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Chiral PCN pincer Ni(II) complex-catalyzed asymmetric hydrophosphination of 2-alkenoylpyridines with diphenylphosphine†

Jin-Ge Li, Bing-Bo Qiu, Hui Jiang, * Mao-Ping Song and Jun-Fang Gong *

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Herein, nine chiral PCN pincer Ni(II) complexes **2** with (phosphine)-(imidazoline) ligands and two complexes **5a** and **5b** bearing (phosphinite)-(imidazoline) ligands were successfully synthesized *via* a "one-pot" phosphination(phosphorylation)/nickelation reaction. All the new complexes were characterized using elemental analysis and NMR spectroscopy. Additionally, the molecular structures of complexes **2a**, **2e** and **5a** were elucidated using X-ray single-crystal diffraction analysis. Their efficacy as enantioselective catalysts for the asymmetric hydrophosphination of 2-alkenoylpyridines was investigated. Using 5 mol% of complex **2a** as the catalyst in the presence of Et_3N, various 2-alkenoylpyridines reacted smoothly with diphenylphosphine to afford structurally diverse chiral pyridine-containing phosphine derivatives in yields up to 99% with an enantioselectivity up to 98% ee. Further transformations of the catalysis products were also studied.

Introduction

Chiral P-containing organic molecules have wide applications in the fields of asymmetric catalysis,[1] materials[2] and pharmaceuticals.[3] A large number of methods have been developed for the construction of these compounds.[4] Among them, organo-[5] or transition-metal-catalyzed[6,7] asymmetric hydrophosphination of electron-deficient alkenes with trivalent secondary or primary phosphines provides a direct and atom-economic approach for the synthesis of chiral phosphines, which are valuable ligands or organocatalysts for enantioselective transformations. In this regard, the cyclopalladated catalysts, particularly pincer Pd catalysts, stand out, and they have shown great potential since their first successful application in the field of asymmetric hydrophosphination in 2010.[6,8,9] For example, the bis(phosphine) PCP Pd pincer complex **A** bearing stereogenic benzylic methylene centers (Chart 1) developed by Duan and co-workers is an extremely powerful and versatile catalyst for hydrophosphination of enones,[9a,i] enals,[9b] α,β-unsaturated *N*-acylpyrroles[9c] and carboxylic esters,[9d] nitroalkenes,[9e] α,β-unsaturated and α,β,γ,δ-unsaturated sulfonic esters[9f,g] with diarylphosphines. Using this catalyst, structurally diverse chiral phosphine derivatives from the 1,4- or 1,6-conjugate addition were generated in high yields with excellent enantioselectivity (≥90% ee). The PCP pincer catalyst **B**, an interesting complex which was prepared *via* catalytic asymmetric hydrophosphination followed by palladation[10a] performed well in hydrophosphination of α,β,γ,δ-unsaturated ketones (dienones) to afford exclusively the 1,4-addition products with excellent enantioselectivity (up to >99% ee).[10b] While the PCP complex **C** containing P-stereogenic centers instead of C-stereogenic centers exhibited good stereocontrol in the hydrophosphination of nitroalkenes[11a] and β,γ-unsaturated α-keto esters[11b] (up to 83% and 93% ee, respectively). Besides the PCP Pd pincers, bis(imidazoline) NCN **D**,[12a] the hybrid (aminophosphine)-(imidazoline) PCN **E** (ref. 12*b*) and (phosphinite)-(imidazoline) PCN **F** (ref. 12*c*) Pd pincers have been proved by us to be effective and stereoselective catalysts for the hydrophosphination of enones (up to 94% ee, 94% ee and 98% ee, respectively). Recently, we have disclosed the synthesis of a series of (phosphine)-(imidazoline) PCN Pd pincers and found that complex **G** (ref. 12*d*) showed promising enantioselectivity

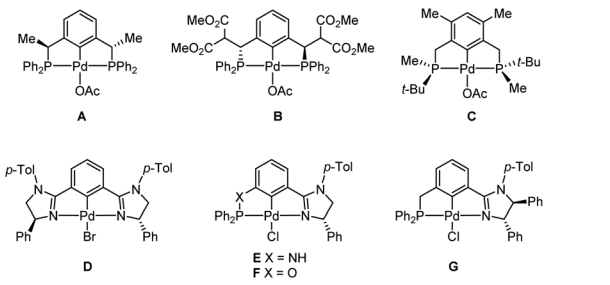

Chart 1 Pincer Pd(II) complexes used in asymmetric hydrophosphination.

College of Chemistry, Pingyuan Laboratory, Zhengzhou University, Zhengzhou 450001, China. E-mail: jiangh@zzu.edu.cn; gongjf@zzu.edu.cn

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in the hydrophosphination of 2-alkenoylpyridines with Ph_2PH (24 examples, 41–87% ee).

As described above, pincer Pd complexes, particularly those with P-donors, have become privileged chiral catalysts for the related asymmetric hydrophosphination. Moreover, pincer Pd-catalyzed hydrophosphination of specially designed substrates followed by the metalation reaction is a relatively simple and efficient route for the construction of new chiral metal (Pd and Ni) pincer complexes.[9a,b,12c,13,14] The obtained Pd and Ni pincers either have intriguing structural characteristics or can be further employed as catalysts with high efficiency for asymmetric hydrophosphination. Notably, the unique and stable terdentate coordination mode of the pincer complexes, which effectively prevents the deactivation of catalysts caused by the coordination of the P-nucleophiles and the P-adducts, is certainly the key factor responsible for the great success of Pd pincers. Despite all these advantages, the precious nature of palladium leads to some limitations for their use in mass production. Therefore, the development of efficient but inexpensive metal catalysts with the pincer backbone for enantioselective hydrophosphination is highly desirable.

In comparison with the well-studied Pd pincer catalysts,[6,9–13] chiral pincer Ni catalysts remain underdeveloped, although Ni is relatively inexpensive and abundant. In this respect, Zhang, Imamoto and co-workers reported that the PCP Ni complex **H** possessing P-stereogenic centers (Chart 2) could catalyze the asymmetric aza-Michael addition of α,β-unsaturated nitriles with moderate enantioselectivity (up to 46% ee).[15] While Kumagai, Shibasaki and co-workers found that CCC Ni complex **I** afforded high levels of stereocontrol in the asymmetric addition of alkylnitriles to aldimines or aldehydes (up to 98%, 95% ee and 96% ee, respectively).[16] In particular, Wang, Duan and co-workers developed unsymmetric PCP′ Ni complex **J** as the catalyst to realize the first highly enantioselective synthesis of P-stereogenic secondary phosphine-boranes by the asymmetric addition of primary phosphine to electron-deficient alkenes such as enones (up to 99% ee and >20 : 1 dr).[14] Recently, they have demonstrated that the PCN Ni complex **K** exhibited excellent enantioselectivity in the asymmetric hydrophosphination of enones with Ph_2PH (up to 98% ee).[17] Overall, the use of chiral pincer nickel complexes in enantioselective transformations is still limited. To develop more chiral Ni pincers as cost-effective and stereoselective catalysts for asymmetric synthesis and also in continuation of our research interest in pincer chemistry,[6c,12,18] we synthesized a series of (phosphine)-(imidazoline) PCN Ni pincers **2** (Scheme 1) and investigated their potential in the catalytic asymmetric hydrophosphination of 2-alkenoylpyridines with Ph_2PH. A variety of pyridine-containing phosphine derivatives were thus generated from the catalytic reactions in good yields and enantioselectivity. It is known that chiral phosphines functionalized by pyridine can serve as bidentate N,P ligands for transition metal-catalyzed asymmetric transformations.[19] Consequently, the obtained catalytic products have potential use in asymmetric catalysis. The results are as follows.

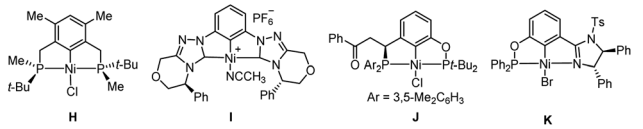


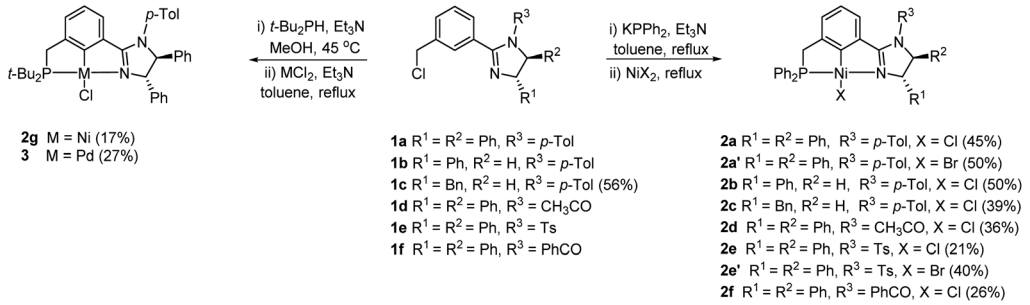
Chart 2 Pincer Ni(II) complexes used in asymmetric reactions.

Results and discussion

Synthesis of chiral (phosphine)-(imidazoline) PCN pincer Ni(II) complexes

The pincer Ni(II) complexes **2a–f** including **2a′** and **2e′** were successfully prepared *via* a "one-pot" phosphination/nickelation reaction (Scheme 1).[20] Thus, chiral imidazoline ligands **1a–f** with different chiral substituents and NR^3 groups, which were synthesized according to the procedure reported previously,[12d] were first phosphinated by treatment with $KPPh_2$ in the presence of Et_3N in refluxing toluene for 12 h. Then, $NiCl_2$ was added and refluxed for another 12 h for C–H nickelation. The corresponding PCN pincer Ni(II) chloride complexes **2a–f** were isolated in 21–50% yields after purification. When $NiBr_2$ was used for nickelation, the bromide complexes **2a′** and **2e′** were obtained in 50% and 40% yields, respectively. In addition, the Ni(II) chloride complex **2g** with a *t*-Bu_2P group instead of a Ph_2P group was prepared by a similar "one-pot" phosphination/nickelation reaction. In this case, the ligand **1a** first reacted with excess *t*-Bu_2PH in MeOH at 45 °C for 24 h, followed by the addition of Et_3N at room temperature and stirring for 0.5 h to complete the phosphination.[21] After evaporation of the solvent under vacuum, the residue was extracted with ether and filtered through a Cellite pad. Then ether and the remaining *t*-Bu_2PH were removed under vacuum. Next, toluene, Et_3N and $NiCl_2$ were added and refluxed for 12 h to achieve C–H nickelation. The expected pincer Ni(II) complex **2g** was successfully obtained albeit in a rather low yield of 17%. Following the same procedure, but using $PdCl_2$ instead of $NiCl_2$, gave the pincer Pd(II) chloride complex **3** in 27% yield. This complex was prepared for comparison with the Ni complexes.

All of the complexes are air- and moisture-stable in both the solid state and solution. The ligand **1c** and the pincer complexes **2** and **3** are new compounds. They were well characterized by elemental analysis (HRMS for the ligand 1c), ^1H NMR, $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR (for the complexes) spectroscopy. For example, in the ^1H NMR spectra of the ligands, a singlet or a triplet with a small coupling constant of 1.8 Hz (for **1c** and **1f**) appears at δ in the range of 7.52–7.87 ppm for the central aryl proton located adjacent to both CH_2Cl and the imidazoline ring, whereas the associated signal disappears in the ^1H NMR spectra of the complexes, suggesting the formation of a Ni–C or Pd–C bond in the pincer complexes. In addition, the appearance of signals corresponding to the protons of Ph_2P or *t*-Bu_2P in the ^1H NMR spectra, the extensive P–C coupling in the $^{13}C\{^1H\}$ NMR spectra and the single resonance at around 43 ppm or 84 ppm in the $^{31}P\{^1H\}$ NMR spectra of the complexes also indicate the formation of the pincer complexes.



