Supporting Information

Chemoselective Reduction of the Phosphoryl Bond of O-Alkyl Phosphinates and Related Compounds: An Apparently Impossible Transformation

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Contents

General Experimental

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 syste in electrospray ionization mode (ESI), also at UCD. The NMR spectra were recorded at 25 °C on Varian VNMRS 300, 400, 500 and 600 MHz spectrometers. 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 using 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. A number of 1H-NMR spectra contain an impurity peak at approximately δ = 0.07 ppm due to the presence of adventitious silicone grease transferred from the lubricated rubber septa.

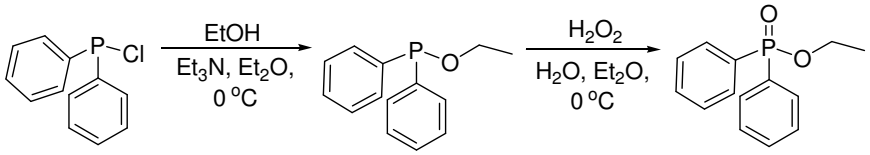
Unless otherwise stated, all reactions were carried out under a N_2 atmosphere in dry glassware using Schlenk-line techniques and all glassware was flame dried prior to use. Air and moisture sensitive liquids and solutions were transferred via syringe. All commercially available solvents were used as supplied unless otherwise stated. All "dry" solvents were dried and distilled by standard procedures or were processed through a Grubbs type still, a Pure Solv-400-3-MD solvent purification system supplied by Innovative Technology Inc. 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 60F254 aluminium plates with realization by UV irradiation or iodine staining. 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 prior to use. Prior to use sieves were heated to ~300 °C, using a heat gun, for 2 minutes while under vacuum in Schlenk-ware. They were allowed to cool to room temperature and this procedure was then repeated (x 3). All products were isolated as oils and so melting points were not obtained.

Synthesis of Materials

P-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine oxide

Compound was previously synthesised and characterised by us.[1]

O-Ethyl *P,P*-diphenylphosphinate



P-Chloro-*P*,*P*-diphenylphosphine (3.0 g, 2.4 mL, 12.7 mmol) was dissolved in diethyl ether (40 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to 0 ^{o}C in an ice-bath and triethylamine (2.13 mL, 15.2 mmol, 1.2 equiv.) was added, followed by ethanol (0.89 mL, 15.2 mmol, 1.2 equiv.). The flask was allowed to warm to room temperature and stirred for 3 hours.

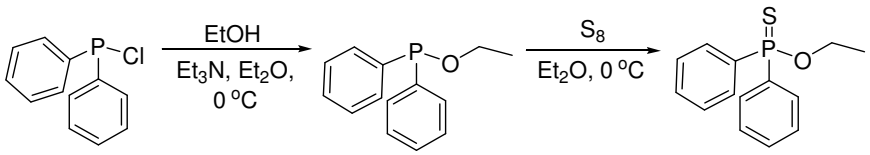
The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a 100 mL round bottomed flask. The flask was cooled to 0 ^{o}C in an ice-bath and de-ionized water (10 mL) was added followed by hydrogen peroxide (35% v/v in water, 1.52 mL, 15.2 mmol, 1.2 equiv.), added slowly to avoid an exotherm. After 30 minutes, the diethyl ether was removed by rotary evaporator (care being taken not to remove any water, as this could lead to concentrated peroxide). The product was extracted from the aqueous solution with DCM (2x20 mL). The organic layer was then washed with water (20 mL) to remove any residual peroxide and, following separation, dried over anhydrous $MgSO_4$ for 5 minutes. The DCM was finally removed *in vacuo* to produce a white solid. The yield was 2.35 g (75%).

^{1}H NMR shifts matched those in the literature [2]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94-7.73 (m, 4H, *o*-ArH)(lit.: 7.81-7.76), 7.58-7.36 (m, 6H, *m/p*-ArH)(lit.:7.48-7.37), 4.21-4.02 (m, 2H, OCH_2)(lit.: 4.11-4.03), 1.36 (t, $^{3}J_{HH}$ = 7 Hz, 3H, $OCCH_3$)(lit.: 1.32, $^{3}J_{HH}$ = 7.1 Hz); ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 31.1 ppm (lit.[2] 31.4).

_O_-Ethyl _P,P_-diphenylphosphinothioate



P-chloro-*P*,*P*-diphenylphosphine (3.0 g, 2.4 mL, 12.7 mmol) was dissolved in diethyl ether (40 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to 0 ^{o}C in an ice-bath and triethylamine (2.13 mL, 15.2 mmol, 1.2 equiv.) was added, followed by ethanol (0.89 mL, 15.2 mmol, 1.2 equiv.). The flask was allowed to warm to room temperature and stirred for 3 hours.

The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a 100 mL round bottomed flask. The flask was cooled to 0 ^{o}C in an ice-bath and elemental sulfur (2.17 g, 68 mmol, 5 equiv.) was added. The mixture was allowed to warm up to room temperature and stirred overnight.

The excess S_8 was removed by vacuum filtration through a Buchner funnel and the solvent was removed *in vacuo.* The product was purified by column chromatography with a silica stationary phase and eluent of cyclohexane/ethyl acetate 96:4. The pure product was a crystalline solid with a yield of 1.92 g (54%). Some loss of yield may have been due to air oxidation during manipulation of the sample.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92-7.82 (m, 2H, *o*-ArH), 7.49-7.35 (m, 3H, *m/p*-ArH), 4.09 (dq, $^{3}J_{PH}$ = 9 Hz, $^{3}J_{HH}$ = 7 Hz, 2H, OCH_2), 1.33 (t, $^{3}J_{HH}$ = 7 Hz, 3H, $OCCH_3$); ppm.

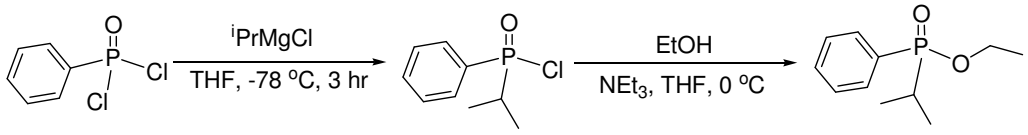
^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ =134.7, 131.8, 131.1, 128.4, 61.1, 16.3; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 81.0 ppm.

HRMS (ES+) $[M+ H]^+$ $C_{14}H_{16}OPS$ Found: 263.0659 Calculated: 263.0853

IR (cm^{-1}): 3058, 2980, 2896, 1480, 1439, 1389

_O_-ethyl _P_-phenyl-_P_-isopropylphosphinate



Phenylphosphinic dichloride (2.14 mL, 3.0 g, 15.4 mmol) was dissolved in dry THF (40 mL) in a dry 100 mL Schlenk round bottomed flask under an atmosphere of N_2. The flask was cooled to -78 °C in an acetone/liq. nitrogen bath and isopropyl magnesium chloride (2M in THF, 9.25 mL, 18.5 mmol, 1.2 equiv.) was added dropwise via syringe. The flask was allowed to warm to room temperature and stirred for 3 hrs. A ^{31}P-NMR of the intermediate at this point showed one major peak at 67 ppm. (Note: In contrast to the other procedures, the salt by-product is soluble in THF and so was not removed at this point.)

The flask was cooled to 0 °C in an ice-bath and dry ethanol (1.1 mL, 18.5 mmol, 1.2 equiv.) was added followed by dry triethylamine (2.6 mL, 18.5 mmol, 1.2 equiv.).The reaction was allowed to warm to room temperature and stirred overnight. In order to remove the triethylammonium chloride, the THF was removed *via* rotary evaporator and the product was dissolved in bench diethyl ether. The salt is insoluble, thereby precipitating and enabling isolation of the product by vacuum filtration. This action of removing the solvent

and re-dissolving in diethyl ether was repeated until most of the salt was judged to have been removed.

The product was purified by column chromatography with a silica stationary phase and eluent of cyclohexane/isopropanol in the ratio 94:6. The yield was 2.73 g (84%).

(Note: the isopropyl CH_3 groups appear as diastereotopic in both proton and carbon NMR)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74-7.63 (m, 2H, *o*-ArH), 7.51-7.34 (m, 3H, *m/p*-ArH), 4.10-3.93 (m, 1H, OCH_2), 3.87-3.73 (m, 1H, OCH_2), 1.97 (dsept, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, 1H, PCH), 1.23 (t, $^3J_{HH}$ = 7 Hz, 3H, $OCCH_3$), 1.10 (dd, $^3J_{PH}$ = 17 Hz, $^3J_{HH}$ = 7 Hz, 3H, $PCCH_3$), 0.98 (dd, $^3J_{PH}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, 3H, $PCCH_3$); ppm.

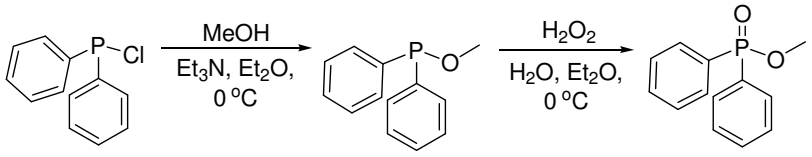
^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ =132.2, 132.0, 129.6, 128.4, 60.5, 28.3, 16.4, 15.5, 15.1; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 53.8 ppm.

HRMS (ES+) $[M]^+$ $C_{11}H_{17}O_2P$ Found: 212.0961 Calculated: 212.0966

IR (cm^{-1}): 2971, 2936, 1647, 1470, 1439, 1389, 1268

_O_-Methyl _P,P_-diphenylphosphinate



P-Chloro-*P*,*P*-diphenylphosphine (3.0 g, 2.4 mL, 12.7 mmol) was dissolved in diethyl ether (40 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to 0^{o}C in an ice-bath and triethylamine (2.13 mL, 15.2 mmol, 1.2 equiv.) was added, followed

by methanol (0.62 mL, 15.2 mmol, 1.2 equiv.). The flask was allowed to warm to room temperature and stirred for 3 hours.

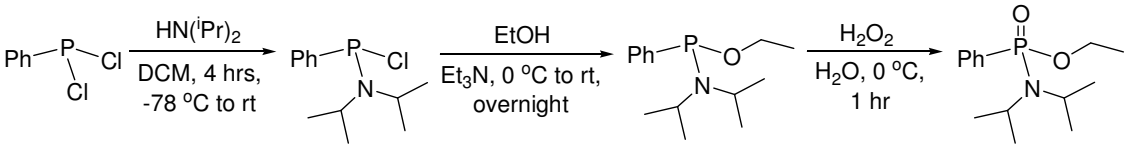
The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a 100 mL round bottomed flask. The flask was cooled to 0 ^{o}C in an ice-bath and de-ionized water (10 mL) was added followed by hydrogen peroxide (35% v/v in water, 1.52 mL, 15.2 mmol, 1.2 equiv.), added slowly to avoid an exotherm. After 30 minutes, the diethyl ether was removed by rotary evaporator (care being taken not to remove any water, as this could lead to concentrated peroxide). The product was extracted from the aqueous solution with DCM (2x20 mL). The organic layer was then washed with water (20 mL) to remove any residual peroxide and, following separation, dried over anhydrous $MgSO_4$ for 5 minutes. The DCM was finally removed *in vacuo* to produce a white solid.

^{1}H NMR shifts matched those in the literature[3]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97-7.24 (m, 10H, ArH)(lit.: 7.77-7.37), 3.74 (d, $^{3}J_{PH}$ = 10 Hz, 3H, OCH_3)(lit.: 3.70, $^{3}J_{PH}$ = 10.1 Hz); ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 33.0 ppm (lit.: 34.908).

_O_-Ethyl _N,N_-diisopropyl _P_-phenylphosphonamidate



P,P-dichloro-*P*-phenylphosphine (10.0 g, 7.6 mL, 0.056 mmol) was dissolved in dry DCM (80 mL) in a dry 250 mL Schlenk flask under an atmosphere of nitrogen. The flask was cooled to -78 ^{0}C in a liq. N_2/acetone bath. Diisopropylamine (17.1 g, 23.7 mL, 0.17 mmol, 3 equiv.) was added slowly and the reaction was stirred for 1 hr. The flask was removed form the cooling bath, allowed to gradually warm to room temperature and was continued to be stirred for a

further 3 hrs. A ^{31}P-NMR taken at this point showed one peak for the desired intermediate as the primary species present.

The Flask was cooled to 0 ^{o}C in an ice bath and triethylamine (20 g, 27.67 mL, 0.2 mmol, 3 equiv.) was added followed by ethanol (3.11 g, 3.95 mL, 0.068 mmol, 1.2 equiv.). The reaction was stirred and allowed to warm gradually to room temperature overnight.

To remove the ammonium salt by-products, deionised water (20 mL), which had been degassed thoroughly with nitrogen, was added to the flask, creating a biphasic mixture. The mixture was stirred vigorously for approx. 10 minutes. The water was removed *via* syringe with care being taken to leave the DCM in the flask. This procedure was repeated two further times.

Deionised water (20 mL) was added followed by hydrogen peroxide (35% v/v in H_2O, 4.5 mL, 0.045 mol, 1.3 equiv.) introduced slowly at 0 ^{o}C in an ice-bath. The reaction was stirred for 1 hr. The mixture was transferred to a separating funnel. The organic layer, DCM, was isolated and washed with water (20 mL) and sat. brine (20 mL). Remaining peroxides in the aqueous layer were quenched by the addition of sodium metabisulphite. The DCM solution was dried with $MgSO_4$, isolated by filtration and the solvent was removed *in vacuo* on a rotary evaporator. The final product was purified with column chromatography with an eluent of cyclohexane/ isopropanol (94:6). The yield was 9 g (63%).

(Note: the $NC(CH_3)$ protons and carbons appear as diastereotopic in NMR)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92-7.26 (m, 5H, ArH), 4.27-3.98 (m, 2H, OCH_2), 3.34 (dsept 2H, $^{3}J_{PH}$ = 18 Hz, $^{3}J_{HH}$ = 7 Hz, NCH), 1.38 (t, 3H, $^{3}J_{HH}$ = 7 Hz, $OCCH_3$), 1.29 (d, 6H, $^{3}J_{HH}$ = 7 Hz, $NC(CH_3)_2$), 1.13 (d, 6H, $^{3}J_{HH}$ = 7 Hz, $NC(CH_3)_2$); ppm.

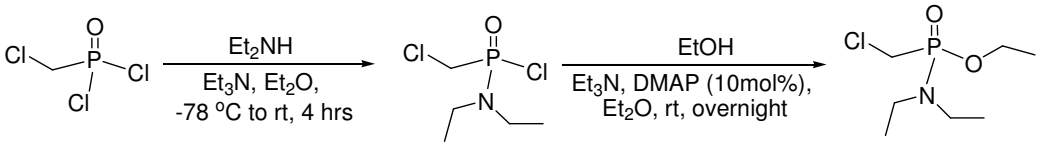
^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ = 133.3, 131.2, 130.8, 128.0, 59.4, 45.6, 23.3, 21.8, 16.3; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 21.3 ppm.

HRMS (ES+) $[M+ H]^{+}$ $C_{14}H_{25}NO_2P$ Found: 270.1623 Calculated: 270.1628

IR (cm^{-1}): 2969, 1405, 1264, 1157

***N,N*-Diethyl-*O*-ethyl-*P*-chloromethylphosphonamidate**



P-(Chloromethyl)phosphonic *P,P*-dichloride (3.0 g, 1.83 mL, 17.93 mmol) was dissolved in diethyl ether (50 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to -78 ^{o}C in an acetone/liq. nitrogen bath and triethylamine (3.8 mL, 26.9 mmol, 1.5 equiv.) was added, followed by diethylamine (1.85 mL, 17.93 mmol, 1.0 equiv.). After one hour the flask was allowed to warm to room temperature and was then stirred for a further 3 hours. A ^{31}P-NMR spectrum of the intermediate showed one major peak at δ = 35.1 ppm (97% conversion by integration).

The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a second dry 100 mL Schlenk flask under a N_2 atmosphere. A second portion of triethylamine (10.0 mL, 70.8 mmol, 4 equiv.) was added followed by dry ethanol (5 mL, 85 mmol, 4.85 equiv.) and 4-dimethylaminopyridine (0.22 g, 1.8 mmol, 10 mol%). The reaction was stirred overnight at room temperature.

The salt by-product was removed by cannula filtration with the solution entering a 100 mL round bottomed flask. The solvent, ether, was removed *in vacuo*. The product was purified by column chromatography with a silica stationary phase and an eluent of cyclohexane/isopropanol in the ratio 94:6. The yield was 2.15 g (52%). (Loss of yield was caused by a side-product, likely formed through double addition to the phosphorus precursor, having a similar R_f to the desired product.)

(Note: the OCH_2 protons appear as diastereotopic in ^{1}H-NMR)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.25-4.08 (m, 1H, OCH_2), 4.07-3.92 (m, 1H, OCH_2), 3.59-3.46 (m, 2H, PCH_2Cl), 3.23-3.09 (m, 4H, NCH_2), 1.39-1.30 (m, 3H, $OCCH_3$), 1.21-1.10 (m, 6H, $NCCH_3$); ppm.

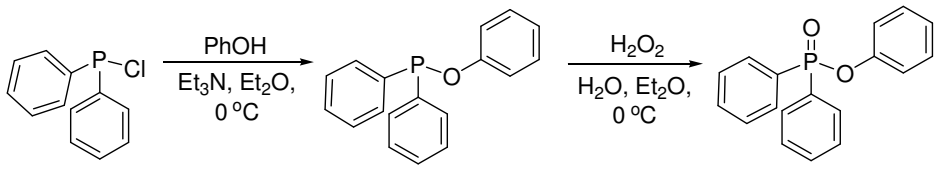
^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ =60.4, 38.8, 34.8, 16.1, 14.1; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 23.8 ppm.

HRMS (ES+) $[M+ Na]^+$ $C_7H_{17}NO_2NaPCl$ Found: 236.0589 Calculated: 236.0583

IR (cm^{-1}): 2976, 2938, 1466, 1384, 1248

_O_-Phenyl _P,P_-diphenylphosphinate



_P_-Chloro-_P_,_P_-diphenylphosphine (3.0 g, 2.4 mL, 12.7 mmol) was dissolved in diethyl ether (40 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to 0 ^{o}C in an ice-bath and triethylamine (2.13 mL, 15.2 mmol, 1.2 equiv.) was added, followed by phenol (1.43 g, 15.2 mmol, 1.2 equiv.). The flask was allowed to warm to room temperature and stirred for 3 hours.

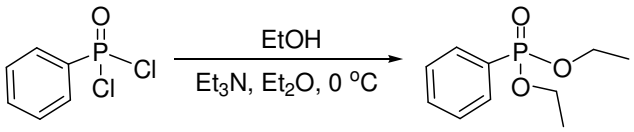
The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a 100 mL round bottomed flask. The flask was cooled to 0 ^{o}C in an ice-bath and de-ionized water (10 mL) was added followed by hydrogen peroxide (35% v/v in water, 1.52 mL, 15.2 mmol, 1.2 equiv.), added slowly to avoid an exotherm. After 30 minutes, the diethyl ether was removed by rotary evaporator (care being taken not to remove any water, as this could lead to concentrated peroxide). The product was extracted from the aqueous solution with DCM (2x20 mL). The organic layer was then washed with water (20 mL) to remove any residual peroxide and, following separation, dried over anhydrous $MgSO_4$ for 5 minutes. The DCM was finally removed _in vacuo_ to produce a white solid. The yield was 3.36 g (90%).

^{1}H NMR shifts matched those in the literature[4]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.21-6.97 (m, 15H, ArH)(lit.: 7.87-7.05); ppm

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 30.0 ppm (lit.: 31.4 ppm).

_O,O_-Diethyl _P_-phenylphosphonate



_P_-Phenylphosphonic P,P-dichloride (3.0 g, 2.14 mL, 15.4 mmol) was dissolved in dry diethyl ether (70 mL) in a dry 100 mL Schlenk flask under an atmosphere of N_2. The flask was cooled to 0 ^{o}C in an ice-bath and triethylamine (5.38 mL, 38.5 mmol, 2.5 equiv.) was added, followed by ethanol (2.69 mL, 46.2 mmol, 3 equiv.). The flask was allowed to warm to room temperature and stirred overnight.

The insoluble salt by-product, triethylammonium chloride, was removed by cannula filtering the solution into a 100 mL round bottomed flask. The solvent was removed *in vacuo*. The resulting yellow oil was dissolved in DCM (30 mL) and extracted with water (2x30 mL) to yield a clear oil which was pure by NMR analysis with a yield of 3.2 g (97%).

^{1}H NMR shifts matched those in the literature[5]

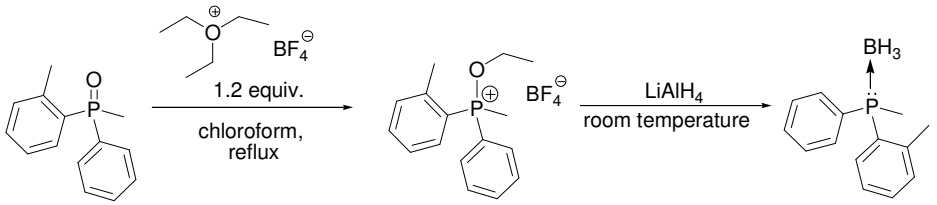
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87-7.77 (m, 2H, *o*-ArH)(lit.: 7.84-7.78), 7.58-7.41 (m, 3H, *m/p*-ArH)(lit.:7.57-7.43), 4.22-4.02 (m, 4H, OCH_2)(lit.: 4.18-4.04), 1.32 (t, $^{3}J_{HH}$ = 7 Hz, 6H, $OCCH_3$)(lit.: 1.32, $^{3}J_{HH}$ = 7.14 Hz); ppm.

^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ =132.3, 131.7, 128.41, 128.38, 62.0, 16.3; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 18.7 ppm (lit.: 18.9).

