Catalyst- and solvent-free hydrophosphination and multicomponent hydrothiophospination of alkenes and alkynes

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Supplementary Information

General

Diphenylphosphine (Aldrich), elemental sulfur, and all the starting alkenes and alkynes were commercially available of the best grade (Aldrich, Acros, Alfa Aesar) and were used without further purification. Infrared analysis was performed with a FT-IR-4100 (ATR) spectrophotometer; wavenumbers are given in cm^{-1}. NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers (300 and 400 MHz for ^{1}H NMR; 75 and 101 MHz for ^{13}C NMR; 122 and 162 MHz for ^{31}P MNR); chemical shifts are given in (δ) parts per million and coupling constants (*J*) in hertz. Mass spectra (EI) were obtained at 70 eV on an Agilent 5973 spectrometer; fragment ions in *m/z* with relative intensities (%) in parentheses. HRMS analyses were carried out on Finnigan MAT95S and Agilent 7200 (Q-TOF) spectrometers. The purity of volatile compounds and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-6890 and Youling 6100 instruments equipped with flame ionization detectors and 30 m capillary columns (0.32 mm diameter, 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{injector}$ = 270 ºC, T_{column} = 60 ºC (3 min) and 60–270 ºC (15 ºC/min); retention times (t_r) are given in min. Thin layer chromatography was carried out on TLC plastic sheets with silica gel 60 F_{254} (Merck). Column and preparative chromatography was performed using silica gel 60 of 40–60 microns and P/UV254, respectively (hexane/EtOAc as eluent). All reactions were performed with new or thoroughly cleaned magnetic bars in order to rule out any catalysis by traces of metals.

Synthesis of deuterated compounds

Deuteriodiphenylphosphine (Ph_2PD) was prepared following a literature procedure,[1] namely: *n*-butyl lithium [1.6 M in hexane, 5.5 mmol (1.1 equiv.)] was added dropwise to a solution of diphenylphosphine (5.0 mmol, 1.0 equiv.) in tetrahydrofuran (5 mL) at 0 °C. After stirring for 1 h at room temperature, 0.2 mL of deuterium oxide were added and stirring was continued for 10 min, followed by the addition of anhydrous magnesium sulfate. The resulting mixture was decanted via cannula and the solvent was removed in vacuo to give deuteriodiphenylphosphine in quantitative yield as a colourless oil.

(Deuterioethynyl)cyclohexane [(D_1)-**4i**] was prepared by stirring ethynylcyclohexane (**4i**) and D_2O, in the presence of copper nanoparticles on carbon, at 70 ºC overnight, followed by standard extractive work-up.[2]

Diphenyl disulfide-catalysed isomerisation of (*Z*)- to (*E*)-alkenes. General procedure.[3]

The *Z* alkene (0.8 equiv.) in THF (2 mL) was heated under reflux for 8 h in the presence of $(PhS)_2$ (0.2 equiv.) and AIBN (0.2 equiv.). The progress of the reaction was monitored by GC

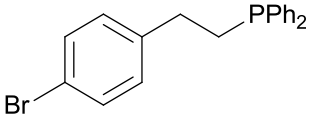
until steady conversion into the *E* isomer. The resulting mixture was diluted with EtOAc (10 mL) and subjected to aqueous workup with water (3×10 mL) and brine (2×10 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The *E/Z* ratio was determined by GC-MS.

General procedure for the hydrophosphination of alkenes 1

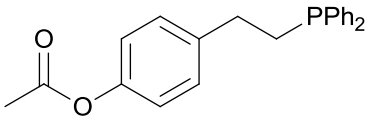
All reactions were performed using tubes in a multi-reactor system under argon. Diphenylphosphine (0.5 mmol, 87 μL) and the alkene (**1**, 0.5 mmol) were stirred during the specified time at room temperature, 70 or 100 ºC (Tables 1–3). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent in vacuo. The reaction crude absorbed on silicagel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure tertiary phosphines **2**. The phosphine oxides **2x**, **2y** and **2z** were purified by preparative chromatography (silica gel, hexane/EtOAc).

Characterisation of compounds 2

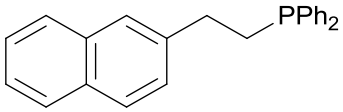
Compounds **2a**,[4] **2b**,[4] **2d**,[4] **2f**,[5] **2g**,[6] **2j**,[7] **2l**,[8] **2m**,[9] **2n**,[4] **2o**,[10] **2p**,[5] **2s**[11] and **2v**[12] were characterised by comparison of their physical and spectroscopic data with those described in the literature. Data for the new compounds or those not fully characterised in the literature, follows:



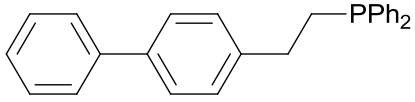
(4-Bromophenethyl)diphenylphosphine (2c): Colourless oil; 150.9 mg (82% yield); t_r 16.59 min; R_f 0.63 (hexane). IR (neat) ν = 3069, 2926, 1489, 1432, 1092, 1014, 803, 735, 694, 646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.31 (m, 12H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.74–2.62 (m, 2H), 2.39–2.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.6 (d, *J* = 13.0 Hz, *C*P), 138.4 (d, *J* = 12.7 Hz, *C*CH_2), 132.8 (d, *J* = 18.5 Hz, *C*HCP), 131.6, 130.1, 128.7 (d, *J* = 23.6 Hz, *C*HCHCP), 128.6, 119.9, 31.8 (d, *J* = 18.1 Hz, CH_2P), 30.2 (d, *J* = 12.9 Hz, *C*H_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –16.2. GC-MS (EI): *m/z* (%) = 370 (34) [M^++2], 369 (56) [M^++1], 368 (35) [M^+], 367 (51), 342 (28), 340 (29), 200 (10), 199 (71), 186 (49), 184 (10), 183 (54), 165 (11), 152 (10), 121 (100), 109 (12), 108 (56), 107 (22), 104 (10), 91 (11), 78 (12), 77 (24), 51 (10). HRMS (EI): *m/z* calcd. for $C_{20}H_{18}BrP$ 368.0329, found 368.0336.



4-[2-(Diphenylphosphanyl)ethyl]phenyl acetate (2e): Colourless oil; 148.0 mg (85% yield); t_r 17.72 min; R_f 0.32 (hexane/EtOAc, 9:1). IR (neat) ν = 3051, 2915, 1760, 1506, 1432, 1367, 1213, 1192, 1164, 1016, 909, 736, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 4H), 7.37–7.28 (m, 6H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 2.75–2.64 (m, 2H), 2.38–2.31 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 148.9, 140.3 (d, *J* = 13.4 Hz, CP), 138.5 (d, *J* = 12.9 Hz, *C*CH_2), 132.8 (d, *J* = 18.5 Hz, *C*HCP), 129.2, 128.7 (d, *J* = 20.8 Hz, *C*HCHCP), 128.6, 121.5, 31.7 (d, *J* = 18.2 Hz, CH_2P), 30.2 (d, *J* = 12.9 Hz, *C*H_2CH_2P), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.9. GC-MS (EI): *m/z* (%) = 349 (13) [M^++1], 348 (61) [M^+], 347 (96), 320 (27), 305 (22), 278 (19), 200 (10), 199 (64), 186 (42), 183 (42), 165 (10), 121 (100), 108 (44), 107 (18), 91 (14), 77 (16). HRMS (EI): *m/z* calcd. for $C_{22}H_{21}O_2P$ 348.1271, found 348.1279.

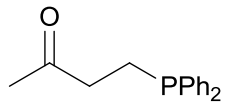


[2-(Naphthalen-2-yl)ethyl]diphenylphosphine (2h): Yellow oil; 154.8 mg (91% yield); t_r 20.90 min; R_f 0.44 (hexane). IR (neat) ν = 3052, 1435, 1178, 1121, 818, 693, 740, 724, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.73 (m, 3H), 7.58 (br s, 1H), 7.49–7.39 (m, 6H), 7.36–7.28 (m, 7H), 2.92–2.82 (m, 2H), 2.47–2.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.2 (d, *J* = 13.3 Hz, CP), 138.6 (d, *J* = 13.0 Hz, *C*CH_2), 133.8, 132.9 (d, *J* = 18.5 Hz, *C*HCP), 132.2, 128.7 (d, *J* = 19.4 Hz, *C*HCHCP), 128.6, 128.2, 127.8, 127.6, 127.2, 126.2, 126.1, 125.4, 32.5 (d, *J* = 17.8 Hz, CH_2P), 30.2 (d, *J* = 13.0 Hz, *C*H_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.7. GC-MS (EI): *m/z* (%) = 341 (15) [M^++1], 340 (72) [M^+], 339 (100), 312 (37), 199 (31), 186 (18), 183 (22), 154 (17), 153 (13), 152 (11), 121 (55), 115 (11), 108 (25). HRMS (EI): *m/z* calcd. for $C_{24}H_{21}O_2P$ 340.1381, found 340.1376.

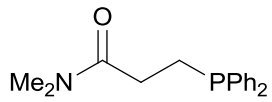


{2-[(1,1'-Biphenyl)-4-yl]ethyl}diphenylphosphine (2i): Colourless oil; 164.8 mg (90% yield); t_r 27.02 min; R_f 0.63 (hexane/EtOAc, 9:1). IR (neat) ν = 3051, 3025, 2925, 1483, 1432, 820, 738, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.45 (m, 2H), 7.43–7.30 (m, 9H), 7.26–7.23 (m, 6H), 7.17–7.13 (m, 2H), 2.72–2.64 (m, 2H), 2.35–2.27 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ

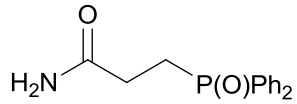
= 141.8 (d, *J* = 13.2 Hz, *C*CH_2), 141.2, 139.1, 138.6 (d, *J* = 13.1 Hz, CP), 132.9 (d, *J* = 18.5 Hz, *C*HCP), 128.9, 128.7 (d, *J* = 19.8 Hz, *C*HCHCP), 128.6, 128.5, 127.3, 127.2, 127.1, 32.0 (d, *J* = 17.9 Hz, CH_2P), 30.3 (d, *J* = 13.0 Hz, *C*H_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.8. GC-MS (EI): *m/z* (%) = 367 (12) [M^++1], 366 (56) [M^+], 365 (100), 339 (12), 338 (48), 199 (40), 186 (29), 183 (30), 180 (19), 166 (11), 165 (25), 152 (13), 121 (66), 108 (30), 77 (12). HRMS (EI): *m/z* calcd. for $C_{26}H_{23}P$ 366.1537, found 366.1547.



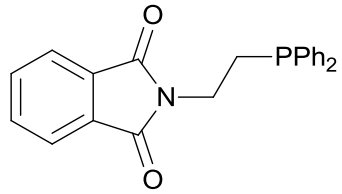
4-(Diphenylphosphanyl)butan-2-one (2k): Colourless oil; 89.6 mg (70% yield); t_r 15.18 min; R_f 0.50 (hexane/EtOAc, 8:2). IR (neat) ν = 3051, 2914, 1714, 1432, 1385, 740, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 4H), 7.36–7.29 (m, 6H), 2.56–2.44 (m, 2H), 2.33–2.24 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.7 (d, *J* = 12.5 Hz, CO), 138.1 (d, *J* = 12.5 Hz, CP), 132.8 (d, *J* = 18.6 Hz, *C*HCP), 128.8 (d, *J* = 22.9 Hz, *C*HCHCP), 128.6, 39.9 (d, *J* = 39.9 Hz, *C*H_2CH_2P), 29.9, 21.4 (d, *J* = 11.2 Hz, CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.6. GC-MS (EI): *m/z* (%) = 256 (56) [M^+], 255 (98), 217 (12), 215 (11), 213 (12), 202 (10), 201 (63), 185 (21), 184 (13), 183 (100), 152 (14), 141 (37), 131 (11), 121 (21), 108 (22), 107 (21). HRMS (EI): *m/z* calcd. for $C_{16}H_{17}OP$ 256.1017, found 256.1007.



3-(Diphenylphosphanyl)-*N*,*N*-dimethylpropanamide (2q): White solid; 99.8 mg (70% yield); m.p. 102.0–106.0 ºC; t_r 16.71 min; R_f 0.32 (hexane/EtOAc, 1:1). IR (neat) ν = 3050, 2918, 1637, 1481, 1430, 1410, 1393, 1267, 1134, 1046, 155, 743, 721, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.42 (m, 4H), 7.34–7.31 (m, 6H), 2.92 (s, 3H), 2.87 (s, 3H), 2.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2 (d, *J* = 14.9 Hz, CO), 138.1 (d, *J* = 12.4 Hz, ArC), 132.7 (d, *J* = 18.5 Hz, ArCH), 128.6 (d, *J* = 26.1 Hz, ArCH), 128.5 (s, ArCH), 37.0 (s, CH_3N), 35.5 (s, CH_3N), 29.7 (d, *J* = 20.4 Hz, CH_2P), 23.1 (d, *J* = 10.4 Hz, *C*H_2CH_2P). ^{31}P NMR (122 MHz, $CDCl_3$): δ = –15.5 ppm. GC-MS (EI): *m/z* (%) = 285 (20) [M^+], 270 (33), 214 (14), 213 (87), 209 (11), 208 (100), 186 (11), 183 (76), 160 (45), 152 (15), 133 (13), 109 (15), 108 (23), 107 (19), 84 (53), 72 (17), 68 (44). HRMS (ES+): *m/z* calcd. for $C_{17}H_{20}NOP$ 285.1283, found 285.1281.

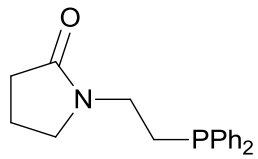


3-(Diphenylphosphoryl)propanamide (2r): White solid; 102.0 mg (75% yield); m.p. 205.4–208.0 ºC; t_r 13.80 min; R_f 0.19 (EtOAc/MeOH, 9:1). IR (KBr) ν = 3313, 3166, 1687, 1433, 1413, 1180, 1119, 751, 694 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 7.86–7.75 (m, 4H), 7.64–7.51 (m, 6H), 2.79–2.66 (m, 2H), 2.53–2.41 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ = 176.3 (d, *J* = 14.9 Hz, CO), 133.6 (d, *J* = 2.8 Hz, ArCH), 132.8 (d, *J* = 100.8 Hz, ArC), 131.9 (d, *J* = 11.9 Hz, ArCH), 130.1 (d, *J* = 107.0 Hz, ArCH), 27.9 (d, *J* = 2.7 Hz, *C*H_2CH_2P), 25.7 (d, *J* = 73.5 Hz, CH_2CH_2P). ^{31}P NMR (122 MHz, CD_3OD): δ = 36.4 ppm. GC-MS (EI): *m/z* (%) = 273 [M^+] (2), 219 (11), 202 (68), 201 (45), 197 (11), 196 (100), 155 (14), 125 (10), 77 (36), 51 (15). HRMS (ES+): *m/z* calcd. for $C_{15}H_{16}NO_2P$ 273.0919, found 273.0923.



***N*-[2-(Diphenylphosphanyl)ethyl]phthalimide (2t)**

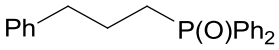
Pale yellow oil; 125.7 mg (70% yield); t_r 22.11 min; R_f 0.62 (hexane/EtOAc, 7:3). IR (neat) ν = 3057, 2911, 1764, 1700, 1432, 1392, 1359, 1315, 1119, 1066, 946, 822, 714, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38–2.44 (m, 2H), 3.80 (dt, *J* = 15.7, 8.5 Hz, 2H), 7.19–7.26 (m, 6H), 7.36–7.41 (m, 4H), 7.58–7.63 (m, 2H), 7.66–7.73 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 27.5 (d, *J* = 14.8 Hz, CH_2P), 35.5 (d, *J* = 23.1 Hz, *C*H_2CH_2P), 123.3, 128.6, 128.8 (d, *J* = 19.2 Hz, *C*HCHCP), 132.8 (d, *J* = 19.0 Hz, *C*HCP), 134.0, 137.5, 137.5 (d, *J* = 12.1 Hz, CP), 168.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –21.5. GC-MS (EI): *m/z* (%) = 360 (25) [M^++1], 359 (100) [M^+], 201 (50), 199 (30), 186 (15), 183 (36), 179 (10), 130 (21), 121 (43), 108 (25), 107 (13), 77 (19). HRMS (EI): *m/z* calcd. for $C_{22}H_{18}NO_2P$ 359.1075, found 359.1072.



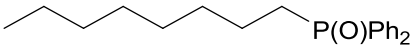
***N*-[2-(Diphenylphosphanyl)ethyl]pyrrolidin-2-one (2u)**

Yellow oil; 115.9 mg (78% yield); t_r 19.57 min; R_f 0.37 (EtOAc). IR (neat) ν = 3050, 2914, 2873, 2360, 2341, 1677, 1432, 1285, 739, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.39 (m, 4H), 7.37–7.28 (m 6H), 3.45–3.39 (m, 2H), 3.34 (t, *J* = 7.0 Hz, 2H), 2.34–2.24 (m, 4H), 1.92–

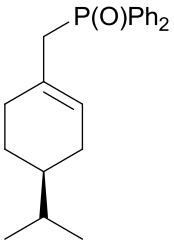
1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.9, 137.9 (d, *J* = 12.2 Hz, CP), 132.8 (d, *J* = 19.0 Hz, *C*HCP), 128.9, 128.7 (d, *J* = 22.4 Hz, *C*HCHCP), 47.6, 40.2 (d, *J* = 22.3 Hz, *C*$H_2$$CH_2$P), 31.0, 26.6 (d, *J* = 14.3 Hz, CH_2P), 17.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –20.7. GC-MS (EI): *m/z* (%) = 297 (40) [M^+], 269 (26), 241 (12), 220 (65), 213 (24), 212 (70), 211 (20), 199 (22), 197 (11), 186 (22), 185 (17), 184 (11), 183 (73), 172 (100), 165 (11), 152 (13), 145 (13), 134 (34), 133 (18), 121 (73), 109 (18), 108 (87), 107 (32), 98 (13), 91 (21), 77 (20), 70 (12), 69 (18), 68 (13), 56 (10). HRMS (EI): *m/z* calcd. for $C_{18}H_{20}NOP$ 297.1283, found 297.1273.



Diphenyl(3-phenylpropyl)phosphine oxide (2x): Colourless oil; 113.6 mg (71% yield); t_r 22.01 min; R_f 0.62 (hexane/EtOAc, 1:1). IR (neat) ν = 3055, 3035, 2928, 2858, 1589, 1490, 1437, 1173, 1119, 978, 745, 720, 616 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.74 (ddd, *J* = 11.6, 8.1, 1.5 Hz, 4H), 7.61–7.52 (m, 6H), 7.30–7.14 (m, 5H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.46–2.37 (m, 2H), 1.90–1.87 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD): δ = 140.9 (s, ArC), 131.8 (d, *J* = 99.7 Hz, ArC), 131.9 (d, *J* = 2.7 Hz, ArCH), 130.7 (d, *J* = 9.7 Hz, ArCH), 128.6 (d, *J* = 11.8 Hz, ArCH), 128.1 (s, ArCH), 128.0 (s, ArCH), 125.8 (s, ArCH), 35.9 (d, *J* = 14.7 Hz, *C*$H_2$$CH_2$P), 27.7 (d, *J* = 72.3 Hz, CH_2P), 23.1 (d, *J* = 3.7 Hz, *C*$H_2$$CH_2$$CH_2$P). ^{31}P NMR (122 MHz, CD_3OD): δ = 37.0 ppm. GC-MS (EI): *m/z* (%) = 320 (7) [M^+], 215 (100), 201 (10), 91 (7), 77 (8). HRMS (ES+): *m/z* calcd. for $C_{21}H_{21}OP$ 320.1330, found 320.1322.



Octyldiphenylphosphine oxide (2y): White solid; 109.9 mg (70% yield); m.p. 54.0–56.0 ºC (hexane/EtOAc); t_r 18.39 min; R_f 0.52 (EtOAc). IR (neat) ν = 3050, 2925, 2854, 1437, 1179, 1118, 746, 720, 693 cm^{-1}. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.80 (ddd, *J* = 11.6, 8.1, 1.5 Hz, 4H), 7.56 (m, 6H), 2.46–2.42 (m, 2H), 1.67–1.03 (m, 12H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CD_3OD): δ = 130.5 (d, *J* = 98.5 Hz, ArC), 130.4 (d, *J* = 2.4 Hz, ArCH), 128.9 (d, *J* = 9.6 Hz, ArCH), 127.1 (d, *J* = 11.7 Hz, ArCH), 29.9 (CH_2), 28.8 (d, *J* = 14.2 Hz, *C*$H_2$$CH_2$P), 27.2 (d, *J* = 3.1 Hz, CH_2), 26.8 (d, *J* = 70.2 Hz, CH_2P), 20.7 (s, CH_2), 19.5 (d, *J* = 4.1 Hz, *C*$H_2$$CH_2$$CH_2$P), 11.5 (s, CH_3). ^{31}P NMR (122 MHz, CD_3OD): δ = 35.4 ppm. GC-MS (EI): *m/z* (%) = 314 (3) [M^+], 257 (10), 229 (11), 216 (55), 215 (100), 202 (60), 201 (34). HRMS (ES+): *m/z* calcd. for $C_{20}H_{27}OP$ 314.1800, found 314.1788.

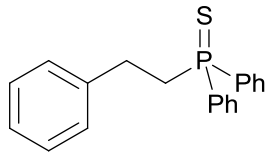


(*S*)-[(4-Isopropylcyclohex-1-en-1-yl)methyl]diphenylphosphine oxide (2z): White solid; 126.8 mg (75% yield); m.p. 143.0–148.0 ºC (hexane/EtOAc); $[\alpha]_D^{26}$ –150.7 (*c* = 0.73, MeOH); t_r 21.98 min; R_f 0.27 (hexane/EtOAc, 1:1). IR (neat) ν = 3048, 2956, 2921, 2851, 1590, 1436, 1187, 1167, 1116, 745, 720, 693 cm^{-1}. ^1H NMR (300 MHz, CD_3OD): δ = 7.83–7.77 (m, 4H), 7.62–7.53 (m, 6H), 5.40 (s, 1H), 3.20 (d, *J* = 13.6 Hz, 2H), 2.04–1.65 (m, 3H), 1.45–1.32 (m, 2H), 1.24–1.12 (m, 3H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, CD_3OD): δ = 134.4 (d, *J* = 98.9 Hz, ArC), 134.1 (d, *J* = 2.4 Hz, ArCH), 134.3 (d, *J* = 98.8 Hz, ArC), 133.0 (d, *J* = 9.5 Hz, ArCH), 132.9 (d, *J* = 9.5 Hz, ArCH), 130.6 (d, *J* = 11.8 Hz, ArCH), 129.9 (d, *J* = 10.0 Hz, C), 129.7 (d, *J* = 10.2 Hz, CH), 41.7 (s, CH), 40.0 (d, *J* = 68.4 Hz, CH_2P), 33.9 (s, CH), 32.8 (d, *J* = 2.5 Hz, CH_2), 31.6 (s, C), 31.1 (d, *J* = 2.5 Hz, CH_2), 28.3 (s, CH_2), 21.1 (s, CH_3), 20.9 (s, CH_3). ^{31}P NMR (122 MHz, CD_3OD): δ = 37.7 ppm. GC-MS (EI): *m/z* (%) = 339 (17) [M^++1], 338 (57) [M^+], 295 (31), 281 (45), 269 (12), 207 (64), 203 (16), 202 (100), 201 (60), 191 (13), 156 (11), 78 (13), 77 (17), 73 (12). HRMS (ES+): *m/z* calcd. for $C_{22}H_{27}OP$ 338.1800, found 338.1789.

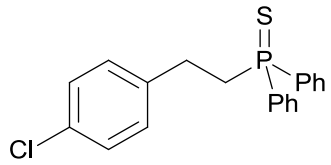
General procedure for the hydrothiophosphination of alkenes 1

All reactions were performed using tubes in a multi-reactor system under air. Diphenylphosphine (0.5 mmol, 87 μL), the alkene (**1**, 0.5 mmol) and elemental sulfur (0.5 mmol, 16.0 mg) were stirred at 70, 100 or 120 ºC overnight (Table 4). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent in vacuo. The reaction crude absorbed on silicagel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure tertiary phosphine sulfides **3**. Compounds **3b**, **3e**, **3x** and **3ac** were purified by preparative chromatography (silica gel, hexane/EtOAc).

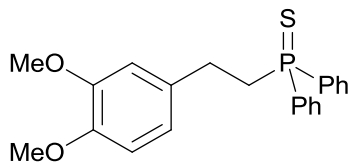
Characterisation of compounds 3



Phenethyldiphenylphosphine sulfide (3a):[13] White solid; 156.2 mg (97% yield); m.p. 105.4–106.4 ºC; t_r 19.36 min; R_f 0.71 (hexane/EtOAc, 7:3). IR (neat) ν = 3051, 2928, 1520, 1435, 1104, 757, 711, 620, 610 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.91 (m, 4H), 7.52–7.41 (m, 6H), 7.29–7.22 (m, 2H), 7.20–7.13 (m, 3H), 2.97–2.86 (m, 2H), 2.81–2.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0 (d, *J* = 16.9 Hz, ArC), 132.7 (d, *J* = 80.0 Hz, ArC), 131.6 (d, *J* = 2.7 Hz, ArCH), 131.2 (d, *J* = 10.1 Hz, ArCH), 128.8 (ArCH), 128.7 (ArCH), 128.3 (ArCH), 126.5 (ArCH), 34.7 (d, *J* = 54.7 Hz, CH_2P), 28.5 (d, *J* = 1.4 Hz, CH_2CH_2P). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 41.9 ppm. GC-MS (EI): *m/z* (%) = 322 (17) [M^+], 219 (14), 218 (100), 185 (24), 183 (26), 140 (22). HRMS (ES+): *m/z* calcd. for $C_{20}H_{20}PS$ 322.0945, $C_{20}H_{20}PS$ 323.1023 [M^++H]; found 323.1029.

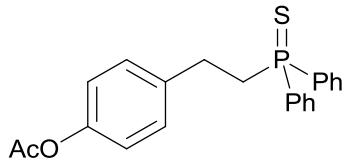


(4-Chlorophenethyl)diphenylphosphine sulfide (3b): Pale yellow oil; 128.2 mg (72% yield); t_r 27.92 min; R_f 0.60 (hexane/EtOAc, 7:3). IR (neat) ν = 3065, 3035, 2928, 2838, 1490, 1436, 1407, 1307, 1071, 1013, 935, 805, 737, 704, 690, 607 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51 (ddd, *J* = 12.9, 7.9, 1.6 Hz, 4H), 7.56–7.36 (m, 6H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.10–6.90 (m, 2H), 2.95–2.80 (m, 2H), 2.79–2.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.2 (d, *J* = 16.4 Hz ArC), 132.5 (d, *J* = 64.4 Hz, ArC), 132.0 (s, ArCH), 131.6 (d, *J* = 2.9 Hz, ArCH), 128.7 (s, ArCH), 130.5 (d, *J* = 10.2 Hz, ArCH), 129.6 (s, ArCH), 128.8 (d, *J* = 11.3 Hz, ArCH), 35.8 (d, *J* = 54.8 Hz, CH_2P), 27.9 (d, *J* = 1 Hz, CH_2). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 41.8 ppm. GC-MS (EI): *m/z* (%) = 356 (7) [M^+], 219 (14), 218 (100), 185 (25), 183 (31), 140 (27), 139 (10). HRMS (ES+): *m/z* calcd. for $C_{20}H_{18}ClPS$ 356.0555, found 356.0571.

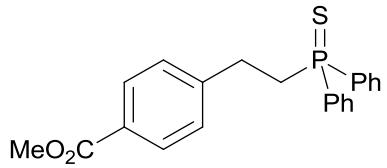


(3,4-Dimethoxyphenethyl)diphenylphosphine sulfide (3aa): Pale yellow solid; 166.2 mg (87% yield); m.p. 102.4–103.8 ºC; t_r 27.58 min; R_f 0.46 (hexane/EtOAc, 7:3). IR (neat) ν = 3050, 2991,

1514, 1467, 1433, 1258, 1236, 1155, 1137, 1102, 1024, 779, 751, 742, 697, 602 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.80 (m, 4H), 7.50–7.41 (m, 6H), 6.77–6.65 (m, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 2.94–2.85 (m, 2H), 2.79–2.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.0 (ArC), 147.6 (ArC), 133.4 (d, *J* = 16.4 Hz, ArC), 132.7 (d, *J* = 79.9 Hz, ArC), 131.6 (d, *J* = 2.6 Hz, ArCH), 131.1 (d, *J* = 10.1 Hz, ArCH), 128.7 (d, *J* = 12.1 Hz, ArCH), 120.1 (ArCH), 111.7 (ArCH), 111.4 (ArCH), 56.0 (CH_3), 55.9 (CH_3), 34.8 (d, *J* = 54.2 Hz, CH_2P), 28.0 (CH_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.8 ppm. GC-MS (EI): *m/z* (%) = 382 (8) [M^+], 218 (18), 185 (10), 183 (14), 165 (14), 164 (100), 140 (11). HRMS (ESI): *m/z* calcd. for $C_{22}H_{23}O_2PS$ 382.1145, $C_{22}H_{24}O_2PS$ 383.1235 [M^++H]; found 383.1238.

