SUPPORTING INFORMATION

Expanding Ligand Space: Preparation, Characterization and Synthetic Applications of Air-Stable, Odorless Di-*tert*-alkylphosphine Surrogates

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1. General Experimental Information

CAUTION: phosphine gas is highly toxic and is spontaneously flammable in air. Procedures that use phosphine gas should only be performed following appropriate training after consultation with local safety advisors, and after completing a thorough risk assessment. All CO-ware apparatus should be inspected for scratches or imperfections prior to use; new CO-ware septa should be used for each reaction, and the manufacturer's guidelines should be followed (no more than 2 injections per septum, using a needle with a diameter of 21g (0.08 mm) or less). CO-ware is recommended for routine use at pressures up to 46 psi, and not above 60 psi; this should be considered when changing reaction scales from those presented in this Supporting Information.

Reagents were purchased from commercial suppliers and used as provided. Me_3SiOTf and methylmagnesium bromide (3.0 M in Et_2O) were stored under anhydrous dinitrogen in sample flasks with J. Young valves. Anhydrous tetrahydrofuran, toluene, dichloromethane and diethyl ether were obtained from in-house solvent purification systems (Inert® ProSolv; dried by passage through activated alumina columns under pressure of Ar). Anhydrous CCl_4 and DBU were obtained by distillation from CaH_2 under an atmosphere of anhydrous dinitrogen. Deuterated solvents were used as supplied. Reactions requiring inert conditions were conducted in flame-dried glassware (apart from NMR tubes and CO-ware two-chamber reactor) under an atmosphere of anhydrous dinitrogen using standard Schlenk techniques.

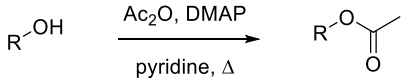
NMR spectra were recorded at 298 K on Bruker Avance-III spectrometers operating at nominal ^{1}H frequencies of 400 and 500 MHz. Chemical shifts (δ) are given in ppm, and are referenced to residual solvent peaks for ^{1}H and $^{13}C\{^{1}H\}$. $CDCl_3$ (7.26 ppm; 77.16 ppm), C_6D_6 (7.16 ppm; 128.06 ppm), CD_3CN (1.94 ppm; 1.32 and 118.26 ppm). External frequency standards are used for ^{11}B ($BF_3.OEt_2$; 0.00 ppm), ^{19}F (CCl_3F; 0.00 ppm) and ^{31}P (85% $H_3PO_{4(aq)}$; 0.00 ppm). Signals are reported as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), heptet (h), multiplet (m), broad (br.), apparent (app.) or combinations thereof. Higher multiplicities are expected in several compounds (*vide infra*), but are reported as multiplets since it was not possible to observe every peak. Due to broadness of peaks, one-bond phosphorus-proton coupling constants measured from the ^{31}P NMR spectra are in many cases not matching the same constant when measured from the ^{1}H spectrum, though the differences are never >0.5%). A 30 second relaxation delay time (D_1) was used for quantitative ^{19}F and ^{31}P NMR spectroscopy.

High-resolution mass spectrometry (HRMS) was performed using a Bruker MicroTOF spectrometer, with an electrospray ionisation (ESI) ion source. Infrared spectra (IR) were recorded on a Bruker Alpha

platinum-ATR with diamond window. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

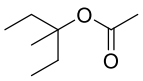
2. Synthesis and Characterisation of *tert*-Alkyl Esters

General procedure for the synthesis of *tert*-alkyl esters (GP1)



A mixture of alcohol (1.0 equiv.), acetic anhydride (1.1-1.5 equiv.) and 4-dimethylaminopyridine (DMAP, 0-0.1 equiv.) in pyridine was heated to 100 °C in a sealed microwave tube overnight. The resulting mixture was diluted with saturated aqueous $NaHCO_3$ solution and extracted with Et_2O (3 ×). The combined organic portions were washed with saturated aqueous $CuSO_4$ solution (3 ×), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Note: care should be exercised to minimise the loss of the more volatile, low molecular weight esters. Crude products were purified by kugelrohr distillation at the temperatures and pressures stated for individual compounds.

3-Methyl-3-pentyl acetate



GP1 was performed using 3-methyl-3-pentanol (6.20 mL, 50.0 mmol), acetic anhydride (7.10 mL, 75.0 mmol), pyridine (6.0 mL) and DMAP (0.611 g, 5.00 mmol). After kugelrohr distillation (40-45 °C, 10 mbar), 3-methy-3-pentyl acetate (5.27 g, 36.5 mmol, 73%) was obtained as a colourless liquid.

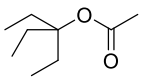
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (s, 3H), 1.90-1.82 (m, 2H), 1.77-1.69 (m, 2H), 1.36 (s, 3H), 0.85 (app. t, *J* = 7.5 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.4, 85.4, 30.4, 22.8, 22.3, 8.0.

ν_{max}(neat)/cm^{-1}: 2974, 2942, 2884, 1730, 1461, 1367, 1246, 1157, 1136, 1017, 940, 848, 610.

HRMS: calcd. for $C_8H_{16}O_2$+Na^+: 167.1043 $[M+Na]^+$; found (ESI^+): 167.1034.

3-Ethyl-3-pentyl acetate



GP1 was performed using 3-ethyl-3-pentanol (6.87 mL, 50.0 mmol), acetic anhydride (7.10 ml, 75.0 mmol), pyridine (6.0 mL), and DMAP (0.611 g, 5.00 mmol). After kugelrohr distillation (45 °C, 1.0 mbar) 3-ethyl-3-pentyl acetate (1.36 g, 8.59 mmol, 43%) was obtained as a colourless liquid.

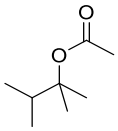
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.99 (s, 3H), 1.81 (q, *J* = 7.5 Hz, 6H), 0.81 (t, *J* = 7.5 Hz, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 170.4, 88.3, 26.9, 27.4, 7.8.

ν_{max}(neat)/cm^{-1}: 2971, 2944, 2884, 1727, 1458, 1366, 1244, 1205, 1138, 1040, 1014, 952, 924, 864, 610.

HRMS: *Neither the parent ion nor any obvious fragments could be observed by ESI-MS.*

2,3-Dimethyl-2-butyl acetate



GP1 was performed using 2,3-dimethyl-2-butanol (3.72 mL, 30.0 mmol), acetic anhydride (4.25 mL, 45.0 mmol), pyridine (5.0 mL) and DMAP (0.366 g, 3.00 mmol). After kugelrohr distillation (r.t., 1.0 mbar), 2,3-dimethyl-2-butyl acetate (2.44 g, 16.9 mmol, 56%) was obtained as a colourless liquid.

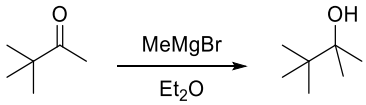
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (h, *J* = 6.9 Hz, 1H), 1.96 (s, 3H), 1.38 (s, 6H), 0.88 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.7, 85.5, 36.2, 22.9, 22.6, 17.4.

ν_{max}(neat)/cm^{-1}: 2972, 1728, 1464, 1368, 1250, 1230, 1140, 1097, 1070, 1017, 939, 897, 820, 609.

HRMS: *Neither the parent ion nor any obvious fragments could be observed by ESI-MS.*

2,3,3-Trimethyl-2-butanol[1]



To a solution of pinacolone (6.25 mL, 50.0 mmol) in anhydrous Et_2O (20 mL) under nitrogen was added methylmagnesium bromide (3.0 M in Et_2O; 20.0 mL, 60.0 mmol). The mixture was stirred at r.t. for 16 h before being quenched with a saturated aqueous solution of NH_4Cl. The resulting biphasic mixture was separated, and the aqueous portion was extracted with Et_2O (3 ×). The organic layers were combined, dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give 2,3,3-trimethyl-2-butanol (5.76 g, 49.6 mmol, 99%) as a colourless liquid. This material was used without further purification.

Characterisation data were consistent with literature values: ^1H[1] and $^{13}C\{^1H\}$[1] NMR.

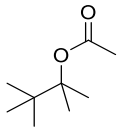
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (s, 1H), 1.18 (s, 6H), 0.94 (s, 9H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 75.1, 37.5, 25.5, 25.4.

ν_{max}(neat)/cm^{-1}: 3466, 2972, 2914, 2876, 1467, 1368, 1152, 1117, 944, 909, 879, 811, 734, 514.

HRMS: *Neither the parent ion nor any obvious fragments could be observed by ESI-MS.*

2,3,3-Trimethyl-2-butyl acetate



GP1 was performed using 2,3,3-trimethyl-2-butanol (2.32 g, 20.0 mmol), acetic anhydride (2.84 mL, 30.0 mmol), pyridine (4.0 mL) and DMAP (0.244 g, 2.00 mmol). After 72 h, a further portion of acetic anhydride (5.68 mL, 60 mmol) was added, and the mixture was stirred for a further 72 h at 100 °C until complete conversion was observed by ^{1}H NMR spectroscopy. After kugelrohr distillation (40-45 °C, 210 mbar), 2,3,3-trimethyl-2-butyl acetate (2.82 g, 17.8 mmol, 89%) was obtained as a colourless liquid.

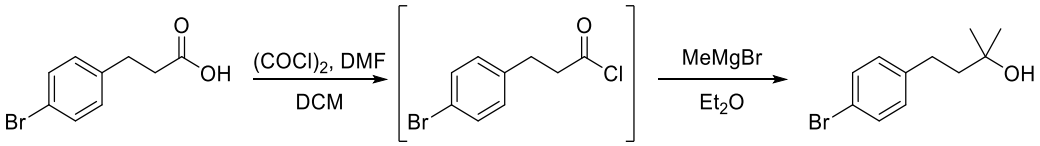
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.97 (s, 3H), 1.48 (s, 6H), 0.95 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 170.7, 86.8, 38.2, 25.1, 22.6, 20.4.

ν_{max}(neat)/cm^{-1}: 2973, 2917, 2879, 1731, 1467, 1367, 1256, 1218, 1171, 1134, 1017, 939, 847, 782, 610, 506, 491.

HRMS: calcd. for $C_9H_{18}O_2$+Na^+: 181.1199 $[M+Na]^+$; found (ESI^+): 181.1182.

2-Methyl-4-(4-bromophenyl)-2-butanol



Dimethylformamide (3 drops) was added to a solution of 3-(4-bromophenyl)propanoic acid (4.12 g, 18.0 mmol) and oxalyl chloride (1.72 mL, 20.0 mmol) in anhydrous dichloromethane (20 mL) under dinitrogen. Vigorous effervescence was observed. The mixture was stirred at r.t. for 1.5 h, then the solvent was removed *in vacuo* and anhydrous Et_2O (20 mL) was added to give a pale yellow solution. Methylmagnesium bromide (3.0 M in Et_2O; 20.0 mL, 60.0 mmol) was added slowly and the resulting mixture was stirred at r.t. for 1 h. A saturated aqueous solution of NH_4Cl was added and the phases were separated. The aqueous phase was extracted with Et_2O (3 ×) and the combined organic portions were dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give 2-methyl-4-(4-bromophenyl)-2-butanol (4.01 g, 16.5 mmol, 92%) as a brown oil which solidified on standing. This material was used without further purification.

Characterisation data were consistent with literature values: ^1H[2] and $^{13}C\{^1H\}$[2] NMR.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.09-7.06 (m, 2H), 2.68-2.64 (m, 2H), 1.78-1.73 (m, 2H), 1.29 (s, 6H), 1.21 (s, 1H).

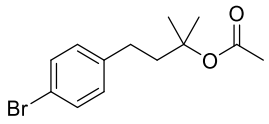
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 141.7, 131.6, 130.2, 119.6, 70.9, 45.7, 30.3, 29.5.

ν_{max}(neat)/cm^{-1}: 3288, 2969, 2929, 2863, 1486, 1402, 1379, 1362, 1262, 1206, 1154, 1124, 1091, 1070, 1010, 908, 834, 801, 761, 631, 521, 484, 452.

HRMS: calcd. for $C_{11}H_{15}{}^{79}BrO+Na^+$: 265.0198 $[M+Na]^+$; found (ESI^+): 265.0193.

m.p./°C: 35-38, lit.[2] 34-37.

2-Methyl-4-(4-bromophenyl)-2-butyl acetate



GP1 was performed using 2-methyl-4-(4-bromophenyl)-2-butanol (3.65 g, 15.0 mmol), acetic anhydride (2.13 mL, 22.5 mmol), pyridine (3.0 mL) and DMAP (0.183 g, 1.50 mmol). After kugelrohr distillation (200-220 °C, 0.3 mbar), 2-methyl-4-(4-bromophenyl)-2-butyl acetate (3.84 g, 13.5 mmol, 90%) was obtained as a yellow liquid.

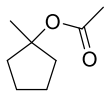
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.08-7.04 (m, 2H), 2.61-2.56 (m, 2H), 2.05-2.00 (m, 2H), 1.97 (s, 3H), 1.49 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.6, 141.2, 135.6, 130.3, 119.7, 81.9, 42.6, 30.0, 26.3, 22.5.

ν_{max}(neat)/cm^{-1}: 2975, 2931, 2870, 1729, 1488, 1455, 1366, 1246, 1201, 1168, 1125, 1094, 1071, 1011, 945, 828, 803, 761, 609, 519, 466.

HRMS: calcd. for $C_{13}H_{17}{}^{79}BrO_2$+Na^+: 307.0304 [M+Na]$^+$; found (ESI$^+$): 307.0303.

1-Methylcyclopentyl acetate



GP1 was performed using 1-methylcyclopentanol (5.01 g, 50.0 mmol), acetic anhydride (7.10 mL, 75.0 mmol), pyridine (6.0 mL) and DMAP (0.611 g, 5.00 mmol). After kugelrohr distillation (r.t., 0.3 mbar), 1-methylcyclopentyl acetate (6.23 g, 46.8 mmol, 88%) was obtained as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[3] and $^{13}C\{^{1}H\}$[3] NMR.

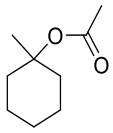
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.10-2.02 (m, 2H), 1.95 (s, 3H), 1.73-1.62 (m, 4H), 1.62-1.56 (m, 2H), 1.52 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 170.8, 89.8, 39.2, 24.4, 23.9, 22.5.

ν_{max}(neat)/cm^{-1}: 2966, 2874, 1731, 1443, 1367, 1337, 1249, 1188, 1122, 1018, 939, 855, 613, 461.

HRMS: *Neither the parent ion nor any obvious fragments could be observed by ESI-MS.*

1-Methylcyclohexyl acetate



GP1 was performed using 1-methylcyclohexanol (6.21 mL, 50.0 mmol), acetic anhydride (5.20 mL, 55.0 mmol) and pyridine (6.0 mL). After kugelrohr distillation (r.t., 0.2 mbar) 1-methylcyclohexyl acetate (6.87 g, 44.0 mmol, 88%) was obtained as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[4] and $^{13}C\{^{1}H\}$[5] NMR, IR.[5]

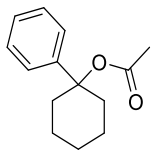
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15-2.08 (m, 2H), 2.00 (s, 3H), 1.58-1.22 (m, 11H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 170.6, 81.9, 36.8, 25.6, 25.5, 22.6, 22.3.

ν_{max}(neat)/cm^{-1}: 2932, 2861, 1730, 1448, 1367, 1285, 1266, 1232, 1155, 1107, 10431, 1017, 964, 945, 918, 870, 809, 611, 467.

HRMS: *Neither the parent ion nor any obvious fragments could be observed by ESI-MS.*

1-Phenylcyclohexyl acetate



GP1 was performed using 1-phenylcyclohexanol (3.52 g, 20.0 mmol), acetic anhydride (2.84 mL, 30.0 mmol), pyridine (4.0 mL) and DMAP (0.244 g, 2.00 mmol). After kugelrohr distillation (120 °C, 0.3-0.4 mbar), 1-phenylcyclohexyl acetate (3.64 g, 16.7 mmol, 83%) was obtained as a pale yellow liquid which solidified on standing.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.30 (m, 4H), 7.25-7.21 (m, 1H), 2.52-2.46 (m, 2H), 2.05 (s, 3H), 1.78-1.70 (m, 3H), 1.69-1.63 (m, 4H), 1.35-1.25 (m, 1H).

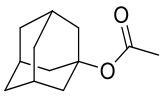
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 169.7, 145.8, 128.4, 127.1, 124.7, 82.6, 36.4, 25.5, 22.3, 22.2.

ν_{max}(neat)/cm^{-1}: 3087, 3059, 3028, 2933, 2860, 1737, 1494, 1448, 1366, 1263, 1227, 1132, 1013, 960, 910, 843, 817, 757, 696, 646, 630, 600, 537.

HRMS: calcd. for $C_{14}H_{18}O_2$+Na^+: 241.1199 $[M+Na]^+$; found (ESI^+): 241.1196.

m.p./°C: 57-59, lit.[6] 58-59.

1-Adamantyl acetate



GP1 was performed using 1-adamantanol (7.61 g, 50.0 mmol), acetic anhydride (7.10 mL, 75.0 mmol), pyridine (8.0 mL) and DMAP (0.612 g, 5.00 mmol). After kugelrohr distillation (135-140 °C, 6-8 mbar) 1-adamantyl acetate (9.71 g, 50.0 mmol, >99%) was obtained as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[5] and $^{13}C\{^{1}H\}$[5] NMR, IR.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18-2.12 (m, 3H), 2.12-2.09 (m, 6H), 1.98 (s, 3H), 1.72-1.64 (m, 6H).

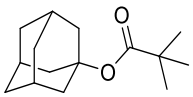
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 170.4, 80.4, 41.4, 36.4, 30.9, 22.9.

ν_{max}(neat)/cm^{-1}: 2910, 2853, 1731, 1456, 1367, 1354, 1241, 1059, 1016, 864.

HRMS: calcd. For $C_{12}H_{18}O_2$+Na^+: 217.1199 $[M+Na]^+$; found (ESI^+): 217.1192.

m.p./°C: 31-32, lit.[5] 31.

1-Adamantyl pivalate



GP1 was performed using 1-adamantanol (3.04 g, 20.0 mmol), pivalic anhydride (5.59 mL, 30.0 mmol), pyridine (4.0 mL), and DMAP (0.244 g, 2.00 mmol). After stirring for 1 week, the crude product was obtained as a mixture with Piv_2O (1.0:0.5). Kugelrohr distillation was used to separate the two species (Piv_2O: 50-60 °C, 0.5 mbar; 1-adamantyl pivalate: 120-126 °C, 0.2 mbar). 1-Adamantyl pivalate (4.01 g, 17.0 mmol, 85%) containing < 5% Piv_2O was obtained in this manner as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[7] and $^{13}C\{^{1}H\}$[7] NMR, IR.[8]

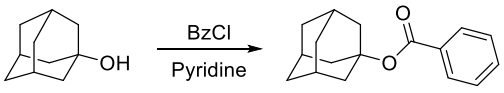
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.18-2.13 (m, 3H), 2.11-2.07 (m, 6H), 1.69-1.63 (m, 6H), 1.14 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 178.0, 79.7, 41.4, 39.4, 36.4, 30.9, 27.4.

ν_{max}(neat)/cm^{-1}: 2909, 2853, 1722, 1479, 1457, 1394, 1355, 1318, 1281, 1161, 1103, 1056, 1004, 969, 940, 917, 872, 814, 770, 573, 427, 407.

HRMS: calcd. For $C_{15}H_{24}O_2$+Na^+: 259.1669 $[M+Na]^+$; found (ESI^+): 259.1673.

1-Adamantyl benzoate



Benzoyl chloride (1.27 mL, 11.0 mmol) was added to a solution of 1-adamantanol (1.52 g, 10.0 mmol) in pyridine (5.0 mL) at r.t. The mixture was stirred at r.t. for 16 h, then an aqueous solution of $NaHCO_3$ (5% w/v, 25 mL) was added. The aqueous phase was separated and extracted with dichloromethane (3 × 20 mL), the organic portions were combined and washed with brine (3 × 20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product as a colourless solid. Recrystallisation from hot methanol gave 1-adamantyl benzoate (2.08 g, 8.12 mmol, 81%) as a colourless crystalline solid.

Characterisation data were consistent with literature values: ^{1}H[9] and $^{13}C\{^{1}H\}$[9] NMR, IR.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.96 (m, 2H), 7.52 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.44-7.38 (m, 2H), 2.28-2.25 (m, 6H), 2.25-2.19 (m, 3H), 1.76-1.67 (m, 6H).

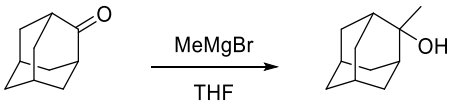
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 165.6, 132.5, 132.3, 129.6, 128.3, 81.2, 41.6, 36.4, 31.1.

ν_{max}(neat)/cm^{-1}: 2907, 2847, 1704, 1453, 1321, 1271, 1178, 1117, 1103, 1070, 1048, 1027, 711, 685.

HRMS: calcd. for $C_{17}H_{20}O_2$+Na^+: 279.1356 $[M+Na]^+$; found (ESI^+): 279.1357.

m.p./°C: 64-65, lit.[11] 66.5-67.

2-Methyl-2-adamantanol[12]



Methylmagnesium bromide (3.0 M in Et_2O; 10.0 mL, 30.0 mmol) was added to a solution of 2-adamantanone (2.25 g, 15.0 mmol) in anhydrous THF (20 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h before a saturated aqueous solution of NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 ×). The organic layers were combined, dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give 2-methyl-2-adamantanol (2.41 g, 14.5 mmol, 97%) as a colourless solid.

Characterisation data were consistent with literature values: ^1H[13] and $^{13}C\{^1H\}$[13] NMR.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.21-2.15 (m, 2H), 1.89-1.84 (m, 2H), 1.82-1.77 (m, 2H), 1.76-1.71 (m, 2H), 1.69-1.65 (m, 4H), 1.58-1.53 (m, 2H), 1.42 (s, 1H), 1.34 (s, 3H).

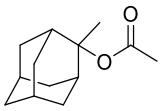
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 74.0, 39.3, 38.4, 35.3, 33.1, 27.7, 27.5, 27.2.

ν_{max}(neat)/cm^{-1}: 3355, 2989, 2888, 2852, 1442, 1374, 1353 ,1334, 1207, 1121, 1079, 1045, 1029, 953, 916, 870, 825, 802, 607, 492, 468, 446.

HRMS: calcd. for $C_{11}H_{18}O+Na^+$: 189.1250 $[M+Na]^+$; found (ESI^+): 189.1236.

m.p./°C: 203-206, lit.[13] 207.

2-Methyl-2-adamantyl acetate



GP1 was performed using 2-methyl-2-adamantanol (2.00 g, 12.0 mmol), acetic anhydride (1.70 mL, 18.0 mmol), pyridine (3.0 mL) and DMAP (0.147 g, 1.20 mmol). After kugelrohr distillation (100 °C, 0.2-0.3 mbar), 2-methyl-2-adamantyl acetate (2.27 g, 10.9 mmol, 91%) was obtained as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[14] and $^{13}C\{^{1}H\}$[14] NMR.

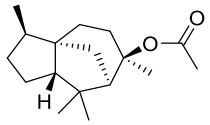
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.28-2.25 (m, 2H), 2.03-1.98 (m, 2H and s, 3H), 1.89-1.84 (m, 2H), 1.81-1.77 (m, 2H), 1.74-1.72 (m, 1H), 1.72-1.68 (m, 3H), 1.61 (s, 3H), 1.58-1.56 (m, 1H), 1.56-1.53 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 170.4, 86.9, 38.3, 36.3, 34.6, 33.2, 27.4, 26.7, 22.4, 22.2.

ν_{max}(neat)/cm^{-1}: 2902, 2860, 1726, 1446, 1363, 1244, 1218, 1104, 1025, 956, 935, 887, 841, 609, 504, 456.

HRMS: calcd. for $C_{13}H_{20}O_2$+Na^+: 231.1356 $[M+Na]^+$; found (ESI^+): 231.1347.

(+)-Cedryl acetate



GP1 was performed using (+)-cedrol (4.45 g, 20.0 mmol), acetic anhydride (2.84 mL, 30.0 mmol), pyridine (4.0 mL) and DMAP (0.244 g, 2.00 mmol). After kugelrohr distillation (130-140 °C, 0.1 mbar), (+)-cedryl acetate (5.20 g, 19.7 mmol, 98%) was obtained as a pale yellow liquid, which solidified on standing.

Characterisation data were consistent with literature values: ^{1}H[15] and $^{13}C\{^{1}H\}$[15] NMR. Note: the literature ^{1}H NMR spectroscopic data only accounts for 25 of the 28 expected protons.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.39 (dd, *J* = 5.2, 1.5 Hz, 1H), 2.03 (ddt, *J* = 13.7, 5.7, 1.7 Hz, 1H), 1.96-1.83 (m, 5H including a singlet at 1.95 ppm), 1.82-1.78 (m, 1H), 1.68-1.60 (m, 2H), 1.55-1.49 (m, 4H including a singlet at 1.54 ppm), 1.46-1.23 (m, 5H), 1.17 (s, 3H), 0.97 (s, 3H), 0.83 (d, *J* = 7.1 Hz, 3H).

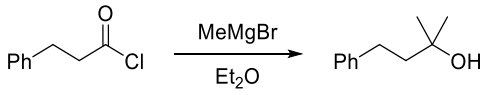
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 170.5, 86.4, 57.0, 56.8, 54.1, 43.5, 41.5, 41.1, 37.1, 33.3, 31.4, 28.6, 27.1, 26.0, 25.4, 22.9, 15.7.

ν_{max}(neat)/cm^{-1}: 2963, 2952, 2934, 2901, 2872, 1722, 1471, 1457, 1364, 1262, 1242, 1117, 1086, 1021, 949, 927, 840, 757, 696, 612, 461.

HRMS: calcd. for $C_{17}H_{28}O_2$+Na^+: 287.1982 $[M+Na]^+$; found (ESI^+): 287.1981.

m.p./°C: 40-42, lit.[15] 44-46.

2-Methyl-4-phenyl-2-butanol



Methylmagnesium bromide (3.0 M in Et_2O; 10.0 mL, 30.0 mmol) was added dropwise to a solution of 3-phenylpropionyl chloride (1.49 mL, 10.0 mmol) in anhydrous Et_2O (20 mL) at r.t. The mixture was stirred at r.t. for 3 h, then a saturated aqueous solution of NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 ×). The combined organic layers were dried ($MgSO_4$), filtered and the solvent was removed *in vacuo* to give 2-methyl-4-phenyl-2-butanol (1.62 g, 9.86 mmol, 99%) as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[16] and $^{13}C\{^{1}H\}$[16] NMR.

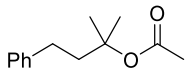
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.23-7.17 (m, 3H), 2.74-2.69 (m, 2H), 1.83-1.78 (m, 2H), 1.30 (app. s, 7H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 142.7, 128.6, 128.5, 125.9, 71.1, 45.9, 30.9, 29.5.

ν_{max}(neat)/cm^{-1}: 3383, 3026, 2968, 2932, 2864, 1604, 1494, 1454, 1376, 1210, 1149, 1071, 1031, 913, 829, 767, 738, 697, 519.

HRMS: calcd. for $C_{11}H_{16}O+NH_4^+$: 182.1539 $[M+NH_4]^+$; found (ESI^+): 182.1534.

2-Methyl-4-phenyl-2-butyl acetate (*d*$_0$-2)



GP1 was performed using 2-methyl-4-phenyl-2-butanol (1.64 g, 10.0 mmol), acetic anhydride (1.42 mL, 15.0 mmol), pyridine (2.0 mL) and DMAP (0.122 g, 1.00 mmol). After kugelrohr distillation (90-100 °C, 0.05-0.06 mbar), 2-methyl-4-phenyl-2-butyl acetate (***d*$_0$-2**) (1.86 g, 9.02 mmol, 90%) was obtained as a colourless liquid.

Characterisation data were consistent with literature values: ^{1}H[17] and ^{13}C{^{1}H}[17] NMR, IR.[17]

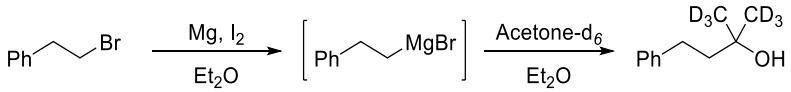
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 2.67-2.62 (m, 2H), 2.10-2.05 (m, 2H), 1.98 (s, 3H), 1.51 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 170.6, 142.2, 128.51, 128.50, 125.9, 82.1, 42.8, 30.5, 26.2, 22.5.

ν_{max}(neat)/cm^{-1}: 3027, 2977, 2936, 2867, 1730, 1604, 1495, 1454, 1366, 1246, 1202, 1169, 1123, 1073, 1017, 945, 822, 765, 742, 698, 611, 517, 464.

HRMS: calcd. for $C_{13}H_{18}O_2$+Na^+: 229.1199 $[M+Na]^+$; found (ESI^+): 229.1200.

2-Methyl-4-phenyl-2-butanol-d_6



A crystal of iodine was sublimed onto magnesium turnings (1.09 g, 45.0 mmol) under nitrogen, then anhydrous Et_2O (30 mL) was added. (2-Bromoethyl)benzene (5.55 g, 30.0 mmol) was added dropwise with stirring to generate 2-phenylethylmagnesium bromide. This mixture was stirred for 0.5 h at r.t. before it was added slowly by cannula transfer to a solution of acetone-d_6 (1.84 mL, 25.0 mmol) in anhydrous Et_2O (30 mL). The mixture was stirred at r.t. for 1 h, then a saturated aqueous solution of NH_4Cl was added. The phases were separated and the aqueous phase was extracted with Et_2O (3 ×). The organic layers were combined, dried ($MgSO_4$), filtered and the solvent was removed *in vacuo*. The crude material was layered onto a pad of silica gel which was eluted sequentially with pentane (to remove the 1,4-diphenylbutane side-product) and Et_2O to give 2-methyl-4-phenyl-2-butanol-d_6 (3.50 g, 20.5 mmol, 82%, >99% deuterium incorporation) as a colourless liquid.

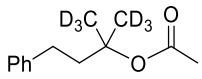
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.22-7.16 (m, 3H), 2.73-2.68 (m, 2H), 1.82-1.77 (m, 2H), 1.25 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 142.7, 128.6, 128.5, 125.9, 70.8, 45.8, 30.9, 28.5 (1:3:6:7:6:3:1 h, J = 19.2 Hz).

ν_{max}(neat)/cm^{-1}: 3376, 3027, 2935, 2863, 2224, 1603, 1497, 1454, 1263, 1175, 1114, 1050, 956, 812, 743, 696, 577, 509, 465, 430.

HRMS: calcd. for $C_{11}H_{10}D_6O$+Na^+: 193.1470 $[M+Na]^+$; found (ESI^+): 193.1477.

2-Methyl-4-phenyl-2-butyl acetate-d_6 (d_6-2)



GP1 was performed using 2-methyl-4-phenyl-2-butanol-d_6 (2.55 g, 15.0 mmol), acetic anhydride (2.13 mL, 22.5 mmol), pyridine (3.0 mL) and DMAP (0.183 g, 1.50 mmol). After kugelrohr distillation (90-100 °C, 0.05-0.06 mbar), 2-methyl-4-phenyl-2-butyl acetate-d_6 (***d*$_6$-2**) (3.06 g, 14.4 mmol, 96%, >99% deuterium incorporation) was obtained as a colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 2.67-2.62 (m, 2H), 2.09-2.04 (m, 2H), 1.98 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.6, 142.3, 128.5, 128.5, 125.9, 81.8, 42.7, 30.4, 25.3 (1:3:6:7:6:3:1 h, *J* = 19.2 Hz), 22.5.

ν_{max}(neat)/cm^{-1}: 3027, 2935, 2866, 2232, 1728, 1498, 1454, 1366, 1252, 1168, 1104, 1041, 1018, 963, 923, 809, 745, 697, 607, 509, 462, 436.

HRMS: calcd. for $C_{13}H_{12}D_6O_2$+Na^+: 235.1576 [M+Na]$^+$; found (ESI$^+$): 235.1576.

3. Determination of Zn_3P_2 Purity and Protonolysis Rate (Manuscript Scheme 2B)

CAUTION: phosphine gas is highly toxic and is spontaneously flammable in air. Procedures that use phosphine gas should only be performed following appropriate training after consultation with local safety advisors, and after completing a thorough risk assessment. A syringe-stop should be employed to ensure that the barrel of the gas-syringe cannot be ejected during the titration.

Solid Zn_3P_2 (for mass see Figure S1) was added to a two-necked flask fitted with septa. The flask was evacuated and backfilled with anhydrous dinitrogen (3 ×) before a gas syringe (50 mL) with a luer lock needle was inserted through one of the septa and purged with N_2 (3 ×). The flask was then disconnected from the Schlenk line and degassed aqueous HCl (5.0 M; 2.0 mL, 10 mmol) was added quickly in one portion using a Luer lock syringe. **CAUTION: gas pressure within the apparatus increases immediately; the plunger of the syringe used to add hydrochloric acid should be held down after the acid has been added and while the syringe is removed carefully from the apparatus.** The time taken for generation of gas was measured in 2.0 mL increments (taking into account the volume of hydrochloric acid (2.0 mL) that was added), and the mixture was stirred until no further gas was released. A solution of $KMnO_4$ in aqueous sulfuric acid (0.50 M in 0.50 M H_2SO_4, 10 mL, 5.0 mmol) was added slowly, and the plunger of the gas syringe was driven back in to allow oxidation of the PH_3 gas. **CARE! exothermic reaction**. After 10 minutes the vessel was opened to air.

Volumetric gas evolution data for two independent experiments are displayed in Figure S1.

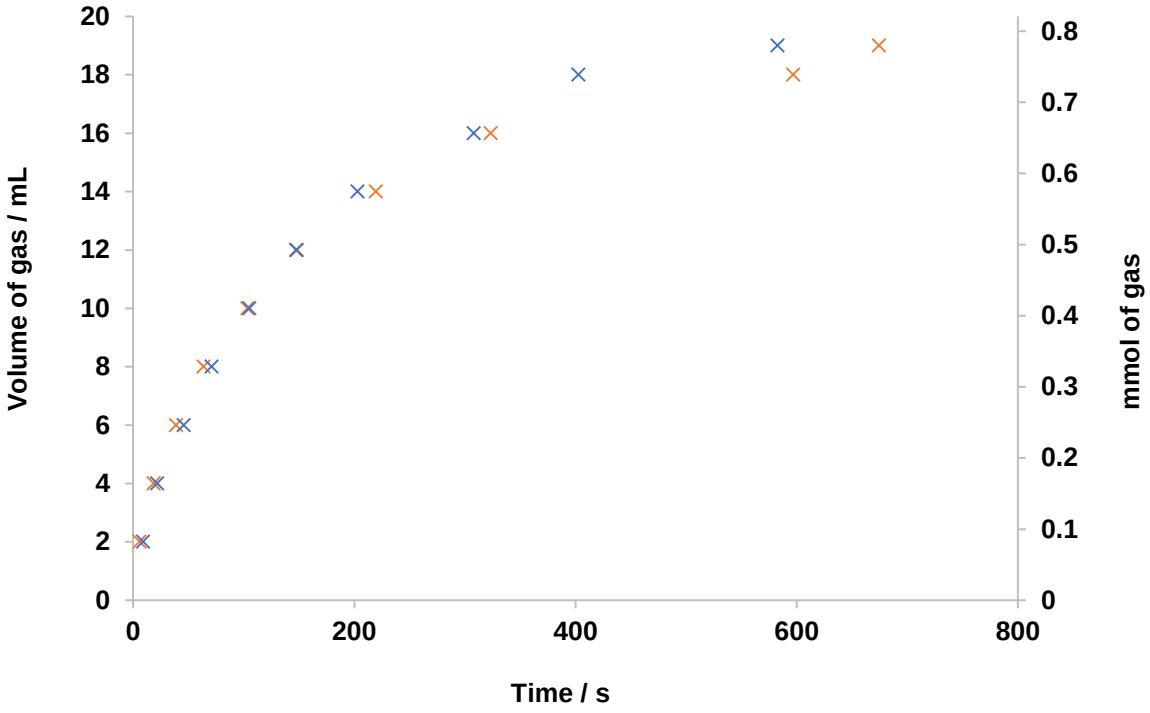
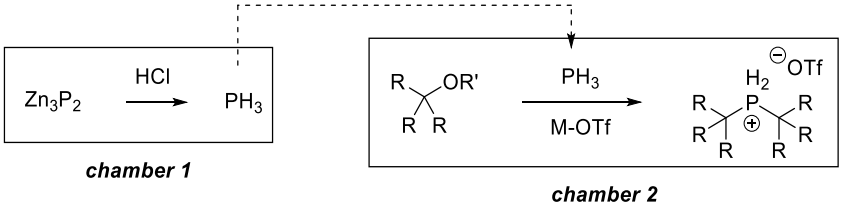


Figure S1. Volumetric gas titration of Zn_3P_2.

Blue – Run 1 (0.128 g Zn_3P_2, 0.496 mmol at 100% purity): 19.0±0.5 mL gas evolved in 583 s. Using PV = nRT (P = 1.00 bar, T = 297 K). n = 0.780 mmol gas. **Purity = 78.6%**.

Orange – Run 2 (0.129 g Zn_3P_2, 0.500 mmol at 100% purity): 19.0±0.5 mL gas evolved in 674 s. Using PV = nRT (P = 1.00 bar, T = 297 K). n = 0.780 mmol gas. **Purity = 78.0%**.

4. Screening of Carbocation Sources (Manuscript Scheme 2C)

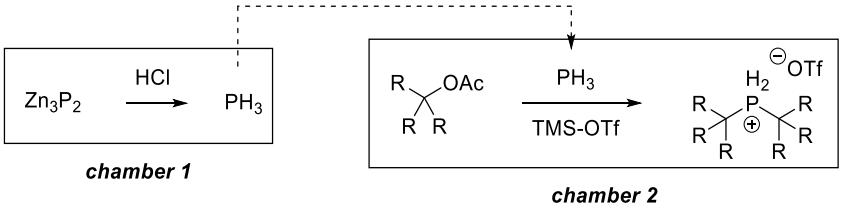


CAUTION: phosphine gas is highly toxic and is spontaneously flammable in air. Procedures that use phosphine gas should only be performed following appropriate training after consultation with local safety advisors, and after completing a thorough risk assessment. All CO-ware apparatus should be inspected for scratches or imperfections prior to use; new CO-ware septa should be used for each reaction, and the manufacturer's guidelines should be followed (no more than 2 injections per septum, using a needle with a diameter of 21g (0.08 mm) or less). CO-ware is recommended for routine use at pressures up to 46 psi, and not above 60 psi; this should be considered when changing reaction scales from those presented in this Supporting Information.

Zinc phosphide (78.0% purity, 0.165 g, 0.50 mmol (to give 1.00 mmol PH_3)) was added to chamber one of a two-chamber reactor (CO-ware, 20 mL total volume, fitted with compatible septa). The reactor was evacuated and backfilled with anhydrous dinitrogen (3 ×). *Tert*-amyl carbocation source (6.00 mmol, 6.00 equiv.) and trimethylsilyl trifluoromethanesulfonate (0.181 mL, 1.00 mmol) or trifluoromethanesulfonic acid (0.088 mL, 1.00 mmol) were added to chamber two. Degassed aqueous hydrochloric acid (5.0 M; 2.0 mL, 10 mmol) was added to chamber one quickly in a single portion using a Luer lock syringe. **CAUTION: gas pressure within the apparatus increases immediately; the plunger of the syringe used to add hydrochloric acid should be held down after the acid has been added and while the syringe is removed carefully from the apparatus.** The reaction was stirred at r.t. for 4 h. The reactor was then opened to air and an aliquot was removed from chamber two for ^{31}P NMR spectroscopic analysis.

5. Synthesis of Di-*tert*-alkylphosphonium Salts 1 (Manuscript Scheme 3)

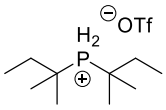
General procedure – Synthesis of di-*tert*-alkylphosphonium salts (GP2)



CAUTION: phosphine gas is highly toxic and is spontaneously flammable in air. Procedures that use phosphine gas should only be performed following appropriate training and after consultation with local safety advisors.

Zinc phosphide (78.0% purity, 0.165 g, 0.50 mmol (to give 1.00 mmol PH_3)) was added to chamber one of a two-chamber reactor (CO-ware, 20 mL total volume, fitted with compatible septa). The reactor was evacuated and backfilled with anhydrous dinitrogen (3 ×). *Tert*-alkyl ester (3.00 mmol, 3.00 equiv.) and trimethylsilyl trifluoromethanesulfonate (0.181 mL, 1.00 mmol) were added to chamber two. Degassed hydrochloric acid (5.0 M; 2.0 mL, 10 mmol) was added to chamber one quickly in a single portion using a Luer lock syringe. **CAUTION: gas pressure within the apparatus increases immediately; the plunger of the syringe used to add hydrochloric acid should be held down after the acid has been added and while the syringe is removed carefully from the apparatus.** The reaction was stirred at r.t. for 4 h. The reactor was then opened to air and washed into a flask with Et_2O. Products that spontaneously precipitated/crystallised from solution were isolated by filtration and washed with Et_2O. If the product did not spontaneously precipitate/crystallise, the reaction was concentrated *in vacuo* before Et_2O was added; if no precipitation/crystallisation occurred at this point, mixtures were placed in a freezer at -25 °C overnight. The isolated phosphonium salts are stable under ambient laboratory conditions for at least a year.

Di-*tert*-amylphosphonium trifluoromethanesulfonate (1a)



Conditions 1: GP2 was performed using *tert*-amyl acetate (0.460 mL, 3.00 mmol). Di-*tert*-amylphosphonium trifluoromethanesulfonate **1a** (0.151 g, 0.466 mmol, 47%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed using *tert*-amyl acetate (0.920 mL, 6.00 mmol). Di-*tert*-amylphosphonium trifluoromethanesulfonate **1a** (0.249 g, 0.768 mmol, 77%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.41 (d, *J* = 472.5 Hz, 2H), 1.89 (dq, *J* = 14.8, 7.4 Hz, 4H), 1.54 (d, *J* = 18.5 Hz, 12H), 1.08 (t, *J* = 7.5 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.7 (q, *J* = 319.8 Hz), 35.5 (d, *J* = 33.6 Hz), 32.9, 24.6, 8.0 (d, *J* = 8.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.47.

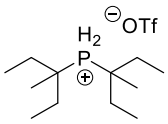
^{31}P NMR (202 MHz, $CDCl_3$): δ 15.25 (tm, *J* = 472.6 Hz).

ν_{max}(neat)/cm^{-1}: 2975, 2424, 1509, 1468, 1418, 1250, 1222, 1153, 1065, 1026, 939, 867, 828, 812, 772, 755, 702, 675, 635, 572, 516, 494, 418.

HRMS: calcd. for $C_{10}H_{24}P^+$: 175.1610 $[M\text{-}OTf]^+$; found (ESI^+): 175.1613.

m.p./°C: 113-115.

Di-(3-methyl-3-pentyl)phosphonium trifluoromethanesulfonate (1b)



Conditions 1: GP2 was performed using 3-methyl-3-pentyl acetate (0.433 g, 3.00 mmol). Di-(3-methyl-3-pentyl)phosphonium trifluoromethanesulfonate **1b** (0.159 g, 0.451 mmol, 45%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed on a 5.0 mmol scale in a 100 mL CO-ware reactor using Zn_3P_2 (78.0% purity, 0.827 g, 2.50 mmol), 3-methyl-3-pentyl acetate (2.16 g, 15.0 mmol), trimethylsilyl trifluoromethanesulfonate (0.905 mL, 5.00 mmol) and degassed hydrochloric acid (5.0 M; 10 mL, 50 mmol). Di-(3-methyl-3-pentyl)phosphonium trifluoromethanesulfonate **1b** (1.14 g, 3.24 mmol, 65%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.36 (d, *J* = 470.1 Hz, 2H), 2.00-1.83 (m, 8H), 1.54 (d, *J* = 18.7 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.7 (q, *J* = 319.7 Hz), 39.8 (d, *J* = 32.0 Hz), 29.6, 22.2, 7.9 (d, *J* = 7.9 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.42.

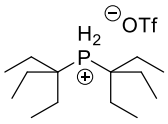
^{31}P NMR (202 MHz, $CDCl_3$): δ 3.45 (tm, *J* = 470.3 Hz).

ν_{max}(neat)/cm^{-1}: 2978, 2949, 2887, 2410, 1460, 1394, 1248, 1222, 1148, 1027, 939, 754, 635, 571, 516.

HRMS: calcd. for $C_{12}H_{28}P^+$: 203.1923 $[M\text{-}OTf]^+$; found (ESI^+): 203.1920.

m.p./°C: 105-109.

Di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate (1c)



Conditions 1: GP2 was performed using 3-ethyl-3-pentyl acetate (0.475 g, 3.00 mmol). Di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (0.336 g, 0.883 mmol, 88%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed on a 5.0 mmol scale in a 100 mL CO-ware reactor using Zn_3P_2 (78.0% purity, 0.827 g, 2.50 mmol), 3-ethyl-3-pentyl acetate (2.37 g, 15.0 mmol), trimethylsilyl trifluoromethanesulfonate (0.91 mL, 5.0 mmol) and degassed hydrochloric acid (5.0 M; 10 mL, 50 mmol). Di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (1.84 g, 4.84 mmol, 97%) was obtained as a colourless crystalline solid.

A triplet of 13-ets is expected in the ^{31}P NMR spectrum, from $^{1}J_{P\text{-}H}$ and $^{3}J_{P\text{-}H}$ couplings respectively. However, the lower intensity peaks of the multiplet are not observed due to poor signal:noise, and as such is reported below as a triplet of multiplets with both coupling constants given.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.21 (d, *J* = 468.9 Hz, 2H), 1.89 (dq, *J* = 17.4, 7.4 Hz, 12H), 1.05 (t, *J* = 7.4 Hz, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.8 (q, *J* = 320.1 Hz), 44.9 (d, *J* = 29.1 Hz), 27.2, 8.0 (d, *J* = 7.1 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.38.

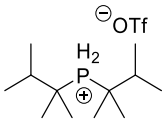
^{31}P NMR (202 MHz, $CDCl_3$): δ -13.43 (tm, *J* = 468.9, 17.3 Hz).

ν_{max}(neat)/cm^{-1}: 2976, 2938, 2885, 2424, 2400, 1456, 1393, 1272 ,1243, 1222, 1153, 1025, 957, 896, 862, 755, 635, 600, 572, 515, 450, 410.

HRMS: calcd. for $C_{14}H_{28}P^+$: 231.2236 $[M\text{-}OTf]^+$; found (ESI^+): 231.2239.

m.p./°C: 115-117.

Bis-(2,3-dimethyl-2-butyl)phosphonium trifluoromethanesulfonate (1d)



GP2 was performed using 2,3-dimethyl-2-butyl acetate (0.433 g, 3.00 mmol). Bis-(2,3-dimethyl-2-butyl)phosphonium trifluoromethanesulfonate **1d** (0.281 g, 0.797 mmol, 80%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.46 (d, *J* = 472.2 Hz, 2H), 2.15 (dh, *J* = 10.8, 6.8 Hz, 2H), 1.52 (d, *J* = 18.8, 12H), 1.09 (d, *J* = 6.8, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.8 (q, *J* = 320.1 Hz), 39.8 (d, *J* = 32.1 Hz), 35.4, 22.7, 17.5 (d, *J* = 6.8 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.37.

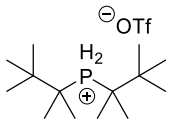
^{31}P NMR (202 MHz, $CDCl_3$): δ 8.02 (tm, *J* = 472.3 Hz).

ν_{max}(neat)/cm^{-1}: 2973, 2415, 1470, 1392, 1377, 1254, 1222, 1157, 1083, 1025, 934, 757, 635, 572, 516, 423.

HRMS: calcd. for $C_{12}H_{28}P^+$: 203.1923 $[M\text{-}OTf]^+$; found (ESI^+): 203.1922.

m.p./°C: 151-154.

Bis-(2,3,3-trimethyl-2-butyl)phosphonium trifluoromethanesulfonate (1e)



GP2 was performed using 2,3,3-trimethyl-2-butyl acetate (0.475 g, 3.00 mmol). Bis-(2,3,3-trimethyl-2-butyl)phosphonium trifluoromethanesulfonate **1e** (0.294 g, 0.773 mmol, 77%) was obtained as a colourless crystalline solid.

A triplet of 13-ets is expected in the ^{31}P NMR spectrum, from $^{1}J_{P\text{-}H}$ and $^{3}J_{P\text{-}H}$ couplings respectively. However, the lower intensity peaks of the multiplet are not observed due to poor signal:noise, and as such is reported below as a triplet of multiplets with both coupling constants given.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.50 (d, *J* = 468.7 Hz, 2H), 1.57 (d, *J* = 18.6 Hz, 12H), 1.18 (s, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.8 (q, *J* = 320.1 Hz), 43.7 (d, *J* = 29.5 Hz), 38.7, 25.8 (d, *J* = 5.7 Hz), 21.9.

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.22.

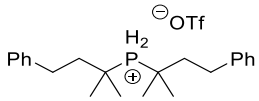
^{31}P NMR (202 MHz, $CDCl_3$): δ -7.25 (tm, *J* = 469.1, 18.6 Hz).

ν_{max}(neat)/cm^{-1}: 2981, 2881, 2430, 1476, 1388, 1250, 1224, 1148, 1029, 964, 755, 636, 572, 516.

HRMS: calcd. for $C_{14}H_{32}P^+$: 231.2236 $[M\text{-}OTf]^+$; found (ESI^+): 231.2235.

m.p./°C: 134-137.

Di-(2-methyl-4-phenyl-2-butyl)phosphonium trifluoromethanesulfonate (1f)



Conditions 1: GP2 was performed using 2-methyl-4-phenyl-2-butyl *iso*butyrate (0.619 g, 3.00 mmol). Di-(2-methy-4-phenyl-2-butyl)phosphonium trifluoromethanesulfonate **1f** (0.398 g, 0.835 mmol, 83%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed on a 5.0 mmol scale in a 100 mL CO-ware reactor using Zn_3P_2 (78.0% purity, 0.827 g, 2.50 mmol), 2-methyl-4-phenyl-2-butyl *iso*butyrate (3.51 g, 15.0 mmol), trimethylsilyl trifluoromethanesulfonate (0.905 mL, 5.00 mmol) and degassed hydrochloric acid (5.0 M; 10 mL, 50 mmol). Di-(2-methyl-4-phenyl-2-butyl)phosphonium trifluoromethanesulfonate **1f** (2.02 g, 4.24 mmol, 85%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.26 (m, 4H), 7.24-7.19 (m, 2H), 7.18-7.14 (m, 4H), 6.57 (d, *J* = 476.5 Hz, 2H), 2.76-2.69 (m, 4H), 2.14-2.05 (m, 4H), 1.60 (d, *J* = 18.4 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 139.7, 129.0, 128.5, 126.8, 120.7 (q, *J* = 319.9 Hz), 41.8, 35.4 (d, *J* = 33.1 Hz), 29.8 (d, *J* = 8.1 Hz), 25.2.

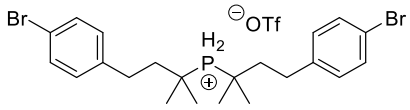
^{19}F NMR (470 MHz, $CDCl_3$): δ -78.34.

^{31}P NMR (202 MHz, $CDCl_3$): δ 14.52 (tm, *J* = 476.6 Hz).

ν_{max}(neat)/cm^{-1}: 3065, 3029, 2965, 2936, 2863, 2427, 2397, 1603, 1498, 1456, 1379, 1273, 1248, 1220, 1152, 1025, 986, 935, 745, 701, 636, 572, 516, 466, 418.

HRMS: calcd. for $C_{22}H_{32}P^+$: 327.2236 $[M\text{-}OTf]^+$; found (ESI^+): 327.2239.

Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium trifluoromethanesulfonate (1g)



GP2 was performed using 2-methyl-4-(4-bromophenyl)-2-butyl acetate (0.856 g, 3.00 mmol). Di-(2-methyl-4-(4-bromophenyl)-2-butyl)phosphonium trifluoromethanesulfonate **1g** (0.401 g, 0.632 mmol, 63%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.64 (d, *J* = 478.1 Hz, 2H), 2.71-2.64 (m, 4H), 2.10-2.00 (m, 4H), 1.62-1.52 (d, *J* = 18.2 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 138.8, 132.0, 130.3, 120.7 (q, *J* = 320.1 Hz), 120.6, 41.9, 35.2 (d, *J* = 31.9 Hz), 29.2 (d, *J* = 8.0 Hz), 25.2.

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.36.

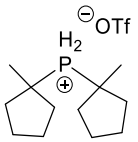
^{31}P NMR (202 MHz, $CDCl_3$): δ 14.43 (tm, *J* = 479.6 Hz).

ν_{max}(neat)/cm^{-1}: 2965, 2943, 2873, 2416, 2391, 1488, 1471, 1402, 1377 ,1252, 1222, 1154, 1071, 1027, 1009, 922, 798, 756, 636, 608, 572, 515, 486, 456.

HRMS: calcd. for $C_{22}H_{30}Br_2P^+$: 483.0446 $[M\text{-}OTf]^+$; found (ESI^+): 483.0448.

m.p./°C: 93-95.

Di-(1-methylcyclopentyl)phosphonium trifluoromethanesulfonate (1h)



Conditions 1: GP2 was performed using 1-methylcyclopentyl acetate (0.427 g, 3.00 mmol). Di-(1-methylcyclopentyl)phosphonium trifluoromethanesulfonate **1h** (0.118 g, 0.339 mmol, 34%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed using 1-methylcyclopentyl acetate (0.853 g, 6.00 mmol). Di-(1-methylcyclopentyl)phosphonium trifluoromethanesulfonate **1h** (0.193 g, 0.554 mmol, 55%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.53 (d, *J* = 478.1 Hz, 2H), 2.21-2.08 (m, 4H), 1.95-1.82 (m, 12H), 1.50 (d, *J* = 18.0 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.7 (q, *J* = 320.0 Hz), 38.6 (d, *J* = 2.7 Hz), 37.3 (d, *J* = 38.7 Hz), 24.4 (d, *J* = 9.1 Hz), 23.7 (d, *J* = 3.4 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.50.

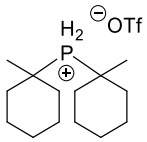
^{31}P NMR (202 MHz, $CDCl_3$): δ 18.22 (tm, *J* = 478.2 Hz).

ν_{max}(neat)/cm^{-1}: 2969 2878, 2442, 2415, 1453, 1390, 1248, 1222, 1147, 1025, 943, 915, 755, 635, 572, 515, 475.40.

HRMS: calcd. for $C_{12}H_{24}P^+$: 199.1610 [M-OTf]$^+$; found (ESI$^+$): 199.1619.

m.p./°C: 58-61.

Di-(1-methylcyclohexyl)phosphonium trifluoromethanesulfonate (1i)



GP2 was performed using 1-methylcyclohexyl acetate (0.469 g, 3.00 mmol). Di-(1-methylcyclohexyl)phosphonium trifluoromethanesulfonate **1i** (0.278 g, 0.739 mmol, 74%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.33 (d, *J* = 469.5 Hz, 2H), 2.05-1.96 (m, 4H), 1.89-1.82 (m, 4H), 1.69-1.60 (m, 16H), 1.45-1.41 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.7 (q, *J* = 320.1 Hz), 36.2 (d, *J* = 33.8 Hz), 35.1, 24.8, 21.6. 20.7 (d, *J* = 9.6 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.41.

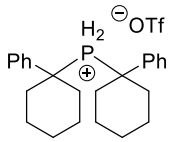
^{31}P NMR (202 MHz, $CDCl_3$): δ 17.44 (tm, *J* = 470.1 Hz).

ν_{max}(neat)/cm^{-1}: 2932, 2862, 2426, 2403, 1460, 1388, 1350, 1250, 1222, 1151, 1025, 988, 968, 941, 920, 847, 756, 635, 613, 571, 515, 466, 440.

HRMS: calcd. for $C_{14}H_{28}P^+$: 227.1923 $[M\text{-}OTf]^+$; found (ESI^+): 227.1928.

m.p./°C: 138-142.

Di-(1-phenylcyclohexyl)phosphonium trifluoromethanesulfonate (1j)



Conditions 1: GP2 was performed using a solution of 1-phenylcyclohexyl acetate (0.655 g, 3.00 mmol) dissolved in degassed anhydrous dichloromethane (2.0 mL), with chamber two heated to 40 °C. Di-(1-phenylcyclohexyl)phosphonium trifluoromethanesulfonate **1j** (0.203 g, 0.369 mmol, 37%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed using 1-phenylcyclohexyl acetate (0.655 g, 3.00 mmol), with chamber two heated to 40 °C. Di-(1-phenylcyclohexyl)phosphonium trifluoromethanesulfonate **1j** (0.291 g, 0.581 mmol, 58%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50-7.44 (m, 4H), 7.43-7.32 (m, 7H, Ar-H + one peak of PH_2 doublet), 6.18 (app. s, 1H, one peak of PH_2 doublet), 2.10-2.00 (m, 4H), 1.89-1.78 (m, 4H), 1.53-1.41 (m, 6H), 1.38-1.23 (m, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 133.6, 130.0 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 3.5 Hz), 128.0 (d, *J* = 5.4 Hz), 120.9 (q, *J* = 320.2 Hz), 42.3 (d, *J* = 31.9 Hz), 33.1, 25.0, 21.0 (d, *J* = 9.7 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.26.

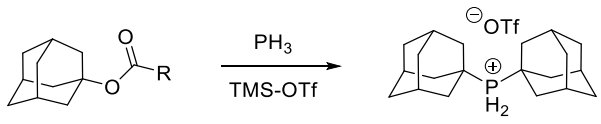
^{31}P NMR (202 MHz, $CDCl_3$): δ 18.28 (tm, *J* = 478.6 Hz).

ν_{max}(neat)/cm^{-1}: 2940, 2858, 2398, 2366, 1448, 1256, 1222, 1142, 1051, 1026, 948, 750, 699, 634, 571, 514, 415.

HRMS: calcd. for $C_{24}H_{32}P^+$: 351.2236 $[M\text{-}OTf]^+$; found (ESI^+): 351.2232.

m.p./°C: 167-170.

Di-(1-Adamantyl)phosphonium trifluoromethanesulfonate (1k)



R = Me, **Conditions 1,4**
R = Ph, **Conditions 2**
R = ^{t}Bu, **Conditions 3**

Conditions 1: GP2 was performed using a solution of 1-adamantyl acetate (0.583 g, 3.00 mmol) dissolved in degassed anhydrous dichloromethane (2.0 mL), with chamber two heated to 40 °C. Di-(1-adamantyl)phosphonium trifluoromethanesulfonate **1k** (0.378 g, 0.835 mmol, 84%) was obtained as a colourless crystalline solid.

Conditions 2: GP2 was performed using a solution of 1-adamantyl benzoate (0.769 g, 3.00 mmol) dissolved in degassed anhydrous dichloromethane (2.0 mL), with chamber two heated to 40 °C. Di-(1-adamantyl)phosphonium trifluoromethanesulfonate **1k** (0.373 g, 0.824 mmol, 82%) was obtained as a colourless crystalline solid.

Conditions 3: GP2 was performed using a solution of 1-adamantyl pivalate (0.709 g, 3.00 mmol) dissolved in degassed anhydrous dichloromethane (2.0 mL), with chamber two heated to 40 °C. Di-(1-adamantyl)phosphonium trifluoromethanesulfonate **1k** (0.380 g, 0.840 mmol, 84%) was obtained as a colourless crystalline solid.

Conditions 4: GP2 was performed on a 5.0 mmol scale in a 100 mL CO-ware reactor using Zn_3P_2 (78.0% purity, 0.827 g, 2.50 mmol), 1-adamantyl acetate (2.91 g, 15.0 mmol), trimethylsilyl trifluoromethanesulfonate (0.905 mL, 5.00 mmol) and degassed hydrochloric acid (5.0 M; 10 mL, 50 mmol). Di-(1-adamantyl)phosphonium trifluoromethanesulfonate **1k** (2.06 g, 4.55 mmol, 91%) was obtained as a colourless crystalline solid.

Note: one of the peaks of the doublet at 35.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum overlaps with the doublet at 35.5 ppm, but can be observed with additional processing.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99 (d, *J* = 469.4 Hz, 2H), 2.21-2.16 (br. m, 12H), 2.14-2.09 (br. m, 6H), 1.84-1.78 (br. m, 12H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 120.8 (q, *J* = 320.4 Hz), 38.9 (d, *J* = 2.0 Hz), 35.5 (d, *J* = 2.0 Hz), 35.4 (d, *J* = 34.8 Hz), 27.5 (d, *J* = 10.4 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.31.

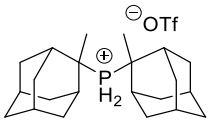
^{31}P NMR (202 MHz, $CDCl_3$): δ 13.04 (t, *J* = 469.6 Hz).

ν_{max}(neat)/cm^{-1}: 2906, 2854, 2424, 2400, 1450, 1345, 1305, 1276, 1245, 1221, 1154, 1022, 973, 944, 898, 755 ,634, 571, 515, 489, 447.40, 417.

HRMS: calcd. for $C_{20}H_{32}P^+$: 303.2236 $[M\text{-}OTf]^+$; found (ESI^+): 303.2258.

m.p./°C: >280, decomposition.

Di-(2-methyl-2-adamantyl)phosphonium trifluoromethanesulfonate (1l)



GP2 was performed using 2-methyl-2-adamantyl acetate (0.625 g, 3.00 mmol). Di-(2-methyl-2-adamantyl)phosphonium trifluoromethanesulfonate **1l** (0.145 g, 0.302 mmol, 30%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.82 (d, *J* = 466.1 Hz, 2H), 2.29-2.19 (m, 12H), 2.16-2.11 (m, 2H), 1.99-1.90 (m, 6H), 1.80-1.68 (m, 14H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 121.9 (q, *J* = 320.2 Hz), 46.0 (d, *J* = 30.1 Hz), 38.6, 35.7 (d, *J* = 1.7 Hz), 33.8 (d, *J* = 3.8 Hz), 31.5 (d, *J* = 8.7 Hz), 26.9, 26.8, 22.2 (d, *J* = 2.5 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.36.

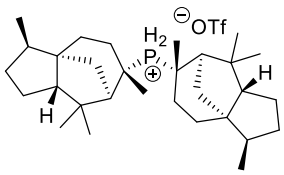
^{31}P NMR (202 MHz, $CDCl_3$): δ -4.30 (tm, *J* = 466.2 Hz).

ν_{max}(neat)/cm^{-1}: 2912, 2869, 2449, 2408, 1462, 1282, 1245, 1223, 1150, 1026, 955, 934 ,755, 635, 572, 516.

HRMS: calcd. for $C_{22}H_{36}P^+$: 331.2549 $[M\text{-}OTf]^+$; found (ESI^+): 351.2553.

m.p./°C: 202-206.

Dicedrylphosphonium trifluoromethanesulfonate (1m)



GP2 was performed using (+)-cedryl acetate (0.793 g, 3.00 mmol) with chamber two heated to 40 °C. Dicedrylphosphonium trifluoromethanesulfonate **1m** (0.419 g, 0.252 mmol, 25%) was obtained as a colourless crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (d, *J* = 465.1 Hz, 2H), 2.42-2.32 (m, 2H), 2.14-1.86 (m, 8H), 1.85-1.73 (m, 12H), 1.63-1.54 (m, 4H), 1.48-1.39 (m, 4H), 1.38-1.25 (m, 8H), 1.10 (s, 6H), 0.89 (d, *J* = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.7 (q, *J* = 320.5 Hz), 57.8, 55.2, 54.7, 47.4 (d, *J* = 13.0 Hz), 46.2 (d, *J* = 25.4 Hz), 43.2 (d, *J* = 6.3 Hz), 41.5, 36.4, 34.0, 30.5, 29.7 (d, *J* = 2.1 Hz), 29.5, 27.0, 25.3, 15.4.

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.26.

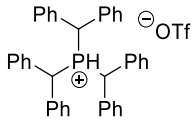
^{31}P NMR (202 MHz, $CDCl_3$): δ 11.18 (tm, *J* = 466.5 Hz).

ν_{max}(neat)/cm^{-1}: 2941, 2871, 2418, 1464, 1392, 1281, 1249, 1225, 1149, 1029, 972, 942, 755, 636, 571, 516.

HRMS: calcd. for $C_{30}H_{52}P^+$: 443.3801 $[M\text{-}OTf]^+$; found (ESI^+): 443.3803.

m.p./°C: 142-144.

Tribenzhydrylphosphonium trifluoromethanesulfonate (1n)



GP2 was performed using a solution of benzhydryl acetate[18] (0.679 g, 3.00 mmol) dissolved in degassed anhydrous dichloromethane (2.0 mL), with chamber 2 heated to 40 °C. Tribenzhydrylphosphonium trifluoromethanesulfonate **1n** (0.516 g, 0.756 mmol, 76%) was obtained as a colourless crystalline solid.

The PH signal in the ^{1}H NMR spectrum (8.82 ppm) appears as a broad doublet of quartets (from coupling to the ^{31}P and benzhydrylic methine protons, respectively), but the resolution is not sufficient to allow accurate measurement of the second coupling constant.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (dm, *J* = 486.8 Hz, 1H) 7.09-7.22 (m, 30H), 5.13 (dd, *J* = 17.4, 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 132.8 (d, *J* = 4.0 Hz), 129.6, 129.1 (d, *J* = 6.9 Hz), 128.5, 121.3 (q, *J* = 320.6 Hz), 46.1 (d, *J* = 34.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -77.89.

^{31}P NMR (162 MHz, $CDCl_3$): δ 20.05 (dq, *J* = 488.9, 17.3 Hz).

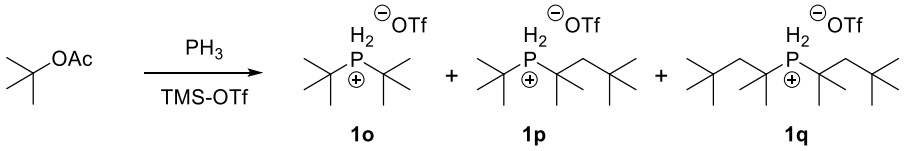
ν_{max}(neat)/cm^{-1}: 3064, 3033, 2910, 2420, 1600, 1586, 1494, 1453, 1255, 1224, 1153, 1029, 929, 744, 693, 637, 572, 511, 475.

HRMS: calcd. for $C_{12}H_{28}P^{+}$: 203.1923 $[M\text{-}OTf]^{+}$; found (ESI^{+}): 203.1920.

m.p./°C: 215-218.

6. Alkylation of PH_3 with *tert*-Butyl Acetate (Manuscript Scheme 4A)

Di-*tert*-butylphosphonium trifluoromethanesulfonate (1o), *tert*-butyl(2,4,4-trimethyl-2-pentyl)phosphonium trifluoromethanesulfonate (1p) and bis-(2,4,4-trimethyl-2-pentyl)phosphonium trifluoromethanesulfonate (1q)



GP2 was performed using *tert*-butyl acetate (0.80 mL, 6.00 mmol). The product distribution was determined by ^{31}P NMR spectroscopic analysis of the reaction mixture (1.0:3.6:5.1 **1o**:**1p**:**1q**) prior to work-up. Work-up as per **GP2** afforded a mixture of **1o**, **1p** and **1q** (0.115 g, 0.32:0.42:0.26 **1o**:**1p**:**1q**) as a colourless crystalline solid. Assignments were confirmed by comparison to literature data (**1o**)[19] or by independent synthesis of pure samples (**1q**, *vide infra*).

Characterisation data for **1o**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (d, *J* = 474.8 Hz, 2H), 1.58 (d, *J* = 18.0 Hz, 18H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 120.6 (q, *J* = 319.9 Hz), 31.3 (d, *J* = 29.5 Hz), 28.0 (d, *J* = 1.8 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ 22.30.

Characterisation data for **1p**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (d, *J* = 472.5 Hz, 2H), 1.84 (d, *J* = 12.6 Hz, 2H), 1.72 (d, *J* = 20.4 Hz, 6H), 1.59 (d, *J* = 17.7 Hz, 9H), 1.10 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 120.6 (q, *J* = 319.9 Hz), 50.3, 37.5 (d, *J* = 31.9 Hz), 34.1 (d, *J* = 12.5 Hz), 32.2 (d, *J* = 32.8 Hz), 31.8, 27.5 (d, *J* = 2.1 Hz), 25.8.

$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ 25.82.

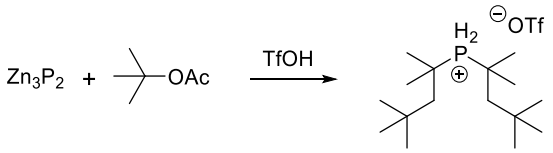
Characterisation data for **1q**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (d, *J* = 470.1 Hz, 2H), 1.86 (d, *J* = 12.0 Hz, 4H), 1.73 (d, *J* = 20.4 Hz, 12H), 1.10 (s, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 120.6 (q, *J* = 319.9 Hz), 50.5, 38.7 (d, *J* = 29.5 Hz), 34.2 (d, *J* = 12.6 Hz), 31.9, 26.2.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 29.56.

Bis-(2,4,4-trimethyl-2-pentyl)phosphonium trifluoromethanesulfonate (1q)



Trifluoromethanesulfonic acid (0.26 mL, 3.00 mmol) was added to a mixture of Zn_3P_2 (0.129 g, 0.39 mmol) and anhydrous, degassed *tert*-butyl acetate (2.5 mL) at r.t. The resulting heavy black suspension was stirred overnight. The mixture was filtered through a plug of cotton wool, eluting with Et_2O, and the resulting biphasic mixture was placed in a freezer at -25 °C overnight. The solids were collected by Büchner filtration, washed with Et_2O and dried under a flow of air to give di-(2,2,4-trimethyl-2-pentyl)phosphonium trifluoromethanesulfonate **1q** (30.4 mg, 74.4 µmol, 9%).

Note that the trifluoromethyl carbon is not observed in the ^{13}C NMR spectrum at this concentration due to low signal:noise, but the presence of the trifluoromethanesulfonate counterion is confirmed by the ^{19}F NMR and IR spectroscopy and IR .

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (d, *J* = 470.2 Hz, 2H), 1.86 (d, *J* = 12.0 Hz, 4H), 1.73 (d, *J* = 20.1 Hz, 12H), 1.10 (s, 18H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 50.7, 38.8 (d, *J* = 29.1 Hz), 34.3 (d, *J* = 12.8 Hz), 32.0, 26.4.

^{19}F NMR (470 MHz, $CDCl_3$): δ -78.31.

^{31}P NMR (202 MHz, $CDCl_3$): δ 29.53 (tm, *J* = 470.0 Hz).

ν_{max}(neat)/cm^{-1}: 2955, 2910, 2875, 2414, 1472, 1399, 1378, 1255, 1223, 1158, 1028, 950, 756, 638, 572, 517.

HRMS: calcd. for $C_{16}H_{36}P^+$: 259.2549 $[M\text{-}OTf]^+$; found (ESI^+): 259.2533.

m.p./°C: 119-121.

7. Isotope Exchange Studies (Manuscript Scheme 4B)

Preparation of 5.0 M DCl in D_2O

Trimethylsilyl chloride (6.35 mL, 50.0 mmol) was added slowly to D_2O (10.0 mL), and the mixture was stirred for 1 h. The resulting biphasic mixture was degassed by sparging with nitrogen, and the aqueous phase was removed by syringe for use in isotope exchange studies.

Reaction of 2-methyl-4-phenylbut-2-yl acetate (*d_0*-2) with PD_3

GP2 was performed using 2-methyl-4-phenylbut-2-yl acetate ***d_0*-2** (0.619 g, 3.00 mmol) and DCl (5.0 M in D_2O). Di-(2-methyl-4-phenylbut-2-yl)phosphonium trifluoromethanesulfonate ***d_n*-1f** (0.245 g) was obtained as a colourless crystalline solid. The isotopic distribution of ***d_n*-1f** prepared in this way was determined by ESI-MS (Figure S2) and ^{1}H NMR spectroscopy (Figure S3).

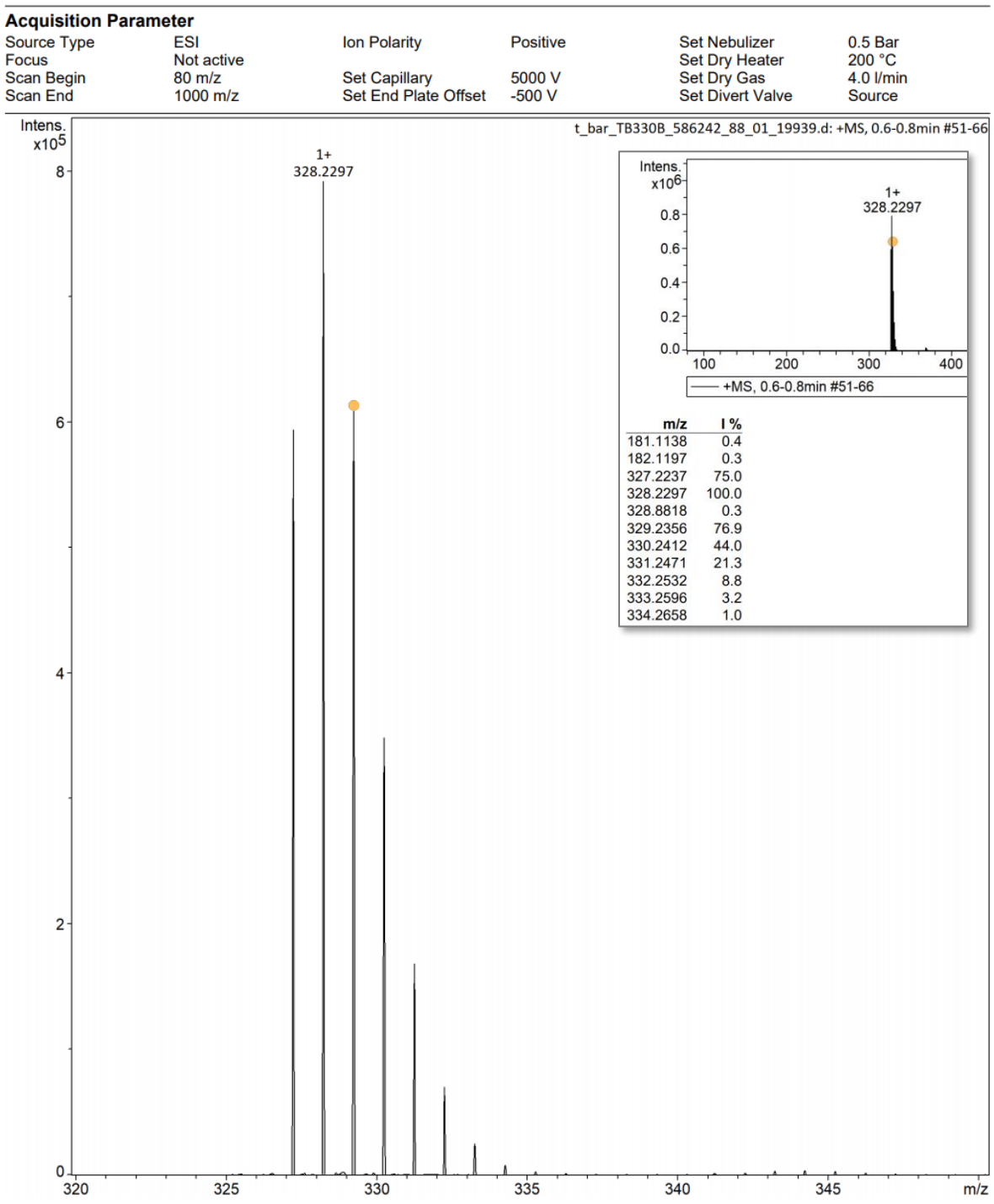


Figure S2. ESI-MS mass distribution for the d_n-**1f** cation prepared from the reaction of d_0-**2** with PD_3.

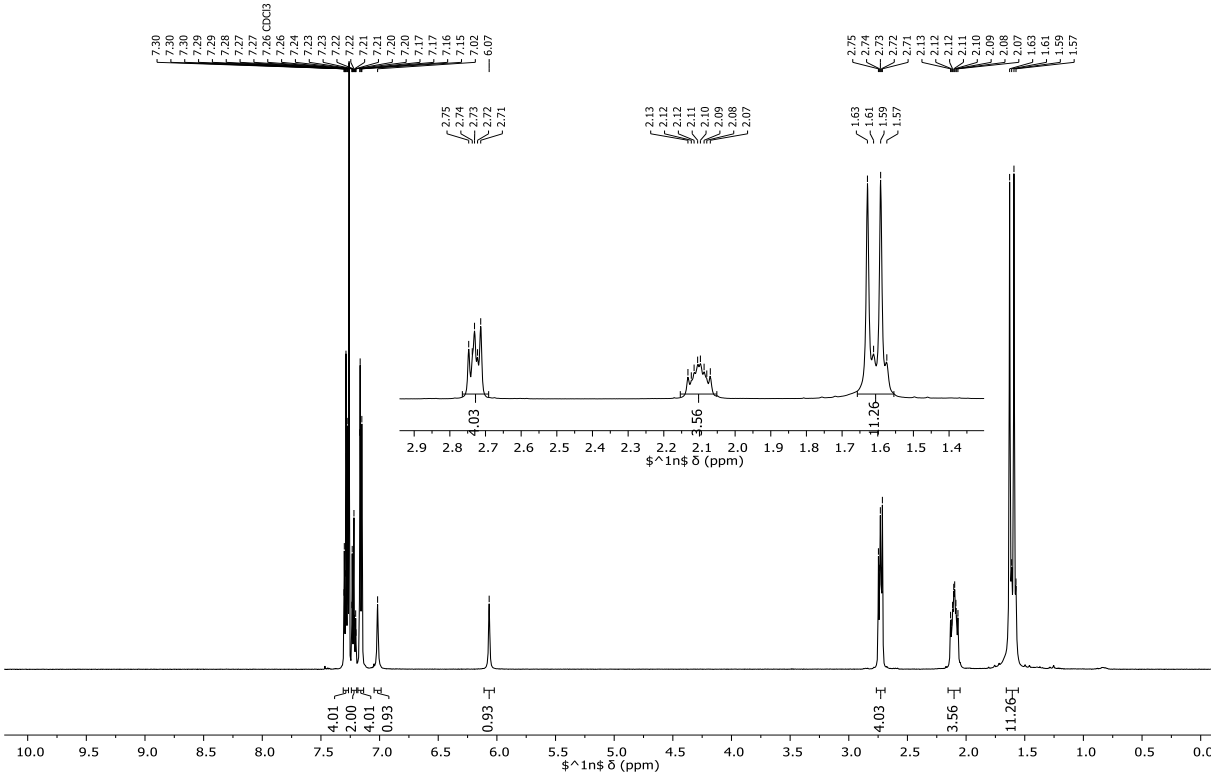


Figure S3. ^{1}H NMR spectrum of $\boldsymbol{d_n}$**-1f** prepared from the reaction of $\boldsymbol{d_0}$**-2** with PD_3.

Reaction of 2-methyl-4-phenylbut-2-yl acetate-d_6 (2-d_6) with PH_3

GP2 was performed using d_6-2-methyl-4-phenylbut-2-yl acetate ***d*$_6$-2** (0.637 g, 3.00 mmol). d_n-Di-(2-methyl-4-phenylbut-2-yl)phosphonium trifluoromethanesulfonate ***d*$_n$-1f** (0.356 g) was obtained as a colourless crystalline solid. The isotopic distribution of ***d*$_n$-1f** prepared in this way was determined by ESI-MS (Figure S4) and ^{1}H NMR spectroscopy (Figure S5).

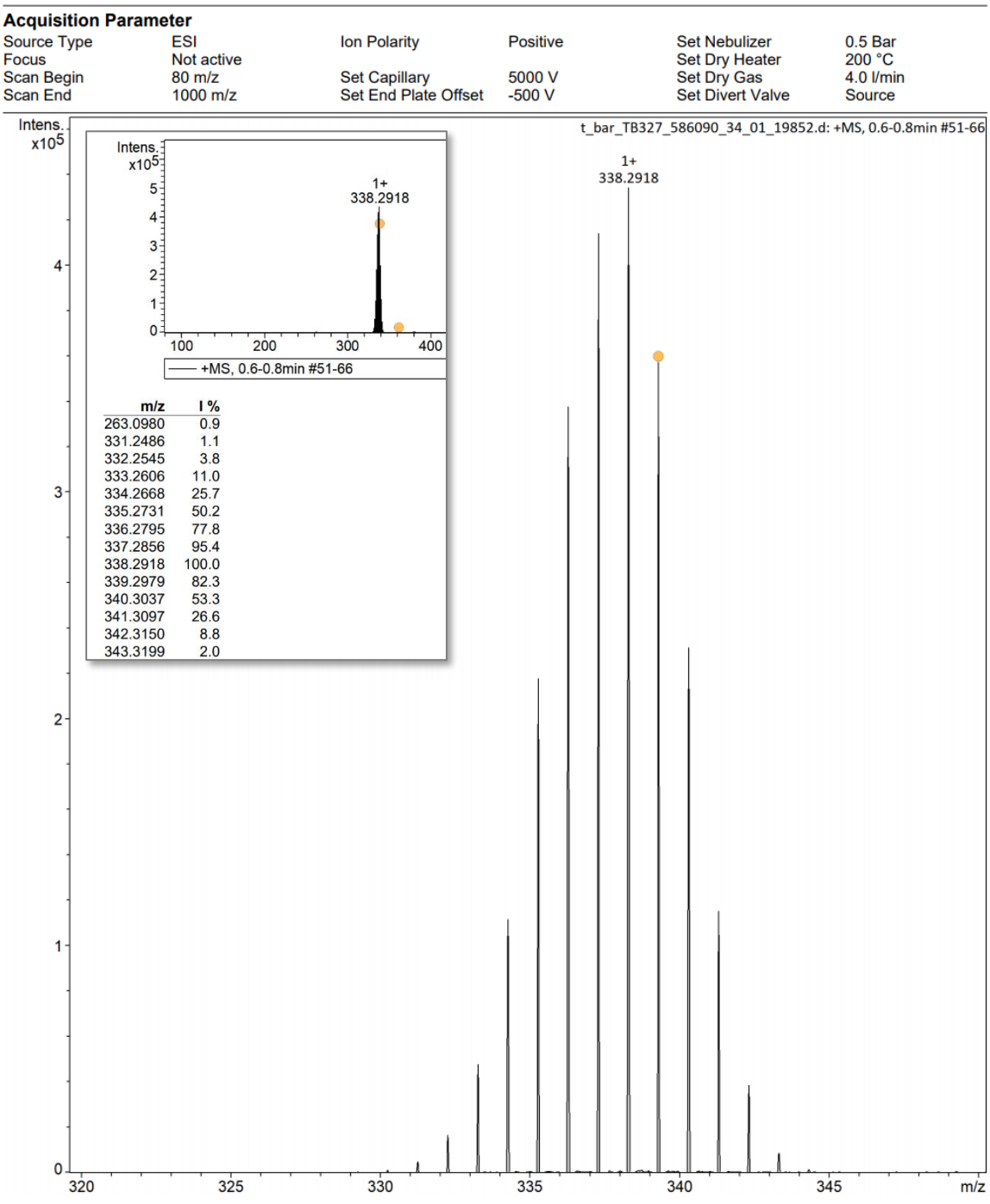


Figure S4. ESI-MS mass distribution for the ***d*$_n$-1f** cation prepared from the reaction of ***d*$_6$-2** with PH_3.

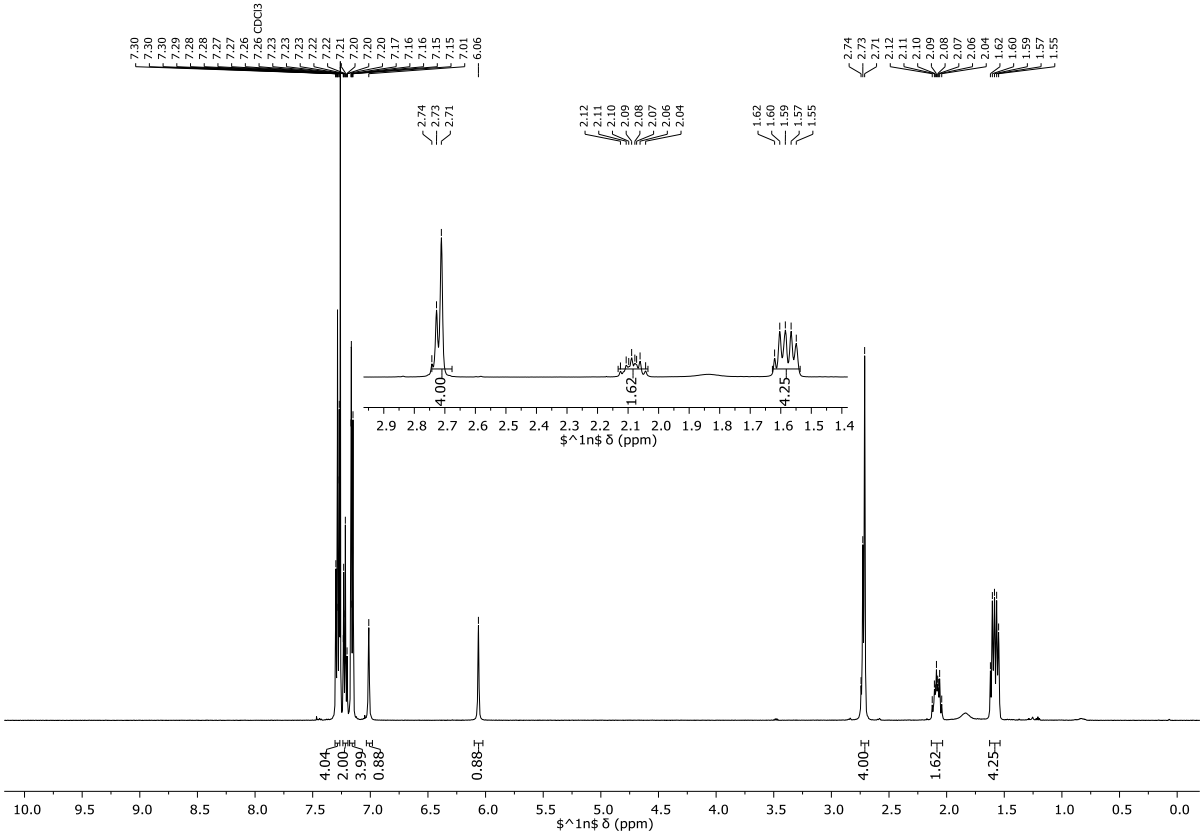


Figure S5. ^{1}H NMR spectrum of $\boldsymbol{d_n}$**-1f** prepared from the reaction of $\boldsymbol{d_6}$**-2** with PH_3.

Reaction of 2-methyl-4-phenylbut-2-yl acetate-d_6 (2-d_6) with PD_3

GP2 was followed, with d_6-2-methyl-4-phenylbut-2-yl acetate **2-d_6** (0.637 g, 3.00 mmol) and DCl (5.0 M in D_2O). d_n-Di-(2-methyl-4-phenylbut-2-yl)phosphonium trifluoromethanesulfonate ***d*$_n$-1f** (0.208 g) was obtained as a colourless crystalline solid. The isotopic distribution of ***d*$_n$-1f** prepared in this way was determined by ESI-MS (Figure S6) and ^{1}H NMR spectroscopy (Figure S7).

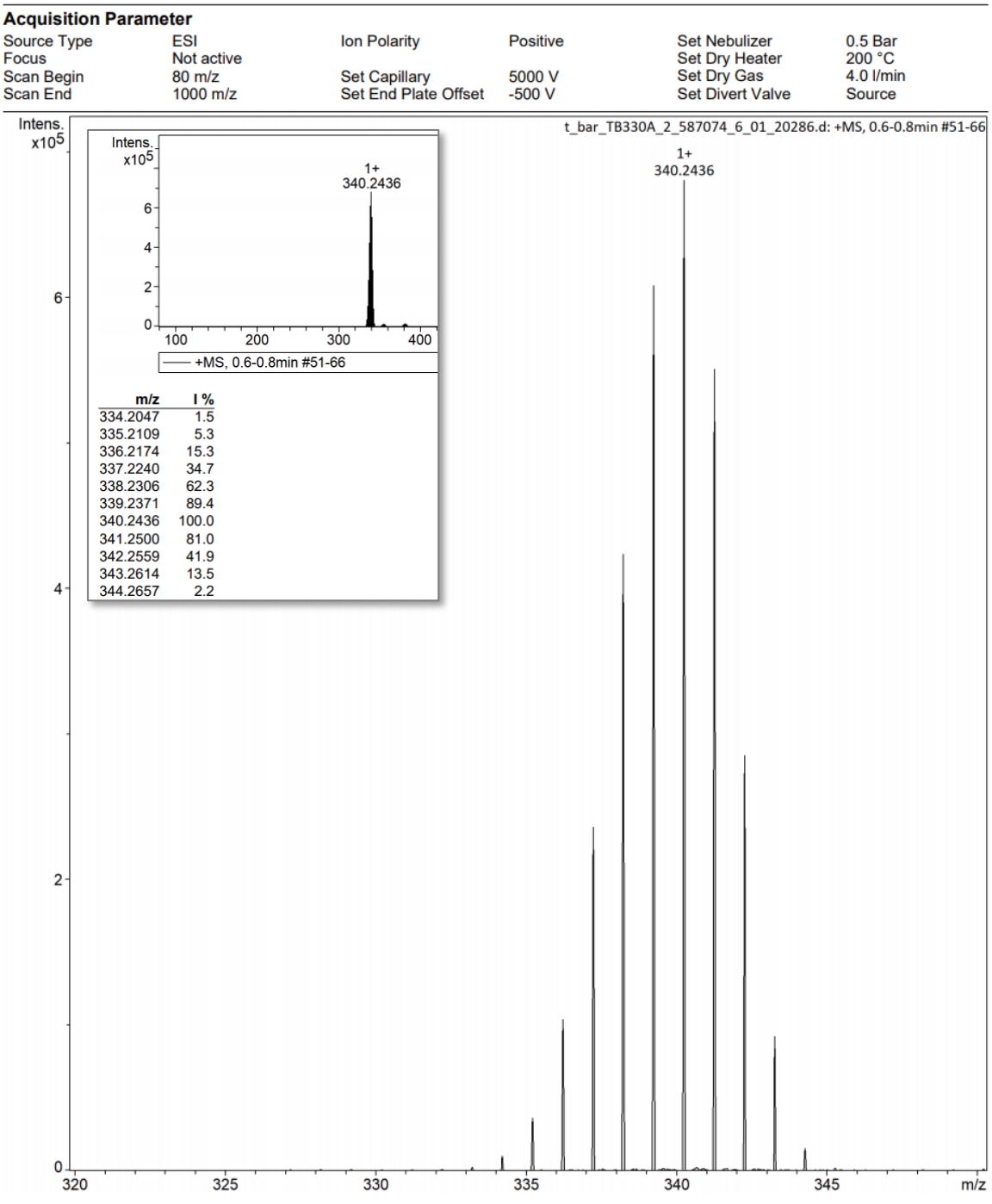


Figure S6. ESI-MS mass distribution for the ***d*$_n$-1f** cation prepared from the reaction of ***d*$_6$-2** with PD_3.

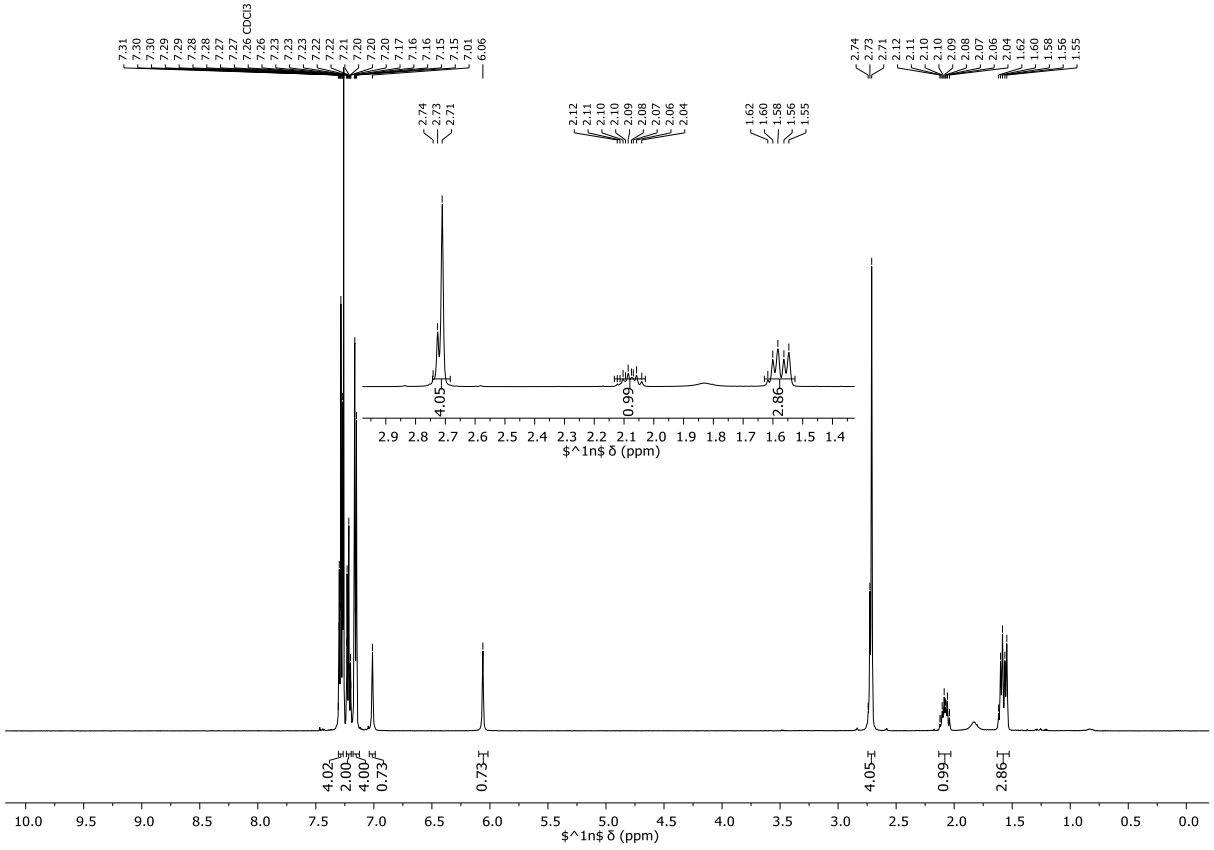
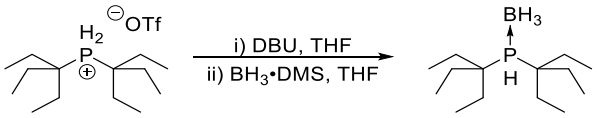


Figure S7. ^{1}H NMR spectrum of $\boldsymbol{d_n}$**-1f** prepared from the reaction of $\boldsymbol{d_6}$**-2** with PD_3.

8. Derivatisation of Di-(3-ethyl-3-pentyl)phosphonium Triflate 1c (Manuscript Scheme 5)

Di-(3-ethyl-3-pentyl)phosphine borane complex



A flame-dried microwave tube containing di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (0.190 g, 0.500 mmol) was evacuated and backfilled with anhydrous dinitrogen (3 ×), then anhydrous degassed THF (2.0 mL) and DBU (83.7 mg, 0.550 mmol) were added. The mixture was stirred at r.t. for 10 minutes before borane dimethylsulfide complex (2.0 M IN THF; 0.50 mL, 1.00 mmol) was added and the mixture was stirred overnight at r.t. The vessel was opened to air, the solvent was removed *in vacuo*, and the resulting crude material was passed through a pad of silica gel (eluent: cyclohexane:Et_2O, 5:1). After concentration *in vacuo*, di-(3-ethyl-3-pentyl)phosphine borane complex (0.118 g, 0.484 mmol, 97%) was obtained as a low-melting colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.41 (dq, *J* = 353.6, 6.9 Hz, 1H), 1.82-1.70 (m, 12H), 0.95 (t, *J* = 7.4 Hz, 18H), 0.90-0.20 (br. m, 3H).

^{11}B NMR (160 MHz, $CDCl_3$): δ -42.5 to -38.5 (m).

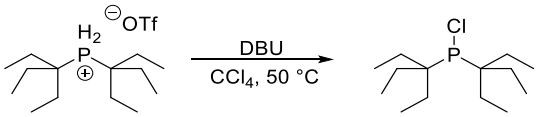
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 42.9 (d, *J* = 20.2 Hz), 28.3 (d, *J* = 1.9 Hz), 8.8 (d, *J* = 5.2 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ 12.66 (dm, *J* = 356.5 Hz).

ν_{max}(neat)/cm^{-1}: 2965, 2939, 2881, 2398, 2368, 1451, 1384, 1330, 1172, 1143, 1064, 1039, 970, 927, 884, 858, 801, 743, 695, 608, 556, 504, 427.

HRMS: calcd. for $C_{14}H_{34}BP+Na^+$: 267.2383 $[M+Na]^+$; found (ESI^+): 267.2381.

Di-(3-ethyl-3-pentyl)chlorophosphine



A flame-dried microwave tube containing di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (0.190 g, 0.500 mmol) was evacuated and backfilled with anhydrous dinitrogen (3 ×), then anhydrous degassed CCl_4 (2.0 mL) and DBU (76.1 mg, 0.500 mmol) were added. The mixture was stirred for 27 h at 50 °C. Stirring was then stopped to allow the biphasic mixture to separate; the lower layer was transferred into a flame-dried Schlenk tube (previously evacuated and backfilled with anhydrous dinitrogen (3 ×)) and the solvent was removed *in vacuo* giving di-(3-ethyl-3-pentyl)chlorophosphine (0.128 g, 0.481 mmol, 96%) as a colourless liquid.

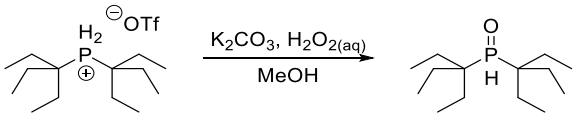
A 13-et is expected in the ^{31}P NMR spectrum, from $^{3}J_{P\text{-}H}$ coupling. This is not observed in full as the lower intensity peaks are not observed due to poor signal:noise and as such is reported below as a multiplet with the coupling constant given.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.84-1.67 (m, 12H), 0.98 (t, *J* = 7.5 Hz, 18H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 46.4 (d, *J* = 51.4 Hz), 27.89 (d, *J* = 15.4 Hz), 9.38 (d, *J* = 10.7 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ 158.34 (m, *J* = 8.9 Hz).

Di-(3-ethyl-3-pentyl)phosphine oxide



A suspension of di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (76.1 mg, 0.200 mmol) and K_2CO_3 (27.6 mg, 0.200 mmol) in methanol (1.0 mL) was stirred for 30 minutes. 30% aqueous H_2O_2 (60 µL, 0.50 mmol) was added and the mixture was stirred for 2 h. A saturated aqueous solution of sodium metabisulfite (0.5 mL) and aqueous hydrochloric acid (1 M; 1.0 mL) were then added. The methanol was removed *in vacuo* and the remaining mixture was extracted with dichloromethane (3 ×). The combined organic portions were concentrated *in vacuo* to give di-(3-ethyl-3-pentyl)phosphine oxide (46.9 mg, 0.190 mmol, 95%) as a colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (d, *J* = 421.4 Hz, 1H), 1.87-1.63 (m, 12H), 1.00 (t, *J* = 7.5 Hz, 18H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 44.5 (d, *J* = 54.8 Hz), 26.0, 8.5 (d, *J* = 6.1 Hz).

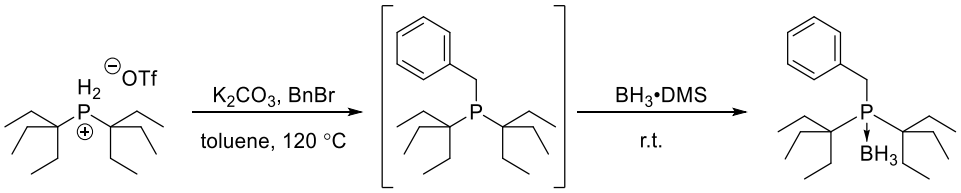
^{31}P NMR (202 MHz, $CDCl_3$): δ 53.88 (dm, *J* = 421.5 Hz).

ν_{max}(neat)/cm^{-1}: 2964, 2940, 2880, 2294, 1460, 1441, 1378, 1333, 1273, 1176, 1158, 1134, 1075, 1033, 997, 983 ,915, 886, 803, 765, 735, 623, 552, 517, 485, 448, 415.

HRMS: calcd. for $C_{14}H_{31}OP+H^+$: 247.2185 $[M+H]^+$; found (ESI^+): 247.2190.

m.p./°C: 34-35.

Di-(3-ethyl-3-pentyl)benzylphosphine borane complex



A flame-dried microwave tube containing di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (0.190 g, 0.500 mmol) and K_2CO_3 (0.207 g, 1.50 mmol) was evacuated and backfilled with dry nitrogen (3 ×) before anhydrous degassed toluene (2.0 mL) and benzyl bromide (85.5 mg, 0.500 mmol) were added. The mixture was stirred overnight at 120 °C, then allowed to cool without stirring so that the suspended solids settled. The supernatant was then transferred to a second flame-dried microwave tube containing borane dimethylsulfide complex (2.0 M in THF; 0.50 mL, 1.00 mmol). Anhydrous degassed toluene (2.0 mL) was added to the solid residue in the first tube, the suspension was stirred and allowed to settle, and the supernatant transferred to the microwave tube containing borane dimethylsulfide complex; this process was repeated a further two times. The mixture containing borane dimethylsulfide was stirred at r.t. for 2 h. The vessel was then opened to air, solvent was removed *in vacuo*, and the resulting crude material was passed through a pad of silica gel (eluent: cyclohexane:Et_2O, 5:1). Removal of solvent *in vacuo* afforded di-(3-ethyl-3-pentyl)benzylphosphine borane complex (0.143 g, 0.426 mmol, 85%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.45 (m, 2H), 7.27-7.15 (m, 3H), 3.31 (d, *J* = 11.8 Hz, 2H), 1.93-1.82 (m, 12H), 1.03-0.17 (m, 21H, including t, *J* = 7.5 Hz)

^{11}B NMR (128 MHz, $CDCl_3$): δ -39.5 to -34.5 (m).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 135.7 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 3.9 Hz), 127.9 (d, *J* = 1.8 Hz), 126.5 (d, *J* = 2.2 Hz), 44.3 (d, *J* = 17.1 Hz), 29.7 (d, *J* = 21.0 Hz), 27.4 (d, *J* = 1.7 Hz), 10.2 (d, *J* = 5.6 Hz).