2g M = Ni (17%)
3 M = Pd (27%)

1a $R^1 = R^2 = Ph$, $R^3 = p$-Tol
1b $R^1 = Ph$, $R^2 = H$, $R^3 = p$-Tol
1c $R^1 = Bn$, $R^2 = H$, $R^3 = p$-Tol (56%)
1d $R^1 = R^2 = Ph$, $R^3 = CH_3CO$
1e $R^1 = R^2 = Ph$, $R^3 = Ts$
1f $R^1 = R^2 = Ph$, $R^3 = PhCO$

2a $R^1 = R^2 = Ph$, $R^3 = p$-Tol, X = Cl (45%)
2a' $R^1 = R^2 = Ph$, $R^3 = p$-Tol, X = Br (50%)
2b $R^1 = Ph$, $R^2 = H$, $R^3 = p$-Tol, X = Cl (50%)
2c $R^1 = Bn$, $R^2 = H$, $R^3 = p$-Tol, X = Cl (39%)
2d $R^1 = R^2 = Ph$, $R^3 = CH_3CO$, X = Cl (36%)
2e $R^1 = R^2 = Ph$, $R^3 = Ts$, X = Cl (21%)
2e' $R^1 = R^2 = Ph$, $R^3 = Ts$, X = Br (40%)
2f $R^1 = R^2 = Ph$, $R^3 = PhCO$, X = Cl (26%)

Scheme 1 Synthesis of the chiral (phosphine)-(imidazoline) PCN pincer Ni(II) complexes **2** and pincer Pd(II) complex **3**.

Molecular structures of the pincer Ni complexes

The PCN pincer coordination mode in these complexes was clearly confirmed by X-ray single-crystal diffraction analysis of the crystal structures of Ni(II) complexes **2a** and **2e**. The molecules of **2a** and **2e**·CH_2Cl_2 are shown in Fig. 1 and 2, respectively. The selected bond lengths and angles are collected in Table 1. The P and N atoms as well as the C atom of the central aryl in the complexes **2a** and **2e** coordinate with the Ni(II) center to form two fused five-membered nickelacycles, where N–Ni–P has a bond angle of around 161° and C–Ni–Cl has a bond angle of around 173°. These two five-membered nickelacycles are almost coplanar with the central aromatic ring and the imidazoline ring. Both the C–Ni–P angles and the C–Ni–N angles are around 83° in the complexes, which are typical for pincers consisting of two fused five-membered metallacycles and reflect the relative steric strain of the system.[12,17,20] The metal–ligand distances and bond angles around the Ni(II) center in complexes **2a** and **2e** are similar to the bond lengths of Ni–C, Ni–N and Ni–P being around 1.89 Å, 1.91 Å and 2.12 Å, respectively, which are comparable to those in the related chiral PCN pincer Ni complexes with (aminophosphine)-(imidazoline) ligand[12b] or (phosphinite)-(imidazoline) ligands.[17] In addition, the metal-tridentate ligand bond lengths in the Ni complex **2a** are all shorter than the corresponding Pd complex,[12d] following the expected pattern of Ni < Pd.

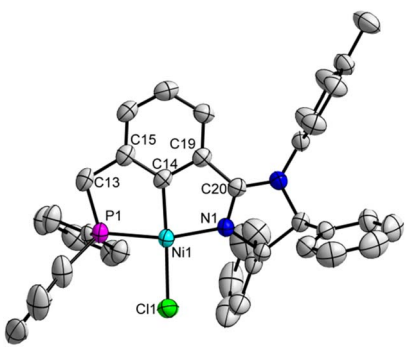


Fig. 1 Molecular structure of complex **2a** with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms are omitted for clarity).

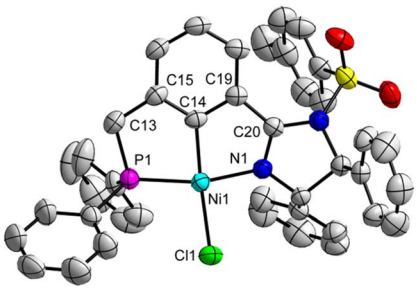


Fig. 2 Molecular structure of complex **2e**·CH_2Cl_2 with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms and the solvent molecule are omitted for clarity).

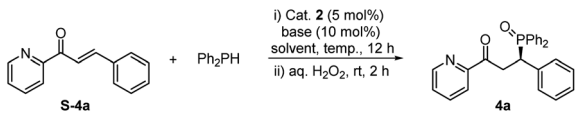
Table 1 Selected bond lengths (Å) and angles (°) for **2a** and **2e**·CH_2Cl_2

	2a	**2e**·CH_2Cl_2
Ni–C	1.885(4)	1.891(4)
Ni–P	2.1182(11)	2.1408(12)
Ni–N	1.913(3)	1.918(3)
Ni–Cl	2.2193(11)	2.2130(12)
C–Ni–P	82.57(12)	83.07(13)
C–Ni–N	83.17(15)	82.29(16)
C–Ni–Cl	173.41(12)	172.81(13)
N–Ni–P	160.98(11)	160.65(11)
P–Ni–Cl	96.37(5)	100.99(5)
N–Ni–Cl	99.19(10)	94.96(11)

Catalytic studies

To evaluate the potential of the newly obtained PCN pincer Ni(II) complexes in asymmetric hydrophosphination, the addition of Ph_2PH to (*E*)-2-(3-phenylacryloyl)pyridine with the Ni pincers as the catalysts was first investigated (Table 2; for the convenience of operation, the P-adduct of this reaction and all the other adducts from hydrophosphination were oxidized to the corresponding phosphine oxides for analysis). Under the same conditions as the PCN Pd pincer **G**-catalyzed hydrophosphination of enones,[12d] the Ni pincer **2a**, which has the same ligands as the **G**, afforded the product **4a** only in 55% yield with 10% ee (entry 1). By contrast, **4a** was obtained in >99% yield with 85% ee with the Pd pincer **G** as the catalyst.[12d] A survey of several solvents other than acetone (entries 2–7) indicated that the catalyst **2a** behaved much better in CH_3CN,

Table 2 Optimization of reaction conditions for the asymmetric hydrophosphination of (*E*)-2-(3-phenylacryloyl)pyridine with diphenylphosphine catalyzed by the PCN pincer Ni(II) complexes **2**[a]

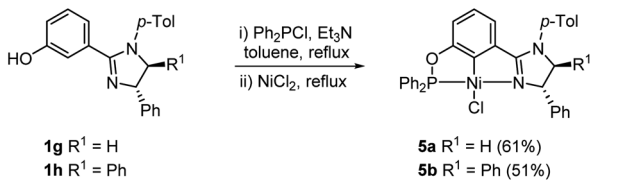


Entry	Cat.	Base	Solvent	Temp. (°C)	Yield[b] (%)	ee[c,d] (%)
1	**2a**	KOAc	Acetone	rt	55	10
2	**2a**	KOAc	DCM	rt	87	0
3	**2a**	KOAc	Toluene	rt	93	20
4	**2a**	KOAc	THF	rt	76	40
5	**2a**	KOAc	MeOH	rt	99	0
6	**2a**	KOAc	*n*-Hexane	rt	85	54
7	**2a**	KOAc	CH_3CN	rt	88	67
8	**2a**	KOAc	CH_3CN	10	88	70
9	**2a**	KOAc	CH_3CN	0	85	86
10	**2a**	KOAc	CH_3CN	−10	78	84
11	**2a′**	KOAc	CH_3CN	0	88	82
12	**2b**	KOAc	CH_3CN	0	75	9
13	**2c**	KOAc	CH_3CN	0	85	6[e]
14	**2d**	KOAc	CH_3CN	0	73	0
15	**2e**	KOAc	CH_3CN	0	62	22
16	**2e′**	KOAc	CH_3CN	0	75	28
17	**2f**	KOAc	CH_3CN	0	52	84
18	**2g**	KOAc	CH_3CN	0	91	2
19	**2a**	Cs_2CO_3	CH_3CN	0	59	32
20	**2a**	$NaHCO_3$	CH_3CN	0	53	24[e]
21	**2a**	NaOH	CH_3CN	0	72	84
22	**2a**	KOH	CH_3CN	0	95	58
23	**2a**	Et_3N	CH_3CN	0	93	92
24	**2a**	**Et_3N**[f]	**CH_3CN**	**0**	**91**	**95**
25	**2a**	Et_3N[g]	CH_3CN	0	95	92
26	**2a**[h]	Et_3N	CH_3CN	0	78	84

[a] Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and (*E*)-2-(3-phenylacryloyl)pyridine (0.3 mmol) in the presence of the pincer Ni complex **2** (5 mol%) and base (10 mol%) in 2 mL of solvent for 12 h. [b] Isolated yield. [c] Determined using chiral HPLC analysis. [d] The major enantiomer of the product **4a** was determined to have the (*R*)-configuration by comparing its optical rotation with that of the same compound in ref. 12*d*. [e] The major enantiomer of the product **4a** has the (*S*)-configuration. [f] Using 20 mol% of Et_3N. [g] Using 30 mol% of Et_3N. [h] Using 3 mol% of catalyst.

giving the product **4a** in 88% yield with 67% ee (entry 7). Lowering the temperature led to higher ee values (entries 8–10) and a good enantioselectivity of 86% ee could be achieved at 0 °C (85% yield, entry 9). With CH_3CN as the solvent and at 0 °C, the performance of the other eight Ni pincers was tested (entries 11–18). The bromide counterpart of **2a** (complex **2a′**) gave a comparable yield (88%) and ee value (82%, entry 11). While changing the chiral substituent from (4*S*,5*S*)-diphenyl to (4*S*)-phenyl or benzyl resulted in rather poor enantioselectivity (entries 12 and 13). The enantioselectivity also varied with the groups on the imidazoline-N and the P donor (entries 14–18). Unfortunately, only complex **2f** with *N*-benzoyl could provide a good enantioselectivity of 84% ee (52% yield, entry 17). Complexes with *N*-acetyl, *N*-Ts or *t*-Bu_2P gave a racemic product or a product with low enantioselectivity (entries 14–16 and 18). Subsequently, with complex **2a** as the best catalyst, various bases including Cs_2CO_3, $NaHCO_3$, NaOH, KOH, and Et_3N were screened (entries 19–23). Pleasingly, using Et_3N as the base, both the yield and enantioselectivity were improved and excellent results were obtained (85% yield with 86% ee *vs.* 93% yield with 92% ee, entry 9 *vs.* 23). Increasing the amount of Et_3N led to a further improvement in the enantioselectivity or the yield (entries 24 and 25) and the best enantioselectivity (95% ee, entry 24) was achieved with 20 mol% of Et_3N. Finally, with a reduction in catalyst loading of **2a** from 5 mol% to 3 mol%, the product **4a** was generated in obviously decreased yields and enantioselectivity (entry 26). Consequently, on the basis of the above-mentioned results, the optimized conditions for the model reaction include using 5 mol% of complex **2a** as the catalyst in the presence of 20 mol% of Et_3N as the base in CH_3CN at 0 °C (entry 24).

In our previous studies, it was found that the (phosphine)-(imidazoline) PCN Pd pincer **G** (Chart 1) exhibited inferior stereocontrol in most cases when compared with the related (phosphinite)-(imidazoline) PCN Pd pincer **F** (Chart 1) in the asymmetric hydrophosphination of 2-alkenoylpyridines.[12c,d] Therefore, to further evaluate the performance of the current Ni catalysts (the Ni analogues of Pd pincer **G**) in asymmetric hydrophosphination, the related chiral (phosphinite)-(imidazoline) pincer Ni(II) complexes **5a** and **5b** (the Ni analogues of Pd pincer **F**) were prepared according to the method reported previously (Scheme 2).[12c] The two new complexes were also well characterized by means of elemental analysis and NMR spectroscopy. The molecular structure of complex **5a** was determined by X-ray single-crystal diffraction analysis (Fig. 3). The catalytic properties of the four complexes, namely the Pd pincer **3** and the three Ni pincers **2a**, **5a** and **5b**, in the reaction of (*E*)-2-(3-phenylacryloyl)pyridine with Ph_2PH under several different conditions were compared (Table 3). The choice of the conditions was based on the current (*vide supra*) and previous results.[12c] When CH_3CN and KOAc were used as the solvent and base, respectively, both the Pd complex **3** and the Ni complex **2a** worked well to afford the product **4a** in high yields and enantioselectivity with the Pd complex **3** being slightly better (entries 1 and 2). The Ni complexes **5a** and **5b** showed higher activity but lower stereoselectivity, especially **5a** (entries 3 and 4). Interestingly, complex **5a** mainly afforded (*S*)-enantiomer of the product **4a**, which was opposite to that of the other three complexes. With Et_3N as the base, the Ni complexes **2a** and **5b** containing the same imidazoline ring provided good results (entries 5 and 8). However, the Pd complex **3** and the Ni complex **5a** behaved poorly, either giving low yield or low enantioselectivity (entries 6



Scheme 2 Synthesis of the chiral (phosphinite)-(imidazoline) PCN pincer Ni(II) complexes **5a** and **5b**.

