Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Simple Unprecedented Conversion of Phosphine Oxides and Sulfides to Phosphine Boranes using Sodium Borohydride

Kamalraj V. Rajendran and Declan G. Gilheany*

Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

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General Experimental

Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory, University College Dublin. IR spectra were obtained on a Varian 3100 FTIR Excalibur series spectrometer. Routine electrospray mass spectra were obtained on a Micromass Quattro spectrometer. High-resolution mass spectra were run on a Waters Micromass GCT system either in (CI) chemical ionization or (EI) electron ionization mode, also at UCD. The NMR spectra were recorded at 25 °C on Varian VNMRS 300, 400, and 500 MHz spectrometers. ^{13}C NMR spectra (^{31}P decoupled) were recorded on a VNMRS 600 MHz spectrometer. All NMR samples of potentially air-sensitive compounds were made up under nitrogen by syringing a small amount of a solution into an NMR tube contained in a long Schlenk tube that was charged with an atmosphere of nitrogen, and then adding dry $CDCl_3$ to dissolve the compound. The NMR tube was then taken out using tweezers. $CDCl_3$ was purchased from Aldrich, and dried by adding to a Young's flask containing activated molecular sieves (4 Å) under an atmosphere of nitrogen. It was then stored under nitrogen in the Young's flask over the molecular sieves.

High-performance liquid chromatography was performed on a Agilent Technologies 1200 series equipped with a 6 column switching device. HPLC grade solvents, purchased from Aldrich and Lennox Supplies Ireland, were used as supplied. All samples were filtered through an Acrodisc CR 13 mm syringe filter with 0.2 µm PTFE prior to injection.

Unless otherwise stated all reactions were carried out under N_2 atmosphere in dry glassware using Schlenk-line techniques and all glassware was flame dried prior to use. Air and moisture sensitive liquids and solutions were transferred *via* syringe. All commercially available solvents were used as supplied unless otherwise stated. All "dry" solvents were dried and distilled by standard procedures[1] or were processed through a Grubbs type still, supplied by Innovative Technology Inc. Pure Solv-400-3-MD solvent purification system. Oxygen free nitrogen was obtained from BOC gases and was used without further drying. Thin layer chromatography (TLC) was performed on Merck pre-coated Kieselgel $60F_{254}$ aluminium plates with realization by UV irradiation. Flash column chromatography was performed on Merck silica 9385, particle size 0.040-0.063 mm. Magnesium turnings for Grignard reactions were heated to 180 °C for at least 24 hours prior to use. Further activation was achieved by heating and stirring vigorously under vacuum for approximately 10 minutes immediately prior to reaction. 4Å Molecular sieves were kept stored in an oven at 180 °C at all times. Prior to use

sieves were heated to ~300 °C, using a heat gun, for 2 minutes while under vacuum. They were allowed to cool to room temperature and this procedure was then repeated.

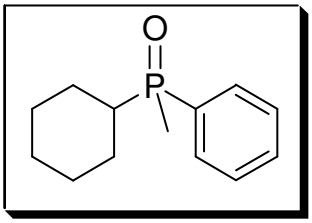
Oxalyl chloride, triphenylphosphine oxide, triphenylphosphine sulfide, tributylphosphine oxide, BINAP, Meerwein's salts, methyl triflate, methyl tosylate, methyl iodide, sulfuryl chloride, methane sulfuryl chloride, thionyl chloride, $NaBH_4$ and other reagents were purchased from Sigma-Aldrich, Fluka or Merck & Co., Inc. (±)-1,2-ethandiylbis[(*o*-anisylphenyl)phenylphosphine oxide and (±)-1,2-ethandiylbis[(*o*-tolylphenyl)phenylphosphine oxide were gifted by Celtic Catalysts Ltd. BINAPO was made from BINAP by oxidation with hydrogen peroxide.[2]

Enatioenriched methylphenyl-*o*-tolylphosphine oxide 93% ee (S), *o*-Anisylmethylphenylphosphine oxide 95 % ee (*R*) were gifted by Celtic Catalysts Ltd. (2-Biphenyl)methylphenylphosphine oxide 81 % ee (*S*), *tert*-Butylmethylphenylphosphine oxide 46 % ee (*S*); 53 % ee (*R*), methylphenyl(mesityl)phosphine oxide 44 % ee (*R*) were synthesied by aysmmetric Appel reaction.[2,3]

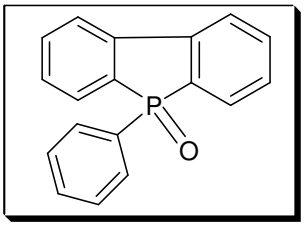
A number of the required phosphines, phosphine oxides, and phosphine sulfides were synthesised previously by us as follows.

Compound	**Reference**
Methylphenyl-*o*-tolylphosphine oxide	2
o-Anisylmethylphenylphosphine oxide	2
Methylphenyl-(2-trifluoromethyl)phenylphosphine oxide	3
(2-Biphenyl)methylphenylphosphine oxide	3
(4-Fluoro-2-methylphenyl)methylphenylphosphine oxide:	3
(2,4-Dimethylphenyl)methylphenylphosphine oxide	3
Methylphenyl(2-*i*-propylphenyl)phosphine oxide:	2
(±)-Methyl-(1-naphthyl)phenylphosphine oxide	3

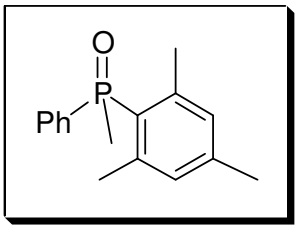
tert-Butylmethylphenylphosphine oxide	2
Cyclohexylmethylphenylphosphine oxide	Made by the same method. Data given below



(±)-Cyclohexylmethylphenylphosphine oxide: From Phosphine (2 g, 9.7 mmol), in a yield of (1.8 g, 84%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.71-7.46 (m, 5H, Ar) 1.68 (d, $^{2}J_{PH}$ = 12.4 Hz, 3H, PCH_3), 1.69-1.16 (m, 11H, *c*-Hexyl) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 40.6 ppm (Lit.[4] -33.1 ppm).

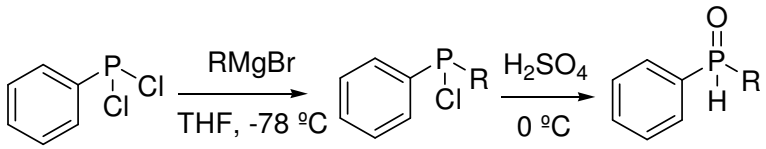


***P*-phenyldibenzophosphole oxide**: From P-phenyl dibenzophosphole[5] (2 g, 7.7 mmol), by oxidation with hydrogen peroxide[2] gave *P*-phenyldibenzophosphole oxide (1.82 g, 86%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80-7.29 (m, 13H, Ar) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 33.5 ppm (lit.[5] 33.8)

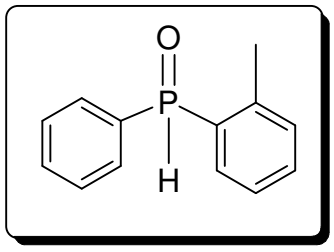


Methylphenyl(mesityl)phosphine oxide[6]: From methylphenyl (mesityl)phosphine[7] (1g, 4.1 mmol) by oxidation with hydrogen peroxide gave methylphenyl(mesityl)phosphine oxide (0.86 g, 81%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64-7.46 (m, 2H, Ar), 7.50-7.38 (m, 3H, Ar), 6.90-6.89 (m, 2H, Ar), 2.41 (s, 6H, *o*-Me), 2.30 (s, 3H, *p*-Me), 1.21 (d, $^{2}J_{PH}$ = 6.0 Hz, 3H, PCH_3); ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 34.6 ppm.

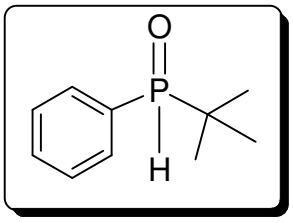
Synthesis of Required Secondary Phosphine oxides



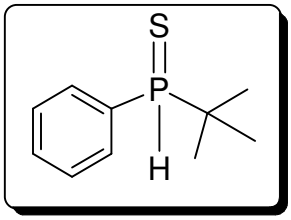
Exemplar: Synthesis of *o*-tolylphenylphosphine oxide:[8] A dry 100 mL two-necked round bottom flask fitted with reflux condenser, nitrogen inlet and outlet and septum was charged with magnesium turnings (0.5 g, 18.7 mmol, 1.1 equiv). 2-Bromotoluene (3.0 g, 17 mmol, 1 equiv) was dissolved in THF (10 mL), and approx. 2 mL of this solution was added to the flask *via* syringe. The mixture was heated to reflux with vigorous stirring until the reaction initiated, at which point the remainder of the solution was added over approximately 30 minutes, also via syringe. After this time the reaction was refluxed for a further 2 hours. The reaction was allowed to cool to room temperature and, it was then transferred through a syringe into a pressure-equalized dropping funnel attached to a flame dried and degassed 100 mL round bottom flask, which had been charged previously with dichlorophenylphosphine (3.0 g, 17 mmol, 1 equiv) and anhydrous THF (10 mL). This solution was cooled to -78 °C using dry ice-acetone mixture and the Grignard solution was added dropwise over 1 hour. The flask was allowed to warm to room temperature and was then stirred for an hour. A 10% aqueous solution of H_2SO_4 (100 mL) was added dropwise to the reaction mixture at 0 °C and the reaction was allowed stirred for an hour. The solvent was removed in *vacuo,* and extracted with dichloromethane (3 ×100 mL), which had been stored over anhydrous magnesium sulfate for 30 min under a nitrogen atmosphere. The extracts were filtered through a sintered funnel under nitrogen, the solvent removed *in vacuo*, phosphine oxide was isolated as colourless oil.



(±)-*o*-tolylphenylphosphine oxide: (3.35 g, 88 %) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13 (d, J_{HP} = 483.8 Hz, 1H), 7.75-7.21 (m, 9H, Ar), 2.35 (s, 3H, $ArCH_3$). ^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 141.4, 132.8, 132.3, 132.2, 131.42, 131.41, 130.8, 129.5, 128.9, 126.0, 20.2. ^{31}P NMR ($CDCl_3$, 121 MHz): δ =21.6 (lit[8] 21.9) ppm. HRMS (CI) Calc. 216.0704; found: 216.0701. HPLC (CHIRALCEL® IA column, 90:10 Heptane - EtOH, 1 mL/min R_t: 18.4 min, 19.9 min.

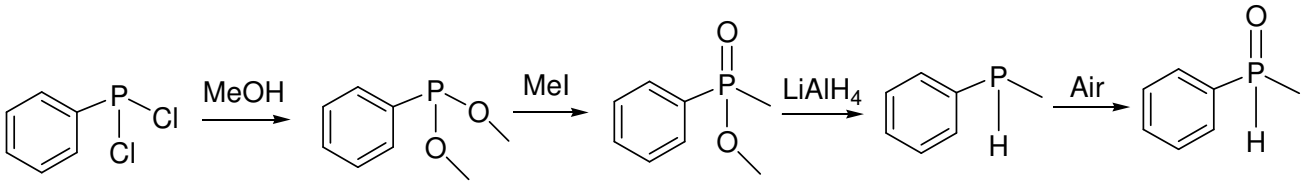


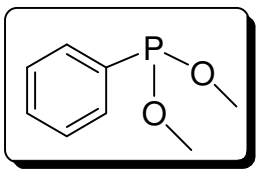
(±)-*tert*-Butyphenylphosphine oxide: From $PhPCl_2$ (3.0 g, 17 mmol, 1 equiv) and ^tBuMgBr (17 mL 1.0 M in THF 1 equiv) by the procedure above gave (±)-*tert*-Butyphenylphosphine oxide (2.65 g, 85 %) ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.68-7.38 (m, 5H, Ar), 7.08 (d, J_{HP} = 458.9 Hz, 1H), 1.15(d, J_{HP}= 16.5 Hz, 9H) ^{13}C NMR {^1H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 132.6, 130.9, 128.4, 127.7, 23.7, 23.6. ^{31}P NMR ($CDCl_3$, 121 MHz): δ =47.4 (lit[8] 47.6) ppm. HRMS (CI) Calc. 182.0861; found: 182.0857. HPLC (CHIRALCEL® IA column, 90:10 Heptane - EtOH, 1 mL/min R_t: 18.4 min, 19.9 min.



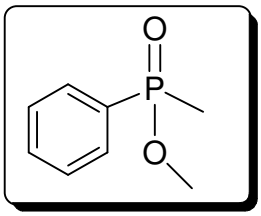
(±)-*tert*-Butyphenylphosphine sulfide: From $PhPCl_2$ (3.0 g, 17 mmol, 1 equiv), ^tBuMgBr (17 mL 1.0 M in THF 1 equiv), $LiAlH_4$(8.5 mL 2.0 M in THF 1 equiv.) and sulphur (0.65 g, 1.2 equiv, 20.4 mmol) by the procedure above gave (±)-*tert*-Butyphenylphosphine sulphide as solid (2.64 g, 78%) ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48-7.18 (m, 5H, Ar), 6.83 (d, J_{HP} = 458.9 Hz, 1H), 0.9 (d, J_{HP}= 16.5 Hz, 9H) ^{31}P NMR ($CDCl_3$, 121 MHz): δ =54.0 (lit[9] 54.0)

Synthesis of methylphenylphosphine oxide[4]

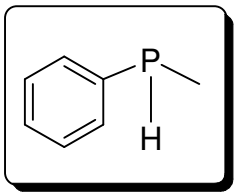




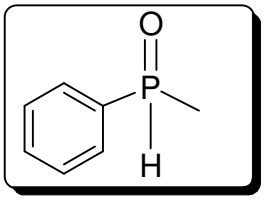
Synthesis of dimethylphenylphosphonite: A 500 mL 2 necked round bottom flask equipped with a pressure equalised dropping funnel attached to a Schlenk line was charged with anhydrous pyridine (80 mL, 0.9 mol), dichlorophenylphosphine (84 g, 0.46 mol) and degassed pentane (250 mL). The stirred solution was cooled to 0 °C and anhydrous methanol (38 mL, 0.93 mol) in degassed pentane (25 mL) was added over a period of 2 hours. The pyridine hydrochloride salt was filtered off under N_2 and the filtrate was concentrated under reduced pressure. The crude grainy colourless liquid product was carried onto the next step without further purification. (38 g, 47 %) ^{31}P NMR ($CDCl_3$, 121 MHz): δ =165.09 ppm.



Synthesis of methyl-methylphenylphosphinate : A 3-neck 250 mL round bottom flask was fitted with a thermometer and two condensers, one of which was connected to a pressure equalised dropping funnel which in turn was connected to a Schlenk lin via a stop-cock adaptor. The flask was charged with a small amount of dimethylphenylphosphonite (3 mL) and a few drops of methyl iodide. The orange mixture was stirred and warmed carefully under a N_2 atmosphere until a very vigorous exothermic reaction began. The phosphonite (35 g, 0.21 mol) was added at a rate sufficient to keep the temperature at roughly 70 °C. It was necessary to periodically add small amount of methyl iodide to maintain a constant reaction. After completer addition the red mixture was stirred at room temperature overnight. Distillation under reduced pressure (98°C @ 0.4 mm Hg) yielded a colourless oil (27.2 g 78%). ^{31}P NMR ($CDCl_3$, 121 MHz): δ =48.7 ppm.

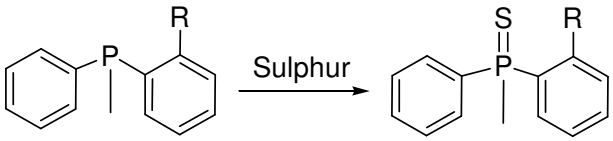


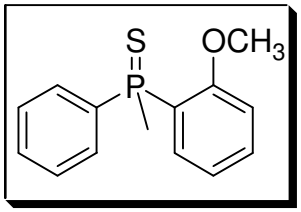
Synthesis of methylphenylphosphine: To a stirred solution of $LiAlH_4$ (1 M soln. In THF 50 mL, 50 mmol) in dry THF (25 mL) at -78 °C was added a solution of a methylphenylphophinate (5.0 g, 29.4 mmol) in dry THF (75 mL) over 1 hour. After warming to room temperature the solution was then refluxed for 4 hours. After removal of THF under reduced pressure, degassed H_2O (20 mL) was added very slowly, followed by degassed aqueous NaOH (20% 20 mL) and finally degassed H_2O (20 mL). The product was extracted into degassed DCM (2 x 100 mL), dried over $MgSO_4$ and the solvent removed under reduced pressure. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = -76.4 ppm.



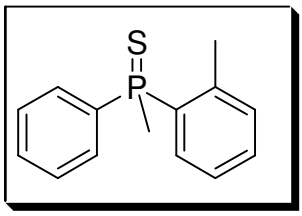
methylphenylphosphine oxide: The phosphine from previous reaction was opened to air and left for 3 days for complete conversion to oxide. (2.9 g 70 %) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80-7.42 (m, 5H, Ar), 7.64 (d, J_{HP} = 484.4 Hz, 1H), 1.81 (d, J_{HP}= 11 Hz, 3H) ^{31}P NMR ($CDCl_3$, 121 MHz): δ =21.2 (lit[8] 20.3).

Synthesis of Required Phosphine Sulfides

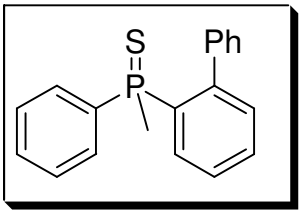




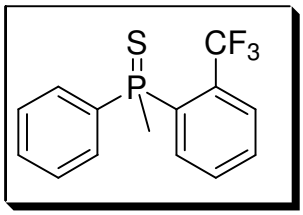
Exemplar Synthesis of (±)-*o*-anisylmethylphenylphosphine sulfide: To a stirred solution of phosphine (0.5 g, 2.1 mmol, 1 equiv) in DCM (30 mL, degassed) at 0 °C (ice bath) sulphur (74 mg, 1.2 equiv) was added through powder funnel. After the addition was complete the suspension was stirred for 2 hrs. Excess sulphur was filtered off and the solvent was removed in *vacuo* to yield light yellow solid. (0.5 g 90%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.20-8.13 (m, 1H, Ar), 7.68-7.63 (m, 2H, Ar), 7.45-7.19 (m, 4H, Ar), 7.07-7.04 (m, 1H, Ar), 6.81-6.78 (m, 1H, Ar), 3.59 (s, 3H, OCH_3), 2.29 (d, $^{2}J_{PH}$ = 14.4 Hz, 3H, CH_3,); ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 35.2 (lit[10] 35.9) ppm.



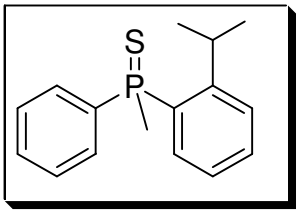
(±)-*o*-tolylmethylphenylphosphine sulfide: From phosphine[2] (2 g, 9.3 mmol), in a yield of (1.9 g, 82%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.48-8.40 (m, 3H, Ar), 8.32-8.24 (m, 4H, Ar), 7.92-7.521 (m, 2H, Ar), 2.75 (s, 3H, $ArCH_3$), 2.32 (d, $^{2}J_{PH}$ = 14.1 Hz, 3H, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 34.7 (lit[11] 34.4) ppm.



(±)-(2-Biphenyl)methylphenylphosphine sulfide : From phosphine[3] (2 g, 7.2 mmol), in a yield of (1.8 g, 81%) ^{1}H NMR ($CDCl_3$, 300 MHz) : δ = 8.60-724 (m, 14H, Ar), 2.29 (d, $^{2}J_{PH}$ = 14.1 Hz, 3H, CH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 37.2 ppm. ^{13}C NMR {^{1}H,^{31}P} (CDCl3, 151 MHz): *δ* = 136.5, 132.8, 132.2, 131.5, 130.4, 129.7, 129.3, 128.8, 127.9, 127.7, 127.3, 126.3, 125.3, 121.1, 23.2 ppm. IR: ν˜ =3185, 2468, 1621, 1342, 1292, 585 (P=S) cm^{-1}. HRMS (EI): C_{19} H_{17} PS Calculated: 308.0788 Found: 308.0781.



(±)Methylphenyl(2-trifluoromethylphenyl)phosphine sulfide : From phosphine[3] (1 g, 5.5 mmol), in a yield of (0.55 g, 87%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01-7.42 (m, 9H, Ar), 2.4 (d, $^{2}J_{PH}$ = 12.2, Hz, 3H, PCH_3) ppm.^{31}P NMR ($CDCl_3$, 121 MHz): δ = 40.6 ppm. ^{13}C NMR {^{1}H,^{31}P} (CDCl3, 151 MHz): *δ* = 136.9, 135.4, 133.1, 132.9, 132.7, 131.8, 131.4, 130.0, 129.4, 127.4, 123.5 (q, *J* = 273.2 Hz), 17.6 ppm. IR: ν˜ =3213, 1649, 1521, 1474, 1232, 595 (P=S) cm^{-1}. HRMS (EI): C_{14} H_{12} F_3PS Calculated: 300.0349 Found: 300.0342.

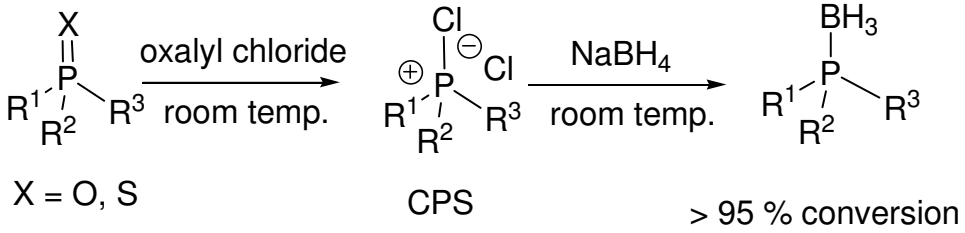


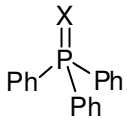
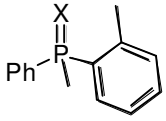
(±)-Methylphenyl(2-*i*-propylphenyl)phosphine sulfide : From phosphine[2] 2 g, 8.2 mmol), in a yield of (1.81 g, 80%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62-7.12 (m, 9H, Ar) 3.24 (quintet, *J* = 6.7 Hz, 1H, CH,), 2.21 (d, $^{2}J_{PH}$ = 14.0 Hz, 3H, PCH_3,), 1.34 (d, *J* = 6.8 Hz 3H, *i*-Pr-Me), 0.92 ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 37.3 ppm. ^{13}C NMR {^{1}H,^{31}P} (CDCl3, 151 MHz): *δ* = 154.3, 136.2, 134.9, 132.9, 131.4, 130.2, 129.2, 128.3, 127.4, 125.5, 32.5, 23.4. 17.6 ppm. IR: ν˜ =3385, 2868, 1521,1592, 1474, 1364, 580 (P=S) cm^{-1}. HRMS (EI): C_{16} H_{19} PS Calculated: 274.0945 Found: 274.0939.

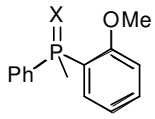
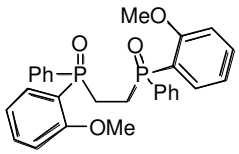
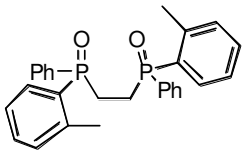
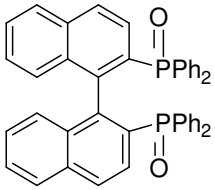
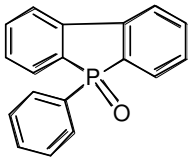
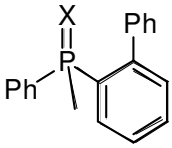
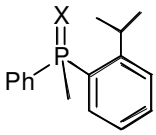
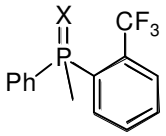
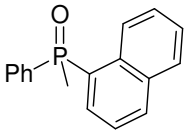
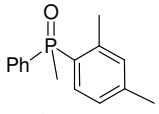
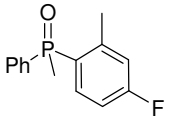
General Procedure for Reduction of Achiral Racemic Tertiary and Secondary phosphine oxide and sulfides using oxalyl chloride and sodium borohydride.

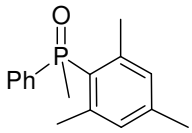
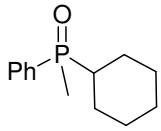
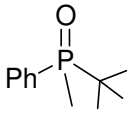
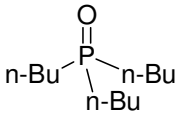
To a stirred solution of phosphine oxide/sulfide (1.0 mmol) in toluene (2 mL) was added oxalyl chloride (1.0 mmol) dissolved in toluene (2 mL) dropwise at room temperature under a nitrogen atmosphere. At this point ^{31}P-NMR of the reaction mixture shows full conversion to chlorophosphosphonium salt (CPS). After 30 min, sodium borohydride (2.1 mmol) dissolved in diglyme (~3 mL) was added dropwise to the reaction mixture. This mixture was stirred for 1 h, where ^{31}P shows full completion of CPS to phosphine borane. The reaction mixture was washed with deionised water (5 mL) and the isolated organic layer was dried over anhydrous MgSO4. The drying agent was removed by filtration, and the solvent was removed *in vacuo* to give colourless oil, which was eluted through a silica plug with 50:50 cyclohexane/ethylacetate. Solvent removal *in vacuo* yielded the pure phosphine borane.

Table A. Reduction of achiral and racemic tertiary phosphine oxides and sulfides.



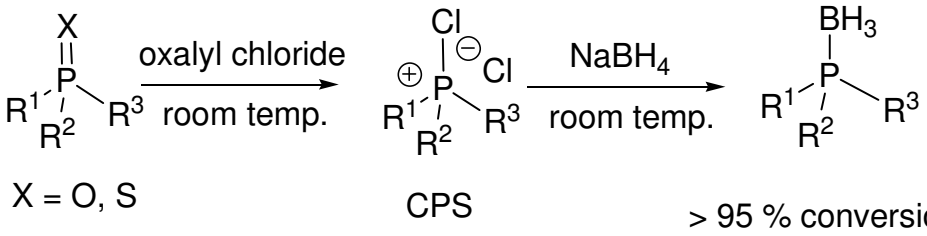
Entry	Starting material	^{31}P-NMR Chemical Shift (ppm) PX[a]	CPS[b]	PB[c]
1		X = O 25.2 X = S 42.1	64.4[23]	21.5
2		X= O 32.5 X= S 34.7	71.0	10.2

3		X= O 28.5 X= S 35.2	70.5	8.4
4		32.4	73.8	18.4
5		34.8	72.1	18.8
6		23.0	62.6	21.4
7		33.5	57.6	25.0
8		X= O 26.9 X= S 37.2	67.1	13.3
9		X= O 32.2 X = S 37.3	70.8	9.1
10		X =O 31.6 X = S 40.6	66.8	18.4
11		33.1	70.2	13.3
12		31.7	71.0	10.5[d]
13		31.0	70.4	10.2[d]

14		34.6	72.0	11.6
15		40.6	91.9	17.1
16		47.0	100.9	25.8
17		56.2	105.1	14.1

[a] : PX: phosphine oxide or sulfide; [b]: CPS: shift assigned as chlorophosphonium salt; [c] : PB phosphine borane, isolated yield > 85%. No other material was apparent in the ^{31}P NMR of the crude reaction mixture. Unless otherwise noted, these are known compounds - literature references given in ESI; [d] : this work.

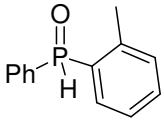
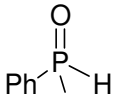
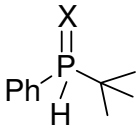
Table B. Reduction of racemic secondary phosphine oxides and sulfide.



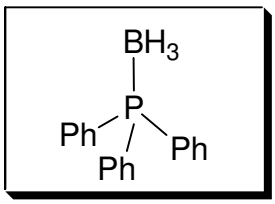
X = O, S

CPS

> 95 % conversion

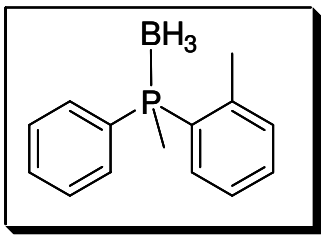
Entry	Starting material	^{31}P-NMR Chemical Shift (ppm)		
		PX[a]	CPS[b]	PB[c]
1		21.6	78.4	-6.3
2		21.2	100.9	-13.5
2		X = O 47.4 X = S 54.0	107.7	31.0

[a] PX: phosphine oxide or sulfide ; [b] CPS: shift assigned as chlorophosphonium salt; [c] PB: phosphine borane, isolated yield > 85%. No other material was apparent in the ^{31}P nmr of the crude reaction mixture. These are known compounds - literature references given in SI.



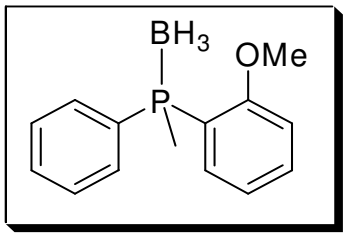
Triphenylphosphine borane : From triphenylphosphine oxide (0.27 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave triphenylphosphine borane. (0.24 g, 88%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.61–7.40 (m, 15H, Ph-H), 1.74–0.83 (br, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ =21.5 (lit.[12]) 20.6 ppm.

Triphenylphosphine borane : From triphenylphosphine sulfide (0.29 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave triphenylphosphine borane. (0.25 g, 92%) ^{31}P NMR ($CDCl_3$, 121 MHz): δ =21.5 (lit.[12] above) 20.6 ppm.



Methylphenyl(*o*-tolyl)phosphine borane : From methylphenyl(*o*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(*o*-tolyl)phosphine borane (0.20 g, 87%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ =7.72–7.14 (m,9 H, Ar), 2.17 (s, 3 H, $ArCH_3$), 1.82 (d, $^2J_{PH}$ = 9.8 Hz, 3 H, CH_3) 1.61–0.72 (br, 3H, BH_3) ppm ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 10.2 (lit[13] 10.9) ppm

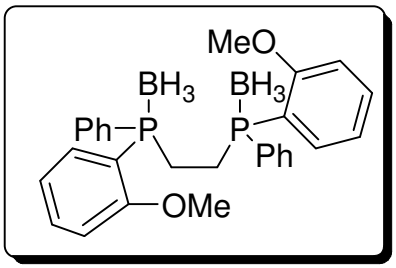
Methylphenyl(*o*-tolyl)phosphine borane : From methylphenyl(*o*-tolyl)phosphine sulfide (0.24 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(*o*-tolyl)phosphine borane (0.21 g, 91%) ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 10.5 (lit[13] 10.9) ppm



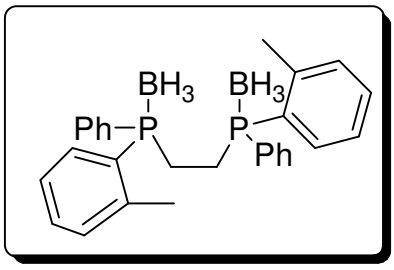
Methylphenyl(*o*-anisyl)phosphine borane : From methylphenyl(*o*-anisyl)phosphine oxide (0.24 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(*o*-anisyl)phosphine borane. (0.22 g, 91%) ^{1}H NMR

($CDCl_3$, 300 MHz): δ =7.90–6.77 (m,9 H, Ar), 3.68 (s, 3 H, Ar-OCH3), 1.94 (d, $^2J_{PH}$ = 10.2 Hz, 3H, CH3) 1.43–0.50 (br, 3H, BH_3) ppm ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 8.4(lit[14] 9.2) ppm.

Methylphenyl(*o*-anisyl)phosphine borane : From methylphenyl(*o*-anisyl)phosphine sulfide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(*o*-anisyl)phosphine borane. (0.21 g, 87%) ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 8.7 (lit[14] 9.2) ppm



(±)-1,2-Ethandiylbis[(*o*-anisylphenyl)phenylphosphine borane: From 1,2-ethandiylbis[(*o*-anisylphenyl)phenylphosphine oxide (0.49 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 2.0 mmol, 2 equiv.) followed by the treatment with $NaBH_4$ in diglyme (6.9 mL, 0.6 M, 4.2 mmol, 4.2 equiv) gave 1,2-ethandiylbis[(*o*-anisylphenyl)phenylphosphine borane (0.42 g, 87%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90-7.83 (m, 2H, Ar), 7.69-7.64 (m, 4H, Ar), 7.49-7.36 (m, 8H, Ar), 7.05-7.00 (m, 2H, Ar), 6.83-6.80(m, 2H, Ar), 3.62 (s, 6H, OCH_3), 1.87 (m, 4H, P-CH_2), 1.22–0.90 (br, 6H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 18.5 ppm (lit[15] 18.8 ppm).



(±)-1,2-Ethandiylbis[(*o*-tolylphenyl)phenylphosphine borane : From 1,2-ethandiylbis[(*o*-tolylphenyl)phenylphosphine (0.46 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 2.0 mmol, 2 equiv.) followed by the treatment with $NaBH_4$ in diglyme (6.9 mL, 0.6 M, 4.2 mmol, 4.2 equiv) gave 1,2-ethandiylbis[(*o*-tolylphenyl)phenylphosphine borane. (0.43 g, 88%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.66-7.60 (m, 2H, Ar), 7.52-7.37 (m, 8H, Ar), 7.30-7.26 (m, 2H, Ar), 7.20-7.18(m, 6H, Ar), 2.14 (s, 6H, CH_3), 2.48 (m, 4H, P-CH_2), 1.26–0.88 (br, 6H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 18.5 ppm (lit.[13] 19.1 ppm)

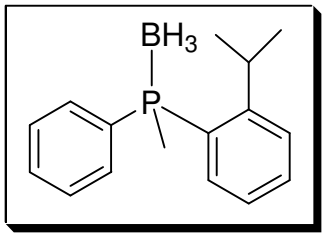
1,1′-Binaphthalene-2,2′-diyl)bis(diphenylphosphineborane):From (1,1′Binaphthalene-2,2′-diyl)bis (diphenylphosphine oxide) (0.33 g, 0.5 mmol, 1 equiv) treated with oxalyl chloride (0.2 mL, 1.0 mmol, 2 equiv.) followed by the treatment with $NaBH_4$ in diglyme (6.9 mL, 0.6 M, 2.1 mmol, 4.2 equiv) gave 1,1′-Binaphthalene-2,2′-diyl)bis(diphenylphosphine borane) (0.29 g, 87%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.82 (dd, *J* = 8.5 Hz, *J* = 2.2Hz, 2H), 7.74-7.52 (m, 20H), 7.41 (m, 2H), 7.39 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H). 1.69–0.72 (br, 6H, BH_3) ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 23.0 (lit[16] 23.0) ppm.

***P*-Phenyldibenzophosphole borane:** From *P*-phenyldibenzophosphole oxide (0.28 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave *P*-phenyldibenzophosphole borane. (0.25 g, 93%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90-7.29 (m, 13H, Ar), 0.90-1.43 (b, m, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 25.0 ppm. ^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 142.3, 132.7, 132.1, 131.0, 130.9, 129.4, 127.9, 127.1, 126.6, 120.3 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.6 ppm. IR (KBr, cm^{-1}) ν: 3053, 2395 (BH_3), 1636, 1593, 1438, 1294, 1164, 1027, 766. HRMS (M $-BH_3$ + H) $^+$ $C_{18}H_{14}P$ Calculated: 261.0833 Found: 261.0828.

(±)-(2-Biphenylyl)methylphenylphosphine borane : From (±)-(2-Biphenyl)methylphenylphosphine oxide (0.29 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (2-Biphenylyl)methylphenylphosphine borane. (0.26 g, 89%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ =7.89-7.82 (m, 5H, Ar), 7.70–7.19 (m, 9 H, Ar), 1.41 (d, $^2J_{PH}$ = 10.1 Hz, 3 H, CH3), 1.56–0.73 (br, 3H, BH_3) ppm. ^{31}P NMR (CDCl3, 121 MHz): δ = 13.3 (lit.[17] 14.4) ppm.

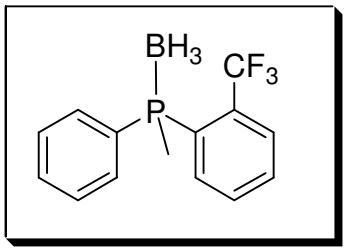
(±)-(2-Biphenyl)methylphenylphosphine borane : From (±)-(2-Biphenyl)methylphenylphosphine sulfide (0.31 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.)

followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (2-Biphenyl)methylphenylphosphine borane. (0.24 g, 85%) . ^{31}P NMR (CDCl3, 121 MHz): δ = 13.8 (lit.[17] 14.4) ppm.



(±)-Methylphenyl(2-*iso*-propylphenyl)phosphine borane: From methylphenyl -(2-*iso*-propylphenyl)phosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(2-*iso*-propylphenyl)phosphine borane. (0.24 g, 92%) ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.67-7.26 (m, 9H, Ar) 3.18 (quintet, J = 6.7 Hz, 1H, CH,), 1.86 (d, $^2J_{PH}$ = 10.0 Hz, 3H, PCH_3,), 1.08 (d, J = 6.8 Hz 3H, *i*-Pr-Me), 0.73 (d, J = 7.4 Hz, 3H, *i*-Pr-Me,); 1.62–0.51 (br, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 300 MHz) : δ = 9.0 ppm (lit[13] 9.7ppm).

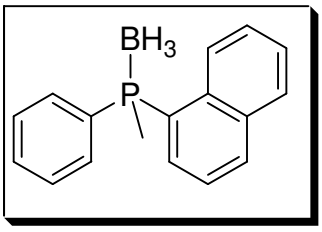
(±)-Methylphenyl(2-*iso*-propylphenyl)phosphine borane: From methylphenyl -(2-*iso*-propylphenyl)phosphine sulfide (0.27 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl(2-*iso*-propylphenyl)phosphine borane. (0.22 g, 86%) ^{31}P NMR ($CDCl_3$, 300 MHz) : δ = 9.3 ppm (lit[13] 9.7ppm).



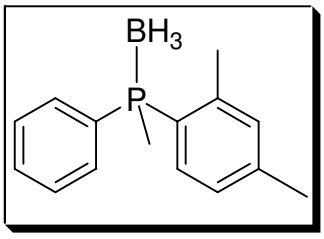
(±)-Methylphenyl (2-trifluoromethylphenyl)phosphine borane[18] : From methylphenyl (2-trifluoromethylphenyl)phosphine oxide (0.28 g, 1.0 mmol, 1 equiv) reated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenyl (2-trifluoromethylphenyl)phosphine borane. (0.26 g, 92%) ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70-7.02 (m, 9H, Ar), 1.91 (d, $^2J_{PH}$ = 9.9 Hz, 3H, PCH_3), 0.65-1.53 (br, m, 3H) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 18.3. (lit[18] 18.7)

(±)-Methylphenyl (2-trifluoromethylphenyl)phosphine borane : From methylphenyl (2-trifluoromethylphenyl)phosphine sulfide (0.30 g, 1.0 mmol, 1 equiv) reated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1

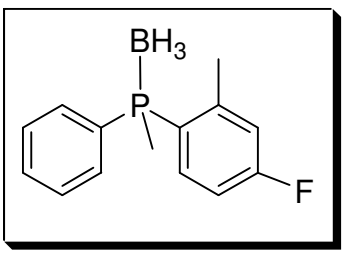
mmol, 2.1 equiv) gave methylphenyl (2-trifluoromethylphenyl)phosphine borane. (0.23 g, 88%) ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 18.5. (lit[18] 18.7)



(±)-Methyl(1-naphthyl)phenylphosphine borane: From (±)-methyl(1-naphthyl)phenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methyl(1-naphthyl)phenylphosphine borane. (0.24 g, 91%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.22 (d, *J* = 8.4 Hz, 1H, Ar), 8.00 (d, *J* = 8.4 Hz, 1H, Ar), 7.91-7.37 (m, 10H, Ar), 2.23 (d, $^2J_{PH}$ = 10.2 Hz, 3H, CH_3) 1.53- 0.62 (br, m, 3H) ppm.^{31}P NMR ($CDCl_3$, 121 MHz): δ = 13.3 ppm (Lit.[17] 14.4 ppm).

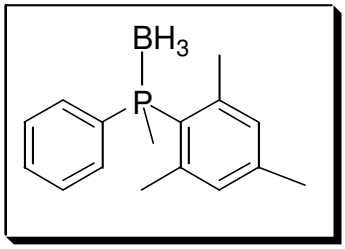


(±)-(2,4-Dimethylphenyl)methylphenylphosphine borane : From (±)-2,4-dimethylphenyl)methylphenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-2,4-dimethylphenyl)methylphenylphosphine borane. (0.24 g, 92%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.64-7.09 (m, 8H, Ar), 2.55 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 1.99 (d, $^2J_{PH}$ = 9.8 Hz, 3H, PCH_3) 0.62-1.67 (b, m, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 10.5 ppm.^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 142.8, 140.6, 138.7, 134.6, 132.6, 133.3, 131.4, 130.7, 128.4, 126.9, 21.3, 21.3, 12.8 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = -36.5 ppm) IR (KBr, cm^{-1}) ν: 3120, 2385 (BH_3), 1626, 1583, 1438, 1320, 1236, 1145, 725. HRMS (M $-BH_3$ + H) $^+$ C_{15} $H_{18}P$ Calculated: 229.1146 Found: 229.1138; HPLC (CHIRALPAK® ASH column, 98:2 heptane: EtOH, 1 mL/min) R_t: 8.0 min, 10.2 min.

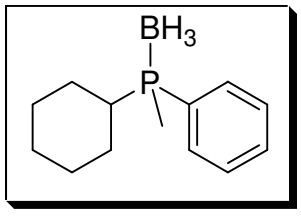


(±)-(4-Fluoro-2-methylphenyl)methylphenylphosphine borane: (±)-(4-fluoro-2-methylphenyl)methylphenylphosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6

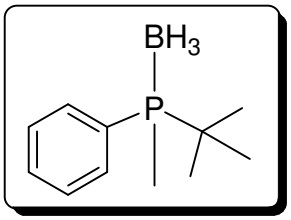
M, 2.1 mmol, 2.1 equiv) gave (±)-(4-fluoro-2-methylphenyl)methylphenylphosphine borane. (0.22 g, 84%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.74-6.89 (m, 8H, Ar), 2.18 (s, 3H, $ArCH_3$), 1.84 (d, $^{2}J_{PH}$ = 9.9 Hz, 3H, CH_3), 0.90-1.57 (br, m, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 10.2 ppm. ^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 163.11 (d, $^{1}J_{PF}$ = 249.3 Hz), 145.3, 137.7, 134.8, 131.2, 129.1, 127.9, 125.3, 118.4, 112.9, 21.7, 12.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = -35.7 ppm. IR (KBr, cm^{-1}) ν: 3020, 2345 (BH_3), 1650, 1493, 1332, 1294, 1121, 1012, 742. HRMS (M –BH_3 + H)$^{+}$ $C_{14}H_{15}PF$ Calculated: 233.0895 Found: 233.0887 HPLC (CHIRALPAK® ASH column, 98:2 heptane: EtOH, 1 mL/min) R_t: 9.0 min, 11.0 min.



