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Iridium Catalysts with Chiral Bicyclic Pyridine–Phosphane Ligands for the Asymmetric Hydrogenation of Olefins

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New bicyclic pyridine–phosphane ligands were prepared, and their iridium complexes were evaluated in asymmetric hydrogenation of trisubstituted olefins with non-coordinating and weakly coordinating substituents. The iridium catalysts showed high reactivity and enantioselectivity for both types of olefins.

Introduction

The asymmetric hydrogenation of olefins with chiral iridium N,P complexes is one of the most efficient and simple methods to create a chiral center.[1] It overcomes the major problem that P,P-ligated rhodium and ruthenium catalysts have in asymmetric hydrogenation, i.e., that these catalysts normally require the substrates to have a good coordinating group next to the C=C double bond. Since Pfaltz and co-workers first introduced chiral N,P complexes based on Crabtree's catalyst,[2] $[(Cy_3P)(pyridine)Ir(COD)]PF_6$ (Cy = cyclohexyl, COD = cyclooctadiene), to hydrogenate unfunctionalized olefins,[3] a number of N,P-ligands have been reported for use in the iridium-catalyzed asymmetric hydrogenation of alkenes with non-coordinating and weakly coordinating substituents.[4,5] Chiral N,P-ligands have also been successfully used in several other chemical transformations, such as allylic substitution and C–C coupling reactions.[6]

During the last few years, chiral bicyclic N,P complexes of iridium based on various heterocyclic scaffolds (Figure 1, **A**–**C**) have been developed by our group,[7,8] and have been used successfully in reactions including asymmetric hydrogenation, Heck coupling,[9] and isomerization of allylic alcohols.[10]

The nitrogen-containing moiety of the N,P-ligands is a heterocycle such as a thiazole or an imidazole, and it acts as an N-donor bonded to the iridium metal. Due to the different electronic properties of the N-donors used, the heterocyclic scaffolds play an important role in tuning the reactivities of the catalysts. The linker between the backbone and phosphorus can also influence the outcome of the hydrogenation reaction. For example, complex **A**, a thiazole iridium complex with an N-linker (Figure 1) hydrogenated fluorinated olefins with higher reactivity and with less C–F-bond cleavage.[7e] Pyridine is one of the most common heterocycles, and its use as an N-donor can be envisioned. In an early report, Pfaltz and co-workers prepared a series of iridium catalysts with pyridine-derived ligands and an oxygen linker.[11] These iridium complexes were very reactive and enantioselective in the hydrogenation of olefins. However, N,P-ligands that have an oxygen linker (O–P) are normally less stable, and this limits their use. N,P-ligands with carbon–phosphorus bonds (C–P) are more stable, which makes them more widely applicable. We envisioned pyridine-derived N,P-ligands with a carbon linker, still maintaining the backbone structure that we had developed earlier. In this paper, we report the preparation of new pyridine-bicyclic N,P-ligands and the evaluation of their iridium complexes in the asymmetric hydrogenation of trisubstituted olefins.

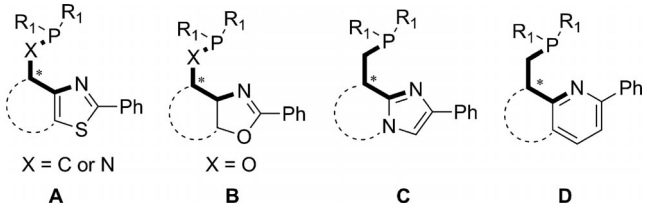

Figure 1. Examples of chiral N,P-ligands used in our group.

Results and Discussion

As shown in Scheme 1, iridium complexes **7a**–**7d** were prepared from the corresponding bicyclic pyridine derivatives, **1a** and **1b**. Compounds **1a** and **1b** were lithiated and