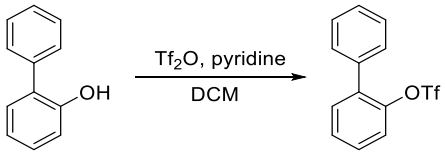
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): 53.31 (m).

ν_{max}(neat)/cm^{-1}: 2969, 2940, 2881, 2399, 2302, 1601, 1496, 1454, 1382, 1339, 1156, 1064, 1032, 914, 819, 769, 699, 601, 559, 470, 435.

HRMS: calcd. for $C_{21}H_{40}BP+Na^+$: 357.2853 $[M+Na]^+$; found (ESI^+): 357.2852.

9. Synthesis and Characterisation of Di-*tert*-alkylbiarylphosphines 3 (Manuscript Scheme 6)

2-Biphenyl trifluoromethanesulfonate [20]



A flame-dried Schlenk tube containing 2-phenylphenol (8.51 g, 50.0 mmol) was evacuated and backfilled with anhydrous dinitrogen (3 ×), then anhydrous degassed dichloromethane (50 mL) and pyridine (4.83 mL, 60.0 mmol) were added. The resulting solution was cooled to 0°C and trifluoromethanesulfonic anhydride (10.1 mL, 50.0 mmol) was added slowly. The mixture was stirred at r.t. for 2 h, then passed through a pad of silica gel (eluent: dichloromethane). The solvent was removed *in vacuo* and the resulting crude material was passed through another pad of silica gel (eluent: 19:1 petroleum ether : Et_2O). Concentration *in vacuo* afforded 2-biphenyl trifluoromethanesulfonate (15.1 g, 50.0 mmol, >99%) as a colourless liquid. This material was used without further purification.

Characterisation data were consistent with literature values: ^{1}H,[20] $^{13}C\{^{1}H\}$,[20] and ^{19}F[20] NMR.

^{1}H NMR (500 MHz, $CDCl_3$): 7.51-7.39 (m, 9H).

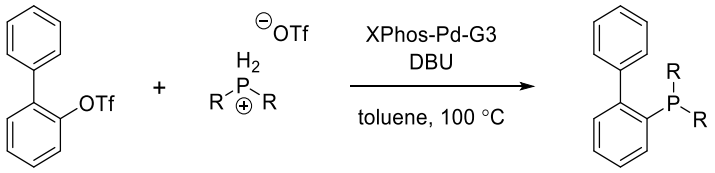
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 147.0, 135.7, 132.1, 129.5, 129.1, 128.7, 128.6, 128.5, 122.2, 118.5 (q, *J* = 320.6 Hz).

^{19}F NMR (470 MHz, $CDCl_3$): δ -74.08.

ν_{max}(neat)/cm^{-1}: 3066, 1477, 1419, 1246, 1203, 1135, 1099, 1046, 1011, 881, 783, 764, 751, 731, 698, 625, 593, 570, 503, 462.

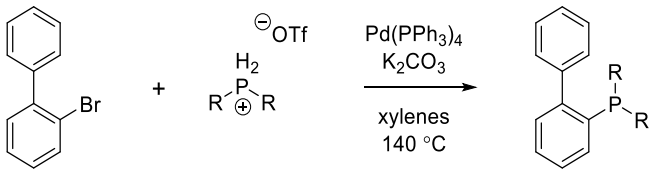
HRMS: calcd. for $C_{13}H_9F_3O_3S+Na^+$: 325.0117 $[M+Na]^+$; found (ESI^+): 325.0118.

General procedure for P-C cross couplings with 2-biphenyl triflate (GP3)



A microwave tube containing XPhosPdG3[21] (8.5 mg, 10 µmol, 2 mol%) and di-*tert*-alkylphosphonium trifluoromethanesulfonate **1** (0.500 mmol) was evacuated and backfilled with anhydrous dinitrogen (3 ×), then degassed toluene (2.50 mL), 2-biphenyl trifluoromethanesulfonate (151 mg, 0.500 mmol), and DBU (0.224 mL, 1.50 mmol) were added. The mixture was stirred at 100 °C for 16 h, then allowed to cool to r.t. The reaction was diluted with Et_2O and washed with water. The aqueous portion was extracted with Et_2O (2 ×), and the combined organic portions were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Recrystallisation from methanol afforded the pure dialkylbiarylphosphine **3**.

General procedure for P-C cross couplings with 2-biphenyl bromide (GP4)

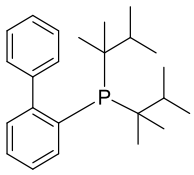


A microwave tube containing $Pd(PPh_3)_4$ (3 mol%), di-*tert*-alkylphosphonium trifluoromethanesulfonate **1** (1.00 equiv.) and K_2CO_3 (3.00 equiv.) was evacuated and backfilled with anhydrous dinitrogen (3 ×), then degassed xylenes (to give $[\mathbf{1}]_0$ = 0.4-0.5 M) and 2-biphenyl bromide (1.20 equiv.) were added. The mixture was stirred at 140 °C for 16 h, then allowed to cool to r.t. The reaction was diluted with Et_2O and washed with water. The aqueous portion was extracted with Et_2O (2 ×), and the combined organic portions were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Recrystallisation from methanol or acetone afforded the pure dialkylbiarylphosphine **3**.

Note: di-*tert*-alkylbiarylphosphines **3** obtained by **GP3** or **GP4** that could not be isolated by recrystallisation were employed directly in the synthesis of the corresponding di-*tert*-

alkylbiarylphosphine selenides **4** and di-*tert*-alkylbiarylphosphine gold(I) chloride complexes **5**. Details of these procedures are provided in Sections S10 and S11, below.

2-(Bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl (3d)



GP3 was performed using bis-(2,3-dimethyl-2-butyl)phosphonium trifluoromethanesulfonate **1d** (0.138 g, 0.500 mmol). 2-(Bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl **3d** (0.098 g, 0.276 mmol, 55%) was isolated as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.34-7.26 (m, 7H), 1.66 (app. dq, *J* = 13.4, 6.9 Hz, 2H), 1.25 (d, *J* = 8.1 Hz, 6H), 0.92 (d, *J* = 8.2 Hz, 6H), 0.84 (d, *J* = 6.8 Hz, 6H), 0.73 (d, *J* = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.9 (d, *J* = 34.5 Hz), 144.0 (d, *J* = 7.2 Hz), 136.6 (d, *J* = 1.7 Hz), 135.7 (d, *J* = 32.3 Hz), 131.0 (d, *J* = 4.1 Hz), 130.7 (d, *J* = 6.5 Hz), 128.4, 127.0, 126.2, 125.7, 39.8 (d, *J* = 31.0 Hz), 35.8 (d, *J* = 22.2 Hz), 23.6 (d, *J* = 9.5 Hz), 23.2 (d, *J* = 6.8 Hz), 18.1 (d, *J* = 12.8 Hz), 17.8 (d, *J* = 14.8 Hz).

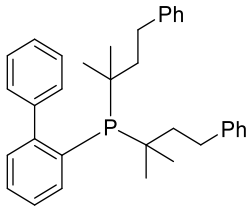
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.14 (s).

ν_{max}(neat)/cm^{-1}: 3051 ,2974, 2958, 2898, 2867, 1463, 1442, 1375 ,1160 ,1122 ,1079, 1050, 1008, 995, 909, 870, 778, 746, 695, 616, 555, 514, 476.

HRMS: calcd. for $C_{24}H_{35}P+H^+$: 355.2549 $[M+H]^+$; found (ESI^+): 355.2544.

m.p./°C: 64-66.

2-(Di-(2-methyl-4-phenyl-2-butyl)phosphino)biphenyl (3f)



GP3 was performed using di-(2-methyl-4-phenyl-2-butyl)phosphonium trifluoromethanesulfonate **1f** (0.238 g, 0.500 mmol). 2-(Di-(2-methyl4-phenyl-2-butyl)phosphino)biphenyl **3f** (0.162 g, 0.338 mmol, 68%) was isolated as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.34 (td, *J* = 7.5, 1.6 Hz, 1H), 7.28-7.21 (m, 10H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.06-7.02 (m, 4H), 2.69-2.62 (m, 2H), 2.57-2.49 (m, 2H), 1.80-1.70 (m, 4H), 1.34 (d, *J* = 10.1 Hz, 6H), 1.16 (d, *J* = 10.3 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.6 (d, *J* = 33.2 Hz), 143.7 (d, *J* = 7.1 Hz), 143.3, 136.9 (d, *J* = 2.5 Hz), 134.7 (d, *J* = 29.2 Hz), 131.0 (d, *J* = 6.4 Hz), 130.8 (d, *J* = 4.1 Hz), 128.7, 128.5, 128.4, 127.2, 126.5, 126.0, 125.6, 45.2 (d, *J* = 20.0 Hz), 36.6 (d, *J* = 28.6 Hz), 30.3 (d, *J* = 13.9 Hz), 27.5 (d, *J* = 11.1 Hz), 27.4 (d, *J* = 12.3 Hz).

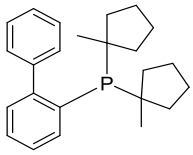
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 13.81 (s).

ν_{max}(neat)/cm^{-1}: 3082, 3057, 3020, 2959, 2939, 2860, 1600, 1582, 1495, 1453, 380, 1362, 1176, 1129, 1069, 1030, 1008, 908, 840, 745, 696, 600, 577, 508, 492, 460.

HRMS: calcd. for $C_{34}H_{39}P+H^+$: 479.2862 $[M+H]^+$; found (ESI^+): 479.2874.

m.p./°C: 85-86.

2-(Di-(1-methylcyclopentyl)phosphino)biphenyl (3h)



GP3 was performed using di-(1-methylcyclopentyl)phosphonium trifluoromethanesulfonate **1h** (0.174 g, 0.500 mmol). 2-(Di-(1-methylcyclopentyl)phosphino)biphenyl **3h** (0.115 g, 0.328 mmol, 66%) was isolated as an off-white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.27-7.38 (m, 7H), 7.23-7.26 (ddd, *J* = 7.4, 4.0, 1.7 Hz, 1H), 1.76-1.86 (m, 2H), 1.42-1.69 (m, 12H), 1.31-1.37 (m, 2H), 1.22 (d, *J* = 8.3 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.9 (d, *J* = 31.3 Hz), 143.9 (d, *J* = 5.9 Hz), 136.4 (d, *J* = 28.1 Hz), 135.7 (d, *J* = 3.2 Hz), 130.9 (d, *J* = 3.2 Hz), 130.8 (d, *J* = 5.9 Hz), 128.3, 127.3, 126.5, 125.9, 42.3 (d, *J* = 23.7 Hz), 40.6 (d, *J* = 24.4 Hz), 40.0 (d, *J* = 17.1 Hz), 25.9 (d, *J* = 7.3 Hz), 24.4 (d, *J* = 8.2 Hz), 23.7 (d, *J* = 7.5 Hz).

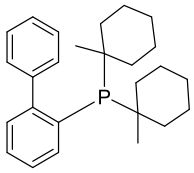
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 18.31 (s).

ν_{max}(neat)/cm^{-1}: 3050, 2954, 2864, 1443, 1376, 1315, 1241, 1216, 1073, 1007, 910, 829, 775, 743, 701, 617, 505, 473.

HRMS: calcd. for $C_{24}H_{31}P+H^+$: 351.2236 $[M+H]^+$; found (ESI^+): 351.2242.

m.p./°C: 79-81.

2-(Di-(1-methylcyclohexyl)phosphino)biphenyl (3i)



GP3 was performed using di-(1-methylcyclohexyl)phosphonium trifluoromethanesulfonate **1i** (0.188 g, 0.500 mmol). 2-(Di-(1-methylcyclohexyl)phosphino)biphenyl **3i** (0.114 g, 0.301 mmol, 60%) was isolated as an off-white crystalline solid. The product could not be separated from 2% residual XPhos (δ_P -12.31 ppm).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.38-7.23 (m, 8H), 1.80-1.72 (m, 2H), 1.66-1.60 (m, 2H), 1.52-1.41 (m, 8H), 1.36-1.29 (m, 6H), 1.26 (d, *J* = 8.8 Hz, 6H), 1.18-1.10 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.8 (d, *J* = 32.6 Hz), 144.1 (d, *J* = 6.7 Hz), 136.8 (d, *J* = 2.4 Hz), 134.5 (d, *J* = 31.0 Hz), 130.9 (d, *J* = 3.9 Hz), 130.8 (d, *J* = 6.1 Hz), 128.3, 127.2, 126.4, 125.5, 37.8 (d, *J* = 18.3 Hz), 37.6, 37.5, 37.4, 26.3, 22.7 (d, *J* = 7.9 Hz), 21.6 (d, *J* = 10.7 Hz).

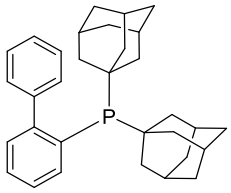
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 25.16 (br. s.).

ν_{max}(neat)/cm^{-1}: 3054, 2916, 2847, 2665, 1442, 1377, 1339, 1284, 1162 ,1123, 1073, 963, 926, 850, 772 ,744, 698, 615, 523, 490 ,461.

HRMS: calcd. for $C_{26}H_{35}P+H^+$: 379.2549 $[M+H]^+$; found (ESI^+): 379.2549.

m.p./°C: 77-79.

2-(Di-(1-adamantyl)phosphino)biphenyl (3k)



GP3 was performed using di-(1-adamantyl)phosphonium trifluoromethanesulfonate **1k** (0.226 g, 0.500 mmol). 2-(Di-(1-adamantyl)phosphino)biphenyl **3k** (0.161 g, 0.354 mmol, 71%) was isolated as an off-white crystalline solid.

Characterisation data were consistent with literature values: ^{1}H,[22] ^{13}C{^{1}H},[22] ^{31}P{^{1}H}[22] NMR, IR.[22]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.40-7.29 (m, 5H), 7.28-7.22 (m, 3H), 1.93-1.82 (m, 18H), 1.68-1.63 (m, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 152.0 (d, *J* = 32.7 Hz), 144.1 (d, *J* = 7.2 Hz), 136.8 (d, *J* = 2.8 Hz), 133.2 (d, *J* = 27.7 Hz), 130.8 (d, *J* = 6.2 Hz), 130.8 (d, *J* = 3.8 Hz), 128.3, 127.2, 126.4, 125.5, 42.0 (d, *J* = 13.0 Hz), 37.5 (d, *J* = 25.6 Hz), 37.1, 29.0 (d, *J* = 8.5 Hz).

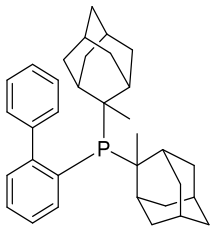
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 21.10 (s).

ν_{max}(neat)/cm^{-1}: 2897, 2844, 2675, 1444, 1342, 1301, 1252, 1101, 1071, 1047, 1008, 970, 825, 770, 744, 696, 552, 504, 471, 426.

HRMS: calcd. for $C_{34}H_{39}P+H^+$: 455.2862 $[M+H]^+$; found (ESI^+): 455.2865.

m.p./°C: 218-223, lit.[22] 222-224.

2-(Di-(2-methyl-2-adamantyl)phosphino)biphenyl (3l)



GP4 was performed using $Pd(PPh_3)_4$ (6.9 mg, 6.0 µmol), di-(2-methyl-2-adamantyl)phosphonium trifluoromethanesulfonate **1l** (96.1 mg, 0.200 mmol), 2-bromobiphenyl (45 µL, 0.240 mmol), K_2CO_3 (82.9 mg, 0.600 mmol) and degassed xylenes (0.5 mL). 2-(Di-(2-methyladamant-2-yl)phosphino)biphenyl **3l** (56.3 mg, 0.117 mmol, 58%) was obtained as an off-white solid after recrystallisation from methanol.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.44-7.18 (m, 8H), 2.83 (d, *J* = 12.4 Hz, 2H), 2.26-2.06 (m, 6H), 1.85-1.71 (m, 6H), 1.66-1.50 (m, 12H), 1.49-1.41 (m, 4H), 1.30 (dt, *J* = 13.1, 2.8 Hz, 2H), 1.00 (dt, *J* = 12.6, 2.9 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 151.1 (d, *J* = 34.2 Hz), 144.1 (d, *J* = 5.3 Hz), 138.0, 134.2 (d, *J* = 38.3 Hz), 131.6 (d, *J* = 6.7 Hz), 131.5 (d, *J* = 3.2 Hz), 128.2, 127.5, 126.3, 125.3, 45.1 (d, *J* = 36.3 Hz), 40.1 (d, *J* = 3.2 Hz), 36.4 (d, *J* = 16.0 Hz), 35.9 (d, *J* = 9.5 Hz), 34.5 (d, *J* = 17.9 Hz), 33.6 (d, *J* = 15.0 Hz), 32.8 (d, *J* = 5.4 Hz), 32.5 (d, *J* = 4.0 Hz), 28.3 (d, *J* = 1.4 Hz), 27.6, 22.5.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -0.09 (s).

ν_{max}(neat)/cm^{-1}: 2896, 2844, 2663, 1441, 1380, 1351, 1304, 1221, 1098, 1072, 1021, 956, 868, 774, 744, 696, 615, 552, 486, 465, 450.

HRMS: calcd. for $C_{34}H_{43}P+H^+$: 483.3175 $[M+H]^+$; found (ESI^+): 483.3180.

m.p./°C: 169-171.

tert-Alkyl Group Contributions to ^{31}P NMR Chemical Shifts

Group contributions of individual *tert*-alkyl substituents to ^{31}P NMR chemical shifts were calculated according to the method of Grim *et al.*[23] The excellent correlation observed between the calculated group contributions and the observed chemical shifts of JohnPhos analogues **3** does not hold for phosphines featuring two substituents at the C_β-position (Figure S8).

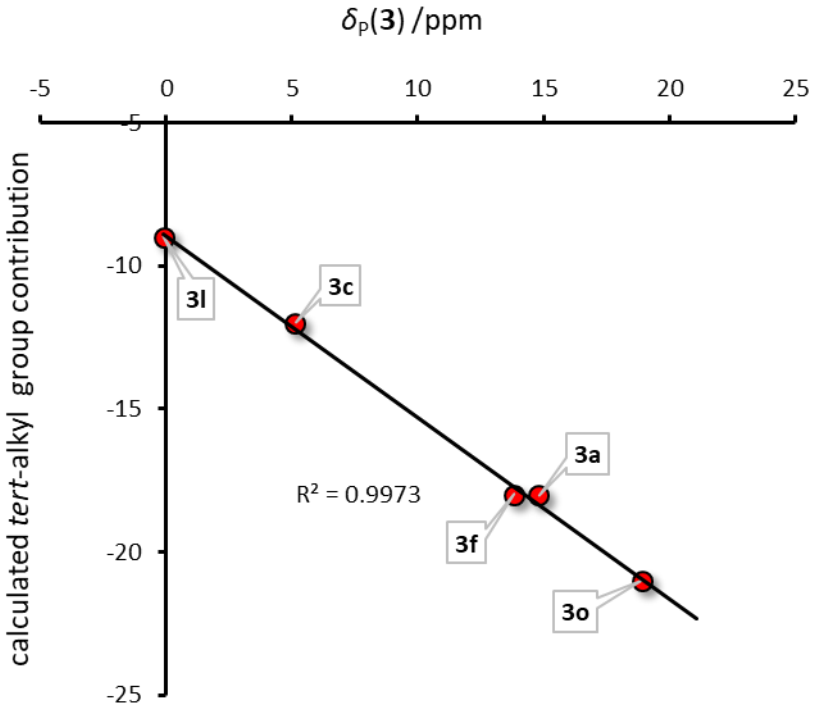
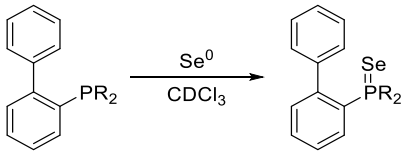


Figure S8. Correlation of calculated *tert*-alkyl group contributions *vs* observed ^{31}P NMR chemical shifts (/ppm) of JohnPhos analogues **3**.

10. Synthesis of Di-*tert*-alkylbiarylphosphine Selenides 4

(Manuscript Scheme 6)

General procedure for the synthesis of di-*tert*-alkylbiarylphosphine selenides (4) (GP5)



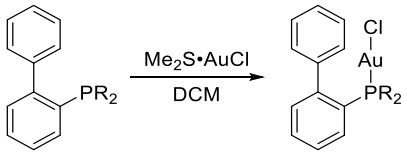
Di-*tert*-alkylbiarylphosphine **3** (*ca* 7 mg pure, or *ca* 2 mg of crude material from the examples where pure material was not obtained, *vide supra*) and selenium powder (20 mg, excess) were added to an NMR tube, which was evacuated and filled with anhydrous dinitrogen (3 ×). Anhydrous degassed $CDCl_3$ (0.60 mL) was added, and the tube was capped under a flow of anhydrous dinitrogen. After sealing with PTFE tape, the mixture was heated to 100 °C overnight. The tube was cooled to r.t., the solids were allowed to settle and a $^{31}P\{^1H\}$ NMR spectrum was recorded. The resulting ^{31}P NMR chemical shifts and $^1J_{P\text{-}Se}$ coupling constants below were measured from these spectra are listed in Table S1.

entry	R	δ_P / ppm	$^1J_{P\text{-}Se}$ /Hz
1	*tert*-amyl **4a**	76.71	732.7
2	3-methyl-3-pentyl **4b**	15.12	708.1
3	3-ethyl-3-pentyl **4c**	11.34	704.0
4	2,3-dimethylbut-2-yl **4d**	15.69	708.2
5	2-methyl-4-phenylbut-2-yl **4f**	73.35	738.8
6	1-methylcyclopentyl **4h**	74.69	723.0
7	1-methylcyclohexyl **4i**	80.39	729.3
8	1-adamantyl **4k**	69.99	726.0
9	2-methyladamant-2-yl **4l**	4.49	702.2

Table S1. ^{31}P NMR chemical shifts (/ppm) and $^1J_{P\text{-}Se}$ coupling constants (/Hz) of di-*tert*-alkylbiarylphosphine selenides **4**, measured as dilute solutions in $CDCl_3$ at 298 K.

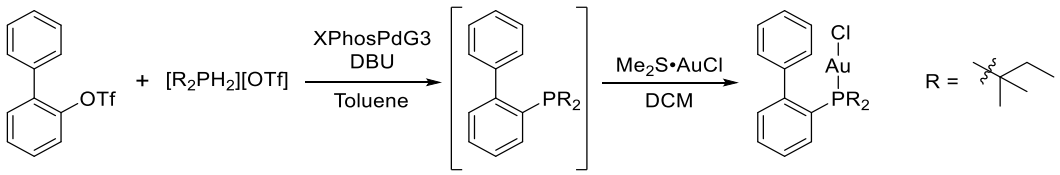
11. Synthesis and Characterisation of Di-*tert*-alkylbiarylphosphine Gold(I) Chloride Complexes 5 (Manuscript Scheme 6)

General procedure for the synthesis of di-*tert*-alkylbiarylphosphinegold(I) chloride complexes (5) (GP6)



Dichloromethane ($[\mathbf{3}]_0$ = 0.1 M) was added to a vial containing di-*tert*-alkylbiarylphosphine **3** (50.0 µmol pure isolated material, or 0.50 mmol crude material from the examples where pure di-*tert*-alkylbiarylphosphine **3** was not obtained (*vide infra*)) and dimethylsulfide gold(I) chloride complex (1 equiv.). The mixture was stirred at r.t. for 1 h then concentrated *in vacuo*. The residue was triturated with pentane and the resulting solid was collected by Büchner filtration; where necessary, the products were further purified by passage through a pad of silica gel or Celite® (eluent: dichloromethane). The di-*tert*-alkylbiarylphosphinegold(I) chloride complexes **5** were obtained as off-white solids.

[(2-Biphenyl)di-*tert*-amylphosphine]gold(I) chloride (5a)



GP3 was performed using di-*tert*-amylphosphonium trifluoromethanesulfonate **1a** (0.138 g, 0.500 mmol). Crude 2-(di-*tert*-amylphosphino)biphenyl **3a** was obtained as a viscous yellow liquid [**^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$):** δ 14.83]. *ca* 2 mg were removed for the synthesis of the selenide **4a** (**GP5**, Section S10) and the remainder was subjected to **GP6**. [(2-Biphenyl)di-*tert*-amylphosphine]gold(I) chloride **5a** (0.146 g, 0.262 mmol, 52%) was obtained as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (td, *J* = 7.4, 1.6 Hz, 1H), 7.59-7.55 (m, 1H), 7.53-7.45 (m, 2H), 7.44-7.40 (m, 2H), 7.29 (ddd, *J* = 7.5, 4.3, 1.8 Hz, 1H), 7.14-7.10 (m, 2H), 1.86 (dt, *J* = 13.3, 7.5 Hz, 2H) 1.78 (dt, *J* = 13.5, 7.6 Hz, 2H), 1.41 (d, *J* = 16.8 Hz, 6H), 1.36 (d, *J* = 15.5 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.5 (d, *J* = 13.1 Hz), 142.4 (d, *J* = 6.5 Hz), 134.1 (d, *J* = 2.7 Hz), 133.5 (d, *J* = 7.3 Hz), 130.6 (d, *J* = 2.3 Hz), 129.3, 128.8, 128.4, 126.7 (d, *J* = 6.8 Hz), 126.0 (d, *J* = 43.4 Hz), 41.8 (d, *J* = 25.3 Hz), 34.4 (d, *J* = 8.2 Hz), 26.5 (d, *J* = 6.5 Hz), 25.5 (d, *J* = 4.0 Hz), 7.6 (d, *J* = 11.8 Hz).

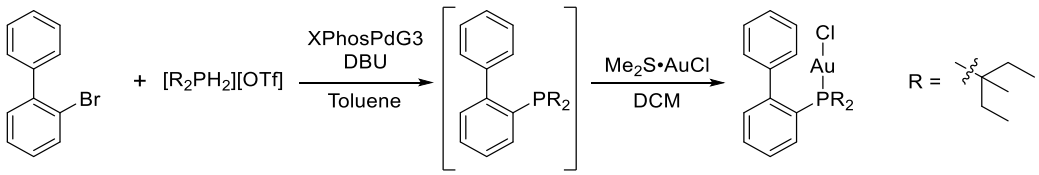
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 65.35 (s).

ν_{max}(neat)/cm^{-1}: 3048, 2964, 2920, 2876, 1462, 1437, 1421, 1411, 1386, 1364, 1140, 1031, 993, 953, 910, 773, 753, 699, 676, 635, 617, 534, 508, 484.

HRMS: calcd. for $C_{22}H_{31}AuClP+Na^+$: 581.1410 $[M+Na]^+$; found (ESI^+): 581.1404, calcd. for $C_{22}H_{31}AuClP+NH_4^+$: 576.1856 $[M+NH_4]^+$; found (ESI^+): 576.1852.

m.p./°C: decomposes *ca* 120 °C.

[(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine]gold(I) chloride (5b)



GP4 was performed using di-(3-methyl-3-pentyl)phosphonium trifluoromethanesulfonate (0.176 g, 0.500 mmol), 2-bromobiphenyl (104 µL, 0.600 mmol), K_2CO_3 (207 mg, 1.50 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 15.0 µmol, 3 mol%) in degassed xylenes (1.0 mL). Crude 2-(di-3-methyl-3-pentylphosphino)biphenyl **3b** was obtained as a viscous yellow liquid [**$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$):** δ 0.05]. *ca* 2 mg were removed for the synthesis of the selenide **4b** (**GP5**, Section S10) and the remainder was subjected to **GP6**. [(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine]gold(I) chloride **5b** (0.257 g, 0.437 mmol, 87%) was obtained as an off-white solid.

Note: the signal in the ^1H NMR spectrum at 7.88-7.92 ppm appears as a poorly resolved td (*cf*. other Au complexes), the resolution is not sufficient to assign coupling constants.

^1H NMR (500 MHz, $CDCl_3$): δ 7.92-7.88 (m, 1H), 7.58-7.54 (m, 1H), 7.52-7.44 (m, 2H), 7.44-7.39 (m, 2H), 7.28 (ddd, *J* = 7.7, 4.4, 1.8 Hz, 1H), 7.17-7.14 (m, 2H), 2.17 (ddq, *J* = 14.8, 11.1, 7.4 Hz, 2H), 1.87-1.73 (m, 4H), 1.72-1.61 (m, 2H), 1.48 (d, *J* = 14.4 Hz, 6H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 150.0 (d, *J* = 13.4 Hz), 142.5 (d, *J* = 6.2 Hz), 135.1 (d, *J* = 2.7 Hz), 134.0 (d, *J* = 7.5 Hz), 130.5 (d, *J* = 2.6 Hz), 129.3, 128.7, 128.4, 126.6 (d, *J* = 41.0 Hz), 126.5 (d, *J* = 6.7 Hz), 45.5 (d, *J* = 23.6), 32.8 (d, *J* = 10.3 Hz), 31.3 (d, *J* = 5.2 Hz), 24.1 (d, *J* = 1.9 Hz), 9.5 (d, *J* = 10.4 Hz), 9.3 (d, *J* = 8.7 Hz).

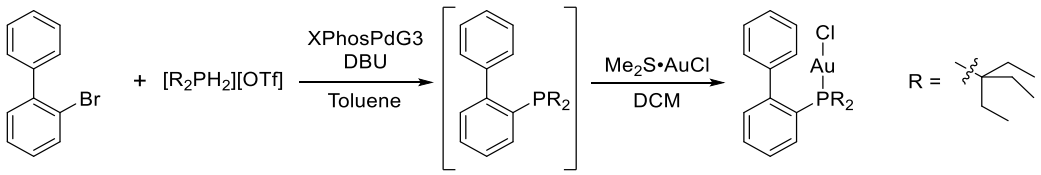
$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 58.34 (s).

ν_{max}(neat)/cm^{-1}: 2967, 2936, 2876, 1460, 1441, 1384, 1121, 1062, 1033, 1006, 779, 750, 698, 615, 532, 506, 495, 457.

HRMS: calcd. for $C_{24}H_{35}AuClP+Na^+$: 609.1723 $[M+Na]^+$; found (ESI^+): 609.1718, calcd. for $C_{24}H_{35}AuClP+NH_4^+$: 604.2169 $[M+NH_4]^+$; found (ESI^+): 604.2162.

m.p./°C: decomposes *ca* 130°C.

[(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine]gold(I) chloride (5c)



GP4 was performed using di-(3-ethyl-3-pentyl)phosphonium trifluoromethanesulfonate **1c** (0.190 g, 0.500 mmol), 2-bromobiphenyl (104 µL, 0.600 mmol), K_2CO_3 (207 mg, 1.50 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 15.0 µmol, 3 mol%) in degassed xylenes (1.0 mL). Crude 2-(di-3-ethyl-3-pentylphosphino)biphenyl was obtained as a viscous yellow liquid [**$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$):** δ 5.16]. *ca* 2 mg were removed for the synthesis of the selenide **4c** (**GP5**, Section S10) and the remainder was subjected to **GP6**. [(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine]gold(I) chloride **5c** (0.166 g, 0.270 mmol, 54%) was obtained as an off-white solid.

^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (app. t, *J* = 7.6 Hz, 1H), 7.56 (app. t, *J* = 7.6 Hz, 1H), 7.51-7.38 (m, 4H), 7.28-7.24 (m, 1H, overlap with residual $CHCl_3$ peak), 7.18 (app. d, *J* = 7.5 Hz, 2H), 2.12 (ddq, *J* = 14.8, 14.8, 7.4 Hz, 6H), 1.97 (ddq, *J* = 14.8, 14.8, 7.4 Hz, 6H), 0.99 (t, *J* = 7.4 Hz, 18H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 149.5 (d, *J* = 13.2 Hz), 142.8 (d, *J* = 6.0 Hz), 135.6 (d, *J* = 2.7 Hz), 134.3 (d, *J* = 7.4 Hz), 130.4 (d, *J* = 2.4 Hz), 129.3, 128.7, 128.4, 127.8 (d, *J* = 37.2 Hz), 126.4 (d, *J* = 6.4 Hz), 50.7 (d, *J* = 19.7 Hz), 30.3 (d, *J* = 6.0 Hz), 10.5 (d, *J* = 8.2 Hz).

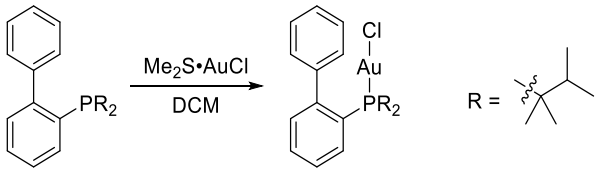
$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 59.91 (s).

ν_{max}(neat)/cm^{-1}: 2966, 2939, 2879, 1583, 1457, 1439, 1383, 1335, 1154, 1122, 1069, 1033, 1006, 909, 839, 777, 750, 699, 671, 615, 547, 526, 507, 493, 465.

HRMS: calcd. for $C_{26}H_{39}AuClP+Na^+$: 637.2036 $[M+Na]^+$; found (ESI^+): 637.2022, calcd. for $C_{26}H_{39}AuClP+NH_4^+$: 632.2482 $[M+NH_4]^+$; found (ESI^+): 632.2465.

m.p./°C: 167-169.

[(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine]gold(I) chloride (5d)



GP6 was performed using 2-(bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl **3d** (17.7 mg, 50.0 µmol). [(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine]gold(I) chloride **5d** (19.7 mg, 33.6 µmol, 67%) was obtained as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.5, 1.5 Hz, 1H), 7.58-7.54 (m, 1H), 7.51 (tt, *J* = 7.4. 1.6 Hz, 1H), 7.46 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.44-7.39 (m, 2H), 7.29 (ddd, *J* = 7.6, 4.4, 1.7 Hz, 1H), 7.20-7.17 (m, 2H), 2.17 (dh, *J* = 10.7, 6.8 Hz, 2H), 1.47 (d, *J* = 13.8 Hz, 6H), 1.45 (d, *J* = 18.4 Hz, 6H) 0.97 (d, *J* = 6.7 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.6 (d, *J* = 13.1 Hz), 142.2 (d, *J* = 6.0 Hz), 135.3 (d, *J* = 2.6 Hz), 134.2 (d, *J* = 7.4 Hz), 130.6 (d, *J* = 2.5 Hz), 129.3, 128.7, 128.4, 127.0 (d, *J* = 40.1 Hz), 126.5 (d, *J* = 6.7 Hz), 45.7 (d, *J* = 23.2 Hz), 35.1 (d, *J* = 4.9 Hz), 26.4 (d, *J* = 9.4 Hz), 23.9, 19.5 (d, *J* = 7.8 Hz), 19.1 (d, *J* = 5.1 Hz).

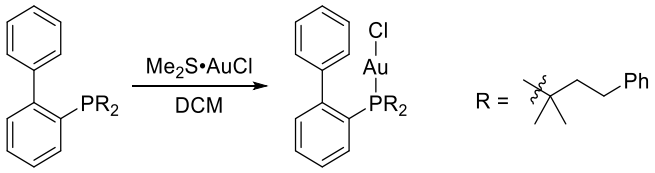
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 58.33 (s).

ν_{max}(neat)/cm^{-1}: 2960, 2874, 1462, 1442, 1392, 1367, 1237, 1156, 1125, 1083, 1007, 908, 780, 756, 699, 678, 616, 541, 511, 465, 416.

HRMS: calcd. for $C_{24}H_{35}AuClP+Na^+$: 609.1723 $[M+Na]^+$; found (ESI^+): 609.1717, calcd. for $C_{24}H_{35}AuClP+NH_4^+$: 604.2169 $[M+NH_4]^+$; found (ESI^+): 604.2164.

m.p./°C: 172-174.

[(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine]gold(I) chloride (5f)



GP6 was performed using 2-(di-(2-methyl-4-phenyl-2-butyl)phosphino)biphenyl **3f** (23.9 mg, 50.0 µmol). [(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine]gold(I) chloride **5f** (24.3 mg, 34.2 µmol, 68%) was obtained as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (td, *J* = 7.6, 1.4 Hz, 1H), 7.57-7.51 (m, 2H), 7.48 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.38-7.33 (m, 2H), 7.31-7.24 (m, 5H, overlap with residual $CHCl_3$ peak), 7.20-7.16 (m, 2H), 7.04 (dd, *J* = 7.7, 1.5 Hz, 6H), 2.69-2.56 (m, 4H), 2.14-1.97 (m, 4H), 1.55 (d, *J* = 16.9 Hz, 6H), 1.54 (d, *J* = 15.3 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.5 (d, *J* = 13.4 Hz), 142.1 (d, *J* = 6.3 Hz), 141.5, 134.2 (d, *J* = 2.5 Hz), 133.8 (d, *J* = 7.4 Hz), 130.9 (d, *J* = 2.4 Hz), 129.3, 128.8, 128.7, 128.5, 128.4, 126.9 (d, *J* = 6.7 Hz), 126.3, 125.5 (d, *J* = 43.3 Hz), 43.8 (d, *J* = 6.7 Hz), 41.9 (d, *J* = 24.2 Hz), 29.8 (d, *J* = 10.4 Hz), 28.1 (d, *J* = 7.6 Hz), 26.9 (d, *J* = 3.7 Hz).

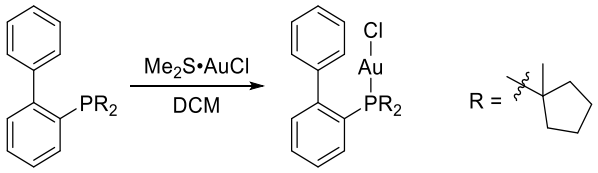
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 63.55 (s).

ν_{max}(neat)/cm^{-1}: 3060, 3024, 2965, 2926, 2853, 1601, 1496, 1453, 1386, 1365, 1200, 1130, 1071, 1008, 906, 776, 745, 717, 697, 617, 573, 531, 511, 414.

HRMS: calcd. for $C_{34}H_{39}AuClP+Na^+$: 733.2036 $[M+Na]^+$; found (ESI^+): 733.2015, calcd. for $C_{34}H_{39}AuClP+NH_4^+$: 728.2482 $[M+NH_4]^+$; found (ESI^+): 728.2467.

m.p./°C: 130-132.

[(2-Biphenyl)di-(1-methylcyclopentyl)phosphine]gold(I) chloride (5h)



GP6 was performed using 2-(di-(1-methylcyclopentyl)phosphino)biphenyl **3h** (17.5 mg, 50.0 µmol). [(2-Biphenyl)di-(1-methylcyclopentyl)phosphine]gold(I) chloride **5h** (21.9 mg, 37.6 µmol, 75%) was obtained as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (td, *J* = 7.6, 1.6 Hz, 1H), 7.58-7.54 (m, 1H), 7.52-7.40 (m, 4H), 7.29 (ddd, *J* = 7.5, 4.3, 1.7 Hz, 1H), 7.18-7.15 (m, 2H), 2.30-2.20 (m, 2H), 2.09-1.99 (m, 2H), 1.83-1.70 (m, 6H), 1.69-1.56 (m, 6H), 1.37 (d, *J* = 14.9 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.0 (d, *J* = 13.5 Hz), 142.3 (d, *J* = 6.3 Hz), 134.2 (d, *J* = 2.8 Hz), 133.3 (d, *J* = 7.4 Hz), 130.5 (d, *J* = 2.4 Hz), 129.5, 128.9, 128.3, 126.8 (d, *J* = 6.9 Hz), 126.8 (d, *J* = 46.5 Hz), 45.9 (d, *J* = 28.6 Hz), 40.6 (d, *J* = 9.3 Hz), 40.4 (d, *J* = 8.4 Hz), 25.9 (d, *J* = 4.9 Hz), 24.3 (d, *J* = 9.8 Hz), 23.4 (d, *J* = 10.2 Hz).

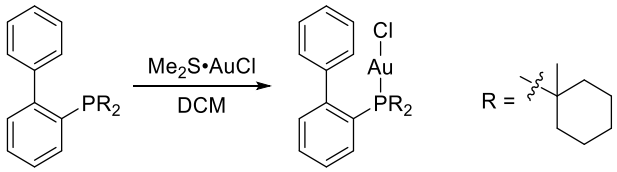
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 58.89 (s).

ν_{max}(neat)/cm^{-1}: 2954, 2867, 1463, 1441, 1424, 1376, 778, 754, 702, 679, 616, 537, 523, 511.

HRMS: calcd. for $C_{24}H_{31}AuClP+Na^+$: 605.1410 $[M+Na]^+$; found (ESI^+): 605.1406, calcd. for $C_{24}H_{31}AuClP+NH_4^+$: 600.1856 $[M+NH_4]^+$; found (ESI^+): 600.1852.

m.p./°C: 160-163.

[(2-Biphenyl)di-(1-methylcyclohexyl)phosphine]gold(I) chloride (5i)



GP6 was performed using 2-(di-(1-methylcyclohexyl)phosphino)biphenyl **3i** (18.9 mg, 50.0 µmol). [(2-Biphenyl)di-(1-methylcyclohexyl)phosphine]gold(I) chloride **5i** (24.8 mg, 40.6 µmol, 81%) was obtained as an off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (td, *J* = 7.1, 1.7 Hz, 1H), 7.60-7.55 (m, 1H), 7.52-7.44 (m, 2H), 7.44-7.40 (m, 2H), 7.30-7.27 (ddd, *J* = 7.4, 2.4, 1.8 Hz, 1H), 7.14-7.10 (m, 2H), 2.13-2.04 (m, 2H), 2.03-1.88 (m, 4H), 1.79-1.72 (m, 2H), 1.65-1.43 (m, 16H), 1.18-1.08 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.8 (d, *J* = 13.0 Hz), 142.5 (d, *J* = 6.5 Hz), 134.5 (d, *J* = 2.4 Hz), 133.6 (d, *J* = 7.2 Hz), 130.4 (d, *J* = 2.3 Hz), 129.4, 128.8, 128.3, 126.5 (d, *J* = 6.4 Hz), 125.2 (d, *J* = 42.2 Hz), 43.2 (d, *J* = 24.2 Hz), 37.6, 37.5 (d, *J* = 1.8 Hz), 25.5 (d, *J* = 1.3 Hz), 21.7 (d, *J* = 4.0 Hz), 21.3 (d, *J* = 7.8 Hz), 21.3 (d, *J* = 7.3 Hz).

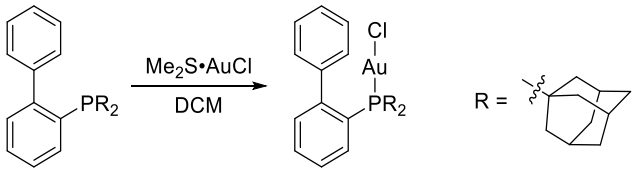
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 71.19 (s).

ν_{max}(neat)/cm^{-1}: 2934, 2866, 2844, 1463, 1441, 1427, 1374, 1345, 1333, 1272, 1255, 1239, 1159, 1146, 1131, 1081, 1030, 1007, 972, 933, 899, 851, 775, 752, 693, 648, 616, 552, 528, 513, 497, 462, 436.

HRMS: calcd. for $C_{26}H_{35}AuClP+Na^+$: 633.1723 [M+Na$^+$]; found (ESI$^+$): 633.1717, calcd. for $C_{26}H_{35}AuClP+NH_4^+$: 628.2169 [M+NH$_4$]$^+$; found (ESI$^+$): 628.2159.

m.p./°C: decomposes *ca* 220 °C.

[(2-Biphenyl)di-(1-adamantyl)phosphine]gold(I) chloride (5k)



GP6 was performed using 2-(di-(1-adamantyl)phosphino)biphenyl **3k** (22.7 mg, 50.0 µmol). [(2-Biphenyl)di-(1-adamantyl)phosphine]gold(I) chloride **5k** (23.7 mg, 34.5 µmol, 69%) was obtained as an off-white solid. The synthesis[24] and crystal structure[25] for **5k** have been reported previously by Stradiotto and co-workers.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (td, *J* = 7.0, 2.0 Hz, 1H), 7.59-7.55 (m, 1H), 7.53-7.47 (m, 2H), 7.45-7.41 (m, 2H), 7.30 (ddd, *J* = 7.0, 4.3, 2.0 Hz, 1H), 7.13-7.09 (m, 2H), 2.22-2.08 (m, 12H), 2.01-1.97 (m, 6H), 1.70-1.65 (m, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 150.9 (d, *J* = 13.1 Hz), 142.5 (d, *J* = 6.4 Hz), 134.5 (d, *J* = 2.4 Hz), 133.6 (d, *J* = 7.3 Hz), 130.5 (d, *J* = 2.3 Hz), 129.4, 128.7, 128.3, 126.4 (d, *J* = 6.5 Hz), 124.0 (d, *J* = 43.7 Hz), 42.7 (d, *J* = 23.6 Hz), 42.3 (d, *J* = 2.7 Hz), 36.4 (d, *J* = 1.6 Hz), 28.7 (d, *J* = 9.9 Hz).

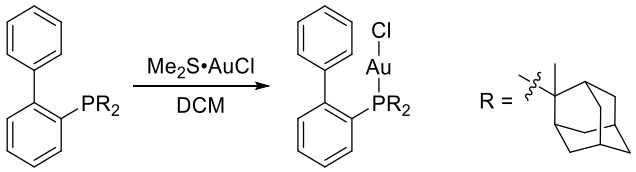
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 61.57 (s).

ν_{max}(neat)/cm^{-1}: 3046, 2901, 2848, 1465, 1449, 1343, 1301, 1275, 1259, 1127, 1044, 969, 905, 773, 752, 730, 694, 547, 531, 517, 488, 453, 433.

HRMS: calcd. for $C_{32}H_{39}AuClP+Na^+$: 709.2036 $[M+Na]^+$; found (ESI^+): 709.2029, calcd. for $C_{32}H_{39}AuClP+NH_4^+$: 704.2482 $[M+NH_4]^+$; found (ESI^+): 704.2448.

m.p./°C: >270.

[(2-Biphenyl)di-(2-methyl-2-adamantyl)phosphine]gold(I) chloride (5l)



GP6 was followed using 2-(di-(2-methyl-2-adamantyl)phosphino)biphenyl **3l** (12.1 mg, 25.0 µmol) and dimethylsulfide gold(I) chloride complex (7.4 mg, 25 µmol). [(2-Biphenyl)di-(2-methyl-2-adamantyl)phosphine]gold(I) chloride **5l** (6.0 mg, 8.4 µmol, 34%) was obtained as an off-white solid.

The ^{1}H and ^{31}P NMR spectra of this compound are complicated by restricted rotation. Variable temperature ^{31}P NMR spectra (DMSO-d_6, 298-368 K) showed four different signals for the complex which tended towards coalescence at higher temperatures (Figure S9).

HRMS: calcd. for $C_{34}H_{43}AuClP+Na^{+}$: 737.2349 $[M+Na]^{+}$; found (ESI^{+}): 737.2344.

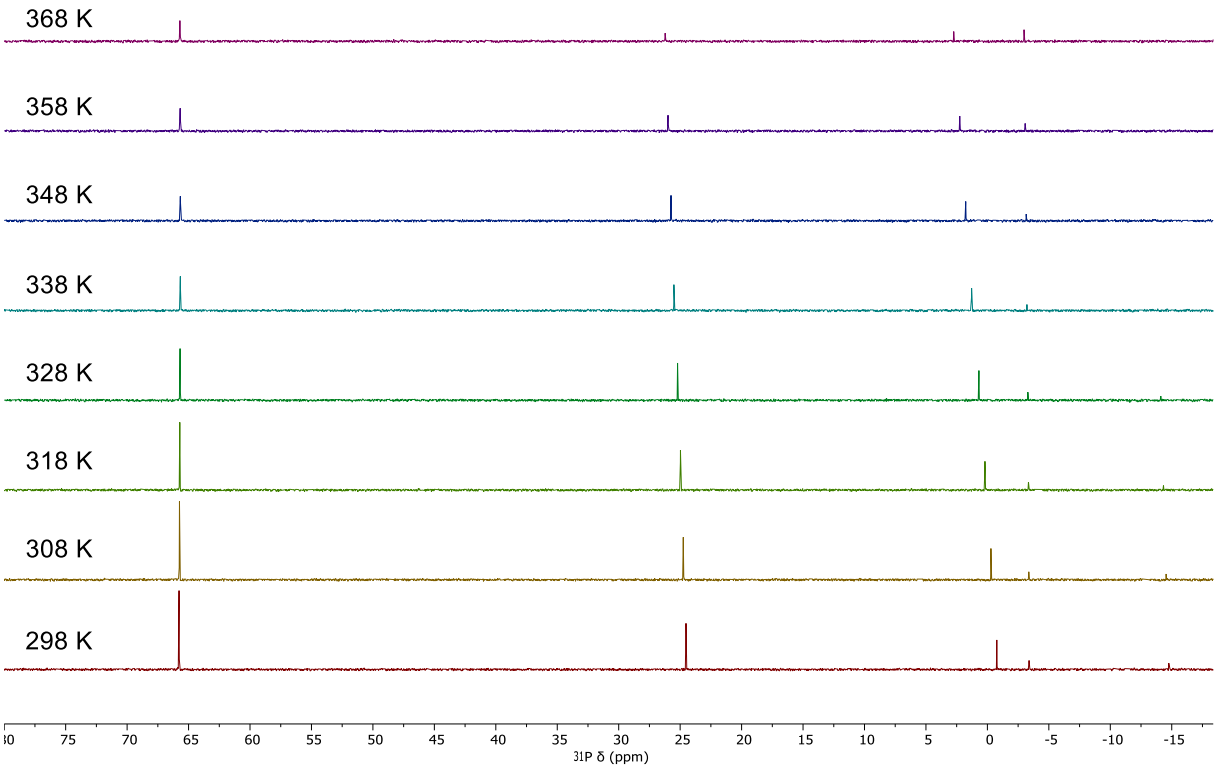
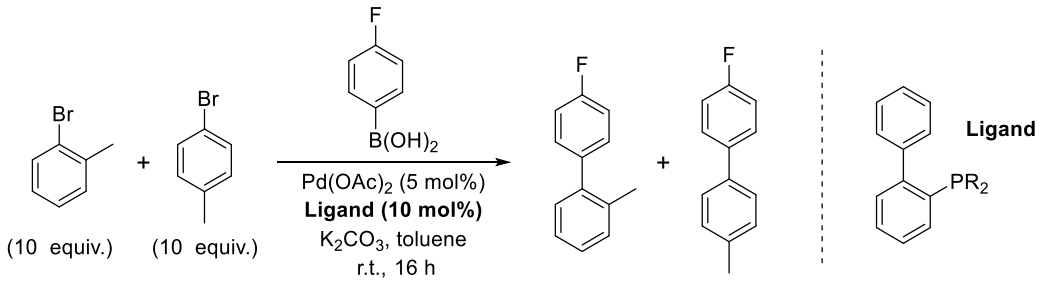


Figure S9. Variable temperature ^{31}P NMR spectra of **5l** in DMSO-d_6.

12. Suzuki-Miyaura Chemoselectivity Study (Manuscript Scheme 7)



Bromotoluene stock solution: 4-bromotoluene (3.42 g, 20.0 mmol) and 2-bromotoluene (3.42 g, 20.0 mmol) were added to a dry Schlenk tube that had previously been evacuated and backfilled with anhydrous dinitrogen (3 ×), and the mixture was made up to 20.0 mL total volume with anhydrous degassed toluene.

Competition reactions: 4-fluorophenylboronic acid (28.0 mg, 0.200 mmol), K_2CO_3 (0.276 g, 2.00 mmol) $Pd(OAc)_2$ (2.25 mg, 10.0 µmol, 5 mol%) and ligand (**3d**, **3f**, **3h**, **3i**, **3k**, **3l**, or **3o** ; 20.0 µ mol, 10 mol%) were added to microwave tubes. The tubes were capped, then evacuated and backfilled with anhydrous dinitrogen (3 ×). Bromotoluene stock solution (2.0 mL) was added to each tube, and the mixtures were stirred at r.t. for 16 h. An aliquot of each reaction was removed, diluted with $CDCl_3$, and the ratio of products was measured by ^{19}F NMR spectroscopy. Four peaks were observed in all cases, the identity of which were confirmed by comparison to authentic samples (Figure S10).

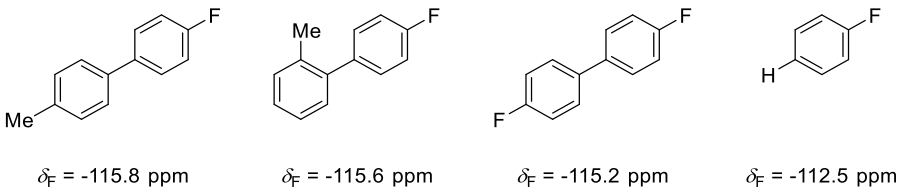
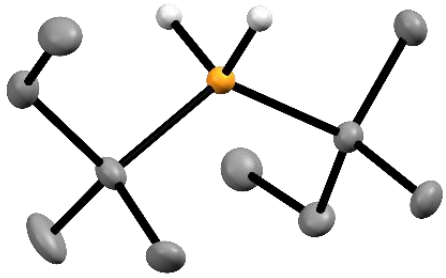


Figure S10. ^{19}F NMR chemical shifts (/ppm, $CDCl_3$) of species observed in Suzuki-Miyaura cross-couplings.

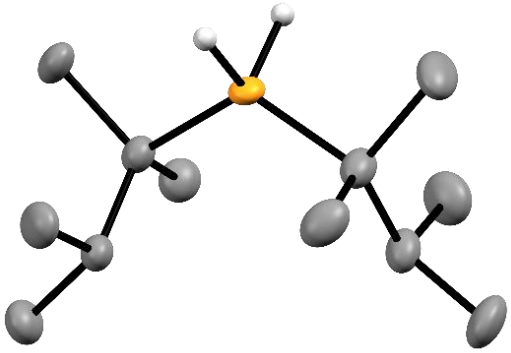
13. X-ray Crystallography Data Tables

Table S2. Crystal data and structure refinement for **1a** (CCDC 1990404; triflate anion and H atoms on C omitted for clarity).



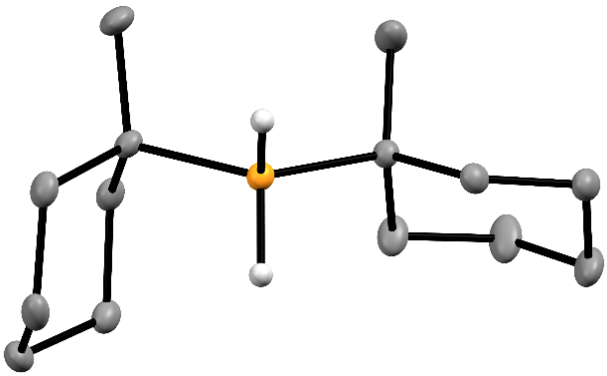
Empirical formula	$C_{11}H_{24}O_3F_3PS$
Formula weight	324.33
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.4780(3)
b/Å	10.4898(2)
c/Å	17.7113(4)
α/°	90.0
β/°	99.9348(18)
γ/°	90.0
Volume/Å^3	3198.51(11)
Z	8
ρ_{calc}g/cm^3	1.347
μ/mm^{-1}	3.067
F(000)	1376.0
Crystal size/mm^3	0.232 × 0.166 × 0.077
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.562 to 147.572
Index ranges	-21 ≤ h ≤ 18, -12 ≤ k ≤ 9, -19 ≤ l ≤ 21
Reflections collected	11217
Independent reflections	6130 [R_{int} = 0.0244, R_{sigma} = 0.0319]
Data/restraints/parameters	6130/0/371
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0852
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.0902
Largest diff. peak/hole / e Å^{-3}	0.39/-0.28

Table S3. Crystal data and structure refinement for **1d** (CCDC 1990405; triflate anion and H atoms on C omitted for clarity).



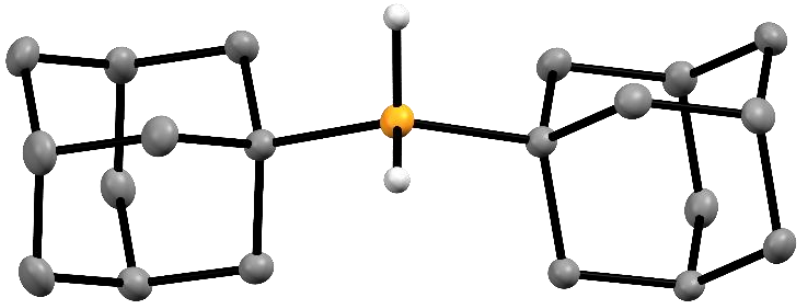
Empirical formula	$C_{13}H_{28}F_3O_3PS$
Formula weight	352.38
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.8317(4)
b/Å	22.6453(9)
c/Å	9.2451(6)
α/°	90
β/°	106.967(6)
γ/°	90
Volume/Å^3	1768.51(17)
Z	4
ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	2.814
F(000)	752.0
Crystal size/mm^3	0.326 × 0.242 × 0.142
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.74 to 147.248
Index ranges	-7 ≤ h ≤ 10, -26 ≤ k ≤ 27, -11 ≤ l ≤ 7
Reflections collected	6294
Independent reflections	3407 [R_{int} = 0.0431, R_{sigma} = 0.0363]
Data/restraints/parameters	3407/1050/333
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0823, wR_2 = 0.2221
Final R indexes [all data]	R_1 = 0.0866, wR_2 = 0.2282
Largest diff. peak/hole / e Å^{-3}	0.93/-0.47

Table S4. Crystal data and structure refinement for **1i** (CCDC 1990406; triflate anion and H atoms on C omitted for clarity).



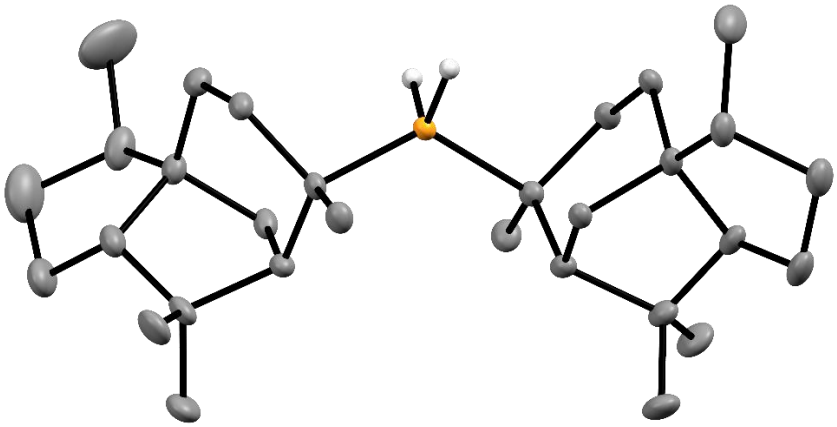
Empirical formula	$C_{15}H_{28}F_3O_3PS$
Formula weight	376.40
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.5000(2)
b/Å	10.6274(2)
c/Å	18.6029(4)
α/°	90
β/°	100.595(2)
γ/°	90
Volume/Å^3	1846.13(7)
Z	4
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	2.735
F(000)	800
Crystal size/mm^3	0.210 x 0.183 x 0.118
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.6260 to 147.5540
Index ranges	-11 ≤ h ≤ 7, -12 ≤ k ≤ 11, -22 ≤ l ≤ 23
Reflections collected	6454
Independent reflections	6454 [R_{int} = 0.0389, R_{sigma} = 0.0461]
Data/restraints/parameters	3553/1/216
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0533; wR_2 = 0.1293
Final R indexes [all data]	R_1 = 0.0574; wR_2 = 0.1341
Largest diff. peak/hole / e Å^{-3}	1.044/-0.673

Table S5. Crystal data and structure refinement for **1k** (CCDC 1990407; triflate anion and H atoms on C omitted for clarity).



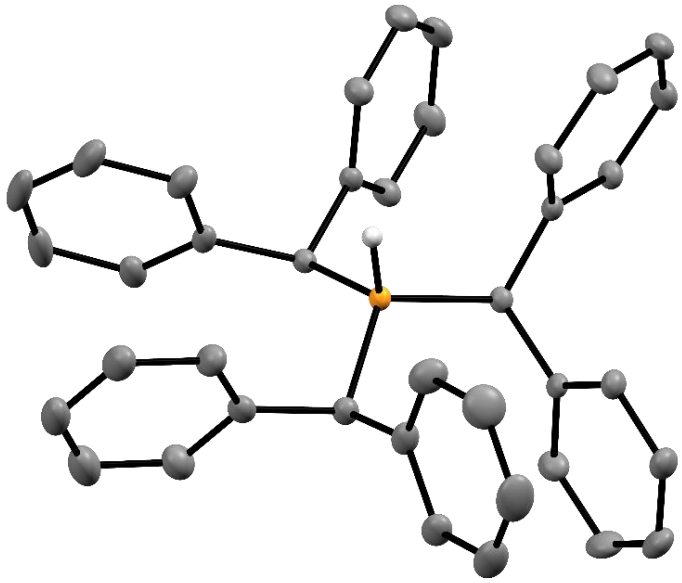
Empirical formula	$C_{21}H_{32}F_3O_3PS$
Formula weight	452.49
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1508(2)
b/Å	18.5177(4)
c/Å	21.1099(5)
α/°	90
β/°	100.488(2)
γ/°	90
Volume/Å^3	4286.10(16)
Z	8
ρ_{calc}g/cm^3	1.402
μ/mm^{-1}	2.457
F(000)	1920
Crystal size/mm^3	0.158 × 0.077 × 0.043
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.396 to 147.522
Index ranges	-12 ≤ h ≤ 13, -23 ≤ k ≤ 20, -26 ≤ l ≤ 17
Reflections collected	28854
Independent reflections	8144 [R_{int} = 0.0676, R_{sigma} = 0.0408]
Data/restraints/parameters	8144/6/539
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0642; wR_2 = 0.1644
Final R indexes [all data]	R_1 = 0.0746; wR_2 = 0.1749
Largest diff. peak/hole / e Å^{-3}	1.836/-0.706

Table S6. Crystal data and structure refinement for **1m** (CCDC 1990408; triflate anion and H atoms on C omitted for clarity).



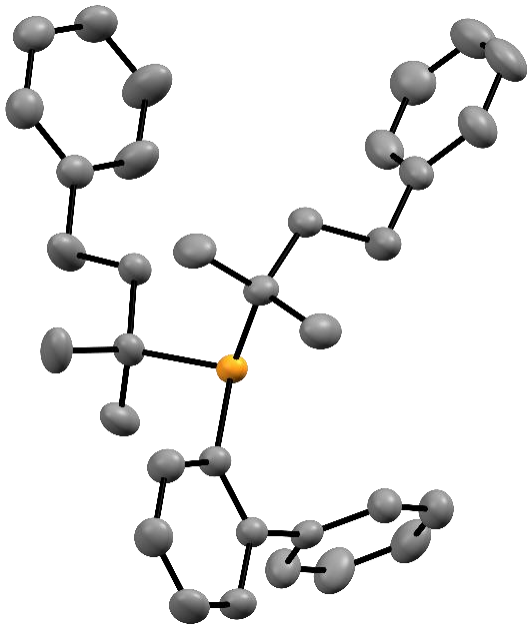
Empirical formula	$C_{31}H_{52}F_3O_3PS$
Formula weight	592.75
Temperature/K	120(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.3620(2)
b/Å	16.8285(3)
c/Å	25.1572(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3116.76(12)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	1.807
F(000)	1280.0
Crystal size/mm^3	0.45 × 0.098 × 0.033
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.028 to 145.772
Index ranges	-8 ≤ h ≤ 7, -20 ≤ k ≤ 20, -31 ≤ l ≤ 29
Reflections collected	18408
Independent reflections	6075 [R_{int} = 0.0897, R_{sigma} = 0.0594]
Data/restraints/parameters	6075/1/366
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1796
Final R indexes [all data]	R_1 = 0.0692, wR_2 = 0.1837
Largest diff. peak/hole / e Å^{-3}	0.67/-0.40
Flack parameter	-0.013(13)

Table S7. Crystal data and structure refinement for **1n** (CCDC 1990409; triflate anion, H atoms on C and one molecule of CH_2Cl_2 omitted for clarity).



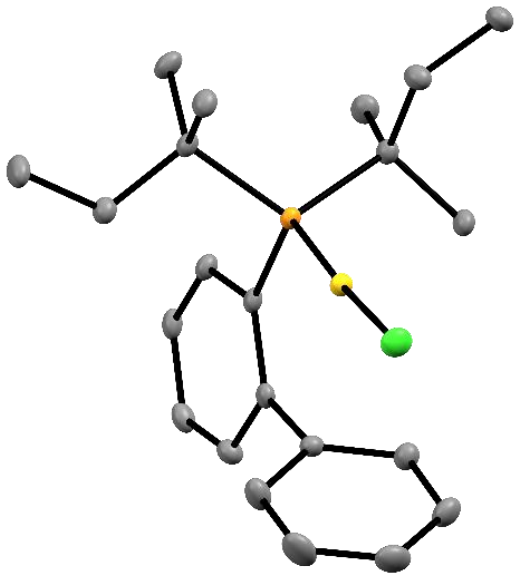
Empirical formula	$C_{40.9}H_{35.8}Cl_{1.8}F_3O_3PS$
Formula weight	759.13
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5515(2)
b/Å	18.5889(2)
c/Å	17.7571(2)
α/°	90
β/°	99.9070(10)
γ/°	90
Volume/Å^3	3756.12(9)
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	2.789
F(000)	1575.0
Crystal size/mm^3	0.574 × 0.213 × 0.052
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.77 to 147.506
Index ranges	-14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -16 ≤ l ≤ 22
Reflections collected	61659
Independent reflections	7546 [R_{int} = 0.0651, R_{sigma} = 0.0278]
Data/restraints/parameters	7546/496/555
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0701, wR_2 = 0.1794
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1818
Largest diff. peak/hole / e Å^{-3}	1.10/-0.63

Table S8. Crystal data and structure refinement for **3f** (CCDC 1990410; H atoms omitted for clarity).



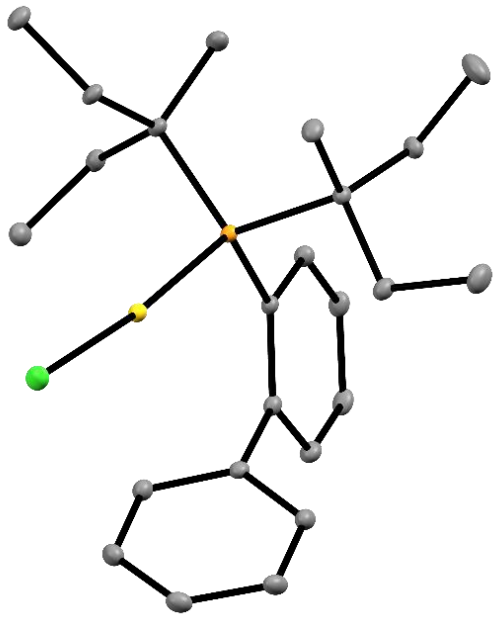
Empirical formula	$C_{34}H_{39}P$
Formula weight	478.62
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.1139(2)
b/Å	12.6246(3)
c/Å	13.5249(3)
α/°	111.882(2)
β/°	109.918(2)
γ/°	96.579(2)
Volume/Å^3	1447.74(6)
Z	2
ρ_{calc}g/cm^3	1.098
μ/mm^{-1}	0.962
F(000)	516.0
Crystal size/mm^3	0.158 × 0.149 × 0.071
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.746 to 144.51
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	23255
Independent reflections	5573 [R_{int} = 0.0280, R_{sigma} = 0.0188]
Data/restraints/parameters	5573/401/375
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.1005
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.1057
Largest diff. peak/hole / e Å^{-3}	0.21/-0.16

Table S9. Crystal data and structure refinement for **5a** (CCDC 1990411; H atoms and one molecule of cyclohexane omitted for clarity).



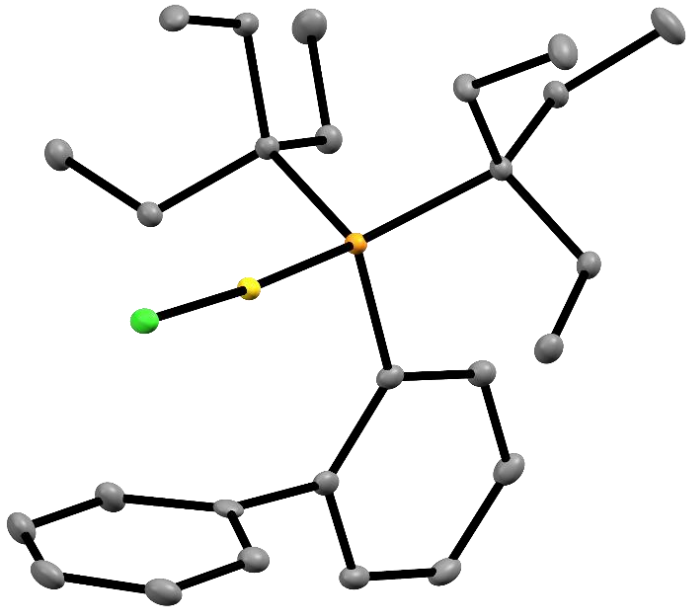
Empirical formula	$C_{47}H_{68}Au_2Cl_2P_2$
Formula weight	1159.78
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.0872(3)
b/Å	14.0744(6)
c/Å	16.7016(5)
α/°	78.850(3)
β/°	81.860(2)
γ/°	78.924(3)
Volume/Å^3	2269.59(14)
Z	2
ρ_{calc}g/cm^3	1.697
μ/mm^{-1}	6.676
F(000)	1144.0
Crystal size/mm^3	0.178 × 0.143 × 0.036
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.988 to 70.126
Index ranges	-16 ≤ h ≤ 15, -22 ≤ k ≤ 22, -26 ≤ l ≤ 26
Reflections collected	64649
Independent reflections	18791 [R_{int} = 0.0359, R_{sigma} = 0.0395]
Data/restraints/parameters	18791/656/631
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0285, wR_2 = 0.0483
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.0539
Largest diff. peak/hole / e Å^{-3}	1.23/-1.66

Table S10. Crystal data and structure refinement for **5b** (CCDC 1990412; H atoms omitted for clarity).



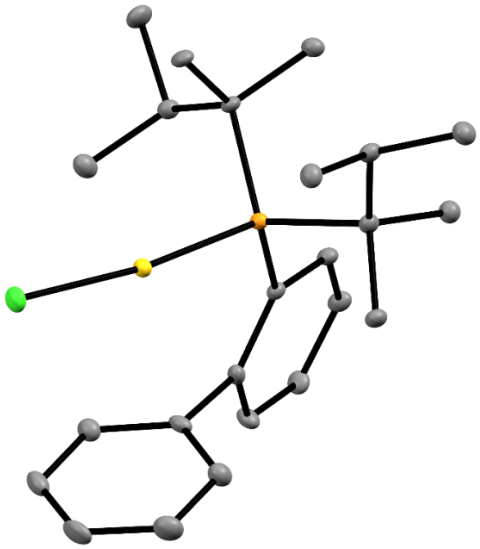
Empirical formula	$C_{24}H_{35}AuClP$
Formula weight	586.90
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0134(2)
b/Å	14.7285(3)
c/Å	15.0955(3)
α/°	90
β/°	92.029(2)
γ/°	90
Volume/Å^3	2224.92(8)
Z	4
ρ_{calc}g/cm^3	1.752
μ/mm^{-1}	6.811
F(000)	1160.0
Crystal size/mm^3	0.261 × 0.23 × 0.095
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.068 to 75.594
Index ranges	-17 ≤ h ≤ 16, -24 ≤ k ≤ 25, -25 ≤ l ≤ 25
Reflections collected	44846
Independent reflections	11484 [R_{int} = 0.0414, R_{sigma} = 0.0390]
Data/restraints/parameters	11484/0/251
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0249, wR_2 = 0.0467
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0506
Largest diff. peak/hole / e Å^{-3}	1.73/-1.56

Table S11. Crystal data and structure refinement for **5c** (CCDC 1990413; H atoms omitted for clarity).



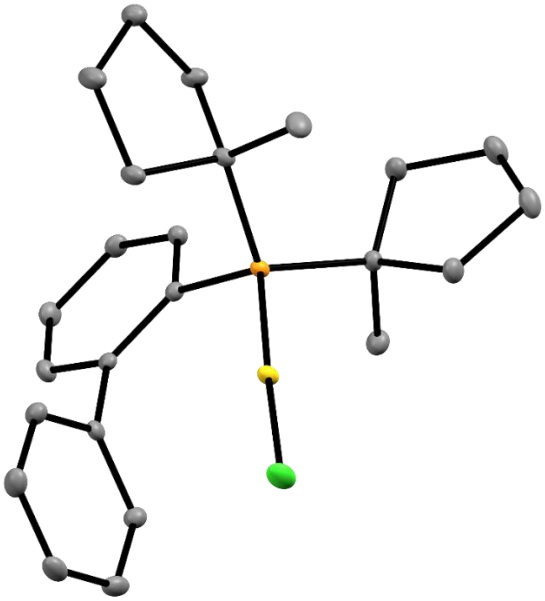
Empirical formula	$C_{26}H_{39}AuClP$
Formula weight	614.96
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0412(4)
b/Å	15.8623(6)
c/Å	15.2487(5)
α/°	90
β/°	91.963(4)
γ/°	90
Volume/Å^3	2427.33(16)
Z	4
ρ_{calc}g/cm^3	1.683
μ/mm^{-1}	6.247
F(000)	1224.0
Crystal size/mm^3	0.099 × 0.089 × 0.052
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.79 to 57.374
Index ranges	-13 ≤ h ≤ 11, -20 ≤ k ≤ 20, -18 ≤ l ≤ 20
Reflections collected	24176
Independent reflections	5556 [R_{int} = 0.0264, R_{sigma} = 0.0232]
Data/restraints/parameters	5556/0/268
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0185, wR_2 = 0.0387
Final R indexes [all data]	R_1 = 0.0223, wR_2 = 0.0399
Largest diff. peak/hole / e Å^{-3}	0.70/-0.72

Table S12. Crystal data and structure refinement for **5d** (CCDC 1990414; H atoms and two molecules of cyclohexane omitted for clarity).



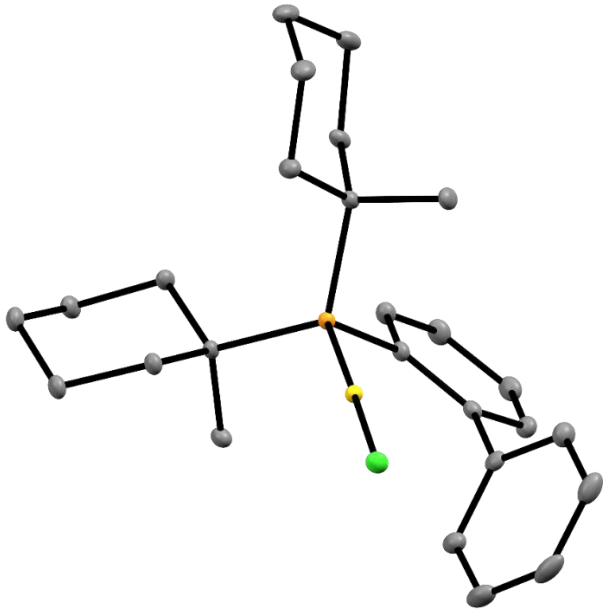
Empirical formula	$C_{30}H_{47}AuClP$
Formula weight	671.06
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.6600(3)
b/Å	11.3550(3)
c/Å	23.7632(7)
α/°	90
β/°	100.803(3)
γ/°	90
Volume/Å^3	2825.42(14)
Z	4
ρ_{calc}g/cm^3	1.578
μ/mm^{-1}	5.374
F(000)	1352.0
Crystal size/mm^3	0.153 × 0.05 × 0.017
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.796 to 65.982
Index ranges	-16 ≤ h ≤ 15, -16 ≤ k ≤ 17, -34 ≤ l ≤ 35
Reflections collected	64955
Independent reflections	9978 [R_{int} = 0.0651, R_{sigma} = 0.0530]
Data/restraints/parameters	9978/102/325
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0566
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.0626
Largest diff. peak/hole / e Å^{-3}	1.97/-1.15

Table S13. Crystal data and structure refinement for **5h** (CCDC 1990415; H atoms and one molecule of water omitted for clarity).



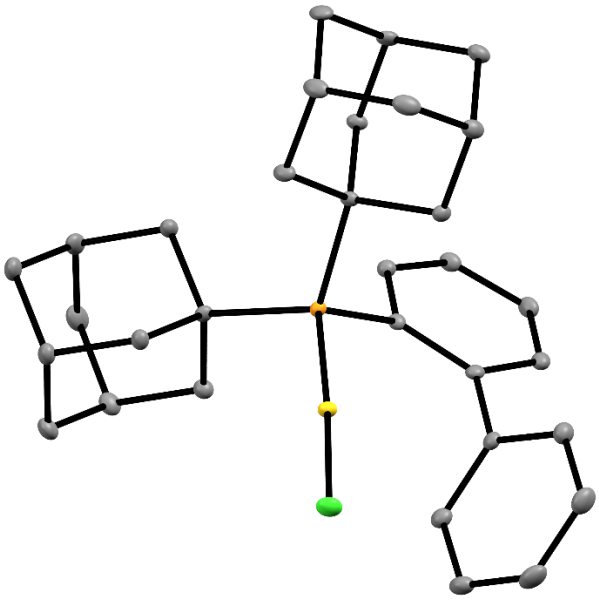
Empirical formula	$C_{24}H_{31.22}AuClO_{0.11}P$
Formula weight	584.85
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.7107(2)
b/Å	9.9662(3)
c/Å	25.5485(6)
α/°	90
β/°	96.659(2)
γ/°	90
Volume/Å^3	2202.97(10)
Z	4
ρ_{calc}g/cm^3	1.763
μ/mm^{-1}	6.879
F(000)	1148.0
Crystal size/mm^3	0.113 × 0.094 × 0.051
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.236 to 57.416
Index ranges	-11 ≤ h ≤ 10, -13 ≤ k ≤ 13, -33 ≤ l ≤ 33
Reflections collected	55140
Independent reflections	5357 [R_{int} = 0.0357, R_{sigma} = 0.0192]
Data/restraints/parameters	5357/105/275
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0168, wR_2 = 0.0322
Final R indexes [all data]	R_1 = 0.0208, wR_2 = 0.0336
Largest diff. peak/hole / e Å^{-3}	0.79/-0.73

Table S14. Crystal data and structure refinement for **5i** (CCDC 1990416; H atoms omitted for clarity).



Empirical formula	$C_{26}H_{35}AuClP$
Formula weight	610.92
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7821(3)
b/Å	20.3690(4)
c/Å	11.1066(3)
α/°	90
β/°	106.794(3)
γ/°	90
Volume/Å^3	2335.20(11)
Z	4
ρ_{calc}g/cm^3	1.738
μ/mm^{-1}	13.597
F(000)	1208
Crystal size/mm^3	0.23 x 0.138 x 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.382 to 148.956
Index ranges	-12 ≤ h ≤ 13, -25 ≤ k ≤ 25, -13 ≤ l ≤ 13
Reflections collected	19303
Independent reflections	4705 [R_{int} = 0.0256, R_{sigma} = 0.200]
Data/restraints/parameters	4705/0/265
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0177; wR_2 = 0.0428
Final R indexes [all data]	R_1 = 0.0188; wR_2 = 0.0433
Largest diff. peak/hole / e Å^{-3}	0.728/-0.966

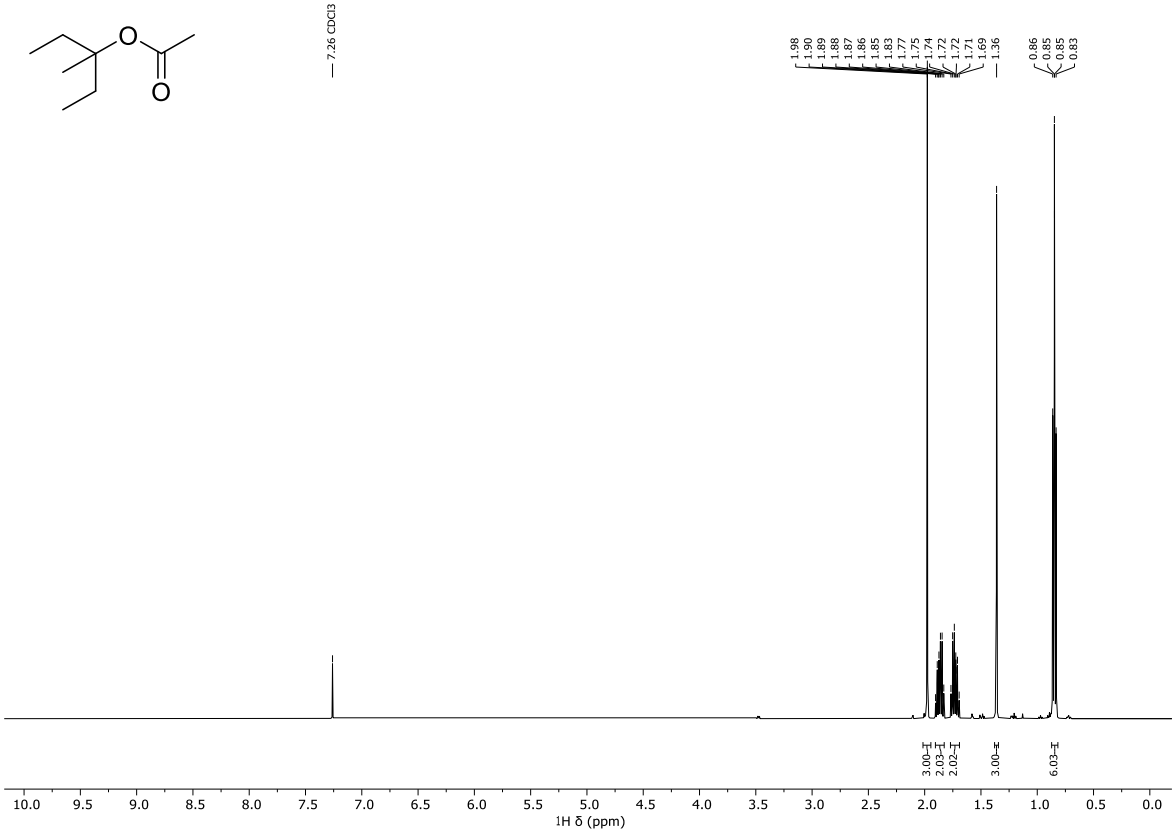
Table S15. Crystal data and structure refinement for **5k** (CCDC 1990417; H atoms omitted for clarity).



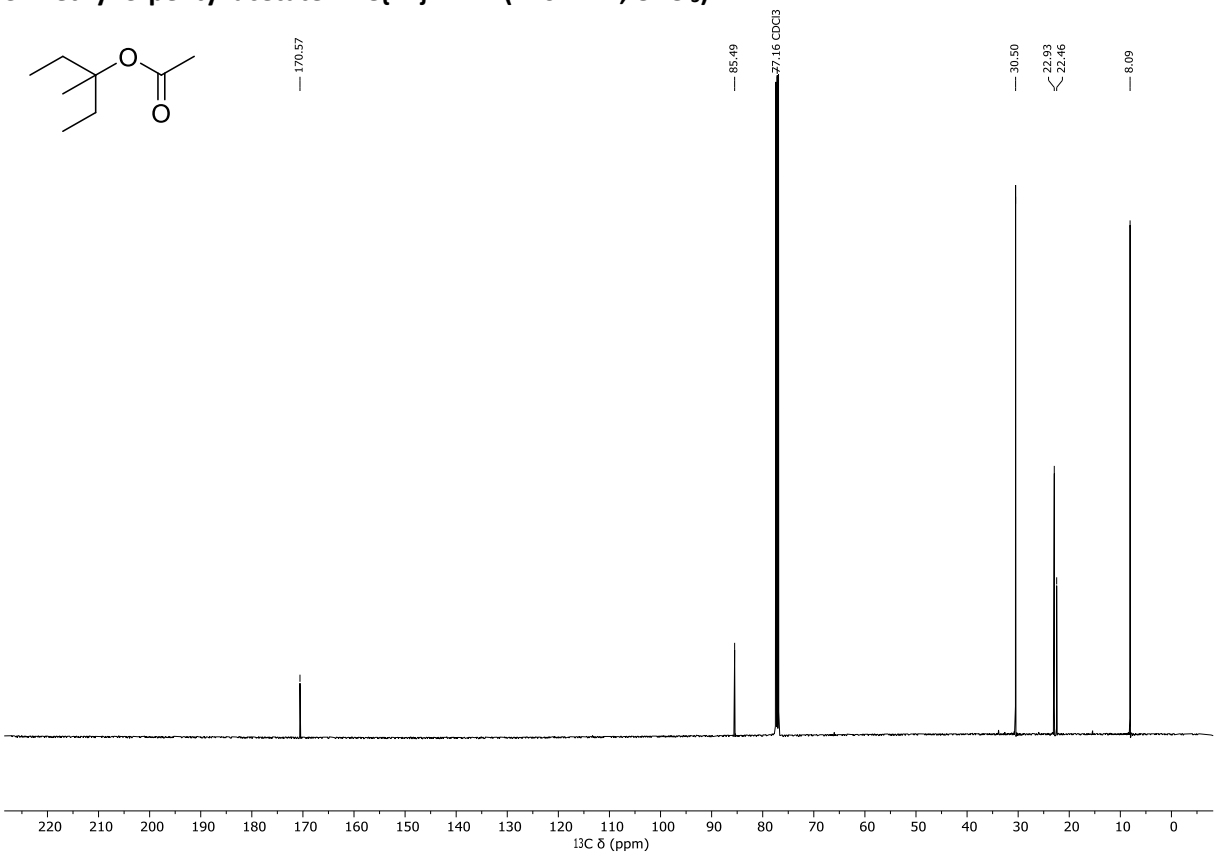
Empirical formula	$C_{32}H_{39}AuClP$
Formula weight	687.02
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.9313(2)
b/Å	15.6446(2)
c/Å	15.2881(2)
α/°	90
β/°	109.268(2)
γ/°	90
Volume/Å^3	2693.83(7)
Z	4
ρ_{calc}g/cm^3	1.694
μ/mm^{-1}	5.640
F(000)	1368.0
Crystal size/mm^3	0.276 × 0.09 × 0.046
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.61 to 75.426
Index ranges	-20 ≤ h ≤ 20, -26 ≤ k ≤ 26, -25 ≤ l ≤ 26
Reflections collected	51837
Independent reflections	13779 [R_{int} = 0.0649, R_{sigma} = 0.0720]
Data/restraints/parameters	13779/0/316
Goodness-of-fit on F^2	0.923
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0687
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.0717
Largest diff. peak/hole / e Å^{-3}	3.37/-1.89

14. NMR Spectra

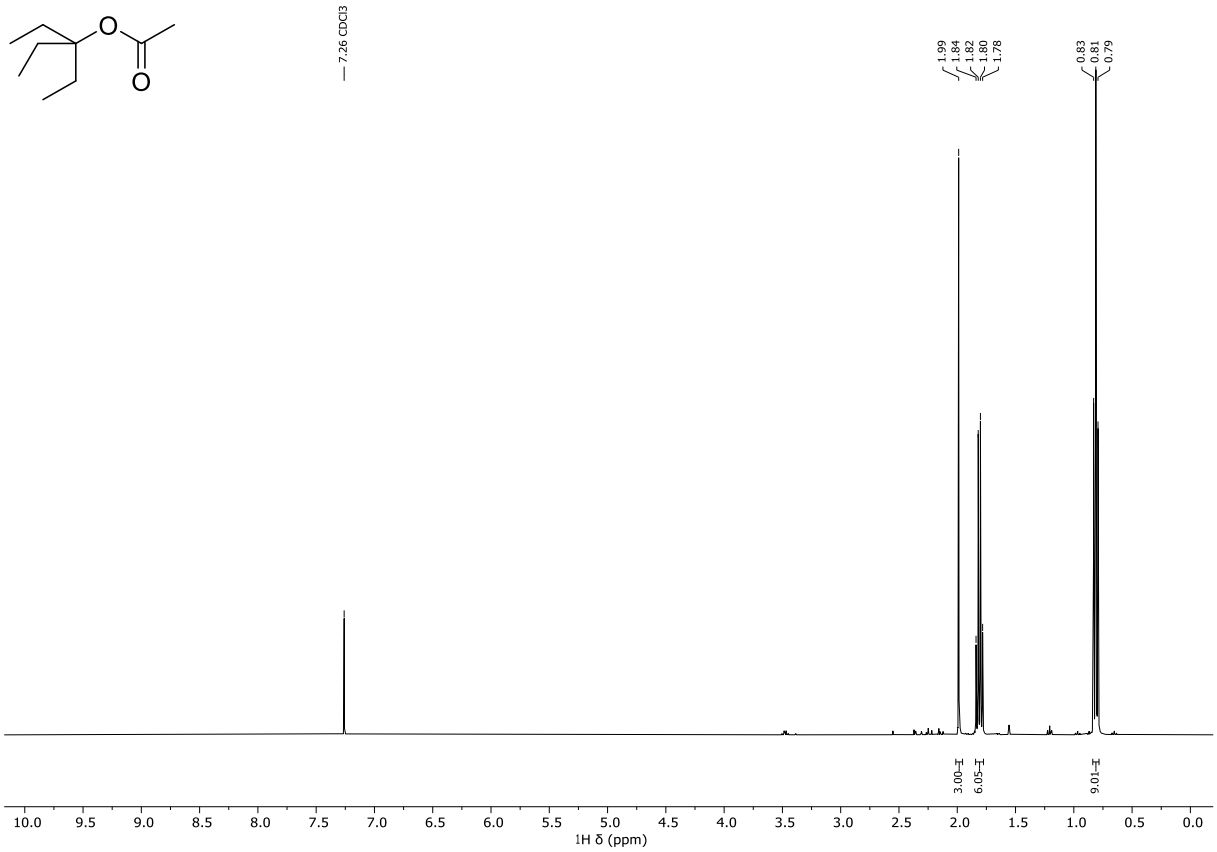
3-Methyl-3-pentyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



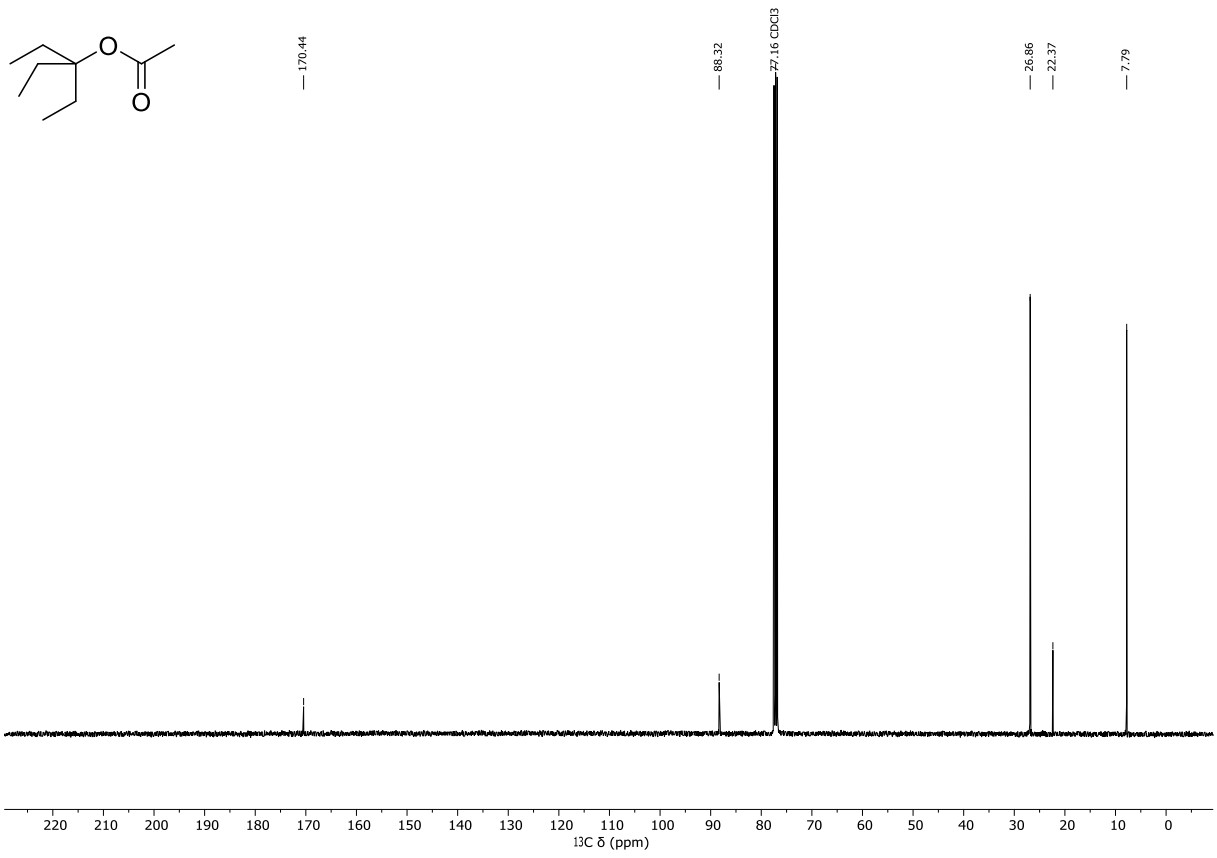
3-Methyl-3-pentyl acetate - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



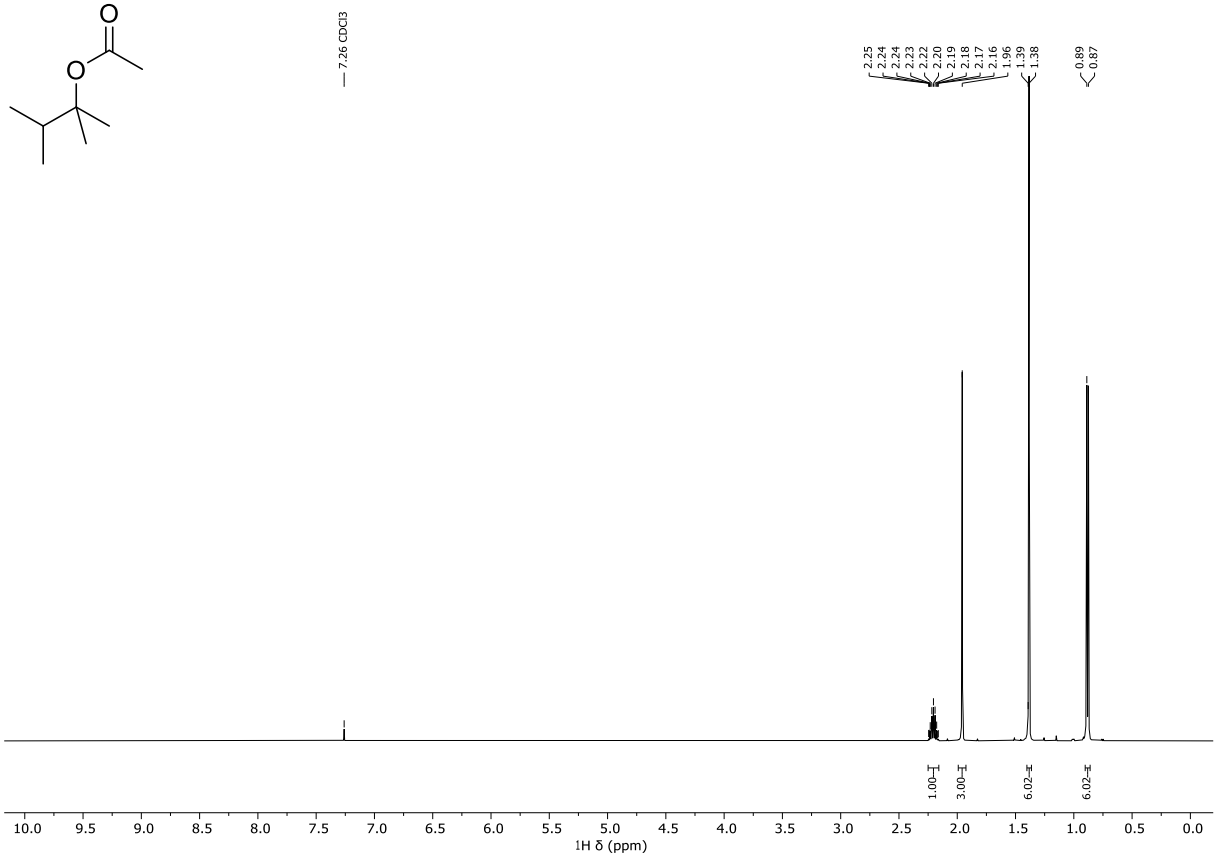
3-Ethyl-3-pentyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



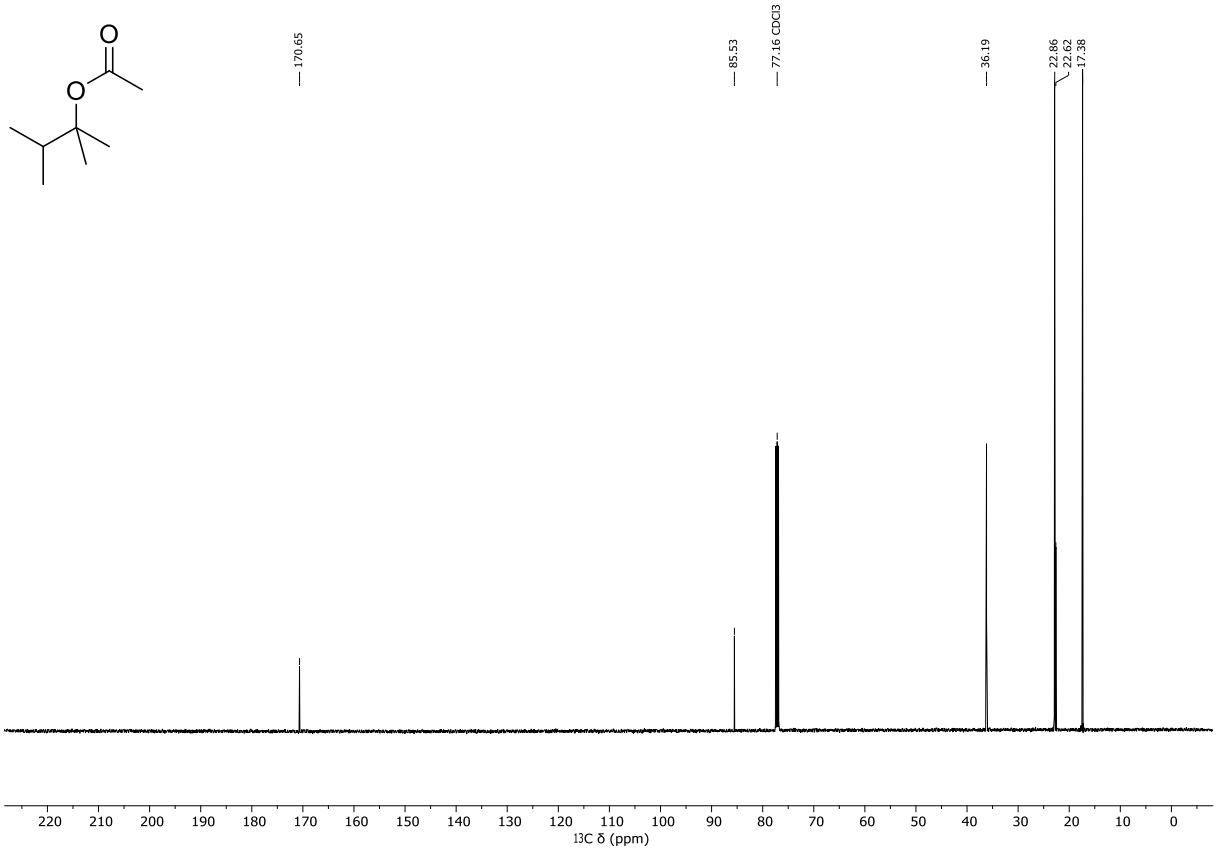
3-Ethyl-3-pentyl acetate - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



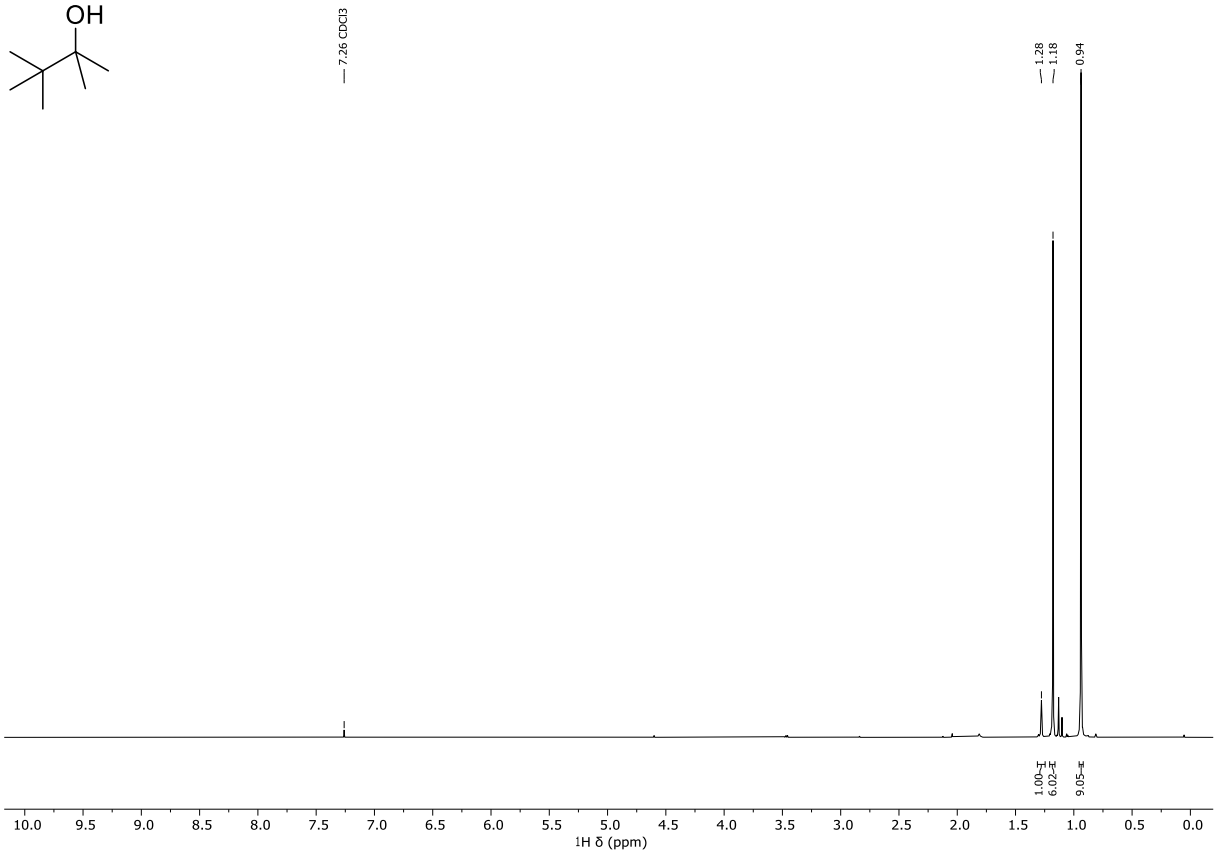
2,3-Dimethyl-2-butyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



