Supplementary Material

A Convenient Synthetic Route to (S_p) Methylphosphine-Borane Derivatives via an Asymmetric Lithiation/Trapping-Reductive Elimination Strategy.

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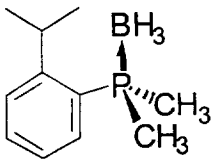
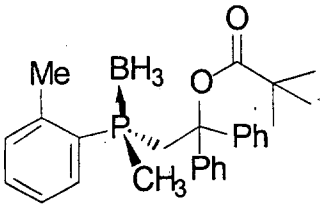


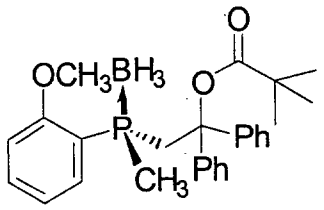
(2-Isopropylphenyl)dimethylphosphine-borane (**1b**). To a cooled (-78 °C) solution of 1-bromo-2-isopropylbenzene[1] (6.1 g, 31mmol) in ether (60 mL) was added *n*-butyllithium (17.0 mL, 31 mmol, 1.8 M in hexanes, 1.0 eq) dropwise. The solution was stirred at -78 °C for 10 min followed by warming to 0 °C for 45 min. The solution was again cooled to -78 °C and chlorodimethylphosphine-borane (3.7 g, 34 mmol, 1.1 eq) was added slowly. The reaction mixture was allowed to warm to ambient temperature after 30 min at -78 °C, and was stirred for 12 h. Water (20 mL) was added and the aqueous phase was extracted with ether (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The crude colorless solid was purified by recrystallization from hot 5% ethyl acetate/ hexanes (~75 mL) yielding 1-(2-isopropylphenyl)-dimethylphosphine-borane (4.8 g, 25 mmol, 80 %) as a colorless solid. mp=84.8-85.9 °C (5% ethyl acetate/ hexanes); IR (KBr) 2958, 2360 (B-H), 1066, 921, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.54 (ddd, J=12.0, 7.8, 1.5 Hz, 1H, Ar-**H**), 7.45 (m, 1H, Ar-**H**), 7.39 (ddd, J=8.0, 3.8, 1.5 Hz, 1H, Ar-**H**), 7.23 (m, 1H, Ar-**H**), 3.51 (apparent sep d, J=6.7 Hz, J_{P-H}=1.2 Hz, 1H, $ArCH(CH_3)_2$), 1.63 (d, J_{P-H}=9.9 Hz, 6H, $P(CH_3)_2$), 1.92 (d, J=6.7 Hz, 1H, $CH(CH_3)_2$), 0.84 (broad apparent

q, J_{B-H}=85.8 Hz, 3H, PBH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.1 (d, J_{P-C}=8.2 Hz), 131.5 (d, J_{P-C}=2.1 Hz), 131.1 (d, J_{P-C}=10.3 Hz), 127.5 (d, J_{P-C}=52.2 Hz), 127.0 (d, J_{P-C}=8.0 Hz), 125.9 (d, J_{P-C}=9.8 Hz), 31.2 (d, J_{P-C}=6.3 Hz, $ArCH(CH_3)_2$), 24.3 (s, $ArCH(CH_3)_2$), 13.6 (d, J_{P-C}=39.4 Hz, $P(CH_3)_2$); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 0.92 (q, J_{B-P}=55 Hz); TLC R_f 0.26 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 179 (M^+-BH_4) 75, 77, 91, 115, 117, 133, 152, 165 (100%), 179, 180; exact mass calculated for $C_{11}H_{16}P$ (M^+-BH_4) requires *m/z* 179.0990 found m/z 179.0990.



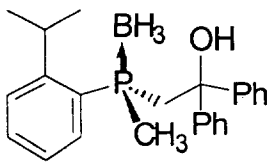
(*S*$_P$)-2-(Methyl-*o*-tolylphosphino-borane)-1,1-diphenylethyl 2,2-Dimethylpropionate (**2c**). To a cooled (-78 °C) solution of (-)-sparteine (2.6 mL, 11 mmol, 1.1 eq) in ether (40 mL) was added *s*-butyllithium (9.2 mL, 11 mmol, 1.2 M, 1.1eq) slowly. The solution was stirred for 10 min and dimethyl-*o*-tolylphosphine-borane (**1c**) (1.7 g, 10 mmol, 1.0 eq) in ether (40 mL) was added dropwise via cannula. The solution was allowed to stir for 3 h and benzophenone (2.0 g, 11 mmol, 1.1 eq) dissolved in THF (10 mL) was added slowly via cannula. The solution was stirred at -78 °C for 1 h, and was then warmed to ambient temperature over 2 h. The solution was again cooled to 0 °C, and trimethylacetyl chloride (1.8 mL, 15 mmol, 1.5 eq) was added in one portion and the solution was allowed to stir as the ice bath warmed to room temperature over 10 h. To the mixture, 5% aqueous sulfuric acid (20 mL) was added and the aqueous phase was extracted with ether (3 x 20 mL). The combined organic phases were washed with saturated sodium bicarbonate (20 mL), brine (20 mL), dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The resulting crude colorless solid was purified by slow vapor recrystallization from ethyl acetate with hexanes providing (*S*$_P$)-2-(Methyl-*o*-tolylphosphino-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2c**) (3.3 g, 7.6 mmol, 76%) as colorless prisms. mp=(with decomposition) 157.3-158.6 °C (ethyl acetate/ hexanes); $[\alpha]_D^{28\ °C}$ -15.3° (c=5.13, sol. dichloromethane); IR (KBr) 3059, 2979, 2439 (B-H), 2396 (B-H), 2337 (B-H), 1709 (C=O), 1157 (broad, C-O), 989, 752, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.40-7.09 (m, 14H, Ar-**H**), 3.83 (dd, *J*=14.9Hz, J_{P-H}=8.8 Hz, 1H, PCH(**H**)C), 3.57 (dd, *J*=14.9, J_{P-H}=11.6 Hz, 1H, PCH(**H**)C), 2.52 (s, 3H, Ar-CH_3), 1.16 (s, 9H, $C(CH_3)_3$), 1.13 (d, J_{P-H}=9.8 Hz, 3H, PCH_3), 0.64

