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International Conference

Catalysis in Organic Synthesis

ICCOS-2012

BOOK OF ABSTRACTS

September 15-20, 2012

Moscow, Russia

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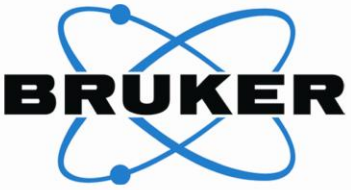

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Index

Plenary Lectures

PL1

DESIGN AND APPLICATIONS OF SELECTIVE CATALYSTS FOR OLEFIN METATHESIS

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Olefin metathesis catalysts have become one of the tools for the efficient synthesis of complex molecules and materials. Until recently, the catalysts demonstrated poor catalyst controlled stereoselectivity. Over the past couple of years, complexes based on molybdenum, tungsten and ruthenium have been discovered that will produce olefins good to excellent selectivity for the generation of *Z* olefins both in cross and in ring closing metathesis. New ligands have been developed that result in different selectivities and open new applications of metathesis in the synthesis of an array of complex molecules. In addition, the complex initiators allow for the synthesis of polymers with controlled structures that precisely control the properties of the materials.

PL2

ASYMMETRIC COUNTERANION DIRECTED CATALYSIS (ACDC): A REMARKABLY GENERAL STRATEGY FOR ENANTIOSELECTIVE SYNTHESIS

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Most chemical reactions proceed via charged intermediates or transition states. Such "polar reactions" can be influenced by the counterion, especially if conducted in organic solvents, where ion pairs are inefficiently separated by the solvent. Although asymmetric catalytic transformations involving anionic intermediates with chiral, cationic catalysts have been realized, analogous versions of inverted polarity with reasonable enantioselectivity, despite attempts, only recently became a reality. In my lecture I will present the development of this concept, which is termed asymmetric counteranion-directed catalysis (ACDC) and illustrate its generality with examples from organocatalysis, transition metal catalysis, and Lewis acid catalysis.

Since 2005, Benjamin List has been a director at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (Germany). He obtained his Ph.D. in 1997 at the Johann-Wolfgang-Goethe-University in Frankfurt am Main. From 1997 until 1998 he conducted postdoctoral research at The Scripps Research Institute in La Jolla (USA) and became an assistant professor there in January 1999. In 2003 he joined the Max-Planck-Institut für Kohlenforschung in Mülheim. He has been an honorary professor at the University of Cologne since 2004.

Professor List's research focuses on organic synthesis and catalysis. He has contributed fundamental concepts to chemical synthesis including aminocatalysis, enamine catalysis, and asymmetric-counter-anion-directed catalysis (ACDC). His group has pioneered several new amine- and amino acid-catalyzed asymmetric reactions originating from his discovery of the proline-catalyzed direct asymmetric intermolecular aldol reaction in 2000. Shortly thereafter, his group has developed the enamine catalysis concept and introduced the first proline-catalyzed asymmetric Mannich reaction. Subsequently, his researchers pioneered novel Michael reactions, α-aminations, enol-exo-aldolizations, and aldehyde α-alkylations. Furthermore, his collaborative efforts have provided a clearer mechanistic understanding of enamine catalysis and established the basis for the design of new reactions and catalysts.
His latest work deals with chiral anions in asymmetric catalysis. In 2006 he introduced the concept of asymmetric counter-anion-directed catalysis (ACDC). This very general strategy for asymmetric synthesis has recently found widespread use in organocatalysis, transition metal catalysis, and Lewis acid catalysis.
The accomplishments of Ben List's group have been recognized with the Synthesis-Synlett Journal Award in 2000, the Carl-Duisberg-Memorial Award in 2003, the Degussa Prize for Chiral Chemistry, the Lieseberg Prize of the University of Heidelberg, and the "Dozentenstipendium" of the German Chemical Industry in 2004. He received the Novartis Young Investigator Award in 2005, the JSPS-Fellowship Award in 2006, the Award of the German Chemical Industry and the Astra Zeneca Research Award in Organic Chemistry in 2007, and was named a Thomson Reuters Citation Laureate in 2009. In 2011 his group has been awarded an Advanced Grant (2.5M€) by the ERC. During the last years he has held many appointments as visiting Professor and named lectureships.

PL3

CHEMISTRY WITH METHANE: CONCEPTS RATHER THAN RECIPES

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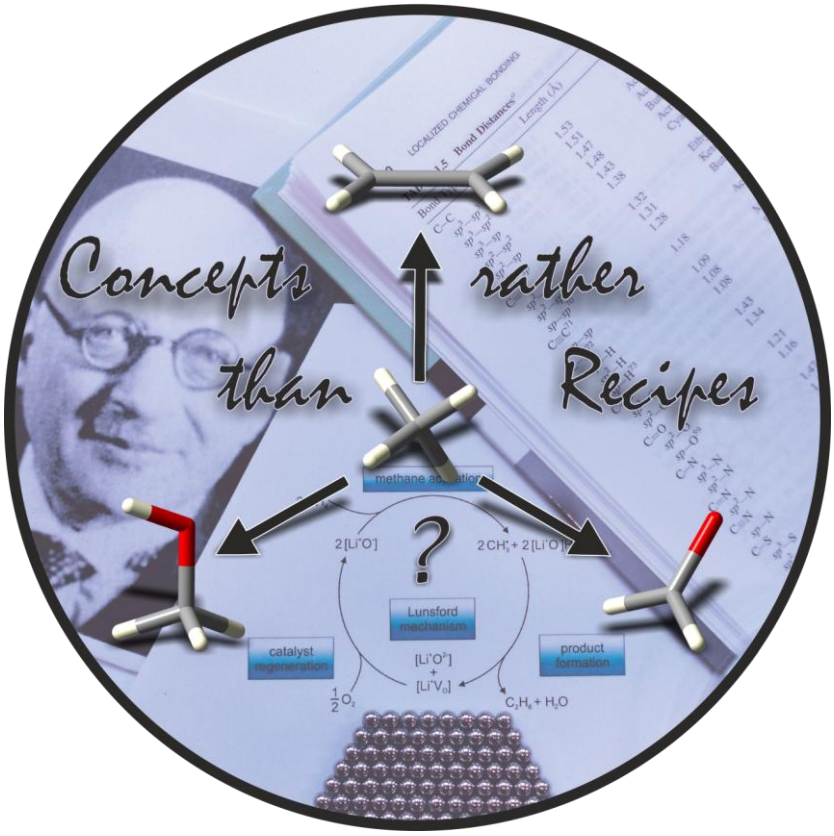
Four seemingly simple transformations related to the chemistry of methane will be addressed from mechanistic and conceptual points of view, i.e.: 1) metal-mediated dehydrogenation to form metal carbene complexes, 2) the hydrogen-atom abstraction step in the oxidative dimerization of methane, 3) the mechanisms of the CH_4 → CH_3OH conversion, and 4) the initial bond scission as well as the rate-limiting step in the selective CH_3OH → CH_2O oxidation. State-of-the-art gas-phase experiments, in conjunction with electronic-structure calculations, permit to identify the elementary reactions at a molecular level and thus to unravel detailed mechanistic aspects. Where appropriate, these results are compared with findings obtained from related, more conventional studies in solution or on surfaces. Three aspects deserve special mentioning: 1) the prominent role of relativistic effects exerted by 5d elements, 2) two-state reactivity as a (new) reaction paradigm, and 3) unparalleled cluster-size and ligand effects on reactivity, all of which matter in the organometallic chemistry with methane at ambient conditions.



PL4

ENHANCING THE SELECTIVITY IN ORGANIC SYNTHESIS OVER HETEROGENEOUS CATALYSTS: BIMETALLIC VS MONOMETALLIC CATALYSTS

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The main benefit in application of supported metal catalysts for the reactions of organic synthesis compared to metal or metal-organic complexes, which consists in their easy separation from reaction mixture containing reagents, reaction products and solvents, goes down by the worse selectivity towards a target product. The reason of this disadvantage is inhomogeneous distribution of active sites on energy because of variation of the chemical state and local structure originating from non-monodispersion of metallic particles, interaction of active component with support, incomplete removal of ligands and other components of a precursor and parent solution, etc. These problems are absent in the case of metal-complex catalysts when all active centers are energetically homogeneous. One of the possible solutions of the problem is the introduction of the second metal to produce bimetallic active component. In this case, dilution of the surface of supported metal particles with the second metal, which, as a rule, is inactive for the reaction studied, allows one to form the active sites of a specific geometry (ensemble effect) and/or to modify the electronic property of an active metal (ligand effect). Possibility of a wide variation of surface composition of bimetallic particles from core-shell structure to homogeneous alloy should be also taken into account.

In this lecture I will illustrate this postulate via examples of literature and our recent researches which demonstrate enhancing the selectivity in a number of reactions over bimetallic catalysts compared to monometallic ones. Among of them are ethylene acetoxylation over Pd-Au vs. Pd catalysts, ethylene epoxidation over Ag-Cu vs. Ag catalysts, selective hydrogenation of acetylene in the presence of ethylene over Pd-Zn vs. Pd catalysts, as well as selective oxidation of glucose to gluconic acid over Au-Pd vs. Au catalysts.

Furthermore, capabilities of surface science methods (XPS, PM-IRAS, XAS, etc.) to study the structure and chemical state of surface sites on the active component particles will be analyzed. It will be shown that not only ratio of different metals, but also reaction conditions are of significance. As consequence, understanding the nature of active sites in the bimetallic catalysts creates the possibility to elucidate the structure-selectivity relationship and regulate the catalyst performance for the reactions of organic synthesis.

PL5

RECENT ADVANCES IN HIGHLY GENERAL AND SELECTIVE SYNTHESES OF ALKENES OF ALL CONCEIVABLE TYPES VIA ALKYNE ELEMENTOMETALATION AND Pd-CATALYZED CROSS-COUPLING

E.-I. Negishi, S. Xu, H. Kamada, E.H. Eun Hoo Kim, A. Oda

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Highly (≥99%) selective synthesis of various conceivable types of mono-, di-, and oligoenes can be achieved via **alkyne elementometalation**, such as **hydro-, carbo-, hetero-, or metallometalation**, followed by Pd-catalyzed alkenylation with ≥99% retention of all structural features. This new alkene synthesis protocol overcomes various difficulties associated with various other methods for alkene syntheses, such as the Wittig reaction and its variants including the Horner-Wadsworth-Emmons olefination, its Still-Gennari and Ando modifications, and the Heck olefination. Critical comparisons indicate that the Negishi alkenylation with alkenylmetals containing Zn or Zr displays superior stereoselectivity in comparison with other Pd-catalyzed cross-coupling protocols, such as Suzuki and Heck reactions.

Syntheses of various types of synthetically challenging di- and oligoenes will be discussed with the ultimate goal of developing the generally applicable synthetic routes to any fundamentally synthesizable alkene-containing compounds with emphasis on biologically and medicinally important compounds of natural or unnatural origin.

PL6

NOVEL METHODS FOR SYNTHESIS AND C-H FUNCTIONALIZATION OF ARENES AND HETEROARENES

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A set of novel efficient transition metal-catalyzed methodologies for synthesis of multisubstituted carbocycles proceeding via a C-H activation pathway has been developed [1, 2]. We have also developed novel methods for *direct* C-H functionalization of electron-rich heterocycles and arenes [3-5]. Next, we explored employment of Si-tethered directing groups for the Pd-catalyzed *directed* C-H halogenation, vinylation, and mono- and bis-oxygenation reactions [6-10]. These Si-tethered directing group are traceless or can easily be converted into a variety of useful functionalities.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

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PL7

NEW PARADIGM IN EXPLORATION OF REACTION PATHWAYS IN ORGANOMETALLIC CATALYSIS

S. Maeda[1], H. Xiao[1], K. Morokuma[2]

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Finding the transition state (TS) as the first-order saddle point on the potential energy surface (PES) has been a central issue in the theoretical study of chemical reaction mechanisms. The full catalytic cycle including all related TSs was first revealed in the late '80th for the Halpern mechanism of olefin hydrogenation by the Wilkinson catalyst [1]. Since then, various catalytic cycles have been studied. Theoretically unveiled TS geometries have provided many important suggestions in designing novel catalysts by experimentalists. Therefore, collaborations between experimental and theoretical chemists toward this goal are nowadays very commonly.

TS structures have been located by geometry optimization [2]. In general, a good initial guess geometry is required. Hence, some TSs totally unknown/unexpected or far from estimates may possibly be missed. It is also hard to judge whether anything TS is missed or not in the search. Thus, fully systematic search is highly desired in particular for complex chemical reactions that may involve multiple reactants in multiple pathways and multiple steps in each pathway.

Hence, We have developed the artificial force induced reaction (AFIR) method [3], which enabled automated exploration of A + B → X (+ Y) type reaction pathways. AFIR was successful in locating all associative pathways starting from a given set of reactant molecules without using any guess in some systems such as the Aldol reaction [4]. Its application to the Passerini multicomponent reaction discovered a new mechanism in this very conventional reaction [5]. Furthermore, we recently achieved semi-automatic determination of a full catalytic cycle of a homogeneous catalysis (hydroformylation reaction of ethylene using $HCo(CO)_3$ as active catalyst) without using any initial guess for the first time by AFIR [6]. In this talk, the AFIR method and some examples of its applications to catalysis will be presented. Perspectives of automated reaction path search methods will also be discussed toward systematic prediction of reaction mechanisms starting only from given reactants and catalysts.

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PL8

DIRECT FUNCTIONALIZATION OF C-H BOND IN AROMATICS: METAL-FREE VS METAL-CATALYZED REACTIONS

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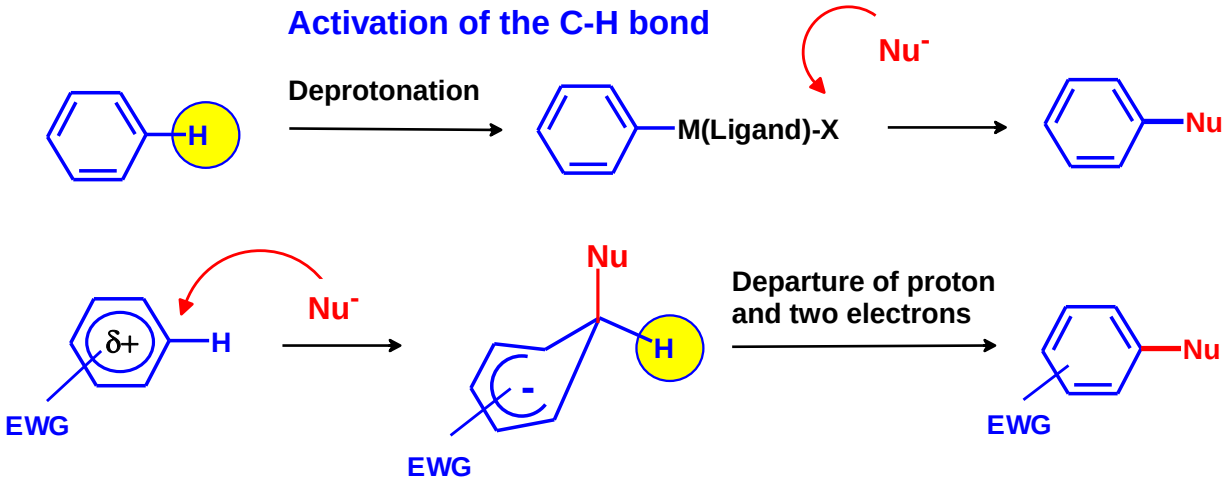
Two principal approaches to incorporate nucleophilic fragments into an aromatic ring through the displacement of hydrogen of the C-H bond will be considered. The first one is based on catalytic activation of the C-H bond, and it involves the step of deprotonation followed by the formation of organometal intermediates which then react with nucleophiles into the final products. Metal-catalyzed cross-coupling reactions proved to be a powerful synthetic tool to form a variety C(sp^2)-X bonds.



The second approach (S_N^H) suggests a direct nucleophilic attack at unsubstituted carbon of an aromatic ring leading to σ^H-adducts followed by oxidation and departure of a proton ("Addition-Elimination" Protocol).[1-3] The metal-free S_N^H reactions provide a good complimentary basis for metal-catalyzed cross-coupling reactions. Recent advances in the field of nucleophilic substitution of hydrogen (S_N^H) enabling one to functionalize the C-H bond in aromatic and heteroaromatic compounds by action of carbon- or heteroatom-centered nucleophilic reagents will be discussed.

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PL9

MOLECULAR COMPLEXITY THROUGH GOLD CATALYSIS

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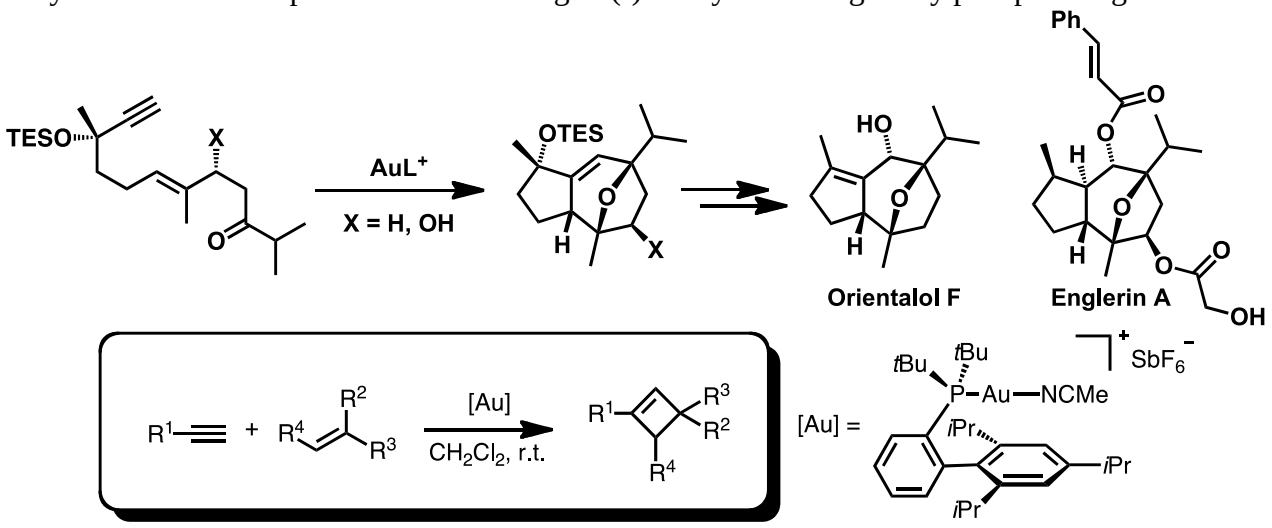
Gold(I) complexes are the catalysts of choice for the selective activation of alkynes under mild conditions,[1] which has been applied for the construction of cyclic systems such as orientalol F and englerin A.[2] Recently we have found that the intermolecular reaction of alkynes with alkenes leads to cyclobutenes in the presence of cationic gold(I) catalysts bearing bulky phosphine ligands.[3]



Extension of these results to the development of new gold(I)-catalyzed cyclopropanation[4] and other intermolecular reactions will be presented.

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PL10

THE POWER OF ASYMMETRIC PHASE TRANSFER CATALYSIS

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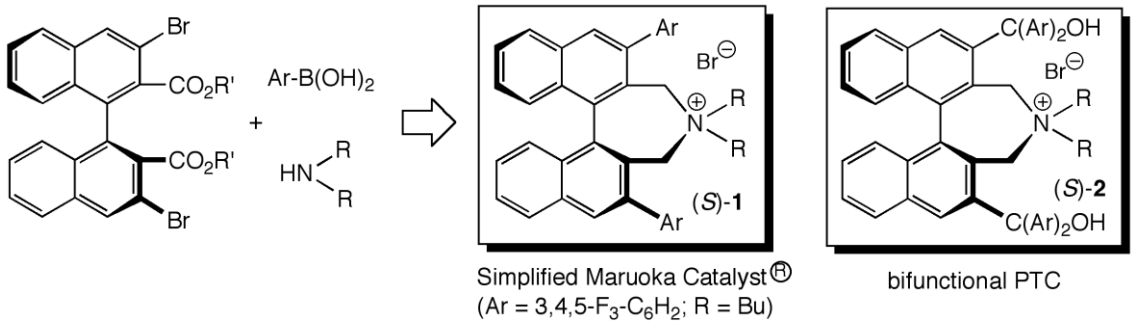
Phase transfer catalysis (PTC) has been recognized as a convenient and highly useful synthetic tool in both academia and industry because of several advantages of PTC (*i.e.*, operational simplicity, mild reaction conditions with aqueous media, environmental consciousness, suitability for large-scale reactions, etc.), which meet the current requirement for practical organic synthesis.[1] In particular, we are interested in the development of various useful asymmetric transformations with high efficiency. Our strategy is based on our recent finding of a very active, chiral phase transfer catalyst of type (*S*)-**1** (Simplified Maruoka Catalyst® with Ar = 3,4,5-F_3-C_6H_2; R = Bu) for the asymmetric alkylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester. [2] Since the catalyst (*S*)-**1** can be readily prepared from three components, *i. e.*, a chiral binaphthyl part, an arylboronic acid ($ArB(OH)_2$), and a secondary amine (R_2NH), the appropriate modification of $ArB(OH)_2$ and R_2NH parts should give newly designed catalysts for the development of novel asymmetric transformations. Accordingly, we recently designed several new catalysts of type **1** for asymmetric Strecker and conjugate addition reactions.[2] Furthermore, by introducing an additional functional group at 3,3'-positions, a series of bifunctional phase transfer catalyst of type (*S*)-**2** were designed for practical asymmetric transformations under essentially neutral conditions.[3]



Simplified Maruoka Catalyst®
(Ar = 3,4,5-F_3-C_6H_2; R = Bu)

bifunctional PTC

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PL

THE APPLICATION OF TRANSITION-METAL-CATALYZED REACTIONS FOR THE SYNTHESIS OF DIVERSE NITROGEN HETEROCYCLES

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The transition-metal-catalyzed reactions have played an important role in organic chemistry for quite sometimes, and this is evidenced by the awards of Noble prizes in chemistry for three years for researches in these areas, first in 2001 and then in 2005 and 2010.
Harnessing the Suzuki-Miyaura reaction to form the biaryl scaffolds, we have transformed these biaryl derivatives to various alkaloids including Buflavine, Aristolactam alkaloids and Eupolauramine and other derivatives. Buflavine belongs to a group of natural *Amaryllidaceae* alkaloids isolated from *Boophane flava* bulbs. It possesses a very rare 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine skeleton composing of a biaryl ring system linked *via* an eight-membered *N*-heterocyclic ring. Aristolactam alkaloids, having a phenanthrene chromophore, are a minor group of natural compounds of pharmacological interest mainly found in the *Aristochiaceae*. Eupolauramine is a structurally unique azaphenanthrene alkaloid isolated from *Eupomatic laurina* which has been found in Australia and New Guineas. As Eupolauramine occurred naturally in only low concentration, the synthesis would provide sufficient material for further biological testing.
Applying the Ring-Closing Metathesis (RCM) reaction to form the ring in various benzoquinolizine derivatives, these key intermediates could be further functionalized to generate other biologically active heterocycles. Benzoquinolizine moiety is embedded in structures of various biologically active alkaloids including Ankorine, Tetrabenazine and Emetine.
Exploiting the palladium-catalyzed C-H activation, the synthesis of multi ring fused indolobenzazocinone derivatives could be accomplished.

The application of various metal catalyzed reactions in the syntheses of the above mentioned alkaloids and other nitrogen heterocycles will be presented.

Invited Lectures

IL1

MECHANISTIC INVESTIGATIONS IN HOMOGENEOUS CATALYSIS

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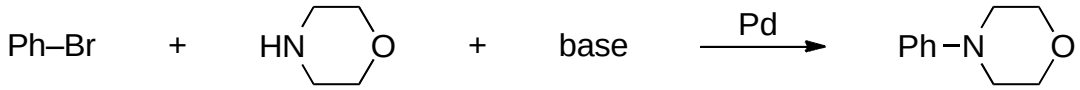
Coupling reactions catalyzed by transition metals are among the most important tools in the toolbox of synthetic organic chemists. Palladium-catalyzed couplings in particular are versatile and well understood. More recently, alternative couplings based on environmentally benign metals like iron have become popular. Our group focuses on mechanistic investigations of known coupling reactions, with the aim to develop improved reaction conditions or even uncover new reactivity. The current talk will exemplify our work in two different areas; the Pd-catalyzed Buchwald-Hartwig coupling of aryls with secondary amines, and the Fe-catalyzed C–C coupling.

Buchwald-Hartwig amination is an established reaction with a well understood mechanism. [1] We work on this reaction within the SYNFLOW consortium, with the aim to enable flow catalysis for coupling an aryl bromide with a cyclic secondary amide. The batch reaction uses *t*-BuOK as a base, forming insoluble KBr, potentially clogging the reactor. The current lecture will disclose our investigations into the detailed role of the base, with the aim to enable a mechanistically informed selection of alternative bases in the reaction.



In the second part of the talk, I will focus on the Fe-catalyzed C–C coupling of Grignard reagents. This reaction, originally investigated by Kochi in the 70's, [2] has had a renaissance in recent years. The current talk will focus on our experimental and computational studies of the reaction mechanism, [3] both for the hetereocoupling and for the mechanistically simpler stoichiometric homocoupling of Grignard reagents. Our recent results give strong indication that the most favorable coupling involves an Fe(I)-Fe(III) cycle, but with several possible side reactions involving other oxidation states on Fe.

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IL2

WHEN ASYMMETRIC AMINOCATALYSIS MEETS THE VINYLOGY PRINCIPLE

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Asymmetric aminocatalysis[1] has greatly expanded the chemist's ability to stereoselectively functionalise unmodified carbonyl compounds. The field has coalesced around two pioneering studies,[2,3] which recognized that chiral amines could activate carbonyl compounds according to fundamental and general reactivity concepts: the LUMO-lowering effect, which is the underlying activation principle of iminium ion catalysis,[2] and the HOMO-raising effect inherent to enamine catalysis.[3] Those activation modes account for the functionalisation of carbonyls at their β and α positions, respectively. The successful marriage of these reactivity concepts to the principle of vinylogy[4] has recently led to the development of novel aminocatalytic activation modes, which allow for the direct, stereoselective, and site-selective functionalization of unsaturated carbonyls at remote positions, such as the γ,[5] δ, and even the ε[6] positions.
Here, some recent contributions from our laboratories are presented.[7]

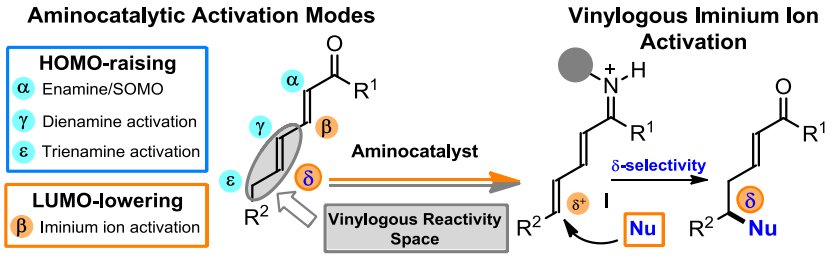

Figure 1. Established activation modes in aminocatalysis and the vinylogous iminium ion strategy

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IL3

VISIBLE LIGHT PHOTOCATALYSIS FOR ORGANIC SYNTHESIS

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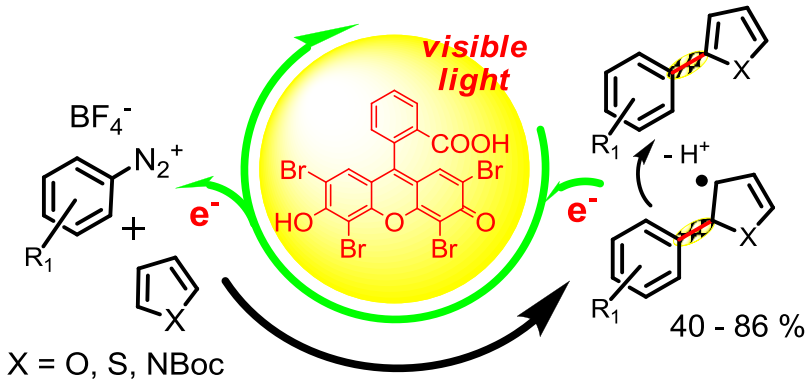
Photoredoxcatalysis uses the energy of visible light to generate redox power for the formation of reactive intermediates in synthesis. Redox-active metal complexes and organic dyes can serve as homogeneous photocatalysts, while organic and inorganic semiconductors are suitable heterogeneous photocatalysts for organic synthesis. Over the last years an increasing number of examples were reported that combine the advantages of energy efficient photocatalysis with the high selectivity, e.g. of organocatalysis. The lecture discusses recent developments in homogeneous and heterogeneous photocatalysis from our laboratory and our attempts to unravel their mechanisms.



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IL4

HELICAL-POLYMER-BASED CHIRAL PHOSPHINE PQXPHOS AS HIGHLY ENANTIOSELECTIVE, CHIRALITY–SWITCHABLE LIGANDS FOR ASYMMETRIC CATALYSIS

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Much effort is being made to establish "next-generation" chiral catalysts for asymmetric organic synthesis. Such catalysts are expected to realize new, innovative catalytic reactions, and to afford not only high enantioselectivity, but also high catalytic activity, better recoverability, and reusability. It is also expected for such new chiral catalysts to possess "a switch" by which the chirality of the catalyst can be interconverted. This feature allows synthetic organic chemist to escape from preparation of two enantiomeric catalysts for stereoselective production of both enantiomers. In this presentation is discussed new poly(quinoxaline-2,3-diyl)-based chiral ligand **PQXphos** (*R*)-**L1**, which show high enantioselectivities (>95% ee for three different reactions), high reusability (up to 8-time reuse), and higher catalyst activity than do the corresponding low-molecular-weight chiral ligands. In addition, the polymer backbone underwent perfect switch of helical chirality by the effect of solvent. This feature could be successfully applied to new catalytic systems in which either enantiomer can be produced with high enantioselectivities from a single chiral ligand, whose helical chirality is easily switchable. Palladium-catalyzed asymmetric reactions including asymmetric hydrosilylation of styrenes,[1] asymmetric biaryl synthesis via Suzuki–Miyaura coupling,[2] and C–C bond cleaving desymmetrization of *meso*-methylenecyclopropanes[3] shall be discussed.[4]

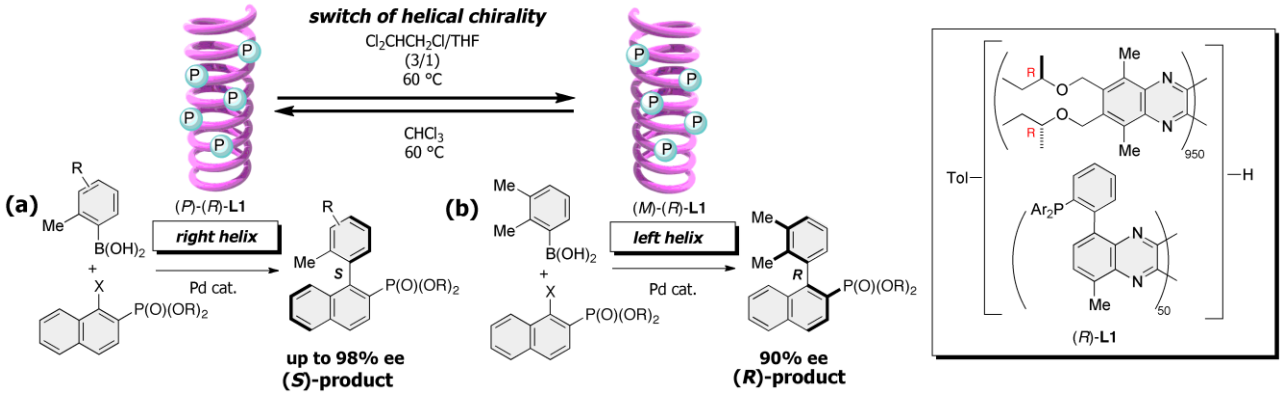

Figure 1 Asymmetric Biaryl Synthesis via Suzuki–Miyaura Coupling in the Presence of PQXphos (*R*)-**L1**. Production of *S*- or *R*-product using either right- or left-handed helical (*R*)-**L1**, whose helical chirality is switchable by solvent effect.

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IL5

ENANTIOPURE HOMOALLYLIC ALCOHOLS AS BUILDING BLOCKS FOR STEREOSELECTIVE SYNTHESIS

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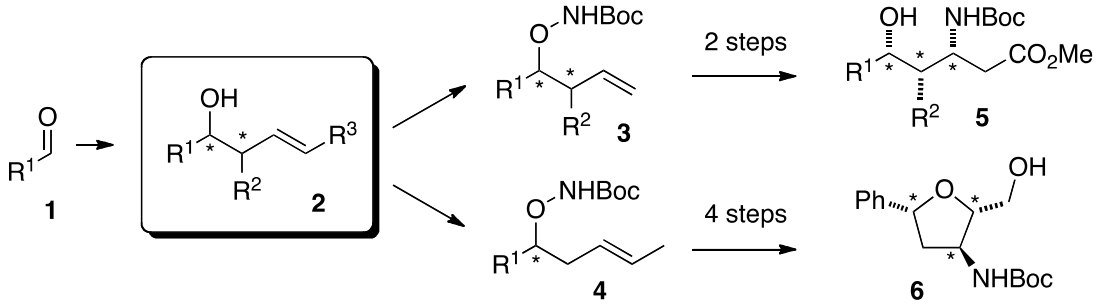
Carbon-carbon and carbon-heteroatom bond formation are the traditional cornerstones of synthetic organic chemistry. Herein, we present our latest endeavor in finding practical solutions for both types of chemical transformations. Asymmetric allylation of aldehydes **1** with allyltrichlorosilane reagents in recent years has become a powerful synthetic tool.[1] We shall overview the existing strategies and reveal new development in the organocatalytic, highly stereo- and enantioselective synthesis of branched and linear homoallylic alcohols **2**.



Scheme: Application of homochiral homoallylic alcohols in synthesis

The resultant homoallylic alcohols **2** can be readily converted to oxamine derivatives **3** and **4**, which offer a variety of ways for further synthetic development. A stereocontrolled Pd-catalysed functionalisation via the construction of a carbon-heteroatom bond will be illustrated by synthesis of β-amino-δ-hydroxy amino acids **5** and aza analogues of *C*-nucleosides **6**. Mechanistic details of these reactions will be discussed.

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IL6

ADAPTIVE CATALYSTS IN ORGANIC SYNTHESIS

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Transition metal mediated catalytic transformations is a well-established and outstanding tool with high impact in the areas of organic synthesis, pharmaceutical and medicinal chemistry, natural product synthesis, material science, and several other fascinating applications. Homogeneous and heterogeneous catalysis in cross-coupling, Heck, carbonylation reactions, and also carbon-heteroatom bond formation has shown tremendous recent growth. Rapid methodology development in the areas of selective construction of C-C and C-Heteroatom bonds revealed unique features about the mechanistic nature of transition metal catalysis: *adaptive interconverion of different active species is taking place during the catalytic transformation.*

In the present study transition-metal-catalyzed reactions are discussed in view of evolution of active species in solution and finding the relationship between the nature of catalyst active species to the efficiency and selectivity of the reaction.[1-8]

The questions of particular importance are catalytic properties related to mononuclear metal complexes and metal clusters in solution, interconversion between homogeneous and heterogeneous catalytic systems, leaching, and stability/recycling of metal catalysts. The optimal strategy to select efficient catalytic system for C-C and C-Heteroatom bonds formation is of major attention.

Possible directions to create next generation of catalytic systems capable for adaptive recognition of the substrate and promoting selective transformation with variety of different substrates will be presented and discussed.

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IL7

METAL NANOPARTICLES: FROM THEIR ORGANOMETALLIC SYNTHESIS TO THEIR APPLICATION IN CATALYSIS

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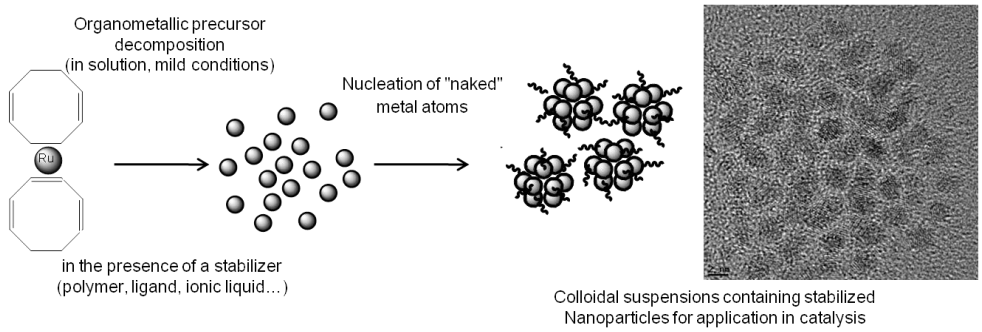
Many efforts are presently devoted to the synthesis of metal or metal oxide nanomaterials. This interest comes from their attractive properties that can find applications in various areas[1] such as catalysis.[2] In our group, the synthesis of metal and metal oxide nano-objects is performed through an organometallic approach.[3] Metal organic complexes are decomposed in solution under mild conditions and in the presence of polymers or ligands as stabilizing agents. Depending on the reaction conditions, nanoparticles of tunable characteristics are formed, the control of which is possible since the reaction parameters have an influence on the nucleation step and/or the growth step during the synthesis.



Our objective is to prepare well-dispersed nanoparticles with a narrow size distribution and a controlled surface composition, these parameters being important for further application. The choice of the ligand used as stabilizer is thus of prime importance as it can influence the characteristics of the nanoparticles as their size, shape, or surface chemistry and consequently, their catalytic properties. Examples of so-obtained nanoparticles will be presented. A particular attention will be devoted to the functionalisation of their surface through an adequate choice of the stabilizer that can lead to application in catalysis in organic[4] or aqueous media[5]. Our approach can also be applied for the deposition of nanoparticles into supports like mesoporous silica[6] or carbon supports,[7] leading thus to supported nanocatalysts.

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IL8

BIMETALLIC Zr, Al- INTERMEDIATES AS ACTIVE CENTERS OF ZIRCONIUM CATALYZED ALKENE HYDRO-, CARBO- AND CYCLOALUMINATION REACTIONS

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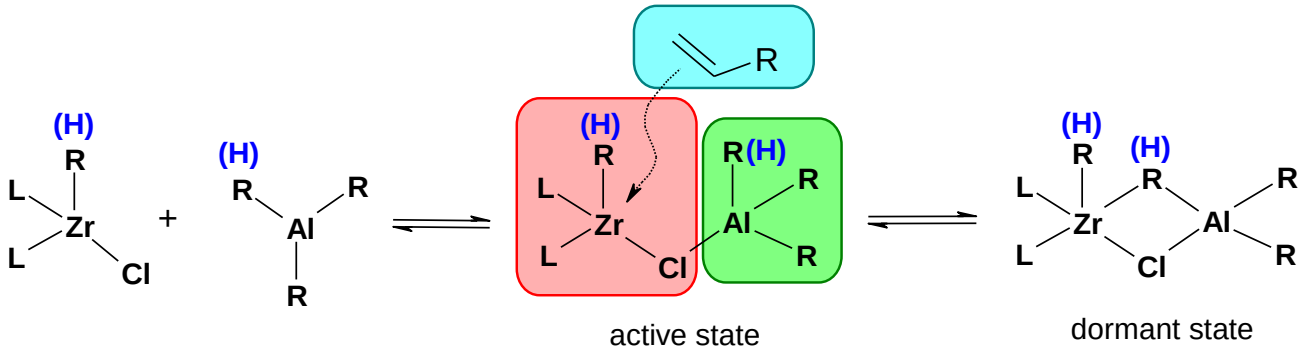
Bimetallic catalytic systems based on transition metal complexes are widely used in modern organic chemistry. Each of these systems shows unique properties and provides high conversion of a substrate, reaction chemo- and stereoselectivity due to the possibility of effective variation in electronic structure and geometry of the catalytically active centers. Bimetallic systems consisting of Ti or Zr complexes and organoaluminum compounds (OAC) are of great importance because they catalyze a wide range of chemical transformations, including Ziegler-Natta polymerization, di- and oligomerization, as well as the hydro-, carbo- and cycloalumination of alkenes and acetylenes [1]. Various Zr,Al-complexes are assumed as the active centers of the reactions [2].

The report presents the results on the experimental and theoretical studies of the role of Zr,Al-bimetallic intermediates in the alkene hydro-, carbo- and cycloalumination, catalyzed with zirconium η^5-complexes. The factors that determine the intermediate reactivity and, consequently, the activity of the catalytic systems, reaction pathway and enantioselectivity are considered. The contribution of intra- and intermolecular processes of σ- ligand exchange between the transition and nontransition metal atoms in the formation of catalytically active centers is discussed. Thus, the mechanisms of zirconium complex catalysis in the alkene hydro-, carbo- and cycloalumination are proposed, which enable to formulate the general approaches to the design of bimetallic Zr,Al-catalytic systems based on balance between electronic and steric factors of the transition metal complex, organoaluminum compound and substrate in the reaction key intermediates.



The authors thank the Russian Foundation of Basic Research for financial support (Grants No. 11-03-00210a, 12-03-363a).

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IL9

SELECTIVE TRANSFORMATIONS OF EPOXIDES AND AZIRIDINES

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The dominant chemistry of epoxides and aziridines is the C-O or C-N bond cleavage under the catalysis of Lewis aicd or transition metal catalyst. In past, the C-C heterolysis of thiese compounds leading to carbonyl or azomethine ylides can be only achieved under photoinduced and thermal conditions. Recently, we developed two novel strategies to chieve the chemoselective C-C bond heterolysis under mild conditions by introduction either two electron-withdrawing groups or one electron-withdrawing group and one alkyne groups, affording to reactive 1,3- or 1,4-dipoles, which can readily react with CO or various dipolarophiles such as aldehydes, imines, olefins, alkynes and nitrones, affording to diverse functionalized heterocyclic compounds. Enantioselective variants of these reactions are also developed and moderate enantioselectivity is obtained.[1] Besided the 1,3-dipolar cycloaddition, a homo-hetero-Nazarov cyclization is also developed.
Besides the C-C bond cleavage of epoxide mentioned above, a rhodium(I)-catalyzed hetero-[5+2] cycloaddition/Claisen rearrangement of yne-vinylic epoxides was recently discovered, in which a C-O bond cleavage takes place.[2] In this lecture we aslo want to show some new progress on the selectively C-C and C-X bond cleavage of epoxides and aziridines. Enantioselective version of some Lewis acid catalyzed e 1,3-dipolar cycloaddition will be also introduced.

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IL10

C-H BORYLATION OF TERMINAL ALKYNES

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This presentation will describe the use of new iridium pincer complexes as catalysts for catalytic dehydrogenative coupling of boranes and terminal alkynes to yield 1-borylalkynes. We will describe the synthesis of the new pincer ligands, their iridium complexes, optimization of catalysis, and isolation of intermediates. This reaction gives convenient access to an important building block that can be utilized in a number of reactions. We will show how 1-borylalkynes can be used in cycloaddition reactions to produce versatile structures retaining carbon-boron bonds for subsequent functionalization.

IL11

CATALYSIS: A KEY ENABLING TECHNOLOGY FOR SUSTAINABLE CHEMICAL PRODUCTION AND FUTURE ENERGY TECHNOLOGIES

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Despite numerous important methodological advancements in all areas of chemistry, still most organic synthesis as well as the industrial production of chemicals can be improved. Currently, more than 80% of all products of the chemical industry are made via catalysis. In this regard, the development of new and more efficient catalysts constitutes a key factor for achieving a sustainable production of all kinds of chemicals today and in the future. Here, several major challenges will be presented in the talk. Furthermore, it will be shown that recently developed molecular-defined as well as nano-structured iron catalysts enable us to perform a multitude of redox processes with high yields and selectivity.[1-10] Specific examples which demonstrate the potential of catalytic processes with bio-relevant metal complexes compared to more traditional catalytic reactions will include hydrogenations and dehydrogenations, as well as oxidation reactions.

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IL12

ASYMMETRIC ORGANOCATALYSIS WITH BIFUNCTIONAL THIOUREAS AND NEWLY DESIGNED HYDROGEN-BOND DONORS

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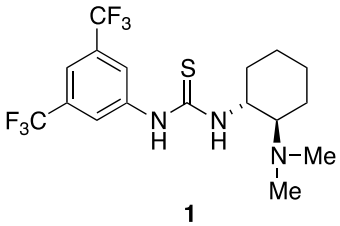
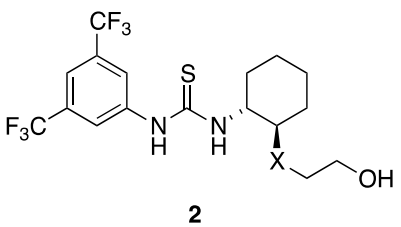
Organocatalyst has attracted considerable attention as a new alternative to enzymes and metallic catalysts. We first became interested in urea and thiourea catalysts as hydrogen-bond donors and have found that bifunctional thiourea 1 bearing a tertiary amino group efficiently promoted various types of enantioselective nucleophilic additions such as Michael addition, aza-Henry reaction, and hydrazination, giving the corresponding products in good yields with high enantioselectivities.1) Later, we also developed several bifunctional thioureas 2 bearing a alcoholic or phenolic hydroxy group which dramatically promoted the 1,4- and 1,2-addition of organoboronic acids into activated quinolines, γ-hydroxy-α,β-unsaturated ketones, and α-imino amides.2) In these reactions, the binary complexes, prepared from the hydroxy thioureas and organoboronic acid, would be active catalysts, in which in situ generated organoboronate moieties may act either as Lewis acids or as nucleophiles.

In contrast to our successful results of asymmetric reactions, the precise mechanism of these organocatalyzed reactions has not been fully understood. Although several reaction mechanisms were proposed by using computational methods, there is actually no experimental evidence based on spectroscopic analysis such as X-ray crystallography and NMR. We then prepared several pseudo-binary complexes of catalyst and reactant to detect unstable reaction intermediates by means of spectroscopic measurements. We eventually succeeded in the structural analysis of an aminothiourea-1,3-diketone complex by X-ray crystallography. Furthermore, to extend the synthetic applicability of hydrogen-bond donor catalysts, we designed new types of bifunctional organocatalysts 3 bearing a new privileged structure. As a result, we discovered that appropriate heterocycles such as quinazolin-4-one and benzothiadiazine-1,1-dioxide bearing a tertiary amino group could be used as multi-functional organocatalysts, giving better results than the original thiourea 1 depending on the reaction types.3)

In my presentation, I will talk about (1) the synthesis and structural analysis of binary complex analogues of catalyst and substrate to identify short-lived reaction intermediates, (2) the synthesis and characterization of new hydrogen-bond donor catalysts 3 bearing a bicyclic skeleton, and (3) the application of these new organocatalysts 3 to a wide range of asymmetric reactions.



1



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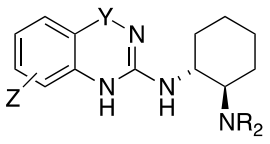

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IL13

SELECTIVE OXIDATION BY SOLID OXIDS - MECHANISMS AND CATALYSTS

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IL14

TRANSITION METAL-CATALYZED TRANSFER HYDROGENATION AS AN EFFICIENT TOOL TO MAKE CARBON-CARBON AND CARBON-HETEROATOM BONDS

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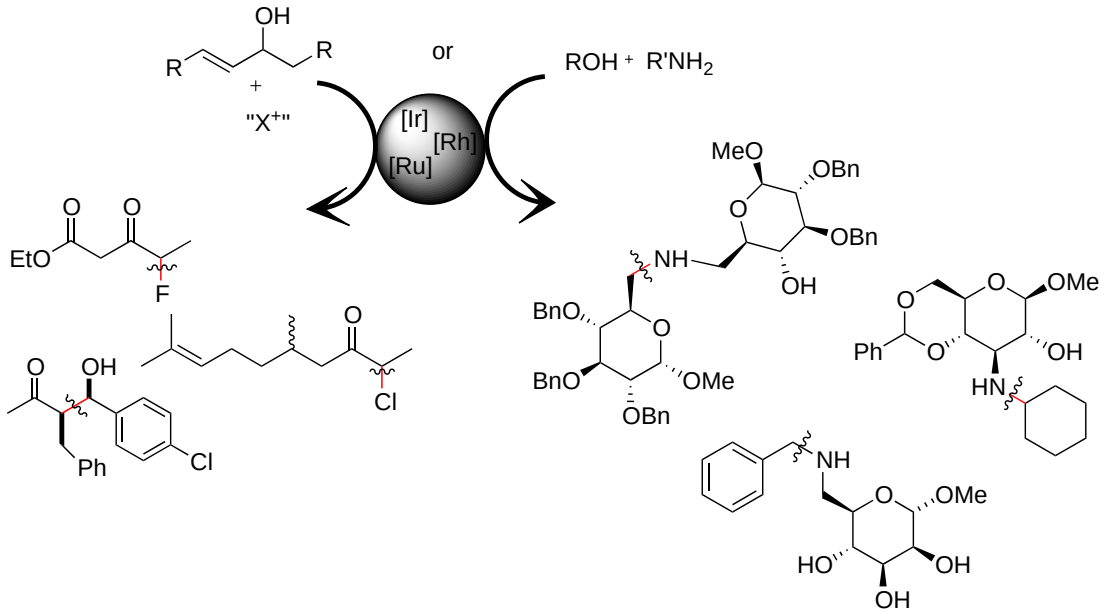
The development of new and efficient catalytic methods to meet the demands of modern synthetic chemistry is extremely important. We describe here our latest results[1] on the formation of C–C, [2] C–F[3] , C–Cl [3] and C–N[4] bonds *via* transfer hydrogenation using rhodium, ruthenium and iridium complexes. Synthetic applications and mechanistic aspects will be described.



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IL15

CHALLENGING ON ORGANIC SYNTHESIS: DIRECT TRANSFORMATION OF UNREACTIVE CHEMICAL BONDS

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To understand of the intrinsic properties of the inert bonds and to meet the requirement of green and sustainable development in organic synthesis, Shi and coworkers made significant contributions in the field of C-H/O/C bond activations and developed efficient synthetic methodologies with high step- and atom- economy.

Due to their easy availability and inert reactivity, direct application of O-containing fine chemicals based on the activation of C-O bond is highly appealing and challenging. Shi and coworkers applied aryl/alkenyl carboxylates and phenolates as coupling partners into different transformations, which showed great potential for direct application of phenol derivatives in organic synthesis.[1] These results not only offer new strategies to construct useful compounds, but also open new windows for understanding the features of inert C-O bonds.

C-H activation is a hot topic providing methodologies to construct diverse organic molecules with high step and atom efficiency. The previous researches in C-H activation mostly focused on the mechanistic studies and cross couplings with organohalides/unsaturated bonds.[2] In Shi's studies, directing group-oriented strategy was successfully applied to approach regioselective C-H activation and the reaction was further extended to heterocylces and general arenes. New concept of oxidative coupling has been introduced to the field of C-H activation and highly selective halogenation, couplings with arylboronic acids, arylsilanes, Grignard reagents based on C-H bond activation, even cross dehydrogenative arylation (CDA) of two arenes were developed.[3] Later on, benzylic and allylic C-H activation was also established to construct C-C bonds.[4] Afterwards, Shi has developed the late and noble transition metal catalysis (Pd, Ir, etc), normal transition metal catalysis (Co, Fe, Nb, Mo, etc)[5] and even transition-metal free process for direct C-H transformations.[6] Very recently, his group reported the beautiful and successful example for the direct addition of aryl C-H to aldehydes and aldimines with the decent studies on their mechanisms.[7]

C-C activation is another challenging field, which might induce the conceptually new organic transformations. Shi group also devote themselves into this field and reported several interesting examples on group transfer of organic molecules by C-C cleavage.[8] These studies are beneficial for understanding the nature of abundant C-C bonds.

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IL16

CALCIUM CATALYZED REACTIONS

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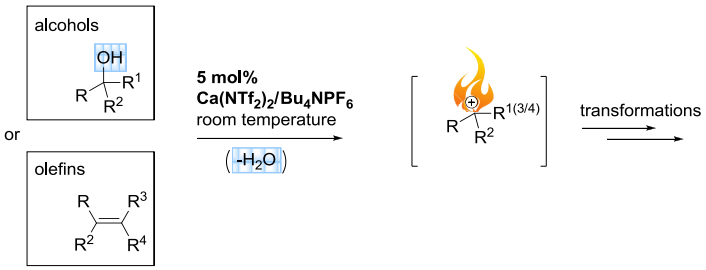
In the past decades, catalysts have been developed almost exclusively on the basis of transition metals. Nowadays, it is increasingly significant to create more sustainable alternatives, wherever possible. Calcium, among other alkaline earth metals, seems to be an ideal candidate for a highly benign metal catalyst. It is essentially free of toxicity and the fifth most frequent element in the earth crust. Surprisingly, its catalytic potential remains hitherto almost unexplored. Therefore, our research focuses on the development of calcium catalyzed reactions.



In the course of the last three years we were the first to successfully apply calcium salts as highly efficient Lewis acidic catalysts in organic synthesis. In direct transformations of environmentally benign π-activated alcohols and olefins with different nucleophiles we demonstrated that our new calcium catalyst is more active than most of the known Lewis acidic catalysts, reflected by a broad substrate scope under very mild reaction conditions. These, and further transformations of the transitional formed reactive carbocationic intermediates, such as cycloisomerization reactions will be presented.

IL17

CATALYTIC MOLECULAR REARRANGEMENTS AS TOOLS FOR C-C BOND FORMATION

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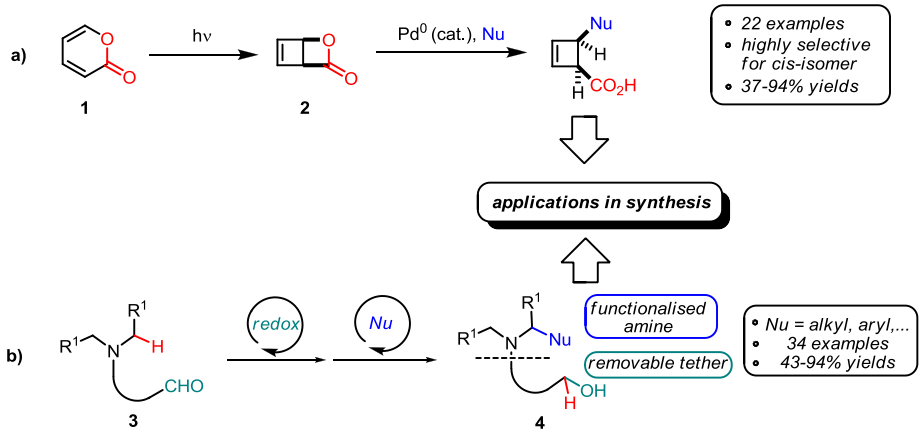
The advent of the 21st century brought about a pressing need for new, efficient and clean strategies for rapid elaboration of molecular complexity. Our group has studied the use of atom-economical transformations, domino pericyclic reactions and redox-neutral rearrangement sequences as particularly appealing means towards achieving those ambitious goals.
In this presentation, we will cover in detail some of our research in these areas, with a focus on catalytic transformations leading to functionalised carbo- and heterocyclic frameworks.[1]
Applications of the methods developed to concise and stereocontrolled total syntheses of natural products shall be presented and discussed.[2]



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IL18

SELECTIVE FORMATION OF C-C CARBON BONDS FROM SATURATED CYCLIC AMINES VIA RUTHENIUM CATALYSIS

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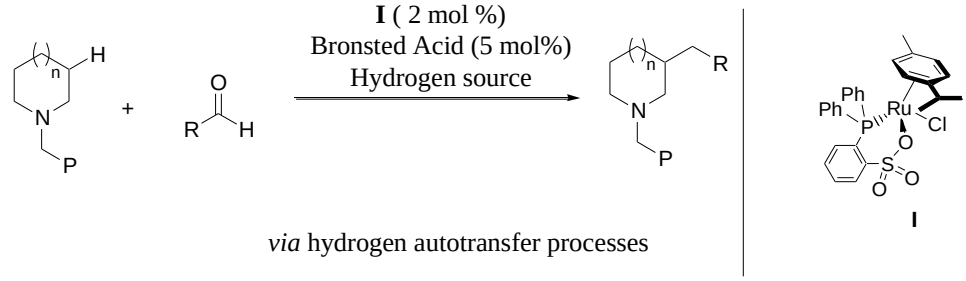
Catalytic activation of aliphatic C-H bond to create new C-C bonds is a topic of current interest. We have recently found a new catalytic system based on a ruthenium(arene) complex featuring a chelating phosphinosulfonate bidentate ligand, which is able to promote cascade hydrogen transfer reactions.[1] Profit has been taken from this catalytic ability to selectively functionalize cyclic amine both at their N-atom[1a] and at C(3) position (Scheme 1)[1a,2]. This transformation involves a sequence of hydrogen transfers, reactive enamine formation, and C-C bond formation.



Scheme 1. C(3) functionalization of cyclic amines

This reaction provides a straightforward access to doubly functionalized aromatic heterocycles and to the preparation of tetrahydroisoquinoline derivatives.[3]

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IL19

ORGANOCATALYSTS AND ENZYMES: COMPLEMENTARY AND COOPERATIVE

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The major part of the lecture will focus on organocatalytic and combined organocatalytic/enzymatic transformations such as (i) the dynamic kinetic resolution (DKR) of azlactones, affording enantiomerically pure α-amino acid derivatives,[1] (ii) KR and DKR of oxazinones, affording enantiomerically pure β^2– and β^3-amino acids,[2] and the stereoselective synthesis of 1,3-diols by combining organocatalytic aldol chemistry with enzymatic reduction.[3] All four types of transformations are of preparative value, and their scopes and mechanisms[4] are discussed. In addition, the lecture will briefly highlight some further recent results relevant to asymmetric organocatalysis: pK_a-values for a series of commonly used chiral Brønsted acids,[5] novel chiral diamine building blocks (such as N-monoprotected *cis*-1,2-diaminocyclohexane, *cis*-DACH)[6], and the conformational analysis of a short peptide (*L*-Leu_6) catalyst for the Juliá-Colonna epoxidation.[7]

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IL20

MICROWAVE EFFECTS IN CATALYSIS

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Microwave activation is widely used to intensify both the catalyst preparation and the mere catalytic reactions. Numerous examples are known in the art related to the application of the microwave irradiation in organic syntheses and, to a lesser extent, in catalysis. Of the utmost interest are the so-called non-thermal effects. The microwave activation can provide a 5-10 times enhancement of the rate of the catalytic processes and a decrease of the light-off temperature of the catalytic reactions. The catalyst preparation is also enjoying the benefits of the microwave approach, because some specific advantages can be used in this case, especially, the microwave drying and mild decomposition of organometallic precursors to produce metal nanoparticles. On the other hand, non-equilibrium effects can be expected while using the microwave treatment, in particular, when MW-absorbing metal nanoparticles are embedded in the insulating matrix of a zeolite or oxide and selective supply of energy to the metal nanoparticles can be expected, while keeping the matrix and the acid or basic sites located at the support surface at a near-room temperature.

The lecture summarizes the progress in the state of the art related to the use of the microwave activation in catalysis using the numerous examples available from the literature and own experimental research. The following reactions deserve special attention:

- Hydrogenation of diverse organic substrates,
- Dehydrogenation of naphthenes
- Oxidative dehydrogenation of light alkanes
- Conversion of methane into valuable products
- Cellulose and lignin conversion

The main features of the MW-assisted processes as compared to the thermally activated reactions are a decrease of the reaction temperature (by 100-150^{o}C), enhancement of the reaction rate, increase of the selectivity, especially in the case of bifunctional catalysts containing both the acidic and metal functions.

Additional advantages of the use of the microwave activation are related to the lower energy consumption for the catalytic processes, increase of the catalyst stability, possibility of stabilization of unusual active phases that are metastable or unstable under the thermal conditions, the possibility of instantaneous switching off of the catalytic reaction once the reaction products leave the MW-zone, which is important in the case of the partial oxidation reactions when the product is usually considered to be more active in complete oxidation than the starting substrate.

Of particular interest is the application of the microwave activation and heating in the processes occurring in ionic liquids that are capable of absorbing the MW energy due to the high value of the tangent of dielectric losses. A wide range of organic syntheses is digested with the goal to reveal positive effects of MW on the conversion, selectivity and other process parameters.

The commercial aspects of the MW-assisted catalysis are discussed.

IL21

Ir-CATALYZED ASYMMETRIC ALLYLIC DEAROMATIZATION REACTIONS

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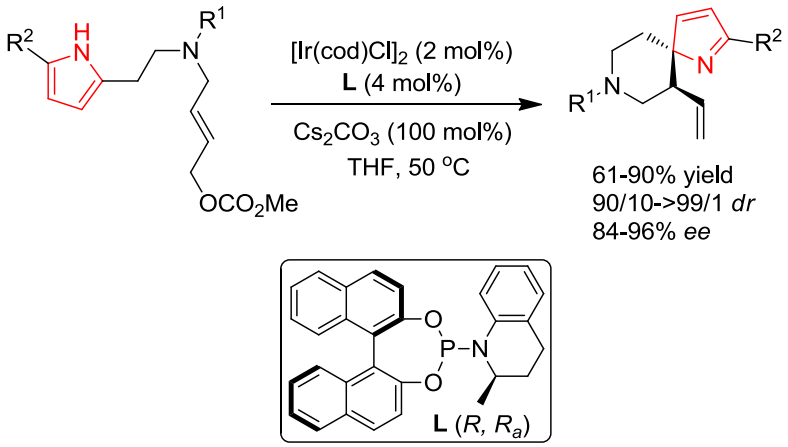
Asymmetric dearomatization reactions are particularly attractive methods in organic synthesis given the facts that the starting materials arenes are highly abundant and readily available, and the dearomatization reaction would provide direct access to compounds bearing quaternary carbon center, or polycylces and spirocycles. Unfortunately, due to the extra stability of "aromaticity" of the arenes, their dearomatization reaction with good enantioselective control has been rarely studied.

In this talk, the progress from the You laboratory on the development of catalytic asymmetric dearomatization processes will be introduced. Direct asymmetric dearomatization reactions of indoles, pyrroles, and phenols were realized with a proper choice of catalysts.



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IL22

TEACHING ENANTIOSELECTIVITY TO C-H BOND ACTIVATIONS

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Reactions involving the activation and subsequent functionalization of relatively inert C-H bonds have considerable synthetic potential because of their economic and ecological benefits. Since the last decade, this has been recognized and a lot of research activities are observed in this area. Significant progress was made in addressing reactivity and selectivity (mainly chemo- and regio-) issues, as well as refining mechanistic understanding of the different pathways.[1] Despite all these advances, asymmetric transformations have so far little precedence.[2] Often harsh conditions, the use of uncommon ligand systems or bar metal salts have hampered developments in this area.
The presentation will focus on our recent developments of activating enantiotopic $C(sp^2)$-H and $C(sp^3)$-H bonds as well as using C-H activations as entry point for enantioselective downstream reactions.[3,4] The design and development of new ligands is essential to the success these transformations as these are not only linked to yield and enantioselectivity, but also heavily impact the reaction outcome itself.

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IL23

ASYMMETRIC CONJUGATE ADDITION OF CARBONYL COMPOUNDS TO UNSATURATED NITRO, SULFONE AND PHOSPHONATE SUBSTRATES

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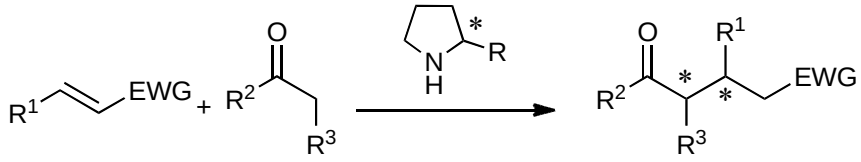
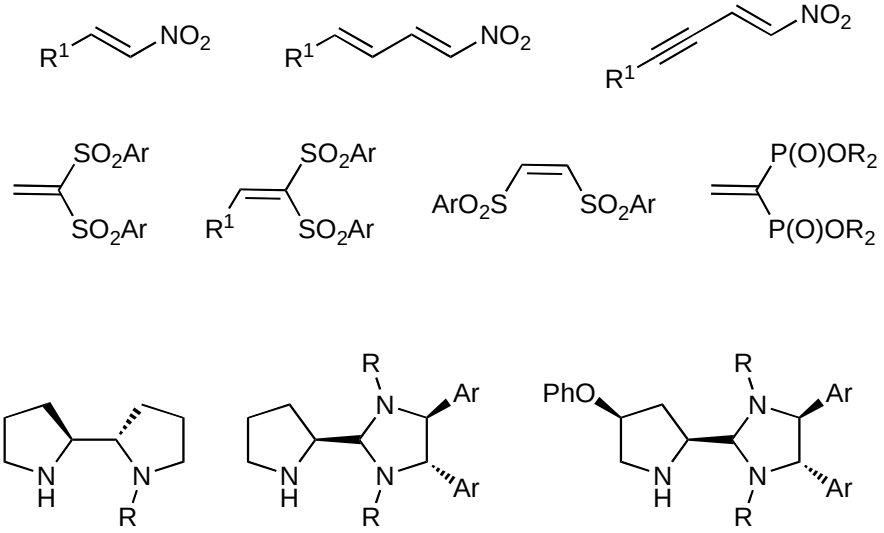
In the field of enamine organocatalysis, many efforts have been directed towards the asymmetric conjugate addition of carbonyl derivatives to various Michael acceptors. We shall describe our contributions to this particular topic and the synthetic applications.[1]



EWG = $-NO_2$, $-SO_2Ar$, $P(O)OR_2$

We will, particularly, stress out the various Michael acceptors,[2] as well as the new organocatalysts we have introduced.[3]



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IL24

HIGHLY STEREOSELECTIVE SYNTHESES WITH CHIRAL DIRHODIUM CATALYSTS

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Dirhodium catalysts with chiral carboxylate or carboxamidate ligands are optimal catalysts for highly enantioselective transformations that involve metal carbene intermediates or occur with Lewis acid activation. This presentation will focus on catalytic processes with easily prepared enoldiazoacetates that include cycloaddition reactions that operate through metal carbene intermediates, and will present clear evidence for the effectiveness of chiral dirhodium(II,III) carboxamidates in hetero-Diels-Alder, dipolar cycloaddition, and carbonyl-ene reactions. Metal vinylcarbene intermediates are susceptible to both [3 + 3]- and [2 + 3]-cycloaddition reactions with nitrones, azomethine ylides, and hydrazones, and stereocontrol that generally exceeds 90% ee is achieved when these reactions are performed with Hashimoto's chiral phthalimide-amino acid ligated dirhodium catalysts. The divergent activities of copper and dirhodium catalysts is evident in these reactions, with copper directing reactant enoldiazoacetates along an acid-catalyzed pathway, and dirhodium taking the reactants through a metal carbene pathway. A more precise understanding of catalysis in these reactions allows predictability in their applications for synthesis.

IL25

SELECTIVITY IN DI-Ru AND DI-Rh-CATALYZED NITRENOID REACTIONS ON BISHOMOALLYLIC SULFAMATES: ALLYLIC C-H INSERTION VS AZIRIDINATION

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Tetra-bridged (carboxylate and hydroxypyridinato) di-Rh and di-Ru complexes catalyze nitrenoid reactions on methyl substituted bishomoallylic sulfamates. These reactions proceed in selective manner and lead to allylic amine and aziridine formation. However, the mechanism and factors controlling the selectivity of these reactions still remain unknown. As such, we studied the mechanisms and factors controlling the allylic amine and aziridine formation in these complexes. These density functional studies show the importance of nature of (1) transition metal atoms, (2) bridging and proximal ligands, (3) substitution in substrate molecule, as well as (4) lower-lying spin states. For example, for [Ru_2(*hp*)$_4$Cl], **1**, (where *hp* = OC_5H_4N, hydroxypyridinato) we have shown that: (i) the energetically most favorable isomer of **1**, the (4,0)-complex with all four pyridine nitrogens coordinated to a single Ru center, has the quartet ground state with 1.71 and 1.06 unpaired α-spins at Ru^1- and Ru^2-centers, respectively; (ii) its Ru^1 center is an intermediate-spin Ru(II), while Ru^2 center is a low-spin Ru(III), (iii) the coordination of NSO_2OR to **1** forms the complex **1.a** with the doublet ground electronic state (an 0.82 unpaired α-spin is located on the Ru^2-center) and the Ru^1=NSO_2OR double bond. Allylic amine formation from the doublet **1.a** proceeds via ΔH=14.82(ΔG=16.74) kcal/mol energy barrier and leads to the quartet state, diradical, intermediate, which later converges to quartet state amine complex with a small energy barrier. The overall process is calculated to be an exothermic by 70.48(65.38) kcal/mol. Aziridination of the **1.a** occurs via a slightly higher, ΔH=15.81(ΔG=18.0) kcal/mol, energy barrier at doublet state transition state and leads to the quartet state (again via a radical pathway) aziridine complex**.** This process is found to be exothermic by 38.68(37.43) kcal/mol. Thus, the energy barrier required for allylic amine formation from **1.a** is 0.99 (1.26) kcal/mol smaller than that for aziridine formation.

For the [Ru_2(*esp*)$_2$(SbF_6)], **2**, we have found a similar picture with the following differences: (i) the calculated α-spins on Ru^1 and Ru centers of **2** are 1.56 and 1.20, respectively; (ii) the ground electronic state of the complex **2**-NSO_2OR, **2.a**, is the doublet state with 1.06 and 0.11 unpaired α-spins on Ru^2 and Ru^1, respectively, and 0.33 unpaired β-spins on N; and (iii) the energy barrier required for allylic amine formation from **2.a** is by 0.25 (0.28) kcal/mol larger than that for aziridine formation.

Comparison of the factors controlling allylic amine and aziridine formation in the di-Ru and di-Rh systems provide more insightful information and will be discussed during the presentation.

IL26

CYCLODEXTRIN FUNCTIONALISATION FOR CATALYSIS

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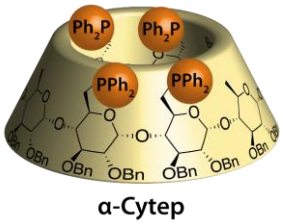
Concave molecules such as cyclodextrins desperately need efficient poly hetero-functionalization methods to fulfil their promises. Based on the discovery of a regioselective debenzylation reaction of sugars, and the understanding of its mechanism,[1] we delineated several strategies to access such cyclodextrins. Bascule-bridging[2] and tandem azide-reduction/deprotection[3] are two complementary ways to reach an unprecedented degree of complexity of functionalization of the primary rim of cyclodextrins allowing the access to a library of diversely functionalised cyclodextrins. The access to such complex structures allows applications in a wide range of areas. We explored some, such as asymmetric catalysis using regioisomers to induce enantioselectivity[4] or tetraphosphine cyclodextrins reaching very high TONs,[5] but it is our strong belief that many other possibilities are offered through this methodology.



α-Cytep

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IL27

COMPUTATIONAL STUDIES ON THE MECHANISMS FOR CARBON-CARBON BOND FORMATION: CROSS-COUPLING AND BEYOND

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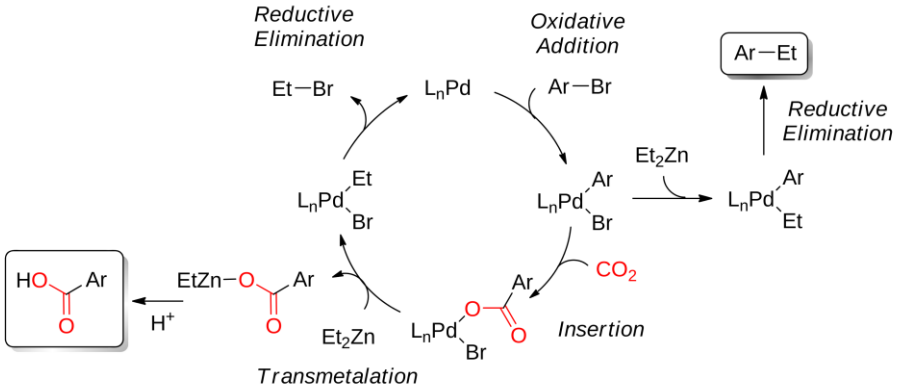
Selective formation of new carbon-carbon bonds under mild conditions is an obvious target for homogeneous catalysis, as it is one of the keys to the synthesis of more complex organic molecules. Palladium-catalyzed cross-coupling reactions are among the most efficient methods for the creation of new carbon-carbon bonds. The mechanism consists of three main steps: oxidative addition, transmetalation and reductive elimination. Our knowledge of these steps has improved in recent years thanks in part to computational studies that will be briefly reviewed. One of the main complications is the existence of a large amount of intermediates and transition states in the catalytic cycle. The presence of large bulky phosphines as ligands also poses particular problems in terms of conformational diversity.



Other catalytic processes for carbon-carbon bond formation, such as direct arylation or carbon dioxide insertion (see scheme), have some mechanistic connections to cross-coupling. They have been also investigated computationally, and their particular features will be highlighted.

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IL28

IONIC LIQUID ORGANOCATALYSTS AS EFFICIENT TOOLS OF GREEN CHEMISTRY

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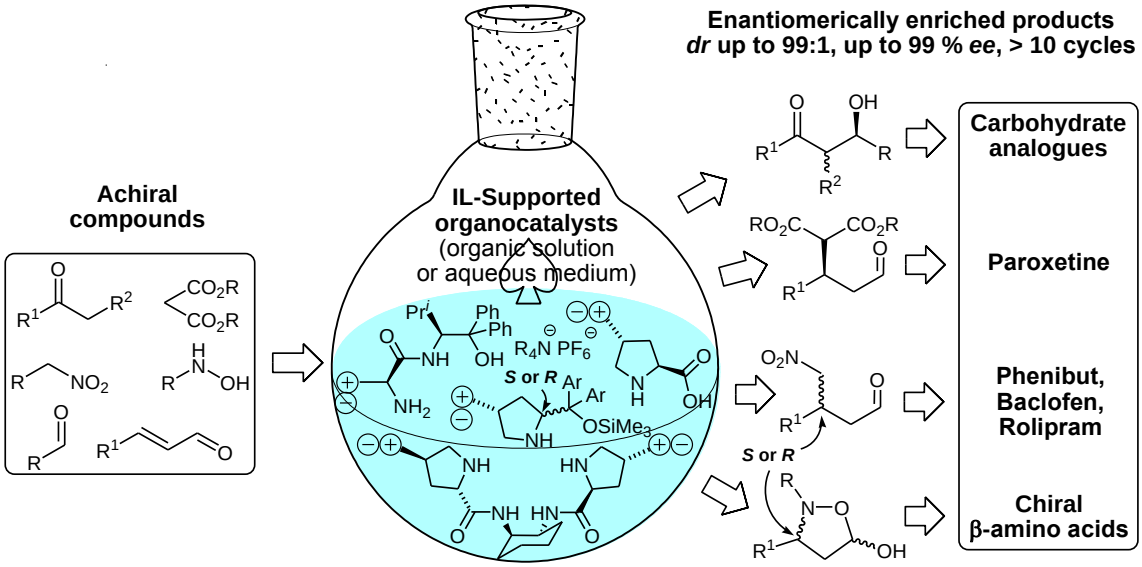
During the last decade, the organocatalysis (catalysis by small, metal-free organic molecules) has attracted considerable attention as it allows regio-, stereo- or enantioselective syntheses of practically useful compounds from available precursors under simple and environmentally safe experimental conditions. However, the separation of generated products and homogeneous organocatalysts remains a challenge. Easily recoverable forms of organocatalysts are mostly needed for industrial applications.

We have developed convenient green chemistry protocols for stereo- and enantioselective reactions of carbonyl compounds (aldol, Michael, etc.) in the presence of organocatalysts (phase-transfer catalysts or catalysts bearing Brønsted or Lewis active sites) modified with ionic groups (ionic liquid (IL) fragments). A catalyst could be attached to the IL-fragment through the electrostatic interaction or tagged to the cation by means of a covalently bonded spacer group. These modifications significantly reduce (but not to zero) solubility of the catalyst in organic and/or aqueous phases and facilitate its recovery. Furthermore, here emerges an opportunity to tune catalyst properties by varying cation and/or anion nature and analyze it by conventional NMR or MS techniques. Carbohydrate analogues, β-amino acids and central nervous system medications have been synthesized with extremely high stereo- and enantioselectivities using the developed catalysts at the key steps. Tetraalkylammonium salts and proline- or prolinamide derivatives could be more than 10 times reused in aldol reactions without any loss in their activity and/or reaction selectivity. However, the activity of O-TMS-prolinol or primary amine-derived catalysts in asymmetric Michael reactions, that involve an iminium-ion formation step, became lower after the third regeneration. Undesirable side reactions that poisoned these catalysts have been revealed by the ESI-MS and solutions (inert atmosphere or acidic reactivation) have been found to increase their operation period.



The work was financially supported by the Department of Chemistry and Material Sciences of RAS (Basic Research Program No. 1) and the Russian Foundation of Basic Research (project 12-03-00420).

IL29

NEW DIRECTIONS IN ORGANOCATALYSIS

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The lecture will demonstrate new directions in organocatalysis by new reactions, concepts and activation modes.

Oral Communications

OC1

DESIGNING ELECTRON-RICH 2,6-DIMETHOXY-SUBSTITUTED N-HETEROCYCLIC CARBENES AS ORGANOCATALYSTS FOR THE HYDROACYLATION OF ELECTRON-NEUTRAL ALKENES

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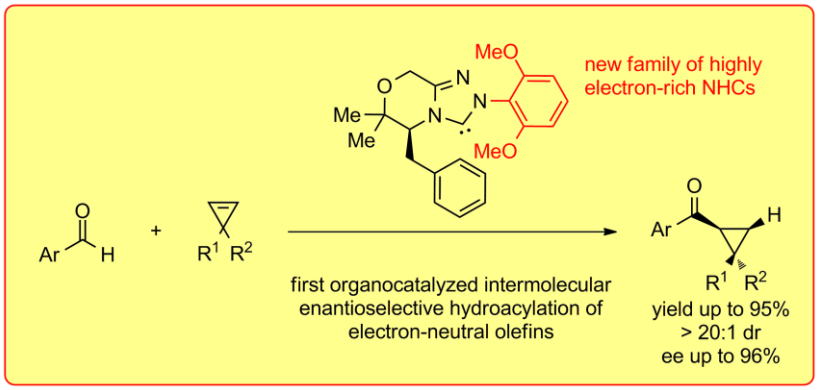
We report the design of a new, highly electron-rich N-heterocyclic carbene (NHC)[1] with a 2,6-dimethoxyphenyl substituent. This NHC enables for the first time the organocatalytic, asymmetric, intermolecular hydroacylation of an electron-neutral alkene, namely a cyclopropene.[2] This reaction yields valuable acylcyclopropanes in high yields and with excellent diastereo- and enantioselectivity starting from various aromatic aldehydes and cyclopropenes. The superb performance of the NHC in this challenging transformation encouraged us to synthesize a series of 2,6-dimethoxy-substituted NHCs and to test these in further hydroacylations.[3] Their performance in even more challenging hydroacylations of unstrained olefins is also reported.



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OC2

TRANSITION METAL COMPLEXES BASED ON 1,8-NAPHTHYRIDINE LIGANDS-PREPARATION AND CATALYSIS

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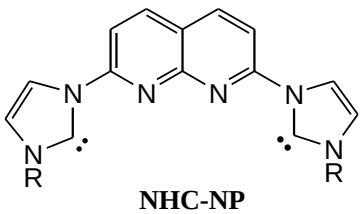
Ligands, that can coordinate two metal centers in close proximity, have received much attention recently. Such dinuclear complexes may show unusual properties and synergism between the two metals during the catalysis.[1] In our recent works, we have studied the coordination chemistry of various metal ions toward a series of l,8-naphthyridine based ligands and their catalysis.

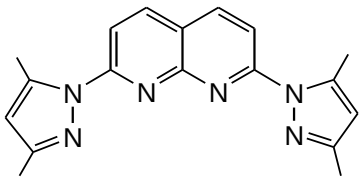
Palladium complex [{Pd_2(**NHC-NP**)$_2Cl_2$}(PF_6)] (**1**) containing NHC ligands was prepared via the carbene transfer reaction. Structural analysis shows that **1** consists of two Pd ions coordinating by two NHC ligands from two **NHC-NP** ligands in *trans* fashion. Due to the geometrical constrain and strong donating ability of NHCs, complex **1** provides an excellent reactivity on the cross coupling product on the Kumada-Corriu reaction of ArBr with cyclohexylmagnesium bromide. [2a]

Reaction of nickel(II) chloride with **Py-NP** in a 2:1 molar ratio gave an excellent yield of chloride-bridged dinickel complexes [{(**Py-NP**)(μ-$Cl)_2Ni_2Cl_2(CH_3OH)_2$}] (**2**). Crystal structure of **2** shows that the distance between nickel atoms is ca. 3.2 Å. This dinickel complex **2** has been tested in the catalytic homo-coupling of terminal alkynes leading to 1,3-diynes with the use O_2 as the oxidant, showing excellent activities. The catalytic activity of this complex is better than those of the mono-nuclear species.[2b]

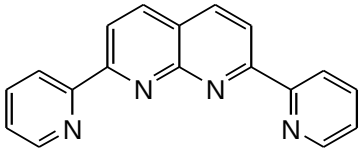
Treatment of a mixture of $Pd_2(dba)_3$ and $(PhCN)_2PdCl_2$ with **Bp-NP** in CH_2Cl_2 at ambient temperature yielded a water-soluble and air stable tripalladium species. Crystal structure shows that this complex is with the composition of [Pd_3(**Bp-NP**)$_2Cl_4$] and three palladium metal ions is arranged in a "L" shape geometry.[2c] This tri-palladium complex can act as a Lewis acid for the promotion of the condensation reaction of carbonyl compounds with indoles. Other metal complexes will also be discussed.



NHC-NP



Py-NP



Bp-NP

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OC3

IODINE- AND BORON TRIFLUORIDE- CATALYZED PEROXIDATION OF ACETALS

A.O. Terent'ev, V.A. Vil', I.B. Krylov, I.A. Yaremenko

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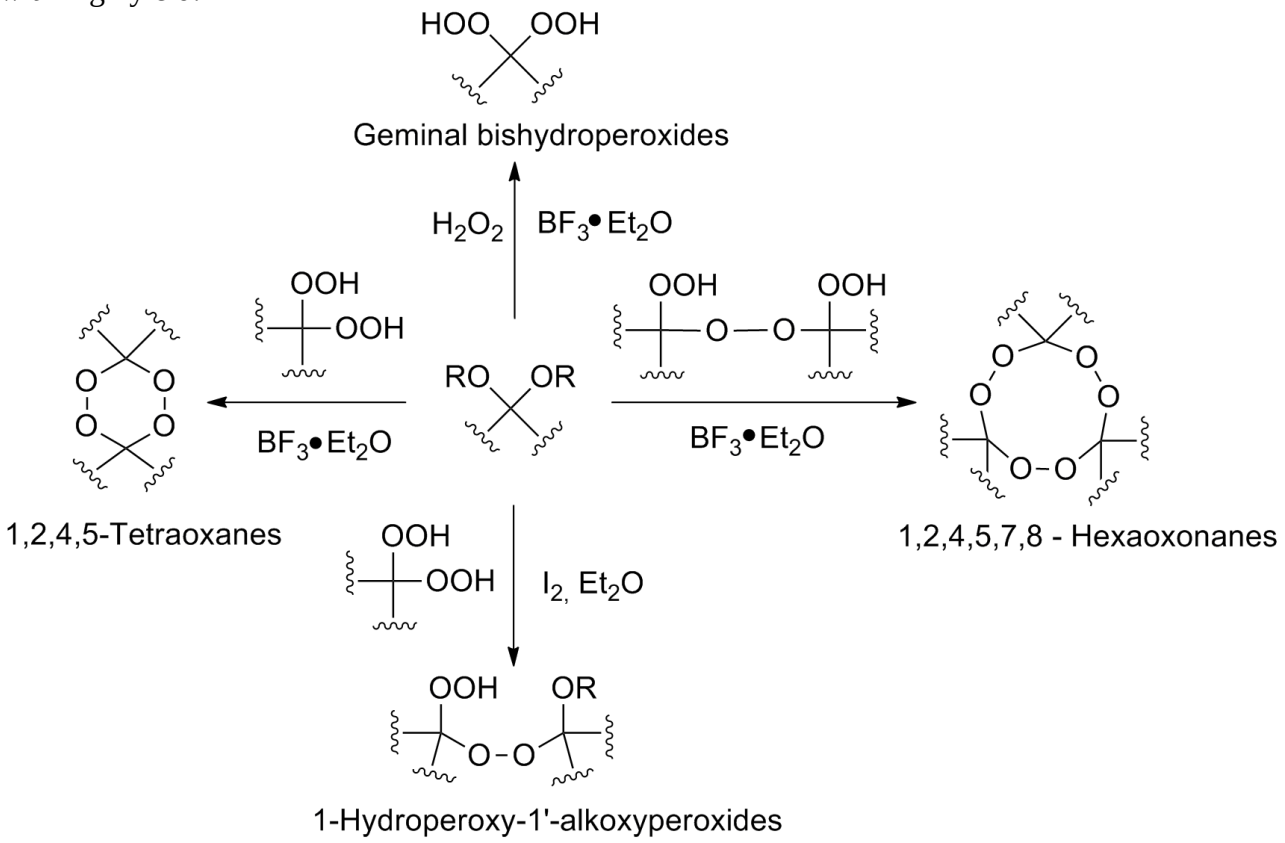
It was found that iodine and boron trifluoride effectively catalyze reaction of acetals with hydrogen peroxide and hydroperoxides. As the result of these reactions gem-bishydroperoxides, tetraoxanes, hexaoxonanes, and 1-hydroperoxy-1-alkoxyperoxides are obtained. The nature of the solvent has an important influence on the formation of target products.
Application of iodine and boron trifluoride makes it possible to prepare peroxides selectively and with high yield.



This work is supported by the Grant of the Russian Foundation for Basic Research (Grant 11-03-00857-a), and the Ministry of education and science of the Russian Federation (Grant 11.519.11.2038).

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OC4

RUTHENIUM-CATALYSED sp^2 C-H BOND ACTIVATION AND FUNCTIONALISATION

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The catalytic functionalisation of inert sp^2 C-H bonds for selective C-C bond cross-couplings has a tremendous importance as it can soon replace the very useful classical catalytic cross-coupling reactions between an organometallic (M = Li, MgX, ZnX, BR_2, SnR_3, …) when regioselectivity is found.

The lecture objective is to present the advantages brought by cheap, air and water stable ruthenium(II) catalysts for cross-coupling reactions from inert C-H bonds, even operating in water as solvent.

- Regioselective syntheses of polyheterocycles and tridentate ligands will be shown, using ruthenium(II)-carboxylate and carbonate systems, and the mechanism of C-H bond deprotonation discussed.
- The direct functionalization of imines as a route to functional ketones and bulky amines via sequential C-H bond arylation/hydrosilylation will be presented.
- The dehydrogenative oxidative cross-coupling reactions involving two sp^2C-H bonds will be demonstrated in alkenylation reactions with ruthenium catalysts and oxidizing partners.
- **Catalysis in water :** Examples of C-H bond functionalization **in water** will be selected.

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OC5

NEW ENANTIOSELECTIVE SYNTHESIS OF SUBSTITUTED NUCLEOSIDES

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Modified nucleosides continue to hold a central position in the chemotherapy of cancer and viral diseases, and in particular, 2′-modified nucleosides play an important role in research aimed at understanding the detailed molecular basis of RNA function. In connection with a program in the antiviral area, we needed to prepare multikilo amounts of uridine derivatives that we diversely functionalized at the 2’ and 4’ positions. Although these compounds are known and have been widely incorporated into modified nucleic acids, no practical synthesis of this interesting building block has been reported, and even its physicochemical properties are not fully described. In this presentation, we will describe the development of successful methodology for the efficient synthesis of such derivatives that allowed the preparation of multi-hundred kilos of the API.

OC6

LABILITY OF INTACYCLIC BONDS OF NOVEL CYCLIC P,N-LIGANDS - PROBLEM OR ADVANTAGE?

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Various P,N-containing heterocyclic and macrocyclic ligands are avaible via Mannich-type condensations in the systems: primary phosphine (secondary diphosphine)/formaldehyde/primary amine(diamine). [1]

During the last decade we found out few unexpected processes demonstrating a lability of P-CH_2-N fragments of these phosphines. It has been found that $P^RP^SC^S$-isomer of 7-membered bisphosphines undergoes a selective stereoconversion with the predominant formation of corresponding $P^RP^RC^S$-isomer. 14-Membered compounds totally dissociate to 1-aza-3,6-diphosphacycloheptanes, whereas a crystallization causes contrary processes. The reaction leading to the exchange of substituents on N-atoms of 16-membered P,N-macrocycles has been shown. The first example of the transformation of 1,5-diaza-3,7-diphosphacyclooctanes on the Au_3 cluster template into 16-membered cyclic aminomethylphosphine ligand was uncovered recently, as well as a row of examples of high yield syntheses of complexes containing P,N-cyclic ligands in the stereoisomeric form differ from the starting ligand.

It has been shown that those ligands could form effective biomemetic electrocatalytic systems for hydrogen oxidation and C-C cross-coupling [3].

This work was supported by RFBR (No.10-03-00380-a, 11-03-12152-ofi_m), President's of RF Grant for the support of leading scientific schools (No.NSh-6667.2012.3), VW Foundation (No 85 625).

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OC7

APPLICATION OF DABCO AS AN EFFICIENT ORGANOCATALYST FOR [4+2] CYCLOADDITION REACTION IN A MICROWAVE-ASSISTED SYNTHESIS OF SUBSTITUTED ANILINES

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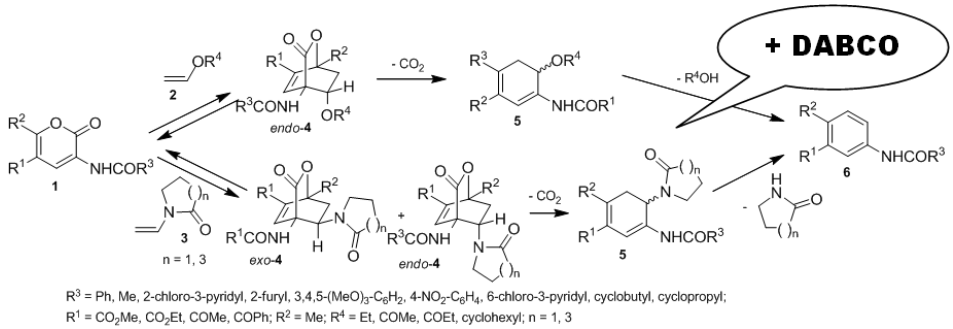
Diels–Alder reaction[1] is still one of the most important tools in organic chemistry and is widely used in construction of six membered rings with high degree of regio- and stereoselectivity. When 2*H*-pyran-2-ones are used as dienes and dienophiles contain groups that could be eliminated during subsequent reaction steps, various reaction pathways are to be considered. We investigated[2] cycloadditions between electron deficient 2*H*-pyran-2-ones **1** and electron rich vinyl-moiety-containing dienophiles **2** or **3** (which serve as synthetic equivalents of acetylene). DABCO showed an obvious acceleration effect on the overall reaction course (**1** → **6**) and was found to be the most appropriate catalyst among many examined. We were able to show that DABCO did not affect the rate of the cycloaddition (**1** → **4**) neither CO_2 extrusion (**4** → **5**), but clearly facilitated the elimination (**5** → **6**) of the group stemming from the dienophile **2** (OR^4, NR_2). To confirm this assumption we independently prepared 2-oxabicyclo[2.2.2]oct-5-ene intermediate **4** (actually, the only way was to apply high-pressure synthesis, because under thermal conditions the elimination of CO_2 is inevitable). Microwave-assisted heating[3] of **4** with DABCO (or without any catalyst) gave us insight in this catalyzed reaction step. When DABCO was added aromatic compound **6** was the only reaction product obtained; this was in clear contrast to the reaction without DABCO, where a mixture of aromatic compound **6** and dihydro compound **5** was produced (in both cases 2-oxabicyclo[2.2.2]oct-5-ene **4** was consumed completely). However, cycloaddition under high pressure conditions proceeded to the same extent and yielded only **4**, regardless of the presence of DABCO as an organocatalyst. At this point it is important to stress that acid catalysis (with Dowex) was in most cases ineffective due to the polymerization propensity of the dienophiles **2**. Furthermore, structures of both intermediates **4** and **5** were unequivocally confirmed by single-crystal X-ray diffraction analyses[4] and the stereoselectivity of the transformations was additionally supported by semiempirical calculations. Further interesting results with acrylonitrile will also be presented.[4]



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OC8

LEWIS ACID CATALYZED (3+N)-CYCLOADDITIONS/ANNULATIONS OF DONOR-ACCEPTOR CYCLOPROPANES

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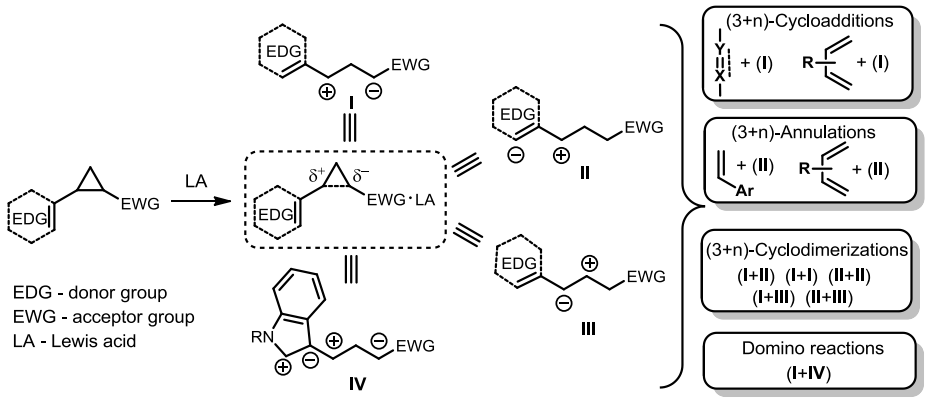
Donor-acceptor (DA) cyclopropanes are equipped with donor and acceptor groups at vicinal positions that selectively polarizes C-C bond between these groups. Lewis acids, used as an catalyst, enhance this polarization allowing for interaction of DA cyclopropanes with nucleophiles, electrophiles and ambiphilic reagents mostly as synthetic equivalents of synthon **I**.[1] Recently, this type of reactivity we have also found in (3+2)-[2] and (3+4)-cycloadditions[3] of DA cyclopropanes to furans, nitriles and conjugated dienes. Moreover, we have discovered several other types of DA cyclopropane reactivity.[4-6] Thus, as synthetic equivalents of synthon **II** they participate in (3+2)- and (3+4)-annulations with styrenes and dienes,[4] respectively. The presence of several nucleophilic and electrophilic centers in DA cyclopropanes allows us to perform their (3+3)-cyclodimerizations, where they react as synthetic equivalents of the synthons **I** and **II** mentioned above.[5a] Unusual behavior of DA cyclopropanes has been found in their (3+2)-cyclodimerization where one molecule of a cyclopropane provides only two carbon atoms (synthon **III**) in a newly formed ring.[5b] For indole-derived DA cyclopropanes we have developed domino cyclodimerization furnishing unprecendent pentaleno[1,6a-b]indole skeleton.[6]



This work was supported by the Russian Foundation of Basic Research (12-03-00717-a).

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p-NITROPHENYL AS ACTIVATING GROUP IN ORGANOCATALYSIS VIA IMINIUM. MECHANISTIC INSIGHTS AND SYNTHETIC APPLICATIONS

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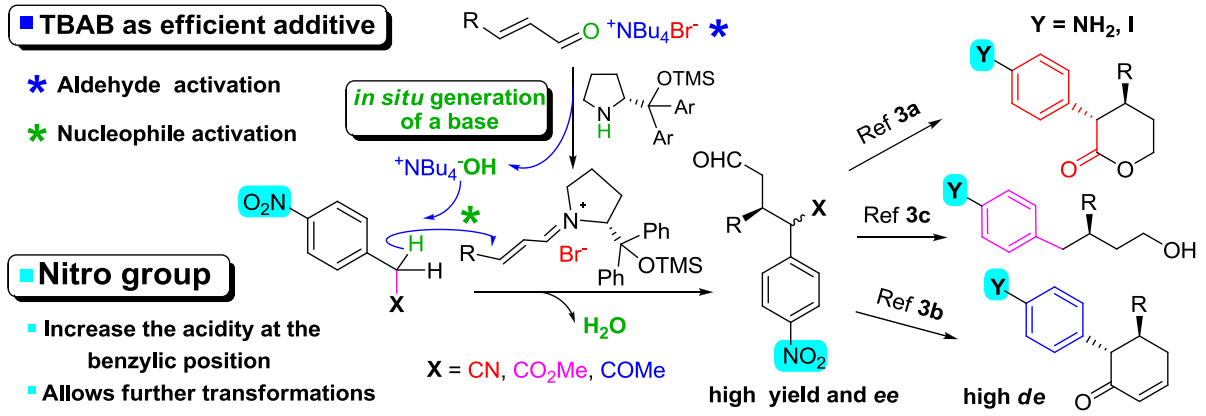
During the past few years, the research area of asymmetric organocatalysis has grown rapidly to become one of the most exciting and modern tools for the synthesis of optically active compounds. [1] In particular, iminium ion catalysis using chiral secondary amines is a powerful method to introduce nucleophiles at the β position of α,β-unsaturated aldehydes *via* enantioselective Michael addition. [2] Nevertheless, some challenges remain unsolved, such as some mechanistic aspects and the structural limitation of the nucleophile.

With the exception of the nitroderivatives, the pro-nucleophilic species require the presence of two geminal electronwithdrawing groups to get the appropriate acidity of the methylenic protons to intervene in organocatalytic processes. We have been able to use arylacetic acid derivatives as new class of nucleophiles in organocatalytic reactions through an iminium intermediate by incorporating a nitro group at the *para* position of the aromatic ring, which confers enough acidity to the benzylic protons. The resulting Michael adducts, which are obtained in high yields and enantioselectivities, are interesting building blocks for the diastereoselective construction of more complex molecules not easily accessible by other routes. [3]



Despite the impressive recent advances in iminium catalysis, some mechanistic features still remain unknown. As a better understanding of the catalytic cycle would allow the design of more efficient processes, we have systematically analyzed all the parameters which can affect the reactivity and enantioselectivity of these reactions. We have rationalized several aspects regarding the nature of the nucleophile, aldehyde, solvent and the role of the additives. Recently we have demonstrated that quaternary ammonium salts are efficient neutral additives in organocatalytic Michael additions to enals[3c], promoting sequentially iminium formation and activation of the nucleophile *via* enolate due to the formation of a base during the reaction course (see scheme above).

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OC10

NEW CATALYSTS FOR ENANTIOSELECTIVE INTRAMOLECULAR HYDROAMINATION

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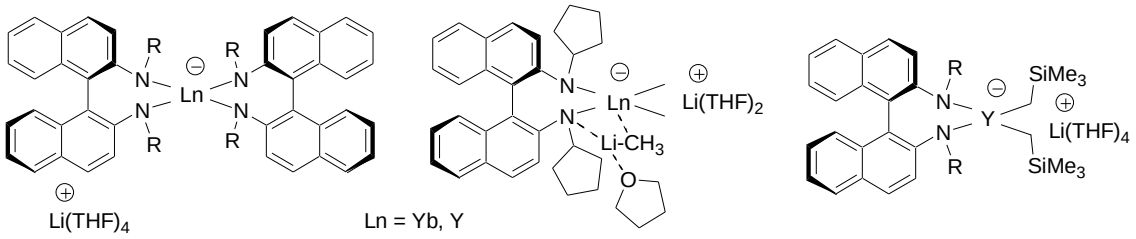
The metal-catalysed asymmetric hydroamination of olefins, formally the addition of a –NH unit on a C=C double bond, [1] perfectly meets the criteria of atom economic reaction. The fine tuning of catalysts to perform this transformation with high enantioselectivities remains at present a real challenge to take up, considering the importance of these compounds in medicinal and natural products chemistry.

In recent years numerous lanthanide and group IV based catalysts proved successful for promoting this transformation but no general solution has been found yet for the synthesis of a wide range of substrates under mild conditions. We have synthesized different new families of efficient lanthanide amide ate complexes based on the binaphthylamido ligand that promoted various hydroamination reactions. [2]

These complexes could promote the formation of several pyrrolidines in up to 87 % ee at RT. Some piperidines were also cyclized and recent results show that sterically demanding 1,2-disubstituted aminoalkenes could also be transformed with up to 78 % ee. [3] These chiral complexes also demonstrated their ability to promote the cyclization of amine-tethered trisubstituted alkenes in up to 55% ee, as the first report of the formation of enantioenriched quaternary centers by an hydroamination reaction. [4]



Finally, other new chiral complexes will be presented that catalyze the intramolecular hydroamination of aminodienes leading to propenyl-pyrrolidine and piperidine with high activities and enantioselectivities.

Particular attention has been drawn towards the synthesis of these catalysts, available in few synthetic steps and mostly used *in situ*. These species are thus promising for their wide application in challenging hydroamination reactions.

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OC11

TOTAL SYNTHESIS AND BIOLOGICAL EVALUATION OF NEW ANTITUMOR ALLOCOLCHICINOIDS

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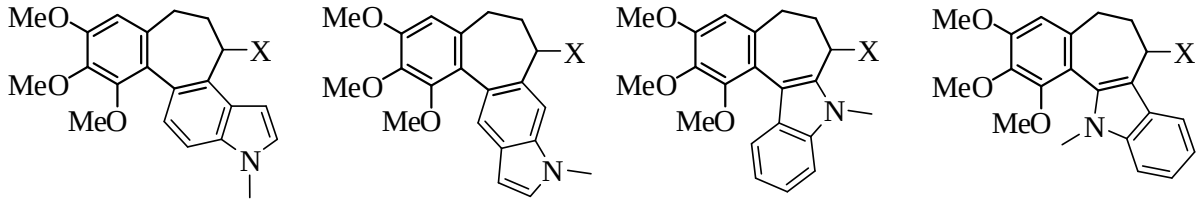
A range of indole-containing allocolchicinoids was synthesized using catalytic approaches:



Several from synthesized compounds manifest antitumor activity at nanomalar or even at subnanomolar concentration range, along with particularly low unspecific cytotoxicity.

Acknowledgements - this work was supported by the DAAD Program (№ A/08/79551), Russian Federal Target Program (16.740.11.0476 and 14.740.12.1382) and RFBR grant 12-03-00214-a.

DIRECT ENANTIOSELECTIVE VINYLOGOUS MICHAEL ADDITION OF 3-ALKYLIDENE OXINDOLES TO NITROOLEFINS CATALYZED BY BIFUNCTIONAL CINCHONA ALKALOID THIOUREAS

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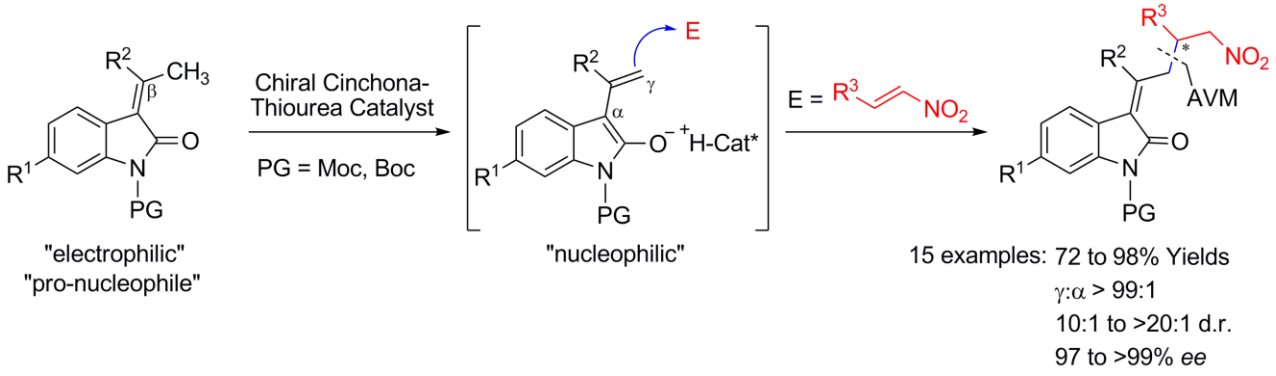
3-Alkylidene oxindoles occupy a preeminent position among the various classes of chemically and medicinally relevant small molecule scaffolds. Their plural functional architecture featuring a lactam carbonyl flanked by a highly substituted exocyclic double bond renders them enabling intermediates to be elaborated into a myriad of useful nitrogen heterocycles of varied complexity.[1] While 3-alkylidene oxindoles are well known for their electrophilic reactivity at the C-β position, an "umpolung" option can also be envisaged, which capitalizes on the vinylogous pro-nucleophilic character of the γ-alkyl group in the ylidene matrices. Continuing our discovery program aimed at unveiling the synthetic potential of novel, oxindole-based vinylogous scaffolds,[2] we developed the first direct, organocatalytic asymmetric vinylogous Michael reaction of differently substituted 3-alkylidene oxindoles with nitroolefins, catalyzed by the consecrated bifunctional cinchona alkaloid-based thioureas.[3] Provided that *N*-carbamoyl protected oxindoles were used, the reaction scope and generality were substantial, and no matter whether there were neutral, electron-withdrawing, or electron-releasing substituents on the reaction components, the reactions performed efficiently, with outstanding levels of regio-, diastereo-, and enantioselectivity.



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OC13

THE SWEET SIDE OF CATALYSIS - CHIRAL LIGANDS FROM SUGARS

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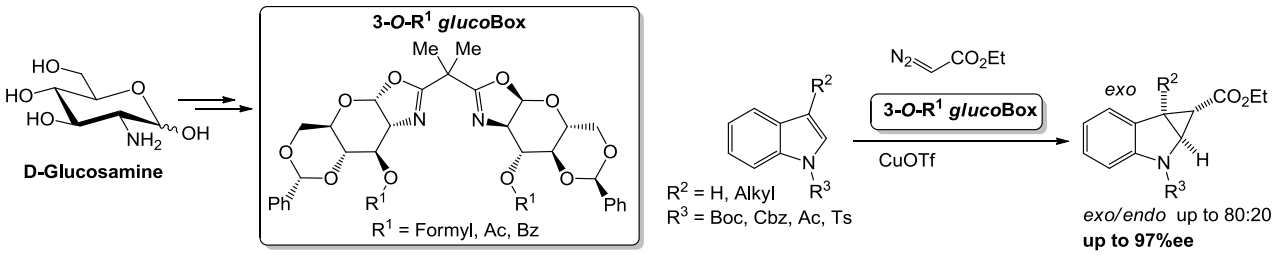
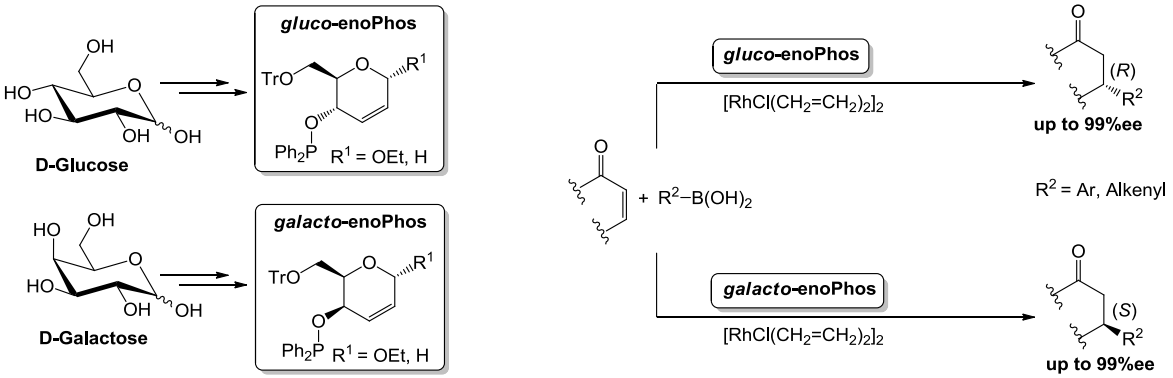
Carbohydrates - the most abundant compounds from the *chiral pool* - have long been disregarded as starting materials for the design of chiral ligands for asymmetric metal catalysis and only recently interest in carbohydrate-derived ligands has significantly increased.[1] We have designed new bis(oxazoline) ligands based on D-glucosamine[2] and olefin-phosphinite ligands based on D-glucose and D-galactose,[3] all of which offer excellent levels of stereoinduction. Our *gluco*Box ligands have achieved up to 97%ee in the asymmetric Cu(I)-catalysed cyclopropanation of indoles,[4] which has not been reported up to now.[5] This reaction can be used for the buildup of quaternary stereocentres.



Ligands *gluco*-enoPhos and *galacto*-enoPhos have been employed in asymmetric Rh(I)-catalysed 1,4-additions of aryl- and alkenylboronic acids to enones,[6] giving products in up to 99%ee in opposite configuration thus acting as a pair of highly efficient *pseudo* enantiomers.[3c]



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OC14

LIBRARIES OF TUNABLE P*-CHIROGENIC PHOSPHACYCLANES: PREPARATION STRATEGIES AND APPLICATIONS IN ENANTIOSELECTIVE CATALYSIS

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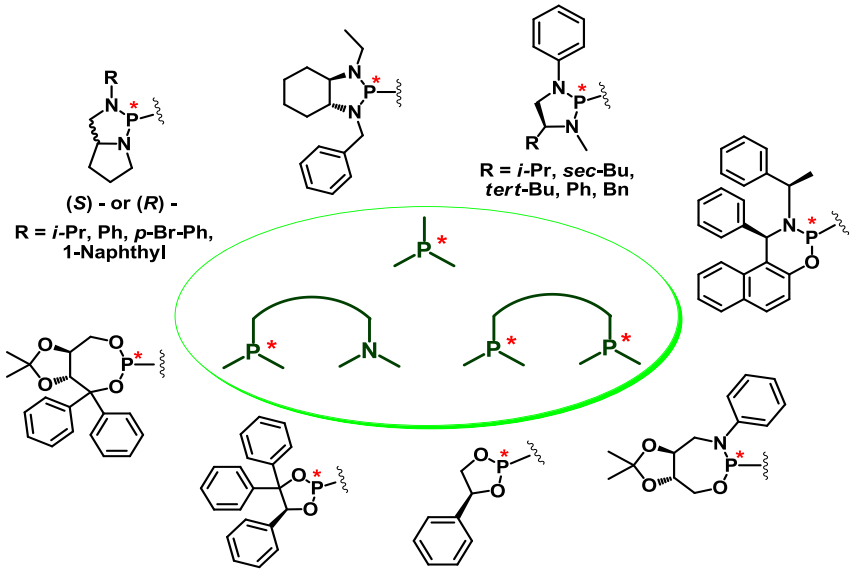
Starting enantiopure synthons (diamines, (aminomethyl)naphthols, aminoalcohols, diols) have been prepared from inexpensive (*S*)- and (*R*)-α-aminoacids, (*R*)-amines, (*R*,*R*)-tartaric and (*S*)-mandelic acids in multigram scale. Based on these synthons, novel groups of P^*-mono-, P^*,*N*- and P^*,P^*-bidentate phosphite-type phosphacyclanes, possessing asymmetric phosphorus atoms, have been created:



The new ligand's libraries have demonstrated good to excellent enantioselectivity in the majority of the important transition metal-catalyzed asymmetric processes. In particular, up to 99% *ee* was achieved in the Pd- and Pt-catalyzed allylation of 1,3-diphenylallyl acetate and cyclohex-2-enyl ethyl carbonate, up to 91% *ee* in the Pd-catalyzed desymmetrization of *N*,*N*-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate, up 99% *ee* in the Rh-catalyzed asymmetric hydrogenation of unsaturated acid esters, up to 99% *ee* in the Rh-catalyzed addition of phenylboronic acid to cyclohexenone. Some products of the aforementioned reactions are a key precursors for the synthesis of chiral unsaturated acid esters and amides, as well as valuable bioregulators (+)-juvabione (insecticide), (+)-wine lactone (fragrance compound), mannostatin A (antiviral drug for the future) and (-)-swainsonine (anticancer drug for the future).

We acknowledge the financial support from the Russian Foundation for Basic Research (Grant No. 11-03-00347-a).

OC15

ASYMMETRIC CATALYSIS IN THE PHARMACEUTICAL INDUSTRY: FROM CASE STUDIES TO CURRENT FRONTIERS AND NEW DIRECTIONS

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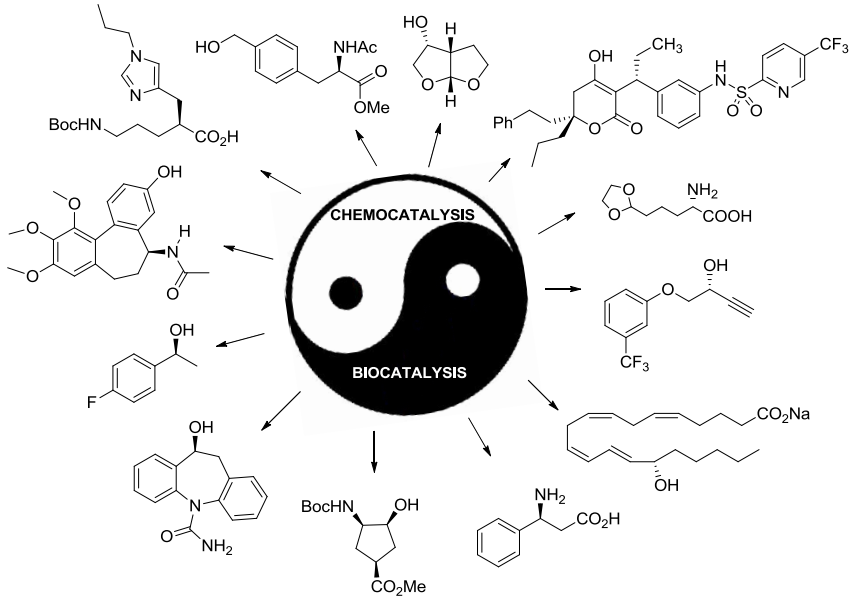
Optically active synthons are ubiquitous in pharmaceutical compounds. The need for large-scale production of highly enantioselective products requires the pharmaceutical industry to develop efficient and economic ways of preparing these intermediates.
At the Chirotech Technology Centre, we focus on the development of chiral synthons for APIs and pharmaceutical intermediates. In the asymmetric synthesis of the compounds of interest we employ state-of-the-art technology and exploit asymmetric catalysis in its most diverse aspects, *e.g.* hydrogenation, hydroformylation, phase transfer catalysis and allylic alkylation with transition metals along with wide transformation scope in biocatalysis.
We continuously aim to expand our established experience in the field of asymmetric catalysis by looking at cutting-edge developments for applied research in the pharmaceutical industry.



Drawing from industrial examples,[1-9] we would like to present case studies of applications of asymmetric catalysis on a commercial scale and discuss our opinions on current frontiers and directions for catalysis within the pharmaceutical industry.

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OC16

CATALYTIC REDUCTIVE DOMINO TRANSFORMATIONS OF 1,2-OXAZINES

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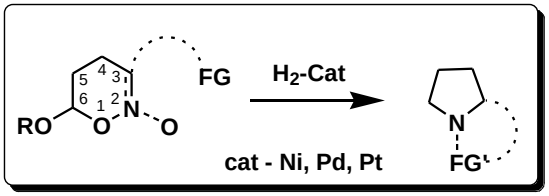
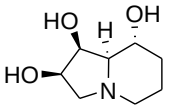
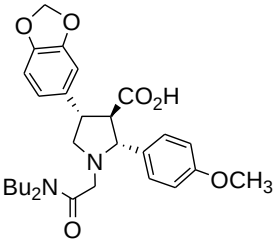
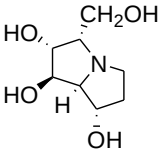
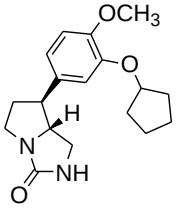
1,2-Oxazines are considered as versatile intermediates in the target-oriented organic synthesis due to their availability and high synthetic potential for the construction of stereochemically complex nitrogen-containing molecules [1]. Probably, the most useful and unique transformation of 1,2-oxazines is the reductive ring contraction to pyrrolidines [1,2]. This multi-step domino reaction proceeds under high-pressure hydrogenation conditions and is catalyzed by heterogeneous transition-metal catalysts. Introduction of functional groups in the 1,2-oxazine ring opens possibilities for the construction of additional rings in the same reductive domino sequence allowing to access various bicyclic scaffolds [1,3].

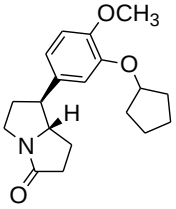


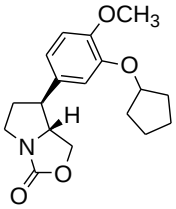

Swainsonine
(Reissig et al, 1995)


ABT-627 Atrasentan
(Reissig et al, 2003)


Alexine
(Gallos et al, 2002)


(+)-and (-)-CMPI


(+)-and (-)-CMPH


(+)-and (-)-CMPO

Highly potent PDE 4B inhibitors

In the presentation the mechanism of 1,2-oxazine reduction to pyrrolidines and recent examples of its application in asymmetric total synthesis developed by us and other research groups are discussed [3].

The financial support from Russian foundation for basic research (grant #11-03-00737a) and President's grant council (grant MK-1361.2011.3) is greatly acknowledged.

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OC17

MECHANISM-BASED ORGANIC AND ORGANOMETALLIC CHEMISTRY OF CARBODIIMIDES

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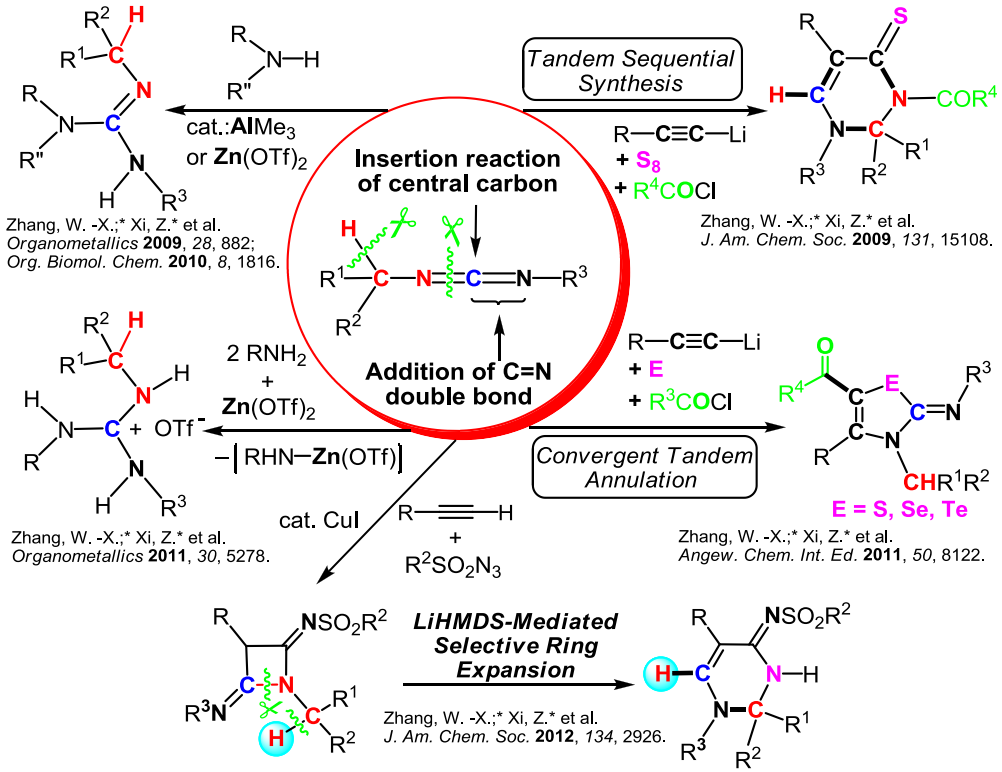
For more than 130 years, carbodiimides (RN=C=NR) have proved versatile reagents since the carbodiimides were first correctly formulated and characterized by Weith. Carbodiimide chemistry mainly included the use as condensing agents in the preparation of nucleotides and peptides, heterocycle synthesis, cycloaddition reactions, biological modification, etc. For organometallic chemists, carbodiimides were used widely to synthesize amidinate/guanidinate ancillary ligands for stabilization of various metal complexes owing to the well established nucleophilic addition process of organometallic reagents to carbodiimides. Scheme 1 summarized our recent development on the metal-promoted carbodiimide chemistry.[1-4] To gain information on these processes, mechanistic studies were carried out by the isolation and characterization of the important reaction intermediates.



Scheme 1

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OC18

A MODULAR APPROACH TO CHIRAL IMIDATES: A NEW CLASS OF NITROGEN-BASED CHIRAL LIGANDS

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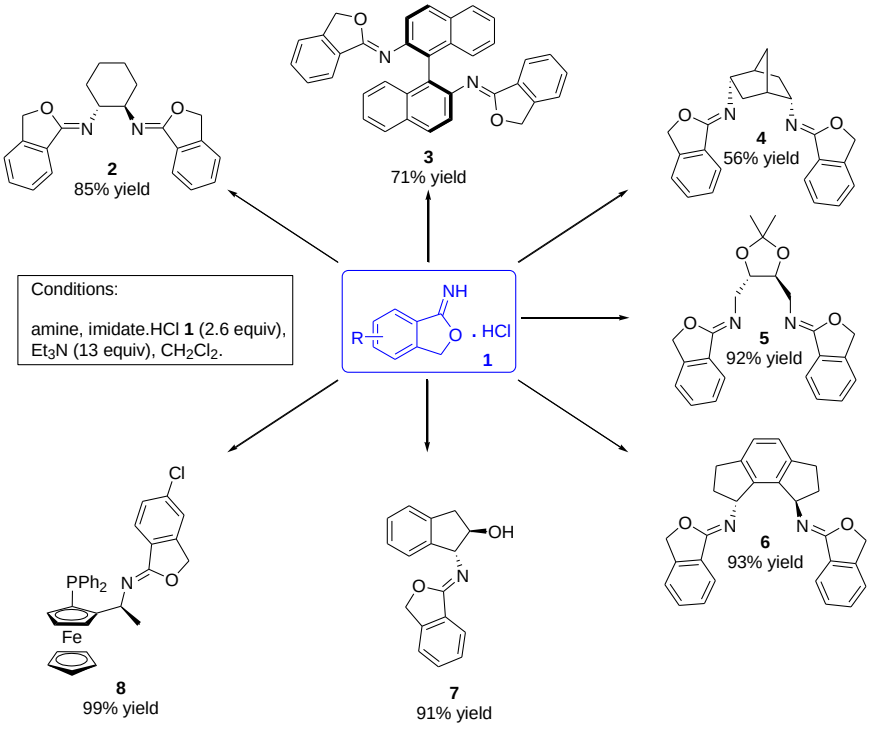
Nitrogen-containing ligands are known as ***cheap, readily accessible and stable*** alternatives for phosphane ligands [1], which are often very sensitive to air and require a multistep synthesis [2]. We wish to present a ***combinatorial approach*** to ***a novel type of nitrogen-based mono- and bidentate ligands*** [3,4]. These ligands are characterized by their ***modular structure***, allowing an ***easy one-step synthesis*** by simply combining two readily variable precursors which are either commercially available, or can be reached in only a few steps: a cyclic imidate **1** and a (chiral) amine, respectively diamine. These ligands show ***promising results*** in e.g. the Cu(I)-catalyzed asymmetric aziridination of methyl cinnamate, in asymmetric diethylzinc additions to benzaldehydes, in the Pd(0)-catalyzed asymmetric allylic alkylation and amination, and in Ir(I)-based asymmetric hydrogenation of alkenes.



