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Rhodium-Catalyzed Enantioselective Hydrogenation of Unsaturated Phosphonates by ClickFerrophos Ligands

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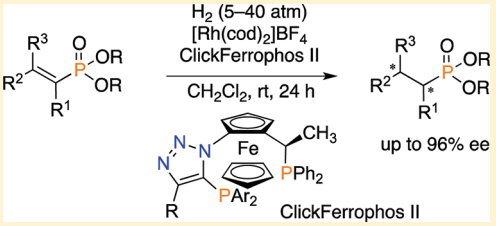
Supporting Information

ABSTRACT: Newly developed ClickFerrophos II ligands were applied in the hydrogenation of α,β-unsaturated phosphonates. The use of a rhodium/ClickFerrophos II catalyst was examined in the hydrogenation of functionalized α,β-unsaturated phosphonates and was revealed to be effective for β-alkyl-β-aryl or β-dialkyl phosphonates, (*Z*)-β-enolester phosphonates, and α-phenylethenyl phosphonates, producing the corresponding chiral phosphonates in good yields with high enantioselectivities (up to 96% ee).



INTRODUCTION

Chiral phosphonic acids and phosphonates are expected to be useful as chiral building blocks of optically active alkenes through the Horner–Wadsworth–Emmons reaction.[1] They are also of biological interest; for example, chiral α- or β-hydroxy phosphonates and α- or β-amino phosphonates can be applied to antibacterial agents,[2] enzyme inhibitors,[3] and intermediates in biosynthetic processes.[4] Chiral 1-arylethylphosphonates are attractive compounds for study in medicinal chemistry because of their biological properties; they act as phosphorus analogues of 2-arylpropionic acids such as ibuprofen and naproxene.[5]

Catalytic asymmetric hydrogenation of α,β-unsaturated phosphonates provides a convenient and efficient way to synthesize chiral phosphonates.[6] Although there have been some reports on the asymmetric hydrogenation of unsaturated phosphonates using chiral rhodium catalysts, the number of effective catalysts is limited, and the quest for new ligands and metal complex catalysts remains a great challenge.

In previous work, we developed chiral ferrocenyl ligands, which we called ClickFerrophos, using click chemistry methodology (CuAAC reaction), and carried out highly enantioselective hydrogenation of alkenes and ketones using rhodium and ruthenium complexes of these ligands.[7] ClickFerrophos I ligands (Figure 1) are 1,5-diphosphines with a structure similar to that of Taniaphos, although they sometimes give better enantioselectivities.[7a] In this study, we developed the new ClickFerrophos II ligands, whose structures are similar to that of Walphos, a well-accepted 1,5-diphosphine ligand used in asymmetric synthesis.[8] We applied ClickFerrophos I and II ligands in rhodium-catalyzed asymmetric hydrogenation of unsaturated phosphonates and found them to be effective, giving the corresponding chiral phosphonates with high enantioselectivity.

RESULTS AND DISCUSSION

The new chiral 1,2,3-triazoleferrocenyl-1,5-diphosphines (ClickFerrophos II), **L3**–**5**, were readily prepared starting from commercially available (*R*)-ferrocenylamine (Ugi's amine) **1**, as illustrated in Scheme 1. Regioselective *ortho*-lithiation of **1** followed by trapping with tosyl azide gave *o*-azideferrocenylamine **2**, which was subjected to click chemistry without isolation,[9] giving *o*-1,2,3-triazoleferrocene **3a** in good yield (60%). Replacement of the dimethylamino group of **3a** with diphenylphosphine produced the ferrocenylethyl phosphine **4a** in good yield (58%) and enantioselectivity (retention/inversion = 14:1).[10] Compound **4a** was treated with *n*-BuLi followed by trapping with diarylphosphine chloride to give 1,5-diphosphines **L3** and **L5** in good to moderate yields (55–69%). **L4** (R = H) was prepared by desilylation of **3b** (R = Me_3Si) by tetrabutylammonium fluoride in THF followed by a similar successive transformation, i.e., replacement of the dimethylamino group by diphenylphosphine and introduction of another phosphine group to the 5-position of the 1,2,3-triazole ring, as

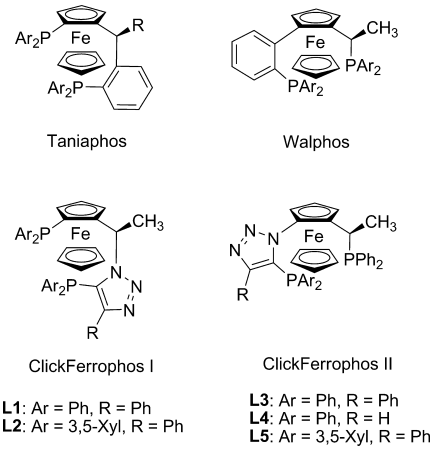


Figure 1. 1,5-Diphosphine ligands.

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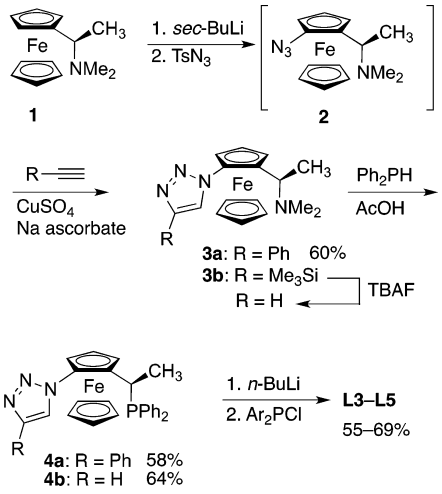
Scheme 1. Preparation of New ClickFerrophos Ligands



described above. We were successful in obtaining a single crystal of **L4** suitable for X-ray analysis. The X-ray crystallographic structure of **L4** is shown in Figure 2.

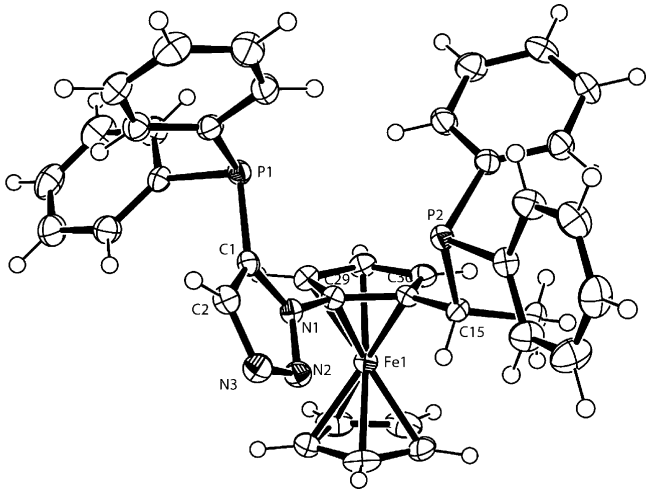
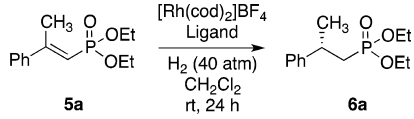


Figure 2. ORTEP drawing of new ClickFerrophos ligand **L4** with thermal ellipsoids drawn at the 50% probability level.

