

# Abstracts

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## Enantioselective Catalysis Using Chiral N,N'-Dioxide Ligands

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N-oxides known for their electron-donating property, have been applied in many reactions as organocatalysts. Recently, we extended N,N'- $\alpha$  dioxides as a new class of chiral ligands chelated with different Lewis acids including Ti(IV), In(III), Cu(I), Sc(III), La(III), Ni(II), Fe(II) etc, and demonstrated that chiral N,N'- $\alpha$  dioxide-metal complex catalysts were highly efficient for a number of asymmetric transformations. Enantioselective cyanation of aldehydes and ketones were firstly realised by the N,N'- $\alpha$  dioxide-Ti(IV) catalyst. The N,N'- $\alpha$  dioxide-In(III) has successfully catalysed asymmetric hetero-Diels-Alder reaction of Danishefsky dienes with aldehydes, asymmetric allylation of ketones as well as asymmetric aminolysis of meso-stilbene oxide. The N,N'- $\alpha$  dioxide-Cu(I) was a novel catalyst for the asymmetric Henry reaction of aldehydes, aldimines and ketimines. The N,N'- $\alpha$  dioxide-Sc(III) complex could catalyse the asymmetric aza-Diels-Alder reaction of aldimines and asymmetric allylation of aldimines. Chiral N,N'- $\alpha$  dioxide coordinated with La(OTf)<sub>3</sub> was effective for the enantioselective direct Michael addition of nitroalkanes to nitroolefins. Asymmetric intramolecular oxa-Michael addition of  $\alpha$ ,  $\beta$ -unsaturated ketones to the synthesis of flavanones and asymmetric carbonyl-ene reaction have been realised by the chiral N,N'- $\alpha$  dioxide-Ni(II) complex. And the chiral Fe(II) complex with N,N'- $\alpha$  dioxide was found to be an efficient catalyst for asymmetric intermolecular oxa-Michael reaction. The detail of the application of these novel chiral ligands in transition-metal-catalysed asymmetric reactions will be presented in my lecture.

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## Cyclisation of Enynes

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The transition metal catalysed cyclisation of enynes has attracted considerable attention in recent years as the transformation of a relatively simple substrate into a more complex product under catalytic conditions without the generation of byproducts means that reactions of this type fulfill many of the demanding criteria now expected in organic chemistry. This lecture will discuss a study of an asymmetric catalytic enyne cyclisation that incorporates carbon monoxide (an asymmetric catalytic Pauson Khand reaction), and will present initial results obtained with other metal-catalysed enyne cyclisations using a bis-phosphonate substituted enyne.

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## Organocatalytic Asymmetric Multicomponent Reactions for the Rapid Synthesis of Structurally Diverse Nitrogen-Containing Molecules

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Nitrogen-containing chiral organic compounds represent important structural motifs with wide occurrence in unnatural and natural compounds exhibiting important biological activities. For example, 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs), Dihydropyridines (DHPs) and related heterocyclic compounds constitute core structural elements in the medicinally relevant compounds and serve as key synthetic intermediates for total synthesis of natural alkaloids exhibiting important biological activities. Chiral pyrrolidines also have widespread applications to the synthesis of biologically active compounds and natural products.  $\beta$ -Amino carbonyls represent another important class of chiral building blocks of pharmaceutically relevant compounds. In view of the synthetic significance of these structural motifs, we have been interested in the development of organocatalytic enantioselective methods to rapidly access them. At this symposium, we will describe our efforts directed at the discovery of asymmetric Biginelli reaction, cycloaddition reactions, and Mannich reactions for manufacturing structurally diverse DHPMs, DHPs, pyrrolidines, and  $\beta$ -amino carbonyls.

## Selectivities in Pd-Catalyzed Asymmetric Allylic Alkylations

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Palladium catalyzed asymmetric allylic alkylation (AAA) is one of the most powerful tools to form carbon-carbon bonds and carbon-hetero atom bonds enantioselectively. A variety of nucleophiles have been applied in this reaction and chiral centers can be produced in allylic substrates, in nucleophiles or in both. In spite of these achievements, some key issues still have to be addressed: regioselectivity is still not fully resolved for monosubstituted allyl substrates, and the carbon nucleophiles are restricted mainly to those "soft", stabilised carbanions.