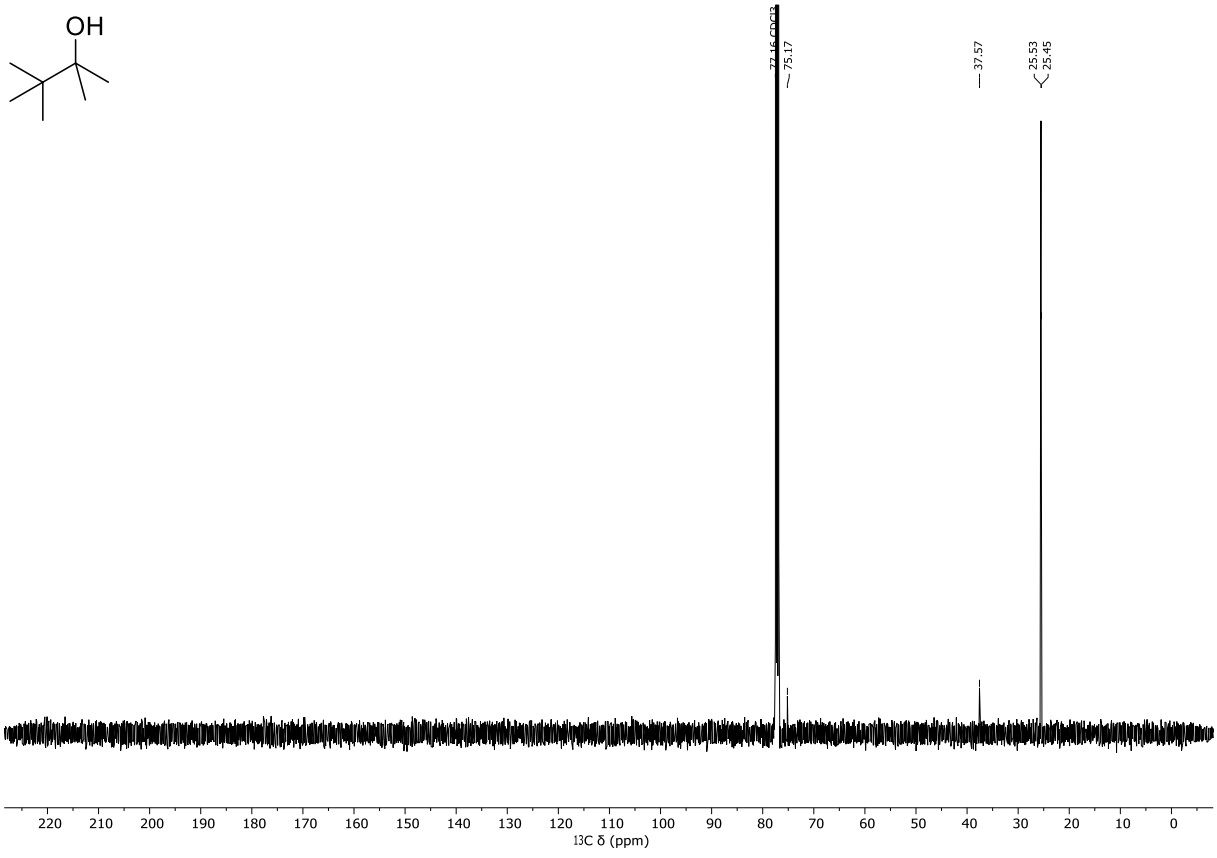
2,3-Dimethyl-2-butyl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



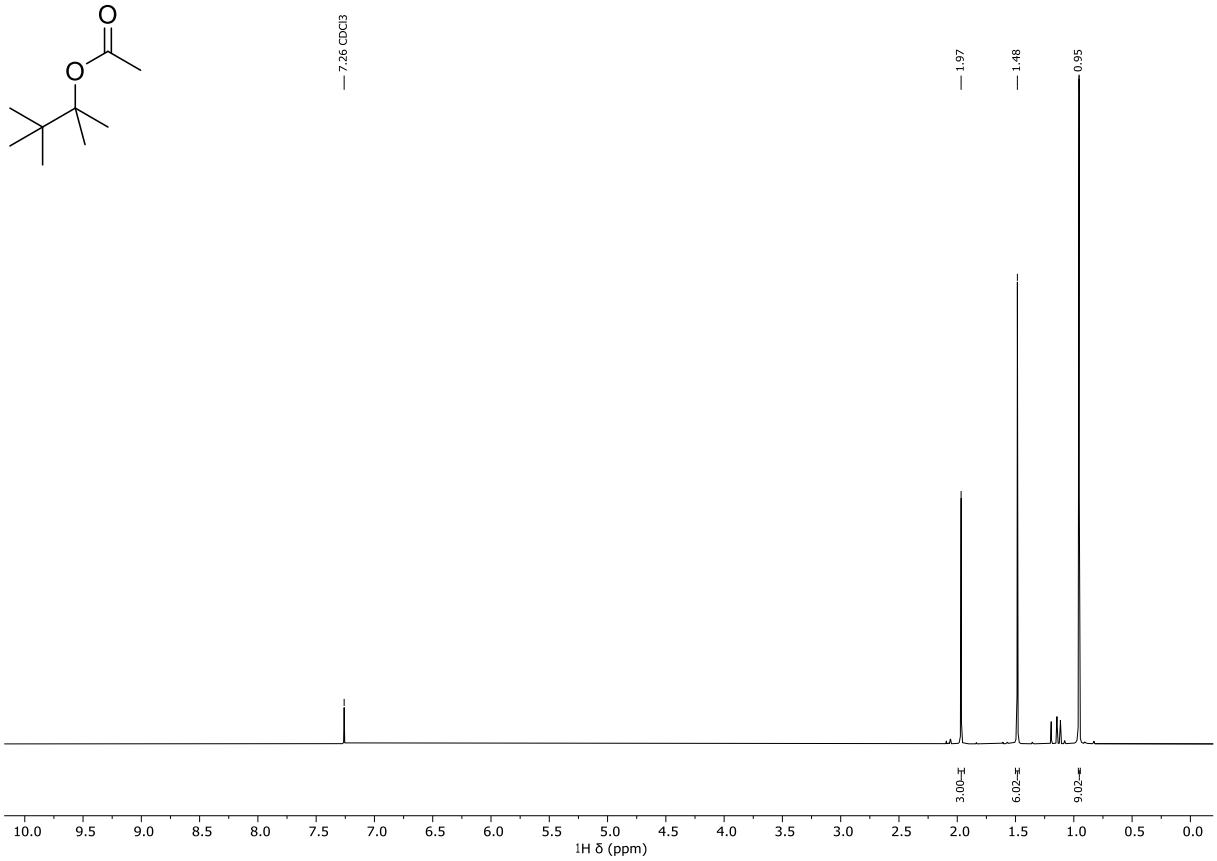
2,3,3-Trimethyl-2-butanol - ^{1}H NMR (500 MHz, $CDCl_3$)



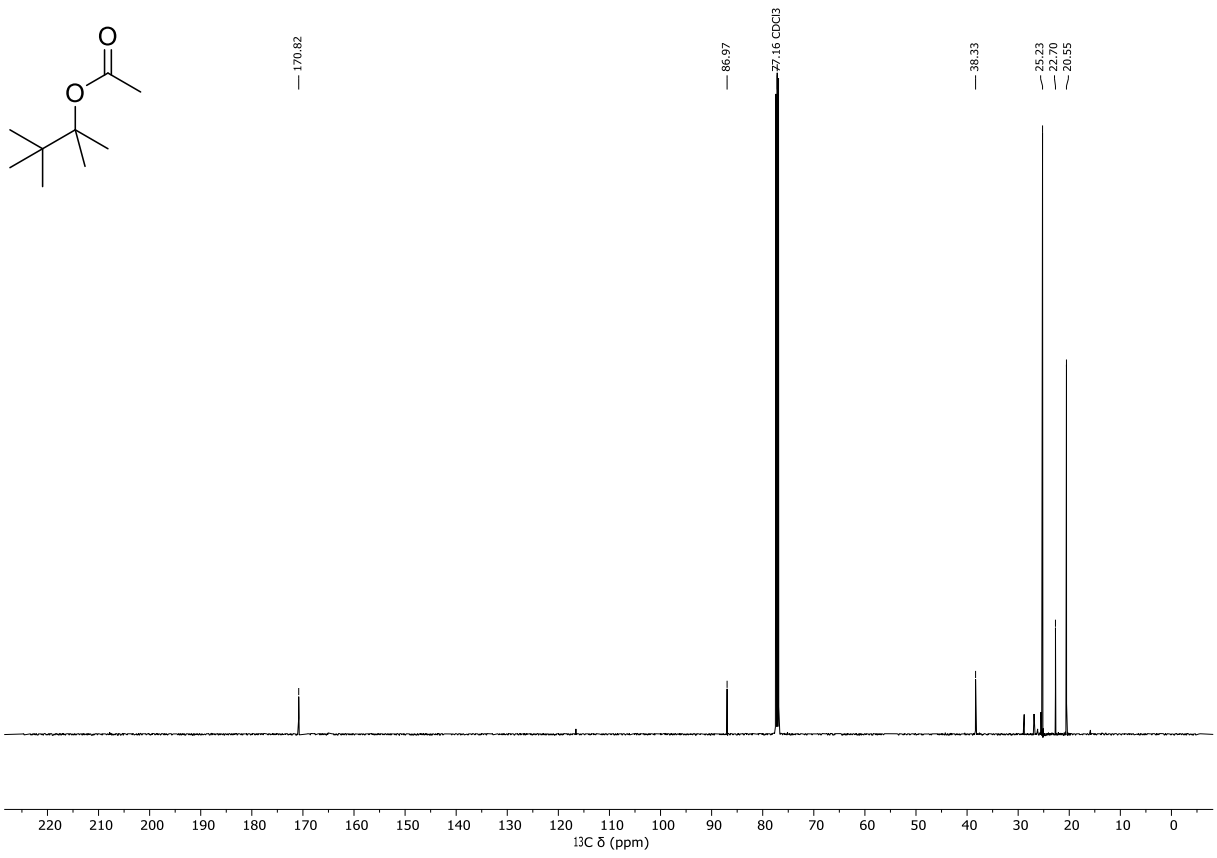
2,3,3-Trimethyl-2-butanol - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



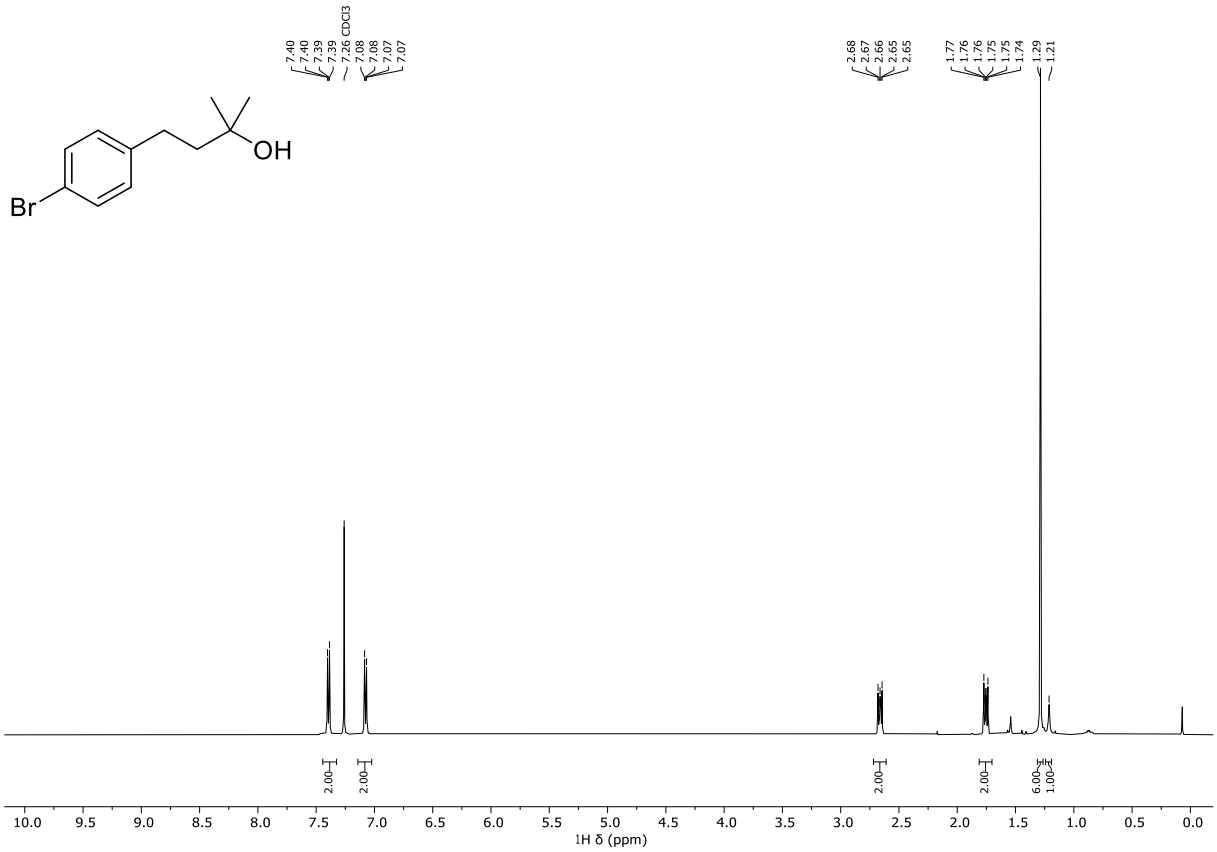
2,3,3-Trimethyl-2-butyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



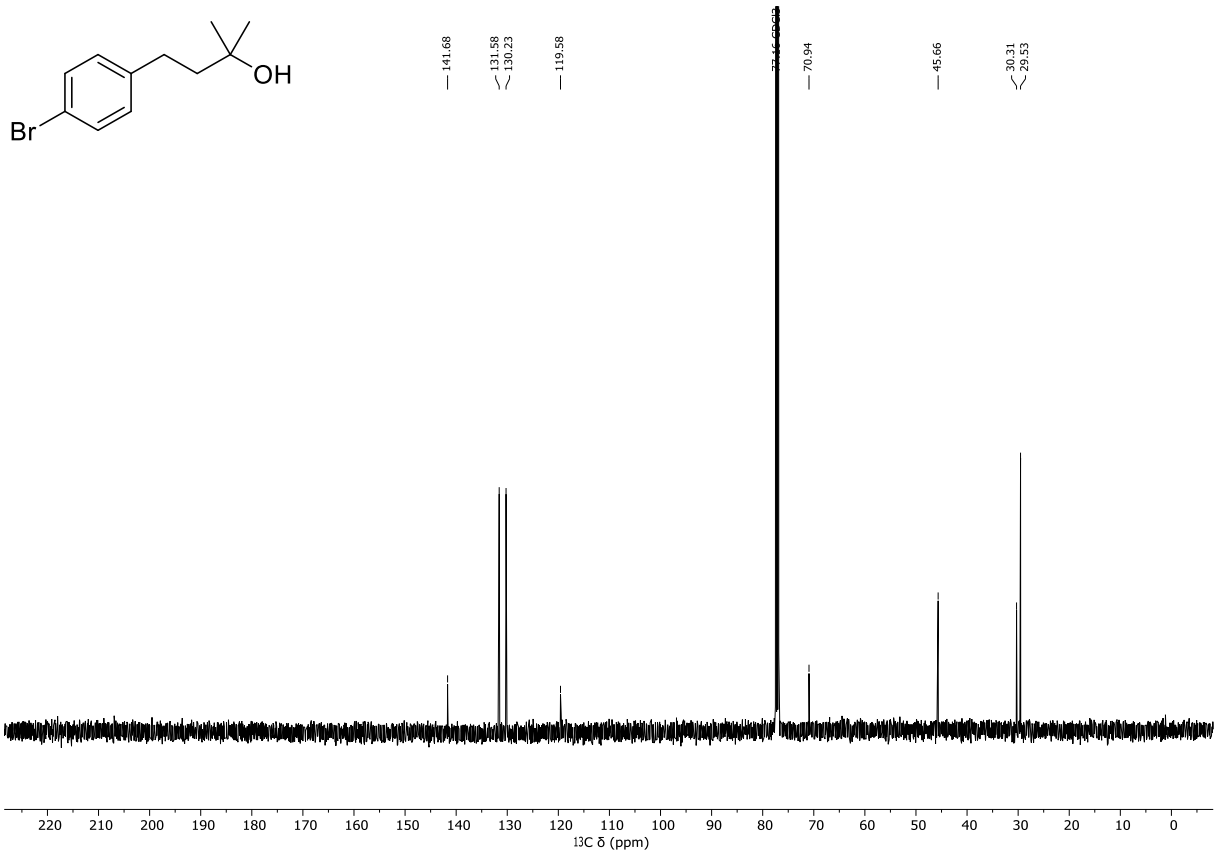
2,3,3-Trimethyl-2-butyl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



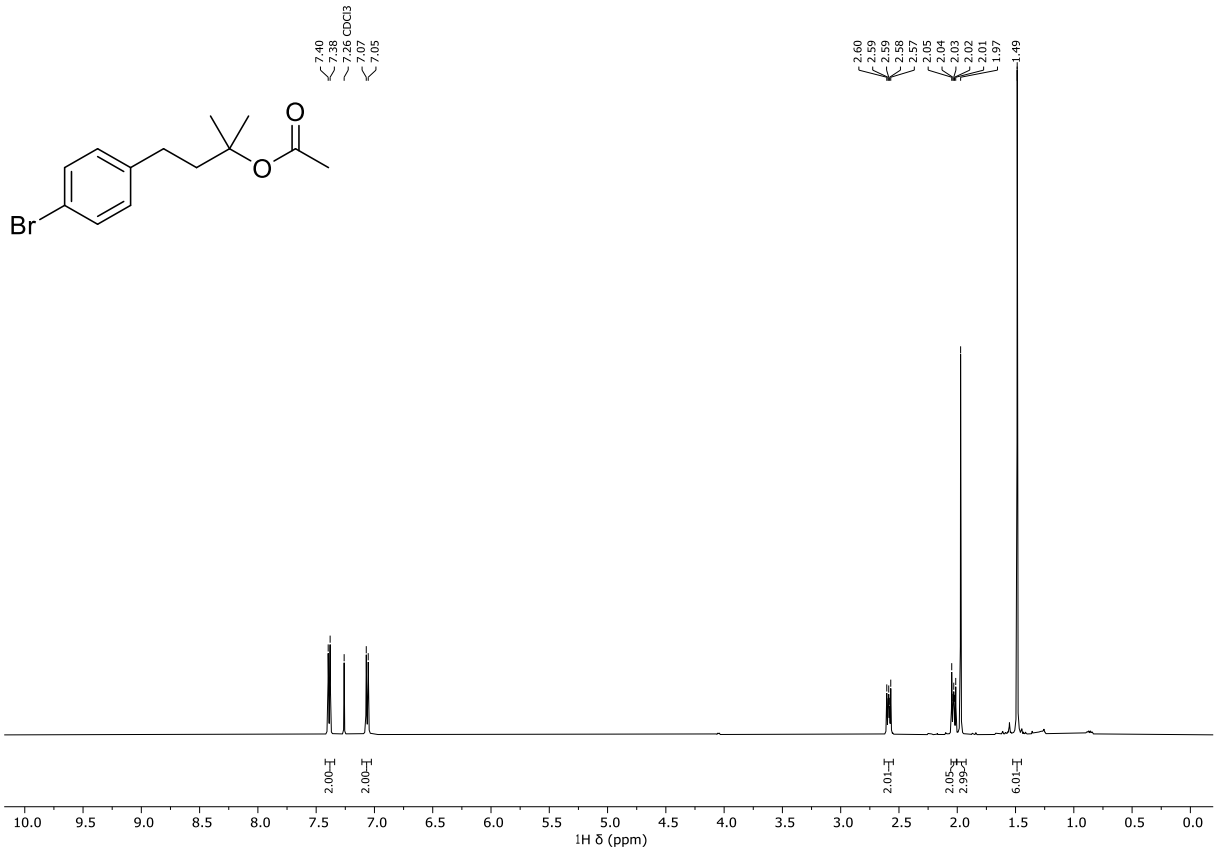
2-Methyl-4-(4-bromophenyl)-2-butanol - ^{1}H NMR (500 MHz, $CDCl_3$)



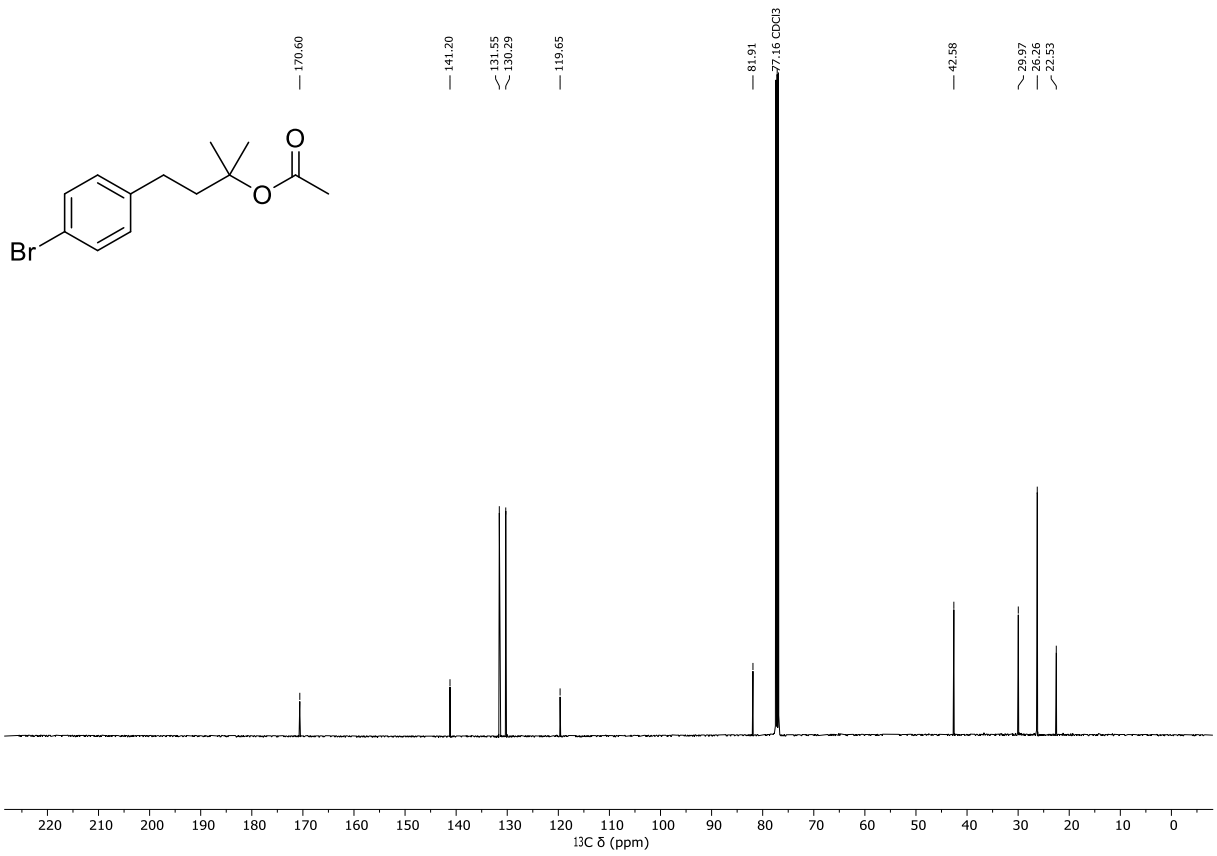
2-Methyl-4-(4-bromophenyl)-2-butanol - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



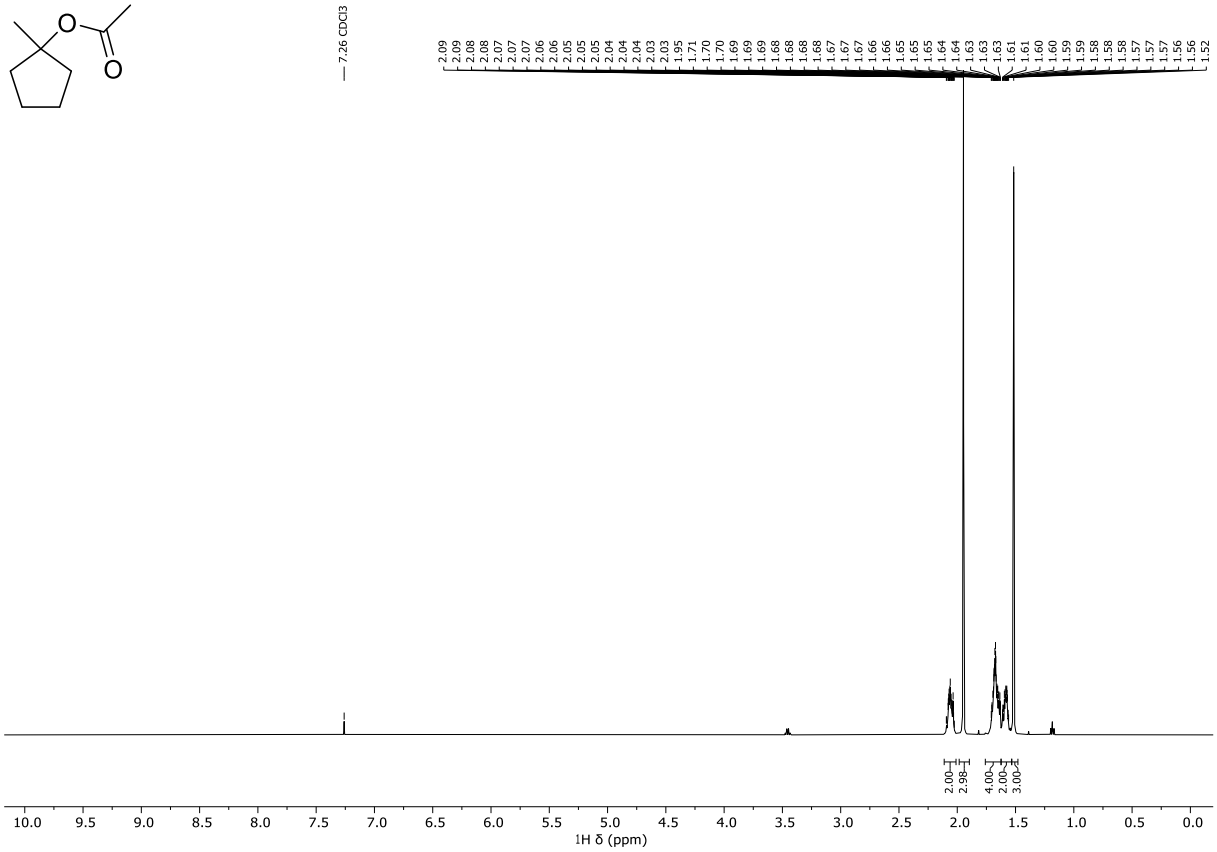
2-Methyl-4-(4-bromophenyl)-2-butyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



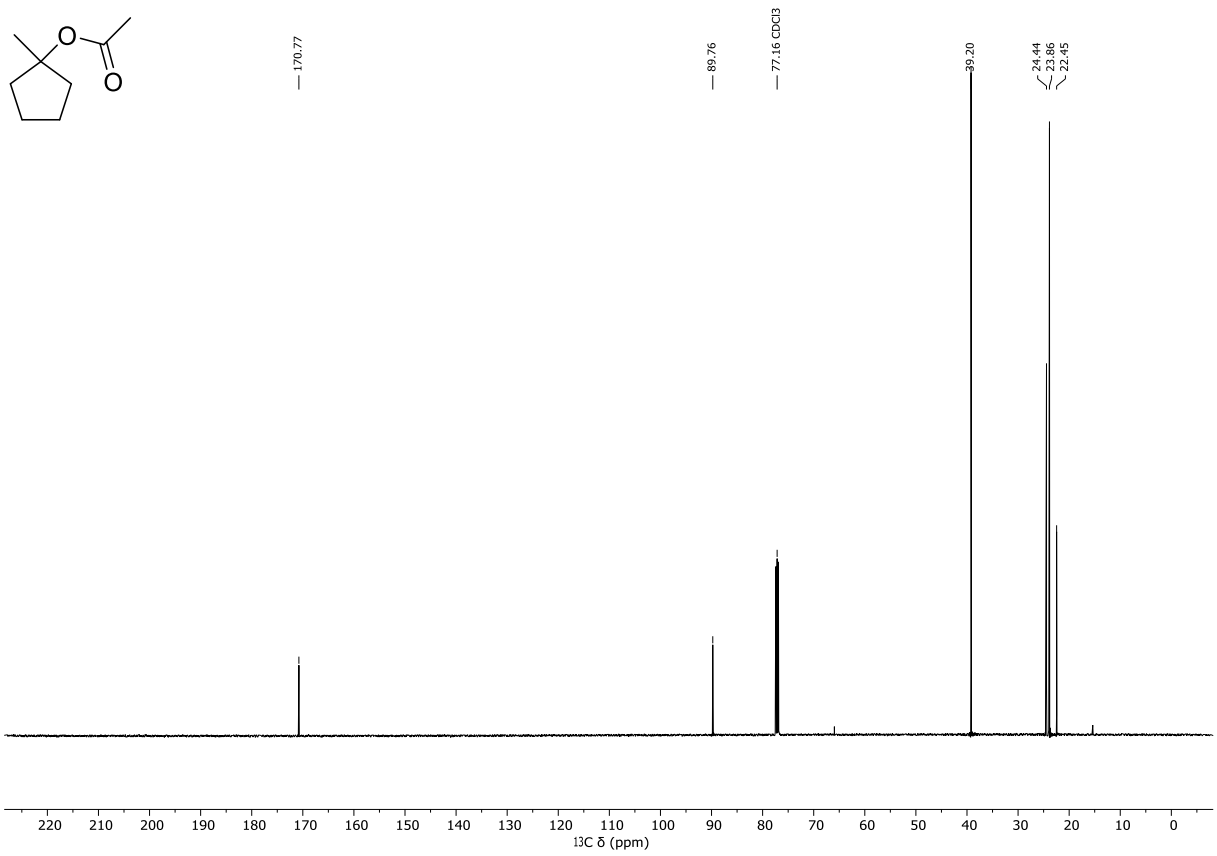
2-Methyl-4-(4-bromophenyl)-2-butyl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



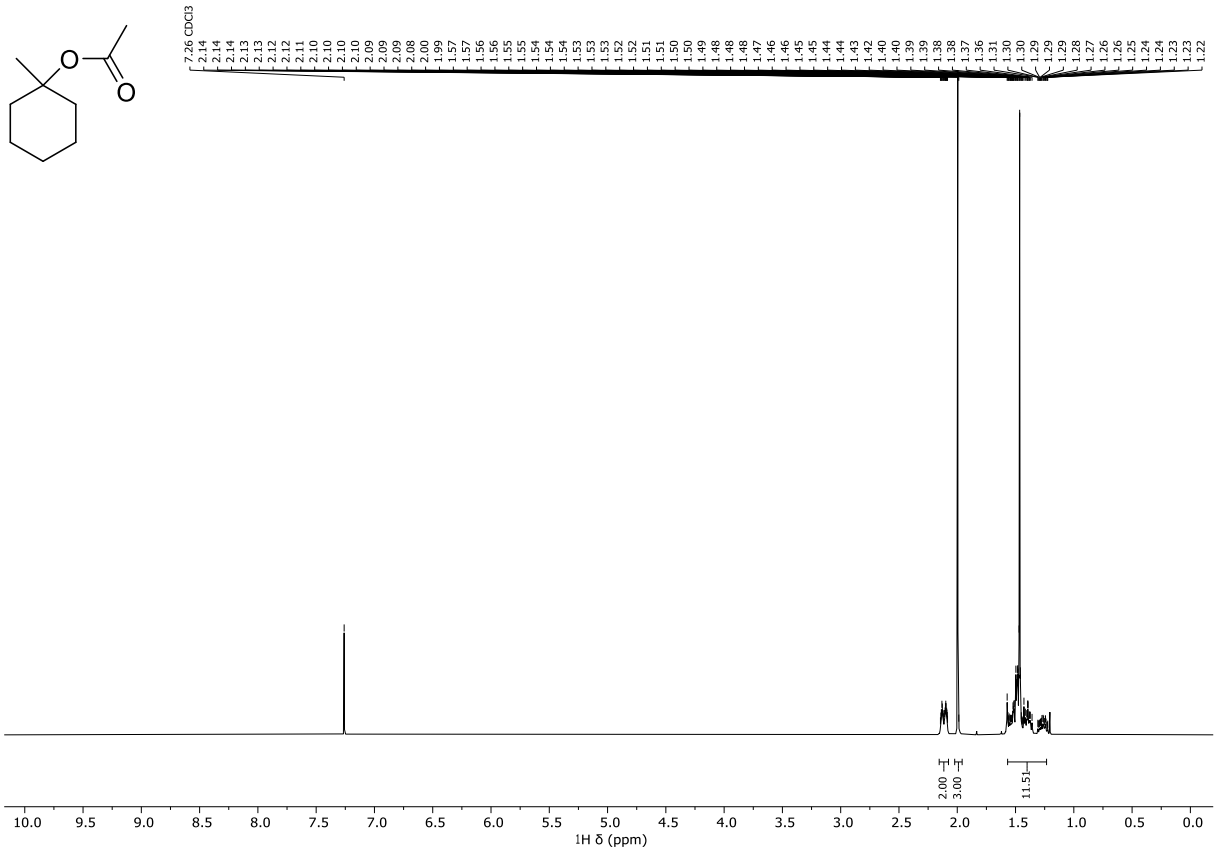
1-Methylcyclopentyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



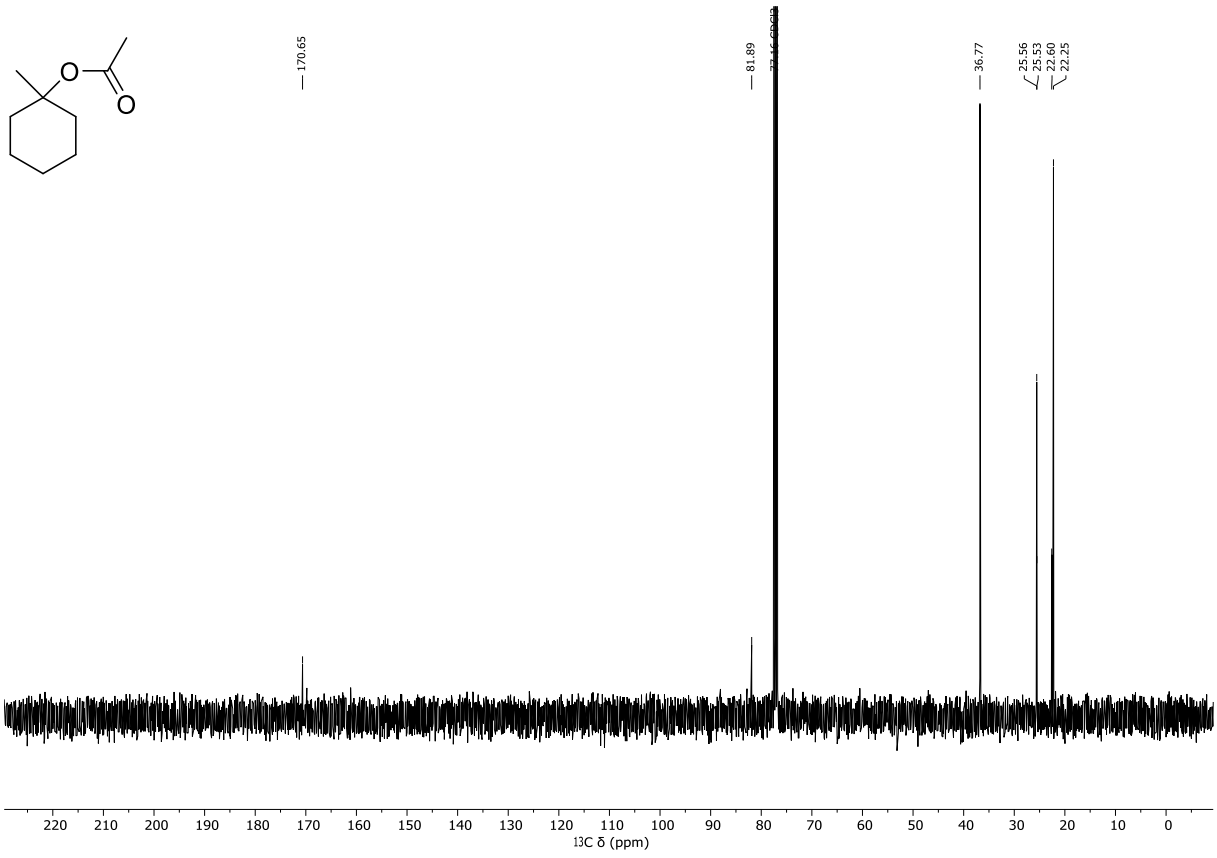
1-Methylcyclopentyl acetate - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



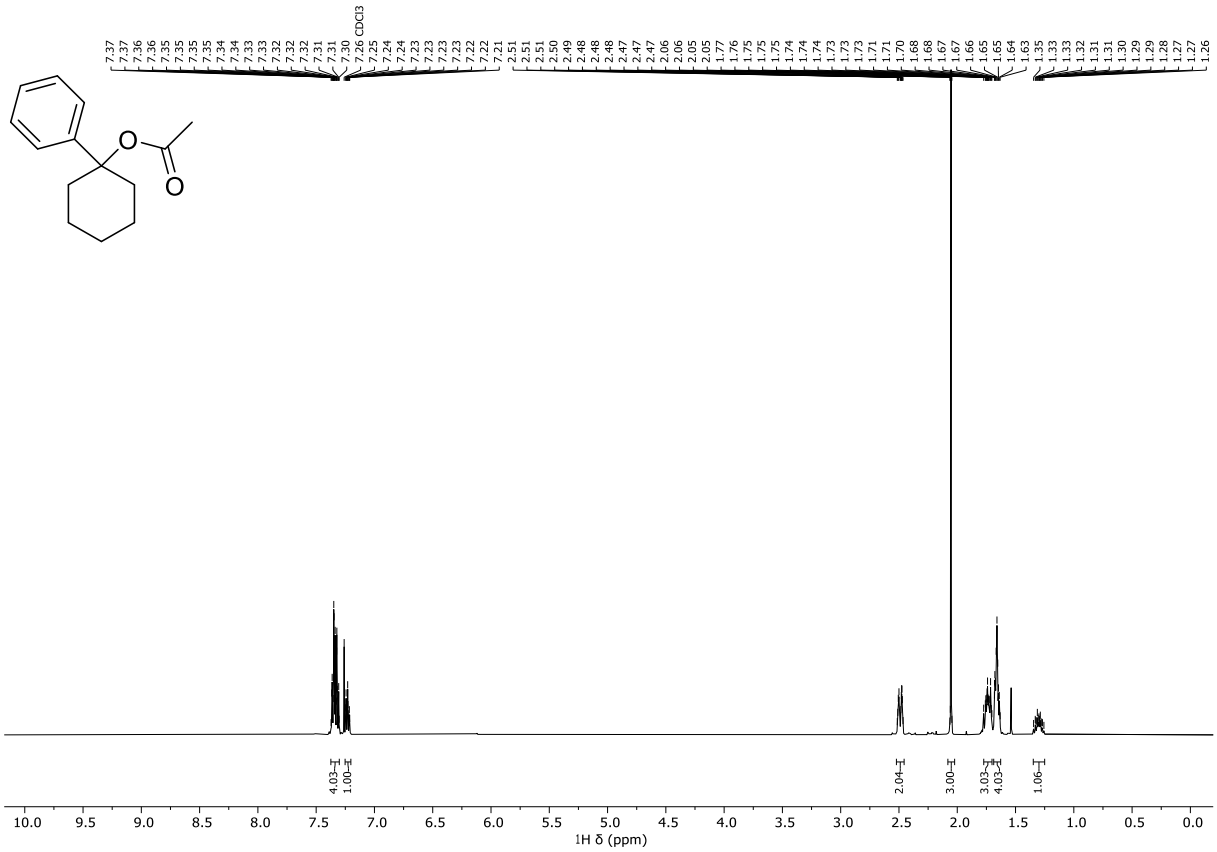
1-Methylcyclohexyl acetate - ^{1}H NMR (400 MHz, $CDCl_3$)



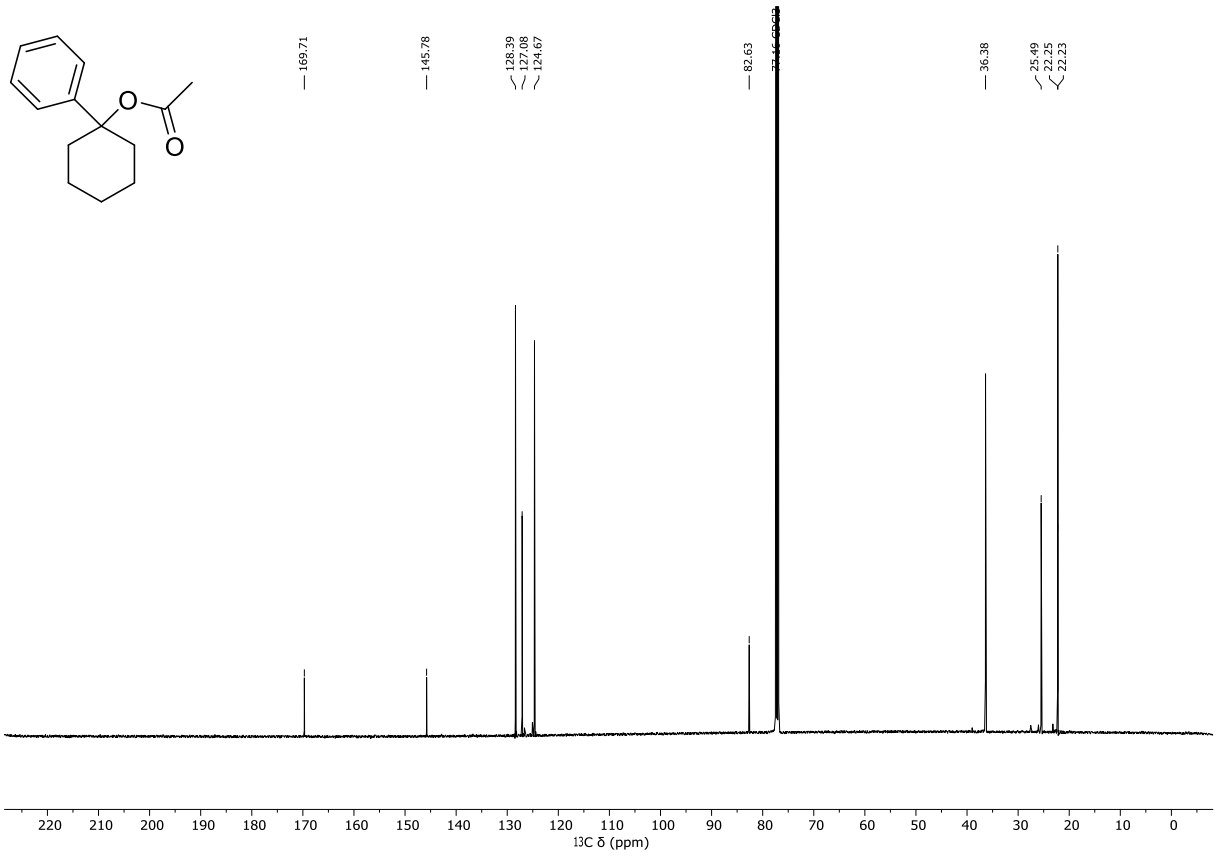
1-Methylcyclohexyl acetate - ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



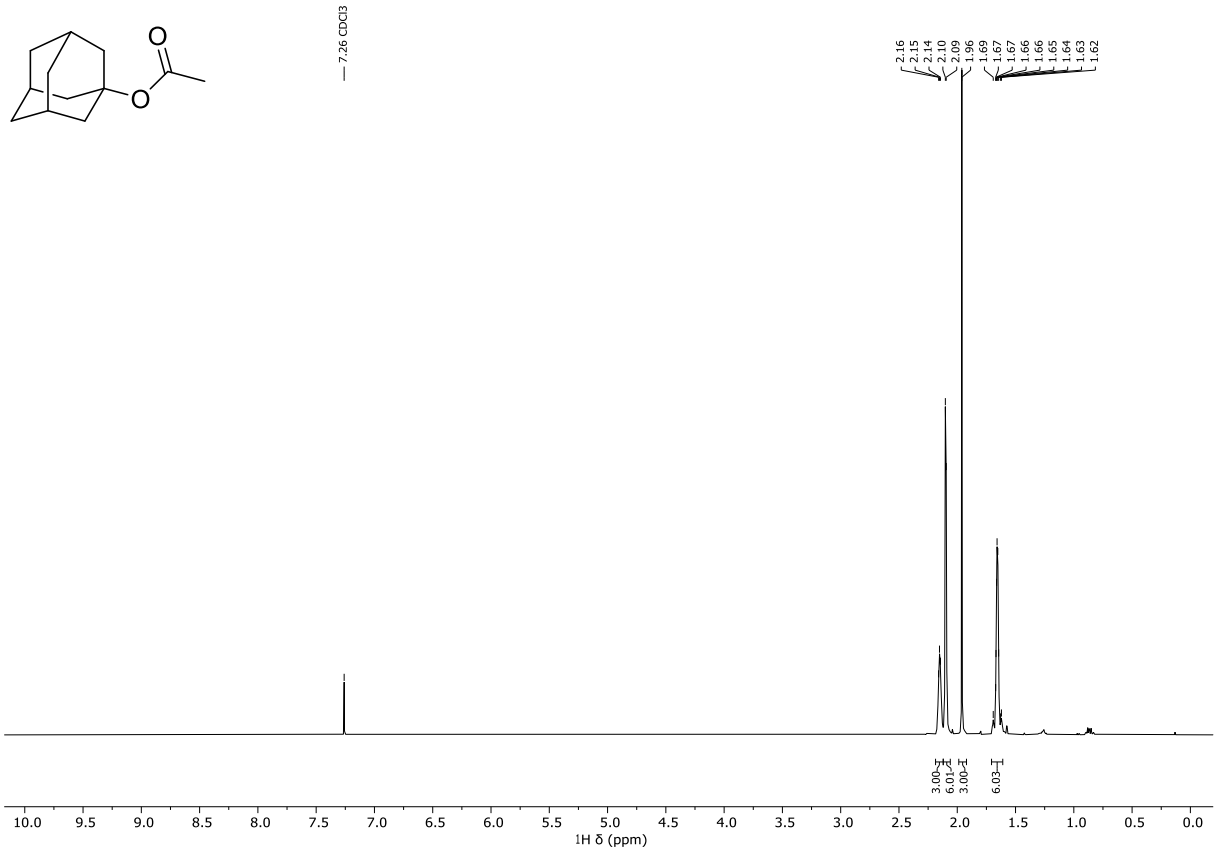
1-Phenylcyclohexyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



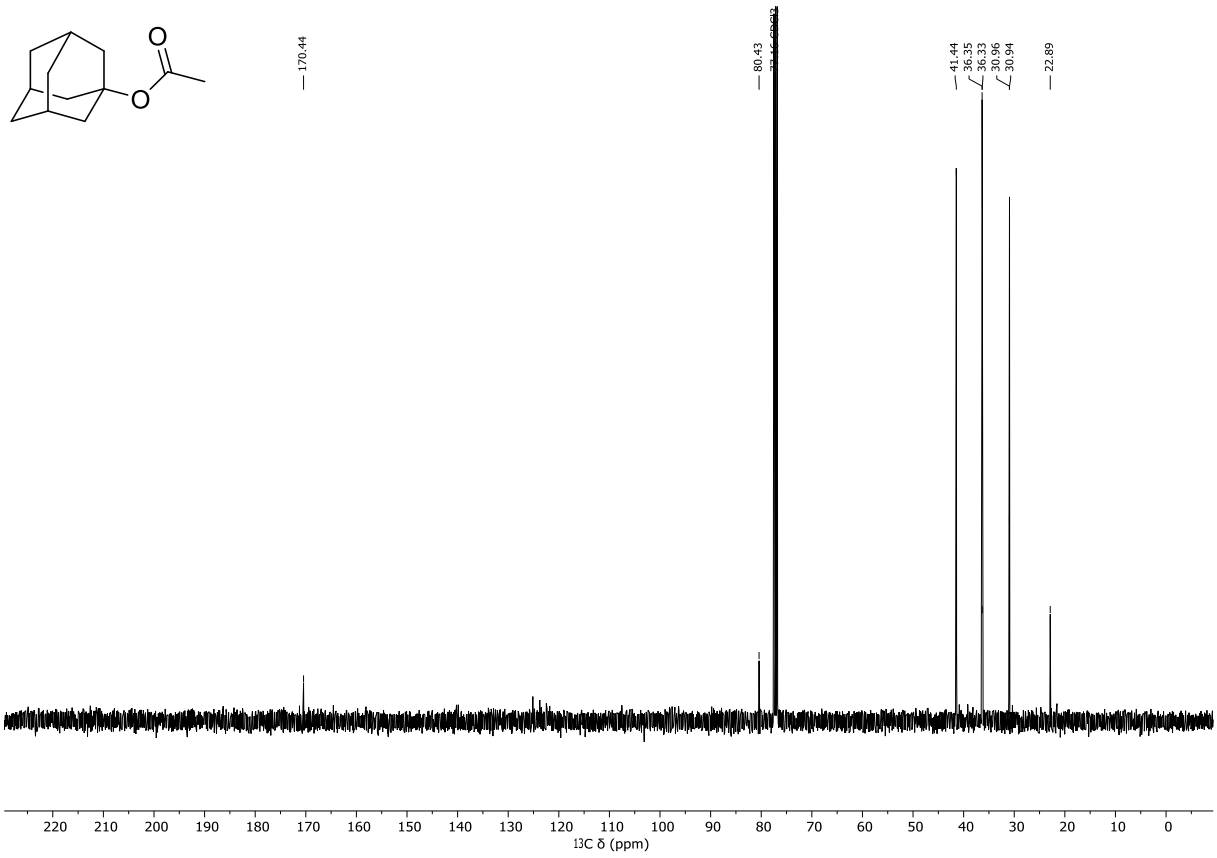
1-Phenylcyclohexyl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



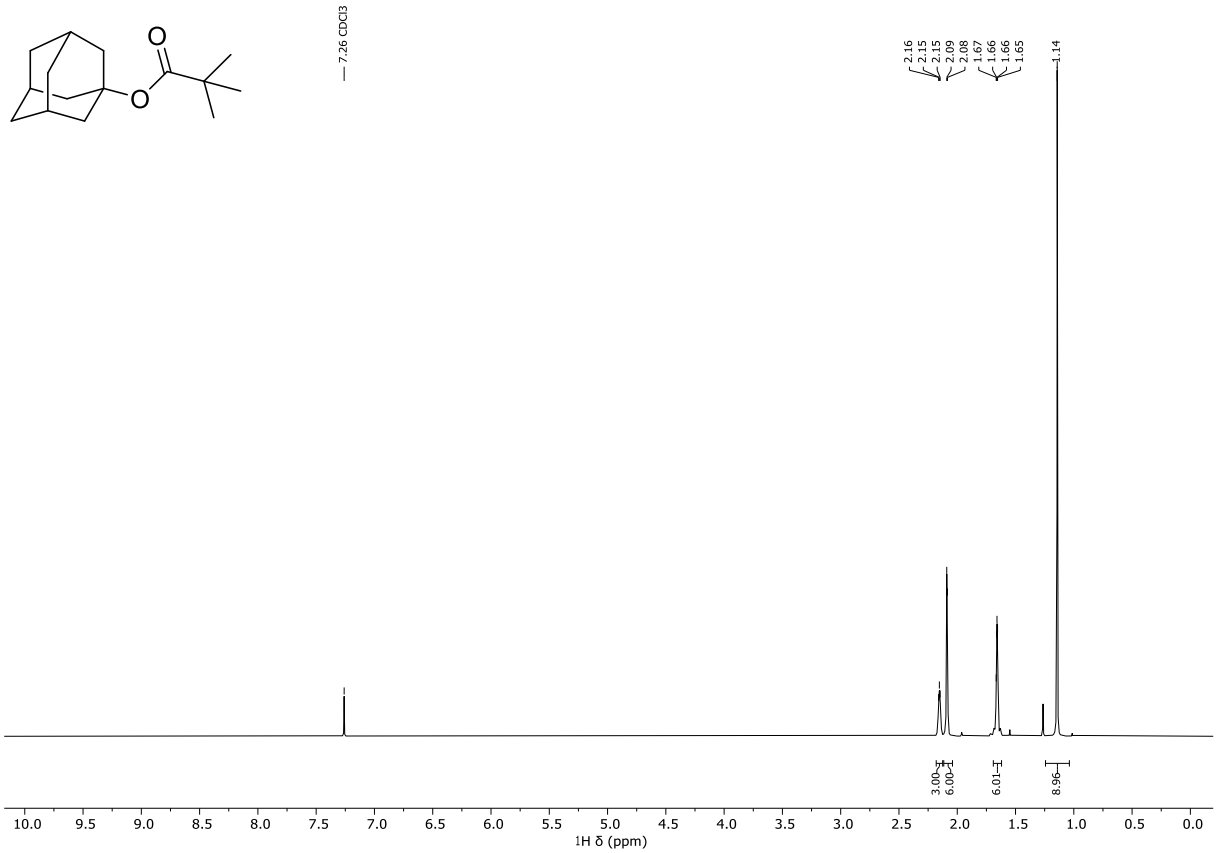
1-Adamantyl acetate - ^{1}H NMR (400 MHz, $CDCl_3$)



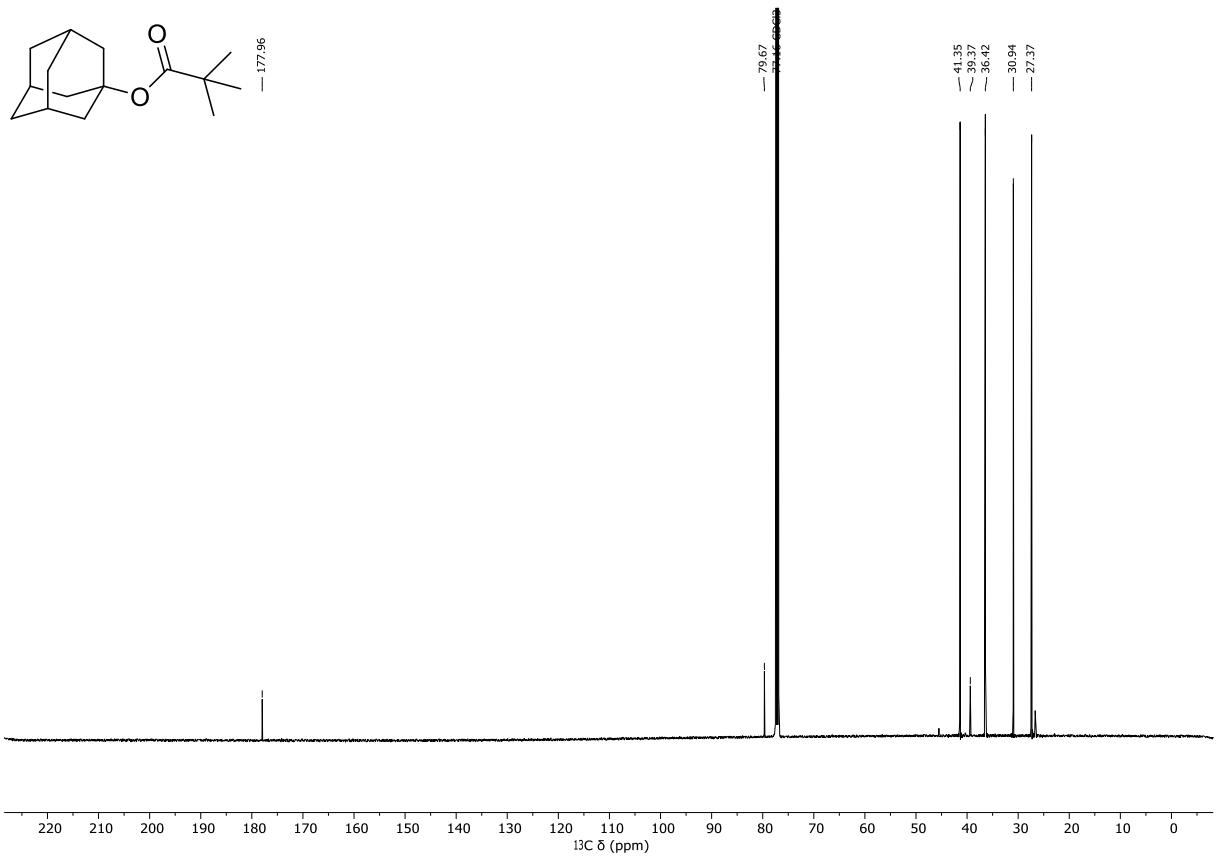
1-Adamantyl acetate - ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



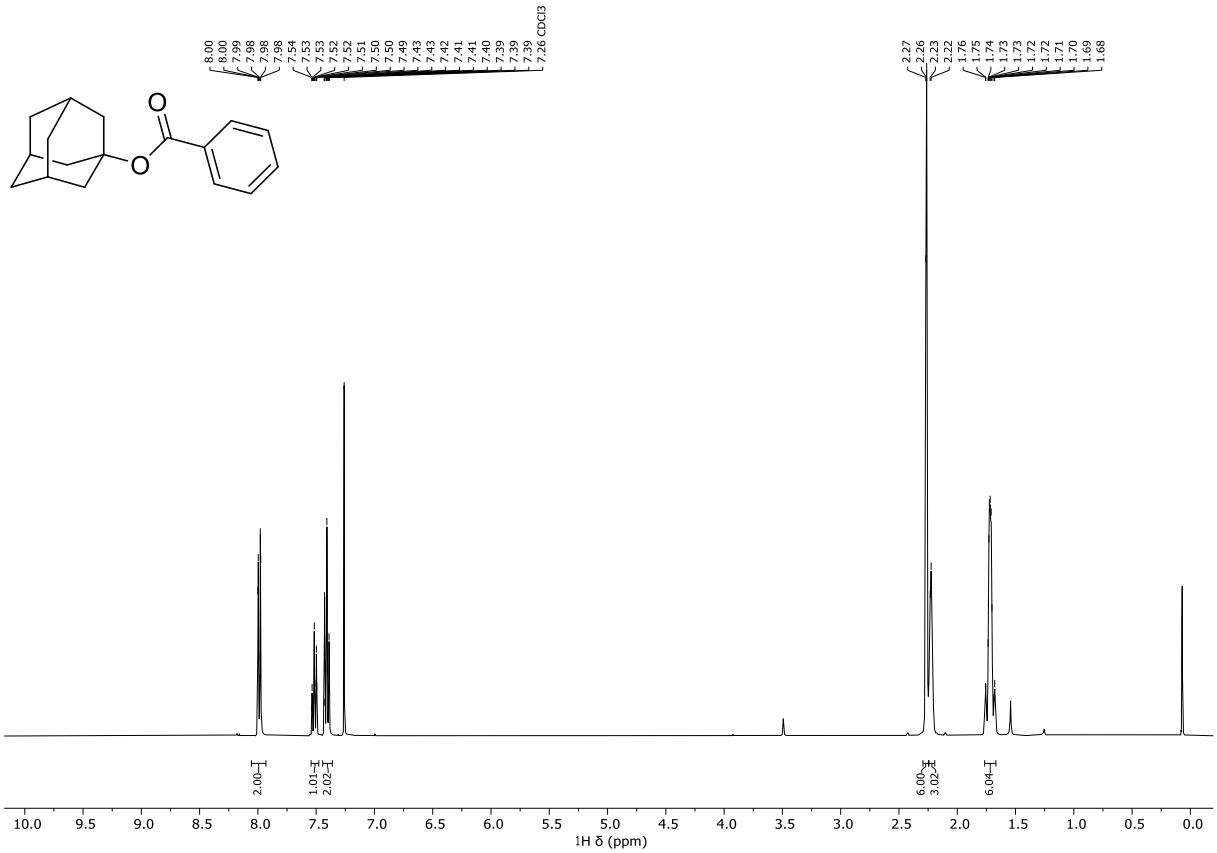
1-Adamantyl pivalate - ^{1}H NMR (500 MHz, $CDCl_3$)



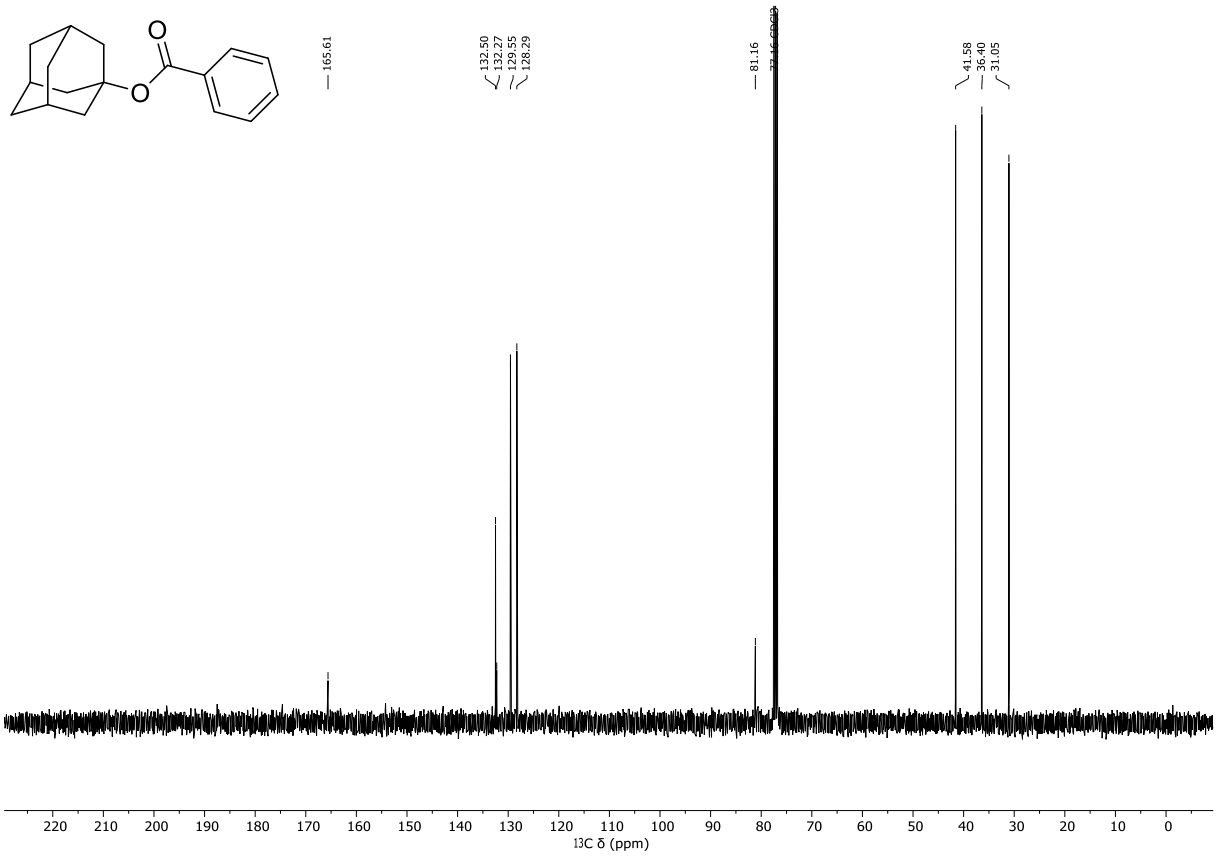
1-Adamantyl pivalate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



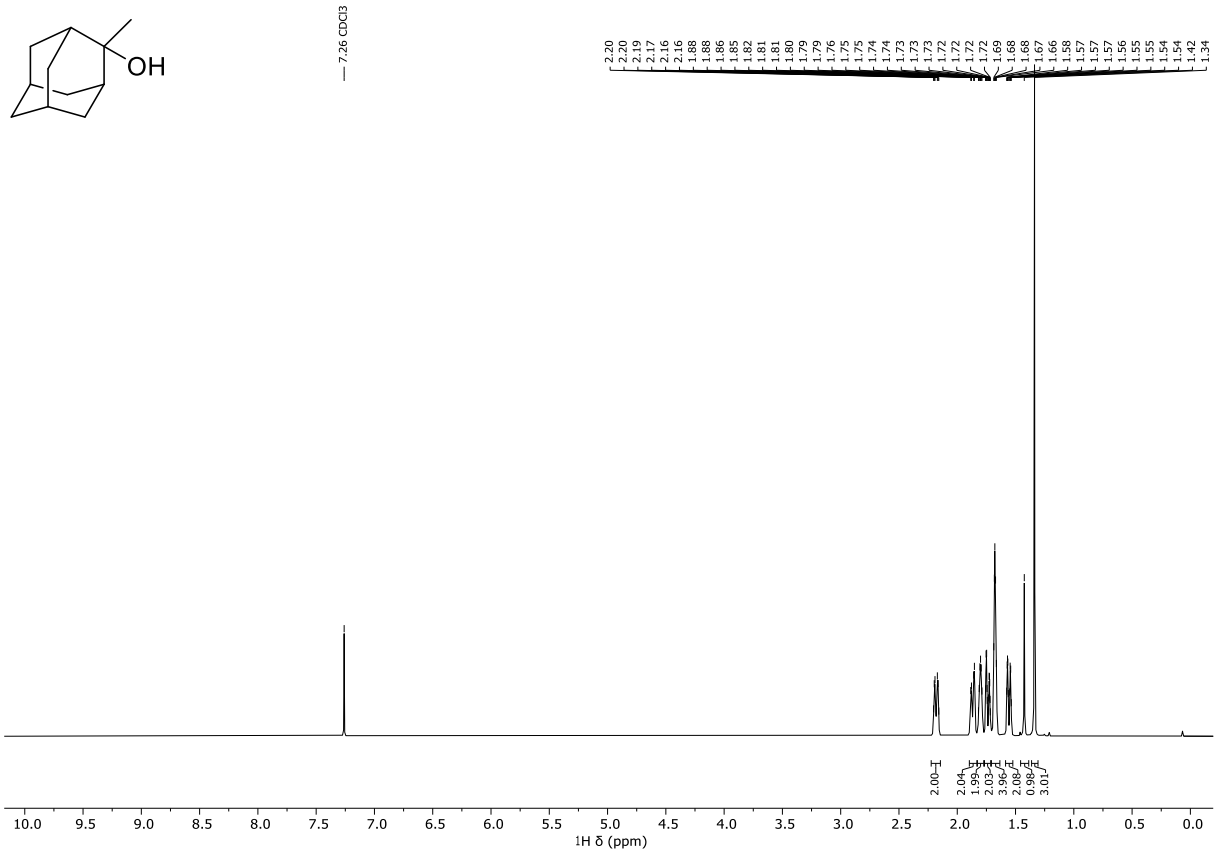
1-Adamantyl benzoate - ^{1}H NMR (400 MHz, $CDCl_3$)



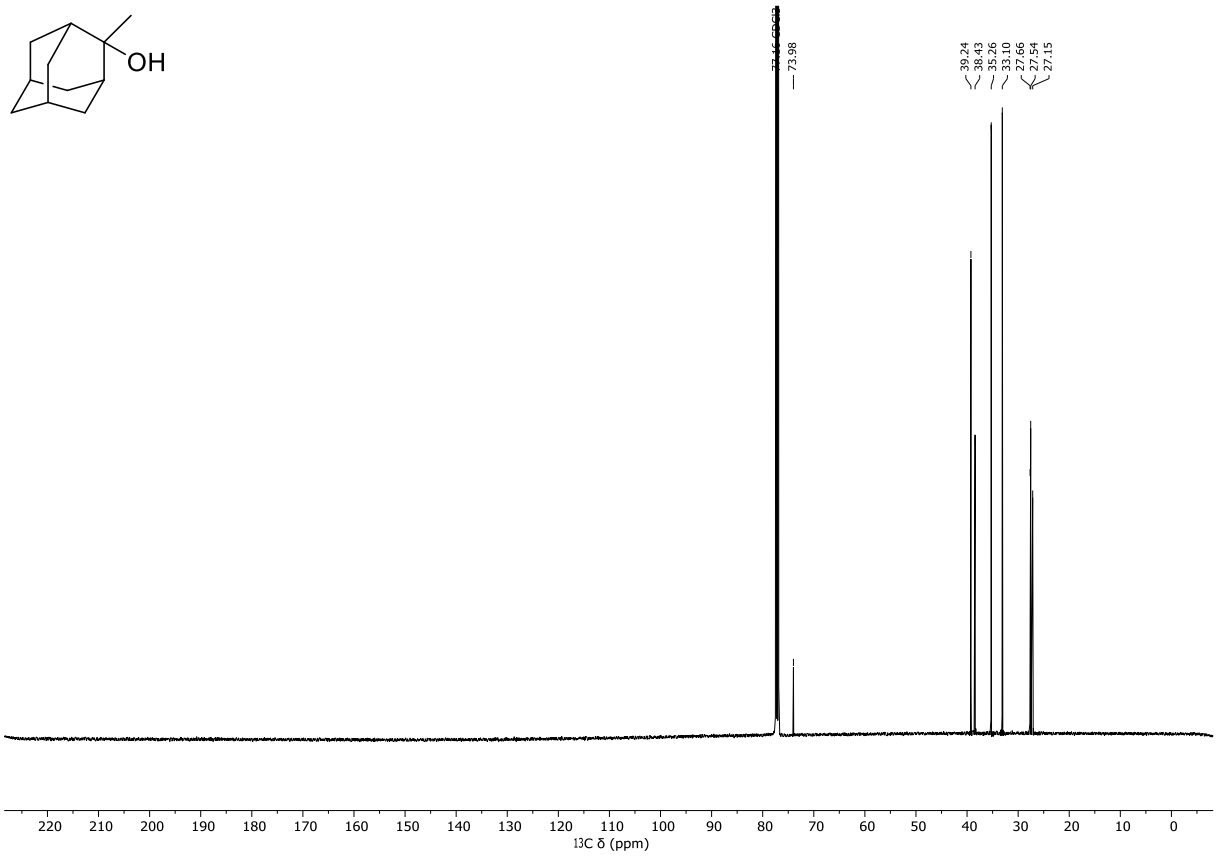
1-Adamantyl benzoate - ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



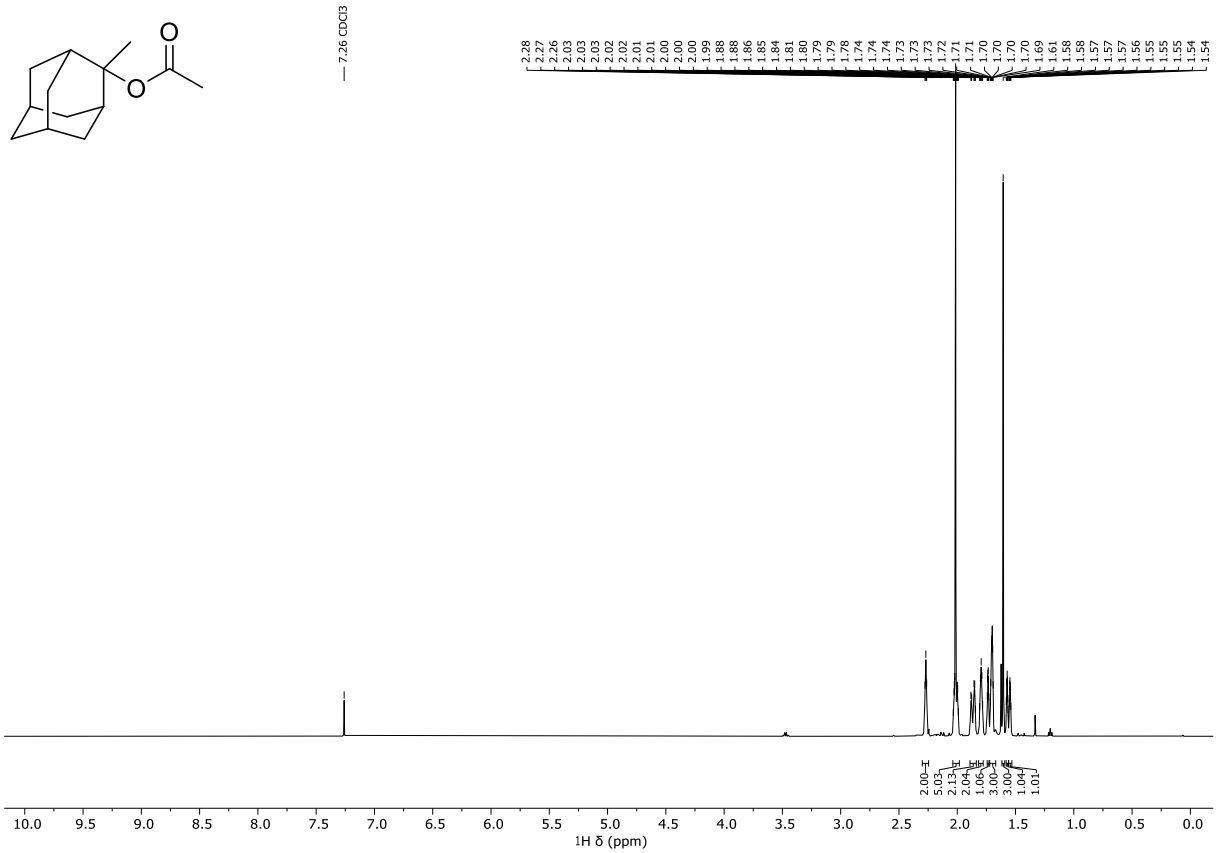
2-Methyl-2-adamantanol - ^{1}H NMR (500 MHz, $CDCl_3$)



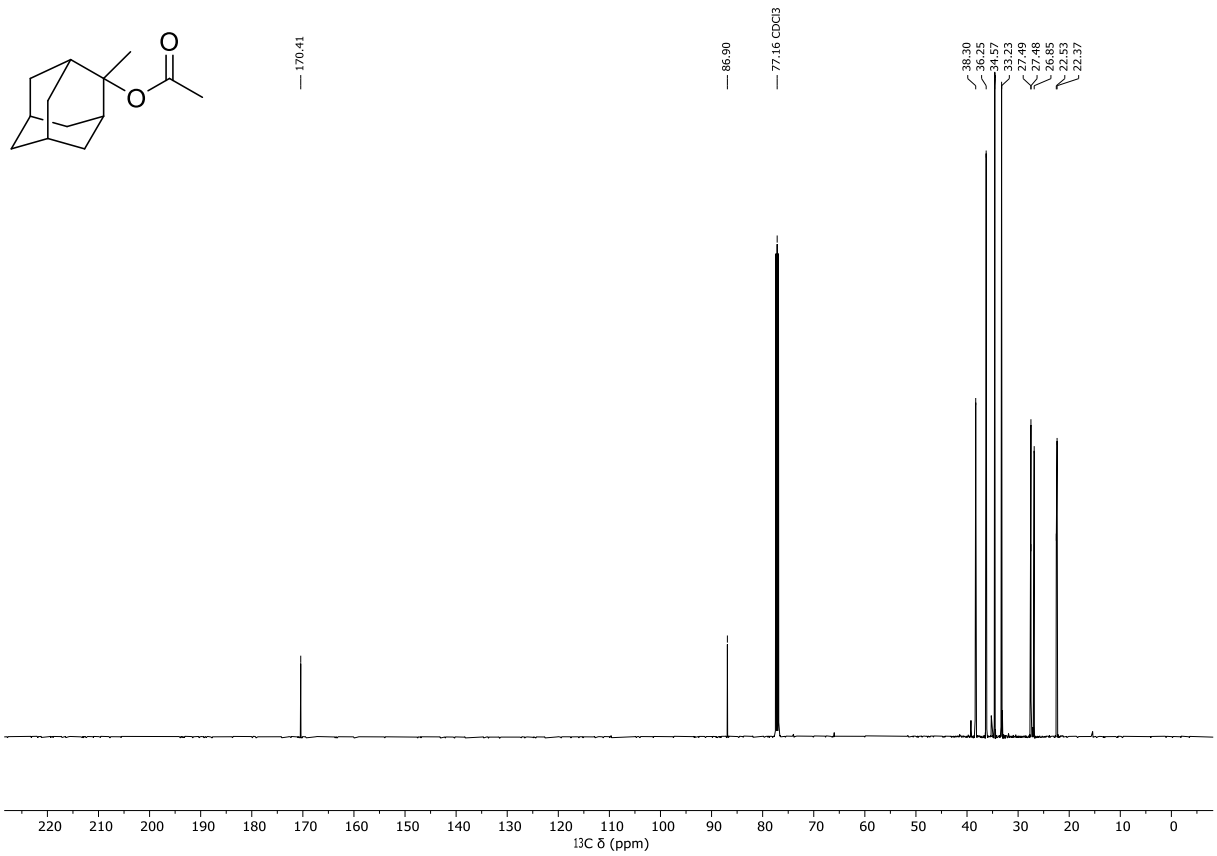
2-Methyl-2-adamantanol - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



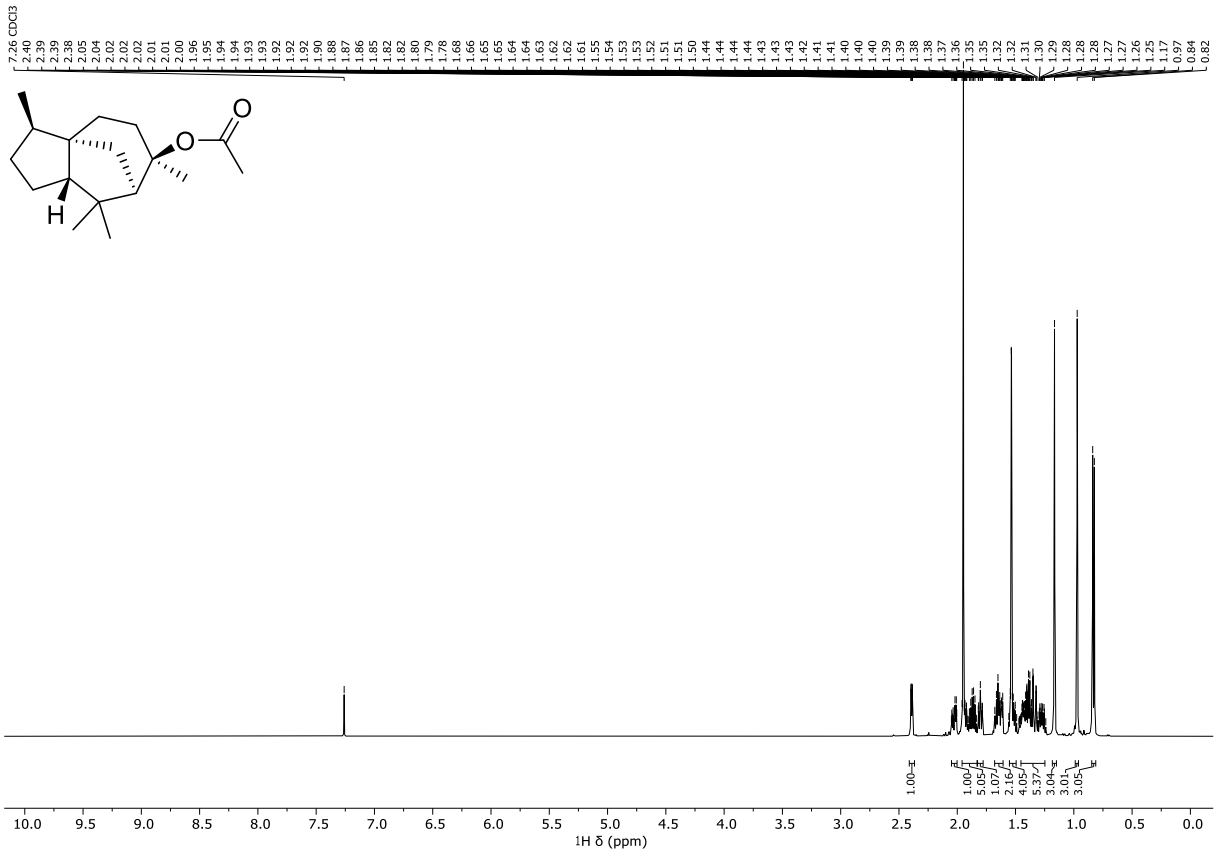
2-Methyl-2-adamantyl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



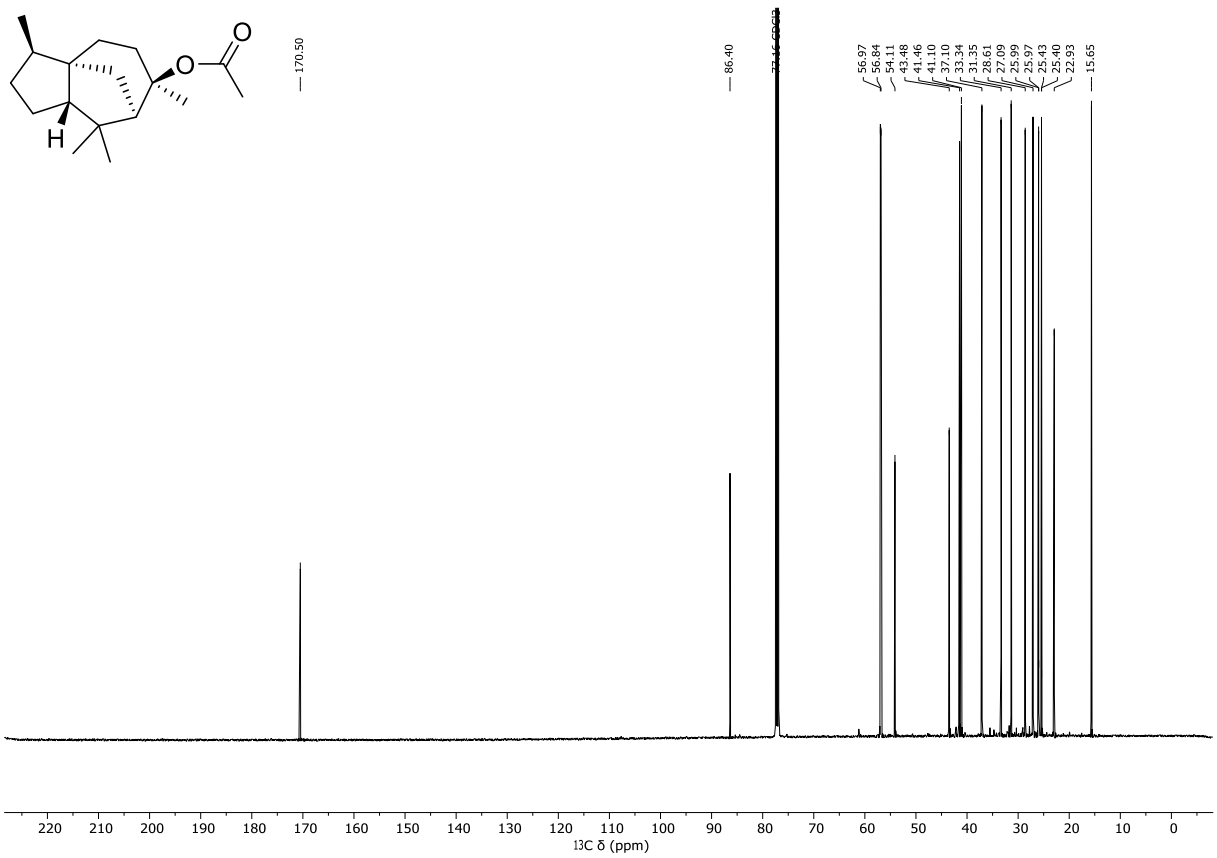
2-Methyl-2-adamantyl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



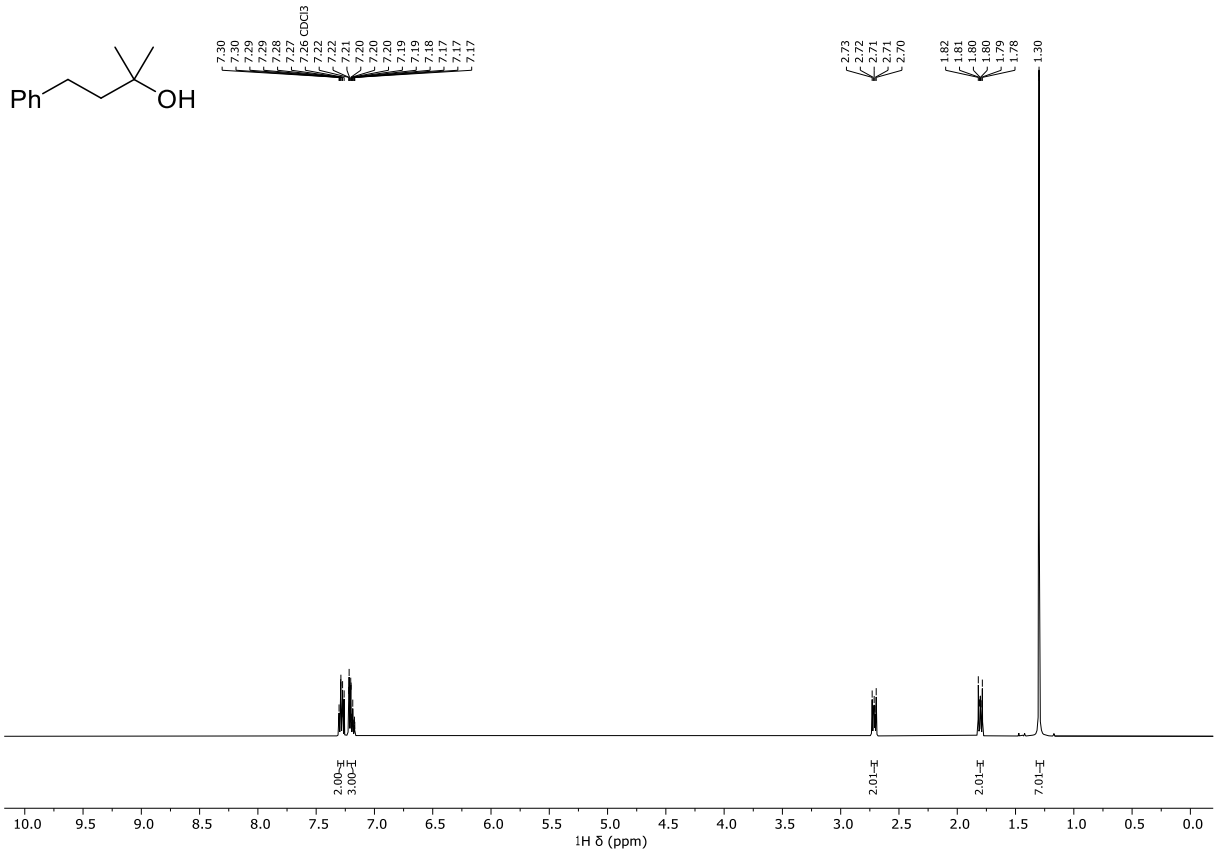
(+)-Cedryl acetate - ^{1}H NMR (500 MHz, $CDCl_3$)



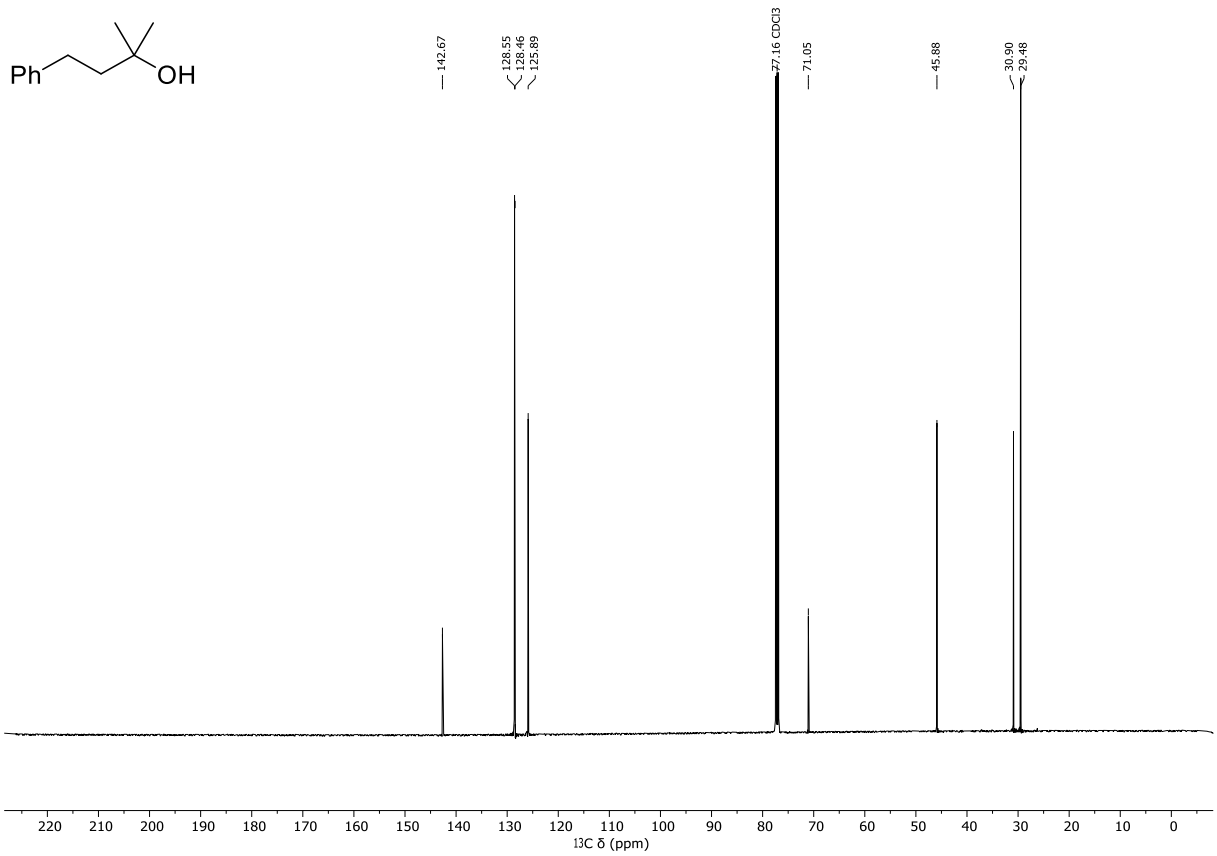
(+)-Cedryl acetate - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



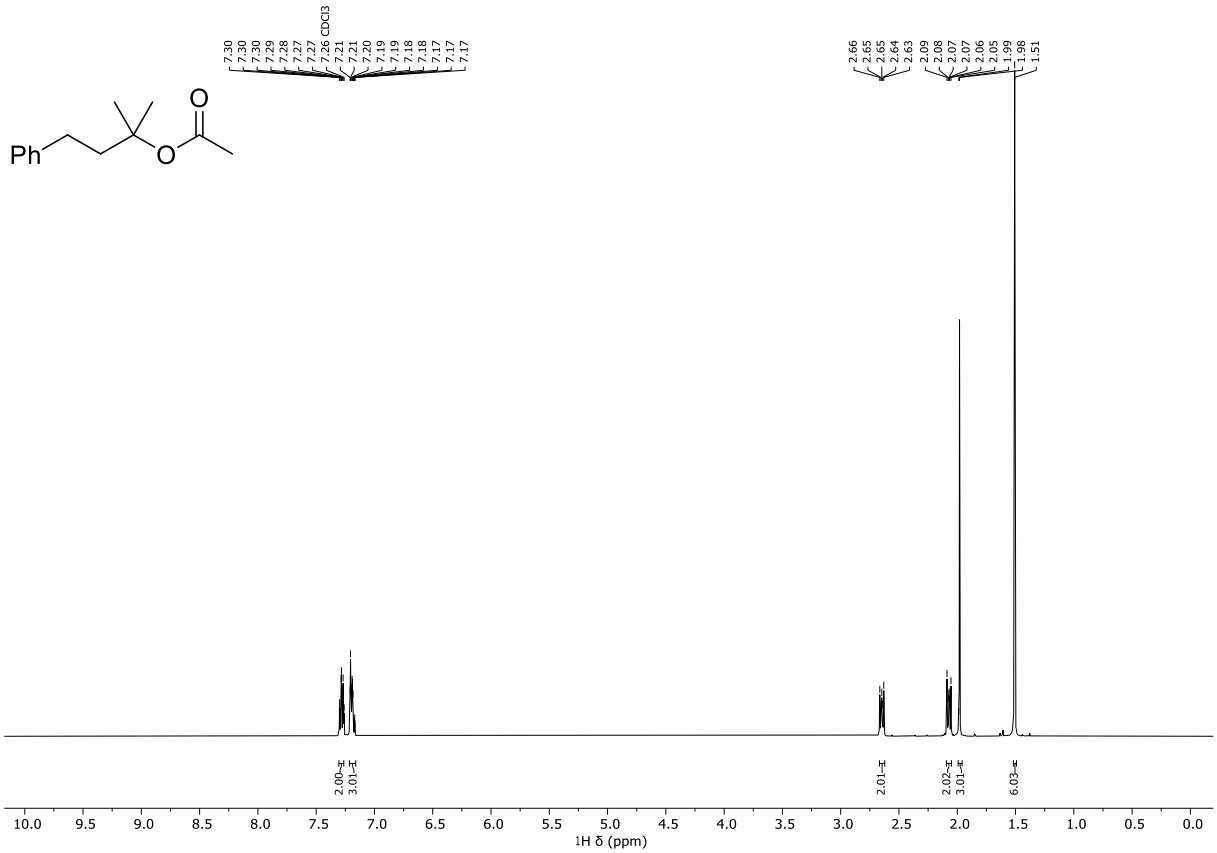
2-Methyl-4-phenyl-2-butanol - ^{1}H NMR (500 MHz, $CDCl_3$)



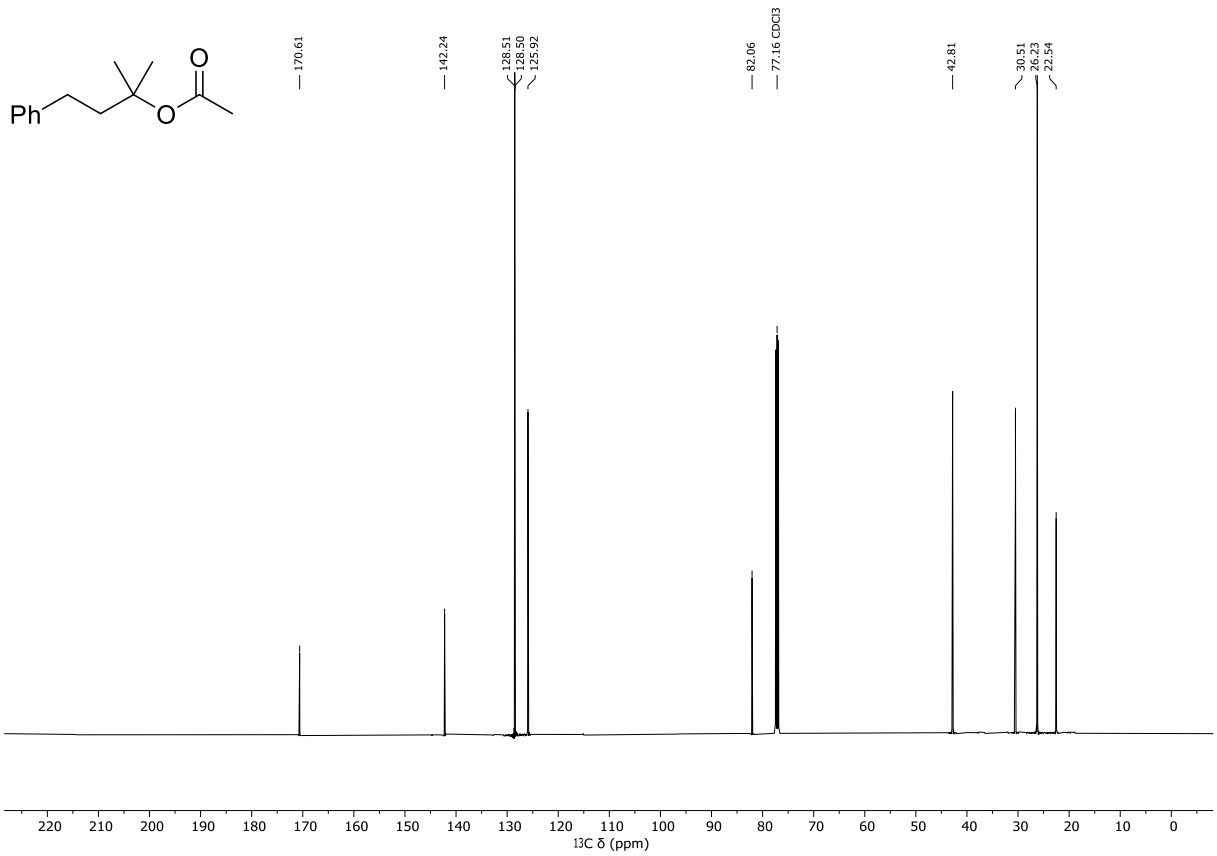
2-Methyl-4-phenyl-2-butanol - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



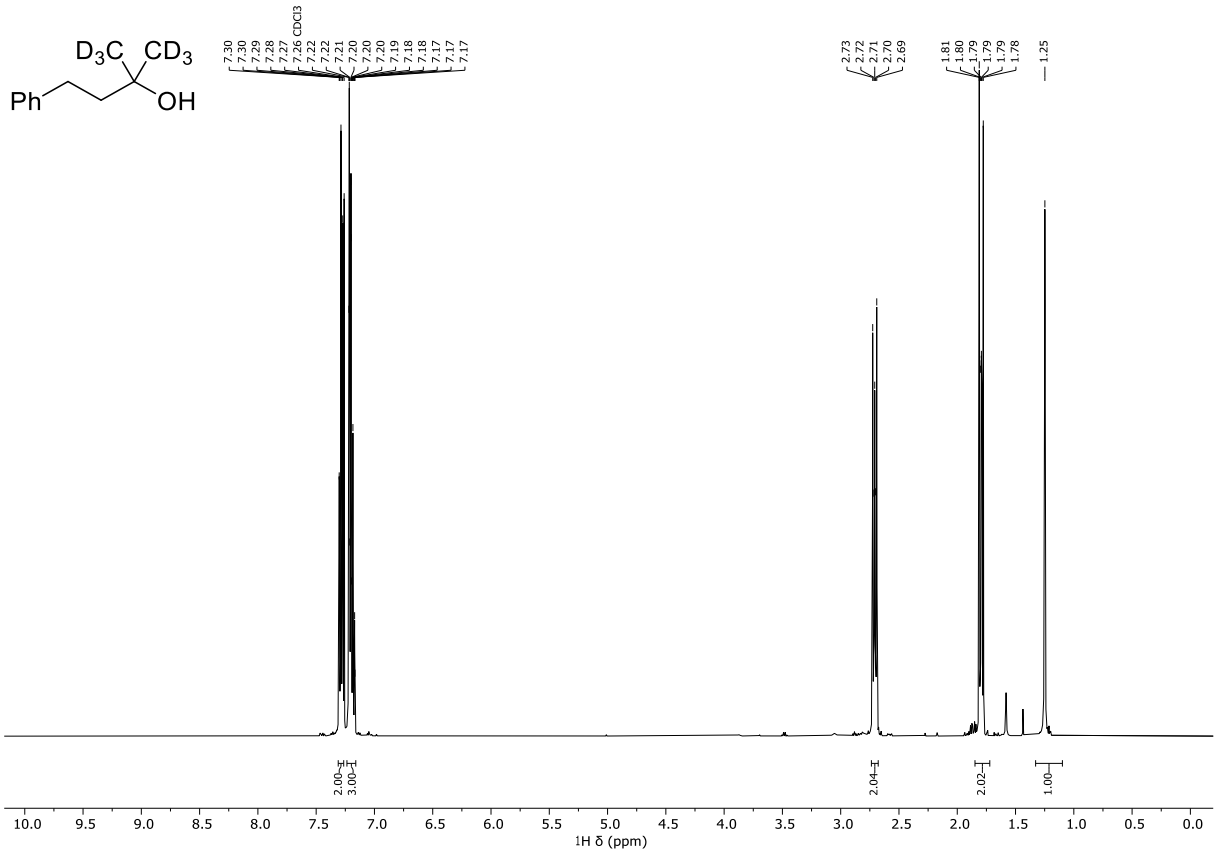
2-Methyl-4-phenyl-2-butyl acetate (d_0-2) - ^{1}H NMR (500 MHz, $CDCl_3$)