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OC19

CYCLIZATION REACTIONS OF ENYNES THROUGH ORGANOMETALLIC Ru COMPLEXES

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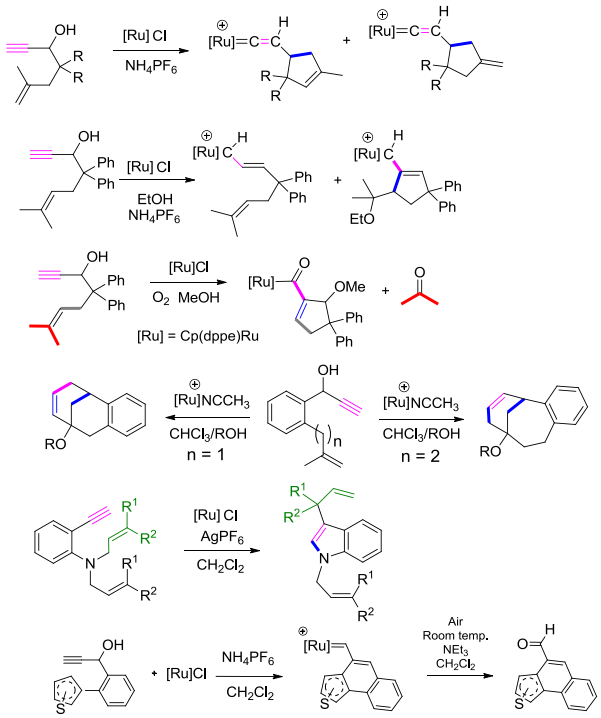
Organometallic Ru Complexes play key role in inducing novel C-C bond formation reactions of acetylenes and various enyne compounds. When the triple bond is accompanied with other unsaturated groups or functional groups with heteroatom, novel reactions take place. Cyclization of enyne compounds could be readily induced by cationic ruthenium complexes. Methyl substituents on the olefinic portion of the organic enyne plays important role in controlling the reaction pathway involving carbocationic intermediates. Interestingly, facile oxygenation reactions are also observed in the ruthenium induced cyclizations.



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OC20

ALKYNE METATHESIS FOR THE SYNTHESIS OF CF_3-CONTAINING AMINO ACID DERIVATIVES

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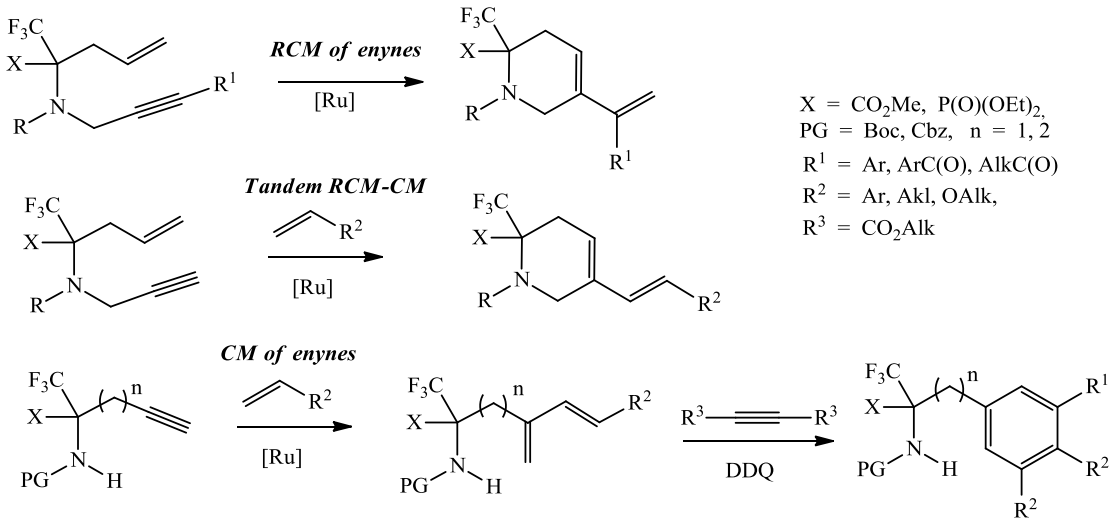
The introduction of trifluoromethyl (CF_3) groups into organic molecules can substantially alter their chemical and metabolic stability, lipophilicity, and binding selectivity because of the strongly electron withdrawing nature and large hydrophobic domain of trifluoromethyl groups.[1] Notably, many biologically active compounds, including the antidepressant *Prozac* and the herbicide *Fusilade*, contain the CF_3 groups as the essential motif.[1] As a result, much attention has been paid to the development of new synthetic methods for the introduction of the CF_3 groups into diverse organic compounds.[1,2]

Recently we have developed highly efficient syntheses of trifluoromethylated cyclic α-amino acid derivatives based on metal-catalyzed cyclotrimerization[3], 1,3-dipolar cycloaddition[4] as well as metathesis-type reations[5]. Now we report on new pathway to CF_3-containing α-amino carboxylic and phosphonic acid derivatives based on enyne cross-metathesis (CM), enyne ring closing metathesis (RCM) as well as tandem enyne RCM-CM.



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This work was financially supported by Russian Foundation of Basic Research (projects №№, 08-03-92504, 12-03-00557).

OC21

RARE EARTH COMPLEXES OF NEW MULTIDENTATE TETHERED PHENOXY-AMIDINATE LIGANDS. APPLICATIONS IN ROP OF LACTIDE

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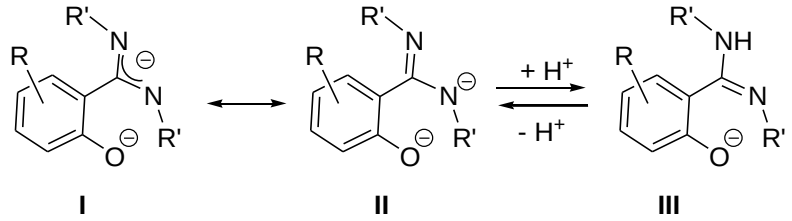
Given the success of the "constrained geometry" Cp-amido complexes of early transition metals in polymerization catalysis, the implementation of new ligand assemblies incorporating tethered anionic moieties can be of both fundamental and practical value.
New multidentate tethered amidine-phenol pro-ligands {4,6-*t*$Bu_2C_6H_2O$-(2-C(N-R)=N-R}H_2 ({LONR}H_2, R = *i*Pr, cyclohexyl (Cy), 2,6-*i*$Pr2C_6H_3$ (Ar)) were synthesized and their coordination chemistry with rare earth metals (Y, Nd, Sm and Yb) has been investigated.[1] Three different approaches were explored to coordinate these (pro)ligands onto rare earths: salt metathesis, and amine and methane elimination reactions. Thus, chloro, amido and alkyl complexes of group 3 metals have been obtained and authenticated. Two alternative coordination modes of this dianionic ligand (I and II) and a protonated mono-anionic form (III) have been evidenced in complexes:



I **II** **III**

Amido complexes of phenoxy-amidinate ligands are active initiators/catalysts, when combined with iPrOH or $PhCH_2OH$ used as co-initiators/chain transfer agents, in the ROP of *rac*-lactide, giving atactic to heterotactic-enriched PLAs. Studies on the catalytic activity of these complexes will be detailed.

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OC22

HETEROGENEOUS PHOTOCATALYSIS IN ORGANIC SYNTHESIS

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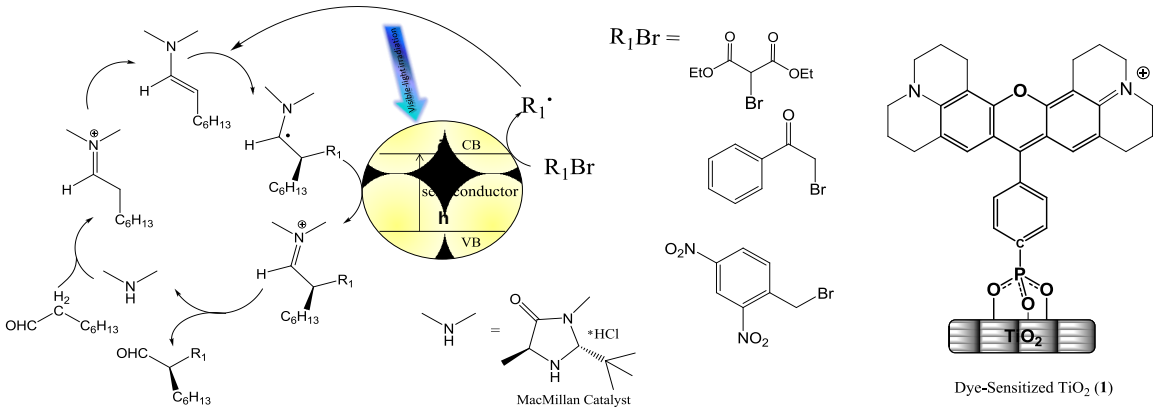
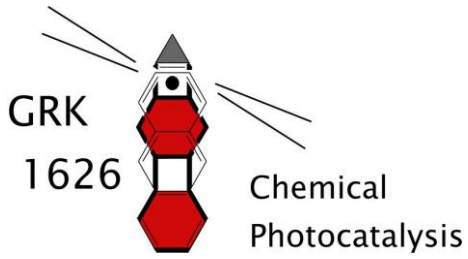
Visible light photocatalysis is a topic of increasing interest for many applications. One way of utilizing the visible range of the solar spectra is the combination of organo- and photoredox catalysis as pioneered by MacMillan [1a]. Using MacMillan´s catalyst in conjunction with inorganic semiconductors as sensitizers, we have investigated the asymmetric C-C coupling of octanal with different bromo-substrates [1].



The range of investigated semiconductors includes the well-known blank TiO_2 (P25), dye-sensitized TiO_2 (**1**) as well as novel $PbBiO_2Br$ semiconductors. The $PbBiO_2Br$ semiconductor was used in two modifications – nanoparticles and bulk material, which have band gaps of 2.56 eV and 2.47 eV, respectively and can be irradiated with 440 nm LEDs. TiO_2 was sensitized by the Phos-Texas Red dye, which was immobilized on the surface and showed an absorption maximum at 560 nm.

The products could be obtained in good to very good yields of up to 84 % ($PbBiO_2Br$ *nano*; 2-bromodiethylmalonate) and with excellent enantioselectivities of up to 96% ($PbBiO_2Br$ *nano*; bromoacetophenon) [2].

Other C-C bond formation reactions are under investigations in our group.



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Financial support: DFG: GRK 1626 – Chemical Photocatalysis

OC23

GREEN AND SUSTAINABLE CATALYSIS BY COPPER AND IRON NANOPARTICLES

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The last decade has witnessed a tremendous growth in the field of nanoscience and nanotechnology. The easy accessibility to nanoparticles has prompted investigations on their applications in catalysis. The recent reports showed amazing level of their performance as catalysts in terms of selectivity, reactivity and improved yields of products. The development of an efficient and industrially and environmentally acceptable catalyst constitutes one of the important goals towards sustainability and economic growth. As a part of our interest in this area we initiated an investigation to explore the potential of environmentally benign and inexpensive copper and Iron nanoparticles in organic reactions, particularly the functionalization of molecules.

Copper nanoparticles have been found to be very efficient catalyst for carbon-heteroatom bond formation. Thus, Copper nanoparticles have been used for the synthesis of aryl sulfides,[1] aryl selenides,[2] aryl and vinyl dithiocarbamates,[3] and aryl amines by reduction of aromatic nitro compounds[4] and azides.[5,6] Iron nanoparticles have been employed for the electrophilic amination of organo-copper reagents leading to the synthesis of functionalized tertiary amines[7] and reduction of nitro groups in water at room temperature.[8]

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OC24

GOLD-PALLADIUM ALLOY NANOPARTICLES SUPPORTED ON ALUMINA AND CARBON AS NOVEL EFFICIENT CATALYSTS FOR SELECTIVE OXIDATION OF GLUCOSE

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At present, gluconic acid or its salts used in the food, pharmaceutical, concrete and other industries are manufactured by enzymatic oxidation of glucose or glucose-containing raw materials produced by biomass conversion. Since the biotechnological processes have serious drawbacks in practice, replacing the enzymes as catalysts for glucose oxidation by an inorganic catalyst is of great interest for a long time. Gold both in form of sol and of supported metal is now considered as the most promising catalyst for gluconate production by aerobic glucose oxidation, showing quite good catalytic activity and selectivity along with the high resistance to deactivation [1]. For selective liquid-phase oxidations of some aldehydes (glyoxal) and alcohols (sorbitol and glycerol), doping of gold with palladium leads to further improvement in the catalytic performance coupled with the reduced catalyst cost [2]. However, the aerobic oxidation of sugars into sugar acids over bimetallic AuPd catalysts is still poorly studied, and the results obtained are rather controversial.

Herein, we report the results of the systematic study of the AuPd catalysts for the oxidation of glucose into sodium gluconate by dioxygen, whose primary goal was to tune the composition and nanostructure of bimetallic particles by changing a Pd/Au ratio in order to achieve optimal catalytic performance. For this purpose, a series of AuPd catalysts containing 1.5-2 at% (Pd+Au) with variation in the bulk Pd/Au ratio from 0.03 to 5.5 mol/mol were prepared by the intentionally designed procedures based on the sequential deposition of metals that allow avoiding their segregation and to obtain uniformly dispersed AuPd particles mainly below 5 nm in size regardless of the relative amount of the two metals. Mesoporous carbon and alumina were chosen as the catalyst supports, since they are preferable for application in the liquid-phase oxidation processes. The catalysts were characterized by XRD, TEM/EDX and XPS, with a special attention to the proof of the formation of the alloyed AuPd particles with the mean Pd/Au composition close to the nominal value for preparation. In turn, EXAFS and electrochemical techniques (CO stripping, copper underpotential deposition) revealed that upon decreasing the Pd/Au ratio, the particle structure changes from a "homophilic" structure (i.e. with a predominance of the number of Au-Au and Pd-Pd bonds over the number of Au-Pd bonds) to a heterogeneous (Au-core-rich and Pd-shell-rich) frame. During testing for the aqueous-phase oxidation of glucose into sodium gluconate by O_2 at 60°C and pH 8, the alloyed AuPd catalysts showed superior activities in combination with good selectivity and higher resistance to deactivation under the test conditions compared to monometallic Pd or Au nanoparticles on the same support. With an increase of the Pd fraction, the activity increases distinctly and reaches a maximum for Pd/Au = 0.2 (±0.03) mol/mol, exceeding the total activity of reference Pd and Au catalysts by a factor of 3 with 95% selectivity towards sodium gluconate at 100% conversion. When compared the samples with a similar Pd/Au composition, those prepared with the alumina support are characterized with higher catalytic activity than the carbon-supported catalysts. The reasons for the synergistic acceleration of glucose oxidation over the AuPd catalysts, as well as for the effects of their Pd/Au composition and the support nature on the catalytic properties are discussed on the basis of the catalyst characterization data.

The work was financially supported by the RFBR (grant No. 11-03-01022).

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OC25

COBALT-CATALYZED MARKOVNIKOV FUNCTIONALIZATION OF TERMINAL ALKYNES

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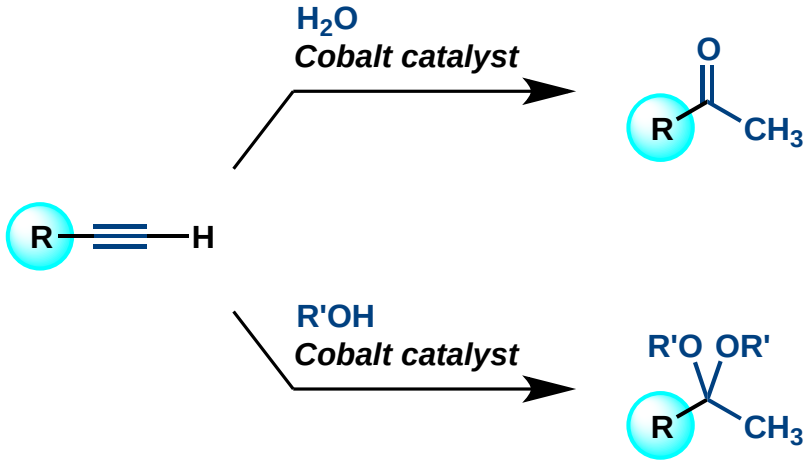
Metal-catalyzed hydration of alkynes is an ideal example of a reaction that incorporates water in organic compounds, affording synthetically important carbonyl compounds in a highly atom-economical manner. The alkyne hydration has been widely used both in laboratory and industrial synthetic chemistry, often based on mercury salts. Alternative catalysts have been sought over the years for other metallic species, and the recent advent of gold-catalyzed hydration of alkynes has attracted considerable interest.

In searching for new and more efficient processes for alkyne hydration based on first row transition metals, we found that several cobalt complexes serve as precatalysts for Markovnikov hydration of terminal alkynes to give the corresponding methyl ketones. Hydroalkoxylation of alkynes proceeded in a similar manner, providing the corresponding acetals. The substrate scope and limitation, as well as possible mechanisms based on spectroscopic, kinetic, and DFT studies will be presented.



R = aliphatic or aromatic

OC26

ASYMMETRIC COUNTERANION-DIRECTED ALKALI METAL CATALYSIS: STEREOCHEMICALLY INERT CHIRAL ALKALI COBALTATES AS CATALYSTS OF C-C BOND FORMATION

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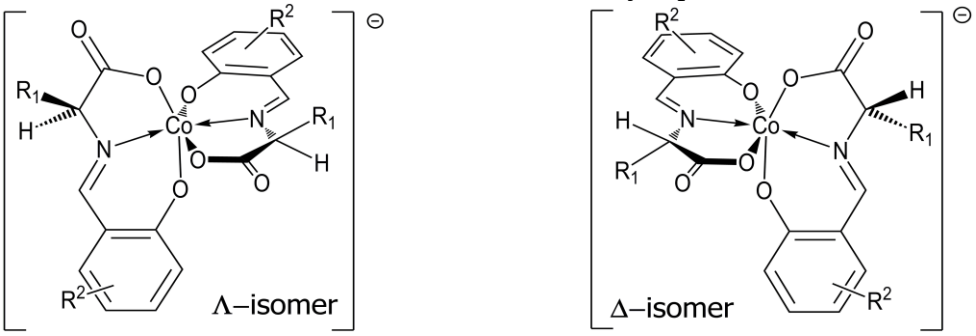
Recently developed asymmetric counteranion-directed catalysis (ACDC) is a novel synthetic strategy. According to it, asymmetric course of a reaction, proceeding via positively charged intermediates, can be secured by introducing chiral counteranions into the catalytic system.[1] The principle was recently broadened to include transition metal catalyzed reactions.[2] Chiral phosphate anions derived from BINOL are commonly employed as chiral anions in the series of ACDC reactions.[1,2]

We report here use of alkali metal cations as Lewis acids in ACDC type of conversions with chiral counteranions derived from stereochemically inert, chiral anionic cobaltate complexes (see figure).[3] The cobaltate complexes exist as two independent meridional Λ- and Δ-diastereomers not interconvertable under the reaction conditions and can be easy separated.



The Lewis acidity of the cation in combination with chiral weakly coordinated anion was enhanced in comparison with traditional metal complexes due to the absence of strongly metal-ligand interactions. Therefore, it can be sufficient to use alkali metals cations as Lewis acids, which are not generally considered to be efficient catalysts in asymmetric transformations.

The novel chiral metallocomplex catalytic systems were tested in asymmetric Michael, hetero-Diels-Alder reactions and trimethylsilylcyanation of aldehydes.

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OC27

A CHIRAL POROUS METAL-ORGANIC FRAMEWORK, (S)-KUMOF-1, AS THE HETEROGENEOUS CATALYST FOR ENANTIOSELECTIVE REACTIONS

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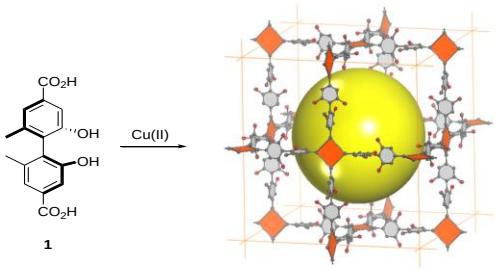
Chiral metal-organic frameworks (MOFs) constitute a unique class of multifunctional hybrid materials and are envisioned as a heterogeneous catalyst for enantioselective reactions. Despite some pioneering works on catalytic enantioselective reaction promoted by chiral MOFs, there is still a need for practical catalysts and many fundamental issues must be answered; 1) the preparation of practically useful chiral MOFs[1] and 2) the evidence of utilization of all active sites in the MOFs.[2]

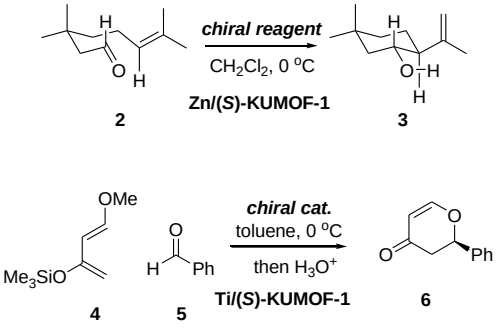
We have designed and synthesized a chiral metal-organic framework, (*S*)-**KUMOF-1** (Cu_2(S)-1)$_2$(H_2O)$_2$, 1 = 2,2'-dihydroxy-6,6'-dimethyl(1,1'-biphenyl)-4,4'-dicarboxylate) of which non-interpenetrating NbO type framework provides a spacious pore (2 × 2 × 2 nm3) and is equipped with potential catalytic sites exposed into the pore. Two reactions, the carbonyl-ene reaction with modified MOF after replacement of the protons on biphenol on the organic links with Zn(II) and the hetero-Diels-Alder reaction with Ti(IV), respectively, were studied.

In this maneuver, we observed that the reaction occurs entirely inside the pores for a given substrate and the reaction rate of the heterogeneous reaction by this specific MOF is comparable to that of its homogeneous counterpart. In addition, it is also observed that the enantioselectivities are significantly improved by extra steric bias provided from the frames of the MOF. These observations reinforce the legitimacy of the strategy of using a chiral MOF as a highly enantioselective heterogeneous catalyst.



1

(*S*)-**KUMOF-1**



2 3 4 5 6

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OC28

NEW INSIGHTS AND DEVELOPMENTS IN PALLADIUM CATALYSIS – A COMBINATION OF THEORY AND EXPERIMENT

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Detailed understanding of catalytic transformations is key to designing better catalysts. This talk will give insights on case studies recently undertaken in our laboratory. Computational chemistry was applied to gain insights on reaction mechanisms, active catalytic species, ligand and additive effects of selected metal-catalyzed transformations in the areas of C-H activation and cross-coupling. Experimental studies were performed in parallel to computational studies to validate computational results and test theoretical predictions. As a result of these investigations, novel reactivities have been uncovered. [1]

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OC29

ESI-MS STUDIES OF OXIDATIVE PALLADO-CATALYZED REACTIONS

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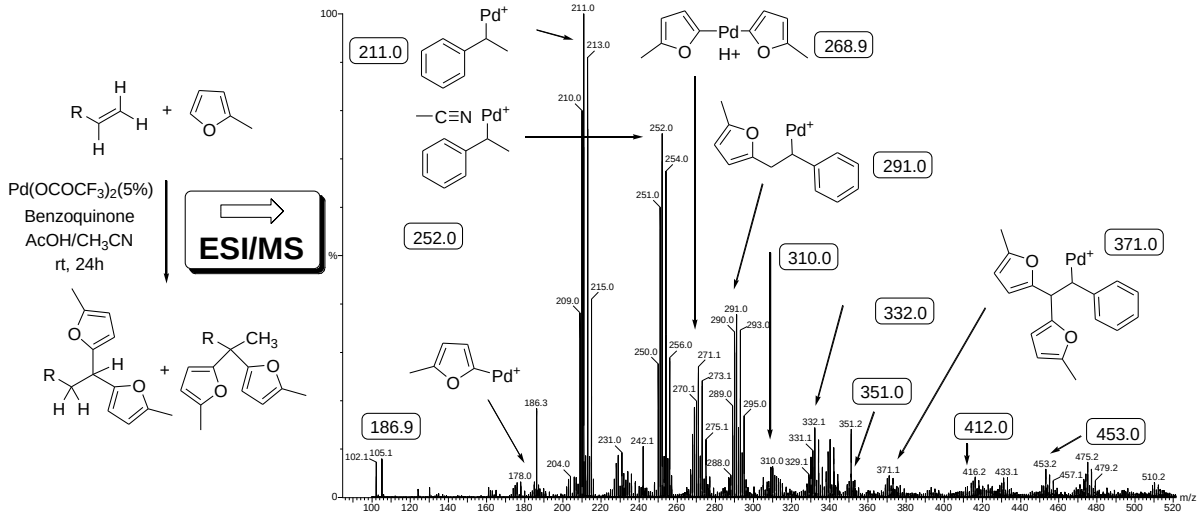
Comprehensive mechanistic investigations usually require kinetic data, identification of catalytic species and a global reaction law. For processes based on combination of different parameters, such as catalytic reactions, the proposition of a mechanism and the selection of the active species for the determination of the rate law may not be accurate. ESI-MS has rapidly become a major tool in identifying reactive intermediates and has achieved great success in mechanistic investigations.[1]
Most of the examples of palladium catalysis consist of nonoxidative methods, especially cross-coupling reactions. Oxidative reactions tend to be more challenging; they require the use of an external oxidant, and the conditions are incompatible with air-sensitive phosphine ligands, which have been critical to the success of the Pd^0-catalysed cross-couplings. As a result, palladium-catalyzed oxidative reactions have received less attention than their nonoxidative counterparts and their mechanisms are less known.
We will present the mechanistic studies developed by ESI-MS in our laboratories over the past years on various pallado-catalyzed reactions.[2] We have for examples shown that dinuclear palladium complexes are more involved as active catalytic intermediates than mononuclear species in the Wacker oxidation of alkenes. The nature of the catalytic species involved in dehydrogenative Heck reactions and in the formation of diarylalkanes will be also discussed.



The formation of difurylalkanes through C-H activation monitored by ESI-MS

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OC30

GEOMETRIC ISOMERISM IN SQUARE PLANAR ORGANOPALLADIUM COMPLEXES WITH UNSYMMETRIC BIDENTATE AMINOPYRIDINE LEADS TO REACTIVITY DIFFERENTIATION IN NORBORNENE INSERTION AND ALTERNATING ETHYLENE-NORBORNENE COPOLYMERIZATION —A KINETIC AND MECHANISTIC APPROACH

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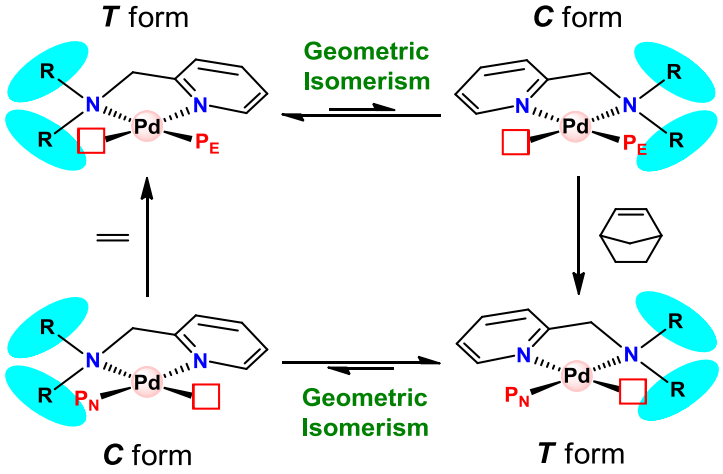
Cationic methylpalladium complexes bearing hetero-functional bidentate ligands of α-aminopyridines have been found to be effective precursors for catalytic alternating copolymerization of ethylene (E) and norbornene (N) under mild conditions.[1] Both of the square planar methyl and norbornyl palladium(II) complexes exhibit facile reversible geometrical isomerization. The geometric isomers show distinct reactivity toward olefin-insertion reactions. Detailed kinetic studies by means of variable-temperature NMR technique on ethylene-insertion, norbornene-insertion, as well as the geometric isomerization have been examined. Corresponding DFT calculations for such fundamental paths have also been investigated. Both approaches reveal consistent results, indicating that the *cis*-isomers undergo olefin insertion more facile than the *trans* analogues. An unprecedented mechanism in which the reversible geometric isomerization and the geometric isomer-distinguished kinetics lead to the alternating E-N copolymerization will be presented.



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OC31

ALTERNATIVE ENERGY INPUT FOR TRANSFER HYDROGENATION USING NHC-IRIDIUM BASED CATALYSTS IN GLYCEROL AS HYDROGEN DONOR AND SOLVENT

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Glycerol is an attracting alternative to conventional volatile organic solvents (VOSs) due to its interesting chemical and physical properties, including good thermal stability, high boiling point and low vapour pressure. However, only few studies have been devoted to the use of glycerol as alternative solvent in organic synthesis.[1] Apart from its use as solvent, we report here the use of glycerol as an environmentally friendly hydrogen donor for transfer hydrogenation (TH) reaction, in the presence of novel iridium catalysts[2,3] under microwave or ultrasounds activation. [3]

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OC32

HOMOGENEOUS CATALYSIS APPLIED TO THE PRODUCTION OF PHARMA MOLECULES

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The main activity of DSM Innovative Synthesis is to design and/or improve synthetic routes towards complex pharmaceuticals molecules for their production on large scale. In numerous cases, homogeneous catalysis appeared to be an enabling tool to shorten the synthesis and render the whole process more efficient and more environmentally friendly – i.e. more sustainable.
In this lecture, we will illustrate the benefit of homogeneous catalysis with real-life substrates. The catalytic technologies that we used include Rh and Ir-catalyzed asymmetric hydrogenation of olefins, enamides and imines, Cu-catalyzed N-arylation, Pd-catalyzed carbonylation.

OC33

DEVELOPMENT OF A NEW ROUTE FOR THE CONSTRUCTION OF HYDRO[9B]AZAPHENALENES VIA ALLYLBORATION AND METATHESIS REACTIONS

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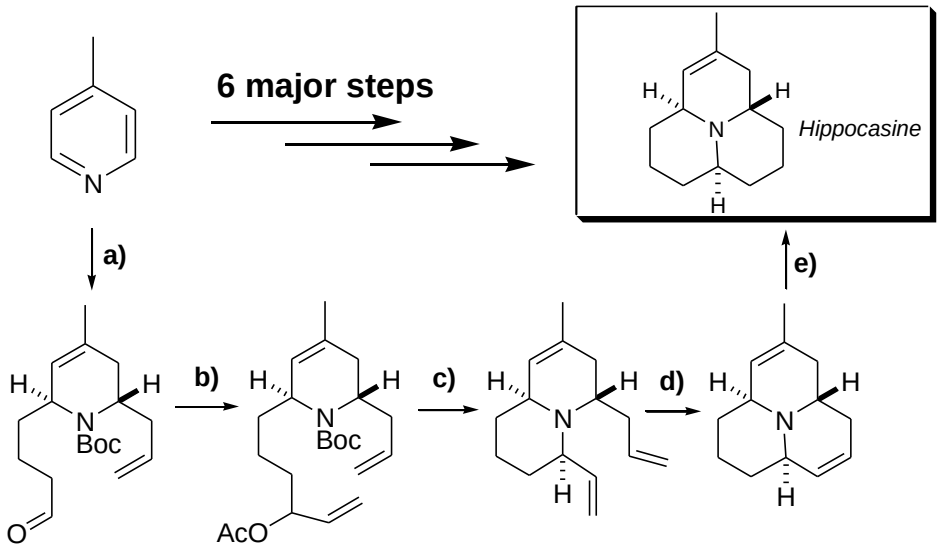
It was found that naturally occurring heterocyclic compounds of hydro[9b]azaphenalene series have a complex powerful effects on insects and animals. There are enough methods directed on creating of [9b]azaphenalene skeleton, however neither of them nor use such efficient methods of the formation of cycles as ring closure metathesis and palladium catalyzed allylic amination. It is well known that for utilization of such methods a specifically designed molecule is required containing several C=C bonds. Efficient method of the introduction of the terminal C=C bonds into heterocycles is alkenyl and allylboration of pyridines. In our approach a construction of hydro[9b]azaphenalenes includes following key steps: a) alkyl,allylboration of corresponding pyridines (*e.g.* 4-picoline) with lithium derivative prepared from 1,1-diethoxy-4-iodobutane and triallylborane. It is worth to note an original atom economy synthesis of 1,1-diethoxy-4-iodobutane and allylic derivatives from $(EtO)_3CH$ and All_3B was developed; b) intramolecular palladium catalyzed allylic amination of amino function with allylic acetate; c) ring closure metathesis reaction with Grubbs' II catalyst.



a) i - tBuLi/I$(CH_2)_3$CH$(OEt)_2$, -78^0 C; All_3B, MeOH; ii - Boc_2O; H^+/H_2O; b) i - VinylMgBr -78^0 C; ii - Ac_2O/Py; c) $[AllPdCl]_2$, 2mol%; d) Grubbs' II, PhMe; e) Pd/C, H_2.

This work was supported by the President of Russian Federation (Sci. School № 7946.2010.3), Presidium of RAS (№ 8, coordinator – V.A. Tartakovsky and № 5, coordinator – A.I. Grigor'ev), Division of Chemistry and Material Sciences RAS (Programme No. 9).

OC34

SYNTHESIS, COORDINATION CHEMISTRY AND CATALYTIC TESTS OF NEW CHIRAL FERROCENYL P,N LIGANDS

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Many efforts have been devoted to the development of asymmetric catalysis because of the significant use of chiral compounds as intermediates of pharmaceuticals and advanced materials.[1] Amongst many ligands which have been tested, planar chiral ferrocenes ligands constitutes a privileged family of ligands for enantioselective catalysis.[2]
We will disclose in this communication the synthesis of a new chiral N-(p-toluenesulfonyl)-containing ferrocenyl ligands and its coordination chemistry with Ru, Ir and Rh precursors yielding in some cases chiral at metal complexes. Moreover, DFT calculations in order to better understand the nature and stabilities of these complexes will be presented. Additionally, preliminary evaluation of the different complexes as catalysts for the asymmetric transfer hydrogenation of ketones[3] will also be disclosed.

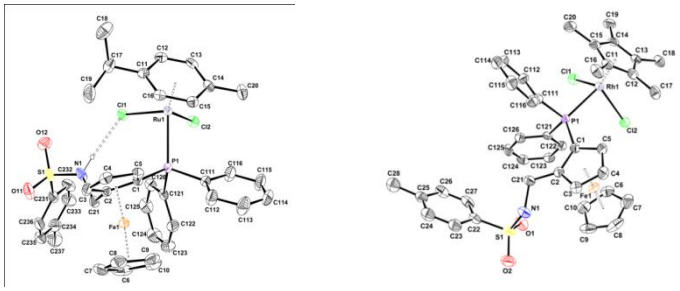

Figure 1. X-ray structure of Ru and Rh complexes containing ferrocenyl P,N ligands

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OC35

BIOCATALYSIS IN FINE ORGANIC SYNTHESIS

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The author analyses the advance and problems in enzyme research for purposes of fine organic synthesis. The present-day organic chemistry has a large set of enzymes of various specificity and nature of chemical reactions (hydrolases, oxido-reductase, isomerase, synthetase, transferase, ligase), which provide unique opportunities in organic synthesis.

The physico–chemical grounds of high selectivity of enzymes as well as the advantages and limitations of enzyme applications in fine organic synthesis are examined.

Studies explored the thermodynamic and kinetic regularities of synthetic reactions in the use of enzyme hydrolysis (alcoholysis) of various compounds, including the application of enzymes in nonaqueous solvents and two-phase systems, and the methods to obtain high yields of products in thermodynamically unfavorable conditions.

Achievements of chemistry of enzymatic synthesis of various compounds are illustrated by a number of particular examples, such as the synthesis of amino acids of natural and unnatural stereochemical configurations, the synthesis of tyrosine and dihydroxyphenylalanine, tryptophan and 5-oxytriptofan, citrulline, urocanic acid and the production of various organic acids.

Particular attention is paid to the synthesis of β-lactamine antibiotics and their various modifications, nucleophosphates, the synthesis of oligo- and polynucleotides and the synthesis of radioactively labeled compounds.

The contemporary chemistry of enzymes in fine organic synthesis has been facing the problem of regeneration of cofactors. The ways of solving this problem are discussed.

A topic analyzed in detail is a number of unique examples of one-step enzymatic synthesis of physiologically active compounds with a deep change in hydrocarbon skeleton (the synthesis of the entire set of natural prostaglandins, lipoxines, leucotrienes and the synthesis of steroids).

In a series of cases, studies examined a possibility of synthesis and hydrolysis of phospho-organic compounds.

Studies analyzed the methodical and technological problems of the use of enzymes in organic synthesis, namely the methods of "protection" of enzymes and their use in organic solvents, the creation of heterogeneous catalysts based on the immobilization of enzymes on inorganic and polymeric carriers as well as the methods for stabilization of enzymes against thermal denaturation. Considerable attention is given to preparing the heterogeneous catalysts based on immobilized microbial cells.

Examples of application of enzyme technology in large-scale organic synthesis are examined.

OC36

GREENING THE ORGANIC PHOSPHORUS CHEMISTRY: BIOCATALYTIC SYNTHESES OF BIOLOGICALLY ACTIVE P-COMPOUNDS

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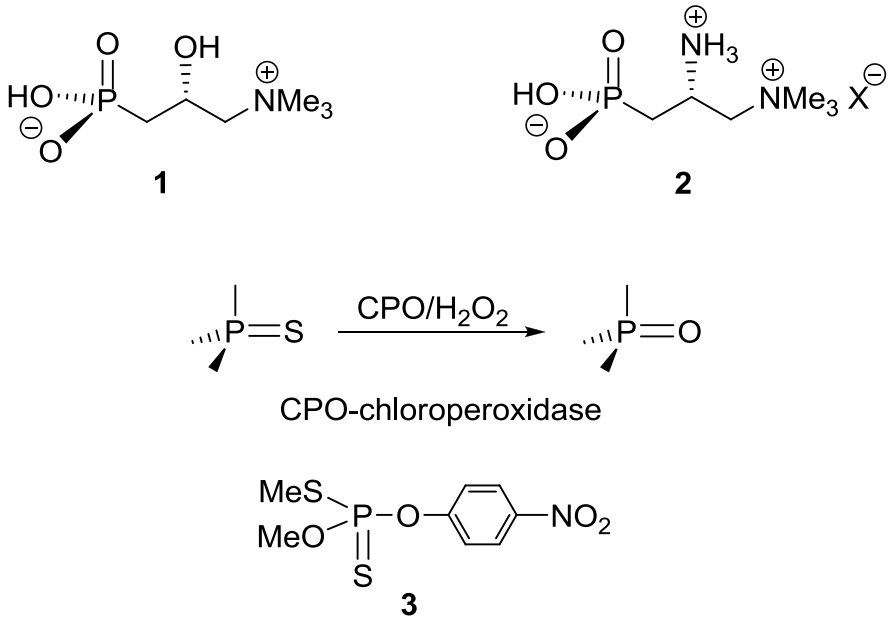
The combination of biocatalytic and chemical synthesis provides a powerful route to specifically designed functionalized molecules. The biocatalytic part serves to generate enantiomerically pure starting materials or intermediate products while chemical reactions are used to transform these compounds into the desired target structures. The value and advantages of this approach to the synthesis of bioactive organic phosphorus compounds will be demonstrated using phosphocarnitine **1** and phosphoemeriamine **2** as examples.[1]



In the last part of this presentation the biocatalytic oxidation of the thiophosphoryl group will be discussed as a short and facile way for the synthesis of chiral enantiopure agrochemicals, as for example the insecticidal dithiophosphate **3**.[2]

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OC37

DIRECT CATALYTIC TREATMENT OF BIOMASS SUBSTRATES TOWARDS HYDROCARBON FUEL COMPONENTS

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Current paper presents the results concerning to development of nanosized heterometallic catalysts and scientific bases of biomass substrates conversion into fuel components over developed catalysts. The peculiarities and regularities of the next processes were studied that resulted in estimation of the most probable reactions pathways:

- Bioalcohols direct conversion into hydrocarbon components of gasoline
- Cross-coupling reactions of bioalcohols mixtures modeling fermentation mixtures resulting in alkanes-olefins fraction formation of gasoline as well as mixtures of ethanol with either glycerol or acetone as respectively biotechnology co-products and cumene method of phenol producing
- One-step and high selective hydrogenation of different compositions rape oils leading to alkanes formation of either gasoline or diesel fractions
- Cellulose hydrogenative liquefaction accompanied with its exhaustive deoxygenation towards hydrocarbon fractions formation with boiling point upper 220°C.

By using XRD, XPS, EXAFS, SEM-EDX methods the genesis of the most active and stable nanosized catalytic systems was studied and mechanism of catalytically active clusters formation was determined.

This work was financially supported by RFBR (№ 12-03-00489-a) and Grants Council of President RF (МК-2917.2012.3, МК-1621.2012.3). Authors thanks Moiseev I.I. and Gekhman A.E. for their great interest and valuable advises to the work.

OC38

RECENT DEVELOPMENTS IN THE HOMOGENEOUS CATALYSIS BY TRANSITION METAL METALLACARBORANES

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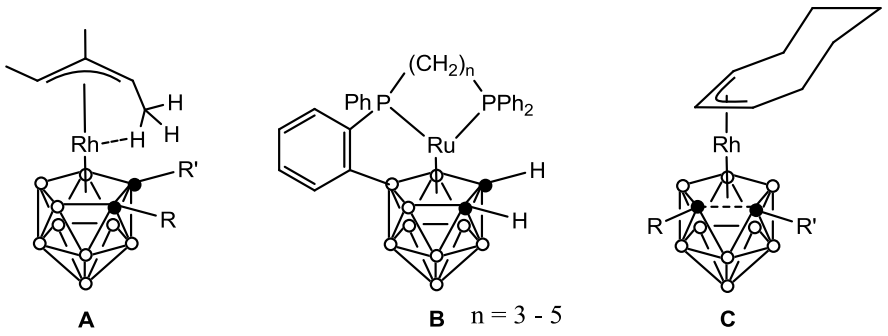
A series of formally 16-electron or 18-electron *closo*- and *exo-nido*-metallacarboranes of rhodium and ruthenium with different types of phosphine/diphosphine as well as cyclic and acyclic hydrocarbon ligands at the metal vertices have been synthesized, structurally investigated by modern physical methods (X-ray diffraction, multinuclear NMR) and explored as efficient catalysts precursors for homogeneous catalyses.

Examples of reactions catalyzed by metallacarboranes and recently studied in our group include: (a) hydroformylation of the model alkenes (styrene, its 4-substituted derivatives, some other alkenes and terpenoids) under syngas using either scCO2 or toluene as solvents and (π-R-allyl)-*closo*-rhodacarboranes (type **A**) as pro-catalysts, where very good to excellent yields with high regioselectivities have been achieved. Remarkably, these rhodacarborane pro-catalysts work very well even without either phosphine or phosphite as co-catalysts;[1] (b) a variety of transition metal metallacarborane systems have been investigated as catalysts for the ATRP processes of vinyl monomers.[2] Among these, some metallacarborane complexes, in particular those based upon 17-electron (paramagnetic) *closo*-ruthena-{C_2B_9}-carboranes (type **B**), display excellent catalytic activities and produce polymeric materials with quite reasonable polydispersity indices as low as 1.15;[3] (c) progress has been made in finding new ways to catalyze asymmetrical hydrogenation of prochiral enamides by the agostic *closo*- and non-agostic *pseudocloso* carborane-based rhodium-cyclooctenyl complexes (type **C**) coupled *in situ* with the chiral phosphoamidite [(S)-PipPhos].[4]



1. K.I. Galkin, S.E. Lubimov, I.A. Godovikov, F.M. Dolgushin, A.F. Smol'yakov, E.A. Sergeeva, V.A. Davankov, I.T. Chizhevsky, *submitted for publication*.

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This work was financially supported by Russian Foundation of Basic Research (project № 12-03-00102).

Posters

P1

PALLADIUM-CATALYZED AMINATION OF DIHALOGENO SUBSTITUTED PYRIDINES AND QUINOLINES WITH ADAMANTANE-CONTAINING AMINES

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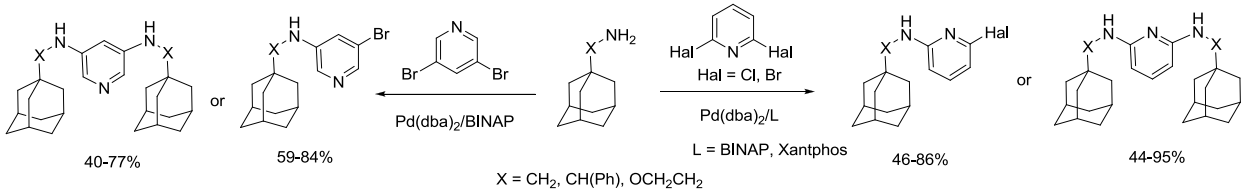
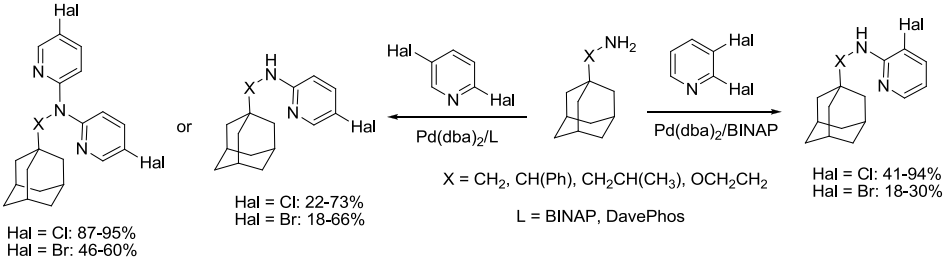
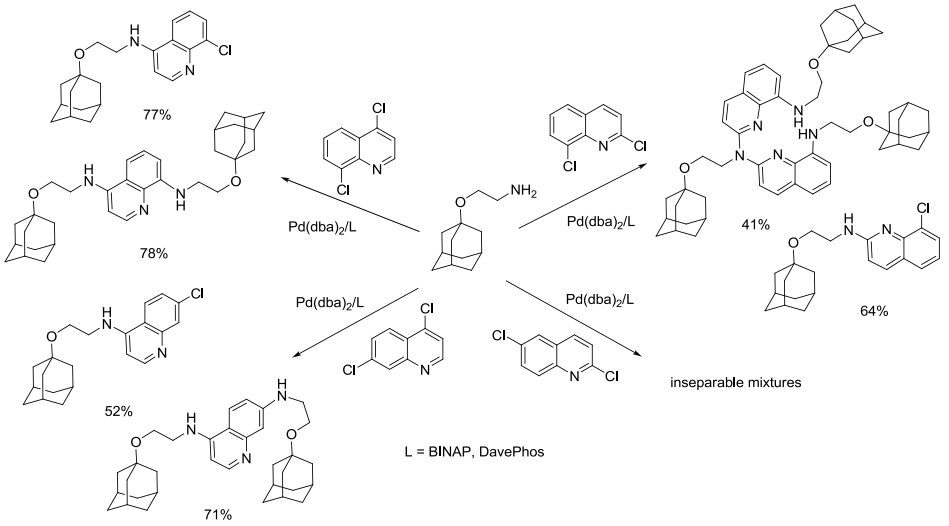
Symmetrical 2,6- and 3,5-dihalopyridines successfully produced mono- and diamino derivatives depending on the stoichiometry of starting compounds. Generally, better results were obtained with 2,6-dichloropyridines in comparison with 2,6-dibromopyridines.



The catalytic substitution of the halogen atom at α-carbon atom of pyridine in 2,3- and 2,5-dihalopyridines was in many cases successful, and better results were achieved with less active dichloropyridines. The most interesting fact is the possibility to synthesize *N,N*-bis(5-halopyridin-2-yl) derivatives of adamantane-containing amines in yields up to 95% using 2,5-dihalopyridines taken in a 4-fold excess.



Diamination of 4,7- and 4,8-dichloroquinolines with the excess of 1-(2-ethoxy)adamantane afforded diaminosubstituted quinolines in high yields while diamination of 2,6- and 2,8-isomers was not selective.



The work was supported by the RFBR grant 10-03-01108.

P2

TRANSITION METAL CATALYZED SYNTHESIS OF NOVEL FIVE- AND SIX-MEMBERED HETEROCYCLIC SYSTEMS

E. Abele, R. Abele, T. Beresneva, J. Visnevska, S. Belyakov, L. Golomba

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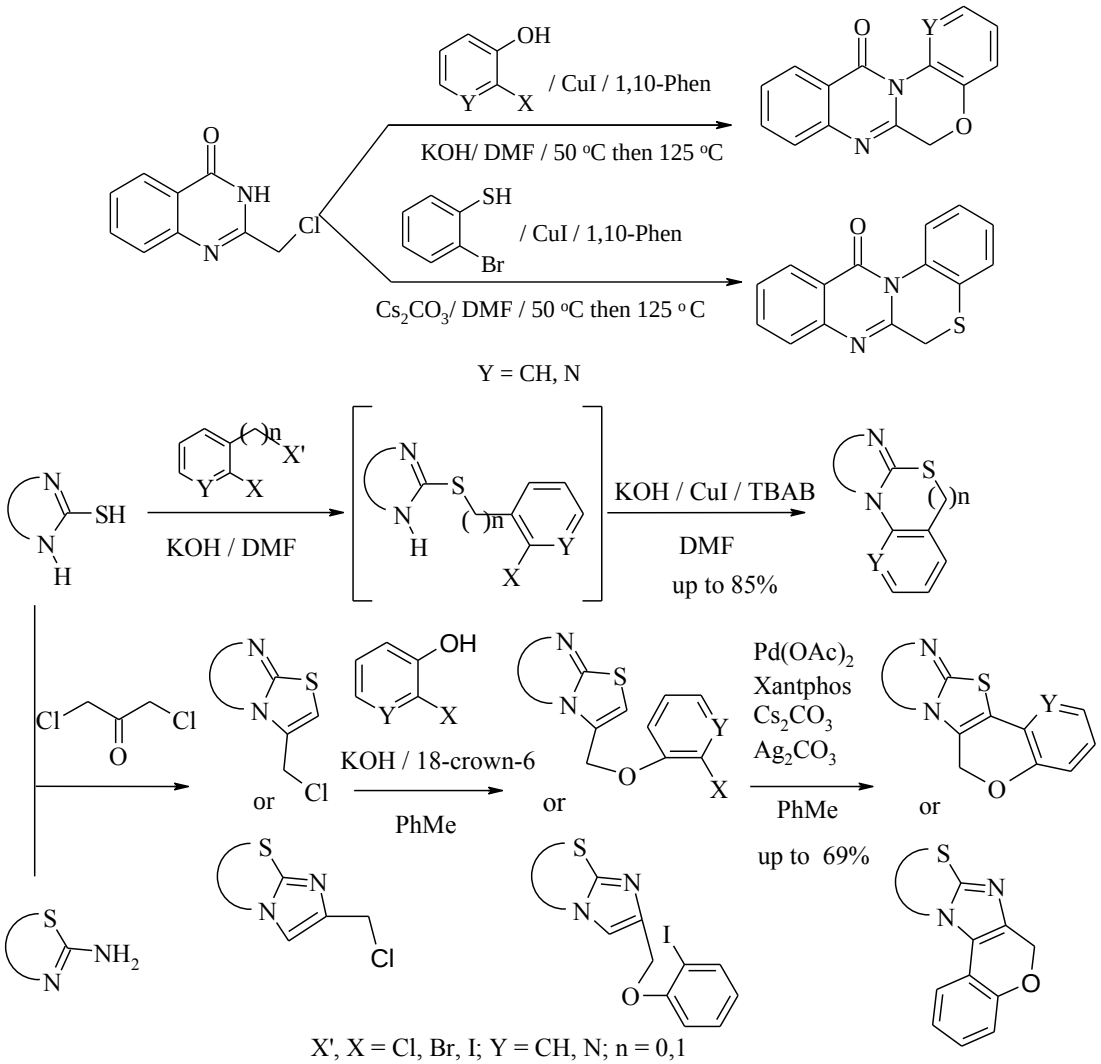
Cu-catalyzed synthesis of polycyclic systems including formation of novel thiazole and thiazine rings is presented.

Polycyclic compounds on the thiazole and imidazole basis were obtained in three steps. The last step is cyclization of o-haloarenes in the system $Pd(OAc)_2$ / Xantphos / Cs_2CO_3 / Ag_2CO_3 / PhMe.



This work was supported by the project of ESF Foundation of Latvia (Project N 2009/0197/1DP/1.1.1.2.0/09/APIA/VIAA/014).

P3

TRANSITION METAL CATALYZED SYNTHESIS OF NOVEL SEVEN-MEMBERED HETEROCYCLIC SYSTEMS

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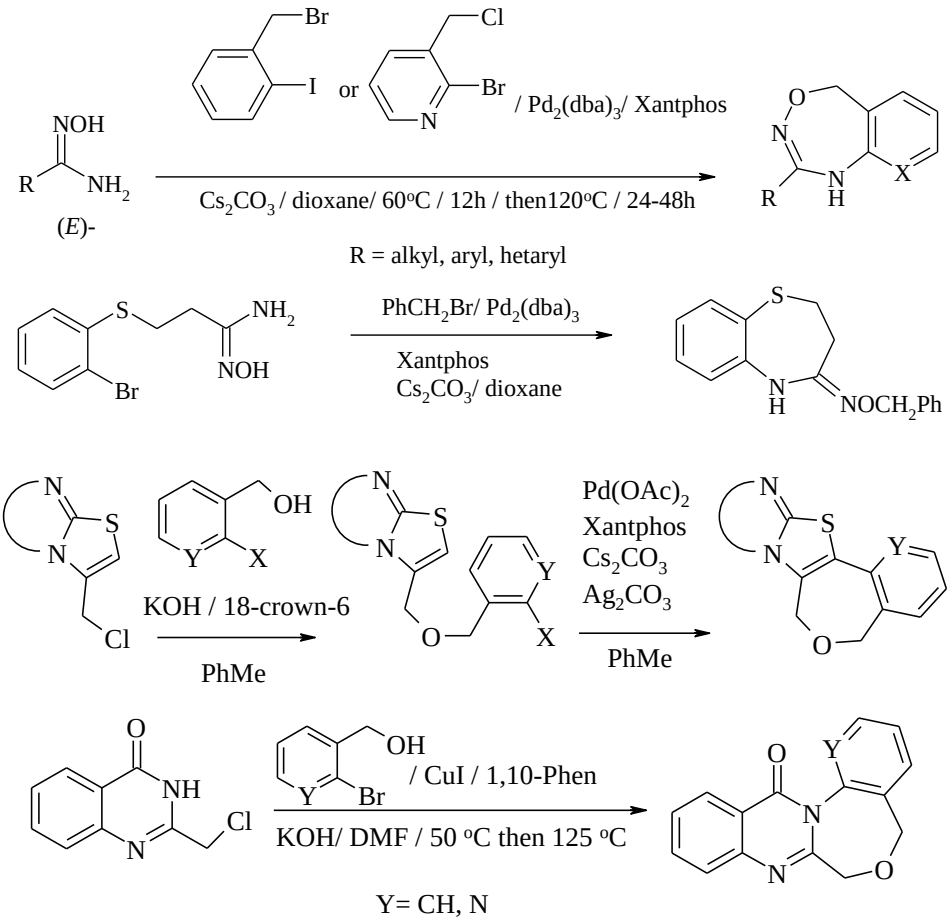
A simple palladium-catalyzed one pot synthesis of novel class of heterocyclic compounds - fused 3-substituted 1,2,4-oxadiazepines from corresponding (*E*)-amidoximes and *o*-iodobenzyl bromide or 2-bromo-3-chloromethylpyridine was developed. It was also demonstrated that the system benzyl bromide / solid Cs_2CO_3 / $Pd_2(dba)_3$ / Xantphos / dioxane was excellent for O-alkylation N-arylation tandem reaction leading to 2,3-dihydro-5*H*-benzo[*b*][1,4]thiazepin-4-one O-benzyloxime in 62% yield by one pot method. Synthesis of polycyclic compounds on the oxepine and 1,4-oxazepine base have been presented too.



This work was supported by the project of ESF Foundation of Latvia (Project N 2009/0197/1DP/1.1.1.2.0/09/APIA/VIAA/014).

P4

HYDROESTERIFICATION OF OLEFINS. PALLADIUM (II) CATALYSTS BEARING PHOSPHOROUS-NITROGEN LIGANDS. PRELIMINARY STUDIES IN BIPHASIC AND HOMOGENEOUS SYSTEMS

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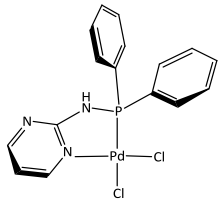
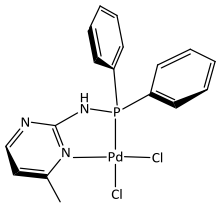
The homogenous catalysis is an important tool in order to obtain organic products: aldehydes, acids and esters. Several research groups in recent years have focused on the task of developing new organometallic compounds with carbene, phosphorus, nitrogen and other types of ligands. During the last time our research group has developed the synthesis and characterization of ruthenium and palladium compounds with phosphorus-nitrogen ligands for diverse applications in homogeneous catalysis. The complex and the ligands were synthesized by Schlenk techniques and characterized by nuclear magnetic resonance and elemental analysis [1,2]. This abstract reports the use of catalysts of palladium (II) with phosphorus-nitrogen ligands, which have proved to be active catalysts in olefin hydroesterification. The catalysts were employed in biphasic and homogeneous media [3,4].

The catalytic reactions were carried out in high pressure reactors using variable pressures and temperatures in order to optimize the reaction conditions. The results show that the prepared catalysts allow conversions between 60-92% at pressures under 50 bar and at 75 º C.

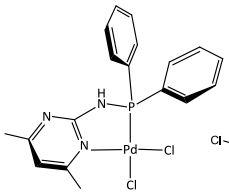
It was observed that this type of ligands directs the reaction to the formation of mainly a branched ester with a 98 ratio, with high chemoselectivity. The reaction requires the addition of low amounts of triphenylphosphine which allows obtaining a catalytic system with high stability under the reaction conditions. For the biphasic systems were studied ligands Na-dTPS, Na-mTPS, plus a serie of derivatives with fluorinated substituents.



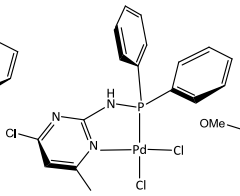
Pd-1



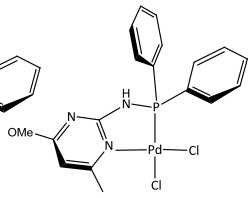
Pd-2



Pd-3



Pd-4



Pd-5

Acknowledgments

The authors acknowledge financial support of Fondecyt-Chile N° 1120149. LIA-MIF Project N° 836, Chile, France and ECOS-CONICYT Nº C07E. G.A. thanks CONICYT for the doctoral scholarship awarded N° 21090186 and for scholarship support for the realization of thesis (N° 24110005). G.A. thanks Vicerrectoría de Asuntos Académicos, Universidad de Chile.

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P5

VINYLIDENE COMPOUNDS OLYGOMERIZATION CATALYZED EXCHANGE RESINS, AS A METHOD FOR CLEANING OCTENE-1

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The major areas of application higher olefins are the production linear low density polyethylene (LLDPE), in which α-olefins are comonomers, and also surface-active agents (surfactants) different classes, oil additives, etc.

The basic requirements for quality α-olefins relate content vinylidene olefin structures that separation by rectification is impossible because of close boiling point. That vinylidene isomers, being the most active and reactive, especially in the reaction. However, their branched structure not give the expected properties of products derived from α-olefins.

The chosen method of treating the fraction of α-olefins C8 of JSC "Nizhnekamskneftekhim" is based on a highly reactive hydrocarbons vinylidene double bonds. Cleaning is the selective oligomerization reaction olefins with tertiary carbon atom, followed by stripping unreacted α-olefins.

The catalyst of oligomerization was used sulfonic Lewatit K-2425, which is a macroporous catalyst with high content of SO3H-groups, pore diameter 240 Å, the total exchange capacity of 5.20 mq / g

Studies have shown that the initial rate of the reaction of oligomerization is more dependent on the reaction temperature, and to a lesser extent on the concentration of catalyst

The values of the initial velocities of the oligomerization reaction, depending on the temperature and the concentration of catalyst.

Temperature, ^{0}C	Catalyst concentration, wt%.		
	5	10	15
	Initial velocity, mol / l·s × 10^5		
60	0,41	0,83	0,75
80	2,08	1,85	1,7
100	2,17	2,07	2,01

Optimal conditions of the selective oligomerization vinylidene hydrocarbons C_8 on sulphocationite Lewatit K-2425: T = 80° C, the concentration of the catalyst 10 wt %. Response time - 3 hours. The conversion vinylidene hydrocarbons in these conditions was 94.66%, and their content was reduced from 1.8 to 0.096 wt%.

Isomer content in a fraction of C_8 α-olefins.

Isomers	Parent fraction	Purified fractions
Linear α-olefins,% wt..	97,31	98,99
Vinylidene hydrocarbons,% wt.	1,8	0,096
With the inside of the double bond,% wt.	0,89	0,914

The work was performed as part of the Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" for 2009-2013, FC № 14.740.11.0383.

P6

HYDROGEN BONDING MEDIATED ENANTIOSELECTIVE ORGANOCATALYSIS ON WATER: SIGNIFICANT RATE ACCELERATION AND ENHANCED STEREOSELECTIVITY

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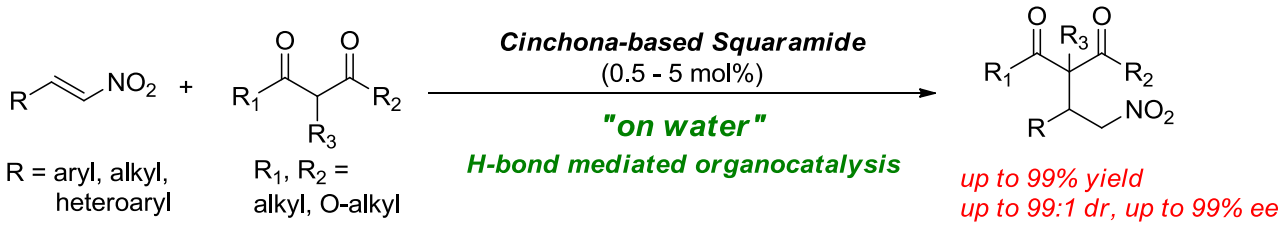
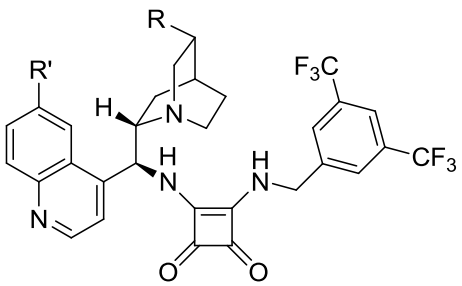
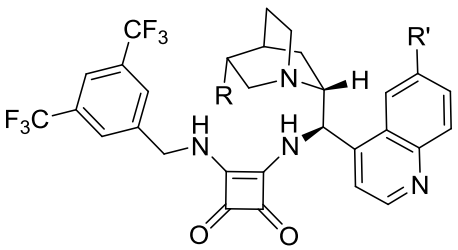
Nature uses water as a solvent for biosynthetic reactions to sustain life. The "hydrophobic effect" is a key element in enzyme catalysis, in determining the structures of proteins and nucleic acids, and in the binding of antigens to antibodies. Due to movements toward green chemistry and an increased scientific effort to mimic nature, tremendous effort has recently been applied toward developing enantioselective organocatalytic reactions in an aqueous environment. Chiral secondary amines have been shown to be viable catalysts in an aqueous environment for several C-C and C-heteroatom bond-forming processes, which proceed via iminium or enanmine intermediates. However, introducing water as a solvent in the hydrogen-bonding-mediated asymmetric catalysis still remains a challenge, because water can interfere with the organocatalysis by its capacity for disrupting hydrogen bonds and other polar interactions. In this symposium, we will present the successful results of H-bonding-mediated enantioselective organocatalysis in an aqueous environment. Enantioselective Michael addition using a bifunctional cinchona-based squaramide organocatalyst was dramatically accelerated in brine compared to the reaction in organic solvents, due to the hydrophobic hydration effect. Remarkably, in most cases, diastereo- and/or enantioselectivity also were enhanced in brine. Catalyst loading at 0.5 mol% was sufficient to complete most reactions within 10 min, affording the Michael adduct in up to >99% yield and >99% ee. [1]





CD-SQA, R = vinyl, R' = H
QN-SQA, R = vinyl, R' = OMe
HQN-SQA, R = ethyl, R' = OMe



CN-SQA, R = vinyl, R' = H
QD-SQA, R = vinyl, R' = OMe
HQD-SQA, R = vinyl, R' = OMe

1. H. Y. Bae, S. Some, J. S. Oh, Y. S. Lee, C. E. Song, *Chem. Commun.* 2011, **47**, 9621–9623

P7

NEW REACTIONS OF ARSINE, BISMUTHINE AND STIBINE WITH ALKOHOLS IN PRESENCE OF METAL COMPLEX CATALYST

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In recent years, we found a number of new organic reactions involving halide platinum (II) and (IV), for example, oxidation of alkanes, arenes, olefins, alcohols, carbon monoxide / 1-2 /.
We first discovered that by passing the mixture of gases AsH_3-Ar, at 50 ° C in an alcoholic solution of the complexes Na_2PtCl_6, known for its high inertness and stability, formed trialkilarsinity $(RO)_3As$ and trialkilarsenaty $(RO)_3AsO$.

$AsH_3 + 3Na_2PtCl_6 + 3ROH \rightarrow 3Na_2PtCl_4 + (RO)_3As + 6HCl$ (1)
$AsH_3 + 3Na_2PtCl_6 + 3ROH \rightarrow (RO)_3AsO + 2Pt + RCl + 7HCl,$ (2)
$SbH_3 + 3Na_2PtCl_6 + 3ROH \rightarrow 3Na_2PtCl_4 + (RO)_3Sb + 6HCl$ (3)
$BiH_3 + 3Na_2PtC_l6 + 3ROH \rightarrow 3Na_2PtCl_4 + (RO)_3Bi + 6HC$ (4)

The rate of reactions (1,3,4) is described by equation (5):

$W = k_1 [Pt(IV)]^{0,5} [Pt(II)]^{0,5} [EH_3]^{0,5} [ROH]^{0,5}$, where E = As, Sb, Bi, (5)

The rate of reaction (2) is described by equation (6):

$W = k_1 [EH_3]^{0,5} [ROH]^{0,5} ([Pt(IV)]^{0,5} [Pt(II)]^{0,5} + k_2 [Pt(II)]$, where E = As, Sb, Bi, (6)

These mechanisms are activated Arsine, Bismuthine and Stibine and can be used to open this type of reactions involving organic compounds and other elements.

Conclusions:
1. First discovery of new reactions of Arsine, Bismuthine and Stibine with alcohols in the presence of metal complex catalyst.
2. The proposed mechanism arsine new reactions of Arsine, Bismuthine and Stibine with alcohols in the presence of metal complex catalyst.

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P8

SYNTHESIS OF AZA-ANALOGUES OF DEOXYPODOPHYLLOTOXIN

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4-Deoxypodophyllotoxin (DPT) is a naturally occurring lignan [1] closely related to the better known podophyllotoxin, which is used for the production of two widely used anticancer drugs, etoposide and teniposide. Deoxypodophyllotoxin has also shown potent cytotoxicity against a series of tumor lines, [2], [3] and its mode of action has been reported to be by inducing cell cycle arrest through tubuline polymerase inhibition, [4] which is complementary to the Topoisomerase inhibitory activity of etoposide and teniposide. Furthermore, it has demonstrated remarkable potential against Herpes simplex virus, has considerable antiproliferative effects, antiplatelet aggregation activity, *in vivo* antiasthmatic activity and even antiallergic activity. Finally, DPT also has a broad spectrum of insecticidal activity.

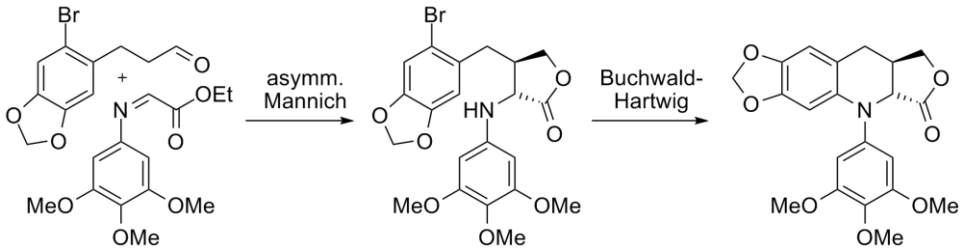

Figure 1: Overview of synthesis strategy

The goal of this project was to synthesize analogues which differ from the parent compound by introduction of a nitrogen atom at the 1-position. This new class of analogues will be synthesized by means of an enantioselective total synthesis. The synthesis can be divided in three distinct parts. At first, the synthesis of 2 achiral precursors, comprising all the atoms required for the backbone of the structures. Second, a stereoselective coupling of these precursors ensures the *trans*-relationship at the lactone ring and preserving this chirality during the final ringclosure to 1-aza-deoxypodophyllotoxin.

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P9

ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ALDEHYDES USING TRANS-3-METHYLENECYCLOPROPANE-1,2-DICARBOXAMIDES AS A CHIRAL LIGANDS-MODIFIED WITH Ti(O-i-Pr)$_4$

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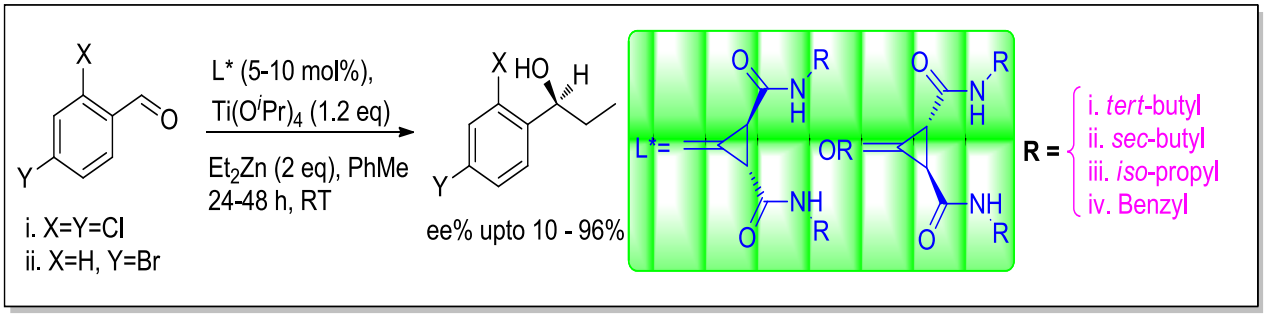

A set of new C_2 symmetry chiral bis-amide ligands (8 ligands) have been easily obtained from *trans*-3-methylenecyclopropane-1,2-dicarboxylic acid (Feist's acid) in a straightforward manner. The modified procedure of the resolution of the (±)-Feist's acid was achieved. These new ligands have been tested as chiral catalysts for the enantioselective addition of diethylzinc to aromatic aldehydes in the presence of Ti(O^{i}Pr)$_4$ as a co-additive. Very good to low enantiomeric accesses (up to 95%) were obtained. The influence of solvent, temperature and the alkyl group substituents has been studied. All new compounds are fully characterized by standard spectroscopic methods including their optical activities.

P10

NEW TRIOXORHENIUM(VII) COMPLEXES BEARING THE WATER-SOLUBLE 1,3,5-TRIAZA-7-PHOSPHAADAMANTANE AS CATALYSTS FOR THE BAEYER-VILLIGER OXIDATION OF KETONES

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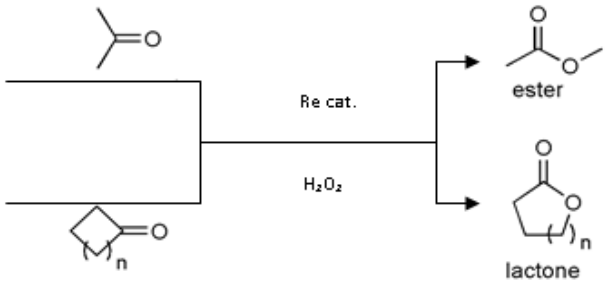
In spite of the very rich coordination chemistry that has been expanded for rhenium [1], the use of complexes with this metal as catalysts is still an underdeveloped field of research. The wide application of [(Me)ReO_3] (MTO) in oxidation catalysis [2], including the BV oxidation of ketones, clearly demonstrates the ability of this metal to form highly active catalysts for oxidation reactions of olefins and other unsaturated substrates.

However, the application of other Re complexes, apart from MTO, is still very limited, although we have found that certain rhenium complexes with oxo- or *N*-ligands (such as, scorpionates, pyrazoles, benzoyl-diazenido, -hydrazido) are capable of catalyzing, in homogeneous systems, under mild or moderate conditions, the oxidation and carboxylation of inert alkanes and Baeyer-Villiger oxidations of ketones [3].

In pursuit of our interest on the above catalytic oxidation reactions, we now report the catalytic activity of the new water soluble and water stable aminophosphine, 1,3,5-triaza-7-phosphaadamantane (PTA) rhenium complexes, [$ReO_3(PTA)_2$](ReO_4)·MeOH (**1**), [ReO_3(Tpm)(PTA)](ReO_4) (**2**) and [$ReO_3(\eta^2$-TPM)(PTA)][ReO_4] (**3**) for the Baeyer-Villiger oxidation of a series of cyclic and acyclic ketones using 35 % hydrogen peroxide as oxidant.



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Acknowledgements This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and projects PTDC/QUI-QUI/102150/2008, PTDC-EQU-EQU-122025-2010 and PEst-OE/QUI/UI0100/2011

P11

OXIDATION OF CYCLOHEXANOL TO CYCLOHEXANONE OVER THE MODIFIED ZEOLITE

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Activity and selectivity of zeolites of different crystalline structure (synthetic and natural) modified with cations of the transition metals have been tested in vapor phase reaction of oxidation of cyclohexanol. Metalzeolites modified with the cations of the different metals were prepared by ion-exchange method. For preparing of catalyst on the basis of natural zeolites at first the dealumination of ones is carrying out by means of acid treatment. A fraction of granulated modified zeolites of about 0.25-0.63 mm of equivalent diametr was used as catalysts. Runs performed at several feed rates and using granules of the catalyst of different sizes showed that external and internal mass transfer effects were negligible under the studied experimental conditions. The test of the activity of these catalysts was carried out in a flow apparatus with the quarts reactor connected directly to the gas chromatograph. The analysis of the products of reaction was performed by gas chromatography, using a column filled with paropak-T (length 3m), and helium as the carrier gas, hot wire detector, program control of the temperature and by apparatus GC-MS of Agilent 7890 brends with mass detector Agilent 5975, using a column filled with HP-5-MS (length 30m). The test of the activity of the specimens of the catalysts was carried out in range of temperature 180-400^{0}C, space velocity by cyclohexanole 0.97-7.0 h^{-1}, and mole ratios of cyclohexanole:air= 1:(5.15-11.35).

The study of the catalytic activity of the modified zeolites in the reaction of oxidation of cyclohexanol shows that the products of this reaction are cyclohexanone, cyclohexene, methylcyclopentadiene and small amounts of carbon dioxide.

The conversion of this alcohol and the selectivity of the process on products of the reaction on these catalysts are marked differently. It has been studied the influence of nature and concentration of cations on the direction of the reactions

It has been established that the proceeding of these reactions on the modified zeolites depends from nature of zeolite, also from nature and concentration of the cations, acid sites on the surface of catalyst and experimental conditions of the process (temperature, space velocity, mole ration of reagents).

On the basis of this investigation the efficient modified zeolite catalyst has been selected for the reaction of oxidation of cyclohexanol into cyclohexanone (at the optimum conditions , the yield of cyclohexanone is 74,5-96.1% at the selectivity 81,9-97.9%).

P12

OXIDATIVE DEHYDROGENATION OF C_1-C_4 ALCOHOLS OVER MODIFIED ZEOLITES

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The oxidative dehydrogenation of aliphatic alcohols is one of the rather perspective method for obtaining of aldehydes and kethones. In general, these processes are carried out at high temperatures on metallic and oxide forms of the transition elements, which exhibit relatively low activity and selectivity.

The present paper is devoted to oxidative dehydrogenation of C1-C4 alcohols in the presence of molecular oxygen over synthetic (A, X, Y, ZSM-5) and natural (clinoptilolite and mordenite), modified by cations of transition elements (Cu^{2+}, Sn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} and Pd^{2+}) for the purpose of high efficiency catalysts for obtaining of corresponding aldehydes.

The catalysts were prepared by ion-exchange method. The amount of modified metals was determined by ionspectral method on ICP-MS Agilent 7700 and it was 0.5-6.0 weight % of zeolite.

The experiments were carried out in a flow apparatus connected directly to the gas chromatograph, at atmospheric pressure and in wide range of temperature, 190-380^{0}C, space velocity, 1000-6000 h^{-1} and molar ratio of reagents, alcohol:O_2:N_2=1:(0.33-5.0):(1.33-5). The analysis of the products was performed by gas-chromotography method.

The results of analysis showed that the reaction of oxidative dehydrogenation of alcohols to corresponding them aldehydes and ketones is accompanied with formation of small amounts of products deep oxidation, dehydration and destruction.

It has been found that methalzeolite catalysts on the basis of synthetic zeolites are more active in these reactions than catalysts prepared on the basis of natural zeolites. The study of influence of the nature of transition element cation on activity of catalysts showed that the Cu and Pd containing catalysts exhibit most activity. It was determined that each of the investigated alcohols has optimum concentration of the transition element cation and the type of zeolite where reached the maximum yield of aldehyde.

As a result, it has been selected efficient metalzeolite catalysts for the oxidative dehydrogenation of methanol, ethanol, propanol, isopropanol, butanol, isobutanol and butanol-2 to the corresponding aldehydes and ketones (formaldehyde, acetaldehyde, propionaldehyde, acetone, butyraldehyde, isobutyric aldehyde and methyl ethyl ketone).

On the selected active catalysts the kinetic laws proceeding of reactions have been investigated and on the basis of results the probable stage mechanism of formation of aldehydes has been suggested. According to mechanism theoretically based kinetic models of the studied reactions have been developed.

P13

SELECTION OF AN ACTIVE ZEOLITE CATALYST FOR OXIDATIVE DEHYDROGENATION OF CYCLOHEXANE TO 1,3-CYCLOHEXADIENE

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The oxidative dehydrogenation of cyclohexane can produce 1,3-cyclohexadiene, potential useful intermediate and monomer for organic synthesis. Cyclohexane is available in large amounts in naphthas. Azerbaijan oil is rich in naphthenic hydrocarbons, in particular cyclohexane.

The production of 1,3-cyclohexadiene is performed industrially in liquid phase. This process is low in energy efficiency, and generates plenty of by-products.

Recently the big attention had been given to the using of modified zeolites for promoting the oxidative dehydrogenation of cyclohexane. But numerous the literature data testify that the main product of the reaction was benzene, water and carbon-dioxide. In the present paper the results of the investigation on selection of high efficiency zeolite catalyst for the reaction of oxidative dehydrogenation of cyclohexane to 1,3-cyclohexadiene are provided.

The following catalysts were used: Azerbaijan natural clinoptilolite (SiO2/Al2O3=α=8.6), mordenite (α=9.6), NaY (α=4.2), NaX (α=2.9), NaA (α=2.9) and CaA (α=1.9), modified with different amounts of methal cations (Cu^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Pd^{2+}, Mn^{2+}, Mg^{2+} and etc.). The catalysts were prepared by ion-exchange method. The amount of modified metals was determined by ICP-MS.

The test of the activity of the prepared zeolite, catalysis was carried out in a flow apparatus with the quarts tube reactor connected directly to the gas chromatograph. The analyses of the products of the reaction was performed by gas chromatography, using a column filled with Paropac-T (length, 3 m). The 1,3-cyclohexadienealso was identified by GC-MS. A study of the catalytic activity of modified zeolites in the reaction of oxidative dehydrogenation of cyclohexane was performed in wide range of temperature, 300-390^{0}C, space velocity, 500-3000 h^{-1} and molar ratio of reagents C_6H_{12}:O_2:N_2=1:(0.24-1.0):(1.62-6.2).

It has been determined that the products of the reaction were cyclohexene, 1,3-cyclohexadiene, benzene, carbon-dioxide and small amounts of cyclohexanol and cyclohexanone. The yields of this products depend on zeolite type, metal cations nature and reaction condition.

Highly efficient catalyst was selected for the reaction of selective oxidative dehydrogenation of cyclohexane to 1,3-cyclohexadiene, on the basis of natural clinoptilolite zeolite and this catalyst showed a better activity and selectivity to the desired product, and the conversion of cyclohexane was 35.8 % while the selectivity to cyclohexadiene was 65.1%.

P14

SYNTHESIS OF 2-ARYL-4,5,6,7-TETRAHYDRO-1H-INDOLES VIA SUBSEQUENT SONOGASHIRA COUPLING/Pd-MEDIATED CYCLIZATION

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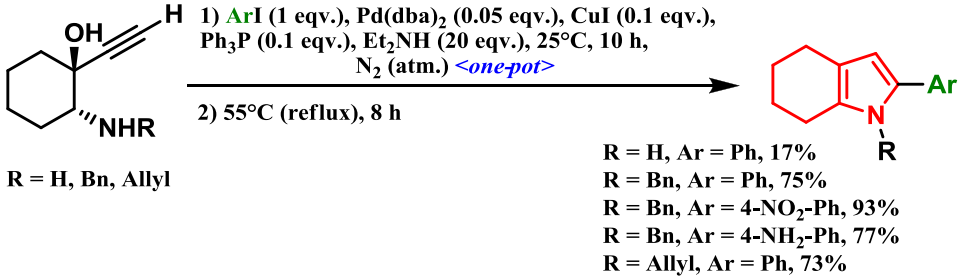
Recent studies in chemistry of indole and its derivatives are focused on development of robust, effective and convenient chemical technology for the synthesis of natural products and their analogs. These compounds can be powerful tools for impacting biology and medicine.
One of the urgent directions in synthetic chemistry is the creating of new pathways leading to substances possessing 4,5,6,7-tetrahydro-1H-indole scaffold. This structural motif is present in two members of Stemona alkaloid family[1] making this ring privileged for library design and drug discovery. Moreover, tetrahydroindole derivatives display a wide spectrum of biological activity such as anti-implantation, hypoglycemic, anti-inflammatory and analgesic, potent neuroleptic (e.g. molindone), anti-tumor, etc. On the other hand, tetrahydroindoles are valuable intermediates applied in the synthesis of natural alkaloids such as goniomitine, arcyriacyanin A, 6,7-secoagroclavine, chuangxinmycin, synthetic drugs like pindolol and highly functionalised indoles.



Palladium-mediated cyclization of amino propargylic alcohols to pyrroles had been initially disclosed by Utimoto[2] et al. In our previous work we have accomplished synthesis of various tetrahydroindoles featuring this methodology[3].
In our present work we have developed *one-pot* sequence based on Sonogashira cross-coupling/Pd-mediated 5-*endo-dig* cyclization and applied this methodology for the gram-scale synthesis of 2-aryl-4,5,6,7-tetrahydroindoles (5 examples). We have estimated that reaction conditions tolerate a wide range of functional groups including nitro and amino moieties. The yield of requisite tetrahydroindoles substantially depends on substituents in aromatic ring and at nitrogen atom.

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P15

NOVEL CHIRAL AMINOCARBENE COMPLEXES DERIVED FROM THE COUPLING OF AMINO ACID ESTERS WITH ISONITRILES

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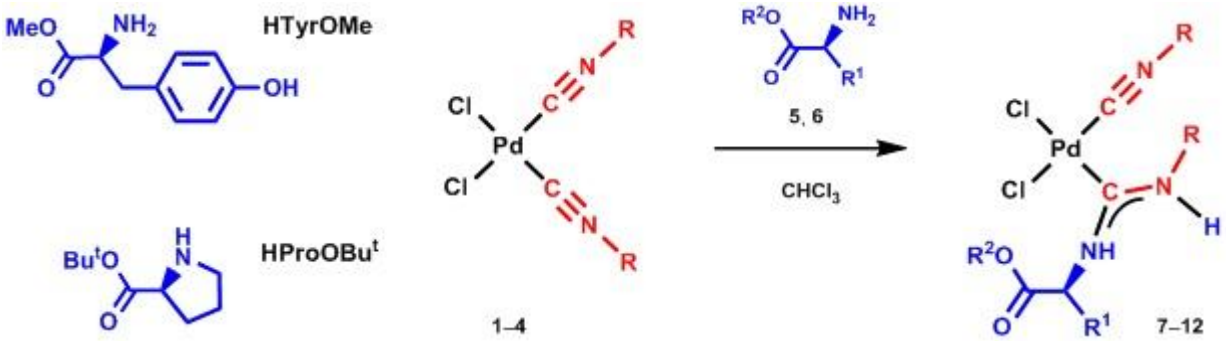
Metal-mediated coupling between one isonitrile ligand in *cis*-[$PdCl_2(CNR)_2$] [R = C_6H_3(2,6-Me_2) **1**, C_6H_3(2-Cl,6-Me) **2**, C_6H_{11} **3**, *t*-Bu **4**] and optically active amino acid esters *L*-HTyrOMe **5** and *L*-HProO(*t*-Bu) **6** proceeds under mild conditions ($CHCl_3$, 20–25 °C) giving chiral aminocarbene species *cis*-$PdCl_2$(CNR)(C(*L*-TyrOMe)NHR) [R = C_6H_3(2,6-Me_2) **7**, C_6H_3(2-Cl,6-Me) **8**], *cis*-$PdCl_2$(CNR)(C{*L*-ProO(*t*-Bu)}NHR) [R = C_6H_3(2,6-Me_2) **9**, C_6H_3(2-Cl,6-Me) **10**, C_6H_{11} **11**, *t*-Bu **12**].



All compounds were fully characterized by elemental analyzes (C, H, N), ESI-MS, IR, 1D (^{1}H and ^{13}C{^{1}H}) and 2D (^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC/^{1}H, ^{13}C-HSQC, ^{1}H, ^{13}C-HMBC) NMR spectroscopic techniques, and by X-Ray diffraction analysis for five complexes. The set of analytical methods indicated that the absolute configuration of the chiral component remains the same in the course of the reaction [1].

Generated aminocarbene complexes were employed as precatalysts for the symmetric Suzuki-Miyaura coupling of aryl bromides BrC_6H_4R-4 with phenylboronic acid giving biaryl species and demonstrated catalytic activity (yields about 50%, TONs up to $5*10^4$) under mild conditions (80 °C, Na_2CO_3, EtOH). Preliminary results showed that compound **9** possess a catalytic activity (yield about 50%, TON about 40) under extremely mild conditions (25 °C, Na_2CO_3, toluene). The catalytical properties of all the obtained chiral carbene species in the asymmetric processes will further be explored and compared to those for previously reported chiral NHC complexes [2].

This project has been supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (Projects PTDC/QUI-QUI/098760/2008 and PTDC/QUI-QUI/109846/2009 and Ph.D. Grant for TBA SFRH/BD/81459/2011).

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P16

Cu(I)-CATALYZED ARYLATION AND HETEROARYLATION OF POLYAMINE

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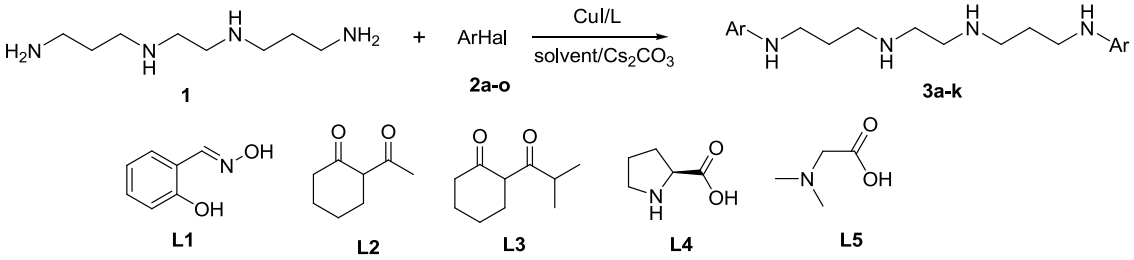
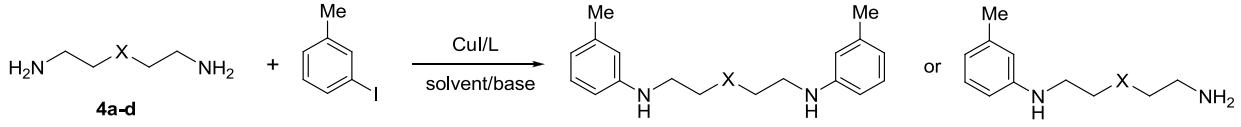
Cu(I)-catalyzed *N,N'*-diarylation of tetraamine **1** with a variety of aryl halides **2a-o** provided corresponding compounds **3a-k** in yields up to 68%, aryl iodides being more reactive than aryl bromides. The reaction conditions were adjusted to favor selective arylation of primary amino groups.



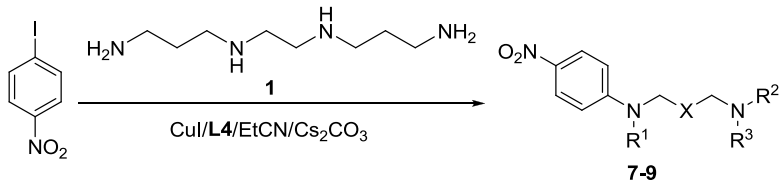
2a: PhBr, CuI/**L4**/MeCN, yield of **3a** 65%
2b: PhI, CuI/**L4**/MeCN, yield of **3a** 59%
2c: *m*-bromotoluene, CuI/**L4**/MeCN, yield of **3b** 55%
2d: *m*-iodotoluene, CuI/**L4**/MeCN, yield of **3b** 67%
2e: 3,5-dimethyliodobenzene, CuI/**L2**/DMF, yield of **3c 54%**
2f: 1,3-dibromobenzene, CuI/**L2**/DMF, yield of **3d** 28%
2g: 1-bromo-3-iodobeznzene, CuI/**L4**/EtCN, yield of **3d** 27%
2h: 1,3-diiodobenzene, CuI/**L4**/EtCN, yield of **3e**, 24%
2i: 4-bromobiphenyl, CuI/**L1**/toluene, yield of **3f** 27%
2j: 4-iodobiphenyl, CuI/**L4**/MeCN, yield of **3f** 43%
2k: 4-acetoxy-4'-iodobiphenyl, CuI/**L4**/EtCN, yield of **3g** 68%
2l: N,N-diethyl-3-iodobenzamide, CuI/**L4**/EtCN, yield of **3h** 58%
2m: 2-bromonaphthalene, CuI/**L3**/DMF, yield of **3i** 28%
2n: 4-iodoanisole, CuI/**L4**/EtCN, yield of **3j** 52%
2o: 4-iodochlorobenzene, CuI/**L4**/EtCN, yield of **3k** 42%

m-Iodotoluene was used as a model reagent for the investigation of the reactivity of tri- and tatraamines **4a-c** under Cu(I)-catalysis conditions.



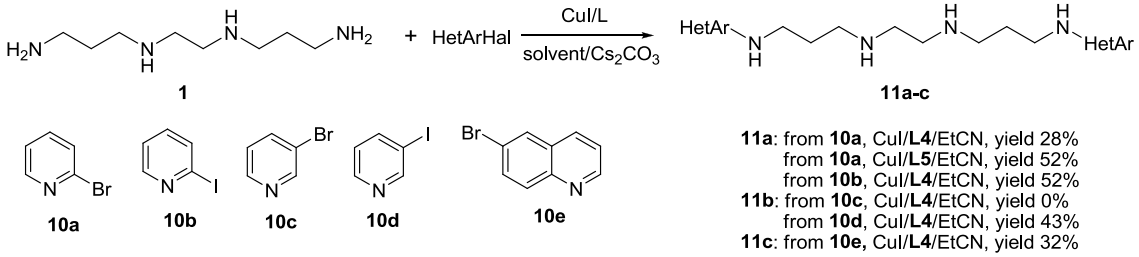
4a: X = CH_2NHCH_2, CuI/**L4**/MeCN, yield of **6a** 78%
4b: X = $NHCH_2CH_2CH_2NH$, CuI/**L4**/EtCN, yield of **5b**, 35%
4c: X = $CH_2NHCH_2CH_2CH_2NHCH_2$, CuI/**L4**/EtCN, yield of **5c**, 18%

The possibility of *N,N*-diarylation of primary amino groups was demonstrated when using *p*-nitroiodobenzene.



with 2.5 equiv. of 4-iodonitrobenzene:
7: $R^1 = R^2 = R^3 = p\text{-}NO_2C_6H_4$, yield (mixture **7** + **8**) 35%
8: $R^1 = R^2 = p\text{-}NO_2C_6H_4$, R^3 = H, yield 33%
9: $R^2 = p\text{-}NO_2C_6H_4$, $R^1 = R^3$ = H, yield 12%
with 5 equiv. of 4-iodonitrobenzene:
yield of pure **7** 22%

N,N'-diheteroarylation reactions of tetraamine **1** was carried out using bromo- and iodosubstituted pyridines and quinoline.



11a: from **10a**, CuI/**L4**/EtCN, yield 28%
from **10a**, CuI/**L5**/EtCN, yield 52%
from **10b**, CuI/**L4**/EtCN, yield 52%
11b: from **10c**, CuI/**L4**/EtCN, yield 0%
from **10d**, CuI/**L4**/EtCN, yield 43%
11c: from **10e,** CuI/**L4**/EtCN, yield 32%

The work was supported by the RFBR grant N 12-03-00796.

PALLADIUM NANOPARTICLES STABILIZED IN THE PHOSPHONIUM IONIC LIQUIDS AS AN EFFECTIVE CATALIST IN SUZUKI REACTION

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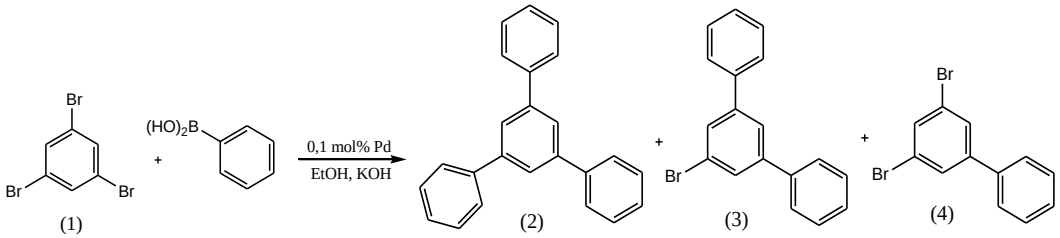
Suzuki cross-coupling catalyzed by transition metals is one of the most important and popular tool of C-C-bond formation in organic synthesis[1]. Phosphonium Ionic Liquids (PILs)[2] are effective and favorable Palladium Nanoparticles (PdNs) stabilizers.

A: X=$(CF_3SO_2)_2N$ R=Alk(C_1-C_{18}), $CH_2COOCH_2CH_3$
B: X=BF_4

Scheme 1. Synthesis of the PILs based on the sterically hindered phosphine

A number of the ionic liquids based on the phosphonium salts was obtained. Synthesized PILs consist of three *tert*-butyl (Scheme 1) or three *n*-butyl substituents and linear alkyl chain of various length or chain with ester group on the phosphorus atom. PdNs stabilized in decyl(tri-*tert*-butyl)phosphonium and decyl(tri-*n*-butyl)phosphonium salts were tested as catalysts in Suzuki reaction (Scheme 2). 1,3,5-tribromobenzene (1) was chosen as a substrate.



Scheme 2. The Suzuki reaction

The results are shown in Table 1. PdNs formation was confirmed by the method of Transparent Electron Microscopy (Fig. 1).

Table 1. Suzuki reaction in PIL presence

№	PILs	Concentration of PILs, mol%	Yield, %		
			(2)	(3)	(4)
1	A	1	38,8	8,0	1,9
2	A	5	55,5	17,2	3,2
3	A	10	43,4	8,0	2,4
4	B	10	57,8	8,6	2,0
5	B	25	68,3	6,0	1,6
6*	B	25	92,0	4,1	0,5

*reaction mixture was heated to 50°C

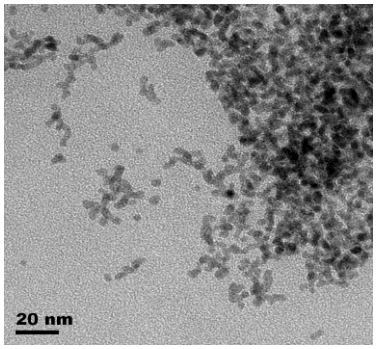


Figure1. Palladium nanoparticles (TEM)

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P18

A SOLID-SUPPORTED ORGANOCATALYST FOR CONTINUOUS-FLOW ENANTIOSELECTIVE ALDOL REACTIONS

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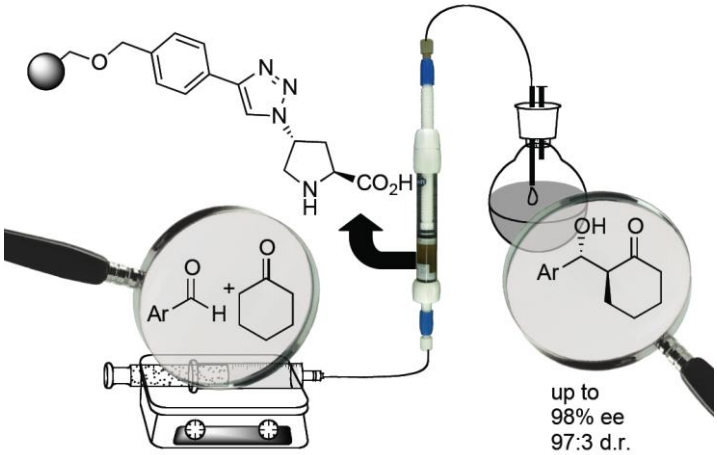
The aldol reaction is one of the most used methods for the formation of new carbon-carbon bonds. Control of the absolute configuration of the newly formed stereocentre is of vital importance for the preparation of asymmetric aldol products since they can be used as important building blocks for pharmaceuticals and natural products. A sustainable and enviromentally friendly method to achieve this aim is by means of organocatalysts, which in turn, can be immobilized onto solid supports to facilitate their use as they can be recovered by direct filtration and reused several times. Furthermore, because of their stability and recyclability, solid-supported organocatalysts are particularly suitable for continuous-flow systems,[1] which allow large-scale synthesis usually accompanied by higher turnover numbers (TONs). Only two examples of stereoselective aldol reactions catalyzed by immobilized catalysts in continuous-flow systems have been reported in the literature until now, however only low levels of productivity and diastereoselectivity could be achieved in both cases.[2]



Our research group has a broad experience in performing single-pass continuous-flow reactions using organocatalysts anchored onto polystyrene resins.[3] Hence, using this kind of systems, the preparation of a polymer-supported proline derivative and its use as a heterogeneous organocatalyst for highly stereoselective aldol reactions in continuous operation[4] will be presented.

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P19

NOVEL METHOD FOR THE SYNTHESIS OF MESO-SUBSTITUTED OLIGOPYRROLES AND CORROLES

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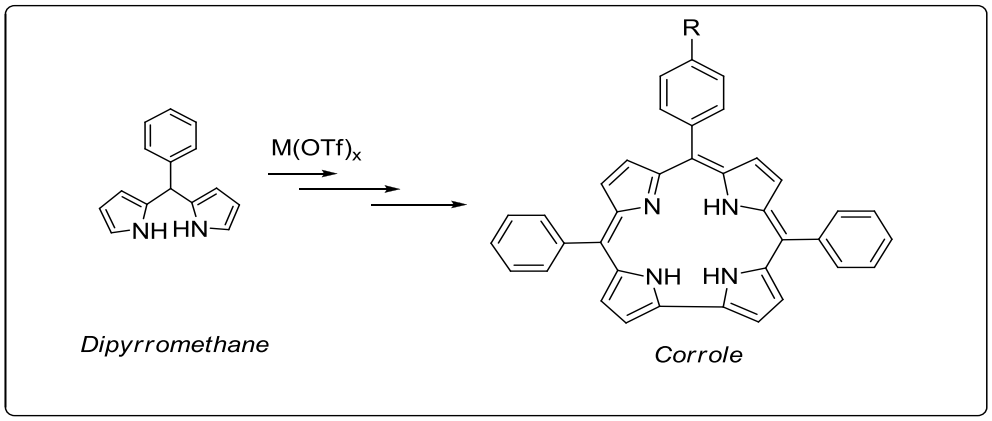
Meso-substituted porphyrins and porphyrin like compounds are important macrocyclic aromatic compounds in organic chemistry. Corrole is one of the most common contracted porphyrin type compound and the first synthesized and isolated macrocylic member of porphyrin derivatives in this class. Corroles take place in some medicinal applications, as catalysts of synthetic transformations, in some vitamins like B12 and as coordinating ligands for metals with high oxidation state.[1] Oligopyrrolic structures also take a wide research area in synthetic studies as the subunits of porphyrins[2a], corroles[2b], expanded porphyrins[2c], etc. Especially pyrrole and dipyrromethane have an efficient role in organic synthesis as the building blocks of macrocyclic structures.[2,3] On the other hand, the usage of tripyrrane and tetrapyrrane compounds is less common because of the difficulties in the synthesis and purification and also storage of these compounds due to their unstable nature.
In this study, we aimed to use dipyrromethane sulfonamides as precursors for the synthesis of *meso*-substituted tripyrrane and tetrapyrrane compounds in the presence of metal triflate catalyst. This procedure allows for the synthesis of unsymmetrical tripyrranes and tetrapyrranes. Tripyrrane and tetrapyrrane are very valuable subunits for the construction of porphyrins, corroles and expanded porphyrins. After the synthesis of tetrapyrranes through dipyrromethane sulfonamides, corroles were synthesized by direct *α-α'* coupling of tetrapyrranes by using suitable oxidizing agent. All compounds were isolated by chromatographic methods and their structures were identified *by* spectroscopic techniques (^{1}H NMR, ^{13}C NMR, FT-IR, HRMS).



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P20

BRANCHED POLYPHENYLENES FOR PLED APPLICATIONS OBTAINED USING METAL-COMPLEX CATALYSIS

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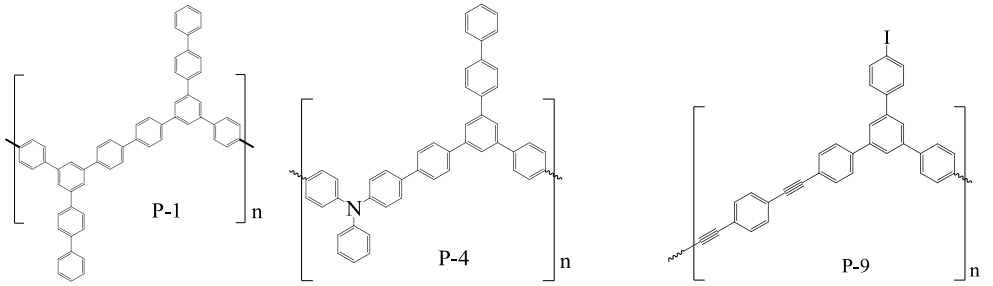
Polymer light-emitting diodes (PLED) draw great attention due to their easy solution process and potentially high efficiency for their application in various fields, such as displays and various lighting applications.[1-2] But so far there is an unsolved problem related to obtaining stable blue emitting polymer materials (2.9 – 2.7 eV). Since the discovery of polyfluorenes, they have been a research interest because of their blue emitting properties.[3] However, their thermal and chemical stability are not good enough for their application as active layers in PLEDs. Most of the synthesized derivatives have a problem related to colour instability due to degradation processes.[4-5]

We introduce novel soluble starlike branched polyphenylenes with exceptional thermal and chemical stability properties which are blue emitters. Thus such polymers can become a good alternative to the development of PLEDs.

A series of starlike branched polyphenylenes (P1 – P7) was synthesized via the method of Ni-catalyzed polycondensation and Suzuki reaction. The obtained polymers were characterized via ^{1}H and ^{13}C spectroscopy, element analysis and FTIR spectroscopy.



A PLED was created on the basis of polymer P-4 as an active layer (Fig. 1). The sample showed excellent performance of thermal and photo-stability, however electroluminescence efficiency of this sample is not high enough and its increase is our task for the near future. On the basis of the polyphenylenes as a host matrix for the iridium organic complex dye a series of PLEDS were built. Current voltage characteristics and electroluminescence spectra were measured.

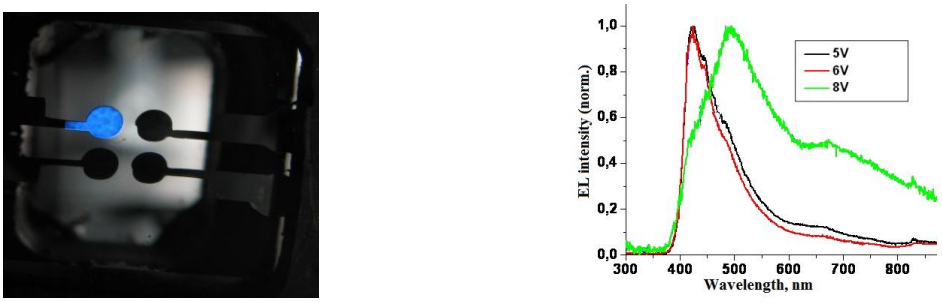


Fig.1. Photo of PLED with P-4 active layer (on the left) and electroluminescence spectra of the devise (on the right)

Via Sonogashira reaction series of blue emitting polyphenylenes with acetylene groups in the polymer backbone (P8 – P12) was synthesized and spectra of their photoluminescence were measured.

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BIOMIMETIC ORGANOCATALYSIS USING MALONIC ACID HALF-THIOESTERS (MAHTs) AS ENOLATE PRECURSORS: MIMICRY OF POLYKETIDE SYNTHASES

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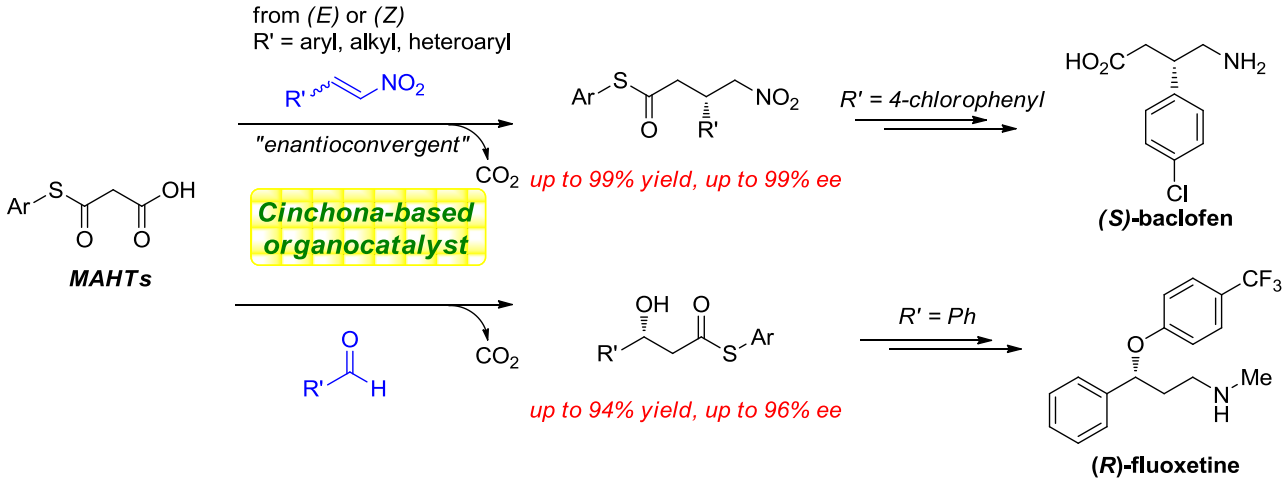
Nature uses the enzymatic activation of malonic acid half thioesters (MAHTs) to generate ester enolates or their equivalents that smoothly undergo the chain elongation step by decarboxylative Claisen condensation. Inspired by these biocatalytic processes, a few groups have independently reported on a Metal-catalyzed aldol reaction and Michael addition reaction using MAHTs as direct thioester enolate donors. Meanwhile, other groups independently demonstrated that organocatalytic asymmetric transformations can also be accomplished with MAHTs via hydrogen bond catalysis using organocatalysts. Unfortunately, the catalytic activity and enantioselectivity achieved in their work were insufficient for synthetic use. In this symposium, we present that some cinchona-based organocatalysts serve as remarkably effective catalysts for biomimetic enantioselective organocatalysis using MAHTs as enolate precursors in asymmetric Michael addition reaction[1] and asymmetric direct aldol reaction. In addition, the synthetic utilities of our protocols are demonstrated in the formal synthesis of (*S*)-baclofen and (*R*)-fluoxetin. Details of the mechanistic hypothesis and the basis for enantioselectivity will also be presented.



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P22

TRIMETHYLSILYL TRIFLATE CATALYZED DIELS-ALDER REACTIONS OF MALEIC ACID ISOIMIDES

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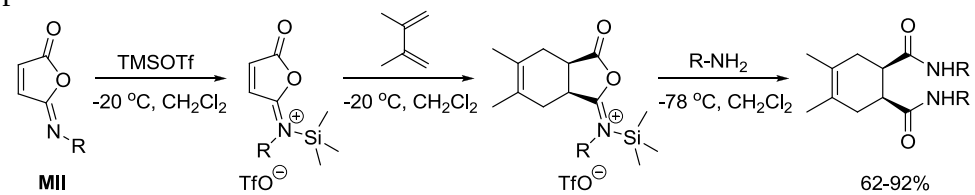
While maleic anhydride remains one of the most widely used dienophiles in Diels-Alder reaction, other maleic acid derivatives, e. g., maleic monoamides are often not reactive enough. However, cyclodehydration of maleic monoamides under strongly acidic conditions yields maleic isoimidium salts, which undergo Diels-Alder reaction with ease [1]. Limited stability of maleic isoimidium salts often poses problems for the synthesis and use of these compounds. Cycloaddition reactions of the parent maleic isoimides (**MII**), while possible in some instances, require long reaction times and elevated temperature, which leads to side reactions. Our aim was to find a catalyst to facilitate Diels-Alder reactions of **MII**. Among the catalysts currently employed to promote cycloaddition reactions, the leading role is still played by metal (including transition metal) catalysts. We wished to avoid using this type of compounds, keeping in line with the current predisposition to environmentally benign synthetic methods. Several highly electrophilic silicon derivatives have been recently claimed to enhance the reactivity of dienophiles in Diels-Alder reactions [2]. We decided to explore the possibility to use trimethylsilyl triflate (TMSOTf) as a potent, yet mild catalyst for Diels-Alder reactions of **MII**.

On treatment with TMSOTf at -20°C, **MII** readily formed 1:1 adducts, as evidenced by spectroscopic data: the carbonyl group and imino group absorption bands in the IR spectra shifted towards higher wave numbers, while the C=C double bond protons in the ^{1}H NMR spectra shifted downfield. The spectral data also supported our hypothesis that TMSOTf could make **MII** more likely to undergo Diels-Alder reactions, as it was evident that the C=C double bond electron density had decreased.

We also wanted to clarify how exactly TMSOTf interacted with **MII**. In view of the considerably greater stability of Si-O bond compared to Si-N bond, it could be envisaged that silicon would preferentially bind to the carbonyl oxygen. Indeed, it has been reported that this is the case, if TMSOTf is added to tertiary amides [3]. However, *ab initio* quantum mechanical calculations revealed that bonding to the imino group nitrogen in **MII** was at least by 8 kcal/mol more favorable. This conclusion was supported by the ^{29}Si NMR spectrum of the adduct, displaying ^{29}Si chemical shift of 7.23 ppm – much more characteristic of a Si-N^{+} than of a Si-O^{+} bond.

As we had proposed, **MII** adducts with TMSOTf reacted smoothly with dienes even at -20°C to yield the corresponding cycloaddition products. Due to their high reactivity they were not isolated, but treated *in situ* with an excess of primary amine, so that maleic diamides were finally obtained in good yields. Analysis of the reaction mixture indicated that the cycloaddition and subsequent ring opening reactions were complete within an hour, occasional lowering of yield being primarily due to isolation procedures.



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P23

NORBORNENE BASED COPPER-CONTAINING COPOLYMERS. SYNTHESIS AND ELECTROLUMINESCENT PROPERTIES

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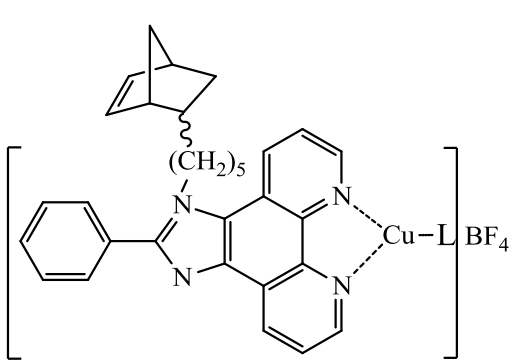
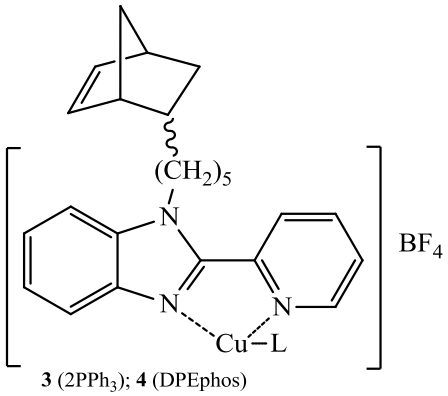
Luminescent copper(I) complexes with norbornene functionalized phenantroline and pyridinylbenzimidazole ligands were synthesized. Compounds **1-4** were isolated as air stable highly soluble yellow solids.

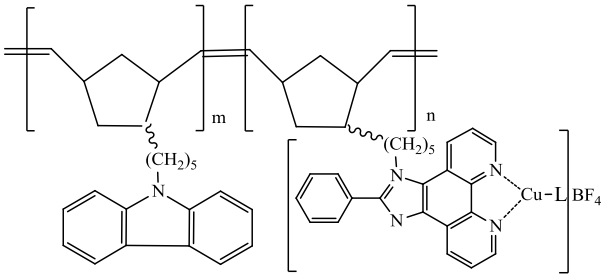


1 (2PPh$_3$); **2** (DPEphos)

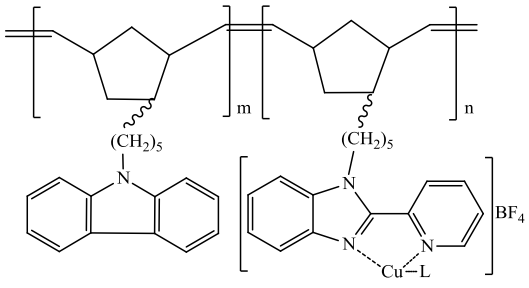


3 (2PPh$_3$); **4** (DPEphos)

Copper-containing monomers **1-4** were copolymerized via ring-opening metathesis polymerization with carbazole substituted norbornene monomer.



m:n = 20:1 **5** (PPh$_3$)$_2$; **6** (DPEphos)



m:n = 1:1 **7** (PPh$_3$)$_2$; **8** (DPEphos)

The resulting copolymers **5-8** were used as emitting materials in organic light-emitting diodes (OLEDs) of the structure ITO/Cu-copolymers/BATH/Alq$_3$/Yb. The OLED devices generated electroluminescence of green and yellow-orange colors with maximum brightness of 37.5 cd/m^2.

This work was supported by the Russian Foundation for Basic Research (Project № 12-03-00250-a).

P24

PALLADIUM-CATALYZED OXIDATIVE ARYLATIVE CARBOCYCLIZATION OF ALLENYNES

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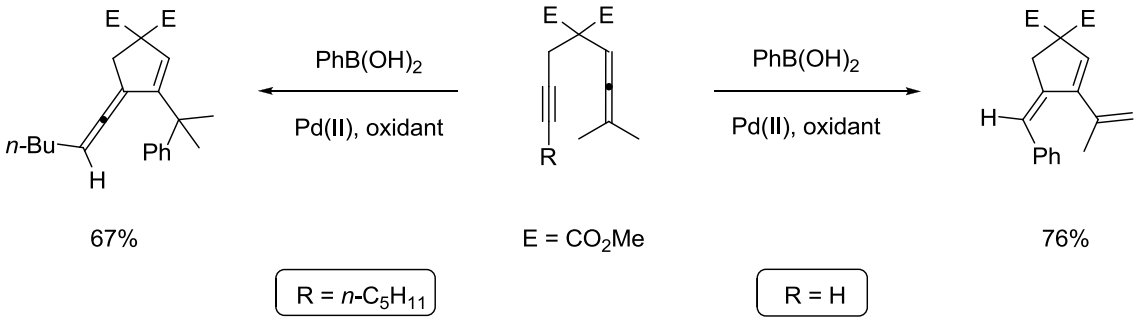
Transition metal-catalyzed cyclizations of allenynes provide efficient and atom-economical routes to polyunsaturated carbo- and heterocycles.[1] An oxidative protocol was developed allowing for the palladium-catalyzed synthesis of arylated carbocyclic structures under mild and insensitive conditions.[2] Using palladium acetate as catalyst and 1,4-benzoquinone as oxidant, a wide range of arylboronic acids is suitable for the cyclization reactions of 1,5-allenynes.
Employing these conditions cross-conjugated trienes were obtained in the case of a terminal or an aryl-substituted alkyne-moiety. However, with alkyl-substituents access to vinylallenic products is provided. Two possible mechanisms were suggested to rationalize the formation of the two different products.



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P25

γ-ALKYLIDENEBUTENOLIDE: A SIMPLE BUILDING BLOCK TO ACCESS THE POLYCYCLIC SCAFFOLDS OF NATURAL PRODUCTS

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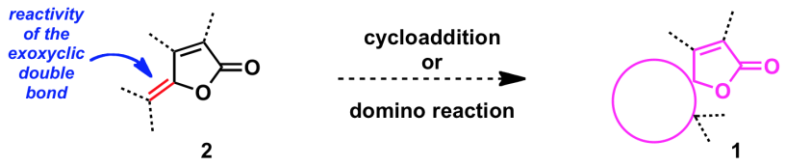
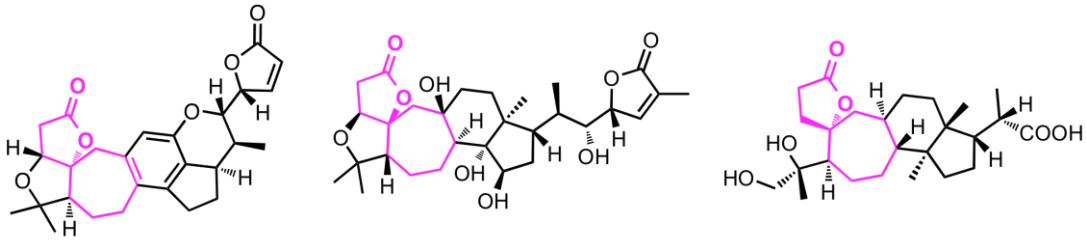
On one hand, natural products containing **spirolactones 1** represent a large class of structurally diverse molecules exhibiting a wide range of biological activities. Having cyclic structures fused at a central carbon provide those molecules with an interesting sterically constrained feature, which is often responsible for the biological activities observed. [1] On the other hand, **γ-alkylidenebutenolide 2** is a very attractive and valuable building blocks and has been used on a number of occasions to access more complex structures.
Accordingly, not only we recently reported a palladium free Sonogashira reaction to reach those moieties (**2**) diastereoselectively [2] but, we have also shown a growing and continued interest in the construction of spirolactones from this species (Diels-Alder [3] or new domino [4] reactions).



The **spiro [6.4] ring system** is a recurring structural motif in natural products from the *Schisandra genus* family. Despite their interesting biological activities (**anti-HIV** for instance), the reason why we decided to focus on developing an approach toward the synthesis of the polycyclic skeleton core of those compounds comes from the fact that such molecules represent a synthetic challenge for organic chemists. Indeed, these polycyclic structures present at least seven stereogenic centres including several quaternary one.



Strategies, synthesis of precursors and cyclisations will be described and discussed.

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P26

DEVELOPMENT OF NEW TYPE CATALYSTS IN DIRECT ASYMMETRIC ALDOL REACTION OF AROMATIC KETONES

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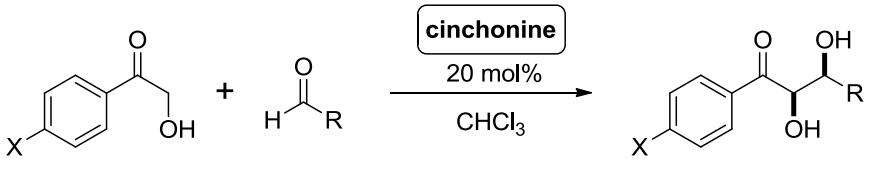
The aldol reaction is one of the most powerful transformations in organic chemistry. This process unites two carbonyl partners to give new carbon-carbon bond with up to two new stereocenters. Since first application of proline as organocatalyst in asymmetric aldol reaction,[1] astonished number of catalysts have been published and many problems with stereochemistry control have been solved.[2] However, there are still some problematic examples of aldol reaction, where classic catalyst are useless. Among others reaction between aromatic ketones and aliphatic aldehydes still constitutes white spot on the aldol reaction map. Only a few works were published in this topic with metal complexes as catalyst.

Now, we show a new application of cinchona alkaloids as organocatalyst in direct asymmetric aldol reaction of aromatic hydroxyketones and aliphatic aldehydes. Results of our work show that cinchona alkaloids could be applied as first example of organocatalyst in asymmetric aldol reaction of aromatic hydroxyketones. Reaction products were obtain with acceptable yield, high diasteroselectivity and moderate enantiomeric excess.



