Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

A Convenient Chromatography-Free Method for the Purification of Alkenes Produced in the Wittig Reaction

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1. General Experimental

All chemicals were supplied by Aldrich, with the exception of Zeoprep silica, 2-methylbenzaldehyde (*o*-tolualdehyde, Fluka), (*tert*-butoxycarbonylmethyl)-triphenylphosphonium bromide (Fluka), 1 mol L^{-1} $LiAlH_4$ in THF (Acros Organics) and Merck standardised alumina 90. All chemicals were used without further purification except diethyl ether, toluene, and THF, which were processed through an Innovative Technology Inc. Pure Solv-400-3-MD solvent purification (Grubbs still) system and stored in Strauss flasks under a nitrogen atmosphere, and ethyl acetate and dichloromethane, which were degassed by passing a stream of dry nitrogen gas (oxygen-free) through the solvent for one hour for the purposes of work-ups in phosphine syntheses. All benzaldehydes (supplied by Aldrich) were checked by NMR for the presence of carboxylic axids, but no trace of acid was found and so the benzaldehydes were used without further purification. Phosphonium salts were dried in a vacuum dessicator over P_2O_5 and, together with KHMDS, NaHMDS, and commercial (*tert*-butoxycarbonylmethyl)triphenylphosphonium bromide, were stored in an MBraun glove box under an atmosphere of argon. Oxalyl chloride was stored under an atmosphere of nitrogen in a Young's flask, and dispensed by nitrogen-flushed syringe. 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylopentodialdofuranose-(1,4) was placed in a Schlenk flask under argon gas, and dissolved in dry THF to give a 0.5 mol L^{-1} solution. This solution was stored in the Schlenk flask under nitrogen at -18 ˚C in a freezer. 2-methylbenzaldehyde (*o*-tolualdehyde) was stored under nitrogen in a sealed Fluka® vessel.

NMR chemical shifts are reported in parts per million (ppm), and coupling constants (*J*) are reported in hertz (Hz). All NMR samples were made up using $CDCl_3$ as solvent. NMR spectra were obtained on Varian Inova and VNMRS 300, 400, 500 and 600 MHz spectrometers, the latter of which is equipped with a triple resonance probe. Double decoupled ^{13}C {^{1}H, ^{31}P} NMR spectra of new phosphonium salts were obtained on the 600 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts were measured relative to tetramethylsilane. ^{31}P NMR chemical shifts were measured relative to an external orthophosphoric acid standard. ^{19}F NMR chemical shifts were measured relative to

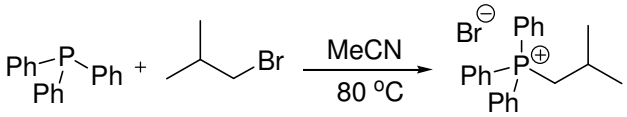
CCl_3F. In the reporting of characterisation details, the NMR signals due to aromatic hydrogen "j" (where j = 1-6) of a benzyl group are referred to as ArH-j and those due to phenyl hydrogens as PhH-j, and likewise the corresponding carbons are referred to as ArC-j and PhC-j respectively. Assignments of signals in ^{1}H and ^{13}C NMR spectra was done by reference to $^{13}C\{^{1}H, ^{31}P\}$, COSY, g HSQCAD, and gHMBCAD NMR spectra. The 1D DPFGSE-NOE NMR technique (Double Pulse Field Gradient Spin Echo Nuclear Overhauser Effect NMR spectroscopy) was used to detect NOE contacts.

High resolution mass spectra were obtained on a LCT electrospray ionisation mass spectrometer or a GCT Premier GC/MS mass spectrometer by electronic or chemical ionisation. Samples were dissolved in acetonitrile or methanol. Melting points were obtained using a Reichert Thermovar melting point apparatus, and are uncorrected. Flash column chromatography was carried out using Aldrich neutral alumina (Brockmann grade I) or Zeoprep silica. TLC was done using Merck pre-coated alumina 90 or silica 60 F-254 plates. Realisation of plates was done by UV irradiation.

All reactions described here were carried out under an atmosphere of nitrogen. The inert atmosphere was established inside a reaction flask by the standard Schlenk pump and fill technique,[1] using a Schlenk manifold that allowed each of five silicone rubber tubes to each be open either to vacuum or to the nitrogen supply by means of a three-way tap (third position is closed to both vacuum and nitrogen). The reaction flask was typically flame dried and attached to the Schlenk manifold by one of the silicone rubber tubes, and evacuated by application of a vacuum pump (Edwards RV5 rotary vane pump) while hot. The flask was allowed to cool under vacuum and then filled with nitrogen. It was then evacuated and re-filled a further two times. This technique was also applied to establish a nitrogen atmosphere in the tubing connected to a sealed Schlenk flask that already contained an inert atmosphere (nitrogen or argon gas). The flask could be opened to the nitrogen supply after the connecting tubing had been evacuated and re-filled three times. When not in use, the the open end of each length of silicone rubber tubing was fitted with a syringe barrel with an attached needle. The needle was inserted through a rubber septum into a conical flask containing dry KOH pellets, and the tip was embedded in amongst the pellets. In this manner the tubing was kept free of ambient moisture.

2. Synthesis of phosphonium salts

P-(*iso*-butyl)triphenylphosphonium bromide[2]



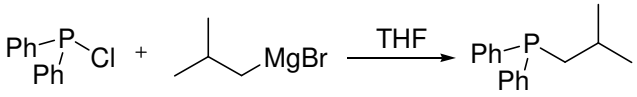
Triphenylphosphine (4.26 g, 16.2 mmol), dry acetonitrile (10 ml), and 1-bromo-2-methylpropane (2 ml, 18.4 mmol) were added to a flame dried Schlenk flask under an atmosphere of nitrogen. Stirring gave a clear solution. The flask was fitted with a reflux condenser (flame dried and connected to nitrogen supply) and the reaction mixture was heated to 80 ˚C for 3 days under a gentle flow of nitrogen. The progress of the reaction was periodically checked by taking a ^{31}P NMR spectrum of a small sample of the reaction mixture diluted with $CDCl_3$. After 3 days, the acetonitrile solvent was removed, and the residue was recrystallised from hot chloroform/ethyl acetate to give white crystals of the product in a yield of 5.5 g (13.8 mmol, 85%). The white crystals thus obtained were placed in a dessicator under nitrogen and dried using phosphorus pentoxide and calcium chloride, and then placed in a glove box under an atmosphere of argon.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 6H, PhH-2), 7.79 (m, 3H, PhH-4), 7.71 (m, 6H, PhH-3), 3.80 (dd, J = 12.9, 6.2, 2H, PCH_2), 2.18 – 1.99 (m, 1H, CHMe$_2$), 1.08 (d, J = 6.7, 6H, CH(CH_3)$_2$).[2]

^{31}P NMR (162 MHz, $CDCl_3$): δ 23.0.

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9 (d, J = 3.0, PhC-4), 133.7 (d, J = 10.0, PhC-2), 130.4 (d, J = 12.5, PhC-3), 119.0 (d, J = 85.3, PhC-1), 30.5 (d, J = 47.4, P-CH_2), 24.6 (d, J = 4.3, CHMe$_2$), 24.34 (d, J = 9.2, CH(CH_3)$_2$).[2]

iso-Butyldiphenylphosphine[3]

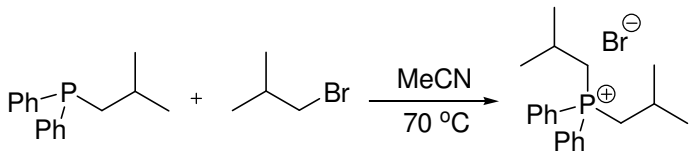


Chlorodiphenylphosphine (8.5 ml, 46.0 mmol) was transferred from a Young's flask to a flame-dried Schlenk tube under a nitrogen atmosphere, and dissolved in dry THF (60 ml). The yellow solution was cooled to 0 ˚C and a 2.0 mol L^{-1} solution of *iso*-propyl magnesium chloride in Et_2O (29 ml, 58 mmol) was added dropwise. The solution became cloudy as addition neared completion. Once addition of the Grignard reagent was complete, the reaction mixture was allowed to warm to room temperature. ^{31}P NMR (inert atmosphere) of a small sample (0.3 ml) of the reaction mixture diluted with dry degassed $CDCl_3$ (0.5 ml) showed it to contain only phosphine (δ_P = -20 ppm). The reaction mixture was quickly poured into a degassed mixture of CH_2Cl_2 (150 ml) and saturated NH_4Cl solution (150 ml) under a nitrogen atmosphere in a separatory funnel. All remaining manipulations were carried out under inert atmosphere. The biphasic mixture was shaken, and then the organic layer was allowed to drain into a flame-dried round bottom flask (connected to nitrogen supply) containing Na_2SO_4. After shaking the resulting mixture, the supernatatnt solution was transferred by cannula into a frit, and filtered into a Schlenk flask connected to the frit to remove the drying agent. The solvent was removed from the filtrate *in vacuo*. The resulting yellow oil was purified by vacuum distillation (10^{-2} mbar, bath temperature 156 ˚C) using a short range distillation apparatus, giving a clear oil (7.5 g, 68%).

^1H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 4H), 7.36 – 7.27 (m, 6H), 1.99 (d, *J* = 7.0, 2H), 1.68 (dd, *J* = 14.3, 7.1, 1H), 1.02 (dd, *J* = 14.0, 6.2, 6H).[3]

^{31}P NMR (121 MHz, $CDCl_3$) δ -19.9 (lit.[3] -19.4)

Di(*iso*-butyl)diphenylphosphonium bromide



iso-Butylduphenylphosphine (4.8 ml, 20 mmol) and *iso*-butyl bromide (6.5 ml, 60 mmol) were dissolved in dry acetonitrile in a flame dried Schlenk flask fitted with a reflux condenser under a nitrogen atmosphere. The solution was stirred for one week at 70 ˚C. Reaction progress was monitored periodically by taking a ^{31}P NMR spectrum of a small sample of the reaction mixture. Once all the phosphine was consumed, the solvent was removed *in vacuo*, and the residue was crytallised from hot chloroform/ethyl acetate. The resulting white crystals were dried under vacuum in a dessicator containing $CaCl_2$ and P_2O_5 and stored under argon gas in a glove box. Yield = 6.8 g (90%).

^{1}H NMR (500 MHz, cdcl$_3$) δ 8.00 – 7.93 (m, 4H), 7.81 – 7.75 (m, 2H), 7.73 – 7.66 (m, 4H), 3.35 (dd, *J* = 12.8, 6.5, 4H), 1.98 – 1.85 (m, 2H), 0.96 (dd, *J* = 6.7, 0.8, 12H).

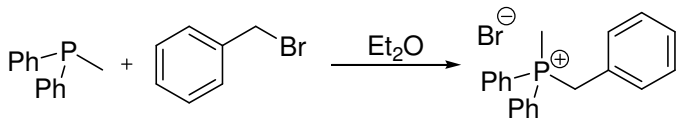
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6 (d, *J* = 3.0), 133.3 (d, *J* = 9.4), 130.2 (d, *J* = 12.0), 118.9 (d, *J* = 80.9), 30.7 (d, *J* = 46.6), 24.3 (dd, *J* = 18.6, 6.8).

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.0.

HRMS: Calc. for $[M]^+ = C_{20}H_{28}P$ 299.1929; found 299.1928 (0.2 ppm).

MP (crystallised from $CHCl_3$/EtOAc) 183-184 °C.

Benzylmethyldiphenylphosphonium bromide[4]



A Schlenk flask was charged with nitrogen using the standard Schlenk pump and fill technique.[1] Methyldiphenylphosphine[5] (3.50 ml, 18.6 mmol) was transferred from a Young's flask to the Schlenk flask by nitrogen-flushed syringe. Dry diethyl ether (30 ml) was added to give a clear solution of the phosphine. Benzyl bromide (2.5 ml, 21 mmol) was then added by syringe. The solution turned a cloudy white colour upon addition. The solution was left to stir for 2 days, after which time a white solid was observed in the flask. The solid was isolated by filtration under suction. This solid was recrystallised from hot chlorform/ethyl acetate and the crystals isolated by filtration under suction. The filtrate was retained and yielded further crystals after standing for a period. The crystals (6.51g , 94% yield) were dried in a vacuum dessicator over P_2O_5 and $CaCl_2$ for several days before being transferred to a glove box under argon.

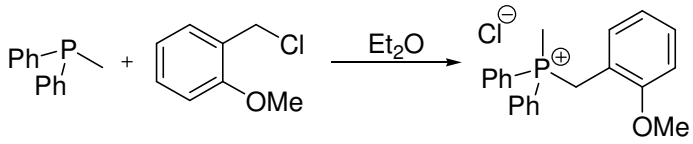
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (m, 4H, ArH-2), 7.70 (m, 2H, ArH-4), 7.60 (m, 4H, PhH-3), 7.27 (m, 2H, ArH-2), 7.20 (m, 1H, ArH-4), 7.13 (m, 2H, ArH-3), 4.91 (d, $^{2}J_{PH}$ = 15.4, 2H, CH_2), 2.70 (d, $^{2}J_{PH}$ = 13.7, 3H, CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ 23.8.

^{13}C NMR (126 MHz, $CDCl_3$): δ 134.5 (d, $^{4}J_{PC}$ = 3.2 Hz, PhC-4), 132.9 (d, $^{2}J_{PC}$ = 9.9 Hz, PhC-2), 130.8 (d, $^{3}J_{PC}$ = 5.6 Hz, ArC-2), 129.8 (d, $^{3}J_{PC}$ = 12.6 Hz, PhC-3), 128.7 (d, $^{4}J_{PC}$ = 3.6 Hz, ArC-3), 128.1 (d, $^{5}J_{PC}$ = 4.2 Hz, ArC-4), 127.4 (d, $^{2}J_{PC}$ = 9.2 Hz, ArC-1), 118.7 (d, $^{1}J_{PC}$ = 85.0 Hz, PhC-1), 30.5 (d, $^{1}J_{PC}$ = 47.6 Hz, CH_2), 7.1 (d, $^{1}J_{PC}$ = 56.4 Hz, CH_3).

HRMS (m/z): Calc. for $[M]^+ = C_{20}H_{20}P$ 291.1303; found 291.1296 (2.4 ppm).

2-Methoxybenzylmethyldiphenylphosphonium chloride



A Schlenk flask was charged with nitrogen using the standard Schlenk pump and fill technique.[1] Methyldiphenylphosphine[5] (4.1 ml, 4.3 g, 21.6 mmol) was transferred from a Young's flask to the Schlenk flask by nitrogen-flushed syringe. Dry diethyl ether (35 ml) was added to give a clear solution of the phosphine. 2-methoxybenzyl chloride (3.3 ml, 3.7 g, 23.8 mmol) was then added by syringe. The solution turned a cloudy white colour upon addition. The solution was left to stir for 2 days, after which time a white solid was observed in the flask. The solid was isolated by filtration under suction. This solid was recrystallised from hot chlorform/ethyl acetate and the crystals isolated by filtration under suction. The filtrate was retained and yielded further crystals after standing for a period. The crystals (7.52 g, 98% yield) were dried in a vacuum dessicator over P_2O_5 and $CaCl_2$ for several days before being transferred to a glove box under argon.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (m, 4H, PhH-2), 7.71 (m, 2H, PhH-4), 7.64 (m, 1H, ArH-6), 7.60 (m, 4H, PhH-3), 7.23 (m, 1H, ArH-4), 6.87 (m, 1H, ArH-5), 6.66 (m, 1H, ArH-3), 4.79 (2H, d, $^2J_{PH}$ = 15.2, CH_2), 3.20 (s, 3H, OCH_3), 2.75 (d, $^2J_{PH}$ = 13.6, 3H, CH_3),

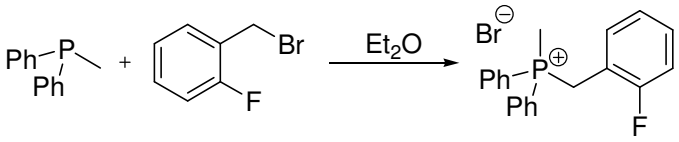
^{31}P NMR (202 MHz, $CDCl_3$): δ 22.9.

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.8 (d, J_{PC} = 5.6, ArC-5), 134.5 (d, J_{PC} = 2.8, PhC-4), 133.0 (d, J_{PC} = 10.1, PhC-2), 132.8 (d, J_{PC} = 5.6, ArC-6), 130.0 (d, J_{PC} = 3.9, ArC-4), 129.7 (d, J_{PC} = 12.3, PhC-3), 121.3 (d, J_{PC} = 3.4, ArC-5), 119.7 (d, $^1J_{PC}$ = 83.6, PhC-1), 115.9 (d, $^2J_{PC}$ = 7.0, ArC-1), 110.3 (d, J_{PC} = 3.3, ArC-3), 54.8 (s, OCH$_3$), 25.4 (d, $^1J_{PC}$ = 48.8, CH$_2$), 8.0 (d, $^1J_{PC}$ = 56.7, CH$_3$).

HRMS (m/z): Calc. for $[M]^+ = C_{21}H_{22}PO$ 321.1408; found 321.1410 (0.6 ppm).

MP (crystallised from $CHCl_3$/EtOAc) 188-191 °C.

2-Fluorobenzylmethyldiphenylphosphonium bromide



A Schlenk flask was charged with nitrogen using the standard Schlenk pump and fill technique.[1] Methyldiphenylphosphine[5] (3.8 ml, 4.05 g, 20 mmol) was transferred from a Young's flask to the Schlenk flask by nitrogen-flushed syringe. Dry diethyl ether (32 ml) was added to give a clear solution of the phosphine. 2-fluorobenzyl bromide (2.65 ml, 4.16 g, 22 mmol) was then added by syringe. The solution turned a cloudy white colour upon addition. The solution was left to stir for 2 days, after which time a white solid was observed in the flask. The solid was isolated by filtration under suction. This solid was recrystallised from hot chlorform/ethyl acetate and the crystals isolated by filtration under suction. The filtrate was retained and yielded further crystals after standing for a period. The crystals (7.59g, 97% yield) were dried in a vacuum dessicator over P_2O_5 and $CaCl_2$ for several days before being transferred to a glove box under argon.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96-7.88 (m, 4H, PhH-2), 7.82-7.77 (m, 1H, ArH-6), 7.76-7.72 (m, 2H, PhH-4), 7.64-7.60 (m, 4H, PhH-3), 7.24 (m, 1H, ArH-4), 7.06 (t, ^2J = 7.6 Hz, 1H, ArH-5), 6.87 (m, 1H, ArH-3), 4.95 (d, $^3J_{PH}$ = 15.4, 2H, CH_2), 2.79 (d, $^3J_{PH}$ = 13.6, 3H, CH_3).

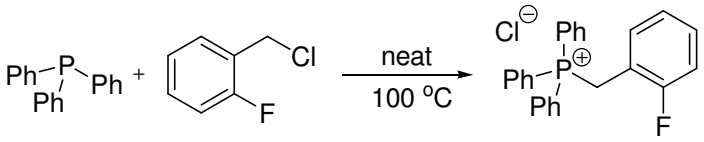
^{31}P NMR (202 MHz, $CDCl_3$): δ 22.5.

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.9 (dd, J_{PC} = 6.1, J_{FC} =247.6 , ArC-2), 135.1 (d, J_{PC} = 3.1, PhC-4), 133.4 (dd, J = 5.1, 2.7, ArC-6), 133.2 (d, J = 10.0, PhC-2), 130.8 (dd, J_{PC} = 3.9, J_{FC} = 8.2, ArC-4), 130.2 (d, J_{PC} = 12.6, PhC-3), 125.2 (app t, J = 3.5, ArC-5), 118.8 (d, J_{PC} = 84.6, PhC-1), 115.7 (dd, J_{PC} = 3.2, J_{FC} = 21.8, ArC-3), 115.2 (dd, J_{PC} = 8.6, J_{FC} =14.9, ArC-1), 24.7 (d, J_{PC} = 49.8, CH$_2$), 8.0 (d, J_{PC} = 56.2, CH$_3$).

HRMS (m/z): Calc. for $[M]^+ = C_{20}H_{19}PF$ 309.1208; found 309.1209 (0.3 ppm).

MP (crystallised from $CHCl_3$/EtOAc) 202-204 °C.

2-fluorobenzyltriphenylphosphonium chloride[6]

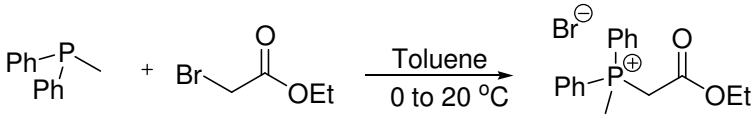


Triphenylphosphine (20.0 g, 76.3 mmol) was added to a Schlenk flask under N_2. The reaction flask containing the triphenylphosphine was then placed in an oil bath and heated to 100 °C. Triphenylphosphine is a liquid at this temperature,[7] and thus can be used as the reaction solvent. 2-fluorobenzyl chloride (14.4 g, 76.3 mmol) was then added. A white solid formed in the flask virtually instantly after addition of the benzyl bromide, and all of the triphenylphosphine was observed to have disappeared. After approximately 10 minutes, the reaction flask was removed from the oil bath and allowed to cool to room temperature. The white solid was difficult to remove from the sides of the flasks, so dichloromethane was added to aid removal of the solid from the flask. The suspension of the salt in the dichloromethane was transferred to a round bottomed flask and the solvent was removed *in vacuo*. The white salt was recrystallised from chloroform/ethyl acetate and the crystals (30.1 g, 88% yield) isolated by filtration under suction.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.51 (m, 15H), 7.36 (m, 1H), 7.16 (m, 1H), 6.85 (app. t, J = 7.5, 1H), 6.72 (app. t, J = 9.1, 1H), 5.35 (d, J = 14.4, 2H).[6]

^{31}P NMR (121 MHz, $CDCl_3$) δ 22.4.

(Ethoxycarbonylmethyl)methyldiphenylphosphonium bromide[8]



A solution of methyldiphenylphosphine (0.60 ml, 0.64 g, 3.2 mmol) in dry toluene (3 ml) was prepared in a Schlenk flask under an atmosphere of nitrogen. This was cooled to 0 °C in an ice bath, and ethyl bromoacetate (0.36 ml, 1.54 g, 3.2 mmol) was added slowly

by syringe. A white solid was seen to form in the reaction mixture almost instantly. The reaction mixture was stirred for overnight at room temperature, after which time only a white solid was present in the reaction flask. This was isolated by filtration, washed extensively with toluene, and then recrystallised from hot chloroform/ethyl acetate to give white crystals, which were dried using phosphorus pentoxide in a vacuum dessicator. The dry crystals (1.01 g, 86%) were stored in a glove box under argon gas.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.87 (m, 4H, PhH-2), 7.84 – 7.72 (m, 2H, PhH-4), 7.71 – 7.59 (m, 4H, PhH-3), 5.11 (d, *J* = 13.9, 2H, PC*H*$_2$), 4.07 (d, *J* = 7.1, 2H, OC*H*$_2$), 3.06 (d, *J* = 14.3, 3H, PC*H*$_3$), 1.10 (t, *J* = 7.1, 3H, OCH_2CH_3).[8]

^{31}P NMR (121 MHz, $CDCl_3$) δ 21.3 (lit.[8] 22).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (d, *J* = 4.0, C=O), 134.9 (d, *J* = 3.0, PhC-4), 132.8 (d, *J* = 10.6, PhC-2), 130.1 (d, *J* = 13.1, PhC-3), 118.9 (d, *J* = 87.9, PhC-1), 62.7 (s, O*C*H$_2$), 32.0 (d, *J* = 57.6, P*C*H$_2$), 13.8 (s, OCH_2CH_3), 9.7 (d, *J* = 56.3, P*C*H$_3$).

3. Procedure for Wittig reaction & phosphine oxide removal

Wittig Reaction

Dry phosphonium salt (1.0 equivalent) and NaHMDS or KHMDS (1.0-1.1 equivalents) were placed in a flame-dried Schlenk flask in a glove box under an atmosphere of argon. The flask was sealed, removed from the glove box and charged with an atmosphere of nitrogen by the pump and fill technique[1] using a Schlenk manifold. Sufficient dry THF was added to give an ylide solution of 0.2 mol L^{-1} concentration. A precipitate of alkali metal halide formed upon stirring and the solution was orange or yellow coloured for non-stabilised and semi-stabilised ylides, and pale yellow or colourless for ester-stabilised ylides. The ylide solution was stirred for one hour for semi-stabilised and ester-

stabilised ylides, 15-20 minutes for non-stabilised ylides. The ylide solution was either maintained at room temperature (20 °C) or cooled to -20 °C or -78 °C (reaction temperature specified for each reaction below), and then the aldehyde (1.0 equivalent, neat or as a solution in dry THF) was added dropwise, causing the ylidic colour to fade.

Work-up

Unless otherwise stated, reactions carried out at low temperature were maintained at that temperature for 15 minutes, then allowed to warm to room temperature (20 °C). All such reactions were stirred for 12 hours at 20 °C, after which time the THF solvent was removed *in vacuo* to give the crude product. Dichloromethane (15 ml) and saturated NH_4Cl solution (5 ml) were added to the mixture, which was transferred to a separatory funnel. The phases were separated and the aqueous layer was washed twice more with dichloromethane (10 ml). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated to give a crude product containing only alkene, phosphine oxide (mostly derived from the Wittig reaction, but some from aqueous hydrolysis of the ylide or starting phosphonium salt), and a small amount of aldehyde. This mixture was characterised by NMR.

This general procedure was employed for all Wittig reactions carried out, with the exception of the reaction of *iso*-propylidenetriphenylphosphorane and cyclopentanecarbaldehyde giving 1-cyclopentyl-3-methylbut-1-ene, where diethyl ether was used in place of THF.

Procedures for removal of phosphine oxide & aldehyde from Wittig crude product

(a) *Cyclohexane procedure*

Oxalyl chloride (1.1-2.0 equivalents) was added to the crude product by nitrogen-flushed syringe. Gas was evolved very vigourously. Cyclohexane (10 ml) was added immediately, causing the formation of a two-phase mixture; the upper phase consisted of a cyclohexane solution (often yellow), the lower a yellow oil or solid containing aldehyde mixed with chlorophosphonium salt. The cyclohexane phase was carefully decanted into another flask. The residue was washed a further five times with cyclohexane (5 ml

aliquots), and the washings were transferred to the second flask. This (clear or yellow) solution was filtered via cannula (using a Whatman GFD grade glass microfibre filter). The cyclohexane filtrate was washed twice with saturated aqueous $NaHCO_3$ to quench & remove the remaining oxalyl chloride, and then twice with a 1 mol L^{-1} aqueous solution of HCl. The resulting solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the product alkene. ^{1}H and ^{31}P NMR analysis of this product showed there to be no aldehyde or phosphorus-containing material present, only *Z* and *E* isomers of alkene. Comparison of the NMR spectra from before & after oxalyl chloride treatment in all cases showed the alkene *Z/E* ratio to be unchanged.

(b) *Cold Et_2O procedure*

The reaction was not subjected to aqueous work-up. The reaction solvent was removed *in vacuo*. To the Schlenk flask containing the crude product (under nitrogen atmosphere) was added oxalyl chloride (1.1-2.0 equivalents), causing the evolution of gas. A yellow solid or viscous oil was formed almost instantaneously, and the reaction mixture was stirred at 20 ºC for five minutes, and then cooled to -78 ºC. Dry degassed Et_2O (15 ml) was added, and the mixture was stirred for a further five minutes. Stirring was then ceased, and the cold ethereal solution was filtered by cannula into a separatory funnel. The residue in the Schlenk flask was washed a further five times with Et_2O (10 ml each), and the washings were filtered by cannula into the separatory funnel. Significant care was necessary during the filtration to keep the tip of the cannula away from the oily residue; thus not all of the Et_2O was transferred in each wash. The filtrate was washed twice with saturated aqueous $NaHCO_3$ (5 ml each) to quench & remove the remaining oxalyl chloride, and then twice with saturated NH_4Cl solution (5 ml each). The resulting solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the product alkene. NMR analysis of this product showed there to be no phosphorus present in the product. Comparison of the NMR spectra from before & after oxalyl chloride treatment in all cases showed the alkene *Z/E* ratio to be unchanged.

Regeneration of phosphine from filtration residue

Note that the best results for phosphine regeneration were obtained if the initial Wittig crude product was subjected to a preliminary aqueous work-up – see the description given above.

The chlorophosphonium salt-containing residue (contained in a Schlenk flask) remaining after removal of the cyclohexane solution of alkene by cannula filtration was charged with nitrogen by the Schlenk pump and fill technique.[1] Dry THF was added and the resulting solution was cooled to -78 °C. A solution of $LiAlH_4$ in THF (1 mol L^{-1}, 1.2 equivalents) was added dropwise, causing the evolution of hydrogen gas from the solution.

After addition was complete, the remaining $LiAlH_4$ was quenched by one of two methods. In the first, degassed ethyl acetate (20 ml) was added to quench excess $LiAlH_4$. The solvent was removed *in vacuo* and a small sample of the residue was removed and analysed by ^{1}H and ^{31}P NMR. Degassed ethyl acetate (20 ml) was added to the residue, and the resulting mixture was then washed with degassed saturated ammonium chloride solution (2 x 10 ml), and dried over $MgSO_4$, all under an atmosphere of nitrogen. In the second method, the reaction mixture was quickly poured into a separatory funnel (connected to nitrogen supply) containing a degassed mixture of dichloromethane (20 ml) and saturared NH_4Cl solution (10 ml). The reaction flask was then washed with degassed dichloromethane and the washings were also transferred. After shaking the biphasic mixture, the organic phase was allowed to run off. The aqueous phase was washed with further degassed dichloromethane (15 ml) and the organic phases were combined, and dried over $MgSO_4$. These procedures were carried out under an atmosphere of nitrogen when handling methyldiphenylphosphine. The second method (CH_2Cl_2/NH_4Cl work-up) was found to result in higher yields of phosphine and lower amounts of side-products.

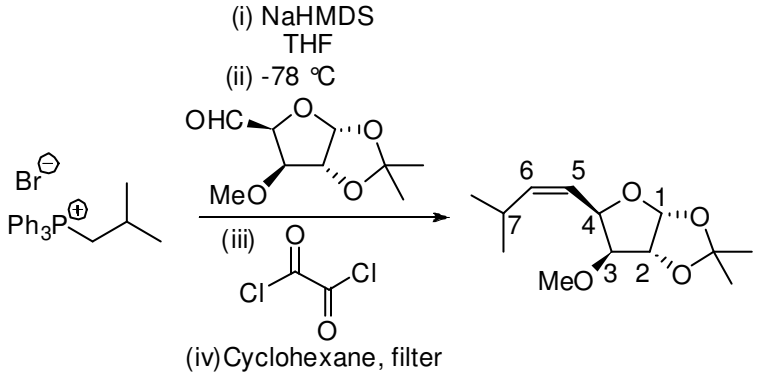
The dried solution of phosphine (in ethyl acetate or dichloromethane) was filtered (using inert atmosphere filtration apparatus,[1] and collecting in a Schlenk flask under nitrogen if dealing with the air-sensitive methyldiphenylphosphine), and the solvent was then

removed *in vacuo*, yielding the phosphine product, generally free of phosphine oxide. Triphenylphosphine was isolated as a white crystalline solid, δ_P ($CDCl_3$, 121 MHz) -5.3; lit[9] -4.8, and methyldiphenylphosphine was isolated as a clear oil δ_P ($CDCl_3$, 121 MHz) -26.8 (lit.[10] -26.3). In instances where small amounts of phosphine oxide were present, it could be removed by elution of the product through a short plug of silica using degassed ethyl acetate, dichloromethane or cyclohexane as solvent. If non-degassed solvents are used for the work-up procedure, significant quantities of phosphine oxide are present in the product arising from oxidation of the phosphine in solution.

4. Characterisation of purified alkenes

The characterisation data for alkenes purified by oxalyl chloride treatment is listed below, and is presented in the order in which the compounds appear in Table 1.

1. Reaction of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylopentodialdo-furanose-(1,4) with *P*-(*iso*-butylidene)triphenylphosphorane. Table 1 entry 1.



From *iso*-butyltriphenylphosphonium bromide (61 mg, 0.15 mmol), KHMDS (28 mg, 0.14 mmol) and 1,2-O-isopropylidene-3-O-methyl-α-D-xylopentodialdofuranose-(1,4) (0.31 ml of a 0.5 mol L^{-1} solution in THF, 0.15 mmol) at -78 °C in THF. The crude product was treated with oxalyl chloride (0.014 ml, 0.17 mmol) and purified using cyclohexane as the filtration solvent to give the *Z*-alkene as a clear oil (34 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (d, *J* = 3.9, 1H, H-1), 5.55 – 5.49 (m, 1H, H-6), 5.48 – 5.41 (m, 1H, H-5), 4.93 (dd, *J* = 8.2, 3.0, 1H, H-4), 4.59 (d, *J* = 3.9, 1H, H-2), 3.59 (d, *J* = 3.1, 1H, H-3), 3.40 (s, 3H, OMe), 2.70 – 2.58 (m, 1H, H-7), 1.52 (s, 3H, acetonide CH_3), 1.34 (s, 3H, acetonide CH_3), 1.01 & 0.99 (2 x d, *J* = 6.6, 6H, CH(CH_3)$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4 (C-6), 120.7 (*C*Me_2), 111.3 (C-5), 104.6 (C-1), 86.2 (C-3), 82.3 (C-2), 75.8 (C-4), 58.2 (OMe), 27.5 (*C*H(CH_3)$_2$), 26.8 & 26.2 (diastereotopic acetonide *C*H_3), 23.3 & 23.0 (diastereotopic CH(*C*H_3)$_2$).

HRMS (m/z): Calc. for $[M]^+ = C_{13}H_{22}O_4$; found 242.1518 (0 ppm).

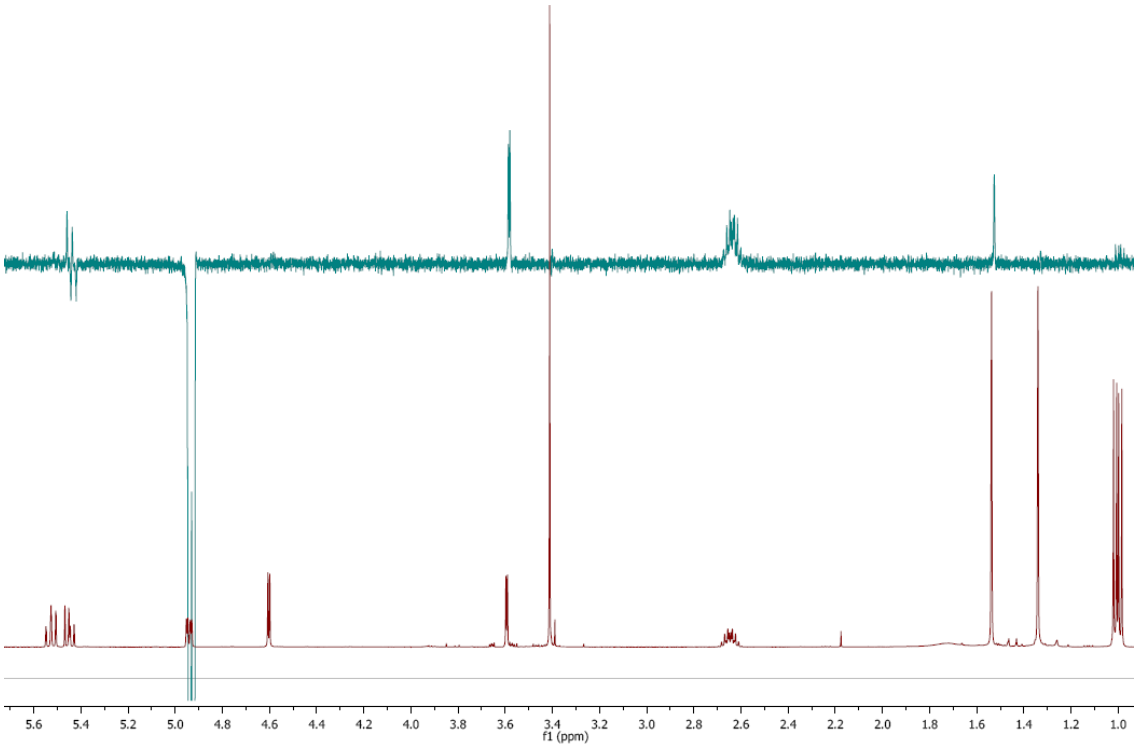
IR: 2970-2850 (m, C-H stretch), 1735 (w), 1658 (w), 1466 (w), 1380 (m, CMe_2 bend), 1261 (m), 1216 (m), 1165 (m), 1118)s), 1081 (s), 1022 (s), 863 (m), 796 (m).

2D NOESY (500 MHz, $CDCl_3$, 800 ms mixing time): NOE contact shown between H-4 and H-3 and between H-4 and H-7.

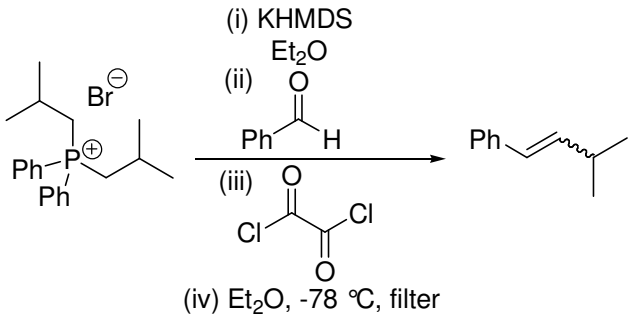
1D DPFGSE-NOE (500 MHz, $CDCl_3$, 800 ms mixing time): The sample was irradiated at the resonance frequency of H-4 (signal at δ 4.93 ppm). NOE contact can be seen with H-3 (δ 3.59), H-7 (δ 2.70-2.58), one of the acetonide methyl groups (δ 1.52) and with the *iso*-propyl methyl groups (δ 1.01-0.99, small contact). See Fig. 1.

From these NOE experiments, the stereochemistry of the alkene double bond is demonstrated to be *Z* (based on NOE contact of H-4 and H-7) and the relative stereochemistry of H-3 and H-4 is shown to be *cis,* as it had been in the starting aldehyde. No epimerisation can have occurred at C-4 under the reaction conditions.

Fig. 1. ^{1}H NMR (bottom) and 1D DPFGSE-NOE spectra of purified *Z*-alkene (top).



2. 3-methyl-1-phenylbut-1-ene.[11] Table 1 entry 2.

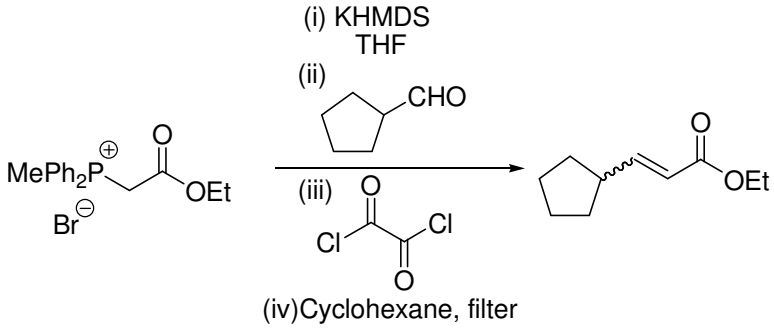


From di(*iso*-butyl)diphenylphosphonium bromide (188 mg, 0.496 mmol), KHMDS (108 mg, 0.541 mmol) and benzaldehyde (60 mg, 0.57 mmol) in Et_2O (5 ml) at 20 °C. The crude product was not subjected to aqueous work-up, but treated with oxalyl chloride (0.07 ml, 0.11 g, 0.8 mmol) and purified using Et_2O at -78 °C as the filtration solvent to give the product alkene (69 mg). NMR analysis of this product showed there to be no phosphorus present in the product, although a small amount of benzaldehyde remained

(3% based on integration in ^{1}H NMR). Taking into account this residual aldehyde, the amount of alkene recovered was 67 mg (93%).

