



Chiral Metal Complexes as Catalysts and Building Blocks of Molecular Scaffolds

The Chinese Academy of Sciences – Croucher Foundation Joint Research Grant

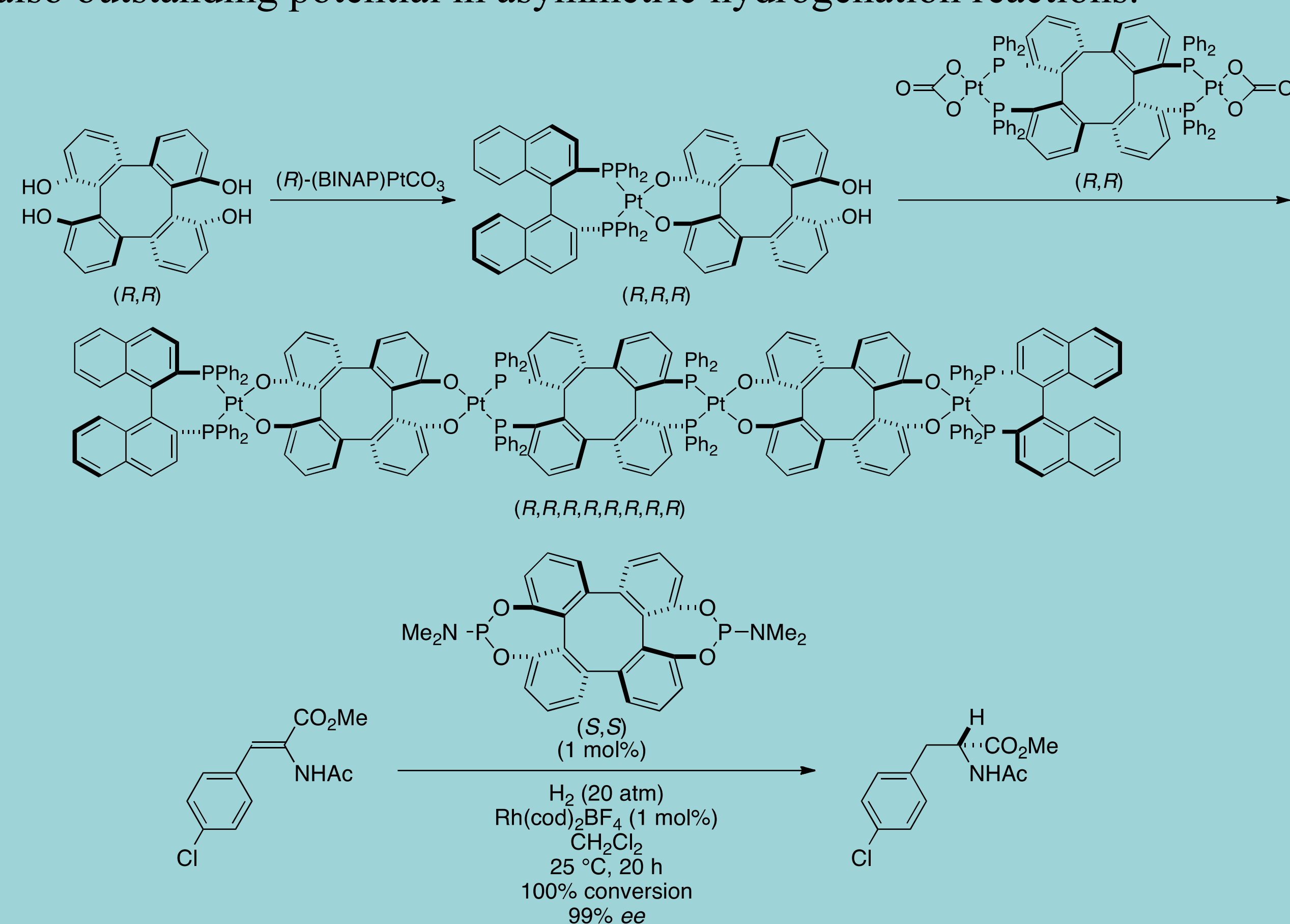
Principal Investigators: Henry N.C. Wong (The Chinese University of Hong Kong)
Xue-Long Hou (Shanghai Institute of Organic Chemistry, CAS)
Co-Investigators: Chi-Ming Che, Man-Kin Wong (The University of Hong Kong)
Zhen-Jiang Xu (Shanghai Institute of Organic Chemistry, CAS)

Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry,
The Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200032, China

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Helical and Rod-like Chiral Platinum Complexes and Asymmetric Hydrogenation (Henry N.C. Wong and Hai-Yan Peng)

