

# Development of Ruthenium Catalysts for the Enantioselective Synthesis of P-Stereogenic Phosphines via Nucleophilic Phosphido Intermediates

Vincent S. Chan, Melanie Chiu, Robert G. Bergman,\* and F. Dean Toste\*

*Department of Chemistry, University of California, Berkeley, California 94720*

## Supporting Information

	Page #
I. General Information	S-2
II. Materials	S-2
III. Experimental	
(a) Procedure for alkoxide optimization	S-3
(b) Procedure for the synthesis of the <i>i</i> Pr-PHOX catalyst ( <b>6</b> )	S-3
(c) Procedure for phosphine alkylation with <b>6</b>	S-4
(d) General procedure for mixed ligand catalyst synthesis	S-5
(e) Typical procedure for asymmetric alkylation	S-6
(f) Characterization data for chiral phosphines	S-6
(g) Procedure for measurement of reaction half-lives	S-31
(h) Procedure for the synthesis of complexes <b>23</b> and <b>24</b>	S-32
(i) NMR spectra for complexes <b>23</b> and <b>24</b>	S-34
IV. References	S-36

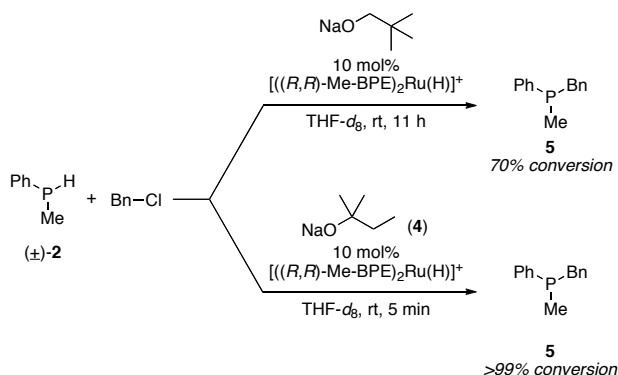
**I. General Information.** Unless otherwise noted, reactions and manipulations were performed at ambient temperature in an inert atmosphere ( $N_2$ ) glovebox, or using standard Schlenk and high-vacuum line techniques. Glassware was oven-dried for at least 8 h at 150 °C or flame-dried under vacuum immediately prior to use. TLC analysis of reaction mixtures was performed on Merck silica gel 60 F<sub>254</sub> TLC plates. Chromatography was carried out on Merck 60 silica gel (32-63  $\mu$ m). All NMR spectra were obtained at ambient temperature using Bruker DRX-500, AVB-400, or AVQ-400 spectrometers.  $^1H$  NMR chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual protiated solvent. Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration).  $^{13}C$  NMR chemical shifts ( $\delta$ ) are reported in ppm relative to the carbon resonance of the deuterated solvent.  $^{31}P$  NMR chemical shifts ( $\delta$ ) are reported in ppm relative to external 85% aqueous  $H_3PO_4$ . Infrared (IR) spectra were recorded on a ThermoNicolet Avatar 370 as a thin film on a ZnSe crystal. Mass spectrometry and elemental analyses were performed at the University of California, Berkeley Micro-Mass/Analytical Facility. Enantiomeric excess was determined using either a Shimadzu 10A VP Series Chiral HPLC with detection at 230, 254 and 280 nm or an Agilent 1100 Series Chiral HPLC with detection at 210, 220, 230, 254, and 280 nm. Samples for chiral HPLC analysis were prepared in neat *i*PrOH (2 mg/mL).

**II. Materials.** Reagents/ligands were purchased from commercial suppliers, checked for purity and used without further purification unless otherwise noted. Liquids were degassed using three freeze-pump-thaw cycles and stored over 4Å activated molecular sieves. Solids were stored in an inert ( $N_2$ ) atmosphere glove box. Tetrahydrofuran, pentane, toluene, diethyl ether and benzene (Fisher) were passed through a column of activated alumina (type A2, size 12 x 32, Purify Co.) under nitrogen pressure and sparged with  $N_2$  prior to use. Benzene- $d_6$  was dried over 4Å sieves. THF- $d_8$  was vacuum transferred from purple sodium benzophenone/ketyl and stored under an inert atmosphere. 1,2-Bis(dimethylphosphino)ethane (dmpe) was purchased from Strem Chemicals and stored in a Schlenk vessel in the glovebox. The 1.0 M  $BH_3$ •THF solution (Aldrich) was transferred to a Schlenk flask equipped with a vacuum stopcock and stored in the glove box.

### III. Experimental

**Procedure for alkoxide optimization (Table 1).** In a nitrogen atmosphere glovebox, a one-dram vial was charged with secondary phosphine complex  $[(dmpe)_2Ru(H)(PMePh)][BPh_4]$  (**3**)<sup>1</sup> (10 mg, 1 equiv) and sodium *tert*-amyloxide **4** (1.3 mg, 1 equiv). Following complete dissolution of the solids with tetrahydrofuran-*d*<sub>8</sub> (0.3 mL), the yellow solution was then transferred to an NMR tube. The tube was capped and deprotonation of **3** to phosphido complex  $(dmpe)_2Ru(H)(PMePh)$  **1**<sup>1</sup> was monitored by <sup>31</sup>P NMR spectroscopy. Solubility of the alkoxide was determined by visual inspection of the reaction solution.

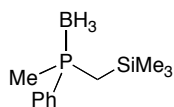
**Scheme S-1.** Determination of the optimal alkoxide base



Based on the initial evaluation of alkoxides (Table 1), both NaOtAm (**4**) and sodium neopentoxide were sufficiently basic and soluble. However, sodium *tert*-amyloxide (**4**) was determined to be optimal, on the basis of its efficiency in the catalytic reaction (Scheme S-1). Sodium neopentoxide was incapable of effecting quantitative alkylation in the presence of catalytic  $[(R,R)\text{-Me-BPE}]_2Ru(H)[BPh_4]$ , whereas complete conversion to benzylmethylphenylphosphine was observed with NaOtAm.

**Procedure for the synthesis of  $[(R)\text{-}iPr\text{-PHOX}]_2Ru(H)[BPh_4]$  (**6**).<sup>1</sup>** To a 50-mL Schlenk vessel with removable Teflon stopcock was added  $(PPh_3)_3Ru(H)(Cl)$ <sup>2</sup> (600 mg, 1 equiv) and (*R*)-*i*Pr-PHOX (485 mg, 2 equiv), which was dissolved in THF (10 mL). The sealed vessel was brought out of the glovebox and then degassed by three freeze-pump-thaw cycles. The reaction was then heated to 105 °C; after 18 h, the solution was cooled to room temperature and concentrated to 5 mL. Under a nitrogen atmosphere, NaBPh<sub>4</sub> (222 mg, 1 equiv) was added as a 1.0 M THF solution. The solution was stirred for 10 h at room temperature, then filtered through a pad of Celite. THF was removed in vacuo to afford a dark orange-red solid. The solid was

then washed with Et<sub>2</sub>O (3 x 1 mL) and benzene (3 x 1 mL). Further purification was accomplished by precipitation of **6** from a saturated THF solution by slow vapor diffusion with Et<sub>2</sub>O at room temperature. The title compound was obtained as a red crystalline solid (564 mg, 74%): mp 209.5–211 °C (dec). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz) δ 8.08 (m, 1H), 8.01 (m 1H), 7.90–7.81 (m 3H), 7.64–7.14 (m, 22H), 6.86 (m, 12H), 6.68 (m, 8H), 5.98 (m, 1H), 4.49 (m, 3H), 4.27 (br t, 1H), 4.22 (m, 1H), 3.98 (br d, 1H), 2.80 (m, 1H), 0.82 (d, *J* = 7.2 Hz, 3H), 0.55 (br s, 4H), 0.33 (d, *J* = 6.8 Hz, 3H), -0.21 (br s, 3H), -20.9 (Ru-*H*, dd, *J* = 27.6, 27.2, 35.8 Hz, 1H). <sup>11</sup>B{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 128 MHz) δ -8.5. <sup>31</sup>P{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 162 MHz) δ 67.4 (d, *J* = 26 Hz), 59.9 (d, *J* = 24 Hz). Anal. Calcd for C<sub>72</sub>H<sub>69</sub>BN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Ru: C 74.03, H 5.95, N 2.40; Found: C 73.65, H 5.98, N 2.39.



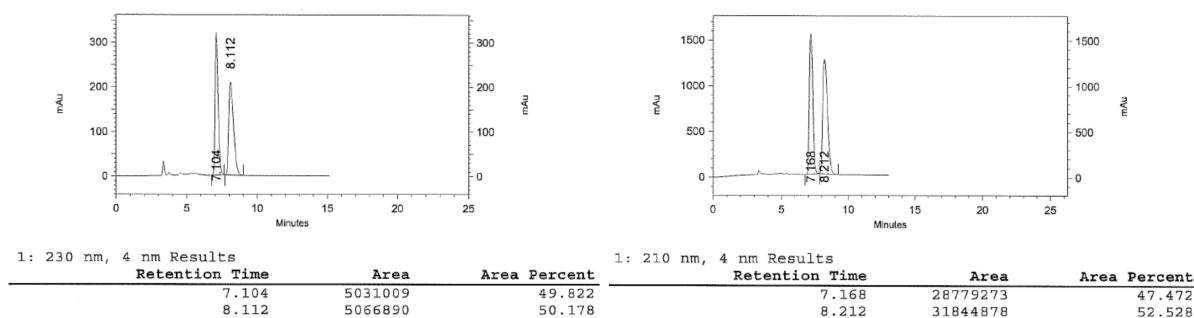
**Methylphenyl(trimethylsilylmethyl)phosphine-borane (8b).**

A one-dram vial was charged with ruthenium catalyst **6** (24 mg, 0.020 mmol, 0.1 equiv) and NaOtAm **4** (27 mg, 0.24 mmol, 1.2 equiv), to which THF (0.8 mL) was added. (Bromomethyl)trimethylsilane (34 μL, 0.24 mmol, 1.2 equiv) was syringed into the solution, which was transferred to an NMR tube. The tube was fitted into a Cajon adapter and brought out of the glovebox. Using standard Schlenk technique, the NMR tube was placed under a positive pressure of nitrogen on a high vacuum manifold. The solution was cooled to -78 °C, and methylphenylphosphine **2** (26 μL, 0.20 mmol, 1.0 equiv) was added directly to the reaction mixture using a Hamilton Gastight syringe. The NMR tube was then flame-sealed under an atmosphere of nitrogen. The contents were mixed by inverting the NMR tube, then warmed to -30 °C. After 60 h, the solution was warmed to rt and brought into the glovebox. The NMR tube was opened and the solution was transferred to a five-dram scintillation vial equipped with a stirbar. A 1.0 M solution of BH<sub>3</sub>•THF (2 mL, 2.0 mmol, 10 equiv) was added and the resulting solution was stirred for 30 min at room temperature. The following work-up was performed outside of the glovebox: excess BH<sub>3</sub> was quenched by slow addition of water and the resulting slurry was then extracted with ethyl acetate (3 x 5 mL). The combined organic phase was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo.

Flash chromatography (gradient from pure hexanes to 60:40 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) furnished the product as a colorless oil (76% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.82–7.80 (m, 2H),



7.51–7.49 (m, 3H), 1.59 (d,  $J = 10$  Hz, 3H), 1.32–1.18 (m, 2H), 0.75 (br q, 3H), 0.07 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  132.6 (d,  $J = 53$  Hz), 131.0 (d,  $J = 10$  Hz), 130.9 (d,  $J = 4$  Hz), 128.6 (d,  $J = 10$  Hz), 15.6 (d,  $J = 39$  Hz), 15.2 (d,  $J = 24$  Hz), 0.3.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  6.8 (q,  $J_{\text{B-P}} = 62$  Hz). IR: 3078, 3057, 2954, 2898, 2376, 2257, 1436, 1416, 1250, 1118, 1056, 897, 844, 790, 745, 695  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{11}\text{H}_{19}\text{BSiP}]^+$  221.1087, Found 221.1090. Separation of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 0.9 mL/min, 91:9 hexanes:*i*-PrOH,  $T_r$  minor 7.17, major 8.21 min) determined the ee to be 5%.



**General procedure for mixed ligand catalyst synthesis.** In a nitrogen atmosphere glovebox, a 25-mL Schlenk vessel with a removable Teflon stopcock was charged with an equivalent of  $(\text{PPh}_3)_3\text{Ru}(\text{Cl})(\text{H})$ ,<sup>2</sup> the desired chiral ligand (1 equiv) and THF (0.3 M relative to ruthenium). The sealed vessel was brought out of the glovebox and then degassed using three freeze-pump-thaw cycles. The reaction mixture was heated to 105 °C for 16 h, then cooled to room temperature and brought back into the glovebox. An equivalent of the desired achiral ligand was added and the reaction mixture was stirred for 1 h at rt. Sodium tetraphenylborate (1 equiv) was then added as a 1.0 M solution in THF. The solution was stirred for 12 h at room temperature, then filtered through a pad of Celite. The volatile organic materials were removed in vacuo to afford the crude product. The resulting solid was washed with  $\text{Et}_2\text{O}$  (3 x 1 mL) and benzene (3 x 1 mL) to remove any  $\text{PPh}_3$ . Further purification was accomplished by precipitation of the Ru(II) complex from a saturated THF solution by slow vapor diffusion with  $\text{Et}_2\text{O}$  at room temperature.

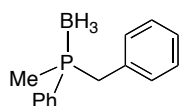
**$[(\text{(R)-MeO-BiPHEP})(\text{dmpe})\text{Ru}(\text{H})][\text{BPh}_4]$  (10).** The air-sensitive product was isolated as an orange solid (97% yield).  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 400 MHz)  $\delta$  7.54–7.19 (m, 38H), 7.01–6.95 (m, 3H), 6.85 (m, 3H), 6.45 (m, 1H), 6.33 (m, 1H), 3.35 (br s, 6H), 1.41–1.28 (br m, 7H), 0.90–

0.82 (m, 4H), 0.60 (br m, 2H), 0.45 (br m, 3H), -13.26 (br m, 1H, Ru-*H*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF-*d*<sub>8</sub>, 162 MHz)  $\delta$  36.0 (br m). HRMS (ESI<sup>+</sup>) calcd for [C<sub>44</sub>H<sub>49</sub>O<sub>2</sub>P<sub>4</sub><sup>100</sup>Ru]<sup>+</sup> 833.1725, 833.1652.

**[(*R*)-DIFLUORPHOS)(dmpe)Ru(H)][BPh<sub>4</sub>] (11).** The air-sensitive product was sparingly soluble in Et<sub>2</sub>O; isolated the catalyst as an orange solid (77% yield).  $^1\text{H}$  NMR (THF-*d*<sub>8</sub>, 400 MHz)  $\delta$  8.03 (br t, 1H), 7.91 (br t, 1H), 7.72 (br m, 1H), 7.51 (br m, 1H), 7.43-7.33 (m, 16H), 7.30-7.23 (m, 13H), 7.16-6.89 (m, 9H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.55 (br m, 1H), 1.29-1.25 (m, 6H), 1.14 (br d, *J* = 7.6 Hz, 3H), 0.88 (m, 1H), 0.65 (br d, *J* = 7.6 Hz, 1H), 0.51 (br d, *J* = 8.0 Hz, 1H), 0.27 (br d, *J* = 8.0 Hz, 3H), 0.04 (d, *J* = 7.2 Hz, 1H), -18.49 (m, 1H, Ru-*H*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF-*d*<sub>8</sub>, 162 MHz)  $\delta$  35.6 (m), 34.1 (m), 30.1 (m), 24.4 (m). HRMS (ESI<sup>+</sup>) calcd for [C<sub>44</sub>H<sub>41</sub>F<sub>4</sub>O<sub>4</sub>P<sub>4</sub>Ru]<sup>+</sup> 935.0930, Found 935.0951.