(broad apparent s, 3H, PBH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.51 (s, *t*-$BuCO_2$)144.4 (d, J_{P-C}=10.3 Hz, ArC), 144.4 (s, ArC), 142.1 (d, J_{P-C}=8.8 Hz, ArC), 132.1 (d, J_{P-C}=9.5 Hz, ArC), 131.7 (s, J_{P-C}=8.5 Hz, ArC), 130.9 (s, ArC), 128.0 (d, J_{P-C}=7.5, ArC), 127.9 (d, J_{P-C}=51.6 Hz, ArC), 127.4 (d, J_{P-C}=3.3 Hz, ArC), 125.9 (d, J_{P-C}=1.2 Hz, ArC), 125.7 (s, ArC), 83.4 (d, J_{P-C}=3.5 Hz, Ph_2CO-), 39.6 (s, C-$C(CH_3)_3$), 34.8 (d, J_{P-C}=30.3 Hz, PCH_2C), 27.0 (s, $C(CH_3)_3$), 22.1 (d, J_{P-C}=4.2 Hz, $ArCH_3$), 11.5 (d, J_{P-C}=40.8 Hz, PCH_3); ^{31}P NMR (101 MHz, $CDCl_3$) δ: 5.95 (very broad s); TLC R_f 0.32 (20% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 418 (M^+-BH_3, 7.1%)57, 77, 91, 138, 154, 165, 180 (100%), 214, 238, 316; exact mass calculated for $C_{27}H_{31}O_2P$ (M^+-BH_3) requires *m/z* 418.2062 found m/z 418.2065; separation of enantiomers by chiral HPLC (CHIRAL PAK® AD, flow rate 1.0 mL/min, 10% *i*-PrOH/ hexanes, t_R= 4.44(major), 5.61 (min) determined the enantiomeric excess of the reaction to be 91 % before recrystallization and >99% after recrystallization.



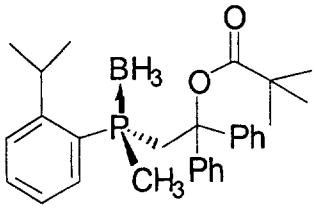
(*S*$_P$)-2-(Methyl-2-methoxyphenylphosphino-borane)-1,1-diphenylethyl 2,2-Dimethylpropionate (**2d**). *s*-Butyllithium (4.6 mL, 5.5 mmol, 1.2 M in cyclohexane, 1.1 eq) was added dropwise to a cooled (-78°) solution of (-)-sparteine (1.3 mL, 5.5 mmol, 1.1 eq) in ether (40 mL). The solution was stirred for 10 min, and dimethyl-(2-methoxyphenyl)phosphine-borane (**1d**) (0.91 g, 5 mmol, 1.0 eq) dissolved in ether (20 mL) was added dropwise via cannula. The reaction mixture was stirred for 3 h at -78 °C , and a solution of benzophenone (1.0 g, 5.5 mmol, 1.1 eq) dissolved in THF (10 mL) was then added slowly via cannula. The reaction mixture was stirred at -78 °C for an additional 1 h, then warmed to 0 °C over 2 h. To the solution at 0 °C, trimethylacetyl chloride (740 μL, 6.6 mmol, 1.2 eq) was added, and the reaction mixture was then warmed to ambient temperature over 10 h. The heterogenous suspension was quenched with 5% aqueous sulfuric acid (20 mL), and the ether and THF were removed in vacuo. To the resulting biphasic residue dichloromethane (50 mL) was added. The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic phases were washed with saturated aqueous sodium bicarbonate (20 mL), brine (20 mL), dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The crude material was purified by slow vapor defusion recrystallization from ethyl acetate with hexanes. The

enantiomerically pure product formed large rhombohedral crystals while the racemic material co-crystallized out as very fine fibrous crystals. The enantiomerically pure crystals of (S_P)-2-(methyl-2-methoxyphenylphosphino-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2d**) (1.0g, 2.3 mmol, 46%) was separated from the racemic crystals by rapidly stirring the solution and pouring the fine racemic crystals away, this was repeated 3 more times with 5% ethyl acetate/ hexanes. mp=(with decomposition) 178.9-179.7 °C (ethyl acetate/ hexanes); $[\alpha]_D^{28\ °C}$ +7.3° (c=5.04, solvent CH_2Cl_2); IR (KBr) 3068, 2966, 2408 (B-H), 2378 (B-H), 2342 (B-H), 1731 (C=O), 1149° (broad, C-O), 978, 760, 696 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) δ: 7.97 (ddd, J=14.0, 7.7, 1.5 Hz, 1H, Ar-**H**), 7.43 (m, 1H, Ar-**H**), 7.25 (m, 1H, Ar-**H**), 7.11-7.06 (m, 2H, Ar-**H**), 6.98 (m, 1H, Ar-**H**), 6.89 (m, 1H, Ar-**H**), 6.78-6.74 (m, 3H, Ar-**H**), 6.69 (m, 1H, Ar-**H**), 6.60 (apparent tq, J=7.9, 0.9 Hz, 1H, Ar-**H**), 6.04 (dd, J=8.25, 3.2 Hz, 1H, Ar-**H**), 4.03 (dd, J=14.4 Hz, J_{P-H}=9.3 Hz, 1H, PCH(**H**)C), 3.97 (apparent t, J_{H-H}=14.4, J_{P-H}=14.4, 1H, PCH(**H**)C), 3.00 (s, 3H, ArOC**H**$_3$), 1.82 (very broad s, 3H, BH_3), 1.36 (s, 9H, C(C**H**$_3$)$_3$), 1.20 (d, J_{P-H}=9.9 Hz, 3H, PC**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 176.6 (s, t-Bu**C**O$_2$), 160.6 (d, J_{P-C}=2.25 Hz, Ar**C**), 145.1 (d, J_{P-C}=7.3 Hz, Ar**C**), 143.6 (d, J_{P-C}=4.7 Hz, Ar**C**), 136.1 (s, Ar**C**), 135.9 (s, Ar**C**) 132.8 (s, Ar**C**), 127.9 (s, Ar**C**), 127.4 (s, Ar**C**), 127.2 (d, J_{P-C}=13.9 Hz, Ar**C**), 126.3 (s, Ar**C**), 125.9 (s, Ar**C**), 120.7 (d, J_{P-C}=12.7 Hz, Ar**C**), 116.4 (d, J_{P-C}=51.4 Hz, Ar**C**), 110.0 (d, J_{P-C}=3.6 Hz, Ar**C**), 83.4 (s, **C**OCPh$_2$), 55.0 (s, ArOCH$_3$), 39.6 (s, **C**(CH$_3$)$_3$), 32.7 (d, J_{P-C}=35.2 Hz, PCH$_2$**C**), 27.1 (s, C(**C**H$_3$)$_3$), 11.7 (d, J_{P-C}=42.8 Hz, PCH$_3$); ^{31}P NMR ($CDCl_3$, 121MHz) δ: 5.14 (d, J_{B-P}=55.8 Hz); TLC R_f 0.25 (20% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 434 (M^+-BH_3, 2.3%) 57, 77, 107, 139, 154, 165, 180 (100%), 193, 230, 332, 346; exact mass calculated for $C_{27}H_{31}O_3P$ (M^+-BH_3) requires m/z 434.2011 found m/z 434.2005; separation of enantiomers by chiral HPLC (CHIRALPAK® AD, flow rate 1.0 mL/min, 10% i-PrOH/ hexanes, t_R= 4.75 (major), 6.55 (min) determined the enantiomeric excess to be >99%.