Accordingly, the ligand ability of new ferrocenyl phosphine ligands (ClickFerrophos II) was investigated in the asymmetric hydrogenation of α,β-unsaturated phosphonates. First, we screened ClickFerrophos ligands **L1**−**5** in the rhodium complex-catalyzed asymmetric hydrogenation of diethyl (*E*)-(2-phenyl-1-propene)phosphonate **5a**. The reaction was typically performed at room temperature for 24 h in CH_2Cl_2 under 40 atm hydrogen using 1 mol % of $[Rh(cod)_2]BF_4$ and an equivalent amount of ligand. The results are summarized in Table 1. The ClickFerrophos ligands worked satisfactorily to give diethyl (*S*)-2-phenylpropyl phosphonate (**6a**) in excellent yields with high enantioselectivities (up to 95% ee). It was found that the phenyl group at the 4-position of the 1,2,3-triazole ring was essential for high enantioselectivity; 4-unsubstituted **L4** gave the product with low ee.[11] The introduction of a sterically demanding phosphine group (bis(3,5-xylyl)phosphine) into the 1,2,3-triazole group increased the enantiomeric excess of the product to 94−95% for both ClickFerrophos I (**L2**) and II (**L5**). As it was difficult to introduce bis(3,5-xylyl)phosphine into the

Table 1. Asymmetric Hydrogenation of Diethyl (*E*)-(2-Phenyl-1-propene)phosphonate[a]



entry	ligand	% yield	% ee[b]
1	**L1**	84	85
2	**L2**	87	94
3	**L3**	99	87
4	**L4**	93	63
5	**L5**	95	95

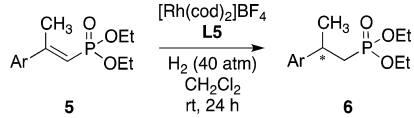
[a] **5a** (0.50 mmol), $[Rh(cod)_2]BF_4$ (0.005 mmol), ligand (0.006 mmol), CH_2Cl_2 (2.0 mL); rt, H_2 (40 atm). [b] Determined by HPLC.

side chain of ferrocene **3**, the ligand efficiency of the two 1,5-di[bis(3,5-xylyl)phosphine]-substituted derivatives could not be evaluated. In a previous asymmetric hydrogenation of an enamide, a rhodium/ClickFerrophos I (**L2**) complex bearing two bis(3,5-xylyl)phosphine units was the most effective ligand.[7b] However, **L5**, bearing one bis(3,5-xylyl)phosphine unit, gave the product with sufficiently high enantioselectivity, so **L5** was considered to be satisfactory for asymmetric hydrogenation of α,β-unsaturated phosphonates.

In the ^{31}P NMR measurements, two phosphine signals of **L3** observed at −30.5 and +2.90 ppm, and they are shifted to +8.60 (dd, J = 31.5, 153.0 Hz) and +40.6 ppm (dd, J = 31.5, 140.3 Hz), respectively, upon mixing with $[Rh(cod)_2]BF_4$, suggesting the *P,P*-chelate complexation.

Since **L5** gave the highest enantioselectivity with a high product yield, it was chosen as a ligand for hydrogenation of various diethyl (*E*)-2-aryl-1-propenephosphonates (**5a**−**j**). The reactions were carried out under the same conditions as described above, and the results are summarized in Table 2.

Table 2. Asymmetric Hydrogenation of Diethyl (*E*)-2-Aryl-1-propenephosphonate[a]



entry	Ar in **5**	% yield	% ee[b] (config)
1	C_6H_5, **5a**	95, **6a**	95 (*S*)-(−)
2[c]	C_6H_5, **5a**	70, **6a**	90 (*S*)-(−)
3	*o*-MeC_6H_4, **5b**	95, **6b**	92 (−)
4	*m*-MeC_6H_4, **5c**	76, **6c**	94 (−)
5	*p*-MeC_6H_4, **5d**	96, **6d**	93 (−)
6	*p*-$MeOC_6H_4$, **5e**	88, **6e**	95 (−)
7	*p*-$NO_2C_6H_4$, **5f**	92, **6f**	95 (−)
8	*p*-FC_6H_4, **5g**	85, **6g**	93 (−)
9	*p*-ClC_6H_4, **5h**	96, **6h**	92 (−)
10	*p*-BrC_6H_4, **5i**	98, **6i**	96 (−)
11	2-Thienyl, **5j**	99, **6j**	95 (−)

[a] **5** (0.50 mmol), $[Rh(cod)_2]BF_4$ (0.005 mmol), **L5** (0.006 mmol), CH_2Cl_2 (2.0 mL); rt, H_2 (40 atm). [b] Determined by HPLC. [c] S/C = 1000.

In all cases, the reactions proceeded quantitatively with excellent enantioselectivity, regardless of the electronic properties or position of the substituents on the aromatic ring, and every product possessed the (−)-configuration. For example, *o*-,

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m-, and *p*-methylphenyl substituents gave high ee at almost the same level as **6a** (entries 3−5), and both *p*-electron-rich (*p*-$MeOC_6H_4$) and electron-poor (*p*-$NO_2C_6H_4$) aryl groups gave excellent enantioselectivity (entries 6 and 7). Asymmetric hydrogenation with (*E*)-(2-thienyl-1-propene)phosphonate, a typical heteroaryl-substituted substrate, also afforded the corresponding product with full conversion and high enantioselectivity. The hydrogenation of **5a** could be carried out with low catalyst loadings (0.1 mol %, S/C = 1000) in a satisfactory yield and ee; 70% yield, 90% ee (entry 2).

Encouraged by these positive results, we examined the scope of α,β-unsaturated phosphonate substrates. ClickFerrophos ligands **L2** and **L5**, which were effective in the hydrogenation of **5a**, were used for hydrogenation of β-alkyl-β-aryl- (**7**), β-dialkyl- (**8**), α-aryl ethenyl- (**9**), and β-phenyl-β,γ-unsaturated phosphonate (**10**) (Figure 3). The results of the hydrogenation

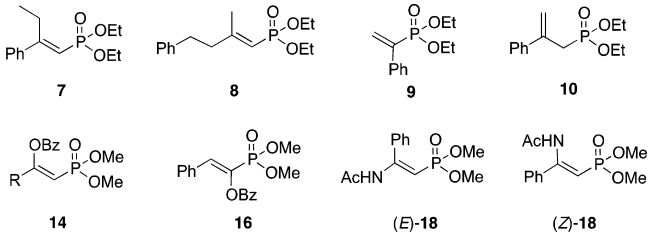
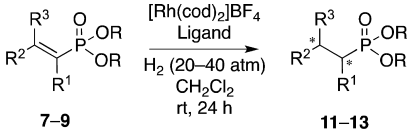


Figure 3. Unsaturated phosphonates.

reactions are summarized in Table 3. Hydrogenation of **7** and **8** gave products with a stereogenic center at the β-position. The

Table 3. Asymmetric Hydrogenation of α,β-Unsaturated Phosphonates[a]



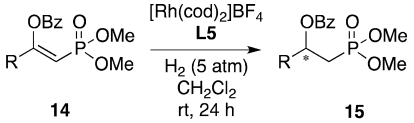
entry	substrate	ligand	product	% yield	% ee[b] (config)
1[c]	7	**L5**	**11**	68	95 (−)
2[c]	8	**L5**	**12**	94	91 (−)
3[d]	9	**L5**	**13**	97	83 (*R*)-(+)
4[d]	9	**L2**	**13**	94	18 (*R*)-(+)
5[e]	9	Taniaphos	**13**	95	17 (nd)
6[d]	9	Walphos	**13**	66	61 (*R*)-(+)

[a]Substrate (0.50 mmol), $[Rh(cod)_2]BF_4$ (0.005 mmol), ligand (0.006 mmol), CH_2Cl_2 (2.0 mL); rt, 24 h. [b]Determined by HPLC. [c]40 atm of H_2. [d]20 atm of H_2. [e]Reference 6i.

results indicated that Rh/**L5** complex was an efficient catalyst in the hydrogenation of **7** and **8**, giving β-phenylbutane- **11** and β-methyl-δ-phenylbutanephosphonate **12** with high enantioselectivity and good yield, respectively (entries 1 and 2).