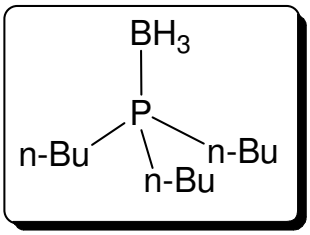
(±)-Methylphenyl(mesityl)phosphine borane: From (±)-methylphenyl(mesityl)phosphine oxide (0.26 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-methylphenyl(mesityl)phosphine borane. (0.21 g, 84%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.49-7.42(m, 2H, Ar), 7.36-7.08 (m, 3H, Ar), 6.84-6.78 (m, 2H, Ar), 2.23 (s, 6H, *o*-Me), 2.20 (s, 3H, *p*-Me), 1.86 (d, $^{2}J_{PH}$ = 9.6 Hz, 3H, PCH_3); 1.38-0.82 (b, m, 3H, BH_3) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 11.6 ppm. ^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 151 MHz): δ = 142.5, 140.0, 134.4, 133.6, 129.9, 129.4, 129.1, 127.7, 127.1, 124.2, 22.9, 19.8, 16.0 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ = -32.5 ppm); IR (KBr, cm^{-1}) ν: 3010, 2356(BH_3), 1746, 1623, 1336, 1320, 1136, 765.



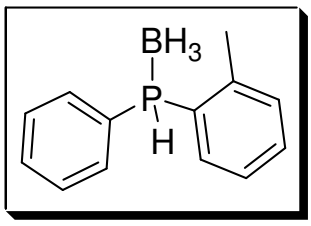
(±)-Cyclohexylmethylphenylphosphine borane: From (±)-(2-Cyclohexylmethylphenylphosphine oxide (0.23 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave **(±)-**cyclohexylmethylphenylphosphine borane. (0.20 g, 90%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73-7.46 (m, 4H, Ar) 1.68 (d, $^{2}J_{PH}$ = 10.4 Hz, 3H, PCH_3), 1.69-1.16 (m, 11H, *c*-Hexyl); 1.46-0.38 (br, m, 3H) ppm ^{31}P NMR ($CDCl_3$, 300 MHz): δ = 17.1 ppm (Lit.[17] 16.2 ppm).



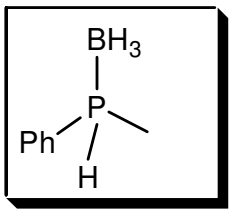
(±)-*tert*-Butylmethylphenylphosphine borane: From (±)-*tert*-Butylmethylphenylphosphine oxide (0.20 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave (±)-*tert*-Butylmethylphenylphosphine borane. (0.17 g, 89%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.68-7.38 (m, 5H, Ar), 1.45 (d, J_{HP}= 10.2 Hz, 3H), 1.09(d, J_{HP}= 16.5 Hz, 9H), 1.12-0.88 (br, m, 3H) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ =25.8 (lit.[19] 25.3) ppm.



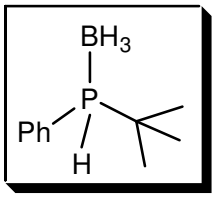
Tri-n-butylphosphine borane : From tri-n-butylphosphine oxide (0.21 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave tri-n-butylphosphine borane. (0.19 g, 86%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.55-1.47 (m, 6H), 1.45-1.32 (m, 12H), 0.85 (t, J_{HP}= 7.5 Hz, 9H), 0.55-0.15(br, m, 3H) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ =14.1 (lit.[20] 14.7) ppm.



Phenyl(*o*-tolyl)phosphine borane : From methylphenyl(*o*-tolyl)phosphine oxide (0.15 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave phenyl(*o*-tolyl)phosphine borane. (0.13 g, 87%) %) ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.82-7.30 (m, 9H, Ar), 6.58 (d, J_{HP} = 385 Hz, 1H), 2.46(s, 3H), 1.65-0.45 (br, m, 3H) ppm. ^{31}P NMR (CDCl3, 121 MHz): δ = -6.3 (lit[21] -3.8) ppm



Methylphenylphosphine borane: From Methylphenylphosphine oxide (0.14 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave methylphenylphosphine borane. (0.12 g, 86%)^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.75-7.44 (m, 9H, Ar), 5.35 (d, J_{HP} = 375 Hz, 1H), 1.67 (d, $^2J_{PH}$ = 12.1 Hz, 3H), 0.68-0.45 (br, m, 3H) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ = -13.5 (lit.[22] -14.6).



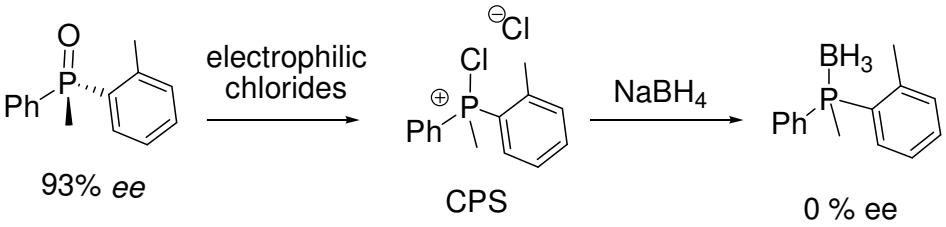
(±)-*tert*-Butylphenylphosphine borane: From *tert*-butylphenylphosphine oxide (0.18 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave *tert*-butylphenylphosphine borane. (0.16 g, 88%) ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80 -7.45 (m, 5H, Ph), 5.25 (q, J_{HP} = 375 Hz, 1H), 1.21 (d, J_{HP} = 15.2 Hz, *t*-Bu, 9H) 1.58-0.32 (m, 3H, BH_3). ^{31}P NMR ($CDCl_3$, 121 MHz): δ =31.0 (lit[19] 32.0) ppm.

(±)-*tert*-Butylphenylphosphine borane: From *tert*-butylphenylphosphine sulfide (0.20 g, 1.0 mmol, 1 equiv) treated with oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.) followed by the treatment with $NaBH_4$ in diglyme (3.4 mL, 0.6 M, 2.1 mmol, 2.1 equiv) gave *tert*-butylphenylphosphine borane. (0.15 g, 86%) ^{31}P NMR ($CDCl_3$, 121 MHz): δ =31.4 (lit[19] 31.9) ppm.

Reduction of Enantioenriched phosphine oxide

Using electrophilic chlorides (*S*)-methylphenyl-*o*-tolylphosphine oxide of 93% ee was subject to the general procedure for reduction with oxalyl chloride and sodium borohydride described above. The results are shown in Table 1.

Table C Reduction of enantiomerically enriched phosphine oxide with electrophilic chlorides under various conditions.



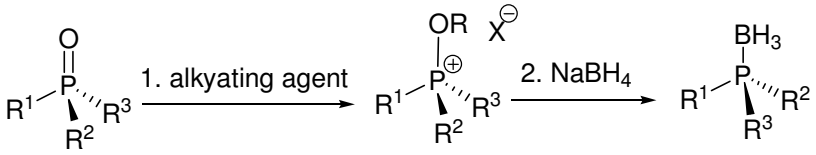
Entry[a]	Electrophilic Chlorides	solvent	PB % ee[b]
1	$(COCl)_2$	Neat	0
2	$(COCl)_2$	Toluene	0
3	$(COCl)_2$	DME[d]	0
4[c]	$(COCl)_2$	Toluene	0
5	$(COCl)_2$	DCM	0
6	$(COCl)_2$	IL[e]	0
7	SO_2Cl_2	Toluene	0
8	$MeSO_2Cl_2$	Toluene	0
9	$SOCl_2$	DCM	0
10	$(COCl)_2$	diethylether	0

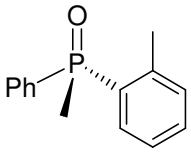
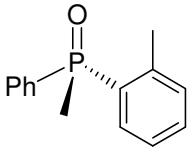
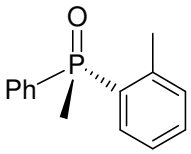
[a] = Both steps in the reaction was done at -78 °C for entries 2-10, r.t. for entry 1.; CPS (by ^{31}P NMR) was same for entries 1-9; for entry 10 CPS was observed at -31 and 71 ppm which found to be covalent and ionic form respectively.[23] [b] = (PB) phosphine borane; % ee was determined by CSP HPLC; yield > 95% except for entry 8 which was 65% (by ^{31}P NMR). [c] = Very slow addition addition of both oxalyl chloride and $NaBH_4$; [d] = DME: dimethoxy ethane [e] =(IL) Ionic liquid (1-methyl-3-octylimidazolium tetrafluroborate;

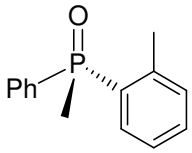
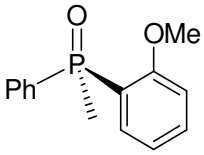
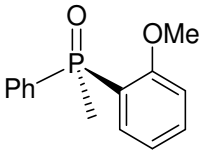
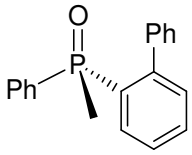
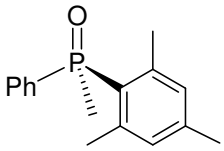
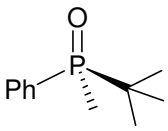
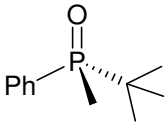
General Procedure for the Stereospecific Conversion of Enantioenriched Phosphine oxide to phosphine borane

To a stirred solution of alkylating agent (1.2 mmol) in DCM or DME (2 mL) phosphine oxide (1.0 mmol) disolved in DCM or DME (2 mL) was added dropwise at room temperature under a nitrogen atmosphere. The reaction mixture was refluxed gently for 2 hrs at which point ^{31}P NMR showed the complete conversion of phosphine oxide to the alkoxyphosphonium salt. After cooling to room temperature, sodium borohydride (3 mmol) dissolved in diglyme (5 mL) was added dropwise to the reaction mixture. This mixture was refluxed gently for 2 h. Once the ^{31}P NMR showed the full conversion of salt to phosphine borane the reaction mixture was washed with deionised water (5 mL), and the isolated organic layer was dried over anhydrous $MgSO_4$. The drying agent was removed by filtration, and the solvent was removed *in vacuo* to give colourless oil, which was eluted through a silica plug using 50:50 cyclohexane/ethylacetate as eluting solvent. Solvent removal *in vacuo* yielded the pure phosphine borane.

Table D. Stereospecific reduction/boronation[a] of enantioenriched phosphine oxide.



Entry	Phosphine oxide	Alkyl. agent	Yield (%)[b]	% ee[c] (config)
1[d,e]	 93% *ee* (*S*)	MeOTf	62	93 (*S*)
2[e]	 93% *ee* (*S*)	MeOTf	73	93 (*S*)
3[f]	 93% *ee* (*S*)	$[Et_3O]BF_4$	76	93 (*S*)

4	 93% *ee* (*S*)	$[Me_3O]BF_4$	71	93 (*S*)
5.[g]	 95% *ee* (*R*)	$[Et_3O]BF_4$	67	95 (*R*)
6.[h]	 95% *ee* (*R*)	$[Me_3O]BF_4$	71	95 (*R*)
7.[i]	 81% *ee* (*S*)	$[Et_3O]BF_4$	68	81 (*S*)
8.[j]	 44 % *ee*	$[Et_3O]BF_4$	67	44 [k]
9.[l]	 53 % *ee* (*R*)	$[Et_3O]BF_4$	63	53 (*R*)
10.	 46 % *ee* (*S*)	$[Et_3O]BF_4$	68	46 (*S*)

[a] Unless otherwise specified the addition of alkylating agent (in DCM) and $NaBH_4$ (in diglyme) was carried at room temperature followed by refluxing; [b] isolated yield; [c] by CSP HPLC, configuration determined as described below; [d] $NaBH_4$ was added at -78 °C; [e] in DME solvent, methoxyphosphonium salt was observed at δ75.9 ppm in ^{31}P NMR; [f] ethoxyphosphonium salt was observed at δ 71.9 ppm in ^{31}P NMR; [g] ethoxyphosphonium salt was observed at δ 70.3 ppm in ^{31}P NMR; [h] methoxyphosphonium salt was observed at δ 73.8 ppm in ^{31}P NMR; [i] ethoxyphosphonium salt was observed at δ 67.8 ppm in ^{31}P NMR [j] ethoxyphosphonium salt was observed at δ 78.3 ppm in ^{31}P NMR; [k] % ee of phosphine oxide,obtained by converting scalemic phosphine borane to scalemic phosphine oxide using DABCO and H_2O_2; config remains to be assigned; [l] ethoxyphosphonium salt was observed at δ 89.8 ppm in ^{31}P NMR.

Table D

Entry 1: (*S*)-Methylphenyl(*o*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with methyl triflate (0.13 mL, 1.2 mmol, 1.2 equiv.) in DME solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(*o*-tolyl)phosphine borane (0.14 g, 62%, 93 % ee (*S*))

Entry 2: (*S*)-Methylphenyl(*o*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1 equiv) was treated with methyl triflate (0.13 mL, 1.2 mmol, 1.2 equiv.) in DME solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave (*S*)-methylphenyl(*o*-tolyl)phosphine borane (0.16 g, 73%, 93 % ee (*S*))

Entry 3: (*S*)-Methylphenyl(*o*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1.0 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(*o*-tolyl)phosphine borane (0.17 g, 76%; 93 % ee (*S*))

Entry 4: (*S*)-Methylphenyl(*o*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 1.0 equiv) was treated with (trimethyloxonium tetrafluoroborate) $[Me_3O]BF_4$ (0.17 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(*o*-tolyl)phosphine borane (0.16 g, 71%; 93 % ee (*S*))

Entry 5: (*R*)-Methylphenyl(anisyl)phosphine oxide (0.25 g, 1.0 mmol, 1.0 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(anisyl)phosphine borane (0.16 g, 67%; 95 % ee (*R*))

Entry 6: (*R*)-Methylphenyl(anisyl)phosphine oxide (0.25 g, 1.0 mmol, 1 equiv) was treated with (trimethyloxonium tetrafluoroborate) $[Me_3O]BF_4$ (0.17 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave methylphenyl(anisyl)phosphine borane (0.17 g, 71%; 95 % ee (*R*))

Entry 7: (*S*)-Methylphenyl(biphenyl)phosphine oxide (0.14 g, 0.5 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (0.11 g, 0.6 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (3 mL, 0.5 M, 1.5 mmol, 3.0 equiv) gave methylphenyl(biphenyl)phosphine borane (95 mg, 68%; 81 % ee (*S*))

Entry 8: (*R*)-Methylphenyl(mesityl)phosphine oxide (85 mg, 0.3 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (73 mg, 0.4 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (2 mL, 0.5 M, 1.0 mmol, 3.0 equiv) gave methylphenyl(mesityl)phosphine borane (52 mg, 67%). For HPLC analysis methylphenyl(mesityl)phosphine borane was treated with DABCO (1.2 equiv) followed by hydrogen peroxide (1.2 equiv) to give (*S*)-Methylphenyl(mesityl)phosphine oxide 44 % ee.

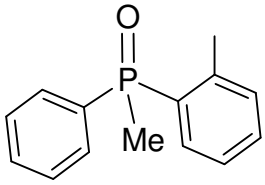
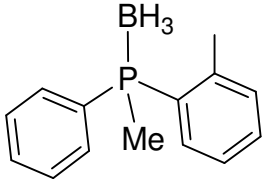
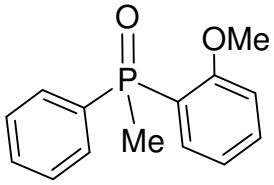
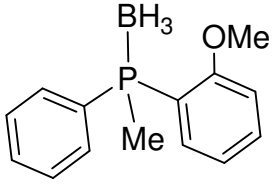
Entry 9: (*R*)- *tert*-Butylmethylphenylphosphine oxide (0.19 g, 1.0 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave *tert*-Butylmethylphenylphosphine borane (0.12 g, 63%; 53 % ee (*R*)

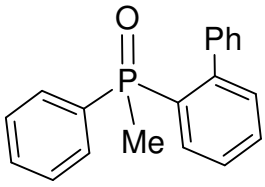
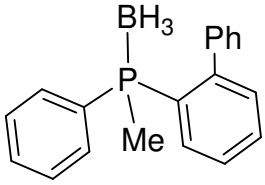
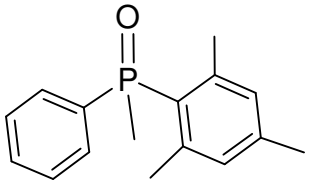
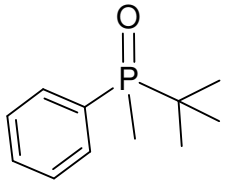
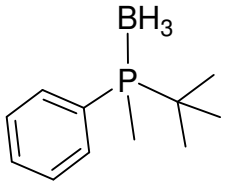
Entry10: (*S*)- *tert*-Butylmethylphenylphosphine oxide (0.19 g, 1.0 mmol, 1 equiv) was treated with (triethyloxonium tetrafluoroborate) $[Et_3O]BF_4$ (0.22 g, 1.2 mmol, 1.2 equiv.) in DCM solvent followed by the treatment with $NaBH_4$ in diglyme (6 mL, 0.5 M, 3.0 mmol, 3.0 equiv) gave *tert*-Butylmethylphenylphosphine borane (0.13 g, 68%; 46 % ee (*S*)

Determination of absolute configurations of phosphine oxide and borane

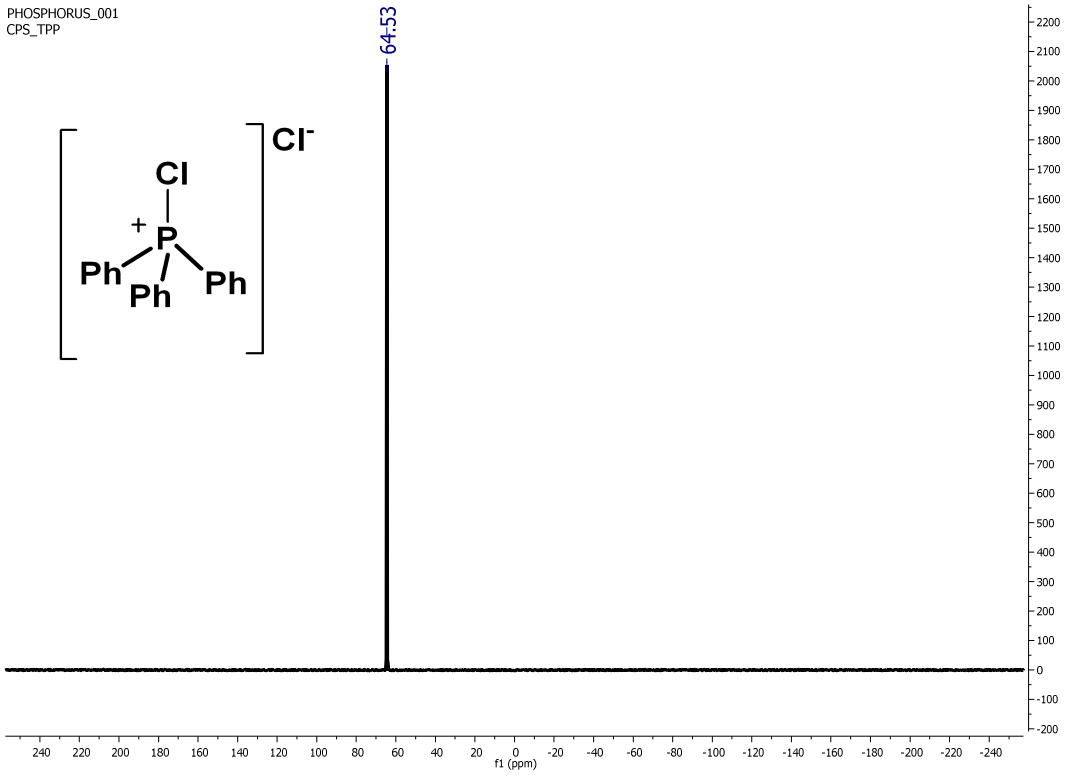
These were assigned according to the literature reported data. Thus 93% (*S*)-methylphenyl*o*-tolyl phosphine oxide and 95 % (*R*)-methylphenylanisylphosphine oxide obtained from Celtic Catalysts Ltd. was confirmed as the (*S*) and (*R*) enantiomer respectively by HPLC comparison with the phosphine oxide obtained from an asymmetric Appel reaction on racemic methylphenyl*o*-tolylphosphine with (+)-menthol and HCA, which gave (*S*)-enantiomer of phosphine oxide,[24] reaction on racemic methylphenylanisylphosphine with (-)-menthol and HCA, which gave (*R*)-enantiomer of phosphine oxide.[25]

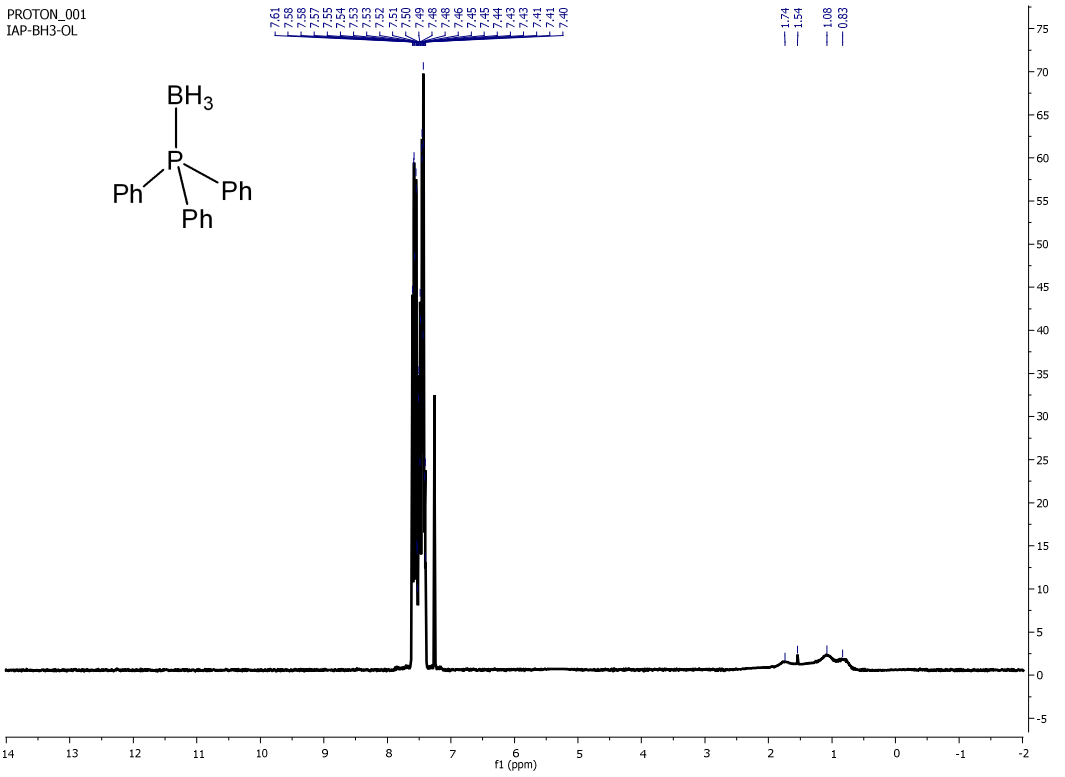
The Absolute configuration of phosphine oxide and phosphine borane were assigned by comparison with the literature reported (cited near the entry no.) HPLC data.

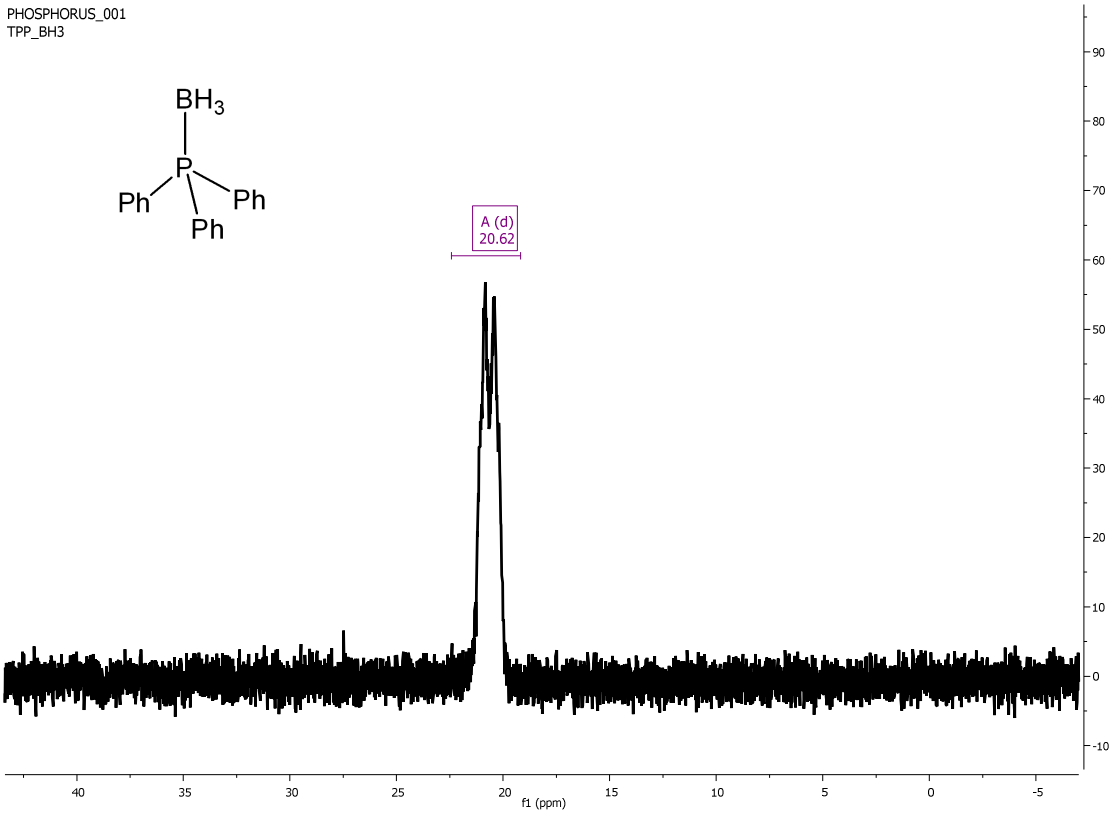
Entry	Phosphine oxide and Phosphine borane	Column	Condition	t1 (min)	t2 (min)
1.[24]		Chiralpak IA	Heptane/Et-OH = 80/20 1 mL/min	7.4 (*S*)	8.4 (*R*)
2. [13]		Chiralpak AS-H	Heptane/Et-OH = 98/02 1 mL/min	10.1 (*R*)	12.5 (*S*)
3.[25]		Chiralpak IA	Heptane/Et-OH = 90/10 1 mL/min	14.6(*R*)	15.9(*S*)
4. [14]		Chiralpak AS-H	Heptane/Et-OH = 98/02 1 mL/min	12.3(*R*)	13.1(*S*)

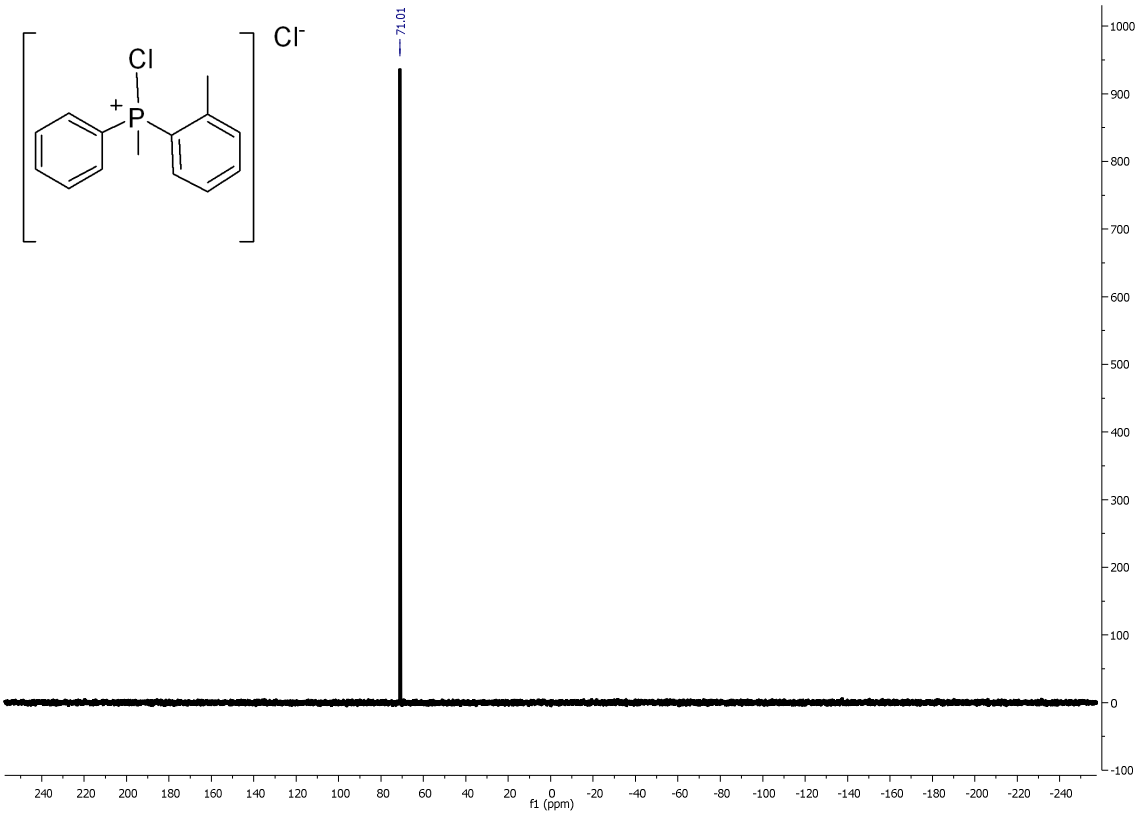
5.[25]		Chiralpak AS-H	Heptane/Et-OH = 90/10 1 mL/min	8.1(*R*)	10.2(*S*)
6.[25]		Chiralpak AS-H	Heptane/Et-OH = 98/02 1 mL/min	11.6 (*R*)	13.1 (*S*)
7.[26]		Chiralpak IA	Heptane/Et-OH = 90/10 1 mL/min	8.9	10.3
8.[27]		Chiralpak IA	Heptane/Et-OH = 90/10 1 mL/min	8.0 (*S*)	10.2 (*R*)
9.[27]		Chiralpak OJH	Heptane/Et-OH = 70/30 1 mL/min	9.0 (*S*)	10.2 (*R*)

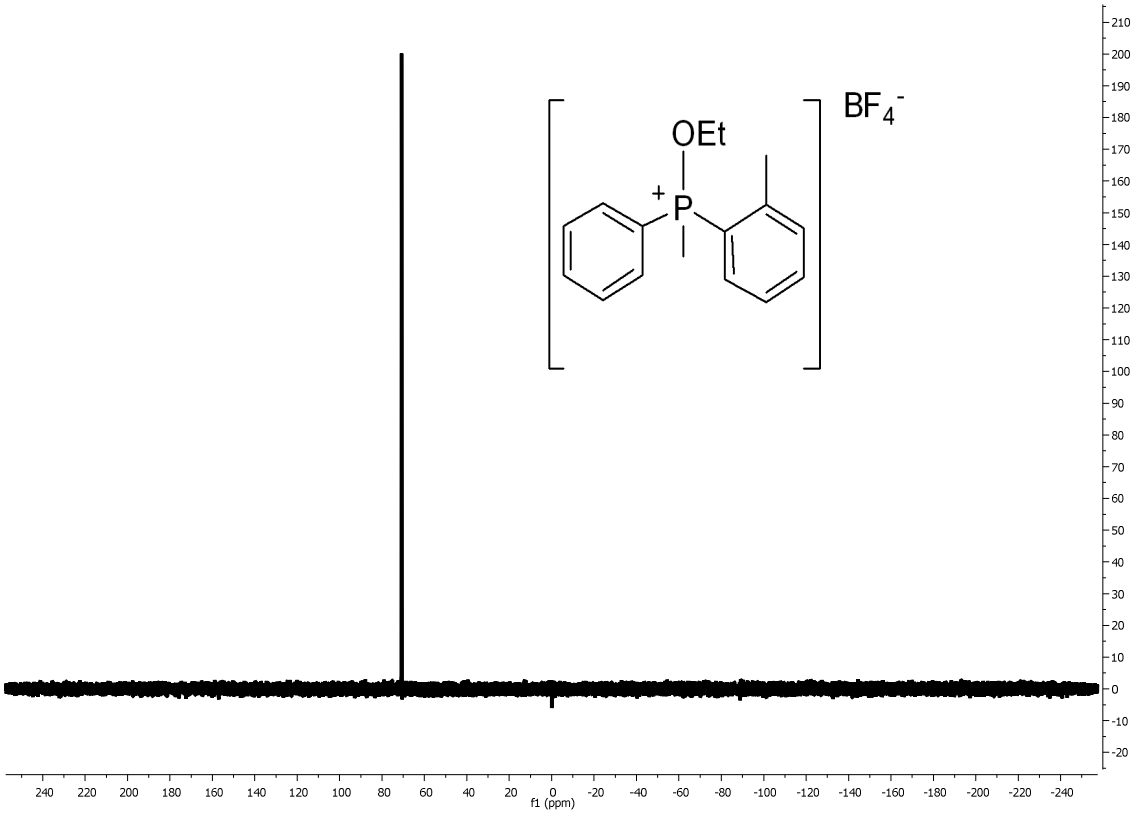
NMR spectra and HPLC traces of phosphine boranes.

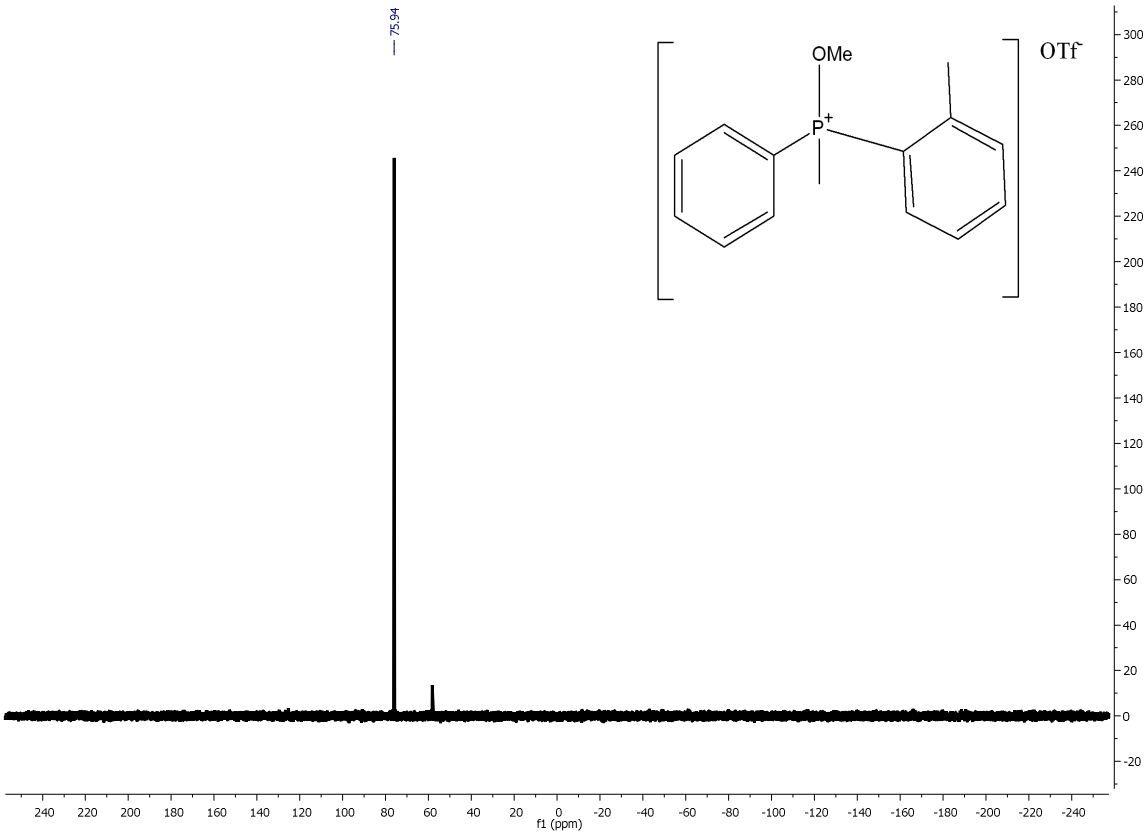


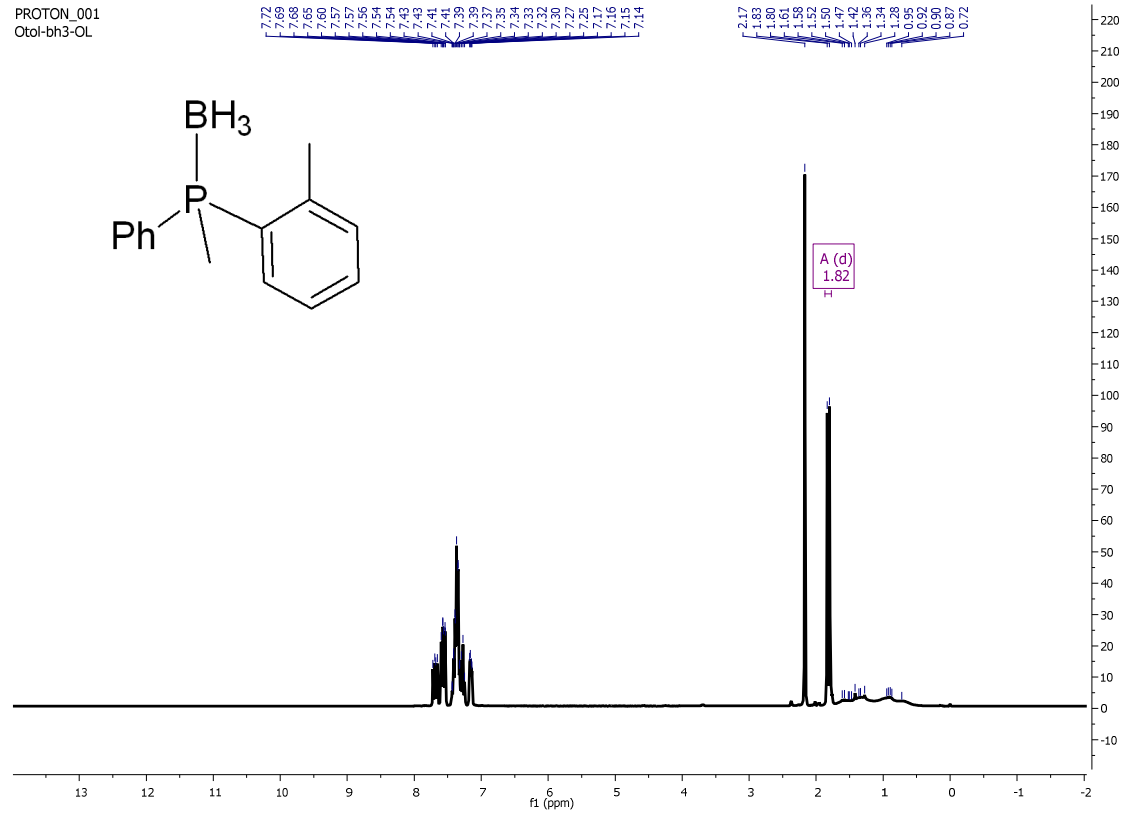


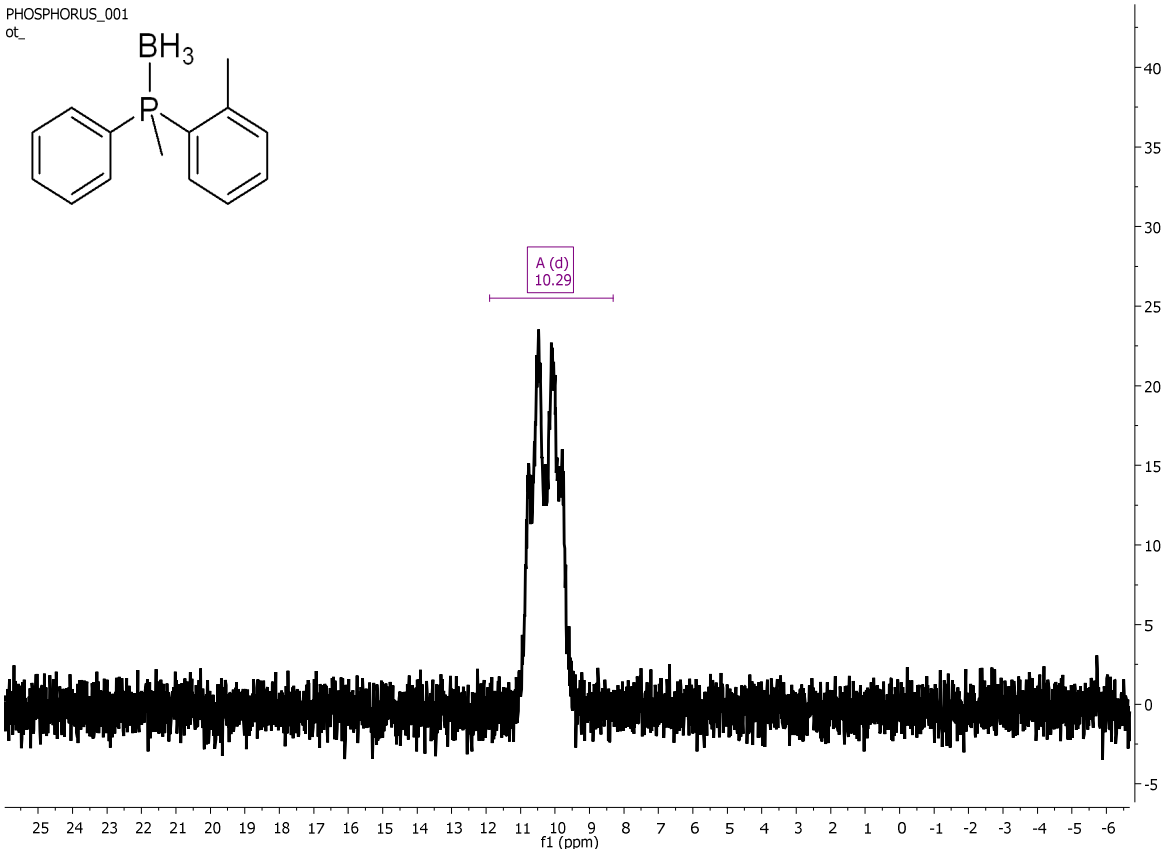

PHOSPHORUS_001
TPP_BH3
BH3
P
Ph
Ph
Ph
A (d)
20.62
f1 (ppm)