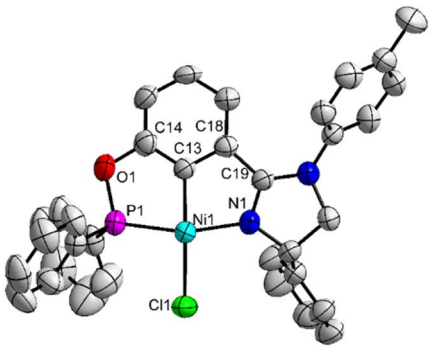
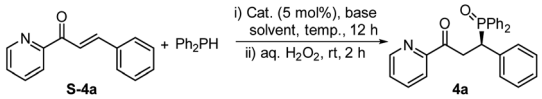


Fig. 3 Molecular structure of complex **5a** with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms are omitted for clarity; one of the two independent molecules is shown).

Table 3 Enantioselective hydrophosphination of (*E*)-2-(3-phenylacryloyl)pyridine with diphenylphosphine catalyzed by the PCN pincer metal complexes **2a**, **3**, **5a** and **5b**[a]



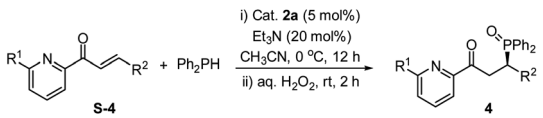
Entry	Cat.	Solvent	Base	Temp. (°C)	Yield[b] (%)	ee[c,d] (%)
1	**2a**	CH_3CN	KOAc	0	85	86
2	**3**	CH_3CN	KOAc	0	87	90
3	**5a**	CH_3CN	KOAc	0	91	30[e]
4	**5b**	CH_3CN	KOAc	0	92	79
5	**2a**	CH_3CN	Et_3N	0	91	95
6	**3**	CH_3CN	Et_3N	0	40	64
7	**5a**	CH_3CN	Et_3N	0	99	27[e]
8	**5b**	CH_3CN	Et_3N	0	99	88
9	**2a**	Toluene	KOAc	0	44	66
10	**5a**	Toluene	KOAc	0	79	0
11	**5b**	Toluene	KOAc	0	61	0
12	**2a**	Toluene	KOAc	−10	43	42
13	**5a**	Toluene	KOAc	−10	58	0
14	**5b**	Toluene	KOAc	−10	53	8

[a] Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and (*E*)-2-(3-phenylacryloyl)pyridine (0.3 mmol) in the presence of the complex **2a**, **3**, or **5** (5 mol%) and Et_3N (20 mol%) or KOAc (10 mol%) in 2 mL of solvent for 12 h. [b] Isolated yield. [c] Determined using chiral HPLC analysis. [d] The major enantiomer of the product **4a** was determined to have the (*R*)-configuration by comparing its optical rotation with that of the same compound in ref. 12*d*. [e] The major enantiomer of the product **4a** has the (*S*)-configuration.

and 7). With toluene and KOAc as the solvent and base, respectively, where the Pd pincer **F** performed very well,[12c] no Ni catalysts could give satisfactory results (entries 9–14). Among them, complex **2a** furnished moderate enantio-selectivity, while the other two Ni pincers even gave (almost) racemic products. Roughly, the Ni pincers **5a** and **5b** were more active but the Ni pincer **2a** was the most stereoselective under the selected conditions.

Among the twelve PCN pincers, namely one Pd and eleven Ni pincers, the Ni pincer **2a** gave the best stereocontrol, therefore, with **2a** as the catalyst, the asymmetric hydrophosphination of a wide range of 2-alkenoylpyridines with Ph_2PH was then examined under the optimized reaction conditions (Table 2, entry 24). As shown in Table 4, substituents either electron-donating or electron-withdrawing on β-phenyl and on 6-position of pyridine in the pyridine-containing α,β-unsaturated ketone substrates were well tolerated with the current system. The substituents include Me, Et, OMe, F, Cl, Br, I and NO_2 and the desired oxidized P-adducts **4b–v** were produced in generally high yields (83–99%, 16 of 21 examples, entries 2–22). The *ortho*-substituent (Me) on β-phenyl of the 2-alkenoylpyridine led to reduced yield (79%), especially reduced enantioselectivity (50% ee), which might be likely due to steric hindrance of the *ortho*-position (entries 2–4). In the case of *p*-F substituted 2-alkenoylpyridine, both the yield and enantioselectivity of the

Table 4 Enantioselective hydrophosphination of 2-alkenoylpyridines with diphenylphosphine catalyzed by the PCN pincer Ni(II) complex **2a**[a]



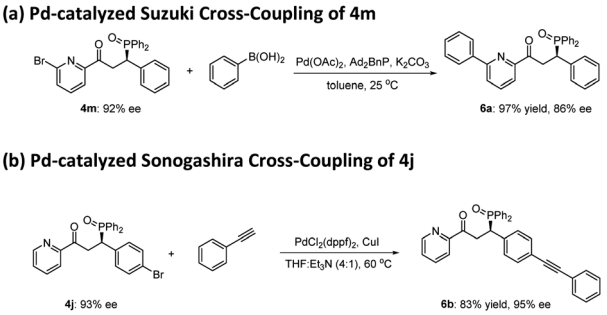
Entry	R^1	R^2	Product	Yield[b] (%)	ee[c,d] (%)
1	H	Ph	**4a**	91	95(85)[e](89)[f]
2	H	*o*-MeC_6H_4	**4b**	79	50(69)[e]
3	H	*m*-MeC_6H_4	**4c**	88	81(80)[e]
4	H	*p*-MeC_6H_4	**4d**	89	91(77)[e](73)[f]
5	H	*p*-EtC_6H_4	**4e**	92	92(87)[e]
6	H	*p*-$OMeC_6H_4$	**4f**	85	92(86)[e](95)[f]
7	H	*m*-ClC_6H_4	**4g**	92	84(82)[e]
8	H	*p*-ClC_6H_4	**4h**	96	86
9	H	*m*-BrC_6H_4	**4i**	99	81(66)[e](85)[f]
10	H	*p*-BrC_6H_4	**4j**	98	93(67)[e](87)[f]
11	H	*p*-IC_6H_4	**4k**	96	90
12	H	*p*-$NO_2C_6H_4$	**4l**	97	85(88)[f]
13	Br	Ph	**4m**	88	92(58)[e]
14	Br	*p*-MeC_6H_4	**4n**	91	98(62)[e]
15	Br	*p*-EtC_6H_4	**4o**	90	82(60)[e]
16	Br	*p*-$OMeC_6H_4$	**4p**	71	78(75)[e]
17	Br	*p*-ClC_6H_4	**4q**	83	91(41)[e]
18	Me	Ph	**4r**	88	91(85)[e]
19	Me	*p*-FC_6H_4	**4s**	60	60
20	Me	*p*-ClC_6H_4	**4t**	93	95(80)[e]
21	Me	*p*-BrC_6H_4	**4u**	79	91
22	Me	*p*-IC_6H_4	**4v**	76	88
23	H		**4w**	90	53(64)[e](46)[f]
24	H		**4x**	98	81(66)[e](82)[f]
25	H	*t*-Bu	**4y**	87	20(n.d.)[e]

[a] Hydrophosphination reactions were performed with Ph_2PH (0.2 mmol) and 2-alkenoylpyridines (0.3 mmol) in the presence of complex **2a** (5 mol%) and Et_3N (20 mol%) in 2 mL of CH_3CN at 0 °C for 12 h. [b] Isolated yields. [c] Determined using chiral HPLC analysis. [d] The absolute configurations of the known products were assigned to be *R* by comparing their optical rotations with those in ref. 12*d*, and the configurations of the new products were assigned by analogy. [e] Results from ref. 12*d*. [f] Results from ref. 12*c*.

product **4s** were moderate (60%, entry 19). Gratifyingly, good to excellent enantioselectivity (78–98% ee) was achieved in all other cases, and in most cases, the enantioselectivity was higher than 90% (entries 3–18 and 20–22). It was found that the stereoselectivity varied with the position and electronic property of the substituent in the substrates. For example, 2-alkenoylpyridines bearing a *meta*-substituent on β-phenyl yielded the corresponding phosphine oxides with lower enantioselectivities than those possessing a *para*-substituent (entry 3 *vs.* 4, 7 *vs.* 8 and 9 *vs.* 10). However, a clear trend for the effect of electronic property of the substituent on the enantioselectivity could not be obtained. In addition to 2-alkenoylpyridines with β-phenyl and β-substituted phenyl, 2-alkenoylpyridines with β-1-naphthyl and even β-heteroaryl such as β-2-thienyl were also suitable substrates for this transformation, furnishing the oxidized P-adducts **4w** and **4x** in excellent yields with moderate to high enantioselectivity (90% yield with 53% ee and 98% yield with 81% ee, respectively, entries 23 and 24). Finally, 2-alkenoylpyridine containing a β-*tert*-butyl (alkyl) group reacted smoothly with Ph_2PH, delivering the product **4y** in 87% yield albeit with a rather modest ee value (20% ee, entry 25).

It should be noted that the PCN Ni pincer **2a** exhibited comparable or better stereocontrol than its Pd analogue, the Pd pincer **G** (Chart 1)[12d] in most cases (Table 4). For example, Ni catalyst **2a** furnished the products **4a**, **4d**, **4i**, **4j**, **4m**, **4n**, **4o**, **4q**, **4t** and **4x** bearing phenyl, substituted phenyl, 6-substituted 2-pyridyl or 2-thienyl in much higher ee values than the Pd catalyst **G** with the same catalyst loading (95% *vs.* 85%, 91% *vs.* 77%, 81% *vs.* 66%, 93% *vs.* 67%, 92% *vs.* 58%, 98% *vs.* 62%, 82% *vs.* 60%, 91% *vs.* 41%, 95% *vs.* 80% and 81% *vs.* 66%, respectively, entries 1, 4, 9, 10, 13–15, 17, 20 and 24). Only in the cases of the products **4b** and **4w** with *o*-MeC_6H_4 or 1-naphthyl, the Ni complex **2a** gave lower enantioselectivity than the Pd complex **G** (50% *vs.* 69% and 53% *vs.* 64%, respectively, entries 2 and 23). However, in comparison with the related PCN Pd pincer **F** (Chart 1),[12c] the Ni pincer **2a** afforded much better enantioselectivity when the β-*p*-MeC_6H_4 enone substrate was subjected to the hydrophosphination (91% *vs.* 73%, entry 4). In other cases, Ni pincer **2a** showed comparable stereocontrol (entries 1,6, 9, 10, 12, 23 and 24). Interestingly, both the Ni pincer **2a** and the Pd pincer **G** yielded (*R*)-**4**, while the Pd pincer **F** provided (*S*)-**4** as the major products in the catalytic reactions. In terms of the catalytic activity, the Ni pincer **2a** was generally lower than the Pd pincer **G**. There is one exception. With **2a** as the catalyst, the reaction of β-*tert*-butyl 2-alkenoylpyridine with Ph_2PH proceeded well and the desired product **4y** was obtained in 87% yield (entry 25). However, in the presence of the catalyst **G** the same reaction gave only trace amounts of the product **4y**. Overall, the current investigations provide a more stereoselective but less expensive catalyst for the asymmetric hydrophosphination of 2-alkenoylpyridines.