Application of the Rh/**L5** complex to the hydrogenation of **9** was successful, giving the (*R*)-1-phenylethylphosphonate **13** in good yield with 83% ee (entry 3). In contrast, the use of **L2** gave the product with full conversion but poor ee (entry 4). It has been reported that Taniaphos ligand, which is structurally similar to **L2**, also gives a low ee % (17%) (entry 5).[6i] We tested Walphos ligand (Ar = Ph), whose structure is similar to **L5** in this reaction for comparison, and found that it gave moderate yield and ee value (entry 6). The hydrogenation of

Table 4. Scope of Asymmetric Hydrogenation of Dimethyl (*Z*)-2-Benzoyloxy-2-arylethenephosphonate[a]



entry	R in **14**	% yield	% ee[b] (config)
1	C_6H_5, **14a**	89, **15a**	93 (*S*)-(−)
2[c]	C_6H_5, **14a**	8, **15a**	nd
3[d]	C_6H_5, **14a**	0, **15a**	nd
4[e]	C_6H_5, **14a**	99, **15a**	88 (*S*)-(−)
5	*p*-MeC_6H_4, **14b**	91, **15b**	96 (−)
6	*p*-$MeOC_6H_4$, **14c**	62, **15c**	93 (−)
7	*p*-ClC_6H_4, **14d**	86, **15d**	94 (−)
8	*p*-BrC_6H_4, **14e**	77, **15e**	88 (−)
9	2-Naphthyl, **14f**	56, **15f**	92 (−)
10	Me, **14g**	96, **15g**	92 (+)

[a]**14** (0.50 mmol), $[Rh(cod)_2]BF_4$ (0.005 mmol), ligand (0.006 mmol), CH_2Cl_2 (2.0 mL); rt, H_2 (5 atm). [b]Determined by HPLC. [c]**L2** was used. [d]Taniaphos was used. [e]Walphos was used.

β,γ-unsaturated phosphonate **10** resulted in the production of an almost racemate of **6a** (92% yield, 2% ee).

We next examined the asymmetric hydrogenation of α- and β-enol ester and β-enamido phosphonates (**14**, **16**, **18**) (Figure 3) by using Rh/**L5** complex. The hydrogenation with (*Z*)-2-benzoyloxy-2-phenylethenephosphonate **14a** by using Rh/**L5** catalyst under 5 atm of hydrogen gave an 89% yield of (*S*)-(−)-**15a** in 93% ee (Table 4, entry 1). We also tested **L2**, Taniaphos, and Walphos ligands for comparison; **L2** gave 8% yield of product, Taniaphos did not give the product, and Walphos gave a good yield and ee value, respectively (entries 2−4).[12] Thus, **L5** was revealed to be a suitable ligand, and the scope of the catalyst was broadened to the various (*Z*)-2-benzoyloxy-2-arylethenephosphonates (**14a−f**). These results are also summarized in Table 4. As seen in the hydrogenation with β-methyl-β-aryl phosphonates **5**, significant influence of phenyl ring substituents on enantioselectivity was not observed, with both electron-donating (entries 5 and 6) and electron-withdrawing (entries 7 and 8) substituents giving high enantioselectivities (88−96% ee). The best ee and yield was obtained in the hydrogenation of **14b** (R = *p*-MeC_6H_4). The 2-naphthyl-substituted substrate led to the corresponding saturated product with somewhat low yield with high ee (entry 9). In the hydrogenation of alkyl enol ester **14g**, high enantioselectivity was also obtained (entry 10). In contrast, the hydrogenation with (*E*)-1-benzoyloxy-2-phenylethenephosphonate **16** using Rh/**L5** afforded poor ee (13% ee) of 1-benzoyloxy-2-phenylethanephosphonate **17** in 83% yield.

The asymmetric hydrogenation (40 atm of H_2) of β-enamido phosphonates (*E*)- and (*Z*)-**18** (Figure 3) was not successful, dimethyl (2-acetamido-2-phenylethyl)phosphonate **19** being obtained in low yields and ee values. The product **19** obtained from (*E*)-**18** had an opposite configuration to that from (*Z*)-**18**; (−)-**19** from (*E*)-**18**, 13% yield, 33% ee, (+)-**19** from (*Z*)-**18**, 10% yield, 35% ee.

CONCLUSION

ClickFerrophos II ligands are efficient for highly enantioselective Rh-catalyzed hydrogenation of functionalized α,β-unsaturated phosphonates such as β-alkyl-β-aryl or β-dialkyl phosphonate, (*Z*)-β-enolester phosphonate, and α-phenyl-

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ethenyl phosphonate. Thus, the scope of the catalyst may be somewhat wider than those of other Rh/chiral phosphine catalysts which are of limited use for certain substrates.[6]

EXPERIMENTAL SECTION

Preparation of 2-(1,2,3-Triazole)ferrocene. In a 100 mL three-neck round-bottom flask containing a magnetic stirring bar were charged [1(*R*)-dimethylaminoethyl]ferrocene **1** (>99% ee) (1.30 g, 5.1 mmol) and dry diethyl ether (20 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *s*-BuLi (1.0 M, 5.8 mL, 5.8 mmol) was then added using a syringe through the septum with magnetic stirring. When the addition was completed, the ice bath was removed, and the mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was cooled in an ice bath, a diethyl ether (2.0 mL) solution of tosyl azide (1.30 g, 6.6 mmol) was injected into the mixture, and the resulting mixture was allowed to warm to room temperature and stirred for 4 h. Then, sodium ascorbate (0.80 g, 4.0 mmol), $CuSO_4$ (0.32 g, 2.0 mmol), water (20 mL), *t*-BuOH (20 mL), and alkyne (6.5 mmol) were successively added to the flask, and the resulting solution was stirred for 24 h. The solution was extracted with dichloromethane (30 mL × 3). The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate/triethyl amine = 80/20/1) to give the (1*R*,2*Sp*)-2-(1,2,3-triazole)-(1*R*)-dimethylaminoethylferrocene **3**.

3a: yield 1.20 g, 3.0 mmol, 60%; orange solid; mp = 30−31 °C; $[\alpha]^{25}_D$ −36.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H, *J* = 6.8 Hz), 2.06 (s, 6H), 3.95 (q, 1H, *J* = 6.8 Hz), 4.24−4.25 (m, 2H), 4.26 (s, 5H), 4.81−4.82 (m, 1H), 7.32 (t, 1H, *J* = 7.4 Hz), 7.44 (t, 2H, *J* = 7.4 Hz), 7.88 (d, 2H, *J* = 7.4 Hz), 8.53 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 12.0, 39.7, 55.2, 64.9, 65.0, 66.0, 70.9, 83.7, 93.3, 122.8, 125.5, 127.9, 128.8, 130.7, 146.7; HRMS calcd for $C_{22}H_{24}FeN_4$ $[M + H]^+$ 401.1423, found 401.1428.

3b: The compound was obtained by desilylation of the 5-trimethylsilyltriazole derivative by tetrabutylammonium fluoride in THF: yield 0.38 g, 1.18 mmol, 30%; orange solid; mp = 169−170 °C; $[\alpha]^{25}_D$ −88.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (d, 3H, *J* = 6.8 Hz), 1.98 (s, 6H), 3.87 (q, 1H, *J* = 6.8 Hz), 4.25−4.27 (m, 2H), 4.26 (s, 5H), 4.77 (s, 1H), 7.70 (s, 1H), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 12.7, 39.7, 55.1, 64.9, 65.1, 66.1, 70.9, 83.6, 93.4, 126.8, 133.0; HRMS calcd for $C_{16}H_{20}FeN_4$ $[M + H]^+$ 325.1110, found 325.1118.