^{1}H NMR (300 MHz, $CDCl_3$) of alkene product (*Z*/*E* = 20:80):
Assigned to *E*-isomer: δ 6.18 (dd, *J* = 15.9, 6.6, 1H, *i*-PrC*H*=C), 2.56-2.37 (m, 1H, C*H*Me_2), 1.09 (d, *J* = 6.7, 6H, CH(CH_3)$_2$).[11]
Assigned to *Z*-isomer: δ 5.47 (dd, *J* = 11.5, 10.3, 1H, *i*-PrC*H*=C), 3.00 – 2.80 (m, 1H, C*H*Me_2), 1.04 (d, *J* = 6.6, 6H, CH(CH_3)$_2$).[11]
Overlapping signals due to both isomers (integrations relative to 1H of *E*-isomer):
δ 7.38-7.14 (m, contains C*H*Cl_3), 6.38-6.26 (m, overlapping dd signals, 1.25H, *E* & *Z* PhC*H*=C).[11]

3. Ethyl 3- cyclopentylprop-2-enoate.[12] Table 1, entry 3.

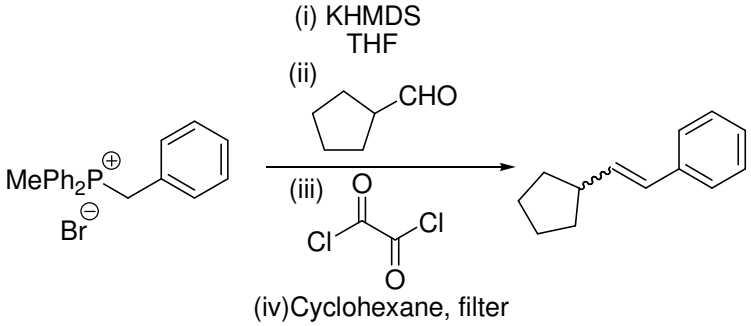


From (ethoxycarbonylmethyl)methyldiphenylphosphonium bromide (101 mg, 0.275 mmol), KHMDS (55 mg, 0.276 mmol) and cyclopentanecarbaldehyde (28 mg, 0.28 mmol) at 20 °C in THF. The crude product was treated with oxalyl chloride (0.03 ml, 0.35 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (42 mg, 91%).

^{1}H NMR (300 MHz, $CDCl_3$) of purified mixture of alkenes (*Z*/*E* = 10:90):
Assigned to *E*-isomer: δ_H 6.94 (dd, *J* = 15.6, 8.0, 1H, H-3), 5.79 (dd, *J* = 15.6, 1.0, H-2).[12]
Assigned to *Z*-isomer: δ_H 6.11 (dd, *J* = 11.3, 10.0, 1H, H-3), 5.69 (d, *J* = 11.5, 1H, H-2).[12]

Other signals were also present in which overlap occurred between the signals of the alkene diastereomers (integrations are relative to 1 H of the *E*-isomer):
δ_H 4.24 – 4.13 (m, 2.22H, C*H*$_2$Me), 2.68 – 2.50 (m, 1.11H, ring H-1), 1.91 – 1.77 (m, 2.3H), 1.77 – 1.51 (m, 4.6H), 1.45-1.32 (m, integration obscured by residual cyclohexane) 1.29 (t, *J* = 7.1, 3.4H, *E* & *Z*-C*H*$_3$).[12]

4. 1-cyclopentyl-2-phenylethene[13,14] Table 1, entry 4



From benzylmethyldiphenylphosphonium bromide (327 mg, 0.880 mmol), KHMDS (176 mg, 0.880 mmol) and cyclopentanecarbaldehyde (90 mg, 0.92 mmol) at 20 °C in THF. The crude product was treated with oxalyl chloride (0.10 ml, 11 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (0.13 g, 87%).

^{1}H NMR (300 MHz, $CDCl_3$) of purified mixture of alkenes (*Z*/*E* = 10:90):

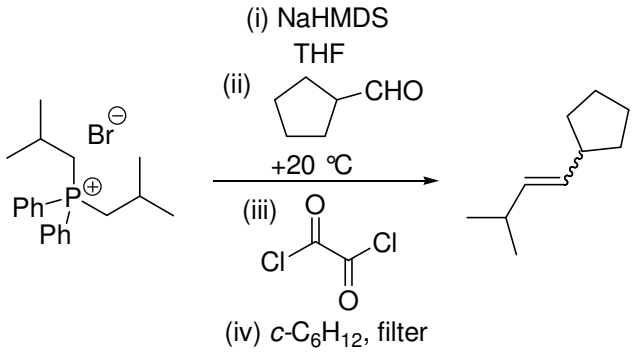
Assigned to *E*-isomer: δ 6.20 (1H, dd, *J* 15.8, 7.6, H-1), 2.68 – 2.49 (1 H, m, -C_5H_9 H-1).[13,14]

Assigned to *Z*-isomer: δ 5.58 (1 H, dd, *J* 11.3, 10.2, H-1), 3.01 – 2.87 (1 H, m, *c*-C_5H_9 H-1).[13,14]

Other signals were also present in which overlap occurred between the signals of the alkene diastereomers (integrations are relative to 1H of the *E*-isomer):

δ 7.38 – 7.24 (4.8 H, m), 7.20-7.14 (1 H, m), 6.43 – 6.30 (1.1 H, m, contains d, *J* 15.9, *E* and *Z* H-2), 1.85 (2.2 H, m), 1.79 – 1.30 (m, *c*-C_5H_9 signals, integration obscured by signals of H_2O and residual cyclohexane).[13,14]

5. 1-cyclopentyl-3-methylbut-1-ene. Table 1 entry 5.



From di(*iso*-butyl)diphenylphosphonium bromide (595 mg, 1.57 mmol), KHMDS (313 mg, 1.57 mmol) and cyclopentanecarbaldehyde (0.16 g, 0.17 ml, 1.6 mmol) by procedure B at 20 °C in THF. The crude product was treated with oxalyl chloride (0.13 ml, 0.20 g, 1.54 mmol) and purified using cyclohexane as the filtration solvent to give the phosphorus-free product as a clear oil, which was immediately characterised. The oil was found to decompose if left to stand, but to be slightly longer-lived if kept in solution. Due to the decomposition of the alkene, accurate HRMS or IR data could not be obtained. The *Z/E* ratio of the alkene product was found to be 12:88.

E-1-cyclopentyl-3-methylbut-1-ene:

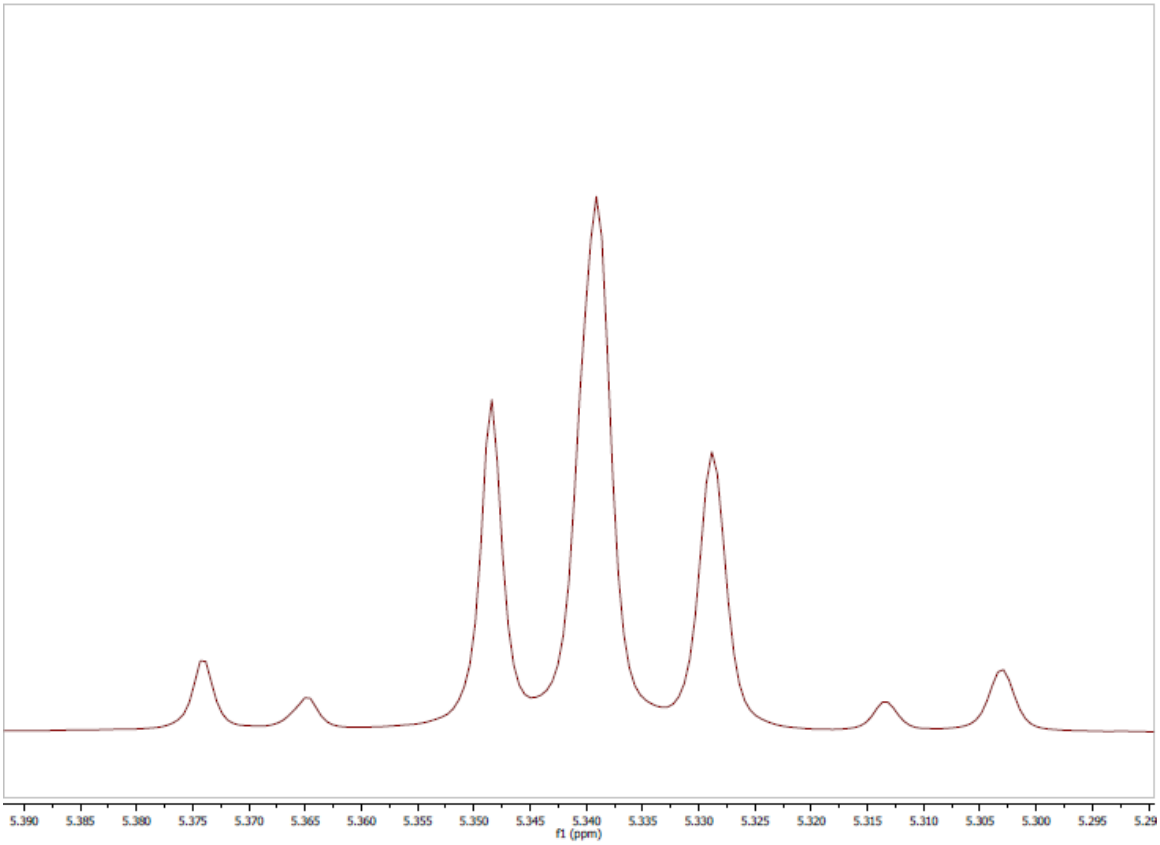
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 – 5.27 (m, *J* ~ 15.4, 5.6, 2H, *H*C=C*H*), 2.41 – 2.30 (m, 1H, *c*-C_5H_9 H-1), 2.27 – 2.17 (m, 1H, C*H*Me_2), 1.80 – 1.49 (m, ~6H, contains small contribution from *Z*-isomer signals, *c*-C_5H_9 ring protons), 1.29 – 1.17 (m, 2H, C_5H_9 ring protons), 0.96 (d, *J* = 6.8, ~6H, CH_3, overlaps with corresponding signal of *Z*-isomer).

The *H*C=C*H* multiplet is shown in Fig. 2. Although second order coupling is clearly present between the two alkene signals, approximate coupling constants of 15.4 Hz and 5.6 Hz can be assigned for *H*C=C*H* coupling and C=C*H*–C*H* coupling respectively.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.6 (C-2), 131.8 (C-1), 43.2 (*c*-C_5H_9 C-1), 33.3 (ring C-2 & C-5), 30.9 (*C*HMe_2), 25.1 (ring C-3 & C-4), 22.7 (CH(C*H*$_3$)$_2$).

1D DPFGSE-NOE NMR showed no NOE contact between either *c*-C_5H_9 H-1 and C*H*Me_2, or *c*-C_5H_9 H-1 and CH$(CH_3)_2$. On the basis of the magnitude of the observed approximate alkene coupling constant (J ~ 15.4 Hz) and the absence of NOE contact between the vicinal alkene substituents, we conclude that the stereochemistry of this alkene is *E*.

Fig. 2. *H*C=C*H* multiplet for *E*-1-cyclopentyl-3-methylbut-1-ene

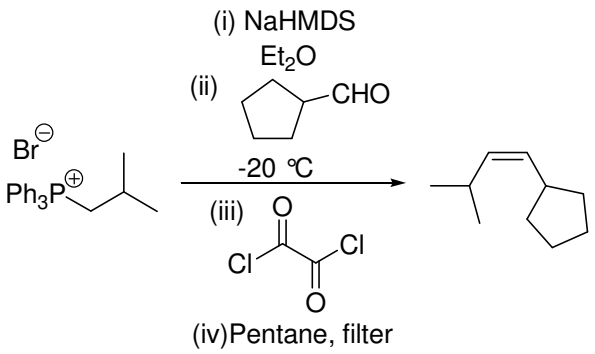


Some signals from the *Z*-alkene were present in the NMR spectra (integrations relative to 1H of *E*-isomer):

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (td, J = 19.6, 10.7, 0.13H, *H*C=C*H*), 2.76 – 2.56 (m, 0.26H, C*H*Me_2 & *c*-C_5H_9 H-1).

^{13}C NMR (126 MHz, $CDCl_3$) δ 34.0 & 25.4 (*c*-C_5H_9 C-2 & C-3), 23.5 (*C*H_3).

6. *Z*-1-cyclopentyl-3-methylbut-1-ene. Table 1 entry 6.



For this reaction, the general procedure was followed with the following modifications: Diethyl ether was used in place of THF, the reaction was carried out at -20 ˚C rather than -78 ˚C, and pentane was used in place of cyclohexane. No reaction of this ylide and aldehyde occurs below approximately -20 °C as judged by a lack of decolourisation of the ylide solution by addition of aldehyde at temperatures lower than this.

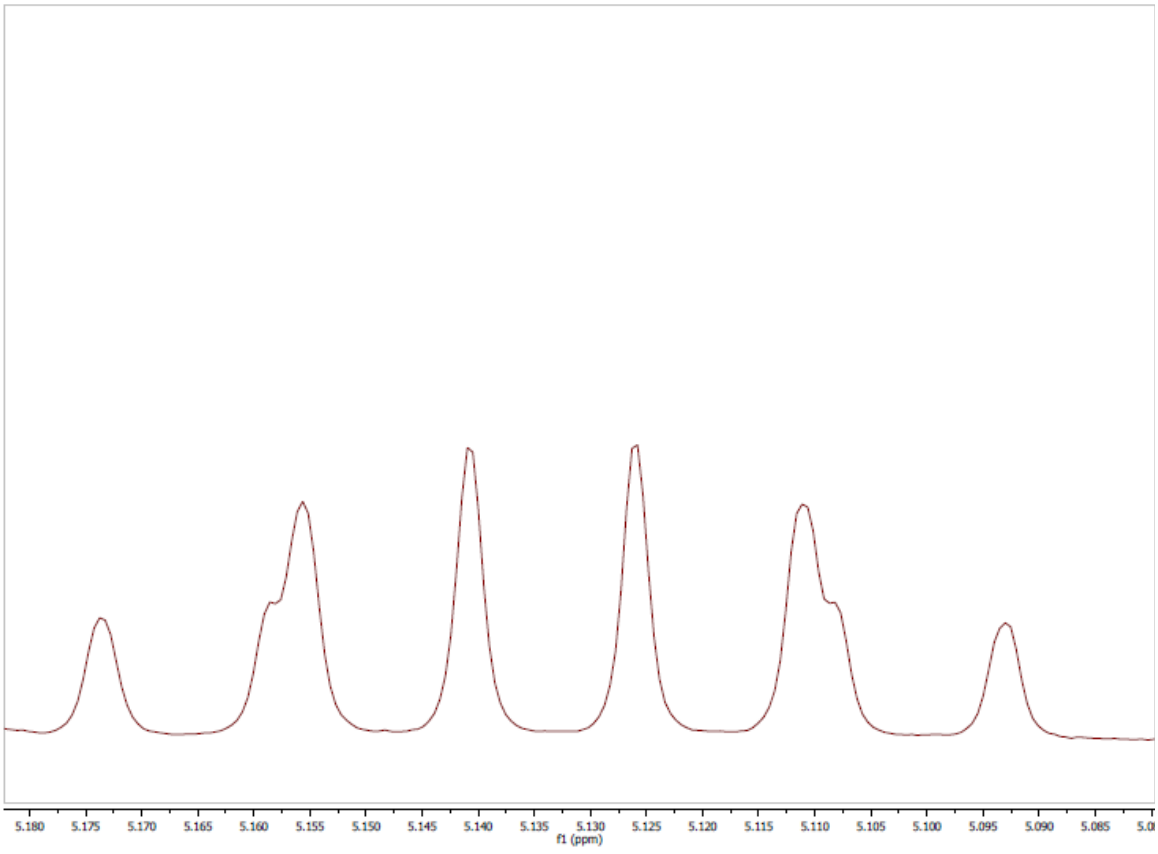
From (*iso*-butyl)triphenylphosphonium bromide (250 mg, 0.63 mmol), NaHMDS (115 mg, 0.63 mmol) and cyclopentanecarboxaldehyde (0.067 ml, 62 mg, 0.63 mmol) at -20 °C in Et_2O. The crude product was treated with oxalyl chloride (0.06 ml, 0.09 g, 0.7 mmol) and purified using pentane as the filtration solvent to give the product as an oil (0.28 g, contains small impurities). The crude product obtained in this way contained only *Z*-alkene and no phosphorus or aldehyde, but decomposed if left to stand.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.20 – 5.06 (m, 2H, *H*C=C*H*), 2.77 – 2.55 (m, 2H, δ 2.77-2.65 *c*-C_5H_9 H-1, δ 2.65-2.55 C*H*Me_2), 1.83 – 1.51 (m, 6H, *c*-C_5H_9 ring hydrogens), 1.30 – 1.12 (m, 2H, *c*-C_5H_9 ring hydrogens), 0.95 (dd, *J* = 6.7, 6H, C*H*$_3$).
^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2 & 132.9 (C=C), 38.3 (*c*-C_5H_9 C-1), 34.0 & 25.4 (*c*-C_5H_9 C-2 & C-3), 26.8 (*C*HMe_2), 23.5 (*C*H_3).

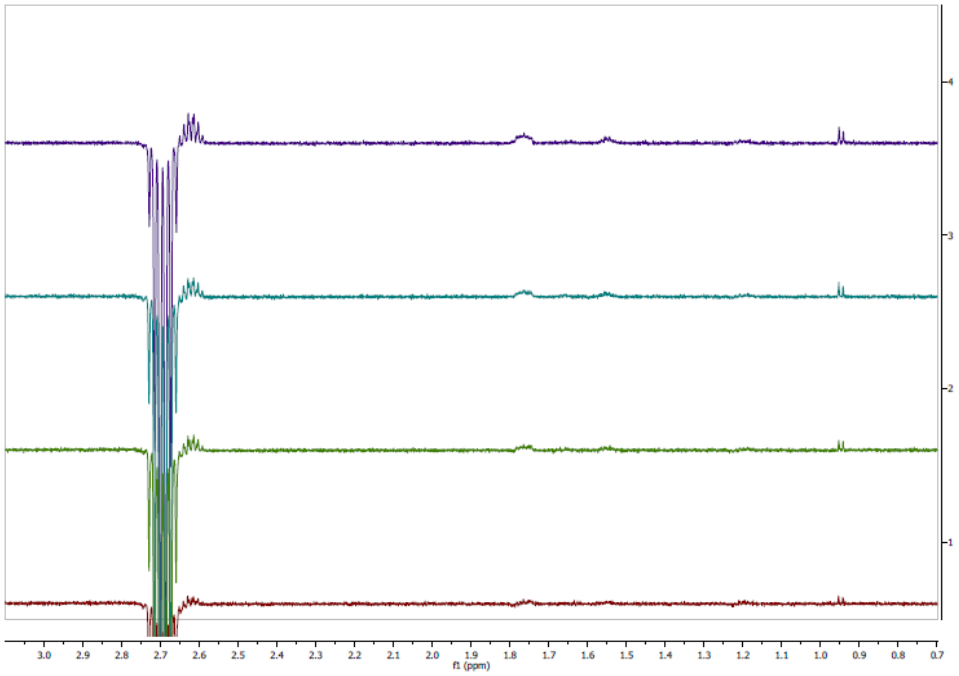
^{1}H NMR of a crude sample of this alkene on a 600 MHz instrument allowed the fine structure of the alkene proton signal (see Fig. 3(a)) to be determined: δ 5.16 (1H, roofed dd, *J* = 10.7, 9.1, *c*-C_5H_9C*H*=C), 5.11 (1H, roofed dd, *J* = 10.7, 9.1, *i*-PrC*H*=C). ^{13}C and gHSQCAD NMR spectra of the same sample on the 600 MHz spectrometer indicate that

the signal at δ_C = 136.2 belongs to *i*-Pr*C*H=C and that at δ_C = 132.9 belongs to *c*-C_5H_9*C*H=C. 1D DPFGSE-NOE experiments were carried out involving irradiation of the *c*-C_5H_9 H-1 (δ 2.77-2.65) and C*H*Me_2 (δ 2.65-2.55) signals. The experiment involving irradiation of the *c*-C_5H_9 H-1 signal indicated NOE contact with the cyclopenyl ring signals, but also with C*H*Me_2, and a small contact with the *iso*-propyl C*H*$_3$ groups (see Fig. 3(b)). The experiment involving irradiation of the C*H*Me_2 signal indicated NOE contact with *c*-C_5H_9 H-1 and the methyl groups (see Fig. 3(c)). On the basis of these experiments we conclude that the stereochemistry of this alkene is *Z*. A 2D NOESY spectrum of the same sample indicated the same NOE contacts.

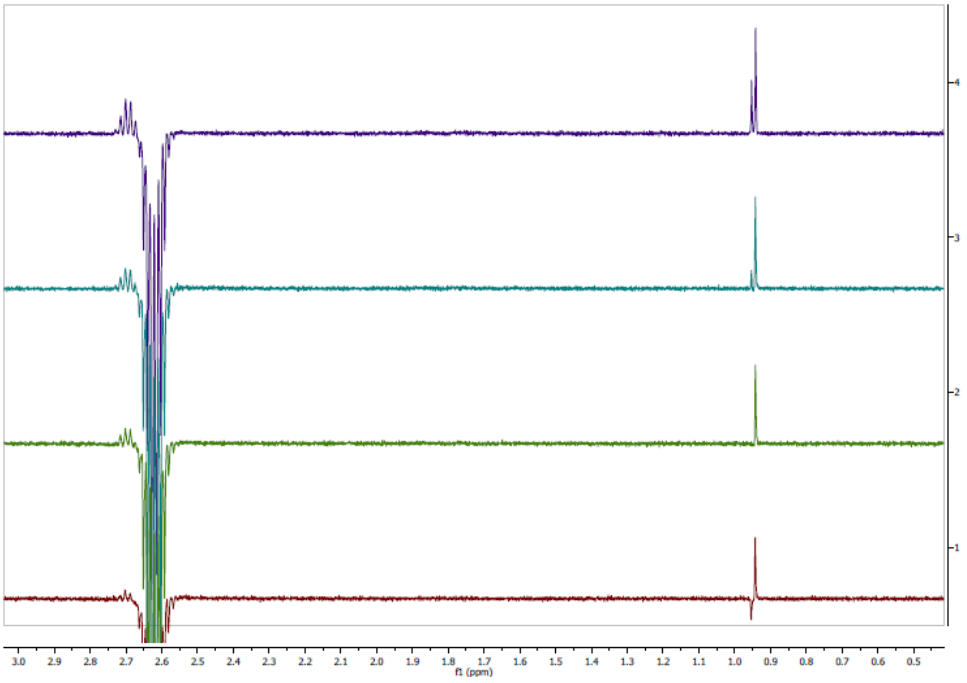
Fig. 3. (a) *H*C=C*H* signal for *Z*-1-cyclopentyl-3-methylbut-1-ene.



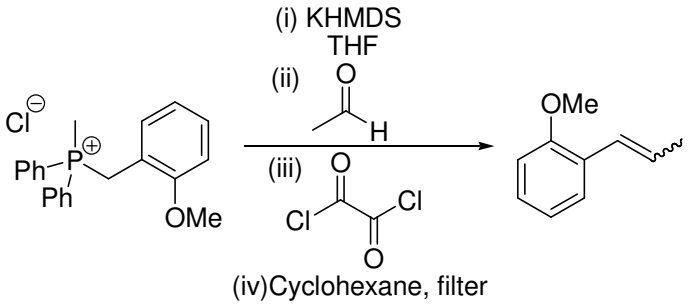
(b) 1D DPFGSE NMR experiments involving irradiation of the signal centred at δ = 2.69 at mixing times 0.5, 1.0, 1.5 and 3.0 seconds (in ascending order).



(c) 1D DPFGSE NMR experiments involving irradiation of the signal centred at δ = 2.62 at mixing times 0.5, 1.0, 1.5 and 3.0 seconds (in ascending order).



7. 1-(2-methoxyphenyl)prop-1-ene.[15,16] Table 1 entry 7.



From 2-methoxybenzylmethyldiphenylphosphonium chloride (470 mg, 1.32 mmol), KHMDS (273 mg, 1.37 mmol) and ethanal (60 mg, 1.36 mmol) at 20 °C in THF. The crude product was treated with oxalyl chloride (0.12 ml, 0.18 g, 1.4 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (165 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$) of purified mixture of alkenes (*Z*/*E* = 15:85):

E-isomer: δ 7.38 (dd, *J* 7.6, 1.3, 1H), 7.19 – 7.15 (m, 1H), 6.85 (app d, *J* 8.1, 1H), 6.71 (dd, *J* 15.8, *ca.* 1.5 (small coupling constant indistinct), 1H), 6.22 (dq, *J* 15.8, 6.6, 1H), 1.89 (dd, *J* 6.6, 1.7, 3H).[15,16]

Z-isomer: δ 7.22 (app t, *J* 7.8, 1H), 6.54 (dd, *J* 11.5, small coupling constant indistinct, 1H), 5.84 (dq, *J* 11.5, 7.1, 1H), 1.82 (dd, *J* 7.1, 1.8, 3H).[16]

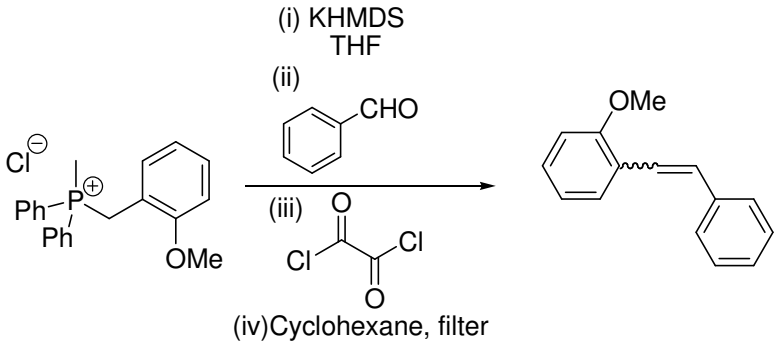
Overlapping signals of the two isomers were also observed (integrations relative to 1 H of *E*-isomer):

δ 6.95-6.86 (m, 1.6H, contains 1 *E*-ArH and 3 *Z*-ArH), 3.84 (3.6H, *E* and *Z* OMe).[15,16]

The residue from filtration of the oxalyl chloride-treated product (a viscous yellow oil) was dissolved in dry THF (2 ml) and treated with a 1 mol L^{-1} solution of $LiAlH_4$ in THF (1.7 ml, 1.7 mmol) at -78 °C. The resulting solution was poured into a degassed mixture of dichloromethane (20 ml) and saturated NH_4Cl (10 ml) in a separatory funnel under an inert atmosphere. After shaking, the organic phase was allowed to drain off into a round

bottom flask (under nitrogen atmosphere) and dried over $MgSO_4$. The aqueous phase was extracted with further degassed dichloromethane (15 ml), and the organic phase was allowed to drain into the round bottom flask. The mixture in the round bottom flask was quickly filtered of the drying agent and residual salts under nitrogen atmosphere through a short plug of silica into a Schlenk flask using inert atmosphere filtration apparatus. The solvent was removed *in vacuo* yielding methyldiphenylphosphine as a clear oil (0.26 g, 98%), δ_P ($CDCl_3$, 121 MHz) -26.8 (lit.[17] -26.3).

8. 2-methoxystilbene.[18,19] Table 1, entry 8.



From 2-methoxybenzylmethyldiphenylphosphonium chloride (152 mg, 0.426 mmol), KHMDS (90 mg, 0.45 mmol) and benzaldehyde (45 mg, 0.43 mmol) by procedure B at 20 °C in THF. The crude product was treated with oxalyl chloride (0.06 ml, 0.7 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil that crystallised on standing (89 mg, 99%).

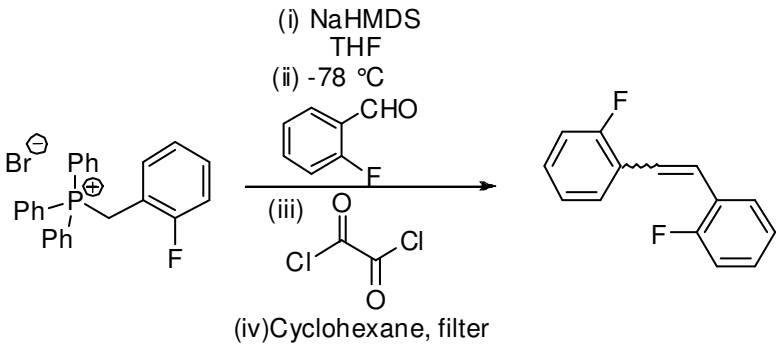
^{1}H NMR (500 MHz, $CDCl_3$) of purified mixture of alkenes (*Z*/*E* = 12:88):

Assigned to *E*-isomer: δ 7.58 (dd, *J* 7.6, 1.0, 1H), 7.52 (d, *J* 7.5, 2H), 7.55 – 7.45 (m, 3H, contains app d, *J* 7.5, *E*-ArH & d, *J* 16.5, *E*-C*H*=C), 7.33 (app t, *J* 7.7, 2H, *E*-ArH), 6.95 (app t, *J* 7.5, 1H), 3.86 (s, 3H, OCH_3).[18]

Assigned to *Z*-isomer: δ 6.74 (app t, *J* 7.4, 1H, *Z*-ArH), 6.69 (d, *J* 12.3, 1H, *Z*-C*H*=C), 6.62 (d, *J* 12.3, *Z*-C*H*=C), 3.79 (s, 3H, OCH_3).[19]

Other overlapping signals of both isomers present (integrations relative to 1 H of *E*-isomer): δ_H 7.25-7.08 (m, 4H of which 3 H is from *E*-isomer and 7 x 0.14 H is from *Z*-isomer, contains app t, *J* 7.6, 2 x *Z*-ArH, and d at δ 7.10, *J* 16.5, *E*-C*H*=C), 6.90-6.85 (m, 1.14 H, contains app d, *J* 8.1, *E*-ArH).[18,19]

9. 2,2'-difluorostilbene.[20,21,22] Table 1 entry 9.



From 2-fluorobenzyltriphenylphosphonium bromide (290 mg, 0.640 mmol), KHMDS (125 mg, 0.63 mmol) and 2-fluorobenzaldehyde (0.067 ml, 0.79 g, 0.64 mmol) in THF at -78 °C. The crude product was treated with oxalyl chloride (0.06 ml, 0.09 g, 0.7 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil that crystallised on standing (0.13 g, 93%).

^{1}H NMR (300 MHz, $CDCl_3$) of alkene mixture:
No signals could be assigned to the *E*-isomer.[20]
Assigned to *Z*-isomer: δ 7.07 – 6.96 (m, 2H), 6.96 – 6.85 (m, 2H), 6.76 (s, 2H, *H*C=C*H*).[22]

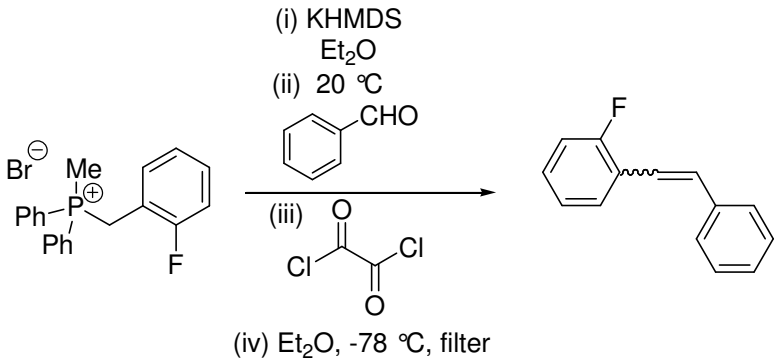
^{19}F NMR (282 MHz, $CDCl_3$) of crude product:

Assigned to *E*-isomer: δ -117.9 - -118.0 (m).

Assigned to *Z*-isomer: δ -115.0 - -115.1 (m).

Integrations indicate a *Z/E* ratio of 94:6.

10. 2-fluorostilbene.[23,24] Table 1 entry 10.



From 2-fluorobenzylmethyldiphenylphosphonium bromide (255 mg, 0.655 mmol), KHMDS (138 mg, 0.692 mmol) and benzaldehyde (72 mg, 0.68 mmol) at 20 °C in Et_2O. The crude product was not subjected to aqueous work-up, but treated with oxalyl chloride (0.08 ml, 0.12 g, 0.9 mmol) purified using Et_2O at -78 ºC as the filtration solvent to give the product as a clear oil that solidified on standing, yielding white crystals (125 mg, 96%).

^{1}H NMR (500 MHz, $CDCl_3$) of purified alkene:

Assigned to *E*-isomer: δ 7.61 (td, *J* = 7.7, 1.4, 1H), 7.54 (d, *J* = 7.3, baseline obscured, *ca.* 2H), 7.37 (t, *J* = 7.6, 2H), 7.28 (d, *J* = 16.4, 2H), 7.18 (m, contains d, *J* = 16.5), 7.14 (t, *J* = 7.5, 1H).[23]

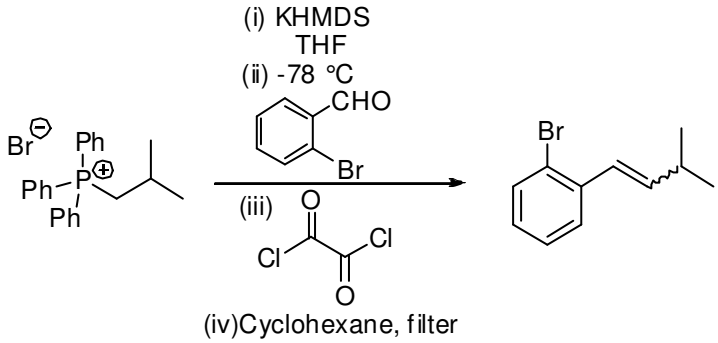
Assigned to *Z*-isomer: δ 6.92 (t, *J* = 7.2, 1H), 6.72 (d, *J* = 12.2, 1H), 6.61 (d, *J* = 12.3, 1H).[24]

Overlapping signal due to both isomers (integration relative to 1H of *E*-isomer): δ 7.10 – 7.00 (m, 1.2H).[23,24]

^{19}F NMR (282 MHz, $CDCl_3$) of purified alkene: δ -114.9 – -115.1 (m, 0.2F), -117.9 – -118.1 (m, 1F).

Integrations indicate a *Z/E* ratio of 17:83.

11. 1-(2-bromophenyl)-3-methylbut-1-ene.[25] Table 1 entry 11.



From (*iso*-butyl)triphenylphosphonium bromide (555 mg, 1.39 mmol), KHMDS (308 mg, 1.54 mmol) and 2-bromobenzaldehyde (0.16 ml, 0.25 g, 1.4 mmol) at -78 °C in THF. The crude product was treated with oxalyl chloride (0.13 ml, 0.20 g, 1.54 mmol) and purified using cyclohexane as the filtration solvent to give the phosphorus-free product as a clear oil (0.28 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$) of purified alkene (*Z*/*E* = 82:18):
Assigned to *E*-isomer: δ 6.67 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 6.8 Hz, 1H), 1.11 (d, *J* = 6.7 Hz, 6H).[25]
Assigned to *Z*-isomer: δ 6.31 (d, *J* = 11.4 Hz, 1H), 5.64 – 5.51 (app t, 1H), 1.01 (d, *J* = 6.6 Hz, 6H).[25]

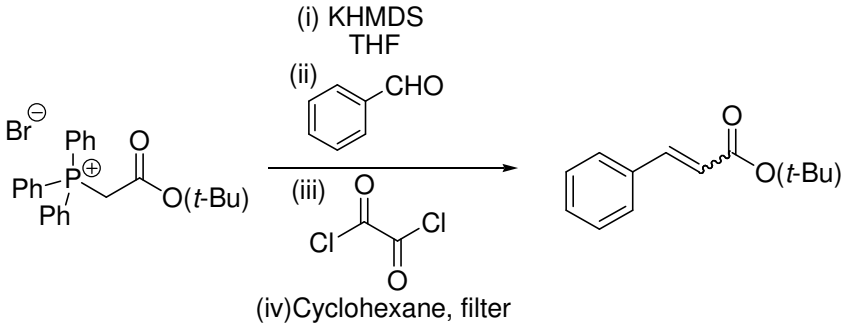
Also present was a multiplet with signals of the *E* and *Z*-isomers overlapping (integration relative to 1H of *Z*-isomer): δ 2.72-2.48 (m, 1.2H, *E* and *Z* C*H*Me_2).

The residue from filtration of the oxalyl chloride-treated product was dissolved in dry THF (5 ml) and treated with a 1 mol L^{-1} solution of $LiAlH_4$ in dry Et_2O (1.7 ml, 1.7 mmol) at -78 °C, giving white crystals of triphenylphosphine (0.29 g, 80%) after work-up with degassed ethyl acetate/NH_4Cl solution and filtration through a short silica plug to remove residual phosphine oxide.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.24 (m).

^{31}P NMR (121 MHz, $CDCl_3$) δ -5.3 (lit.[9] -4.8).

12. *tert*-Butyl 3-phenylprop-2-enoate. [26,27] Table 1 entry 12.



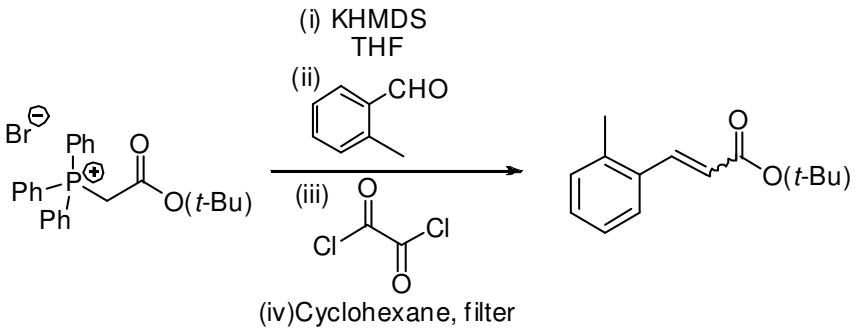
From (*tert*-butoxycarbonylmethyl)methyldiphenylphosphonium bromid[28] (247 mg, 0.598 mmol), KHMDS (143 mg, 0.72 mmol) and benzaldehyde (69 mg, 0.65 mmol) at 20 °C in THF. The crude product was treated with oxalyl chloride (0.08 ml, 0.9 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (106 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) of mixture of enoates (*Z*/*E* = 4:96):
Assigned to *E*-isomer: δ 7.59 (d, *J* = 16.0, 1H, not baseline separated), 7.54-7.48 (m, 2H, ArH), 7.38-7.34 (m, 3H), 6.37 (d, *J* = 16.0, 1H), 1.54 (s, 9H, *t*-Bu).[26]

Assigned to *Z*-isomer: δ 6.86 (d, *J* = 12.6, 1H), 5.88 (d, *J* = 12.6, 1H).[27] *t*-Bu signal (δ 1.43) is obscured by residual cyclohexane.

The residue from filtration of the oxalyl chloride-treated product (a pale yellow solid) was dissolved in dry THF (5 ml) and treated with a 1 mol L^{-1} solution of $LiAlH_4$ in THF (1.1 ml, 1.1 mmol) at -78 °C, giving white crystals of triphenylphosphine (138 mg, 88%) after work-up with degassed ethyl acetate/NH_4Cl solution. δ_P (121 MHz, $CDCl_3$) -5.3 (lit.[9] -4.8).

13. *tert*-Butyl 3-(2-methylphenyl)prop-2-enoate.[29] Table 1 entry 13.



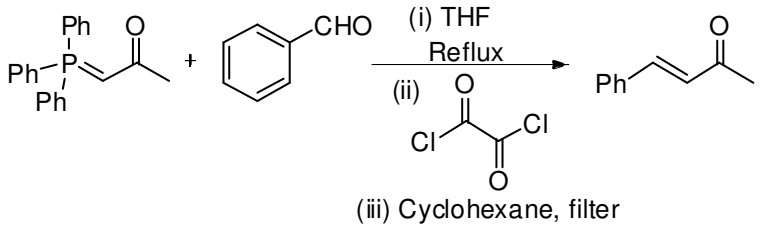
From (*tert*-Butoxycarbonylmethyl)triphenylphosphonium bromide[28] (328 mg, 0.794 mmol), KHMDS (167 mg, 0.834 mmol) and 2-methylbenzaldehyde (95 mg, 0.79 mmol) at 20 ºC in THF. The crude product was treated with oxalyl chloride (0.10 ml, 1.2 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (0.15 g, 88%).

^{1}H NMR of purified product (integrations relative to 1 H of *E*-isomer): δ_H (500 MHz, $CDCl_3$) 7.88 (1 H, d, *J* 15.9, *E*-H-3), 7.55-7.53 (1 H, m, *E*-ArH), 7.27 – 7.22 (contains C*H*Cl_3 signal, m, *E*-ArH), 7.21-7.16 (2 H, m, *E*-ArH), 7.02 (0.03 H, d, *J* 12.1, *Z*-H-3), 6.29 (1 H, d, *J* 15.9, *E*-H-2), 5.95 (0.03 H, d, *J* 12.1, *Z*-H-2), 2.43 (3 H, s, *E*-CH_3), 2.27 (0.1 H, s, *Z*-CH_3), 1.54 (9 H, s, *E*-C(CH_3)$_3$), 1.30 (0.27 H, s, *Z*- C(CH_3)$_3$).[29]

The *Z/E* ratio of the alkene was determined to be 3:97 by comparison of the relative integrations of the signals assigned to each isomer.