In recent years we have developed several kinds of chiral ligands with multiple chiral elements based upon the framework of ferrocene. These ligands showed their superior properties to control regio-, diastereo- and enantio-selectivities in Pd-catalyzed AAA reactions using monosubstituted allyl and dienyl esters as substrates, "hard" carbanions including cyclic and acyclic ketones and acyclic amides as nucleophile. Highly regio-, diastereo and enantio-selectivities were realised. The impact of structure of ligands, the additives, the bases as well as the solvents on the selectivities is discussed.

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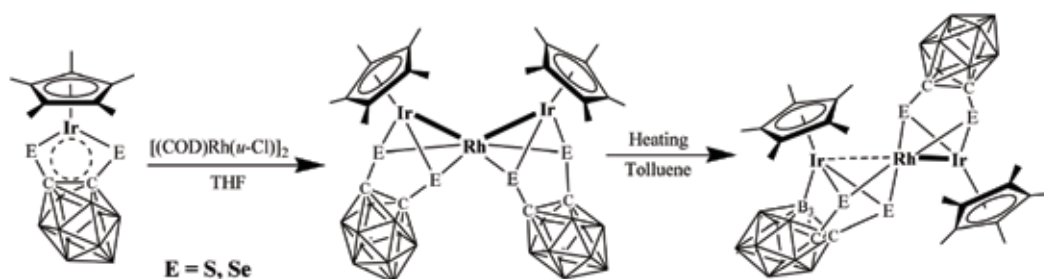
## Organometallic Chemistry of 1,2-Dichalcogenolato Carboranes

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Half-sandwich transition metal complexes ( $\text{Cp}^*\text{M}$ ,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous  $\text{Cp}^*$  rings. In the protected space below the  $\text{Cp}^*$  ligands, 1,2-dichalcogenolato carborane ligands can be accommodated, e.g. 16-electron "pseudo-aromatic" mono-nuclear rhodium and iridium complexes  $\text{Cp}^*\text{M}(\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10})$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{E} = \text{S}, \text{Se}$ ), and they can be used as starting materials to react with low valence transition metal complexes to give heteronuclear complexes  $\{\text{Cp}^*\text{M}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2\text{Mo}(\text{CO})_2$ ,  $\{\text{Cp}^*\text{M}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2\text{W}(\text{CO})_2$  and  $\text{Cp}^*\text{M}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})][\text{CO}(\text{CO})_3]_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{E} = \text{S}, \text{Se}$ ) which contain metal-metal bonds.



$\text{Cp}^*\text{Ir}(\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10})$  reacts with  $[(\text{COD})\text{RhCl}]_2$  to form *cis*- $\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2\text{Rh}$  and in refluxing toluene solution, the *cisoid* complex can be converted in more than 90% yield to corresponding *transoid*  $\text{trans}-\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_9)]\}\text{Rh}\{\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$  which contains a boron-iridium bond.

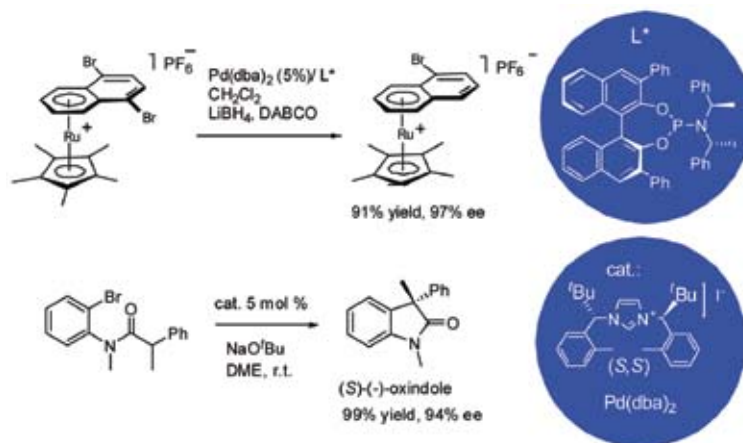
## Asymmetric Catalysis with Bulky Chiral Monodentate Phosphoramidate- and NHC-Ligands

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This lecture will detail the development of novel catalysts and ligands for asymmetric synthesis. The focus will be on bulky chiral monodentate ligands and applications will include the desymmetrisation of meso – arene complexes and palladium-catalysed asymmetric intramolecular  $\alpha$ -arylation of amides to yield oxindoles.