Preparation of 2-(1,2,3-Triazole)ferrocenylmonophosphine. The compound **3a** (0.95 g, 2.4 mmol) was placed in a 50 mL of sealed tube and dissolved in acetic acid (15 mL) under argon. Diphenylphosphine (0.75 g, 4.3 mmol) was added, and the reaction mixture was heated to 110 °C and stirred for 18 h. After the reaction mixture was heated to room temperature, the acetic acid solution was diluted with dichloromethane (20 mL), washed with saturated aq $NaHCO_3$ (20 mL × 3) and brine, dried ($MgSO_4$), and filtered, and solvent was removed on a rotary evaporator to leave an orange residue. The crude product was purified by column chromatography (Al_2O_3, hexane/ethyl acetate = 7/1) to provide the mono phosphine **4**.

4a: yield 0.76 g, 1.4 mmol, 58%; orange solid; mp = 71−72 °C; $[\alpha]^{25}_D$ −3.55 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (dd, 3H, *J* = 7.1, 16.0 Hz), 3.91 (quint, 1H, 7.0 Hz), 4.28 (t, 1H, *J* = 2.6 Hz), 4.31 (s, 5H), 4.39 (m, 1H), 4.42 (m, 1H), 6.60 (s, 1H), 6.70 (t, 2H, *J* = 7.0 Hz), 6.89 (t, 2H, *J* = 7.3 Hz), 7.08 (t, 1H, *J* = 7.3 Hz), 7.31−7.38 (m, 4H), 7.42 (t, 2H, *J* = 7.3 Hz), 7.50−7.54 (m, 2H), 7.72 (d, 2H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 19.5 (d, *J* = 24.2 Hz), 28.2 (d, *J* = 12.8 Hz), 63.4, 65.1, 65.7 (d, *J* = 5.8 Hz), 70.6, 87.5 (d, *J* = 6.3 Hz), 92.7, 121.9, 125.4, 127.7, 127.8 (d, *J* = 6.8 Hz), 127. 9, 128.6 (d, *J* = 7.2 Hz), 128.7, 129.3, 130.4, 133.3 (d, *J* = 18.7 Hz), 133.9 (d, *J* = 20.2 Hz), 135.2 (d, *J* = 15.3 Hz), 136.6 (d, *J* = 16.9 Hz), 146.2; ^{31}P NMR ($CDCl_3$) δ 7.54; HRMS calcd for $C_{32}H_{28}FeN_3P$ $[M + Na]^+$ 564.1262, found 564.1264.

4b: yield 0.23 g, 0.49 mmol, 64% (from 0.25 g of **3b**); orange solid; mp = 165−166 °C; $[\alpha]^{25}_D$ +117 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.6−1.2 (br, 3H), 1.70 (dd, 3H, *J* = 7.2, 16.5 Hz), 4.27 (s, 5H), 4.30 (t, 1H, *J* = 2.6 Hz), 4.38 (m, 1H), 4.58 (quint, 1H, *J* = 7.2 Hz), 4.64 (s, 1H), 6.60 (s, 1H), 6.82 (t, 2H, *J* = 8.0 Hz), 6.98 (t, 2H, *J* = 8.0 Hz), 7.18 (t, 1H, *J* = 7.5 Hz), 7.38 (s, 1H), 7.49−7.56 (m, 3H), 7.84 (t, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 16.6 (d, *J* = 5.1 Hz), 27.2 (d, *J* = 25.6 Hz), 62.7, 65.4, 67.8 (d, *J* = 1.5 Hz), 70.8, 81.6 (d, *J* = 5.4 Hz), 92.7 (d, *J* = 1.7 Hz), 124.9, 126.6 (d, *J* = 52.4 Hz), 127.8 (d, *J* = 9.7 Hz), 128.5 (d, *J* = 52.9 Hz), 128.9 (d, *J* = 9.6 Hz), 130.0 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 2.2 Hz), 132.3 (d, *J* = 8.6 Hz), 132.6, 133.2 (d, *J* = 8.4 Hz); ^{31}P NMR ($CDCl_3$) δ 25.8; HRMS calcd for $C_{26}H_{27}BFeN_3P$ $[M + Na]^+$ 502.1277, found 502.1278.

Preparation of 2-(1,2,3-Triazole)ferrocenyldiphosphine (ClickFerrophos II). In a 20 mL Schlenk tube containing a magnetic stirring bar were charged **4** (100 mg, 0.19 mmol) and dry THF (2.5 mL) under a slight pressure of nitrogen. The flask was cooled at −78 °C, and a hexane solution of *n*-BuLi (1.6 M, 0.12 mL, 0.20 mmol) was then added using a syringe through the septum with magnetic stirring. After 10 min, diarylphosphine chloride (0.24 mmol) was injected into the mixture at −78 °C and stirred for 2 h. The mixture was allowed to warm to room temperature and then stirred for an additional 24 h. The reaction was quenched with saturated NH_4Cl, and the solution was then extracted with dichloromethane (20 mL × 3). The combined extracts were washed (brine), dried (Na_2SO_4), and filtered, and the solvent was removed on a rotary evaporator to leave an orange residue. The crude product was purified by column chromatography on Al_2O_3 (hexane/ethyl acetate = 10/1) to give pure diphosphine (ClickFerrophos II) as an orange solid.

L3: yield 93 mg, 0.13 mmol, 69%; orange solid; mp = 74−75 °C; $[\alpha]^{25}_D$ −53.6 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (dd, 3H, *J* = 7.0, 7.0 Hz), 3.75 (s, 1H), 3.89 (dq, 1H, *J* = 2.0, 7.0 Hz), 3.97 (t, 1H, *J* = 2.7 Hz), 4.22 (m, 1H), 4.31 (s, 5H), 6.78−6.92 (m, 5H), 6.99−7.09 (m, 5H), 7.24−7.36 (m, 10H), 7.46 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 14.7, 28.5 (d, *J* = 20.3 Hz), 64.0, 66.1 (d, *J* = 3.7 Hz), 67.6 (d, *J* = 10.2 Hz), 70.9, 88.1 (d, *J* = 19.3 Hz), 92.8, 127.2, 127.3 (d, *J* = 18.7 Hz), 127.4, 127.7 (d, *J* = 7.1 Hz), 127.8 (d, *J* = 5.9 Hz), 128.1, 128.3 (d, *J* = 4.3 Hz), 128.8, 128.9, 129.0 (d, *J* = 10.8), 130.9, 131.6 (d, *J* = 15.5 Hz), 132.0 (d, *J* = 4.4 Hz), 131.1 (d, *J* = 4.3 Hz), 132.4, 132.5 (d, *J* = 10.8 Hz), 133. Two (d, *J* = 10.8 Hz), 133.7 (d, *J* = 9.6 Hz), 134.2 (d, *J* = 20.5 Hz), 135.2 (d, *J* = 2.5 Hz), 135.4 (d, *J* = 2.4 Hz), 137.4 (d, *J* = 18.9 Hz), 152.8 (d, *J* = 4.1 Hz); ^{31}P NMR ($CDCl_3$) δ −30.5 (d, *J* = 20.1 Hz), 2.9 (d, *J* = 20.2 Hz); HRMS calcd for $C_{44}H_{37}FeN_3P_2$ $[M + H]^+$ 726.1885, found 726.1873.