The residue from filtration of the oxalyl chloride-treated product (a pale yellow solid) was dissolved in dry THF (2 ml) and treated with a 1 mol L^{-1} solution of $LiAlH_4$ in THF (1.2 ml, 1.2 mmol) at -78 °C, giving white crystals of triphenylphosphine (0.20 g , 95%) after work-up with degassed CH_2Cl_2/NH_4Cl solution. δ_P (121 MHz, $CDCl_3$) -5.3 (lit.[9] -4.8).

14. 4-phenylbut-3-en-2-one.[30] Table 1 entry 14.



To a solution of acetonylidenetriphenylphosphorane[28] (872 mg, 2.74 mmol) in dry THF at 20 ˚C was added benzaldehyde (0.28 ml, 0.29 g, 2.7 mmol) dropwise. The reaction was refluxed (oil bath heated to 70 ˚C) while stirring overnight. The THF solvent was then removed *in vacuo*. The crude product was treated with oxalyl chloride (0.20 ml, 0.30 g, 2.4 mmol) and purified using cyclohexane as the filtration solvent to give the product as an oil (0.35 g, 88%).

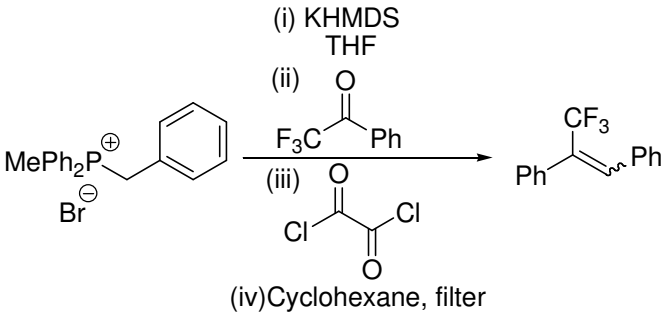
^{1}H NMR (300 MHz, $CDCl_3$) of mixture of enones:

Assigned to *E*-isomer: δ 7.60 – 7.36 (m, 6H, aromatic H & H-4), 6.72 (d, J = 16.3, 1H, H-3), 2.38 (s, 3H, CH_3).[30]

Assigned to *Z*-isomer: δ 6.90 (1H, d, ^3J = 12.7 Hz, H-4), 6.20 (1H, d, ^3J = 12.7 Hz, H-3), 2.14 (3H, s, CH_3).[30]

Integrations indicate *Z/E* ratio of 3:97.

15. 3,3,3-trifluoro-1,2-diphenylprop-1-ene.[31,32,33] Table 1 entry 15.

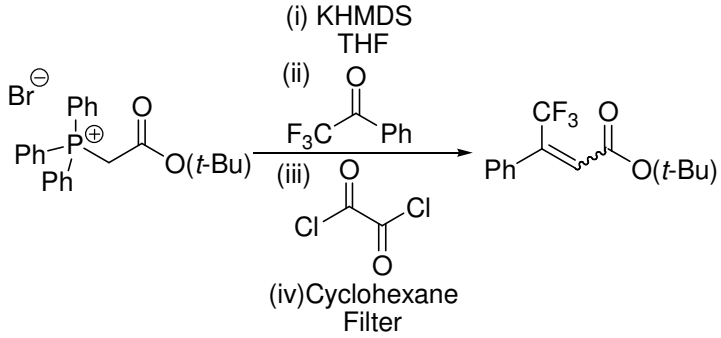


From benzylmethyldiphenylphosphonium bromide (179 mg, 0.482 mmol), KHMDS (97 mg, 0.482 mmol) and 2,2,2-trifluoroacetophenone (90 mg, 0.52 mmol) at 20 ºC in THF. The crude product was treated with oxalyl chloride (0.06 ml, 0.7 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (0.11 g, 92%).

^{1}H NMR (500 MHz, $CDCl_3$) of purified product:
Assigned to *E*-isomer: δ 7.25 – 7.17 (m, 1H), 7.15 (app t, *J* = 7.4, 1H), 7.00 (app d, *J* = 7.5, 1H).[31] No signals could be unambiguously assigned to the *Z*-isomer.[32]

^{19}F NMR (282 MHz, $CDCl_3$) of purified product:
δ -56.3 (s, 0.13F, *Z*-isomer),[32,33] -65.6 – -66.2 (m, 1F, *E*-isomer).[31,33] Integrations indicate a *Z/E* ratio of 12:88.

16. *tert*-Butyl 4,4,4-trifluoro-3-phenylprop-2-enoate.[34,35] Table 1 entry 16.



From (*tert*-Butoxycarbonylmethyl)triphenylphosphonium bromide (394 mg, 0.954 mmol), KHMDS (190 mg, 0.952 mmol) and 2,2,2-trifluoroacetophenone (172 mg, 0.99 mmol) at 20 ºC in THF. The crude product was treated with oxalyl chloride (1.1 ml, 1.3 mmol) and purified using cyclohexane as the filtration solvent to give the product as a clear oil (233 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$) of purified product:
Assigned to *E*-isomer: δ 6.53 (app d, *J* = 1.4, 1H).[34]
Assigned to *Z*-isomer: δ 6.28 (s, 0.17H).[35]

Overlapping signals of the two isomers (integrations relative to 1H of *E*-isomer):
δ 7.44 – 7.35 (m, 4H), 7.30 – 7.23 (m, contains C*H*Cl_3 signal), 1.22 (s, 10.6H, *t*-Bu).

^{19}F NMR (282 MHz, $CDCl_3$) of purified product (integrations based on *E*-isomer):
δ -59.7 (s, 0.17F, *Z*-isomer), -67.5 (s, 1F, *E*-isomer, lit.[34] –67.98).

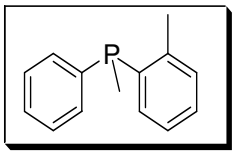
Integrations of signals assigned to the two isomers in both the ^{1}H and the ^{19}F NMR indicate a *Z/E* ratio of 15:85.

The residue from filtration of the oxalyl chloride-treated product (a pale yellow solid) was dissolved in dry THF (5 ml) and treated with a 1 mol L^{-1} solution of $LiAlH_4$ in THF (1.5 ml, 1.5 mmol) at -78 °C, giving white crystals of triphenylphosphine (0.22 g , 88%) after work-up with degassed ethyl acetate/NH_4Cl solution and filtration through a short silica plug. δ_P (121 MHz, $CDCl_3$) -5.4 (lit.[9]-4.8).

5. Reduction of phosphine chalcogenides

General Procedure: To a stirred solution of phosphine chalcogenide (1 equivalent) in toluene (to give a solution of 0.1 mol L^{-1} concentration) was added oxalyl chloride (1 equiv) dissolved in toluene (10 mL) dropwise at room temperature under a nitrogen atmosphere. After 10 minutes, a solution of $LiAlH_4$ in THF (1M, 1.2 equivalents) was added dropwise to the reaction mixture. This mixture was stirred for 30 minutes. The reaction mixture was evaporated under reduced pressure, then degassed ethyl acetate (20 mL) and degassed NH_4Cl solution (20 mL) were added. The phases were separated, and the aqueous layer was extracted with ethyl acetate (20 mL). The combined organic phases were dried over $MgSO_4$, filtered through a silica plug to remove residual phosphine oxide and concentrated *in vacuo* to give phosphine.

Reduction of methylphenyl(*o*-tolyl)phosphine oxide.

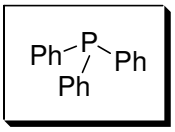


Chlorophosphonium salt was formed from methylphenyl(*o*-tolyl)phosphine oxide (1.0 g, 4.3 mmol) and oxalyl chloride (0.37 mL, 4.3 mmol), and reduced using a solution of $LiAlH_4$ (5.16 mL, 1.0 M in THF, 5.16 mmol), giving methylphenyl(*o*-tolyl)phosphine as a colourless oil (0.78 g, 85%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53-7.24 (m, 9H, Ar), 2.53 (s, 3H, $ArCH_3$), 1.75 (d, $^2J_{PH}$ = 4.1 Hz, 3H, CH_3).

^{31}P NMR ($CDCl_3$, 121 MHz): δ -36.2 (lit.[36] -35.2).

Reduction of triphenylphosphine oxide:

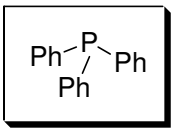


Chlorophosphonium salt was formed from triphenylphosphine oxide (0.27 g, 1.0 mmol, 1 equiv) and oxalyl chloride (0.10 mL, 1.0 mmol, 1 equiv.), and reduced using a solution of $LiAlH_4$ (1.2 mL, 1.0 M in THF, 1.2 mmol), giving triphenylphosphine (0.23 g, 88%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61–7.35 (m, 15H, Ph-H).

^{31}P NMR ($CDCl_3$, 121 MHz): δ -4.5 (lit.[9] -4.8).

Reduction of triphenylphosphine sulfide

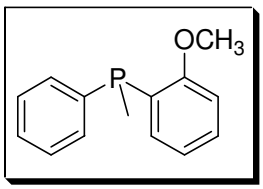


Chlorophosphonium salt was formed from triphenylphosphine sulfide 0.29 g, 1.0 mmol, 1 equiv) and oxalyl chloride (0.10 mL, 1.0 mmol, 1 equiv.), and reduced using a solution of $LiAlH_4$ (1.2 mL, 1.0 M in THF, 1.2 mmol), giving triphenylphosphine (0.23 g, 88%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61–7.35 (m, 15H, Ph-H).

^{31}P NMR ($CDCl_3$, 121 MHz): δ -4.6 (lit.[9] -4.8).

Reduction of (*o*-methoxyphenyl)methylphenylphosphine oxide



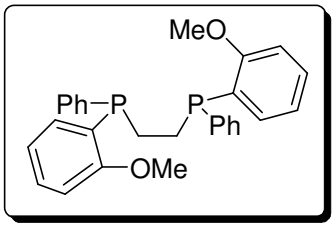
Chlorophosphonium salt was formed from (*o*-methoxyphenyl)methylphenylphosphine oxide (0.24 g, 1.0 mmol, 1 equiv) and oxalyl chloride (0.1 mL, 1.0 mmol, 1 equiv.), and reduced using a solution of $LiAlH_4$ (1.2 mL, 1.0 M in THF, 1.2

mmol), giving *o*-methoxyphenyl)methylphenylphosphine (0.19 g, 83%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.42 (m, 2H, Ar), 7.37-7.25 (m, 4H, Ar), 7.06-7.02 (m, 1H, Ar), 6.93-6.82 (m, 2H, Ar), 3.78 (s, 3H, OCH_3), 1.59 (d, $^2J_{PH}$ = 4.1 Hz, 3H, CH_3).

^{31}P NMR ($CDCl_3$, 121 MHz): δ -36.6 (lit.[36] –35.2).

Reduction of (±)-1,2-ethandiylbis[(*o*-anisyllphenyl)phenylphosphine oxide:

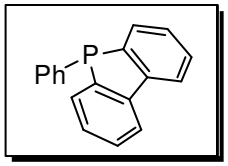


Chlorophosphonium salt was formed from 1,2-ethandiylbis[(*o*-anisylphenyl)phenylphosphine oxide (0.49 g, 1.0 mmol, 1 equiv) and oxalyl chloride (0.20 mL, 2.0 mmol, 2 equiv.), and reduced using a solution of $LiAlH_4$ (2.4 mL, 1.0 M in THF, 2.4 mmol), giving(±)-1,2-ethandiylbis[(*o*-anisylphenyl)phenylphosphine(0.39 g, 81%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.00-9.93 (m, 2H, Ar), 7.78-7.71 (m, 4H, Ar), 7.49-7.27 (m, 8H, Ar), 7.10-7.05 (m, 2H, Ar), 6.86-6.78(m, 2H, Ar), 3.58 (s, 6H, OCH_3), 1.48 (m, 4H, P-CH_2).

^{31}P NMR ($CDCl_3$, 300 MHz): δ -22.9 (lit.[37] -21.0).

Reduction of *P*-phenyl-5*H*-dibenzophosphole oxide[38]



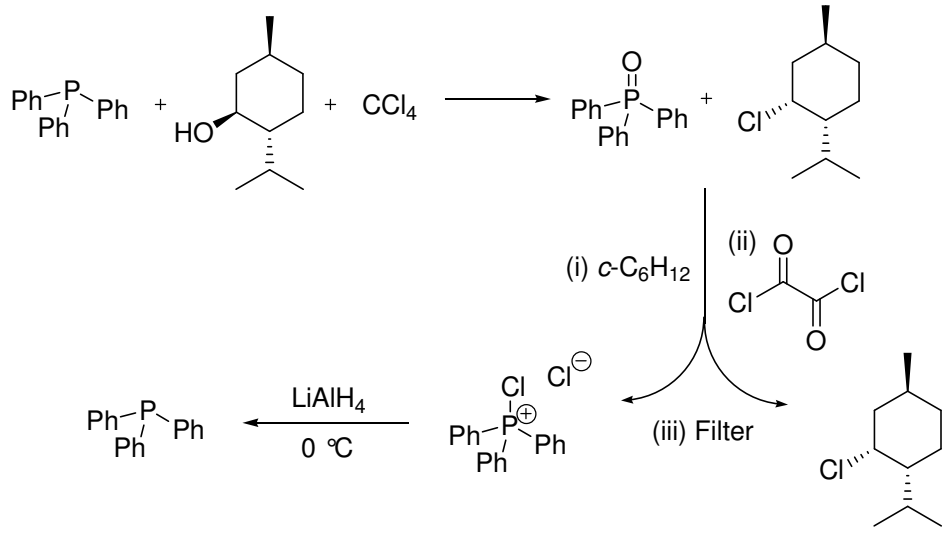
Chlorophosphonium salt was formed from *P*-phenyldibenzophosphole oxide (0.28 g, 1.0 mmol, 1 equiv) and oxalyl chloride (0.10 mL, 1.0 mmol, 1 equiv.), and and reduced using a solution of $LiAlH_4$ (1.2 mL, 1.0 M in THF, 1.2 mmol), giving *P*-phenyl-5*H*-dibenzophosphole (0.21 g, 81%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92-7.29 (m, 13H, Ar).

^{31}P NMR ($CDCl_3$, 121 MHz): δ -7.0 (lit.[39] -9.5).

6. Synthesis & isolation of neomenthyl chloride under Appel-type conditions and reduction of phosphine oxide by-product

Reaction of Ph_3P + CCl_4 + (-)-menthol



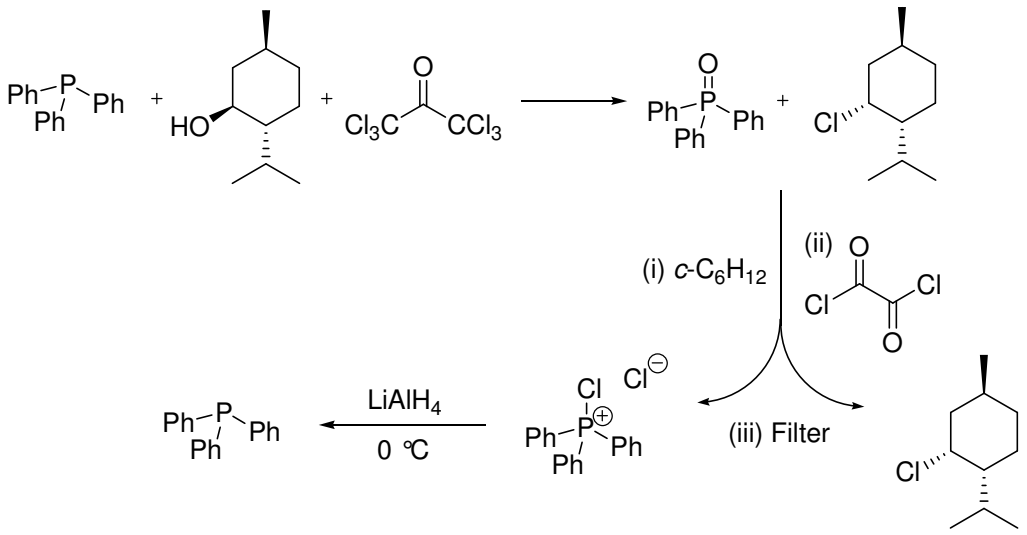
Triphenylphosphine (1.0 g, 3.8 mmol, 1 equiv.) and (-)-menthol (0.59 g, 3.5 mmol) were dissolved in dry toluene (20 ml) in a flame dried Schlenk tube under an atmosphere of nitrogen. CCl_4 (0.4 mL, 3.8 mmol) was added drop-wise to the reaction mixture which was then refluxed for 30 minutes. Completion of the reaction was confirmed by ^{31}P NMR analysis of a small sample of the reaction mixture (^{31}P NMR δ 25.2 ppm).

The toluene reaction solvent was removed *in vacuo* and cyclohexane (10 mL) was added to the residue. Oxalyl chloride (0.3 mL, 3.8 mmol) was added dropwise to the reaction mixture which caused the formation of a white precipitate of chlorophosphonium salt. The supernatant liquid was removed by cannula filtration. The residue was washed (2x 10 mL) twice with cyclohexane and the washings removed by cannula filtration. The combined cyclohexane filtrate was washed with water (20 mL x 2). The separated organic phase was then dried over anhydrous $MgSO_4$. Filtration to remove the drying agent and evaporation of the solvent *in vacuo* yielded neomenthyl chloride (0.55 g, 83 %).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 4.74 (m, 1H), 2.02–1.91 (m, 1H), 1.88–1.78 (m, 1H), 1.68–1.56 (m, 2H), 1.48–1.39(m, 2H), 1.33–1.28 (m, 2H), 1.05–1.01 (m, 1H) 0.87 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, CH_3), 0.84 (d, $^{3}J_{H,H}$ = 6.7 Hz, 3H, CH_3), 0.71 (d, $^{3}J_{H,H}$ = 6.9 Hz, 3 H, CH_3).[40]

The solid residue remaining after cannula filtration of the reaction mixture was dissolved in THF (10 ml) and cooled to 0 ˚C. A solution of $LiAlH_4$ in THF 1.0 M (3.8 mL, 3.8 mmol) was added dropwise to the mixture, which was then stirred for 30 minutes while warming to room temperature. Ethyl acetate (10 ml) was added to quench the $LiAlH_4$, followed by saturated aqueous NH_4Cl (10 ml). The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous phase was washed twice more with ethyl acetate (10 ml each wash). The combined organic phases were dried over $MgSO_4$, filtered through a silica plug to remove residual phosphine oxide and concentrated *in vacuo* to give phosphine (3.4 g, 89%).
^{31}P NMR (162 MHz): δ -4.8 (lit.[9] 4.8).

Reaction of Ph_3P + hexachloroacetone (HCA) + (-)-menthol



Triphenylphosphine (1.0 g, 3.8 mmol, 1 equiv.) and (-)-menthol (0.59 g, 3.5 mmol) were dissolved in dry toluene (20 ml) in a flame dried Schlenk tube under an atmosphere of nitrogen. HCA (0.4 mL, 3.8 mmol) was added drop-wise to the reaction mixture which

was then refluxed for 30 minutes. Completion of the reaction was confirmed by ^{31}P NMR analysis of a small sample of the reaction mixture (^{31}P NMR δ 25.2 ppm).

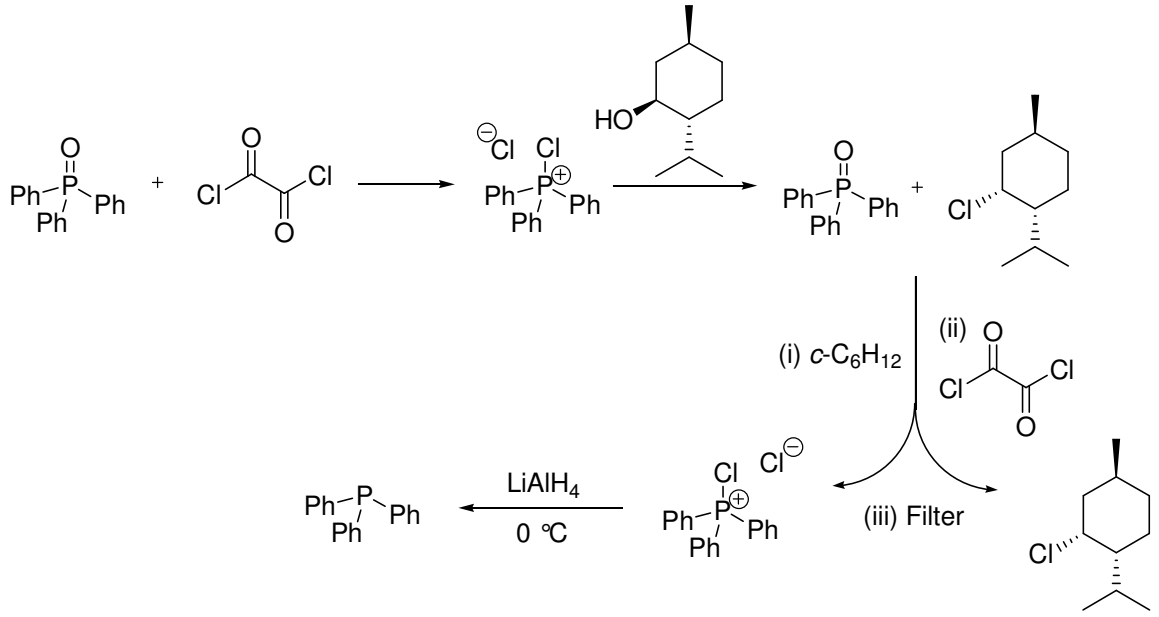
The toluene reaction solvent was removed *in vacuo* and cyclohexane (10 mL) was added to the residue. Oxalyl chloride (0.32 mL, 3.8 mmol) was added dropwise to the reaction mixture which caused the formation of a white precipitate of chlorophosphonium salt. The supernatant liquid was removed by cannula filtration. The residue was washed (2x 10 mL) twice with cyclohexane and the washings removed by cannula filtration. The combined cyclohexane filtrate was washed with water (20 mL x 2). The separated organic phase was then dried over anhydrous $MgSO_4$. Filtration to remove the drying agent and evaporation of the solvent *in vacuo* yielded neomenthyl chloride (0.52, 78%).

^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 4.85 (m, 1 H), 2.06–1.98 (m, 1 H), 1.94–1.84 (m, 1 H),1.73–1.64 (m, 2 H), 1.51–1.45(m, 2H), 1.41–1.34 (m, 2H), 1.07–1.02 (m, 1H) 0.91(d, $^3J_{H,H}$ = 6.4 Hz, 3H, CH_3), 0.86 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 0.78 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, CH_3).[40]

The solid residue remaining after cannula filtration of the reaction mixture was dissolved in THF (10 ml) and cooled to 0 ˚C. A solution of LiAlH4 in THF 1.0 M (3.8 mL, 3.8 mmol)was added dropwise to the mixture, which was then stirred for 30 minutes while warming to room temperature. Ethyl acetate (10 ml) was added to quench the $LiAlH_4$, followed by saturated aqueous NH_4Cl (10 ml). The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous phase was washed twice more with ethyl acetate (10 ml each wash). The combined organic phases were dried over $MgSO_4$, filtered through a silica plug to remove residual phosphine oxide and concentrated *in vacuo* to give phosphine product (3.43 g, 90%).

^{31}P NMR (162 MHz): δ -4.6 (lit.[9] -4.8).

Reaction of triphenylphosphine oxide + oxalyl chloride + (-)-menthol



Triphenylphosphine oxide (1.0 g, 3.5 mmol) was dissolved in dichloromethane (10 ml) in a flame dried Schlenk tube under an atmosphere of nitrogen. Oxalyl chloride (0.30 mL, 3.5 mmol) was added drop wise to the reaction mixture resulting in the formation of a white precipitate. (^{31}P NMR δ 64.5 ppm). (-)-Menthol (0.56 g, 3.5 mmol) was added to the reaction mixture through a powder funnel, causing the reaction mixture to become clear. The complete formation of alkoxyphosphonium salt was confirmed by ^{31}P NMR of a small sample of the reaction mixture (^{31}P NMR δ 58.9). The reaction was allowed to stir for 30 minutes. Completion of the reaction was confirmed by ^{31}P NMR analysis of a small sample of the reaction mixture (^{31}P NMR δ 25.2).

The toluene reaction solvent was removed *in vacuo* and cyclohexane (10 mL) was added to the residue. Oxalyl chloride (0.30 mL, 3.5 mmol) was added dropwise to the reaction mixture which caused the formation of a white precipitate of chlorophosphonium salt. The supernatant liquid was removed by cannula filtration. The residue was washed (2x 10 mL) twice with cyclohexane and the washings removed by cannula filtration. The combined cyclohexane filtrate was washed with water (20 mL x 2). The separated organic phase was then dried over anhydrous $MgSO_4$. Filtration to remove the drying agent and evaporation of the solvent *in vacuo* yielded neomenthyl chloride (0.49 g, 80 %).

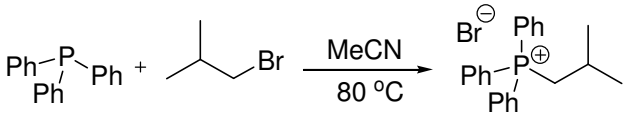
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 4.77 (m, 1 H), 2.02–1.91 (m, 1H), 1.88–1.78 (m, 1 H),1.68–1.56 (m, 2H), 1.48–1.39(m, 2H), 1.33–1.28 (m, 2H), 1.04–1.01 (m, 1H) 0.85 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, CH_3), 0.83 (d, $^{3}J_{H,H}$ = 6.7 Hz, 3H, CH_3), 0.70 (d, $^{3}J_{H,H}$ = 6.9 Hz, 3 H, CH_3).[40]

The solid residue remaining after cannula filtration of the reaction mixture was dissolved in THF (10 ml) and cooled to 0 ˚C. A solution of $LiAlH_4$ in THF 1.0 M (3.5 mL, 3.5 mmol) was added dropwise to the mixture, which was then stirred for 30 minutes while warming to room temperature. Ethyl acetate (10 ml) was added to quench the $LiAlH_4$, followed by saturated aqueous NH_4Cl (10 ml). The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous phase was washed twice more with ethyl acetate (10 ml each wash). The combined organic phases were dried over $MgSO_4$, filtered through a silica plug to remove residual phosphine oxide and concentrated *in vacuo* to give phosphine. (0.78 g, 86 %).

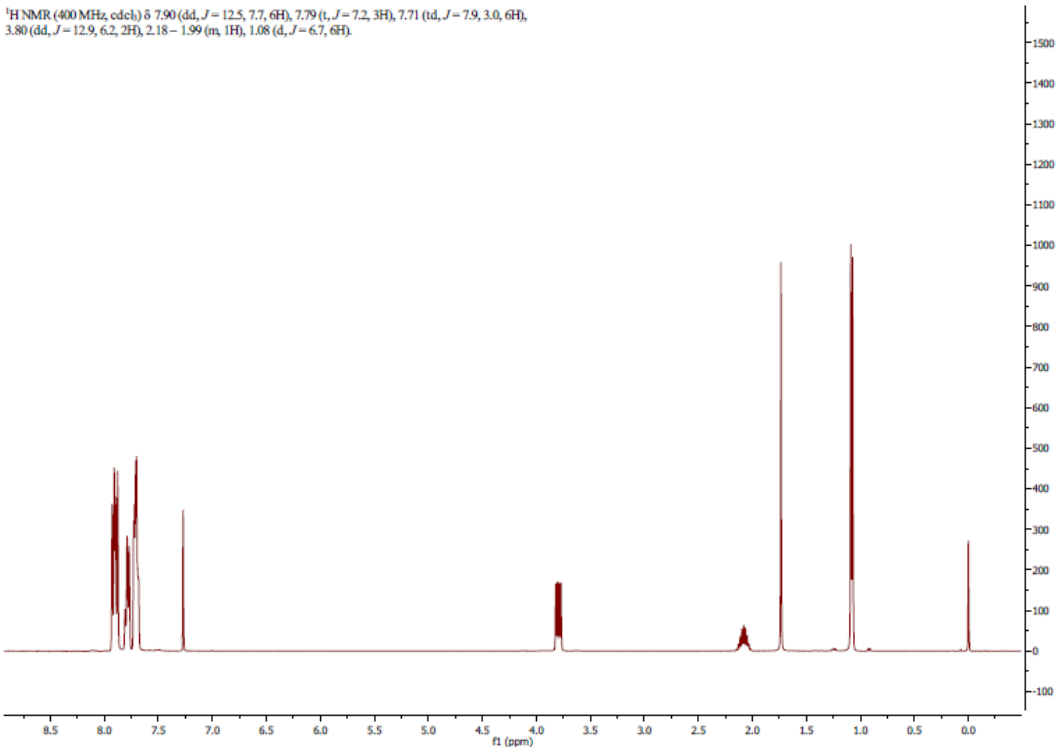
^{31}P NMR (162 MHz): δ -4.5 (lit.[9] -4.8).

7. NMR spectra of phosphonium salts

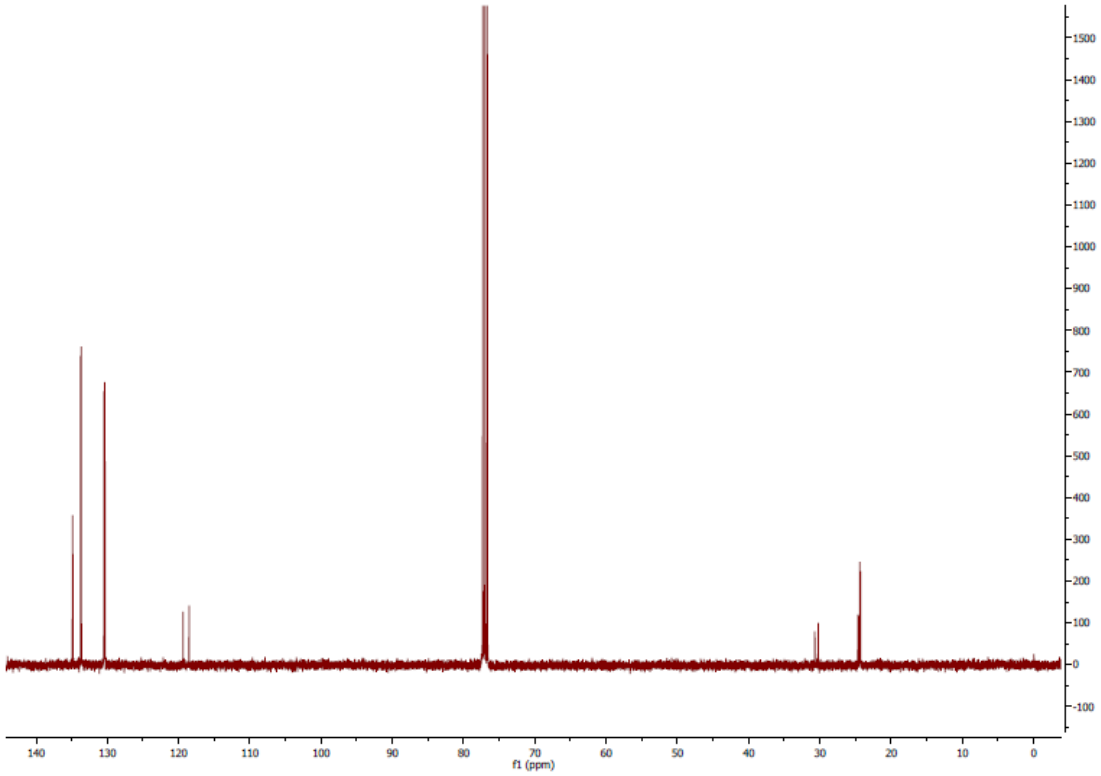
P-(*iso*-butyl)triphenylphosphonium bromide



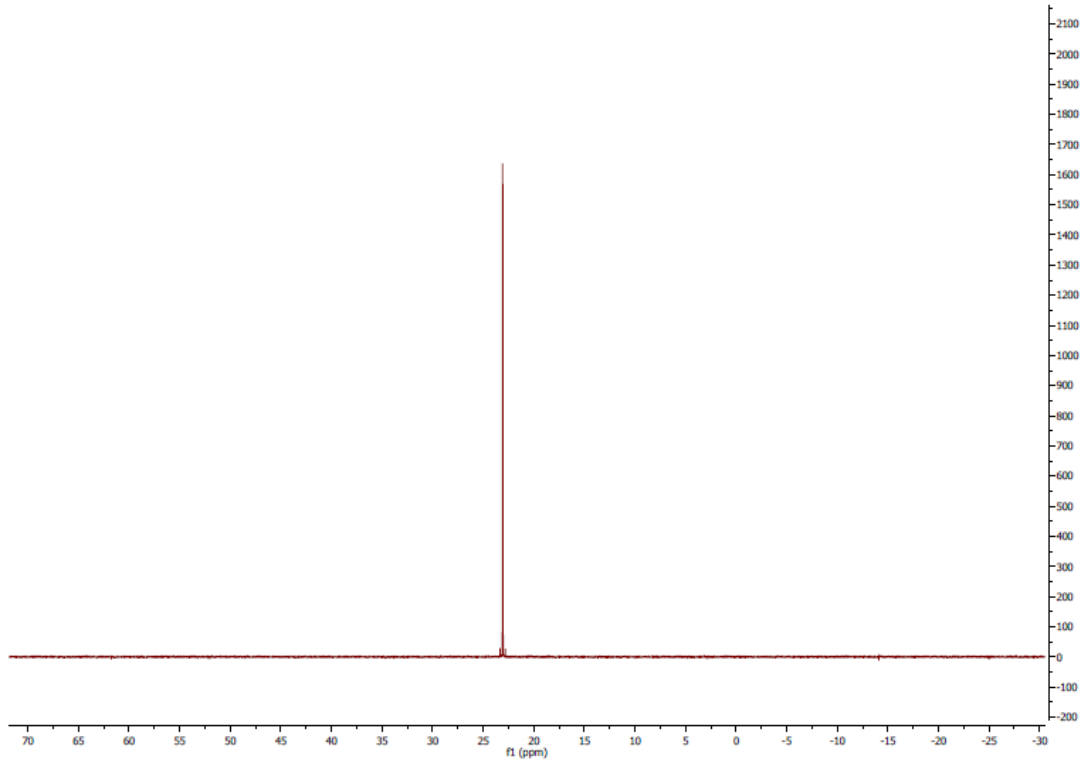
^{1}H NMR



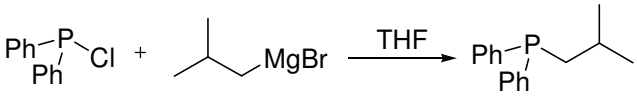
^{13}C NMR



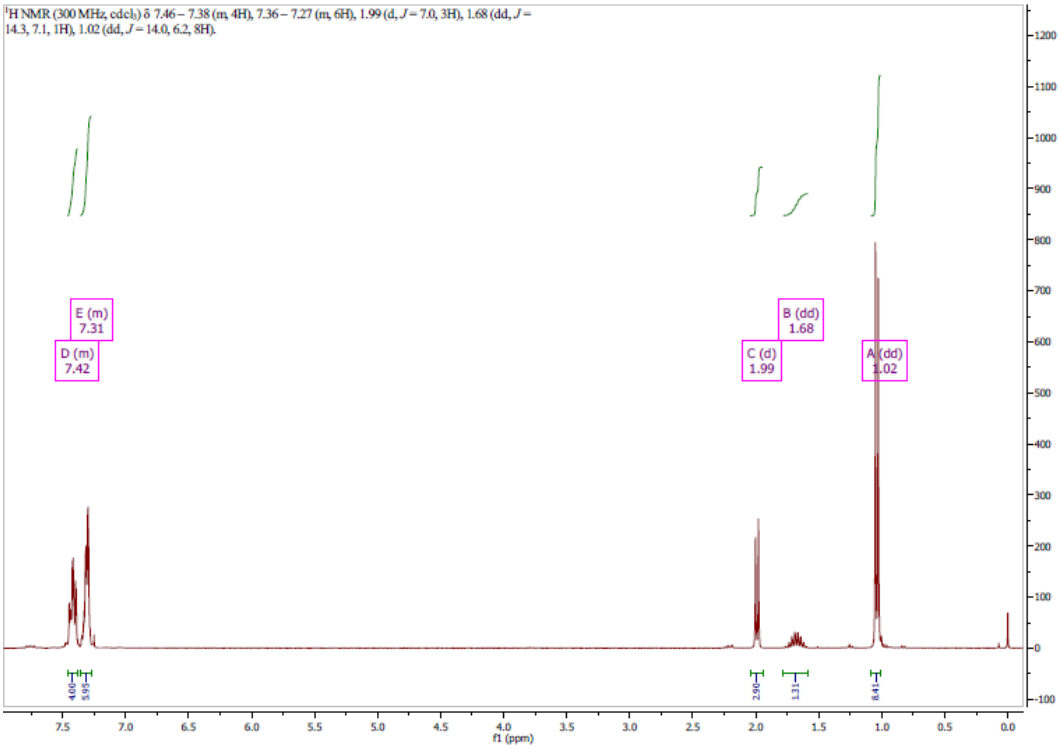
^{31}P NMR



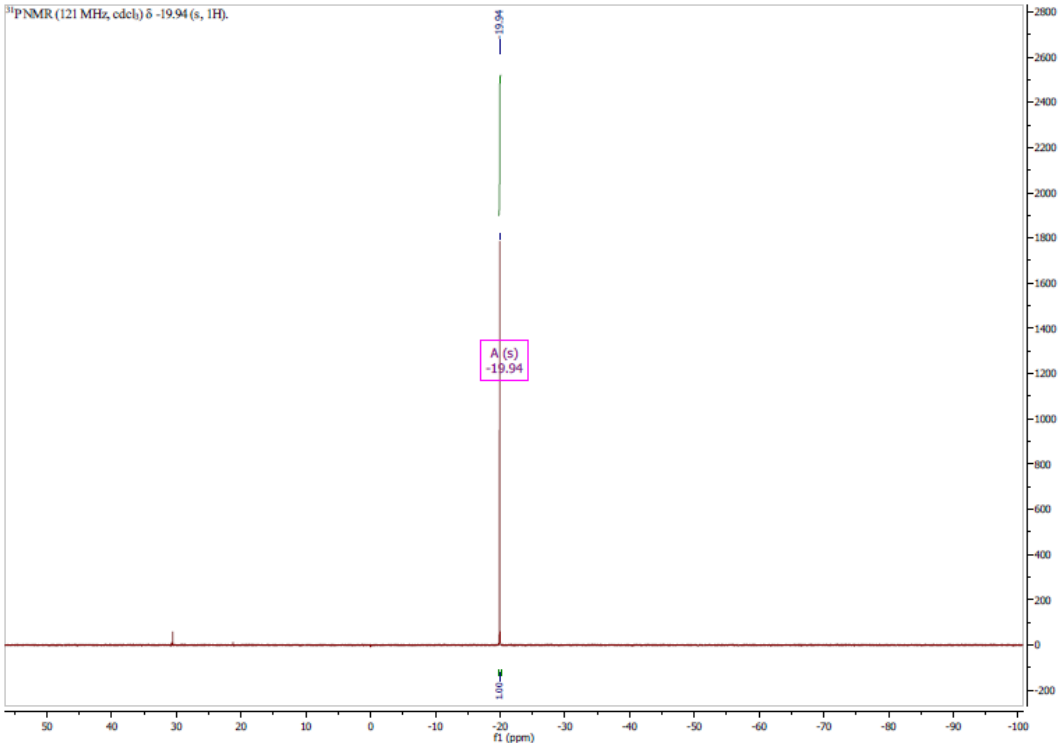
iso-Butyldiphenylphosphine



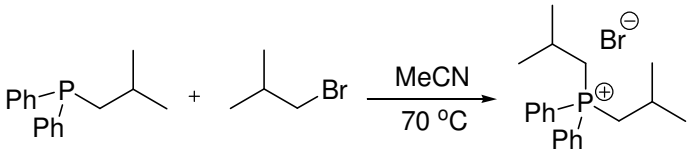
^{1}H NMR



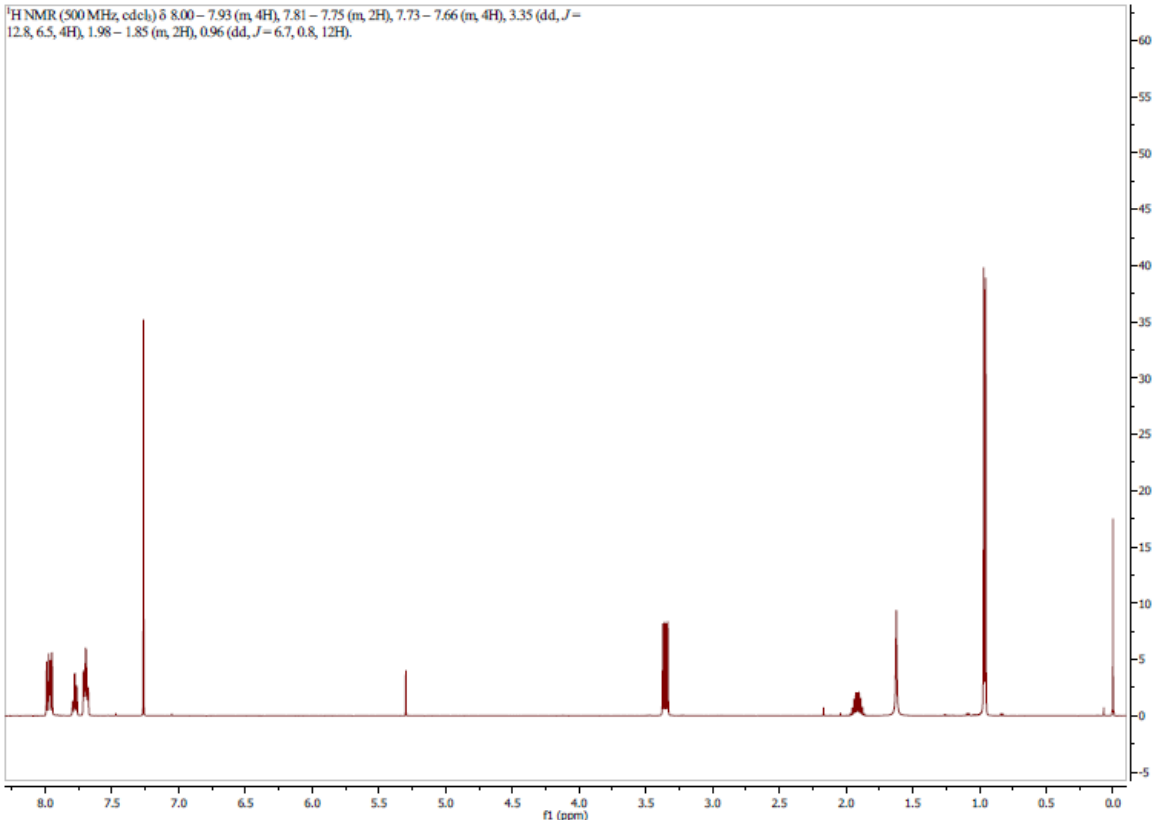
^{31}P NMR



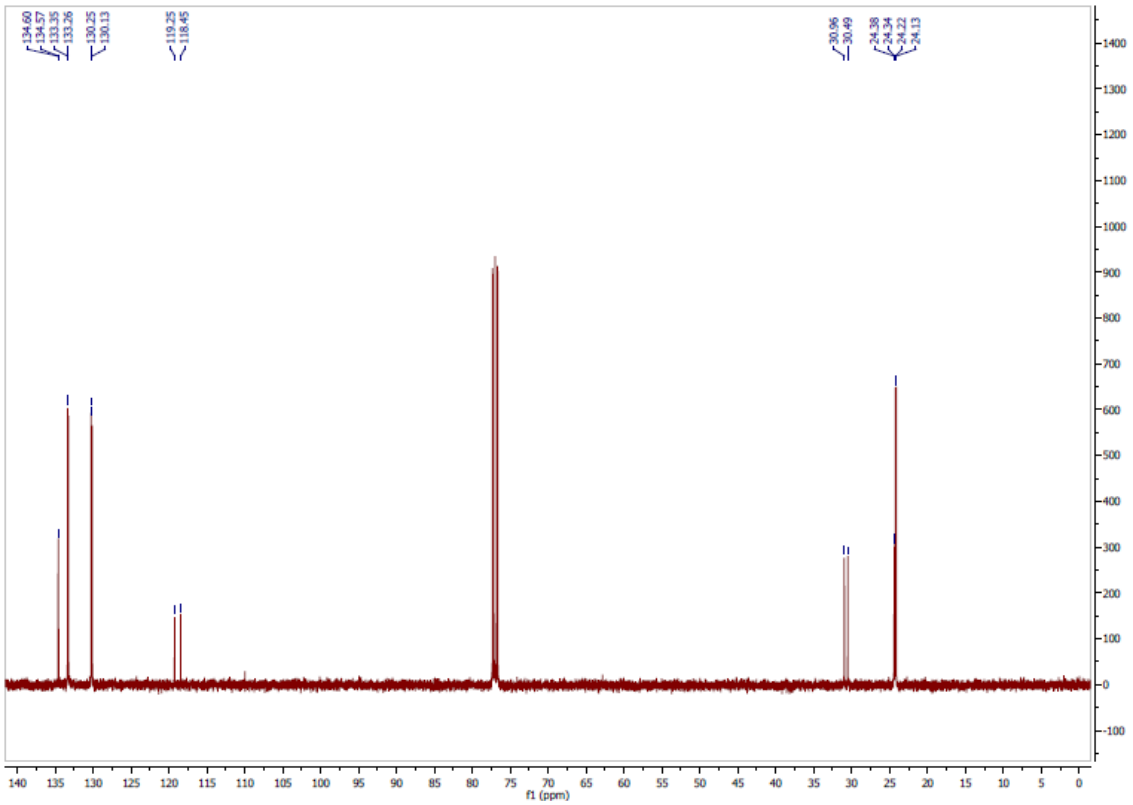
Di(*iso*-butyl)diphenylphosphonium bromide