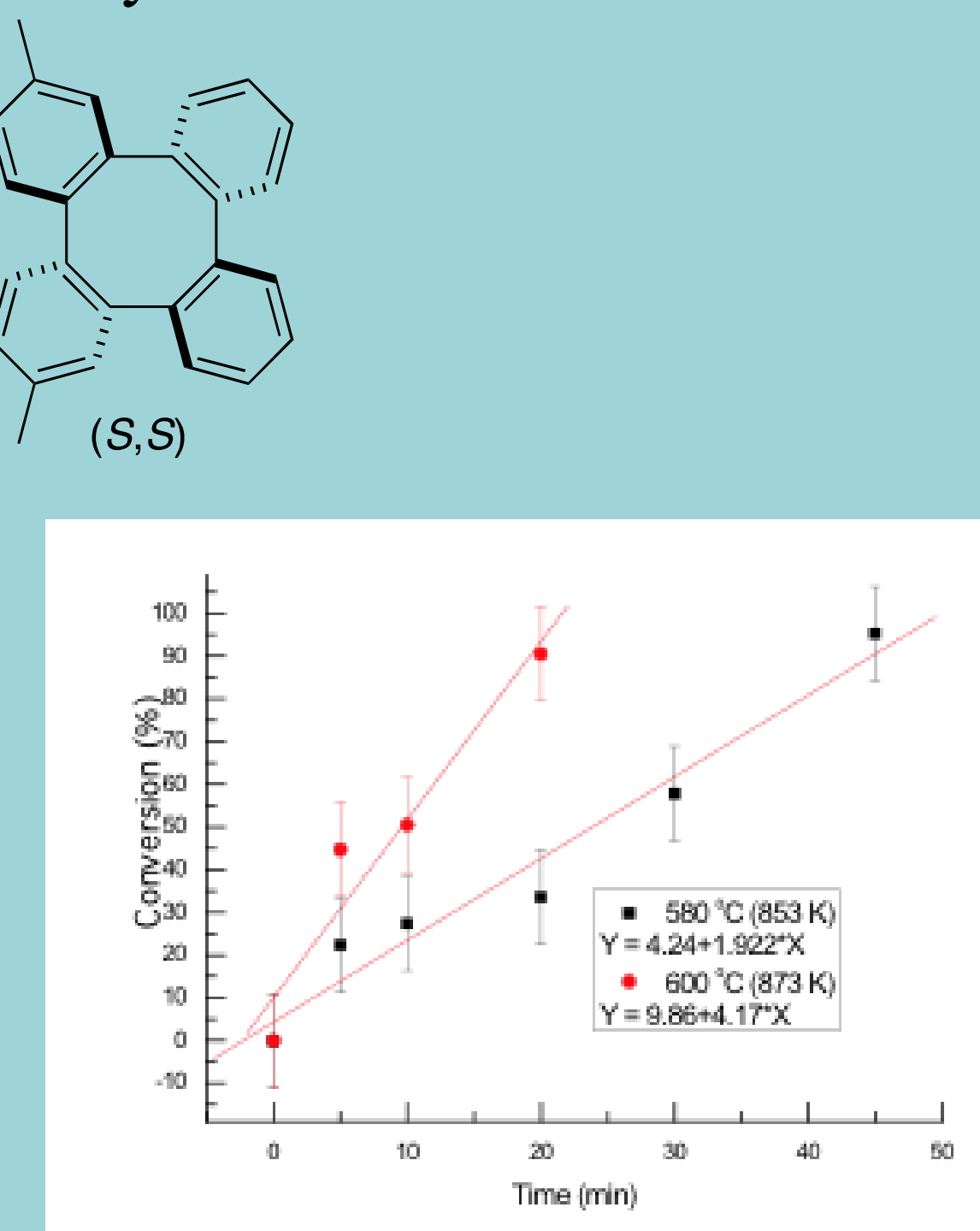
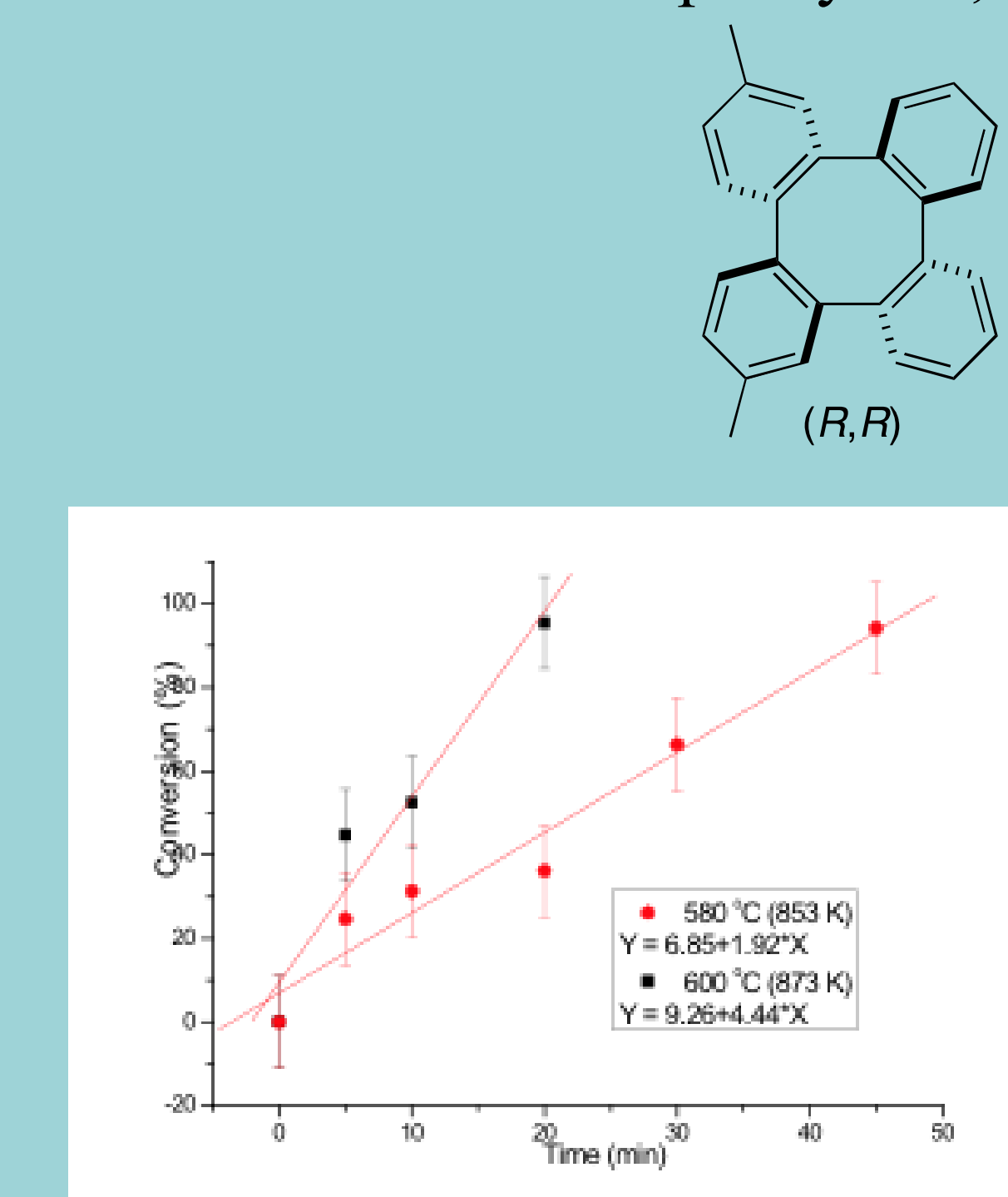
Chiral tetrahydroxytetraphenylene building blocks were employed in preparing platinum complexes, leading to the identification of novel molecular scaffolds with helical and rod-like structures. A rhodium complex has shown also outstanding potential in asymmetric hydrogenation reactions.