L4: yield 69 mg, 0.11 mmol, 58%; orange solid; mp = 158−159 °C; $[\alpha]^{25}_D$ −34.2 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (dd, 3H, *J* = 7.1, 8.0 Hz), 3.97 (t, 1H, *J* = 2.7 Hz), 3.98−4.04 (m, 2H), 4.22 (m, 1H), 4.23 (s, 5H), 7.12−7.46 (m, 21H); ^{13}C NMR ($CDCl_3$) δ 16.0 (d, *J* = 5.4 Hz), 28.1 (d, *J* = 18.1 Hz), 64.3, 66.0 (d, *J* = 11.5 Hz), 66.1 (d, *J* = 4.3 Hz), 70.7, 87.7 (d, *J* = 18.8 Hz), 92.2, 127.6, 127.8 (d, *J* = 7.3 Hz), 128.0 (d, *J* = 5.0 Hz), 128.5 (d, *J* = 6.9 Hz), 128.9, 129.0, 129.1 (d, *J* = 15.1 Hz), 129.7, 132.0 (d, *J* = 16.1), 133.2 (d, *J* = 2.0 Hz), 133.5 (d, *J* = 2.1 Hz), 133.7 (d, *J* = 20.3 Hz), 134.7 (d, *J* = 7.3 Hz), 134.8, 135.1, 136.9 (d, *J* = 17.9 Hz), 138.4 (d, *J* = 17.0 Hz), 140.2. ^{31}P NMR ($CDCl_3$) δ −37.0 (d, *J* = 16.1 Hz), 4.6 (d, *J* = 16.0 Hz); HRMS calcd for $C_{38}H_{33}FeN_3P_2$ $[M + H]^+$ 650.1572, found 650.1576. The solid recrystallized from hexane/CH_2Cl_2 was suitable for X-ray analysis, CCDC 847021.

L5: yield 72 mg, 0.10 mmol, 55%; orange solid; mp = 83−84 °C; $[\alpha]^{25}_D$ −57.7 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (dd, 3H, *J* = 6.9, 6.9 Hz), 1.86 (s, 6H), 2.32 (s, 6H), 3.80 (s, 1H), 3.83 (q, 1H, *J* = 6.9 Hz), 4.01 (t, 1H, *J* = 2.7 Hz), 4.33 (m, 1H), 4.35 (s, 5H), 6.52 (s, 1H), 6.66 (d, 2H, *J* = 7.8 Hz), 6.92 (t, 2H, *J* = 8.3 Hz), 6.98−7.04 (m, 6H), 7.22−7.32 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 15.1, 20.9, 21.4, 28.1 (d, *J* = 19.7 Hz), 64.0, 66.2 (d, *J* = 4.3 Hz), 67.7 (d, *J* = 10.7 Hz), 70.8, 88.3 (d, *J* = 20.0 Hz), 92.9, 126.8, 127.3 (d, *J* = 23.5 Hz), 127.6 (d, *J* = 7.1 Hz), 128.2 (d, *J* = 4.5 Hz), 128.8, 128.9, 129.8, 130.0 (d, *J* = 4.7 Hz), 130.2 (d, *J* = 4.5 Hz), 130.7, 130.8 (d, *J* = 13.9 Hz), 131.3, 131.6 (d, *J* = 15.7 Hz), 132.1 (d, *J* = 21.2 Hz), 133.4, (d, *J* = 8.4 Hz), 134.5 (d, *J* = 20.7 Hz), 135.1 (d, *J* = 1.8 Hz), 135.3

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(d, J = 1.8 Hz), 137.1 (d, J = 6.6 Hz), 137.5 (d, J = 28.5 Hz), 138.2 (d, J = 7.3 Hz), 152.9 (d, J = 4.3 Hz); ^{31}P NMR ($CDCl_3$) δ −31.5 (d, J = 18.0 Hz), 2.7 (d, J = 18.0 Hz); HRMS calcd for $C_{48}H_{45}FeN_3P_2$ $[M + H]^+$ 782.2511, found 782.2515.

General Procedure for Asymmetric Hydrogenation of α,β-Unsaturated Phosphonates. The following provide a typical experimental procedure of asymmetric hydrogenation of α,β-unsaturated phosphonate. In a 20 mL Schlenk tube containing a stirring bar, $[Rh(COD)_2]BF_4$ (2.0 mg, 1.0 mol %) and **L5** (4.3 mg, 1.1 mol %) were dissolved in degassed dichloromethane (2.0 mL) under nitrogen at room temperature. After being stirred at room temperature for 30 min, the dichloromethane solution was transferred to the autoclave containing α,β-unsaturated phosphonate (0.50 mmol, S/C = 100). The autoclave was purged three times with hydrogen and the hydrogen pressure set at 40 atm. The reaction was carried out for 24 h with magnetic stirring. The pressure was released to atmospheric pressure, and the solution was transferred to a round-bottom flask. The solvent was removed on a rotary evaporator to leave the residue which was subjected to PTLC (hexane/ethyl acetate = 1/1 as eluent) to give a pure product. The product was fully characterized by spectroscopic methods with reference to spectra of the known compound.

Diethyl (*S*)-2-phenylpropylphosphonate (6a): 95% ee; $[\alpha]^{28}_D$ −19.4 (c 0.80, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, minor enantiomer t_R = 15.3 min; major enantiomer t_R = 17.2 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.1 Hz), 1.24 (t, 3H, J = 7.1 Hz), 1.39 (d, J = 7.0 Hz, 3H), 1.98−2.13 (m, 2H), 3.19−3.24 (m, 1H), 3.88−4.02 (m, 4H), 7.17−7.24 (m, 3H), 7.26−7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, J = 1.5 Hz), 16.3 (d, J = 1.5 Hz), 23.5 (d, J = 9.3 Hz), 34.2 (d, J = 138.4 Hz), 34.6 (d, J = 3.5 Hz), 61.1 (d, J = 6.3 Hz), 61.3 (d, J = 6.5 Hz), 126.3, 126.6, 128.5, 146.6 (d, J = 11.1 Hz); ^{31}P NMR ($CDCl_3$) δ 30.2.

Diethyl 2-(2-Methylphenyl)propylphosphonate (6b): 92% ee; $[\alpha]^{28}_D$ −12.4 (c 0.50, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, minor enantiomer t_R = 9.8 min; major enantiomer t_R = 11.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.1 Hz), 1.24 (t, 3H, J = 7.1 Hz), 1.36 (d, 3H, J = 6.9 Hz), 2.00−2.14 (m, 2H), 2.38 (s, 3H), 3.45−3.54 (m, 1H), 3.85−4.05 (m, 4H), 7.07−7.20 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.2, 16.3, 19.4, 22.8 (d, J = 9.0 Hz), 29.3, 33.6 (d, J = 138.1 Hz), 61.2 (d, J = 6.5 Hz), 61.3 (d, J = 6.5 Hz), 125.1, 126.0, 126.2, 130.3, 134.9, 144.7 (d, J = 11.7 Hz); ^{31}P NMR ($CDCl_3$) δ 30.7; HRMS calcd for $C_{14}H_{24}O_3P$ $[M + H]^+$ 271.1463, found 271.1466.