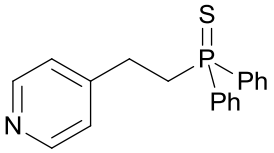


4-[2-(Diphenylphosphorothioyl)ethyl]phenyl acetate (3e): Yellow semi-solid; 123.5 mg (65% yield); t_r 35.63 min; R_f 0.35 (hexane/EtOAc, 7:3). IR (neat) ν = 3052, 2961, 2919, 2849, 1754, 1507, 1436, 1367, 1259, 1192, 1164, 1100, 1013, 909, 808, 799, 738, 690, 610 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (ddd, *J* = 12.9, 7.8, 1.7 Hz, 4H), 7.49–7.48 (m, 6H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.96–2.86 (m, 2H), 2.78–2.69 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.7 (s, CO), 149.2 (s, ArC), 138.6 (d, *J* = 16.8 Hz ArC), 132.6 (d, *J* = 80.0 Hz, ArC), 131.7 (d, *J* = 2.9 Hz, ArCH), 131.2 (d, *J* = 10.2 Hz, ArCH), 129.3 (s. ArCH), 128.8 (d, *J* = 12 Hz, ArCH), 121.8 (s, ArCH), 34.6 (d, *J* = 54.9 Hz, CH_2P), 27.9 (d, *J* = 1.3 Hz, CH_2), 14.3 (s, CH_3). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 41.8 ppm. GC-MS (EI): *m/z* (%) = 380 (15) [M^+], 219 (18), 218 (100), 217 (11), 185 (26), 183 (30), 140 (25), 139 (11). HRMS (ES+): *m/z* calcd. for $C_{22}H_{21}O_2PS$ 380.1000, found 380.0992.

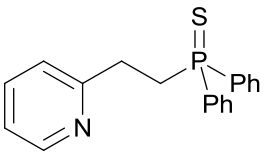


Methyl 4-[2-(diphenylphosphorothioyl)ethyl]benzoate (3ab): Pale yellow semi solid; 184.3 mg (97% yield); t_r 26.49 min; R_f 0.60 (hexane/EtOAc, 7:3). IR (neat) ν = 3055, 2927, 1752, 1507, 1435, 1367, 1192, 1164, 1102, 909, 736, 710, 690, 609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.80 (m, 4H), 7.53–7.42 (m, 6H), 7.19–7.13 (m, 2H), 6.98–6.93 (m, 2H), 2.97–2.87 (m, 2H), 2.79–2.69 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7 (CO), 149.2 (ArC), 138.6 (d, *J* = 16.9 Hz, ArC), 132.6 (d, *J* = 80.2 Hz, ArC), 131.7 (d, *J* = 2.6 Hz, ArCH),

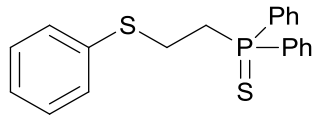
131.2 (d, *J* = 10.1 Hz, ArCH), 129.3 (ArCH), 128.2 (d, *J* = 12.0 Hz, ArCH), 121.8 (ArCH), 34.6 (d, *J* = 54.7 Hz, CH_2P), 27.9 (*C*H_2CH_2P), 21.2 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.8 ppm. GC-MS (EI): *m/z* (%) = 380 (9) [M^+], 219 (13), 218 (100), 217 (11), 185 (28), 183 (28), 140 (29), 139 (12). HRMS (ESI): *m/z* calcd. for $C_{22}H_{21}O_2PS$ 380.1000, $C_{22}H_{22}O_2PS$ 381.1078 [M^++H]; found 381.1068.



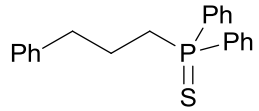
Diphenyl[2-(pyridin-4-yl)ethyl]phosphine sulfide (3f): Pale brown solid; 145.4 mg (90% yield); m.p. 86.2–87.7 ºC; t_r 19.36 min; R_f 0.43 (hexane/EtOAc, 2:8). IR (neat) ν = 3035, 2927, 1598, 1437, 1414, 1103, 993, 937, 804, 763, 741, 703, 693, 620, 611 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.49–8.41 (m, 2H), 7.90–7.80 (m, 4H), 7.56–7.42 (m, 6H), 7.12–7.06 (m, 2H), 3.00–2.89 (m, 2H), 2.80–2.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.9 (ArCH), 149.8 (ArC), 132.6 (d, *J* = 81.5 Hz, ArC), 131.8 (d, *J* = 2.9 Hz, ArCH), 131.1 (d, *J* = 10.2 Hz, ArCH), 128.8 (d, *J* = 12.1 Hz, ArCH), 123.7 (ArCH), 33.4 (d, *J* = 55.7 Hz, CH_2P), 27.9 (*C*H_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 41.9 ppm. GC-MS (EI): *m/z* (%) = 323 (4) [M^+], 218 (28), 185 (22), 183 (29), 140 (21), 139 (14), 107 (16), 106 (100), 77 (10). HRMS (ESI): *m/z* calcd. for $C_{19}H_{18}NPS$ 323.0898, $C_{19}H_{19}NPS$ 324.0976 [M^++H]; found 324.0979.



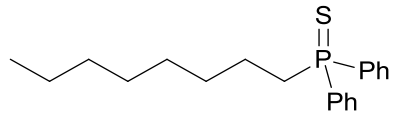
Diphenyl[2-(pyridin-2-yl)ethyl]phosphine sulfide (3g): Pale brown solid; 153.4 mg (95% yield); m.p. 100.5–103.0 ºC; t_r 18.18 min; R_f 0.70 (EtOAc). IR (neat) ν = 3055, 2917, 2858, 1589, 1436, 1102, 998, 939, 762, 752, 734, 710, 690, 622, 610 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51–8.46 (m, 1H), 7.93–7.82 (m, 4H), 7.56–7.39 (m, 7H), 7.17–7.11 (m, 1H), 7.10–7.05 (m, 1H), 3.19–3.10 (m, 2H), 3.03–2.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.1 (d, *J* = 16.1 Hz, ArC), 149.4 (ArCH), 136.5 (ArCH), 132.7 (d, *J* = 80.1 Hz, ArC), 131.6 (d, *J* = 2.7 Hz, ArCH), 131.2 (d, *J* = 10.1 Hz, ArCH), 128.7 (d, *J* = 12.1 Hz, ArCH), 123.4 (ArCH), 121.6 (ArCH), 31.9 (d, *J* = 56.7 Hz, CH_2P), 30.7 (*C*H_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.7 ppm. GC-MS (EI): *m/z* (%) = 323 (1) [M^+], 183 (11), 107 (11), 106 (100). HRMS (ESI): *m/z* calcd. for $C_{19}H_{18}NPS$ 323.0898, $C_{19}H_{19}NPS$ 324.0976 [M^++H]; found 324.0985.



Diphenyl[2-(phenylthio)ethyl]phosphine sulfide (3v):[14] Pale yellow oil; 141.6 mg (80% yield); t_r 22.49 min; R_f 0.69 (hexane/EtOAc, 7:3). IR (neat) ν = 3050, 1574, 1479, 1435, 1103, 733, 708, 687, 620, 609 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.72 (m, 4H), 7.53–7.42 (m, 8H), 7.28–7.24 (m, 2H), 7.22–7.17 (m, 1H), 3.20–3.10 (m, 2H), 2.78–2.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.0 (ArC), 132.3 (d, *J* = 80.2 Hz, ArC), 131.8 (d, *J* = 3.0 Hz, ArCH), 131.1 (d, *J* = 10.3 Hz, ArCH), 129.6 (ArCH), 129.3 (ArCH), 128.9 (d, *J* = 12.2 Hz, ArCH), 126.6 (ArCH), 32.7 (d, *J* = 51.2 Hz, CH_2P), 26.8 (CH_2CH_2P). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 40.5 ppm. GC-MS (EI): *m/z* (%) = 357 (21) [M^+], 219 (15), 218 (100), 217 (14), 185 (31), 183 (36), 140 (31), 139 (28), 109 (15), 107 (10), 77 (14), 63 (11). HRMS (ESI): *m/z* calcd. for $C_{20}H_{19}PS$ 354.0666, $C_{20}H_{20}PS$ 355.0744 [M^++H]; found 355.0754.

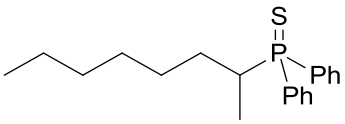


Diphenyl(3-phenylpropyl)phosphine sulfide (3x): Orange oil; 112.6 mg (67% yield); t_r 24.19 min; R_f 0.57 (hexane/EtOAc, 7:3). IR (neat) ν = 3045, 3026, 2918, 2848, 1494, 1437, 1118, 906, 723, 683 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.73 (ddd, *J* = 12.8, 8.0, 1.5 Hz, 4H), 7.46–7.28 (m, 6H), 7.24–7.12 (m, 5H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.44–2.23 (m, 2H), 2.01–1.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8 (s, ArC), 132.8 (d, *J* = 80.0 Hz, ArC), 131.4 (d, *J* = 2.5 Hz, ArCH), 131.0 (d, *J* = 10.1 Hz, ArCH), 128.6 (d, *J* =12.2 Hz, ArCH), 128.5 (s, ArCH), 128.4 (s, ArCH), 126.1 (s, ArCH), 36.3 (d, *J* = 16.7 Hz, CH_2CH_2P), 31.7 (d, *J* = 74.8 Hz, CH_2P), 23.7 (d, *J* = 1.7 Hz, $CH_2CH_2CH_2P$). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 42.6 ppm. GC-MS (EI): *m/z* (%) = 336 (19) [M^+], 231 (10), 219 (14), 218 (100), 217 (12), 199 (23), 185 (16), 183 (24), 140 (14). HRMS (ES+): *m/z* calcd. for $C_{21}H_{21}PS$ 336.1102, found 336.1097.

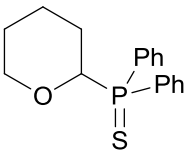


Octyldiphenylphosphine sulfide (3y): Yellow semi solid; 74.3 mg (45% yield); t_r 16.17 min; R_f 0.71 (hexane/EtOAc, 9:1). IR (neat) ν = 3042, 2923, 2853, 1550, 1435, 1102, 739, 690, 621, 610 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.78 (m, 4H), 7.51–7.41 (m, 6H), 2.48–2.39 (m, 2H), 1.67–1.57 (m, 2H), 1.42–1.33 (m, 2H), 1.29–1.17 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 133.2 (d, *J* = 79.5 Hz, ArC), 131.5 (d, *J* = 2.6 Hz, ArCH), 131.2 (d,

J = 10.0 Hz, ArCH), 128.7 (d, *J* = 11.8 Hz, ArCH), 32.7 (d, *J* = 56.4 Hz, CH_2P), 31.9, 30.8, 30.7, 29.2, 22.7 (5 × CH_2), 22.3 (d, *J* = 2.5 Hz, *C*H_2CH_2P), 14.2 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.7 ppm. GC-MS (EI): *m/z* (%) = 330 (6) [M^+], 219 (15), 218 (100), 217 (13), 185 (17), 183 (20), 140 (18), 139 (13). HRMS (ESI): *m/z* calcd. for $C_{20}H_{27}PS$ 330.1571, $C_{20}H_{28}PS$ 331.1649 [M^++H]; found 331.1659.



Octan-2-yldiphenylphosphine sulfide (3y'): Yellow semi solid; 90.7 mg (55% yield); t_r 16.51 min; R_f 0.79 (hexane/EtOAc, 9:1). IR (neat) ν = 3025, 2957, 2927, 2858, 1539, 1435, 1095, 716, 688, 652 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.90 (m, 4H), 7.52–7.41 (m, 6H), 3.58–3.45 (m, 1H), 1.67–1.48 (m, 2H), 1.35–1.13 (m, 8H), 1.28 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 135.4 (d, *J* = 84.9 Hz, ArC), 131.8 (dd, *J* = 3.1, 1.3 Hz, ArCH), 131.6 (dd, *J* = 11.2, 6.7 Hz, ArCH), 128.6 (dd, *J* = 13.2, 1.1 Hz, ArCH), 44.2 (d, *J* = 1.3 Hz, CHP), 38.3 (d, *J* = 5.3 Hz, CH_2), 31.8, 29.1, 26.6 (3 × CH_2), 23.1 (d, *J* = 5.3 Hz, CH_3), 22.7 (CH_2), 14.2 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 61.8 ppm. GC-MS (EI): *m/z* (%) = 330 (1) [M^+], 252 (10), 251 (38), 250 (52), 219 (18), 218 (87), 217 (100), 185 (25), 183 (35), 140 (22), 139 (50), 77 (10), 63 (12). HRMS (ESI): *m/z* calcd. for $C_{20}H_{27}PS$ 330.1571, $C_{20}H_{28}PS_2$ 331.1649 [M^++H]; found 331.1647.



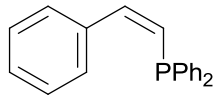
Diphenyl(tetrahydro-2*H*-pyran-2-yl)phosphine sulfide (3ac): White solid; 90.6 mg (60% yield); m.p. 148.0–151.0 ºC (hexane/EtOAc); t_r 17.85 min; R_f 0.70 (hexane/EtOAc, 7:3). IR (neat) ν = 3046, 2947, 2901, 2861, 1437, 1313, 1105, 1098, 1080, 1037, 757, 746, 708, 692, 646 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (ddd, *J* =12.5, 8.1, 1.5 Hz, 2H), 7.85 (ddd, *J* =12.5, 8.1, 1.5 Hz, 2H), 7.51–7.41 (m, 6H), 4.34–4.29 (m, 1H), 4.09–4.06 (m, 1H), 3.51–3.45 (m, 1H), 2.16–2.11 (m, 1H), 1.93–1.90 (m, 1H), 1.56–1.53 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.1 (d, *J* = 9.7 Hz, ArCH), 132.2 (d, *J* = 78.4 Hz, ArC), 131.7 (d, *J* = 9.7 Hz, ArCH), 129.2 (d, *J* = 78.4 Hz, ArC), 128.4 (d, *J* = 12.0 Hz, ArCH), 128.1 (d, *J* = 12.0 Hz, ArCH), 79.8 (d, *J* = 74.7 Hz, CHP), 70.2 (d, *J* = 10.6 Hz, CH_2O), 25.5 (s, CH_2), 24.5 (s, CH_2), 23.4 (d, *J* = 13.2 Hz, CH_2). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 43.2 ppm. GC-MS (EI): *m/z* (%) = 302 (8) [M^+], 219 (17), 218

(100), 186 (16), 185 (18), 183 (26), 140 (12), 139 (17), 107 (12), 85 (80), 67 (15), 57 (14), 55 (14). HRMS (ES+): *m/z* calcd. for $C_{17}H_{19}OPS$ 302.0894, found 302.0887.

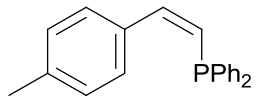
General procedure for the hydrophosphination of alkynes 4

All reactions were performed using tubes in a multi-reactor system under argon. Diphenylphosphine (0.5 mmol, 87 μL) and the alkyne (**4**, 0.5 mmol) were stirred at 70 ºC overnight (Table 5). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent in vacuo. The reaction crude absorbed on silicagel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure alkenyl phosphines **5**.

Characterisation of compounds 5

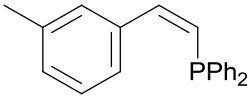


(*Z*)-Diphenyl(styryl)phosphine (5a):[15] White solid; 113.8 mg (79% yield); m.p. 79.5–81.0 ºC; t_r 12.33 min; R_f 0.49 (hexane). IR (KBr) ν = 3068, 3043, 3027, 1593, 1560, 1491, 1474, 780, 739, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.40 (m, 6H), 7.37–7.24 (m, 10H), 6.46 (dd, *J* = 12.7, 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.2 (d, *J* = 19.1 Hz, *C*H=CHP), 139.5 (d, *J* = 9.6 Hz, ArCP), 137.6 (d, *J* = 2.3 Hz, ArC), 132.9 (d, *J* = 18.9 Hz, ArCH), 129.6 (d, *J* = 17.0 Hz, CH=*C*HP), 129.5 (ArCH), 128.7 (ArCH), 128.6 (ArCH), 128.2 (ArCH). ^{31}P NMR (121 MHz, $CDCl_3$): δ = –24.8 ppm. GC-MS (EI): *m/z* (%) = 288 [M^+] (68), 287 (100), 183 (16), 179 (13), 178 (21), 167 (16), 133 (16), 108 (15), 107 (15). HRMS (ES+): *m/z* calcd. for $C_{20}H_{17}P$ 288.1068, found 288.1071.

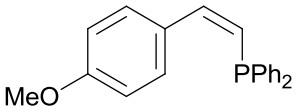


(*Z*)-(4-Methylstyryl)diphenylphosphine (5b): White solid; 110.2 mg (73% yield); m.p. 86.2–90.2 ºC; t_r 15.00 min; R_f 0.74 (hexane/EtOAc, 9.5:0.5). IR (neat) ν = 3064, 2970, 1475, 1422, 790, 733, 690, 682, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.39 (m, 6H), 7.34–7.29 (m, 7H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.38 (dd, *J* = 12.6, 3.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.2 (d, *J* = 19.3 Hz, *C*H=CHP), 139.6 (d, *J* = 9.5 Hz, ArC), 138.2 (ArC), 134.3 (ArC), 132.8 (d, *J* = 18.9 Hz, ArCH), 129.6 (d, *J* = 8.5 Hz, ArCH), 128.9 (ArCH), 128.6 (d, *J* = 6.7 Hz, ArCH), 128.5 (ArCH), 128.4 (d, *J* = 15.6 Hz, CH=*C*HP), 21.4 (CH_3). ^{31}P NMR (162

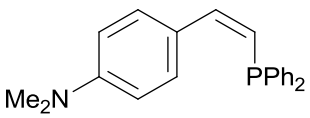
MHz, $CDCl_3$): δ = –24.8 ppm. GC-MS (EI): *m/z* (%) = 303 [M^++1] (15), 302 (75) [M^+], 301 (100), 178 (10). HRMS (ES+): *m/z* calcd. for $C_{21}H_{19}P$ 302.1224, $C_{21}H_{20}P$ 303.1303 [M^++H]; found 303.1302.



(*Z*)-(3-Methylstyryl)diphenylphosphine (5c): White solid; 132.8 mg (88% yield); m.p. 59.7–61.2 ºC; t_r 14.84 min; R_f 0.74 (hexane/EtOAc, 9.5:0.5). IR (neat) ν = 3065, 2977, 1599, 1476, 1432, 799, 738, 693, 683, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.42 (m, 4H), 7.36–7.28 (m, 9H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.44 (dd, *J* = 12.7, 2.6 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.2 (d, *J* = 18.9 Hz, *C*H=CHP), 139.6 (d, *J* = 9.7 Hz, ArC), 137.7 (ArC), 136.9 (d, *J* = 2.3 Hz, ArC), 132.9 (d, *J* = 19.0 Hz, ArCH), 130.5 (d, *J* = 7.4 Hz, ArCH), 129.4 (d, *J* = 16.0 Hz, CH=*C*HP), 128.9 (ArCH), 128.7 (d, *J* = 6.8 Hz, ArCH), 128.6 (ArCH), 128.1 (ArCH), 126.7 (d, *J* = 8.9 Hz, ArCH), 21.6 (CH_3) . ^{31}P NMR (162 MHz, $CDCl_3$): δ = –24.5 ppm. GC-MS (EI): *m/z* (%) = 302 (65) [M^+], 303 (12), 301 (100). HRMS (ES+): *m/z* calcd. for $C_{21}H_{19}P$ 302.1224, $C_{21}H_{20}P$ 303.1303 [M^++H]; found 303.1310.

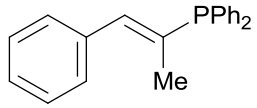


(*Z*)-(4-Methoxystyryl)diphenylphosphine (5d): White solid; 136.7 mg (86% yield); m.p. 137.3–138.9 ºC; t_r 16.80 min; R_f 0.66 (hexane/EtOAc, 9.5:0.5). IR (neat) ν = 3068, 2927, 2848, 1603, 1507, 1178, 1027, 747, 239, 694 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 6H), 7.35–7.30 (m, 7H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.31 (dd, *J* = 12.6, 2.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.7 (ArC), 143.8 (d, *J* = 19.3 Hz, *C*H=CHP), 139.6 (d, *J* = 9.3 Hz, ArC), 132.8 (d, *J* = 18.7 Hz, ArCH), 131.2 (d, *J* = 8.9 Hz, ArCH), 129.9 (ArC), 128.7 (d, *J* = 6.6 Hz, ArCH), 128.6 (ArCH), 126.9 (d, *J* = 15.1 Hz, CH=*C*HP), 113.7 (ArCH), 55.4 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –24.7 ppm. GC-MS (EI): *m/z* (%) = 319 [M^++1] (22), 318 (100) [M^+], 317 (83), 210 (24), 209 (13), 207 (21), 197 (17), 183 (10), 167 (12), 165 (12), 138 (10). HRMS (ES+): *m/z* calcd. for $C_{21}H_{19}OP$ 318.1174, $C_{21}H_{20}OP$ 319.1252 [M^++H]; found 319.1266.

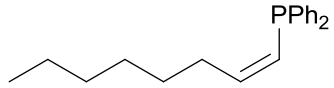


***N,N*-Dimethyl-4-[(*Z*)-2-(diphenylphosphino)vinyl]aniline (5e)**: Yellow solid; 143.9 mg (87% yield); m.p. 156.0–158.8 ºC; t_r 20.56 min; R_f 0.55 (hexane/EtOAc, 9.5:0.5). IR (neat) ν = 3050,

2887, 1611, 1519, 1432, 1199, 1158, 736, 694 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 6H), 7.34–7.27 (m, 7H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.15 (dd, *J* = 12.6, 3.0 Hz, 1H), 2.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.4 (ArC), 144.3 (d, *J* = 19.2 Hz, *C*H=CHP), 140.1 (d, *J* = 9.5 Hz, ArC), 132.8 (d, *J* = 18.6 Hz, ArCH), 131.0 (d, *J* = 9.4 Hz, ArCH), 128.6 (ArCH), 128.5 (d, *J* = 14.7 Hz, CH=*C*HP), 125.5 (ArC), 123.8 (d, *J* = 14.2 Hz, ArCH), 111.8 (ArCH), 40.4 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –23.9 ppm. GC-MS (EI): *m/z* (%) = 332 [M^++1] (18), 331 (74) [M^+], 330 (18), 229 (19), 223 (100), 207 (11). HRMS (ES+): *m/z* calcd. for $C_{22}H_{22}NO$ 331.1490, $C_{22}H_{23}NO$ 332.1568 [M^++H]; found 332.1576.

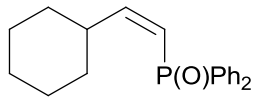


Diphenyl[(*E*)-1-phenylprop-1-en-2-yl]phosphine (5g):[16] White solid; 96.6 mg (64% yield); m.p. 84.9–88.8 ºC; t_r 14.39 min; R_f 0.71 (hexane/EtOAc, 9.5:0.5). IR (neat) ν = 3045, 2957, 1570, 1476, 1431, 741, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 15H), 7.25–7.21 (m, 1H), 1.79 (dd, *J* = 2.8, 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3 (d, *J* = 29.1 Hz, *C*H=CP), 137.5 (d, *J* = 6.5 Hz, ArC), 136.9 (d, *J* = 12.2 Hz, ArC), 134.1 (d, *J* = 20.9 Hz, CH_3*C*P), 133.3 (d, *J* = 18.7 Hz, ArCH), 129.5 (d, *J* = 7.4 Hz, ArCH), 128.5 (ArCH), 128.4 (d, *J* = 6.4 Hz, ArCH), 127.9 (ArCH), 127.5 (ArCH), 24.5 (d, *J* = 4.0 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.4 ppm. GC-MS (EI): *m/z* (%) = 303 [M^++1] (11), 302 (67) [M^+], 301 (100), 183 (14), 108 (12). HRMS (ES+): *m/z* calcd. for $C_{21}H_{19}P$ 302.1224, $C_{21}H_{20}P$ 303.1303 [M^++H]; found 303.1307.

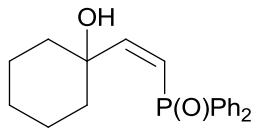


(*Z*)-Oct-1-en-1-yldiphenylphosphine (5h): Colourless oil; 91.8 mg (62% yield); t_r 11.62 min; R_f 0.84 (hexane/EtOAc, 9:1). IR (neat) ν = 3072, 3047, 2949, 2929, 2851, 1617, 1437, 370 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.36 (m, 4H), 7.34–7.27 (m, 6H), 6.43 (ddt, *J* = 23.8, 11.3, 7.3 Hz, 1H), 6.21–6.13 (m, 1H), 2.50–2.37 (m, 2H), 1.45–1.17 (m, 8H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.2 (d, *J* = 24.4 Hz, *C*H=CHP), 139.7 (d, *J* = 9.2 Hz, ArC), 132.7 (d, *J* = 18.7 Hz, ArCH), 128.5 (d, *J* = 6.6 Hz, ArCH), 128.3 (ArCH), 127.8 (d, *J* = 9.0 Hz, CH=*C*HP), 31.8 (CH_2), 31.2 (d, *J* = 21.1 Hz, *C*H_2CH), 29.3 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3). ^{31}P NMR (122 MHz, $CDCl_3$): δ = –31.4 ppm. GC-MS (EI): *m/z* (%) = 296 [M^+] (7), 253 (20), 240 (14), 239 (68), 226 (24), 225 (15), 200 (26), 199 (23), 187 (16), 186 (100), 185 (10), 183 (62), 152 (12), 147 (17), 145 (10), 133 (38), 129 (16), 128 (15), 121 (11), 117 (17), 116 (21),

115 (51), 109 (64), 108 (91), 107 (39), 105 (11), 91 (56), 83 (12), 77 (14), 65 (12), 51 (10). HRMS (ES+): *m/z* calcd. for $C_{20}H_{25}P$ 296.1694, found 296.1698.



(*Z*)-(2-Cyclohexylvinyl)diphenylphosphine oxide (5i): White solid; 95.0 mg (61% yield); m.p. 140.0–143.6 ºC; t_r 18.15 min; R_f 0.42 (hexane/EtOAc, 3:7). IR (neat) ν = 3061, 3021, 2918, 2839, 1619, 1435, 1181, 1118, 718, 691, 604 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.68 (m, 4H), 7.60–7.33 (m, 6H), 6.47 (ddd, *J* = 40.7, 12.9, 10.5 Hz, 1H), 5.99 (dd, *J* = 25.3, 12.9 Hz, 1H), 2.98 (q, *J* = 10.8 Hz, 1H), 1.73–1.44 (m, 5H), 1.32–0.93 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.6 (*C*H=CHP), 134.7 (d, *J* = 103.7 Hz, ArC), 131.4 (d, *J* = 2.8 Hz, ArCH), 130.9 (d, *J* = 9.9 Hz, ArCH), 128.4 (d, *J* = 12.0 Hz, ArCH), 119.1 (d, *J* = 101.2 Hz, CH=*C*HP), 39.1 (d, *J* = 7.5 Hz, *C*HCH$_2$), 32.1 (d, *J* = 1.8 Hz, CH$_2$), 25.7 (CH$_2$), 25.0 (CH$_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.2 ppm. GC-MS (EI): *m/z* (%) = 311 (15) [M^++1], 310 (73) [M^+], 207 (21), 202 (100), 201 (23), 183 (12), 155 (17), 125 (7), 77 (7). HRMS (ES+): *m/z* calcd. for $C_{20}H_{23}OP$ 310.1487, found 310.1485.



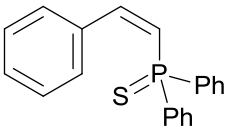
(*Z*)-[2-(1-Hydroxycyclohexyl)vinyl]diphenylphosphine oxide (5j): White solid; 93.0 mg (60% yield); m.p. 145.3–147.0 ºC; t_r 20.20 min; R_f 0.63 (hexane/EtOAc, 3:7). IR (neat) ν = 3244, 3236, 2930, 1437, 1157, 1116, 990, 732, 710, 694, 655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (ddd, *J* = 12.2, 8.0, 1.4 Hz, 4H), 7.55–7.32 (m, 6H), 6.87 (dd, *J* = 40.6, 14.0 Hz, 1H), 6.25 (s, 1H), 5.94 (dd, *J* = 24.7, 14.0 Hz, 1H), 1.96–1.20 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.2 (*C*H=CHP), 133.0 (d, *J* = 107.0 Hz, ArC), 131.8 (d, *J* = 2.7 Hz, ArCH), 131.1 (d, *J* = 10.1 Hz, ArCH), 128.6 (d, *J* = 12.2 Hz, ArCH), 118.1 (d, *J* = 98.3 Hz, CH=*C*HP), 71.7 (d, *J* = 6.6 Hz, CO), 37.9, 25.5, 21.7 (CH$_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.7 ppm. GC-MS (EI): *m/z* (%) = 309 [M^+–17] (22), 308 (100) [M^+–18], 292 (14), 279 (21), 231 (17), 203 (11), 202 (29), 201 (19), 183 (30), 155 (20), 141 (11), 125 (12), 91 (12), 77 (20). HRMS (ES+): *m/z* calcd. for $C_{20}H_{23}O_2P$ 326.1436, $C_{20}H_{21}OP$ [M^+–18] 308.1330, found 308.1316.