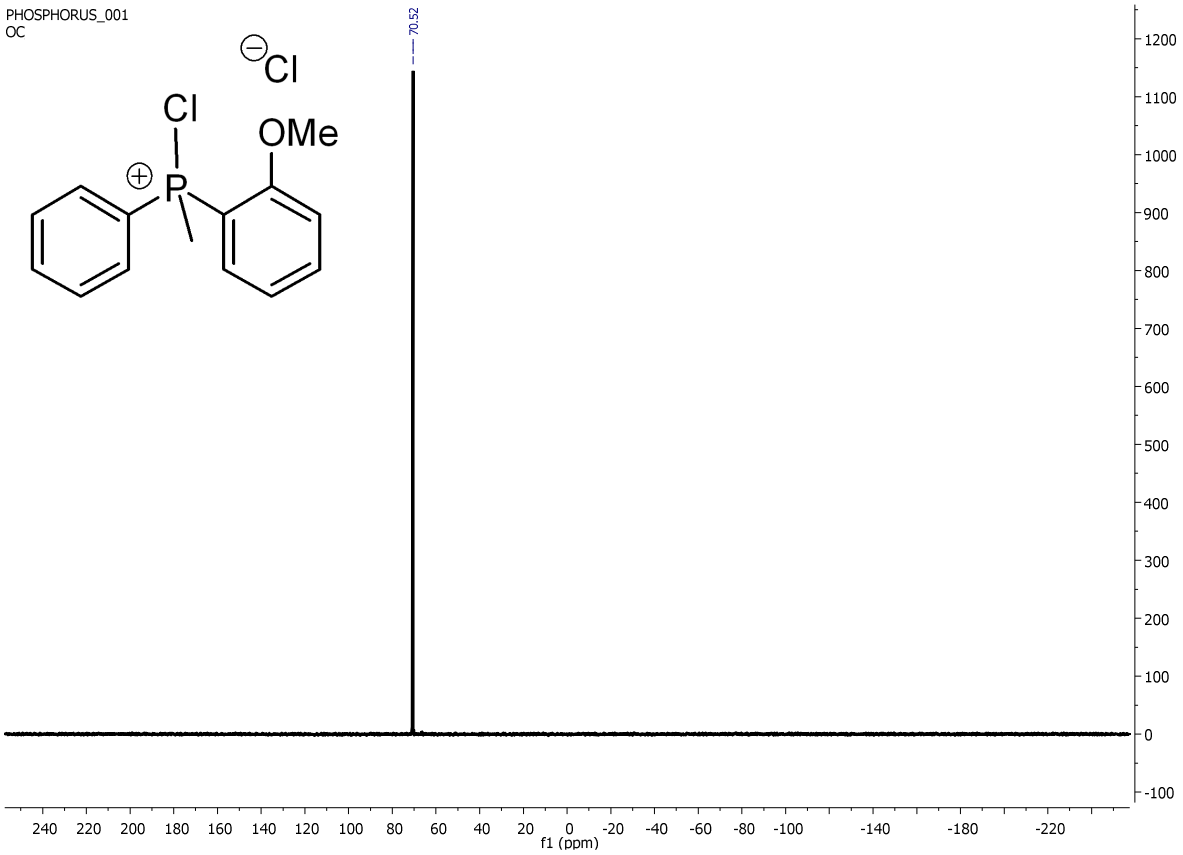

Cl
P
Cl-
71.01
f1 (ppm)

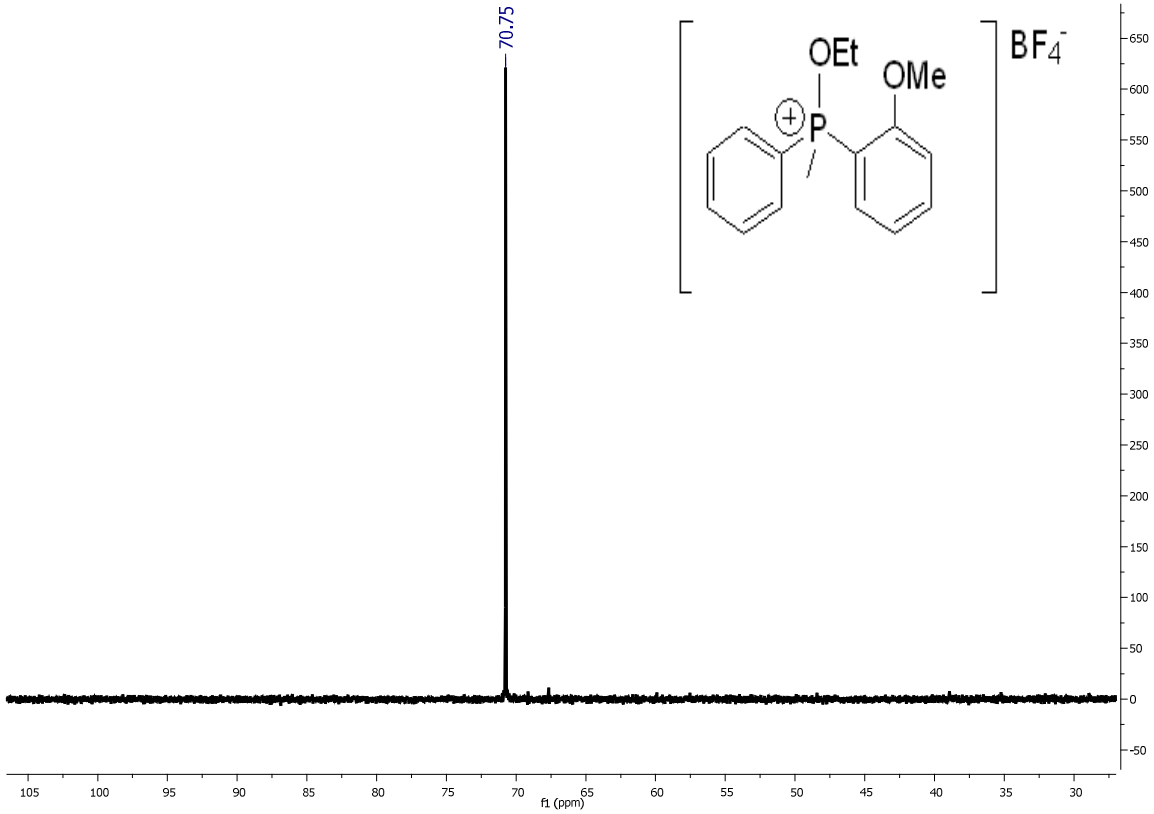

OEt
P
+
BF4-
f1 (ppm)

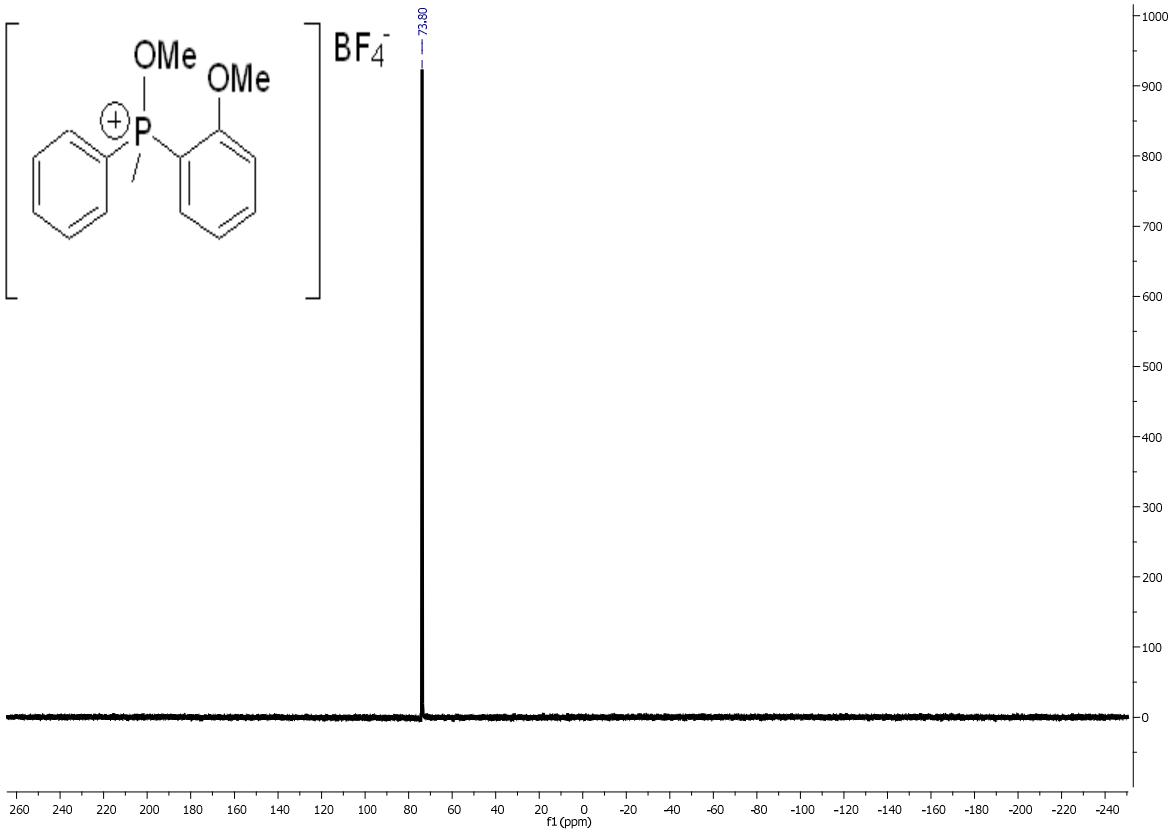

75.94
OMe
P+
OTf-
f1 (ppm)

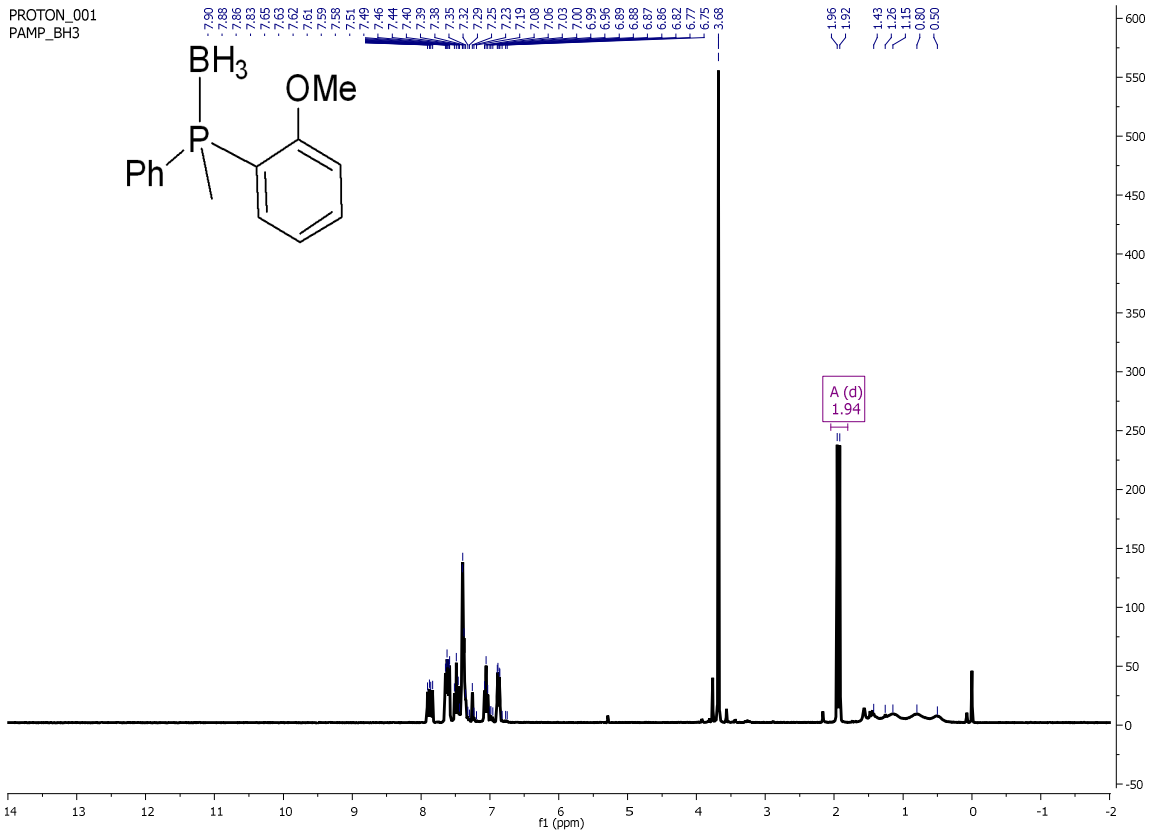

PROTON_001
Otol-bh3-OL
BH3
P
Ph
A (d)
1.82
H
f1 (ppm)

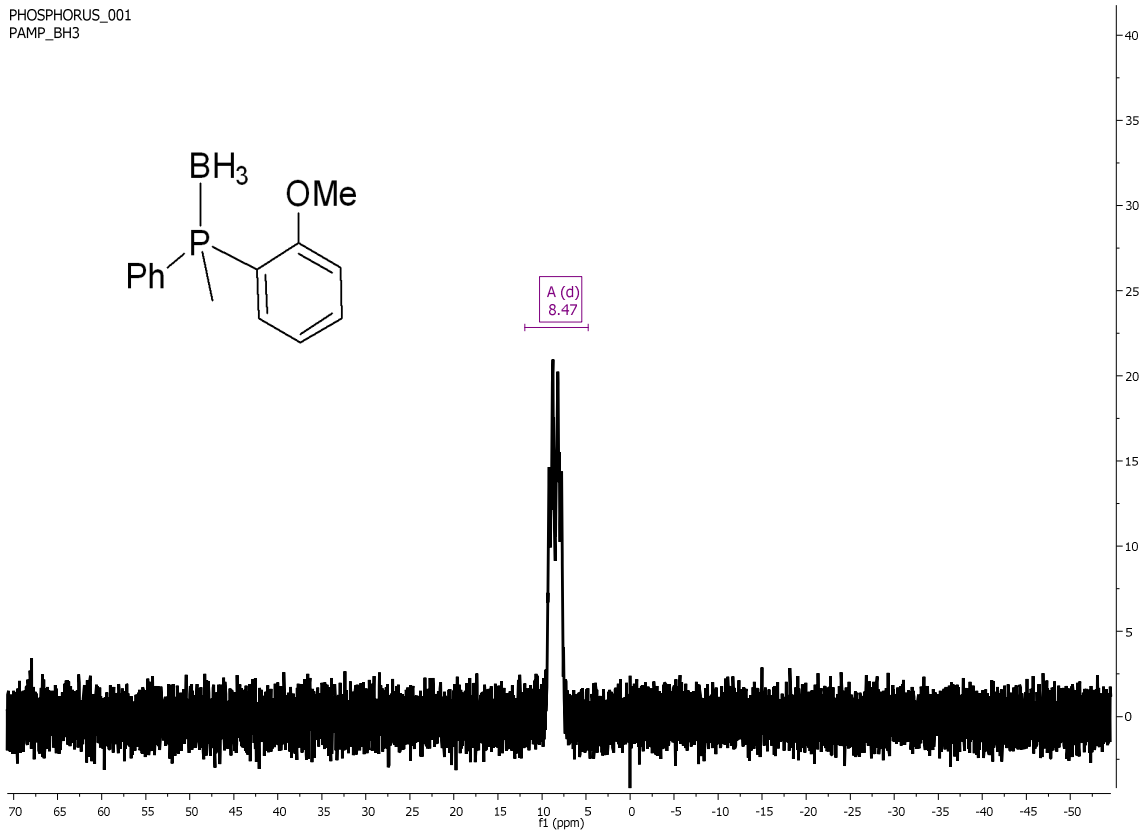

PHOSPHORUS_001
ot_
BH3
P
A (d)
10.29
f1 (ppm)

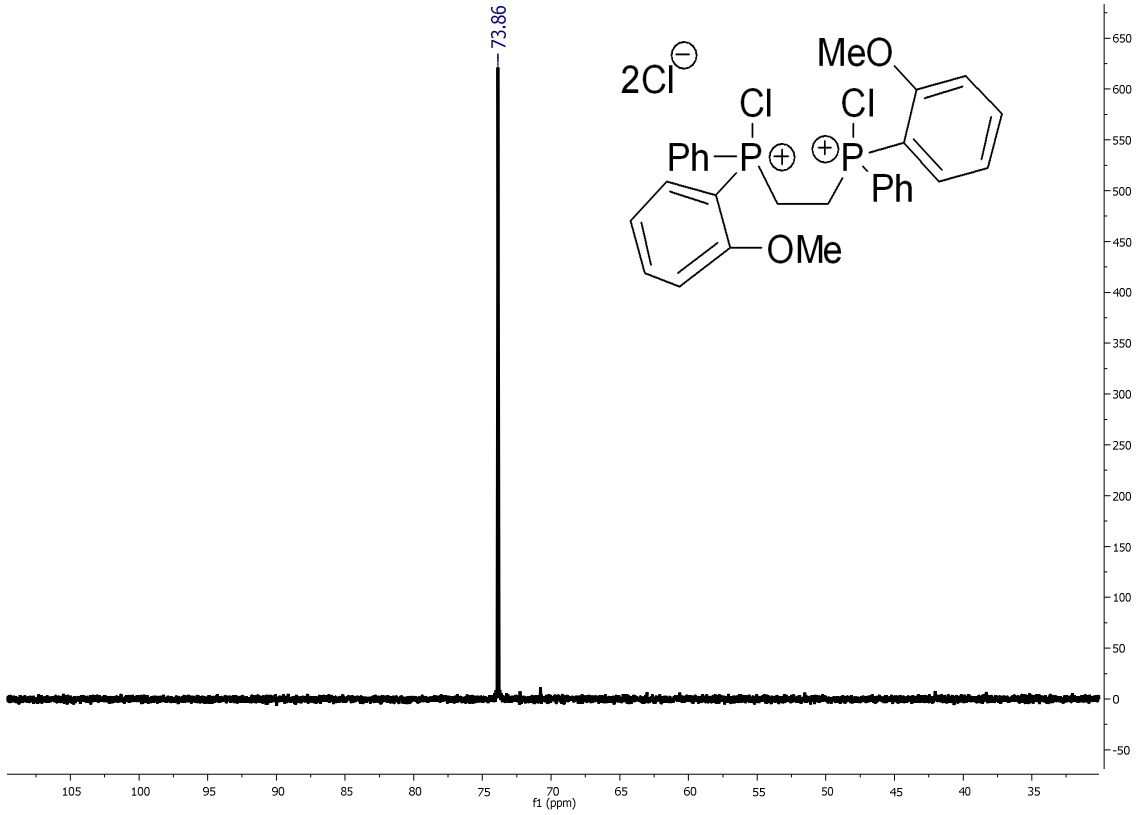

PHOSPHORUS_001
OC
70.52
Cl
Cl
OMe
P
f1 (ppm)

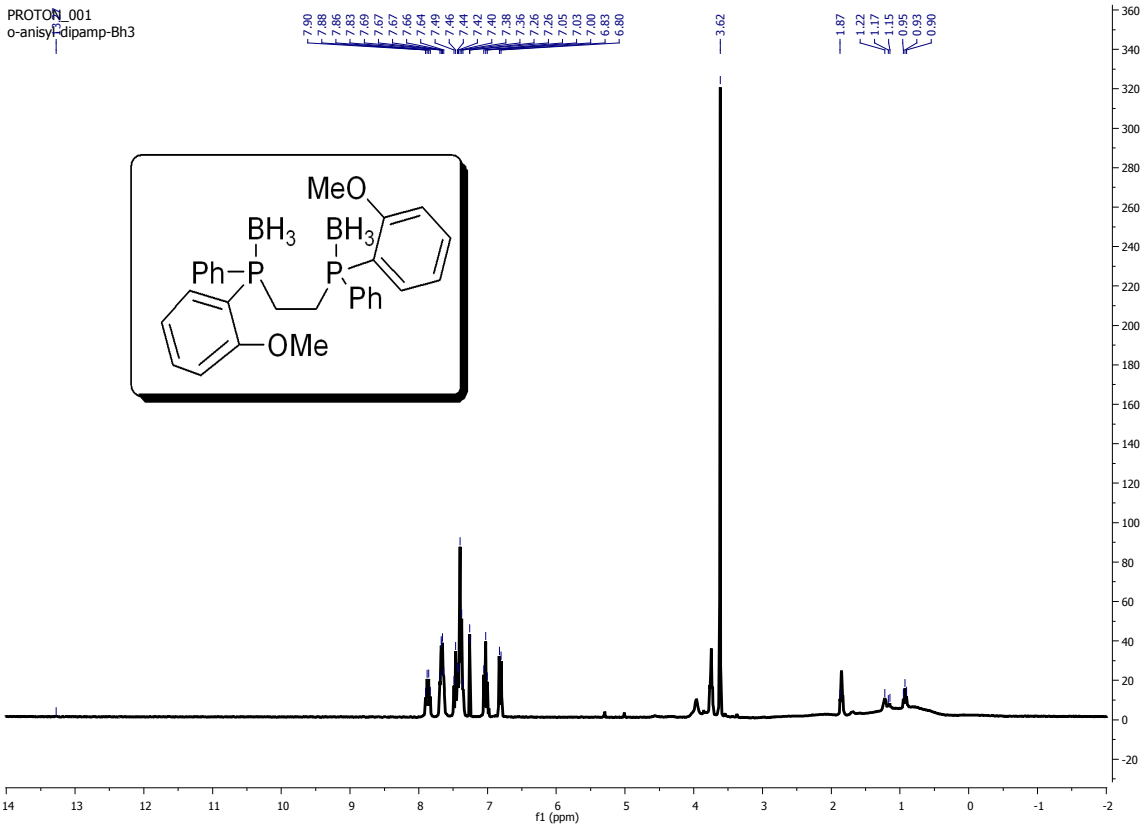

70.75
OEt
OMe
P
BF4
f1 (ppm)

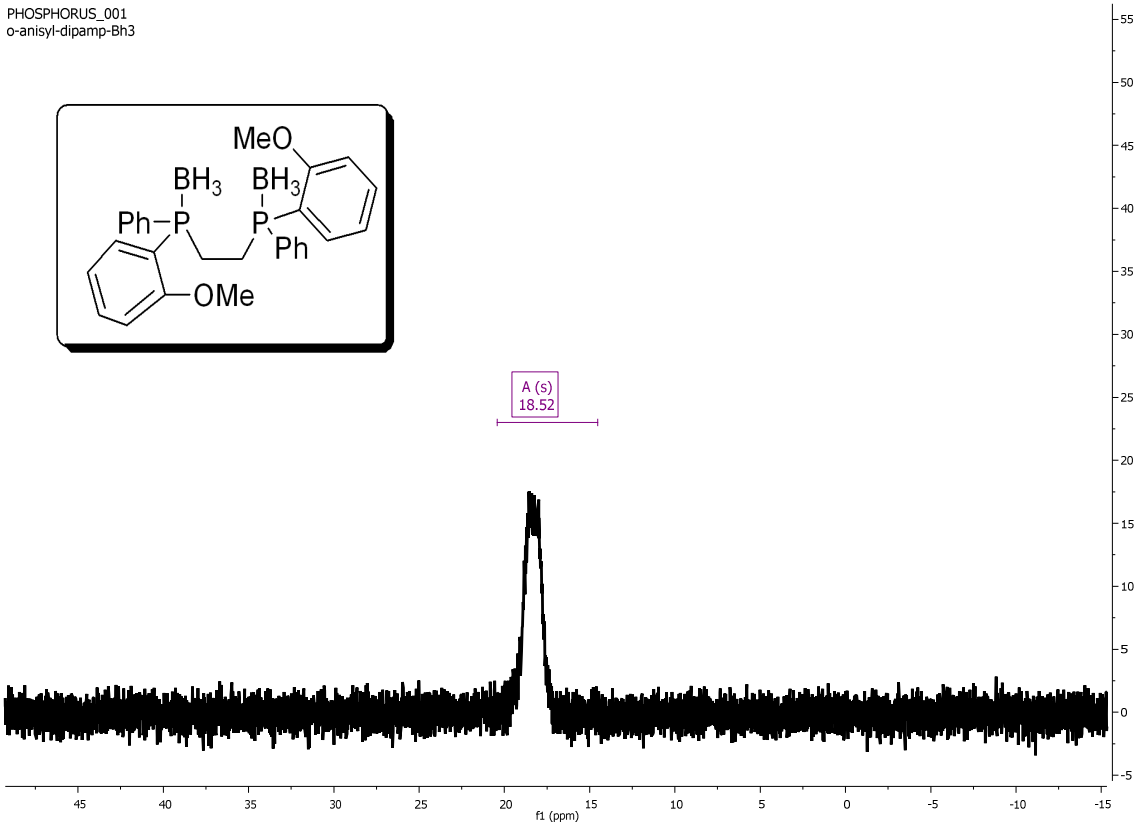

OMe
OMe
P
BF4-
73.80
f1 (ppm)

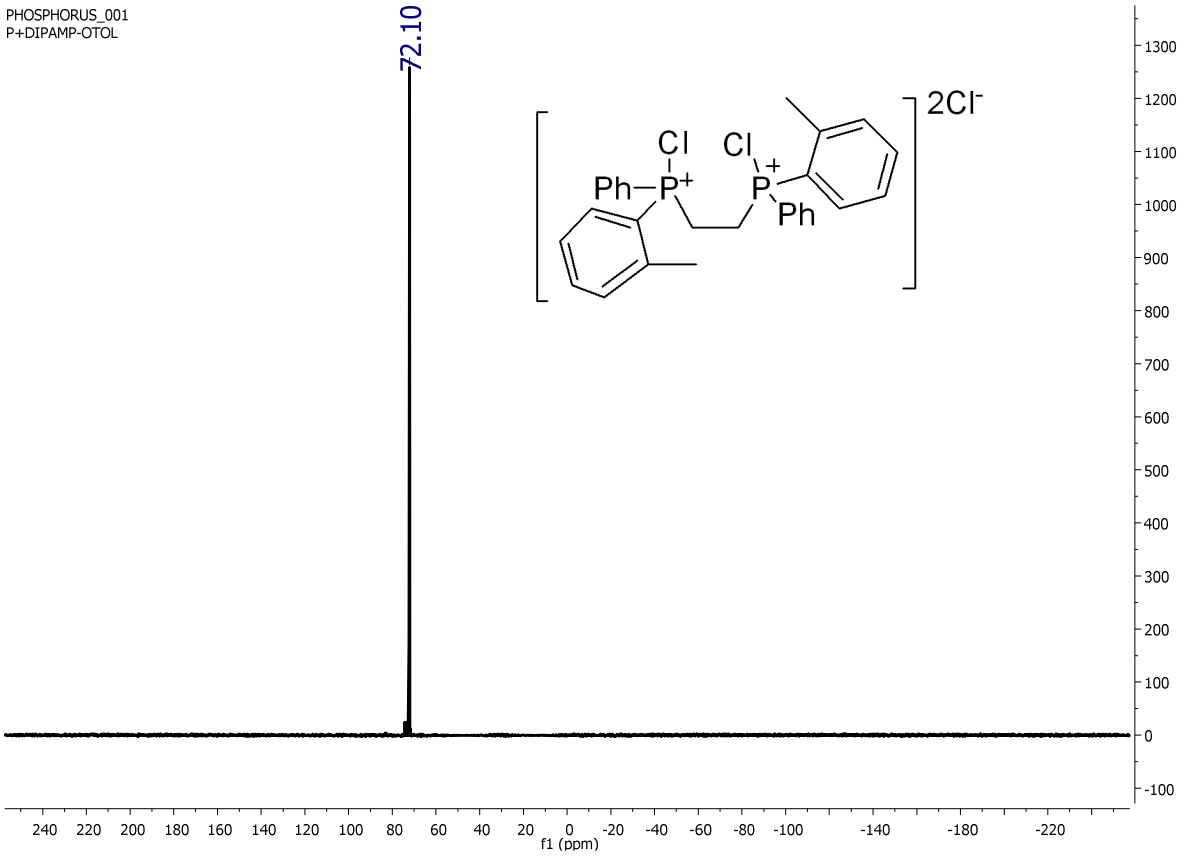

PROTON_001
PAMP_BH3
BH3
OMe
P
Ph
A (d)
1.94
f1 (ppm)

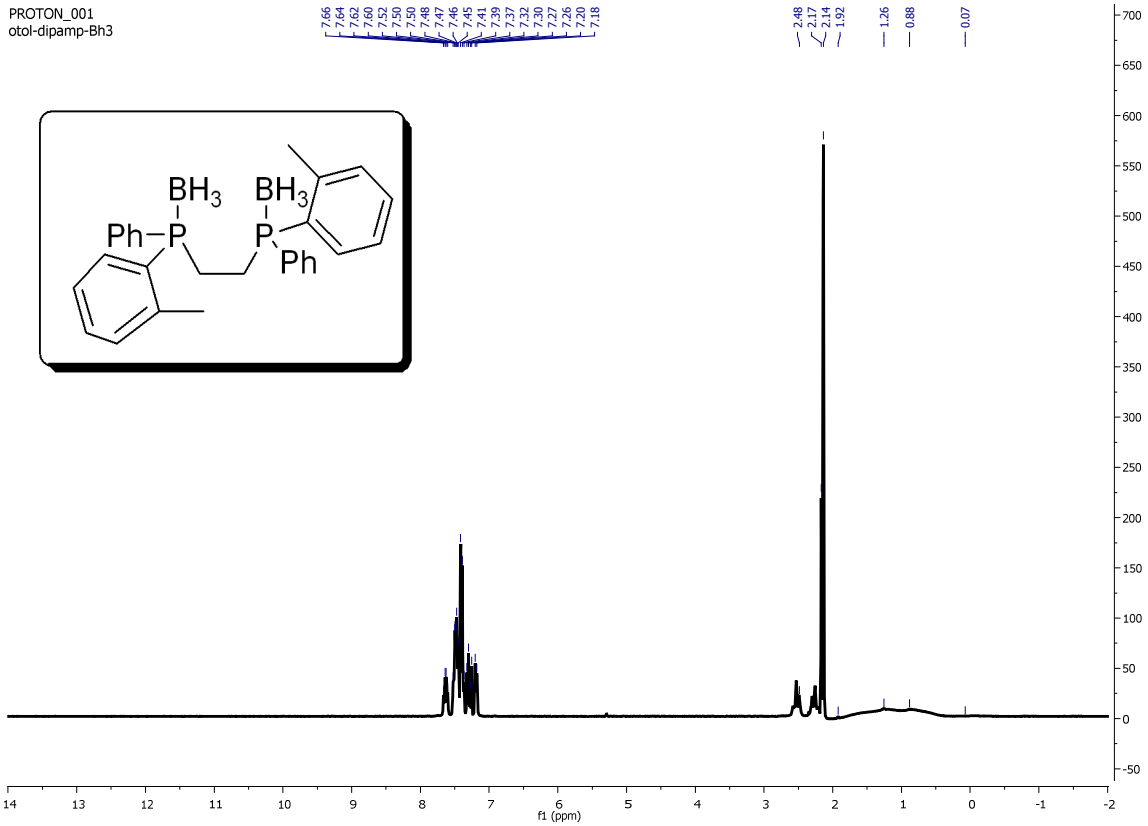

PHOSPHORUS_001
PAMP_BH3
BH3
OMe
P
Ph
A (d)
8.47
f1 (ppm)

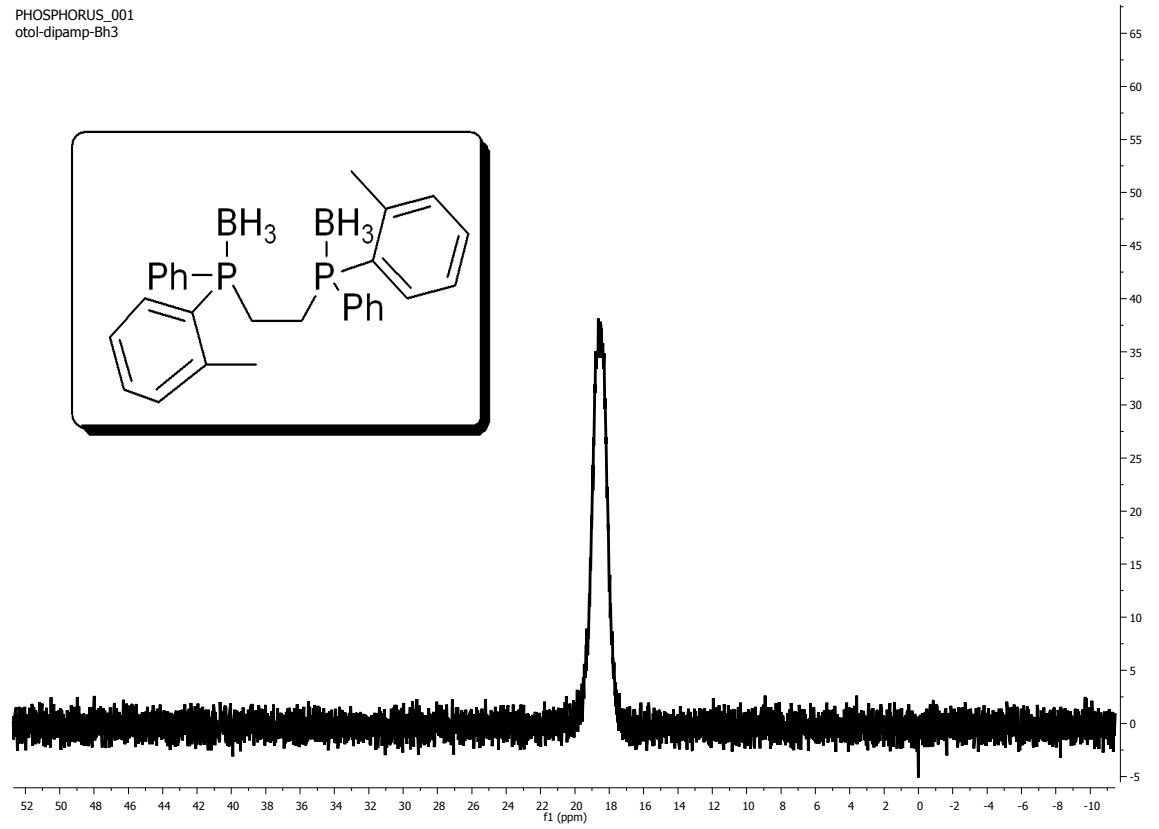

73.86
2Cl
MeO
Cl
Cl
Ph
P
P
Ph
OMe
f1 (ppm)

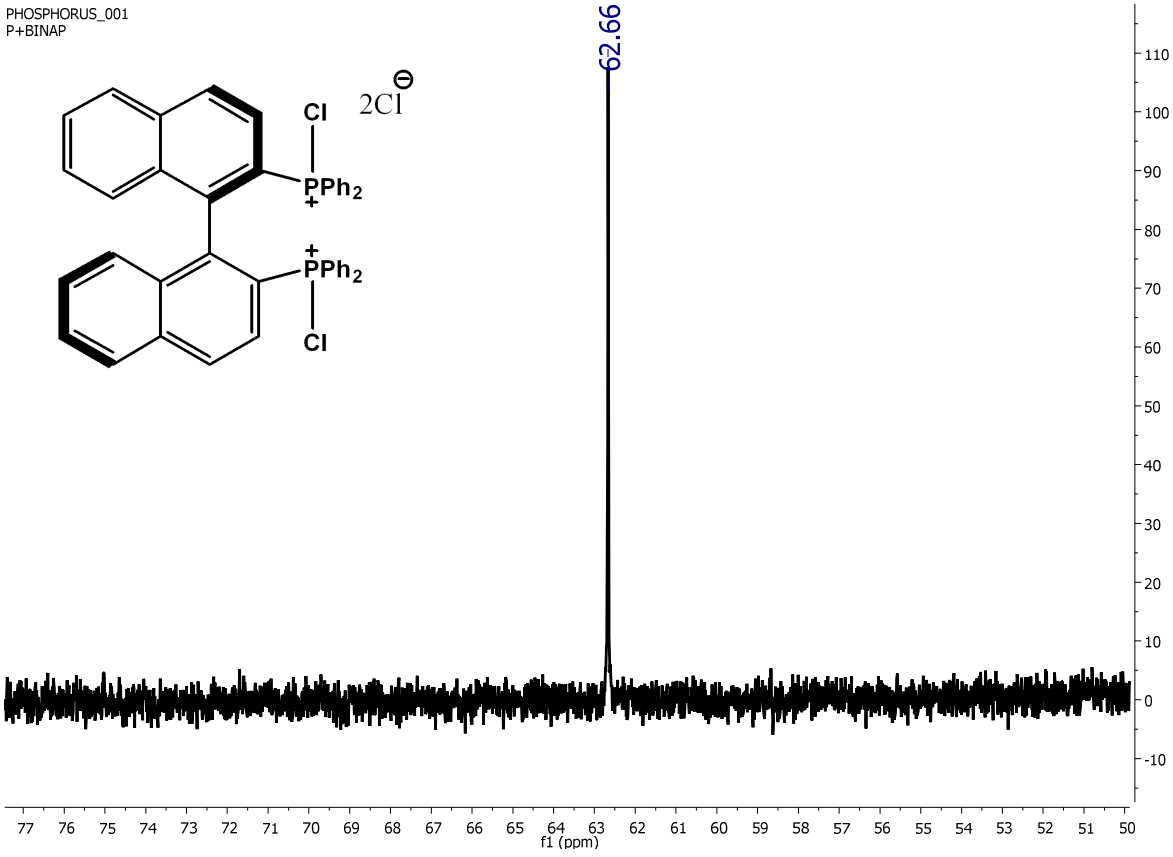

PROTON_001
o-anisyl-dipamp-Bh3
7.90
7.88
7.86
7.83
7.69
7.67
7.67
7.66
7.64
7.49
7.46
7.44
7.42
7.40
7.38
7.36
7.26
7.26
7.05
7.03
7.00
6.83
6.80
3.62
1.87
1.22
1.17
1.15
0.95
0.93
0.90
MeO
BH3
BH3
Ph–P
P
Ph
OMe
f1 (ppm)

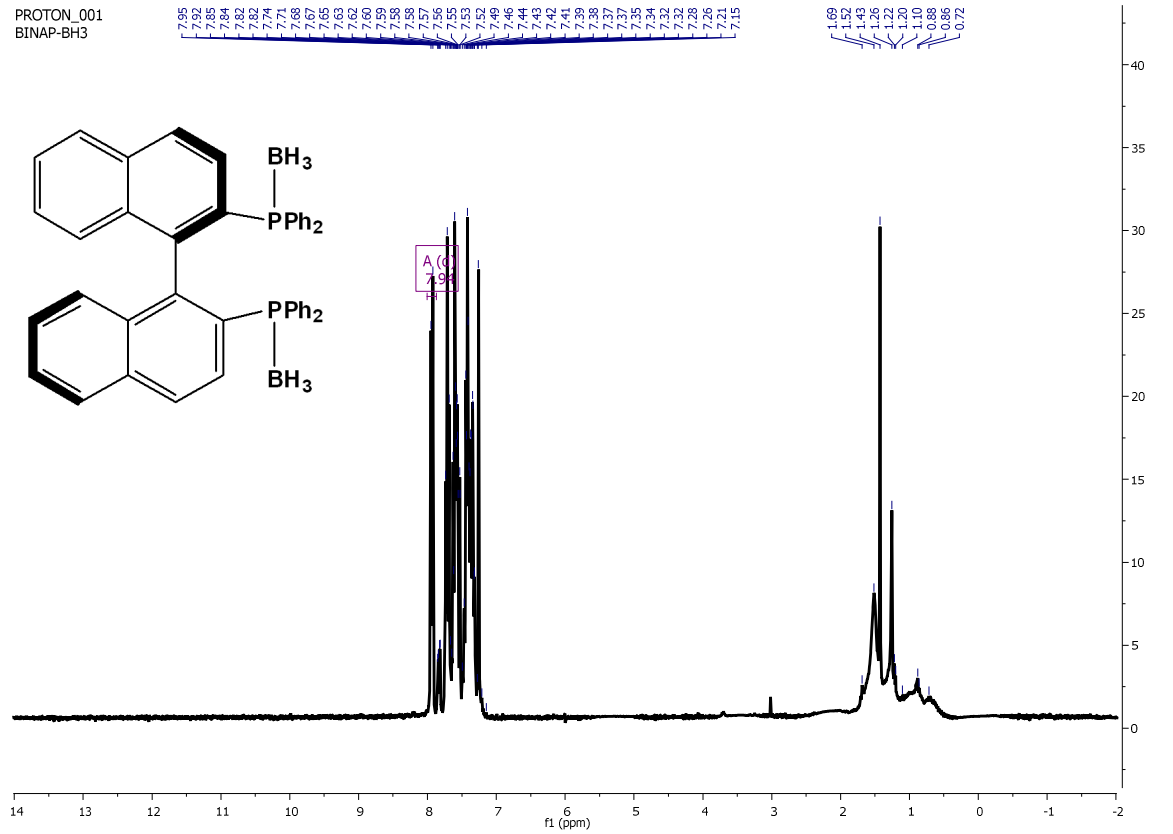

PHOSPHORUS_001
o-anisyl-dipamp-Bh3
MeO
BH3
BH3
Ph–P
P
Ph
OMe
A (s)
18.52
f1 (ppm)

