EDGE ARTICLE

Enantioselective copper-catalyzed hydrophosphination of alkenyl isoquinolines†‡

Qingjing Yang,[a] Jian Zhou[ab] and Jun (Joelle) Wang 🆔 *[b]

An enantioselective hydrophosphination of alkenyl isoquinolines is developed by using a copper–chiral diphosphine ligand catalyst. It provides a direct and atom-efficient approach to prepare a variety of chiral phosphines with an isoquinoline unit in good yields and high enantioselectivities. In addition, these chiral phosphine products are useful bidentate P,N-ligands which showed potential application in asymmetric catalysis.

Chiral organophosphorus compounds play a significant role in bioactive molecules, agrochemistry, and functional materials.[1] In addition, they are also broadly applied in transition metal catalysis and organocatalysis as chiral ligands and chiral catalysts.[2] Compared with conventional methods using a stoichiometric amount of chiral starting materials or chiral reagents,[3] asymmetric catalytic approaches have attracted increasing attention in the construction of chiral phosphines. Among them, catalytic asymmetric hydrophosphination is one of the most direct and atom-economical ways for preparation of optically active phosphines.

Pd-Catalyzed asymmetric hydrophosphination of α,β-unsaturated compounds (including α,β-unsaturated aldehydes, ketones, esters, pyrrole amides, sulfonic esters, and sulfonamides) with secondary phosphines has emerged as a versatile method for the construction of chiral phosphine compounds (Scheme 1a).[4] Other transition metal complexes such as chiral Ni,[5] Pt,[6] Cu[7] and Mn[8] catalysts and organocatalysts[9] were also applied in the asymmetric hydrophosphination of electron-deficient alkenes, recently. However, examples where heteroarenes were employed in alkene activation have not appeared due to the relatively poor reactivity of alkenylheteroarenes. In 2021, Terada reported hydrophosphinylation of β-unsubstituted alkenylheteroarene *N*-oxides with SPO (secondary phosphine oxide) catalyzed by their chiral bis(guanidino)iminophosphorane organosuperbase (Scheme 1b).[10] The subsequent reduction of the phosphine oxide product could give quinoline phosphine. Inspired by Yin's recent elegant work on the Cu/TANIAPhos-catalyzed enantioselective
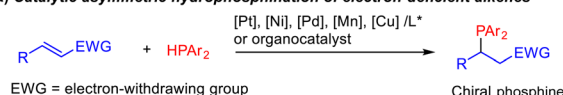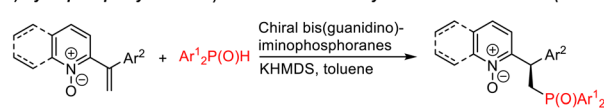
hydrophosphination of α,β-unsaturated amides in which the olefin moiety is sluggishly activated by the adjacent carboxamide group (Scheme 1c),[7a] we envisioned that the long-time unsolved asymmetric hydrophosphination of intrinsic low electrophilic alkenyl-heteroarenes might be realized with a suitable Cu/chiral phosphine catalyst because of its relative stability in the presence of excess HPPh$_2$. Furthermore, the chiral tertiary phosphine products bearing a N-heteroaromatic ring themselves are potentially useful chiral bidentate P,N-ligands in asymmetric catalysis.

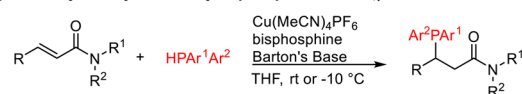**Scheme 1** Examples of asymmetric hydrophosphination of electron-deficient alkenes and asymmetric hydrophosphination to alkenyl azaarenes.

[a]*Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen, 518055, China*

[b]*Department of Chemistry, Hong Kong Baptist University, Kowloon, Hong Kong, China. E-mail: junwang@hkbu.edu.hk*