General procedure for the hydrothiophosphination of alkynes 4

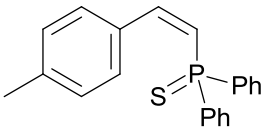
All reactions were performed using tubes in a multi-reactor system under air. Diphenylphosphine (0.5 mmol, 87 μL), the alkyne (**4**, 0.5 mmol) and elemental sulfur (0.5 mmol, 16.0 mg) were

stirred at 70 ºC overnight (Table 6). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent in vacuo. The reaction crude absorbed on silicagel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure alkenyl phosphine sulfides **6**.

Characterisation of compounds 6

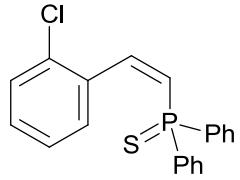


(*Z*)-Diphenyl(styryl)phosphine sulfide (6a):[17] White solid; 153.6 mg (96% yield); m.p. 104.0–105.0 ºC; t_r 18.15 min; R_f 0.65 (hexane/EtOAc, 7:3). IR (neat) ν = 3046, 2986, 2926, 1595, 1489, 1434, 1097, 782, 727, 700, 688, 656, 620 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.81 (m, 4H), 7.54–7.46 (m, 3H), 7.37–7.26 (m, 6H), 7.08–6.97 (m, 3H), 6.41 (dd, *J* = 17.8, 13.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.6 (d, *J* = 2.1 Hz, *C*H=CHP), 134.6 (d, *J* = 7.0 Hz, ArC), 133.1 (d, *J* = 85.4 Hz, ArC), 131.3 (d, *J* = 10.5 Hz, ArCH),131.2 (d, *J* = 3.1 Hz, ArCH), 130.3 (ArCH), 128.9 (ArCH), 128.4 (d, *J* = 12.6 Hz, ArCH), 127.6 (ArCH), 123.2 (d, *J* = 81.8 Hz, CHP). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 30.3 ppm. GC-MS (EI): *m/z* (%) = 321 (23) [M^++1], 320 (100) [M^+], 319 (12), 287 (15), 218 (63), 211 (31), 185 (27), 183 (61), 140 (20), 133 (37), 107 (11). HRMS (ES+): *m/z* calcd. for $C_{20}H_{17}PS$ 320.0789, $C_{20}H_{18}PS$ 321.0867 [M^++H]; found 321.0877.

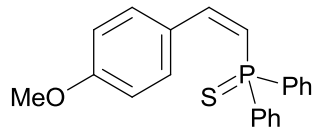


(*Z*)-(4-Methylstyryl)diphenylphosphine sulfide (6b):[17] Pale yellow solid; 130.3 mg (78% yield); m.p. 118.0–122.0 ºC; t_r 18.15 min; R_f 0.57 (hexane/EtOAc, 8:2). IR (neat) ν = 3050, 3000, 1591, 1436, 1099, 823, 741, 715, 709, 691, 631, 601 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.86 (m, 4H), 7.45–7.41 (m, 3H), 7.37–7.30 (m, 6H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.34 (dd, *J* = 18.0, 13.6 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.8 (d, *J* = 1.8 Hz, *C*H=CHP), 139.2 (ArC), 133.4 (d, *J* = 85.4 Hz, ArC), 131.7 (d, *J* = 6.8 Hz, ArCH), 131.3 (d, *J* = 10.9 Hz, ArCH), 131.1, 130.6, 128.5, 128.4 (4 × ArCH), 121.7 (d, *J* = 82.2 Hz, CHP), 21.4 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.4 ppm. GC-MS (EI): *m/z* (%) = 335 (19) [M^++1], 334 (78) [M^+], 301 (12), 226 (11), 225 (67), 218 (62), 185 (45), 184 (14), 183 (100), 179 (11),

178 (10), 152 (13), 147 (51), 140 (37), 139 (14), 134 (17), 133 (14), 115 (24), 104 (14), 77 (12), 65 (11), 63 (15), 51 (11). HRMS (ES+): *m/z* calcd. for $C_{18}H_{19}PS$ 334.0945, $C_{18}H_{20}PS$ 335.1023 [M^++H]; found 335.1028.

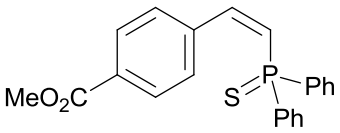


(*Z*)-(2-Chlorostyryl)diphenylphosphine sulfide (6k): Pale yellow solid; 164.6 mg (93% yield); m.p. 83.2–86.7 ºC; t_r 20.11 min; R_f 0.72 (hexane/EtOAc, 8:2). IR (neat) ν = 3060, 2991, 1467, 1435, 1097, 1051, 744, 736, 720, 704, 693, 675, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.77 (m, 4H), 7.59 (d, *J* = 13.3 Hz, 1H), 7.48 (d, *J* = 13.3 Hz, 1H), 7.33–7.26 (m, 6H), 7.07 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.94 (td, *J* = 7.6, 1.6 Hz, 1H), 6.84 (td, *J* = 7.6, 1.0 Hz, 1H), 6.60 (dd, *J* = 18.2, 13.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.1 (d, *J* = 2.7 Hz, *C*H=CHP), 133.5 (d, *J* = 7.2 Hz, ArC), 132.8 (ArC), 132.3 (ArCH), 132.4 (d, *J* = 85.5 Hz, ArC), 131.4 (d, *J* = 10.4 Hz, ArCH), 131.3 (ArCH), 129.9 (ArCH), 128.5 (ArCH), 128.4 (d, *J* = 12.6 Hz, ArCH), 126.1 (d, *J* = 81.8 Hz, CHP), 126.0 (ArCH). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5 ppm. GC-MS (EI): *m/z* (%) = 354 (1) [M^+], 320 (24), 319 (100), 183 (17). HRMS (ES+): *m/z* calcd. for $C_{20}H_{16}ClPS$ 354.0399, $C_{20}H_{17}ClPS$ 355.0477 [M^++H]; found 355.0480.

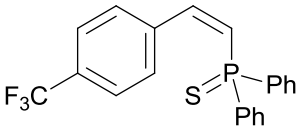


(*Z*)-(4-Methoxystyryl)diphenylphosphine sulfide (6d): Yellow solid; 157.5 mg (90% yield); m.p. 75.2–77.4 ºC; t_r 21.19 min; R_f 0.58 (hexane/EtOAc, 7:3). IR (neat) ν = 3045, 3006, 2957, 2927, 2838, 1604, 1585, 1435, 1310, 1260, 1170, 1097, 1031, 839, 751, 741, 718, 705, 691, 651, 628 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 4H), 7.53–7.49 (m, 2H), 7.40–7.29 (m, 7H), 6.61–6.56 (m, 2H), 6.24 (dd, *J* = 18.0, 13.6 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.3 (ArC), 146.5 (d, *J* = 1.8 Hz, *C*H=CHP), 133.5 (d, *J* = 85.4 Hz, ArC), 132.6 (ArCH), 131.3 (d, *J* = 10.6 Hz, ArCH), 131.2 (d, *J* = 3.0 Hz, ArCH), 128.5 (d, *J* = 12.5 Hz, ArCH), 127.3 (d, *J* = 6.9 Hz, ArCH), 119.9 (d, *J* = 82.7 Hz, CHP), 113.1 (ArCH), 55.3 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.4 ppm. GC-MS (EI): *m/z* (%) = 351 (21) [M^++1], 350 (89) [M^+], 318 (10), 317 (13), 242 (16), 241 (100), 218 (47), 210 (12), 185 (38), 184 (11), 183 (76), 165 (14), 163 (36), 152 (13), 150 (14), 140 (29), 139 (10), 133 (17), 121 (10), 107 (13), 77 (11),

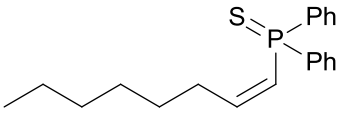
63 (12). HRMS (ES+): *m/z* calcd. for $C_{21}H_{19}OPS$ 350.0894, $C_{21}H_{20}OPS$ 351.0972 [M^++H]; found 351.0968.



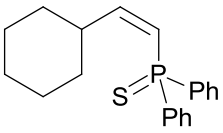
(*Z*)-Methyl 4-[2-(diphenylphosphorothioyl)vinyl]benzoate (6l): Pale yellow solid; 173.8 mg (92% yield); m.p. 109.9–114.4 ºC; t_r 25.16 min; R_f 0.33 (hexane/EtOAc, 8:2). IR (neat) ν = 3042, 2995, 2946, 1715, 1608, 1437, 1275, 1100, 871, 707, 689, 637, 608 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.80 (m, 4H), 7.73–7.66 (m, 2H), 7.58–7.51 (m, 2H), 7.50–7.46 (m, 1H), 7.41–7.27 (m, 6H), 6.56 (dd, *J* = 17.3, 13.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6 (ArC), 145.0 (d, *J* = 2.1 Hz, *C*H=CHP), 138.9 (d, *J* = 7.0 Hz, ArC), 132.7 (d, *J* = 85.6 Hz, ArC), 131.5 (d, *J* = 2.7 Hz, ArCH), 131.3 (d, *J* = 10.7 Hz, ArCH), 130.0 (ArCH), 129.9 (ArC), 128.8 (ArCH), 128.5 (d, *J* = 12.6 Hz, ArCH), 126.1 (d, *J* = 80.6 Hz, CHP), 52.2 (CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.9 ppm. GC-MS (EI): *m/z* (%) = 379 (16) [M^++1], 378 (61) [M^+], 269 (18), 238 (11), 219 (13), 218 (90), 207 (15), 191 (15), 185 (44), 184 (15), 183 (100), 178 (14), 152 (12), 140 (32), 139 (14), 134 (13), 133 (14), 129 (10), 108 (10), 107 (15), 63 (11). HRMS (ES+): *m/z* calcd. for $C_{22}H_{19}O_2PS$ 378.0843, $C_{22}H_{20}O_2PS$ 379.0922 [M^++H]; found 379.0920.



(*Z*)-Diphenyl[4-(trifluoromethyl)styryl]phosphine sulfide (6f): Yellow solid; 58 mg (30% yield); m.p. 150.2–152.7 ºC; t_r 19.53 min; R_f 0.42 (hexane/EtOAc, 8:2). IR (neat) ν = 3056, 2919, 2848, 1436, 1321, 1115, 1097, 1065, 858, 717, 704, 689, 615 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.66 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50–7.15 (m, 9H), 6.60 (dd, *J* = 17.3, 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 144.2 (d, *J* = 2.5 Hz, *C*H=CHP), 137.9 (d, *J* = 8.2 Hz, ArC), 132.3 (d, *J* = 85.5 Hz, ArC), 131.9 (m, ArC), 31.4 (d, *J* = 3.0 Hz, ArCH), 131.2 (d, *J* = 10.7 Hz, ArCH), 130.0 (d, *J* = 1.0 Hz, ArCH), 128.4 (d, *J* = 12.6 Hz, ArCH), 126.6 (d, *J* = 80.5 Hz, CHP), 124.4 (q, *J* = 3.8 Hz, ArCH) 123.7 (q, *J* = 272.0 Hz, ArC). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.8 ppm. GC-MS (EI): *m/z* (%) = 389 (23) [M^++1], 388 (100) [M^+], 356 (81), 355 (93), 279 (16), 218 (63), 201 (29), 191 (15), 185 (30), 184 (11), 183 (78), 140 (20), 108 (22), 107 (14). HRMS (ES+): *m/z* calcd. for $C_{21}H_{16}F_3PS$ 388.0662, found 388.0652.



(*Z*)-Oct-1-en-1-yldiphenylphosphine sulfide (6h):[17] Colorless oil; 147.6 mg (90% yield); t_r 15.69 min; R_f 0.66 (hexane/EtOAc, 8:2). IR (neat) ν = 3042, 2951, 2924, 2854, 1611, 1435, 1100, 735, 717, 706, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.83 (m, 4H), 7.50–7.40 (m, 6H), 6.58 (ddt, *J* = 42.9, 12.4, 7.6 Hz, 1H), 6.27 (ddt, *J* = 23.5, 12.4, 1.5 Hz, 1H), 2.29 (qdd, *J* = 7.6, 2.9, 1.5 Hz, 2H), 1.35–1.06 (m, 8H), 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (*C*H=CHP), 134.6 (d, *J* = 84.2 Hz, ArC), 131.4 (ArCH), 131.3 (d, *J* = 9.0 Hz, ArCH), 128.6 (d, *J* = 12.4 Hz, ArCH), 123.0 (d, *J* = 84.5 Hz, CHP), 31.6 (CH_2), 31.0 (d, *J* = 9.4 Hz, CH_2), 28.9, 28.4, 22.6 (CH_2), 14.2 (CH_3). ^{31}P NMR (122 MHz, $CDCl_3$): δ = 28.4 ppm. GC-MS (EI): *m/z* (%) = 328 (29) [M^+], 271 (43), 219 (17), 218 (100), 217 (35), 185 (16), 183 (35), 139 (13). HRMS (ES+): *m/z* calcd. for $C_{20}H_{25}PS$ 328.1415, $C_{20}H_{26}PS$ 329.1493 [M^++H]; found 329.1498.



(*Z*)-(2-Cyclohexylvinyl)diphenylphosphine sulfide (6i): Pale yellow solid; 97.8 mg (60% yield); m.p. 63.8–66.8 ºC; t_r 16.20 min; R_f 0.58 (hexane/EtOAc, 9:1). IR (neat) ν = 3040, 2929, 2920, 1611, 1099, 734, 719, 708, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 4H), 7.49–7.39 (m, 6H), 6.42–6.24 (m, 1H), 6.17 (dd, *J* = 23.6, 12.4 Hz, 1H), 2.76–2.61 (m, 1H), 1.60–1.49 (m, 5H), 1.29–1.23 (m, 1H), 1.02–0.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 157.8 (ArC), 134.8 (d, *J* = 84.2 Hz, ArC), 131.3 (d, *J* = 10.5 Hz, ArCH), 131.2 (d, *J* = 3.1 Hz, *C*H=CHP), 128.6 (d, *J* = 12.4 Hz, ArCH), 121.3 (d, *J* = 84.6 Hz, CHP), 39.3 (d, *J* = 31.3 Hz, CH), 31.1 (d, *J* = 1.0 Hz, CH_2), 25.8, 25.1 (CH_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.8 ppm. GC-MS (EI): *m/z* (%) = 326 (29) [M^+], 219 (19), 218 (100), 217 (20), 185 (28), 183 (47), 140 (25), 139 (16), 133 (12), 109 (10), 108 (14), 107 (10). HRMS (ES+): *m/z* calcd. for $C_{20}H_{23}PS$ 326.1258, $C_{20}H_{24}PS$ 327.1336 [M^++H]; found 327.1340.

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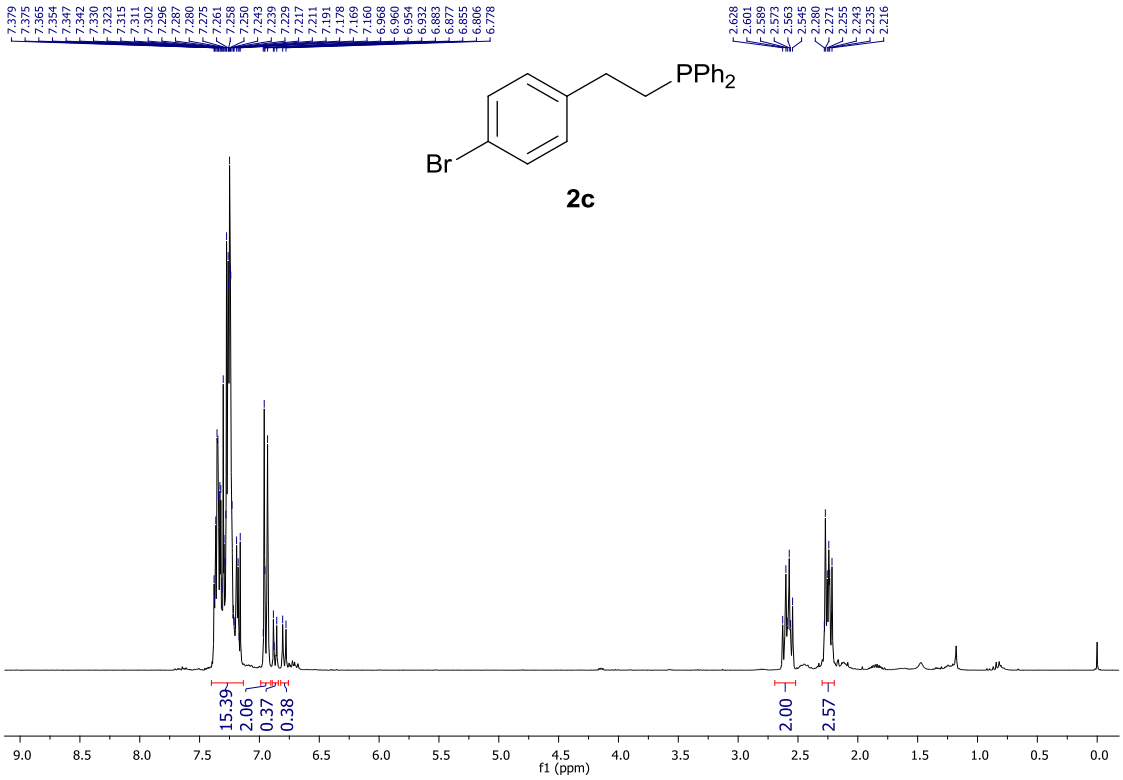
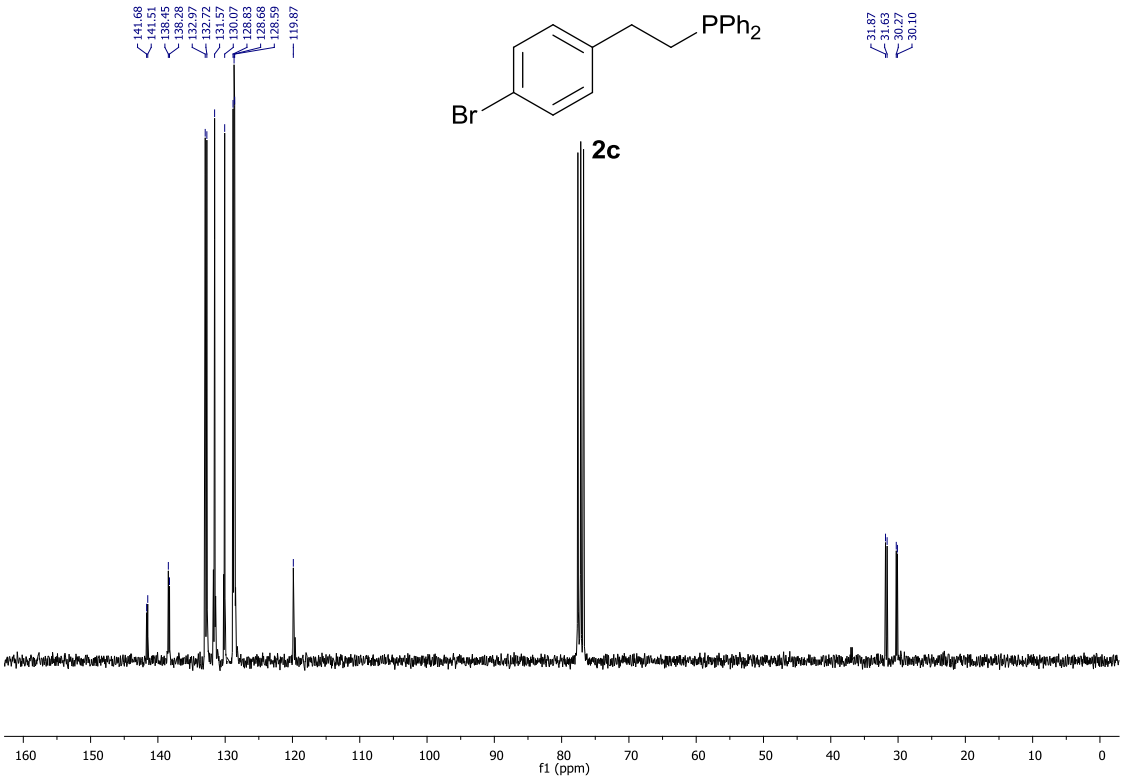
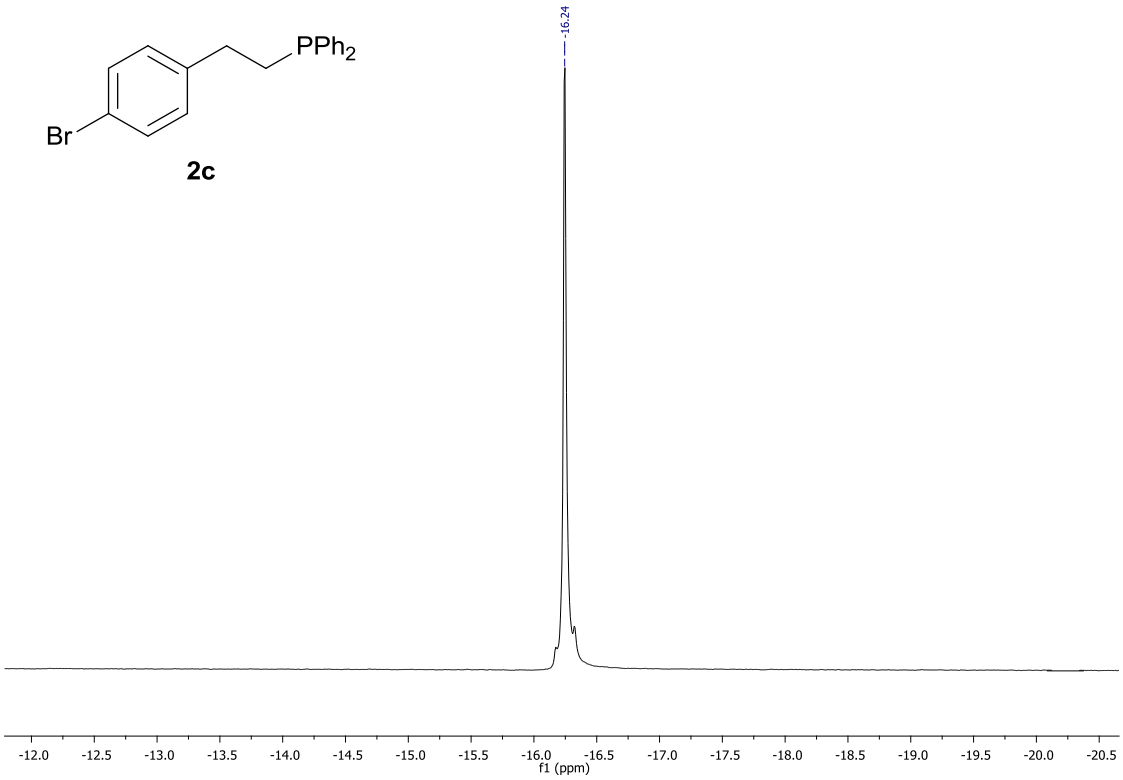
NMR spectra of new compounds 2



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Br
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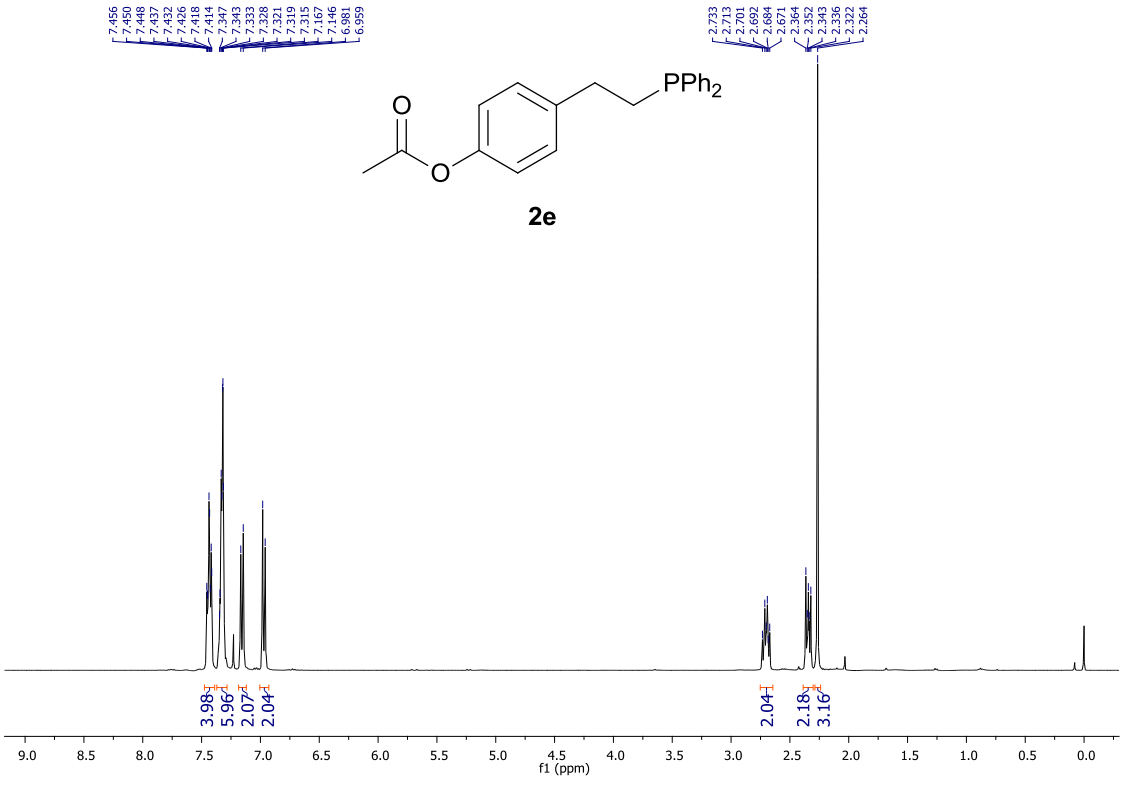
f1 (ppm)