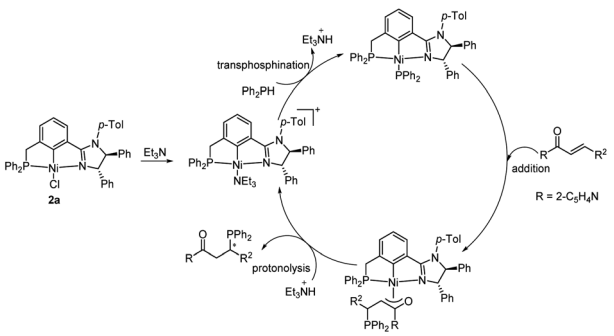
To further explore the practical potential of the above-described method, transformation reactions of the catalysis products were carried out (Scheme 3). The Br-substituent on the pyridine of the oxidized P-adduct **4m** could be smoothly converted to phenyl by the Pd-catalyzed Suzuki coupling reaction, furnishing the product **6a** in excellent yield without any obvious loss in enantioselectivity (86% ee, Scheme 3a). The Br-substituent of **4j** could also be transformed to alkynyl by the Pd/Cu-catalyzed Sonogashira coupling reaction and the desired product **6b** was obtained in 83% yield without any loss of enantioselectivity (95% ee, Scheme 3b). Similar to the catalysis products, these transformed products are potentially useful chiral N,O-[12c] or N,P-ligands.



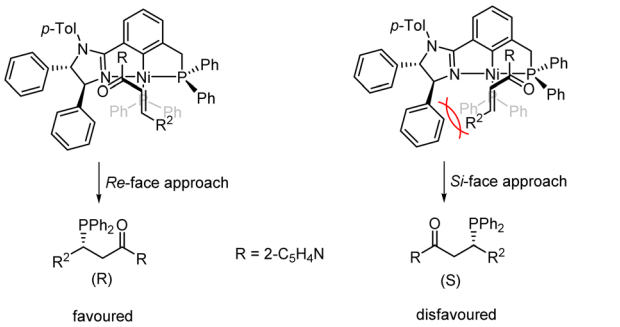
Scheme 3 (a) Suzuki and (b) Sonogashira cross-coupling reactions of **4m** and **4j**, respectively, to afford **6a** and **6b**.

Based on the related studies[9a,12c,14,17] as well as our experimental results, a plausible catalytic cycle for the current asymmetric hydrophosphination is proposed and shown in Scheme 4. The reaction would be initiated by replacement of the chloride in the PCN pincer Ni catalyst **2a** by Et_3N to generate the chiral cationic Ni–NEt_3 complex. Then, transphosphination between the Ni–NEt_3 complex with diphenylphosphine affords the nickel phosphido intermediate (Ni-PPh_2). The subsequent intermolecular, nucleophilic addition of the diphenylphosphido group on nickel to 2-alkenoylpyridine occurs to produce the oxa-π-allylnickel intermediate, which undergoes protonolysis with Et_3N^+H to form the P-adduct along with the regeneration of the active pincer Ni–NEt_3 catalyst.

According to the stereochemical outcomes of the current hydrophosphination reactions as well as literature reports on the pincer Pd-catalyzed asymmetric hydrophosphination of enones,[12c,d] a possible pathway for the formation of (*R*)-**4** was proposed (Scheme 5). To minimize the unfavorable steric repulsions between the R^2 substituent at the β-position of the enone and the (4*S*)-phenyl group on the imidazoline ring of the catalyst, the enone substrate approaches the Ni-PPh_2



Scheme 4 Proposed mechanism of asymmetric hydrophosphination.



Scheme 5 Possible stereochemical pathway for the formation of (*R*)-**4**.

intermediate with its *Re*-face preferentially. This facial selectivity leads to the formation of the products **4** with (*R*)-configuration as the major enantiomers.

Conclusions

In summary, we have developed unsymmetrical chiral PCN pincer Ni(II) complexes as less expensive and stereoselective catalysts for the asymmetric hydrophosphination of 2-alkenoylpyridines with Ph_2PH. During the investigations, twelve chiral pincer complexes, namely one Pd(II) and eleven Ni(II) pincers were successfully synthesized and well characterized. All the complexes were able to catalyze the stated hydrophosphination, among which the Ni complex **2a** afforded the best stereocontrol. Using complex **2a** as the catalyst, various pyridine-functionalized chiral phosphine oxides with structural diversity were produced in generally high yields with good to excellent enantioselectivity. Furthermore, the obtained chiral phosphine oxides could be readily transformed by metal-catalyzed coupling reactions to provide new and potentially useful chiral ligands for asymmetric catalysis.

Experimental section

General information

Solvents were dried using standard methods and freshly distilled prior to use if needed. Chiral ligand **1** (ref. 12*d* and 20*b*) and enone substrates[22] were prepared according to the methods reported in the literature. All other chemicals were commercially available and used without further purification. NMR spectra were recorded using a Bruker DPX-600, DPX-400, or DPX-300 spectrometer with $CDCl_3$ as the solvent, TMS as the internal standard for ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR and 85% H_3PO_4 as the external standard for $^{31}P\{^1H\}$ NMR. HRMS was determined using a Waters/Agilent Q-Tof Micro MS/MS System ESI spectrometer. The enantiomeric excesses of (*R*)- and (*S*)-enantiomers were determined by HPLC analysis over a chiral column using a UV detector. The melting points were measured using a WC-1 instrument and uncorrected. Elemental analyses were performed using a Thermo Flash EA 1112 elemental analyzer. Optical rotations were recorded using an SGW®-2 polarimeter.

The analytical data of the new ligand **1c** are as follows.

(*S*)-4-Benzyl-2-(3-(chloromethyl)phenyl)-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazole (1c). Yellow oil (420.0 mg, 56% based on the 3-chloromethylbenzamido alcohol). $[\alpha]_D^{20} = -21$ (*c* 0.386, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.52 (t, J = 1.8 Hz, 1H, ArH), 7.31–7.11 (m, 8H, PhH and ArH), 6.84 (d, J = 8.2 Hz, 2H, NArH), 6.45 (d, J = 8.4 Hz, 2H, NArH), 4.50–4.42 (m, 3H, CH_2Cl and NCH), 3.92 (app t, J = 9.8 Hz, 1H, NCH_2), 3.60 (dd, J = 7.1, 9.5 Hz, 1H, NCH_2), 3.16 (dd, J = 4.5, 13.6 Hz, 1H, CH_2), 2.76 (dd, J = 8.6, 13.6 Hz, 1H, CH_2), 2.15 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 161.5, 140.2, 138.2, 137.5, 133.5, 131.4, 130.0, 129.5, 129.3, 129.1, 128.8, 128.42, 128.36, 126.4, 122.9, 65.1, 58.4, 45.8, 42.2, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{24}H_{24}ClN_2^+$: 375.1623, found: 375.1627.

Synthesis of the chiral (phosphine)-(imidazoline) PCN pincer nickel(II) complexes 2a–f, 2a′ and 2e′

Ligand **1** (0.5 mmol) was added to a 25 mL dry Schlenk flask in an argon atmosphere. Et_3N (139 μL, 1.0 mmol), $KPPh_2$ (1.2 mL, 0.5 M in THF) and anhydrous toluene (10 mL) were then added. The resulting mixture was refluxed for 12 h. Then, $NiCl_2$ (194 mg, 1.5 mmol) or $NiBr_2$ (328 mg, 1.5 mmol) was added and the reaction mixture was refluxed for another 12 h. After cooling, filtration, and evaporation, the residue was purified by column chromatography on silica gel using CH_2Cl_2/EtOAc (50/1) as an eluent to produce the corresponding PCN pincer complex **2a–f**, **2a′** and **2e′**.

(2-((4*S*,5*S*)-4,5-Diphenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) chloride (2a). Yellow solid (153.0 mg, 45%). Mp: 286–288 °C. $[\alpha]_D^{20} = +52$ (*c* 0.115, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H, PPhH), 7.86–7.83 (m, 2H, PPhH), 7.55–7.53 (m, 2H, ArH), 7.43–7.28 (m, 15H, PPhH and ArH), 7.05–7.00 (m, 4H, ArH), 6.75–6.72 (m, 1H, ArH), 6.31 (d, J = 7.6 Hz, 1H, ArH), 5.27 (d, J = 4.9 Hz, 1H, NCH), 4.74 (d, J = 4.9 Hz, 1H, NCH), 3.78 (d, J = 10.4 Hz, 2H, CH_2P), 2.31 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.5, 165.6 (d, J = 30.8 Hz), 147.4 (d, J = 21.4 Hz), 144.4, 140.9, 138.0, 136.6 (d, J = 4.4 Hz), 133.5 (d, J = 10.4 Hz), 132.6 (d, J = 10.0 Hz), 132.2 (d, J = 39.8 Hz), 131.8 (d, J = 41.1 Hz), 130.4, 130.14, 130.05, 129.1, 128.7, 128.5 (d, J = 9.9 Hz), 128.4, 127.25, 127.19, 127.1, 126.7 (d, J = 19.4 Hz), 126.4, 124.3, 124.0, 80.4, 72.2, 42.5 (d, J = 38.5 Hz), 21.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 42.5. Anal. calcd for $C_{41}H_{34}ClN_2NiP \cdot 0.35CH_2Cl_2$: C, 69.99; H, 4.93; N, 3.95. Found: C, 70.06; H, 4.78; N, 3.79.

(2-((4*S*,5*S*)-4,5-Diphenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) bromide (2a′). Yellow solid (181.1 mg, 50%). Mp: 290–292 °C. $[\alpha]_D^{20}$ = +50 (*c* 0.119, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.01–7.98 (m, 2H, PPhH), 7.86–7.79 (m, 2H, PPhH), 7.54 (d, J = 7.1 Hz, 2H, ArH), 7.44–7.29 (m, 14H, PPhH and ArH), 7.04–6.74 (m, 6H, ArH), 6.32 (d, J = 7.6 Hz, 1H, ArH), 5.39–5.27 (m, 1H, NCH), 4.75–4.73 (m, 1H, NCH), 3.79–3.76 (m, 2H, CH_2P), 2.30 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.8, 167.4 (d, J = 29.9 Hz), 147.3 (d, J = 21.5 Hz), 144.5, 140.8, 138.0, 136.5 (d, J = 6.1 Hz), 133.8 (d, J = 10.5 Hz), 132.7 (d, J = 9.8 Hz), 132.4 (d, J = 41.8 Hz), 131.8 (d, J = 42.6 Hz), 130.5, 130.2, 130.1, 129.1, 128.7,

128.5 (d, J = 10.0 Hz), 128.4, 127.3, 127.2, 126.8 (d, J = 18.9 Hz), 126.5, 126.4, 124.3, 124.2, 80.5, 73.0, 43.6 (d, J = 38.2 Hz), 21.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 42.5. Anal. calcd for $C_{41}H_{34}BrN_2NiP$: C, 67.99; H, 4.73; N, 3.87. Found: C, 68.06; H, 4.63; N, 3.67.

(*S*)-(2-((Diphenylphosphino)methyl)-6-(4-phenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)phenyl)nickel(II) chloride (2b). Yellow solid (150.9 mg, 50%). Mp: 141–142 °C. $[\alpha]_D^{20}$ = +27 (c 0.105, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 7.97–7.94 (m, 2H, PPhH), 7.85–7.82 (m, 2H, PPhH), 7.56 (d, J = 8.2, 2H, ArH), 7.41–7.34 (m, 8H, PPhH and ArH), 7.27 (d, J = 7.3 Hz, 1H, ArH), 7.21–7.15 (m, 4H, ArH), 6.97 (d, J = 7.6 Hz, 1H, ArH), 6.71 (t, J = 7.6 Hz, 1H, ArH), 6.33 (d, J = 7.6 Hz, 1H, ArH), 5.40 (dd, J = 3.8, 10.8 Hz, 1H, NCH), 4.44 (app t, J = 10.3 Hz, 1H, NCH_2), 3.94 (dd, J = 3.8, 9.8 Hz, 1H, NCH_2), 3.77–3.68 (m, 2H, CH_2P), 2.39 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.6, 165.4 (d, J = 31.0 Hz), 147.2 (d, J = 21.1 Hz), 144.2, 137.9, 137.5, 136.5, 133.5 (d, J = 10.3 Hz), 132.5 (d, J = 10.0 Hz), 132.3 (d, J = 42.5 Hz), 131.6 (d, J = 40.4 Hz), 130.5 (d, J = 2.4 Hz), 130.3, 130.1 (d, J = 2.2 Hz), 128.6 (d, J = 9.4 Hz), 128.5 (d, J = 11.7 Hz), 127.1, 126.7, 126.53, 126.51 (d, J = 19.0 Hz), 124.3, 124.0, 64.8, 61.9, 42.5 (d, J = 38.8 Hz), 21.2. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 42.6. Anal. calcd for $C_{35}H_{30}ClN_2NiP\cdot 0.5CH_2Cl_2$: C, 65.98; H, 4.84; N, 4.34. Found: C, 66.08; H, 4.72; N, 4.21.