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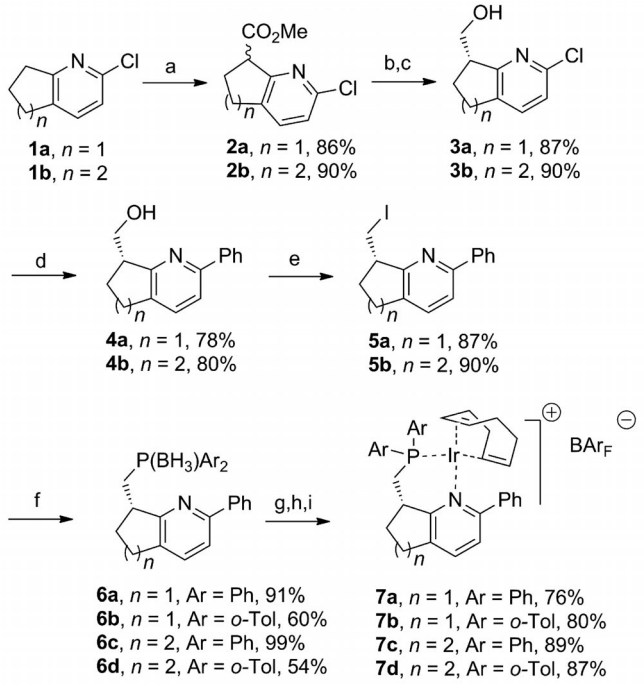
treated with dimethyl carbonate to give racemic esters **2a** and **2b**, which were resolved by preparative HPLC (Chiralcel OD-column, 20 × 250 mm). Optically pure pyridine esters were further reduced to alcohols **3a** and **3b** by DIBAL-H (diisobutylaluminium hydride), and the phenyl groups were introduced by Suzuki coupling reactions. Alcohols **4a** and **4b** were converted into the corresponding iodinated compounds (i.e., **5a** and **5b**) by treatment with iodine, triphenylphosphane, and a catalytic amount of imidazole. Borane-protected N,P-ligands **6a**–**6d** were obtained by substitution with in-situ-prepared $Ar_2P(BH_3)Li$ (Ar = Ph or *o*-Tol). Chiral HPLC confirmed that no racemization occurred during any of the manipulations with the chiral compounds. The protecting group was removed by treatment with diethylamine. The free N,P-ligands were subsequently treated with $[Ir(COD)Cl]_2$ to form the iridium complexes, and anion exchange was achieved by addition of $NaBAr_F{\cdot}3H_2O$ to give iridium N,P complexes **7a**–**7d**.



Scheme 1. Preparation of iridium complexes **7a**–**7d**. Reaction conditions: a) diisopropylamine, BuLi, $(MeO)_2CO$, Et_2O, –30 °C then room temp.; b) preparative HPLC (Chiralcel OD-column, 20 × 250 mm; hexane/2-propanol, 99:1; 3 mL min^{-1}); c) DIBAL-H, Et_2O, –78 °C; d) $PhB(OH)_2$, DPPF (1,1′-bis(diphenylphosphanyl)-ferrocene), $PdCl_2$, K_2CO_3, toluene, H_2O, reflux; e) I_2, PPh_3, imidazole, CH_2Cl_2, room temp.; f) $Ar_2P(BH_3)H$, BuLi, THF, –78 °C; g) diethylamine, room temp.; h) $[Ir(COD)Cl]_2$, CH_2Cl_2, room temp.; i) $NaBAr_F{\cdot}3H_2O$, H_2O.

The newly prepared iridium complexes (i.e., **7a**–**7d**) were evaluated in the asymmetric hydrogenation of trisubstituted olefins. As shown in Table 1, complexes **7a** and **7b**, containing a five-membered ring, generally showed better reactivity and selectivity. For the unfunctionalized substrates (Table 1, entries 1–3), complexes **7a** and **7b** gave higher conversions and better enantioselectivities. Complexes **7c** and **7d**, with similar ligand structures but based on six-membered rings, gave significantly lower reactivity or selectivity.

trans-α-Methylstilbene (Table 1, entry 1) gave full conversion to the product with 99% *ee* using **7b**. With **7a**, substrates **9** and **10** (Table 1, entries 2 and 3) were fully converted into the corresponding products with 93 and 91% *ee*, respectively. With functionalized olefins, **7a** and **7b** performed better than **7c** and **7d**. Complex **7a** gave the best results for substituted functionalized olefins **11** and **13** as well (Table 1, entries 4 and 6). β-Substituted allylic alcohol **12** (Table 1, entry 5) was the only exception, and this substrate was hydrogenated by **7c** with full conversion to the product with 99% *ee*. The difference in reactivity between the five- and six-membered-ring catalysts was obvious when α-methylcinnamic ester **14** was used as a substrate: **7c** and **7d** gave less than 5% conversion, whereas 99% conversion was achieved using **7b**. For the other two α-functionalized olefins (Table 1, entries 8 and 9), full conversions were achieved using **7b** to give the products with 75 and 76% *ee*.

We have previously developed a selectivity model to rationalize and predict the absolute configuration of the product of hydrogenation.[12] The olefin coordinates *trans* to phosphorus, which is in agreement with other proposed mechanisms.[13] As shown in Figure 2a, the phenyl group on the pyridine ring occupies quadrant 3, which is the most hindered quadrant. Quadrants 1 and 4 are the least hindered sites, and are *trans* to each other. The ligand partly occupies quadrant 2, and its steric bulk makes this quadrant semi-hindered. In Figure 2b, a simplified model, using *trans*-α-methylstilbene as an example, the smallest substituent, hydrogen, should be positioned in the most hindered quadrant 3, and the most sterically demanding substituents, the two phenyl rings, will be located in quadrants 1 and 4. This selectivity model predicts the stereochemical outcome of the hydrogenation reaction (Figure 2, c), which is in agreement with the experimental results. In the case of conjugated α,β-unsaturated esters, electronic effects should be taken into consideration. The hydrogenation product of *trans*-α-methyl cinnamate (Table 1, entry 7) gave the (*R*)-mismatched configuration with the selectivity model, which is opposite to what was observed experimentally. This is a