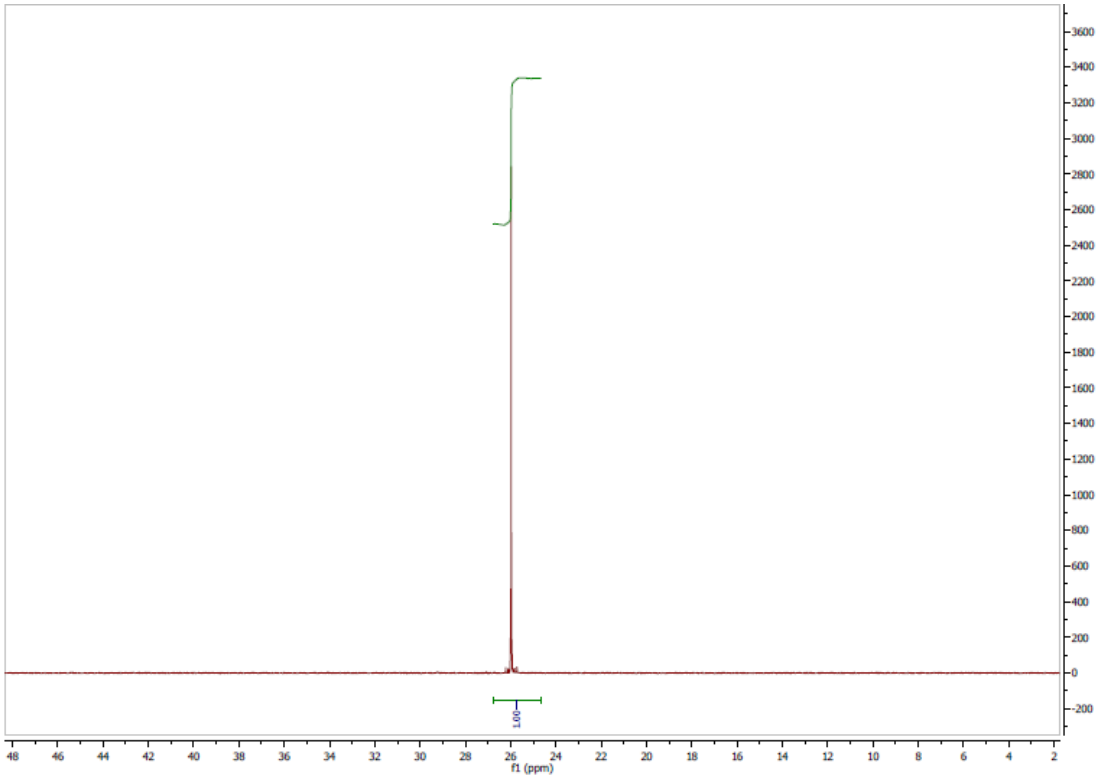
^{1}H NMR



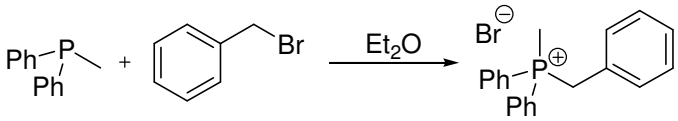
^{13}C NMR



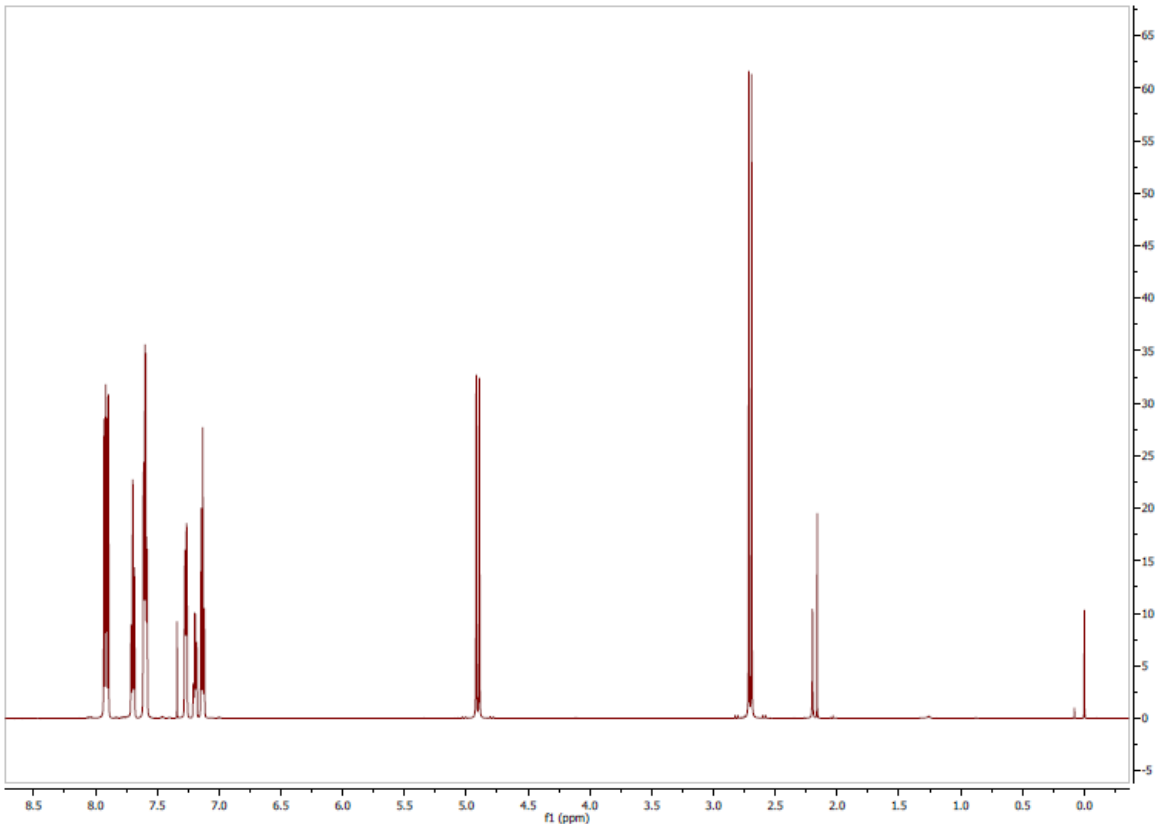
^{31}P NMR



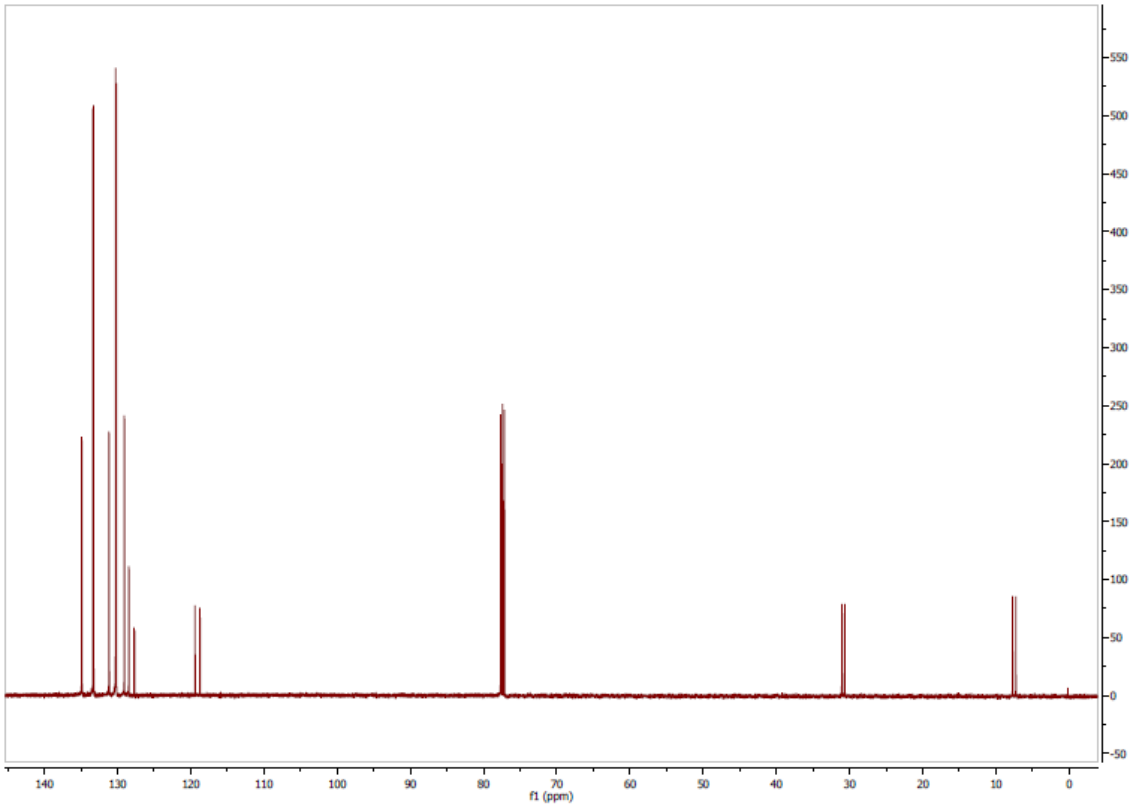
Benzylmethyldiphenylphosphonium bromide



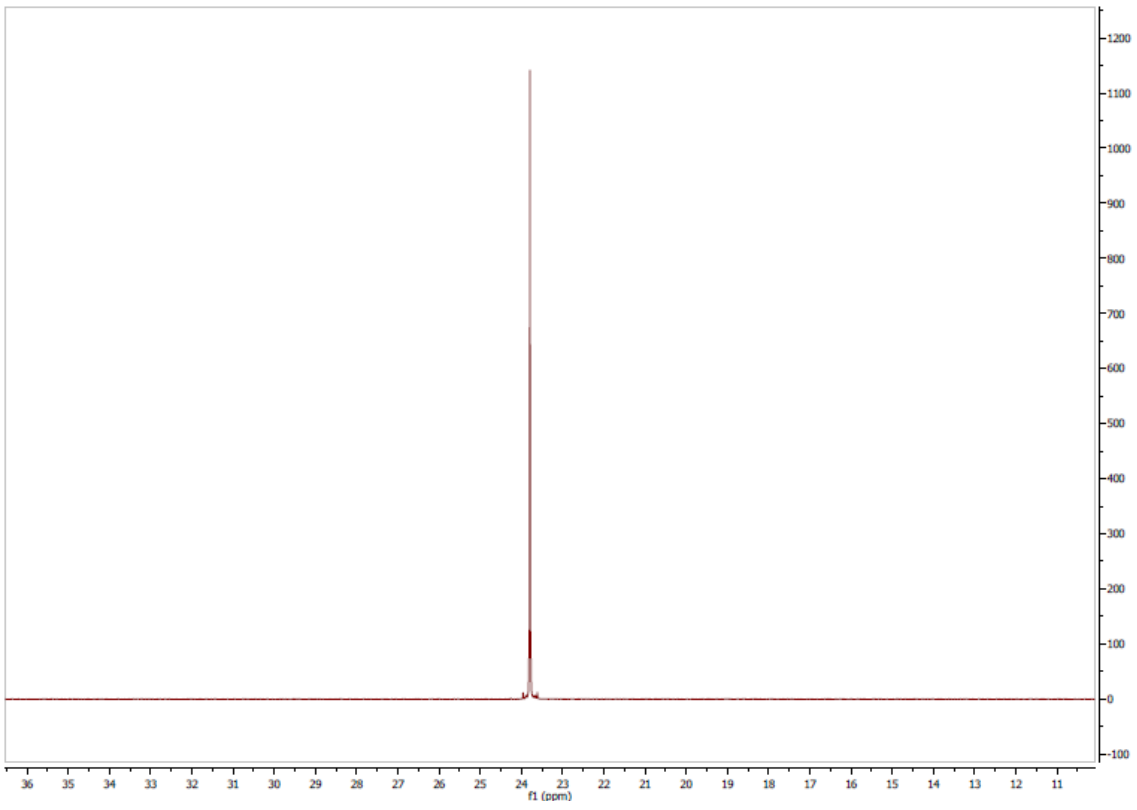
^{1}H NMR



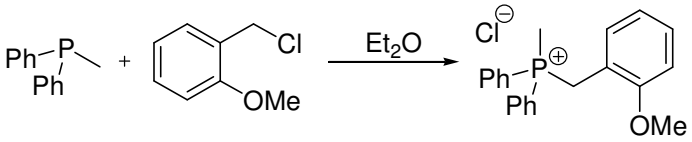
^{13}C NMR



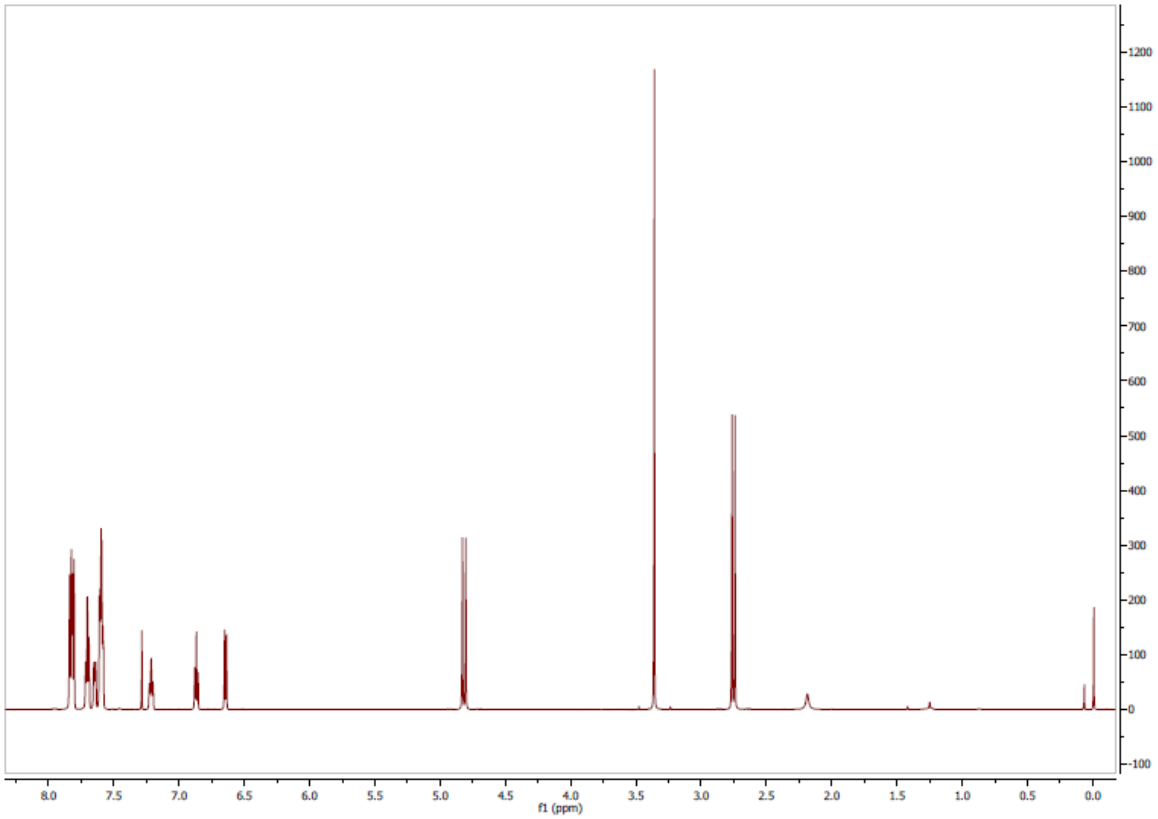
^{31}P NMR



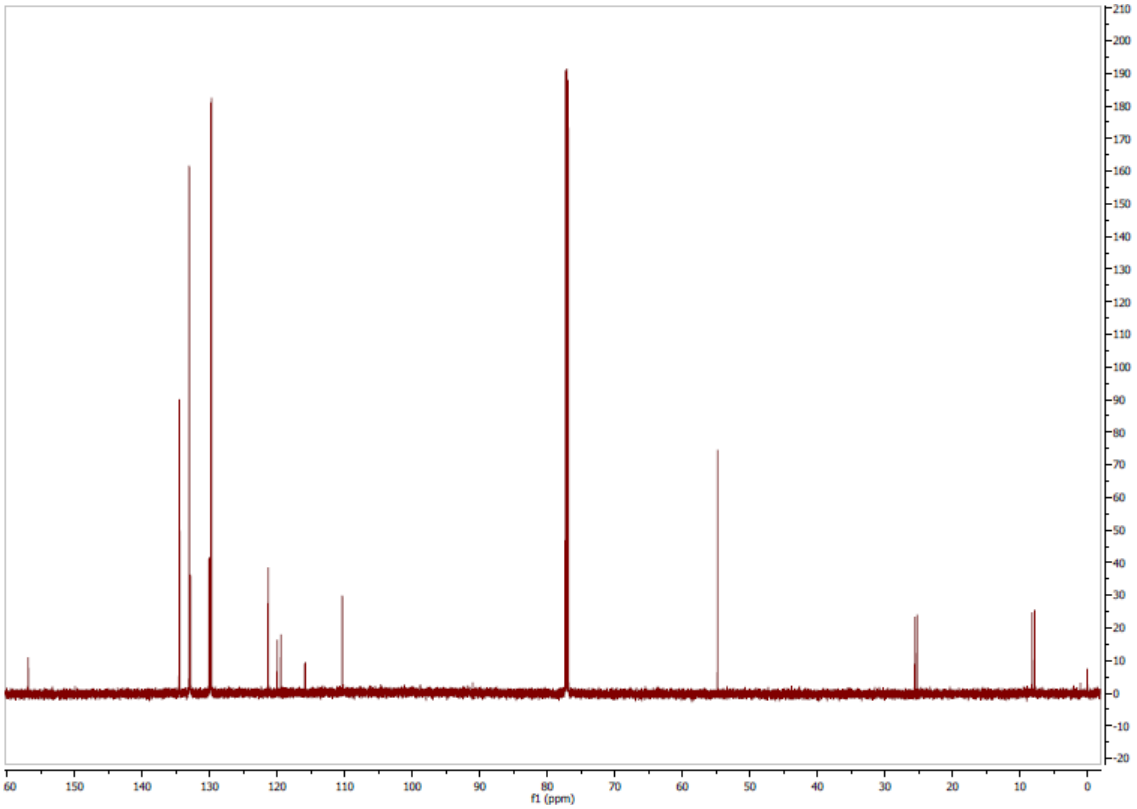
2-Methoxybenzylmethyldiphenylphosphonium chloride



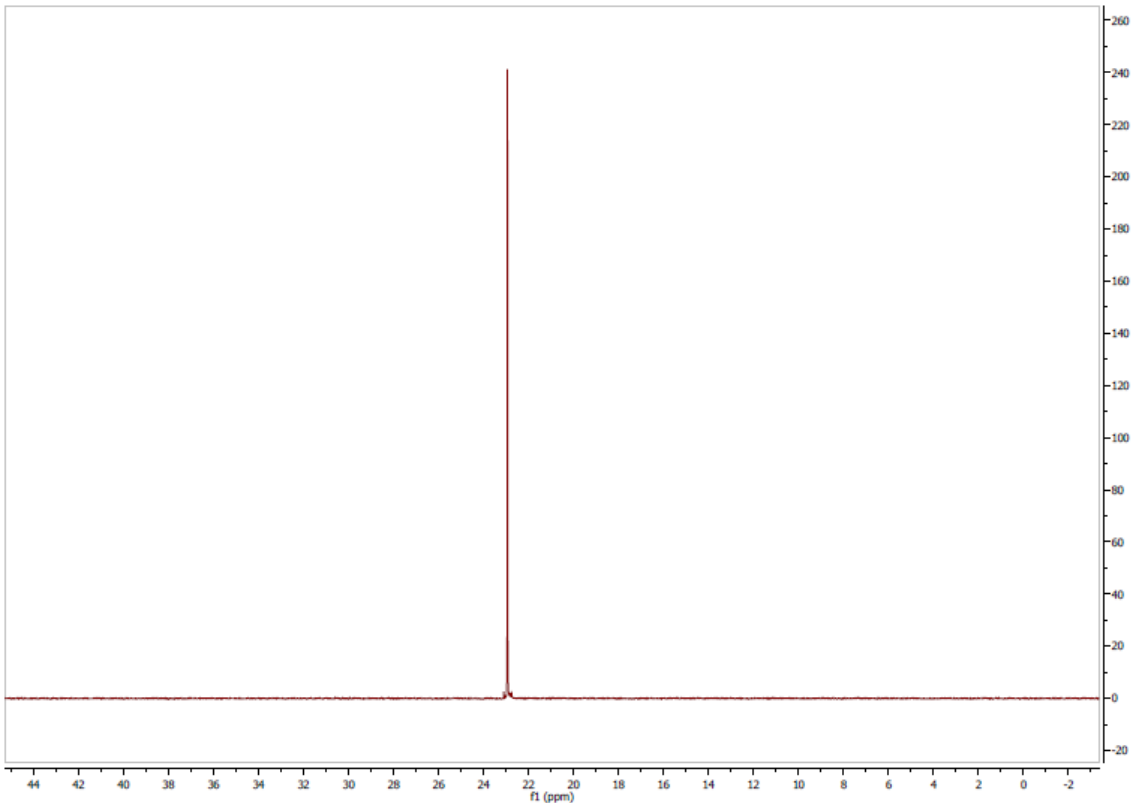
^{1}H NMR



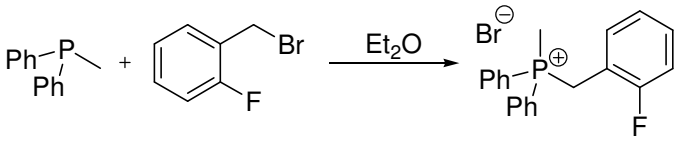
^{13}C NMR



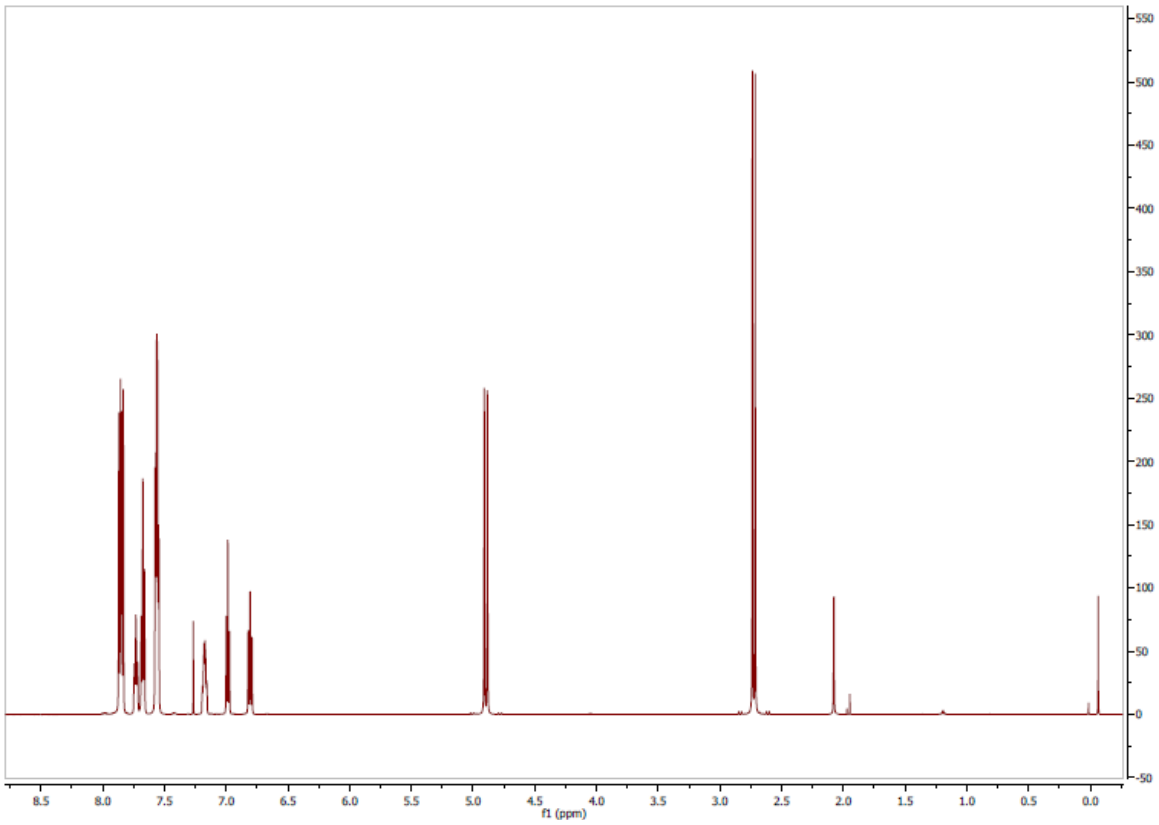
^{31}P NMR



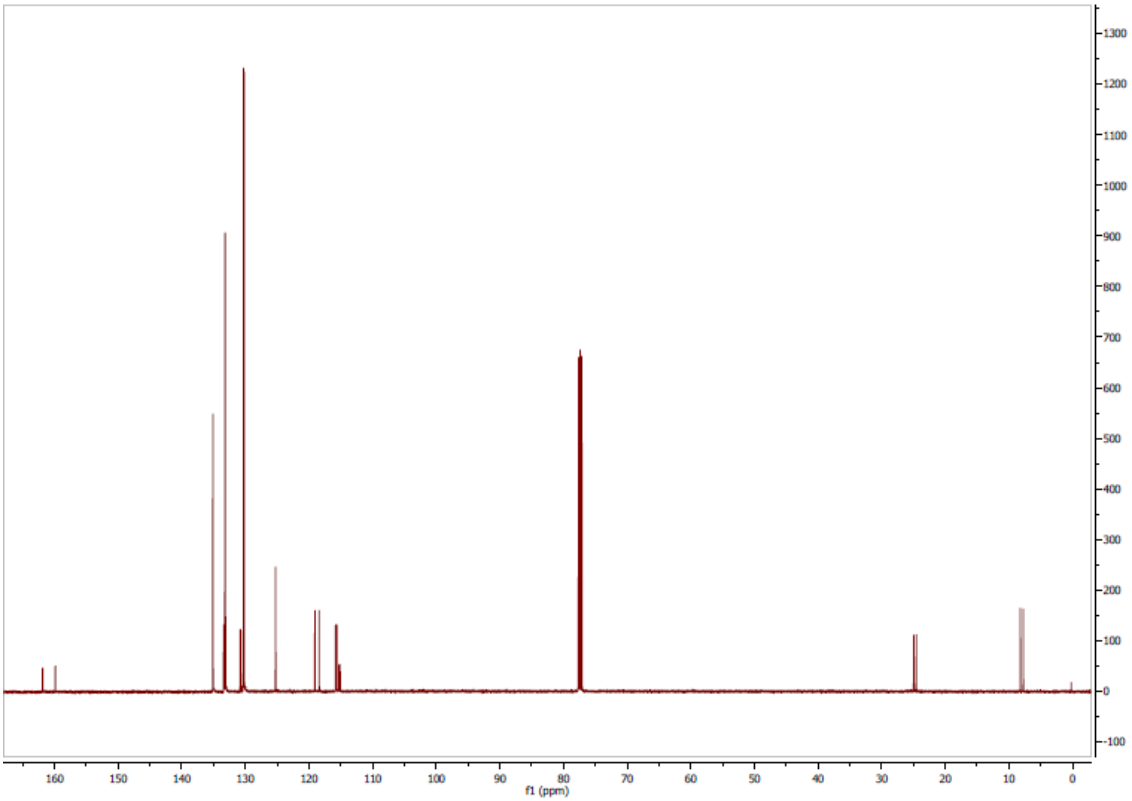
1b. 2-Fluorobenzylmethyldiphenylphosphonium bromide



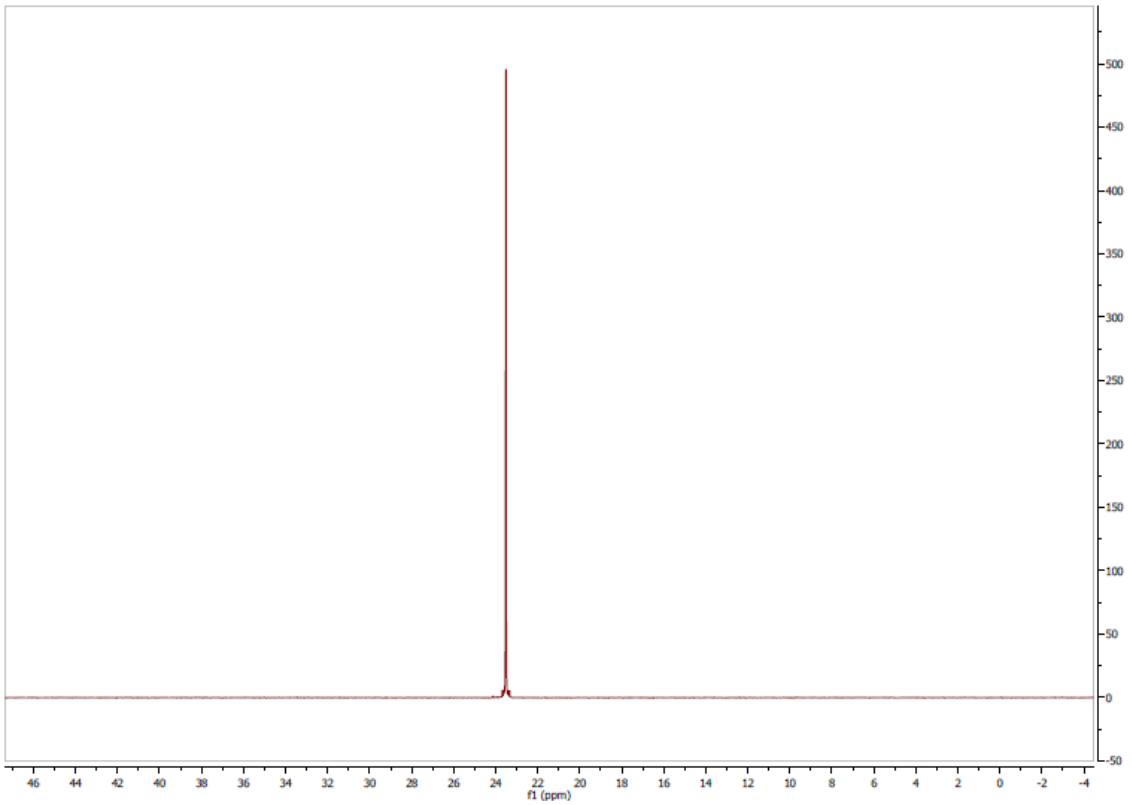
^{1}H NMR



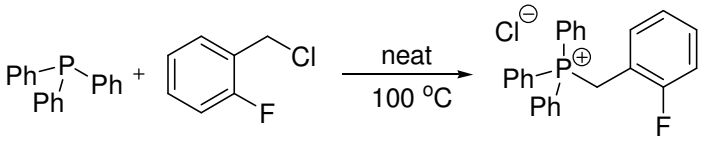
^{13}C NMR



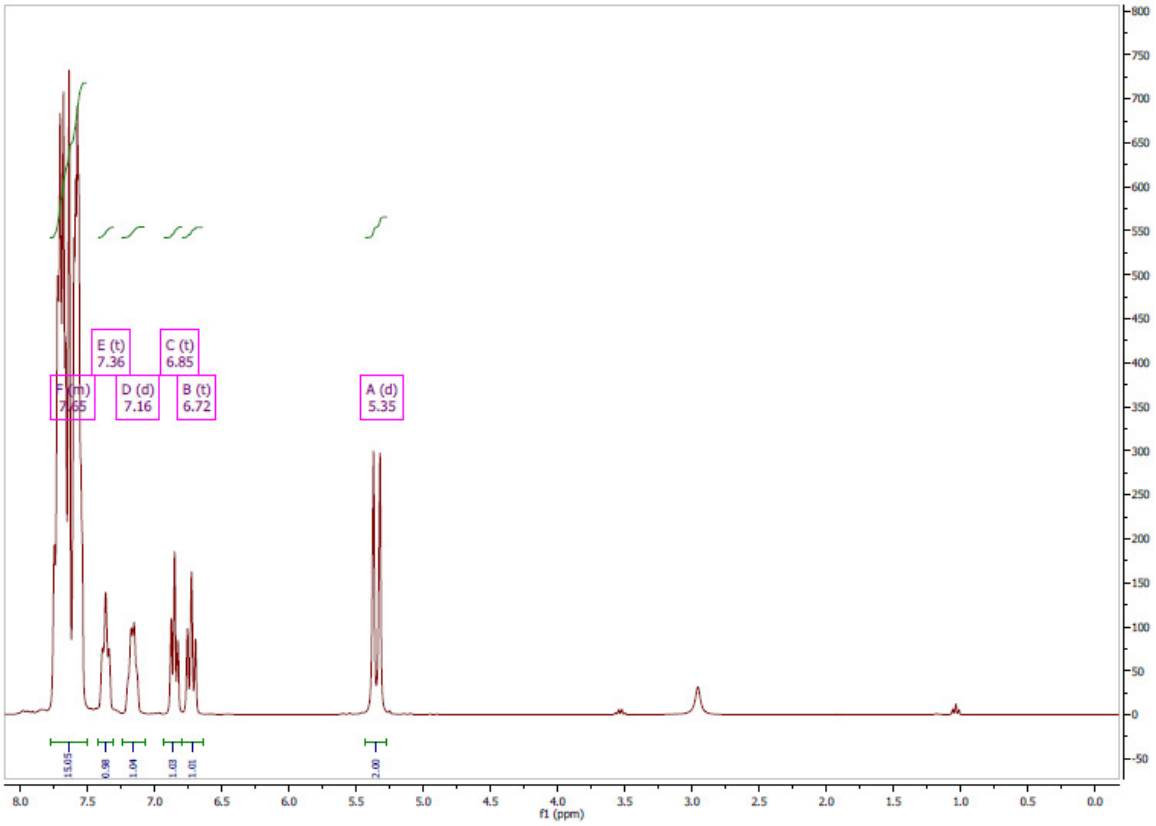
^{31}P NMR



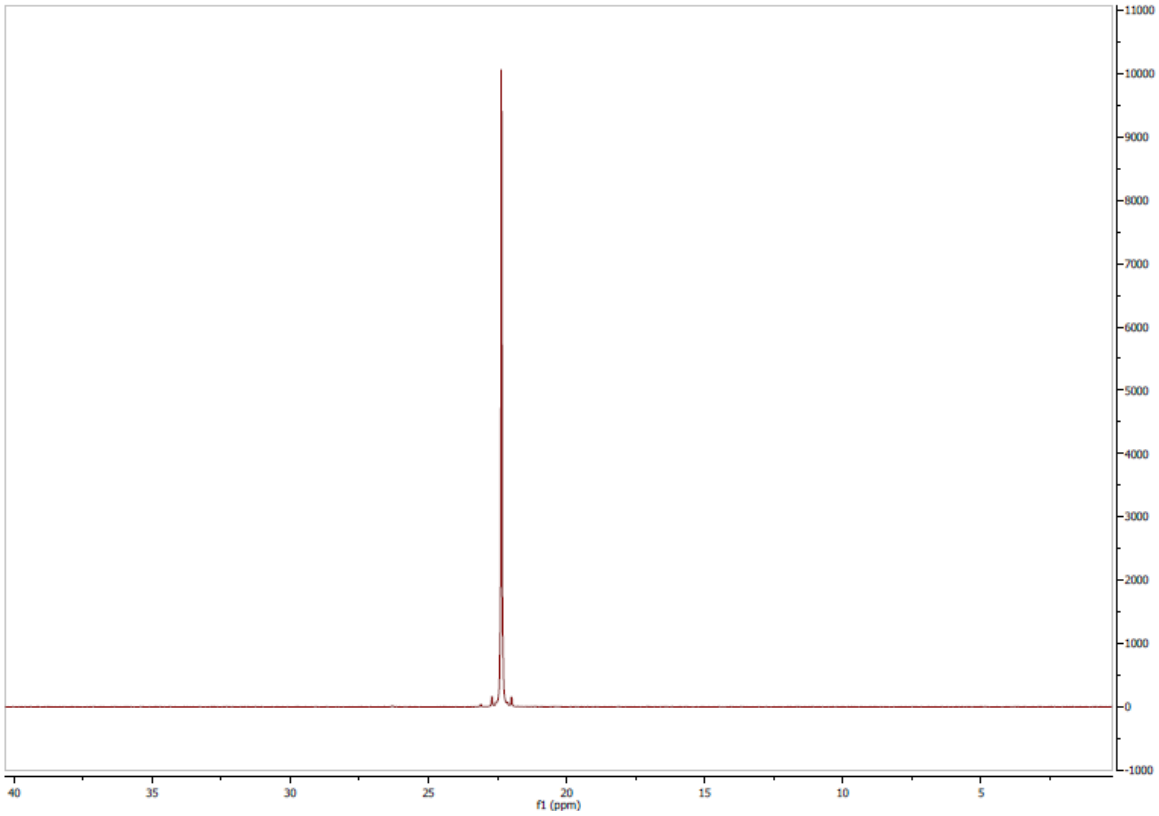
2-fluorobenzyltriphenylphosphonium chloride