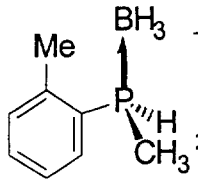
(S_P)-2-[Methyl-(2-i-propylphenyl)phosphino-borane]-1,1-diphenyl-ethan-1-ol (**5b**). s-Butyllithium (0.46 mL, 0.55 mmol, 1.2 M, 1.1 eq) was added dropwise to a cooled (-78 °C) solution of (-)-sparteine (0.13 mL, 0.55 mmol, 1.1 eq) in ether (2.0 mL). After 10 min a

solution of dimethyl-(2-*i*-propylphenyl)-phosphine-borane (**1b**) (0.097 g, 0.50 mmol, 1.0 eq) in ether (2.0 mL) was added dropwise via cannula. The reaction mixture was stirred for 3 h at -78 °C and a solution of benzophenone (0.10 g, 5.5 mmol, 1.1 eq) in THF (0.5 mL) was added slowly via cannula. The reaction mixture was stirred at -78 °C for an additional 1 h and then warmed slowly to 0 °C for an additional 2 h. To the solution, 5% aqueous sulfuric acid (1.0 mL) was added in one portion. The aqueous phase was extracted with ether (3 × 2 mL), and the combined organic phases were washed with saturated sodium bicarbonate (1mL) and brine (1 mL) then dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The crude oil was then purified by flash chromatography on silica gel (gradient elution with 0-5% ethyl acetate/ hexanes) yielding ($\underline{S}_P$)-2-[methyl(2-*i*-propylphenyl)phosphino-borane]-1,1-diphenylethan-1-ol (**5b**) as an oil that gradually solidified over time. mp=(with decomposition) 84.5-91.3 °C (hexanes); $[\alpha]_D^{25\ °C}$ +2.3° (c=4.01, sol. $CDCl_3$); IR (KBr) 3463 (broad, O-H), 3059, 2956, 2405 (B-H), 2366 (B-H), 1059 (C-O), 992, 764, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.49 (m, 14H, Ar-**H**), 4.37 (s, 1H, OH), 3.50 (sep, *J*=6.3 Hz, 1H, $CH(CH_3)_2$), 3.10 (apparent d, *J*= 11.1 Hz, 2H, PCH_2C), 1.33 (d, *J*=6.3 Hz, 3H, $C(CH_3)$), 1.32 (d, J_{P-H}=10.5 Hz, 3H, PCH_3), 1.26 (d, *J*=6.3 Hz, 3H, $C(CH_3)$), 1.79 (very broad s, 3H, BH_3); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 152.8 (d, J_{P-C}=8.2 Hz, Ar**C**), 146.3 (d, J_{P-C}=7.1 Hz, Ar**C**), 146.0 (d, J_{P-C}=4.8 Hz, Ar**C**), 132.6 (d, J_{P-C}=12.3 Hz, Ar**C**),131.8 (d, J_{P-C}=2.4 Hz, Ar**C**), 128.3 (s, Ar**C**), 128.1 (s, Ar**C**), 127.3 (d, J_{P-C}=8.1 Hz, Ar**C**), 127.2 (d, J_{P-C}=8.1 Hz, Ar**C**), 127.0 (d, J_{P-C}=55.1 Hz, Ar**C**), 126.2 (s, Ar**C**), 126.0 (s, Ar**C**), 125.8 (s, Ar**C**), 125.6 (s, Ar**C**), 77.7 (s, Ph_2COH), 41.2 (d, J_{P-C}=30.9 Hz, PCH_2), 31.4 (d, J_{P-C}=5.2 Hz, $C(CH_3)$), 24.6 (s, $C(CH_3)$), 24.4 (s, $C(CH_3)$), 13.1 (d, J_{P-C}=40.8 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 2.7 (apparent broad d, J_{B-P}=71.1 Hz); TLC R_f 0.22 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 360 (M^+-BH_5) 51, 77, 91, 105, 115, 165 (100%), 178, 179, 180, 242; exact mass calculated for $C_{24}H_{25}OP$ (M^+-BH_5, 40%) requires *m/z* 360.1643 found m/z 360.1642; separation of the enantiomers of the product with chiral HPLC (CHIRALPAK® AD, 2% *i*-PrOH/ hexanes, 1.0 mL/ min, t_R= 9.73 (major), 12.74 min) indicated a ee of >99%.