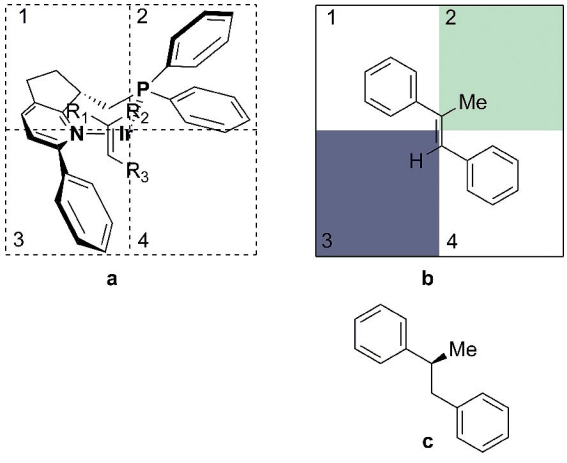
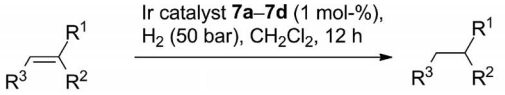
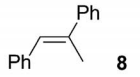
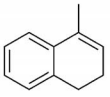
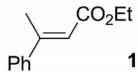
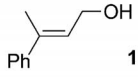
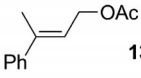
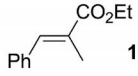
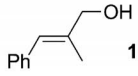
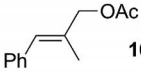


Figure 2. Selectivity model used to predict the absolute configuration.

Table 1. Asymmetric hydrogenation of trisubstituted olefins with **7a**–**7d**.



		7a		7b		7c		7d	
Entry	Substrate	conv.	*ee*	conv.	*ee*	conv.	*ee*	conv.	*ee*
1	 **8**	84%	97% (*S*)	99%	99% (*S*)	17%	76% (*S*)	26%	87% (*S*)
2	 **9**	99%	93% (*S*)	99%	90% (*S*)	91%	35% (*S*)	99%	90% (*S*)
3	 **10**	99%	91% (*R*)	99%	76% (*R*)	87%	77% (*R*)	97%	48% (*R*)
4	 **11**	94%	80% (*S*)	99%	78% (*S*)	17%	50% (*S*)	35%	65% (*S*)
5	 **12**	99%	94% (*S*)	99%	84% (*S*)	99%	99% (*S*)	99%	87% (*S*)
6	 **13**	99%	94% (*S*)	99%	79% (*S*)	99%	90% (*S*)	99%	92% (*S*)
7	 **14**	46%	78% (*R*)	99%	77% (*R*)	< 5%		< 5%	
8	 **15**	33%	99% (*S*)	99%	75% (*S*)	42%	31% (*S*)	62%	66% (*S*)
9	 **16**	48%	77% (*S*)	99%	76% (*S*)	50%	14% (*S*)	67%	46% (*S*)

common phenomenon with some α-methyl cinnamate substrates, and is probably due to a strong electronic effect that prevents hydride insertion at the electron-rich terminus on the C=C double bond, and leads to the formation of a sterically disfavored but electronically favored product.

Conclusions

In this study, bicyclic pyridine–phosphane ligands were prepared, and their iridium complexes were evaluated as catalysts for the asymmetric hydrogenation of various olefins. Good conversions and enantioselectivities were obtained. In most cases, five-membered-ring-containing iridium complexes **7a** and **7b** were better catalysts than six-membered-ring-containing complexes **7c** and **7d**. We found that these catalysts gave results competitive with those obtained with other heterocyclic iridium complexes. The carbon–phosphorus bond in these ligands makes them relatively stable and allows their isolation and their "in situ" use for other reactions.

Experimental Section

General Methods: All reagents used were commercially available. CH_2C_2 was freshly distilled from CaH_2 under nitrogen. THF was freshly distilled from sodium benzophenone under nitrogen. Chromatographic separations were performed on Kieselgel 60H silica gel (particle size: 0.063–0.100 mm). Thin layer chromatography (TLC) was performed on aluminum plates coated with Kieselgel 60 (0.20 mm, UV254), and plates were visualized under ultraviolet light (ν = 254 nm), or by staining with ethanolic phosphomolybdic acid and heating. ^{1}H NMR spectra were recorded at 500 or 300 MHz in $CDCl_3$, and were referenced internally to the residual $CHCl_3$ peak (δ = 7.26 ppm). ^{13}C NMR spectra were recorded at 100 or 75 MHz in $CDCl_3$, and were referenced to the central peak of $CDCl_3$ (δ = 77.0 ppm). ^{31}P NMR spectra were recorded at 121.47 MHz in $CDCl_3$. Chemical shifts are reported in ppm (δ scale). Enantiomeric excesses were determined either using HPLC with a chiral column and a diode array detector at 220 and 254 nm, or by GC with a chiral column and an MS detector. Optical rotations were recorded with a thermostatted polarimeter using a sodium lamp (589 nm) and a 1.0 dm cell. HRMS (ESI) data were obtained using a Bruker microTOF-Q II instrument operating at ambient temperature. IR spectra were measured using a Perkin–Elmer FTIR instrument.