(*S*)-(2-(4-Benzyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino) methyl)phenyl)nickel(II) chloride (2c). Yellow solid (120.5 mg, 39%). Mp: 122–124 °C. $[\alpha]_D^{20}$ = −175 (c 0.111, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.04–8.01 (m, 2H, PPhH), 7.94–7.91 (m, 2H, PPhH), 7.46–7.38 (m, 8H), 7.21–7.12 (m, 5H), 6.94–6.83 (m, 3H), 6.65 (t, J = 7.6 Hz, 1H, ArH), 6.14 (d, J = 7.6 Hz, 1H, ArH), 4.53–4.49 (m, 1H, NCH), 4.03 (t, J = 10.1 Hz, 1H, NCH_2), 3.80–3.69 (m, 3H, NCH_2 and CH_2P), 3.37 (dd, J = 3.3, 13.3 Hz, 1H, CH_2), 3.05 (dd, J = 8.1, 13.3 Hz, 1H, CH_2), 2.36 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 168.9, 164.7 (d, J = 30.5 Hz), 147.3 (d, J = 21.5 Hz), 138.1, 137.5, 137.3, 136.8, 133.1 (d, J = 10.1 Hz), 132.8 (d, J = 10.1 Hz), 132.1 (d, J = 40.7 Hz), 131.9 (d, J = 40.6 Hz), 130.5 (d, J = 2.4 Hz), 130.3 (d, J = 2.4 Hz), 130.1, 128.7 (d, J = 9.9 Hz), 128.6 (d, J = 9.9 Hz), 128.1, 126.3 (d, J = 19.3 Hz), 126.2, 124.0, 123.9, 60.4, 59.8, 42.8 (d, J = 38.7 Hz), 41.2, 21.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 43.0. Anal. calcd for $C_{36}H_{32}ClN_2NiP$: C, 69.99; H, 5.22; N, 4.53. Found: C, 69.74; H, 5.50; N, 4.09.

(2-((4*S*,5*S*)-1-Acetyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) chloride (2d). Yellow solid (113.7 mg, 36%). Mp: 262–264 °C. $[\alpha]_D^{20}$ = −38 (c 0.102, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 7.6 Hz, 1H, ArH), 7.91–7.88 (m, 2H, PPhH), 7.79–7.76 (m, 2H, PPhH), 7.47–7.31 (m, 16H), 7.14–7.08 (m, 2H, ArH), 5.25 (s, 1H, NCH), 5.13 (s, 1H, NCH), 3.82 (d, J = 10.7 Hz, 2H, CH_2P), 2.05 (s, 3H, $COCH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 169.8, 169.1, 166.2 (d, J = 29.5 Hz), 147.0 (d, J = 21.4 Hz), 141.1, 139.4, 136.9, 133.3 (d, J = 10.5 Hz), 132.7 (d, J = 9.9 Hz), 131.4 (d, J = 41.4 Hz), 131.3 (d, J = 42.4 Hz), 130.6 (d, J = 2.5 Hz), 130.4 (d, J = 2.5 Hz), 129.7, 129.1, 128.9, 128.6 (d, J = 10.7 Hz), 128.5 (d, J = 10.8 Hz), 128.4, 128.1, 127.8 (d, J = 19.4 Hz), 126.2, 125.1, 125.0, 73.3, 72.2, 42.3 (d, J = 38.5 Hz), 24.4. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 42.7. Anal. calcd for $C_{32}H_{30}ClN_2NiOP$: C, 68.44; H, 4.79; N, 4.43. Found: C, 68.20; H, 4.66; N, 4.22.

(2-((4*S*,5*S*)-4,5-Diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) chloride (2e). Yellow solid (78.1 mg, 21%). Mp: 153–154 °C. $[\alpha]_D^{20}$ = −33 (c 0.100, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, J = 7.7 Hz, 1H, ArH), 7.94–7.90 (m, 2H, PPhH), 7.73–7.70 (m, 2H, PPhH), 7.46–7.30 (m, 13H), 7.23–7.20 (m, 1H), 7.17–7.09 (m, 6H), 7.03 (d, J = 8.0, 2H, ArH), 5.38 (d, J = 2.5 Hz, 1H, NCH), 5.30 (d, J = 2.5 Hz, 1H, NCH), 3.83–3.80 (m, 2H, CH_2P), 2.36 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 167.3, 166.1 (d, J = 29.3 Hz), 147.5 (d, J = 21.1 Hz), 145.0, 141.9, 140.3, 136.0, 135.3, 133.5 (d, J = 10.4 Hz), 132.4 (d, J = 10.0 Hz), 131.5 (d, J = 41.5 Hz), 131.1 (d, J = 42.5 Hz), 130.7 (d, J = 2.5 Hz), 130.4 (d, J = 2.5 Hz), 130.0, 129.2, 128.7, 128.6 (d, J = 10.0 Hz), 128.5, 128.0 (d, J = 19.4 Hz), 127.7, 127.3, 127.1, 126.2, 126.0, 125.1, 75.8, 70.5, 42.4 (d, J = 38.6 Hz), 21.6. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 43.1. Anal. calcd for $C_{41}H_{34}ClN_2NiO_2PS\cdot CH_2Cl_2$: C, 60.86; H, 4.38; N, 3.38. Found: C, 61.05; H, 4.33; N, 3.19.

(2-((4*S*,5*S*)-4,5-Diphenyl-1-tosyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) bromide (2e′). Yellow solid (157.7 mg, 40%). Mp: 150–152 °C. $[\alpha]_D^{20}$ = −28 (c 0.105, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, J = 7.6 Hz, 1H, ArH), 7.94–7.91 (m, 2H, PPhH), 7.74–7.71 (m, 2H, PPhH), 7.47–7.30 (m, 13H), 7.23–7.10 (m, 7H), 7.03 (d, J = 7.9, 2H, ArH), 5.38 (s, 1H, NCH), 5.30 (s, 1H, NCH), 3.83–3.80 (m, 2H, CH_2P), 2.36 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 167.3, 166.1 (d, J = 29.3 Hz), 147.5 (d, J = 21.1 Hz), 145.0, 141.9, 140.3, 136.0, 135.3, 133.5 (d, J = 10.5 Hz), 132.5 (d, J = 10.0 Hz), 131.5 (d, J = 41.6 Hz), 131.1 (d, J = 42.7 Hz), 130.7, 130.4, 130.0, 129.2, 128.7, 128.6 (d, J = 9.7 Hz), 128.5, 128.0 (d, J = 19.3 Hz), 127.7, 127.3, 127.1, 126.2, 126.0, 125.1, 75.8, 70.5, 42.4 (d, J = 38.4 Hz), 21.6. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 43.1. Anal. calcd for $C_{41}H_{34}BrN_2NiO_2PS\cdot 0.5CH_2Cl_2$: C, 60.00; H, 4.25; N, 3.37. Found: C, 60.24; H, 4.22; N, 3.15.

(2-((4*S*,5*S*)-1-Benzoyl-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-6-((diphenylphosphino)methyl)phenyl)nickel(II) chloride (2f). Yellow solid (90.2 mg, 26%). Mp: 160–162 °C. $[\alpha]_D^{20}$ = +26 (c 0.107, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ 7.86–7.83 (m, 2H, PPhH), 7.76–7.73 (m, 2H, PPhH), 7.40–7.23 (m, 18H), 7.15–7.11 (m, 4H), 7.02 (d, J = 7.6 Hz, 1H, ArH), 6.91 (dt, J = 1.3, 7.7 Hz, 1H, ArH), 5.20 (d, J = 2.2 Hz, 1H, NCH), 5.00 (d, J = 2.2 Hz, 1H, NCH), 3.76 (d, J = 10.6 Hz, 2H, CH_2P). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 170.9, 170.6, 165.8 (d, J = 30.8 Hz), 147.0 (d, J = 21.1 Hz), 140.6, 140.2, 136.9, 133.9, 133.3 (d, J = 10.4 Hz), 132.7 (d, J = 10.0 Hz), 132.6, 131.5 (d, J = 41.3 Hz), 131.3 (d, J = 42.5 Hz), 130.6 (d, J = 2.4 Hz), 130.4 (d, J = 2.4 Hz), 129.4, 129.0, 128.62 (d, J = 10.1 Hz), 128.58 (d, J = 9.4 Hz), 128.4, 128.0, 127.5 (d, J = 19.2 Hz), 127.2, 126.4, 125.7, 124.7, 75.0, 72.9, 42.5 (d, J = 39.1 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 42.8. Anal. calcd for $C_{41}H_{32}ClN_2NiO_2P\cdot 0.75CH_2Cl_2$: C, 66.20; H, 4.46; N, 3.70. Found: C, 66.06; H, 4.55; N, 3.40.

Synthesis of the PCN pincer metal complexes 2g and 3

Under an argon atmosphere, di-*tert*-butylphosphine (0.2 mL, 1.1 mmol) was added to a solution of **1a** (218.1 mg, 0.5 mmol) in

MeOH (5 mL, deoxygenated prior to use) in a 25 mL Schlenk flask. The solution was heated and stirred at 45 °C for 24 h and then cooled to room temperature. Degassed Et_3N (0.5 mL) was added and the mixture was stirred for 0.5 h. After evaporation of the solvent under vacuum, the residue was extracted with ether and filtered through a Cellite pad. After removal of diethyl ether under vacuum, the flask was heated at 60 °C for 1 h under vacuum to remove the remaining di-*tert*-butyl phosphine. The residue was transferred to a 25 mL dry Schlenk tube, and then anhydrous toluene (10 mL), Et_3N (83 μL, 0.6 mmol) and $PdCl_2$ (106 mg, 0.6 mmol) or Et_3N (139 μL, 1 mmol) and $NiCl_2$ (194 mg, 1.5 mmol) were added under an argon atmosphere, and the reaction mixture was refluxed for 12 h. After cooling, filtration, and evaporation, the residue was purified by column chromatography on silica gel with CH_2Cl_2/EtOAc (50/1) as the eluent to produce the corresponding PCN pincer complexes **2g** or **3**.

(2-((Di-*tert*-butylphosphino)methyl)-6-((4*S*,5*S*)-4,5-diphenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)phenyl)nickel(II) chloride (2g). Yellow solid (54.3 mg, 17%). Mp: 116–118 °C. $[\alpha]_D^{20}$ = +18 (*c* 0.109, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.1 Hz, 2H, PhH), 7.38–7.24 (m, 9H), 7.04–6.92 (m, 4H), 6.67 (dt, J = 1.3, 7.6 Hz, 1H, ArH), 6.26 (d, J = 7.6 Hz, 1H, ArH), 5.26 (d, J = 4.8 Hz, 1H, NCH), 4.70 (d, J = 4.8 Hz, 1H, NCH), 3.10 (d, J = 8.7 Hz, 2H, CH_2P), 2.29 (s, 3H, CH_3), 1.45 (d, J = 13.0 Hz, 9H, *t*-Bu_2H), 1.44 (d, J = 13.2 Hz, 9H, *t*-Bu_2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.0, 165.0 (d, J = 27.9 Hz), 149.7 (d, J = 18.4 Hz), 144.9, 141.0, 137.7, 136.8, 136.1 (d, J = 1.3 Hz), 129.9, 129.0, 128.5, 128.3, 127.2, 127.1, 127.0, 126.2, 126.0 (d, J = 16.3 Hz), 123.6, 123.3, 80.2 (d, J = 1.9 Hz), 71.7, 34.6 (d, J = 25.8 Hz), 34.4 (d, J = 24.7 Hz), 33.6 (d, J = 30.3 Hz), 29.6 (d, J = 3.6 Hz), 29.3 (d, J = 3.2 Hz), 21.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 83.8. Anal. calcd for $C_{37}H_{42}ClN_2NiP \cdot 0.2CH_2Cl_2$: C, 68.02; H, 6.55; N, 3.98. Found: C, 68.02; H, 6.51; N, 4.26.