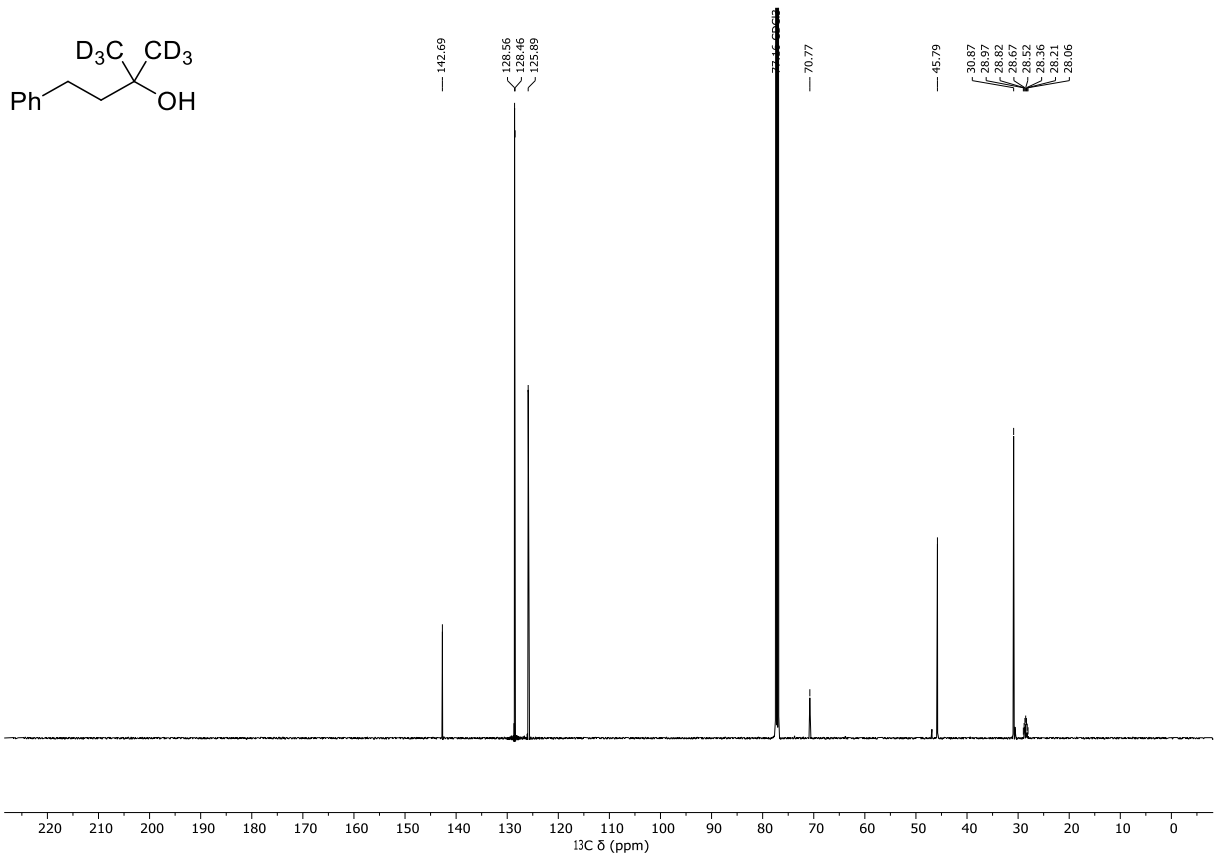
2-Methyl-4-phenyl-2-butyl acetate (d_0-2) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



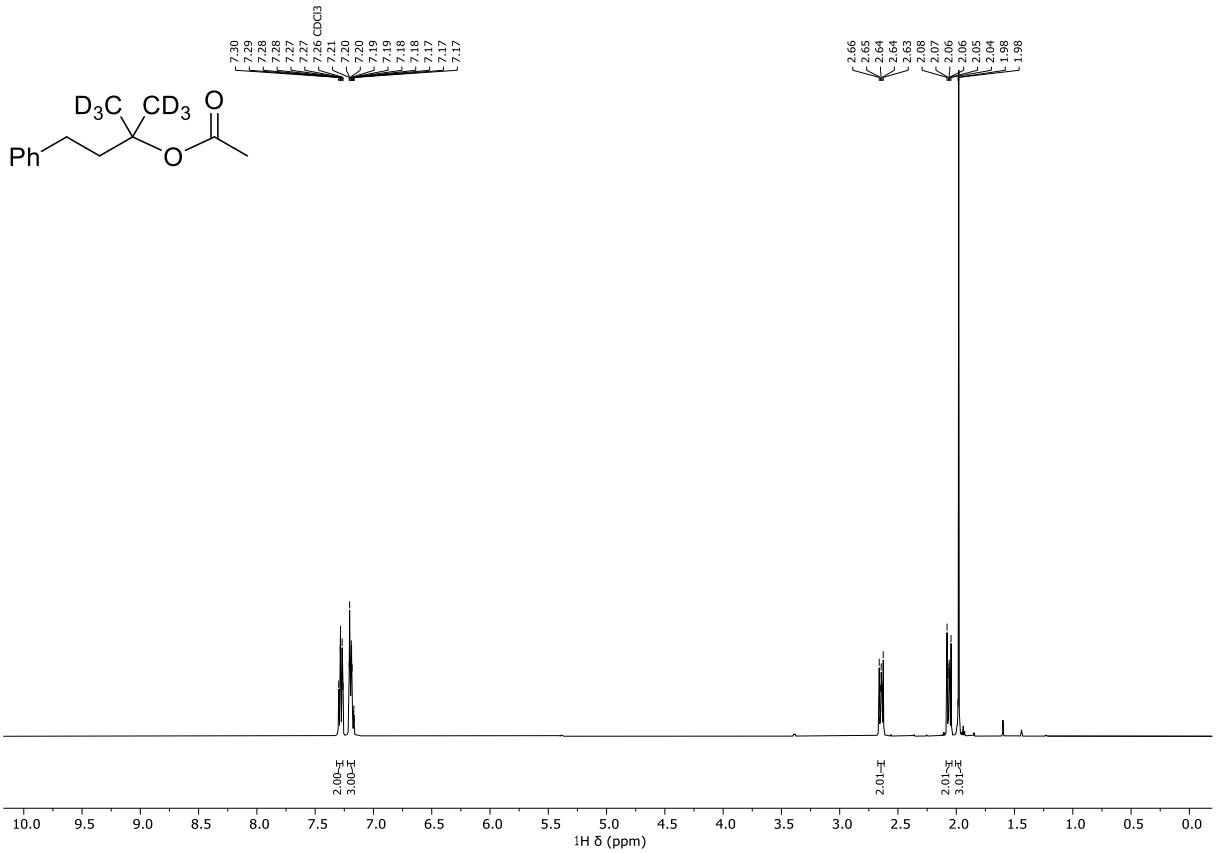
2-Methyl-4-phenyl-2-butanol-d_6 - ^{1}H NMR (500 MHz, $CDCl_3$)



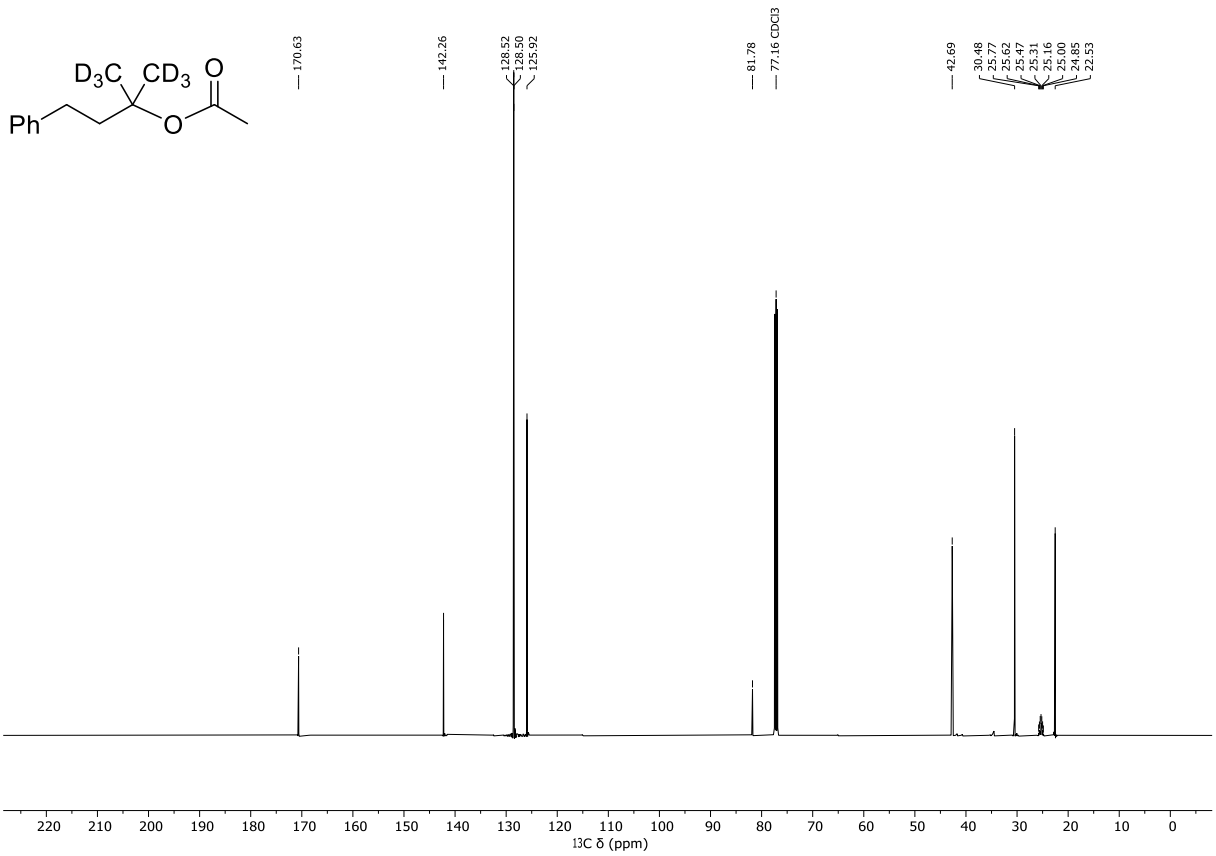
2-Methyl-4-phenyl-2-butanol-d_6 - $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



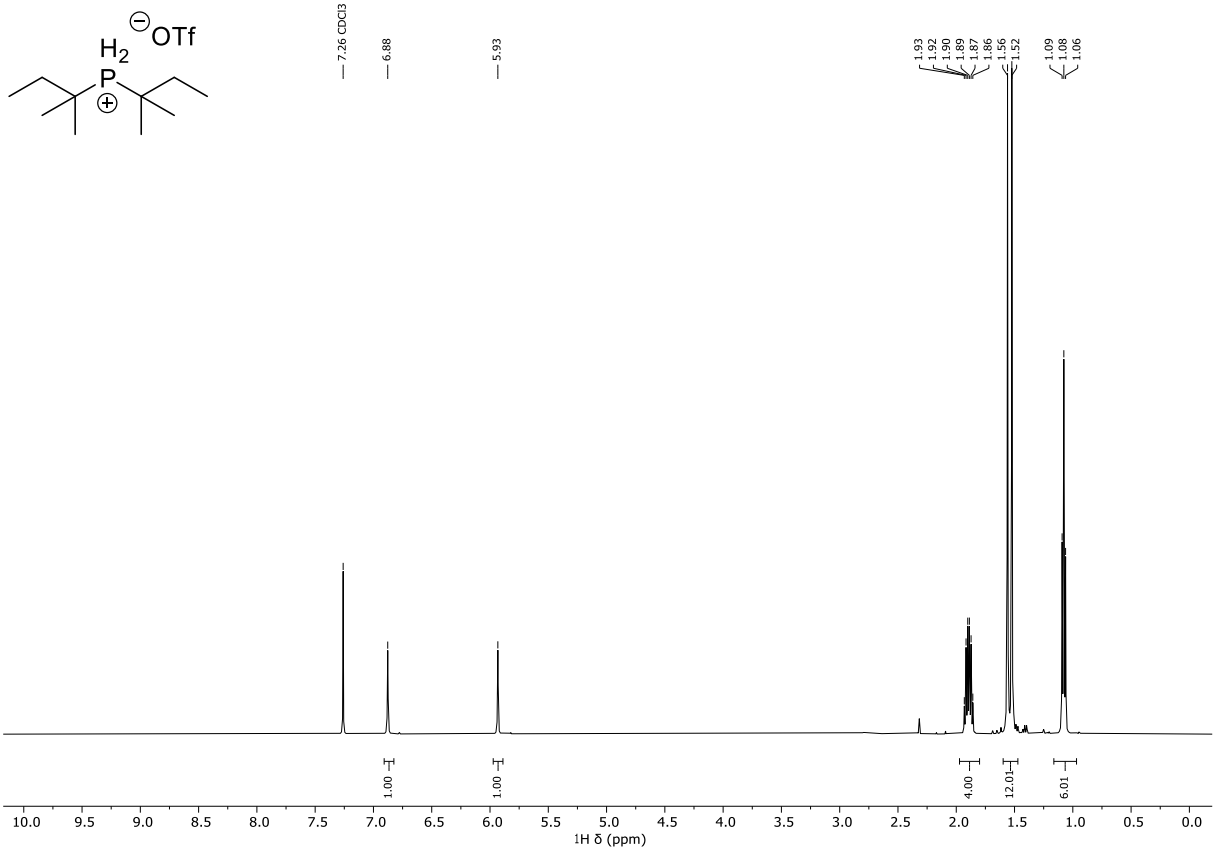
2-Methyl-4-phenyl-2-butyl acetate-d_6 (d_6-2) - ^{1}H NMR (500 MHz, $CDCl_3$)



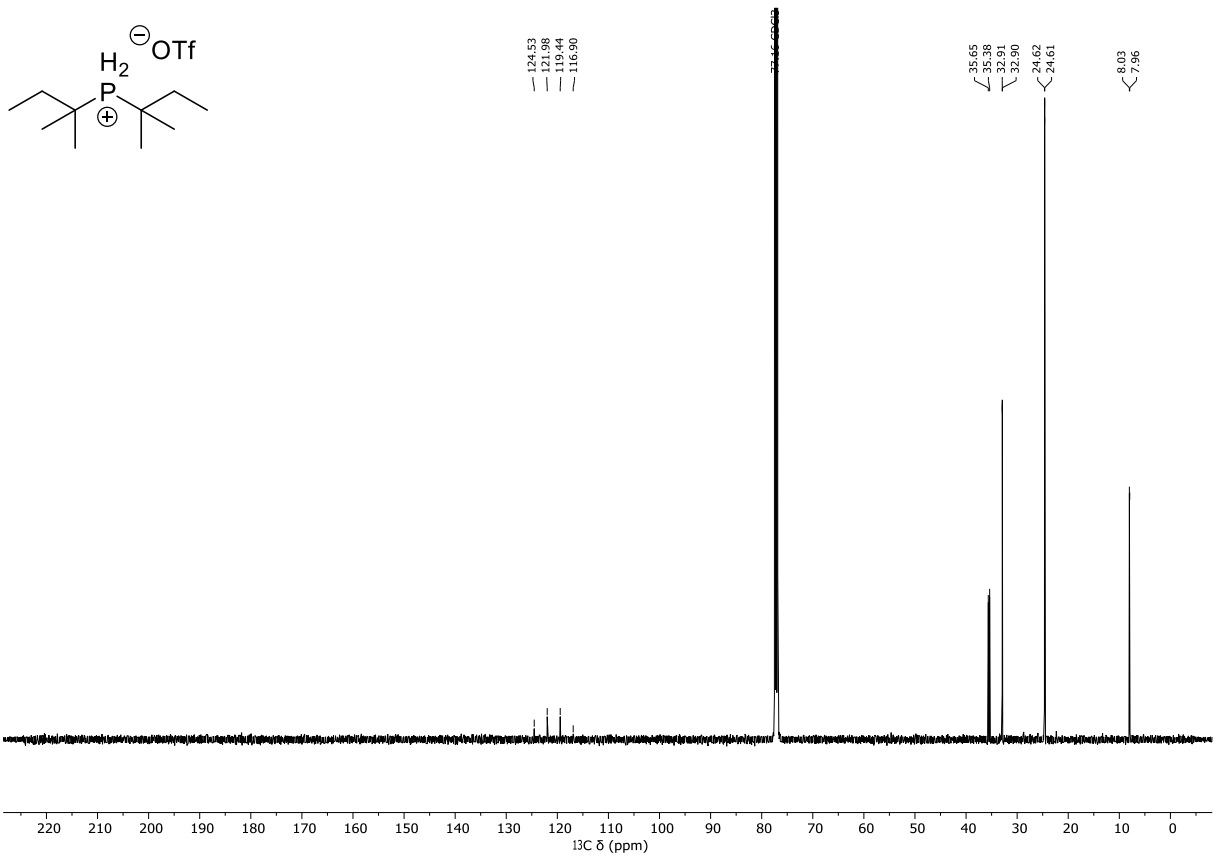
2-Methyl-4-phenyl-2-butyl acetate-d_6 (d_6-2) - $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



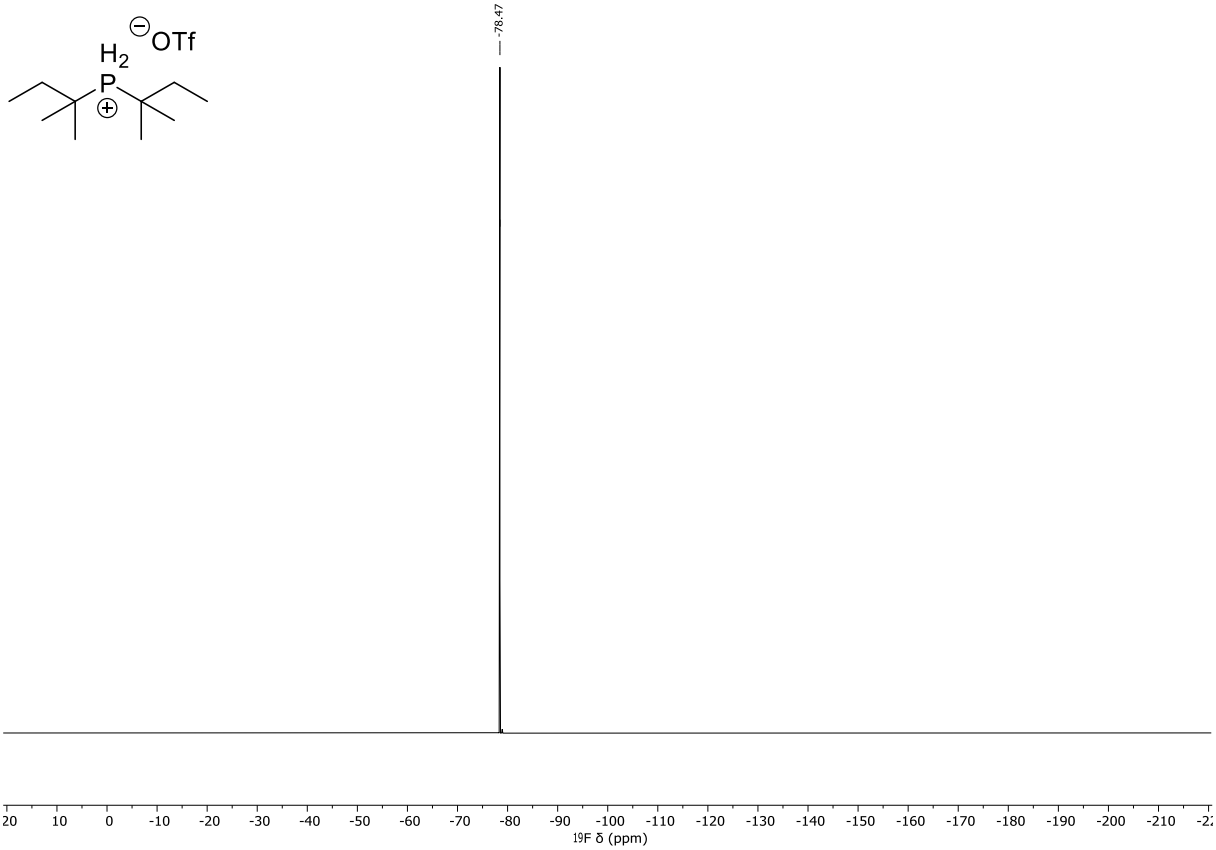
Di-*tert*-amylphosphonium triflate (1a) - ^{1}H NMR (500 MHz, $CDCl_3$)



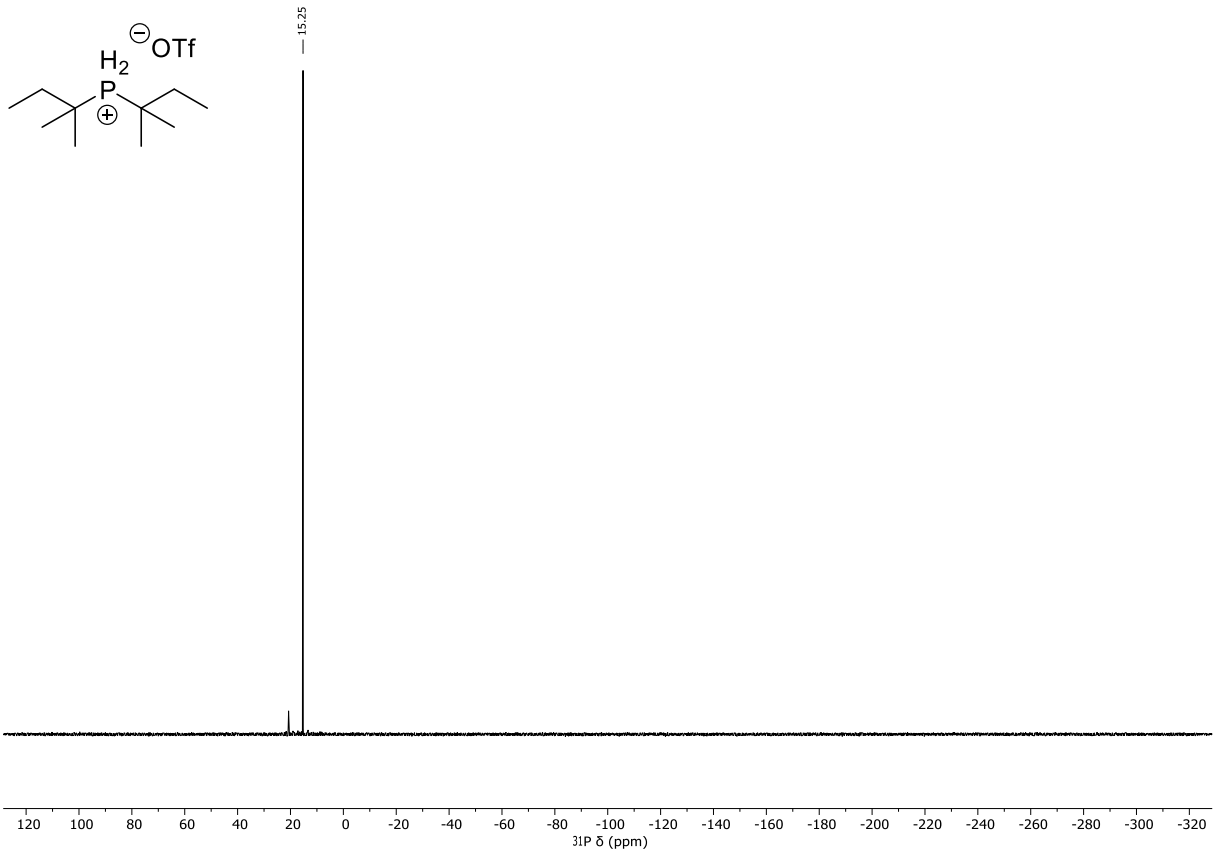
Di-*tert*-amylphosphonium triflate (1a) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



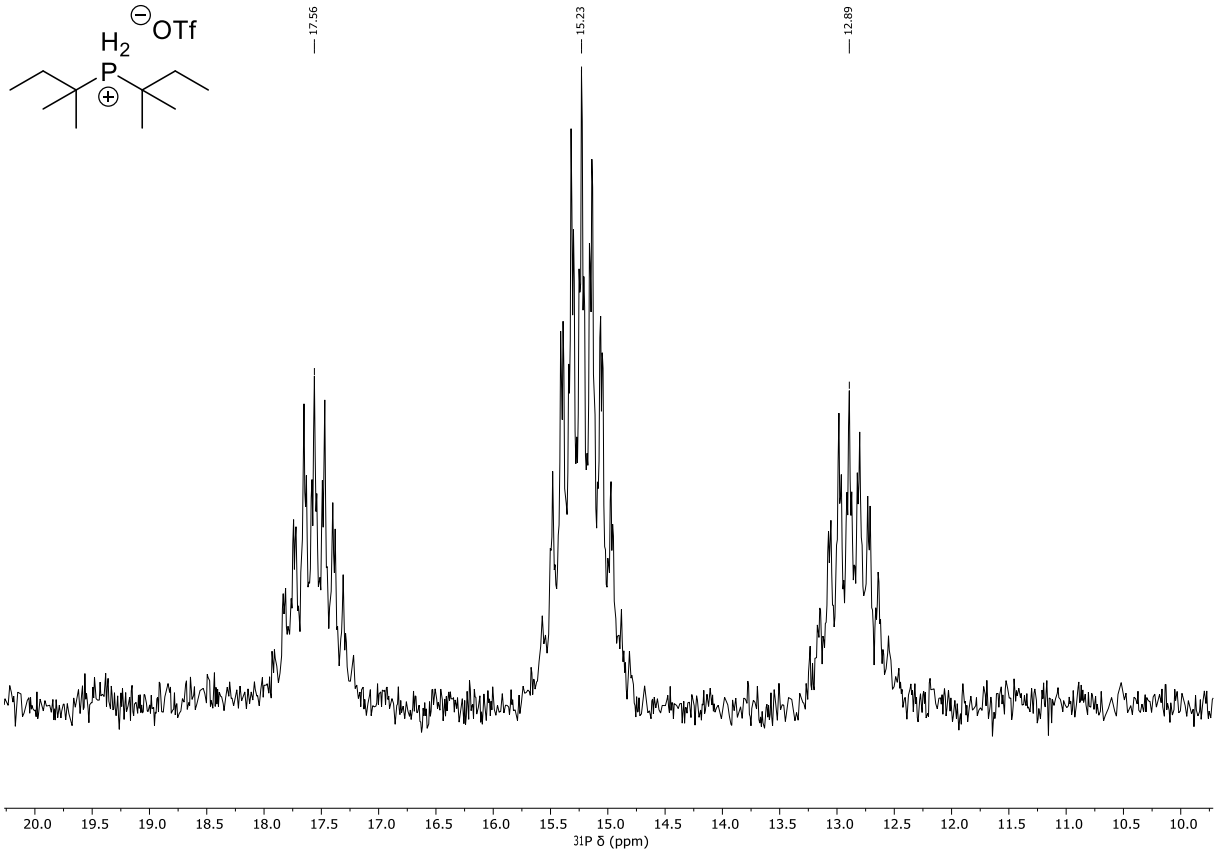
Di-*tert*-amylphosphonium triflate (1a) ^{19}F NMR (470 MHz, $CDCl_3$)



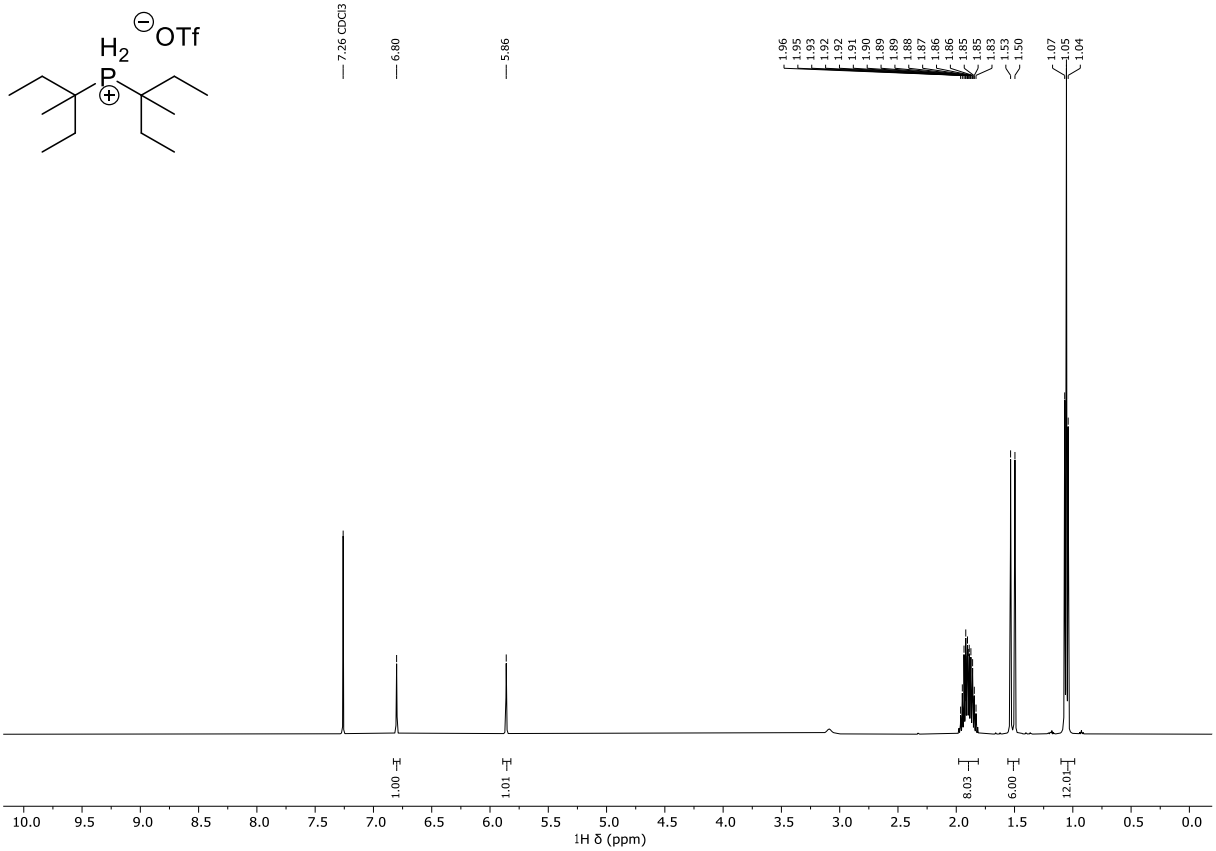
Di-*tert*-amylphosphonium triflate (1a) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



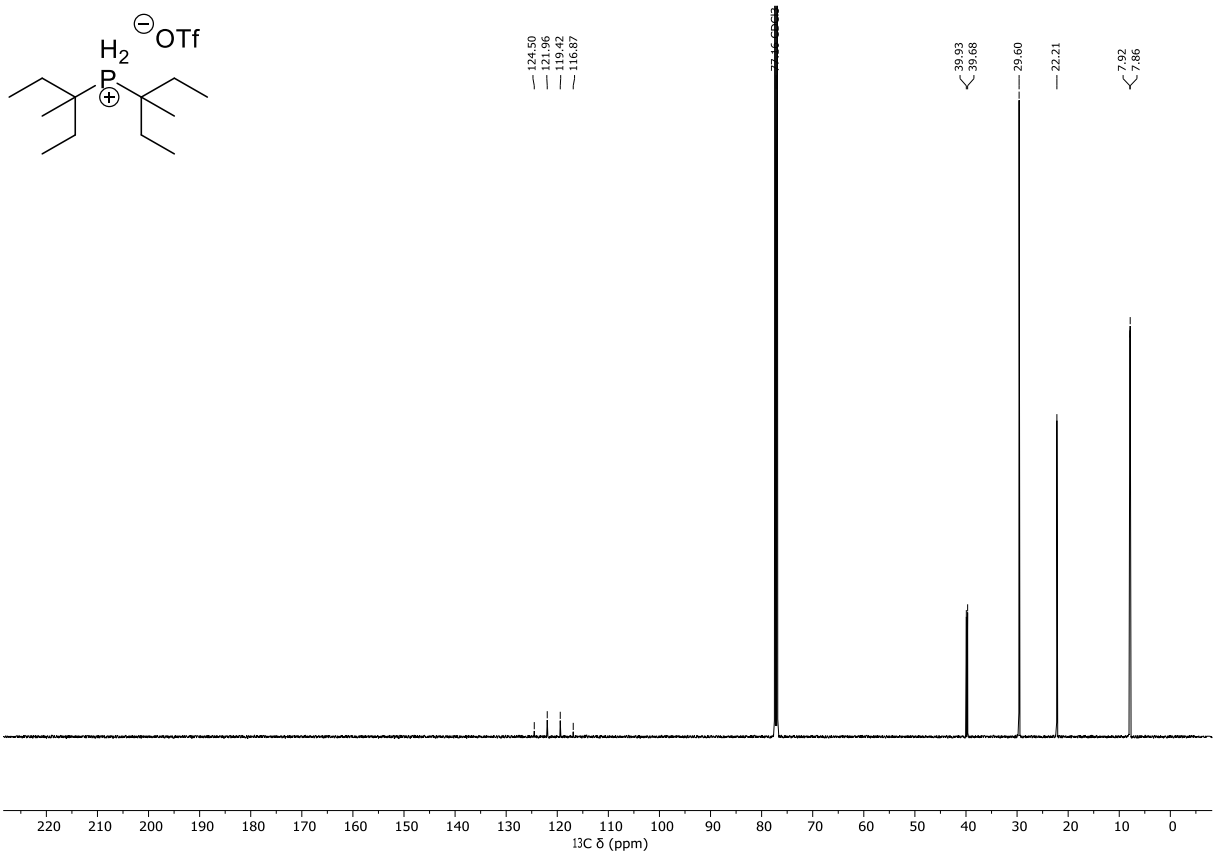
Di-*tert*-amylphosphonium triflate (1a) ^{31}P NMR (202 MHz, $CDCl_3$)



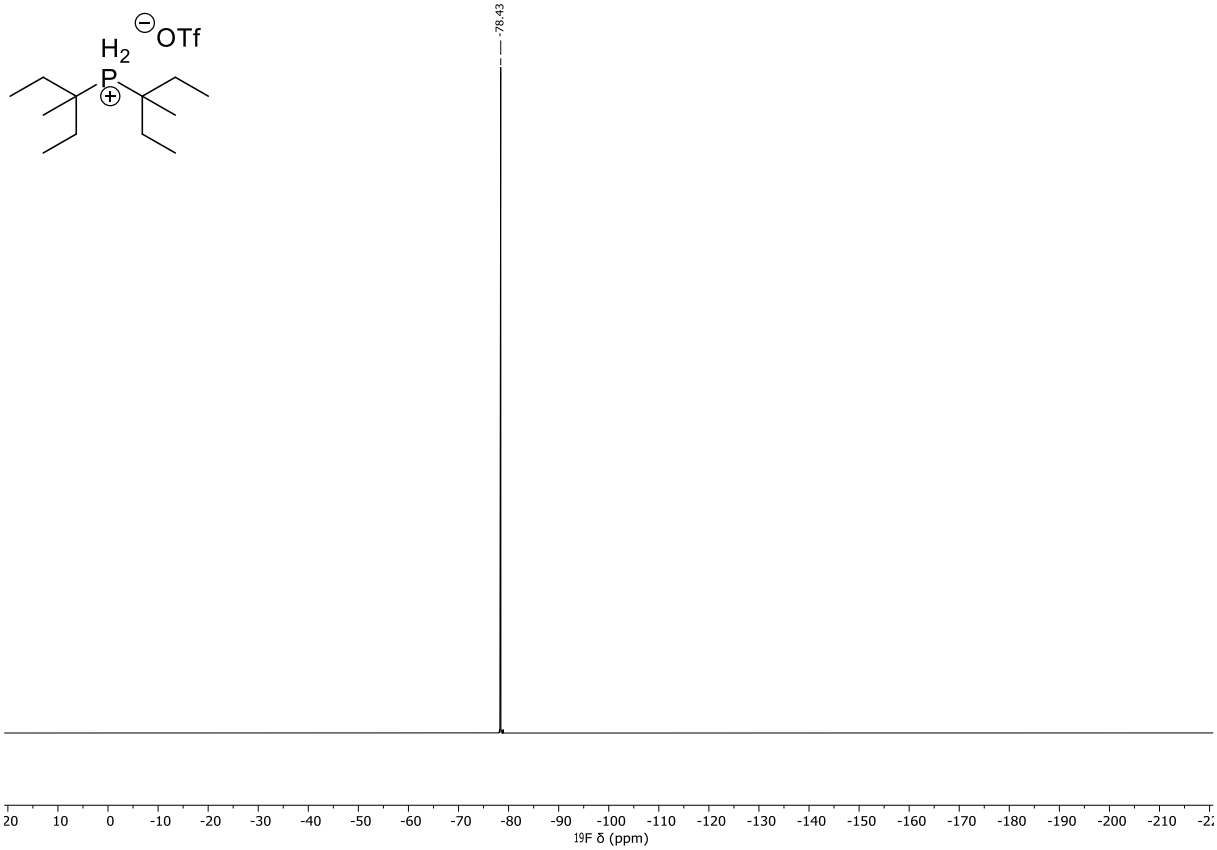
Di-(3-methyl-3-pentyl)phosphonium triflate (1b) - ^{1}H NMR (500 MHz, $CDCl_3$)



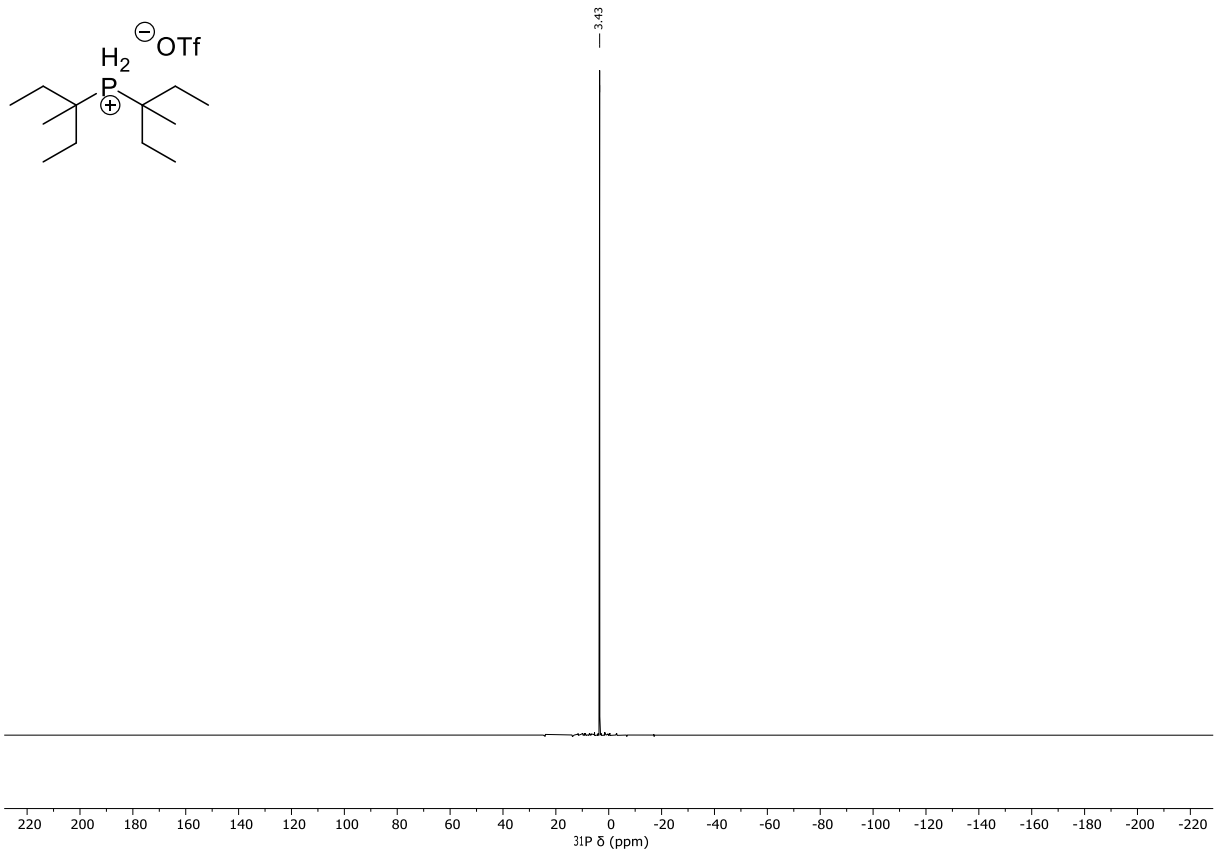
Di-(3-methyl-3-pentyl)phosphonium triflate (1b) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



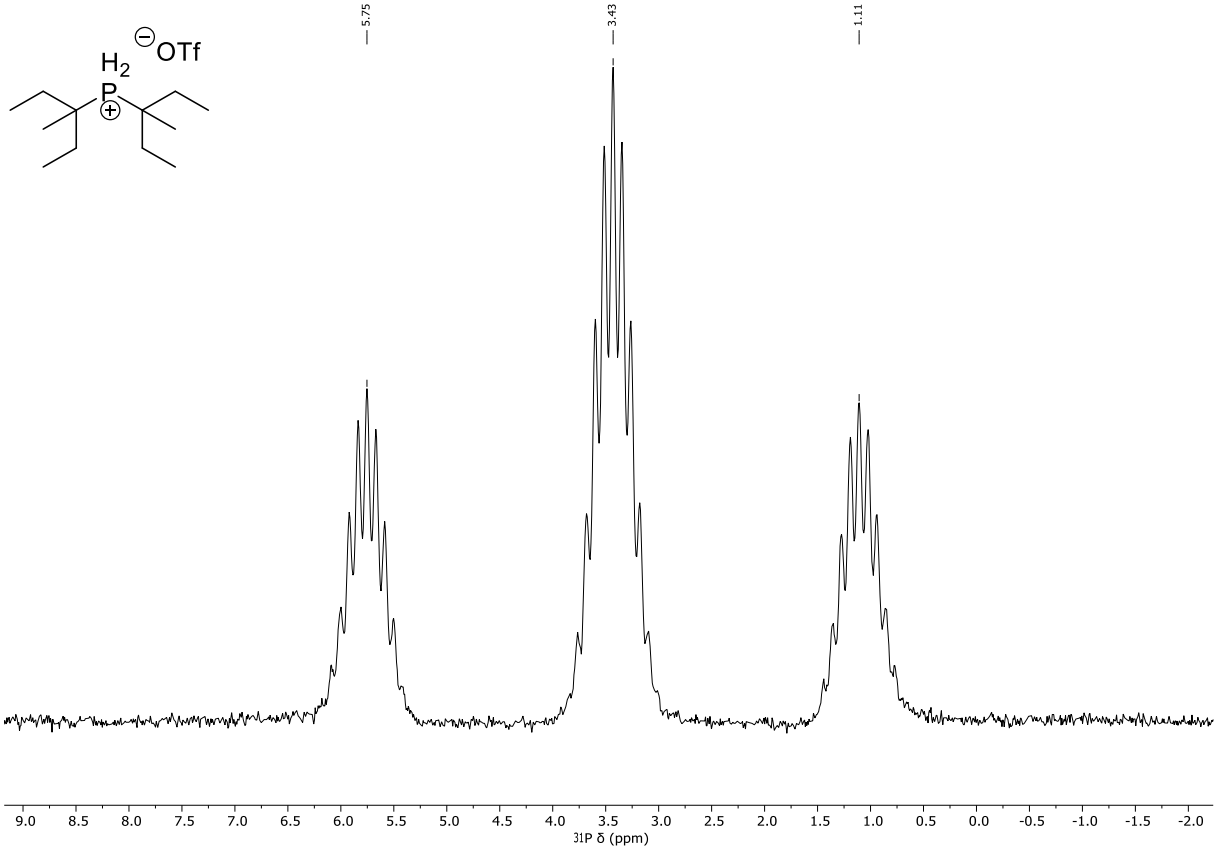
Di-(3-methyl-3-pentyl)phosphonium triflate (1b) ^{19}F NMR (470 MHz, $CDCl_3$)



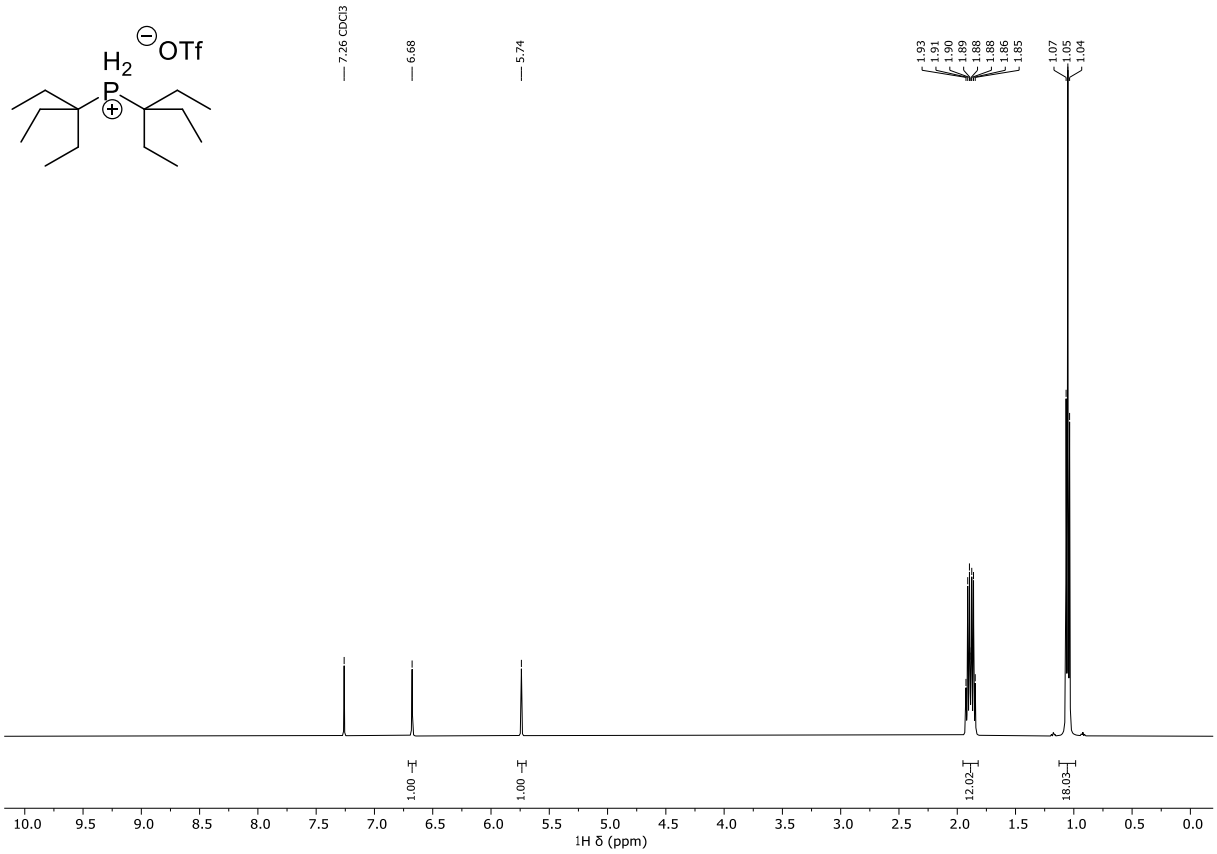
Di-(3-methyl-3-pentyl)phosphonium triflate (1b) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



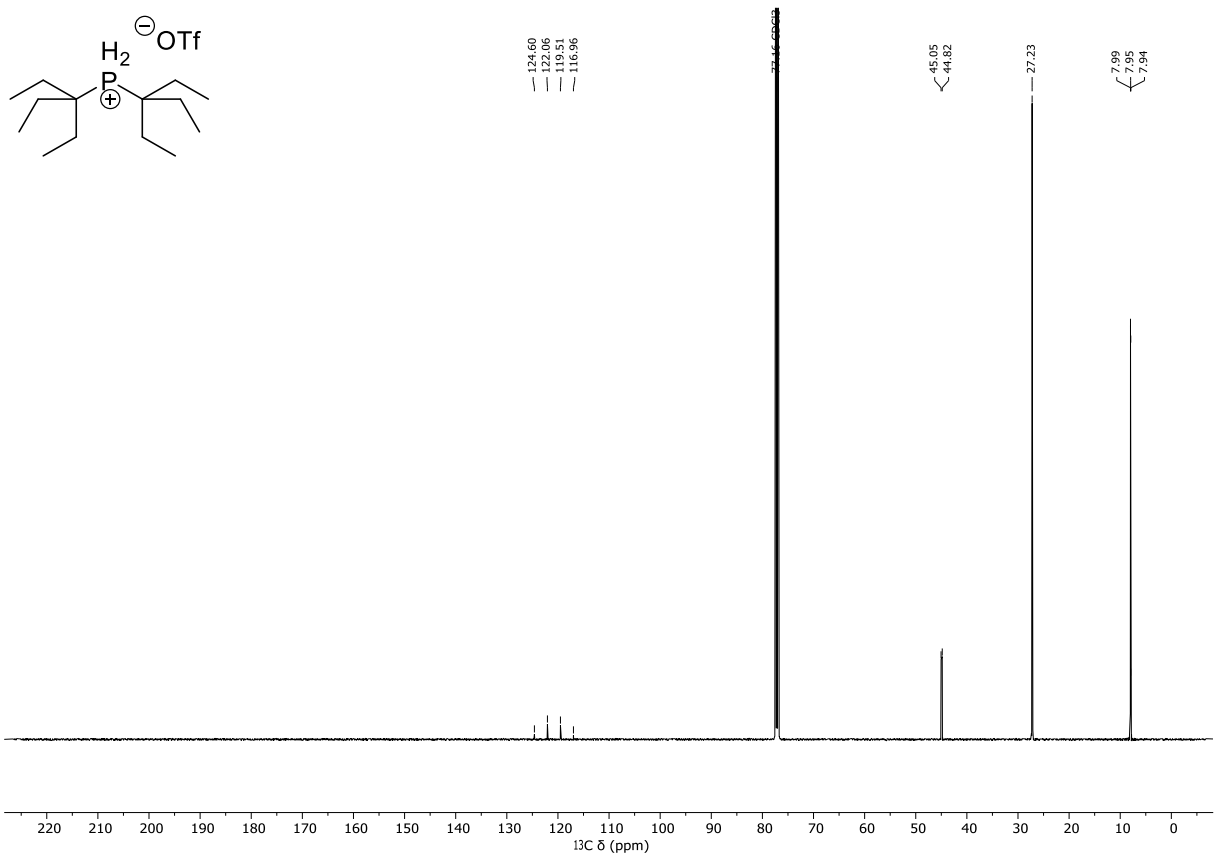
Di-(3-methyl-3-pentyl)phosphonium triflate (1b) ^{31}P NMR (202 MHz, $CDCl_3$)



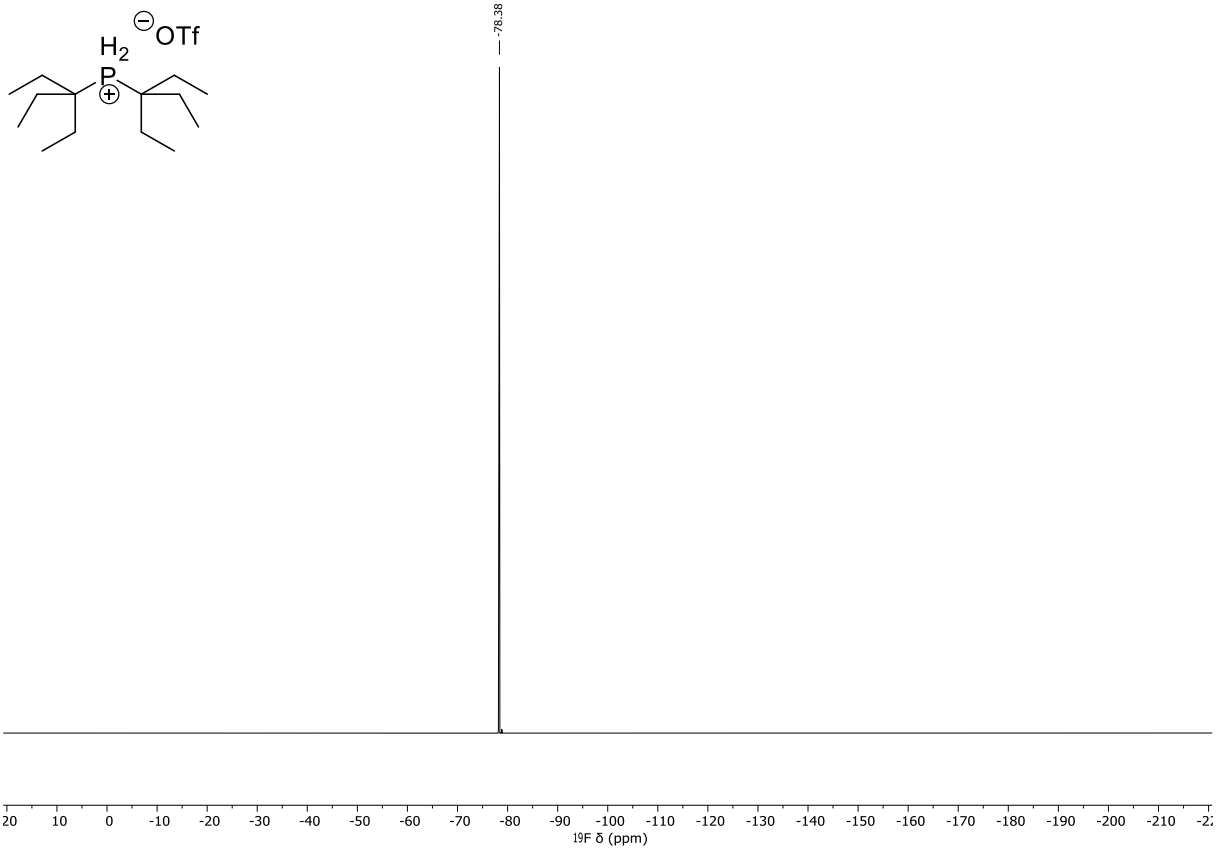
Di-(3-ethyl-3-pentyl)phosphonium triflate (1c) - ^{1}H NMR (500 MHz, $CDCl_3$)



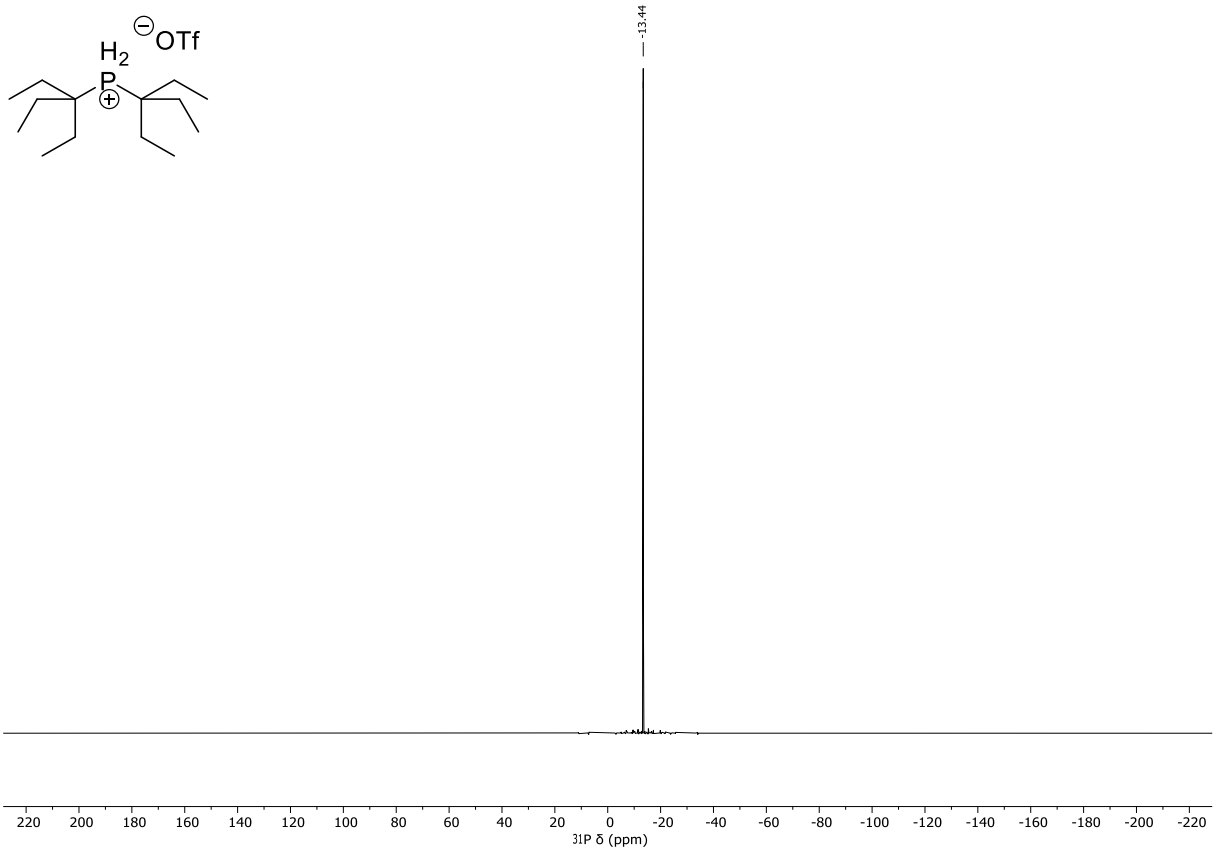
Di-(3-ethyl-3-pentyl)phosphonium triflate (1c) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



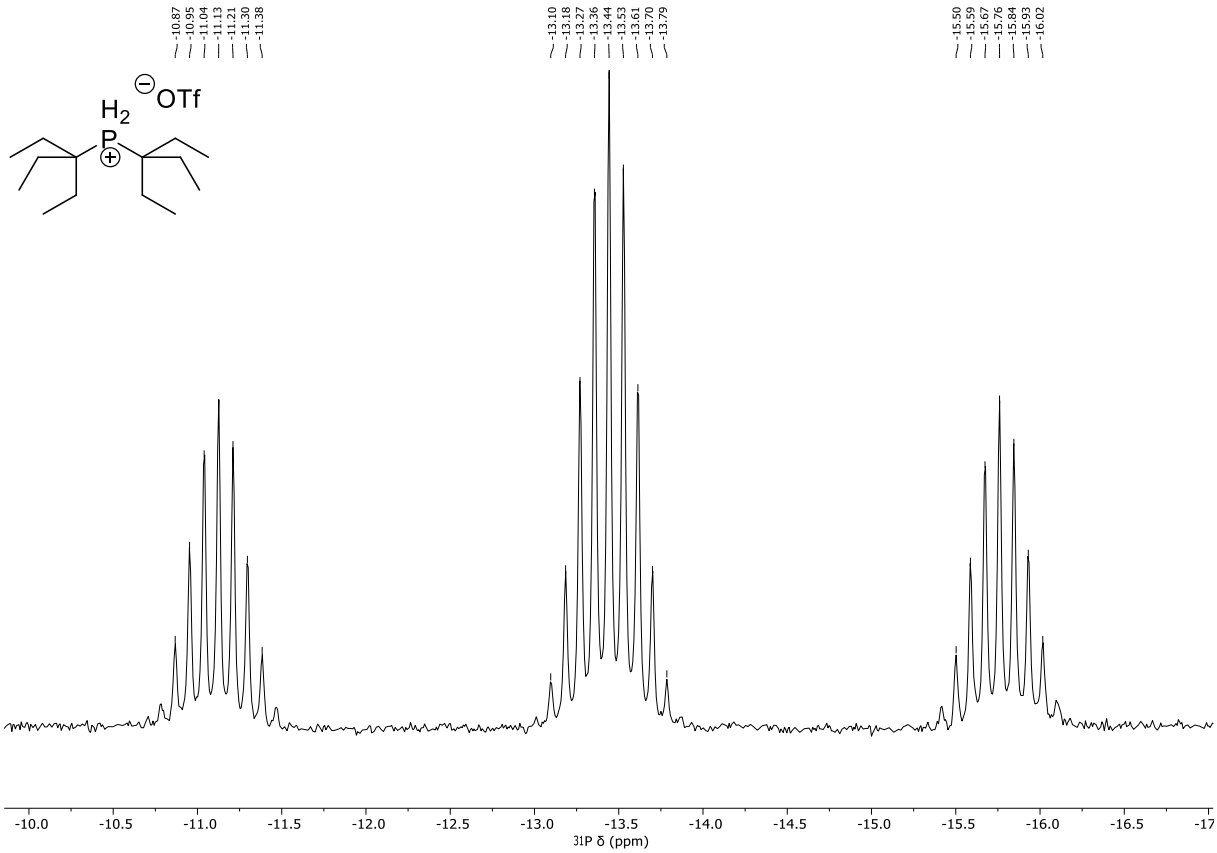
Di-(3-ethyl-3-pentyl)phosphonium triflate (1c) ^{19}F NMR (470 MHz, $CDCl_3$)



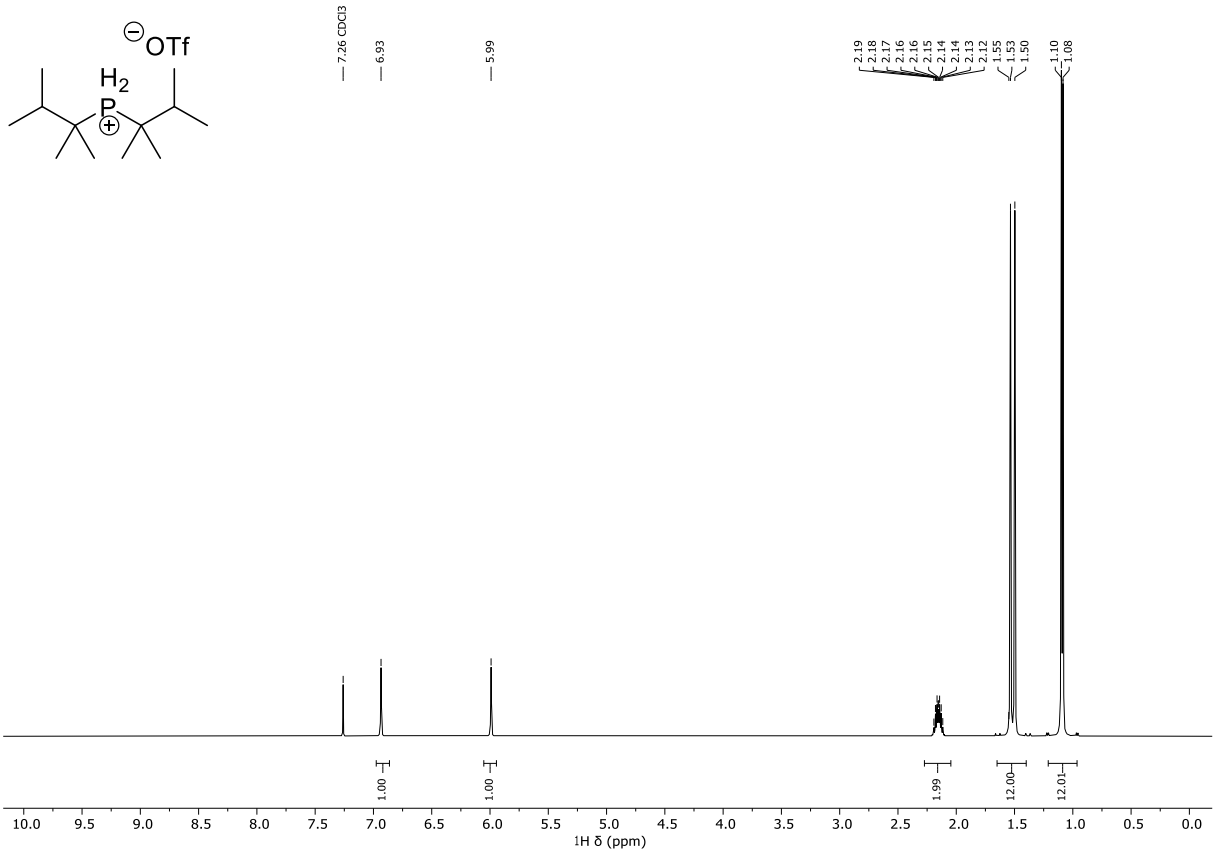
Di-(3-ethyl-3-pentyl)phosphonium triflate (1c) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



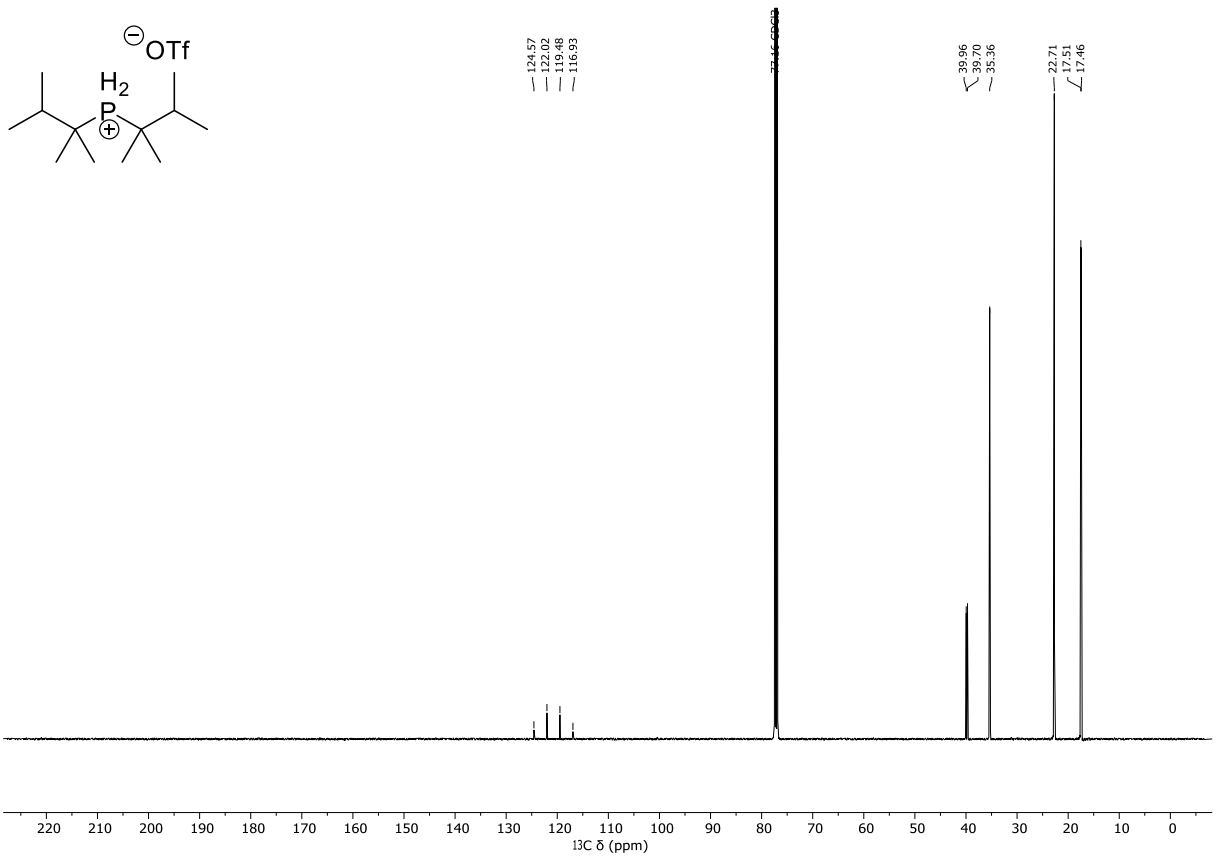
Di-(3-ethyl-3-pentyl)phosphonium triflate (1c) ^{31}P NMR (202 MHz, $CDCl_3$)



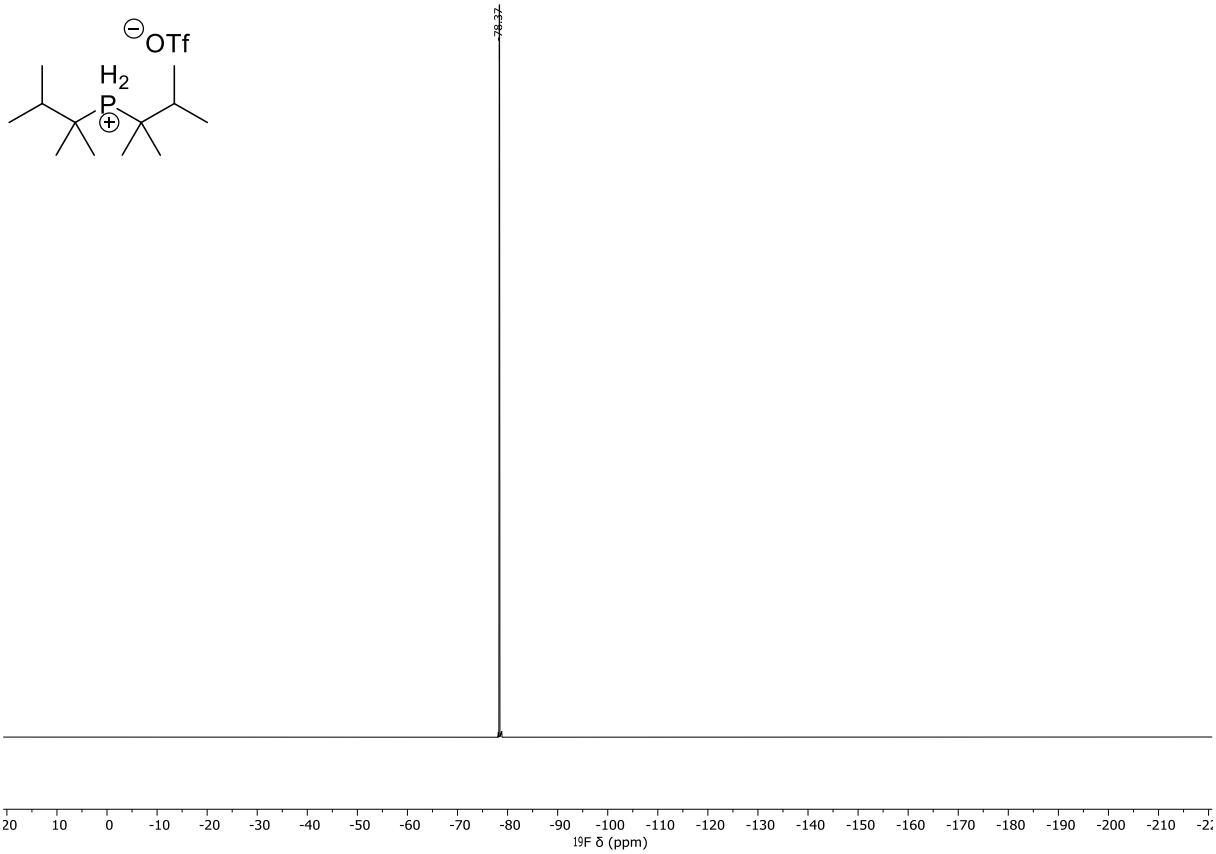
Bis-(2,3-dimethyl-2-butyl)phosphonium triflate (1d) - ^{1}H NMR (500 MHz, $CDCl_3$)



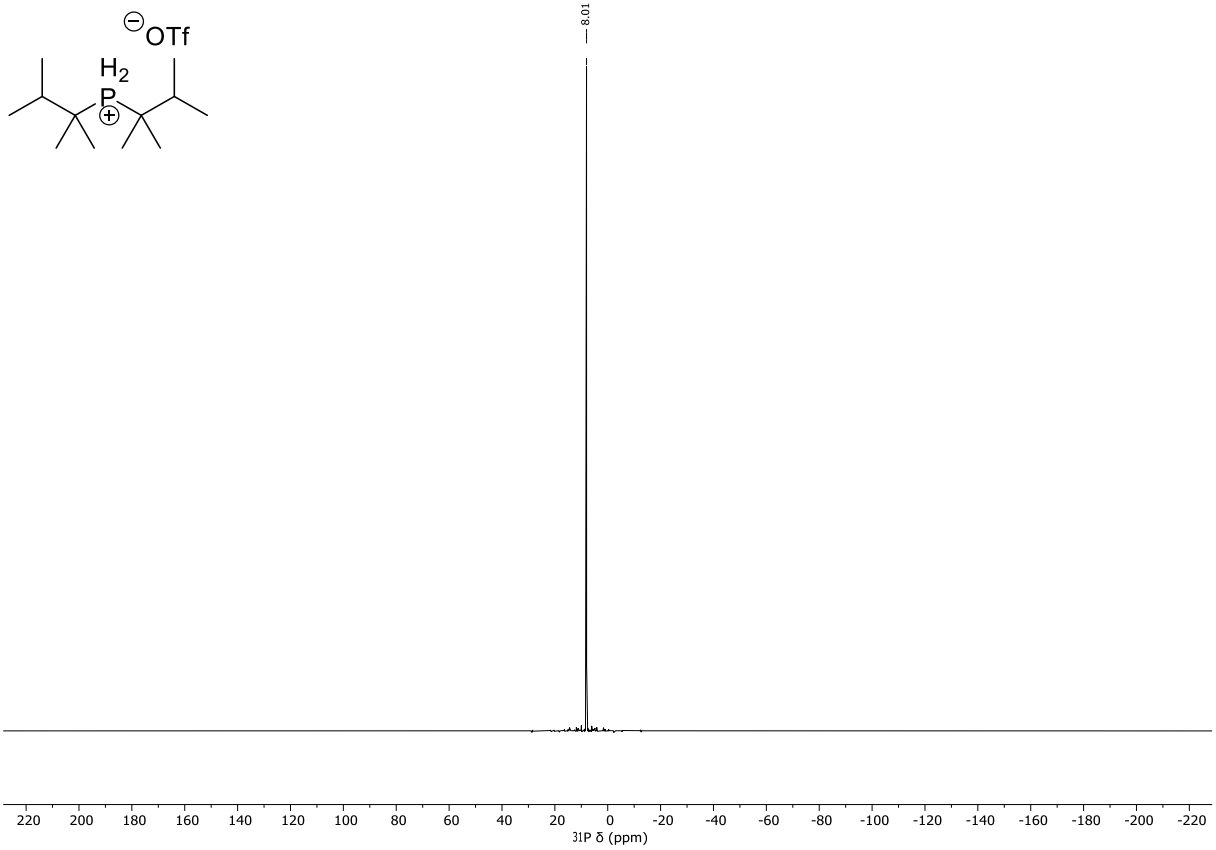
Bis-(2,3-dimethyl-2-butyl)phosphonium triflate (1d) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



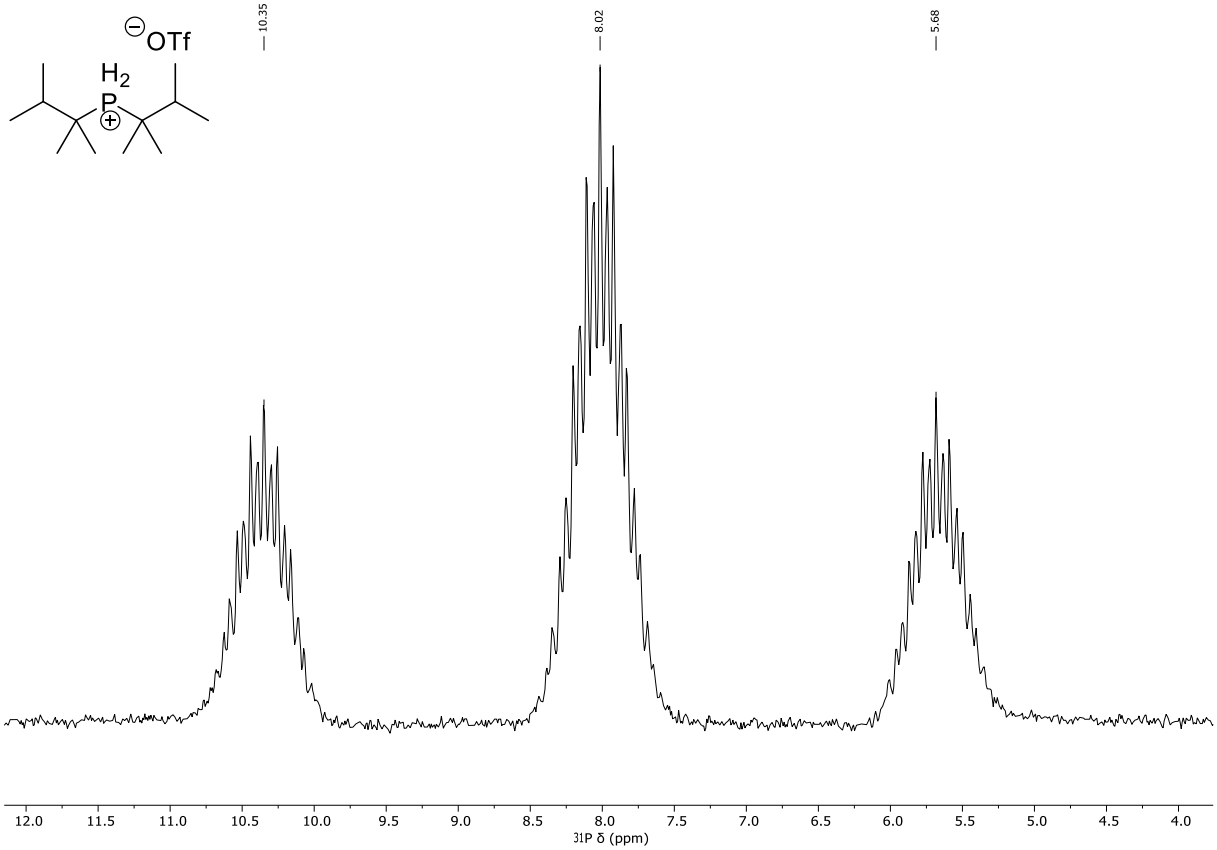
Bis-(2,3-dimethyl-2-butyl)phosphonium triflate (1d) ^{19}F NMR (470 MHz, $CDCl_3$)



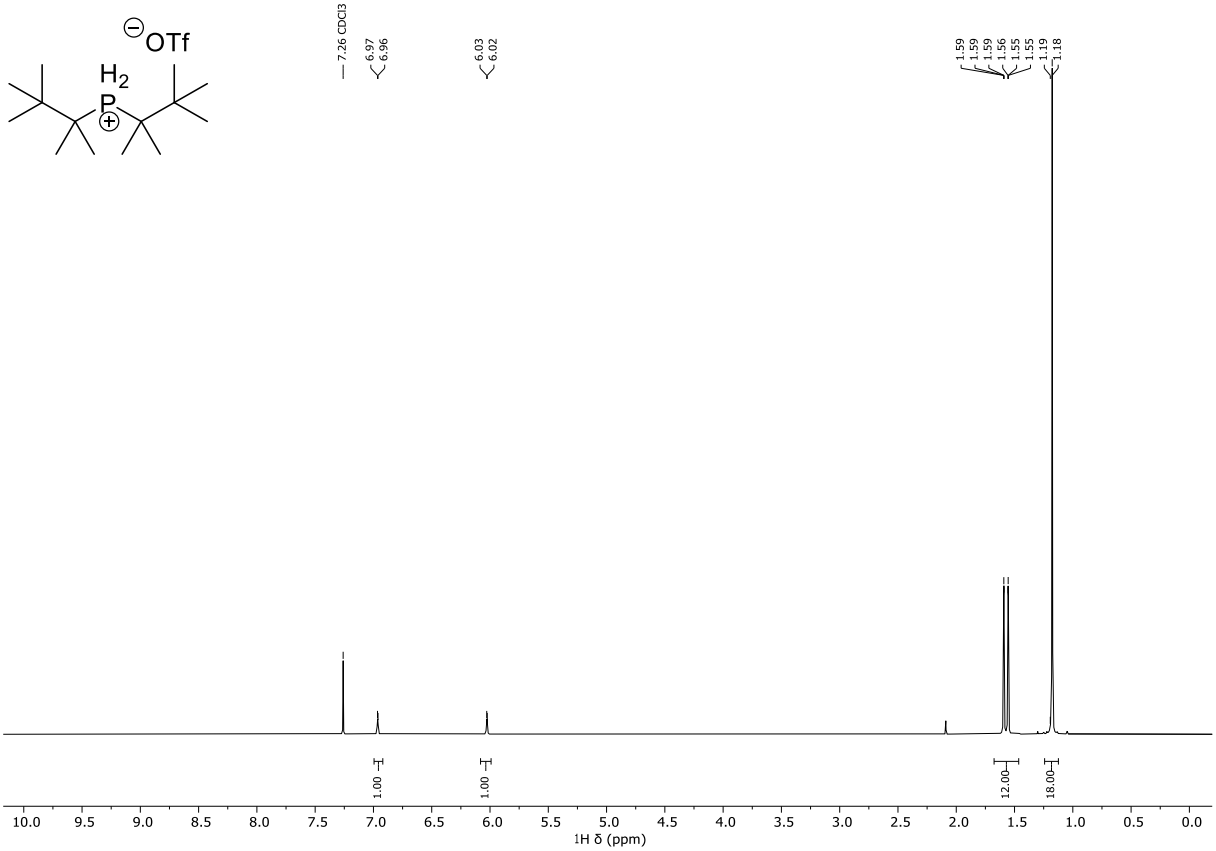
Bis-(2,3-dimethyl-2-butyl)phosphonium triflate (1d) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



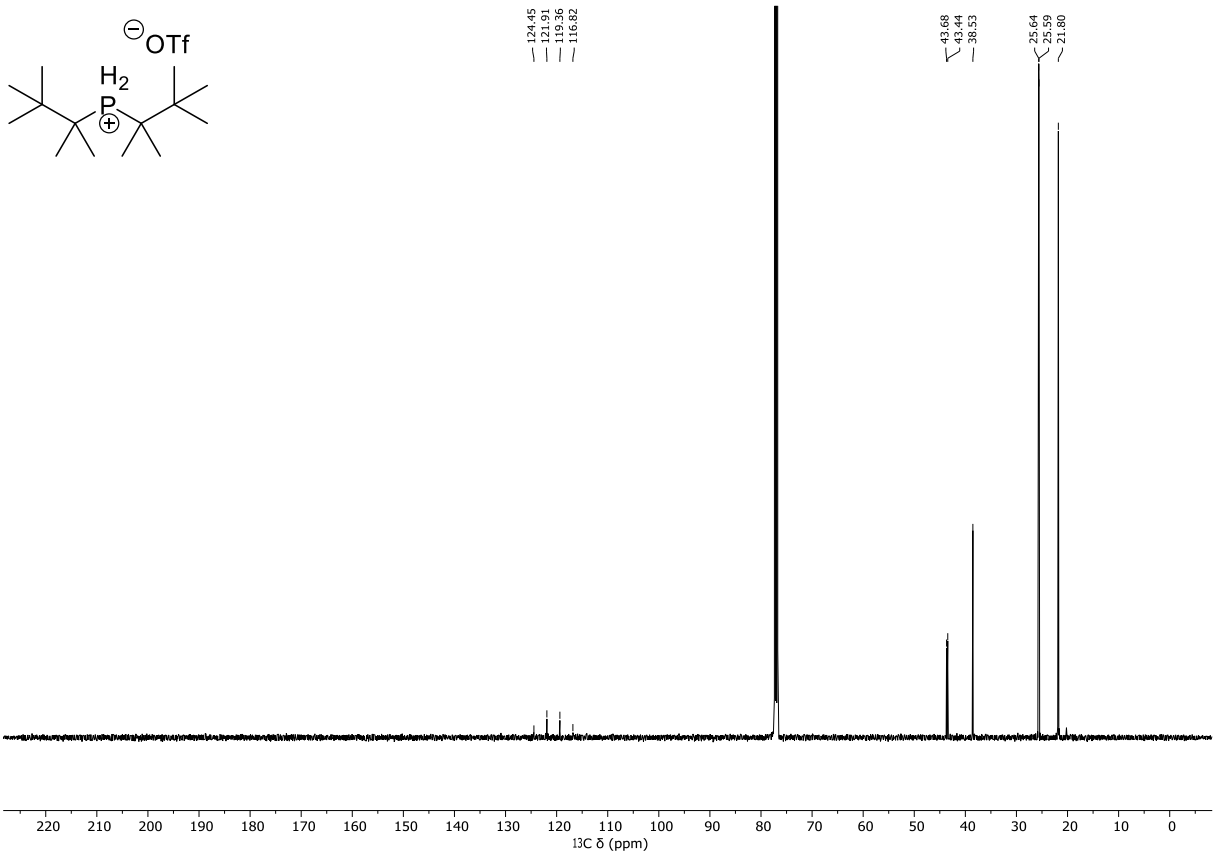
Bis-(2,3-dimethyl-2-butyl)phosphonium triflate (1d) ^{31}P NMR (202 MHz, $CDCl_3$)



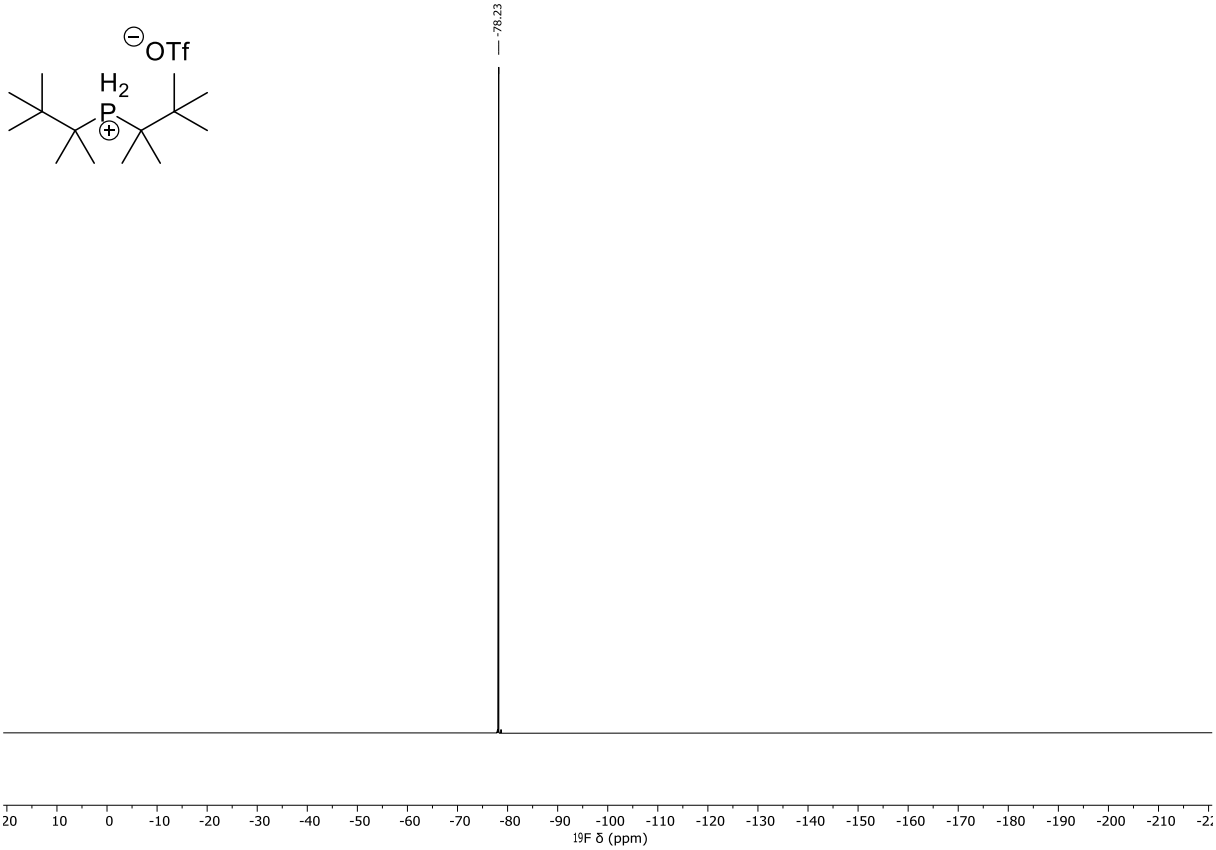
Bis-(2,3,3-trimethyl-2-butyl)phosphonium triflate (1e) - ^{1}H NMR (500 MHz, $CDCl_3$)



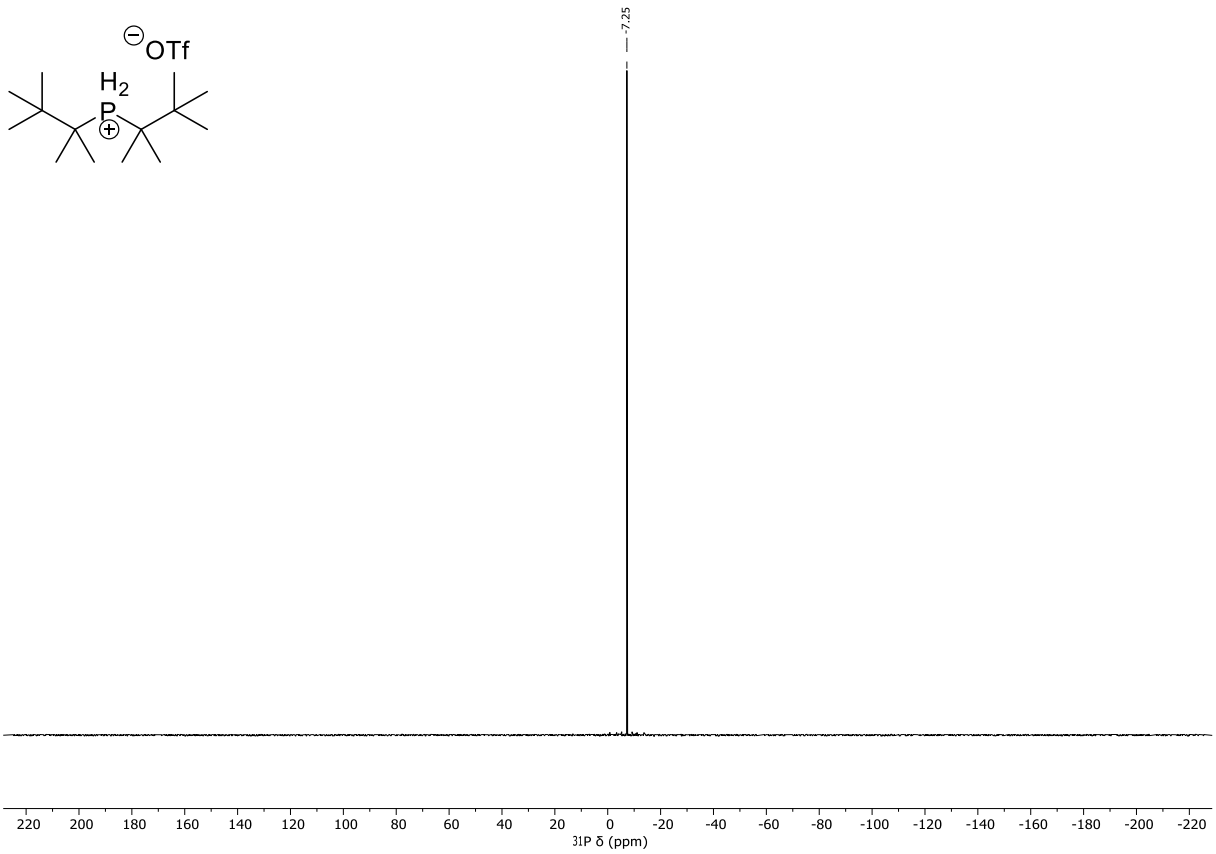
Bis-(2,3,3-trimethyl-2-butyl)phosphonium triflate (1e) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



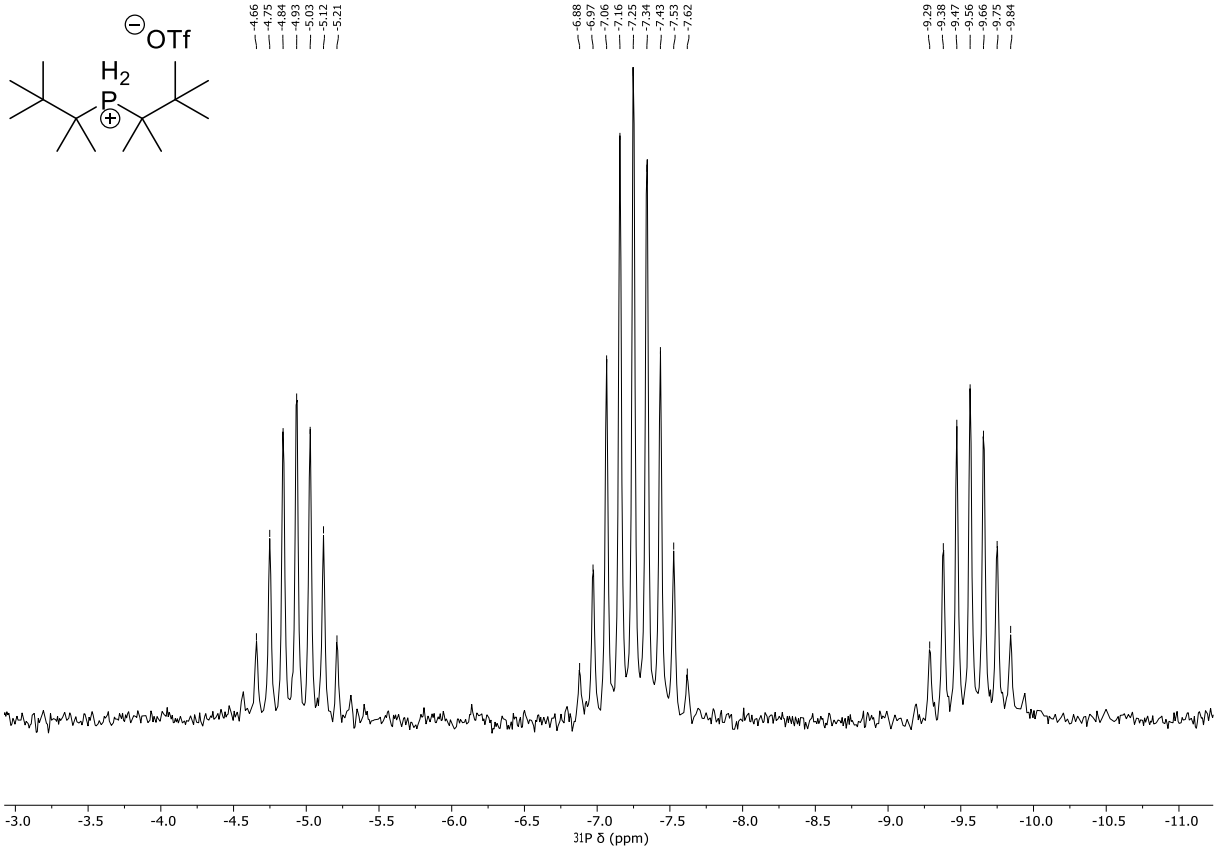
Bis-(2,3,3-trimethyl-2-butyl)phosphonium triflate (1e) ^{19}F NMR (470 MHz, $CDCl_3$)



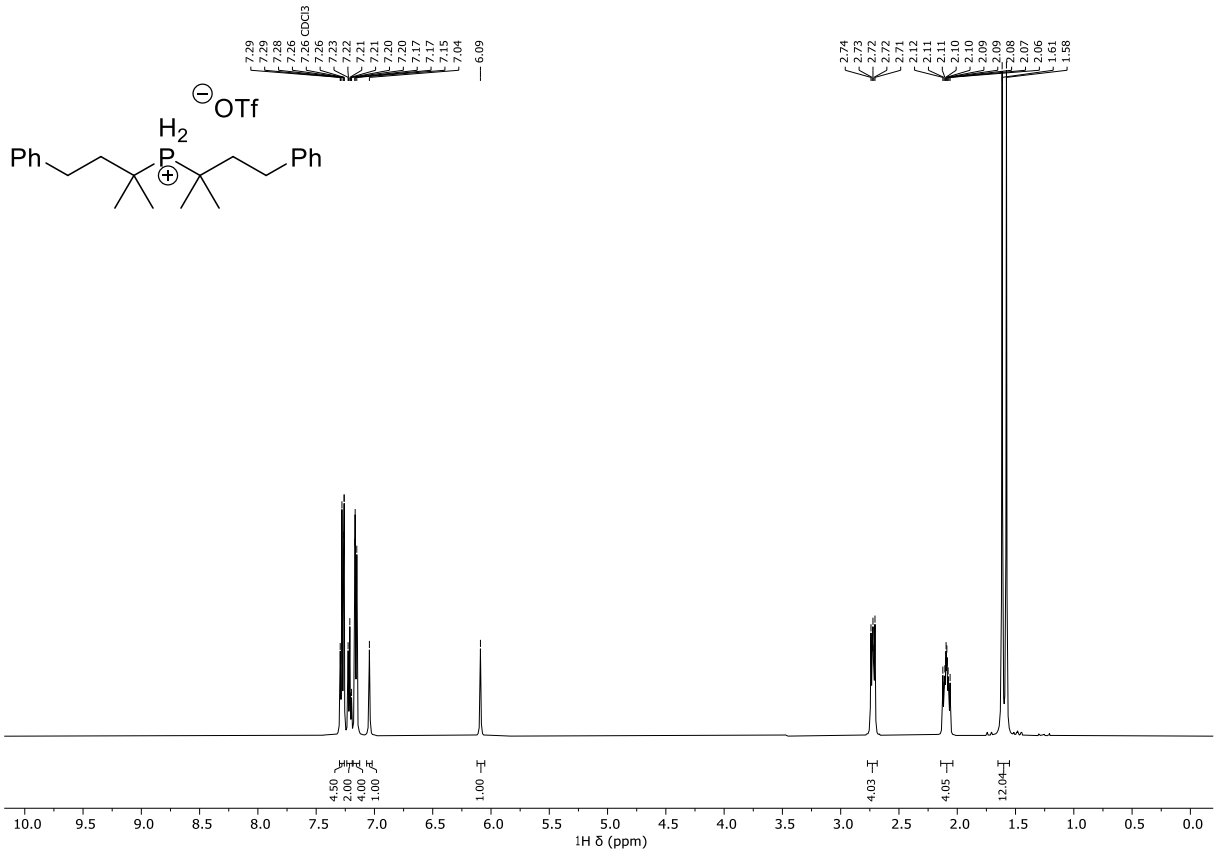
Bis-(2,3,3-trimethyl-2-butyl)phosphonium triflate (1e) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



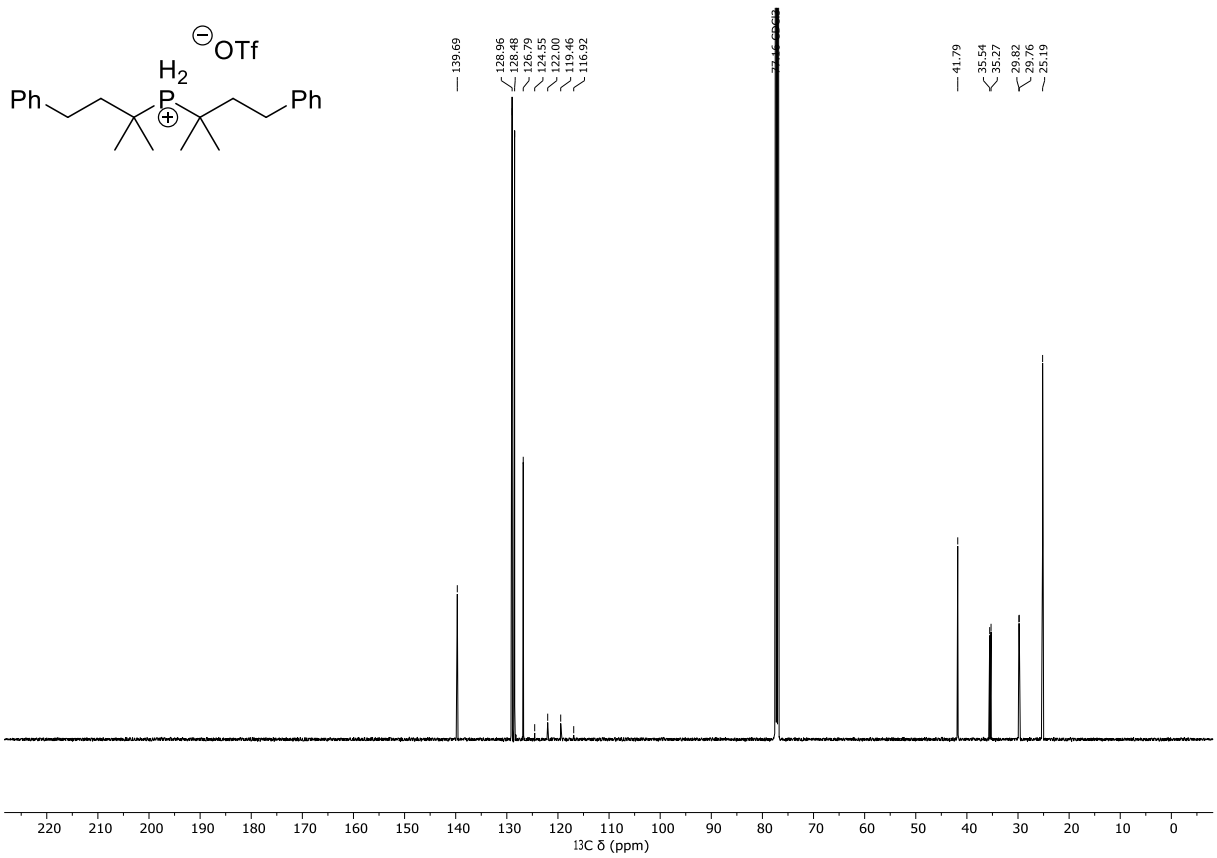
Bis-(2,3,3-trimethyl-2-butyl)phosphonium triflate (1e) ^{31}P NMR (202 MHz, $CDCl_3$)