^{1}H NMR

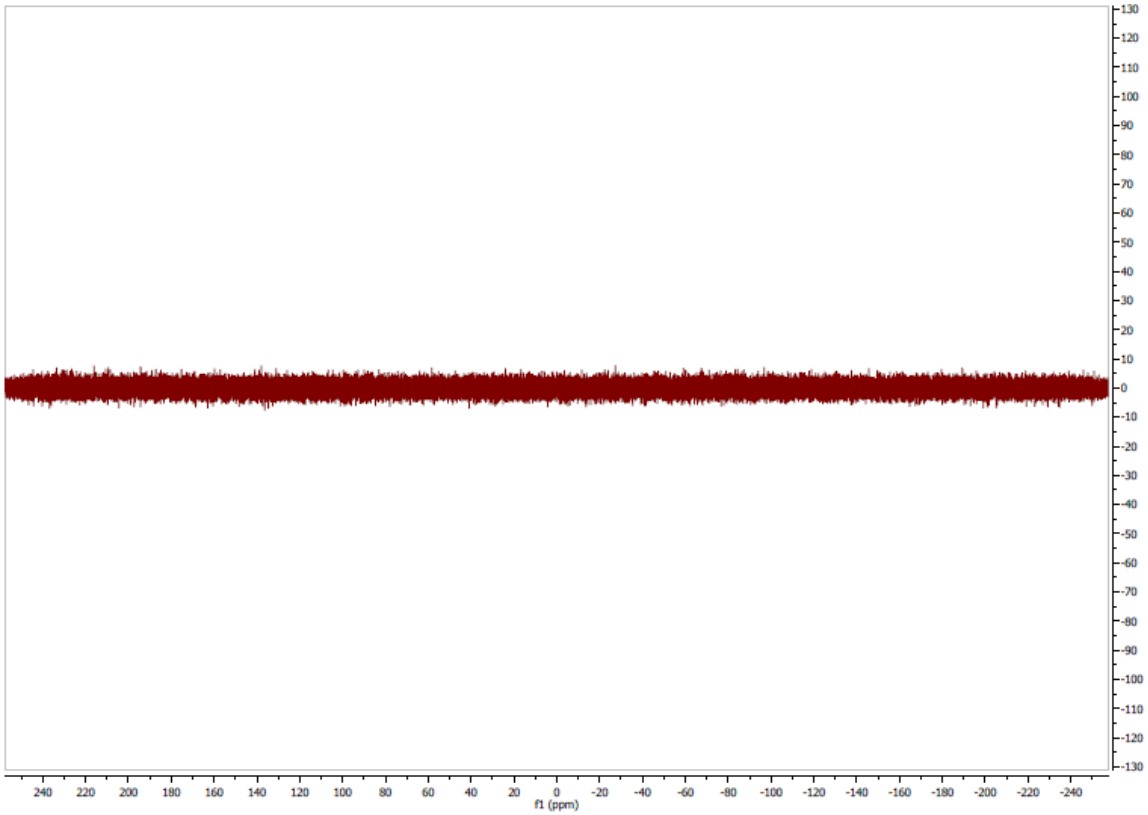


^{31}P NMR

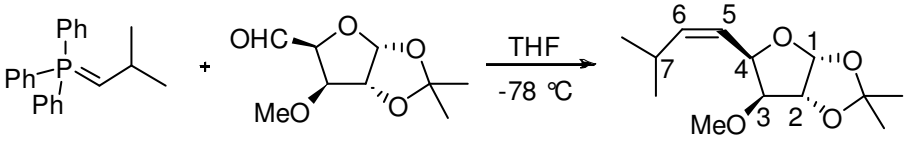


8. NMR spectra of purified alkenes and regenerated phosphines from Wittig reactions

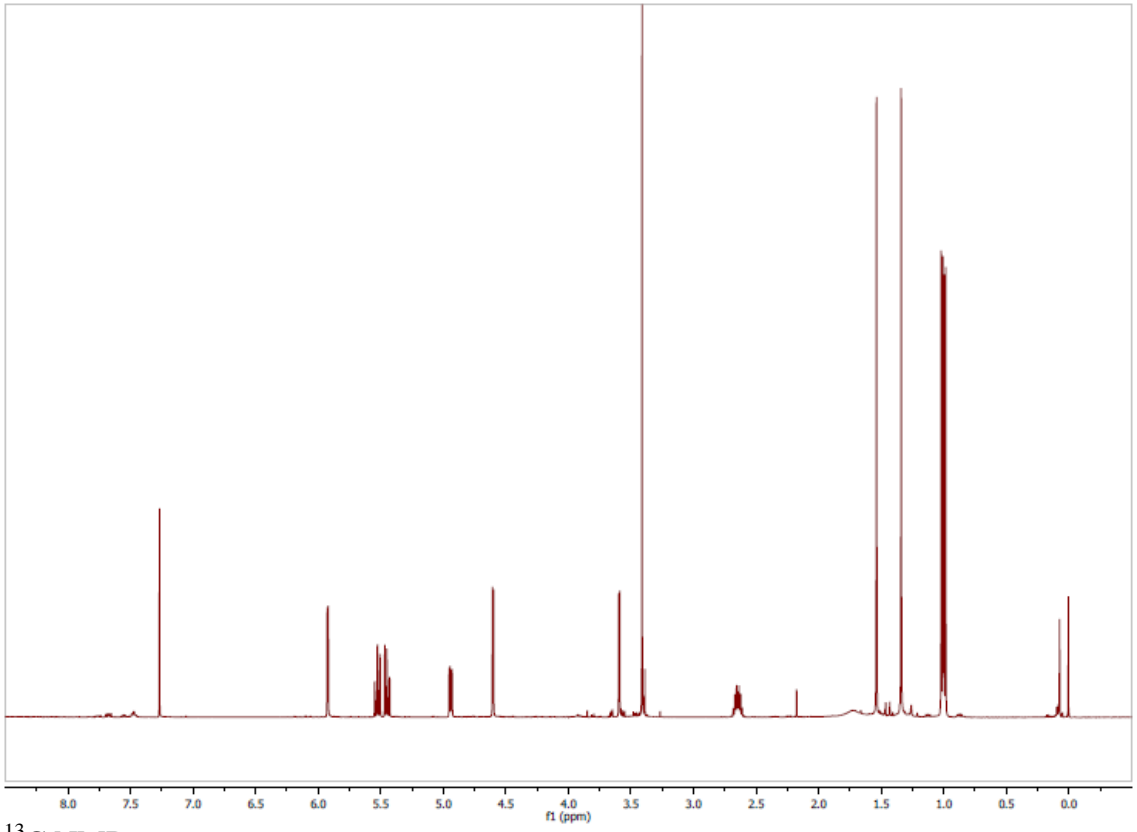
The ^{31}P NMR spectrum of all purified alkenes appeared like the one shown below, showing the absence of phosphorus-containing material.



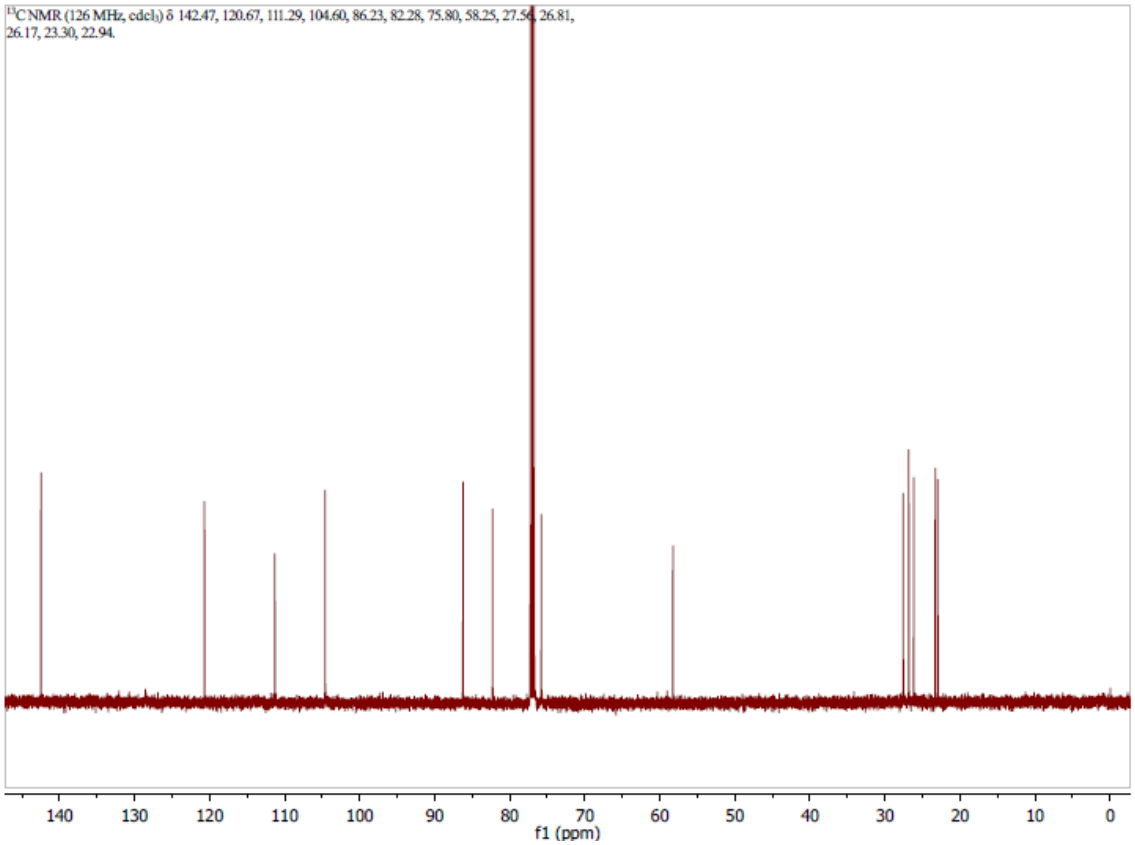
1. Reaction with *P*-(*iso*-butylidene)triphenylphosphorane. Table 1 entry 1.



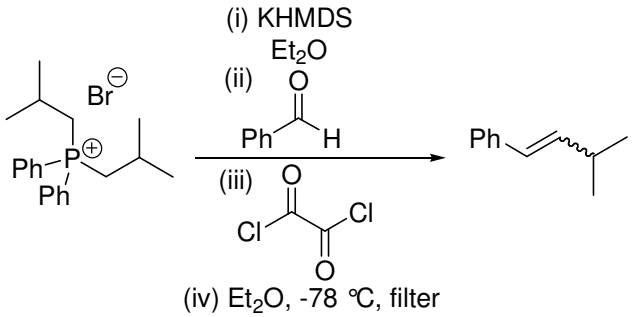
^{1}H NMR of purified alkene



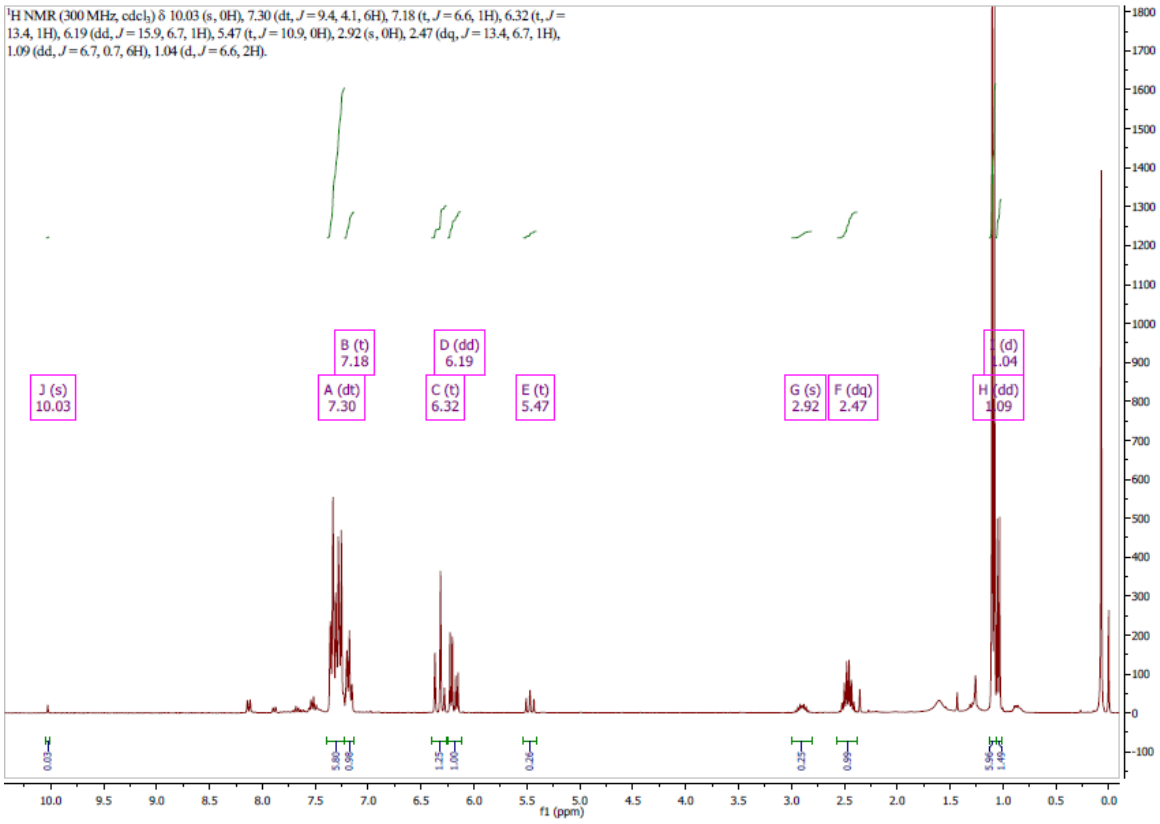
^{13}C NMR



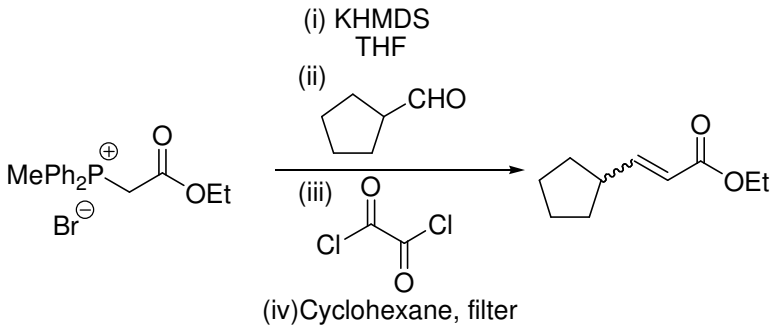
2. 3-methyl-1-phenylbut-1-ene. Table 1 entry 2.



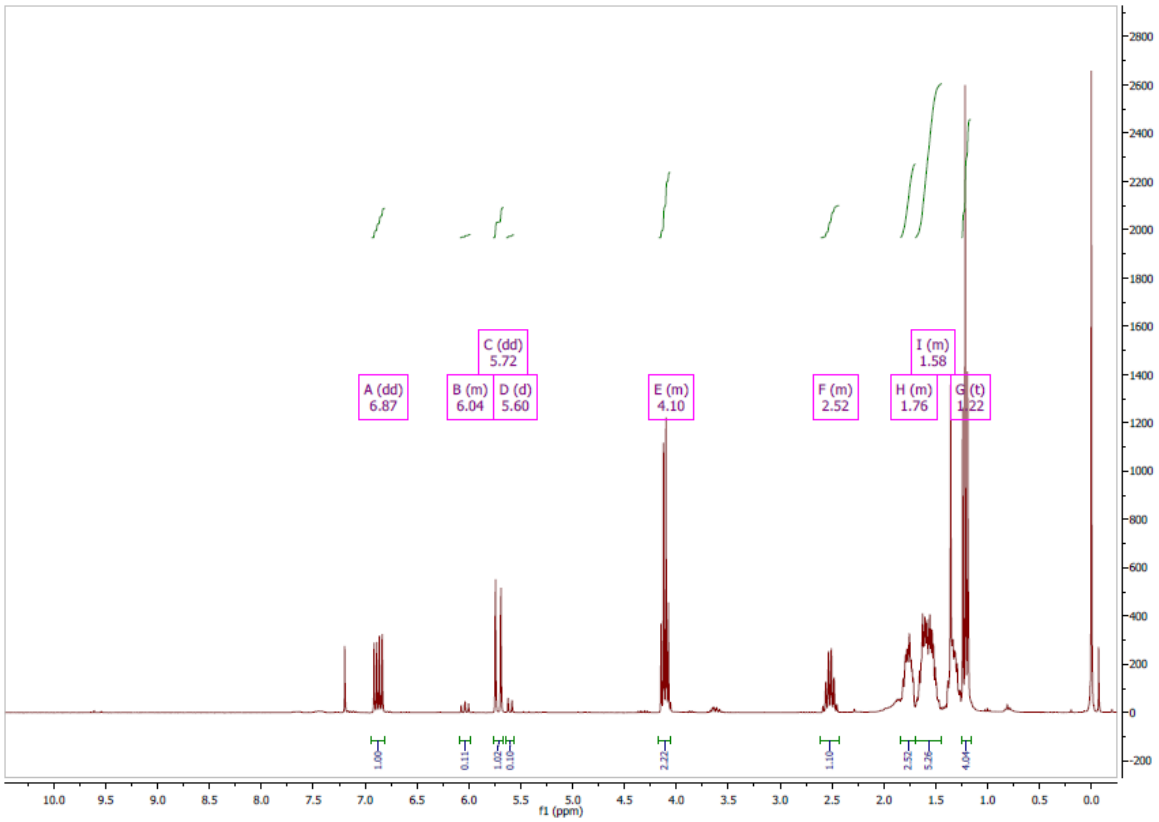
^{1}H NMR



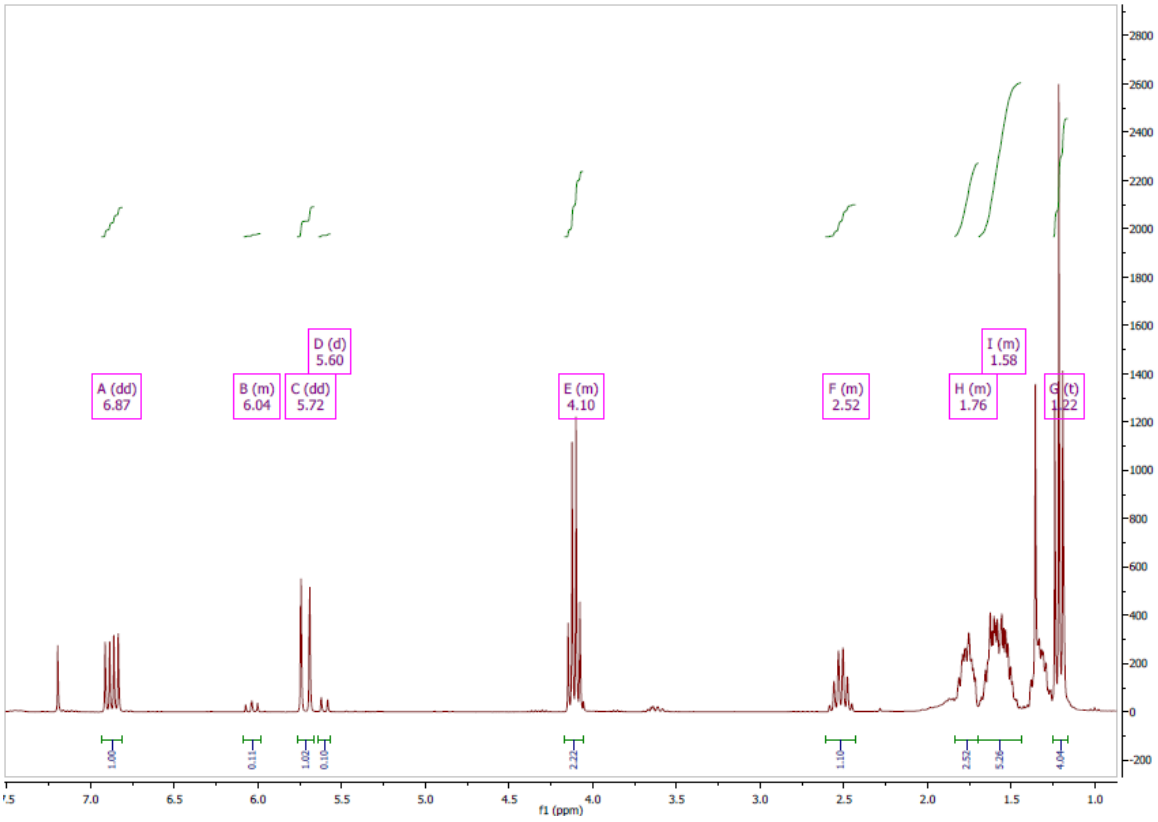
3. Ethyl 3- cyclopentylprop-2-enoate. Table 1, entry 3.



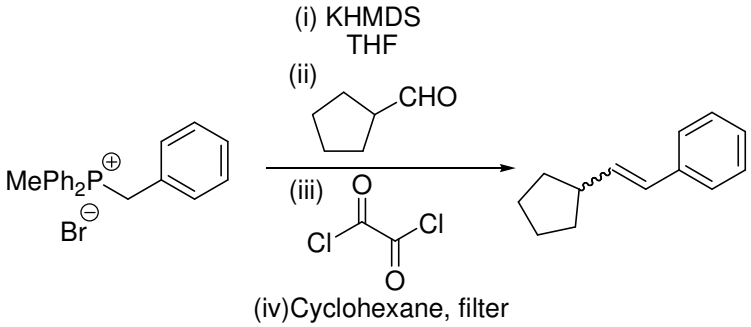
^{1}H NMR:



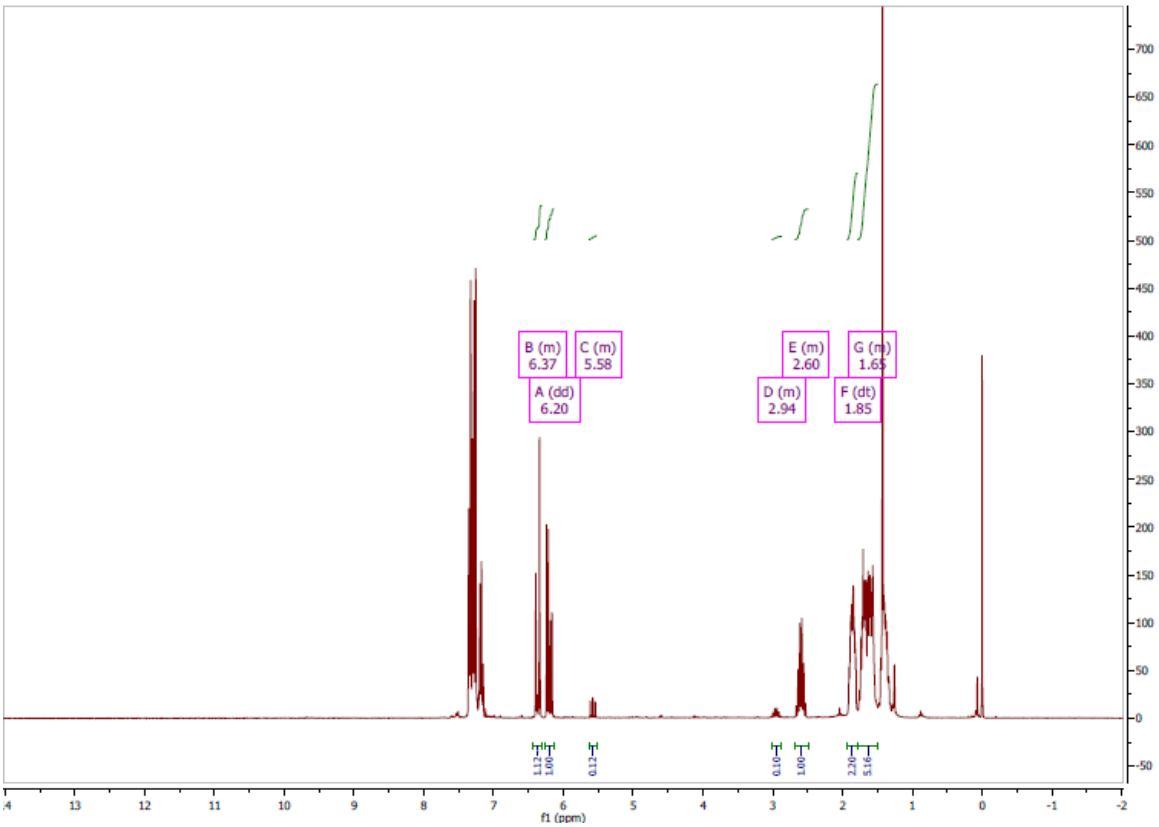
Close-up on δ 1.0-7.5 ppm region



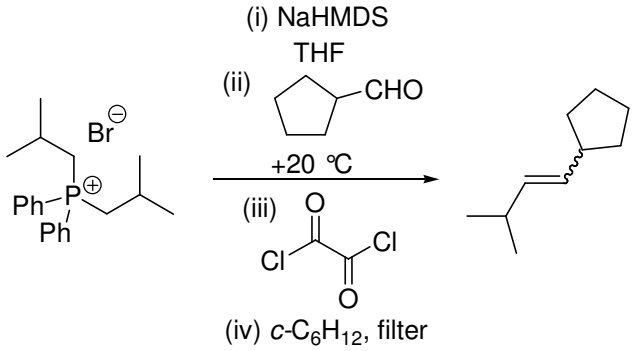
4. 1-cyclopentyl-2-phenylethene. Table 1, entry 4



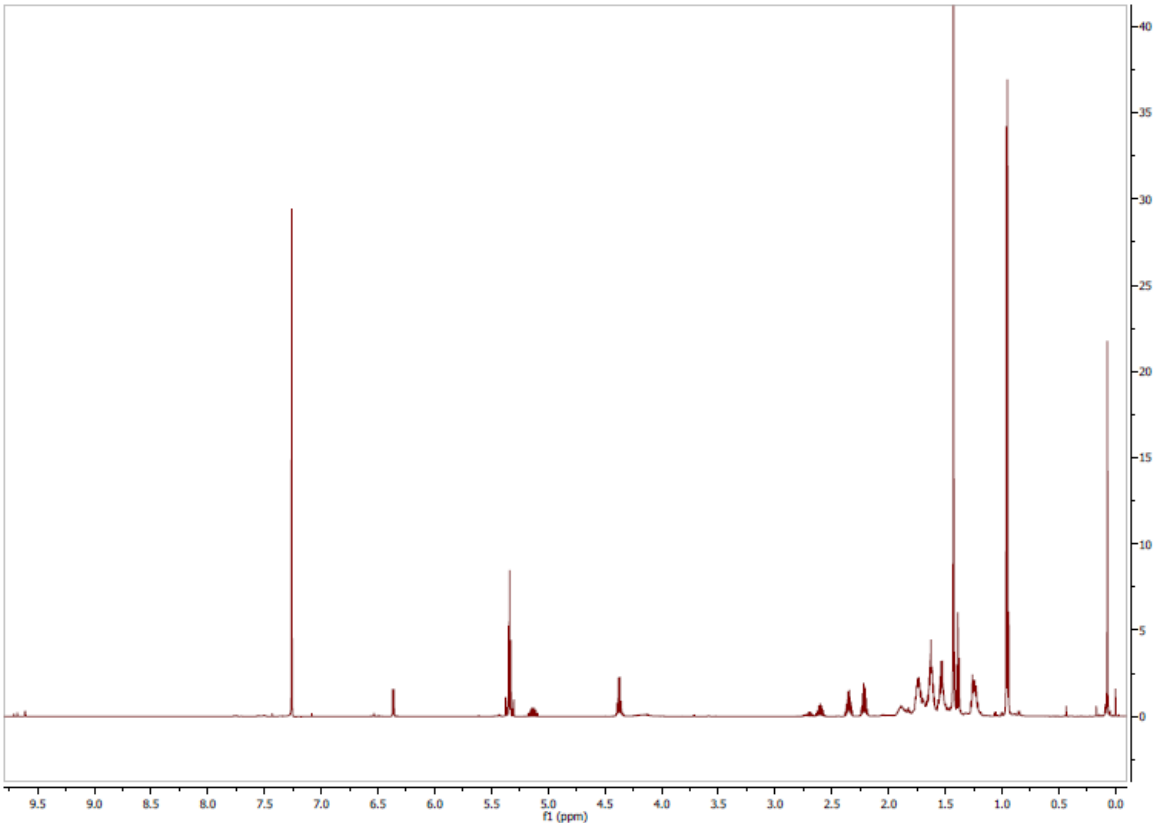
^{1}H NMR



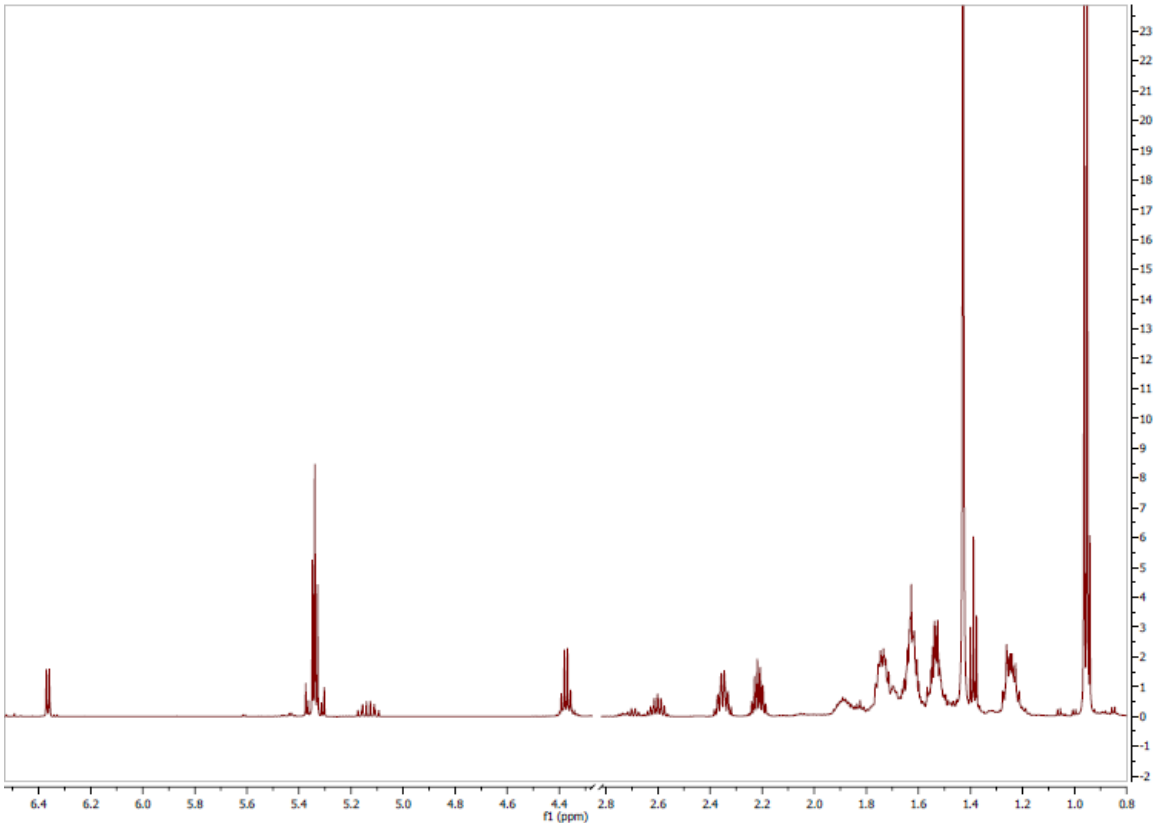
5. 1-cyclopentyl-3-methylbut-1-ene. Table 1 entry 5.



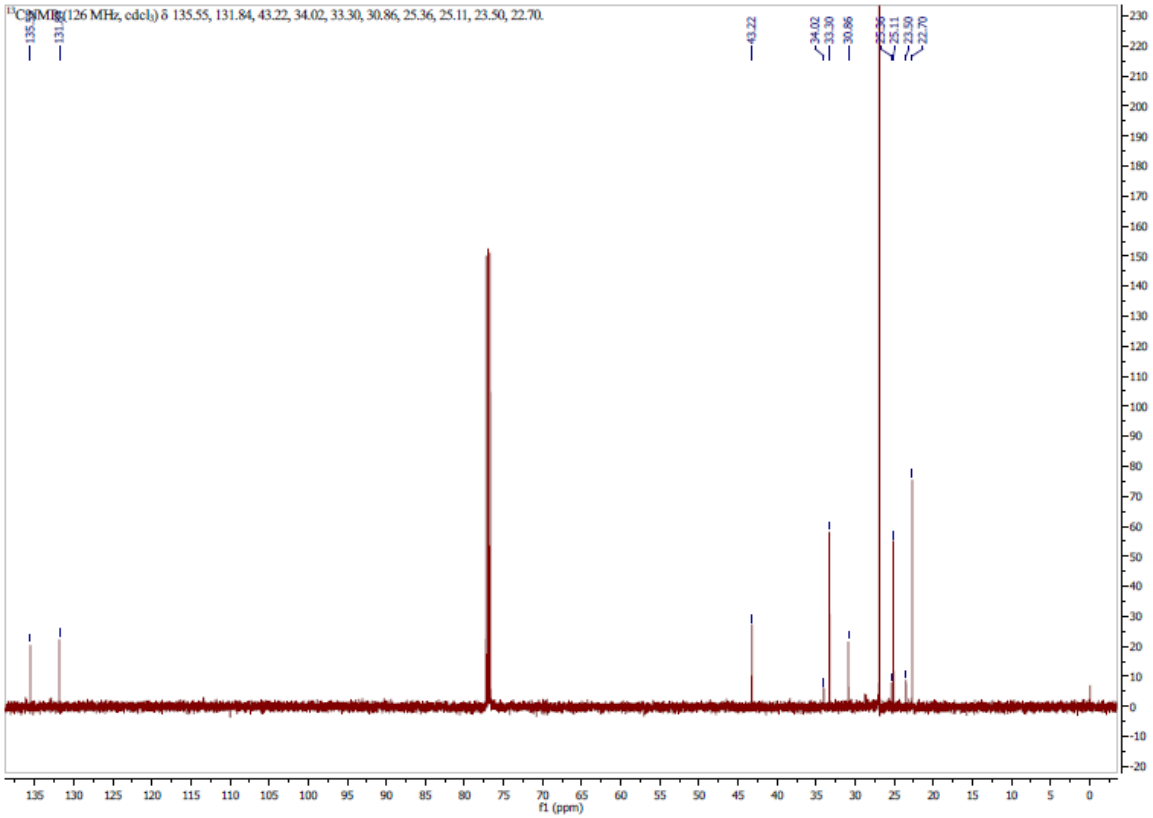
^{1}H NMR



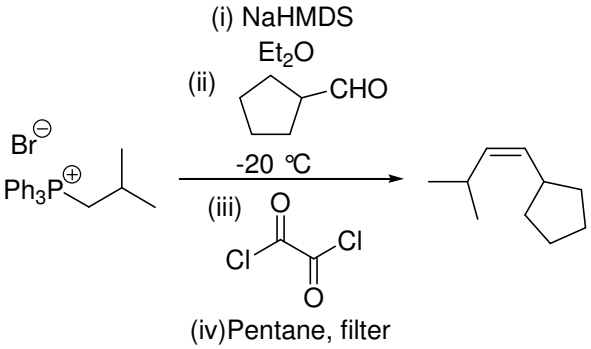
^{1}H NMR close up on regions δ 0.8-2.8 and 4.3-6.5 ppm.



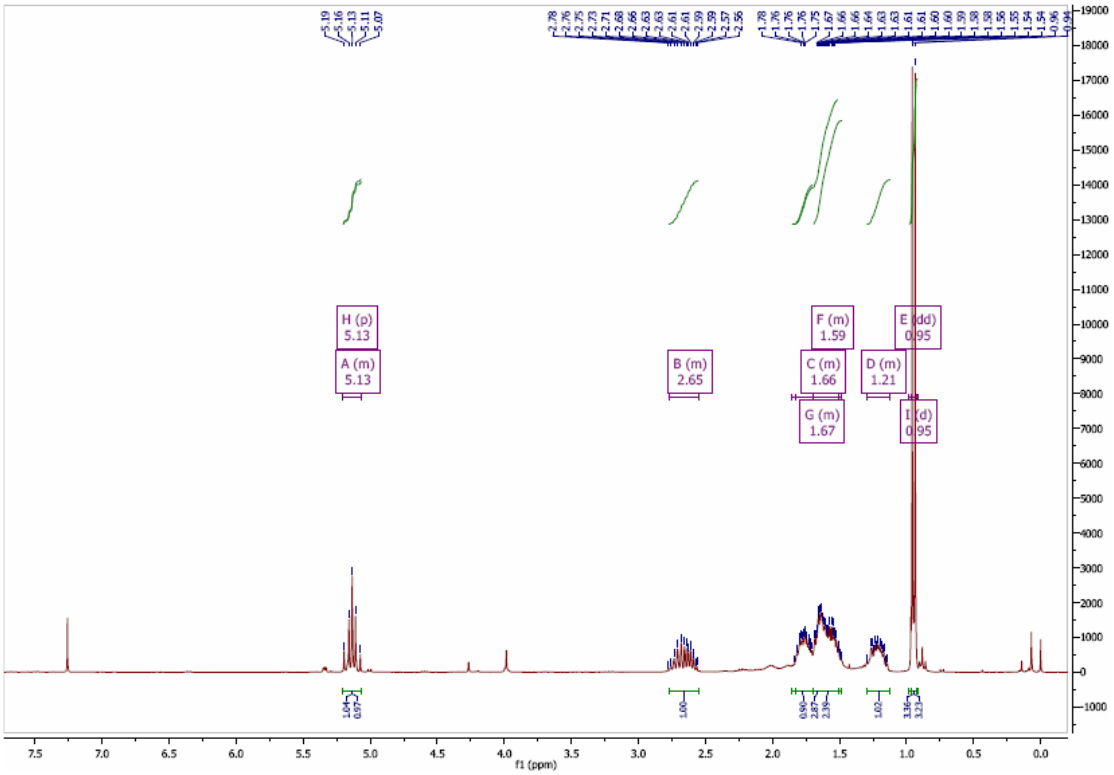
^{13}C NMR



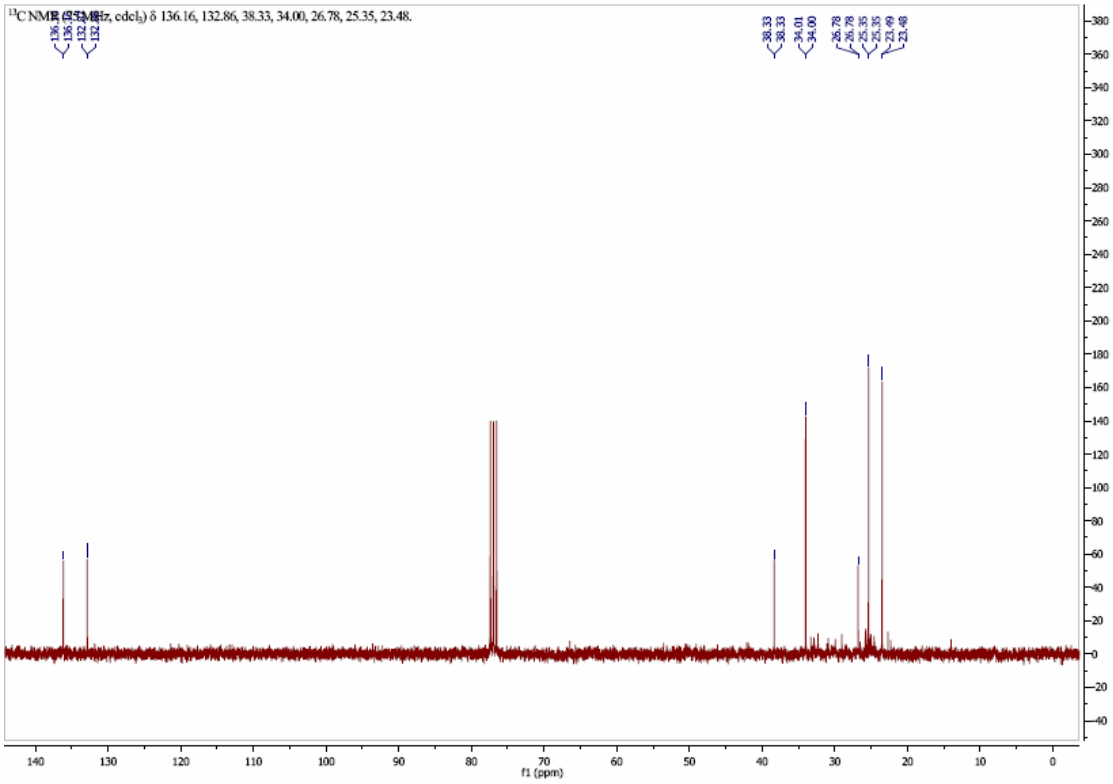
6. *Z*-1-cyclopentyl-3-methylbut-1-ene. Table 1 entry 6.