Diethyl 2-(3-Methylphenyl)propylphosphonate (6c):[6a] 94% ee; $[\alpha]^{28}_D$ −18.8 (c 0.50, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 97/3, flow rate = 0.3 mL/min, minor enantiomer t_R = 31.7 min; major enantiomer t_R = 33.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.1 Hz), 1.25 (t, 3H, J = 7.1 Hz), 1.39 (d, 3H, J = 6.9 Hz), 1.97−2.15 (m, 2H), 2.33 (s, 3H), 3.12−3.23 (m, 1H), 3.88−4.05 (m, 4H), 7.00−7.03 (m, 3H), 7.17−7.20 (t, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3 (d, J = 2.0 Hz), 16.4 (d, J = 2.0 Hz), 21.4, 23.4 (d, J = 8.7 Hz), 34.2 (d, J = 138.2 Hz), 34.5 (d, J = 3.6 Hz), 61.1 (d, J = 6.5 Hz), 61.2 (d, J = 6.5 Hz), 123.5, 127.0, 127.4, 128.3, 138.0, 146.7 (d, J = 12.3 Hz); ^{31}P NMR ($CDCl_3$) δ 30.3.

Diethyl 2-(4-Methylphenyl)propylphosphonate (6d):[6a] 93% ee; $[\alpha]^{28}_D$ −12.7 (c 0.10, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, minor enantiomer t_R = 20.4 min; major enantiomer t_R = 22.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.1 Hz), 1.25 (t, 3H, J = 7.1 Hz), 1.37 (d, 3H, J = 7.0 Hz), 2.00−2.10 (m, 2H), 2.31 (s, 3H), 3.12−3.24 (m, 1H), 3.91−4.04 (m, 4H), 7.11−7.13 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J = 2.0 Hz), 16.3 (d, J = 2.0 Hz), 20.9, 23.5 (d, J = 8.8 Hz), 34.2 (d, J = 3.6 Hz), 34.4 (d, J = 138.0 Hz), 61.2 (d, J = 6.5 Hz), 61.4 (d, J = 6.5 Hz), 126.4, 129.1, 135.8, 143.7 (d, J = 12.6 Hz); ^{31}P NMR ($CDCl_3$) δ 30.3.

Diethyl 2-(4-methoxyphenyl)propylphosphonate (6e):[6a] 95% ee; $[\alpha]^{28}_D$ −22.8 (c 0.90, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, minor enantiomer t_R = 18.7 min; major enantiomer t_R = 21.2 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.1 Hz), 1.25 (t, 3H, J = 7.1 Hz), 1.36 (d, 3H, J = 6.9 Hz), 1.95−2.13 (m, 2H), 3.12−3.24 (m, 1H), 3.78 (s, 3H), 3.90−4.04 (m, 4H), 6.84 (d, 2H, J = 8.6 Hz), 7.15 (d, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2, 16.3, 23.6 (d, J = 9.5 Hz), 33.7 (d, J = 3.0 Hz), 34.5 (d, J = 131.1 Hz), 55.2, 61.2 (d, J = 6.5 Hz), 61.4 (d, J = 6.5 Hz), 113.8, 127.5, 138.8 (d, J = 12.2 Hz), 158.1; ^{31}P NMR ($CDCl_3$) δ 30.3.

Diethyl 2-(4-nitrophenyl)propylphosphonate (6f): 95% ee; $[\alpha]^{28}_D$ −33.5 (c 0.60, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 96/4, flow rate =1.0 mL/min, minor enantiomer t_R = 39.2 min; major enantiomer t_R = 43.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.1 Hz), 1.26 (t, 3H, J = 7.1 Hz), 1.42 (d, 3H, J = 6.9 Hz), 2.04−2.14 (m, 2H), 3.31−3.39 (m, 1H), 3.91−4.06 (m, 4H), 7.41 (d, 2H, J = 8.7 Hz), 8.18 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J = 3.3 Hz), 16.3 (d, J = 3.3 Hz), 23.3 (d, J = 10.1 Hz), 33.9 (d, J = 140.3 Hz), 34.8, 61.4 61.5, 123.8, 127.7, 146.6, 154.1 (d, J = 10.5 Hz); ^{31}P NMR ($CDCl_3$) δ 28.8; HRMS calcd for $C_{13}H_{21}NO_5P$ $[M + H]^+$ 302.1157, found 302.1153.

Diethyl 2-(4-fluorophenyl)propylphosphonate (6g):[6a] 93% ee; $[\alpha]^{28}_D$ −17.5 (c 0.70, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol =99/1, flow rate =0.8 mL/min, minor enantiomer t_R = 42.0 min; major enantiomer t_R = 45.7 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.1 Hz), 1.25 (t, 3H J = 7.1 Hz), 1.36 (d, 3H, J = 7.0 Hz), 2.00−2.09 (m, 2H), 3.21−3.24 (m, 1H), 3.90−4.03 (m, 4H), 6.96 (dd, 2H, J = 8.6, 8.6 Hz), 7.18 (dd, 2H, J = 8.6, 5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J = 2.5 Hz), 16.3 (d, J = 2.5 Hz), 23.7 (d, J = 10.3 Hz), 34.0 (d, J = 3.4 Hz), 34.4 (d, J = 138.8 Hz), 61.2 (d, J = 6.6 Hz), 61.4 (d, J = 6.6 Hz), 115.2 (d, J = 21.1 Hz), 128.1 (d, J = 7.8 Hz), 142.2 (dd, J = 3.4, 11.2 Hz), 161.4 (d, J = 244.0 Hz); ^{31}P NMR ($CDCl_3$) δ 29.8.

Diethyl 2-(4-chlorophenyl)propylphosphonate (6h):[6a] 92% ee; $[\alpha]^{28}_D$ −22.9 (c 0.10, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, minor enantiomer t_R = 15.1 min; major enantiomer t_R = 16.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.1 Hz), 1.25 (t, 3H, J = 7.1 Hz), 1.36 (d, 3H, J = 6.9 Hz), 1.99−2.08 (m, 2H), 3.18−3.22 (m, 1H), 3.90−4.05 (m, 4H), 7.17 (d, 2H, J = 8.5 Hz), 7.27 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J = 3.0 Hz), 16.3 (d, J = 3.0 Hz), 23.5 (d, J = 10.3 Hz), 34.1 (d, J = 139.1 Hz), 34.2 (d, J = 3.8 Hz), 61.3 (d, J = 6.5 Hz), 61.4 (d, J = 6.5 Hz), 128.1, 128.5, 132.0, 145.0 (d, J = 11.4 Hz); ^{31}P NMR ($CDCl_3$) δ 30.0.

Diethyl 2-(4-bromophenyl)propylphosphonate (6i):[6a] 96% ee; $[\alpha]^{25}_D$ −24.8 (c 1.0, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, minor enantiomer t_R = 24.9 min; major enantiomer t_R = 27.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.36 (d, J = 6.9 Hz, 3H), 1.99−2.07 (m, 2H), 3.16−3.21 (m, 1H), 3.91−4.05 (m, 4H), 7.11 (d, 2H, J = 8.5 Hz), 7.42 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.2 (d, J = 3.0 Hz), 16.3 (d, J = 3.0 Hz), 23.5 (d, J = 10.3 Hz), 34.2 (d, J = 138.9 Hz), 34.3 (d, J = 3.5 Hz), 61.3 (d, J = 6.5 Hz), 61.5 (d, J = 6.5 Hz), 120.0, 128.5, 131.5, 145.6 (d, J = 11.6 Hz); ^{31}P NMR ($CDCl_3$) δ 29.6.