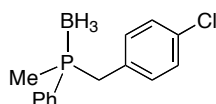
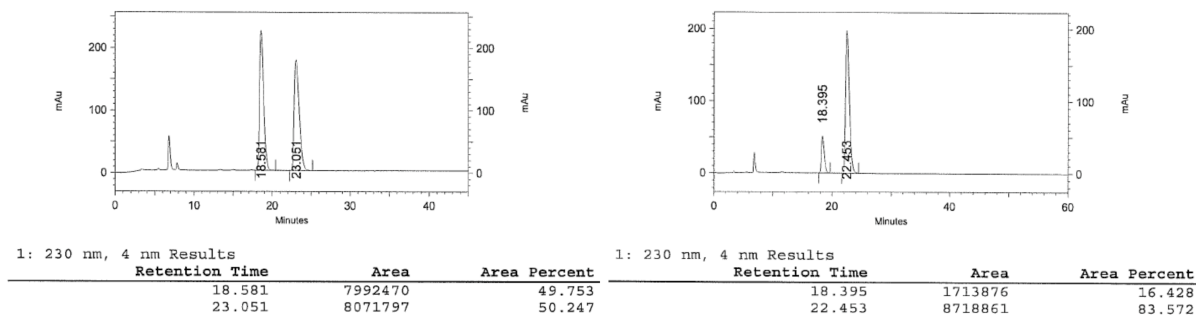
**Typical procedure for the asymmetric alkylation with mixed ligand catalyst.** In a nitrogen atmosphere glovebox, a one-dram scintillation vial was charged with MeO-BiPHEP/dmpe catalyst **10** (7.0 mg, 0.0061 mmol, 0.07 equiv), sodium *tert*-amyloxide **4** (12 mg, 0.10 mmol, 1.2 equiv) and THF (0.30 mL). Methylphenylphosphine (**2**) (11  $\mu\text{L}$ , 0.087 mmol, 1.0 equiv) and benzyl chloride (12  $\mu\text{L}$ , 0.10 mmol, 1.2 equiv) were syringed into the solution, and the vial was capped. The reaction solution was stirred at room temperature for 90 min. A 1.0 M solution of BH<sub>3</sub>•THF (0.87 mL, 0.87 mmol, 10 equiv) was added to the mixture and the resulting solution was stirred for 30 min at room temperature. The reaction mixture was quenched outside of the glovebox by the slow addition of water; the resulting aqueous solution was extracted with ethyl acetate (4 x 5 mL). The combined organic phase was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (conditions indicated below).

**Tables 9 & 10: Chiral phosphines prepared with (*R*)-MeO-BiPHEP/dmpe catalyst (10).**

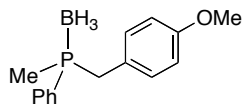
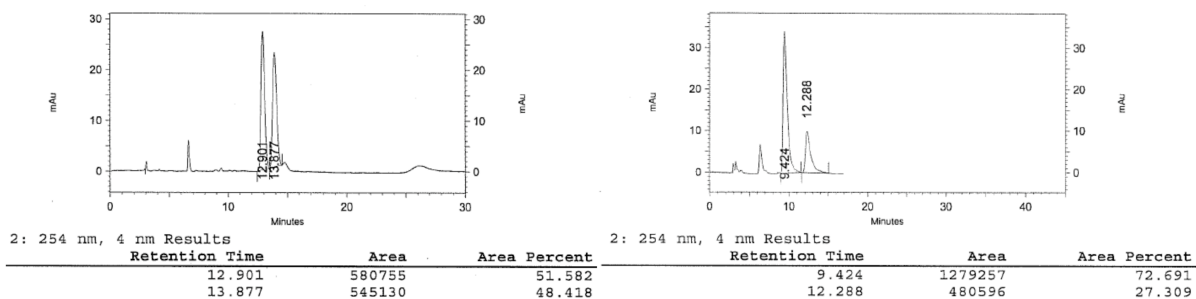


**Benzylmethylphenylphosphine-borane (5).** Silica gel flash column chromatography (80:20 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) afforded the product as a white solid (92% yield). NMR spectral data agreed with literature values:<sup>1</sup>  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.63–7.41 (m, 5H), 7.21 (m, 3H), 6.92 (m, 2H) 3.21 (d, *J* = 8.4 Hz, 2H), 1.51 (d, *J* = 10 Hz, 3H), 0.69 (br q,

3H). Separation of enantiomers was achieved via chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 85:15 hexanes:*i*PrOH,  $T_r$  minor 18.40, major 22.45 min) and the ee determined to be 68%. On cooling the reaction to -30 °C, the phosphine-borane **5** was recovered in 75% ee.

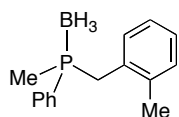
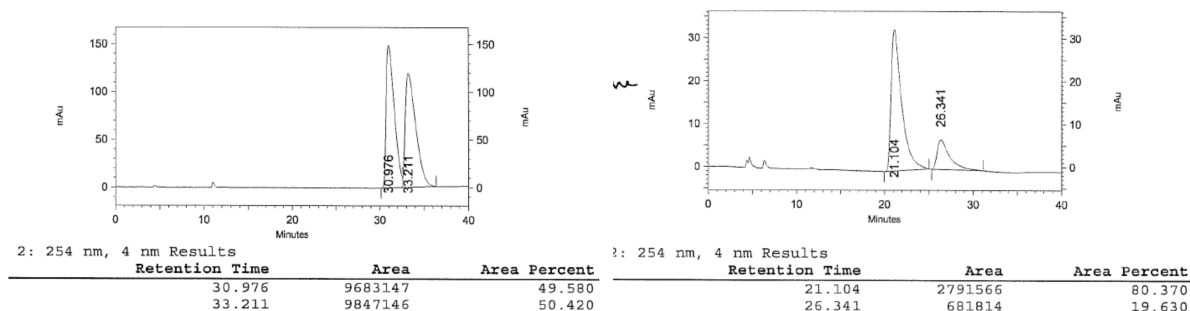


**(4-Chlorobenzyl)methylphenylphosphine-borane (7a).** Silica gel flash column chromatography (75:25 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) afforded the product as an off-white solid (97% yield). NMR spectral data agree with literature values:<sup>1</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.58–7.42 (m, 5H), 7.18 (d,  $J$  = 8 Hz, 2H), 6.84 (d,  $J$  = 6.8 Hz, 2H), 3.17 (d,  $J$  = 10.8 Hz, 2H), 1.53 (d,  $J$  = 9.6 Hz, 3H), 0.77 (br q, 3H). Separation of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.1 mL/min, 96:4 hexanes:*i*PrOH,  $T_r$  major 9.43, minor 12.30 min) determined the ee to be 45%.

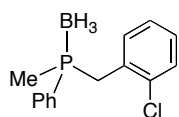


**(4-Methoxybenzyl)methylphenylphosphine-borane (7c).** Silica gel flash column chromatography (60:40 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) afforded the product as a white solid (96% yield). NMR spectral data agree with literature values:<sup>3</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.58–7.48 (m, 3H), 7.44–7.41 (m, 2H), 6.83 (d,  $J$  = 8.0 Hz, 2H), 6.75 (d,  $J$  = 8.0 Hz, 2H), 3.78 (s, 3H), 3.15

(d,  $^2J_{\text{P-H}} = 10.4$  Hz, 2H), 1.49 (d,  $^2J_{\text{P-H}} = 10.0$  Hz, 3H), 0.65 (br q, 3H). Separation of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.0 mL/min, 98:2 hexanes:*i*PrOH,  $T_{\text{r}}$  major 21.10, minor 26.34 min) determined the ee to be 61%.



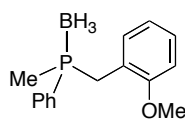
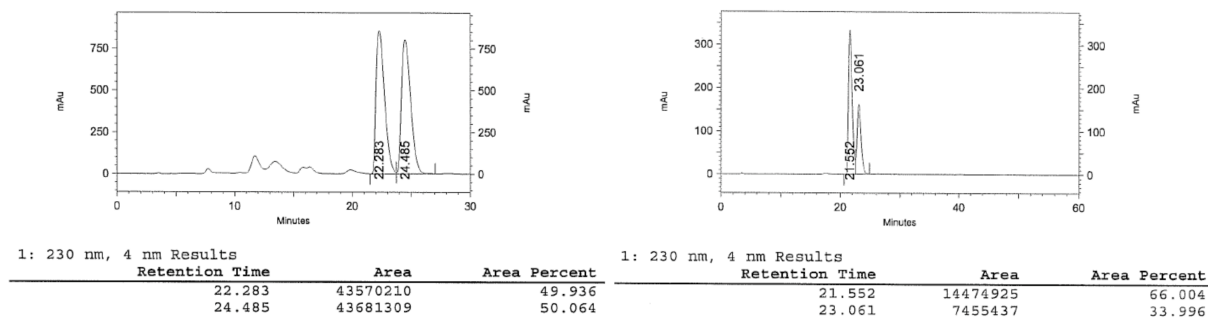
**Methyl(2-methylbenzyl)phenylphosphine-borane (7d).** The crude product was filtered through a plug of silica gel:  $R_{\text{f}}$  (80:20 hexanes: $\text{CH}_2\text{Cl}_2$ ) 0.16. The yield was not determined. NMR spectral data agree with literature values:<sup>1</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.52 (m, 3H), 7.41 (m, 2H), 7.17–7.07 (m, 3H), 6.89 (m, 1H), 3.24 (m, 2H), 1.96 (s, 3 H), 1.56 (d,  $J = 10$  Hz, 3H), 0.83 (br q, 3H). Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 0.9 mL/min, 94:6 hexanes:*i*PrOH,  $T_{\text{r}}$  major 33.25, minor 76.17 min) determined the ee to be 56%.



**(2-Chlorobenzyl)methylphenylphosphine-borane (12a).**

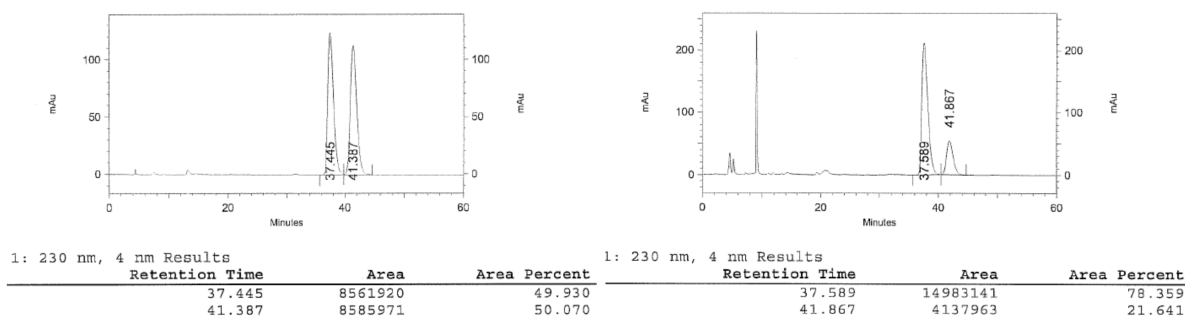
Silica gel flash column chromatography (75:25 hexanes: $\text{CH}_2\text{Cl}_2$ ) afforded the product as a colorless residue (89% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.65–7.60 (m, 2H), 7.55–7.50 (m, 1H), 7.46–7.41 (m, 2H), 7.46–7.41 (m, 1H), 7.21–7.11 (m, 2H), 7.07–7.03 (m, 1H), 3.50–3.37 (m, 2H), 1.55 (d,  $J = 10.0$  Hz, 3H), 0.71 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  134.1 (d,  $J = 4$  Hz), 132.3 (d,  $J = 9$  Hz), 131.9 (d,  $J = 3$  Hz), 131.7 (d,  $J = 9$  Hz), 131.5 (d,  $J = 3$  Hz), 129.5 (d,  $J = 2$  Hz), 129.3 (d,  $J = 29$  Hz), 128.6 (d,  $J = 10$  Hz), 128.4 (d,  $J = 2$  Hz), 126.6 (d,  $J = 2$  Hz), 32.4 (d,  $J = 31$  Hz), 8.9 (d,  $J = 38$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  12.9 (m). IR: 3058, 2918, 2379, 2338, 1474, 1437, 1063, 902, 749, 693  $\text{cm}^{-1}$ . HRMS (FAB<sup>+</sup>) calcd for  $[\text{C}_{14}\text{H}_{14}\text{BCIP}]^+$  259.0615, Found

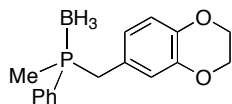
259.0608. Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 95:5 hexanes:*i*PrOH,  $T_r$  major 21.55, minor 23.06 min) determined the ee to be 32%.



**(2-Methoxybenzyl)methylphenylphosphine-borane (12b).** Silica gel flash

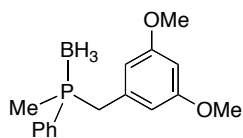
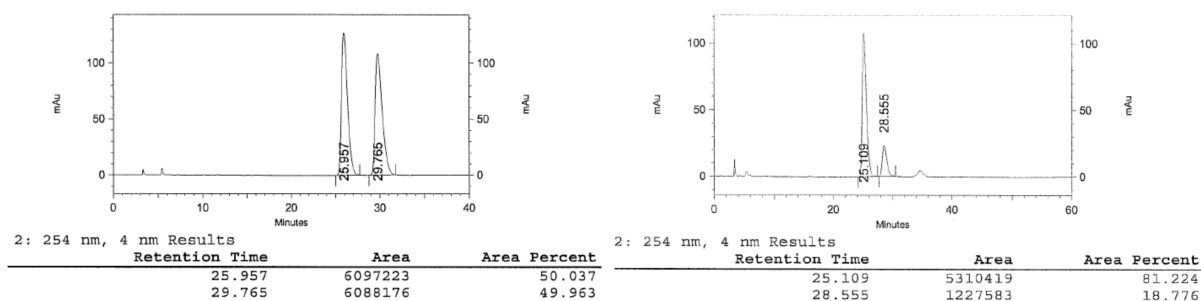
column chromatography (93:7 hexanes:EtOAc) afforded the product as a colorless residue (79% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.63–7.41 (m, 5H), 7.21 (m, 3H), 6.92 (m, 2H), 3.21 (d,  $J$  = 8.4 Hz, 2H), 1.51 (d,  $J$  = 10 Hz, 3H), 0.69 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  131.7 (d,  $J$  = 9 Hz), 131.2 (d,  $J$  = 4 Hz), 130.9 (d,  $J$  = 2 Hz), 129.5 (d,  $J$  = 53 Hz), 128.3, 128.2, 128.1, 120.9 (d,  $J$  = 8 Hz), 120.1 (d,  $J$  = 2 Hz), 110.1 (d,  $J$  = 2 Hz), 54.7, 29.2 (d,  $J$  = 32 Hz), 8.7 (d,  $J$  = 38 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.9 (q,  $J_{\text{B-P}}$  = 63 Hz). IR: 3058, 3026, 3003, 2960, 2835, 2375, 2252, 1600, 1495, 1437, 1249, 1063, 905, 754, 693  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{15}\text{H}_{17}\text{BOP}]^+$  255.1110, Found 255.1108. Separation of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 1.0 mL/min, 90:10 hexanes:*i*PrOH,  $T_r$  major 37.59, minor 41.87 min) determined the ee to be 56%.





