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Development of a Novel Multifunctional N,P Ligand for Highly Enantioselective Palladium-Catalyzed Asymmetric Allylic Etherification of Alcohols and Silanols

Fei Ye,[a] Zhan-Jiang Zheng,[a] Li Li,[a] Ke-Fang Yang,[a] Chun-Gu Xia,[b] and Li-Wen Xu*[a, b]

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Over the last four decades, catalytic asymmetric transformations mediated by bio-, transition-metal, and organic catalysts have served as a powerful means to access a wide range of optically pure compounds.[1] In particular, tremendous efforts have been devoted to transition-metal-based asymmetric catalysis because it is one of the most attractive and practical approaches owing to its high selectivity and atom-economic nature.[2] This approach usually relies on the successful design and synthesis of chiral ligands. In this regard, phosphine-and-nitrogen-containing ligands are extremely attractive for asymmetric catalysis because they are easily prepared from readily available amino acids, chiral amines, or chiral alcohols.[3] Despite the explosive and impressive advances in this field, the design and synthesis of structurally novel and readily accessible phosphine ligands for highly efficient and enantioselective transformations remains a formidable challenge.[1–3] This challenge has motivated chemists to search for novel and simple synthetic approaches to structurally diverse backbones for chiral ligands. Accordingly, in terms of the importance of palladium catalysis in asymmetric synthesis, the development of novel phosphine ligands still needs substantial exploration for highly enantioselective asymmetric transformations to be more practical.

In palladium catalysis, the palladium-catalyzed asymmetric allylic alkylation (AAA, also namely the Tsuji–Trost reaction) is one of the most powerful reactions for construction of carbon–carbon and carbon–heteroatom bonds.[4] In this context, although numerous chiral ligands has been reported for regioselective and enantioselective allylic alkylation with relatively good performance,[4,5] the palladium-catalyzed asymmetric allylic alkylation or etherification (AAE) of alcohols and 1,3-diphenyl-2-propenyl acetate has not been widely reported with high levels of enantioselectivity owing to the mismatch of poor nucleophilicity of alcohols with respect to chiral metal–ligand complexes.[4a,6] Notably, in 2008, Chan and co-workers reported a palladium-catalyzed asymmetric allylic etherification of 1,3-diphenyl-2-propenyl acetate with alcohols in moderate to high yields (58–98%) and good to excellent levels of enantioselectivity (83–96% *ee*) by using the ($S_p R$)-FerroNPS ligand.[7] Meanwhile, the research groups of Hou, Ding, Fukuzawa, Du, and others[8] have also demonstrated independently that various bidentate phosphine or phosphite ligands associated with palladium centers afford chiral allylic ethers in moderate to good levels of enantioselectivity and diastereoselectivity. However, this useful process to provide chiral allylic ethers still needs substantial improvement in its level of enantioselectivity and chemical yield to be more practical.

Inspired by these studies and encouraged by our recent findings on multidentate phosphine ligands that promote highly efficient, enantioselective copper catalysis,[9] we developed a new class of multidentate and multifunctional phosphine ligands for palladium catalysis and asymmetric allylic alkylation, including allylic etherification (AAE). In an effort to develop low-cost, easy-to prepare phosphine ligands, we herein report our recent results on the design and synthesis of a new cyclic tertiary-diamine-containing diphosphine ligands having two nitrogen atoms (CycloN2P2-Phos), a ligand that can be prepared from the very cheap and readily accessible *trans*-1,2-diaminocyclohexane; we also report the application of this ligand in the palladium-catalyzed asymmetric allylic etherification (AAE) of 1,3-diaryl-2-propenyl acetate with alcohols and silanols.