2c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7.414
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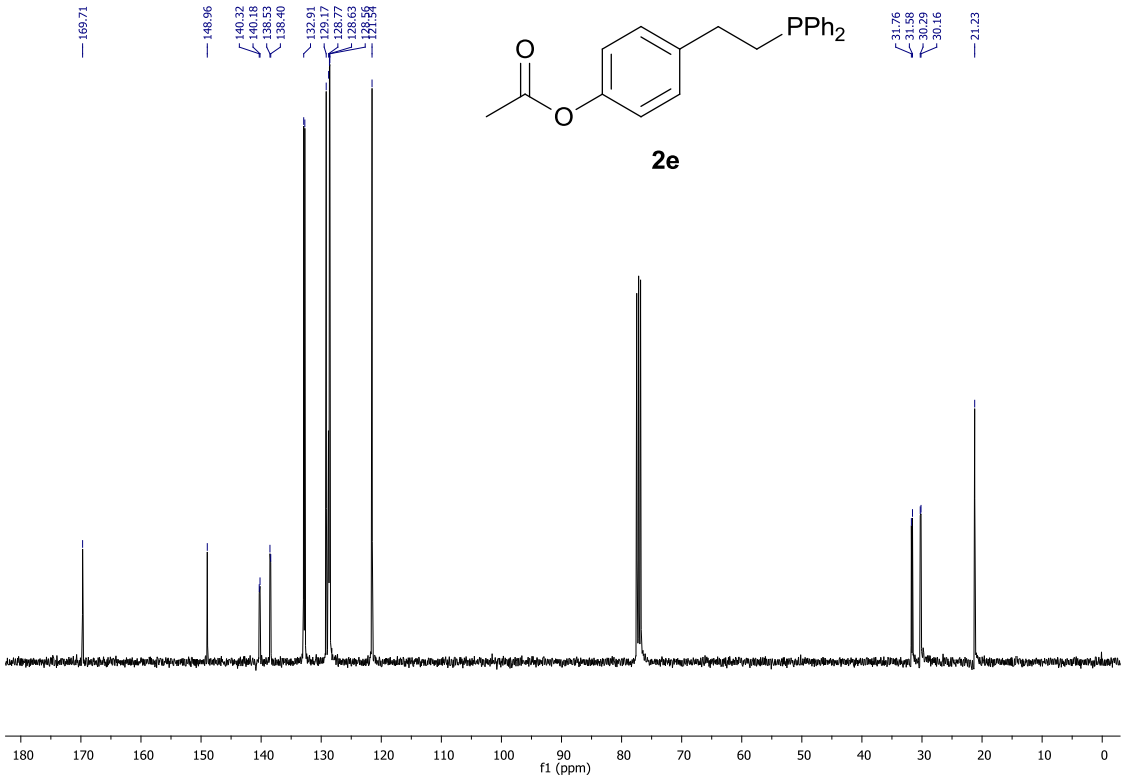
7.343
7.333
7.328
7.321
7.319
7.315
7.167
7.146
6.981
6.959
2.733
2.713
2.701
2.692
2.684
2.671
2.364
2.352
2.343
2.336
2.322
2.264
PPh2
O
O
3.98
5.96
2.07
2.04
2.04
2.18
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2e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140.32
140.18
138.53
138.40
132.91
129.17
128.77
128.63
128.56
121.54
31.76
31.58
30.29
30.16
21.23
PPh2
O
O
2e
180
170
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150
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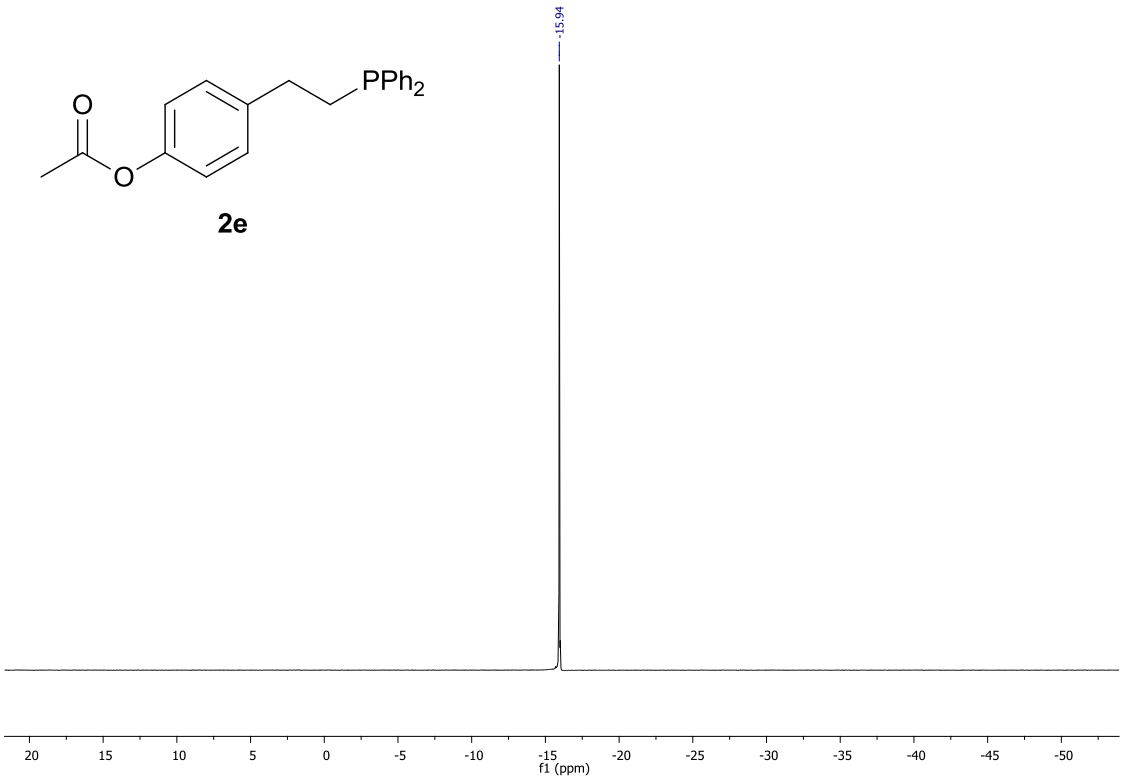
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-15.94
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O
O
2e
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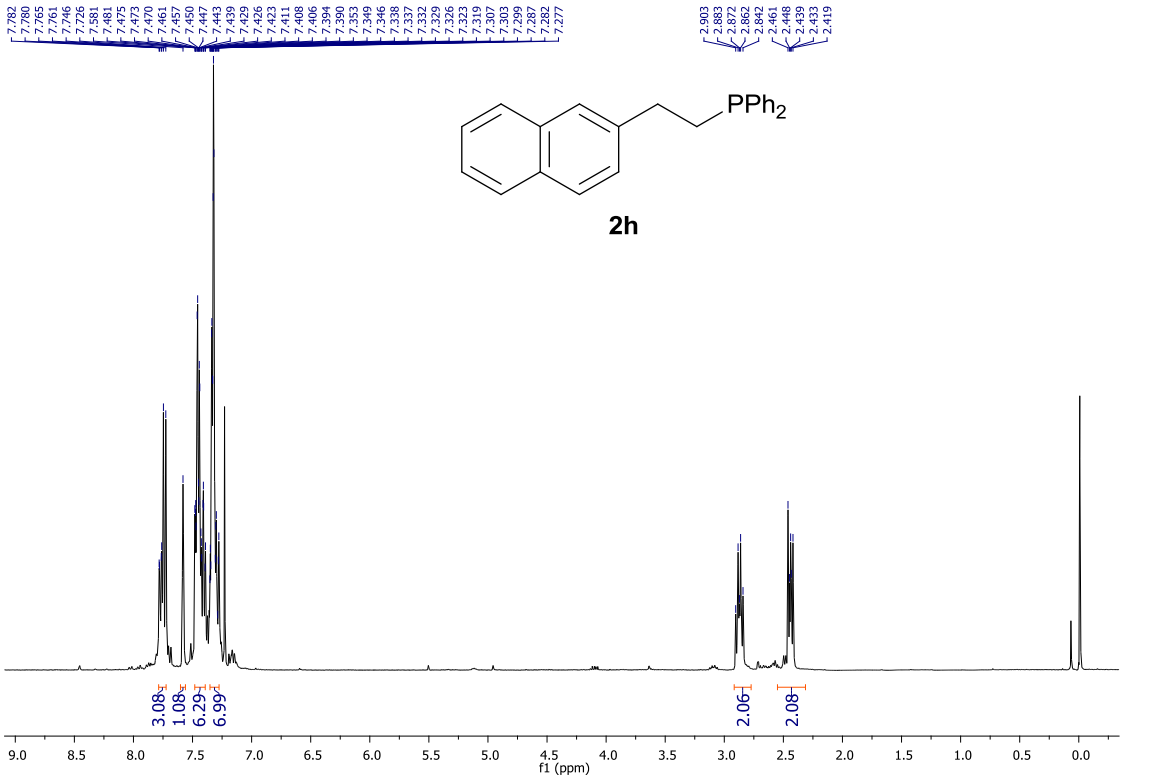
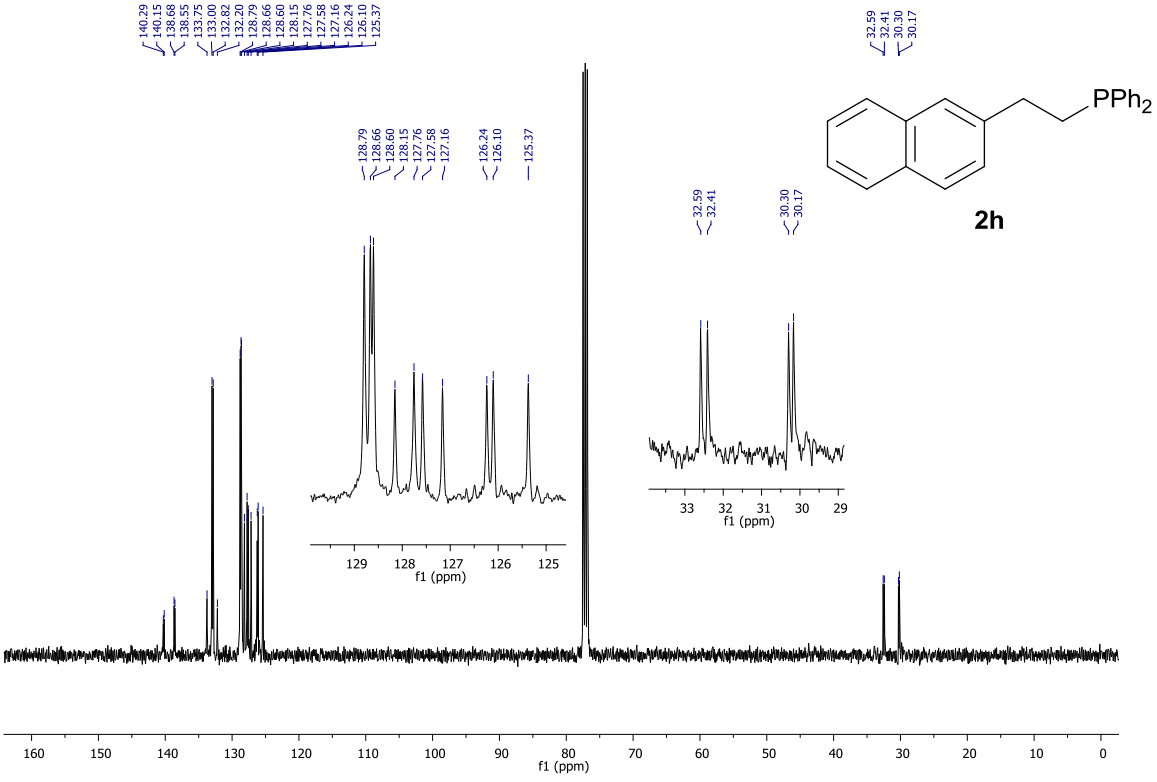
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


PPh2
2h
f1 (ppm)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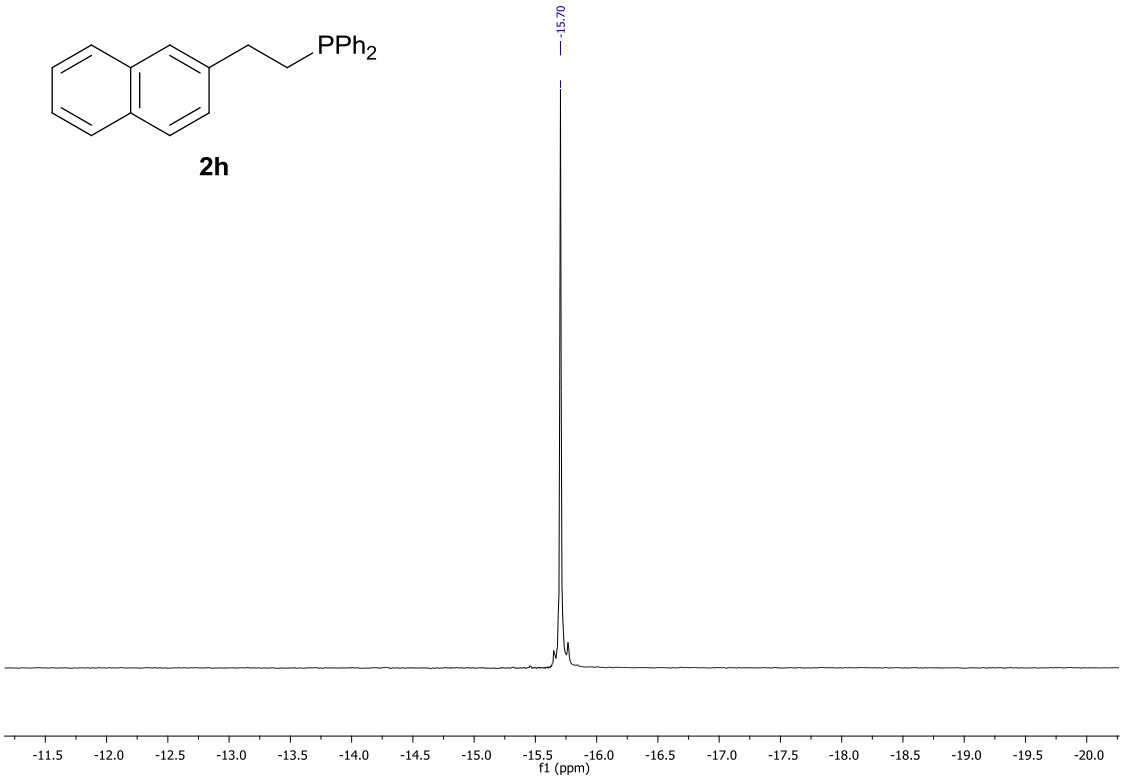
2h
f1 (ppm)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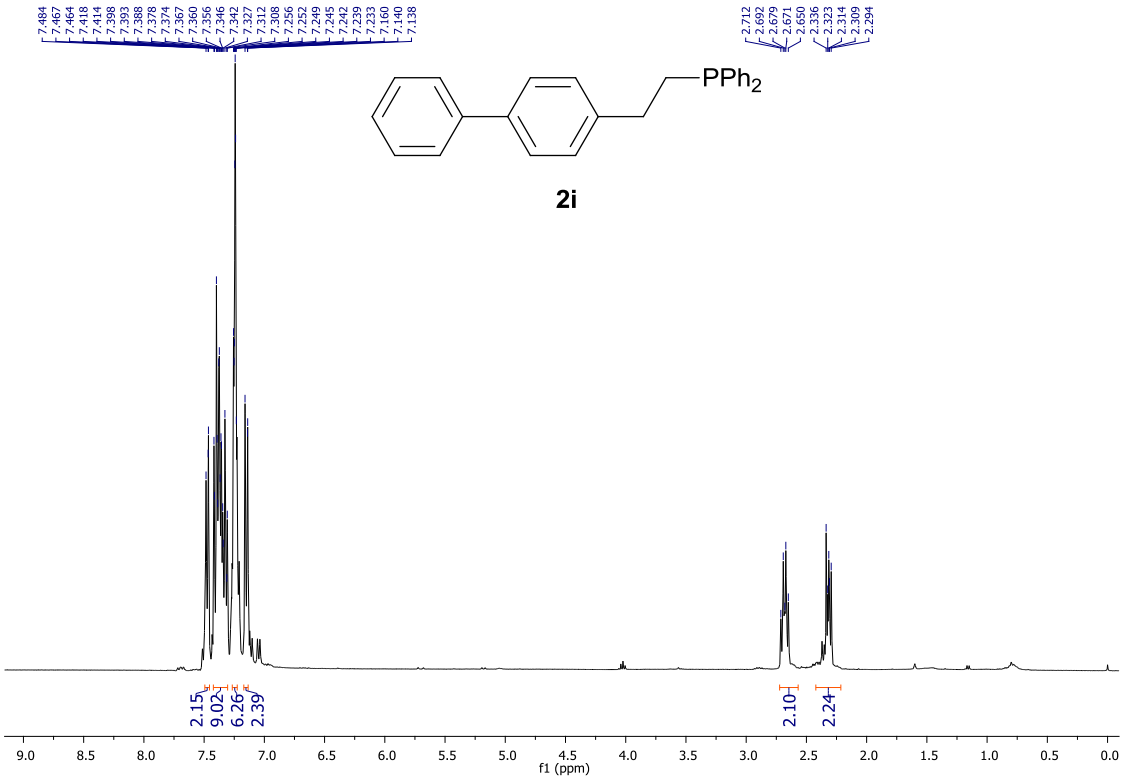
2h
-15.70
-11.5 -12.0 -12.5 -13.0 -13.5 -14.0 -14.5 -15.0 -15.5 -16.0 -16.5 -17.0 -17.5 -18.0 -18.5 -19.0 -19.5 -20.0
f1 (ppm)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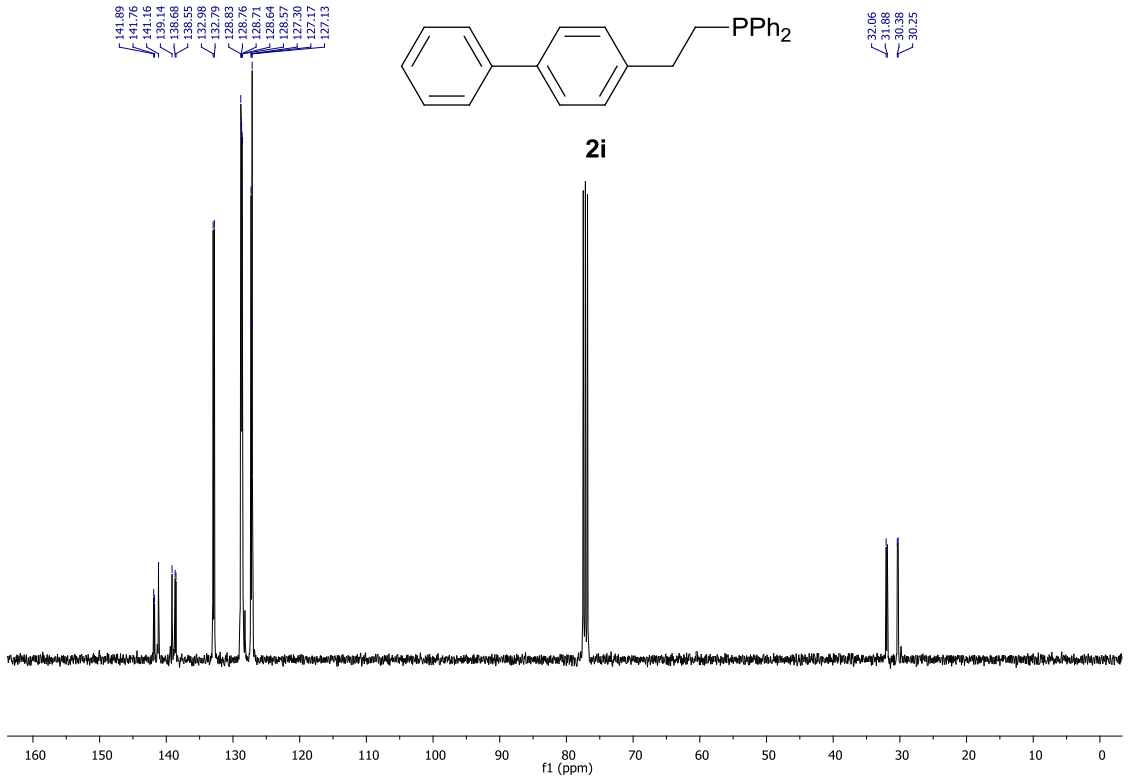
2.712 2.692 2.679 2.671 2.650 2.336 2.323 2.314 2.309 2.294
PPh2
2i
2.15 9.02 6.26 2.39 2.10 2.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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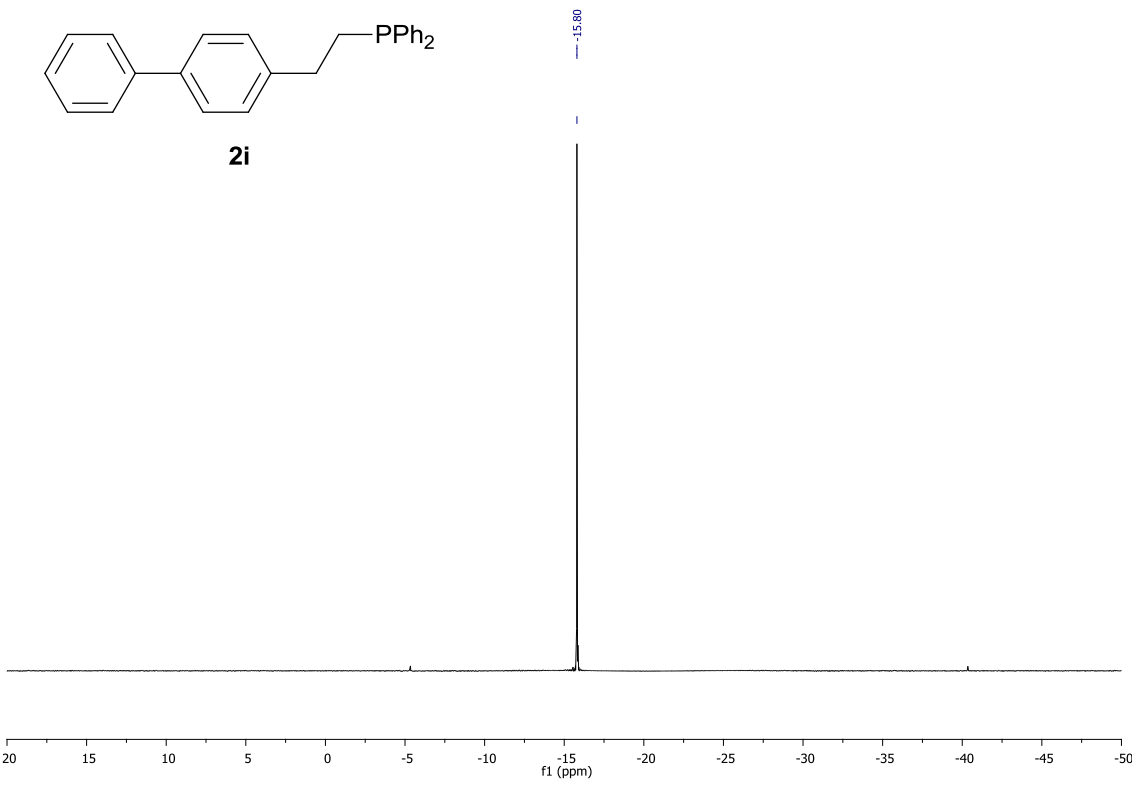
139.14
138.68
138.55
132.98
132.79
128.83
128.76
128.71
128.64
128.57
127.30
127.17
127.13
32.06
31.88
30.38
30.25
PPh2
2i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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2i
-15.80
20
15
10
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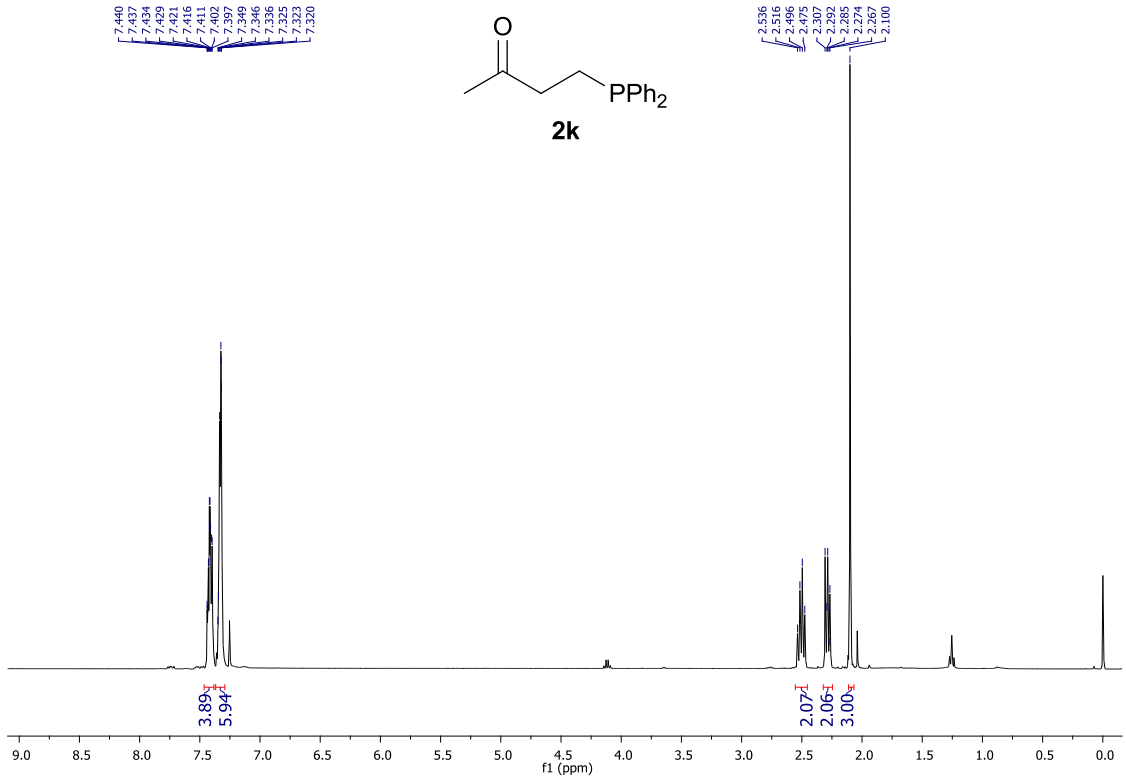
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)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7.434
7.429
7.421
7.416
7.411
7.402
7.397
7.349
7.346
7.336
7.325
7.323
7.320
O
PPh2
2k
2.536
2.516
2.496
2.475
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2.292
2.285
2.274
2.267
2.100
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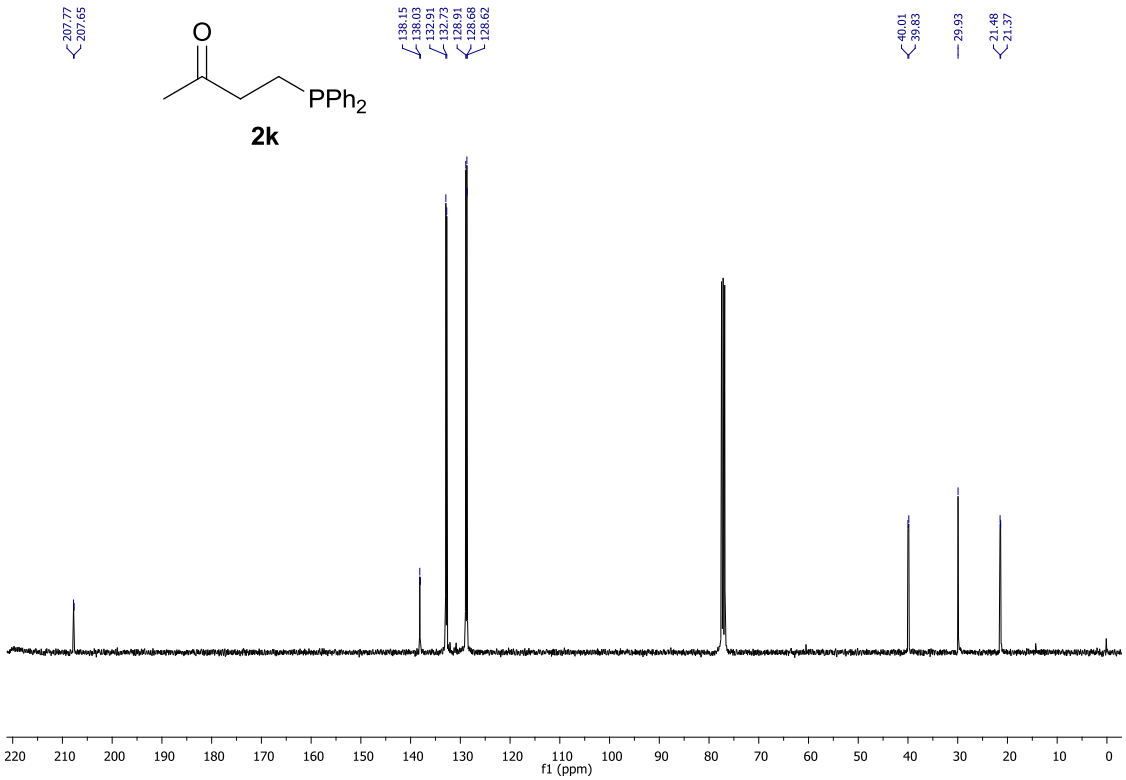
5.94
2.07
2.06
3.00
f1 (ppm)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207.65
O
PPh2
2k
138.15
138.03
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132.73
128.91
128.68
128.62
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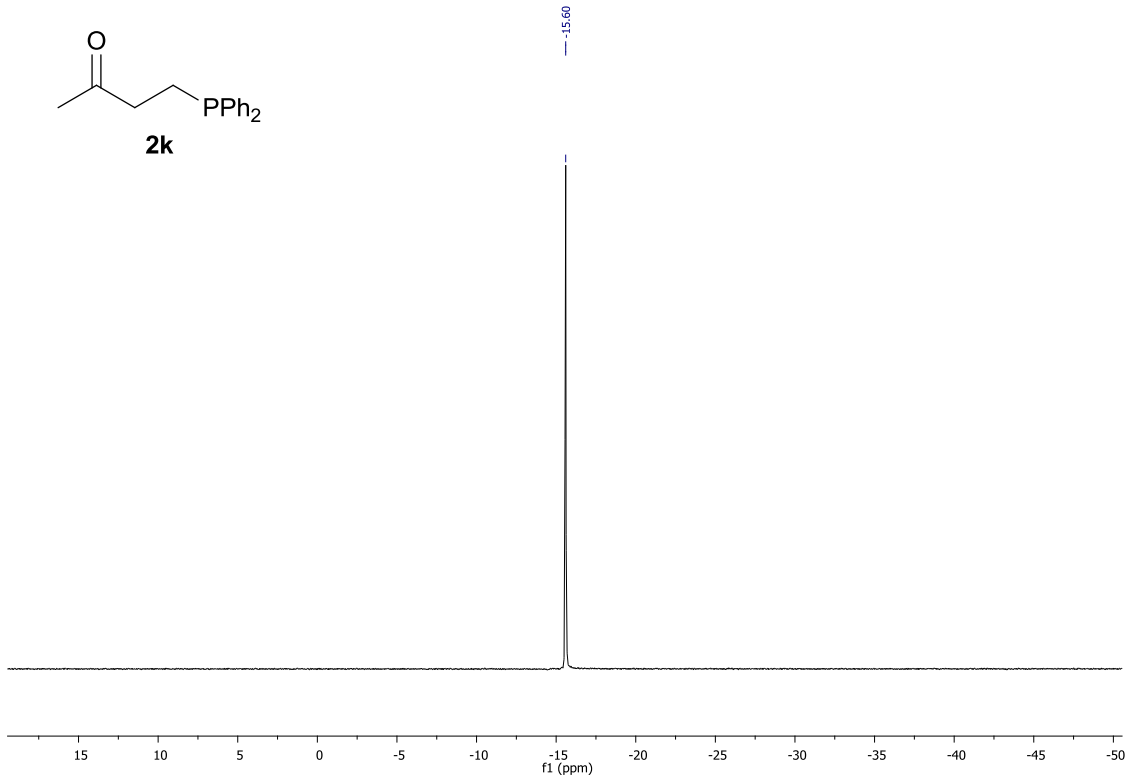
39.83
29.93
21.48
21.37
f1 (ppm)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PPh2
2k
-15.60
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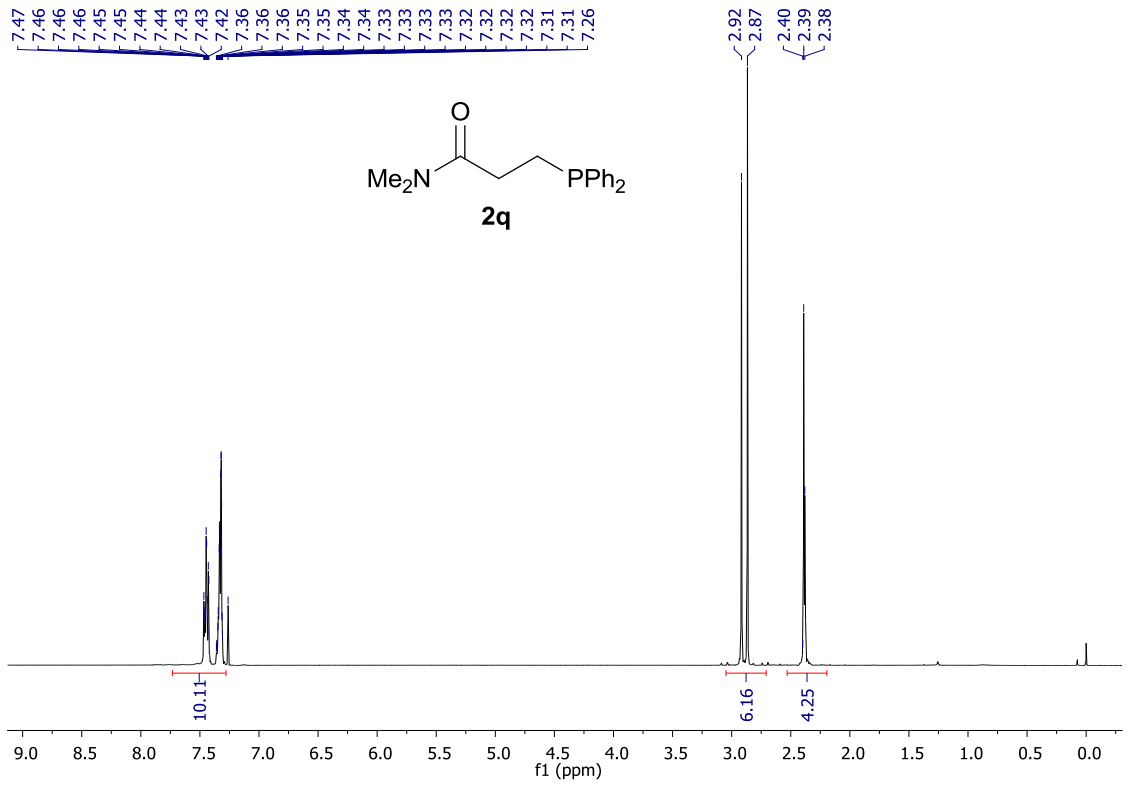
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)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7.46
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7.45
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7.44
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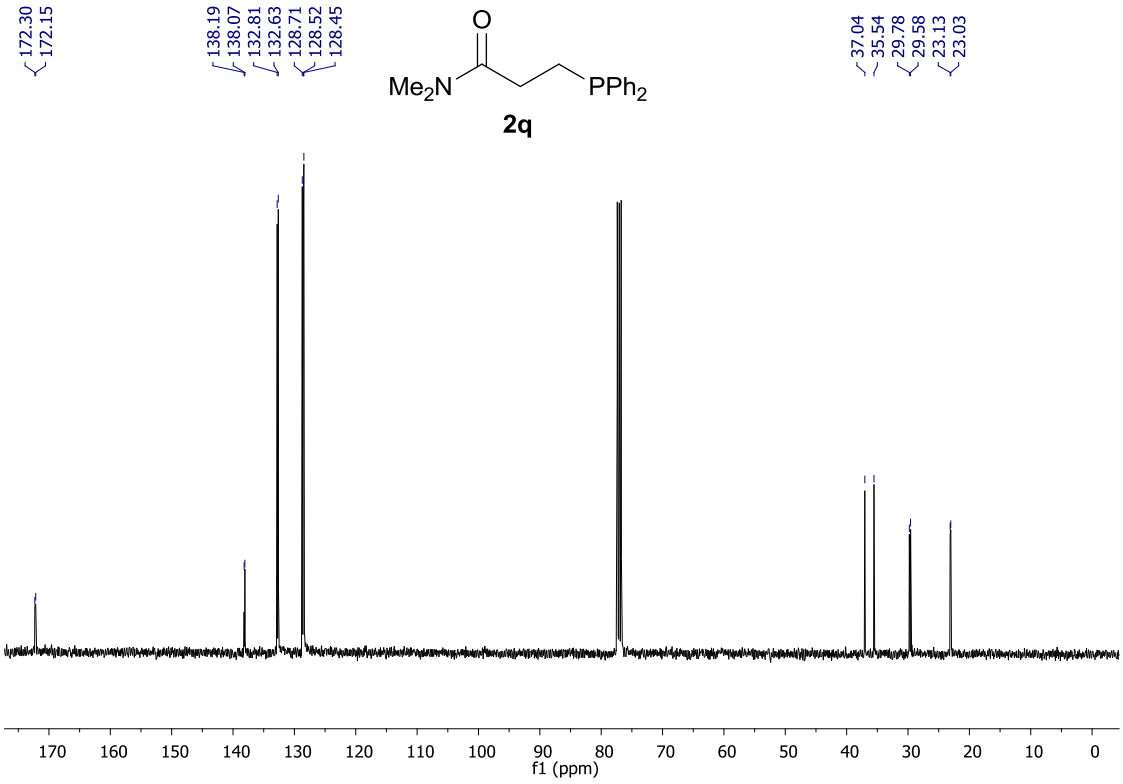
7.42
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.26
2.92
2.87
2.40
2.39
2.38
O
Me2N
PPh2
2q
10.11
6.16
4.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.07
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128.52
128.45
37.04
35.54
29.78
29.58
23.13
23.03
O
Me2N
PPh2
2q
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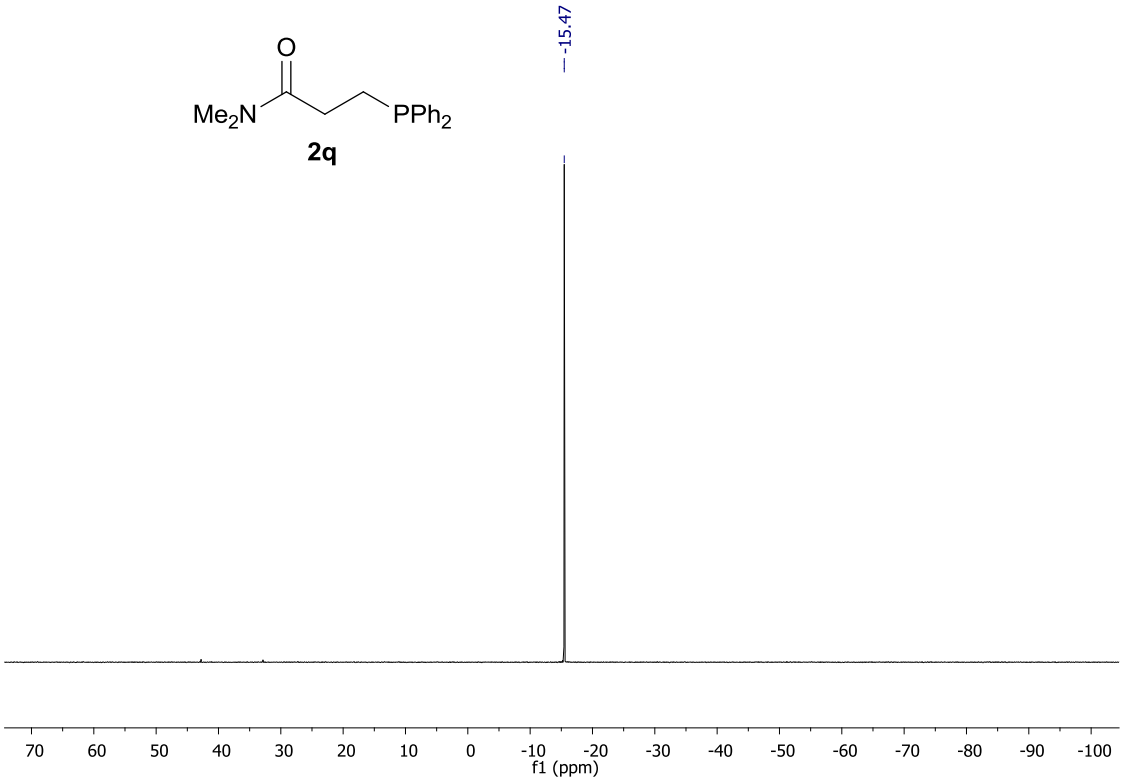
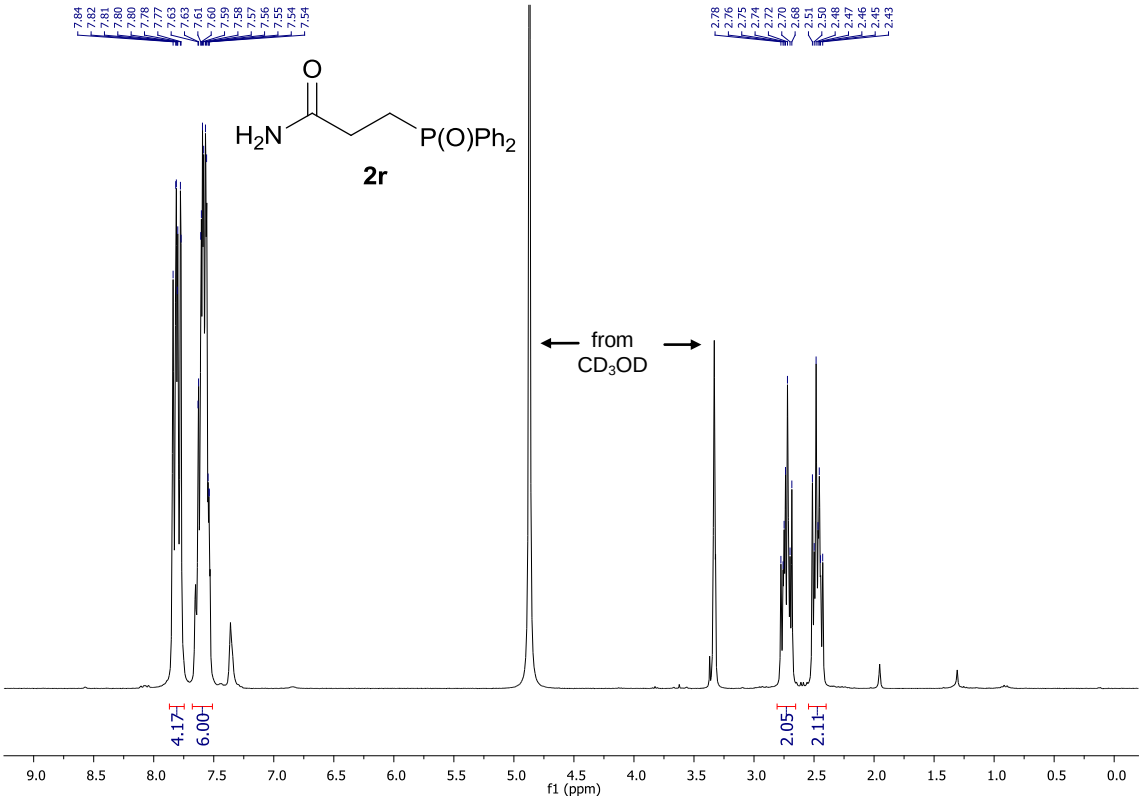
f1 (ppm)