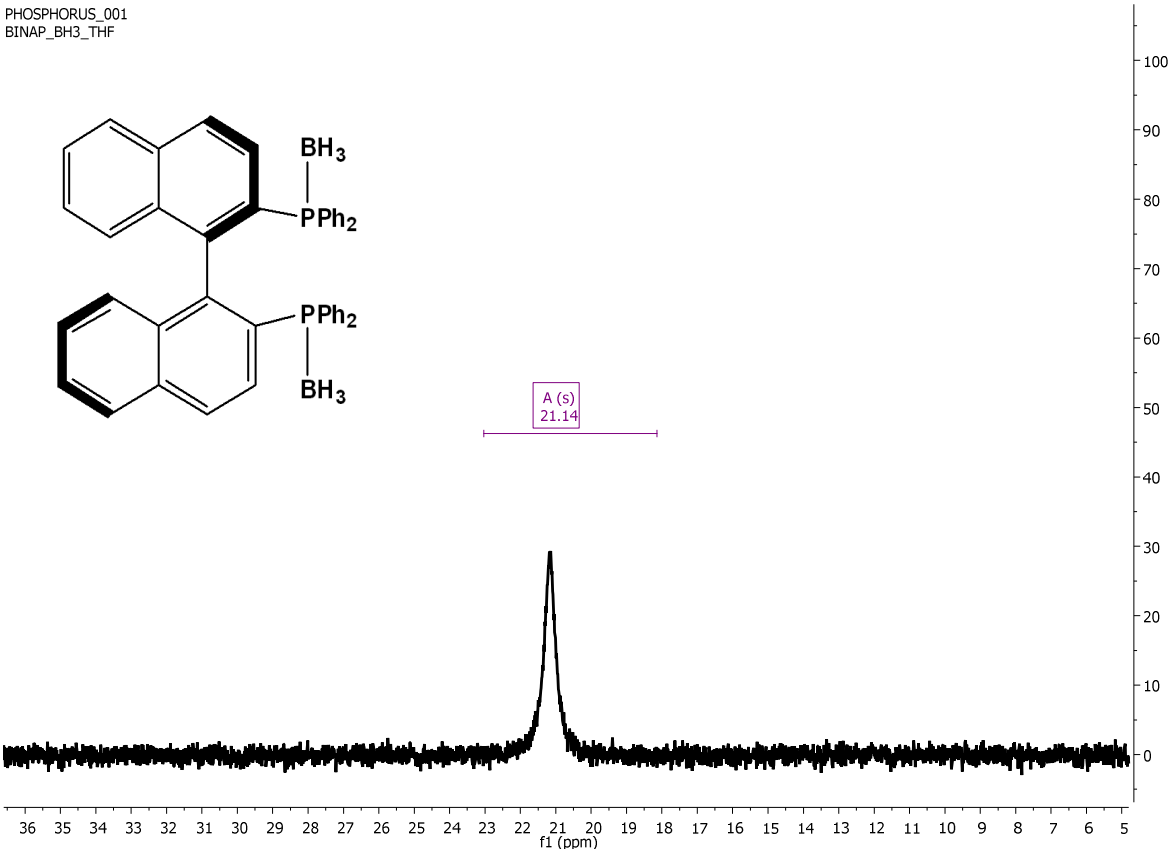

PHOSPHORUS_001
P+DIPAMP-OTOL
72.10
2Cl-
Cl
Cl
Ph—P+
P+
Ph
f1 (ppm)


PROTON_001
otol-dipamp-Bh3
BH3
BH3
Ph—P
P
Ph
f1 (ppm)


PHOSPHORUS_001
otol-dipamp-Bh3
BH3
BH3
Ph–P
P
Ph
f1 (ppm)


PHOSPHORUS_001
P+BINAP
62.66
2Cl
Cl
PPh2
PPh2
Cl
f1 (ppm)


PROTON_001
BINAP-BH3
7.95 7.92 7.85 7.84 7.82 7.82 7.74 7.71 7.68 7.67 7.65 7.63 7.62 7.60 7.59 7.58 7.58 7.57 7.56 7.55 7.53 7.52 7.49 7.46 7.44 7.43 7.42 7.41 7.39 7.38 7.37 7.37 7.35 7.34 7.32 7.32 7.28 7.26 7.21 7.15
1.69 1.52 1.43 1.26 1.22 1.20 1.10 0.88 0.86 0.72
BH3
PPh2
PPh2
BH3
A (s)
7.94
f1 (ppm)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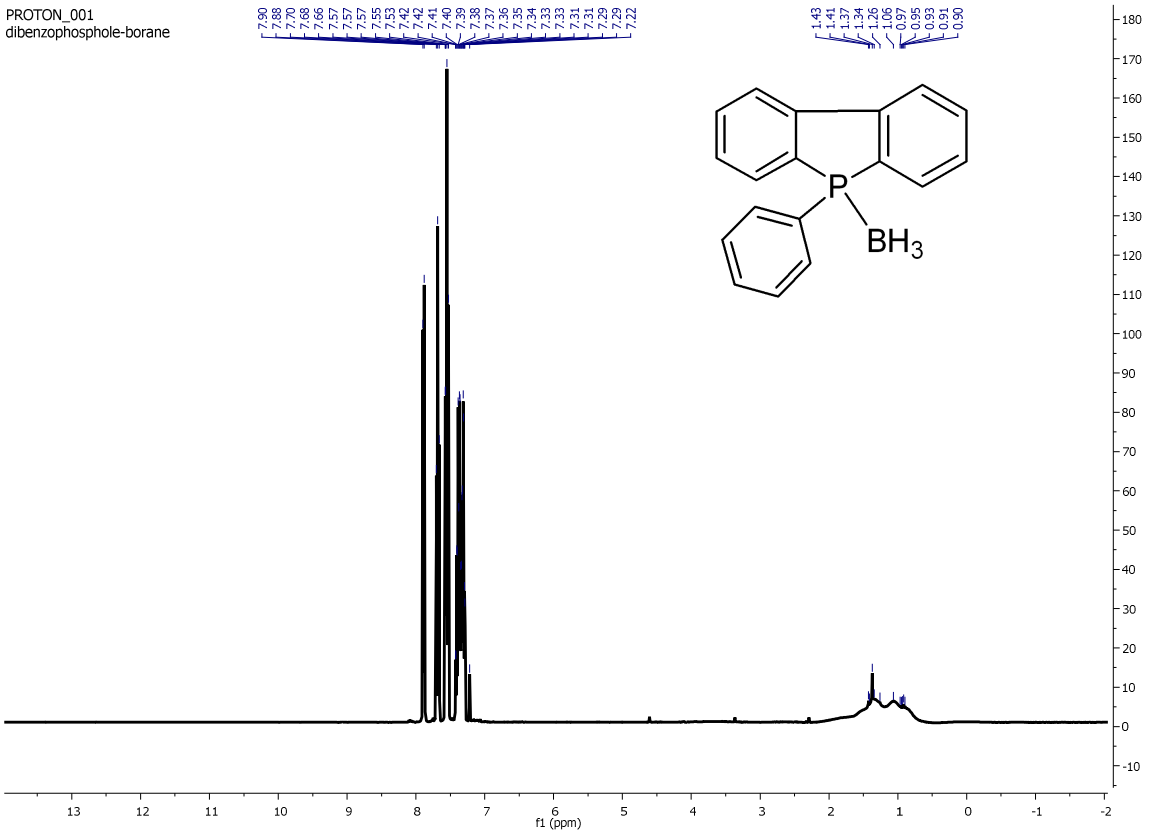
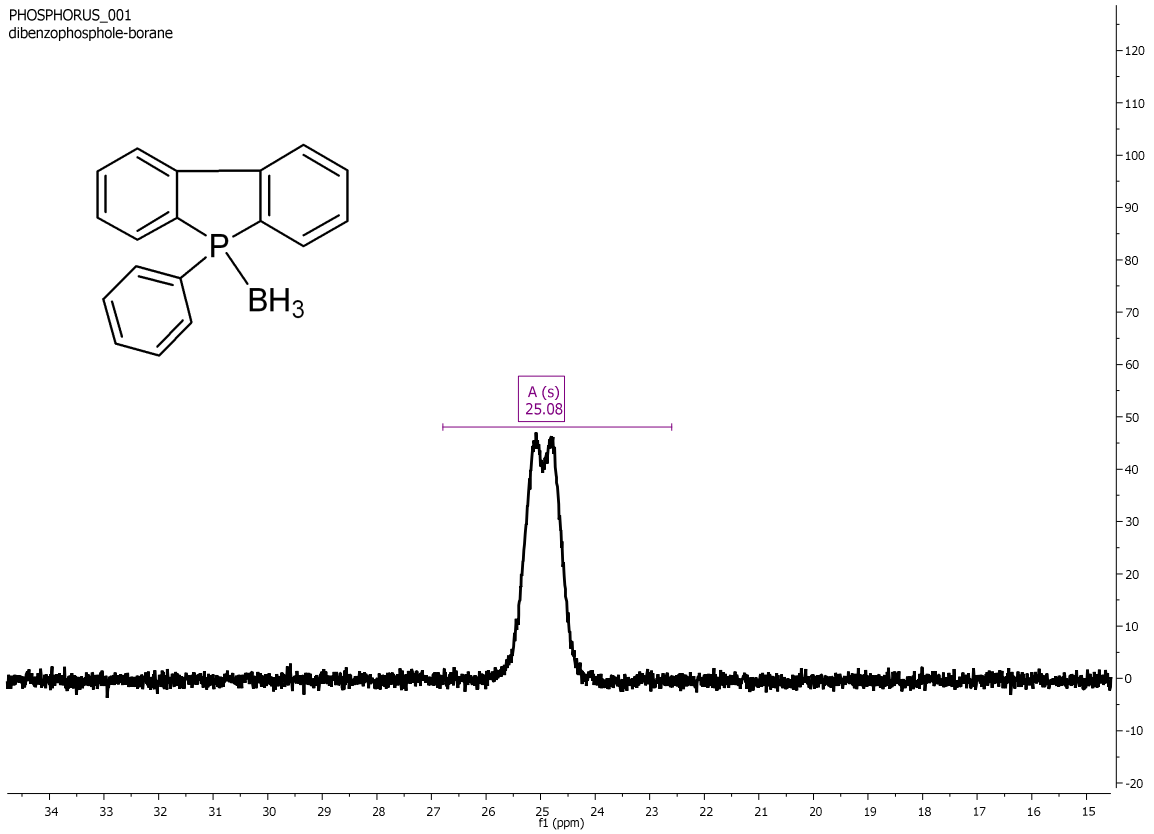
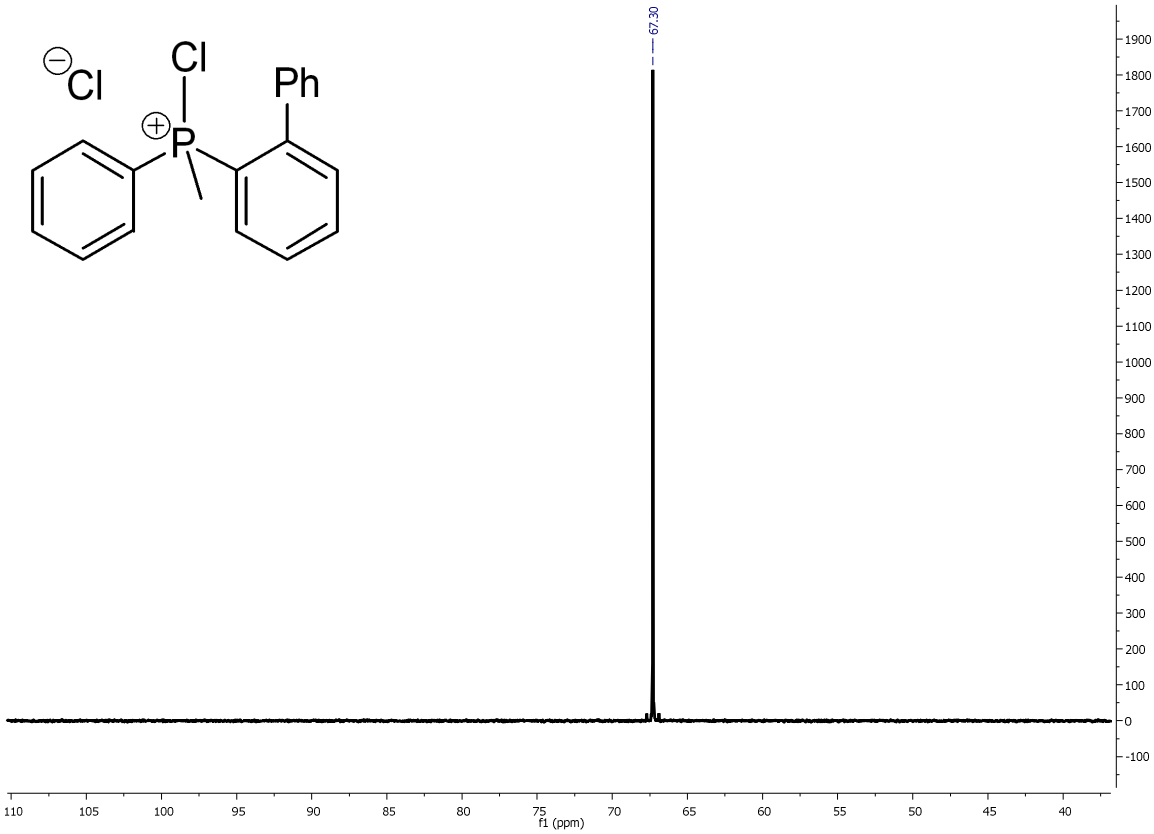
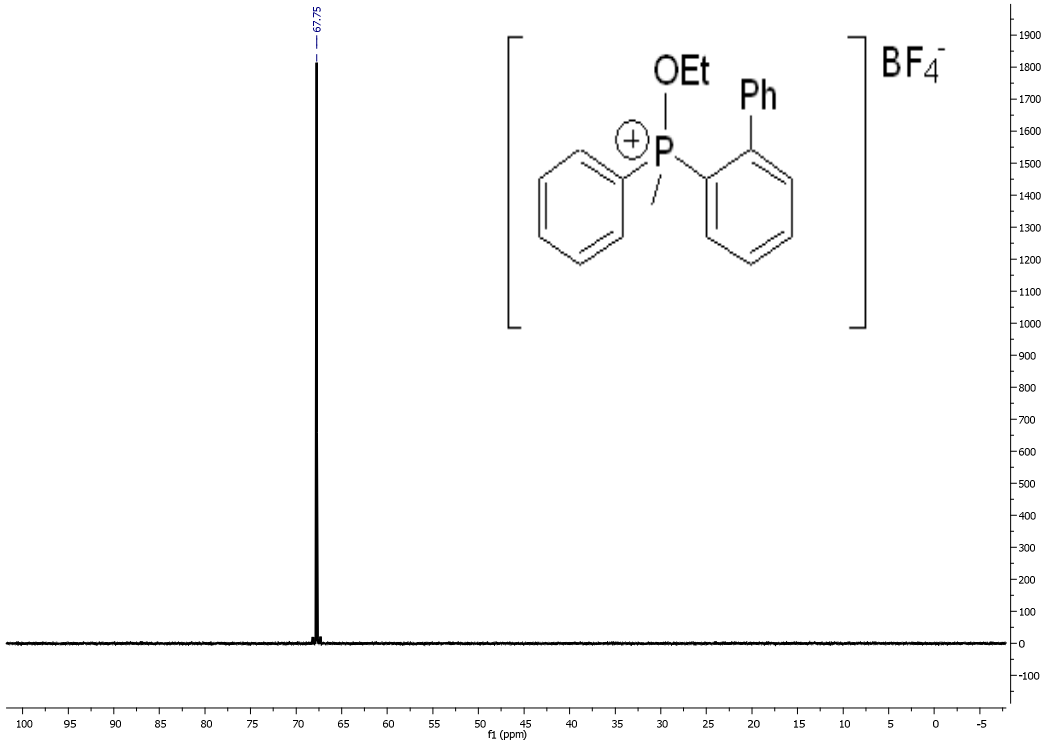
BINAP_BH3_THF
BH3
PPh2
PPh2
BH3
A (s)
21.14
f1 (ppm)

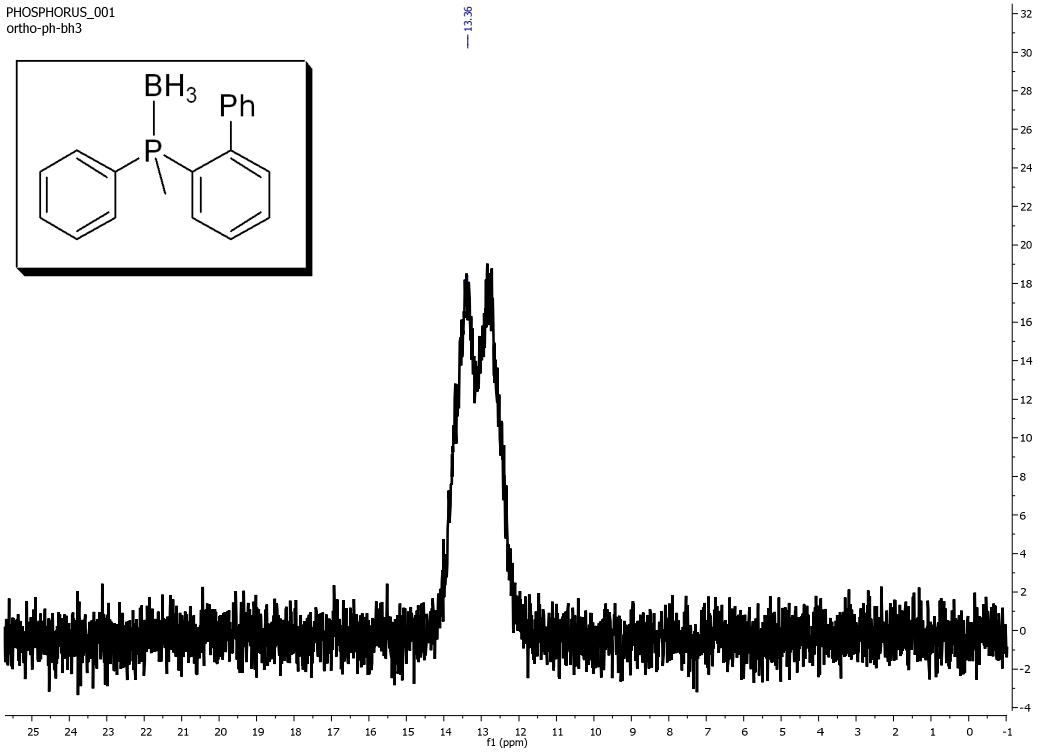

57.61
P
Cl
Cl
f1 (ppm)

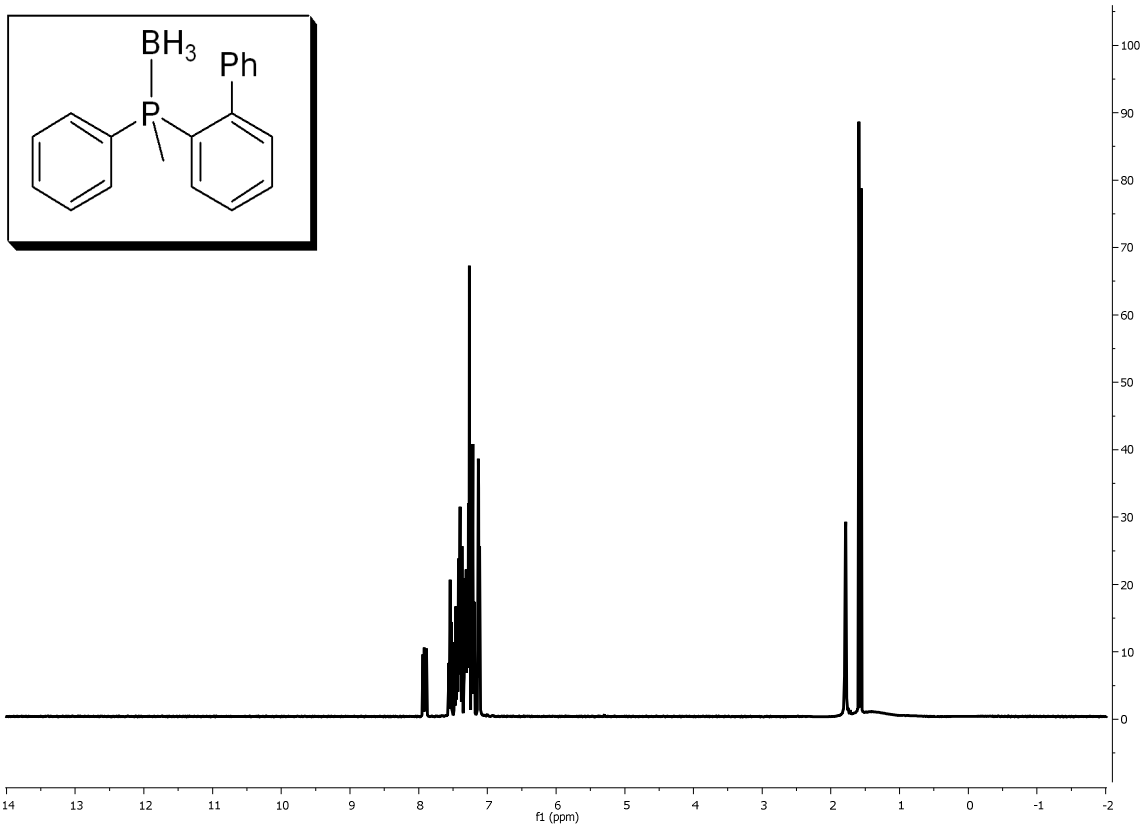

PROTON_001
dibenzophosphole-borane
7.90
7.88
7.70
7.68
7.66
7.57
7.57
7.57
7.55
7.53
7.42
7.42
7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.31
7.31
7.29
7.29
7.29
7.22
1.43
1.41
1.37
1.34
1.26
1.06
0.97
0.95
0.93
0.91
0.90
P
BH3
f1 (ppm)

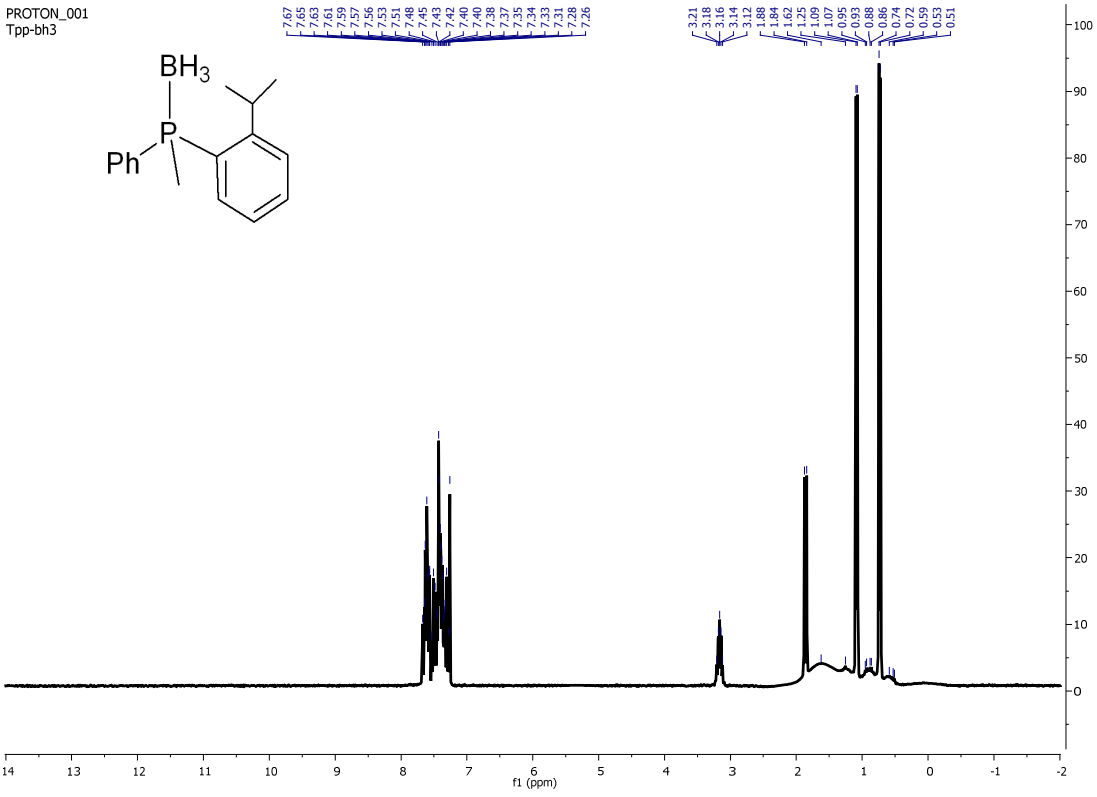

PHOSPHORUS_001
dibenzophosphole-borane
P
BH3
A (s)
25.08
f1 (ppm)

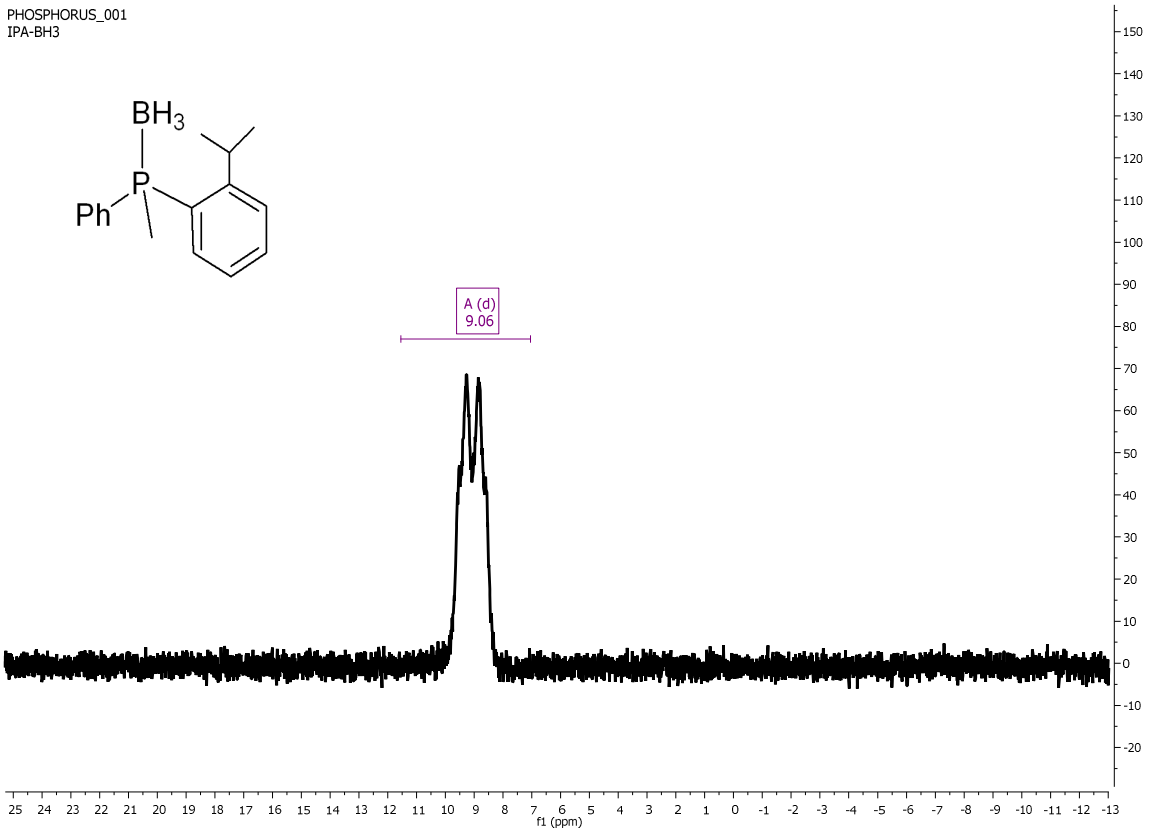

Cl
Cl
Ph
P
67.30
f1 (ppm)

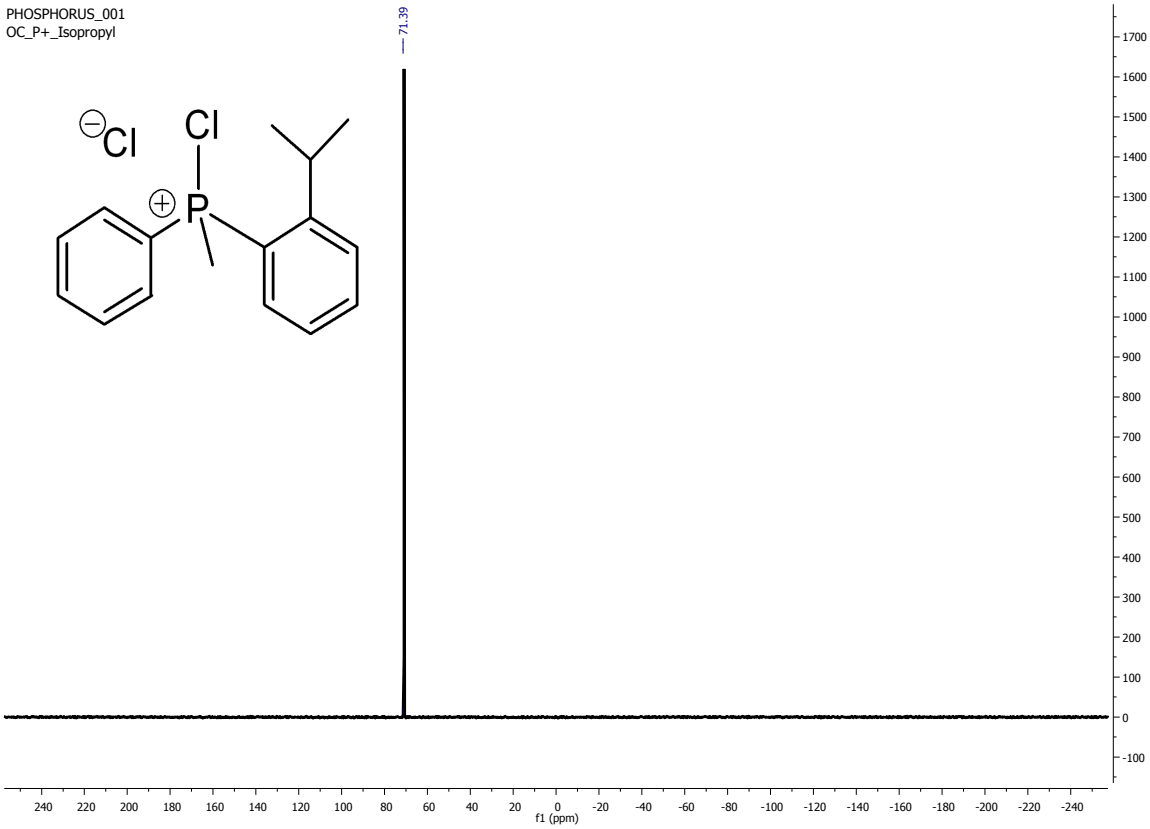

67.75
OEt
Ph
P
BF4-
f1 (ppm)

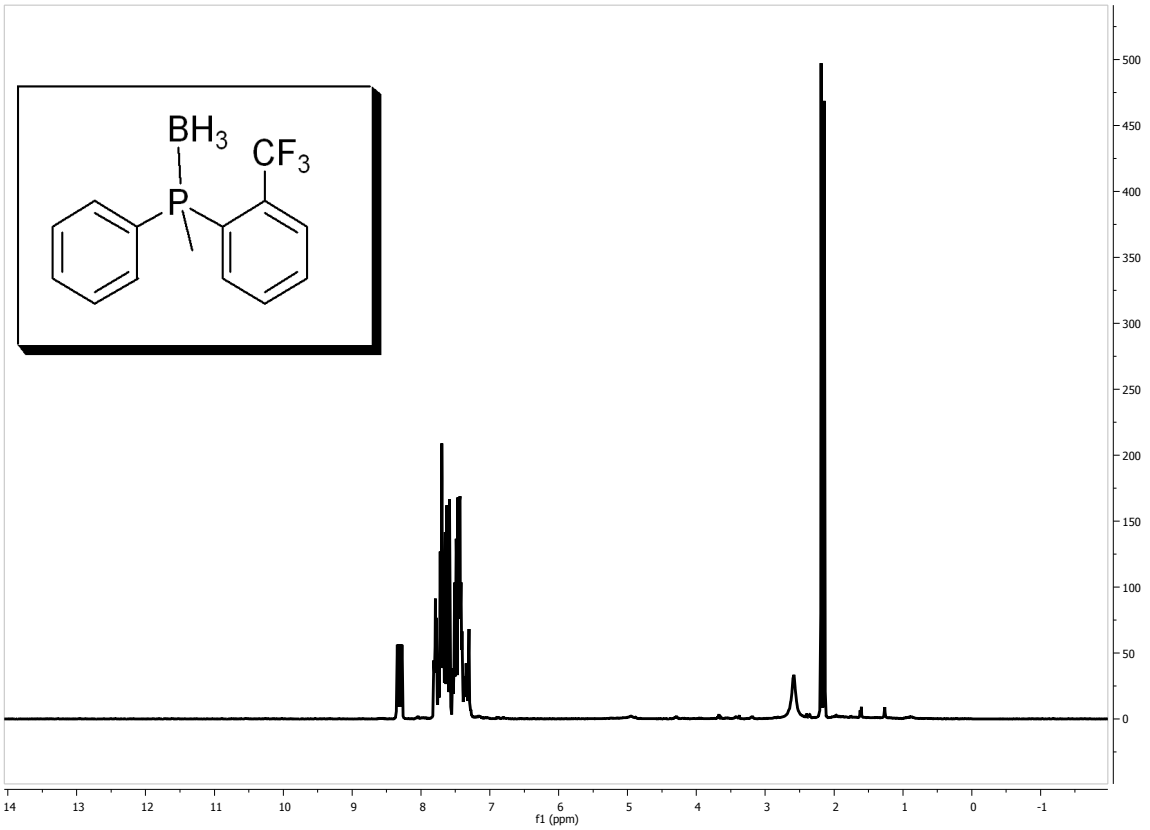

PHOSPHORUS_001
ortho-ph-bh3
13.36
BH3
Ph
P
f1 (ppm)

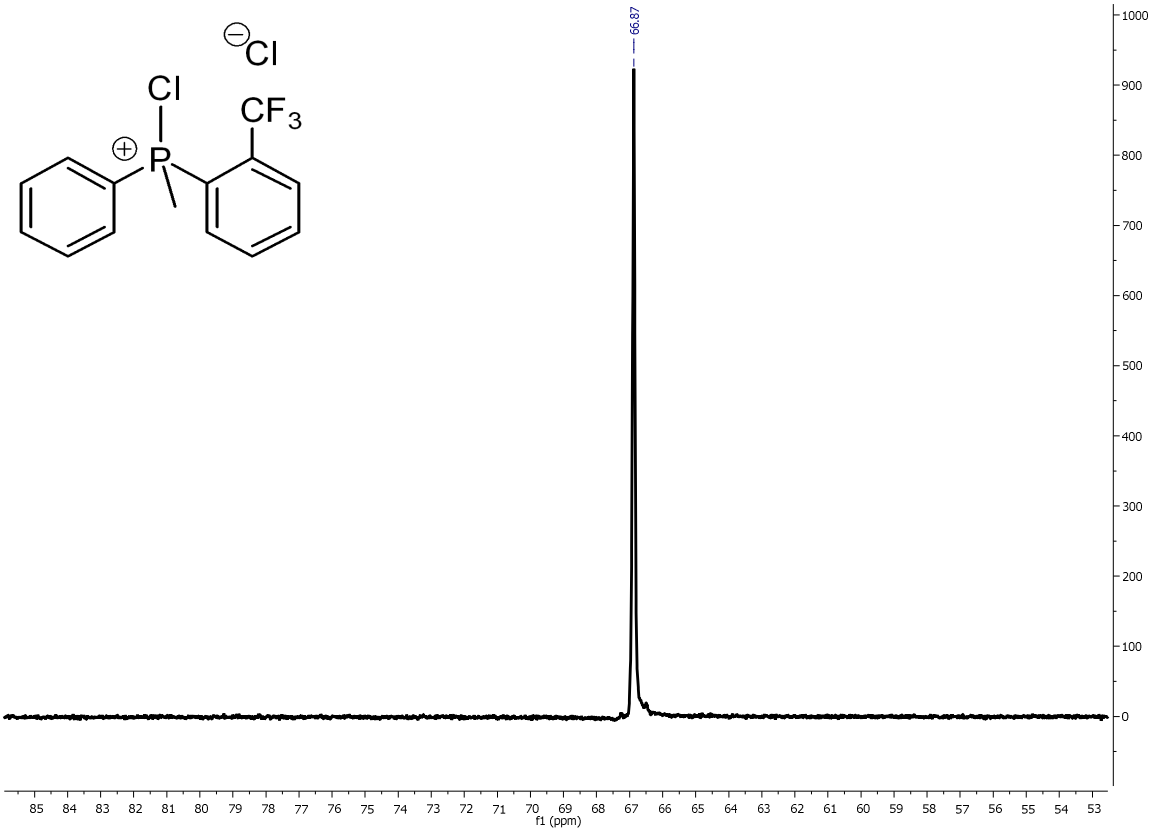

BH3
Ph
P
f1 (ppm)

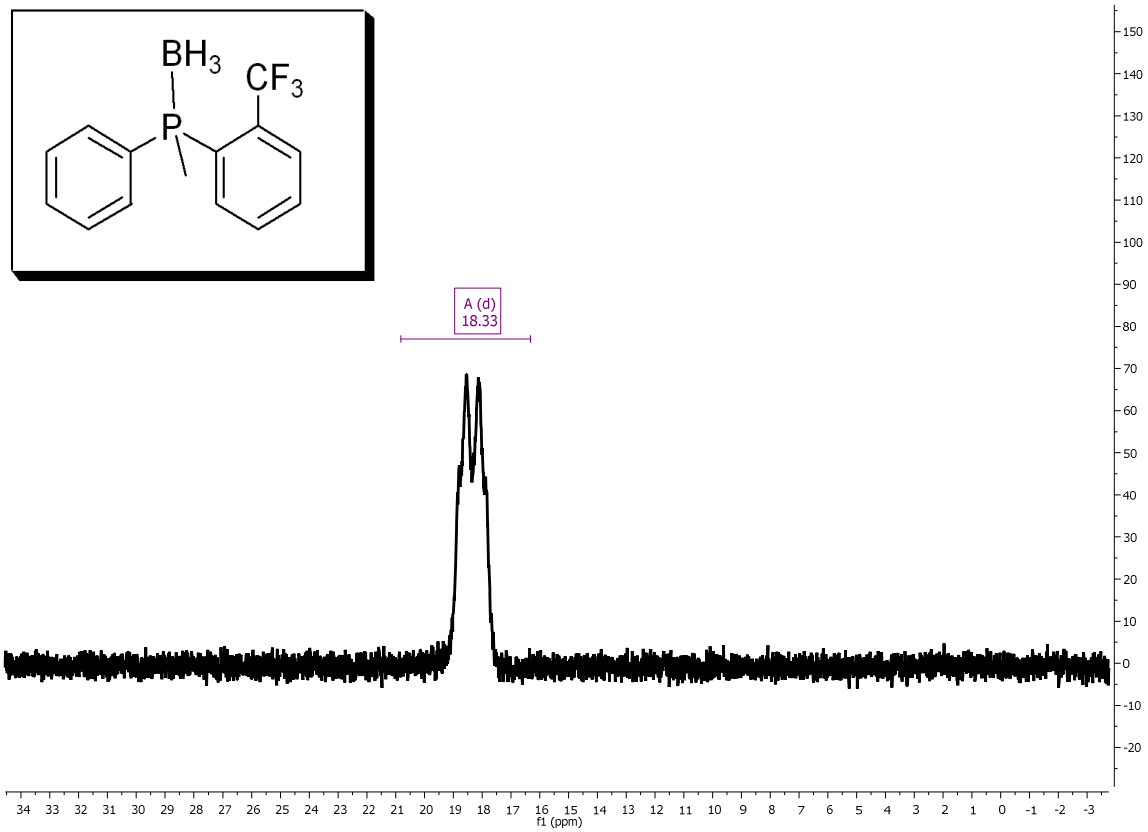

PROTON_001
Tpp-bh3
BH3
P
Ph
f1 (ppm)


PHOSPHORUS_001
IPA-BH3
BH3
P
Ph
A (d)
9.06
f1 (ppm)

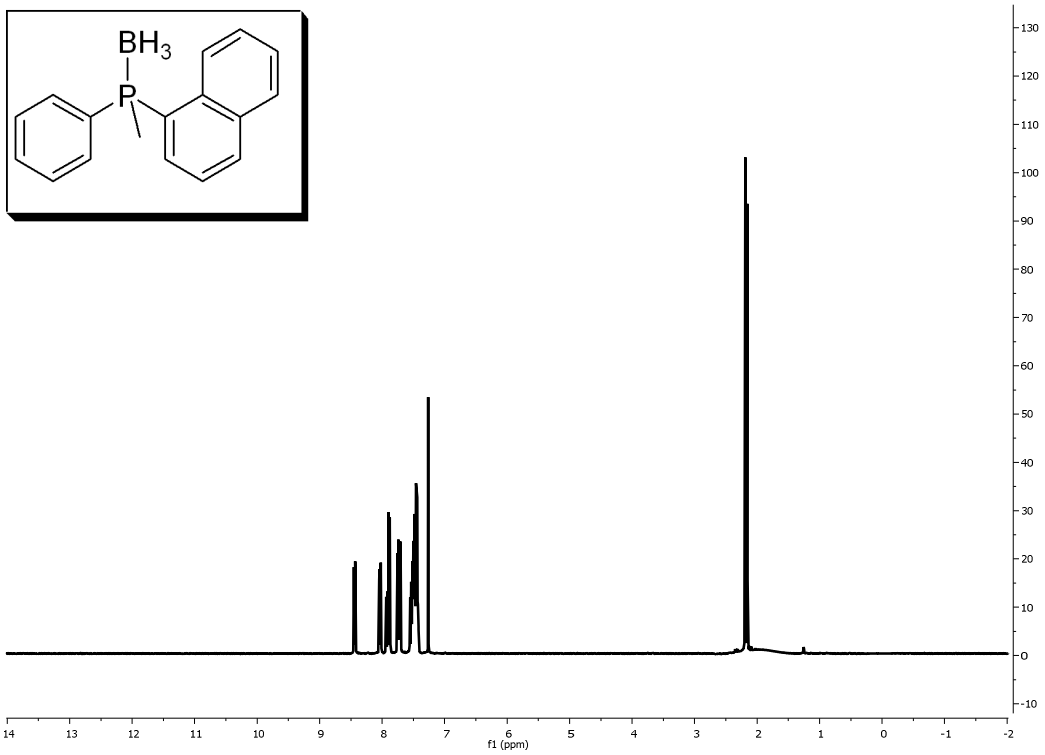

PHOSPHORUS_001
OC_P+_Isopropyl
71.39
Cl
Cl
P
f1 (ppm)