Reduction of Phosphine, Phosphinate, Phosphinothioate and Phosphonamidate

P-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine borane



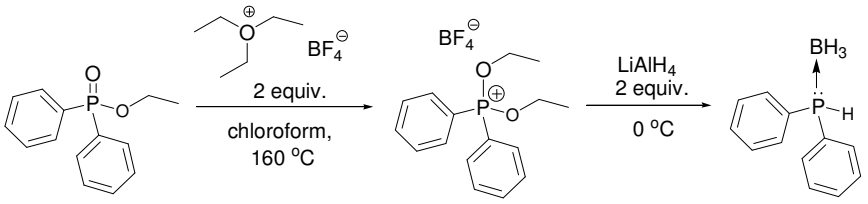
93% ee (*S*)
Ar = *ortho*-tolyl

93% ee (*S*)
90% yield

Dry *P*-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine oxide (0.23 g, 1.0 mmol, 93% ee with *S* config.) was dissolved in dry chloroform (2 mL) in a dry 10 mL Schlenk flask under an atmosphere of nitrogen. Triethyloxonium tetrafluoroborate (0.22 g, 1.2 mmol, 1.2 equiv.) was added, the flask was closed and the mixture was heated to reflux for 2 hours. The mixture was then allowed to cool to room temperature. ^{31}P-NMR spectroscopy at this point shows one peak, corresponding to the phosphonium tetrafluoroborate salt, at δ = 71 ppm. Lithium aluminium hydride (1 M in THF, 1.0 mL, 1.0 mmol, 1 equiv.) was added the reaction was left to stir overnight. Following this any excess $LiAlH_4$ was carefully quenched with water (10 mL) and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to yield pure *P*-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine borane (.21 g, 91%; 93% ee (*S*)).

Product was previously synthesised and characterised by us.[6]

***P,P*-diphenylphosphine borane**



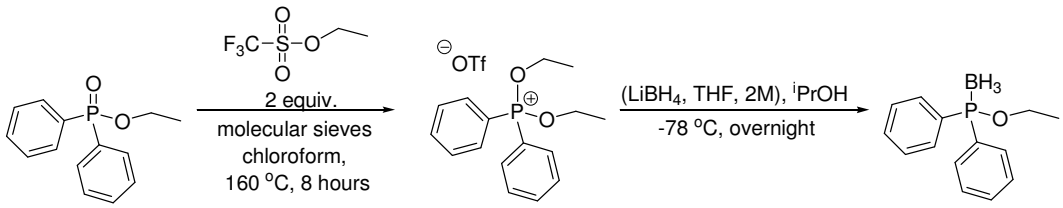
Dry ethyl diphenylphosphinate (0.246 g, 1.0 mmol) was dissolved in dry chloroform (2 mL) in a dry 10 mL Young's tube under an atmosphere of nitrogen. Triethyloxonium tetrafluoroborate (0.38 g, 2 mmol, 2 equiv.) was added, the flask was screwed tightly closed and flask was submerged in an oil-bath only up to the level of the solvent. The mixture was heated to 160 ^{o}C for 5 hours. The mixture was then allowed to cool to room temperature. ^{31}P-NMR spectroscopy at this point shows one peak, corresponding to the phosphonium tetrafluoroborate salt intermediate, at δ = 40.3 ppm.

The flask was cooled to 0 ^{o}C in an ice-bath and lithium aluminium hydride (1 M in THF, 2.0 mL, 2.0 mmol, 2 equiv.) was added. The reaction was left to stir overnight. Following this any excess $LiAlH_4$ was carefully quenched with water (10 mL) and the aqueous layer was extracted with DCM (3 x 10 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* to yield pure *P,P*-diphenylphosphine borane (.17 g, 84%).

NMR analysis matched that in the literature[7]

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90-7.38 (m, 10H, ArH), 6.30 (dq, $^{1}J_{PH}$ = 379 Hz, $^{3}J_{HH}$ = 7 Hz, 1H, PH), 1.54-0.52 (br, 3H, BH_3); ppm.

***O*-Ethyl *P,P*-diphenylphosphinite borane** (initial conditions)



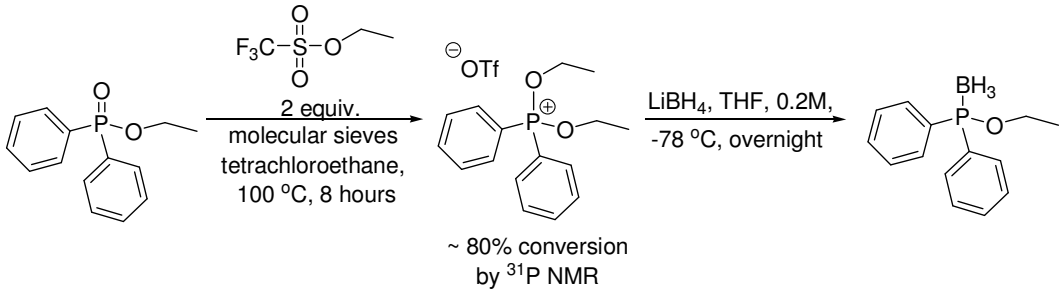
Dry ethyl diphenylphosphinate (400 mg, 1.64 mmol) was dissolved in dry chloroform (4.0 mL) in a dry 100 mL Schlenk tube that contained 4 Å molecular sieves (3.6 g), activated by flame drying for approximately one minute followed by being placed under high vacuum for ca. 30 minutes. Dry ethyl triflate (0.44 mL, 3.39 mmol, 2 equiv.), stored in a Young's flask, was added and tube was closed tight under an atmosphere of N_2. (Note: ethyl triflate is potentially highly toxic and care should be taken to always handle it in a fumehood and to quench any residue carefully using an aqueous solution of sodium hydroxide). The flask was placed in an oil-bath such that the level of the solvent in the tube matched the level of the oil, i.e. only the very bottom of the flask was submerged. This portion of the flask was heated to 160 ^{o}C for 8 hours. A Perspex blast shield was placed in forward of the whole apparatus as a protective measure against sudden, and potentially explosion, shattering of the glass, while under pressure.

Following this the flask was allowed to cool to room temperature (as a precaution the tube was opened slowly while wearing a thick oven-glove). A ^{31}P-NMR showed one major peak, for the dialkoxyphosphonium salt, at δ = 55.7 ppm, with the remainder as starting phosphinate. (Note: the peak for the phosphinate can often be broadened to the point of being nearly indistinguishable from the base-line.)

Lithium borohydride (2.0 M in THF, 1.92 mL, 3.84 mmol, 2.5 equiv.) was placed in a dry 100 mL Schlenk flask, followed by the additional of isopropanol (17.3 mL). The flask was cooled to -78 ^{o}C with acetone/liq. N_2 and the DiAPS solution was added slowly, via syringe leaving the molecular sieves behind. The reaction of lithium borohydride with the excess ethyl triflate can be quite exothermic, so it is important to add the DiAPS solution slowly. The Young's tube, in which the alkylation reaction took place, was washed out with dry isopropanol (2x1 mL) with the washings added to the reduction reaction.

The reaction was allowed to warm up slowly overnight. Note: a gradual warm up to room temperature aids conversion to product. The product had a conversion of 80% as measured by ^{31}P-NMR, relative to the starting phosphinate. (the mass balance was made up almost exclusively by unreacted starting phosphinate)

***O*-Ethyl *P,P*-diphenylphosphinite borane** (final optimised conditions)



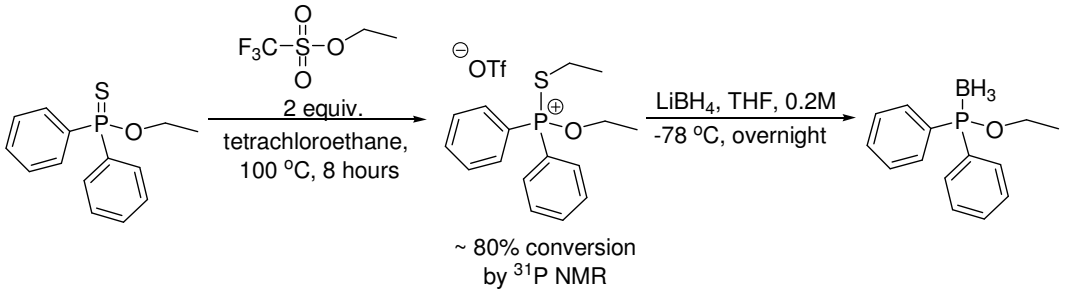
Exemplar A: Dry ethyl diphenylphosphinate (400 mg, 1.64 mmol) was dissolved in dry tetrachloroethane (4.0 mL) in a dry 100 mL Schlenk tube that contained activated molecular sieves (3.6 g). Dry ethyl triflate (0.44 mL, 3.39 mmol, 2 equiv.), taken from a Young's flask, was added and tube was closed tight under an atmosphere of N_2. (Note: ethyl triflate is potentially highly toxic and care should be taken to always handle it in a fumehood and to quench it carefully using an aqueous solution of sodium hydroxide). The flask was placed in an oil-bath such that the level of the solvent in the tube matched the level of the oil, i.e. only the very bottom of the flask was submerged. This portion of the flask was heated to 100 °C for 8 hours. This time period is quite strict with any deviation in either direction leading to a lowering of the conversion.

Following this the flask was allowed to cool to room temperature. A ^{31}P-NMR showed one major peak, for the dialkoxyphosphonium salt, at δ = 55.7 ppm, with the remainder as starting phosphinate. (Note: the peak for the phosphinate can often be broadened to the point of being nearly indistinguishable from the base-line.)

Lithium borohydride (2.0 M in THF, 1.92 mL, 3.84 mmol, 2.5 equiv.) was placed in a dry 100 mL Schlenk flask and diluted down to 0.2 M with dry THF (17.3 mL). The flask was cooled to

-78 ^{o}C with acetone/liq. N_2 and the DiAPS solution was added slowly, *via* syringe leaving the molecular sieves behind. The reaction of lithium borohydride with the excess ethyl triflate can be quite exothermic, so it is important to add the DiAPS solution slowly. The Young's tube, in which the alkylation reaction took place, was washed out with dry THF (2x1 mL) with the washings added to the reduction reaction.

The reaction was allowed to warm up slowly overnight. Note: a gradual warm up to room temperature aids conversion to product. The product was purified with a short plug of silica with an eluent of cyclohexane/ethyl acetate 90:10, with a yield of 0.29 g (73%).



An identical procedure was followed with ethyl diphenylthiophosphinate (400 mg, 1.53 mmol) as the starting material with a yield of ethyl diphenylphosphinite borane of 0.27 g (72%). The same product was obtained as with ethyl diphenylphosphinate, namely ethyl diphenylphosphinite. The mass balance was not the starting material, as ordinarily observed, but the rearranged starting material, whereby the ethyl group has migrated to the sulfur, forming a P=O bond.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78-7.68 (m, 4H, *o*-ArH), 7.51-7.37 (m, 6H, *m/p*-ArH), 4.06 (dq, $^{3}J_{HH}$ = 7 Hz, $^{3}J_{PH}$ =8 Hz, 2H, OCH_2), 1.32 (t, $^{3}J_{HH}$ = 7 Hz, 3H, $OCCH_3$), 1.54-0.52 (m, 3H, BH_3); ppm.

^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ =132.4, 131.8, 131.2, 128.6, 63.6, 16.7; ppm.

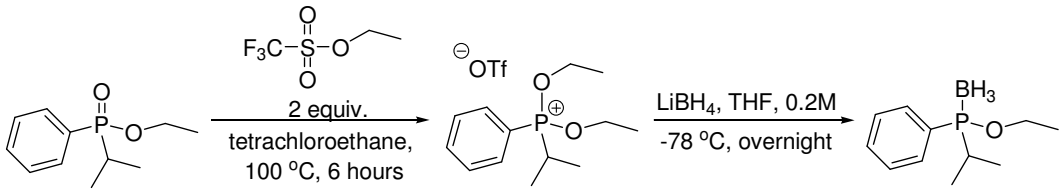
^{31}P NMR ($CDCl_3$, 162 MHz): δ = 103.7 (br) ppm.

^{11}B NMR ($CDCl_3$, 128 MHz): δ = -40.4 (d, $^{1}J_{PB}$ = 67 Hz, 1B, BH_3) ppm.

HRMS (ES+) $[M - BH_3 + H]^+$ $C_{14}H_{16}OP$ Found: 231.0947 Calculated: 231.0939

IR (cm^{-1}): 2980, 2386 (P-B), 1438

_O_-Ethyl _P_-phenyl-_P_-isopropylphosphinite borane



>99% conversion
by ^{31}P NMR

Exemplar A was applied to dry *O*-ethyl *P,P*-phenylisopropylphosphinate (400 mg, 1.88 mmol), with the alteration that the first step, alkylation, was run for 6 hours. Following this, a ^{31}P-NMR showed one peak, for the dialkoxyphosphonium salt, at δ = 75.7 ppm. ^{31}P-NMR analysis with 1024 scans, which affords a very good signal to noise ratio, showed no remaining phosphinate starting material, i.e. >99% conversion.
Following reduction, the desired product was purified with a short plug of silica with an eluent of cyclohexane/ethyl acetate 90:10, with a yield of 0.32g (80%).

(Note: the isopropyl CH_3 groups appear as diastereotopic in both ^1H and ^{13}C NMR)
^1H NMR ($CDCl_3$, 400 MHz): δ = 7.76-7.68 (m, 2H, *o*-ArH), 7.55-7.43 (m, 3H, *m/p*-ArH), 4.09-3.98 (m, 1H, OCH_2), 3.91-3.79 (m, 1H, OCH_2), 2.11 (dsept, $^2J_{PH}$ = 12 Hz, $^3J_{HH}$ = 7 Hz, 1H, PCH_1), 1.28 (t, $^3J_{HH}$ = 7 Hz, 3H, $OCCH_3$), 1.16 (dd, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 3H, $PCCH_3$), 1.00 (dd, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 3H, $PCCH_3$), 1.11-0.20 (m, 3H, BH_3); ppm.

^{13}C NMR {^1H, ^{31}P} ($CDCl_3$, 101 MHz): δ =131.6, 131.2, 130.7, 128.4, 63.5, 29.3, 16.6, 15.7, 15.4; ppm.

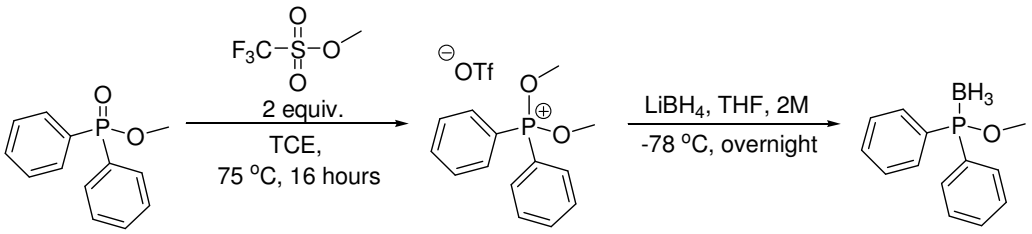
^{31}P NMR ($CDCl_3$, 162 MHz): δ = 119.3 ppm.

^{11}B NMR ($CDCl_3$, 128 MHz): δ = -43.5 (d, $^{1}J_{PB}$ = 67 Hz, 1B, BH_3) ppm.

HRMS (ES+) $[M+ H -BH_3]^+$ $C_{11}H_{18}OP$ Found: 197.1095 Calculated: 197.1095

IR (cm^{-1}): 2978, 2384 (P-B), 1438

_O_-Methyl _P,P_-diphenylphosphinite borane



Exemplar A was applied to dry *O*-methyl *P,P*-diphenylphosphinate (400 mg, 1.85 mmol), with the alteration that the first step, alkylation, was run for 16 hours at 75 °C. Following this, a ^{31}P-NMR showed one peak, for the dialkoxyphosphonium salt, at δ = 60.6 ppm. Following reduction, the desired product was purified with a short plug of silica with an eluent of cyclohexane/ethyl acetate 90:10, with a yield of 0.24g (60%).

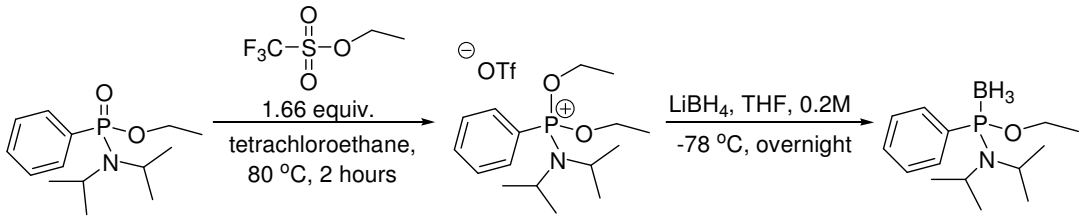
NMR data matched that in the literature[8]
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79-7.68 (m, 4H, *o*-ArH) (lit.: 7.84-7.71), 7.55-7.41 (m, 6H, *m*/*p*-ArH) (lit.: 7.62-7.44), 3.74 (d, $^{3}J_{PH}$ = 12 Hz, 3H, OCH_3) (lit.: 3.78, $^{3}J_{PH}$ = 12Hz), 1.51-0.49 (m, 3H, BH_3) (lit.: 1.90-0.20); ppm.

^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ = 131.9, 131.6, 131.3, 128.6, 54.0; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 107.4 (br) (lit.: 109.0) ppm.

^{11}B NMR ($CDCl_3$, 128 MHz): δ = -40.9 (d, $^{1}J_{PB}$ = 67 Hz, 1B, BH_3) ppm.

***O*-Ethyl N,N-diisopropyl *P*-phenylphosphonamidite borane**



Exemplar A was applied to dry *O*-Ethyl N,N-diisopropyl *P*-phenylphosphonamidite borane (400 mg, 1.49 mmol), with the alterations that the first step, alkylation, was run at 80 °C for 2 hours with ethyl triflate (0.33 mL, 2.47 mmol, 1.66 equiv.). Following this, a ^{31}P-NMR showed one major peak, for the dialkoxyphosphonium salt, with 87% conversion, with the remainder as starting phosphinate.

Following reduction, the desired product was purified with a short plug of silica with an eluent of cyclohexane/ethyl acetate 90:10, with a yield of 0.2 g (50%).

(Note: the NC(CH_3) protons and carbons appear as diastereotopic in NMR)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77-7.36 (m, 5H, ArH), 4.27-4.15 (m, 1H, OCH_2), 4.10-3.99 (m, 1H, OCH_2), 3.59 (dsept, 2H, $^3J_{PH}$ = 15 Hz, $^3J_{HH}$ = 7 Hz, NCH), 1.40 (t, 3H, $^3J_{HH}$ = 7 Hz, $OCCH_3$), 1.22 (d, 6H, $^3J_{HH}$ = 7 Hz, $NC(CH_3)_2$), 1.18 (d, 6H, $^3J_{HH}$ = 7 Hz, $NC(CH_3)_2$), 0.86 (br, q, 3H, BH_3); ppm.

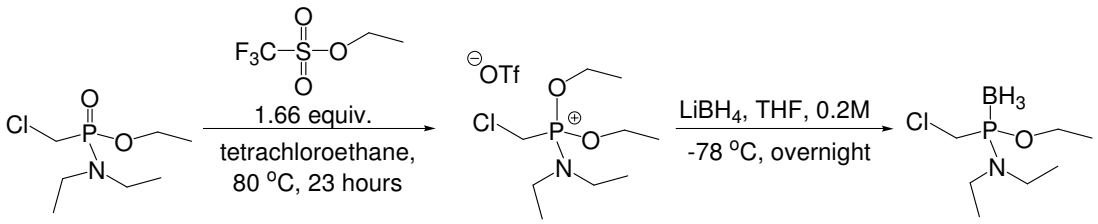
^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ = 134.7, 130.9, 130.6, 128.1, 61.6, 47.8, 23.5, 22.8, 16.5; ppm.

^{31}P NMR ($CDCl_3$, 162 MHz): δ = 105.7 (br, q) ppm.

^{11}B NMR ($CDCl_3$, 128 MHz): δ = -36.9 (d, $^1J_{PB}$ = 77 Hz, 1B, BH_3) ppm.

IR (cm^{-1}): 2969, 2385 (P-B), 1643

***N,N*-Diethyl-*O*-ethyl-*P*-chloromethylphosphonamidite borane**



Exemplar A was applied to dry *N,N*-diethyl-*O*-ethyl-*P*-chloromethylphosphonamidate (400 mg, 1.88 mmol), with the alterations that the first step, alkylation, was run at 80 ^{o}C for 23 hours with ethyl triflate (0.42 mL, 3.12 mmol, 1.66 equiv.). Following this, a ^{31}P-NMR showed one major peak, for the dialkoxyphosphonium salt, at δ = 42.0 ppm, with 58% conversion, with the remainder as starting phosphinate.

Following reduction, the desired product was purified with a short plug of silica with an eluent of cyclohexane/ethyl acetate 90:10, with a yield of 0.13g (32%)

(Note: the OCH_2 protons appear as diastereotopic in the proton NMR)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.08-3.93 (m, 1H, OCH_2), 3.92-3.78 (m, 1H, OCH_2), 3.58-3.49 (m, 2H, PCH_2Cl), 3.25-3.07 (m, 4H, NCH_2), 1.27 (t, $^{3}J_{HH}$ = 8 Hz, 3H, $OCCH_3$), 1.13 (t, $^{3}J_{HH}$ = 7 Hz, 6H, $NCCH_3$), 1.04-0.12 (m, 3H, BH_3); ppm.

^{13}C NMR {^{1}H, ^{31}P} ($CDCl_3$, 101 MHz): δ = 62.0, 39.4, 36.7, 16.4, 14.3; ppm.

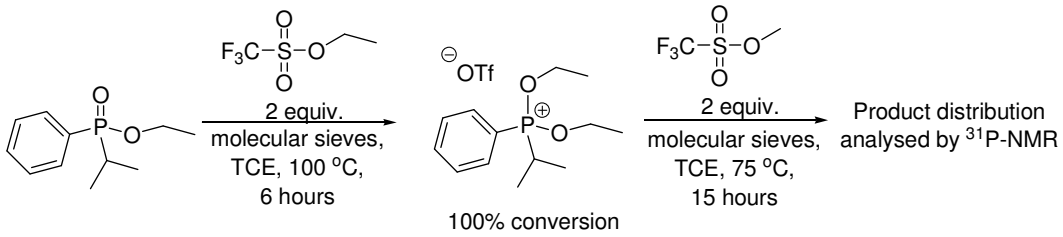
^{31}P NMR ($CDCl_3$, 162 MHz): δ = 115.4 ppm.