Barrier for Ring Inversion of Tetraphenylene (Henry N.C. Wong and Hui Huang)

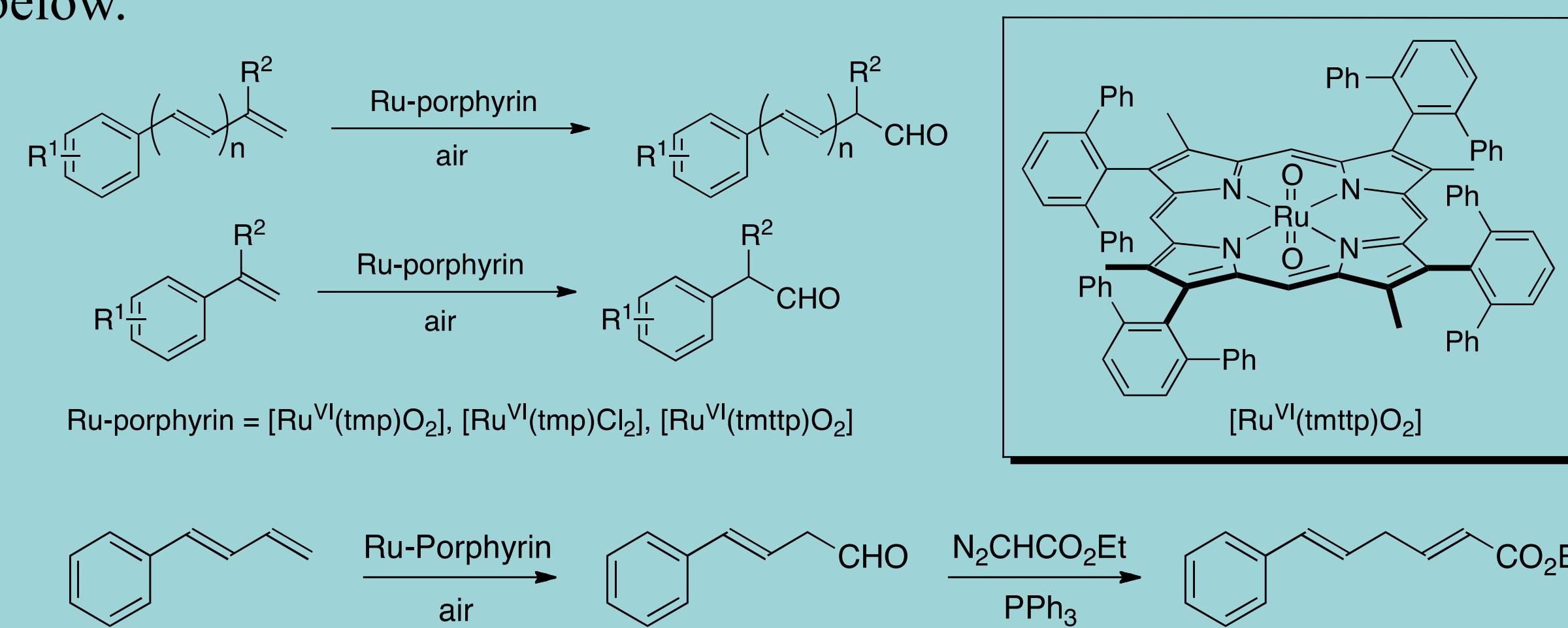
There has been controversy in the ring inversion barrier of tetraphenylene. In 1971, a value of 5.7 ± 1 kcal/mol had been obtained by making use of NMR spectroscopy on a derivative of tetraphenylene [Figeys, H.P.; Dralants, A. *Tetrahedron Lett.* **1971**, 3901], while a year later, Allinger reported a much larger value of 222 kcal/mol using CNDO/2 computation [Finder, C.J.; Chung, D.; Allinger, N.L. *Tetrahedron Lett.* **1972**, 4677]. Also in 1972, Mislow measured the racemization of a partially resolved derivative of tetraphenylene and concluded that the value should be greater than 45 kcal/mol [Gust, D.; Senkler, G.H., Jr.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1345]. Our own contribution in this field came from the racemization study of an enantiomerically pure derivative of benzotetraphenylene, which led to a value of 67.2 ± 0.8 kcal/mol [Rashidi-Ranjbar, P.; Man, Y.-M.; Snadström, J.; Wong, H.N.C. *J. Org. Chem.* **1989**, 54, 4888].

We undertook the synthesis of the optically pure enantiomeric (R,R)- and (S,S)-2,7-dimethyltetraphenylenes. The two methyl groups would help to make the molecule chiral, but would not influence the inversion barrier. These two enantiomers gave good CD spectra, as well as are separable on a chiral HPLC column (OD column, hexane/*i*-PrOH 99.3/0.7, 0.7 mL/min., UV 220 nm). Heating of (S,S)-2,7-dimethyltetraphenylene at 600 °C showed that it decomposed to form triphenylene without racemization. Therefore, the activation energy of this decomposition process can be taken as the lowest limit of the proposed inversion barrier. After careful experimentation, the kinetics of decomposition of 2,7-dimethyltetraphenylenes and its parent tetraphenylene were obtained, and the results are shown in Figure 1 and Figure 2. The activation energies were finally determined to be 62.8 kcal/mol for 2,7-dimethyltetraphenylene and 58.2 kcal/mol for tetraphenylene, respectively.