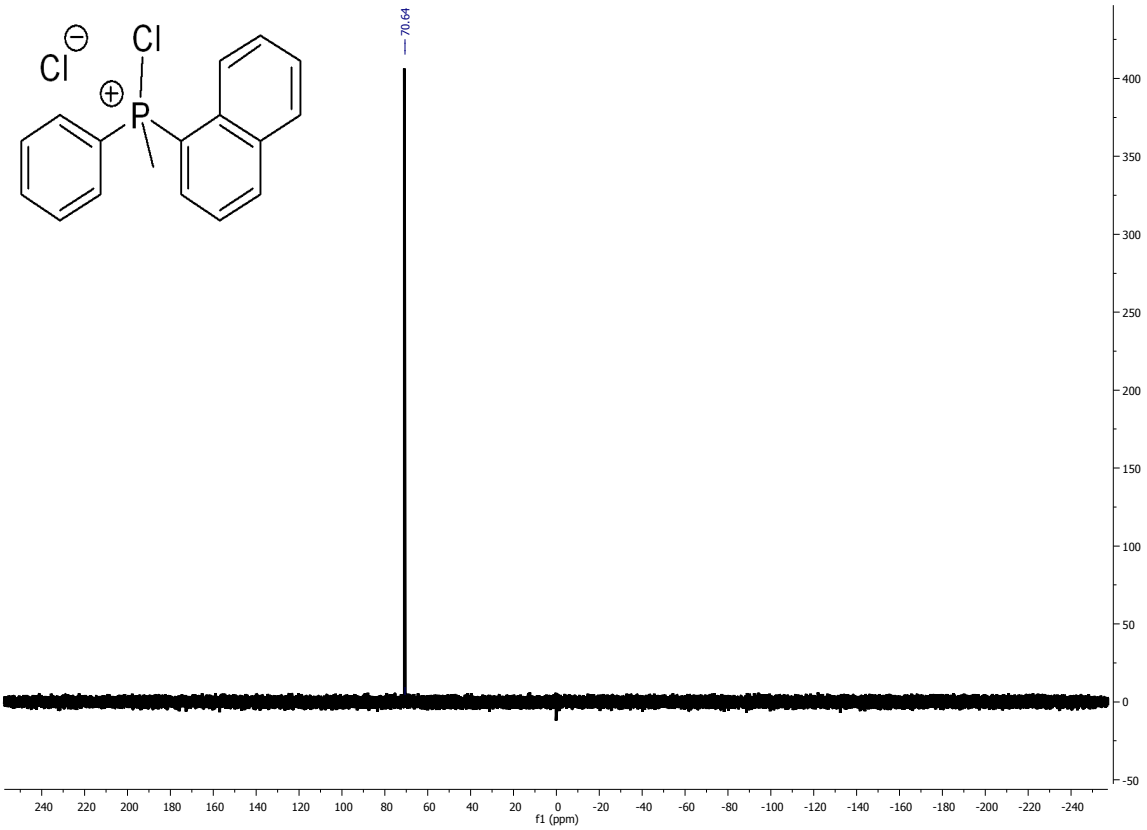

BH3
CF3
P
f1 (ppm)

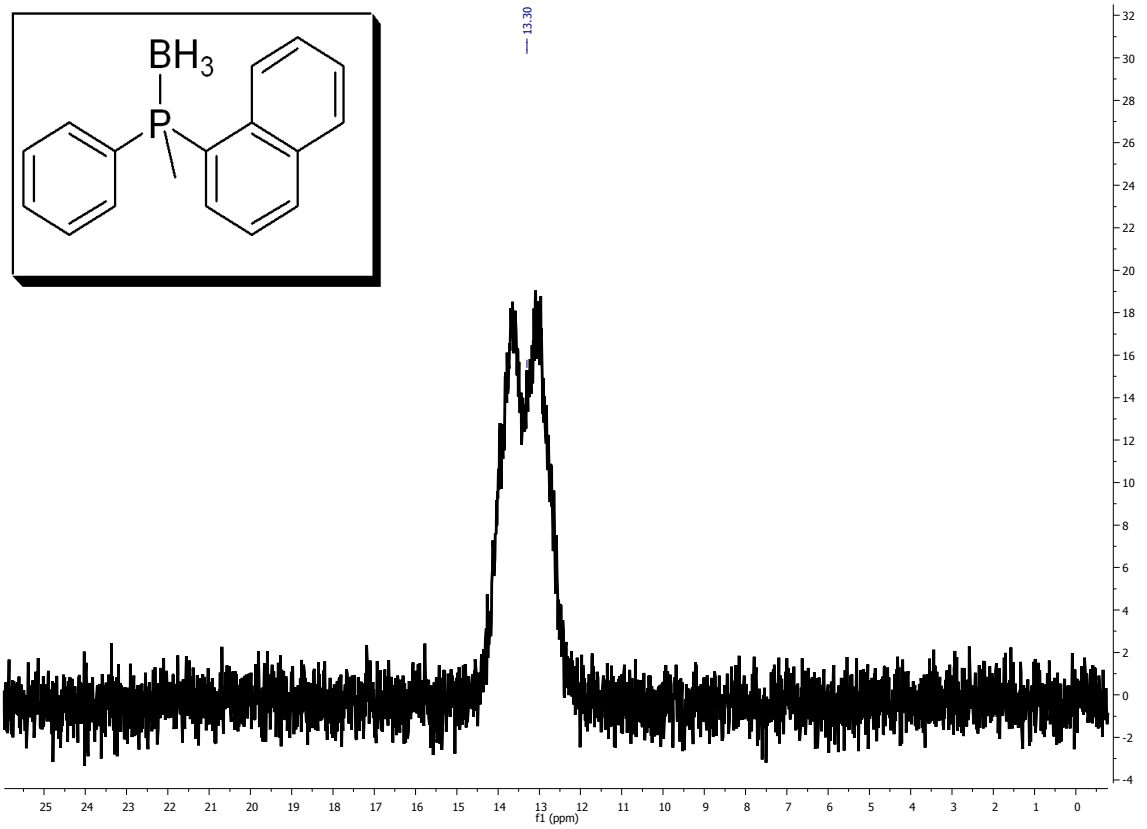

Cl
Cl
CF3
P
66.87
f1 (ppm)

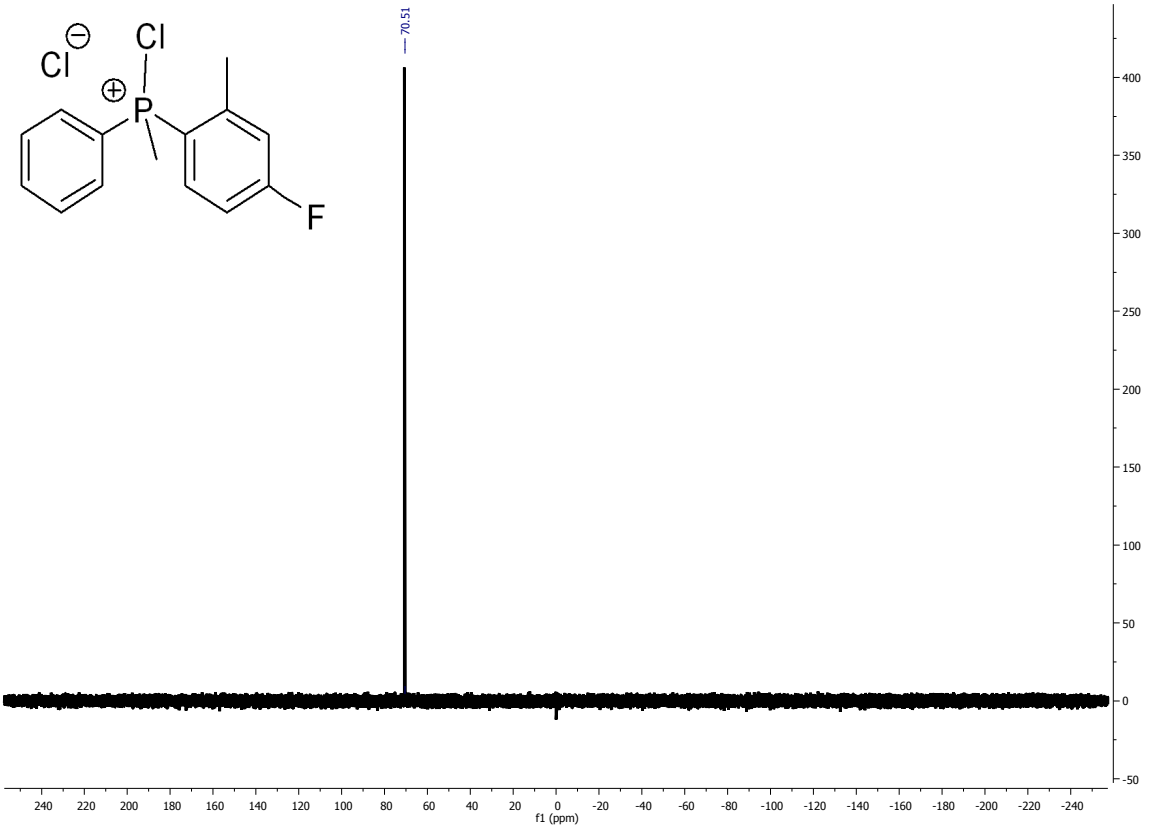

BH3
CF3
P
A (d)
18.33
f1 (ppm)

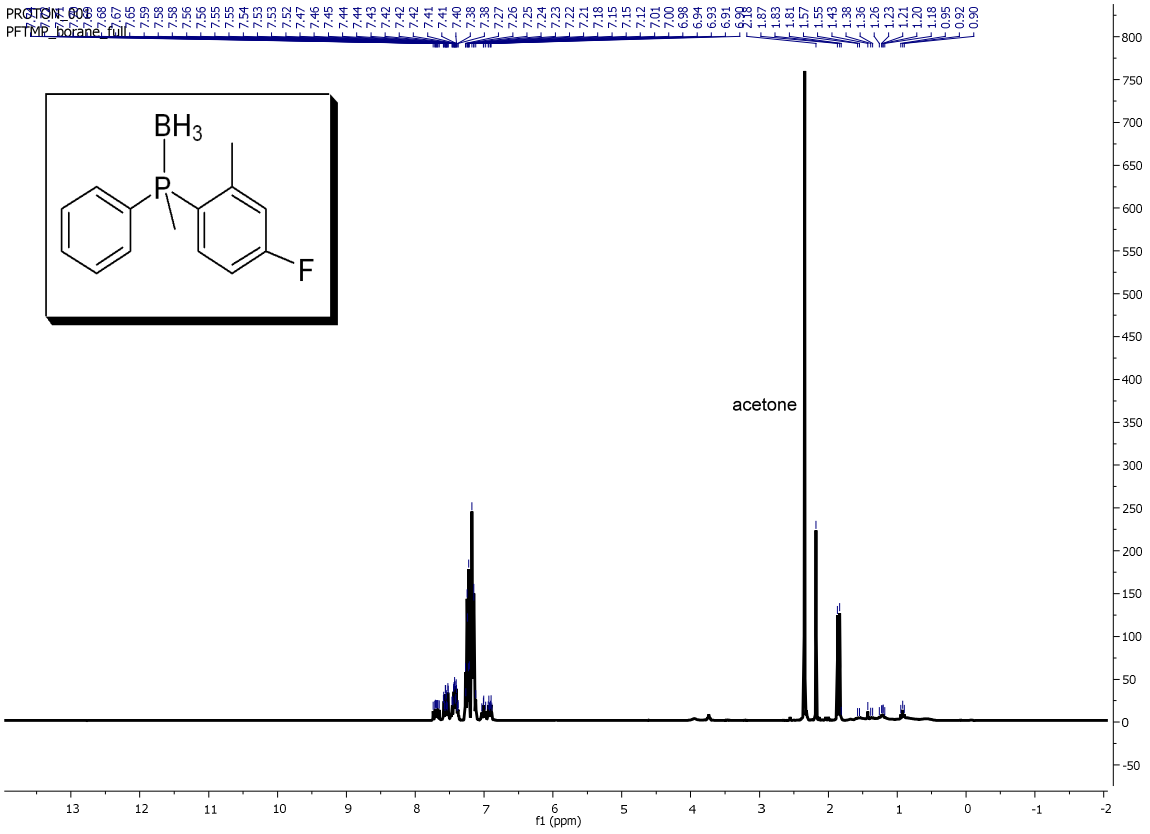
#

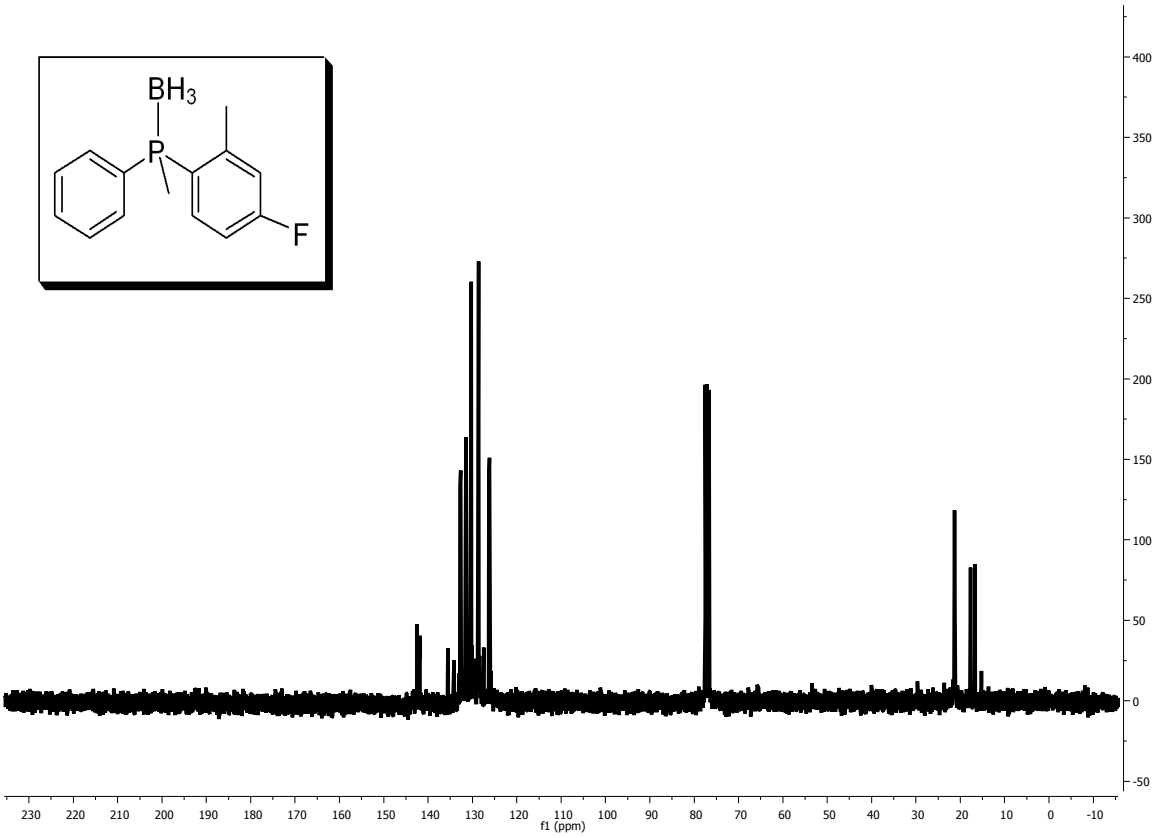

BH3
P
f1 (ppm)


Cl
Cl
P
70.64
400
350
300
250
200
150
100
50
0
-50
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

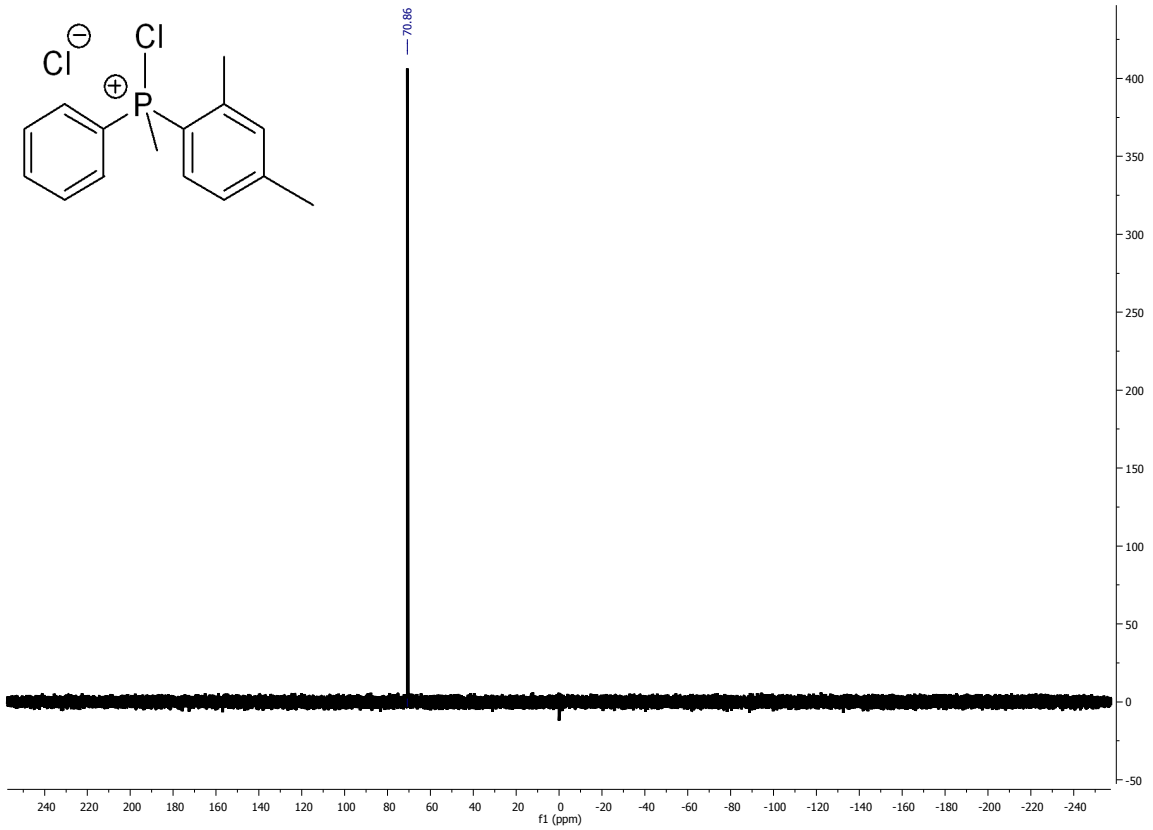

BH3
P
13.30
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

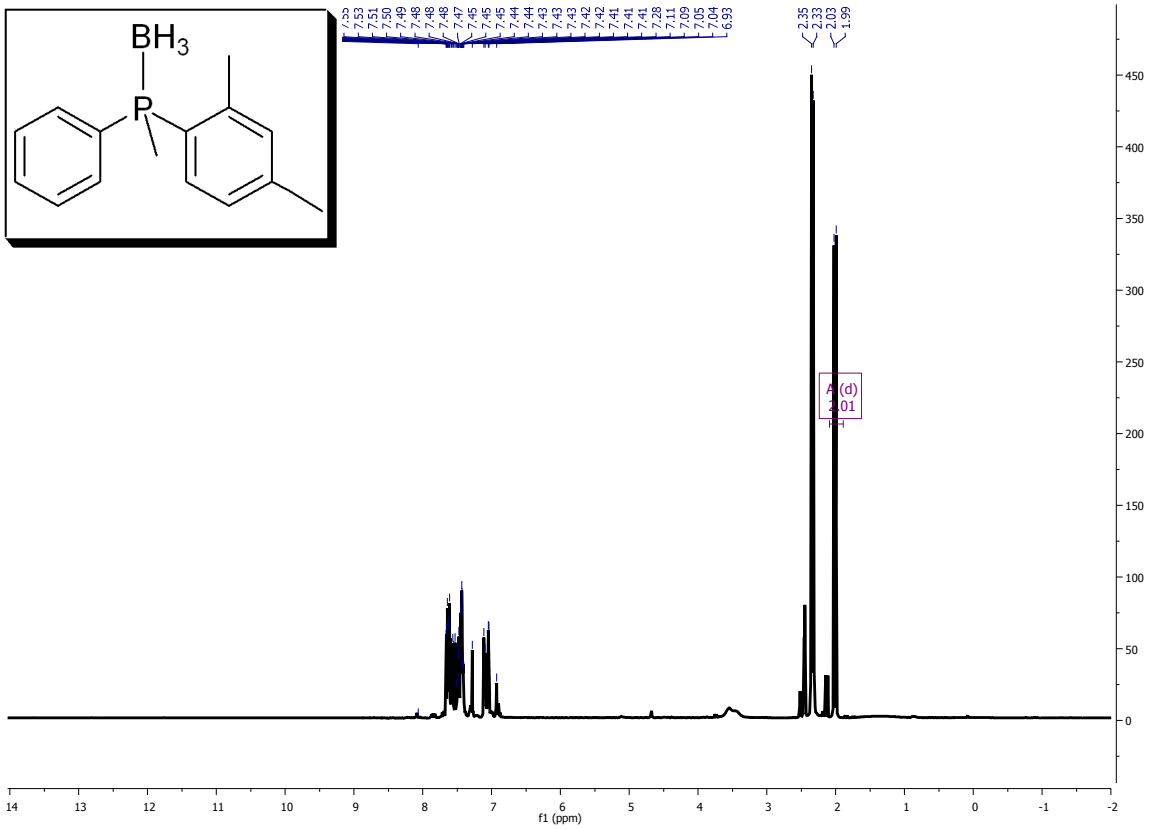

Cl
Cl
P
F
70.51
f1 (ppm)

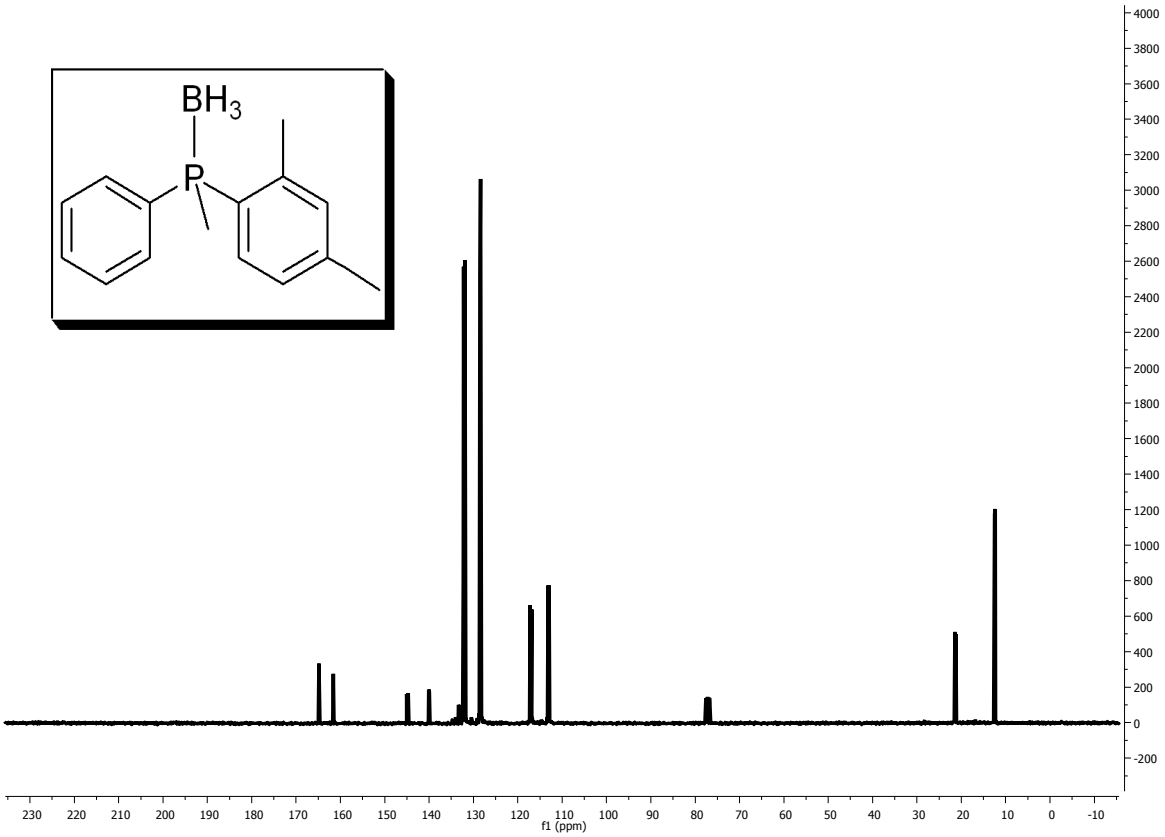

PROTON_603
PFTMP_borane_full
BH3
P
F
acetone
f1 (ppm)

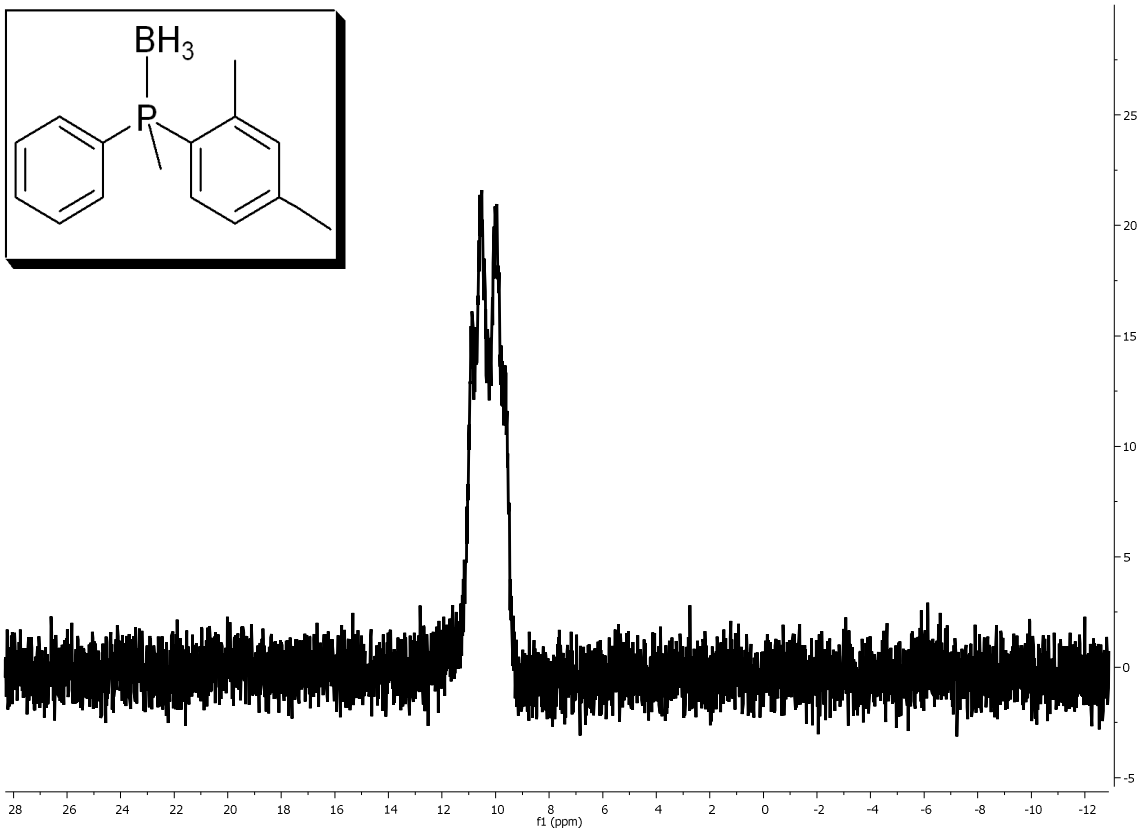

BH3
P
F
400
350
300
250
200
150
100
50
0
-50
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

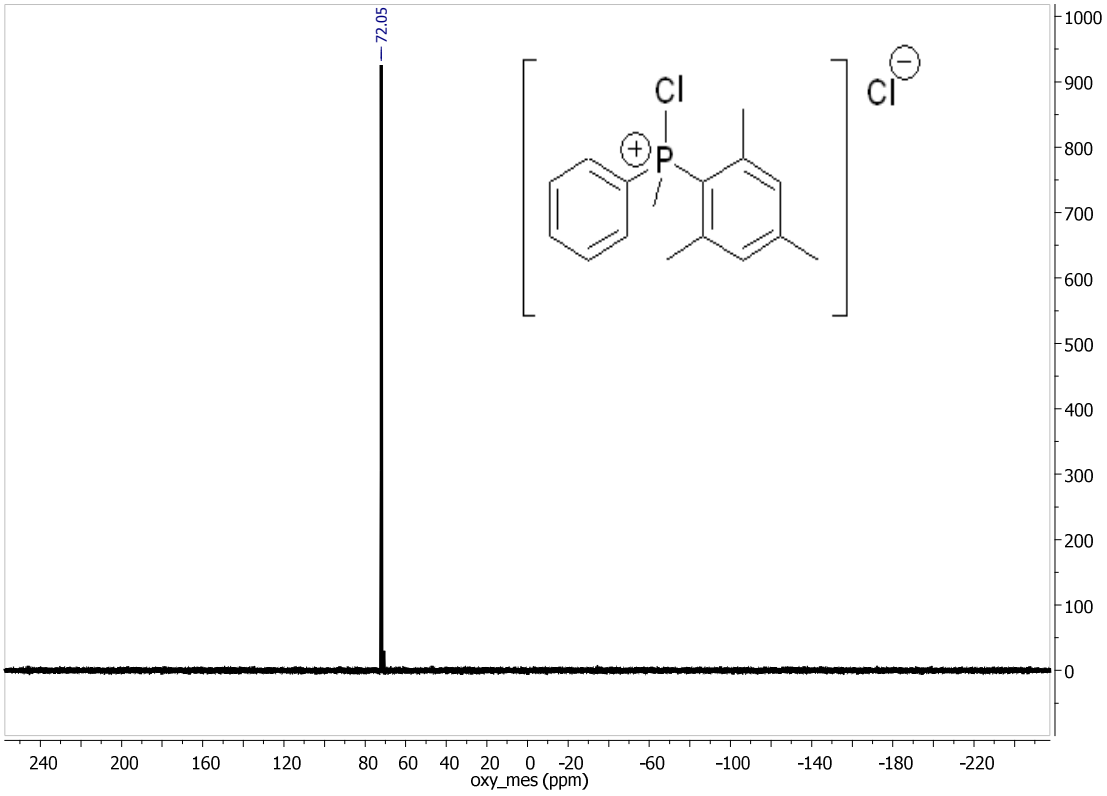

PHOSPHORUS_001
PFTMP_borane_full
BH3
P
F
A (d)
10.23
25
20
15
10
5
0
-5
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

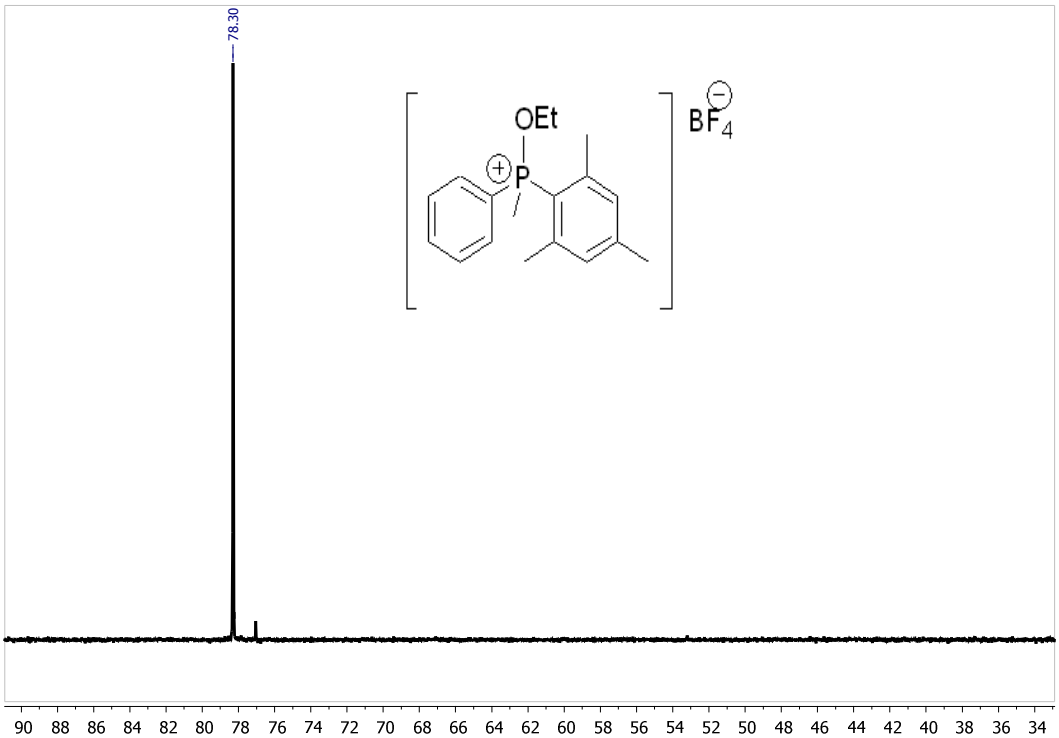

Cl
Cl
P
70.86
f1 (ppm)

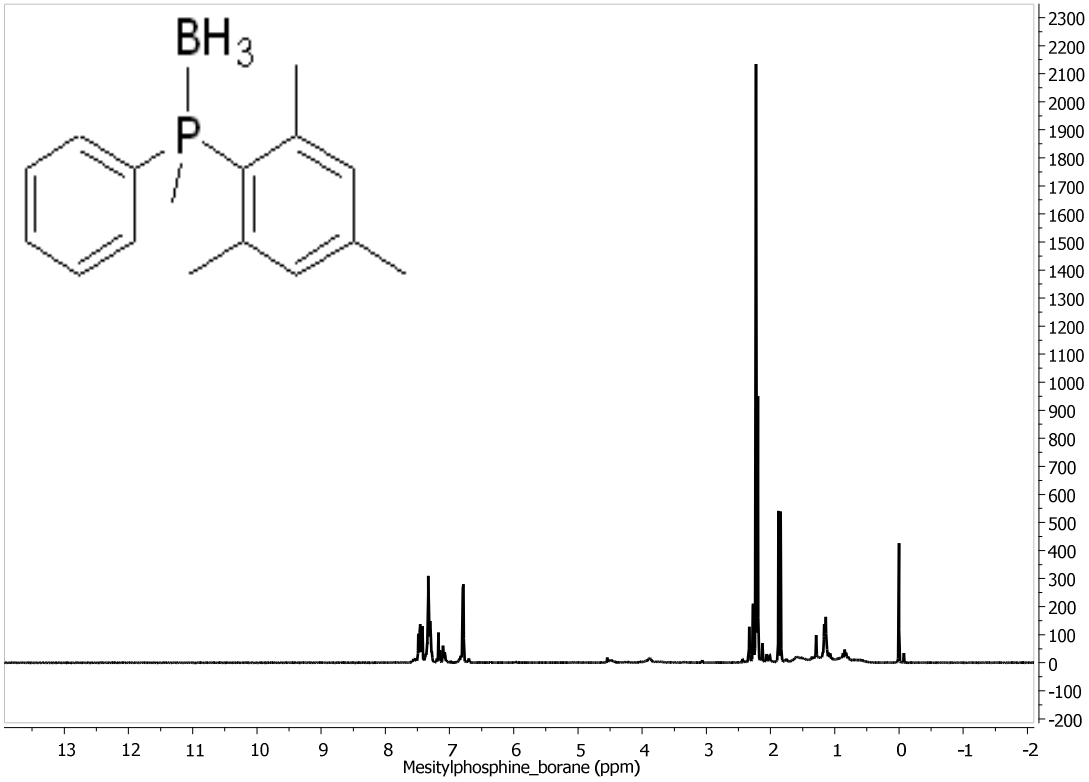

BH3
P
7.53
7.51
7.50
7.49
7.48
7.47
7.45
7.44
7.43
7.42
7.41
7.28
7.11
7.09
7.05
7.04
6.93
2.35
2.33
2.03
1.99
A (d)
2.01
f1 (ppm)

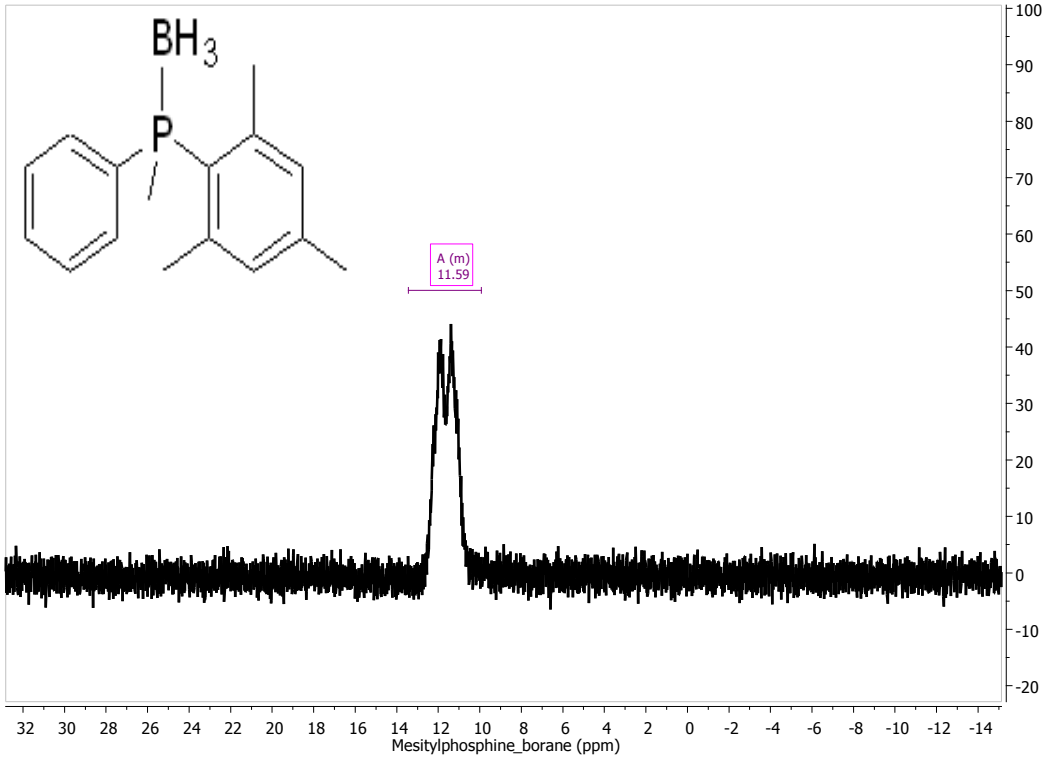

BH3
P
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

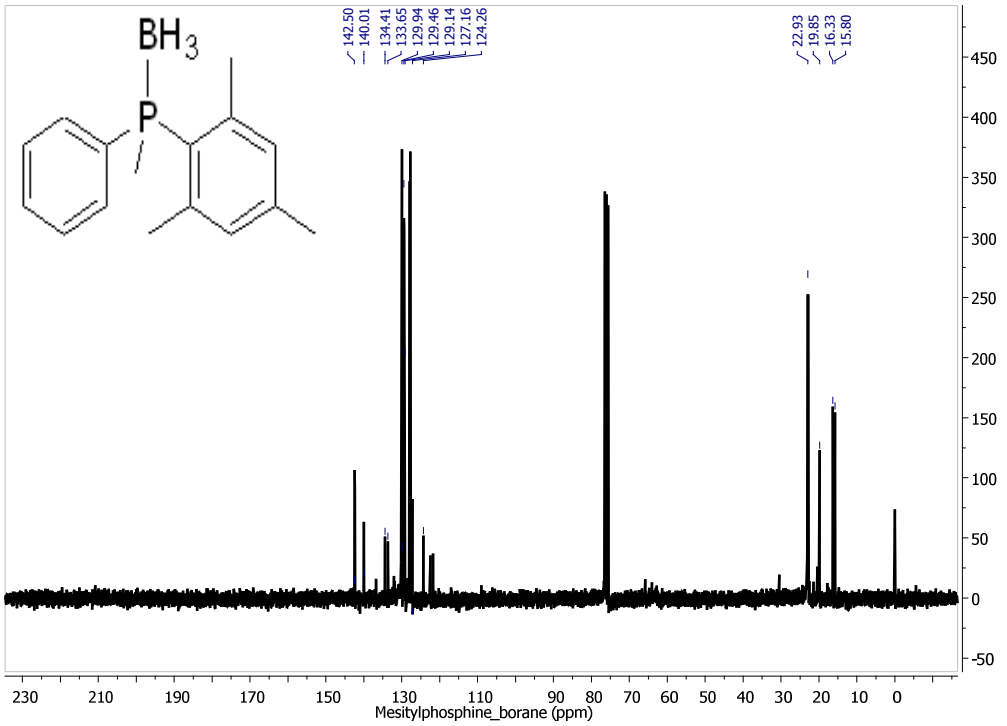

BH3
P
25
20
15
10
5
0
-5
28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12
f1 (ppm)