^{11}B NMR ($CDCl_3$, 128 MHz): δ = -42.5 (d, $^{1}J_{PB}$ = 78 Hz, 1B, BH_3) ppm.

HRMS (ES+) $[M\text{-}BH_3+ H]^+$ $C_7H_{18}NOPCl$ Found: 198.0819 Calculated: 198.0815

IR (cm^{-1}): 2981, 2393 (P-B), 1453, 1383

Reversibility of the Alkylation Reaction

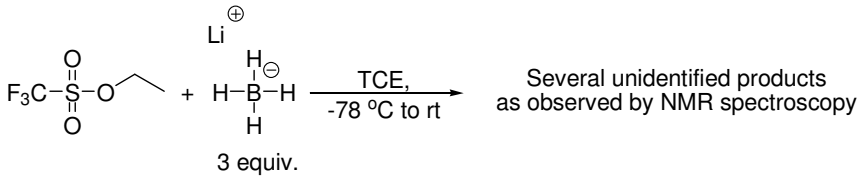


O-Ethyl *P*-phenyl-*P*-isopropylphosphinate (200 mg, 0.94 mmol) was reacted with ethyl triflate (0.24 ml, 1.88 mmol, 2.0 equiv.) according to exemplar A. To the resulting DiAPS solution was added methyl triflate (0.21 mL, 1.88 mmol, 2.0 equiv.) and the reaction was heated to 75 °C for 15 hours.

A ^{31}P-NMR spectrum of the reaction mixture showed three products at δ = 75.9, 78.2 and 80.5 ppm. This experiment proves that the alkylation of *O*-ethyl *P*-phenyl-*P*-isopropylphosphinate with ethyl triflate is a reversible process.

Investigations of Side Reactions occurring during Reduction Reaction

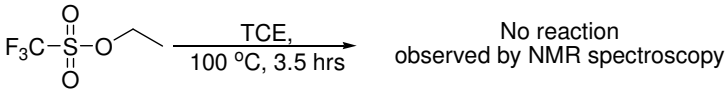
Reaction of ethyl triflate with lithium borohydride



Ethyl triflate (75 mg, 0.05 mL, 0.421 mmol) was dissolved in dry tetrachloroethane (0.4 mL) in a dry 100 mL Young's tube. The flask was cooled to -78 ^{o}C in a dry ice/acetone bath and lithium borohydride (2.0 M in THF, 0.63 mL, 1.26 mmol, 3 equiv.) was added via syringe. The reaction was stirred for one hour before being removed from the bath and allowed to warm to room temperature. The reaction was them stirred for a further 2.5 hours.

A ^{11}B-NMR spectrum of the mixture showed four products at δ = -42.9, -26.5, -1.4 and 18.5 ppm. The products were not identified.

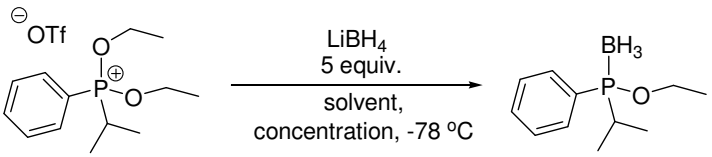
Heating of ethyl triflate in tetrachloroethane



Ethyl triflate (75 mg, 0.05 mL, 0.421 mmol) was dissolved in dry tetrachloroethane (0.4 mL) in a dry 100 mL Young's tube. The flask was heated to 100 ^{o}C for 3.5 hours. The reaction was allowed to cool to room temperature and a ^{19}F-NMR spectrum of the reaction showed that no reaction had taken place. The ^{19}F NMR shift of ethyl triflate is δ = -75 ppm.

Solvent study of $LiBH_4$ reaction

Effect of concentration of the reductant and solvent[a] on conversion to phosphinite borane from phosphinate with $LiBH_4$[b]



Solvent[c]	Concentration (M) [d]	Conversion to PB (%)[e]
MeOH	0.5	29
EtOH	0.5	42
IPA	0.5	73
IPA	0.2	51[f]
THF	2	0
THF	0.5	46
THF	0.2	80
THF	0.1	80
Et_2O	0.2	14[g]
MeCN	0.2	36
Et_3N	20 equiv.[h] in THF	0

[a] all solvents accompanied by THF, as originating from $LiBH_4$ solution (2.5 mL) [b] 5 equiv. of $LiBH_4$ were used in each case [c] solvents were thoroughly dried before use [d] values are the absolute concentration of the $LiBH_4$ in mixed solvent, or neat THF, prior to the addition of DiAPS [e] as measured by ^{31}P-NMR with 3 second relaxation delay, from starting phosphinate [f] conversion to phosphinate is lower, but conversion to phosphinite borane desired product is also lowered due to emergence of sec-phosphine borane side-product [g] $LiBH_4$ was dissolved in neat diethyl ether, no THF [h] 20 equiv. relative to phosphinate.

From the table above it is clear that there is both a strong concentration and a solvent effect in operation in the reduction reaction.

Employing non-sterically hindered alcohols, methanol and ethanol, as the solvent is detrimental to the yield, likely through a side reaction of the alcohol with the reductant. Isopropanol as previously stated is a good solvent, with 73% conversion at 0.5 M. Surprisingly, given later results, lowering the concentration further to 0.2 M also lowers the conversion, due to the emergence of a side-product, the secondary phosphine borane *P*-phenyl-*P*-isopropylphosphine borane. The exact cause of this side reaction is not known. Tetrahydrofuran is also a good solvent with the yield now inversely proportional to the concentration, ranging from 0% at 2 M to 80% at 0.2 M. The mass balance is made up by the reformed starting phosphinate. This concentration effect eventually ceases, as decreasing the concentration further, e.g. from 0.2 to 0.1 M, carries no benefit. Diethyl ether and acetonitrile are not good solvents to employ, possibly due to the low polarity of the former and the nitrogen of the latter becoming alkylated instead of the phosphoryl bond. Triethylamine completely disrupts the reaction, again probably due to transfer of the alkyl group from the phosphonium salt to the amine nitrogen.

HPLC chromatographs and NMR spectra of starting materials and products

CSP-HPLC chromatographs of racemic *P*-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine oxide and borane

```
==================================================================
Acq. Operator   : General sequence              Seq. Line :   4
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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
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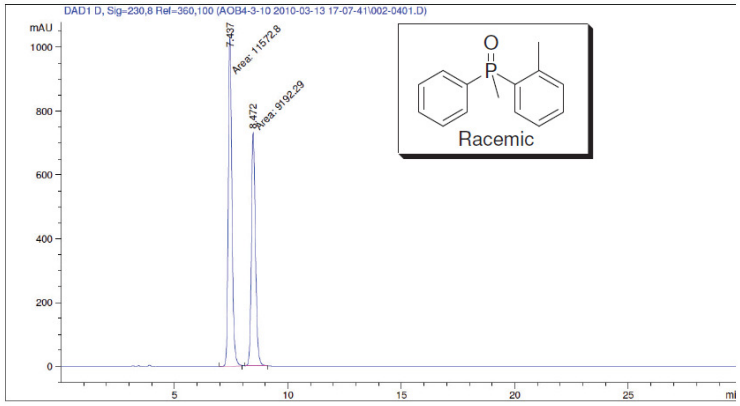


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==================================================================

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
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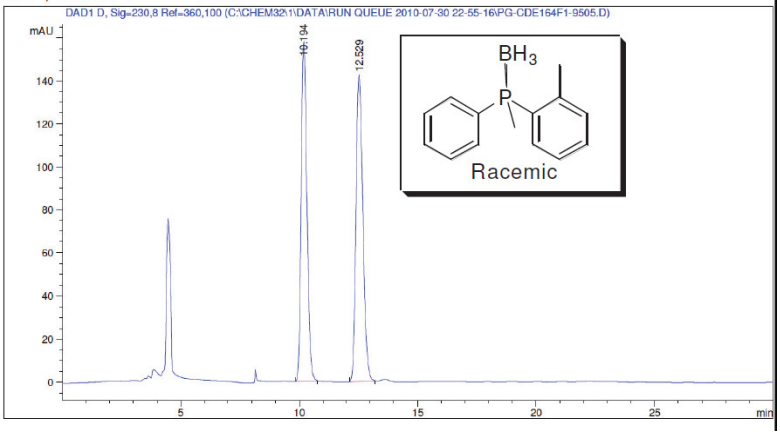

CSP-HPLC chromatograph of *P*-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine oxide with 93% ee (*S*)

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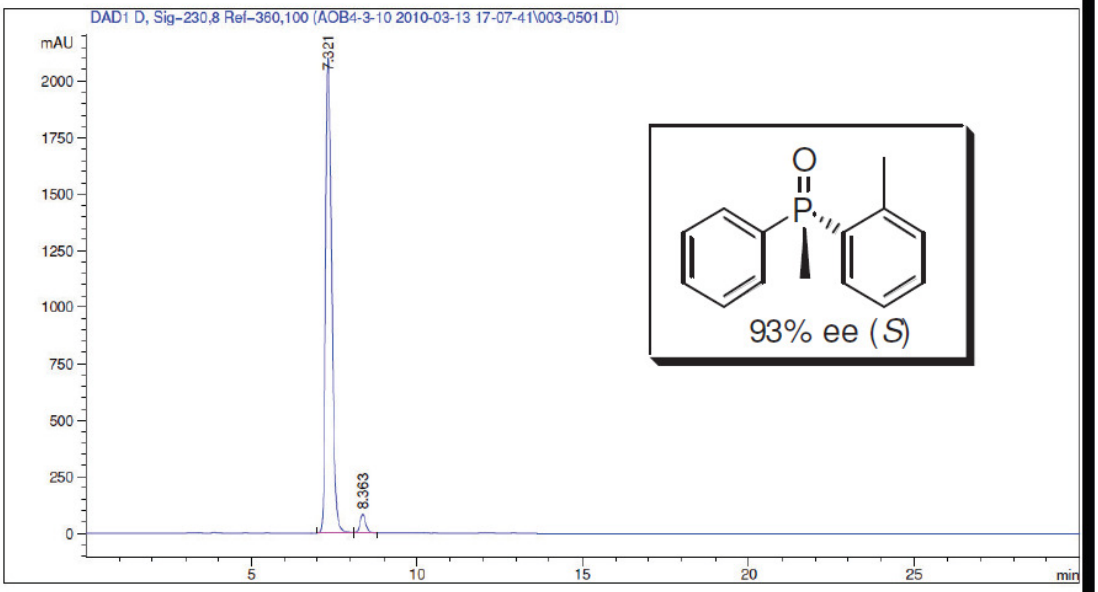


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================================================================
                      Area Percent Report
================================================================

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
```

CSP-HPLC chromatograph of *P*-methyl-*P*-phenyl-*P*-(*ortho*-tolyl)phosphine borane with 93% ee (*S*)