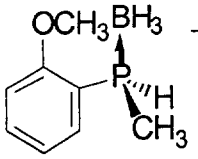
(*S*$_P$)-2-(Methyl-2-*i*-propylphenylphosphino-borane)-1,1-diphenylethyl 2,2-Dimethylpropionate (**2b**). *s*-Butyllithium (4.6 mL, 5.5 mmol, 1.2 M, 1.1 eq) was added dropwise to a cooled (-78 °C) solution of (-)-sparteine (1.3 mL, 5.5 mmol, 1.1 eq) in ether (20 mL). After 10 min a solution of dimethyl(2-*i*-propylphenyl)phosphine-borane (**1b**) (0.97 g, 5.0 mmol, 1.0 eq) in ether (20 mL) was added dropwise via cannula. The reaction mixture was stirred for 3 h and a solution of benzophenone (1.0 g, 5.5 mmol, 1.1 eq) in THF (5 mL) was added slowly via cannula. The solution was stirred at -78 °C for an additional 1 h and then warmed slowly to 0 °C over 2 h. At 0 °C pivaloyl chloride (0.98 mL, 1.5 mmol, 1.5 eq) was added in one portion. The solution was stirred at 0 °C for 3 h, then it was warmed to ambient temperature for 7 h. The reaction mixture was then concentrated in vacuo and dichloromethane (50 mL) and 5% aqueous sulfuric acid (20 mL) were added. The aqueous phase was extracted with methylene chloride (3 × 20 mL). The combined organic phases were washed with saturated sodium bicarbonate (20 mL) and brine (20 mL), then dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The resulting crude colorless solid was purified by crystallization from hot hexanes, and the residual material from the supernatant was purified by flash chromatography (gradient elution 0-5% ethyl acetate/hexanes) yielding (*S*$_P$)-2-(methyl-2-*i*-propylphenylphosphino-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2b**) (1.6 g, 3.5 mmol, 70%) as a colorless solid. mp=(with decomposition) 133-136 °C (hexanes); $[\alpha]_D^{25\ °C}$ +20° (c=5.01, sol. THF); IR (KBr) 3057, 2966, 2428 (B-H), 2382 (B-H), 2339 (B-H), 1733 (C=O), 1146 (broad, C-O), 991, 760, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.42-7.36 (m, 4H, Ar-**H**), 7.32-7.11 (m, 10H, Ar-**H**), 4.03 (dd, *J*=14.7 Hz, J_{P-H}=6.6 Hz, 1H, PC**H**(H)C), 3.51 (apparent p d, *J*=6.6 Hz, J_{P-H}=1.2 Hz, 1H, C**H**$(CH_3)_2$), 3.20 (apparent t, $J_{P-H,\ H-H}$=14.7 Hz, 1H, PC**H**(H)C), 1.30 (d, *J*=6.6 Hz, 3H, CH(C**H**$_3$)), 1.28 (s, 9H, C$(CH_3)_3$), 1.27 (d, *J*=6.6 Hz, 3H, CH(C**H**$_3$)), 0.97 (d, J_{P-H}=9.6 Hz, 3H, PC**H**$_3$), 0.75 (apparent broad s, 3H, B**H**$_3$); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 176.7 (s, *t*-BuCO_2), 153.4 (d, J_{P-C}=9.9 Hz, Ar-**C**), 144.9 (d, J_{P-C}=7.1 Hz, Ar**C**), 144.3 (d, J_{P-C}=3.7 Hz, Ar**C**), 131.2 (s, Ar**C**), 130.7 (d, J_{P-C}=8.3 Hz, Ar**C**), 128.3 (d, J_{P-C}=55.1 Hz, Ar**C**), 128.2 (s, Ar**C**), 128.0 (s, Ar**C**),127.5 (s, Ar**C**), 127.3 (d, J_{P-C}=4.2 Hz, Ar**C**), 126.1 (s, Ar**C**), 125.9 (s, Ar**C**),

125.8 (s, ArC), 125.7 (s, ArC), 83.3 (d, J_{P-C}=2.3 Hz, (d, J=2.3 Hz, Ph_2CO-), 39.7 (s, $C(CH_3)_3$), 36.1 (d, J_{P-C}=30.1 Hz, PCH_2), 31.1 (d, J_{P-C}=6.4 Hz, $CH(CH_3)_2$), 27.1 (s, $C(CH_3)_3$), 24.8 (s, $C(CH_3)$), 24.3 (s, $C(CH_3)$), 11.5 (d, J_{P-C}=39.8 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 5.29 (broad s); TLC R_f 0.31 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 343 (M^+-BH_3-$C_5H_9O_2$, 6×10^{-3}%) 151, 167, 181 (100%), 242, 317, 329, 331; exact mass calculated for $C_{24}H_{24}P$ (M^+-BH_3-$C_5H_9O_2$) requires *m/z* 343.1616 found m/z 343.1620; due to the lack of separation of the enantiomers by chiral HPLC (CHIRALPAK® AD or CHIRALCEL® OD-H columns), the ee was determined to be >99% ee by correlation to (*R*)-2-(methyl-2-*i*-propylphenylphosphine-borane)-1,1-diphenylethan-1-ol (**5b**).