Diethyl 2-(thiophene-2-yl)propylphosphonate (6j):[6a] 95% ee; $[\alpha]^{28}_D$ −19.0 (c 0.10, $CHCl_3$); HPLC conditions: Chiralpak AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, minor enantiomer t_R = 17.3 min; major enantiomer t_R = 19.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.1 Hz), 1.28 (t, 3H, J = 7.1 Hz), 1.48 (d, 3H, J = 6.9 Hz), 2.06 (ddd, 1H, J = 5.6, 15.3, 18.6 Hz), 2.15−2.21 (ddd, 1H, J = 8.5, 15.3, 17.6 Hz), 3.48−3.59 (m, 1H), 3.98−4.08 (m, 4H), 6.85−6.86 (m, 1H), 6.89−6.91 (m, 1H), 7.13 (d, 1H, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3, 16.4, 24.2 (d, J = 7.0 Hz), 30.4 (d, J = 2.0 Hz), 35.7 (d, J = 138.0 Hz), 61.4 (d, J = 7.0 Hz), 61.5 (d, J = 6.0 Hz), 122.9, 123.0, 126.5, 150.9 (d, J = 15.0 Hz); ^{31}P NMR ($CDCl_3$) δ 29.2.

Diethyl 2-phenylbutylphosphonate (11):[6a] 95% ee; $[\alpha]^{28}_D$ −11.9 (c 0.70, $CHCl_3$); HPLC conditions: Chiralcel OJ-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, major enantiomer t_R = 8.9 min; minor enantiomer t_R = 10.3 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, 3H, J = 7.2 Hz), 1.14 (t, 3H, J = 7.2 Hz), 1.20 (t, 3H, J = 7.2 Hz), 1.60−1.66 (m, 1H), 1.82−1.87 (m, 1H), 2.06−2.14 (m, 2H), 2.87−2.97 (m, 1H), 3.76−3.96 (m, 4H), 7.17−7.21 (m, 3H),

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7.27−7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.8, 16.2 (d, J = 6.4 Hz), 16.3 (d, J = 6.4 Hz), 30.6 (d, J = 12.7 Hz), 32.6 (d, J = 139.1 Hz), 41.9 (d, J = 3.6 Hz), 61.2 (d, J = 6.5 Hz), 61.4 (d, J = 6.5 Hz), 126.3, 127.6, 128.3, 144.4 (d, J = 8.4 Hz); ^{31}P NMR ($CDCl_3$) δ 30.5.

Diethyl 2-methyl-4-phenylbutylphosphonate (12):[6a] 91% ee; $[\alpha]^{28}_D$ −11.4 (c 0.50, $CHCl_3$); HPLC conditions: Chiralcel OJ-H, n-hexane/2-propanol = 98/2, flow rate = 0.7 mL min^{-1}, major enantiomer t_R = 19.7 min; minor enantiomer t_R = 22.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, 3H J = 6.7 Hz,), 1.30 (t, 6H, J = 7.1 Hz), 1.56−1.67 (m, 2H), 1.73−1.88 (m, 2H), 1.94−1.99 (m, 1H), 2.58−2.66 (m, 2H), 4.02−4.09 (m, 4H), 7.14−7.18 (m, 3H), 7.24−7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.4, 16.5, 20.8 (d, J = 7.5 Hz), 28.0 (d, J = 4.0 Hz), 32.7 (d, J = 138.0 Hz), 33.0, 40.0 (d, J = 13.6 Hz), 61.2 (d, J = 6.4 Hz), 61.3 (d, J = 5.8 Hz), 125.7, 128.2, 128.3, 142.2; ^{31}P NMR ($CDCl_3$) δ 31.7.

Diethyl 1-phenylethylphosphonate (13):[6i,j] 83% ee; $[\alpha]^{28}_D$ +4.8 (c 0.10, $CHCl_3$); HPLC conditions: chiralpak AD-H, n-hexane/2-propanol = 98/2, flow rate = 0.5 mL/min (210 nm), minor enantiomer t_R = 26.2 min; major enantiomer t_R = 30.6 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, 3H, J = 6.9 Hz), 1.27 (t, 3H, J = 6.9 Hz), 1.58 (dd, 3H, J = 18.5, 7.4 Hz), 3.19 (dq, 1H, J = 22.5, 7.4 Hz), 3.75−4.11 (m, 4H), 7.22−7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.6 (d, J = 5.0 Hz), 16.3 (d, J = 5.6 Hz), 16.4 (d, J = 5.9 Hz), 38.6 (d, J = 136 Hz), 61.9 (d, J = 6.9 Hz), 62.4 (d, J = 6.9 Hz), 126.9, 128.3, 128.5 (d, J = 6.5 Hz), 138.0 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$) δ 29.2.

Dimethyl 2-benzoyloxy-2-phenylethylphosphonate (15a):[6h] 93% ee; $[\alpha]^{28}_D$ −4.2 (c 0.60, $CHCl_3$); HPLC conditions: Chiralcel OJ-H, n-hexane/2-propanol = 91/9, flow rate = 1.0 mL/min, major enantiomer t_R = 26.0 min; minor enantiomer t_R = 32.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (ddd, 1H, J = 5.5, 15.5, 18.8 Hz), 2.70 (ddd, 1H, J = 6.5, 15.5, 17.2 Hz), 3.62 (d, 3H, J = 5.9 Hz), 3.64 (d, 3H, J = 5.9 Hz), 6.30 (ddd, 1H, J = 5.5, 6.5, 9.0 Hz), 7.30−7.58 (m, 8H), 8.10 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 32.1, 33.5, 52.3 (d, J = 6.8 Hz), 52.5 (d, J = 7.3 Hz), 71.4 (d, J = 2.2 Hz), 126.4, 128.4, 128.5, 128.7, 129.9, 133.1, 139.7 (d, J = 10.7 Hz), 165.2; ^{31}P NMR ($CDCl_3$) δ 28.1.

Dimethyl 2-benzoyloxy-2-(4-methylphenyl)ethylphosphonate (15b):[6h] 96% ee; $[\alpha]^{25}_D$ −2.7 (c 0.60, $CHCl_3$); HPLC conditions: chiralcel IB, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 9.6 min; minor enantiomer t_R = 11.2 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 1H) 2.41 (ddd, 1H, J = 5.4, 15.5, 18.8 Hz), 2.70 (ddd, 1H, J = 8.6, 17.1, 17.1 Hz), 3.62 (d, 3H, J = 5.5 Hz), 3.65 (d, 3H, J = 5.5 Hz), 6.27 (ddd, 1H, J = 5.5, 8.8, 8.8 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.55 (t, 1H, J = 7.5 Hz), 8.07 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1, 32.2 (d, J = 140.2 Hz), 52.3 (d, J = 6.5 Hz), 52.5 (d, J = 7.7 Hz), 71.3, 126.4, 128.3, 129.3, 129.7, 130.0, 133.0, 136.8 (d, J = 10.9 Hz), 138.3, 165.2; ^{31}P NMR ($CDCl_3$) δ 28.2.

Dimethyl 2-benzoyloxy-2-(4-methoxyphenyl)ethylphosphonate (15c):[6h] 93% ee; $[\alpha]^{25}_D$ −2.1 (c 0.10, $CHCl_3$); HPLC conditions: Chiralcel IB, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 14.8 min; minor enantiomer t_R = 17.6 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (ddd, 1H, J = 5.8, 15.5, 18.7 Hz), 2.70 (ddd, 1H, J = 8.3, 15.5, 17.5 Hz), 3.62 (d, 3H, J = 7.3 Hz), 3.65 (d, 3H, J = 7.3 Hz), 3.79 (s, 3H), 6.27 (ddd, 1H, J = 5.9, 8.5, 8.5 Hz), 6.87−6.91 (m, 2H), 7.39−7.45 (m, 4H), 7.53−7.57 (m, 1H), 8.07 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 32.6 (d, J = 140.0 Hz), 52.3 (d, J = 3.1 Hz), 52.5 (d, J = 2.7 Hz), 55.2 (d, J = 3.2 Hz) 71.1 (d, J = 2.6 Hz), 114.0, 128.0, 128.3, 129.7, 130.1, 131.9 (d, J = 10.3 Hz), 133.0, 159.6, 165.2; ^{31}P NMR ($CDCl_3$) δ 28.2.