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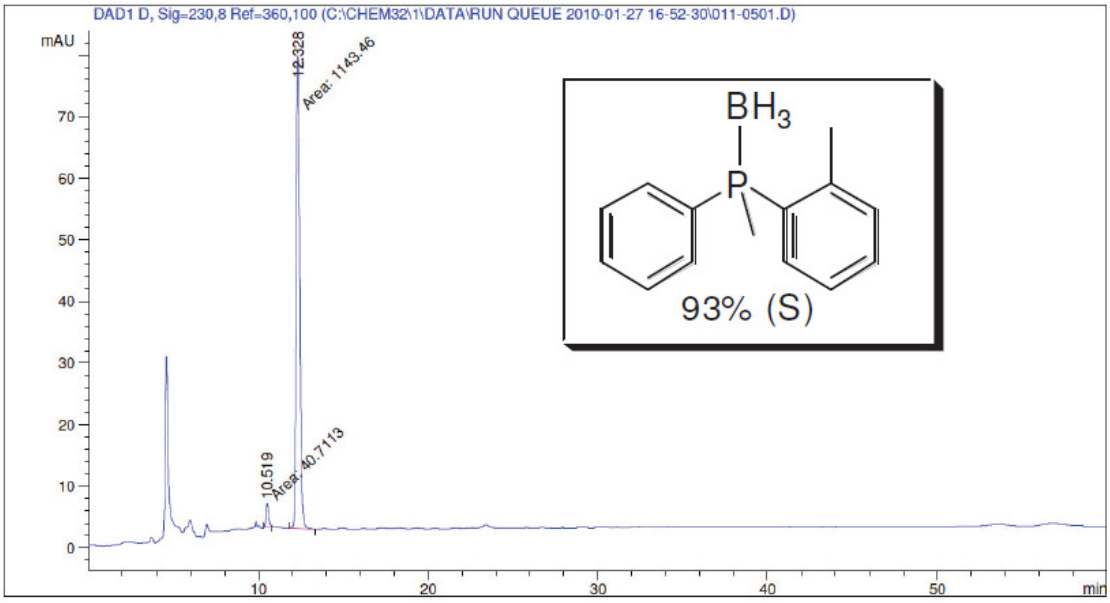


```
======================================================================
                        Area Percent Report
======================================================================

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
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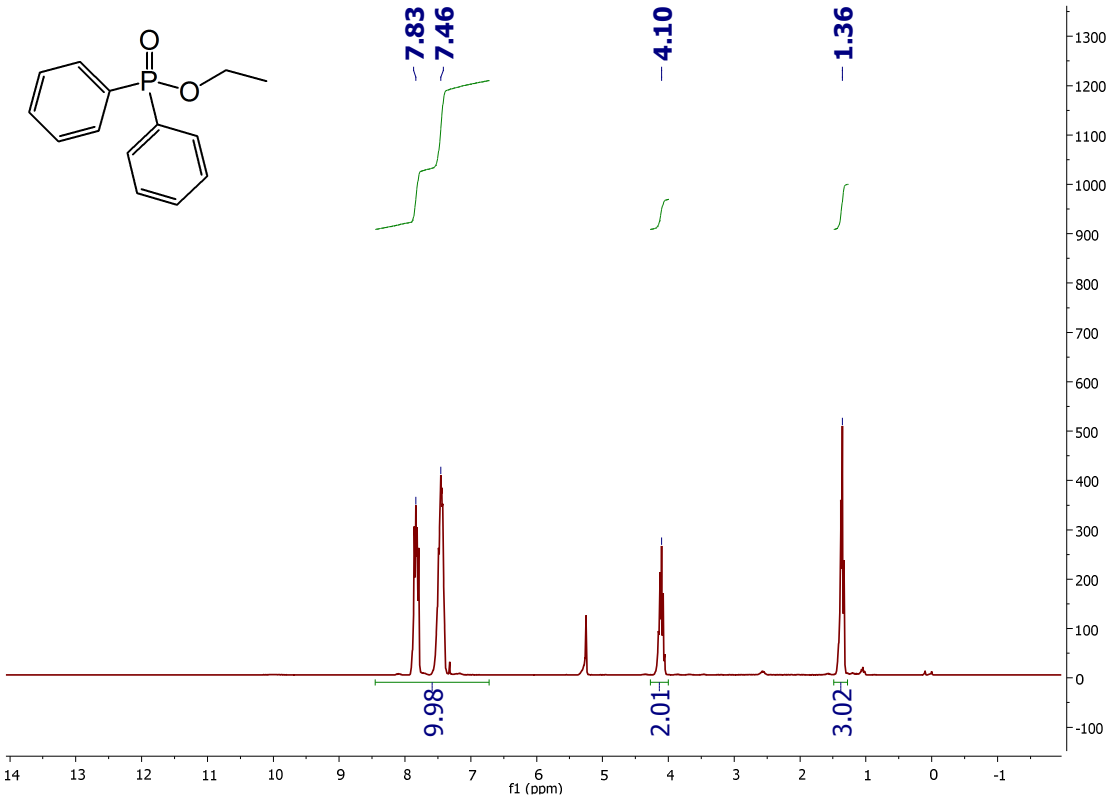
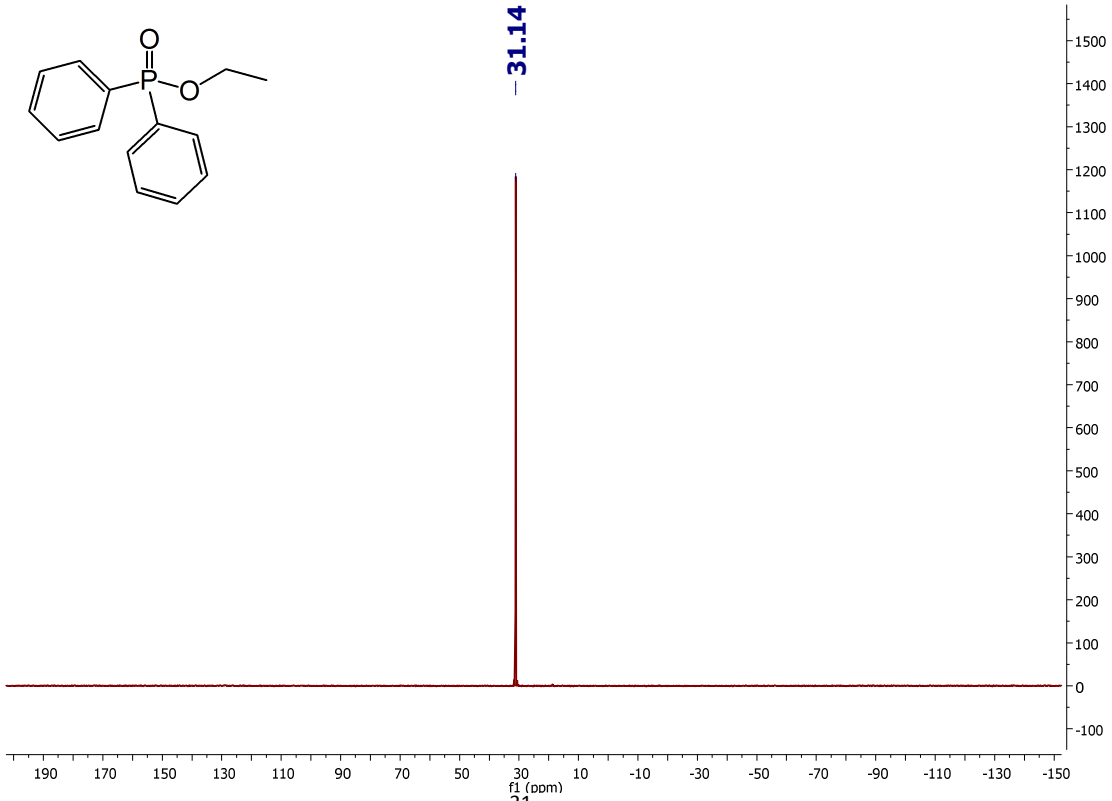


^{1}H-NMR



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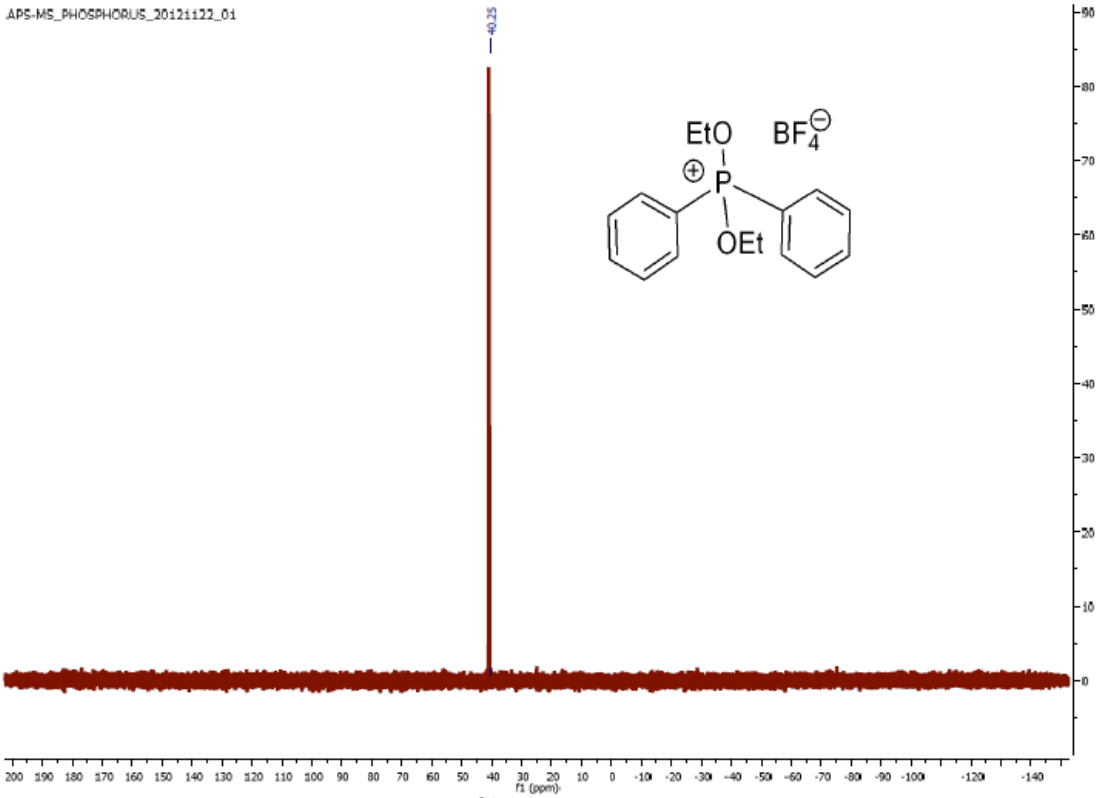

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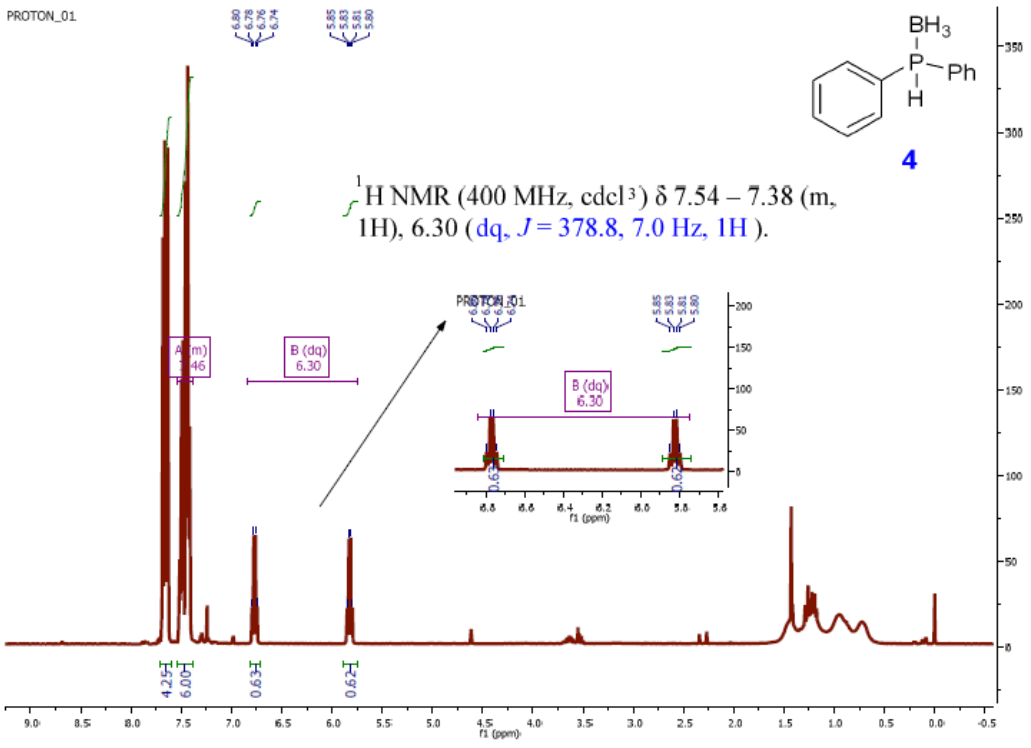

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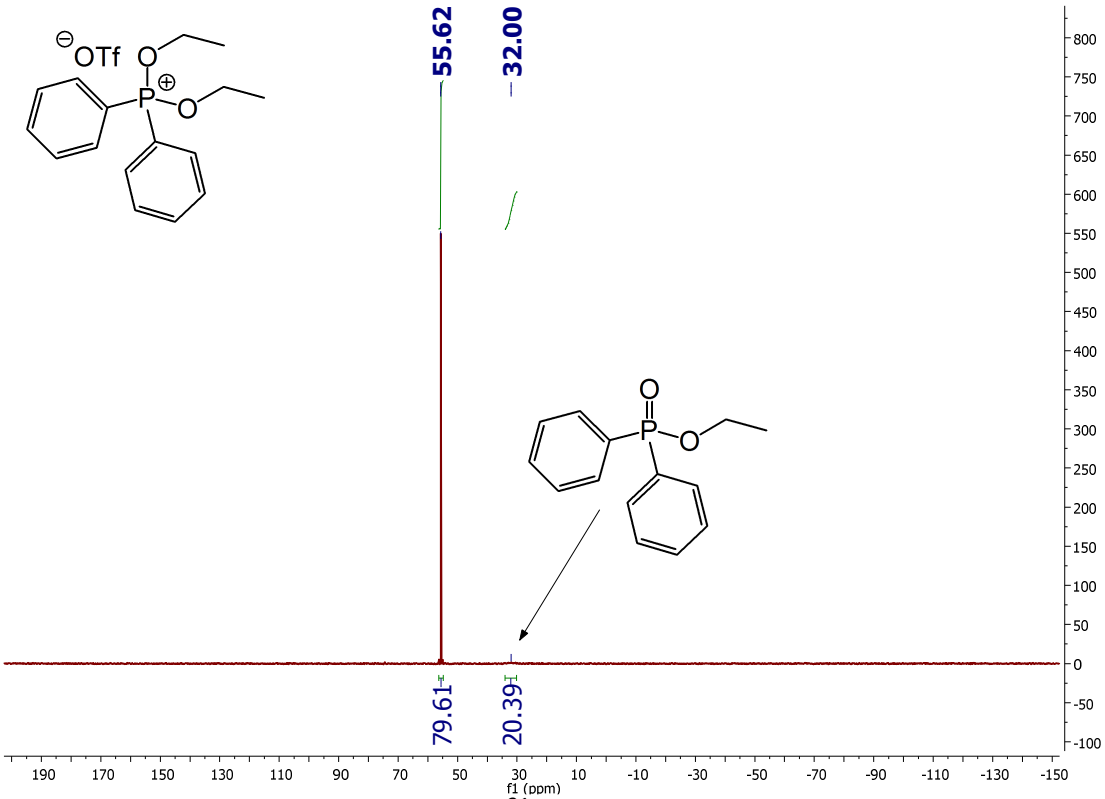

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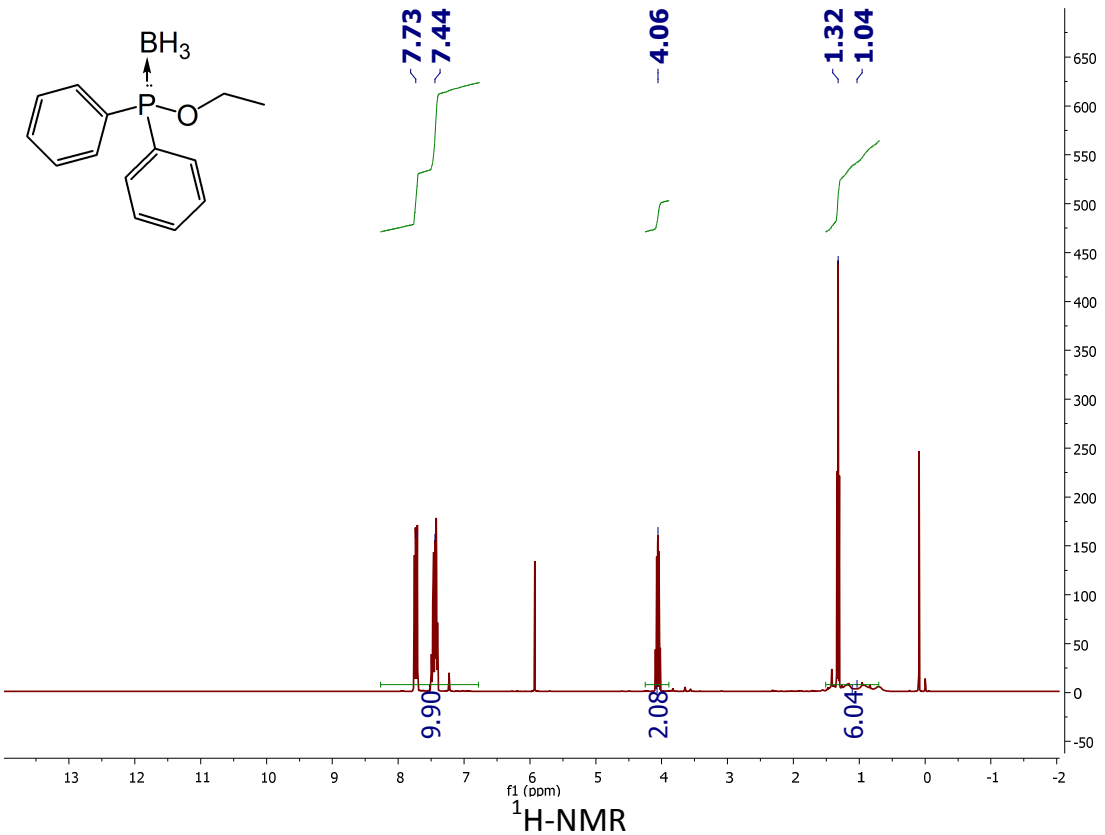

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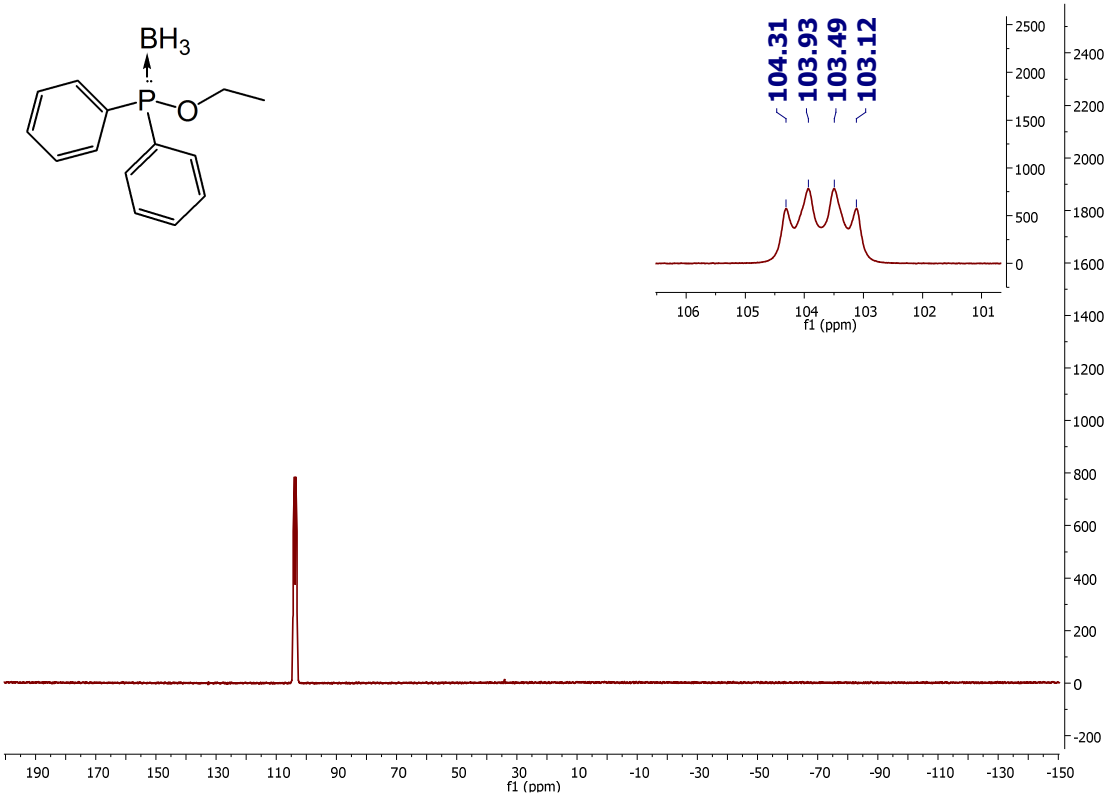

