Catalytic Asymmetric Deprotonation of Phosphine Boranes and Sulfides as a Route to *P*-Stereogenic Compounds

Jonathan J. Gammon, Steven J. Canipa, Peter O'Brien, Brian Kelly and Sven Taylor

Department of Chemistry, University of York, Heslington, York YO10 5DD

Fax: +44 1904 432516; Tel: +44 1904 432535; E-mail: paob1@york.ac.uk

Full Experimental Procedures and Characterisation Data/NMR spectra:

General

Water is distilled water. Et_2O, THF and toluene were freshly distilled from benzophenone ketyl. (–)-Sparteine and diamine **3** were distilled from CaH_2 before use. Petrol refers to the fraction of petroleum ether with a boiling range of 40-60 °C. Brine refers to a saturated aqueous solution. All reactions were carried out under O_2 free Ar using oven-dried and/or flame-dried glassware. Flash column chromatography was carried out using Fluka Silica gel 60 (0.035-0.070 mm particle size). Thin layer chromatography was carried out using Merck F_{254} alumina-backed silica plates. Proton (400 MHz), carbon (100.6 MHz) and phosphorus (109 MHz) NMR spectra were recorded on a Jeol ECX-400 or a Jeol EX 270 instrument with internal deuterium lock. Chemical shifts are quoted as parts per million and referenced to $CHCl_3$ (7.27). Carbon and phosphorus NMR spectra were recorded with broadband proton decoupling. Carbon NMR spectra were assigned using DEPT experiments. Infra-red spectra were recorded on an ATI Matteson Genesis FT-IR spectrometer. Optical rotations were recorded at room temperature (20 °C) on a Jasco DIP-370 polarimeter (using the sodium D line; 259 nm) and $[\alpha]_D$ measurements are given in units of 10^{-1} deg cm^2 g^{-1}. Melting points were measured on a Gallenkamp melting point apparatus. Chiral stationary phase HPLC was performed on an Agilent 1200 series instrument and a multiple wavelength, UV/Vis diode array detector. *tert*-Butyldimethyl phosphine borane **1** was prepared according to a literature procedure.[1]

General Procedure A: Lithiation-substitution of *tert*-butyldimethylphosphine borane 1 using a stoichiometric amount of (–)-sparteine (1.2 eq.).

Alkyllithium (1.1 eq.) was added dropwise to a stirred solution of (–)-sparteine (1.2 eq.) in Et_2O (3 mL) at –78 ^oC under Ar. After stirring for 15 min at –78 ^oC, a solution of phosphine borane **1** (120 mg, 0.94 mmol) in Et_2O (2 mL) was added dropwise over 10 min *via* a syringe. The resulting solution was stirred at –78 ^oC for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added *via* a syringe and the resulting solution allowed to warm to rt over 16 h. 1 M $HCl_{(aq)}$ (10 mL) and EtOAc (10 mL) were added and the layers separated. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with 1 M $HCl_{(aq)}$ (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a yellow oil.

General Procedure B: Lithiation-substitution of *tert*-butyldimethylphosphine borane 1 using a substoichiometric amount of (–)-sparteine (0.2 eq.).

Alkyllithium (1.1 eq.) was added dropwise to a stirred solution of (–)-sparteine (0.2 eq.) in Et_2O (10 mL) at –78 ^oC under Ar. After stirring for 15 min at –78 ^oC, a solution of phosphine borane **1** (120 mg, 0.94 mmol) in Et_2O (5 mL) was added dropwise over 10 min *via* a syringe. The resulting solution was stirred at –78 ^oC for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added *via* a syringe and the resulting solution allowed to warm to rt over 16 h. 1 M $HCl_{(aq)}$ (10 mL) and EtOAc (10 mL) were added and the layers separated. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with 1 M $HCl_{(aq)}$ (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a yellow oil.

General Procedure C: Lithiation-substitution of *tert*-butyldimethylphosphine borane 1 using alkyllithium (1.1 eq.).

A solution of phosphine borane **1** (120 mg, 0.94 mmol) in Et_2O (2 mL) was added dropwise over 10 min *via* a syringe to a stirred solution of alkyllithium (1.1 eq.) in Et_2O (3 mL) at –78 ^oC under Ar. The resulting solution was stirred at –78 ^oC for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added *via* a syringe and the resulting solution allowed to warm to rt over 16 h. 1 M

$HCl_{(aq)}$ (10 mL) and EtOAc (10 mL) were added and the layers separated. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with 1 M $HCl_{(aq)}$ (10 mL), water (10 mL) and brine (10 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a yellow oil.

General Procedure D: Lithiation-substitution of *tert*-butyldimethylphosphine sulfide 4 using a stoichiometric amount of (–)-sparteine (1.2 eq.).

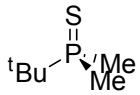
Alklyllithium (1.1 eq.) was added dropwise to a stirred solution of (–)-sparteine (1.2 eq.) in Et_2O (3 mL) at –78 ˚C under Ar. After stirring for 15 min at –78 ˚C, a solution of phosphine sulfide **4** (100 mg, 0.67 mmol) in Et_2O (10 mL) was added dropwise over 10 min *via* a syringe. The resulting solution was stirred at –78 ˚C for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added dropwise *via* a syringe and the resulting solution was allowed to warm to rt over 16 h. 1 M $HCl_{(aq)}$ (6 mL) was added and the mixture stirred for 15 min to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with 1 M $HCl_{(aq)}$ (5 mL), water (5 mL) and brine (5 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a colourless oil.

General Procedure E: Lithiation-substitution of *tert*-butyldimethylphosphine sulfide 4 using a substoichiometric amount of (–)-sparteine (0.05-0.2 eq.).

Alklyllithium (1.1 eq.) was added dropwise to a stirred solution of (–)-sparteine (0.05-0.2 eq.) in Et_2O (10 mL) at –78 ˚C under Ar. After stirring for 15 min at –78 ˚C, a solution of phosphine sulfide **4** (300 mg, 2.00 mmol) in Et_2O (20 mL) was added dropwise over 10 min *via* a syringe. The resulting solution was stirred at –78 ˚C for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added dropwise *via* a syringe and the resulting solution was allowed to warm to rt over 16 h. 1 M $HCl_{(aq)}$ (18 mL) was added and the mixture stirred for 15 min to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with 1 M $HCl_{(aq)}$ (15 mL), water (15 mL) and brine (15 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a colourless oil.

General Procedure F: Lithiation-substitution of *tert*-butyldimethylphosphine sulfide 4 using alkyllithium (1.1 eq.).

Alklyllithium (1.1 eq.) was added dropwise over 10 min *via* a syringe to a stirred solution of phosphine sulfide **4** (100 mg, 0.67 mmol) in Et_2O (15 mL) at −78 ˚C under Ar. The resulting solution was stirred at −78 ˚C for 3 h. Then, $Me_2PhSiCl$ (1.1 eq.) was added dropwise *via* a syringe and the resulting solution was allowed to warm to rt over 16 h. 1 M $HCl_{(aq)}$ (6 mL) was added and the mixture stirred for 15 min to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with 1 M $HCl_{(aq)}$ (5 mL), water (5 mL) and brine (5 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a colourless oil.



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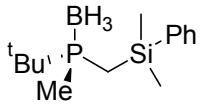
***tert*-Butyldimethylphosphine sulfide 4**

A solution of methylmagnesium bromide (55 mL of a 3 M solution in Et_2O, 164.0 mmol, 2.6 eq.) in THF (55 mL) was added to a stirred solution of *tert*-butyldichlorophosphine (10.0 g, 63.0 mmol, 1.0 eq.) in THF (100 mL) at −10 ˚C under Ar. The resulting heterogeneous mixture was stirred at rt for 5 h. Sulfur (2.6 g, 82.0 mmol, 1.3 eq.) was added and the mixture was heated at 80 ˚C for 5 min. After cooling to rt, the mixture was poured onto ice/water (120 mL) and conc. $HCl_{(aq)}$ (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (30 mL), water (30 mL) and brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a yellow solid. Purification by recrystallisation from hexane (50 mL) gave phosphine sulfide **4** (5.88 g, 62%) as a white solid, mp 206-207 ˚C (lit.,[2] 203 ˚C); R_F(4:1 petrol-EtOAc) 0.1; IR (NaCl) 3020, 2975, 1215, 940, 910, 755 (P=S), 670, 630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.64 (d, J = 12.5 Hz, 6H, PMe), 1.22 (d, J = 16.5 Hz, 9H, $PCMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 32.5 (d, J = 52.5 Hz, P*C*Me_3), 24.3 (PC*Me*$_3$), 16.3 (d, J = 51.5 Hz, PMe); $^{31}P\{1H\}$ NMR (109 MHz, $CDCl_3$) δ: 54.2; (EI) *m/z* 150 (M^+, 45), 94 (100), 79 (25), 57 (35), 41 (40); HRMS (EI) *m/z* calcd for $C_6H_{15}PS$ M^+ 150.0632, found 150.0629. Spectroscopic data consistent with that reported in the literature.[2]