**((2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)methyl)methylphenylphosphine-**

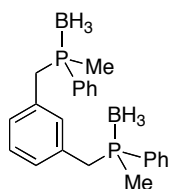
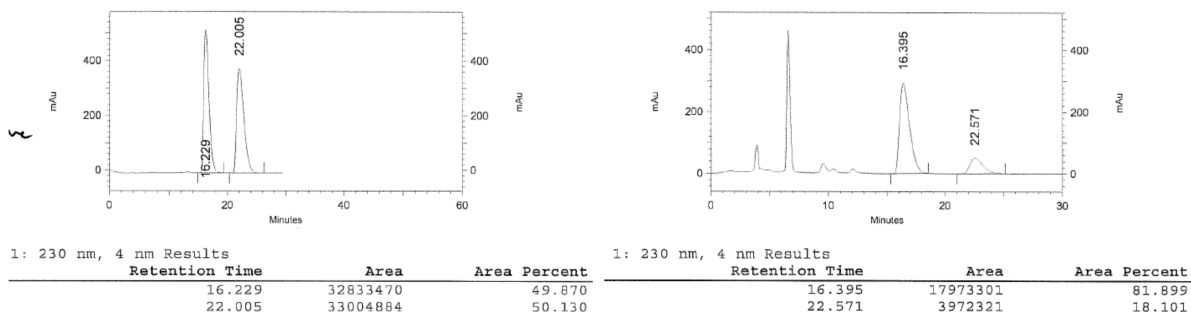
**borane (12c).** Silica gel flash column chromatography (93:7 hexanes:EtOAc) afforded the product as a white residue (90% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.60-7.55 (m, 2H), 7.50 (m, 1H), 7.42 (m, 2H), 6.69 (d,  $J = 8.4$  Hz, 1H), 6.45 (s, 1H), 6.37 (d,  $J = 8.4$  Hz, 1H), 4.12 (d,  $J = 7.2$  Hz, 4H), 3.14-3.04 (m, 2H), 1.49 (d,  $J = 9.6$  Hz, 3H), 0.66 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  143.1 (d,  $J = 2$  Hz), 142.5 (d,  $J = 2$  Hz), 131.6 (d,  $J = 9$  Hz), 131.2 (d,  $J = 2$  Hz), 128.9 (d,  $J = 52$  Hz), 128.5 (d,  $J = 9$  Hz), 125.1 (d,  $J = 8$  Hz), 122.6 (d,  $J = 4$  Hz), 118.3 (d,  $J = 4$  Hz), 116.9 (d,  $J = 2$  Hz), 64.1, 35.0 (d,  $J = 32$  Hz), 8.8 (d,  $J = 39$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.2 (m). IR: 3055, 2980, 2930, 2876, 2372, 2254, 1588, 1506, 1288, 1062, 886, 692, 609  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{16}\text{H}_{17}\text{BO}_2\text{P}]^+$  283.1059, Found 283.1058. Separation of enantiomers by chiral HPLC (Chiralcel OD-H Column, flow rate 1.0 mL/min, 97:3 hexanes: $i$ PrOH,  $T_r$  major 25.11, minor 28.54 min) determined the ee to be 62%.



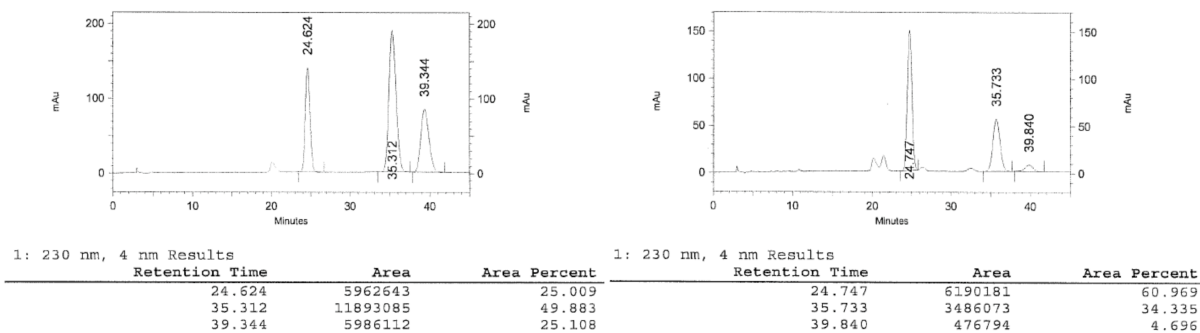
**(3,5-Dimethoxybenzyl)methylphenylphosphine-borane (12d).**

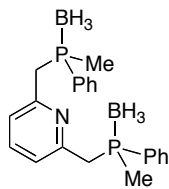
Silica gel flash column chromatography (90:10 hexanes:EtOAc) afforded the product as a white solid (98% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.60-7.55 (m, 2H), 7.52-7.48 (m, 1H), 7.45-7.41 (m, 2H), 6.31 (d,  $J = 2.0$  Hz, 1H), 6.04 (t,  $J = 2.0$  Hz, 2H), 3.65 (s, 6H), 3.14 (d,  $^2J_{\text{P-H}} = 9.6$  Hz, 2H), 1.52 (d,  $^2J_{\text{P-H}} = 9.6$  Hz, 3H), 0.71 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  160.3 (d,  $J = 3$  Hz), 134.3 (d,  $J = 8$  Hz), 131.7 (d,  $J = 9$  Hz), 131.2 (d,  $J = 3$  Hz), 128.8 (d,  $J = 52$  Hz), 128.5 (d,  $J = 10$  Hz), 107.5 (d,  $J = 4$  Hz), 99.2 (d,  $J = 3$  Hz), 55.1, 36.1 (d,  $J = 31$  Hz), 8.6 (d,  $J = 39$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.5 (m). IR: 3057, 3001, 2958, 2837, 2377, 2253, 1606, 1463, 1434, 1323, 1206, 1155, 1060, 930, 903, 845, 740, 693  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for

$[\text{C}_{16}\text{H}_{19}\text{BO}_2\text{P}]^+$  285.1216, Found 285.1225. Separation of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.0 mL/min, 95:5 hexanes:*i*PrOH,  $T_r$  major 16.40, minor 22.57 min) determined the ee to be 63%.

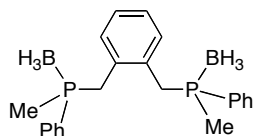
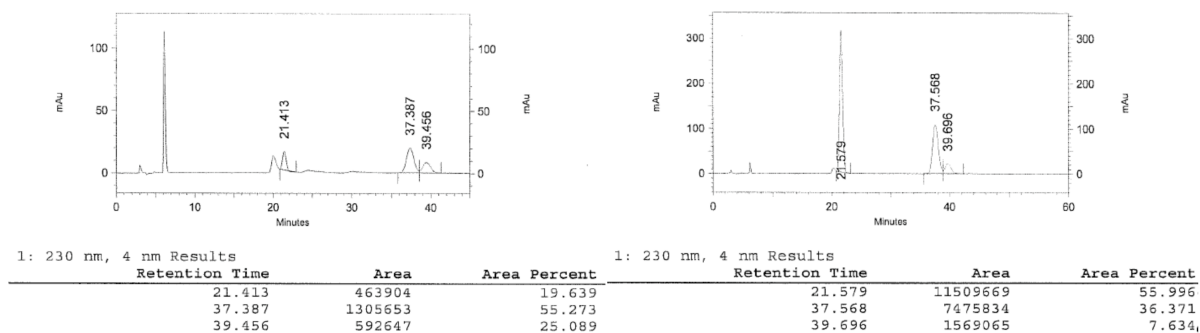


**1,3-Bis((methylphenylphosphino-borane)methyl)benzene (7h).** Silica gel flash column chromatography (80:20 hexanes:EtOAc) afforded the product as a colorless residue (87% yield). NMR spectral data agreed with literature values:<sup>1</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.58–7.42 (m, 10H), 7.02 (t  $J$  = 7.6 Hz, 1H), 6.76–6.63 (m, 3H), 3.12 (m, 4H), 1.52–1.44 (m, 6H), 1.08–0.42 (m, 6H). Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.1 mL/min, 95:5 hexanes:EtOH;  $C_2$ :  $T_r$  major 24.75, minor 39.84 min; meso:  $T_r$  35.73 min) determined the ee to be 87%. The ratio of  $C_2$ :meso diastereomers was found to be 65:35. At -30 °C, the ee was measured to be 93% with a 69:31  $C_2$ :meso dr.



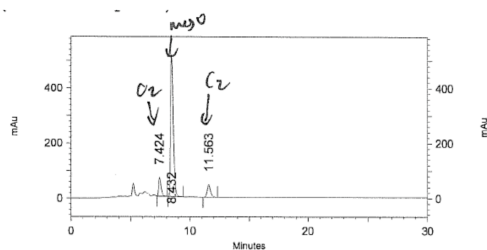


**2,6-Bis((methylphenylphosphino-borane)methyl)pyridine (7i).** Silica gel flash column chromatography (65:35 hexanes:EtOAc) afforded the product as a colorless residue (99% yield). NMR spectral data agree with literature values:<sup>1</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.68–7.59 (m, 4H), 7.54–7.40 (m, 7H), 6.87–6.81 (m, 2H), 3.38–3.34 (m, 4H), 1.62–1.49 (m, 6H), 0.78 (br q, 6H). Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.1 mL/min, 95:5 hexanes:EtOH; C<sub>2</sub>: T<sub>r</sub> major 21.58, minor 39.70 min; meso: T<sub>r</sub> 37.57 min) determined the ee to be 76%. Ratio of C<sub>2</sub>:meso diastereomers found to be 64:36.



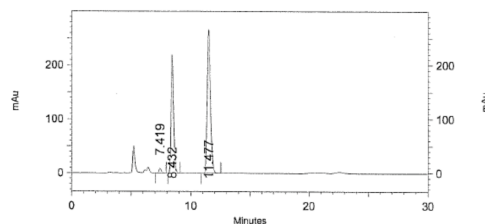
**1,2-Bis((methylphenylphosphino-borane)methyl)benzene (7j).** Silica gel flash column chromatography (70:30 hexanes:EtOAc) afforded the product as an off-white solid (96% yield). NMR spectral data agree with literature values:<sup>1</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.55–7.43 (m, 6H), 7.42–7.38 (m, 4H), 7.08 (m, 2H), 6.80 (m, 2H), 3.01 (m, 4H), 1.50 (m, 6H), 1.02–0.31 (m, 6H). Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 80:20 hexanes:iPrOH; C<sub>2</sub>: T<sub>r</sub> minor 7.42, major 11.48 min; meso: T<sub>r</sub> 8.43 min) determined the ee to be 96%. Ratio of C<sub>2</sub>:meso diastereomers found to be 62:38.





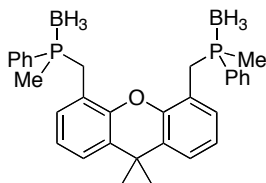
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
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8.432	8166152	81.494
11.563	876072	8.743



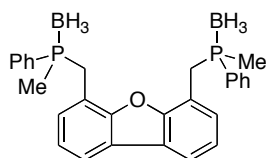
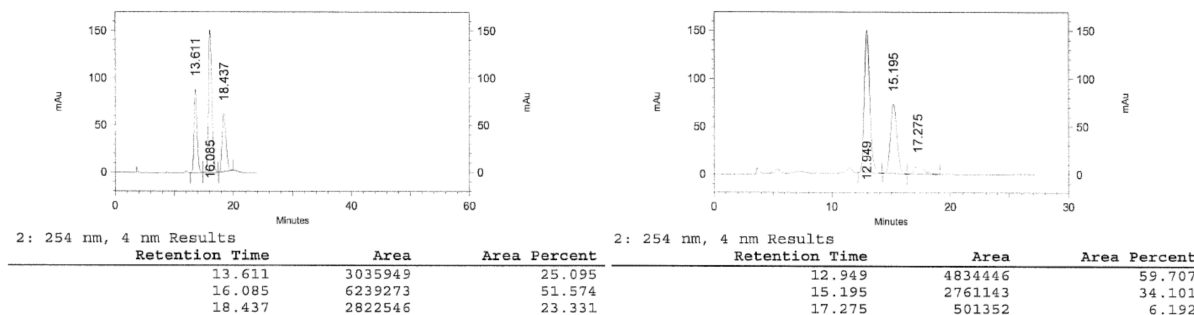
1: 230 nm, 4 nm Results

Retention Time	Area	Area Percent
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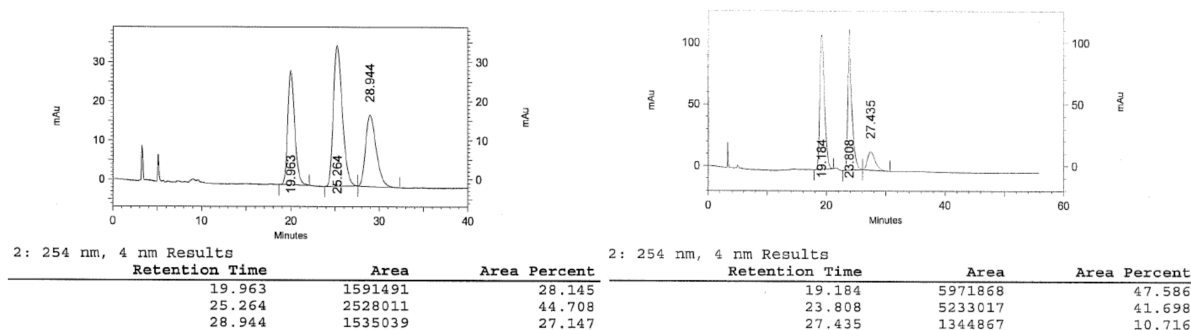


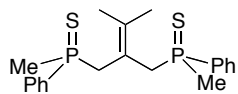
### (9,9-Dimethyl-9H-xanthene-4,5-

**diyl)bis(methylene)bis(methylphenylphosphine-borane) (13a).** Silica gel flash column chromatography (93:7 hexanes:EtOAc) afforded the product as a white foam (99% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56-7.49 (m, 4H), 7.36-7.28 (m, 8H), 7.02-6.98 (m, 2H), 6.88-6.86 (m, 2H), 3.44-3.25 (m, 4H), 1.60-1.55 (m, 12H), 0.75 (br m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  147.6 (m), 131.7 (dd,  $J = 2$ , 9 Hz), 131.3, 130.2, 129.1 (dd,  $J = 4$ , 8 Hz), 129.0 (d,  $J = 52$  Hz), 128.5 (dd,  $J = 4$ , 10 Hz), 124.9 (dd,  $J = 3$ , 8 Hz), 122.8, 119.9 (dd,  $J = 2$ , 8 Hz), 34.2, 32.6, 32.1, 31.4, 29.5 (d,  $J = 31$  Hz), 29.4 (d,  $J = 31$  Hz), 9.4 (d,  $J = 39$  Hz), 9.3 (d,  $J = 39$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.8 (br m). IR: 3057, 2970, 2918, 2372, 2243, 1436, 1061, 902, 729, 692, 579  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{31}\text{H}_{33}\text{B}_2\text{OP}_2]^+$  505.2193, Found 505.2202. Separation of enantiomers by chiral HPLC (Chiralcel OD-H Column, flow rate 1.0 mL/min, 98:2 hexanes:EtOH;  $\text{C}_2$ :  $T_r$  major 12.95, minor 17.27 min; meso:  $T_r$  15.19 min) determined the ee to be 83%. Ratio of  $\text{C}_2$ :meso diastereomers found to be 66:34. At  $-30^\circ\text{C}$ , the ee was measured to be 87% with a 68:32  $\text{C}_2$ :meso dr.