-15.47
O
Me2N
PPh2
2q
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)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7.81
7.80
7.80
7.78
7.77
7.63
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.54
2.78
2.76
2.75
2.74
2.72
2.70
2.68
2.51
2.50
2.48
2.47
2.46
2.45
2.43
O
H2N
P(O)Ph2
2r
from
CD3OD
4.17
6.00
2.05
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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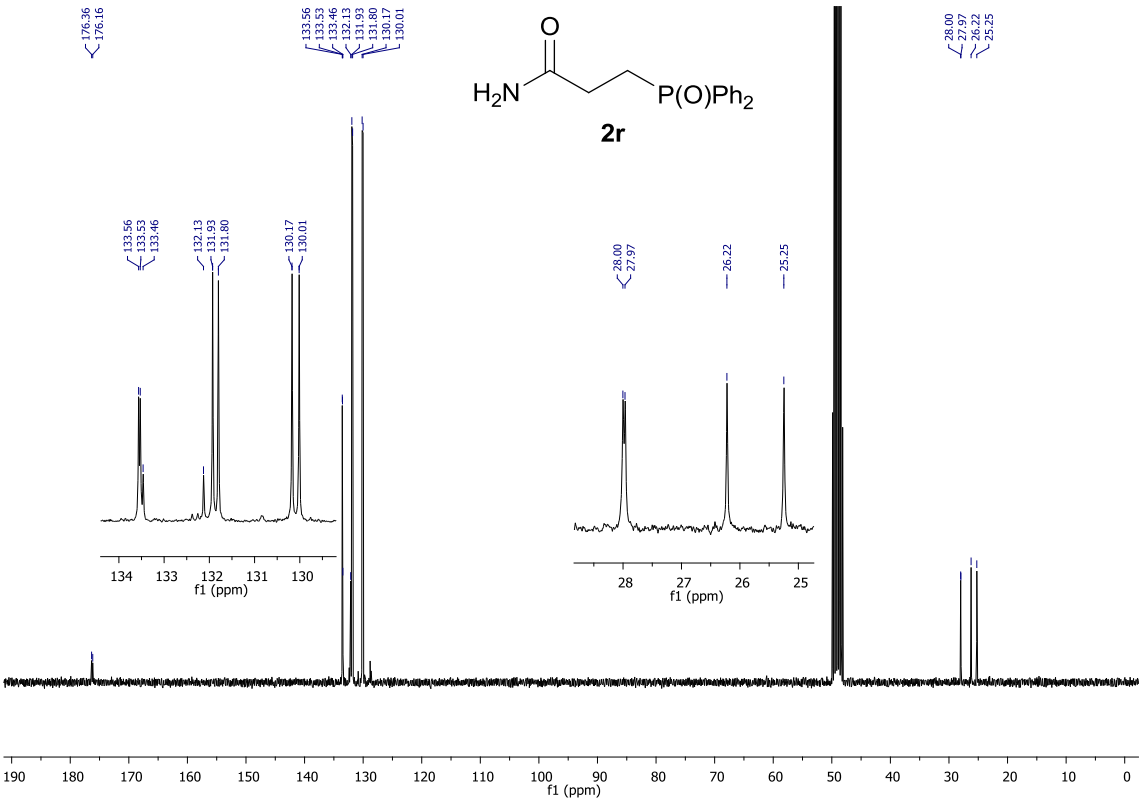
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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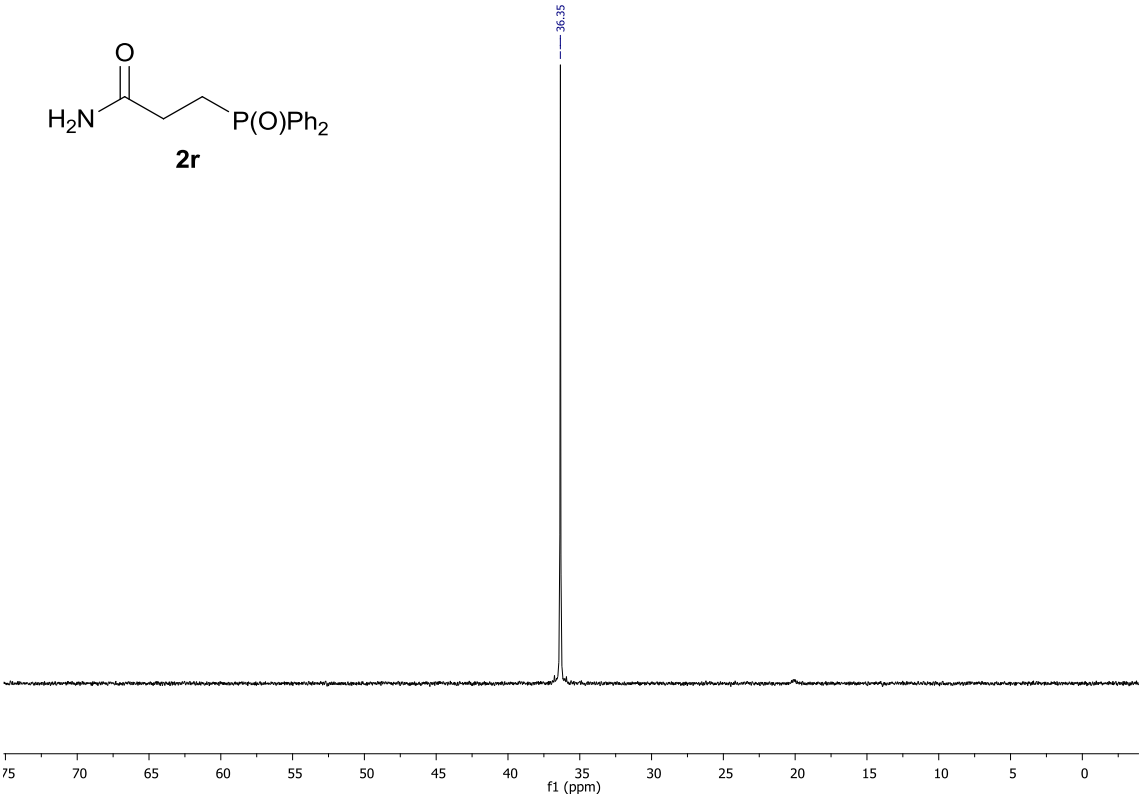
176.16
133.56
133.53
133.46
132.13
131.93
131.80
130.17
130.01
28.00
27.97
26.22
25.25
O
H2N
P(O)Ph2
2r
134
133
132
131
130
f1 (ppm)
28
27
26
25
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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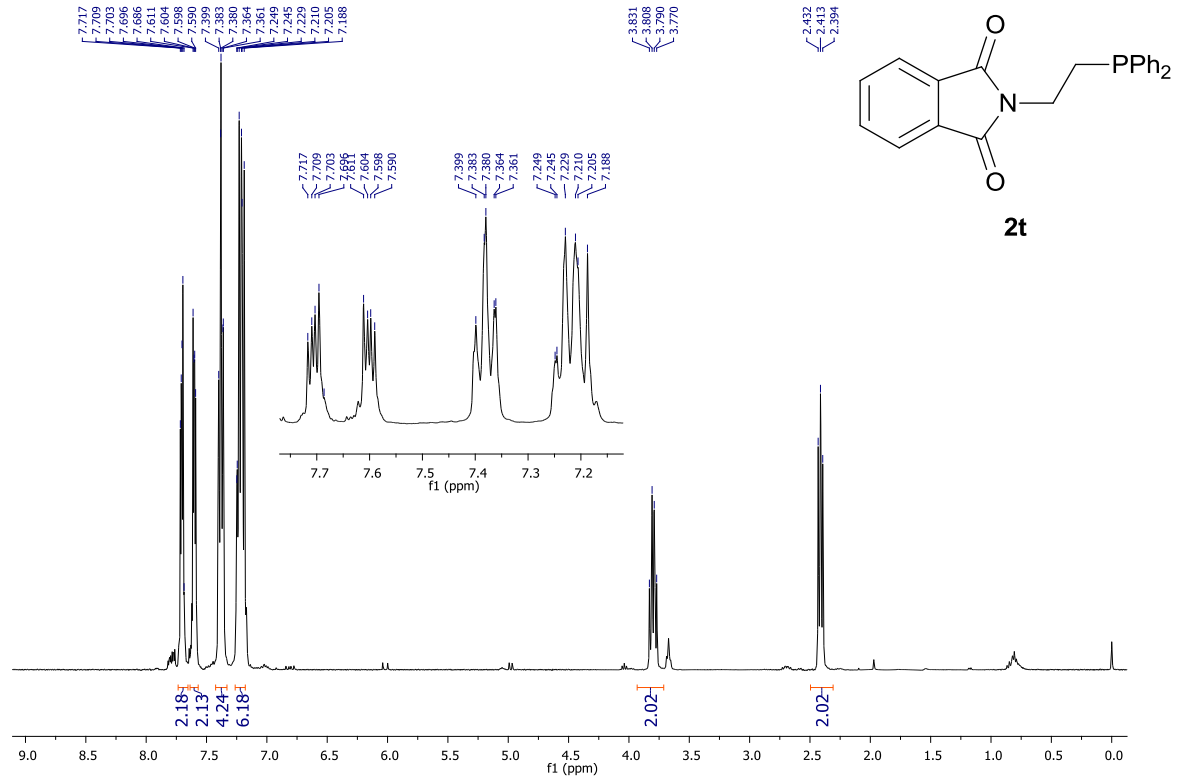
H2N
P(O)Ph2
2r
36.35
f1 (ppm)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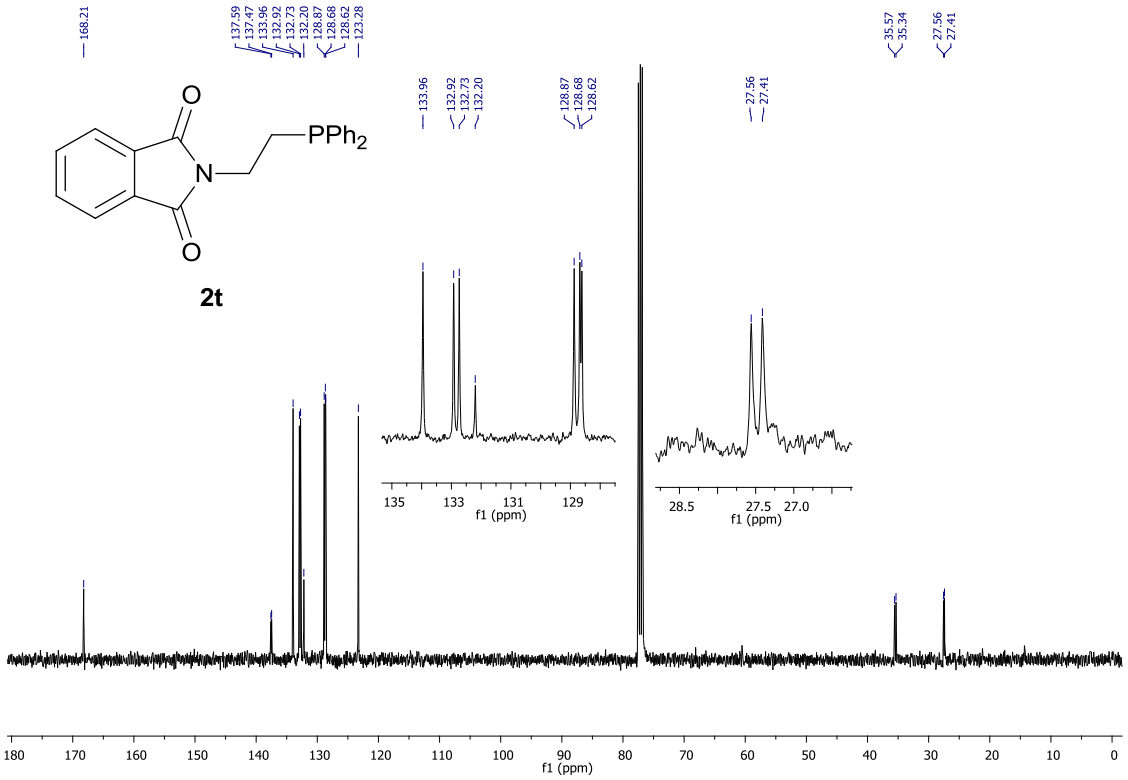
7.598
7.590
7.399
7.383
7.380
7.364
7.361
7.249
7.245
7.229
7.210
7.205
7.188
3.831
3.808
3.790
3.770
2.432
2.413
2.394
O
N
O
PPh2
2t
2.18
2.13
4.24
6.18
2.02
2.02
f1 (ppm)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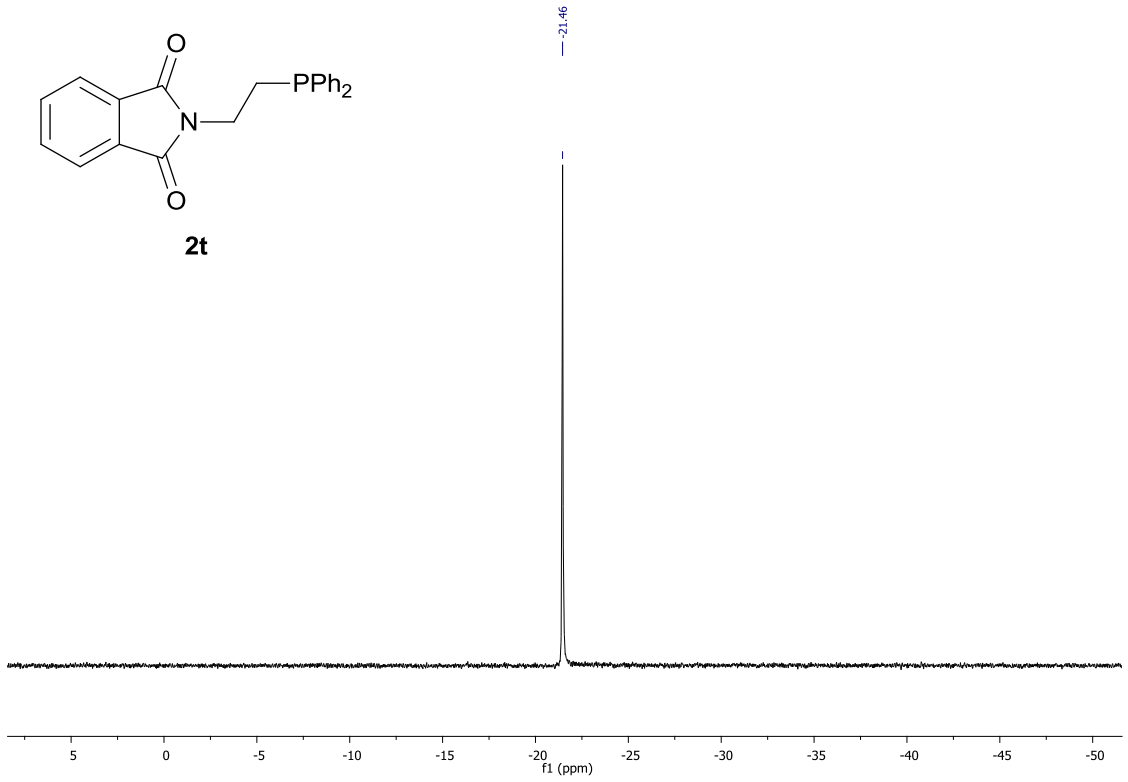
132.20
128.87
128.68
128.62
123.28
35.57
35.34
27.56
27.41
O
N
PPh2
O
2t
f1 (ppm)
f1 (ppm)
f1 (ppm)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N
PPh2
O
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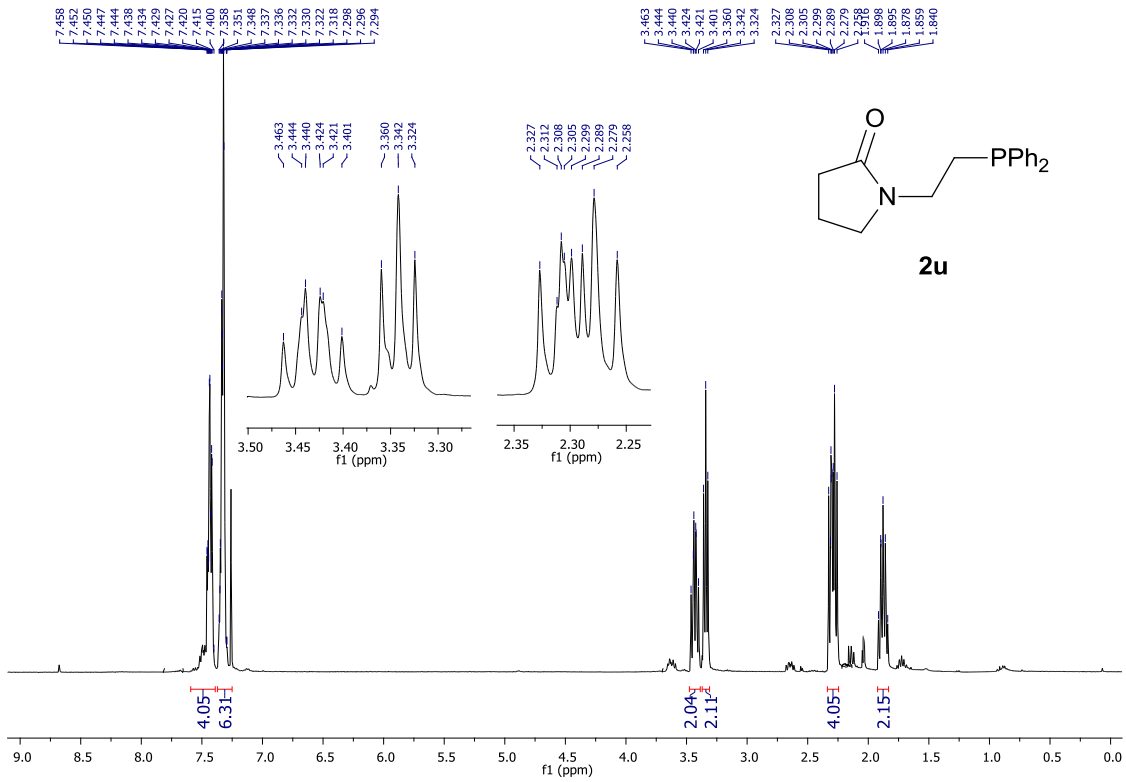
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7.415
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7.358
7.351
7.348
7.337
7.336
7.332
7.330
7.322
7.318
7.298
7.296
7.294
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3.444
3.440
3.424
3.421
3.401
3.360
3.342
3.324
2.327
2.308
2.305
2.299
2.289
2.279
1.918
1.898
1.895
1.878
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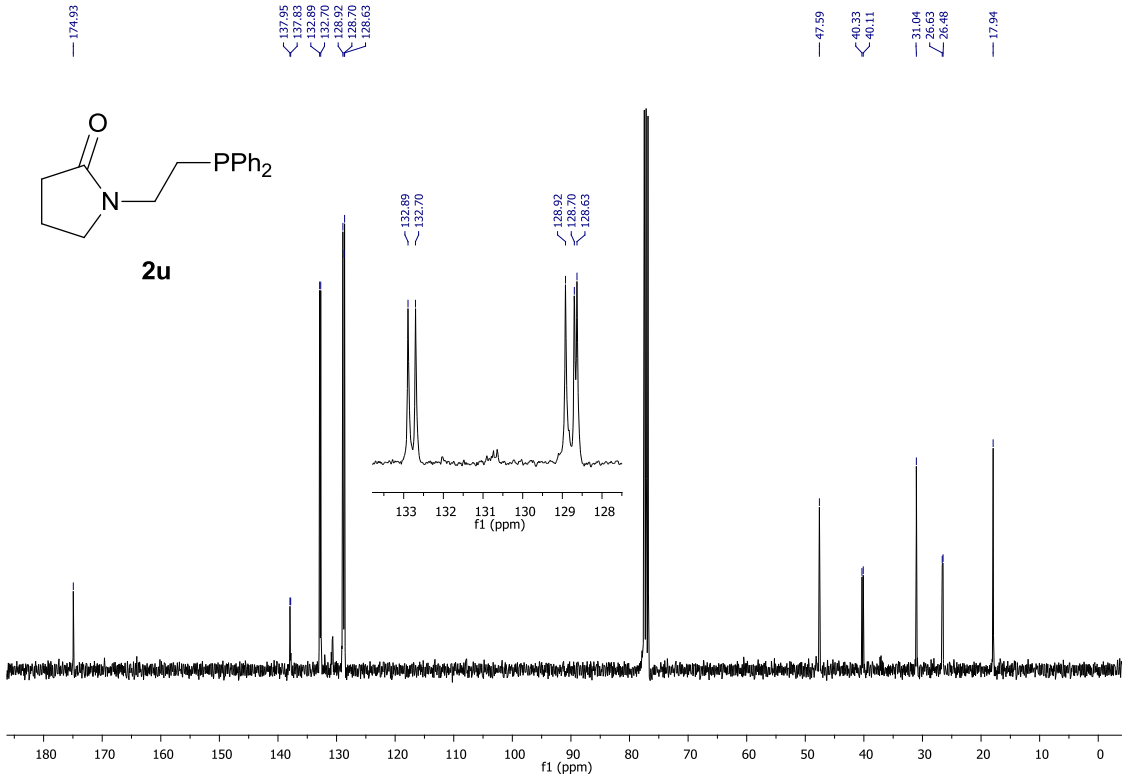
4.05
2.15
f1 (ppm)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132.89
132.70
128.92
128.70
128.63
47.59
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40.11
31.04
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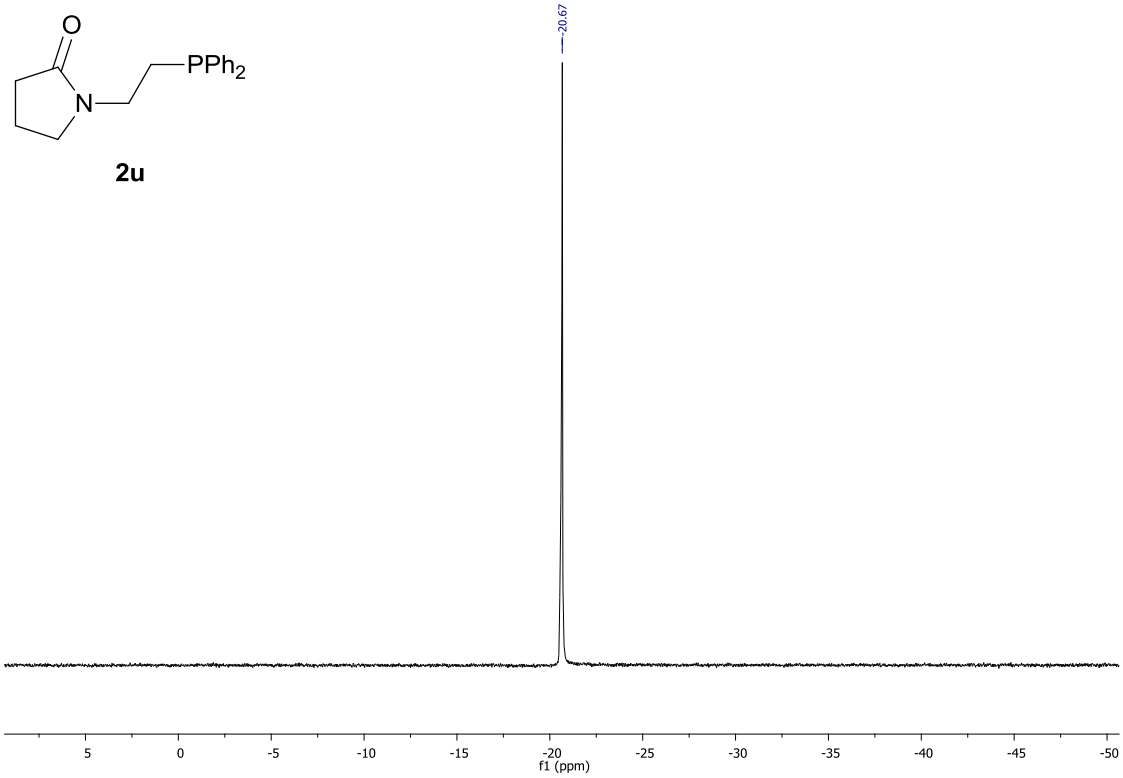
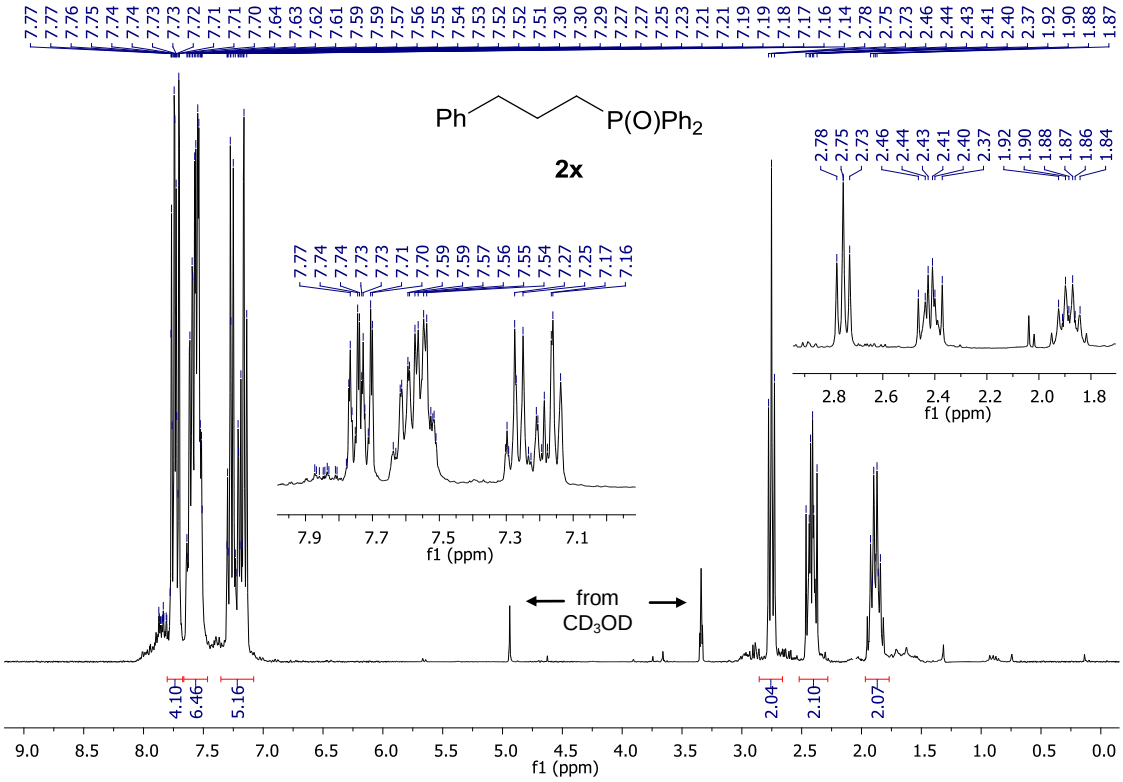
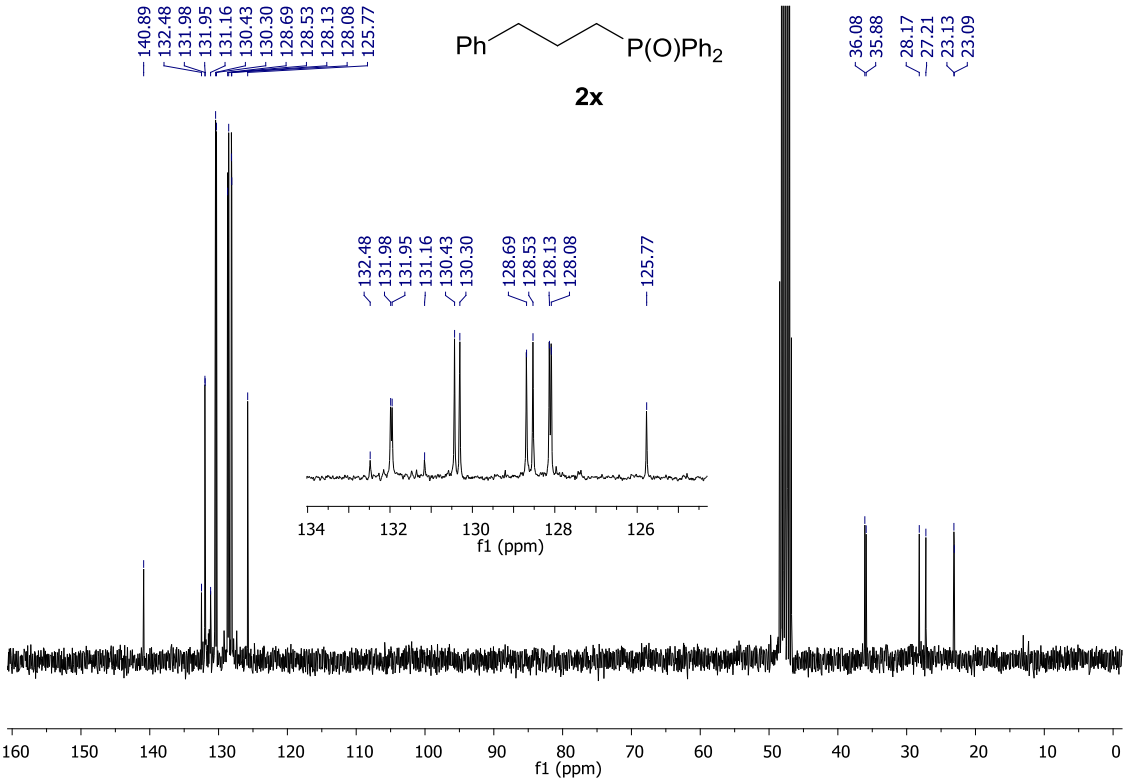
26.48
17.94
O
PPh2
N
2u
f1 (ppm)