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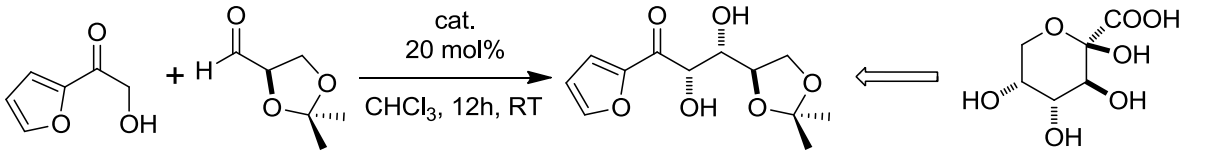
Application of mentioned reaction gives opportunity to synthesis *de novo* of ketohexoses like 2-keto-D-gluconic acid which is component of *Acetobacter* bacteria cell membrane.[4]



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2-keto-D-gluconic acid

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P27

APPLYING HYDROFORMYLATION TO THE SYNTHESIS OF ALKALOIDS

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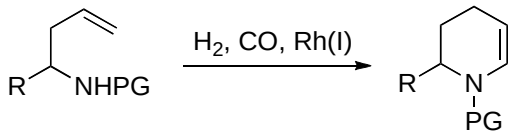
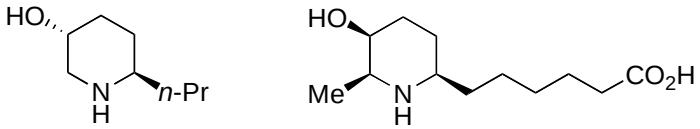
2 - University of Heidelberg
roderick@ntu.edu.sg

Hydroformylation is a remarkably mild and tolerant method for the formation of a new C-C bond and generating aldehyde functionality. [1] With an appropriately placed protected amine in the substrate, tandem condensation occurs to give a cyclic enamine derivative.



The electron rich double bond of the enamine derivative allows further functionalisation. Using dihydroxylation, which proceeds with surprising diastereoselectivity, and stereoelectronically controlled iminium chemistry, we have been able to prepare a number of piperidine alkaloids including pseudoconhydrine [2] and azimic acid.



1 **2**

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P28

CARBOHYDRATE-DERIVED PHOSPHORAMIDITE LIGANDS FOR ENANTIOSELECTIVE Cu-CATALYZED 1,4-CONJUGATE ADDITION OF DIETHYLZINC TO ENONES

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The enantioselective copper-catalyzed conjugate addition is one of the most important methods for the formation of new stereogenic center. Leading role among chiral ligands used for this reaction play phoshoramidite ligands based on the atropoisomeric binaphtols and chiral amines. There are only single examples of phoshoramidite ligands based on carbohydrate-derived amines, all other are mixed phosphonic-phosphoramidite ligands. Having in mind that most of successful phosphoramidite ligands were based on a single phosphorous atom, we decided to synthesized carbohydrate-derived ligands having the structure **I** (Figure 1), in which one can control the asymmetric induction by varying steric demands of protecting group R-R".

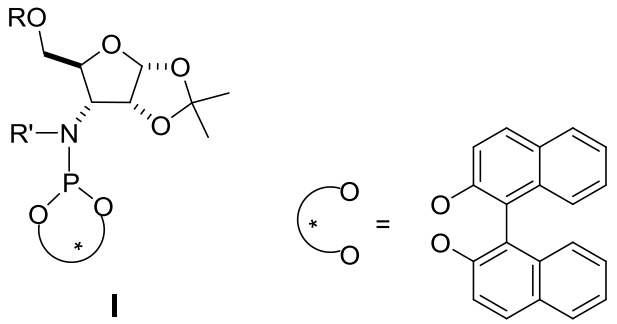

Fig. 1

We have synthesized library of ligands with various protecting group R and R' (hydrogen or alkyl) and used them for the enantioselective conjugate addition of Et_2Zn to chalcone and cyclohexenone. Best results were obtained for ligands with *tert*-butyldimethylsilyl as the R group and benzyl (77% ee for chalcone) or cyclohexylmethyl (57% ee for cyclohexenone) as R' groups. This results position our ligands among the best sugar-derived ligands for copper-catalyzed conjugate addition.

P29

SCALABLE ENANTIO- AND STEREOSELCTIVE ROUTE TO OCTAHYDROCYCLOHEPTA[b]PYRROL-4(1H)-ONE SCAFFOLD VIA THE AZA-COPE-MANNICH REARRANGEMENT

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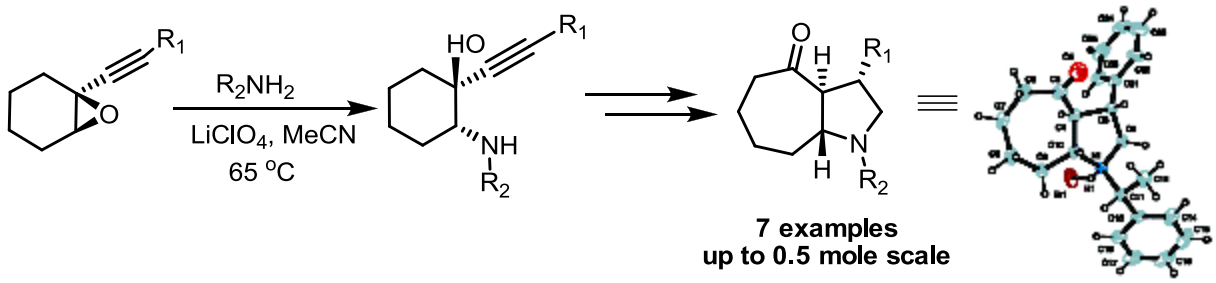
Aza-Cope-Mannich reaction is a powerfull tool for construction of complex molecules containing pyrrolidine ring[1]. Various natural products and biologically active compounds were synthesized during past years[2] using this transformation. Many biologically relevant compounds, such as hexahydroindoles and octahydropyrroles can be prepared in streoselective fashion[3]. For this and others cycloalkano[b]fused pyrrolidines two types of ring junction are possible. Since preparation of *cis*- fused compound is well known, we aimed to create an approach to *trans*-fused heterocycles.
In our present work we have developed enantio- and stereoselctive approach to the octahydrocyclohepta[b]pyrrol-4(1H)-one scaffold. The method based on Aza-Cope-Mannich rearrangement of *trans*-2-amino-2-ethenylcyclohexanols which resulted in only one of 4 possible diastereomers. In order to extend this approach to the preparation of these scaffolds in enantiomerically pure form, we required a method for preparing (1R,2R)-trans-2-aminocyclohexanole in a large scale. This intermediate had previously been obtained by asymmetric Shi epoxidation, which proceeded in high overall efficiency. The salient features of the route include epoxide opening and aza-Cope-Mannich reaction.



Overall efficiency of this process allows us to prepare 100 g quantities of target compounds for subsequent modification and preparation of compound libraries for high- throughput screening.

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P30

THE CATALYTIC TRANSFORMATION OF THE 3-ALKYLSULPHANYL-2-ARYLAZO-3-CYCLOALKYLAMINO-ACRYLONITRILES

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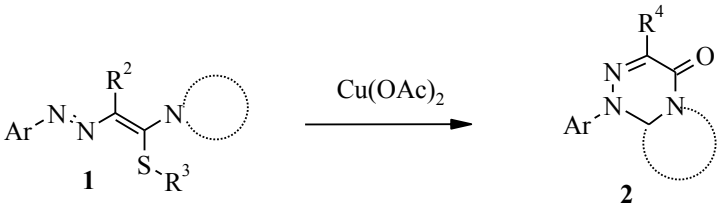
1,2,4-Triazines and its derivatives condensed with one or more heterocyclic rings found application in many fields such as pharmaceutical, herbicidal, pesticides and dyes.[1]
Recently we have discovered that 3-alkylsulphanyl-2-arylazo-3-cycloalkylaminoacrylonitriles **1** can transform into the mono- or bicyclic 1,2,4-triazines in the mild conditions.[2]



R^1 = Me, Benzyl, Allyl, Propargyl R^2 = CN, Ph

Systematic studies of the reaction allowed us to elucidate the main tendencies of the process and established the effect of several catalists like $Cu(OAc)_2$, $Hg(OAc)_2$. These observations helped us to expand the scope of the reaction discovered to prepare series of mono- and bicyclic 1,2,3-triazine derivatives.

We thank the RFBR (grant 11-03-00579-a, 10-03-96-084-r_ural-a) for financial support.

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P31

THE UNUSUAL BEHAVIOR OF A DISULFIDE DERIVATIVE DURING NMR, IR AND MS ANALYSIS

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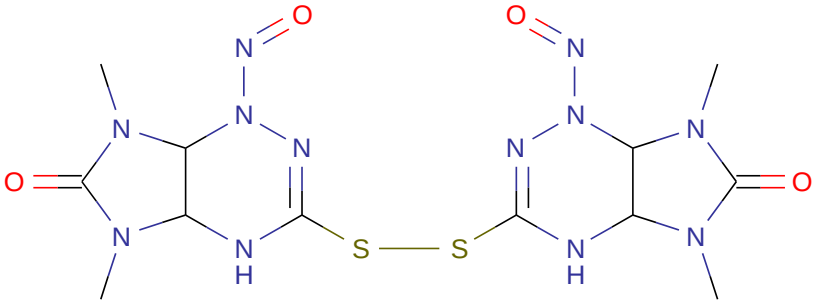
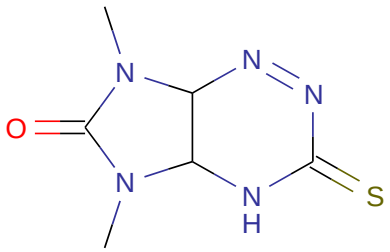
The spectral characterization of new-synthesized compounds is a routine procedure in modern chemistry. However, due to high complexity of spectral data the calculations within the framework of density functional theory (DFT) are acknowledged to be useful for spectra interpretation [1]. This work is dealt with comprehensive experimental (NMR, IR, MS) and theoretical analysis of disulfide (**1**) aimed at understanding of its structural perturbations in course of spectra acquisition.



(1)



(2)

It was shown that (**1**) represents a double set of signals both in ^{1}H/ ^{13}C NMR and IR spectra. Noticeably, the latter also draws a relatively high distance between two NH bands. Systematically, in ESI-MS spectrum a common pattern for two substances is observed, where one can see the contaminating molecular ion of the mass that is just 30 a.m.u. less than a half mass of **(1).** Its presumable structure **(2)** correlates well with second set of NMR signals and IR bands in corresponding spectra. Thus, according to ESI-MS, IR and 1D NMR data we observed a mixture of **(1)** and (**2**). However, the advanced NMR studies, namely DOSY, have shown indistinguishable diffusion coefficients and, moreover, EXSY evidenced for the chemical exchange with $\Delta G^{\#}_{298}$ = 78.8±0.5 kJ/mole, that can be well explained by hindered rotation of NO-groups according to DFT calculations. Comparing DFT-calculated vibrational frequencies and signal intensities of **(1)** and experimental IR-data, the hydrogen bonding of NH-protons leading to asymmetry of **(1)** in the solid state can be concluded. That explains the double set of bands characterized by noticeable difference of two NH wavenumbers mentioned above. Finally, advanced study by HPLC-MS and MS/MS is in favor of **(1)** decomposition during ionization in mass-spectrometer giving **(2)**.
Summing up, the observed double set of spectral data is due to completely different reasons. Structural spectral analysis combined with DFT calculations has demonstrated its credibility.

The financially support from the Russian Foundation for Basic Research Project No. 11-03-01055 and from the Chemistry and Materials Science Department of the Russian Academy of Sciences (basic research program "Medicinal and Biomolecular Chemistry") is greatly appreciated.

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P32

IMMOBILIZATION OF CHIRAL ORGANOCATALYSTS ON POLY(METHYLHYDROSILOXANE)

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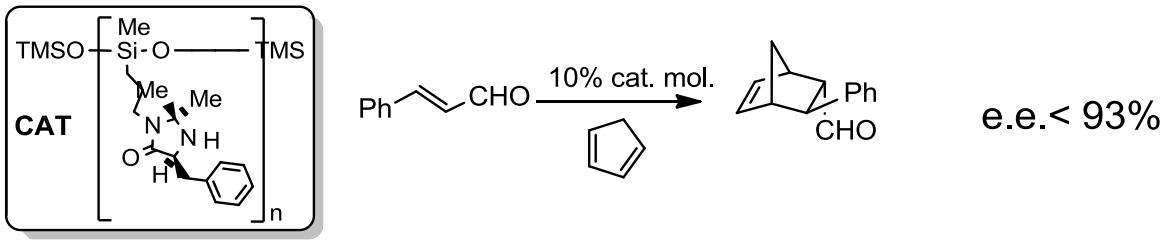
Anchoring of a chiral catalyst on a polymer support offers a clear advantages in recovering and recycling of the precious catalytic species, streamlining the reaction work up and facilitating the isolation of the product. The choice of the support is crucial. In particular, soluble supports have been the subject of an extensive investigation effort because they allow the development of anchored catalysts that better mimic the non-supported catalyst, often leading to higher chemical and stereochemical efficiency.

Among a variety of available soluble supports, polymethylhydrosiloxane (PMHS) has many positive features: it is a commercially available, inexpensive polymer, that can be readily functionalized, and its solubility properties can be properly tuned by a judicious choice of the organic residues to be attached to the polymeric backbone. Here, we report our preliminary results on the preparation and application of two PMHS-supported enantiomerically pure bifunctional organocatalysts.

Catalysts derived from PMHS-supported imidazolidinone **5** and different acids can be conveniently employed to promote Diels-Alder cycloadditions of α,β–unsaturated aldehydes with cyclopentadiene. The immobilization on the polymer greatly simplified the catalyst recovery. Recycling experiments showed that the supported catalyst maintains its stereochemical efficiency for up to five reaction cycles. A properly modified Takemoto's catalyst was succesfully anchored to poly(methylhydrosiloxane) and employed in the stereoselective addition of activated carbon nucleophiles to nitrostyrene.



P33

ASYMMETRIC ALKENE CYCLOMETALLATION BY $EtAlCl_2$ AND Mg, CATALYZED WITH CHIRAL ZIRCONIUM COMPLEXES

T.V. Berestova, T.A. Raznicina, I.V. Molchankina, L.V. Parfenova, L.M. Khalilov, U.M. Dzhemilev

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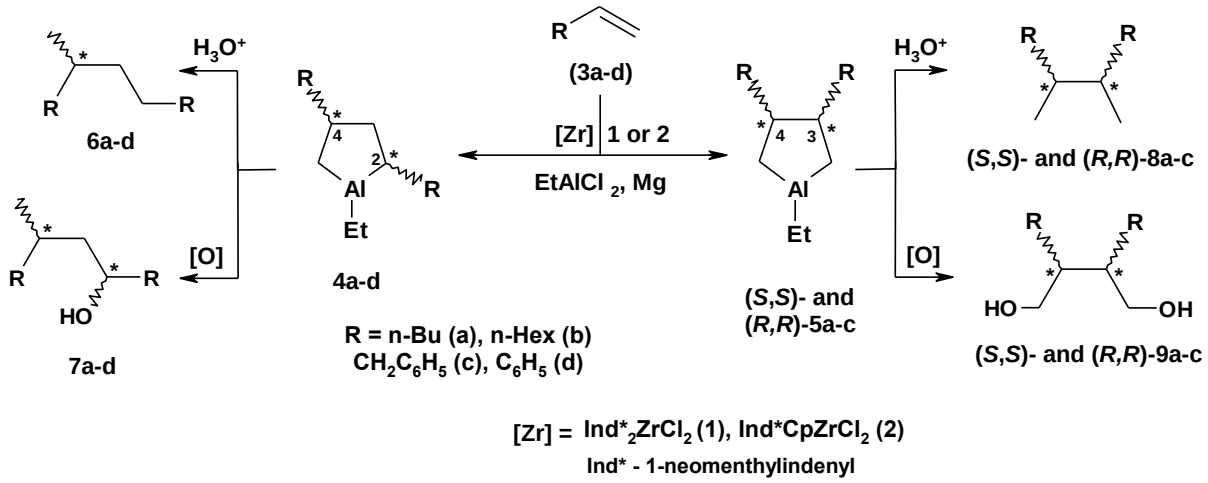
Catalytic cyclometallation of terminal alkenes by $EtAlCl_2$ and Mg (powder), catalyzed with Cp_2ZrCl_2, is the effective route to *trans*-3,4-dialkyl-1-ethylaluminacyclopentanes [1]. It is expected that application of chiral zirconocenes in the reaction could give enantiomerically enriched disubstituted aluminacyclopentanes, which further may be transformed into practically important optically active monomers for organic and organometallic chemistry.
Herein we studied chemo-, regio- and enantioselectivity of the reaction of alkenes **3a-d** with $EtAlCl_2$ and Mg, catalyzed with Zr η^5-complexes $Ind^*{}_2ZrCl_2$ (Ind^*-neomenthylindenyl) (**1**), $CpInd^*ZrCl_2$ (**2**) (scheme 1).

Scheme 1



It is shown that reaction with terminal alkenes **3a-c** is followed by the formation of *trans*-3,4-dialkyl(benzyl)-1-ethylaluminacyclopentanes (**5a-c**) with yield of 27-63% (6-36%*ee*). Application of styrene **3d** in the reaction provides 2,4-diphenyl-1-ethylaluminacyclopentane (**4d**) with yield 28%, which was hydrolyzed to the (1*R*,*S*)-1,3-diphenylbutane (**6d**) (33-41%*ee*).
The structures of the disubstituted aluminacyclopentanes **4** and **5** were established by the means of one- and two-dimensional NMR spectroscopy and GC-MS of the hydrolysis (**6**, **8**), deuterolysis and oxidation (**7**, **9**) products.

The authors thank the Russian Foundation of Basic Research (Grant No. 12-03-00363a) for financial support.

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P34

DIOXINDOLE IN ASYMMETRIC CATALYTIC SYNTHESIS: NEW ROUTES TO ENANTIOENRICHED 3-SUBSTITUTED 3-HYDROXYOXINDOLES AND APPLICATION TO THE SYNTHESIS OF MAREMYCIN A

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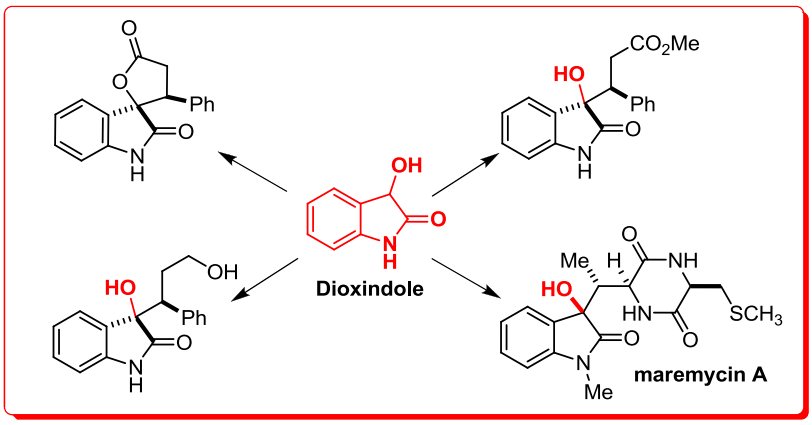
Many biological active compounds and natural products possess an oxindole framework with a hydroxyl-bearing tetrasubstituted stereocenter at C3. [1] This has provided the impetus for developing highly stereoselective routes to this particular target structure. [2] Here, we describe an unprecedented synthetic strategy to access 3-substituted 3-hydroxyoxindole derivatives in excellent yields and enantioselectivities. [3] We have discovered that dioxindole (3-hydroxy-2-oxindole) is characterized by a strong nucleophilic behaviour that has allowed the development of an asymmetric Michael addition to α,β-unsaturated aldehydes, driven by iminium ion activation, using a catalyst loading as little as 1 mol%. The chemistry provides a direct and easy access to valuable spiro oxindole γ-butyrolactones and 3-substituted 3-hydroxyoxindole derivatives in excellent yields and enantioselectivities (up to 99%). The preparation of maremycin A testifies to the potential usefulness of this previously unexplored reactivity in natural product synthesis.



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P35

HETEROGENEOUS CATALYSIS WITH IMMOBILIZED PALLADIUM NANOPARTICLES ON METAL-ORGANIC FRAMEWORKS (Pd@MOF)

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Due to the growing need for sustainable development, enormous efforts to develop environmentally friendly and efficient catalytic systems have been made. In this context, heterogeneous catalysis offers great advantages from an industrial and environmental point of view. Heterogeneous catalysts can be separated from the reaction media, they can be recycled more easily than homogeneous catalysts, and the production of waste can be minimized. We describe here our latest results on the synthesis and characterization of a novel heterogeneous catalyst that consists of palladium nanoparticles incorporated in a functionalized metal-organic framework (MIL-101(Cr), **Figure 1**).[1]

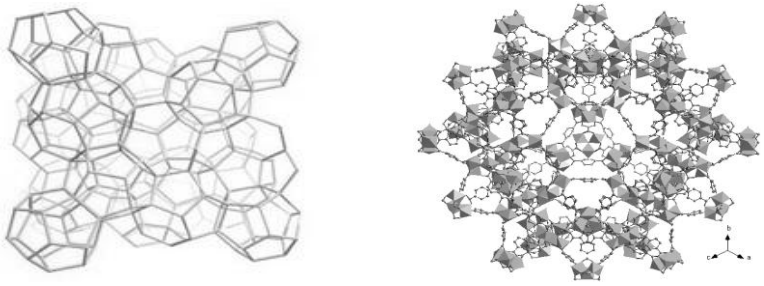

Figure 1. Zeotype architecture of MIL-101(Cr) (left) and structure of the large cage (right).

We also present the catalytic activity of the palladium catalyst (**Figure 2**) in the aerobic oxidation of alcohols.[2]

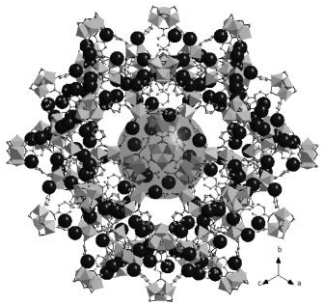

Figure 2. Palladium nanoparticles inside functionalized MIL-101(Cr).

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P36

PALLADIUM CATALYZED DIRECT AND REGIOSELECTIVE ARYLATIONS OF INDOLES, BENZOFURAN AND BENZOTHIOPHENE WITH ARYLDIAZONIUM SALTS

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Aryldiazonium tetrafluoroborates are thermostable, easy-to-prepare electrophiles that have been increasingly employed in cross-coupling reactions in the last decade. Their application in the Heck-Matsuda reactions allow the development of fast, smooth and phosphine-free methods when compared to more conventional couplings.[1] Regarding direct arylation of (hetero)aromatics, a process which does not require the activation (pre-functionalization) of the coupling partners, aryldiazonium tetrafluoroborates have been successfully employed as radical sources.[2]

To the best of our knowledge, the only published report of transition metal-catalyzed heteroaromatics arylation with aryldiazonium salts is the one from Colas and Goeldner,[3] who employed palladium-catalyzed arylation of benzofuran as a probe for testing the quality of freshly prepared aryldiazonium trifluoroacetates. So far, there are only two examples of these reactions with somewhat poor yields. Therefore, a comprehensive study regarding transition metal-catalyzed direct arylation of (hetero)aromatics with aryldiazonium tetrafluoroborates remains a considerable challenge.

We describe herein a direct method that allows successfully arylation of electron-rich heteroaromatics in moderate to good yields within short reaction times under smooth conditions. Moreover, we were able to surpass the high nucleophilicity of indoles, preventing their attack on the aryldiazonium salt to form diazo dyes. Reaction of aryldiazonium tetrafluoroborates with indoles yielded the desired arylated products almost exclusively. Mechanistic investigations pointed to the formation of a highly electrophilic cationic arylpalladium species which are attacked by the electron-rich heteroaromatics.

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P37

BIMETALLIC (Cu,Na) CAGE-LIKE SILSESQUIOXANES AS UNIVERSAL CATALYSTS FOR CARBONYL COMPOUNDS TRANSFORMATIONS

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2 - A.N.Nesmeyanov Institute of Organoelement Compounds of RAS, Laboratory of Asymmetric Catalysis, Moscow, Russia
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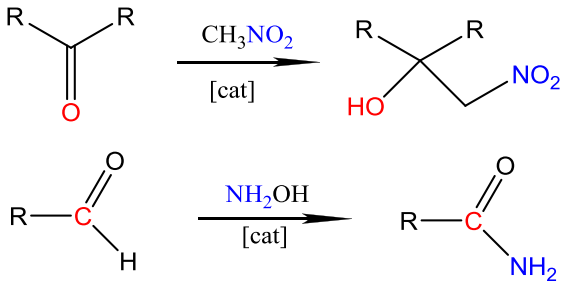
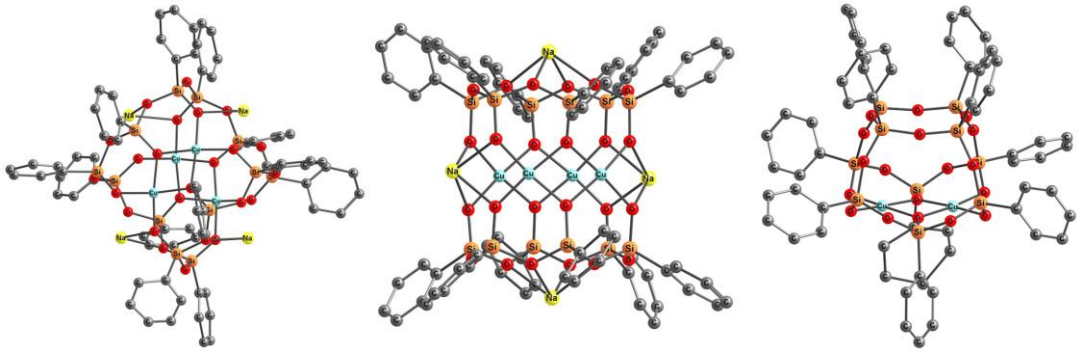
There is no doubt that cage-like metallasiloxanes should be mentioned among the most attractive objects of contemporary organosilicon chemistry due to their unusual molecular architecture, magnetic and catalytic properties [1, 2]. Now we represent a first case of successful application of several Cu,Na-silsesquioxane cages as catalysts for carbonyl-containing compounds' transformations:



Catalysts:



We revealed that Cu,Na-containing cages are active catalysts for aldehydes and even ketones transformations by Henry reaction (which is much more rare thing than for aldehydes transformations). Also we showed an activity of such cages in less known reaction of amides synthesis. Several peculiarities of studied processes, e.g. influence of cage structures, mechanism of catalysis (homo, hetero and in the absence of any solvent) will be described in detail.

This work was supported by RFBR (project № № 11-03-00646)

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P38

INTRAMOLECULAR SILA-MATTESON REARRANGEMENT: A GENERAL ACCESS TO SILYLATED HETEROCYCLES

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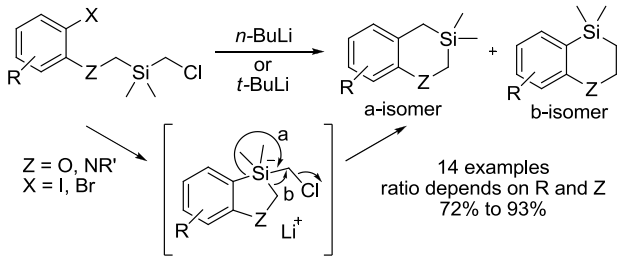
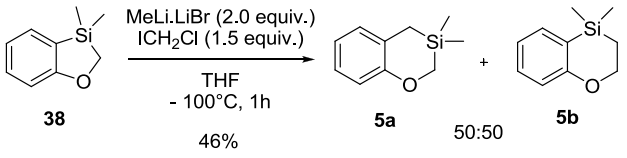
Replacing a carbon atom with a silicon can be regarded as a way to develop innovative new drugs. Despite the large similarities between these elements, significant advantages on the physiological and biological properties were observed and C/Si swap of known drug skeletons has been widely investigated in the last two decades. This increasing interest of silylated derivatives and the lack of general synthetic procedures, prompted us to focus on the preparation of new silylated heterocycles.



During this study, we observed that the intramolecular cyclisation furnished not only the desired products (a-isomer) but also their regioisomers (b-isomer). A mechanism involving a hypervalent-silicon species which would evolve either by migration of the aromatic ring (path a) or the CH_2-Si bond (path b) was confirmed by the formation of both isomers from the siladihydrobenzofuran.



Screening of various experimental conditions and substrates suggested that the isomers ratio is mainly governed by the intrinsic reactivity of the pentaorganosilicate species, and more precisely by the nature of the substituents borne by the aromatic ring. Interestingly, a good correlation between the isomers ratio and the Hammett constants of these aromatic substituents could be established. A further study on the nitrogen protecting group effect was also undertaken and showed its significant influence.

This intramolecular silicon-version of the Matteson rearrangement applies to a large variety of substrates and gives a general, efficient and versatile access to new silylated heterocycles.

François, C.; Boddaert, T.; Durandetti, M.; Querolle, O.; Van Hijfte, L.; Meerpoel, L.; Angibaud, P.; Maddaluno, J. *Org. Lett*. **2012**, *14*, 2074-2077.

PROSPECTS OF SYNTHETIC ELECTROCHEMISTRY IN THE DEVELOPMENT OF UNUSUAL OXIDATION STATE METAL CATALYSTS FOR C-CF AND P-CF BONDS FORMATION REACTIONS AND HYDROGEN-EVOLVING ACTIVITY

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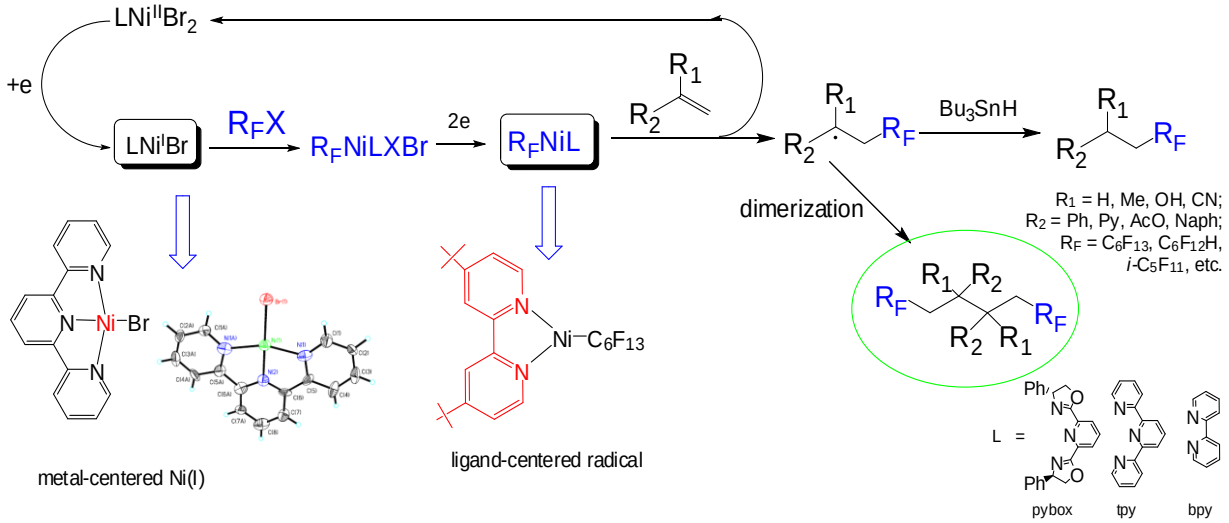
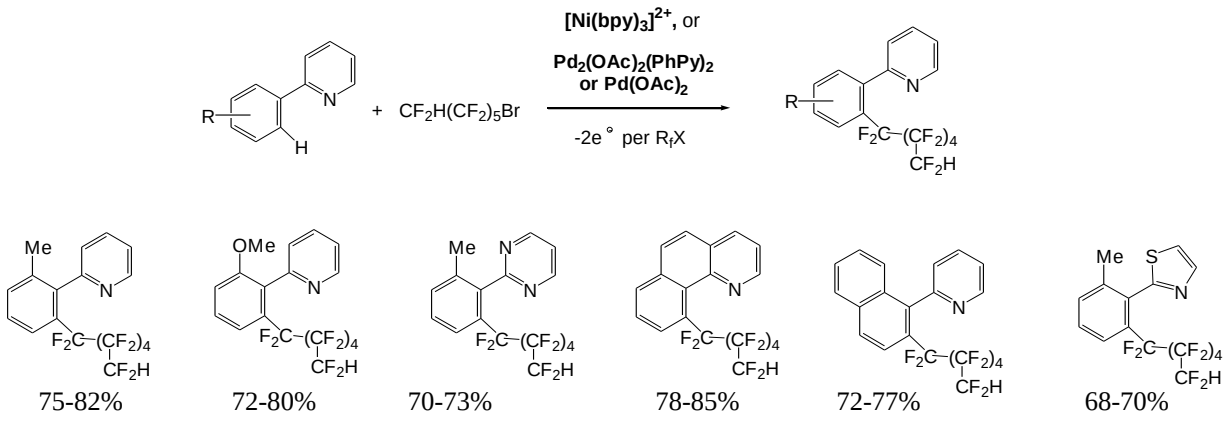
Achievements of electrosynthesis mediated by nickel and palladium complexes in unusual oxidation states will be demonstrated. Important advances are associated with the development of synthetic approaches to the C = C, P-Cl, P-P and C-H bonds functionalization in the one-step mild conditions. The leading role of electrochemistry in the development of biomimetic catalysts for oxidation of hydrogen in the coordination sphere of the complex or H_2 evolution will be discussed.





P40

DIRECT AND EFFECTIVE IRON/NHC CATALYZED HYDROSILYLATION OF ALDEHYDES, KETONES AND TERTIARY AMIDES

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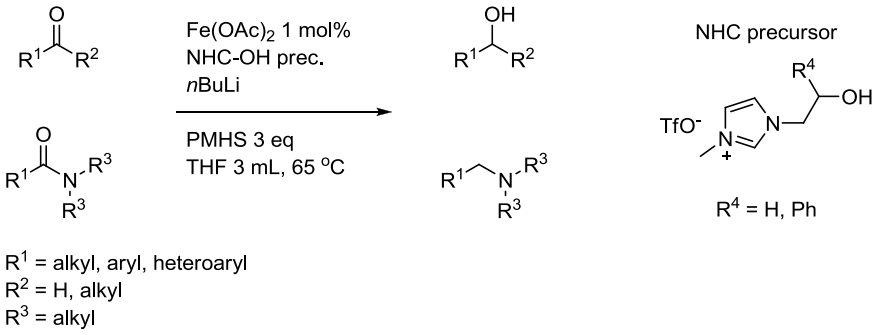
The reduction of carbonyl compounds alcohols is a common and most useful method for the formation of alcohols. There are numerous transition metal catalyzed methods for this transformation, but most catalysts today are derived from heavy or rare metals and the toxicity and high price of those are drawbacks for large scale synthesis. There is a demand for the use of non-toxic and less expensive metals, and iron, which has a high natural abundance, is environmentally and biologically benign and inexpensive has become one of the most interesting alternatives. In particular, a number of iron catalyzed hydrosilylation protocols have been presented during the last years.[1]

Here we show a new iron/*N*-heterocyclic carbene (NHC) catalyzed hydrosilylation protocol, where an active catalyst was formed *in situ* from structurally simple hydroxyethyl imidazolium salts together with an iron source, and the inexpensive and benign silane polymethylhydrosiloxane (PMHS).[2] The potentially bidentate ligand shows an enhanced catalytic activity to similar systems, and the scope of the reaction is very wide. The highly active hydroxyethyl NHC system was also proven to work well for the reduction of tertiary amides to amines, a transformation where it is highly attractive to avoid the use of reactive hydride reagents.



Scheme 1 Direct hydrosilylation of carbonyl compounds catalyzed by *in situ* generated iron/NHC complexes

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P41

"GREEN" CROSS-COUPLING REACTIONS CATALYZED BY MESOPOROUS OXIDES SUPPORTED 1,2-AZOLE-PALLADIUM COMPLEXES

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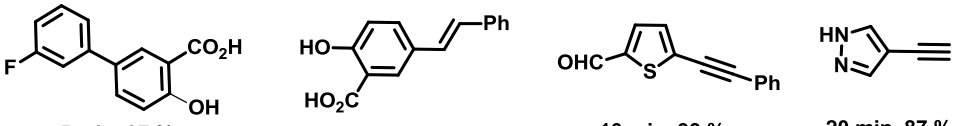
The palladium-catalyzed the Suzuki–Miyaura, the Mizoroki-Heck and the Sonogashira reactions represent straightforward and highly effective tools for carbon–carbon bond formation in the synthesis of biaryls and arylated unsaturated compounds. Herein, we report for the first time a simple and fast method for preparation of highly active, recyclable palladium catalysts from 1,2-azole ligands and mesoporous oxides through a modified sol–gel procedure. In comparison to common sol–gel entrapment methods, the key feature of ours is the use of complexes of Pd(II) with 1,2-azoles, efficient catalyst for fast hydrolysis and gelation of tetraethoxysilane (TEOS), and microwave drying of gel. The catalyst preparation procedure may be carried out easily within the one hour.First of all we prepared 1,2-azole palladium complexes $PdCl_2(L)$ or $PdCl_2(L)_2$ {L = 5-(*p*-tolyl)isoxazol-3-amine, [5-(*p*-tolyl)isoxazol-3-yl]methanamine, 5-(*p*-tolyl)isoxazole-3-carbaldehyde oxime, 4,5-dichloroisothiazole-3-carbohydrazide, 4,5-dichloro-N'-phenylisothiazole-3-carbohydrazide, etc.}. The new complexes are high-turnover-number catalysts for cross-coupling reactions with low palladium loading (0.0001–0.1%) in neat water, as the most "green" solvent, under an air atmosphere. Remarkably high TON of 1000000 and TOF of 12000000 h^{-1} were achieved.Then the silica gel entrapping palladium complex $PdCl_2(L)$ or $PdCl_2(L)_2$ were prepared by a one-pot procedure: (1) vigorous agitation of mixture of MeOH, TEOS, 1,2-azole ligands, and aqueous solution of Na_2PdCl_4; (2) treating the resulting light brownish suspension with ammonium fluoride or 3-aminopropyltriethoxysilane; (3) drying the resulting gel in a microwave oven at a power of 600–850 W within 8-10 min. The resulting palladium/1,2-azole/SiO_2 composites are denoted as $PdCl_2(L)_n@SiO_2$. They are quite leach-proof, highly porous materials (BET surface areas up to 900 m^2/g, and average pore diameters of 10-17 nm) and completely air stable for some months. The amount of palladium entrapped by silica was found to be ~0.1 mmol/g or ~1 wt% (*ca.* 99% of the palladium loading).

The $PdCl_2(L)_n@SiO_2$ catalysts were applied to carbon–carbon cross-coupling reactions of aryl halides with arylboronic acids, olefins and terminal acetylenes in aqueous media. At 0.1 mol% of Pd loading, all the reactions proceeded smoothly to give cross-coupling products in high isolated yields in water at 100 °C for 5-20 minutes without any inert gas protection in the presence of various bases (Na_2CO_3, K_2CO_3, K_3PO_4, NaOH, and KOH). From the standpoint of industry and green chemistry, water has clear advantages as a solvent for use in this type of reactions because it is cheap, readily available, and nontoxic. The reusability of the catalysts was tested in the Suzuki–Miyaura reaction between 4-methoxyphenylboronic acid and 3-bromobenzoic acid; $PdCl_2(L)_n@SiO_2$ could be reused 10 times without losing activity. Examples of the biaryl, olefin, and acetylene compounds synthesized are presented below.



5 min, 97 % | 20 min, 92 % | 10 min, 93 % | 20 min, 87 %

We thank the Belarusian Republican Foundation for Basic Research (X12P-024) and the Russian Foundation for Basic Research (12-08-90025-Bel_a) for financial support of this work.

P42

A CATALYTIC MULTICOMPONENT COUPLING REACTION FOR THE ENANTIOSELECTIVE SYNTHESIS OF SPIROACETALS

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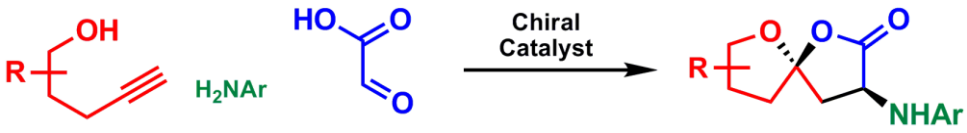
Natural products are an exceptional source of drug leads and a continuous inspiration for the design of small-molecule libraries for drug discovery.[1] In this context, spiroacetals have been found as a key structural unit in many biologically active and structurally diverse natural products.[2] In this context, we have recently reported a new strategy for the synthesis of functionalized chroman spiroacetals,[3] that was further exploited in the total synthesis of the bioactive natural product (−)-berkelic acid.[4] Following our interest in this field, we became particularly interested in the development of a "reagent-controlled" asymmetric synthesis of spiroacetals. It should be stressed that despite the unquestionable interest of optically active spiroacetals, as far as we know, only three strategies for the enantioselective synthesis of these compounds from achiral substrates have been reported to date.[5] So, the scarcity of catalytic asymmetric methods for the enantioselective synthesis of spiroacetals motivated us to investigate on this issue. Thus, we envisaged that the three-component coupling reaction of alkynols, arylamines and glyoxylic acid in the presence of an appropriate chiral catalyst should lead to [5,5]-spiroacetal derivatives in a enantioselective way.[6] Here, we present our recent advances on the development of this new reaction.



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6 Some support for our proposed strategy was found in a multicomponent coupling reaction reported by R. Lavilla and col. See: O. Jiménez, G. de la Rosa, R. Lavilla, Angew. Chem. Int. Ed. 2005, 44, 6521-6525.

ENANTIOSELECTIVE SYNTHESIS OF TETRAHYDROQUINOLINES THROUGH A ONE-POT MULTICATALYTIC AND MULTICOMPONENT PROCESS INVOLVING AN ASYMMETRIC POVAROV REACTION

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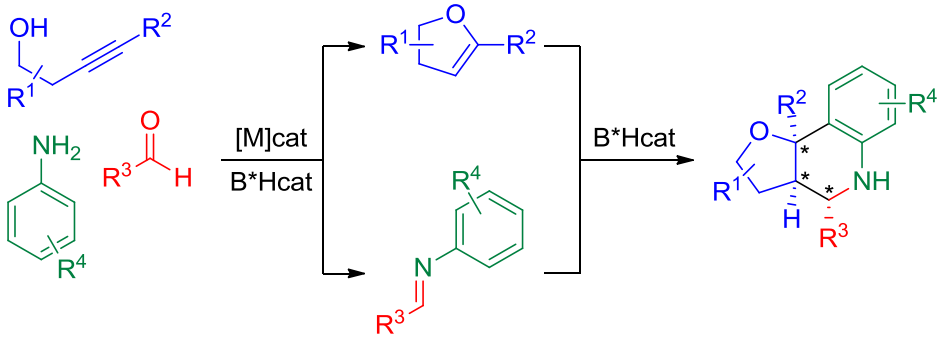
Tetrahydroquinolines are heterocyclic molecular frameworks found in many biologically active natural products, pharmaceuticals and other compounds with interesting applications. [1], [2] The synthesis of this important class of organic molecules has attracted the interest of both synthetic and medicinal chemists.[2] Probably, the most commonly used strategy in tetrahydroquinoline synthesis is the inverse-electron demand [4+2] cycloaddition between a *N*-arylimine (diene) and an electron-rich olefin (dienophile) known as the Povarov reaction.[3] In this context, we considered the cooperative transition-metal and Brønsted acid catalytic process shown in Scheme 1 as a potentially simple and useful method for the enantioselective synthesis of functionalized furo[3,2-*c*]quinoline derivatives through a one-pot multicatalytic and multicomponent process involving an asymmetric Povarov reaction. To achieve our goal, we require the use of differently substituted dihydrofuran derivatives and an appealing strategy would involve its in situ generation. [4] In this approach both reactants for the Povarov reaction, the enol ether and the *N*-arylimine, are formed in situ. Thus, we hypothesized that an intramolecular hydroalkoxylation of alkynols promoted by an appropriate metal catalyst [M] would provide the dihydrofuran. In the other hand, condensation of aldehydes and anilines catalysed by a Brønsted acid (B*H) would afford the required imines. If this Brønsted acid (B*H) were chiral it could also catalyse the asymmetric reaction between the dihydrofuran and the imine to get the tetrahydroquinolines in an enantiomerically enriched form (Scheme 1).



Scheme 1

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P44

HIGHLY EFFICIENT IMMOBILIZED ORGANOCATALYSTS FOR ASYMMETRIC EPOXIDATION OF TRANS-METHYLCINNAMATE

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2 - University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia
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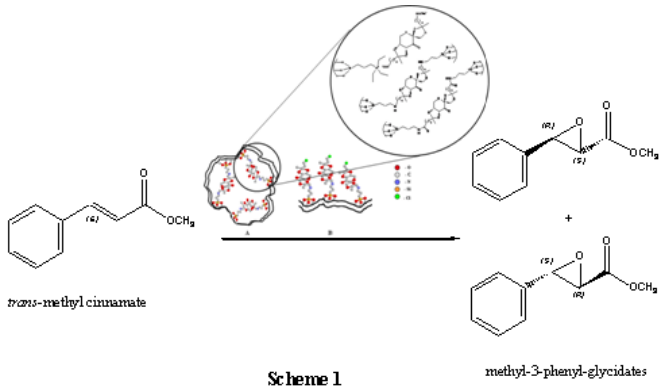
Chiral glycidates are recognized as key intermediates crucial for synthesizing many important drugs and natural products as well. In recent years dramatic development of methods for this purpose was observed, especially in the field of metal-catalyzed epoxidations [1]. For metal-free asymmetric epoxidation (e.g., organocatalysis) current methodology relies mainly on the development of chiral ketones (e.g., so called Shi ketone prepared from cheap renewable materials as D-fructose [2]). Such procedures seem to be the most advantageous in the asymmetric epoxidation of a variety of non-functionalized olefins, dienes, enynes, and hydroxyalkenes with >90% ee [3]. Nevertheless, considering the concept of green chemistry and taking the current constraints into account, one of the prospects for organocatalysis is heterogeneous approach. The practical advantageous of heterogeneous organocatalysis was successfully demonstrated with the few examples reported in literature but this field is still undeveloped. Taking into account the above informations, the current trends in synthetic chemistry and our interest in both asymmetric catalysis and green chemistry, the main concern of the present work was to prepare novel chiral ketone based solid materials as efficient enantioselective heterogeneous organocatalysts. It has taken into consideration three strategies: i) the grafting of chiral ketones onto the surface of mesoporous silica; ii) the use of chiral ketones as pillars for the synthesis of Chiral-Metal-Organic-Frameworks (CMOFs), and iii) the grafting of organocatalyst onto coated magnetically recoverable nanocatalysts with functionalized silica. The prepared catalysts were exhaustively characterized and tested in the asymmetric epoxidation of commercially available and inexpensive *trans*-methyl cinnamates to (*2R,3S*)-phenyl glycidates (e.g., Scheme 1).



Scheme 1

As a function of the preparation methodology, the nature of the support and the structure of the chiral ketone, heterogeneous organocatalysts with well-defined and specifically located active sites and improved enantioselectivity properties were obtained. In this context it will be taken into discussion a series of criteria as: the economy of the catalyst, the stability and handling of the catalysts, recycling issues, enantioselectivity, activity, and catalyst loading.

Acknowledgements:
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P45

DESIGN AND SYNTHESIS OF NEW RUTHENIUM BIPYRIDYL COMPOUNDS FOR APPLICATION AS DYE-SENSITIZED SOLAR CELLS

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Among the metal complexes, ruthenium complexes have shown the best photovoltaic properties: a broad absorption spectrum, suitable excited and ground state energy levels, relatively long excited-state lifetime, and good chemical and electrochemical stability. Both 2,2'-bipyridyl ligands can be adjusted with different substituents to improve photovoltaic efficiency.
The ancillary 2,2'-bipyridyl ligand (with alkyl, alkoxyl chain and other substituents) can be modified to increase the molar extinction coefficient, suppress dye aggregation on the semiconductor, and optimize the redox potential of the photosensitizer. The introduction of two hydrophobic alkyl chains on the bipyridyl ligands has shown greater thermal stability in the amphiphilic heteroleptic ruthenium sensitizers.[1]
The best efficiencies, that are reached using these ruthenium sensitizers, are near 11% and are obtained by C101, B1, C106 and B11 complexes.[2],[3] From these results a new family of ruthenium sensitizers is being developed in order to reach more efficiency and solubility in organic solvents. This new family of complexes displays a bipyridyl with thiophene substituents and branched alkyl chains.[4]

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P46

OXIDATION CATALYSIS WITH A RUTHENIUM-ALUMINIUM METAL–ORGANIC FRAMEWORK

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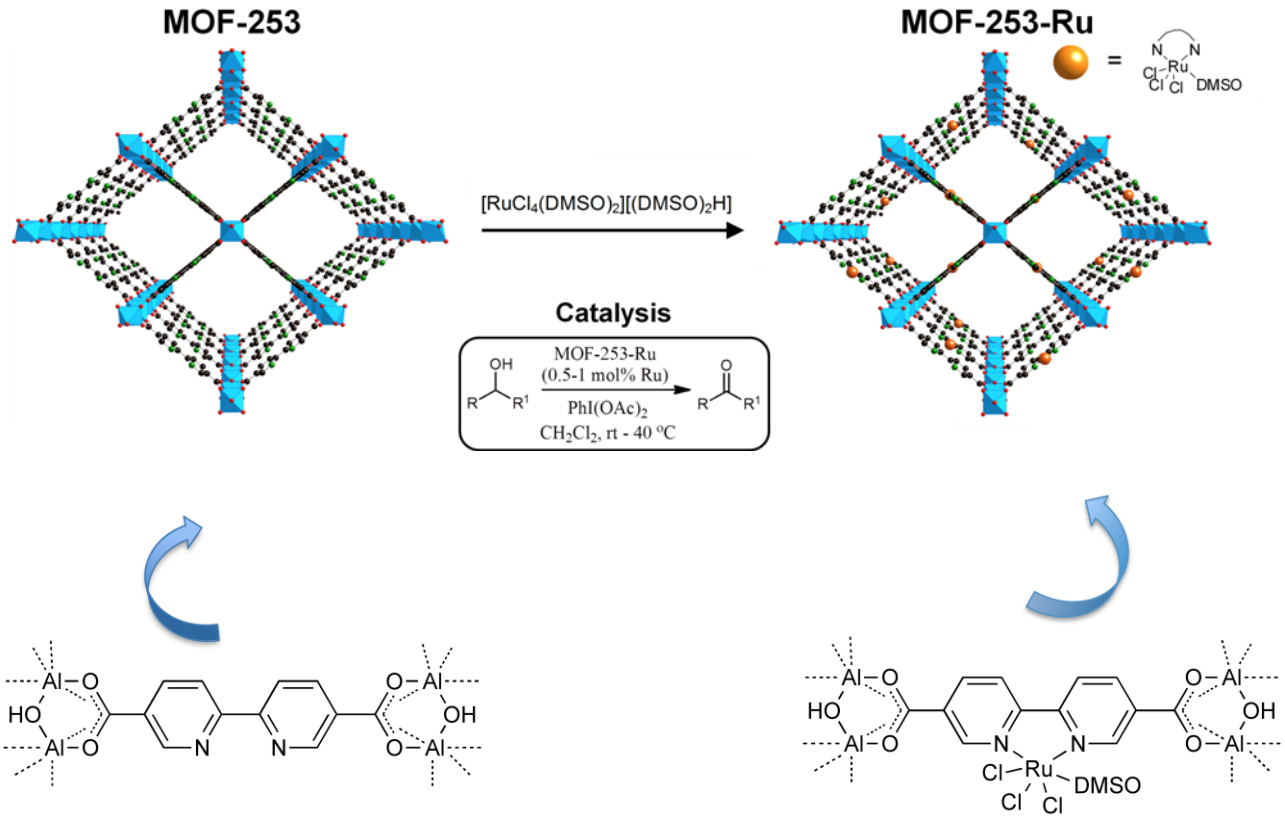
Aluminium-based metal–organic frameworks (MOFs) exhibit high chemical stability compared to copper and zinc MOFs. In this work, a ruthenium complex has been grafted by post-synthetic modification onto MOF-253,[1] a porous Al-MOF containing open bipyridine sites on the linkers. The resulting MOF-253-Ru was used as a catalyst for the oxidation of a wide range of alcohols into their corresponding carbonyl compounds in high yields.[2] Remarkably, primary alcohols were selectively oxidised to aldehydes at room temperature and in short reaction times. MOF-253-Ru catalyst can be recycled without significant loss of activity, crystallinity or surface area.



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THE DIRECT CATALYTIC ENANTIOSELECTIVE VINYLOGOUS ALDOL REACTION OF ALPHA-BRANCHED ENALS WITH ISATINS

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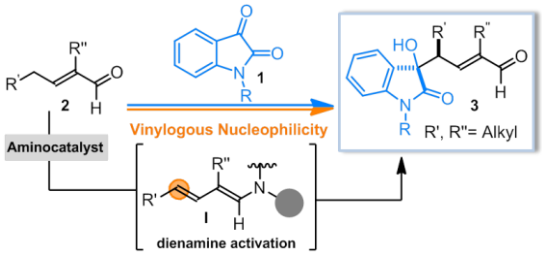
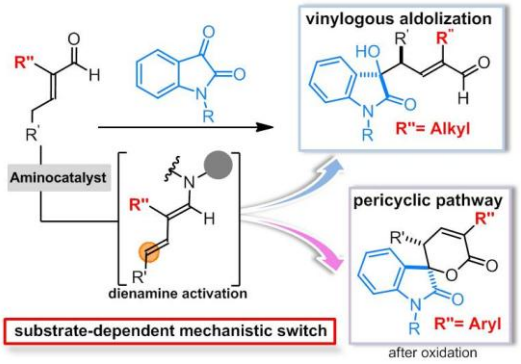


We report herein the direct vinylogous aldol[1] reaction of α-substituted α,β-unsaturated aldehydes with isatins using a chiral secondary amine as catalyst. The use of γ-dienolizable unmodified α,β-unsaturated carbonyl substrates as "extended dienolates" directly leads to densely functionalized δ-hydroxylated α,β-unsaturated carbonyl moieties that are molecular elements featuring in a large number of natural products. In this context, different α-substituted enals are well tolerated and a wide pool of isatin derivatives can be employed, regardless of their electronic properties.

Mechanistic studies point to two divergent pathways to be operative, depending on the substitution pattern of the enal starting material employed. In the case of alkyl substituent, dienamine intermediates participate in vinylogous nucleophilic attack, leading to δ-hydroxylated products. In case of α-aryl substituted enals the *in situ* generated dienamine presumably act as dienes in a Hetero-Diels-Alder like pathway, leading to the formation of spirooxindole lactol.



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P48

OXOMOLYBDENUM(VI) COMPLEXES CATALYZED CHEMOSELECTIVE OXIDATION OF SULFIDES TO SULFOXIDES

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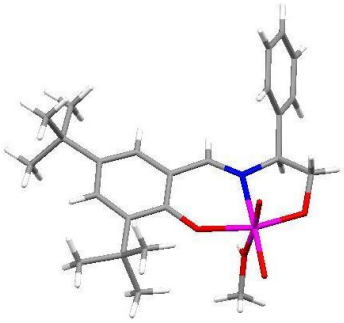
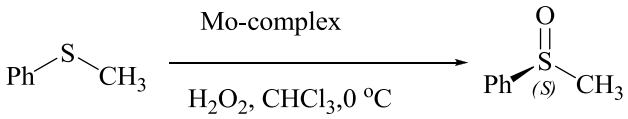
Oxo-molybdenum and related compounds promoted chemical transformation in organic synthesis has been of current interest.[1] Molybdenum oxide chloride has been found as a successful catalyst for selective oxidation of sulfides to sulfoxide and sulfones with hydrogen peroxide oxidant which is reported from our group. The catalyst shows remarkable tolerance towards various functional groups particularly alkene, aldehyde, imine, oxime and alcohol.[2] This result motivated us to develop the chiral oxomolybdenum compounds for asymmetric sulfoxidation reactions. In this direction, few chiral cis-dioxomolybdenum(VI)-(ONO) complexes of Schiff bases have been synthesized.[3] These complexes were tested for catalytic asymmetric sulfoxidation reactions using hydrogen peroxide as oxidant at low temperature. The reaction proceeds with high chemoselectivity towards sulfoxide formation along with good to moderate enantiomeric excess. Incorporation of phenyl substitution at β-position of the amino alcohol gave good enantiomeric excess rather than the benzyl substituted complex. ESI-MS study of the reaction mixture clearly indicates the formation of oxoperoxoMo(VI) complexes which is considered to be the active catalyst. The investigation of the ESI-MS was also carried out for the reaction mixture of phenyl methyl sulfide with hydrogen peroxide in presence of catalyst after the completion of oxidation proves the recovery of the catalysts during catalytic cycle. Further modification on the catalyst for studying the electronic effect of the ligands is being currently investigated.





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UNEXPECTED FORMATION OF N-ALKYLPYRIDINIUM SALTS AS AN ALTERNATIVE WAY TO ETHANOLAMINE TOSYLATION IN PYRIDINE

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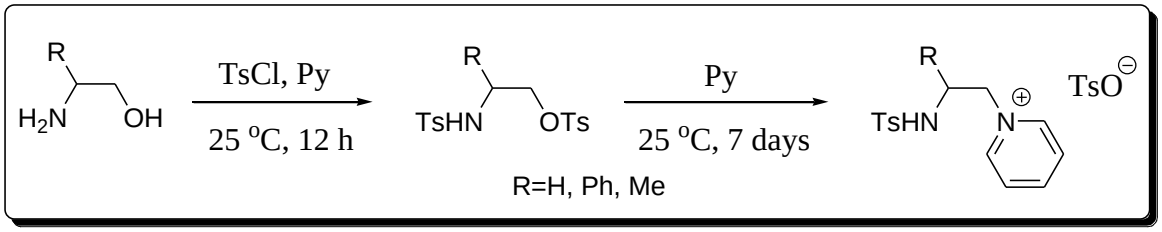
The ligands based on ethanolamines widely used in organometallic and coordination chemistry [1]. The tosylation reaction of ethanolamines results to semiproducts in synthesis of such ligands.
The classical method of tosylation of monoethanolamines usually results in N,O-ditosylation [2]. However, in some cases the alcohol tosylation gives the products with substitution of TsO group by nucleophiles present in reaction medium [3]. In this study we have established that tosylation of monoethanolamines in a medium of pyridine under increased reaction time (compared to the classical method) leads to the unexpected formation of novel N-alkylpyridinium tosylates.



The structure of the compounds obtained was established by multinuclear NMR spectroscopy and X-ray analysis (R = H).

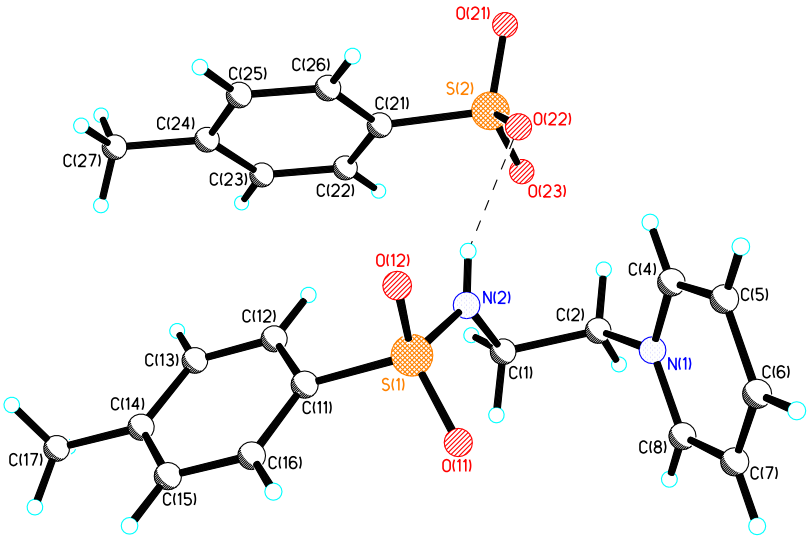


Figure. Molecular structure of the compound (R = H).

This work is supported by the RFBR (12-03-00206-a) and by President Grant for Young Russian Scientists *(МД-3634.2012.3).*

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P50

METAL-FREE CATALYTIC HYDROGENATION OF POLAR AND NON-POLAR DOUBLE AND TRIPLE BONDS

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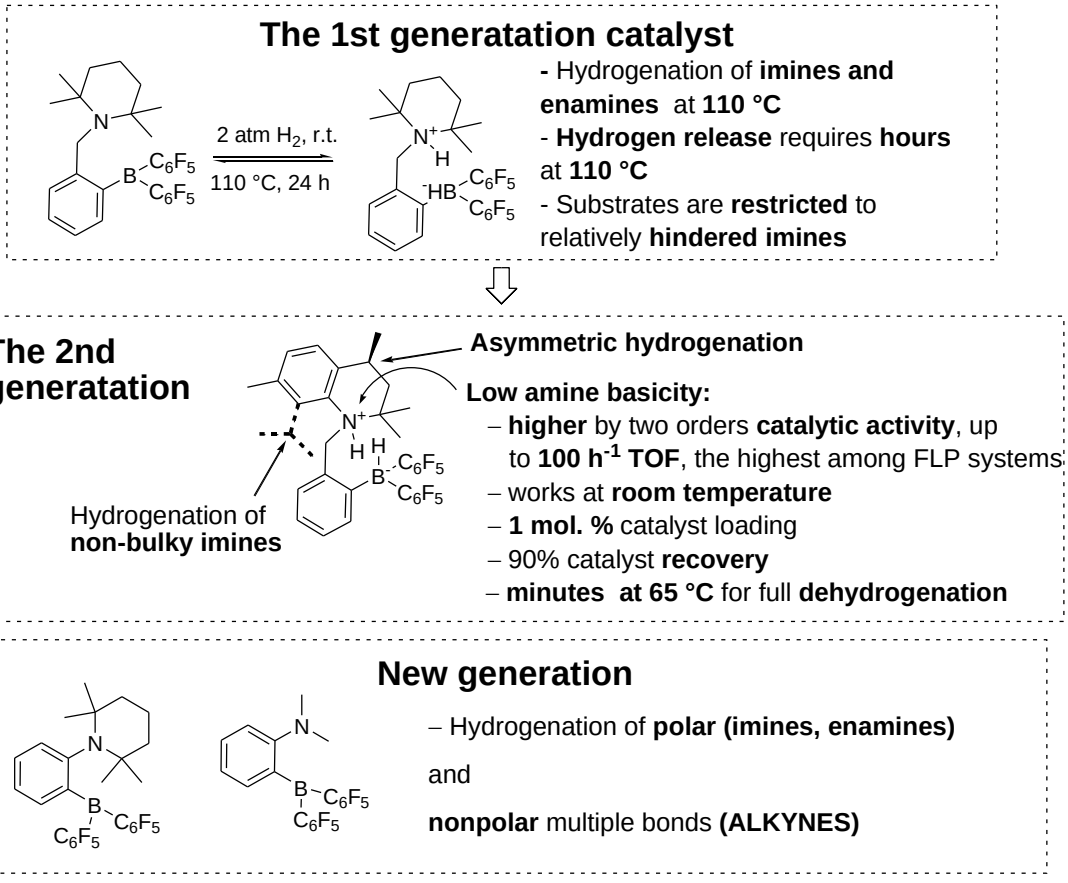
Hydrogenation of unsaturated bonds is one of the principal reactions in organic chemistry. A recent approach to the activation of hydrogen using powerful but sterically "*frustrated*" *Lewis* acid-base *pairs* (FLPs) opened up a new way to catalytic hydrogenation. A combination of Lewis acidic and basic parts in one molecule gives rise to intramolecular systems able to activate H_2 reversibly. For the first time *ansa*-aminoboranes have been reported by our group.



We have shown, that *ansa*-bridged aminoborane FLPs are advantageous over respective intermolecular pairs, especially, when applied as hydrogenation catalysts. The amine moiety of the *ansa*-aminoboranes can be greatly varied giving rise to catalysts with advanced properties: high activity, asymmetric induction, catalyst recycling, substrate selectivity or universality, etc. One of our most remarkable recent findings is a facile catalytic hydrogenation of alkynes under mild conditions using a new generation of the *ansa*-aminoboranes.

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P51

Ru(II) AND Os(II) BASED SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

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Dye-sensitized solar cells (DSSCs) have practically considered as a feasible alternative to conventional amorphous silicon solar cells. As a result, numerous organometallic sensitizers have been designed and synthesized, among which the most common sensitizers are ascribed to N3, N719 and black dye, respectively. Recently, we reported a new family of ruthenium(II) and osmium(II) complexes containing functionalized azolate chelate, together with *bis*(4,4'-dicarboxy-2,2'-bipyridine) or even 4,4',4''-tricarboxy-2,2':6',2''-terpyridine, respectively. These azolate coupled group 8 metal sensitizers were synthesized and subsequently characterized using photophysical methods and spectroscopic means. Upon optimization, some of our Ru(II)-based sensitizers, even without the utilization of thiocyanate ancillary**,** could produce a conversion efficiency of ≥10%, the results of which are superior to that of N719 and black dye reference solar cells prepared in our studies.

P52

DEVELOPMENT OF NOVEL NICKEL-BASED PHOSPHINE-FREE CATALYTIC SYSTEM FOR SELECTIVE SYNTHESIS OF MONOSELENOSUBSTITUTED DIENES

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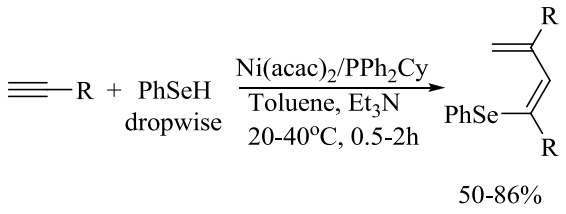
Addition of chalcogen-containing molecules to multiple bonds of alkenes and alkynes is a convenient one-step method of heterofunctionalization of organic substrates, which are valuable synthones in organic synthesis [1]. Nowadays, use of transition metal catalysis allows to perform addition of E-H and E-E bonds (E = S, Se) to unsaturated compounds with selective formation of functionalized products with predetermined structure. Usually, these reactions lead to the formation of substituted alkenes [2, 3]. In several cases formation of mono- and bis- heterosubstituted dienes was observed [4, 5].

In our study, it was shown that the use of catalytic system based on nickel complexes in the addition of selenols to triple bond of terminal alkynes led to the formation of not only vinylselenides, but also to a new type of organic compounds – monoselenosubstituted dienes. The key factors which determine chemoselectivity of the developed catalytic system are: 1) use of sterically hindered phosphine ligand; 2) dropwise addition of phenylselenol; 3) excess of alkyne. Also, it was found, that addition of catalytic amounts of triethylamine positively influenced on selectivity of diene formation (scheme 1).



Scheme 1. Addition of selenol to terminal alkynes.

We have found that reaction could be carried out in phosphine-free conditions, in the presence of only triethylamine. The control of reaction selectivity by addition of base and phosphine ligands will be discussed.

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P53

PHOTOCATALYTIC AEROBIC OXIDATION OF DIHYDROACRIDINES IN THE PRESENCE OF NANOSIZED COMPOSITE MATERIALS

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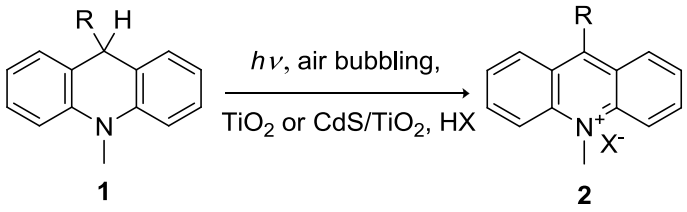
It is known that TiO_2 initiates oxidation of a variety of organic compounds with molecular oxygen. According to the literature TiO_2 is active as photocatalyst only in the UV range. In case of dye-sensitized and transition metal-doped TiO_2 the use of visible light becomes also possible. Cadmium sulfide is still widely used to sensitize TiO_2 for the visible light driven applications. Significant improvement of photochemical properties can be reached by preparing an appropriate microstructure of the composite CdS/TiO_2 material.

We extend for the first time our studies on application of nanocrystalline TiO_2 and/or CdS/TiO_2 composites as photocatalysts for visible-light-induced oxidation of dihydroacridines as a σ^H-adducts of the reaction of nuclephilic substitution of hydrogen in (hetero)arenes. This approach proved to be successful in the series of acridines.



R = -Ph; -CN; $-CH_2NO_2$
$X^- = CF_3COO^-, Cl^-, HSO_4^-$

Scheme 1. Oxidation of C-9 substituted dihydroacridines

It is worth to note that the observed transformations of dihydroacridines into the corresponding acridinium cations by action of air oxygen in the presence of CdS/TiO2 composites and irradiation appear to be the first examples of visible-light-catalyzed oxidations of the σH-adducts, as the key intermediates of the SNH reactions. Effects of reaction conditions (temperature, concentration of TiO2 or CdS/TiO2 and the nature of a mineral acid) on yields of products have been discussed.

The spectral data used in this study were obtained at the «Integrated research and expert assessment of organic materials» laboratory (Ural Federal University, Ekaterinburg, Russia). The research was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-5505.2012.3, Grant MK-1901.2011.3), the Russian Foundation for Basic Research (Project No. 10-03-00756-a), the Ural Branch of Russian academy of Sciences (project No. 12-P-234-2003), the research was carried out in terms of Ural Federal University development program with the financial support of young scientists.

P54

SYNTHESIS OF PLANAR CHIRAL FERROCENES

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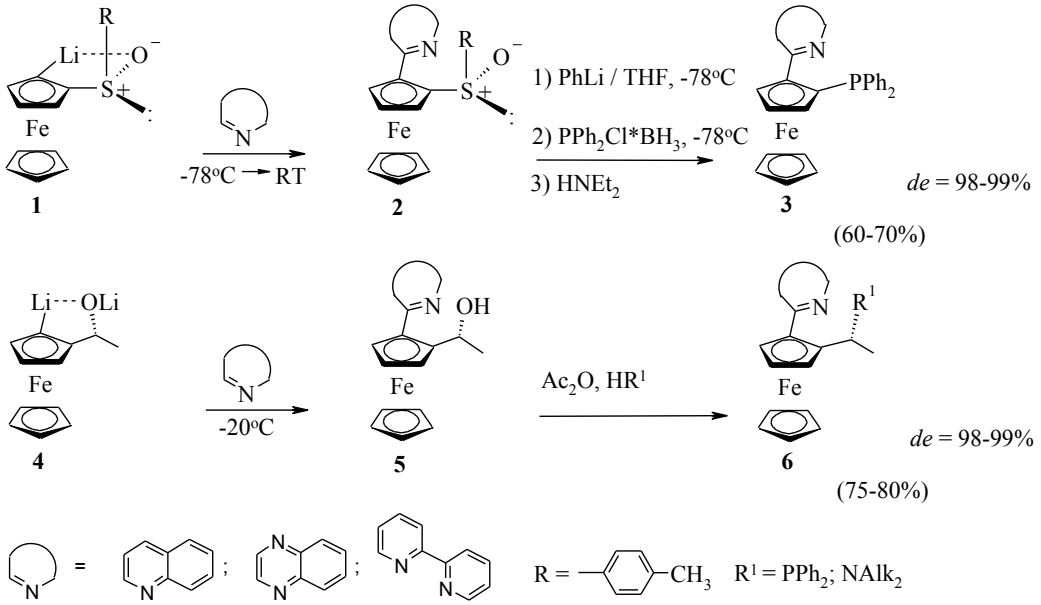
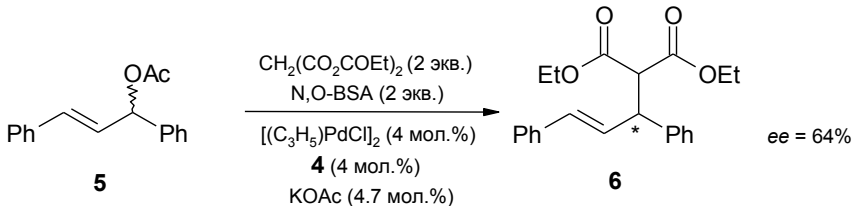
Planar chiralferrocene ligands have been shown to be efficient stereocontrol elements in many metal centred asymmetric catalytic reactions due to their stability, ease of introduction of planar chirality and interesting electronic properties of ferrocene unit. For the synthesis of compounds **4** the substances which contain asymmetric fragments in their structures are often used. We selected ferrocenyl containing chiral sulfoxide and alcohol since lithiocompaunds **1,4** have been synthesized by the region- and stereoselective metallation (CIPE effect) in the presence of LDA or BuLi. The S_N^H reactions of lithium derivatives **1** have been found to lead to optical pure planar chiral ferrocenes **3**, **4** (Scheme 1). The substances from the S_N^H reactions are formed with comparable yields.



Scheme 1. S_N^H reaction of the lithium derivatives with mono- and diazines

Ligands were applied to Pd-catalyzed allylic alkylation reaction with quantitative yield and ee 64%.



Scheme 2. Reaction of allylic alkylation

The optical purities of **3**, **4**, **6** were determined by HPLC on columns with chiral sorbents.

The spectral data used in this study were obtained at the «Integrated research and expert assessment of organic materials» laboratory (Ural Federal University, Ekaterinburg, Russia). The research was financially supported by the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-5505.2012.3, Grant MK-1901.2011.3), the Russian Foundation for Basic Research (Project No. 10-03-00756-a), the research was carried out in terms of Ural Federal University development program with the financial support of young scientists.

P55

NEW SYNTHETIC APPROACH FOR EXPANDED PORPHYRINS

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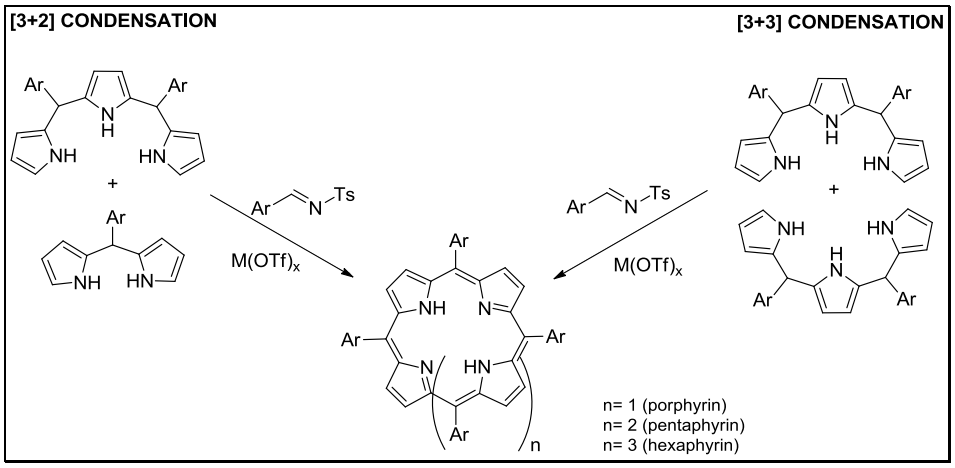
Expanded porphyrins have attracted considerable attention because of their widespread applications in chemistry. Expanded porphyrins generally contain a larger number of meso-like bridging atoms, a greater number of pyrrolic subunits, or both.[1] The complexing ability of these macrocycles with metals make them as potential photosynthesizers in photodynamic therapy (PDT), contrast agents in magnetic resonance imaging (MRI), building blocks in nonlinear optical materials, etc.[2] The most important precursors for the synthesis of meso-substituted expanded porphyrins are oligopyrrolic structures such as dipyrromethanes and tripyrranes.[3]

Metal triflates are Lewis acids known for being highly active, inexpensive, non-toxic, and reusable catalysts.[4] Our recent studies showed that triflates are also highly active catalysts in the reactions of heteroaromatic compounds with *N*-Tosyl imines and can be used in the synthesis of porphyrins and their subunits.[5]

In this study, it was aimed to achieve the synthesis of expanded porphyrins by using [3+2] and [3+3] condensation reactions of tripyrranes and dipyrromethanes with *N*-Tosyl imines in the presence of metal triflate catalysts. Different reaction conditions were investigated for the construction of expanded porphyrins and visualization of reactions were carried out by Mass Spectroscopy.



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P56

HIGHLY ENANTIOSELECTIVE CARBOCYCLIZATIONS BY COMBINATION OF AMINE AND HETEROGENOUS METAL CATALYSTS

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The first examples of one-pot highly enantioselective dynamic kinetic asymmetric transformations involving α,β-unsaturated aldehydes, propargylated nucleophiles and Pd (II) nanocatalyst. [1] These DYKATs, which proceed by a combination of catalytic iminium activation, enamine activation and Pd (II) nanoparticles supported on aminopropyl-modified siliceous mesocellular foam (MCF) catalyzed enyne cycloisomerization, gives access to functionalized cyclopentanes, dihydrofurans and 2,5 –dihydropyrroles with up to 98% ee. The Pd (II) nonocatalyst was found to be remarkably stable and could be recycled many times with no leaching of the metal into solution or any change in activity

P57

ORTHO CARBOXYBENZENEDIAZONIUM SALTS IN CROSS COUPLING REACTIONS

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Ortho carboxybenzenediazonium salts are widely used as sources of benzynes in both polar and pericyclic chemistry. [1] Recently, we have demonstrated that these arenediazonium salts can also be employed as effective electrophiles in Heck-Matsuda couplings. Our studies revealed that the Heck adducts can be obtained in good yields under low catalyst loadings - 0.5 % mol of palladium acetate. The methodology was successfully applied in an "one-pot" synthesis of isocoumarins and phthalides (figure 1). [2]

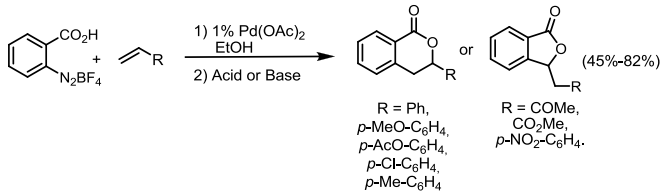

Figura 1 - Selective preparation of of isocoumarins and phthalides.

In view of its practicality, we decided to extend the scope of this protocol to perform practical synthesis of other functional compounds. Many vinylic systems considered hard-to-react substrates for cross-coupling reactions, such as 1,1-disubstituted olefins [3], and those bearing phosphonate ester and boronic acids provided the coupling adducts in good yields. Efforts are ongoing to explore other *ortho* functionalized aryldiazonium salts.

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P58

FACILE AND SOLVENT FREE SYNTHESIS OF XANTHENES AND BENZOXANTHENE DERIVATIVES USING SIMPLE IONIC LIQUIDS

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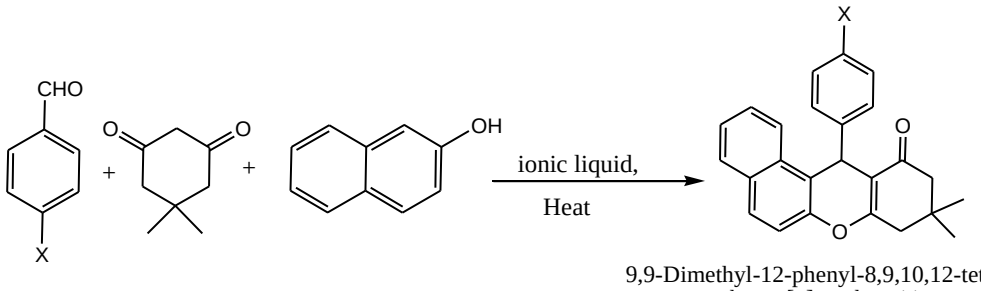
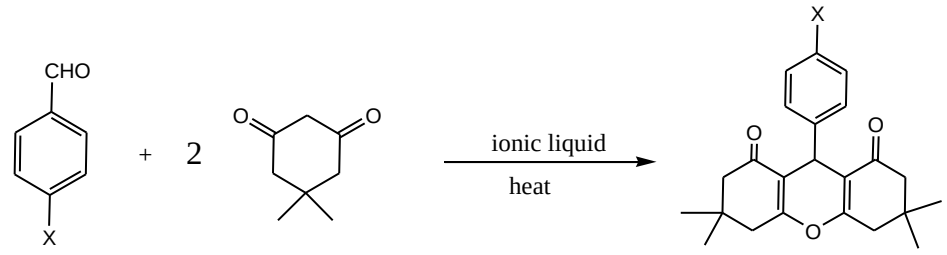
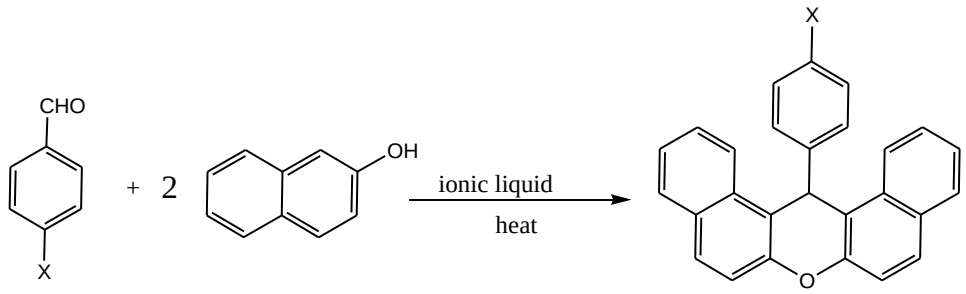
The synthesis of xanthenes, especially benzo xanthenes has attracted great interest in recent years due to their wide range of biological and pharmaceutical properties such as antiviral, antibacterial, and anti-inflammatory activities as well as sensitizers in photodynamic therapy.
A facile, efficient and environment-friendly protocol for the synthesis of 9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydro-benzo[a]xanthen-11-one, 3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione and 14-Phenyl-14H-dibenzo[a,j]xanthene by a one-pot condensation of 2-Naphthol, 5, 5- dimethyl-1,3-cyclohexadione and aromatic aldehydes promoted by simple ionic liquid under solvent-free conditions is reported.
The synthetic approach offer the advantages of clean reaction, simple methodology, short reaction time, high yield, easy purification, and easy preparation of the catalysts.



9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one



3,3,6,6-Tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione



14-Phenyl-7,14-dihydro-dibenzo[*a*,*j*]xanthene

P59

GOLD(I)/ZINC(II) CATALYZED TANDEM HYDROAMINATION/ANNULATION REACTION OF 4-YNE-NITRILES

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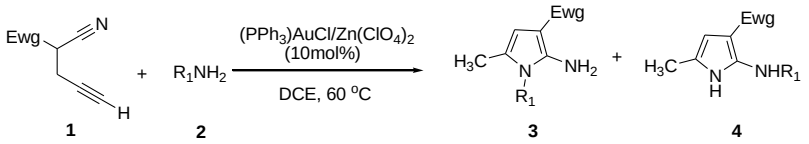
Over the past six years, gold catalysis has been shown to be a powerful tool in organic synthesis. Cationic gold (I) and gold (III) show unique activities towards unactivated alkenes, alkynes, allenes, 1.3-dienes and enynes promoting the nucleophilic addition of a variety of functional groups both inter- and intramolecularly.[1] In that respect, a great number of gold catalyzed tandem reactions of various systems with external nucleophiles that enable the formation of cyclic systems are present in the literature.[2] Especially transformations including the catalytic addition of N-H bonds across C-C multiple bonds (hydroamination) that are catalyzed by both gold(I) and gold(III) complexes have found wide application for the generation of new C-N bonds. In the course of our research to develop new methodologies for the synthesis of nitrogen containing heterocycles that are promoted by transition metal catalysts, we recently demonstrated Zn (II) salts to be effective catalysts for the activation of both the C=O bond and CN triple bond.[3]

In light of our previous investigation wherein nitriles could be activated towards nucleophilic attacks by Zn(II) salts, we report herein a conceptually new synthetic approach to substituted pyrroles via a cooperative Au(I)/Zn(II)-catalyzed sequential inter/intramolecular hydroamination reaction of 4-yne-nitriles with various amines.

The most notable aspect of the present reaction is the sequential activation of nitriles as pronucleophiles and alkynes as electrophiles, which enables the rapid assembly of a range of 2-amino substituted pyrroles with high efficiency. 2-Aminopyrroles have been found to show interesting biological properties or have been used as precursors for known drugs, in which they have found use as synthetic precursors for the acyclic nucleoside analogs of the pyrrolo[2,3-d]pyrimidine ring system.



1 **2** **3** **4**

In this simple one pot assembly, readily obtained α-propargyl methyl nitriles (4-yne-nitriles) **1** and a series of aliphatic and aromatic amines **2** as nucleophiles, are used as starting materials to produce pyrrole **3** and **4** with high diversity (Scheme).

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P60

CHIRAL NHC-RHODIUM(I) COMPLEXES FOR THE TRANSFER HYDROGENATION OF ACETOPHENONE

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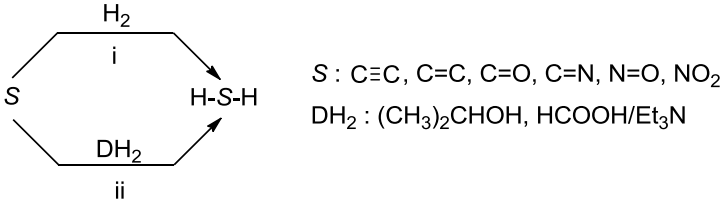
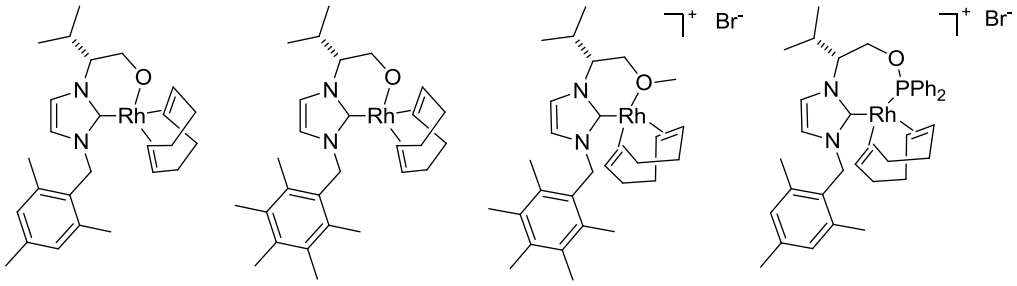
Transition metal-catayzed transfer hydrogenation of carbonyl compounds is one of the most important reactions in pharmaceutical and chemical industries. Many NHC ligands are known to be active catayst for the transfer hydrogenation reaction.[1] Whereas direct hydrogenation (route i) of unsaturated compounds (*S*) is more widely applied, transfer hydrogenation (route ii) is a powerfull alternative in view of its easy of handling, the easy availability of hydrogen donor (DH_2), low cost of reducing agents and safety.[2] The asymmetric transfer hydrogenation (ATH) of prochiral ketones is highly efficient method to obtain enantiomerically enriched alcohols. However, there are very few report describing the use of chiral NHCs in asymmetric transfer hydrogenation. In general, moderate to good conversions were obtained but enantioselectivities were poor to moderate.[3]



In this study, ionic and neutral chiral NHC-Rh(I) complexes (**I**-**III**) were prepared and characterized by spectroscopic techniques, and were evaluated as catalysts for transfer hydrogenation of acetophenone.



Ia **Ib** **II** **III**

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P61

CHIRAL NHC-RHODIUM(I) COMPLEXES AND THEIR APPLICATIONS IN THE ARYLATION OF ALDEHYDES

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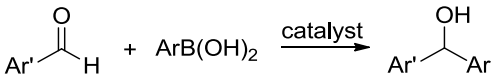
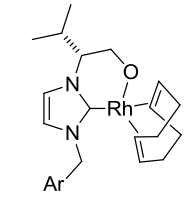
Diarylmethanols are important structural motives for the synthesis of biologically and pharmaceutically active compounds.[1] The addition of organometallic reagents to aryl aldehydes has been the general method to obtain the diarylmethanols. Organolithium, organomagnesium, organozinc and organocopper compounds are the most frequently used organometallics. However, limitations to their applications arise from the nature of the reagents, which are usually toxic and sensitive to air and moisture.[2] Therefore, 1,2-addition of boronic acids to aldehydes catalyzed by various metal complexes has attracted considerable attention following the seminal report by Miyaura et. al. in 1998.[3] Since then several catalysts have been developed and NHC complexes, has become a very useful approach to prepare such compounds.[4]

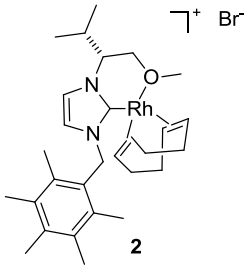


With regard to the synthesis of chiral diarylmethanols, the asymmetric arylation of aldehydes with boronic acids in the presence of chiral NHC complexes has attracted much attention.[5] Chiral neutral (1) and cationic NHC-Rh(I) complexes (2, 3) were prepared and characterized by spectroscopic techniques. These were used as catalysts for the 1,2-addition of phenylboronic acid to aldehydes.



Ar = $C_6H_2Me_3$-2,4,6
C_6Me_5

1



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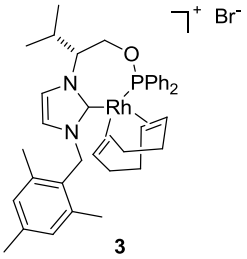

3

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PALLADIUM CATALYSED CARBONYLATION OF TERMINAL ALKENES TO α,β-UNSATURATED ESTERS

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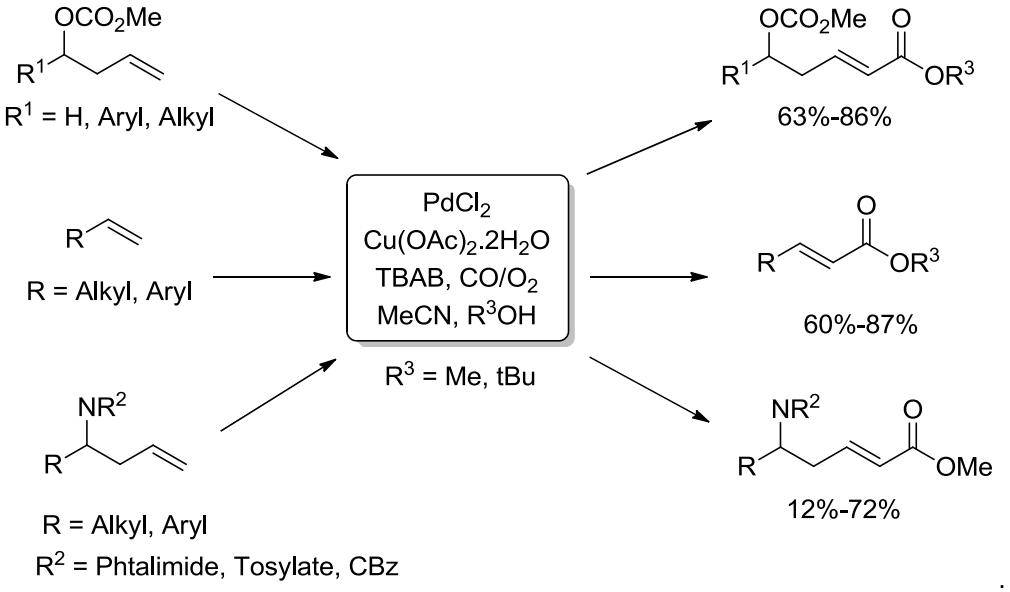
Oxidative carbonylation of terminal alkenes to produce α,β-unsaturated esters is an attractive alternative to cross metathesis. In previous reports,[1] mixtures of mono and dicarbonylated products were often obtained. Another challenge resides in the effective reoxidation of Pd(0) to Pd (II) to permit an efficient catalytic system. Selective oxidative carbonylation of styrene to the cinnamate derivative was reported by Bianchini[2] using a Pd(II)(dppe) complex under acidic conditions; however, the reaction required high CO pressure and elevated temperature.

Scheme



Herein, we present a mild protocol for the carbonylation of terminal functionalised and non-functionalised alkenes to α,β-unsaturated esters (Scheme). The reaction conditions were optimised to achieve practical yield and high chemoselectivity. Importantly, the reactions proceeded at atmospheric pressure of CO and O_2. Combination of Cu(II) with oxygen was found to be crucial for the efficient reoxidation of Pd. Further details on optimisation of the reaction conditions and the reaction scope will be discussed. Synthetic application of the developed method to the synthesis of a vanilloid receptor-1 antagonist (TRPV-1) will be also presented.

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P63

MOLECULAR ORIGAMI – STEREOSELECTIVE SYNTHESIS OF COMPLEX HETEROCYCLES THROUGH SKELETAL REARRANGEMENT OF ENZYMATICALLY DESYMMETRIZED BUILDING BLOCKS

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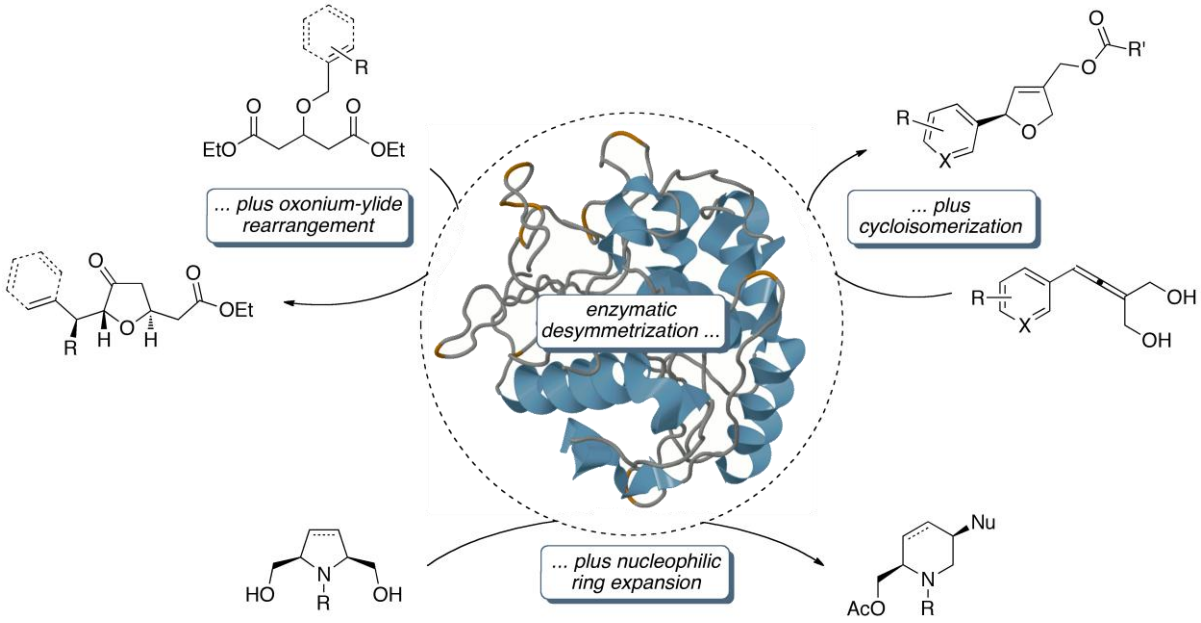
In constant search of highly selective protocols for the preparation of optically pure chiral molecules, organic chemists have shown growing interest in the use of biocatalysts – and lipases in particular – to accomplish this ever-demanded task. In this context, bifunctional symmetric substrates have to be considered exceptionally valuable as their desymmetrization is not only offering rapid access to chiral non-racemic target structures but also leads to the selective protection of one of the enantiotopic groups, hence allowing for an orthogonal functionalization.[1]
The direct connection of enzymatic desymmetrizations with a second potentially symmetry-breaking transformation represents the center of our research efforts. Thus, molecular complexity of the resulting products is substantially increased offering new possibilities for their application in organic synthesis. Exemplarily, we are presenting our recent progress in the sigmatropic rearrangement of desymmetrized glutarates [2], the cycloisomerization of axially chiral allenols [3], as well as implementations in natural product synthesis.



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P64

CATALYTIC SYNTHESIS OF FUNCTIONAL SUBSTITUTED 2,2-ARYLMETHYLENE-BIS-(3-HYDROXY-5,5-DIMETHYLCYCLOHEX-2-ENONES) AND 3,3,6,6-TETRAMETHYL-9-ARYL-3,4,5,6,7,9-HEXAHYDRO-1H-XANTHENE-1,8(2H)-DIONES

E.A. Dikusar, V.I. Potkin, N.G. Kozlov, A.P. Polikarpov, A.A. Shunkevich

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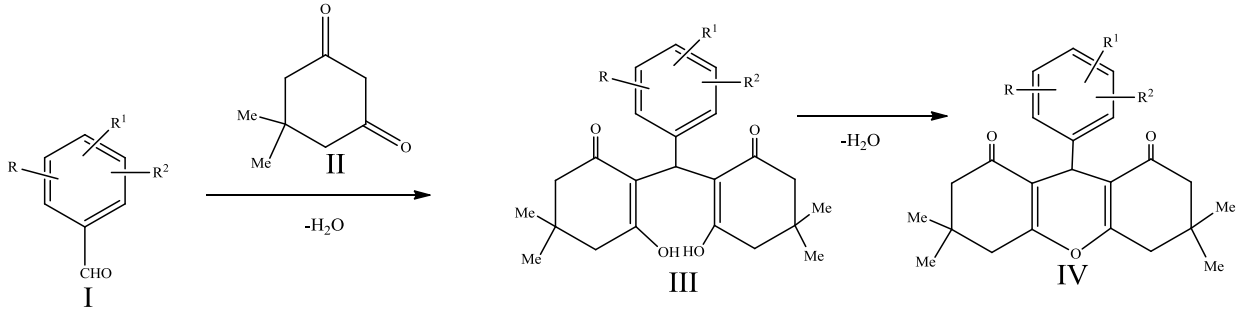
Benzaldehydes vanillin series (I) - vanillin, vanillal, as well as their homologs, analogs and derivatives thereof may serve as convenient and accessible synthons for chemical modification and obtaining on their basis of biologically active compounds in a wide range of practical applications [1], including functional substituted xanthenes, with a pronounced fungicidal and insecticidal activity, as well as the xanthene dyes [2].



Functionally substituted 2,2[1]-arylmethylene-*bis*-(3-hydroxy-5,5-dimethylcyclohex-2-enones) (III) were synthesized with a yield of 75-80% by the condensation of benzaldehydes vanillin series (I) with dimedone (II) in methanol in the presence of polymeric fibrous anion exchanger "FIBAN AK-22". Functionally-substituted xanthenes (IV) were synthesized in quantitative yield about 100% by dehydration of the dioles (III), carried out by refluxing in benzene with azeotropic removing of water formed in the presence of a fibrous sulfonic “FIBAN K-1“. Xanthenes (IV) contained in its structure the fragments of isoxazole, isothiazole and carborane heterocycles and clusters. The catalysts of the process - fibrous ion exchangers "FIBAN AK-22" and "FIBAN K-1" were developed and produced in the Institute of Physical Organic Chemistry National Academy of Sciences of Belarus in commercial scale for the purification of air and waste waters from harmful impurities in the filters of the deep cleaning of ammonia, amines, nitrogen heterocycles, aerosol bases, including in clean rooms in electronic and pharmaceutical industries, in deionized water purification, concentration of ions for the analysis of dilute solutions, in the synthesis of methyl tert-alkyl esters, olefins isomerization, alcohols dehydration [3] .

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CONCISE AND EXPEDITIOUS STRATEGY TOWARD OXYGENATED TERPHENYLS VIA PHENOL OXIDATION-REAROMATIZATION PROCESS

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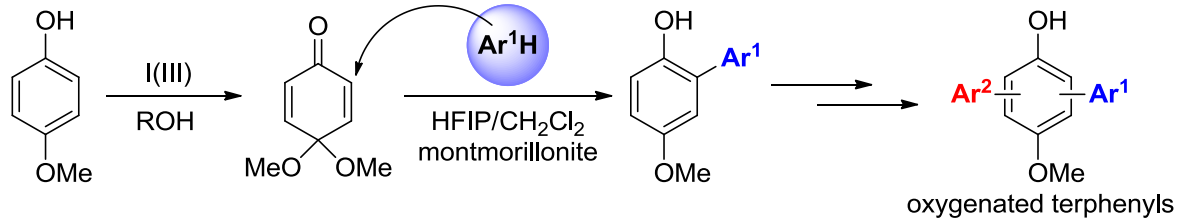
Oxygenated terphenyls and their derivatives exist in naturally occurring compounds. Generally, their constructions rely on metal-catalyzed coupling reactions using metal and halogen prefunctionalized substrates.[1)] Recently, direct carbon-hydrogen bond coupling reactions have been investigated to reduce the synthetic steps. However, those reactions have some problems in reaction controls, such as surplus arylation and the difficulty of introduction of two different aryl groups. Thus, terphenyl synthesis still demands a more concise strategy. Recently, we reported a novel approach to the construction of oxygenated biaryls by nucleophilic addition of aromatic nucleophiles to quinone monoacetals.[2)] This method involves two important steps; oxidation of phenols to the quinone monoacetals and its bond-forming rearomatization process. Quinone monoacetals were synthesized by treatment of the phenols with an oxidant such as hypervalent iodine reagent in methanol. Subsequently, biaryls were obtained by nucleophilic addition of aromatic nucleophiles to quinine monoacetals by the aid of montmorillonite clay in the mixture of hexafluoroisopropanol (HFIP) and dichloromethane.
At this conference, we present a new strategy toward oxygenated terphenyls by means of repetitive arylation *via* phenol oxidation-rearomatization process.



repetitive arylation via oxidation/rearomatization

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P66

NEW SYNTHESIS UTILIZING DESIGNER OXO-BRIDGED HYPERVALENT IODINE SPECIES

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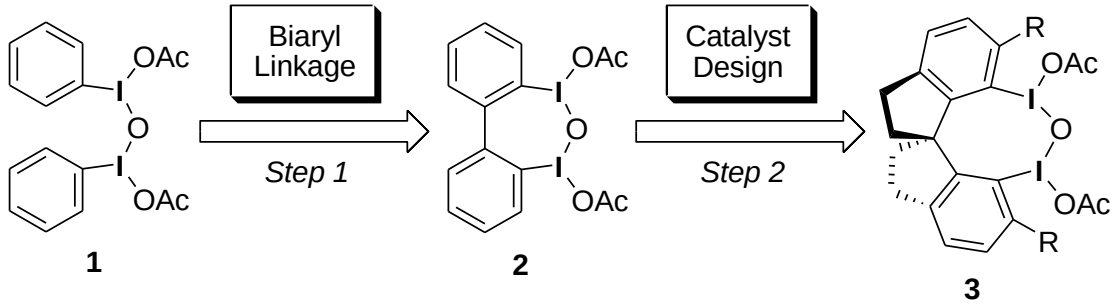
Hypervalent iodine reagent has become one of the promising tools in developing environmentally benign oxidations due to their low toxicities and easy handling.[1)] Our research purpose is to enhance the synthetic value of the reagent as useful alternative to highly toxic heavy metal oxidants and even rare metals, by pioneering their new reactivity and efficient utilization. Thus, we have developed several metal catalyst-free bond formations and functionalizations for aromatic rings, carbon-carbon unsaturated bonds, and aliphatic carbon-hydrogen bonds *via* selective one- or two-electron oxidation pathways using phenyliodine diacetate (PIDA, $PhI(OAc)_2$) and bis (trifluoroaceatate) (PIFA, $PhI(OCOCF_3)_2$).[2)] We also have designed new hypervalent iodine reagents and catalysts based on adamantane or methane structures showing high reactivities and recyclabilities.[3)]

In this conference, we will present the recent development of μ-oxo-bridged hypervalent iodine compounds **1**-**3** for efficient oxidative transformations. The μ-oxo iodine **1** exhibited excellent oxidizing behaviour over common reagents, PIDA and PIFA, during the phenolic oxidations.[4)] Catalytic and asymmetric utilizations have become possible by the modifications of **1** to the designer μ-oxo iodines **2** and **3**.[5)]



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P67

ELECTROCATALYTIC DESIGN OF MEDICINALLY RELEVANT SPIROCYCLIC BARBITURATES

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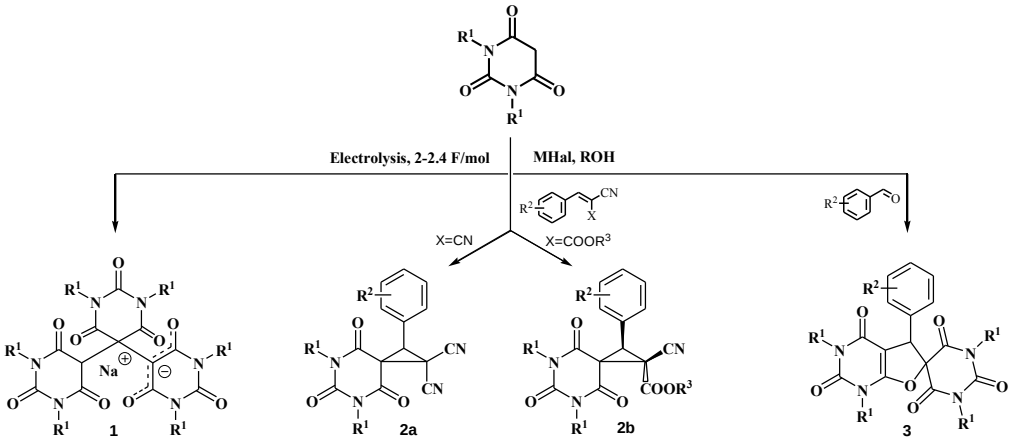
Pyrimidine-2,4,6-triones (barbiturates) belong to a widely-spread group of drugs used as sedative, narcotic, anticonvulsant and antiepileptic agents.[1] Spirobarbiturates have attracted special attention of organic and pharmaceutical community due to unique structural assembly and associated spectrum of biological properties including neuropharmacological effects[2] and inhibition of MMP and TNF-α converting enzymes.[3]

In a course of our study we have focused on electrochemical transformations of barbituric acids due to their pronounced pharmacological properties. It was found that electrolysis of barbituric acids in alcohols in the presence of sodium halides in an undivided cell leads to corresponding sodium salt of condensed barbituric trimer **1** in 75–90% yields. The salt could be easilly converted to disodium salt or to neutral linear trimer under action of NaOH or HCl, respectively. Addition of Michael or Knoevenagel acceptors changes a route of electrocatalytic process giving rise to spirocyclic barbiturates of type **2** in 45–93% or type **3** in 70–85% yields as a result of complex cascade electrochemically promoted cyclizations. It was shown that the linear sodium salt **1** could be also converted into spirocyclic barbiturate of type **3** bearing spiroconjugated barbituric fragment instead of aryl ring by direct chemical oxidation with Br_2 in alkaline alcoholic solution. Noteworthy, the combined electrolysis of barbituric acids and benzylidenecyanoacetates in methanol in an undivided cell in the presence of sodium bromide allows stereoselective formation of spirocyclopropylbarbiturates **2b** with (*E*)-configuration of aryl and alkoxycarboxylate substituents in 45–71% yields. Structures of type **1** and **2b** were confirmed by a single-crystal X-ray diffraction study.



The developed electrocatalytic processes represent a prominent one-step approach to medicinally privileged spirocyclic barbiturate derivatives of a promising utility. Mild chemical nature of mediatory electrolysis allows good substance yields and superior stereoselectivity. Finally, the developed procedure utilizes simple equipment and undivided cell, and is valuable from the viewpoint of environmentally benign synthesis and large-scale processes.

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P68

NICKEL ACETYLACETONATE – AN EFFICIENT CATALYST IN REACTIONS OF METHYLENE ACTIVE CARBONYL COMPOUNDS WITH CYANAMIDES

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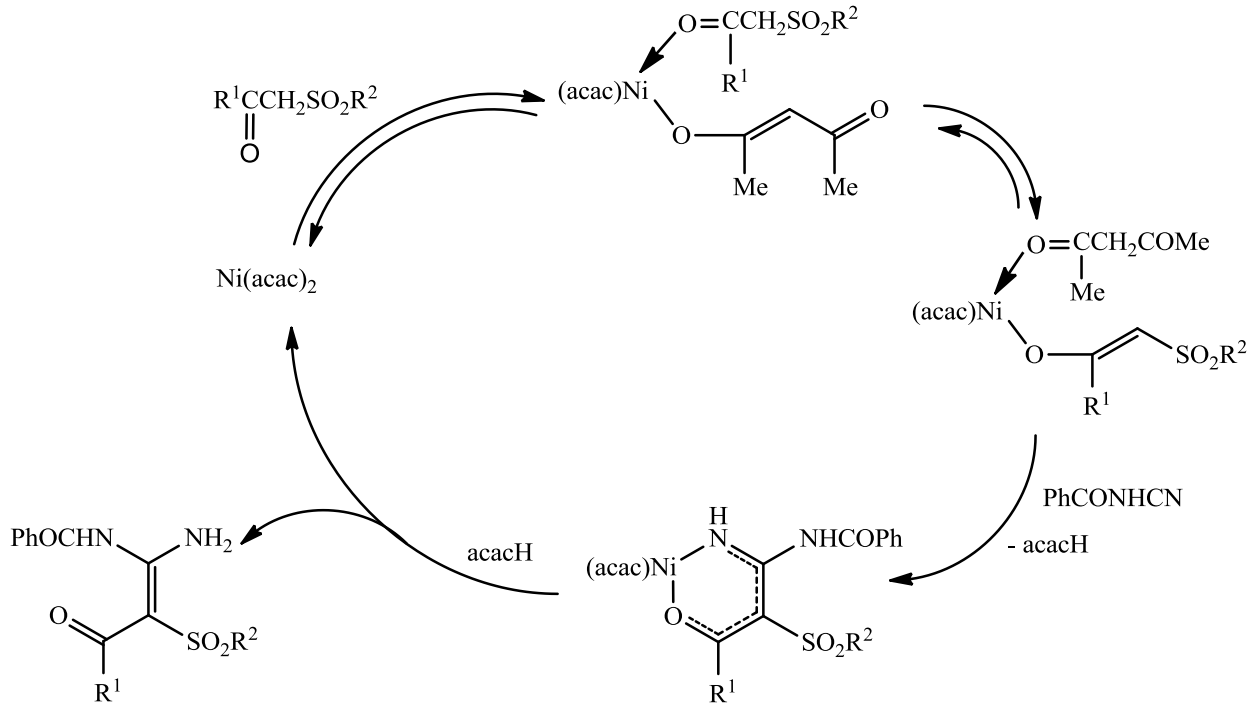
Addition of methylene active carbonyl compounds to C≡N bond fails under acidic or basic conditions. However, as it was shown earlier [1] the reaction of β-diketones and β-oxo esters proceeds under mild conditions in the presence of catalytic amounts of nickel acetylacetonate.
It was established that the key intermediates in these transformations are the β-diketonate type chelates which can add to the activated C≡N bond unlike the corresponding free ligands.
Although 1,3-cycloalkanediones, barbituric acids, β-oxo sulfones and 1-arylpyrazoline-5-ones are not able to form chelates of this kind, the addition products easily can be obtained using $Ni(acac)_2$ as catalyst.
Obviously, in this case the reactive intermediates are nickel enolates formed from the corresponding carbonyl compounds. Thus, for example, the transformation of β-oxo sulfones with benzoyl cyanamide may be represented in the following manner:



Any evidences of C≡N bond activation through the coordination interaction between $Ni(acac)_2$ and cyanamide were not found.

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P69

NOVEL TMS-BASED CATALYSTS FOR SYNTHESIS OF MIXED ALCOHOLS

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In recent time many attention was attracted to alternative fuels such as alcohols. Conventional oxide catalysts used for alcohols synthesis are very sensitive to the presence of ultra-low sulphur amount in the feed sulphur. One of the ways to overcome this difficulty is to use systems based on widely used for hydrodesulphurization (HDS) transition metal sulphide (TMS) catalysts, modified for alcohol synthesis by addition of potassium. The aim of the present work is to investigate a structure of sulphide catalyst active sites in mixed alcohol synthesis (MAS). As a conceptual basis for this work the model of dynamic nature of the active sites of TMS catalysts was taken [1].

The results of investigation into the effect of carrier structure allowed us to assume that morphological characteristics and nature of the carriers essentially affect the catalytic activity. Information about a role of K in the catalytic activity was obtained by testing the samples with K content in the range 0-15 wt. %. With increasing of K content selectivity changes from HC to alcohols. Main part of the liquid products consists of C_1-C_4 alcohols (>85 wt. %), ethanol and propanol has concentrations more than methanol. Potassium concentration affects substantially HDS and HYD activities. In these reactions K represents itself a poison and primary poisons HYD active sites. Addition of K up to 10 wt. % reduces catalysts HDS activity in small extent, but reduces HYD activity. Poisoning of C-S hydrogenolysis sites occurs by increasing K concentration to 15 wt. %,. Basing on TEM data (Fig. 1) we suggested that K ions intercalates between two neighboring MoS_2 layers. Above 10 wt. % K "glues" MoS_2 slabs by basal planes growing layers number. Further increase of K content from 10 to 15 wt. % initiates growth of an average crystallite length via "sticking" by laterals.

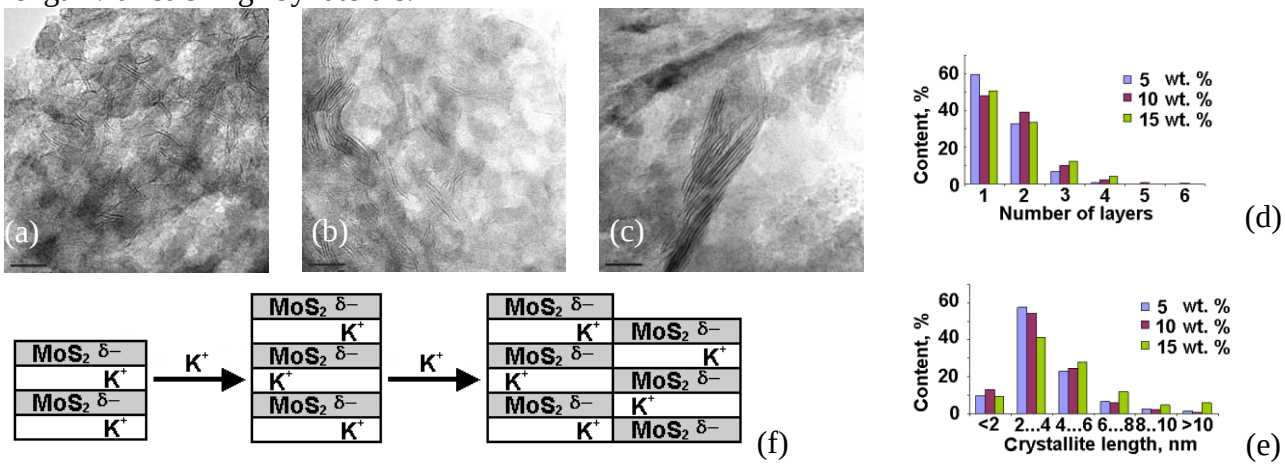

Fig. 1. The TEM-images of the samples with different K content: (a) – 5 wt. %, (b) – 10 wt. %, (c) – 15 wt. %. Statistical distribution of layers number and length of MoS_2 crystallites: (d) – crystallites layers number distribution, (e) –crystallites length distribution. "Sticking" of MoS_2 crystallites (f).

Potassium affects active phase morphology and modifies the active sites of the TMS catalysts.

It was shown that Co-promoted catalyst more selective to alcohols than unpromoted one. The observed Co promoting activity in MAS and HDS led us to conclusion about similarity in the nature of the active sites operating in both reactions.

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P70

HIGHLY ENANTIOSELECTIVE ORGANOCATALYTIC TRIFLUOROMETHYL CARBINOL SYNTHESIS - A CAVEAT ON REACTION TIMES AND PRODUCT ISOLATION

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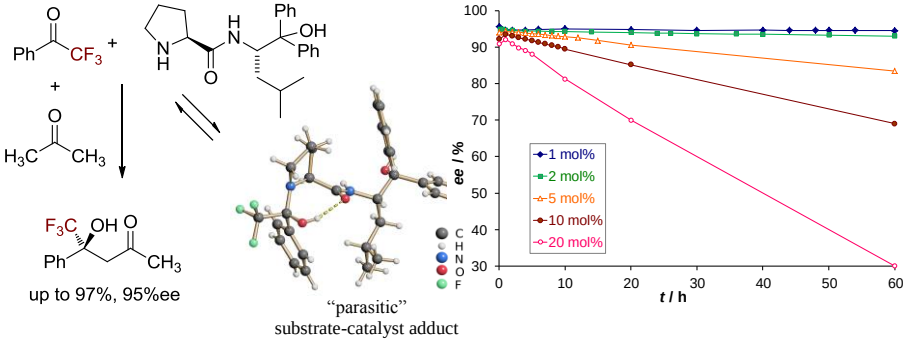
The asymmetric organocatalytic aldol reaction serves as one of the most powerful carbon-carbon bond forming methods, providing access to *β*-hydroxycarbonyl compounds in an enantio- selective fashion.[1] Herein, we describe aldol reactions with trifluoroacetophenones as acceptors, yielding chiral α-aryl, α-trifluoromethyl tertiary alcohols, valuable intermediates in organic synthesis. Of the various organocatalysts examined, Singh's catalyst [(2*S*)-N-[(1*S*)-1-hydroxydiphenylmethyl)-3-methylbutyl]-2 pyrrolidinecarboxamide] was found to efficiently promote this organocatalytic transformation in a highly enantioselective manner.[2] Detailed reaction monitoring (^{19}F-NMR, HPLC) showed that up to full conversion, the catalytic transformation proceeds under kinetic control and affords up to 95 % ee in a time-independent manner.[3] At longer reaction times, the catalyst effects racemization. For the product aldols, even weak acids (such as ammonium chloride) or protic solvents can induce racemization, too. Thus, acid-free workup, at carefully chosen reaction time, is crucial for the isolation of the aldols in high (and stable) enantiomeric purity. As evidenced by ^{19}F-NMR, X-ray structural analysis, and independent synthesis of a stable intramolecular variant, Singh's catalyst reversibly forms a catalytically inactive ("parasitic") intermediate, namely a N,O-hemiacetal with trifluoroacetophenones. X-ray crystallography also allowed the determination of the product aldols' absolute configuration (*S*).



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P71

AN EFFICIENT ORGANOCATALYTIC METHOD FOR HIGHLY ENANTIOSELECTIVE MICHAEL ADDITION OF MALONATES TO ENONES CATALYZED BY READILY ACCESSIBLE PRIMARY AMINE-THIOUREA

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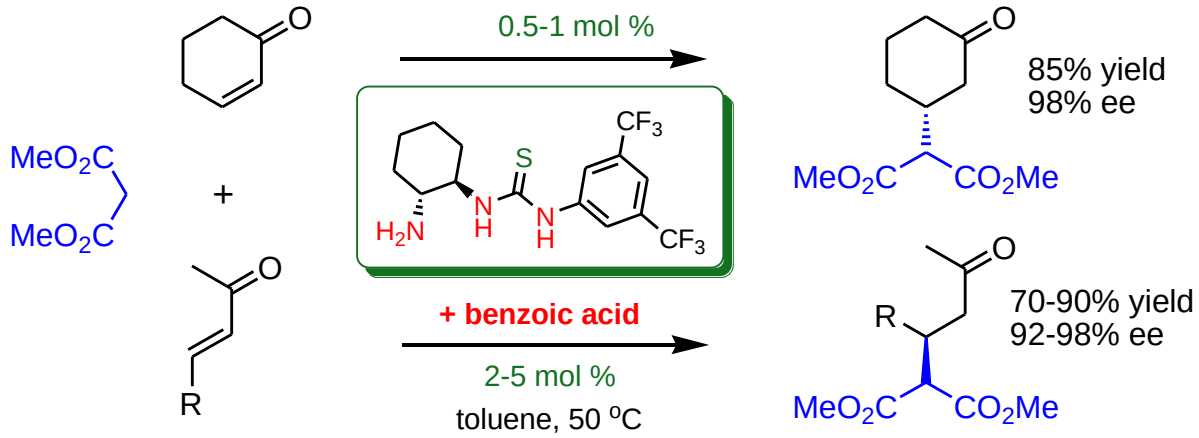
Asymmetric organocatalysis promoted by primary amines has been recognized in recent years as a very attractive tool for the synthesis of chiral molecules.[1] In our studies we focused attention on the organocatalytic Michael reactions[2] with this type of catalysts based on iminium activation. Of particular interest are reactions operating with low loading (≤ 5 mol %)[3] of easily accessible primary amines.

We observed that simple and readily available primary amine-thioureas derived from 1,2-diaminocyclohexane were very efficient catalysts for the addition of malonates to various enones. Our results confirmed that the presence of additional basic site (e.g. tertiary amine) in the primary amine-thiourea catalyst structure is not essential for efficiency of this reaction.[4]



In this communication we report practical and highly enantioselective Michael addition of malonates to enones catalyzed by simple and readily available bifunctional primary amine-thiourea derived from 1,2-diaminocyclohexane. The addition of weak acids and temperature increase (*ca.* 50 °C) improved efficiency of the Michael reaction. This approach allows for the efficient synthesis of 1,5-ketoesters with good yields, excellent enantioselectivities and low loading (0.5-5 mol %) of simple chiral primary amine-thiourea catalysts, and is applicable in multi-gram scale synthesis.

Acknowledgment We are grateful to the Polish Ministry of Science and Higher Education (Grant Iuventus Plus 2010 022170) for financial support.

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P72

HETEROCYCLISATION BY INTRAMOLECULAR ANTI-CARBOLITHIATION OF CHLOROALKYNES

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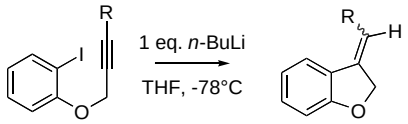
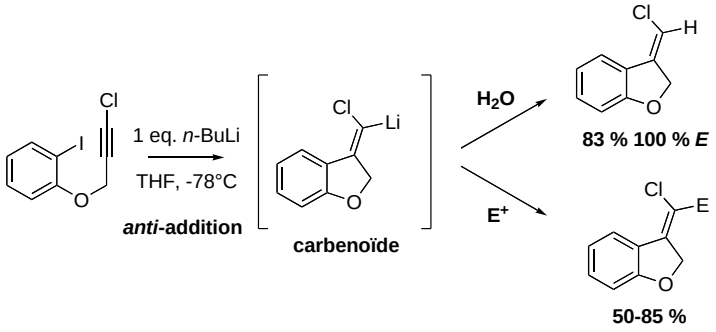
For the past 30 years, carbometallation methodologies using organolithium reagents have been greatly developed.[1] However, intramolecular additions of aryllithium to a triple bond are not very common, due to the dependence of the moiety on the unsaturation. Indeed, until the 90's, this chemistry was limited to acetylenic derivatives bearing phenyl[2] or silyl[3] groups, able to stabilize the vinyllithium intermediate. In our case, we have recently described a method providing highly functionalized heterocycles by intramolecular carbolithiation of an acetylenic triple bond bearing an acetal appendage.[4] Moreover, it was the first time that a direct *anti*-addition was observed, induced by a rotatory chelation of the acetal and confirmed by DFT calculations.[4b,c] We thus decided to evaluate the scope of this reaction by modifying the terminal propargylic substituent borne by arylethers and study their propensity to cyclize under carbanionic conditions.[5]
In order to explore this new reactivity, we decided to replace the acetal by other chelating groups, such as ethers, halogens or sulphur.



