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Asymmetric hydrogenation of alkenes with planar chiral 2-phosphino-1-aminoferrocene-iridium(I) complexes

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ABSTRACT

The first highly enantioenriched and enantiopure planar chiral 2-phosphino-1-aminoferrocene ligands and their Ir(COD)BAr_F complexes are reported. The ligands display bidentate coordination behavior towards iridium, as indicated by trends in ^{31}P and ^{1}H NMR spectra of the phosphine moieties and the α to nitrogen substituents of the amines. All of the new complexes showed good reactivity as catalysts in promoting asymmetric hydrogenation of several prochiral alkenes, with enantioselectivities up to 92%. Iridium complexes of dimethylaminoferrocene derivatives containing *P*–Ar groups [PPh_2 and $P(o\text{-tol})_2$] gave the highest levels of asymmetric induction.

1. Introduction

Iridium complexes with chiral bidentate *P,N* ligands [1] represent a class of catalysts that have significantly expanded the application range of asymmetric hydrogenation [2]. Based on the original cationic catalyst designed by Crabtree et al. in 1977 [3] for the hydrogenation of hindered alkenes (**1**, Fig. 1), Pfaltz and co-workers have made significant contributions to this area by the development Ir(I) complexes containing chiral phosphino- or phosphinito-oxazoline ligands (**2**, **3**) [4]. Combined with non-coordinating counterions such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr_F), which inhibit deactivation of the metal [5], a broad range of catalysts tailored to ever increasing types of substrates may developed by changes to chiral ligand structures. To this end, Andersson et al. and Bolm and Lu have reported ligand motifs containing *N*-phosphine (**4**) [6] or sulfoximine (**5**) [7] groups, while Zhou has investigated phosphino-oxazolines with spirocyclic chiral centers (**6**) [8]. Ferrocenyl *P,N* ligands [9] which possess elements of both planar and central chirality, such as oxazoline **7** [10] and pyridyl derivative **8** [11], have also been investigated.

Despite the predominance of *P,N*-donor ligands in asymmetric iridium catalyzed hydrogenation, the majority of ligands as outlined in Fig. 1 have sp^2-hybridized nitrogen donors. In contrast, our group has reported that the Ir(COD)BAr_F coordination complex of racemic 2-diphenylphosphino-1-dimethylaminoferrocene (**9a**), which has an sp^3-hybridized nitrogen donor, catalyzes hydrogenation and hydroamination of alkenes [12]. Based on those results and our recent development of an asymmetric synthesis of 2-substituted-1-aminoferrocenes [13], we describe in this paper the synthesis of enantioenriched and enantiopure Ir(COD)BAr_F complexes of several 2-phosphino-1-aminoferrocene ligands [14,15] and assess their effectiveness in catalytic asymmetric hydrogenation of alkenes. The ligands used in this study differ somewhat from previous ferrocene-based systems (e.g., **7** and **8**) in that they are exclusively planar chiral and have ligating heteroatoms that are directly attached to the cyclopentadienyl (Cp) ring rather than in pendant groups.

2. Results and discussion

All new enantioenriched and enantiopure 2-phosphino-1-aminoferrocene ligands (**9a**–**c** and **15**) were synthesized by asymmetric lithiation of Lewis acid-base adducts **10** or **13** with isopropyllithium in the presence of **11** and 2-dimethylaminoethanol (DMAE), followed by addition of chlorophosphine electrophiles (Scheme 1) [13]. The ammonium salts **12a**–**c**·HBF_4 and **14**·HBF_4 were then prepared by sequential addition of elemental sulfur and a slight excess of $HBF_4{\cdot}OEt_2$. Ammonium fluoroborate salts **12a**·HBF_4 and **14**·HBF_4 were recrystallized to enantiomeric purity

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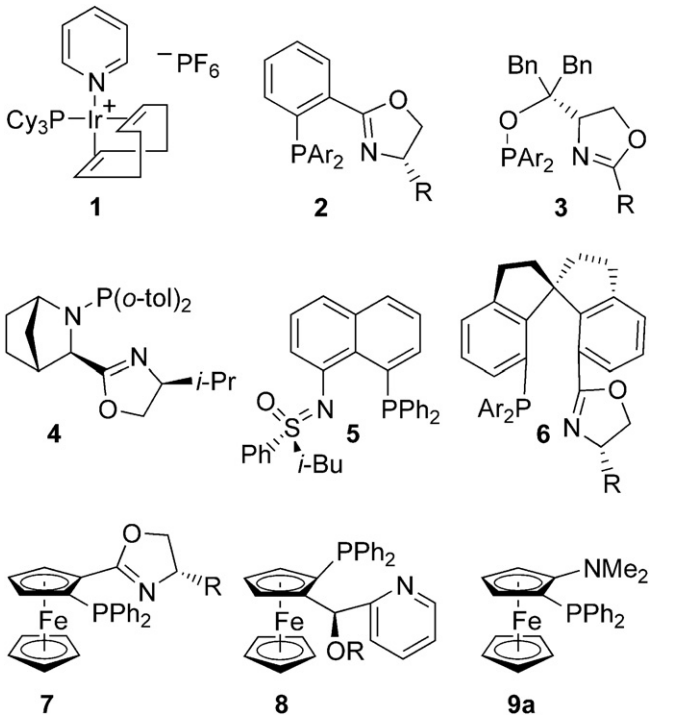


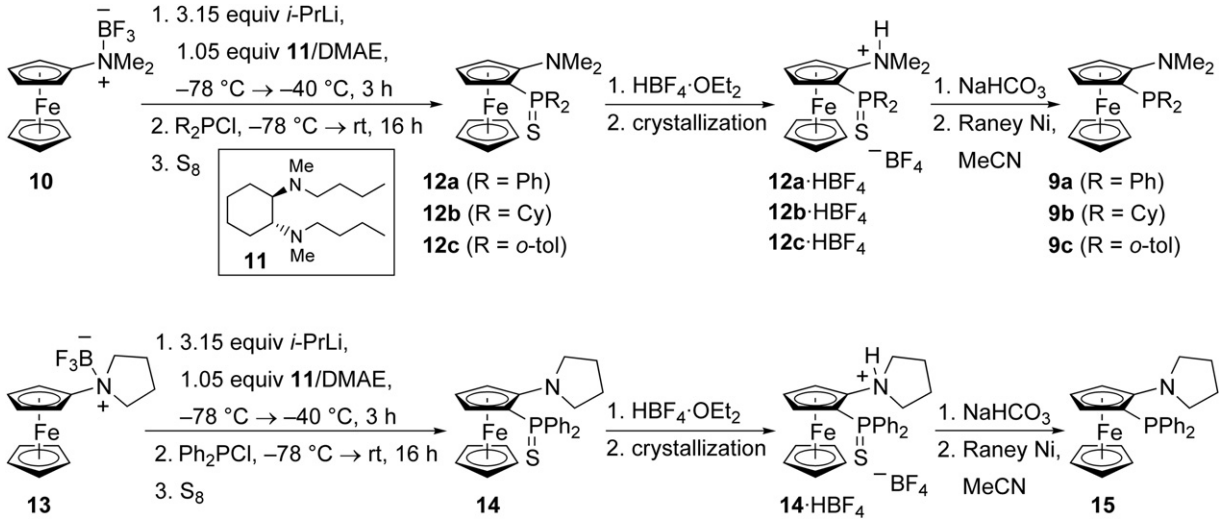
Fig. 1. Crabtree's catalyst (**1**) and chiral ligands (**2-9a**) used in iridium catalyzed hydrogenation.

by diffusion of diethyl ether into a dichloromethane solution of each salt. In a similar manner, dicyclohexylphosphine sulfide **12b** was enriched from 70 to 84% ee by recrystallization of **12b**·HBF_4, whereas *o*-tol derivative **12c**·HBF_4 could not be enriched beyond 78% ee by this method. In any case, neutralization of each ammonium salt with sodium bicarbonate and desulfurization (Raney nickel) afforded planar chiral ligands **9a**–**c** and **15** of sufficient structural diversity to enable assessment of their iridium complexes in asymmetric hydrogenation of alkenes. To the best of our knowledge, ligands **9a** and **15** are the first enantiomerically pure 2-phosphino-1-aminoferrocenes to be reported [16].