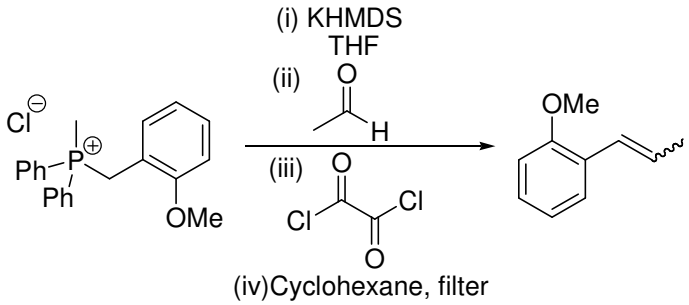
^{1}H NMR


H (p)
5.13
A (m)
5.13
B (m)
2.65
F (m)
1.59
C (m)
1.66
G (m)
1.67
D (m)
1.21
E (dd)
0.95
I (d)
0.95
f1 (ppm)

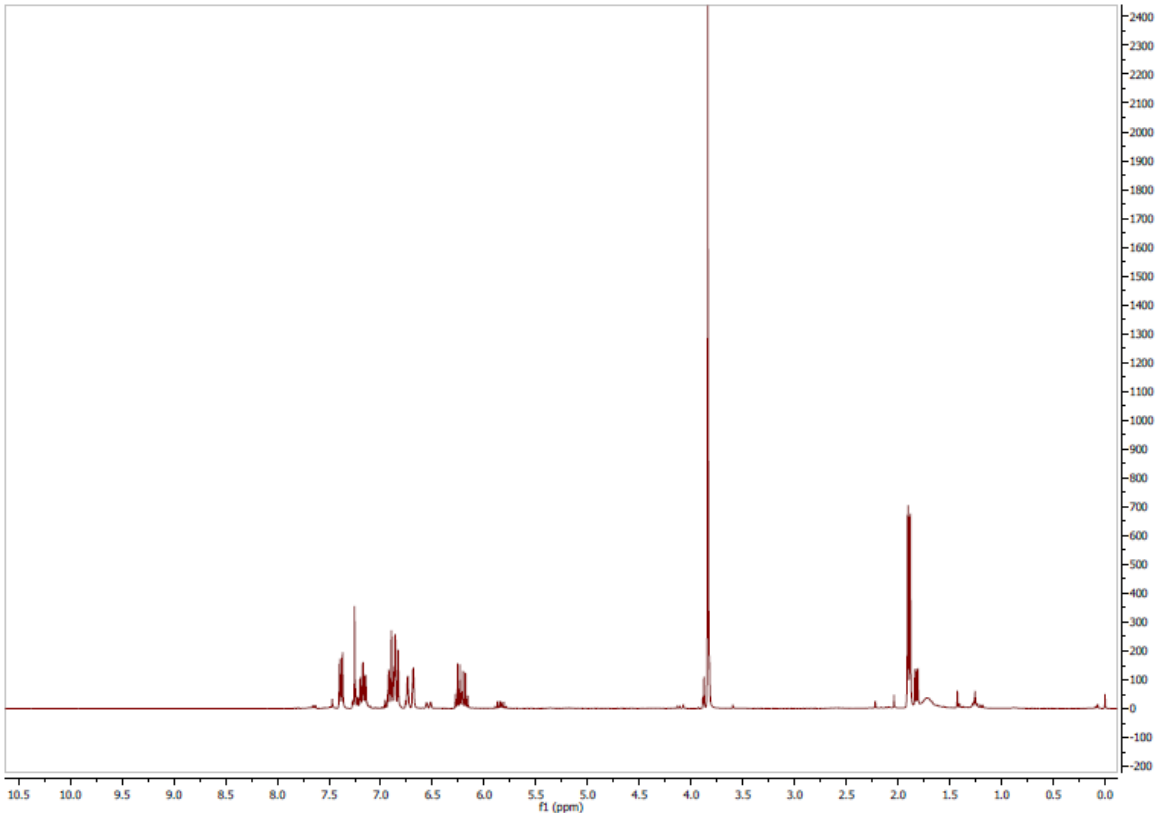
^{13}C NMR



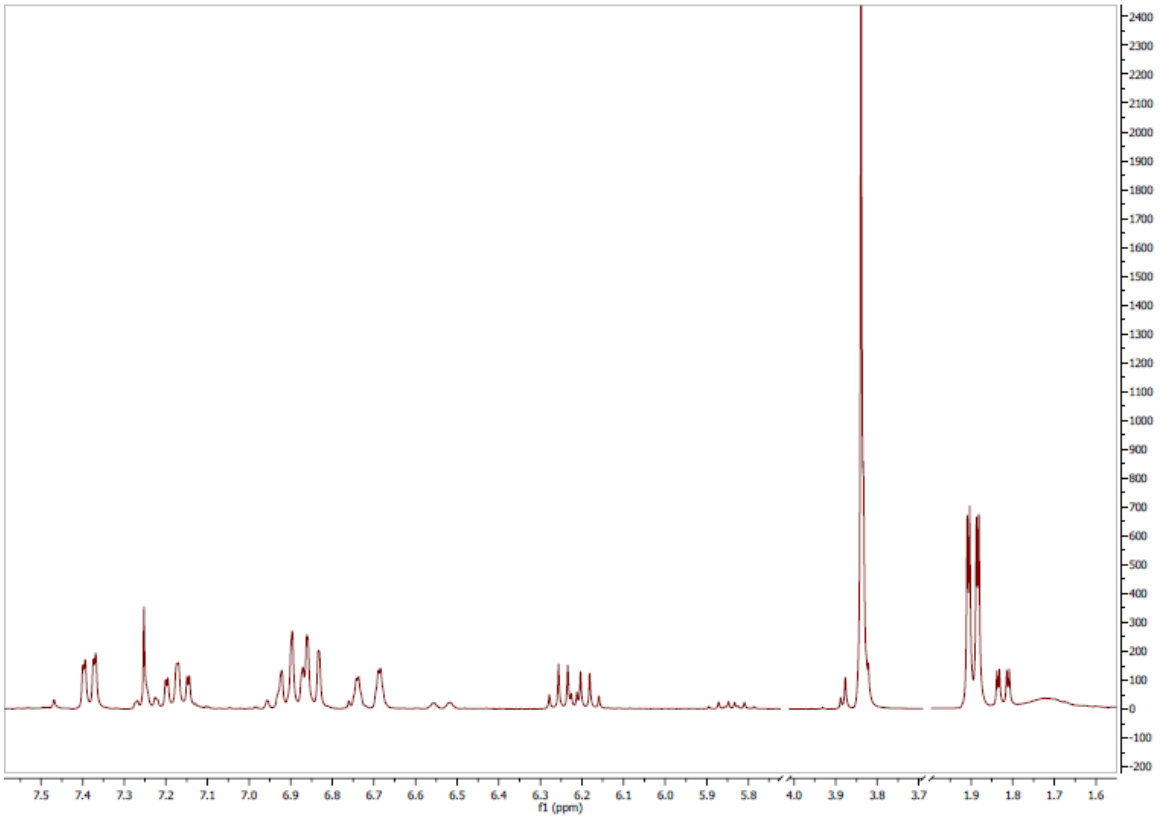
7. 1-(2-methoxyphenyl)prop-1-ene. Table 1 entry 7.



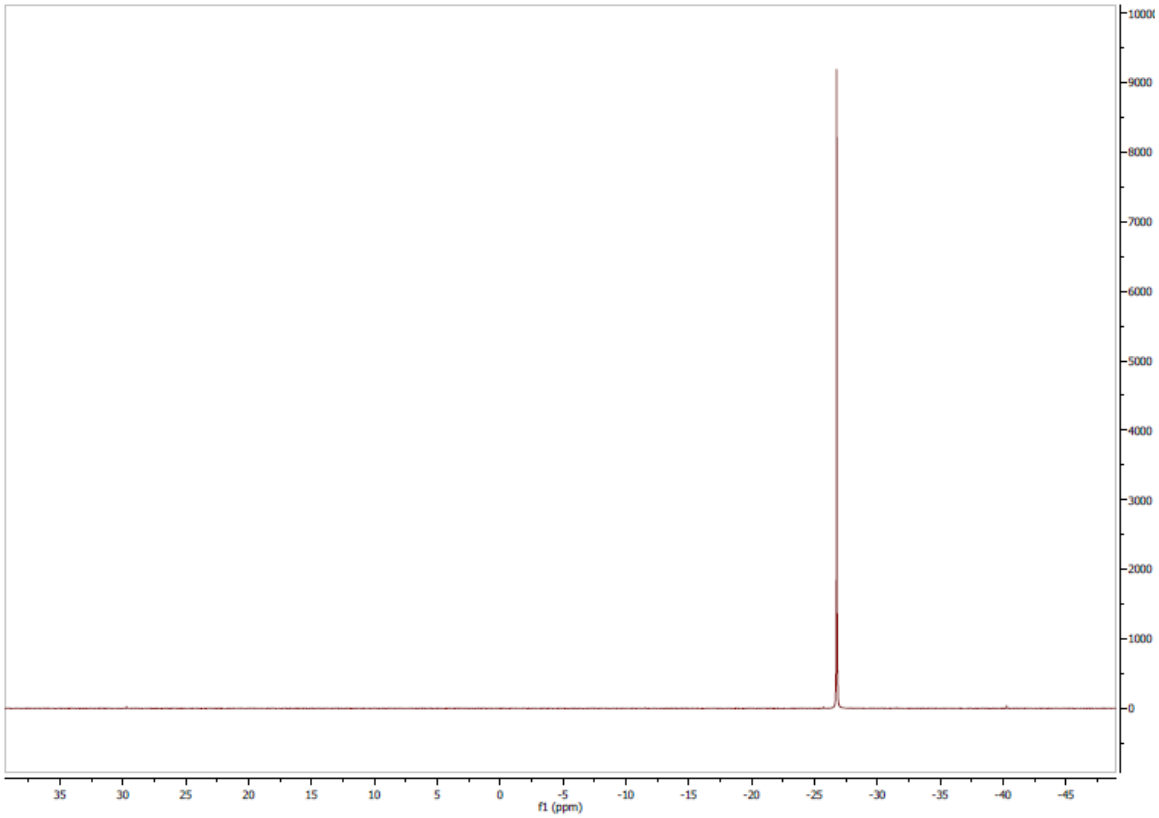
^{1}H NMR



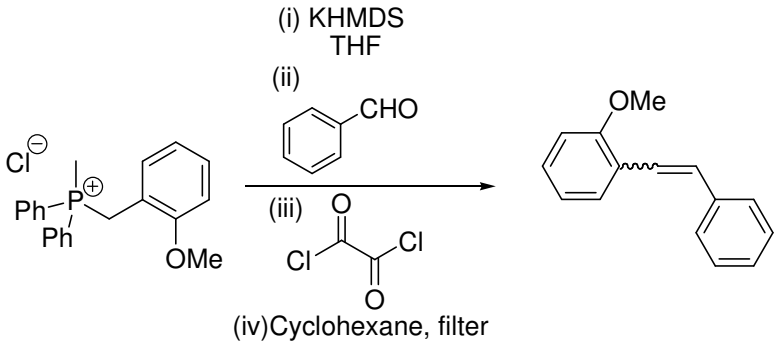
^{1}H NMR close up on δ 2.7-4.0 and 5.7-7.8 ppm regions



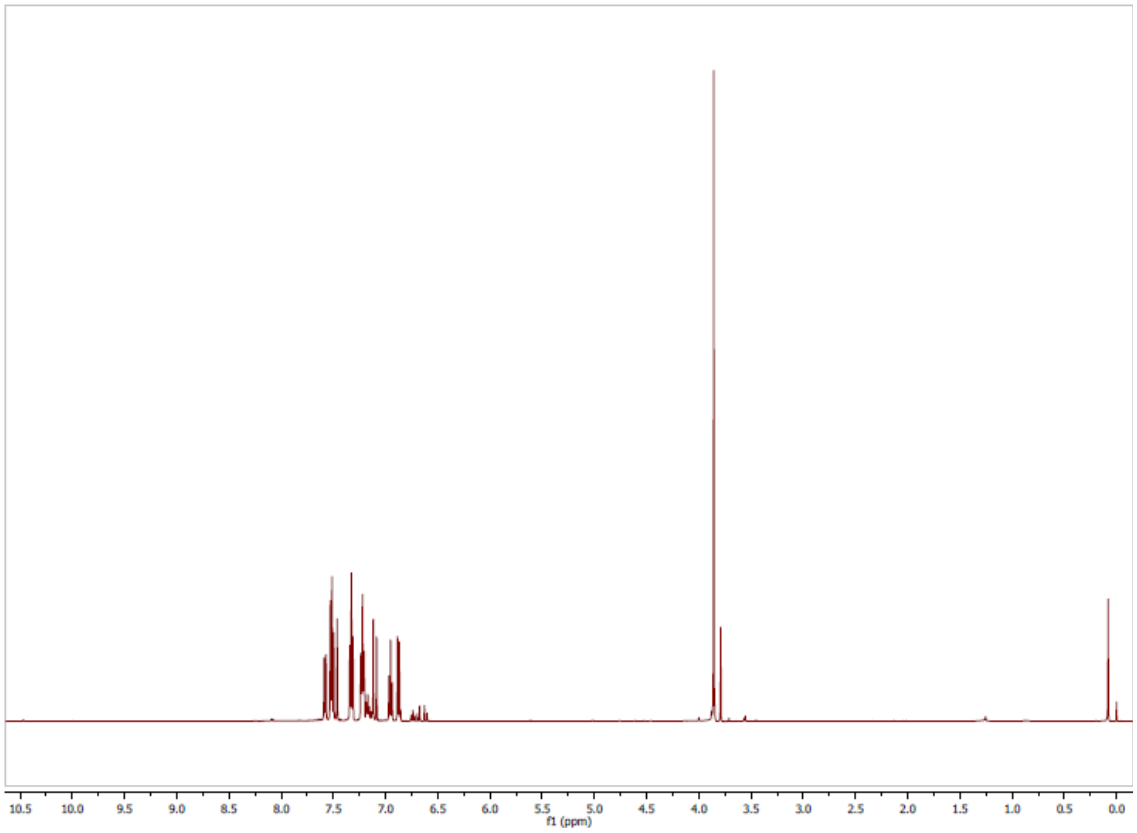
^{31}P NMR of regenerated methyldiphenylphosphine



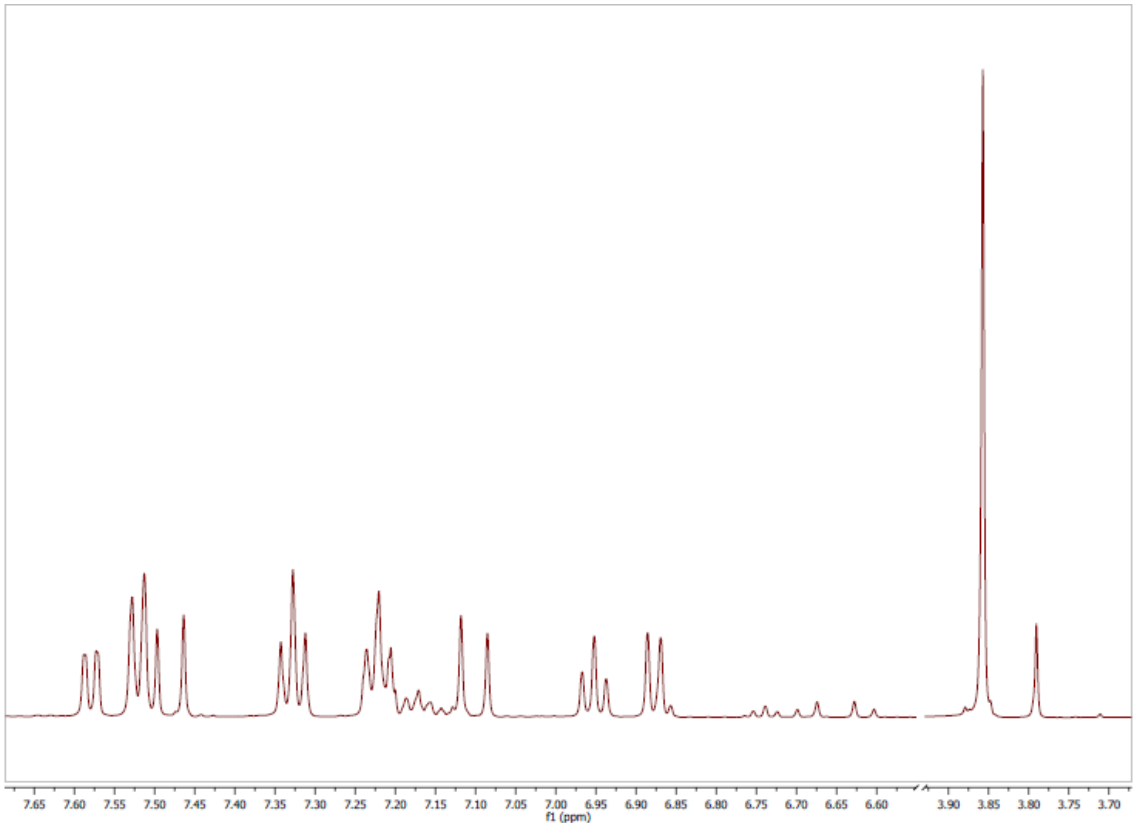
8. 2-methoxystilbene. Table 1, entry 8.



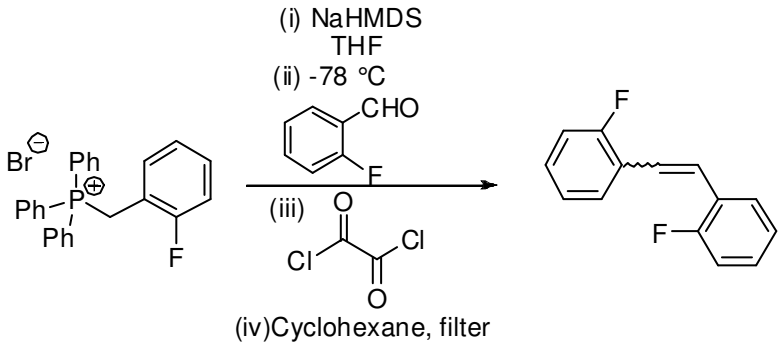
^{1}H NMR



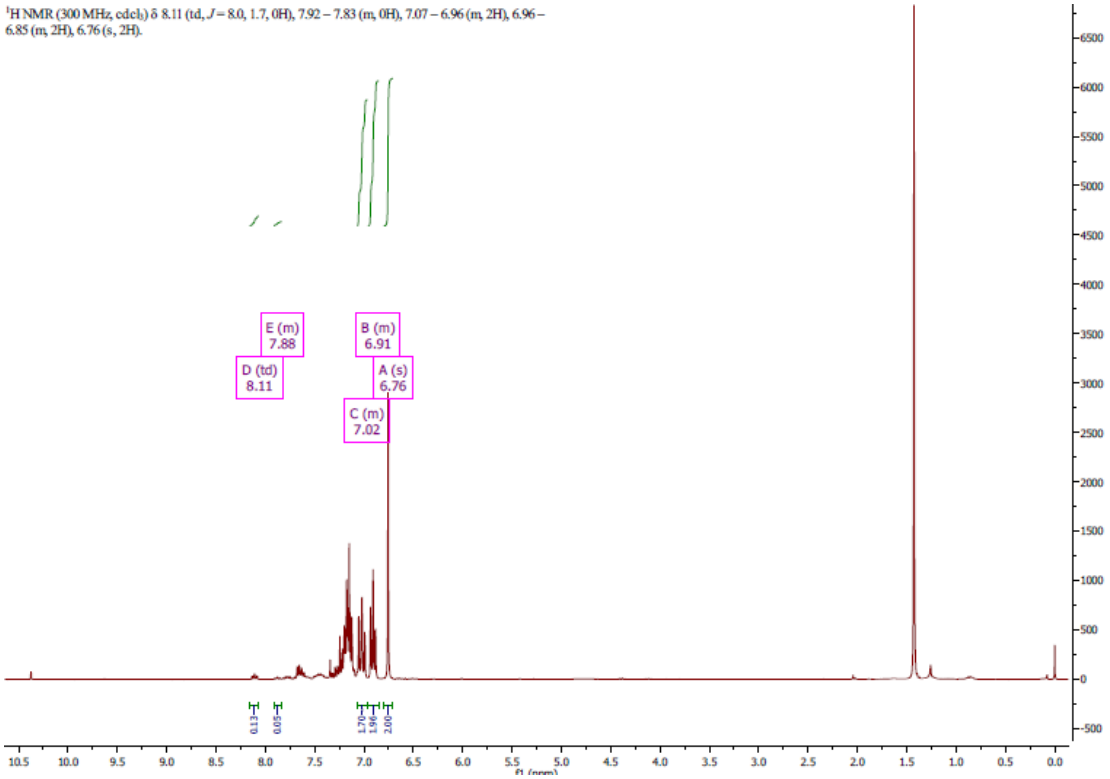
^{1}H NMR close up of δ 3.7-4.0 and 6.5-7.8 ppm.



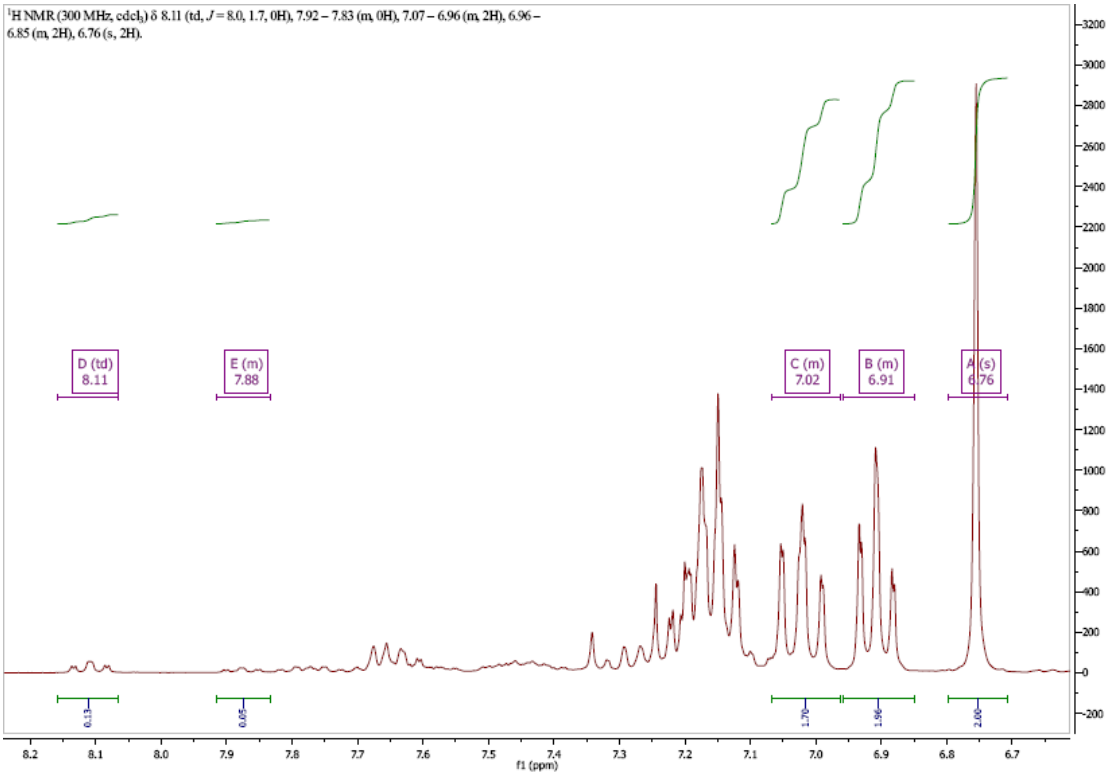
9. 2,2'-difluorostilbene. Table 1 entry 9.



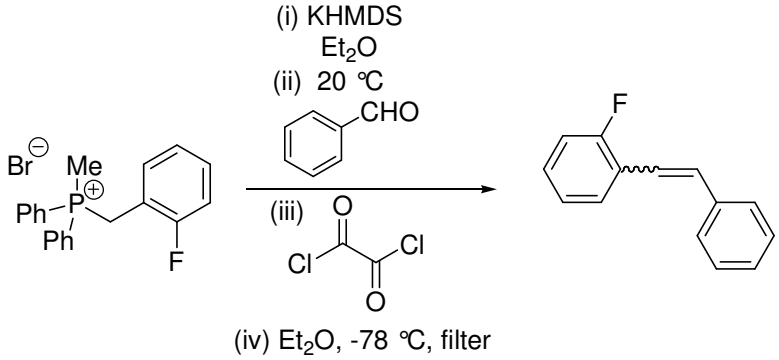
^{1}H NMR



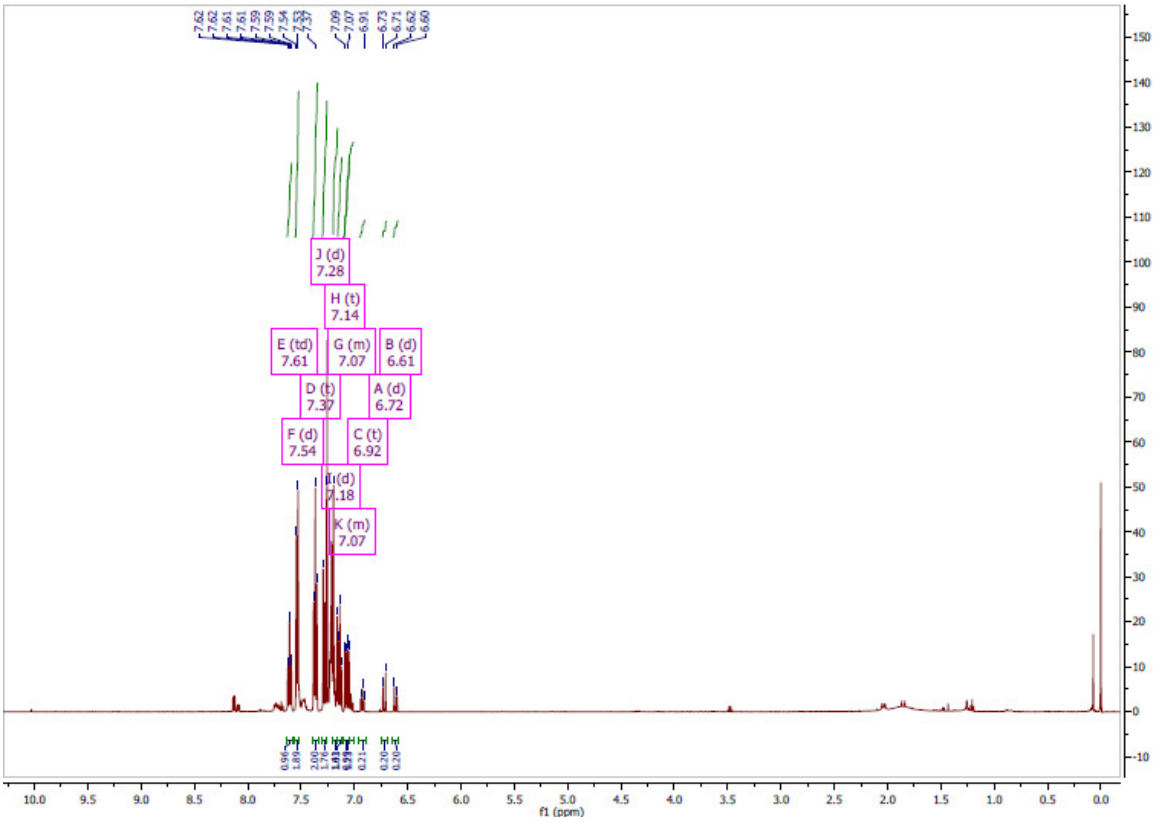
^{1}H NMR δ 6.7-8.2 ppm



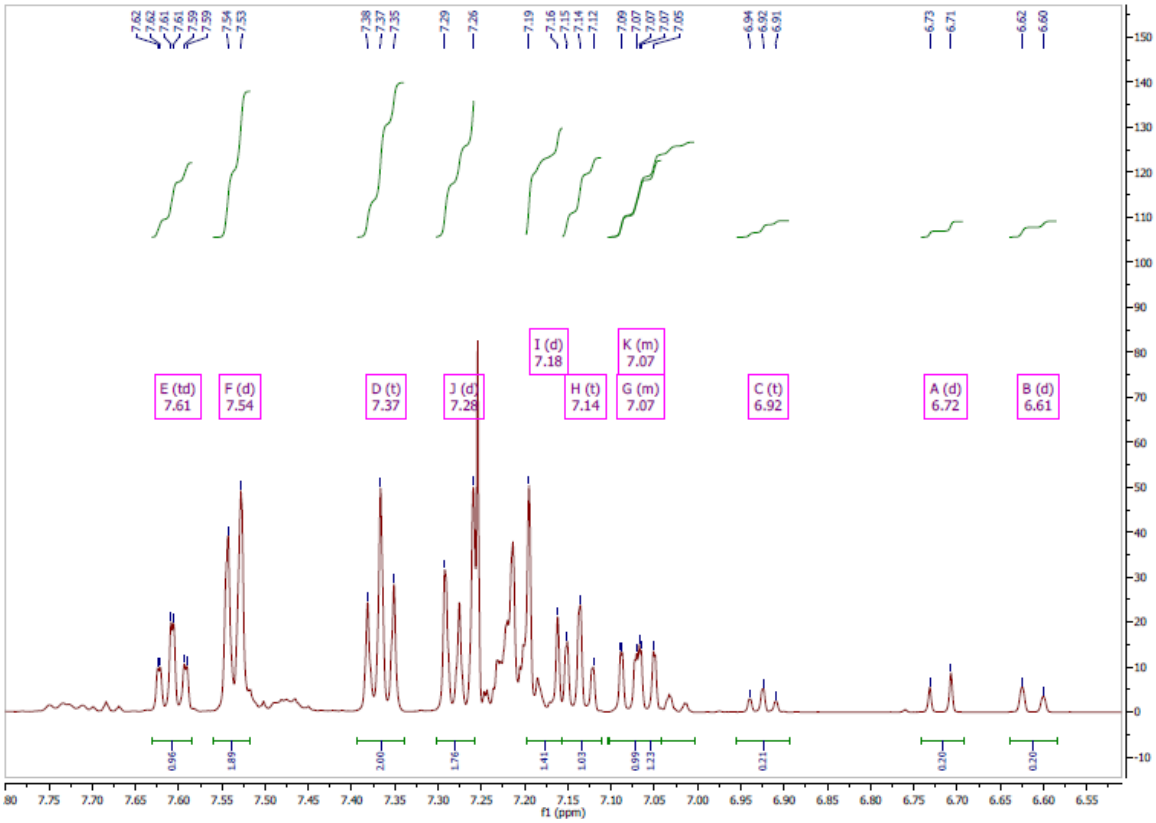
10. 2-fluorostilbene. Table 1 entry 10



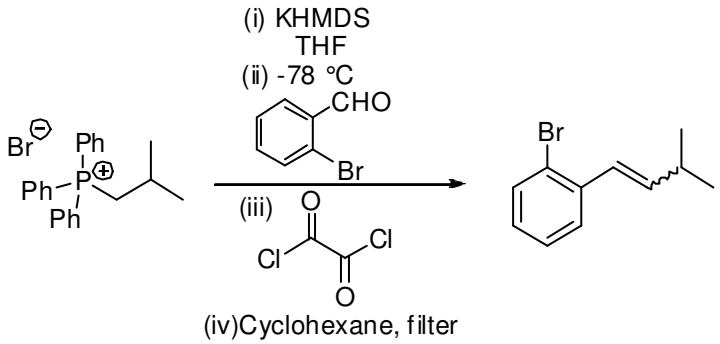
^{1}H NMR



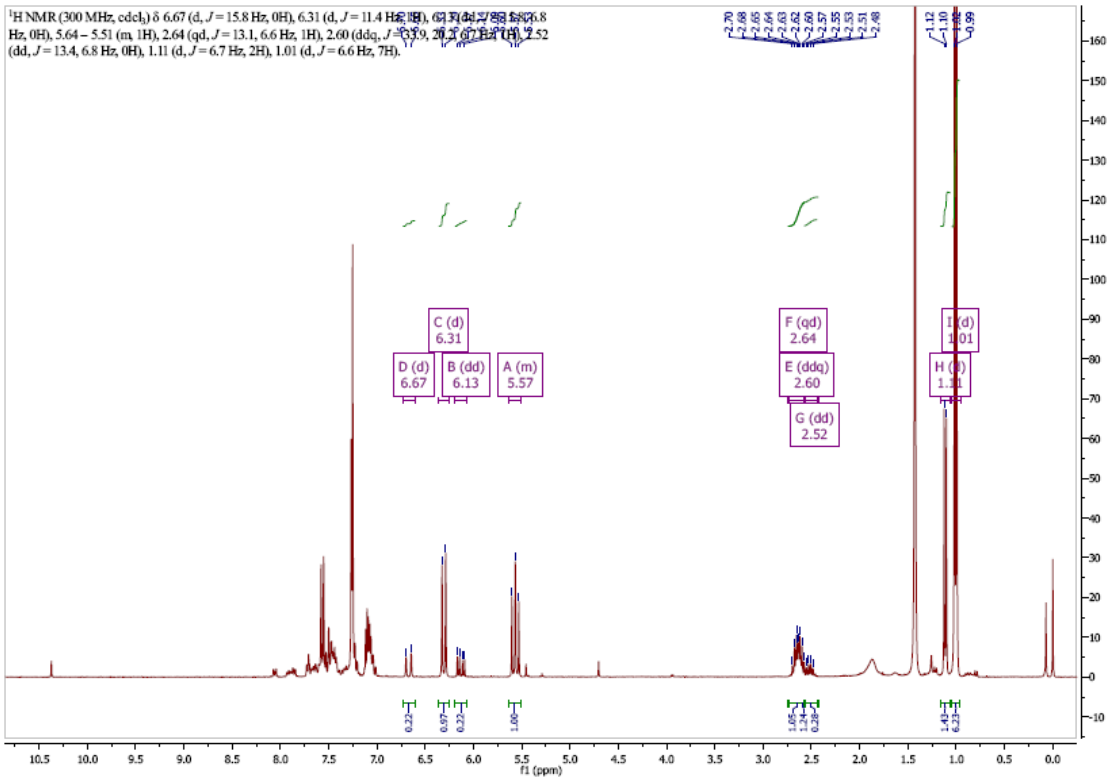
^{1}H NMR close up on δ 6.5-7.8 ppm region.



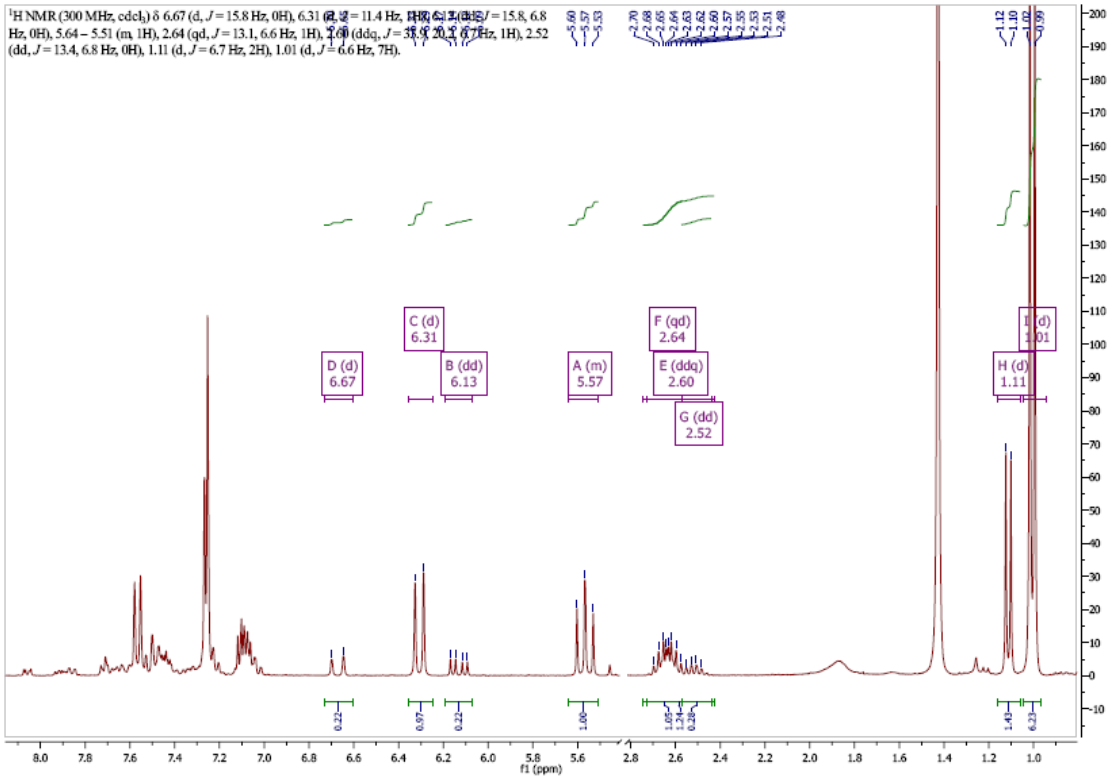
11. 1-(2-bromophenyl)-3-methylbut-1-ene. Table 1 entry 10.