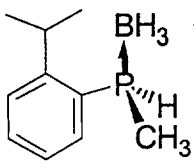


(S_P)-Methyl(2-methylphenyl)phosphine-borane (**3c**). Into a cooled (-78 °C) solution of lithium naphthalenide (5.0 mL, 0.50 M in THF, 2.5 mmol, 3 eq) was added a solution of (S_P)-2-(Methyl-*o*-tolylphosphino-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2c**) (224 mg, 0.5 mmol, 1.0 eq) in THF (5.0 mL) was added dropwise via cannula. The mixture was allowed to stir for 10 min and a solution of THF, MeOH and AcOH (8:1:1) (0.5 mL) was added very slowly. To the solution, saturated ammonium chloride (2 mL) water (2 mL) and ether (5 mL) were then added. The aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The amorphous crude solid was purified by flash column chromatography (5% ethyl acetate/ hexanes for elution), yielding (S_P)-methyl(2-methylphenyl)phosphine-borane (**3c**) (71 mg, 0.47 mmol, 94%) as a colorless oil. $[\alpha]_D^{27\ °C}$ -26° (c=1.00, solvent $CDCl_3$); IR (film, NaCl), 3060, 2921, 2385 (broad, B-H), 1064 (sharp), 997 (sharp), 928, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.69 (dd, J=13.6, 7.8 Hz, 1H, Ar-**H**), 7.51 (m, 1H, Ar-**H**), 7.31-7.25 (m, 2H, Ar-**H**), 5.66 (apparent d septet, J_{P-H}=371.7 Hz, J=6.3 Hz, 1H, P-**H**), 2.51 (s, 3H, ArCH_3), 1.60 (apparent dd, J_{P-H}=11.0 Hz, J=6.3 Hz, 3H, PCH_3), 0.80 (q, J_{B-H}=90.2 Hz, 3H, BH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.8 (d, J_{P-C}=3.8 Hz, ArC), 132.7 (d, J_{P-C}=14.5 Hz, ArC), 313.6 (s, ArC), 130.7 (d, J_{P-C}=7.2 Hz, ArC), 126.4 (d, J_{P-C}=11.7 Hz, ArC), 125.4 (d, J_{P-C}=54.2 Hz, ArC), 20.7 (d, J_{P-C}=5.2 Hz, $ArCH_3$), 7.22 (d, J_{P-C}=38.3 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 121 Hz) δ: -24.1 (broad q, J_{B-C}=43.0 Hz); TLC R_f 0.26

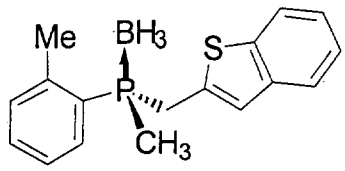
(20% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 138 (M^+-BH_3, 38%) 65, 69, 77, 78, 79, 91 (100%), 92, 121, 124, 138; exact mass calculated for $C_8H_{11}P$ (M^+-BH_3) requires *m/z* 138.0598 found m/z 138.0592.



(S_P)-Methyl(2-methoxyphenyl)phosphine-borane (**3d**). Into a cooled (-78 °C) solution of lithium naphthalenide (5.0 mL, 0.50 M in THF, 2.5 mmol, 3 eq) a solution of (S_P)-2-(methyl-2-methoxyphenylphosphino-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2d**) (224 mg, 0.5 mmol, 1.0 eq) in THF (5.0 mL) was added dropwise via cannula. The solution was allowed to stir for 10 min, and a mixture of THF, MeOH and AcOH (8:1:1, 0.5 mL) was added very slowly. To the solution was added saturated aqueous ammonium chloride (2 mL), water (2 mL) and ether (10 mL). The aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. The amorphous crude solid was purified by flash column chromatography on silica gel (gradient elution 5-10% ethyl acetate/ hexanes) yielding (S_P)-methyl-(2-methoxyphenyl)phosphine-borane (**3d**) (83 mg, 0.49 mmol, 99%) as a colorless oil. $[\alpha]_D^{24\ °C}$ -90° (c=1.08, THF); IR (film, NaCl) 3069, 2941, 2386 (broad, B-H), 998 (sharp), 921 (broad), 755 (broad) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.75 (ddd, *J*=13.8, 7.5, 1.5 Hz, 1H, Ar-**H**), 7.49 (apparent t, *J*=8.4 Hz, 1H, Ar-**H**), 7.03 (apparent dt, *J*=7.5, 1.5, 1H, Ar-**H**), 6.92 (dd, *J*=8.4, 3.3 Hz, 1H, Ar-**H**), 5.67 (apparent d septet, J_{P-H}=385.2 Hz, *J*=6.3 Hz, 1H, P-**H**), 3.89 (s, 3H, Ar-CH_3), 1.54 (dd, J_{P-H}=11.4 Hz, *J*=6.3 Hz, 3H, PCH_3), 0.76 (very broad q, J_{B-H}=94.5 Hz, 3H, BH_3); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 160.7 (s, Ar**C**), 134.8 (d, J_{P-C}=14.5 Hz, Ar**C**), 133.7 (s, Ar**C**), 121.1 (d, J_{P-C}=12.4 Hz, Ar**C**), 114.2 (d, J_{P-C}=54.8 Hz, Ar**C**), 110.3(d, J_{P-C}=4.0 Hz, Ar**C**), 55.7 (s, ArCH_3), 7.0 (d, J_{P-C}=39.8 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 300 MHz) δ: -30.8 (apparent dd, J_{B-P}=58.6, 46.0 Hz); TLC R_f 0.18 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 153 (M^+-BH_4, 9%) 51, 65, 69, 77, 91 (100%), 95, 107, 109, 121, 139; exact mass calculated for $C_8H_{10}OP$ (M^+-BH_4) requires *m/z* 153.0469 found m/z 153.0465.