Based on these design considerations and our prior experience in the construction of chiral organophosphorus compounds,[11] we began our study by examining the hydrophosphination of alkenyl isoquinoline **1a** with diphenyl phosphine **2a** in the presence of a copp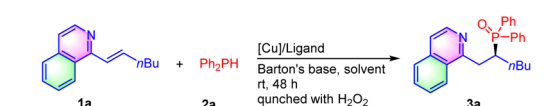er complex and Barton's base in toluene at room temperature (Table 1). (R)-Binap (**L1**) gave the bench-stable secondary phosphine oxide **3a** in 85% yield by the *in situ* oxidation of the labile secondary phosphine product with hydrogen peroxide, avoiding their isolation and purification while maintaining their structural diversity. However, the enantioselectivity of **3a** was very poor (entry 1). Other biphosphine ligands-(R)-Segphos (**L2**), (R)-difluorophos (**L3**), (R, R)-BDPP (**L4**), (R, R)-Ph-BPE (**L5**) and (R, R)-Me-Duphos (**L6**) resulted in low yields and enantio-control (entries 2–6). Catalyzed by (R, R)-QuinoxP* (**L7**), 68% ee was obtained with 77% yield (entry
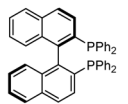
7). To our delight, the reaction with (R, R)-BenzP* (**L8**) provided the hydrophosphination product **3a** in 88% yield with 83% ee (entry 8). Therefore, (R, R)-BenzP* (**L8**) was chosen for further optimization. Other Cu precursors, such as $Cu(MeCN)_4BF_4$, $Cu(OAc)_2$, $Cu(ClO_4)_2 \cdot 6H_2O$, and $Cu(OTf)_2$, were employed, indicating that $Cu(MeCN)_4PF_6$ was the best choice (entry 8 vs. entries 9–12). Next, we examined the effect of a solvent on the reaction. It was showed that the reactions in THF, 1,4-dioxane, DME, and anisole provided product **3a** with similar high yields, but the reaction in anisole gave the highest ee (entries 13–16). Other bases, including DABCO, K_2CO_3, and KOAc, were then tested, and led to a slight decrease of the reaction yields (entries 17–19). On increasing the molar ratio of Barton's base/**1a** from 1 : 1 to 1.5/1, the ee of product **3a** was enhanced to 87% (entry 20). Finally, product **3a** was obtained in 94% yield with 90% ee by lowering the temperature to 0 °C (entry 21).

With the optimal conditions, the substrate scope of substituted alkenyl isoquinolines was then investigated (Table 2). As for β-alkyl substituted alkenyl isoquinolines, both linear alkyl (**3b** and **3c**), benzyl (**3d**) and cyclopropanyl (**3e**) reacted efficiently with diphenyl phosphine **2a** to afford the corresponding products in 80–96% yields with 80–86% ee. The absolute configuration of product **3e** was confirmed as (R) by X-ray crystal structure analysis.[12] Interestingly, there was only 1,4-addition when the conjugate divinyl isoquinoline **1f** was investigated, and the hydrophosphination product **3f** was obtained in 70% yield with 86% ee. Subsequently, substrates with aryl groups were also evaluated. The 1-styrylisoquinoline **1g** reacted smoothly under the reaction conditions, providing the product **3g** in 87% yield and 92% ee. A wide range of alkenyl isoquinolines with an electron-donating group (**3h** and **3i**) or an electron-withdrawing group (**3j**, **3k**, **3l**, **3m**, and **3n**) at the *para*-position of the phenyl ring were tolerated. In general, the reactions afforded products in moderate to excellent yields with moderate to high enantioselectivity. A good outcome was also achieved upon introducing a methyl group at the *meta*-position of the aryl group of the substrate (**3p**). The reaction of **1q** containing a 2-naphthyl substituent proceeded to afford **3q** with a decreased yield and enantioselectivity (70% yield and 77% ee). Substrates with a heteroaryl, such as 2-furanyl (**3r**), 3-furanyl (**3s**), 3-thienyl (**3t**), and 3-pyridinyl (**3u**), were well-tolerated under this catalytic condition. The 2-pyridinyl (**3v**) or 4-pyridinyl (**3w**) substituted substrate also worked well to deliver products in excellent yields, but led to an obvious decrease in enantioselectivities. The reaction between α-phenyl-substituted **1x** and Ph₂PH was attempted, affording the product **3x** in 93% yield and 53% ee. It was found that quinoline **1y** also could be hydrophosphinated with this catalyst at 60 °C to provide the product **3y** in 73% yield with 54% ee. Furthermore, alkenyl pyridines were also compatible with the reaction conditions to deliver the corresponding products in good yields and enantioselectivities (**3z** and **3aa**).
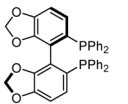
The substitute groups on isoquinolines were also evaluated (Table 2). Substrates with electron-donating groups (Me and OMe) or with electron-withdrawing groups (F and Br) at the 4- (**3ab** and **3ac**), 5-(**3ad**), and 6-positions (**3ae**, **3af**, **3ag** and **3ah**) of the isoquinoline ring were well-tolerated affording products in