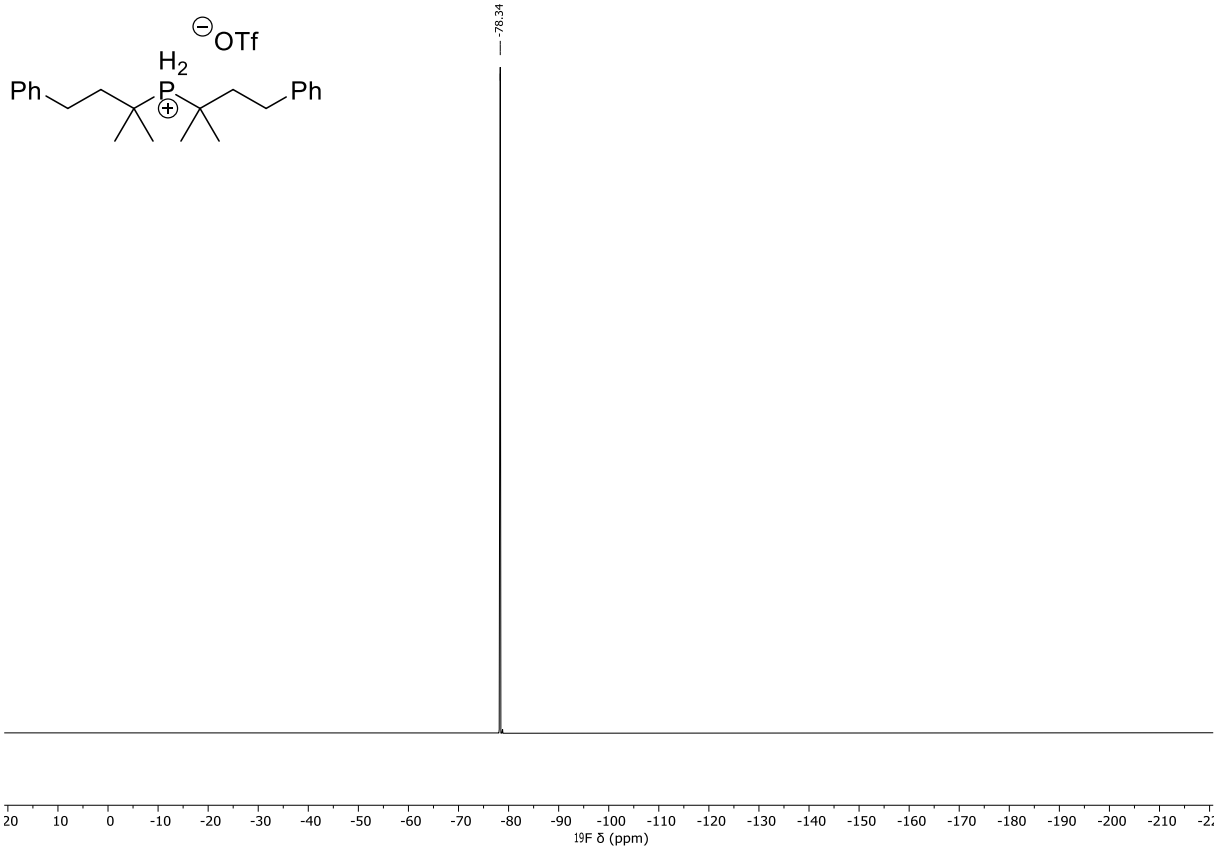
Di-(2-methyl-4-phenyl-2-butyl)phosphonium triflate (1f) - ^{1}H NMR (500 MHz, $CDCl_3$)



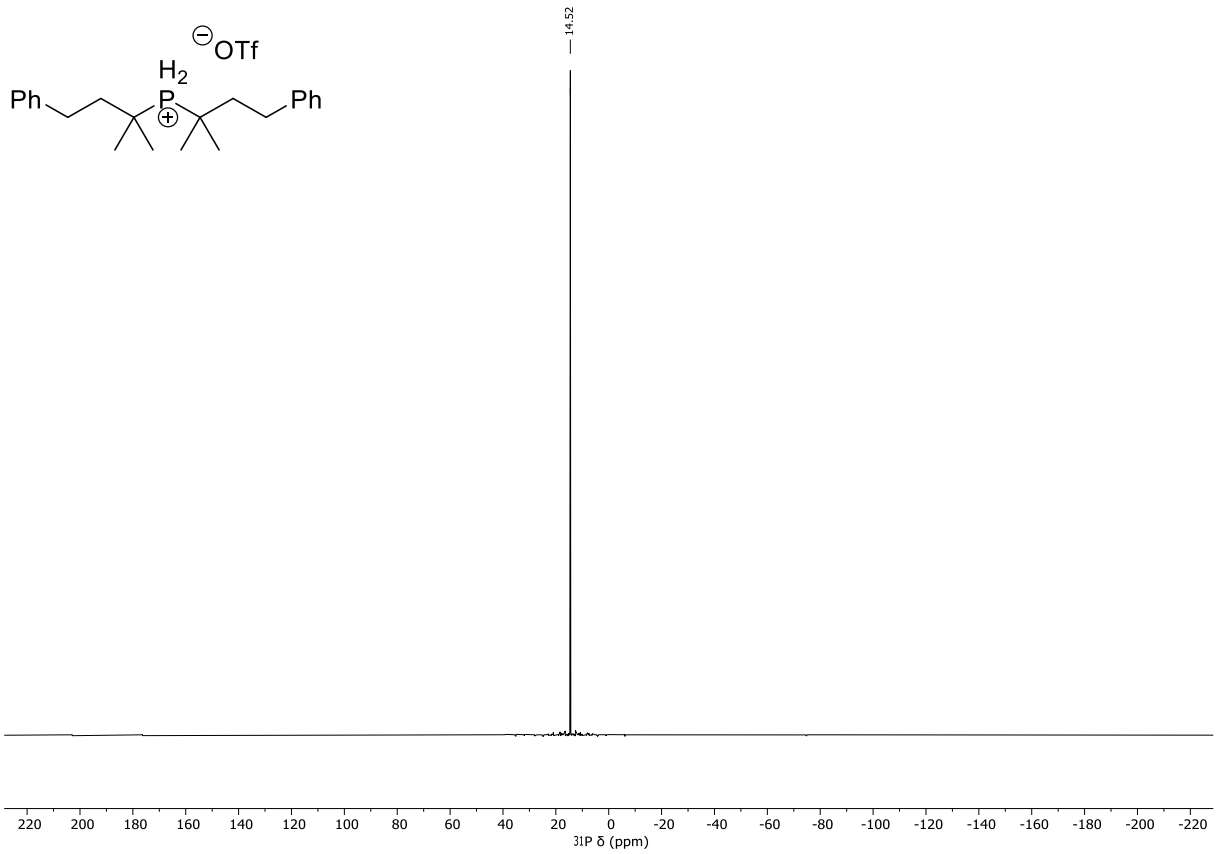
Di-(2-methyl-4-phenyl-2-butyl)phosphonium triflate (1f) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



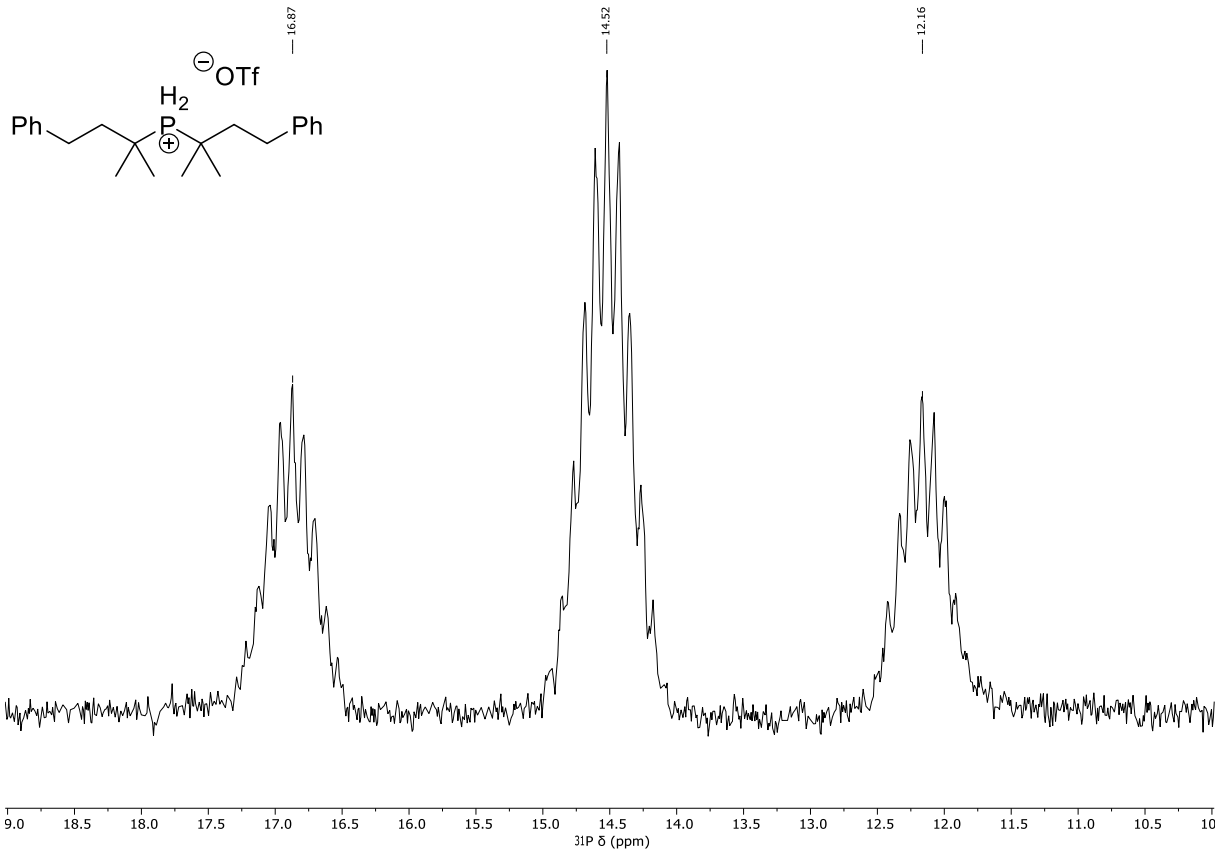
Di-(2-methyl-4-phenyl-2-butyl)phosphonium triflate (1f) ^{19}F NMR (470 MHz, $CDCl_3$)



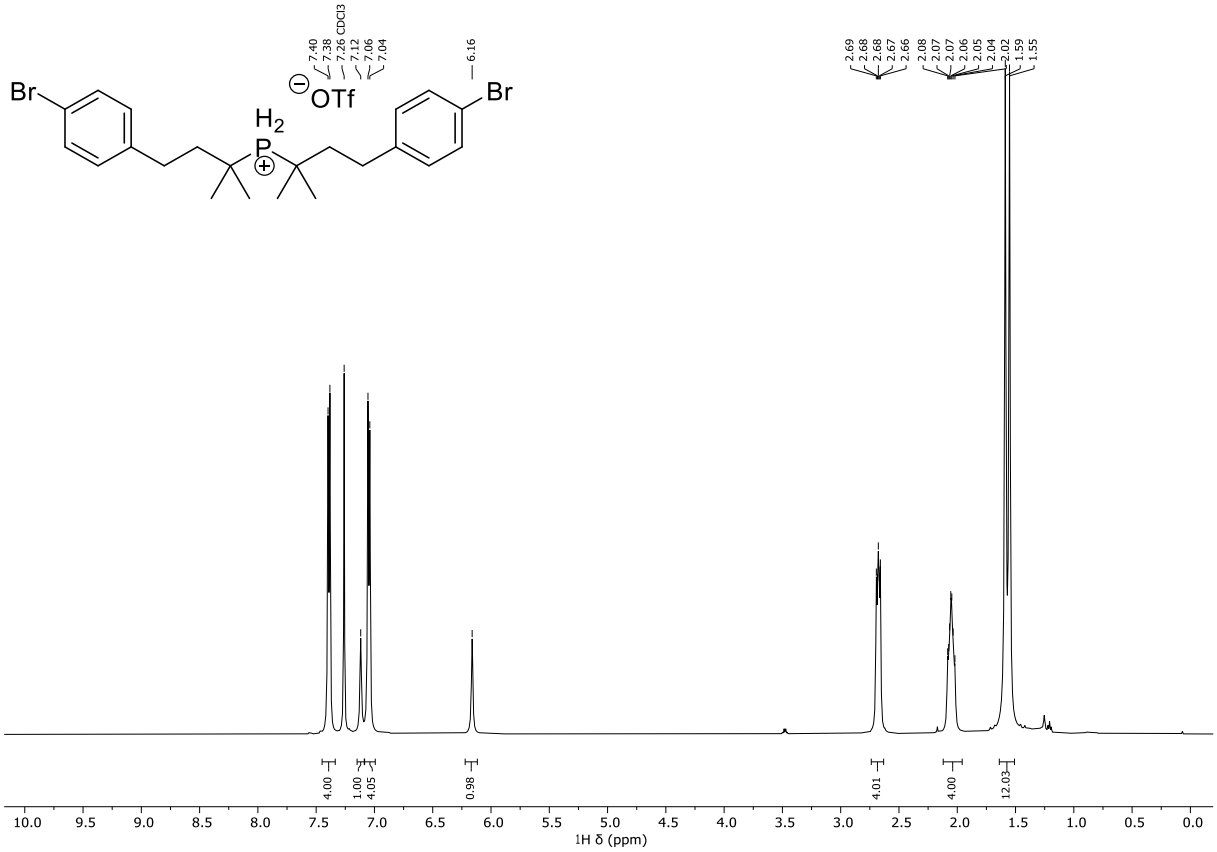
Di-(2-methyl-4-phenyl-2-butyl)phosphonium triflate (1f) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



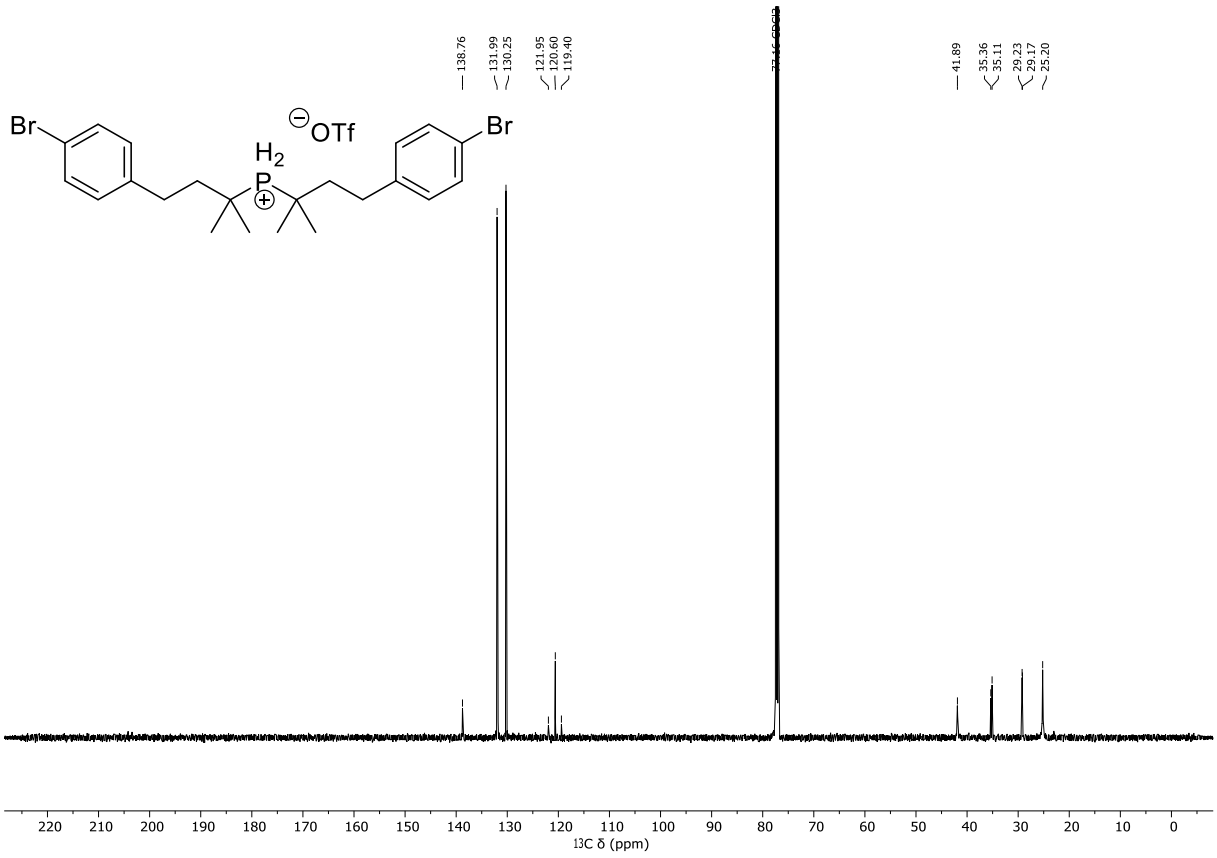
Di-(2-methyl-4-phenyl-2-butyl)phosphonium triflate (1f) ^{31}P NMR (202 MHz, $CDCl_3$)



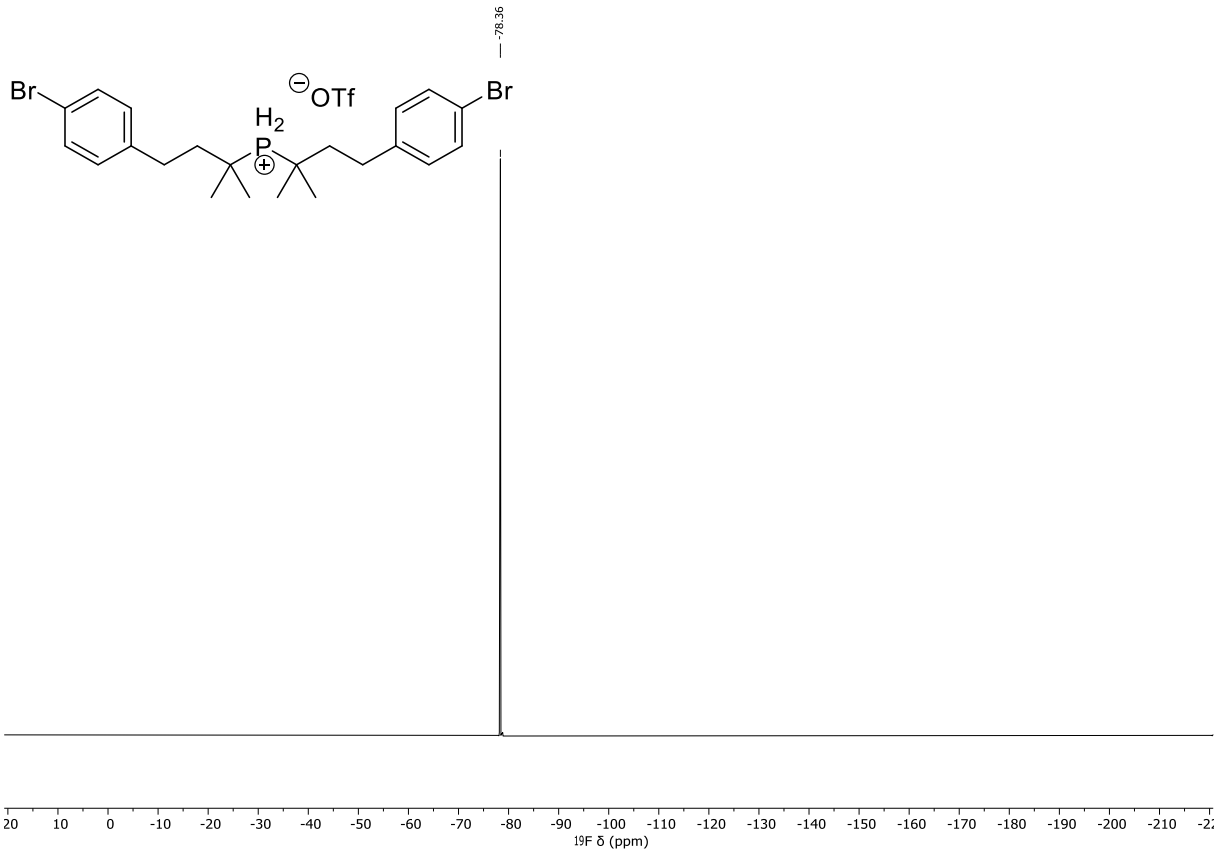
Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium triflate (1g) - ^{1}H NMR (500 MHz, $CDCl_3$)



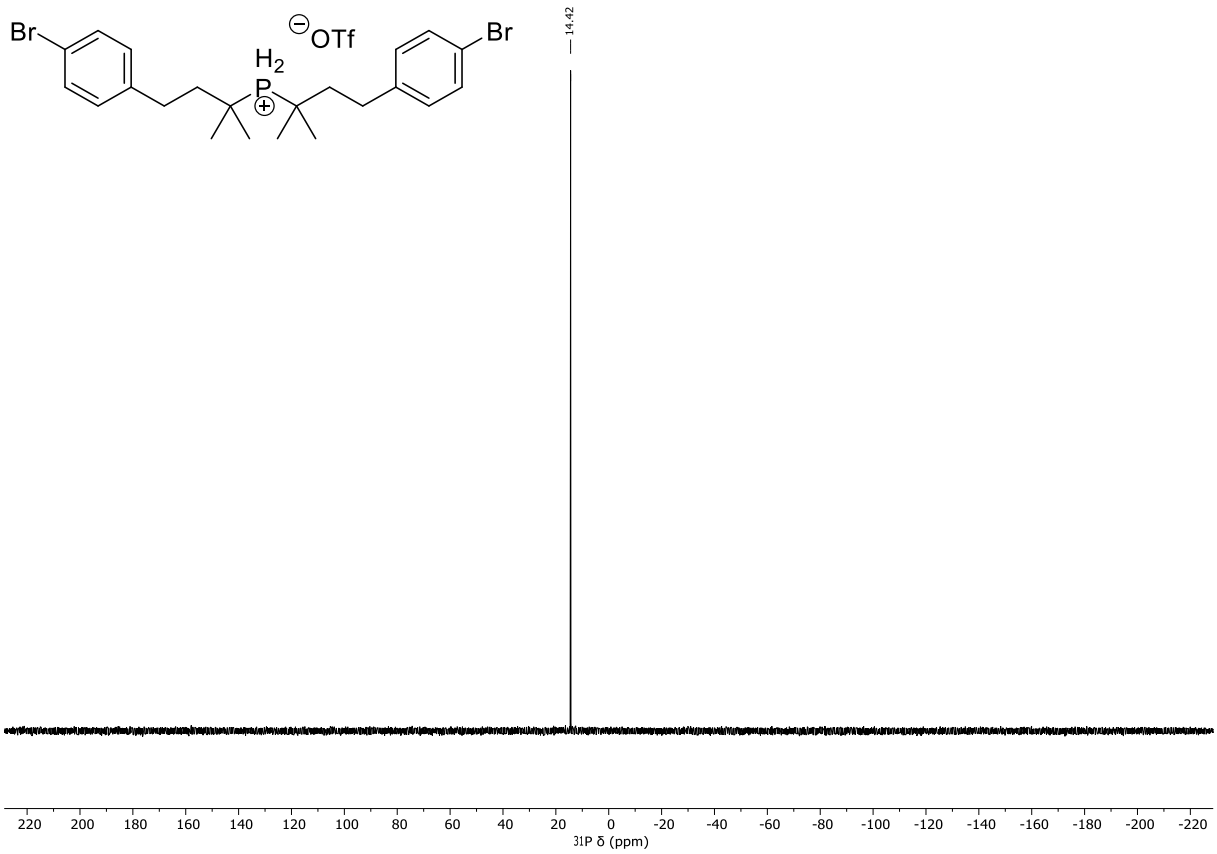
Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium triflate (1g) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



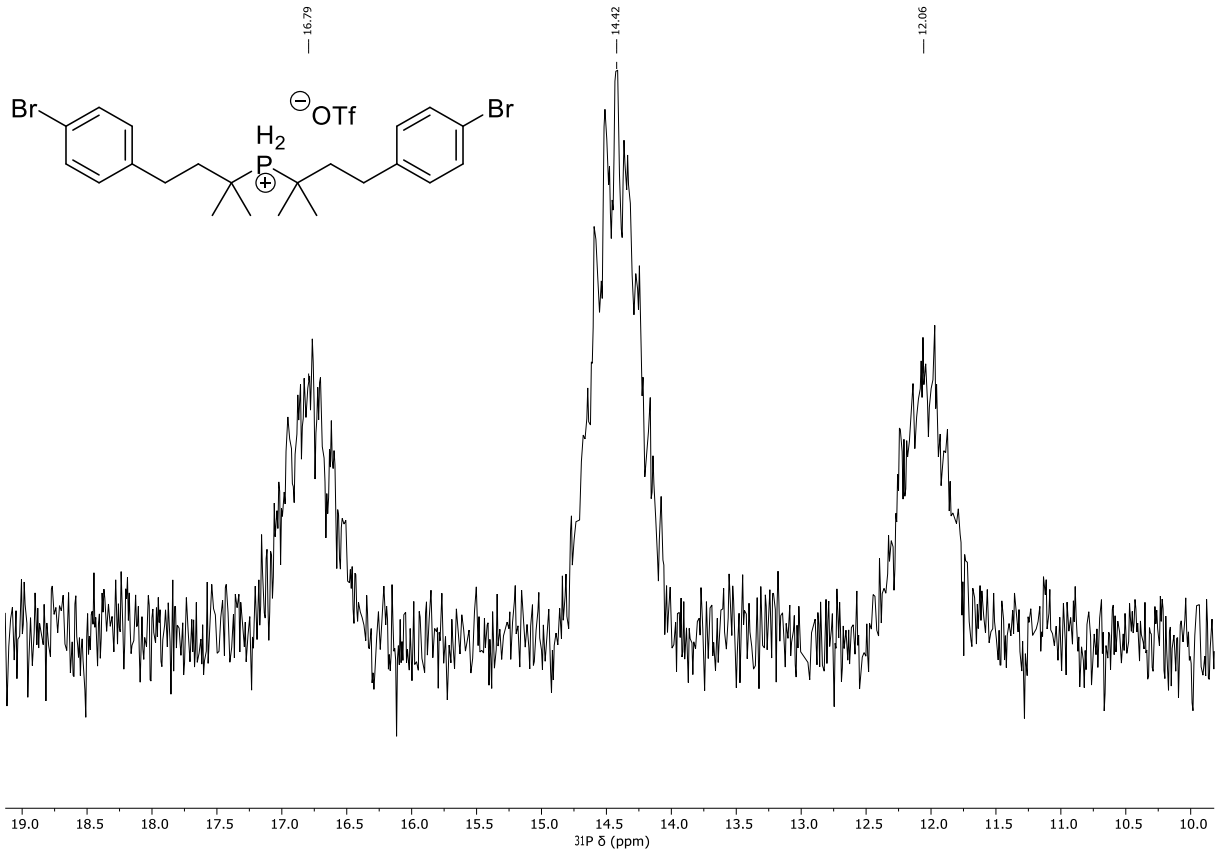
Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium triflate (1g) ^{19}F NMR (470 MHz, $CDCl_3$)



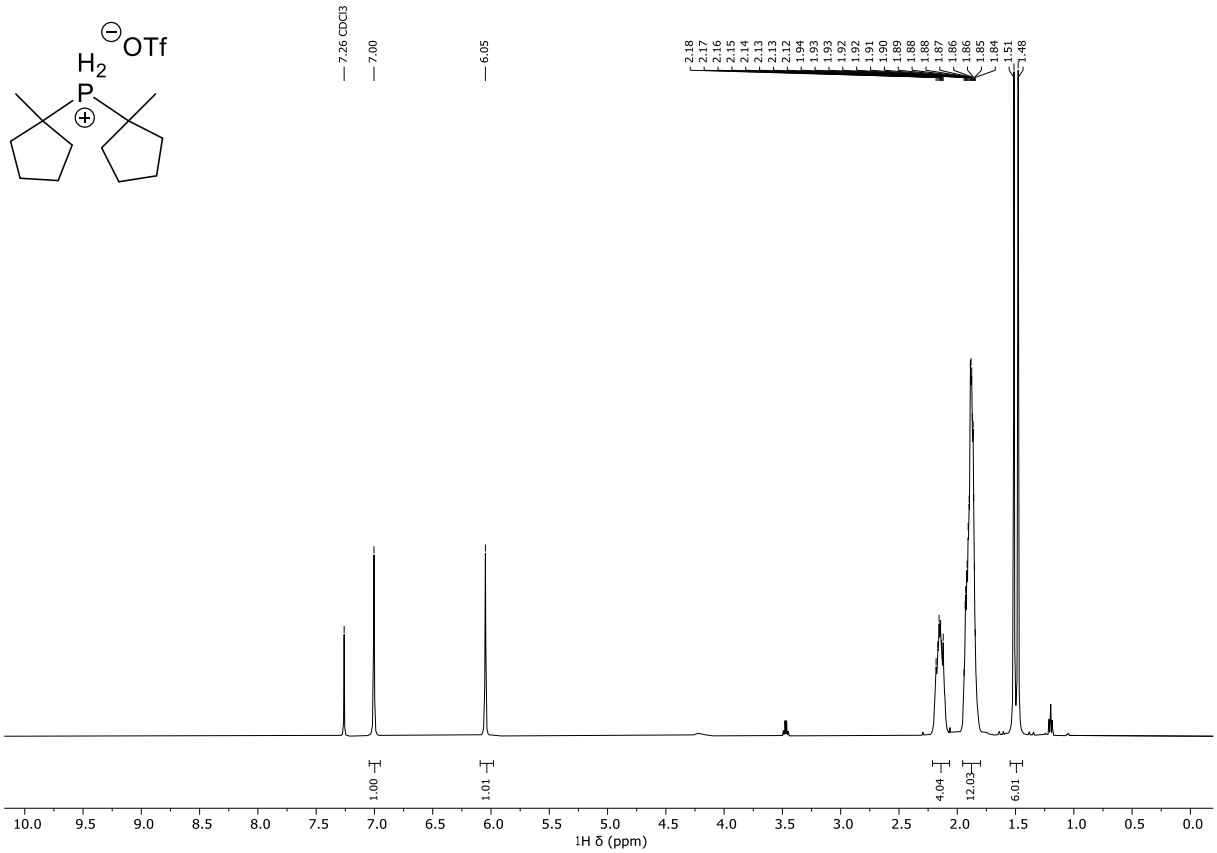
Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium triflate (1g) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



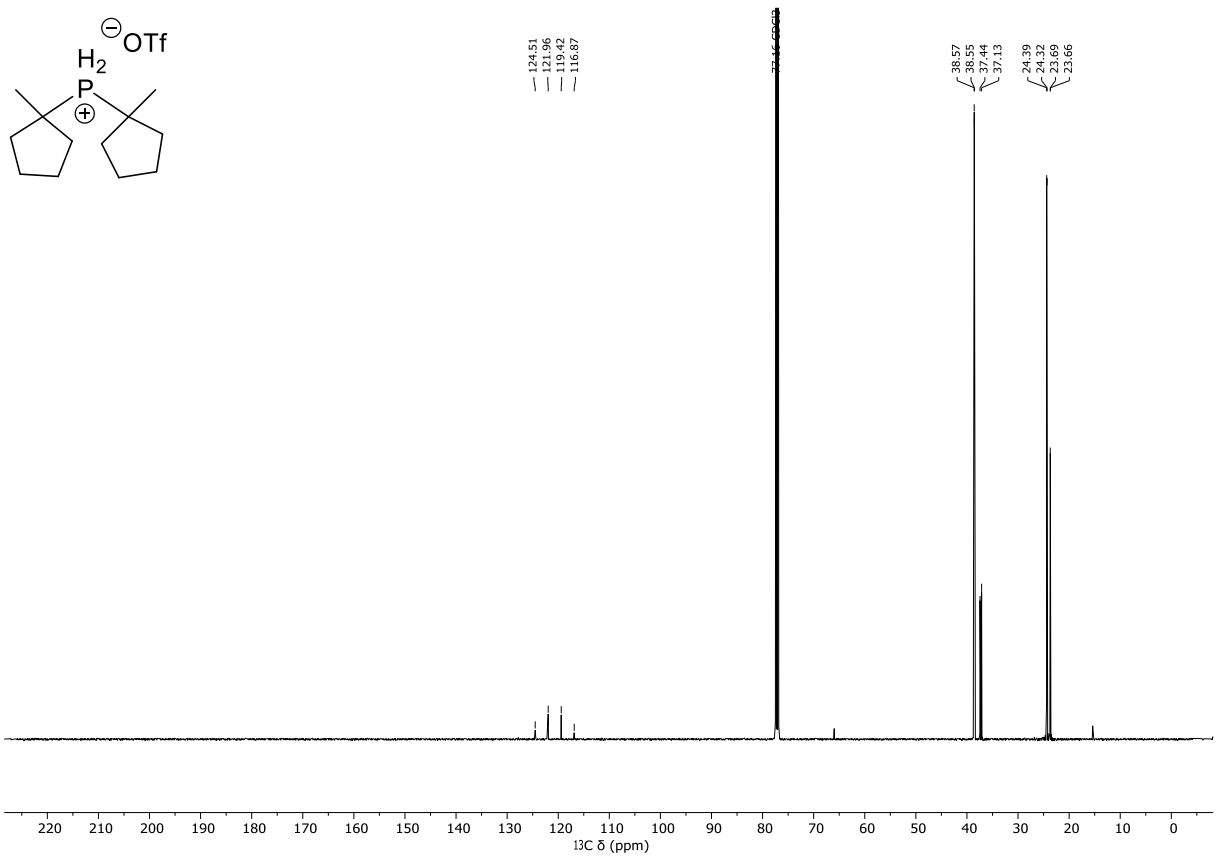
Di-(2-Methyl-4-(4-bromophenyl)-2-butyl)phosphonium triflate (1g) ^{31}P NMR (202 MHz, $CDCl_3$)



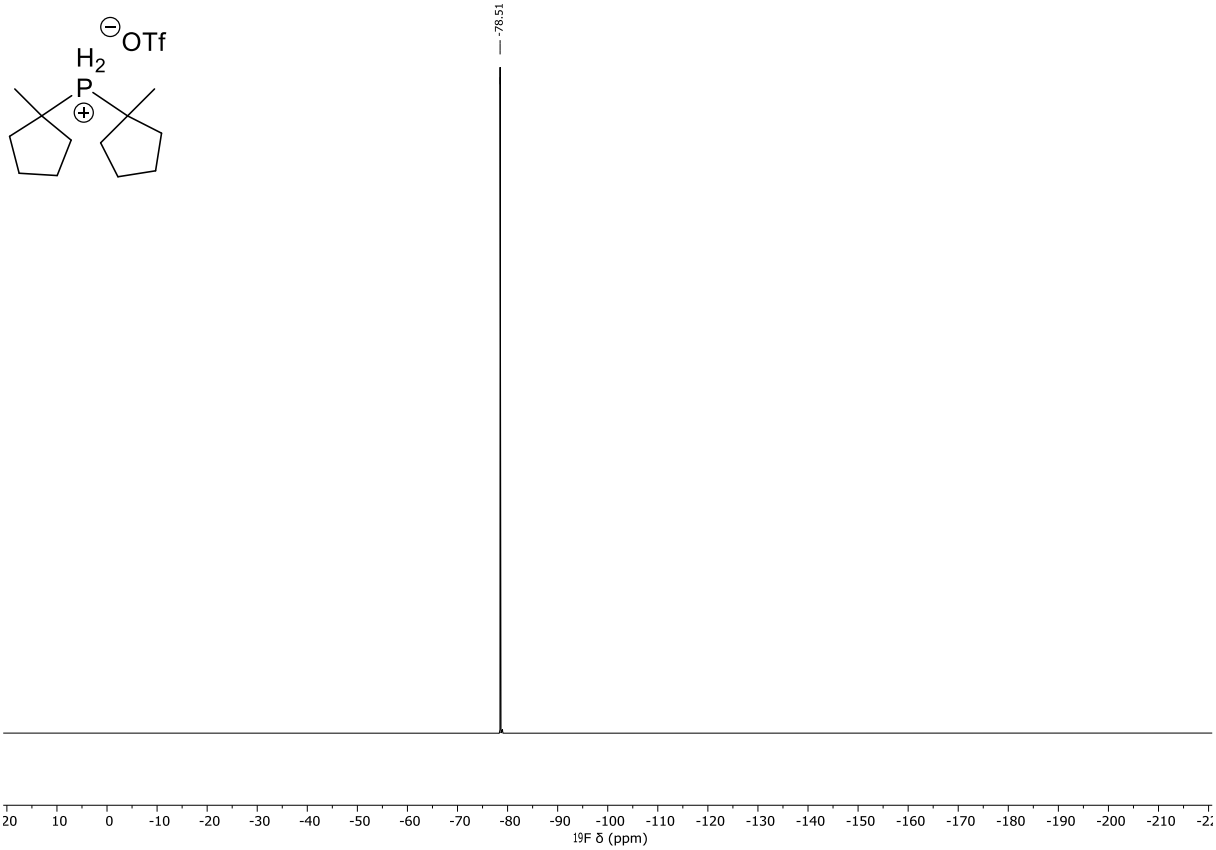
Di-(1-methylcyclopentyl)phosphonium triflate (1h) - ^{1}H NMR (500 MHz, $CDCl_3$)



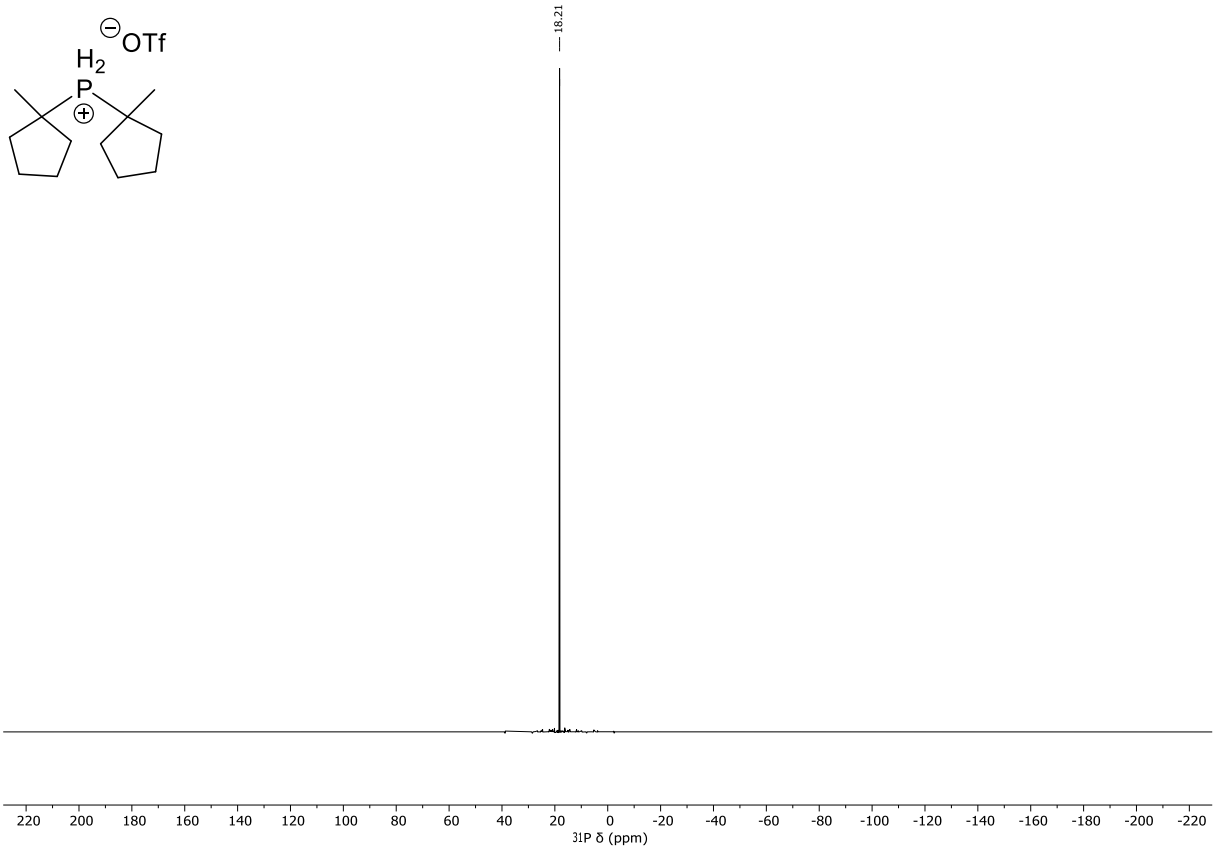
Di-(1-methylcyclopentyl)phosphonium triflate (1h) - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



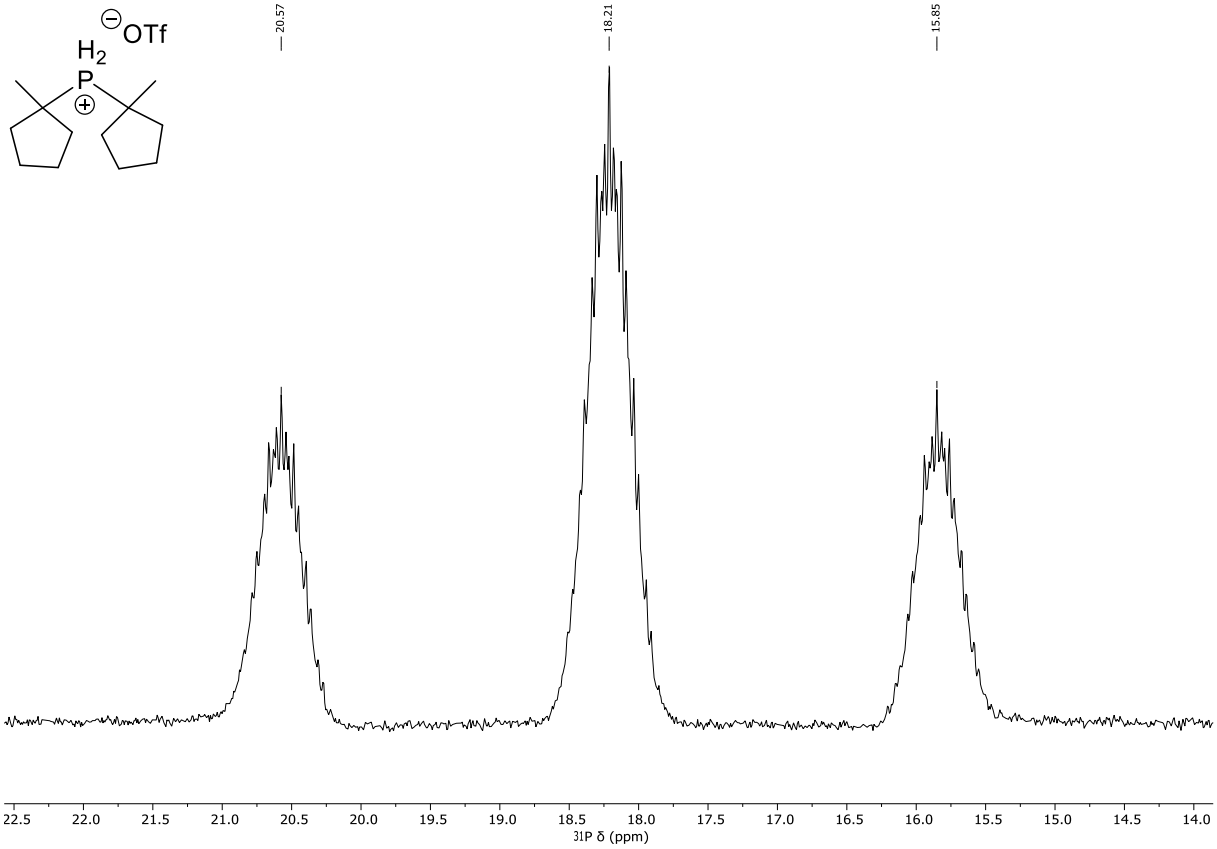
Di-(1-methylcyclopentyl)phosphonium triflate (1h) ^{19}F NMR (470 MHz, $CDCl_3$)



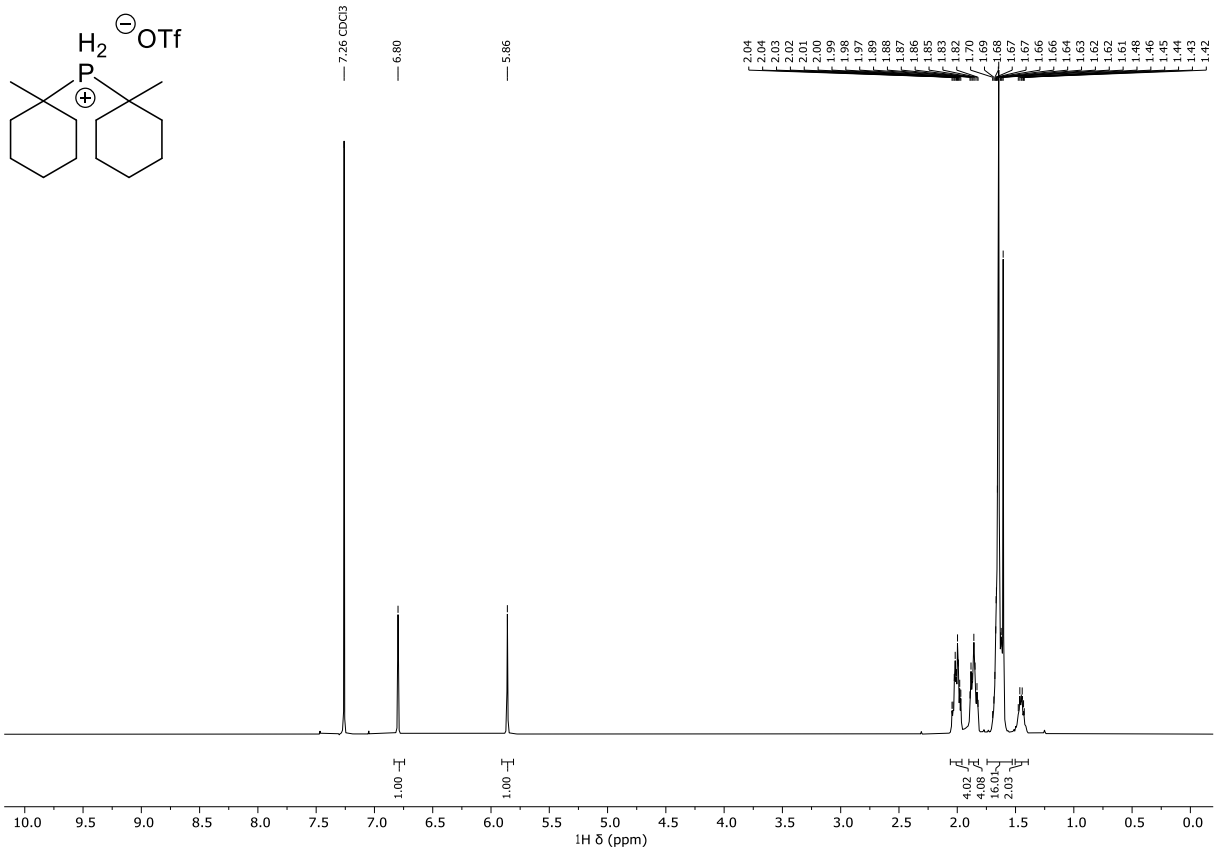
Di-(1-methylcyclopentyl)phosphonium triflate (1h) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



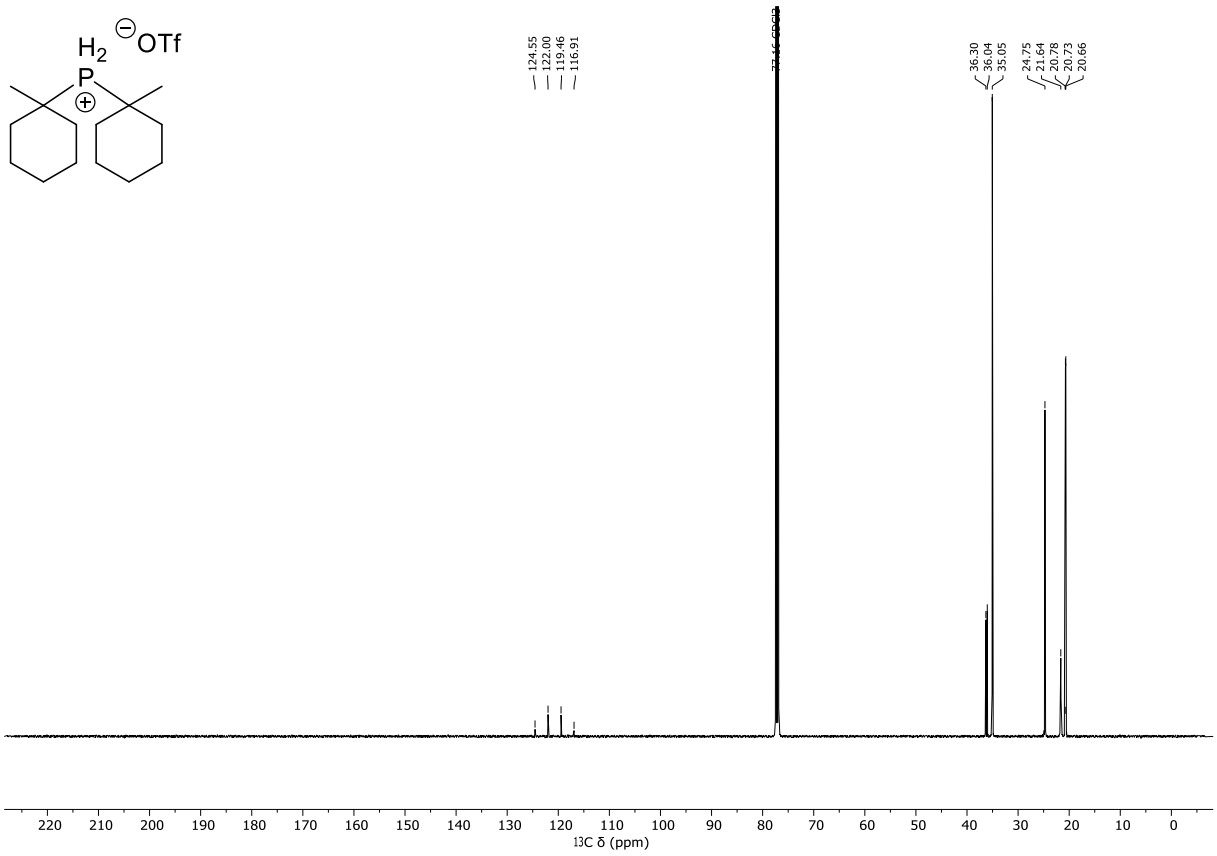
Di-(1-methylcyclopentyl)phosphonium triflate (1h) ^{31}P NMR (202 MHz, $CDCl_3$)



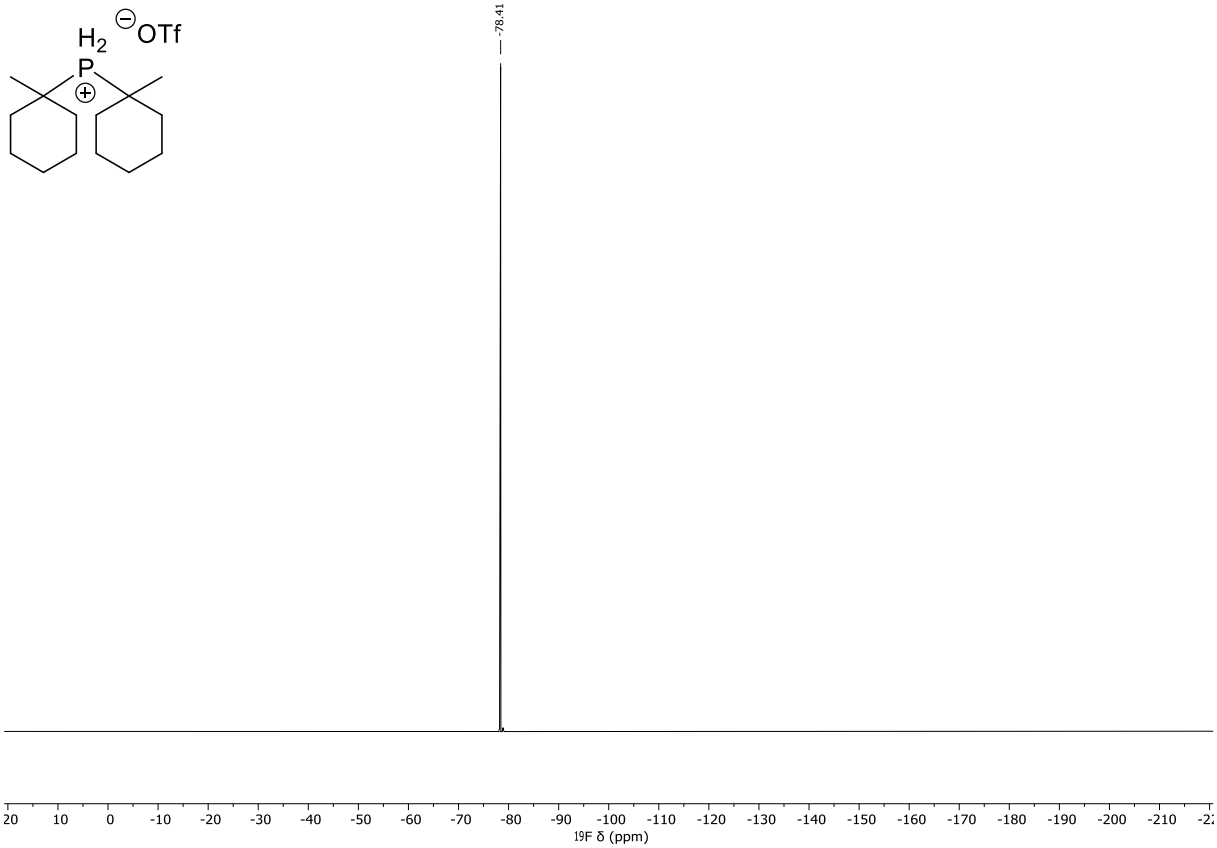
Di-(1-methylcyclohexyl)phosphonium triflate (1i) - ^{1}H NMR (500 MHz, $CDCl_3$)



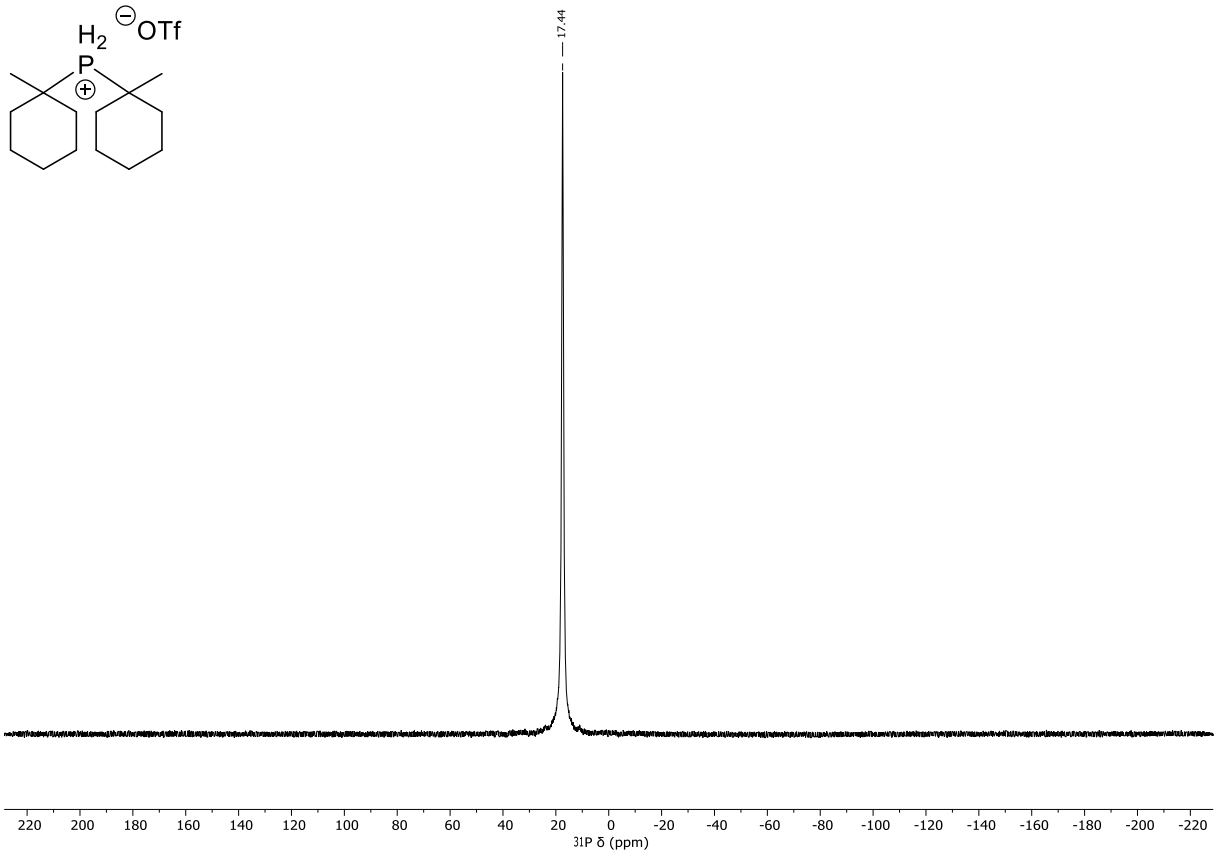
Di-(1-methylcyclohexyl)phosphonium triflate (1i) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



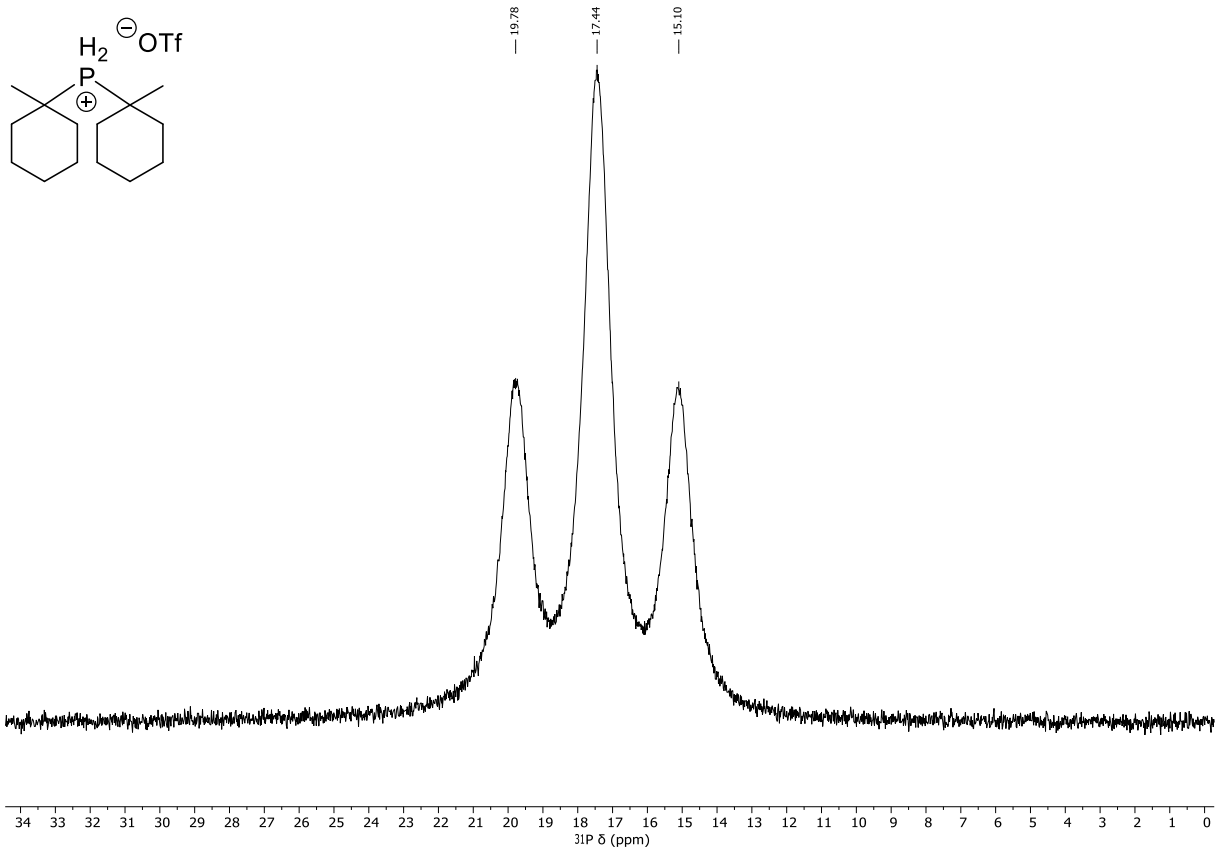
Di-(1-methylcyclohexyl)phosphonium triflate (1i) ^{19}F NMR (470 MHz, $CDCl_3$)



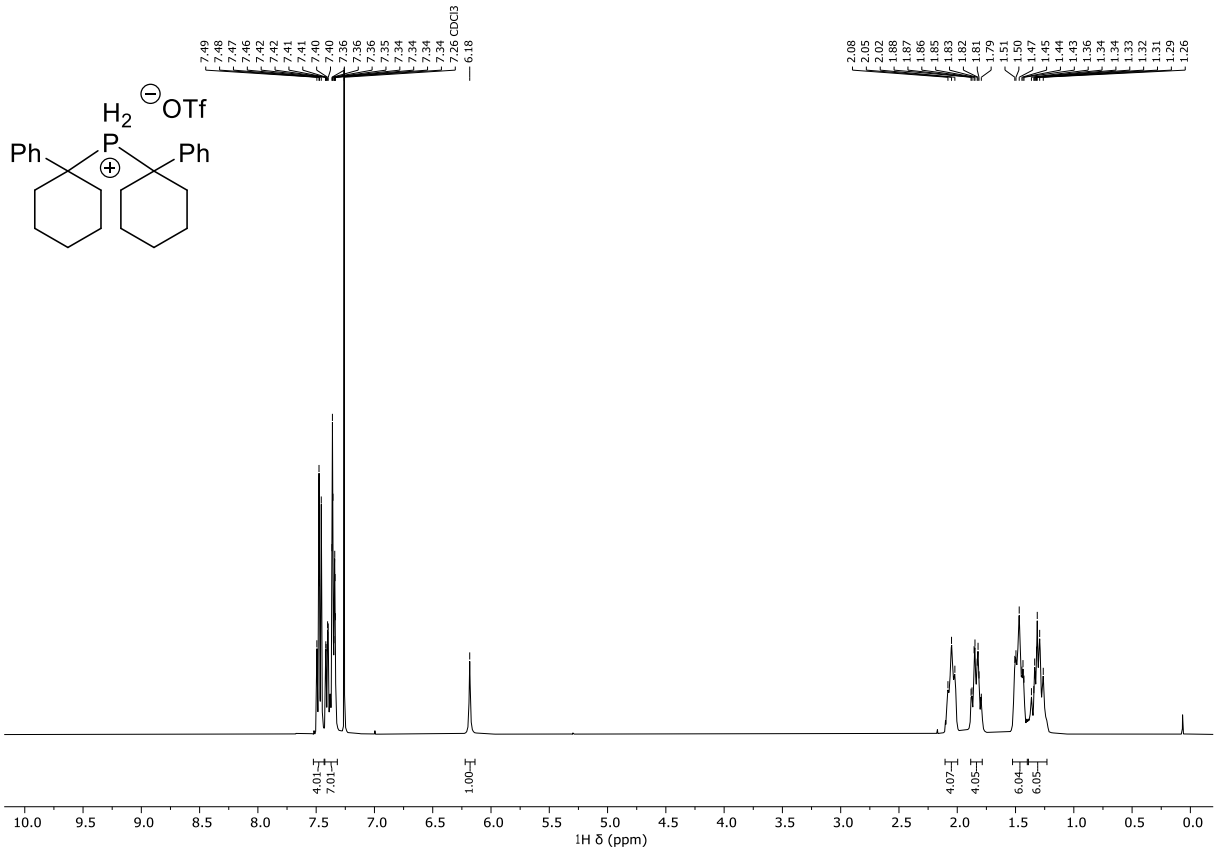
Di-(1-methylcyclohexyl)phosphonium triflate (1i) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



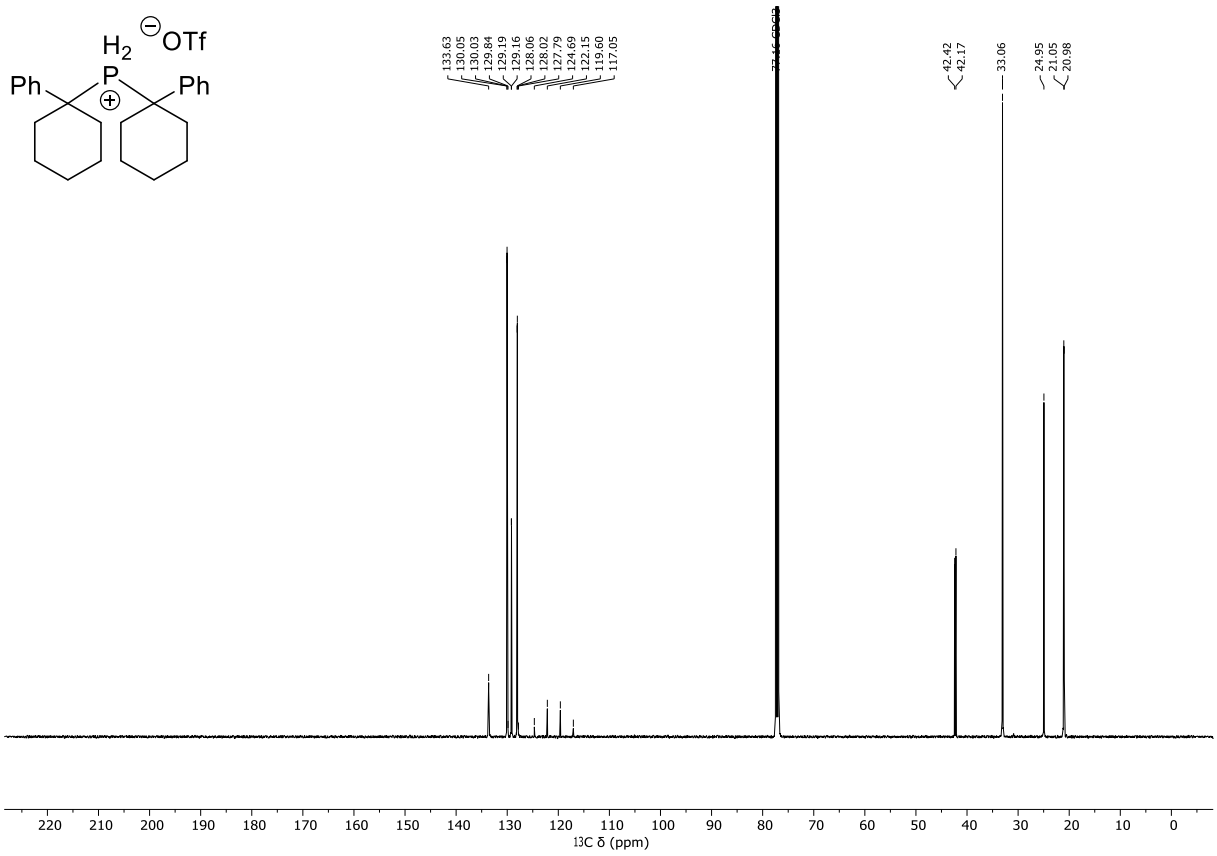
Di-(1-methylcyclohexyl)phosphonium triflate (1i) ^{31}P NMR (202 MHz, $CDCl_3$)



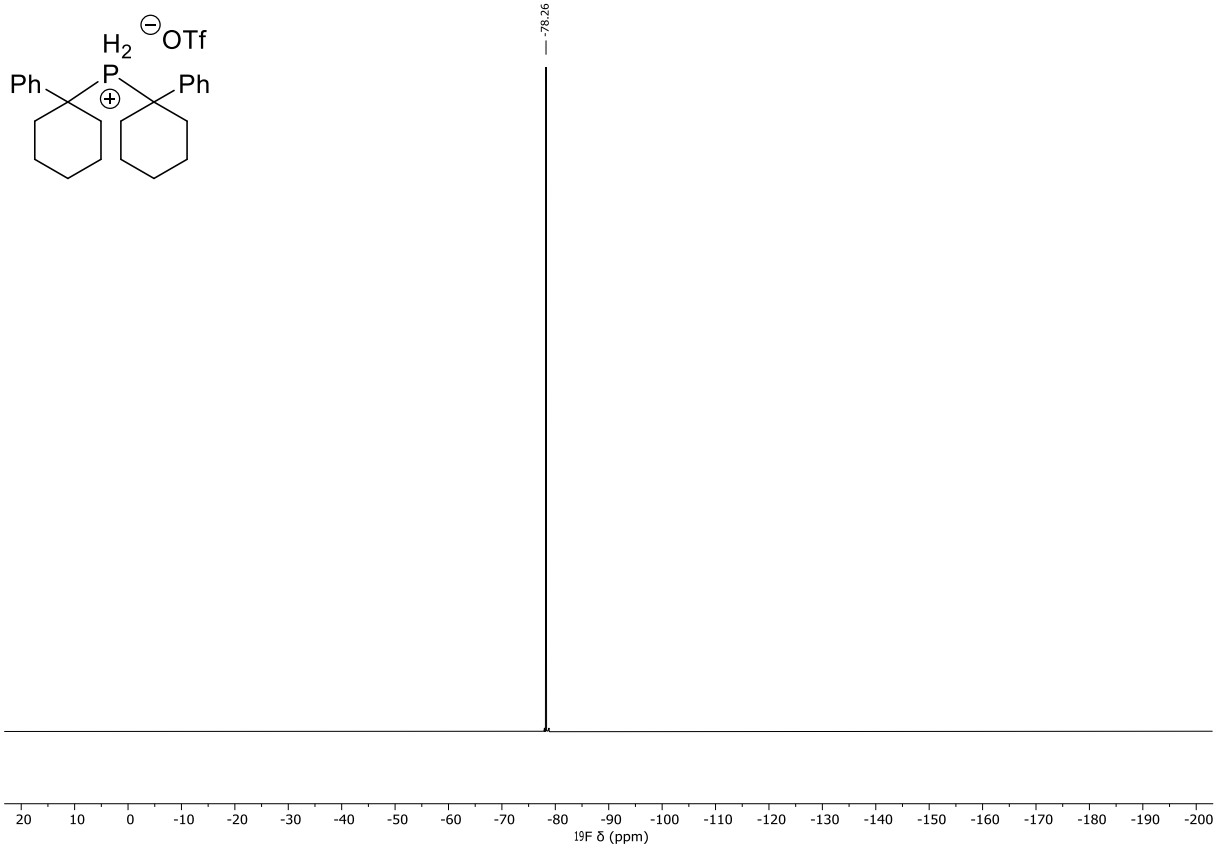
Di-(1-phenylcyclohexyl)phosphonium triflate (1j) - ^{1}H NMR (500 MHz, $CDCl_3$)



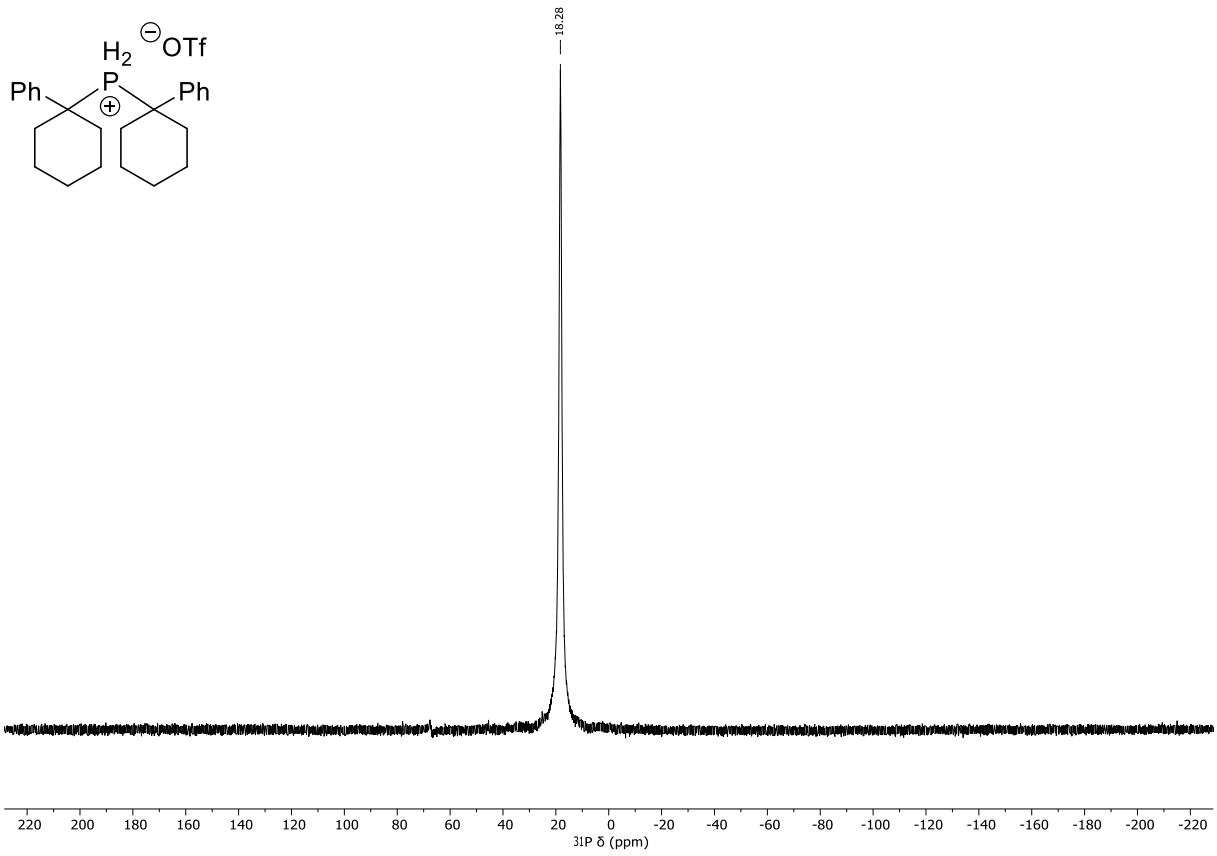
Di-(1-phenylcyclohexyl)phosphonium triflate (1j) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



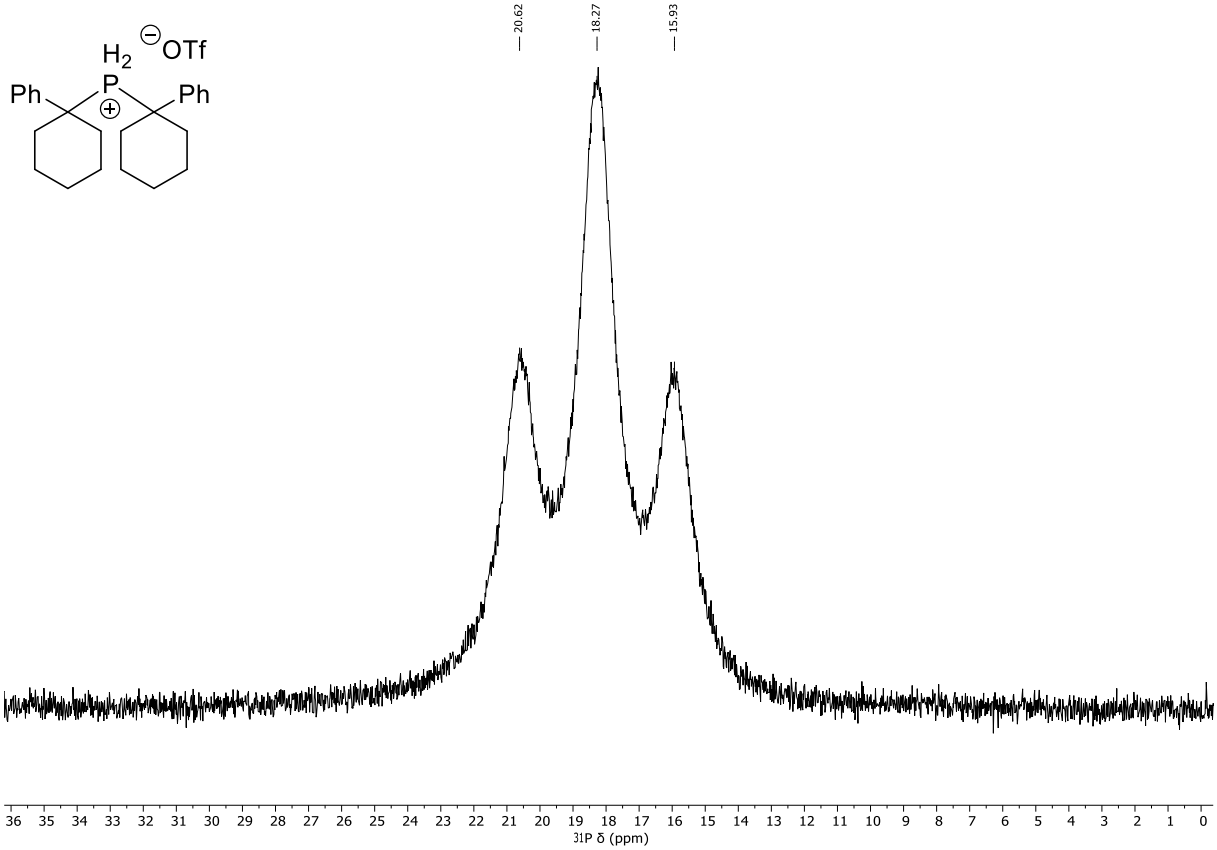
Di-(1-phenylcyclohexyl)phosphonium triflate (1j) ^{19}F NMR (470 MHz, $CDCl_3$)



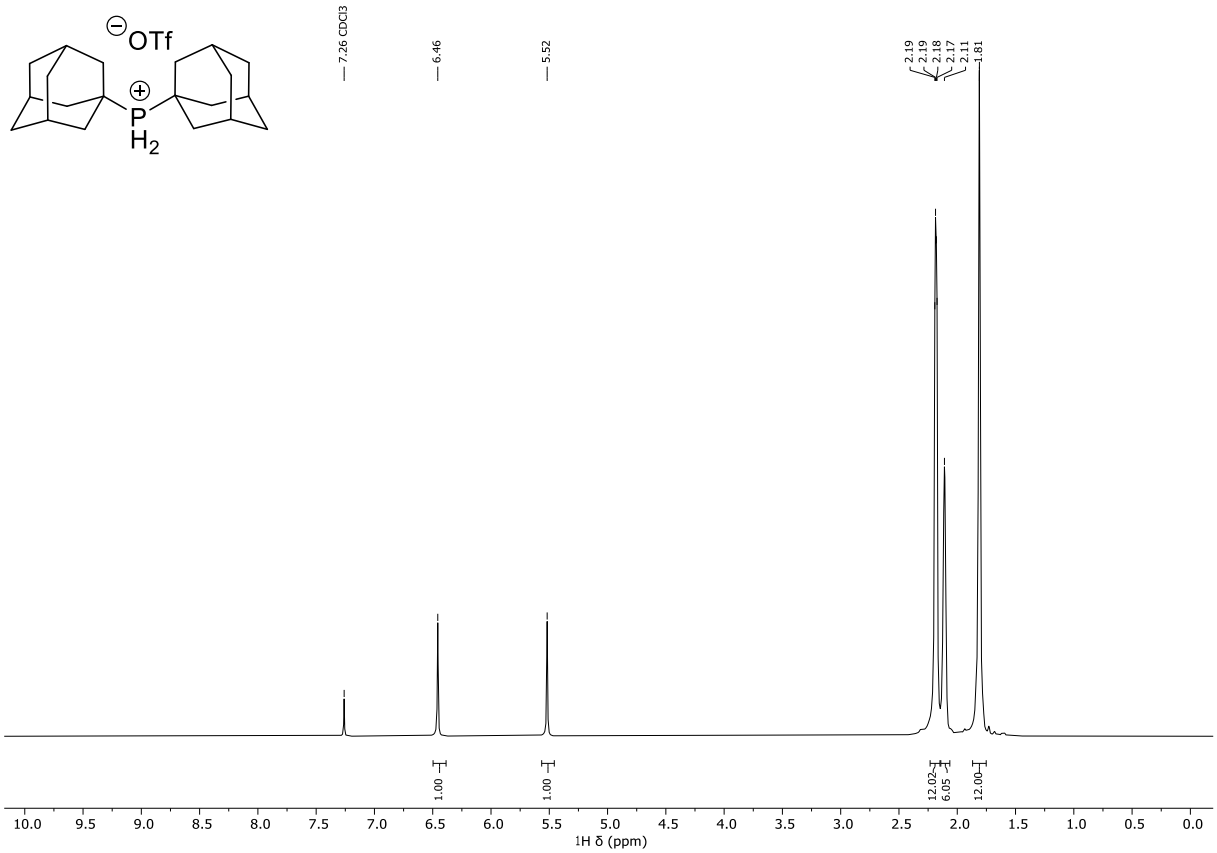
Di-(1-phenylcyclohexyl)phosphonium triflate (1j) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



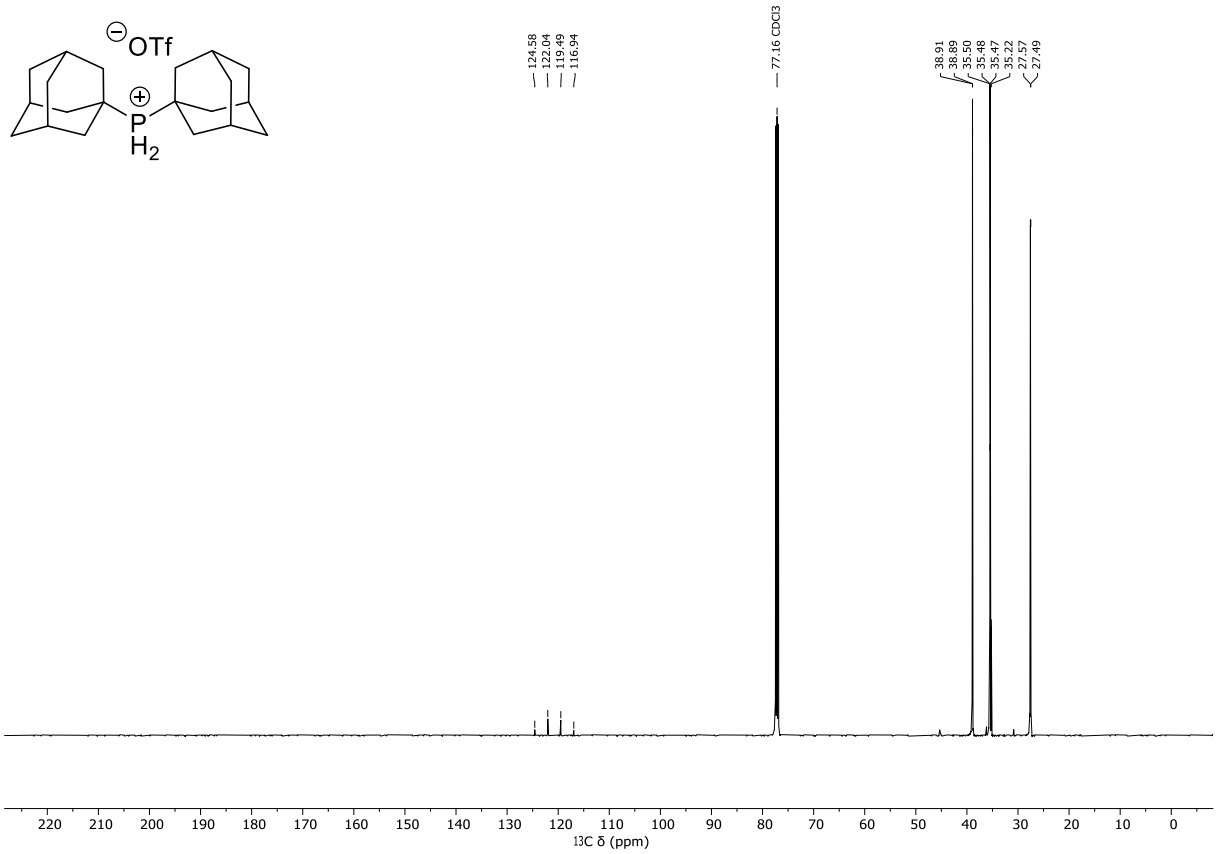
Di-(1-phenylcyclohexyl)phosphonium triflate (1j) ^{31}P NMR (202 MHz, $CDCl_3$)



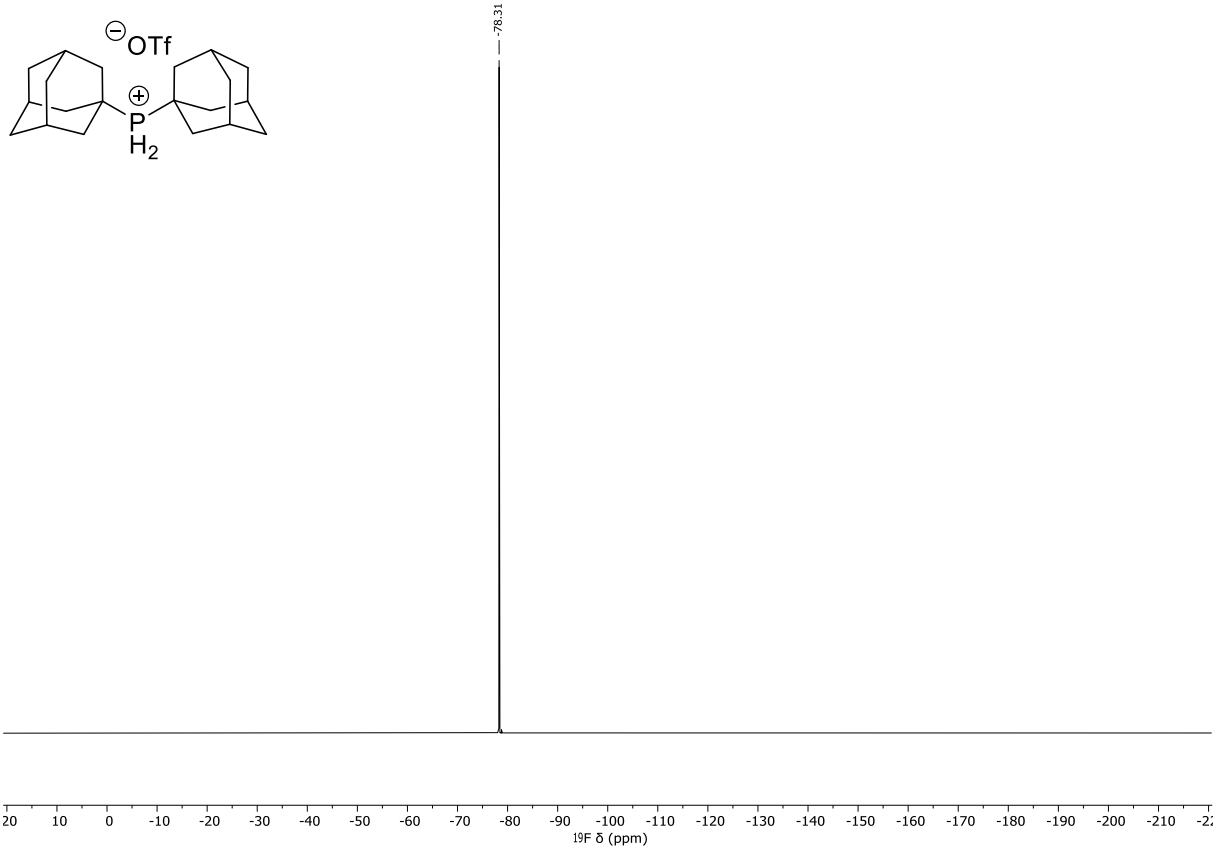
Di-(1-Adamantyl)phosphonium triflate (1k) - ^{1}H NMR (500 MHz, $CDCl_3$)



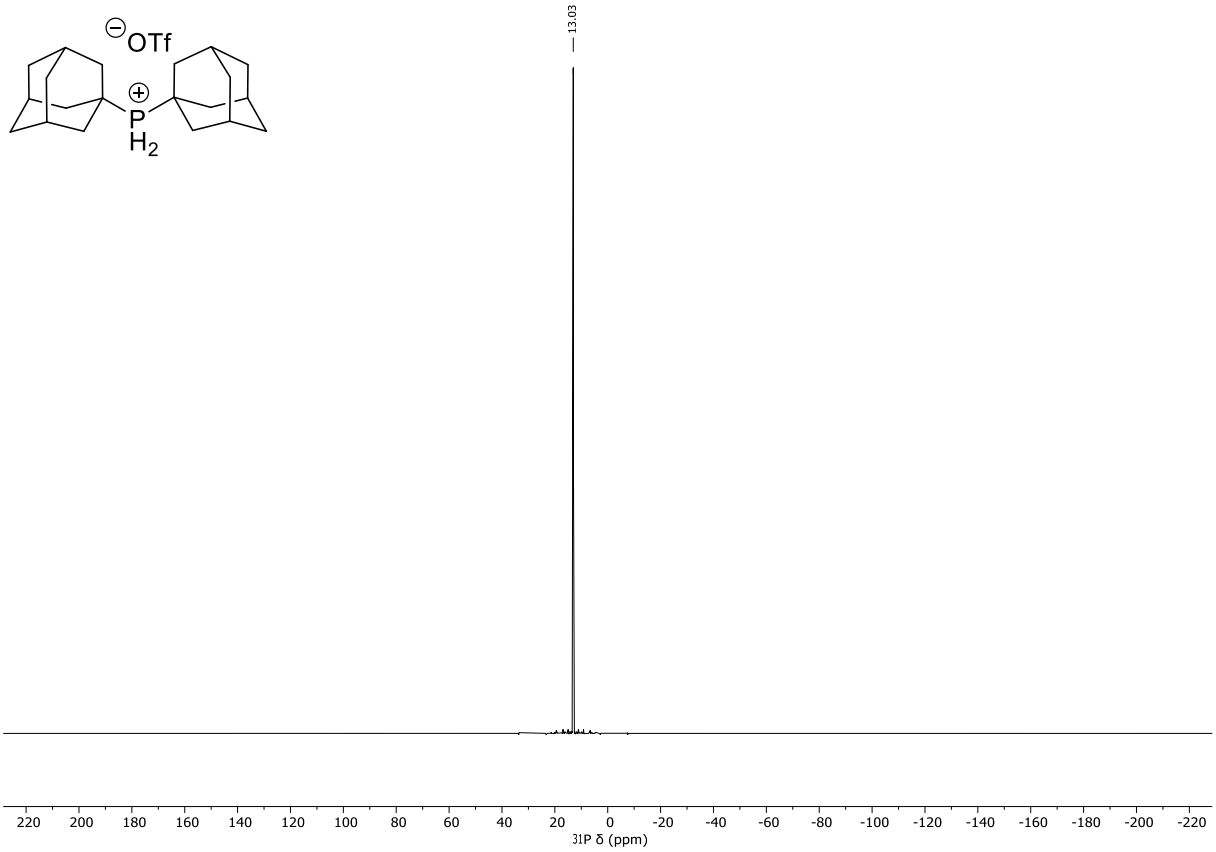
Di-(1-Adamantyl)phosphonium triflate (1k) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



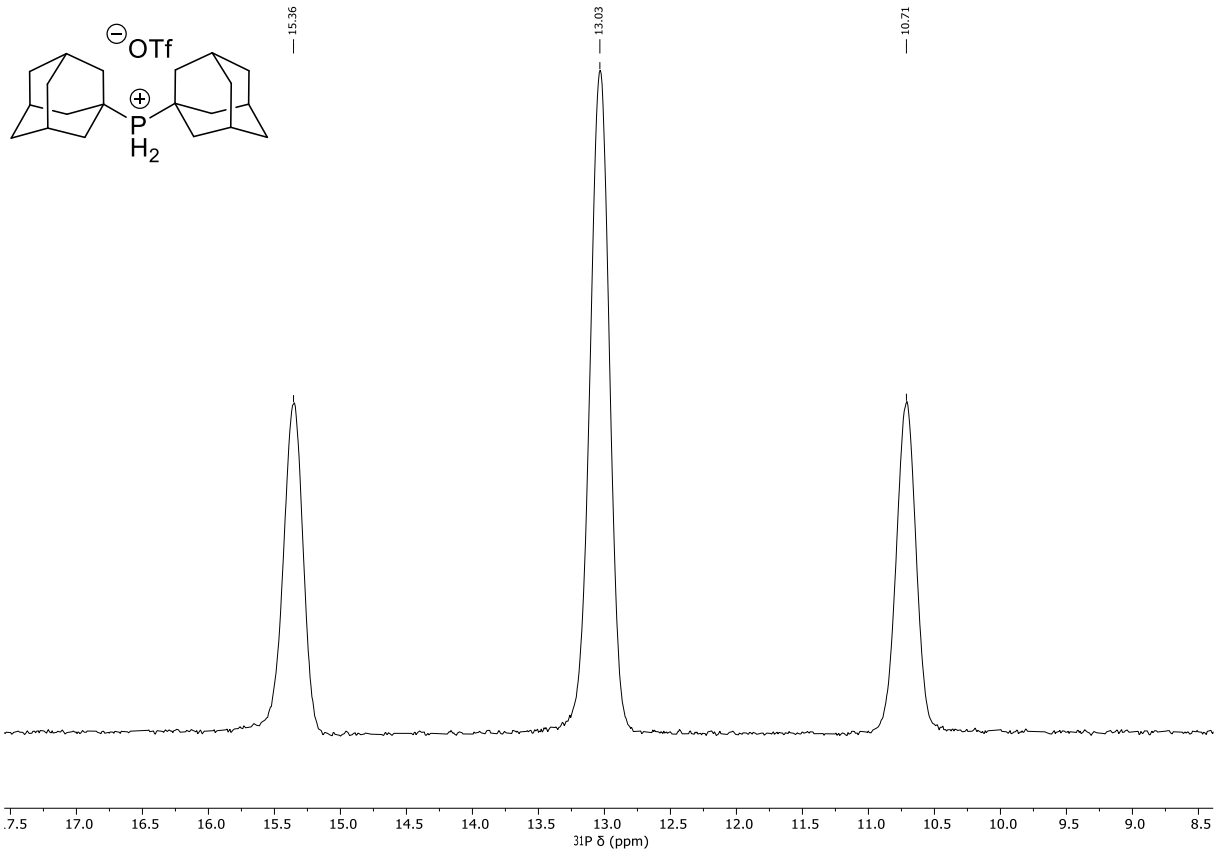
Di-(1-Adamantyl)phosphonium triflate (1k) ^{19}F NMR (470 MHz, $CDCl_3$)



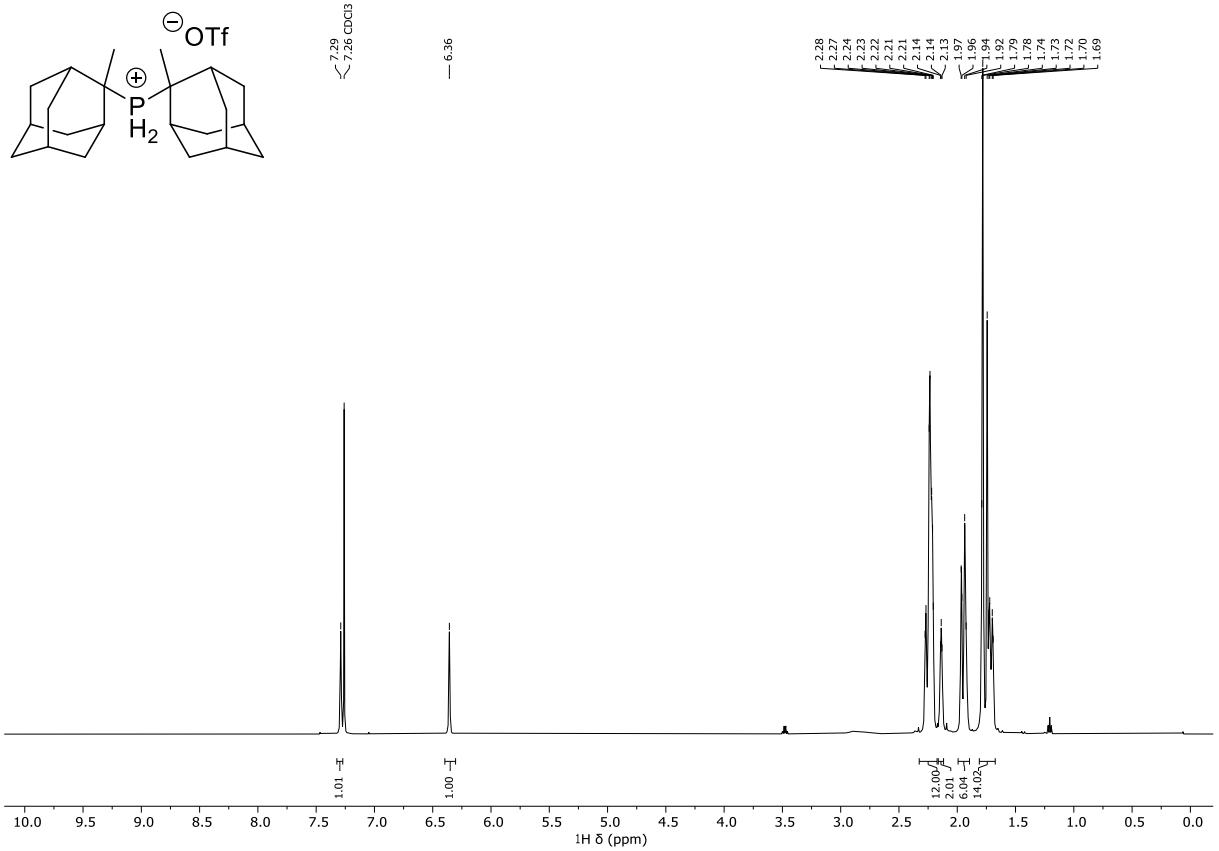
Di-(1-Adamantyl)phosphonium triflate (1k) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



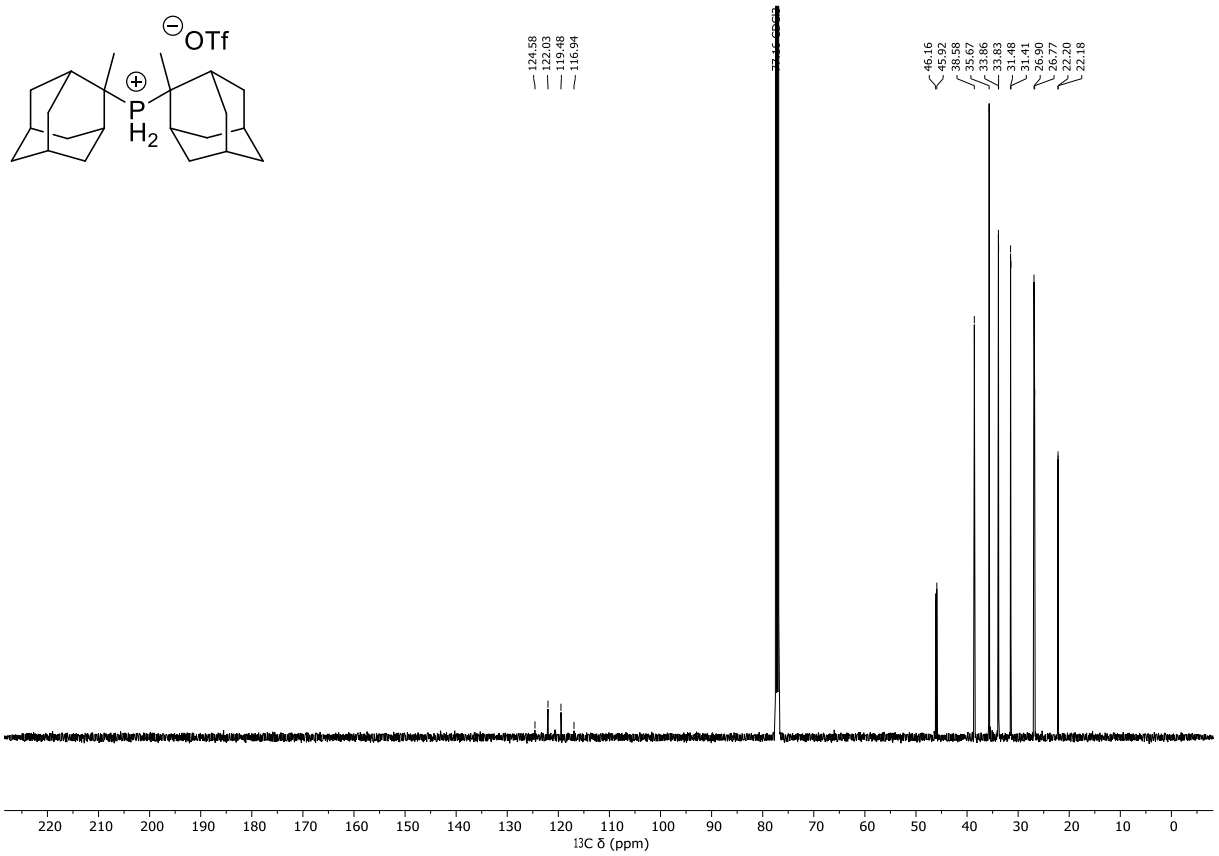
Di-(1-Adamantyl)phosphonium triflate (1k) ^{31}P NMR (202 MHz, $CDCl_3$)