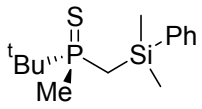


(*R*)-**5**

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(1.2 eq. (–)-sparteine, Table 1, entry 1)

Using general procedure **A**, (–)-sparteine (213 mg, 0.91 mmol) and *s*-BuLi (0.63 mL of a 1.32 M solution in cyclohexane, 0.83 mmol) in Et_2O (2 mL), phosphine borane **1** (100 mg, 0.76 mmol) in Et_2O (3 mL) and $Me_2PhSiCl$ (0.14 mL, 0.83 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (149 mg, 74%, 92:8 er) as a colourless oil which slowly crystallised to a white solid, mp 40-42 ^oC; $[\alpha]_D$ +8.1 (*c* 1.00 in $CHCl_3$); R_F(4:1 petrol-EtOAc) 0.3; IR (NaCl) 2960, 2375, 1426, 1265, 1114, 1060, 904, 887, 822, 738, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.54 (m, 2H, Ph), 7.40-7.38 (m, 3H, Ph), 1.12 (d, *J* = 13.5 Hz, 9H, CMe_3), 1.06-0.97 (m, 2H, PCH_2), 1.00 (d, *J* = 10.0 Hz, 3H, PMe), 0.56 (s, 3H, SiMe), 0.52 (q, *J* = 93.0 Hz, 3H, BH_3), 0.50 (s, 3H, SiMe); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.4 (d, *J* = 4.5 Hz, *ipso*-Ph), 133.5 (Ph), 129.4 (Ph), 128.0 (Ph), 28.3 (d, *J* = 33.0 Hz, *C*Me_3), 24.5 (d, *J* = 2.5 Hz, C*Me*$_3$), 7.6 (d, *J* = 21.5 Hz, PCH_2), 7.2 (d, *J* = 35.5 Hz, PMe), –0.4 (d, *J* = 2.5 Hz, SiMe), –1.5 (SiMe); MS (ESI, NH_3) *m*/*z* 265 [$(M - H)^+$]; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{28}BPSi$ $(M - H)^+$ 265.1713, found 265.1706; HPLC: Daicel Chiracel OD, 1:99 v/v *i*PrOH-hexane, 0.1 mL min^{-1}, 254 nm, 52.7 min [(*R*)-**5**], 56.3 min [(*S*)-**5**].



(*S*)-**6**

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(1.2 eq. (–)-sparteine, Table 1, entry 2)

Using general procedure **D**, (−)-sparteine (204 mg, 0.87 mmol) and *s*-BuLi (0.60 mL of a 1.32 M solution in cyclohexane, 0.80 mmol) in Et_2O (2 mL), phosphine sulfide **4** (109 mg, 0.73 mmol) in Et_2O (7 mL) and $Me_2PhSiCl$ (135 mg, 0.80 mmol) gave the crude product as a

colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (153 mg, 74%, 84:16 er) as a colourless oil, R_F(4:1 petrol-EtOAc) 0.4; $[\alpha]_D$ +30.1 (*c* 1.15 in $CHCl_3$); IR (NaCl) 3070, 2960, 1460, 1425, 1365, 1295, 1250, 1110, 885, 820, 735, 710, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.56 (m, 2H, Ph), 7.38-7.36 (m, 3H, Ph), 1.49-1.38 (m, 1H, PCH_AH$_B$), 1.37 (d, *J* = 12.0 Hz, 3H, PMe), 1.26-1.18 (m, 1H, PCH$_A$$H_B$), 1.18 (d, *J* = 16.5 Hz, 9H, $PCMe_3$), 0.63 (s, 3H, SiMe), 0.53 (s, 3H, SiMe); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 138.7 (d, *J* = 4.5 Hz, *ipso*-Ph), 134.0 (Ph), 129.8 (Ph), 128.3 (Ph), 34.6 (d, *J* = 50.5 Hz, *C*Me_3), 24.5 (d, *J* = 12.0 Hz, CMe_3), 16.6 (d, *J* = 51.5 Hz, PMe), 15.7 (d, *J* = 39.0 Hz, PCH_2), –0.2 (d, *J* = 3.5 Hz, SiMe), –1.3 (SiMe); $^{31}P\{1H\}$ NMR (109 MHz, $CDCl_3$) δ: 56.8; MS (EI) *m/z* 284 (M^+, 20), 269 [$(M - Me)^+$, 15], 227 [$(M - CMe_3)^+$, 30], 207 [$(M - Ph)^+$, 10], 150 [$(M - SiMe_2Ph)^+$, 100], 135 [$(M - CH_2SiMe_2Ph)^+$, 60]; HRMS (EI) *m/z* calcd for $C_{14}H_{25}PSSi$ M^+ 284.1184, found 284.1186; HPLC: Daicel Chiracel OD, 99:1 v/v hexane-*i*PrOH, 0.4 mL min^{-1}, 230 nm, 16.8 min [(*S*)-**6**], 19.5 min [(*R*)-**6**].

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(0.2 eq. (–)-sparteine, Table 1, entry 3)

Using general procedure **B**, (–)-sparteine (70 mg, 0.30 mmol) and *s*-BuLi (1.24 mL of a 1.32 M solution in cyclohexane, 1.64 mmol) in Et_2O (10 mL), phosphine borane **1** (197 mg, 1.49 mmol) in Et_2O (5 mL) and $Me_2PhSiCl$ (0.28 mL, 1.64 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (302 mg, 76%, 74:26 er) as a colourless oil which slowly crystallised to a white solid, $[\alpha]_D$ +4.6 (*c* 1.05 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.2 eq. (–)-sparteine, Table 1, entry 4)

Using general procedure **E**, (–)-sparteine (95 mg, 0.41 mmol, 0.2 eq.) and *s*-BuLi (1.72 mL of a 1.32 M solution in cyclohexane, 2.28 mmol) in Et_2O (2 mL), phosphine sulfide **4** (310 mg, 2.07 mmol) in Et_2O (14 mL) and $Me_2PhSiCl$ (388 mg, 2.28 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as

eluent gave adduct (*S*)-**6** (439 mg, 75%, 60:40 er) as a colourless oil, $[\alpha]_D$ +9.4 (*c* 1.10 in $CHCl_3$).

***rac*-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane *rac*-5**

(no ligand, Table 1, entry 5)

Using general procedure **C**, *s*-BuLi (0.63 mL of a 1.32 M solution in cyclohexane, 0.83 mmol) in Et_2O (2 mL), phosphine borane **1** (100 mg, 0.76 mmol) in Et_2O (3 mL) and $Me_2PhSiCl$ (0.14 mL, 0.83 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct *rac*-**5** (141 mg, 70%) as a colourless oil which slowly crystallised to a white solid.

***rac*-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane *rac*-6**

(no ligand, Table 1, entry 6)

Using general procedure **F**, *s*-BuLi (0.56 mL of a 1.32 M solution in cyclohexane, 0.73 mmol), phosphine sulfide **4** (100 mg, 0.67 mmol, 1.0 eq.) in Et_2O (7 mL) and $Me_2PhSiCl$ (125 mg, 0.73 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct *rac*-**6** (156 mg, 83%) as a colourless oil.

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(1.2 eq. (–)-sparteine, Table 1, entry 7)

Using general procedure **A**, (–)-sparteine (265 mg, 1.13 mmol) and *n*-BuLi (0.46 mL of a 2.25 M solution in hexanes, 1.04 mmol) in Et_2O (2 mL), phosphine borane **1** (124 mg, 0.94 mmol) in Et_2O (3 mL) and $Me_2PhSiCl$ (0.17 mL, 1.04 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (191 mg, 76%, 89:11 er) as a colourless oil which slowly crystallised to a white solid.

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(1.2 eq. (–)-sparteine, Table 1, entry 8) and

Using general procedure **D**, (–)-sparteine (187 mg, 0.80 mmol, 1.2 eq.) and *n*-BuLi (0.33 mL of a 2.25 M solution in hexanes, 0.73 mmol, 1.1 eq.) in Et_2O (2 mL), phosphine sulfide **4** (100 mg, 0.67 mmol, 1.0 eq.) in Et_2O (7 mL) and $Me_2PhSiCl$ (125 mg, 0.73 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (167 mg, 88%, 88:12 er) as a colourless oil.

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(0.2 eq. (–)-sparteine, Table 1, entry 9)

Using general procedure **B**, (–)-sparteine (117 mg, 0.50 mmol) and *n*-BuLi (1.14 mL of a 2.40 M solution in hexanes, 2.75 mmol) in Et_2O (10 mL), phosphine borane **1** (329 mg, 2.50 mmol) in Et_2O (5 mL) and $Me_2PhSiCl$ (0.46 mL, 2.75 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (138 mg, 21%, 84:16 er) as a colourless oil which slowly crystallised to a white solid.