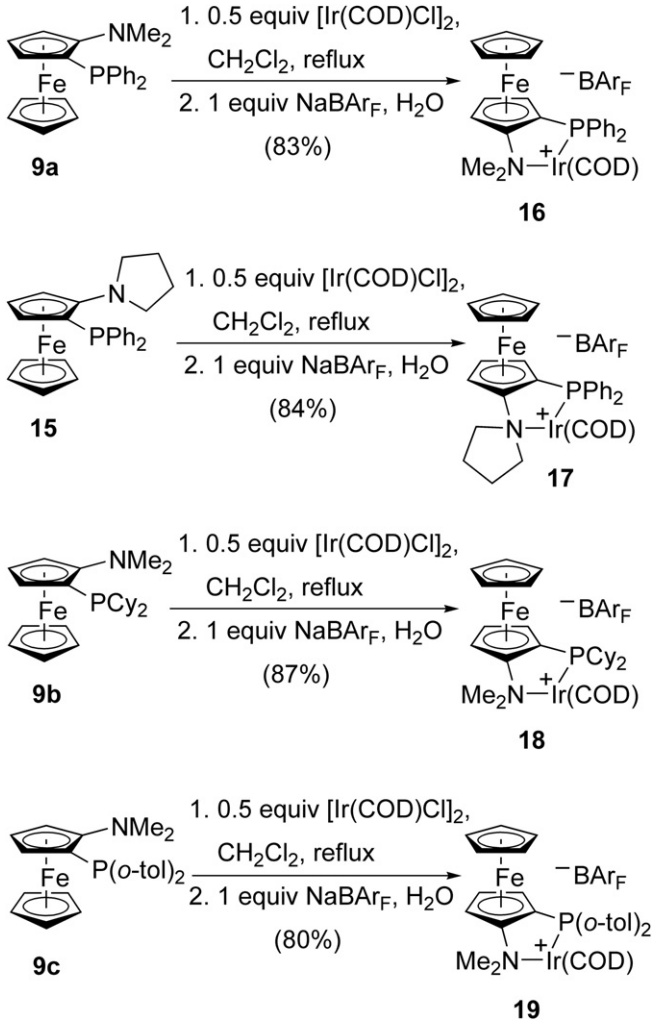
With ligands **9a**–**c** and **15** in hand, cationic iridium complexes **16**–**19** were prepared by reaction with $[Ir(COD)Cl]_2$ followed by *in situ* anion exchange using sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate ($NaBAr_F$, Scheme 2). Previously, we reported the X-ray crystal structure of racemic **16** in which the ligand was shown to behave as a bidentate *P,N* donor to give a five-membered chelate ring [12]. The bidentate coordination of the ligand in racemic **16** was also evident in its ^{31}P and ^1H NMR spectra where a downfield shift was observed for the phosphorus signal (^{31}P δ 15.0) in addition to non-equivalent amino methyl singlets [$^1H(NMe_2)$ δ 3.13, 2.69] in comparison to the free ligand [^{31}P δ −20.4; $^1H(NMe_2)$ δ 2.69] [12]. The same spectroscopic trend was observed in new complexes **17**–**19**. Thus, **18**–**19** displayed analogous downfield shifts of their ^{31}P NMR signals (**18**: δ 18.6; **19**: δ 17.6, 12.9 [17]) and diastereotopic NMe_2 singlets in ^1H NMR (**18**: δ 3.07, 2.83; **19**: δ 3.50, 3.47, 3.07, 3.00) [17] versus the free ligands [**9b**: ^{31}P δ −11.2 and $^1H(NMe_2)$ δ 2.75; **9c**: ^{31}P δ −39.8 and $^1H(NMe_2)$ δ 2.67]. Complex **19** was a 1:1 mixture of bidentate conformational isomers, as confirmed by low temperature (−10 °C) NMR experiments [17]. Ferrocenylpyrrolidine ligand **15** featured a ^{31}P NMR signal at δ −11.2 and a four-hydrogen ^1H NMR multiplet for the α to nitrogen methylene groups at δ 3.20–3.10, which shifted accordingly in complex **17** [^{31}P δ 14.4; ^1H (Nα-$(CH_2)_2$) δ 3.31–3.15 (m, 3H) and 2.60–2.56 (m, 1H)].

Iridium complexes **16**–**19** were employed in asymmetric hydrogenation of several prochiral alkenes (**20a**–**g**, Scheme 3). For consistency, all experiments were conducted in dichloromethane under 62 bar pressure of hydrogen at room temperature for 72 h with a catalyst loading of 2 mol% [18]. Initial results using enantiopure catalyst **16** were very encouraging: *trans*-1,2-diphenylpropene (**20a**) was hydrogenated to **21a** in 96% isolated yield and 84% ee favoring the *R* enantiomer. Even better selectivities were obtained with cinnamate esters **20b** and **20c**, which provided the β-chiral esters **21b** and **21c** in excellent yields and 91–92% ee. Respectable selectivities were also observed with cinnamates **20d** and **20e** to give α-chiral esters **21d** and **21e** in 82–83% ee. Hydrogenation of amide **20f** and allylic alcohol **20g** with **16** afforded **21f** and **21g** with lower levels of asymmetric induction (48 and 18% ee, respectively). Changing the solvent to toluene, chloroform or 1,2-dichloroethane did not improve the yield or selectivity of these reactions.

In an effort to improve selectivity and to identify reactivity trends the remaining catalysts **17**–**19**, which incorporate structural variations at the amine or phosphine substituents, were evaluated in asymmetric hydrogenation of the same substrates. Although pyrrolidine-containing catalyst **17** gave an identical result as **16** in hydrogenation of **20a**, significantly lower enantioselectivities were observed for β-chiral products **21b** and **21c** (61% ee). In fact,



Scheme 1. Asymmetric synthesis of 2-phosphino-1-aminoferrocenes **9a**–**c** and **15**.



Scheme 2. Preparation of planar chiral 2-phosphino-1-aminoferrocene-Ir(I) complexes.

changing the position of the methyl group as in substrates **20d** and **20e** provided α-chiral esters **21d** and **21e** as racemates, a huge decrease in selectivity compared to complex **16**. Similar decreases were seen with amide **20f** and alcohol **20g**, the latter to give **21g** in 12% ee favoring the *S* rather than *R* enantiomer. It is clear from these experiments that the bulkier pyrrolidine moiety of **17** is detrimental to the selectivity of hydrogenation.

Based on the preceding results, complexes **18** and **19** with differing phosphine substituents were investigated. With **18** (84% ee), products **21a**–**e** were obtained in 48–58% ee, which is lower than the levels of selectivity observed with **16**, even accounting for the lower enantiomeric purity of the precatalyst. Slightly higher selectivity was observed for product **21g** (23% ee). More interesting results were attained with **19** (78% ee). Thus, hydrogenation of **20a**–**e** gave products **21a**–**e** in 73–78% ee, mirroring the higher levels of induction seen with **16**. Complex **19** was less selective however with esters **20d** and **20e** (21 and 29% ee, respectively). Interestingly, hydrogenation of **20g** with **19** afforded **21g** in significantly better 49% ee in comparison to **16** (18% ee), continuing a steric trend that was hinted at with complex **18**. This last result must be tempered by the possibility that a diastereomeric dimeric form of the active catalyst, produced *in situ* from scalemic **19**, is enhancing the enantioselectivity. Nonetheless, it is encouraging that the relative levels of enantioselectivity with **19** rival (**20b** and **20c**) or even surpass (**20a** and **20g**) complex **16** for several substrates.

3. Conclusion

In summary, we have prepared the first highly enantioenriched and enantiopure planar chiral 2-phosphino-1-aminoferrocenes and synthesized their Ir(COD)BAr_F complexes. The ligands in each case appeared to be bidentate towards the metal, as indicated by trends in ^{31}P and ^{1}H NMR observed previously for racemic **16**. All of the new complexes showed good reactivity as catalysts in promoting asymmetric hydrogenation of several prochiral alkenes, with enantioselectivities as high as 92%. These results are encouraging considering that they represent the first use of such exclusively planar chiral *P,N* ligands, where both heteroatoms are directly attached to a ferrocene Cp ring, in asymmetric catalysis [12,16]. Structural variations to the ligands showed that changes to the phosphine moiety are probably more productive in enhancing the selectivity of hydrogenation than changing the amine functionality (**17**), which leads to severe decreases in asymmetric induction for many substrates. Although not enantiomerically pure, it was notable that P(*o*-tol)$_2$-containing complex **19** produced higher relative or absolute levels of asymmetry than PPh_2-containing complex **16** for substrates **20a** and **20g**. Based on these results, further investigations of ligands **9a**, **9c** and their *P*-aryl congeners in metal-mediated asymmetric catalysis are warranted and currently underway in our group.

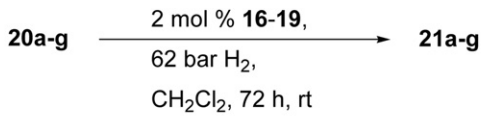
4. Experimental

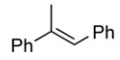
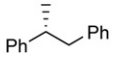
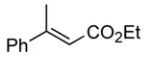
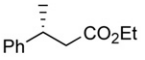
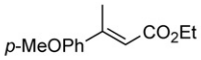
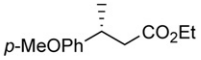
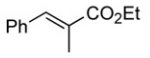
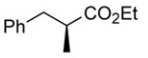
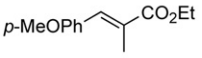
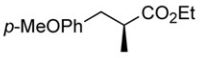
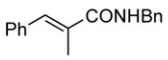
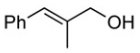
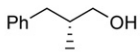
4.1. General