R= CR_2OR, Cl, Br, Ph, SPh, $SiMe_3$...

In case of chloropropyne, we obtained efficiently the *anti*-addition product, and the vinyllithium intermediate had been successfully trapped with various electrophiles. Coupling reactions of this intermediate have also permits the formation of vinyl stannane, silane or boronic acid. In addition, the carbolithiation leads to an interesting gem-chlorolithium carbenoid species, which was successfully exploited for its electrophilic and nucleophilic properties.



Indeed, we decided to take advantage of this lithium chloride intermediate by activating the chloride in some palladium-catalyzed cross-coupling reaction, leading to di-substituted exocyclic dihydrovinylbenzofuran. These results will be presented at the congress.

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P73

NEW CATALYSTS FOR THE SIMULTANEOUS CONTROL OF REGIO- AND ENANTIOSELECTIVITY IN HYDROXY- AND ALKOXY-CARBONYLATION

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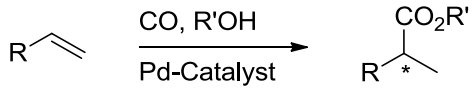
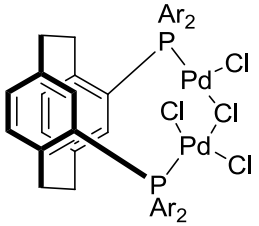
Over the last three decades palladium catalysed hydroxycabonylation has become well established as a useful tool for the synthesis of commodity and fine chemicals.[1] Asymmetric hydroxy and alkoxy-carbonylation allow the formation of more complex, enantio-enriched carboxylic acids and esters from cheap, simple alkene starting materials.



The simultaneous control of chemo-, regio- and enantioselectivity has been problematic, with the vast majority of catalysts providing near racemic products and requiring very harsh conditions, in terms of pressure and temperature. Until very recently the best reproducible result from the literature gave an e.e. of just 43 % for the hydroxycarbonylation of an aryl-alkene.[2]



We have found an unusual class of di-palladium precatalysts that can perform the hydroxycarbonylation of styrene with e.e.'s as high as 80 % and the methoxycarbonylation of the same substrate with an e.e. of 91 %.[3] While our initial efforts were highly enantioselective, regioselectivity was still a problem. More recently, we have since developed catalysts which can overcome this issue, delivering high branched selectivity while maintaining a high level of enantioselectivity for the reaction of a number of different substrates.[4] Highlights and current work towards even more active and selective catalysts shall be presented.

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P74

CATALYTIC CYCLOALUMINATION AS A NEW APPROACH FOR STEROID MODIFICATION

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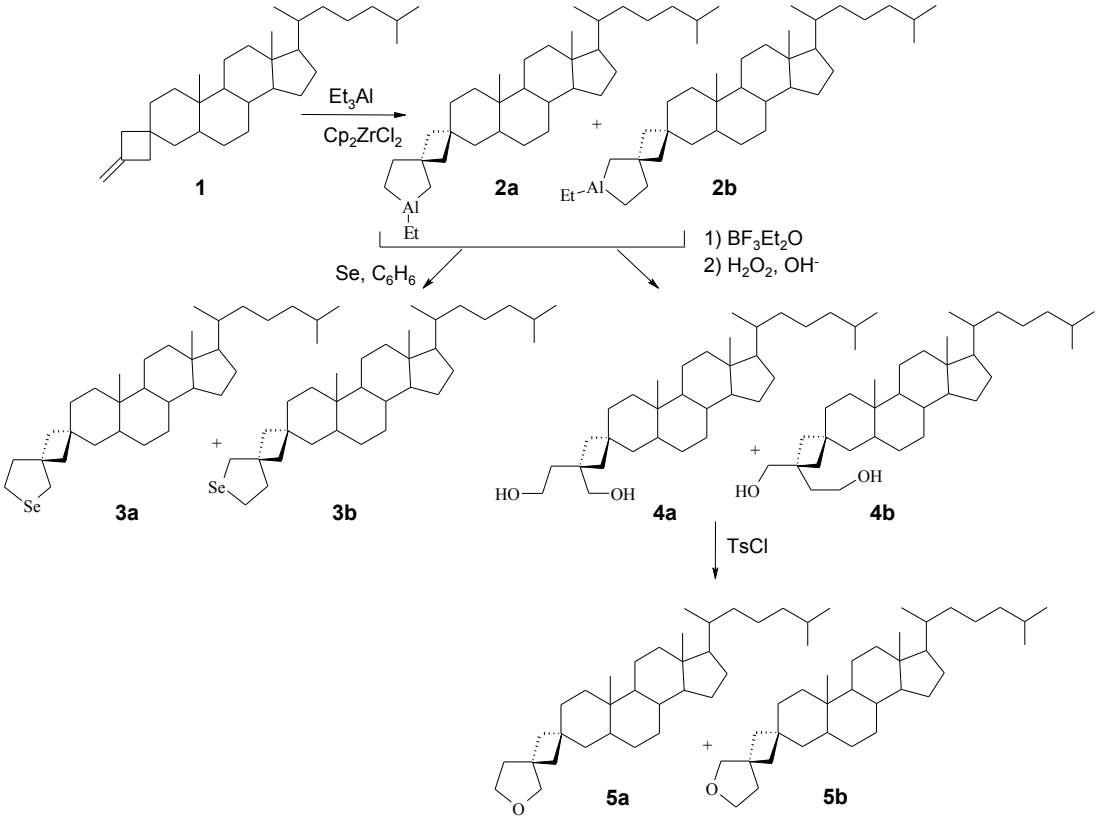
The development of new modification methods for natural and synthetic steroids remains actual problem in organic chemistry since the resulting derivatives may possess various types of biological activities.

We believe that the cycloalumination reaction of unsaturated compounds, which was developed in our laboratory and was found wide application in synthesis of mono- and bifunctional hydrocarbons as well as carbo- and heterocyclic compounds, is one of approaches for incorporation of carbo- and heterocyclic fragments or functional groups in a steroid molecule [1,2].

In this report, this new approach for steroid modification is demonstrated on the example of 3'-methylene-spiro[(5α)-cholestane-3,1'-cyclobutane] **1**, which enters into the Cp_2ZrCl_2-catalyzed cycloalumination reaction with Et_3Al to afford diastereomeric pair of spiro[(5α)-cholestane-3,2'-(6'-ethyl-6'-alumina-spiro[3.4]octane)] **2a** and **2b**. The latters undergo transformations to both selenophane derivatives **3a,b** when treated with Se in benzene solution and tetrahydrofurane derivatives **5a,b** through oxidation with hydrogen peroxide followed by cyclization of resulting diols **4a,b.**



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ASYMMETRIC CROSS-ALDOL REACTION OF PYRUVIC DERIVATIVES: BIOMIMETIC SYNTHESIS OF ULOSONIC ACIDS

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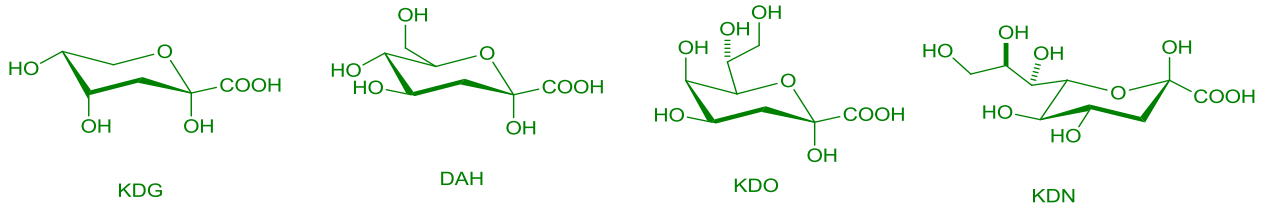
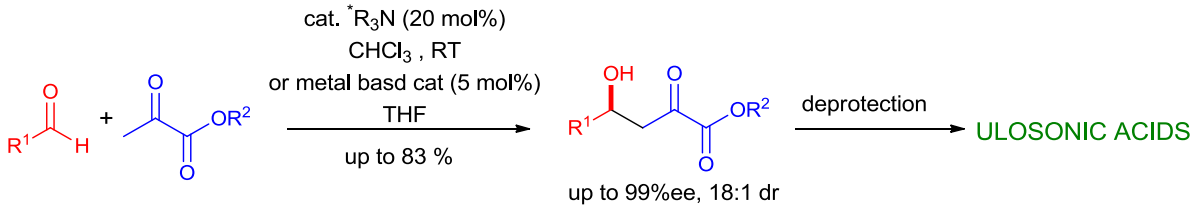
Among the variants of asymmetric aldol reactions, pyruvate-dependent aldol reactions are of particular interest, as these processes are vital in the formation of 3-deoxy-2-ulosonic acids, which are essential sugar units for many biological processes and transformations. The phosphorylated form of KDG is a part of the Entner–Doudoroff pathway while the 7-phosphate of the DAH is a key intermediate in the biosynthesis of aromatic amino acids via the shikimate pathway. The KDO has been found in Gram-negative bacteria lipopolysaccharides (LPS). Naturally occurring KDN is significantly involved in the pathogenesis of microorganisms and various disease states.[1]



Recently, we have successfully developed stereoselective catalytic synthesis of ulosonic acid precursors through direct aldol reaction of sugar aldehydes with pyruvic derivatives. In this protocol C3 pyruvic aldehyde dimethyl acetal or 2-acetylthiazole were utilized as masked pyruvate synthons. Our methodology promoted by chiral metal complexes acting as type II aldolases can be seen as resembling the natural pathway of substrate activation.[2] Even so, the need for direct methodology using pyruvate esters has remained a challenging task. The protocols associated with the names of Jørgensen, Dondoni and Yamamoto are disappointing towards cross-aldol reaction and involves only homoaldolizations or reaction with highly reactive chloral hydrate.[3]

Herein, we are also presenting a broad scope catalytic approach to direct aldol reaction between pyruvate esters and various aldehydes. Cinchona- alkaloids and metal based catalysts have been utilized to achieve excellent yields and stereocontrol (up to 99% ee and 18:1 dr). The presented methodology was used to synthesized higher ulosonic acids by the reaction between the esters and sugar aldehydes via an attractive biomimetic approach.[4]



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P76

SUPPORTED MODEL CATALYSTS FOR OXIDATION OF ALCOHOLS

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The oxidation of alcohols to their corresponding carbonyl compounds, are important and widely used reactions either on laboratory scale or industrial scale.[1] Oxidation of alcohols is normally carried out using either stoichiometric amounts of inorganic oxidants such as chromate or permanganate,[2] or expensive homogeneous catalysts. Both having disadvantages such as liberation of large amounts of byproducts and difficulty separation.

The use of platinum and palladium heterogeneous catalysts for the oxidation of alcohols are environmentally more friendly and have widely been investigated, either unpromoted or promoted by Pb^0 or Pb^{II},[3] or Bi^0 or Bi^{III}.[4] Other metals can also be used as promoters such as Co^{II} or Co^{III},[5] and Sn^{IV}.[6]

To obtain a homogeneous dispersion of two different metals on a solid support surface is very difficult, since like metals tend to aggregate together. The distribution of the two different metals and the catalytic activity of such a bimetallic heterogeneous catalyst strongly depend on the method of preparation of the catalyst. Promoting of palladium catalyst with bismuth-oxoacetate to produce a bimetallic heterogeneous catalyst increases the catalytic oxidation compared to the monometallic palladium supported on carbon.[7]

It has been shown that a bimetallic single source catalyst precursor resulted in a more homogeneous distribution of the two metals and a higher catalytic activity was observed compared to catalysts prepared by the physical mixing of two separate mono-metallic precursors.[8]

This presentation reports the use of $[Pd^{II}Co^{II}(\mu\text{-}OOCCH_3)_4]\cdot H_2O\cdot 2CH_3COOH$ as a single source catalyst precursor for preparation of the $Pd^{IV}Co^{III}/SiO_2$ bimetallic heterogeneous catalyst, which was successfully used in for oxidation of an ocadecanol to its corresponding carbonyls.

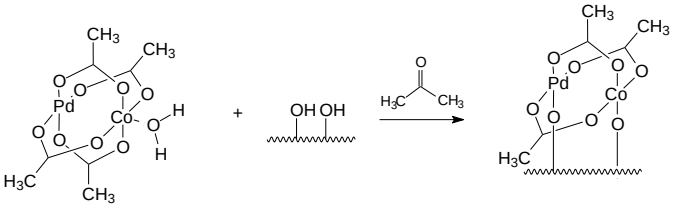

Figure 1: Grafting of the Pd-Co bridging tetraacetate onto the solid support.

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P77

CuAAC REACTION IN STEROID CHEMISTRY NEW AMPHIPHILIC LIGANDS AND POTENTIAL DRUGS

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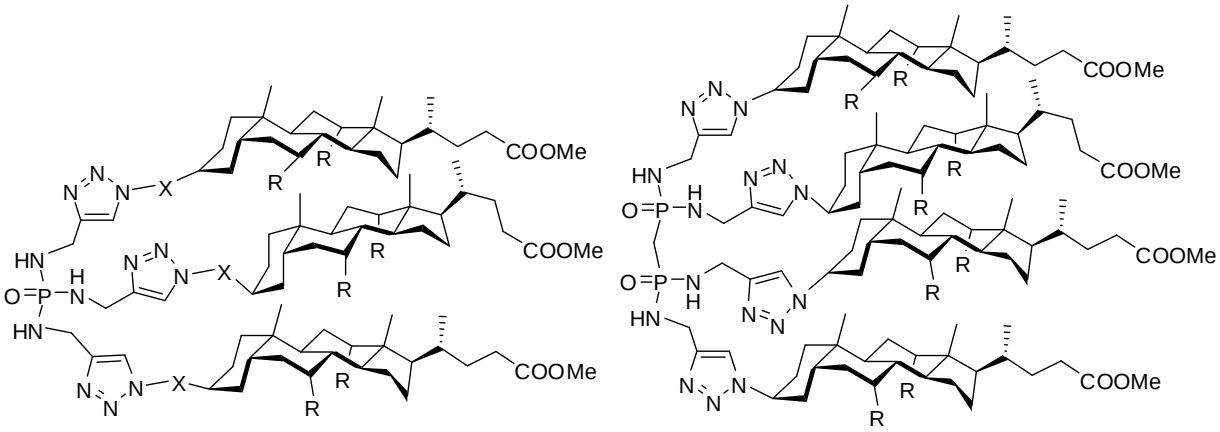
Bile acids provide unique possibilities for the construction of new amphiphilic molecules due to the presence of rigid framework with lipophilic and hydrophilic sides. Recently copper-catalyzed 1,3-dipolar cycloaddition of azides to alkynes (CuAAC) have been proposed for the preparation of bile acid-containing amphiphilic ligands [1]. We have synthesized several steroid-containing macrocycles using this protocol [2]. However the yields of macrocyclization step usually haven't exceeded 20-25%.

Here we demonstrate that CuAAC reaction can be applied for the easy and high-yielding access to pincer, tri-, and tetrapodal ligands, containing phosphoric **1** and methylenediphosphonic **2** acid linkers.

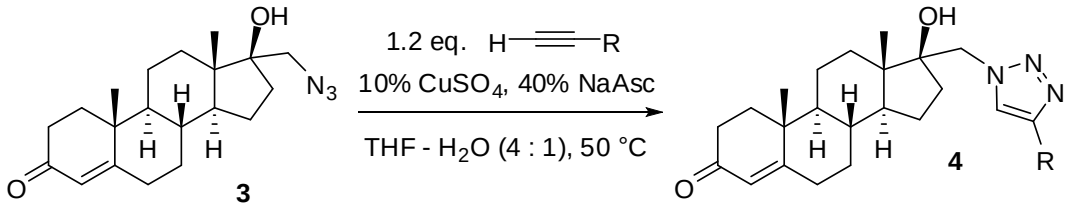


1a: R=H
1b: R=OH

2

Some of the synthesized molecules (e.g. **1a**) form gels in both DMSO and benzene at low concentrations.

CuAAC reaction was also used for the preparation of triazolylsteroids – potential 17-hydroxylase inhibitors.



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CATALYTIC PROPERTIES OF HETEROBIMETALLIC COMPLEXES DERIVED FROM CYCLOPENTADIENYL-RUTHENIUM AND GROUP 10 POCOP PINCER COMPOUNDS

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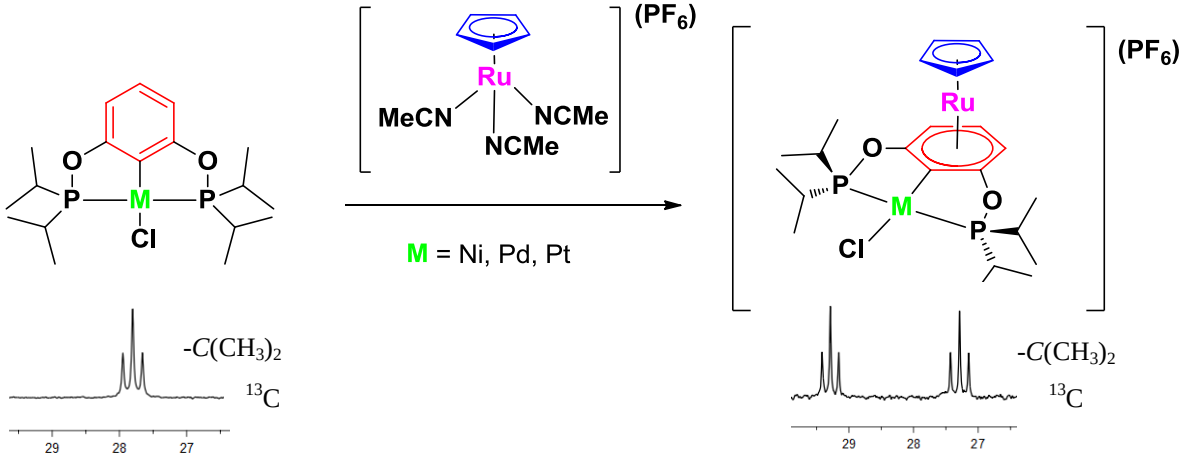
A series of heterobimetallic complexes was prepared by η^6-coordination of the $[CpRu]^+$ fragment to the aromatic ring of pincer complexes of nickel, palladium and platinum. Their molecular structures were determined by single-crystal X-ray diffraction. The analysis in solid state and dissolution clearly showed that the coordination occurs in an orthogonal fashion and, as a consequence, both faces of the pincer complexes become nonequivalent and thus generates diastereotopicity. The electrochemical behavior of the new complexes was studied, showing that the new bimetallic species are much less electron-rich than the POCOP precursors [1]. The heterobimetallic compounds were used as homogeneous catalysts in different cross-coupling reactions and showed enhanced activity when compared to their monometallic counterparts.



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Financial support from PAPIIT (IN204812) and CONACyT (153151) is acknowledged.

DEVELOPMENT OF NOVEL N–HETEROCYCLIC CARBENE CATALYSTS AND DIRECT CHEMOSELECTIVE CROSSED ACYLOIN CONDENSATIONS CATALYSED BY N–HETEROCYCLIC CARBENES

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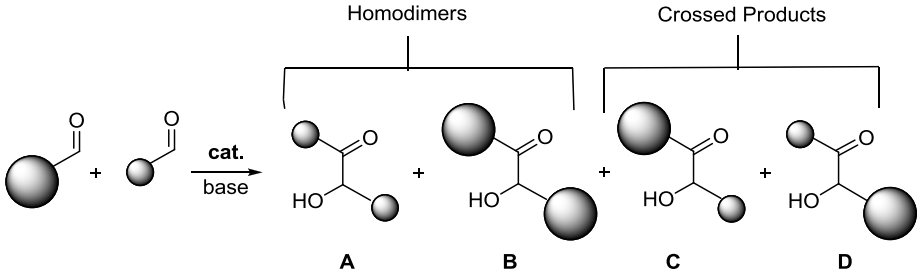
Our aim is to design highly tuneable triazolium salt precatalysts which are capable of promoting asymmetric reactions involving acyl anion equivalents such as in the benzoin condensation. When two different aldehydes are allowed to react in the presence of an achiral catalyst, there are four possible outcomes each yielding two enantiomers.



Scheme 1. Challenges associated with crossed acyloin condensation

An artificial chiral catalyst capable of promoting only one enantiomer of one possible product in this potentially useful process has not yet been reported. We have designed synthetic routes in order to obtain novel monofunctional and bifunctional chiral triazolium salts. These precatalysts possess an *N*-Heterocyclic carbene moiety as shown in the general structure (Figure 1) which incorporate: a) an azide b) a triazole ring and c) an amide in order to ascertain the factors that determine both chemoselectiviy and enantioselectivity in the coupling process.

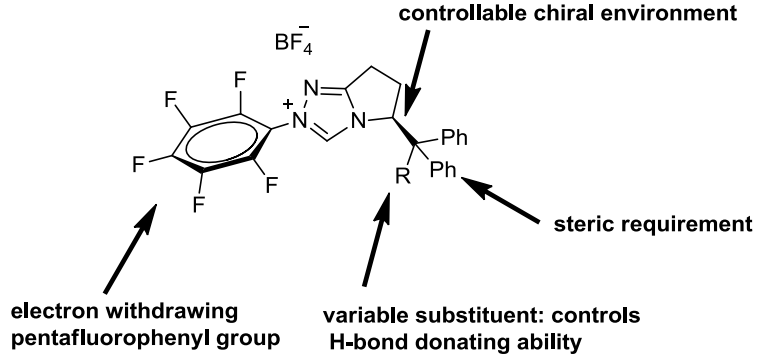


Figure 1. Structural backbone of triazolium precatalysts

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P80

CONTINUOUS FLOW ASYMMETRIC α-AMINATION OF ALDEHYDES

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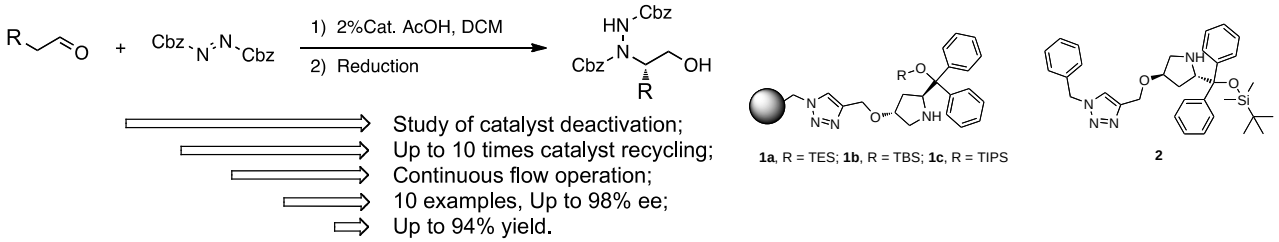
Chiral α-amino carbonyl derivatives are important intermediates in organic synthesis as they can be easily transformed into bioactive compounds.[1] There is thus great interest in developing catalytic, direct strategies for the α-amination of carbonyl compounds and, in particular, organocatalytic methods that avoid the use of toxic metals.[2] Although great improvements in this reaction have been reported in recent years,[2c, 2d] the development of an efficient catalyst, which can be reusable and even applied to continuous flow operation remains a challenge.[2c]



We have successfully developed polystyrene-supported diphenylprolinol silyl ether as catalysts for α-amination reactions. Very high conversions and enantioselectivities can be achieved in very short reaction time with only 2 mol%, and even 1 mol% of catalyst loading. Based on the study of the catalyst deactivation reaction, the underlying chemical process has been identified, and a simple solution to the deactivation problem has been developed. Under the optimal reaction conditions, the catalyst has been recovered and reused in 10 consecutive reaction cycles, leading to an accumulated TON value of 480. The introduction of the TBS unit as a more stable protecting group of the tertiary alcohol in the catalytic unit (**1b**) allowed application to continuous flow conditions for extended periods of time. Catalyst **1b** exhibited very highly selectivity for linear aldehydes in the presence of α- or β-branched ones, which allows the selective amination of the linear component in aldehyde mixtures resulting from Rh-catalyzed hydroformylation of propene.[3]

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P81

GOLD(I)-CATALYZED INTERMOLECULAR CYCLOADDITIONS OF ALLENAMIDES

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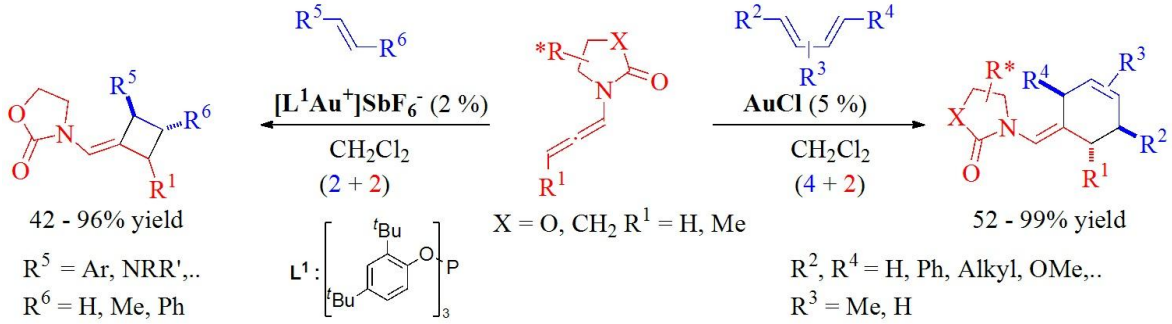
In recent years there have been extraordinary advances in the development of Au-catalyzed processes. [1] In this context, our group has recently demonstrated the possibility of using allenes as three or two carbon components in intramolecular Au-catalyzed [4C+3C] and [4C+2C] cycloadditions.[2]

Herein, we describe our results on the development of Au-catalyzed (4 + 2) intermolecular cycloaddition between a variety of dienes and allenamides, which is efficiently catalyzed by AuCl.[3] Curiously, in some cases, (2 + 2) cycloadducts were also detected as minor side products. On these bases, and considering the synthetic and medicinal relevance of these cyclobutanic systems, we specifically pursued the development of a Au-catalyzed intermolecular (2 + 2) cycloaddition. As a result, we found that these (2 + 2) cycloadditions between allenamides and alkenes can be efficiently achieved using a gold complex incorporating a bulky phosphite ligand, providing excellent yields of a variety of (2 + 2) adducts, with complete regio-, chemo- and stereo-selectivity.[4] Analysis of their scopes, possible mechanistic scenarios as well as the development of asymmetric versions of these types of cycloadditions, will also be discussed.



HF acknowledges FCT for a doctoral fellowship SFRH/BD/60214/2009.

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P82

IONIC LIQUIDS – EFFECTIVE CATALYSTS AND REACTION MEDIA FOR THE SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES

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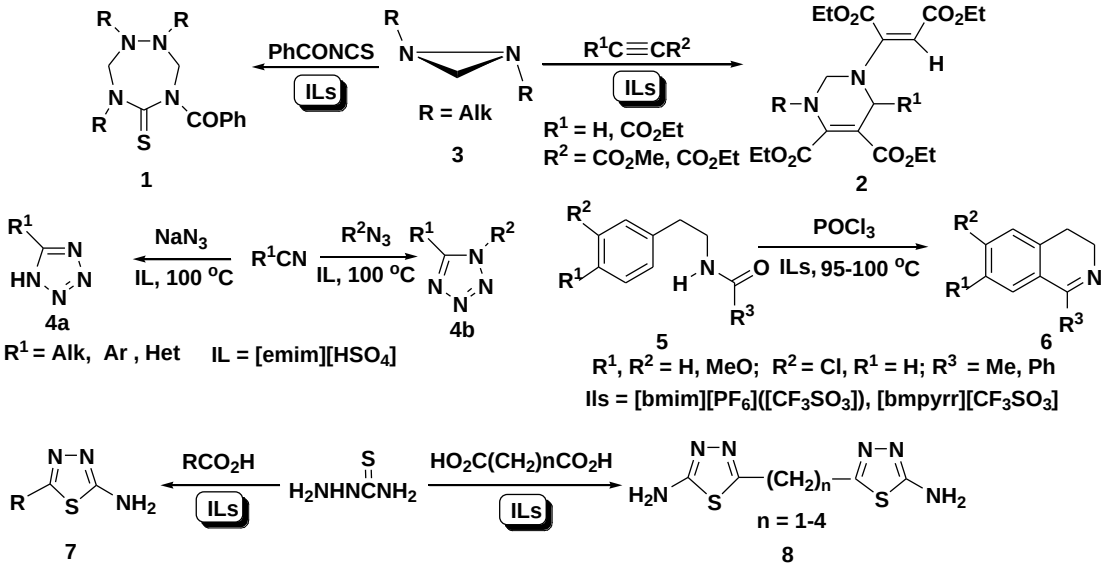
Heterocycles derivatives play bigger and bigger part in different fields of science and technology (medicine, agriculture, electronic).Therefore a development of new, more effective methods for the synthesis of heterocyles does not lose of its urgency. One of the prospective approaches to solve this task is the using of ionic liquids (ILs) as reactive media and catalysts, since ILs hasten different heterolytic processes, and some of them have acidic or basic character and are be able to reveal a catalytic activity. Beside ILs are fire-resistant, have limited vapor pressure and recyclable (green chemistry).

Last past years we have developed several new methods for the synthesis of different nitrogen-containing heterocycles with the using of ILs. Thus, absolutely unique ring expansion reactions – a formation of tetrazepanthiones[1a] **1** and tetrahydropyrimidines **2**, have been found at an interaction of 1,2-disubstituted diaziridines **3** with benzoyl isocyanate and DEAD[1b] or methyl propyolate[1c] in ILs, accordingly. The general method for the preparation of 5-mono- and 1,5-disubstituted tetrazoles **4a** and **4b** heve been developed on the basis of NaN_3 and $AlkN_3$ condensation with different nitriles without addition of any other acidic catalysts.[2] ILs, containing $[CF_3SO_3]$-anion, effectively catalyse the formation of 3,4-dihydroisoquinolines **6** according to Bishler-Napieralski reaction by cyclodehydration of *N*-acyl-2-arylethylamines **5** with $POCl_3$ as dehydration reagent.[3] The 2-aminothiadiazoles **7** and **8** were successfully synthesized under the action of thiosemicarbazide on different mono- and dicarboxylic acids in so-called acidic IL [bmim][HSO_4].[4] The analogical studies are now in a progress.



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4. *Mendeleev Commun.*, 2011, **21**, 331.

P83 (GM8)

COMBINED COMPUTATIONAL AND SPECTRAL APPROACH TO THE STUDY OF REACTION MECHANISMS WITH HYDRIDES: HOW TO PROGRESS AND AVOID FAILURE

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Mechanistic investigations of reactions involving metal hydrides are very important for catalysis, chemistry, and biochemistry [1]. The computations are needed not only to support experimental studies but also to explain observed phenomena and predict behavior of certain species. Examples from hydride chemistry where single method is not sufficient for description of system will be discussed.

- Combination of theoretical and experimental data acquired on the hydrogen bonding, proton transfer and H_2 evolution kinetics and thermodynamics allows explanation of the $Cp^*MoH(CO)(PMe_3)_2$ behavior upon protonation in the mid-polar solvent in terms of the specific solute-solvent interactions [2].
- The structure of [RhX(diene)(P,SR)] with ferrocenyl phosphine-thioethers ligands (diene = norbornadiene, 1,5-cyclooctadiene; P,SR = $CpFe(1,2\text{-}\eta^5\text{-}C_5H_3(PPh_2)(CH_2SR)$; R = *t*Bu, Ph, Bz, Et; X=Cl, BF_4) was established with a combination of experimental IR and computational DFT investigations and points to an equally four coordinate square planar geometry with the diene ligand, the chlorine and the phosphorus atoms in the coordination sphere and with a dangling thioether function. However, a second isomeric form featuring a 5-coordinated square planar geometry with the thioether function placed in the axial position is easily accessible in some cases.
- The metal involvement in dihydrogen bond based on purely computed electronic parameters (NBO, Kohn-Sham MO and AIM analysis) for Cp*MH(dppe) (M=Fe, Ru, Os) adopted for explanation of the proton transfer kinetic product changing from non-classical $M(\eta^2\text{-}H_2)$ for Fe and Ru to classical *cis*-$M(H)_2$ for Os in these hydrides [3,4].
- Identification of high energetic intermediates with low interconversion barriers in reactions of proton transfer to the $Cp^*MoH_3(dppe)$, $Cp^*MoH(PMe_3)_3$ and CpRuH(dppe) by computations, allows full description of hydrogen atom migration mechanism.

Acknowledgements: this work was supported by the RFBR (11-03-01210), CNRS-RFBR bilateral grant, the GDRI "Homogeneous Catalysis for Sustainable Development" and by Division of Chemistry and Material Sciences of RAS.

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P84

METAL-CATALYZED C–H FUNCTIONALIZATION FOR THE SYNTHESIS OF LACTONES

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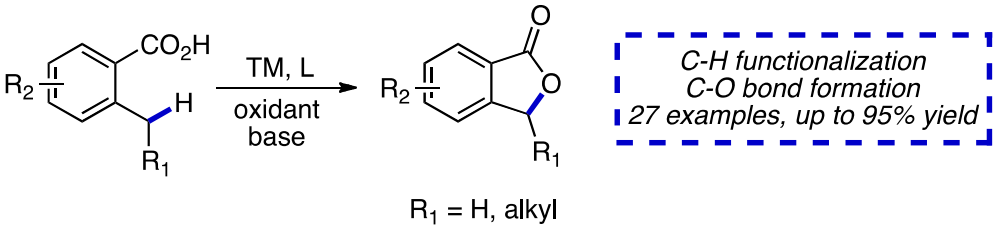
Developing new methodologies in terms of step, atom and redox economy is at the center of organic chemistry. In this context C–H bond functionalization, generally aided by transition metal complexes, has emerged as one of the most powerful tools for achieving this purpose[1]. On the other hand, designing efficient protocols for the formation of C–O bonds still remains an important challenge[2]. Recently, our research group has reported the direct C–H functionalization/C–O bond formation protocol for the synthesis of valuable lactones, using cheap and abundant carboxylic acids as directing groups[3]. This method is characterized by their wide substrate scope, including challenging substrate combinations with particularly sensitive functional groups and a diverse set of substitution patterns. Besides, deuterium labeled experiments revealed an unusual isotope effect[4], suggesting that C–H bond cleavage might not be involved in the rate limiting step of the process.



Scheme 1. Lactone synthesis via C–H functionalization

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P85

ALKYNE ACTIVATION WITH CARBOPHILIC LEWIS ACID CATALYST FOR THE SYNTHESIS OF FURAN AND PYRROLIDINE DERIVATIVES

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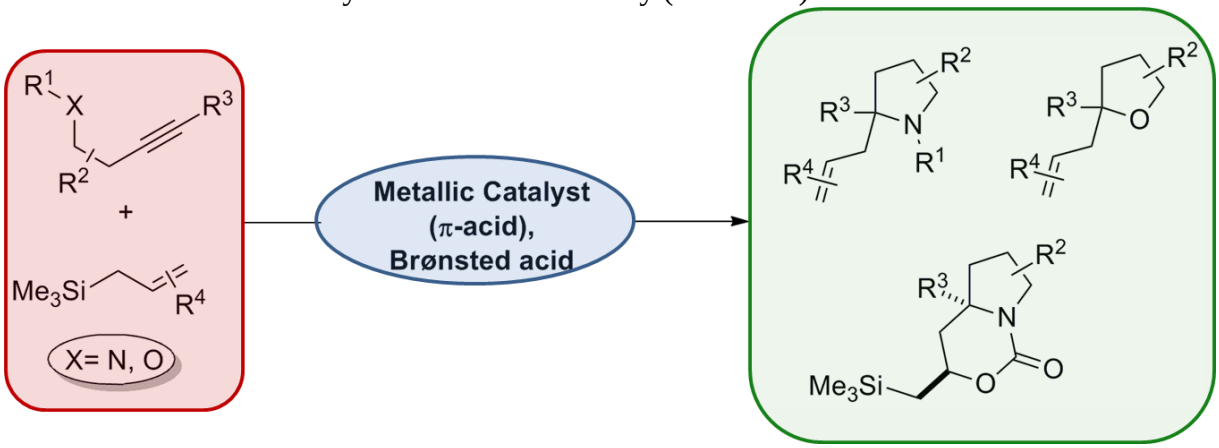
Tandem (domino or cascade) reactions have emerged as very attractive tools in organic chemistry as they allow several bond-forming and/or cleaving events to occur in a single synthetic operation, thus minimizing the cost and waste associated with one-reaction/one-vessel approaches. The development of these reactions offer the opportunity of building up complex molecules, frequently with high stereoselectivity, from simple and easily available substrates.[1] In this context, catalytic cascade reactions involving an initial activation of a carbon-carbon triple bond by a carbophilic Lewis acid (π-acid) are particularly interesting. Moreover, metal-catalyzed intramolecular addition of heteroatoms to alkynes provides a rapid and efficient access to a variety of heterocyclic compounds.[2]

Following our interest in this type of transformations,[3] we have developed a multicomponent and multicatalytic cascade reaction of hydroalcoxylation or hydroamination / nucleophilic addition using allyltrimethylsilane derivatives as carbonated nucleophiles. This methodology has allowed the synthesis of 2,2-disubstituted pyrrolidine or tetrahydrofuran derivatives as well as pyrrolooxazinones in a totally diastereoselective way (Scheme 1).



Scheme 1

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P86

NEW CHIRAL NHC LIGANDS FOR THE COPPER-CATALYZED ASYMMETRIC CONJUGATE ADDITION OF GRIGNARD REAGENTS

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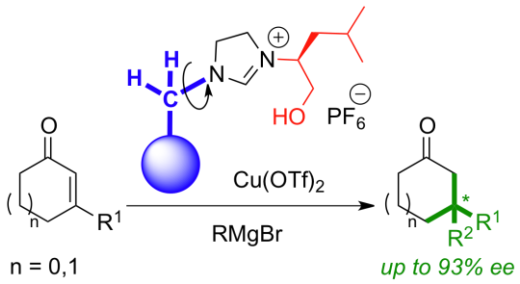
Since asymmetric conjugate additions (A.C.A.) represent a powerful methodology allowing direct access to enantioenriched ketones, we kept our attention on some specific remaining challenges.[1] At this time, only few copper-catalysed nucleophiles were able to be introduced selectively on trisubstitued enones, promoted by various types of NHC's chiral ligands.[2] This work discloses recent advances in the A.C.A. of the highly desirable Grignard reagents to β-substituted cyclic enones.[3]
Several ligands have been synthetized in high yields and involved in catalysis for the addition of ethylmagnesium bromide leading to chiral 3,3-cyclohexanone (up to 93% *ee*). The best ligand was then engaged in optimized conjugate additions of various Grignard reagents allowing for the formation of quaternary centers with high level of regio- and enantioselectivity with only 0.75mol % of catalyst loading. Noteworthy is the addition of alkylmagnesium bromide for the construction of 3,3-cyclopentanone (up to 86% *ee*), highlighted by useful chiral synthon synthesis. Such level of selectivity for A.C.A. of alkylmagnesium bromide to 5-membered rings is unprecedented.



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P87

IMIDAZOLIUM AND BENZIMIDAZOLIUM SALTS BASED ON DI- AND TRITERPENES

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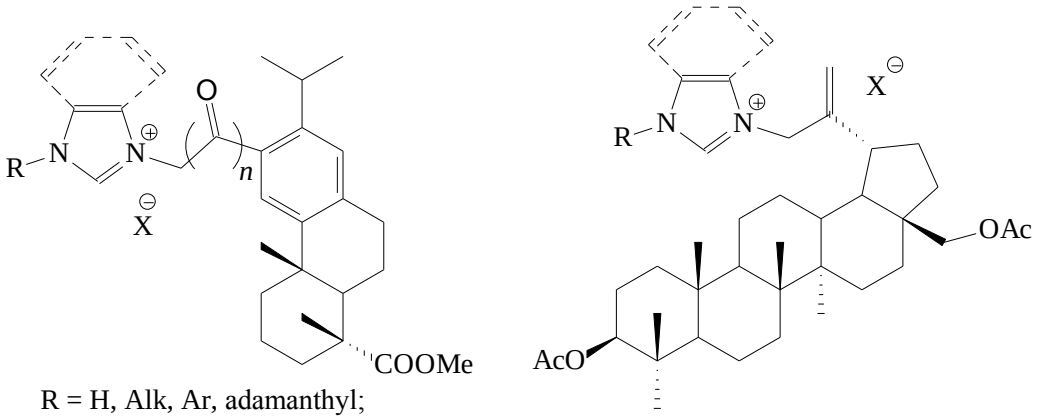
Transition-metal-catalyzed cross-coupling is one of the most fundamental and important reactions widely employed in organic chemistry. Recently N-heterocyclic carbenes (NHC) have found widespread application as ligands for Pd-mediated cross-coupling reactions in laboratory and industry. Imidazolium and benzimidazolium salts are usually used for generation of NHC. Tuning the steric and electronic factors is the most reliable way for seeking an «ideal ligand».
We have synthesized about ~ 80 new imidazolium and benzimidazolium salts based on diterpene or triterpene framework [1]. Synthesis was performed by heating the corresponding imidazole and diterpene (or triterpene) chloro- (or bromo-) derivative in MeCN under reflux. Diterpene compounds were solidified after treating by hot ethylacetate; triterpene derivatives were purified by column chromatography on silica gel.



R = H, Alk, Ar, adamanthyl;
n = 0,1; X = Cl, Br, BF_4

N-Heterocyclic carbenes generated from imidazolium salts *in situ* were successfully used as NHC ligands for Suzuki-Miyaura, Heck and Sonogashira reactions. The peculiarities of synthesis and catalysis by new ligands are the subject of our report.
We have established the profound effect of simple imidazoles (1-adamantyl-3*H*-imidazole, 4-adamantyl-3*H*-imidazole, 1-*t*-butyl-3*H*-imidazole, benzimidazole) on cross-coupling reactions. Obviously, in such cases 1-alkyl-3*H*-imidazoles are stabilizing ligands for Pd(0) species by itself, without any N-heterocyclic carbene.
This work was supported by Russian Fund of Basic Research, project No. 12-03-00276.

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P88

$Al(OTf)_3$: AN ENVIRONMENTALLY BENIGN CATALYST FOR DIRECT NUCLEOPHILIC SUBSTITUTION OF THE HYDROXY GROUP OF PROPARGYLIC ALCOHOLS

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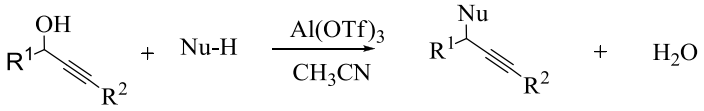
Substitution of the hydroxy group of propargylic alcohols by nucleophiles gives access to functionalized alkynes which can be readily converted into a variety of other functional groups.[1] As a result of the wide synthetic applicability associated with the alkyne functional group, the propargylic alcohol substitution reaction has played a major role in organic synthesis. In this regard, the most useful methodologies are based on transition-metal,[2] Lewis[3] and Brønsted acid[4] catalyzed/ mediated substitution reactions. Many of these and other methods[5] are, however, hampered by the cost and availability of the catalysts, excessive catalyst loading and/or limited nucleophile applicability. While a few catalyst systems ($FeCl_3$ in CH_3CN, $MoCl_5$ in DCM, and phosphomolybdic acid on silica) have been reported for propargylic alcohol substitution reactions in decent yields[6], none of these allow for C-C bond formations. In view of the synthetic importance of these propargylic synthons, the development of a general and convenient method for their synthesis is desired.

In this presentation we would like to disclose our results with regards to the $Al(OTf)_3$-catalyzed direct substitution of propargylic hydroxy groups with various aromatic and heteroatomic nucleophiles including indole to afford the corresponding products in excellent yields.



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P89

RUTHENIUM COMPLEXES OF 1,10-PHENANTHROLINE DERIVATIVES AND THEIR CATALYTIC PROPERTIES

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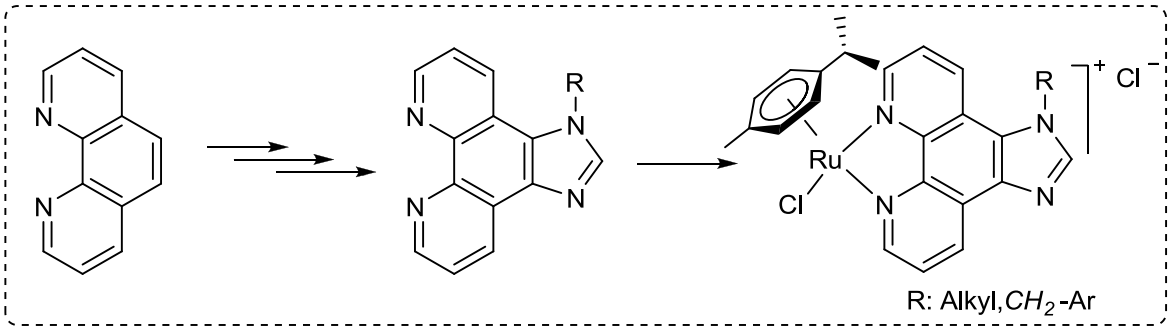
(η^6-Arene)ruthenium(II) complexes have been subject to intensive studies for many years due to their interesting coordination chemistry and catalytic properties.[1] Furthermore interest in the chemistry of half-sandwich (η^6-arene)-ruthenium(II) complexes received considerable attention owing to their interesting anti-tumor activity.[2]

The reduction of ketones using catalytic hydrogenation transfer conditions with 2-propanol as hydrogen source has been largely investigated in the last years and several ruthenium complexes have proven to be efficient catalyst precursors in transfer hydrogenation.[3]

We have studied and catalytic properties of five new complexes (Scheme 1) isolated from the reaction between [Ru(η^6-arene)Cl_2]$_2$ dimers and derivatives of 1,10 phenanthroline.



Scheme 1. Reaction steps of Ru(II) complexes

Firstly, starting from phenanthroline 1,10-phenanthroline-5,6-dione was synthesized afterwards benzimidazole derivatives, 1*H*-imidazo-[4,5-*f*][1,10]phenanthroline formed by ring closing process by means of NH_4OAc and formaldehyde, interaction with this ligand and the alkyl halide in basic medium, afforded N-substituted benzimidazole derivatives, 1-R-1*H*-imidazo[4,5*f*][1.10]phenanthroline was synthesized. Reaction of obtained ligands with [Ru(*p*-cymene)Cl_2]$_2$ gave water soluble ruthenium complexes according to the steps are shown in Scheme 1.

The new ruthenium(II) complexes have been employed as catalyst for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source and results were compared.

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P90

NOVEL DIPOLES AND DIPOLAROPHILES IN 1,3-DIPOLAR CYCLOADDITION OF AZOMETHINE YLIDES

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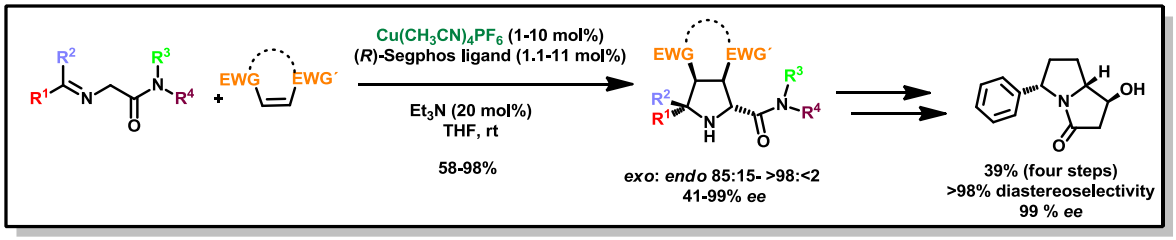
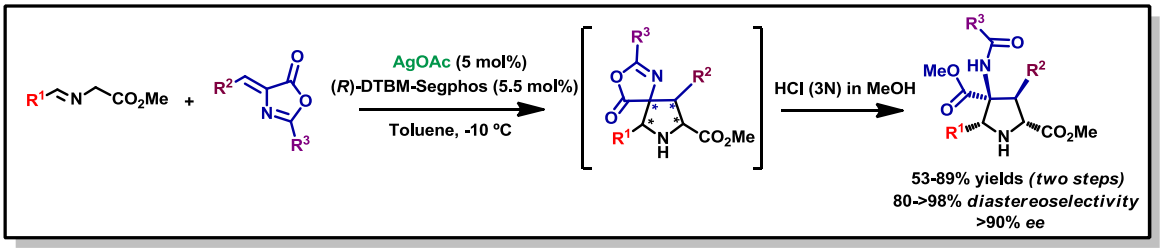
Pyrrolidine derivatives have attracted great attention in recent years owing to both their abundance in bioactive natural and unnatural products, as well as their applications as chiral ligands and organocatalysts in asymmetric synthesis. [1] Their importance has prompted the development of different approaches for their enantioselective synthesis. Among them, the 1,3-dipolar cycloaddition of azomethine ylides with activated alkenes represents a powerful and atom economy strategy. However, despite the impressive progress and the high levels of asymmetric induction achieved, the variety of suitable dipole and dipolarophile partners is rather limited till the last few years. [2] Consequently the utility of the catalytic enantioselective 1,3-dipolar cycloadditions of azomethine ylide would be significantly extended if it could be applied to other dipoles and dipolarophiles.

Very recently, we have reported that 2-amidopyrrolidines can be accessed in excellent yields, *exo*-selectivities, and enantioselectivities when using α-iminoamides as azomethine ylide precursors using Cu^{I}-Segphos complexes as catalyst system. [3] The synthetic usefulness of this methodology has been demonstrated by the preparation of substituted pyrrolizidines, a common structural motif in many natural products (Scheme 1).

Pyrrolidines with 4,4-amino acid substitution can be rapidly assembled in a modular and high selectively manner using oxazolones as new dipolarophiles. After a broad screening of reaction conditions and chiral ligands we found that the best diastereoselectivity and enantioselectivity were obtained using Ag^{I}-DTBM-Segphos as catalyst system. The treatment of the obtained α-quaternary azlactones with HCl in methanol afforded the corresponding N-protected amino acid methyl esters with high yield and selectivity (Scheme 2).



Scheme 1



Scheme 2

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P91

ENANTIOSELECTIVE SUZUKI-MIYAURA CROSS-COUPLING REACTION CATALYZED BY CHIRAL CN-PALLADACYCLES

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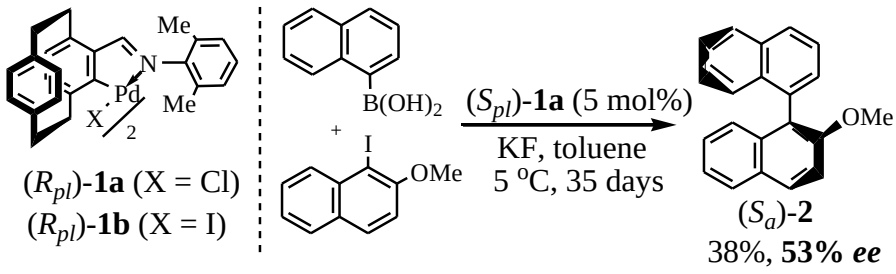
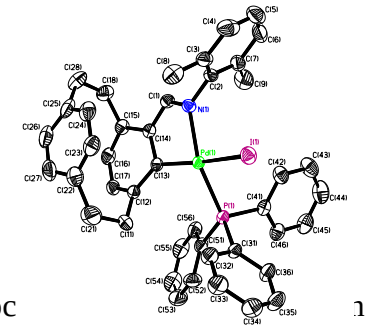
Unique activity of cyclopalladated compounds (CPC′s) in classical homogeneous catalysis has stimulated use of their chiral representatives as enantioselective catalysts.[1] However, by contrast with impressive achievements in CPC-catalyzed asymmetric Overman′s rearrangements, cross-coupling catalysis by chiral palladacycles is poorly developed, with numerous reported failures in this field. Our research is devoted to development of an enantioselective Suzuki cross-coupling reaction catalyzed by palladacycles.

First of all, we have found that only the *CN*-palladacycles offer an opportunity to realize this process under extremely mild conditions. Thus, model reaction of *para*-tolyl bromide with phenyl boronic acid may be conducted at –18 °C, if cyclopalladated *N*,*N*-dimethylaminomethylferrocene is used as catalyst.[2] Further we have performed screening a broad set of chiral CPC′s in the reaction of 2-methoxynaphthyl-1 iodide with 1-naphthaleneboronic acid affording atropoisomeric 1,1′-bi-naphthyl **2**, with main attention focused on the catalysts of planar chirality. As the result, we have achieved maximum enantioselectivity (up to 53% *ee*) using non-metallocenic cyclopalladated imine dimer (R_{pl})-**1a** as catalyst at low temperature. To note, this optical yield exceeds the known values of 26-40% *ee* obtained previously for the same reaction with pincer CPC′s.[3,4]



(R_{pl})-**1a** (X = Cl)
(R_{pl})-**1b** (X = I)

(S_a)-**2**
38%, **53% *ee***



The optimal optical yield was obtained in toluene in air, the reaction oc 1 period and any indications on the palladium black formation. Cyclopalladated catalyst was recovered in nearly quantitative yield (96%) in the form of its μ-iodide analogue (R_{pl})-**1b**. The structure of the latter was unambiguously confirmed by spectral and X-ray diffraction study of its mononuclear PPh_3 derivative (R_{pl})-**1c**. Results of several mechanistic experiments may be considered as an indirect evidence against the operation of the classical catalytic cycle, based on the Pd^{II}/Pd^{0} redox processes; the intact state of the palladacycle seems to be a rather probable.

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P92

DRY (CARBON DIOXIDE) REFORMING OF METHANE ON SYSTEMS CONTAINING NANOPARTICLES OF Ni, Fe AND MNO_2

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The reforming of natural gas with CO_2 (the DRM process) is a very attractive reaction in terms of both the academic study of syngas production and industrial utilization.
The dry (carbon dioxide) reforming of methane (DRM) on catalytic systems containing nanoparticles of Ni matrixing in Al_2O_3 as well as Fe and MnO_2 molded onto a ZrO_2 supporter is studied. Experiments were conducted in a flow catalytic apparatus at atmospheric pressure. The catalytic activity was determined by applying a mixture of [CH_4: CO_2] = 1:1. Analysis of the products was carried out by chromatography on a Kristall 2000M instrument. The rate of formation of reaction products W (mol/h*$g_{.af}$) was measured after reaching steady state and calculated per unit mass of metal (active) phase of the catalyst.
DRM on a system of nanoparticles of nickel at a temperature of 1123 has allowed to reach out to 87% of theoretical. However, catalyst activity decreased over time and from experiment to experiment, due to partial carbonization and / or to the formation of nickel aluminate.
Catalytic systems containing iron nanoparticles have shown significant activity in the carbon dioxide conversion of methane at temperatures above 900 K. At 1023 K the conversion of methane was about 21%. The introduction of an equivalent amount of manganese oxide, greatly improving the conversion of CH_4 at 1173 K it was 67%.
Analysis of CO_2 in the gas phase showed that the conversion of the latter was slightly lower than that of methane in all the systems studied. It was observed increase in the concentration of carbon dioxide in the gas phase in the temperature range 823-923K on Fe-MnO_2/ZrO_2. This may be due to the occurrence of adverse Boudouard reaction: $2CO = C + CO_2$. One can not exclude the interaction of chemisorbed CO with atomic oxygen surface (MnO_2), accompanied by desorption of carbon dioxide.
The results obtained on nickel- and iron-containing systems, in general, consistent with the mechanism of UKM discussed in [4]. There's supposed to successive dissociation of CH_4 on the surface of the particles with the formation of CH_X and C and their interaction with the adsorbed atom O. The lack of water in the reaction products indicates that the stage of formation of OH-Z and interaction with the N-Z does not occur, and when the dissociative adsorption of methane on a few metal atoms form the activated complex formed by C-[x (H-nZ)]. In samples with MnO_2, the CO reaction product is formed, probably and according to [1,4], resulting in reductive decomposition of manganese carbonate in its interaction with carbon (or carbide or CH_X) or H_2.
Catalytic processing of data in the coordinates of the Arrhenius equation to calculate the activation energy has allowed the conversion of methane and CO formation, which amounted to 35-45 kJ / mol and 49-88 kJ / mol, which proved to be somewhat lower than data obtained in applied and bulk catalysts [1-3] , which may indicate the influence of the structure of the active phase and an increase in catalytic activity with increasing dispersion.

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P93

COBALT-CATALYZED REDUCTIVE ALKYLATION OF ARYL HALIDES OR ALLYLIC ACETATES

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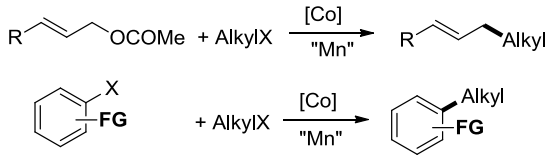
Transition metal catalyzed C-C bond formation reactions have profoundly changed the methodologies in organic synthesis. Palladium remains the metal of choice for such transformations; nevertheless its cost has motivated the search for alternatives both in academic and industrial research groups. Several other metals such as nickel, iron, copper, and cobalt have been proposed with success in this research area. In our research, we have privileged the use of cobalt which is eco-compatible and cheap. $CoBr_2$ was shown to be very efficient even sometimes superior to other metals for carbon-carbon bond formation allowing the synthesis of functionalized molecules in mild conditions. [1]
Recently we reported the first Cobalt-catalyzed direct alkylation of various aryl halides [2] or allylic acetates.[3] These methods are very straightforward, and environmentally friendly. It is efficient for the coupling of a large variety of functionalized alkyl halides (primary, secondary, and tertiary) with substituted aryl halides or allylic acetates. Good to excellent yields are obtained in presence of various functionalities.



In this communication, the scope, the regioselectivity of these reactions together with a possible mechanism based on experimental observation will be presented.

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P94

MODULAR SYNTHESIS OF HELICAL CATIONIC DYES

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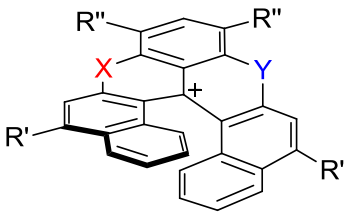
Fluorescent dyes are essential tools in biological studies.[1] Quite a few interesting organic frameworks possess this important characteristic among which are cationic helicenes. These derivatives are intrinsically polar due to their charge but their lipophilicity (and biological properties) can be addressed through the nature of the attached side chain(s).

X, Y = O
X, Y = NR
X = O, Y = NR



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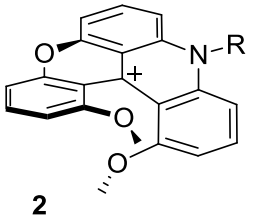

2

Herein, we report on the synthesis of novel cationic [6] helicenes and their modular post-synthesis functionalization. Compound **2**, from the same family of extremely stable carbocations,[2] is also a new type of helicene. Compounds of type **1** and **2** are readily prepared and are highly fluorescent.

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P95

NEW LIGANDS BASED ON AMINO DERIVATIVES OF BILE ACIDS

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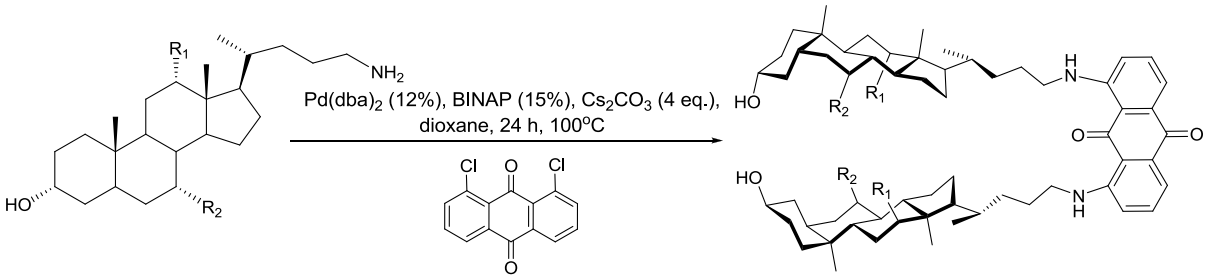
Bile acids are known to possess unique facial amphiphilic properties. Therefore it is possible to construct different molecular receptor and ligands based on bile acids derivatives [1]. Pincer-like bis-amino steroidal ligands are under special interest. Combination of hydrophilic and hydrophobic surfaces makes these compounds attractive for complex formation both with inorganic and organic molecules (including DNA) [2].

Previously, we developed successful approach for obtaining bile acids based macrocycles in palladium-catalyzed reaction [3, 4]. But the necessity of including group with $C(sp^2)$-Hal bound into bile acid under investigation is a drawback of this method.

The technique of direct copper- and palladium-catalyzed arylation of bile acids amino derivatives was developed in this work. We have shown, that 3- and 24-amino compounds can be successfully transformed into corresponding pincer-like steroidal ligands by copper- and palladium-catalyzed reactions.



1: R_1 = H, R_2 = H **88%**
2: R_1 = H, R_2 = OH **74%**
3: R_1 = OH, R_2 = OH **34%**

Complex formation of ligands **1**, **2** and **3** with fluorine and copper ions was investigated via ^{1}H-NMR (F^-) and spectrophotometric (Cu^{2+}) titration. The high affinity of steroidal ligand to F^- and Cu^{2+} was demonstrated.

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P96

CATALYTIC ADDITION AND METATHESIS POLYMERIZATION OF SILYL-SUBSTITUTED NORBORNENES AND TRICYCLONONENES AS INSTRUMENTS OF POLYMER DESIGN

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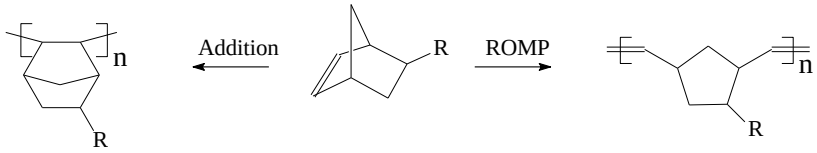
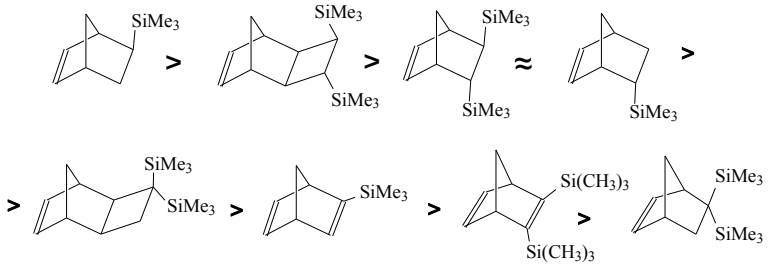
Silicon-containing norbornenes and tricyclo[4.2.1.$0^{2,5}$]nonenes are suitable substrates for organic and polymer synthesis. The presences of double bond in the strain norbornene fragment and active silyl-groups as well as the capability to participate in metathesis and addition polymerization provide synthetic opportunities for design of polymers with desired properties. We developed catalytic polymerization of new Si-substituted norbornenes, norbornadienes and tricyclononenes (the norbornene-type monomers – SiNB's) as a method of synthesis of polymers with high gas permeability [1].



Metathesis polymerization (ROMP) of SiNB's was realized with help of different W- and Ru-catalysts. Microstructure control (ratio of cis/trans double bond) of polynorbornenes was achieved by the use of $RuCl_3$, WCl_6/1,1,3,3-tetramethyldisilacyclobutane, $Cl_2(PCy_3)_2Ru$=CHPh catalysts. The molecular weight regulation was provided on Grubbs-catalysts of 1-st and 2-nd generation. It was determined the substantial influence of number, regio and stereo position of bulky Me_3Si-substituents on SiNB's activity in ROMP. The activity of SiNB's in ROMP on Grubbs-catalyst $Cl_2(PCy_3)_2Ru$=CHPh reduced in the range:



Addition polymerization (AP) of SiNB's was carried out in the presence of Ni(II) or Pd(II) salts (naphtenate, acetate) and MAO or $B(C_6F_5)_3$ as activators. Norbornenes and norbornadienes with two Me_3Si- substituents turned out to be inactive in the studied conditions. At the same time AP of disubstituted tricyclononenes proceeded with rather good yields of highly molecular weight polymers. In the presentation the impact of number and position of Me_3Si-substituents on SiNB's activity in catalytic polymerization is analyzed on the basis of quantum-chemical calculations of electronic, energy and structural characteristics of the studied monomers. Obtained from the calculations the reactivity indexes of the monomers correlated well with the range of their activity in the polymerization processes. The synthesized polymers demonstrated high gas-transport properties, especially addition polynorbornenes. They are the promising materials for membrane gas separation – environmentally friendly process.

This work was partly supported by Russian Foundation of Basic Research (Grant 10-08-01303-a).

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P97

GLYCO-ENOPHOS – CARBOHYDRATE-DERIVED LIGANDS FOR ASYMMETRIC CATALYSIS

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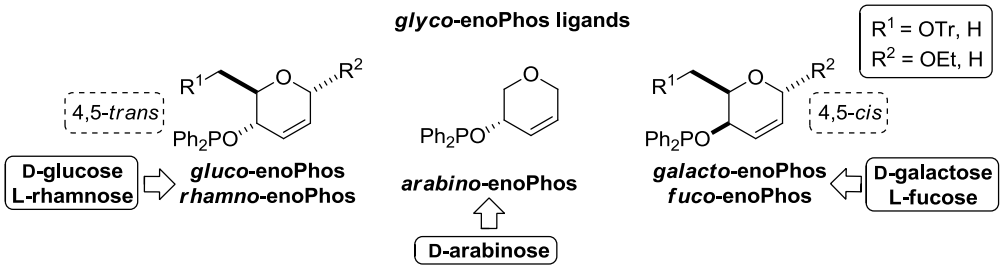
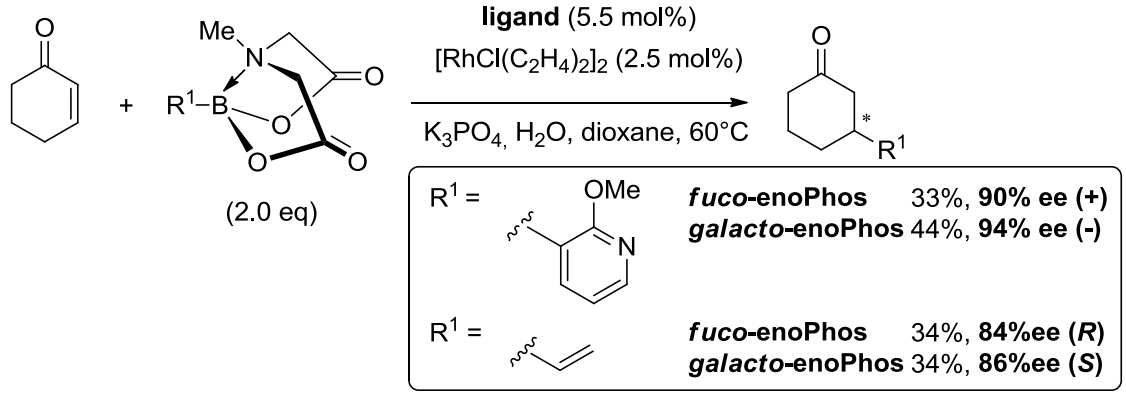
In the last decades the design of novel ligand structures for asymmetric catalysis has become an important field in organic chemistry. Hybrid ligands containing olefinic and phosphorous-based donor sites have emerged as powerful stereodirecting tools in asymmetric transformations. [1] With a series of olefin phosphinite hybrid ligands derived from inexpensive and enantiopure monosaccharides, [2] we have developed efficient pairs of *pseudo* enantiomeric ligands, which act give excellent stereoselectivity in asymmetric rhodium-catalysed 1,4-additions. [3]



Currently we are testing our new ligands in the rhodium-catalysed 1,4-addition of more challenging nucleophiles with MIDA boronates [4] to cyclohexenone. As a first promising result we have obtained the addition products of 2-methoxypyridyl and vinyl MIDA boronates in high enantioselectivity.



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P98

CALCIUM FLUOR- AND HYDROXY-APATITES MODIFIED OR NOT AS CATALYSTS FOR C-C BOND FORMATION

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Apatites, mostly fluoro- (FAP) and hydroxyl-apatites (HAP), are of considerable interest in numerous research areas. Several authors have demonstrated recently the usefulness of apatites modified by transition metal ions as heterogeneous catalysts but the role of apatite is not clear.
We have shown previously that Ru^{3+} containing HAP and FAP, which are known as catalysts for alcohols oxidation, are multi-phase materials. The mechanism leading to such materials was elucidated as a dissolution re-precipitation process. In this case the catalytic entity is a ruthenium rich phase, the apatite itself does not catalyze the oxidation reaction. In the case of lanthanum modified apatites which are potential catalysts for the C-C bond formation in the Michael reaction, the situation remained unclear about the active species acting as catalyst. Moreover, as for Ru-modified apatite, we have found that the La(III) ions are not introduced in the apatite structure but exist as an independent La(III) phosphate phase. In these conditions, we decided to investigate the catalytic properties of different apatites and the phases formed during the reaction of lanthanum (III) salt on these apatites. It was shown that non-modified HAPs with various Ca/P ratio and specific surface areas itself are efficient catalysts for the Michael reaction in smooth conditions (room temperature without solvent). Mechanism studies using deuteroxyapatites, led us to conclude that hydroxyl groups (OH) located on the surface of the apatites are responsible of their catalytic activity. The systematic study of C-C bond formation by Glaser, Suzuki, and Heck reactions using modified or not apatites is in progress.

P99

CHLORO(1,5-CYCLOOCTADIENE)[1,3-DIISOPROPYL(5,6-DIMETHYL)BENZIMIDAZOL-2-YLIDENE]IRIDIUM(I) AS A HIGHLY EFFICIENT CATALYST FOR TRANSFER HYDROGENATION OF CARBONYL DERIVATIVES

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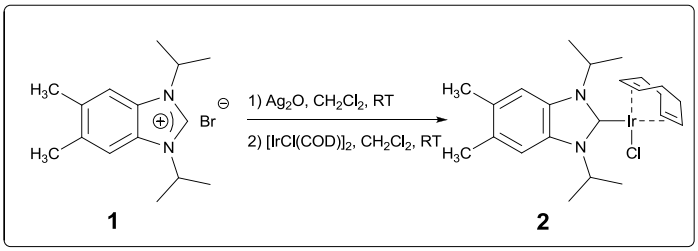
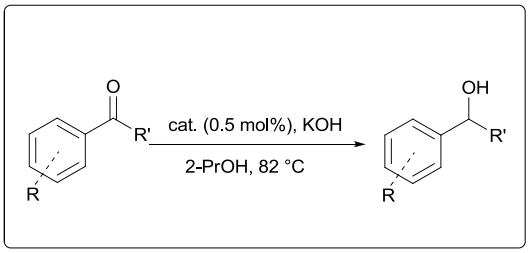
The transition metal complexes of N-heterocyclic carbenes (NHCs) have been the focus of intense research in organometallic chemistry and homogeneous catalysis.[1] The electronic and steric parameters of NHC complexes can be modified easily, and they have greater stability toward air, moisture and heating when compared with phosphine analogues.[2] Thus, iridium, rhodium and ruthenium complexes bearing NHCs have been employed as catalysts for number of catalytic reduction reactions such as, hydrogenation, transfer hydrogenation (TH), and hydrosilylation.3 TH reactions require typically a hydrogen donor such as 2-propanol together with a strong base and transition metal catalyst, and is preferred for large-scale industrial use in the hope of developing a greener process by reducing waste production and energy use and lowering toxicity.4 It has been found that, NHC complexes of iridiumI show superior activities when compared with their rhodiumI analogues.[5]

In this study, iridium^{I} complex (**2**) derived from corresponding 1,3-diisopropyl-(5,6-dimethyl)benzimidazolium bromide salt (**1**) was synthesized (Scheme 1) and applied for catalytic TH reaction of various carbonyl compounds (Scheme 2). As a result, *i*Pr group attached to 5,6-dimethylbenzimidazole ligand found to be very active catalyst for NHC-Ir catalyzed TH reaction with a variety of substrate scale and up to 1200 h^{-1} TOF was achieved.



Scheme 1. Synthesis of NHC-Ir complexes



Scheme 2. NHC-Ir catalyzed TH reaction

Table 1. TH of carbonyl compounds catalyzed by **2**.

Entry	Substrate	Time (min)	Conversion (%)	TOF (h^{-1})
1	Acetophenone	10	100	1200
2	2'-Chloroacetophenone	15	97	776
3	3,4-Dimethylacetophenone	30	93	372
4	4-Methoxyacetophenone	30	91	364
5	Benzaldehyde	30	100	400
6	2,4,6-Trimethylbenzaldehyde	30	100	400
7	2-Methoxybenzaldehyde	60	87	174
8	3,4,5-Trimethoxybenzaldehyde	120	56	56

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P100

SYNTHESIS OF BIMETALLIC RHODIUM(I) COMPLEXES CONTAINING TRIDENTATE TRIAMINE LIGANDS: AS CATALYSTS FOR TRANSFER HYDROGENATION OF KETONES

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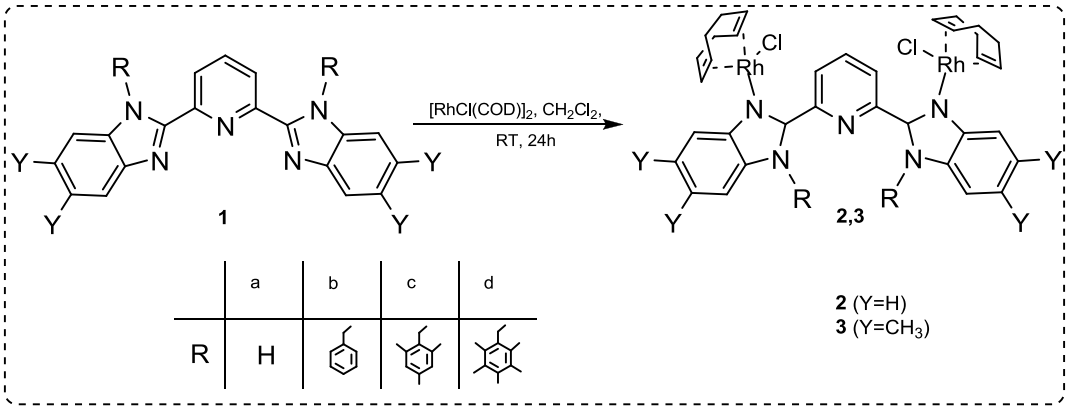
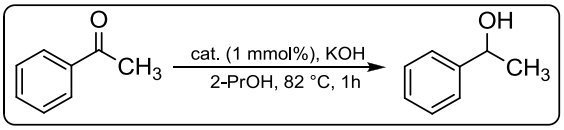
It is well known that imidazole-containing molecules can easily coordinate to metal ions as well as act as hydrogen-bond acceptors or donors in coordination chemistry. In addition, benzimidazole-based organic ligands and their metal complexes continue to attract interest as components in homogeneous catalysis[1]. These applications have attracted many experimentalists and theorist to investigate the spectroscopic and structural properties of benzimidazole[2–4] and some of its derivatives. Contrary to the rich literature reporting rhodium(I) complexes with π-acid ligands, the complexation of Rh(I) with terdentate aromatic N-donor ligands has poorly been explored[5].
In this study, we synthesized bimetallic Rhodium(I) complexes [{Rh(COD)Cl}$_2$L] (Scheme1) derived from tridentate triamine (´N^N^N´) ligands and characterized by one- and twodimensional NMR spectroscopies, and single-crystal X-ray diffraction. These complexes were used as catalytys in transfer hydrogenation reaction of ketones (Table 1) .



Scheme 1. Synthesis of [{Rh(COD)Cl}$_2$L] complexes

Table1: [{Rh(COD)Cl}$_2$L] catalysed TH reaction



Entry	Cat.	Conv. (%)	Entry	Cat.	Conv. (%)
1	**2a**	88	5	**3a**	90
2	**2b**	82	6	**3b**	84
3	**2c**	86	7	**3c**	89
4	**2d**	94	8	**3d**	98

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P101

DECOMPOSITION OF ARENEDIAZONIUM SALTS IN THE PRESENCE OF Fe(0)-NANOCATALYST UNDER MICROWAVE IRRADIATION

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Arenediazonium salts ArN_2+–OTs (ADT) are one of the most important building blocks in the classical organic synthesis and perspective reagents for C-C bond formation [1]. Diazonium salts have high reactivity in various processes and one of modern trend of diazonium salt's chemistry is c-c coupling reactions, which usually carry out in the presence of palladium catalysts [2], meanwhile the important shortage of this method is high cost of catalysts. Hypothetically compounds of other transition metals are able to substitute palladium, for instance, iron compounds [3]. In literature there is no data about diazonium salts decomposition in the presence of Fe-catalyst.
We examined reactivity of ADT over Fe(III) compounds and demonstrated that presence of Fe(III) changes quantitative and qualitative composition of decomposition products depending on solvents, temperature, type of catalyst and its percentage. Especially we should pay attention to the fact that iron (III) compound show high reactivity in olefins arylation reactions, this was shown by the example of styrene, but this compounds have not sufficient selectivity. As is generally known, in Pd-catalyzed reactions with diazonium salts Pd (0) initiates further reactions, which lead to formation of final product. Based on this fact in our reactions we used iron nanoparticles as source of Fe(0), which we obtained according to the method [4]. We showed that arenediazonium dodecyl sulfate is able to react with styrene in water under microwave irradiation at 85°C over 5 weights % of catalyst, we obtained stilbene with satisfactory yield. This is the first example of reaction between diazonium salts and styrene in the presence of Fe(0) catalyst. Reaction is carried out very rapidly (about 20 minutes) and conform to green chemistry condition.
Consequently, diazonium salts combined with iron nanoparticles are promising reagents for further research of their decomposition and arylation reaction. We can talk about assumption that this catalyst can become low-cost alternative to palladium compounds.

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P102

FROM ESTERS TO ALCOHOLS AND BACK

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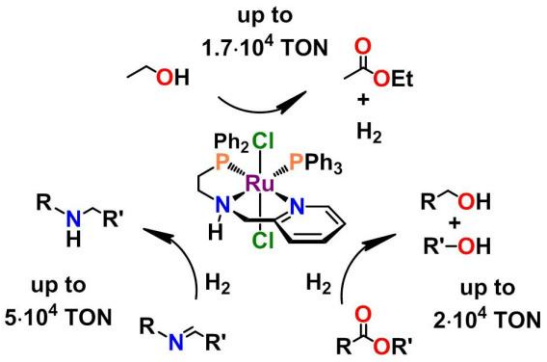
Reduction of esters is a common reaction in organic chemistry, however, the classical methods using main-group hydrides are hazardous and they are accompanied by excessive formation of chemical waste. New pincer-type ruthenium and osmium catalysts from our laboratory: MHCl(CO)(NNHP), $[MH(CO)(NNP)]_2$, and $RuCl_2(PR_3)$(NNHP) facilitate a green ester reduction process affording alcohols under hydrogen gas, under basic or neutral conditions, with practically no by-product waste. The same catalysts are efficient for hydrogenation of compounds with polar double bonds (e.g. imines) and for acceptorless dehydrogenative coupling (ADC) of primary alcohols, $C_nH_{2n+1}OH$ (n > 1), affording symmetrical esters. $RuCl_2(PPh_3)$(NNHP) is a particualrly outstanding air-stable ruthenium catalyst that has unprecedented efficiency for ethanol dehydrogenation to ethyl acetate under reflux (TON up to 17,000) and for hydrogenation of esters and imines at 40 °C while using as low as 50 ppm [Ru].



P103

SYNTHESIS OF D-GLUCOSOAMINE DERIVATIVES AND THEIR APPLICATION AS ORGANOCATALYSTS IN THE ASYMMETRIC MICHAEL REACTION

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Currently we are the witnesses of chemists' enormous interest in enantioselective and enantiospecific organic reactions. In order to obtain enantiomerically pure compounds we applied asymmetric catalysis methodology [1]. In spite of many years' intensive experiments in this field, we do not have a simple and universal procedure for making a desired catalyst of optimal properties. However, we do know that a good precursor for such catalyst should be characterized by a low price and high availability, and as a result, in our research, we used D-glucosoamine hydrochloride. Recycling D-glucosoamine is very important from ecological point of view as it is a major product of chitin depolymerization which is a renewable resource so-called biomass. So we concentrated on creating organocatalysts from sugars, hoping that it will be a promising catalyst for enantioselective Michael reaction. In order to achieve that, we synthesized a family of sugar compounds containing the thiourea functionality. The obtained compounds have been used, with very good results, as organocatalysts in the asymmetric Michael reaction.

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"Carbohydrates as renewable raw materials in the synthesis of products with high added value" no. POIG.01.01.02-14-102/09-02

P104

PRIMARY AMINO ACID DERIVED POLYMER SUPPORTED ORGANOCATALYSTS

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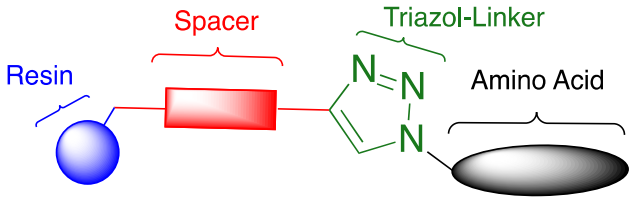
Towards the objective of more sustainable chemistry, the immobilization of organocatalysts represents an attractive technique, which allows simple recovery and reuse of the catalysts leading to a substantial reduction of the effective catalyst loading accompanied by simplified work-up procedures. Because of their stability and recyclability, solid-supported organocatalysts are particularly suitable for continuous flow systems[1], which allow large-scale synthesis of important building blocks for pharmaceuticals and natural products. While proline has been employed for years as highly selective organocatalyst, examples of reactions catalyzed by amino acids bearing primary amino groups have only recently been reported.[2] Until now, however, no immobilized versions of this compound class have been tested in enantioselective catalysis.



In this work, anchoring strategies for the preparation of a series of novel polystyrene (PS) supported amino acid derivatives have been developed. Copper-mediated Huisgen cycloaddition (click chemistry) is used as supporting strategy[3] to develop solid supported catalysts, which work in water and in organic solvents. The evaluation of these functionalized resins in different organocatalytic processes (aldol-type, Mannich-type, Michael-type etc.) depending on the nature of the supported amino acid is currently in progress. Furthermore, the suitability of these catalysts for single pass-continuous flow processes will be explored.

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P105

CATALYTIC ASYMMETRIC DIRECT MANNICH REACTION OF GLYCINATE SCHIFF BASES WITH IN SITU GENERATED ALIPHATIC ENOLIZABLE IMINES

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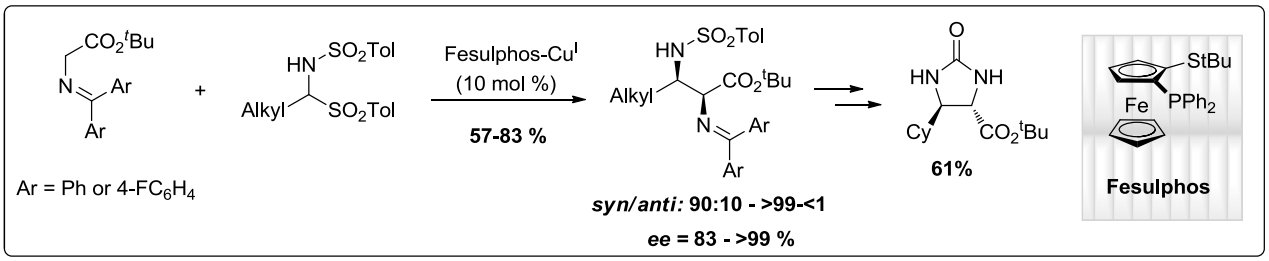
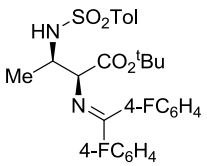
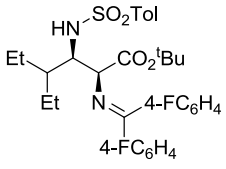
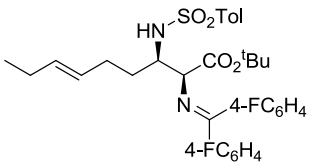
Optically active *α,β*-diamino acids are important structural motifs found in peptide-based drugs and other bioactive compounds, and also serve as versatile synthetic building blocks. [(1)] The direct Mannich reaction between glycine ester Schiff bases and imines is arguably the most attractive and atom-efficient catalytic asymmetric route to non-proteinogenic *α,β*-diamino acids.[(2)] Despite very efficient organometallic-based and metal-free procedures have been devised showing high levels of absolute and relative stereocontrol, there are still limitations to be solved. For example, aliphatic enolizable imines are challenging substrates as they tend to undergo self-condensation. Therefore, only isolated examples of the Mannich reaction of glycinate derivatives utilizing aliphatic imines as substrates are reported.[(3)] Furthermore, achieving high diastereo- and enantiocontrol remain unresolved for this type of substrates.

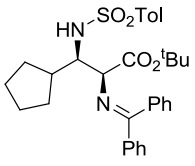
Very recently, our research group has reported the Cu^{I}-Fesulphos-catalyzed asymmetric direct Mannich reaction of glycinate derivatives with aromatic aldimines, leading to orthogonally protected *α,β*-diamino acid derivatives with either *anti*- or *syn*- configuration in a highly diastereo- and enantiocontrolled manner.[(4)] However, enolizable aliphatic aldimines proved to be unsuitable substrates under these conditions. Herein we describe a practical solution to this limitation by using *N*-Ts protected α-amidoalkyl-*p*-tolylsulfones as stable equivalents of *N*-Ts aliphatic imines. The corresponding *β*-alkyl-*α,β*-diamino acid derivatives are isolated with good yields and excellent diastereo- and enantiocontrol. The preparation of a known imidazolidinone via sequential double amino deprotection served to confirm both the relative and absolute configuration.




74% , *ee* = > 99%
***syn/anti* = >99:<1**


70% , *ee* = 97%
***syn/anti* = >99:<1**


78% , *ee* = > 99%
***syn/anti* = 90:10**


83% , *ee* = > 99%
***syn/anti* = >99:<1**

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P106

EXPANDING THE SCOPE OF MINOR ENANTIOMER RECYCLING

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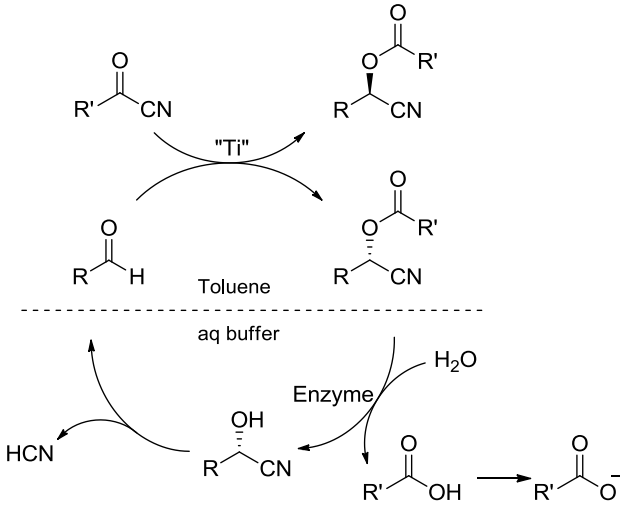
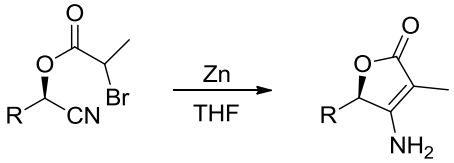
We have recently developed a recycling procedure where the undesired product enantiomer is transformed back to the prochiral starting material and thereby given another chance in the catalytic reaction (Scheme 1). This method is used for the preparation of *O*-acylated cyanohydrins with excellent ee:s and yields. [1] A chiral titanium salen catalyst is used for the forward reaction while the minor enantiomer is hydrolyzed selectively by an enzyme to give the free cyanohydrin; in the two-phase system used for the reaction the hydrolysis product spontaneously eliminates HCN to give back the starting aldehyde. The driving force for this unidirectional cycle is the continuous addition of the acyl cyanide and the subsequent formation of carboxylate ions.



Scheme 1 – Minor enantiomer recycling of *O*-acylated cyanohydrins.

Current work is concentrated on using bromo-functionalised aldehydes and acyl cyanides in the minor enantiomer recycling procedure. Synthesis of *O*-acylated ω-bromocyanohydrins was shown to be useful in yielding highly enantioenriched 2-cyanotetrahydrofuran and 2-cyanotetrahydropyran. [2] Use of a racemic α-bromo-substituted acyl cyanide provides the product as a mixture of two diastereomers with high selectivity and in high yield. The resulting *O*-acylated cyanohydrins proved to be useful in the synthesis of aminofuranones using an intramolecular Blaise reaction (Scheme 2).



Scheme 2 – **Intramolecular Blaise reaction.**

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REACTIONS OF 1,3-DIENE COMPLEX OF Ru(0) WITH CONJUGATED CARBONYLS, 1,3-DIENES OR 1,2-DIENES: STRAIGHTFORWARD ACCESS TO UNSATURATED CARBONYL COMPOUNDS BY A Ru(0) CATALYST

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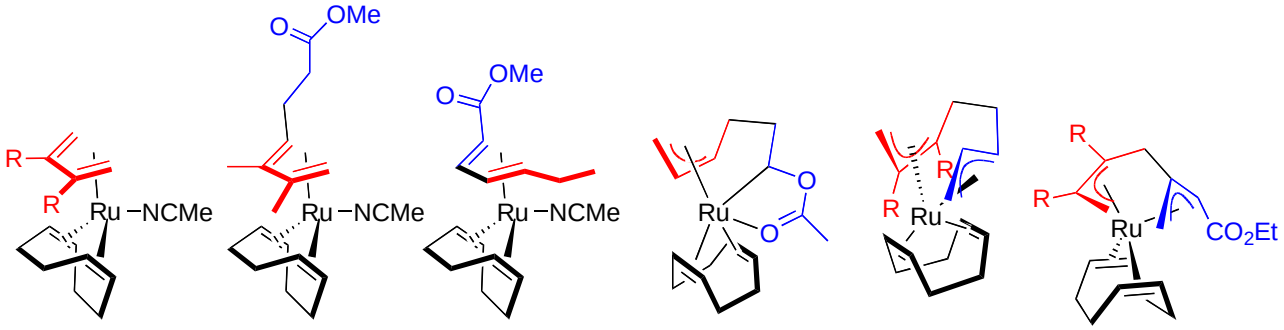
We have studied selective C–C bond forming reactions by 1,3-diene complexes of Ru(0) through an oxidative coupling mechanism.[1,2] In this contribution, we disclose the stoichiometric and catalytic reactions of 1,3-diene with substituted alkenes, 1,3-dienes, or 1,2-dienes at Ru(0). Reactions of complexes **1a** and **1b** with methyl acrylate produced new 1,3-diene complexes of Ru(0) **2aa** and **2ba** in 95% and 97% yields, respectively. Since **1b** gives an oxidative coupling product η^1:η^3:κ^1*O*-metallacycle **2bb** by the reaction with vinyl acetate, **2aa** and **2ba** are probably produced by oxidative coupling reaction followed by internal proton migration. Similar oxidative coupling reactions occurred to give **2ac** and **2bc** by the reactions of **1a** and **1b** with 1,3-butadiene, whose stereochemistry indicates the coordinated *cisoid*-1,3-diene to react with *transoid*-1,3-diene. With 1,2-dienes such as ethyl 2,3-butadienoate, *rac-prone,supine-anti*-(2*R*,5*R*)-**2ad** and -**2bd** were exclusively obtained as single diastereomers. This stereochemistry indicates prior coordination of 1,2-diene, wherein the Ru(0) distinguishes the regio and prostereogenic face in orthogonal π–planes in 1,2-diene before the nucleophilic attack of the 1,3-diene on the coordinated 1,2-diene.



1a (R = Me)
1b (R = H)

2aa

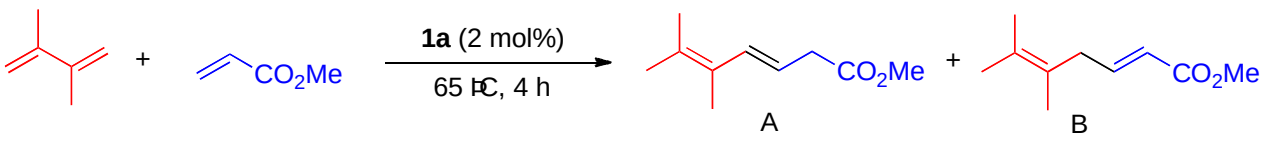
2ba

2bb

2ac (R = Me)
2bc (R = H)

2ad (R = Me)
2bd (R = H)

Among these oxidative coupling products, the Ru(0) complexes catalyzed cross dimerization of 1,3-dienes with conjugated carbonyl compounds. As a typical example, **1a** (2 mol%) catalyzed cross dimerization of 2,3-dimethyl-1,3-butadiene with methyl acrylate at 65 ˚C in 97% yield. A series of catalytic cross dimerizations of 1,3-dienes and detailed mechanism involving isotopic labeling experiments will be discussed.



A B

97% (A/B = 73/27)

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P108

RHODIUM-CATALYZED CROSS DEHYDROGENATIVE COUPLING (CDC) OF HETEROCYCLES

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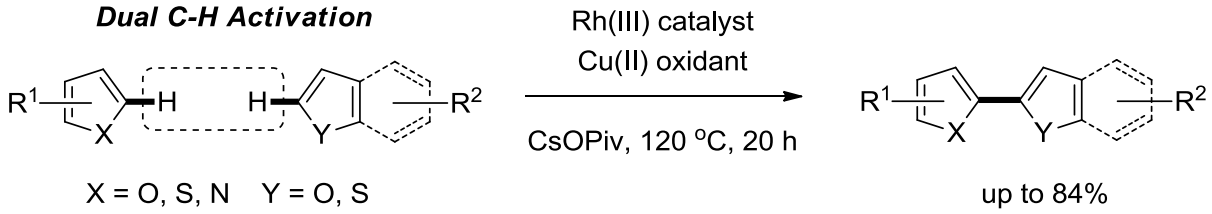
The selective construction of a carbon-carbon bond between two organic fragments is one of the most fundamental processes in organic chemistry. In recent years, significant research attention has been devoted to the development of transition metal-catalyzed cross-coupling reactions between unfunctionalized substrates where both coupling partners derive via C-H activation (CDC).[1] These processes benefit from higher atom-economy and cost-efficiency compared to conventional coupling methodologies between pre-functionalized substrates, whilst exhibiting superior environmental profiles. The successful development of CDC reactions, however, raises the dual challenges of encouraging the reactivity of stable C-H bonds and controlling selectivity for the desired cross-coupled product over homo-dimers of each coupling partner.
As part of our study into transition metal-catalyzed CDC reactions of aromatic compounds,[2] our attention was drawn to the selective cross-coupling of heterocycles to afford bis(heteroarenes). These compounds are of interest to the pharmaceutical and materials industries and are often difficult to access via conventional coupling methodologies. The combination of a rhodium(III) catalyst and a copper(II) oxidant led to the highest yields of the coupled products whilst very high levels of regioselectivity were observed for a range of furan, thiophene and pyrrole substrates.[3] Moreover, high selectivity for the cross-coupled products over the homo-dimers was generally observed. Details of this investigation and related studies from our group will be presented.



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[3] For reviews of Rh(III)-catalyzed C-H activation, see: a) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* 2012, DOI: 10.1039/c2cs15281a; b) T. Satoh, M. Miura, *Chem. Eur. J.* 2010, *16*, 11212-11222.

P109

RUTHENIUM CATALYZED SYNTHESIS OF LACTAMS AND PYRROLES FROM MULTI-COMPONENT REACTIONS OF UNSATURATED ALDEHYDES, AMINES, CO AND ALKENES

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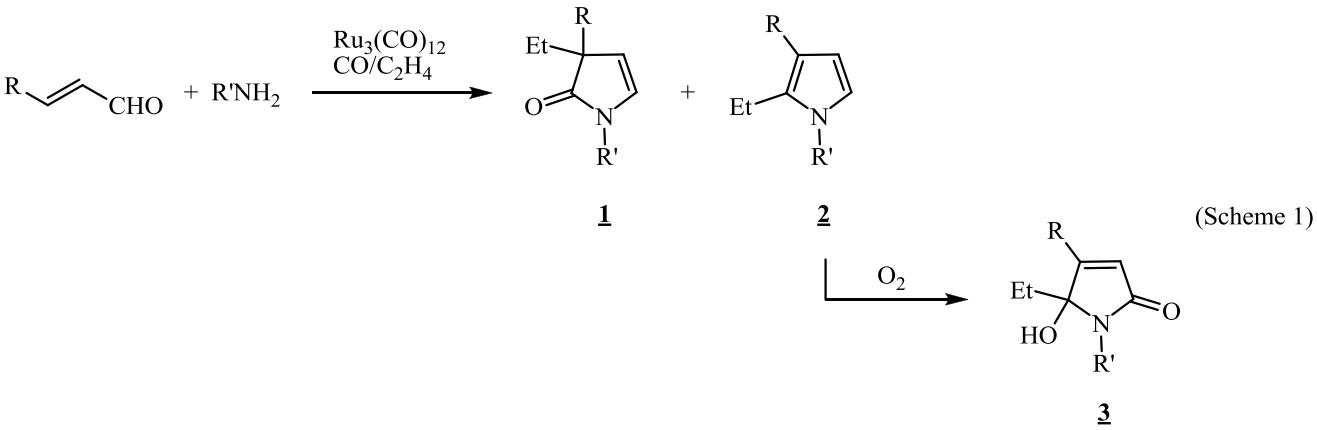
The reaction of α,β-unsaturated imines with primary amines, CO and ethylene (or terminal alkenes in general) in the presence of $Ru_3(CO)_{12}$ yields mixtures of the corresponding chiral γ-lactam, **1**, and a 2,3-disubstituted pyrrole derivative, **2** (Scheme 1).[1,2] The chemoselectivity of this reaction is highly depending on the polarity of the solvent with saturated hydrocarbons leading to the isolation of the lactam in almost quantitative yields whereas the use of methanol gives rise to the formation of the pyrrole in yields of up to 75%.[3] Pyrrole derivatives **2** may easily be oxidized to produce 5-hydroxy-pyrrol-2-one derivatives, **3**.[4]

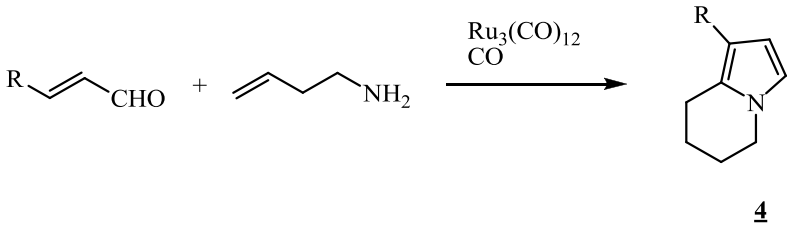
According to the results of DFT calculations on the mechanism of the catalytic formation of compounds **1** the catalytically active species is a mononuclear electronically and coordinatively unsaturated $Ru(CO)_4$ fragment. Upon coordination of the intermediate imine, that is formed by the



(Scheme 1)

condensation of the aldehyde and the amine, a metal assisted C-H activation in β-position with respect to the C-N double bond is triggered. The rate determining step then is the insertion of CO into the ruthenium carbon bond resulting from this C-H activation reaction.[5]

If the alkenyl and the amine functions are included in the same substrate molecule only the formation of tetrahydroindolizines, **4**, which correspond to the pyrrole derivatives **2** shown in Scheme 1, are formed in good yields (Scheme 2).[6]



(Scheme 2)

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[6] T. Biletzki, W. Imhof, in preparation.

P110

ENANTIODIVERGENT INTRAMOLECULAR ALDOL REACTION DEPENDING ON A CONFORMATIONAL CHANGE OF CHIRAL TRIAMINE

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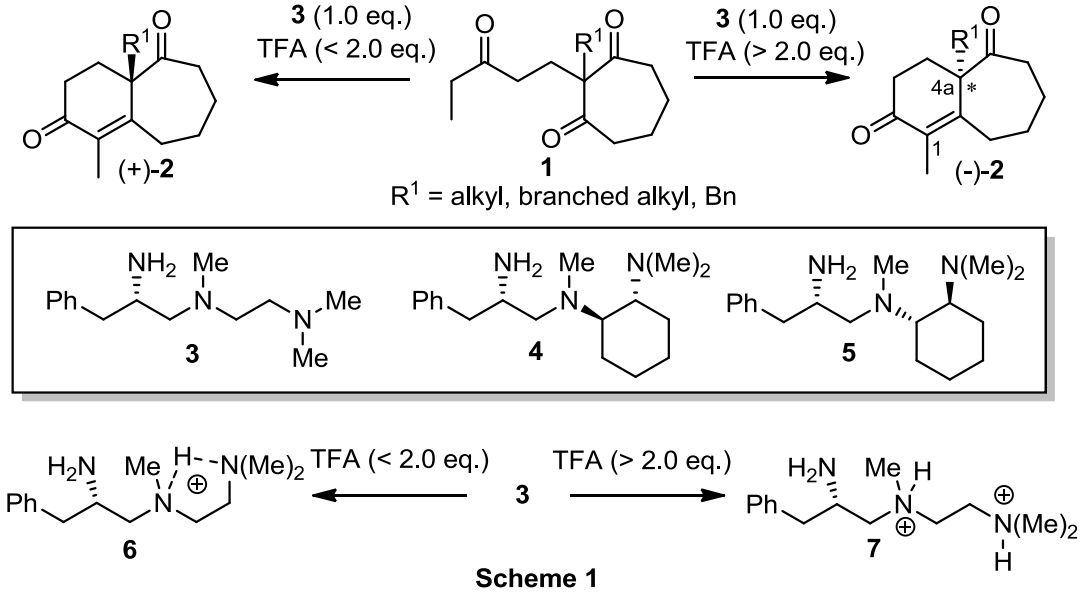
We have studied the intramolecular aldol reaction of trione (**1**), mediated by versatile amino acids, to construct a new chiral Wieland-Miescher ketone analog (**2**) bearing a 7-membered ring.[1] However, most of amino acids decomposed to corresponding achiral amines *via* a decarboxylation during the reaction. Therefore, new chiral mediators to promote the aldol reaction of **1** effectively have been still required.

Herein we report that the aldol reaction using a chiral triamine (**3**)[2] proceeded to give (+)- and (-)-**2** respectively in an enantiodivergent fashion depending on the amount of acid co-catalyst. Thus, the reaction using a stoichiometric amount of **3** in the presence of less than 2.0 equivalent of trifluoroacetic acid (TFA) afforded enone [(+)-**2**] predominantly. On the other hand, in the case of using more than 2.0 equivalent of TFA, (-)-**2** was obtained accompanied with a complete inversion of enatioselectivity. Next, we prepared conformationally restricted chiral triamines (**4**) and (**5**). The aldol reaction using **4** or **5** did not reveal the enantiodiversity. These results suggested that the enantiodiverse behavior of **3** was due to the conformational change of ethylene diamine moiety in **3**. Thus, under the condition less than 2.0 equivalent of TFA, **3** existed as **6** with the folding conformation of ethylene diamine unit. Conformation of **3** was switched to the extending one (**7**) caused to the formation of diammonium ion under the presence of more than 2.0 equivalent of TFA. The enantiodiversity was hardly affected by versatile substituents (R^1) such as branched alkyl and benzyl on a cycloheptanedione in **1** (Scheme 1).



Scheme 1

References

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P111

SYNTHESIS OF N-CONTAINING PHOSPHONATES BY THE MICHAEL ADDITION OF PYRROLE TO CYANO VINYLPHOSPHONATES

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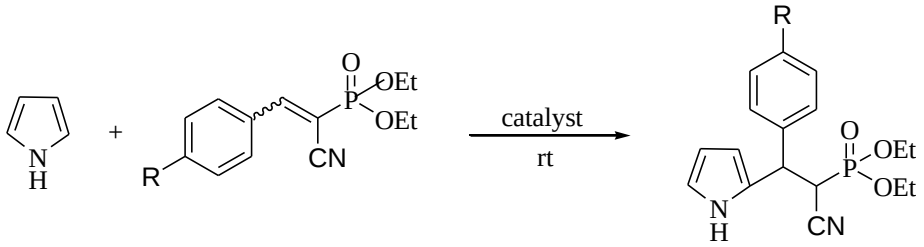
Synthesis of phosphonate derivatives continue to attract considerable interest because of their biologically important properties and synthetic aspects.[1] Derivatives of phosphonates have activities as insecticides, herbicides, fungicides, plant growth regulators and drugs to treat bone disorders and also effective transition-state analogue inhibitors for a variety of enzymes.[2]

In literature there are many methods for the synthesis of phosphonates. Among these methods, Michael addition is the most useful one. Vinylphosphonates, containing electron-withdrawing groups at the α-position are valuable Michael acceptors.[3] For this reason, we describe here the synthesis of phosphonates by the Michael addition of pyrrole to cyano vinylphosphonates.

In this study, cyano vinylphosphonates were synthesized by the condensation reaction of diethyl cyanomethylphosphonate and aromatic aldehydes in the presence of piperidine. Michael addition of pyrrole to cyano vinylphosphonates were performed by using various catalysts, in different solvents, at rt. The novel phosphonates were obtained in 69-96% yields as a diastereomeric mixture in the presence of $Sc(OTf)_3$ as catalyst.



R = H, CF_3, CH_3, F, Cl, Br, CN, NO_2

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P112

HYPERVALENT IODINE(III) MEDIATED OXIDATIVE CROSS-COUPLING LEADING TO FUNCTIONALIZED BIARYLS

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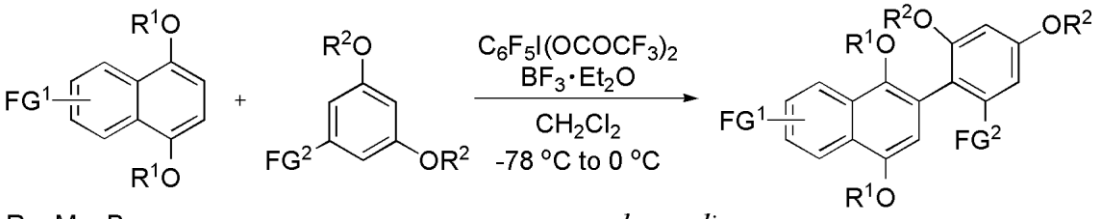
Biaryl backbone is the important common structure of various functional materials such as natural products, pharmaceuticals and optoelectric materials. The coupling of two unfunctionalized arenes, that is, oxidative cross-coupling has received much attention as the most straightforward approach to the synthesis of biaryls, but practical method has not been reported for a long period because of the uncontrollable homo-coupling.[1)] On the other hand, our continuous synthetic studies concerned with hypervalent iodine(III) reagents, such as $PhI(OCOCF_3)_2$ (PIFA), as the environmentally-friendly oxidants[2)] have recently led to discover that the reagents allow to cause the metal-free and selective oxidative cross-coupling using alkylarenes or heteroaromatics as the substrates.[3)]
At this conference, we present the development of the cross-coupling between two phenylethers leading to the poly oxy-functionalized biaryls which are frequently found in natural products. The problematic homo-coupling and over-oxidization were successfully suppressed by employing fluorinated iodine reagent $C_6F_5I(OCOCF_3)_2$ and desired cross-coupling products were obtained in excellent yields. The coupling occurred in a wide range of functional groups and the obtained biaryl compound could be easily elaborated to the synthesis of naturally occurring skeleton by utilizing the functional group.[4)]



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P113

NEW SYNTHETIC APPROACH FOR TRANSITION-METAL-CATALYZED C-P BOND CONSTRUCTION

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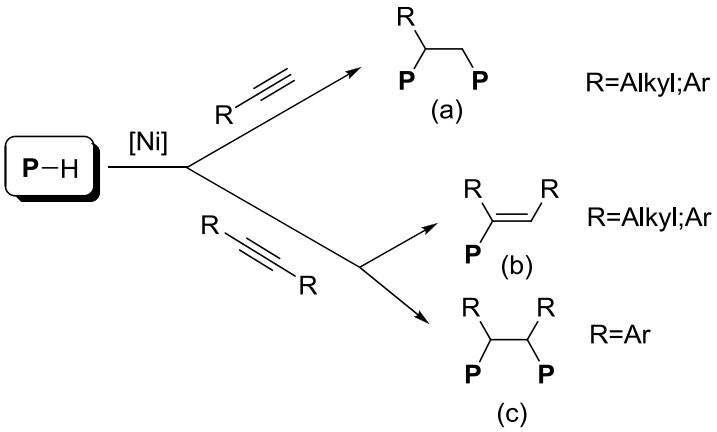
Transition-metal-catalyzed element-hydrogen (E-H) addition to unsaturated compounds is a rapidly developing area of organic chemistry. Finding of effective catalytic systems based on readily available transition metal complexes is a common strategy for the development of this area. Catalytic reactions involving a broad range of different heteroelements are widely used in modern chemistry.

Carbon-phosphorus bond formation is an area of special interest, because the synthesized organic phosphorus derivatives are in demand as useful derivatives in nucleic acid chemistry, as versatile reagents in synthesis, as flame retardants and building blocks in polymer sciences.[1]

A number of mechanistic studies revealed that Pd and Ni catalysts are efficient for atom-economic C-P bond construction.[2-4] The next step is development of practical and efficient synthetic methods for selective preparation of phosphorus derivatives using this catalytic approach.



We have investigated Ni-catalyzed transformation involving alkynes and varying amounts of H-phosphonates. Addition of two molecules of H-phosphonate to terminal alkynes catalyzed by Ni complexes leads to formation of bisphosponates **(a)**. Addition of H-phosphonate to internal alkynes catalyzed by Ni complexes gives vinyl products as well as the bisphosponates. In case of vinyl addition product is obtained with excellent E\Z stereoselectivity **(b)**. Product **(c)** is obtained when two molecules of H-phosphonate reacted with internal alkyne.

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P114

METAL-FREE ARYLATION OF OXYGEN NUCLEOPHILES WITH DIARYLIODONIUM SALTS

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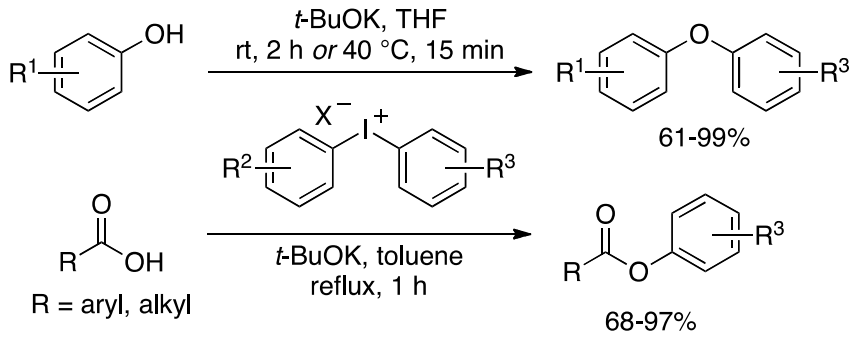
Diaryl ethers and aryl esters are common structural motifs in pharmaceuticals and agrochemicals.[1] Many natural products containing the diaryl ether substructure have received considerable attention, including vancomycin and other glycopeptide antibiotics, as well as anti-HIV agents like chloropeptin. Despite an immense focus on the synthesis of these compound classes, *ortho*-substituted diaryl ethers and sterically hindered aryl esters remain difficult to obtain for applications in life science and the polymer industry. [2]

We have developed methodology for the electrophilic arylation of phenols, carboxylic acids and sulfonic acids with diaryliodonium salts. The reaction conditions are mild, metal-free, and avoid the use of halogenated solvents, additives or excess reagents.

The arylated products are obtained in good to excellent yields in short reaction times. Sterical hindrance is very well tolerated, both in the nucleophile and in the diaryliodonium salt. The scope includes bulky *ortho*- and halo-substituted products, which are difficult to obtain by metal-catalyzed protocols. Many functional groups are tolerated, including carbonyl groups, heteroatoms and alkenes.[3-5]



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P115

NOVEL APPROACHES TOWARD HIGHLY FUNCTIONALIZED 2-IMIDAZOLINES

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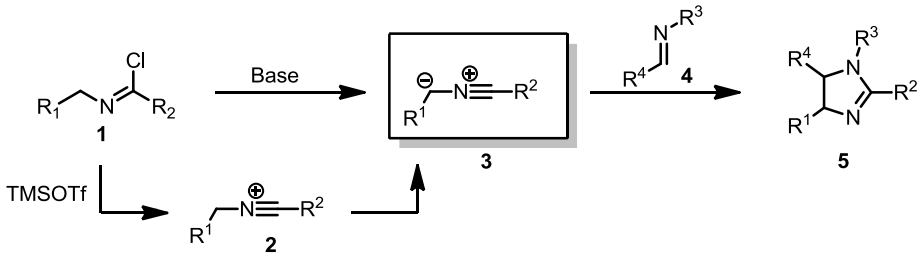
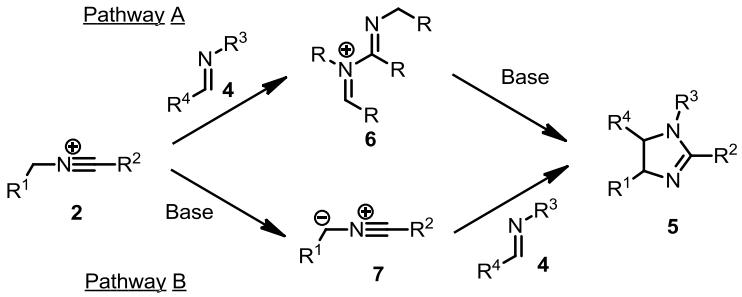
Functionalized 2-imidazolines **5** have great potential as ligands in asymmetric transition metal catalysis and as organocatalysts.[1] They are also of pharmaceutical interest due to their wide variety of biological activities.[2] Although several methods for the synthesis of **5** have been reported, a direct route toward tetrasubstituted 2-imidazolines in one step has not yet been described. Nitrilium ions **2** and the corresponding ylids **3** are versatile reactive intermediates,[3,4] but so far these have not been used in the synthesis of complex *N*-heterocycles. We envisioned that the reaction of these intermediates with imines **4** in the presence of a base would provide efficient access to functionalized 2-imidazolines **5**.



Scheme 1

Using **2** or **3** we were able to develop a simple one-step protocol toward **5**. A deeper understanding of the reaction mechanism leading to **5** is essential for the determination of factors governing the scope and stereoselectivity of the reaction. Experimental and theoretical investigations to this end will be discussed that focus on the identification of possible reaction intermediates (**6** and **7**) for the plausible reaction pathways A and B (scheme 2).



Scheme 2

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P116

ONE-POT SYNTHESES OF DIBENZOBICYCLO[b,f][3.3.1]-NONA-5a,6a-DIENE-6,12-DIONE

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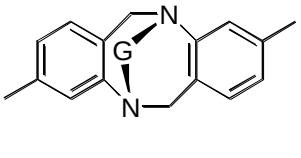
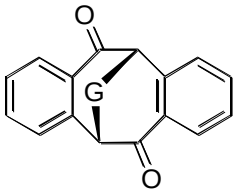
Tröger's base **1** is a small, chiral molecule which has been used widely as a cleft in supramolecular chemistry with a view towards the preparation of many novel specific receptors [1]. Dibenzobicyclo[b,f][3.3.1]nona-5a,6a-diene-6,12-dione **2** can be regarded as analogues of Tröger's base.

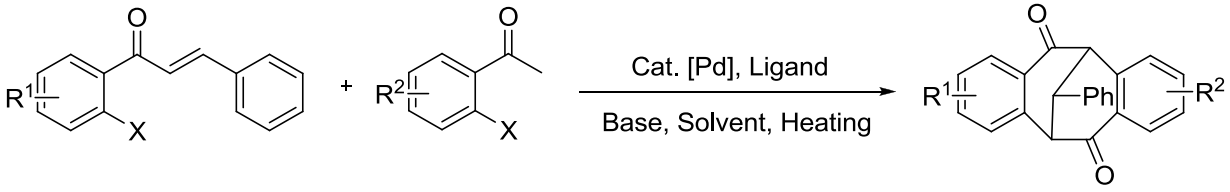


1



2

In last ten years, the dione **2** framework has been identified as a versatile supramolecular building block [2], and chemists were committed to synthesize a range of functionalized derivatives of dione. In this work, we will report our new progress in the synthesis of dione **2** via Palladium-catalyzed process as shown below.



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P117

AMINOALCOHOLS AS EFFICIENT ORGANOCATALYSTS IN ALDOL REACTION OF ISATINS WITH ACETONE. MECHANISTIC STUDIES AND SYNTHESIS OF NATURAL PRODUCTS

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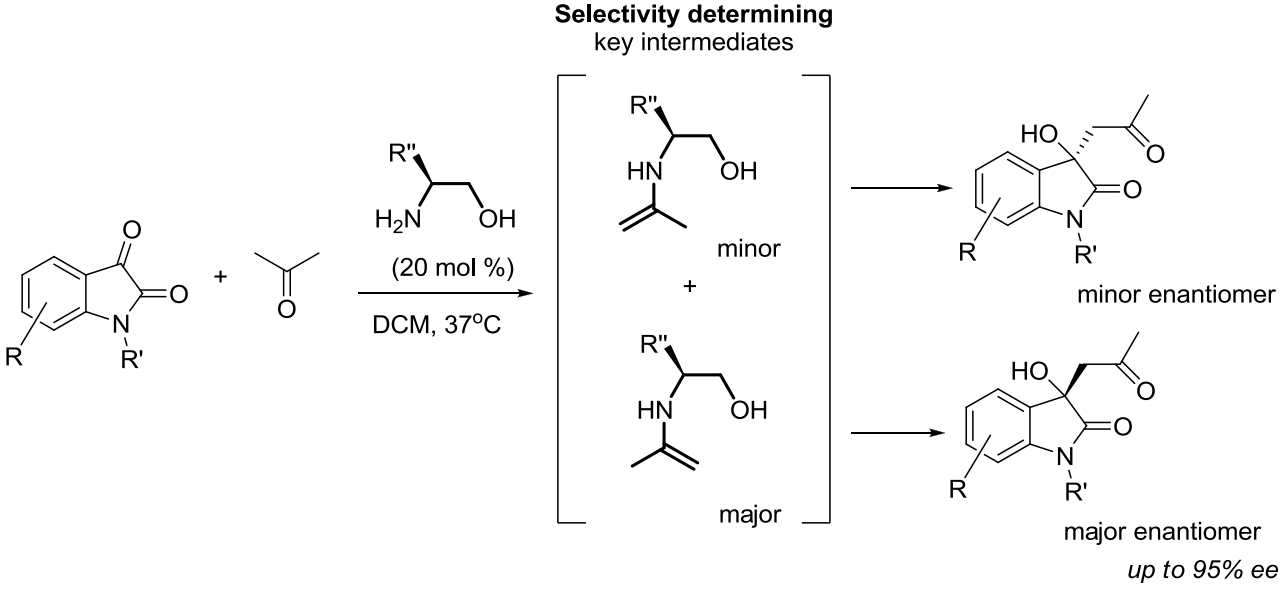
A great success was attained in the asymmetric organocatalytic reactions between an aldehyde and a ketone. In contrast, the ketone-ketone cross-aldol reactions are rare.[1] The amino alcohols, reported to date as organocatalysts, typically featured a secondary amine moiety, whereas the diamines usually contained a combination of one secondary and one tertiary amino group or one primary and one tertiary. In our preliminary communication,[2] vicinal amino alcohols with a primary amino group at the chiral center, were identified as the most efficient organocatalysts in a challenging ketone-ketone aldol condensation between isatins and acetone, by far superior to proline and its congeners.

Scheme



Herein, we provide an orchestration of our original findings, show new examples of this successful aldol reaction, and present a detailed discussion of the mechanism, based on kinetic studies, isotopic labeling, and DFT calculations. Formation of the *syn*-enamine with high selectivity over its *anti*-isomer could be a unique feature of primary aminoalcohols (**Scheme**), and it also provides high enantioselectivity of the reaction. The method developed was employed in the syntheses of Convolutamydine A, a natural product shown to exhibit anti-leukemia activity, and an alkaloid Speranskatine A. Details on optimisation of the reaction conditions and the scope of the reaction will be also presented.

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P118

SIMULATION OF CHEMICAL KINETIC NETWORKS – A TOOL FOR THE ANALYSIS OF COMPLEX CATALYTIC CYCLES. A CASE STUDY OF CONTEMPORANEOUS DUAL CATALYSIS

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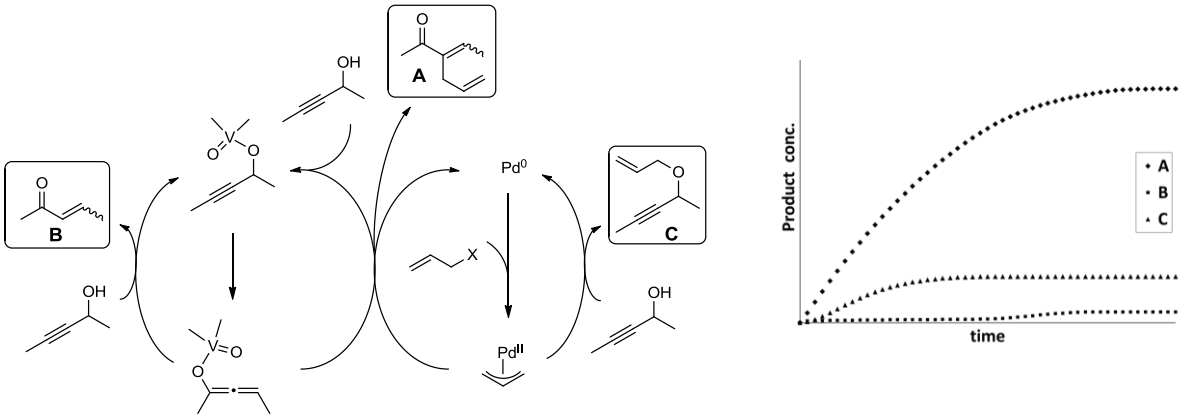
A growing number of reactions with more and more complex mechanisms are nowadays being studied computationally. While DFT methods are able to provide an access to detailed free energy profiles of such reactions, the issue of obtained data analysis becomes an apparent problem. Even a qualitative analysis of the free energy profiles for mechanisms involving two or more coupled catalytic cycles is often impossible, especially in cases when the effect of concentrations needs to be taken into account.