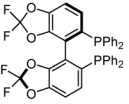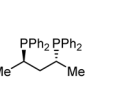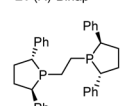**Table 1** Optimization of reaction conditions[a]
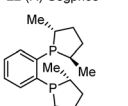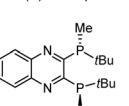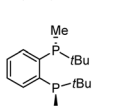
Entry	[Cu]	Ligand	Solvent	Yield[b] (%)	ee[c] (%)
1	$Cu(MeCN)_4PF_6$	**L1**	Toluene	85	3
2	$Cu(MeCN)_4PF_6$	**L2**	Toluene	51	32
3	$Cu(MeCN)_4PF_6$	**L3**	Toluene	52	20
4	$Cu(MeCN)_4PF_6$	**L4**	Toluene	44	40
5	$Cu(MeCN)_4PF_6$	**L5**	Toluene	30	−35
6	$Cu(MeCN)_4PF_6$	**L6**	Toluene	11	7
7	$Cu(MeCN)_4PF_6$	**L7**	Toluene	77	68
8	$Cu(MeCN)_4PF_6$	**L8**	Toluene	88	83
9	$Cu(MeCN)_4BF_4$	**L8**	Toluene	36	83
10	$Cu(OAc)_2$	**L8**	Toluene	48	86
11	$Cu(ClO_4)_2 \cdot 6H_2O$	**L8**	Toluene	74	66
12	$Cu(OTf)_2$	**L8**	Toluene	41	73
13	$Cu(MeCN)_4PF_6$	**L8**	THF	86	84
14	$Cu(MeCN)_4PF_6$	**L8**	1,4-Dioxane	91	83
15	$Cu(MeCN)_4PF_6$	**L8**	DME	93	82
16	$Cu(MeCN)_4PF_6$	**L8**	Anisole	92	85
17[d]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	20	73
18[e]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	35	70
19[f]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	24	68
20[g]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	90	87
21[h]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	91	86
22[g,i]	$Cu(MeCN)_4PF_6$	**L8**	Anisole	94	90

[a] Reaction conditions: [Cu] (10 mol%), ligand (11 mol%), **1a** (0.2 mmol), **2a** (0.3 mmol), Barton's base (1.0 eq.), solvent (1.0 mL). [b] Isolated yields. [c] The ee values were determined by chiral HPLC. [d] DABCO. [e] K_2CO_3. [f] KOAc. [g] 1.5 eq. Barton's base. [h] 2.0 eq. Barton's base. [i] 0 °C.

Table 2 Substrate scope[a]

3a, R = nBu, 94% yield, 90% ee
3b, R = nPr, 96% yield, 86% ee[b,c]
3c, R = nPentyl, 95% yield, 84% ee[b,d]
3d, R = Bn, 80% yield, 80% ee

3e, 92% yield, 82% ee[b]

CCDC 2201645 [3e]

3f, 70% yield, 86% ee[b]

3g, R = H, 87% yield, 92% ee
3h, R = Me, 88% yield, 91% ee[d]

3i, R = OMe, 80% yield, 83% ee[b,d]
3j, R = F, 64% yield, 83% ee[d]
3k, R = Cl, 80% yield, 74% ee[d]
3l, R = Br, 70% yield, 84% ee[c]
3m, R = OCF₃, 94% yield, 81% ee
3n, R = CF₃, 90% yield, 74% ee[b,c]
3o, R = Ph, 66% yield, 80% ee

3p, 89% yield, 81% ee[d]

3q, 70% yield, 77% ee[b,d]

3r, 83% yield, 88% ee[c]
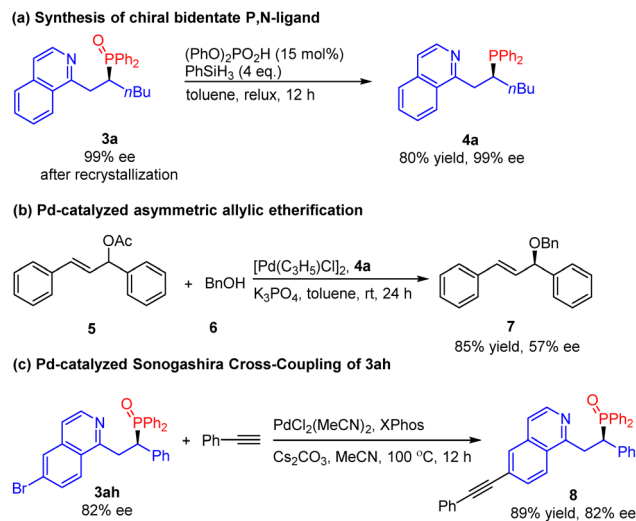
3s, X = O, 93% yield, 87% ee[b,c]
3t, X = S, 72% yield, 84% ee[b]

3u, 86% yield, 91% ee

3v, 92% yield, 71% ee[c]

3w, 97% yield, 79% ee[c]

3x, 93% yield, 53% ee[b]

3y, 73% yield, 54% ee[e]

3z, R = nBu, 76% yield, 87% ee[e]
3aa, R = Ph, 65% yield, 84% ee[e]

3ab, R = Me, 75% yield, 78% ee[b]
3ac, R = Br, 78% yield, 79% ee[d]

3ad, 77% yield, 86% ee[b]

3ae, R = Me, 73% yield, 87% ee[b]
3af, R = OMe, 82% yield, 89% ee[b]
3ag, R = F, 88% yield, 82% ee[b]
3ah, R = Br, 78% yield, 80% ee[d]

3ai, 97% yield, 88% ee[b]

3aj, 91% yield, 86% ee[c]

[a] Reaction conditions: Cu(MeCN)₄PF₆ (10 mol%), ligand (11 mol%), **1** (0.2 mmol), **2** (0.3 mmol), Barton's base (0.3 mmol), anisole (1.0 mL). Isolated yields. The ee values were determined by chiral HPLC. [b] Room temperature. [c] 24 h. [d] 72 h. [e] 60 °C.