Preparation of Carboxylated Pyridine Derivitives 2a and 2b: *n*BuLi (2.5 M in hexane; 2.0 equiv.) was added to a solution of **1a** or **1b** (1.0 mmol) and diisopropylamine (1.0 mmol) in dry Et_2O (20 mL) at –30 °C under an argon atmosphere. The mixture was stirred at –30 °C for 1 h, and then dimethyl carbonate (1.1 mmol) was added. The solution was stirred at –30 °C for 1 h, then it was allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was quenched by the addition of ammonium chloride (saturated aqueous solution), and the aqueous phase was extracted with Et_2O. The combined organic extracts were washed further with brine, dried with $MgSO_4$, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (pentane/ethyl acetate = 10:1) to give pure **2a** or **2b**. The racemic mixtures were separated by preparative HPLC (Chiralcel OD-column, 20 × 250 mm; hexane/2-propanol, 99.5:0.5; 3 mL min^{-1}).

Methyl (*S*)-2-Chloro-6,7-Dihydro-5*H*-cyclopenta[*b*]pyridine-7-carboxylate [(*S*)-2a]: Obtained in 86% yield. $[\alpha]_D^{25}$ = 21.1 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 4.09 (dd, *J* = 6.0, 8.5 Hz, 1 H), 3.75 (s, 3 H), 3.11 (m,1 H), 2.90 (m, 1 H), 2.45 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.3, 162.3, 150.0, 136.5, 135.3, 122.9, 52.5, 51.0, 29.2, 28.2 ppm. IR (neat): $\tilde{\nu}$ = 1731, 1568, 1421, 1164, 823 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{11}ClNO_2$ [M + H]$^+$ 212.0478; found 212.0473.

Methyl (*S*)-2-Chloro-5,6,7,8-tetrahydroquinoline-8-carboxylate (2b): Obtained in 90% yield. $[\alpha]_D^{25}$ = 26.34 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 8 Hz, 1 H), 7.16 (d, *J* = 8 Hz, 1 H), 3.98 (m, 3 H), 3.76 (s, 3 H), 2.85 (m, 1 H), 2.76 (m, 1 H), 2.25 (m, 1 H), 2.12 (m, 1 H), 1.95 (m, 1 H), 1.83 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.1, 154.2, 148.2, 140.0, 131.5, 122.8, 52.3, 47.8, 27.7, 26.7, 19.9 ppm. IR (neat): $\tilde{\nu}$ = 2948, 1732, 1566, 1442, 1430, 1161, 1135, 1003, 814 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{12}ClNO_2Na$ [M + Na]$^+$ 248.0454; found 248.0449.

Preparation of Pyridine Alcohols 3a and 3b: DIBAL-H (1.0 M in THF; 2.5 equiv.) was added dropwise to a solution of ester **2a** or **2b** (1.0 mmol) in THF (10 mL), at –78 °C under an argon atmosphere. After the addition was complete, the reaction mixture was stirred at –78 °C for a further 2 h, and then it was allowed to warm up to room temperature over 1 h. After the reaction was complete, ammonium chloride (saturated aqueous solution) was added, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with brine, dried with $MgSO_4$, and filtered. The crude product was purified by flash column chromatography (dichloromethane/methanol = 20:1) to give the pure product.

(*S*)-(2-Chloro-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-7-yl)methanol (3a): Obtained in 87% yield. $[\alpha]_D^{25}$ = 8.2 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 3.90 (m, 1 H), 3.81 (dd, *J* = 7.5, 10.5 Hz, 1 H), 3.47 (br. s, 1 H), 3.35 (m, 1 H), 2.92 (m, 2 H), 2.28 (m, 1 H), 1.84 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 149.3, 136.3, 135.1, 122.1, 65.5, 46.9, 28.9, 26.5 ppm. IR (neat): $\tilde{\nu}$ = 2940, 1568, 1418, 1237, 1167, 1033, 875, 8181 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{11}ClNO$ [M + H]$^+$ 184.0529; found 184.0524.