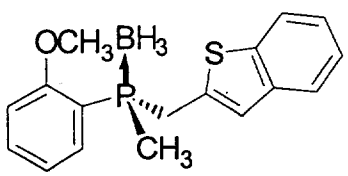


(S_P)-Methyl(2-*i*-propylphenyl)phosphine-borane (**3b**). A solution of (S_P)-2-(methyl-2-*i*-propylphenylphosphine-borane)-1,1-diphenylethyl 2,2-dimethylpropionate (**2b**) (230 mg, 0.50 mmol, 1.0 eq) in THF (5.0 mL) was added to a cooled (-78 °C) solution of lithium naphthalenide (5.0 mL, 2.5 mmol, 0.5 M, 5.0 eq). The solution was allowed to stir for 10 min and a mixture of THF, MeOH and AcOH (8:1:1, 0.5 mL) was added very slowly. To the solution was added saturated aqueous ammonium chloride (2 mL) water (2 mL) and ether (10 mL). The aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were washed with brine then dried ($MgSO_4$), filtered and concentrated in vacuo. The amorphous crude solid was purified by flash column chromatography on silica gel (5% ethyl acetate/ hexanes for elution) yielding (S_P)-methyl-(2-*i*-propylphenyl)phosphine-borane (**3b**) (85 mg, 0.47 mmol, 94%) as a colorless oil. $[\alpha]_D^{27\ °C}$ -2.3° (c=1.26, sol. THF); IR (film, NaCl) 3059, 2963, 2378 (broad, B-H), 1064 (broad), 997 (sharp), 929 (broad), 761 (broad) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.64 (ddd, *J*=13.6, 7.7, 1.5 Hz, 1H, Ar-**H**), 7.48 (m, 1H, Ar-**H**), 7.39 (m, 1H, Ar-**H**), 7.26 (m, 1H, Ar-**H**), 5.70 (apparent d sep., J_{P-H}=372.3 Hz, *J*=6.2 Hz, 1H, P**H**), 3.27 (apparent sep, *J*=6.9 Hz, 1H, ArC**H**$(CH_3)_2$), 1.61 (dd, J_{P-H}=10.8 Hz, *J*=6.2 Hz, 3H, PCH_3), 1.29 (apparent t, *J*=6.9 Hz, 6H, ArCH$(CH_3)_2$), 0.84 (broad q, J_{B-H}=95.4 Hz, PBH_3); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 152.1 (d, J_{P-C}=4.9 Hz, Ar**C**), 132.8 (d, J_{P-C}=14.0 Hz, Ar**C**), 132.1 (d, J_{P-C}=2.5 Hz, Ar**C**), 126.6 (s, Ar**C**), 132.1 (d, J_{P-C}=6.9 Hz, Ar**C**), 124.4 (d, J_{P-C}=54.9 Hz, Ar**C**), 31.5 (d, J_{P-C}=5.7 Hz, ArC**H**$(CH_3)_2$), 24.3 (s, C(CH_3)), 24.0 (s, C(CH_3)), 8.5 (d, J_{P-C}=38.2 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: -27.8 (broad q, J_{B-P}= 41.2 Hz); TLC R_f 0.21 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 166 (M^+-BH_3, 58%) 69, 77, 91 (100%), 109, 115, 123, 133, 138, 151, 166; exact mass calculated for $C_{10}H_{15}P$ (M^+-BH_3) requires *m/z* 166.0911 found m/z166.0910.

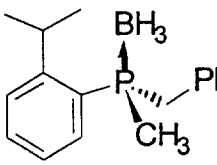


(S_P)-Benzo[*b*]thiophene-2-ylmethyl(2-methylphenyl)methyl-phosphine-borane (**4c**). *n*-Butyllithium (290 μL, 0.49 mmol, 1.7 M in hexanes, 1.1 eq) was added dropwise to a cooled

(-78 °C) solution of (S_P)-methyl-(2-methylphenyl)-phosphine-borane (**3c**) (68 mg, 0.44 mmol), HMPA (170 μL, 0.98 mmol, 2.0 eq), and THF (1.0 mL). The mixture was stirred for 5 min and a solution of 2-chloromethylbenzo[*b*]thiophene (90 mg, 0.49 mmol, 1.1 eq) in THF (1.0 mL) was added dropwise via cannula slowly. The solution was allowed to stir for 10 h at -78 °C and water (3.0 mL) was added in one portion. The aqueous phase was extracted with ether (3 × 2 mL), the combined organic phases were washed with brine (3 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The amorphous white solid was then purified by flash column chromatography (gradient elution with 0-5% ethyl acetate/ hexanes) yielding (S_P)-benzo[*b*]thiophene-2-ylmethyl(2-methylphenyl)methylphosphine-borane (**4c**) (110 mg, 0.38 mmol, 71%) as a colorless crystalline solid. mp=91.2-92.9 °C (ethyl acetate/ hexanes); $[\alpha]_D^{27\,°C}$ -99° (c=0.99, sol. THF); IR (KBr) 3055, 2911, 2400 (B-H), 2357 (B-H), 2333 (B-H), 1434, 1065 (sharp), 914 (sharp), 744 (sharp) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.67-7.59 (m, 2H, Ar-**H**), 7.45-7.37 (m, 2H, Ar-**H**), 7.29-7.16 (m,4H, Ar-**H**), 6.87 (d, J=2.9 Hz, 1H, Ar-**H**), 3.67 (dd, J=15.3 Hz, J_{P-H}=9.51 Hz, 1H, PCH(**H**)Ar), 3.54 (dd, J=15.3 Hz, J_{P-H}=8.7 Hz, 1H, PCH(**H**)Ar), 2.67 (s, 3H, Ar-C**H**$_3$), 1.64 (d, J=9.5Hz, 3H, PC**H**$_3$), 1.04 (very broad q, J_{B-H}=122.7 Hz, 3H, B**H**$_3$); ^{13}C NMR ($CDCl_3$, 75MHz) δ: 142.1 (d, J_{P-C}=9.2 Hz, Ar**C**), 139.5 (d, J_{P-C}= 2.4 Hz, Ar**C**), 139.4 (d, J_{P-C}=1.4 Hz, Ar**C**), 134.8 (d, J_{P-C}=9.2 Hz, Ar**C**), 132.6 (d, J_{P-C}=9.3 Hz, Ar**C**), 131.7 (d, J_{P-C}=8.6 Hz, Ar**C**), 131.6 (d, J_{P-C}=1.5 Hz, Ar**C**), 126.2 (d, J_{P-C}=34.4 Hz, Ar**C**), 126.1 (d, J_{P-C}=4.8 Hz, Ar**C**), 124.3 (s, Ar**C**), 124.0 (s, Ar**C**), 123.8 (d, J_{P-C}=6.0 Hz, Ar**C**), 123.0 (s, Ar**C**), 121.9 (s, Ar**C**), 29.5 (d, J_{P-C}=31.2 Hz, P**C**H$_2$Ar), 22.1 (d, J_{P-C}=4.2 Hz, Ar**C**H$_3$), 10.2 (d, J_{P-C}=39.4 Hz, P**C**H$_3$); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 12.03 (apparent broad d, J_{B-H}=63.6 Hz); TLC R_f 0.19 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 283 (M^+-BH_3, 3%) 125, 139 (100%), 147, 154, 283; exact mass calculated for $C_{17}H_{16}PS$ (M^+-BH_4) requires *m/z* 283.0710 found m/z 283.0768; separation of the enantiomers by chiral HPLC (CHIRALPAK® AD, flow rate 1.0 mL / min, 10% *i*-PrOH/ hexanes, t_R= 7.67 (major), (8.72 min) determined the enantiomeric excess to be >99%.