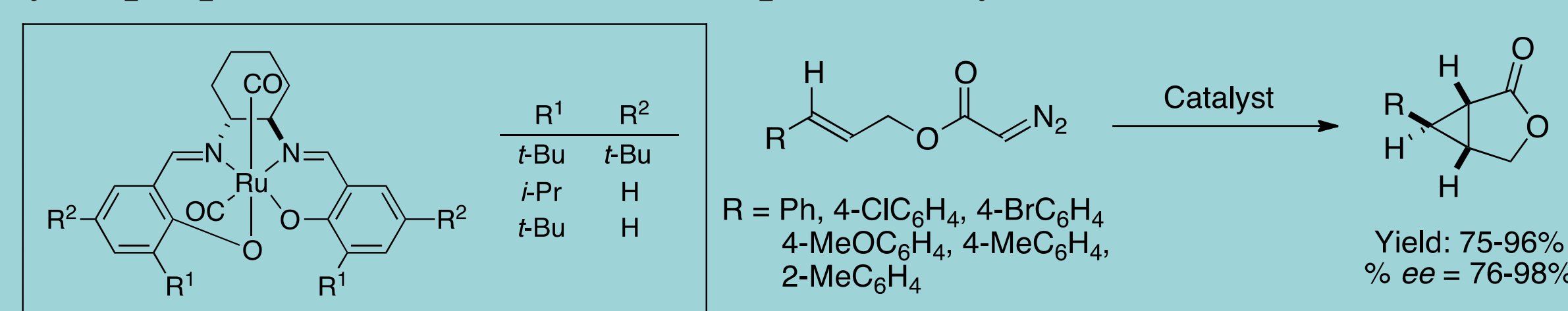
A Mild Method for Highly Selective Conversion of Terminal Alkenes into Aldehydes with Ruthenium(IV)-Porphyrin Catalysts (Chi-Ming Che and Man-Kin Wong)

The Wacker-type oxidation of alkenes to carbonyl compounds is one of the most important reactions in organic synthesis. It was found that the aerobic oxidation of a wide variety of terminal alkenes with [Ru^{VI}(por)Cl₂] as catalyst (por = tmp) afforded aldehydes in up to 99% yield with 100% substrate conversion without C=C bond cleavage. A more robust catalyst [Ru^{VI}(tmtp)O₂] has recently been developed for this novel type of catalytic aerobic oxidation. The freshly generated aldehydes can be converted *in situ* to α,β-unsaturated esters as shown below.



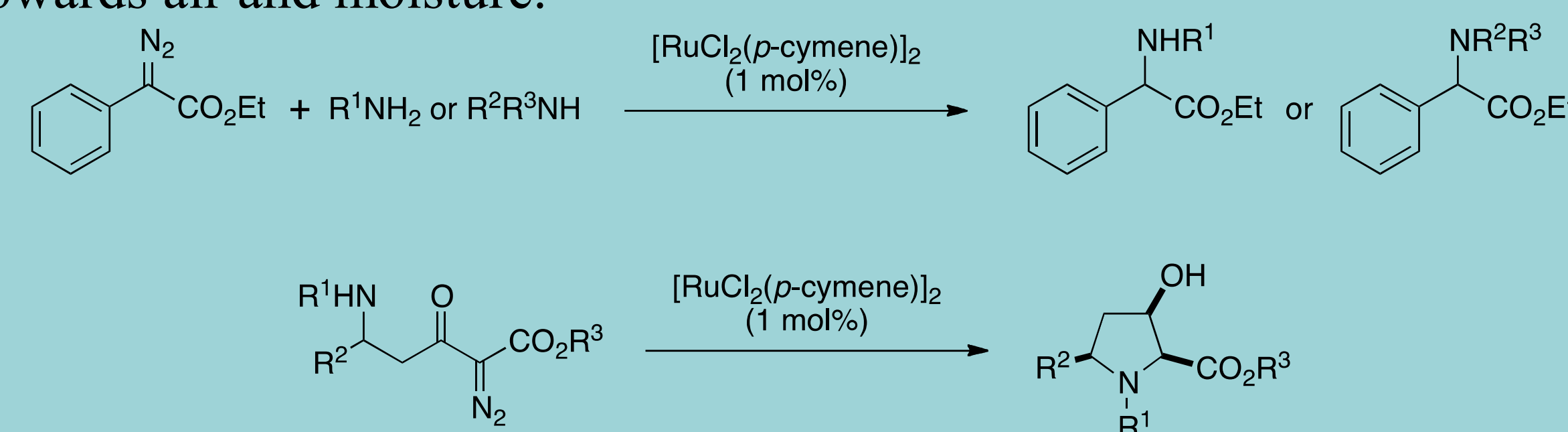
cis-β-Bis(carbonyl) ruthenium-salen Complexes: Asymmetric Intramolecular Cyclopropanation (Chi-Ming Che, Man-Kin Wong and Zhen-Jiang Xu)

Several chiral *cis*-β-bis(carbonyl) ruthenium-salen complexes were prepared and their X-ray crystal structures were determined. These complexes were found to be highly efficient in asymmetric intramolecular cyclopropanation of *trans*-allylic diazoacetates. Desired cyclopropanes were obtained in up to 96% yield and 98% ee.