Scheme 2 Synthesis applications.

(a) Synthesis of chiral bidentate P,N-ligand

(b) Pd-catalyzed asymmetric allylic etherification

(c) Pd-catalyzed Sonogashira Cross-Coupling of 3ah

73–93% yields with 78–89% ee. Finally, we turned our attention towards the scope of diarylphosphines **2**. Hydrophosphination with (p-Me-C₆H₄)₂PH and (3,5-Me-C₆H₃)₂PH led to the corresponding products **3ai** and **3aj** with excellent yields and good enantioselectivities. However, other phosphines, such as (o-Me-C₆H₄)₂PH, (p-MeO-C₆H₄)₂PH, (p-F-C₆H₄)₂PH and Cy₂PH, were not suitable for the reaction and only trace expected products were detected.

Chiral bidentate P,N-ligands are one of the most important family of ligands widely used in asymmetric catalysis.[13] Therefore, there is an increasing demand for the efficient synthesis of chiral bidentate P,N-ligands. However, most of the protocols for the synthesis of chiral P,N-ligands focused on the chiral

resolution or required tedious multistep synthesis.[14] Herein, the reduction of phosphine oxide product **3a** with phenylsilane in the presence of diphenyl phosphate provided phosphine **4a** in 80% yield without loss of enantiomeric purity (Scheme 2). Subsequently, we examined our P,N-ligand **4a** in the Pd-catalyzed asymmetric allylic etherification of benzyl alcohol, obtaining the desired product **7** in good yield (85%) and moderate ee (57%). In addition, the product **3ah** could also be transformed by Pd-catalyzed Sonogashira cross-coupling. The corresponding alkynylation product **8** was obtained in excellent yield without a decline in enantiopurity.

A possible mechanism for the reaction was proposed based on the literature (Scheme 3).[7a,b,15] Chiral copper complex **V** is formed by Cu(MeCN)₄PF₆ and (R, R)-BenzP*. Coordination between HPPh₂ and chiral copper complex **V** generates complex **I**, which undergoes deprotonation in the presence of Barton's base to produce the nucleophilic copper(I)-diphenylphosphide species **II**. Then, the alkene tethered with isoquinoline coordinates to complex **II** and affords the Cu–phosphido-alkene
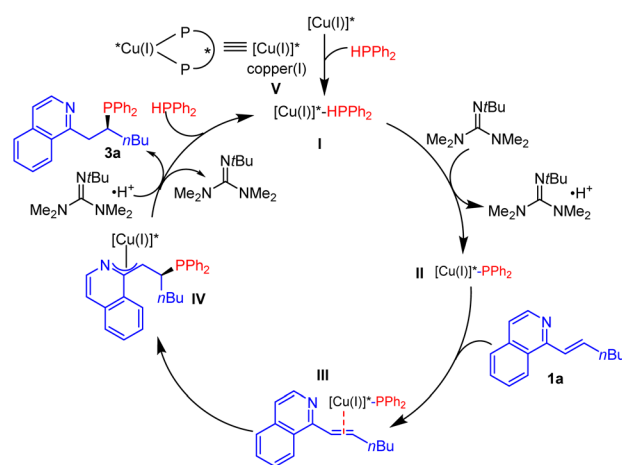
Scheme 3 Proposed catalytic cycle.

complex **III**. Next, asymmetric addition of the diarylphosphido group on copper to the alkenyl-substituted isoquinoline provides an aza-π-allylcopper intermediate **IV**, which is protonated to release the phosphination product **3a** and regenerates copper complex **V** for the next catalytic cycle.

In summary, we have established an operationally simple and highly enantioselective Cu(ɪ)-catalyzed hydrophosphination reaction of alkenyl-substituted isoquinolines. This method afforded a direct and atom efficient access to chiral phosphines with an isoquinoline unit in high yields and enantioselectivities in most cases. Furthermore, the product was showcased as a new chiral P,N-type ligand in palladium-catalyzed asymmetric allylic etherification. Further work on the structure modification and application of these chiral phosphine products in other asymmetric reactions is underway in our laboratory.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.‡

Author contributions

Dr Q. Yang performed the experiments and prepared the supplementary information. J. Zhou collected some data. Prof. J. Wang conceived and directed the project. Q. Yang and J. Wang wrote the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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