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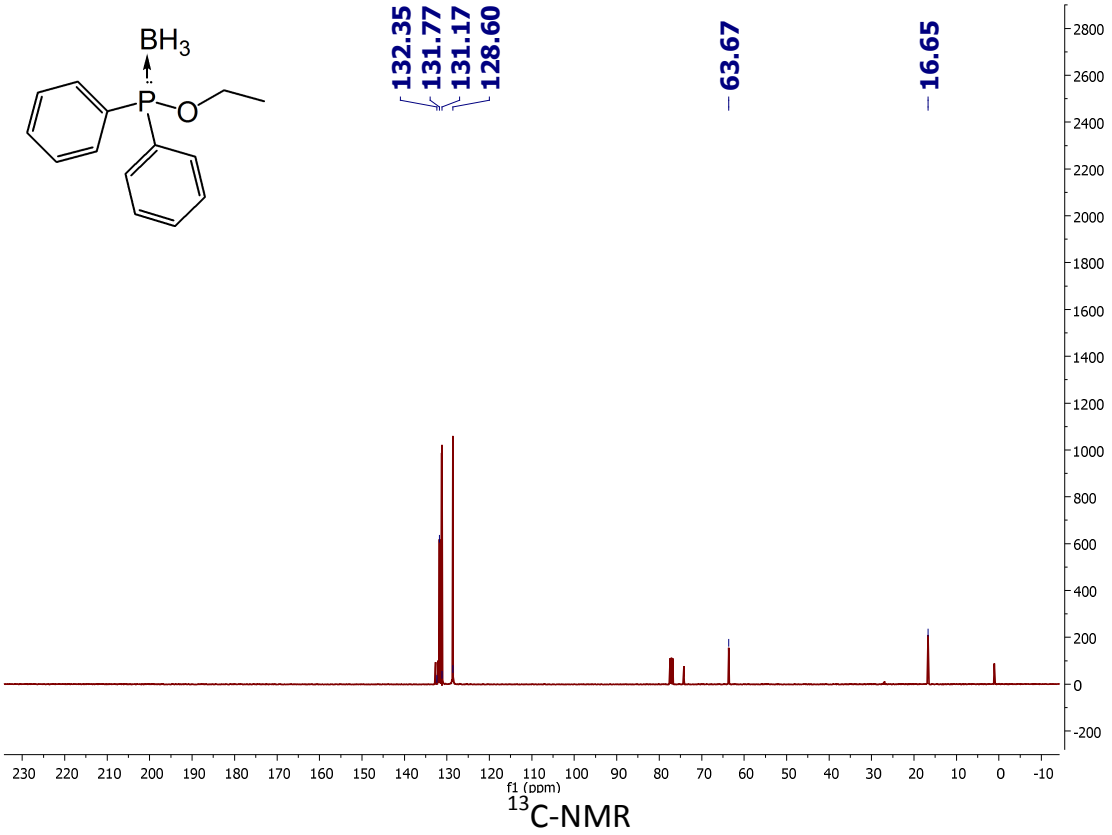

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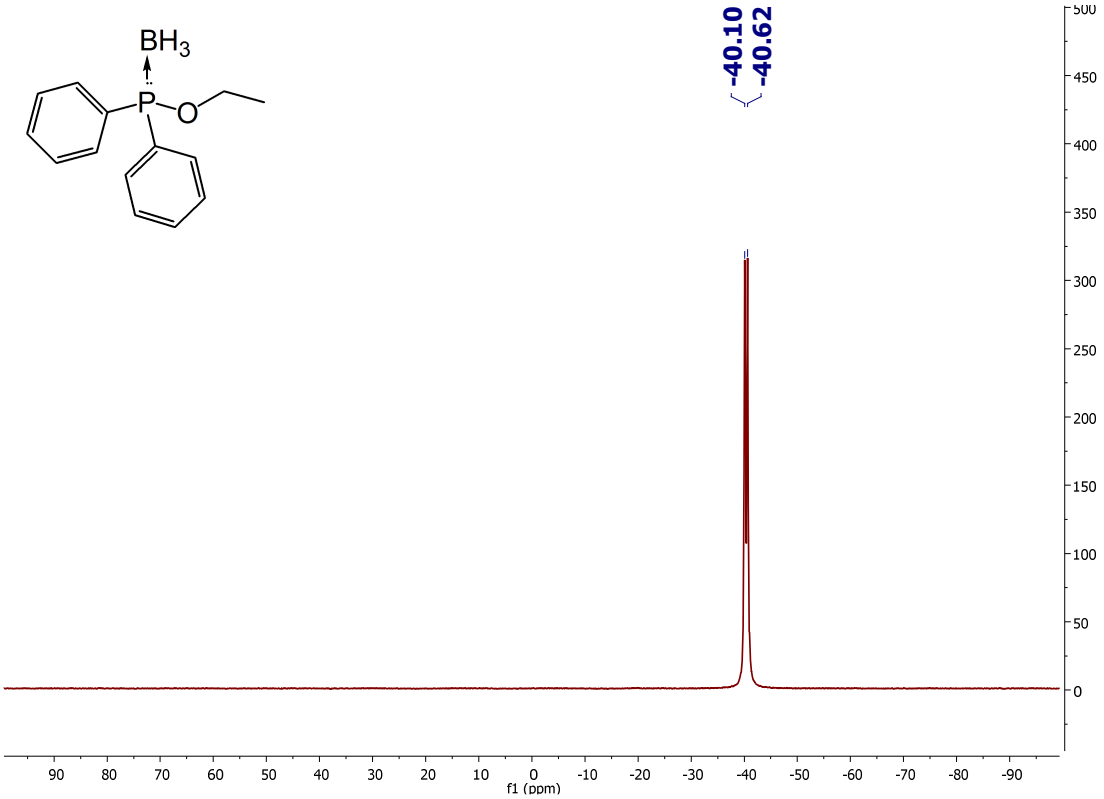

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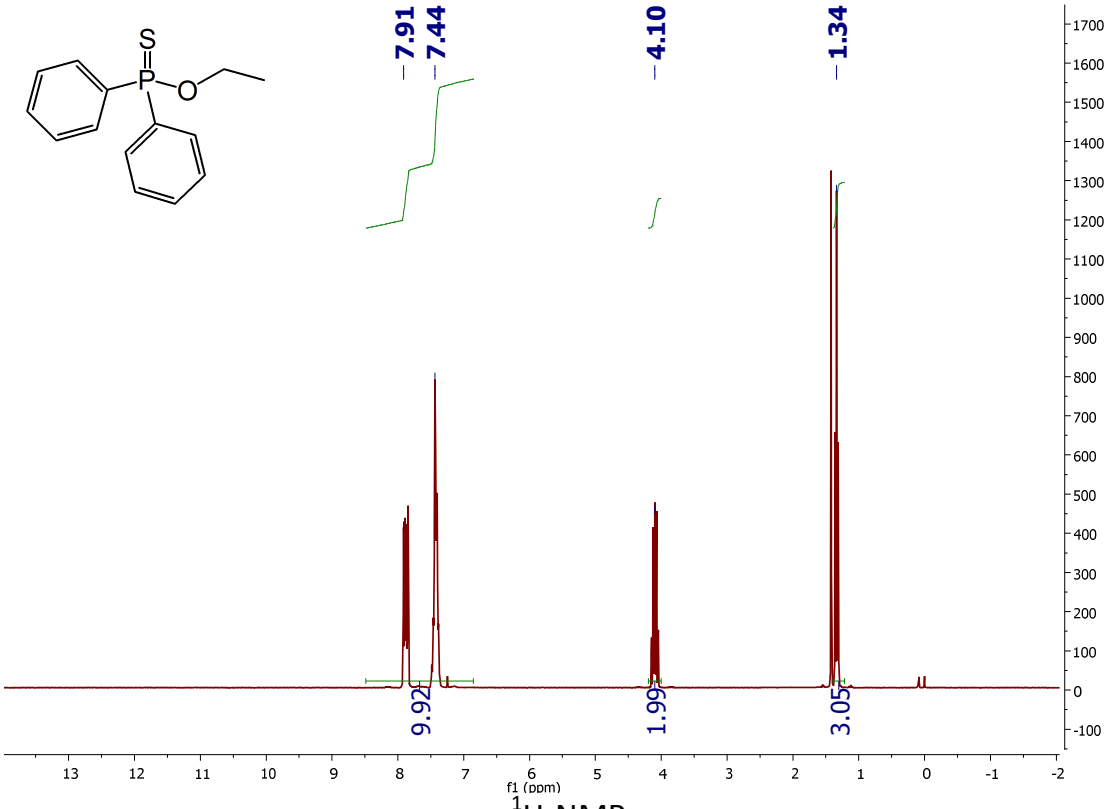

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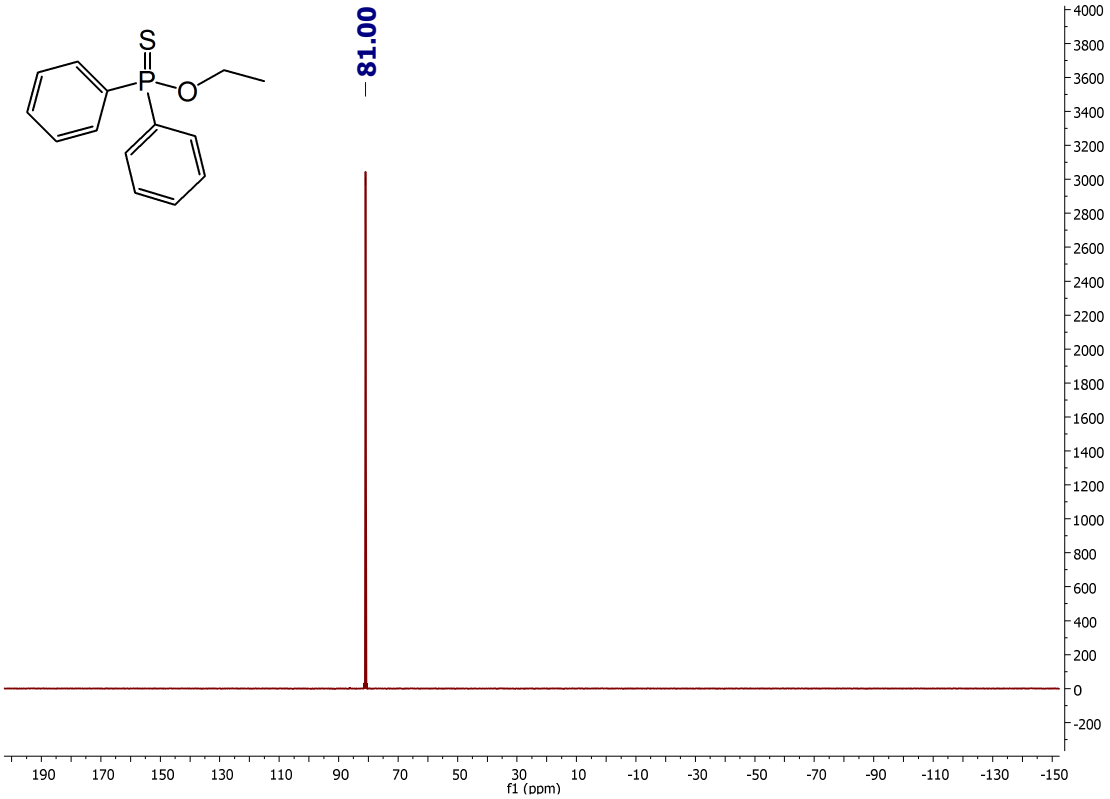

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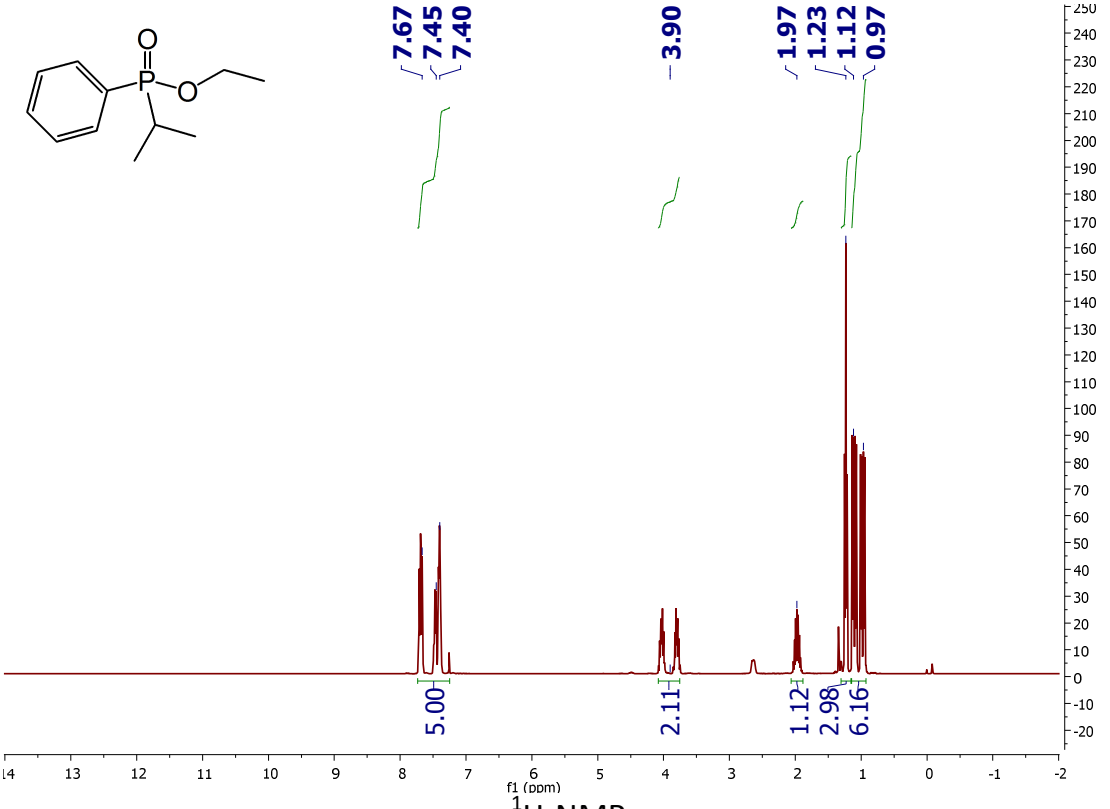

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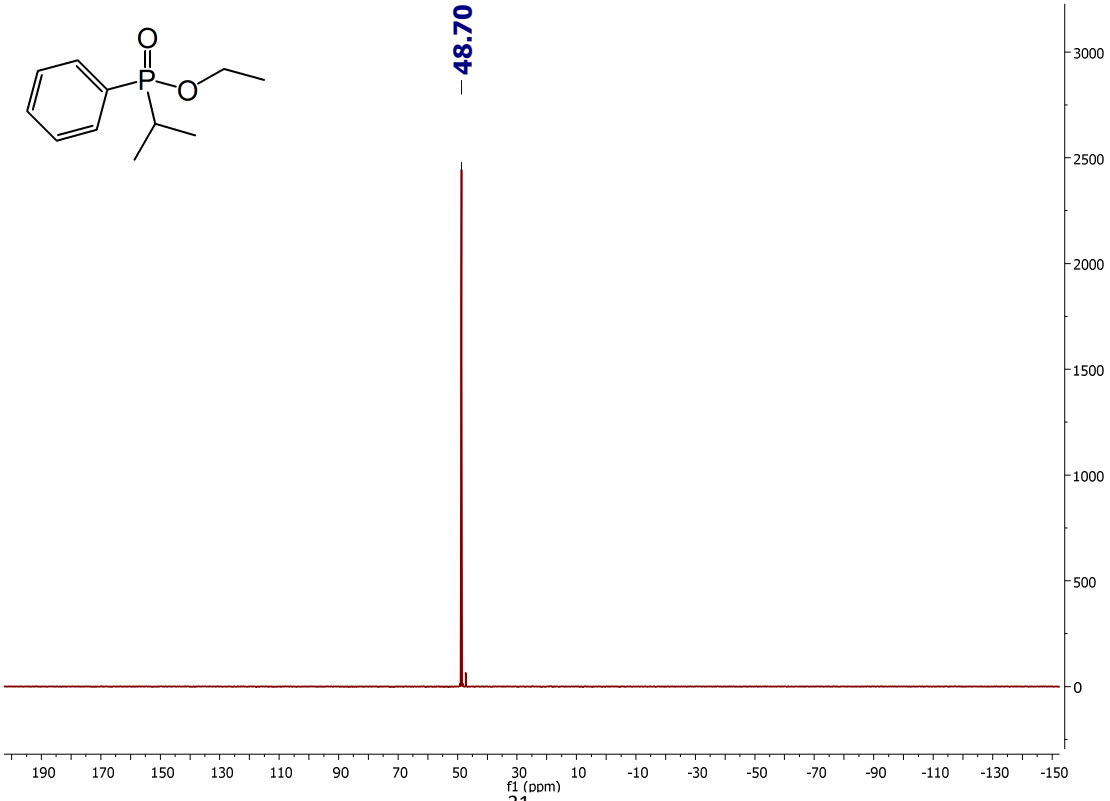

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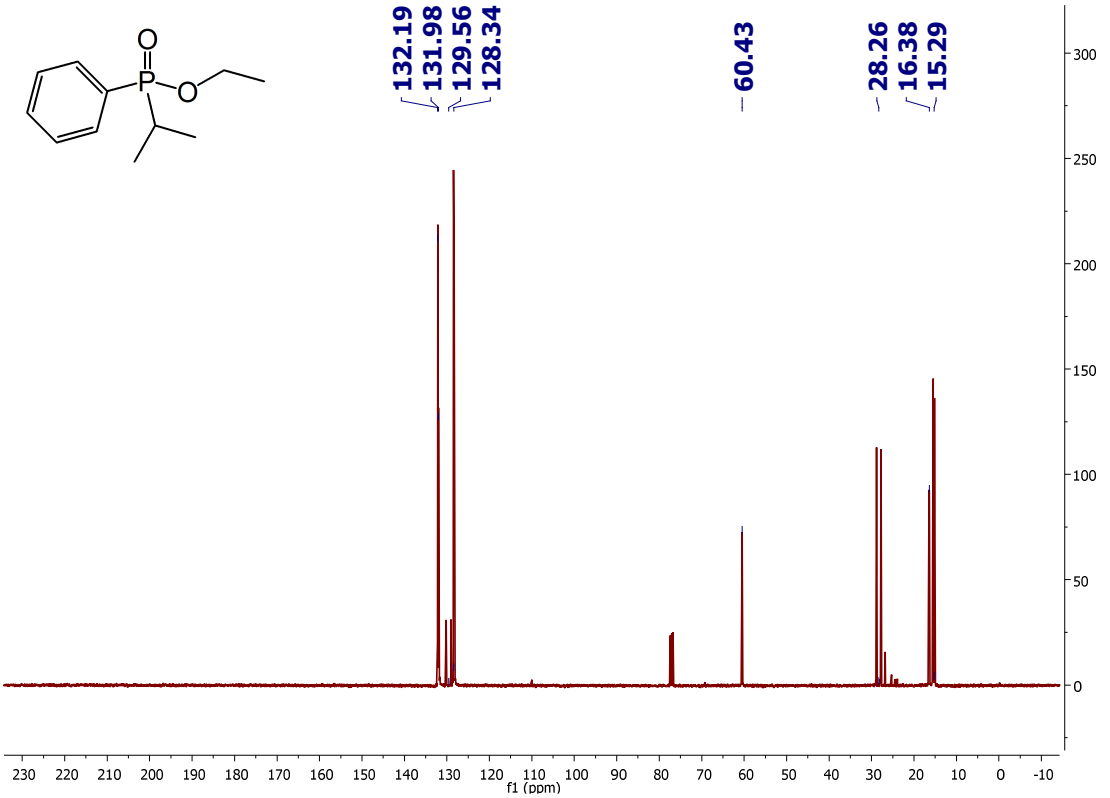

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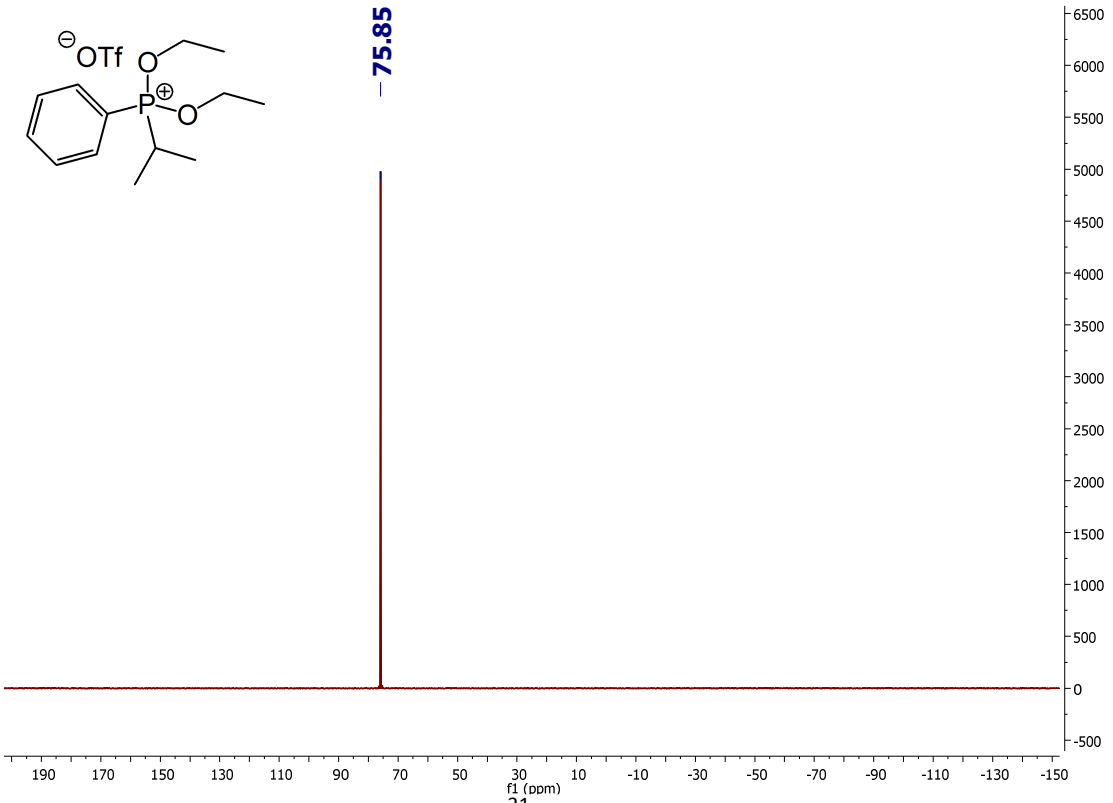

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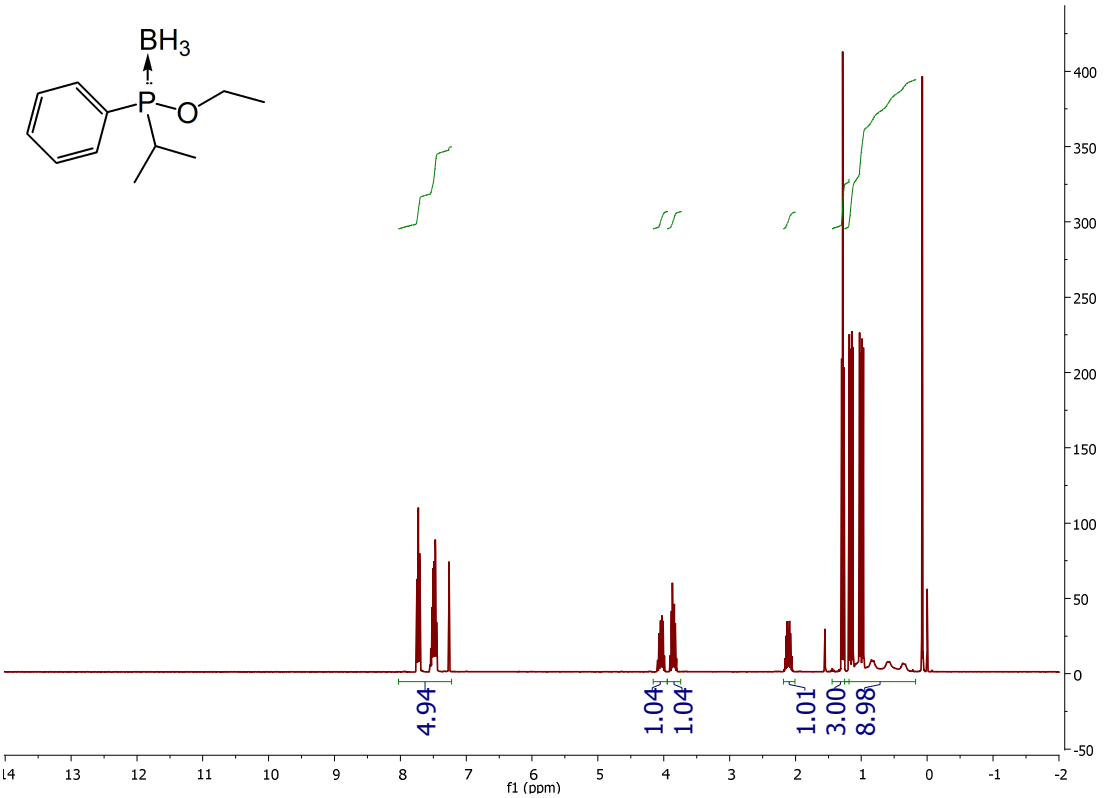

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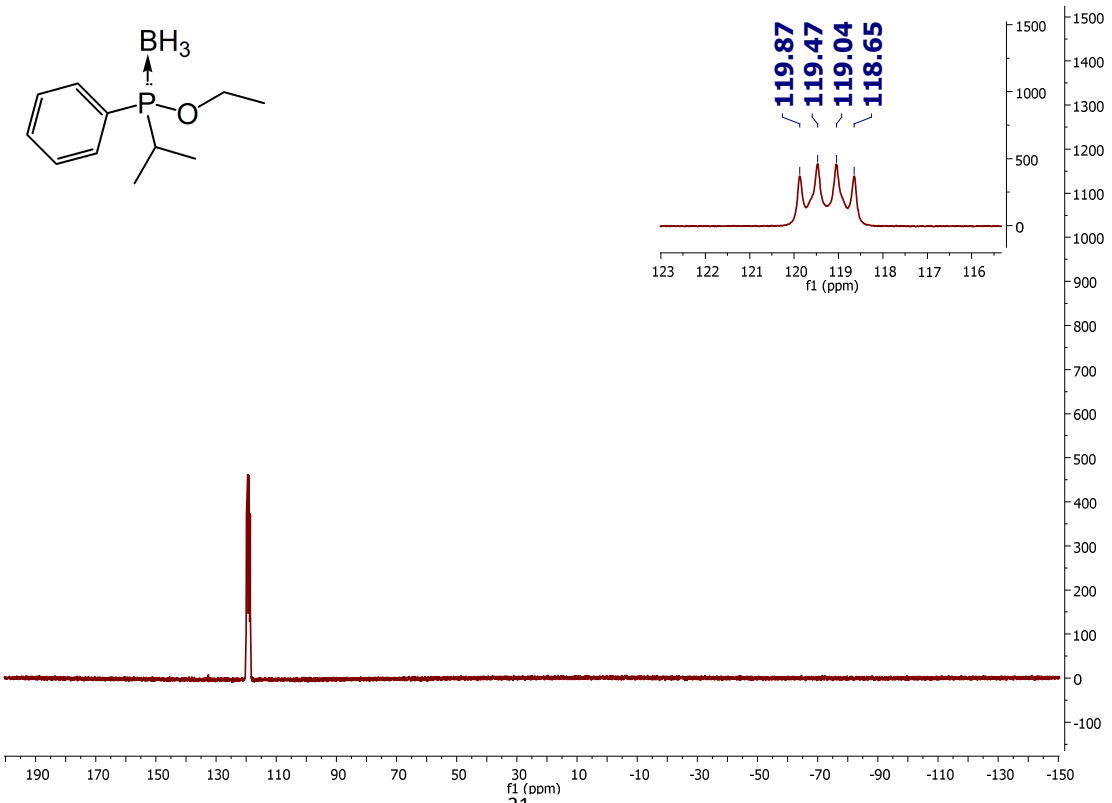

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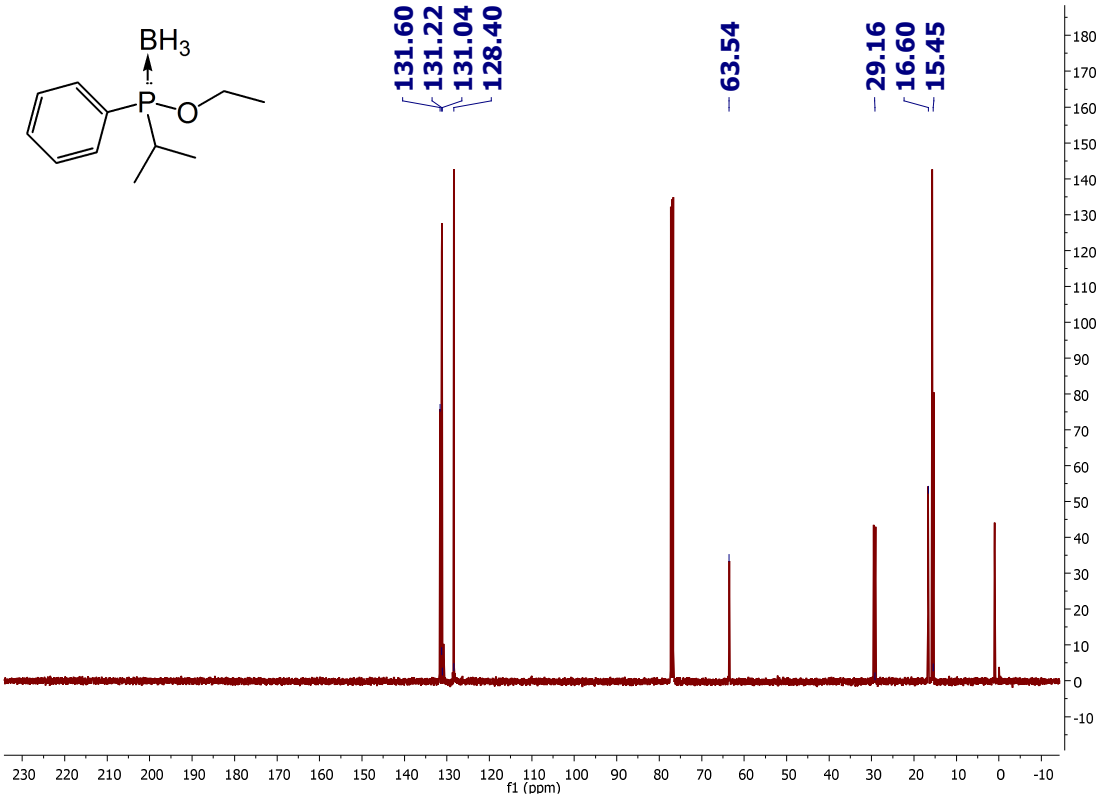