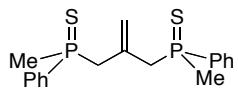
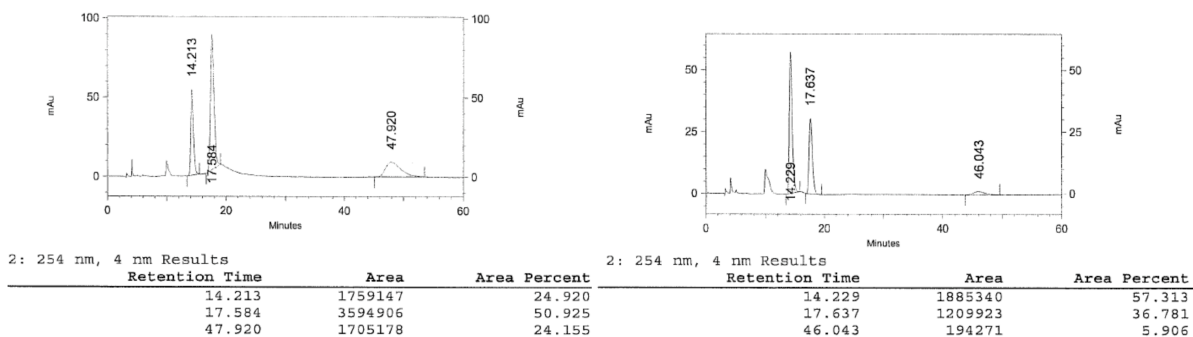
**(13b).** Silica gel flash column chromatography (90:10 hexanes:EtOAc) afforded the product as a white solid (>99% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.80 (d,  $J$  = 7.2 Hz, 2H), 7.58 (m, 4H), 7.41 (m, 2H), 7.35 (m, 4H), 7.23 (dt,  $J$  = 7.1, 6.8 Hz, 2H), 7.06 (br m, 2H), 3.51-3.38 (m, 4H), 1.51 (m, 6H), 0.89 (br m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  154.1, 131.6 (d,  $J$  = 9 Hz), 131.4, 129.3 (d,  $J$  = 9 Hz), 128.7, 128.6 (d,  $J$  = 10 Hz), 124.1, 123.0, 119.7, 116.8 (d,  $J$  = 7 Hz), 29.7 (d,  $J$  = 31 Hz), 9.3 (d,  $J$  = 38 Hz), 9.1 (d,  $J$  = 38 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  11.3 (br). IR: 3058, 2923, 2853, 2372, 1434, 1414, 1189, 1053, 792, 735, 691, 585  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{28}\text{H}_{27}\text{B}_2\text{OP}_2]^+$  463.1723, Found 463.1722. Separation of enantiomers by chiral HPLC (Chiralcel OD-H Column, flow rate 1.0 mL/min, 95:5 hexanes: $i$ PrOH;  $\text{C}_2$ :  $T_r$  major 19.18, minor 27.44 min; meso:  $T_r$  23.81 min) determined the ee to be 64%. Ratio of  $\text{C}_2$ :meso diastereomers found to be 58:42.





**(13c).** Silica gel flash column chromatography (70:30 hexanes:EtOAc)

afforded the product as a pale yellow residue (>99% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.90-7.81 (m, 4H), 7.52-7.43 (m, 6H), 3.33-3.19 (m, 4H), 2.03-1.90 (m, 6H), 1.52 (m, 3H), 1.41 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  136.0 (m), 133.1 (dm), 131.6 (d,  $J = 13$  Hz), 130.7 (m), 128.6 (m), 115.8 (m), 39.4 (d,  $J = 66$  Hz), 39.3 (d,  $J = 65$  Hz), 21.9 (app t), 21.8 (app t), 21.1 (dm).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  37.8, 37.6. IR: 3056, 2987, 2911, 1435, 1111, 884, 731, 691, 582  $\text{cm}^{-1}$ . HRMS ( $\text{EI}^+$ ) calcd for  $[\text{C}_{20}\text{H}_{26}\text{P}_2\text{S}_2]^+$  392.0951, Found 392.0947. Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.0 mL/min, 90:10 hexanes:EtOH;  $\text{C}_2$ :  $T_r$  major 14.23, minor 46.03 min; meso:  $T_r$  17.64 min) determined the ee to be 80%. The ratio of  $\text{C}_2$ :meso diastereomers was found to be 63:37.

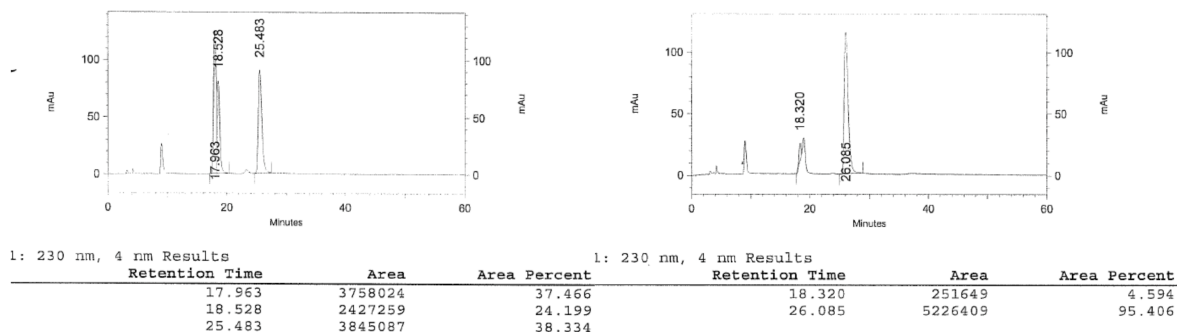


**(2-Methylenepropane-1,3-diyl)bis(methylphenylphosphine sulfide) (13d).**

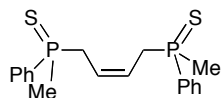
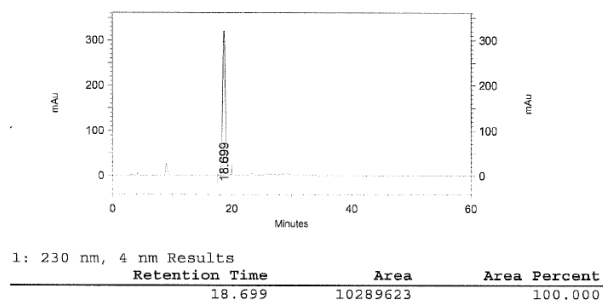
Separation of the  $\text{C}_2$  and meso diastereomers was accomplished by silica gel flash column chromatography (75:25 hexanes:EtOAc). The meso diastereomer was recovered as a colorless residue (46% yield) and the  $\text{C}_2$  diastereomer as a yellowish residue (54% yield). The  $\text{C}_2$ :meso dr was measured to be 55:45 by  $^1\text{H}$  NMR spectroscopy of the crude product. Separation of enantiomers by chiral HPLC (Chiralcel AD-H Column, flow rate 1.0 mL/min, 90:10 hexanes:*i*PrOH;  $\text{C}_2$ :  $T_r$  minor 18.32, major 26.09 min; meso:  $T_r$  18.70 min) determined the ee to be 92%.

Characterization data for the  $\text{C}_2$  diastereomer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.88-7.82 (m, 4H), 7.50-7.44 (m, 6H), 4.93 (dd,  $J = 5.2, 5.6$  Hz, 2H), 3.17 (m, 4H), 1.99 (d,  $J = 12.0$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  132.1 (m), 131.6, 130.7 (m), 130.2 (m), 128.5 (m),

120.8 (m), 42.7 (d,  $J = 53$  Hz), 20.6 (d,  $J = 58$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  35.5. IR: 3052, 2980, 2902, 1632, 1436, 1110, 905, 741, 692, 610  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{18}\text{H}_{23}\text{P}_2\text{S}_2]^+$  365.0716, Found 365.0712.



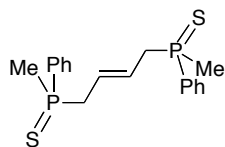
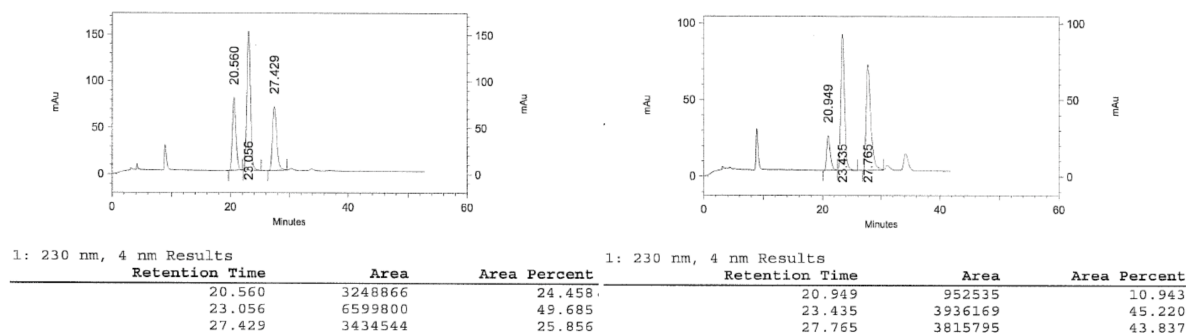
Characterization data for the meso diastereomer:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.92-7.86 (m, 4H), 7.52 (m, 6H), 4.84 (dd,  $J = 5.5, 5.5$  Hz, 2H), 3.25 (m, 2H), 3.12 (m, 2H), 1.93 (d,  $J = 12.5$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  131.1 (m), 131.7, 130.8 (m), 130.2 (m), 128.6 (m), 120.7 (m), 42.8 (d,  $J = 51$  Hz), 20.8 (d,  $J = 56$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 202 MHz)  $\delta$  35.7. IR: 3052, 2903, 1436, 1110, 895, 741, 692, 611  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{18}\text{H}_{23}\text{P}_2\text{S}_2]^+$  365.0716, Found 365.0715.



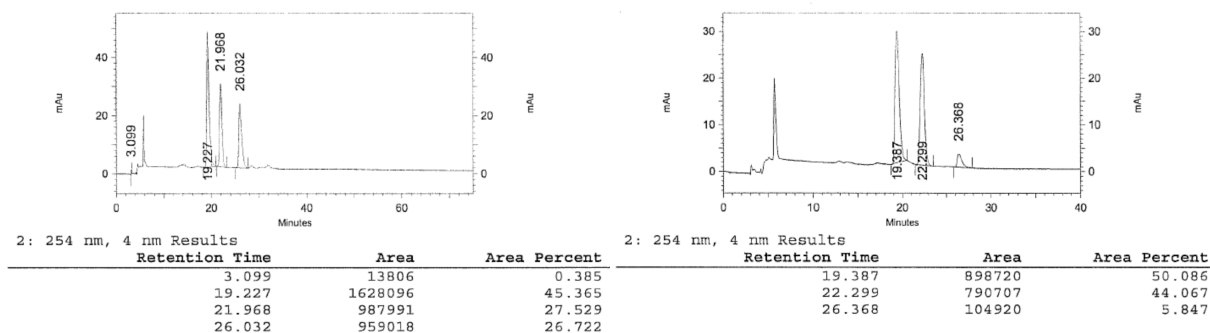
**(Z)-1,4-bis(methylphenylphosphorothioyl)but-2-ene (13e).** Silica gel flash

column chromatography (65:35 hexanes:EtOAc) afforded the product as a brown residue (81% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.86-7.81 (m, 4H), 7.52-7.46 (m, 6H), 5.62 (m, 2H), 2.88 (m, 4H), 1.93 (dd,  $J = 11.5, 11.5$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  132.0 (d,  $J = 15$  Hz), 131.6 (d,  $J = 5$  Hz), 138.4 (d,  $J = 15$  Hz), 130.4 (m), 128.5 (m), 124.1 (m), 35.4 (d,  $J = 54$  Hz), 19.9 (d,  $J = 56$  Hz), 19.9 (d,  $J = 56$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  38.1. IR: 3052, 2976, 2907, 1435,

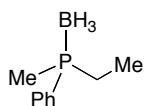
1111, 889, 743, 693, 607  $\text{cm}^{-1}$ . HRMS ( $\text{EI}^+$ ) calcd for  $[\text{C}_{18}\text{H}_{22}\text{P}_2\text{S}_2]^+$  364.0638, Found 364.0635. Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 90:10 hexanes:*i*PrOH;  $\text{C}_2$ :  $T_r$  minor 20.95, major 27.77 min; meso:  $T_r$  23.44 min) determined the ee to be 60%. The ratio of  $\text{C}_2$ :meso diastereomers was found to be 55:45.



**(*E*)-1,4-bis(methylphenylphosphorothioyl)but-2-ene (13f).** Silica gel flash column chromatography (65:35 hexanes:EtOAc) afforded the product as an orange residue (80% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.89-7.78 (m, 4H), 7.50-7.45 (m, 6H), 5.55 (br s, 1H), 5.48 (br s, 1H), 2.89-2.86 (br m, 4H), 1.93 (d,  $J = 12.4$  Hz, 3H), 1.84 (d,  $J = 12.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  132.3 (br d), 132.0 (br d), 131.6 (d,  $J = 9$  Hz), 131.2 (br d), 130.5 (m), 128.6 (m), 125.6 (m), 40.5 (m), 39.9 (m), 19.9 (m), 19.3 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  38.0, 37.9. IR: 3052, 2962, 1436, 1106, 908, 889, 730, 688, 588  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{18}\text{H}_{23}\text{P}_2\text{S}_2]^+$  365.0716, Found 365.0715. Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 85:15 hexanes:EtOH;  $\text{C}_2$ :  $T_r$  major 22.30, minor 26.43 min; meso:  $T_r$  19.39 min) determined the ee to be 77%. The ratio of  $\text{C}_2$ :meso diastereomers was found to be 49:51.