((2-((Di-*tert*-butylphosphino)methyl)-6-((4*S*,5*S*)-4,5-diphenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)phenyl)palladium(II)) chloride (3). Yellow solid (92.8 mg, 27%). Mp: 136–138 °C. $[\alpha]_D^{20}$ = +42 (*c* 0.131, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.0 Hz, 2H, PhH), 7.39–7.24 (m, 9H), 7.12–7.04 (m, 4H), 6.73 (dt, J = 1.3, 7.7 Hz, 1H, ArH), 6.41 (d, J = 7.8 Hz, 1H, ArH), 5.40 (d, J = 5.3 Hz, 1H, NCH), 4.70 (d, J = 5.3 Hz, 1H, NCH), 3.33–3.17 (m, 2H, CH_2P), 2.30 (s, 3H, CH_3), 1.42 (d, J = 14.1 Hz, 9H, *t*-Bu_2H), 1.41 (d, J = 14.0 Hz, 9H, *t*-Bu_2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.2 (d, J = 2.6 Hz), 165.7, 149.0 (d, J = 16.5 Hz), 143.7, 141.0, 137.8, 137.5, 135.4, 130.1, 129.0, 128.5, 128.3, 127.3, 127.2, 127.1, 126.7 (d, J = 20.6 Hz), 126.4, 125.2, 123.4, 80.1 (d, J = 3.0 Hz), 73.6 (d, J = 2.3 Hz), 35.1 (d, J = 16.4 Hz), 35.0 (d, J = 16.8 Hz), 34.3 (d, J = 27.9 Hz), 29.3 (d, J = 4.8 Hz), 29.2 (d, J = 4.4 Hz), 21.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 91.1. Anal. calcd for $C_{37}H_{42}ClN_2PPd$: C, 64.63; H, 6.16; N, 4.07. Found: C, 64.73; H, 6.11; N, 4.23.

Synthesis of the PCN pincer nickel(II) complexes 5a and 5b

Under an argon atmosphere, to a solution of **1g** or **1h** (0.5 mmol) and Et_3N (69.5 μL, 0.5 mmol) in toluene (5 mL) was added Ph_2PCl (0.5 mmol). The resulting mixture was refluxed for 3 h. $NiCl_2$ (194.4 mg, 1.5 mmol) was then added and the reaction mixture was refluxed for 12 h. After cooling, filtration and evaporation, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to produce the corresponding PCN pincer Ni(II) complexes **5a** or **5b**.

(*S*)-2-(4-Phenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)-6-(diphenylphosphinoxy) phenylnickel(II) chloride (5a). Yellow solid (184.7 mg, 61%). Mp: 214–218 °C. $[\alpha]_D^{20}$ = +85 (*c* 0.071, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.97 (m, 4H, PPhH), 7.53 (d, J = 7.6 Hz, 2H), 7.48–7.34 (m, 8H), 7.29–7.16 (m, 5H), 6.78–6.72 (m, 2H, ArH), 6.19 (d, J = 6.8 Hz, 1H, ArH), 5.34 (dd, J = 4.0, 10.9 Hz, 1H, NCH), 4.50 (app t, J = 10.9 Hz, 1H, NCH_2), 3.96 (dd, J = 4.0, 9.9 Hz, 1H, NCH_2), 2.40 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 169.8, 163.8 (d, J = 15.3 Hz), 150.4 (d, J = 35.8 Hz), 143.7, 138.1, 136.8, 133.1, 132.7, 132.0 (d, J = 13.2 Hz), 131.6 (d, J = 13.0 Hz), 131.5, 131.4, 130.4, 128.60, 128.58 (d, J = 11.0 Hz), 127.3, 126.6, 126.4, 125.7, 120.2, 113.6 (d, J = 13.7 Hz), 64.9, 62.1, 21.2. $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 150.7. Anal. calcd for $C_{34}H_{28}ClN_2NiOP$: C, 67.42; H, 4.66; N, 4.62. Found: C, 67.14; H, 5.08; N, 4.32.

(*S*,*S*)-2-(4,5-Diphenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-imidazol-2-yl)-6-(diphenylphosphinoxy)phenylnickel(II) chloride (5b). Yellow solid (173.9 mg, 51%). Mp: 164–166 °C. $[\alpha]_D^{20}$ = +121 (*c* 0.034, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.98 (m, 4H, PPhH), 7.51–7.28 (m, 17H), 7.06 (m, 3H), 6.80–6.76 (m, 2H, ArH), 6.18–6.14 (m, 1H, ArH), 5.22 (d, J = 5.0 Hz, 1H, NCH), 4.78 (d, J = 5.0 Hz, 1H, NCH), 2.31 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 178.8, 169.6, 163.9, 143.9, 140.5, 138.3, 137.0, 136.0, 133.0, 132.5, 132.0 (d, J = 13.2 Hz), 131.6 (d, J = 12.8 Hz), 131.4, 130.1, 129.1, 128.7, 128.6, 128.5, 127.5, 127.1, 126.3, 125.8, 120.2, 113.7 (d, J = 13.6 Hz), 80.5, 72.4, 21.2. $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$): δ 150.4. Anal. calcd for $C_{40}H_{32}ClN_2NiOP$: C, 70.46; H, 4.73; N, 4.11. Found: C, 70.13; H, 4.94; N, 3.85.

General procedure for the enantioselective hydrophosphination of enones with diphenylphosphine

A mixture of the pincer Ni catalyst **2a** (5 mol%) and Et_3N (5.5 μL, 20 mol%) in anhydrous CH_3CN (2 mL) was stirred at room temperature for 0.5 h under an argon atmosphere. Ph_2PH (37.2 mg, 0.2 mmol) was then added and stirring was continued for 0.5 h. After addition of the enone (0.3 mmol), the resulting mixture was stirred at 0 °C for an additional 12 h and then directly oxidized with a H_2O_2 aqueous solution (30%, 60 μL). The mixture was stirred at room temperature for 2 h and then saturated $Na_2S_2O_3$ aqueous solution was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried with anhydrous Na_2SO_4 and the volatiles were removed under reduced pressure. Purification by column chromatography on silica gel (CH_2Cl_2/EtOAc: 5/1) provided the desired chiral phosphine oxides **4**.

(*R*)-3-(Diphenylphosphinyl)-3-phenyl-1-(pyridin-2-yl)propan-1-one (4a).[12c,d,23] Pale yellow solid (74.9 mg, 91%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 12.4 min (minor), 15.5 min (major), 95% ee. $[\alpha]_D^{20}$ =

+116 (*c* 0.077, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 5.2 Hz, 1H), 7.94–7.89 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.63 (dt, J = 1.7, 7.7 Hz, 1H), 7.46–7.39 (m, 5H), 7.33–7.16 (m, 6H), 7.07–6.99 (m, 3H), 4.41–4.27 (m, 2H), 3.54–3.47 (m, 1H).

(*R*)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(*o*-tolyl) propan-1-one (4b).[12d] Pale yellow solid (67.3 mg, 79%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 11.1 min (minor), 16.4 min (major), 50% ee. $[\alpha]_D^{20}$ = +164 (*c* 0.081, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.51 (d, J = 4.6 Hz, 1H), 7.95–7.92 (m, 2H), 7.71 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.60 (dt, J = 1.7, 7.7 Hz, 1H), 7.50–7.44 (m, 3H), 7.29–7.23 (m, 2H), 7.20–7.16 (m, 2H), 7.10–7.07 (m, 3H), 6.95 (t, J = 7.4 Hz 1H), 6.79 (d, J = 7.5 Hz, 1H), 4.61–4.57 (m, 1H), 4.34 (ddd, J = 5.3, 10.8, 18.5 Hz, 1H), 3.52 (ddd, J = 2.7, 10.6, 18.5 Hz, 1H), 1.90 (s, 3H).

(*R*)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(*m*-tolyl) propan-1-one (4c).[12d] Pale yellow solid (74.9 mg, 88%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 11.0 min (minor), 14.5 min (major), 81% ee. $[\alpha]_D^{20}$ = +128 (*c* 0.186, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.61 (d, J = 4.4 Hz, 1H), 7.99–7.96 (m, 2H), 7.82 (td, J = 1.1, 7.9 Hz, 1H), 7.70 (dt, J = 1.8, 7.7 Hz, 1H), 7.50–7.47 (m, 5H), 7.39–7.33 (m, 2H), 7.27–7.24 (m, 2H), 7.10–7.09 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.6 Hz, 1H), 4.45–4.32 (m, 2H), 3.60 (ddd, J = 2.7, 11.0, 18.2 Hz, 1H), 2.17 (s, 3H).

(*R*)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(*p*-tolyl) propan-1-one (4d).[12c,d] Pale yellow solid (75.7 mg, 89%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (85/15) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 8.6 min (minor), 10.9 min (major), 91% ee. $[\alpha]_D^{20}$ = +82 (*c* 0.202, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.53 (d, J = 4.7 Hz, 1H), 7.92–7.88 (m, 2H), 7.74 (td, J = 1.2, 7.8 Hz, 1H), 7.62 (dt, J = 1.8, 7.7 Hz, 1H), 7.46–7.39 (m, 5H), 7.32–7.26 (m, 2H), 7.21–7.18 (m, 2H), 7.12 (dd, J = 2.0, 8.2 Hz, 2H), 6.85 (d, J = 7.9 Hz, 2H), 4.39–4.24 (m, 2H), 3.49 (ddd, J = 2.7, 10.7, 18.2 Hz, 1H), 2.12 (s, 3H).

(*R*)-3-(Diphenylphosphinyl)-3-(4-ethylphenyl)-1-(pyridin-2-yl) pr-opan-1-one (4e).[12d] Pale yellow solid (81.0 mg, 92%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 12.5 min (minor), 16.8 min (major), 92% ee. $[\alpha]_D^{20}$ = +126 (*c* 0.067, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 4.5 Hz, 1H), 7.93–7.88 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.63 (dt, J = 1.8, 7.7 Hz, 1H), 7.44–7.39 (m, 5H), 7.33–7.26 (m, 2H), 7.20–7.13 (m, 4H), 6.88 (d, J = 7.9 Hz, 2H), 4.40–4.24 (m, 2H), 3.50 (ddd, J = 2.3, 10.9, 17.9 Hz, 1H), 2.42 (q, J = 7.6 Hz, 2H), 1.04 (t, J = 7.6 Hz, 3H).

(*R*)-3-(Diphenylphosphinyl)-3-(4-methoxyphenyl)-1-(pyridin-2-yl)propan-1-one (4f).[12c,d] Pale yellow solid (75.0 mg, 85%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (85/15) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 11.3 min (minor), 14.2 min (major), 92% ee. $[\alpha]_D^{20}$ = +101 (*c* 0.069, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.61 (d, J = 4.8 Hz, 1H), 8.00–7.97 (m, 2H), 7.82 (td, J = 1.1, 7.8 Hz, 1H), 7.70 (dt, J = 1.7, 7.7 Hz, 1H), 7.52–7.48 (m, 5H), 7.40–7.34 (m, 2H), 7.29–7.22 (m, 4H), 6.67 (d, J = 8.7 Hz, 2H), 4.44–4.30 (m, 2H), 3.68 (s, 3H), 3.53 (ddd, J = 2.6, 10.4, 18.0 Hz, 1H).

(*R*)-3-(3-Chlorophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)propan-1-one (4g).[12d] Pale yellow solid (82.1 mg, 92%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (85/15) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 8.8 min (minor), 11.1 min (major), 84% ee. $[\alpha]_D^{20}$ = +146 (*c* 0.127, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.61–8.60 (m, 1H), 8.01–7.96 (m, 2H), 7.83 (d, J = 7.8 Hz, 1H), 7.71 (dt, J = 1.7, 7.7 Hz, 1H), 7.54–7.47 (m, 5H), 7.41–7.35 (m, 2H), 7.31–7.26 (m, 4H), 7.06–7.05 (m, 2H), 4.45–4.31 (m, 2H), 3.57 (ddd, J = 2.0, 10.7, 17.7 Hz, 1H).