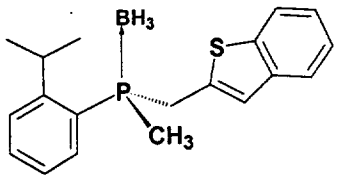


(S_P)-Benzo[*b*]thiophene-2-ylmethyl(2-methoxyphenyl) methyl-phosphine-borane (**4d**). *n*-Butyllithium (310 μL, 0.52 mmol, 1.6 M in hexanes, 1.1 eq) was added dropwise to a cooled (-78 °C) solution of (S_P)-Methyl-(2-methoxyphenyl)phosphine-borane (**3d**) (79 mg, 0.47 mmol) and THF (1.0 mL). The solution was stirred for 5 min and a solution of 2-chloromethylbenzo[*b*]thiophene in THF (1.0 mL) was added dropwise via cannula. The solution was allowed to stir for 10 h at -78 °C then water (1.0 mL) was added in one portion. The aqueous phase was extracted with ether (3 × 1 mL), the combined organic phases were washed with brine (3 mL), dried ($MgSO_4$), filtered (celite) and concentrated in vacuo. The yellow oil was then purified by flash column chromatography (gradient elution 0-5% ethyl acetate/ hexanes) yielding (S_P)-benzo[*b*]thiophene-2-ylmethyl-(2-methoxyphenyl)methylphosphine-borane (**4d**) (130 mg, 0.41 mmol, 88%) as a colorless oil. $[\alpha]_D^{24\ °C}$ +83 (c=1.00, THF); IR (film, NaCl) 3056, 2966, 2372 (broad, B-H), 1247 (C-O), 1062 (sharp), 901, 754 (broad) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.73 (ddd, *J*=13.8, 7.8, 1.7 Hz, 1H, Ar-**H**), 7.67- 7.60 (m, 2H, Ar-**H**), 7.48 (m, 1H, Ar-**H**), 7.29-7.14 (m, 2H, Ar-**H**), 7.03-6.92 (m, 2H, Ar-**H**), 3.95 (s, 3H, ArOC**H**$_3$), 3.73 (dd, J_{P-H}=14.6 Hz, *J*=11.7 Hz, 1H, PCH(**H**)Ar), 3.65 (dd, J_{P-H}=14.6 Hz, *J*=10.7 Hz, PCH(**H**)Ar), 1.63 (d, J_{P-H}=10.2 Hz, 1H, PC**H**$_3$), 0.78 (apparent q, J_{B-H}= Hz, 3H, PB**H**$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 161.4 (s, Ar**C**), 139.6 (d, J_{P-C}=12.5 Hz, Ar**C**), 136.2 (d, J_{P-C}=14.7 Hz, Ar**C**), 135.6 (d, J_{P-C}=6.8 Hz, Ar**C**), 133.9 (s, Ar**C**), 124.0 (s, Ar**C**), 123.7 (d, J_{P-C}=1.9 Hz, Ar**C**), 123.6 (s, Ar**C**), 122.9 (s, Ar**C**), 121.8 (s, Ar**C**),121.1 (d, J_{P-C}=12.2 Hz, Ar**C**), 115.3 (d, J_{P-C}=50.0 Hz, Ar**C**), 110.6 (s, Ar**C**), 110.5 (s, Ar**C**), 55.4 (s, $ArOCH_3$), 28.3 (d, J_{P-C}=35.1 Hz, PCH_2Ar), 9.7 (d, J_{P-C}=39 Hz, PCH_3); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 12.4 (broad apparent d, J_{B-P}=73.6 Hz); TLC R_f 0.25 (20% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 300 (M^+-BH_3, 32%) 77, 91, 107, 121, 147 (100%), 153, 166, 245, 283, 300; exact mass calculated for $C_{17}H_{17}OPS$ (M^+-BH_3) requires *m/z* 300.0738 found m/z 300.0733; separation of enantiomers with chiral HPLC (CHIRALPAK® AD, 10% *i*-PrOH/ hexanes, 1.0mL/ min, t_R= 8.6 (major), (10.7 min) demonstrated a ee of >99%.



(*S*$_P$)-benzyl(2-*i*-propylphenyl)methylphosphine-borane (**6**).

n-Butyllithium (280 μL, 0.51 mmol, 1.8 M, 1.1 eq) was added to a cooled (-78 °C) solution of (*S*$_P$)-(2-*i*-propylphenyl)methylphosphine-borane (**3b**) (84 mg, 0.47 mmol, 1.0 eq), HMPA (163 μL, 0.94 mmol, 2.0 eq) and THF (2.0 mL). The solution was allowed to stir for 5 min at -78 °C and benzyl bromide (61 μL, 51 mmol, 1.1 eq) was added dropwise. The reaction mixture stirred at -78 °C for 10 h, then water (1.0 mL) was added in one portion. The aqueous phase was extracted with ether (3 × 1 mL) and the combined organic phases were washed with brine then dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The crude solid was then purified by flash column chromatography (gradient elution 0-5% ethyl acetate/ hexanes) yielding (*S*$_P$)-benzyl(2-*i*-propylphenyl)methylphosphine-borane (**6**) (150 mg, 0.41 mmol, 81%) as a colorless solid. mp= 101.8-102.3 °C (cyclohexane), $[\alpha]_D^{23\ °C}$ -73° (c=1.02, sol. MeOH); IR (KBr) 3060, 2962, 2393 (B-H), 2355, 1063 (broad), 1024, 758, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ: 7.49-7.42 (m, 2H, Ar-**H**), 7.21-7.13 (m, 5H, Ar-**H**), 6.90-6.88 (m, 2H, Ar-**H**), 3.71 (p, *J*=6.9 Hz, 1H, Ar-C**H**$(CH_3)_2$), 3.35-3.22 (m, 2H, PC$\mathbf{H}_2$Ph), 1.44 (d, J_{P-H}=9.3 Hz, 3H, PC$\mathbf{H}_3$), 1.33 (d, *J*=6.9 Hz, 3H, C(C$\mathbf{H}_3$)), 1.28 (d, *J*=6.9 Hz, 3H, C(C$\mathbf{H}_3$)), 0.87 (very broad s, 3H, B$\mathbf{H}_3$); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 153.6 (d, J_{P-C}=9.8 Hz, Ar**C**), 132.7 (d, J_{P-C}=7.5 Hz, Ar**C**), 131.9 (d, J_{P-C}=7.8 Hz, Ar**C**), 131.7 (s, Ar**C**), 129.5 (d, J_{P-C}=4.0 Hz, Ar**C**), 128.3 (s, Ar**C**), 127.2 (d, J_{P-C}=8.4 Hz, Ar**C**), 126.9 (d, J_{P-C}=1.9 Hz, Ar**C**), 126.0 (d, J_{P-C}=49.9 Hz, Ar**C**), 125.9 (d, J_{P-C}=9.0 Hz, Ar**C**), 35.3 (d, J_{P-C}=30.2 Hz, PC$\mathbf{H}_2$Ph), 31.3 (d, J_{P-C}=6.2 Hz, Ar**C**), 24.8 (s, C(C$\mathbf{H}_3$)), 24.2 (s, C(C$\mathbf{H}_3$)), 10.2 (d, J_{P-C}=41.1 Hz, PC$\mathbf{H}_3$); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 8.5 (broad apparent d, J_{B-P}=68.8 Hz, Ar**C**); TLC R_f 0.34 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 256 (M^+-BH_3, 100%) 65, 91, 109, 133, 149, 165, 176, 213, 227, 241, 256 (100%); exact mass calculated for $C_{17}H_{12}P$ (M^+-BH_3) requires *m/z* 256.1381 found m/z 256.1377; separation of enantiomers with chiral HPLC (CHIRALPAK® AD, 3% *i*-PrOH/ hexanes, 1.0mL/ min, t_R= 5.57 (major), 6.10 (min) demonstrated a ee of >99%.