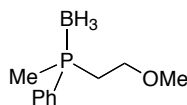
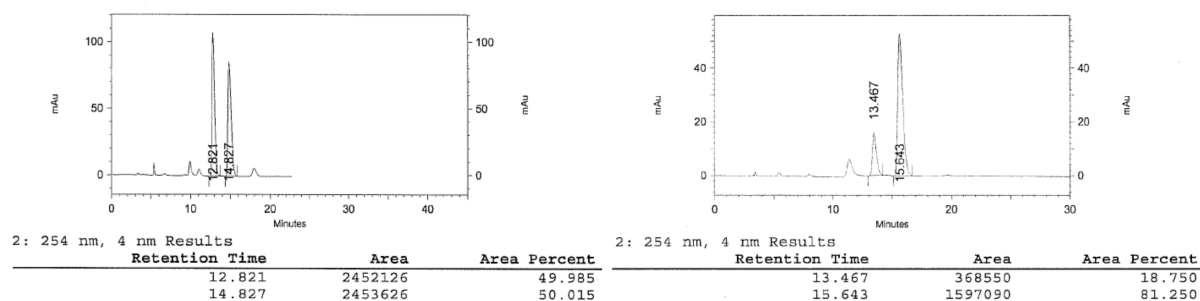


**Tables 11 & 12: Chiral phosphines prepared with DIFLUORPHOS/dmpe catalyst (11).**



**Ethylmethylphenylphosphine-borane (8a).**

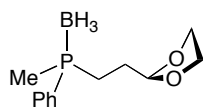
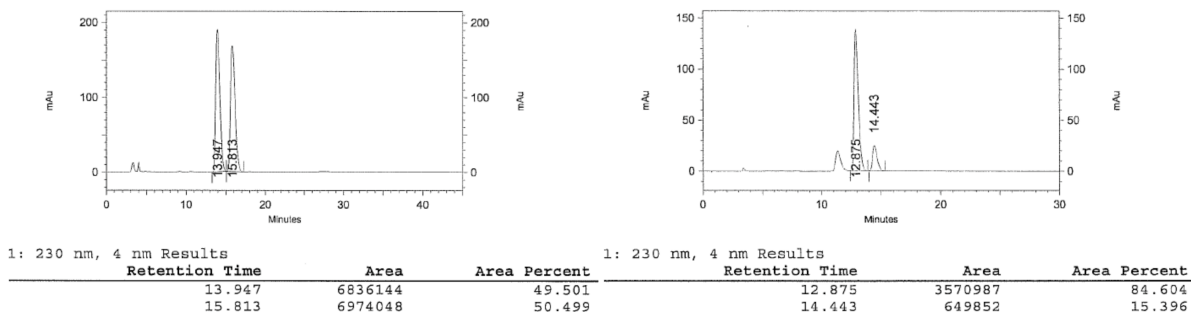
Silica gel flash column chromatography (95:5 hexanes:EtOAc) afforded the product as a colorless oil (97% yield). NMR spectral data agree with literature values:<sup>1</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.74–7.65 (m, 2H), 7.47 (m, 3H), 1.83 (m, 2H), 1.54 (d, *J* = 10.4 Hz, 3H), 1.09–0.39 (m, 6H, CH<sub>3</sub> + BH<sub>3</sub>). Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 91:9 hexanes:*i*PrOH, T<sub>r</sub> minor 13.46, major 15.64 min) determined the ee to be 66%.



**(2-Methoxyethyl)methylphenylphosphine-borane (14a).**

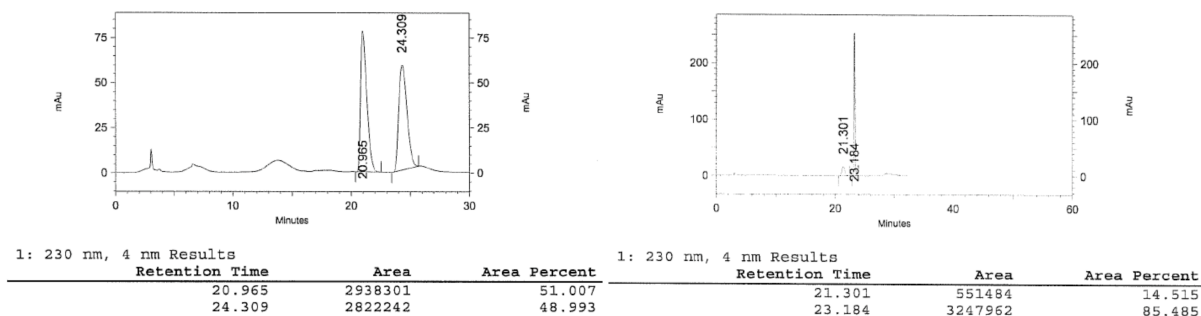
Silica gel flash column chromatography (85:15 hexanes:EtOAc) afforded the product as a colorless residue (88% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.76–7.71 (m, 2H), 7.53–7.44 (m, 3H), 3.69–3.60 (m, 1H), 3.51–3.42 (m, 1H), 3.27 (s, 3H), 2.21–2.07 (m, 2H), 1.62 (d, *J* = 10.4 Hz, 3H), 0.61 (br q, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) δ 131.5, 131.4, 129.7 (d, *J* = 54 Hz), 128.9 (d, *J* = 10

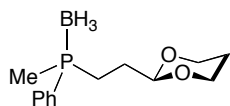
Hz), 67.2, 58.6, 28.1 (d,  $J = 36$  Hz), 11.5 (d,  $J = 38$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  7.4 (q,  $J = 66$  Hz). IR: 3057, 2984, 2923, 2892, 2829, 2371, 1437, 1113, 1065, 893, 744, 693, 585  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{10}\text{H}_{17}\text{BOP}]^+$  195.1110, Found 195.1104. Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 91:9 hexanes:*i*PrOH,  $T_r$  major 12.87, minor 14.44 min) determined the ee to be 68%.



**(2-(1,3-Dioxolan-2-yl)ethyl)methylphenylphosphine-borane (14b).**

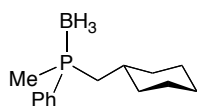
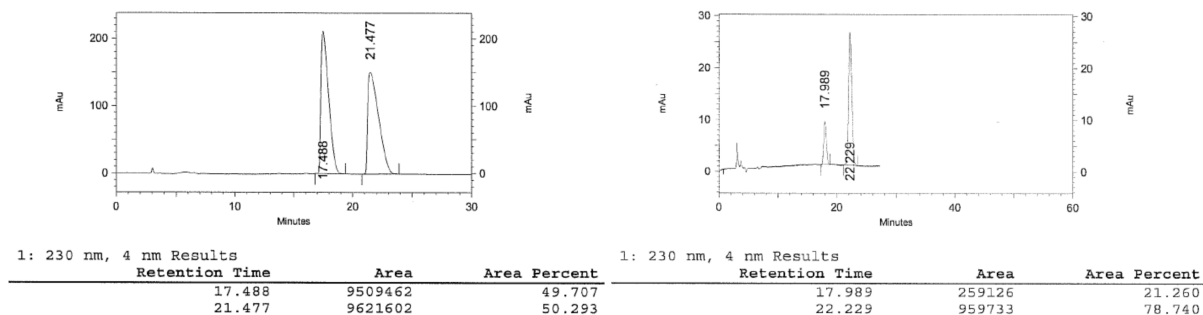
Silica gel flash column chromatography (70:30 hexanes:EtOAc) afforded the product as a colorless residue (84% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.74-7.69 (m, 2H), 7.52-7.45 (m, 3H), 4.88 (t,  $J = 4.4$  Hz, 1H), 3.95-3.81 (m, 4H), 2.03-1.66 (m, 4H), 1.56 (d,  $J = 10.4$  Hz, 3H), 0.61 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  131.5 (d,  $J = 9$  Hz), 131.4, 129.3 (d,  $J = 53$  Hz), 128.9 (d,  $J = 10$  Hz), 103.5, 103.4, 65.1, 27.3, 21.1 (d,  $J = 38$  Hz), 10.8 (d,  $J = 39$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.8 (q,  $J_{\text{B-P}} = 68$  Hz). IR: 3057, 2960, 2885, 2371, 2254, 1436, 1132, 1065, 898, 744, 693, 581  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{12}\text{H}_{19}\text{BO}_2\text{P}]^+$  237.1216, Found 237.1221. Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.1 mL/min, 96:4 hexanes:*i*PrOH,  $T_r$  minor 21.30, major 23.18 min) determined the ee to be 71%.





**(2-(1,3-Dioxan-2-yl)ethyl)methylphenylphosphine-borane (14c).**

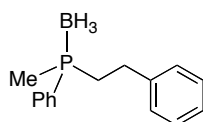
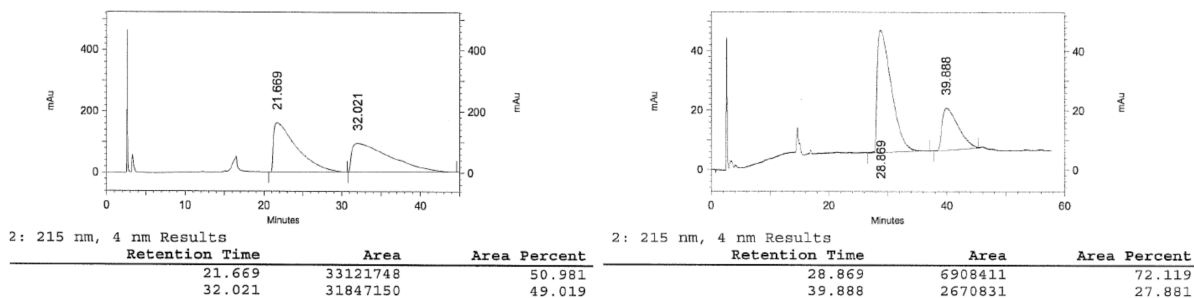
Silica gel flash column chromatography (72:28 hexanes:EtOAc) afforded the product as a colorless residue, which solidified on standing (82% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.73-7.68 (m, 2H), 7.50-7.41 (m, 3H), 4.49 (t,  $J$  = 4.8 Hz, 1H), 4.06-4.00 (m, 2H), 3.73-3.63 (m, 2H), 2.05-1.88 (m, 3H), 1.81-1.60 (m, 2H), 1.53 (d,  $J$  = 10.0 Hz, 3H), 1.31-1.25 (m, 1H), 0.59 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  131.5 (d,  $J$  = 9 Hz), 131.3, 129.4 (d,  $J$  = 55 Hz), 128.8 (d,  $J$  = 9 Hz), 101.1, 101.0, 66.8 (d,  $J$  = 2 Hz), 28.7, 25.7, 21.5 (d,  $J$  = 38 Hz), 10.7 (d,  $J$  = 39 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.5 (m). IR: 3052, 2965, 2932, 2853, 2372, 1437, 1241, 1146, 1129, 1066, 898, 745, 694  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{13}\text{H}_{21}\text{BO}_2\text{P}]^+$  251.1372, Found 251.1373. Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.1 mL/min, 96:4 hexanes:*i*PrOH,  $T_r$  minor 17.99, major 22.23 min) determined the ee to be 57%.



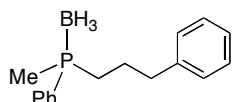
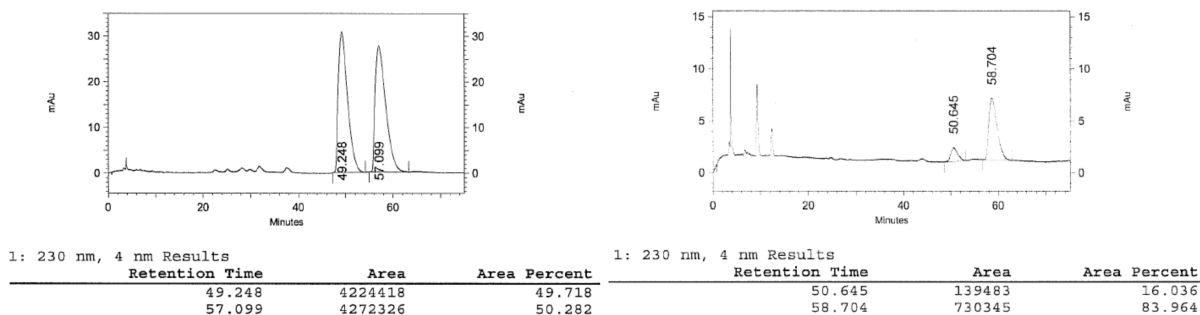
**(Cyclohexylmethyl)methylphenylphosphine-borane (14d).**

Silica gel flash column chromatography (70:30 hexanes: $\text{CH}_2\text{Cl}_2$ ) afforded the product as a colorless residue, which solidified on standing (77% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.77-7.72 (m, 2H), 7.50-7.44 (m, 3H), 1.85-1.58 (m, 8H), 1.53 (d,  $J$  = 10.4 Hz, 3H), 1.26-0.41 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  131.3 (d,  $J$  = 9 Hz), 131.0 (d,  $J$  = 2 Hz), 130.9 (d,  $J$  = 53 Hz), 128.7 (d,  $J$  = 9 Hz), 35.1 (d,  $J$  = 34 Hz), 35.0 (d,  $J$  = 8 Hz), 34.7 (d,  $J$  = 7 Hz), 25.9 (d,  $J$  = 3 Hz), 25.8, 12.6 (d,  $J$  = 39 Hz), 1.0.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  7.0 (q,  $J_{\text{B-P}}$  = 63 Hz). IR: 3055, 2923, 2850, 2368, 1437, 1060, 740, 692  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{14}\text{H}_{21}\text{BP}]^+$  231.1474, Found 231.1472. Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.25 mL/min, pure hexanes,  $T_r$  major 28.82, minor 39.92 min) determined the ee to be 45%.



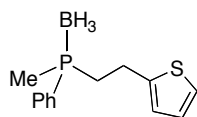
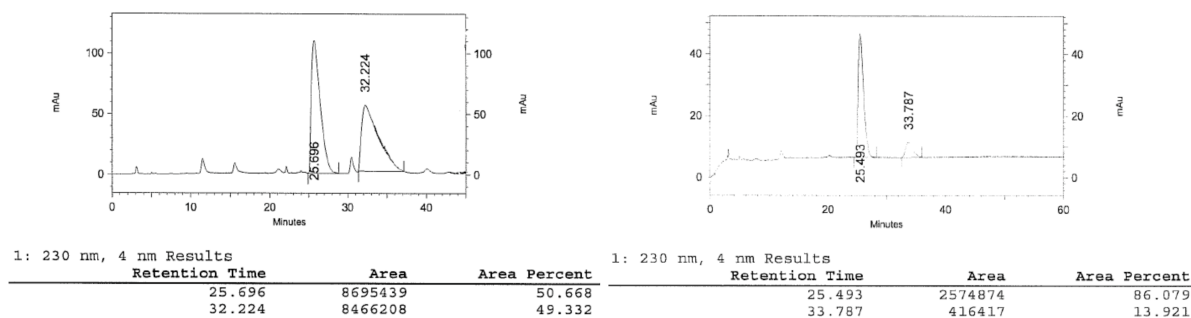


**Methyl(2-phenethyl)phenylphosphine-borane (14e).** Silica gel flash column chromatography (60:40 hexanes:CH<sub>2</sub>Cl<sub>2</sub>) afforded the product as a colorless residue (35% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.77-7.72 (m, 2H), 7.56-7.49 (m, 3H), 7.35-7.31 (m, 2H), 7.26-7.25 (m, 1H), 7.18-7.15 (m, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.94-1.78 (m, 4H), 1.58 (d, *J* = 10.4 Hz, 3H), 0.83 (br q, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) δ 141.1 (d, *J* = 14 Hz), 131.5, 131.4, 129.5 (d, *J* = 53 Hz), 129.0 (d, *J* = 10 Hz), 128.7, 128.1, 126.4, 29.5 (d, *J* = 35 Hz), 29.2, 11.0 (d, *J* = 38 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz) δ 9.3 (m). IR: 3060, 3027, 2924, 2852, 2376, 1437, 1063, 902, 744, 698 cm<sup>-1</sup>. HRMS (FAB<sup>+</sup>) calcd for [C<sub>15</sub>H<sub>17</sub>BP]<sup>+</sup> 239.1161, Found 239.1160. Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 98:2 hexanes:*i*PrOH, T<sub>r</sub> minor 50.65, major 58.70 min) determined the ee to be 68%.