O
PPh2
N
2u
-20.67
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)


Ph
P(O)Ph2
2x
from
CD3OD
4.10
6.46
5.16
2.04
2.10
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.95
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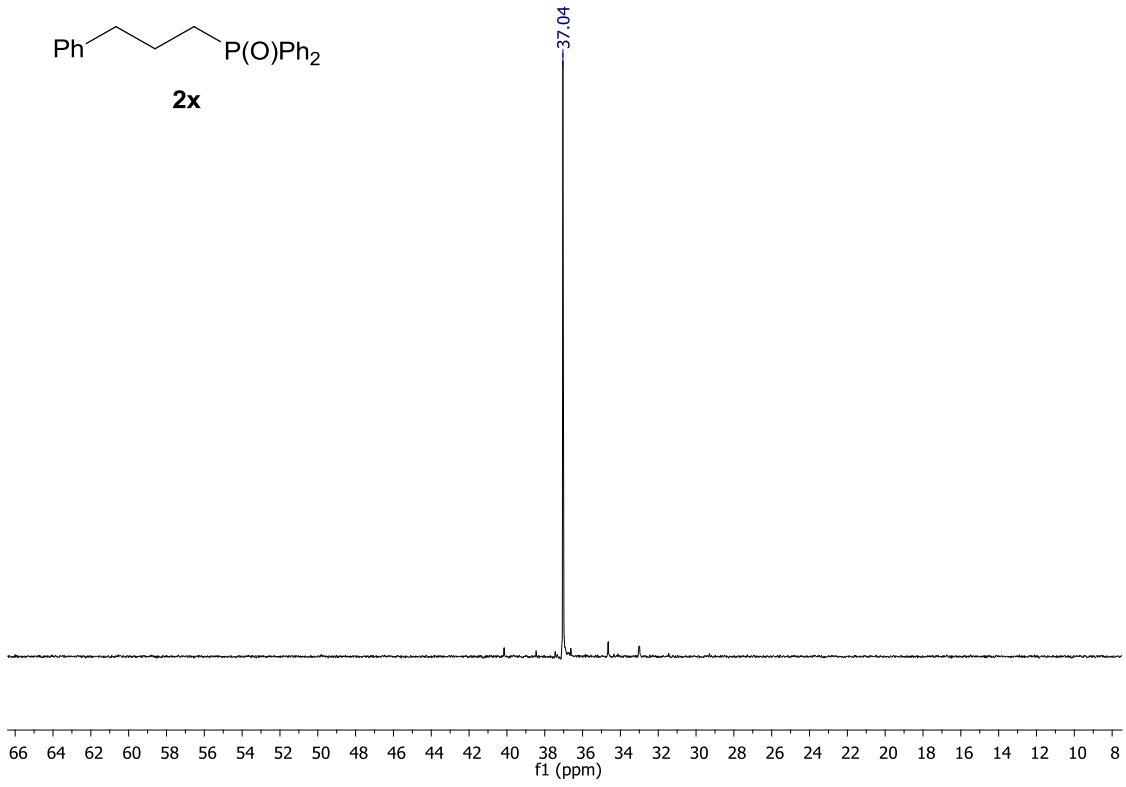
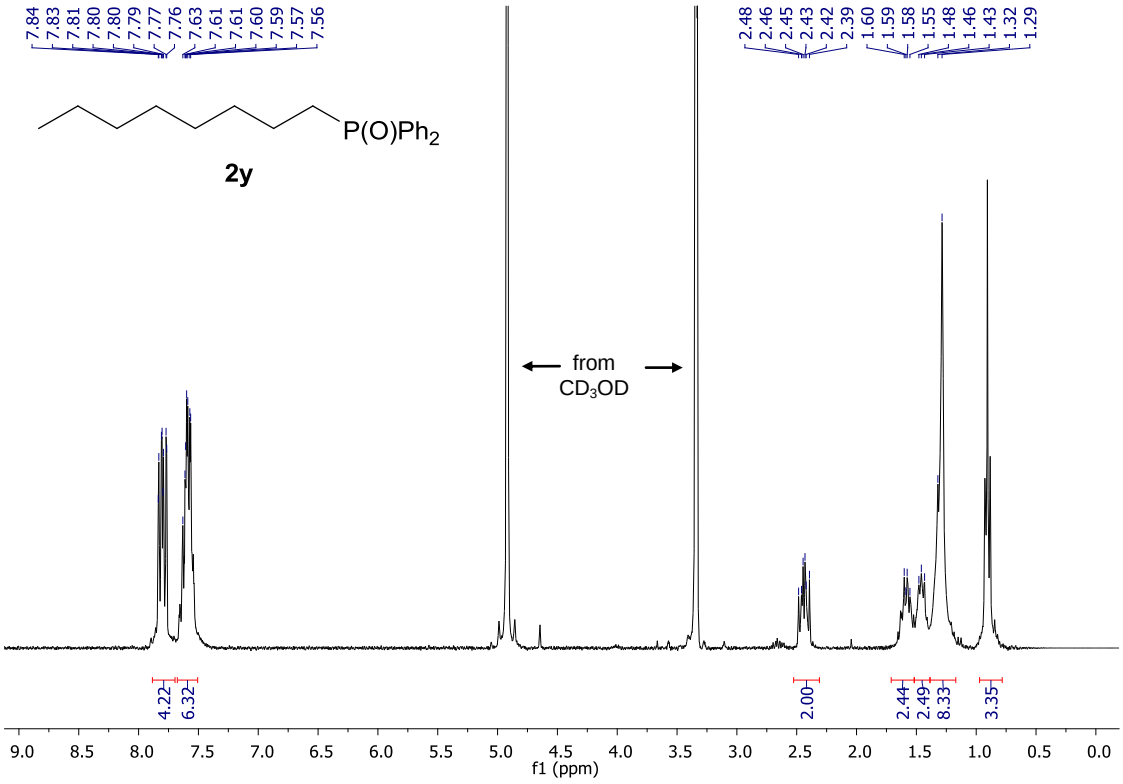
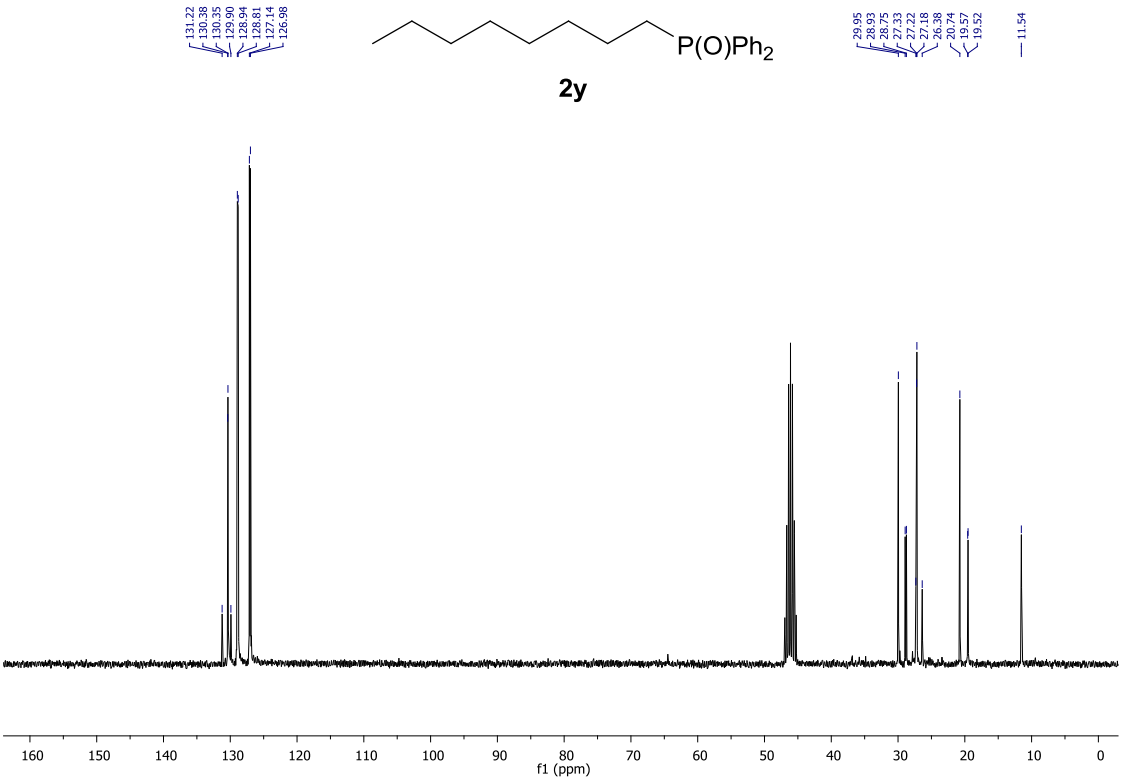
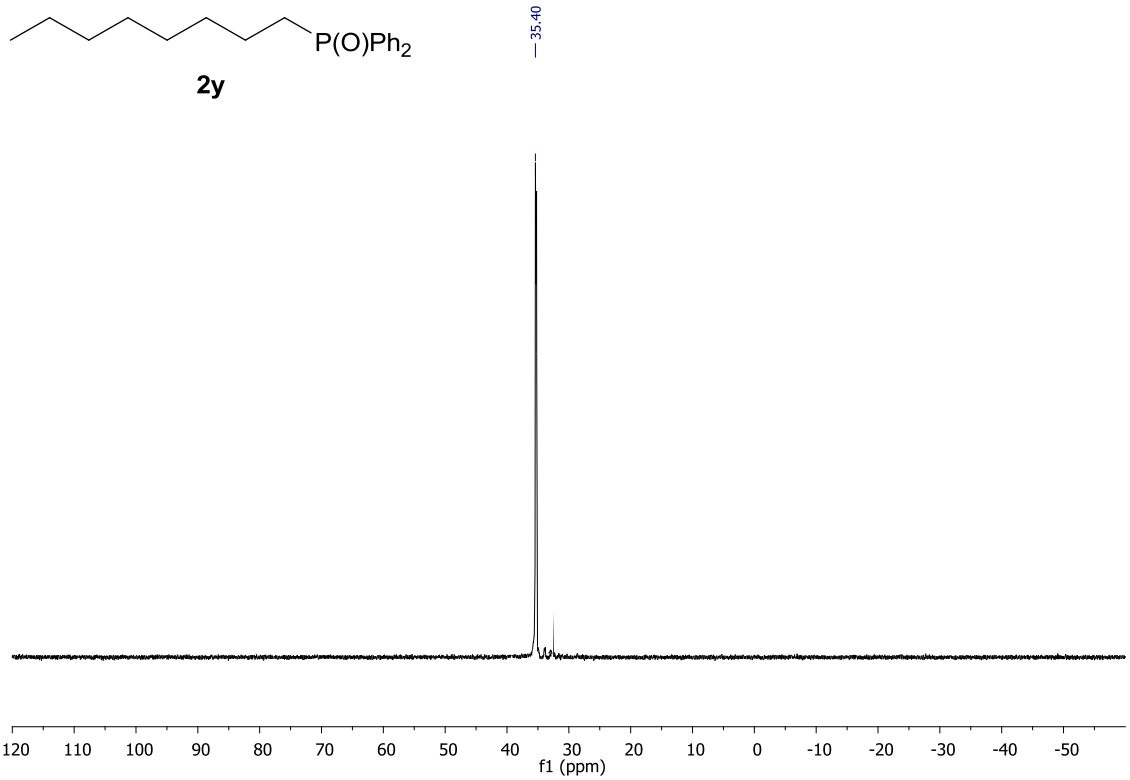
130.43
130.30
128.69
128.53
128.13
128.08
125.77
Ph
P(O)Ph2
2x
36.08
35.88
28.17
27.21
23.13
23.09
132.48
131.98
131.95
131.16
130.43
130.30
128.69
128.53
128.13
128.08
125.77
134
132
130
128
126
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

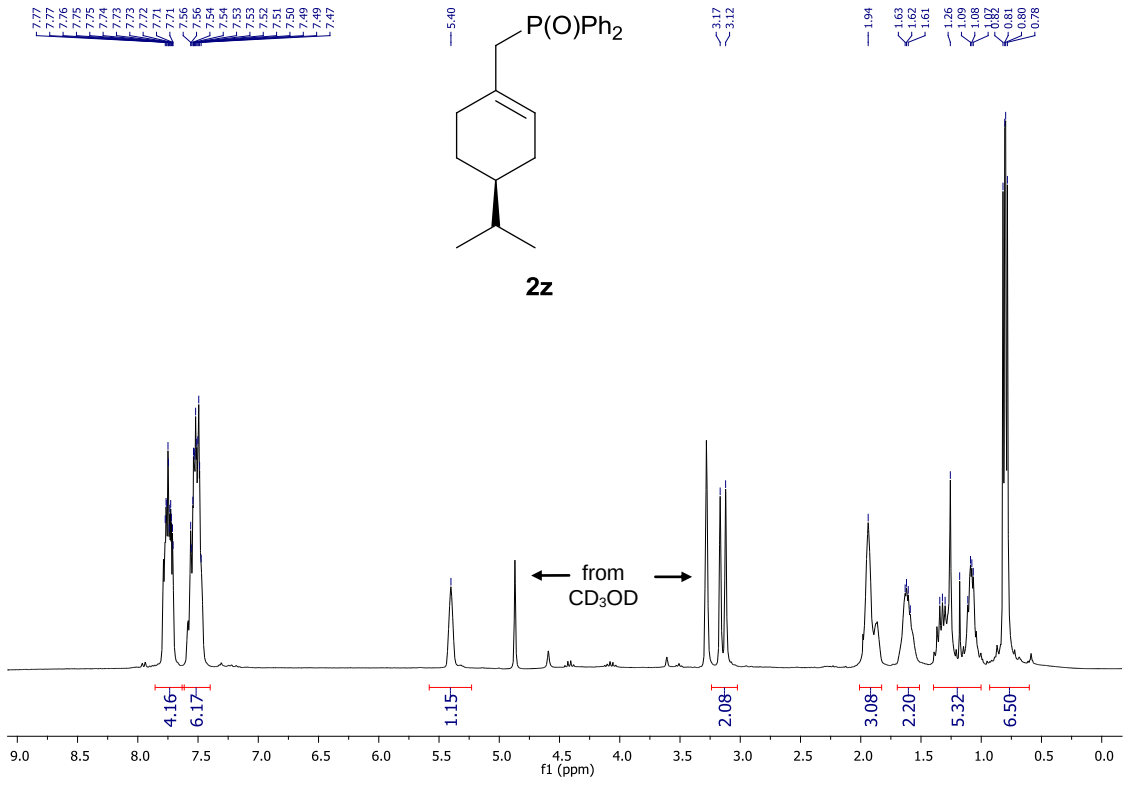

Ph
P(O)Ph2
2x
37.04
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
f1 (ppm)


7.84
7.83
7.81
7.80
7.80
7.79
7.77
7.76
7.63
7.61
7.61
7.60
7.59
7.57
7.56
2.48
2.46
2.45
2.43
2.42
2.39
1.60
1.59
1.58
1.55
1.48
1.46
1.43
1.32
1.29
P(O)Ph2
2y
from
CD3OD
4.22
6.32
2.00
2.44
2.49
8.33
3.35
f1 (ppm)

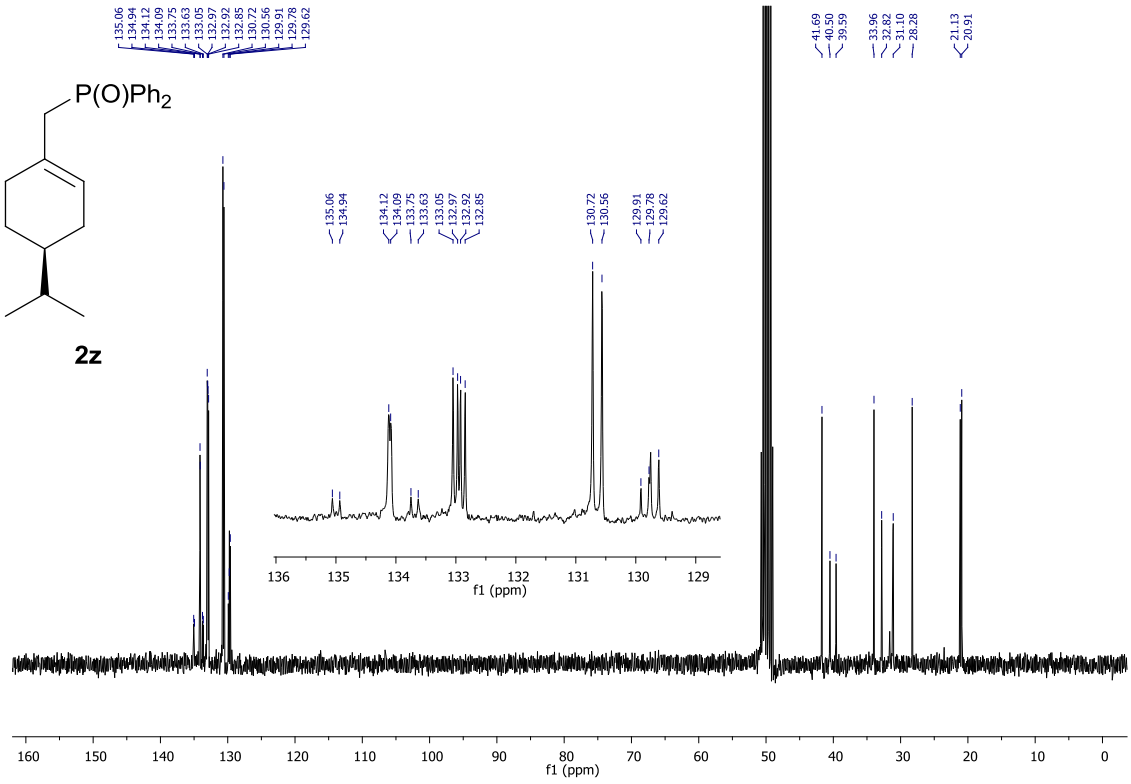

131.22
130.38
130.35
129.90
128.94
128.81
127.14
126.98
P(O)Ph2
2y
29.95
28.93
28.75
27.33
27.22
27.18
26.38
20.74
19.57
19.52
11.54
f1 (ppm)