Dimethyl 2-benzoyloxy-2-(4-chlorophenyl)ethylphosphonate (15d): 94% ee; $[\alpha]^{27}_D$ −15.5 (c 1.0, $CHCl_3$); HPLC conditions: Chiralcel IB, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 11.2 min; minor enantiomer t_R = 13.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (ddd, 1H, J = 5.8, 15.5, 18.8 Hz), 2.66 (ddd, 1H, J = 8.2, 15.6, 17.5 Hz), 3.63 (d, 3H, J = 7.0 Hz), 3.65 (d, 3H, J = 7.0 Hz), 6.27 (ddd, 1H, J = 6.0, 8.6, 8.6 Hz), 7.33 (d, 2H, J = 8.5 Hz), 7.40−7.47 (m, 4H), 7.57 (t, 1H, J = 7.4 Hz), 8.06 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 32.5 (d, J = 140.9 Hz), 52.4 (d, J = 6.4 Hz), 52.5 (d, J = 6.4 Hz), 70.8, 127.9 128.4, 128.8, 129.6, 129.7, 133.2, 134.3, 138.3 (d, J = 10.4 Hz), 165.1; ^{31}P NMR ($CDCl_3$) δ 27.6; HRMS calcd for $C_{17}H_{19}ClO_5P$ $[M + H]^+$ 369.0659, found 369.0656.

Dimethyl 2-benzoyloxy-2-(4-bromophenyl)ethylphosphonate (15e):[6h] 88% ee; $[\alpha]^{24}_D$ −16.2 (c 1.0, $CHCl_3$); HPLC conditions: Chiralcel IB, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 11.7 min; minor enantiomer t_R = 14.2 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (ddd, 1H, J = 5.8, 15.5, 18.8 Hz), 2.66 (ddd, 1H, J = 8.3, 15.5, 17.5 Hz), 3.63 (d, 3H, J = 7.2 Hz), 3.66 (d, 3H, J = 7.2 Hz), 6.25 (ddd, 1H, J = 5.9, 8.6, 8.6 Hz), 7.34 (d, 2H, J = 8.5 Hz), 7.43−7.51 (m, 4H), 7.57 (t, 1H, J = 7.4 Hz), 8.06 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 32.5 (d, J = 140.8 Hz), 52.3 (d, J = 3.1 Hz), 52.5 (d, J = 2.7 Hz), 70.8, 122.5 128.2, 128.4, 129.6, 129.7, 131.8, 133.2, 138.8 (d, J = 10.5 Hz), 165.1; ^{31}P NMR ($CDCl_3$) δ 27.6.

Dimethyl 2-benzoyloxy-2-(β-naphthyl)ethylphosphonate (15f):[6h] 92% ee; $[\alpha]^{22}_D$ −38.8 (c 0.34, $CHCl_3$); HPLC conditions: Chiralcel IB, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 15.5 min; minor enantiomer t_R = 18.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (ddd, 1H, J = 5.4, 15.6, 18.9 Hz), 2.80 (ddd, 1H, J = 8.6, 17.1, 17.1 Hz), 3.62 (d, 3H, J = 11.7 Hz), 3.65 (d, 3H, J = 11.3 Hz), 6.50 (ddd, 1H, J = 5.5, 8.9, 8.9 Hz), 7.43−7.51 (m, 4H), 7.57 (t, 2H, J = 8.0 Hz), 7.81−7.87 (m, 3H), 7.94 (s, 1H), 8.11 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 33.2 (d, J = 140.6 Hz), 52.4, 52.6, 71.6, 123.8, 125.8, 126.4, 127.6, 128.1, 128.4, 128.7, 129.7, 129.9, 133.0, 133.1, 133.2, 137.0, 137.1, 165.2; ^{31}P NMR ($CDCl_3$) δ 28.2.

Dimethyl 2-benzoyloxypropanephosphonate (15g):[6h] 92% ee; $[\alpha]^{20}_D$ +33.4 (c 0.70, $CHCl_3$); HPLC conditions: Chiralcel OJ-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, major enantiomer t_R = 10.6 min; minor enantiomer t_R = 12.5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (d, 3H, J = 6.3 Hz), 2.16 (ddd, 1H, J = 7.0, 15.3, 18.6 Hz), 2.38 (ddd, 1H, J = 6.1, 15.3, 19.1 Hz), 3.73 (d, 3H, J = 8.9 Hz), 3.75 (d, 3H, J = 8.9 Hz), 5.43 (ddd, 1H, J = 6.4, 12.7, 12.7 Hz), 7.44 (t, 2H, J = 7.4 Hz), 7.56 (t, 1H, J = 7.4 Hz), 8.05 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1 (d, J = 7.9 Hz), 32.3 (d, J = 140.1 Hz), 52.5, 52.5, 128.3, 129.5, 130.1, 133.0, 165.6; ^{31}P NMR ($CDCl_3$) δ 29.2.

Dimethyl 1-benzoyloxy-2-phenylethylphosphonate (17):[6d−g] 13% ee; $[\alpha]^{28}_D$ −16.6 (c 1.0, $CHCl_3$); HPLC conditions: Chiralcel OD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min (210 nm), minor enantiomer t_R = 10.4 min; major enantiomer t_R = 19.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19−3.28 (m, 1H), 3.32−3.38 (m, 1H), 3.77 (d, 3H, J = 10.7 Hz), 3.78 (d, 3H, J = 10.7 Hz), 5.77 (ddd, 1H, J = 12.2, 7.4 Hz, 4.0 Hz), 7.15−7.27 (m, 5H), 7.42 (t, 2H, J = 7.9 Hz), 7.56 (t, 1H, J = 7.4 Hz), 8.0 (d, 2H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$) δ 35.7, 53.2 (d, J = 6.3 Hz), 53.4 (d, J = 8.8 Hz), 68.5 (d, J = 166 Hz), 126.9, 128.4, 128.5, 129.0, 129.1, 129.7, 133.3, 136.0 (d, J = 13.7 Hz), 165.0 (d, J = 4.5 Hz). ^{31}P NMR ($CDCl_3$) δ 22.5.

Dimethyl 2-acetylamino-2-phenylethylphosphonate (19):[6b,c] 33% ee; $[\alpha]^{28}_D$ −10.5 (c 0.12, $CHCl_3$); HPLC conditions: Chiralcel OD-H, n-hexane/2-propanol = 85/15, flow rate = 0.5 mL/min, minor enantiomer t_R = 21.5 min; major enantiomer t_R = 25.5 min; ^{1}H NMR (400.0 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.23−2.46 (m, 2H), 3.37 (d, 3H, J = 11.0 Hz,), 3.67 (d, 3H, J = 11.0 Hz), 5.39 (ddd, 1H, J = 23.9, 13.3, 7.2 Hz), 7.09 (br s, 1H), 7.25−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 23.2, 31.7 (d, J = 139 Hz), 48.5 (d, J = 4.3 Hz), 52.1 (d, J = 6.7 Hz), 52.3 (d, J = 6.8 Hz), 126.0, 127.5, 128.6, 141.0 (d, J = 8.2 Hz), 169.4; ^{31}P NMR ($CDCl_3$) δ 29.7.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for new ClickFerrophos II ligands **L3**−**L5** and chiral phosphonate compounds; crystallographic data for **L4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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