(*R*)-3-(4-Chlorophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)propan-1-one (4h). Pale yellow solid (85.5 mg, 96%). Mp: 194–196 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (95/5) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 28.8 min (minor), 33.8 min (major), 86% ee. $[\alpha]_D^{20}$ = +132 (*c* 0.083, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.52 (d, J = 4.8 Hz, 1H), 7.92–7.89 (m, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.63 (dt, J = 1.7, 7.7 Hz, 1H), 7.46–7.41 (m, 5H), 7.33–7.28 (m, 2H), 7.22–7.19 (m, 4H), 7.01 (d, J = 8.4 Hz, 2H), 4.37–4.25 (m, 2H), 3.45 (ddd, J = 2.5, 10.4, 18.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 198.6 (d, J = 13.7 Hz), 152.6, 149.0, 136.7, 134.4 (d, J = 5.6 Hz), 132.9 (d, J = 3.1 Hz), 132.0 (d, J = 2.9 Hz), 131.6 (d, J = 2.9 Hz), 131.5 (d, J = 23.7 Hz), 131.4 (d, J = 8.7 Hz), 131.2 (d, J = 5.4 Hz), 131.0 (d, J = 8.8 Hz), 130.8 (d, J = 23.8 Hz),128.9 (d, J = 11.4 Hz), 128.3 (d, J = 2.1 Hz), 128.2 (d, J = 11.8 Hz), 127.4, 121.8, 40.9 (d, J = 68.8 Hz), 38.2. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 33.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{22}ClNO_2P^+$: 446.1071, found: 446.1066.

(*R*)-3-(3-Bromophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)propan-1-one (4i).[12c,d] Pale yellow solid (96.7 mg, 99%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 13.2 min (minor), 17.7 min (major), 81% ee. $[\alpha]_D^{20}$ = +83 (*c* 0.132, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 4.6 Hz, 1H), 7.92–7.87 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.63 (dt, J = 1.7, 7.7 Hz, 1H), 7.45–7.40 (m, 5H), 7.33–7.28 (m, 3H), 7.25–7.19 (m, 3H), 7.13 (d, J = 7.3 Hz, 1H), 6.92 (t, J = 7.8 Hz, 1H), 4.36–4.21 (m, 2H), 3.49 (ddd, J = 1.9, 10.8, 17.7 Hz, 1H).

(*R*)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-(pyridin-2-yl)propan-1-one (4j).[12c,d] Pale yellow solid (96.1 mg, 98%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (95/5) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 31.6 min (minor), 36.5 min (major), 93% ee. $[\alpha]_D^{20}$ = +86 (*c* 0.151, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.51

(d, J = 4.6 Hz, 1H), 7.92–7.88 (m, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.62 (dt, J = 1.8, 7.7 Hz, 1H), 7.46–7.40 (m, 5H), 7.32–7.27 (m, 2H), 7.22–7.13 (m, 6H), 4.36–4.24 (m, 2H), 3.45 (ddd, J = 2.5, 10.4, 18.1 Hz, 1H).

(*R*)-3-(Diphenylphosphinyl)-3-(4-iodophenyl)-1-(pyridin-2-yl) pr-opan-1-one (4k). Pale yellow solid (103.0 mg, 96%). Mp: 200–202 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (95/5) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 30.7 min (minor), 35.8 min (major), 90% ee. $[\alpha]_D^{20}$ = +103 (*c* 0.098, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 4.6 Hz, 1H), 7.93–7.88 (m, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.64 (dt, J = 1.7, 7.7 Hz, 1H), 7.47–7.29 (m, 9H), 7.24–7.19 (m, 2H), 7.01 (dd, J = 1.9, 8.5 Hz, 2H), 4.35–4.23 (m, 2H), 3.50–3.40 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 198.6 (d, J = 13.6 Hz), 152.5, 149.0, 137.2 (d, J = 2.1 Hz), 136.7, 135.7 (d, J = 5.8 Hz), 132.0 (d, J = 2.9 Hz), 131.9 (d, J = 5.6 Hz), 131.8 (d, J = 23.0 Hz), 131.6 (d, J = 2.8 Hz), 131.4 (d, J = 8.7 Hz), 131.0 (d, J = 8.8 Hz), 130.8 (d, J = 25.7 Hz), 128.9 (d, J = 11.3 Hz), 128.3 (d, J = 11.6 Hz), 127.4, 121.8, 92.8 (d, J = 3.4 Hz), 41.1 (d, J = 68.5 Hz), 38.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.1. HRMS (positive ESI): $[M+H]^+$ calcd for $C_{26}H_{22}INO_2P^+$: 538.0427, found: 538.0424.

(*R*)-3-(Diphenylphosphinyl)-3-(4-nitrophenyl)-1-(pyridin-2-yl) pr-opan-1-one (4l).[12c] Pale yellow solid (88.4 mg, 97%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (85/15) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 17.2 min (minor), 21.4 min (major), 85% ee. $[\alpha]_D^{20}$ = +123 (*c* 0.151, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 4.6 Hz, 1H), 7.95–7.89 (m, 4H), 7.75 (d, J = 7.6 Hz, 1H), 7.65 (dt, J = 1.7, 7.7 Hz, 1H), 7.49–7.44 (m, 7H), 7.36–7.29 (m, 2H), 7.24–7.20 (m, 2H), 4.51–4.33 (m, 2H), 3.50 (ddd, J = 2.4, 10.2, 18.3 Hz, 1H).

(*R*)-1-(6-Bromopyridin-2-yl)-3-(diphenylphosphinyl)-3-phenylpr-opan-1-one (4m).[12d] Pale yellow solid (86.4 mg, 88%). The enantiomeric excess was determined using a Daicel Chiralcel AD-H column with *n*-hexane/2-propanol (80/20) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 25.1 min (minor), 33.3 min (major), 92% ee. $[\alpha]_D^{20}$ = +51 (*c* 0.081, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.99–7.93 (m, 2H), 7.65 (d, J = 6.9 Hz, 1H), 7.49–7.43 (m, 5H), 7.39–7.34 (m, 2H), 7.26–7.12 (m, 5H), 7.05–6.97 (m, 3H), 4.40–4.35 (m, 1H), 4.15–3.97 (m, 1H), 3.49 (ddd, J = 3.0, 10.1, 17.7 Hz, 1H).

(*R*)-1-(6-Bromopyridin-2-yl)-3-(diphenylphosphinyl)-3-(*p*-tolyl)propan-1-one (4n).[12d] Pale yellow solid (92.0 mg, 91%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 14.7 min (minor), 21.1 min (major), 98% ee. $[\alpha]_D^{20}$ = +87 (*c* 0.091, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.05–8.01 (m, 2H), 7.75 (dd, J = 1.4, 7.2 Hz, 1H), 7.59–7.47 (m, 7H), 7.35–7.33 (m, 1H), 7.27–7.24 (m, 2H), 7.15 (dd, J = 2.0, 8.2 Hz, 2H), 6.93 (d, J = 7.9 Hz, 2H), 4.46–4.42 (m, 1H), 4.16–4.10 (m, 1H), 3.56 (ddd, J = 3.1, 10.0, 17.6 Hz, 1H), 2.19 (s, 3H).

(*R*)-1-(6-Bromopyridin-2-yl)-3-(diphenylphosphinyl)-3-(4-ethylp-henyl)propan-1-one (4o).[12d] Pale yellow solid (93.5 mg, 90%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (85/15) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 9.2 min (minor), 13.4 min (major), 82% ee. $[\alpha]_D^{20}$ = +121 (*c* 0.224, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.63 (dd, J = 1.3, 7.3 Hz, 1H), 7.46–7.35 (m, 7H), 7.24–7.21 (m, 1H), 7.13 (dt, J = 2.9, 7.7 Hz, 2H), 7.09 (dd, J = 2.0, 8.2 Hz, 2H), 6.85 (d, J = 7.9 Hz, 2H), 4.37–4.34 (m, 1H), 4.09–4.04 (m, 1H), 3.47 (ddd, J = 3.1, 10.2, 17.7 Hz, 1H), 2.39 (q, J = 7.6 Hz, 2H), 1.00 (t, J = 7.6 Hz, 3H).

(*R*)-1-(6-Bromopyridin-2-yl)-3-(diphenylphosphinyl)-3-(4-metho-xyphenyl)propan-1-one (4p).[12d] Pale yellow solid (74.0 mg, 71%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (80/20) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 9.8 min (minor), 13.9 min (major), 78% ee. $[\alpha]_D^{20}$ = +124 (*c* 0.198, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.05–8.02 (m, 2H), 7.75 (dd, J = 1.4, 7.1 Hz, 1H), 7.59–7.46 (m, 7H), 7.35–7.33 (m, 1H), 7.28–7.24 (m, 2H), 7.19 (dd, J = 2.0, 8.8 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 4.44–4.40 (m, 1H), 4.15–4.09 (m, 1H), 3.67 (s, 3H), 3.54 (ddd, J = 3.1, 9.7, 17.4 Hz, 1H).

(*R*)-1-(6-Bromopyridin-2-yl)-3-(4-chlorophenyl)-3-(Diphenylpho-sphinyl)propan-1-one (4q).[12d] Pale yellow solid (87.3 mg, 83%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (97/3) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 52.8 min (minor), 64.0 min (major), 91% ee. $[\alpha]_D^{20}$ = +78 (*c* 0.275, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.05–8.02 (m, 2H), 7.77 (dd, J = 1.6, 7.0 Hz, 1H), 7.61–7.57 (m, 2H), 7.55–7.53 (m, 3H), 7.51–7.48 (m, 2H), 7.38–7.35 (m, 1H), 7.30–7.27 (m, 2H), 7.23 (dd, J = 2.0, 8.6 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 4.45–4.41 (m, 1H), 4.18–4.12 (m, 1H), 3.54 (ddd, J = 3.0, 9.8, 17.7 Hz, 1H).

(*R*)-3-(Diphenylphosphinyl)-1-(6-methylpyridin-2-yl)-3-phenylpr-opan-1-one (4r).[12d] Pale yellow solid (75.0 mg, 88%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (95/5) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 18.8 min (minor), 23.4 min (major), 91% ee. $[\alpha]_D^{20}$ = +134 (*c* 0.208, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 7.96–7.92 (m, 2H), 7.56 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.45–7.37 (m, 5H), 7.28–7.25 (m, 3H), 7.19–7.16 (m, 3H), 7.06–6.99 (m, 3H), 4.41–4.31 (m, 2H), 3.46 (ddd, J = 1.7, 10.9, 17.3 Hz, 1H), 2.50 (s, 3H).

(*R*)-3-(Diphenylphosphinyl)-3-(4-fluorophenyl)-1-(6-methylpyri-din-2-yl)propan-1-one (4s). Pale yellow solid (53.0 mg, 60%). Mp: 208–210 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (98/2) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 41.6 min (minor), 52.3 min (major), 60% ee. $[\alpha]_D^{20}$ = +142 (*c* 0.077, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.03–8.00 (m, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.7 Hz,1H), 7.55–7.46 (m, 5H),

7.37–7.24 (m, 6H), 6.82 (t, J = 8.7 Hz, 2H), 4.46–4.36 (m, 2H), 3.49 (ddd, J = 2.0, 10.4, 17.6 Hz, 1H), 2.57 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 198.0 (d, J = 13.8 Hz), 160.8 (dd, J = 2.7, 245.7 Hz), 157.1, 151.1, 135.8, 131.2, 131.0 (d, J = 2.8 Hz), 130.5–130.34 (m), 130.33 (d, J = 94.9 Hz), 129.9 (d, J = 8.8 Hz), 127.9 (d, J = 11.1 Hz), 127.1 (d, J = 11.8 Hz), 126.0, 117.8, 114.0 (dd, J = 2.1, 21.5 Hz), 39.8 (d, J = 69.2 Hz), 37.2, 23.3. $^{19}F\{^1H\}$ NMR (565 MHz, $CDCl_3$): δ −115.5. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{24}FNO_2P^+$: 444.1523, found: 444.1522.