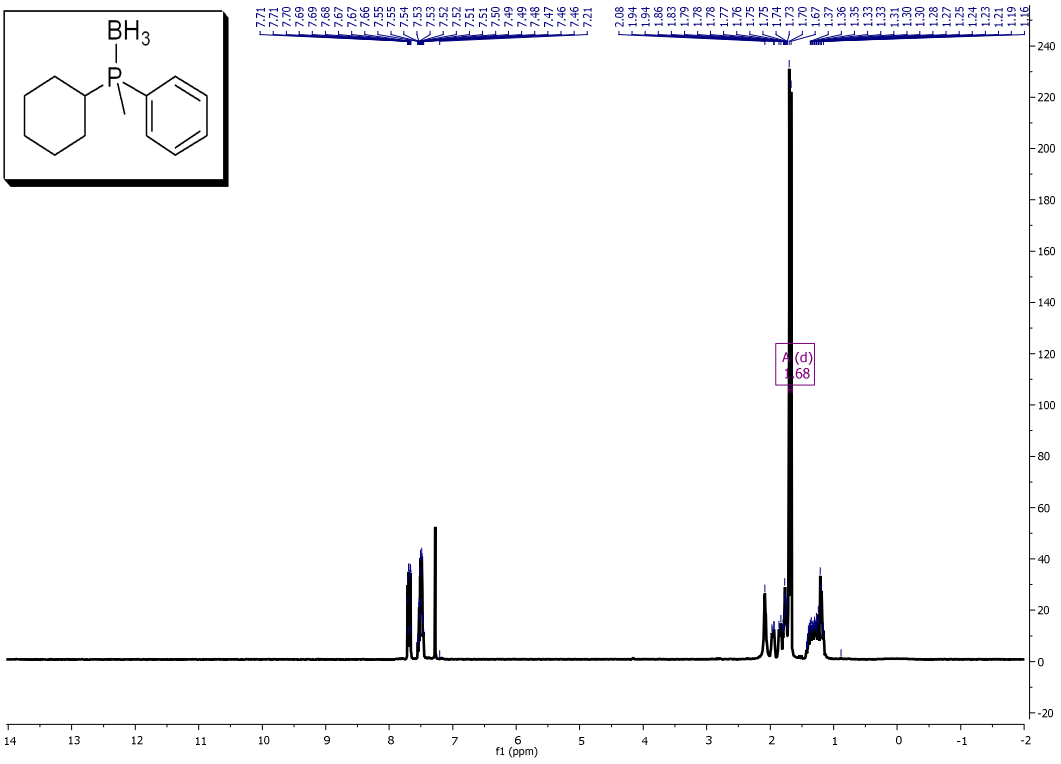

72.05
Cl
P
Cl
1000
900
800
700
600
500
400
300
200
100
0
240
200
160
120
80
60
40
20
0
-20
-60
-100
-140
-180
-220
oxy_mes (ppm)

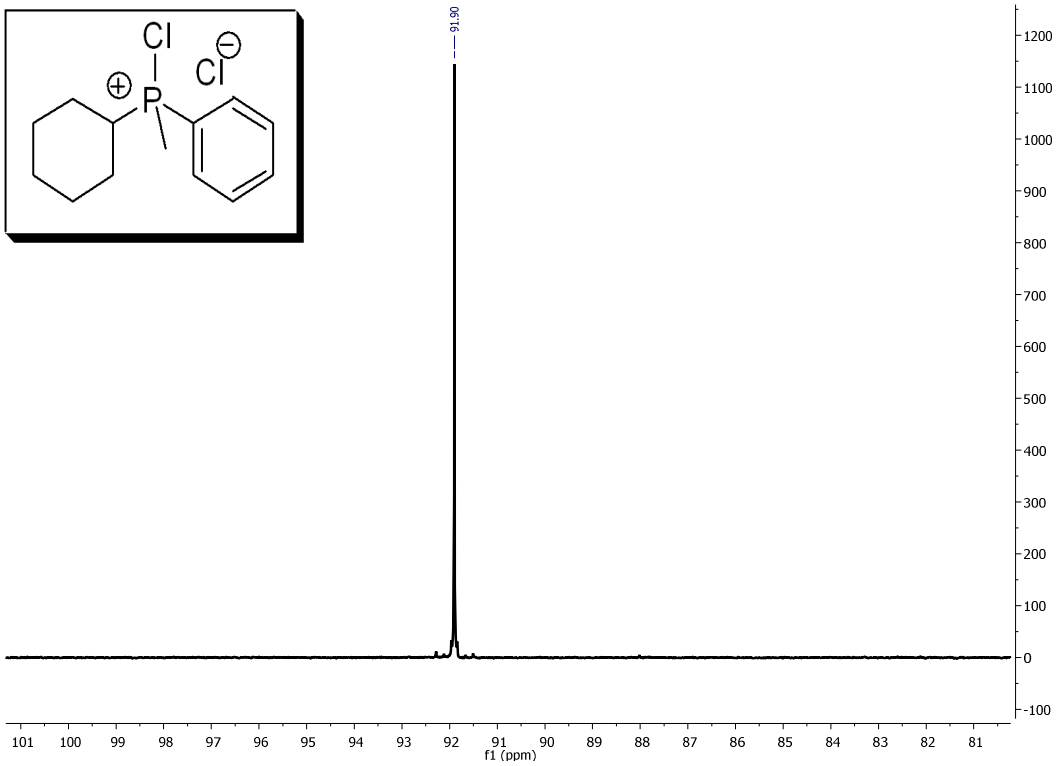

78.30
OEt
P
BF4
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34

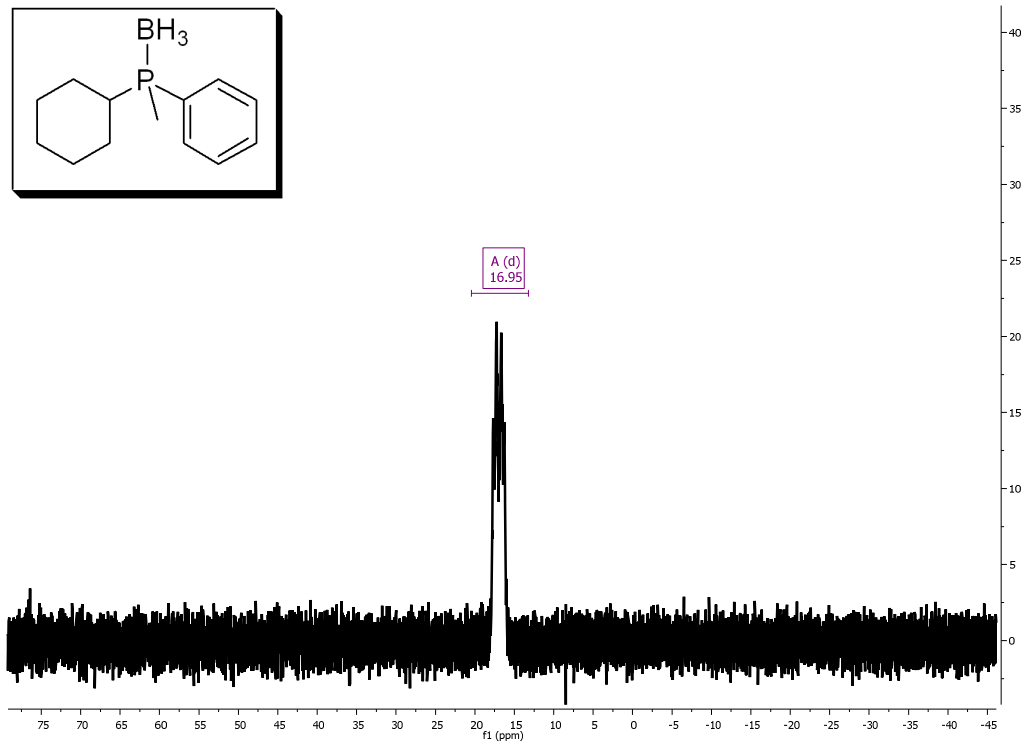

BH3
P
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
Mesitylphosphine_borane (ppm)

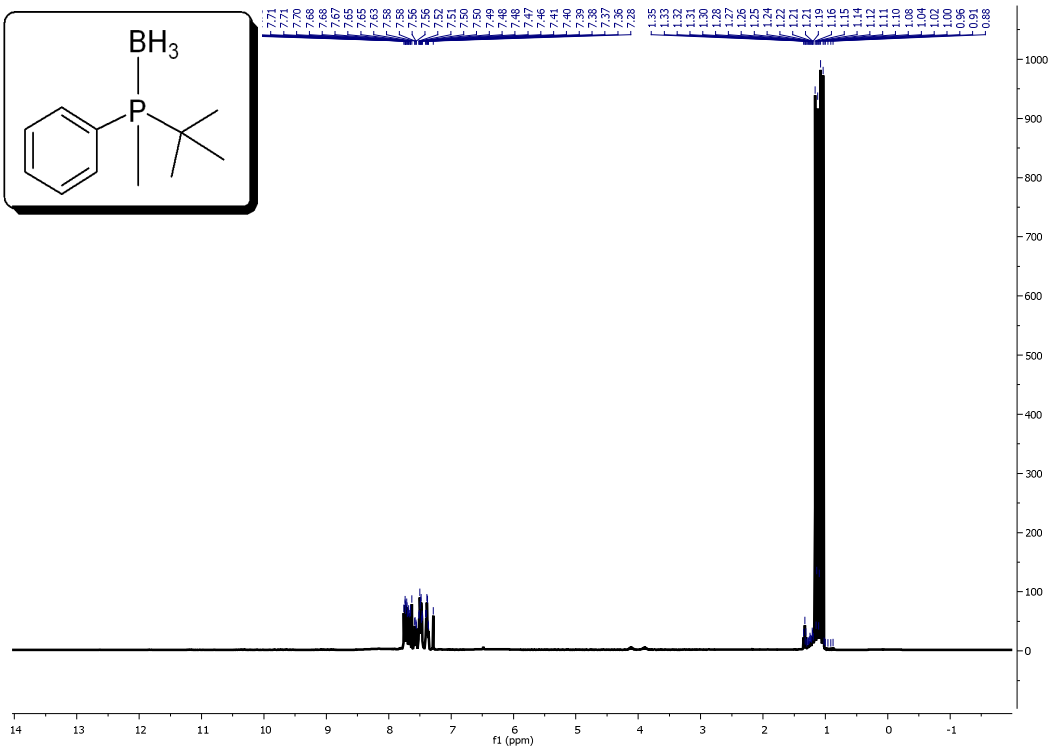

BH3
P
A (m)
11.59
100
90
80
70
60
50
40
30
20
10
0
-10
-20
32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14
Mesitylphosphine_borane (ppm)


BH3
P
142.50
140.01
134.41
133.65
129.94
129.46
129.14
127.16
124.26
22.93
19.85
16.33
15.80
Mesitylphosphine_borane (ppm)

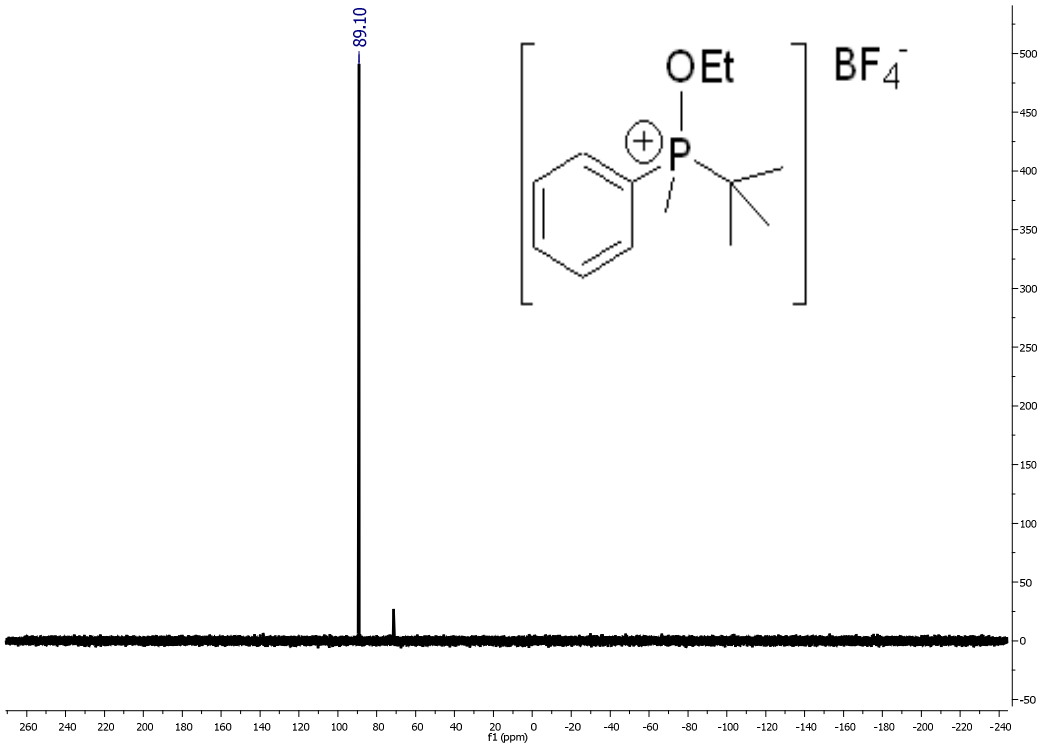

BH3
P
A (d)
2.68
f1 (ppm)

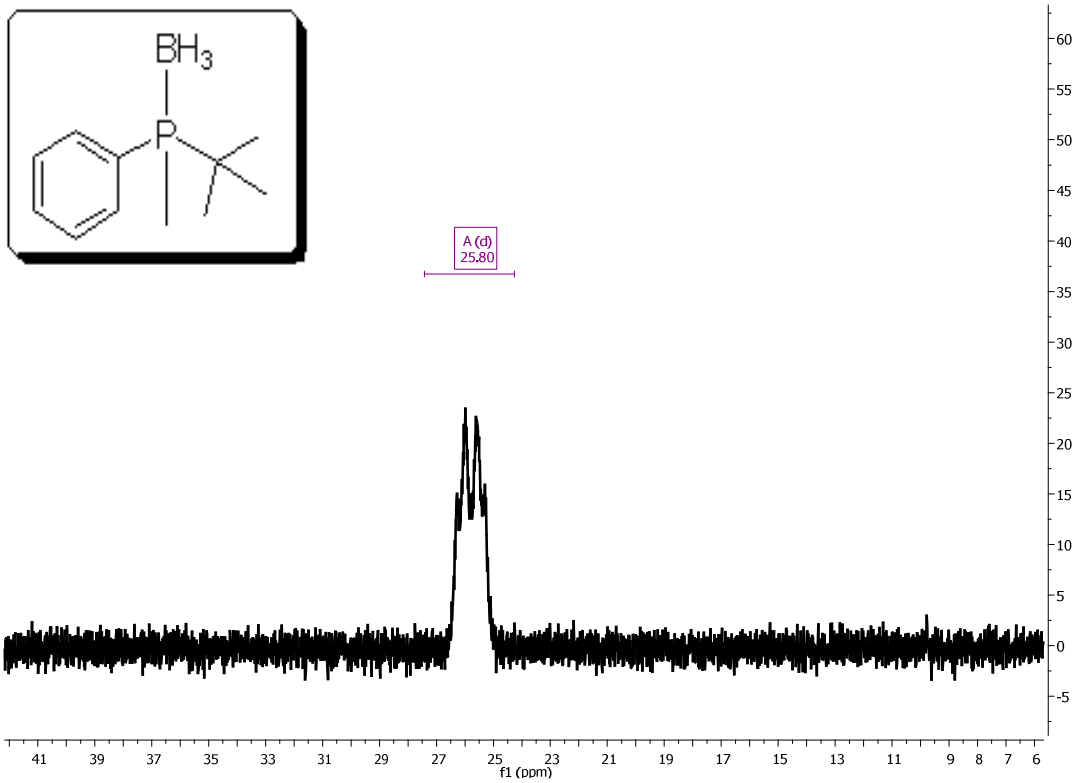

Cl
Cl
P
91.90
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
101 100 99 98 97 96 95 94 93 92 91 90 89 88 87 86 85 84 83 82 81
f1 (ppm)

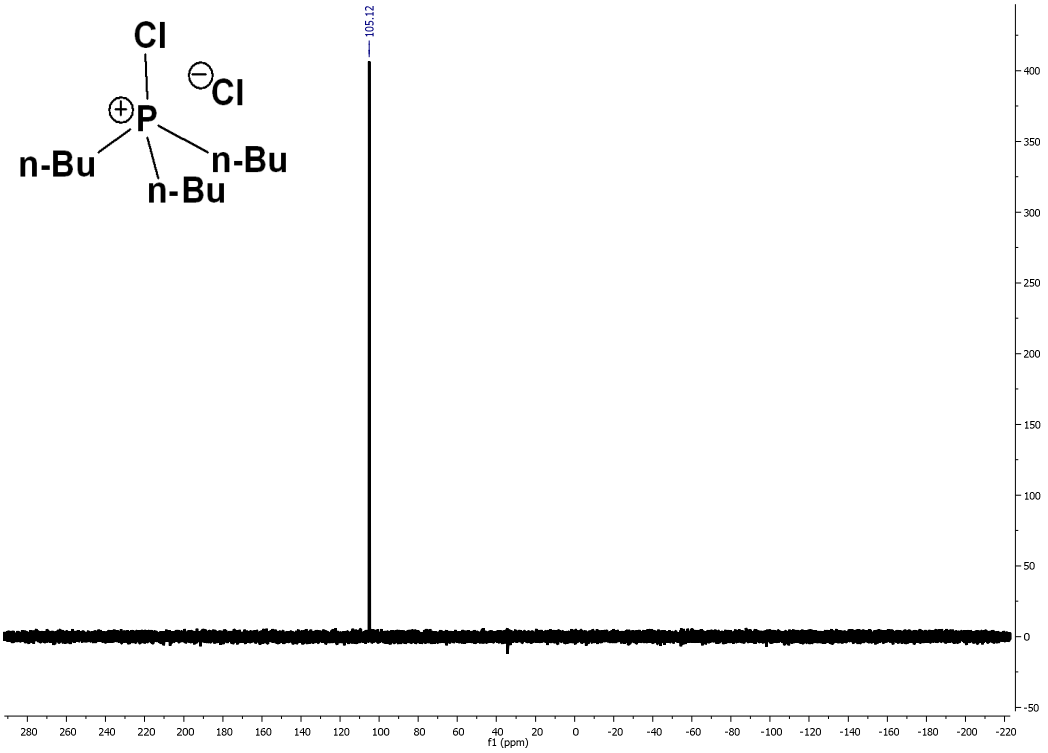

BH3
P
A (d)
16.95
40
35
30
25
20
15
10
5
0
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

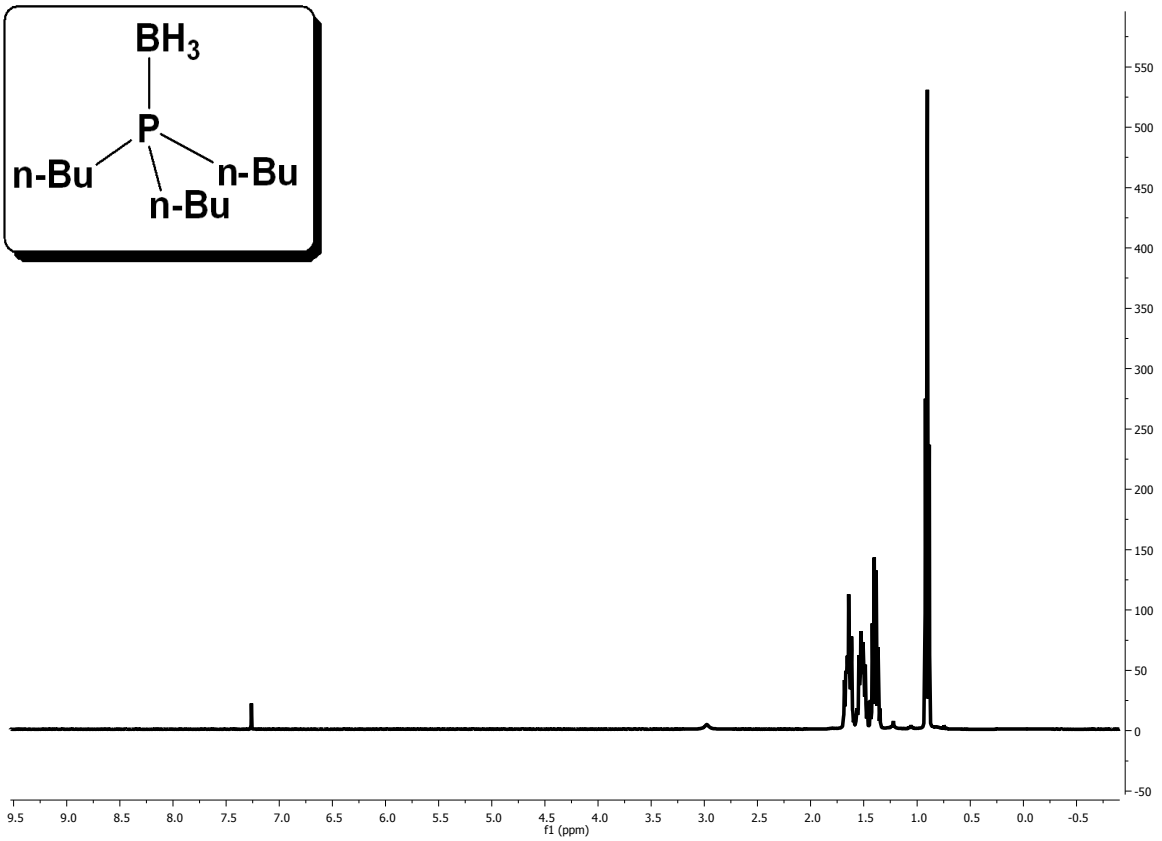

BH3
P
f1 (ppm)

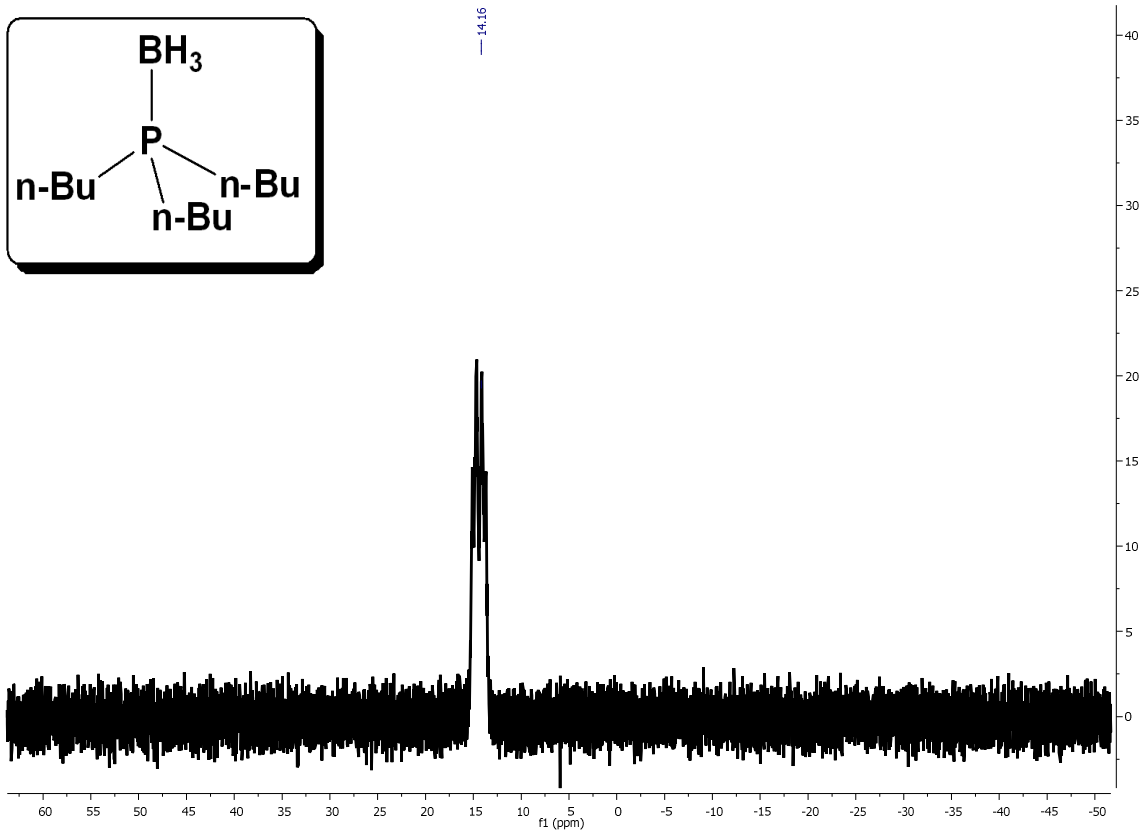

Cl
Cl
P
100.90
f1 (ppm)

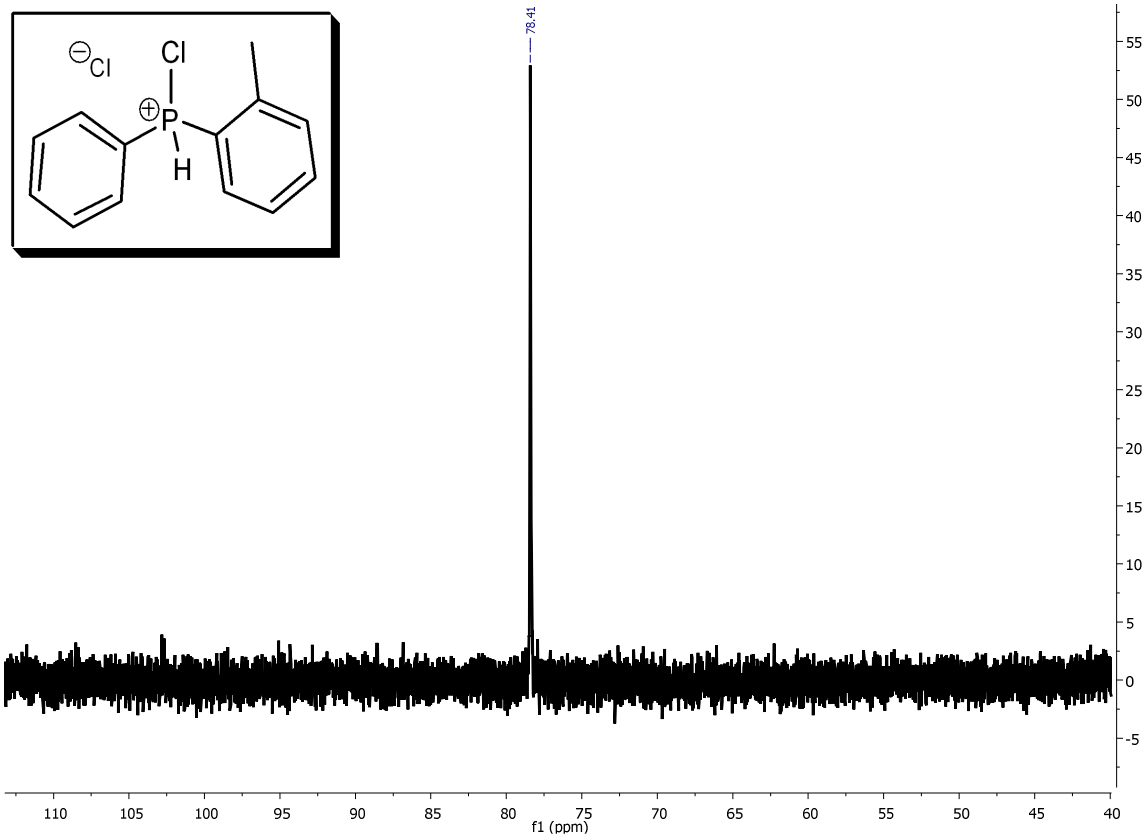

89.10
OEt
P
BF4-
f1 (ppm)

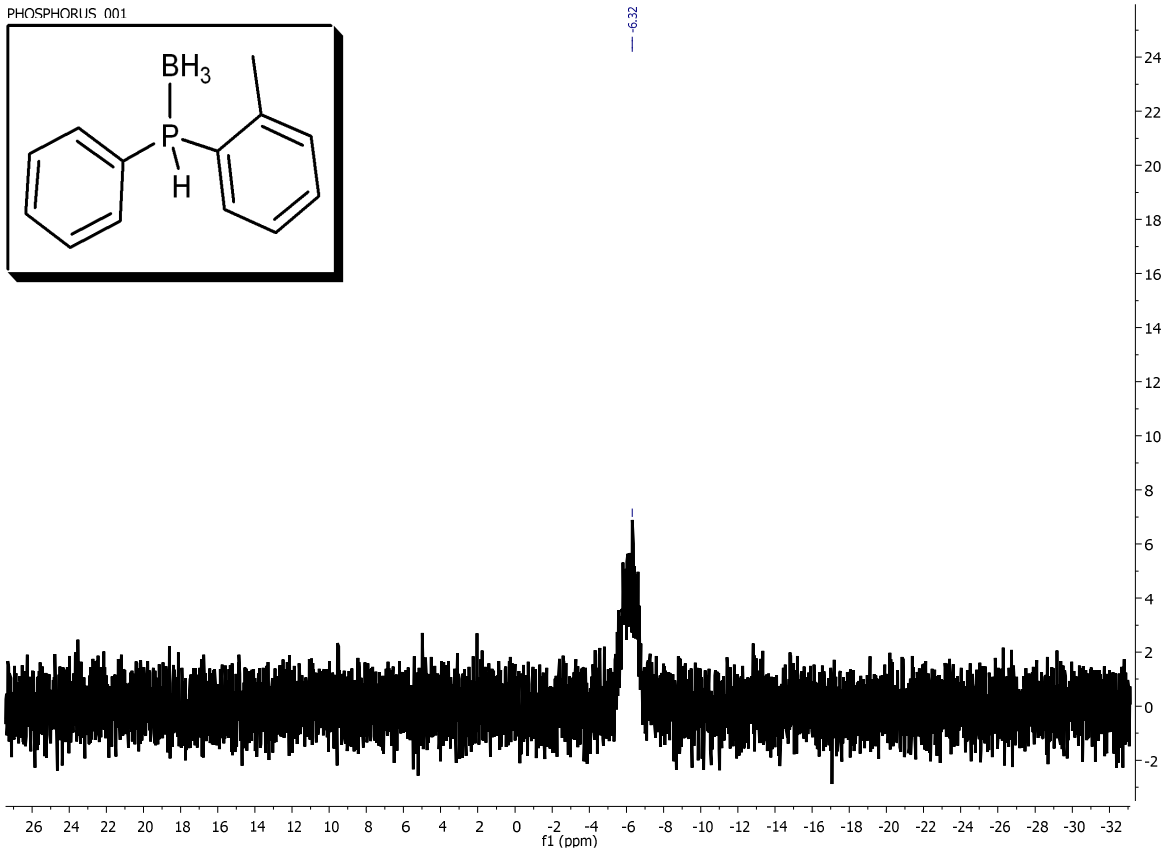

BH3
P
A (d)
25,80
f1 (ppm)

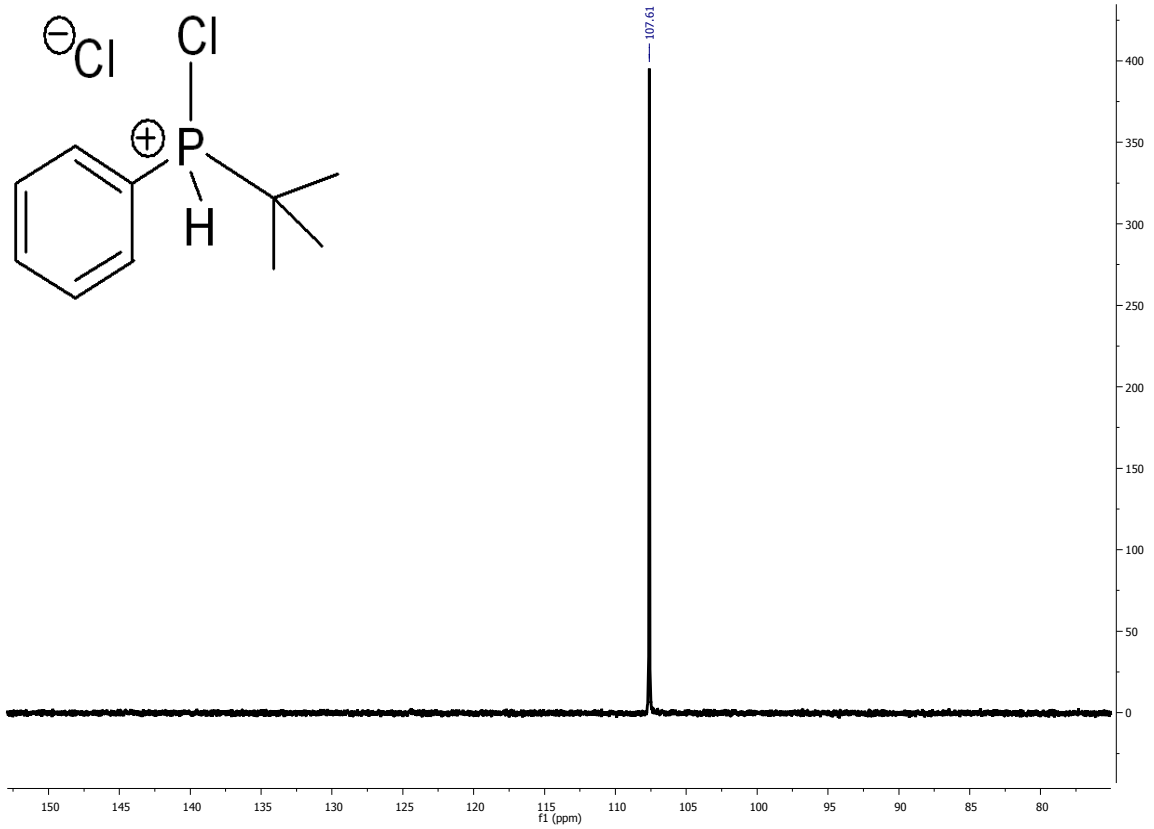

Cl
Cl
P
n-Bu
n-Bu
n-Bu
105.12
f1 (ppm)

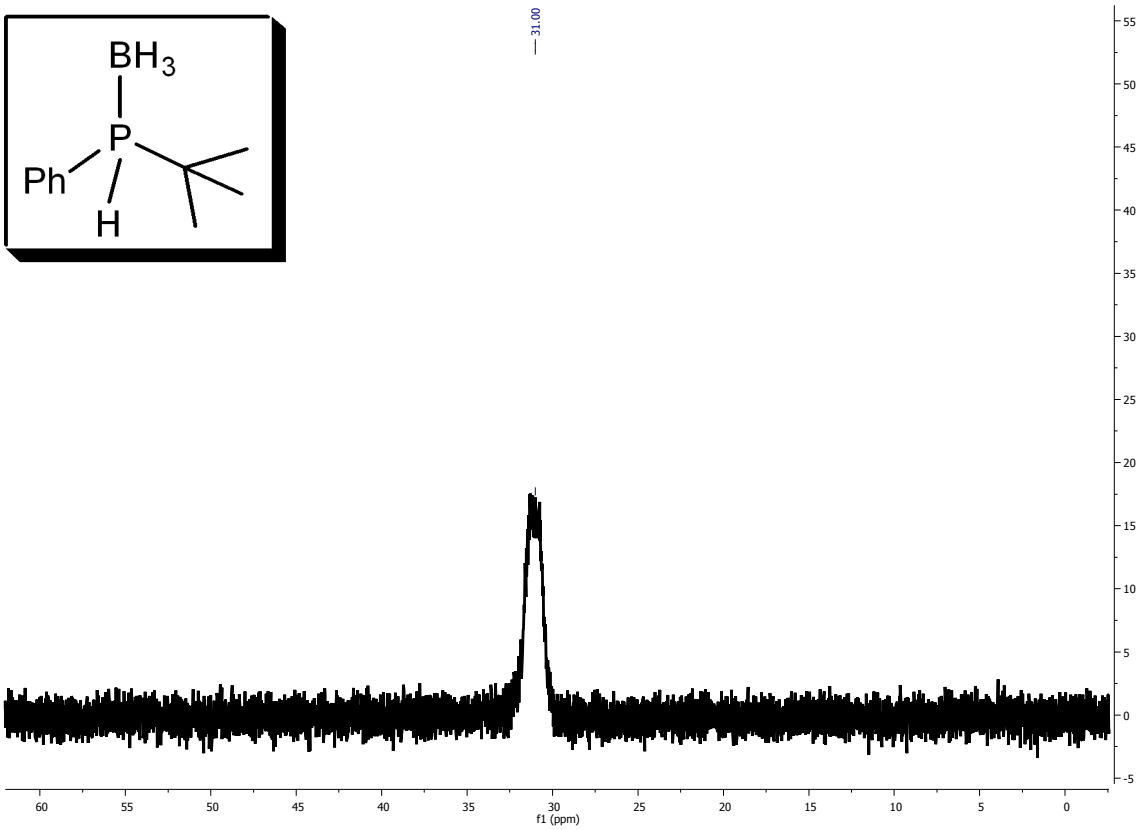

BH3
P
n-Bu
n-Bu
n-Bu
f1 (ppm)

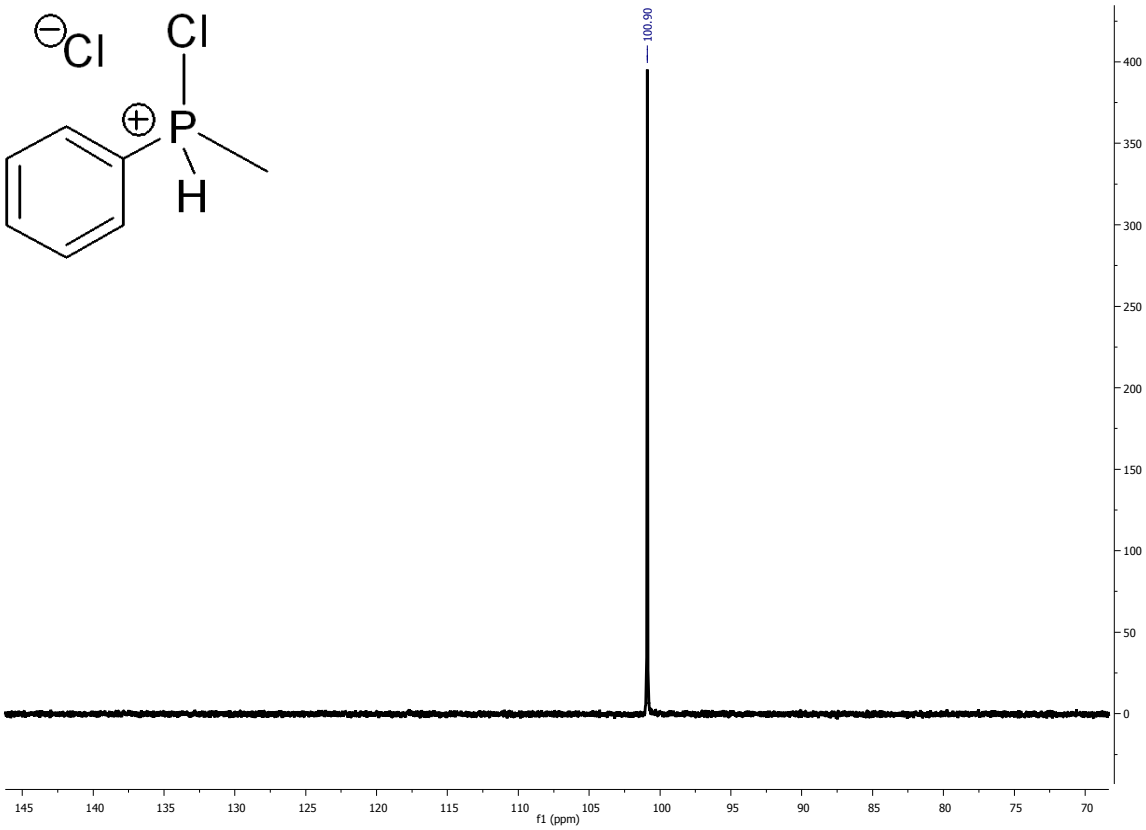

BH3
P
n-Bu
n-Bu
n-Bu
14.16
f1 (ppm)

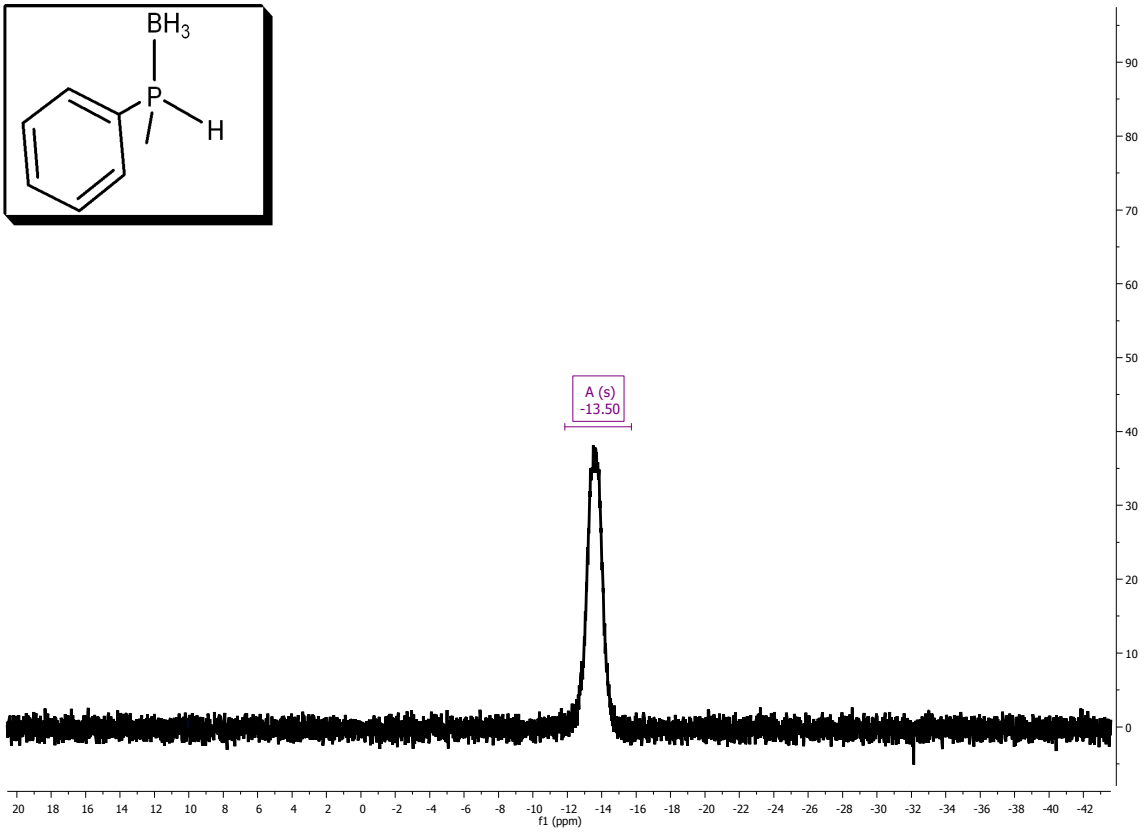

Cl
Cl
P
H
78.41
f1 (ppm)