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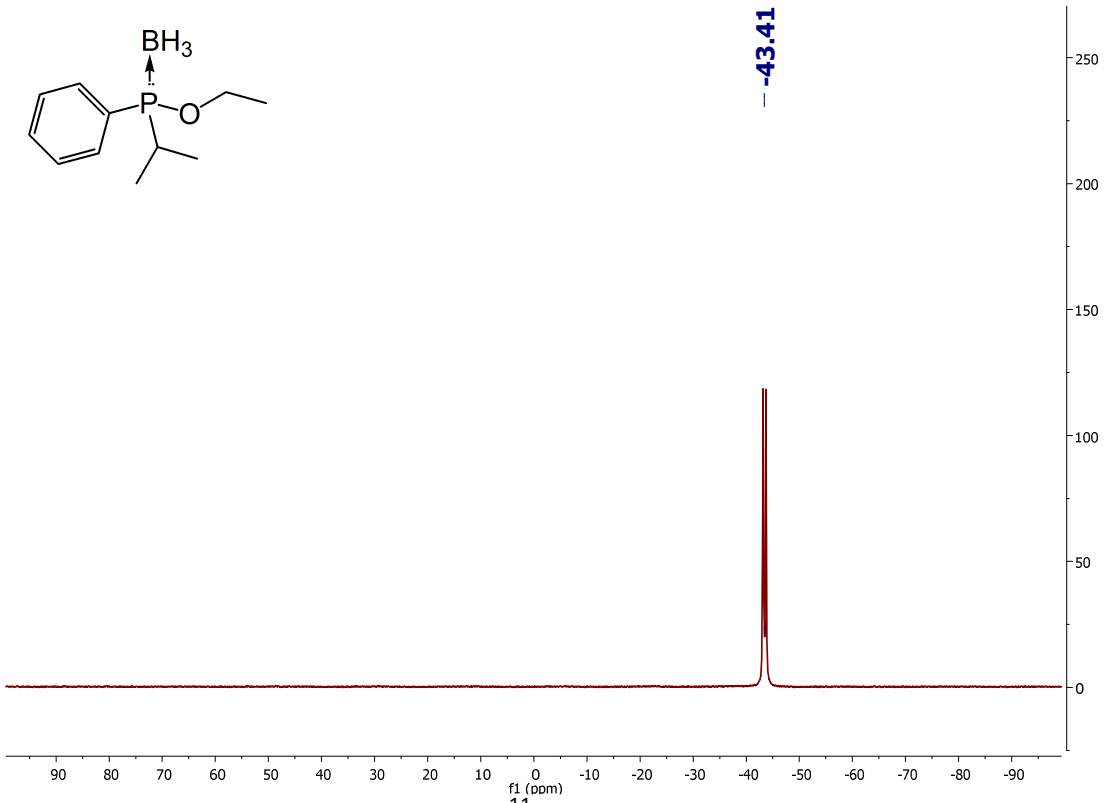

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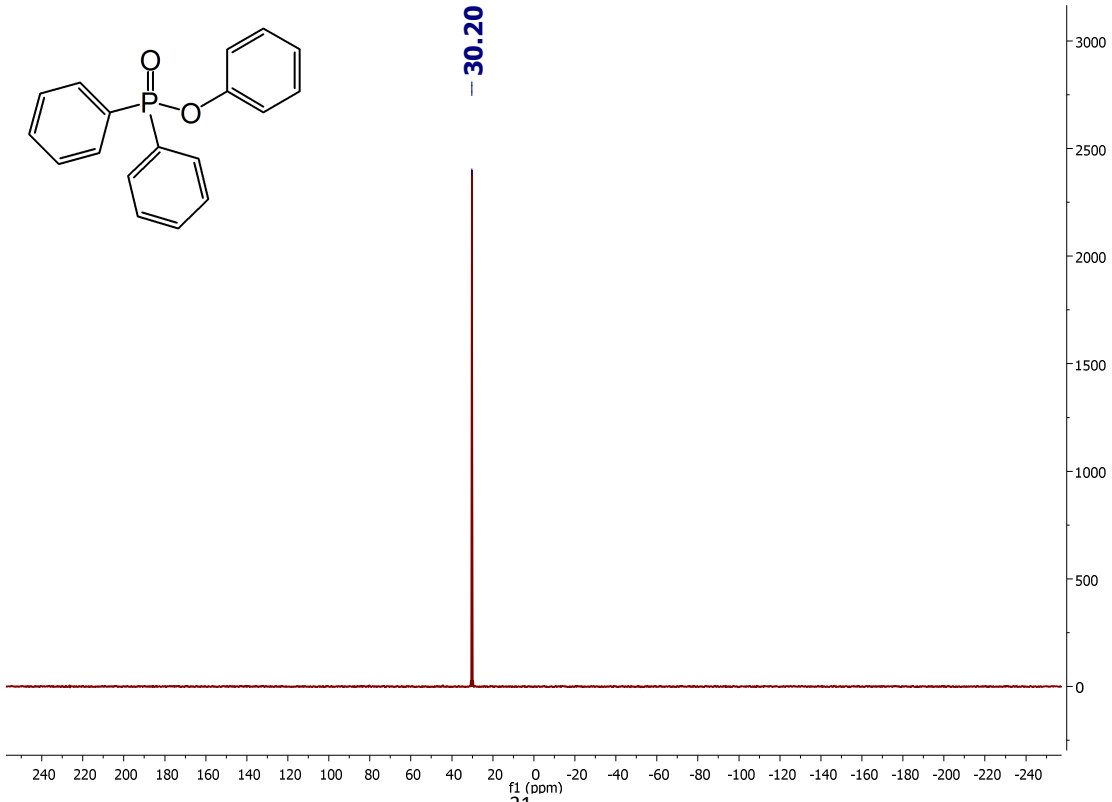

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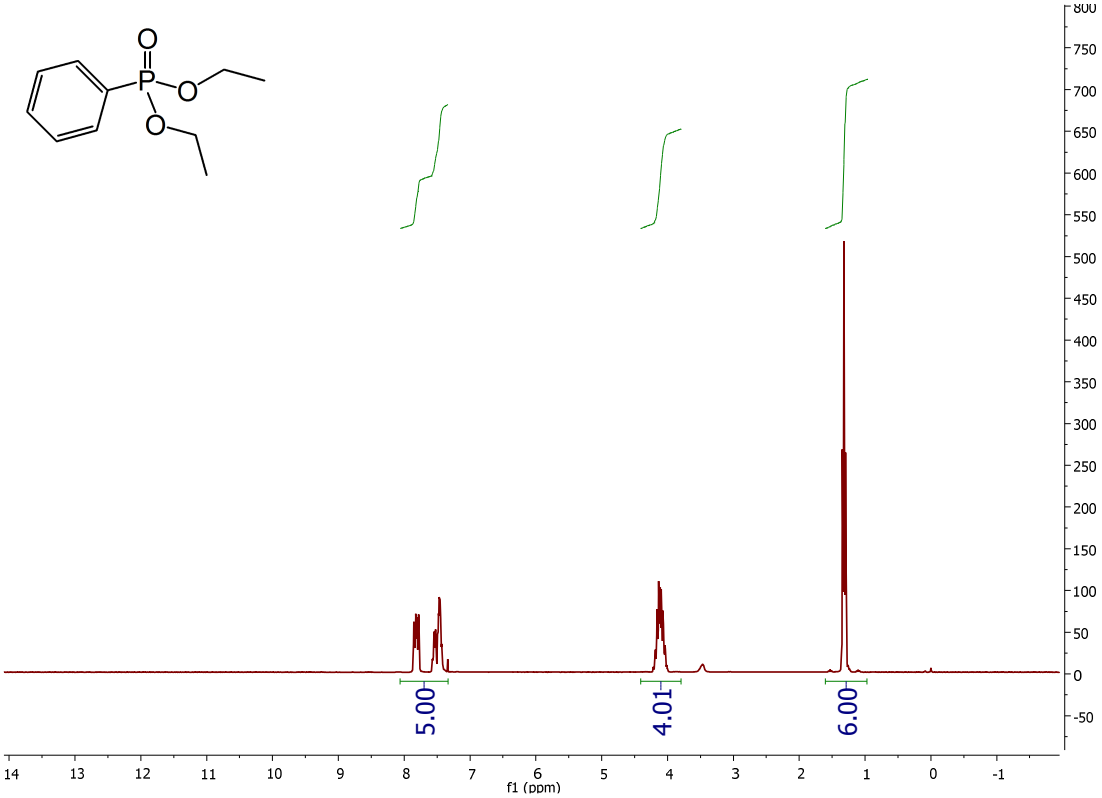

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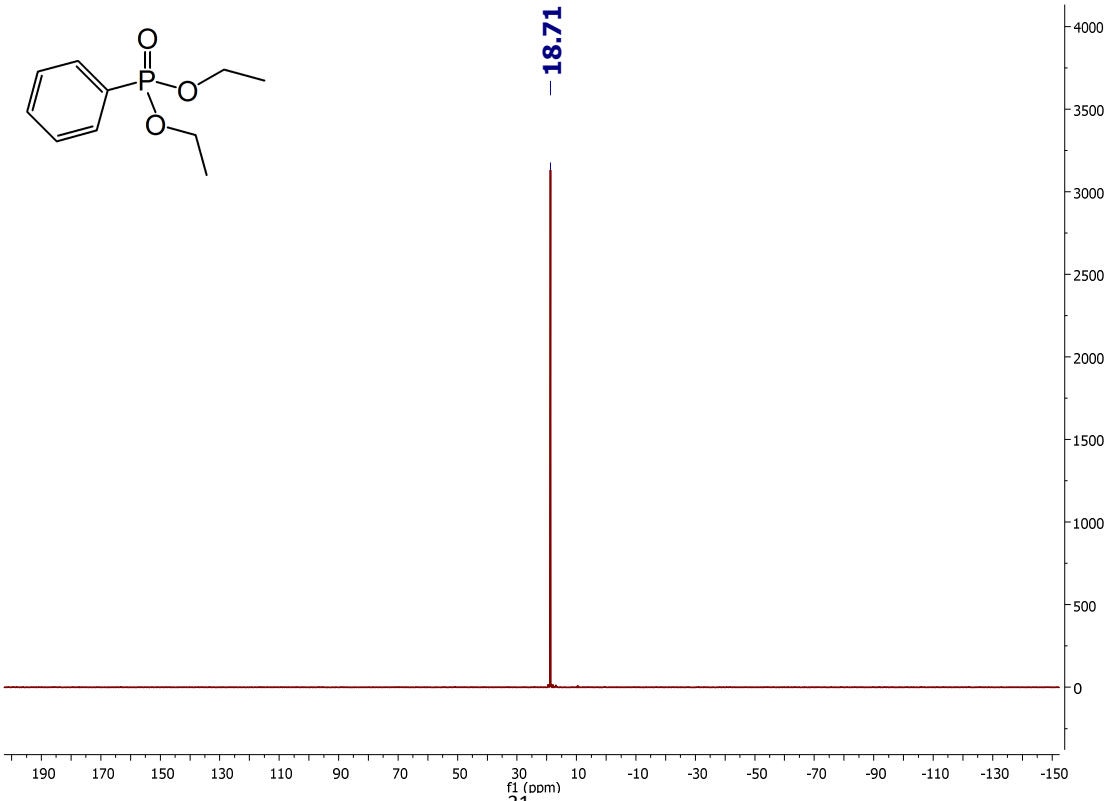

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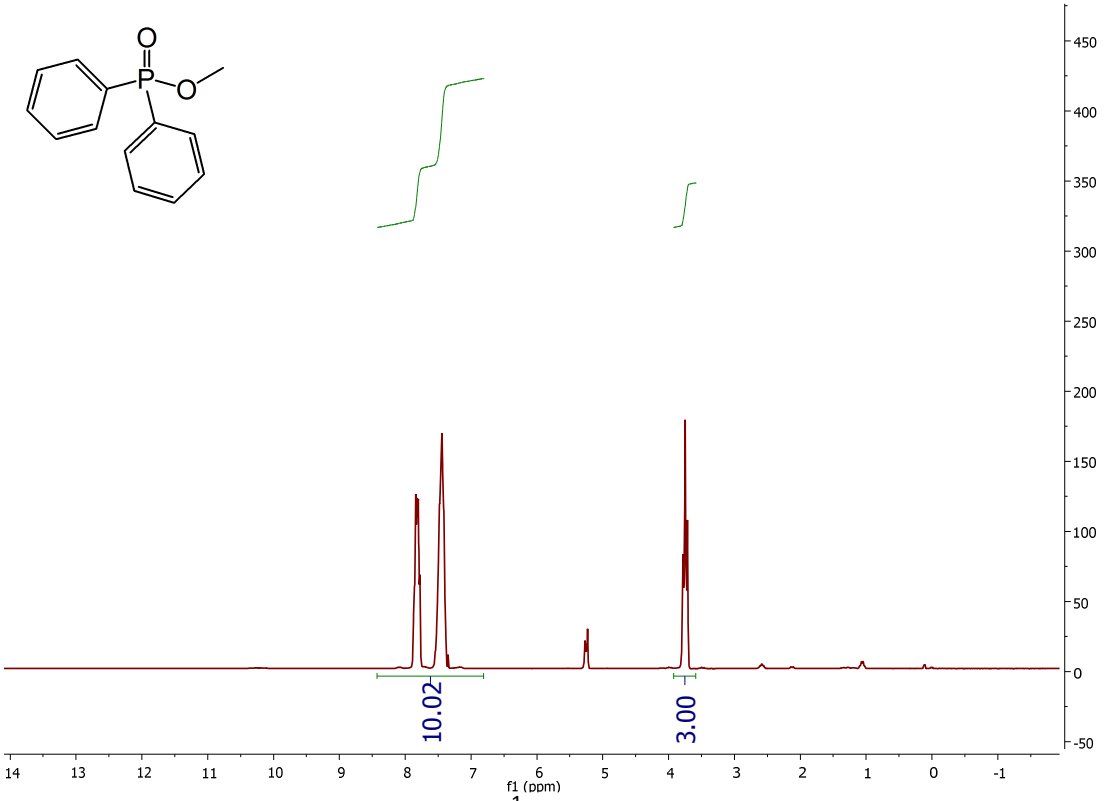

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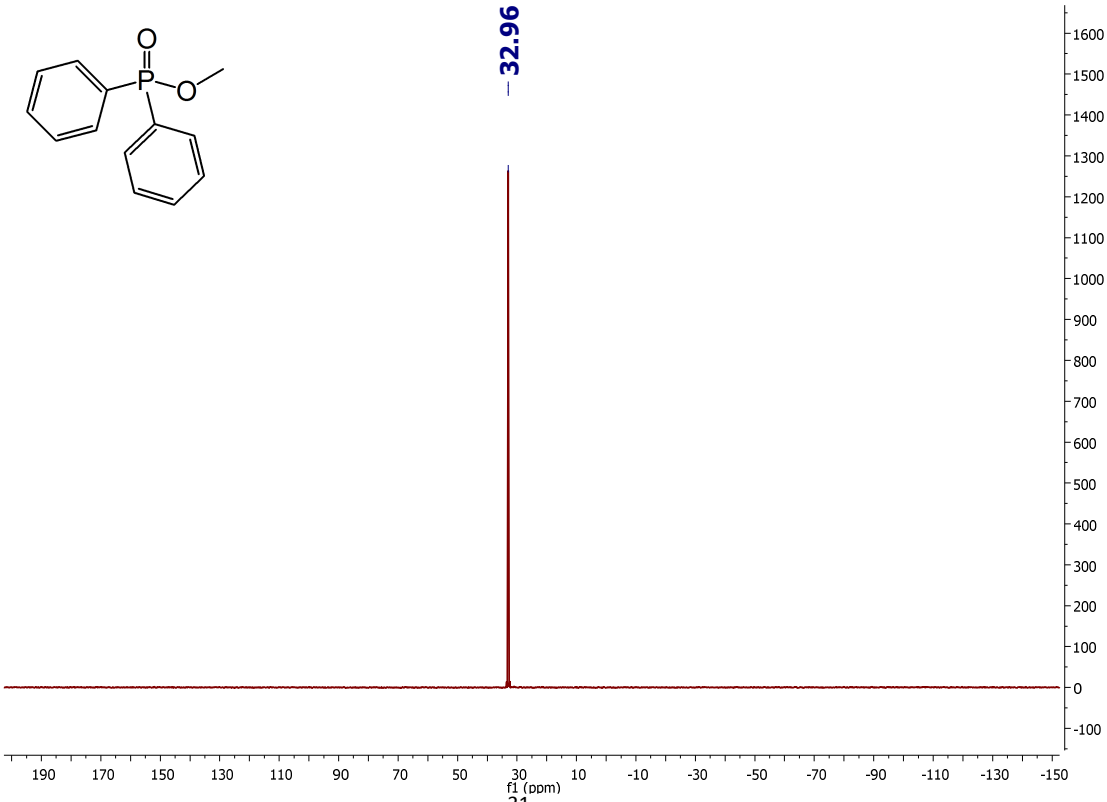

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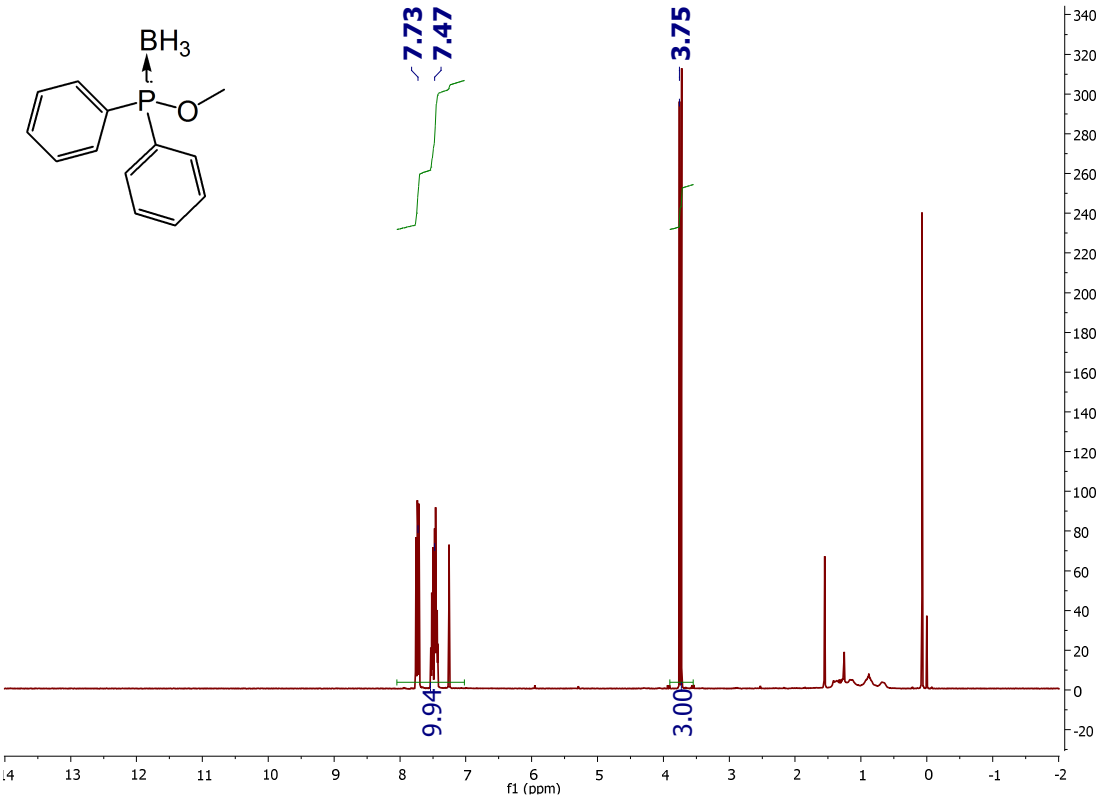

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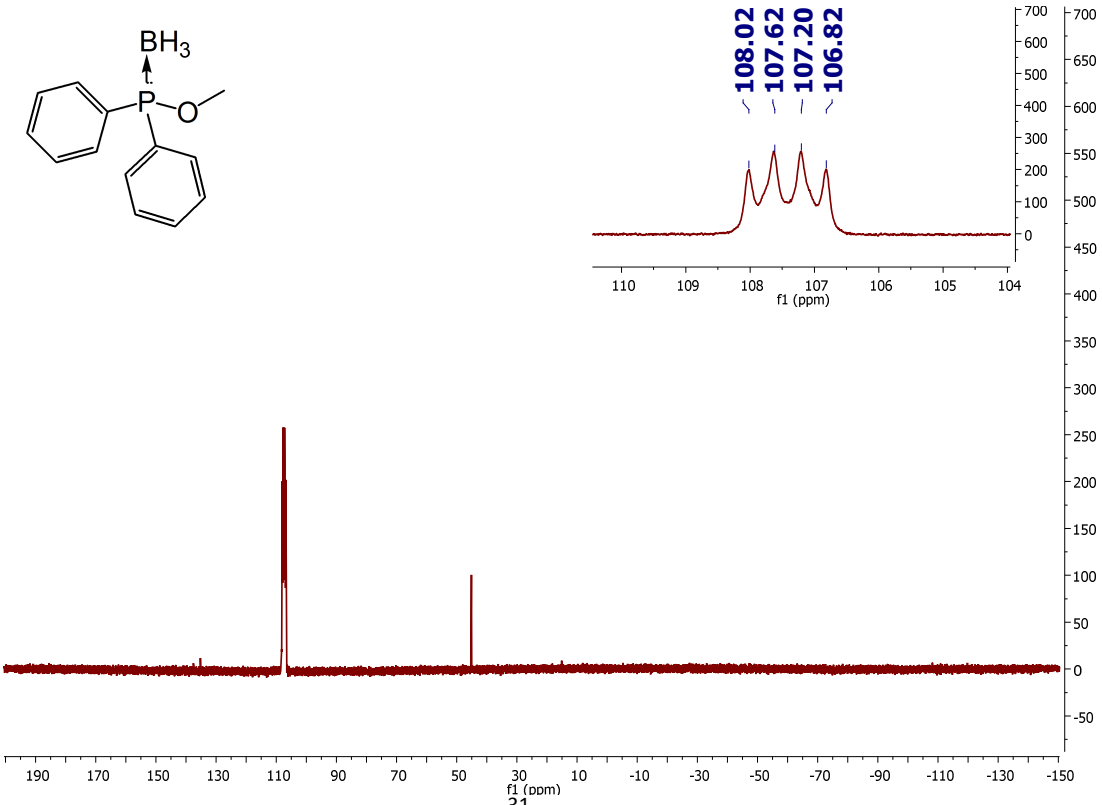

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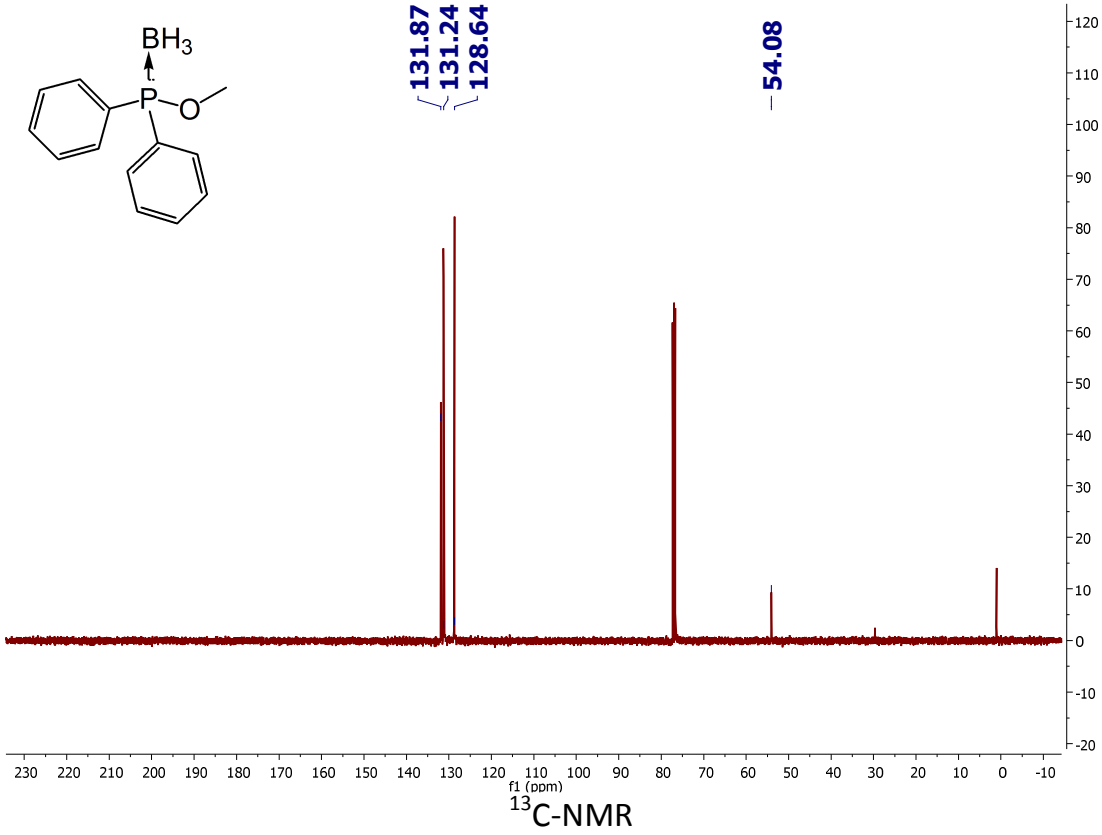

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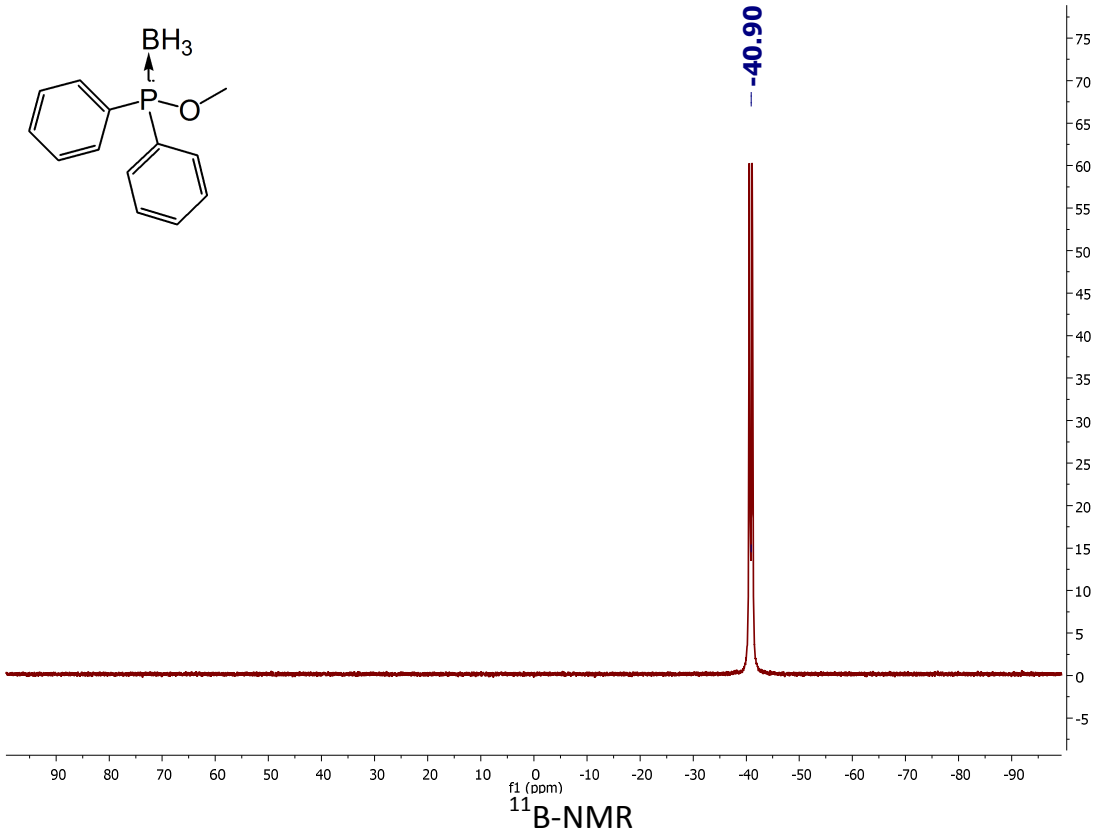

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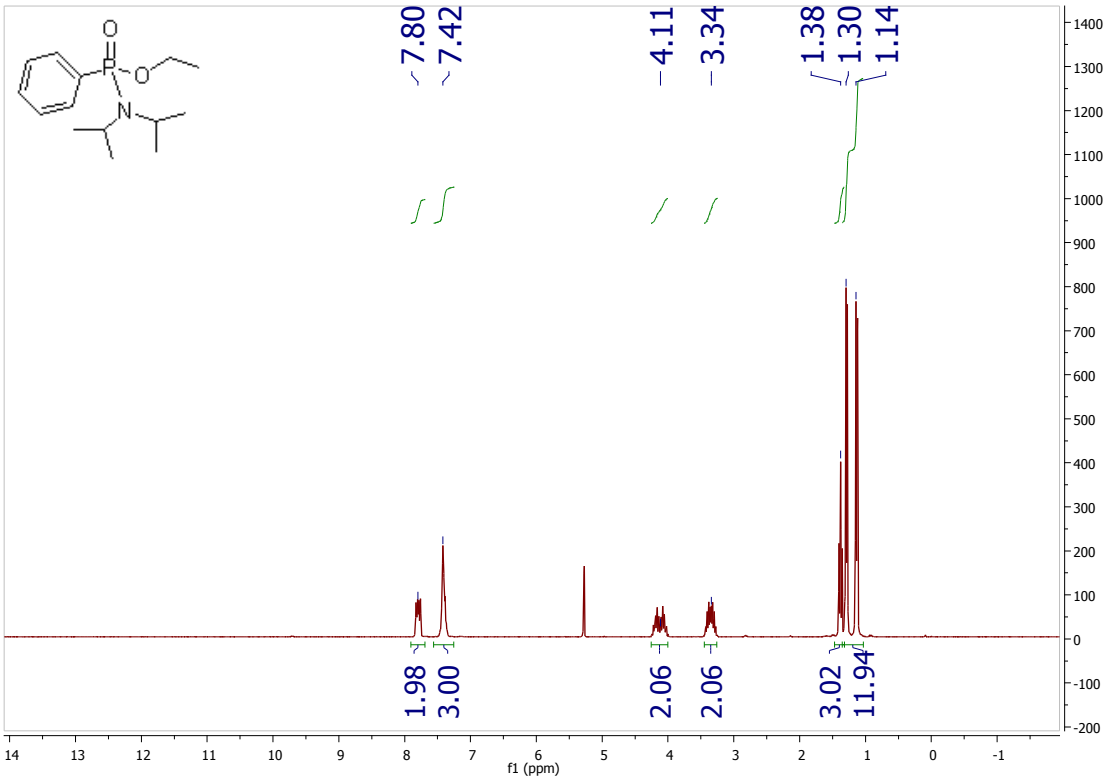