## Development of New Synthetic Methods and Their Applications for the Synthesis of Natural Products

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This presentation describes our recent efforts in the development of several new synthetic methodologies and their applications for the synthesis of natural and bio-active products.

Emphasis will be given on the efficient synthesis of optically active amines which include vicinal C<sub>2</sub>-symmetrical diamines, vicinal unsymmetrical diamines, *syn/anti* amino-alcohols and homoallylic amines based on the strategy of *N*-*tert*-butansulfamide auxiliary-mediated nucleophilic addition or new scaffolded Rh-diene catalysed asymmetric synthesis. Another topic is the new approaches for the synthesis of 3-substituted phthalides and axial atropisomeric biaryls. In the meantime, the usages of these synthetic methods are illustrated by the synthesis of several natural or bio-active products.

## Design of High-Performance Organocatalysts for Practical Asymmetric Synthesis

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The design of new catalysts and new organic transformations in an environmentally benign manner is increasingly important in recent years for the construction of new and useful chiral molecules from simple organic resources. In this context, organocatalysis has recently emerged as a field of research providing practical alternative or complementary technologies to the more traditional transition metal catalysed systems. Accordingly, we have rationally designed various environmentally benign chiral organocatalysts such as chiral phase transfer catalysts, chiral bifunctional organocatalysts, and chiral Brønsted acid catalysts, starting from commercially available optically pure (R)- or (S)-binaphthol. These binaphthyl-modified chiral organocatalysts have been successfully applied for the development of various types of new catalytic asymmetric transformations including asymmetric alkylation, asymmetric conjugate addition, asymmetric direct aldol reactions, asymmetric Mannich reactions, asymmetric epoxidation, asymmetric hydroxyamination, etc. Quite recently, a new approach for the design of chiral bifunctional organocatalysts derived from a *cis*-diamine core structure has been developed in a highly practical manner. The detail of this new catalyst design in addition to the application to asymmetric aldol synthesis will be presented in my lecture.

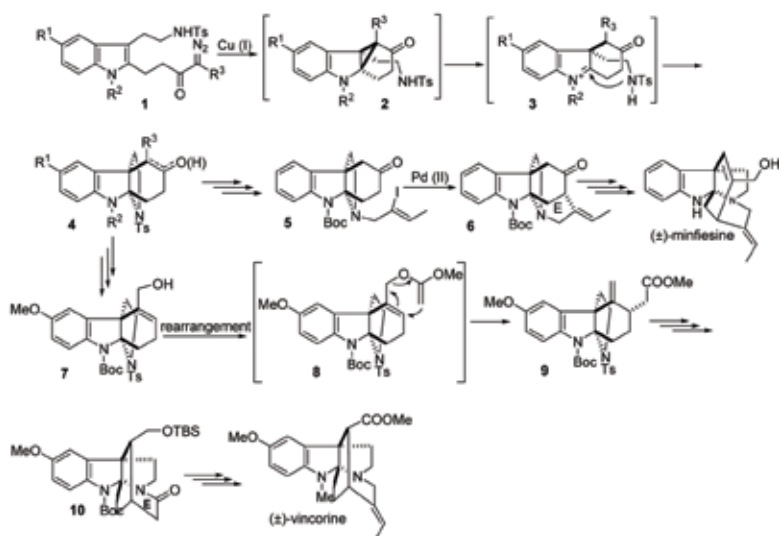
## Total Synthesis of (±)-Minfiensine and (±)-Vincorine

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A highly efficient method was developed for the assembly of a tetracyclic skeleton via a three-step one-pot cascade reaction of cyclopropanation, ring opening and ring closure. The methodology developed was successfully applied to accomplish the total synthesis of indole alkaloids (±)-minfiensine and (±)-vincorine.



This work was supported by NSFC (20632030 and 20825207) and the State Key Laboratory of Bio-organic and Natural Products Chemistry, CAS.

## Transition Metal-Catalysed Reaction of Diazo Compounds, Alkynes and Allenes

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1) Pd-catalysed reaction of  $\alpha$ -diazo carbonyl compounds

Pd complexes are popular catalysts in organic reactions, and  $\alpha$ -diazocarbonyl compounds are well-known to be catalysed by various transition metals. However, there are only sporadic reports on Pd-catalysed reaction of  $\alpha$ -diazocarbonyl compounds. We have recently launched a program to explore the utilisation of Pd complexes in the catalytic reaction of  $\alpha$ -diazocarbonyl compounds and some of these transformations will be described.