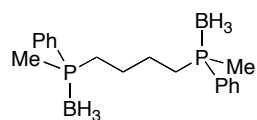
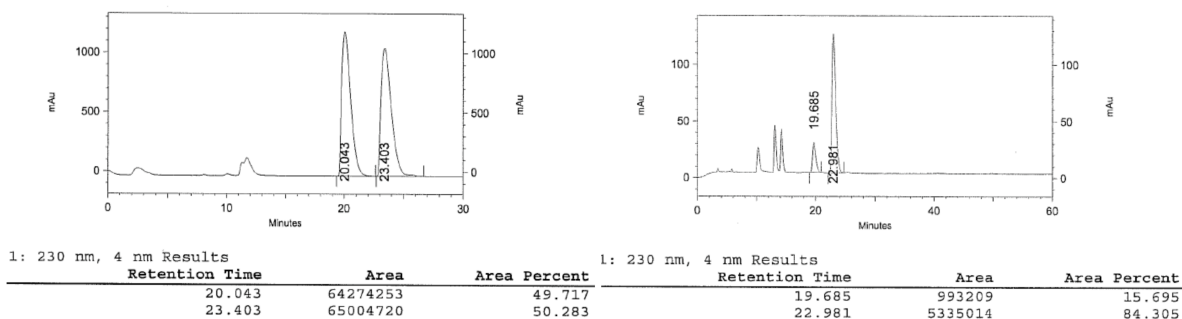


**Methylphenyl(3-phenylpropyl)phosphine-borane (14f).** Silica gel flash column chromatography (93:7 hexanes:EtOAc) afforded the product as a colorless residue (91% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.77-7.72 (m, 2H), 7.56-7.49 (m, 3H), 7.35-7.31 (m, 2H), 7.26-7.25 (m, 1H), 7.18-7.15 (m, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.94-1.78 (m, 4H), 1.58 (d, *J* =

10.4 Hz, 3H), 0.80 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  140.7, 131.3 (d,  $J = 9$  Hz), 131.1 (d,  $J = 2$  Hz), 129.5 (d,  $J = 53$  Hz), 128.7 (d,  $J = 10$  Hz), 128.4, 128.3, 126.0, 36.6 (d,  $J = 13$  Hz), 26.6 (d,  $J = 36$  Hz), 24.5, 10.8 (d,  $J = 39$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.1 (m). IR: 3059, 3026, 2945, 2864, 2369, 1603, 1436, 1063, 893, 742, 696, 592  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{16}\text{H}_{19}\text{BP}]^+$  253.1317, Found 253.1318. Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.1 mL/min, 92:8 hexanes:*i*PrOH,  $T_r$  major 25.49, minor 33.79 min) determined the ee to be 72%.

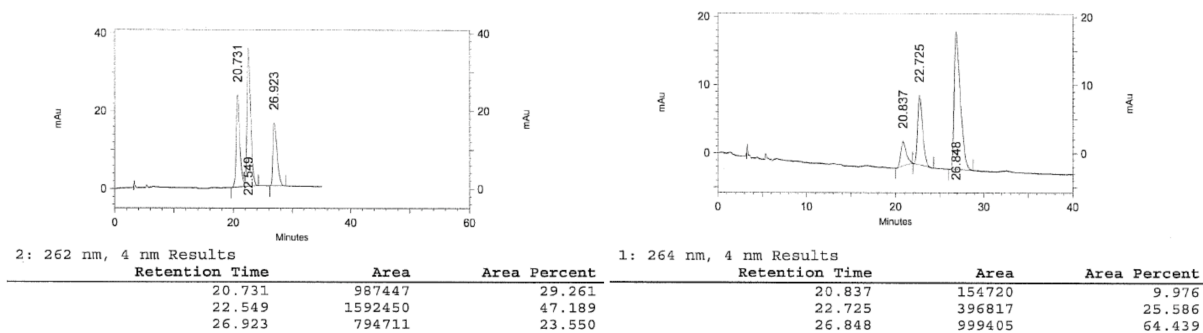


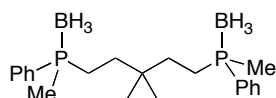
**Methylphenyl(2-(thienyl)ethyl)phosphine-borane (14g).** Silica gel flash column chromatography (93:7 hexanes:EtOAc) afforded the product as a colorless residue (84% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.79-7.74 (m, 2H), 7.56-7.47 (m, 3H), 7.12 (dd,  $J = 0.8$ , 5.2 Hz, 1H), 6.89 (m, 1H), 6.78 (m, 1H), 3.15-3.05 (m, 1H), 2.95-2.85 (m, 1H), 2.33-2.20 (m, 2H), 1.58 (d,  $^2J_{\text{P-H}} = 10.0$  Hz, 3H), 0.72 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  143.6 (d,  $J = 15$  Hz), 131.4, 131.3, 129.0 (d,  $J = 53$  Hz), 128.9 (d,  $J = 10$  Hz), 126.8, 124.4, 123.5, 29.6 (d,  $J = 34$  Hz), 23.6, 10.7 (d,  $J = 38$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.2 (m). IR: 3105, 3057, 2985, 2917, 2854, 2375, 2254, 1437, 1416, 1117, 1064, 903, 743, 694  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{13}\text{H}_{15}\text{BPS}]^+$  247.0882, Found 247.0880. Separation of enantiomers by chiral HPLC (Chiralcel OJ-H Column, flow rate 1.0 mL/min, 90:10 hexanes:*i*PrOH,  $T_r$  minor 19.69, major 22.98 min) determined the ee to be 69%.



### 1,4-Bis(methylphenylphosphino-borane)butane (15a).

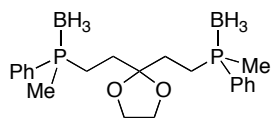
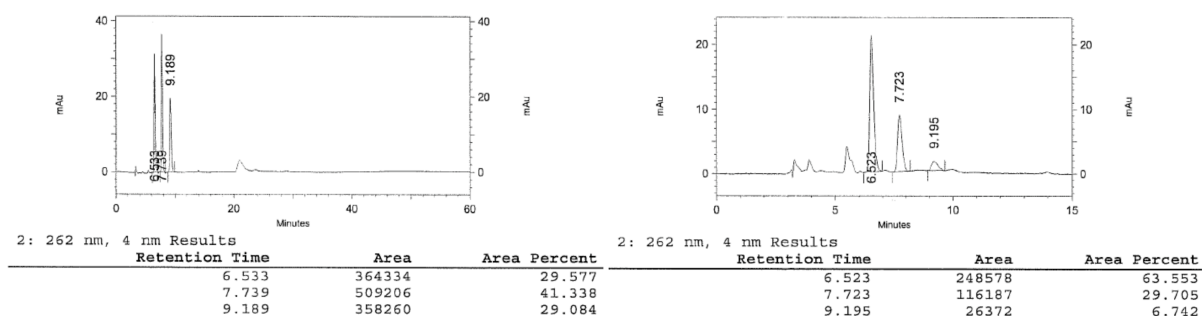
Silica gel flash column chromatography (80:20 hexanes:EtOAc) afforded the product as a white solid (95% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.71-7.64 (m, 4H), 7.52-7.43 (m, 6H), 1.83-1.76 (m, 4H), 1.54-1.49 (m, 8H), 1.41 (m, 2H), 0.86 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  131.3 (d,  $J = 4$  Hz), 131.2 (d,  $J = 3$  Hz), 128.8 (d,  $J = 4$  Hz), 128.7 (d,  $J = 4$  Hz), 129.3 (d,  $J = 66$  Hz), 27.2, 26.8, 24.4, 24.3, 10.8 (d,  $J = 49$  Hz), 10.8 (d,  $J = 49$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  8.9 (m). IR: 3048, 2943, 2368, 1437, 1118, 1061, 907, 783, 743, 693, 585  $\text{cm}^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[\text{C}_{18}\text{H}_{29}\text{B}_2\text{P}_2]^+$  329.1931, Found 329.1927. Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 95:5 hexanes:EtOH;  $C_2$ :  $T_r$  minor 20.84, major 26.85 min; meso:  $T_r$  22.73 min) determined the ee to be 73%. The ratio of  $C_2$ :meso diastereomers was found to be 74:26.





**(3,3-Dimethylpentane-1,5-diyl)bis(methylphenylphosphine-borane)**

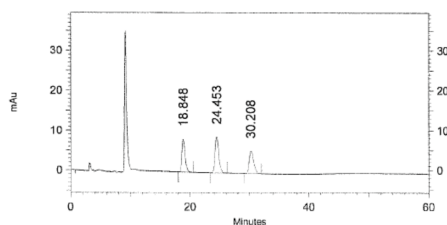
**(15b).** Silica gel flash column chromatography (85:15 hexanes:EtOAc) afforded the product as a white solid (54% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.74-7.68 (m, 4H), 7.50-7.45 (m, 6H), 1.71-1.62 (m, 4H), 1.53 (dd,  $J$  = 9.6, 9.2 Hz, 6H), 1.38 (m, 2H), 1.14 (m, 2H), 0.80 (s, 6H), 0.62 (br m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  131.5 (m), 129.5 (d,  $J$  = 67 Hz), 129.4 (d,  $J$  = 67 Hz), 128.9 (d,  $J$  = 5 Hz), 128.8 (d,  $J$  = 5 Hz), 33.2 (m), 33.1 (m), 26.6, 21.9 (d,  $J$  = 46 Hz), 11.2 (d,  $J$  = 49 Hz), 11.0 (d,  $J$  = 48 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.1 (m). IR: 3058, 2962, 2913, 2373, 2343 1435, 1064, 895, 735, 689, 591  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{21}\text{H}_{35}\text{B}_2\text{P}_2]^+$  371.2400, Found 371.2410. Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 95:5 hexanes:EtOH;  $\text{C}_2$ :  $T_{\text{r}}$  major 6.52, minor 9.15 min; meso:  $T_{\text{r}}$  7.72 min) determined the ee to be 84%. The ratio of  $\text{C}_2$ :meso diastereomers was found to be 71:29.



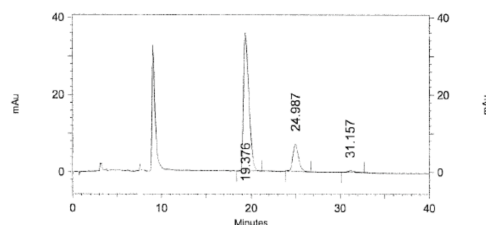
**(2,2'-(1,3-Dioxolane-2,2-diyl)bis(ethane-2,1-diyl))bis(methylphenylphosphine-borane)**

**(15c).** Silica gel flash column chromatography (65:35 hexanes:EtOAc) afforded the product as a white powder (58% yield). The product was isolated as a mixture of the two diastereomers:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.74-7.67 (m, 4H), 7.54-7.44 (m, 6H), 3.90-3.81 (m, 4H), 1.93-1.74 (m, 6H), 1.59-1.52 (m, 8H), 0.86 (br q, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  131.5 (d,  $J$  = 7 Hz), 131.4 (d,  $J$  = 7 Hz), 129.5 (br d), 128.9 (d,  $J$  = 4 Hz), 128.8 (d,  $J$  = 4 Hz), 110.1 (m), 65.0 (d), 29.8 (d), 21.6, 21.2, 11.2 (d,  $J$  = 48 Hz), 11.1 (d,  $J$  = 48 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.9 (m). IR: 3056, 2966, 2894, 2372, 2343, 1435, 1219, 1071, 1043, 900, 740, 690, 591  $\text{cm}^{-1}$ . HRMS ( $\text{FAB}^+$ ) calcd for

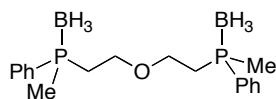
$[C_{21}H_{33}B_2O_2P_2]^+$  401.2142, Found 401.2150. Separation of enantiomers by chiral HPLC (Chiralpak AD-H Column, flow rate 1.0 mL/min, 90:10 hexanes:*i*PrOH;  $C_2$ :  $T_r$  major 19.38, minor 27.77 min; meso:  $T_r$  31.16 min) determined the ee to be 97%. The ratio of  $C_2$ :meso diastereomers was found to be 82:18.



Retention Time	Area	Area Percent
18.848	305573	30.513
24.453	400147	39.957
30.208	295732	29.530

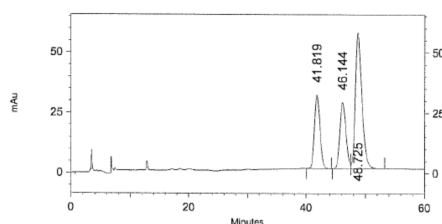


Retention Time	Area	Area Percent
19.376	1462521	81.274
24.987	319091	17.732
31.157	17887	0.994

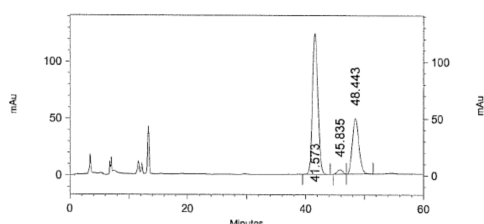


### 2,2'-Oxybis(ethane-2,1-diyl)bis(methylphenylphosphine-borane)

(**15d**). Silica gel flash column chromatography (75:25 hexanes:EtOAc) afforded the product as a colorless oil (>99% yield). The product was isolated as a mixture of the two diastereomers:  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.72-7.68 (m, 4H), 7.53-7.44 (m, 6H), 3.67-3.56 (m, 2H), 3.51-3.41 (m, 2H), 2.10-2.02 (m, 4H), 1.57 (d,  $J$  = 10.4 Hz, 3H), 1.53 (d,  $J$  = 10.4 Hz, 3H), 0.71 (br q, 6H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  131.3, 131.2, 129.5 (dd,  $J$  = 54, 16 Hz), 128.7 (dd,  $J$  = 10, 2 Hz), 65.4, 27.9 (d,  $J$  = 36 Hz), 27.9 (d,  $J$  = 36 Hz), 11.5 (d,  $J$  = 39 Hz), 11.5 (d,  $J$  = 38 Hz).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ , 162 MHz)  $\delta$  7.0 (m). IR: 2954, 2920, 2852, 2368, 1436, 1113, 1064, 901, 742, 692  $cm^{-1}$ . HRMS (FAB $^+$ ) calcd for  $[C_{18}H_{29}B_2OP_2]^+$  345.1880, Found 345.1885. Separation of enantiomers by chiral HPLC (Chiralpak AS-H Column, flow rate 1.0 mL/min, 97:3 hexanes:EtOH;  $C_2$ :  $T_r$  major 41.57, minor 45.84 min; meso:  $T_r$  48.44 min) determined the ee to be 94%. The ratio of  $C_2$ :meso diastereomers was found to be 68:32.