Facing an increasing number of such situations, we turned our attention to numerical simulations as a comprehensive method for the analysis of complex mechanistic networks. The network connectivity defines a set of ordinary differential equations that can be numerically integrated, given the initial concentrations and rate constants from the DFT calculations. As a result time propagation of concentrations of the reaction substrates, products, and intermediates is obtained. The simulation constitutes a theoretical reproduction of an actual experimental reaction *in silico*.

As a proof of principle, the simulation technique has been applied to investigate a reaction involving so-called contemporaneous dual catalysis, being a combination of vanadium-catalyzed Meyer-Schuster rearrangement and palladium-catalyzed allylic substitution.[1] Its mechanism is composed of multiple overlapping catalytic cycles. Formation of the desired product (**A**) requires a reaction between two catalytic intermediates, whereas possible side-products **B** and **C** are formed in reactions of a respective catalytic intermediate with a stoichiometric reagent. The knowledge of barriers for each of these reactions is not sufficient to predict the selectivity, since the relative rates of the alternative products formation are also dependent on the (variable with conversion) concentrations of all the species involved. The simulation, on the other hand, not only satisfactory reproduced the experimental results, but also provided important insights into many aspects of the mechanism and enabled to propose possible improvements in the catalytic system.



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P119

TRANSFER HYDROGENATION OF KETONES IN WATER CATALYZED BY RUTHENIUM AND RHODIUM SURFACE ACTIVE COMPLEXES

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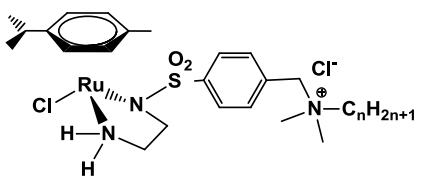
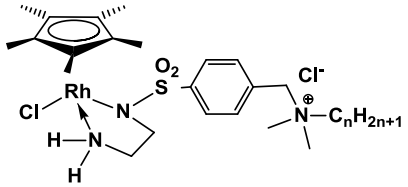
Catalytic transfer hydrogenation (TH) of ketones catalyzed by ruthenium and rhodium amine-amide complexes has proved to be a versatile route to a variety of prochiral alcohols. Particularly, the complexes bearing a chiral diamine such as [(*p*-Cym)RuCl(Ts-DPEN)] (Noyori's) and [Cp*RhCl(Ts-DPEN)] (Xiao's) are well known as catalysts for asymmetric transfer hydrogenation (ATH). These catalysts have been efficiently used in aqueous media together with HCOONa as a reductant, however their solubility in water limits their potential. Here we report on a new catalytic micellar system for TH of ketones in water based on RuL^n and RhL^n complexes with achiral Ts-EN ligand bearing a quaternary ammonium group with long alkyl chain.

The micelle forming catalysts with C_{16}-alkyls, namely RuL^{16} and RhL^{16}, demonstrate enhanced activity in water; the micellar effect is especially pronounced for more hydrophobic ketones. The C_8-based catalysts RuL^8 and RhL^8 do not form micelles alone, though their activity can be greatly improved by imbedding them into the micelles formed by anionic surfactants. The effect of the nature of surfactant and of the solvent on the activity of RuL^n and RhL^n will be discussed.



RuL^n, n = 8, 16



RhL^n, n = 8, 16

The authors thank the EC for financial support through MODUCAT project (FP7 PIIF-GA-2009-236423). COST Action CM0802 (PhoSciNet) is also thanked for mobility funding.

P120

A POLYSTYRENE-SUPPORTED SQUARAMIDE ORGANOCATALYST

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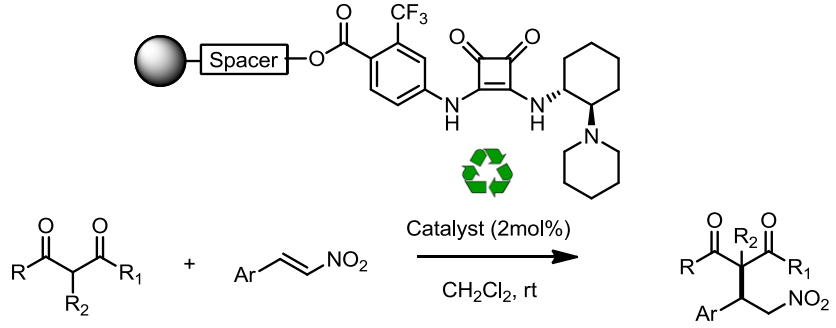
The squaramides are rigid four-membered ring with very important electron delocalization, which makes them very efficient, directional hydrogen-bond donors.[1] In literature there are several examples of homogeneous squaramide organocatalysis used in different reactions.[2] In this study first time a chiral squaramide has been supported onto a polystyrene (PS) resin through a copper-catalyzed azide–alkyne cycloaddition (CuAAC)[3] reaction and used as a very active, easily recoverable and highly reusable organocatalyst for the asymmetric Michael addition of 1,3-dicarbonyl compounds to β-nitrostyrenes. The PS-supported squaramide could be recycled up to 10 times.



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P121

HIGHLY SELECTIVE CATALYTIC SYNTHESIS OF (*E*,*E*)-1,4-DIIODOBUTA-1,3-DIENE VIA ATOM-EFFICIENT REACTION OF ACETYLENE WITH IODINE

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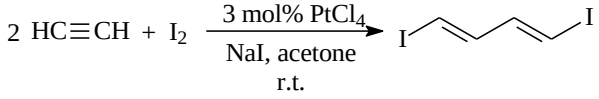
Transition-metal-catalyzed cross-coupling reactions are well-known synthetic tools for the carbon-carbon and carbon-heteroatom bond formation. These reactions play an outstanding role in the natural product synthesis due to their perfect selectivity and tolerance to wide range of functional groups; moreover, they allow one step assembly of complex structures from readily available building blocks. 1,4-Diiodo-1,3-dienes are the excellent reagents for incorporation of 1,3-diene fragments into organic moieties for the synthesis of unsaturated cyclic structures, linear dienes and polyunsaturated compounds [1]. There is a number of methods for the preparation of substituted 1,4-diiodo-1,3-dienes from alkynes but all these methods are not suitable for unsubstituted acetylene so a special procedure for the 1,4-diiodobuta-1,3-diene should be designed.
We have developed first practical procedure for the synthesis of (*E*,*E*)-1,4-diidobuta-1,3-diene from acetylene and iodine in a one step highly selective atom-efficient catalytic reaction (Scheme 1) [2].



Scheme 1. Synthesis of (*E*,*E*)-1,4-diidobuta-1,3-diene from acetylene and iodine.

We have found that the choice of solvent plays a crucial role on the outcome of the reaction. The reaction was carried out in acetone and resulted in high product yield and selectivity towards formation of the desired (*E*,*E*) isomer. Good solubility of acetylene is another important advantage of acetone as a solvent. We have also established the influence of platinum precursor, taken amount of sodium iodide and iodine as well as reaction temperature on the selectivity and the product yield.
Under the optimized conditions catalytic synthesis of (*E*,*E*)-1,4-diidobuta-1,3-diene was carried out using 3 mol% of $PtCl_4$. After isolation and purification we obtained solid crystalline product of 99+% purity which was directly suitable for single-crystal X-ray analysis. Molecular structure of the product is shown below (Figure 1).

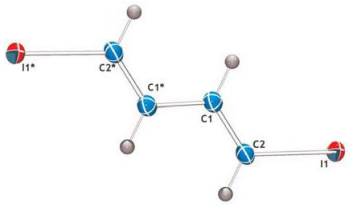


Figure 1. Molecular structure of (*E*,*E*)-1,4-diidobuta-1,3-diene determined by X-ray analysis.

Our further studies showed different stability of synthesized diene toward isomerisation and decomposition in acetone, methanol, chloroform, benzene and DMSO. We also performed mechanistic study of the reaction and the key intermediate of the catalytic cycle containing (*E*)-PtCH=CHI vinyl group was detected by NMR monitoring of the reaction [2].

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P122

5-ARYL-3-(β-AMINOETHYL)-1,2,4-OXADIAZOLES IN BOULTON-KATRIZKY REARRANGEMENT

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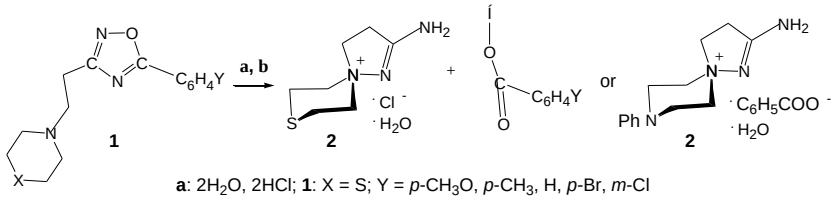
Substituted 1,2,4-oxadiazoles undergo Boulton-Katrizky rearrangement in DMF at 150 ^{o}C or without solvents at 240 ^{o}C with the formation of pyrazolines and pyrazoles of planar structure [1]. After hydrolysis in milder conditions with acid and base catalysis using X-ray diffraction we have observed a similar rearrangement of 5-aryl-3-(β-aminoethyl)-1,2,4-oxadiazoles **1**, but pyrazolinic cycle was involved in the creation of spirogeterocyclic system of **2**: 2-amino-8-thia(or 8-phenylamino)-1-aza-5-azoniaspiro[4.5]dec-1-ene chloride hydrate (or benzoate hydrate) [2]:



a: $2H_2O$, 2HCl; **1**: X = S; Y = *p*-CH_3O, *p*-CH_3, H, *p*-Br, *m*-Cl
b: $2H_2O$; **1**: X = PhN; Y = H

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P123

SYNTHESIS OF N-(1,5,3-DITHIAZEPAN-3-YL)- AND N-(1,5,3-DITHIAZOCYNAN-3-YL)AMIDES IN PRESENCE OF LANTANIDE CATALYSTS

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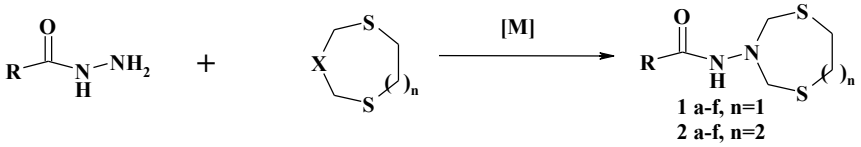
Heterocyclic compounds with *N*-amide substituents are of interest as antituberculous, anti-inflammatory, antitumoral and diuretic agents as well as extractants, sorbents and analytical reagents.

As a continuation of our research on the synthesis of *S,N*-containing heterocycles and aiming to develop an effective method to obtain *N*-(1,5,3-dithiazepan-3-yl)- and *N*-(1,5,3-dithiazocynan-3-yl)amides, we have studied catalyzed by salts and complexes of transition rare-earth metals reactions of transamination of *N*-*tert*-butyl-1,5,3-dithiazepane and *N*-*tert*-butyl-1,5,3-dithiazocynane, and recyclization of 1-oxa-3,6-dithiacycloheptane and 1-oxa-3,7-dithiacyclooctane by hydrazides of isonicotinic, nicotinic, *o*- and *m*-methoxybenzoic acids and by methoxy- and *t*-butoxycarbazates.

We have established, that transamination of *N*-*tert*-butyl-1,5,3-dithiazepane and *N*-*tert*-butyl-1,5,3-dithiazocynane by hydrazides of carboxylic acids proceeds most effectively in presence of YbF_3 (5 mol%) with a ratio of $RC(O)NHNH_2$: *N*-*tert*-butyl-1,5,3-dithiazepane (N-*tert*-butyl-1,5,3-dithiazocynane) : [M] equal 10:10:0.5, leading in certain conditions (80°C, 48 h) to a selective formation of corresponding N-substituted 7- and 8-membered heterocycles in 45-80% yield.



1 a-f, n=1
2 a-f, n=2

R = *p*-C_5H_4N (a), *m*-C_5H_4N (b), *o*-$CH_3OC_6H_4$ (c), *m*-$CH_3OC_6H_4$ (d), OCH_3 (e), $OC(CH_3)_3$ (f);
X = *t*-Bu, [M] = YbF_3; X = O, [M] = $SmCl_3*6H_2O$

The report at the same time will present the results on the synthesis of *N*-(1,5,3-dithiazepan-3-yl)-**1a-d** and N-(1,5,3-dithiazocynan-3-yl)-amides **2a-d**, said compounds obtained by means of recyclization of 1-oxa-3,6-dithiacycloheptane and 1-oxa-3,7-dithiacyclooctan by hydrazides of corresponding carboxylic acids in presence of catalyst $SmCl_3 \cdot 6H_2O$.

The approach thus proposed enables synthesis of *N*-substituted 1,5,3-dithiazepanes and 1,5,3-dithiazocynanes of various structure in high yields and selectivity.

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The authors thank the Russian Foundation of Basic Research for financial support (grants 11-03-00101-a, 11-03-97011-r_Povolzh′e_a).

P124

NMR-STUDIES OF THE MECHANISM OF CARBOHYDRATES CONVERSION TO 5-HYDROXYMETHYLFURFURAL IN NATIVE-IMIDAZOLIUM IONIC LIQUIDS

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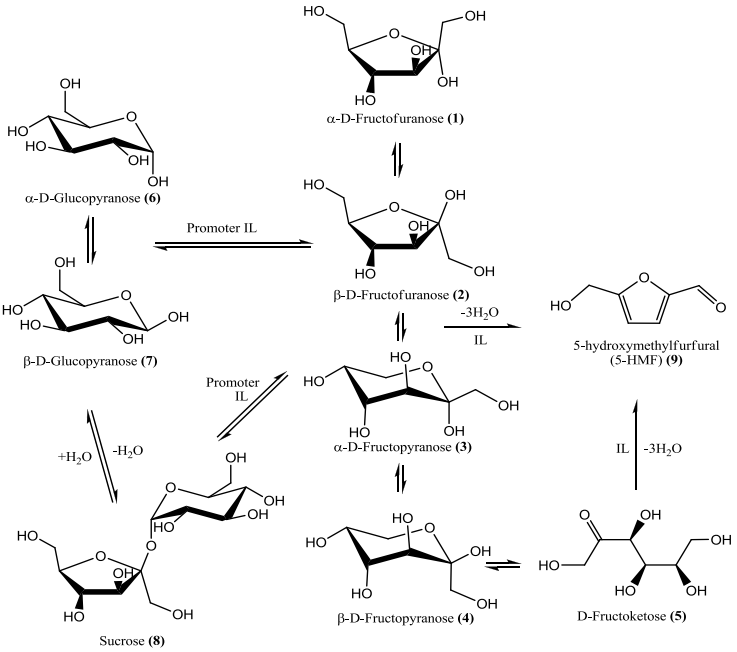
In recent years, cellulose conversion to 5-hydroxymethylfurfural (5-HMF) has received increased attention since carbohydrates constitute 75% of the world's renewable biomass and 5-HMF is considered a key intermediate between petroleum-based industrial organic chemistry and bio-based carbohydrate chemistry. Moreover, 5-HMF and its derivatives are currently used to make plastics and fine chemicals. [1] The goal of our research was to understand mechanistic nature of carbohydrates conversion to 5-HMF in native imidazolium-based ionic liquids at molecular level using specially developed NMR setup. This NMR approach promotes overcoming of the challenging problem in observation of NMR signals and helps to understand the mechanisms of reaction in native state ionic liquid systems at molecular level. [2] The application of ionic liquids suitable for use as solvent allows to avoid 5-HMF decomposition to levulinic and formic acid. While boric compounds are very promising promoters for biomass conversion because of non-toxic, metal-free and low price advantages. Surprisingly, boron trioxide was a highly efficient reagent, which combines both functions – as promoter for glucose conversion into fructose and as dehydration agent for 5-HMF formation. Applying developed NMR approach direct monitoring of the studied reaction with glucose was successfully achieved and resulted in comprehensive detection of reagent conversion, formation of product, interconversion of B_2O_3, detection of borate complex, and the anomeric forms of carbohydrates using not only 1D but also 2D NMR measurements. Surprisingly, dissolution of fructose in ionic liquid, unlike glucose, led to appearance of open fructoketose form and furnished significant change in the anomeric composition in comparison with known data for water solution.[1]



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P125

HOMOGENEOUS CATALYTIC POLYFLUOROALKYLATION OF ORGANIC SUBSTRATES (THIOPHENOLS, PHENOLS, AZOLES) WITH DIFFERENT FREONS

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A possibility of the homogeneous catalytic selective fluoroalkylation of thiophenols, phenols and some azoles with different freons: F114B2 ($BrCF_2CF_2Br$), F113 ($ClCF_2CFCl_2$), and F113B2 ($BrCF_2CFClBr$) using organic bases and electron transfer mediator under mild conditions was shown.

In these activating systems the bases (in particular, substituted pyridines) enhanced electron-donating and nucleophilic ability of substrates by forming complexes of proton-donating S-H, O-H and N-H groups with pyridines. This assumption was verified by demonstration of the dependence of electrochemical oxidation peak potential of substrates on the basicity of different pyridines. Introducing of electron transfer mediator (in particular, sulfur dioxide) from nucleophile (complex of substrate with nitrogen base) to freon resulted in efficient generation of active fluoroalkyl radicals, that are capable to polyfluoroalkylate the aromatic ring of phenols and azoles or heteroatom of thiophenols yielding polyfluoroalkylarylsulfides.

We observed dependence between yields of fluoroalkylation products and pyridine basicity as it was found by us for fluoroalkylation of thiophenols with $BrCF_2CF_2Br$ in the presence of pyridines with different pK_a:

Amines	pK_a	Product yields,% $CH_3C_6H_4SCF_2CF_2Br$
2-chloropyridine	0,72	-
p-acetylpyridine	3,18	-
pyridine	5,23	78
2,5-lutidine	6,25	96
γ-collidine	7,60	98
pyridine*	5,23	28
γ-collidine *	7,60	46

* – p-dinitrobenzene is added

The range of pK_a, which promotes the homogeneous catalytic fluoroalkylating process, was estimated for every freon. The significant influence of freon structure on the possibility and selectivity of fluoroalkylation process was demonstrated.

The radical nucleophilic mechanism of $S_{RN}1$ type for these processes was proposed; some studies of it were confirmed experimentally.

P126

ALUMINUM COMPLEXES BASED ON TRIDENTATE NITROGEN DONOR LIGANDS AS PERSPECTIVE CATALYSTS OF RING-OPENING POLYMERIZATION OF HETEROCYCLES

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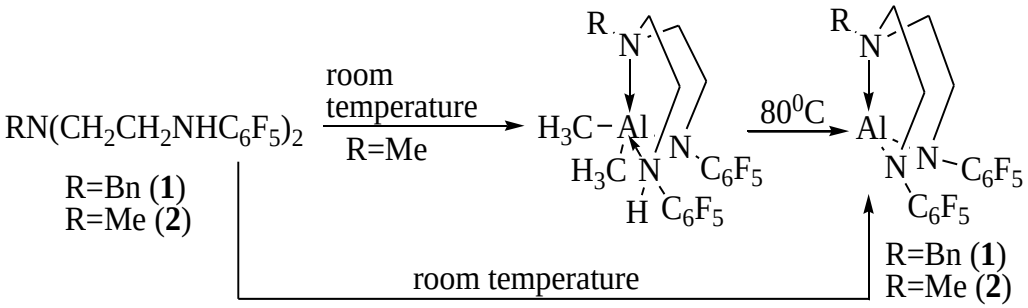
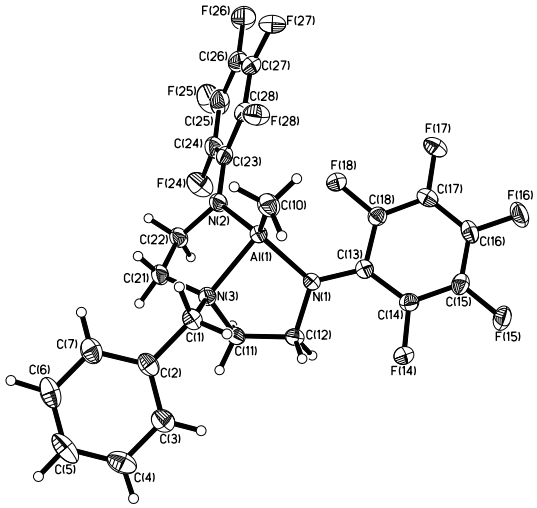
Biodegradable and biocompatible materials are of great importance today [1]. The most convenient and efficient method to obtain such materials is the ring opening polymerization (ROP) of cyclic esters. There has been particular attention over the past decade on the development of new catalytic systems for this process. Tetracoordinated group 13 derivatives are promising catalysts for the ring-opening polymerization of heterocycles (propylene oxide and (*D*, *L*)-lactide) [2].
Tridentate nitrogen donor ligands ($RN(CH_2CH_2NHR')_2$) can be used for stabilizing four-coordinate aluminum center [3]. We synthesized novel complexes of aluminum based on the related ligands. It has been shown that replacement of alkyl substituent at one nitrogen atom in the ligand has a great influence on the course of the reaction.



The crystal structure of the compound **1** was studied by X-ray analysis.



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P127

METAL-FREE OXIDATIVE CROSS-COUPLING REACTION OF AROMATIC COMPOUNDS

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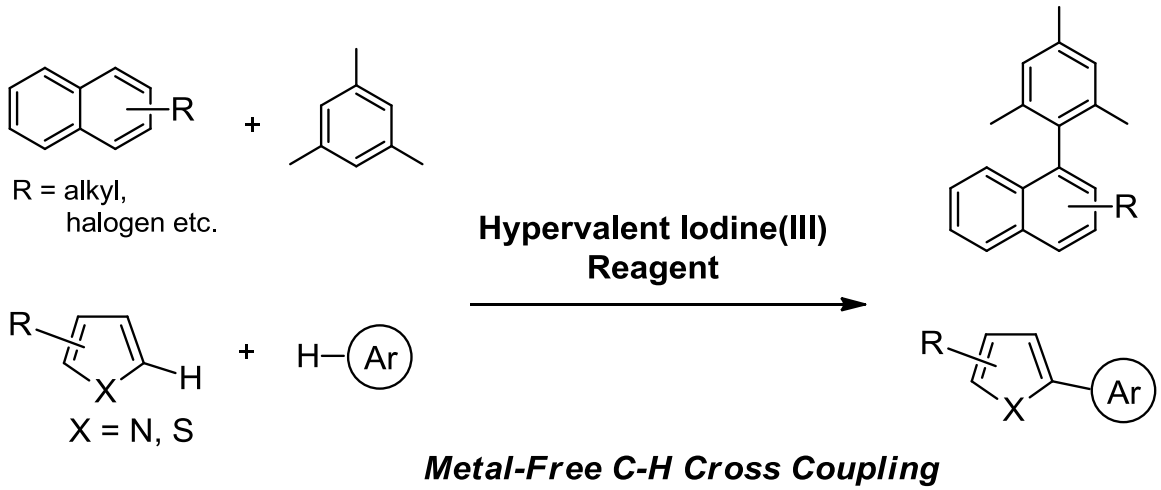
Biary unit is a key structure in a large number of natural products and π-conjugated organic materials. Therefore, the development of novel cross-coupling reaction leading to biaryls is one of the important subjects in modern organic chemistry. In particular, oxidative cross-coupling reaction of aromatic compounds is considerably attractive and regarded as a convenient straightforward route to the synthesis of biaryls without the pre-functionalization of substrates, i.e., halogenation and metallation.

Recently, we have reported metal-free cross-coupling reactions of unfunctionalized aromatic compound using hypervalent iodine reagent.[1), 2)] At this conference, recent progress in the field of metal-free oxidative cross-coupling reactions of aromatic compounds using hypervalent iodine(III) reagents, is presented. [3)]



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P128

HYDROGENATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF Pt-AND Pd-CONTAINING CARBON NANOMATERIALS

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Carbon nanomaterials (CNM) are of potential interest as supports catalysts of reaction of fine chemicals. They have a number of advantages over other heterogeneous supports: uniformity and orderly structure, high specific surface area and the possibility of modification her by the various functional groups [1]. All this makes all metal centers homogeneous and accessible to the substrate molecules, which in turn leads to the rational use of precious metals.

Pt-and Pd-containing CNM were synthesized by impregnation CNM (multiwalled nanotubes (MWNT), nanofibers (NF) or nanodiamonds (ND)) by aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ or K_2PdCl_4 respectively, in the presence of a reducing agent. Depending on the nature of CNM the cluster size Pt and Pd was from 2 to 6 nm. The catalytic activity was studied in model reactions of hydrogenation of unsaturated organic compounds (allyl alcohol and cyclohexene), nitrobenzene, 4-(propylidenamino)benzoic acid and halogenated aryls (m- and p-dichlorobenzene, chlorobenzene, bromobenzene, etc.). The choice of substrates was dictated either by practical value of the products obtained (secondary amines asymmetric structures that are formed in the hydrogenation of Schiff bases), or by the opportunity to compare the parameters of the proposed catalysts with known (nitrobenzene, allyl alcohol, cyclohexene) and hydrogenating dehalogenation is the only environmentally friendly and versatile way utilization halogenated organics.

It is shown that under mild conditions (P_{H_2}=0.1 MPa, T=298-318 K, solvent - aliphatic alcohols), these substrates are restored entirely without formation of intermediate and by-products. When hydrogenating dehalogenation observed cleavage of halogen while maintaining the aromatic system. According to the results, Pt-and Pd-containing CNM are active in these reactions, the most active catalysts obtained on the basis of ND. For example, in the hydrogenation of nitrobenzene Pt/ND and Pd/ND were more active than Pt/MWNT in 2-26 times, than Pt/NF in 3-16 times, than Pt/C (E-TEK) in 2-11 times and than commercial Pd/C in 12-60 times. In the hydrogenation of azomethine Pt/ND and Pd/ND were more active than commercial Pd/C in 13-45 times, and dehalogenation, for example, m-dichlorobenzene - almost 8 times. The most effective is the use in the process of liquid-phase catalytic hydrogenation of Pt- and Pd-CNM with a relatively low weight percentage of metal. The catalyst remains operational after repeated use with no apparent loss of activity. For example, in the hydrogenation of nitrobenzene, cyclohexene or allyl alcohol after 5 consecutive substrate loading, reaction rate has not changed.

Thus, Pt-and Pd-containing CNM have high catalytic activity and stability in the liquid-phase hydrogenation reactions of >C=C<, $-NO_2$, >C=N-, >C-Cl, >C-Br bonds, etc.

The work was supported by Russian Foundation for Basic Research (Grant №12-03-97546-r_centr_a).

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P129

PALLADIUM-CATALYZED AMINATION IN THE SYNTHESIS OF MACROTRICYCLIC CRYPTANDS

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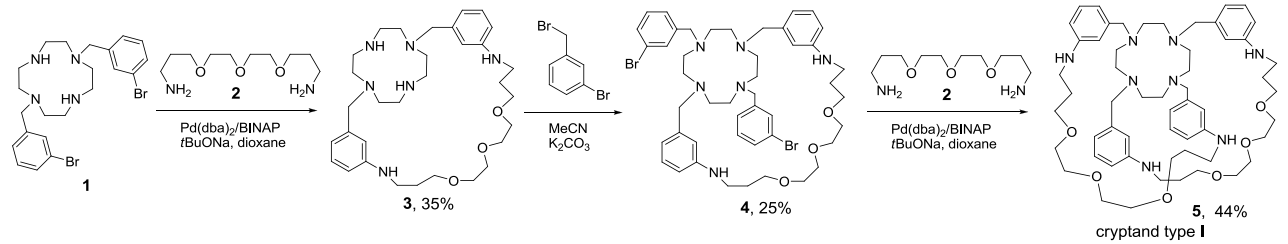
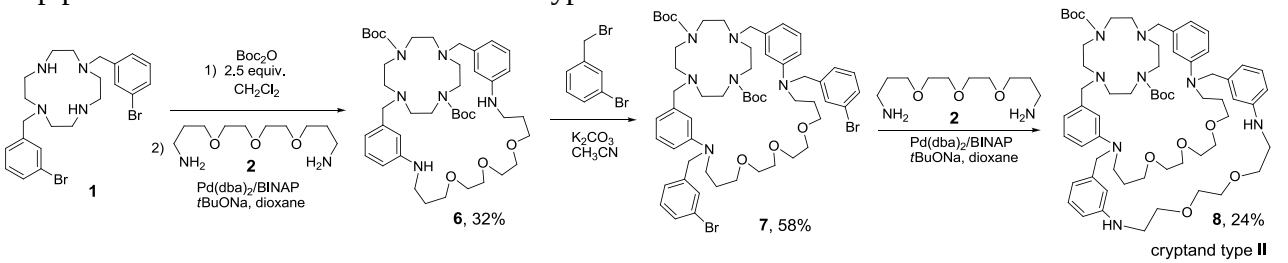
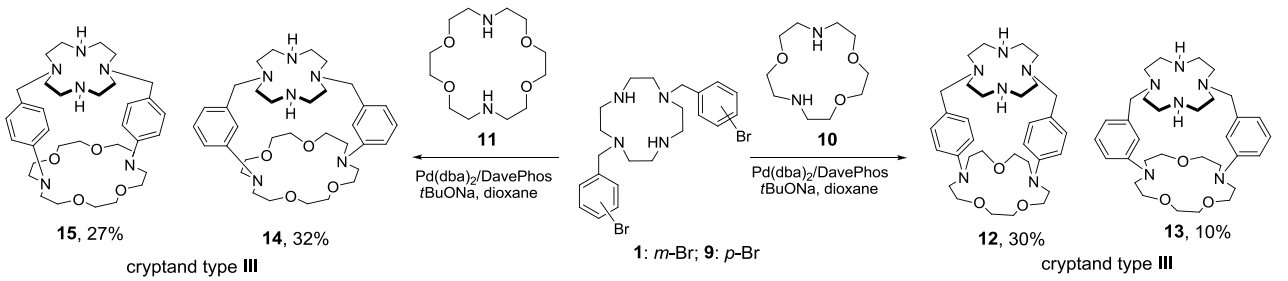
We have proposed various approaches to macrotricyclic cryptands using Pd-catalyzed amination at the macrocyclization steps. Cryptands of type **I** (spherical) were synthesized from 1,7-bis(3-bromobenzyl)-cyclen **1** in three steps by constructing the second macrocycle in compound **3**, modifying it with two *m*-bromobenzyl substituents with the formation of tetrabenzyl cyclen unit in compound **4**, and furnishing the third macrocycle at the last step (cryptand **5**).



Cryptands of type **II** were obtained by protecting two nitrogen atoms in 1,7-bis(3-bromobenzyl)cyclen **1** with BOC groups and introducing the resulting compound in a similar three-step procedure with the formation of the cryptand **8**.



Cryptands **12**-**15** of type **III** (cylindrical) were synthesized *via* one-step procedure from 1,7-bis(bromobenzyl) substituted cyclens **1** and **9** and diazacrown ethers **10** and **11**.



P130

TITANIUM (+4) AND VANADIUM (+3) AND (+5) COMPLEXES WITH OO-TYPE LIGANDS AS ALPHA-OLEFIN CATALYSTS

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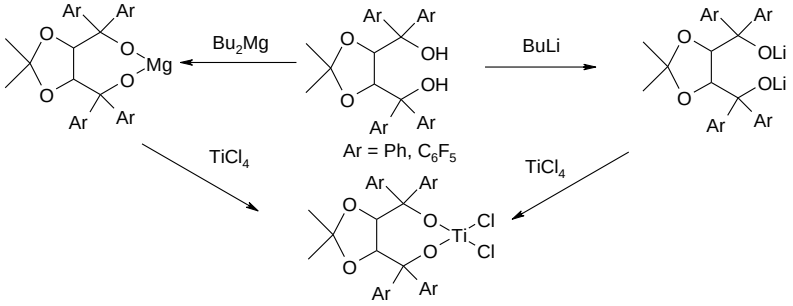
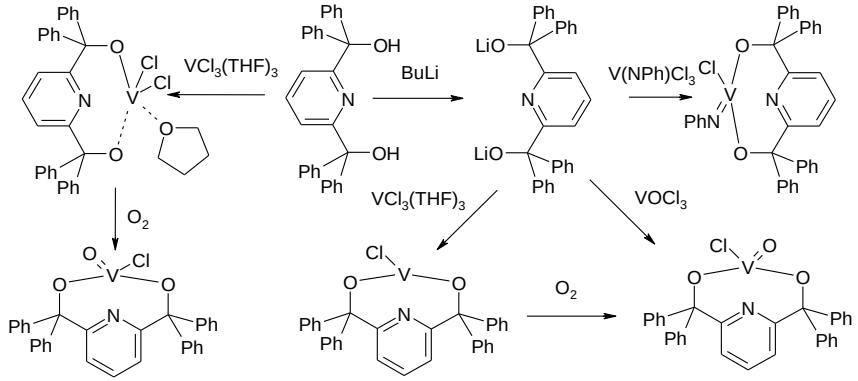
Series of novel titanium dichloride complexes on the base of tetraaryl–1,3–dioxolan-4,5–dimethanol have been developed. The structure and properties of complexes - precursors have been studied as well as their immobilizers by traditional methods – elemental analysis, IR, NMR-spectroscopy and X-ray. Tests of synthesized compounds have carried out to define catalyst activity in homogeneous and heterogeneous polymerization of olefin polymerization. As screening models we used homogeneous and heterogeneous ethylene and propylene polymerization in toluene medium with methylalumoxane (MAO) and triisobutylaluminium (TIBA) as co-catalyst. It has been shown that synthesized compounds are effective catalysts of these processes (120 to 1500 kg [PE]/(mol[Ti]*h), 100 to 500 kg [PE]/(mol[V]*h)). The created steric environment around the atom of the metal influences on the value of the integral activity as well on the value of catalytic and thermic stability both homogeneous and heterogeneous catalytic systems.



Coordination compounds of vanadium (+3) and (+5) with 2,6-bis(diphenylhydroxymethyl)pyridine have been synthesized. Composition and properties of the obtained complexes have been evaluated by NMR, IR spectroscopy, chromatography, X-ray diffraction, and elemental analysis. Catalytic activity of vanadium (+3) and (+5) complexes in this reaction varied between 34 and 578 kg [PE]/(mol[V]*h) after activation with diethylaluminum chloride, depending on the V/Al ratio.



We are grateful to Russian Foundation for Basic Research (project nos. 11-03-12172, 11-03-00297 and 12-03-00974).

P131

VISIBLE LIGHT INDUCED M-C BOND FORMING REDUCTIVE ELIMINATION OF HETERODINUCLEAER ORGANOPLATINUM-MANGANESE COMPLEX

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Heterodinuclear organotransition metal complexes attract considerable interests in relation to cooperative effects of different transition metals in catalysis. Use of light energy in selective chemical reactions and catalysis are also unsolved important subject in these fields. Heterodinuclear (2,2'-bipyridine)- or (4,4'-di-tert-butyl-2,2'-bipyridine)triorgano- platinum-manganesepentacarbonyl complexes (*t*-Bu_2-bpy)R_3Pt-Mn$(CO)_5$, which have been prepared by the simple metathetical reactions of the corresponding triorgano(nitrato)platinum(IV) complexes with sodium pentacarbonylmanganate in THF, were found to show facile Mn-Me bond forming reductive elimination on visible light irradiation under ambient conditions.[1] No significant effecst of the added *t*-Bu_2bpy ligand, $[Mn(CO)_5]^-$ anion, and radical scavenger on both rates under dark and irradiation of light were observed, excluding possible mechanisms involving prior ligand dissociation and heterolytic Pt-Mn bond cleavage processes. This visible light iradiation would cause electron promotion from the HOMO (Pt-Mn bond) to the LUMO (bpy π^*), leading to facile methyl transfer reaction from Pt to Mn.
Synthesis and mechanistic insights of light induced reductive elimination of heterodinuclear organoplatinum-manganese complexes will be discussed.

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P132

NEW APPLICATION OF KULINKOVICH REACTION

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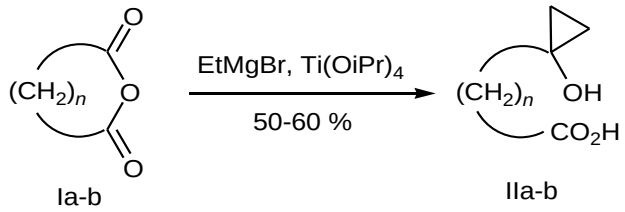
Kulinkovich reaction [1] is widely used for the synthesis of cyclopropanols which by subsequent transformations lead to important compounds with biological properties and with synthetic utility [2]. Cyclopropanation of the substituted acid esters or other acid derivatives was carried out leading to functionalized cyclopropanols [3]or aminocyclopropanes [4].
We report here that reaction of the dicarboxylic acid anhydrides **Ia,b** with ethylmagnesium bromide in the presence of titanium tetra(isopropoxide) gives the cyclopropanols **IIa,b** with carboxylic function located at the end of alkyl group.



n = 2 (a), 3 (b)

We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Project No 12-03-01008-a).

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P133

MODIFICATION OF STEROIDS BY COPPER-CATALYZED CROSS-COUPLING REACTIONS

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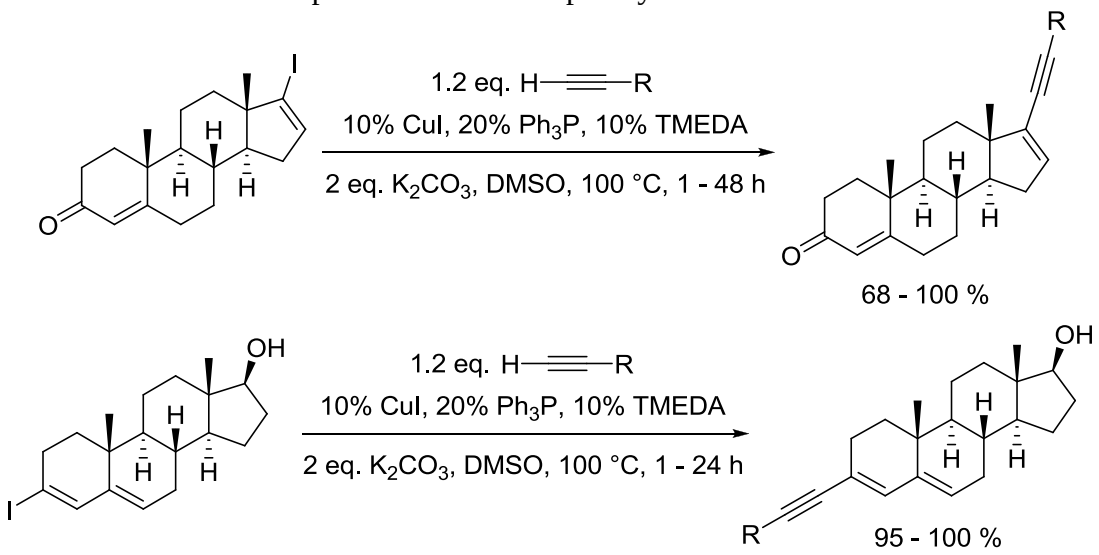
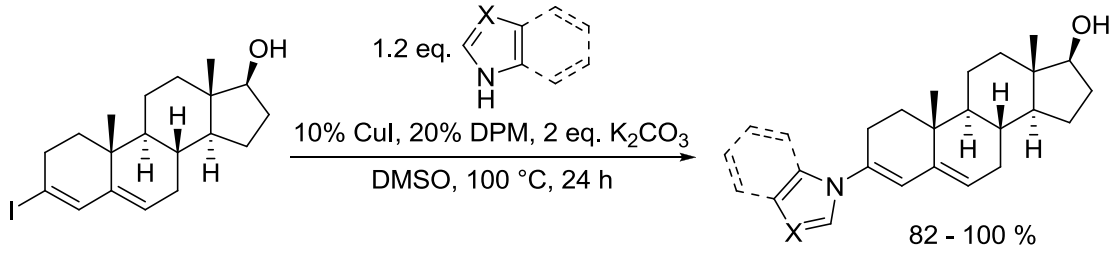
Steroids possess a unique position among other natural compounds due to their high biological activity and involvement into the most important processes in living organisms. Modification of steroids is a «fine-tuning instrument» which provides access to the influence on pharmacological properties of the substance obtained. Palladium-catalyzed cross-coupling reactions have been applied to steroids modification recently [1]. However, a high cost of the metal and appropriate phosphine ligands is an obvious drawback of these protocols. Therefore, the development of alternative catalytic methods of steroids functionalization is an actual synthetic problem.

Herein, for the first time we have investigated the copper-catalyzed cross-coupling reaction of 3- and 17-iodosteroids with terminal acetylenes and NH-heterocycles. The influence of reaction conditions on the conversion and the amount of undesirable halogen reduction by-product was studied.

The cross-coupling of steroidal vinyl iodides with aromatic acetylenes was found to proceed efficiently in the presence of Ph_3P as a ligand. In the case of less reactive acetylenes a new biligand catalytic system based on Ph_3P and TMEDA was proposed. Improved conditions have permitted to avoid the formation of the side product almost completely.



We have designed an effective technique for the copper-catalyzed cross-coupling reaction of steroidal vinyl iodides with a variety of nitrogen heterocycles (indole, imidazole, indazole and carbazole). The best result was achieved using dipivaloylmethane (DPM) as a ligand.



This work was supported by RFBR (grant № 11-03-00265-a).

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P134

ENANTIOSELECTIVE ALKENE CARBO- AND CYCLOMETALLATION BY $AlEt_3$, CATALYZED WITH NEOMENTHYLINDENYL Zr COMPLEXES

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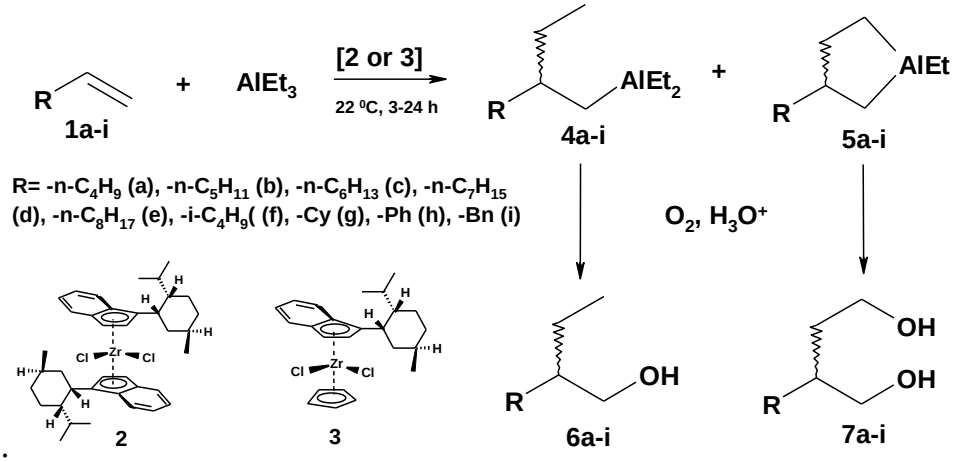
The catalysis of the reaction of $AlEt_3$ with terminal alkenes by chiral zirconium complexes provides enantiomerically enriched carbo- and cycloalumination products [1, 2]. Present work is devoted to a detailed study of the effect of substrate (**1a-i**) and catalyst (**2**, **3**) structure on chemo- and enantioselectivity of the reaction.

It is shown that alkenes (**1a-i**) react with $AlEt_3$ in the presence of 8 mol% of complex **2** in dichloromethane to give carboalumination products **4a-i** with yield up to 78% and enantiomeric excess 50-70% with a predominance of *S*-enantiomers.



The same reaction in benzene or in the absence of a solvent runs with high conversion 70-99% and yield of **5a-i** up to 62%, however, the enantiomeric excess of the cycloalumination products is 7-12%ee, *S*. The replacement of benzene with hexane increases the enantiomeric excess of **5a-i** up to 24-40%ee, whereas the yield reduces to 6-12%. The involvement of styrene in the reaction changes the absolute configuration of *β*-chiral center in the ethylalumination product **4h**. Reaction of terminal alkenes with $AlEt_3$, catalyzed by complex **3**, yields cycloalumination products **5** with *R*-configuration of the *β*-chiral center with yield of 20-60% and enantiomeric excess up to 12%ee.

The absolute configurations of *β*-chiral centers in carboalumination products **4a-i** and aluminacyclopentanes **5a-i** were established by the analysis of specific rotation angles of the oxidation and hydrolysis products **6a-i** and **7a-i**. The alcohols **6a-i** and **7a-i** were involved in the reactions with either *R*-MTPA [3] or (*R*) - 2 - phenylselenopropanoic acid (*R*-PSPA) [4] providing information about the enantiomeric excess of the products.

The authors thank the Russian Foundation of Basic Research (Grant No.12-03-00363a) for financial support.

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P135 (GM9)

HYDROGENATION OF Rh(I) DIENE COMPLEXES AS A WAY TO CATALYTICALLY ACTIVE SPECIES

E.M. Kozinets[1], O.A. Filippov[1], N.V. Belkova[1], E.S. Shubina[1], M. Fekete[2], E. Manoury[3], R. Poli[3], S.B. Duckett[2]

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2 - University of York, Department of Chemistry,United Kingdom
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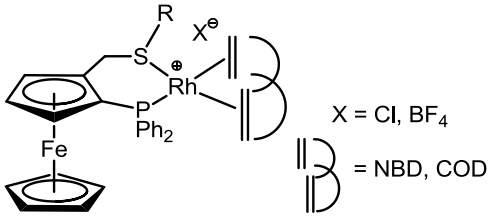
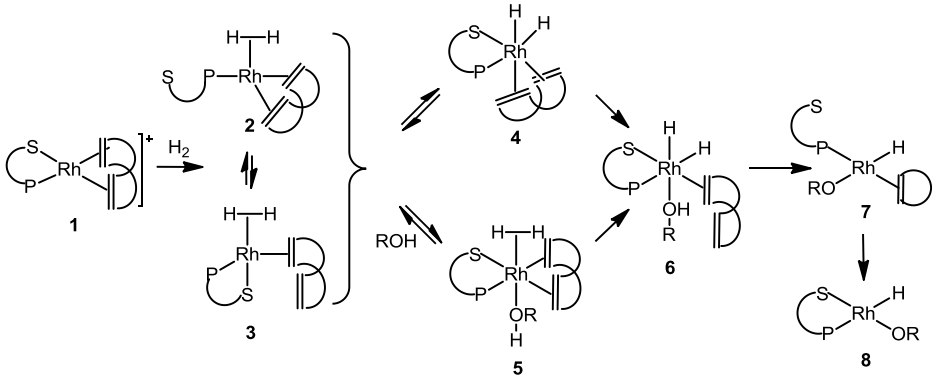
Iridium complexes with diphenylphosphinoferrocenyl thioether ligands are effective catalysts for ketone asymmetric hydrogenation[1]. Their rhodium analogues (**1**, R = ^{t}Bu, Et, Ph, Bz) are good structural and functional models for studying the mechanism of this reaction. The hydrogenation of these precatalytic species under stoichiometric conditions (1-3 bars H_2) was studied by NMR and UV/Vis spectroscopy. The hydrogenation rate is influenced by the nature of the diene ligand, anion and substituent near sulfur atom. The effect of solvent and added base (pyridine, MeONa) on the hydrogenation was also investigated. Presence of pyridine stabilizes a dihydride species and changes the hydrogenation kinetics. The structures of dihydrides were determined by parahydrogen NMR measurements. The data obtained shed light on the mechanism of Rh(I) diene complexes activation (**Scheme 1**) and show the peculiarities of this reaction in comparison to the related bisphosphine complexes[2].





Scheme 1

Acknowledgment: We thank the CNRS and the RFBR for support through a bilateral grant, the GDRI "Homogeneous Catalysis for Sustainable Development", and the French Embassy in Moscow for the financial support of joint PhD thesis for EMK.

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P136 (GM6)

DESYMMETRIZATION OF A LIGAND STRUCTURE AS MEANS TO IMPROVE CATALYTIC AND PHOTOOPTICAL PROPERTIES OF PINCER METALLOCOMPLEXES

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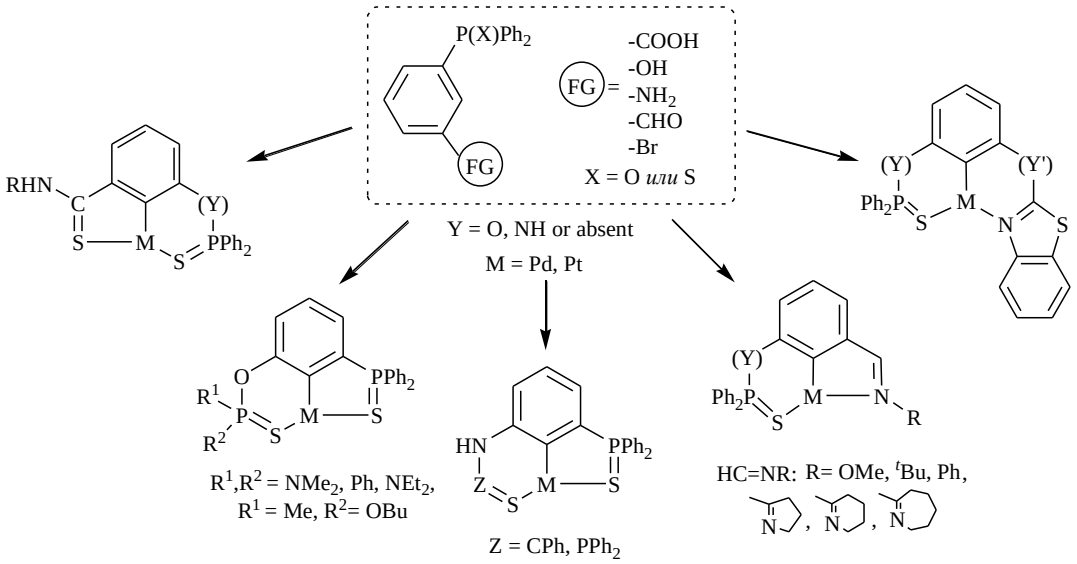
An extending areas of application of pincer complexes, for which easy to perform structural modifications allow fine tuning of electronic and steric properties, attracts more and more interest. Among the strategies used to improve the chemical and physical properties of these compounds, desymmetrization of a pincer structure, affording YEX complexes possible to combine properties of the parent symmetric systems or exhibit the unique ones, holds a special position. Developed by us recently effective synthetic routes to a few new families of hybrid SCY (Y=S', N) ligands bearing thiophosporyl groups in combination with thiocarbamide or azomethine or azole heterocyclic moieties as coordination arms, provided the basis for systematic comparable study of catalytic and luminescent properties of their 5,5-and 6,6-membered Pd and Pt complexes.1 Note that these complexes were readily obtained by direct metallation either in solution or under solid phase conditions suggested for the first time for pincer products, and desymmetrization of a ligand structure facilitated this process.



Furthermore, the catalytic activity of Pd-complexes, tested under identical conditions for the Suzuki-Miyaura cross-coupling of aryl halides with phenylboronic acid, was found to increase along with desymmetrization of a complex structure in a series 5,5-SCS'<5,6-SCS'<5,5-SCN<5,6-SCN<5,6-SCNHet, i.e. passing from complexes with 5,5,-membered fused metallocycles to 5,6-membered ones and to the derivatives having donor atoms of different nature. Similarly, desymmetrization of a complex structure increased the luminescent properties of complexes both at 77K and at ambient temperature. The detectable emission at 300 K for all studied complexes indicates that non-radiative decay pathways have been greatly reduced in the hybrid 5,6-membered complexes compared to the 5,5-membered ones and, further, to their symmetric prototypes.

References

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P137

HIGH-SURFACE ACTIVATED CARBON-CATALYZED SYNTHESIS OF ISOINDOLES: A SIMPLE WAY TO AVOID USING PRECIOUS METALS

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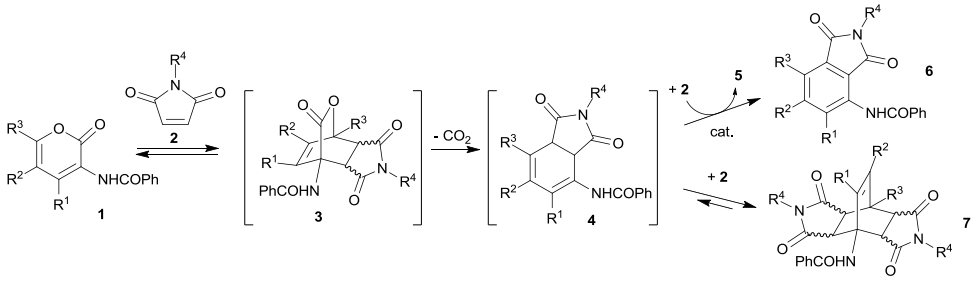

Isoindoles represent an important class of compounds with wide scope of applications and biological activity.[1] 2*H*-Pyran-2-ones and their fused analogues could represent attractive precursors for the synthesis of isoindole derivatives.[2,3] The synthesis we envisaged includes the cycloaddition between the appropriately substituted 2*H*-pyran-2-ones **1** and *N*-substituted maleimides **2**, yielding the primary CO_2-bridged derivatives **3**. With the thermally induced, spontaneous, retro-Diels−Alder elimination of the CO_2 from **3** the cyclohexadienes **4** are obtained, which can further be aromatized into the desired isoindole products **6**. The second molecule of *N*-substituted maleimide **2** acts as the scavenger for the hydrogen that is liberated in the aromatization of **4** consequently yielding isoindoles **6** and concomitantly forming the *N*-substituted succinimides **5**. The other possible scenario is the cycloaddition of a new molecule of dienophile **2** on the intermediate **4** (which enters in the reaction sequence as a new diene system) leading to the formation of the bicyclo[2.2.2]octene by-product 7.4 One might expect that both cycloaddition steps (1 ⇆ 3, 4 ⇆ 7) are reversible, but the irreversible elimination of CO2 from 3 shifts the first cycloaddition reaction far away from the starting compound 1. The second cycloaddition (i.e., 4 ⇆ 7) should also be reversible, therefore enabling the eventually formed double cycloadduct 7 to be transformed back into the intermediate **4** and so having another chance for the aromatization into **6**, but the reversibility of this step is highly dependent upon the temperature and substitution patterns of **1**.[2,3]

In the whole reaction sequence (cycloaddition/elimination/dehydrogenation) the catalyst predominantly influences the dehydrogenation step, which is essential to avoid the formation of bicyclo[2.2.2]octenes **7**. A comparison of the effect of various dehydrogenation catalysts and reaction conditions leads to the conclusion that Darco KB, as the metal-free catalyst with the highest specific surface area (playing the key role for the hydrogen transfer), and decalin as the solvent in a closed vessel, represent the most successful conditions for alternative synthesis of isoindole derivatives **6** via "evergreen" Diels–Alder reaction. The optimized conditions[2] were successfully applied for the synthesis of a set of over 20 novel isoindoles of the type 6. Within this research field we have also investigated the possibility of similar conversion of other systems, for example 9,10-dihydroanthracene.[5]

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[5] To be published.

P138

THE ROLE OF OXIDIZING AGENT ON THE MECHANISM OF CATALYTICAL CARBONYLATION OF ANILINE

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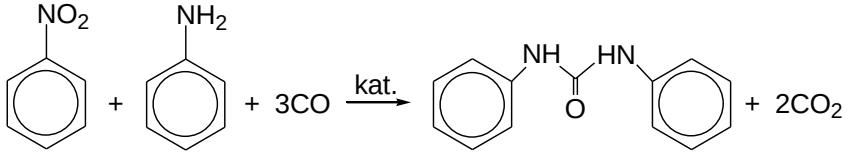
Carbamates and ureas are industrially important products and intermediates (in the synthesis of isocyanates, pesticides, pharmaceutics) traditionally prepared through the so-called phosgene route. The use of extremely toxic phosgene is major disadvantage of this reaction, therefore, new alternative methods are still being explored. Among possible catalytical alternatives, processes of amines carbonylation in the presence of various oxidants have a potential for a large scale. Palladium(II) complexes with N-donor ligands are considered as good catalysts for the carbonylation reactions [1]. There is a general agreement that catalytic activity of metal complexes with nitrogen containing ligands depends on electron density on the palladium atom and a strategy to design (and to obtain) more active catalysts is based on incorporation of new ligands to manipulate the steric and electronic effects around the palladium center.
In our work we carried out several syntheses of palladium(II) complexes of general structure $PdCl_2(X_nPy)_2$ and we investigated the relationships between the structure and electronic properties of X_nPy and catalytic activity of $PdCl_2(X_nPy)_2$ complexes in carbonylation of aniline (model amine). We studied substituent effect in X_nPy on the rate determining step of aniline (AN) carbonylation carried out in presence of two oxidizing agents: nitrobenzene (process 1) and molecular oxygen (process 2).



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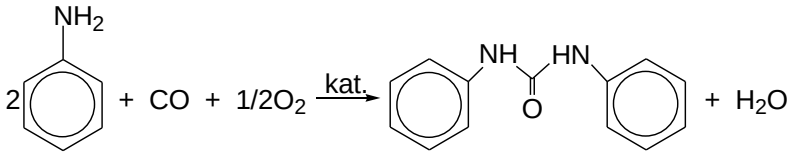

(2)

Electron withdrawing / donating properties of X_nPy ligands were correlated with activities of $PdCl_2(X_nPy)_2$ complexes in presence of Fe / I_2 as co-catalyst. We observed an increase of conversions and yields with increasing X_nPy ligand basicity in the system employing NB as oxidant whereas the opposite tendency was noticed when NB was replaced with O_2. On the basis of presented results we propose two different mechanisms of AN carbonylation [2,3].We optimized reaction conditions in order to obtain high catalyst selectivity toward N,N'-diphenylurea.

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P139

CHIRAL PRIMARY AMINE TAGGED TO IONIC GROUP: THE FIRST IMMOBILIZED ORGANOCATALYST FOR ASYMMETRIC ADDITIONS OF C-NUCLEOPHILES TO α,β-ENONES

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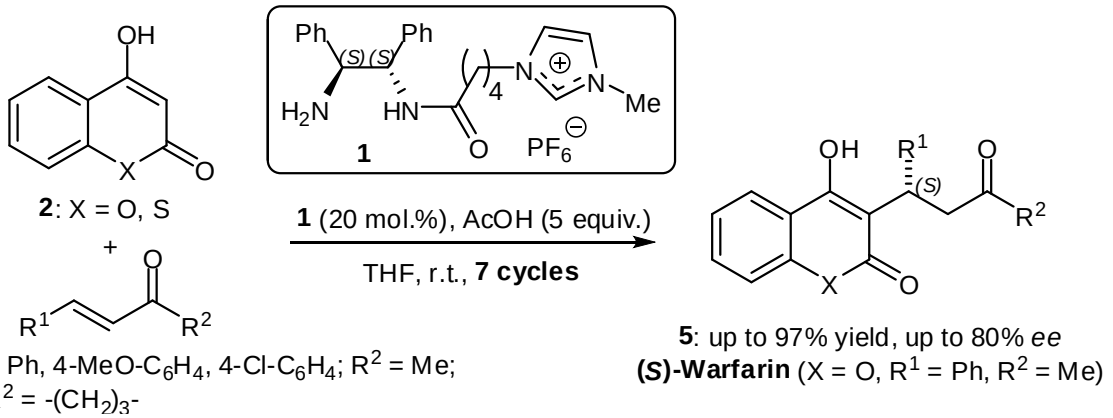
The asymmetric organocatalysis is a rapidly developing area of organic chemistry. However, the majority of modern organocatalysts are rather expensive. Normally, they are needed in a significant amount (10-20 mol. %) which is actually lost during the product isolation, therefore, the development of immobilized recoverable organocatalyst versions remains challenging. Asymmetric Michael reactions are among the most popular organocatalytic transformations as they allow a simple and efficient synthesis of enantiomers of clinically useful medications. Recently, several polymer- or ionic liquid-supported organocatalysts (α,α-diarylprolinol silyl ethers) for reactions of C-nucleophiles with α,β-unsaturated aldehydes have been synthesized [1]. However, these catalysts exhibit poor catalytic performance in corresponding reactions that involve α,β-unsaturated ketones.
Herein we report on the first immobilized organocatalyst **1** for asymmetric Michael reactions of C-nucleophiles with α,β-enones which contain primary amino group along with ionic fragment. In the presence of this catalyst and an acidic co-catalyst (AcOH), hydroxycoumarin and its sulfur-containing analog **2** react with benzylideneacetone derivatives **3** or cyclohexenone **4** to afford corresponding Michael adducts **5** with high yields (up to 97%) and reasonable enantioselectivity (up to 80%). Application of this methodology allowed a simple synthesis of the most active (S)-enantiomer (*ee* 80%) of clinically useful anticoagulant warfarin from available starting compounds in a single step.



The catalyst is easily recoverable and efficiently reusable three times, though, afterwards its activity and stereodifferentiating ability gradually decline. The analysis of recovered catalyst samples by ESI-MS allowed us to reveal undesirable side reactions that poisoned the catalyst, and propose an approach to its reactivation. This information may be useful for the development of robust immobilized organocatalysts for asymmetric Michael reactions involving the iminium ion formation step.

This work was financially supported by the President of the Russian Federation (grant for young Ph.D. No. 3551.2012.3), the Department of Chemistry and Material Sciences of Russian Academy of Sciences (Basic Research Program No. 1) and the Russian Foundation of Basic Research (project 12-03-00420).

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P140

ENANTIOSELECTIVE ADDITION OF CARBON ACIDS TO α-NITROALKENES: THE FIRST ASYMMETRIC AMINOCATALYTIC REACTION IN LIQUEFIED CARBON DIOXIDE

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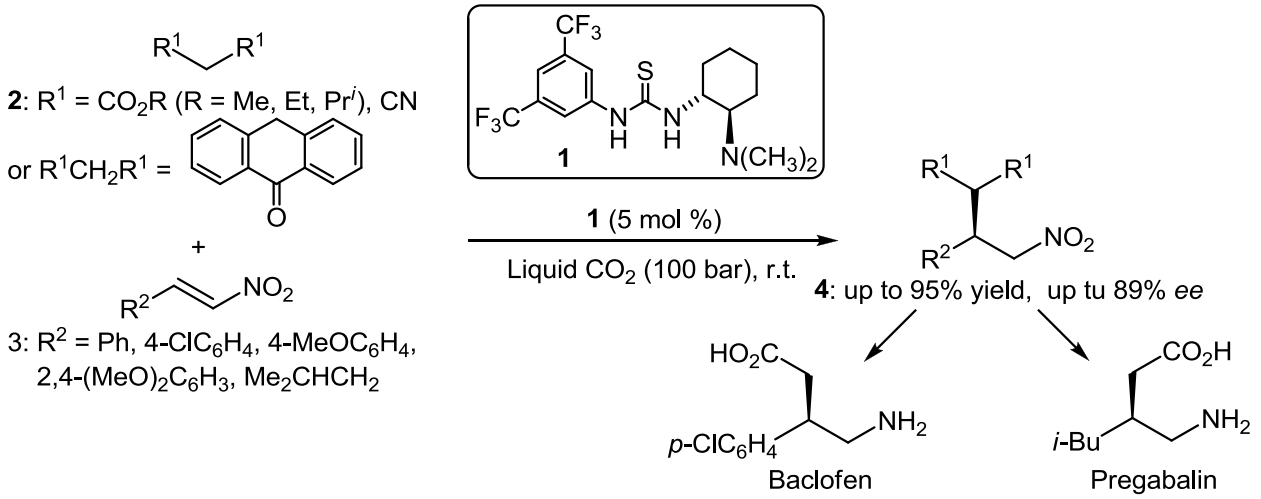
The asymmetric organocatalysis is a powerful tool for enantioselective synthesis of organic compounds. In the presence of small chiral molecules, commonly amines, prochiral compounds generate chiral products in high yields and with excellent enantioselectivities. However, to the best of our knowledge, no asymmetric aminocatalytic reactions in carbon dioxide medium, which is extensively used as a green solvent in various chemical reactions, have been so far communicated. Moreover, a possibility of performing these reactions in liquefied CO_2 was under question because of the by-production of carbamic acid salts from primary or secondary amines and CO_2, which deactivate the catalyst. An undesirable interference of carbon dioxide with the hydrogen bond network generated by organocatalyst and reagents in the transition state might also create problems.

We were happy to discover that enantioselective Michael reactions between carbon acids and α-nitroalkenes are catalyzed efficiently by Takemoto's bifunctional tertiary amine–thiourea derivative **1** in the liquid CO_2 medium [1]. Nucleophiles **2** (dialkylmalonates, malononitrile or anthranone) enantioselectively react with electron-deficient alkenes **3** (β-nitrostyrene derivatives bearing electron-donating or electron-withdrawing groups on the aromatic ring or 1-nitro-4-methylpentene) at ambient temperature and CO_2 pressure 100 bar to afford the corresponding Michael adducts **7**. As a rule, the yields and *ee*s of adducts **7** in the CO_2 medium were comparable with or even higher than in conventional organic solvents (e.g., toluene) and the procedure is scalable. The experiments in an autoclave equipped with sapphire windows showed that the reactions were homogeneous under the proposed conditions. This methodology is applicable to the synthesis of intermediates for the production of most active (*R*)-enantiomer of therapeutically useful $GABA_B$ receptor agonist baclofen, and a chiral anticonvulsant pregabalin.



The work was financially supported by the Presidium of Russian Academy of Sciences (Basic Research Program No. 8) and the Russian Foundation of Basic Research (project 11-03-12163).

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P141

DEVELOPMENT OF PRIMARY AMINE BASED ORGANOCATALYSTS FOR ASYMMETRIC ALDOL AND MICHAEL REACTION

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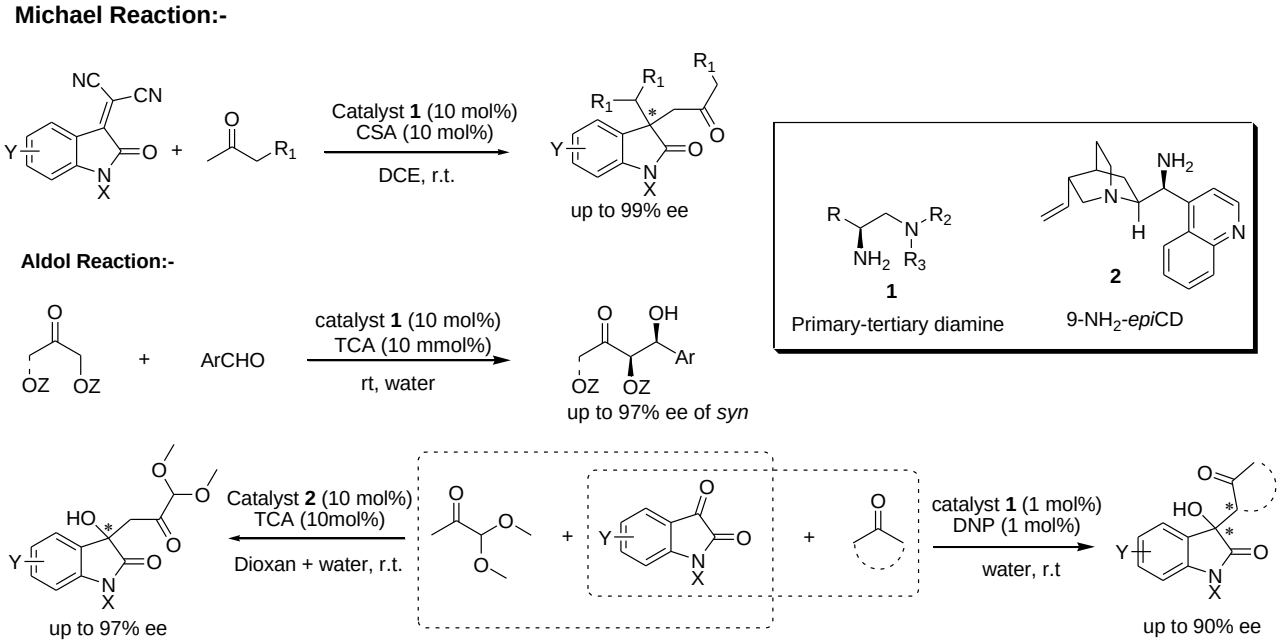
Chiral secondary amine-based organocatalysts have proven to be an extremely powerful catalyst, and have dominated the field of amino catalysis. Recently, aminocatalysis using chiral primary amine-based organocatalysts besides derived from natural amino acids, *Cinchona* alkaloids and other chiral amines have received renewed attention and have become the focus of intensive research endeavours. The primary amino functions, *vis*-a-*vis* the secondary pyrrolidine moiety, provide unique reactivity and stereoselectivity in direct asymmetric aldol reaction and Michael reaction.

The Aldol and Michael reaction represents one of the most powerful carbon-carbon bond-forming reactions for both natural and synthetic chemistry. Over the past few years, we have successfully explored chiral secondary amine based protonated prolinamides for enantioselctive direct cross aldol reaction and *cinchona* alkaloid derived organocatalyst for Michael reaction.[1] In the present study, we have designed and synthesized primary amino acid derived primary-tertiary diamine organocatalysts (**1**) for asymmetric direct cross aldol reaction[2] and Michael reaction. We have also studied the direct cross aldol reaction of pyruvic aldehyde dimethyl acetal with isatins catalyzed by *cinchona* alkaloid derived organocatalyst **2** (**Scheme 1**). The details of these investigations will be presented.



Scheme 1

References:-

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P142

TANDEM CATALYSIS BY LIPASE AND AN ORGANOCATALYST

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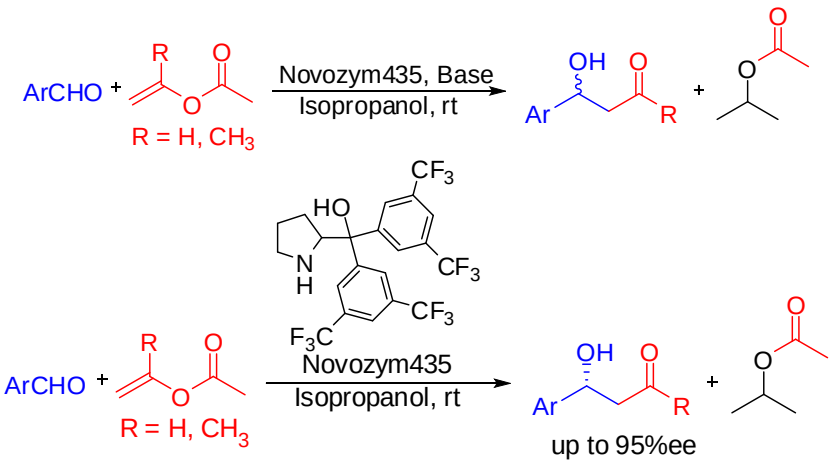
Tandem catalysis involving biocatalysts such as lipases have recently generated considerable interest due to enhanced efficacy of the reaction process and ease of handling, preferably in a single reactor. Recently, novozym435 in tandem catalysis with Ru was successfully employed in the synthesis of chiral polymers.[1] The aldol reaction is one of the most exploited carbon-carbon bond forming reactions in organic synthesis, while acetaldehyde or acetone are the most important precursors for two and three carbon elongation.[2] Despite remarkable progress in homogeneous and heterogenous catalysis including organocatalysis, the aldol reaction of acetaldehyde still remains an interesting challenge, which may act either as a nucleophile or electrophile, owing to its unsubstituted α-position, thereby leading to the formation of side products from dehydration, self condensation etc.

We have used novozym435 tandemly with organocatlyst in aldol reaction of acetaldehyde. The reaction apparently involves lipase catalyzed *in situ* generation of active form of acetaldehyde and acetone from vinyl acetate and isopropenyl acetate respectively followed by organocatalyzed aldol reaction with aromatic aldehydes for the preparation of β-hydroxy aldehyde/ketones. The result of our investigation will be presented.[3] The methodology further opens the field of organocatalysis, wherein the tandem reactions in presence of biocatalysts may facilitate the development of newer strategies in organic synthesis. Further we have got high enantioselectivity after using appropriate organocatalyst with suitable enzyme(**Scheme 1**).



Scheme 1

References:

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P143

NOVEL TITANIUM(+4) COMPLEXES WITH BIDENTATE PHENOL ALCOHOL LIGANDS IN ETHYLENE POLYMERIZATION

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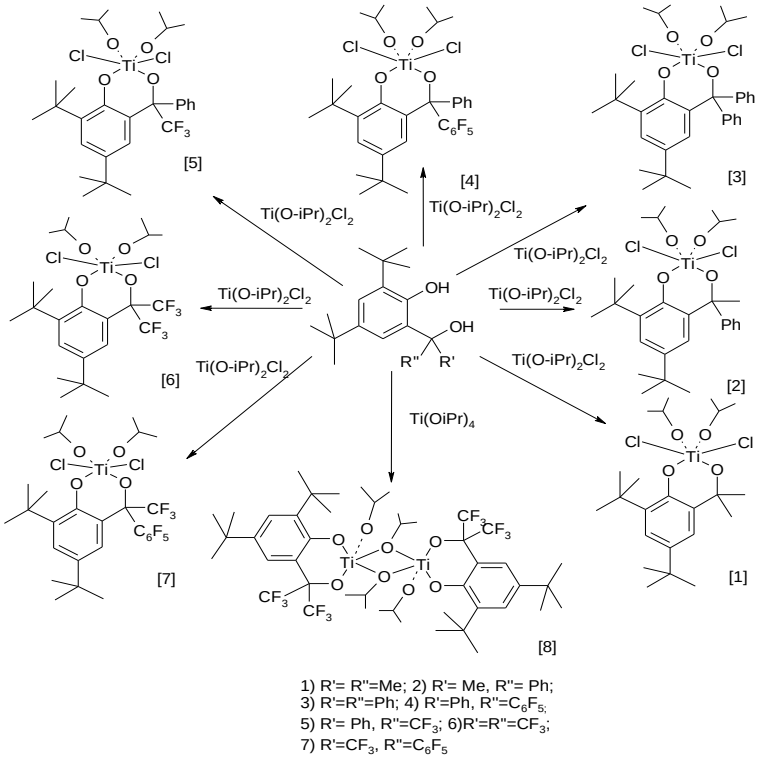
Mononuclear dichloride diisopropoxide complexes (**1-7**) and binuclear (**8**) of titanium(IV) isopropoxide with a bidentate phenol alcohol ligands were obtained.



1) R'= R''=Me; 2) R'= Me, R''= Ph;
3) R'=R''=Ph; 4) R'=Ph, R''=C_6F_5;
5) R'= Ph, R''=CF_3; 6)R'=R''=CF_3;
7) R'=CF_3, R''=C_6F_5

The structures of the complexes were confirmed by X-ray diffraction. The dimeric structure of complex **8** is typical of alkoxy compounds and contains the bridging fragment Ti(μ-OPri)$_2$Ti; the coordination polyhedron of the Ti atom is a distorted tetragonal pyramid. In complex **6,7** the Ti atom has a distorted octahedral environment made up of the O atoms of the ligand, the Cl atoms, and the O atoms of two coordinated propan-2-ol molecules. The catalytic properties of complexes **1-8** in ethylene polymerization were studied with such promoters as polymethylaluminoxane (MAO), trimethylaluminum, triisobutylaluminum, diethylaluminum chloride, and Et_2AlCl—$MgBu_2$ (from 300 to 1100 kg of polyethylene (PE)/(mol of Ti) h atm). The dichloride diisopropoxide complexes obtained from the same ligand and $Ti(O\text{-}iPr)_2Cl_2$ were catalytically active in the presence of MAO, i-Bu_3Al, and Me_3Al. For the catalytic system containing the dichloride diisopropoxide complex, the best promoter is Me_3Al (1100 kg of PE/(mol of Ti) h atm). The polymer obtained on all the catalytic systems is linear polyethylene characterized by high molecular weights (Mw = 593900—2000000 g mol^{-1}) and high polydispersity indices (Mw/Mn = 2.8—15). Various conjectures were made about why lithium and magnesium chlorides have the promoting effects.

We are grateful to Russian Foundation for Basic Research (project nos. 11-03-12172, 11-03-00297 and 12-03-00974).

P144

PORGANOCATALYTIC MICHEAL REACTIONS, DESYMMETRIZATION AND DOMINO HECK REACTIONS

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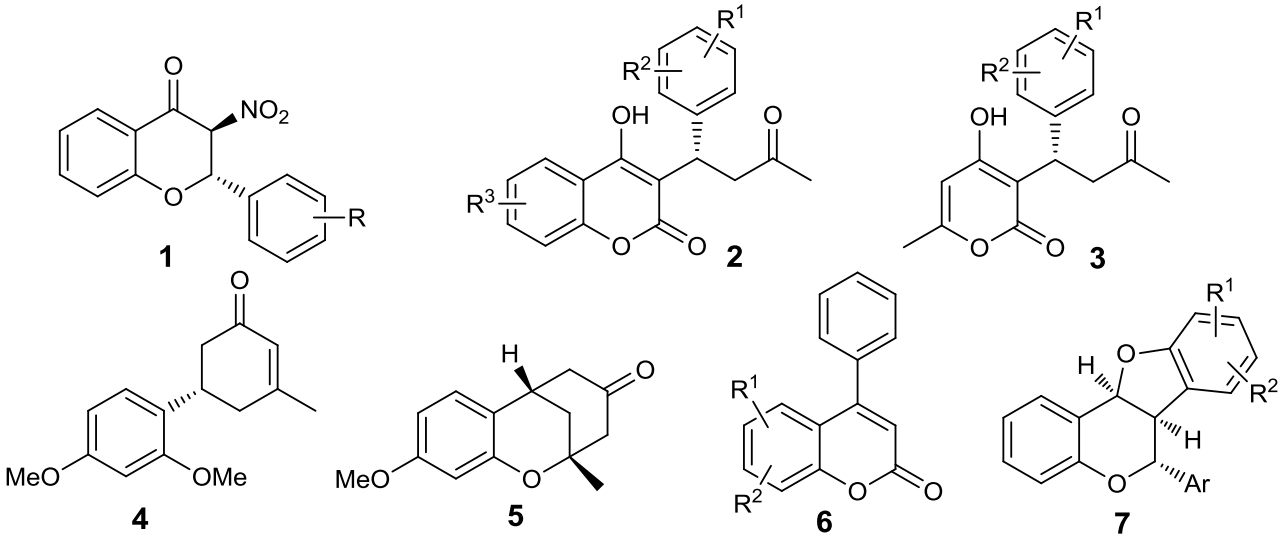
Organocatalytic enantioselective intramolecular oxa-Michael reactions were studied for the preparation of 3-nitroflavanone derivatives (**1**) using the cinchona alkaloid-derived thiourea organocatalyst **2**.[1] Enantioselective organocatalytic Michel additions of 4-hydroxycoumarins and 4-hydroxy-6-methyl-2*H*-pyran-2-one to α,β-unsaturated ketones were carried out with quinine-derived primary amine organocatalysts to produce warfarin analogs **2** and **3** with versatile substitution pattern.[2] Organocatalytic enantioselective desymmetrization produced derivative **4**, which can serve as a precursor for the preparation of the 2,6-methano-2-methylbenzoxocin-4-one derivative **5**.[3] Domino Heck lactonization[4] and Heck oxyarylation[5] reactions were explored for the preparation 4-arylcoumarin (**6**) and racemic 6-arylpterocarpan (**7**) derivatives, respectively.



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P145

PILOT TESTING OF THE NEW DOMESTIC ZHKD-TYPE CATALYSTS FOR DEHYDROGENATION OF ISOAMYLENES TO ISOPRENE

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The KDOM-08 catalyst, being presently used at the Synthetic Rubber Plant, OAO Nizhnekamskneftekhim for dehydrogenation of isoamylenes to isoprene, allows insufficient isoprene yield over the entire period of its industrial performance. In order for process efficiency to be increased, the more stable and reactive catalysts are needed. Within the framework of RF Government Resolution No.218, the new ZHKD-1 and ZHKD-2 ferric potassium catalysts were developed by enhancing the formulation and optimizing phase composition due to correct choice of the ratio of initial components. To estimate possible adoption to the new domestic ferric potassium catalysts, pilot tests of ZHKD-1 and ZHKD-2 catalysts were performed at the Synthetic Rubber Plant, OAO Nizhnekamskneftekhim during isoamylene dehydrogenation to isoprene in adiabatic fixed-bed catalytic flow reactors. The KDOM-08 catalyst, 25 tons of which is used in the reactor No.1 of the first system, served as the reference one. ZHKD-1 and ZHKD-2 catalysts were fed into concurrent reactors Nos. 7 and 8 of the fourth system.

In industry, catalysts operate under severe conditions, with raw feedstock and steam feed rates being ever-changing to increase the target product yield and to lower energy consumption for isoprene production. Therefore, in order to carry out a comparative testing of catalyst performance, the two regimes of their operation were chosen, namely at lower (1-2 t/h) and greater (2.6-3.0 t/h) raw feedstock feeding corresponding to various times of interaction between reaction mixture and catalyst.

It was shown that the KDOM-08 catalyst is able to work more efficiently under industrial conditions at feed rates of 1-2 t/h during 1-3 thousand hours, which is followed by decreasing in performance characteristics due to gradual deactivation of catalyst. By isoprene yield, ZHKD-1 and ZHKD-2 catalysts are more superior to their industrial counterpart. It was also shown that in case of ZHKD-2 catalyst, the more efficient workability is observed even at longer feeding time (4-5 thousand hours) at feed rates of 1-2 t/h, while in case of ZHKD-1 catalyst, the best activity (30-33%) and selectivity (87-92%) are observed during 5 thousand hours at greater feed rates of 2.3-3.0 t/h.

Analysis of catalyst workability over the last 1000 hours showed that at the same process temperatures (619°C) and the same raw feedstock feed rates (2.5 t/h), ZHKD-1 and ZHKD-2 catalysts were used under less dilution of raw feedstock with steam (6.1 t/t) compared with the KDOM-08 catalyst (6.8 t/t). Redesigning of reactors Nos. 7 and 8 enabled lowering the catalyst load from 25 down to 17 tons and facilitated almost twofold increase in daily isoprene yield per 1 ton of catalyst. It seems obvious that due to the increased activity and selectivity as well as the lowered loading volume, using ZHKD-1 and ZHKD-2 catalysts makes economic sense.

This work was supported by the RF Ministry of Education and Science.

P146

EFFECT OF HIGH PRESSURE ON ASYMMETRIC ORGANOCATALYTIC MICHAEL AND FRIEDEL-CRAFTS REACTIONS

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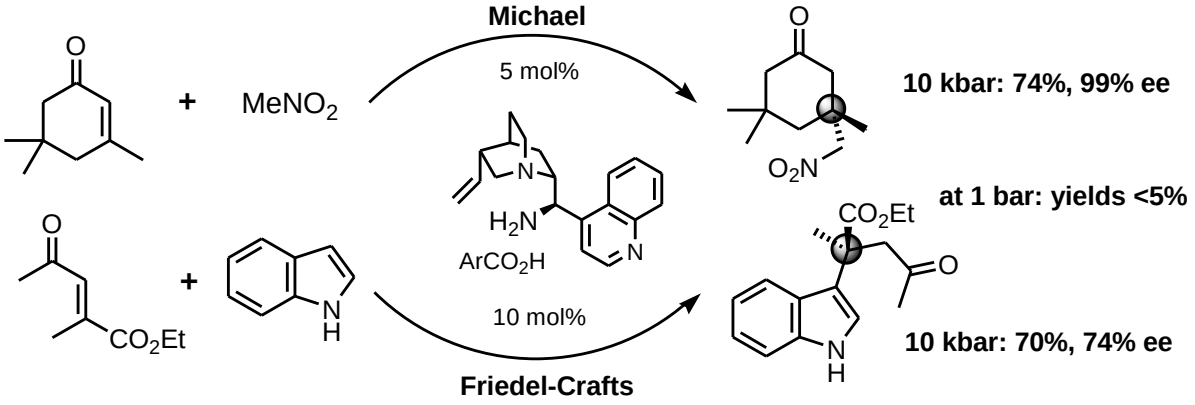
The high-pressure methodology in liquid systems has been quite well recognized as a very powerful tool in organic synthesis,[1] but the influence of pressure on asymmetric metallo- and organocatalytic reactions still remains a poorly explored area of catalysis.[1] These facts, as well as the remarkable progress made in organocatalysis in recent years,[2] prompted us to study the effect of pressure on selected difficult organocatalytic reactions e.g. requiring high loading of catalyst and long reaction time. Increased pressure, can also assists in overcoming reactions ineffective under thermal conditions because of steric constrains and electronic effects. In our high-pressure studies we focused attention on challenging 1,4-conjugate additions of carbon nucleophiles to prochiral β,β-disubstituted Michael acceptors enabling the generation of quaternary stereogenic centers (Scheme).[3]



In this communication we demonstrate the positive effect of hydrostatic pressure (up to 10 kbar) on enantioselective 1,4-conjugate additions of C-nucleophiles to prochiral sterically congested β,β-disubstituted enones catalyzed by simple chiral amines. We have found that high pressure remarkably accelerate selected Michael[4] and Friedel-Crafts[5] reactions with good to high enantioselectivity.

Acknowledgements: Financial support from the Polish National Science Centre (Grant No. N N204 145740) is gratefully acknowledged.

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P147

A NEW CLASS OF CHIRAL POSITIVELY CHARGED METAL COMPLEXES AS ASYMMETRIC CATALYSTS OF C-C BOND FORMATION

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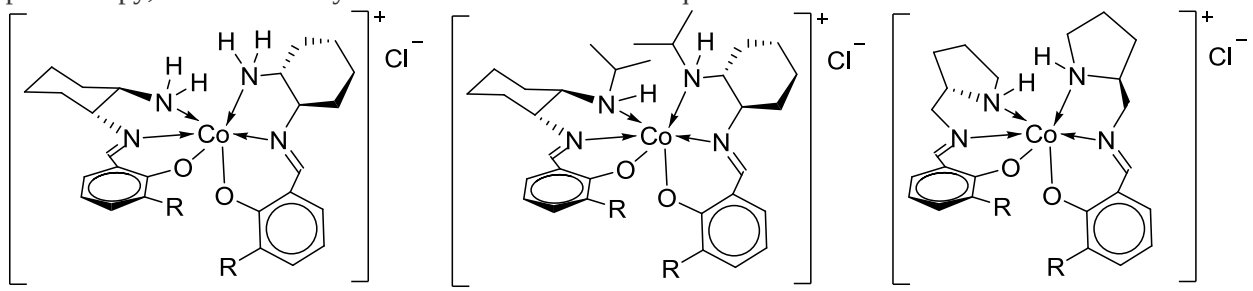
Phase-transfer asymmetric catalysis is a convenient and versatile method for obtaining enantiomerically enriched compounds. Phase-transfer catalysts derived from the *Cinchona* alkaloids have been employed as inexpensive and attractive organocatalysts in enantioselective PTC processes. [1] The disadvantage of these catalysts is that they suffer from stability issues and are difficult to modify.[2] Our work is dedicated to the creation and study of a new class of positively charged hydrophobic stereochemically inert metal complexes that can be used as catalysts to construct C-C bonds enantioselectively.

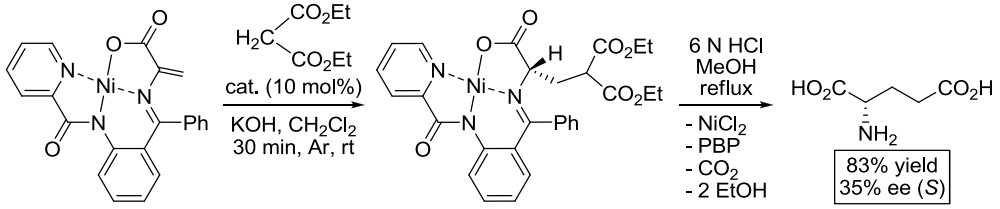
To construct the catalysts of this new class we used ligands that consist of the Schiff-bases of salicyl aldehyde derivatives and chiral diamines. Mixing these ligands with $Na_3[Co(CO_3)_3]\cdot 3H_2O$ readily affords the complexes depicted in Figure 1, solely with Λ-configuration. All complexes are characterized by IR spectroscopy, elemental analysis and various NMR techniques.



R= -H, -OMe, $-CH_2-CH=CH_2$

Figure 1. Chiral cationic complexes (Λ-configurations)

The catalytic activity of the obtained complexes was tested in a Michael reaction (Scheme 1) and a cyanosylilation of benzaldehyde using trimethylsilyl cyanide. Preliminary results indicate that both reactions can be catalyzed with this system in a stereoselective manner. (*S*)-glutamic acid was obtained in 83% yield with 35% enantiomeric excess (ee).



Scheme 3: Michael addition of diethyl malonate on achiral Ni(II) complex

All three catalysts were tested in the trimethylsilylcyanation of benzaldehyde. The latter was converted into the silylated cyanohydrin with up to 27% ee.

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P148

PHOTOCATALYTIC CARBON–CARBON BOND ACTIVATION OF KETONES BY RHODIUM(III) PORPHYRINS

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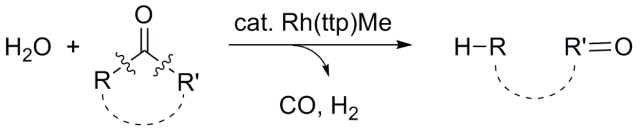
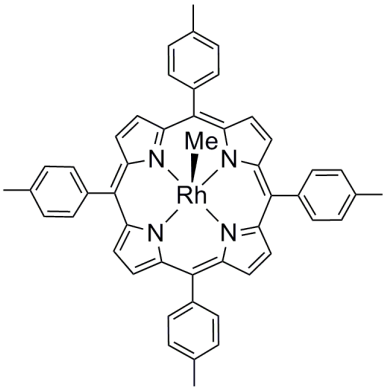
Catalytic cleavage of unactivated carbon-carbon bond is an attractive yet very challenging aspiration in organometallic chemistry. Traditionally, the catalytic carbon carbon bond activation (CCCA) was accomplished under thermal conditions. However, the high temperature required is energy-intensive and it introduces the selectivity problems. Recently, the goal has been achieved with the help of the abundant natural resources: light and water. To pursue a mild, selective and catalytic bond cleavage, light has been introduced into the reaction. We discovered the selective CCCA of unstrained ketones by rhodium(III) porphyrins to yield the corresponding O-incorporated organics. In the presence of water, the photocatalysis was achieved under ambient conditions with good turnovers. Through mechanistic studies, we propose Rh(ttp)OH as a key intermediate and water acts as an oxidizing agent.





Structure of Porphyrin, Rh(ttp)Me

Acknowledgement
We thank the Research Grants Council of Hong Kong for financial support.

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P149

CONTINUOUS-FLOW SELECTIVE HYDROGENATIONS USING BIMODAL TITANIA MONOLITHS-BASED CATALYSTS

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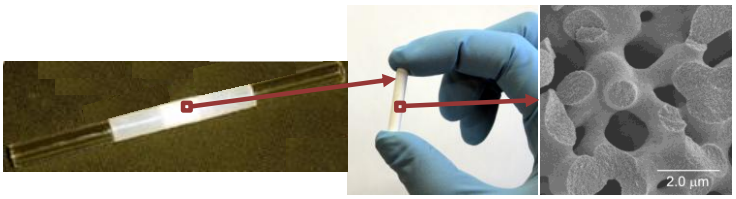
Continuous-flow catalytic processes represent a convenient alternative to heterogeneous phase batch systems in terms of efficiency, safety, waste emission, purification, automation, space and energy consumption, [1] thus providing a considerable contribution to the sustainability of long-term production of chemical compounds, particularly fine-chemicals. [2]Monolith-based reactors have significant advantages compared to conventional packed-bed systems, including improved fluid dynamics, better heat and mass transfer, lower pressure drop, narrow residence time distribution, which ultimately result in higher productivities. [3]Herein we report the first example of monolithic mesoreactor based on metal nanoparticles (MNPs) supported onto bimodal porous titania and its use in catalytic processes under continuous flow conditions.
Single-phase anatase monoliths were prepared, featuring a reproducible open-cell structure with a dual porosity: 1) uniformly distributed flow-through macropores of average diameter 2 μm, 2) diffusive mesopores of 6.0 nm size, connected through 4.1 nm windows due to the interstices of TiO_2 nanocrystallites (6-7 nm), within a skeleton of ca. 1 μm thickness (Fig. 1).



Entry	Reactor	Catalyst	TOF [h^{-1}]	STY [kg l^{-1} h^{-1}]
1	Batch	Pd@TiO_2 ground monolith	932	0.01
2	Flow Packed bed	Pd@mesoporous TiO_2	295	0.47
3		Pd@TiO_2 ground monolith	1131	0.95
4	Flow Monolith	Pd@TiO_2 monolith	1673	4.02
5		Pd@SiO_2 monolith	272	0.27

Fig 1. Monolith: Cladded, as-prepared and SEM image (left). Productivities for batch and flow CHX hydrogenation (right).
The as-prepared Pd@TiO_2 cladded monoliths were employed as catalyst in continuous flow hydrogenation reactions. Various substrates were chosen to illustrate the efficiency of Pd@TiO_2 monoliths in hydrogenation reactions in terms of both space-time-yield and selectivity. The efficiency of the Pd@TiO_2 monolith catalysts was compared with that of parent systems, both in batch (stirred tank) and flow (packed bed) reactors, under similar reaction conditions. Representative results for the hydrogenation of cyclohexene (CHX) are reported in Fig. 1 in terms of turnover frequency (TOF = $mol_{product}$ / mol_{Pd} x h) and space-to-time yield (STY = $kg_{product}$ / $litre_{reactor\ volume}$ x h).
The monolithic catalysts exhibited excellent performance and long-term stability, as no significant conversion decrease was observed over several hours. In the hydrogenation of cyclohexene, the catalysts retained > 99 % of its starting activity after 3 days time-on-stream, providing an overall TON > 125000. Pd leaching in solution was below the detection limit in any case (ICP-OES).

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P150

ASYMMETRIC CATALYSIS OF DIELS-ALDER REACTIONS WITH IN SITU GENERATED HETEROCYCLIC ORTHO-QUINODIMETHANES

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The Diels-Alder reaction is probably the most powerful technology in the synthetic repertoire for single-step constructions of complex chiral molecules. The synthetic power of this fundamental pericyclic transformation has greatly increased with the emergence of asymmetric catalytic variants, and research aimed at further expanding its potential is still exciting and fascinating the chemical community. Here, we document the first asymmetric catalytic Diels-Alder reaction of *in situ* generated heterocyclic *ortho*-quinodimethanes (*o*QDMs), reactive diene species that have never before succumbed to a catalytic approach. Asymmetric aminocatalysis, that uses chiral amines as catalysts, is the enabling strategy to induce the transient generation of indole-, pyrrole- or furan-based *o*QDMs from simple starting materials, while directing the pericyclic reactions with nitroolefins and methyleneindolinones toward a highly stereoselective pathway. The approach provides straightforward access to polycyclic heteroaromatic compounds, which would be difficult to synthesize by other catalytic methods, and should open new synthetic pathways to complex chiral molecules using nontraditional disconnections.

P151

GOLD-CATALYZED HYDROAMINATION OF ALKYNES AND ALLENES WITH AMMONIA AND HYDRAZINE: A MECHANISTIC PERSPECTIVE

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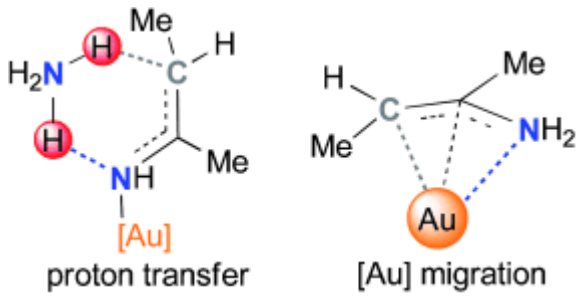
The formation of nitrogen-carbon bonds represents a highly valuable synthetic method to prepare important chemical products. Hydroamination is a simple way of making carbon-nitrogen bonds with atom economy and different transition metal homogenous catalysts have been used to this aim. However, despite the economic interest of using small N-nucleophiles, particularly ammonia and hydrazine, efficient processes for combining these molecules with simple organic molecules are still scarce. In presence of transition metal centers ammonia and hydrazine readily form Werner complexes, which are usually inert.

In the last years gold has been identified as an efficient hydroamination catalyst.[1] Recently, Bertrand and co-workers described the hydroamination of a variety of unactivated alkynes and allenes with both NH_3 and H_2NNH_2 catalyzed by gold complexes prepared with a cyclic (alkyl)(amino)carbene (CAAC).[2,3]

Following our previous work on the mechanism of gold-catalyzed hydroaminations,[4] we have performed the theoretical investigation of the hydroamination with ammonia and hydrazine catalyzed by the Bertrand's gold-CAAC complex.[5] The mechanistic study has identified two key factors, which account for the efficiency of the gold-CAAC complex in the addition of N-H bonds to CC multiple bonds. On one hand, the excess nucleophile (NH_3 or N_2H_4) assists in the proton transfer, and on the other an unforeseen [Au] migration allows a feasible enamine–imine tautomerization.



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P152

ELECTROCATALYTIC TRANSFORMATION OF AVAILABLE ALCOHOLS AND CARBONYL COMPOUNDS TO VALUABLE ACIDS ON NiO(OH) ANODE

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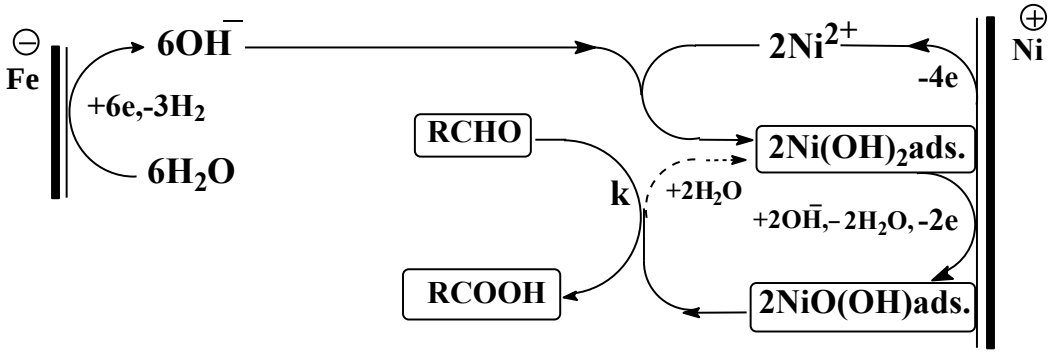
Integrated research efforts have been performed[1-5] with a focus on the development of high performance (65-95% yield) processes based on green chemistry principles to prepare acids for practical applications such as glutaric (antibacterial, antiviral, and fungicidal activity), pyrazolecarbonic (semiproducts in the synthesis of insecticides and acaricides alkylaromatic (semiproducts in the synthesis of a broad scope of pharmaceuticals and odoriferous substances) acids by electro-oxidative transformation of, accordingly, 1,5-pentanediol, 4-formylpyrazoles and alkylaromatic alcohols with two or more CH_2 groups in the side chain. The reactions performed in an undivided cell on the Ni anode in aqueous alkali medium. They are environment-friendly and easily scalable processes of the heterogeneous electrocatalysis with NiO(OH) as an oxidizer-catalyst that self-regenerates on the anode surface according to the next principle scheme:



The regularities of electrocatalytic oxidation on the NiO(OH) electrode and their relationship to the structure of initial compounds will been discussed.

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P153

AN ENTRY TO CARBAPENAMS VIA ASYMMETRIC KINUGASA REACTION INVOLVING CYCLIC NITRONES DERIVER FROM SUGARS AND TERMINAL ACETYLENES

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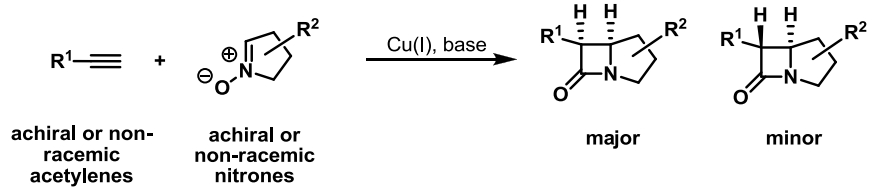
The copper(I) mediated reaction of nitrones and terminal acetylenes, which is known as Kinugasa reaction, represents an attractive method of direct formation of the β-lactam ring.[1,2] This reaction can be performed in many ways including diastereo- and enantioselective versions. In most cases, as 1,3-dipoles simple acyclic nitrones have been used.[3] Number of reactions involving cyclic ones is limited.

3.



Herein, we present our recent studies on Kinugasa reaction involving cyclic nitrones readily available from hydroxy acids or pentoses and terminal acetylenes either achiral or bearing a stereogenic center.[4] All investigated reactions proceeded in good yield and with high diastereoselectivity providing an attractive entry to carbapenams of a potential biological activity.[5] The stereochemical pathway of the reaction and influence of geometry and substitutions in one or both reactants on direction and magnitude of asymmetric induction will be discussed.

This project was financed by the Europen Union within the Europen Regional Development Fund, project POIG. 01.01.02.-14-102/09

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P154

ASYMMETRIC COUNTERANION-DIRECTED HOSOMI-SAKURAI REACTION

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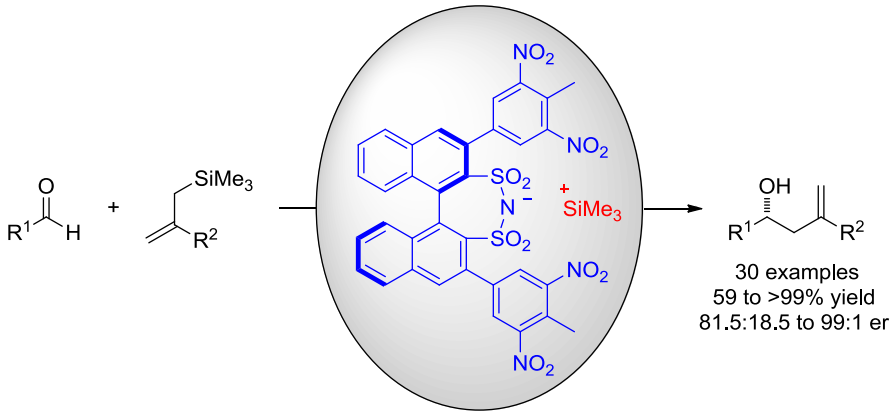
Asymmetric allylation reactions are amongst the most useful reactions in organic synthesis and have been used to evaluate the potential of catalysts and catalytic concepts for asymmetric synthesis.[1] The development of enantioselective Lewis-acid catalysts faces the problem of non-enantioselective TMS^+ catalysis after initial activation by the chiral Lewis-acid.[2] Our group has developed the concept of asymmetric counteranion-directed catalysis (ACDC).[3] The underlying idea is to use ion-pairing between a cationic reaction intermediate or transition state and a chiral counteranion to induce enantioselection. We recently extended the applicability of this concept to organo Lewis-acid catalysis and realized counteranion-directed enantioselective Mukaiyama aldol reactions, as well as, vinylogous and bisvinylogous Mukaiyama aldol reactions.[4]



We here report an enantioselective Hosomi-Sakurai allylation of aromatic aldehydes. The key to this method is turning the TMS^+ catalysis of the Hosomi-Sakurai reaction into the desired catalytic regime and employing asymmetric counteranion-directed catalysis.

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P155

APPLICATION OF TRANSITION METAL CATALYSIS FOR THE SYNTHESIS OF 2-ARYL SUBSTITUTED 1-AMINOCYCLOPROPANE PHOSPHONATES

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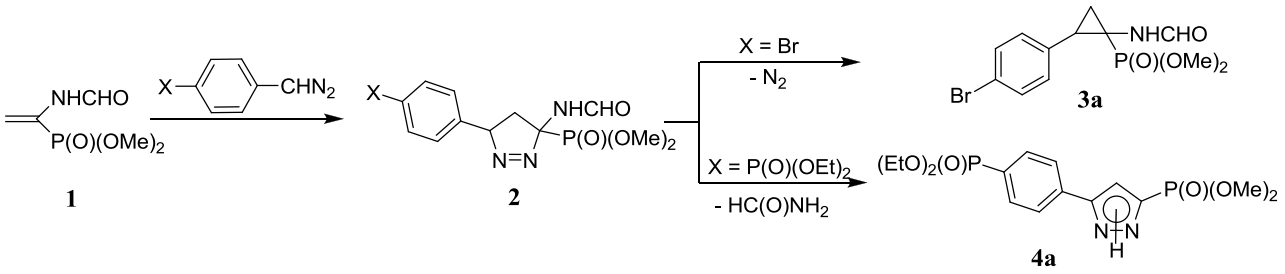
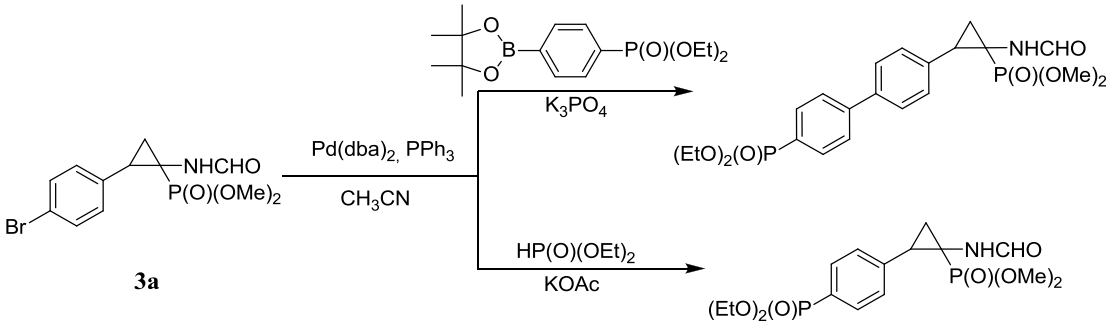
1-Aminocyclopropanephosphonates[1] (ACP) are of interest as phosphorus isosters of 1-aminocyclopropane carboxylic acids playing important role in living organisms. Their great potentialities for practical use stimulate the development of novel synthetic approaches to ACP and their derivatives. 1,3-Dipolar cycloaddition reaction of aryldiazomethanes with dimethyl 1-(formylamino)ethylenephosphonate (**1**) affords 5-substituted dimethyl 3-(formylamino)-4,5-dihydro-3H-pyrazol-3-phosphonates (**2**).[2] Their deazetization provides a straightforward access to 2-aryl substituted ACP (**3**). This method is essentially limited by the electronic demands of the substituent on aromatic ring: in the case of electron withdrawing groups a elimination of formamide, rather than nitrogen, takes place with 5-aryl-3-pyrazolphosphonates (e. g. **4a**) formation.



In this context the elaboration of methods for post-modification of some readily accessible 2-aryl substituted ACP is very desirable. We have shown that dimethyl 2-(4-bromophenyl)-1-formylaminocyclopropanephosphonate **3a** can serve as a convenient precursor for a family of 2-aryl substituted ACP by palladium catalyzed cross-coupling reactions of carbon-carbon and carbon-heteroatom bonds formation, some examples are given below. In each case pertinent conditions (pre-catalyst, ligand, base, solvent, temperature) were found to obtain the target products in high yields in both small and large scale experiments.



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P156

NEW METHOD OF SYNTHESIS OF COMBRETASTATIN A-4 ANALOGS

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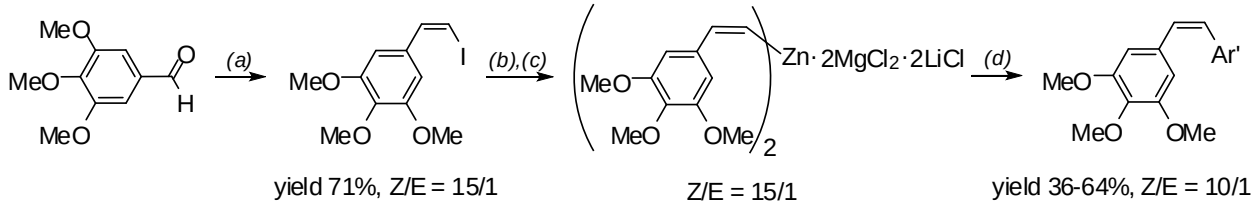
Combretastatin A-4 (CA-4), isolated from South African tree *Combretum caffrum*, is one of the most potent antivascular and antimitotic agents acting at the colchicine binding site of tubulin, that has shown excellent activity against multidrug resistant cancer cells. Due to their unique anticancer properties and simple structures, these *Z*-stilbenes have drawn significant attention of medicinal chemists as lead structures for the design of novel antitumour agents. It has been demonstrated that *Z*-combretastatins manifest much higher biological activity than the corresponding *E*-isomers. However, CA-4 and its analogs are prone to thermal *Z*/*E*-isomerisation, even during the course of synthesis. This indicates a strong need for the development of convenient, mild and stereoselective methods for preparation of such electron-rich *Z*-stilbenes.

We have developed mild and stereoselective approach to Z-stilbenes, using palladium-mediated Negishi cross-coupling reaction of Z-alkenylzinc reagents with different arylhalogenides. Proposed method permits to synthesize CA-4 analogs, bearing different substitution pattern in good yield (36-64%) and high stereosellectivity (Z/E = 10:1) *via* the sequence of three-step one-pot reactions (Scheme 1). Newly prepared compounds manifested good cytotoxicity against HBL100 epithelial cell lines (IC_{50} = 0.022 - 10.3 μM).



Scheme 1. Synthesis of combretastatin A-4 analogs. *Reagents and conditions:* (a) $^{-}IPh_3P^{+}CH_2I$, NaHMDS, THF, -20 °C – 45 min, -78 °C – 3 h, 71% (Z/E = 15:1); (b) *i*-PrMgCl·LiCl solution in THF, -40 °C, 15 min, (Z/E = 15:1); (c) $ZnCl_2$ solution in THF, NMP, -40 °C, 1 min, (Z/E = 15:1); (d) Ar'X, (A-^{ta}Phos)$_2PdCl_2$ (2 mol %), rt, 0.5-17 h, (Z/E = 10:1 (e) At the stage of the cross-coupling reaction phenolic groups were protected as TBS-ethers, free amino groups as Boc-amides.

Acknowledgements. This work was supported by German Academic Research Service (A/08/81119), Federal Targeted Programme "Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009-2013" (16.740.11.0476).

P157

SYNTHESIS OF OXYGENATED ADDITIVES TO DIESEL FUELS BASED ON VEGETABLE OILS

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Preparation of oxygen-containing additives for diesel fuels is especially important due to strict environmental standards for motor fuels and their combustion products. Equally important in this case is also a selection of raw materials for such additives.

From this perspective, special interest are the glycol ethers triglycerides of vegetable oils, containing in its composition a hydroxyl group, which is both a supplier of oxygen in the later stages of the combustion of fuels and, and influencing the lubricants and anti-static properties of the fuels.

The synthesis of ethylene and propylene glycol esters of fatty acids of cottonseed, sunflower and corn oils were carried out under the following conditions: 90 -95^{o}C, reaction time 10 h, the ratio of fatty acid / glycol is 1:4 using the catalysts of KU-2-8 (H-form) , lithium hydroxide and "Seokar-600." The highest activity among the used catalysts showed of KU-2-8 and lithium hydroxide. Yield of ethers in their use was 87%.

Properties of the glycol esters of fatty acids are presented in table. 1

Table 1 Properties of the glycol esters of fatty acids

indicators	**Ethylene glycol ester of fatty acids of vegetable oils**			**Propylene glycol esters of fatty acids of vegetable oils**		
	cottonseed oil	**sunflower oil**	**corn oil**	**cottonseed oil**	**sunflower oil**	**corn oil**
Density at 20 ° C, kg/m3	960,4	956,6	958,7	970,2	967,3	969,5
Acid number, mg KOH / g	7,3	8,6	9,1	7,8	8,9	8,3
Kinematic viscosity at 20 °C, mm^2 / sec	6,45	6,37	6,39	6,92	6,86	6,72
Pour point, ° C	-16	-18	-18	-15	-16	-16
refraction coefficient η^{20}_{D}	1,3648	1,3677	1,3689	1, 4243	1,4267	1,4253
Iodine number gI_2 / g	33,87	52,1	49,60	31,2	50,32	48,23

P158

CHEMOENZYMATIC ENANTIOSELECTIVE TOTAL SYNTHESIS OF THE NORLIGNANS HYPERIONE A AND B

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In 2010, Mu *et al.* reported on the isolation of two novel diastereomeric norlignans from *Hypericum chinese*, a herb which has broad application in traditional chinese medicine.[1] Their structure has been proposed to consist of a central tetrahydrofuran core flanked by two piperonyl-containing substituents in 2- and 4-position, however, the absolute configurations remained unknown.
Here, we present the first enantioselective synthesis of Hyperione A and B based on a lipase-catalyzed desymmetrization.[2] Biocatalytic conversion of a prochiral piperonyl-substituted allenic diol produced the axially chiral key intermediate in enantiopure form. In the following steps, silver-catalyzed cyclosiomerization and grignard-addition selectively furnished the 2,4-disubstituted tetrahydrofuran moiety, which was finally transformed to the natural products.[3]

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P159

HOMOGENEOUS AND HETEROGENEOUS SYNTHESIS OF AMINES CATALYZED BY N-HETEROCYCLIC CARBENE IRIDIUM COMPLEXES

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The development of new methods to prepare amines is very important due to the large number of molecules with biological activity that contain amino functionalities. Our continuous interest in the development of efficient, atom-economical and environmentally friendly processes has prompted us to investigate the synthesis of highly active catalysts for the alkylation of amines using alcohols as latent electrophiles.[1]

We have designed and prepared a family of novel iridium complexes containing bidentate *N*-heterocyclic carbenes (NHC) (Figure 1). The complex with the best catalytic activity is one of the most highly active and efficient catalytic systems for the alkylation of amines with alcohols known to date, and affords a variety of *sec*- and *tert*-amines in excellent yields in short reaction times.[2] Solid supported versions of the catalyst have been also synthesized and tested in the reaction. Mechanistic studies will also be presented.[3]

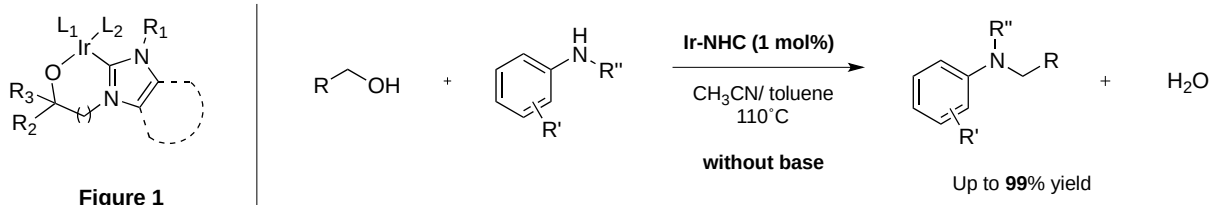

Figure 1

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3. R. Marcos, A. Bartoszewicz, P.-O. Norrby, B. Martín-Matute, *unpublished results.*

P160

CATALYSIS OF TRANSESTERIFICATION AND BENZOIN CONDENSATION BY N-HETEROCYCLIC CARBENES

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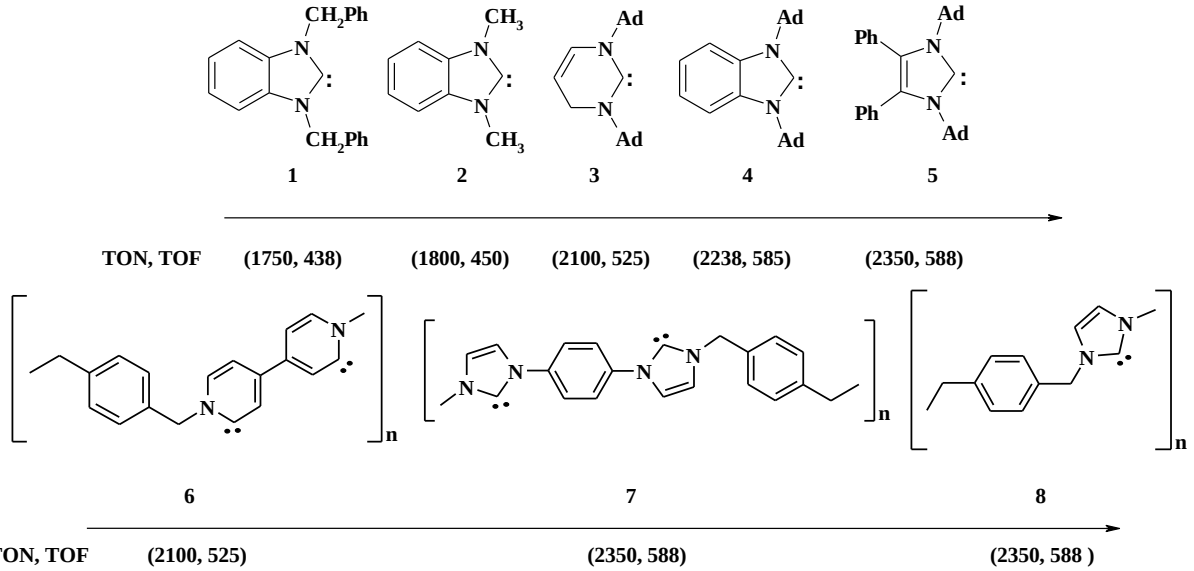
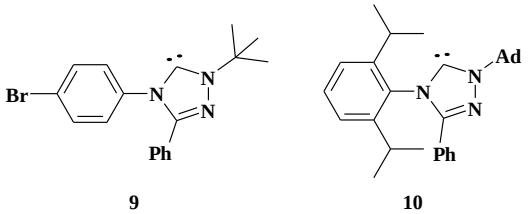
Transesterification is one of the interesting reactions catalyzed by N-heterocyclic carbenes, mild and effective method for the preparation of esters, particularly, for producing of biodiesel fuel. It was found that the transformation of esters successfully proceeds in alcohol excess in the presence of 1,3-disubstituted imidazole-2-ylidenes using 4.4 mol % of carbene catalyst with maximum yield in 85 % [1]. High yields were also achieved in the presence of molecular sieves and excess quantities of esters [2]. But the catalytic efficiency of the indicated carbenes was sufficiently low (TON until 60, TOF until 30 h^{-1}). We studied the catalytic properties of a series of mono-, bis- and polycarbenes in the model transesterification of ethylbenzoate to methylbenzoate in the tenfold methanol excess at room temperature (23°C). The reaction was carried out for 4 h using 0.04 mol % of catalyst [3]. The most efficient carbene catalysts are found to be **4, 5** among the monocarbenes and **7, 8** among the polycarbenes (TON until 2350, TOF until 588 h^{-1}).



Another organocatalytic reaction involving N-heterocyclic carbenes is the benzoin condensation of aldehydes. The transformations of benzaldehyde into benzoin and furfural into furoin were chosen in our research as model. It should be noted insufficient catalytic efficiency of carbenes **9**, **10**. Nevertheless, it was achieved good efficiency in the experiments using 1-5 mol % of compounds **4**, **5** (TON until 62, TOF until 6.5 h^{-1}).



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P161

AN UNDECANUCLEAR IRON(III) CARBOXYLATE AS AN EFFICIENT CATALYST FOR CYCLIC AND LINEAR ALKANE OXIDATION

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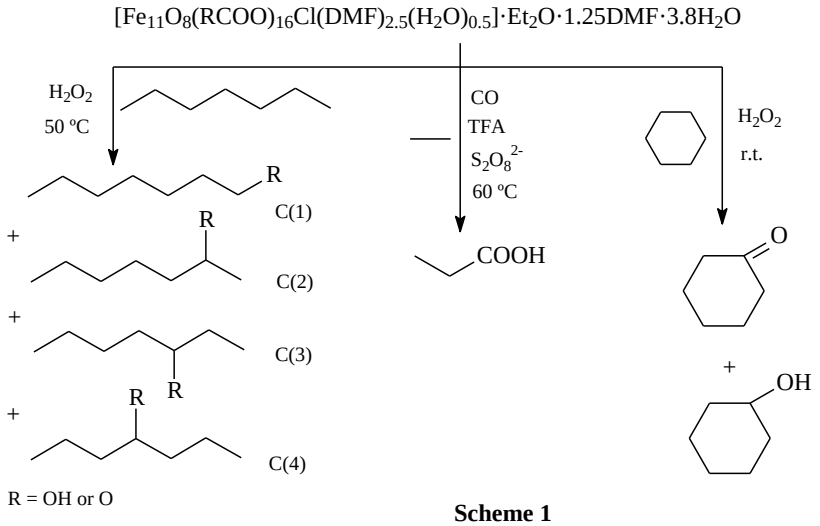
Following our general research line focused on the development of new catalytic systems for the oxidative functionalization of hydrocarbons, complex $[Fe_{11}O_8(RCOO)_{16}Cl(DMF)_{2.5}(H_2O)_{0.5}]\cdot Et_2O \cdot 1.25DMF\cdot 3.8H_2O$ **1** was tested as a catalyst for the peroxidative oxidation of cyclohexane and *n*-heptane by H_2O_2, and for the carboxylation of ethane to the corresponding carboxylic acid (Scheme 1).



Scheme 1

The system **1**/pyrazinecarboxylic acid (Hpca)/ H_2O_2 exhibits a remarkable catalytic activity towards the oxidation of cyclohexane to cyclohexanol (main product) and cyclohexanone, via formation of cyclohexyl hydroperoxide. Overall turnover numbers (TON, moles of product/mol of catalyst) and yields up to *ca*. 3500 and 20% (relative to the alkane), respectively, have been achieved at room temperature after 6 h reaction time. Moreover, catalyst recycling was possible from the liquid medium.

1 is also active for the peroxidative oxidation of *n*-heptane, yielding heptanol and heptanone with the regioselectivity of 1:9:10:10 for C(1):C(2):C(3):C(4) in accord with a radical mechanism.

Furthermore, **1** shows some catalytic activity (TON = 5, yield = 3.2%) for the oxidation of ethane, to acetic acid, in a single-pot process, under mild conditions, and high selectivity towards that acid (only detected product).

The easy accessibility of this undecanuclear iron complex and its catalytic potency makes it a suitable candidate for large-scale oxidations of various alkanes.

Acknowledgements This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and projects PTDC/QUI-QUI/102150/2008, PTDC-EQU-EQU-122025-2010 and PEst-OE/QUI/UI0100/2011 and Austrian Science Fund (project number P19629-N19).