(*S*)-(2-Chloro-5,6,7,8-tetrahydroquinolin-8-yl)methanol (3b): Obtained in 87% yield. $[\alpha]_D^{25.0}$ = 8.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 3.82–3.76 (m, 2 H), 2.99 (m, 1 H) 2.77–2.66 (m, 2 H), 1.98–1.91 (m, 2 H), 1.71 (m, 1 H), 1.47 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3, 147.5, 139.9, 131.4, 121.9, 67.0, 42.4, 28.2, 25.8, 21.2 ppm. IR (neat): $\tilde{\nu}$ = 2940, 1568, 1418, 1237, 1167, 1033, 875, 8181 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{11}ClNO$ [M + H]$^+$ 184.0529; found 184.0524.

Preparation of 4a and 4b: Alcohol **3a** or **3b** (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), and $DPPF{\cdot}PdCl_2{\cdot}CH_2Cl_2$ (0.1 mmol) were added to toluene (20 mL), and then K_2CO_3 (2.0 mmol) and H_2O (1 mL) were added. The mixture was heated to reflux under an argon atmosphere overnight. After the reaction was complete, the reaction mixture was cooled to room temperature and extracted with diethyl ether. The combined organic extracts were washed with brine, dried with $MgSO_4$, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (pentane/ethyl acetate = 5:1) to give the pure product.

(*S*)-(2-Phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-7-yl)methanol (4a): Obtained in 78% yield. $[\alpha]_D^{25}$ = 29.3 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.0 Hz, 2 H), 7.54 (m, 2 H), 7.45 (m, 2 H), 7.38 (m, 1 H), 4.98 (br. s, 1 H), 3.99 (m, 1 H), 3.86 (t, *J* = 10 Hz, 1 H), 3.48 (m, 1 H), 2.93 (dd, *J* = 5.5, 9.5 Hz, 2 H), 2.28 (m, 1 H), 1.71 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 155.2, 139.1, 135.7, 133.2, 128.7, 126.7, 118.9, 66.6, 46.1, 29.3, 26.1 ppm. IR (neat): $\tilde{\nu}$ = 2941, 1586, 1572, 1431, 1226, 1025, 833, 747, 692 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{16}NO$ [M + H]$^+$ 226.1232; found 226.1226.

(*S*)-(2-Phenyl-5,6,7,8-tetrahydroquinolin-8-yl)methanol (4b): Obtained in 80% yield. $[\alpha]_D^{25}$ = 27.7 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7 Hz, 2 H), 7.58–7.50 (m, 4 H), 7.38 (m, 1 H), 3.82–3.87 (m, 2 H), 3.14 (m, 1 H), 2.82–2.78 (m, 2 H), 2.03–1.96 (m, 2 H), 1.77 (m, 1 H), 1.45 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 154.1, 139.1, 138.3, 131.1, 129.0, 126.8, 118.7, 100.3, 67.9, 42.1, 28.7, 26.4, 21.9 ppm. IR (neat): $\tilde{\nu}$ = 3352, 2935, 1563, 1442, 1428, 1137, 1032, 992, 870, 837 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ [M + H]$^+$ 240.1388; found 240.1383.

Iodination of 4a and 4b: Iodine (3.0 mmol), triphenylphosphane (3.0 mmol), and imidazole (3.0 mmol) were added to a solution of compound **4a** or **4b** (1.0 mmol) in dry dichloromethane (15 mL). The mixture was stirred at room temperature overnight. After the reaction was complete, the mixture was diluted with dichloromethane and washed with sodium thiosulfate (saturated aqueous). The separated organic phase was washed with brine, dried with $MgSO_4$, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (pentane/diethyl ether = 5:1) to give the pure product.

(*S*)-7-(Iodomethyl)-2-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (5a): Obtained in 87% yield. $[\alpha]_D^{25}$ = 18.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (m, 2 H), 7.55 (m, 2 H), 7.47 (m, 2 H), 7.40 (m, 1 H), 3.89 (m, 1 H), 3.51 (m, 2 H), 2.95 (m, 2 H), 2.5 (m, 1 H), 1.96 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 156.4, 139.9, 135.8, 133.6, 129.0, 128.9, 127.1, 119.2, 47.8, 31.5, 28.4, 12.3 ppm. IR (neat): $\tilde{\nu}$ = 1586, 1571, 1442, 1431, 1163, 832, 765, 691 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{15}IN$ [M + H]$^+$ 336.0249; found 336.0244.

(*S*)-8-(Iodomethyl)-2-phenyl-5,6,7,8-tetrahydroquinoline (5b): Obtained in 90% yield. $[\alpha]_D^{25}$ = 31.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.5 Hz, 2 H), 7.52 (d, *J* = 8 Hz, 1 H), 7.47–7.42 (m, 3 H), 7.39 (m, 1 H), 3.96 (dd, *J* = 3, 6.5 Hz, 1 H), 3.81 (t, *J* = 9 Hz, 1 H), 3.11 (m, 1 H), 2.80–2.77 (m,

2 H), 2.09 (m, 1 H), 1.92–1.89 (m, 2 H), 1.81 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 154.7, 139.5, 137.8, 131.3, 128.8, 128.6, 126.9, 118.4, 42.6, 29.9, 29.2, 20.8, 14.9 ppm. IR (neat): $\tilde{\nu}$ = 2937, 1558, 1459, 1448, 1178, 831, 758, 689 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}IN$ $[M + H]^+$ 350.0406; found 350.0400.