All reagents were purchased from commercial sources and used as received unless otherwise indicated. Tetrahydrofuran (THF) and diethyl ether were freshly dried and distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen. MTBE was distilled over $LiAlH_4$ under an atmosphere of nitrogen. Boron trifluoride etherate and dichloromethane were distilled from CaH_2 under argon prior to use. Isopropyllithium was prepared according to a published procedure [19] and was titrated against *N*-benzylbenzamide to a blue endpoint [20]. Reactions were performed under argon in flame- or oven-dried glassware using syringe-septum cap techniques or Schlenk conditions unless otherwise indicated. Column chromatography was performed on silica gel 60 (70–230 mesh) or neutral alumina. NMR spectra were obtained on a Bruker Avance 300 or 600 MHz instrument and are referenced to TMS or to the residual proton signal of the deuterated solvent for ^{1}H spectra, and to the carbon multiplet of the deuterated solvent for ^{13}C spectra according to published values. Pressurized reactions were performed with a Parr 4760 bomb. Enantiomeric ratios were determined on an Agilent 1100 series HPLC at $\lambda = 254$ nm with Chiralcel OD-H, Chiralcel OB-H, or Chiralpak AS-H columns, or on a Hewlett–Packard 6890 GC with a Chirasil DEX-CB column, and were compared against racemic material. FT-IR spectra were obtained on an ATI Mattson Research Series spectrometer as KBr pellets for solids or on KBr discs for liquids. Optical rotations were measured on a Rudolph Research Autopol III automatic polarimeter. Mass spectra were obtained on an MSI/Kratos Concept 1S Mass Spectrometer. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

4.2. (*S*)-(−)-2-Diphenylphosphino-1-dimethylaminoferrocene [(*S*)-**9a**]

The synthesis of enantiomerically pure ammonium salt **12a**·HBF_4 from **10** has been reported elsewhere [13]. A flask containing a biphasic suspension of (*S*)-**12a**·HBF_4 (140 mg, 0.26 mmol) in sat. aqueous $NaHCO_3$ (5 mL) and diethyl ether (10 mL) was sonicated for 1 min or until all the solid dissolved. The layers were separated and the aqueous



	alkene, **20**	product, **21**	% yield (% ee) with **16** (99% ee)	% yield (% ee) with **17** (99% ee)	% yield (% ee) with **18** (84% ee)	% yield (% ee) with **19** (78% ee)
a			96 (84)	96 (84)	98 (49)	99 (78)
b			94 (91)	98 (61)	87 (55)	97 (75)
c			99 (92)	83 (61)	96 (58)	99 (73)
d			88 (82)	74[a] (0)	94 (48)	96 (21)
e			98 (83)	79[a] (0)	95 (56)	93 (29)
f			96 (48)	98 (16)	96 (12)	95 (11)
g			95 (18)	96 (12[b])	99 (23)	96 (49)

[a] percent conversion; [b] (*S*)-**21g** is major enantiomer.

Scheme 3. Asymmetric hydrogenation of alkenes **20a**–**g** with catalysts **16**–**19**.

phase was extracted with diethyl ether. The combined ether layer was washed with water, brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give enantiopure aminophosphine sulfide (*S*)-**12a** (116 mg, 99%): mp 120–122 °C; $[\alpha]_D^{20}$ +62.4 (*c* 0.85, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:*i*-PrOH, 1.0 mL/min) determined a 99.7:0.3 er (>99% ee) [t_R(minor) 6.72 min, t_R(major) 7.39 min]. A mixture of the intermediate aminophosphine sulfide and freshly activated Ni-Al catalyst [21] (1.44 g, 16.8 mmol) in acetonitrile (25 mL) under argon was heated at 60 °C for 3 h. The reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite, washing with acetonitrile. Removal of the solvent *in vacuo* afforded aminophosphine (*S*)-**9a** (118 mg, 85%) as an orange wax: $[\alpha]_D^{20}$ −213 (*c* 0.81, $CHCl_3$). Spectroscopic data was in agreement with racemic **9a** reported previously [12].

4.3. (S)-(−)-[2-(Diphenylphosphino)ferrocenyl]-1-pyrrolidine [(S)-15]

The synthesis of enantiomerically pure ammonium salt **14**·HBF_4 from **13** has been reported elsewhere [13]. A flask containing a biphasic suspension of (*S*)-**14**·HBF_4 (170 mg, 0.30 mmol) in sat. aqueous $NaHCO_3$ (5 mL) and diethyl ether (10 mL) was sonicated for 1 min or until all the solid dissolved. The layers were separated and the aqueous phase was extracted with diethyl ether. The combined ether layer was washed with water, brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give enantiopure aminophosphine sulfide (*S*)-**14** (150 mg, 98%): mp 216–218 °C; $[\alpha]_D^{20}$ +60.9 (*c* 0.89, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:*i*-PrOH, 1.0 mL/min) determined a >99.5:0.5 er (>99% ee) [t_R(major) = 5.83 min, t_R(minor) = 7.12 min]. A mixture of intermediate aminophosphine sulfide (*S*)-**14** and freshly activated Ni-Al catalyst [21] (1.41 g, 16.4 mmol) in acetonitrile (25 mL) under argon was heated at 60 °C for 3 h. The reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite, washing with acetonitrile. Removal of the solvent *in vacuo* afforded the free aminophosphine (*S*)-**15** (91 mg, 78%) as an orange solid: mp 118–120 °C; $[\alpha]_D^{20}$ −137.3 (*c* 0.75, $CHCl_3$); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −16.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.38–7.35 (m, 3H), 7.26–7.18 (m, 5H), 4.12 (s, 5H), 4.03 (q, 1H, J = 1.5 Hz), 3.99 (t, 1H, J = 2.4 Hz), 3.26 (m, 1H), 3.20–2.12 (m, 4H), 1.90–1.81 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.7 (d, J^{1331}_{C-P} = 12.1 Hz), 137.9 (d, J^{1331}_{C-P} = 11.3 Hz), 135.3 (d, J^{1331}_{C-P} = 21.9 Hz), 132.3 (d, J^{1331}_{C-P} = 18.1 Hz), 128.9, 128.1 (d, J^{1331}_{C-P} = 5.3 Hz), 128.0 (d, J^{1331}_{C-P} = 3.8 Hz), 116.7 (d, J^{1331}_{C-P} = 16.6 Hz), 68.0, 67.9 (d, J^{1331}_{C-P} = 3.8 Hz), 64.7, 62.1 (d, J^{1331}_{C-P} = 12.8 Hz), 60.2 (d, J^{1331}_{C-P} = 3.8 Hz), 52.4, 52.3, 24.9, 24.8; EIMS [*m*/*z*(%)] 439 (100, M^+); HRMS (EI) calcd for $C_{26}H_{26}NP^{56}Fe$: 439.1152; found 439.1159; Anal. calcd for $C_{26}H_{26}NP^{56}Fe$: C, 71.08; H, 5.97. Found: C, 71.21; H, 5.92.

4.4. (S)-(−)-2-Dicyclohexylphosphinothioyl-1-dimethylaminoferrocene [(S)-12b]

A solution of (*R*,*R*)-**11** (233 mg, 0.916 mmol) in *t*-BuOMe (4.5 mL) was cooled to −40 °C, treated sequentially with *i*-PrLi (1.40 mL, 1.98 M

in pentane, 2.76 mmol) and 2-dimethylaminoethanol (82 mg, 0.917 mmol) in *t*-BuOMe (4.5 mL), and stirred for 15 min at that temperature. The solution was transferred by cannula to a mixture of **10** at −78 °C [prepared by addition of $BF_3{\cdot}OEt_2$ (115 μL, 0.916 mmol) to a solution of dimethylaminoferrocene (200 mg, 0.873 mmol) in *t*-BuOMe (9 mL) at 0 °C and stirring for 10 min]. The mixture was allowed to warm slowly to −40 °C over approximately 3.5 h and held at that temperature for an additional hour. After cooling back to −78 °C, $ClPCy_2$ (390 μL, 1.77 mmol) was added and the mixture was allowed to warm slowly to room temperature. The reaction mixture was diluted with Et_2O and worked-up by addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with Et_2O (3 × 15 mL) and the combined organic extract was washed with H_2O (15 mL), brine (15 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the crude aminophosphine, which was passed through a plug of silica gel, eluting with 90:10 hexane:Et_2O. To the crude material in a dry round bottom flask under argon was added sulfur powder (700 mg, 21.8 mmol) and toluene (15 mL), and the mixture was heated at 40 °C for 2 h. After cooling to room temperature, the reaction mixture was gravity filtered to remove excess sulfur and the filtrate was pre-adsorbed on silica gel *in vacuo*. Flash column chromatography (silica gel, 95:5 hexane:EtOAc) gave (*S*)-**12b** (215 mg, 54%) as an orange wax: $[\alpha]_D^{20}$ −51.2 (*c* 1.7, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:EtOAc, 1.0 mL/min) determined an 85.1:14.9 er (70% ee) [t_R(minor) = 7.99 min, t_R(major) = 8.48 min]; IR (KBr, thin film) ν_{max} 2929, 2851, 1644, 1635, 1475, 1447, 1413, 1383, 1320, 1156, 1109, 1035, 1003, 850, 821, 755, 638 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 60.7; ^1H NMR (300 MHz, $CDCl_3$) δ 4.48 (q, 1H, J = 2.7 Hz), 4.35 (s, 5H), 4.34 (m, 1H), 4.30 (q, 1H, J = 1.5 Hz), 2.65 (s, 6H), 2.55 (m, 2H), 2.09 (m, 1H), 1.93 (m, 4H), 1.82–1.61 (m, 7H), 1.16 (m, 5H), 1.13 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 116.1 (d, J^{1331}_{C-P} = 7.6 Hz), 70.7, 70.6 (d, J^{1331}_{C-P} = 7.6 Hz), 62.7 (d, J^{1331}_{C-P} = 62.7 Hz), 66.6 (d, J^{1331}_{C-P} = 9.8 Hz), 62.3 (d, J^{1331}_{C-P} = 8.3 Hz), 43.4, 39.4 (d, J^{1331}_{C-P} = 50.6 Hz), 37.3 (d, J^{1331}_{C-P} = 51.3 Hz), 28.2 (d, J^{1331}_{C-P} = 2.3 Hz), 27.4 (d, J^{1331}_{C-P} = 3.0 Hz), 27.3, 27.1 (d, J^{1331}_{C-P} = 6.0 Hz), 26.8 (d, J^{1331}_{C-P} = 6.0 Hz), 26.6 (d, J^{1331}_{C-P} = 3.8 Hz), 26.5, 26.0 (d, J^{1331}_{C-P} = 2.3 Hz), 26.0 (d, J^{1331}_{C-P} = 3.2 Hz), 25.9 (d, J^{1331}_{C-P} = 3.8 Hz); EIMS [*m*/*z*(%)] 457 (100, M^+), 308 (23), 229 (16); HRMS (FAB) calcd for $C_{24}H_{36}NPS^{56}Fe$: 457.1655, found 457.1662.