ENANTIOSELECTIVE SYNTHESIS OF 4-AMINO[4H]CHROMENES AND 4-ISOXAZOLINES AND BY ACTIVATION OF ALKYNALS WITH DIPHENYLMETHYLPYRROLIDINES DERIVATIVES

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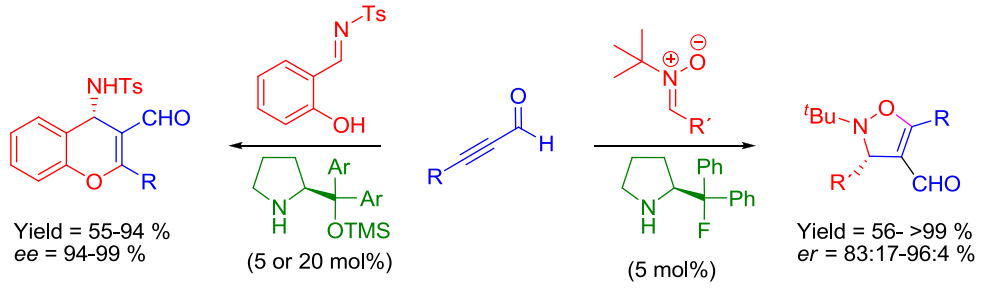
4-Aminochromanes are a class of structures which are integrated in hundred of natural and bioactive compounds. Their importance is reflected in the existence of dozens of patents related to 4-aminochromanes and also exhibit interesting biological properties (e.g. antiobiotic). Finally, the 4-aminochromanol moiety is also important and dozens of medicinal studies as well as the synthesis of related products have been reported. [1] In the first part of this communication, we present the first highly enantioselective oxa-Michael/aza-Baylis-Hillman tandem reaction between 2-alkynals and tosylimines leading to optically active 4-amino-[4H]-chromenes. This reaction takes place in less than 2 hours with high yields and excellent enantioselectivies. The catalytic loading could be reduced to 5 mol% with slight increase in reaction times (left, Scheme).[2]



On the other hand, 4-Isoxazolines or 2,3-dihydroisoxazoles are compounds exhibiting interesting pharmacological properties (antiflamatory action and mitotic kinesin inhibition), along with other biological acitivities. They have also been used as synthons for preparing 1,3-aminoalcohols, aziridines, β-lactames and a wide variety of heterocycles.[3] In the second part of this communication, we will present the first organocatalytic enantioselective 1,3-dipolar reaction between arylnitrones and alkynals catalyzed by (*S*)-2-(fluorodiphenylmethyl)pyrrolidine to yield 4-isoxazolines (2,3-dihydroisoxazoles). It takes place in 1-2 days with high enantiomeric excess, excellent yields and low catalyst loading (1-5 mol%).

Financial support from Spanish Government (CTQ-2009-12168) and CAM ("programa AVANCAT CS2009/PPQ-1634") is gratefully acknowledged. J. A. And S. D. T. thank the MICINN for "Ramon y Cajal" contracts. L. M. thanks the Ministerio de Educación y Ciencia for a predoctoral fellowship. We gratefully acknowledge computational time provided by the Centro de Computación Científica at the Universidad Autónoma de Madrid CCC-UAM.

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P163

ON THE STRUCTURE ORGANIZATION OF CATALYTIC ACTIVE HETEROLIGAND NICKEL COMPLEXES IN HYROCARBONS OXIDATIONS

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The problem of selective oxidation of alkylarenes to hydroperoxides is economically sound. Hydroperoxides are used as intermediates in the large-scale production of important monomers (propylene oxide and styrene are synthesized from α-phenyl ethyl hydroperoxide, and cumyl hydroperoxide is the precursor in the synthesis of phenol and acetone (the world productions are ~ 10^6 ton/ year).

For the first time we proposed and developed a method of modifying transition metals complexes ML^1_n [M = Ni, Fe: L^1 = acac, enamac], with electron-donating mono- or polydentate exo ligands-modifiers L^2 (L^2 = DMF, HMPA, MSt (M=Na, Li), R_4NBr, crown-ethers) aimed at enhancing the selectivity of liquid-phase oxidation of alkylarenes (ethylbenzene and cumene) to the corresponding hydroperoxides. The activity of systems $\{ML^1_n + L^2\}$ is associated with the fact that during the ethylbenzene oxidation the real active catalytic particles heteroligand $M^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ ("A") complexes, which are products of oxygenation of the primary $(M^{II}L^1_2)_x(L^2)_y$ complexes, are formed to be involved in the oxidation process.

On the other hand we discovered unusual effect of significant increase in efficiency of binary systems $\{Ni^{II}(acac)_2+L^2\}$ (electron-donating ligand-modifier L^2 = MSt (M=Na, Li), MP (MP=N-methylpirrolidon-2), HMPA) as the selective catalyst of ethylbenzene oxidation into α-phenyl ethyl hydroperoxide (PEH), with the introduction of the third component – phenol in catalytic system. The formation of heteroligand triple complexes $Ni^{II}(acac)_2\cdot L^2\cdot PhOH$ as active catalytic particles was established.

The formation of the stable supramolecular structure with assistance of intermolecular H-bonds seems to be responsible for the preserve of high activity of catalysts – heterobinuclear heteroligand triple complexes $Ni^{II}(acac)_2\cdot L^2\cdot PhOH$ and heteroligand complexes $Ni^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ ("A"), during oxidation of alkylarens (ethyl benzene, cumene) by dioxygen into hydro peroxides.

For the fist time with use of AFM (Atomic Force Microscopy) we observed the self-assembly-driven growth due to H-bonding of complexes with special prepared silicon surfaces and formation supramolecular nanostructures on the basis of complexes $Ni_2(OAc)_3(acac)MP\cdot 2H_2O$ (complexes "A", L^1=acac, L^2=MP) due to directional inter-molecular H-bonds, apparently at participation of H_2O molecules, acac, acetate groups, MP, and also on the basis of triple complexes $Ni^{II}(acac)_2\cdot L^2\cdot PhOH$ with assistance of intermolecular (phenol-carboxylate) H-bonds and, possibly, other non-covalent interactions.

These data confirm the very probable supramolecular structures appearance on the basis of heterobinuclear heteroligand triple complexes $Ni^{II}(acac)_2\cdot NaSt\cdot PhOH$ in the course of the ethyl benzene oxidation with dioxygen, catalyzed by three-component catalytic system $\{Ni^{II}(acac)_2+NaSt+PhOH\}$ (or heteroligand complexes $Ni^{II}_xL^1_y(L^1_{ox})_z(L^2)_n(H_2O)_m$ ("A"), real catalysts formed during of the ethyl benzene oxidation with dioxygen, catalyzed by binary systems $\{Ni^{II}(acac)_2+L^2\}$), and may explain the stability of active forms of catalysts and hence the high values of the conversion of the ethyl benzene into α-phenyl ethyl hydro peroxide at the selectivity S_{PEH} preservation at the level not below S_{PEH} = 90 % in this process.

P164

SYNTHESIS OF ALPHA-CF_3-SUBSTITUTED CARBONYL COMPOUNDS USING ELECTROPHILIC CF_3-TRANSFER REAGENTS

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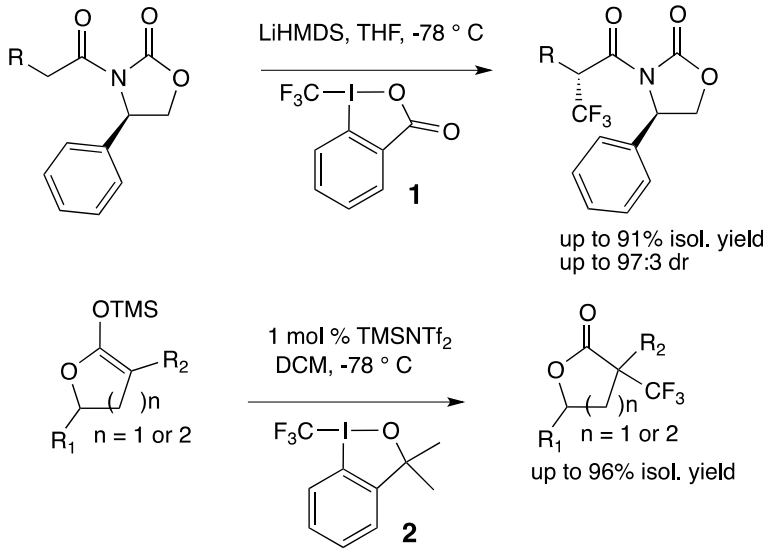
The present work provides more detailed insight into α-trifluoromethylation of enolisable carbonyl substrates.



Evans-type acyl-oxazolidinones were trifluoromethylated with **1** via their corresponding lithium enolates in good to excellent isolated yields and diastereomeric ratios up to 97:3[1]. The trifluoromethylated products were subjected to a series of further racemisation-free synthetic transformations leading to related valuable CF_3-substituted building blocks.
Moreover, trimethylsilylketene acetals derived from 5- and 6-membered lactones underwent efficient $TMSNTf_2$-catalysed trifluoromethylation with**2**with catalyst loadings as low as 1 mol%, thus opening straightforward access to products containing quaternary carbon centres which are otherwise difficult to synthetize. Based on our experimental observations, we have good reason to believe that trifluoromethylation of trimethylsilyl ketene acetals proceeds through the intermediacy of activated O-silylated **2**with more pronounced iodonium character.
The scope of these transformations, a plausible reaction mechanism and intrinsic reactivity patterns of both reagents towards enolisable carbonyl compounds will be discussed.

[1] V. Matoušek, A. Togni, V. Bizet and D. Cahard, *Org. Lett.*,**2011**, *13* (21), 5762-5765

P165

VINYL ACETALS TO BETA-ALKOXY KETONES BY TEBBE METHYLATION AND ACID-INDUCED REARRANGEMENT

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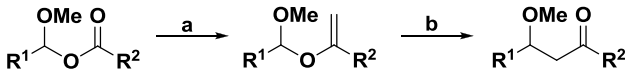
Titanium carbenoids are useful reagents for transformation carbonyl groups into alkenes. They are small and nonbasic, but above all because they will convert carboxylic acid derivatives into the corresponding hetero-substituted alkenes.[1] A range of titanium carbenoids have been used to methylenate esters, but the reagent used by Tebbe, has particular advantages: it is easy to prepare and the workup following reaction often involves simple precipitation of the titanium-containing side products.

One application of titanium carbenoids is in the Petasis−Ferrier rearrangement.[2] It involves methylenation of a 1,3-dioxan-4-one with Tebbe or Petasis reagent to give an enol ether, which rearranges under Lewis-acidic conditions to give a 2,6-*syn*-disubstituted tetrahydropyranone. Surprisingly, rearrangement of linear vinyl acetals, which would be expected to provide a route to β-alkoxy ketones, has not been reported.

We developed a method that allows easy conversion of vinyl acetals into β-hydroxy ketones, which are important building blocks in the synthesis.



a) Tebbe olefination
b) Lewis acid

This project was financed by the European Union within the European Regional Development Fund, Project POIG.01.01.02.-14-102/09.

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P166

HYDRODECHLORINATION OF POLYCHLORINATED BIPHENYLS USING PALLADIUM CATALYSTS

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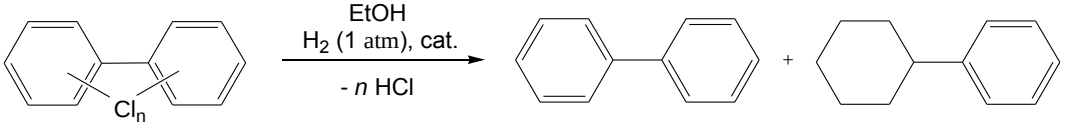
We have previously shown the possibility of PCB hydrodechlorination using a variety of palladium-containing catalysts: palladium-carbon composition produced by method of levitation melting and evaporation (C/Pd) [1]; palladium on Sibunit (Pd/Sibunit) [2] and the commercial palladium on carbon (Pd/C). All these catalysts were active in the hydrodechlorination reaction. In this paper, we compare their activity in reactions of hydrodechlorination of PCB and biphenyl hydrogenation:



Hydrodechlorination of PCB was conducted by about 30% conversion under the same conditions – a catalyst suspended in an alcohol solution of PCB and hydrogen was passed (40-45 ml/min) at room temperature for 5 hours. The catalyst after the reaction was centrifuged, washed three times with ethanol. All liquid products are evaporated. The data obtained are presented in table 1.

Table 1. The results of hydrodechlorination of PCB on various catalysts.

Catalyst	Conversion of PCB in, %		Total conversion of PCB, %
	biphenyl	phenylcyclohexane	
C/Pd	9	12	21
Pd/Sibunit	35	3	38
Pd/C	24	4	28

Thus, the activity of catalysts in the reaction of hydrodechlorination of PCB decreases in the range of Pd/Sibunit > Pd/C > C/Pd. The range of catalysts in the hydrogenation of biphenyl to phenylcyclohexane has the opposite order: C/Pd > Pd/C > Pd/Sibunit. The average adsorption on the catalyst is 3-7%, which does not affect the decrease in yields (this is a small value though adsorption on activated carbons is 45-250%, depending on the type of porosity). The catalyst should be washed for purification and further use. On all catalysts, mainly PCB sorbed with sorption selectivity decreases in the range of C/Pd> Pd/C> Pd/Sibunit, which corresponds to the reduction of palladium in the catalyst. Probably the PCB is on the surface of the catalyst in the form of complexes with palladium.

Pd/Sibunit remain active for three cycles, but after the first use the activity decreases slightly as the particle size of palladium increased from 2.6 to 3.9 nm. It should be noted that the use of specially prepared catalysts (2% Pd/Sibunit) with a particle size of 3 and 7 nm, the total conversion of PCB is 10 and 23%. Thus, increasing the particle size increases the activity of the palladium catalyst. In this case, the lower activity of the smaller particles may be due to their lower stability or their location in the far depths of the support.

This work was carried out with a financial support of the Urals Branch of Russian Academy of Sciences (project № 12-M-34-2036).

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P167

3,4-DIHYDROQUINAZOLINE BEARING RUTHENIUM(II) COMPLEXES FOR TRANSFER HYDROGENATION REACTION

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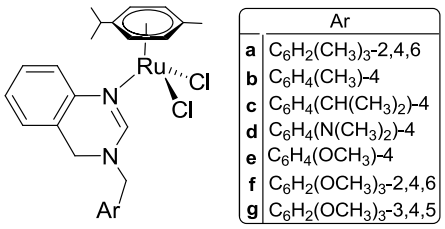
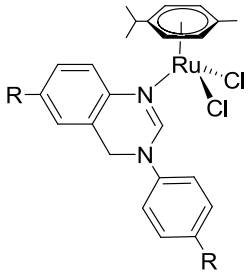
The Ru(II) complexes with ligands bearing N-donor atoms are attracting interest of researchers due to their potential to promote the catalytic reaction of organic compounds.[1-5]The Ru(II) complexes containing N-bonded heterocycles, such as N-alkybenzazole, N-alkylimidazoline and N-alkyl-1,4,5,6-tetrahydropyrimidine were prepared and used successfully as catalysts for transfer hydrogenation.[6-7] Recent studies showed that complexes derived from six-membered heterocyclic rings such as tetrahydropyrimidine exhibit superior activity as compared with five-membered analogues[8] and that the substitution pattern on the heterocyclic ring is also an important factor to affect the catalytic activity. Therefore, it seems of interest to examine the influence of benzene annulation at the 5,6-position of the reduced pyrimidines having alkyl- and aryl- substituents at the nitrogen atom.

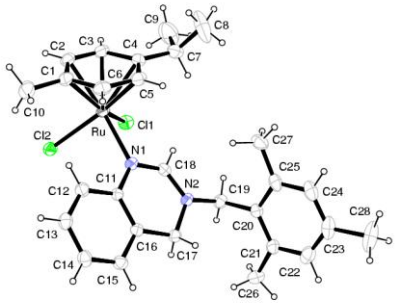


	Ar
a	$C_6H_2(CH_3)_3$-2,4,6
b	$C_6H_4(CH_3)$-4
c	$C_6H_4(CH(CH_3)_2)$-4
d	$C_6H_4(N(CH_3)_2)$-4
e	$C_6H_4(OCH_3)$-4
f	$C_6H_2(OCH_3)_3$-2,4,6
g	$C_6H_2(OCH_3)_3$-3,4,5

1



R= CH_3 : **2** ; OCH_3 : **3**



Molecular structure of **1a**

In this study, N-coordinated 3,4-dihydroquinazoline ruthenium(II) complexes (**1**-**3**) were synthesized and characterized by spectroscopic methods. The single-crystal of the Ru (II) complex **1a** was used for the determination of crystal structure. Furthermore, the resulting piano-stool complexes were evaluated as transfer hydrogenation catalysts for reduction of acetophenone in the presence of 2-propanol and KOH at 82^{o}C.

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P168

SYNTHESIS OF KALBRETORINE VIA DECARBOXYLATIVE IODINATION OF 7H-PYRROLO[3,2,1-de]PHENANTHRIDINE-4,5-DICARBOXYLIC ACID

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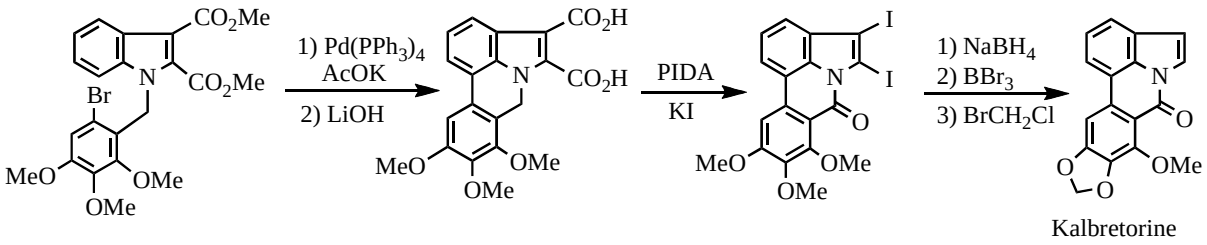
Pratosine, hippadine, and kalbretorine are 7*H*-pyrrolo[3,2,1-*de*]phenanthridone alkaloids, isolated from various species of *Amaryllidaceae*. This family has significant biological activities; for example, hippadine inhibits fertility in male rats [1] and kalbretorine shows antitumor activity.[2] In a previous paper, we reported the synthesis of pratosine and hippadine by the palladium-catalyzed intramolecular cyclization of methyl 1-(2-bromo-4,5-dimethoxybenzyl)indole-2-carboxylate protected 2-position of the indole moiety by an ester group.[3] However, the synthesis of pratosine and hippadine by decarboxylation of the corresponding 7*H*-pyrrolo[3,2,1-*de*]phenanthridine- 4,5-dicarboxylic acids was resulted in low yields. [4] Here, we report the simple synthesis of kalbretorine by the palladium-catalyzed intramolecular cyclization of dimethyl 1-(6-bromobenzyl)- indole-2,3-dicarboxylate derivative and decarboxylative iodination.

The treatment of dimethyl 1-(6-bromo-2,3,4-trimethoxybenzyl)indole-2,3-dicarboxylate in the presence of tetrakis(triphenylphoshine)palladium(0) and potassium acetate in hot dioxane gave the corresponding dimethyl 7*H*-pyrrolo[3,2,1-*de*]phenanthridine-4,5-dicarboxylate. The hydrolysis of the ester by lithium hydroxide gave the corresponding dicarboxylic acid, which could be converted to the diiodo compound via the decarboxylative iodination and oxidation using phenyliodine diacetate and potassium iodide. The diiodo compound could be converted into kalbretorine by the reduction and demethylation, followed by methylenedioxylation.



Kalbretorine

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P169

WELL DEFINED IRON COMPLEXES AS EFFICIENT CATALYSTS FOR HYDROSILYLATION REACTIONS OF CARBON-HETEROATOM DOUBLE BONDS

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Due to high natural abundance, benign environmental impact, and low cost, iron has emerged as an interesting potential surrogate in catalytic processes for classical precious transition metals such as palladium, ruthenium or rhodium. The last decade have seen a rise of its use as the catalyst and efficient processes are now able to compete with other metal-catalyzed ones.[1] Recently, some groups have described well-defined iron(II) complexes, mainly in the area of reduction catalysis[2] such as hydrogenation or hydrogen transfer. In the area of hydrosilylation, two main strategies were usually employed: one based on the use of iron salts (often $Fe(OAc)_2$ *in situ* associated with nitrogen, phosphine or thiophene ligands), and the other one on well-defined iron complexes as pre-catalysts such as bis(pyridylimino)isoindole pincer iron(II) catalyst, or tridentate pyridinediimine iron(0) bis(dinitrogen) complexes. [3]
In our continuing work to develop new methodologies using iron as catalyst, we report herein the application of well defined iron complexes, such as *N*-Heterocyclic Carbene[4] or Phosphine[5] Piano-Stool Iron Complexes as efficient catalysts for hydrosilylation reactions of aldehydes, ketones, and imines.

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P170

SELECTIVE ACYLATION AND ALKYLATION OF PHENOLIC HYDROXYLS MEDIATED BY METAL FLUORIDES

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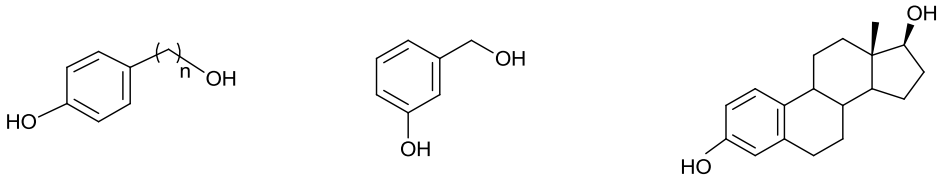
In organic synthesis, esters and ethers are among the most frequently employed protective groups for hydroxy functionalities present in various natural and synthetic compounds. These protective groups are introduced and removed under a great variety of conditions. However, it is usually difficult to conduct a selective acylation or alkylation of compounds bearing multiple hydroxyls. Therefore, various reagents and auxiliaries have been developed for such a transformation, which is still a fundamental but important topic in synthetic organic chemistry. As a part of our continuing study on the selective derivatization of poly-hydric compounds, we have examined the acylation and alkylation of compounds carrying both alcoholic and phenolic hydroxyls as depicted below.



It is easier to selectively acylate an alcoholic hydroxyl in the presence of a phenolic one, while the reverse is much more difficult, because the latter hydroxyl is less nucleophilic than the former. Thus, the acylation of the phenolic hydroxy group is usually performed under basic conditions where the phenolate is produced. A method for acylating phenolic hydroxyls under nearly neutral conditions is undoubtedly more desirable, especially in cases in which labile functional groups exist together in the molecule. The lipase-catalyzed acylation of (hydroxyalkyl)phenols took place predominantly at the alcoholic hydroxyl and the deacylation of their diesters at the phenolic hydroxyl site, both yielding alcoholic monoesters as the sole products. The fluoride ion has long been recognized as an efficient base for the promotion of various types of base-assisted reactions in organic synthesis. We envisaged that a selective acylation of the phenolic hydroxyl of (hydroxyalkyl)phenols could be achieved by choosing an appropriate combination of a metal fluoride and an acylating agent. It was gratifying to finally find that highly selective acylations were achieved by the use of vinyl carboxylates in the presence of rubidium fluoride.

The alkylation of (hydroxyalkyl)phenols with alkyl halides in the presence of metal fluorides such as cesium fluoride took place exclusively at the phenolic hydroxyl group. We found that microwave irradiation reduced the reaction time to a great extent compared with that under conventional heating. Moreover, the use of metal fluorides embedded on Celite resulted in shorter reaction times without affecting the specificity towards the phenolic hydroxyl.

P171

REACTIONS OF PHOSPHINE LIGANDS WITH ORGANIC SUBSTRATES IN AQUEOUS MEDIA

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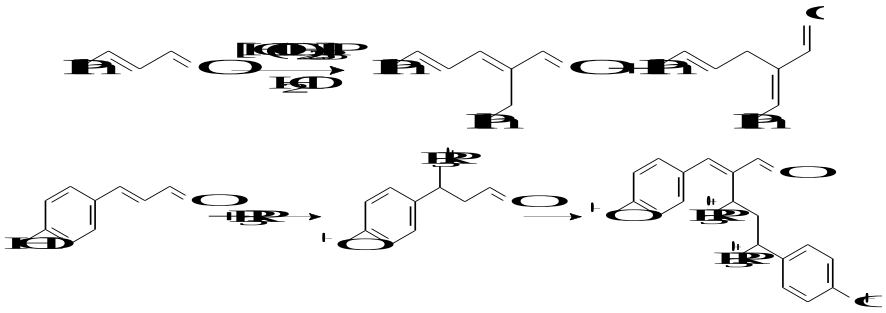
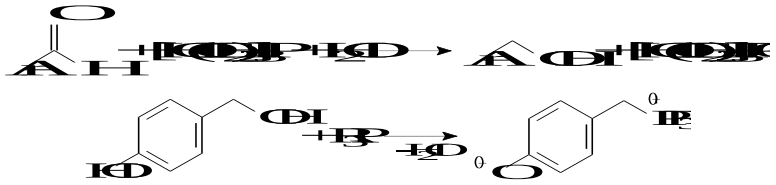
Investigations by Prof. James group into aqueous, transition metal-catalyzed hydrogenation of wood lignin and lignin model compounds revealed that water-soluble phosphines are themselves excellent bleaching agents for pulps. Interaction of phosphines with conjugated carbonyl components of lignin is likely involved in the bleaching process. In order to understand the bleaching effect we investigated reactions of tertiary phosphines with lignin model compounds. The topic is also of interest within homogeneous catalysis in aqueous media involving unsaturated organic substrates using transition metal-phosphine systems.

We discovered that cinnamaldehydes, in the presence of $[HO(CH_2)_3]_3P$, undergoes self-condensation into the two isomeric products. Lignin-type aldehydes, which contain a *p*-OH-group, react with tertiary phosphines to afford bisphosphonium zwitterion products.



$[HO(CH_2)_3]_3P$ catalyses cross-condensation reaction of cinnamaldehydes with ketones.

Effective reduction of the benzaldehydes to the corresponding benzyl alcohols with concomitant oxidation of the phosphine to the phosphine oxide takes place in water in the presence of $[HO(CH_2)_3]_3P$. The 2- or 4-hydroxybenzyl alcohols in reaction with tertiary phosphines in aqueous media afford zwitterionic phosphobetaine products.



Mechanisms of the processes mentioned above as well as reactions of tertiary phosphines with cinnamyl alcohols, cinnamic acids and esters, quinones are discussed.

Acknowledgements - We thank the Natural Sciences and Engineering Research Council of Canada for financial support via a Discovery Grant.

P172

HYDROGENATION OF ENAMINES CATALYZED BY NICKEL NANOPARTICLES

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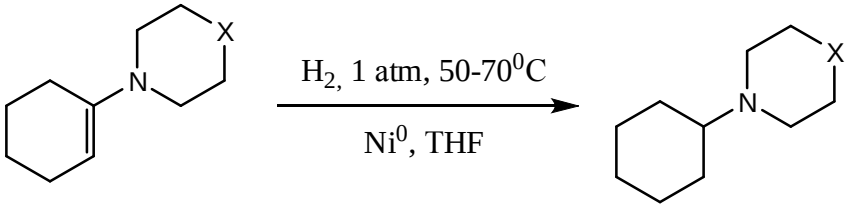
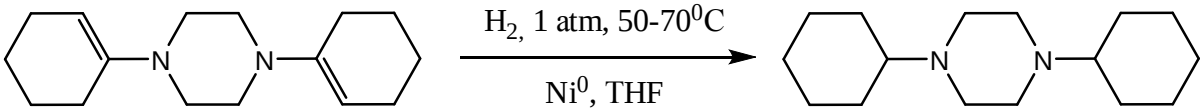
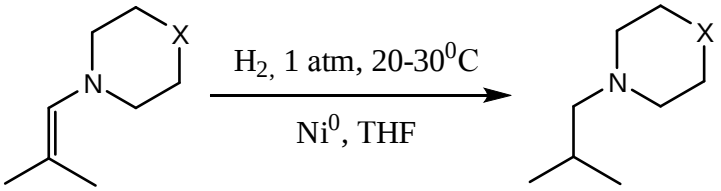
In this article presented results of investigations for the quest of convenient method of enamines hydrogenation by hydrogen in "soft" conditions, using non-expensive catalytic systems. It was found, that nickel nanoparticles, prepared *in-situ* by nickel (II) chloride reduction are accessible catalyst, making possible enamines hydrogenation in tertiary amines in liquid phase and atmospheric pressure and not high reaction temperature.



X= -CH_2-, -O-



The yields of tertiary amines are 85-90%.
Hydrogenation of enamines, synthesized from aldehydes, proceeds smoothly even at room temperature.



X= -CH_2-, -O-

The hydrogenation method investigated can be used for synthesis of tertiary amines.

P173

LIQUID-PHASE ALKENE HYDROGENATION BY ATMOSPHERIC PRESSURE HYDROGEN USING CATALYSIS BY METAL NANOPARTICLES

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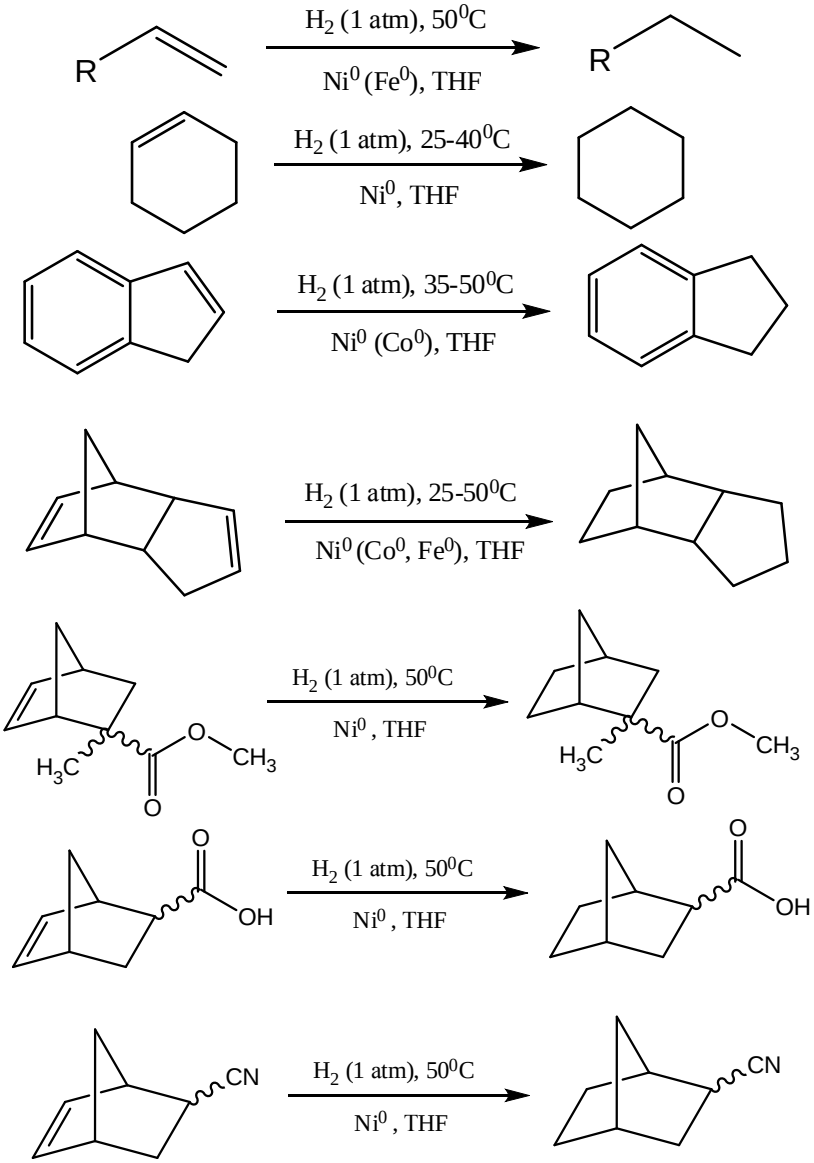
Hydrogenation of double carbon-carbon bonds often needs high temperatures and hydrogen pressures, or use of expensive and rare catalysts. We found, that metal nanoparticles (Ni, Co, Fe) are useful and cheap catalysts for hydrogenation on number of alkenes.
Linear, cyclic, polycyclic and functionalized alkenes were used as starting materials. It was found, that hydrogenation proceeds at 1 atm of hydrogen and room or slightly elevated temperatures during 4-6 hours.



Discovered method may be used for selective hydrogenation of unsaturated substances.

P174

DENSITY FUNCTIONALS PERFORMANCE IN THE ACTIVATION OF H_2 BY Au_3 AND Ag_3 CLUSTERS

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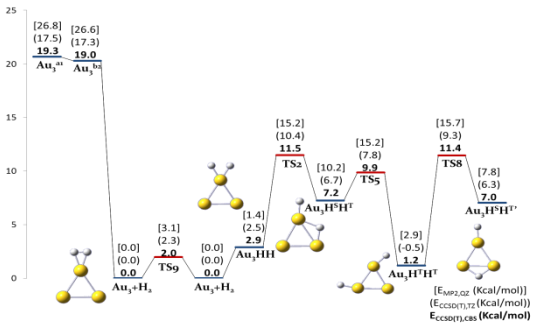
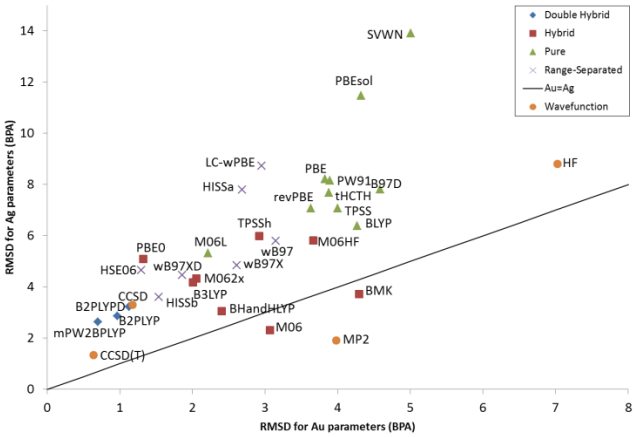
Heterogeneous catalysts are a critical part of industrial chemistry, primarily as a tool for more economically and ecologically efficient chemical processes. It is thus desirable to develop theoretical methods that can predict trends in catalytic activity and predict active catalyst for industrially important reactions. We have thus chosen to undertake a benchmarking study of various methods on the dissociation of molecular hydrogen on small gold and silver clusters. The simulation of the reactivity of H_2 over small noble metal clusters is interesting both for elucidating the participation of the small clusters and also as model for the metal-hydrogen interactions in nanoparticles and surfaces. (A previous study by Gordon and coworkers of this reaction included high-level calculations and three semilocal DFT functionals.[1])



A benchmark study of the performance of DFT methods for the calculation of these mechanisms was perfomed. A wide range of DFT functionals have been selected for this work including a local functional; 9 semi-local functionals; 8 hybrid functionals; 7 range separated hybrid functionals; 3 double-hybrids including the HF-like exchange and MP2-like correlation; and some new developed 3.5 rung functionals including both the exact and a semi-local one-particle density matrices. Wave function methods are also included for comparison purposes.



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P175

BETTI BASE DERIVATIVES: ENANTIOSELECTIVE SYNTHESIS AND STUDY AS ORGANOCATALYSTS

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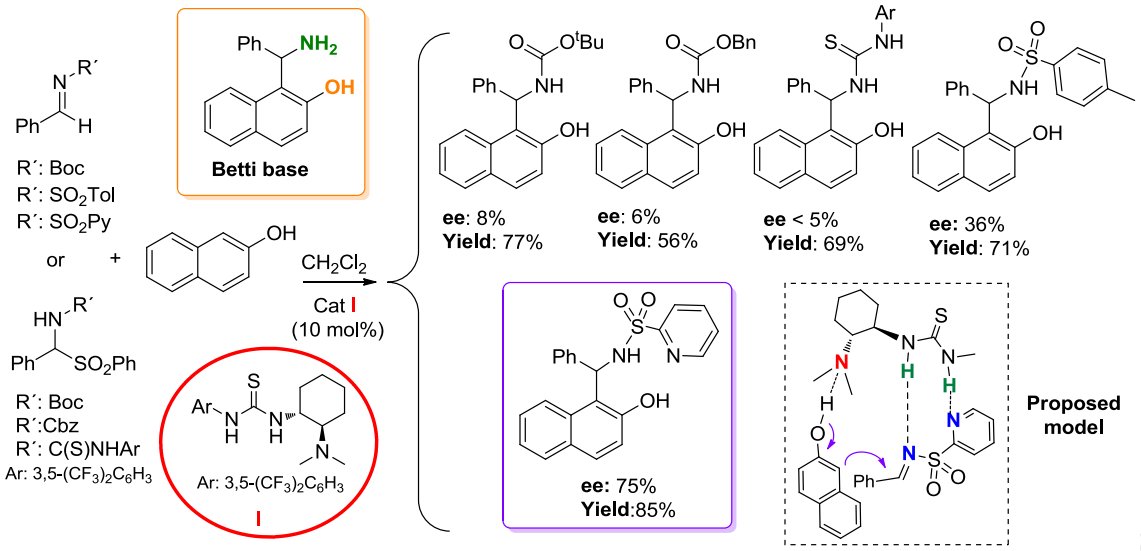
We consider the Betti base [1] a privilege structure, not only for its biological interest [2] but also because it contains a 1,3-aminonaphthol moiety which offers numerous possibilities of transformation by modifying its amino and/or phenolic group. It would be interesting to prepare these compounds enantiomerically pure and used them as new organocatalysts.
In order to obtain a variety of substrates containing this structure, we have performed an enantioselective aza-Friedel-Crafts reaction between 2-napthol [3] and different activated imines or their precursor α-amidosulfones. Our approach is based on the use of a bifunctional catalyst that simultaneously activates both nucleophile and electrophile. So far, the best results have been achieved with *N*-sulfonylpyridylimine [4] as electrophile, and Takemoto´s catalyst **I** which contains a basic center and a thiourea unit.



Scheme 1.

A plausible reaction model is represented in scheme 1, the thiourea unit of the catalyst could coordinate both pyridine and iminic nitrogens, and the terciary amine would activate the 2-naphtol. Some of these structures are being studied as enantioselective organocatalysts in several reactions with promising results.

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P176

LIGAND EFFECTS IN THE INTRAMOLECUAR GOLD CATALYZED HYDROARYLATION OF IODOALKYNES

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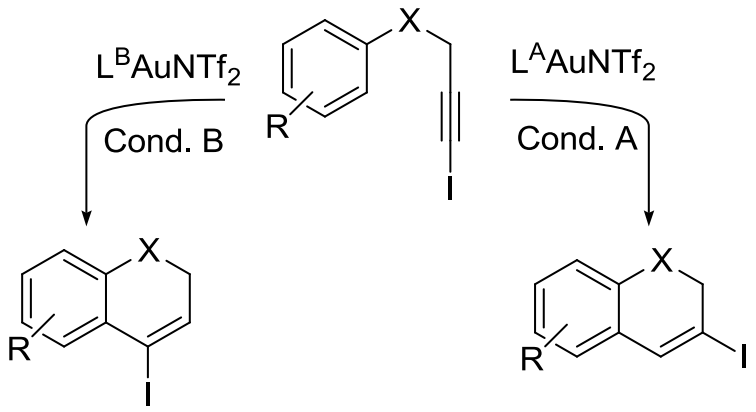
Diversity oriented syntheses is directed to the preparation of families of compounds with structural flexibility[1].

To this regard, we have developed an efficient method for the synthesis of biological interesting scaffolds. Thus, iodosustituted 1,2-dihydroquinolines[2] have been regioselectively obtained through a ligand-controlled process.

The reaction, catalyzed by gold(I) complexes, is tuned according to the electronic effects of the ligands,[3] driving the hydroarylation[4] through two different reaction pathways.



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P177

RESIN-SUPPORTED METAL NANOPARTICLES FOR HYDROGENATION REACTIONS; RECYCLABILITY, SELECTIVITY AND APPLICATION TO CONTINUOUS FLOW SYSTEMS

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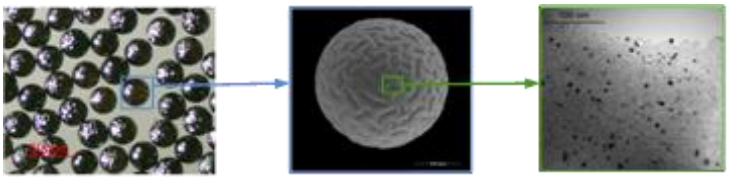
The research in the field of fine-chemicals synthesis by solid-supported metal nanoparticles (MNPs) catalysts attracts steadily increasing interest due to the possibility to couple high activity with ease of separation, catalyst reuse or continuous processing. Therefore, this offers a green and cost-effective alternative to homogeneous and conventional heterogeneous catalysts in an industrial segment blemished by the highest E-factors. However, known preparation methods for supported MNPs suffer from one or more drawbacks, including poor reproducibility, lack of control over NP size and shape, complex or unfriendly synthetic procedures. In order to make their industrial application acceptable, more sustainable routes for MNPs synthesis than those currently used, and involving minimal reagents and mild conditions, are thus required.
In this work we report the process for the immobilization of metal nanoparticles (MNPs) onto ion exchange resins including a deep study of the recyclability, reusability, selectivity and versatility of the developed catalyst. The solid support is the inexpensive and commercially available DOWEX®; gel type resin (styrene-divinylbenzene cross-linked copolymer) in a broad range of varieties (micro-, macroporous, % cross-linking agent, bead size or ionic form), where different precious metals such as palladium, platinum and rhodium have been immobilized.
The synthesis of nanoparticles lies in the immobilization of the metal precursor (ionic interaction) followed by the reduction with H_2 in MeOH. The catalysts have been tested in hydrogenation reactions using very mild conditions (1bar H_2 and room temperature) where they showed to be selective to partial hydrogenation with substrates like cyclooctadiene (97% selectivity to cyclooctene at 98% conversion), selective to C=C hydrogenation in the presence of other functional groups in the case of important substrates like isophorone (73 % selectivity to insaturated ketones at 93% conversion), among others. Special attention requires the hydrogenation of 3-hexyn-1-ol, showing high selectivity to the leaf alcohol fragrance *cis*-3-hexen-1-ol in batch conditions (97% selectivity at 91% conversion). The life time of these catalysts proved in batch for this reaction and their easy integration to reactor equipments allowed us the application to continuous-flow synthesis.
The characterization of MNPs was carried out by using ESEM-EDS, ICP, TEM, XRD and SAXS.



Optical microscopy image ESEM image TEM image

Figure 1. Supported Pd^0 NPs onto DOWEX

In short, we have developed an easy methodology to prepare tethered catalysts, which do not require any pre-catalyst treatment, can be quantitatively recovered and conveniently reused up to 6 times simply after decantation, with negligible metal leaching, highly selective and applicable to continuous flow processes.

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EFFICIENT SPIROCYCLIZATION THROUGH PHENOLIC OXIDATIONS USING HYPERVALENT IODINE (III) REAGENTS AND ITS APPLICATION TO NATURAL PRODUCT

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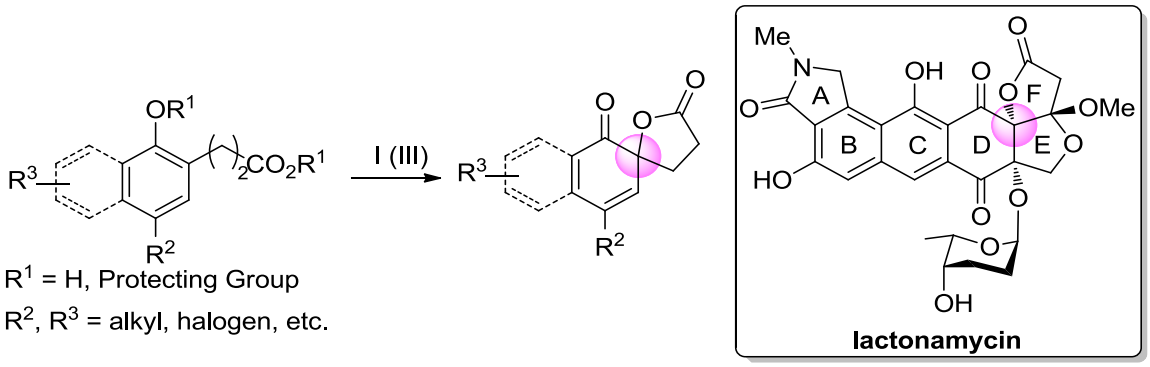
The spirolactone and its derivatives have received much attention as useful intermediates for the synthesis of a variety of structurally diverse organic compounds, due to their unique structures. Additionally, these spirolactone cores frequently show an important relationship with biological properties of natural products. Therefore, there exists a continuing interest in the convenient synthesis of *o*-spirolactone cores in organic chemistry. However, these compounds, for all their utilities, are generally difficult to handle due to their high propensity toward dimerization *via* cycloaddition. Therefore, there has been no report of the efficient and high functional group for the compatibilities of *o*-spirocyclization with natural product synthesis.
On the other hand, hypervalent iodine oxidation of phenol derivatives has been used widely for total synthesis of natural products. We applied the oxidative coupling of various phenolic derivatives to the synthesis of several pharmacologically interesting natural products.[1, 2)] At this conference, we present the synthesis of *o*-spirolactones *via* the intramolecular cyclization of naphthols and phenols protected by silyl group using hypervalent iodine reagents. Further application to the synthesis of lactonamycin core is also described.



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METAL-FREE OXIDATIVE COUPLING REACTION: THE EFFICIENT SYNTHESIS OF BITHIOPHENES USING HYPERVALENT IODINE REAGENT

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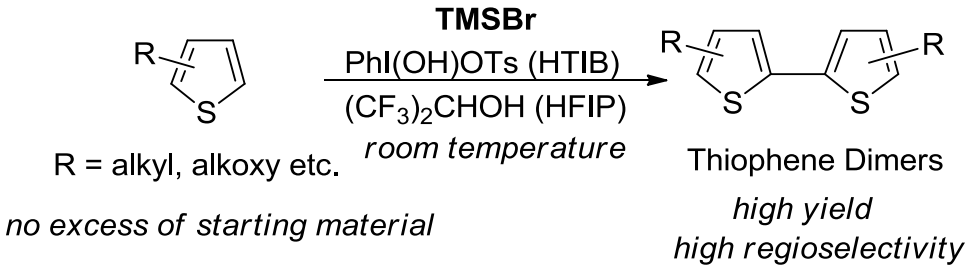
The oligo- and polythiophene derivatives have gained recognition as important materials due to their useful physical properties, such as electrical conductivity and electroluminescence. 2, 2'-Bithiophenes are one of the most important classes of compounds for synthesizing oligo- and poly-thiophenes, since they are polymerized under mild conditions due to their lower oxidation potential compared to thiophene itself, and predominantly yield a higher-quality α-linked polymer. Therefore, the development of convenient coupling reaction for giving 2, 2'- bithiophenes is one of the important subjects in modern organic chemistry. On the other hand, the oxidative biaryl coupling reaction of thiophenes is a significantly attractive, convenient and straightforward route to the synthesis of bithiophenes due to its operational simplicity by avoiding the preparation of the corresponding halogenated and metalled thiophenes. However, electrochemical oxidation or heavy metal oxidants cannot be utilized not only for inducing oxidative coupling for dimerization, but for oligomerization, due to the lower oxidation potential of the formed dimers compared to the corresponding initial monomers.

Recently, our research group has been involved in the development of the hypervalent iodine(III)-induced cross-coupling reactions of heteroaromatic compounds.[1)] In the poster session, we present a study of the oxidative biaryl coupling reaction for the synthesis of substituted bithiophenes (Scheme 1). [2)]



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P180

NITROSONIUM ION PROMOTED IODINATION AND 1,2-IODOFUNCTIONALIZATION OF CYCLOHEXENE AND CALIXARENES

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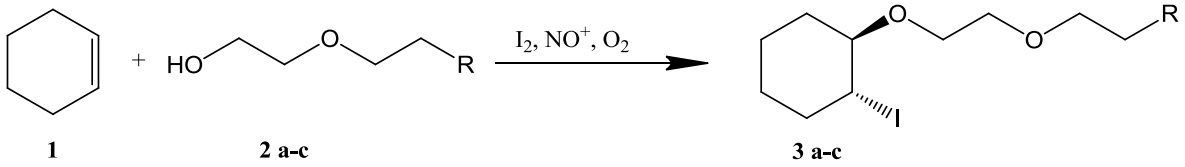
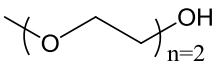
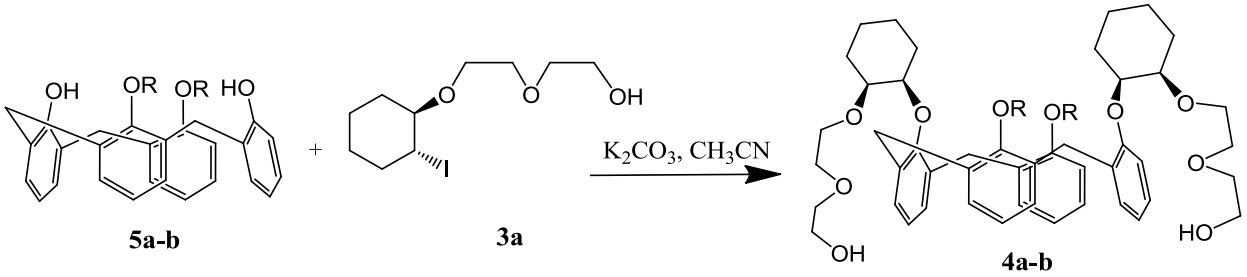
The addition of halogens to multiple bonds is one of the fundamental reactions of organic chemistry.[1] Now we report on a condvenient method for the iodination of cyclohaxene which utilized the nitrosonium ion NO^+ as a catalyst and O_2 as stoichiometric oxidant.



1 **2 a-c** **3 a-c**

2-3 R = OH (**a**),  **(b),** Cl (**c**)

The promoting influence of AlkONO, calixarene*N_2O_4 or $NO^+BF_4^-$ on the addition of I_2 and ethyle glycole derivatives **2** couples to cyclohexane **1** in the presente of O_2 was optimisation.



5a-b **3a** **4a-b**

4-5: R = H (**a**) -CH_2-CH=CH_2 (**b**)

We used compounds **3** for synthesis of derivatives of calixarenes **4.** The details will be presented.

We thank to the RFBR (grant 10-03-00095-a) for the financial supporting of this research.

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P181

ANION-INDUCED ENANTIOSELECTIVE CYCLIZATION OF DIYNAMIDES TO PYRROLIDINES BY CATIONIC GOLD COMPLEXES

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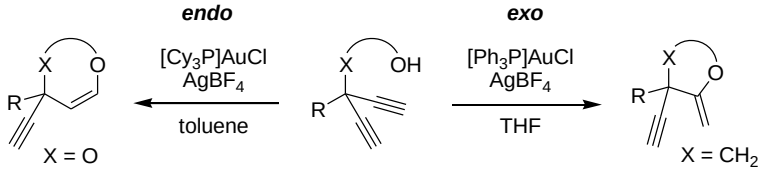
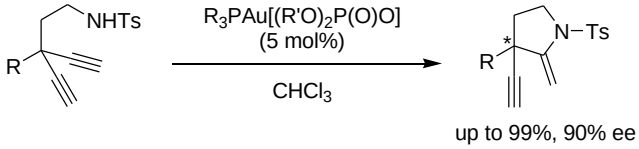
In recent years, gold complexes have been employed extensively for the activation of alkenes, alkynes, and allenes towards the attack of various *O*-, *N*-, *S*-, or *C*-nucleophiles.[1] These transformations occur with high chemoselectivity, high functional group tolerance, and mild reaction conditions to allow access to a variety of new compound classes such as aromatic and aliphatic, saturated and unsaturated heterocycles. In stark contrast to this increasing number of applications for gold catalysts in method development and applications in complex natural product synthesis, corresponding enantioselective processes employing optically active gold complexes as well as mechanistic investigations aiming at an understanding of the fundamental reasons for stereoselectivity are more limited in number.[2] In this context, gold complexes employing chiral phosphine ligands and chiral phosphate anions have been demonstrated as effective and selective catalysts for the transformation of allenes, alkenes, and enynes. In contrast, stereocontrol in the case of diynes has proven difficult so far, in particular in the case of terminal alkynes. In the past, we have focussed on the development of a new method for the gold-catalyzed desymmetrization of 1,4-diynes.[3] Herein, we have shown that intramolecular, nucleophilic cyclization of 3-alkoxy-1,4-diynes results in selective *endo*-cyclization, whereas 3-alkyl-1,4-diynes provide access to the corresponding unsaturated heterocycles by *exo*-cyclization.



Initial studies showed that for the desymmetrization of terminal 1,4-diynes neither chiral phosphine nor carbene ligands led to gold catalysts which permitted highly enantioselective ring closure to unsaturated heterocycles.[4] It was shown however that gold complexes incorporating chiral anions derived from BINOL were successfully employed in the desymmetrization of diynamides to pyrrolidines in selectivities up to 90% ee under appropriate reaction conditions.



References:

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[4] For an example of silver-catalyzed desymmetrizations of internal diynes, see S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada *Bull. Chem. Soc. Jpn.* 2011, *84*, 698.

P182

IMINES HYDROGENATION USING Ru(II) COMPLEXES CONTAINING POLYPYRIDINE LIGANDS

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2 - Universidad de Chile, Facultad de Ciencias Quhmicas y Farmacuuticas, Casilla 233, Santiago 1, Chile
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Complexes of ruthenium are good alternative for hydrogenation of functional groups such as ketones, imines and nitriles[1]. However, the imines hydrogenation is a very complex process because this kind of substrate has a strong donor character and it can acts a a ligand, doing the homogeneous catalytic process unfavorable[2]. In this work, we report the synthesis and characterization of some Ru(II) complexes derivate from the $[Ru(CO)_2Cl_2]n$ and $[RuCl_2(\eta^6$-p-cymene)] precursors, containing nitrogen ligands of different donor character. The compounds were characterized by spectroscopic techniques (^{1}H and ^{31}P-NMR, IR) and elemental analysis. The results give support for the proposed formulation for the prepared complexes. The compounds were used as catalysts in the transfer hydrogenation reaction of some imines derivates from N-benzyllidenaniline. Conversions over 95% were obtained.

Acknowledgements: We thank Fondecyt-Chile(Grants 1120685 and 1120149) and LIA (Chile-France).

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P183

LITHIUM – HALOGEN EXCHANGE INITIATED INTRAMOLECULAR ARYLLITHIUM ADDITIONS TO DIHYDROPYRIDONES

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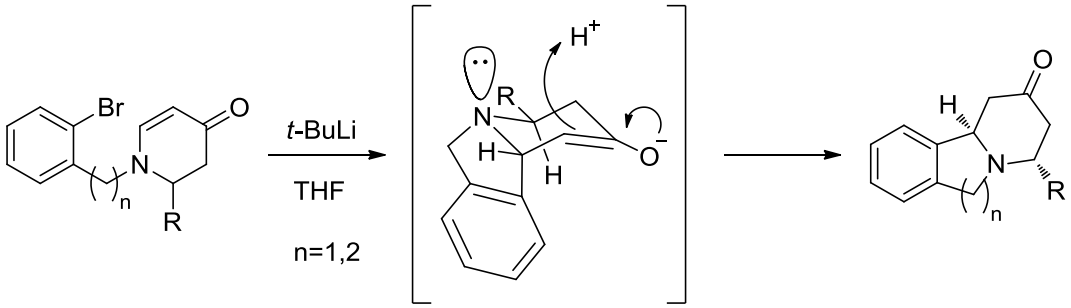
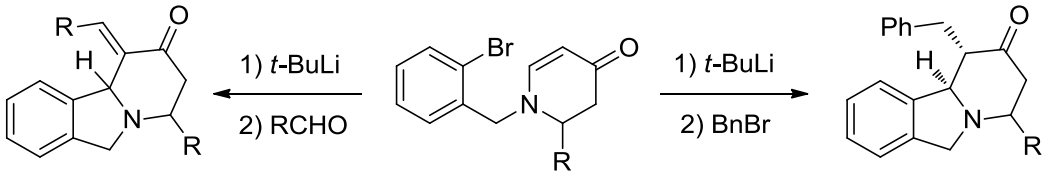
We have discovered a new method of synthesis of benzoquinolizidines and related homologues based on the lithium – halogen exchange initiated conjugate addition of aryllithium to dihydropyridones (Scheme 1).



Scheme 1.

The mechanism suggests that the enolate intermediate is protonated on the top face (axial addition). When we made a tandem reaction with the enolate trapped by a different electrophile (BnBr), the product is also that of axial attact, while the reaction with aldehydes to give the corresponding enones (Scheme 2).



Scheme 2.

P184

MULTICOMPONENT ELECTROCATALYTIC CHAIN TRANSFORMATION OF HETEROCYCLIC C-H ACIDS

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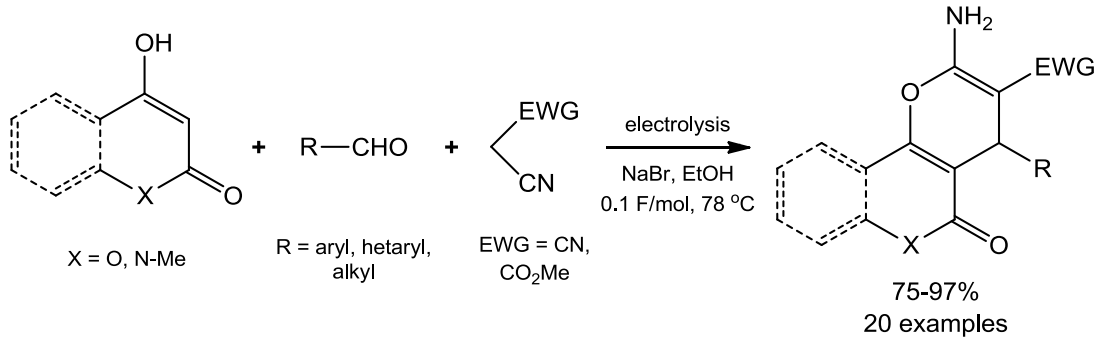
Functionally substituted pharmacologically active bi- or tricyclic heterocyclic systems containing 4*H*-pyran ring, and their derivatives based on pyrano[3,2-*c*]quinoline or pyrano[3,2-*c*]coumarine scaffolds have received considerable attention in the field of medicinal chemistry due to their useful biological properties, such as spasmolytic, diuretic, anticoagulant, and antianaphylactic activity [1]. Recently, 4*H*-pyrans with fused quinolin-2-one ring were established to cause apoptosis in HeLa and MCF-7 human cancer cell lines [2]. Consequently, the incorporation of the two structural features, such as coumarins or quinolons and 4*H*-pyrans, may have significance to the design of new therapeutic agents [3]. Thus, the synthesis of substituted 4*H*-pyrans and allied analogues currently is of great importance.

In the present study we report our results on multicomponent electrocatalytic chain transformation of heterocyclic C-H acids (4-hydroxy-6-methyl-2-pyrone, 4-hydroxycoumarin-2-one or 1-methyl-4-hydroxy-quinolin-2-one), aldehydes and malononitrile or methyl cyanoacetate into substituted pharmacologically active bi- or tricyclic heterocyclic systems in high yields (Scheme 1). The reaction is performed in ethanol in the presence of sodium bromide as an electrolyte.

Scheme 1.



The developed electrocatalytic process offers facile and effecient way to create substituted farmacologically active bi- or tricyclic heterocyclic systems – prominent compounds with different biomedical applications. The electrocatalytic procedure utilizes common equipment and undivided cell. It is easily carried out, reaction products were isolated by simple filtration without any further purification.

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CHEMOSELECTIVE HYDRATION OF TERMINAL ALKYNES CATALYZED BY COBALT(III) PORPHYRIN COMPLEX

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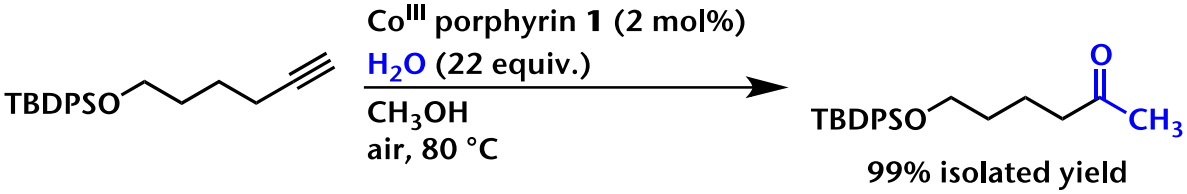
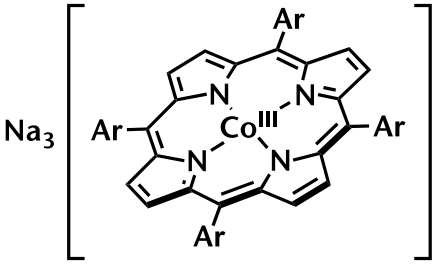
Markovnikov-type hydration of terminal alkynes represents a powerful method for the synthesis of methyl ketones using water as a reagent, mainly based on mercury and gold catalysts. However, hydration of terminal alkynes bearing acid-sensitive functional groups still remains as a challenge in selective organic synthesis, as the functional groups are not well tolerated under the typical hydration conditions.

In addressing this issue, we here report a method for chemoselective hydration of terminal alkynes in the presence of water-soluble cobalt(III) porphyrin complex **1**. In the presence of 2 mol% of catalyst **1**, terminal alkyne containing alkyl *tert*-butyldiphenylsilyl(TBDPS) ether group was hydrated without loss of the TBDPS ether functionality, and the corresponding methyl ketone was obtained in 99% isolated yield. Other functional groups, such as ester, amide, ether, cyano, cyclic acetal, and glycosyl linkage were well tolerated under the hydration conditions. The catalyst can be easily separated from the product and is reusable for several times.



TBDPS = *tert*-butyldiphenylsilyl



1 (Ar = C_6H_4-*p*-SO_3)

P186

LEWIS ACID AND ORGANOCATALYZED DIMERIZATION OF DONOR-ACCEPTOR CYCLOPROPANES

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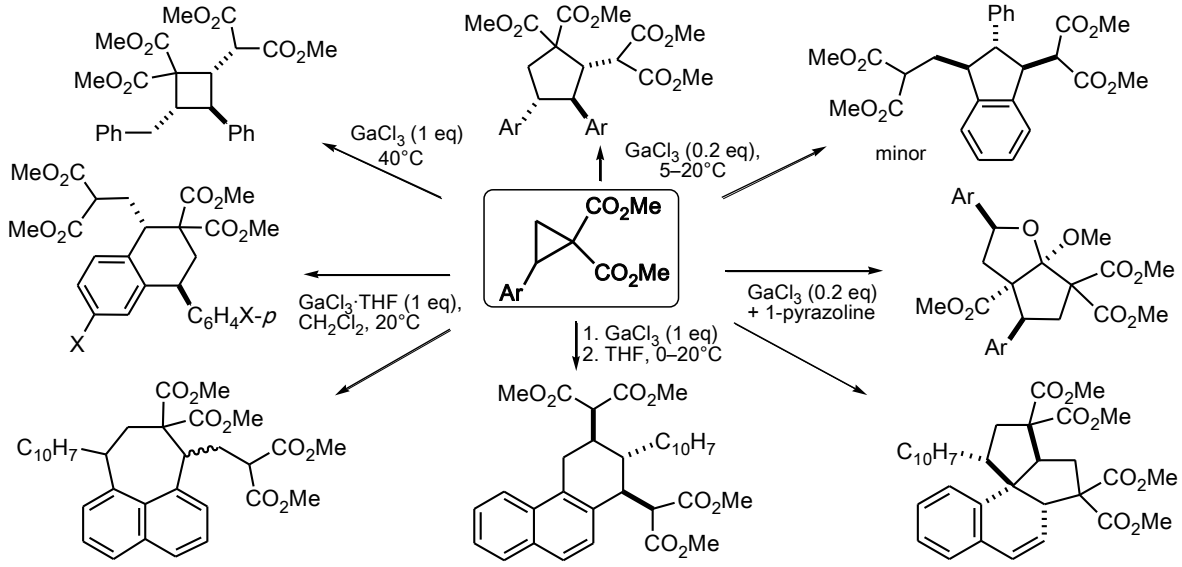
The new paths for the dimerization of donor-acceptor cyclopropanes (dimethyl 2-arylcyclopropane-1,1-dicarboxylates) under action of $GaCl_3$, $GaCl_3 \cdot THF$ and $GaCl_3$ in the presence of dimethyl 3,5-dimethyl-1-pyrazoline-3,5-dicarboxylate, as a specific organocatalyst, have been found. To date we obtained 10 different types of the cyclic products corresponding to cyclopropane dimers, most of them can be prepared selectively. These processes occur as [2+2]-, [3+2]-, [3+3]-, [4+2]-, [4+3]- and [5+3]-annelation, as well as the 1,5-cyclization cascades in which 4, 5, 6, 7, and 8-membered carbo- and heterocycles can be formed. Thus, a treatment of donor-acceptor cyclopropanes with anhydrous $GaCl_3$ in dichloromethane gives polysubstituted cyclopentanes and cyclobutanes in yields higher than 70%. In the presence of the $GaCl_3$•THF complex an efficient formation of tetraline and dihydrocycloheptanaphthalene derivatives takes place.



We have also found that if a tetra-substituted 1-pyrazoline derivative is additionally used in a $GaCl_3$-promoted reaction, DA cyclopropanes undergo another unusual conversion. As a result of this reaction, the C=O fragment of one of the ester groups is incorporated into the cyclic system of the product to give polyfunctional 2-oxabicyclo[3.3.0]octanes. Interestingly, dimethyl 2-(1-naphthyl)cyclopropanedicarboxylate at the same conditions yields pentaleno[6a,1-*a*]naphthalene derivative stereoselectively as a result of *ipso*-attack and 1,5-cyclization. Thus, unique pathways of diverse dimerization of DA cyclopropanes on treatment with $GaCl_3$ and $GaCl_3$–organocatalyst have been demonstrated using esters of 2-aryl(hetaryl)cyclopropanedicarboxylic acids. The reaction mechanisms were studied by NMR spectroscopy and a number of intermediates were detected.

This study was financially supported by the Russian Federation President Council for Grants (NSh-604.2012.3) and by the Division of Chemistry and Materials Science of the Russian Academy of Sciences.

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P187

NEW IONIC LIQUIDS – VERY ACTIVE CATALYSTS IN TRANSESTERIFICATION OF FAME WITH HIGHER ALCOHOLS AND POLYOLS

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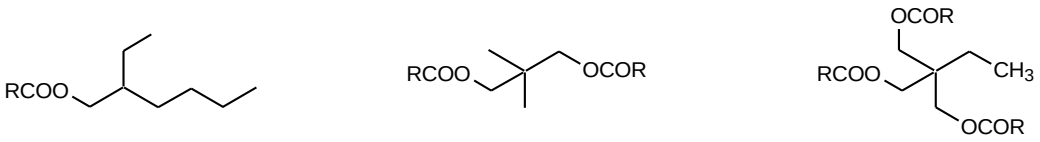
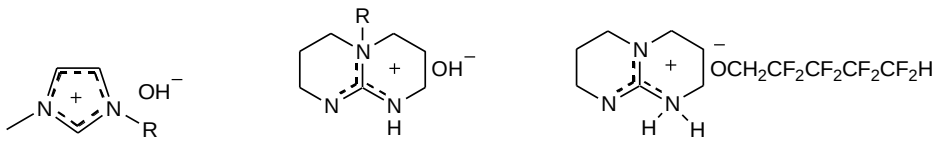
Vegetable oils as lubricants have been widely used for many years due to the high biodegradability and good lubricating properties [1]. Their disadvantage, however, was low oxidative and hydrolytic stability [2-5]. In order to improve the oxidative and hydrolytic stability vegetable oils were subjected to chemical modification. Of the many methods of modifying vegetable oils commonly used is the transesterification of other alcohols and glycols such as 2-ethylhexyl alcohol (2-EH), neopentyl glycol (NPG) and trimethylol propane (TMP), from which the most important are the esters of TMP.



For the synthesis of of esters of TMP mostly transesterification of methyl esters (FAME) and TMP towards enzymatic catalysts (lipase) [5] or alkaline (sodium methoxide) [6] are used. The resulting product, however, contains about 30% of unreacted methyl esters and about 45 wt% triester, which has a critical effect on the lubricating properties of the product. A similar situation occurs in the case of esters of NPG and 2-EH.

In our study we found that the use of ionic liquids as catalysts allows to obtain a product containing triester nearly 80% by weight. The total content of di-and tri-TMP exceeds 90% at a minimum content of FAME, which avoids the cumbersome distillation under a deep vacuum. Specially designed ionic liquids were used, both acidic and alkaline. New alkaline ionic liquids were obtained from both N-methylimidazole, and cyclic guanidine derivative. As anions were: OH and perfluoroalkyl chain. Acidic ionic liquids were obtained from the N-methylimidazole.



In the case of esters of TMP and 2-EH FAME conversion exceeded 90%. In the case of esters of neopentyl glycol (NPG) results were slightly worse. FAME conversion was about 80%.

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P188

SYNTHESIS OF LUBRICANT FATTY ESTERS OVER SULFONIC ACID-FUNCTIONALIZED SILICAS

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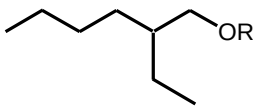
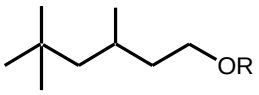
Esters of higher alcohols and fatty acids C_{12}-C_{20} derived from renewable raw materials as well as fatty acids produced by chemical synthesis are an important group of products of great practical importance. These esters, both vegetable and chemical and aliphatic alcohols (C_8-C_{18}) are widely used in cosmetics, as well as components of lubricants [1,2].





R = $C_{17}H_{33}CO$, $C_{17}H_{35}CO$

The basic method of synthesis is the esterification of the alcohol with acid over homogeneous acid catalysts, such as H_2SO_4, or H_3PO_4 RSO_3H [3-6]. Homogeneous catalysts are very effective, but require careful washing from the reaction mixture and also adversely affect the color of the products, which reduces their functional properties. Advantageous alternative to these processes is the use of heterogeneous catalysts. Zeolites HY, H-Beta, H-ZSM-5 and sulfonated synthetic silicates SBA-15 and MCF were examined in the reactions of esterification of fatty acids and polyols, but mainly in glycerol [7-9]. This communication presents the results of studies on the synthesis of fatty acid esters and alcohols, C_8-C_9. These esters are used as components of oil bases. The catalysts used are easily accessible and easy to synthesize with commercial silicas functionalized with alkylsulfonic group, however, in these studies silicas of a wide range of pore size were used, which could have a significant impact on the course of esterification. As fatty acids both rapeseed oleic acid and synthetic isostearic acid were used.

Sulfonated silicas proved to be very effective catalysts for the esterification. For both, oleic and izostearic acid conversion exceeded 90%. Much higher conversion was obtained for the catalyst based on narrow pore silica (22Å). For the ester of 2-ethylhexyl alcohol was even > 99%, while for wide pore silica (120Å) was only 93-95%. Sulfonated narrow pore silica was also characterized by a higher selectivity. This behavior of the catalyst indicates that the esterification process takes place on its surface. Narrow pore silica has a larger surface area, so you can get almost twice the concentration of sulfonic groups on its surface. The main advantage of these catalysts was low (<3%) content of undesirable by-products in the product and the acceptable bright color (30-40 J). Conversion of> 99% can be obtained, for example it is true for acidic ion exchange resins, but their content of by-products reached 9%, which is very unfavorable. Catalyst based on silica can be effectively recycled back into the process without the need of washing, which is of great practical importance. After four cycles of recurrence of the fatty acid conversion decreased slightly from 99% to 97%.

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P189

SYNTHESIS OF FLUORESCENT COUMARIN-SACCHARIDE CONJUGATES

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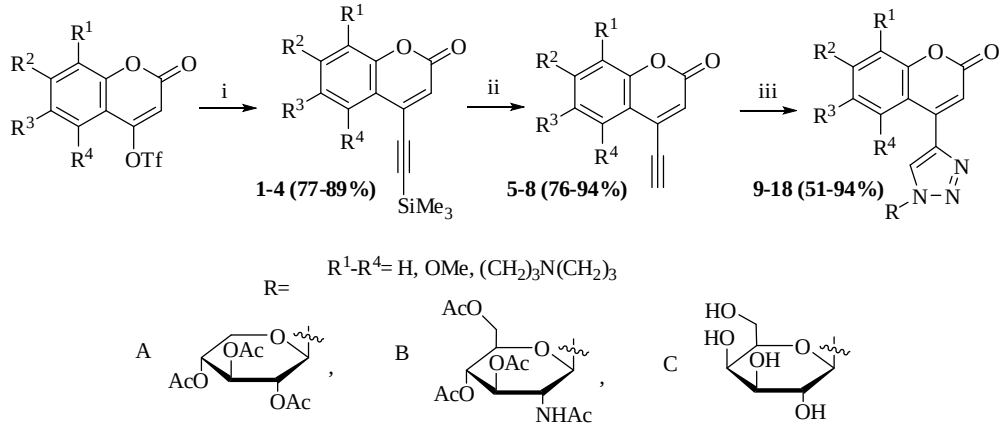
Coumarins are present in plant, microorganism, and animal sources and manifest a wide range of pharmacological activities, including antitumor, antibacterial and antiviral properties.[1]
Compounds **9–18** can serve as good models for the fluorescent detection of carbohydrate receptors on the surface of pathogens, for example, for the recognition some types of cancers[2] using binding of galactose, glucose, or xylose residues to corresponding receptors on the targeted pathogen.
A series of coumarin triazolylglycosides were synthesized[3] starting from 4-trifluoromethanesulfonates comarins in good yields via Sonogashira cross-coupling and copper-mediated 1,3-dipolar cycloaddition reactions of carbohydrate azides.



Scheme 1. Reagents and conditions: (i) Me_3SiCCH (1.1 equiv.), $Pd(Ph_3P)_4$ (0.05 equiv.), CuI (0.1 equiv.), *i*-Pr_2NEt (2 equiv.), MeCN, rt, 2 h; (ii) Bu_4NF in THF, rt, 15 min; (iii) 4a-d (1.1 equiv.), CuI (0.2 equiv.), THF/EtOH/H_2O (1:1:1), 60 °C, 15 h.

Several of the products show strong luminescence [relative quantum yield (Rhodamine 6G as standart) near 0.7] in the 490–560 nm region and are compatible with surface imaging applications.
A standard cytotoxic assay with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT assay)[4] showed no toxic effects of water soluble compound **11** (R^1-R^4=$(CH_2)_3N(CH_2)_3$, R=*C*) in micromolar concentrations on HeLa cells. In this connection fluorophore **11** may be of interest and is compatible with surface imaging applications.[5]
This work was supported by Federal Targeted Programme ‘Scientific and Scientific-Pedagogical Personnel of the Innovative Russia in 2009–2013’ (16.740.11.0476 and 14.740.12.1382) and the Russian Foundation for Basic research (№ 12-03-00214-a).

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P190

CATALYTIC ASYMMETRIC α–HYDROXYLATION OF PYRANOINDOLIZINE DERIVATIVES USING GUANIDINE–UREA BIFUNCTIONAL ORGANOCATALYST

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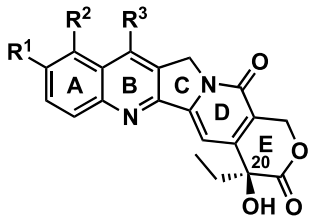
Camptothecin (**1**) (CPT) is a natural product isolated from *Camptotheca acuminata* in 1966.[1] CPT shows potent antitumor activity by inhibiting topoisomerase I, and today, two synthetic CPT derivatives of topotecane (**2**) and irinotecan (**3**) have been clinically used for a cancer chemotherapy. One of a structural feature of CPT (**1**) is an E-ring lactone bearing optically active tertiary hydroxyl group at C20, which is mandatory for the antitumor activity. In this paper, we will describe organocatalytic asymmetric synthesis of C,D,E-ring system of **6**, which is one of a key intermediate of **1** on the basis of Friedlander condensation methodology.[2]



Camptothecin (**1**); R^1=R^2=R^3=H
Topotecan (**2**); R^1=OH,R^2=CH_2NMe_2,R^3=H
Irinotecan (**3**); R^1=OCOPipPip,R^2=H,R^3=Et

We recently have developed guanidine–(thio)urea bifunctional organocatalysts, and reported some enantioselective reactions including carbon-carbon bond forming reactions and oxidation of olefins.[3] In this context, we applied the guanidine-urea catalyst **4** for the oxidation of **5** at C20. Thus, oxidation of **5** with cumene hydrogen peroxide (CHP) in the presence of **4** (10 mol%) was examined, and we found α-hydroxylated **6** was obtained in 95% yield with 84% ee as a desired stereoisomers. In this reaction, guanidine and urea groups in **4** is proposed to interact with lactone **5** and CHP, respectively, and stereochemistry is controlled by flexible linear chiral spacer (Figure 1). Catalyst optimization and substrate scope of this catalysis will also be presented.

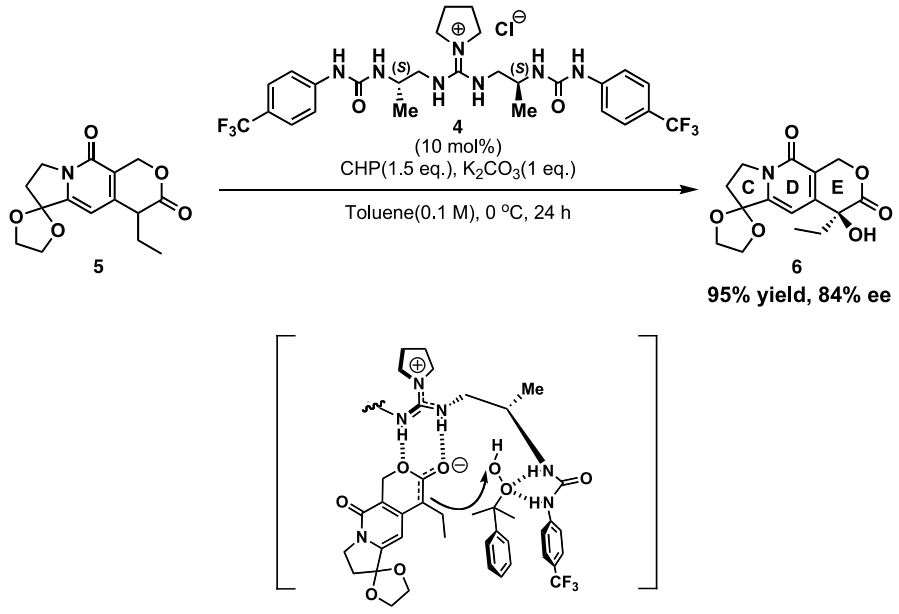


Figure 1

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P191

FIRST ENANTIOSELECTIVE CYCLOPROPANATION OF INDOLES USING GLUCOBOX LIGANDS

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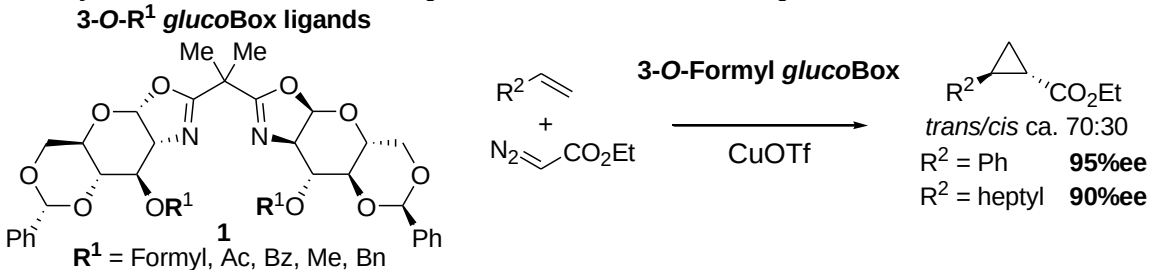
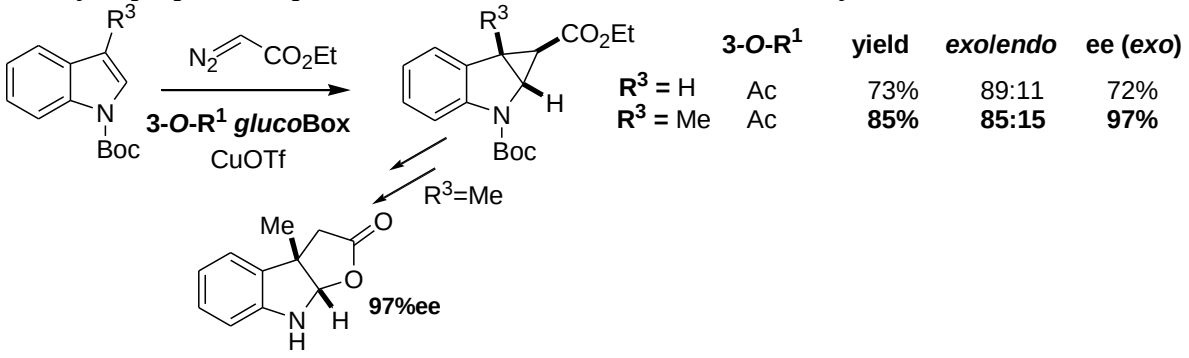
Bis(oxazolines) are among the most successful chiral ligands for metal-catalysed asymmetric reactions.[1] We have introduced carbohydrate-based bis(oxazolines) and found that both, steric demand as well as electronic nature of the 3-*O*-substituents exert strong impact on the enantioselectivity of asymmetric cyclopropanation reactions. As a result of these studies we have designed optimised ligand 3-*O*-formyl *gluco*Box giving cyclopropanation products of both activated styrene and non-activated aliphatic olefin substrates in up to 95%ee.[2]



After the successful application of ligand 3-*O*-formyl *gluco*Box in the stereoselective synthesis of the natural product grenadamide,[2c] we are now exploring carbohydrate-based bis(oxazolines) in the asymmetric cyclopropanation of *N*-acyl indoles, a reaction for which up to now only racemic[3] and diastereoselective[4] protocols have been reported. With *N*-Boc indole we have obtained first promising results. The reaction with 3-methyl *N*-Boc indole yielded the cyclopropanation product containing a quaternary stereocentre in high yield, good *exo*/*endo* selectivity and excellent 97%ee.[5] The cyclopropanation product is a valuable intermediate for the synthesis of indole alkaloids.



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P192

ENANTIOSELECTIVE COOPERATIVE ORGANOCATALYSIS USING A HIGH-PERFORMANCE CHIRAL ANION GENERATOR

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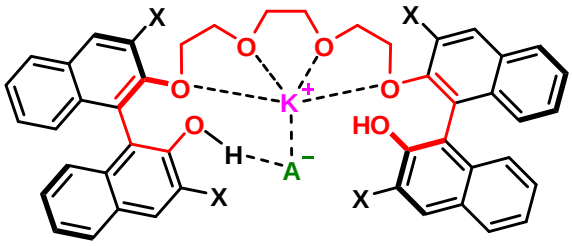
Cooperative catalysis, the simultaneous binding and activation of reacting partners resulting in both the pre-organization of the substrates and stabilization of the transition state structures, is a fundamental principle in enzymatic catalysis. For cooperative catalysis using small organic molecules, we recently developed a new structural motif for multifunctional catalysts that can be used to generate a chiral anion from an inorganic salt in "one phase". Using this chial anion generator as an organocatalyst, excellent catalytic activity and enantioselectivity have been achieved for a range of organic reactions. The single crystal X-ray structure of the complex of the catalyst and a potassium salt (e.g. KF) provides interesting insight into the origin of the catalytic activity and stereoselectivity.[1,2]



Chiral Bis-Hydroxy Polyether
Chiral Anion Generator

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LINEAR POLYSTYRENE-STABILIZED Pt NANOPARTICLES FOR AEROBIC ALCOHOL OXIDATION AND HYDROGEN-TRANSFER REDUCTION IN AQUEOUS MEDIA

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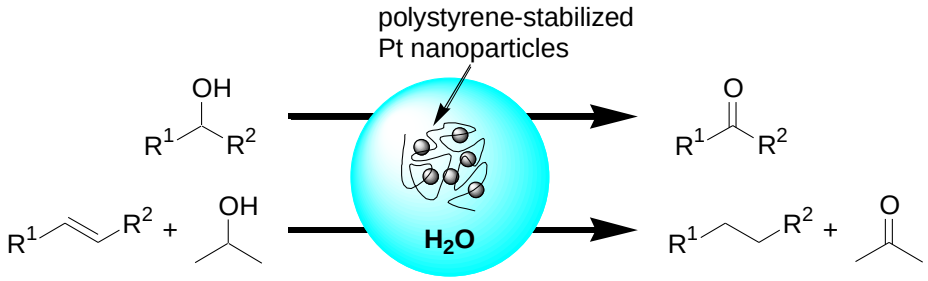
The oxidation of alcohols is one of the most important transformations in organic synthesis because the corresponding carbonyl compounds serve as important and versatile intermediates for the synthesis of fine chemicals.[1] Transfer hydrogenation, which uses H donors instead of hazardous H_2, is also an attractive methodology.[2] Recently, we found that linear polystyrene was capable of stabilizing PdO nanoparticles (PdONPs), and that the resultant polystyrene-stabilized PdONPs have high catalytic activities for C-C coupling reactions in water.[3,4] Now, we report the preparation and application of polystyrene-stabilized PtNPs for aerobic alcohol oxidation in water and hydrogen-transfer reduction to prove its efficiency in promoting the reaction with high recyclability.



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P194

LINEAR POLYSTYRENE-STABILIZED PdO NANOPARTICLES CATALYZED MIZOROKI-HECK REACTION IN WATER

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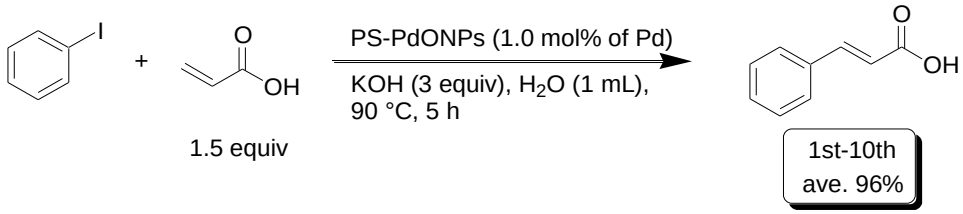
The coupling reaction of vinyl or aryl halides with various alkenes in the presence of palladium catalyst is known as Mizoroki-Heck reaction and represents a powerful tool for building up a new carbon-carbon bond.[1] Recently, attention has focused on the use of palladium nanoparticles (PdNPs) as catalyst in organic synthesis.[2] On the other hand, the use of water as a reaction medium for organic synthesis has recently received much attention, because water is a readily available, safe, and environmentally benign solvent.[3] Recently, we found that PdO nanoparticles (PdONPs) are readily stabilized on linear polystyrene, and the resultant polystyrene-stabilized PdONPs have high catalytic activities for Suzuki and copper-free Sonogashira coupling reactions in water.[4] Now, we report polystyrene-stabilized PdONPs exhibited high catalytic activity for Mizoroki-Heck reaction under air in water and recycled without loss of activity.



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P195

CATALYTIC AEROBIC PRODUCTION OF IMINES EN ROUTE TO MILD, GREEN, AND CONCISE DERIVATIZATIONS OF AMINES

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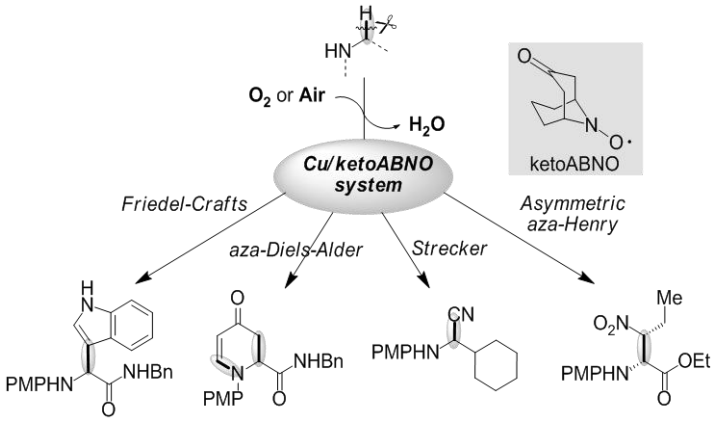
The recent worldwide concern for the environment has inspired chemists to utilize aerobic oxygen as a stoichiometric oxidant in artificial chemical reactions aimed at environmentally benign, streamlined complex molecule synthesis.[1] Continuous escalation of the oxidation level of synthetic intermediates contributes to the minimal use of protective groups that are not included in target compounds.[2] Molecular oxygen is the most ideal stoichiometric oxidant for such oxidative transformations, because it is abundant and produces H_2O as the sole side product.

Amines are primordial structures ubiquitously observed in bioactive molecules. Classically two methods are used to elaborate complex amines; 1) nucleophilic addition to imines or iminium ions and 2) *N*-alkylation or cross coupling. The reactions occur at the nitrogen atom. Alternatively, *direct aerobic oxidative transformation of amines* is the α-position of a substituent on the nitrogen atom is modified via C–C bond-formation with generated transient imine intermediates from amines by aerobic oxidation. The method will provide a new entry to amine synthesis.

We will present a general and synthetically useful catalytic aerobic dehydrogenation of amines to imines using the combination of a sterically less-demanding and electron-deficient new *N*-oxyl radical (ketoABNO) and copper(I) salt.[3] This mild transformation allowed for extension to a direct α-derivatization of secondary amines involving sequential C–C bond-formation to the resulting imines, including a catalytic asymmetric variant. Mechanistic insight into this novel catalytic system will be also the scope of our presentation.



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P196

CATALYTIC OXIDATION OF THIOLS IN IONIC LIQUID USING ORGANIC MEDIATORS

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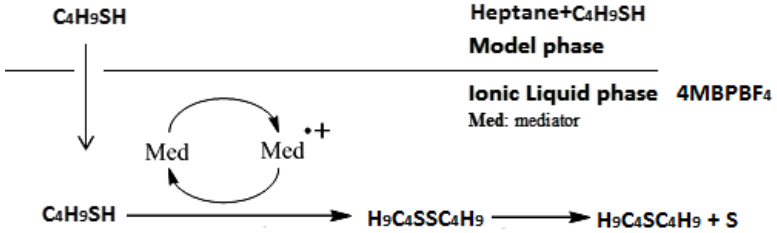
Research devoted to thiols trace concentration extraction from hydrocarbons is significant because of their toxicity as well as new fuel standards development. Ionic liquids are perspective new thiol extragents from nonpolar agents [1].

Ionic liquid extraction of thiols (1-butyl-4-methylpyridynium tetrafluorborate – $4MBPBF_4$) and transformation of thiols to non-toxic disulfides and sulfides by the use of electromediator systems is studied. One of special properties of ionic liquids are high electroconductivity and wide polarization potential values interval [2].

Thereof high electroconductivity thiols oxidation by different electromediators without supplemental electrolite application occurred in the ionic liquid. Electromediators are catalytic systems which brings in minimal quantities and not consumes in chemical combustions [3]. Mediators were aromatic amines (tri-p-tolylamine, tri-p-bromophenylamine, 2,2`,4,4`-tetramethoxyphenylamine, N,N,N`,N`-tetramethyl-1,4-phenylenediamine, phenoxazine). Electrochemical oxidation of C_4H_9SH was occurred at mediator's oxidation potential that allowed to minimize power inputs in 0.5-0.8V. Consequently electrolysis occurs dibutyldisulfide formation thereupon dibutylsulfide (1,7V) as products of one-electron oxidation, fragmentation and dimerization of thiols. Products identification was made with cyclic voltammetry, IR-spectroscopy and gas chromatography.

Demercaptanization scheme with ionic liquid and electromediators usage on the example of model system (heptan+butylthiol) is given below:



The study was financially supported by RFBR (12-03-00513a), grant of the President of RF (MK-923.2012.3), federal special-purpose programme "Scientific and pedagogical personnel of innovative Russia" 2009-2013 (GK № 16.740.11.0594).

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P197

DEVELOPMENT OF RAPID PROCEDURE FOR NMR MONITORING OF ENANTIOMERIC EXCESS IN ORGANOCATALYTIC REACTIONS

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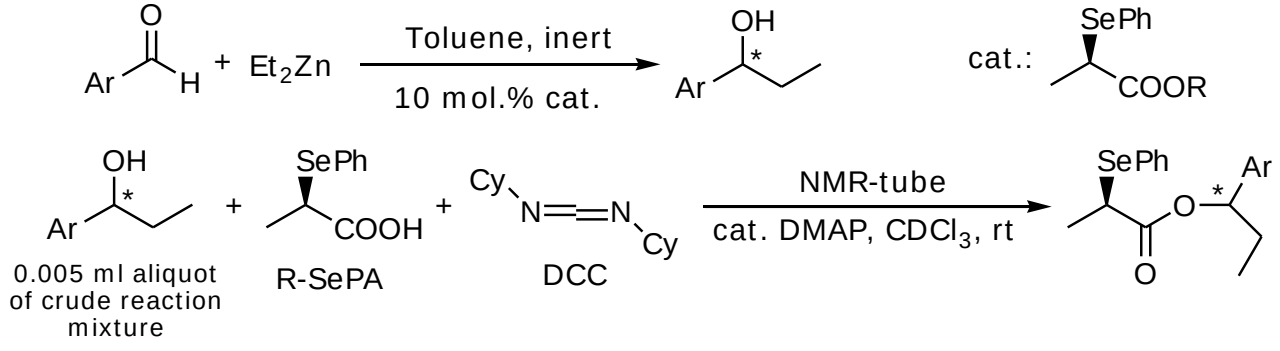
Determination of enantiomeric purity and absolute configuration of chiral molecules is an important task in modern asymmetric synthesis and catalysis as well as in drug design and investigation of natural compounds[1]. Nowadays chiral HPLC and NMR spectroscopy are widely used for determination of enantiomeric excess in asymmetric reactions[2]. Usually additional manipulations to purify crude reaction mixtures are necessary (quenching, extraction, solvent evaporation) prior to analysis by both of the methods. Enantiomers are indistinguishable in NMR therefore special derivatization procedures to prepare diastereomers with chiral auxiliary reagents are required. All these steps are time-consuming and require additional reagents to be used.

Recently we have developed convenient derivatization procedure directly in NMR tube using well-known chiral derivatizing agents (CDA) such as MTPA or MPA and newly synthesized Se-based chiral acid for analysis of chiral alcohols and amines[3]. Preliminary purification of diastereomers formed isn't needed to obtain NMR spectra (both 1D and 2D) of high quality which allows determination of enantiomeric purity of various chiral alcohols and amines with high accuracy within several minutes including sample preparation time.

Here we present novel rapid procedure for real-time NMR monitoring of enantiomeric excess during an asymmetric reaction. Using a model reaction of reductive ethylation of arylaldehydes with Et_2Zn (Scheme 1) we have developed a convenient and reliable protocol to transform enantiomers in a crude reaction mixture into diasrereomers suitable for NMR analysis with minimal additional manipulations. No time-consuming procedures such as extraction or solvent evaporation were needed that allowed to reduce sample preparation time up to 10-15 minutes. Presence of solvent or other components of the reaction mixture didn't influence derivatization procedure and quality of NMR spectra. The ee values measured during NMR monitoring were in a good agreement with those obtained by NMR or HPLC after completion of the reaction and ordinary work-up. Practical aspects of the developed protocol as well as scope and limitations will be discussed.



Scheme 1. Model catalytic reaction and real-time determination of enantiomeric excess by NMR.

The work was supported by the RFBR grant No. 12-03-01094.

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P198

TRIS(TRIAZOYL)METHANOL LIGANDS FOR COPPER (I)-CATALYZED AZIDE ALKYNE CYCLOADDITION REACTIONS

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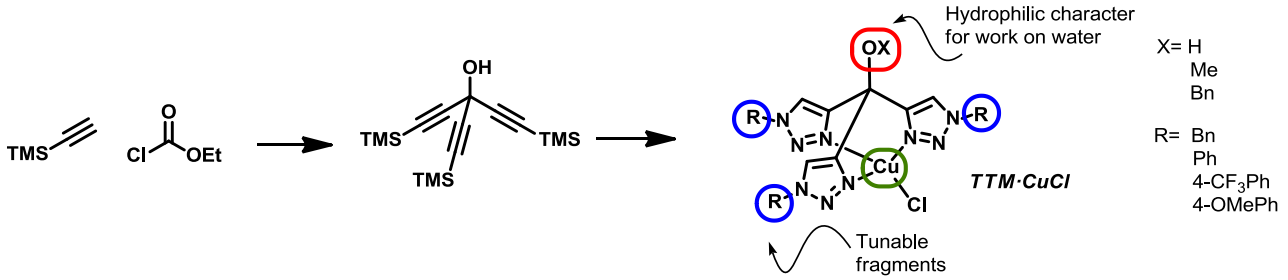
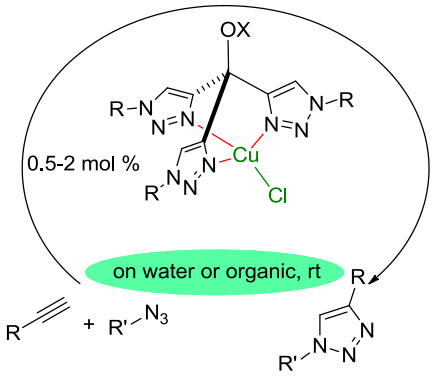
The concept of click chemistry is closely linked to the development of the universally applicable copper-catalyzed alkyne–azide cycloaddition (CuAAC).[1-2] If a criticism can be made to the original CuAAC procedures, it would be related to usage of fairly high amounts of copper catalyst. To overcome this problem, ligand stabilized Cu(I) species have been developed.[3-4]
Tris(1-benzyl-1H-1,2,3-triazol-4-yl)methanol (**TTM**), a highly efficient modular ligand family for CuAAC reactions, has been developed using click chemistry.[5-6] Cu(I) complex and its various derivatives are stable in water and under air; it is active at low catalyst loadings (0.5 mol%) and in both aqueous and purely organic media. In addition, short reaction times at room temperature, and compatibility with free amino groups make **TTM·CuCl** derivatives an outstanding catalyst for CuAAC. Herein, we present the effects of tunable fragments and hydrophilic effect of the –OH group with diverse set of ligands.



As a result of screening different functional groups in the backbone of the catalyst; the system was optimized to work under organic, mixture of organic-aqueous and also in perfluorinated solvents with synthetically useful isolated yields. This investigation expands the applicability of the catalyst.



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P199

HIGHLY ENANTIOSELECTIVE NITROALDOL REACTIONS CATALYZED BY COPPER(II) COMPLEXES DERIVED FROM SUBSTITUTED 2-(PYRIDIN-2-YL)IMIDAZOLIDIN-4-ONE LIGANDS

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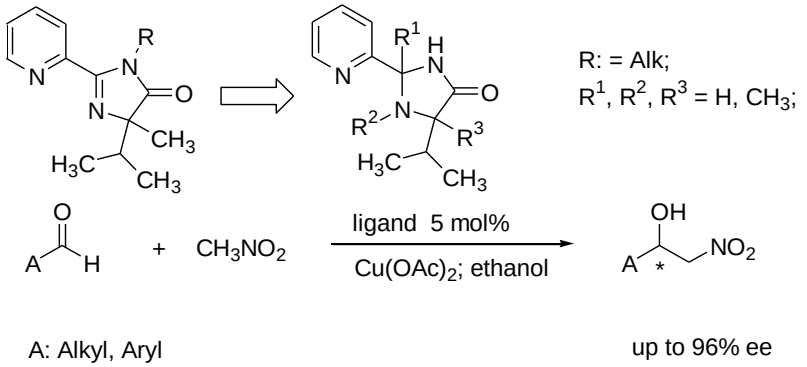
The nitroaldol (Henry) reaction represents one of the basic processes in organic synthesis for producing a carbon-carbon bond and is a key step in the synthesis of many significant compounds. The asymmetric variant of the Henry reaction plays a significant role in the synthesis of pharmaceutical precursors, in particular. The general procedure of this asymmetric synthesis requires the application of a suitable optically pure chiral ligand, often in combination with metal ions. In the case of the nitroaldol reaction, complexes with Cu(II) have proven particularly useful.
The Cu(II) complexes derived from 2-(pyridin-2-yl)-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-ones, which we prepared earlier, were also efficient catalysts for Henry reaction.[1] However, in the case of these complexes, the resulting enantioselectivity was only low (maximum 19% ee). Thanks to the sp^3 configuration at the 2-carbon atom, the imidazolidin-4-ones are less rigid than the substituted 4,5-dihydro-1*H*-imidazol-5-ones.[2] A similar example was encountered in the catalysis of the Henry reaction in the case of Cu(II) complexes derived from substituted pyridylimidazolidines as compared with the Cu(II) complexes derived from pyridylimidazolines.



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P200

ORGANOCATALYTIC SYNTHESIS OF DEOXYKETOSES AND IMINOSUGARS

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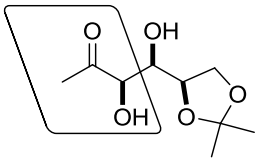
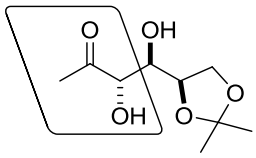
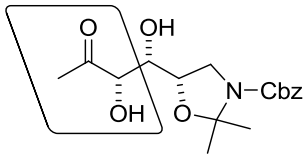
The 1,2-diol unit occurs very often in complex natural products like carbohydrates, iminosugars or alkaloids. Development of enantioselective methodologies for preparation of these molecules have been at the forefront of modern catalytic asymmetric synthesis.
Iminosugars are monosacharide analogues in which the ring oxygen has been replaced by a nitrogen atom. In case of special construction, compounds from this family have potentially therapeutic applications either use in treatment of diabetes, cancer, AIDS, viral infections and metabolic disorders.[1]
Aldol reaction is one of the most useful method of stereoselective formation new carbon-carbon bond. Now, when the researches of organocatalytic aldol reaction reached high level of sophistication, we could try to use whose methodology to the synthesis of more complex molecules.

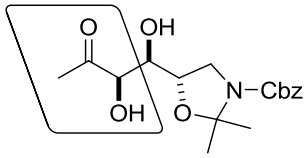


deoxysorbose



deoxytagatose





Here, we present organocatalytic direct activation of hydroxyacetone donors and aldehydes (Garner's aldehyde, (R)-glyceraldehydes and protected (S)-isoserinal aldehyde) by using proline- and serine-based catalyst.2 We tested several popular aminoacid and chiral amine like catalyst in these reaction. The product was obtained with good yield and high diastereoisomeric excess. Desired products with two stereogenic centers have been generated with high level of diastereo- and enantioselectivity. Additionaly to enamine-based mechanism we present substrate activation by using non-chiral amines under asymmetric substrate-based control.

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P201

ESTERIFICATION OF GLYCEROL OVER 12-TUNGSTOPHOSPHORIC ACID ANCHORED TO DIFFERENT SUPPORTS: A GREEN AND SUSTAINABLE APPROACH

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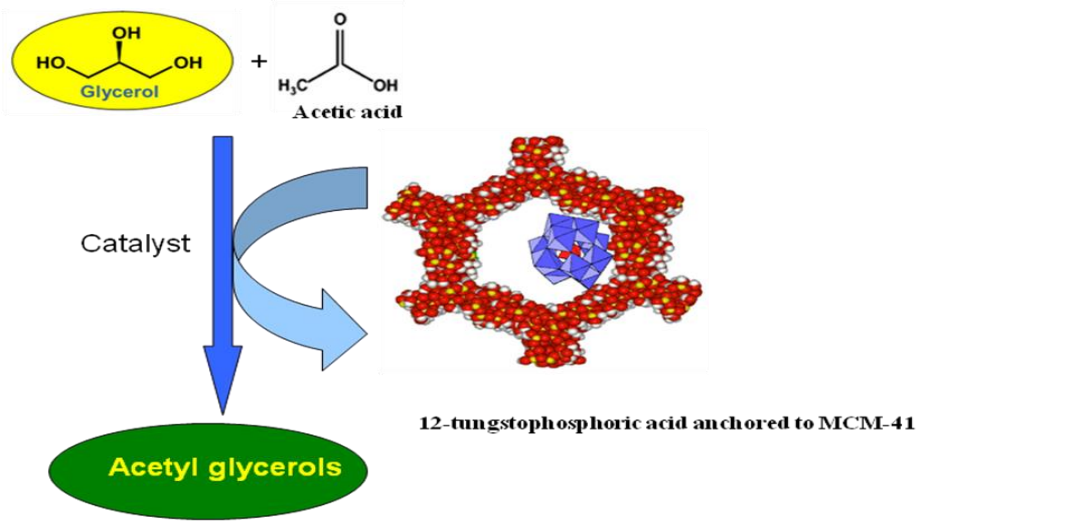
Catalysis represents a key approach to green chemistry in the activation and utilization of bio-renewable chemical feed stocks, crucially important for sustainable society. In recent years increase in biodiesel production has resulted in the accumulation of glycerol, obtained as byproduct. This not only creates a glut in the market but also affects the overall economics of biodiesel production. Hence a search for direct conversion of glycerol to value added products is a current important demand of the society.

The direct conversion of glycerol to high value chemicals would be of great interest from environmental and economic view point [1]. In this regard, use of an ecofriendly catalyst would enhance the activity for the direct conversion of glycerol to value added products, by minimization of waste. Among all, acetylation of glycerol with acetic acid is most important as its application ranges from cosmetics to transportation fuel additives, especially triacetin is promising as it can be added into the formulation of biodiesel. Keeping this in mind, an attempt was made to carry out esterification of glycerol into glycerin esters over environmentally benign catalyst under green conditions.



A green and sustainable approach towards synthesis of acetyl glycerols

The present work consists of synthesis and characterization of 12-tungstophosphoric acid anchored to different support, MCM-41 and Zirconia. The catalytic activity was evaluated for liquid phase esterification of glycerol with acetic acid by varying different reaction parameters such as mole ratio, amount of catalyst and reaction time. The superiority of the present work lies in getting good conversions and selectivity for triacetin. Also catalysts were regenerated and recycled up to four cycles.

Reference:

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P202 (GM4)

POLYETHYLENE GLYCOL AS POLYMERIC SUPPORT IN ASYMMETRIC SYNTHESIS

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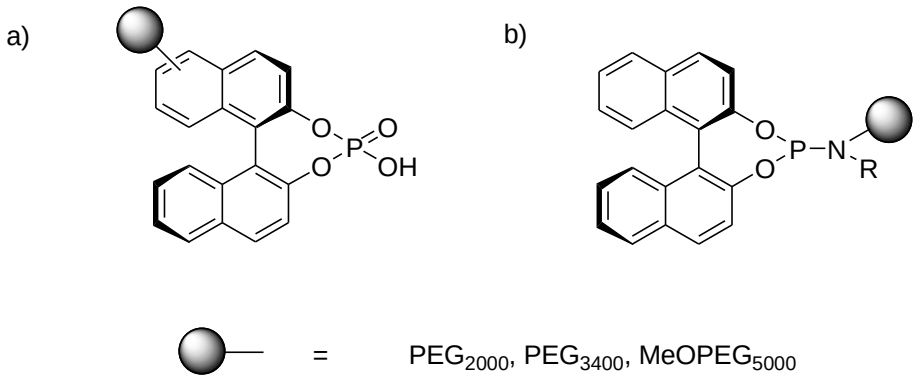
In recent years, the use of soluble polymer-supported reagents and catalysts[1] has gained significant attention as an alternative to traditional solid-phase synthesis.
The present work presents new types of organic catalysts, including chiral phosphoric acids (Scheme 1, a) and phosphoramidites (Scheme 1, b) linked to a polymeric support, possessing catalytic activity and stereo-differentiating ability, easily removed from the reaction mixture and suitable for several catalytic cycles. Polyethylene glycol (PEG) was chosen as polymeric support due to its good solubility in polar solvents and facile isolation by precipitation with diethyl ether.
Scheme 1.



The catalysts were tested in enantioselective addition reaction of diethyl phosphite to multiple C=N bond (Pudovik reaction) leading to precursors of phosphonic acid, in the reaction of transfer hydrogenation of ketimines and homogeneous Pd-catalyzed arylation of imines
The catalytic activity and recyclability were evaluated and will be presented.

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P203

NOVEL RUTHENIUM CATALYST FOR CYCLOTRIMERIZATION OF ALKYNES

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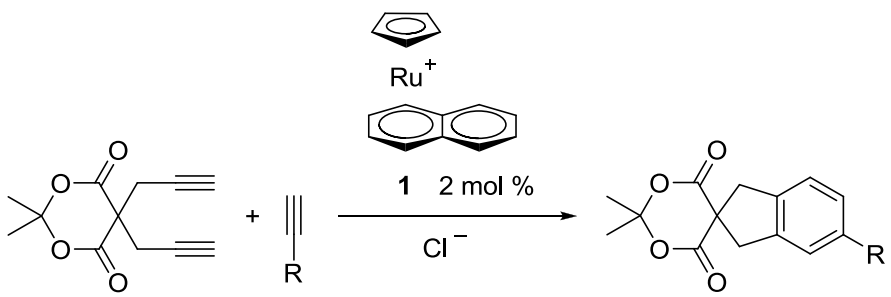
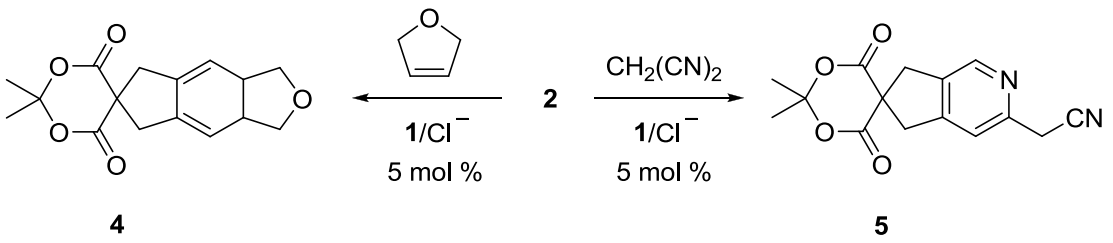
Cyclotrimerization of alkynes is simple and effective method for synthesis of substituted aromatic compounds. We have found that ruthenium naphthalene complex $[CpRu(C_{10}H_8)]^+$ **(1**) in the presence of Cl^- anion generate unsaturated species [CpRuCl] which catalyze cyclotrimerization of dyine **2** with various alkynes to give benzene derivatives **3a**–**i** in 50–80% yields. Reaction proceeds in air at room temperature with 100% conversion in 1–3 h in the presence of 2 mol % of catalyst precursor **1**.



	R	yield
a	C_4H_9	85
b	C_6H_{13}	87
c	Ph	76
d	Me_3Si	54
e	H	56
f	$(CH_2)_2Br$	70
g	$(CH_2)_3OH$	75
h	CH_2OMe	63
i	CH_2OAc	69

Some functional groups in propargylic position of alkynes (R = CH_2OH, COOMe, CH_2NMe_2, CH_2Br) inhibit cyclotrimerization. However, reaction of **2** with protected derivatives of propargyl alcohol (R = CH_2OMe, CH_2OAc) gives **3h**,**i** in good yields. Cyclotrimerization of **2** with 2,5-dihydrofuran or malononitrile in the presence of **1** and Cl^- (5 mol %) gives cyclohexadiene **4** (64%) and pyridine **5** (92%), respectively. In overall, the catalytic activity of **1** in alkyne transformations is similar to that of the popular catalyst Cp*Ru(cod)Cl, while the tolerance to the functional groups is somewhat lower.



This work was supported by Grant for Young Scientists of the President of Russian Federation (grant # МК-684.2011.3).

P204

NEW ASYMMETRIC METHODOLOGIES FOR THE AZA-QUATERNARY MOTIF

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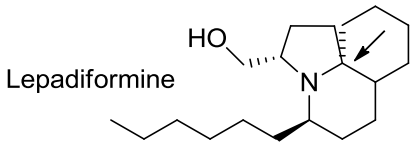
Two contrasting methodologies for accessing the aza-quaternary motif in chiral, non-racemic form will be presented. These will include an auxiliary-based diastereoselective alkylation sequence from malonate comparing with an organocatalysis approach using β-ketoesters in conjunction with a novel hydrazide catalyst.

Within the prolifically bioactive alkaloid field, one finds an abundance of chiral, aza-quaternary centres embedded in the alkaloid structures (Figure 1) that are of interest to medicinal chemistry programmes.



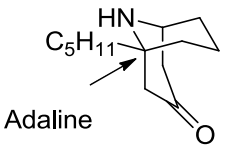
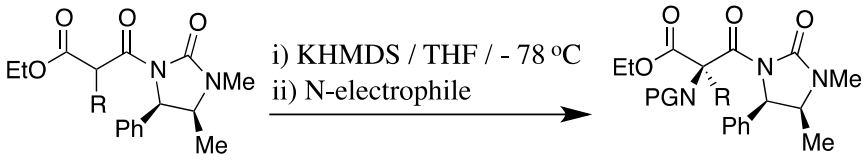


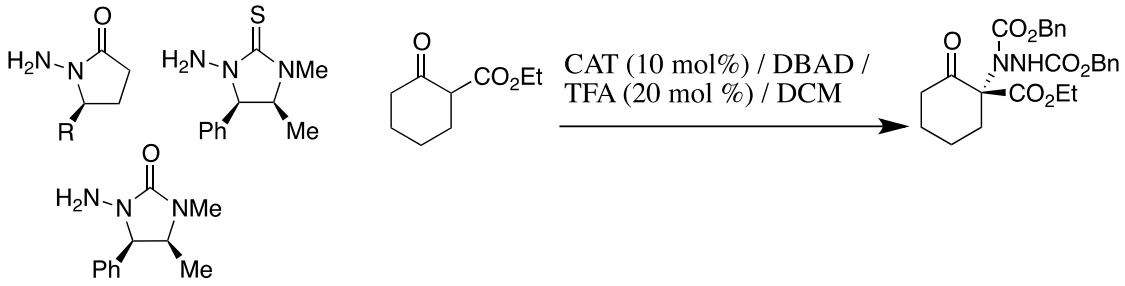
Figure 1: Alkaloids containing aza-quaternary structural motifs

This presentation will describe our efforts towards developing two new contrasting methodologies for accessing aza-quaternary motifs in homochiral form. While the one approach involves using malonate as a cheap starting source with an ephedrine-based imidazolidinone auxiliary in a diastereoselective alkylation sequence, the other is based on an organocatalysis approach using novel hydrazide catalysts with β-ketoesters, Scheme 1.

1) **Diastereoselective alkylation**



2) **Organocatalysis with hydrazide catalysts**



Scheme 1: Two contrasting methodologies for accessing the aza-quaternary motif in homochiral form

P205

ACTIVITY AND SELECTIVITY OF MAGNESIUM FLUORIDE-SUPPORTED PLATINUM GROUP METALS IN REDUCTION OF CHLORONITROBENZENE TO CHLOROANILINE

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The practical importance of chloronitrobenzene hydrogenation results from the large variety of applications of products of the above reaction – chloroanilines which are employed for the manufacture of pharmaceuticals, plant protection agents, dyes and pigments.
From among many methods for chloronitrobenzene reduction to chloroaniline (CAN), the most efficient one is the catalytic method. It is realized as a periodic process in tank reactors (autoclaves) under increased pressure of hydrogen (2-10 MPa). The achievement of 100% selectivity to chloroaniline is a challenging task and this is why an intensive search for catalysts of possibly the highest selectivity is conducted. Recently, good effects were obtained by using unconventional catalytic supports (γ-Fe_2O_3 and SnO_2) [1, 2]. In our study we have employed another untypical support – MgF_2. Ruthenium catalysts based on the latter support were investigated in hydrogenation of *ortho*-chloronitrobenzene to *ortho*-chloroaniline under conventional conditions in a pressure tank reactor (autoclave) as well as under APR conditions (Aqueous-Phase Reforming – APR [3]). Both reactions (APR and nitrogen group reduction) proceed at the same time under identical conditions in a flow reactor. This fact made it possible to eliminate expensive and hazardous compressed hydrogen.
Under conventional conditions of the reaction (autoclave), the Pt/MgF_2 catalysts appeared to be 30 times more active than Ru/MgF_2. It was established that there was impossible to achieve 100% selectivity at a complete conversion of chloronitrobenzene. A higher selectivity (99%) was achieved while using ruthenium catalysts. Over Ru/MgF_2 catalysts tested in APR/HYD conditions (Aqueous-Phase Reforming/Hydrogenation), it was possible to reach 100% selectivity to chloroaniline even at a complete conversion of chloronitrobenzene, although their activity was lower compared to Pt/MgF_2 catalysts.

Table 1. Activity and selectivity of MgF_2-supported platinum group metals in reduction of ortho-chloronitrobenzene to ortho-chloroaniline.

Catalyst	Apparent reaction rate, $g_{CNB}/g_{cat.}\cdot h$	Selectivity to *ortho*-CAN, %	Possibility of achieving 100% selectivity at 100% conversion
	Autoclave/H₂		
Ru/MgF_2	~2.0	97-99	No
Pt/MgF_2	~60.0	~97	No
	APR/Hyd		
Ru/MgF_2	0.24	**~100**	**Yes**
Pt/MgF_2	0.29	76	No

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Acknowledgements

The financial support of the project N N204 181640 by the Polish Ministry of Scientific Research and Information Technology is gratefully appreciated.

P206 (GM5)

CATALYZED OLEFIN HYDROMINATION BY SIMPLE PLATINUM SALTS: NEW MECHANISTIC FEATURES

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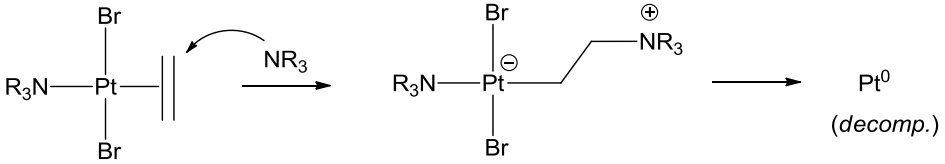
The intermolecular addition of an N-H bond across the C-C double bond in non activated olefins is a current economical and scientific challenge. Our group has introduced one of the best and especially simplest catalytic systems, consisting of bromide-activated platinum(II) salts, for the addition of anilines to ethylene and higher olefins.[1] Experimental and computational studies have elucidated the mechanism of the catalytic cycle.[2] A puzzling point of this catalytic system is the effect of Brønsted basicity on catalytic activity: while more basic anilines yield lower TON, the catalyst decomposition to metallic Pt is also shown to be accelerated by stronger bases. DFT calculations yield similar barriers for the addition of $PhNH_2$ and Et_2NH to C_2H_4, while the latter yields no hydroamination product at all.[3] The decomposition seems to occur after formation of the zwitterionic intermediate resulting from the amine addition to the coordinated olefin (scheme). Recent studies into the catalyst decomposition mechanism and ways to prevent it will be reported. The effect of ligands on the selectivity of the reaction will also be highlighted.



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P207

A NEW METHOD FOR THE SYNTHESIS OF (N AZOLYLALKYL)ALKAN/(AREN)AMIDES BY ALKYLATION OF AZOLES WITH 2-ALKYL/(ARYL)-4,5-DIHYDROOXAZOLES OR 2-ALKYL/(ARYL)-5,6-DIHYDROOXAZINES

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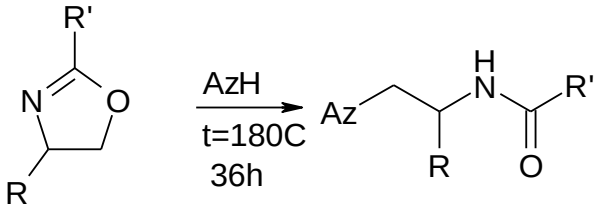
The N-(ω- azolylalkyl)arylamides exhibited high antiaggregative activity[1]. On the other hand obtained of hydrolysis of N-(2-azolylethyl)alkanamides the N-(2-aminoethyl)azoles [2] are valuable starting materials for the preparation of antiaggregation[3], hypotensive[1], anti-HIV[4] and antibacterial drugs.



We synthesized of N-(2-azolylethyl)alkan/(aren)amides and N-(3-azolylpropyl)alkan/(aren)amides by acid-catalyzed ring opening in 2-alkyl/(aryl)-4,5-dihydrooxazoles and 2-alkyl/(aryl)-5,6-dihydrooxazines in presence of azoles.

With $ZnCl_2$ as a catalyst the yields of amides varied from 50 to 87%, highest yield being reached with commercial 2-ethyl-4,5-dihydrooxazole.

The yields of N-[2(-imidazol-1yl)ethyl]propanamides were lower than the yields of analogous triazole and benzimidazole products.

Alkylation of azolees with oxazoline in a steel pressure vessel allowed us to elevate the reaction temperature and raise the conversion of the starting reagents. The yields of amides were increased to 75-86% versus 20-60% under atmospheric pressure.

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P208

ALKYLATION OF AMINES BY ALCOHOLS USING NICKEL AND COBALT NANOPARTICLES AS CATALYSIS

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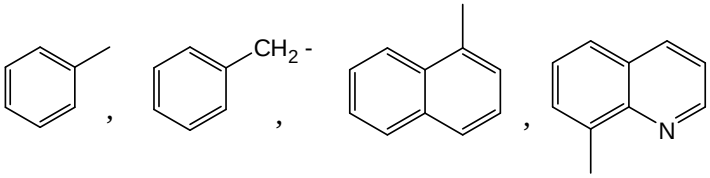
It was found an ability of alkylation by alcohols of direct aromatic and aliphatic amines using nickel or cobalt nanoparticles as catalysts. It was discovered that by this reaction secondary and sometimes tertiary amines may be obtained.

$$RNH_2 + R^1OH \xrightarrow[-H_2O]{Ni^0\ (Co^0)} RNHR^1$$

R= 

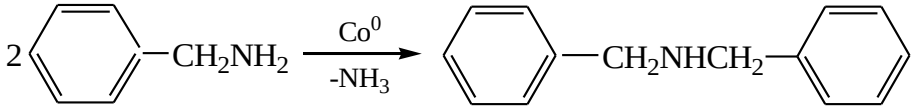
R^1= C_6H_{13} , C_8H_{17} , $C_6H_5CH_2$

Reaction proceeds at 150ºC and higher temperatures, and method discovered is applicable at laboratory conditions for high-boiling amines and alcohols.

Structures of obtained secondary amines are proved by NMR and CMS.

The possible mechanism of alkylation is so-called “hydrogen borrowing”, postulated for analogical reactions, using iridium or palladium complexes as catalysts.

It is shown, that using of nickel and especially cobalt nanoparticles besides primary aliphatic amine alkylation leads to side reaction of their disproportionation. This is proved by disproportionation of benzylamine in absence of alcohol.



The method for synthesizing of secondary amines is high-promising because high surface area of nanoparticles makes possible using smaller amounts of them, and nanoparticles themselves can be easily prepared from simple metal salts, and may be synthesized *in-situ*.