PHOSPHORUS_001
BH3
P
H
-6.32
f1 (ppm)


Cl
Cl
P
H
107.61
f1 (ppm)


BH3
P
Ph
H
31.00
f1 (ppm)


Cl
Cl
P
H
100.90
f1 (ppm)

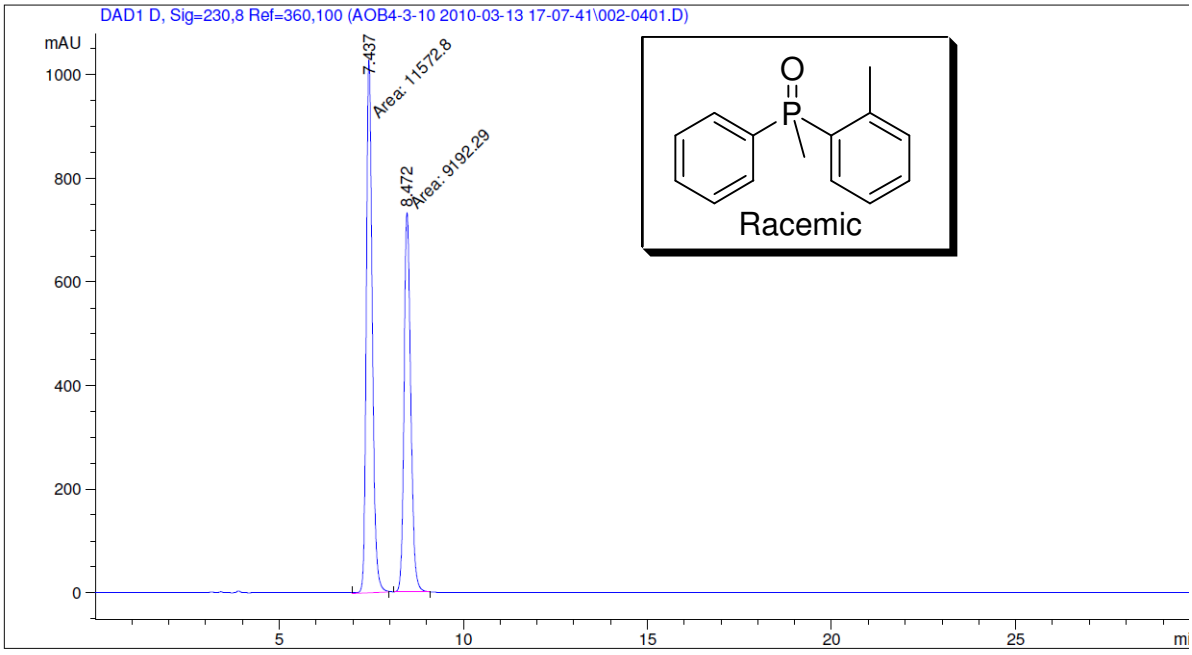


Supporting HPLC Traces

Entry 2 in Table A

Racemic methylphenyl*o*-tolylphosphine oxide

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   4
Acq. Instrument : Kev HPLC 1                    Location : Vial 2
Injection Date  : 3/13/2010 6:22:51 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\AOB4-3-10 2010-03-13 17-07-41\ISO_80_20_30MIN_1MLMIN.M
Last changed    : 3/13/2010 6:22:39 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\AOB4-3-10 2010-03-13 17-07-41\002-0401.D\DA.M (ISO_80_20_
                  30MIN_1MLMIN.M)
Last changed    : 7/8/2009 9:49:45 AM by General sequence
Method Info     : Isocratic at 80/20 heptane/EtOH for 30min at 1ml/min
```

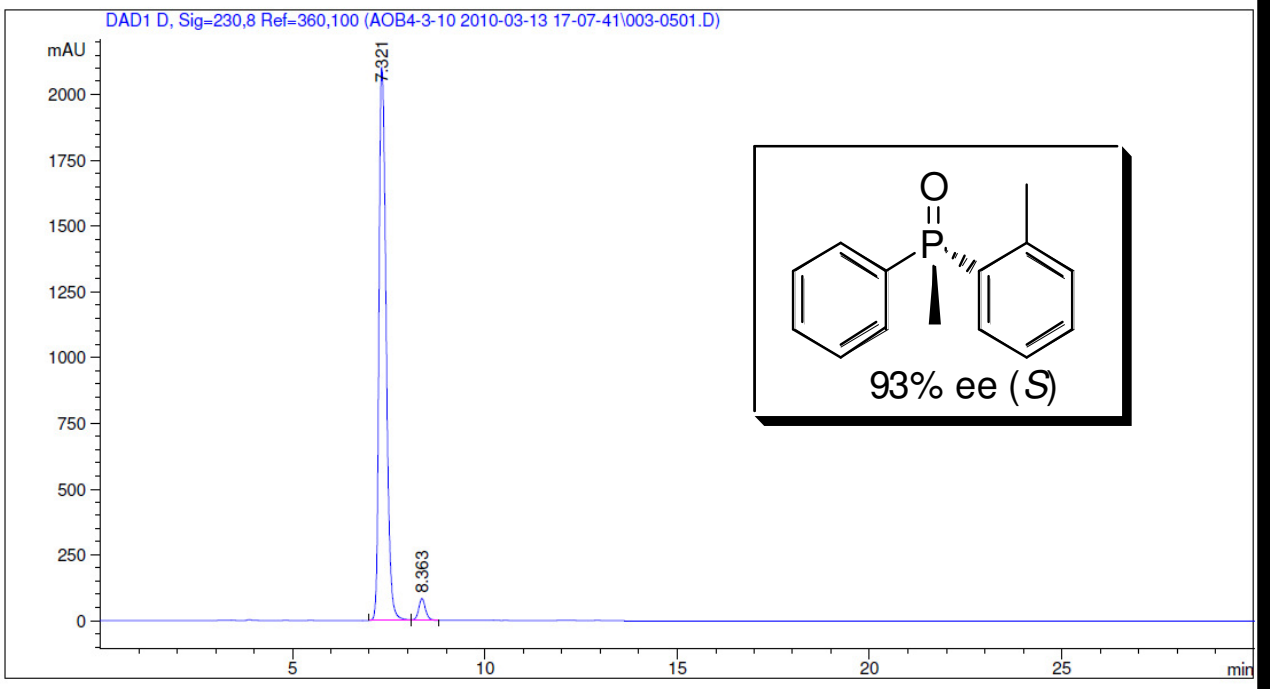



```
======================================================================
                      Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100
```

Entry 1-4 in Table D

Scalemic methylphenyl*o*-tolylphosphine oxide used as starting material

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   5
Acq. Instrument : Kev HPLC 1                    Location : Vial 3
Injection Date  : 3/13/2010 7:04:04 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\AOB4-3-10 2010-03-13 17-07-41\ISO_80_20_30MIN_1MLMIN.M
Last changed    : 3/13/2010 7:03:52 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\AOB4-3-10 2010-03-13 17-07-41\003-0501.D\DA.M (ISO_80_20_
                  30MIN_1MLMIN.M)
Last changed    : 3/15/2010 10:58:35 AM by General sequence
Method Info     : Isocratic at 80/20 heptane/EtOH for 30min at 1ml/min
```

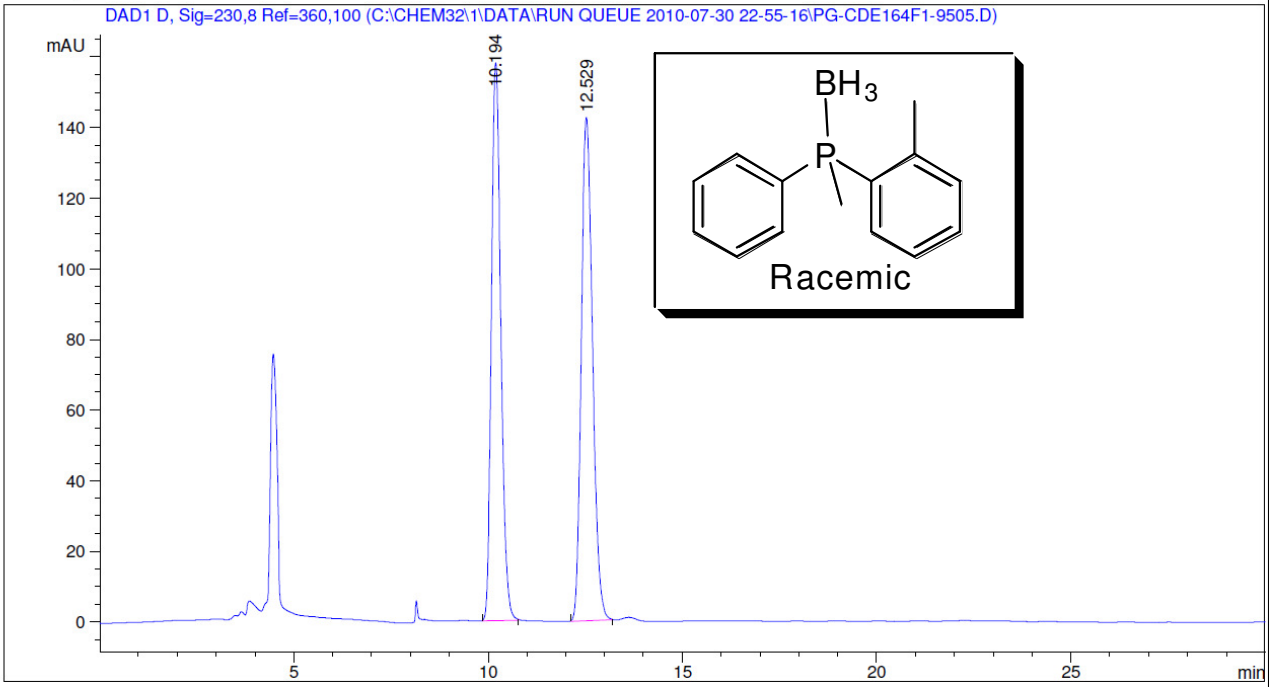



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.321 BV    0.2061 2.74307e4  2103.87964  96.3471
   2   8.363 VB    0.1894 1040.00745   83.42152   3.6529
```

Entry 2 in Table A

Racemic methylphenyl*o*-tolylphosphine phosphine borane

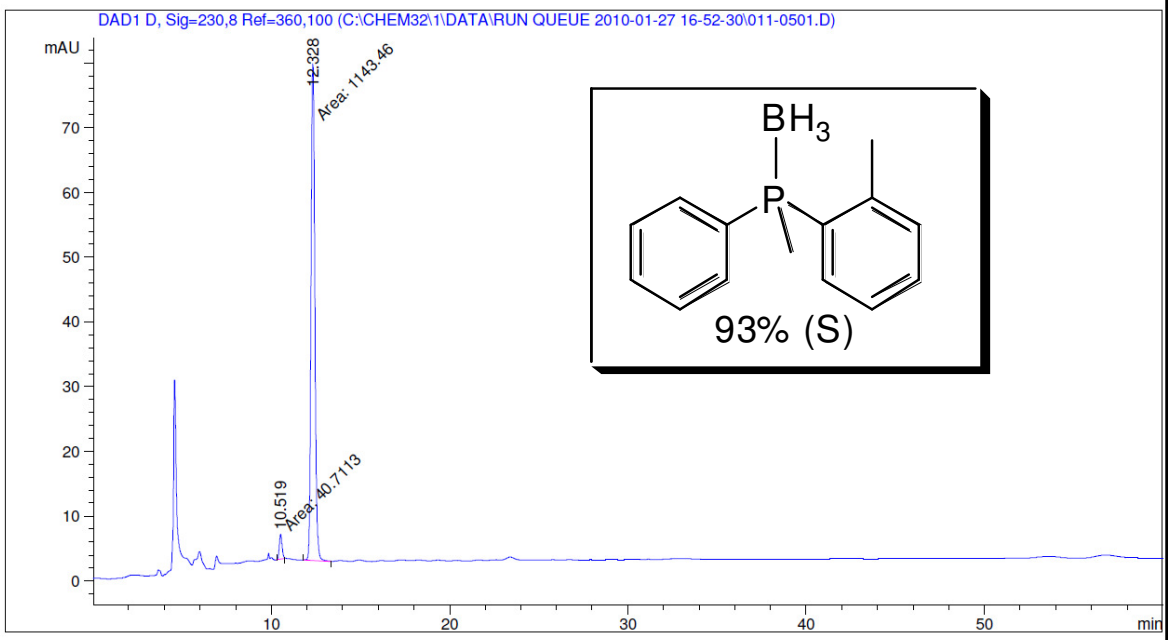
```
======================================================================

Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      24.9             24.9   °C
Column Temp. (right)    :      26.0             26.0   °C
Pressure                :      54.1             54.5   bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       4                4

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       1.75          1193.6   h
DAD 1, Visible Lamp     :      OFF              11.2   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```



Entry 1 and 2 in Table D

Scalemic methylphenyl*o*-tolylphosphine borane obtained by using MeOTF as alkylating agent and $NaBH_4$ as reductant

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   5
Acq. Instrument : Kev HPLC 1                    Location : Vial 11
Injection Date  : 1/27/2010 5:27:07 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-01-27 16-52-30\ISO_98_02_60MIN_1MLMIN.M
Last changed    : 1/27/2010 5:26:56 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/28/2010 8:54:49 PM by General sequence
Method Info     : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min
```

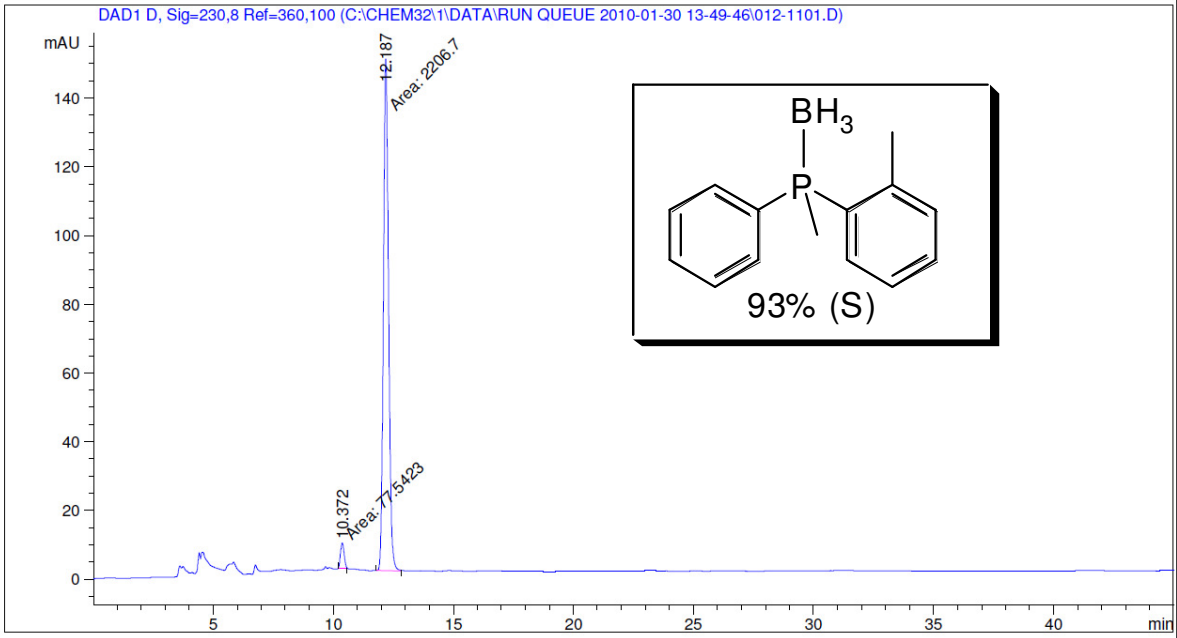



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.519 MM    0.1778   40.71126    3.81536   3.4379
   2  12.328 MM    0.2483 1143.46362   76.75564  96.5621
```

Entry 3 in Table D

Scalemic methylphenyl*o*-tolylphosphine borane obtained by using $[Et_3O]^+BF4^-$ as alkylating agent and $NaBH_4$ as reductant

```
=====================================================================
Acq. Operator   : General sequence              Seq. Line :  11
Acq. Instrument : Kev HPLC 1                    Location : Vial 12
Injection Date  : 1/30/2010 4:22:14 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-01-30 13-49-46\ISO_98_02_45MIN_1MLMIN.M
Last changed    : 1/30/2010 4:22:04 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/28/2010 8:54:49 PM by General sequence
Method Info     : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min
```

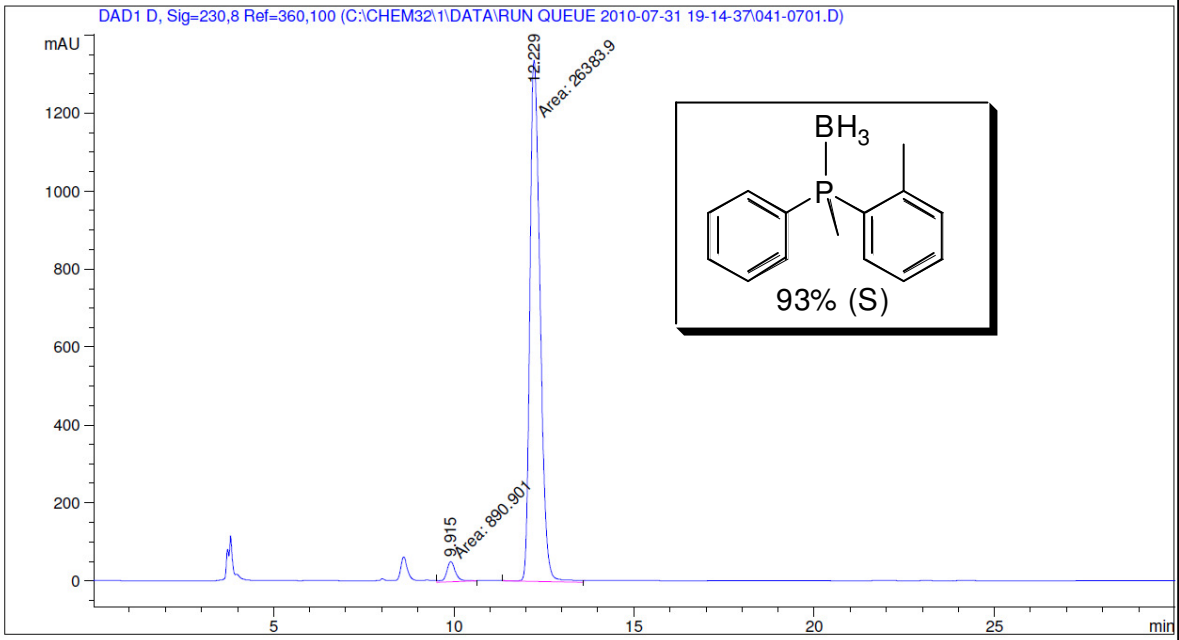



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.372 MM    0.1752   77.54230    7.37590   3.3947
   2  12.187 MM    0.2471 2206.69824  148.81880  96.6053
```

Entry 4 in Table D

Scalemic methylphenyl*o*-tolylphosphine borane obtained by using $Me_3O]^+ BF_4$ as alkylating agent and $NaBH_4$ as reductant

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   7
Acq. Instrument : Kev HPLC 1                    Location : Vial 41
Injection Date  : 7/31/2010 10:11:53 PM              Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-07-31 19-14-37\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 7/31/2010 10:11:43 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/28/2010 8:54:49 PM by General sequence
Method Info     : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min
```

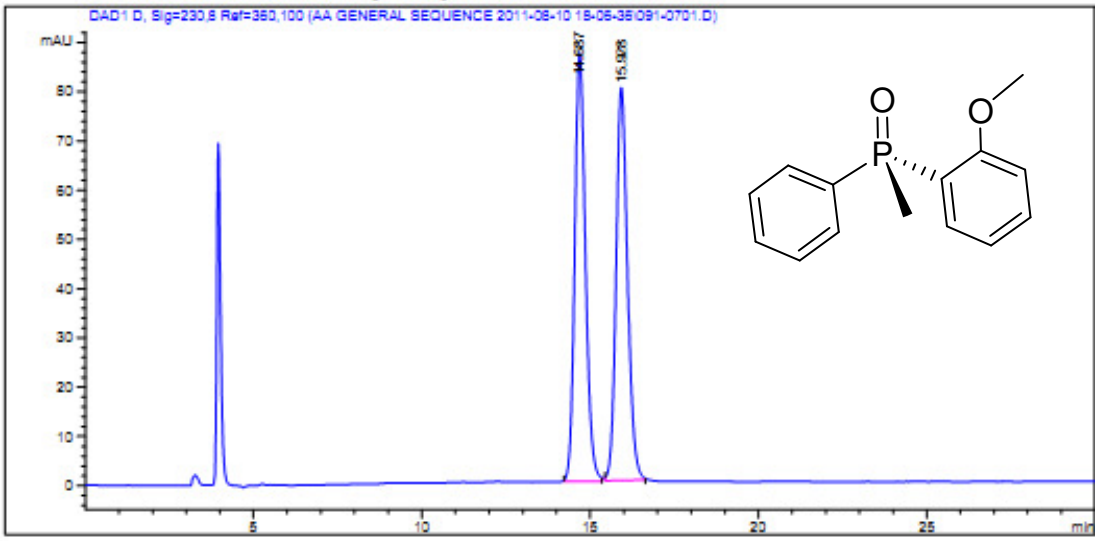



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.915 MM    0.2885  890.90057   51.46819   3.2664
   2  12.229 MM    0.3290 2.63839e4  1336.55017  96.7336
```

Entry 3 in Table A

Racemic (±)anisylmethylphenylphosphine oxide

```
Acq. Operator   : DGG                          Seq. Line :   7
Acq. Instrument : HPLC1                         Location : Vial 91
Injection Date  : 8/10/2011 7:34:12 PM             Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-08-10 18-06-36\ISO_90_10_30MIN_
                  1MLMIN.M
Last changed    : 9/25/2010 3:52:29 PM by General sequence
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_80_20_15MIN_1MLMIN.M
Last changed    : 8/4/2011 6:16:04 PM by DGG
                  (modified after loading)
Method Info     : Isocratic at 80/20 heptane/EtOH for 15min at 1ml/min

Additional Info : Peak(s) manually integrated
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 D, Sig=230,8 Ref=360,100
```

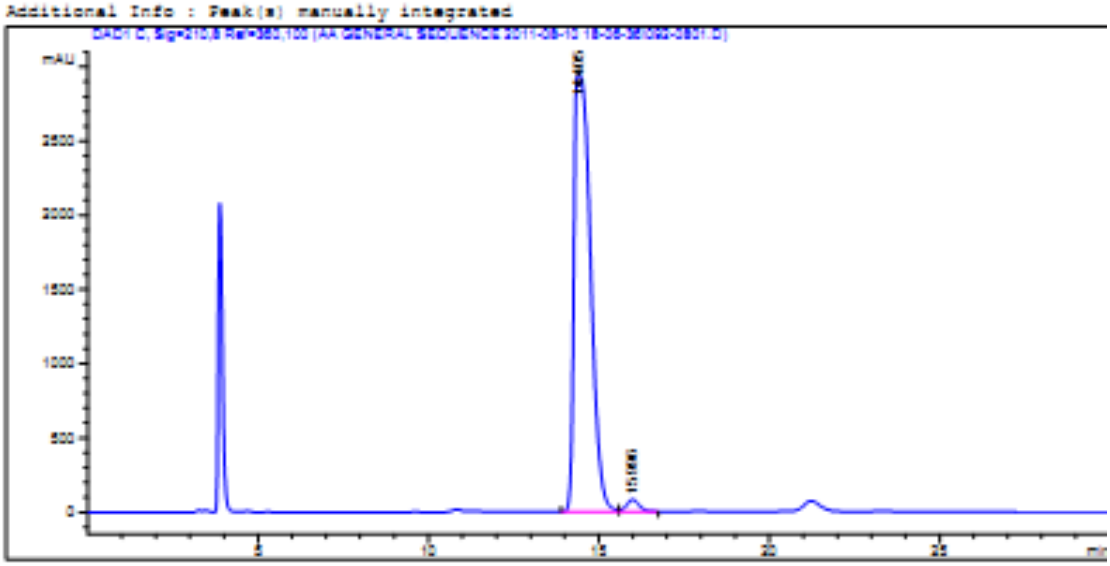
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.697	BB	0.3342	1909.66724	86.95485	50.3048
2	15.928	BB	0.3617	1886.52759	79.84065	49.6952
Totals :				3796.19482	166.79550	

```
                        *** End of Report ***
```

Entry 5-6 in Table D

Scalemic anisylmethylphenylphosphine oxide 95.7 % ee (R)

```
Acq. Operator   : CGG                          Seq. Line :   8
Acq. Instrument : HPLC1                         Location : Vial 92
Injection Date  : 8/10/2011 8:05:12 PM             Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-08-10 18-06-36\ISO_90_10_30MIN_
                  1MLMIN.M
Last changed    : 9/25/2010 3:52:29 PM by General sequence
Analysis Method : C:\CHEM32\1\METHODS\10_FLOW 0,5 MLMIN METHODS\ISO_99_01_15MIN_0_5MLMIN.M
Last changed    : 9/7/2011 12:36:50 PM by CGG
                  (modified after loading)
Method Info     : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min

Additional Info : Peak(s) manually integrated
```

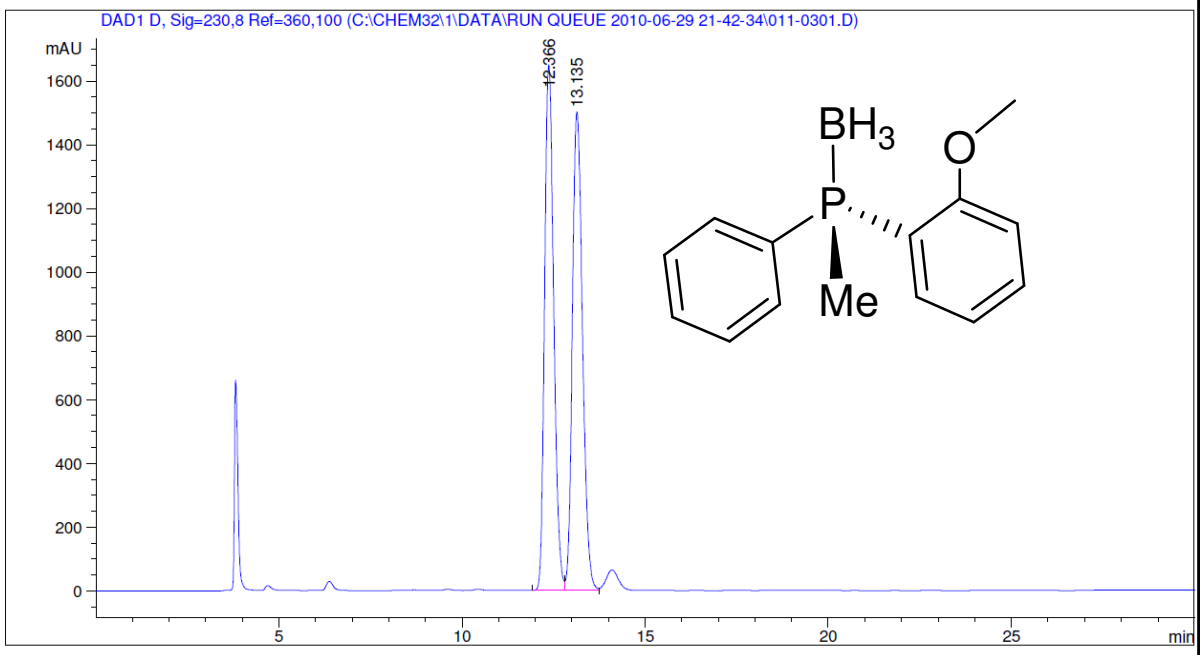



```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100


Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|--------|----|--------|----------|----------|--------|
   1  14.405 VV    0.4367 9.93322e4  2951.40729  97.8821
   2  15.996 VB    0.3938 2149.28979   82.53716   2.1179

Totals :                  1.01481e5  3033.94438

                          *** End of Report ***
```

Entry 3 in Table A

Racemic (±)anisylmethylphenylphosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   3
Acq. Instrument : Kev HPLC 1                    Location : Vial 11
Injection Date  : 6/29/2010 10:17:16 PM             Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-06-29 21-42-34\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/29/2010 10:17:05 PM by General sequence
Analysis Method : C:\CHEM32\1\METHODS\01_COLUMN METHODS\STABILISE_98_02_10MIN_1MLMIN.M
Last changed    : 6/29/2010 9:32:43 PM by General sequence
Method Info     : Stabilise column at 99/1 heptane/EtOH for 10min at 1ml/min
```

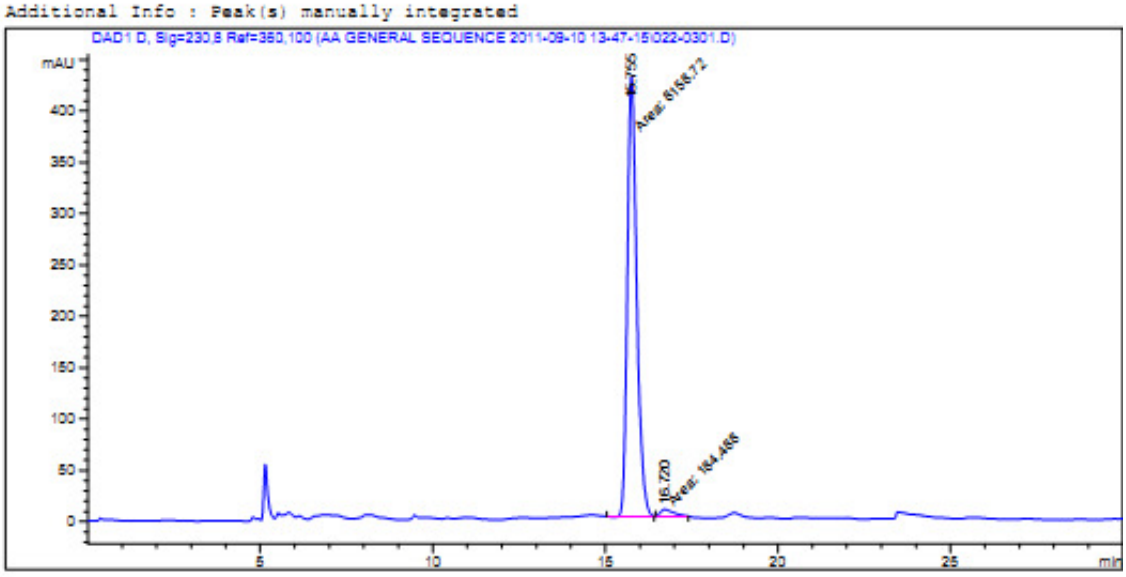



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.366 BV    0.2707 2.86744e4  1650.24219  49.7663
   2  13.135 VV    0.3028 2.89437e4  1502.02356  50.2337
```

Entry 5 and 6 in Table D

Scalemic anisylmethylphenylphosphine borane 95.6 % ee

```
=====================================================================
Acq. Operator   : DGG                          Seq. Line :   3
Acq. Instrument : HPLC1                         Location : Vial 22
Injection Date  : 9/10/2011 2:00:49 PM             Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-09-10 13-47-15\ISO_99_02_30MIN_
                  1MLMIN.M
Last changed    : 2/25/2011 9:47:10 AM by KV
Analysis Method : C:\CHEM32\1\METHODS\10_FLOW 0,5 MLMIN METHODS\ISO_99_01_15MIN_0_5MLMIN.M
Last changed    : 9/7/2011 12:36:50 PM by DGG
                  (modified after loading)
Method Info     : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min

Additional Info : Peak(s) manually integrated
```

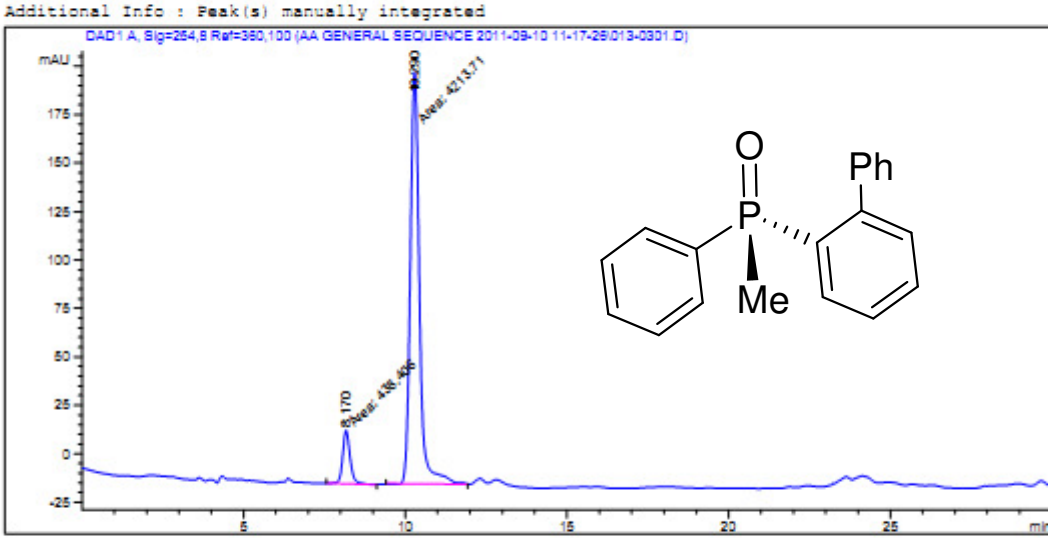



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.755 MM    0.3171 9158.71533  428.82748  97.7888
   2  16.720 MM    0.4489  184.48784    6.84908   2.2112

Totals :                  9343.20317  435.67657

=====================================================================
                        *** End of Report ***
```

Entry 7 in Table D

Scalemic (2-Biphenyl)methylphenylphosphine oxide 81 % ee (*S*)

```
======================================================================
Acq. Operator   : DGG                          Seq. Line :   3
Acq. Instrument : HPLC1                         Location : Vial 13
Injection Date  : 9/10/2011 11:30:59 AM            Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-09-10 11-17-26\ISO_80_20_30MIN_
                  1MLMIN.M
Last changed    : 4/1/2011 10:02:37 AM by K
Analysis Method : C:\CHEM32\1\METHODS\10_FLOW 0,5 MLMIN METHODS\ISO_99_01_15MIN_0_5MLMIN.M
Last changed    : 9/7/2011 12:36:50 PM by DGG
                  (modified after loading)
Method Info     : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min

Additional Info : Peak(s) manually integrated
```

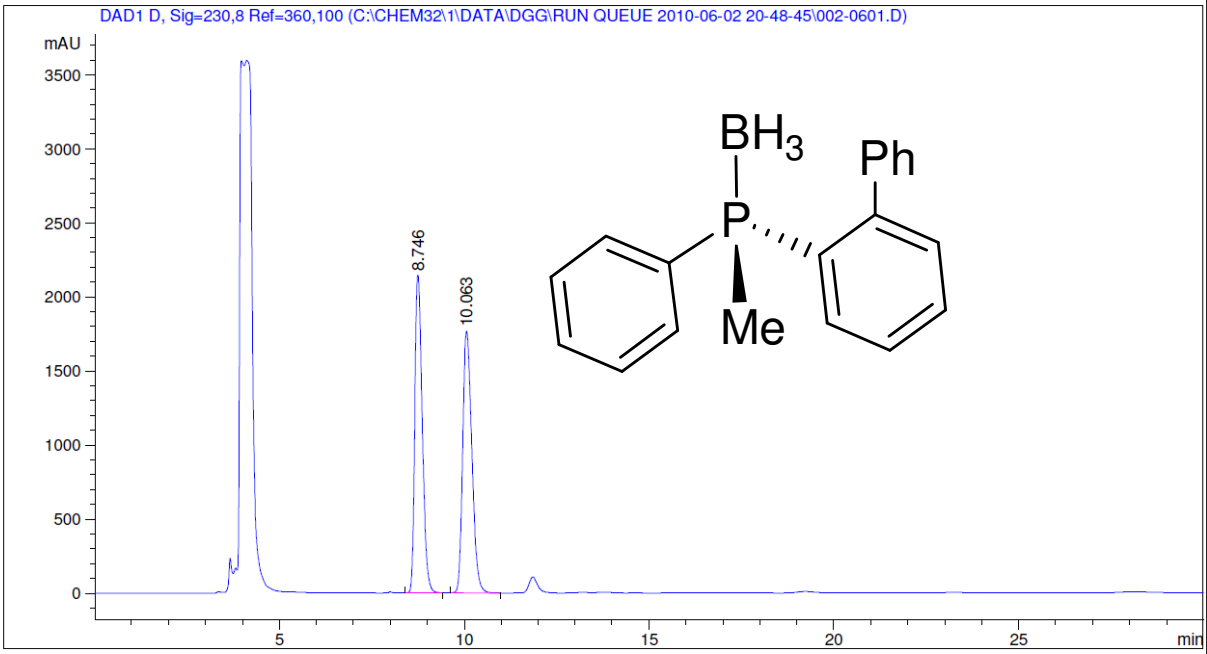



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,8 Ref=360,100


Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.170 MM    0.2664  439.40555   27.42945   9.4238
   2  10.290 MM    0.3307 4213.71143  212.37991  90.5762

Totals :                  4652.11697  239.80936

======================================================================
                        *** End of Report ***
```

Entry 8 in Table A

Racemic (±)-(2-Biphenyl)methylphenylphosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   6
Acq. Instrument : Kev HPLC 1                    Location : Vial 2
Injection Date  : 6/2/2010 10:34:56 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-04-21 18-10-30\RUN QUEUE 2010-06-02 20-48-
                  45\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/2/2010 10:34:46 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 5/20/2010 11:50:38 AM by General sequence
Method Info     : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min
```

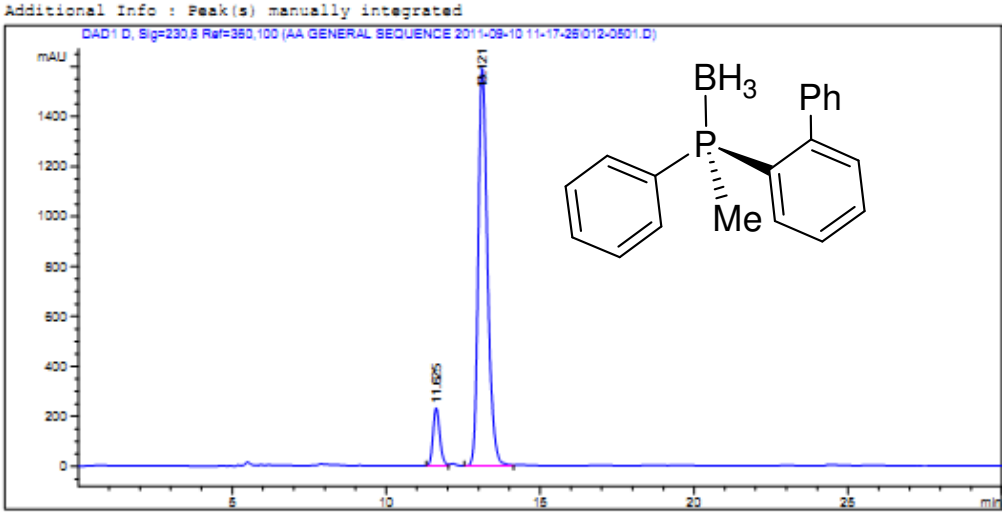



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.746 VB    0.2174 3.00823e4  2148.21655  49.6276
   2  10.063 BB    0.2695 3.05337e4  1767.96008  50.3724
```

Entry 7 in Table D

Scalemic (2-Biphenyl)methylphenylphosphine borane 81 % ee(S)

```
======================================================================
Acq. Operator   : DGG                          Seq. Line :   5
Acq. Instrument : HPLC1                         Location : Vial 12
Injection Date  : 9/10/2011 12:12:29 PM            Inj :   1
                                               Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-09-10 11-17-26\ISO_98_02_30MIN_
                  1MLMIN.M
Last changed    : 2/25/2011 9:47:10 AM by KV
Analysis Method : C:\CHEM32\1\METHODS\10_FLOW 0,5 MLMIN METHODS\ISO_99_01_15MIN_0_5MLMIN.M
Last changed    : 9/7/2011 12:36:50 PM by DGG
                  (modified after loading)
Method Info     : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.625	BV	0.2372	3552.69263	231.29472	9.5416
2	13.121	VV	0.3252	3.36810e4	1589.36267	90.4584
Totals :				3.72337e4	1820.65739	

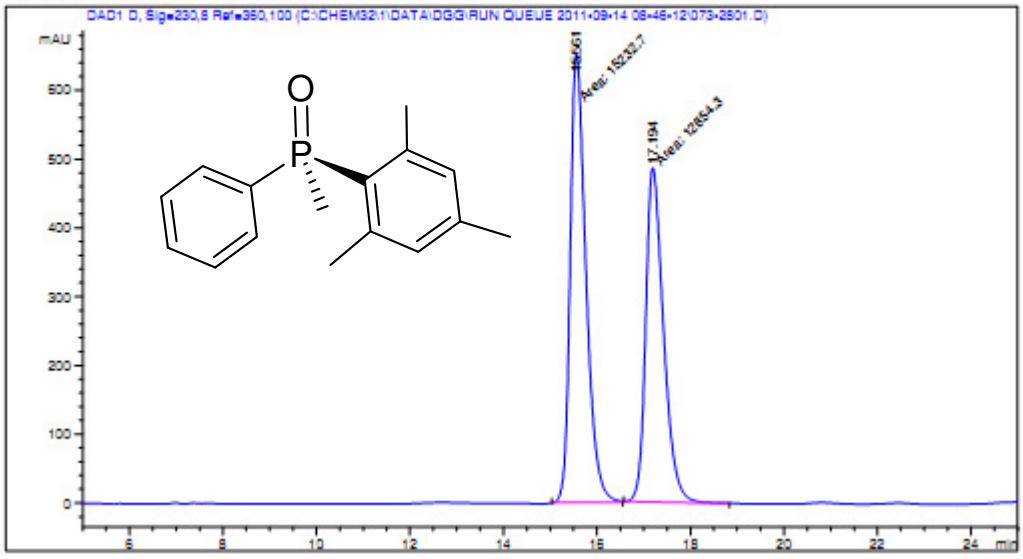
```
======================================================================
                        *** End of Report ***
```