trans-1,2-Diaminocyclohexane is very important chiral molecule that has been applied widely as the precursor of organocatalysts or chiral diamine-based ligands in asymmetric catalysis.[10] In this regard, it was anticipated that the synergy between and Lewis basic nature of two nitrogen centers of the chiral 1,2-diaminocyclohexane backbone would lead to catalysts of superior performance in a variety organic transformations.[11] In addition, chiral *trans*-1,2-diaminocyclohexane is a versatile intermediate for the syntheses of various phosphine ligands that have been developed previously by, for example, the research groups of Trost[12] and Ding,[13] who have contributed greatly to the development of diamine-based phosphine ligands (Figure 1). Realizing the power of *trans*-1,2-diaminocyclohexane-derived phosphine ligands when applied in asymmetric catalysis, we designed and synthesized a novel multifunctional phosphine

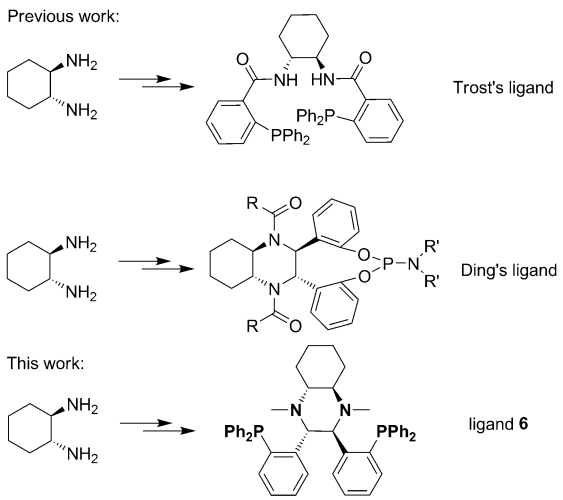

Figure 1. *trans*-1,2-Diaminocyclohexane-derived phosphine ligands.

[a] F. Ye,[+] Dr. Z.-J. Zheng,[+] Dr. L. Li, Dr. K.-F. Yang, Prof. Dr. L.-W. Xu
Key Laboratory of Organosilicon Chemistry and
Material Technology of Ministry of Education
Hangzhou Normal University, Hangzhou 310012 (P. R. China)
Fax: (+86) 571-28865135
E-mail: liwenxu@hznu.edu.cn

[b] Prof. C.-G. Xia, Prof. Dr. L.-W. Xu
State Key Laboratory for Oxo Synthesis and Selective Oxidation
Lanzhou Institute of Chemical Physics (LICP)
Chinese Academy of Sciences (CAS)
Lanzhou, 730000 (P. R. China)

[+] These authors contributed equally to this work

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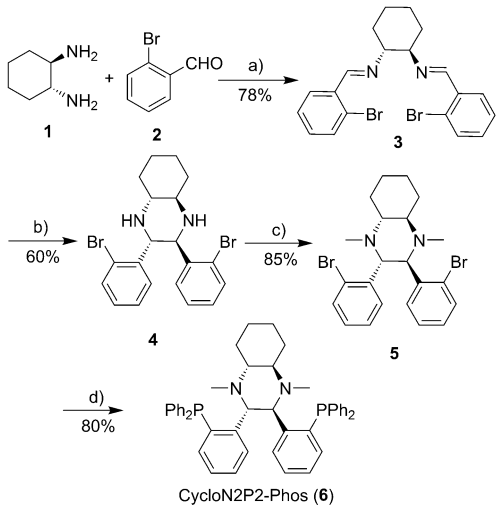