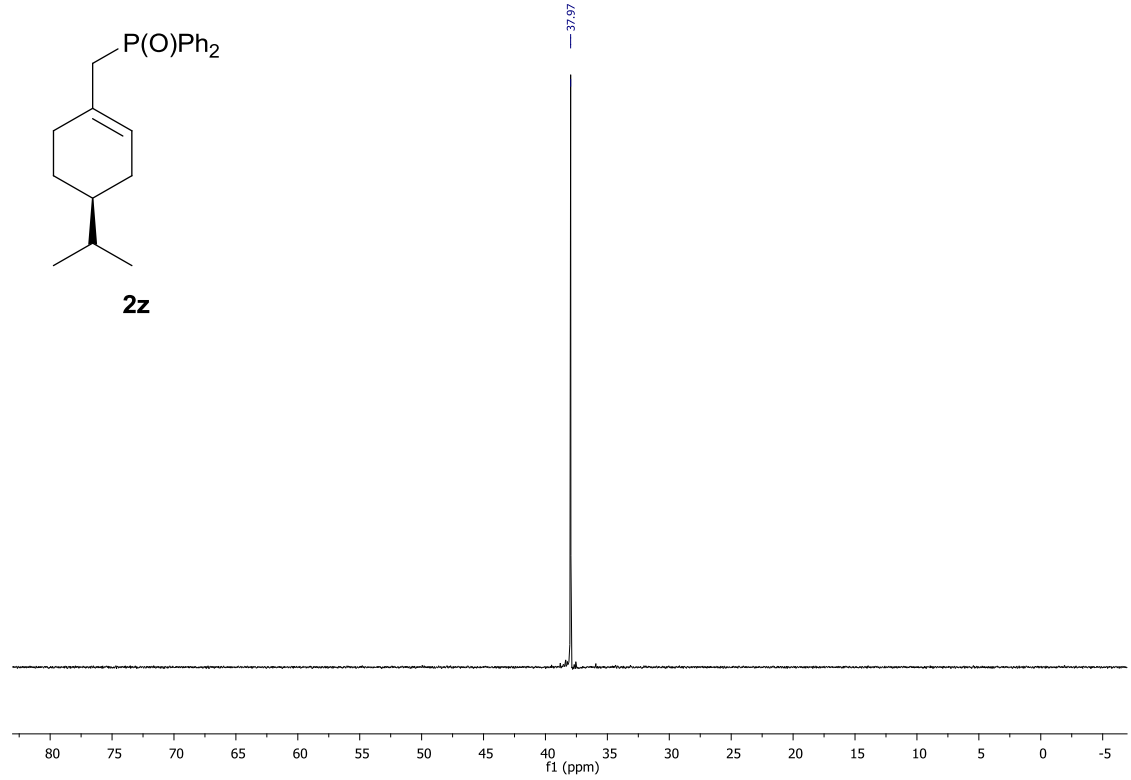

P(O)Ph2
35.40
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

2y

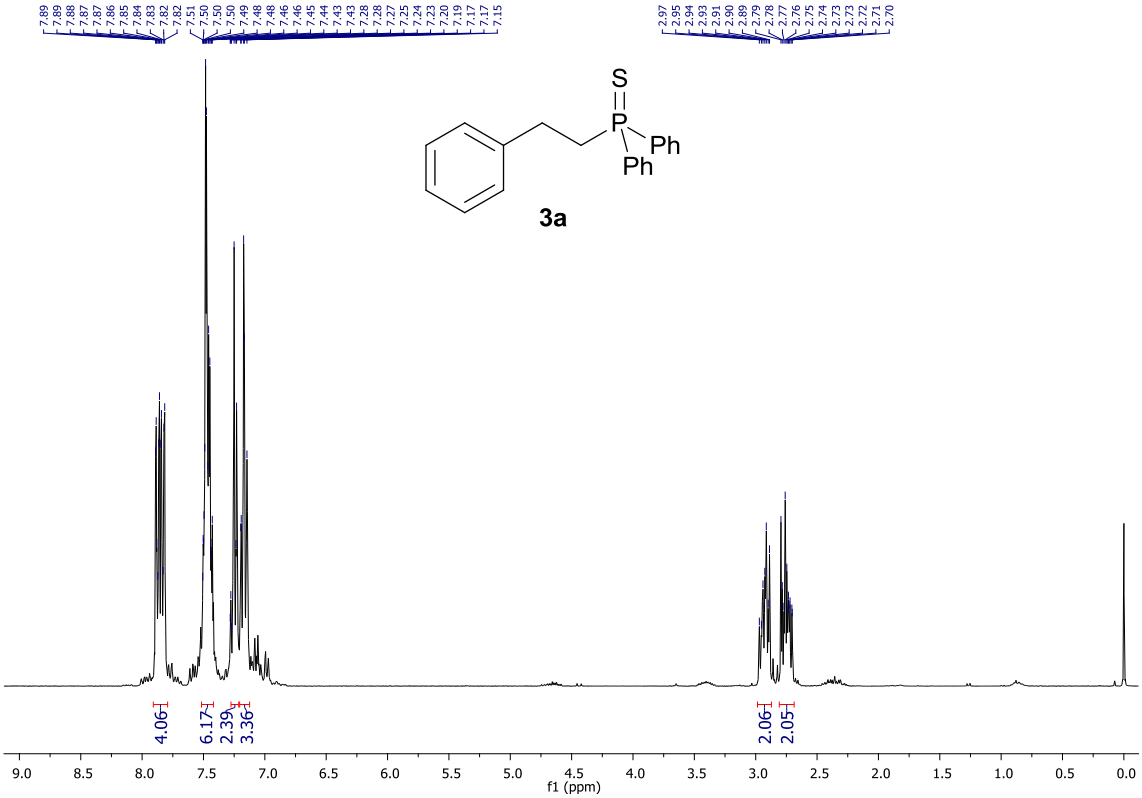

7.77 7.77 7.76 7.75 7.75 7.74 7.73 7.73 7.72 7.71 7.71 7.56 7.56 7.54 7.54 7.53 7.53 7.52 7.51 7.50 7.49 7.49 7.47
5.40
P(O)Ph2
3.17 3.12
1.94
1.63 1.62 1.61
1.26 1.09 1.08 1.07 0.82 0.81 0.80 0.78
from CD3OD
4.16 6.17 1.15 2.08 3.08 2.20 5.32 6.50
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

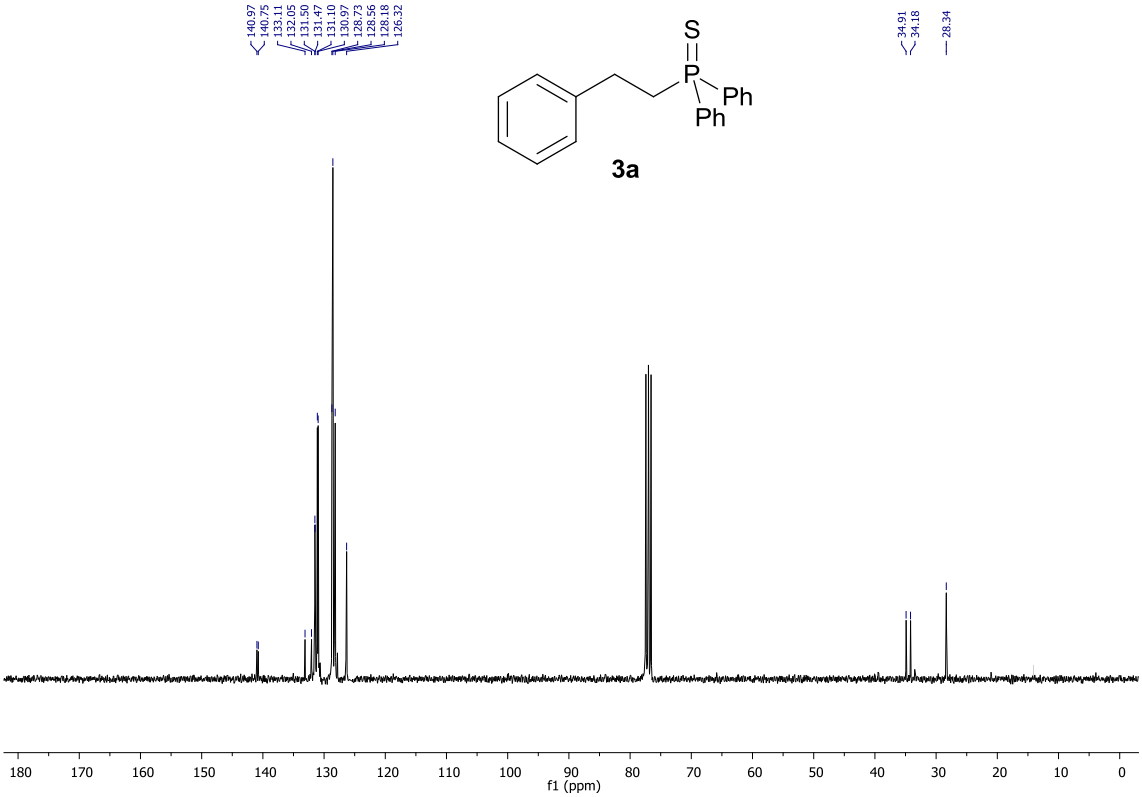
2z

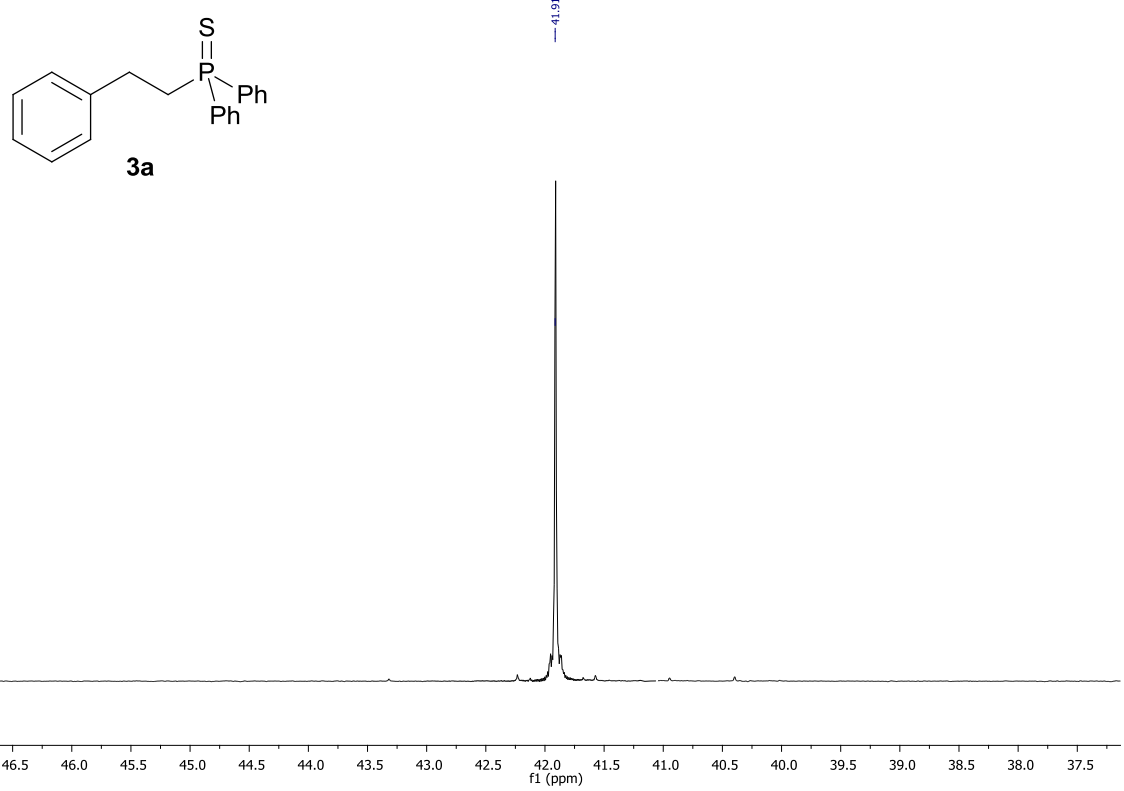

135.06
134.94
134.12
134.09
133.75
133.63
133.05
132.97
132.92
132.85
130.72
130.56
129.91
129.78
129.62
41.69
40.50
39.59
33.96
32.82
31.10
28.28
21.13
20.91
P(O)Ph2
2z
f1 (ppm)

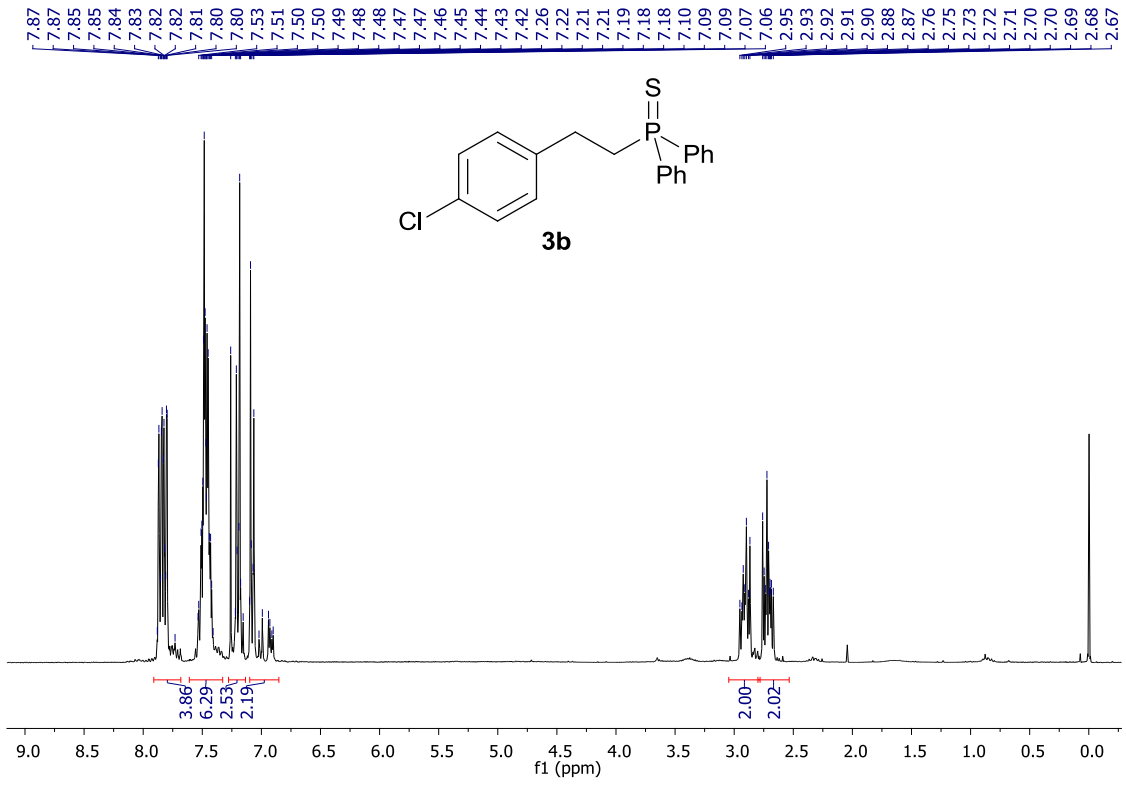

37.97
P(O)Ph2
2z
f1 (ppm)

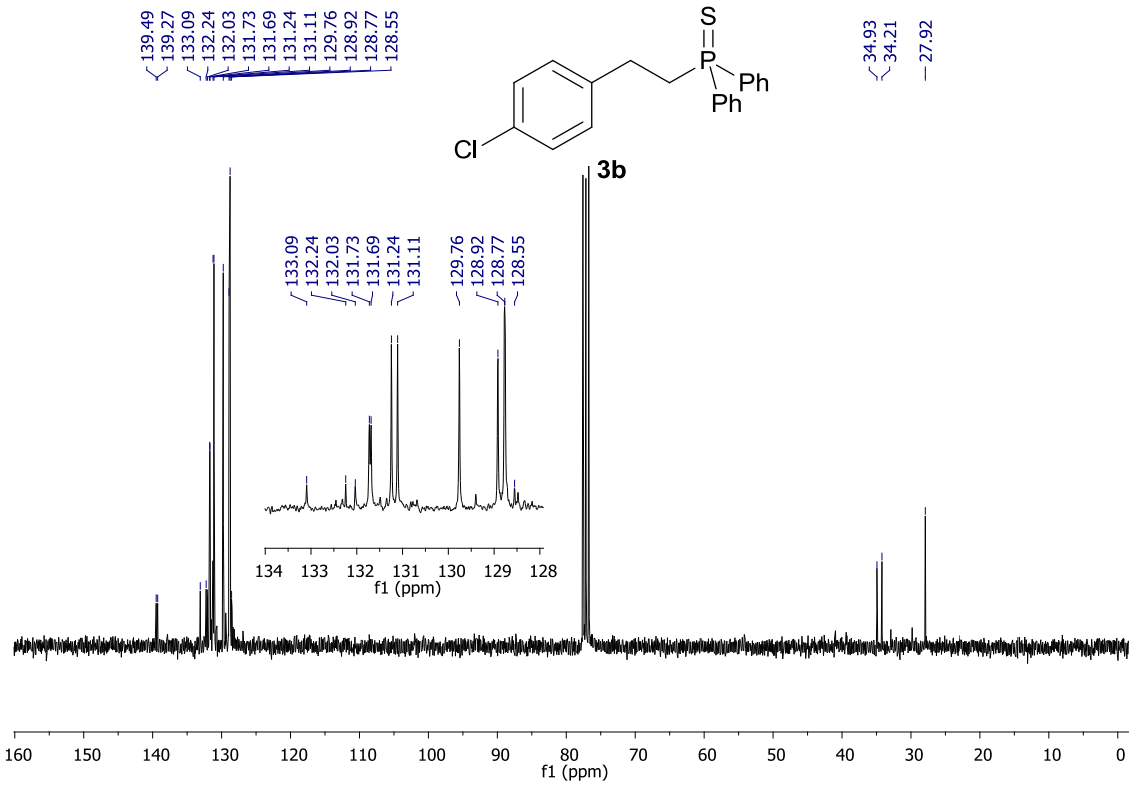
NMR spectra of compounds 3

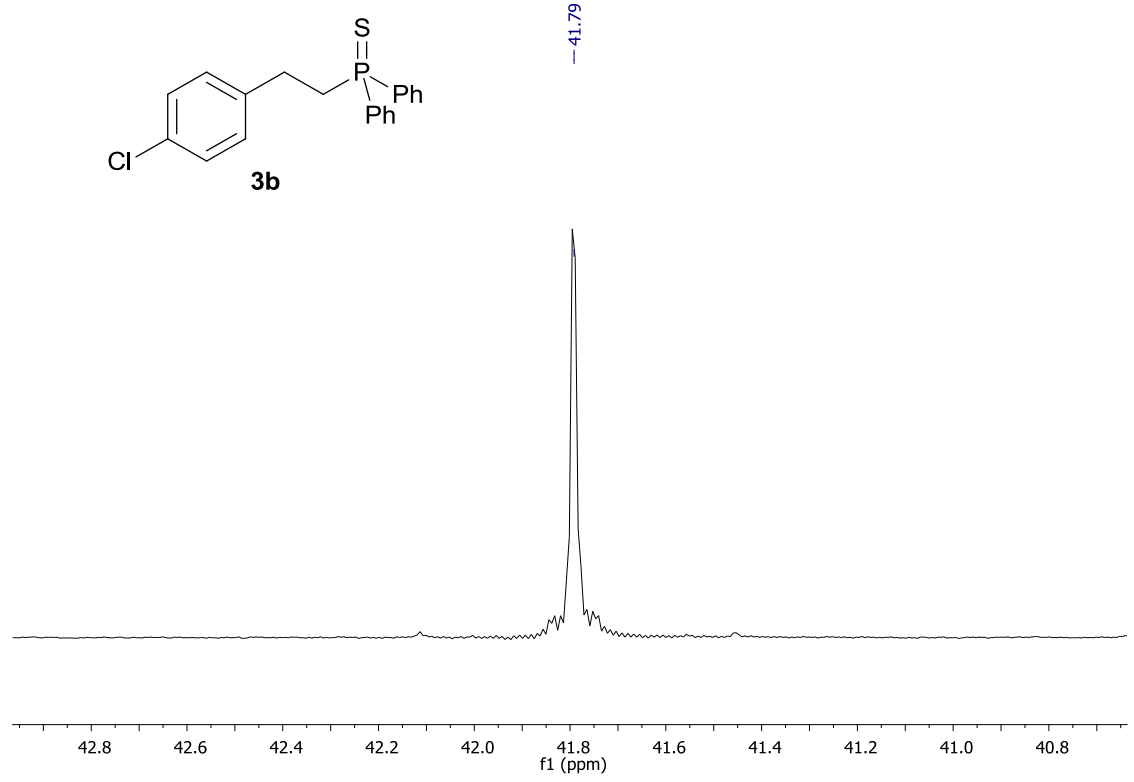


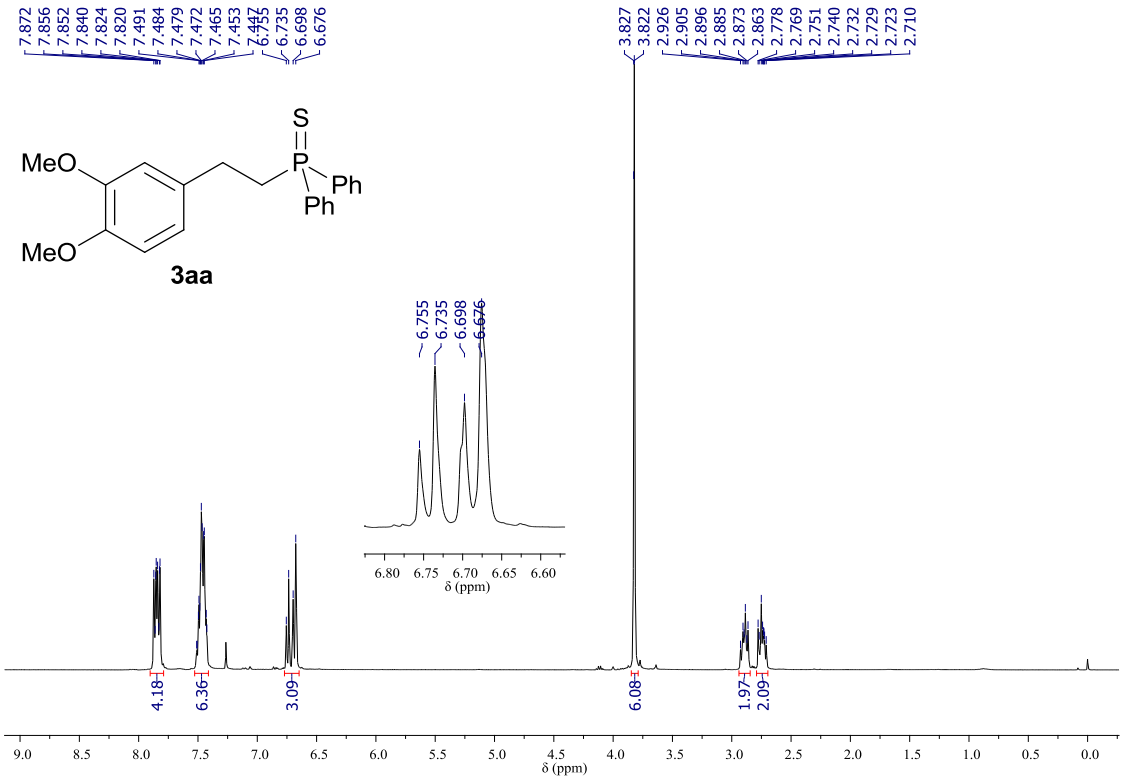


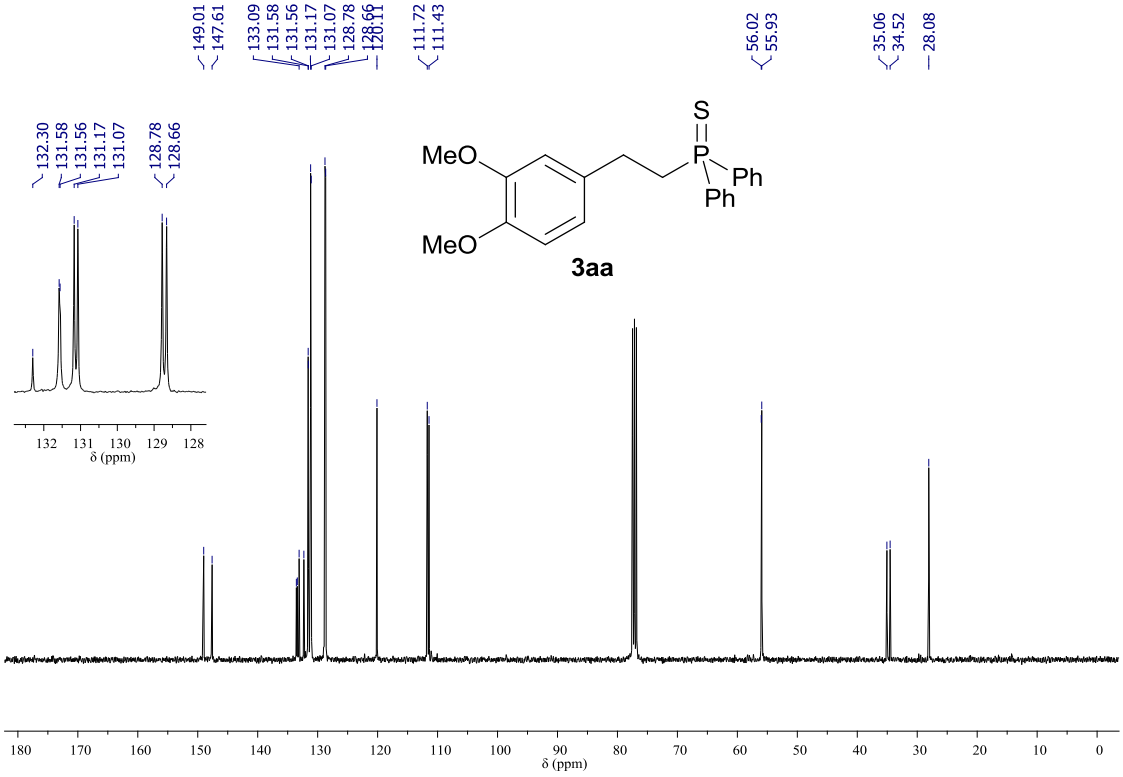

S
P
Ph
Ph
3a
41.91
46.5 46.0 45.5 45.0 44.5 44.0 43.5 43.0 42.5 42.0 41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5
f1 (ppm)

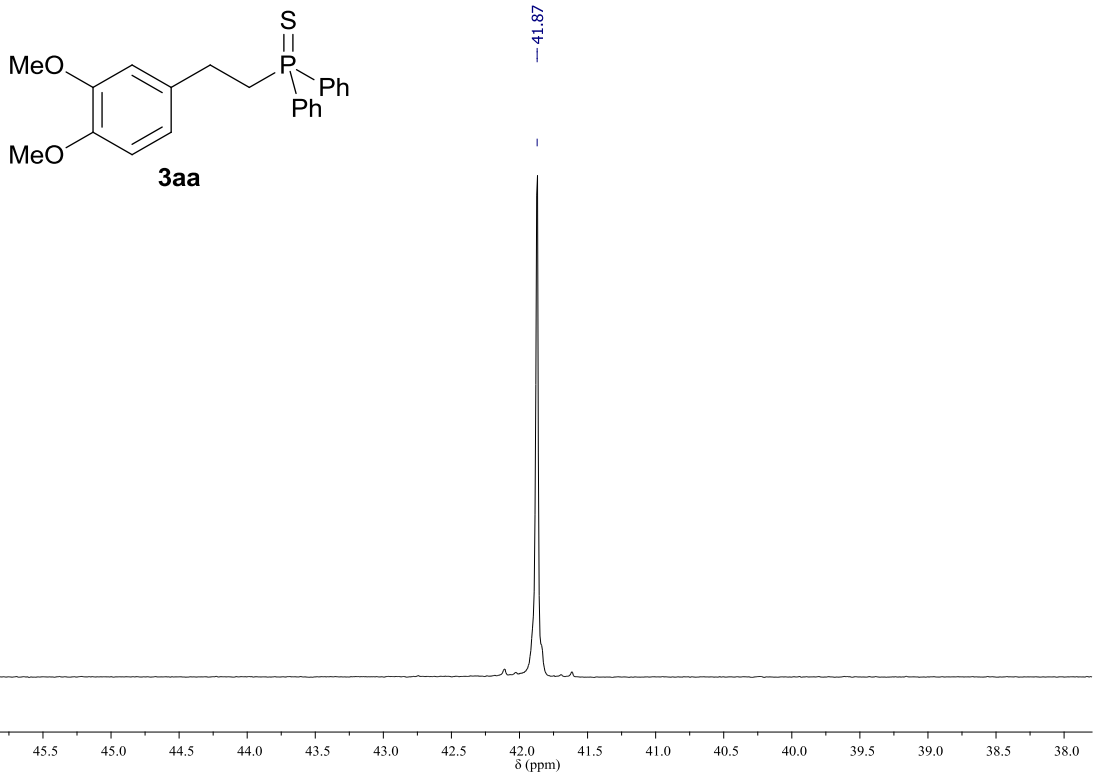

7.87 7.87 7.85 7.85 7.84 7.83 7.82 7.82 7.81 7.80 7.80 7.53 7.51 7.50 7.50 7.49 7.48 7.48 7.47 7.47 7.46 7.45 7.44 7.43 7.42 7.26 7.22 7.21 7.21 7.19 7.18 7.18 7.10 7.09 7.09 7.07 7.06 2.95 2.93 2.92 2.91 2.90 2.88 2.87 2.76 2.75 2.73 2.72 2.71 2.70 2.70 2.69 2.68 2.67
S
P
Ph
Ph
Cl
3b
3.86 6.29 2.53 2.19 2.00 2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