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.2 eq. (–)-sparteine, Table 1, entry 10) and (0.2 eq. (–)-sparteine, Table 2, entry 2)

Using general procedure **E**, (–)-sparteine (87 mg, 0.37 mmol, 0.2 eq.) and *n*-BuLi (0.91 mL of a 2.25 M solution in hexanes, 2.04 mmol, 1.1 eq.) in Et_2O (2 mL), phosphine sulfide **4** (278 mg, 1.86 mmol) in Et_2O (14 mL) and $Me_2PhSiCl$ (349 mg, 2.04 mmol) gave the crude product as colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (432 mg, 82%, 83:17 er) as a colourless oil, $[\alpha]_D$ +26.4 (*c* 0.95 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(no ligand, Table 1, entry 12) and (Table 2, entry 5)

Using general procedure **F**, *n*-BuLi (0.32 mL of a 2.25 M solution in hexanes, 0.73 mmol, 1.1 eq.), phosphine sulfide **4** (100 mg, 0.67 mmol, 1.0 eq.) in Et_2O (7 mL) and $Me_2PhSiCl$ (125 mg, 0.73 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct *rac*-**6** (85 mg, 45%) as a colourless oil.

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(1.2 eq. (–)-sparteine, Table 1, entry 14)

Using general procedure **D**, (–)-sparteine (180 mg, 0.77 mmol) and Me_3SiCH_2Li (0.70 mL of a 1 M solution in pentane, 0.70 mmol) in Et_2O (2 mL), phosphine sulfide **4** (96 mg, 0.64 mmol) in Et_2O (7 mL) and $Me_2PhSiCl$ (120 mg, 0.70 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (167 mg, 92%, 88:12 er) as a colourless oil, $[\alpha]_D$ +32.1 (*c* 1.05 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.2 eq. (–)-sparteine, Table 1, entry 15)

Using general procedure **E**, (–)-sparteine (91 mg, 0.39 mmol) and Me_3SiCH_2Li (2.14 mL of a 1 M solution in pentane, 2.14 mmol) in Et_2O (2 mL), phosphine sulfide **4** (291 mg, 1.94 mmol) in Et_2O (14 mL) and $Me_2PhSiCl$ (364 mg, 2.14 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (435 mg, 79%, 82:18 er) as a colourless oil, $[\alpha]_D$ +27.1 (*c* 1.00 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(no ligand, Table 1, entry 16)

Using general procedure **F**, Me_3SiCH_2Li (0.73 mL of a 1 M solution in pentane, 0.73 mmol, 1.1 eq.) and phosphine sulfide **4** (100 mg, 0.67 mmol, 1.0 eq.) in Et_2O (7 mL) and $Me_2PhSiCl$ (125 mg, 0.73 mmol) gave the crude product as a clear oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct *rac*-**6** (33 mg, 18%) as a colourless oil.

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.1 eq. (–)-sparteine, Table 2, entry 3)

Using general procedure **E**, (−)-sparteine (80 mg, 0.34 mmol) and *n*-BuLi (1.56 mL of a 2.4 M solution in hexanes, 3.74 mmol) in Et_2O (2 mL), phosphine sulfide **4** (512 mg, 3.40 mmol) in Et_2O (25 mL) and $Me_2PhSiCl$ (640 mg, 3.74 mmol, 1.1 eq.) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (714 mg, 74%, 84:16 er) as a colourless oil, $[\alpha]_D$ +28.1 (*c* 1.10 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.05 eq. (–)-sparteine, Table 2, entry 4)

Using general procedure **E**, (−)-sparteine (48 mg, 0.20 mmol) and *n*-BuLi (1.8 mL of a 2.5 M solution in hexanes, 4.51 mmol) in Et_2O (2 mL), phosphine sulfide **4** (615 mg, 4.10 mmol, 1.0 eq.) in Et_2O (25 mL) and $Me_2PhSiCl$ (771 mg, 4.51 mmol, 1.1 eq.) gave the crude product as a clear oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (1.021 g, 88%, 74:26 er) as a colourless oil, $[\alpha]_D$ +22.6 (*c* 0.90 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(1.2 eq. (–)-sparteine, toluene, Table 2, entry 6)

Using general procedure **D**, (–)-sparteine (197 mg, 0.84 mmol) and *n*-BuLi (0.32 mL of a 2.4 M solution in hexanes, 0.77 mmol) in toluene (2 mL) phosphine sulfide **4** (105 mg, 0.70 mmol) in toluene (7 mL) and $Me_2PhSiCl$ (132 mg, 0.77 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (180 mg, 90%, 89:11 er) as a colourless oil, $[\alpha]_D$ +28.5 (*c* 1.00 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(0.2 eq. (–)-sparteine, toluene, Table 2, entry 7)

Using general procedure **E**, (–)-sparteine (90 mg, 0.38 mmol, 0.2 eq.) and *n*-BuLi (0.88 mL of a 2.4 M solution in hexanes, 2.10 mmol) in toluene (2 mL), phosphine sulfide **4** (288 mg, 1.90 mmol) in toluene (14 mL) and $Me_2PhSiCl$ (359 mg, 2.1 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (479 mg, 89%, 83:17 er) as a colourless oil, $[\alpha]_D$ +28.8 (*c* 1.10 in $CHCl_3$).

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

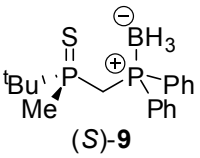
(0.05 eq. (–)-sparteine, toluene, Table 2, entry 8)

Using general procedure **E**, (–)-sparteine (27 mg, 0.125 mmol) and *n*-BuLi (1.00 mL of a 2.5 M solution in hexanes, 2.50 mmol) in toluene (2 mL), phosphine sulfide **4** (346 mg, 2.31 mmol) in toluene (8 mL) and $Me_2PhSiCl$ (430 mg, 2.51 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct (*S*)-**6** (576 mg, 88%, 85:15 er) as a colourless oil.

(*S*)-*tert*-Butylmethylphosphinothioyl(methyl)dimethylphenylsilane (*S*)-6

(no ligand, toluene, Table 2, entry 9)

Using general procedure **F**, *n*-BuLi (0.30 mL of a 2.4 M solution in hexanes, 0.73 mmol) and phosphine sulfide **4** (100 mg, 0.67 mmol) in toluene (7 mL) and $Me_2PhSiCl$ (124 mg, 0.73 mmol) gave the crude product as a colourless oil. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave adduct *rac*-**6** (102 mg, 54%) as a colourless oil and recovered phosphine sulfide **4** (40 mg, 40%) as a white solid.

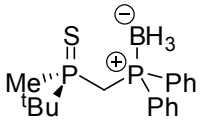


(*S*)-**9**

(*S*)-*tert*-Butylmethylphosphinesulfide-diphenylphosphinomethaneborane (*S*)-9

n-BuLi (0.88 mL of a 2.4 M solution in hexanes, 2.1 mmol) was added dropwise to a stirred solution of (–)-sparteine (25 mg, 0.11 mmol) in toluene (5 mL) at −78 ˚C under Ar. After stirring for 15 min at −78 ˚C, a solution of phosphine sulfide **4** (316 mg, 2.1 mmol) in toluene (21 mL) was added dropwise over 20 min *via* a syringe. The resulting mixture was stirred at −78 ˚C for 3 h. Then, chlorodiphenylphosphine (463 mg, 2.1 mmol) was added dropwise *via* a syringe and the resulting solution was allowed to warm to rt over 16 h. The solution was cooled to 0 ˚C and $BH_3.Me_2S$ (1.6 mL of a 2.0 M solution in THF, 3.15 mmol) was added dropwise *via* a syringe. After stirring at rt for 3 h, 1 M $HCl_{(aq)}$ (15 mL) was added slowly over 10 min (CAUTION – vigorous effervescence) and the resulting mixture was stirred for 15 min at rt to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (20 mL), water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography with toluene then 90:10 toluene-EtOAc as eluent gave adduct (*S*)-**9** (566 mg, 77%, 85:15 er) as a white crystalline solid, mp 176-177 °C; $[\alpha]_D$ −26.3 (*c* 0.93 in $CHCl_3$); R_F(90:10 toluene-EtOAc) 0.5; IR (NaCl) 2960, 2380, 1464, 1437, 1365, 1159, 1104, 1057, 892, 793, 740, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86 (ddd, J = 11.5, 8.5, 1.0 Hz, 2H, Ph), 7.56 (ddd, J = 11.0, 8.0, 1.5 Hz, 2H, Ph), 7.48-7.29 (m, 6H, Ph), 2.92 (q, J = 14.5 Hz, 1H, PCH_AH_B), 2.64 (ddd, J = 14.5, 10.5, 9.0 Hz, 1H, PCH_AH_B), 1.56 (d, J = 12.5 Hz, 3H, PMe), 1.14 (d, J = 17.0