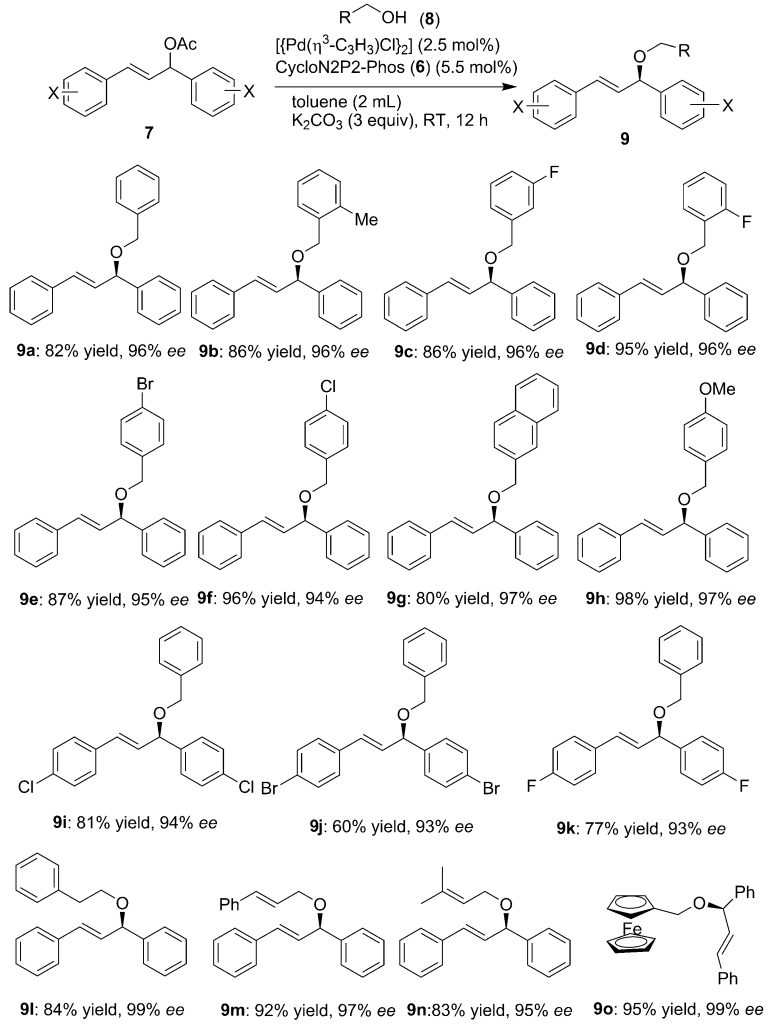
Scheme 1. Synthesis of CycloN2P2-Phos (**6**). Reaction conditions: a) EtOH, 12 h; b) Mn powder, CF_3COOH, CH_3CN, 0–20 °C; c) NaH, CH_3I, THF, 0 °C; d) *n*BuLi, $ClPPh_2$, THF, −40 °C.

ligand (Figure 1); we envisaged the assembly of two phosphorus groups on the chiral 1,2-diaminocyclohexane backbone, thus representing a modular construction of novel multifunctional ligands with four heteroatom centers.

As shown in Scheme 1, novel multifunctional P ligand CycloN2P2-Phos, which contains four stereogenic sp^3 carbon centers, can be prepared via Schiff base **3**, which is formed by the simple condensation of *trans*-1,2-diaminocyclohexane with 2-bromobenzaldehyde. Schiff base **3** was then converted into the dibromo diphenylpiperazine **4** by intramolecular reductive coupling reaction.[14] Notably, the intramolecular reductive coupling of **3** leads to only one diastereoisomer (>99:1 d.r.). The conversion of secondary amine **4** to tertiary amine **5** was performed by treatment with MeI in the presence of strong base. Subsequent bromide–lithium exchange followed by reaction with $ClPPh_2$ gave desired new phosphine ligand CycloN2P2-Phos (**6**). In ligand **6**, variation of the tertiary amine moieties may lead to secondary interactions between phosphine ligand and the substrate that may promote the asymmetric transformation.