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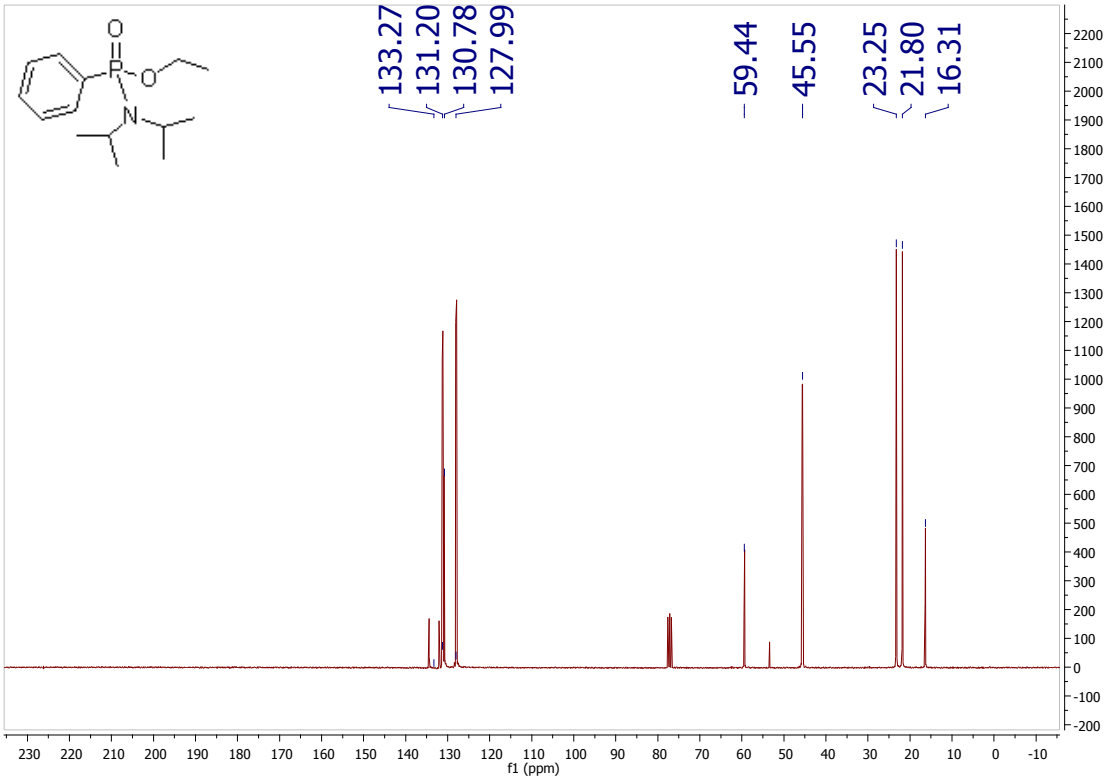

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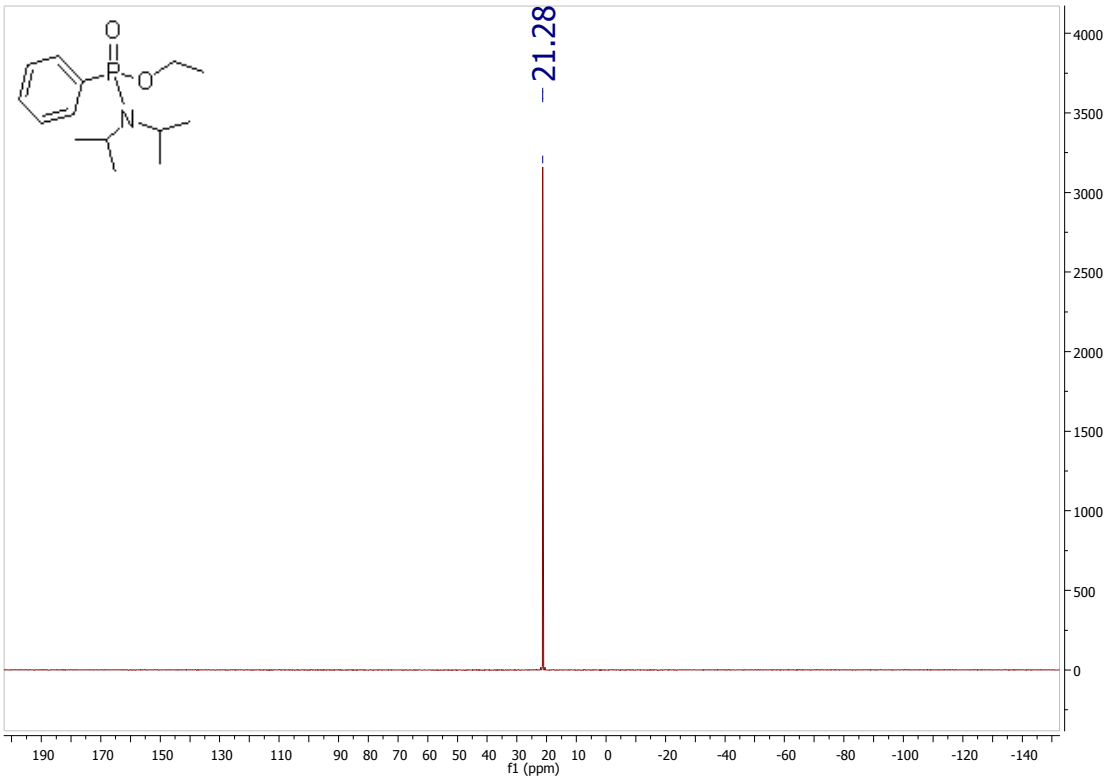

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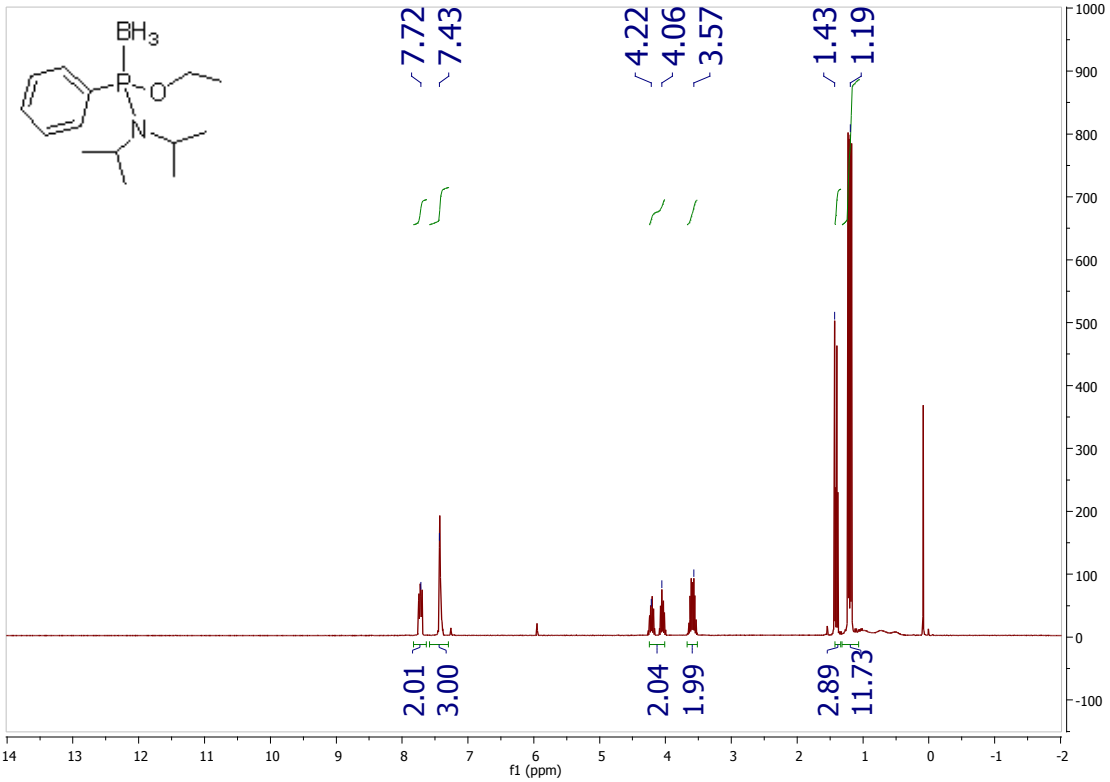

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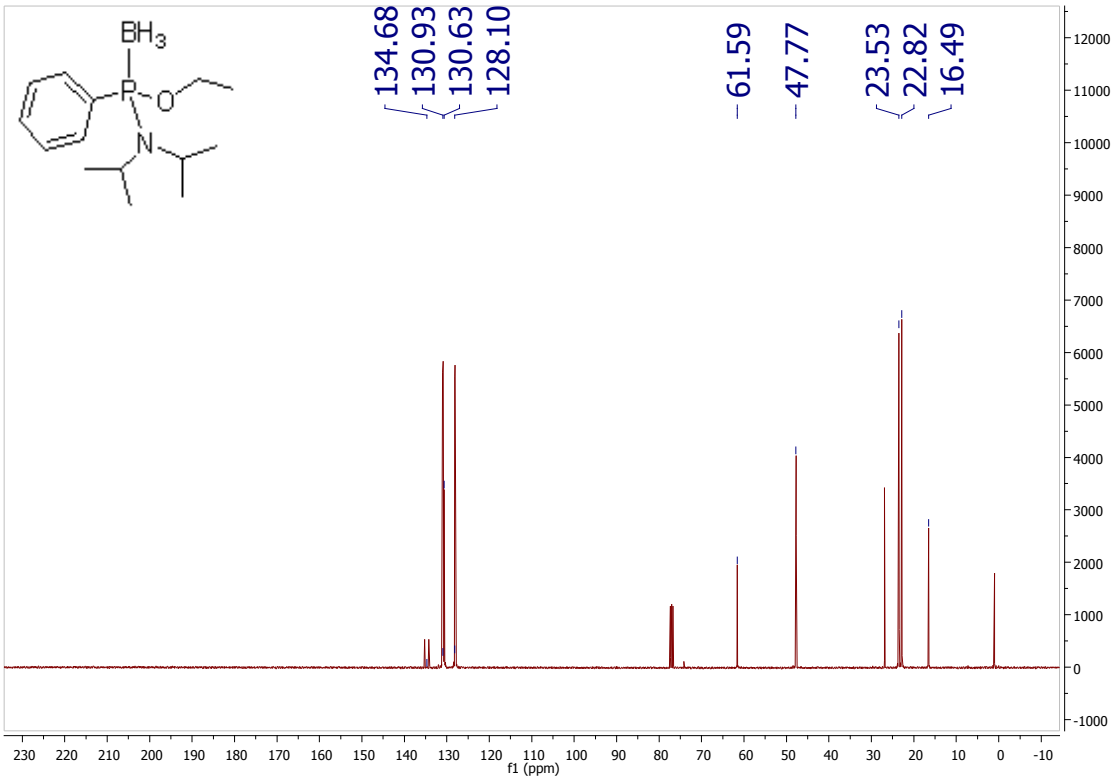

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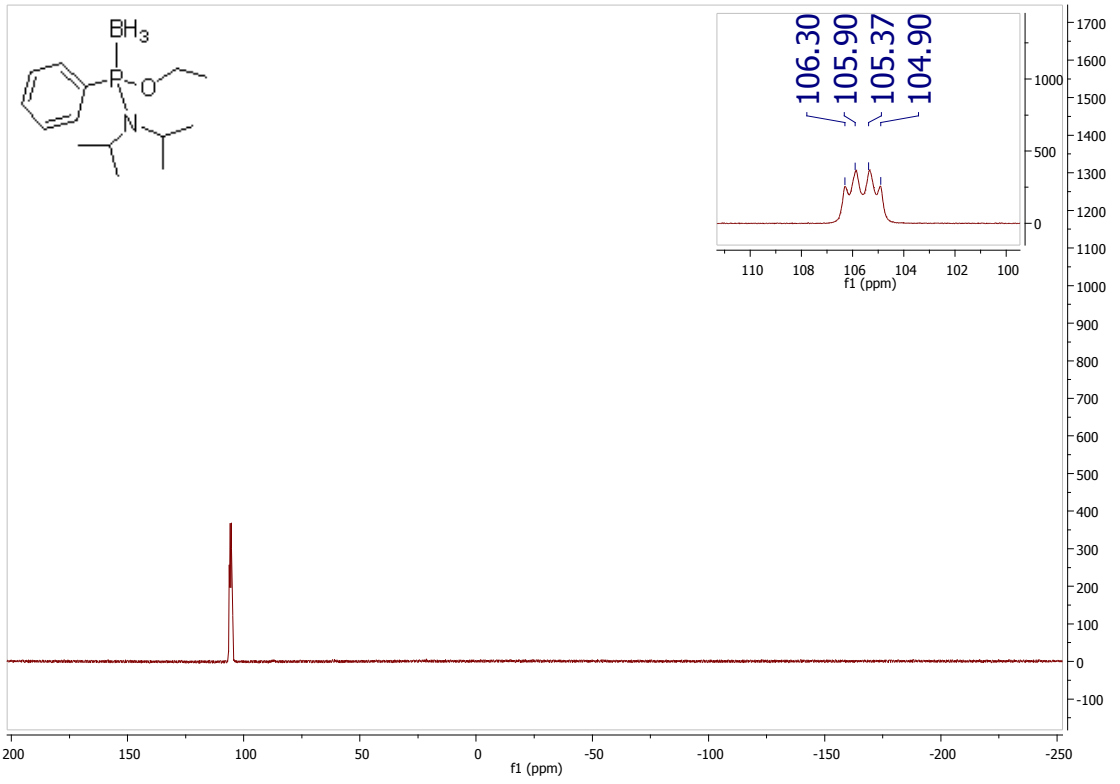

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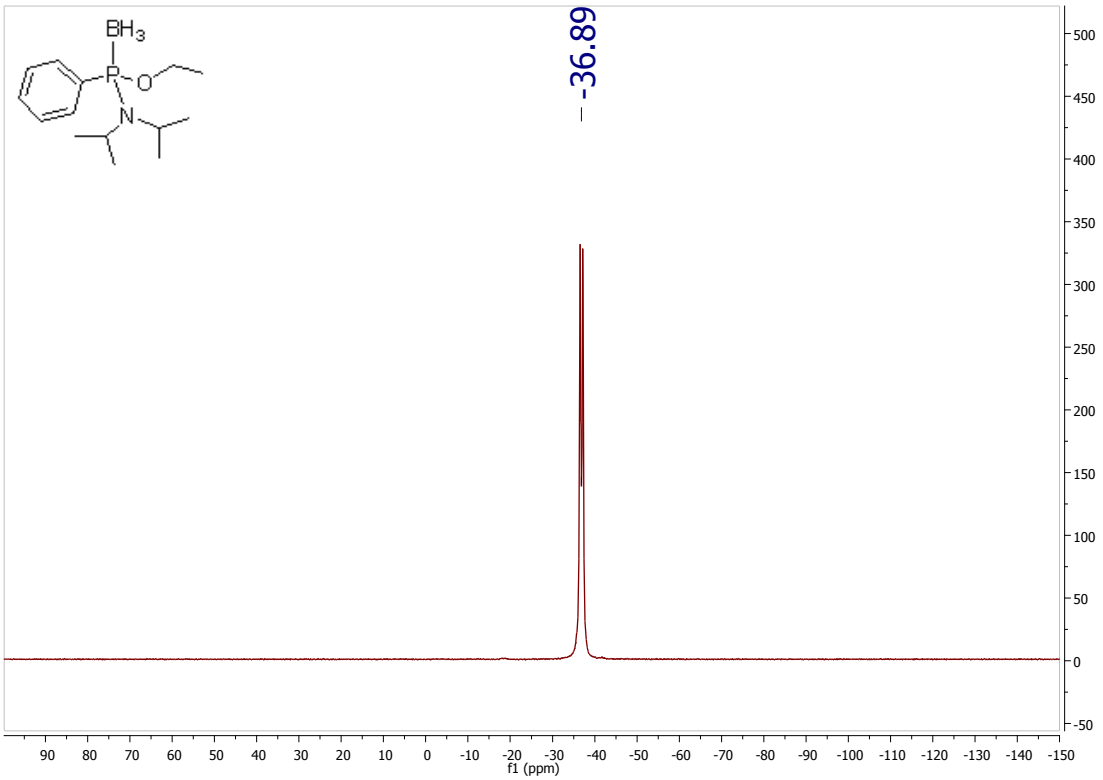

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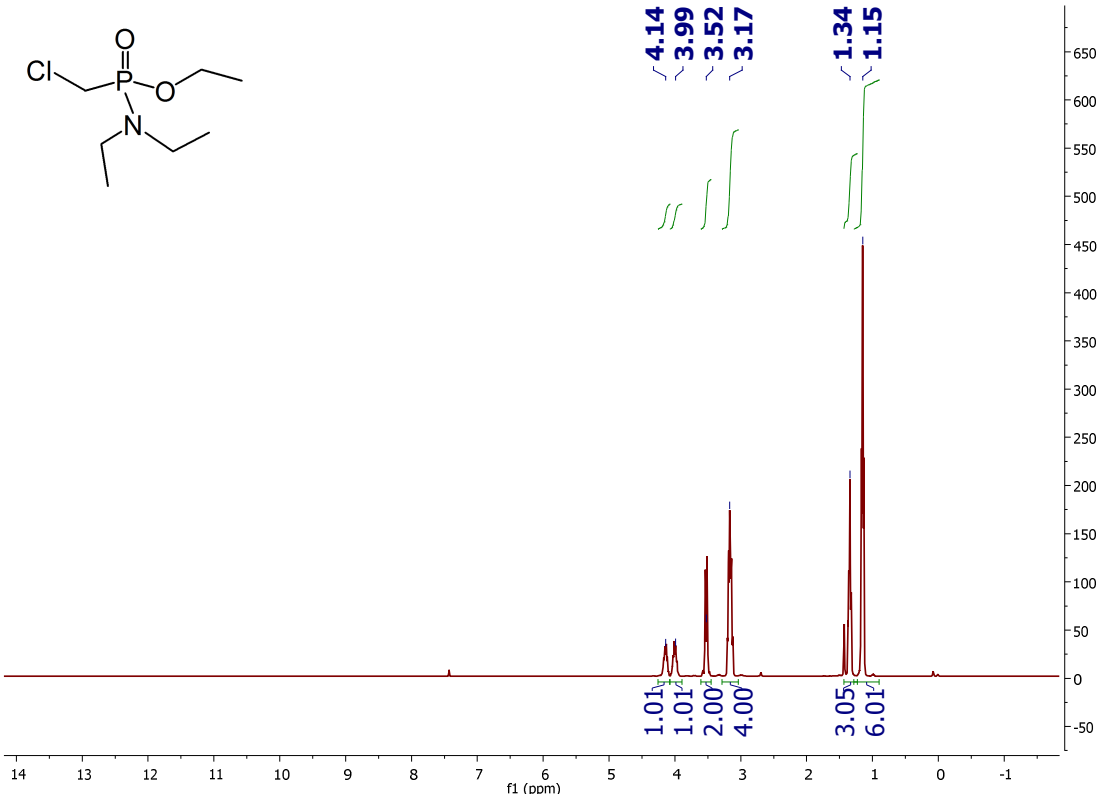

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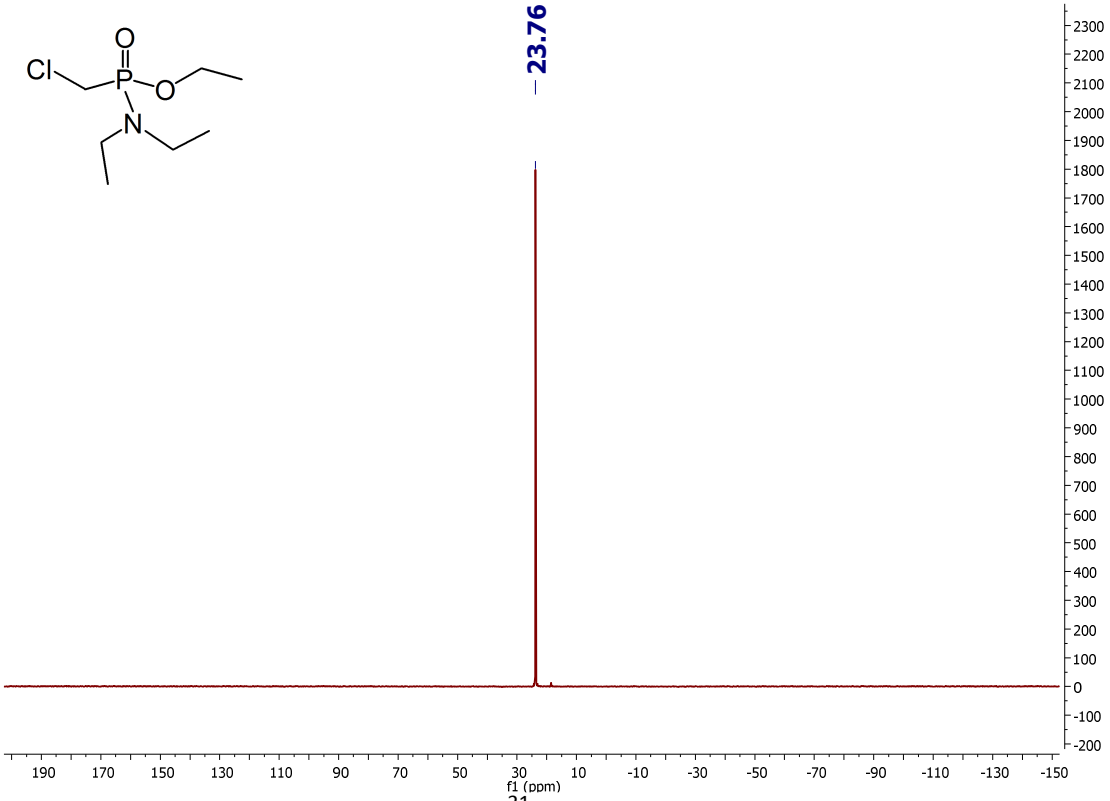

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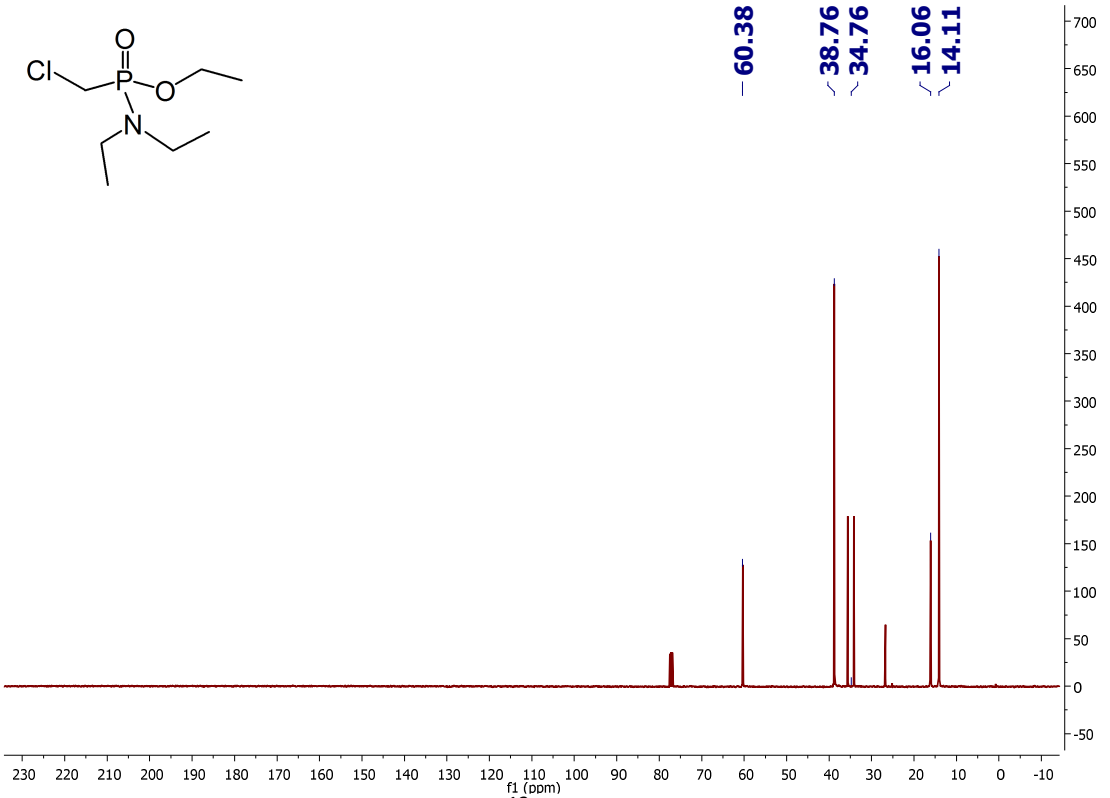

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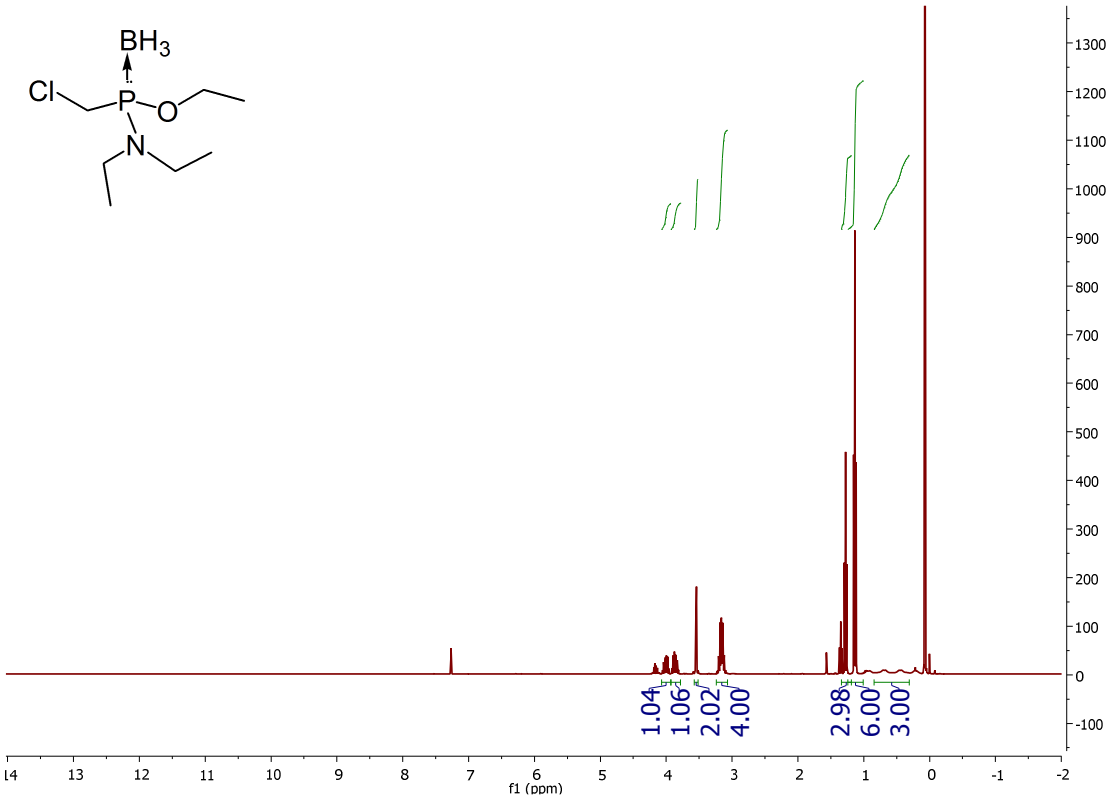