4.5. (*S*)-(−)-[2-(Dicyclohexylphosphinothioyl)ferrocenyl]-1-dimethylammonium tetrafluoroborate [(*S*)-**12b**·HBF_4]

A solution of (*S*)-**12b** (180 mg, 0.394 mmol) in Et_2O (20 mL) at 0 °C open to air was treated with $HBF_4{\cdot}Et_2O$ (76 μL, 0.56 mmol). An immediate color change was observed with formation of a yellow precipitate. The solution was allowed to stir for 10 min, after which the solid was collected by suction filtration, washed with ice-cold Et_2O, and dried *in vacuo* to afford ammonium salt **12b**·HBF_4 (212 mg, 99%) as a yellow powder: mp 84–89 °C; $[\alpha]_D^{20}$ −43.2 (*c* 1.0, $CHCl_3$). Two recyrstallizations via liquid–liquid diffusion of Et_2O into a solution of **12b**·HBF_4 in CH_2Cl_2 afforded further enantiomerically enriched product with the following properties: mp 104–106 °C; $[\alpha]_D^{20}$ −51.3 (*c* 1.0, $CHCl_3$); IR (KBr) ν_{max} 3037, 2933, 2856, 2652, 2564, 2423, 1450, 1217, 1176, 1110, 1053, 851, 754, 608 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 56.7; ^1H NMR (300 MHz, $CDCl_3$) δ 12.01 (s, 1H), 5.45 (t, 1H, J = 1.2 Hz), 4.78 (q, 1H, J = 1.5 Hz), 4.57 (s, 5H), 4.35 (d, 1H, J = 2.4 Hz), 3.58 (d, 3H, J = 5.1 Hz), 3.11 (d, 3H, J = 5.1 Hz), 2.59 (m, 1H), 2.50–2.45 (m, 1H), 2.41–2.31 (m, 1H), 2.05 (m, 3H), 1.85–1.70 (m, 5H), 1.58–1.35 (m, 8H), 1.17 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 110.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 7.6 Hz), 72.5, 70.4 (d, $J^{13}_{C-}{}^{31}_{P}$ = 8.3 Hz), 69.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 8.3 Hz), 64.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.8 Hz), 62.85 (d, $J^{13}_{C-}{}^{31}_{P}$ = 75.6 Hz), 49.2, 48.7, 44.5 (d, $J^{13}_{C-}{}^{31}_{P}$ = 48.3 Hz), 39.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 47.6 Hz), 27.6 (d, $J^{13}_{C-}{}^{31}_{P}$ = 3.2 Hz), 27.4, 27.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.8 Hz), 27.1 (d, $J^{13}_{C-}{}^{31}_{P}$ = 3.8 Hz), 26.3 (d, $J^{13}_{C-}{}^{31}_{P}$ = 8.3 Hz), 26.2 (d, $J^{13}_{C-}{}^{31}_{P}$ = 5.3 Hz), 25.9 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.8 Hz), 25.8 (d, $J^{13}_{C-}{}^{31}_{P}$ = 6.0 Hz) 25.7 (d, $J^{13}_{C-}{}^{31}_{P}$ = 3.8 Hz), 25.3; FABMS [*m*/*z*(%)] 458 (95, M^+), 229 (100); HRMS (FAB) calcd for $C_{24}H_{37}NPS^{56}Fe$: 458.1733, found 458.1732; Anal. calcd for $C_{24}H_{37}NPSFeBF_4$: C, 52.87; H, 6.84. Found: C, 52.17; H, 6.72.

4.6. (*S*)-(−)-2-Dicyclohexylphosphino-1-dimethylaminoferrocene [(*S*)-**9b**]

A flask containing a biphasic suspension of **12b**·HBF_4 (190 mg, 0.34 mmol) in Et_2O (10 mL) and 1M $NaHCO_3$ (5 mL) was sonicated for 1 min or until the solid dissolved. The layers were separated and the aqueous phase was extracted with diethyl ether (2 × 10 mL). The combined ether layer was washed with water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* before passing through a plug of silica gel, eluting with 1:1 hexane:EtOAc, to give the enriched aminophosphine sulfide (*S*)-**12b** (89 mg, 82%) as an orange wax: $[\alpha]_D^{20}$ −64.8 (*c* 0.51, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:EtOAc, 1.0 mL/min) determined an 92.1:7.9 er (84% ee) [t_R(minor) = 8.00 min, t_R(major) = 8.44 min]. A mixture of the aminophosphine sulfide and freshly activated Ni-Al catalyst [21] (646 mg, 7.54 mmol) in acetonitrile (15 mL) under argon was heated to 60 °C for 2 h. The reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite, washing with acetonitrile. Flash column chromatography (silica gel, 90:10 hexane:Et_2O) afforded (*S*)-**9b** as a moderately air-sensitive an orange oil (62 mg, 99%): $[\alpha]_D^{20}$ −14.3 (*c* 0.55, $CHCl_3$); IR (KBr) ν_{max} 3095, 2922, 2849, 2781, 1488, 1448, 1419, 1332, 1182, 1141, 1106, 1053, 999, 813, 614 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −11.2; ^1H NMR (300 MHz, $CDCl_3$) δ 4.23 (s, 5H), 4.10 (s, 1H), 4.04 (q, 1H, J = 2.4 Hz), 3.91 (m, 1H), 2.75 (s, 6H) 2.42 (m, 1H), 1.86 (m, 4H), 1.73–1.53 (m, 6H), 1.47–1.19 (m, 10H), 0.89–0.81 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 118.1 (d, J^{1331}_{C-P} = 13.6 Hz), 67.9, 67.2 (d, J^{1331}_{C-P} = 3.8 Hz), 63.9 (d, J^{1331}_{C-P} = 23.4 Hz), 63.4, 61.3 (d, J^{1331}_{C-P} = 2.3 Hz), 44.9, 44.8, 35.2 (d, J^{1331}_{C-P} = 14.3 Hz), 33.8 (d, J^{1331}_{C-P} = 11.3 Hz), 32.5, 32.2, 30.3 (d, J^{1331}_{C-P} = 14.3 Hz), 29.7 (d, J^{1331}_{C-P} = 10.6 Hz), 29.3 (d, J^{1331}_{C-P} = 6.8 Hz), 27.7 (d, J^{1331}_{C-P} = 12.1 Hz), 27.5 (d, J^{1331}_{C-P} = 6.8 Hz), 27.5 (d, J^{1331}_{C-P} = 13.6 Hz), 27.3 (d, J^{1331}_{C-P} = 7.6 Hz), 26.5 (d, J^{1331}_{C-P} = 8.3 Hz); EIMS [*m*/*z*(%)] 425 (100, M^+), 342 (13), 260 (27), 138 (16); HRMS (EI) calcd for $C_{24}H_{36}NP^{56}Fe$: 425.1934; found 425.1935. NMR data for racemic **9b** was previously reported in acetone-d_6 [12].

4.7. (*S*)-(+)-2-Di-ortho-tolyl-phosphinothioyl-1-dimethylaminoferrocene [(*S*)-**12c**]

A solution of (*R*,*R*)-**11** (235 mg, 0.922 mmol) in *t*-BuOMe (4.5 mL) was cooled to −40 °C, treated sequentially with *i*-PrLi (1.25 mL, 2.25 M in pentane, 2.81 mmol) and 2-dimethylaminoethanol (86 mg, 0.970 mmol) in *t*-BuOMe (4.5 mL), and stirred for 20 min at that temperature. The solution was transferred by cannula to a mixture of **10** at −78 °C [prepared by addition of $BF_3{\cdot}OEt_2$ (115 μL, 0.917 mmol) to a solution of dimethylaminoferrocene (200 mg, 0.873 mmol) in *t*-BuOMe (13 mL) at 0 °C and stirring for 10 min]. The mixture was allowed to warm slowly to −40 °C over approximately 2.5 h and then held at that temperature for an additional hour. After cooling back to −78 °C, a solution of $ClP(o\text{-tol})_2$ (548 mg, 2.20 mmol) in *t*-BuOMe (4 mL) was added and the mixture was allowed to warm slowly to room temperature. The reaction mixture was diluted with Et_2O and worked-up by addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic extract was washed with water (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford the crude aminophosphine. Flash column chromatography (silica gel, 90:10 hexane:EtOAc) was performed to remove (*R*,*R*)-**11**, which gave intermediate (*S*)-**9c** (232 mg, 60%) as an orange wax: ^{31}P NMR