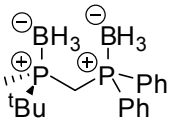
Hz, 9H, CMe_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 133.5 (d, *J* = 10.5 Hz, Ph), 132.0 (d, *J* = 2.5 Hz, Ph), 131.5 (d, *J* = 9.5 Hz, Ph), 131.3 (d, *J* = 2.5 Hz, Ph), 131.1 (d, *J* = 56.5 Hz, *ipso*-Ph), 131.2, (d, *J* = 56.5 Hz, *ipso*-Ph), 128.9 (d, *J* = 10.0 Hz, Ph), 128.7 (d, *J* =10.5 Hz, Ph), 54.2 (dd, *J* = 51.0, 3.0 Hz, P*C*Me_3), 25.9 (dd, *J* = 36.0, 24.5 Hz, PCH_2), 24.1 (d, *J* = 2.0 Hz, PC*Me*$_3$), 15.6 (d, *J* = 55.0 Hz, PMe); $^{31}P\{1H\}$ NMR (161 MHz, $CDCl_3$) δ: 56.0 ($PCMe_3$), 15.3 (PPh_2); MS (ESI) *m/z* 349 [$(M + H)^+$, 95], 347 [$(M – H)^+$, 100]; HRMS (ESI) *m/z* calcd for $C_{18}H_{28}BP_2S$ $(M + H)^+$ 349.1475, found 349.1467; HPLC: Daicel Chiracel AD, 99:1 v/v hexane-*i*PrOH, 1.0 mL min^{-1}, 28.0 min [(*S*)-**9**], 34.3 min [(*R*)-**9**].



(*R*)-**9**

(*R*)-*tert*-Butylmethylphosphinesulfide-diphenylphosphinomethaneborane (*R*)-9

n-BuLi (0.88 mL of a 2.4 M solution in hexanes, 2.1 mmol, 1.0 eq.) was added dropwise to a stirred solution of diamine **3** (25 mg, 0.11 mmol, 0.05 eq.) in toluene (5 mL) at −78 ˚C under Ar. After stirring at −78 ˚C for 15 min, a solution of phosphine sulfide **4** (316 mg, 2.1 mmol, 1.0 eq.) in toluene (21 mL) was added dropwise over 20 min *via* a syringe. The resulting mixture was stirred at −78 ˚C for 3 h. Then, chlorodiphenylphosphine (463mg, 2.1 mmol, 1.0 eq.) was added dropwise *via* a syringe and the mixture was allowed to slowly warm to rt over 16 h. The solution was cooled to 0 ˚C and $BH_3.Me_2S$ (1.7 mL of a 2.0 M solution in THF, 3.3 mmol) was added dropwise *via* a syringe. After stirring at rt for 3 h, 1 M $HCl_{(aq)}$ (15 mL) was added slowly over 10 min (CAUTION – vigorous effervescence) and the resulting mixture was stirred for 15 min at rt to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (20 mL), water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography with toluene then 90:10 toluene-EtOAc as eluent gave adduct (*R*)-**9** (658 mg, 86%, 78:22 er) as a white crystalline solid, $[\alpha]_D$ +19.1 (*c* 1.05 in $CHCl_3$). A sample of the product (353 mg) was recrystallised from chloroform-petrol to give adduct *rac*-**9** (184 mg, 52%, 50:50 er) as white needles. The filtrate was evaporated under reduced pressure to give adduct (*R*)-**9** (169 mg, 48%, 99:1 er) as a white crystalline solid, mp 156-157 °C.

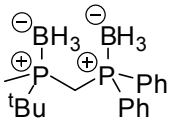


(*S*)-**10**

(*S*)-*tert*-Butylmethylphosphineborane-diphenylphosphinomethaneborane (*S*)-10

Si_2Cl_6 (1.73 mL of a 1.86 M solution in toluene, 3.22 mmol) was added dropwise to a stirred solution of phosphine sulfide (*R*)-**9** (150 mg, 0.43 mmol, 78:22 er) in toluene (15 mL) at rt under Ar. The resulting solution was stirred and heated at 80 ˚C for 2 h. After cooling to rt, the solution was added dropwise *via* cannula to degassed 30% w/w $NaOH_{(aq)}$ (15 mL) under Ar at 0 ˚C. The resulting solution was stirred and heated at 50 ˚C until the aqueous layer became clear. The organic top layer was transferred *via* cannula to a flame-dried flask. The remaining aqueous layer was extracted with degassed toluene (10 mL) and the organic top layer was transferred *via* cannula to the same flame-dried flask. This process was repeated twice (2 × 10 mL of degassed toluene). The combined organic extracts were washed with degassed 30% w/w $NaOH_{(aq)}$ (10 mL) under Ar and the organic top layer was transferred *via* cannula to a flame-dried flask containing $MgSO_4$. The solution was then transferred *via* cannula to a flame-dried flask and $BH_3.Me_2S$ (0.65 mL of a 2.0 M solution in THF, 1.3 mmol) was added dropwise *via* a syringe. The resulting solution was stirred at rt for 2 h. Then, 1 M $HCl_{(aq)}$ (15 mL) was added slowly over 10 min and the resulting mixture was stirred for 15 min at rt to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (20 mL), water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography with 95:5 petrol-EtOAc then 85:15 petrol-EtOAc as eluent gave adduct (*S*)-**10** (125 mg, 88%, 79:21 er) as a white crystalline solid, mp 167-169 ˚C; $[\alpha]_D$ +13.5 (*c* 1.15 in $CHCl_3$); R_F(80:20 petrol-EtOAc) 0.4; IR (NaCl) 2959, 2383, 2343, 1464, 1437, 1368, 1165, 1105, 1062, 895, 809, 740, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.91-7.85 (m, 2H, Ph), 7.65-7.41 (m, 8H, Ph), 2.74 (td, *J* = 15.0, 6.5 Hz, 1H, PC$H_A$$H_B$), 2.35 (ddd, *J* = 15.0, 13.0, 10.0 Hz, 1H, PC$H_A$$H_B$), 1.31 (d, *J* = 10.0 Hz, 3H, PMe), 1.19 (d, *J* = 14.0 Hz, 9H, CMe_3), 1.07- –0.26 (m, 6H, PBH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 133.2 (d, *J* = 10.0 Hz, Ph), 132.2 (d, *J* = 2.5 Hz, Ph), 131.3 (d, *J* = 9.5 Hz, Ph), 131.2 (d, *J* = 2.5 Hz, Ph), 129.0 (d, *J* = 4.5 Hz, Ph), 128.8 (d, *J* = 5.0 Hz, Ph), 126.7 (d, *J* = 56.0 Hz, *ipso*-Ph), 28.9 (dd, *J* = 32.0, 3.5 Hz, P*C*Me_3), 24.8 (d, *J* = 2.5 Hz, PC*Me*$_3$), 18.2 (t, *J* = 25.5 Hz, PCH_2), 6.0 (d, *J* = 33.5 Hz,

PMe); ^{31}P NMR (109.3 MHz, $CDCl_3$) δ: 29.5 (d, J = 65.5 Hz, Ph_2PBH_3), 14.9 (d, J = 65.5 Hz, ^{t}BuPBH$_3$); MS (ESI) *m/z* 353 [(M + Na)$^+$, 100]; HRMS (ESI) *m/z* calcd for $C_{18}H_{30}B_2P_2$ (M + Na)$^+$ 353.1907, found 353.1901; HPLC: Daicel Chiracel OD, 98:2 v/v hexane-*i*PrOH, 1.0 mL min^{-1}, 9.1 min [(*S*)-**10**], 10.3 min [(*R*)-**10**].

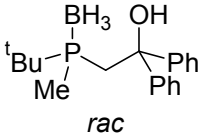


rac-**10**

***rac-tert*-Butylmethylphosphineborane-diphenylphosphinomethaneborane *rac*-10**

s-BuLi (0.77 mL of a 1.3 M solution in cyclohexane, 1.0 mmol) was added dropwise to a stirred solution of phosphine borane **1** (132 mg, 1.0 mmol) in THF (14 mL) at 0 ˚C under Ar. The resulting mixture was stirred at 0 ˚C for 1 h. Then, chlorodiphenylphosphine (220 mg, 1.0 mmol) was added and the solution was stirred at 0 ˚C for 2 h. Then, $BH_3.Me_2S$ (0.55 mL of a 2.0 M solution in THF, 1.1 mmol) was added dropwise. After stirring at rt for 3 h, 1 M $HCl_{(aq)}$ (15 mL) was added slowly over 10 min and the resulting mixture was stirred for 15 min at rt to give a homogeneous biphasic solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (20 mL), water (20 mL) and brine (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product as a white solid. Purification by flash chromatography with 95:5 petrol-EtOAc then 85:15 petrol-EtOAc as eluent gave adduct *rac*-**10** (251 mg, 76%) as a white crystalline solid, mp 174-177 ˚C.