Ruthenium-Catalyzed One-Pot Carbenoid N-H Insertion Reactions (Chi-Ming Che, Man-Kin Wong and Zhen-Jiang Xu)

Aryl- and aliphatic substituted 3-hydroxyprolines (14 examples) and other amino esters (36 examples) were prepared utilizing [RuCl₂(*p*-cymene)₂]-catalyzed one-pot intramolecular and intermolecular carbenoid N-H insertion reactions. The hydroxyprolines were produced in high diastereoselectivities. These catalytic reactions are tolerant towards air and moisture.

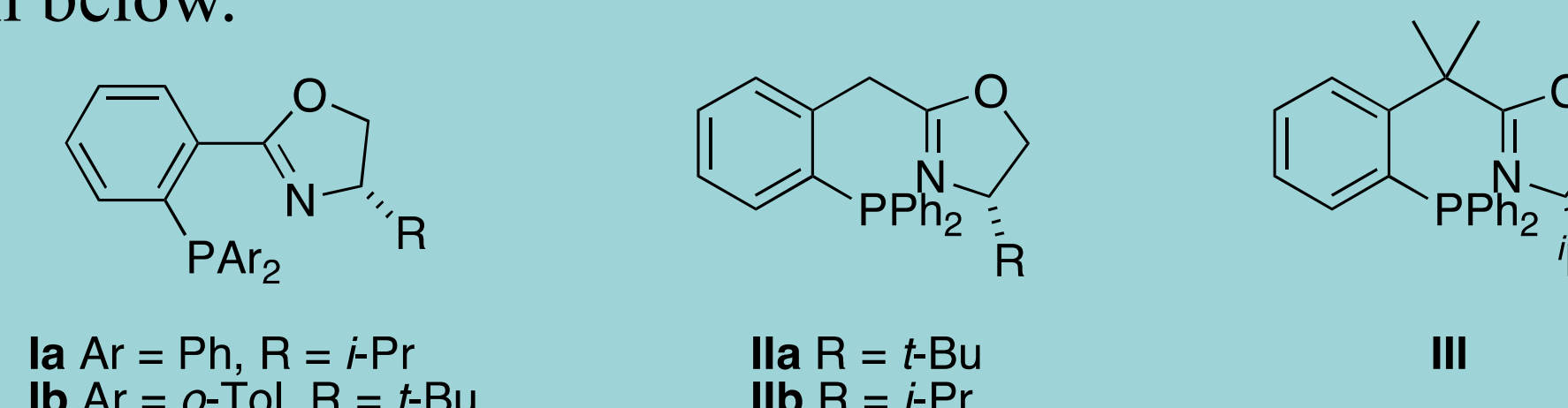


Publications

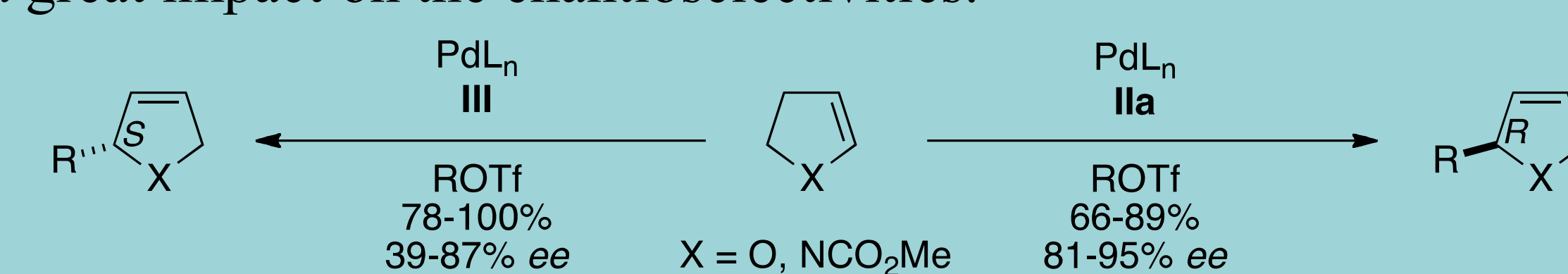
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Benzylic Substituted Ligands in Asymmetric Heck Reaction and Asymmetric Hydrogenation (Xue-Long Hou, Yun-Dong Wu, Qian Peng and Wen-Qiong Wu)