(75.5 MHz, $CDCl_3$) δ −39.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–6.94 (m, 8H), 4.23 (s, 1H), 4.11 (s, 6H), 3.62 (s, 1H), 2.90 (s, 3H), 2.67 (s, 6 H), 2.11 (s, 3H). To (*S*)-**9c** (254 mg, 0.576 mmol) in a dry round bottom flask under argon was added sulfur powder (185 g, 57.6 mmol) and toluene (6 mL), and the mixture was heated at 40 °C for 2 h. After cooling to room temperature, the reaction mixture was gravity filtered to remove excess sulfur and the filtrate was pre-adsorbed on silica gel *in vacuo*. Flash column chromatography (silica gel, 90:10 hexane:Et_2O) gave (*S*)-**12c** (321 mg, 99%) as an orange foam: mp 60–64 °C; $[\alpha]_D^{20}$ +31.7 (*c* 1.0, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:*i*-PrOH, 1.0 mL/min) determined an 88:12 er (76% ee) [t_R(minor) = 5.36 min, t_R(major) = 5.83 min]; IR (KBr) ν_{max} 3097, 3055, 2951, 2925, 2854, 2783, 1732, 1591, 1566, 1493, 1454, 1421, 1383, 1327, 1276, 1146, 1107, 1055, 1006, 819, 756, 713, 687, 647, 609, 581, 532, 474 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 43.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69–8.63 (m, 1H), 7.88–7.81 (m, 1H), 7.45–7.42 (m, 2H), 7.21–7.10 (m, 4H), 4.40 (s, 6H), 4.08 (s, 1H), 3.73 (s, 1H), 2.79 (s, 6H), 2.12 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75.5 MHz, $CHCl_3$) δ 141.3 (d, J^{1331}_{C-P} = 10.6 Hz), 140.4 (d, J^{1331}_{C-P} = 8.3 Hz), 134.7 (d, J^{1331}_{C-P} = 13.6 Hz), 134.2, 133.1, 132.7 (d, J^{1331}_{C-P} = 12.1 Hz), 131.8 (d, J^{1331}_{C-P} = 10.6 Hz), 131.5 (d, J^{1331}_{C-P} = 15.1 Hz), 131.4 (d, J^{1331}_{C-P} = 9.8 Hz), 130.9 (d, J^{1331}_{C-P} = 3.0 Hz), 126.0 (d, J^{1331}_{C-P} = 13.6 Hz), 125.5 (d, J^{1331}_{C-P} = 12.8 Hz), 117.9 (d, J^{1331}_{C-P} = 8.3 Hz), 72.0 (d, J^{1331}_{C-P} = 13.6 Hz), 69.8, 66.0 (d, J^{1331}_{C-P} = 28.7 Hz), 64.9 (d, J^{1331}_{C-P} = 11.3 Hz), 64.1 (d, J^{1331}_{C-P} = 8.3 Hz), 46.7, 22.5 (d, J^{1331}_{C-P} = 3.8 Hz), 21.5 (d, J^{1331}_{C-P} = 5.3 Hz); EIMS [*m*/*z*(%)] 473 (M^+, 100), 441 (21); HRMS (EI) calcd for $C_{26}H_{28}NPS^{56}Fe$: 473.1029; found 473.1032; Anal. calcd for $C_{26}H_{28}NPSFe$: C, 65.97; H, 5.96. Found: C, 65.74; H, 5.97.

4.8. (*S*)-(−)-2-(Di-ortho-tolyl-phosphinothioyl)ferrocenyl-1-dimethylammonium tetrafluoroborate [(*S*)-**12c**·HBF_4]

A solution of (*S*)-**12c** (190 mg, 0.401 mmol) in Et_2O (20 mL) at 0 °C open to air was treated with $HBF_4 \cdot Et_2O$ (66 μL, 0.485 mmol). An immediate color change was observed with formation of a yellow precipitate. The solution was allowed to stir for 10 min, after which the solid was collected by suction filtration, washed with cold Et_2O, and dried *in vacuo* to afford ammonium salt (*S*)-**12c**·HBF_4 (210 mg, 93%) as a yellow powder: mp 137–139 °C; Attempts to enantiomerically enrich this salt by recrystallization using vapor diffusion of Et_2O into a dichloromethane solution were unsuccessful: $[\alpha]_D^{20}$ −46.9 (*c* 0.5, acetone); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 38.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.60 (bs, 1H), 8.84–8.79 (m, 1H), 7.62 (m, 3H), 7.46–7.42 (m, 1H), 7.26 (m, 2H), 7.05–6.97 (m, 1H), 5.59 (s, 1H), 4.78 (s, 1H), 4.28 (s, 6H), 3.66 (d, 3H, *J* = 4.8 Hz), 3.12 (d, 3H, *J* = 4.5 H), 2.21 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75.5 MHz, acetone-d_6) δ 142.1 (d, J^{1331}_{C-P} = 10.6 Hz), 140.9 (d, J^{1331}_{C-P} = 9.1 Hz), 135.8 (d, J^{1331}_{C-P} = 15.1 Hz), 134.2 (d, J^{1331}_{C-P} = 3.0 Hz), 134.1 (d, J^{1331}_{C-P} = 55.1 Hz), 133.5 (d, J^{1331}_{C-P} = 4.5 Hz), 133.4 (2 × d), 131.6 (d, J^{1331}_{C-P} = 11.3 Hz), 128.2 (d, J^{1331}_{C-P} = 53.6 Hz), 127.6, 127.4, 109.6 (d, J^{1331}_{C-P} = 9.8 Hz), 73.6, 72.4 (d, J^{1331}_{C-P} = 9.1 Hz), 71.3 (d, J^{1331}_{C-P} = 9.8 Hz), 67.3 (d, J^{1331}_{C-P} = 67.3 Hz), 66.5 (d, J^{1331}_{C-P} = 6.8 Hz), 50.2, 47.6, 22.8 (d, J^{1331}_{C-P} = 3.0 Hz), 20.9 (d, J^{1331}_{C-P} = 6.0 Hz); FABMS [*m*/*z*(%)] 474 (M-BF_4, 100), 229 (94), HRMS (FAB) calcd for $C_{26}H_{29}NPS^{56}Fe$: 474.1107; found 474.1072.

4.9. (*S*)-(−)-2-Di-ortho-tolyl-phosphino-1-dimethylaminoferrocene [(*S*)-**9c**]

A flask containing a biphasic suspension of (*S*)-**12c**·HBF_4 (190 mg, 0.34 mmol) in Et_2O (10 mL) and 1M $NaHCO_3$ (7 mL) was sonicated for 1 min or until the solid dissolved. The layers were separated and the aqueous phase was extracted with diethyl ether (2 × 10 mL). The combined ether layer was washed with water, brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Elution of the crude material through a plug of silica gel with 70:30 hexane:EtOAc solvent gave the aminophosphine sulfide (113 mg, 71%) with spectroscopic data matching (*S*)-**12c** above: $[\alpha]_D^{20}$ +31.3 (*c* 0.5, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 99:1 hexane:*i*-PrOH, 1.0 mL/min) determined an 89:11 er (78% ee) [t_R(minor) = 5.60 min, t_R(major) = 6.09 min]. A mixture of intermediate aminophosphine sulfide (*S*)-**12c** (90 mg, 0.19 mmol) and freshly activated Ni-Al catalyst [21] (814 mg, 9.51 mmol) in acetonitrile (20 mL) under argon was heated at 60 °C for 2 h. The reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite, washing with acetonitrile. Flash column chromatography (silica gel, 90:10 hexane:Et_2O) afforded (*S*)-**9c** as an orange solid (85 mg, 99%): mp 115–118 °C; $[\alpha]_D^{20}$ −133 (*c* 0.5, $CHCl_3$); IR (KBr) ν_{max} 3052, 2950, 1923, 2843, 2778, 1488, 1451, 1417, 1330, 1105, 1051, 1000, 813, 750, 463 cm^{-1}; ^{31}P NMR (75.5 MHz, $CDCl_3$) δ −39.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–6.94 (m, 8H), 4.23 (s, 1H), 4.11 (s, 6H), 3.62 (s, 1H), 2.90 (s, 3H), 2.67 (s, 6H), 2.11 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.4 (d, J^{1331}_{C-P} = 29.4 Hz), 140.3 (d, J^{1331}_{C-P} = 24.2 Hz), 139.3 (d, J^{1331}_{C-P} = 14.3 Hz), 136.0, 135.3 (d, J^{1331}_{C-P} = 10.6 Hz), 131.8, 129.8 (d, J^{1331}_{C-P} = 11.3 Hz), 129.7, 129.7, 129.0, 127.5, 125.4 (d, J^{1331}_{C-P} = 15.1 Hz), 119.0 (d, J^{1331}_{C-P} = 18.1 Hz), 69.0 (d, J^{1331}_{C-P} = 3.0 Hz), 68.4, 65.2 (d, J^{1331}_{C-P} = 12.1 Hz), 65.1, 61.1 (d, J^{1331}_{C-P} = 2.3 Hz), 45.4, 45.3, 22.1 (d, J^{1331}_{C-P} = 24.9 Hz), 20.8 (d, J^{1331}_{C-P} = 19.6 Hz); EIMS [*m*/*z*(%)] 441 (100, M^+); HRMS (EI) calcd for $C_{26}H_{28}NPS^{56}Fe$: 441.1308; found 441.1311.