Experimental for the reactions referred to in the references.



rac

***rac-P*-(2,2-Diphenyl-2-hydroxyethyl)-*P*-methyl-*tert*-butyl-phosphine borane**

(Reference 12, 1.1 eq. *n*-BuLi, –50 ^{o}C)

Using general procedure **C**, *n*-BuLi (0.39 mL of a 2.14 M solution in hexanes, 0.83 mmol) in Et_2O (2 mL), phosphine borane **1** (100 mg, 0.76 mmol) in Et_2O (3 mL) and benzophenone (152 mg, 0.83 mmol) in Et_2O (3 mL) at –50 ^{o}C gave the crude product as a white solid.

Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave the title compound (27 mg, 11%) as a white solid, R_F(4:1 petrol-EtOAc) 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.46 (m, 4H, Ph), 7.35-7.29 (m, 4H, Ph), 7.26-7.20 (m, 2H, Ph), 4.58 (s, 1H, OH), 2.88 (t, J = 14.5 Hz, 1H, PCH_AH$_B$), 2.67 (dd, J = 14.5 Hz, 6.5 Hz, 1H, PCH$_A$$H_B$), 1.17 (d, J = 13.5 Hz, 9H, CMe_3), 0.74 (d, J = 10.0 Hz, 3H, PMe), 0.88-0.23 (m, 3H, BH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 147.7 (d, J = 8.5 Hz, *ipso*-Ph), 145.3 (d, J = 1.5 Hz, *ipso*-Ph), 128.3 (Ph), 128.2 (Ph), 127.2 (Ph), 125.3 (Ph), 34.2 (d, J = 28.5 Hz, PCH_2), 28.0 (d, J = 36.0 Hz, CMe_3), 24.7 (d, J = 2.5 Hz, CMe_3), 6.5 (d, J = 34.5 Hz, PMe) (some aromatic signals not resolved and one carbon overlaps with $CDCl_3$). Spectroscopic data consistent with that reported in the literature.[3]

***rac*-*P*-(2,2-Diphenyl-2-hydroxyethyl)-*P*-methyl-*tert*-butyl-phosphine borane**

(Reference 12, 1.1 eq. *n*-BuLi, –42 °C)

Using general procedure **C**, *n*-BuLi (0.35 mL of a 2.14 M solution in hexanes, 0.74 mmol) in Et_2O (2 mL) phosphine borane **1** (89 mg, 0.68 mmol) in Et_2O (3 mL) and benzophenone (135 mg, 0.74 mmol) in Et_2O (3 mL) at –42 °C gave the crude product as a white solid. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave the title compound (61 mg, 29%) as a white solid.

***rac*-*P*-(2,2-Diphenyl-2-hydroxyethyl)-*P*-methyl-*tert*-butyl-phosphine borane**

(Reference 12, 1.1 eq. *n*-BuLi, 0 °C)

Using general procedure **C**, *n*-BuLi (0.27 mL of a 2.45 M solution in hexanes, 0.67 mmol) in Et_2O (2 mL) phosphine borane **1** (80 mg, 0.61 mmol) in Et_2O (3 mL) and benzophenone (121 mg, 0.67 mmol) in Et_2O (3 mL) at 0 °C gave the crude product as a white solid. Purification by flash chromatography with 19:1 petrol-EtOAc as eluent gave the title compound (97 mg, 51%) as a white solid.

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(Reference 14, 0.2 eq. (–)-sparteine, –50 °C)

Using general procedure **B**, (–)-sparteine (94 mg, 0.41 mmol) and *n*-BuLi (0.92 mL of a 2.40 M solution in hexanes, 2.21 mmol) in Et_2O (10 mL), phosphine borane **1** (264 mg, 2.01 mmol) in Et_2O (5 mL) and $Me_2PhSiCl$ (0.37 mL, 2.21 mmol) gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (262 mg, 49%, 80:20 er) as a colourless oil which slowly crystallised to a white solid.

(*R*)-*tert*-Butylmethylphosphineborane(methyl)dimethylphenylsilane (*R*)-5

(Reference 15, 1.2 eq. (–)-sparteine)

Using general procedure **A**, (–)-sparteine (213 mg, 0.91 mmol) and Me_3SiCH_2Li (0.83 mL of a 1.00 M solution in pentane, 0.83 mmol) in Et_2O (10 mL), phosphine borane **1** (100 mg, 0.76 mmol) in Et_2O (5 mL) and $Me_2PhSiCl$ (0.14 mL, 0.83 mmol) at –20 °C gave the crude product as a yellow oil. Purification by flash chromatography with 98:2 petrol-Et_2O as eluent gave adduct (*R*)-**5** (151 mg, 75%, 75:25 er) as colourless oil which slowly crystallised to a white solid, $[\alpha]_D$ +0.6 (*c* 1.10 in $CHCl_3$).

References

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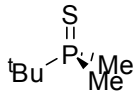
2. G. Haegele and W. Kuchen, W. *Chem. Ber.* 1970, **103**, 2885.