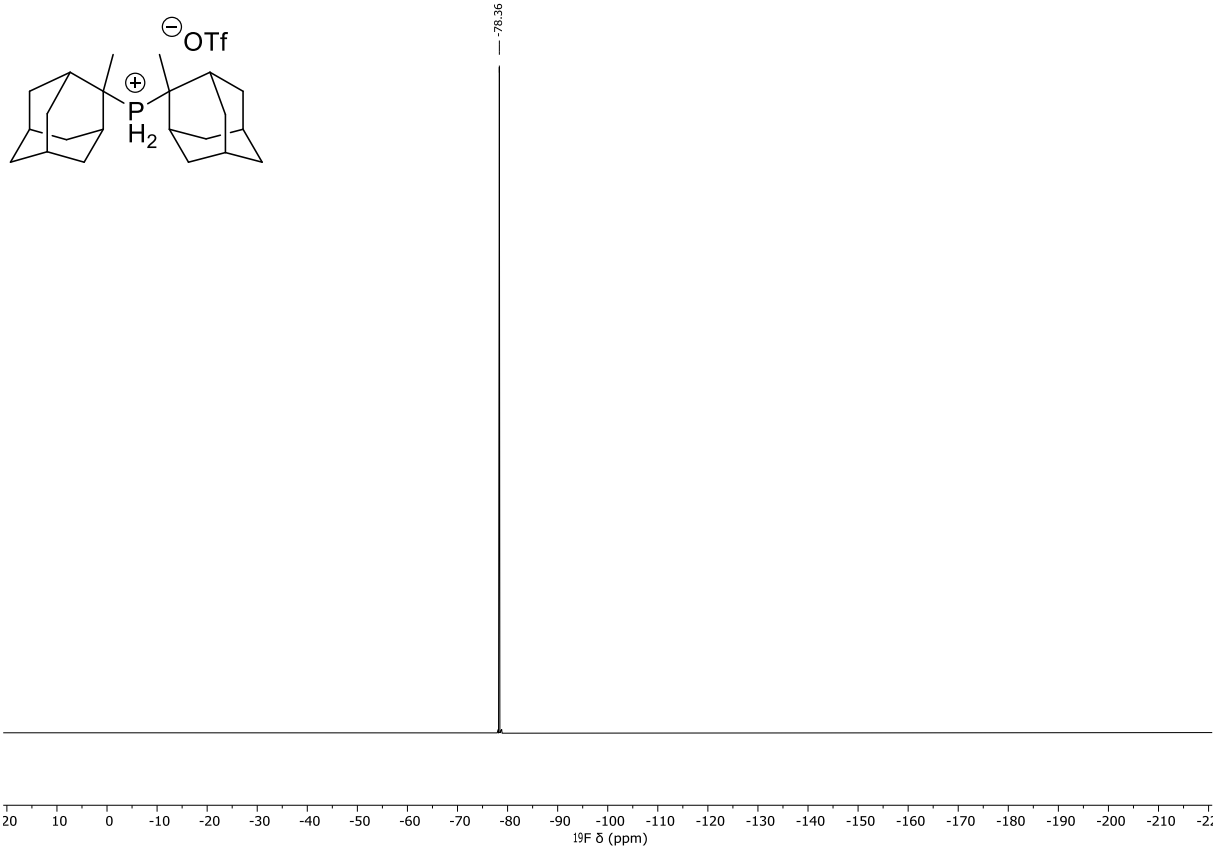
Di-(2-methyl-2-adamantyl)phosphonium triflate (1l) - ^{1}H NMR (500 MHz, $CDCl_3$)



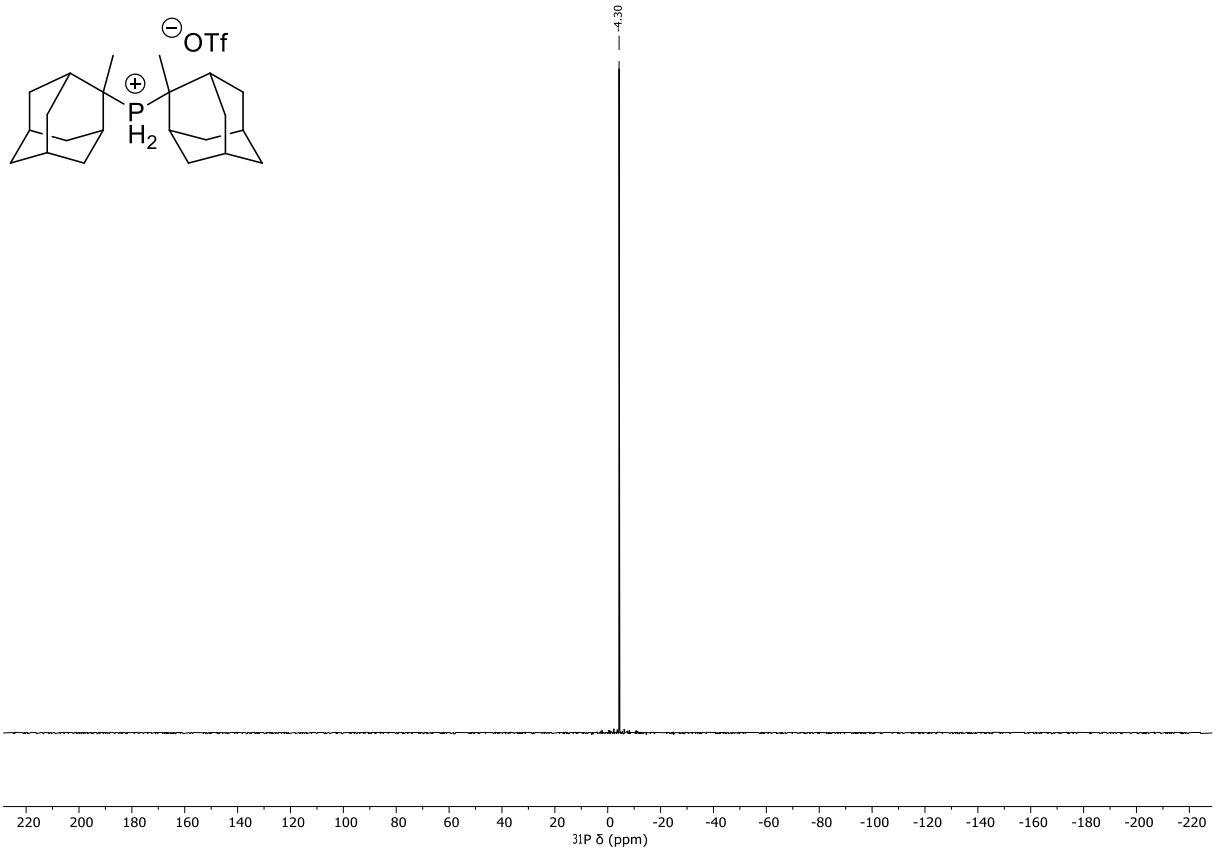
Di-(2-methyl-2-adamantyl)phosphonium triflate (1l) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



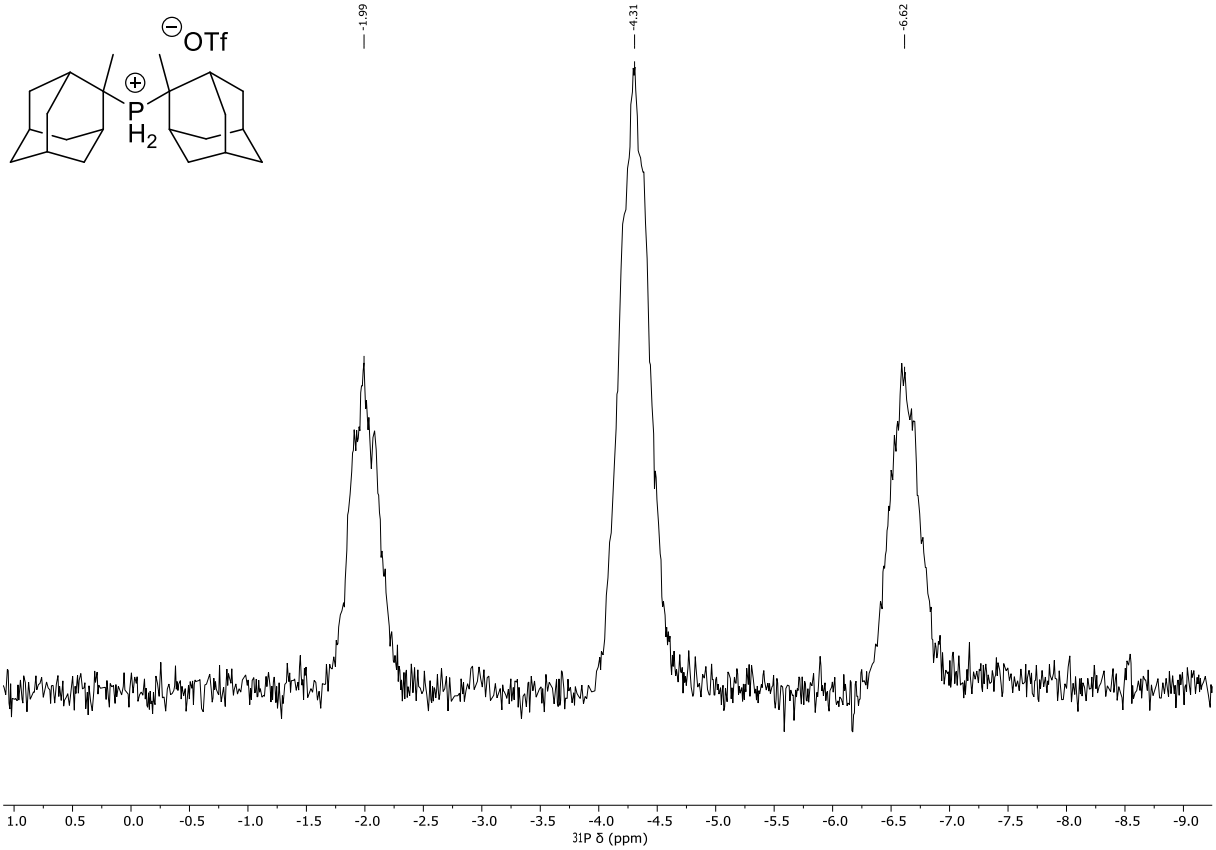
Di-(2-methyl-2-adamantyl)phosphonium triflate (1l) ^{19}F NMR (470 MHz, $CDCl_3$)



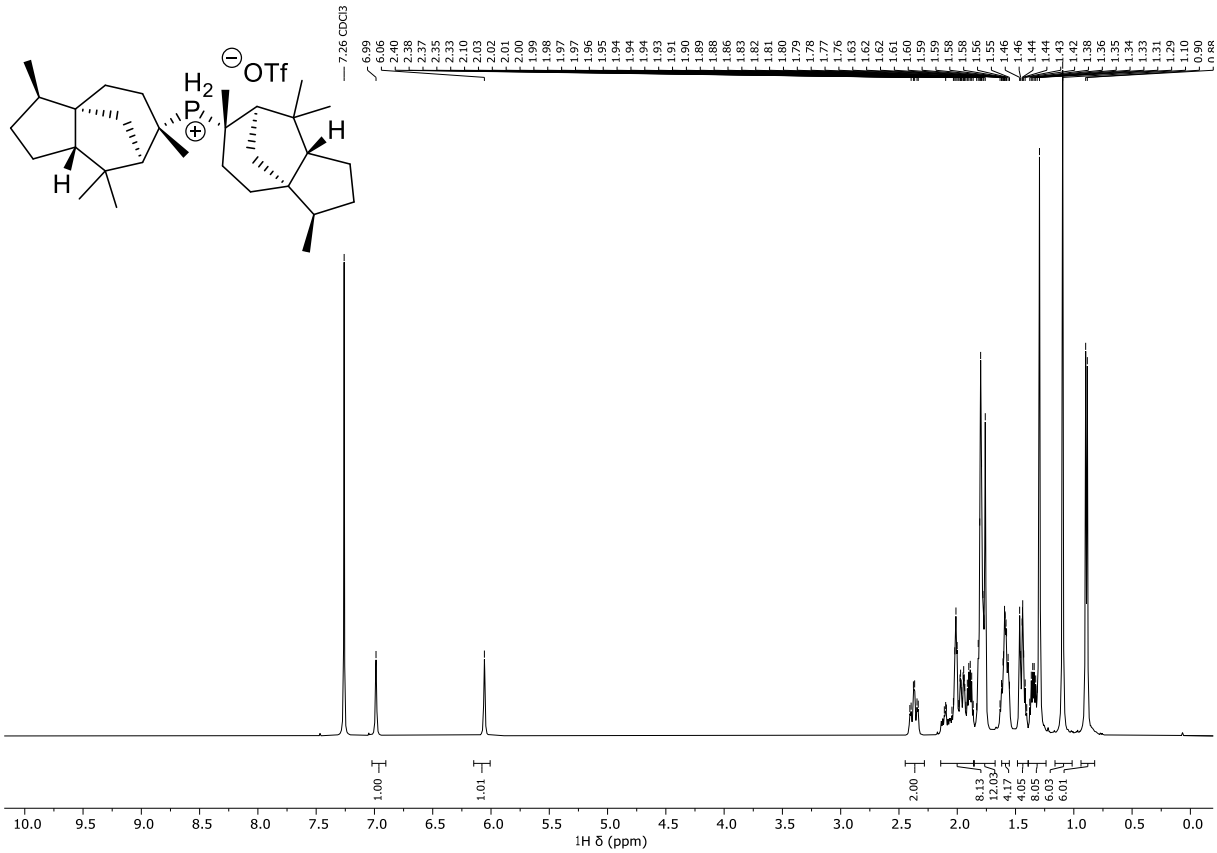
Di-(2-methyl-2-adamantyl)phosphonium triflate (1l) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



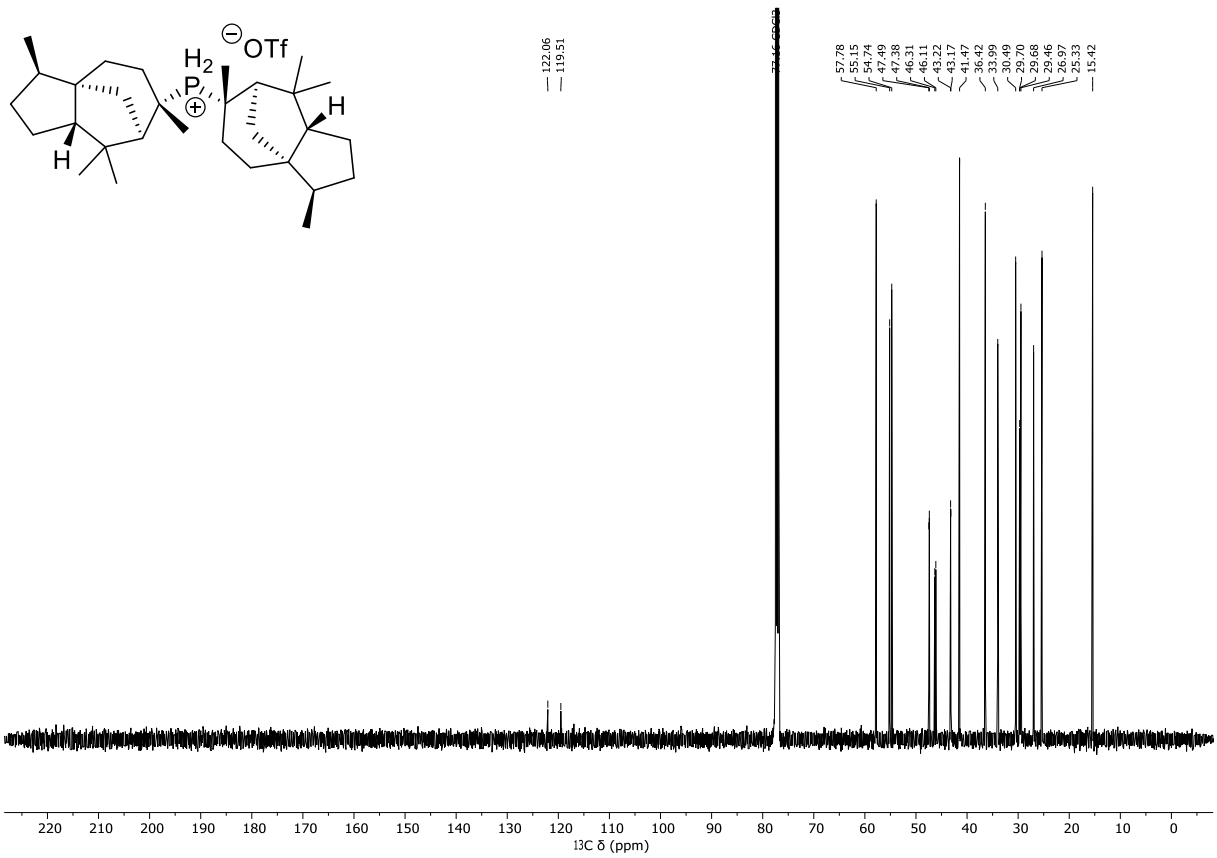
Di-(2-methyl-2-adamantyl)phosphonium triflate (1l) ^{31}P NMR (202 MHz, $CDCl_3$)



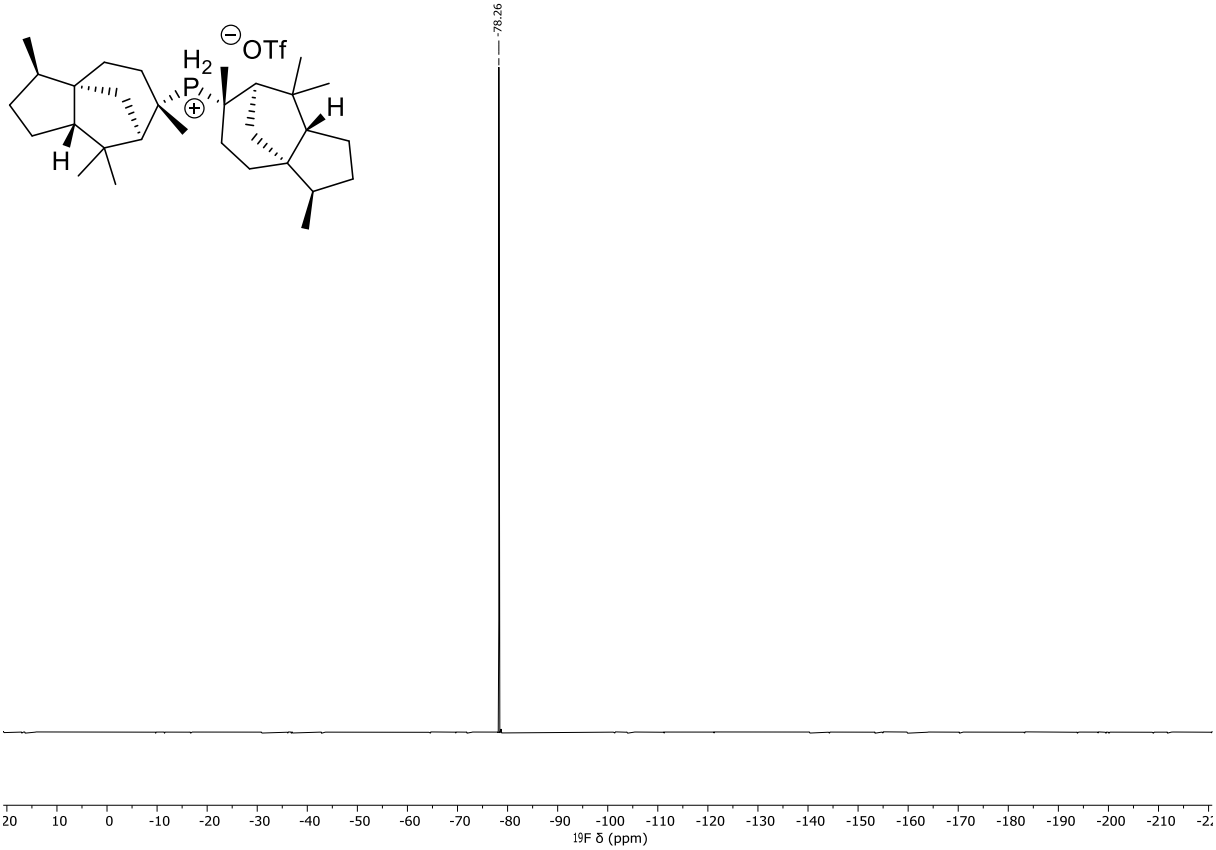
Dicedrylphosphonium triflate (1m) - ^{1}H NMR (500 MHz, $CDCl_3$)



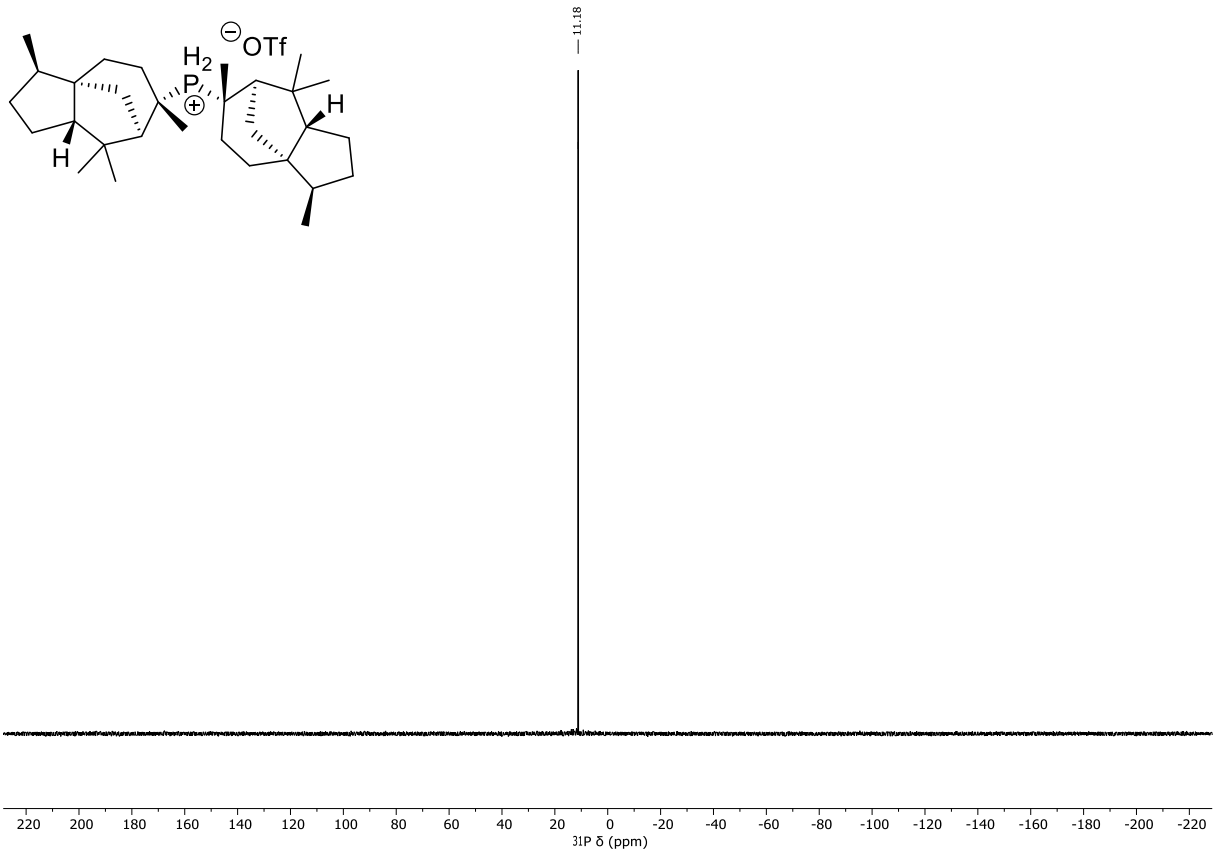
Dicedrylphosphonium triflate (1m) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



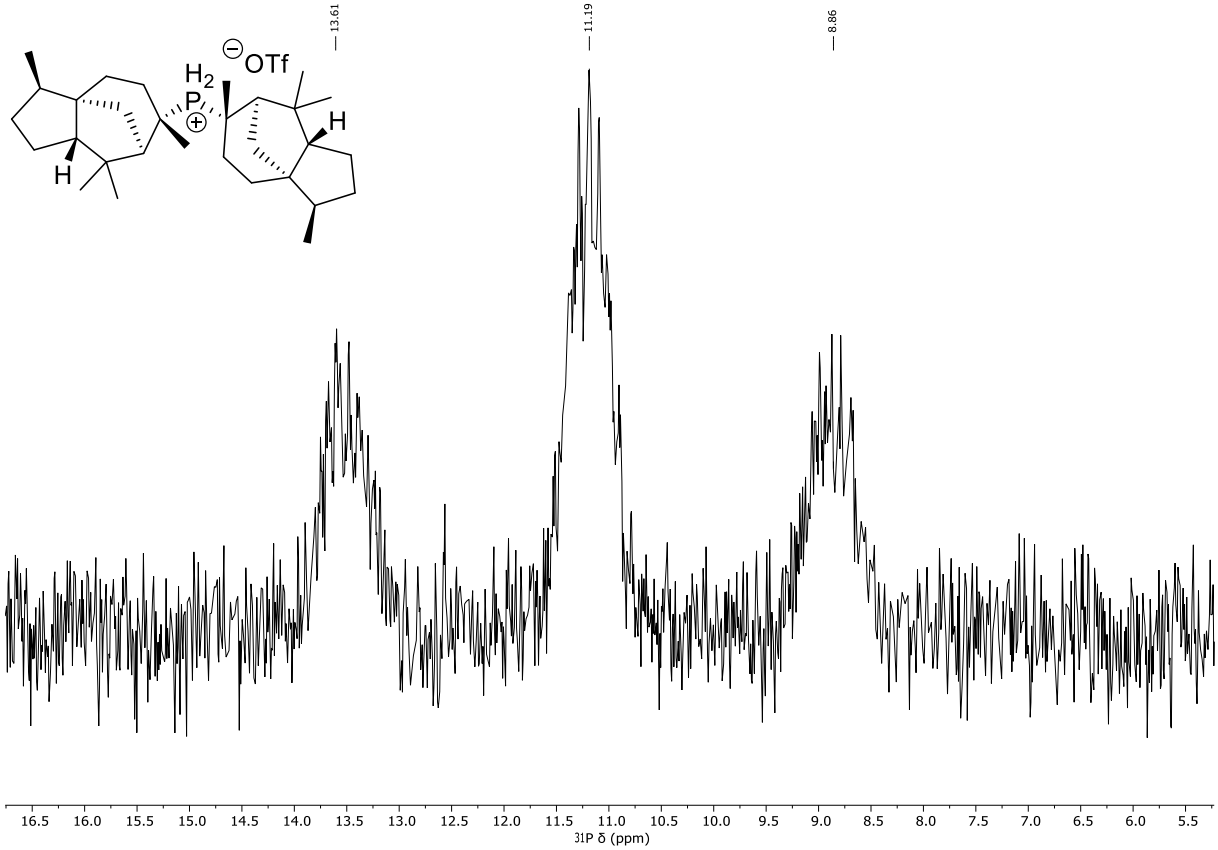
Dicedrylphosphonium triflate (1m) ^{19}F NMR (470 MHz, $CDCl_3$)



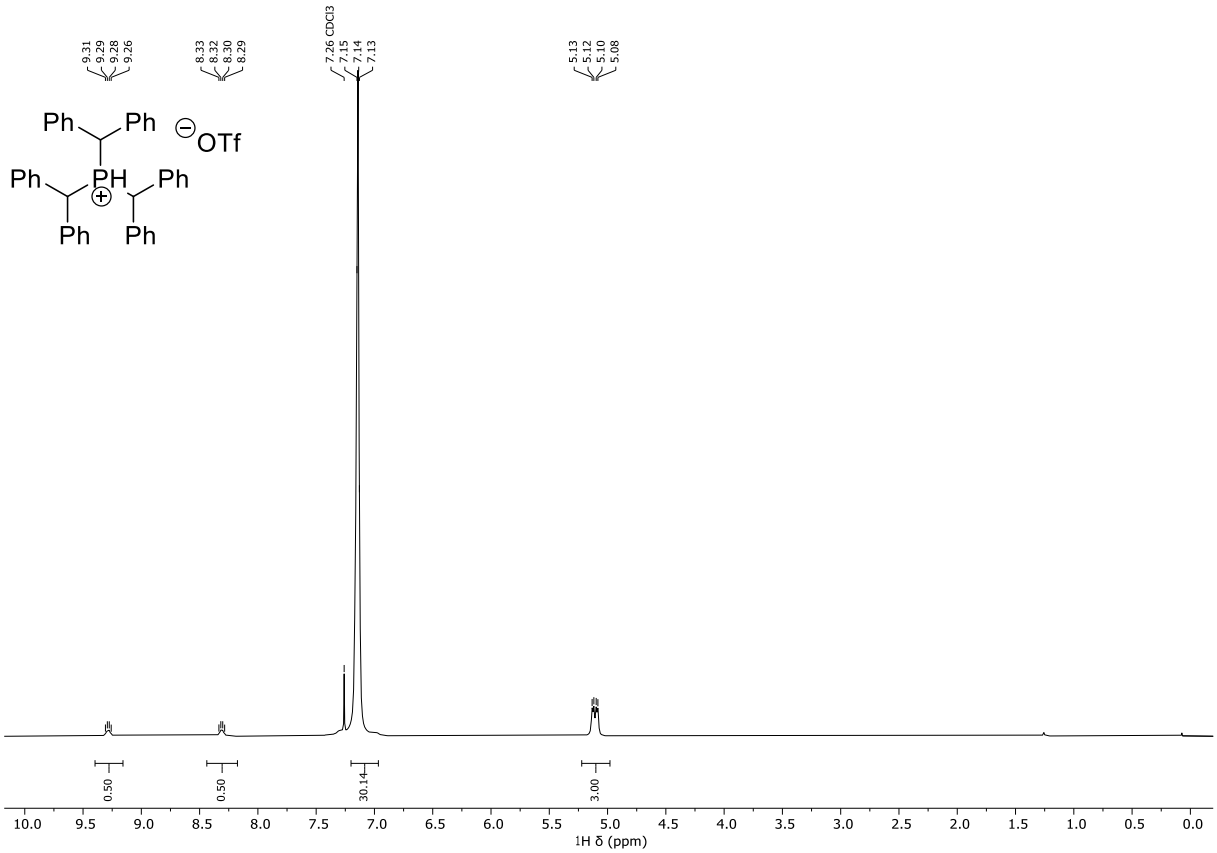
Dicedrylphosphonium triflate (1m) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



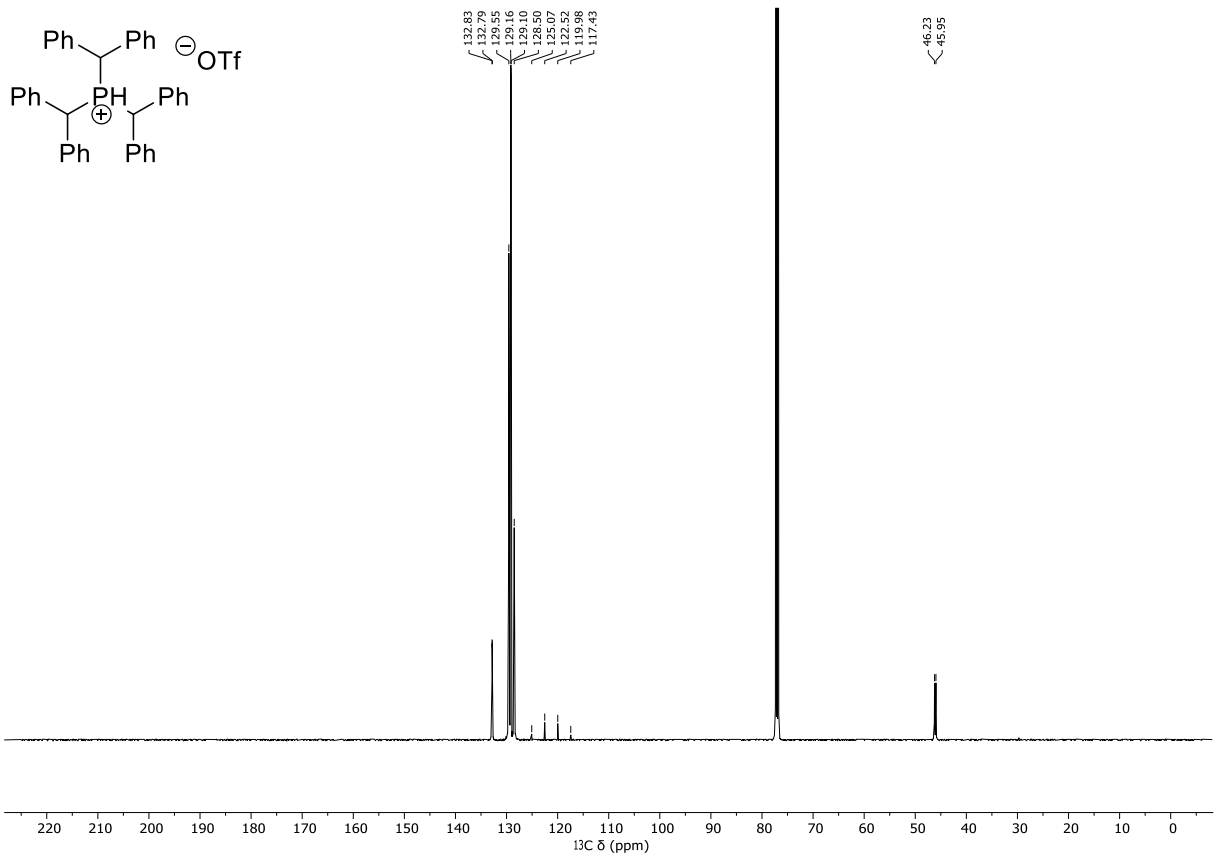
Dicedrylphosphonium triflate (1m) ^{31}P NMR (202 MHz, $CDCl_3$)



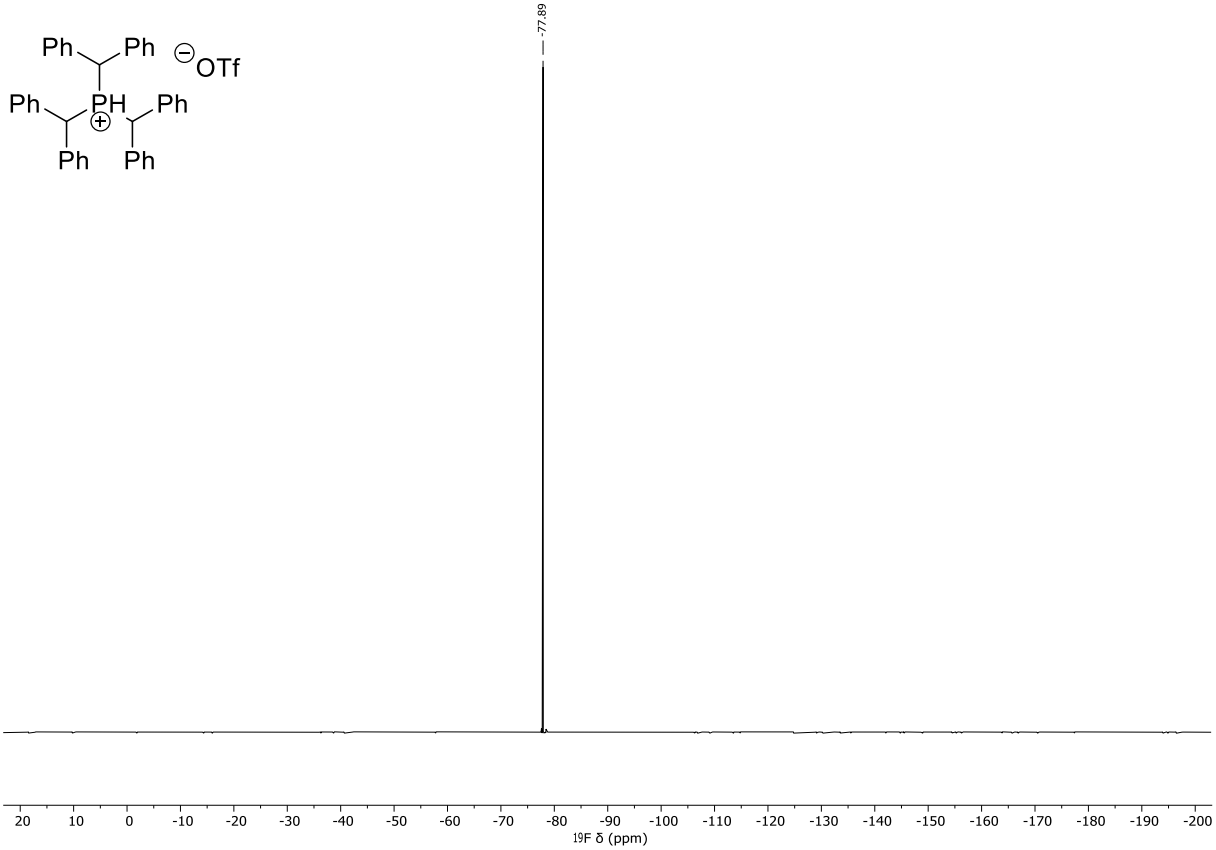
Tribenzhydrylphosphonium triflate (1n) - ^{1}H NMR (500 MHz, $CDCl_3$)



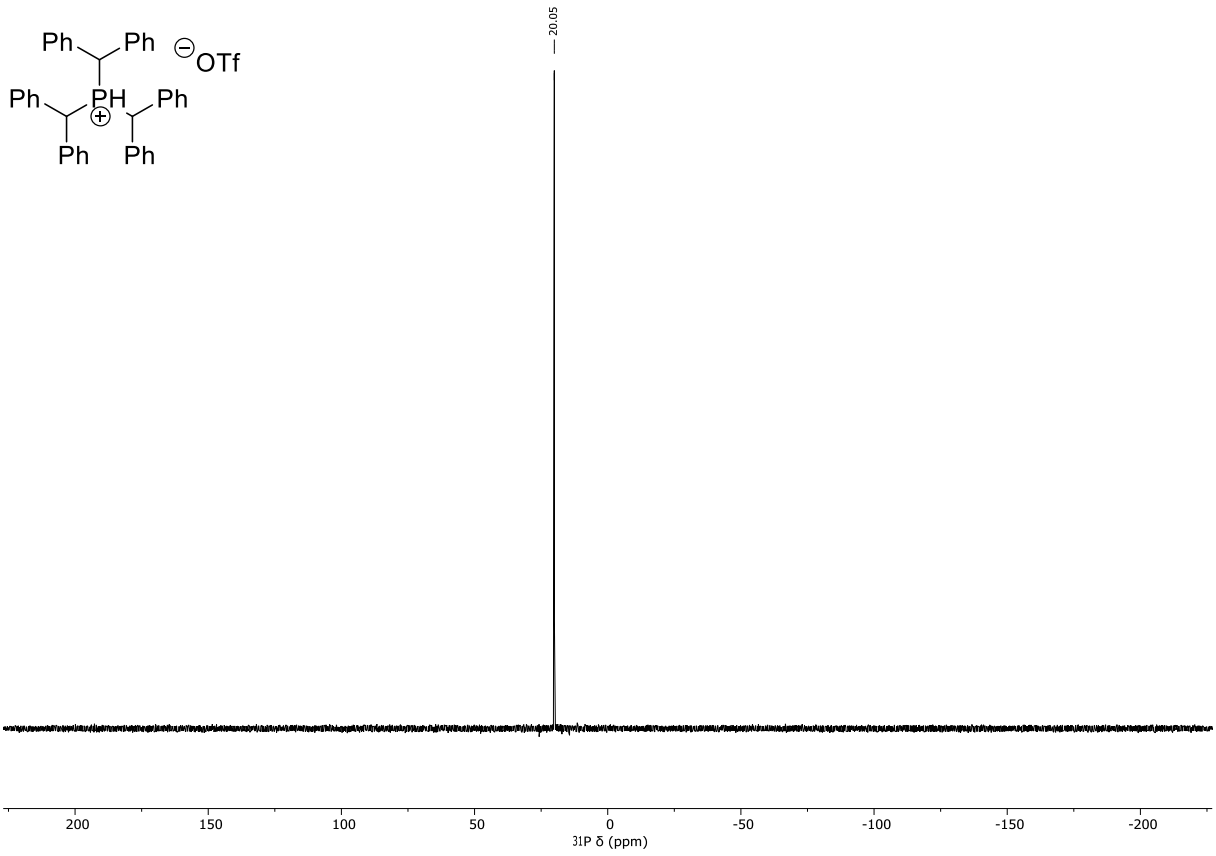
Tribenzhydrylphosphonium triflate (1n) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



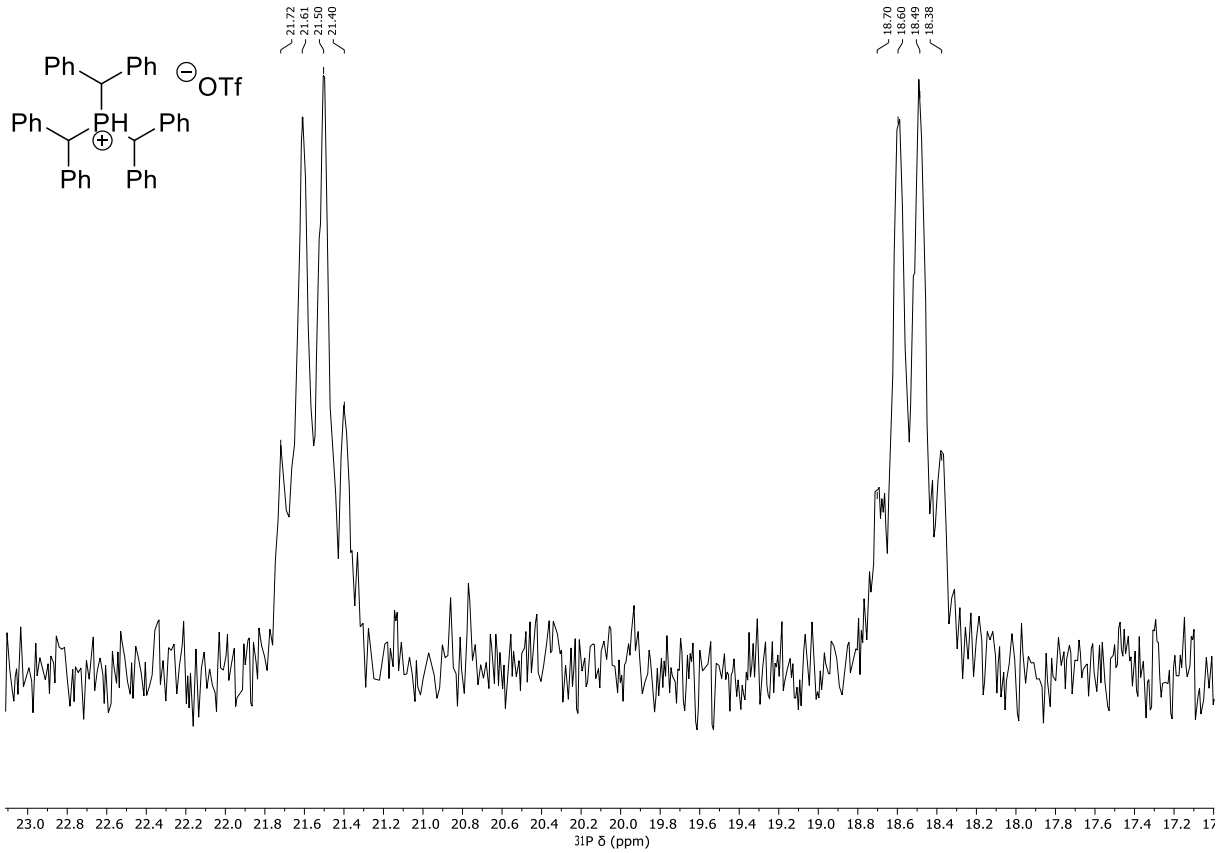
Tribenzhydrylphosphonium triflate (1n) ^{19}F NMR (376 MHz, $CDCl_3$)



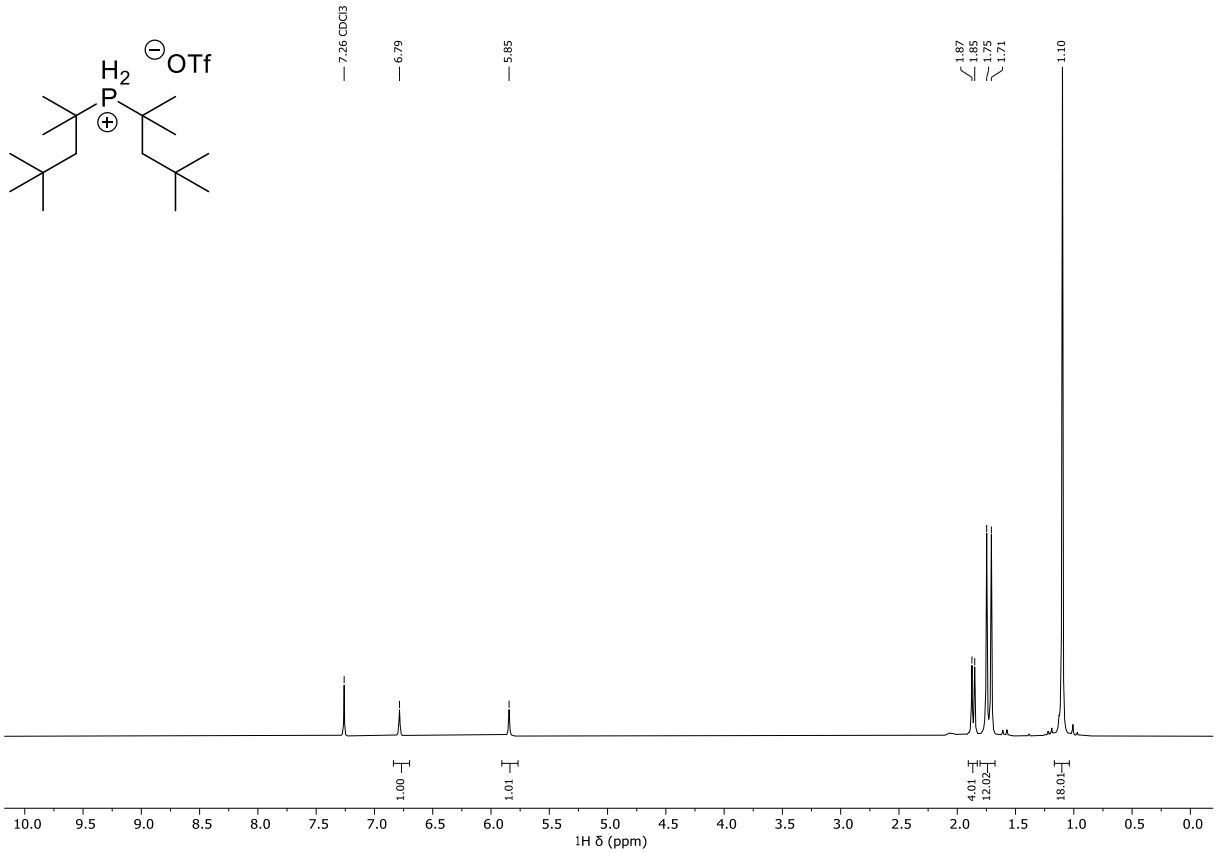
Tribenzhydrylphosphonium triflate (1n) $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$)



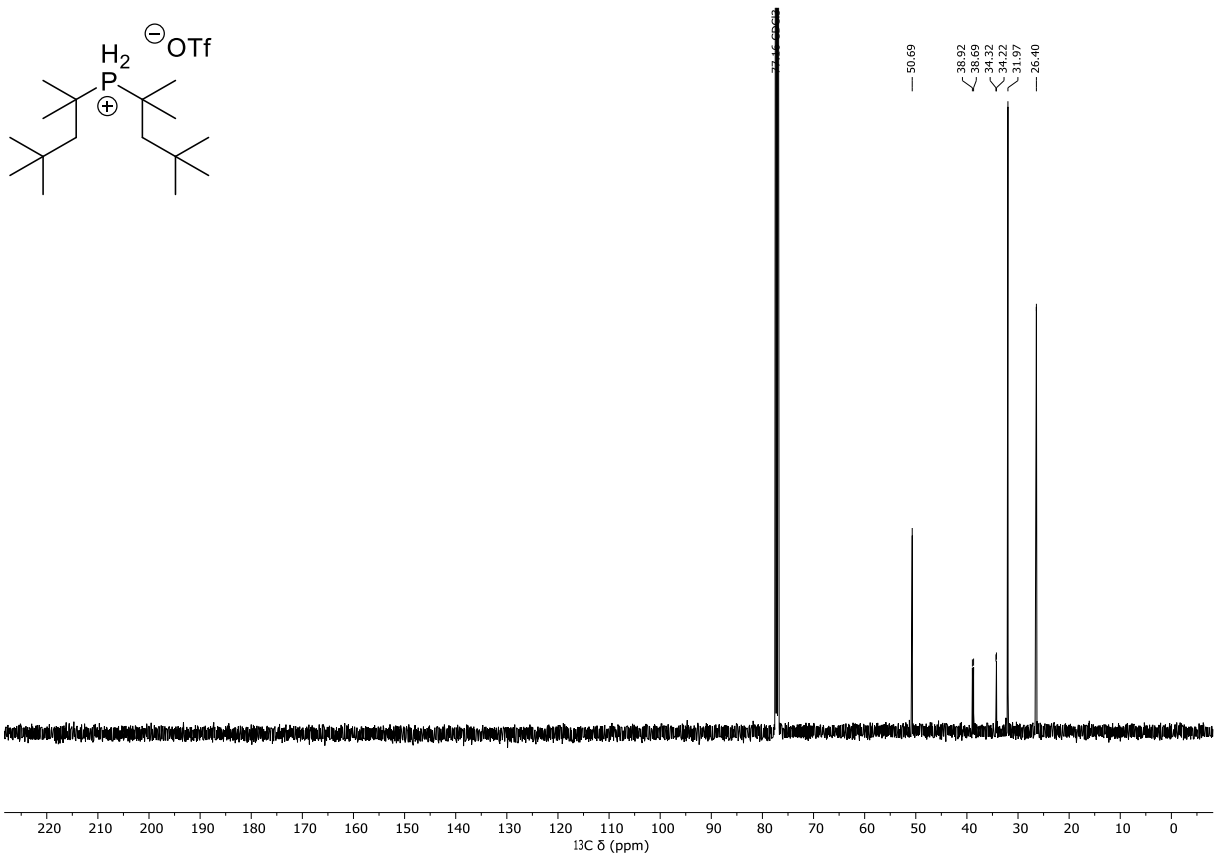
Tribenzhydrylphosphonium triflate (1n) ^{31}P NMR (162 MHz, $CDCl_3$)



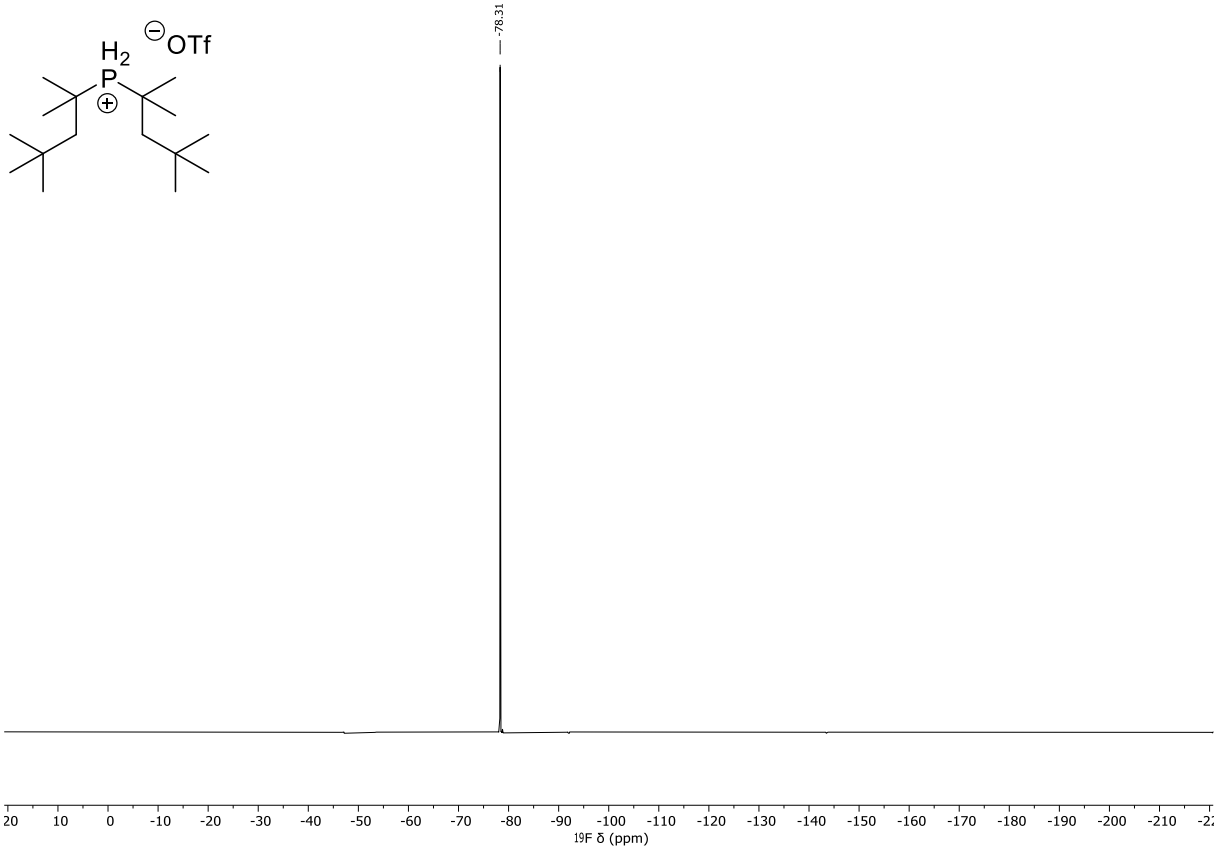
Bis-(2,4,4-trimethyl-2-pentyl)phosphonium triflate (1q) - ^{1}H NMR (500 MHz, $CDCl_3$)



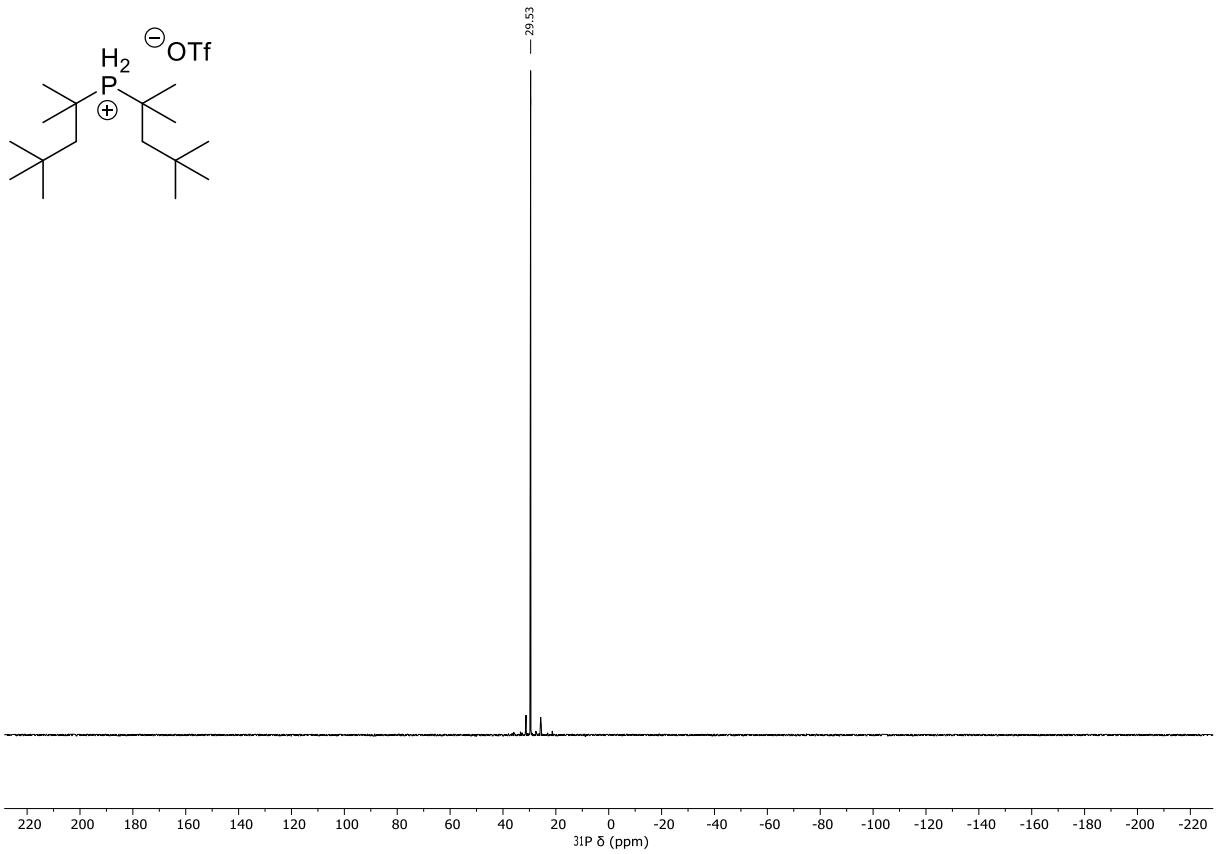
Bis-(2,4,4-trimethyl-2-pentyl)phosphonium triflate (1q) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



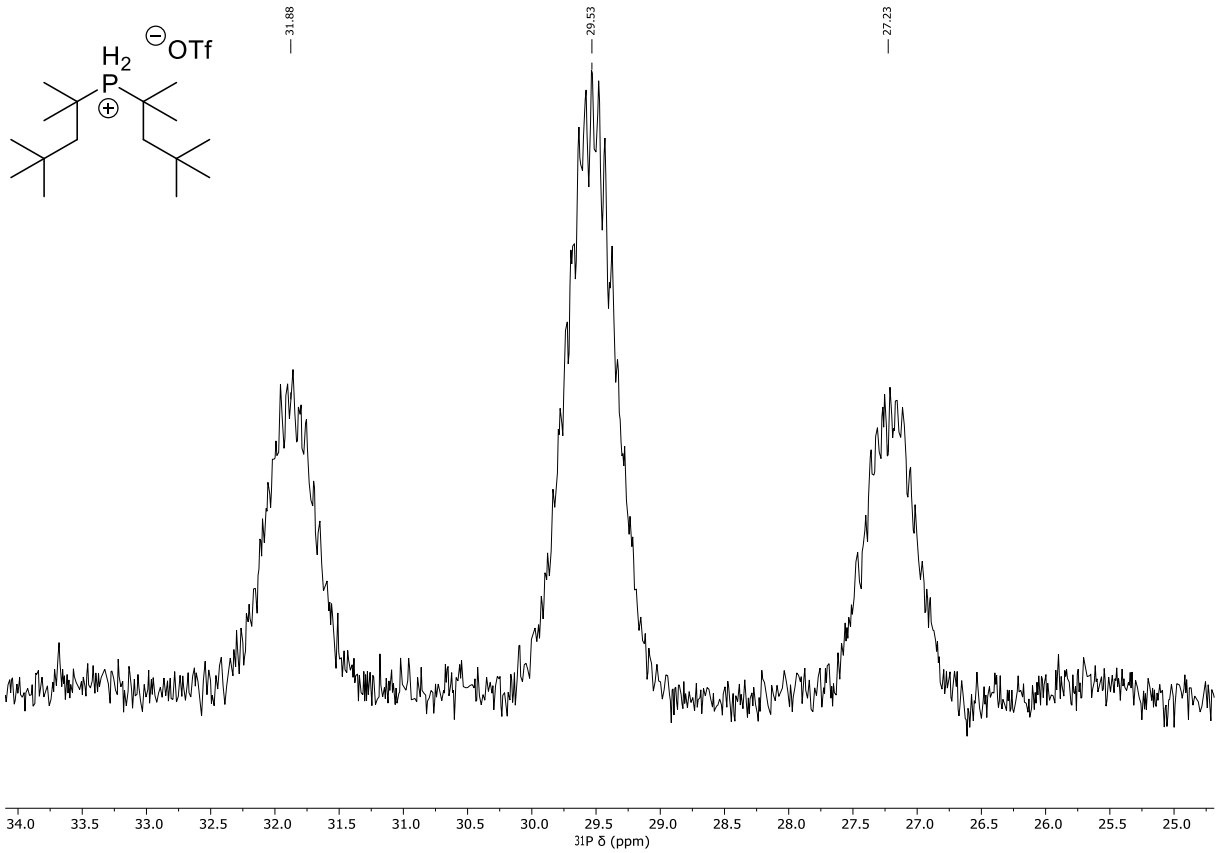
Bis-(2,4,4-trimethyl-2-pentyl)phosphonium triflate (1q) ^{19}F NMR (470 MHz, $CDCl_3$)



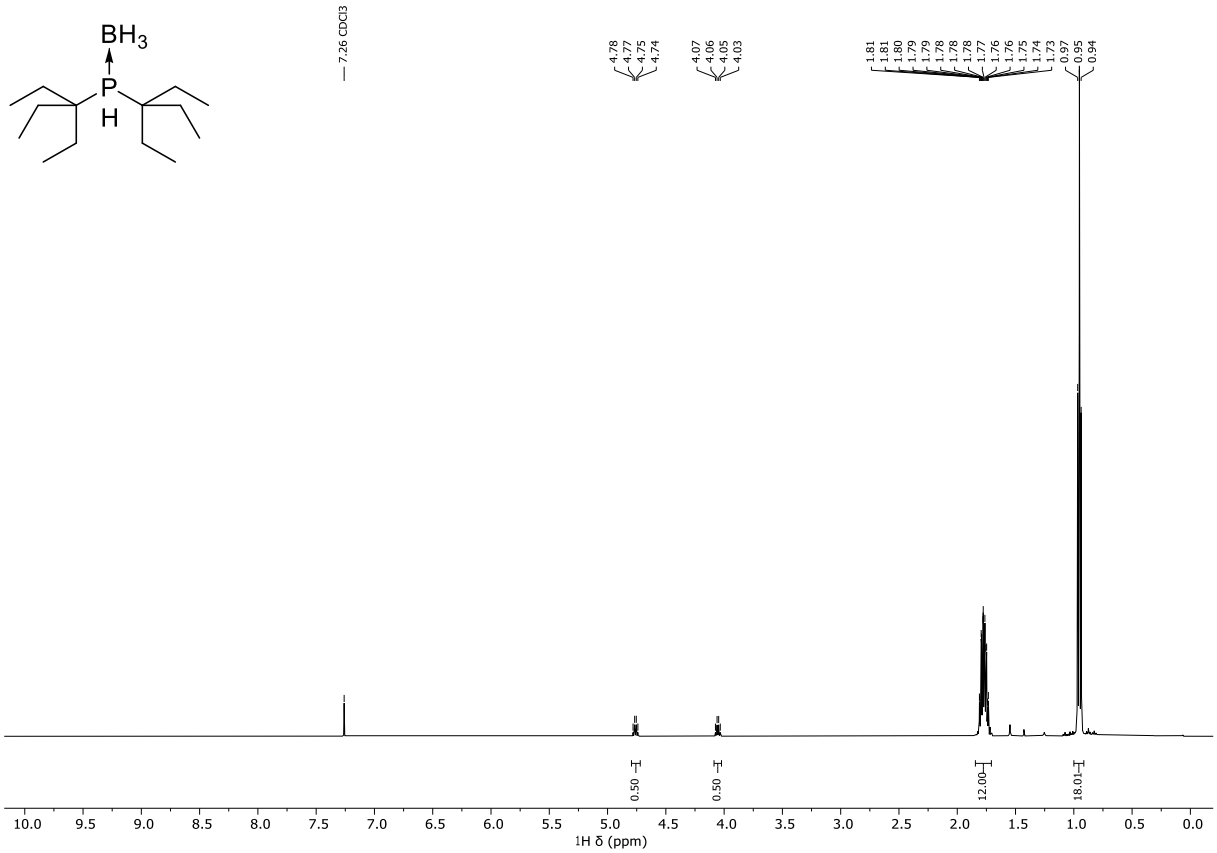
Bis-(2,4,4-trimethyl-2-pentyl)phosphonium triflate (1q) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



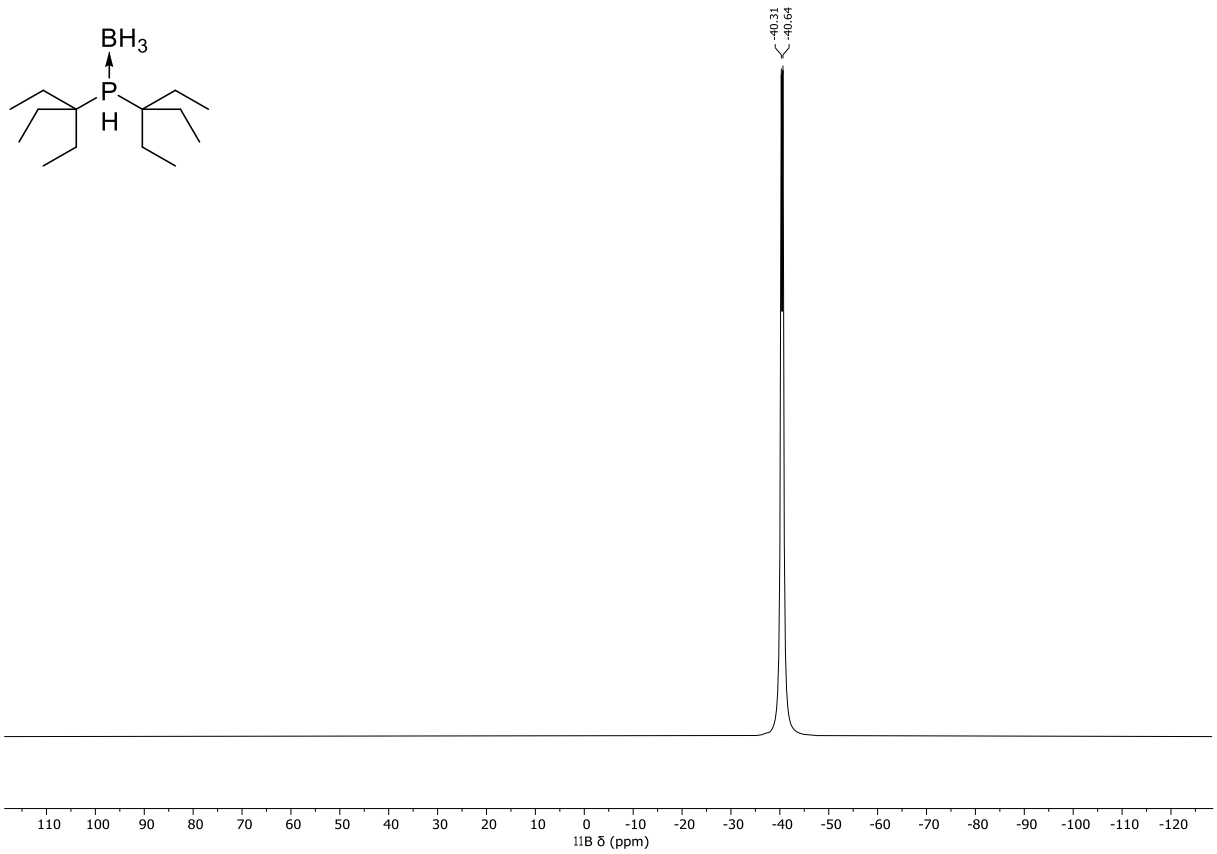
Bis-(2,4,4-trimethyl-2-pentyl)phosphonium triflate (1q) ^{31}P NMR (202 MHz, $CDCl_3$)



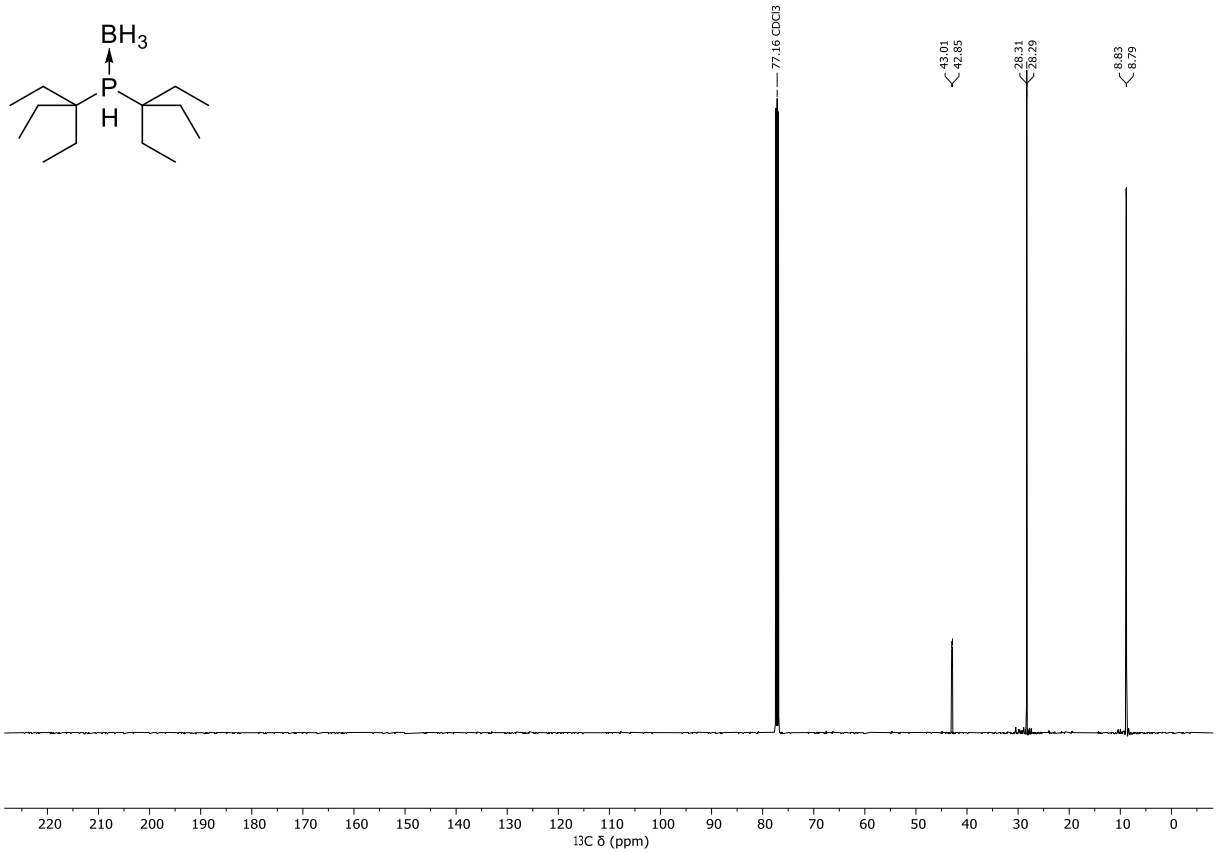
Di-(3-ethyl-3-pentyl)phosphine borane complex - ^{1}H NMR (500 MHz, $CDCl_3$)



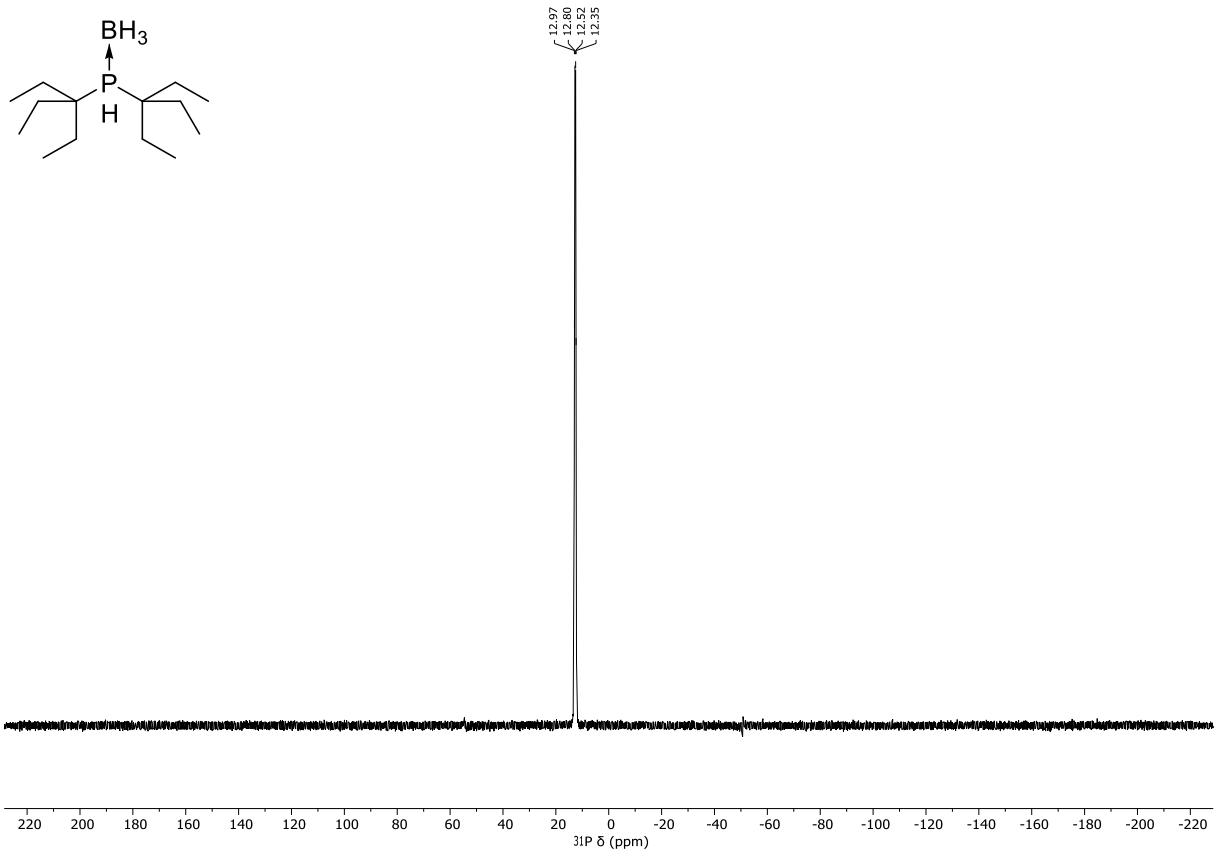
Di-(3-ethyl-3-pentyl)phosphine borane complex ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$)



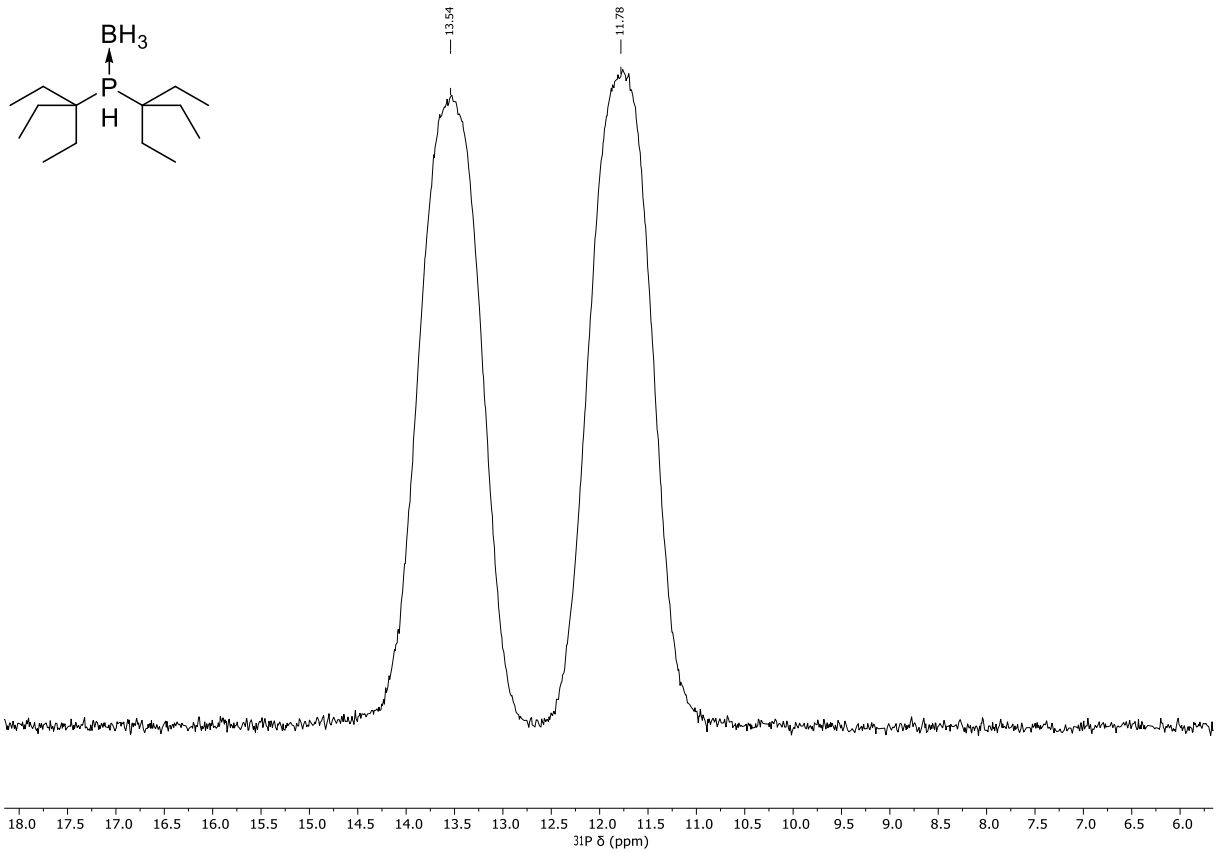
Di-(3-ethyl-3-pentyl)phosphine borane complex - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



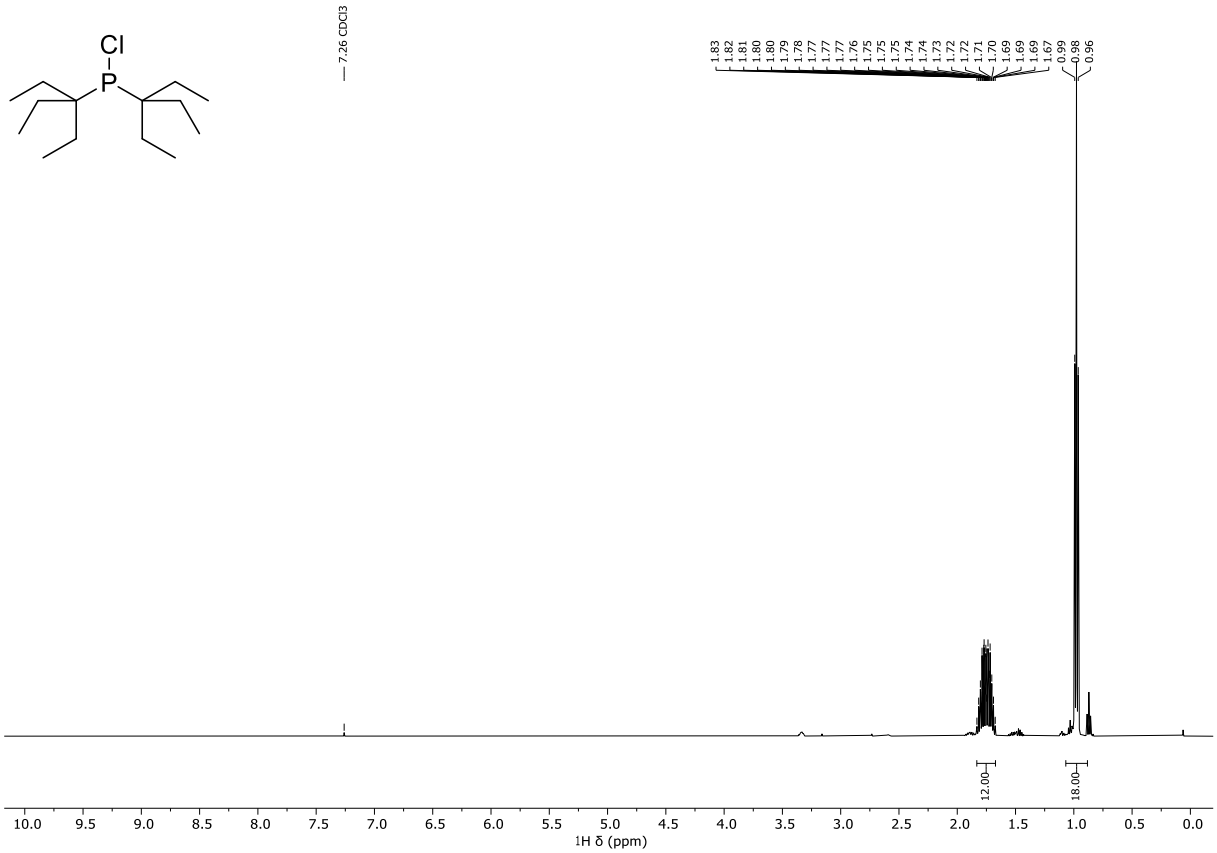
Di-(3-ethyl-3-pentyl)phosphine borane complex $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



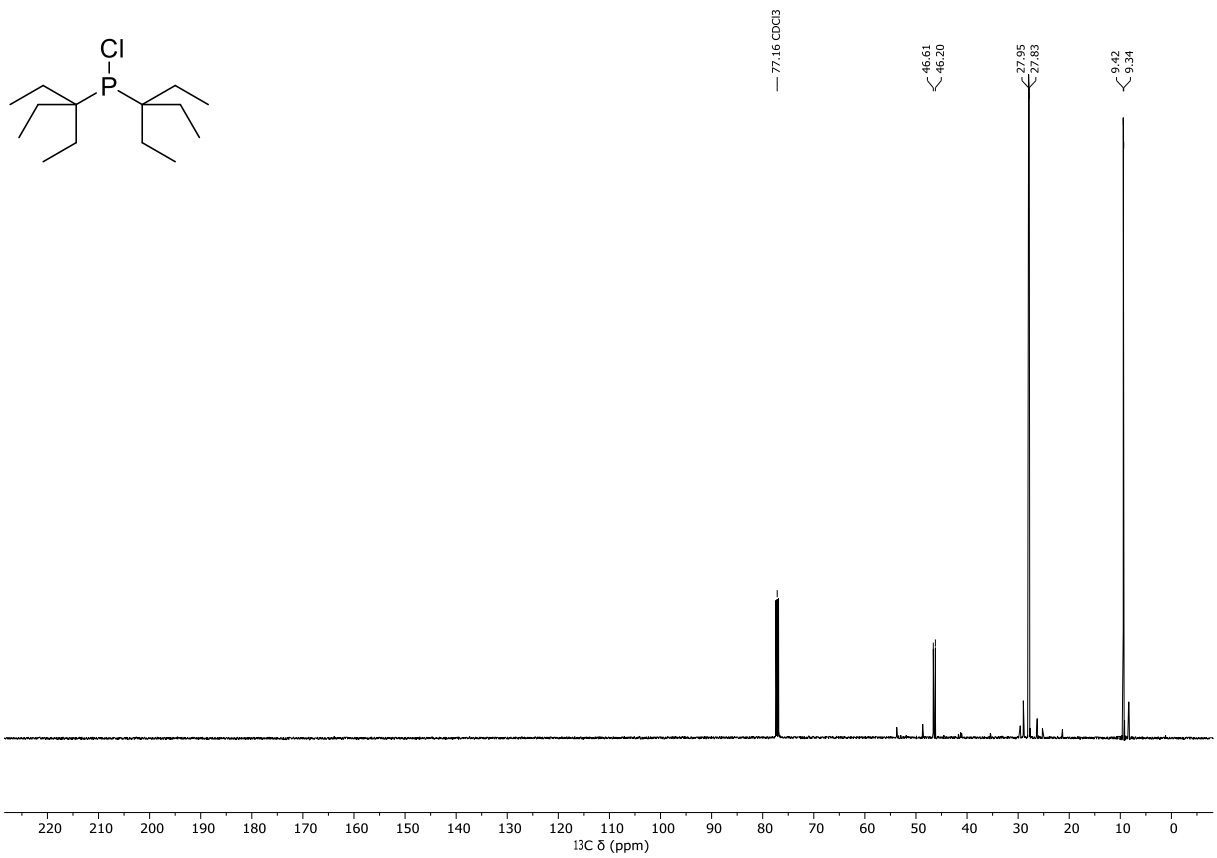
Di-(3-ethyl-3-pentyl)phosphine borane complex ^{31}P NMR (202 MHz, $CDCl_3$)



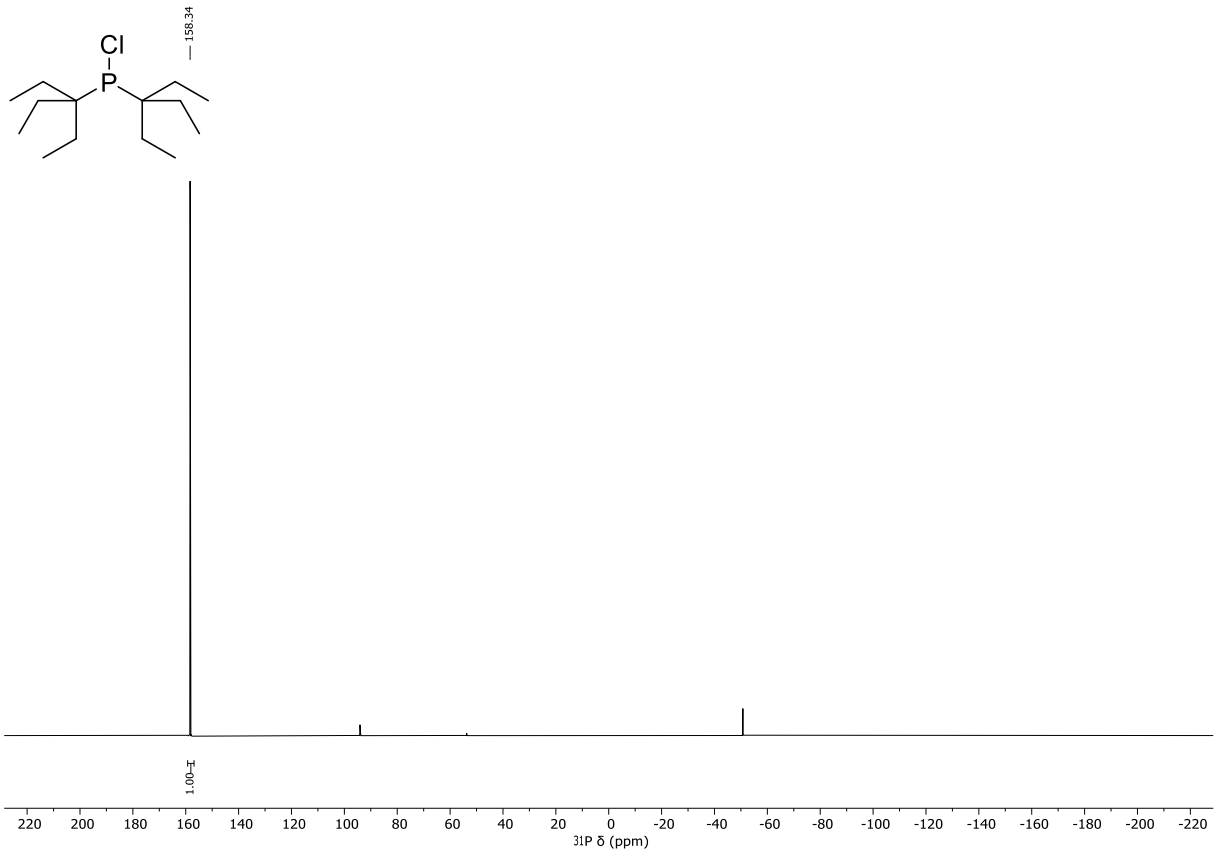
Di-(3-ethyl-3-pentyl)chlorophosphine - ^{1}H NMR (500 MHz, $CDCl_3$)



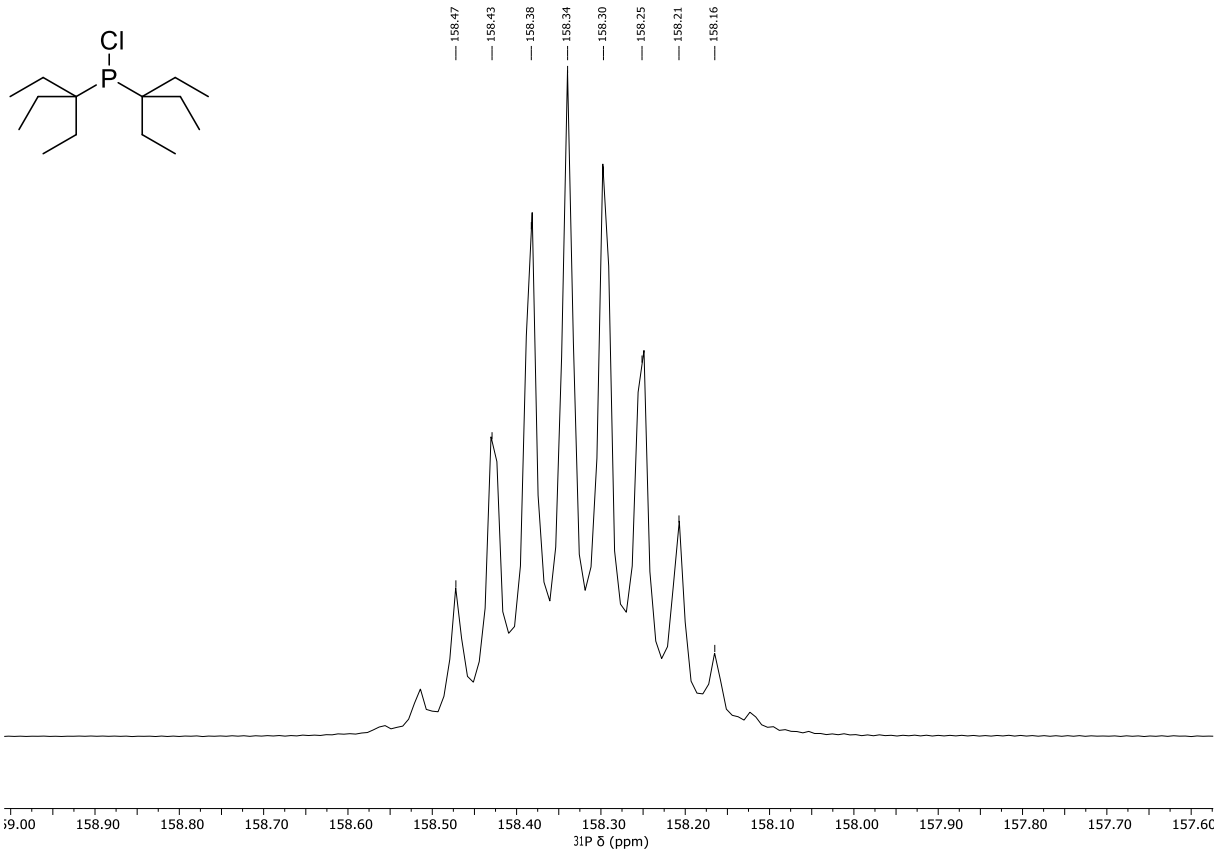
Di-(3-ethyl-3-pentyl)chlorophosphine - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



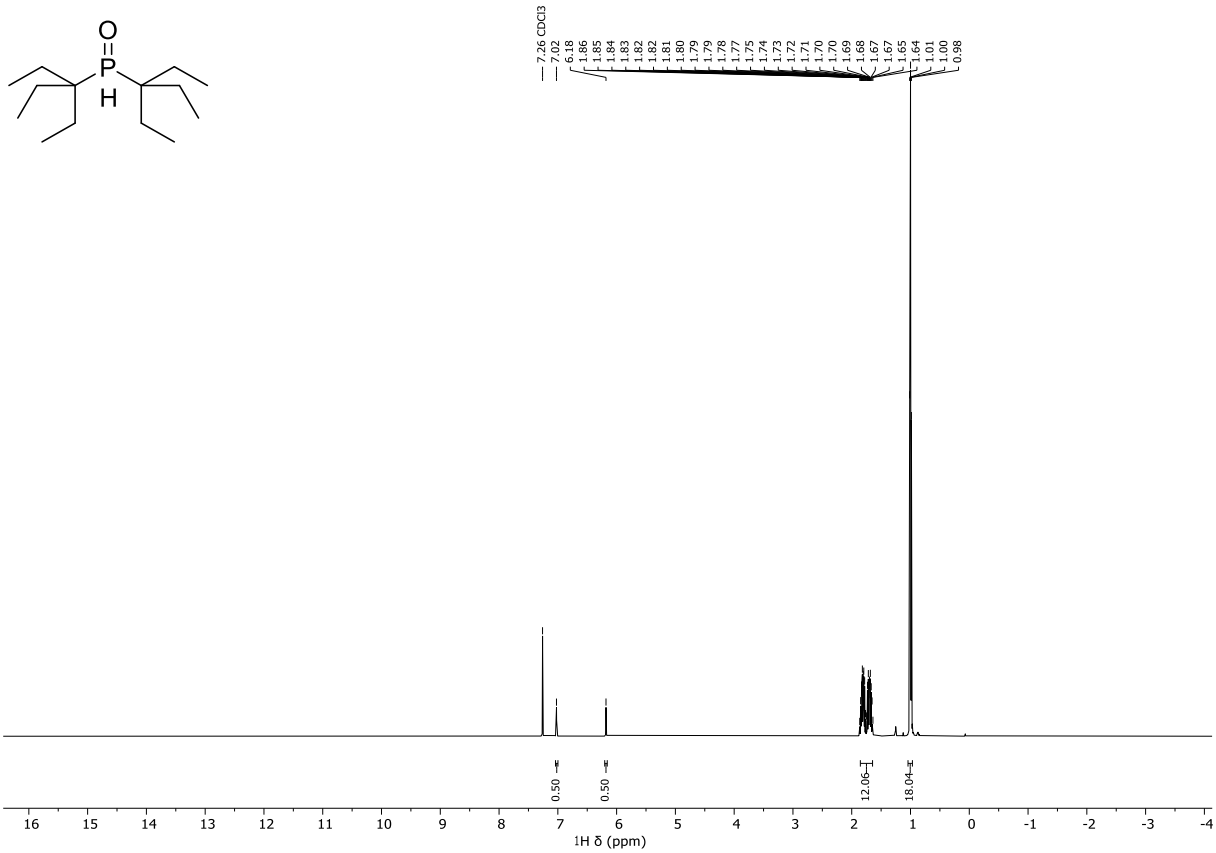
Di-(3-ethyl-3-pentyl)chlorophosphine $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



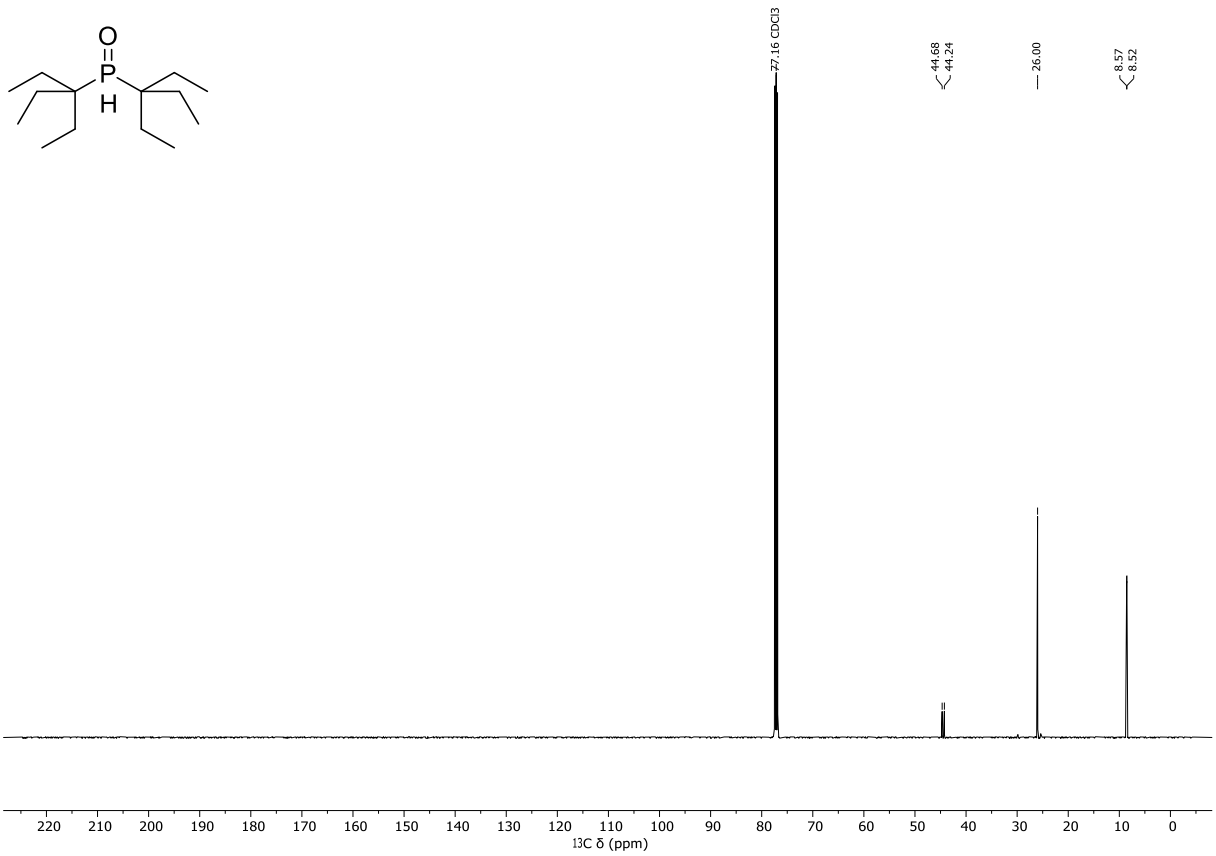
Di-(3-ethyl-3-pentyl)chlorophosphine ^{31}P NMR (202 MHz, $CDCl_3$)



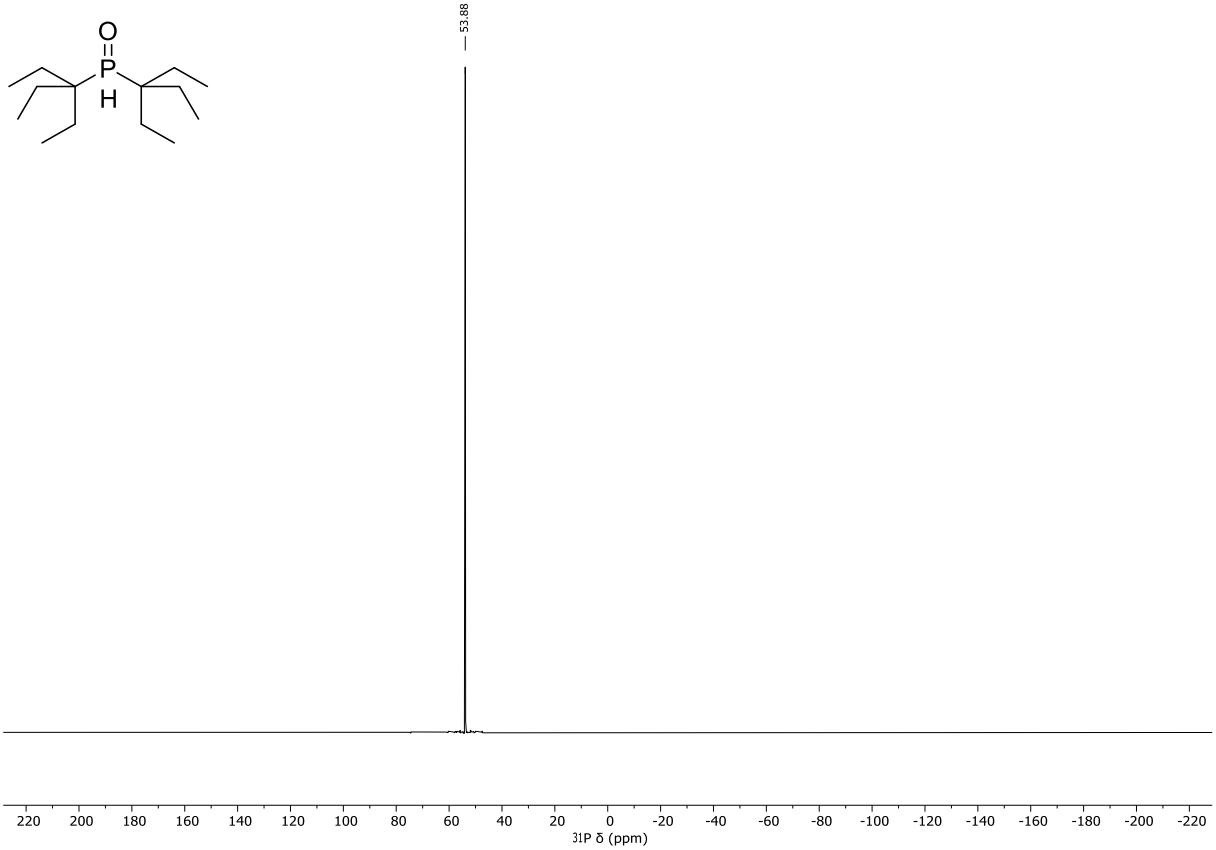
Di-(3-ethyl-3-pentyl)phosphine oxide - ^{1}H NMR (500 MHz, $CDCl_3$)



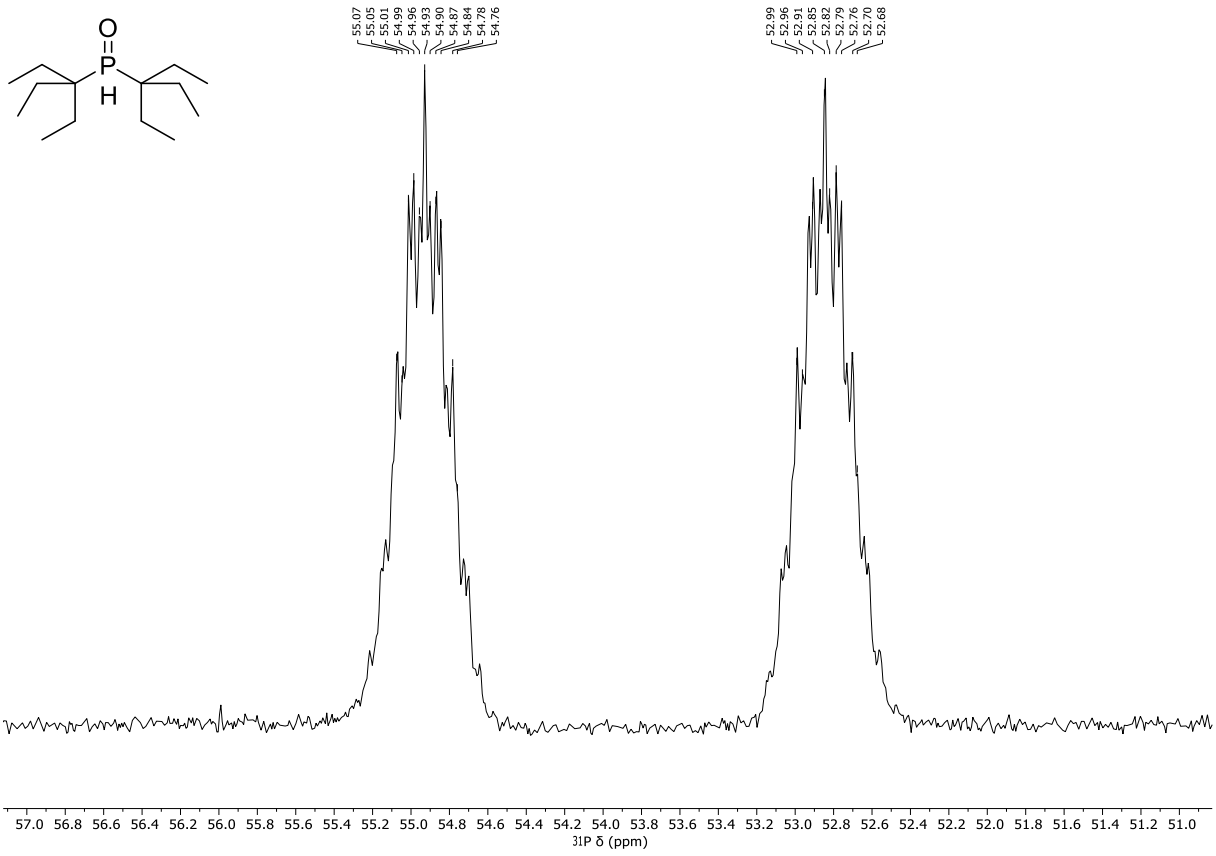
Di-(3-ethyl-3-pentyl)phosphine oxide - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