4.10. (*S*)-(+)-2-Diphenylphosphino-1-dimethylaminoferrocene iridium(cyclooctadiene) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate [(*S*)-(**16**)]

A solution of $[Ir(COD)Cl]_2$ (81 mg, 0.12 mmol) and (*S*)-**9a** (100 mg, 0.24 mmol) in dry CH_2Cl_2 (4 mL) was heated at reflux for 1 h. After cooling to room temperature, $NaBAr_F$ (322 mg, 0.36 mmol) and deionized H_2O (4 mL) were added, resulting in a color change from orange to red. The mixture was stirred for 15 min, after which the layers were separated. The aqueous layer was washed with CH_2Cl_2 (3 × 5 mL) and the combined organic extract was washed with water (5 mL). The solution was concentrated almost to dryness on a rotary evaporator and then passed through a plug of silica gel, eluting with additional CH_2Cl_2. Removal of the solvent *in vacuo* afforded (*S*)-**16** (316 mg, 83%) as an orange solid: mp 168–172 °C; $[\alpha]_D^{20}$ +8.7 (*c* 1.04, acetone). ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 15.0; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (m, 10H), 7.57–7.42 (m, 12H), 5.03 (m, 1H), 4.90 (t, 1H, *J* = 2.7 Hz), 4.57 (m, 1H), 4.47 (s, 1H), 4.41 (s, 1H), 4.31 (s, 5H), 4.05 (m, 1H), 3.51 (m, 1H), 3.12 (s, 3H), 2.69 (s, 3H), 2.39–2.33 (m, 4H), 2.04 (m, 1H), 1.92–1.90 (m, 2H), 1.78–1.74 (m, 1H); All other spectroscopic data was in agreement with racemic **16** reported previously [12].

4.11. (*S*)-(−)-[2-(Diphenylphosphino)ferrocenyl]-1-pyrrolidine iridium(cyclooctadiene) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate [(*S*)-**17**]

A solution of $[Ir(COD)Cl]_2$ (61 mg, 0.091 mmol) and aminophosphine (*S*)-**15** (80 mg, 0.182 mmol) in dry CH_2Cl_2 (5 mL) was heated at reflux for 1.5 h. After cooling to room temperature, the solution was concentrated to provide crude (*S*)-(+)-[2-(diphenylphosphino)ferrocenyl]-1-pyrrolidine iridium(cyclooctadiene) chloride (138 mg, 98%) as an orange solid which was used for the anion exchange without further purification: mp >230 °C; $[\alpha]_D^{20}$ +71.5 (*c* 1.0 $CHCl_3$); FABMS [*m*/*z* (%)] 740 (56, M-Cl), 738 (100), 737 (45), 736 (76), 734 (39), 630 (25), 391 (27), 149 (55); HRMS (FAB) calcd for $C_{34}H_{38}NP^{56}Fe^{193}Ir$ 740.1720, found 740.1760. To a flask containing the chloride salt (90 mg, 0.116 mmol) was added $NaBAr_F$ (129 mg, 0.145 mmol), CH_2Cl_2 (6 mL), and deionized water (6 mL) under argon. The mixture was stirred for 15 min at room temperature over

which time the color changed from orange to red. The layers were separated, the aqueous layer extracted with CH_2Cl_2 (3 × 3 mL), and the combined organic was washed with deionized water (1 × 2 mL). The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 and filtered through a plug of silica gel, eluting with CH_2Cl_2 to give (*S*)-**17** (158 mg, 85%) as an orange solid: mp 128–129 °C; $[\alpha]_D^{20}$ −140 (*c* 0.61, $CHCl_3$); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.4; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −62.34; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 8H), 7.67–7.56 (m, 5H), 7.53 (s, 4H), 7.48–7.42 (m, 5H), 4.87 (bm, 1H), 4.84 (t, 1H, J = 2.7 Hz), 4.50 (s, 5H), 4.45 (m, 1H), 4.44 (m, 1H), 4.31 (m, 1H), 4.04 (bm, 1H), 3.77 (bm, 1H), 3.31–3.15 (m, 3H), 2.60–2.56 (m, 1H), 2.38–2.18 (m, 4H), 2.08–1.83 (m, 7H), 1.73–1.65 (m, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 161.70 (q, J^{1311}_{C-B} = 49.8 Hz), 133.3 (d, J^{1331}_{C-P} = 12.1 Hz), 133.0 (d, J^{1331}_{C-P} = 40.7 Hz), 132.0, 131.8 (d, J^{1331}_{C-P} = 10.6 Hz), 129.7 (d, J^{1331}_{C-P} = 9.1 Hz), 129.2 (d, J^{1331}_{C-P} = 10.6 Hz), 128.9 (q, J^{1319}_{C-F} = 30.2 Hz), 128.8, 126.5 (d, J^{1331}_{C-P} = 58.9 Hz), 124.5 (q, J^{1319}_{C-F} = 273.1 Hz), 121.6 (d, J^{1331}_{C-P} = 22.6 Hz), 117.5, 91.3 (d, J^{1331}_{C-P} = 7.5 Hz), 90.9 (d, J^{1331}_{C-P} = 12.1 Hz), 74.1 (d, J^{1331}_{C-P} = 6.0 Hz), 72.3, 68.8 (d, J^{1331}_{C-P} = 96.6 Hz), 66.5, 65.9, 61.1 (d, J^{1331}_{C-P} = 9.1 Hz), 60.7, 58.64, 57.98, 32.6, 32.4 (d, J^{1331}_{C-P} = 4.5 Hz), 29.8, 28.8, 24.5, 22.2; FABMS [*m*/*z* (%)] 740 (M-BAr_F, 39), 738 (100); HRMS (FAB) calcd for $C_{34}H_{38}NP^{56}Fe^{193}Ir$: 740.1720; found 740.1730.

4.12. (*S*)-(−)-2-Dicyclohexylphosphino-1-dimethylaminoferrocene iridium(cyclooctadiene) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate [(*S*)-**18**]

A solution of $[Ir(COD)Cl]_2$ (22.5 mg, 0.034 mmol) and (*S*)-**9b** (28.5 mg, 0.067 mmol) in dry CH_2Cl_2 (1.5 mL) under argon were heated at reflux for 1.5 h. After cooling to room temperature, the solution was concentrated to provide crude (*S*)-(−)-2-dicyclohexylphosphino-1-dimethylaminoferrocene iridium(cyclooctadiene) chloride (51 mg, 99%) as an orange solid which was used for the anion exchange without further purification: mp >230 °C; $[\alpha]_D^{20}$ −25.1 (*c* 0.64, $CHCl_3$); FABMS [*m*/*z* (%)] 726 (77, M-Cl), 724 (100), 722 (67), 450 (31), 394 (31), 229 (14); HRMS (FAB) calcd for $C_{32}H_{48}NP^{56}Fe^{193}Ir$: 726.2503, found 726.2464. To a flask containing chloride salt (25 mg, 0.033 mmol) was added $NaBAr_F$ (36 mg, 0.041 mmol), CH_2Cl_2 (1 mL), and deionized water (1 mL) under argon. The mixture was stirred for 15 min at room temperature resulting in a color change from orange to red. The layers were separated, the aqueous layer extracted with CH_2Cl_2 (3 × 1.5 mL), and the combined organic extract was washed with deionized water (2 mL). The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 and filtered through a plug of silica gel, eluting with CH_2Cl_2, to give (*S*)-**18** (46 mg, 88%) as a bright orange solid: mp 159–160 °C; $[\alpha]_D^{20}$ −4.2 (*c* 0.53, $CHCl_3$); IR (KBr) ν_{max} 3036, 2929, 2857, 1641, 1634, 1612, 1464, 1454, 1355, 1278, 1162, 1127, 888, 839, 760, 713, 682, 670 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 18.6; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −62.32; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 8H), 7.53 (s, 4H), 4.90 (bm, 1H), 4.84 (t, 1H, J = 3.0 Hz), 4.39 (s, 6H), 4.29 (bm, 1H), 4.23 (bm, 1H), 4.13 (d, 1H, J = 2.4 Hz), 3.75 (bm, 1H), 3.07 (s, 3H), 2.83 (s, 3H), 2.54 (bm, 1H), 2.41–2.11 (m, 5H), 2.05–2.01 (m, 4H), 1.95 (m, 1H), 1.87–1.68 (m, 12H), 1.62–1.56 (m, 1H), 1.45–1.34 (m, 3H), 1.25–1.18 (m, 4H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 161.7 (q, J^{1311}_{C-B} = 49.8 Hz), 134.8, 128.9 (q, J^{1319}_{C-F} = 27.1 Hz), 125.7 (d, J^{1331}_{C-P} = 22.6 Hz), 124.5 (q, J^{1319}_{C-F} = 273 Hz), 117.5, 91.8 (d, J^{1331}_{C-P} = 10.6 Hz), 88.8 (d, J^{1331}_{C-P} = 12.1 Hz), 74.8 (d, J^{1331}_{C-P} = 4.5 Hz), 71.3, 70.1 (d, J^{1331}_{C-P} = 45.3 Hz), 67.6, 59.3, 58.1 (d, J^{1331}_{C-P} = 9.1 Hz), 57.9, 57.1, 52.3, 39.3 (d, J^{1331}_{C-P} = 25.7 Hz), 38.6, (d, J^{1331}_{C-P} = 30.2 Hz), 33.6 (d, J^{1331}_{C-P} = 3.0 Hz), 32.0 (d, J^{1331}_{C-P} = 3.0 Hz), 31.0, 30.6, 29.8 (d, J^{1331}_{C-P} = 6.0 Hz), 29.6, 28.8, 27.9, 27.3 (d, J^{1331}_{C-P} = 9.1 Hz), 27.1 (d, J^{1331}_{C-P} = 13.5 Hz), 27.1 (d, J^{1331}_{C-P} = 10.6 Hz), 27.1, 27.0 (d, J^{1331}_{C-P} = 10.6 Hz), 25.7, 25.4; FABMS [*m*/*z* (%)] 726 (58, M-BAr_F), 725 (41) 724 (100), 723 (41), 722 (89), 721 (29), 720 (48), 612 (25), 610 (25), 530 (34), 528 (35), 451 (35), 450 (59), 449 (47), 448 (45), 447 (27), 406 (28), 392 (47), 345 (35), 343 (36), 330 (28), 229 (29); HRMS (FAB) calcd for $C_{32}H_{48}NP^{56}Fe^{193}Ir$: 726.2503; found 726.2526.