P209

QUANTITATIVE ESTIMATION FOR REACTIVITY OF NITRILES COORDINATED TO Pt(II) IN REACTIONS WITH AZIDES

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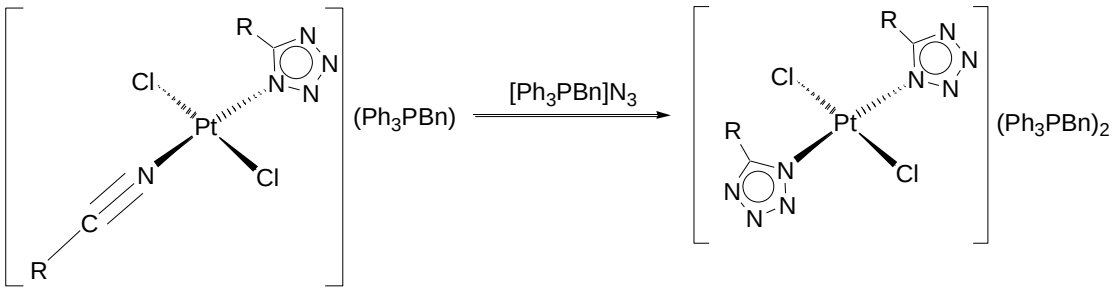
It has been shown that the coordination of RCN to the metals of the platinum group considerably increased the nitrile reactivity in reactions with azides [1]. In this work kinetic of azidation of nitriles coordinated to Pt(II) was studied by gas chromatography method. The synthesis was carried out with triphenylbenzylphosphonium azide in nitromethane at 1-10 °C (Scheme).



R = Me, Et, Ph

Scheme

Rate constants for the second-order reactions were determined in range 0.1-0.4 $l \cdot mol^{-1} \cdot sec^{-1}$. It has been founded that rate of reactions with Pt(II) in some times higher than classical 1,3-dipolar cycloaddition. Considering the significant acceleration of the process, it is presumable that the azidation mechanism of nitriles coordinated to platinum may be distinct from that of the noncoordinated nitriles.

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P210

MECHANISM OF CATALYTIC OXIDATION OF PHENOLIC COMPOUNDS USING POLYOXOMETALATES AS CATALYST

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Refusal from environmentally unsafe compounds and technologies observed in the production of fibrous semimanufactured goods of vegetable origin appears through replace the traditional delignification agents to more environmentally friendly agents. It is an important task for the pulp and paper industry. Molecular oxygen, hydrogen peroxide, peroxyacids are used as an environmentally friendly oxidants. One of the ways of intensification of such productions is use of catalysts, in particular, polyoxometalates. However, information of the mechanism of the process is not enough. In order to develop a mechanism of the catalytic oxidation of lignin compounds there was studied kinetics of the oxidation of phenolic compounds which simulating the structural unit of lignin (ferulic acid, vanillic alcohol sinapic acid etc.) in the presence of oxidants (O_2, H_2O_2, CH_3COOOH) using as a catalyst $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$. Influence of pH, nature and concentration of the oxidized substance, nature and concentration of the oxidant, concentration of catalyst and temperature were researched on the kinetics of the process by spectrophotometric analysis (Specord 200 Analytic Yena), the reaction products were identified, a scheme for the mechanism of the process were developed [1,2].

On the basis of studies it is established that oxidative interaction of polyoxometalates (POM_{ox}) with an oxidizing agent, activated hydrogen ion to form a carbocation (AH^+) (1), courses in the presence of O_2 (2,3). Regeneration of the reduced form of the catalyst ($HPOM_{red}$) is coursed by dissolved molecular oxygen (4):

$A+ H^+$	$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$	AH^+	(1)	$A+ H^+$	$\underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}}$	AH^+	(1')
$AH^+ + POM_{ox}$	$\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$	$[\ AH^+ \cdot POM_{ox}\ ]$	(2)	$POM_{ox}+2nROOH$	$\underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}}$	$POM_{ox}(O_2)_n+nROH$	(2')
$[\ AH^+ \cdot POM_{ox}\ ]$	$\overset{k_3}{\rightarrow}$	$A^+ + HPOM_{red}$	(3)	$AH^+ + POM_{ox}(O_2)_n$	$\underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}}$	$[\ AH^+ \cdot POM_{ox}(O_2)_n]$	(3')
$HPOM_{red} + O_2$	$\overset{k_4}{\rightarrow}$	$POM_{ox} + HO_2^-$	(4)	$[\ AH^+ \cdot POM_{ox}(O_2)_n\ ]$	$\overset{k_4'}{\rightarrow}$	$A^+ + HPOM_{red}(O_2)_{n-1}$	(4')
				$HPOM_{red}(O_2)_{n-1} + ROOH$	$\overset{k_5'}{\rightarrow}$	$POM_{ox}(O_2)_n + ROH$	(5')

In the presence of peroxide compounds carbocation is oxidized under the action of peroxocomplex $POM_{ox}(O_2)_n$ (3', 4'). Regeneration of this peroxocomplex is coursed through its interaction with peracetic acid or hydrogen peroxide (5'). Products of the catalytic oxidation were investigated using GC/MS analyses (Shimadzu QP-2010 Plus).

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P211

POLYMER-SUPPORTED DENDRITIC ORGANOCATALYSTS FOR THE BAYLIS-HILLMAN REACTION

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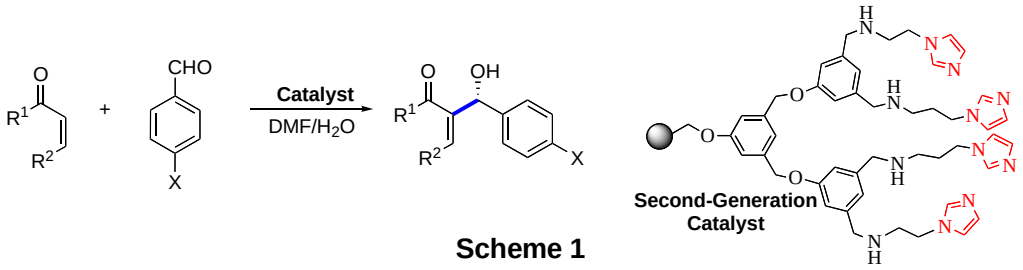
Immobilization of well-defined catalytic units onto insoluble support promises significant environmental and economic benefits. Organocatalysts became highly popular in the last decade due to the easy accessibility of building blocks for their construction, relatively low cost, and diverse and intellectually appealing mechanisms of action. During the past few years our group explored a number of new polymer-supported organocatalysts, exposing the high sensitivity of these systems to the mode of their immobilization.[1]-[3]

One of the most interesting organocatalytic systems, we explored, is that based on N-alkylated imidazoles and directed at Morita-Baylis-Hillman reaction (Scheme 1). Lately, the popularity of this atom economical carbon-carbon bond-forming transformation increased enormously, due to its operational simplicity, functional group tolerance and high number of reactive functional groups in a typical reaction product.

We discovered that the introduction of a polyether dendritic interface between the polymer core and the imidazole units dramatically enhances their catalytic activity in the reaction of conjugated olefins with aromatic aldehydes. For the reaction of methyl vinyl ketone with the strongly electrophilic aldehydes the yields are doubled or tripled, while the less activated aldehydes, as well as less active unsaturated ketones or esters, were forced to react only by the higher generation dendritic catalysts. Moreover, the yields and chemoselectivities displayed by the supported dendritic catalysts exceeded by large those obtained with their simple soluble analogues. Noteworthy, water as a co-solvent demonstrated a tremendous acceleration effect on this transformation for all supported catalytic systems based on N-alkyl imidazoles.



Scheme 1

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P212

NITROGEN AND OXYGEN DIRECTED RUTHENIUM(II)/CARBOXYLATE-CATALYZED ARYLATION OF sp^2 C-H BONDS

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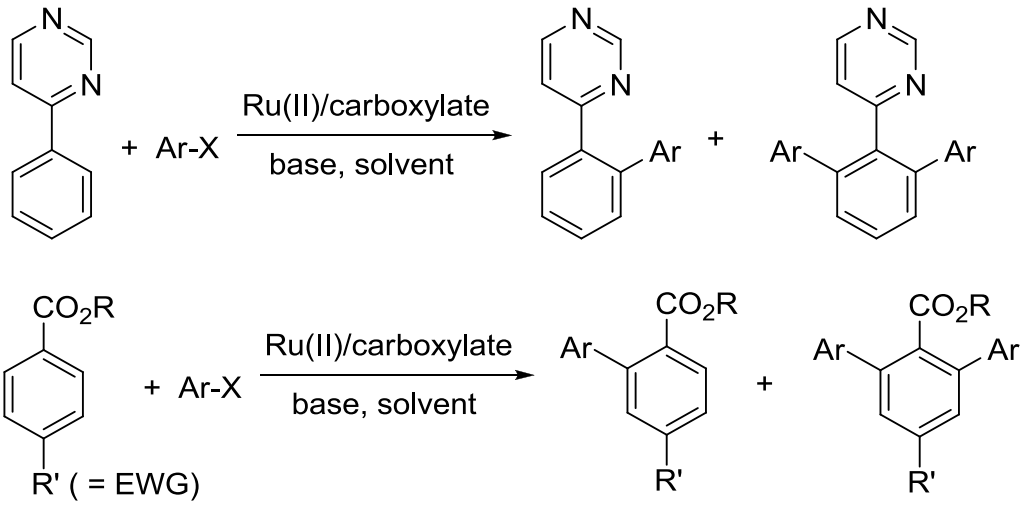
Methodologies for regioselective carbon-carbon bond-forming reactions usually employ transition metal-catalyzed cross-couplings between organic (pseudo)halides and organometallic reagents.[1] These organometallic compounds are frequently not commercially available or rather expensive, and can lead to the formation of undesired by-products. On the other hand, the direct arylation *via* C-H bond activation represents an ecologically more friendly and economically attractive alternative due to minimizing atomic waste.[2]

We have demonstrated that phenylpyrimidines can be directly arylated *via* C-H bond activation by using a new Ru(II)/carboxylate catalyst system with both, electron-rich and electron-poor organic halides.[3] The pyrimidine nitrogen atom acts as a directing group thus facilitating the mono- and diarylation on the ortho positions of the phenyl substituent. The same methodology was applied for the oxygen-directed arylation of benzoic acid derivatives.



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P213

ENANTIOSELECTIVE SYNTHESIS OF 2,3-DIHYDROQUINAZOLINONES AND CYCLOTHIAZIDES

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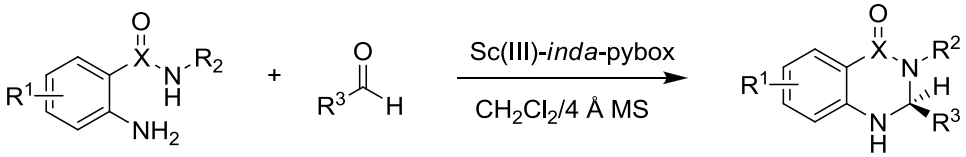
2,3-dihydroquinazolinones (DHQZ) and Cyclothiazides are an important class of heterocycles with a significant applications in pharmaceuticals. It is noteworthy that *S*-stereoisomer of 2,3-DHQZs are more potent tubulin inhibitors when compared to *R*-stereoisomers.[1] Since the chiral aminal centre present in 2,3-DHQZs, and cyclothiazides is prone to racemization there was no success in the catalytic enantioselective synthesis of 2,3-DHQZs until recently[2]. Brønsted acid catalyses reported by List and Rueping lacked substrate diversity. Apart from these reports of Brønsted acid catalyses there is no catalytic method available to effect the asymmetric synthesis of 2,3-DHQZs. That prompted us, for developing the first metal catalyzed enantioselective synthesis of 2,3-DHQZs and Cyclothiazides using scandium-(III)-*inda*-pybox as a catalyst, and we were able to achieve the enantioselective synthesis of various 2-aryl, alkyl, 2,3-diaryl substituted 2,3-DHQZs[3] as well as various 3-aryl and alkyl substituted Cyclothiazides with good to excellent enantioselectivity and admired yield. This study paves the way to synthesize optically pure form of 2,3-DHQZs and Cyclothiazides as well to expand the scope of optimizing pharmacokinetic properties of these compounds towards various drug targets.

Scheme 1 Enantioselective synthesis of 2,3-DHQZs and cyclothiazides



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P214

THE HEAVIER MAIN-GROUP ELEMENTS AND TRANSITION METALS: THEORY AND COMPUTATION OF ACTIVE COMPLEXES

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Many important catalyzed bond-transformations involve donor-acceptor interactions at the reaction center - the transition metal and, only relatively recently, the heavier main-group elements.[1] The so-called frustrated Lewis pairs (FLPs), i.e. the combinations between sterically hindered Lewis acids (LAs) and sterically hindered Lewis bases (LBs), became of interest since the discovery of hydrogen activation, i.e. heterolytic cleavage of H_2, and hydrogen transfer reactions with the metal-free FLP catalysts (Scheme 1), as well as reactions between FLPs and small organic or inorganic molecules.[2]

To identify and better understand the nature and reactivity of LA-LB complexes, mechanistic studies including quantum-chemical calculations have been performed by a number of groups. Our calculations[3] have already pointed out a few important mechanistic aspects. The conformation of the LA-LB complex has a large effect on its reactivity towards H_2. For example, based on calculations of a series of $R'_2P\text{-}BR_2$ compounds with the dative π-bond, we have pointed out that the reactivity depends on the geometry of the P and B centers because of the properties of the π-type overlap between the adjustment lone pair of P and empty p-orbital of B. Also, a balance between acidity and basicity of the fragments in the LA-LB complex is essential for thermodynamics (reaction energy change) and kinetics (barrier) of hydrogen activation. Complexes HLA-LBH reduce unsaturated carbon-hetero atom bonds in quite a broad range of substrates. One prominent example is the reduction of imines by zwitterionic complex $(R^{2'})_2PH\text{-}C_6F_4\text{-}BH(R^2)_2$. For the catalytic reduction of imines to amines by such a complex, and its analogs, with H_2, the proposed mechanism has been refined just recently. Complementary to the research focused on the hydrogen transfer to carbon-nitrogen unsaturated bonds, we investigate the dynamics of carbonyl-borane FLPs. In our earlier DFT study, we have suggested the possibility of catalytic reduction of carbonyl compounds with $B(C_6F_5)_3$ and H_2 in a manner similar to the reduction of C=N bonds (imines) in the presence of only $B(C_6F_5)_3$ and H_2. Recently, our suggestion has been confirmed by experiment. This motivated further computational mechanistic studies - recent results and perspective are to be presented.

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P215 (GM3)

NEW RARE-EARTH COMPLEXES INCORPORATING MULTISUBSTITUTED AMIDINATE-BASED AND RELATED LIGANDS

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Two new amidine proligands that contain a pendant Lewis base in the side arm (Fig. 1), were synthesized and successfully employed for the preparation of the bisalkyl rare earth complexes [2-MeOC$_6$H$_4$NC(*t*Bu)N(2,6-R$_2$C$_6$H$_3$)]Ln(CH$_2$SiMe$_3$)$_2$(L)*n* {Ln = Y, Lu; R = Me, *i*Pr; L = THF}. [1]

The X-ray crystallography revealed that intramolecular coordination of the 2-MeOC$_6$H$_4$ group occurred in {L^1}Lu(CH$_2$SiMe$_3$)$_2$(THF) (Fig. 2). Treatment of the latter with DME afforded a six-coordinate DME adduct with pendant methoxy group. The reaction of proligand L^{2}H with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at -50 °C yielded yttrium bisalkyl complex {L^2}Y(CH$_2$SiMe$_3$)$_2$(THF) (Fig. 3), which above -30 °C in toluene solution quantitatively transformed to alkyl/benzyl complex by an intramolecular C–H bond activation reaction. Being highly sensitive, this product underwent adventitious oxidation reaction forming selectively alkyl/benzoate complex.

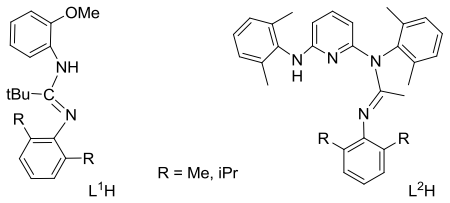

Figure 1. Multidentate amidinate ligands.

The bisalkyl complexes {L^1}Ln(CH$_2$SiMe$_3$)$_2$(THF), in combination with [Ph$_3$C][B(C$_6$F$_5$)$_4$]/Al*i*Bu$_3$, were evaluated as precatalysts for isoprene polymerization. These catalytic systems afforded polyisoprenes with moderate activities and stereoselectivities. The results of polymerization activity tests will be reported in details.

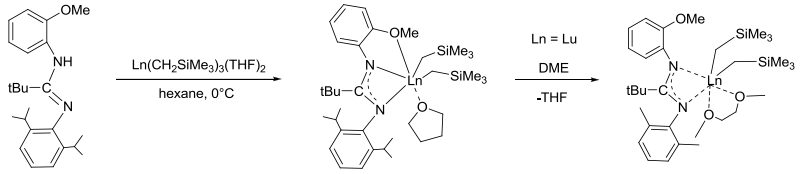

Figure 2. Synthesis of bisalkyl complexes of yttrium and lutetium.

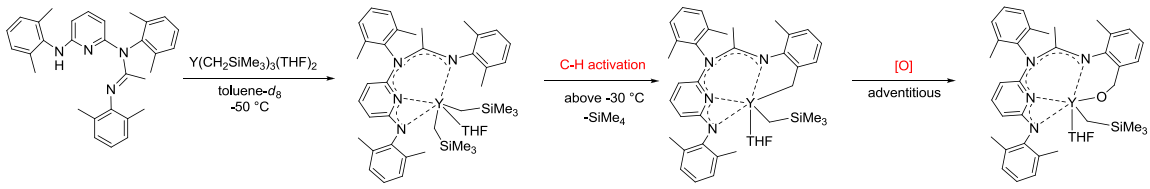

Figure 3. Preparation of bisalkyl and alkyl/benzyl complexes.

Acknowledgements -This work is supported by the Russian Foundation for Basic Research (Grant Nos. 11-03-00555-a), Program of the Presidium of the Russian Academy of Science (RAS), and the RAS Chemistry and Material Science Division.

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P216

ZINC AND COPPER COMPLEXES OF SCHIFF BASE AMINOISOBORNEOL: EFFICIENT CATALYSTS FOR ASYMMETRIC PHENYLACETYLENE ADDITION AND ASYMMETRIC HENRY REACTION OF ALDEHYDES

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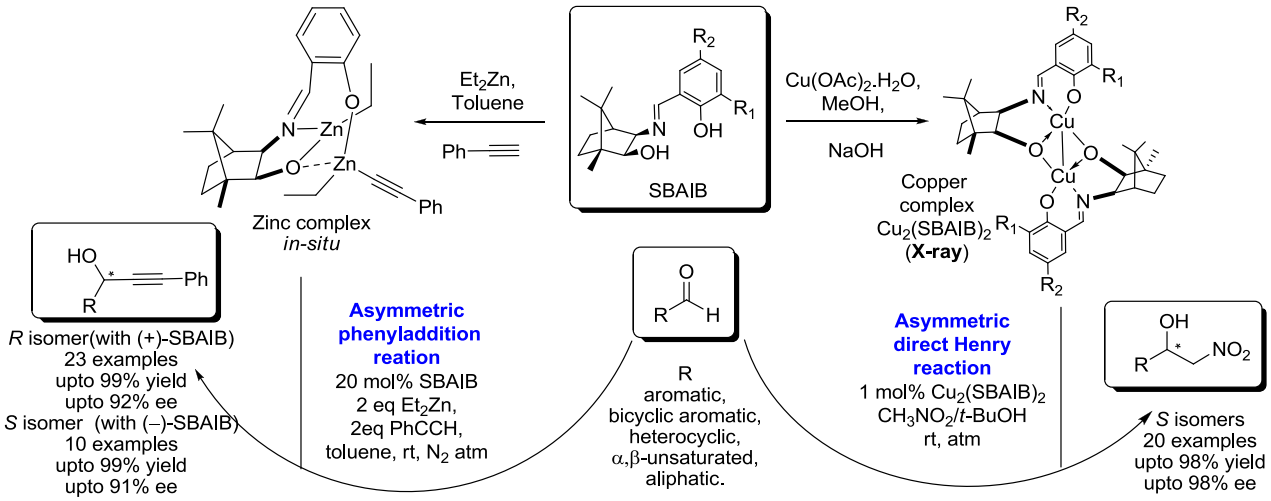
A Series of tridentate Schiff base aminoisoborneol (SBAIB) are synthesis from both (1*R*) and (1*S*)-camphor. As an application of these chiral ligands in asymmetric synthesis, numerous (*R)* and (*S)*-propargylic alcohols are obtained in excellent yield (up to 99%) and ee (up to 92%) when 20 mol% of SBAIB used as a catalyst to generate *in-situ* zinc complex with diethylzinc and phenylacetylene in the reaction of aldehydes. This work also displays the clarification in prolonged configuration conflict of some of the propargylic alcohols.

New seven copper complexes of SBAIB are synthesized and screened for direct Henry reaction. Among these complexes, when the conditions are optimized, the 1 mol% of $Cu_2(SBAIB\text{-}4)_2$ is found to be an excellent catalyst for practically simple, air and moisture tolerant asymmetric direct Henry reaction. The resulting bifunctional *β*-hydroxynitroalkanes (Henry adducts) are obtained in excellent yield (up to 99%) with excellent ee (up to 98%).



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P217

RHODIUM-CATALYZED HOMOGENEOUS REDUCTIVE AMIDATION OF ALDEHYDES

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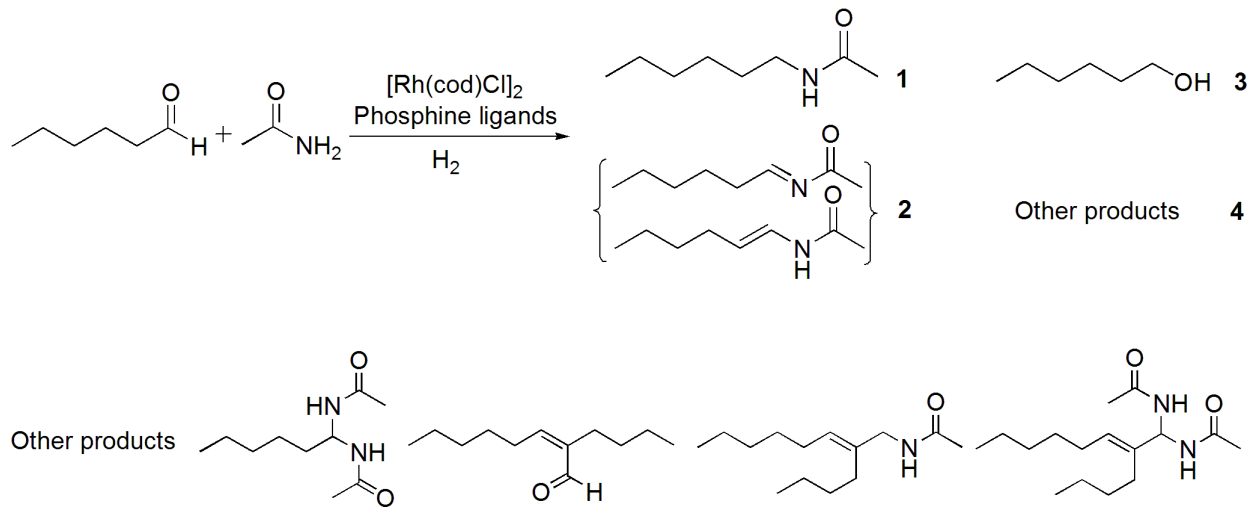
The aim of our research is the development of a cascade catalytic hydroamidomethylation reaction. The main challenge of this research is to develop a catalyst for one-pot hydroformylation reaction and subsequent intermolecular reductive amidation reaction in the presence of syngas. The desired condensation between intermediate aldehyde(s) and amide moieties to produce N-acylimine/enamide intermediates will be crucial to success. We report the selective, facile and atom-efficient catalytic intermolecular reductive amidation reaction. Different rhodium precursors in combination with several monodentate and bidentate phosphine ligands with varying stereo electronic properties were studied in this catalytic reaction. It appears that the reaction proceeds via the formation of enamide and imide intermediates. Optimal results in the catalytic reductive amidation of hexanal with acetamide reveal an excellent overall hexanal conversion of 95%, with more than 90% selectivity for the desired N-hexylacetamide, obtained at a ratio of acetamide/hexanal near unity. Only negligible amounts of by-products derived from aldol condensation, aldehyde hydrogenation and amide di-coupling reactions, were observed.



Acknowledgements: This research was performed within the framework of the CatchBio program. We gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

P218

PHOTOCATALYTIC PROPERTIES OF SUPRAMOLECULAR METAL TETRAPYRROLE COMPLEXES

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Complexes of tetrapyrrolic macroheterocycles (TPMHC) with non-transition and d^{10}-metals (*e.g.*, Mg, Al, Zn) are able to generate rare long-lived (τ_r = 0.1-2 ms) triplet excited states. Some of these metal complexes, first of all phthalocyanines, absorb light of the red region of the visible spectrum (600-900 nm) and they are exclusive stable and non-toxic. Because of these properties TPMHC are special group of promising compounds for photocatalytic processes for environmentally friendly technologies, fine organic synthesis and photodynamic therapy. An association of TPMHC effects on their photophysical and photochemical properties significantly. To control association and to influence on photocatalytic properties of TPMHC directionally it is promising to include them in a variety of supramolecular systems and nanoparticles [1-3].

We developed methods for obtaining supramolecular complexes of different TPMHC with hydrophilic polymers (polyvinylpyrrolidone, polyvinyl alcohol, polyethyleneglycol), adsorption of TPMHC on micro- and nanosized silica, hydroxyapatite, bentonite clays and formation of phthalocyanine nanoparticles and their composites. Stability parameters of these systems and their photophysical properties according to the composition were determined. Optical and luminescent properties of metal TPMHC essentially depend on the nature of the local environment. For a number of complexes photosensitizing activity in $^1O_2$ generation, reactive oxygen radical forms and H_2O_2 was shown. Mechanism of this process depends on the pH. Activity of TPMHC decreases at their association because of triplet-triplet annihilation: ^{3}TPMHC* + ^{3}TPMHC* $\rightarrow$ ^{1}TPMHC* + ^{1}TPMHC. This feature is useful for development of photocatalytic processes in the absence of photooxidative destruction. However, for rigid oxidative reactions the association of TPMHC should be suppressed. Thus, TPMHC-TPMHC and TPMHC-carrier interaction leads to a change of the HOMO-LUMO transition energies and the orbital nature of the radiative state of TPMHC. In addition, activity of TPMHC supramolecular complexes as electron donors in redox processes involving bicarbonate and phosphate anions, pyridine nucleotides, vitamin K_3 and dyes was studied. It is shown that many photochromic substances in different relative amounts can act as energy donors and electron acceptors.

Some novel complexes of TPMHC have been tested at oxidation of anthracene and tryptophan, and flavin reduction. Theses photocatalysts were extremely stable. Supramolecular structures based on molecular and nanoscale TPMHC can be used for different photocatalytic processes with high turnover.

The work was supported by Grant of President of the Russian Federation for State support of young Russian scientists - Candidates of sciences No MK-227.2011.3, Russian Foundation for Basic Research No 12-03-01081-a, RAS Presidium Program No 28, Project of International Science and Technology Center No 3910 and Grant of support of Leading Scientific Schools No NSh-6605.2012.3.

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P219 (GM7)

FUNCTIONALIZATION OF PTA: A CLASS OF WATER SOLUBLE NEUTRAL PHOSPHINES FOR USE IN ACQUEOUS PHASE CATALYSIS

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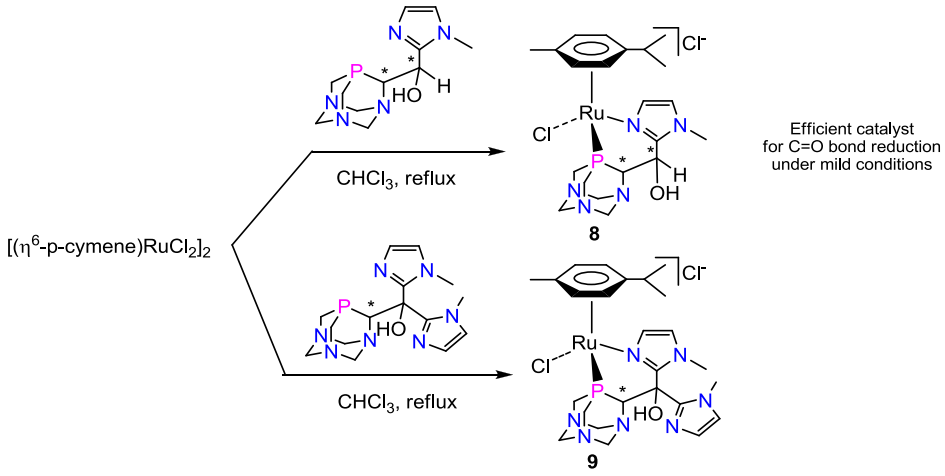
The widespread use of water soluble organometallic complexes in catalysis is often limited by the availability of suitable ligands, such as hydrosoluble phosphines. PTA (1,3,5-triaza-7-phosphaadamantane) has been shown as a versatile amphiphilic cage aminophosphine.[1]
Hereby the synthesis of a small library of derivatives based on PTA functionalization in 6-position ("upper rim") will be presented. Coordination chemistry and catalytic data related to the activity of Ir(I) and Ru(II) complexes with some of these ligands in hydrogenation reactions under very mild conditions using transfer hydrogenation and hydrogenation (30 bar H_2) protocols will be also reported.[2]



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P220

ROLE OF THE COCATALYST IN THE MULTICHIRAL COBALT(III)-COMPLEX-MEDIATED KINETIC RESOLUTION OF RACEMIC EPOXIDES USING CO_2 AS REAGENT

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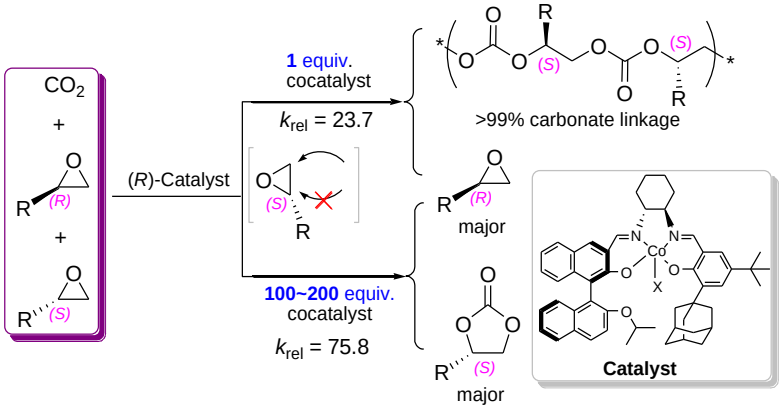
Enantiopure epoxides are important intermediates for synthesizing a wide variety of biologically and pharmaceutically target compounds.[1] Their preparation is mainly via two routes: the enantioselective epoxidation of olefins and the kinetic resolution of *racemic* epoxides by nucleophilic ring-opening reactions.[2] The latter method focuses on highly enantioenriched epoxides resulting from inexpensive or easily accessible commercial starting materials. The representative example is the metal-salen-catalyzed hydrolytic kinetic resolution of terminal epoxides developed by Jacobsen and coworkers,[3] while the kinetic resolution of *racemic* epoxides with CO_2 as reagent via the enantioselective coupling presents an attractive alternative (Scheme 1).[4] The latter affords enantiopure epoxides and optically active organic carbonates. Moreover, excess CO_2 can be easily removed from the reaction system.



Inspired by the ground-breaking work of Jacobsen and coworkers, who employed chiral salenCo(III) catalysts for the hydrolytic kinetic resolution of terminal epoxides, our group reported the first example of the synthesis of optically active cyclic propylene carbonate by a catalytic kinetic resolution process of *racemic* epoxides using CO_2 as reagent.[4] The process involves the simple use of a chiral salenCo(III)X/quaternary ammonium halide catalyst systems under extremely mild and solvent-free conditions. Indeed, in the cobalt(III) complex-catalyzed CO_2/epoxide coupling, both cyclic and polymeric products were often observed in the reaction mixture, and in some cases selective formation of polycarbonates was realized by altering the nature of the cocatalyst.[5] We have reported the effect of the cocatalyst of binary catalyst systems based on chiral salenCo(III) complexes on product selectivity and enantioselectivity. This study has resulted in significant increase in catalytic activity and the achievement of selective formation of only one desired product. Prior to this point many of these results have remained poorly understood, in particularly, the effect of the cocatalyst on product enantioselectivity.[6] Herein we will provide details of mechanistic studies on the role of cocatalyst in the enantioselective coupling of *racemic* epoxides with CO_2 using multichiral Co(III) complexes.

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P221

HETEROARYL VINYLSULFONES AS MICHAEL ACCEPTORS VIA ENAMINE CATALYSIS. ENANTIOSELECTIVE ORGANOCATALYTIC FORMAL ALLYLATION OF BRANCHED ALDEHYDES

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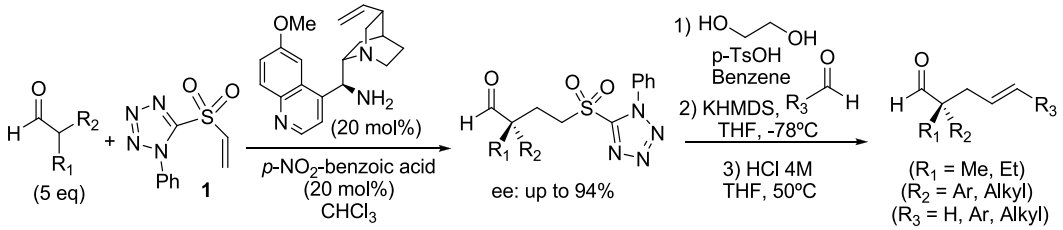
Since the turn of the millennium, the field of asymmetric **organocatalysis** has been the focus of immense research and development, [1] becoming a powerful tool for the synthesis of optically active compounds. The search of **new nucleophiles and electrophiles** which can be used in the field of organocatalysis is essential, in order to allow new interesting and useful transformations in organic chemistry.

The **sulfonyl moiety** is an interesting group [2] due to the many possibilities of transformation and/or elimination that offers and it has been employed in organocatalytic processes [3] as electron withdrawing group, to increase the nucleophilicity or electrophilicity of a parent reagent.

We present herein the first use of **heteroaromatic vinylsulfones** in organocatalytic processes (**Scheme 1**) [4]. The 1-phenyl-1*H*-tetrazole (PT) substituent offers a higher reactivity than traditional aromatic sulfones and interesting possible transformations such as Julia-Kocienski reaction, only feasible with heteroaromatic substituents. Michael addition *via enamine activation* of a variety of α,α-disubtituted aldehydes to the vinylsulfone **1** using cinchone type catalyst affords the Michael adducts in good yields and high enantioselectivities (*ee* up to 94%).



Scheme 1

The Julia-Kocienski olefination of the obtained Michael adducts gives the corresponding γ,δ-unsaturated α,α-disubstituted aldehydes in a highly stereoselective three step sequence which implies only one final column chromatography. The entire process constitutes a formal regio, stereo and enantioselective organocatalytic method for the α-allylation of α,α-disubtituted aldehydes, which is a difficult direct transformation. [5]

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P222

C-H BOND ACTIVATION - A TOOL FOR DERIVATIZING COMPLEX MOLECULES

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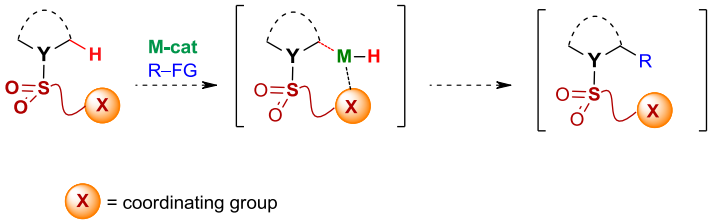

A chemical process of broad synthetic potential is the direct and selective functionalization of ubiquitous but inert sp^3 C–H bonds. Although these transformations are by far less developed than traditional synthetically mature C–C-bond forming reactions, recent contributions have unlocked a new era in this field.[1]

This talk aims at cover pioneering practical strategies for the structural diversification of aliphatic scaffolds *via* the coordination-directed C–H bond activation at remote positions.[2] Following this strategy, our research group has demonstrated the role of *N*-heterosulfonyl derivatives. These protecting groups activate and direct the metal complex to a specific alkane segment of the substrate.[3] Once the reaction is over, they can be easily removed from the reaction products under relatively mild conditions.

The possibility of functionalizing alkane segments in complex organic substrates is perhaps the most challenging aspect of this area. Improvements in substrate scope and reaction conditions are vital to establish this strategy as true synthetic alternatives. Mechanistic insights, focusing on steps and factors controlling the activity and selectivity, will be discussed.

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P223

SYNTHESIS OF OPTICALLY ACTIVE WARFARIN

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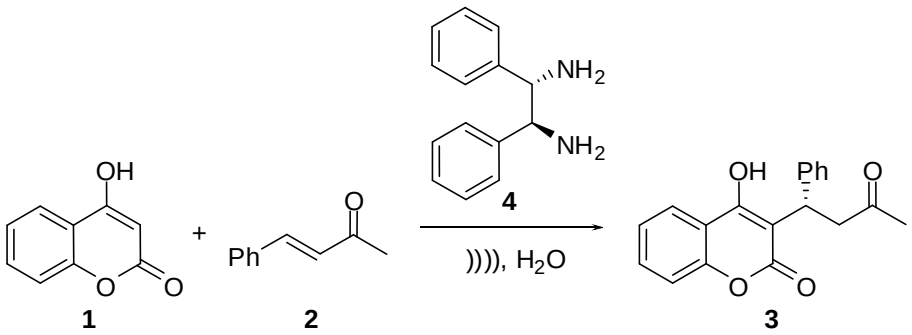
Warfarin (**3**) is a Vitamin K antagonist, inhibiting Vitamin K epoxide reductase and thereby decreasing blood coagulation by preventing the Vitamin K-dependent synthesis of blood-clotting proteins. In the form of its sodium salt it is one of the most widely prescribed anticoagulants for prevention of thrombosis and embolism. Although currently prescribed as the racemate, activity and metabolism are markedly dissimilar for the two enantiomers, the (*S*) enantiomer being more active than the (*R*) enantiomer by a factor of 2–5. Efficient asymmetric syntheses of warfarin are therefore of great interest.[1] The methods of synthesis without metal complexes are more desirable for future therapeutical applications.

Here we present an example of the straightforward synthesis of chiral warfarin via Michael addition of 4-hydroxycumarin (**1**) to benzylideneacetone (**2**) on water using commercially available primary amine (**4**) as a catalyst. After one crystallization from hexane we obtained optically pure warfarin.[2]



Water is a desirable solvent for catalysis with respect to environmental concerns, safety, and cost. The variety of interactions between water and substrates (hydrogen bonding or interactions related to polarity, acidity, hydrophobicity, etc.) make water interesting from an industrial as well as laboratory perspective. In this regard, processes using water as a reaction medium have recently attracted a great deal of attention.[3]

Sonication enables the rapid dispersion of solids on water surface allowing better contact between water and reactants. The use of ultrasounds as a means of accelerating reactions is an important technique and one which is rapidly developing for green processes.[4]

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P224

CYANO-1,4-DIKETONE PRONUCLEOPHILES: NHC-CATALYZED CYCLOADDITION REACTION WITH YNALS

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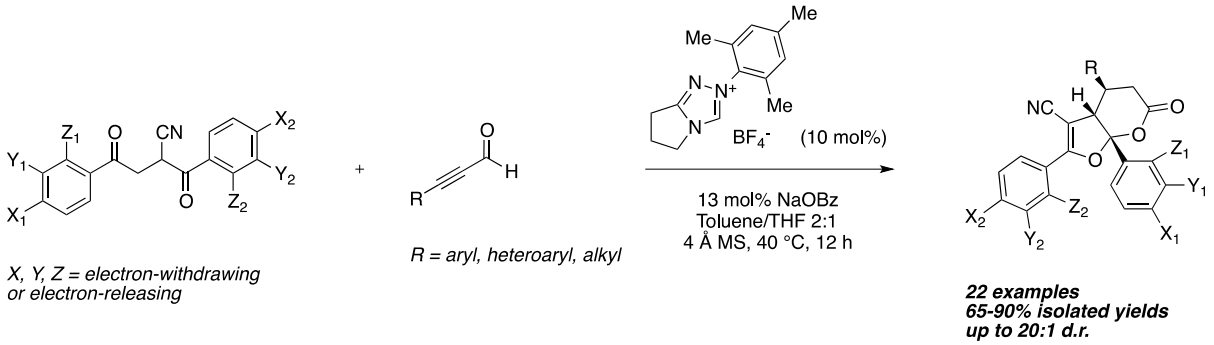

Recently, *N*-Heterocylic Carbenes (NHCs) have emerged as remarkably powerful catalytic entities in the field of synthetically relevant organic transformation. Besides being reputed as powerful σ-donor ligands for transition metals, these divalent carbon nucleophiles also behave as versatile organocatalysts of their own right. Thereby, numerous metal-free, NHC-catalyzed transformations, shedding light on the multiple facets of NHC reactivity, have been reported over the past years.

Herein, we disclose the first highly diastereoselective cycloaddition reaction between α-cyano-1,4-diketones and ynals, mediated by catalytic amounts of a triazolium salt precatalyst and co-catalytic amounts of a weak carboxylate base. The title transformation proceeds smoothly under mild reaction conditions and generates 3 contiguous stereogenic centers, one of which is quaternary. This reaction tolerates a wide variety of electronically distinct substituents on both reaction partners, and affords privileged cyclic ketal scaffolds in 65-90% isolated yields and with up to 20:1 diastereomeric preference. The obtained compounds are interesting candidates for the synthesis of the ginkgolide class of monoterpenoids.

Research on the development of an enantioselective variant of this transformation is ongoing actively in our lab.

P225

SYNTHESIS AND BIOLOGICAL ACTIVITY OF DERIVATIVES 4-ALKYLCYCLOHEXANCARBOXYLIC AND 4-ALKYLCYCLOHEXANOYLBENZOIC ACIDS

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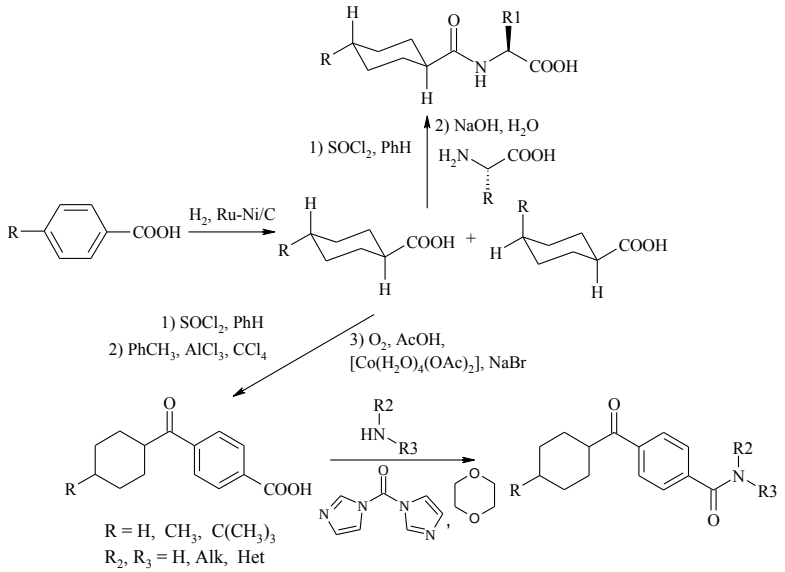
We synthesized a number of new compounds with structure containing a 4-alkylcyclohexanoyl group, which have biological activity [1].



The crucial stages of the production of these compounds are a catalytic reaction stereoselective hydrogenation of the p-alkylbenzoic acids and liquid-phase oxidation 4-alkylcyclohexyltolylketones by oxygen. The oxidation of 4-alkylcyclohexyltolylketones was carried out in acetic acid medium using oxygen [2] with the cobalt-bromide catalyst. The corresponding 4-alkylcyclohexanoylbenzoic acids were obtained with the yield about 90-95% on the reacted substrate. The obtained products structure was confirmed with ^{1}H NMR spectroscopy.

For the first time valence transformations of the catalyst components in 4-cyclohexyltolylketone oxidation are investigated by the electronic spectroscopy method, as well directly during reaction, as with artificial mixtures of reacting system. It was shown that the $Co^{+2}\ldots Br^{-}$ complex is formed at the beginning of reaction. Then a rapid consumption of the formed complex begins due to catalysts valence forms ratio is changed. The complex disappearance caused by bromine consumption and the formation of benzylbromide. There is a trivalent cobalt form accumulation then, which passed to a bivalent form again at the subsequent stage.

In this work were obtained derivatives with respect to the carboxyl group of 4-alkylcyclohexan- and 4-alkylcyclohexanoylbenzoic acids. Then acute toxicity and analgesic properties (using the chemical painful irritation model in mice) were investigated in cooperation with the Department of Pharmacology of the Yaroslavl State Medical Academy (Yaroslavl). Results of the experiments demonstrated that these compounds have a low toxicity and significant analgesic effect.

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P226

DEVELOPMENT OF NEW POLYMER-SUPPORTED ORGANOCATALYSTS FOR ASYMMETRIC ALDOL REACTIONS

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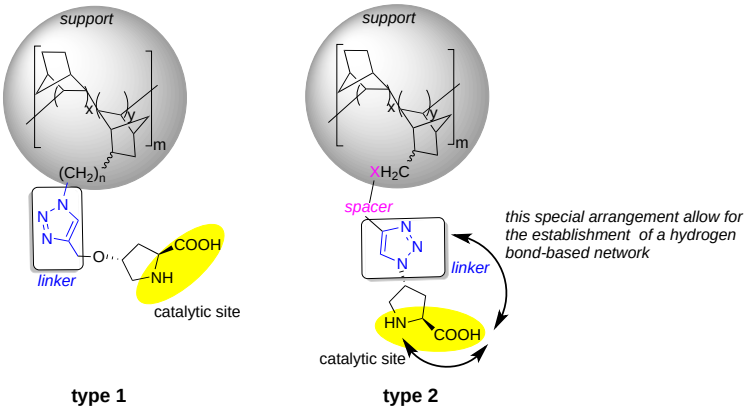
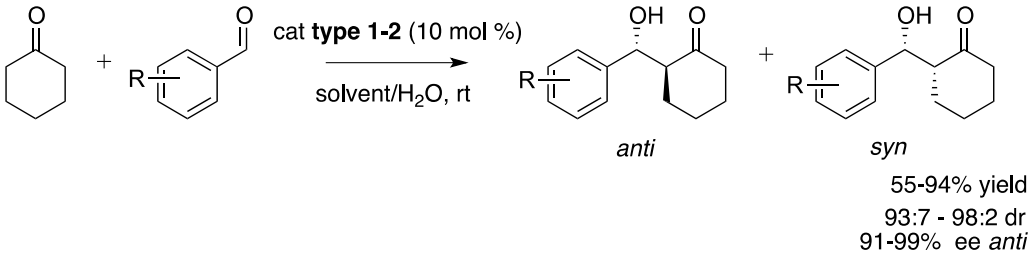
The polynorbornene skeleton is a chemically stable structure that has been previously described as support for reagents and catalysts. To the best of our knowledge, the use of polynorbornene supports in organocatalytic transformations has not been previously reported.[1] In this context and based in the idea of extend the proline-catalyzed direct asymmetric aldol reaction to include novel classes of reusable catalysts, we have been developed a new family of catalytic polymers bearing proline as chiral inductor.



We selected natural hydroxypoline as our starting material and the cooper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)[2] reaction as the covalent strategy for the anchoring of the pyrrolidine moiety onto a polynorbornene support.[3] Following the approach introduced by our group[4] we have been prepared two families of new catalysts (type 1 and 2 in the figure).
Polynorbornene-supported prolines has shown excellent performance in asymmetric aldol reaction of cyclohexanone with aromatic aldehydes in an aqueous environment.



The stability and robustness of the obtained catalysts has been also illustrated by the possibility of extending its use for up to seven cycles in the aldol reaction of cyclohexanone and *p*-nitrobenzaldehyde.

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P227

THE SYNTHESIS AND CATALYTIC PROPERTIES OF RUTHENIUM(II) COMPLEXES CONTAINING PYRIDINE LIGAND

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Ruthenium complexes gain great interest due to stability and structural novelty in catalytic applications [1-2]. Ruthenium has various oxidation states (from 0 to 8). Therefore, it is useful for catalytic reaction [3].

In this work, two new ruthenium(II) complexes containing pyridine ligand with branched alkyl side group [$RuCl_2$(*p*-cymene)L] (L:Pyridine derivatives) were synthesized and characterized by using UV/Vis, FTIR, NMR spectroscopy and cyclic voltammetry. The catalytic efficiency of ruthenium(II) complexes were studied in transfer hydrogenation of acetophenone derivatives in the presence of 2-propanol at 82 ^{o}C. The influence of molecular side groups on pyridine ligands were investigated and a significant difference were observed in catalytic reactivity between the complexes. Yield up to 82% were obtained.

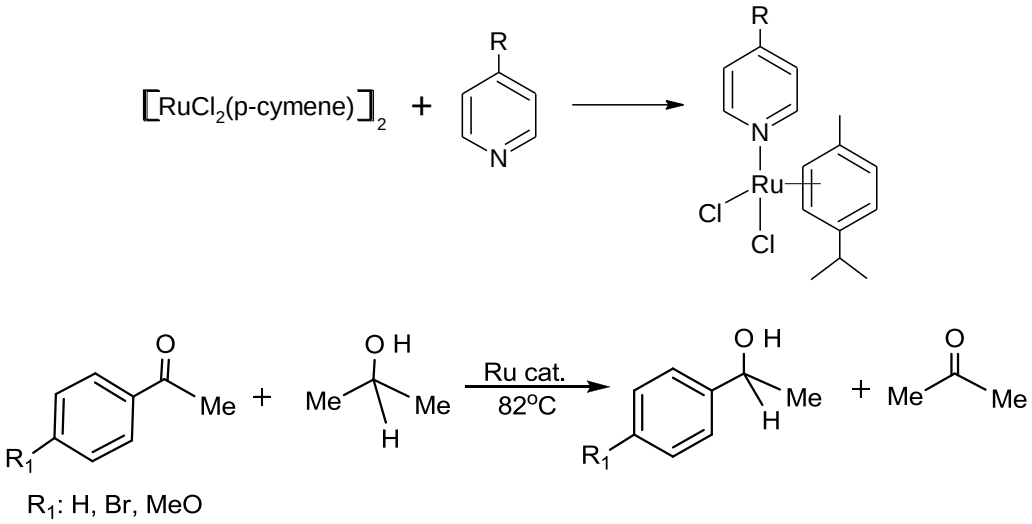

Figure: Synthetic route followed in the synthesis of ruthenium complexes (R: branched alkyl side groups) and transfer hydrogenation reaction.

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P228

MANGANESE COMPLEXES OF *o*-PHTHALALDEHYDE-AMINO ACID SALEN-LIKE LIGANDS: SYNTHESES AND APPLICATION IN ASYMMETRIC EPOXIDATION OF OLEFINS

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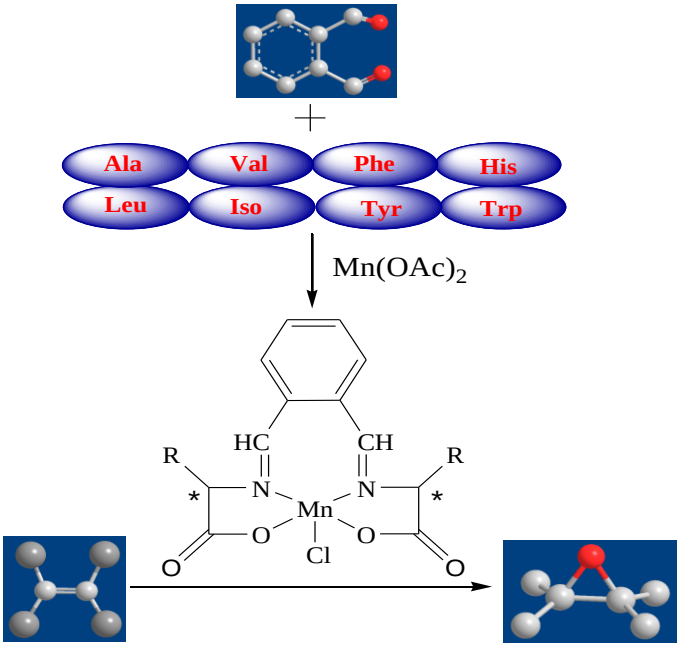
Various salen-like *o*-phthalaldehyde-amino acid (OPAA) ligands were synthesized through the formation of Schiff base between the aldehyde(-CHO) of o-phthalaldehyde (OPA) and amino group(-NH_2) of amino acids (AA). The manganese complexes of OPAA ligand (OPAA-Mn(III)) were used in the asymmetric epoxidation of styrene, indene, α-methylstyrene, 6-cyano-2,2-dimethylchromene, trans-stilbene and 4-octene. Optimized conditions were evaluated against these OPAA-Mn(III) catalysts. NaClO served as an oxidant, NH_4OAc as the axial base and CH_2Cl_2 as the reaction medium. The reaction took place at -15 °C in a heterogeneous system. The best result, 100% ee, was obtained using OPPhe-Mn(III) as a catalyst in the asymmetric epoxidation of trans-stilbene. The axial base NH_4OAc was not found to be essential when the OPHis-Mn(III) catalyst was used because OPHis-Mn(III) contains a N atom of imodazole ring that can perform axial base action. Meanwhile, the addition of CH_3I for the epoxidation of trans-stilbene by OPHis-Mn(III) reduced the reaction time through the formation of quaternary ammonium unit. We used ultraviolet-visible (UV-vis) spectroscopy techniques to investigate catalytic mechanism by monitoring the spectrum of OPPhe-Mn(III) in catalytic process with addition of NaClO.



THE STRUCTURE OF INTERMEDIATES IN PHOSPHINE-CATALYZED REACTIONS OF ELECTRON-DEFICIENT ALKENES DEDUCED FROM KINETIC AND QUANTUM CHEMICAL INVESTIGATIONS

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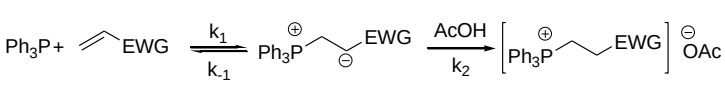
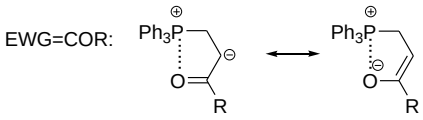
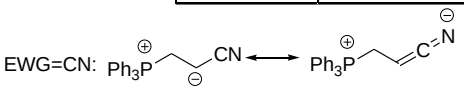
Phosphine-catalyzed reactions of electron-deficient alkenes have been recognized as effective tools for the preparation of various practically useful compounds [1]. The key step of these transformations is the generation of phosphonium zwitterionic intermediate via addition of tertiary phosphine to activated alkene. However, direct isolation and characterization of these zwitterions have still remained an elusive goal. To get information about their structure, the mechanism of tertiary phosphines quarternization with unsaturated carboxylic acids and their functional derivatives was studied using kinetic and quantum chemical approaches.



$W=(k_1/k_{-1})k_2[Ph_3P][=\text{-EWG}][AcOH]=k_{III}[Ph_3P][=\text{-EWG}][AcOH]$

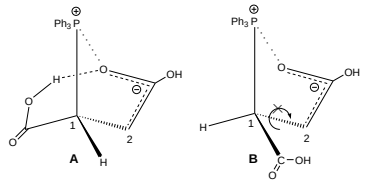
EWG	$k_{III}*10^3$, l^2 mol^{-2} s^{-1}
CO_2H	8.18
CO_2Me	0.89
$CONH_2$	0.62
CN	0.16





It was shown that the quarternization process is described by third-order kinetic equation, which includes the concentration of proton-donor solvent – acetic acid. The reaction rate unexpectedly is not controlled by electrophilicity of unsaturated substrate (see table). Low reactivity of acrylonitrile can be understood taking into account that generated zwitterion is incapable for stabilization by intramolecular electrostatic P···N interaction. Thus, the study allowed to give kinetic evidence that intramolecular P···O interaction takes part in stabilization of the intermediates generated from carbonyl-containing electrophiles; this question is actively debated at present [2,3].

Unique information about spatial structure of the intermediate provided effect of anhimeric assistance – reaction rate acceleration by neighboring group participation, – which was revealed for reactions with unsaturated carboxylic acids having additional carboxylic group in *cis*-position, e.g. maleic and *cis*-aconitic acids. Similar effect for *trans*-isomeric acids was not observed. The use of esters of maleic and fumaric acids in kinetic study allowed to prove that the origin of the anomalous behavior of *cis*-isomeric acids proceeds from additional stabilization of generated zwitterion by intramolecular hydrogen bond (**A**). In case of isomeric fumaric acid such stabilization becomes impossible, since electrostatic P···O interaction inhibits free rotation around C1–C2 single bond (**B**).



The conclusion about spatial structure of the intermediate was also confirmed by quantum chemical computations of the reaction mechanism at B3LYP/6-31+G(d,p) level of theory showed that electrostatic P···O interaction dramatically stabilizes the zwitterion.

This work was supported by a grant from the President of Russia (MK-1316.2012.3).

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P230

CHIRAL POLYOLS AS CATALYSTS OF ASYMMETRIC C-C BOND FORMATION REACTIONS

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The creation of a chain of intramolecular hydrogen bonded hydroxyl groups could be expected to facilitate the proton transfer, accompanying the C-C bond formation, as Figure 1 illustrates. Some analogy can be found in fast proton transport along one-dimensional water chains confined in carbon nanotubes.[1]

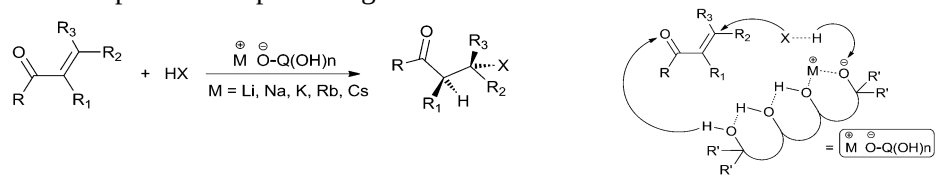

Figure 1. Schematic presentation of a Michael reaction of a CH-acid (XH) catalyzed by a polyalcoholate (polyphenolate) species with the nucleophile/electrophile proton migration facilitated by the multifunctional catalyst.

We have chosen Li, Na and K salts of (*S*)- or (*R*)-3,3'-bis[bis-(phenyl)hydroxymethyl]-2,2'-dihydroxy-dinaphthalene-1,1' (**BIMBOL**) as catalysts of a model reaction of asymmetric Michael addition of malonic ester and other nucleophiles to cyclohex-2-enone.

Among other alcohols and phenols it was only BIMBOL that was an efficient catalyst of the reaction producing Michael adducts with 90% ee.[2]

Other reactions tested with BIMBOL as a catalyst include PTC alkylations of amino acid precursors as shown in Fig. 2 and enantioselective epoxide ring opening with anilines (Fig. 3).

The asymmetric alkylation was conducted in CH_2Cl_2 in the presence of KOH and furnished different amino acids in high yield and reasonably high ee (up to 88%).

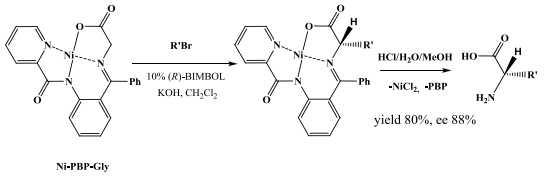

Figure 2. BIMBOL promoted asymmetric alkylation of.

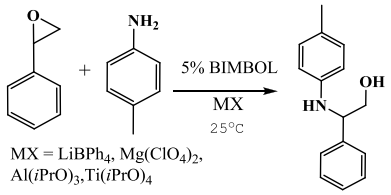

Figure 3. BIMBOL catalyzed ring opening of styrene oxide a glycine Ni(II) complex

The ring opening of styrene oxide with anilines was not catalyzed by BIMBOL at room temperature. However, the addition of Li or Mg salts promoted its catalytic activity. The reaction was stereoselective furnishing only one isomer. Unfortunately, the asymmetric induction was not observed. The induction and catalytic activity of the system was greatly increased when $Ti(O^iPr)_4$ was added to BIMBOL in a ratio 1:1. The forming catalyst was highly active even at a ratio of substrate/catalyst 1000/1. The ee of the final product varied, depending on the conditions, but reached 90% in some cases.

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P231

THE BLOCK CATALYSTS OF NEW GENERATION FOR CLEANING OF EXHAUST GASES OF MOTOR TRANSPORT

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The most effective method of cleaning of exhaust gases of internal combustion engines of cars is the catalytic method. As catalysts of oxidation of CO, hydrocarbons and decomposition of nitrogen oxide, basically, precious metals on carriers which possess high catalytic activity, by thermal stability to poisons are used. Positive experience of use of the catalysts of exhaust gases cleaning motor transport put on block carriers has led to new generations of industrial catalysts for the control of emissions both moving, and constant sources of pollution. Recently block carriers with the honey comb structure of channels are used with the big popularity not only in cleaning of exhaust gases of motor transport, but also in processing of associated and natural gases in a commodity output. For this reason to carriers the new demands are presented: this increase in number of cells at surface unit, stability to heats and mechanical durability.

The method of preparation of the honey comb carrier developed at our laboratory allowed to prepare continuous sheet block carriers of various type of the size. So, we had been prepared the honey comb carriers in diameter of 500 mm for cleaning of waste gases of diesel engines-generators by capacity 2.5 Mw. Such carriers at identical volume of ceramic and metal blocks on 30 % it was easier than them, had more than 75 cells/sm^2 and that was important, the softening temperature made 1800^0C, while at cordierite - $1100\text{-}1300^0$C.

For obtaining of high disperse colloid platinum and a palladium used polyethylene glycol PEG-10000 were used in this work. The colloid was prepared through dissolution of PEG-10000 in the distilled water in a current 2d days. The need quantity of salts of platinum preliminary dissolved in water and a palladium into water solution PEG-10000 was entered.

Samples of catalysts were investigated by means of electronic microscope EM-125K by a method of one-stage remarks. In the sample with Pt the small congestions of dense particles, congestions of dense particles which do not grow together in units are observed, and dispersed on a carrier surface.

By data of electron-microscopic researches in the sample with Pt are observed the small studied catalysts differ high dispersion (8-10 nanometers), uniform distribution of particles of metal on the carrier.

Preliminary results have shown stability catalytic properties of new systems on a basis of metals colloids.

The most active catalyst has been tested in complex cleaning of exhaust gases of hydrocarbons and nitrogen oxides for a diesel engine - the generator. Its activity has made on CO-100 %, CH_x-97 %, NO_x-56.3 %.

The developed effective catalysts of cleaning of exhaust gases of motor transport and exhaust gases of the industrial enterprises from toxic impurity on the metal carrier correspond under characteristics to standard EURO-3. The developed catalytic neutralizers have passed successful tests at the various enterprises.

Thus the developed technology of catalysts-ecologically pure at the expense of replacement of nitrates and chlorides of metals by organic compounds and highly profitable at the expense of decrease in the maintenance of precious metals in the catalyst.

Ru/PNNP CATALYZED ASYMMETRIC AZIRIDINATION: RECENT PROGRESS

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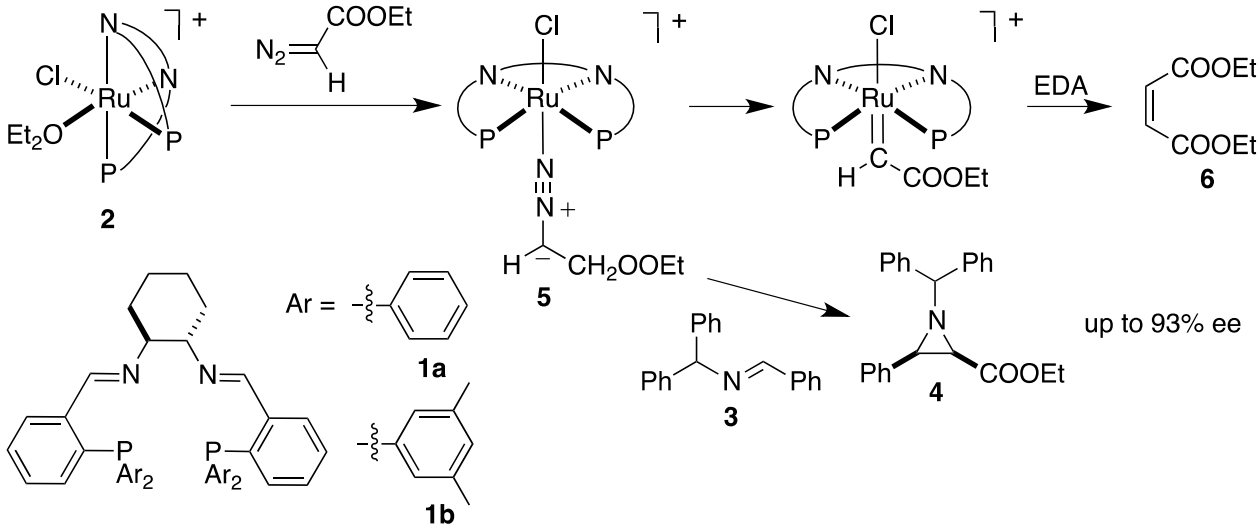
Chiral aziridines are valuable synthons as strain-activated electrophilic precursors to amines as they give ring opening with excellent stereo- and regiocontrol. Our group reported[1] that [RuCl(OEt$_2$)(**1a**)]PF$_6$ (**2a**PF$_6$), formed by chloride abstraction from [RuCl$_2$(**1a**)] with (Et$_3$O)PF$_6$ (1 equiv), catalyzes the asymmetric aziridination of imine **3** with ethyl diazoacetate (EDA) to give aziridine **4** in 26% yield and 84% ee under a strict gradient protocol of temperature. NMR spectroscopic studies showed that EDA coordinates to ruthenium to give the diazoester complex **5**. The latter species either transfers carbene to the imine or decomposes to a carbene complex, which is responsible for the formation of diethyl maleate (**6**), the only byproduct observed, and therefore also for the low yield of aziridine.



Since bulky ligands are known to inhibit carbene formation from diazoester complexes,[2] we prepared a series of substituted PNNP and used them in catalytic aziridination. We found out that the counterion is pivotal, as PF_6^- hydrolyzes upon activation of [RuCl$_2$(**1b**)] with (Et$_3$O)PF$_6$. The resulting acid catalyzes a nonenantioselective aza-Darzens reaction between imine and EDA.[3] Therefore, we screened different anions (PF_6^-, BF_4^-, and SbF_6^-). The aziridine yield reached 45% with little impact on enantioselectivity in the case of **2a**BF$_4$ (78% ee) at 0 °C using an excess of EDA (4 equiv). With ligand **1b**, [RuCl(OEt$_2$)(**1b**)]SbF$_6$ (10 mol%) gave aziridine **4** in 46% yield but the enantioselectivity was reduced to 66% ee. Eventually, **2b**BF$_4$ gave aziridine **4** with 35% yield and 93% ee, which is the best result obtained with a transition metal catalyst. Finally, the reactions with *m*- and *p*-substituted imines will be presented.

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P233

THE ROLE OF PALLADIUM NANOPARTICLES IN CROSS-COUPLING REACTIONS

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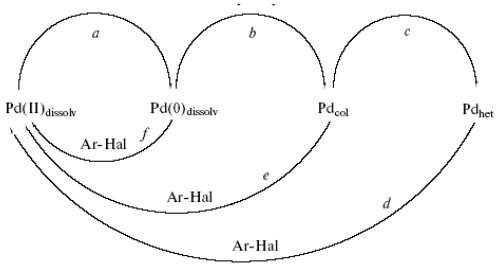
The cross-coupling reactions are of greatest importance and are the focus of researchers' attention [1]. The nature of catalysis in the cross-coupling reactions has been keenly discussed in the literature since the late 1990s. For the Heck reaction (coupling of aryl halides with olefins) the authors of some reviews [2,3] came to the conclusion that homogeneous catalysis in this reaction is most likely, irrespective of the nature of the catalyst precursor generating active species. All authors believe that the same species are involved in the reaction (Scheme 1), namely, dissolved molecular complexes of Pd(0) and Pd(II), Pd nanoparticles (Scheme 1, Pd_{col}) in solution and/or on the supports surface, and larger particles of palladium metal. The heterogeneous palladium species including "dissolved" Pd nanoparticles are only sources of active molecular complexes that are directly involved in the catalytic cycle. It is believed that all active and inactive species generated by the catalyst precursor undergo interconversions during the catalytic reaction and the most important role in these conversions is played by the aryl halide (Scheme 1).



Scheme 1.

However, there is still no consensus to the nature of catalysis in the cross-coupling reactions with the other nucleophiles (alkines, amines, organometallic compounds). Some researchers hold to the hypothesis that these reactions occur via a homogeneous catalytic mechanism, while others believe that the reactions are heterogeneous and involve catalysis on the surface of palladium nanoparticles as well.

In presented study in order to verify various hypotheses about catalysis nature of cross-coupling reactions, we applied a new kinetic approach: measurements of the differential selectivity of active species formed in situ from homogeneous and heterogeneous catalyst precursors in the competitive reaction of two or more aryl halides. Both of the conceptions discussed in the literature - purely homogeneous catalysis and purely heterogeneous catalysis – are not consistent with the observed dependence of the selectivity of forming catalyst on the nature of the catalyst precursor. Most likely, Suzuki and Kumada cross-coupling reactions involving aryl bromides and chlorides proceed simultaneously via homogeneous and heterogeneous catalytic mechanisms. At the same time, the reaction involving aryl iodides most likely occurs via pure homogeneous catalytic mechanism.

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P234

TADDOL-BASED PHOSPHORAMIDITE LIGANDS IN THE Ni-CATALYSED ASYMMETRIC CYCLOISOMERISATION OF 1,6-DIENES

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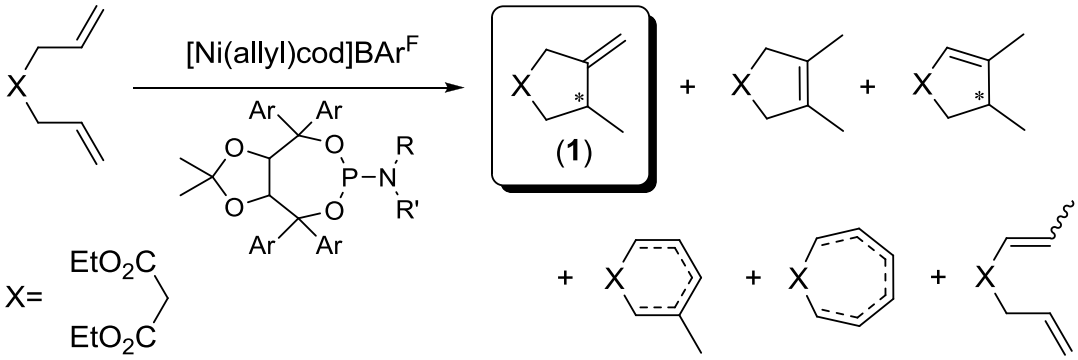
The asymmetric cyclosisomerisation of dienes can be a powerful tool for the synthesis of chiral carbo- and heterocycles containing a double bond for further functionalisations, but is up to now limited to a low number of promising examples.[1,2] In our past work, we applied an azaphospholene ligand and different BINOL-based phosphoramidite ligands in this transformation, observing moderate to good enantioselectivities at relatively low activities.[3-5] Encouraged by the past and recent work of Alexakis,[6] Rovis,[7] Suginome[8] and Fürstner[9], who showed that TADDOL-based ligands may lead to more active and selective catalysts than their BINOL-based analogues in several transformations, we started a detailed study on the use of TADDOL-derived phosphoramidite ligands[10] in the Ni-catalysed asymmetric cycloisomerisation of 1,6-dienes.
Herein, we present our results on the asymmetric cycloisomerisation of 1,6-dienes using monodentate phosphoramidite ligands based on a TADDOL-derived backbone. We describe the optimisation of the ligand structure including the TADDOL-framework as well as the amine part of the ligand using diethyldiallylmalonate as model-substrate for the reaction. Furthermore the substrate scope was extended to other diallylic substrates, achieving overall remarkable high activities and selectivites towards **1** at moderate to good enantioselectivities.



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P235

KINETICS OF MONOPHOSPHITE MODIFIED HYDROFORMYLATION OF OLEFINS

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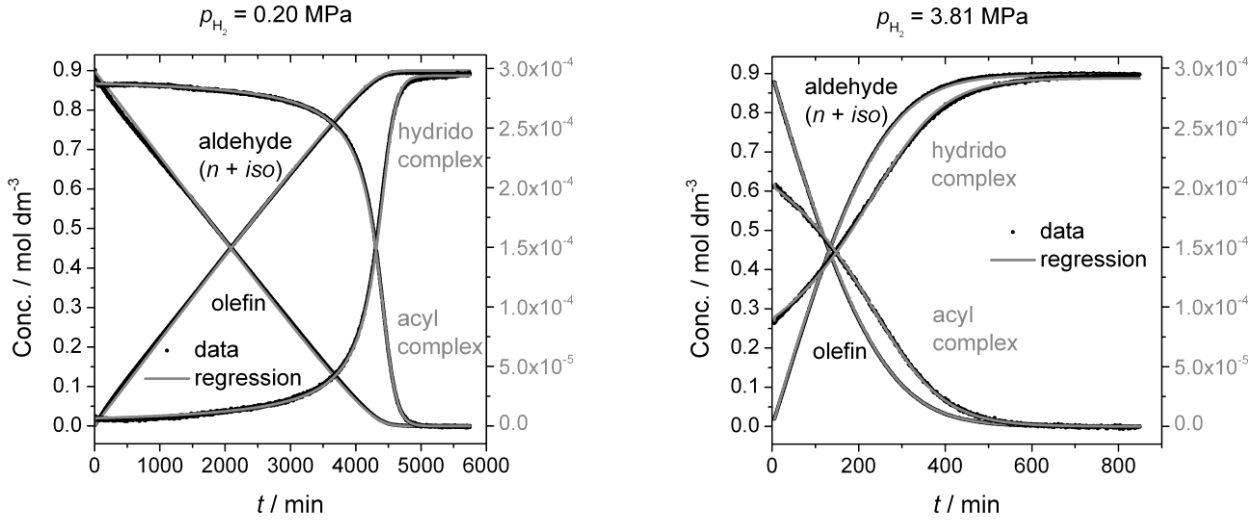
The kinetics of the hydroformylation of 3,3-dimethyl-1-butene with a rhodium monophosphite catalyst has been studied. Time-dependent concentration profiles covering the full olefin conversion range were derived from in situ high pressure FTIR spectroscopic data for both, pure organic components and catalytic intermediates by the Pure Component Decomposition algorithm. These profiles fit to Michaelis-Menten type kinetics with competitive and uncompetitive side reactions involved. The characteristics found for the influence of hydrogen concentration verify that the pre-equilibrium towards the catalyst substrate complex is not established. It has been proven experimentally that the hydrogenolysis of the intermediate acyl complex remains rate limiting even at high conversions when the rhodium hydride is the predominant resting state and the reaction is nearly of first-order with respect to olefin. Results from in situ FTIR and HP NMR spectroscopy and from DFT calculations support the coordination of only one phosphite ligand in the dominating intermediates and a preferred axial position of the phosphite in the electronically saturated, *tbp*-structured acyl rhodium complex.



Hydroformylation of 3,3-dimethyl-1-butene. Concentration profiles of monophosphite rhodium hydride and acyl intermediates and for educt, products (aldehyde sum), compared to results of simultaneous integration/regression of a set of differential equations representing a Michaelis-Menten type mechanism.

P236

NEW CHIRAL ZWITTERIONIC PHOSPHOROUS HETEROCYCLES: SYNTHESIS, STRUCTURE, PROPERTIES AND CATALYTIC ACTIVITY

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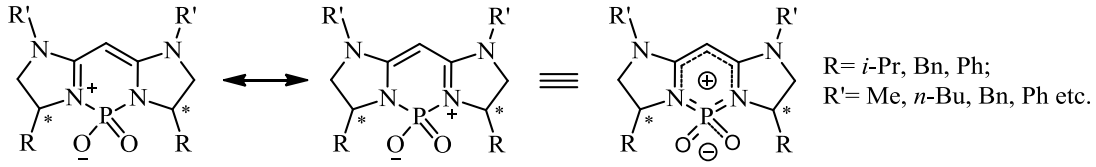
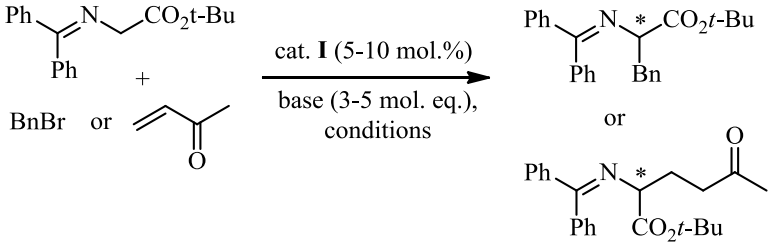
Zwitterionic heterocycles containing negatively charged $PO_2^{\ominus}$ fragment along with positively charged *sp*^{2}-nitrogen atom are rarely known in the literature.[1] The architecture allows specific distribution of charges on oxygen centres (–) and nitrogen (+), which may be able to facilitate reactions requiring either nucleophilic molecular activation (addition of silylated pronucleophiles) or quaternized nitrogen atom (phase transfer processes).
In this presentation, the catalytic activities of a new class of heterocycles **I** (Scheme 1) are described, which were prepared by the incorporation of $PO_2^{\ominus}$ motif into the methylene bridged bis(imidazoline) chiral scaffold[2] derived from readily available amino acids.



(S,S)- or (R,R)-**I**

Scheme 1 New chiral zwitterionic phosphorous heterocycles **I**

Compounds **I** were tested in asymmetric alkylation and Michael addition reactions under phase transfer conditions (Scheme 2), where some enantioselectivity can be observed.



Scheme 2 Some examples of phase transfer reactions catalysed by **I**

The potential applications of these zwitterions in other types of asymmetric transformations will also be briefly described.

This research was supported by a Marie Curie Intra European Fellowship to AES within the 7th European Community Framework Programme (Project 252247).

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PALLADIUM AND RHODIUM CATALYZED ASYMMETRIC REACTIONS USING DIAMIDOPHOSPHITE LIGANDS BASED ON (*S*)-N-(PYRROLIDIN-2-YLMETHYL)ANILINE

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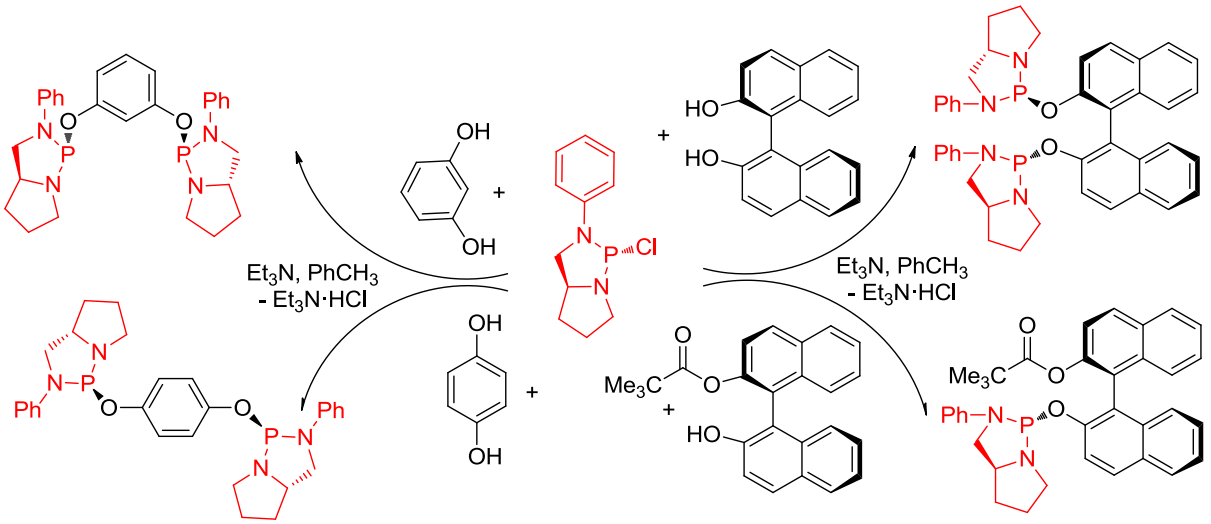
The development of asymmetric transition metal catalyzed reactions has played a significant role in allowing synthetic access to optically pure compounds, especially to biologically important molecules. The dramatic growth of enantioselective catalysis calls for continuation of the search for new and improved chiral ligands.
In contrast to phosphine ligands, whose syntheses can often require multiple steps, phosphite-type compounds can be assembled in a much easier way by simple condensation processes, in particular, by reacting phenols, alcohols or amines with phosphorus halides. Thus, bisphosphites can be readily prepared by reaction between different phosphorochloridites and diols.
Readily available diamidophosphites with *P**-stereocentres have been prepared using (*S*)-*N*-(pyrrolidin-2-ylmethyl)aniline as simple and cheap starting material:



Ligands have shown high efficiency in some asymmetric catalytic processes, namely:
- Pd-catalyzed enantioselective allylation of (*E*)-1,3-diphenylprop-2-enyl acetate(up to 99% *ee*)
- Pd-catalyzed allylic alkylation (*E*)-1,3-diphenylprop-2-enyl ethyl carbonate (up to 92% *ee*)
- Pd-catalyzed desymmetrization of *N*,*N*-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate (up to 70% *ee*)
- Rh-catalyzed asymmetric hydrogenation of prochiral methyl esters of unsaturated acids, in particular dimethyl itaconate and (*Z*)-methyl 2-acetamido-3-phenylacrylate (up to 99% *ee*).

Note, that enantioselective Pd-catalyzed allylic substitution is a novel and highly efficient strategy in the total synthesis of enantiopure natural products, such as (+)-juvabione, (–)-wine lactone, mannostatin A and (–)-swainsonine.

P238

FINE-TUNING OF PROMOTERS FOR EFFICIENT ALKOXYCARBONYLATION OF VINYL ACETATE

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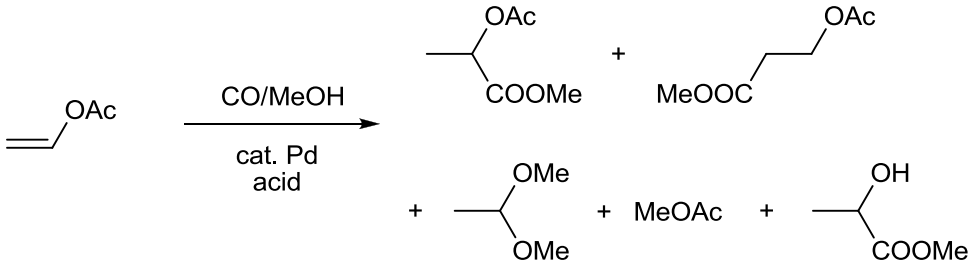
Alkoxycarbonylation of vinyl acetate seems to be a promising chemical venue to lactic acid esters which are important chemicals and synthetic building blocks for food and polymer industry. Manufacturing of large amount of lactates is limited by the currently performed biochemical synthesis that generates also massive amounts of calcium sulfate as a waste product. This problem makes the research of alternative pathways to lactates attractive.
Despite of some successes achieved in recent years, the alkoxycarbonylation of vinyl acetate is still far from industrial requirements. Large amounts of expensive and air-sensitive phosphine ligands are necessary to catalyse this transformation effectively.1 Nevertheless some promising results with low loads of simple phosphines in the presence of promoters were published.2 However these systems demand further improvement concerning activity and conversion.



Herein we report on our results on the Pd-catalyzed methoxycarbonylation of vinyl acetate in the presence of different additives.[3] Triphenylphosphine was used as ligand for palladium because it is especial attractive in terms of stability and cost. Three large families of promoters were tested: Brønsted-acids, Lewis acids and none acidic promoters, such as nitrogen heterocycles and 1,3-dicarbonyl compounds. The effect of 1,3-dicarbonyl compounds and nitrogen heterocyclic compounds was investigated and clarified. Superior results in terms of yield and conversion were obtained with aluminium triflate as promoter. By application of 0.4 mol% of Pd-catalyst a yield of 72 % was achieved.

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P239 (GM10)

CONFORMATIONAL FLEXIBILITY OF A PCP PINCER IRIDIUM HYDRIDE CATALYST OF ALCOHOL DEHYDROGENATION

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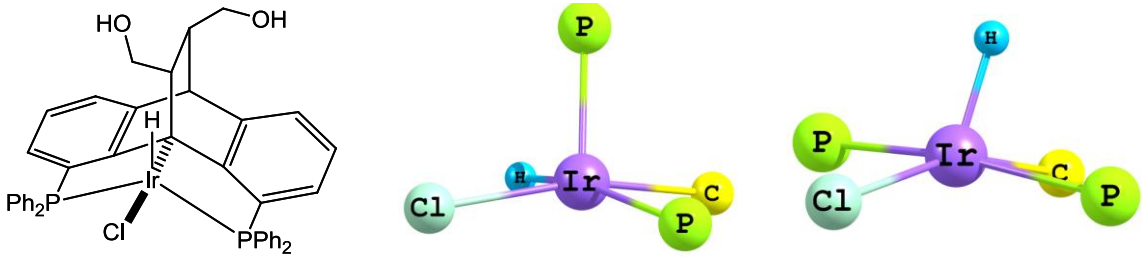
Recently, a new class of bifunctional dibenzobarrelene-based pincer complexes has been demonstrated to exhibit catalytic activity in various processes [1]. In this communication we present the first results of combined variable temperature IR and NMR spectroscopic as well as DFT studies on the PC(sp^3)P pincer iridium hydride complex **1**, being a catalyst of acceptorless alcohol dehydrogenation [2].



1 **2** **3**

The detailed spectroscopic and computational analysis showed the existence of three basic isomers having different geometry around the metal center: **2** and two isomers of type **3** with a *syn*- and *anti*-position of the hydride ligand. Due to the flexibility of the $–CH_2OH$ sidearms each isomer can form several conformers which feature different intramolecular interactions, e.g. dihydrogen bonding of the hydride ligand with the proton of CH and OH groups. Rupture of these bonds and formation of stronger hydrogen bonds with more acidic/basic centers was demonstrated upon addition of trifluoroethanol or NEt_3 in dichloromethane. The equilibrium between isomers shifts in the presence of different bases/coordinating reagents (pyridine, acetonitrile, DMSO, NEt_3), some of which were used as auxiliary base in catalysis [2]. It was established that NEt_3 stabilizes the catalytically active conformer whereas pyridine addition leads to the formation of the non-active species.

This work was financially supported by the Russian Foundation for Basic Research (project No. 11-03-01210) and by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD) (projects No. C-2011b-4 and C-2012a-4).

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P240

SYNTHESIS OF INDOLE-DERIVED ALLOCOLCHICINE ANALOGS EXHIBITING STRONG APOPTOSIS-INDUCING ACTIVITY

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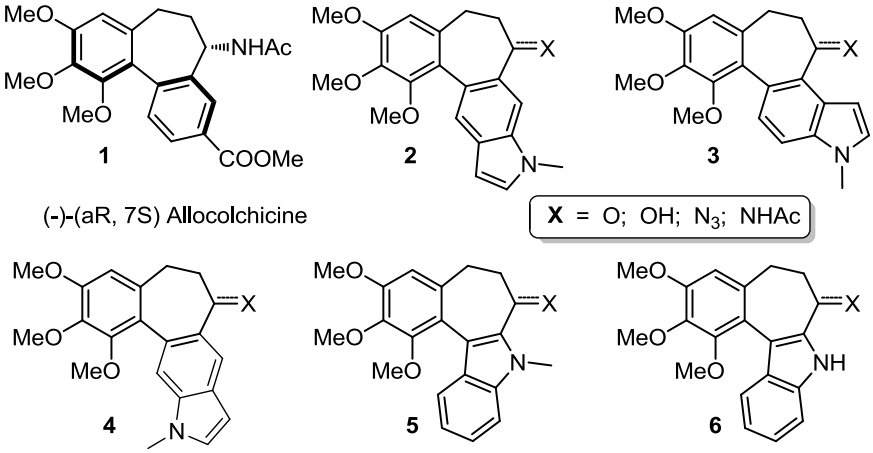
(-)-Colchicine, the major alkaloid from *Colchicum autumnale*, is known for decades as an efficient antimitotic agent able to inhibit microtubule formation (tubulin polymerization) in living cells, thus causing mitosis arrest in the metaphase. While high toxicity has prevented its use as an antitumor agent, colchicine still represents an important lead structure for drug discovery. Allocolchicine (**1)** is a constitutional isomer of colchicine bearing a six membered aromatic C-ring instead of the tropolone moiety. Allocolchicine itself as well as its analogues show promising biological activities similar to colchicines. Herein we report the synthesis of a series of novel allocolchicine analogs **2**-**6** containing *1H*-indolyl fragment.



The fused four-membered carbocyclic skeleton in compounds **2**, **3** and **4** was constructed via Suzuki – Miyaura cross-coupling reaction and subsequent Friedel – Crafts annulation. In turn, Weinreb ketone synthesis and subsequent direct intramolecular C-H arylation reaction gave access to compounds of type **5**. The key ring forming steps for type **6** compounds were aldol condensation and direct intramolecular C-H arylation.

Preliminary biological screening of compounds **2**, **3** on BJAB tumor cell line revealed high antimitotic and apoptose-inducing activity (nanomolar or subnanomolar concentration range) along with particularly low unspecific cytotoxicity as determined by LDH-release assay.

	colchicine	**2** (X = O)	**3** (X = O)	**2** (X = OH)	**3** (X = OH)	**2** (X = NHAc)	**3** (X = NHAc)
IC_{50} [μM]	0.02	0.0025	< 0.001	0.03	0.008	0.08	0.03
AC_{50} [μM]	0.03	0.005	< 0.001	0.1	0.01	0.5	0.05

Acknowledgements to German Academic Exchange Service (DAAD № A/08/79551), Russian Foundation for Basic Research (12-03-00214-a) and Russian Federal Target Program (16.740.11.0476 and 14.740.12.1382).

P241

ETHYLBENZENE DISPROPORTIONATION OVER THE MODIFIED ZEOLITE CATALYSTS

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The disproportionation of ethylbenzene over zeolite catalysts is one of the advanced methods of diethylbezenes (DEB) production. The chemical modification of zeolites accompanying with alterations of their acidic or shape selective properties is one of the possible ways of zeolites para-selectivity improving. In this context development of the para-selective catalysts for ethylbenzene disproportionation process performs the most interest.

The main goal of this paper was to study the effect of zeolites ZSM-5 and BEA modification on their physico-chemical characteristics and catalytic properties in the ethylbenzene disproportionation process. Catalysts based on the ZSM-5 and BEA zeolites, modified with Ni, Co, Cr, Mg, P, were tested on the flowing type laboratory unit. Active components were included to the catalysts at the stage of extrusion.

The tests conditions and catalytic characteristics of the original and modified zeolite catalysts are represented in table 1.

Table 1 – Catalytic activity of the modified zeolite catalysts in ethylbenzene disproportionation (t= 350 ^{o}C, molar ratio H_2/Ethylbenzene=2:1, WHSV= 2,0 hour^{-1}, τ= 1 hour.)

Catalyst	**ΣEt_2Ph in catalizate, % weight**	**Conversion, %**	**Selectivity, %**	**Mane products yield, % weight**
H-BEA (65%)	13,4	32,4	92,6	30,1
Ni-BEA (65%)	14,6	26,2	98,1	25,7
Cr-BEA(65%)	16,3	44,9	90,2	40,5
HZSM-5 (65%)	19,6	47,6	88,8	42,3
Ni-HZSM-5 (65%)	23,1	40,4	96,8	39,1
Cr-HZSM-5 (65%)	20,8	42,9	93,6	40,3

Therefore, it may be concluded that:

- The catalysts based on the original and modified zeolite ZSM-5 have the highest catalytic activity (conversion 40,4-47,6 %) in ethylbenzene disproportionate reaction. Their catalytic activity can be ranged as HZSM-5 < Cr-HZSM-5 < Ni-HZSM-5.
- The Cr-BEA catalyst was most active among the based on the BEA zeolite catalysts (conversion 44,9 %, selectivity 90,2 %). Activity range of zeolite BEA catalysts looks like this:

Ni-BEA < H-BEA < Cr-BEA.

P242

DESIGN OF NEW HYDROGEN BOND-DONATING PHASE TRANSFER CATALYSTS

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In the last two decades organocatalysis has assumed a very important role in the field of enantioselective chemical transformations.[1] The reason this discipline has attracted so much attention is principally due to the robust character, lower toxicity and higher functional group compatibility of organic molecules in comparison to metals and their respective complexes.[1]
Many catalysts in this domain owe their catalytic efficacy to an ability to stabilise developing negative charge in the transition state.[1] In 2003 Takemoto *et al*. presented the first thiourea-based bifunctional organocatalysts, a class of molecule able to simultaneously activate both the electrophile and the nucleophile.[2] Since then many bifunctional catalysts have been developed and exploited. Of these, the cinchona alkaloid core structure has proven a particularly useful structural template.[1]
Phase transfer catalysis is another area of organic chemistry where simple organic molecules are employed to bring about efficient asymmetric transformations.[3] Since Starks[4] introduced the term 'phase transfer catalysis' many tetraalkylammonium or phosphonium salt-based catalysts have been prepared and studied.[3] In particular, in the last few years the potential power of a strategy based on the use of phase-transfer catalysts which also capable of Hydrogen-bond donation has become to be realised (Figure 1). [5,6]

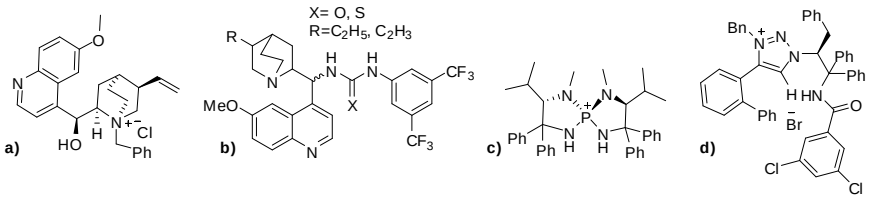

Figure 1. a) First asymmetric phase transfer catalysts (O'Donnell), b) (Thio)urea-based bifunctional organocatalysts (Chen, Connon, Dixon, Soos), c) and d) Hydrogen bond-donating phase transfer catalysts (Ooi).

Here we present the preliminary results of a study aimed at designing new such structures which represent a marriage of effective phase transfer and hydrogen bond-donating modes of action. Finally our aim is to apply the new catalysts synthesised to novel chemical transformation in an asymmetric fashion.

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P243

A SIMPLE METHOD FOR THE ASSIGNMENT OF THE RELATIVE STEREOCHEMISTRY OF CLAVAMS AND CARBAPENAMS

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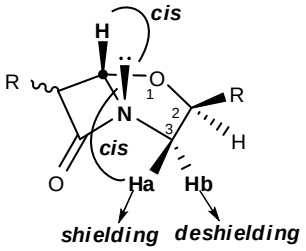
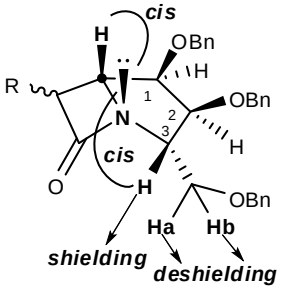
We propose a simple method for determination of the relative stereochemistry of 2-substituted clavams[1] and carbapenams based on nuclear Overhauser effect (NOE) experiments and assignment of the diastereotopicity of protons attached to the C-3 atom.





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P244

TETHERING IN INTERMOLECULAR OLEFIN METATHESIS: SYNTHESIS OF MEDIUM-SIZED HETEROCYCLES

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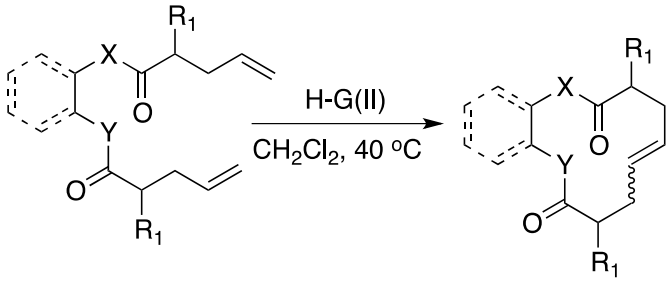
The concept of tethering in intermolecular olefin methathesis has proved to be beneficial and is a well-established synthetic strategy.[1] This approach also addresses two major drawbacks of the cross-metathesis strategy, i.e., *E*/*Z* stereoselectivity and an excess of one of the reaction partners in the process. A temporarily installed unit connecting two fragments enables the formation of different ring sizes and can be disposed of from the system after the completion of the desired transformation. The selection of a disposable unit is based on the nature of the substrates and the applied reaction conditions in the specific transformation. The tethering unit should be stable during the synthetic operations and should be a functional group that is compatible with the catalytic system.

Model cross and ring-closing metathesis strategies toward the C1–C8-linear carbon skeleton are presented.[2] The introduction of a one, two, or four-atom tether enables the formation of 9, 10, and 12-membered rings in good-to-excellent yields and stereoselectivity. Furthermore, the study revealed that the cross metathesis approach and the formation of medium ring sizes (9 and 10) *via* ring-closing metathesis are much less favorable.



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P245

β-CYCLODEXTRIN WITH α-AMINO ACID DERIVATIVES – NEW POTENT CHIRAL HYBRIDS

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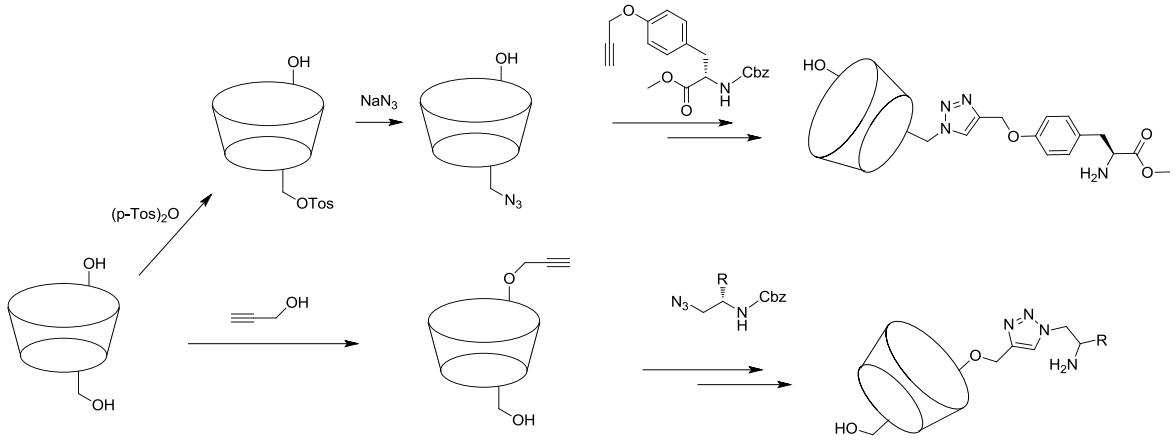
The problem of cyclodextrin derivatization has been solved 14 years ago, since Bittman et al. [1] presented efficient and selective approach to mono-6-substituted β-cyclodextrin; obviously as the new challenge appeared the issue of selective bis-derivatization. Although several solutions had been proposed, the best way for obtaining the single bis-derivatized products was elaborated by Pearce and Sinay [2]. On the other hand, introduction of highly specific coupling – Sharpless' click chemistry – gives an opportunity to combine compounds with many functional groups (often not orthogonal).

Here we present an example of combining these two methods in order to create new functional hybrids which can potentially behave like molecular carriers as well as artificial enzymes. Therefore, we formed a library of β-cyclodextrin derivatives, containing α-amino acid derivatives as side-chains on either primary and secondary site of the cyclodextrin rim.



Some examples of aplication of these compounds as molecular recognition vessels are to be reported.

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"Carbohydrates as renewable raw materials in the synthesis of products with high added value" no. POIG.01.01.02-14-102/09-02

P246

STEREOSELECTIVE SYNTHESIS OF CYCLOBUTANE DERIVATIVES FROM OLEFINS AND ALLENES BY HOMOGENOUS GOLD CATALYSIS

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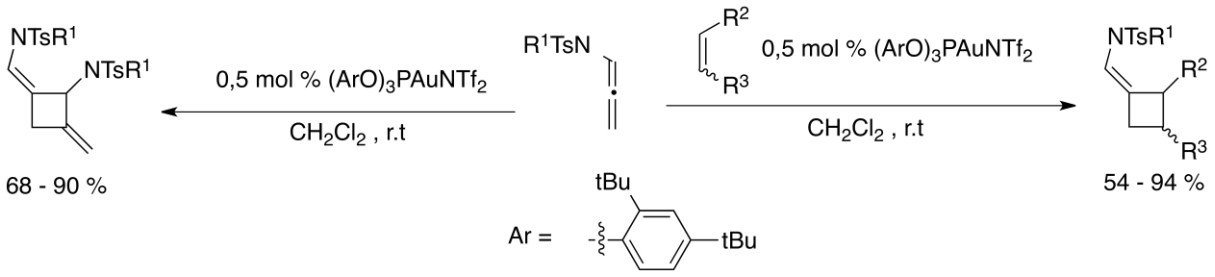
In the last decade gold catalysis has emerged as a useful tool for the synthesis of different scaffolds from accessible starting materials bearing on alkyne or allene moieties.[1]
We report here that the addition of catalytic amounts of a phosphite-based gold(I) catalyst efficiently triggers the intermolecular [2+2] cycloaddition of allenes and alkenes[2] substituted by electron-donor groups. The reaction is fast and furnishes cyclobutane derivatives in a stereoselective manner using low catalyst loadings. Besides, the same catalyst selectively affords homodimerization products from the starting allene, a process that could be conveniently tuned by addition of norbornene. An asymmetric version of this process will be discussed.



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P247

SYNTHESIS OF BIOLOGICAL ACTIVE ISOVALERIC ACID ESTERS BY HYDROALKOXYCARBONYLATION OF ISOBUTYLENE

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Hydroalkoxycarbonylation of isobutylene, a product of oil refining, with carbon monoxide and an alcohol in the presence of homogeneous metal complexes catalysts makes it possible to synthesize easily and conveniently in one step isovaleric acid esters, which possess biological activity and are components of pharmaceutical compositions or valuable intermediates for their synthesis. Some isovalerate esters possess a characteristic odor and are used as fragrance compounds in the manufacture of perfumes, cosmetics, and food essences.

We applied hydroalkoxycarbonylation of isobutylene with carbon monoxide and mono(noly)hydric alcohols in the presence of catalytic systems based on the phosphinpalladium complexes ($Pd(PPh_3)_4$-PPh_3-TsOH, $Pd(Acac)_2$-PPh_3-TsOH) to prepare of biological active isovaleric acid esters: l-menthylisovalerate (possesses spasmolytic properties; it used as main active component of the spasmolytic medicine "Validolium"), ethylisovalerate (possesses aromatic (fruit) odor; intermediate product for obtaining sedative and spasmolytic medicines "Ethyl ester of α-bromisoveleric acid" and "Corvololium"), cyclohexylisovalerate (bactericide activity (against Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa); antifungus activity (against Candida albicans)), benzylisovalerate (bactericide activity (against Escherichia coli, Staphylococcus aureus)) and monoglyceryde of isovaleric acid (bactericide activity (against Escherichia coli, Pseudomonas aeruginosa); antifungus activity (against Candida albicans)).

The reaction were performed in a stainless-stell autoclave (20 atm, 100^0C, 4 h). The reaction was performed without solvent. The [alcohol]:[isobutylene]:[Pd]:[PPh_3]:[p-TsOH] ratio was 435:565:1:7:12. The autoclave at room temperature was charged with the catalytic system and alcohol. The autoclave was hermetized, purged in duplicate with carbon monoxide for deaeration, and charged with olefine, after which required carbon monoxide pressure was effected, and stirring and heating were started. The reaction products were isolated by fractional distillation. The yields of the target products were 14,7-96,0%. The selectivity in linear reaction products was 100%. Such a high regioselectivity is apparently provided both by the structure of the starting alkene (isobutylene) and by the reaction mechanism. The most probable is a hydride mechanism. Evidence for this proposal comes from the observation of an exceptionally strong effect of the p-TsOH addition, which being a proton donor, facilitates formation of the primary active hydride complexes of the catalytic cycle.

P248

POLYMER-STABILIZED METAL NANOPARTICLES – AN EFFECTIVE CATALYSTS FOR ORGANIC SYNTHESIS

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The achieving of high selectivity, activity and technological performance of catalytic systems is the most complicated problem of catalysis. Traditional catalysts are easy regenerated and separated from the reaction mixture and provide relatively high selectivity, but the low surface area and the high content of the noble metals result in their high cost. Nanocatalysts have large surface area-to-volume ratio of the metal, which allows utilizing effectively the expensive metals and providing the higher activity and selectivity compared to the traditional ones. However, without a suitable support the metal nanoparticles aggregate reducing the surface area and restricting the control over the particle size.

Polymers which contain complexes or metal nanoparticles may be used as the catalysts in a variety of organic reactions as they combine the advantages both of homogeneous (high activity and selectivity) and heterogeneous (easy recovery from the reaction mixture and a possibility of regeneration) catalysts. Catalytic properties of such systems may be changed by varying the type of polymeric matrix and characteristics of complexes or metal nanoparticles.

This study is aimed to the development and investigation of novel metal-polymeric systems which are catalytically active and selective in main reaction of organic synthesis, such as, oxidation and hydrogenation reactions in synthesis of vitamin intermediates and medicinal preparations.

The methods of nanoparticles formation in nanostructured polymers were combined into the groups depending on the medium:

nanoparticle formation in amphiphilic block-copolymers (polyethylene oxide-block-poly(2-vinylpyridine) (PEO-P2VP) and polystyrene -block – poly(4-vinylpyridine) (PS-P4VP) were chosen). It is necessary to emphasize that the heterogeneous nanocatalysts on the base PEO-P2VP and PS-P4VP deposited on alumina were also synthesized;

formation of metal nanoparticles in polyelectrolyte systems (polydiallyldimethyl ammonium chloride (PDADMAC) was investigated as the examples of cationic polyelectrolyte);

metal nanoparticles formation in cavities (pores) of a polymeric matrix (hypercrosslinked polystyrene (HPS) was investigated).

Catalytic properties of the synthesized nanostructured composites were studied in selective hydrogenation of long-chain acetylenic alcohols, enantioselective hydrogenation of ethylpyruvate to (R)-ethyllactate and in direct partial oxidation of D-glucose and L-sorbose and full oxidation of phenol. Kinetic investigation and physical-chemical analysis (NMR, XPS, XRD, TEM, AFM, FTIR, BET) of catalytic systems and substrates were conducted and the hypothesis of the reaction mechanisms was proposed. It was shown that the interaction of active component of the catalyst with the solvent, support, modifier and substrate was taken place. It was confirmed that selective hydrogenation and oxidation take place via multiligands reaction complex. Substrate activation occurs by transfer of electron density from active component of the catalyst. For all investigated colloid and deposited catalysts the diameter of metal-nanoparticles was determined to be equal to 2-3 nm. Investigated methods for polymer-containing nanocomposites synthesis allowed to develop highly active, selective (selectivity reached up to 99% at 100% conversion) and stable catalytic systems of hydrogenation, enantioselective hydrogenation and selective and direct oxidation reactions.

P249

SYNTHESIS AND APPLICATION OF CATIONIC PALLADIUM COMPLEXES [(acac)Pd(L^1)(L^2)]A IN TRANSFORMATIONS OF ALKENES AND DIENES

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The cationic palladium complexes are widely used as catalyst precursors in a variety of olefin transformations [1]. For more than 50 years palladium compounds have been intensively used as active and selective catalysts for reactions of many difficult substrates providing new useful synthetic organic products [2]. General routes for the synthesis of cationic palladium complexes [(acac)Pd$(L)_2$]BF_4 (L = PAr_3, A = BF_4 or ClO_4) require use of triphenylmethyl tetrafluoroborate [3], tetrafluoroboric acid etherate [4], or combination of Tl(acac) and silver salt with weakly coordinated anion [5].

We report here the novel effective route for synthesis of the cationic palladium complexes of general formula [(acac)Pd(L^1)(L^2)]A or [(acac)Pd(L^L)]A, where L^1, L^2 = PCy_3, $P(i\text{-}Pr)_3$, PBu_3, MeCN, $HNEt_2$, $HNBu_2$, $HNOct_2$, morpholine; L^L=dppm, dppp, dppb, dppf, cod, phen, bipy, (2,6-*i*-PrPh)$_2$DABMe$_2$, (2,6-MePh)$_2$DABMe$_2$, and A=BF_4 or CF_3SO_3. The new compounds were characterized by elemental analysis, IR and ^{1}H-, ^{13}C-, ^{11}B-, ^{19}F- and ^{31}P-NMR, X-ray diffraction methods.

Prepared complexes [(acac)Pd(L^1)(L^2)]A or [(acac)Pd(L^L)]A were used in combination with boron trifluoride etherate as highly effective catalyst systems for polymerization of norbornene, 5-alkyl-norbornenes, 5-phenylnorbornene, methylbicyclo[2.2.1]hept-5-ene-2-carboxylate, selective dimerization of styrene, alkene dimerization and cross-coupling with alcohols. It was shown that complexes [(acac)Pd(L^1)(L^2)]A or [(acac)Pd(L^L)]A can be used as single catalyst for addition polymerization of norbornene, telomerization of butadiene and isoprene with secondary amines, and selective dimerization of vinylarenes.

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IRIDIUM- CATALYZED ASYMMETRIC TANDEM REACTION OF MESO-DIOLS AND ALDEHYDES

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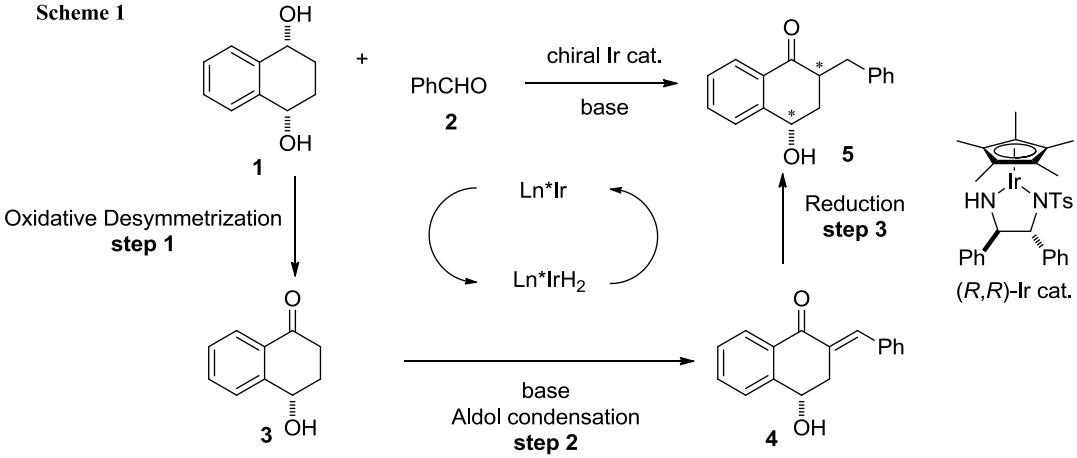
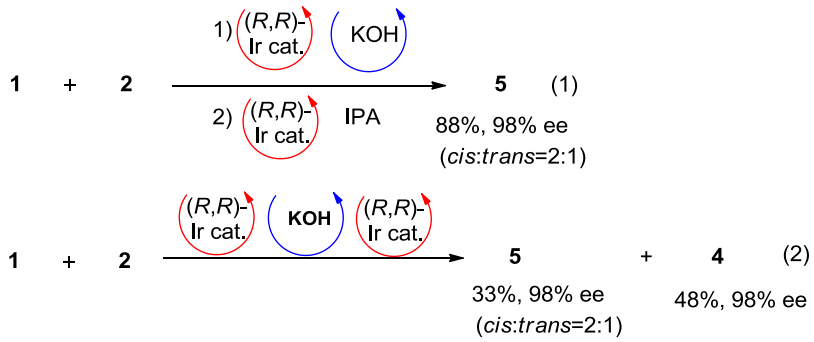
The development of tandem catalyst processes is one of the main properties for the modern synthetic organic chemistry. They lead to reduce the solvent, reagent, purification steps for green chemistry.[1] Recently we have reported oxidative desymmetrization of *meso*-diols using chiral iridium complex catalysts.[2] The reaction is safe and environmentally friendly process without use of stoichiometric amount of heavy metals. We also applied this reaction for the synthesis of otteliones, tubulin polymerization inhibitors.[3] We report here that asymmetric tandem coupling of *meso*-diols and aldehyde using chiral Ir catalyst. This tandem reaction consists of oxidative desymmetrization of meso-diols (Scheme 1, step1), aldol condensation with aldehyde (step 2), reduction of enone (step 3).

A mixture of *meso*-diol **1**, benzaldehyde **2**, chiral Ir complex (10 mol %) and KOH (50 mol %) in dioxane was stirred for 1 h at 50 °C, then 2-propanol (IPA) was added and the mixture was further stirred at the same temperature. After 2 h. the desired benzyl ketone **5** was obtained with 98% ee in 88% yield (eq 1). Asymmetric hydrogen autotransfer reaction without additional hydrogen donor such as IPA gave **5** with 97% ee in 33% yield together with enone **4** with 98% ee in 48% yield (eq 2).

Scheme 1





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P251

DIRECT CHEMOSELECTIVE SYNTHESIS OF POLYHYDROXYLATED QUINOLIZIDINE ENAMINONES FROM INERT SUGAR-DERIVED LACTAMS

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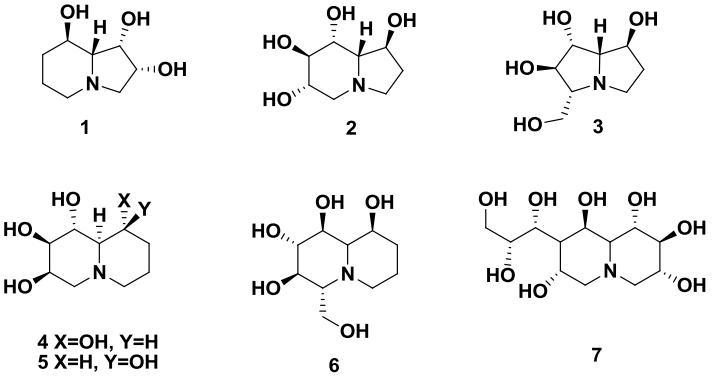
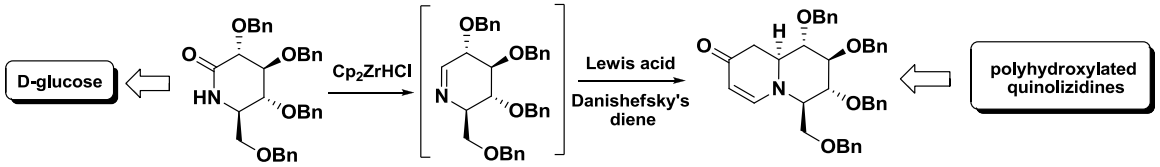
The synthesis of polyhydroxylated indolizidine, pyrrolizidine and quinolizidine is well visible trend in current carbohydrate chemistry. [1] Among these iminosugars, swainsonine (**1**), [2] castanospermine (**2**), [3] and alexine (**3**) [4] and fully synthestic polyhydroxylated quinolizidines **4-6 [5]** have attracted significant interest due to their biological activities as glycosidase inhibitors.



Based on our previous experience we proposed a new method for the synthesis of polyhydroxylated quinolizidine enaminones starting from 6-membered cyclic imines derived from commercially available sugars.



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P252

NEW CATALYTIC ROUTE TO (*E*)-UNSATURATED KETONES

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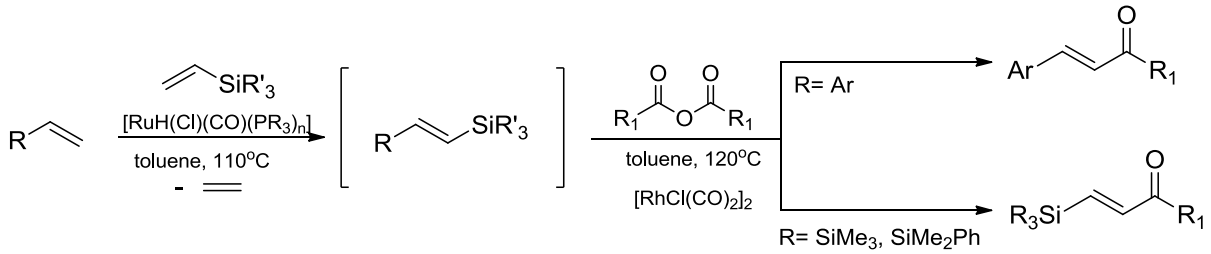
α,β-Unsaturated ketones have been widely applied as useful key reagents in organic synthesis. Their use as substrates for a number of reactions such as Michael addition, hydrogenation, epoxidation, cycloaddition, Morita-Baylis-Hillman reaction etc., has stimulated their synthetic advancements [1]. In the past two decades, we have developed the silylative coupling of olefins with vinyl-substituted organosilicon compounds occurring in the presence of complexes containing initially or generating in situ M-H and M-Si bonds [2]. The ruthenium-catalyzed silylative coupling in combination with subsequent rhodium-catalyzed desilylative acylation (Narasaka coupling) appears to be a valuable step to provide functionalized unsaturated carbonyl compounds.
In the communication, we present our recent results on the synthetic applications of the catalytic silylative coupling reaction for the stereoselective synthesis of *α,β*-unsaturated ketones such as (*E*)-styryl ketones [3] and (*E*)-*β*-silylvinyl ketones [4] which are interesting building blocks in organic synthesis.



Acknowledgment. Financial support from the Ministry of Science and Higher Education (Poland); NN 204 148540 is gratefully acknowledged.

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P253

BICYCLIC ENAMINONES AS BUILDING BLOCKS IN THE SYNTHESIS OF AZAPHENALENES AND RELATED COMPOUNDS

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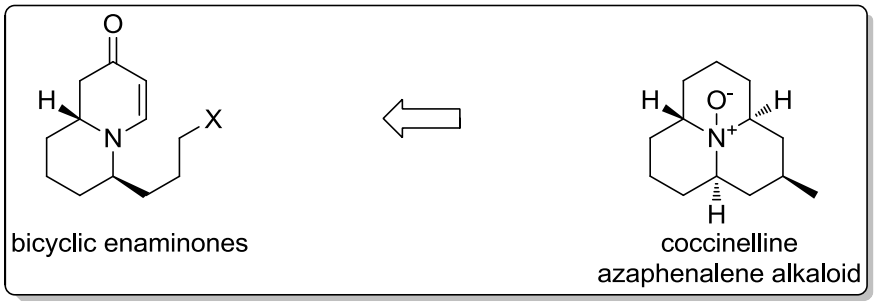
Enaminones are versatile starting materials for the synthesis of many classes of organic compounds [1]. Use of Danishefsky's diene with imines led to generate bicyclic enaminones from easily available azaheterocyclic compounds as precursors of imines [2]. Our ongoing program is aimed on usage of these moieties in further transformations resulting in tricyclic skeleton of azafenalene alkaloids, which are common defensive substances of ladybird beetles family (*Coccinellideae*) [3]. due to their interesting structure and potentially benefitial biological activities this class of natural compounds is of interest of our research group.

This project was financed by the European Union within the European Regional Development Fund, project POIG. 01.01.02.-14-102/09



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P254

CONVERSION OF ALCOHOLS INTO AMINES USING HOMOGENOUS RUTHENIUM CATALYSTS

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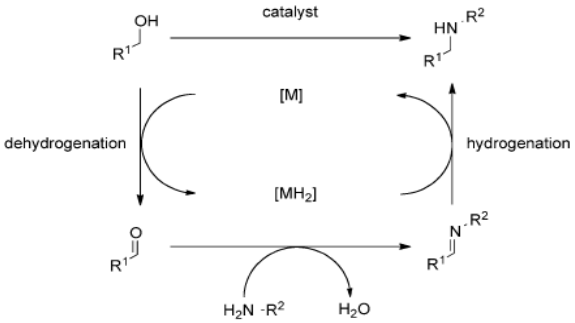
Amines are conventionally synthesized by the alkylation of alkyl halides with ammonia or amines, but over-alkylations are common leading to mixtures of primary, secondary, tertiary amines as well as quaternary ammonium salts. [1]

The direct alkylation of amines with alcohols has been known since the beginning of the 20th century.[2] This is an attractive and promising alternative method to traditional alkylating procedures due to several factors , it is a safer and non-toxic procedure which generates water as a by-product and avoids production of wasteful products, alcohols are inexpensive and more readily available than the corresponding toxic halides or carbonyl compounds and the selectivity of the reaction can be controlled with the catalyst.[3,4]

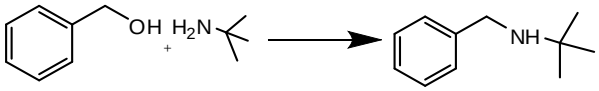


The alcohol is activated by oxidation to give an aldehyde or ketone, which then undergoes a condensation reaction with the amine nucleophile.Subsequent hydrogenation of the resulting imine with the initially generated hydrogen yields the desired amine product

This method had been extensively explored using different homogenous and heterogeneous catalysts. The disadvantages of the known homogeneous catalysts similarly to heterogeneous systems , are the high temperatures and long reaction times to obtain optimum yields which are not desired for industrial processes.

In this paper, we investigated synthesis of amines by the amination of alcohol applying organometallic catalysts based on ruthenium in moderate conditions. Ruthenium catalysts were found to be inactive in the absence of a phosphine ligand, Hence a number of bidentate ligands such as bis(diphenylphosphino)ferrocene (dppf) diphenylphosphinopropane (dppp) and Xantphos were tested.Primary amines have been converted into secondary amines, and secondary amines into tertiary amines, using primary alcohols. Secondary alcohols require more forcing conditions than primary alcohols but are still effective alkylating agents in the presence of these catalysts. Subsequently, it was discovered that the addition of additives such as molecular sieves and suitable base had beneficial effect on these reactions and were therefore placed in our investigation.

The reaction of t-butylamine and benzyl alcohol with $[Ru(\rho\text{-cymene})Cl_2]_2$ was chosen as a model reaction, among the ligands it was found that dppf gave the best conversions.



Excellent yields were obtained by heating a equivalent solution of the alcohol and amine at reflux in toluene in the presence of 2.5 mol% of $[Ru(\rho\text{-cymene})Cl_2]_2$, 5 mol% dppf 10 mol% K_2CO_3 and 3Å MS for 24 hours under argon atmosphere. The reactions were monitored by GC-MS in order to study the alkylation process in detail.