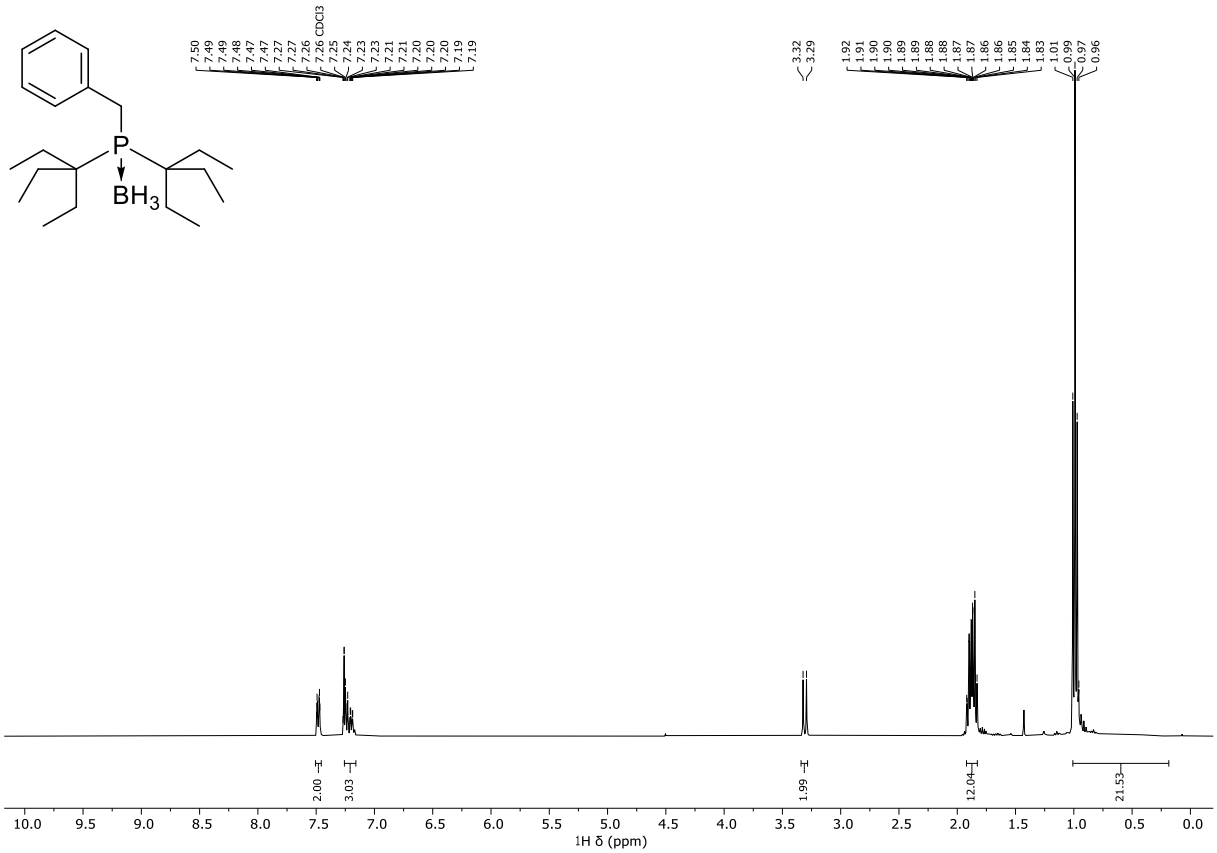
Di-(3-ethyl-3-pentyl)phosphine oxide $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



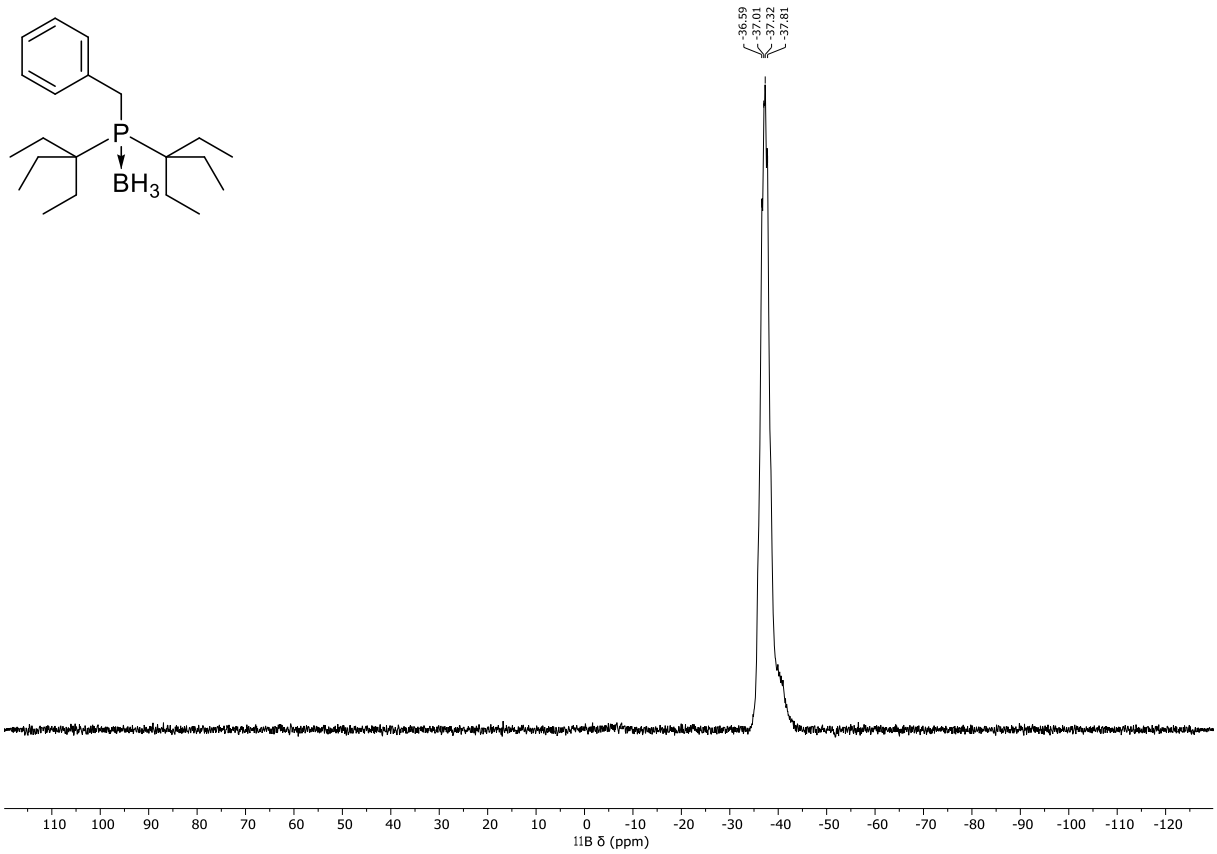
Di-(3-ethyl-3-pentyl)phosphine oxide ^{31}P NMR (202 MHz, $CDCl_3$)



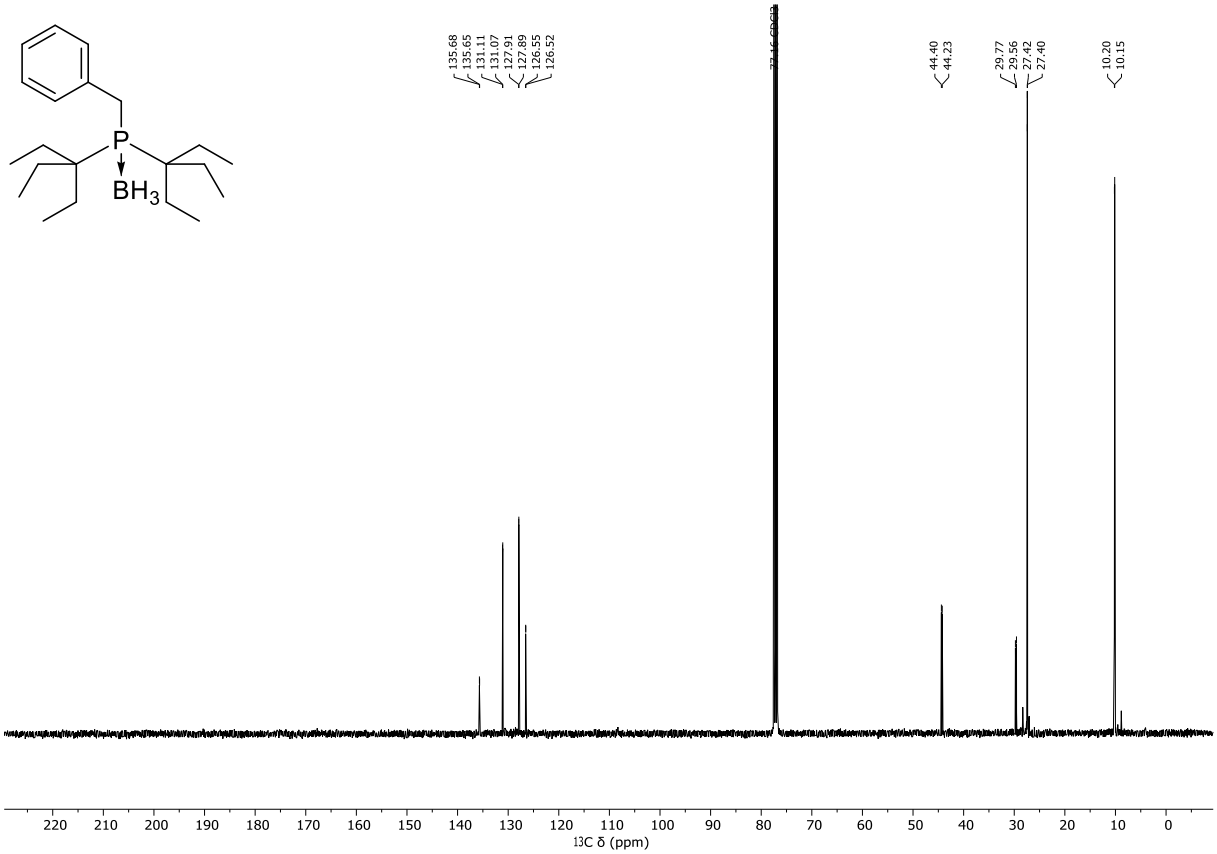
Di-(3-ethyl-3-pentyl)benzylphosphine borane complex - ^{1}H NMR (400 MHz, $CDCl_3$)



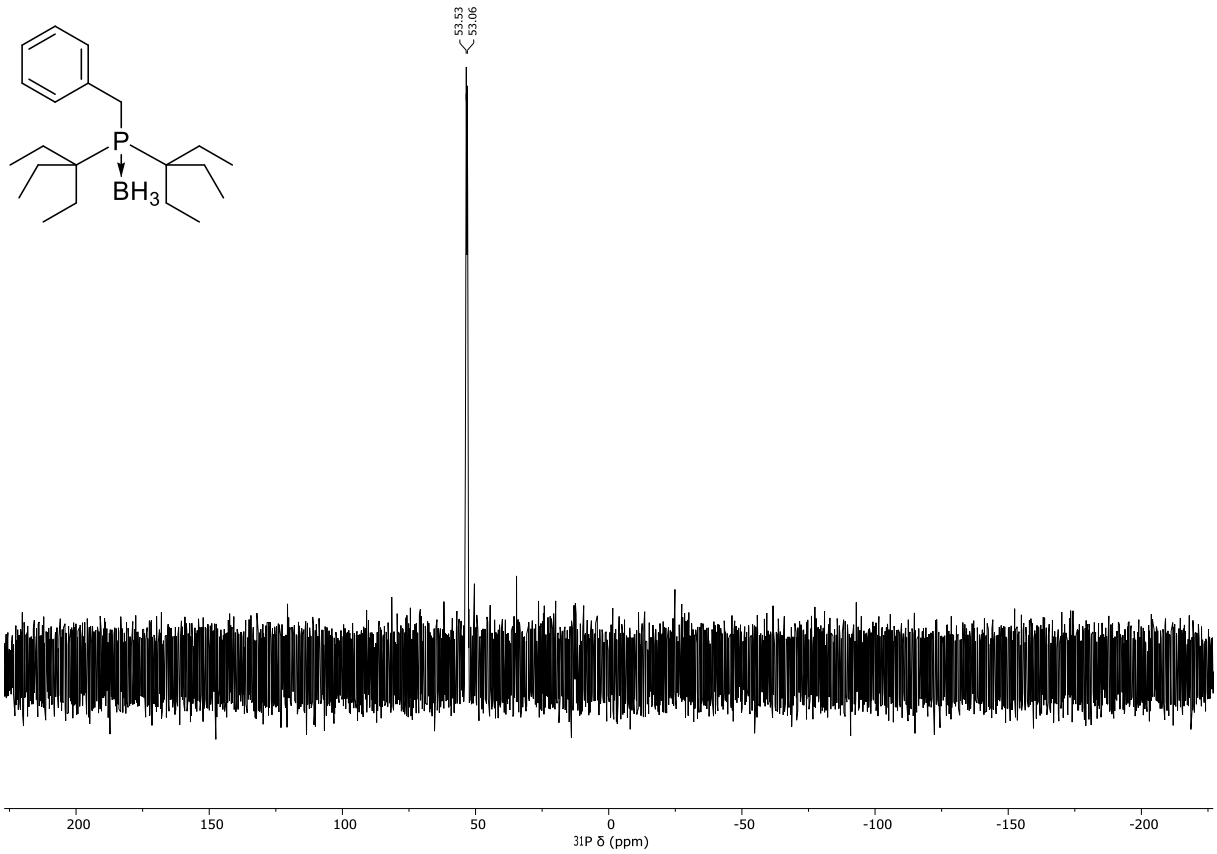
Di-(3-ethyl-3-pentyl)benzylphosphine borane complex ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$)



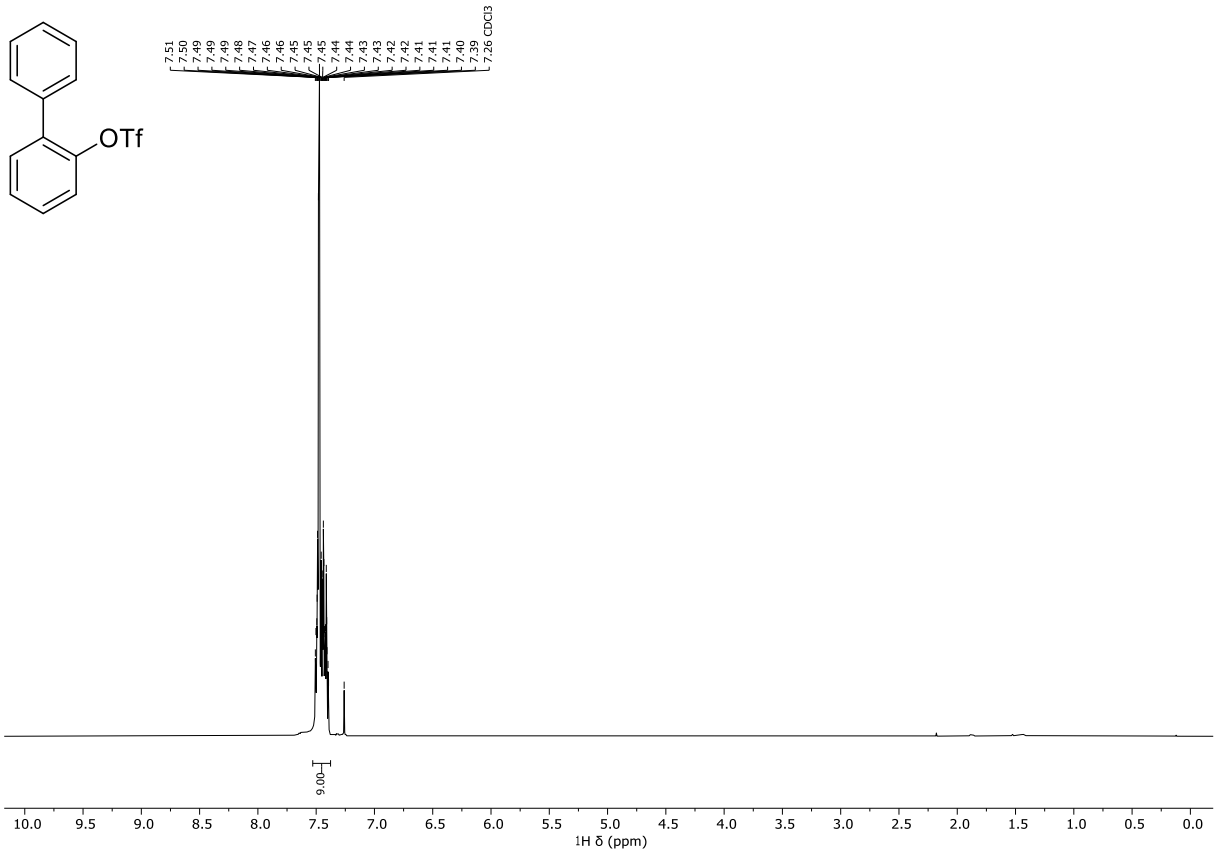
Di-(3-ethyl-3-pentyl)benzylphosphine borane complex - $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



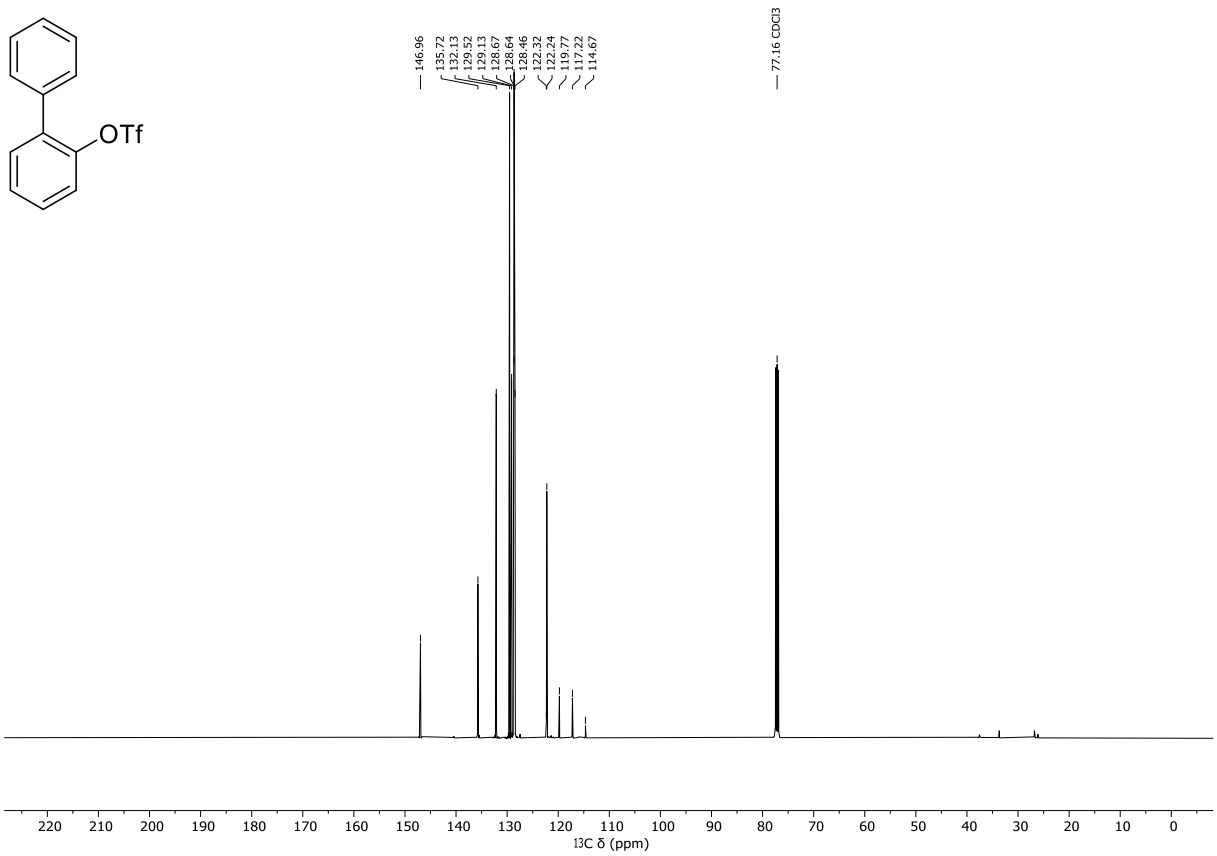
Di-(3-ethyl-3-pentyl)benzylphosphine borane complex $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$)



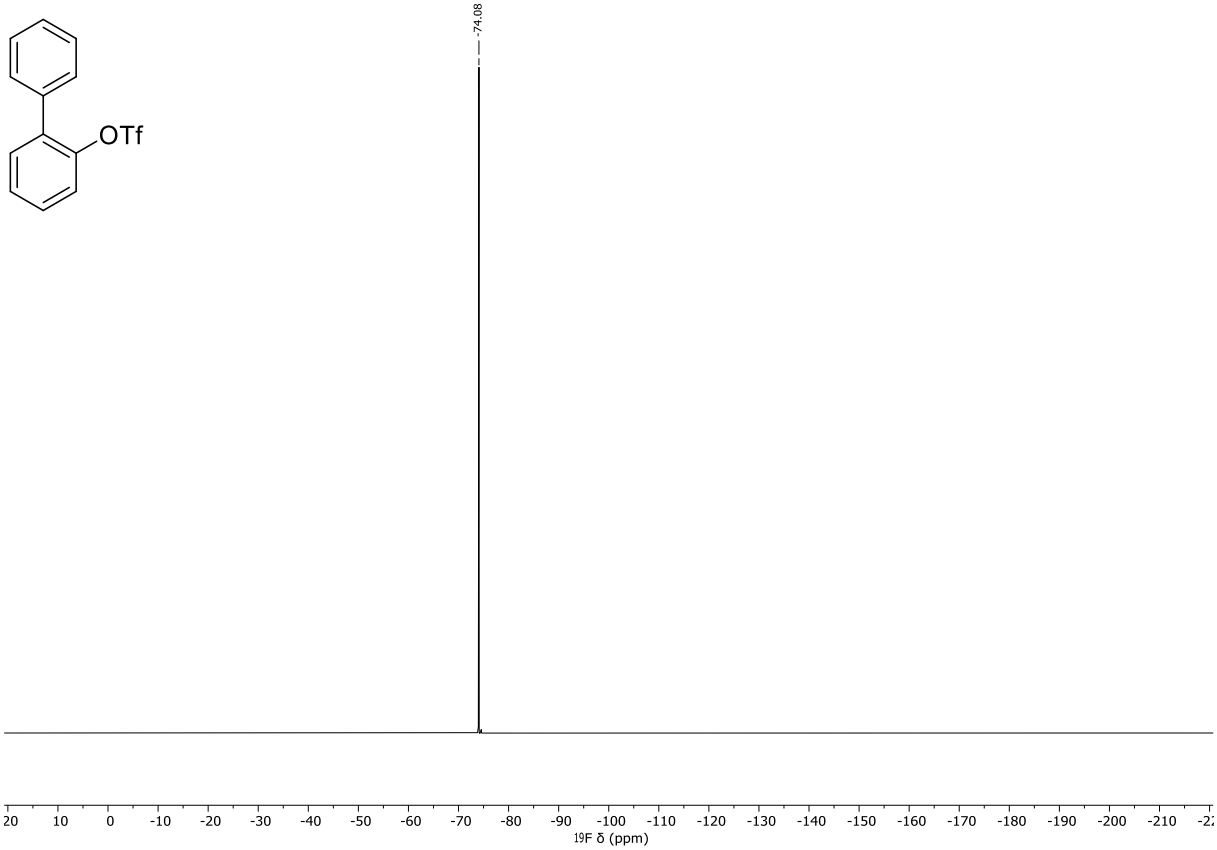
2-Biphenyl triflate - ^{1}H NMR (500 MHz, $CDCl_3$)



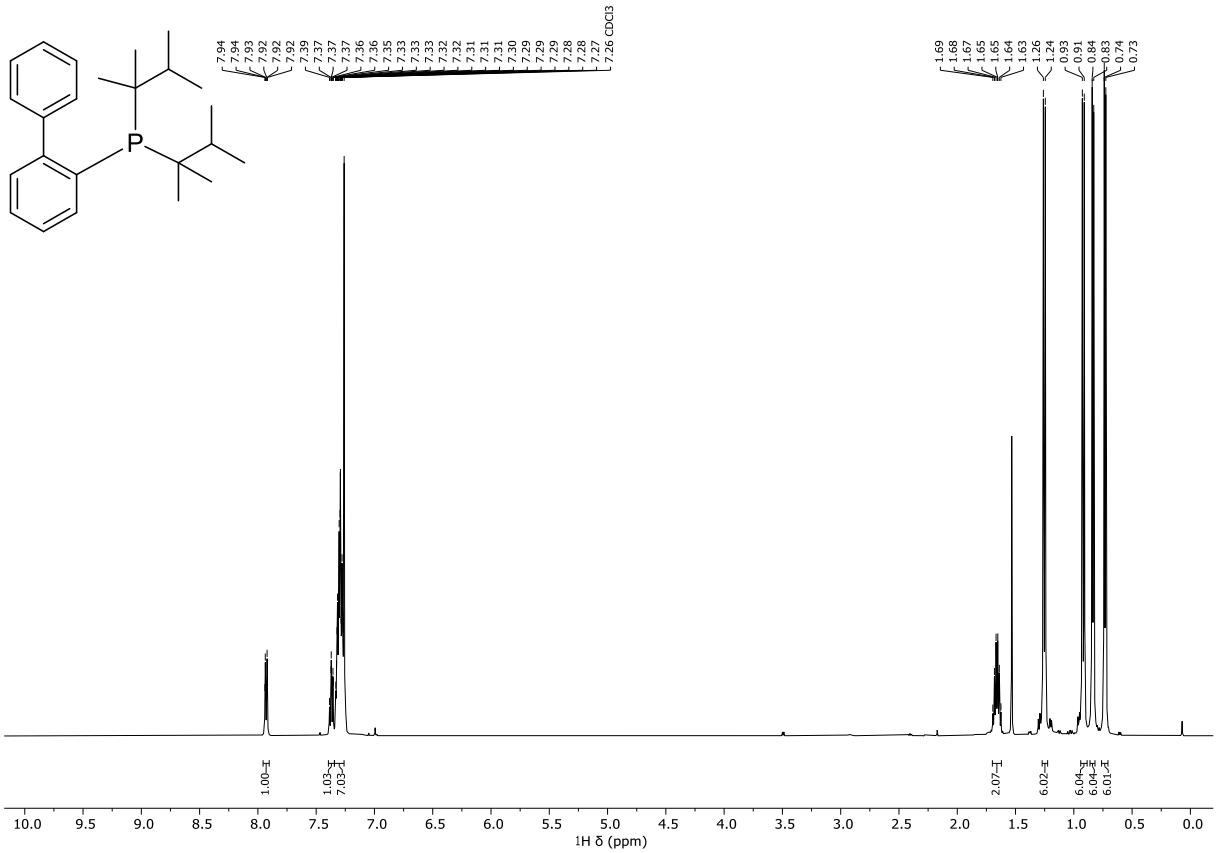
2-Biphenyl triflate - $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



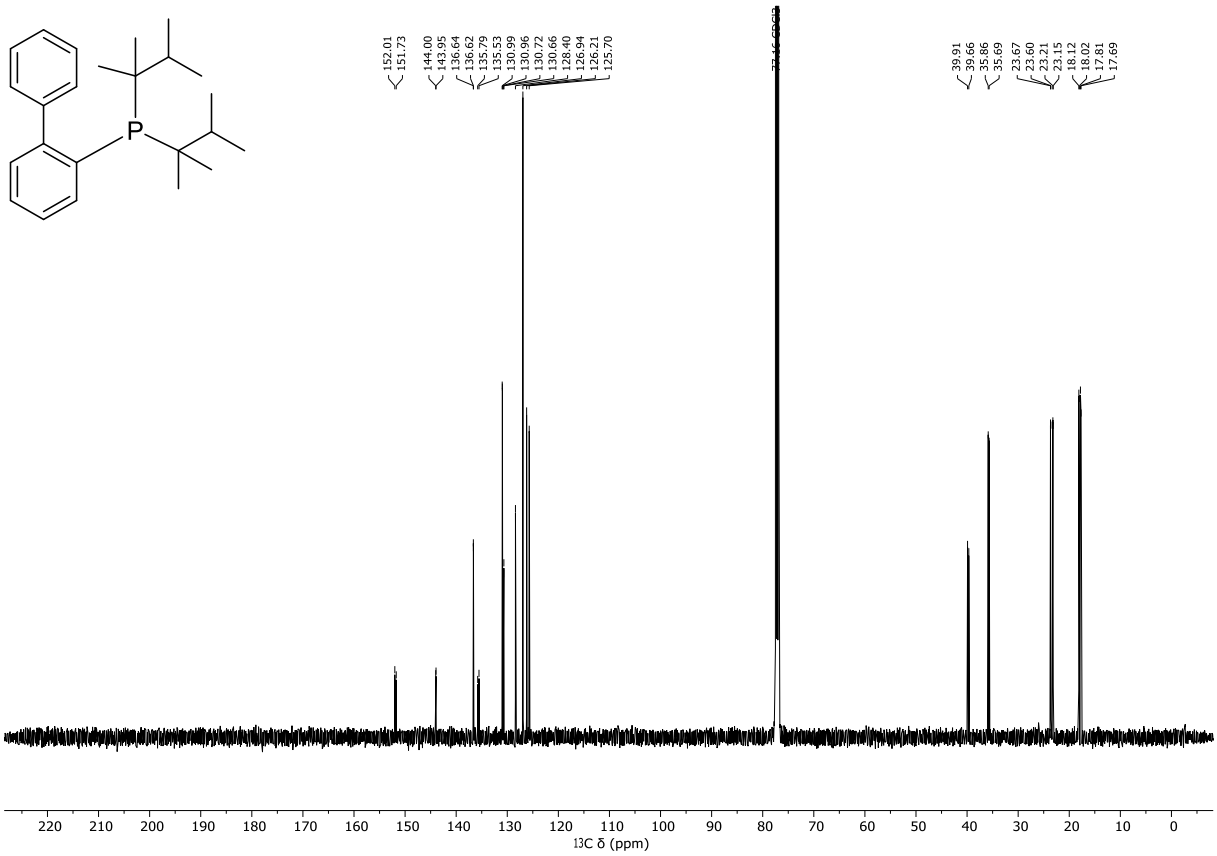
2-Biphenyl triflate ^{19}F NMR (470 MHz, $CDCl_3$)



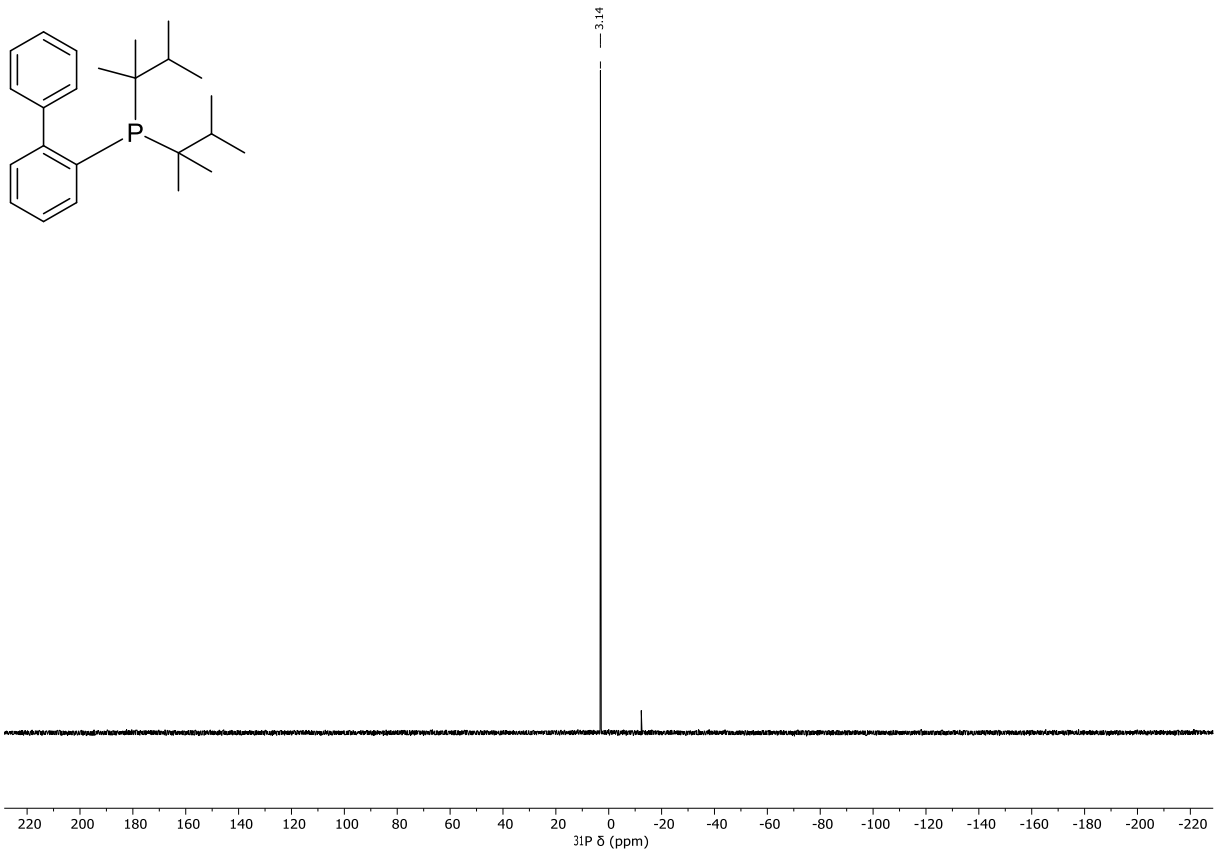
2-(Bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl (3d) - ^{1}H NMR (500 MHz, $CDCl_3$)



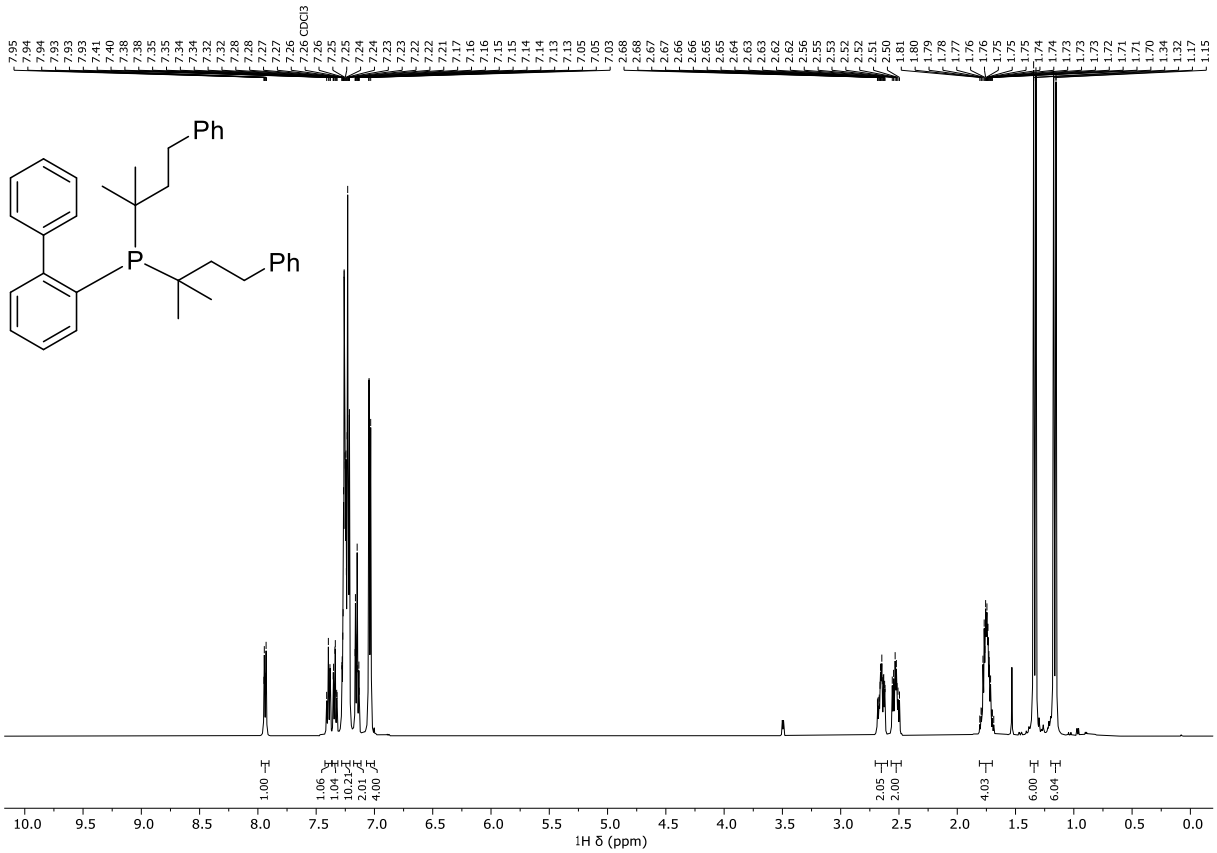
2-(Bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl (3d) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



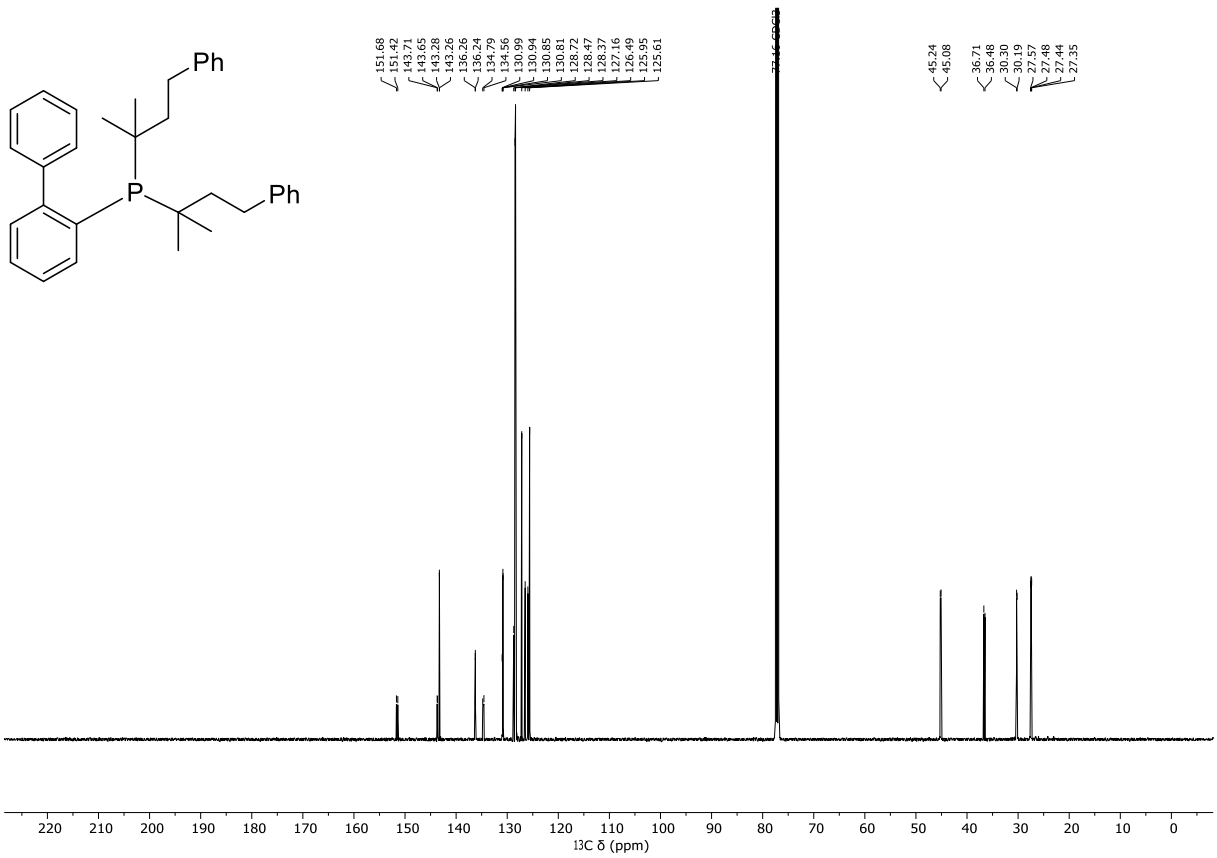
2-(Bis-(2,3-dimethyl-2-butyl)phosphino)biphenyl (3d) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



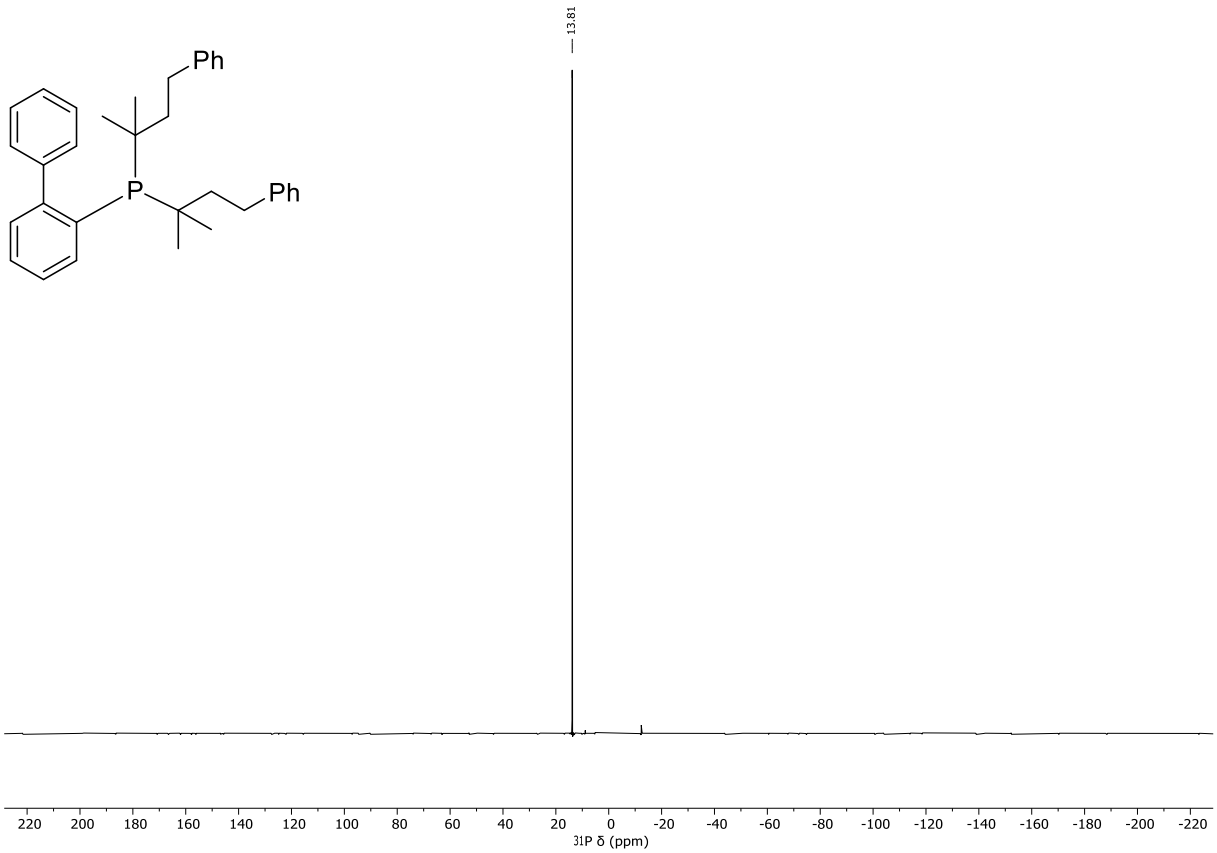
2-(Di-(2-methyl-4-phenyl-2-butyl)phosphino)biphenyl (3f) - ^{1}H NMR (500 MHz, $CDCl_3$)



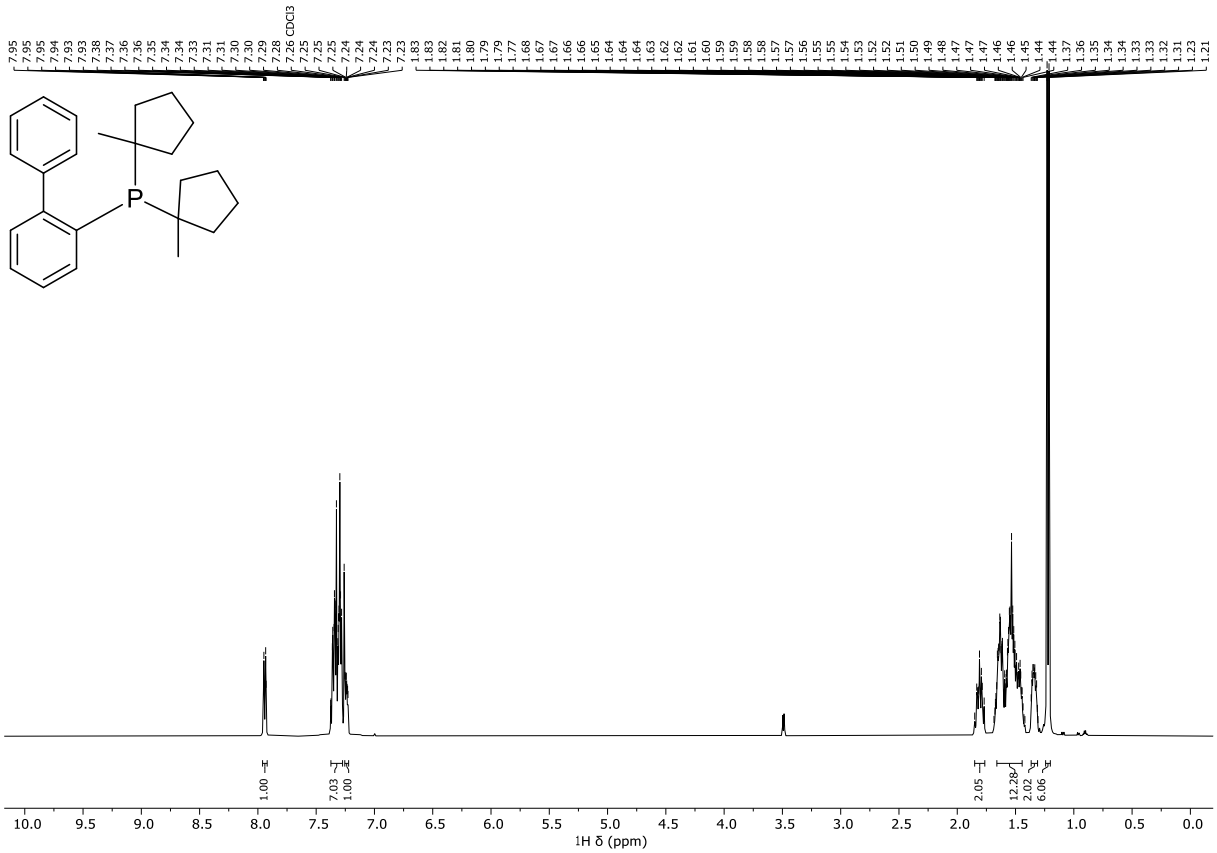
2-(Di-(2-methyl-4-phenyl-2-butyl)phosphino)biphenyl (3f) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



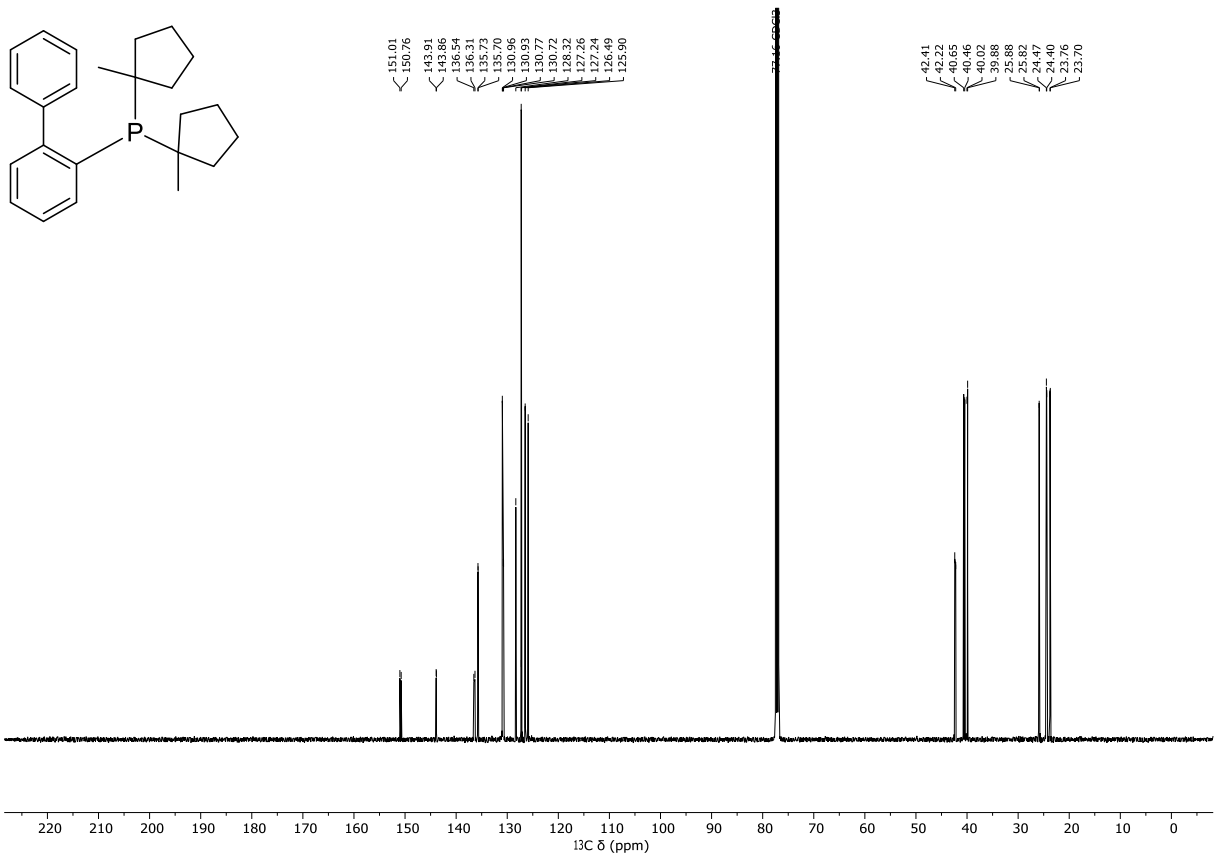
2-(Di-(2-methyl-4-phenyl-2-butyl)phosphino)biphenyl (3f) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



2-(Di-(1-methylcyclopentyl)phosphino)biphenyl (3h) - ^{1}H NMR (500 MHz, $CDCl_3$)

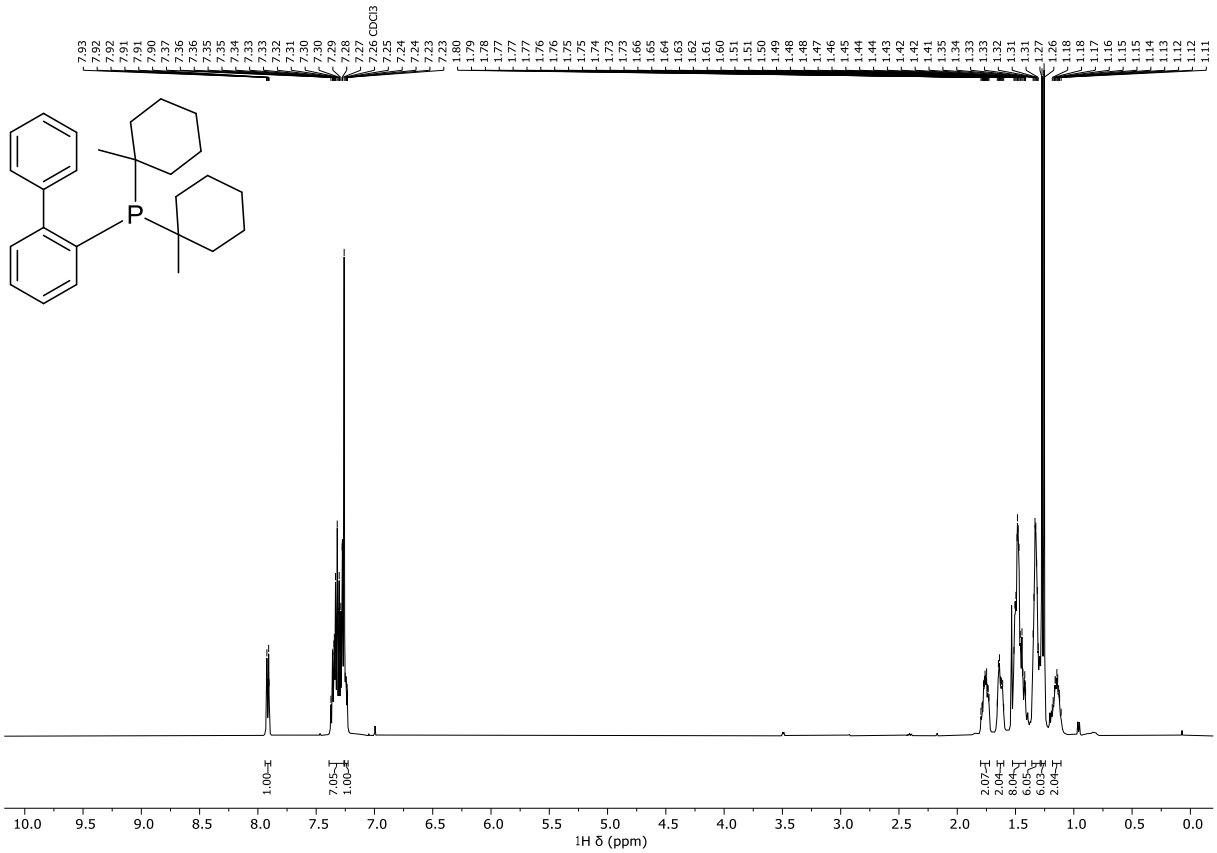


2-(Di-(1-methylcyclopentyl)phosphino)biphenyl (3h) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

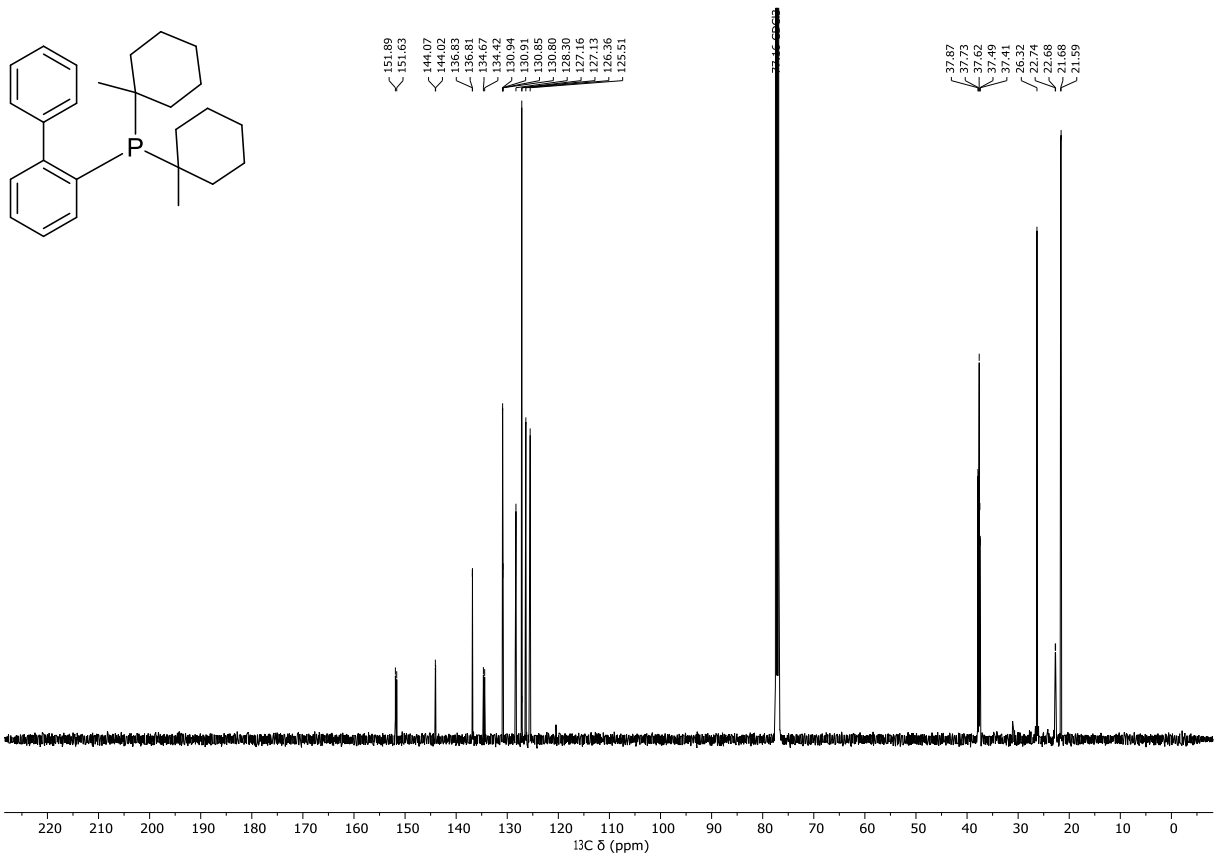


2-(Di-(1-methylcyclopentyl)phosphino)biphenyl (3h) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)

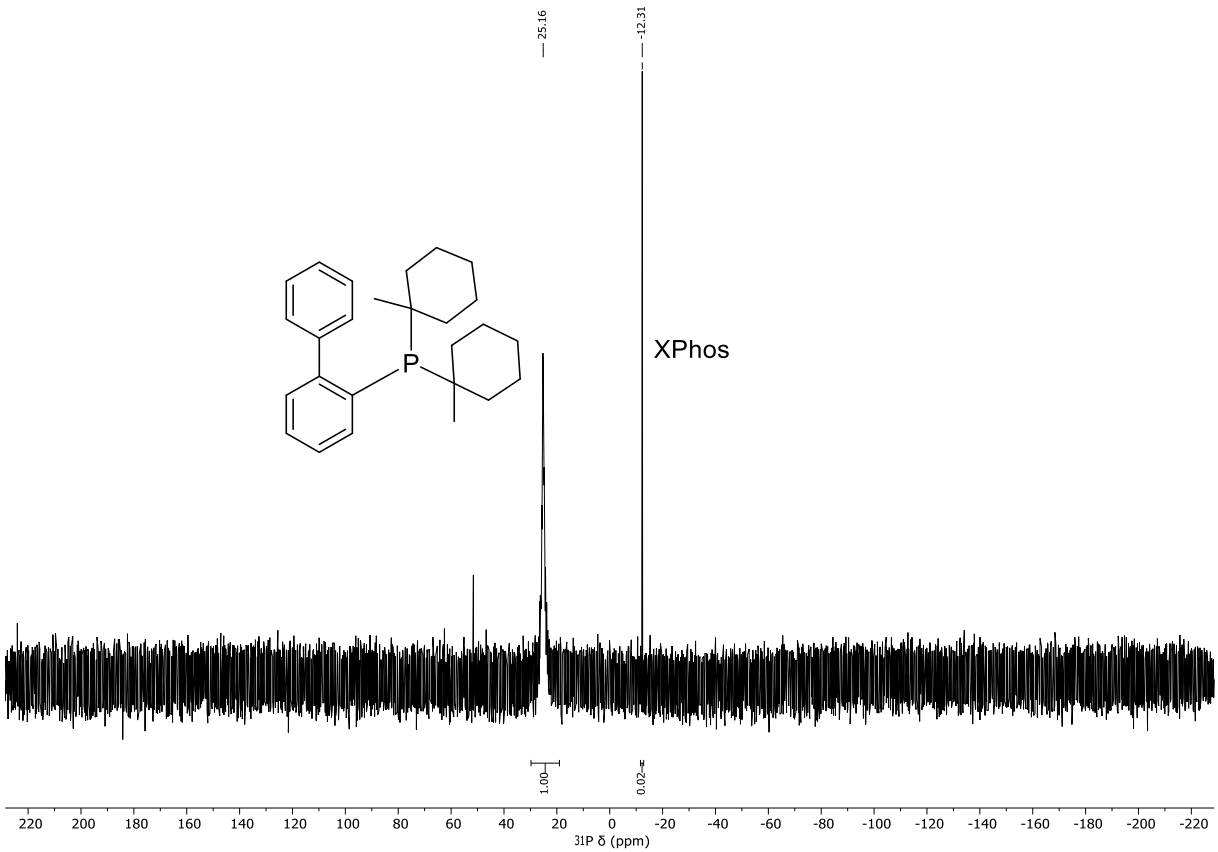
2-(Di-(1-methylcyclohexyl)phosphino)biphenyl (3i) - ^{1}H NMR (500 MHz, $CDCl_3$)



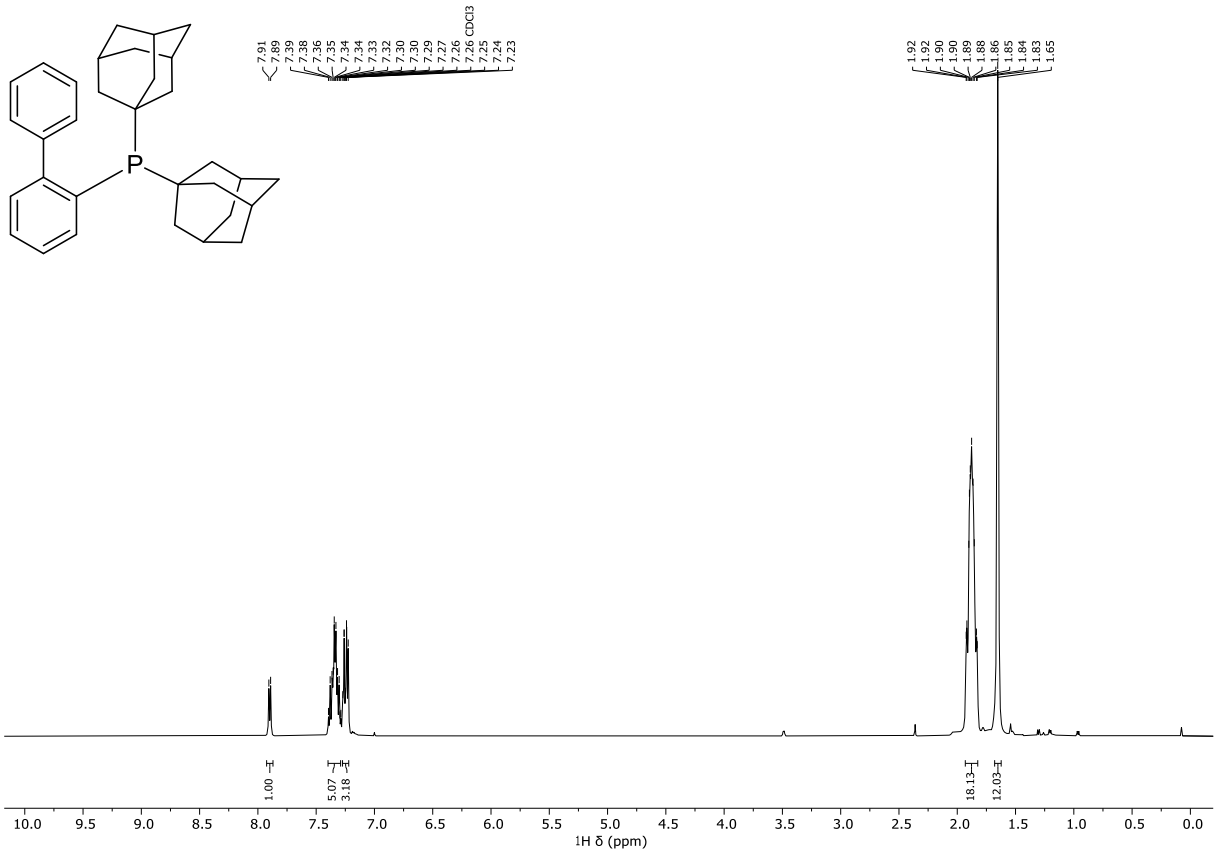
2-(Di-(1-methylcyclohexyl)phosphino)biphenyl (3i) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



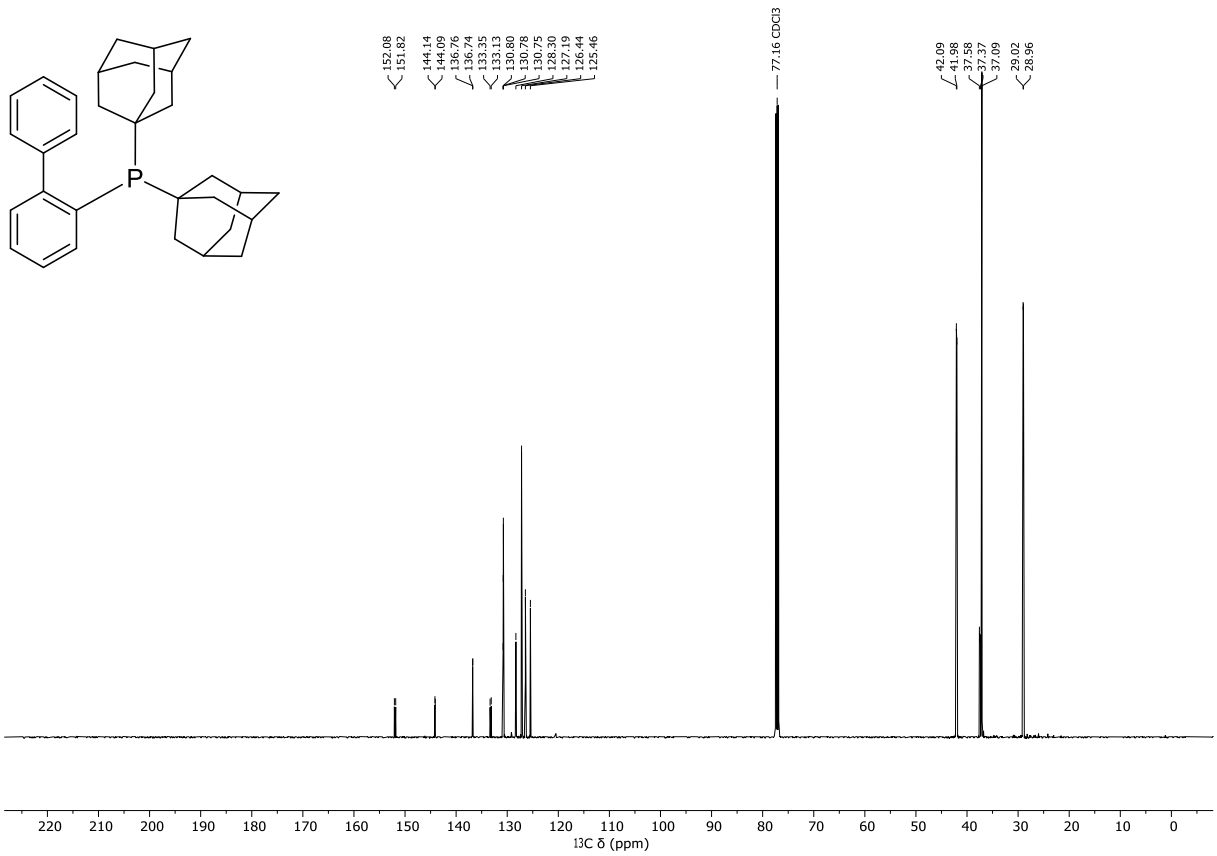
2-(Di-(1-methylcyclohexyl)phosphino)biphenyl (3i) + 2% XPhos (δ_P -12.31 ppm) $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$)



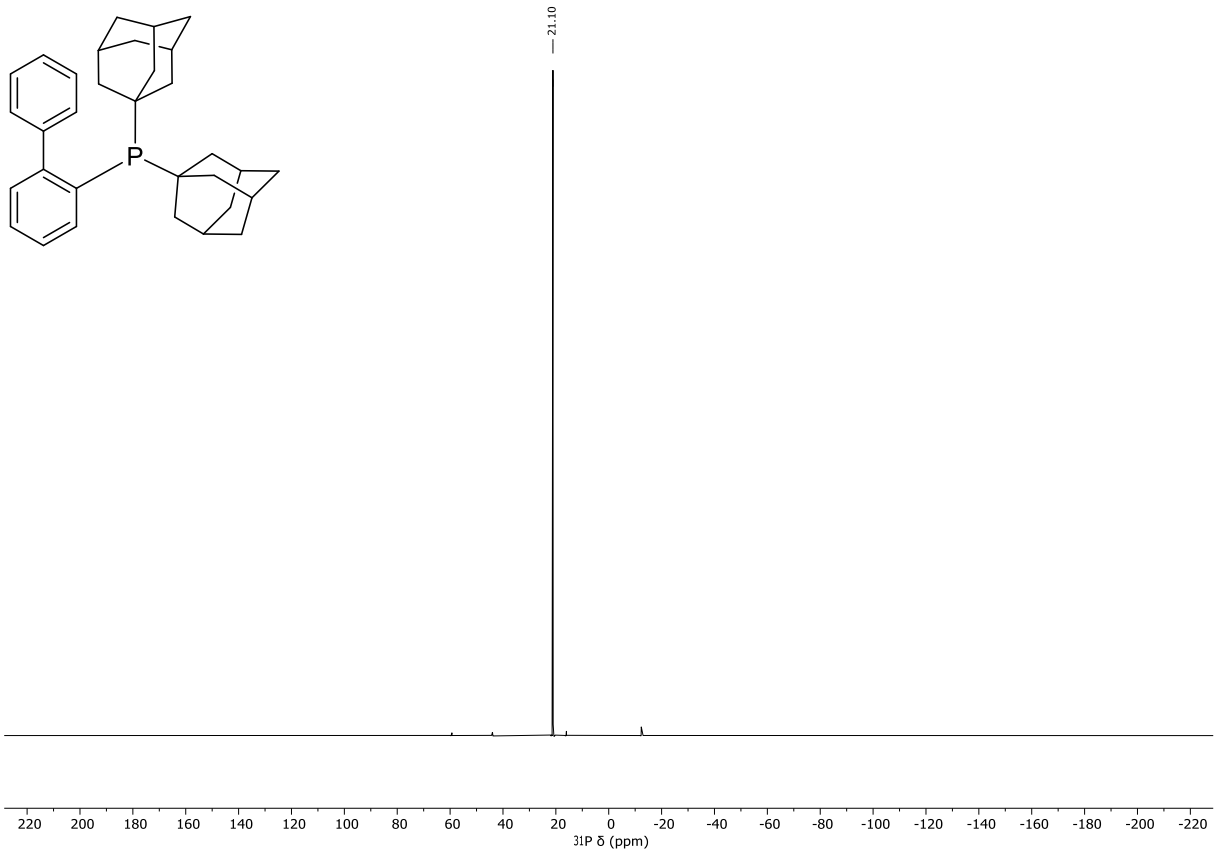
2-(Di-(1-adamantyl)phosphino)biphenyl (3k) - ^{1}H NMR (500 MHz, $CDCl_3$)



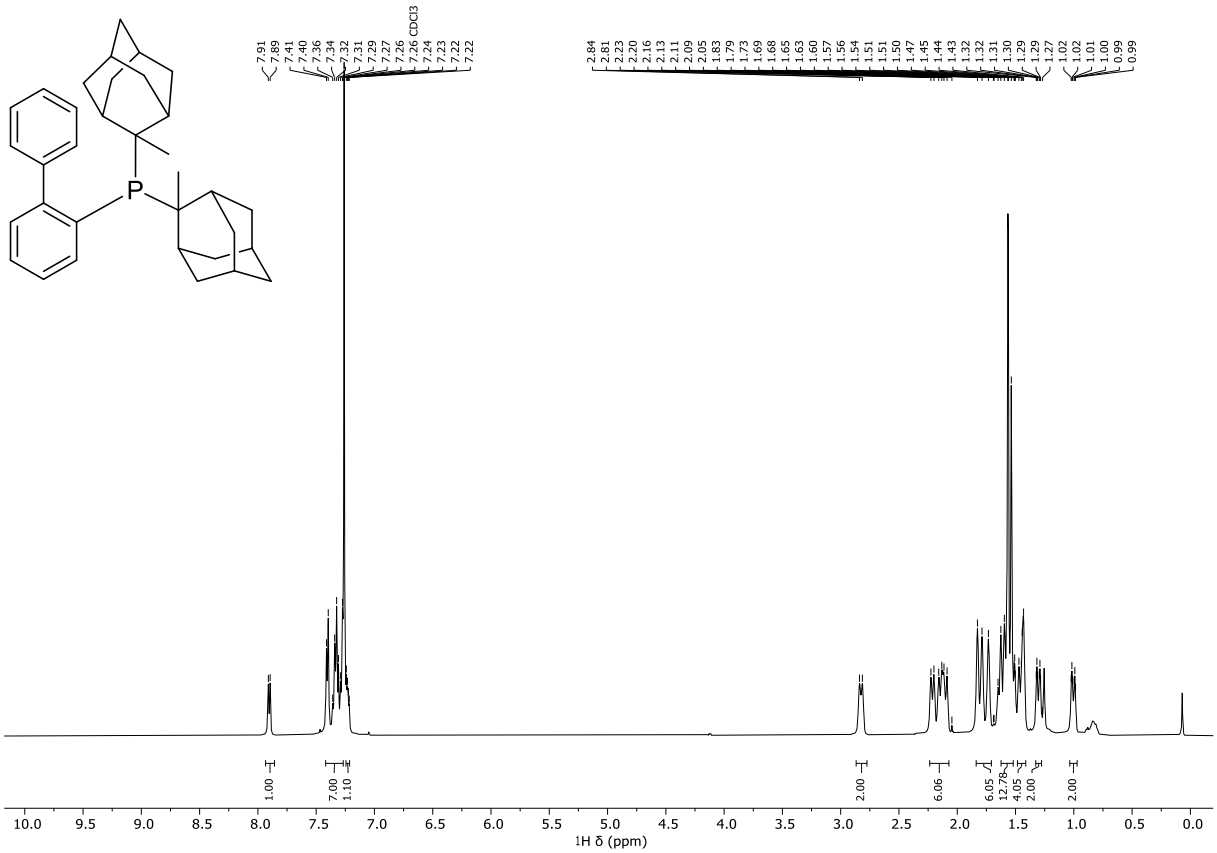
2-(Di-(1-adamantyl)phosphino)biphenyl (3k) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



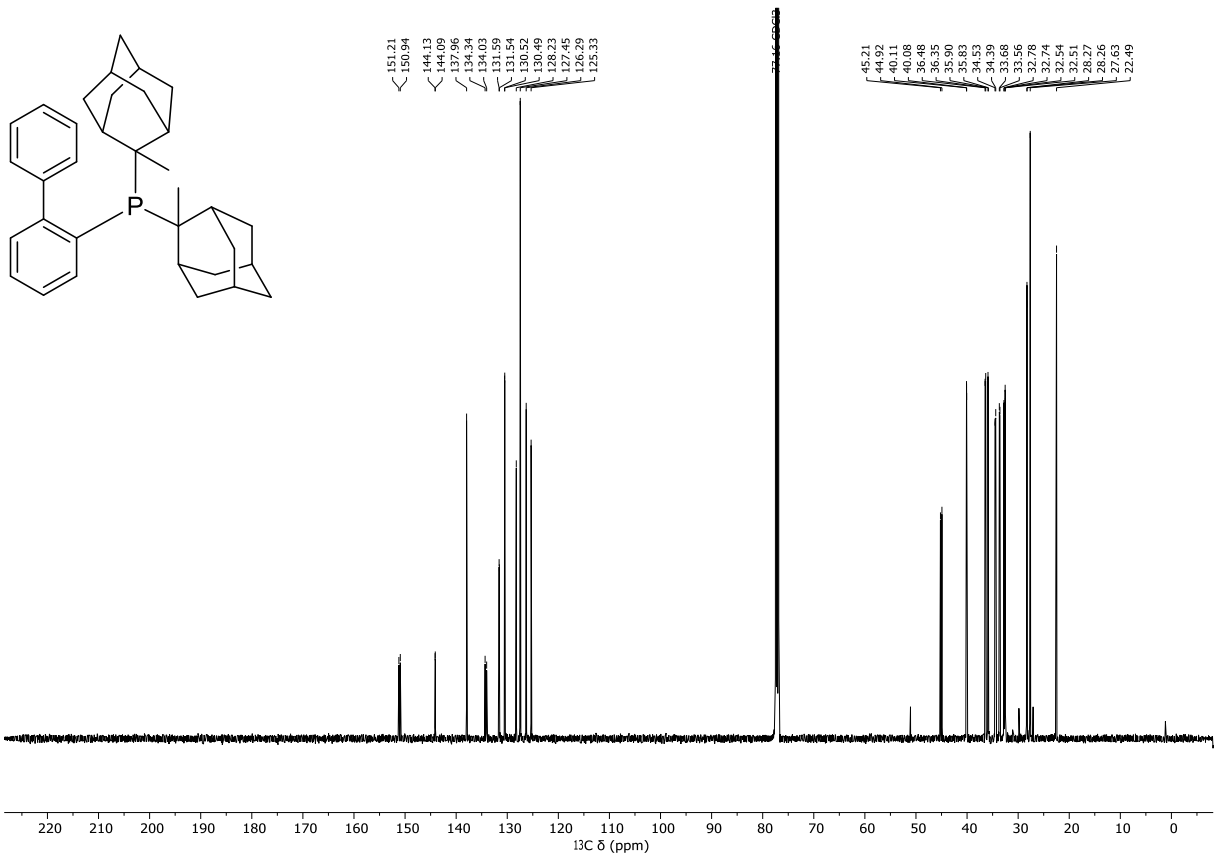
2-(Di-(1-adamantyl)phosphino)biphenyl (3k) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



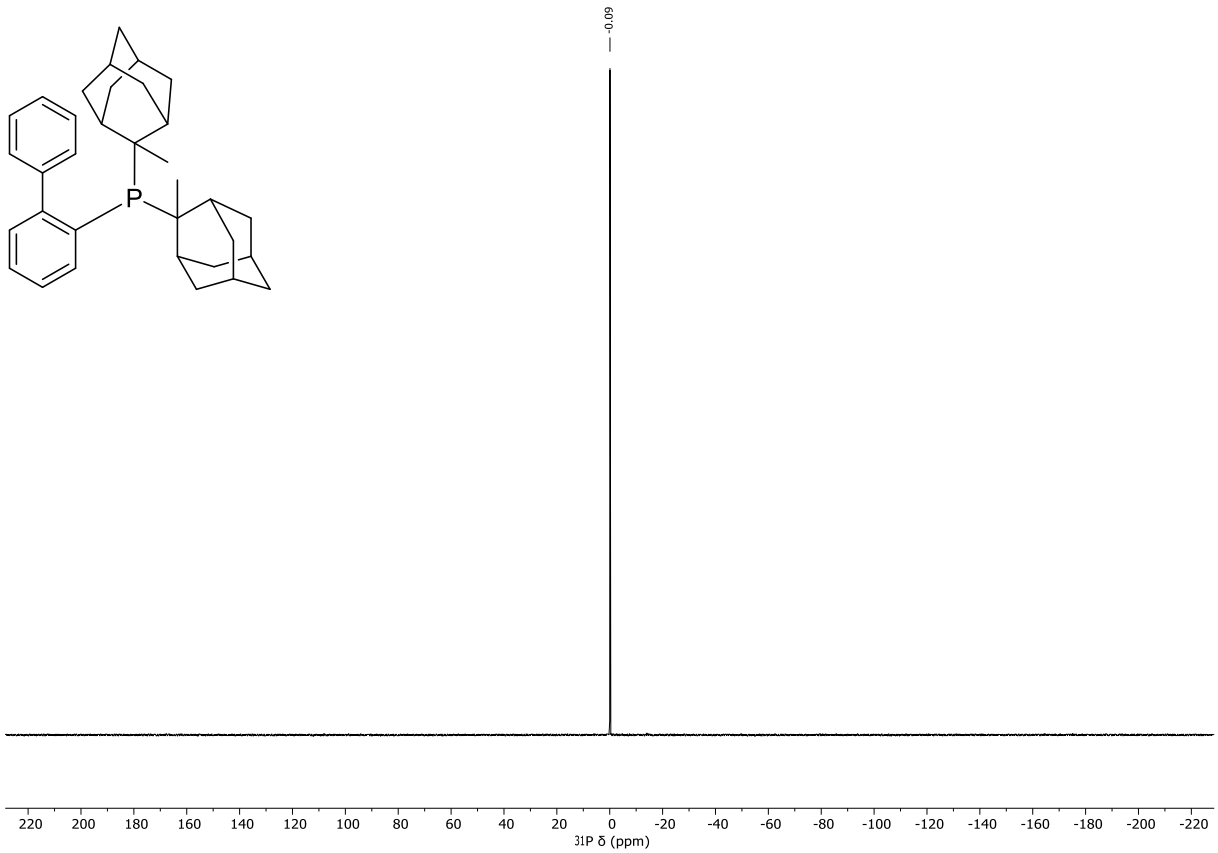
2-(Di-(2-methyl-2-adamantyl)phosphino)biphenyl (3l) - ^{1}H NMR (500 MHz, $CDCl_3$)



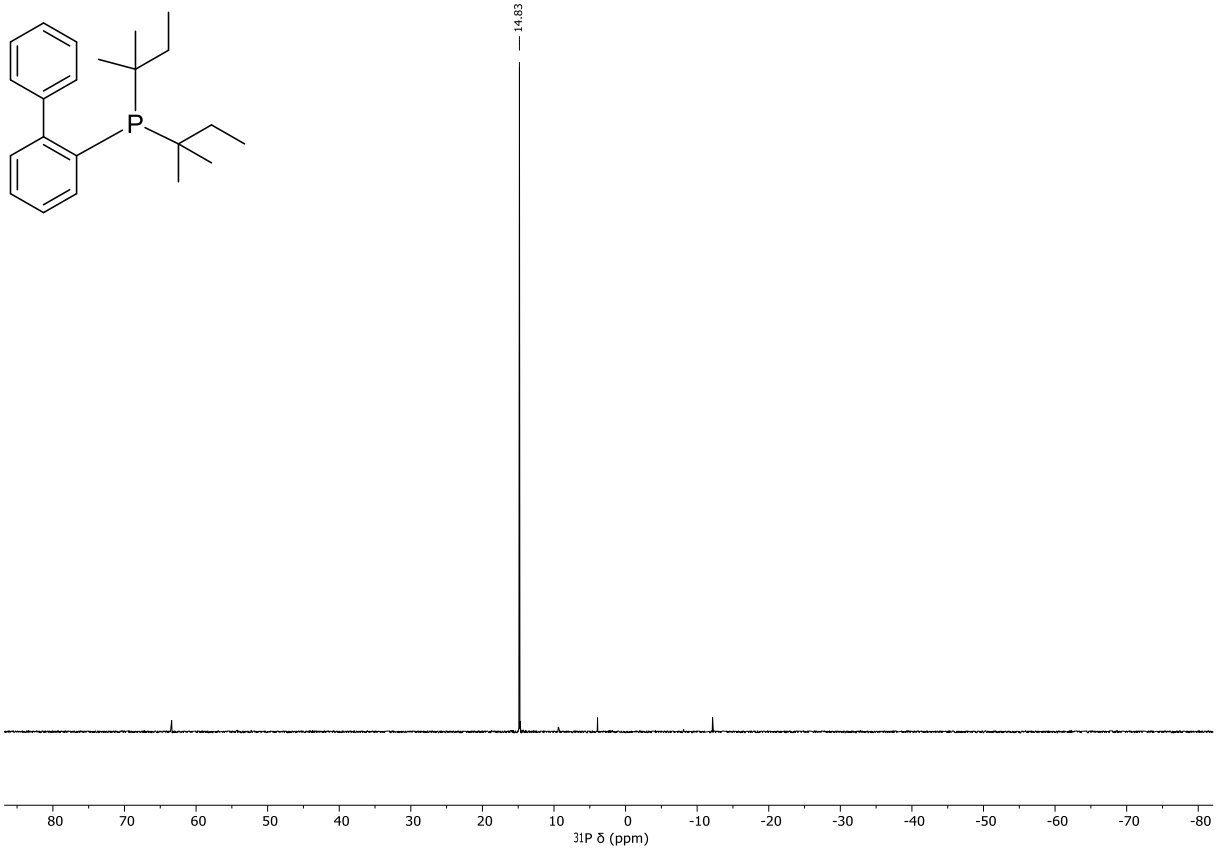
2-(Di-(2-methyl-2-adamantyl)phosphino)biphenyl (3l) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



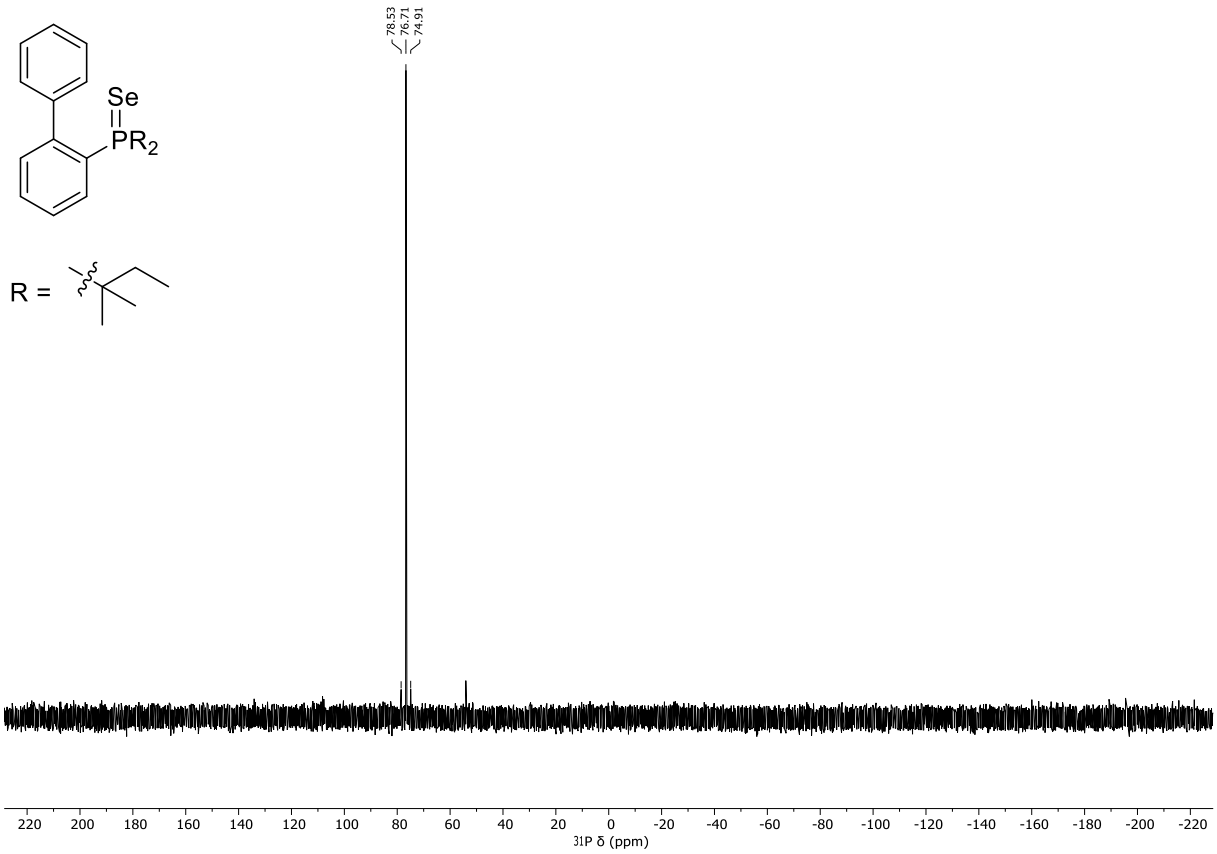
2-(Di-(2-methyl-2-adamantyl)phosphino)biphenyl (3l) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



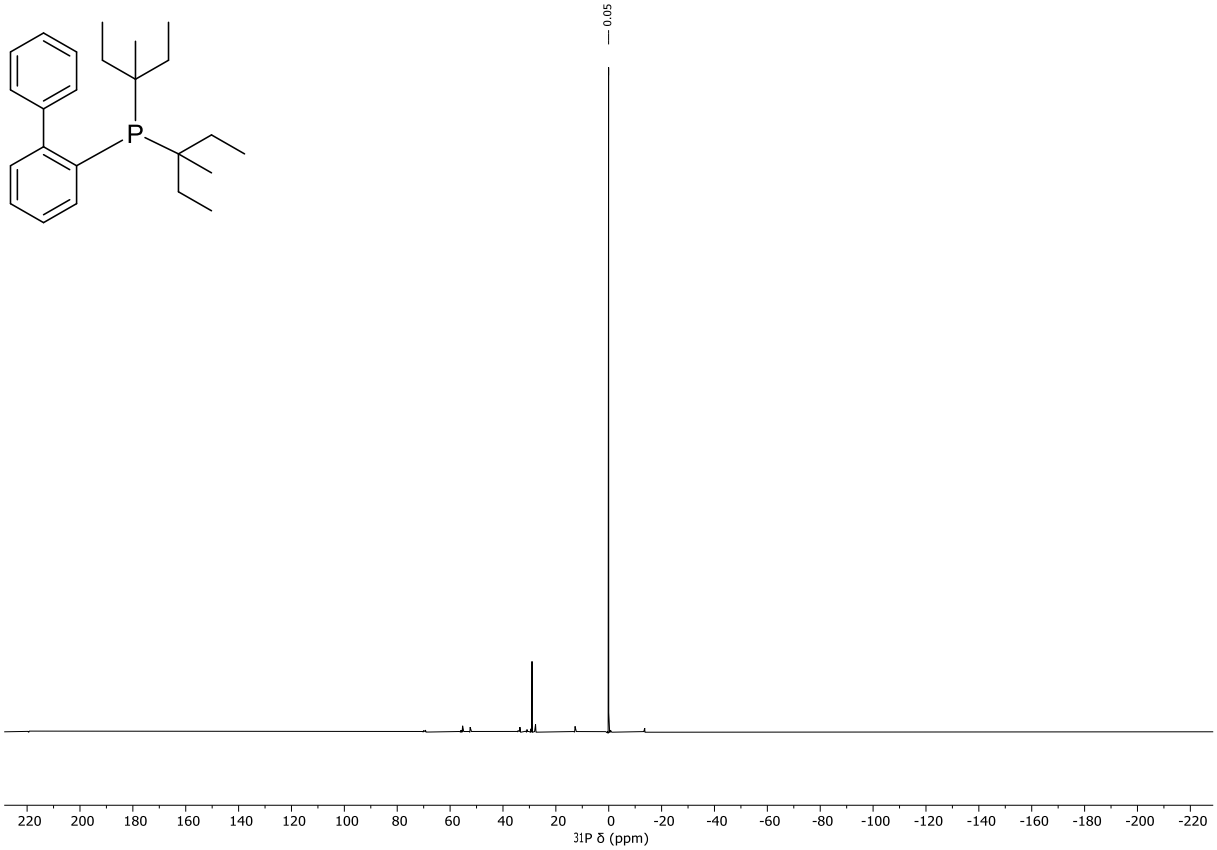
Crude 2-(di-(*tert*-amyl)phosphino)biphenyl (3a) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



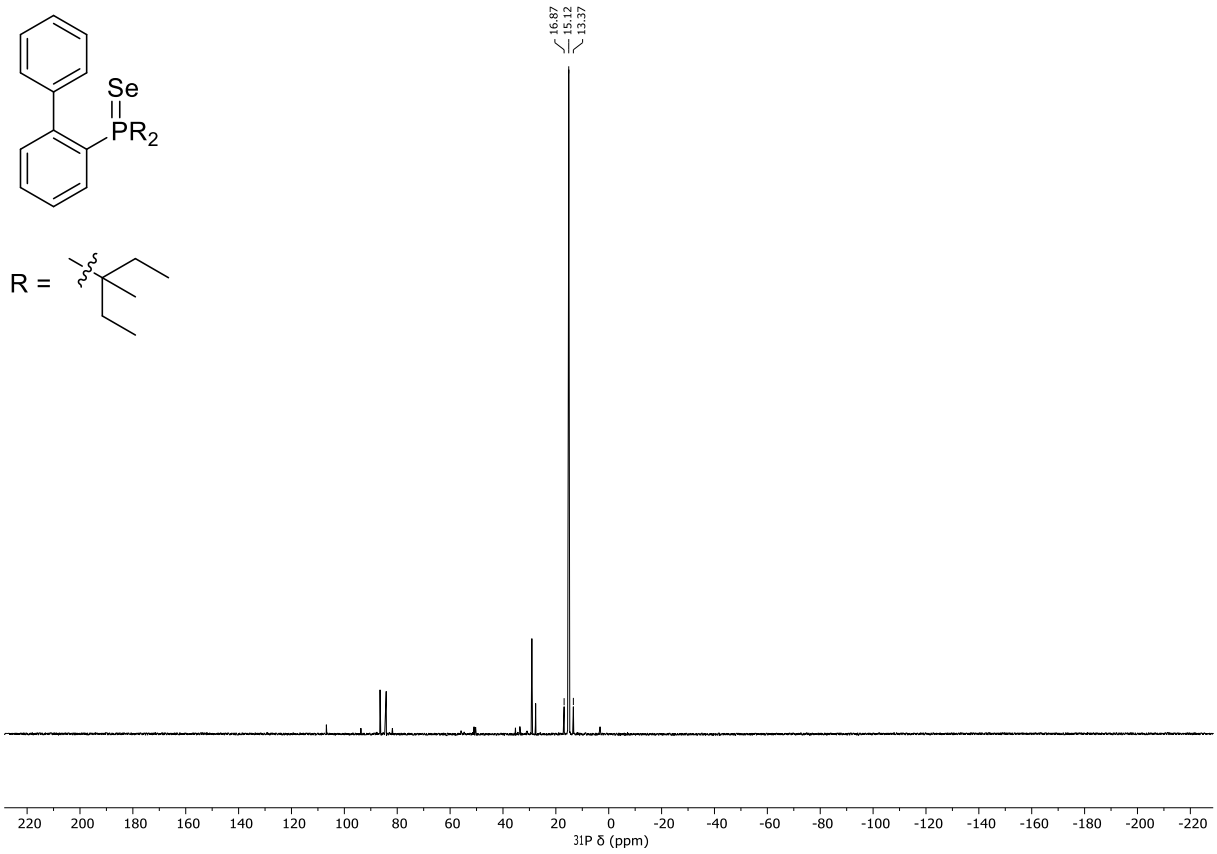
(2-Biphenyl)di-*tert*-amylphosphine selenide (4a) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



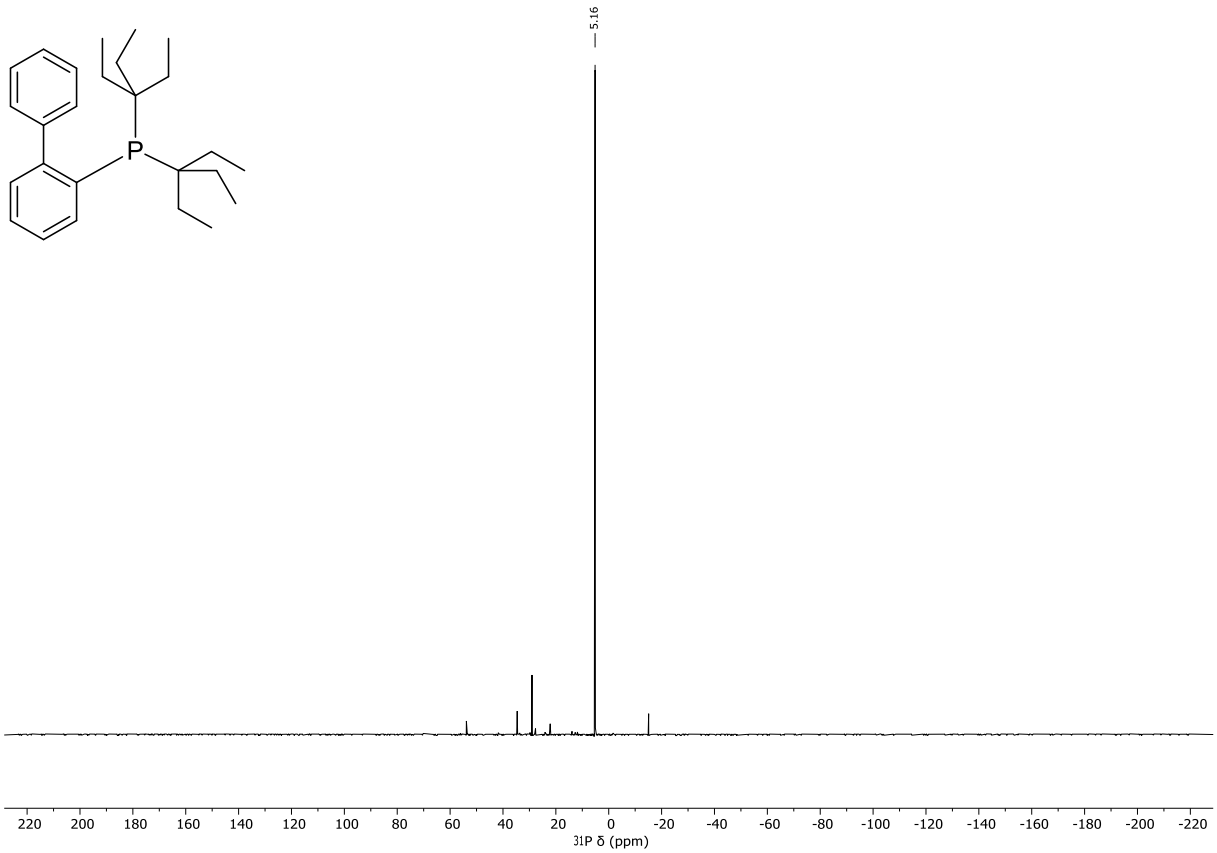
Crude 2-(Di-(3-methyl-3-pentyl)phosphino)biphenyl (3b) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



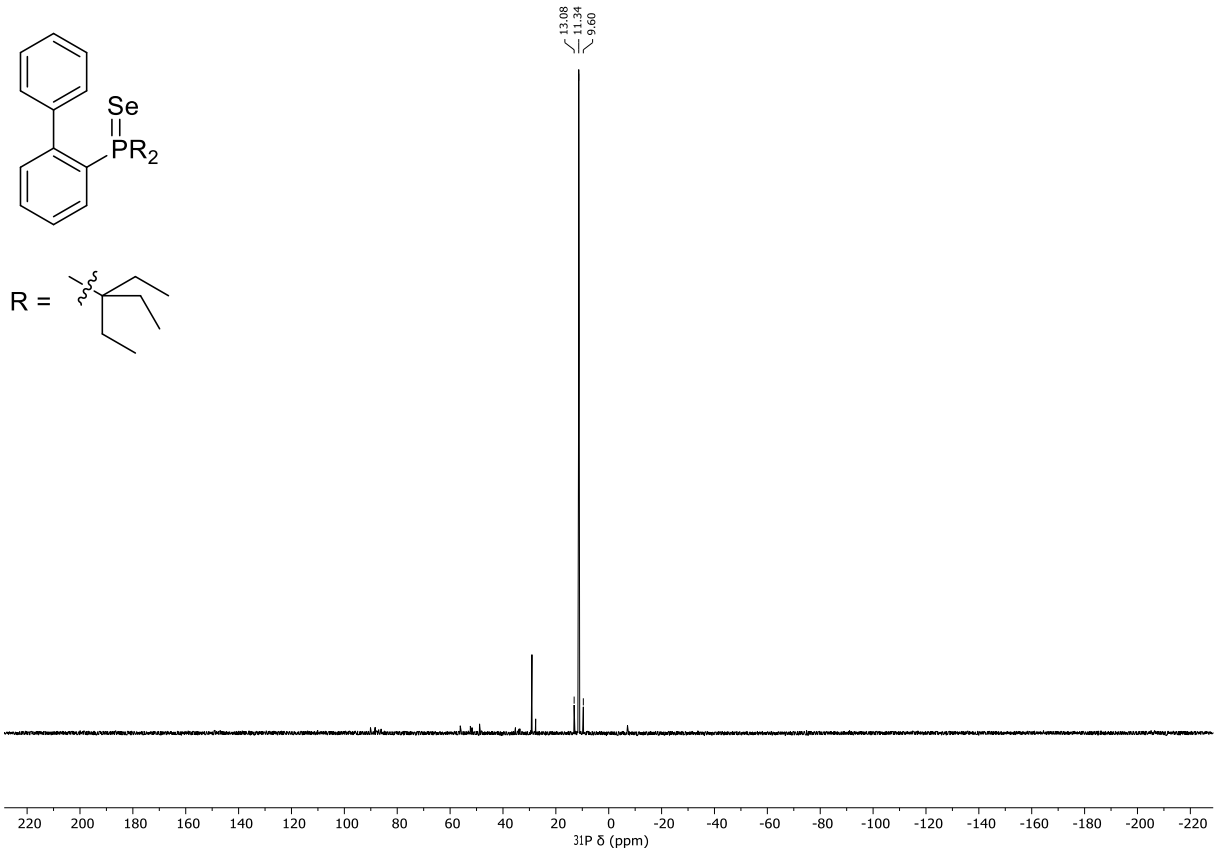
(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine selenide (4b) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