(S_P)-Benzo[*b*]thiophene-2-ylmethyl(2-*i*-propylphenyl)methyl-phosphineborane (**4b**). *n*-Butyllithium (280 μL, 0.51 mmol, 1.8 M, 1.1 eq) was added dropwise to a cooled (-78 °C) solution of (S_P)-(2-*i*-propylphenyl)methylphosphine-borane (**3b**) (83 mg, 0.46 mmol, 1.0 eq), HMPA (160 μL, 0.92 mmol, 2.0 eq) and THF (1.0 mL). The solution was allowed to stir for 5 min at -78 °C and a solution of 2-chloromethylbenzo[*b*]thiophene (93 mg, 51 mmol, 1.1 eq) in THF (1.0 mL) was added dropwise via cannula. The reaction mixture stirred at -78 °C for 10 h then water (1.0 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 1 mL) and the combined organic phases were washed with brine then dried ($MgSO_4$), filtered (silica gel) and concentrated in vacuo. The crude solid was then purified by flash column chromatography (gradient elution 0-2% ethyl acetate/ hexanes) yielding (S_P)-Benzo[*b*]thiophene-2-ylmethyl-(2-*i*-propylphenyl)methylphosphine-borane (**4b**) (147 mg, 0.41 mmol, 81%) as a colorless solid. mp=141-143 °C (5% ethyl acetate/ hexanes); $[\alpha]_D^{25\ °C}$ -119° (c=5.00, sol. THF); IR (KBr) 3055, 2965, 2379 (broad, B-H), 2348 (B-H), 1071 (broad), 912, 748 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.67-7.60 (m, 2H, Ar-**H**), 7.32-7.44 (m, 2H, Ar-**H**), 7.26-7.15 (m, 4H, Ar-**H**), 6.87 (d, *J*=2.4 Hz, 1H, Ar-**H**), 3.69 (apparent pen, *J*=6.6 Hz, 1H $ArCH(CH_3)_2$), 3.63 (dd, *J*=15.3 Hz, J_{P-H}=8.9 Hz, 1H, PC(**H**)HAr), 3.56 (dd, *J*=15.3 Hz, J_{P-H}=8.0 Hz, 1H, PC(**H**)HAr), 1.58 (d, J_{P-H}=9.3 Hz, 3H, PCH_3), 1.35 (d, *J*=6.6 Hz, 3H, C(CH_3)), 1.34 (d, *J*=6.6 Hz, 3H, C(CH_3), 0.97 (apparent broad d, J_{B-H}=97.5 Hz, 3H, BH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.7 (d, J_{P-C}=10.3 Hz, Ar**C**), 139.5 (s, Ar**C**), 135.0 (d, J_{P-C}=9.6 Hz, Ar**C**), 132.0 (d, J_{P-C}=11.8 Hz, Ar**C**), 132.0 (s, Ar**C**), 127.3 (d, J_{P-C}=8.6 Hz, Ar**C**), 126.1 (d, J_{P-C}=9.1 Hz, Ar**C**), 125.3 (d, J_{P-C}=49.7 Hz, Ar**C**), 124.3 (s, Ar**C**), 124.1 (s, Ar**C**), 123.9 (s, Ar**C**), 123.8 (s, Ar**C**), 123.0 (s, Ar**C**), 121.9 (s, Ar**C**), 31.5 (d, J_{P-C}=6.2 Hz, $ArCH(CH_3)_2$), 30.6 (d, J_{P-C}=30.5 Hz, PCH_2), 24.7 (s, C(CH_3)), 124.3 (s, AC(CH_3)), 10.4 (d, J_{P-C}=40.4 Hz, $APCH_3$); ^{31}P NMR ($CDCl_3$, 101 MHz)δ: 9.97 (d, J_{P-C}=61.5 Hz); TLC R_f 0.30 (10% ethyl acetate/ hexanes); LRMS: m/z (E. I.) 312 (M^+-BH_3, 58%) 77, 103, 115, 133, 147 (100%), 165, 176, 282, 297, 312; exact mass calculated for $C_{19}H_{21}PS$ (M^+-BH_3) requires *m/z* 312.1090 found m/z 312.1090; The % ee could not be determined by chiral HPLC (CHIRALPAK® AD or CHIRALCEL® OD-H columns) or chiral NMR shift reagents (europium

tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]) due to lack of resolution of enantiomers. The ee would be expected to be >99% by analogy to (S_P)-benzylmethylphenylphosphine-borane (**6**) (*vide supra*).