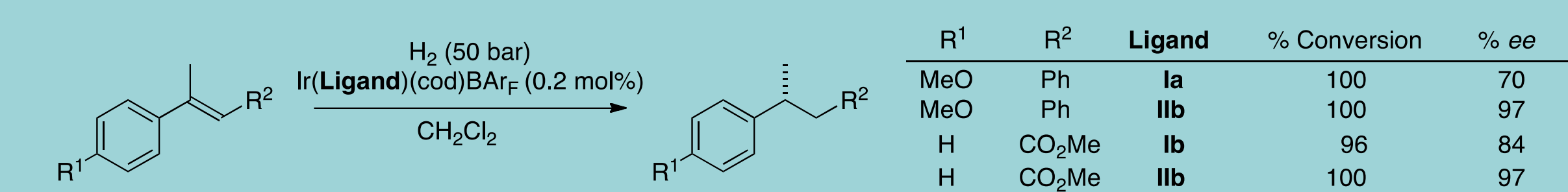
It was discovered that ligands with substituents at the benzylic position showed higher catalytic activities in asymmetric reactions. The structures of some ligands that were synthesized in this program are shown below.



Switch of enantioselectivities was observed for asymmetric Heck reactions of 2,3-dihydrofuran using ligand IIa or III. These results demonstrate that methyl groups at the benzylic position have a great impact on the enantioselectivities.



Ligands Ia, Ib and IIb are all suitable for asymmetric hydrogenation of unfunctionalized alkenes. Higher ee% was observed for IIb that features a benzylic structure.

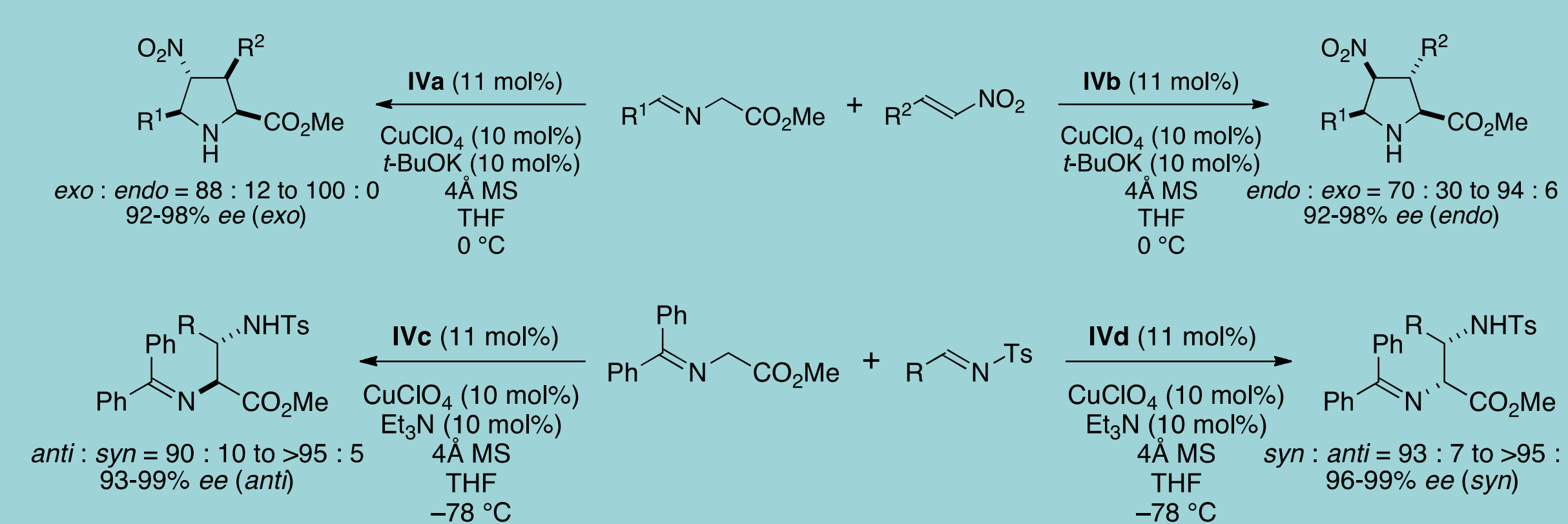


Ferrocene Ligands in Asymmetric Synthesis (Xue-Long Hou, Yun-Dong Wu, Qian Peng, Xiao-Xia Yan, Wen-Hua Zheng and Kai Zhang)

Several ferrocene-based chiral *P,N*-ligands were prepared. Their structures are shown below.