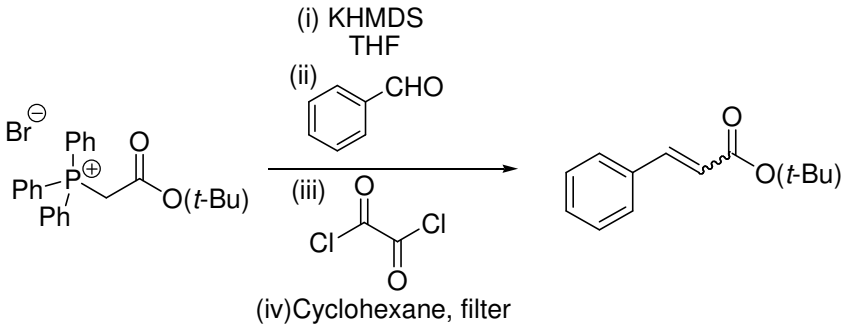
^{1}H NMR



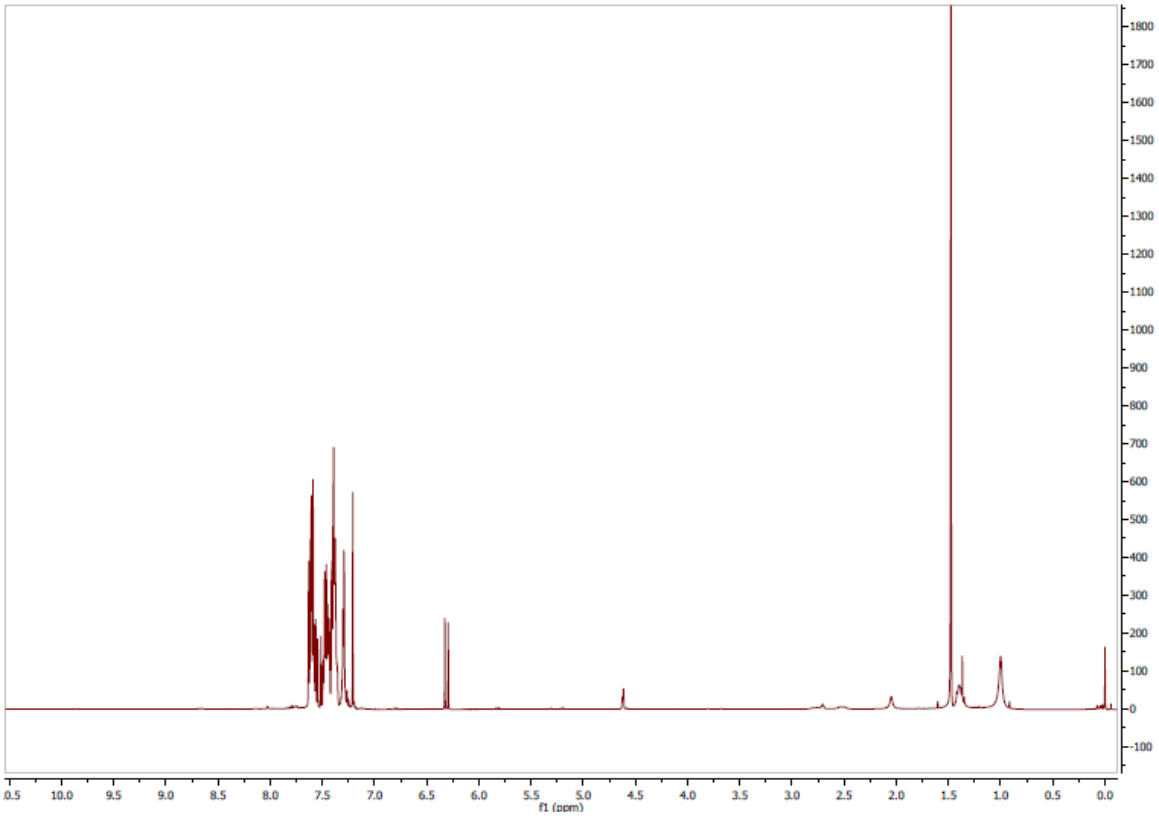
^{1}H NMR close up on δ 0.9-2.8 and 5.5-8.0 ppm regions.



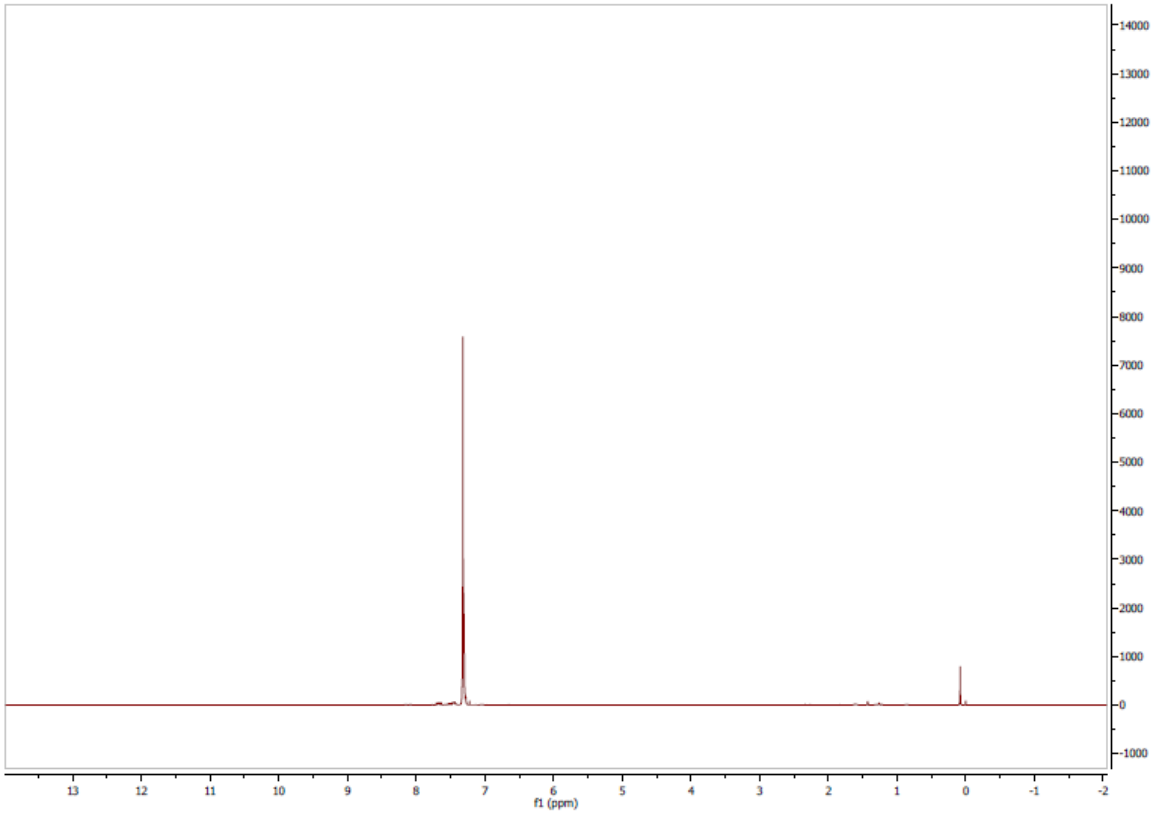
12. ***tert*-Butyl 3-phenylprop-2-enoate**. Table 1 entry 11.



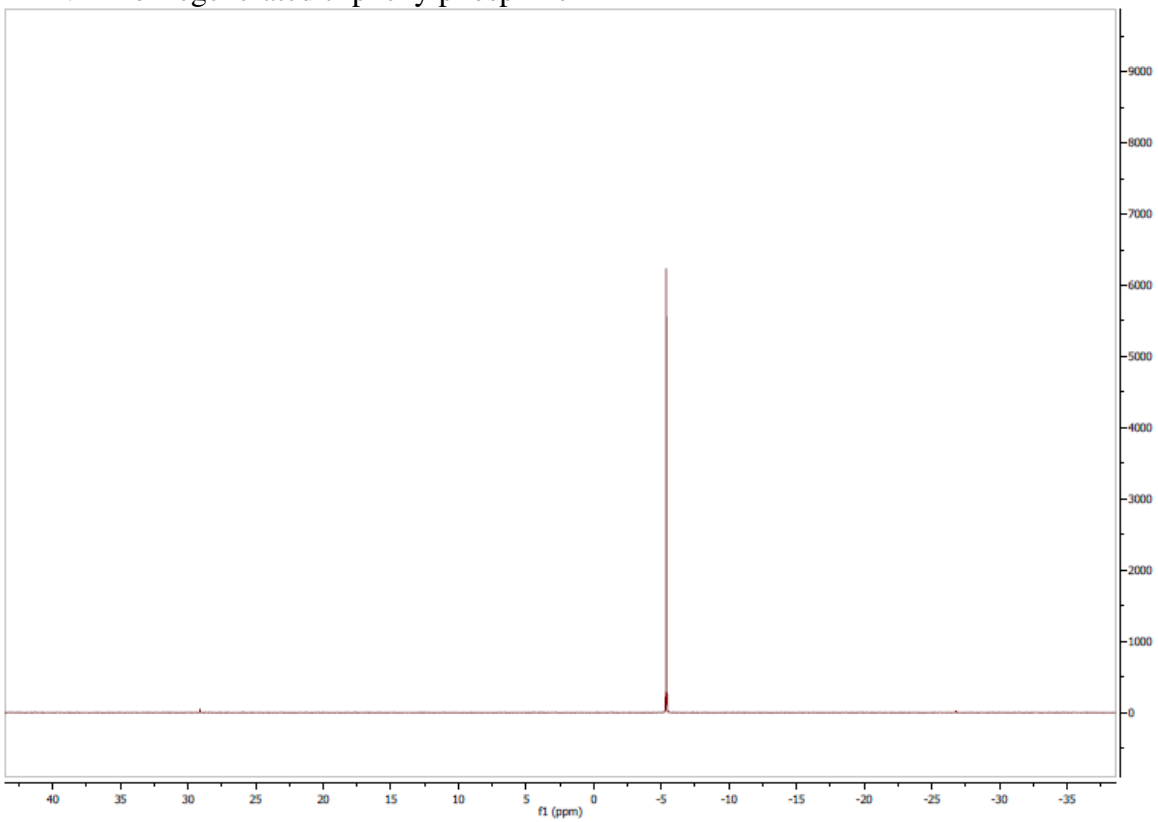
^{1}H NMR



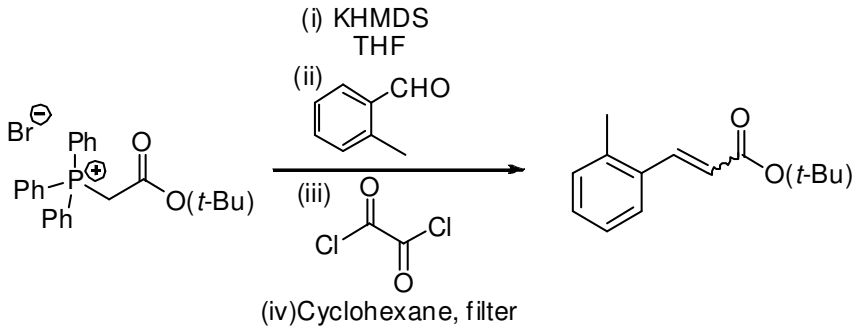
^{1}H NMR of regenerated triphenylphosphine



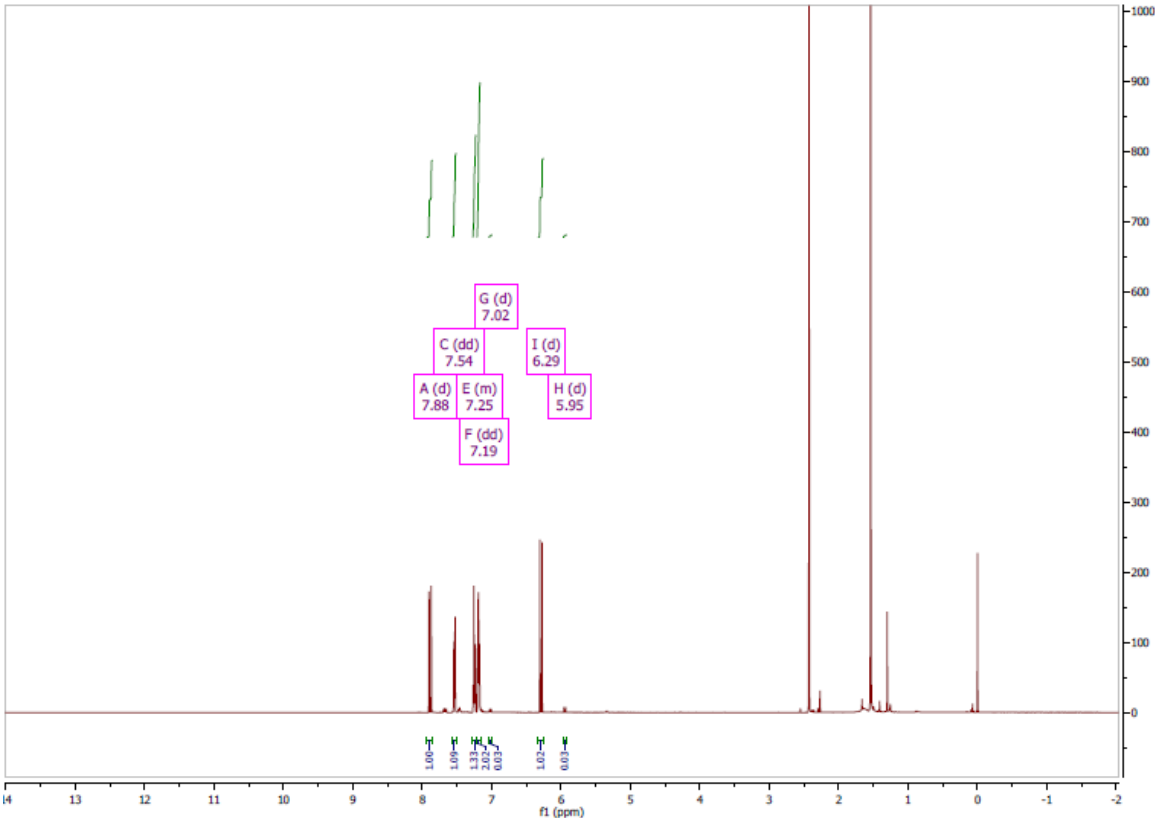
^{31}P NMR of regenerated triphenylphosphine



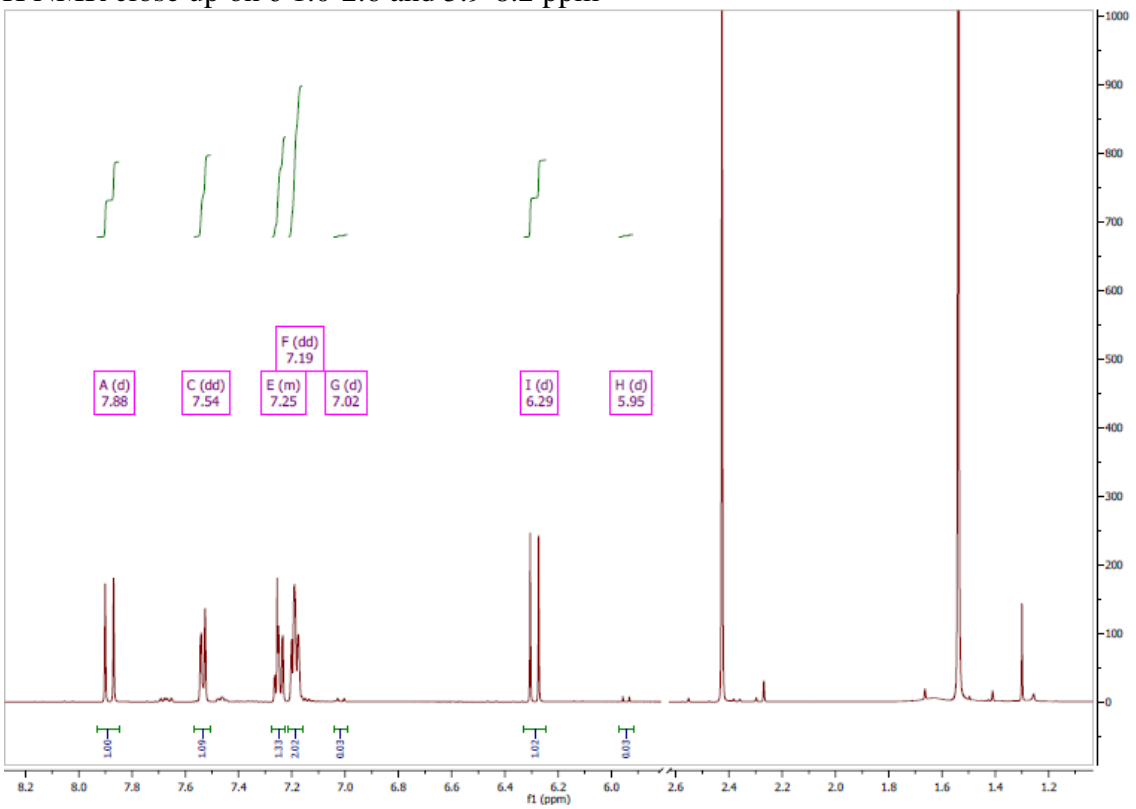
13. *tert*-Butyl 3-(2-methylphenyl)prop-2-enoate. Table 1 entry 12.



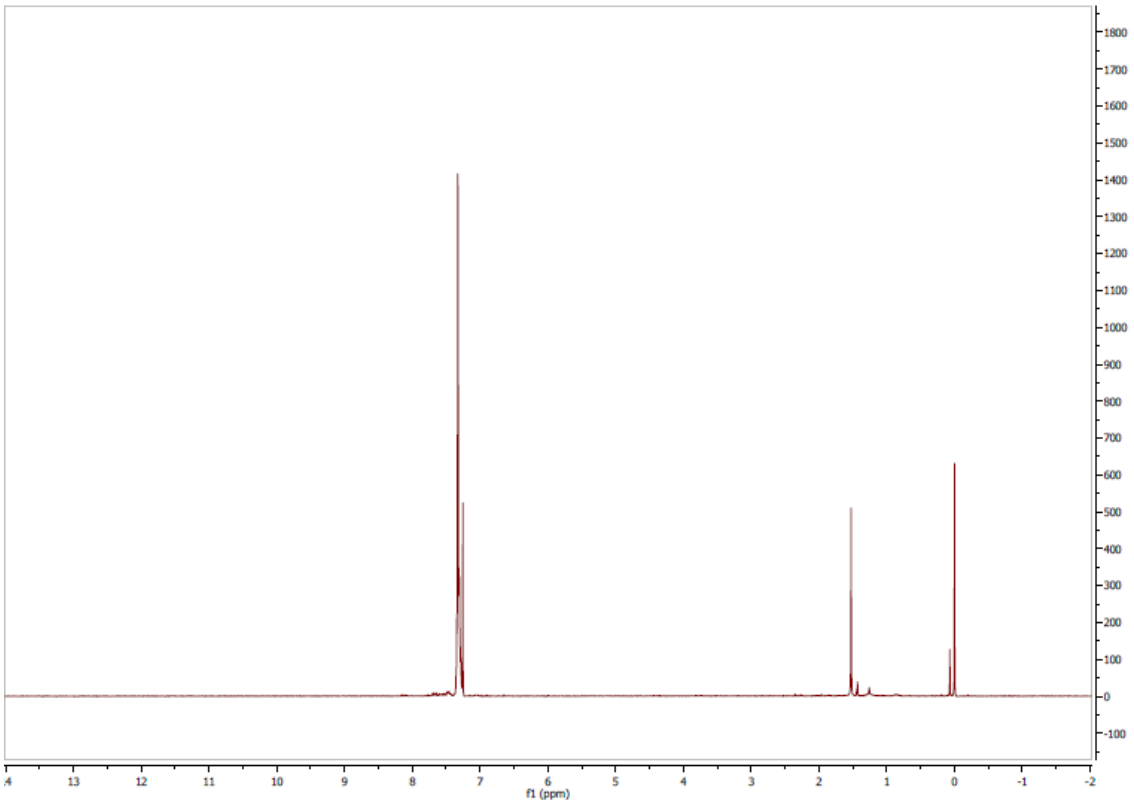
^{1}H NMR



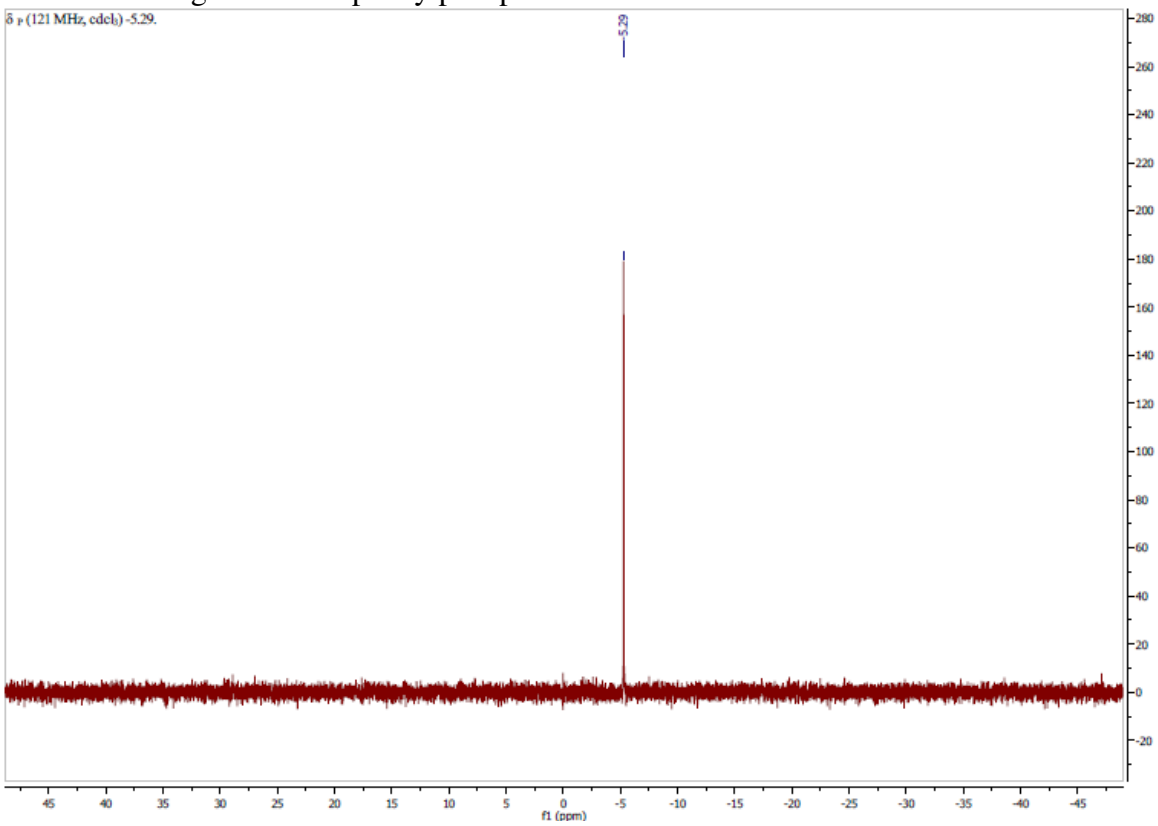
^{1}H NMR close up on δ 1.0-2.6 and 5.9-8.2 ppm



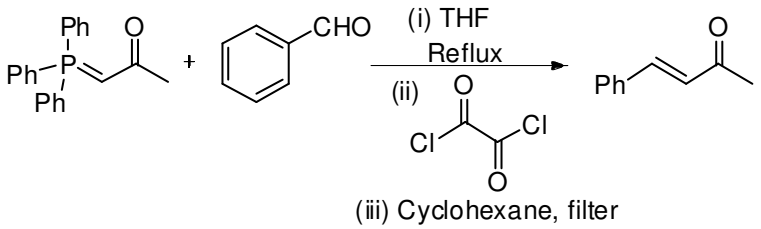
^{1}H NMR of regenerated triphenylphosphine



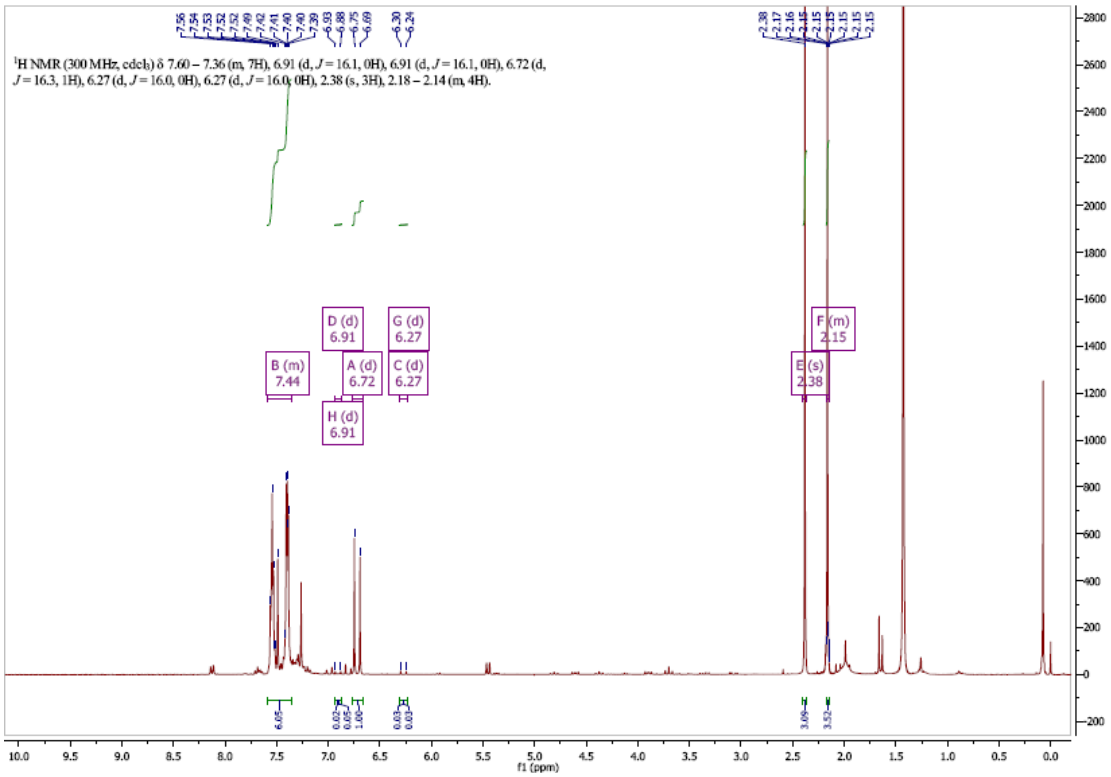
^{31}P NMR of regenerated triphenylphosphine



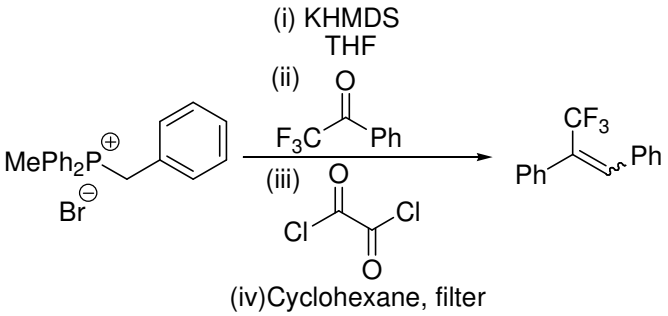
14. 4-phenylbut-3-en-2-one. Table 1 entry 14.



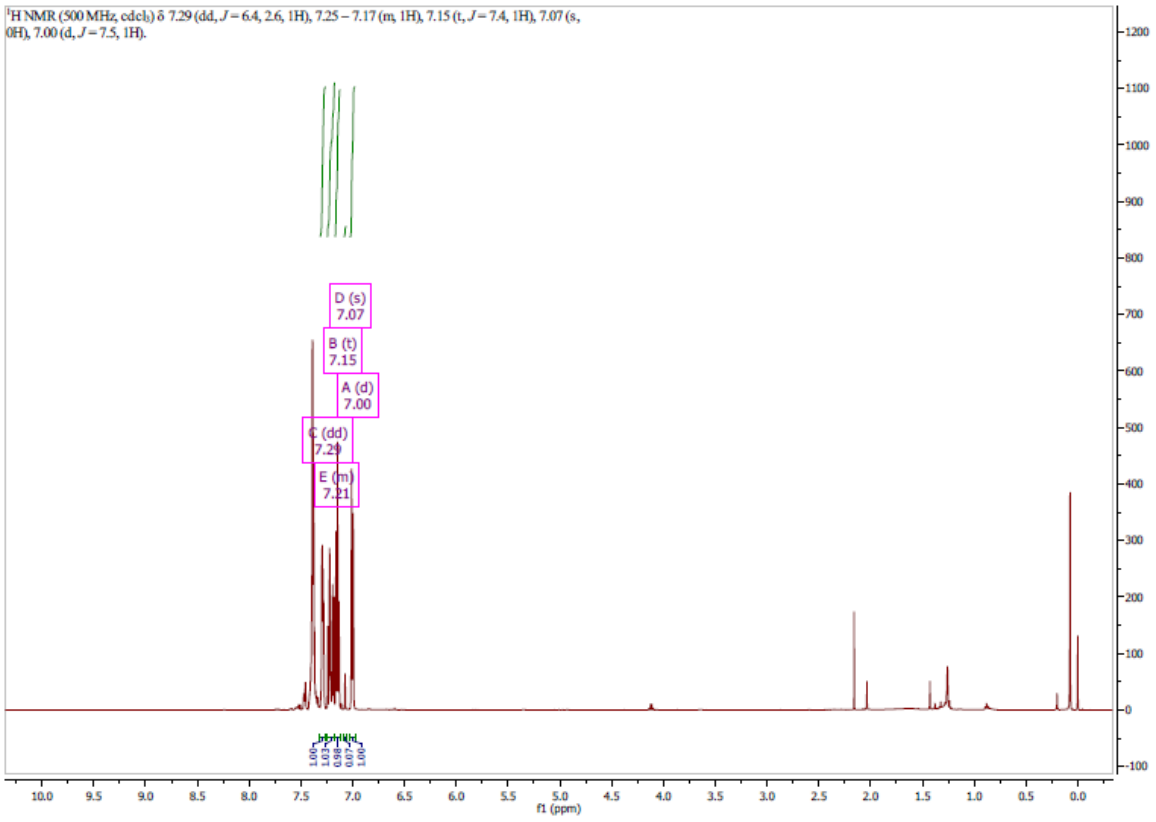
^{1}H NMR



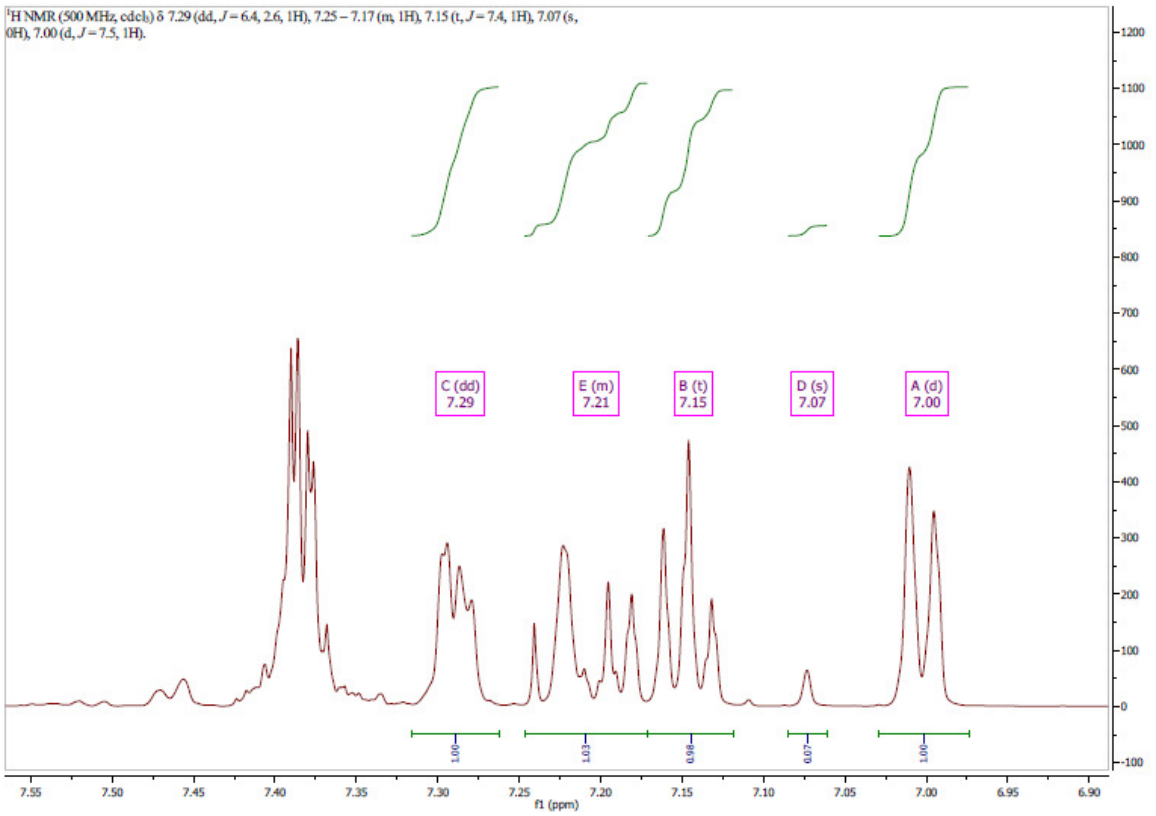
15. 3,3,3-trifluoro-1,2-diphenylprop-1-ene. Table 1 entry 15.



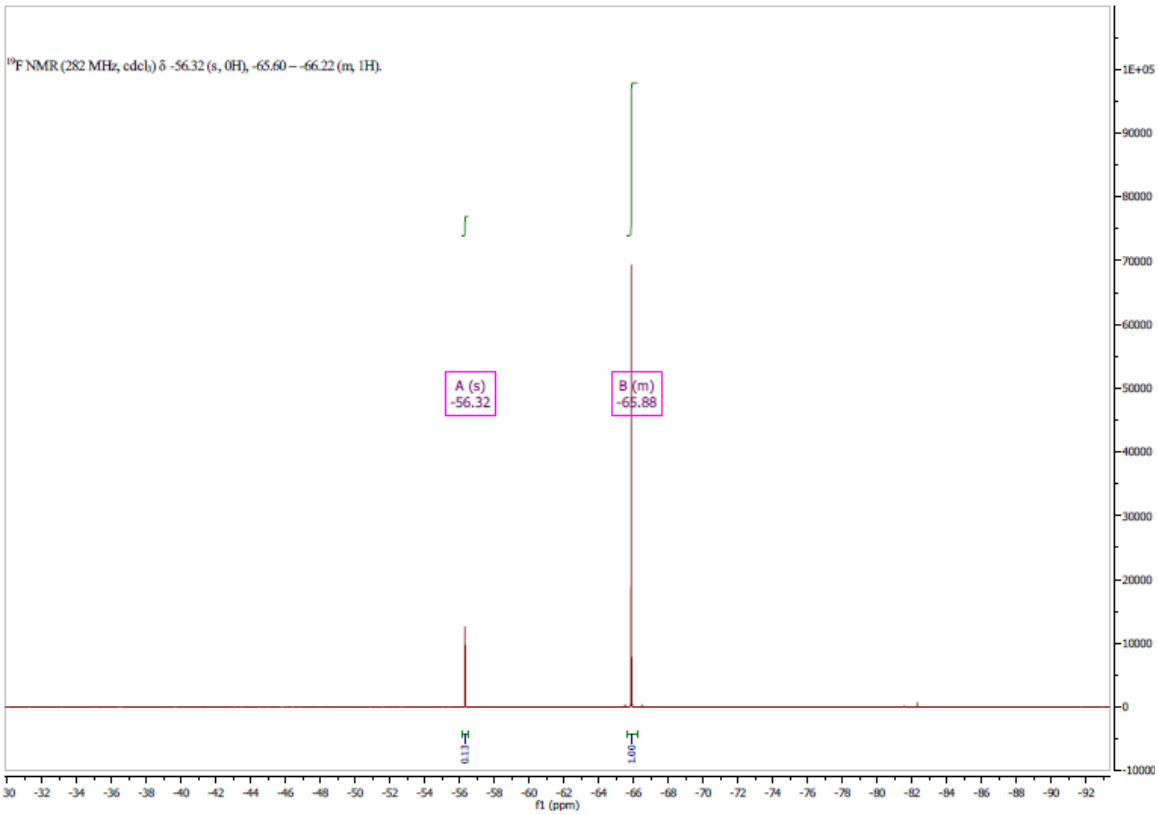
^{1}H NMR



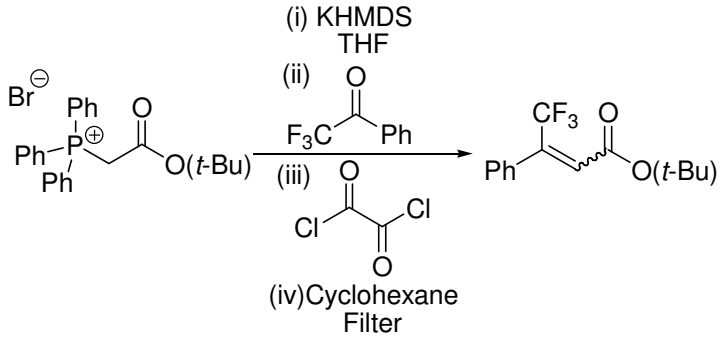
^{1}H NMR close up on aromatic region



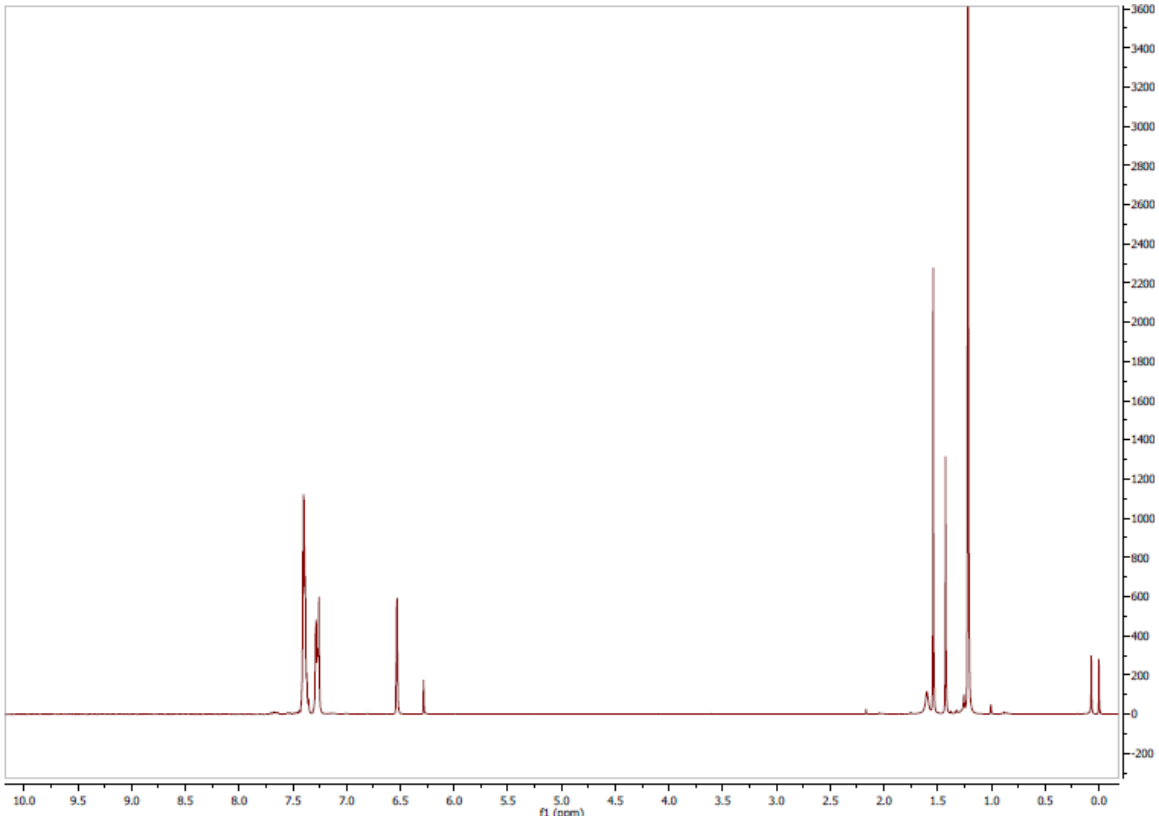
^{19}F NMR



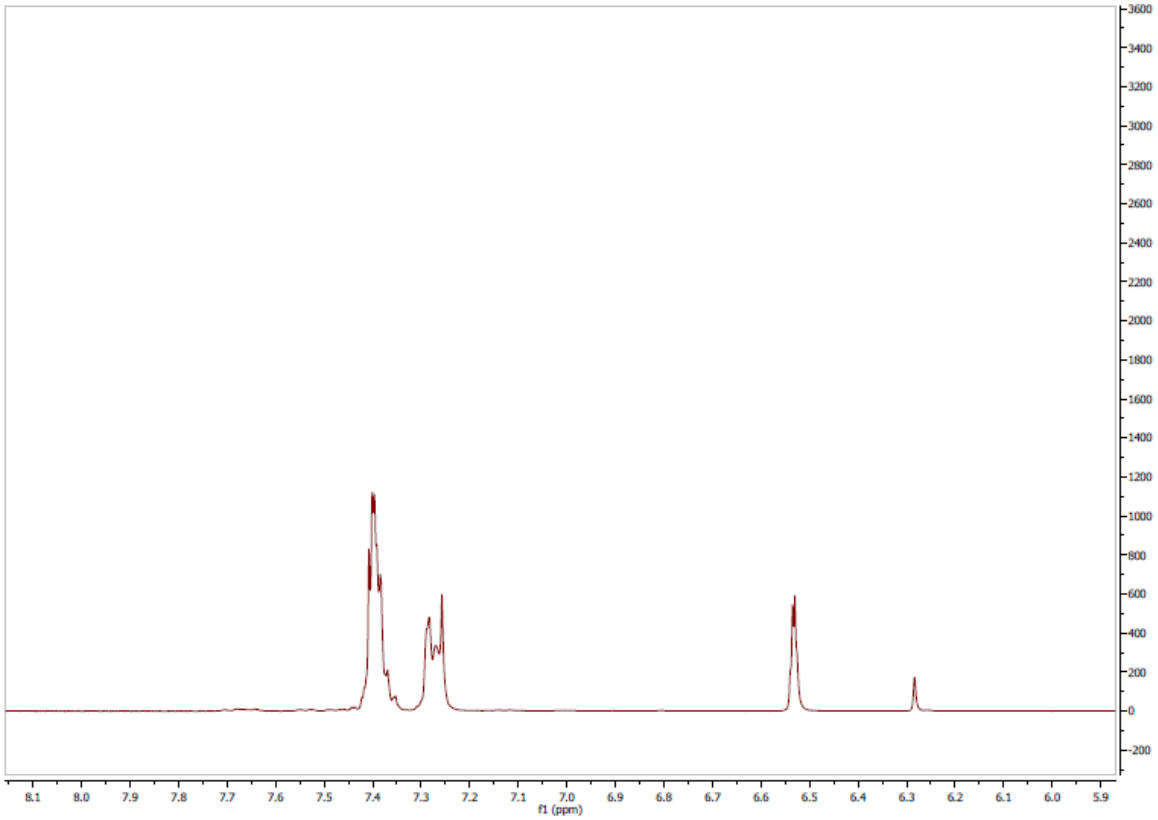
16. *tert*-Butyl 4,4,4-trifluoro-3-phenylprop-2-enoate. Table 1 entry 16.