4.13. (*S*)-(−)-2-Di-ortho-tolyl-phosphino-1-dimethylaminoferrocene iridium(cyclooctadiene) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [(*S*)-**19**]

A solution of $[Ir(COD)Cl]_2$ (29.6 mg, 0.044 mmol) and (*S*)-**9c** (39 mg, 0.088 mmol) in dry CH_2Cl_2 (2 mL) under argon was heated at reflux for 1.5 h. After cooling to room temperature, the solution was concentrated to provide crude (*S*)-(−)-2-di-*ortho*-tolyl-phosphino-1-dimethylaminoferrocene iridium(cyclooctadiene) chloride (67 mg, 99%) as an orange-red solid: mp >230 °C; $[\alpha]_D^{20}$ −49.1 (*c* 1.02, $CHCl_3$); FABMS [*m*/*z*(%)] 742 (M-Cl, 88), 740 (77), 630 (59), 629 (50), 628 (100); HRMS (FAB) calcd for $C_{34}H_{40}NP^{56}Fe^{193}Ir$: 742.1877; found 742.1831. To a flask containing the chloride salt (35 mg, 0.045 mmol) was added $NaBAr_F$ (50 mg, 0.056 mmol), CH_2Cl_2 (1.5 mL) and deionized water (1.5 mL) under argon. The mixture was stirred for 15 min at room temperature over which time the color changed from orange to red. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 1.5 mL), and the combined organic extract was washed with deionized water (2 mL). The solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2 and filtered through a plug of silica, eluting with CH_2Cl_2, to give (*S*)-**19** (58 mg, 81%) as an orange solid: mp 161–163 °C; $[\alpha]_D^{20}$ −27.4 (*c* 0.50, $CHCl_3$); IR (KBr) ν_{max} 3063, 2927, 2856, 1611, 1467, 1355, 1279, 1162, 1127, 908, 888, 834, 758, 713, 682, 671 cm^{-1}; ^{31}P NMR (243 MHz, acetone-d_6, −10 °C, 1:1 mixture of bidentate conformers): δ 17.6, 12.9; ^{1}H NMR (600 MHz, acetone-d_6, −10 °C, 1:1 mixture of bidentate conformers) δ 9.31 (dd, 1H, J^{131}_{H-P} = 13.2, J^{11}_{H-H} = 7.8 Hz), 9.25 (bs, 1H), 8.57 (bs, 1H), 7.82 (s, 2 × 8H), 7.71 (bs, 1H), 7.71 (s, 2 × 4H), 7.60 (q, 2H, J^{11}_{H-H} = 7.8 Hz), 7.47 (t, 2 × 1H, J^{11}_{H-H} = 7.2 Hz), 7.45–7.37 (m, 2 × 2H), 7.33 (t, 1H, J^{11}_{H-H} = 7.2 Hz), 7.26 (bs, 1H), 7.24 (t, 1H, J^{11}_{H-H} = 7.2 Hz), 7.14 (bs, 1H), 5.66 (bs, 1H), 5.28 (bs, 1H), 5.17 (bs, 1H), 5.13 (s, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 5.04 (s, 1H), 4.81 (bs, 1H), 4.80 (s, 1H), 4.63 (s, 1H), 4.57 (s, 5H), 4.30 (s, 5H), 4.14 (s, 1H), 3.87 (s, 1H), 3.72 (s, 1H), 3.50 (s, 3H), 3.47 (s, 3H), 3.46 (bs, 1H), 3.07 (s, 3H), 3.00 (s, 3H), 2.63 (bm, 2H), 2.52 (bs, 3H), 2.44–2.38 (bm, 1H), 2.36–2.29 (bm, 2H + 1H), 2.26–2.19 (bm, 2H), 2.18–2.12 (bm, 1H), 2.04 (s, 3H), 2.02 (bm, 1H), 1.99 (bs, 3H), 1.97 (bm, 1H), 1.92 (s, 3H), 1.84 (bm, 2 × 1H), 1.77–1.74 (bm, 2H), 1.54–1.52 (bm, 1H); ^{13}C NMR (150.9 MHz, acetone-d_6, −10 °C, 1:1 mixture of bidentate conformers) δ 162.4 (q, J^{1311}_{C-B} = 49.8 Hz), 142.4 (d, J^{1331}_{C-P} = 9.1 Hz), 142.2 (d, J^{1331}_{C-P} = 4.5 Hz), 140.5 (bd, J^{1331}_{C-P} = 12.1 Hz), 139.4 (bd, J^{1331}_{C-P} = 22.6 Hz), 137.2 (bd, J^{1331}_{C-P} = 21.1 Hz), 136.0 (bd, J^{1331}_{C-P} = 13.6 Hz), 135.4, 133.6 (d, J^{1331}_{C-P} = 9.1 Hz), 133.3 (d, J^{1331}_{C-P} = 7.5 Hz), 133.1 (d, J^{1331}_{C-P} = 7.5 Hz), 133.0 (d, J^{1331}_{C-P} = 1.5 Hz), 132.7 (d, J^{1331}_{C-P} = 6.0 Hz), 132,6 (d, J^{1331}_{C-P} = 1.5 Hz), 132.5 (d, J^{1331}_{C-P} = 6.0 Hz), 131.6, 130.7 (d, J^{1331}_{C-P} = 48.3 Hz), 129.8 (qq, J^{1319}_{C-F} = 31.7, 3.0 Hz), 128.3 (d, J^{1331}_{C-P} = 58.9 Hz), 127.4 (d, J^{1331}_{C-P} = 15.1 Hz), 127.2 (d, J^{1331}_{C-P} = 13.6 Hz), 127.1 (d, J^{1331}_{C-P} = 10.6 Hz), 126.5 (d, J^{1331}_{C-P} = 27.2 Hz), 125.7 (d, J^{1331}_{C-P} = 24.1 Hz), 125.2 (q, J^{1319}_{C-F} = 271.6 Hz), 118.3 (sept, J^{1319}_{C-F} = 4.5 Hz), 93.8 (bs), 92.1 (d, J^{1331}_{C-P} = 12.1 Hz), 91.6 (bs), 89.1 (bs), 75.8 (bs), 74.5 (d, J^{1331}_{C-P} = 6.0 Hz), 73.2, 72.7, 72.5 (d, J^{1331}_{C-P} = 19.6 Hz), 71.9 (d, J^{1331}_{C-P} = 22.6 Hz), 68.2, 65.8, 63.8 (bs), 61.8 (bs), 60.7 (d, J^{1331}_{C-P} = 10.6 Hz), 60.2 (d, J^{1331}_{C-P} = 9.1 Hz), 60.1 (bs), 59.1 (bs), 57.9, 57.8, 53.0, 51.1, 34.2, 33.9 (bs), 32.0 (bs), 31.5, 31.3, 31.1 (bs), 29.1 (bs), 28.4, 23.3 (2 × d, J^{1331}_{C-P} = 4.5 Hz), 22.3 (bd, J^{1331}_{C-P} = 3.0 Hz), 21.9 (d, J^{1331}_{C-P} = 3.0 Hz); FABMS [*m*/*z* (%)] 742 (62, M-BAr_F), 740 (61), 630 (54), 629 (49), 628 (100); HRMS (FAB) calcd for $C_{34}H_{40}NP^{56}Fe^{193}Ir$ 742.1876, found 742.1915; Anal. calcd for $C_{66}H_{52}NP^{56}Fe^{193}IrBF_{24}$: C, 49.39; H, 3.27. Found: C, 48.74; H, 3.25.