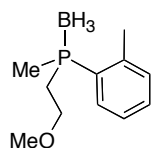


Retention Time	Area	Area Percent
41.819	1944144	23.547
46.144	1965767	23.808
48.725	4346690	52.645

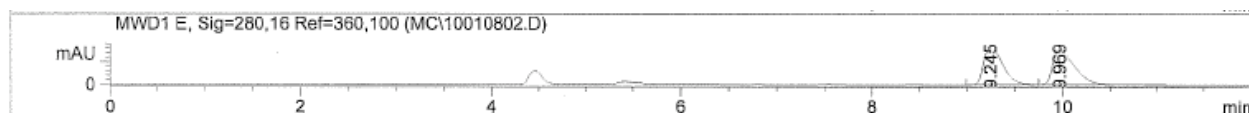


Retention Time	Area	Area Percent
41.573	7987058	66.547
45.835	236930	1.974
48.443	3778200	31.479

**Scheme 2. Chiral phosphines prepared from methyl(2-tolyl)phosphine.**



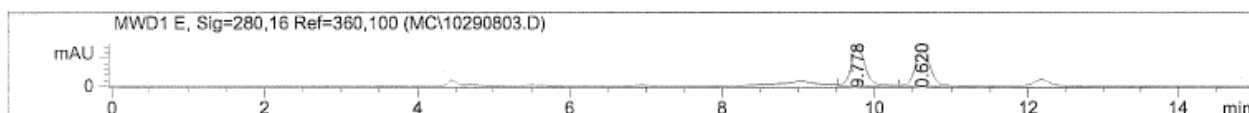
**(2-Methoxyethyl)methyl(2-tolyl)phosphine-borane (17).** Silica gel flash column chromatography (80:20 hexanes/EtOAc) afforded the product as a white solid (40% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.68-7.63 (m, 1H), 7.39-7.35 (m, 1H), 7.24-7.21 (m, 2H), 3.65-3.56 (m, 1H), 3.47-3.38 (m, 1H), 3.26 (s, 3H), 2.62 (s, 3H), 2.31-2.16 (m, 2H), 1.82 (d,  $J = 12.8$  Hz, 3H), 0.83 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  141.8 (d,  $J = 7$  Hz), 132.9 (d,  $J = 12$  Hz), 131.7 (d,  $J = 8$  Hz), 131.4, 127.1 (d,  $J = 51$  Hz), 126.1 (d,  $J = 10$  Hz), 67.4, 58.5, 27.0 (d,  $J = 35$  Hz), 22.0 (d,  $J = 4$  Hz), 11.8 (d,  $J = 40$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  7.33 (m). HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{15}\text{H}_{20}\text{BP}]^+$  239.1165, Found 234.1161. Separation of enantiomers by chiral HPLC (Chiralpak AS-H column, flow rate 0.95 mL/min, 95:5 hexanes:EtOH,  $T_r$  major 9.78 min, minor 10.62) determined the ee to be 3%.



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.245	VV	0.2149	1.18675e4	860.37921	49.4150
2	9.969	VP	0.2533	1.21485e4	740.90460	50.5850

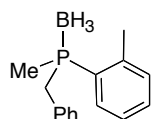
Totals : 2.40160e4 1601.28381



Signal 5: MWD1 E, Sig=280,16 Ref=360,100

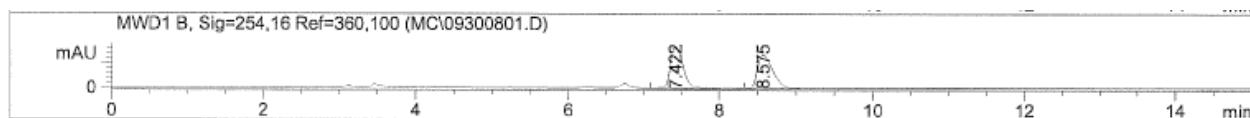
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.778	VV	0.1920	463.03659	36.98829	51.4830
2	10.620	VB	0.1978	436.36023	33.97942	48.5170

Totals : 899.39682 70.96771



**Benzylmethyl(2-tolyl)phosphino-borane (18).** Silica gel flash column chromatography (90:10 hexanes/EtOAc) afforded the product as a white solid (46% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.44-7.35 (m, 2H), 7.29-7.28 (m, 1H), 7.22-7.19 (m, 4H), 6.95-9.93

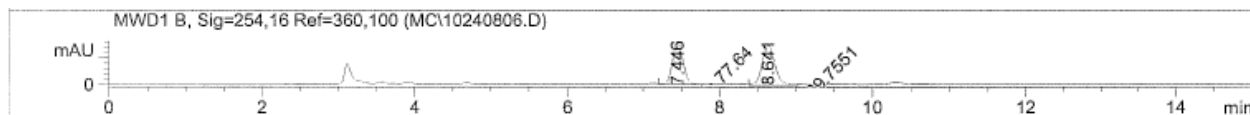
(m, 2H), 3.42-3.23 (m, 2H), 2.64 (s, 3H), 1.57 (d,  $J = 9.6$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  142.3 (d,  $J = 9$  Hz), 132.6 (d,  $J = 9$  Hz), 131.7 (d,  $J = 9$  Hz), 131.4 (d,  $J = 2$  Hz), 129.6 (d,  $J = 4$  Hz), 128.3 (d,  $J = 2$  Hz), 127.0, 126.8 (d,  $J = 46$  Hz), 126.0 (d,  $J = 10$  Hz), 34.4 (d,  $J = 31$  Hz), 22.2 (d,  $J = 4$  Hz), 10.1 (d,  $J = 40$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  10.89 (m). HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{15}\text{H}_{20}\text{BP}]^+$  239.1169, Found 239.1165. Separation of enantiomers by chiral HPLC (Chiralpak AS-H column, flow rate 1.0 mL/min, 95:5 hexanes:EtOH,  $T_r$  minor 7.42, major 8.58 min) determined the ee to be 7%.



Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.422	VV	0.1736	4745.66895	427.15326	50.0340
2	8.575	VB	0.2178	4739.22168	337.45212	49.9660

Totals : 9484.89063 764.60538

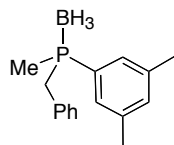


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.446	MM	0.1641	77.64000	7.88431	46.3813
2	8.641	MM	0.1983	89.75513	7.54291	53.6187

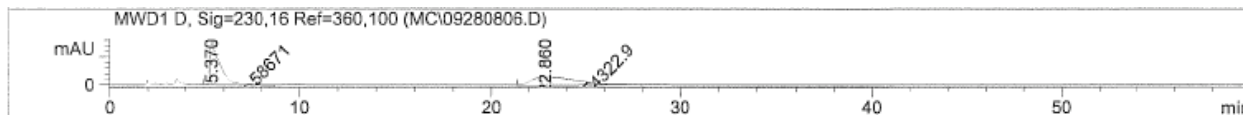
Totals : 167.39513 15.42722

**Table 13. Chiral phosphines prepared from methyl(3,5-xylyl)phosphine.**



**Benzylmethyl(3,5-xylyl)phosphino-borane (20a).** Silica gel flash column chromatography (95:5 hexanes/EtOAc) afforded the product as a white solid (89% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.24-7.22 (m, 3H), 7.14-7.12 (m, 3H), 6.95-6.93 (m, 2H), 3.17 (dd,  $J = 11.2, 5.6$  Hz, 2H), 2.32 (s, 6H), 1.47 (d,  $J = 9.9$  Hz, 3H), 0.77 (br q, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.2 (d,  $J = 9$  Hz), 133.1 (d,  $J = 2$  Hz), 132.5 (d,  $J = 7$  Hz), 129.8 (d,  $J = 4$  Hz), 129.4, 129.3, 128.3 (d,  $J = 53$  Hz), 128.2 (d,  $J = 2$  Hz), 126.9 (d,  $J = 3$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.56 (m). HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{16}\text{H}_{22}\text{BP}]^+$  253.1316,

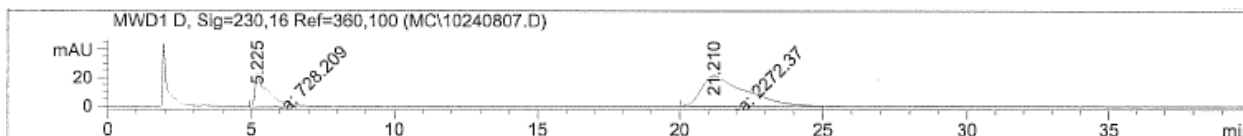
Found 253.1317. Separation of enantiomers by chiral HPLC (Chiralcel OJ column, flow rate 1.5 mL/min, 80:20 hexanes/*i*PrOH,  $T_r$  minor 5.25, major 21.21 min) determined the ee to be 56%.



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.370	MM	0.6187	5.86710e4	1580.40588	51.9241
2	22.860	MM	2.8364	5.43229e4	319.20209	48.0759

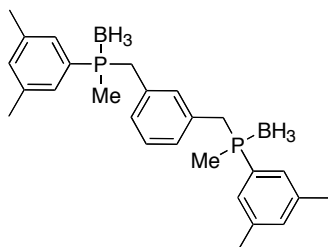
Totals : 1.12994e5 1899.60797



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.225	MM	0.4764	1833.37952	64.13612	21.2702
2	21.213	MM	1.8320	6786.07617	61.73817	78.7298

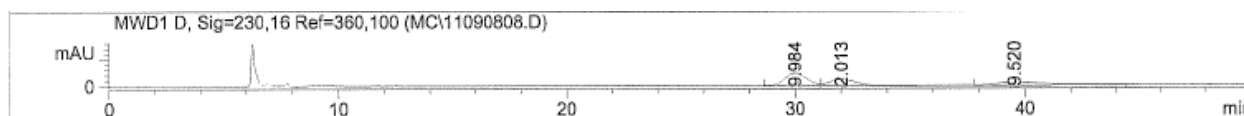
Totals : 8619.45569 125.87430



**1,3-Bis((methyl(3,5-xylyl)phosphino-borane)methyl)-benzene (20b).** Silica gel flash chromatography (80:20 hexanes/EtOAc) afforded the product as a white solid (88% yield). The product was isolated as a mixture of two diastereomers.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.14-7.04 (m, 8H), 6.89-6.88 (m, 1H), 6.83-6.82 (m, 1H), 2.94-2.81 (m, 4H), 2.30-2.28 (m, 12H), 1.45 (d,  $J$  = 9.7 Hz, 3H), 1.44 (d,  $J$  = 9.5 Hz, 3H), 0.62 (br q, 6H). NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  138.4 (d,  $J$  = 11 Hz), 133.2, 132.0 (m), 131.2 (m), 129.2 (m), 128.7, 128.2, 126.9 (m), 32.7 (d,  $J$  = 30 Hz), 32.5 (d,  $J$  = 30 Hz), 21.2 (d,  $J$  = 2 Hz), 9.8 (d,  $J$  = 39 Hz), 9.7 (d,  $J$  = 38 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.57 (m). HRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{26}\text{H}_{38}\text{B}_2\text{P}_2]^+$  434.2590, Found 434.2596. Separation of enantiomers by chiral HPLC (Chiralpak AS-H column, flow rate 0.5 mL/min, 97:3 hexanes/EtOH,  $T_r$  minor 28.68, major



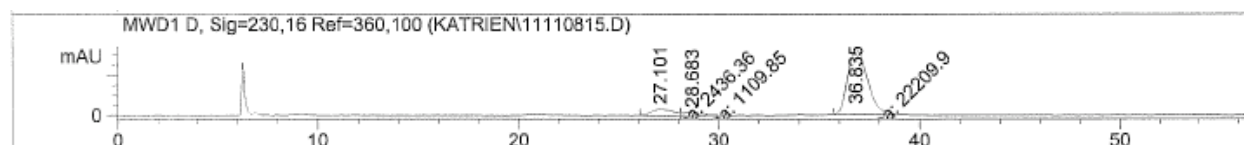
36.84, meso 27.10 min) determined the ee to be 91%. The ratio of  $C_2$ :meso diastereomers was found to be 90:10.



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.984	VV	1.0506	1.66167e4	243.35249	43.8905
2	32.013	VB	1.2924	1.10815e4	126.69525	29.2702
3	39.520	VV	2.4429	1.01612e4	55.52855	26.8393

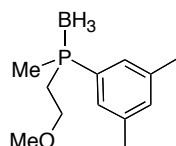
Totals : 3.78594e4 425.57629



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

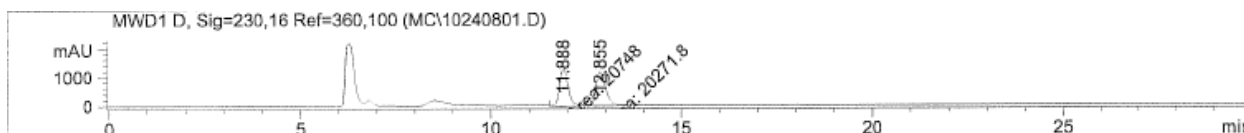
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.101	MF	1.3150	2436.35913	30.88005	9.4593
2	28.683	FM	1.1695	1109.85217	15.81694	4.3091
3	36.835	MM	1.1330	2.22099e4	326.69775	86.2316

Totals : 2.57561e4 373.39475



**(2-Methoxyethyl)methyl(3,5-xylyl)phosphine-borane (20c).** Silica gel

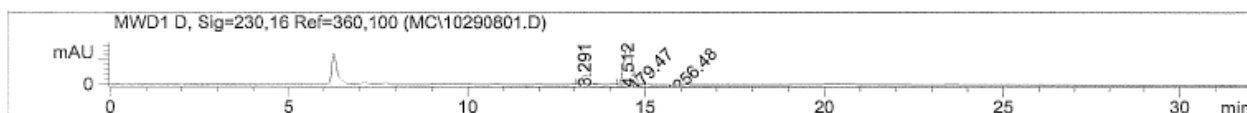
flash chromatography (80:20 hexanes/EtOAc) afforded the product as a clear residue (80% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.33 (s, 1H), 7.30 (s, 1H), 7.13 (s, 1H), 3.68-3.60 (m, 1H), 3.50-3.41 (m, 1H), 3.30 (s, 3H), 2.36 (s, 6H), 2.16-2.09 (m, 2H), 1.60 (d,  $J$  = 10.4 Hz, 3H), 0.68 (br q, 3H).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  6.30 (m). HRMS ( $\text{FAB}^+$ ) calcd for **[C<sub>12</sub>H<sub>12</sub>BOP]<sup>+</sup>** 223.14255, Found 223.1423. Separation of enantiomers by chiral HPLC (Chiralpak AS-H column, flow rate 0.5 mL/min, 97:3 hexanes/*i*PrOH,  $T_r$  minor 13.29, major 14.51 min) determined the ee to be 66%.