Preparation of Borane-Protected N,P-Ligands 6a–6d: *n*BuLi (2.5 M in hexane; 1.5 equiv.) was added to a solution of $Ar_2P(BH_3)H$ (Ar = Ph or *o*-Tol; 0.5 mmol) in dry THF (15 mL) at –78 °C under an argon atmosphere. The solution was stirred for 10 min at –78 °C, and then for a further 1 h at room temperature. Substrate **5a** or **5b** (0.4 mmol) was dissolved in THF, and the solution was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred at 0 °C for a further 1 h. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. When the reaction was complete, $NaHCO_3$ (saturated aqueous solution) was added, and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with brine, dried with $MgSO_4$, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (pentane/diethyl ether = 10:1) to give the pure product.

(*S*)-7-[(Diphenylphosphanyl)methyl]-2-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine Borane Adduct (6a): Obtained in 91% yield. $[\alpha]_D^{25}$ = 17.5 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 12.0 Hz, 2 H), 7.94 (m, 2 H), 7.78 (m, 2 H), 7.55–7.43 (m, 11 H), 3.61 (m 1 H), 3.46 (m, 1 H), 2.80 (m, 2 H), 2.43 (m, 1 H), 1.67 (m, 1 H), 1.4–0.6 (br. m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3 (d, *J* = 13.6 Hz), 155.7, 139.7, 135.1, 132.9, 132.5 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 2.7 Hz), 129.1, 128.9, 128.8, 128.7, 126.9, 118.6, 41.1, 33.0, 30.2 (d, *J* = 3.8 Hz), 29.1 ppm. ^{31}P NMR: δ = 16.6 ppm. IR (neat): $\tilde{\nu}$ = 2379, 1587, 1435, 1107, 1061, 736, 693 cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{27}BNP$ $[M + H]^+$ 406.2010; found 406.1890.

(*S*)-7-[(Di-*o*-tolylphosphanyl)methyl]-2-phenyl-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine Borane Adduct (6b): Obtained in 60% yield. $[\alpha]_D^{25}$ = 3.3 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18–8.02 (m, 3 H), 7.89 (m, 1 H), 7.58–7.10 (m, 11 H), 3.82 (t, *J* = 15.0 Hz, 1 H), 3.32 (m, 1 H), 2.81 (m, 2 H), 2.36 (m, 2 H), 2.26 (s, 3 H), 2.12 (s, 3 H), 1.71 (m, 1 H), 1.7–0.8 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5 (d, *J* = 14.2 Hz), 155.5, 142.3 (d, *J* = 5.2 Hz), 139.6, 135.2, 134.2, 132.9, 132.8, 131.9 (d, *J* = 8.3 Hz), 131.5 (d, *J* = 15 Hz), 128.7, 126.9, 126.6 (d, *J* = 7.5 Hz), 118.5, 40.9, 33.1, 29.6, 29.1, 21.8 (d, *J* = 4.5 Hz) ppm. ^{31}P NMR: δ = 17.5 ppm. IR (neat): $\tilde{\nu}$ = 2373, 1585, 1442, 1135, 1061, 823, 737, 693 cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{32}BNP$ $[M + H]^+$ 436.2365; found 436.2365.

(*S*)-8-[(Diphenylphosphanyl)methyl]-2-phenyl-5,6,7,8-tetrahydroquinoline Borane Adduct (6c): Obtained in 99% yield. $[\alpha]_D^{25}$ = 3.0 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12–8.02 (m, 4 H), 7.78–7.71 (m, 2 H), 7.53–7.38 (m, 11 H), 3.76 (dt, *J* = 0.2, 14.7 Hz, 1 H), 3.30 (m, 1 H), 2.77 (m, 2 H), 2.28 (m, 2 H), 1.90–1.71 (m, 3 H), 1.50–0.82 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.7 (d, *J* = 12.7 Hz), 154.3, 139.8, 137.8, 133.0 (d, *J* = 8.7 Hz), 132.1 (d, *J* = 8.7 Hz), 131.2, 131.1, 128.9, 128.8, 128.7, 126.8, 118.0, 37.1 (d, *J* = 1.4 Hz), 31.0 (d, *J* = 3.6 Hz), 30.1, 28.9, 20.6 ppm. ^{31}P NMR: δ = 16.8 ppm. IR (neat): $\tilde{\nu}$ = 3676, 2988, 2380, 1459, 1065, 736, 692 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{39}BNP$ $[M + H]^+$ 422.2209; found 422.2208.