3. M. J. Johansson, L. Schwartz, M. Amedjkouh and N. Kann, *Tetrahedron: Asymmetry* 2004, **15**, 3531.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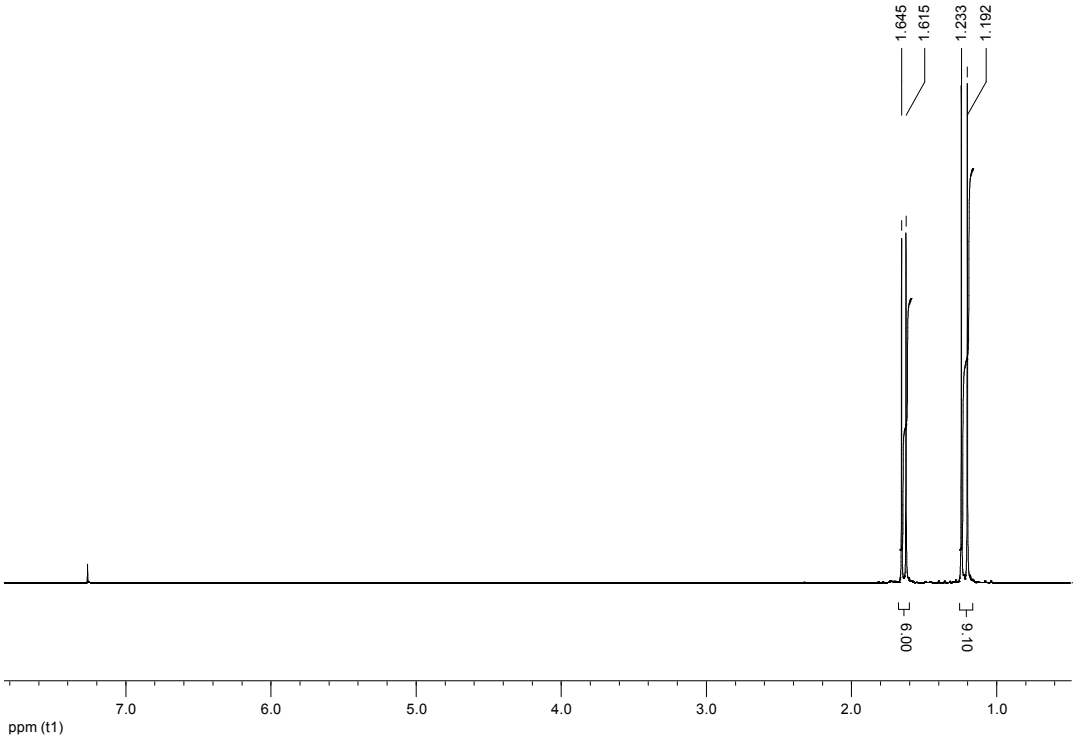
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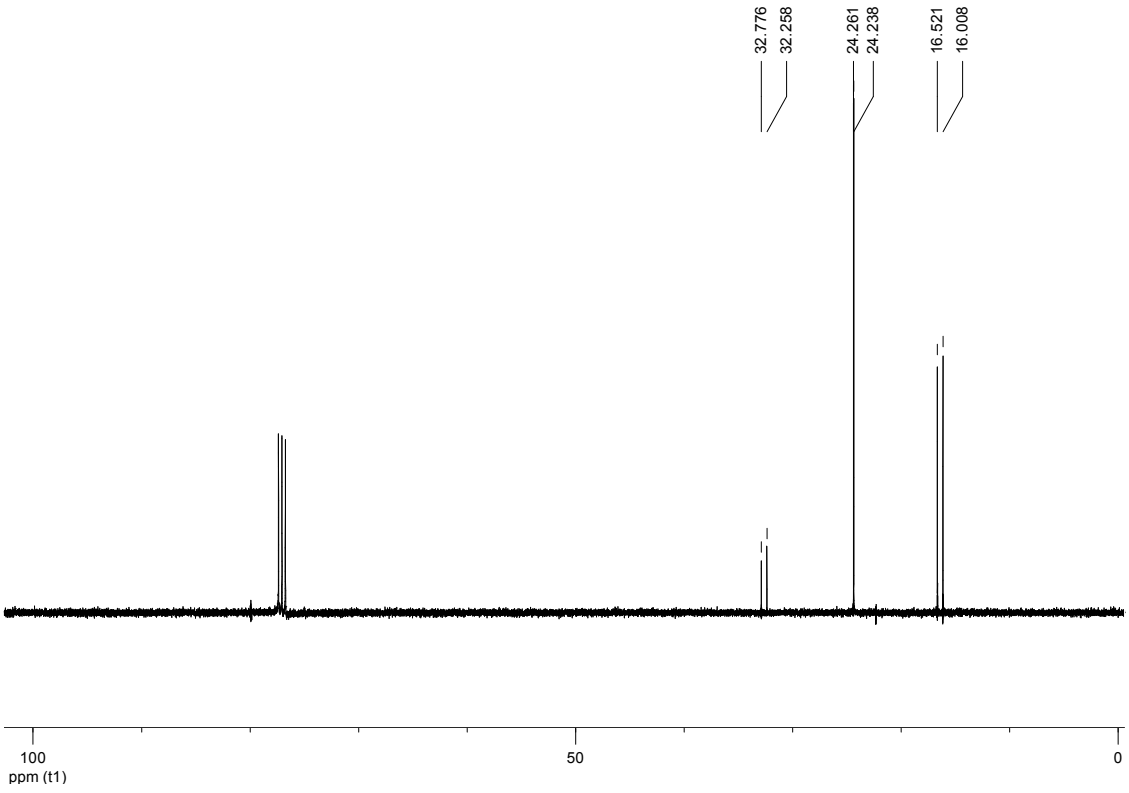
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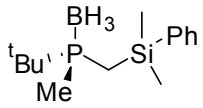
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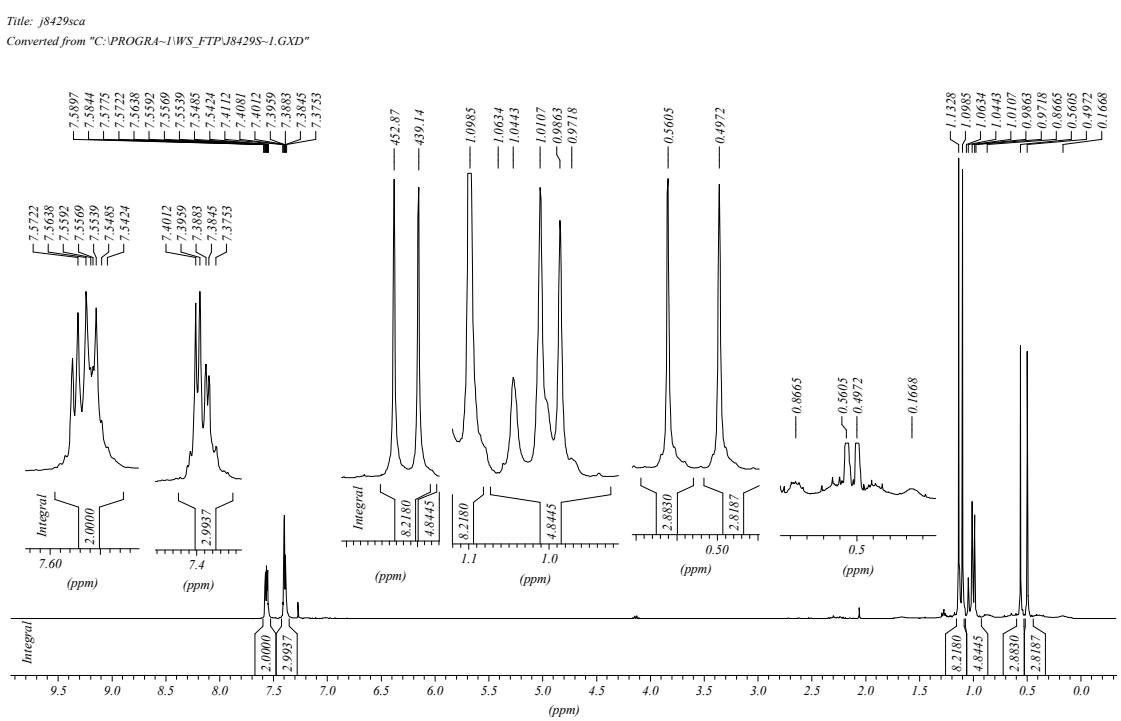