It was found that diastereoselectivity of reactions can be tuned by changing the electronic property of the ligands. For example, copper-catalyzed 1,3-dipolar cycloaddition of azomethine ylides with nitroalkenes furnished either *exo*- or *endo*-pyrrolidines, depending on the electronic property of the the Ar groups on IVa and IVb. The same phenomenon was also observed for Mannich reaction as shown below.



Palladium-catalyzed asymmetric allylic alkylation (AAA) reactions utilizing ferrocene-based ligands Va and Vb were reported to give high regio-, diastereo- and enantio-selectivities. It was also revealed that α-carbanions of acyclic amides are suitable nucleophiles in palladium-catalyzed AAA reactions, leading to high enantioselectivity as demonstrated below. Lithium chloride was found to be essential for high yields and high enantioselectivities.

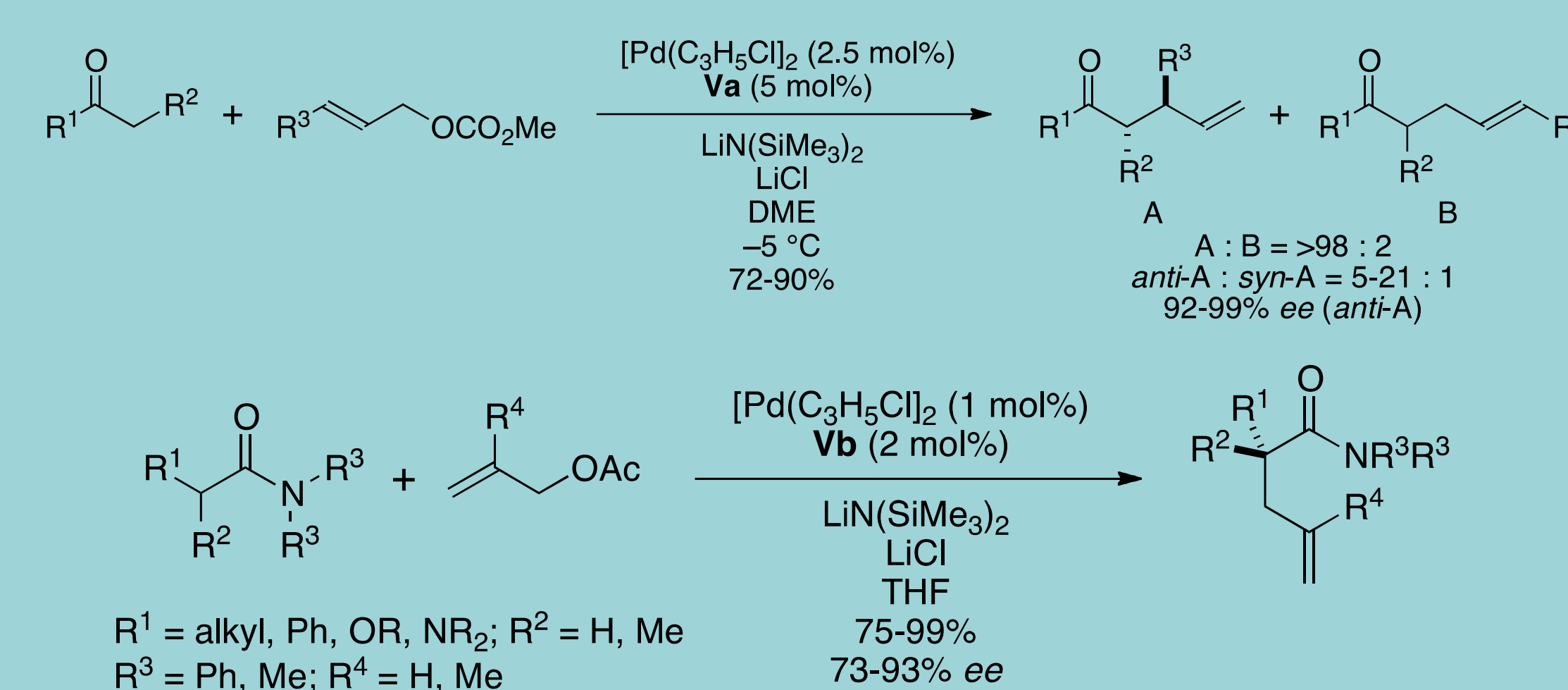


Figure 1. Kinetics of Decomposition of 2,7-Dimethyltetraphenylene at 580 °C and 600 °C

Figure 2. Kinetics of Decomposition of Tetraphenylene at 580 °C and 600 °C