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LIGAND INFLUENCE ON THE STABILITY AND ACTIVITY OF NOVEL COBALT COMPLEXES FOR [2+2+2] CYCLOADDITION REACTIONS

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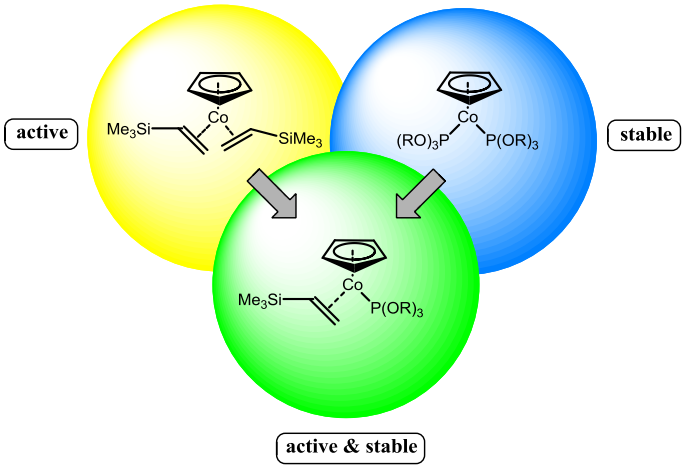
Transition metal-catalyzed [2+2+2] cycloaddition reactions are a convenient method for the synthesis of benzene or pyridine derivatives in a highly atom-economical manner.[1] As work from our group previously showed, cobalt complexes of the type [CpCo(olefin)$_2$] are excellent catalysts for these cycloaddition reactions. Especially [CpCo(H_2C=CHSiMe_3)$_2$] proved to be not only an excellent catalyst but also a great precursor for the convenient synthesis of a variety of different [CpCo(olefin)$_2$]-complexes.[2]
One drawback of [CpCo(H_2C=CHSiMe_3)$_2$] (**1**) is its thermal instability and the rapid degradation of the complex above –40 °C, which makes the handling of the catalyst somewhat tricky. To improve the stability of precatalyst **1** without interfering too strongly with its capability to rather easily generate the catalytically active species, we set out to prepare CpCo(I)-complexes, which have one of their olefin ligands substituted for a ligand that would be able to provide sufficient stability as well as reactivity. In due course we synthesized room temperature-stable complexes of the general type [CpCo(H_2C=CHSiMe_3)(phosphite)] as well as [CpCo(phosphite)$_2$] and screened their respective activities in cyclotrimerization experiments of diynes with nitriles. Here the mixed olefin-phosphite complexes exhibit an excellent combination of thermal stability and high activity in [2+2+2] cycloaddition reactions.[3]



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AMINOCATALYTIC ENANTIOSELECTIVE 1,6-ADDITIONS OF ALKYL THIOLS THROUGH VINYLOGOUS IMINIUM ION ACTIVATION OF CYCLIC DIENONES

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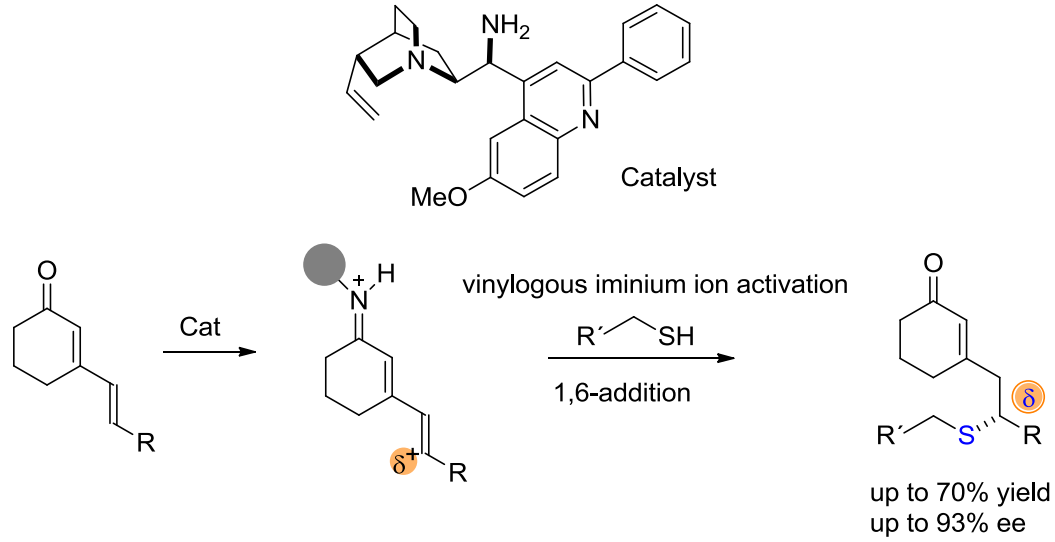
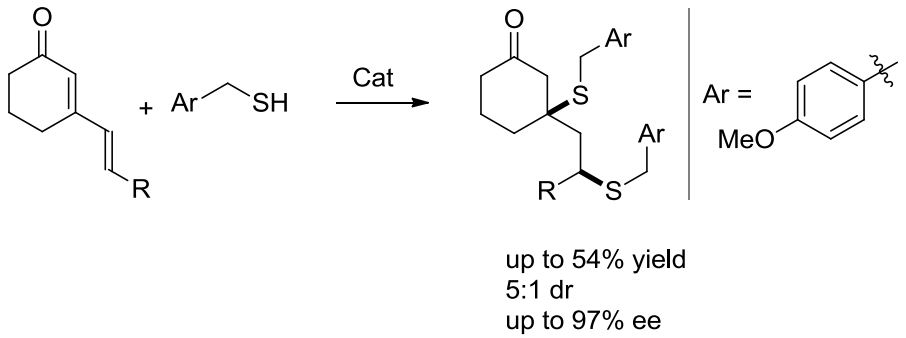
We have discovered that the LUMO-lowering activating effect can be transmitted through the conjugated π-system of 2,4-dienones upon selective condensation with a chiral amine. The resulting aminocatalytic activation mode, termed vinylogous iminium ion catalysis, contributes a strategy for the direct, stereoselective δ-functionalization of unsaturated carbonyl compounds. Specifically, the 1,6-addition of alkyl thiols to β-substituted cyclic dienones catalyzed by a cinchona-based primary amine proceeds with high stereocontrol and δ-site selectivity[1].



In addition, a cascade reaction was successfully implemented by using a large excess of the thiol and prolonging the reaction time. This change in the reaction conditions allowed the synthesis of more sophisticated adducts with moderate diastereoselectivity but high control over the absolute configuration.



[1] *Angew.Chem.Int.Ed.* **2012**. 51, 6439–6442

P257

CATALYTIC CARBON-CARBON BOND HYDROGENATION WITH WATER CATALYZED BY RHODIUM PORPHYRINS

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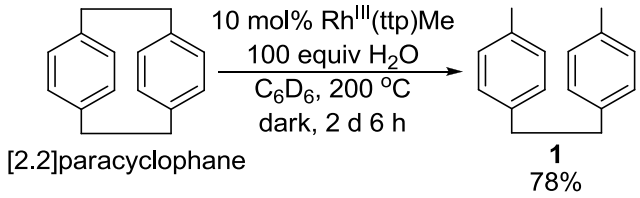
Hydrocracking of fossil fuels increases the fuel quality by bringing up the H/C ratio, however in harsh and acidic conditions of temperature about 400 ^{o}C and pressure over 50 bar.[1] Making such process milder can reduce the energy input and hence negative environmental impacts. Water is a cheap and attractive hydrogen source via water splitting.[2] Recently, we have reported the selective carbon-carbon bond activation of cyclooctane.[3] Now we successfully achieved the catalytic carbon-carbon bond hydrogenation under neutral medium, using water as the hydrogen source. The benzylic carbon-carbon bond of [2.2]paracyclophane was catalytically cleaved and hydrogenated to produce 4,4'-dimethylbibenzyl **1** in good yield.



Acknowledgement
We thank the Direct Grant of Chinese University of Hong Kong for the financial support.

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P258

ROLE OF LEWIS ACIDS IN THE TUNGSTEN-IMIDO-CATALYSED DIMERISATION OF α-OLEFINS: A COMPUTATIONAL MECHANISTIC STUDY

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The complete catalytic cycle for dimerisation of ethylene – chosen as a prototypical α-olefin – by a tungsten–imido compound has been explored computationally. This study was conducted by using a reliable DFT method for the experimentally employed catalyst compound and the Lewis acid cocatalyst, as well as by taking bulk solvent effects into explicit consideration. The aptitude for Lewis adduct formation in catalytically relevant tungsten–imido species has been scrutinised. Specific catalyst–cocatalyst interactions through Lewis acid association at the W=NR functionality are identified, with four-membered chelates identified as being most favourable. The chelate formation is seen to have a pronounced influence on the catalytic ability of tungsten–imido compounds. The identified specific catalyst–cocatalyst associations are the key for the understanding of the observed dimerisation activity, thereby demonstrating what crucial role the Lewis acid is playing in achieving an efficient catalysis. This study furthermore provides a general understanding of the fact that only cocatalysts of $AlCl_nR_m$ type can mediate the dimerisation, whilst AlR_3 Lewis acids are not useful.

P259 (GM2)

RARE EARTH COMPLEXES FOR SYNTHESIS OF BIODEGRADABLE AND BIOCOMPATIBLE POLYMERS

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New multidentate tethered amidine-phenol pro-ligands {4,6-*t*Bu$_2$C$_6$H$_2$O-(2-C(N-R)=N-R}H$_2$ ({LON^R}H$_2$, R = *i*Pr, cyclohexyl (Cy), 2,6-*i*Pr$_2$C$_6$H$_3$ (Ar)). Amine elimination reactions between {LON^{iPr}}H$_2$ or {LON^{Cy}}H$_2$ and Ln[N(SiMe$_3$)$_2$]$_3$ afforded the corresponding phenoxy-amidinate amides {LON^R}LnN(SiMe$_3$)$_2$ (Ln = Y, R = *i*Pr, **1**; R = Cy, **2**; Ln = Nd, R = Cy, **3**), whereas the same reaction between{LON^{Ar}}H$_2$ and Y[N(SiMe$_3$)$_2$]$_3$, under various conditions, always yielded the homoleptic tris(phenoxy-amidinate) complex {LO^{H}N^{Ar}}$_3$Y (**4**). Amido complexes **1**, **2** and **3** are effective initiators for the ring-opening polymerization (ROP) of *racemic* lactide (*rac*-LA), giving atactic or heterotactic-enriched (P_r up to 76%) polymers with high molecular weights (M_n up to 158,800 g.mol^{-1}), but broad molecular weight distributions (M_w/M_n = 1.5-2.8). Effective immortal ROP of *rac*-LA was feasible by combining complex **1** with 5-50 equiv. of isopropanol or benzyl alcohol, affording PLAs with well controlled molecular weights and narrow polydispersities (M_w/M_n = 1.11-1.38).

The reactions of Ln(BH$_4$)$_3$(THF)$_2$ with an equimolar amount of the dilithium derivative of a bridged bis(amidine) containing a conformationally rigid naphthalene linker afforded heterobimetallic *ansa*-bis(amidinate) lanthanide borohydrides [1,8-C$_{10}$H$_6${NC(*t*Bu)N-2,6-Me$_2$-C$_6$H$_3$}$_2$]Ln(BH$_4$) (μ-BH$_4$)Li(THF)$_2$ (Ln = Nd, **5**; Sm, **6**). Compounds **5** and **6** are active in the ring-opening polymerization (ROP) of racemic lactide at 20 °C, acting as single-site diinitiators with the two borohydride groups operative, and providing polymers with a slight heterotactic bias (P_r = 0.54-0.62), controlled molecular weights and relatively narrow polydispersities (M_w/M_n = 1.5-1.7).

A series of borohydrido [*o*-C$_6$H$_4${NC(*t*Bu)NC$_6$H$_2$-2,6R$_2$]Ln(BH$_4$)(THF)$_2$ (R = Me, *i*Pr; Ln = Y, Nd, Sm) and alkoxy [*o*-C$_6$H$_4${NC(*t*Bu)NC$_6$H$_2$-2,6R$_2$]Ln(O*t*Bu)(L)$_n$ (R = Me, *i*Pr; Ln = Y, Nd, Sm; L = THF, n=2; L = DME, n = 1) rare earth complexes supported by ansa-bis(amidinate) ligand system with conformationally rigid *o*-phenylene linker was synthesized and structurally characterized. These complexes proved to be efficient initiators of ring-opening polymerization of *rac*-lactide.

Bis(guanidinate) alkoxy complexes {(Me$_3$Si)$_2$NC(NPr^i)$_2$}$_2$LnO*t*Bu (Ln=Y (**7**), Lu (**8**)) were estimated as initiators for ring-opening polymerization of *rac*-lactide at 130°C in bulk to give atactic polylactides with M_n up to 33000 g/mol. Total conversion of 500 equivalents of monomer was reached in 2 h when **7** was used as an initiator. Complex **7** allows conversion of up to 2500 equivalents of monomer within 8 h. The obtained polylactides demonstrate monomodal molecular mass distribution with rather narrow polydispersities M_w/M_n=1.46-1.84. The experimental molecular weights are noticeably (3-11 times) lower compared to calculated values.

Acknowledgements
This work is supported by the Russian Foundation for Basic Research (Grant No 11-03-00555-a)

P260

Cu(II) COMPLEXES OF BETTI BASE : THE CATALYST FOR THE EPOXIDATION OF OLEFINS UNDER MILD CONDITIONS

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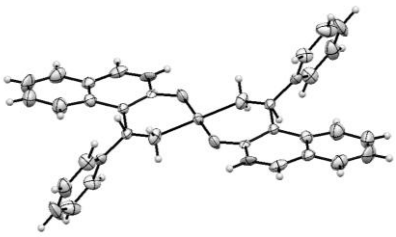
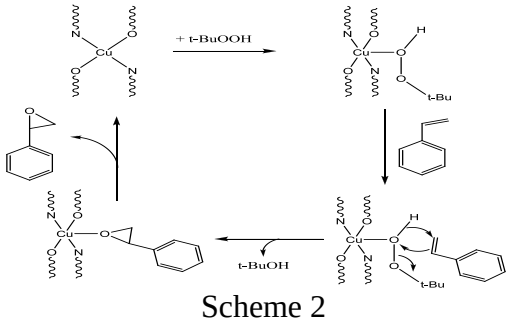
The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals. Among several catalytic procedures for optically active epoxides, the asymmetric epoxidation of unfunctionalized alkenes catalysed by chiral (salen)Mn(III) complexes, initially developed by Jacobsen and Katsuki , is considered to be one of the most effective methods discovered in the last 20 years[1]. In the Jacobsons catalyst, the special orientation of the chiral ligand formed the basis for induction of chirality in the product. The survey of literature reveals a continuous search for chiral ligand which can efficiently catalyse asymmetric reaction.The multi component reaction between 2-naphthol, aryl aldehydes and ammonia or amines yields aminobenzylnaphthols, in a process known as the Betti reaction, was first uncovered at the beginning of the 20th century by Mario Betti, an Italian chemist [2]. The aminobenzylnaphthols could be easily resolved into their enantiomers and can act as excellent coordinating ligands. Recently, a large library of aminonapthylphenols obtained by the Betti reaction and their applications have been reviewed categorically by Naso and co-workers under the title of ‘‘The Betti base: the awakening of a sleeping beauty’’ [3]. In this review it is appropriately mentioned that, ‘‘in spite of the number of structures reported, that are important from the stereochemical point of view, and of the work performed so far, the synthetic potential of the Betti base family has been uncovered only to a small extent’’.

Hence, to discover the potential of Betti base, we have synthesized Cu(II) complexes with optically active and racemic bettibases[4](Scheme 1). These complexes were screened for their catalytic activity for asymmetric epoxidation of styrene using TBHP as an oxidant. In the present presentation we report some our findings. Epoxidation reaction using ***Cu(II) complexes with racemic mixture of Bettibase as catalyst in acetonitrile yields 27% of styrene epoxide with 28%ee, R-styrene oxide being in excess.*** The overall conversion of styrene is 96 %, with 62% of benzaldehyde. The Cu(II) complexes with optically pure Bettibase are found to be less enantioselective(6-14 % ee) but yield better quantities of styrene oxide (70%). Electrochemical studies were carried out to understand the reaction mechanism (Scheme 2).



Scheme 1



Scheme 2

[1] *Comprehensive Asymmetric Catalysis I-III (Incl. Supplement 1+2)* (Eds.: E.N. Jacobsen, A. Pfaltz, H. Yamamoto) **2004**, Springer, Heidelberg.
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P261

GAS PHASE STUDIES OF THE COMPLEXATION OF NICKEL(II) IONS BY PHENYLPYRIDINES

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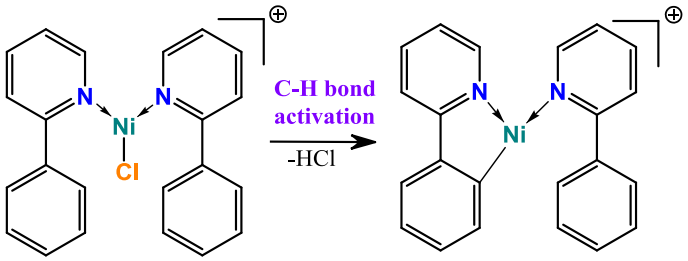
Despite the considerable progress in organometallic chemistry, there are major gaps in our understanding of mechanistic details, especially in comparison with classical organic chemistry. Complexes of late transition metals with organic molecules are a particularly attractive field of study as they are encountered in different kinds of metal-mediated transformations[1].
ESI-MS, ion mobility and CID experiments were performed for ions generated from dilute solutions of 2-, 3- and 4-phenyl pyridines with $NiCl_2$ in methanol.
Electrospray ionization mass spectra show the generation of Ni(II) complexes with phenyl pyridines (both singly and doubly charged). Of the regioisomeric phenylpyridines, 2-phenyl pyridine behaves in a drastically different way, compared to 3- and 4-phenyl pyridines.
Furthering this observation, ion mobility studies of the complex at *m/z* 403 ($[NiCl(phpy)_2]^+$) were performed, in combination with calculations using density functional theory methods. CID measurements show the occurrence of C-H bond activation, which is most pronounced in the case of 2-phenyl pyridine.



403 *m/z* 367 *m/z*

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P262

SYNTHESIS OF POROUS MAGNETIC CARBONIC MATERIAL FROM MODIFIED WOOD SAWDUST

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Synthesis of porous composites with magnetic properties from renewable natural resources and its processing waste is of great importance for solution of some problems in ecology (oil-spill recovery, water purification and etc.), biomedicine, electronics, metallurgy and catalysis. In this paper the study of magnetic porous materials preparation from modified sawdust is presented and possible using of them for noble metals extraction and catalysis.

Wood sawdust was used as a starting material in order to synthesize the porous magnetic materials. The sawdust was impregnated with different reagents ($FeCl_3$, $ZnCl_2$, KOH, H_3PO_4) and their mixtures. Obtained composites were shaped in pills and then undergone a thermal treatment at 200-800°C. Some of theirs were washed with water. The sample modified with chlorides of iron and zinc was found to be the best obtained mixture for porous magnetic material synthesis.

It was established that the maximum surface area (1350 m^2/g) of charcoal obtained from this starting mixture was observed during carbonization at 400°C and accompanied with exothermic process and zinc ferrite formation. Moreover, the water-washed charcoals obtained during carbonization up to 300-600°C have three orders greater specific surface area than non-washed.

An analysis of charcoals by X-ray shown that low-temperature sample (400°C) contains crystalline phase of magnetite such as $(Zn_{0,29}\ Fe_{0,71})Fe_2O_4$; high-temperature sample (800°C) contains zinc-free magnetite and maghemite.

A magnetic hysteresis was observed during the magnetic test of synthesized samples. The magnetic parameters (coercive force, saturation magnetization, residual magnetization) were calculated using the hysteresis loop. Obtained values were close to magnetic parameters of zinc ferrite.

The sorption capacity of synthesized materials during the extraction of gold, palladium and platinum from chloride solutions was found to be higher than the sorption capacity of manufactured nonmagnetic sorbent. It was detected also that the sorption capacity of charcoals depended strongly on the temperature of carbonization of the starting material. The best sorption of gold was observed at samples treated at 400°C, and platinum and palladium - at 800°C.

Thus, modified sawdust with chlorides of iron and zinc was selected as sorbent with the most successful combination of porosity and magnetic properties. Treatment temperature influences the magnetic properties of the material; zinc-containing fragments remove from the charcoal with a temperature rise, and a content of iron oxides in the product go up. It is supposed that synthesized materials can be used for recovery of noble metals by magnetic separation because of its magnetic properties and high adsorption capacity.

P263

CUPPER (II) TRIFLATE - CATALYZED C(sp) – C(sp^3) BOND FORMATION BY COUPLING REACTION OF TRIPHENYLMETHANOL AND 1-ALKYNES

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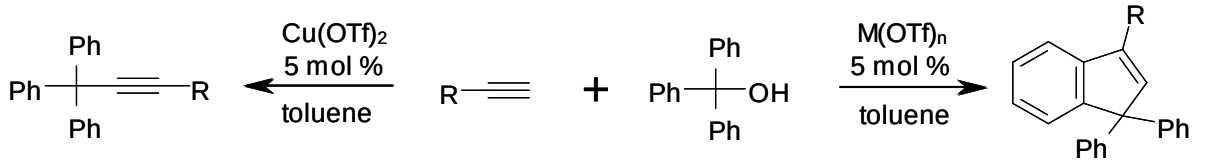
Compounds with triarylmethylethynyl unit show a range of interesting physical properties, in particular, there are descriptions of molecular gyroscopes containing outlined compounds. The molecular gyroscopes are able to maintain rotation in space by gaining energy [1]. There are ways of obtaining the above-noted compounds by using lithium- or magnesium organic compounds or by means of a metal-complex catalysis method.
We were interested in a synthesis of a compound with triarylmethylethynyl unit using the coupling reaction of an alcohol with 1-alkynes and applying the methodology is developed in the present time [2].
Before we showed that the reaction of triphenylcarbinol with 1-alkynes allowed to obtain 3-aryl-1,1-diphenylindenes using catalysts such as $Ga(OTf)_3$, $In(OTf)_3$, and $Sc(OTf)_3$. In this case, the yield was up to 80% [3].



yield up to 95 %

yield up to 80 %

M = Ga, In, Sc
R = Ph, 4-Cl-C_6H_4, 4-NO_2-C_6H_4, 3-NO_2-C_6H_4, 2,4-Cl_2-C_6H_3

If only $Cu(OTf)_2$ is used as a catalyst in this reaction, 3-aryl-1,1-triphenylpropynes can be obtained with the yield up to 95%. The reaction takes place by boiling into toluene for 3 h. Using nitromethane as a solvent reduces a reaction time up to 45 minutes. Applying other compounds of cupper such as $CuCl_2$, $Cu(BF_4)_2$, $Cu(OTs)_2$ is not effectively.
The reaction product is extracted by flash chromatography using a mixture of hexane-ethyl acetate (20:1) as an eluent.

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3. Patent RU 2440963

P264

REMOVABLE DIRECTING GROUPS AS TOOLS FOR REACTIVITY AND SELECTIVITY CONTROL

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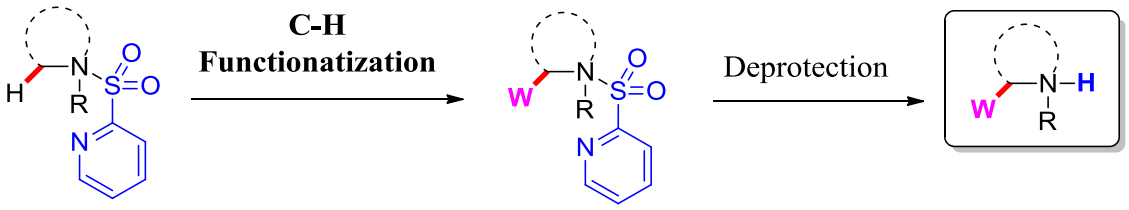
Metal-catalyzed selective C-H activation is leading to a paradigm shift in organic synthesis[1]. This new strategic approach relies on selective modification of ubiquitous C-H bonds of organic compounds instead of the standard approach of conducting transformations on pre-existing functional groups (typically a halogen or an insaturation). The major challenges associated with this chemistry are to render it catalytic in the metal complex, as well as to achieve high chemo- and regiocontrol of its insertion into C-H bonds. Most of the successful reported applications have solved this problem by using a metal-coordinating functionality that aids in the carbometallation of a proximal C-H bond.

However, in spite of the tremendous strides made, an intense search for easily attachable and removable directing groups, combining high reactivity and selectivity, continue to broaden the application of these processes in preparative organic chemistry.

In this line, our group embarked on the selective metal-catalyzed C-H functionalization of substrates bearing a coordinating 2-pyridylsulfonyl moiety as directing group[2]. This strategy has a dual effect: a) it usually enhances the reactivity and the selectivity of the process by means of pre-association of the metal catalyst to the *N*-coordinating group; b) the sulfur-based auxiliary can be readily removed, thus acting as a *temporary activating group.*

Most of the transformations have been investigated on nitrogen-containing compounds due to their importance as constituents of a myriad of natural products and biologically active molecules. In this talk, some selected advances and mechanistic discussions will be presented.



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P265

COPPER- AND PHOSPHINE-FREE CATALYTIC SYSTEMS FOR SONOGASHIRA COUPLING BASED ON PALLADIUM ACYCLIC AMINOCARBENE SPECIES

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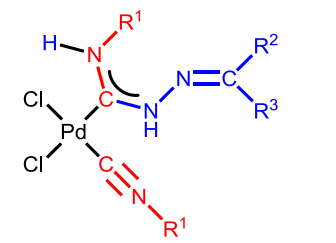
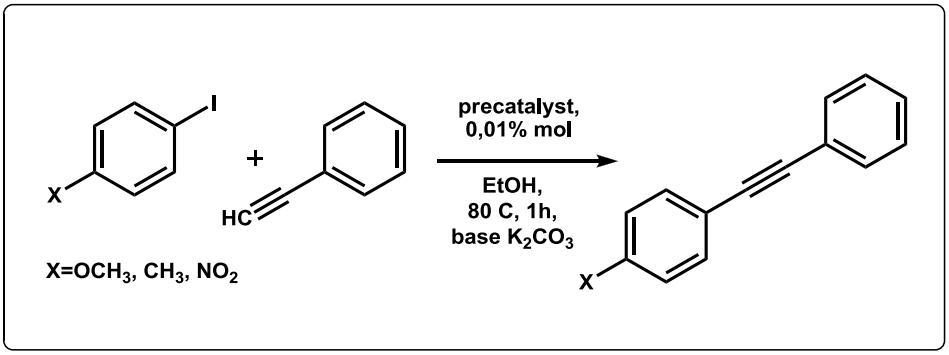
Catalytic activity of *cis*-[$PdCl_2${$C(N(H)N=CR^2_2)=N(H)R^1$}$(C{\equiv}NR^1)$] in Sonogashira reaction of aryl iodides with terminal alkynes was evaluated. Catalysts were obtained in good (80–85%) isolated yields via the metal-mediated reaction between equimolar amounts of *cis*-[$PdCl_2(C{\equiv}NR^1)_2$] and various hydrazones in $CHCl_3$ under reflux conditions for 8h [1].
Our Sonogashira protocol employs ethanol as an environmental-benign solvent and potassium carbonate as a cheap inorganic base base, and does not require the use of either phosphine or copper co-catalyst.



R^1 = Cy, *t*Bu,Xyl, 2-Cl-6-Me-C_6H_4
R^2= R^3=Ph; R^2=H, R^3=C_6H_4OH;
R^2,R^3=fluorenyl



The yields of target products were up to 98% even at the catalyst loading as low as 0.01 mol% guaranteeing the TONs of up to $3{,}7\times10^4$. The catalytic system is also able to operate at room temperature with the catalyst loading of 1 mol% and potassium phosphate as a base (yields up to 95% and TONs up to 95).

This project has been supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal (Projects PTDC/QUI-QUI/098760/2008 and PTDC/QUI-QUI/109846/2009). Authors thank Dr. M. F. C. Guedes da Silva (IST, Portugal) for the X-ray diffraction studies.

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P266

CATALYTIC PROPERTIES OF Fe-M (M = Au, Pd, Cu) NANOCOMPOSITES PRODUCED VIA THE METAL VAPOR SYNTHESIS

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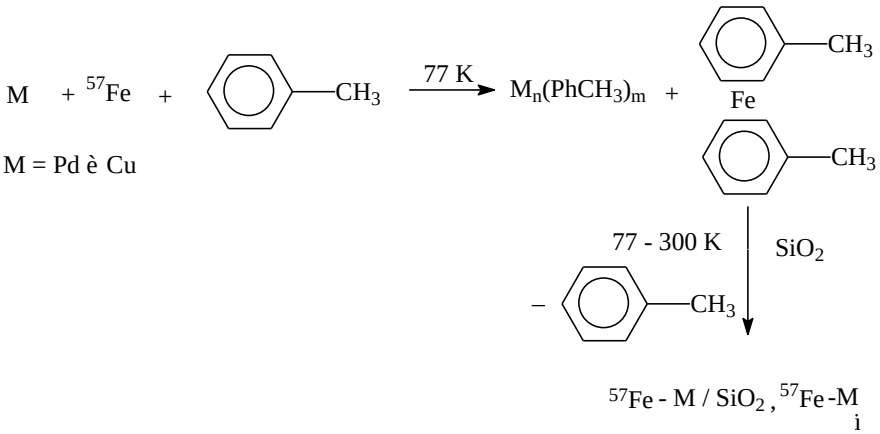
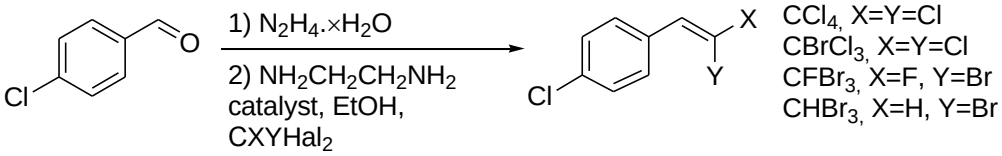
The activity of mono (Fe, Cu, Pd, Au) and bimetallic Fe-M (M = Au, Pd, Cu) nanocomposites produced via the metal vapor synthesis (MVS) has been studied in various catalytic processes: low-temperature oxidation of CO, catalytic olefination reaction, etc.
The MVS yields organosols containing either target metal nanoparticles or thermally labile complexes, which are converted into metal nanoparticles upon very mild heating. These organosols can be used for the modification of mesoporous supports or for catalytic reactions [1].



The catalytic systems have been tested for the first time in the catalytic olefination reaction (COR) based on the interaction of carbonyl-derived hydrazones with polyhaloalkanes in the presence of catalyst [2].



The Fe-M nanocomposites, both blacks and supported catalysts have been elucidated in detail with Mössbauer spectroscopy, X-ray and synchrotron techniques: XPS, XRD, and EXAFS.
This work was supported by Russian Foundation for Basic Research (grants Nos. 10-03-00897, 11-03-91169 and 11-03-00298) and Russian Academy of Sciences (DCMS Program № 6)

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P267

A NEW APPROACH TO THE SYNTHESIS OF N-ARYL-1,3,5-DITHIAZINANES AND N-ARYL-1,5,3-DITHIAZEPINANES

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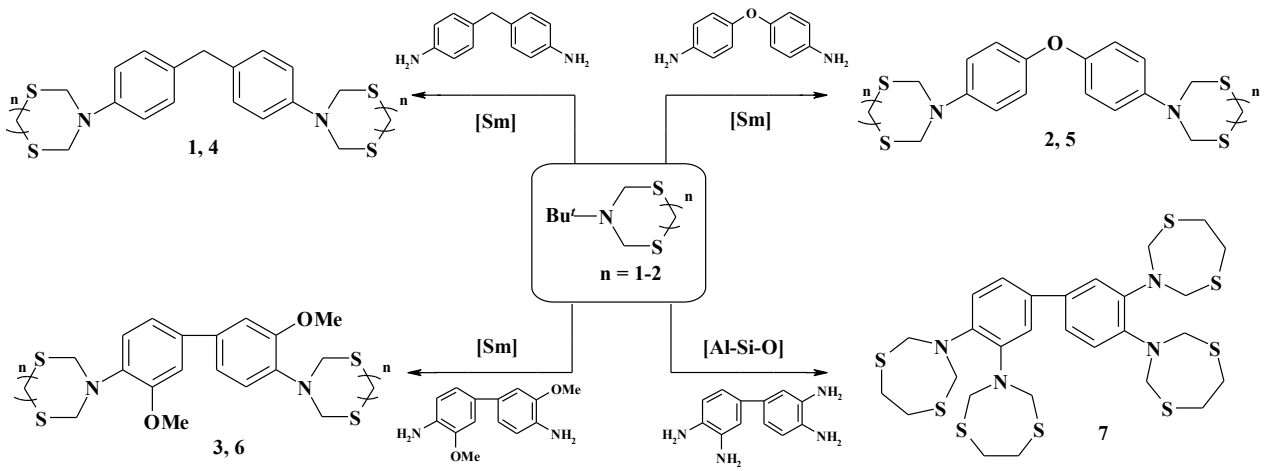
Sulfur- and nitrogen-containing heterocycles are of special interest as potential biocides and fungicides. They are also used as selective complexones and sorbents of noble metals. As recently shown,[1,2] catalytic trans-amination of *N*-methyl-1,3,5-dithiazinane with arylamines is an efficient method for synthesizing of *N*-aryl-1,3,5-dithiazinanes.

In continuation of our previous work, as well as in order to develop the novel approach to the selective synthesis of *N*-aryl-substituted *bis*-1,3,5-dithiazinanes and *bis*-1,5,3-dithiazepinanes, we have studied the catalytic reaction of aromatic diamines with *N*-*tert*-butyl-1,3,5-dithiazinane and *N*-*tert*-butyl-1,5,3-dithiazepinane.

We have established that aromatic diamines (4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenyloxide, 3,3'-dimetoxybenzidine) entered into reaction with *N*-*tert*-butyl-1,3,5-dithiazinane or *N*-*tert*-butyl-1,5,3-dithiazepinane under the action of 5 mol % $Sm(NO_3)_3 \cdot 6H_2O$ (20°C, 3h, $CHCl_3$, 1:2 molar ratio) with selective formation of the corresponding *N*-aryl-*bis*-1,3,5-dithiazinanes **1–3** and *N*-aryl-*bis*-1,5,3-dithiazepinanes **4–6** in 70–85% yield. The reaction of 3,3′-diaminobenzidine with *N*-*tert*-butyl-1,5,3-dithiazepinane (1:4 molar ratio) under the action of catalytic amounts of AlSiO leads to *N*-aryl-*tetrakis*-1,5,3-dithiazepinane **7** in 50% yield.



The structures of novel *N*-aryl-1,3,5-dithiazinanes **1–3** and *N*-aryl-1,5,3-dithiazepinanes **4–7** were proved by means of multinuclear NMR spectroscopy and MALDI TOF-MS.

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The authors thank the Russian Foundation of Basic Research for financial support (grants 11-03-00101-a, 11-03-97011-r_Povolzh′e_a).

P268

DEHYDROGENATIVE HECK REACTION OF FURANS AND THIOPHENES WITH STYRENES UNDER MILD CONDITIONS

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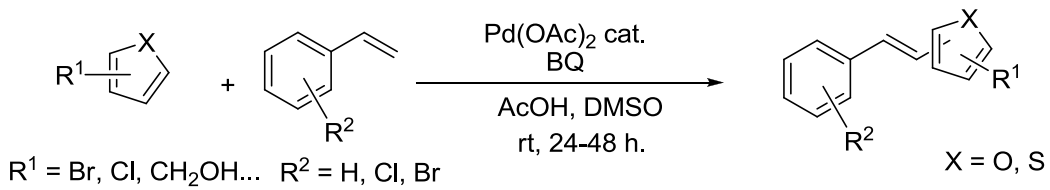
The Pd-catalyzed direct cross-couplings of arenes with alkenes through C-H activation, also called intermolecular Dehydrogenative Heck Reactions (DHRs), have drawn much attention in recent years. [1] These transformations are of interest in term of atom economy, since the result of the DHRs is the formation of a C-C bond from two C-H bonds.
The use of olefins bearing an electron withdrawing group, such as acrylates, acrylamides, acrylonitriles, and unsaturated carbonyl derivatives, is generally required to achieve fair yields. Styrenes are more electron-rich compounds and are a notoriously difficult substrate class due to facile polymerization and cleavage under palladium oxidative conditions. Among the arenes used in DHRs, furans and thiophenes have received little attention because the former are acid sensitive and the latter require elevated temperatures, due to their higher aromatic resonance energy and stability.
In 2008, we have reported the synthesis of difurylalkanes through the bis-coupling of 2-alkylfurans with various alkenes, including styrenes. [2] Then, we reported a dehydrogenative coupling of furans and styrenes leading to Heck-type products in medium to good yields and with high regio- and stereoselectivities, which allowed the use of chlorinated and fluorinated substrates. [3]
The previous transformation occured under mild conditions but nevertheless, brominated substrates were reluctant to react. Glorius et al. have recently shown that brominated compounds can be formed with no proto-debromination using Rh catalysts; however few examples have been reported and the scope of substrates remains to be developed. [4] A recent example has been reported by Zhang et al. using palladium catalysts, but the method requires the presence of a removable pyridylsulfinyl group on the arenes. [5] We will present the DHRs, under mild conditions, of furans and thiophenes with styrenes, including brominated substrates. [6] The influence and the role of the oxidizing agent on the activity of the catalyst will be also discussed.



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P269

CATALYTIC HYDROGENATION OF ALICYCLIC UNSATURATED COMPOUNDS OF VARIOUS FUNCTIONALITY

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The pattern of hydrogenation reaction of unsaturated alicyclic compounds of various functionality with liquid phase hydrogen, using fine-dispersed palladium catalyst applied on amorphous carbon (1 % Pd/C), has been studied.

Thin composite layers of amorphous carbon-palladium ensure nano-dimension of metal particles (20-900 nm) and, therefore high activity of the said catalyst. With this catalyst, the process of hydrogenation is carried out in the perfect-mixing reactor in mild conditions, i.e. at atmospheric pressure and 40 – 80 °C temperature.

In hydrogenation of cycloolefines possessing two double bonds in a molecule, the catalyst selectivity was noticed. The analysis of the results of hydrogenation of 1,5-cyclooctadiene and dicyclopentadiene (tricylo-[5.2.1.$0^{2..6.}$]decadiene-3.8) shows the target products of the reaction are cyclooctene and dicyclopenten (tricyclo[5.2.1.$0^{2.6}$]decen-3).

1 % Pd/C is successfully applied for hydrogenation of unsaturated alicyclic compounds with oxygen-containing groups in molecule. For strained eight membered rings, the reactivity of the compound being hydrogenated decreases in the following way**:** 5,6-epoxy-cis-cyclooctene > 5-cyclooctene- 1,2-diol > 4- cyclooctene-1-one > cyclooctene

The presence of oxygen-containing group in the structure of the compound being hydrogenated facilitates saturation of the double bond. It boosts the ability of the molecule to adsorb on the catalyst surface.

Unsaturated epoxide and ketone are known to change into alcohol in the process of heterogeneous catalyst hydrogenation, as both are bifunctional compounds. It is worth mentioning that only double bond of molecule is hydrogenated selectively when applying 1 % Pd/C. Effective energy of activation of the reaction of C_8 unsaturated compounds hydrogenation using 1 % Pd/C is 39,6 ± 1,6 kJ/mole.

The orders of reaction for individual reagents have been determined. The reaction has zero order for unsaturated compound and first order for catalyst, independently of the structure of the compound being hydrogenated. The data obtained show that the mechanism of the process of unsaturated alicyclic compounds hydrogenation is determined by the nature of the catalyst used.

Saturation of double bond of 5,6-epoxy-cis-cyclooctene with hydrogen over 1 % Pd/C is noticed to be accompanied by practically quantitative yield of saturated epoxide.

The detailed analysis of the products of 5,6-epoxy-cis-cyclooctene hydrogenation into epoxicyclooctene (IR-, 1H NMR spectroscopy) has shown formation of an intermediate compound which is a structural isomer of the original unsaturated epoxide (cis-trans-isomerization).

Applicability 1 % Pd/C for hydrogenation of double bonds of unsaturated alicyclic compounds having oxygen-containing groups and containing 12 atoms of carbon in a ring (C_{12}) has been demonstrated.

The reactivity of these compounds is characterized by less value than the strained C_8 rings. Saturation of double bonds of 9,10-epoxi-1,5 cis, trans-cyclododecadiene demands increasing of reaction temperature from 333 K to 373 K.

Besides the raise of the temperature, saturation of double bonds of unsaturated ketone C_{12} (4,8-cyclododecadiene -1-one) also needs in replacement of hydrocarbon solvent with 1-propanol. Hydrogenation of unsaturated diol C12 (5,9 – cyclododecadiene-1,2 diol) runs efficiently at increased pressure of hydrogen.

NANO-PALLADIUM ON AMINO-FUNCTIONALIZED MESOCELLULAR FOAM: AN EFFICIENT CATALYST FOR SUZUKI REACTIONS AND TRANSFER HYDROGENATIONS

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Nanoparticles have recently attracted an increasing amount of interest because of their unique properties and numerous applications in a variety of fields.[1] In chemistry, heterogenous catalysts based on transition metal nanoparticles have shown to be efficient and selective for a wide range of organic transformations under mild conditions. Particularly in the large-scale synthesis of pharmaceuticals, highly stabilized nanoparticle catalysts can provide solutions to many practical problems.

Recently, we have developed a novel heterogenous catalyst based on Pd nanoparticles immobilized on amino-functionalized siliceous mesocellular foam (Pd(0)-AmP-MCF) (Fig 1).[2] Herein, we report on its use in Suzuki cross-coupling reactions and in transfer hydrogenations of alkenes using microwave irradiation.

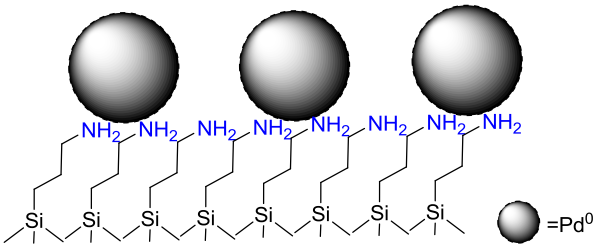

Figure 1: Schematic representation of the Pd(0)-AmP-MCF.

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P271

TOWARDS THE SYNTHESIS OF 1-AZA-ANALOGUES OF PODOPHYLLOTOXIN

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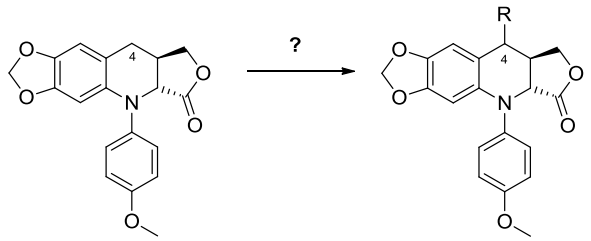
Podophyllotoxin is a naturally occurring toxin belonging to the family of the cyclolignans. It is well known for its antineoplastic and antiviral properties.[1] These interesting features have stimulated research over the past decades towards the synthesis of analogues with the goal to develop new products with better clinical profiles such as less side-effects.[2] Three closely related products were already developed and are currently in clinical use, namely etoposide, teniposide and etopophos. Their clinical use is still associated with toxic side effects such as hair loss, constipation and nausea. The development of more potent analogues still is and remains a valuable research goal.

In this context, the 1-aza-analogues are proposed. These analogues differ from the parent compound by introduction of a nitrogen atom at the 1-position. The 4-deoxy-podophyllotoxin aza analogue was synthesized before in our lab (**1**). The problem we faced was the functionalization of the 4-position.(**2**) Because direct functionalization did not work, we tried 4 different synthetic routes to introduce this functionality in an earlier stage of the synthesis making use of an asymmetric Mannich reaction and an asymmetric Michaël addition.



1 **2**

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P272

SYNTHETIC, STRUCTURAL AND REACTIVITY INVESTIGATIONS OF ALUMINIUM BISTRIFLATE COMPLEXES

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A diverse range of compounds containing triflate (OTf) ligands, such as LiOTf[1], $Zn(OTf)_2$[2] and $Sc(OTf)_3$[3], have been employed as successful Lewis acid catalysts or stoichiometric reagents in various organic transformations. However, the use of classical organic-based ligands with these triflate-containing complexes has been scarce and predominantly investigated *in situ*[4] providing a very limited amount of structural information on the active species. The importance of structural features of these triflate-containing Lewis acids could be of immense importance when attempting to improve their activities. Therefore, we set our goal on investigating the synthesis, structural features and reactivity properties of various ligand-supported aluminium bistriflate complexes with a general formula $LAl(OTf)_2$ (L = terphenyls, amidinates, β-diketiminates etc.).
The preparation of the targeted aluminium bistriflate complexes is best achieved by first synthesizing the cooresponding dihalopresoursors $LAlCl_2$ followed by the chloride-for-triflate ligand exchange using AgOTf.[5] Structural investigations of several target compounds $LAl(OTf)_2$ demonstrated the ligand importance in designing these complexes.
Lastly, we investigated potential catalytic activities of the target aluminium bistriflate complexes as alternatives for more expensive Au-based Lewis acids in several organic transformations.

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P273

REACTIONS OF BRIDGED TETRAOXANES

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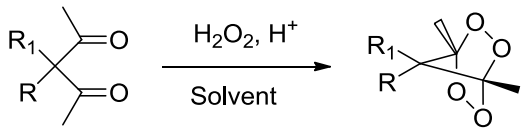
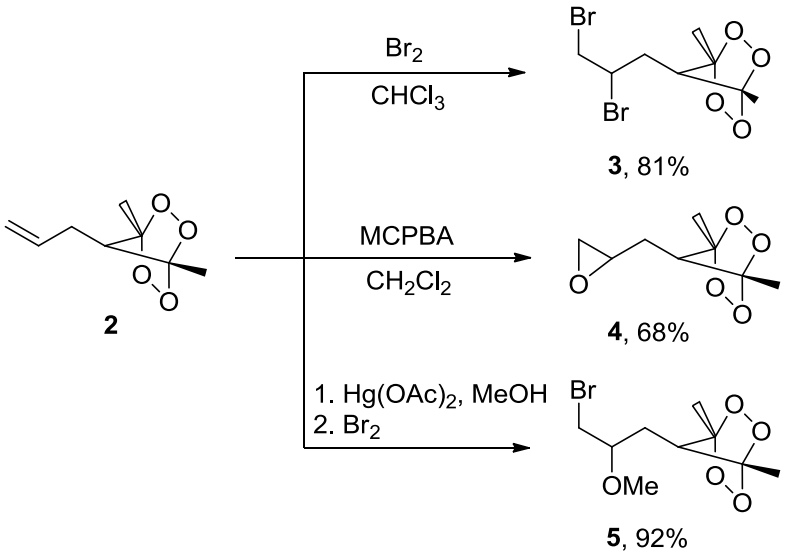
In recent years, it was found that organic peroxides are promising compounds for use as drugs and the study of their properties is an urgent task, and 1,2,4,5-tetraoxanes - one of the most promising classes of organic peroxides, which shows the different types of biological activity. Previously, we developed a method of synthesis of bridged 1,2,4,5-tetraoxanes based on reaction β-dicarbonyl compounds **1** with hydrogen peroxide (Scheme 1) [1].



1 **2**

Scheme 1. Synthesis of 1,2,4,5-tetraoxanes **2** from β-diketones **1** and hydrogen peroxide.

With the aim of evaluating the stability of the peroxide bonds in tetraoxanes to reagents widely used in organic synthesis and determining the structures, which are of interest for biological activity assays, we performed the following reactions involving the functional groups in the bridging fragment of tetraoxanes **2**: halogenation, oxidation, alkoxymercuration, hydrolysis, and amidation. In all of these reactions, the tetraoxane ring remained intact (Scheme 2). In these reactions, the tetraoxane ring is quite stable and thus the starting structures can be easily modified in such a way that the peroxide fragment remains intact. Tetraoxanes are not decomposed by bromine, MCPBA, $Hg(OAc)_2$, amines, or KOH.



Scheme 2. Reaction with retaining of peroxide fragment.

This work is supported by the Grant of the Russian Foundation for Basic Research (Grant 11-03-00857-a), and the Ministry of education and science of the Russian Federation (Grant 11.519.11.2038).

P274

STEREOSELECTIVE AMINE-CATALYZED CARBOLIGATION

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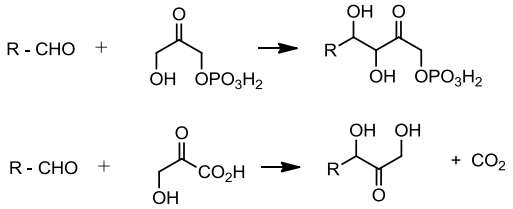
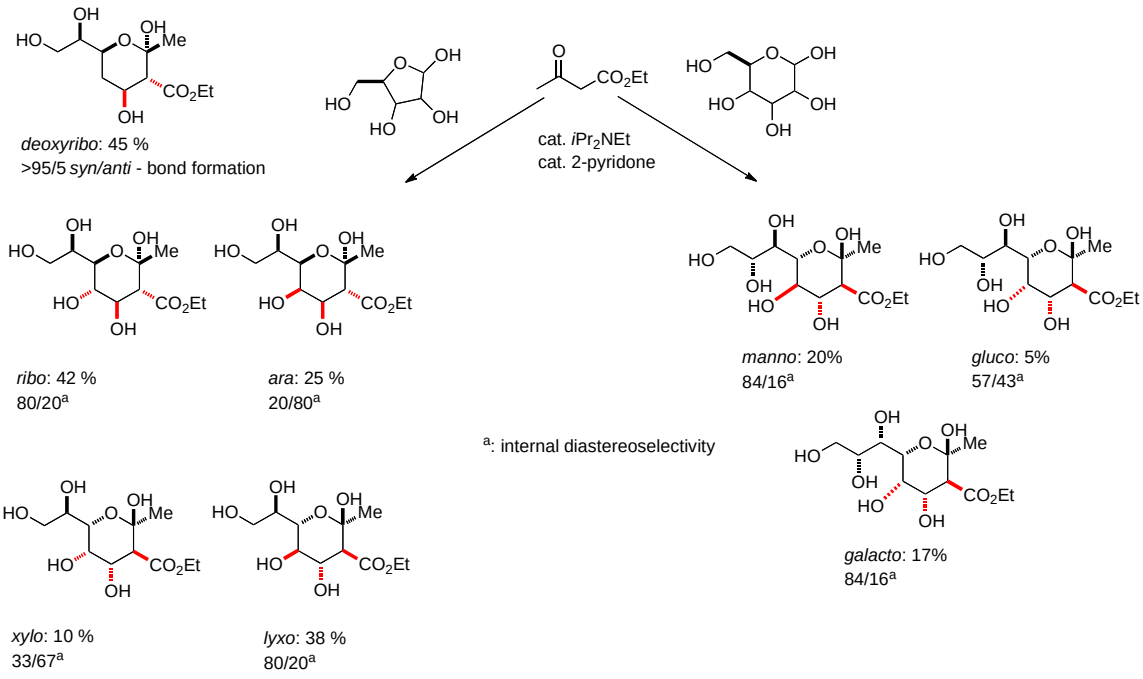
Chain elongated carbohydrates – higher carbon sugars – are important compounds with biologically fundamental properties. Nature realizes these important transformations, apparently effortless, through a deployment of distinctly working aldolases and ketolases with extremely high degrees of stereoselectivity. However this high specificity is limited to a small number of substrates. Also, not all possible stereoisomers can be accessed by enzymatic transformations.



We have developed an organocatalyzed aldol addition of unprotected carbohydrates to 1.3-dicarbonyl compounds without using the classical tedious protecting and deprotecting procedure. In addition condensation reaction and subsequently rearrangements are avoided following this protocol.



These investigations show great advantages in terms of time and atom economy. Also, this operationally simple transformation mimics aldolase-catalyzed transformations, which were identified in many biochemical processes. Further optimization and enlargement of this methodology to more general C-C bond formation processes of unprotected carbohydrates are under way.

Benjamin Voigt , Ulf Scheffler and Rainer Mahrwald , ***Chem. Commun.***, 2012,**48**, 5304-5306

P275

THE PROMOTING EFFECT OF IRON OXIDES ON THE SYNTHESIS OF DIARYL ETHERS

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Diaryl ethers synthesis is usually performed in a heterophase conditions (reagents, which dissolved in aprotic bipolar solvent and the insoluble deprotonated agent), therefore, its modification by addition of promoting additives, which is conducive to further formation of effective nanoreactors, is quite actual. The data about influence of iron complexes in the solid-phase nucleophilic substitution reactions has been presented in literature [1-2]. It can be assumed, that iron inorganic compounds, including those in the solid phase, may have promoting effect. Meanwhile, the probable structural centers (including surface defects) have activating effects.

As a model for the study of aromatic nucleophilic substitution of the traditional substrate with *O*-nucleophiles were chosen as the reaction of 4-nitroclorinebenzene with phenolate, formed *in situ* by the interaction of phenol with potassium carbonate. As the promoting solid-state additive was used hematite (Fe_2O_3). Genesis of solid samples is acquired the important meaning, because passing of the process is determined in important degree by the localization of reaction zone on the surface of separation phases of products and reactants. Genesis determines the topology of surface and localization of the active center. We conduct some experiences with using different samples of hematite. And this experiences showed, those additives of the specified solid-state component accelerates the process. The greatest influence on the studied process provides iron(III) oxide, obtained from ferrous sulfate and past supplementary mechanical processing.

Table 1

Characteristics and genesis of the specimens Fe_2O_3.

Genesis	Fe_2O_3 prepared from $FeSO_4$	Fe_2O_3 prepared from $Fe(OH)_2$	Fe_2O_3 prepared from Mohr's Salt	Fe_2O_3 prepared from $FeCO_3$
Characteristics	S = 4,5 м^2/g	S = 20,3 м^2/g	S = 10,5 м^2/g	S = 7,8 м^2/g

Similar results were obtained for the interaction of 4-nitrochlorobenzene with 4-nitrochlorobenzene, 4-nitrophenolate, and p-cresol. It has been detected, that reaction with stated *O*-nucleophiles proceeds much more intense, than interaction with using phenol, both using of additives Fe_2O_3 and without them. The presence of substituents slightly reduces the effect of hematite samples adding in the reaction system, but the general trend of hematite adding influence remains during promoting action.

A preliminary interpretation of this effect could be next. Iron oxide performs supporting role. It comes as a promoter action of potassium carbonate. This effect may be to ionizing effects on the crystal lattice of potassium carbonate in places of contact phases or by antidiffusion potassium and iron ions in the surface layers of the lattice of hematite and potassium carbonate, respectively. Presumably, that this effect leads to a weakening of ties of K-O and Fe-O in the crystalline phases, which does not reducible to date in the literature data on similar systems.

The effect of the fine crystal structure of hematite on the course of research reaction has been investigated. It appears from the analysis, that the efficiency of the promoting additives is determined in a large extent by amount of basic centers on the surface. It shows that interaction of iron oxide with phenol in the course of reaction is possible.

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P276

PREPARATION AND CATALYTIC HYDROGENATION OF 3-PYRROLINE-2-ONES

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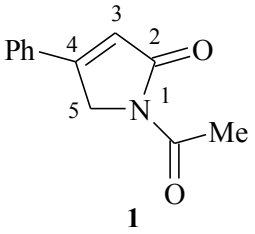
During past decade there was observed increased interest in the SAR investigations aimed at the search of new nootropic pharmaceuticals for the treatment of CNS disorders, which include: cognition/memory, epilepsy and seizures, neurodegenerative deseases, stroke/ischaemia and stress/anxiety. The key role in their treatment belong to so called racetams sharing pyrrolidin-2-one pharmacophore. Its structural derivatization had led to the creation and implementation in medicine several cognition enhancing drugs. However the discovery of new effective pharmaceuticals improving neurotransmission in human brain and as result mental and cognitive abilities remains actual even nowadays.

Our previous investigations in this field of medicinal chemistry included the preparation of 4*R*- and 4*S*-stereo isomers of (4-phenyl-2-oxopyrrolidin-1-yl)-acetamide (phenotropil) and their comparable pharmaceutical investigation. During their following continuation we have synthesized 3-pyrroline-2-ones **1**-**4** variously substituted in N1, C4 and C5 positions for the purpose of their following converstion into biologically active derivatives by the hydrogenation of C3-C4 double bond.



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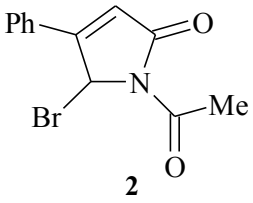

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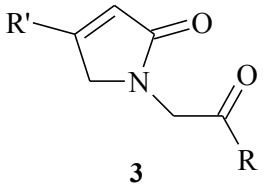

3

R=OEt, NH_2 R'=Ph, OEt, OMe

Hydrogenation of 3-pyrroline-2-ones **1**-**4** was carried out in the presence of following catalysts: Raney Ni, Pd/C, $Pd(OH)_2$, $Pd(OAc)_2$, PtO_2, RuO_2 and $RhCl(PPh_3)_3$ in the range of 5÷10 atm presssure ar 40^{o}C in ethanol. In general mentioned conditions were favourable for the saturation of double bond and the formation of pyrrolidin-2-one derivatives. In addition in the presence of Raney Ni and Pd/C catalysts there was observed the splitting of N-acetyl group in compound **1**. In the case of pyrrolidin-2-one **2** paralel to the reduction of double bond and the splitting of N-acetyl group there was observed the substitution of bromine by hydrogen.

P277

SUPRAMOLECULAR COMPLEXES OF NEW N_4-DONOR LIGAND CONTAINING AN ANTHRACENE MOIETY WITH POTENTIAL APPLICATIONS AS CATALYSTS

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Investigation on metal organic complexes represents one of the most active areas of material science and chemical research. Supramolecular complexes exhibit interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, host-guest chemistry, ion exchange, nonlinear optics, etc. They also can have catalytic properties in many chemical reactions [1]. For example dinuclear Pd(II) complex with quaterpyridine ligand has application in asymmetric allylic substitution reactions [2]. Complexes of Co(II) and Ni(II) with N_6-donor ligand containing quaterpyridine moiety are effective catalysts for ethylene oligomerisation reaction [3].
Quaterpyridine ligands are known to formation many types of supramolecular architectures such as mononuclear complexes, dinuclear helicates [4] and polynuclear architectures [5]. The ligand **L** (figure 1) have been obtained in a multistep synthesis via Pd(0)-catalysed Suzuki-Miyaura and Stille-type coupling reaction. Supramolecular complexes have been obtained by self-assembly of **L** and different transition metal ions. Catalytic properties of obtained compounds in different reactions have investigated.

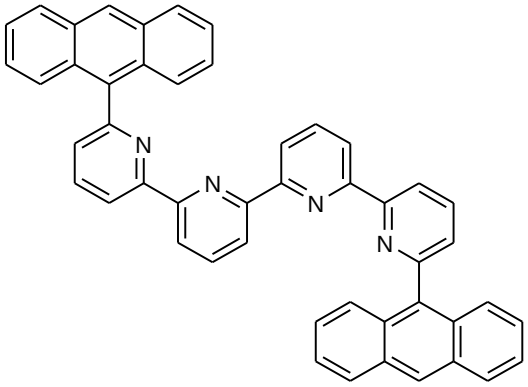

Figure 1 The ligand **L**

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Acknowledgments:

Project supported by: grant IP2011 058871 from the Polish Ministry of Higher Education and Science

P278

METALATIVE COUPLING / SUZUKI COUPLING – SEQUENTIAL REACTION IN THE SYNTHESIS OF π–CONJUGATED UNSATURATED ORGANIC MOLECULAR AND MACROMOLECULAR COMPOUNDS

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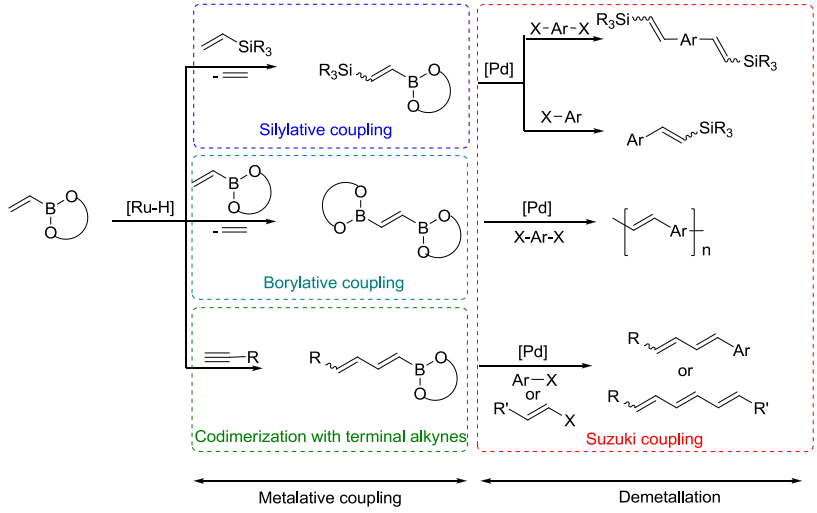
Main group substituted olefins constitute an indispensable tool in modern organic synthesis. The diversity of the reaction, which allows the substitution of i.e. silyl, boryl or stannyl moieties with broad range of functional groups cause a continuous increase in application of such unsaturated compounds [1]. These organometallic reagents have found application in palladium catalyzed C-C bond formation reactions (Suzuki, Hiyama, Sonogashira), which play an important role in the synthesis of complex organic molecules, natural compounds analogous or pharmaceuticals [2].
In the communication we present our recent results on the synthetic application of vinylboranes in organometallic and organic synthesis. The application of transition metal catalyzed processes discovered in our group [3]: silylative and borylative coupling [4] as well as codimerization of vinylboronates [5] with terminal alkynes in combination with demetalative reactions (Suzuki coupling) provide highly π-conjugated organic molecular and macromolecular compounds. The appropriate choice of the process conditions allowed for regio- and stereoselective formation of desired products. The increased emphasis on economy in organic reactions (reduction of the time-consuming and expensive product isolation steps, the amount of used solvents etc) imposes on chemist to run reactions in tandem or longer sequences. The processes presented in the communication can be successfully applied in sequential, one pot formation of desired conjugated products via metalative/demetalative coupling without necessity of isolation of intermediates.



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Acknowledgement: This work was supported by the Ministry of Science and Higher Education of Poland (Grant NN 204265538).

P279

MODULAR SYNTHESIS OF pH-SENSITIVE HELICAL DYES

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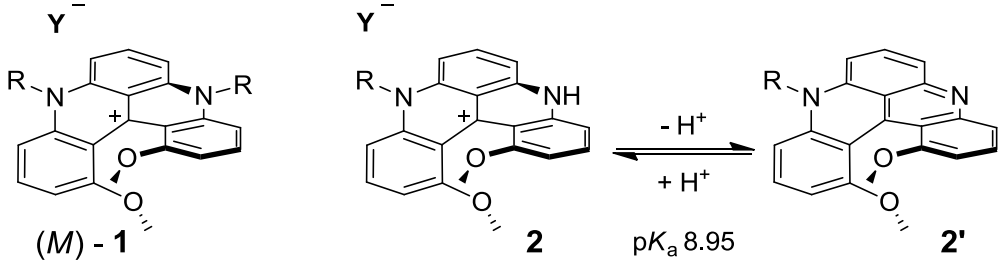
Helicenes are *ortho*-condensed polyaromatic compounds which are chiral due to the helical conformation of their backbone.[1] Whereas hundreds of neutral helicenes can be found in the literature, only few cationic derivatives have been reported.[2] Previously, we have shown that cationic diaza[4]helicenes of type **1** can be readily prepared and resolved; these moieties displaying high barriers of racemization ($\Delta G^{\ddagger}$ 172.8 kJmol^{-1} at 200 °C).[3,4]



Herein, we report the chemical (pH-sensitive, pK_a 8.95) and physical properties of novel quinacridine-based [4]helicenes **2**. We also report the extension of this chemistry to neutral dioxa-aza, diaza-oxa and triazatriangulenes.[3] Applications of such derivatives in synthetic chemistry will also be presented.

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P280

EXPLOITING CATALYSIS TO GENERATE SPIROCYCLIC ALKALOIDS

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Spirocyclic alkaloids are prevalent in nature and several, such as those isolated from marine invertebrates, inhibit cell division and show anti-tumor activity. A number of different spirocyclic systems are represented including the spiropyrrolidine skeleton found in the ascidian-derived cylindricine A and the spiropiperidine framework found in cylindricine B (Figure 1). The tricyclic marine alkaloids (fasicularin, lepadiformine and the cylindricines) isolated from sea squirts (ascidians) all possess a common ring system incorporating a spiropyrrolidine skeleton (Figure 1). Fasicularin possesses substantial cytotoxicity (IC_{50} ~ 14 μg/ml) against Vero cells.

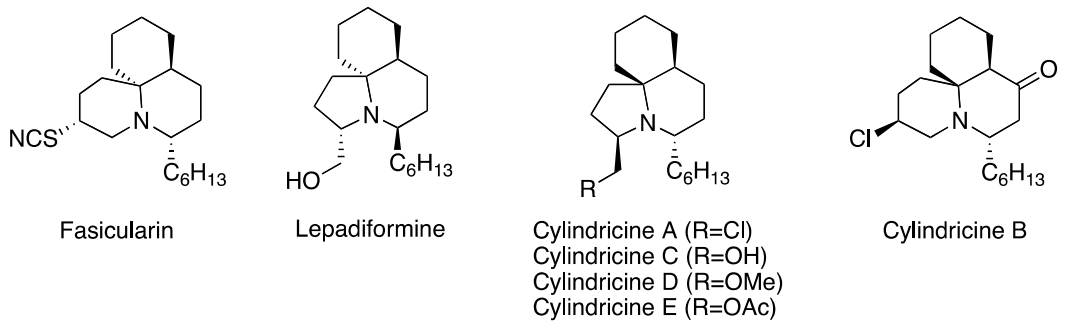

Fig. 1 Marine tricyclic alkaloids

In this paper we will describe a general, two-step method for the synthesis of enantiomerically pure, spirocyclic pyrrolidines and piperidines (Figure 2). Cross metathesis of methylene cycloalkanes with protected allylglycines gave intermediates which on treatment with triflic acid gave the spirocyclic pyrrolidines. Ring expansion methodology was then used to access spirocyclic piperidine analogues. Analogous chemistry employing α-substituted methylene cycloalkanes, required for the construction of the final ring and native perhydroquinoline ring system, was surprisingly unsuccessful. Relay metathesis to generate the required cross product was similarly unfruitful and a new strategy to facilitate this reaction needed to be adopted and was later found to be generically useful for the cross metathesis of difficult coupling partners. This work will presented in this paper.

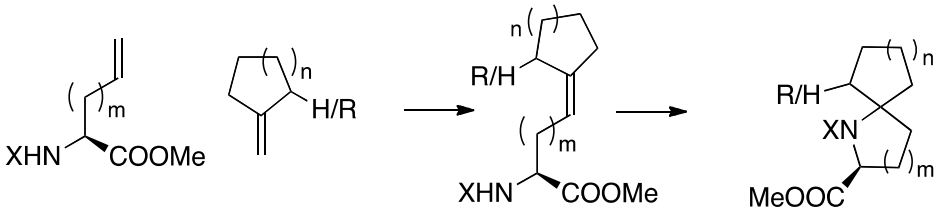

Fig. 2: Spirocycle synthesis *via* cross metathesis and acid promoted cyclisation

P281

CATALYTIC ASYMMETRIC FISCHER INDOLIZATION

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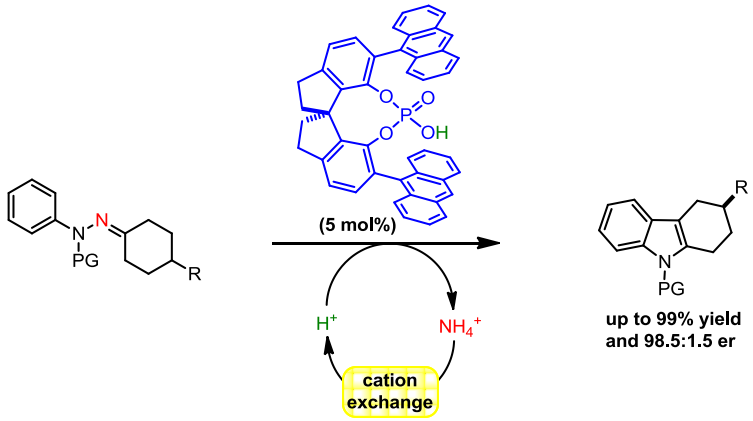
Since its discovery almost 130 years ago, the Fischer indolization of phenyl hydrazones has been extensively studied and has consistently proved to be among the most widely used methods for the synthesis of indoles.[1] Despite this interest, no catalytic asymmetric variant had been reported to date. Here we report the first such example, giving access to 3-substituted tetrahydrocarbazoles in high yields and enantioselectivities. Crucial to the method is the removal of the catalyst-poisoning ammonia by-product by an ion exchange resin.[2]



Subsequent studies have shown the method to be applicable to the modular, enantioselective synthesis of polyaromatic indoles exhibiting helical chirality. It has also been expanded to facilitate the synthesis of a panel of functionally diverse indolines in an enantioselective manner.

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P282

APPLICATION OF COBALT-CATALYZED [2+2+2] CYCLOADDITION REACTIONS

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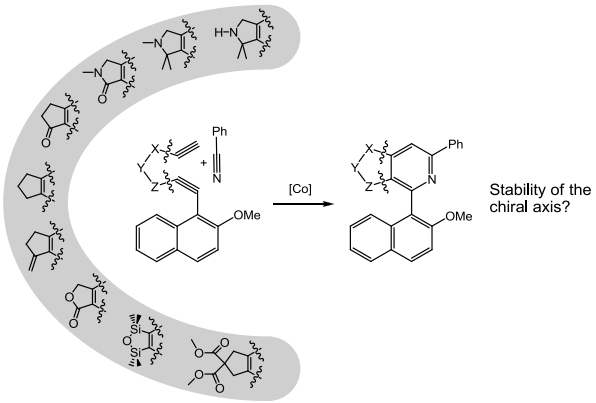
The transition metal-catalysed [2+2+2] cycloaddition reaction is a very useful and valuable member of the synthetic chemists toolbox for the construction of complex organic structures.[1] Access to a significant increase of molecular complexity is granted by the concurrent or successive formation of several bonds leading to the cyclic products. This opportunity has been seized recently, e.g. in several elegant natural product syntheses.
Cobalt complexes belong to the first generation of catalyst systems for cyclotrimerisation reactions, which have been evaluated in complex synthetic endeavours. Photochemical energy input allows the use of mild reaction conditions and sensitive chiral substrates as well as the direct conversion of gaseous coupling partners like acetylene.[2] Here, the application of chiral Co-catalysts for the successful selective preparation of atropisomeric biaryls starting from nitriles and diynes will be discussed. The investigation details the structural requirements of the coupling partners as well as the chiral biaryl products.[3,4] Interestingly, the formed biaryl products show a distinct behaviour concerning the stability of the biaryl axes with the formation of different ring sizes and their substitution pattern. Furthermore, the reaction of chiral diynes with nitriles using achiral catalysts under different conditions furnishes diastereomeric atropisomers, which turned out to be separable easily via chromatography. The features of the cycloaddition reaction as well as the follow-up chemistry will be discussed.[5]



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P283

SYNTHESIS OF 3-FLUORO-3-ARYL OXINDOLES VIA THE DIRECT ENANTIOSELECTIVE CATALYTIC ALPHA-ARYLATION OF AMIDES

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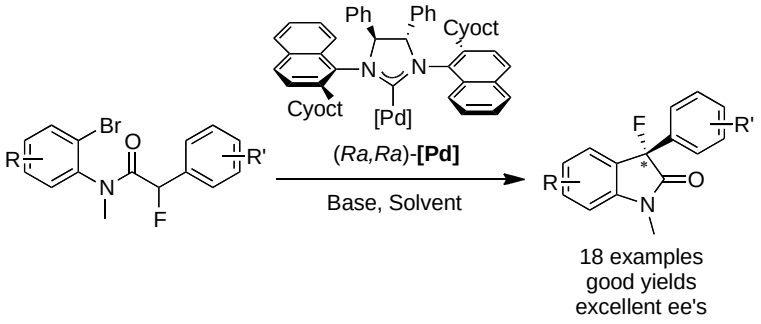

Monodentate N-heterocyclic carbene (NHC) ligands have become ubiquitous in organometallic chemistry and catalysis.[1] Conversely, development of chiral monodentate NHC ligands that induce high selectivity in asymmetric metal catalysis is still at an early stage with relatively few reports detailing enantioselectivities of 90% ee and higher. The main difficulties in designing efficient ligands of this type reside in placing stereocontrol elements at positions near the metal center without affecting the overall reactivity of the catalysts.
We have developed a new catalytic method for the enantioselective construction of carbon-fluorine bonds that relies on an asymmetric α-arylation protocol and have demonstrated its efficacy for the direct synthesis of 3-fluoro-3-aryl oxindoles. These target molecules were obtained in good yields and with excellent enantioselectivities when employing a new NHC ligand with a chiral N-heterocycle and naphthyl side chains that is easily accessed in virtually enantiopure form as a single diastereomer.[2]

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N-HETEROCYCLIC CARBENE SCANDIUM COMPLEXES MEDIATED 1-ALKENE POLYMERIZATION AND COPOLYMERIZATION WITH 1,5-HEXADIENE

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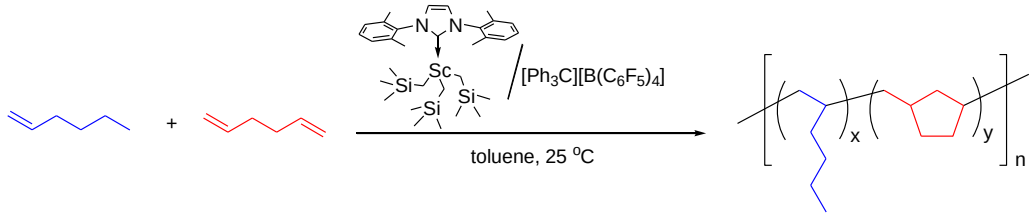
The development of single-site rare-earth metal catalysts for olefin polymerization has attracted considerable attention in recent decade.[1] Especially, scandium catalysts have been proved to be efficient in producing a variety of high performance polyolefin products, such as highly syndiospecific polymerization of styrene, copolymerization ethylene with styrene, conjugated dienes or cycloolefin.[2] However, only very limited catalyst systems concerned the efficient polymerization/copolymerization of higher α-olefins (as 1-hexene) and α,ω-diolefins (as 1,5-hexadiene). Recently, we have found novel NHC-stabilized scandium trialkyl complexes, that initiate the homopolymerization of higher α-olefins with high activity, and first random copolymerization of 1-hexene with 1,5-hexadiene when activated with 2 equiv. of $[Ph_3C][B(C_6F_5)_4]$.



1,5-hexadiene content 26.6 - 98.6 mol%

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(1) (a) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404. (b) Nishiura, M.; Hou, Z. *Nat. Chem.* **2010**, *2*, 257. (c) Zimmermann, M.; Anwander, R. *Chem. Rev.* **2010**, *110*, 6194. (d) Edelmann, F. T. *Coord. Chem. Rev.* **2011**, *255*, 1834.

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P285

PALLADIUM-CATALYZED AMINATION IN THE SYNTHESIS OF HYBRID POLYMACROCYCLIC SYSTEMS

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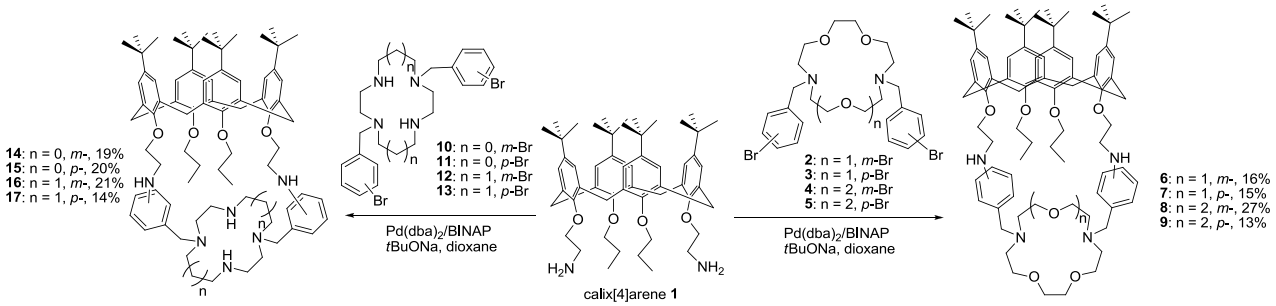
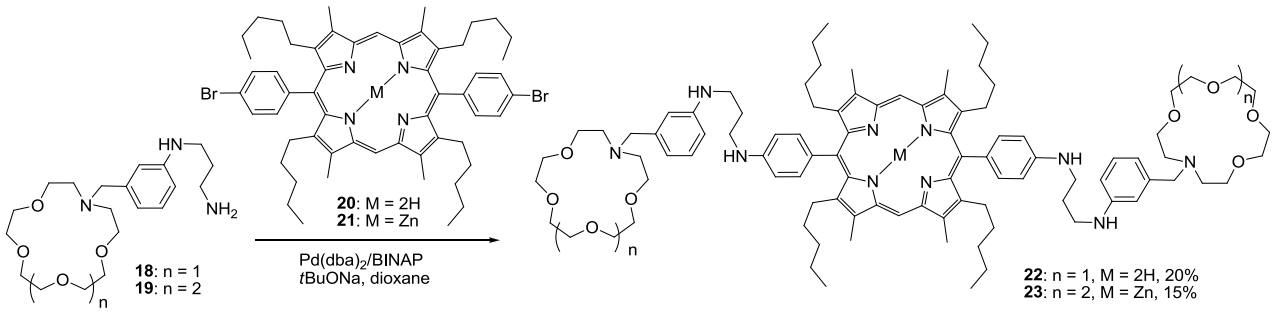
Pd-catalyzed amination was successfully applied to the synthesis of hybrid macrotricyclic systems by reacting diaminocalyx[4]arene **1** with a variety of bis(bromobenzyl) substituted diazacrown ethers **2-5**, cyclens **10, 11** and cyclams **12**, **13**. Macrotricycles **6-9** comprising diazacrown moieties were obtained in 13-27% yields whereas their analogs with tetraazamacrocycles **14-17** in 14-21% yields.



Bis(bromophenyl)substituted porphyrins are valuable substrates in the Pd-catalyzed amination as they can be modified with linear and cyclic oxadiamines. E.g., the reaction of a free-base bis(3-bromophenyl)porphyrin with excess trioxadiamine afforded bis(trioxadiamine) derivative in 30% yield, while mono(4-bromophenyl) substituted porphyrin reacted with the same diamine only in the form of its Zn complex. Azacrown ethers modified with diaminobenzyl substituent (**18** and **19**) were introduced in the Pd-catalyzed reactions with bis(4-bromophenyl)porphyrin **20** and its Zn complex **21** and produced hybrid trismacrocyclic compounds **22** and **23** comprising porphyrin and two azacrown macrocycles.



The work was supported by the RFBR grant 12-03-00796.

SILVER-CATALYZED CARBON DIOXIDE INCORPORATION REACTIONS ON ALKYNE DERIVATIVES

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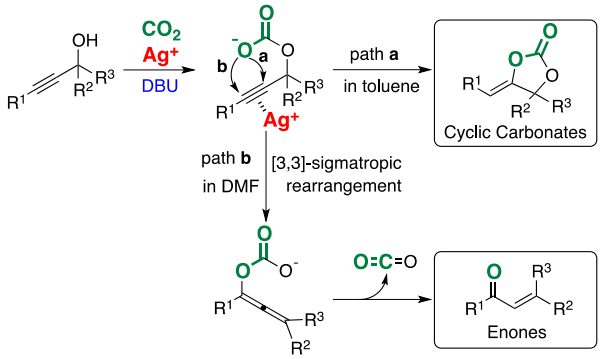
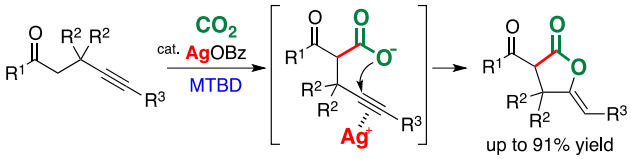
A silver/DBU system was developed for the effective catalyst to activate alkyne derivatives as π-Lewis acid. The reaction of carbon dioxide with propargylic alcohols and propargylic amines afforded the corresponding cyclic carbonate and oxazolidinone, respectively, in high yields under mild conditions (Scheme 1, path **a**)[1]. In a polar solvent, such as DMF, the [3,3]-sigmatropic Meyer-Schuster-type rearrangement of the propargylic alcohol was mediated by carbon dioxide to afford the corresponding α,β-unsaturated carbonyl compounds in high yields (Scheme 1, path **b**)[2]. The silver salt combined with the chiral Schiff base ligand could be applied to enantioselective carbon dioxide incorporation into various bispropargylic alcohols to produce the corresponding cyclic carbonate *via* desymmetrization in high yields with high enantioselectivity.[3, 4]



Based on these observations, the present catalyst system was successfully applied to ketone derivatives containing an alkyne group at an appropriate position in the presence of base. It was found that the carbonate intermediate derived from the enolate and carbon dioxide in the presence of MTBD (7-methyl-triazabicyclo[4.4.0]dec-5-ene) was cyclized on alkyne by AgOBz catalyst to afford the corresponding lactone derivative in high yield under mild conditions.



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P287

ENANTIOSELECTIVE N-ACYLATION OF LACTAMS AND THIOLACTAMS IN THE PRESENCE OF AMIDINE-BASED CATALYSTS

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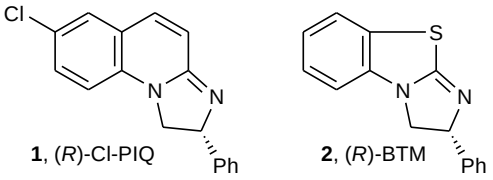
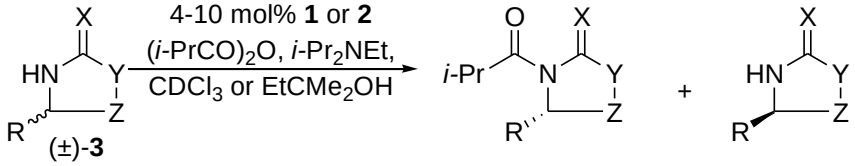
In 2006, our group disclosed the first example of enantioselective catalytic N-acylation of amides achieved using amidine-based catalysts Cl-PIQ **1** and BTM **2:** kinetic resolution of chiral 4-aryl-oxazolidinones (see structure **3**, R = aryl, X = Z = O, Y = CR^1_2). [1] Recently, we extended this methodology to several new classes of lactams and thiolactams. [2] The currently known scope of this transformation and structure-reactivity/enantioselectivity trends will be presented.





X = O, S
YZ = OCR^1_2, CH_2O, CH_2S, $CH_2NCO_2R^3$, CR^4_2
R = aryl, alkenyl, alkynyl, CO_2R^5

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P288

SELECTIVE SYNTHESIS OF CYCLIC PEROXIDES FROM TRIKETONES AND H_2O_2

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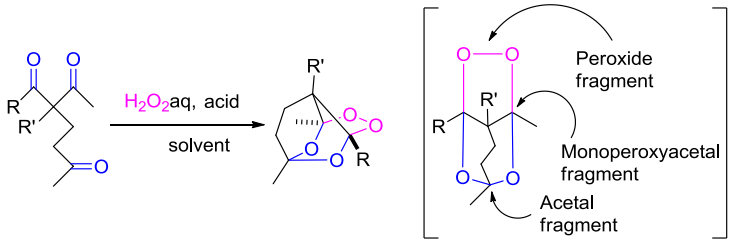
In the past decades, the chemistry of organic peroxides has attracted considerable attention from physicians and pharmacologists because these compounds were found to have antimalarial, antihelmintic, and antitumor activities. The interest in the synthesis of radical polymerization initiators and drugs gave impetus to the development of methods for the synthesis of peroxides with the use of carbonyl compounds, their derivatives, and H_2O_2 as the starting reagents.

A method for the assembly of tricyclic structures containing the peroxide, monoperoxyacetal, and acetal moieties was developed based on the acid-catalyzed reaction of β,δ-triketones with H_2O_2. The tricyclic compounds are produced in 39−90% yields and can be easily isolated from the reaction mixture. The reaction is scaled up to several grams.

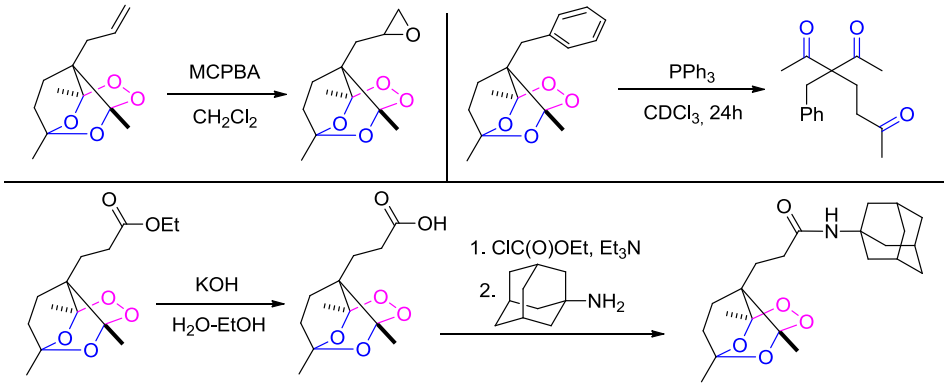
The resulting tricyclic compounds are unusual in that they contain one acetal and two monoperoxyacetal moieties, which are as a rule unstable and can undergo peroxidation in the presence of water and hydrogen peroxide under acidic conditions, and acetals are susceptible to hydrolysis (Scheme 1).

Scheme 1. Synthesis of Tricyclic Peroxides



To assess the resistance of tricyclic peroxides to reagents used in organic synthesis and to determine the structures, which are interesting to test for biological activity, we performed the halogenation, oxidation, alkaline hydrolysis, amidation, and reduction (Scheme 2).

Scheme 2. Reactions of Tricyclic Peroxides



This work is supported by the Grant of the Russian Foundation for Basic Research (Grant 11-03-00857-a), and the Ministry of education and science of the Russian Federation (Grant 11.519.11.2038).

Reference

*Alexander O. Terent'ev, Ivan A. Yaremenko, Vladimir V. Chernyshev, Valery M. Dembitsky, Gennady I. Nikishin. Selective synthesis of cyclic peroxides from triketones and H_2O_2. // J. Org. Chem. 2012, **77**, 1833-1842.*

P289

TRIS(DIBENZYLIDENEACETONE)DIPALLADIUM AS A PRECURSOR OF SOLUBLE METAL COMPLEXES AND NANOPARTICLES: POSSIBILITIES FOR HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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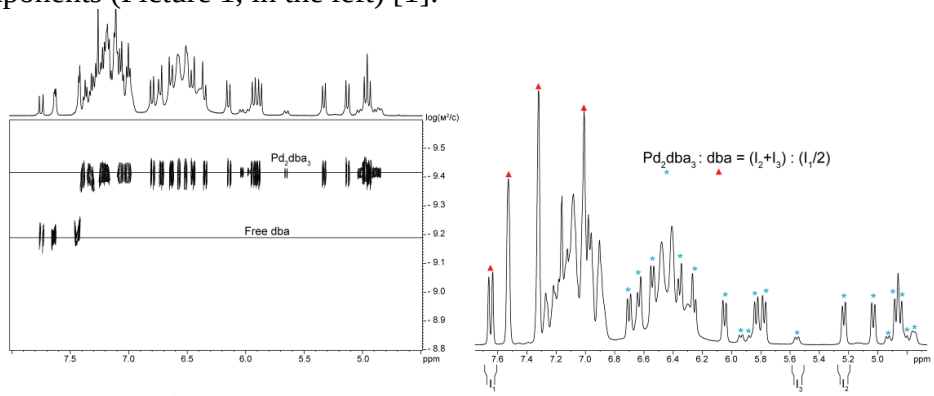
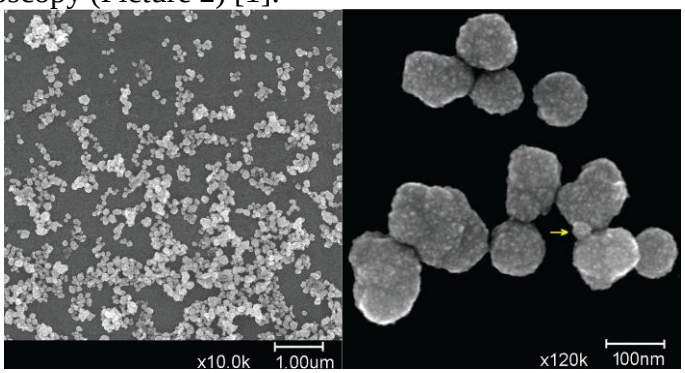
Pd_2dba_3 is a well-known and widely used precursor to generate Pd^0 active species for catalysis or more advanced palladium compounds for organometallic chemistry applications. In spite of being widely used, a little is known about the complex structure and stability. Apart from this it was reported that Pd^0 is subject to decomposition yielding Pd black. Therefore it was important to understand the nature of particles (homo- or heterogeneous) existing in Pd_2dba_3 solutions.
^{1}H DOSY NMR spectroscopy allowed us to discriminate complex ^{1}H spectrum of Pd_2dba_3 into two principal components (Picture 1, in the left) [1].



Picture 1. ^{1}H DOSY NMR and simple 1D proton NMR for Pd_2dba_3

Subsequent analysis of COSY and COSY-LR data mapped major ^{1}H resonances to twelve individual olefin protons. 2D NOESY experiment indicated that three ligands in complex existed in s,*cis*-s,*cis* conformation. On the basis of complex structural investigation performed we suggested simple and reliable method to determine Pd_2dba_3 purity (Picture 1, in the right).
We showed that in solid state Pd_2dba_3 is stable for several months, while in solution it decomposes relatively quickly yielding insoluble precipitate. The composition of precipitate as established by ICP-MS and powder X-ray diffraction studies. The morphology of particles was investigated with scanning electron microscopy (Picture 2) [1].



Picture 2. SEM image obtained from Pd_2dba_3 decomposition products.

The present study has clearly shown that the content of catalytically active species in Pd_2dba_3 may significantly vary, thus leading to estimation of incorrect values of mol %, TON, and TOF actually employed in the reaction [1].

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P290

SILVER(I)-CATALYZED CARBOXYLATION OF ORGANOBORONIC ESTERS WITH CO_2

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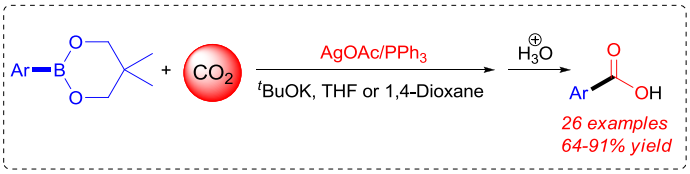
The incorporation of CO_2 into organic substrates to provide high value-added chemicals has gained much attention, since CO_2 is an abundant, inexpensive, and renewable carbon resource.[1] Recently, transition-metal catalyzed carboxylation of less reactive carbon and other nucleophiles with CO_2 were successfully developed.[2] Those catalytic reactions show high efficiency, broad substrate scope and good applicability, allowing more convenient access to various functionalized carboxylic acids and derivatives. Among these carbon nucleophiles, organoboronic acids and their derivatives are particularly attractive substrates due to their ease of handling, broad availability and functional group compatibility. Carboxylation of organoboronic esters with CO_2 catalyzed by $[Rh(OH)(cod)]_2$/dppp, CuI/bisoxazoline or N-heterocyclic carbene complexes have been discovered.[3] Herein, we present the carboxylation of a variety of arylboronic esters with CO_2 using a simple and efficient $AgOAc/PPh_3$ catalyst (Scheme 1). This catalytic system showed wide substrate scopes and various functionalized carboxylic acids could be obtained in good yield.



Scheme 1. Ag(I)-catalyzed carboxylation of organoboronic esters with CO_2

References:

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STEREOSELECTIVE CATALYTIC SYSTEMS BASED ON PRINCIPLE NEW CHIRAL PHOSPHINE-DIAMIDOPHOSPHITES LIGANDS

S.V. Zheglov[1], K.N. Gavrilov[1], M.G. Maksimova[1], O.V. Potapova[1], S.I. Zakharov[1], A.N. Volov[2]

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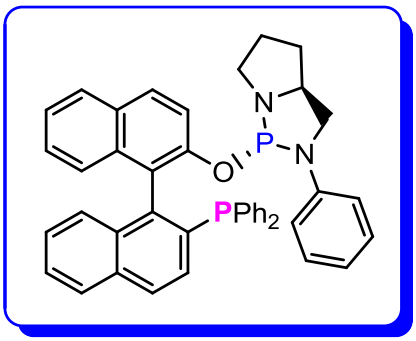
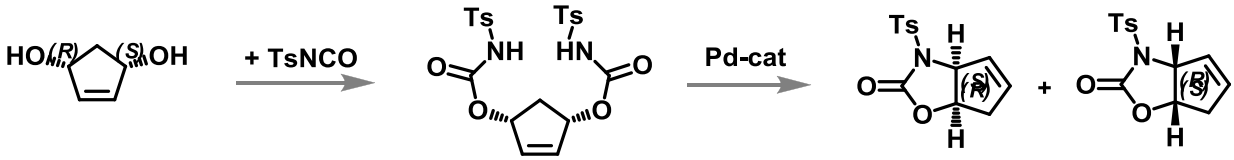
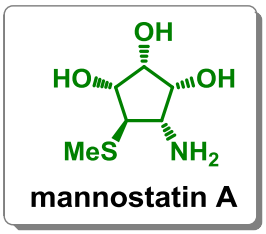
2 - A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS, Moscow, Russian Federation
s.zheglov@rsu.edu.ru

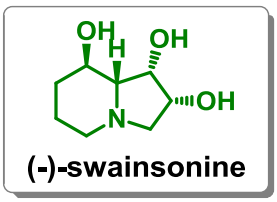


The new (R)- and (S)-BINOL-based previously unknown *P*,*P*-bidentate phosphine-diamidophosphites were synthesized. They combine the advantages of both phosphine and phosphite systems, and have a pronounced structural and electronic asymmetry. Novel phosphine-diamidophosphites provided high enantioselectivity in the Pd-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate with various nucleophiles (*ee* up to 95%).

In addition, at this stage of research accomplishing up to 63% *ee* in the desymmetrization of *N*,*N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate was achieved. The products of the two latter reactions are a key precursors for the synthesis of valuable bioregulators (+)-juvabione (insecticide), (+)-wine lactone (fragrance compound), mannostatin A (antiviral drug for the future) and (-)-swainsonine (anticancer drug for the future).







ONE-POT SYNTHESIS OF FUSED ISOQUINOLINES AND γ-CARBOLINES VIA Rh(III)-CATALYZED C–H ACTIVATION AND INTRAMOLECULAR CYCLIZATION

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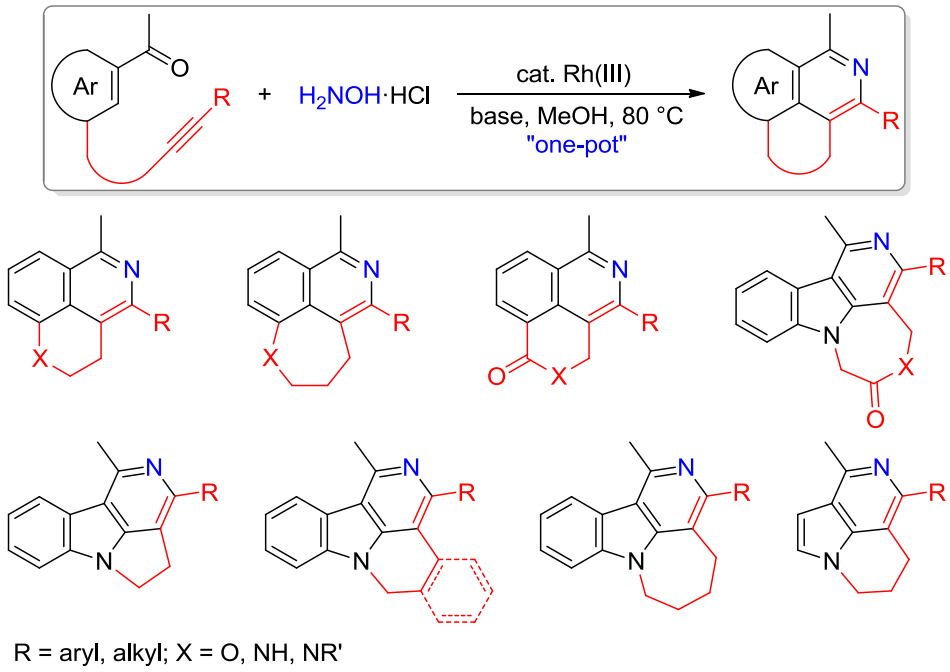
Rh(III)-catalyzed C–H activation has emerged as a versatile tool in syntheses of heterocycles in the past five years [1]. Generally, the reactions proceed in an intermolecular fashion via alkyne or alkene insertion to the metallacyclic intermediates. Herein, we disclose an efficient synthesis of fused rings via Rh(III)-catalyzed intramolecular cyclization. By using rational designed bifunctional substrates, fused ring products were obtained via cascade reaction involving ketone–hydroxylamine condensation, C–H activation and intramolecular cyclization.

This protocol enables rapid assembly of multi-substituted fused isoquinolines and γ-carbolines in a "one-pot" [2] and "external-oxidant-free" [3] approach. Currently, expanding this strategy to other fused ring systems, building diverse libraries of these new heterocyclic compounds and evaluating their biological activities are ongoing.



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P293

TRANSITION-METAL-FREE CATALYTIC SYNTHESIS OF 2,5-DISUBSTITUTED FURAN VIA HYDROLYSIS/CYCLIZATION OF 1, 3-BUTADIYNES

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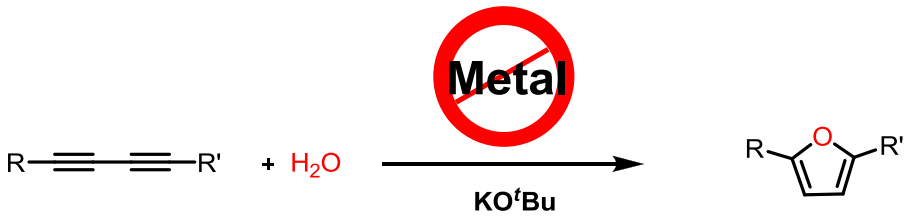
Substituted furans are pharmaceutically important fragments, widely found in natural product, as well as synthetic active biological molecules [1], and numerous protocols have been developed including the use of transition metal catalysts and functionalized alkynes [2]. Thus, the development of an alternative approach toward substituted furans is highly desirable, and transition-metal-free methods appear particularly attractive. Recently, a number of groups reported significant progress of constructing heterocyclic compounds [3]. Herein, we report that hydrolysis and cyclization of 1, 3-butadiynes can be achieved in the presence of *t*-BuOK base at 80 ^{o}C without a transition-metal catalyst to afford 2,5-disubstituted furans.



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P294

++PALLADIUM-CATALYZED γ-ARYLATION OF KETONES VIA β-CARBON ELIMINATION

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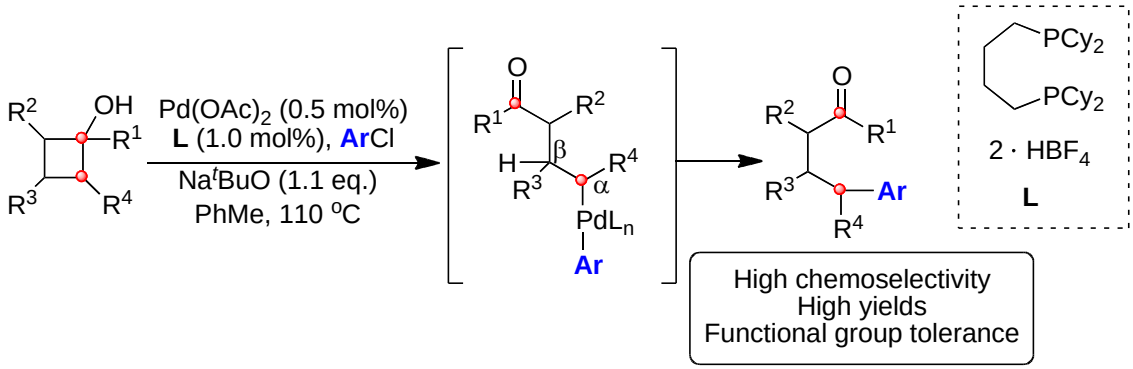
In the last few years, activation of C-C bonds has become of extreme interest to organic chemists.[1] The development of widely applicable and high tolerating catalytic methods for the activation of such bonds is still highly desirable. Mainly due to the reason that most of the methods available now involve the use of stochiometric amounts of metal complexes.[2]
Recently, our research group has reported some progress directed towards the activation of C-C bonds. Thus, we reported the Pd-catalyzed ketone γ-arylation via C-C cleavage with aryl chlorides (Scheme 1).[3] This method is characterized by the wide substrate scope, including challenging substrate combinations with particularly sensitive functional groups and a diverse set of substitution patterns. Strikingly, the protocol avoids competitive β-Hydrogen elimination, thus opening new perspective to be implemented in the near future.



Scheme 1. Metal-catalyzed activation of C-C bonds.

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P295

CATALYTIC HYDROGENATION OF CARBON DIOXIDE AND BICARBONATES WITH A WELL-DEFINED COBALT DIHYDROGEN COMPLEX

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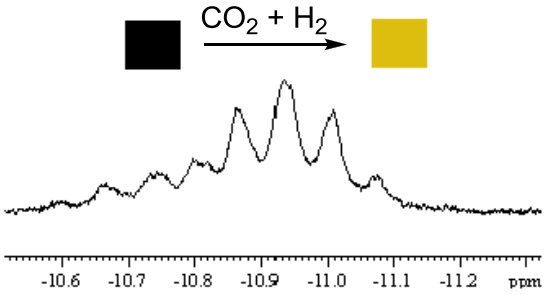
Using a well-defined cobalt dihydride catalyst, we have shown [1] that it is possible to hydrogenate bicarbonates and CO_2 in high yields and TONs. Applying this active catalyst, significantly improved TONs for hydrogenation of bicarbonates and CO_2 compared to other non-precious metal-based catalysts have been achieved. Our cobalt complex is competitive or even superior in comparison with many known precious metal systems for the hydrogenation of CO_2. Notably, it is possible to perform reductions of carbon dioxide at comparably low pressures of H_2 and CO_2 (5 bar), giving the best TONs so far reported under such mild conditions. This represents a good starting point to further improve the hydrogenation at more ambient conditions with low-cost metals. Based on high pressure NMR and catalysis experiments with different kind of hydrid spezies of the complex, we propose that mixing of the PP_3 ligand and the cobalt precursor $Co(BF_4)_2 \cdot 6H_2O$ resulted in a defined dihydride complex $[Co(H_2)PP_3]^+$ BF_4^- which participates in the catalytic cycle.



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P296

HYDROGENATION OF TOLUENE OVER Ni PARTICLES SUPPORTED ON MgF_2, MgO AND MgF_2-MgO SYSTEM

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Hydrogenation of aromatic compounds is an industrially and environmentally interesting reaction. The major applications of aromatic hydrogenation are in the production of aromatic-free fuels and solvents. In diesel fuel aromatic compounds are responsible for undesired particle emissions in exhaust gases. Restrictive standards of the contents of aromatics in diesel fuels have prompted the search for more active and selective catalysts of the C-C bond hydrogenation. One of the metal a commonly used in hydrogenation of aromatic hydrocarbons is nickel. The choice of nickel is mainly due to its availability and reasonable cost compared to noble metals. The performance of nickel catalysts in hydrogenation reaction significantly depends on the type of support, determining the development of specific surface area of the metal, mechanical strength and thermal stability as well as the compatibility with the nickel phase.

The subject of this study are the new toluene hydrogenation nickel catalysts supported on magnesium fluoride or a binary MgF_2-MgO system. Magnesium fluoride has been used as a support of metal phase active and selective in hydrogenation of benzene [1] and toluene [2] or selective reduction of chloronitrobenzene to chloroaniline [3]. MgF_2 is classified as a good mesoporous support having well-developed porous structure, high chemical inertness, thermal stability and hardness [4]. Unfortunately, magnesium fluoride has the specific surface area not greater than 40 $m^2 \cdot g^{-1}$. Therefore, attempts have been made to devise a method of synthesis ensuring a greater specific surface area. One of such methods is to modify MgF_2 with magnesium oxide.

The MgF_2-MgO system of different quantitative composition was tested as a potential support for nickel catalysts to be used in hydrogenation of toluene. The catalytic performance of the system was studied as a function of the MgF_2/MgO ratio in the support and the reaction conditions. The hydrogenation reaction was performed at temperatures ranging from 75 to 225°C, for the catalysts activated in hydrogen at different temperatures (400-550°C). The activity of Ni/MgF_2-MgO catalysts was compared to those of Ni/MgF_2, Ni/MgO – Figure 1. The highest activities were obtained for the catalysts supported on MgF_2-MgO, containing 60 mol.% MgF_2, especially after activation at 500°C. The catalytic activity of nickel supported on magnesium oxo-fluoride in toluene hydrogenation was much higher than those of Ni on the commonly used Al_2O_3 or SiO_2 supports.

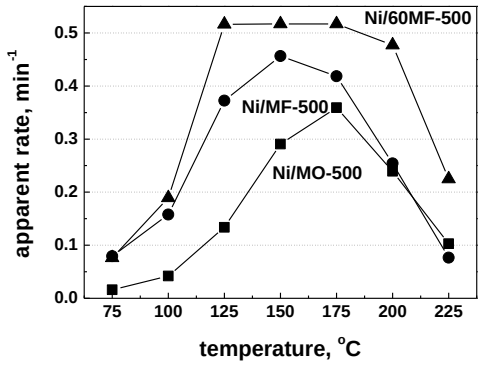

Figure. 1. The effect of reaction temperature on apparent rate of nickel catalysts in toluene hydrogenation reaction after 1h in each temperature.

We thank the Polish Ministry of Scientific Research and Information Technology for financial support under the projects N N204 141339 and N N204 214140.

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P297

MECHANISM OF DECENES FORMATION IN ETHYLENE TRIMERIZATION REACTION

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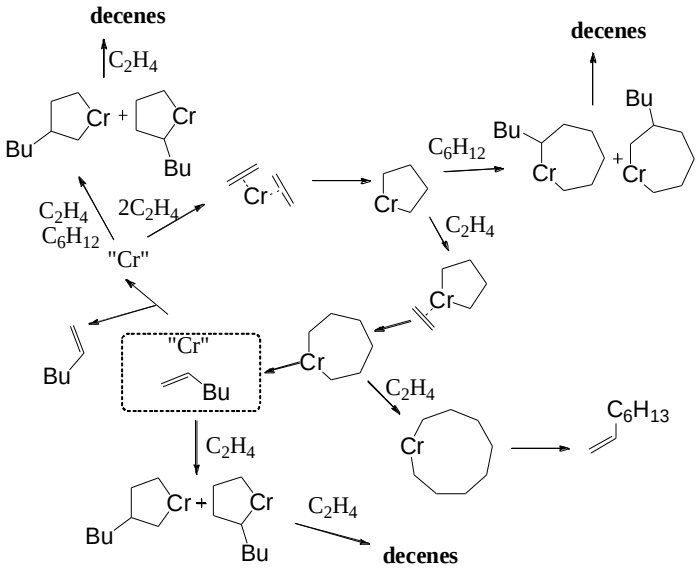
Ethylene trimerization reaction receives significant attention due to its applicability for industrial synthesis of polyethylene comonomer, hexene-1, with selectivity about 90%. First commercial plant utilizing this reaction was launched in Qatar in 2004. The reaction is catalyzed by various homogenous chromium catalysts, activated by aluminiumorganic compounds such as triethylaluminium (TEA), diethyl aluminium chloride (DEAC), or methylalumoxane. It is generally accepted that mechanism of the reaction includes metallacyclic intermediates[1]. The observed high selectivity on hexene-1 is explained as preferable elimination from chromacycloheptane, rather from chromacyclopentane.

Isomeric decenes are the second major product, which is formed in co-trimerization reaction of hexene-1 with two ethylene molecules. Various ways of metallacycle formation using hexene-1, as well as two possible ways of elimination for every substituted chromacycloheptane, are responsible for formation of six main decene isomers. Generally, they are undesirable by-products for the industrial process and their formation should be minimized. However, decenes are used for poly-alpha-olephine preparation and one may need to obtain higher amount of these products.

We studied decenes formation using previously developed enhanced chromium-pyrrole catalyst[2], which has very high activity and good selectivity in ethylene trimerization. It was established that formation rate for every decene linearly increases with increase of hexene-1 concentration. However, we found that at low hexene-1 concentrations, decene formation is independent of hexene-1 concentration. Moreover, there are both hexene-dependent and hexene-independent components in total decene formation rate.



We explain this hexene-independent decenes formation as resulting from back-coordination of just formed hexene-1 molecule to the regenerated catalyst in the end of the catalytic cycle. This can happen within solvent cage, so macroscopic concentration of hexene-1 does not affect this process. Three possible ways of decenes formation, including the proposed back-coordination, are shown on Fig. 1.

The hexene-independent way of decene-1 formation demonstrates that decenes formation is not just a competing process, but rather an intrinsic part of ethylene trimerization reaction.

Fig. 1. Suggested mechanism of decenes formation in ethylene trimerization reaction.

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P298

CATALYTIC FUNCTIONALIZATION OF GEM-DICHLOROCYCLOPROPANES

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Simplicity of production of gem-dichlorocyclopropanes in comparison to other compounds determines an interest to development of methods of production of wide range of polysubstituted carbo- and heterocyclic compounds based on it. We investigated functionalisation and transformation of alkenyl- and polyhalogenalkyl-gem-dichlorocyclopropanes. Catalytical functionalization of dibond in vinyl-gem-dichlorocyclopropanes is realized with preservation of cycle. Their use for the alkylation of aromatic compounds in the presence of Friedel-Crafts catalysts gave corresponding arylalkylcyclopropanes quantitative yield. The oxidation in the presence of salts of metals with several common oxidation states leaded to corresponding aldehydes and acids (in some cases – in the form of acetales and esters, respectively). During the radical polymerization and copolymerization cyclopropane fragments are absent which is explained by conversion of intermediate radicals with ring opening.

Under conditions of phase-transfer catalysis alcohols and phenols are able to react by endocyclic C-Cl-bonds with formation of corresponding ketals. In case of chloromethyl-gem-dichlorocyclopropanes and 1,2,2-trichlorocyclopropanes the main products of reaction are derivatives of corresponding methylenecyclopropylketones. By the example of 1,1-dichloro-2-bromocyclopropane it is demonstrated that full substitution of halogens is accompanied by ring opening and main products are corresponding derivatives of substituted acetylenic aldehydes.

Probable mechanisms of functionalisation and transformation of gem-dichlorocyclopropanes and possibilities of using of these reactions in terms of organic synthesis are discussed in report.

P299 (GM1)

POLY(ETHYLENE GLYCOL)S : GREEN SOLVENTS FOR RING-CLOSING METATHESIS

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Evelina Colacino, Jean Martinez, Frédéric Lamaty

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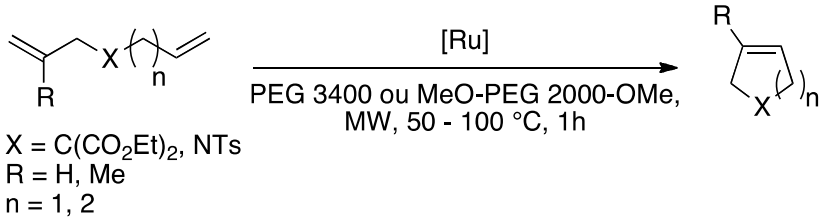
Poly(ethylene glycol)s (PEGs) [1] are an interesting environment-friendly alternative to classical solvents due to their low toxicity and costs.[2] Their combination with metals and metallic salts provide powerful reaction systems for a wide variety of transformations.[3] Our team has shown in the last years that PEGs could be used as solvents in organometallic catalysis for the Sonogashira,[4] the Mizoroki-Heck[5] or Ullmann[6] couplings. We are reporting herein our results regarding Ring-Closing Metathesis (RCM) in PEG.

We have shown previously in the development of a PEG-supported synthesis that the presence of the polymer was not detrimental to the RCM in PEG. We have performed a detailed study of this reaction with various catalysts and PEGs under microwave irradiation.[8]



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Authors Index

C

D

E

F

G

H

I

J

K

L

M

N

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P

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R

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T

U

V

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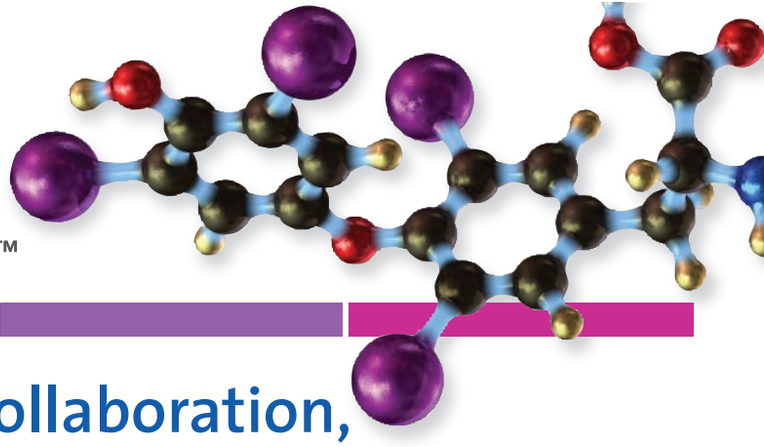

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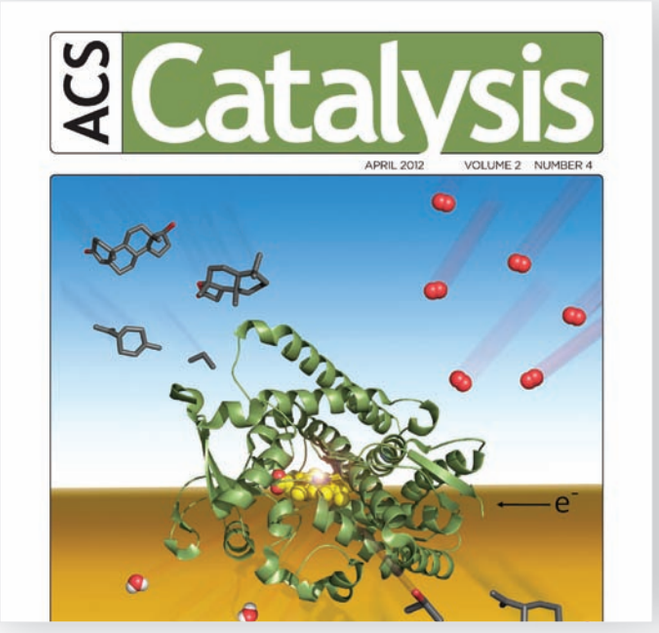

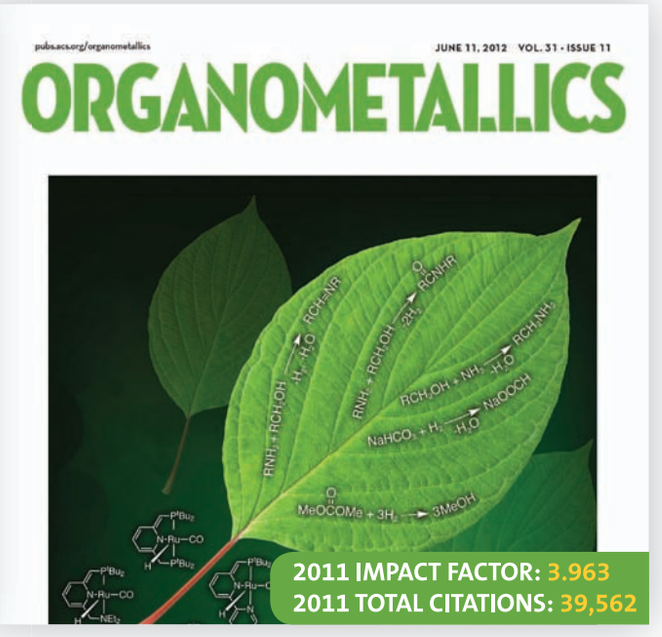

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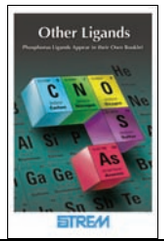
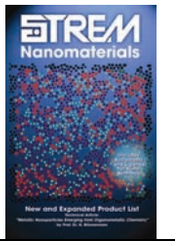
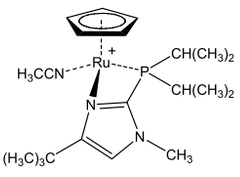




New Catalysts and Ligands



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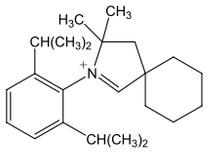

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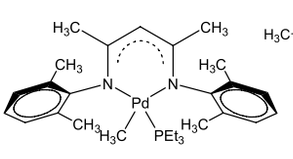

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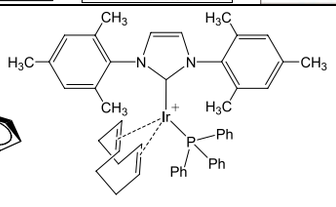

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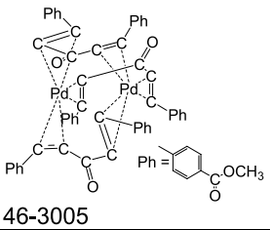

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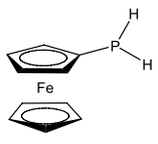

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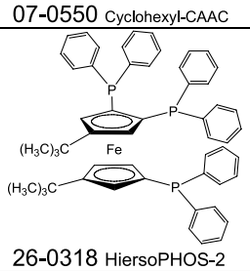

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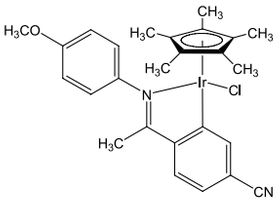

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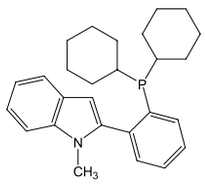

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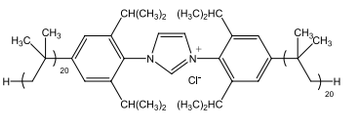

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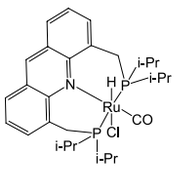

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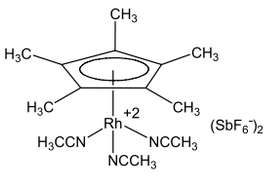

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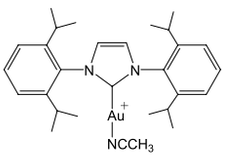

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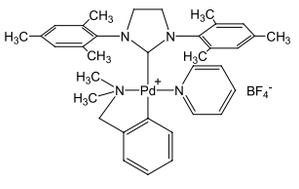

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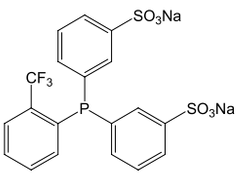
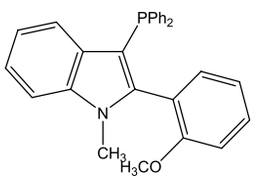


15-0577 o-DANPHOS

New P Ligands



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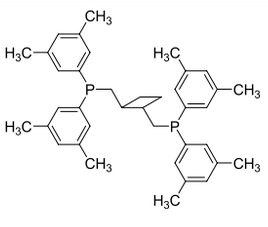

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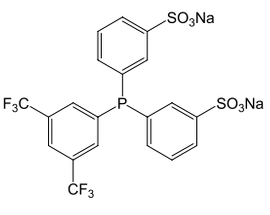

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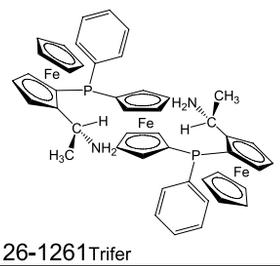

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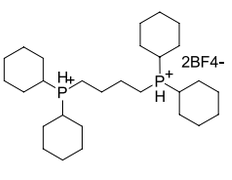

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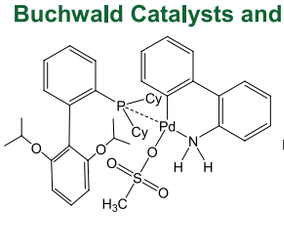
Buchwald Catalysts and Ligands



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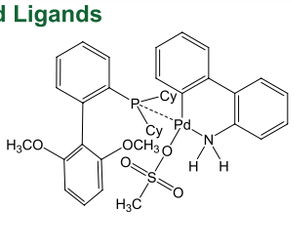

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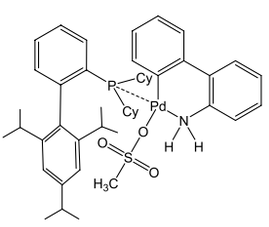
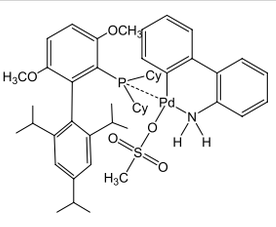
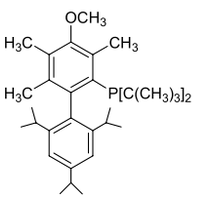


46-0320 from XPhos

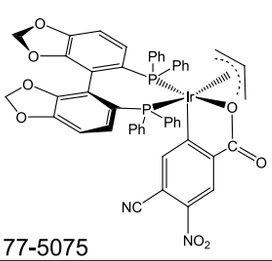


46-0322 from BrettPhos



15-1063

Ligands and Catalysts (Manufactured under license of Takasago patents).



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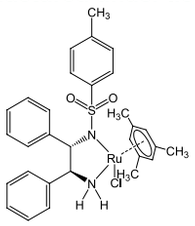

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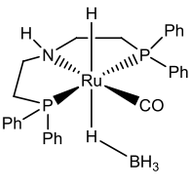

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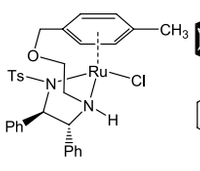

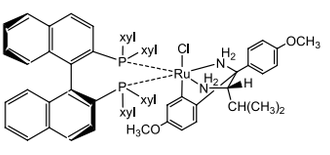

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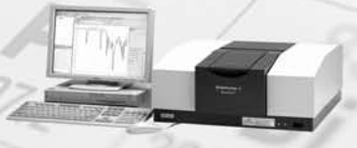

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