(*R*)-**5**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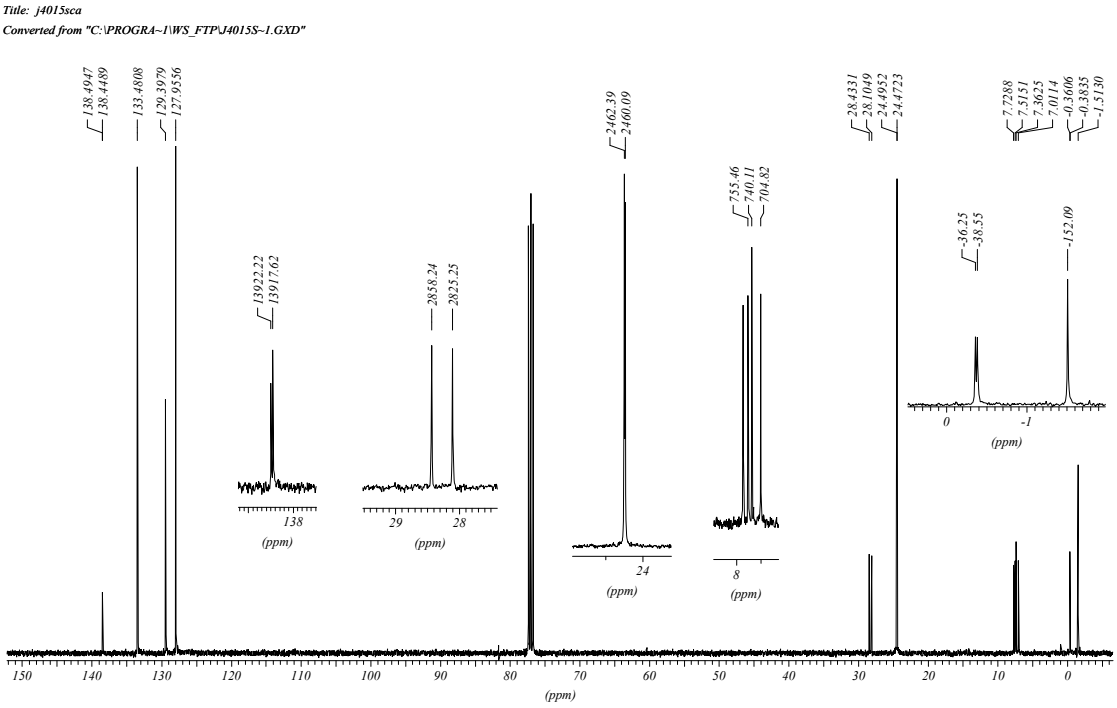
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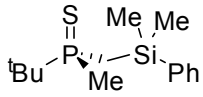
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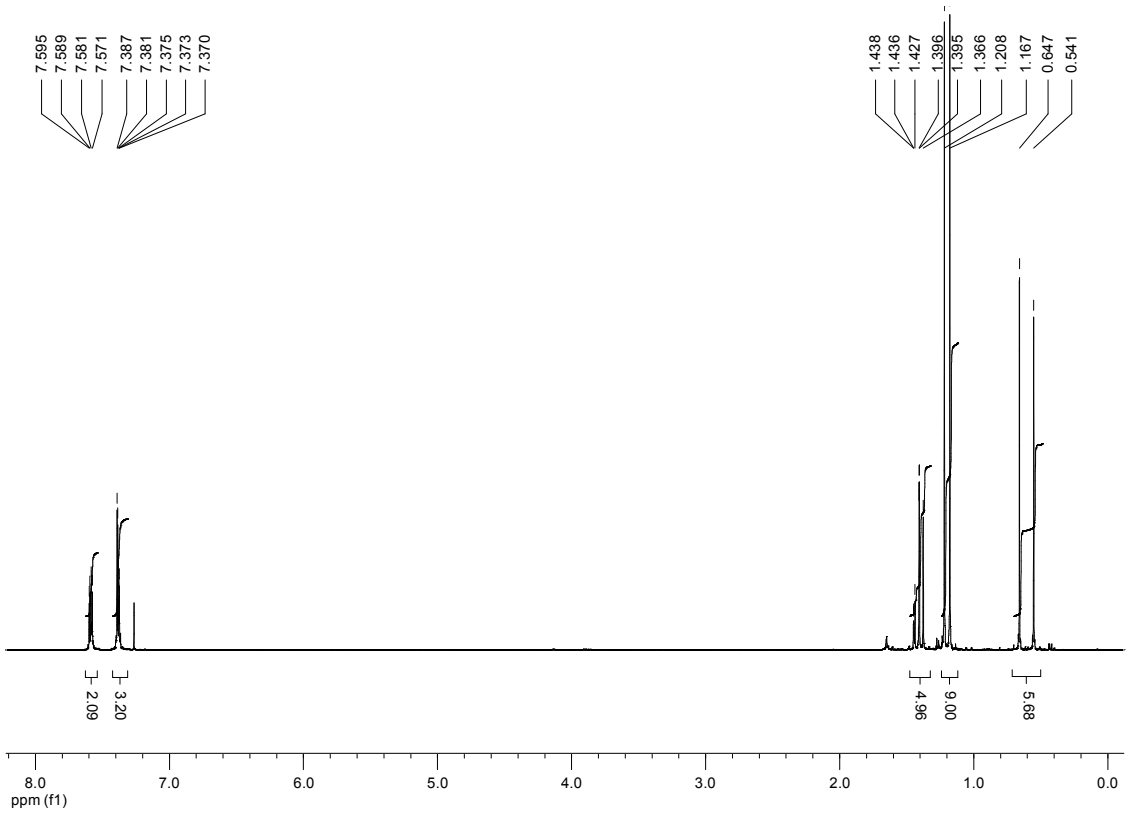
(*S*)-**6**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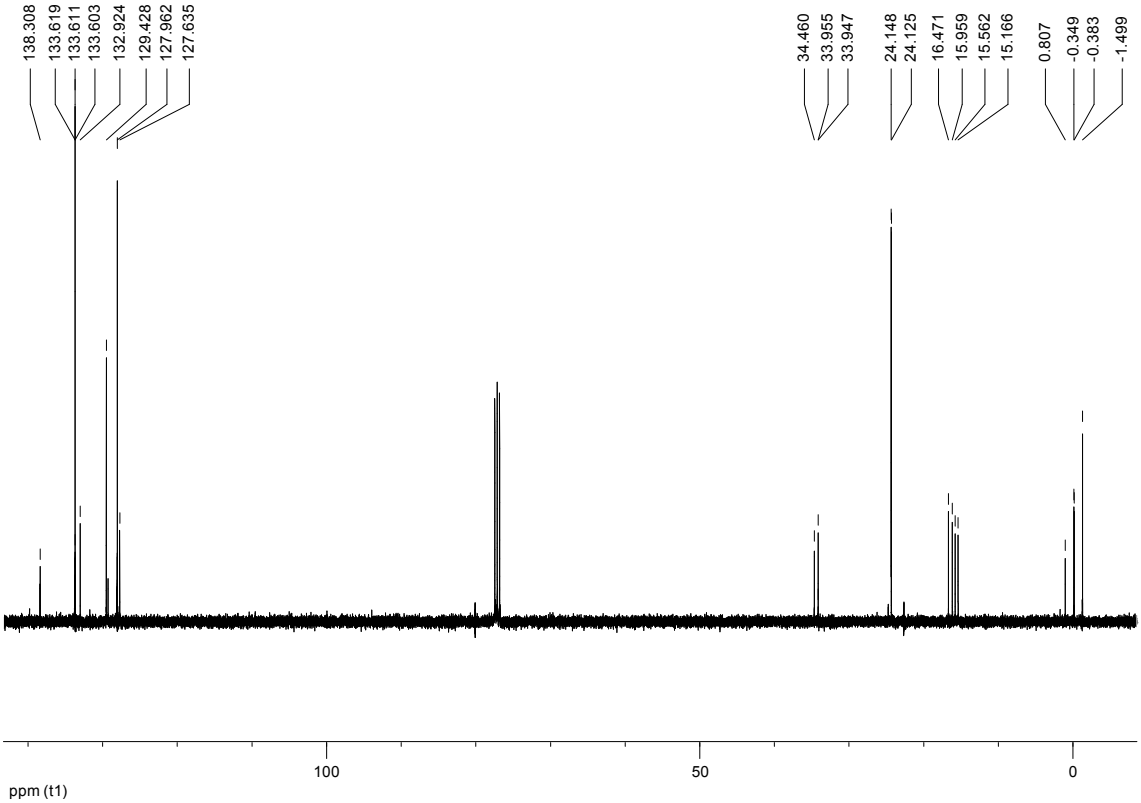
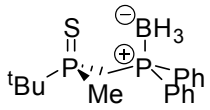
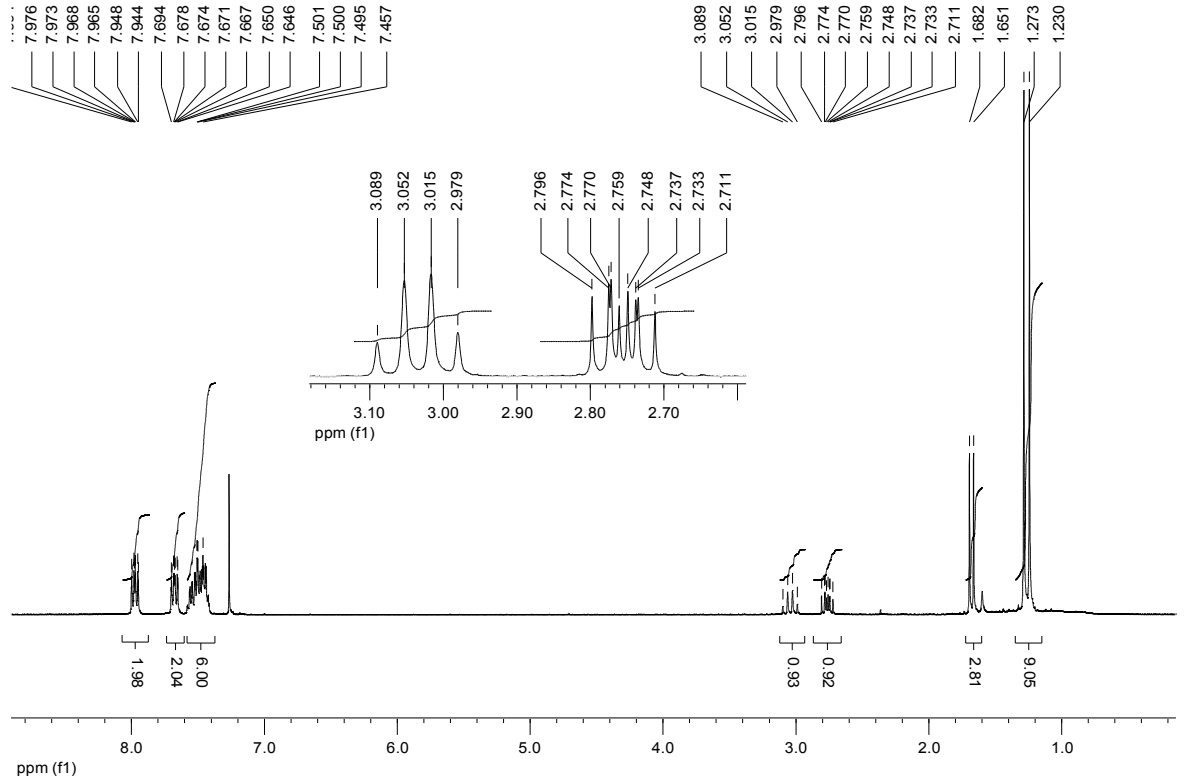
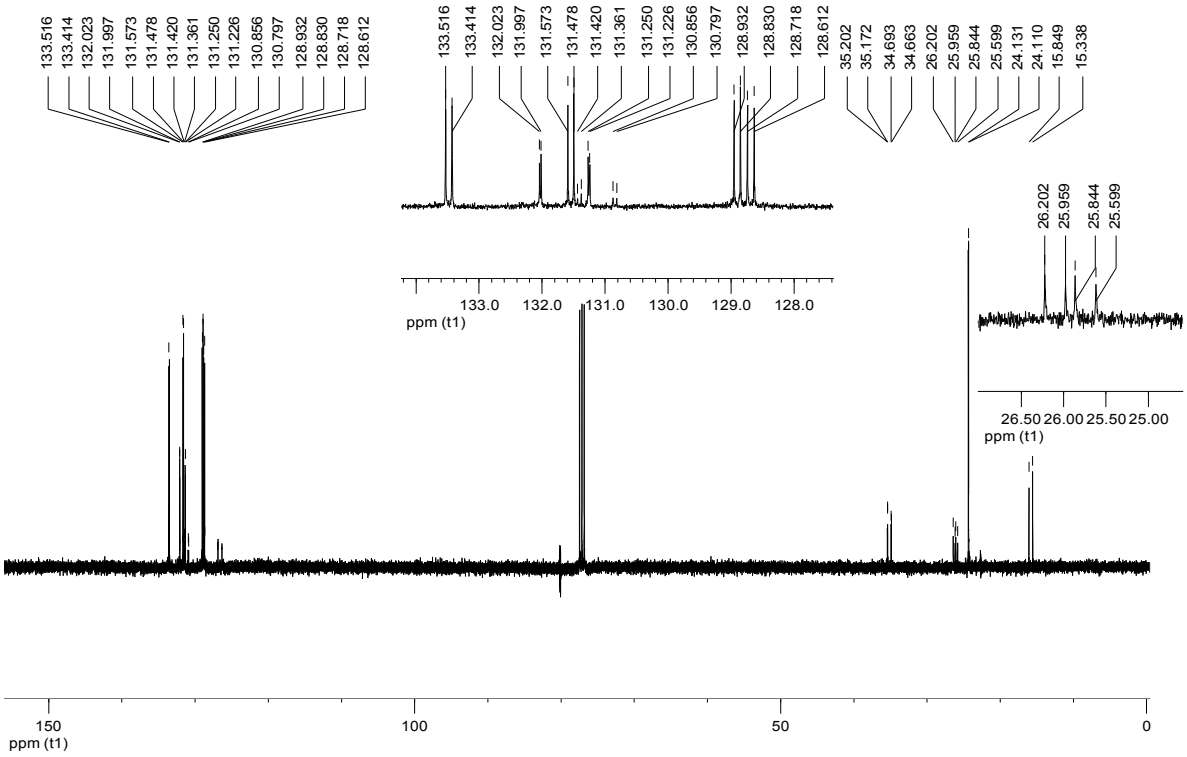
ppm (f1)