(*S*)-8-[(Di-*o*-tolylphosphanyl)methyl]-2-phenyl-5,6,7,8-tetrahydroquinoline Borane Adduct (6d): Obtained in 54% yield, $[\alpha]_D^{25}$ = 13.2 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (dd, *J* = 8.1, 14.1 Hz, 1 H), 7.98 (m, 2 H), 7.82 (dd, *J* = 7.8, 12.3 Hz, 1 H), 7.52–7.11 (m, 11 H), 3.88 (t, *J* = 15.6 Hz, 1 H), 3.11 (m, 1 H), 2.77 (m, 2 H), 2.40 (m, 1 H), 2.24 (s, 3 H), 2.10 (s, 3 H), 1.87 (m, 2 H), 1.6801.57 (br. m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 142.9 (d, *J* = 4.2 Hz), 142.0 (d, *J* = 6.3 Hz), 138.0, 134.9, 132.4 (d, *J* = 12.0 Hz), 132.0 (d, *J* = 8.3 Hz), 131.8 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 2.3 Hz), 131.0 (d, *J* = 2.3 Hz), 128.8, 126.8, 126.7, 126.53 (d, *J* = 1.5 Hz), 118.1, 37.3, 30.5, 29.9, 29.1, 21.9 (d, J_{CP} = 4.3 Hz), 20.6 ppm. ^{31}P NMR: δ = 18.0 ppm. IR (neat): $\tilde{\nu}$ = 3057. 2927, 2380, 1458, 1064, 909, 741 cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{34}BNP$ $[M + H]^+$ 449.2480; found 449.2440.

Preparation of Iridium Complexes 7a–7d: The borane-protected N,P-ligand (1 mmol) was dissolved in Et_2NH (10 mL for 1 mmol of substrate), and the mixture was stirred at room temperature under argon overnight. The Et_2NH was removed under vacuum, the residue was filtered through a short column of deactivated silica gel (pentane/diethyl ether, 1:1), and then the solvent was removed. The free N,P-ligand and $[Ir(COD)Cl]_2$ were dissolved in dichloromethane under argon. This solution was heated to reflux for 1 h. The mixture was allowed to cool to room temperature, and then water and $NaBAr_F{\cdot}3H_2O$ were added, and the resulting mixture was stirred vigorously for 2 h at room temperature. The organic phase was separated and washed with brine, dried with $MgSO_4$, and filtered. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (pentane/dichloromethane = 3: 2) to give the pure product.

Complex 7a: Obtained in 76% yield. $[\alpha]_D^{25}$ = 2.9 (*c* = 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.43 (m, 27 H), 7.24–7.17 (m, 2 H), 4.35 (m, 2 H), 4.16 (m, 1 H), 3.06 (m, 2 H), 2.84 (m, 4 H), 2.22–1.61 (m, 8 H), 1.24 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7 (d, *J* = 2.0 Hz), 161.9 (dd, *J* = 50.0 Hz), 160.4, 139.4, 138.3, 136.4, 134.9, 133.7, 132.5, 132.4, 132.1, 131.6, 131.3, 130.6 (d, *J* = 10.0 Hz), 130.1, 129.8, 129.7, 129.4, 129.3, 129.2, 128.8 (m), 128.4, 126.4 (d, *J* = 20.0 Hz), 125.5, 122.9, 119.3, 117.6, 92.6 (d, *J* = 7.5 Hz), 83.6 (d, *J* = 17.3 Hz), 68.6, 66.6, 46.7 (d, *J* = 5.5 Hz), 36.6 (d, *J* = 4.8 Hz), 34.6, 30.0, 29.8, 29.3, 28.8, 28.7, 28.1, 24.4 ppm. ^{31}P NMR: δ = 12.7 ppm. IR (neat): $\tilde{\nu}$ = 2924, 1610, 1454, 1437, 1352, 1272, 1115, 885, 836, 744, 712, 694, 681 cm^{-1}. HRMS (ESI): calcd. for $C_{35}H_{36}IrNP$ $[M - BAr_F]^+$ 694.2215; found 694.2211.