Entry 14 in Table A

Racemic methylphenyl(mesityl)phosphine oxide

```
Acq. Operator   :                                  Seq. Line :  28
Acq. Instrument : Kev HPLC 1                        Location : Vial 73
Injection Date  : 9/14/2011 5:45:55 PM                   Inj :  1
                                                  Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\DGG\RUN QUEUE 2011-09-14 08-46-12\ISO_90_10_30MIN_1MLMIN.M
Last changed    : 9/14/2011 5:45:44 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\14_OTHER METHODS\GARY\RI 98_2_30MIN_1MLMIN.M
Last changed    : 9/14/2011 1:45:45 PM
                  (modified after loading)
Method Info     : 98/02  for 30 min at 1ml/min
                  RI detector on
```

```
Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      24.0             23.9   °C
Column Temp. (right)    :      25.2             25.1   °C
Pressure                :      50.9             51.3   bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       1                1

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       9.01           3126.3   h
DAD 1, Visible Lamp     :      OFF               97.5   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```

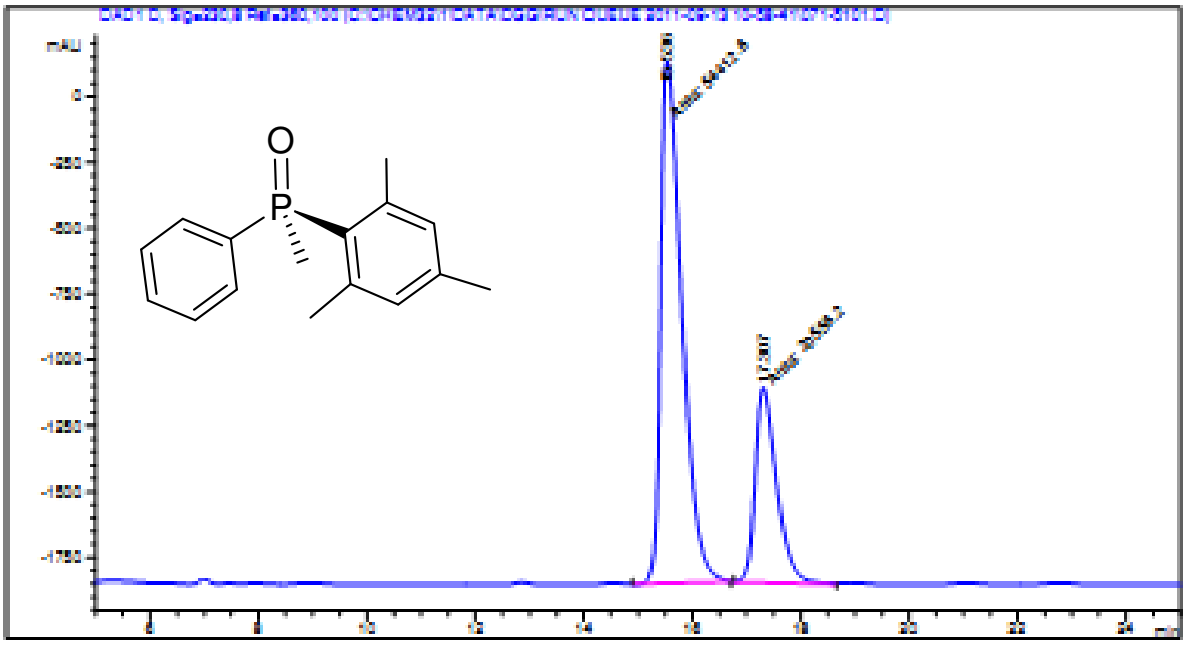


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.561	MM	0.3886	1.52327e4	653.39349	54.2340
2	17.194	MM	0.4407	1.28543e4	486.17926	45.7660
Totals :				2.80870e4	1139.57275	

Entry 8 in Table D

Scalemic methylphenyl(mesityl)phosphine oxide 44 % ee (R)

```
Valve 1 Position        :       1                 1

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       15.51           3116.3   h
DAD 1, Visible Lamp     :       Off               87.5   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```




```
Signal 1: DAD1 C, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height    Area
  #   [min]        [min]   [mAU*s]     [mAU]      %
----|--------|----|--------|----------|----------|--------|
   1  15.536 MM    0.4578 5.44126e4  1981.13867  72.5803
   2  17.307 MM    0.4630 2.05562e4   739.92206  27.4197

Totals :                  7.49688e4  2721.06073

-------------------------------------------------------------------------------
```

Entry 8 in Table D

Scalemic methylphenyl(mesityl)phosphine oxide 44 % ee (*S*)

Instrument Conditions	:	At Start	At Stop	
Column Temp. (left)	:	23.5	23.5	°C
Column Temp. (right)	:	24.5	24.5	°C
Pressure	:	46.3	52.1	bar
Flow	:	1.000	1.000	ml/min
Valve 1 Position	:	1	1	

Detector Lamp Burn Times:	Current On-Time	Accumulated On-Time	
DAD 1, UV Lamp :	16.04	3116.8	h
DAD 1, Visible Lamp :	OFF	87.5	h

Solvent Description :
PMP1 , Solvent A : Heptane
PMP1 , Solvent B : EtOH

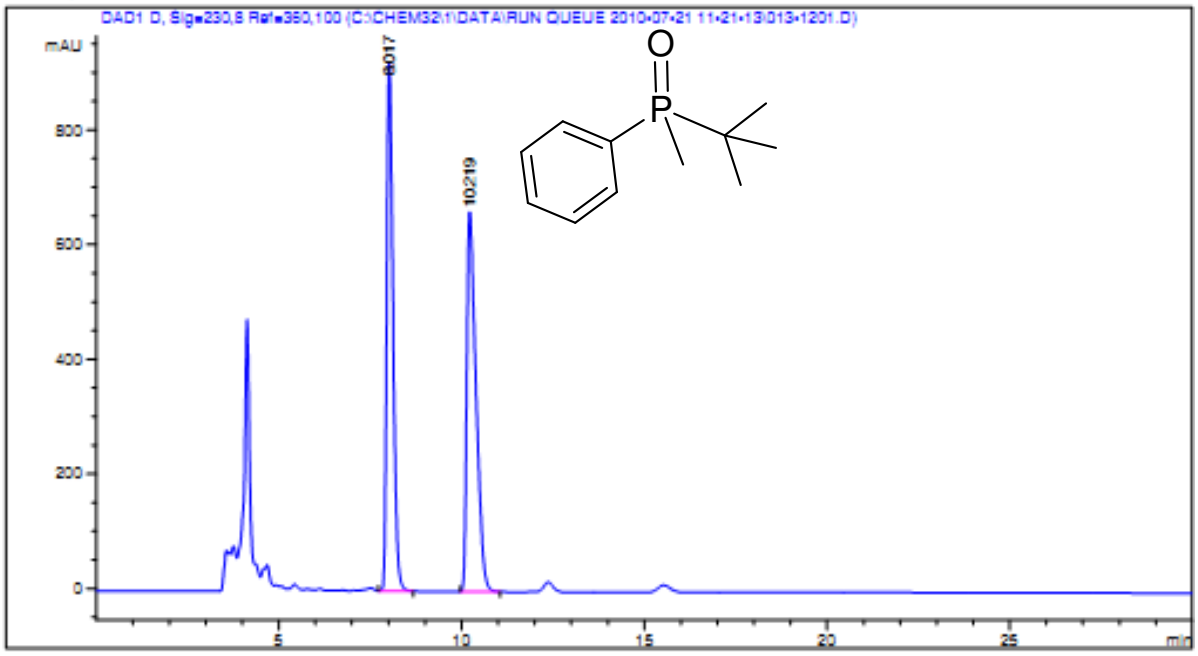
Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.691	MM	0.3806	1.52565e4	668.03705	27.5083
2	17.146	MM	0.4912	4.02051e4	1364.27258	72.4917
Totals :				5.54616e4	2032.30963	

Entry 16 in Table A

Racemic -*tert*-Butylmethylphenylphosphine oxide

```
Instrument Conditions    :    At Start           At Stop
Column Temp. (left)      :      28.3              28.4    °C
Column Temp. (right)     :      29.3              29.4    °C
Pressure                 :      70.1              71.1    bar
Flow                     :       1.000             1.000 ml/min
Valve 1 Position         :       5                 5

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp           :       4.99           1156.3    h
DAD 1, Visible Lamp      :      OFF               11.2    h

Solvent Description      :
PMP1 , Solvent A         : Heptane
PMP1 , Solvent B         : EtOH
```

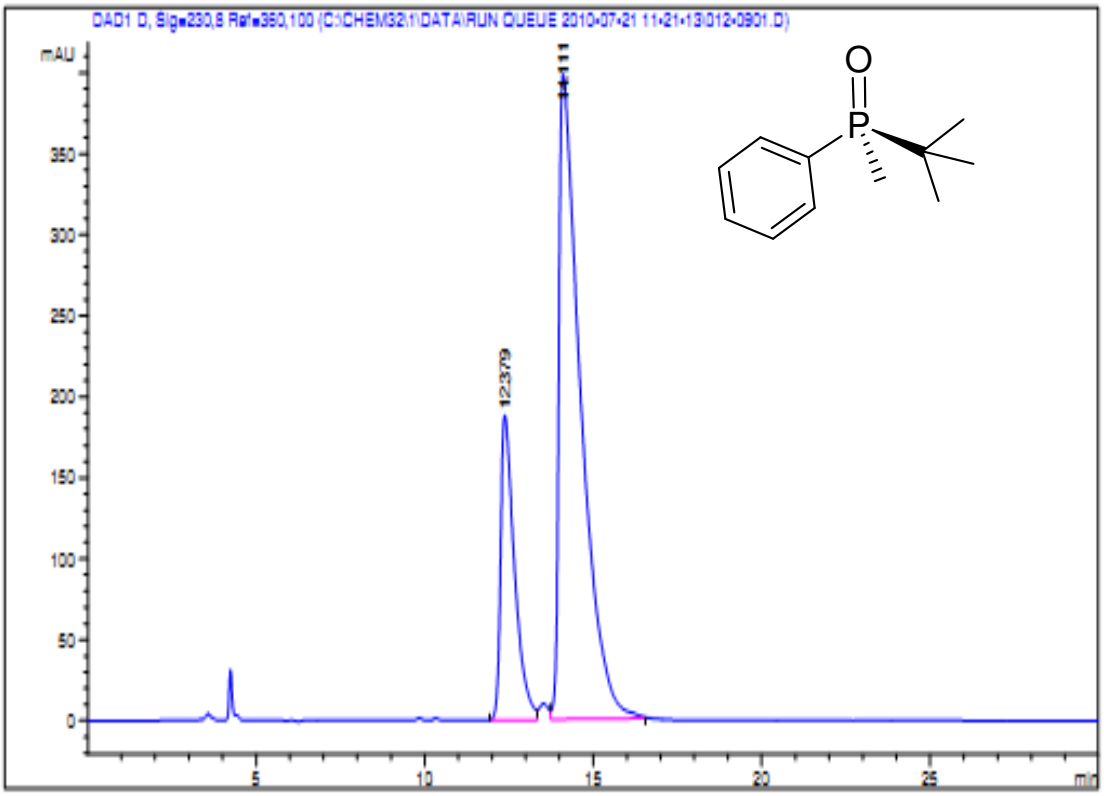


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.017	VB	0.1821	1.09237e4	923.13629	48.4947
2	10.219	BB	0.2665	1.16018e4	661.75677	51.5053
Totals :				2.25255e4	1584.89307	

Entry 9 in Table D

Scalemic (*R*)-*tert*-Butylmethylphenylphosphine oxide 53 % ee

```
Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       3.66           1155.1   h
DAD 1, Visible Lamp     :      OFF               11.2   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```

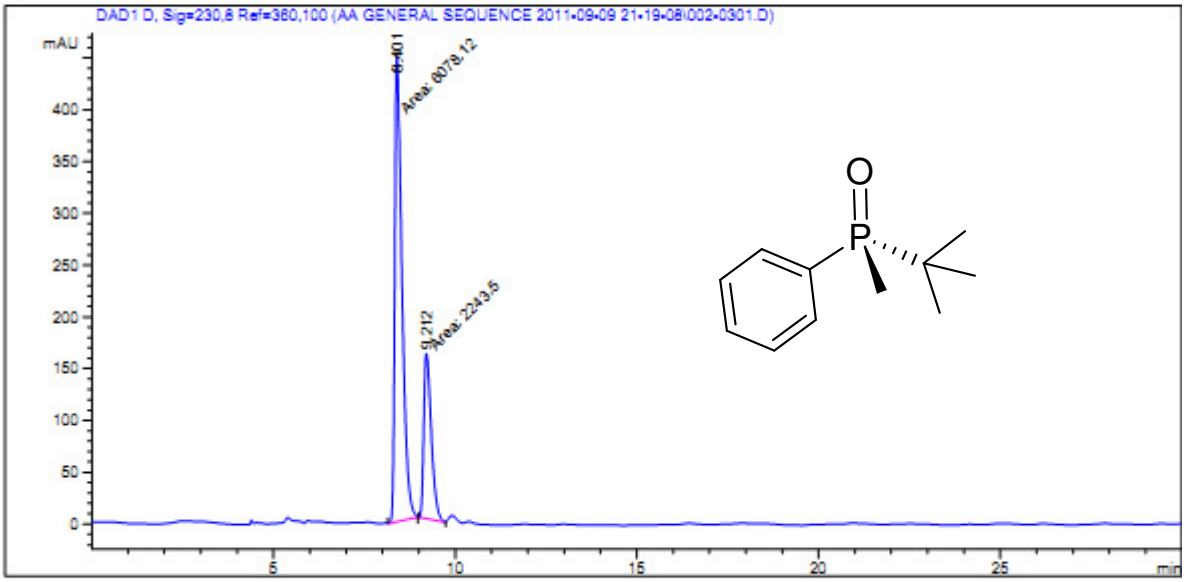



```
Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.379 BV    0.4211 5409.17627  199.34335  23.2056
   2  14.111 VB    0.6644 1.79007e4   399.26746  76.7944

Totals :                  2.33098e4   596.61081
```

Entry 10 in Table D

Scalemic (*S*)-*tert*-Butylmethylphenylphosphine oxide 46 % ee

```
------------------------------------------------------------------------
Acq. Operator    : DGG                          Seq. Line :   3
Acq. Instrument : HPLC1                          Location : Vial 2
Injection Date  : 9/9/2011 9:32:41 PM                 Inj :   1
                                                Inj Volume : 5.000 µl
Acq. Method     : C:\CHEM32\1\DATA\AA GENERAL SEQUENCE 2011-09-09 21-19-08\ISO_90_10_30MIN_
                  1MLMIN.M
Last changed    : 9/25/2010 3:52:29 PM by General sequence
Analysis Method : C:\CHEM32\1\METHODS\10_FLOW 0,5 MLMIN METHODS\ISO_99_01_15MIN_0_5MLMIN.M
Last changed    : 9/7/2011 12:36:50 PM by DGG
                  (modified after loading)
Method Info     : Isocratic at 99/01 heptane/EtOH for 15min at 0.5ml/min

Additional Info : Peak(s) manually integrated
```




```
------------------------------------------------------------------------
                        Area Percent Report
------------------------------------------------------------------------

Sorted By             :      Signal
```

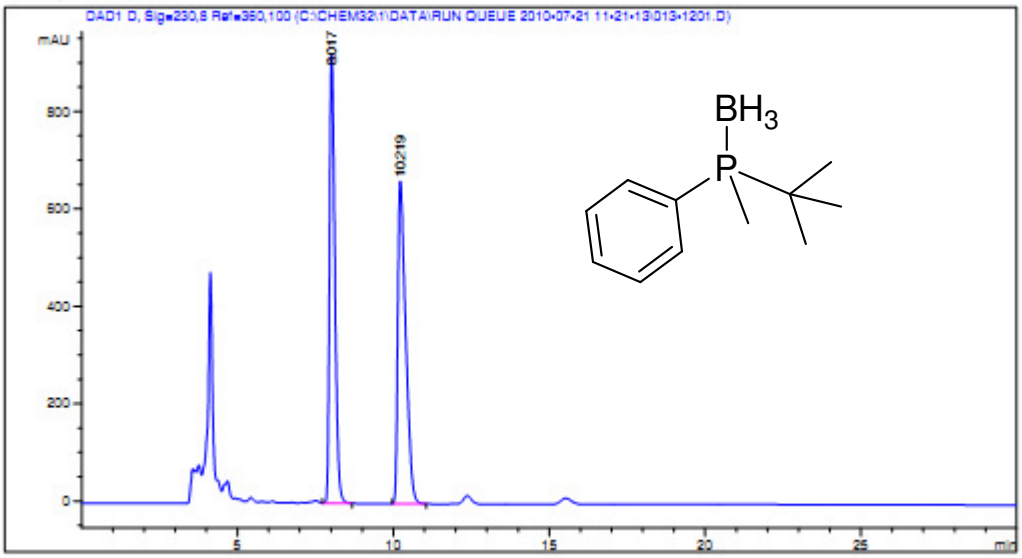
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.401	MM	0.2253	6078.11670	449.64005	73.0401
2	9.212	MM	0.2347	2243.49780	159.30034	26.9599
Totals :				8321.61450	608.94038	

```
------------------------------------------------------------------------
                        *** End of Report ***
```

Entry 16 in Table A

Racemic -*tert*-Butylmethylphenylphosphine borane

```
Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      28.3             28.4    °C
Column Temp. (right)    :      29.3             29.4    °C
Pressure                :      70.1             71.1    bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       5                5

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       4.88           1156.3   h
DAD 1, Visible Lamp     :      OFF               11.2    h

Solvent Description     :
PMPi , Solvent A        : Heptane
PMPi , Solvent B        : EtOH
```

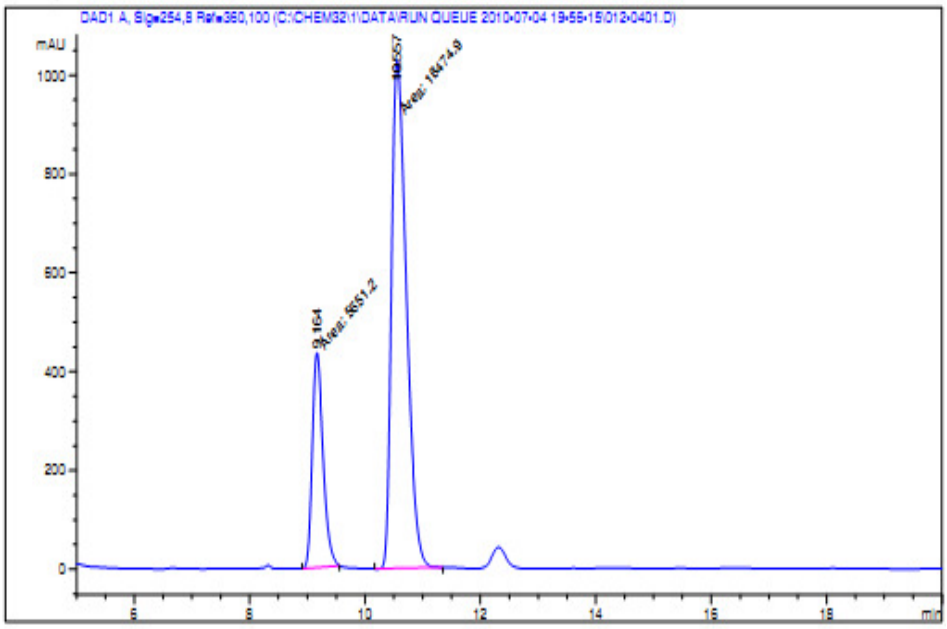



```
Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.017 VB    0.1921 1.09237e4   923.13629  48.4947
   2  10.219 BB    0.2665 1.16018e4   661.75677  51.5053

Totals :                  2.25255e4  1584.89307
```

Entry 9 in Table D

Scalemic (*R*)-*tert*-Butylmethylphenylphosphine borane 53 % ee

```
---------------------------------------------------------------------

Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      29.2             29.2   °C
Column Temp. (right)    :      30.6             30.7   °C
Pressure                :      72.5             76.8   bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       4                4

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       1.41           1101.8   h
DAD 1, Visible Lamp     :      OFF               11.2   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```

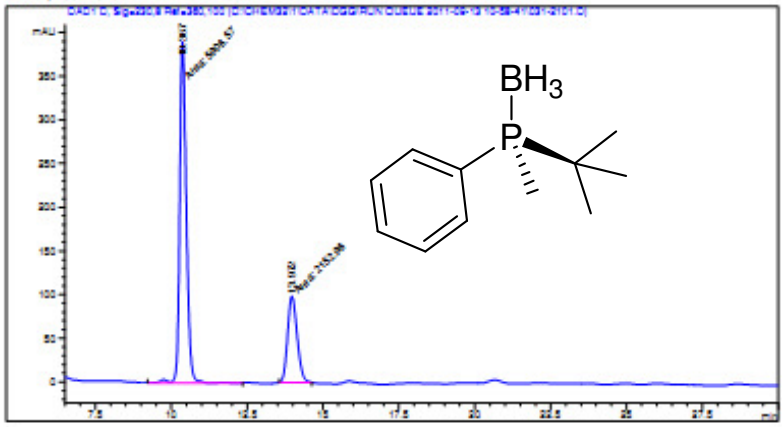



```
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.164 MM    0.2163 5651.20459  435.51163  23.4236
   2  10.557 MM    0.2992 1.84749e4  1028.95654  76.5764

Totals :                  2.41261e4  1464.46817

---------------------------------------------------------------------
```

Entry 10 in Table D

Scalemic (*S*)-*tert*-Butylmethylphenylphosphine borane 46 % ee

```
Acq. Operator   :                              Seq. Line :  21
Acq. Instrument : Kav HPLC 1                    Location : Vial 31
Injection Date  : 9/13/2011 5:34:20 PM             Inj :  1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\DGG\RUN QUEUE 2011-09-13 10-58-41\ISO_70_30_30MIN_1MLMIN.M
Last changed    : 9/13/2011 5:34:09 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\14_OTHER METHODS\GARY\RI 98_2_30MIN_1MLMIN.M
Last changed    : 9/14/2011 10:48:10 PM
                  (modified after loading)
Method Info     : 98/C2  for 30 min at 1ml/min
                  RI detector on

Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      24.0             24.1   °C
Column Temp. (right)    :      25.1             25.2   °C
Pressure                :      68.1             73.8   bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       5                5

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       6.60           3107.4   h
DAD 1, Visible Lamp     :      OFF             87.5   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```

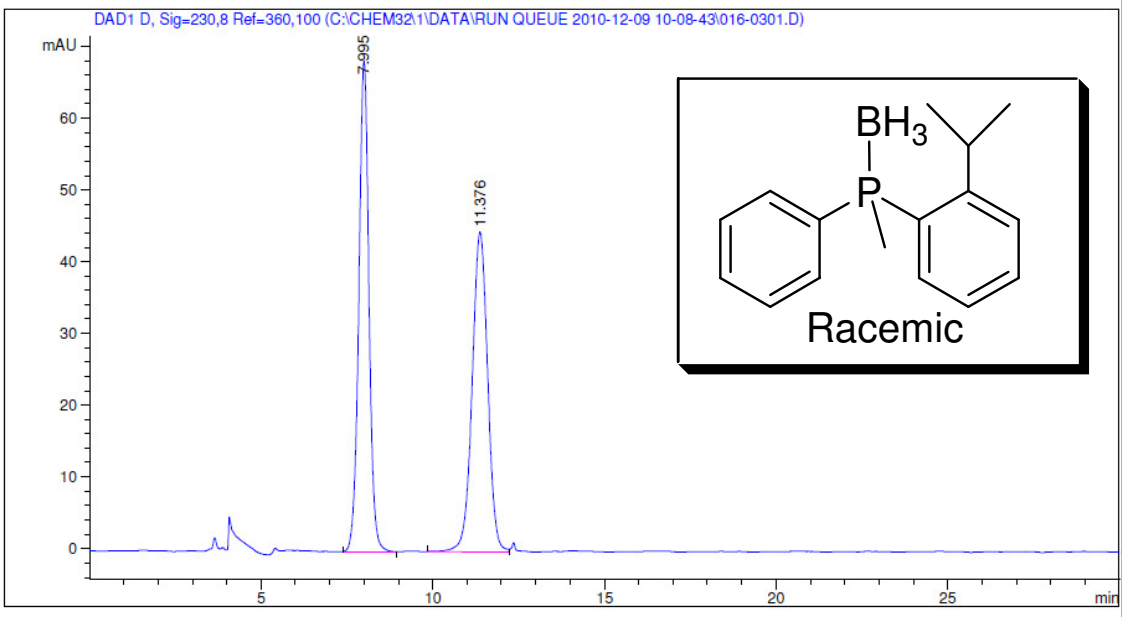



```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.367 MM    0.2521 5906.56689  390.52283  73.2867
   2  13.972 MM    0.3639 2152.96362   98.60745  26.7133

Totals :                  8059.53052  489.13028
```

Entry 9 in Table A

Racemic (±)-methylphenyl(2-*i*-propylphenyl)phosphine borane

```
==================================================================
Acq. Operator   : General sequence              Seq. Line :   3
Acq. Instrument : Kev HPLC 1                    Location : Vial 16
Injection Date  : 12/9/2010 10:41:45 AM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-12-09 10-08-43\ISO_99_01_30MIN_1MLMIN.M
Last changed    : 12/9/2010 10:41:34 AM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\01_COLUMN METHODS\SELECT IA COLUMN.M
Last changed    : 11/30/2010 9:11:53 AM by General sequence
                  (modified after loading)
Method Info     : Select IA column
```

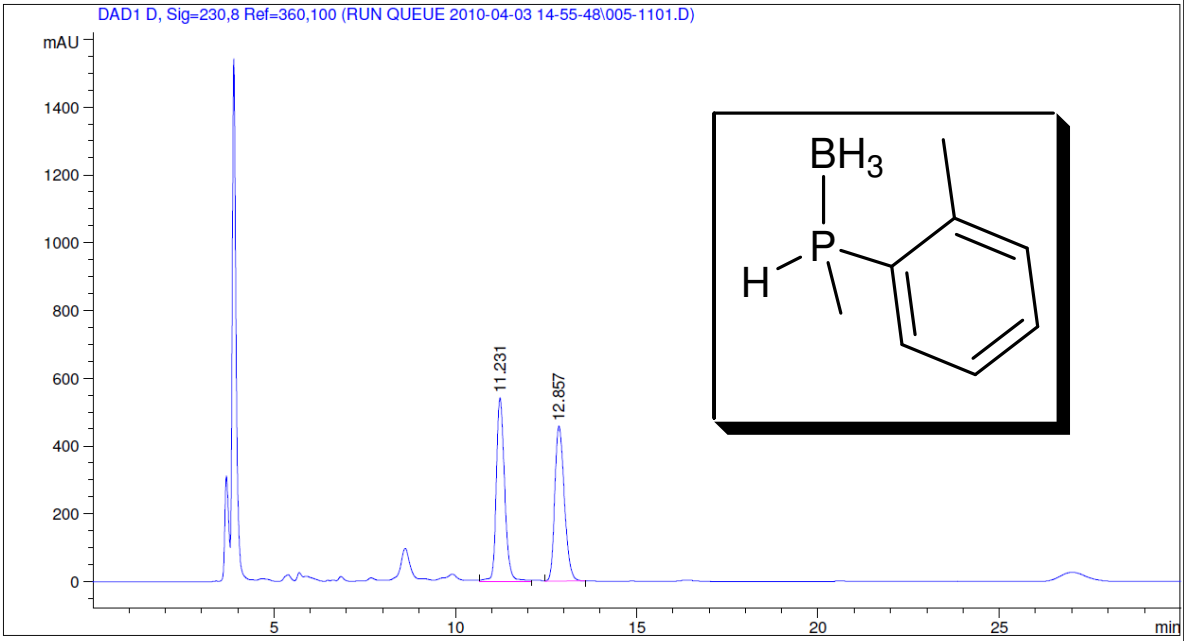



```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.995 BB    0.3106 1399.54749   68.43586  49.9362
   2  11.376 BV    0.4867 1403.12354   44.63789  50.0638
```

Entry 1 in Table B

Racemic (±)methyl(*o*-tolyl)phosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :  11
Acq. Instrument : Kev HPLC 1                    Location : Vial 5
Injection Date  : 4/3/2010 8:07:36 PM                 Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-04-03 14-55-48\ISO_97_03_30MIN_1MLMIN.M
Last changed    : 4/3/2010 5:22:21 PM by General sequence
Analysis Method : C:\CHEM32\1\DATA\RUN QUEUE 2010-04-03 14-55-48\005-1101.D\DA.M (ISO_97_03_
                  30MIN_1MLMIN.M)
Last changed    : 3/22/2010 9:23:07 AM by General sequence
Method Info     : Isocratic at 97/03 heptane/EtOH for 30min at 1ml/min
```

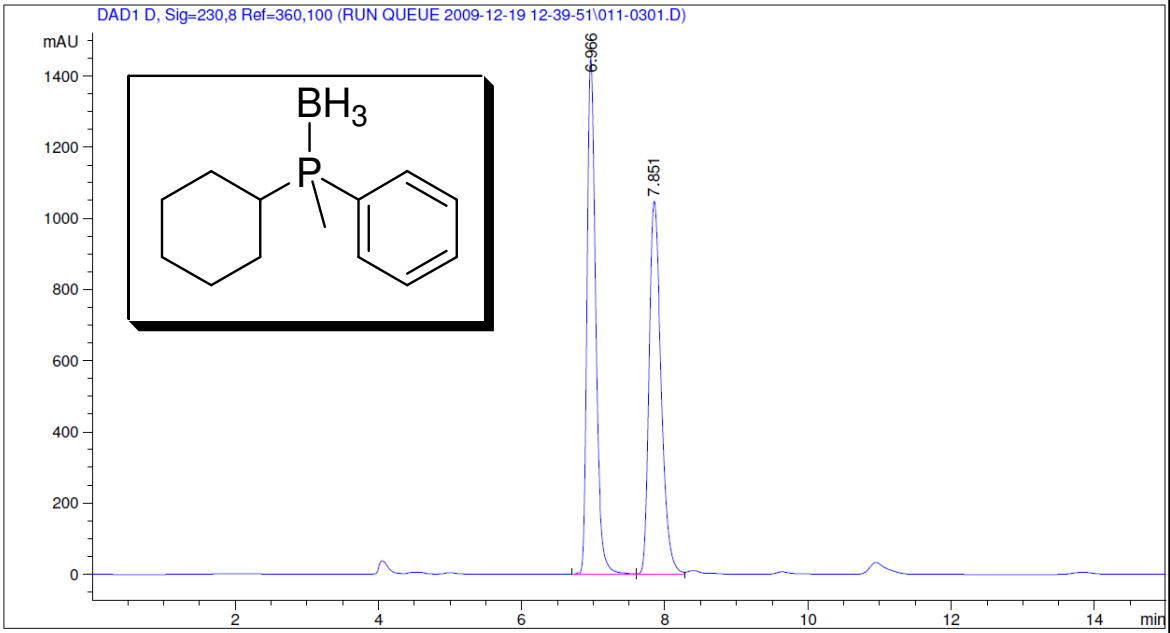



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.231 BB    0.2433 8590.73535  540.99377  50.5975
   2  12.857 VB    0.2840 8387.83105  457.26364  49.4025
```

Entry 15 in Table A

Racemic(±)-Cyclohexymethylphenylphosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   3
Acq. Instrument : Kev HPLC 1                    Location : Vial 11
Injection Date  : 12/19/2009 12:54:02 PM             Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2009-12-19 12-39-51\ISO_96_04_15MIN_1MLMIN.M
Last changed    : 12/19/2009 12:53:52 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\RUN QUEUE 2009-12-19 12-39-51\011-0301.D\DA.M (ISO_96_04_
                  15MIN_1MLMIN.M)
Last changed    : 12/19/2009 3:45:55 PM by General sequence
Method Info     : Isocratic at 95/04 heptane/EtOH for 15min at 1ml/min

Sample Info     : ASH 96 4 pen ethan
```

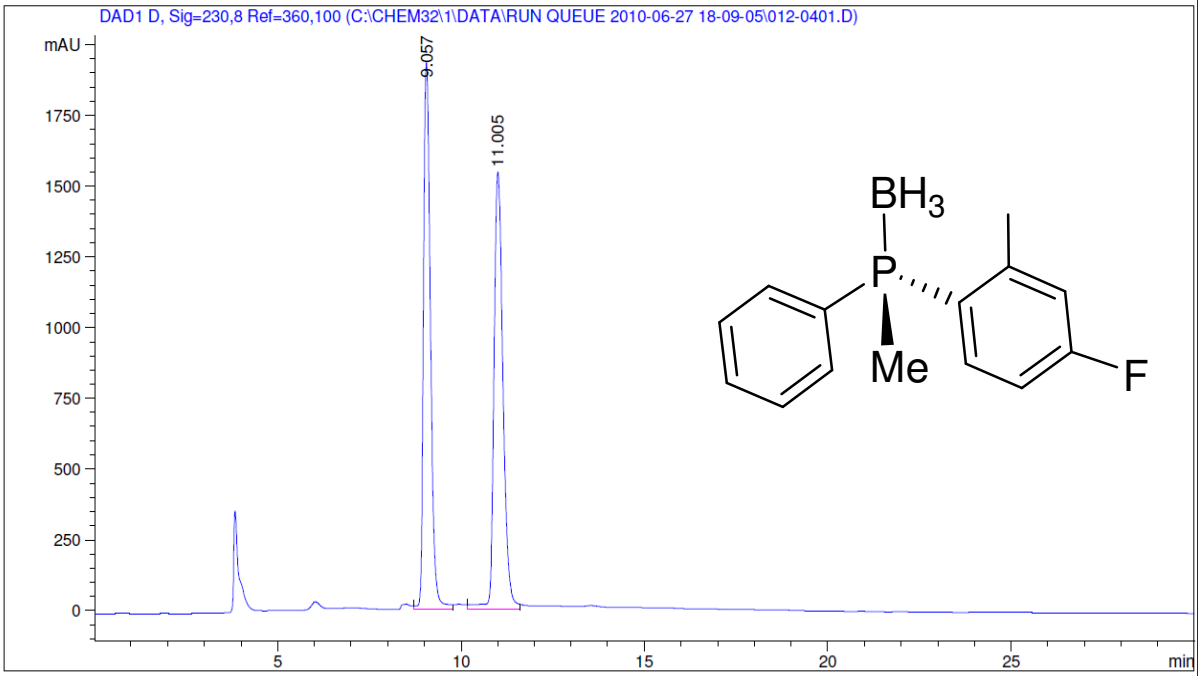



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.966 BV    0.1268 1.20409e4  1451.20239  49.6250
   2   7.851 VV    0.1819 1.22229e4  1049.30774  50.3750
```

Entry 13 in Table A

Racemic(±)-(4-Fluoro-2-methylphenyl)methylphenylphosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   4
Acq. Instrument : Kev HPLC 1                    Location : Vial 12
Injection Date  : 6/27/2010 7:23:21 PM               Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-06-27 18-09-05\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/27/2010 7:23:09 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\03_QUICKSTART 1 MLMIN METHODS\ISO_98_02_30MIN_1MLMIN.M
Last changed    : 6/23/2010 10:22:59 AM by General sequence
                  (modified after loading)
Method Info     : Isocratic at 98/02 heptane/EtOH for 30min at 1ml/min
```

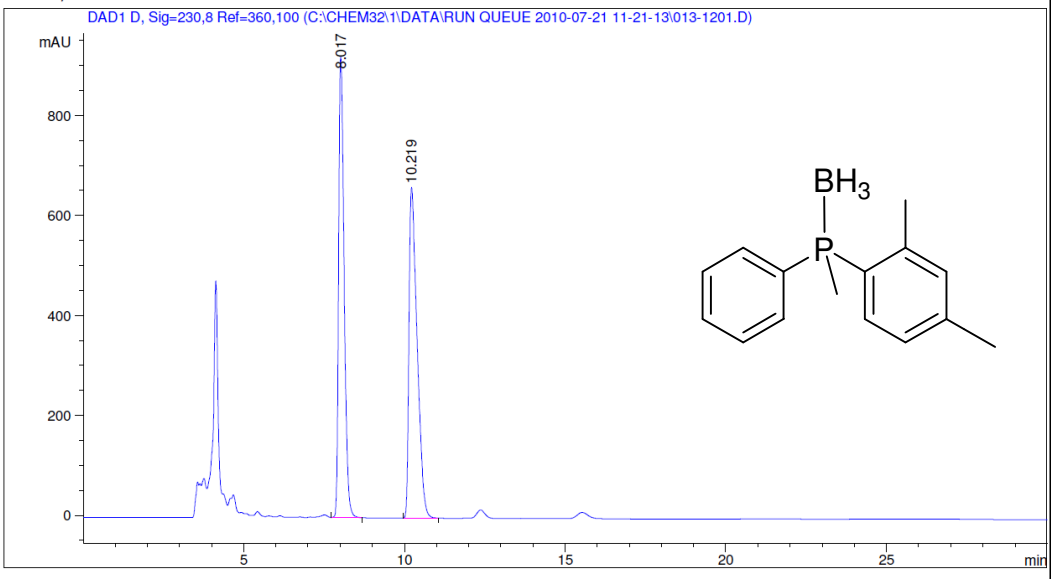



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.057 VB    0.2060 2.55190e4  1933.06165  49.0175
   2  11.005 VBA   0.2663 2.65420e4  1545.97217  50.9825
```

Entry 12 in Table A

Racemic(±)-(4-methyl-2-methylphenyl)methylphenylphosphine borane

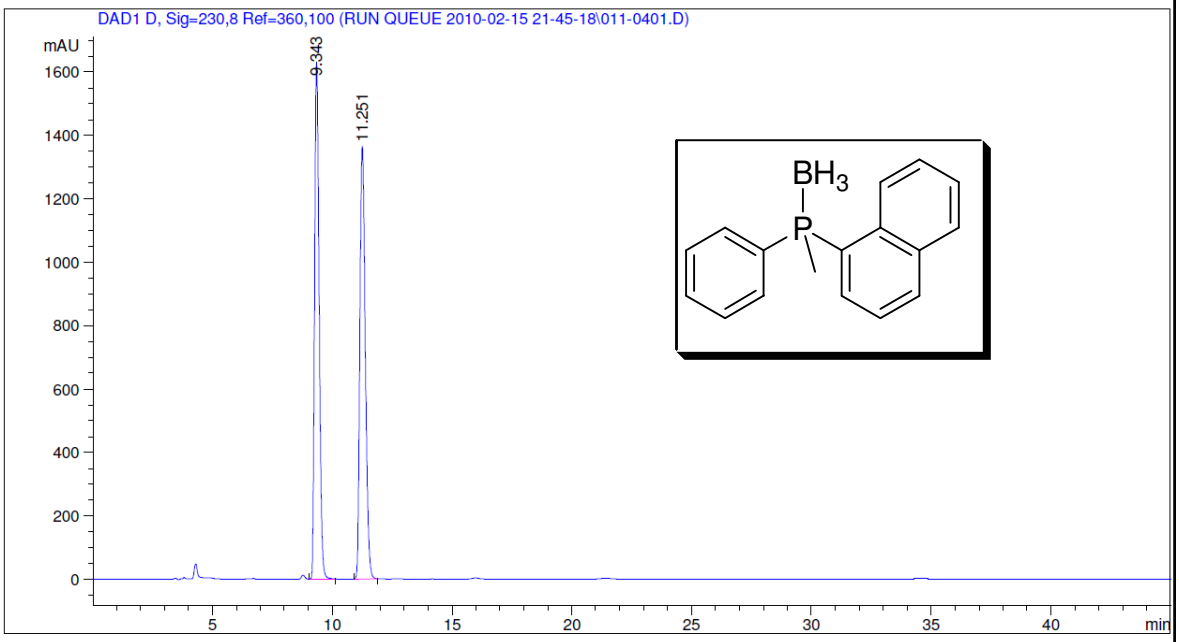
```
======================================================================
Acq. Operator   : General sequence              Seq. Line :  12
Acq. Instrument : Kev HPLC 1                    Location : Vial 13
Injection Date  : 7/21/2010 4:03:40 PM               Inj :   1
                                                Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-07-21 11-21-13\ISO_70_30_30MIN_1MLMIN.M
Last changed    : 7/21/2010 4:03:30 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\01_COLUMN METHODS\STABILISE_98_02_10MIN_1MLMIN.M
Last changed    : 7/5/2010 9:52:01 AM by General sequence
                  (modified after loading)
Method Info     : Stabilise column at 99/1 heptane/EtOH for 10min at 1ml/min

======================================================================

Instrument Conditions   :    At Start          At Stop
Column Temp. (left)     :      28.3             28.4   °C
Column Temp. (right)    :      29.3             29.4   °C
Pressure                :      70.1             71.1   bar
Flow                    :       1.000            1.000 ml/min
Valve 1 Position        :       5                5

Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
DAD 1, UV Lamp          :       4.88          1156.3   h
DAD 1, Visible Lamp     :      OFF              11.2   h

Solvent Description     :
PMP1 , Solvent A        : Heptane
PMP1 , Solvent B        : EtOH
```



Entry 11 in Table A

Racemic(±)-(±)-methyl-(1-naphthyl)phenylphosphine borane

```
======================================================================
Acq. Operator   : General sequence              Seq. Line :   4
Acq. Instrument : Kev HPLC 1                    Location : Vial 11
Injection Date  : 2/15/2010 10:40:38 PM              Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\Chem32\1\DATA\RUN QUEUE 2010-02-15 21-45-18\ISO_98_02_45MIN_1MLMIN.M
Last changed    : 2/15/2010 10:40:28 PM by General sequence
                  (modified after loading)
Analysis Method : C:\CHEM32\1\DATA\RUN QUEUE 2010-02-15 21-45-18\011-0401.D\DA.M (ISO_98_02_
                  45MIN_1MLMIN.M)
Last changed    : 2/16/2010 10:09:50 AM by General sequence
Method Info     : Isocratic at 98/02 heptane/EtOH for 45min at 1ml/min
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=230,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.343 VB    0.2055 2.14471e4  1630.19421  49.8742
   2  11.251 BB    0.2462 2.15553e4  1365.22644  50.1258
```

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