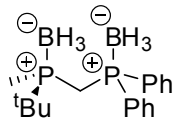

138.308
133.619
133.611
133.603
132.924
129.428
127.962
127.635
34.460
33.955
33.947
24.148
24.125
16.471
15.959
15.562
15.166
0.807
-0.349
-0.383
-1.499
100
50
0
ppm (t1)


S
BH3
tBu
P
P
Ph
Me
Ph

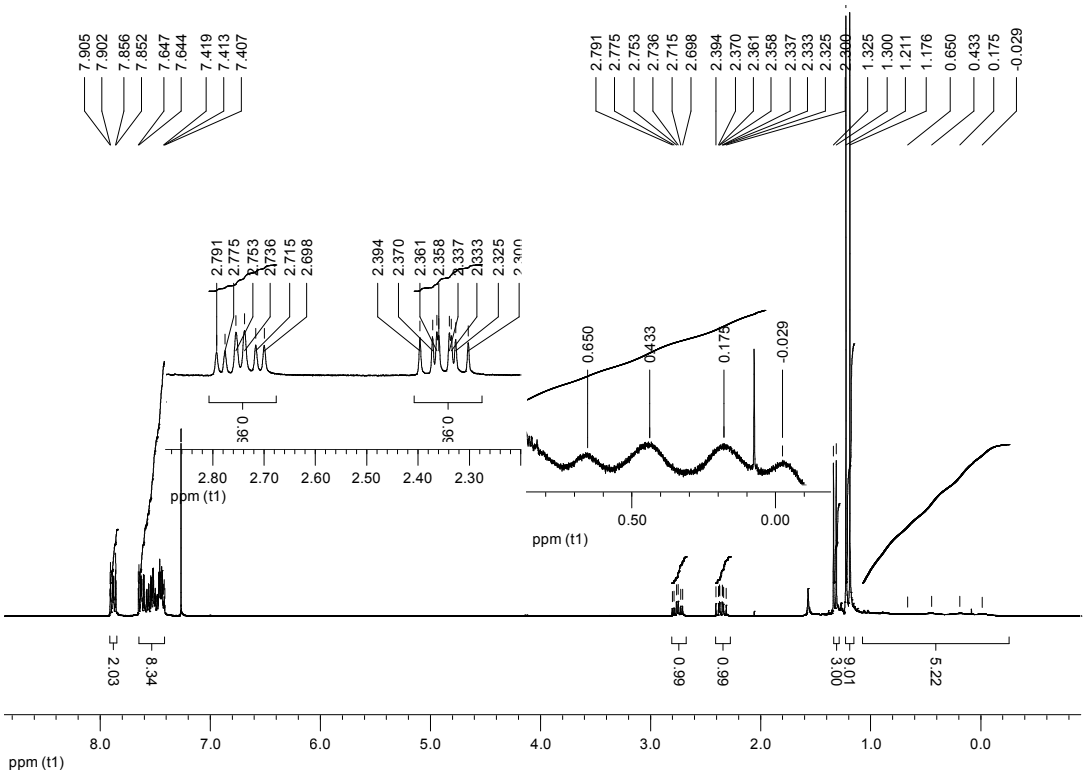
(*S*)-**9**

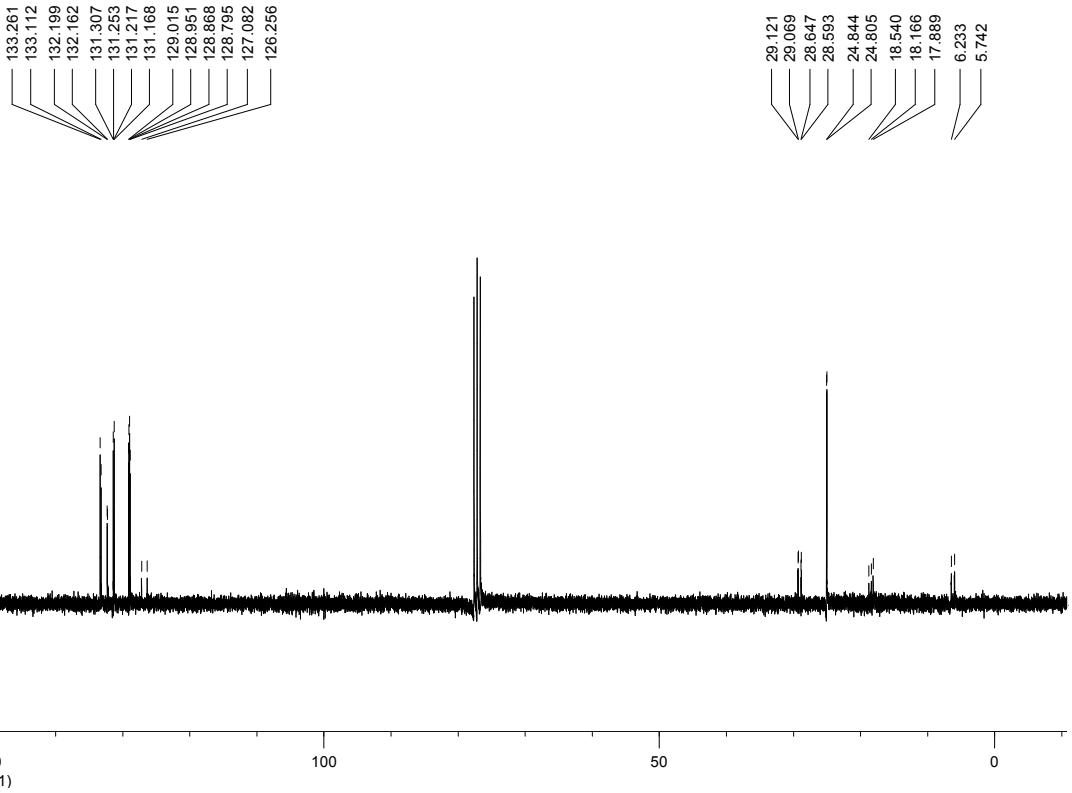

7.976
7.973
7.968
7.965
7.948
7.944
7.694
7.678
7.674
7.671
7.667
7.650
7.646
7.501
7.500
7.495
7.457
3.089
3.052
3.015
2.979
2.796
2.774
2.770
2.759
2.748
2.737
2.733
2.711
1.682
1.651
1.273
1.230
1.98
2.04
6.00
0.93
0.92
2.81
9.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


133.516
133.414
132.023
131.997
131.573
131.478
131.420
131.361
131.250
131.226
130.856
130.797
128.932
128.830
128.718
128.612
35.202
35.172
34.693
34.663
26.202
25.959
25.844
25.599
24.131
24.110
15.849
15.338
150
100
50
0
ppm (t1)


BH3
BH3
P
P
Ph
Ph
tBu

(*S*)-**10**


7.905
7.902
7.856
7.852
7.647
7.644
7.419
7.413
7.407
2.791
2.775
2.753
2.736
2.715
2.698
2.394
2.370
2.361
2.358
2.337
2.333
2.325
1.325
1.300
1.211
1.176
0.650
0.433
0.175
-0.029
2.03
8.34
0.99
0.99
3.00
9.01
5.22
ppm (t1)


133.261
133.112
132.199
132.162
131.307
131.253
131.217
131.168
129.015
128.951
128.868
128.795
127.082
126.256
29.121
29.069
28.647
28.593
24.844
24.805
18.540
18.166
17.889
6.233
5.742
ppm (f1)