2) Transition metal-catalysed reaction of alkynes

The chemistry of transition metal complex activated alkynes has witnessed increasing development in recent years. Among the various catalytic systems, Pt(II) and Au(I) complexes have attracted particular attention due to their high affinity to  $\pi$ -system of the alkyne substrates. Given the high affinity of Pt(II) and Au(I) to alkynes, we have envisioned a thio group can function as an internal nucleophile that triggers the formation of metal carbene intermediate. We will describe the investigation of transition metal-catalysed reaction of propargylic sulfides.

3) Transition metal-catalysed reaction of allenyl sulfides

The transition metal-catalysed reactions of allene derivatives bearing  $\alpha$ -constituents, such as hydroxy, ketone, carboxy, thio and amino groups, have led to the development of many synthetically useful transformations. In connection to our study on [2,3]-sigmatropic rearrangement of sulfide ylide generated from metal carbene and propargylic sulfides, we have studied the transition metal-catalysed reaction of the rearrangement product allenyl sulfides. The reaction proceeds through an unprecedented 1,4-migration of thio group, presumably generating a metal carbene species, which is trapped intramolecularly by carbonyl group to afford furan derivatives as the final products. When the carbonyl substituent is replaced by an acetylenyl group, the reaction gives benzene derivatives. The formation of benzene derivative presumably involves a metallacyclobutene intermediate, which is formed by a [2+2] cycloaddition of the Ru carbene to the alkyne moiety. Examples will be described.

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## Heterocalixaromatics, New Generation Macrocyclic Host Molecules in Supramolecular Chemistry

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The sophistication of the design and synthesis of novel and functional macrocyclic host molecules has always been one driving force to promote the major advances in supramolecular chemistry. In recent years, we have been investigating the supramolecular chemistry of heteroatom-bridged calixaromatics or heterocalixaromatics. In comparison with conventional calixarenes, introduction of oxygen and/or nitrogen atoms as the bridge linkages in calix(hetero)aromatics has resulted in a wide variety of fine bridge-tuned macrocyclic cavities because oxygen and, particularly, nitrogen atoms can adopt  $sp_3$  and/or  $sp_2$  hybrid configurations to form different degrees of conjugation with the neighbouring (hetero)aromatics. In this presentation, I will report the highly efficient synthesis of various aza- and/or oxa-bridged calixaromatics using our established fragment-coupling strategy. The effect of heteroatom linkages on the conformational structures and on the size of macrocycles will be discussed. Construction of polyfunctionalised macrocyclic heterocalixaromatics will be emphasised. Finally, I will demonstrate the potential applications of heterocalixaromatics in the recognition of cation, anion and neutral molecular species.

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## Photocyclodimerization of 2-Naphthalene Derivatives

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The development of efficient and selective methods for organic synthesis is always the main concern of chemists. While many elegant and efficient strategies have been developed for a variety of thermal reactions, there are still few examples in the photochemical transformations. Over the years, much effort has been paid to the improvement of the selective photochemical transformation both in solution and in the solid state. The achievements have demonstrated that the selectivity control in the excited state is a fascinating subject, and photochemistry has gradually matured to a stage that can offer attractive synthetic routes. Since the excited molecule possesses an excess energy content as a result of photon absorption, it is accepted that the thermodynamically favourable products accessible to a photo excited molecule are far greater than those accessible to a ground-state molecule. The fact that light absorption, rather than heat, activates a photochemical reaction allows for selectivity of activation and also allows for the ability to initiate reactions even at very low temperatures.

In this contribution, we will present our recent work on photocyclodimerisation of 2-naphthalene derivatives. The photochemical cyclodimerisation of anthracenes is one of the most established reactions, while the photocyclodimerisation of naphthalene derivatives is limited in scope. Unlike anthracene, naphthalene itself does not undergo photocyclodimerisation. Only some substituted naphthalene derivatives have been reported to give cubane-like photocyclodimers. Herein, our recent studies: (1) formation of cubane-like photocyclodimers from 2-naphthalene- carbonitrile; (2) highly efficient cucurbit[8]uril-templated intramolecular photocycloaddition of 2-naphthalene-labelled poly(ethylene glycol) in aqueous solution; (3)  $\gamma$ -cyclodextrin-directed enantioselective photocyclodimerisation of methyl 3-methoxyl-2-naphthoate, will be highlighted.

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