Complex 7b: Obtained in 80% yield. $[\alpha]_D^{25}$ = 24.5 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.39 (m, 26 H), 7.12 (m, 1 H), 4.42 (m, 1 H), 4.21 (m, 2 H), 3.07 (m, 3 H), 2.95–2.40 (m, 6 H), 2.32–2.06 (m, 5 H), 2.05–1.90 (m, 3 H), 1.43–1.23 (m, 2 H), 1.23–1.00 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7, 162.0 (dd, *J* = 50.0 Hz), 160.9, 142.48, 140.51, 139.5, 138.6, 136.3, 135.0, 133.8, 133.1, 132.6, 132.2, 131.8 (d, *J* = 2.7 Hz), 131.4, 130.2, 129.8, 129.3, 129.01–128.86 (m), 128.53–128.42 (m), 128.18, 127.02 (d, *J* = 10.0 Hz), 126.6, 126.4, 122.9, 119.4, 117.7 (m), 93.9, 85.2, 67.2 (d, *J* = 5.0 Hz), 66.4 (m), 46.6 (d, *J* = 5.6 Hz), 36.9 (m), 34.4, 30.4, 30.2, 29.9, 28.7, 28.4 (m), 27.9 (m), 24.6, 23.3 (m), 23.1 ppm. ^{31}P NMR: δ = 20.8 ppm. IR (neat): $\tilde{\nu}$ = 2925, 1610, 1452, 1436, 1353, 1273, 1117, 886, 839, 745, 681 cm^{-1}. HRMS (ESI): calcd. for $C_{37}H_{40}IrNP$ $[M - BAr_F]^+$ 708.2371; found 722.2524.

Complex 7c: Obtained in 89% yield. $[\alpha]_D^{25}$ = 15.7 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79–7.63 (m, 10 H), 7.63–7.48 (m, 12 H), 7.48–7.39 (m, 5 H), 7.34–7.28 (m, 2 H), 4.52 (m, 1 H), 4.31 (m, 1 H), 4.10 (m, 1 H), 3.14 (m, 1 H), 2.84 (m, 2 H), 2.70 (m, 1 H), 2.55 (m, 1 H), 2.51–2.32 (m, 2 H), 2.19 (m, 1 H), 2.08–1.84 (m, 3 H), 1.81–1.67 (m, 3 H), 1.40–1.31 (m, 1 H), 1.15–1.04 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.6 (dd, *J* =

50.0 Hz), 160.2, 141.2, 138.8, 135.0, 133.2 (d, J = 10.5 Hz), 132.6–132.1 (m), 132.0–131.4 (m), 130.6–130.2 (m), 129.9, 129.8, 129.6, 129.5, 129.3, 128.9, 126.7, 124.8, 124.2, 123.0, 119.3, 117.7, 88.0, 69.5, 68.8, 41.0, 36.1, 35.8, 32.2, 32.1, 29.9, 29.4, 28.3, 23.6, 20.0 ppm. ^{31}P NMR: δ = 3.7 ppm. IR (neat): $\tilde{\nu}$ = 2923, 1609, 1461, 1436, 1353, 1274, 1118, 886, 838, 738, 712, 681, 695 cm^{-1}. HRMS (ESI): calcd. for $C_{36}H_{38}IrNP$ $[M - BAr_F]^+$ 722.2528; found 708.2367.

Complex 7d: Obtained in 87% yield. $[\alpha]_D^{25}$ = 10.0 (c = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84–7.67 (m, 12 H), 7.67–7.55 (m, 3 H), 7.55–7.49 (m, 5 H), 7.49–7.26 (m, 6 H), 7.23–7.11 (m, 1 H), 4.68–4.33 (m, 2 H), 4.19 (m, 1 H), 3.01–2.67 (m, 1 H), 2.67–2.36 (m, 4 H), 2.23–2.00 (m, 5 H), 1.95–1.83 (m, 2 H), 1.83–1.48 (m, 5 H), 1.22–0.94 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6 (dd, J = 50 Hz), 169.0, 141.0, 139.2, 135.1, 132.7, 131.7, 131.5, 130.2, 129.8–129.3 (m), 128.5–129.0 (m), 127.1, 127.0–126.6 (m), 125.8, 123.0, 119.4, 117.7, 41.0 (d, J = 6 Hz), 36.5, 34.8, 31.8 (m), 30.8, 30.2, 29.4, 28.2, 24.0, 23.1, 22.7, 19.6 ppm. ^{31}P NMR: δ = 40.7 ppm. IR (neat): $\tilde{\nu}$ = 2951, 1609, 1461, 1353, 1272, 1115, 886, 838, 736, 712, 681, 669 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{42}IrNP$ $[M - BAr_F]^+$ 736.2684; found 736.2681.

General Procedure for Asymmetric Hydrogenation: Ir complex (1.0 mol-%) and substrate (0.25 mmol) were added into a vial, followed by dichloromethane (1 mL). The vial was placed in a high-pressure hydrogenation apparatus. The reactor was purged three times with H_2 (1 bar), then it was filled with H_2 (50 bar). The reaction mixture was stirred at room temperature for 12 h. Then the H_2 pressure was released, and the solvent was removed in vacuo. The crude product was filtered through a short plug of silica. Conversions were determined by ^{1}H NMR spectroscopy, and enantiomeric excesses were determined by GC–MS or HPLC with a chiral column.[4]

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for all key intermediates and final products.

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