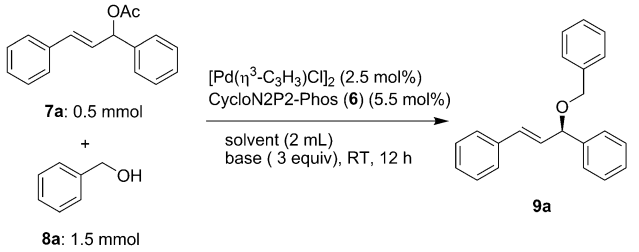
With CycloN2P2-Phos (**6**) in hand, we first examined the efficiency and selectivity of the palladium-catalyzed asymmetric allylic etherification of alcohols. To optimize the reaction conditions, the allylic etherification of 1,3-diphenyl-2-propenyl acetate (**7a**) with benzyl alcohol (**8a**) was used. Initially, the reaction was carried out at room temperature (25 °C) by using 2.5 mol% palladium catalyst [{Pd(η^3-C_3H_3)Cl}$_2$] (5 mol% Pd) and 5.5 mol% CycloN2P2-Phos (**6**). After a preliminary examination of the reaction parameters, such as base and solvent (see Table 1), it was found that toluene and K_2CO_3 were the best choice solvent and base, respectively. The palladium-catalyzed allylic etherification of **7a** and **8a** at room temperature (25 °C) afforded high levels of enantioselectivity (96% *ee*) and good yield (82%; Table 1).

Based on the above study, the palladium-catalyzed asymmetric allylic etherification of various alcohols with allylic acetates **7** were evaluated under the optimized conditions.



Scheme 2. Pd/CycloN2P2-Phos-catalyzed asymmetric allylic etherification of various alcohols with allylic acetates.

Table 1. Initial screening of the asymmetric allylic etherification of 1,3-diphenyl-2-propenyl acetate with benzyl alcohol.[a]



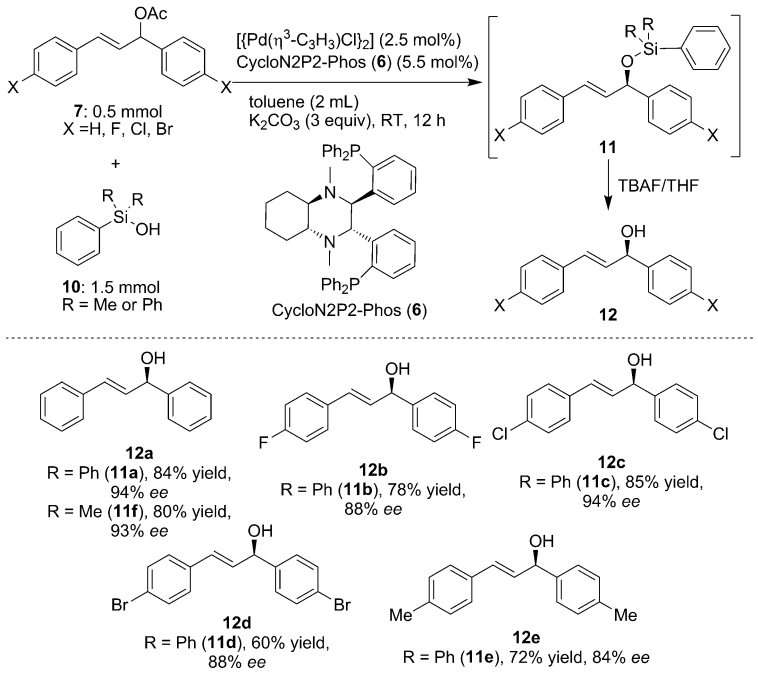
Entry	Solvent	Base	T [°C]	Yield[b] [%]	*ee*[c] [%]
1	toluene	Cs_2CO_3	25	85	91
2	toluene	Cs_2CO_3	0	65	91
3	toluene	Na_2CO_3	25	<10	–[d]
4	toluene	BSA[e]	25	<10	–
5	toluene	KOAc	25	<10	–
6	toluene	K_2CO_3	25	82	96
7	toluene	K_2CO_3	0	<20	–
8	THF	K_2CO_3	25	20	–
9	CH_2Cl_2	K_2CO_3	25	82	92
10	CH_3CN	K_2CO_3	25	34	90
11	Et_2O	K_2CO_3	25	65	94