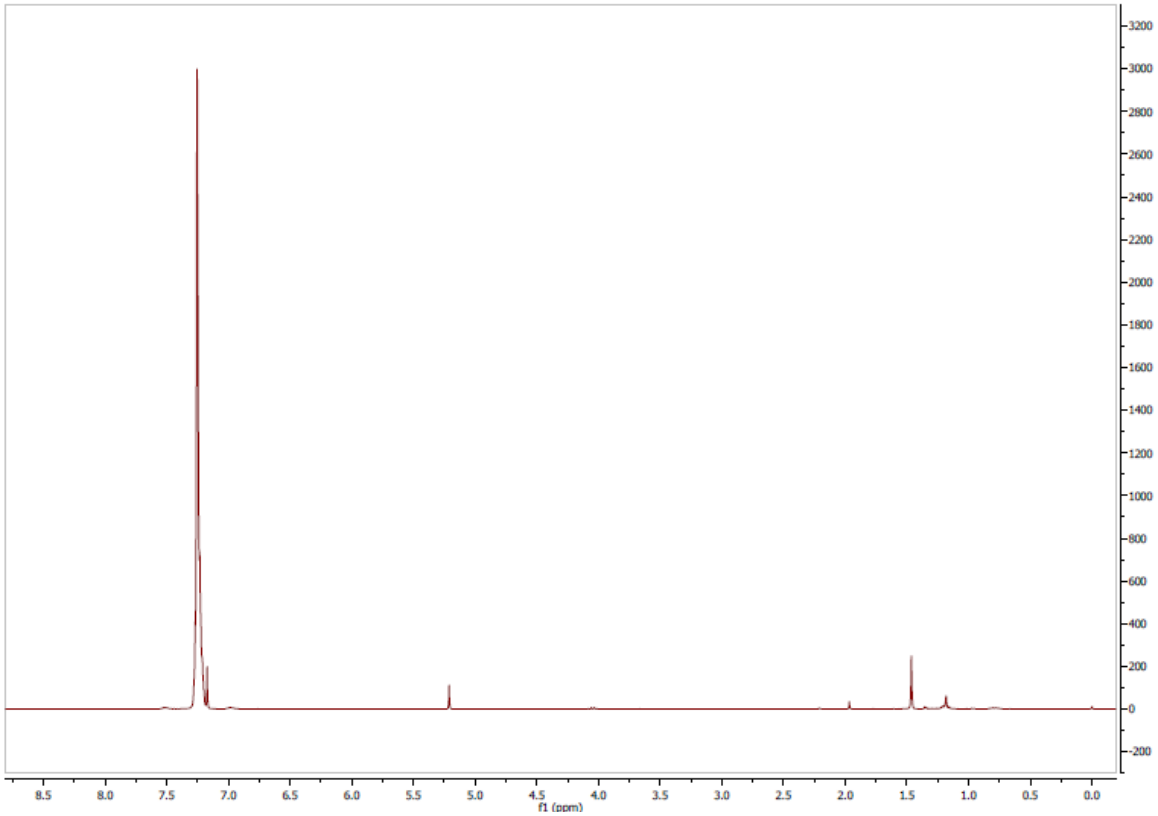
^{1}H NMR



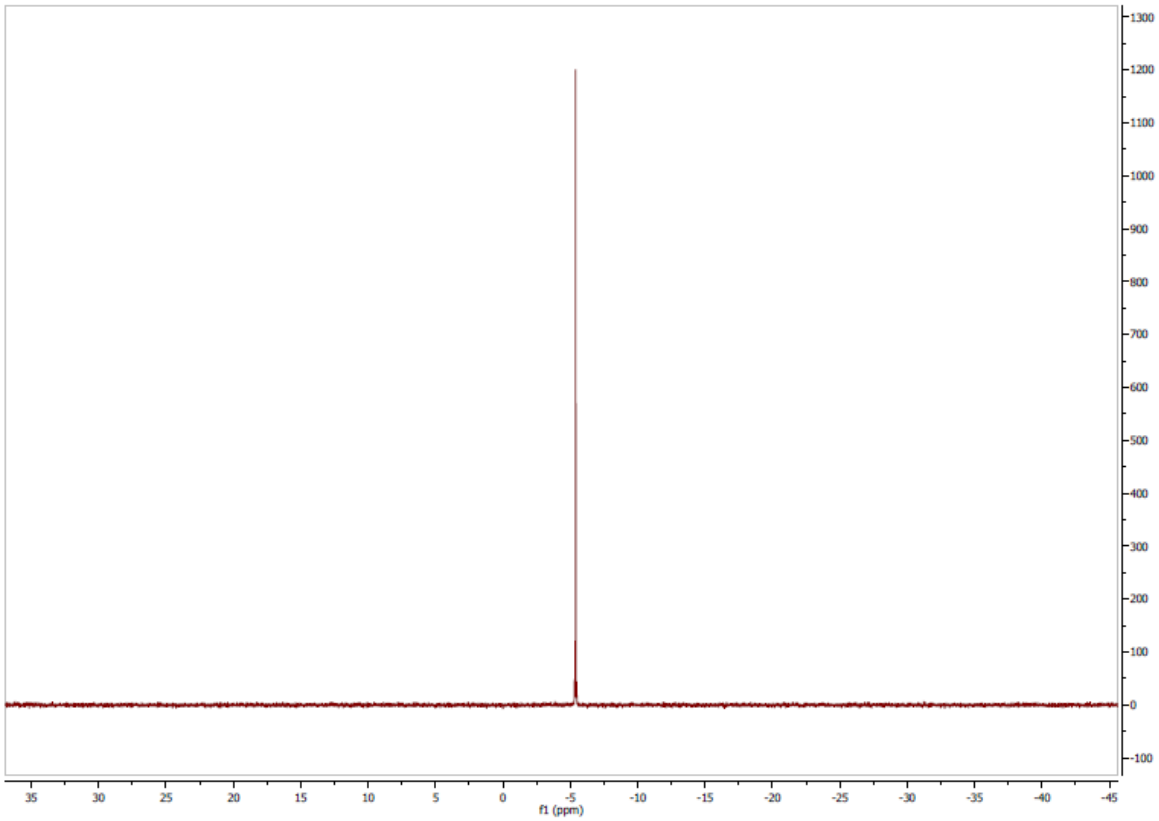
^{1}H NMR close up on δ 5.7-8.1 ppm region.



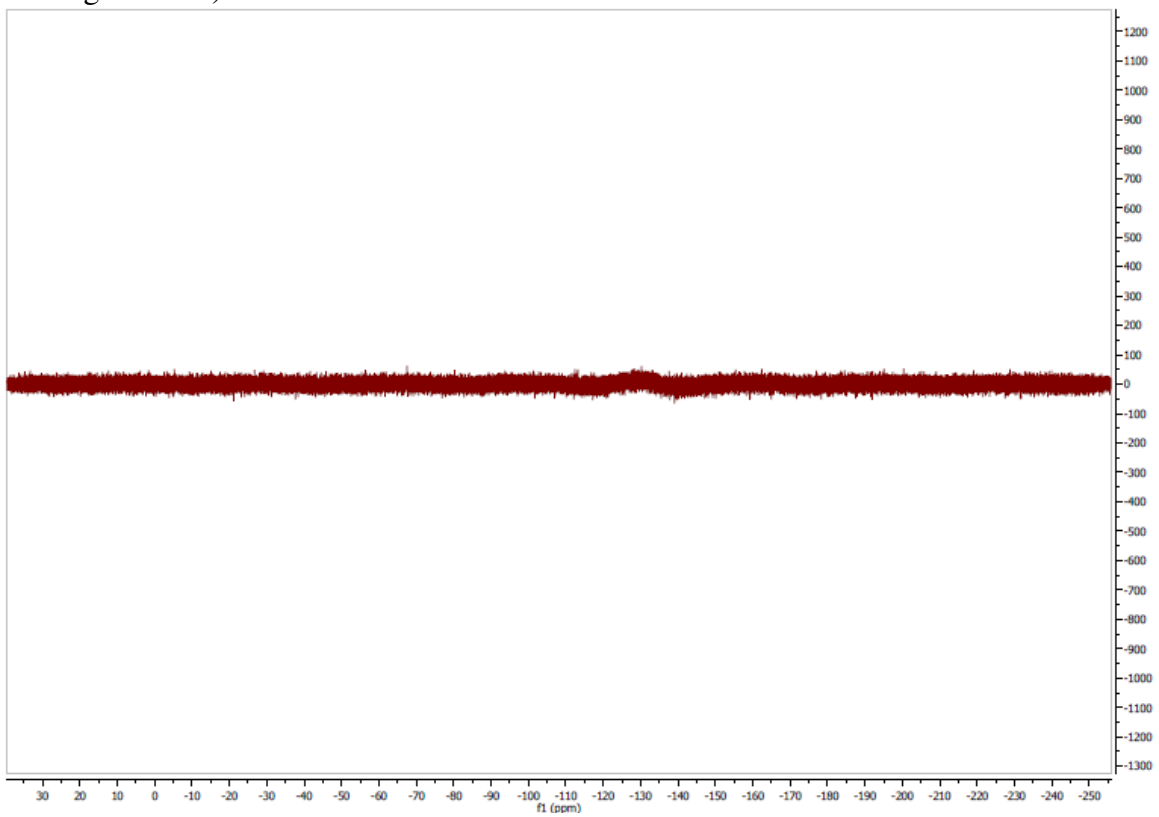
^{1}H NMR of regenerated triphenylphosphine



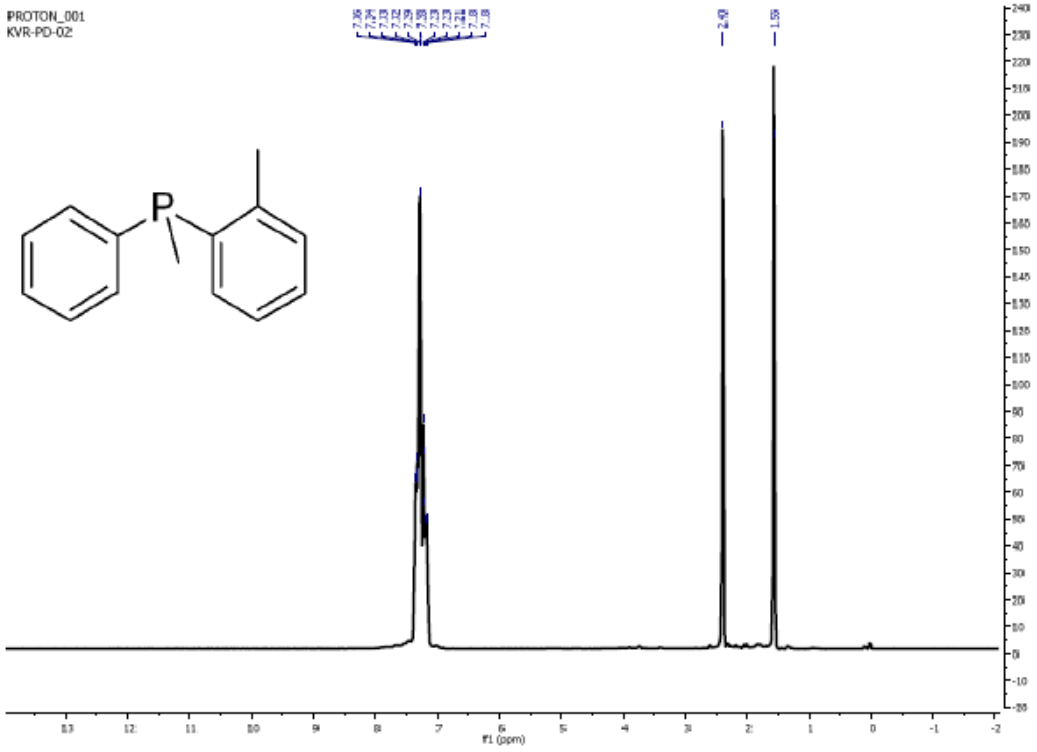
^{31}P NMR of regenerated triphenylphosphine



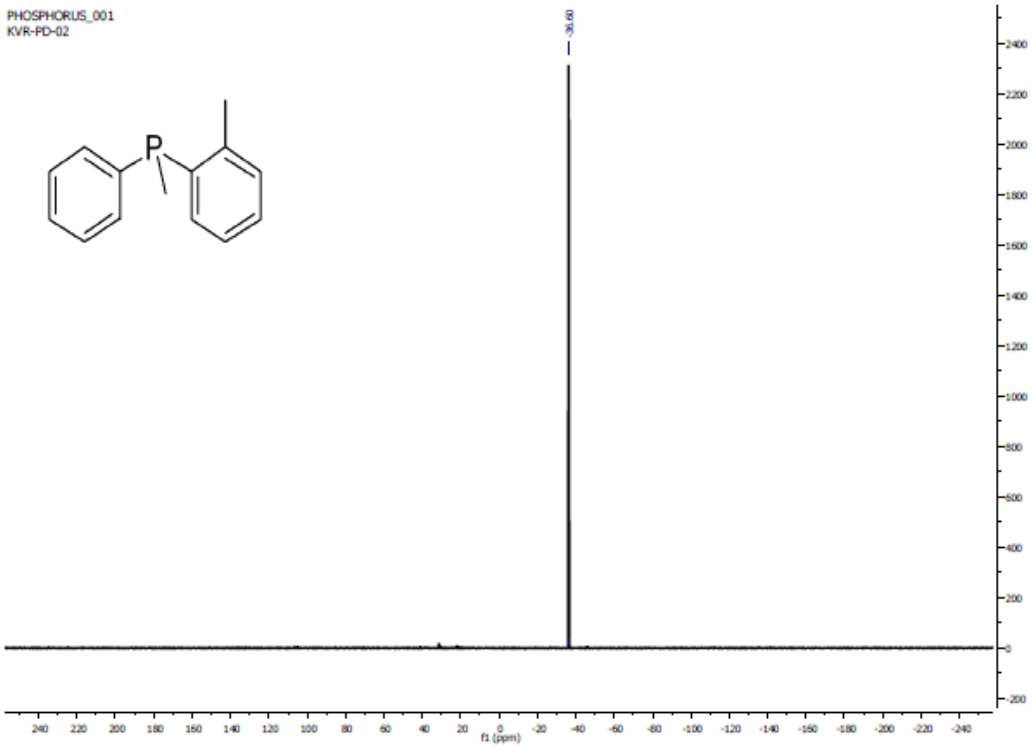
^{19}F NMR of regenerated triphenylphosphine (showing absence of alkene and ketone starting material).



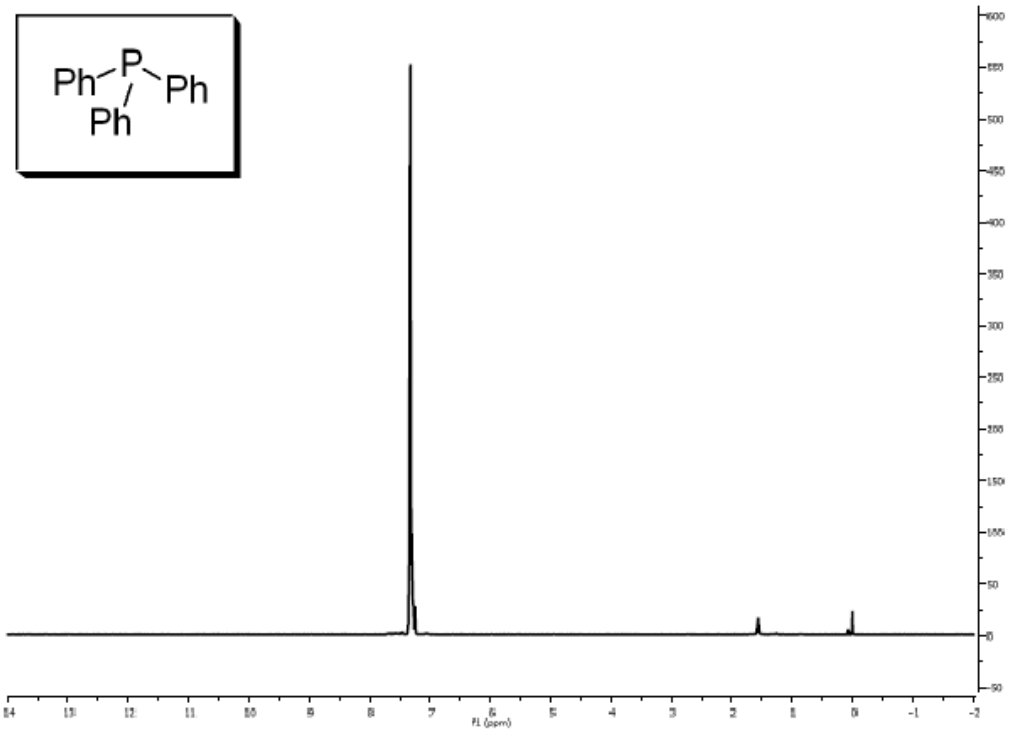
9. NMR spectra of phosphines produced by reduction of phosphine chalcogenides



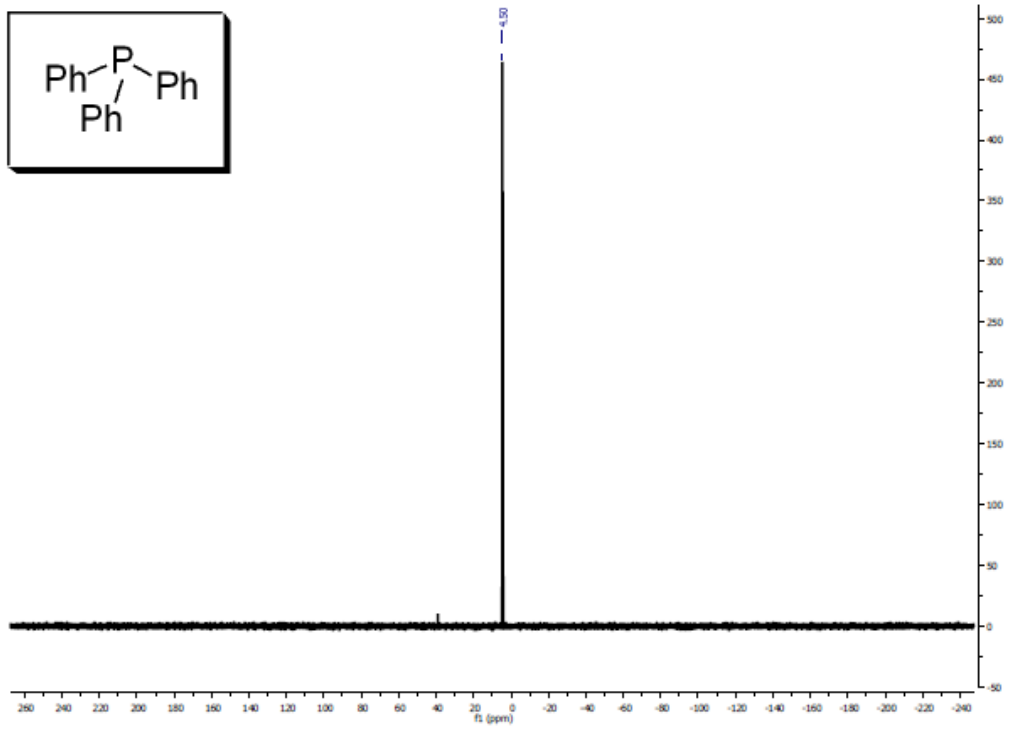
^{1}H-NMR of methylphenyl(*o*-tolyl)phosphine



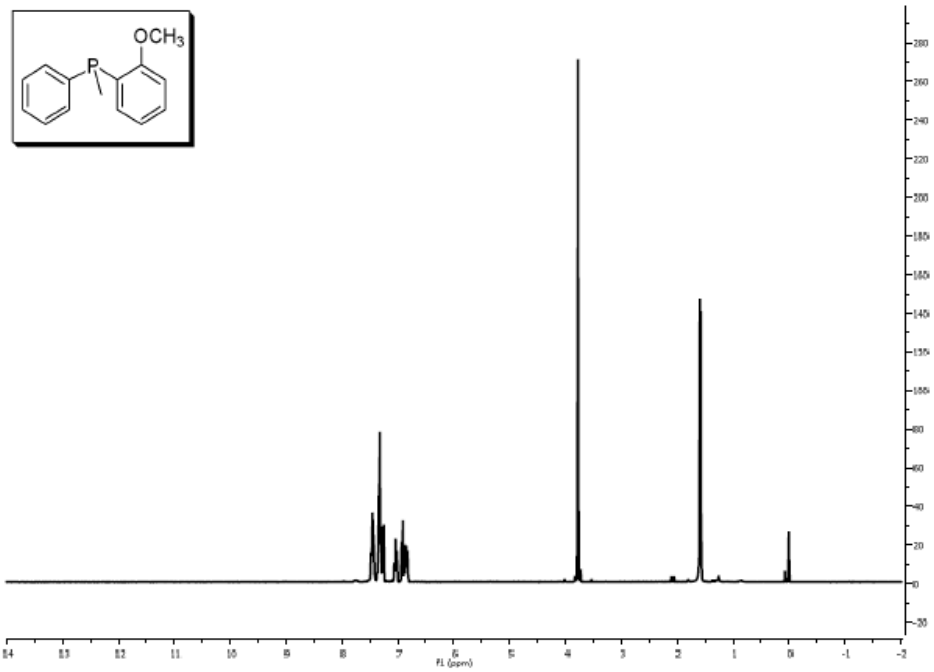
^{31}P-NMR of methylphenyl(*o*-tolyl)phosphine



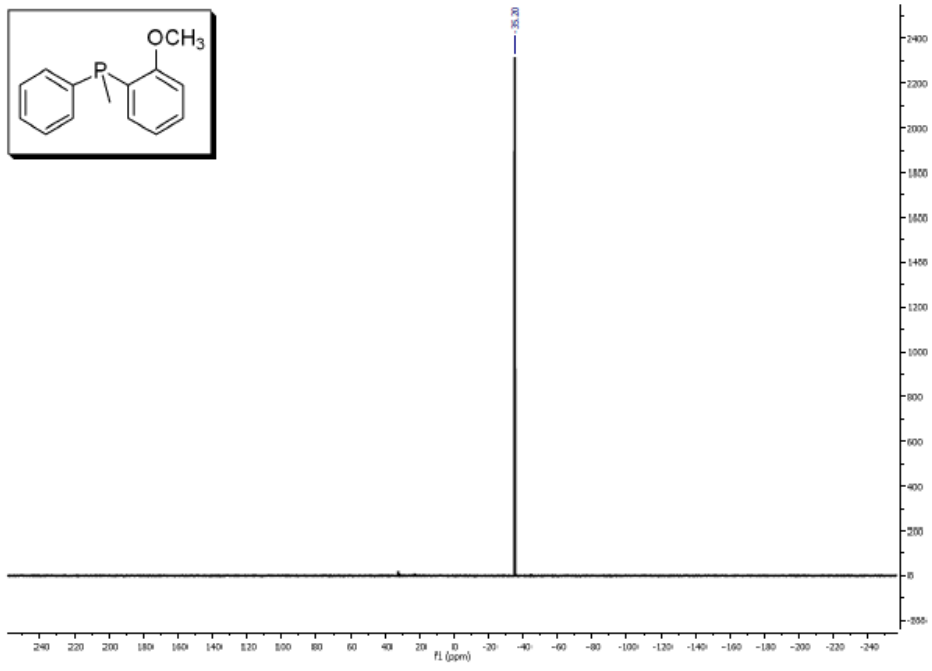
^{1}H-NMR of triphenylphosphine



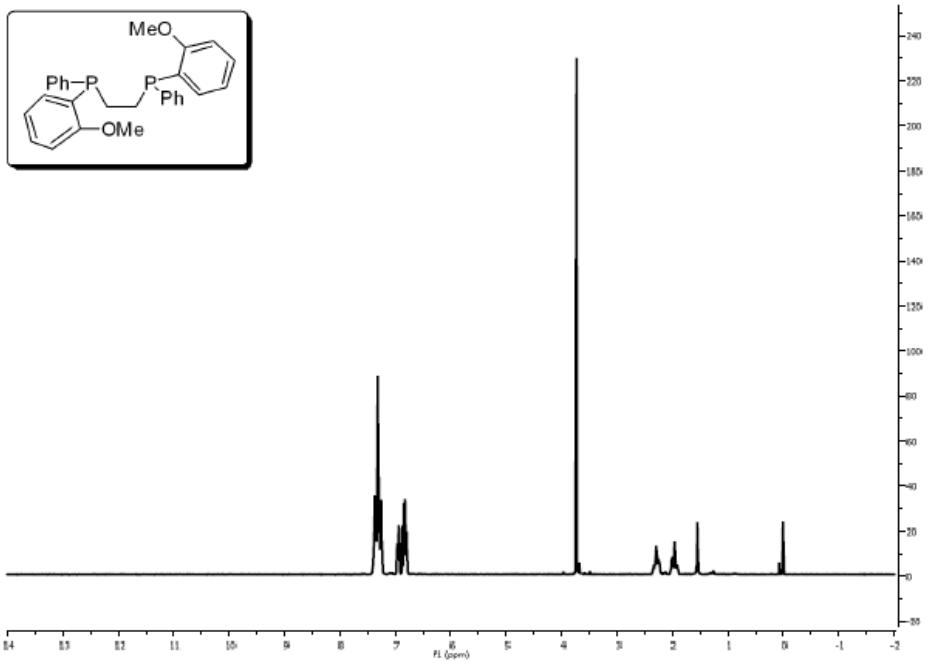
^{31}P-NMR triphenylphosphine



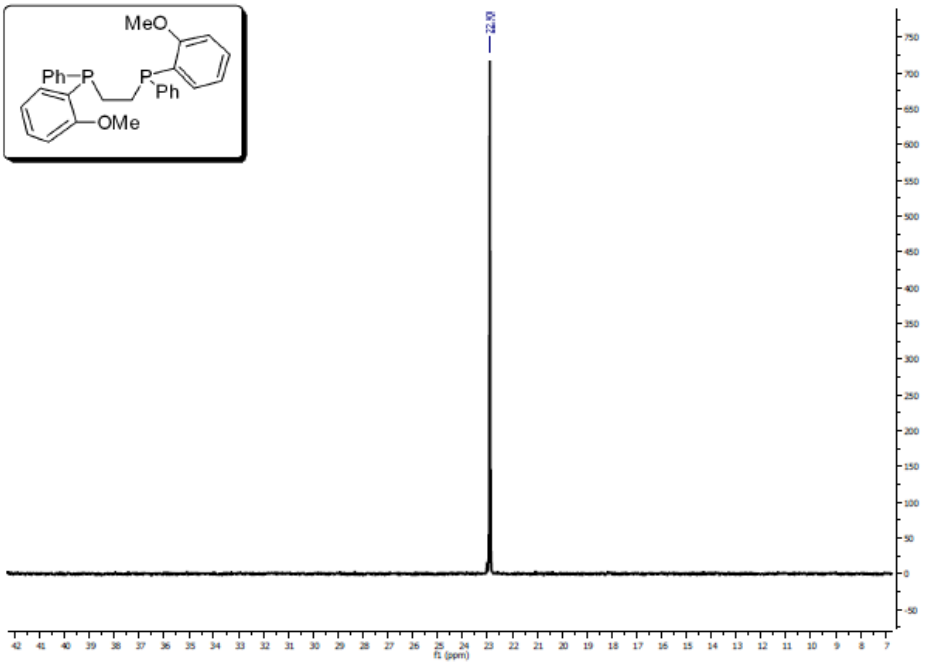
^{1}H-NMR of (*o*-methoxyphenyl)methylphenylphosphine



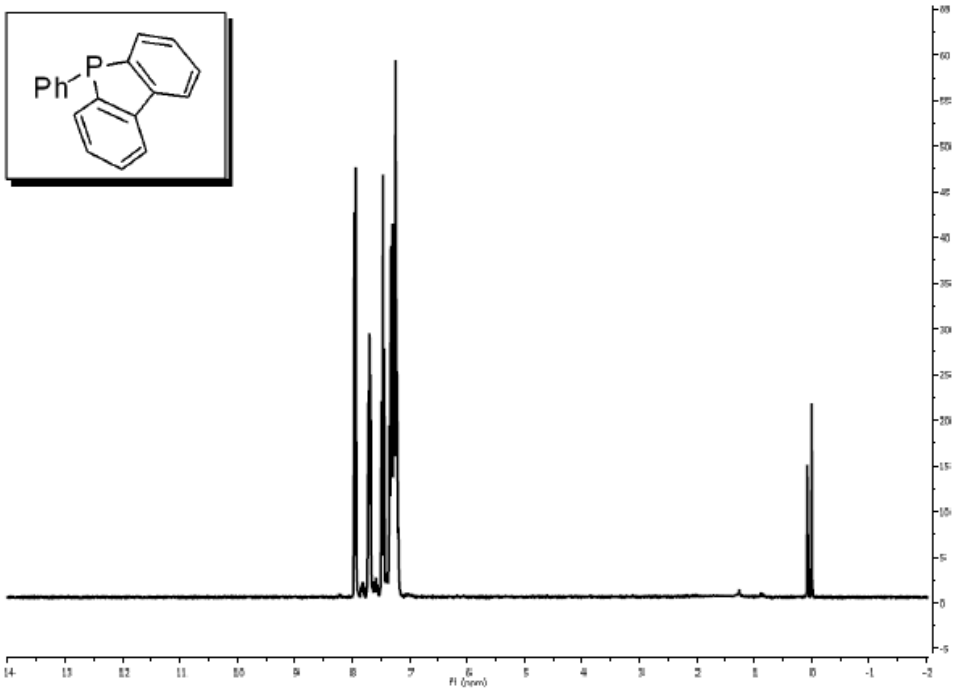
^{31}P-NMR of (*o*-methoxyphenyl)methylphenylphosphine



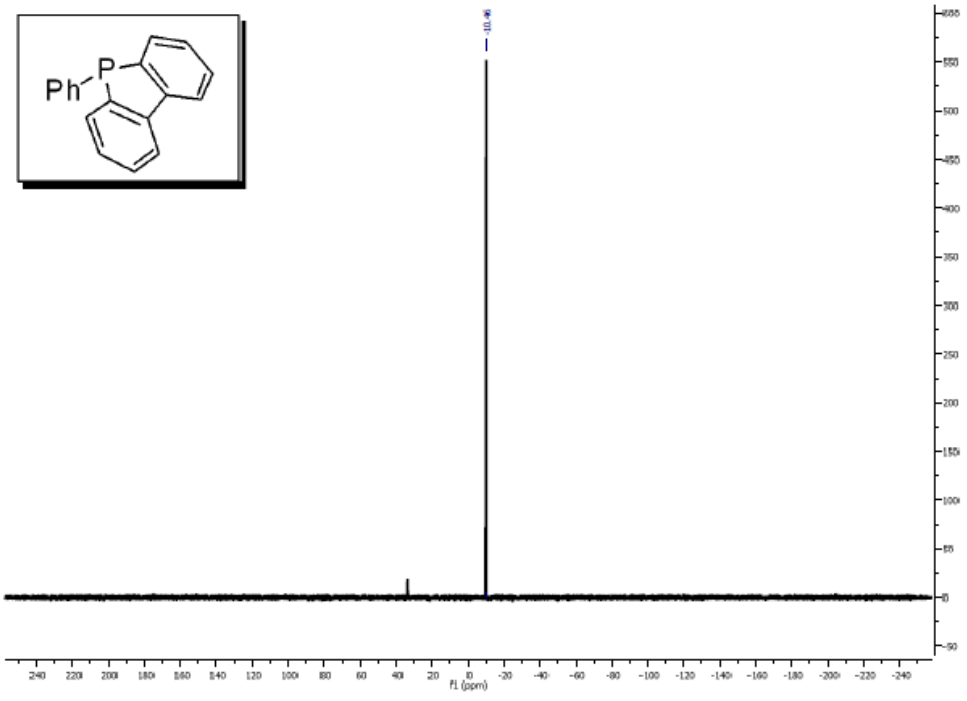
^{1}H-NMR of (±)-1,2-ethandiylbis[(*o*-anisyllphenyl)phenylphosphine



^{31}P-NMR of (±)-1,2-ethandiylbis[(*o*-anisyllphenyl)phenylphosphine



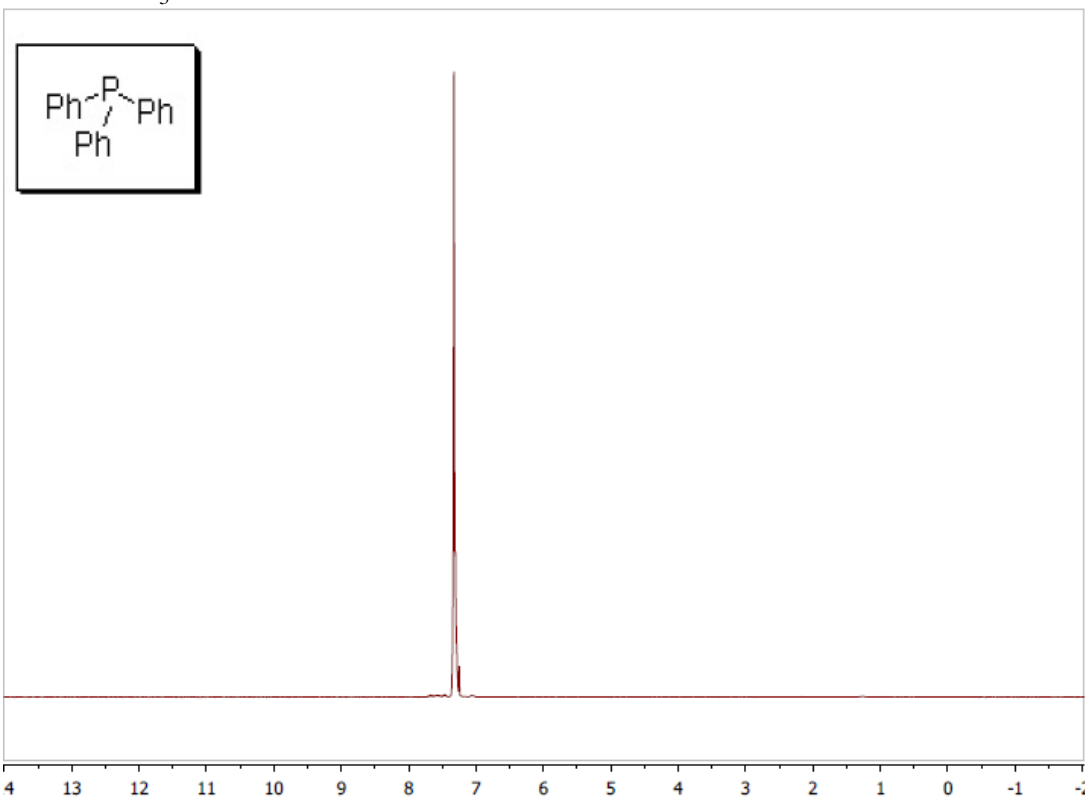
^{1}H-NMR of *P*-phenyl-5*H*-dibenzophosphole



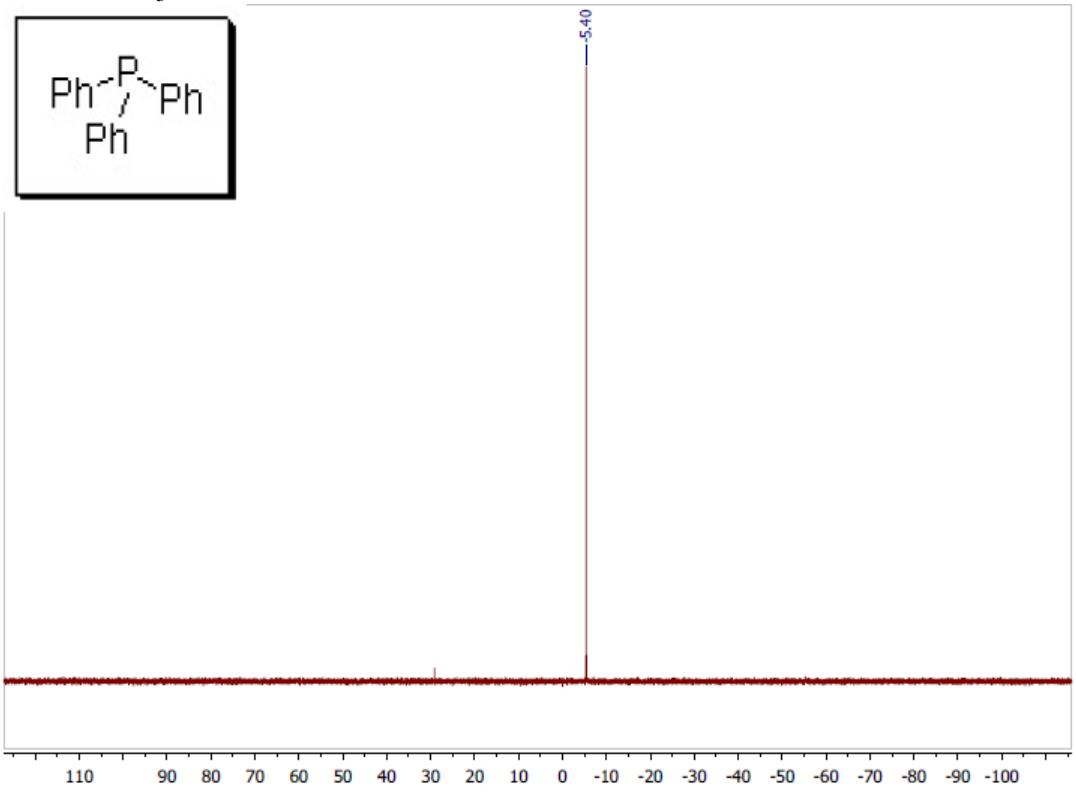
^{31}P-NMR of *P*-phenyl-5*H*-dibenzophosphole

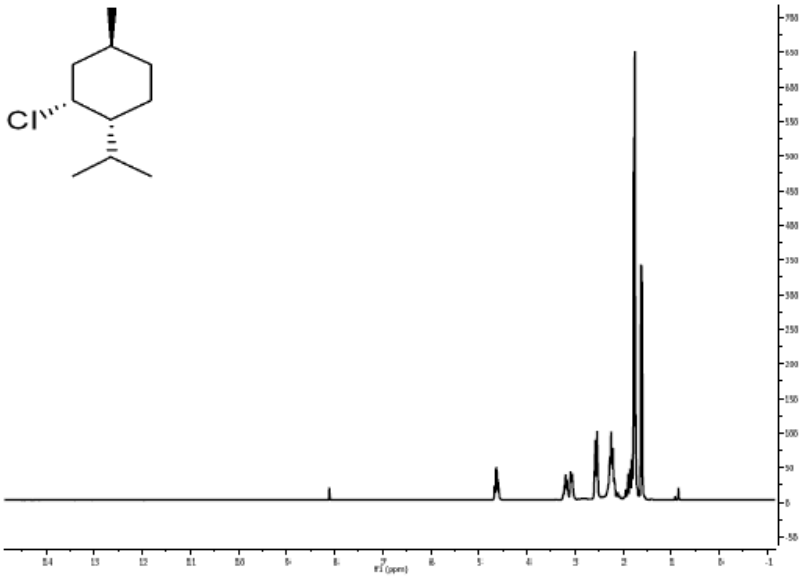
10. NMR spectra of purified products from Appel-type reactions

^{1}H NMR of Ph_3P



^{31}P NMR of Ph_3P





^{1}H-NMR of neomenthyl chloride

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