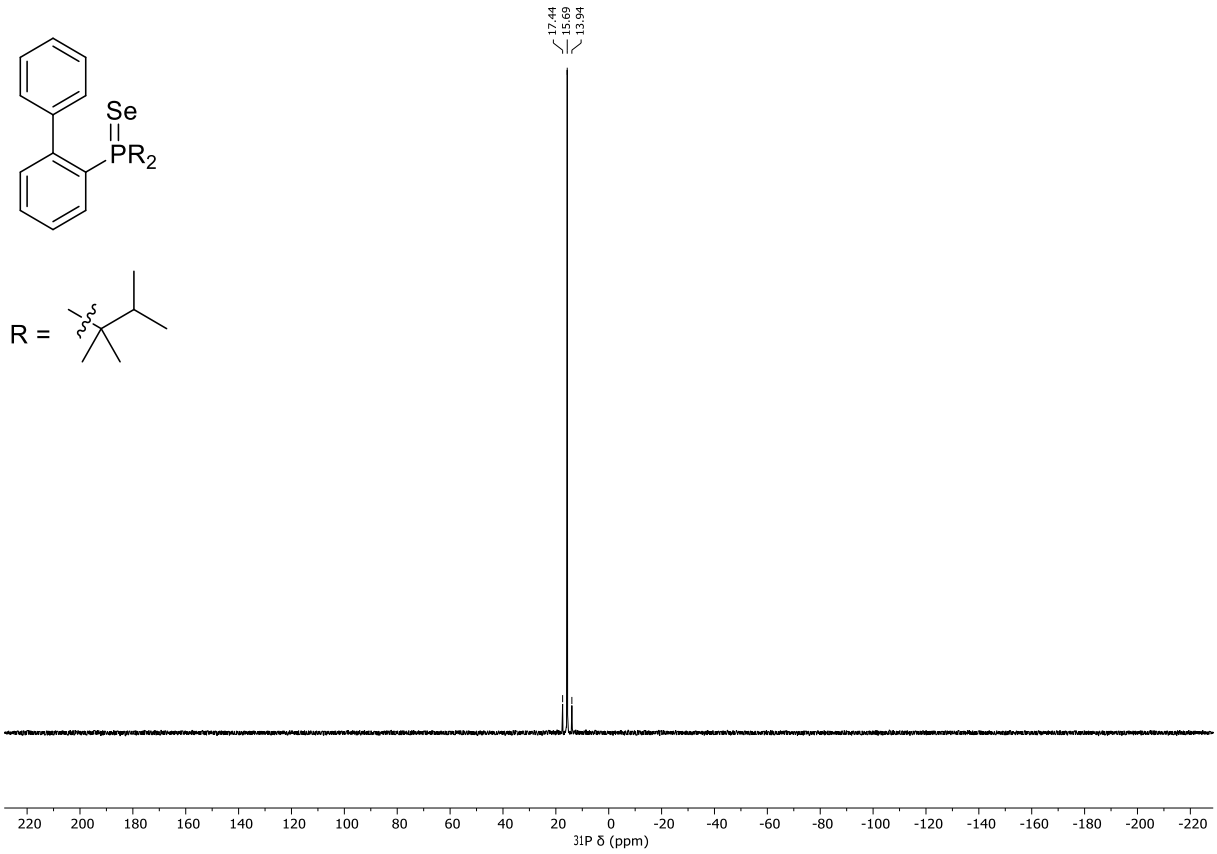
Crude 2-(Di-(3-ethyl-3-pentyl)phosphino)biphenyl (3c) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



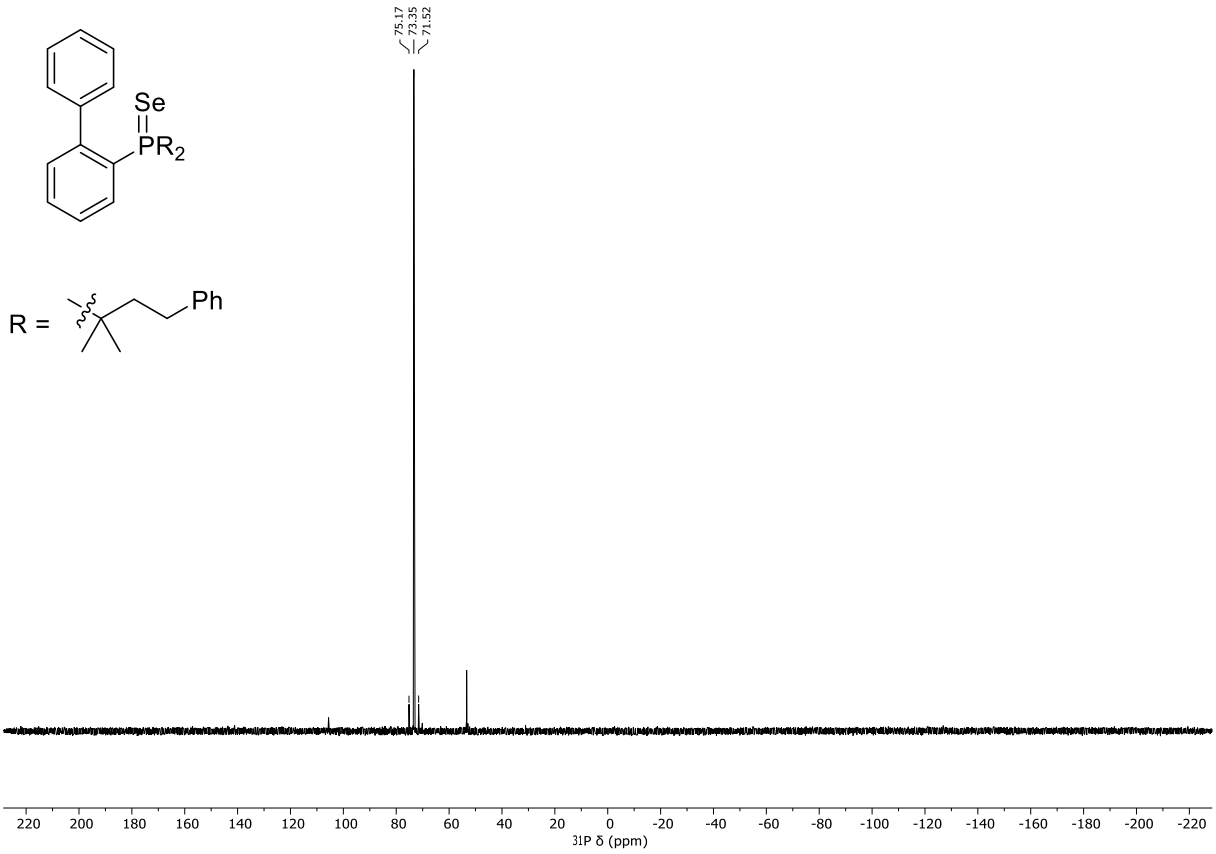
(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine selenide (4c) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



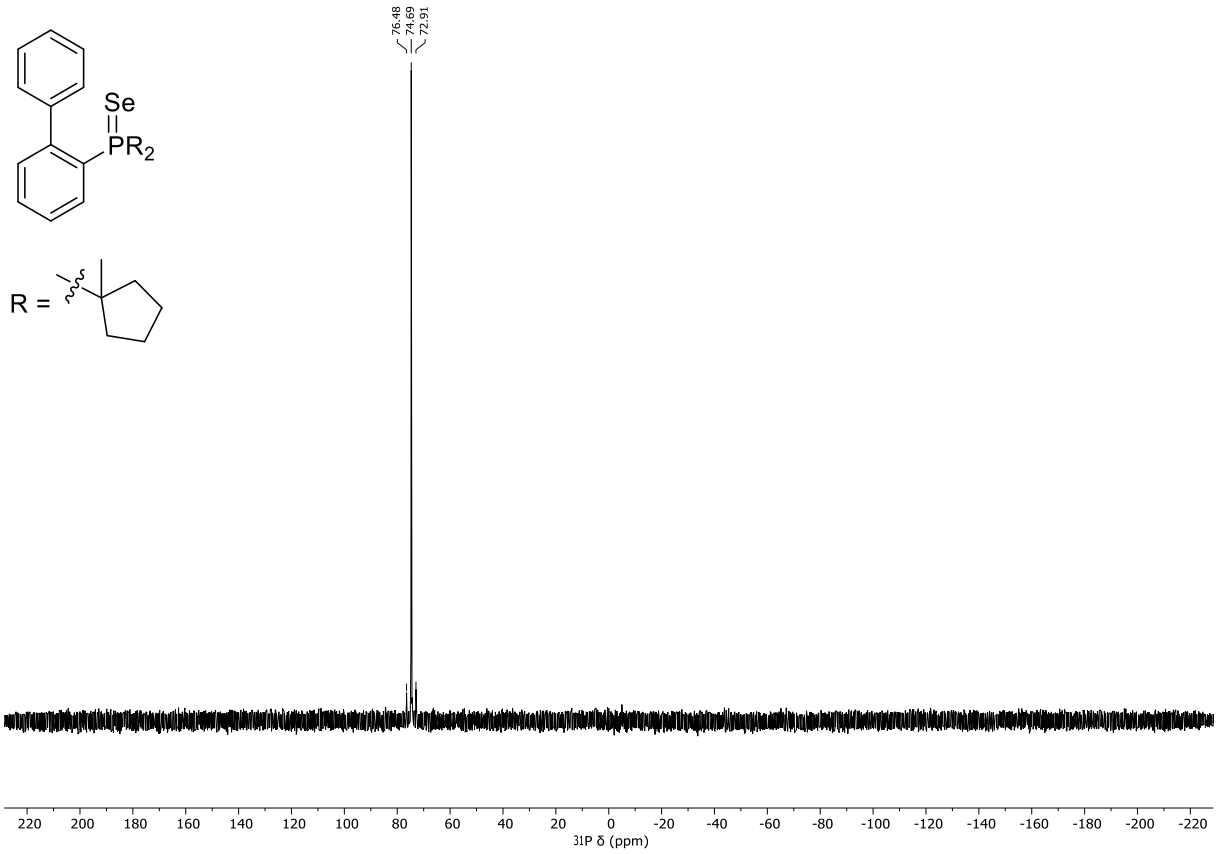
(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine selenide (4d) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



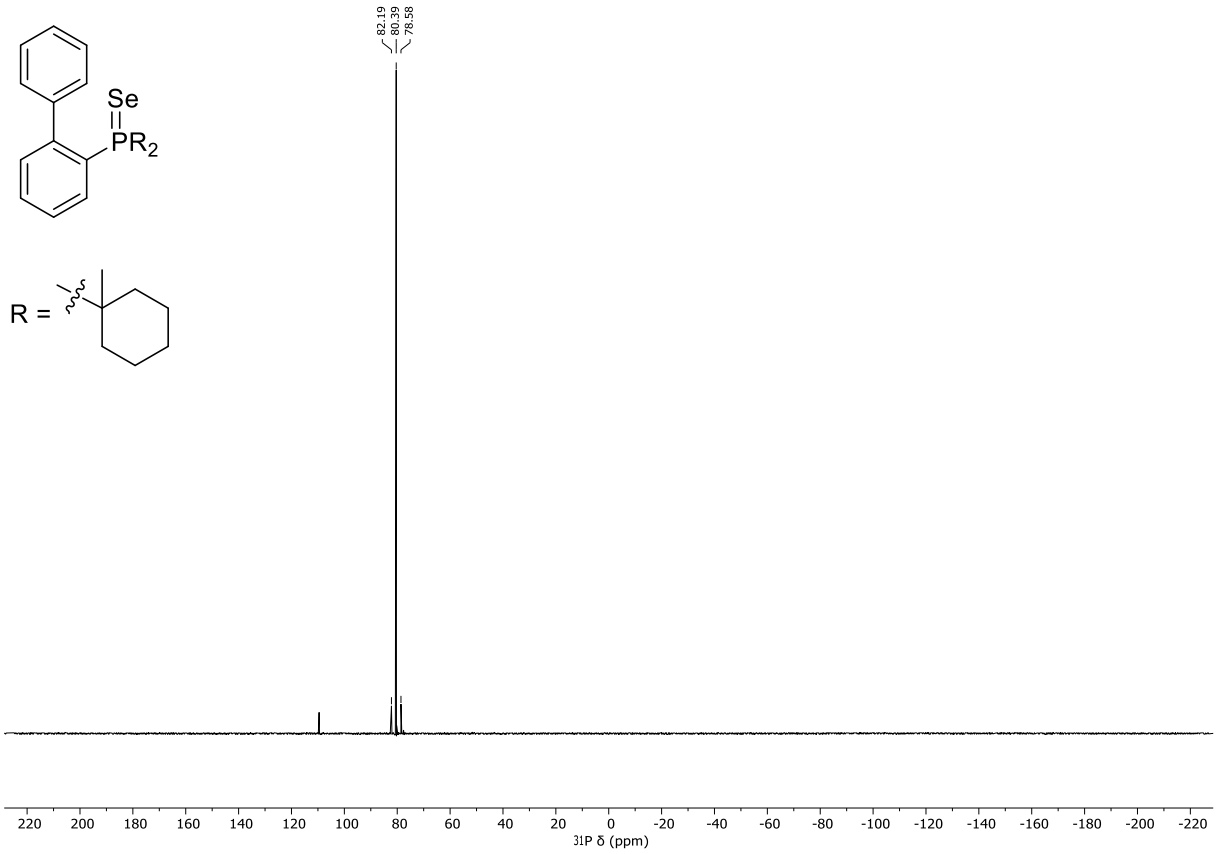
(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine selenide (4f) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



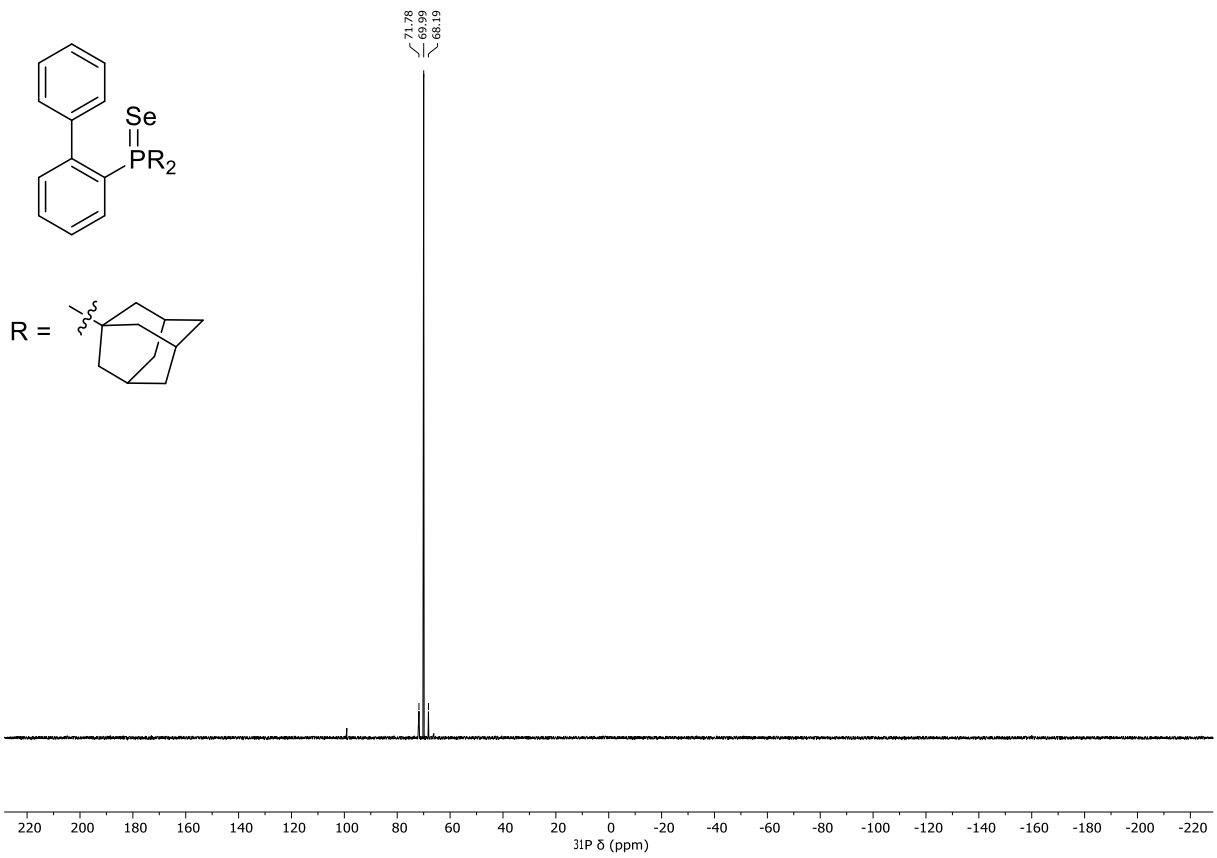
(2-Biphenyl)di-(1-methylcyclopentyl)phosphine selenide (4h) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



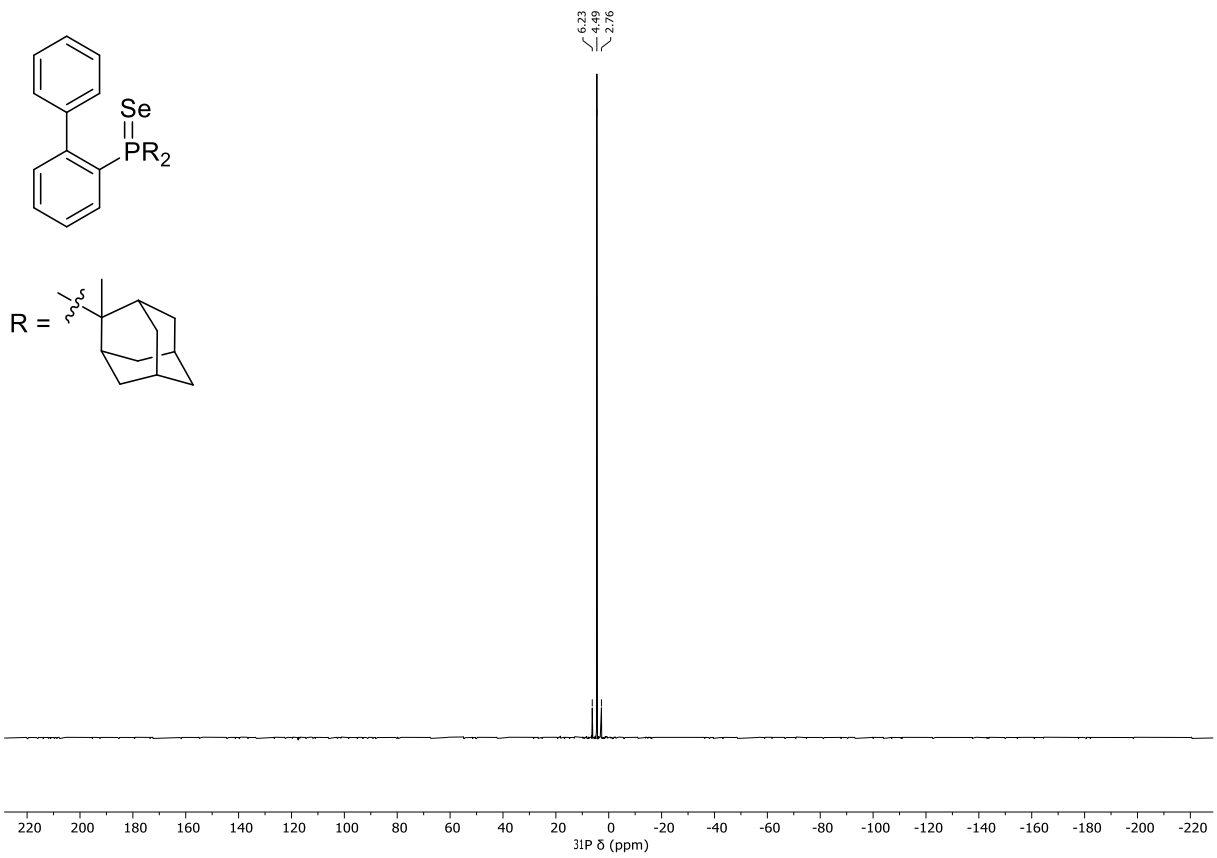
(2-Biphenyl)di-(1-methylcyclohexyl)phosphine selenide (4i) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



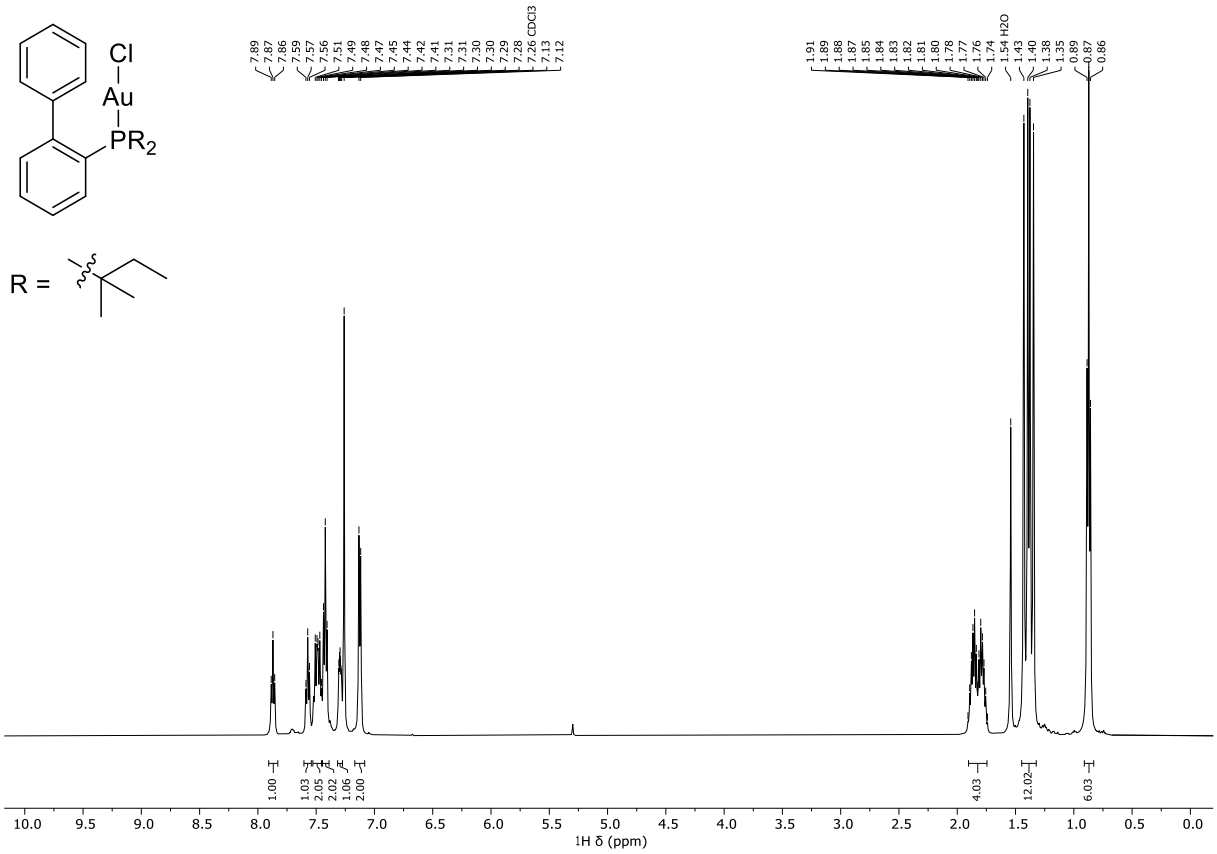
(2-Biphenyl)di-(1-adamantyl)phosphine selenide (4k) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



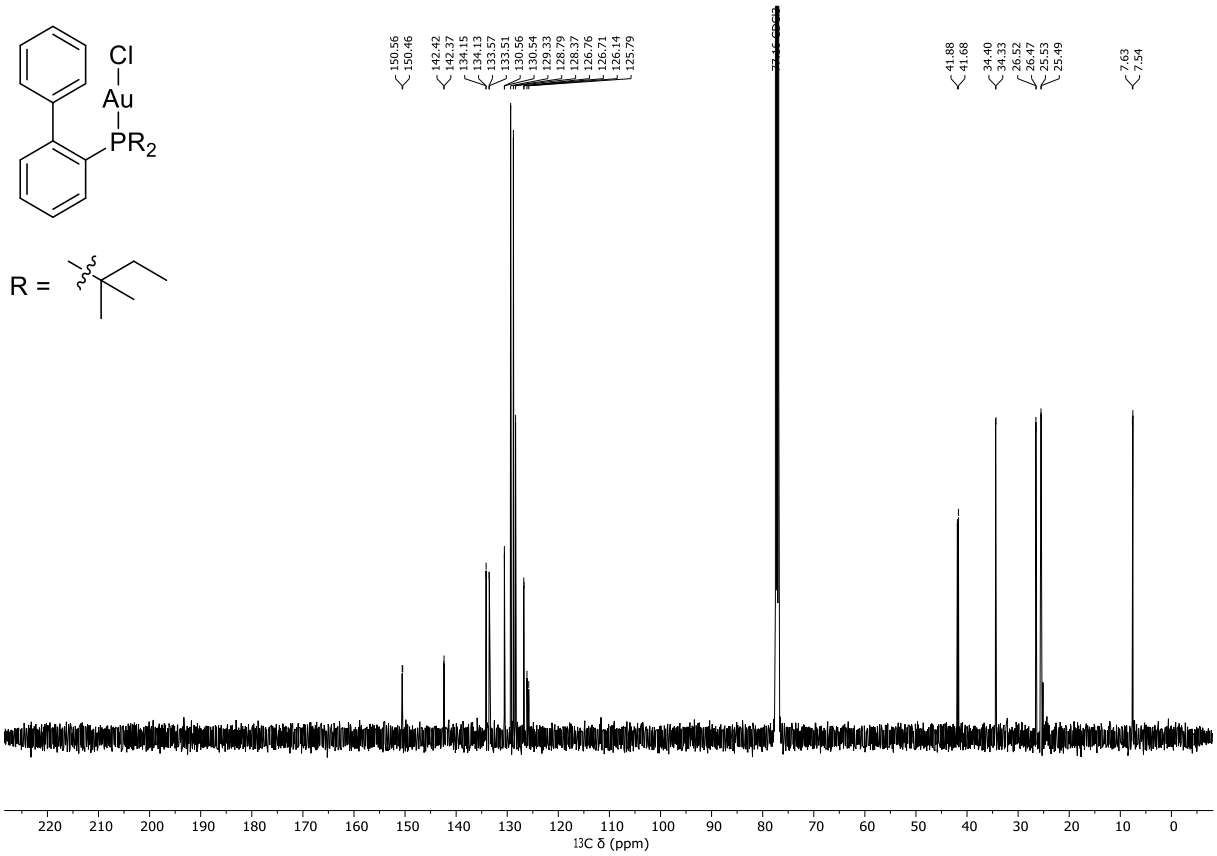
(2-Biphenyl)di-(2-methyl-2-adamantyl)phosphine selenide (4l) reaction mixture $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



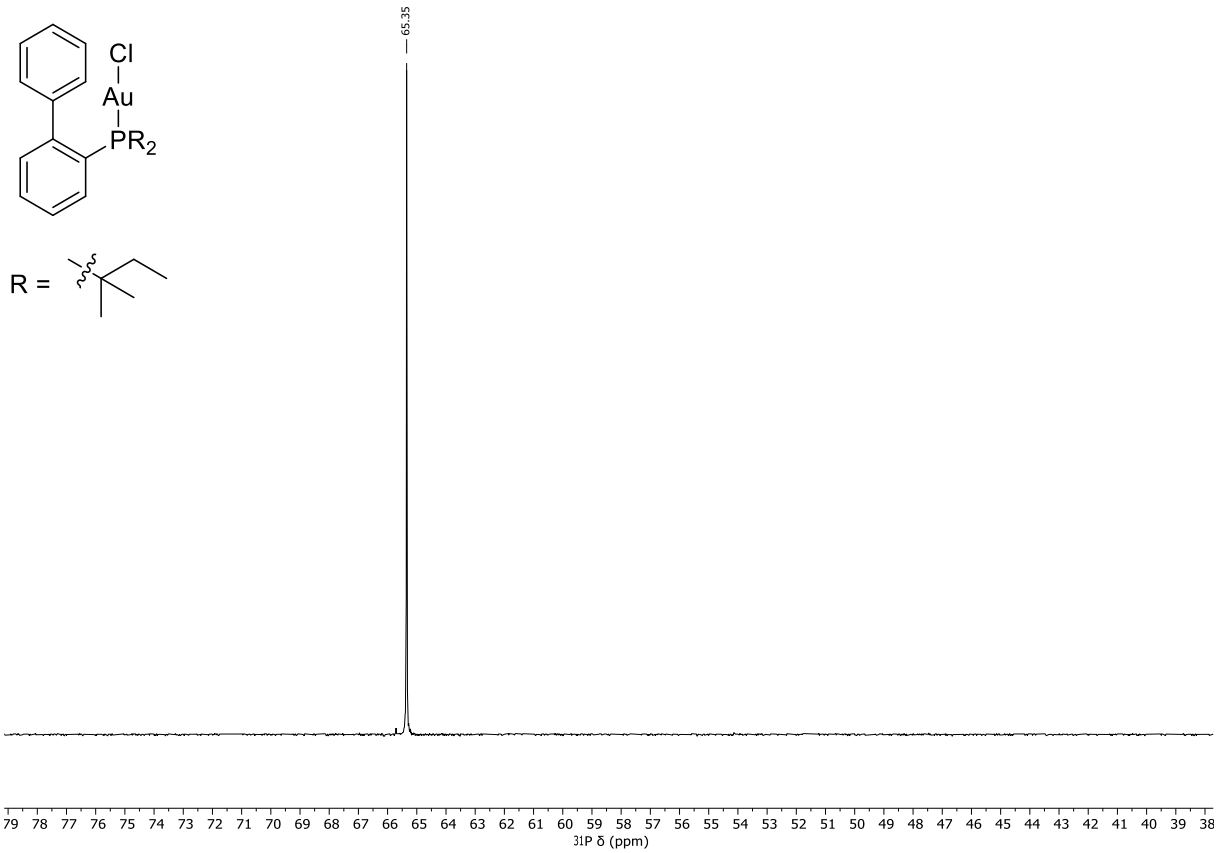
[(2-Biphenyl)di-tert-amylphosphine]gold(I) chloride (5a) - ^{1}H NMR (500 MHz, $CDCl_3$)



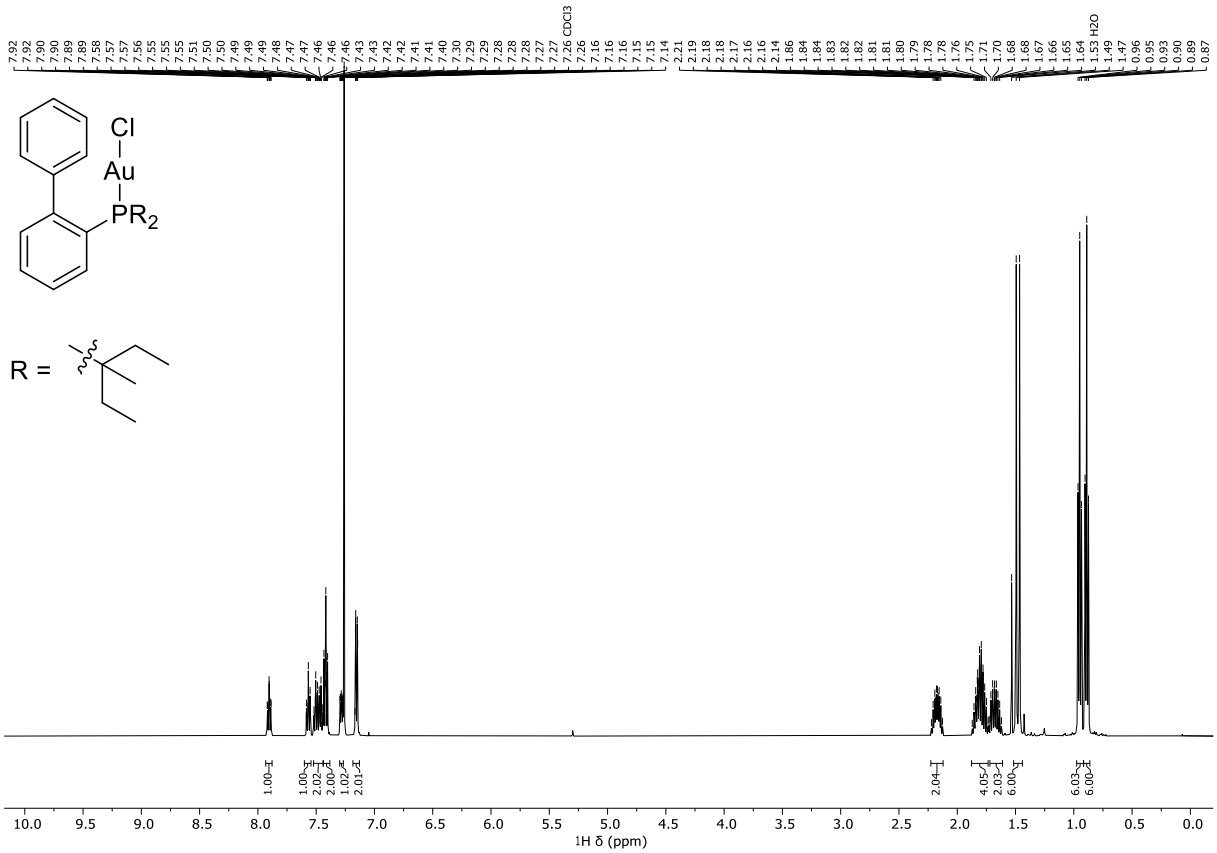
[(2-Biphenyl)di-tert-amylphosphine]gold(I) chloride (5a) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



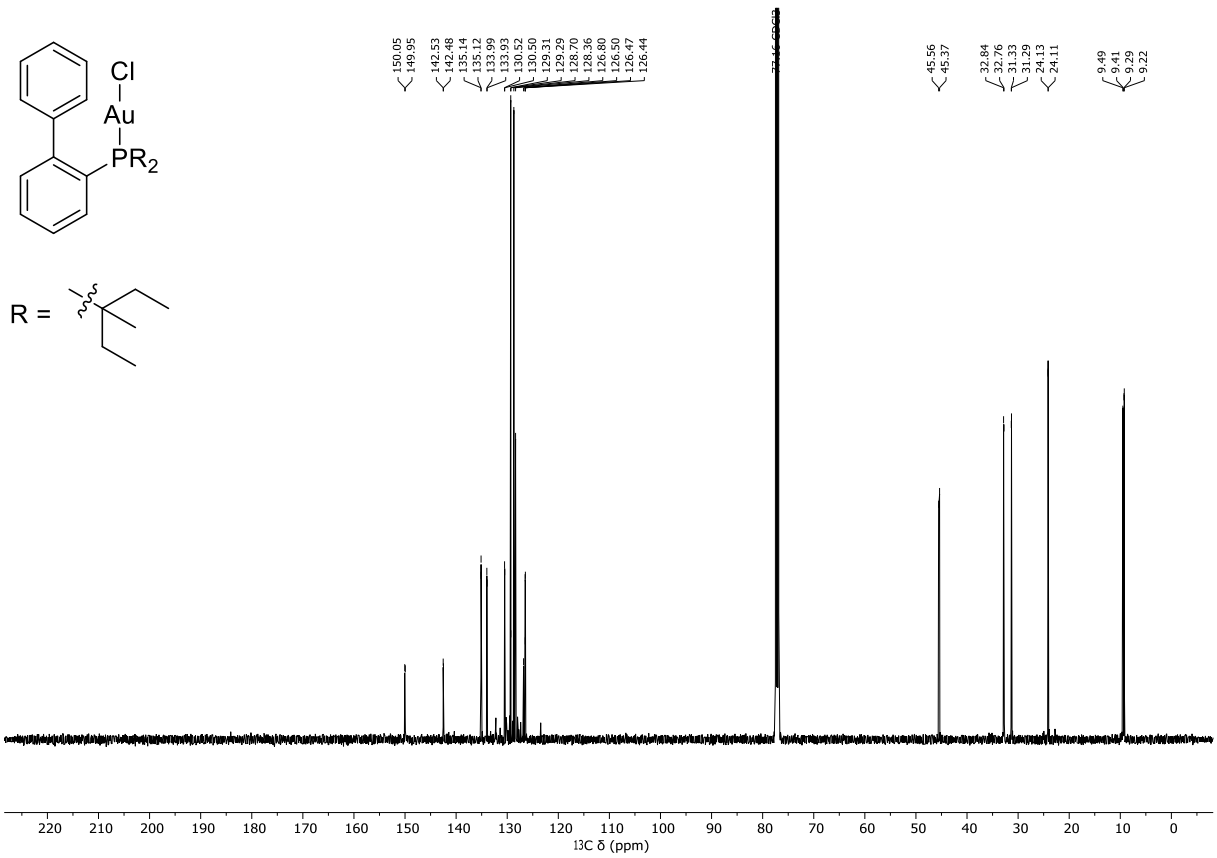
[(2-Biphenyl)di-tert-amylphosphine]gold(I) chloride (5a) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



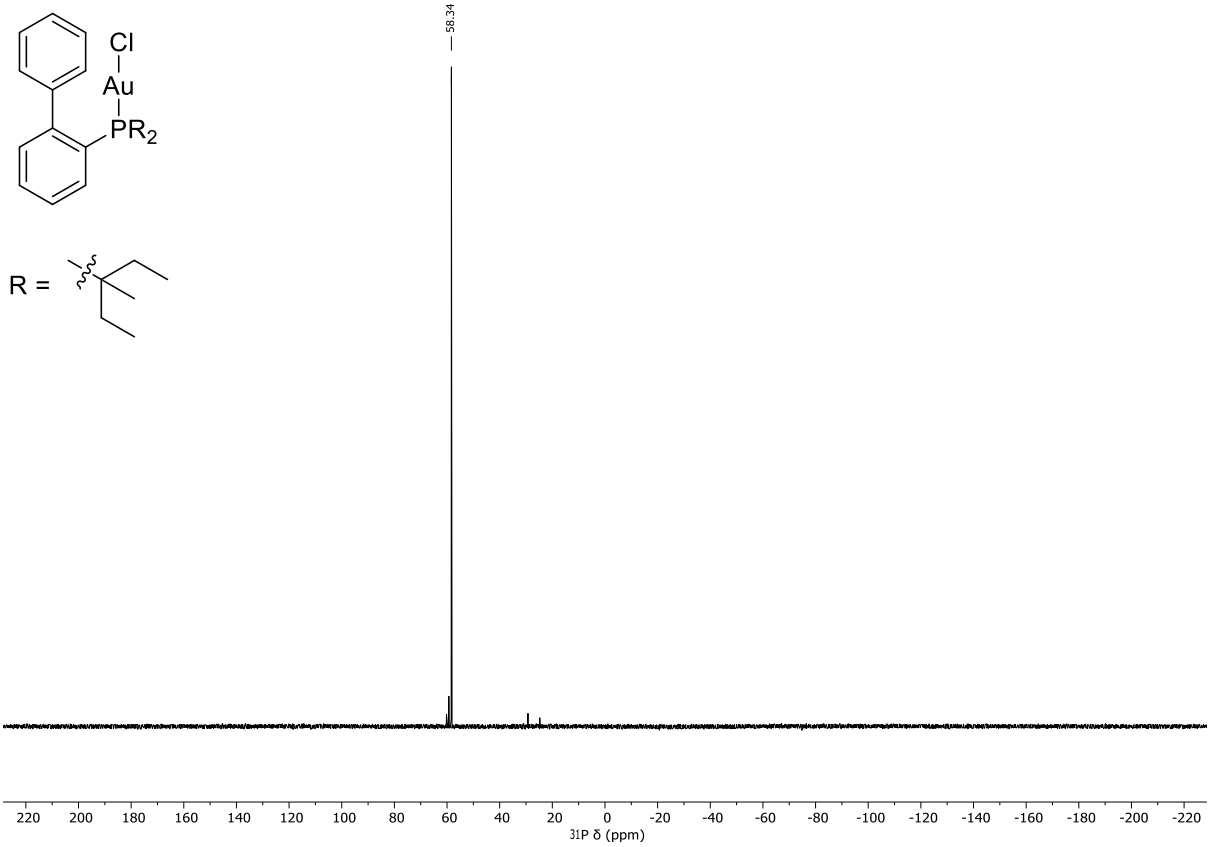
[(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine]gold(I) chloride (5b) - ^{1}H NMR (500 MHz, $CDCl_3$)



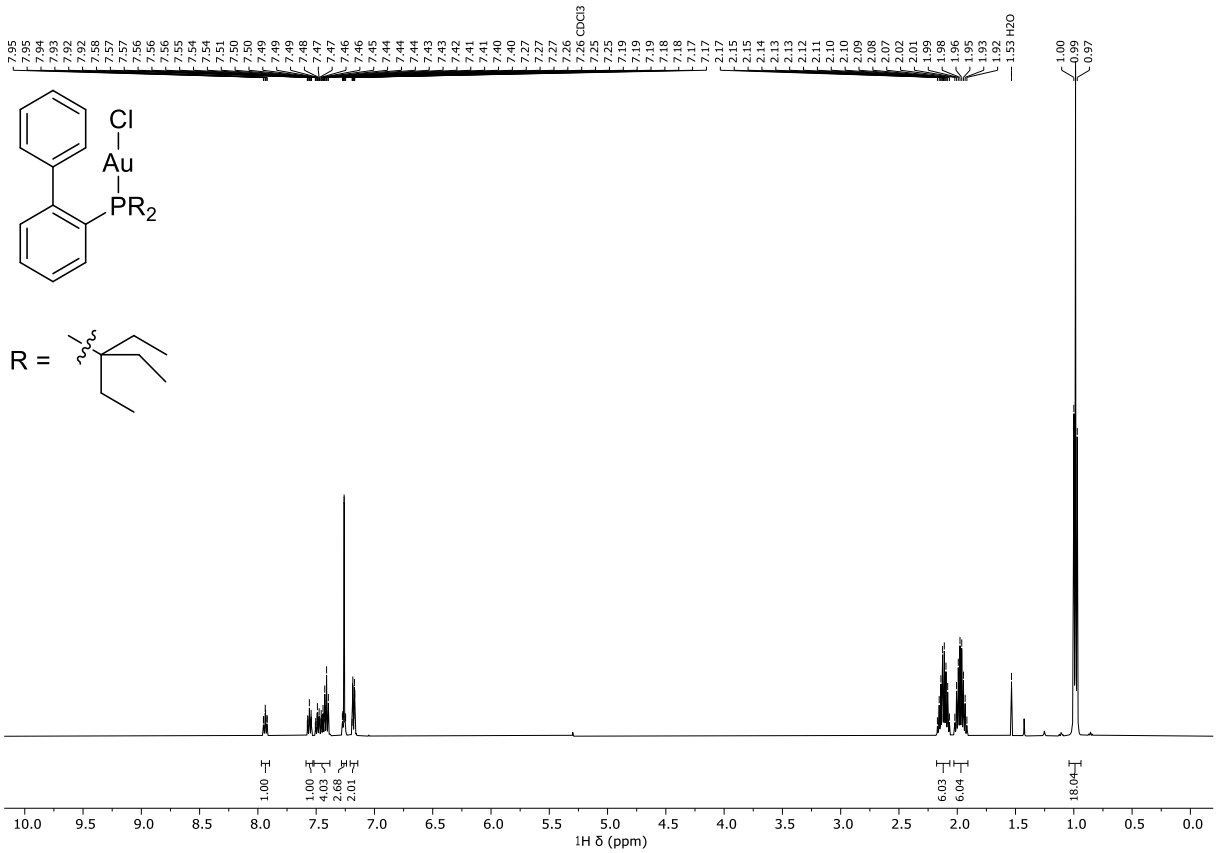
[(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine]gold(I) chloride (5b) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



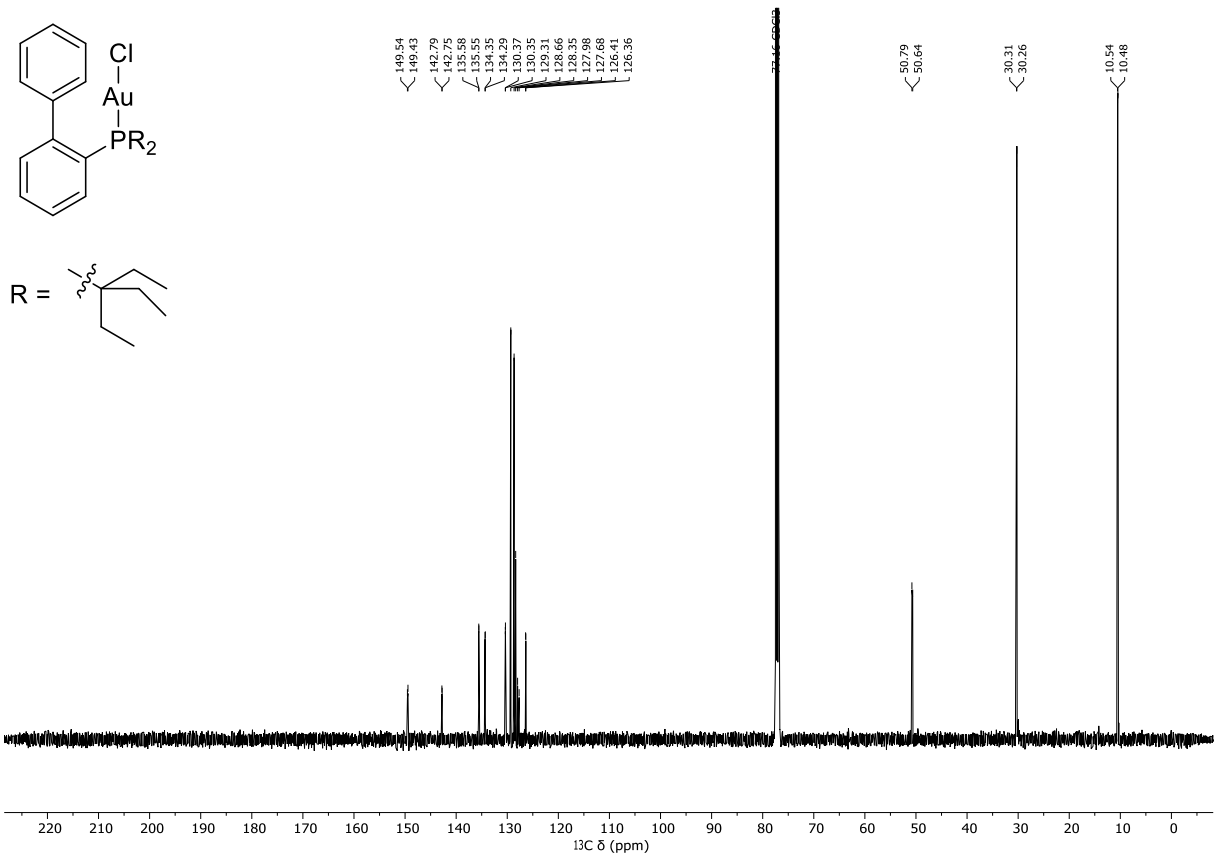
[(2-Biphenyl)di-(3-methyl-3-pentyl)phosphine]gold(I) chloride (5b) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



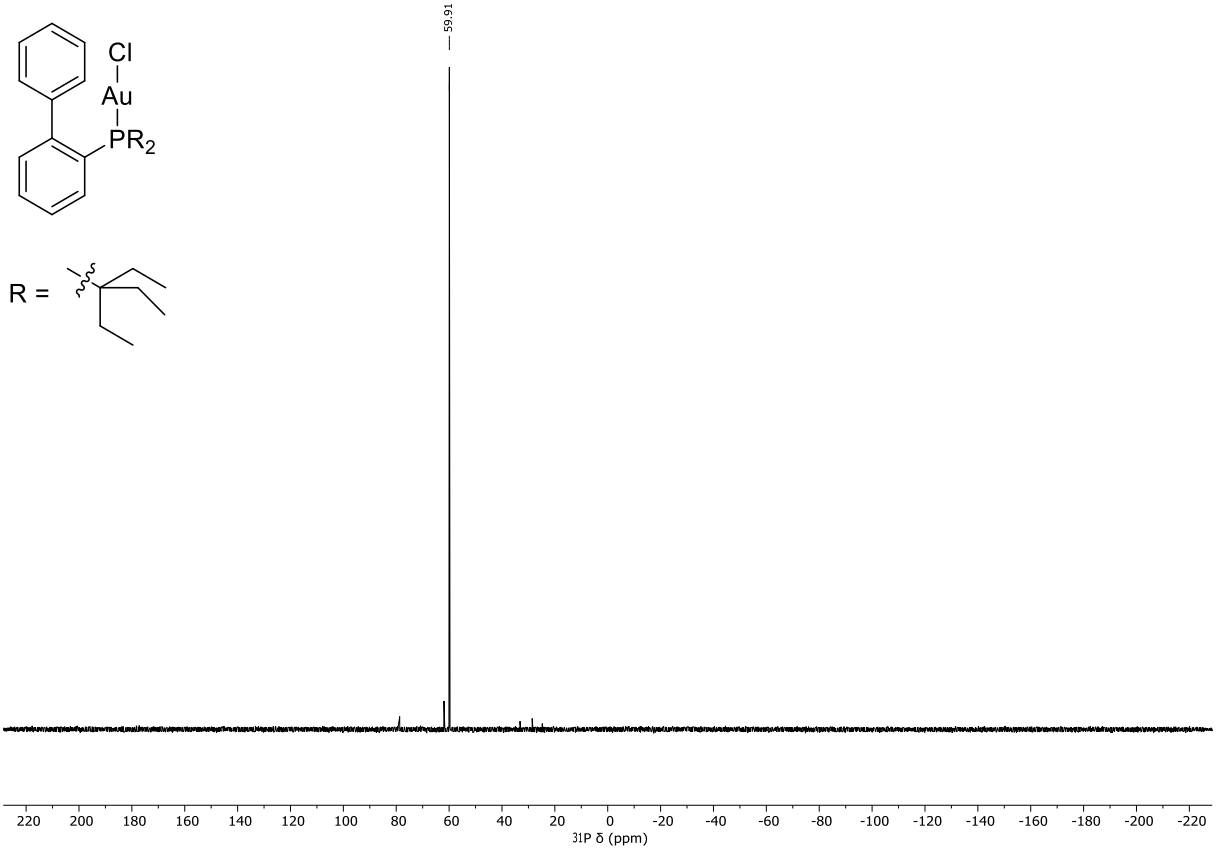
[(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine]gold(I) chloride (5c) - ^{1}H NMR (500 MHz, $CDCl_3$)



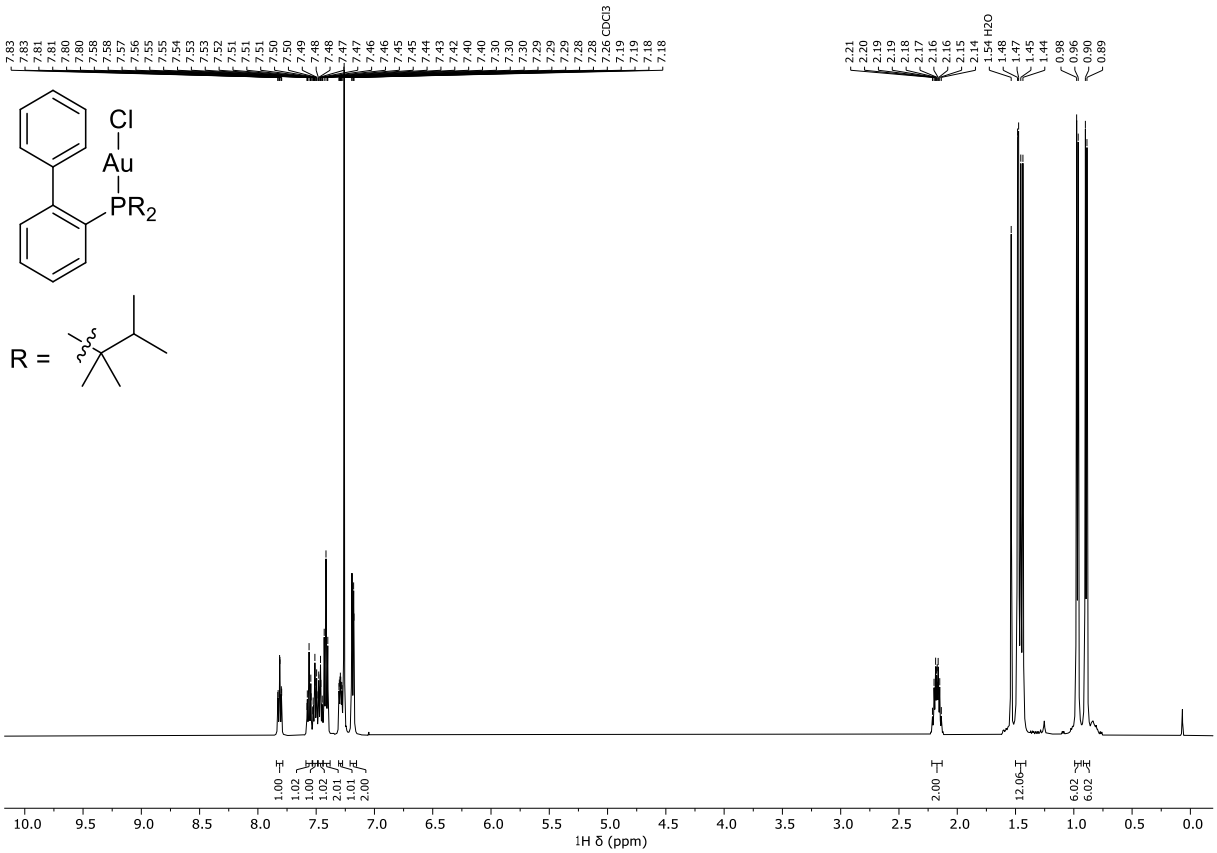
[(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine]gold(I) chloride (5c) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



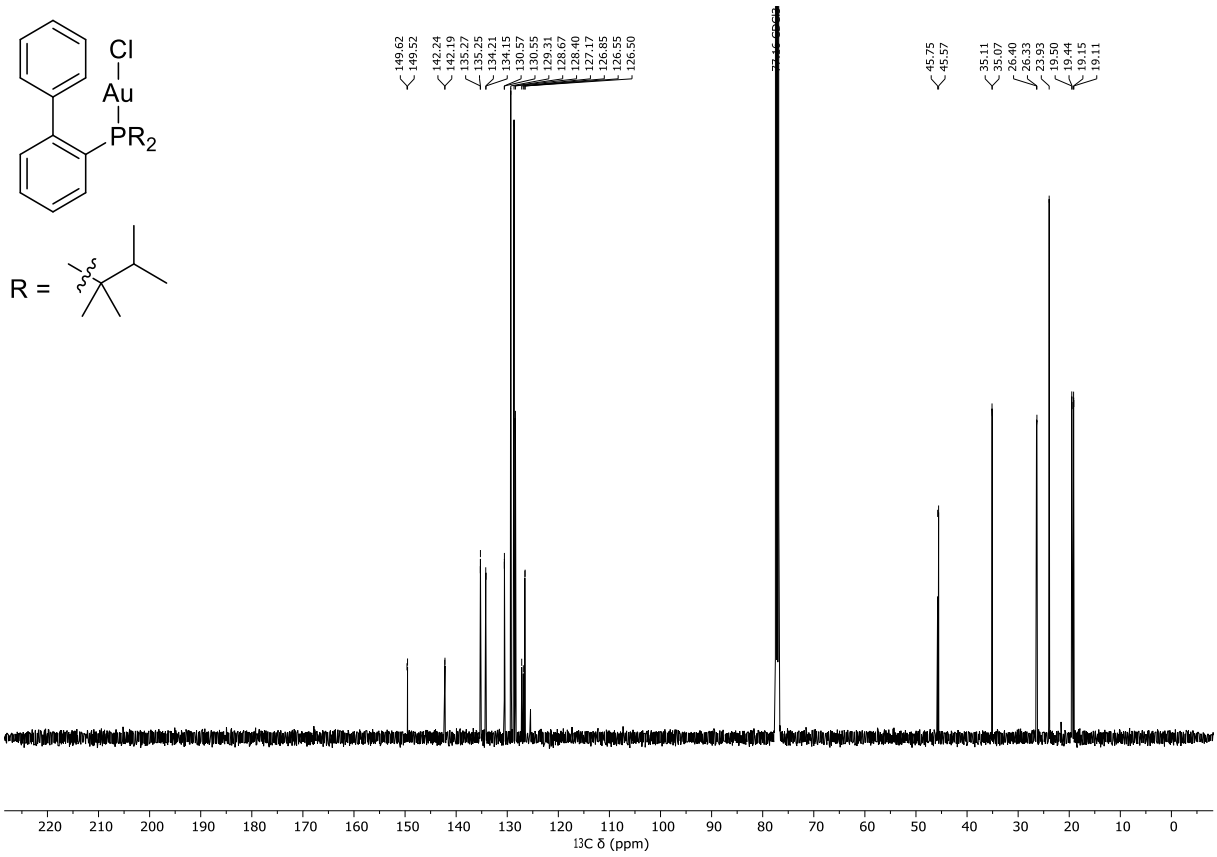
[(2-Biphenyl)di-(3-ethyl-3-pentyl)phosphine]gold(I) chloride (5c) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



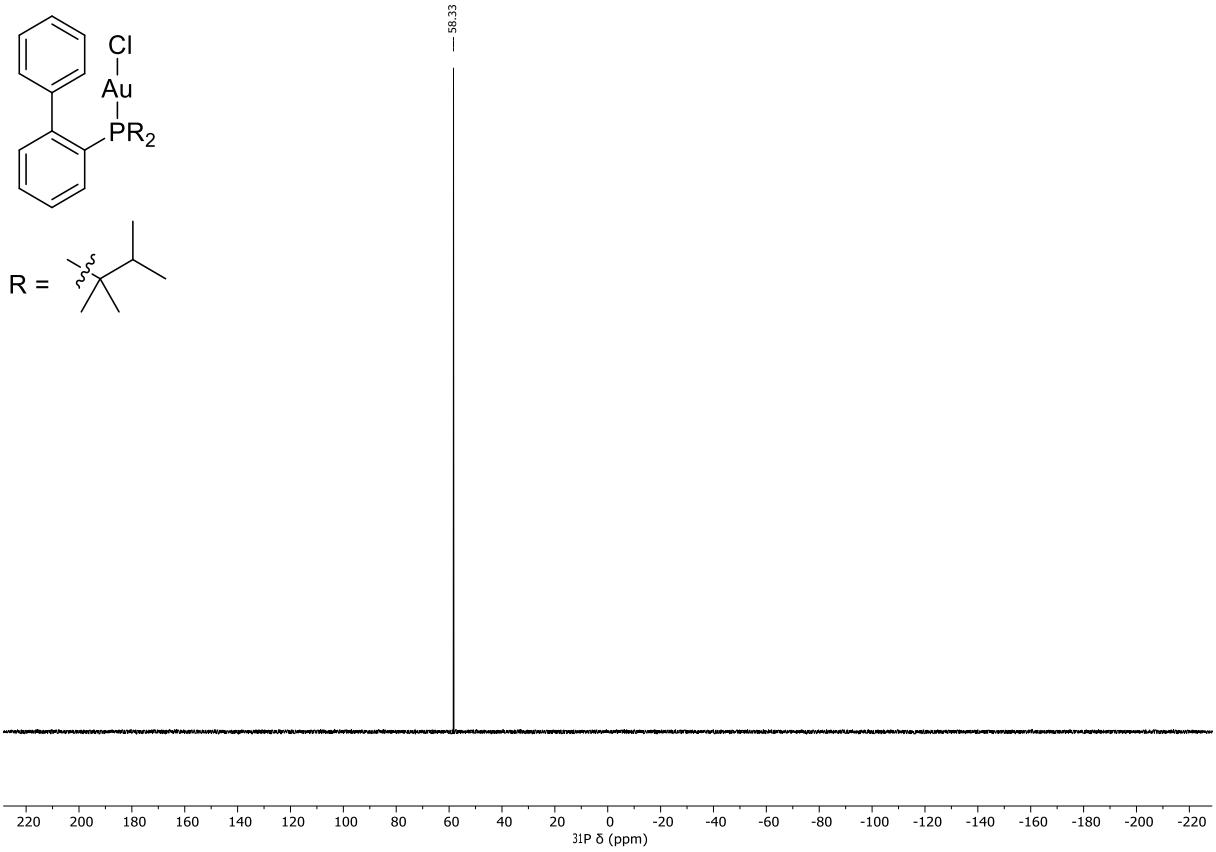
[(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine]gold(I) chloride (5d) - ^{1}H NMR (500 MHz, $CDCl_3$)



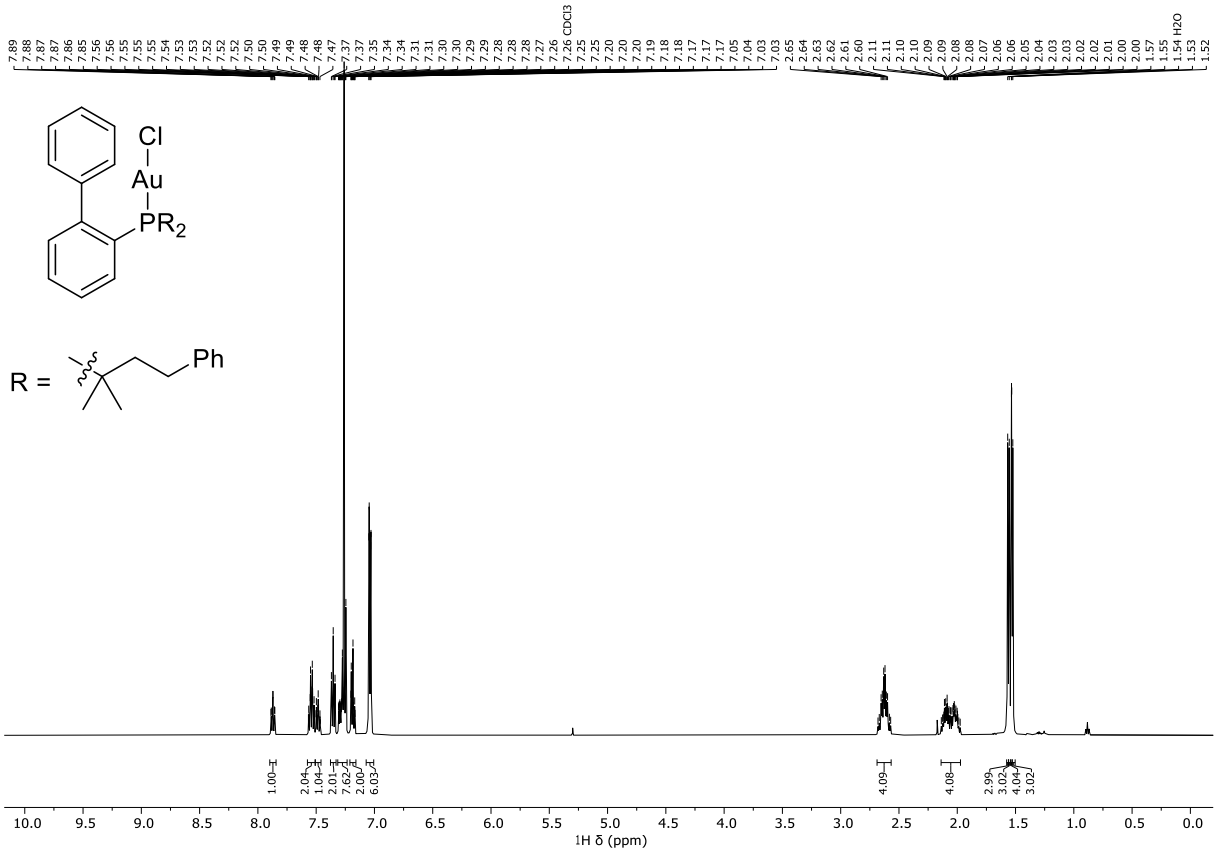
[(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine]gold(I) chloride (5d) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



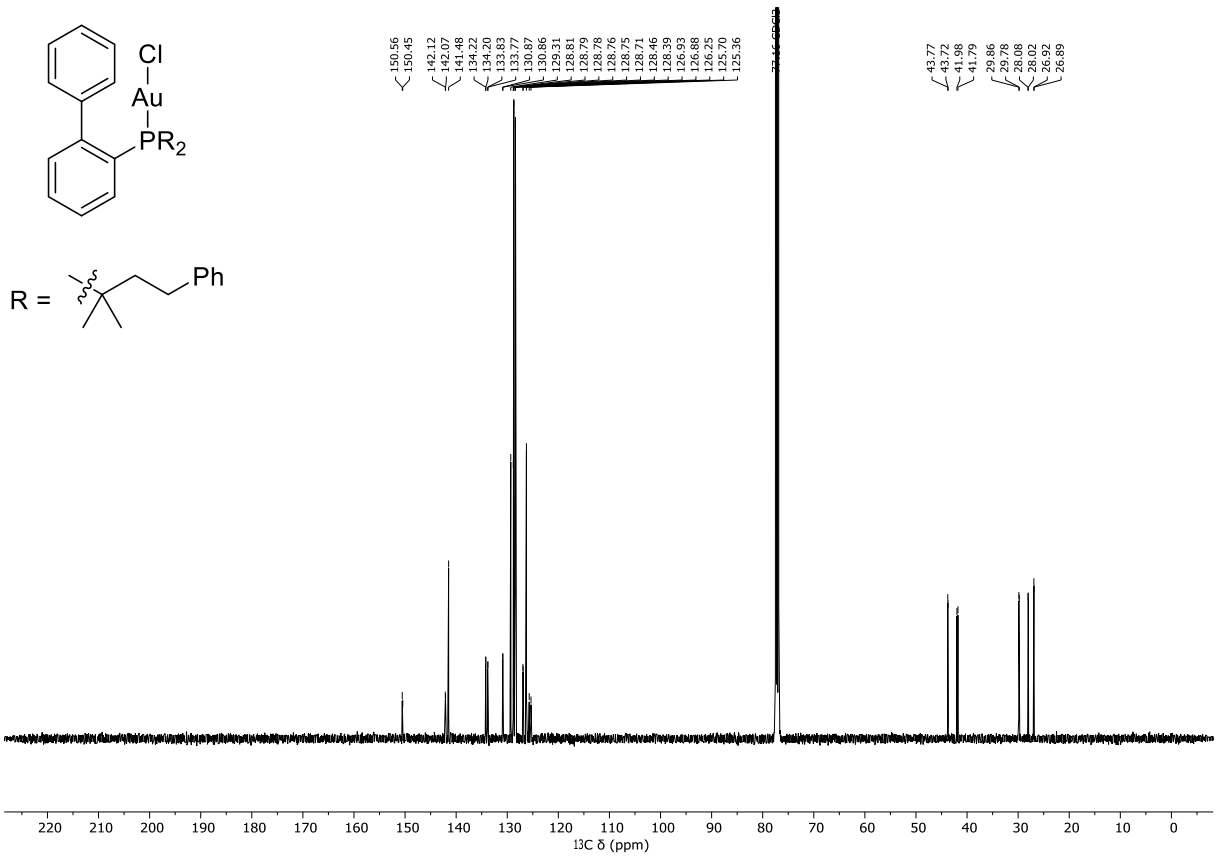
[(2-Biphenyl)bis-(2,3-dimethyl-2-butyl)phosphine]gold(I) chloride (5d) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



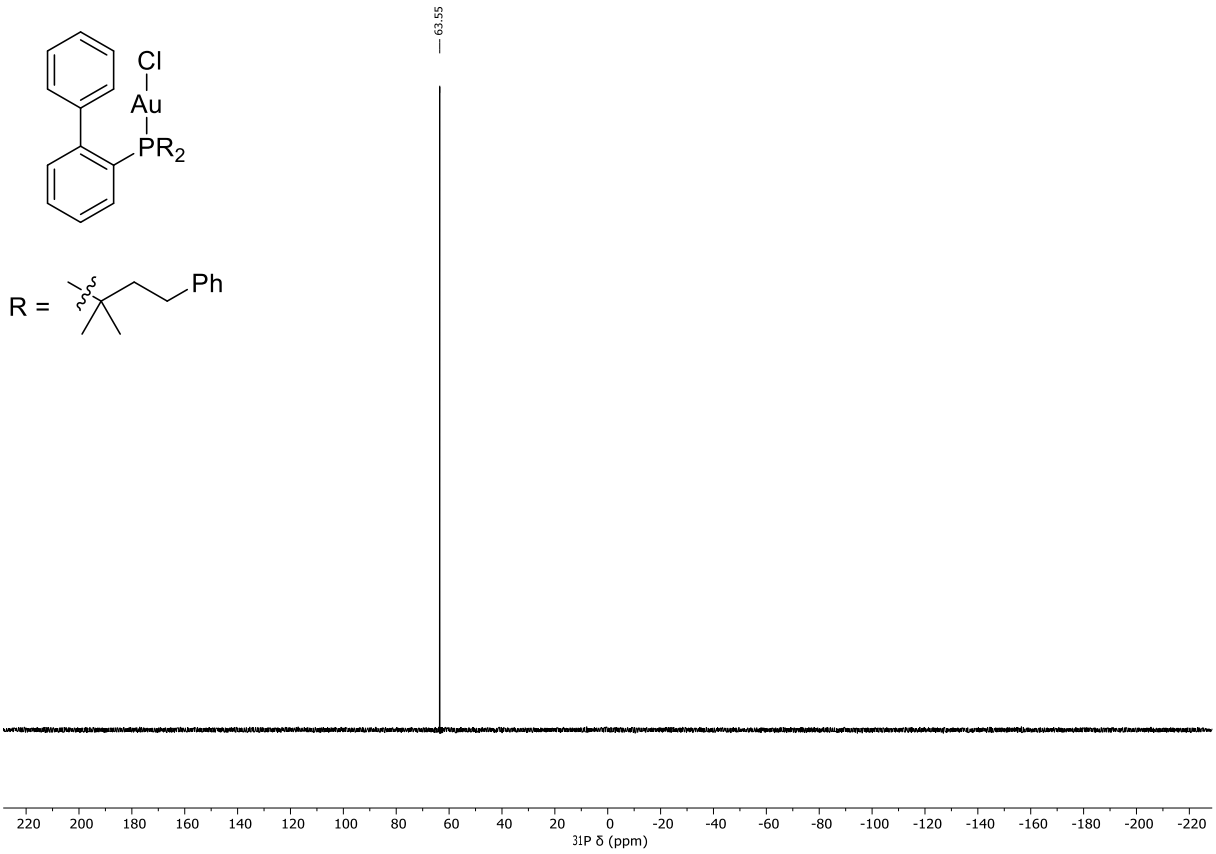
[(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine]gold(I) chloride (5f) - ^{1}H NMR (500 MHz, CDCl$_3$)



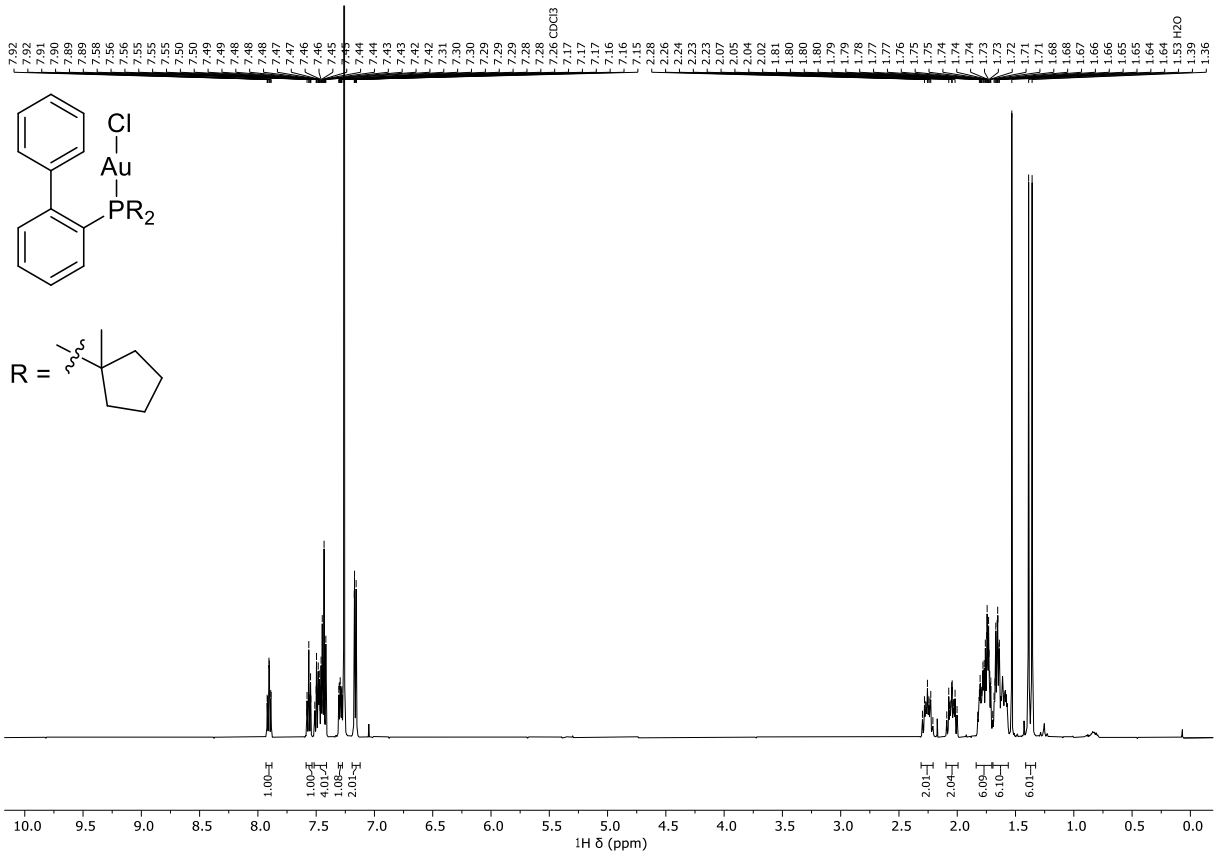
[(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine]gold(I) chloride (5f) - ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



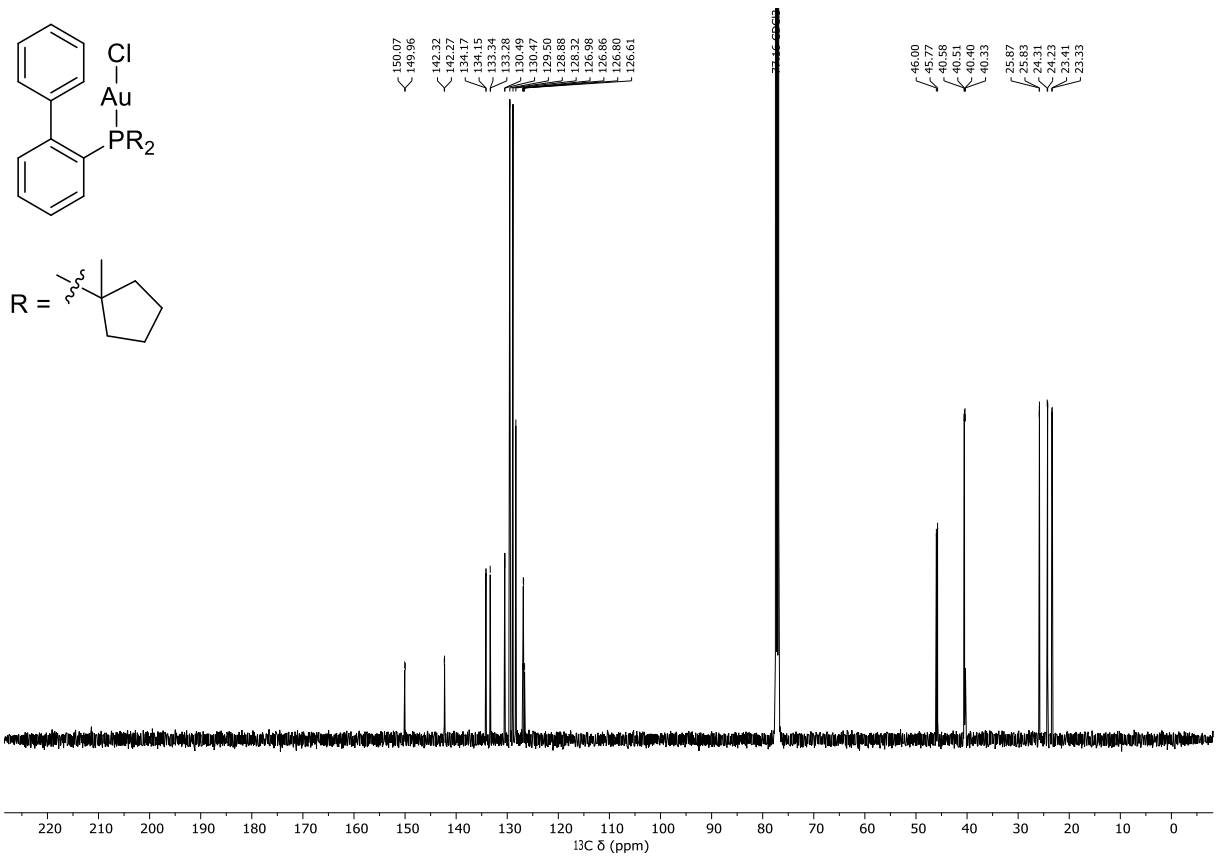
[(2-Biphenyl)di-(2-methyl-4-phenyl-2-butyl)phosphine]gold(I) chloride (5f) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



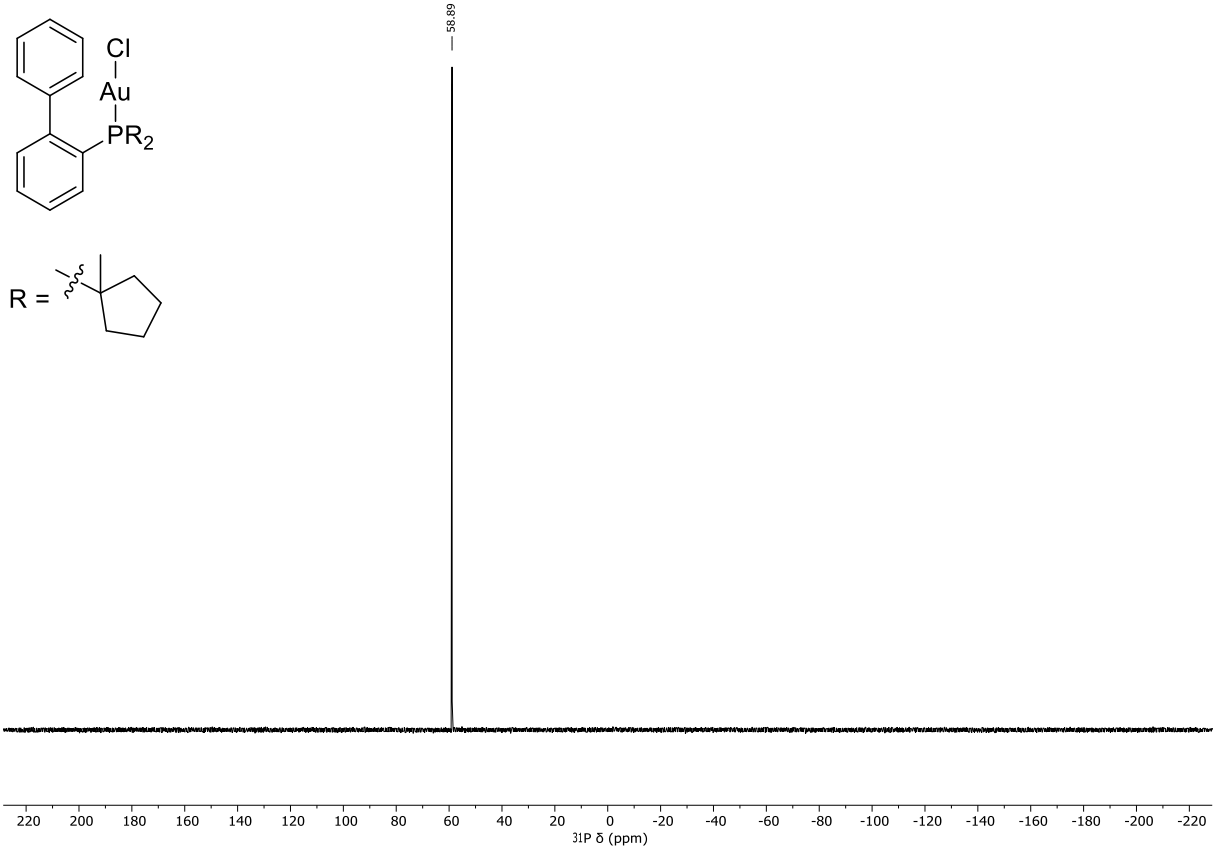
[(2-Biphenyl)di-(1-methylcyclopentyl)phosphine]gold(I) chloride (5h) - ^{1}H NMR (500 MHz, $CDCl_3$)



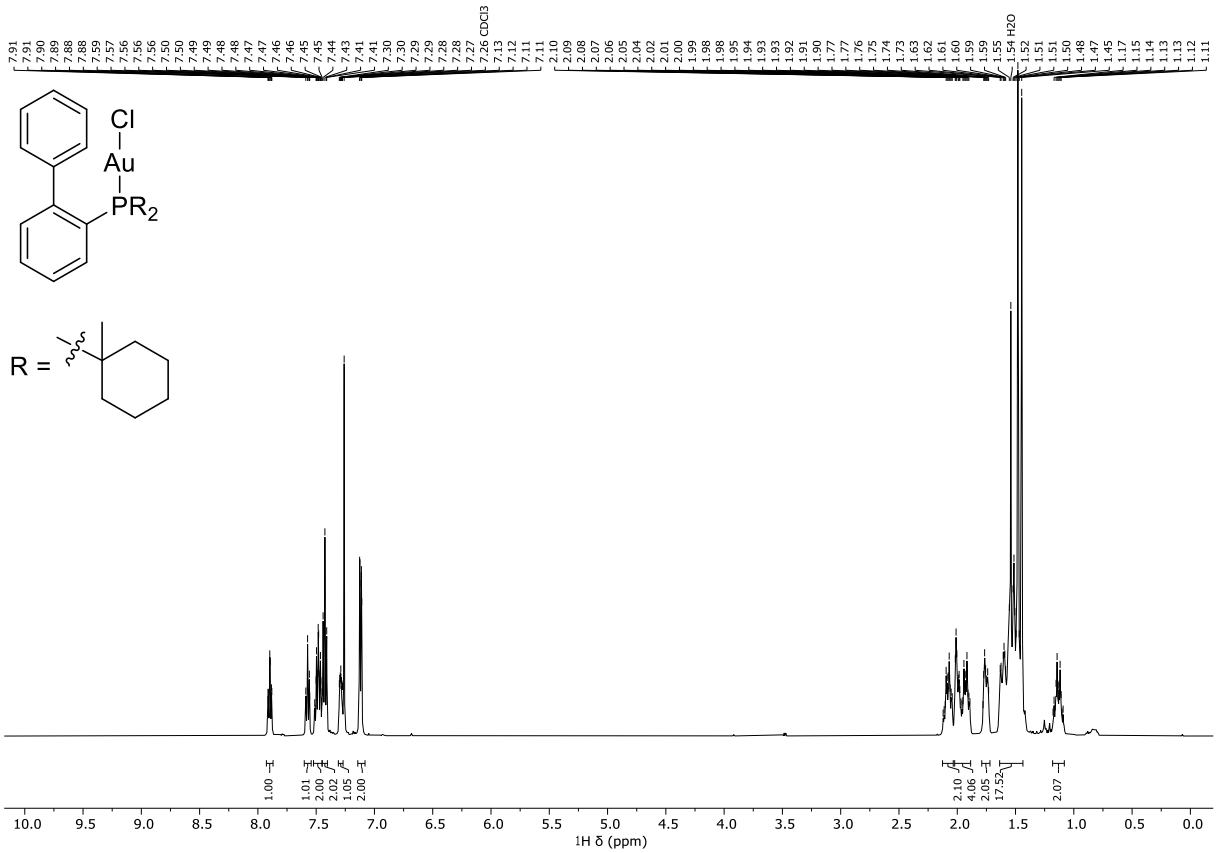
[(2-Biphenyl)di-(1-methylcyclopentyl)phosphine]gold(I) chloride (5h) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



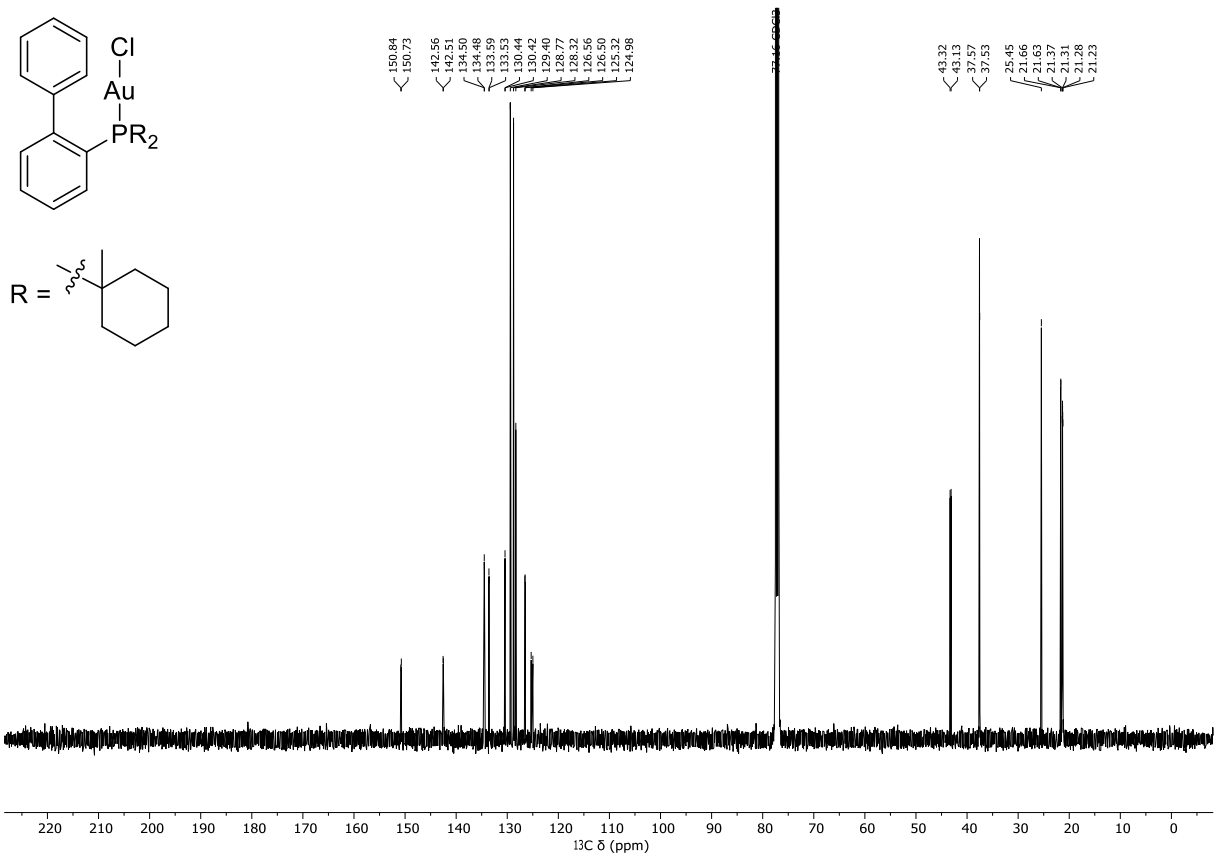
[(2-Biphenyl)di-(1-methylcyclopentyl)phosphine]gold(I) chloride (5h) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



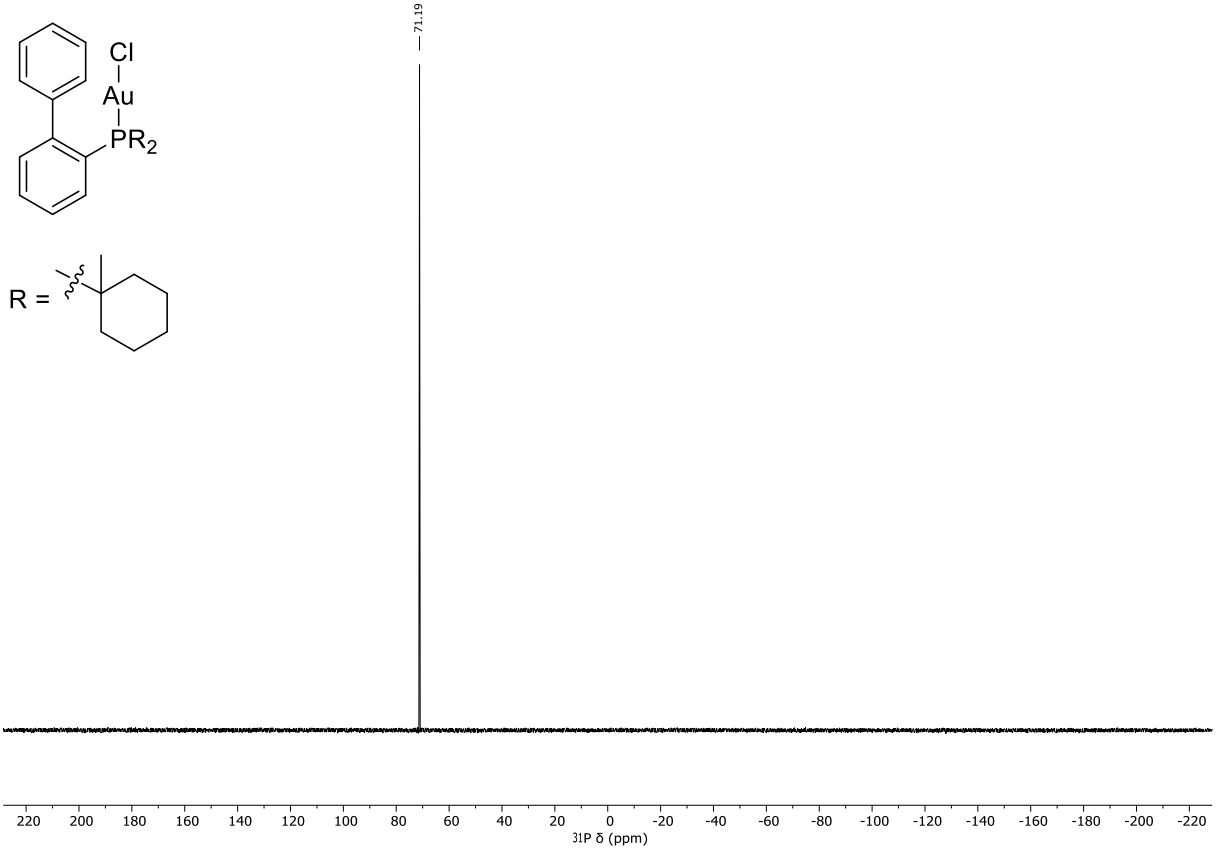
[(2-Biphenyl)di-(1-methylcyclohexyl)phosphine]gold(I) chloride (5i) - ^{1}H NMR (500 MHz, $CDCl_3$)



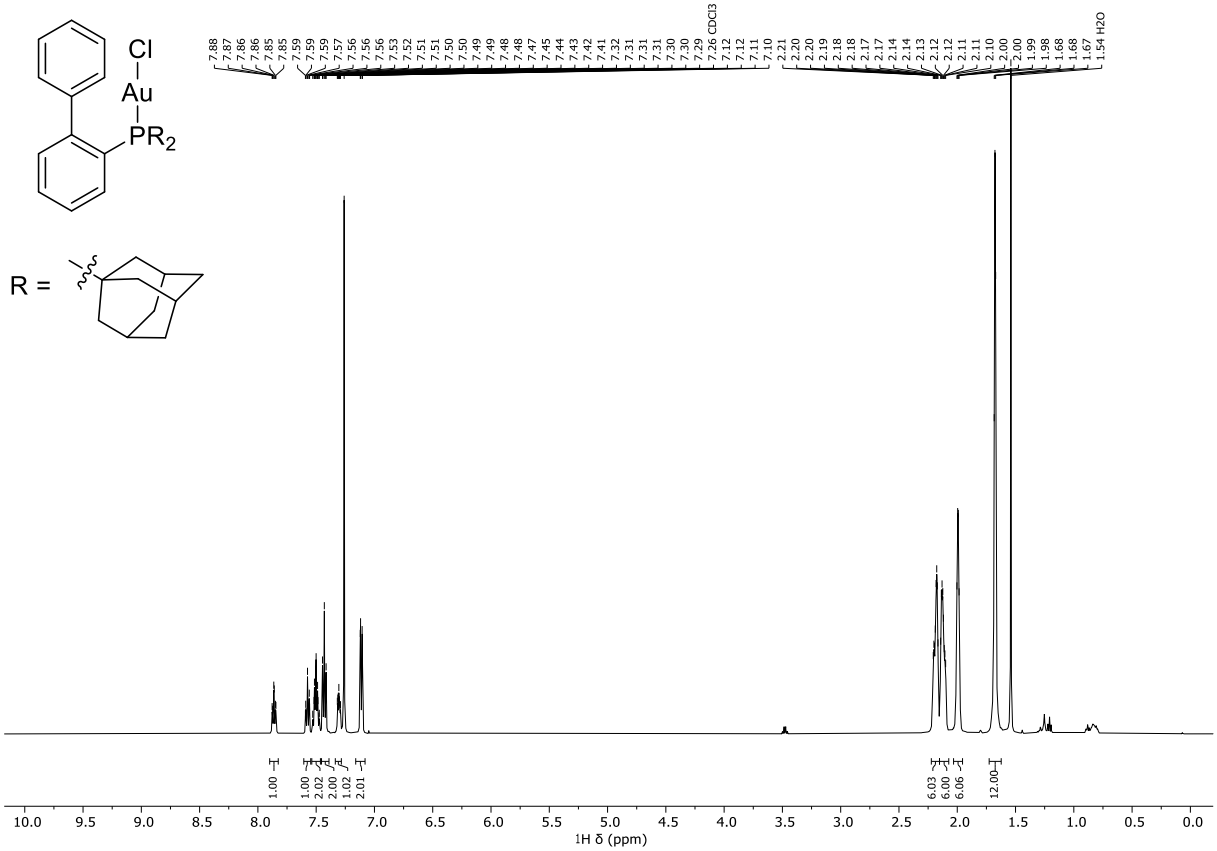
[(2-Biphenyl)di-(1-methylcyclohexyl)phosphine]gold(I) chloride (5i) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



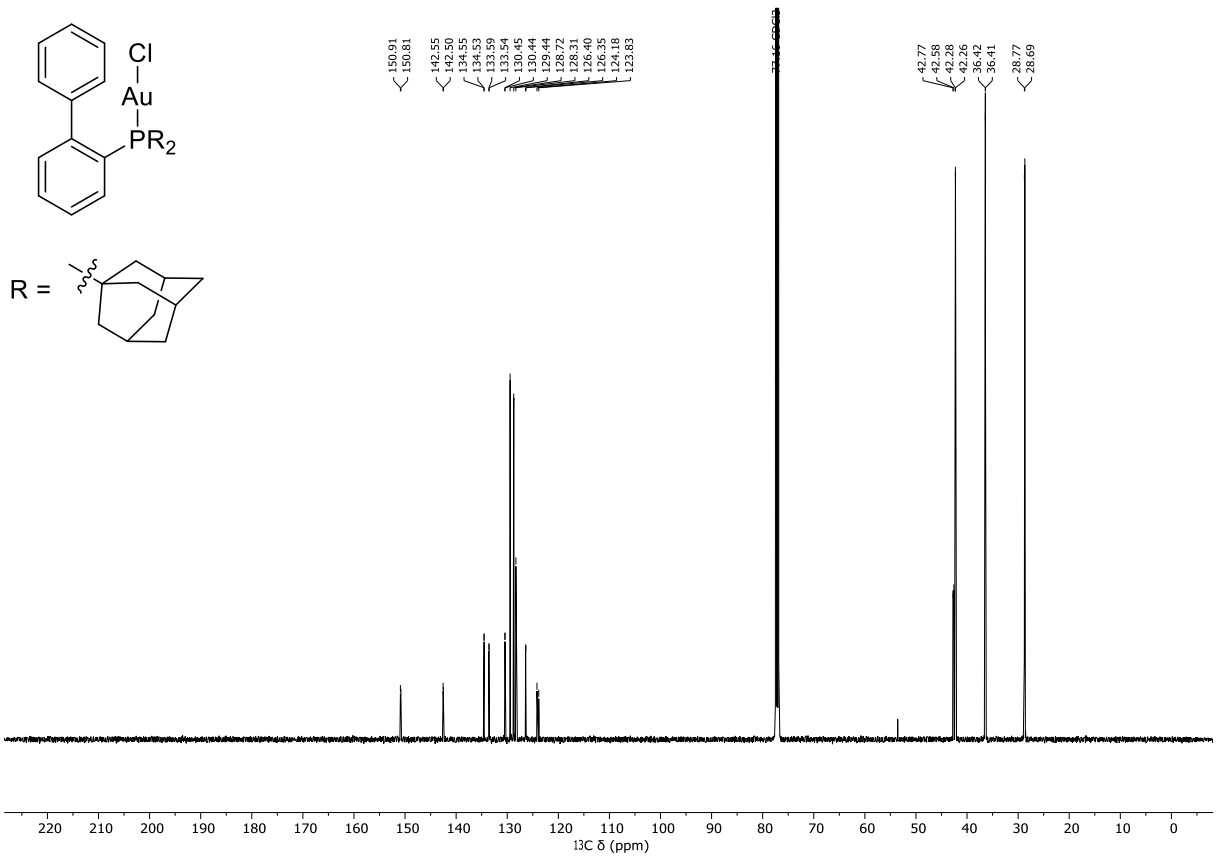
[(2-Biphenyl)di-(1-methylcyclohexyl)phosphine]gold(I) chloride (5i) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



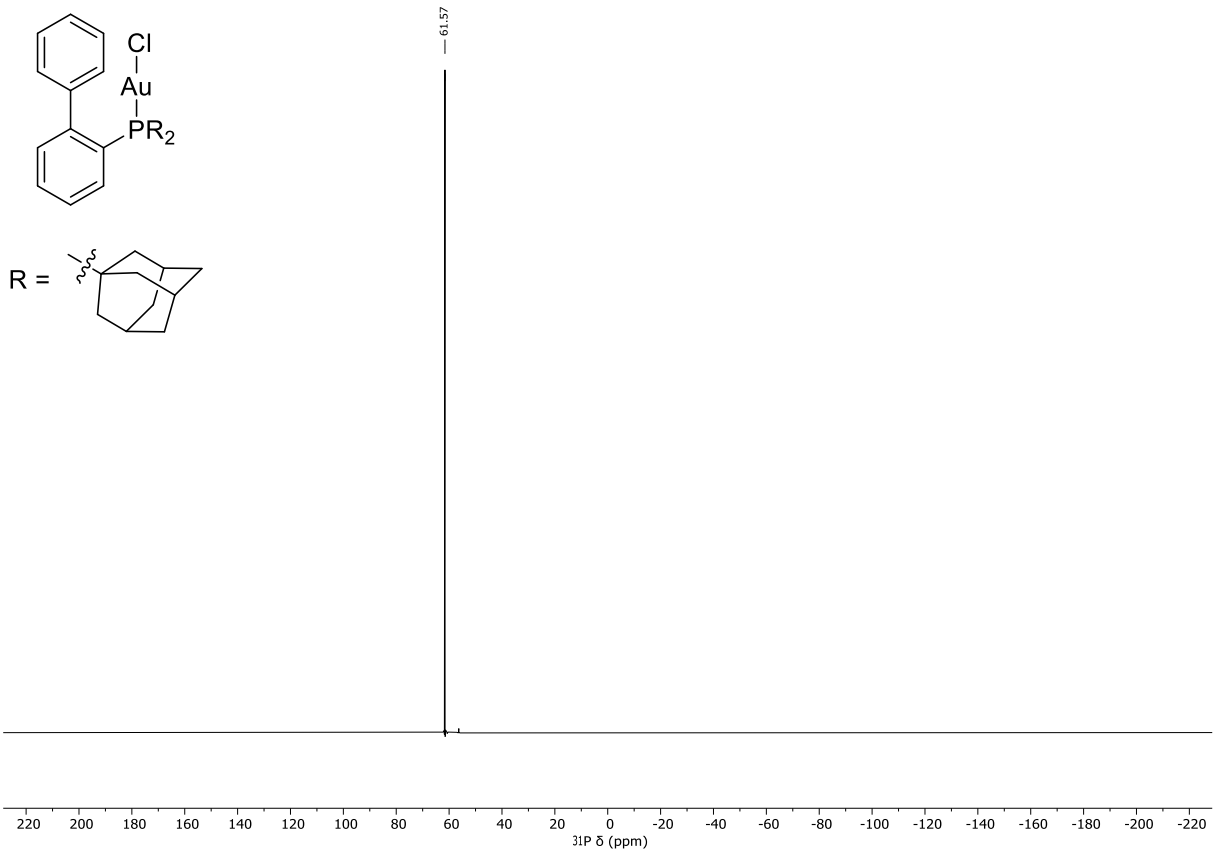
[(2-Biphenyl)di-(1-adamantyl)phosphine]gold(I) chloride (5k) - ^{1}H NMR (500 MHz, $CDCl_3$)



[(2-Biphenyl)di-(1-adamantyl)phosphine]gold(I) chloride (5k) - ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



[(2-Biphenyl)di-(1-adamantyl)phosphine]gold(I) chloride (5k) $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$)



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