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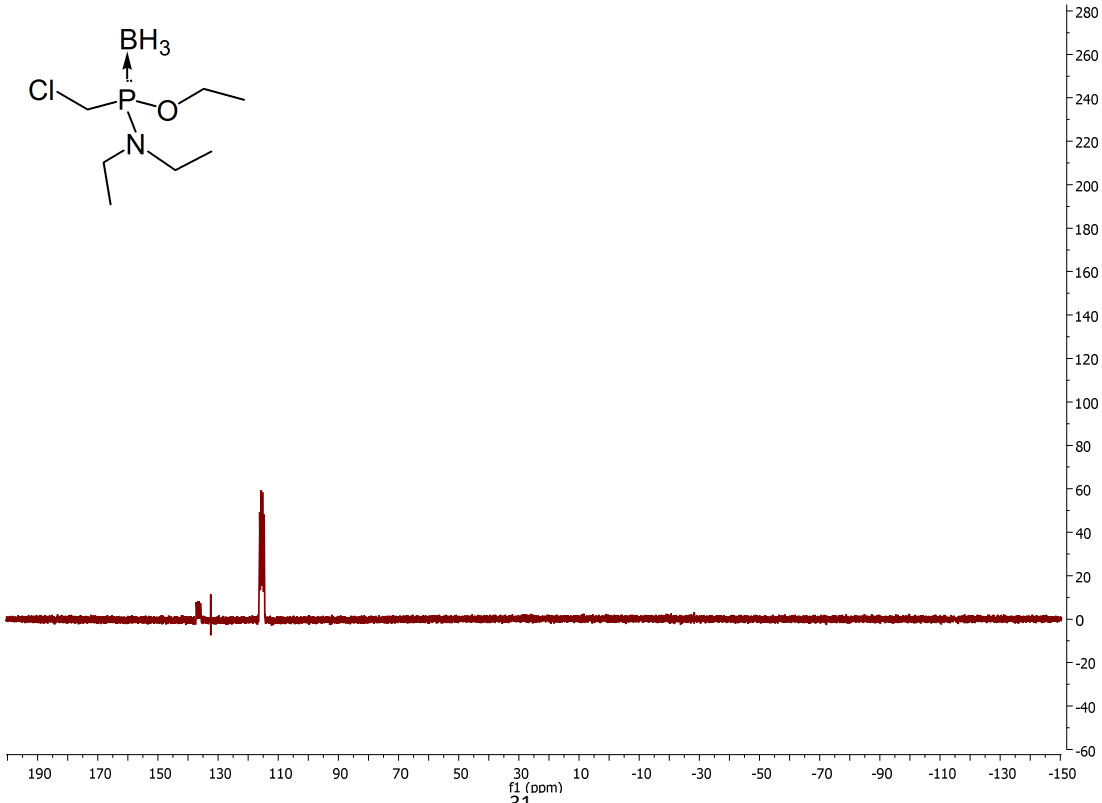

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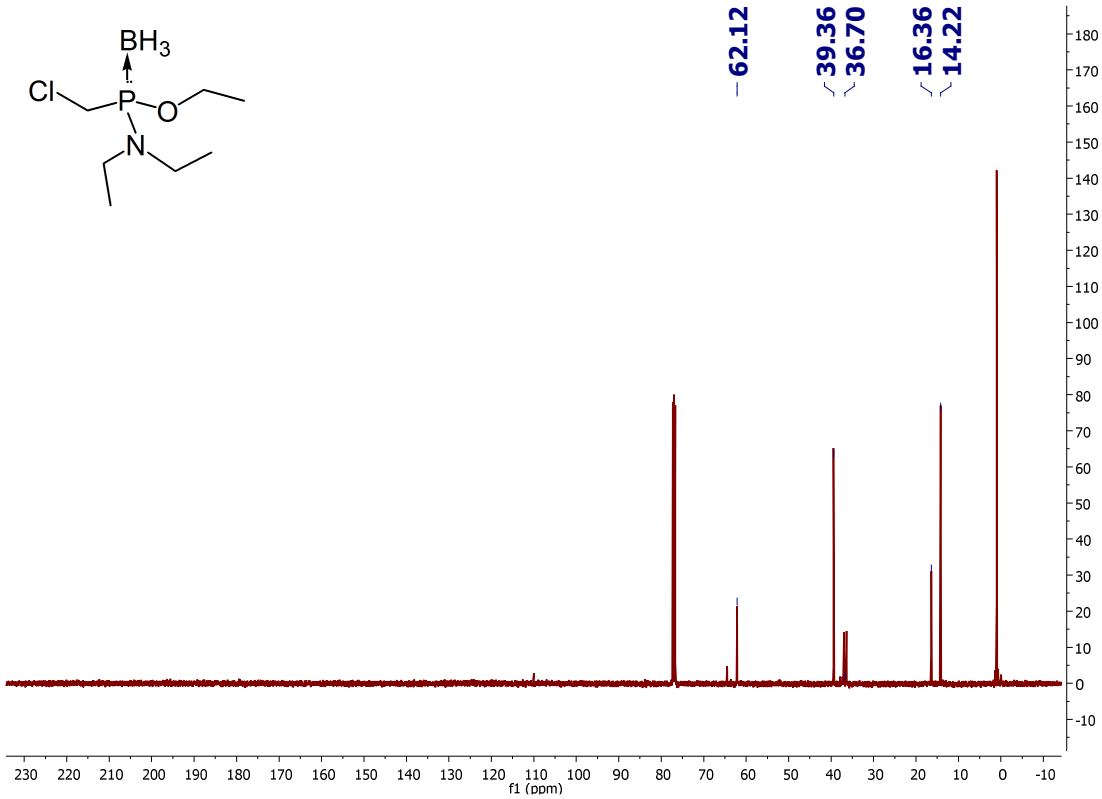

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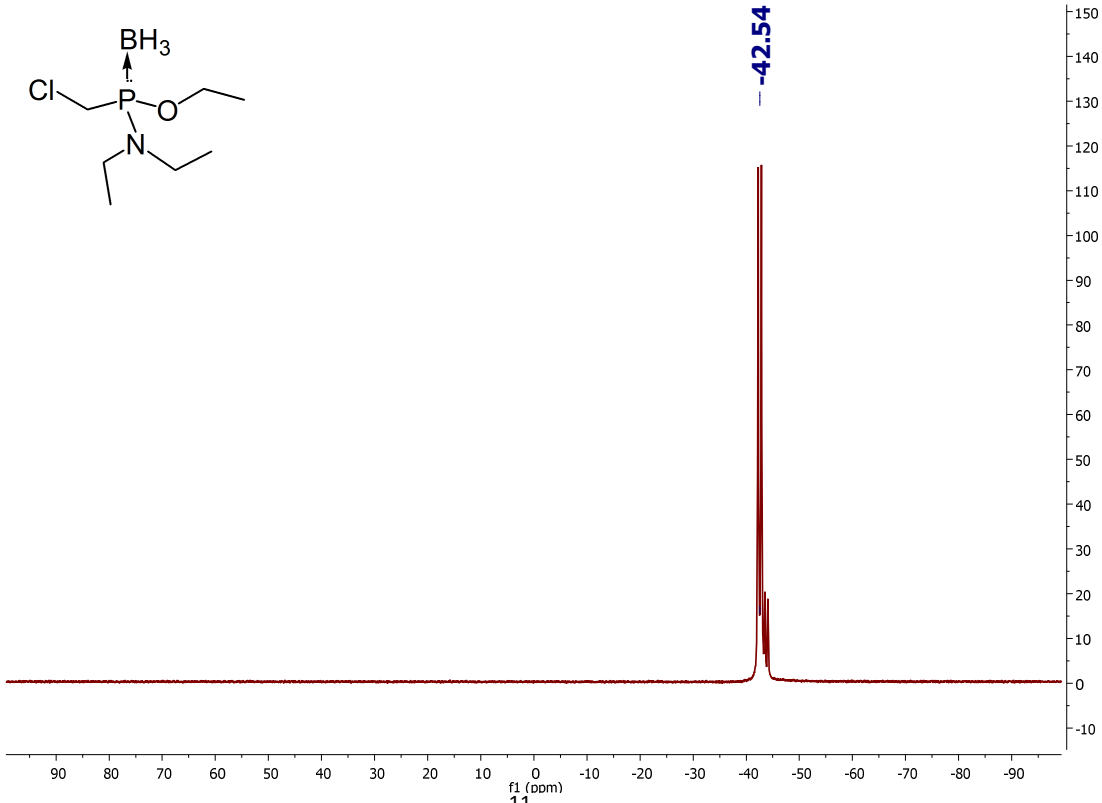

^{11}B-NMR

References

1. E. Bergin, C. T. O'Connor, S. B. Robinson, E. M. McGarrigle, C. P. O'Mahony, D. G. Gilheany, *J. Am. Chem. Soc.* **2007**, *129*, 9566-9567.
2. T. Wang, S. Sang, L. Liu, H. Qiao, Y. Gao, Y. Zhao, *J. Org., Chem.* 2014, **79**, 608.
3. W. Goldeman, T. K. Olszewski, B. Boduszek, W. Sawka-Dobrowolska, *Tetrahedron* 2006, **62**, 4506.
4. B. Xiong, X. Feng, L. Zhu, T. Chen, Y. Zhou, C.-T. Au, S.-F. Yin, *ACS Catal.* 2015, ***5***, 537.
5. T. Hirao, T. Masunaga, Y. Ohshiro, T. Agawa, *Synthesis* 1981, **1**, 56.
6. K. V. Rajendran, D. G., Gilheany, Chem. Commun**.**, 2012, **48**, 817.
7. G. Baccolini, C. Boga, M. Mazzacurati and F. Sangirardi, Org. Lett., 2006, **8**, 1677.
8. M. Stankevic, K. M. Pietrusiewicz, *Synthesis* 2005, **8**, 1279.