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.888	MM	0.2641	2.07480e4	1309.25085	50.5804
2	12.855	MM	0.2910	2.02718e4	1161.03088	49.4196

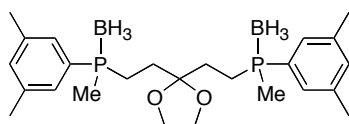
Totals : 4.10197e4 2470.28174



Signal 4: MWD1 D, Sig=230,16 Ref=360,100

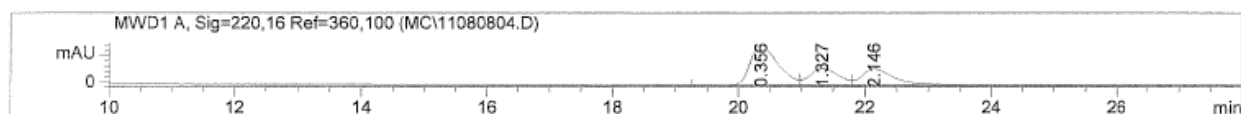
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.291	MM	0.2464	1479.47107	100.07114	16.9354
2	14.512	MM	0.2899	7256.48145	417.13815	83.0646

Totals : 8735.95251 517.20930



**(2,2'-(1,3-Dioxolane-2,2-diyl)bis(ethane-2,1-diyl))bis(methyl(3,5-**

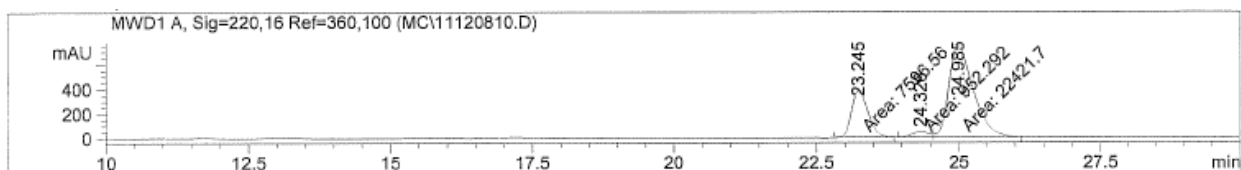
**xylyl)phosphine-borane) (20d).** Silica gel flash chromatography (80:20 hexanes/EtOAc) afforded the product as a clear residue (52% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.30-7.27 (m, 4H), 7.13-7.10 (m, 2H), 3.89-3.85 (m, 4H), 2.37-2.35 (m, 12H), 1.84-1.75 (m, 6H), 1.62-1.57 (m, 2H), 1.52 (d,  $J = 10.0$  Hz, 3H), 1.50 (d,  $J = 10.5$  Hz, 3H), 0.66 (br q, 6H).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 162 MHz)  $\delta$  9.41 (m). LRMS ( $\text{FAB}^+$ ) calcd for  $[\text{C}_{25}\text{H}_{42}\text{B}_2\text{O}_2\text{P}_2]^+$  457.28, Found 457.28. Separation of enantiomers by chiral HPLC (Chiralpak IB column, flow rate 0.5 mL/min, 98:1.5:0.5 hex/*i*PrOH/EtOH,  $T_r$  minor 24.33, major 24.99, meso 23.25 min) determined the ee to be 92%. The ratio of  $C_2$ :meso diastereomers was found to be 74:26.



Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.356	VV	0.4604	1.18818e4	393.38052	52.3636
2	21.327	VV	0.5006	5173.41162	161.12733	22.7994
3	22.146	VB	0.5243	5635.74756	159.49045	24.8369

Totals : 2.26910e4 713.99831



Signal 1: MWD1 A, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.245	MM	0.3304	7596.56104	383.19556	24.5283
2	24.326	MF	0.3646	952.29211	43.53408	3.0748
3	24.985	FM	0.5036	2.24217e4	742.03992	72.3968
Totals :				3.09706e4	1168.76956	

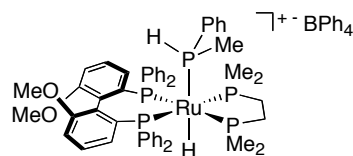
### Scheme 3. General procedure for measuring half-lives of ruthenium-catalyzed reactions.

In a nitrogen-atmosphere glovebox, a solution of NaOtAm (12 mg, 0.10 mmol, 1.2 equiv) in THF-*d*<sub>8</sub> (0.20 mL) was taken up in an airtight syringe equipped with a needle. The needle was stoppered with a rubber septum and set aside. Separately, an NMR tube was charged with a solution of MeO-BIPHEP/dmpe catalyst **10** (7.0 mg, 0.0061 mmol, 0.07 equiv), benzyl chloride (12  $\mu$ L, 0.10 mmol, 1.2 equiv), and substrate phosphine (0.087 mmol, 1.0 equiv) in THF-*d*<sub>8</sub> (0.30 mL). A sealed capillary containing a 0.05 M solution of zirconocene dichloride in C<sub>6</sub>D<sub>6</sub> (external standard) was placed inside the NMR tube. The NMR tube was fitted to an Ultra-Torr Cajon adaptor, and both the NMR tube and the syringe containing NaOtAm were brought out of the glovebox. The Cajon was flushed onto a Schlenk line, and the contents of the NMR tube were frozen in liquid nitrogen. Under a positive pressure of nitrogen, the solution of NaOtAm was added to the contents of the NMR tube. The NMR tube was then flame-sealed under vacuum, and the reaction was monitored at room temperature by <sup>1</sup>H and <sup>31</sup>P NMR for the disappearance of substrate phosphine and the appearance of product phosphine.

**General procedure for measuring half-lives of base-mediated background reactions.** In a nitrogen-atmosphere glovebox, a solution of NaOtAm (12 mg, 0.10 mmol, 1.2 equiv) in THF-*d*<sub>8</sub> (0.20 mL) was taken up in an airtight syringe equipped with a needle. The needle was then stoppered with a rubber septum and set aside. Separately, an NMR tube was charged with a solution benzyl chloride (12  $\mu$ L, 0.10 mmol, 1.2 equiv) and substrate phosphine (0.087 mmol, 1.0 equiv) in THF-*d*<sub>8</sub> (0.30 mL). A sealed capillary containing a 0.05 M solution of zirconocene dichloride (external standard) was placed inside the NMR tube. The NMR tube was fitted to an Ultra-Torr Cajon adaptor, and both the NMR tube and the syringe containing NaOtAm were brought out of the glovebox. The Cajon was flushed onto a Schlenk line, and the contents of the NMR tube were frozen in liquid nitrogen. Under a positive pressure of nitrogen, the solution of NaOtAm was added to the contents of the NMR tube. The NMR tube was then flame-sealed

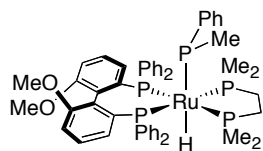
under vacuum, and the reaction was monitored at room temperature by  $^1\text{H}$  and  $^{31}\text{P}$  NMR for the disappearance of substrate phosphine and the appearance of product phosphine.

**Scheme 4. Synthesis of MeO-BiPHEP/dmpe methylphenylphosphine and phosphido complexes.**



**$[(R)\text{-MeO-BiPHEP})(\text{dmpe})\text{Ru}(\text{H})(\text{HPPhMe})][\text{BPh}_4]$**

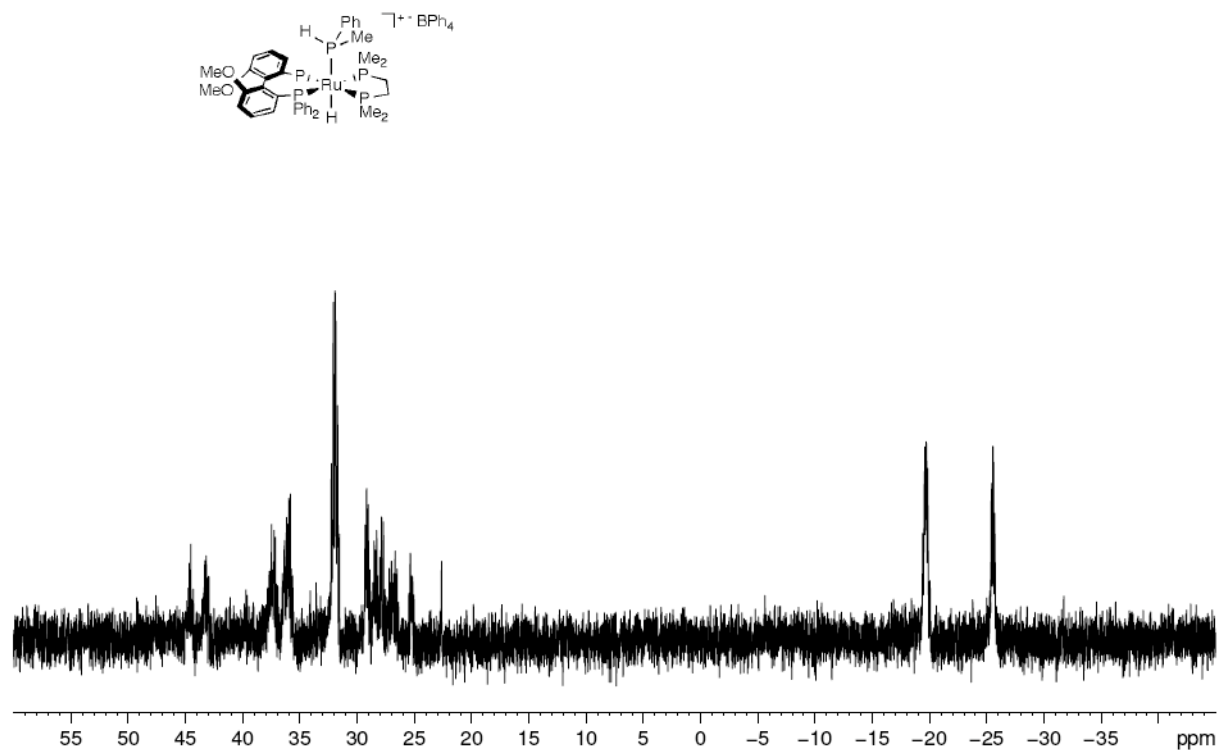
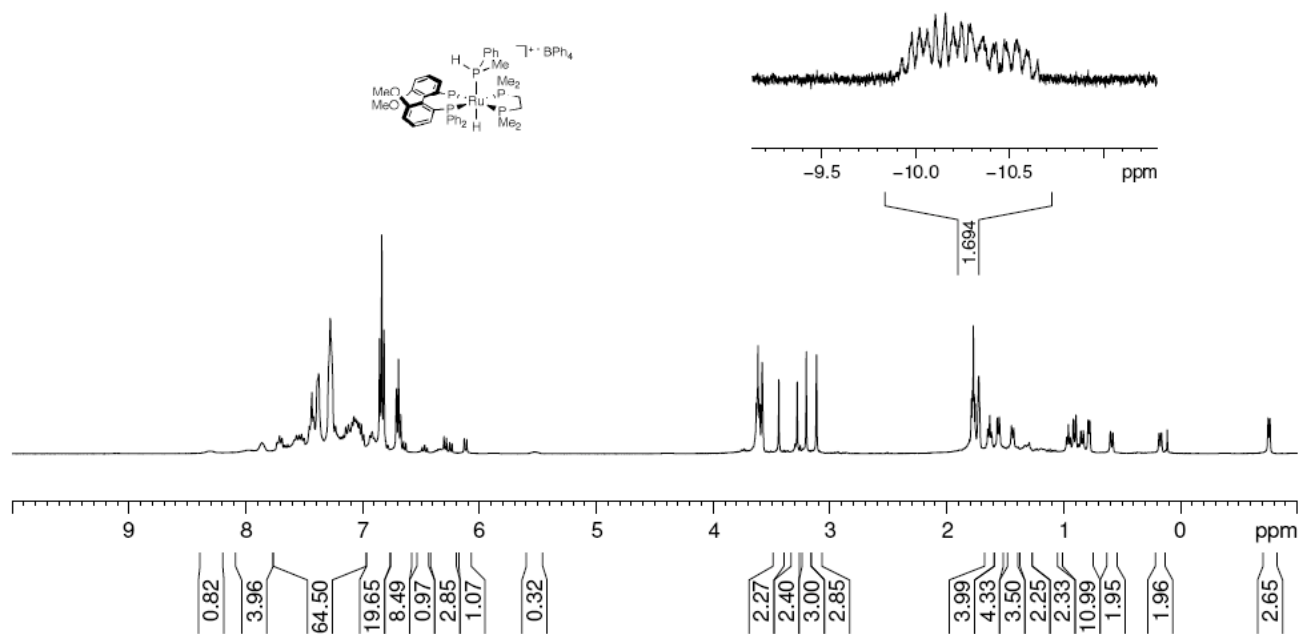
**(23).** In a nitrogen atmosphere glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with a solution of **10** (249 mg, 0.218 mmol, 1.0 equiv) in THF (5 mL). Methylphenylphosphine (28  $\mu\text{L}$ , 0.218 mmol, 1.0 equiv) was added via micropipette. The reaction mixture was stirred for 30 min, then concentrated in vacuo. The resulting crude product was purified via silica gel flash chromatography (80:20 pentane/Et<sub>2</sub>O, then THF). A product with NMR spectra consistent with **23** was obtained as a light peach solid (88% yield) and as a mixture of diastereomers (3:2 d.r.).  $^1\text{H}$  NMR (THF-*d*<sub>8</sub>, 400 MHz)  $\delta$  8.32 (br m, 0.7H), 7.99-7.00 (m, 58H), 6.93-6.82 (m, 17H), 6.69 (m, 7H), 6.48 (t,  $J$  = 8.7 Hz, 0.7H), 6.30 (d,  $J$  = 8.3 Hz, 1H), 6.25 (d,  $J$  = 8.6 Hz, 0.7 Hz), 6.13 (d,  $J$  = 8.3 Hz, 1H), 5.94 (br m, 0.7H), 3.45 (s, 2H), 3.29 (s, 2H), 3.21 (s, 3H), 3.13 (s, 3H), 1.64 (t,  $J$  = 6.5 Hz, 2H), 1.58 (d,  $J$  = 7.3 Hz, 3H), 1.45 (d,  $J$  = 7.21, 2H), 1.38-1.16 (m, 2.7H), 0.96 (t,  $J$  = 6.7 Hz, 2H), 0.92 (d,  $J$  = 8.6 Hz, 3H), 0.85 (d,  $J$  = 8.3 Hz, 2H), 0.79 (d,  $J$  = 5.4 Hz, 3H), 0.60 (d,  $J$  = 9.1 Hz, 2H), 0.18 (d,  $J$  = 8.4 Hz, 2H), -0.76 (d,  $J$  = 5.9 Hz, 3H), -10.3 (m, 1.7H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF-*d*<sub>8</sub>, 162 MHz)  $\delta$  43.9 (m), 36.5 (m), 33.7 (m), 31.9 (m), 29.2-25.3 (m), -19.7 (m), -25.5 (m).



**$[(R)\text{-MeO-BiPHEP})(\text{dmpe})\text{Ru}(\text{H})(\text{PPhMe})]$  (**24**).**

In a nitrogen atmosphere glovebox, an NMR tube was charged with a solution of **23** (78 mg, 0.062 mmol, 1.0 equiv) in THF-*d*<sub>8</sub> (0.300 mL). A solution of NaHMDS (12 mg, 0.068 mmol, 1.1 equiv) in THF-*d*<sub>8</sub> (0.300 mL) was added, yielding a deep red, clear solution. Within 10 minutes, the desired product was observed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR as a mixture of two isomers (9:1), and HMDS. The NMR data reported here correspond to the major isomer.  $^1\text{H}$  NMR (THF-*d*<sub>8</sub>, 400 MHz)  $\delta$  8.37

(br m, 1H), 8.06 (br m, 2H), 7.63-7.37 (m, 4H), 7.25-7.09 (m, 8H), 7.07-6.87 (m, 10H), 6.76 (t,  $J = 7.89$  Hz, 1H), 6.65 (t,  $J = 7.34$  Hz, 2H), 6.52 (t,  $J = 6.97$  Hz, 1H), 6.43 (d,  $J = 8.25$  Hz, 1H), 6.05 (d,  $J = 7.89$  Hz, 1H), 3.31 (s, 3H), 3.19 (s, 3H), 1.12 (d,  $J = 7.70$  Hz), 1.05 (d,  $J = 7.52$  Hz, 3H), 0.89 (d,  $J = 2.75$  Hz, 3H), 0.37 (d,  $J = 6.97$  Hz, 3H), -0.03 (d,  $J = 7.52$  Hz, 3H), -12.25 (m, 1H).  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF- $d_8$ , 162 MHz)  $\delta$  39.3-36.9 (m) 34.8 (m), 33.2 (m), 31.8 (m), 30.1 (m), -84.7 (m).





#### IV. References

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