[a] Conditions: 1,3-diphenyl-2-propenyl acetate (0.5 mmol), [{Pd(η³-C_3H_3)Cl}$_2$] (2.5 mol%), ligand **6** (5.5 mmol%), benzyl alcohol (1.5 mmol), base (3.0 equiv), in solvent (2 mL). [b] Yields obtained upon chromatography. [c] The *ee* value was determined by HPLC on a chiral stationary phase, and the absolute configuration was established by correlation with literature data; see ref [6c]. [d] The enantioselectivity was not determined (ND). [e] BSA = *N*,*O*-bis(trimethylsilyl)acetamide.

As shown in Scheme 2, the reaction proceeded smoothly to afford the desired chiral ethers in good to excellent yields and with high levels of enantioselectivity (93–99% *ee*). Notably, the use of ligand **6** in the asymmetric allylic etherification of allylic alcohols **8m** and **8n** led to the isolation of chiral unsymmetric diallyl ethers, **9m** and **9n**, in good to excellent yields, 92% and 83%, and high levels of enantioselectivity, 97 and 95% *ee*, respectively (Scheme 2). Interestingly, the palladium-catalyzed asymmetric allylic etherification of ferrocene-based alcohol **8o** gave the chiral ether **9o** in excellent yield and enantioselectivity (95% yield and 99% *ee*), a transformation that could be a useful transformation in organic synthesis because of the importance of ferrocene-based derivatives.

Encouraged by the excellent results obtained, we then turned our attention to the asymmetric allylic etherification of allylic acetate with silanols. Notably, no catalytic asymmetric method has been reported to date for the preparation of chiral silyl ethers by using palladium-catalyzed allylic etherification of allylic acetate with silanols. To investigate this transformation using ligand **6**, we selected two aryl silanols as representative substrates. As shown in Scheme 3, the palladium-catalyzed allylic etherification was carried out following the optimized method, that is, [{Pd(η³-C_3H_3)Cl}$_2$] and CycloN2P2-Phos in toluene. The desired silyl ether **11** could be obtained in excellent yields (>90%); however, the determination of enantioselectivity was not easy because of unsuccessful resolution through HPLC using a chiral column. Thus, the *ee* values of **11** were confirmed indirectly by using the corresponding chiral allylic alcohols **12**. Alternatively, it was shown that direct synthesis of chiral allylic alcohols **12** through desilylation of **11** could be performed smoothly. These representative secondary allylic alcohols were isolated in good yields and with high levels of enantioselectivity (up to 94% *ee*; Scheme 3). Indeed, this procedure, asymmetric allylic etherification with silanols and subsequent desilylation, represents one of the best protocol for the synthesis of chiral aromatic allylic alcohols.[15]

In summary, we have investigated a new multidentate phosphine, CycloN2P2-Phos, which is derived from chiral *trans*-1,2-diaminocyclohexane. This scaffold has several features: it is extremely air stable, it contains multiple stereogenic centers, it contains two tertiary amine moieties, and it is easily prepared. We demonstrated its effectiveness as a chiral phosphine ligand in the palladium-catalyzed asymmetric allylic etherification (AAE) of alcohols and silanols, the products being isolated in good to excellent yields and with high levels of enantioselectivity (up to 99% *ee*). To the



Scheme 3. Pd/CycloN2P2-Phos-catalyzed asymmetric allylic etherification of allylic acetate with silanols.

best our knowledge, the use of the palladium complex of CycloN2P2-Phos currently affords the highest levels of enantioselectivity in the palladium-catalyzed asymmetric allylic etherification (AAE) of alcohols and silanols>. Further applications of the Pd/CycloN2P2-Phos complex, in conjunction with detailed mechanistic investigations will be reported in the near future.

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Keywords: allylic etherification · asymmetric catalysis · chiral ligands · palladium · silanols

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