4.14. (R)-(−)-1,2-Diphenylpropane (**21a**)

A solution of *trans*-methyl stilbene **20a** (30 mg, 0.15 mmol) and iridium catalyst (*S*)-**16** (4.9 mg, 0.0031 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21a** (29 mg, 96%) as a colorless oil: $[\alpha]_D^{20}$ −48.3 (*c* 0.86 $CHCl_3$) [lit [22]. $[\alpha]_D^{20}$ −73.7 (*c* 1.0, $CHCl_3$)]; Chiral GC analysis (Chirasil DEX-CB; 100 °C for 5 min, 0.5 °C/min increase to 140 °C, hold at 140 °C for 5 min, 2 °C/min increase to 180 °C, hold at 180 °C for 10 min) determined an enantiomeric ratio (er) of 91.8:8.2 (84% ee) [t_R(major) = 64.32 min, t_R(minor) 64.61 = min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.30 (m, 3H), 7.24–7.20 (m, 2H), 7.14 (d, 2H, J = 7.2 Hz), 3.13–2.98 (m, 2H), 2.82 (q, 1H, J = 7.8 Hz), 1.31 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.0, 140.8, 129.1, 128.3, 128.1, 127.0, 126.0, 125.8, 45.0, 41.8, 21.1.

4.15. (R)-(−)-Ethyl 3-phenylbutanoate (**21b**)

A solution of *trans*-ethyl 3-phenylbut-2-enoate **20b** (57 mg, 0.29 mmol) and iridium catalyst (*S*)-**16** (9.4 mg, 0.0060 mmol, 2.0 mol %) in CH_2Cl_2 (3 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21b** (54 mg, 94%) as a colorless oil: $[\alpha]_D^{20}$ −23.5 (*c* 0.94, $CHCl_3$) [lit [23]. $[\alpha]_D^{20}$ −24.7 (*c* 1.12, $CHCl_3$)]; CSP HPLC analysis (Chiralcel OB-H; eluent: 99.5:0.5 hexane/*i*-PrOH, 0.5 mL/min) determined an enantiomeric ratio (er) of 95.3:4.7 (91% ee) [t_R(major) = 11.99 min, t_R(minor) = 14.09 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.17 (m, 5H), 4.08 (q, 2H, J = 6.9 Hz), 3.35–3.23 (sx, 1H, J = 7.2 Hz), 2.66–2.50 (m, 2H), 1.31 (d, 3H, J = 6.9 Hz), 1.19 (t, 3H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.4, 145.7, 128.4, 126.7, 126.3, 60.2, 43.0, 36.5, 21.8, 14.1.

4.16. (R)-(−)-Ethyl 3-(4-methoxyphenyl)butanoate (**21c**)

A solution of *trans*-ethyl 3-(4-methoxyphenyl)but-2-enoate **20c** (58 mg, 0.26 mmol) and iridium catalyst (*S*)-**16** (8.4 mg, 0.0053 mmol, 2.0 mol %) in dry CH_2Cl_2 (3 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21c** (58 mg, 99%) as a colorless oil: $[\alpha]_D^{20}$ −26.7 (*c* 1.0, $CHCl_3$); CSP HPLC analysis[24] (Chiralcel OB-H; eluent: 99.5:0.5 hexanes/*i*-PrOH, 0.5 mL/min) determined an enantiomeric ratio (er) of 96:4 (92% ee) [t_R(major) = 21.73 min, t_R(minor) = 28.91 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, 2H, J = 8.4 Hz), 6.84 (d, 2H, J = 8.7 Hz), 4.07 (q, 2H, J = 6.9 Hz), 3.78 (s, 3H), 3.24 (sx, 1H, J = 7.2 Hz), 2.61–2.46 (m, 2H), 1.27 (d, 3H, J = 6.9 Hz), 1.18 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.4, 158.0, 137.8, 131.4, 127.6, 113.8, 60.1, 55.1, 43.2, 35.7, 21.9, 14.1.

4.17. (S)-(+)-Ethyl 2-methyl-3-phenylpropanoate (**21d**)

A solution of *trans*-ethyl 2-methyl-3-phenylacrylate **20d** (34 mg, 0.18 mmol) and iridium catalyst (*S*)-**16** (5.7 mg, 0.0036 mmol, 2.0 mol %) in CH_2Cl_2 (1.8 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21d** (30 mg, 88%) as a colorless oil: $[\alpha]_D^{20}$ +28.4 (*c* 1.0, $CHCl_3$); CSP HPLC analysis [6d] (Chiralcel OB–H; eluent: 99.5:0.5 hexane/*i*-PrOH, 0.5 mL/min) determined an enantiomeric ratio (er) of 91:9 (82% ee) [t_R(minor) = 8.52 min, t_R(major) = 10.10 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.16 (m, 5H), 4.09 (q, 2H, J = 6.9 Hz), 3.08–2.98 (m, 1H), 2.79–2.64 (m, 2H), 1.21 (d, 3H, J = 7.2 Hz), 1.16 (d, 3H, J = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 176.1, 139.4, 128.9, 128.3, 126.2, 60.2, 41.4, 39.7, 16.7, 14.1.

4.18. (S)-(+)-Ethyl 3-(4-methoxyphenyl)-2-methylpropanoate (**21e**)

A solution of *trans*-ethyl 3-(4-methoxyphenyl)-2-methylacrylate **20e** (30 mg, 0.14 mmol) and iridium catalyst (*S*)-**16** (4.5 mg, 0.0029 mmol, 2.0 mol %) in CH_2Cl_2 (1.4 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21e** (30 mg, 98%) as a colorless oil: $[\alpha]_D^{20}$ +24.5 (*c* 1.25, $CHCl_3$); CSP HPLC analysis [6d] (Chiralcel OB-H; eluent: 99.5:0.5 hexane/i-PrOH, 0.5 mL/min) determined an enantiomeric ratio (er) of 91.5:8.5 (83% ee) [t_R(minor) = 9.01 min, t_R(major) = 9.76 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, 2H, J = 8.7 Hz), 6.81 (d, 2H, J = 8.7 Hz), 4.09 (q, 2H, J = 7.2 Hz), 3.78 (s, 3H), 3.01–2.90 (m, 1H), 2.73–2.57 (m, 2H), 1.19 (t, 3H, J = 7.2 Hz), 1.13 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 176.2, 158.1, 131.4, 129.9, 113.7, 60.2, 55.2, 41.7, 38.8, 16.7, 14.2.

4.19. (S)-(+)-N-Benzyl-2-methyl-3-phenylpropanamide (**21f**)

A solution of *trans*-*N*-benzyl-2-methyl-3-phenylacrylamide **20f** (30 mg, 0.12 mmol) and iridium catalyst (*S*)-**16** (3.8 mg, 0.0024 mmol, 2.0 mol %) in dry CH_2Cl_2 (1.2 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred stir for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21f** (29 mg, 96%) as a pale yellow oil: $[\alpha]_D^{20}$ +23.2 (*c* 0.93, $CHCl_3$) [lit [25]. $[\alpha]_D^{20}$ +52.3 (*c*, 1.2 $CHCl_3$)]; CSP HPLC analysis (Chiralcel OD-H; eluent: 95:5 hexane:*i*-PrOH, 1.0 mL/min λ = 210 nm) determined an enantiomeric ratio (er) of 73.8:26.2 (48% ee) [t_R(major) = 26.53 min, t_R(minor) = 29.99 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.16 (m, 9H), 7.04–7.01 (m, 2H), 5.66 (bs, 1H), 4.32 (m, 2H), 2.98 (dd, 1H, J = 13.2, 8.7Hz), 2.70 (dd, 1H, J = 13.5, 6.3 Hz), 2.47 (sx, 1H, J = 6.6 Hz), 1.23 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 175.3, 139.8, 138.1, 128.5, 128.4, 127.5, 127.2, 126.2, 43.9, 43.3, 40.5, 17.8.

4.20. (R)-(+)-2-Methyl-3-phenylpropan-1-ol (**21g**)

A solution of *trans*-2-methyl-3-phenylpropenol **20g** (34.2 mg, 0.23 mmol) and iridium catalyst (*S*)-**16** (7.3 mg, 0.0046 mmol, 2.0 mol %) in dry CH_2Cl_2 (2.4 mL) in a vial under argon was sealed in an autoclave. The autoclave was evacuated and back-filled with hydrogen three times, pressurized to 62 bar, and the mixture was stirred for 72 h at room temperature. The solvent was removed *in vacuo* and the crude reaction mixture was passed through silica gel, eluting with 90:10 hexane:EtOAc, to give **21g** (33 mg, 95%) as a clear oil: $[\alpha]_D^{20}$ +1.36 (*c* 1.06, $CHCl_3$) [lit [26]. $[\alpha]_D^{20}$ −11.1 (*c* 0.86, $CHCl_3$) for (*S*)-enantiomer]; CSP HPLC analysis (Chiralcel OD-H; eluent: 95:5

hexane:*i*-PrOH, 1.0 mL/min) determined an enantiomeric ratio (er) of 59.2:40.8 (18% ee) [t_R(minor) = 8.73 min, t_R(major) = 10.52 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.17 (m, 5H), 3.51 (m, 2H), 2.76 (dd, 1H, J = 13.5, 6.3 Hz), 2.43 (dd, 1H, J = 13.5, 8.1 Hz), 1.95 (oct, 1H, J = 6.3 Hz), 1.47 (bs, 1H), 0.93 (d, 3H, J = 6.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 140.6, 129.1, 128.2, 125.8, 67.6, 39.6, 37.7, 16.4.

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Appendix A. Supplementary information

Spectroscopic data (^{1}H, ^{31}P and ^{13}C NMR) for sulfides **12b** and **12c**, salts **12b**·HBF_4 and **12c**·HBF_4, ligands **9a**–**9c** and **15**, complexes **16**–**19**, plus HSQC data for fluxional complex **19** at −10 °C. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2010.08.042.

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