(*R*)-3-(4-Chlorophenyl)-3-(diphenylphosphinyl)-1-(6-methylpyri-din-2-yl)propan-1-one (4t).[12d] Pale yellow solid (85.5 mg, 93%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (98/2) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 44.6 min (minor), 53.2 min (major), 95% ee. $[\alpha]_D^{20}$ = +123 (*c* 0.071, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.03–7.99 (m, 2H), 7.63 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.7 Hz,1H), 7.52–7.49 (m, 5H), 7.37–7.35 (m, 1H), 7.29–7.23 (m, 5H), 7.09 (d, J = 8.4 Hz, 2H), 4.46–4.36 (m, 2H), 3.49 (ddd, J = 2.0, 10.5, 17.6 Hz, 1H), 2.57 (s, 3H).

(*R*)-3-(4-Bromophenyl)-3-(diphenylphosphinyl)-1-(6-methylpyri-din-2-yl)propan-1-one (4u). Pale yellow solid (79.8 mg, 79%). Mp: 210–212 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (98/2) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 46.2 min (minor), 56.3 min (major), 91% ee. $[\alpha]_D^{20}$ = +131 (*c* 0.083, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.02–7.99 (m, 2H), 7.63 (d, J = 7.2 Hz, 1H), 7.57 (t, J = 7.7 Hz,1H), 7.53–7.49 (m, 5H), 7.37–7.35 (m, 1H), 7.29–7.22 (m, 7H), 4.45–4.36 (m, 2H), 3.49 (ddd, J = 1.8, 10.5, 17.3 Hz, 1H), 2.56 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 198.9 (d, J = 13.8 Hz), 158.1, 152.1, 136.8, 135.0 (d, J = 5.6 Hz), 132.0 (d, J = 2.7 Hz), 131.8 (d, J = 67.0 Hz), 131.6 (d, J = 5.6 Hz), 131.5 (d, J = 2.8 Hz), 131.4 (d, J = 8.6 Hz), 131.2 (d, J = 2.1 Hz), 130.97, 130.96 (d, J = 8.8 Hz), 128.9 (d, J = 11.2 Hz), 128.2 (d, J = 11.7 Hz), 127.1, 121.1 (d, J = 3.2 Hz), 118.9, 41.1 (d, J = 68.6 Hz), 38.1, 24.3. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.5. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{24}BrNO_2P^+$: 504.0723, found: 504.0720.

(*R*)-3-(Diphenylphosphinyl)-3-(4-iodophenyl)-1-(6-methylpyri-din-2-yl)propan-1-one (4v). Pale yellow solid (84.0 mg, 76%). Mp: 220–222 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (98/2) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 49.1 min (minor), 59.1 min (major), 88% ee. $[\alpha]_D^{20}$ = +90 (*c* 0.081, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 7.93–7.90 (m, 2H), 7.54 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.7 Hz,1H), 7.44–7.41 (m, 5H), 7.36 (d, J = 8.4 Hz, 2H), 7.29–7.26 (m, 1H), 7.21–7.18 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.01 (dd, J = 2.0, 8.5 Hz, 2H), 4.34–4.26 (m, 2H), 3.42–3.38 (m, 1H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 197.8 (d, J = 13.8 Hz), 157.1, 151.0, 136.2 (d, J = 2.1 Hz), 135.8, 134.7 (d, J = 5.8 Hz), 131.0 (d, J = 2.6 Hz), 130.9 (d, J = 5.5 Hz), 130.8 (d, J = 64.5 Hz), 130.5 (d, J = 2.7 Hz), 130.3 (d, J = 8.6 Hz), 130.1 (d, J = 58.2 Hz), 129.9 (d, J = 8.8 Hz), 127.9 (d, J = 11.4 Hz), 127.2 (d, J = 11.7 Hz), 126.0, 117.9, 91.7 (d, J = 3.3 Hz), 40.1 (d, J = 68.3 Hz), 37.0, 23.3. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.5. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{27}H_{24}INO_2P^+$: 552.0584, found: 552.0582.

(*R*)-3-(Diphenylphosphinyl)-3-(naphthalen-2-yl)-1-(pyridin-2-yl)propan-1-one (4w).[12c,d] Pale yellow solid (83.1 mg, 90%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 13.9 min (minor), 18.9 min (major), 53% ee. $[\alpha]_D^{20}$ = +80 (*c* 0.069, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 4.8 Hz, 1H), 8.02–7.96 (m, 4H), 7.64–7.52 (m, 4H), 7.45–7.42 (m, 3H), 7.35–7.18 (m, 6H), 6.99 (t, J = 7.4 Hz, 1H), 6.88–6.84 (m, 2H), 5.39–5.33 (m, 1H), 4.44–4.35 (m, 1H), 3.59 (ddd, J = 3.2, 10.9, 18.4 Hz, 1H).

(*R*)-3-(Diphenylphosphinyl)-1-(pyridin-2-yl)-3-(thiophen-2-yl) pr-opan-1-one (4x).[12c,d] Pale yellow solid (81.9 mg, 98%). The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 16.2 min (minor), 21.4 min (major), 81% ee. $[\alpha]_D^{20}$ = +87 (*c* 0.120, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 8.62–8.61 (m, 1H), 7.98–7.95 (m, 2H), 7.86 (d, J = 8.2 Hz, 1H), 7.74–7.71 (m, 1H), 7.62–7.59 (m, 2H), 7.53–7.49 (m, 3H), 7.42–7.40 (m, 2H), 7.34–7.31 (m, 2H), 7.01–6.97 (m, 2H), 6.79–6.77 (m, 1H), 4.85–4.81 (m, 1H), 4.32 (ddd, J = 5.2, 10.8, 18.3 Hz, 1H), 3.59 (ddd, J = 2.9, 10.0, 18.3 Hz, 1H).

(*R*)-3-(Diphenylphosphinyl)-4,4-dimethyl-1-(pyridin-2-yl) pentan-1-one (4y). Yellow oil (68.2 mg, 87%). The enantiomeric excess was determined using a Daicel Chiralcel As–H column with *n*-hexane/2-propanol (90/10) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 6.1 min (minor), 10.2 min (major), 20% ee. $[\alpha]_D^{20}$ = +16 (*c* 0.307, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, J = 4.6 Hz, 1H), 8.06–8.02 (m, 2H), 7.75–7.68 (m, 4H), 7.50–7.47 (m, 3H), 7.37 (ddd, J = 1.4, 4.7, 7.4 Hz, 1H), 7.15–7.07 (m, 3H), 3.74–3.66 (m, 1H), 3.55–3.47 (m, 2H), 1.06 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 199.8 (d, J = 5.9 Hz), 152.4, 148.7, 136.4, 135.7 (d, J = 93.1 Hz), 134.0 (d, J = 94.7 Hz), 131.22 (d, J = 8.4 Hz), 131.16 (d, J = 2.8 Hz), 130.9 (d, J = 8.4 Hz), 130.7 (d, J = 2.7 Hz), 128.5 (d, J = 11.5 Hz), 127.9 (d, J = 11.1 Hz), 127.1, 121.7, 41.5 (d, J = 70.7 Hz), 35.7 (d, J = 2.3 Hz), 34.8, 29.8 (d, J = 6.0 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 34.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{24}H_{27}NO_2P^+$: 392.1774, found: 392.1773.

Synthesis of 6a

First, **4m** (98 mg, 0.2 mmol), phenylboronic acid (44 mg, 0.36 mmol), K_2CO_3 (60.8 mg, 0.44 mmol), Ad_2BnP (1.9 mg, 2.4 mol%) and $Pd(OAc)_2$ (0.9 mg, 2.0 mol%) were added to a 10 mL dry Schlenk tube under an argon atmosphere. Anhydrous toluene (0.1 M, 2 mL) was then added and the reaction mixture was stirred at 25 °C for 2 h. The completion of the reaction was monitored by TLC and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was collected, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc: 5/1) to give **6a** as a white powder.

(*R*)-3-(Diphenylphosphinyl)-3-phenyl-1-(6-phenylpyridin-2-yl)pr-opan-1-one (6a). White solid (94.5 mg, 97%). Mp: 238–240 °C. The enantiomeric excess was determined using a Daicel Chiralcel AD-H column with *n*-hexane/2-propanol (80/20) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 22.3 min (minor), 26.0 min (major), 86% ee. $[\alpha]_D^{28}$ = +183 (*c* 0. 086, CH_2Cl_2). ^{1}HNMR (600 MHz, $CDCl_3$): δ 7.96 (d, J = 7.1 Hz, 2H), 7.93–7.89 (m, 2H), 7.75 (dd, J = 2.4, 6.4 Hz, 1H), 7.68–7.65 (m, 2H), 7.45–7.37 (m, 8H), 7.28–7.24 (m, 3H), 7.18–7.15 (m, 2H), 7.05–6.98 (m, 3H), 4.46–4.40 (m, 2H), 3.61–3.54 (m, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 198.1 (d, J = 13.5 Hz), 155.5, 151.6, 137.0, 136.5, 134.8 (d, J = 5.9 Hz), 131.0 (d, J = 58.0 Hz), 130.9 (d, J = 2.7 Hz), 130.5 (d, J = 8.4 Hz), 130.4 (d, J = 52.9 Hz), 130.3 (d, J = 2.7 Hz), 130.1 (d, J = 8.7 Hz), 129.0 (d, J = 5.5 Hz), 128.5, 127.9, 127.8 (d, J = 11.3 Hz), 127.1 (d, J = 2.1 Hz), 127.0 (d, J = 11.7 Hz), 126.0, 122.7, 119.1, 40.6 (d, J = 68.3 Hz), 37.0. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{32}H_{27}NO_2P^+$: 488.1774, found: 488.1778.

Synthesis of 6b

$Pd(dppf)Cl_2$ (0.01 mmol) was added to a mixture of **4j** (98 mg, 0.2 mmol), CuI (0.02 mmol), phenylacetylene (0.24 mmol) and THF/NEt_3 (4 mL/1 mL) under an argon atmosphere. The mixture was stirred at 60 °C overnight. The solution was then diluted with CH_2Cl_2, washed three times with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2: 1/2) to give **6b** as a white powder.

(*R*)-3-(Diphenylphosphinyl)-3-(4-(phenylethynyl)phenyl)-1-(pyri-din-2-yl)propan-1-one (6b). White solid (85.0 mg, 83%). Mp: 206–208 °C. The enantiomeric excess was determined using a Daicel Chiralcel OD-H column with *n*-hexane/2-propanol (95/5) at a flow rate of 1.0 mL min^{-1} and detected at a UV wavelength of 228 nm. Retention times: 31.2 min (minor), 36.0 min (major), 95% ee. $[\alpha]_D^{28}$ = +164 (*c* 0.085, CH_2Cl_2). ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.6 Hz, 1H), 8.02–7.98 (m, 2H), 7.82 (d, J = 7.9 Hz, 1H), 7.69 (dt, J = 1.7, 7.7 Hz, 1H), 7.56–7.45 (m, 7H), 7.39–7.27 (m, 11H), 4.51–4.36 (m, 2H), 3.61–3.54 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 198.6 (d, J = 13.5 Hz), 152.6, 149.0, 136.7, 136.3 (d, J = 5.9 Hz), 132.0 (d, J = 2.7 Hz), 131.9 (d, J = 26.9 Hz), 131.6, 131.5 (d, J = 13.4 Hz), 131.4 (d, J = 6.5 Hz), 131.1 (d, J = 8.9 Hz), 131.0 (d, J = 22.2 Hz), 130.0 (d, J = 5.5 Hz), 128.8 (d, J = 11.4 Hz), 128.3, 128.21, 128.20 (d, J = 11.7 Hz), 127.4, 123.2, 121.8, 89.5, 89.2 (d, J = 1.9 Hz), 41.7 (d, J = 68.5 Hz), 38.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 33.1. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{34}H_{27}NO_2P^+$: 512.1774, found: 512.1778.

Data availability

The data are available within the article or its ESI.† The crystallographic data for **2a**, **2e** and **5a** have been deposited at the CCDC under numbers 2284819, 2287268 and 2424928 and can be obtained from **https://www.ccdc.cam.ac.uk/structures/** (free of charge).

Author contributions

Jin-Ge Li: investigation; data curation; writing (original draft). Bing-Bo Qiu: investigation. Hui Jiang: funding acquisition; supervision. Mao-Ping Song: funding acquisition; supervision. Jun-Fang Gong: conceptualization; methodology; writing (review & editing); funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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