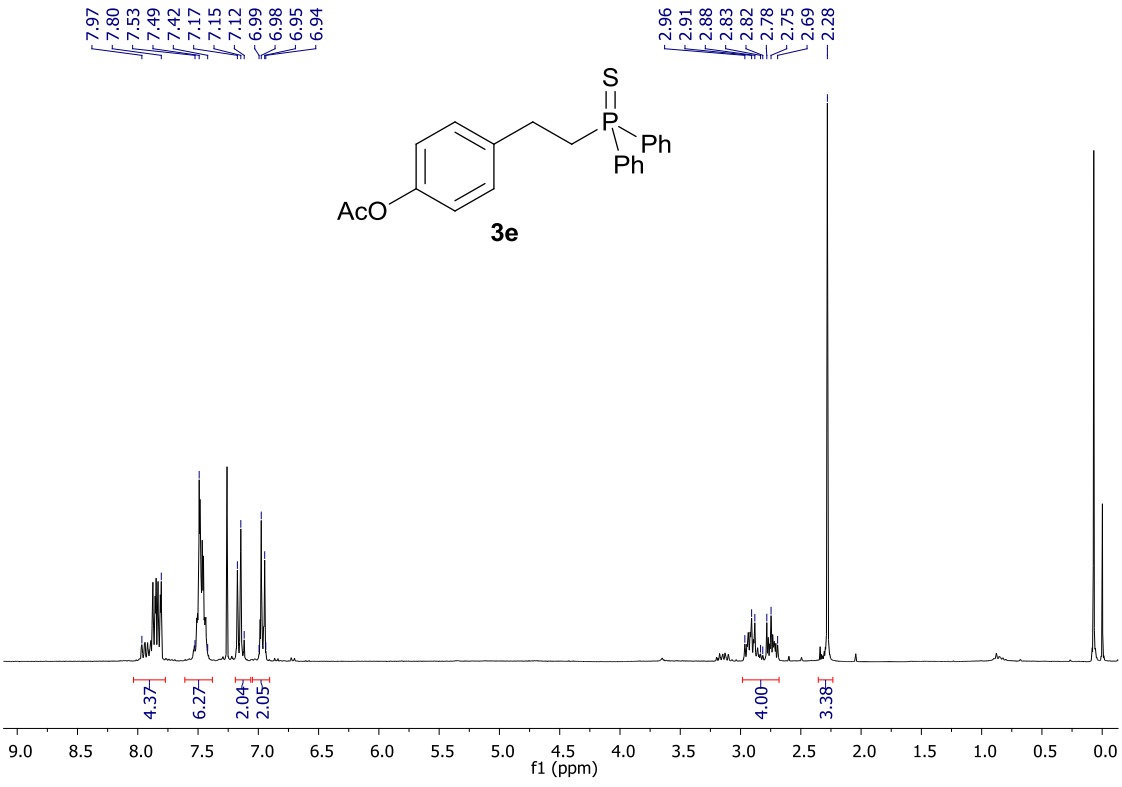

139.49
139.27
133.09
132.24
132.03
131.73
131.69
131.24
131.11
129.76
128.92
128.77
128.55
34.93
34.21
27.92
S
P
Ph
Ph
Cl
3b
133.09
132.24
132.03
131.73
131.69
131.24
131.11
129.76
128.92
128.77
128.55
134 133 132 131 130 129 128
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

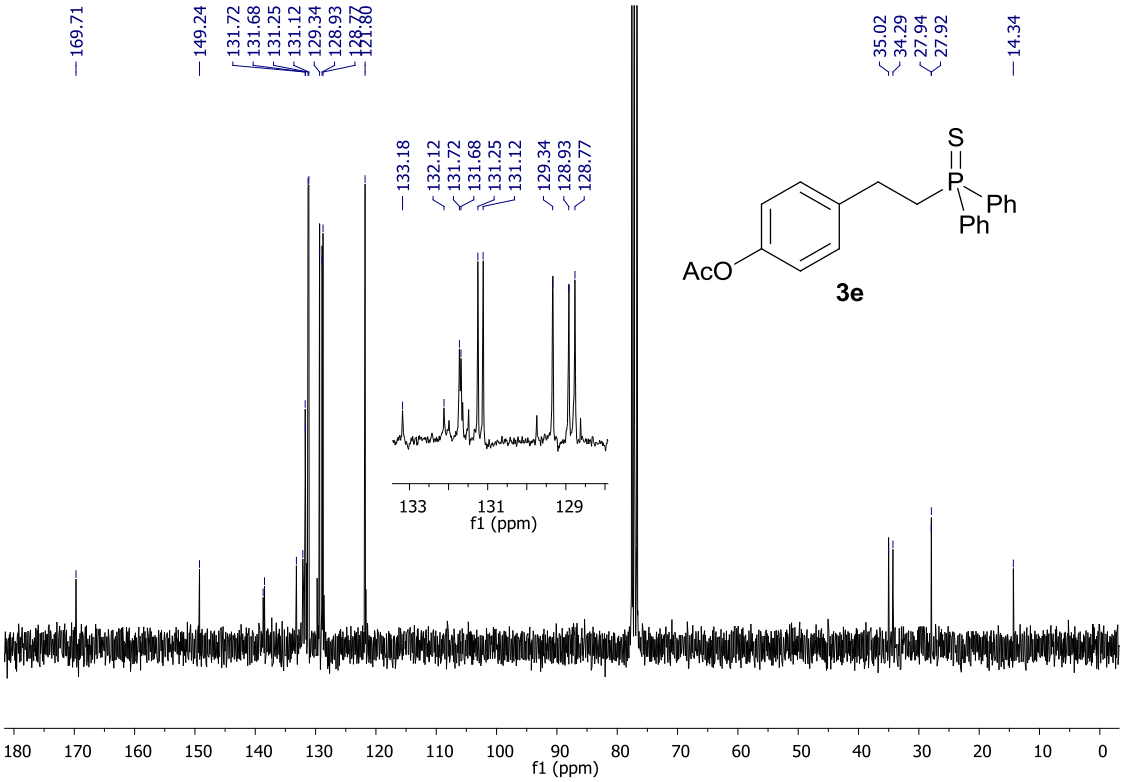

S
P
Ph
Ph
Cl
3b
41.79
42.8 42.6 42.4 42.2 42.0 41.8 41.6 41.4 41.2 41.0 40.8
f1 (ppm)

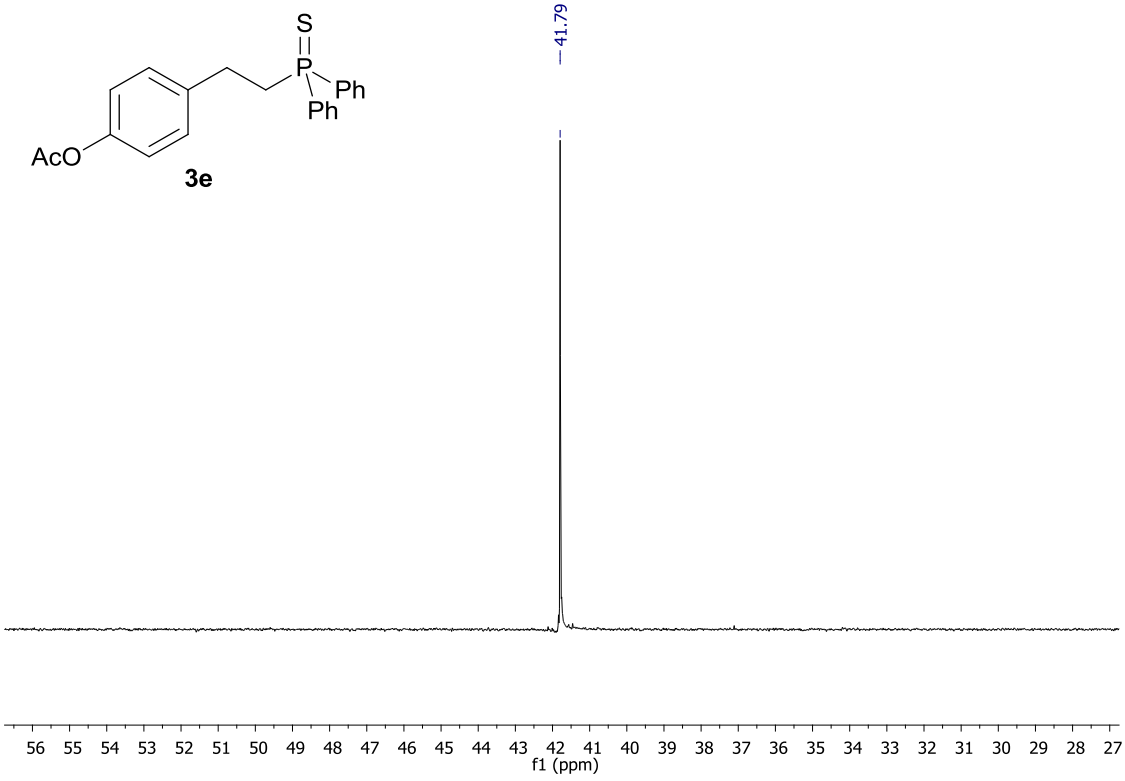

7.872
7.856
7.852
7.840
7.824
7.820
7.491
7.484
7.479
7.472
7.465
7.453
6.735
6.698
6.676
3.827
3.822
2.926
2.905
2.896
2.885
2.873
2.863
2.778
2.769
2.751
2.740
2.732
2.729
2.723
2.710
MeO
MeO
S
P
Ph
Ph
3aa
6.755
6.735
6.698
6.676
6.80 6.75 6.70 6.65 6.60
δ (ppm)
4.18
6.36
3.09
6.08
1.97
2.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

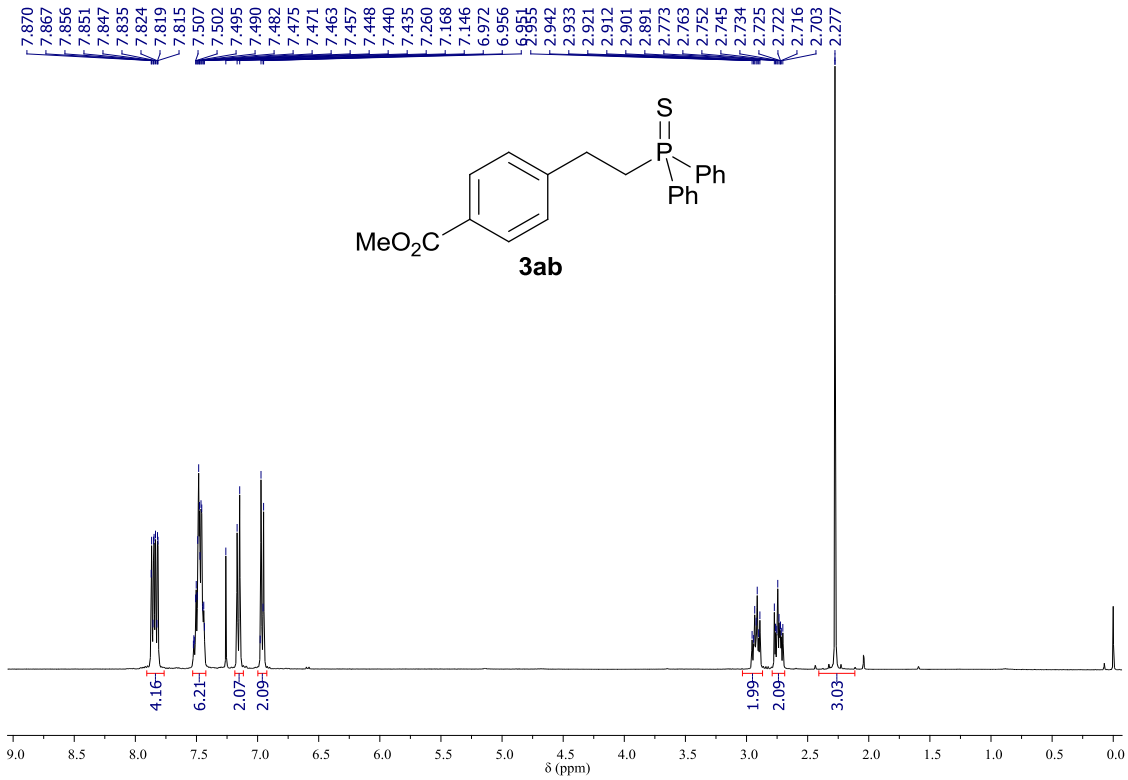

149.01
147.61
133.09
131.58
131.56
131.17
131.07
128.78
128.66
120.11
111.72
111.43
56.02
55.93
35.06
34.52
28.08
132.30
131.58
131.56
131.17
131.07
128.78
128.66
132 131 130 129 128
δ (ppm)
MeO
MeO
S
P
Ph
Ph
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

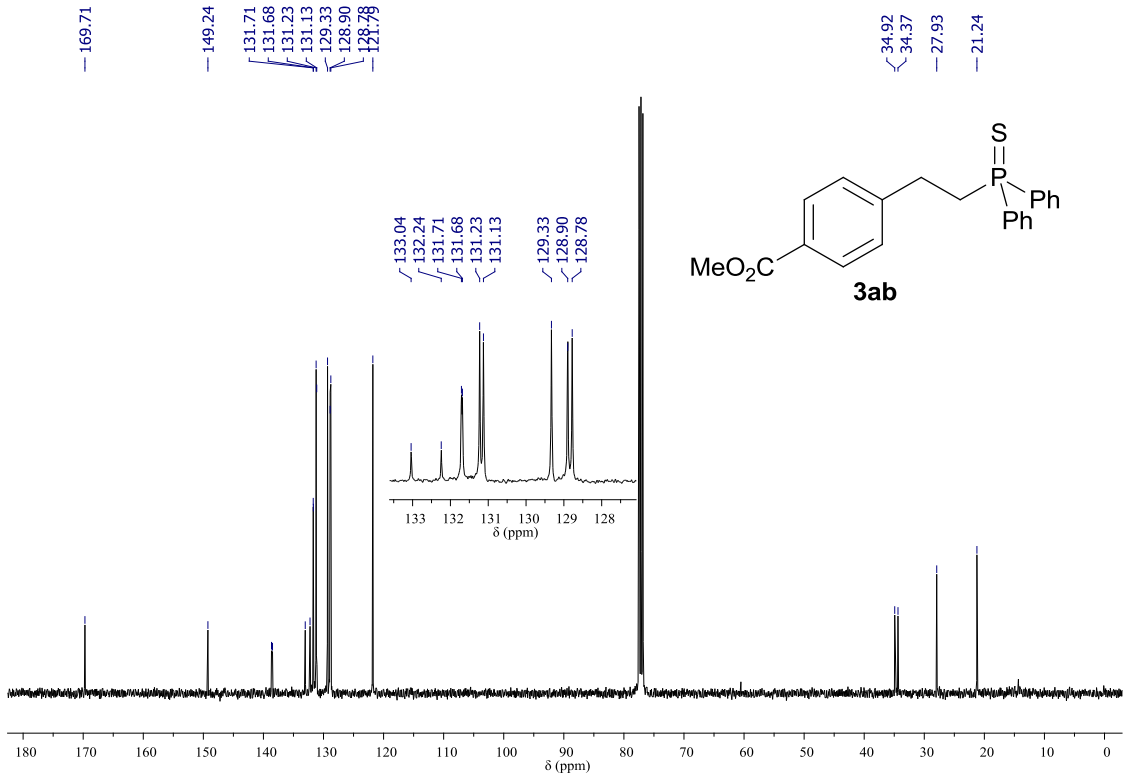

MeO
MeO
S
P
Ph
Ph
3aa
41.87
45.5
45.0
44.5
44.0
43.5
43.0
42.5
42.0
41.5
41.0
40.5
40.0
39.5
39.0
38.5
38.0
δ (ppm)

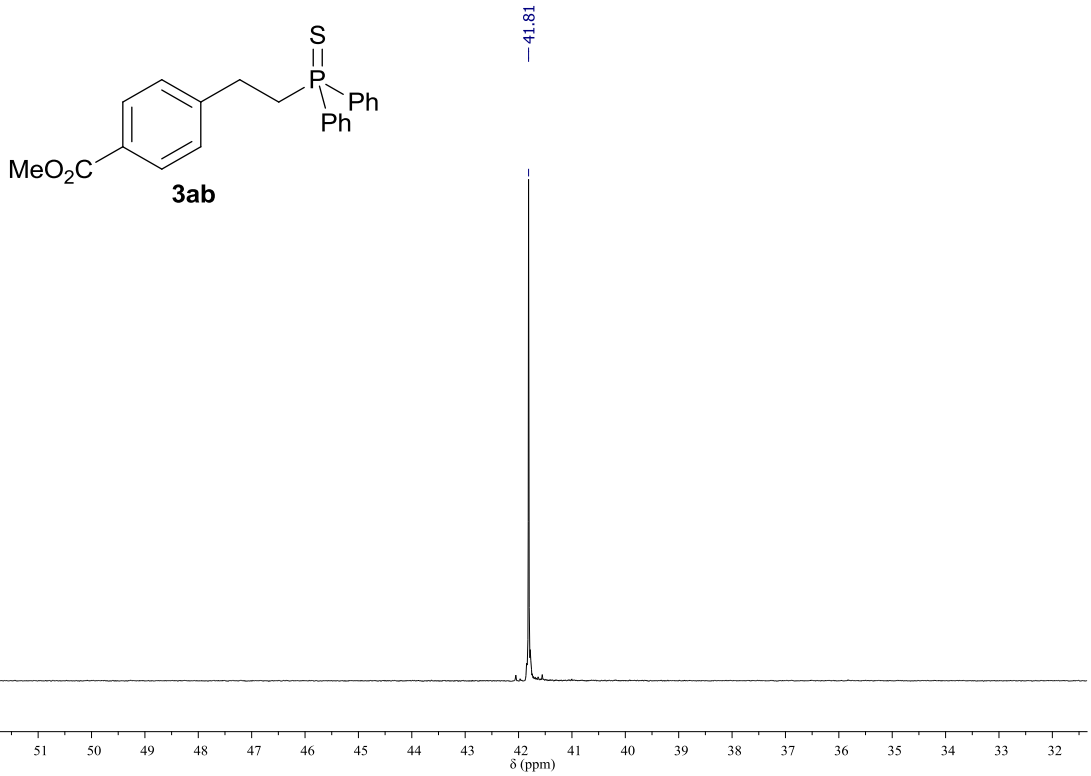

7.97
7.80
7.53
7.49
7.42
7.17
7.15
7.12
6.99
6.98
6.95
6.94
2.96
2.91
2.88
2.83
2.82
2.78
2.75
2.69
2.28
AcO
S
P
Ph
Ph
3e
4.37
6.27
2.04
2.05
4.00
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

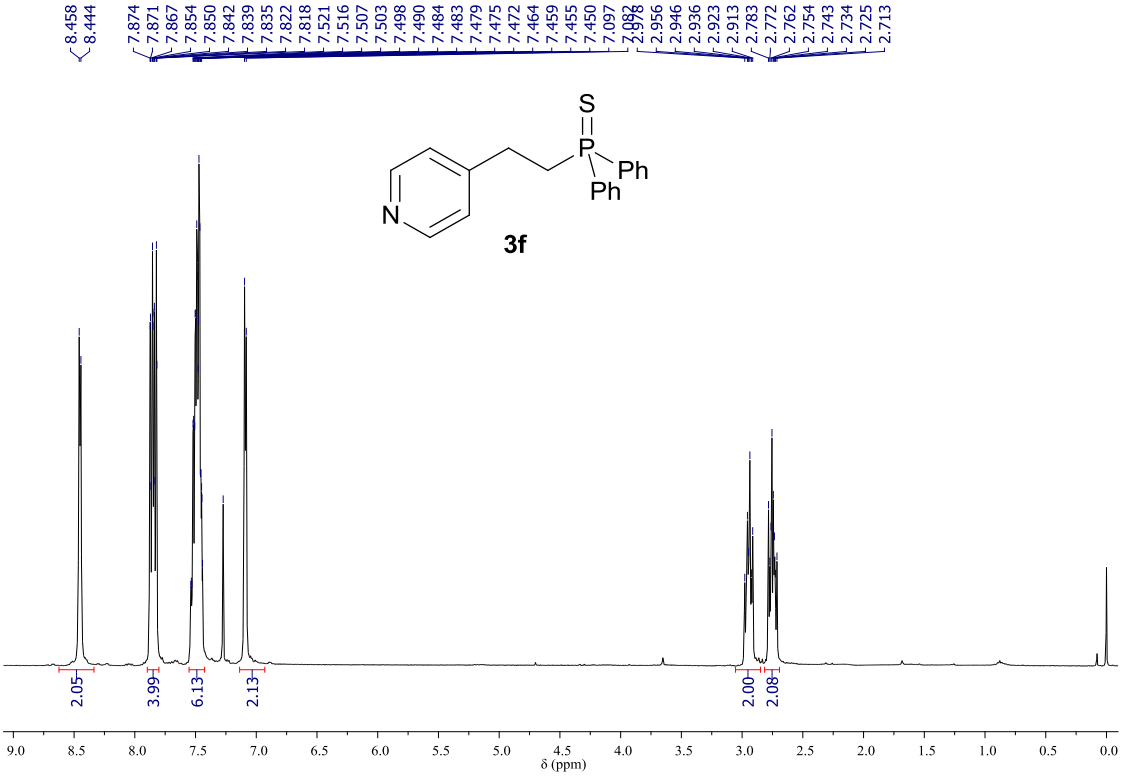

169.71
149.24
131.72
131.68
131.25
131.12
129.34
128.93
128.77
121.80
35.02
34.29
27.94
27.92
14.34
133.18
132.12
131.72
131.68
131.25
131.12
129.34
128.93
128.77
133
131
129
f1 (ppm)
S
P
Ph
Ph
AcO
3e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

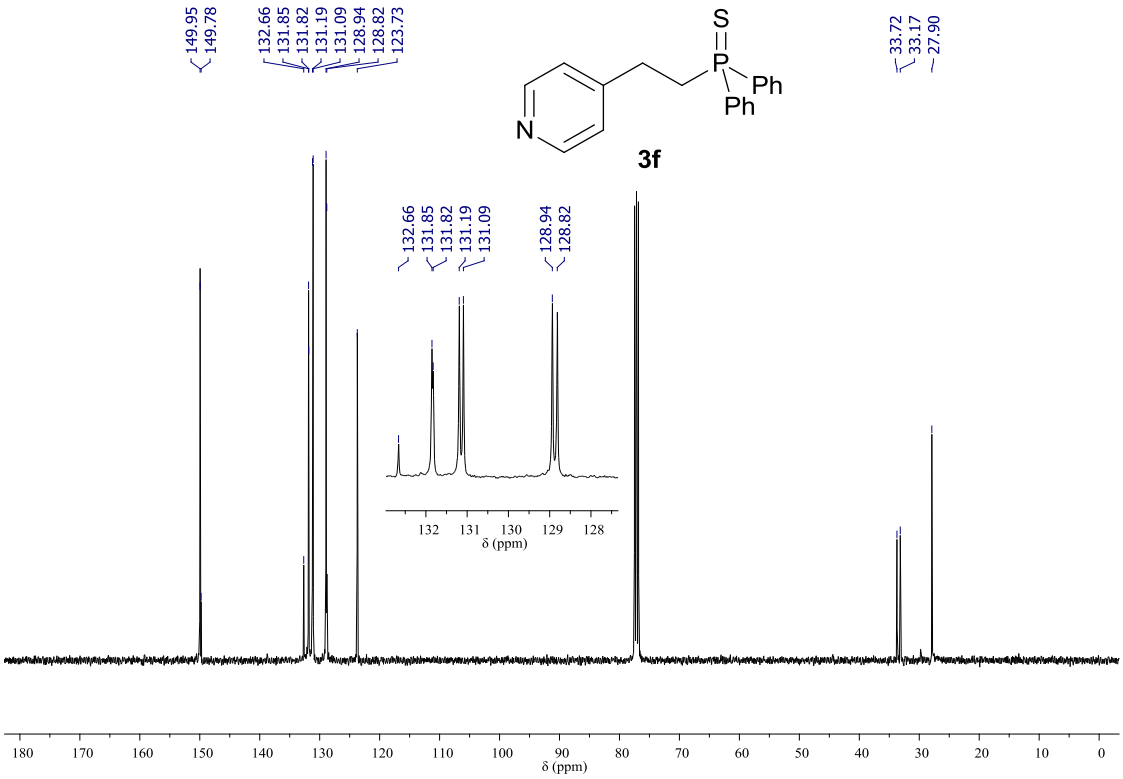

S
P
Ph
Ph
AcO
3e
41.79
56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27
f1 (ppm)

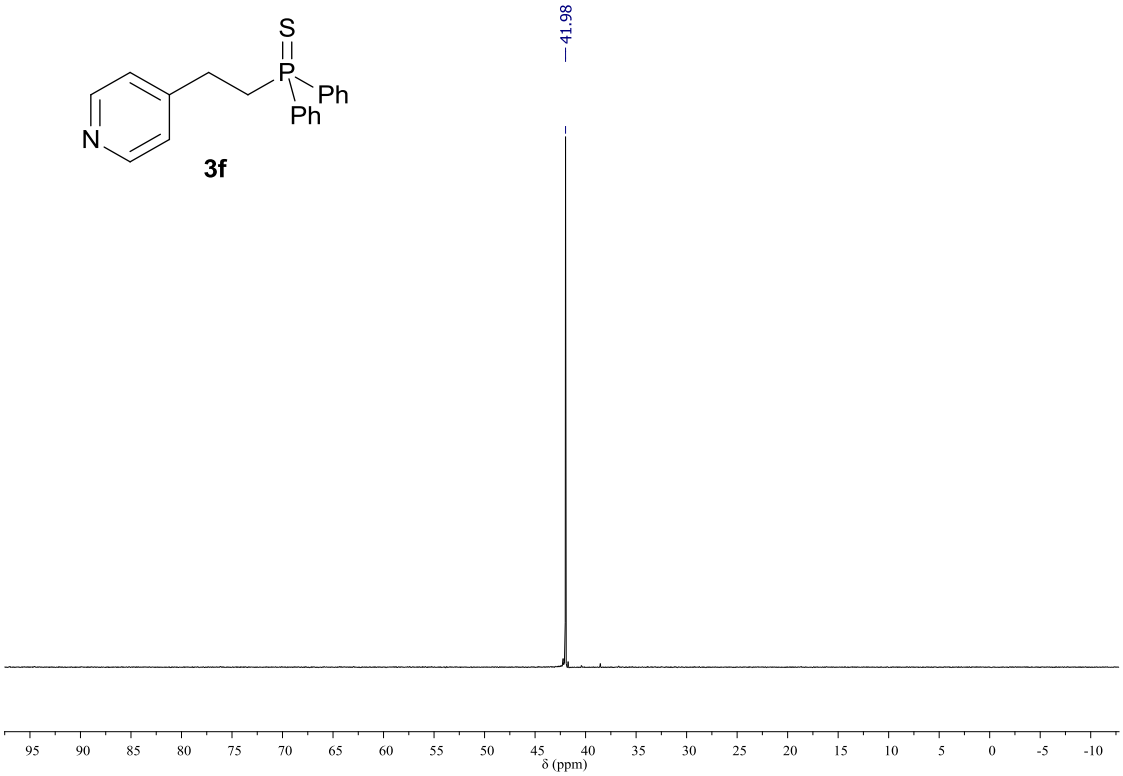

7.870
7.867
7.856
7.851
7.847
7.835
7.824
7.819
7.815
7.507
7.502
7.495
7.490
7.482
7.475
7.471
7.463
7.457
7.448
7.440
7.435
7.260
7.168
7.146
6.972
6.956
6.951
2.955
2.942
2.933
2.921
2.912
2.901
2.891
2.773
2.763
2.752
2.745
2.734
2.725
2.722
2.716
2.703
2.277
S
P
Ph
Ph
MeO2C
3ab
4.16
6.21
2.07
2.09
1.99
2.09
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

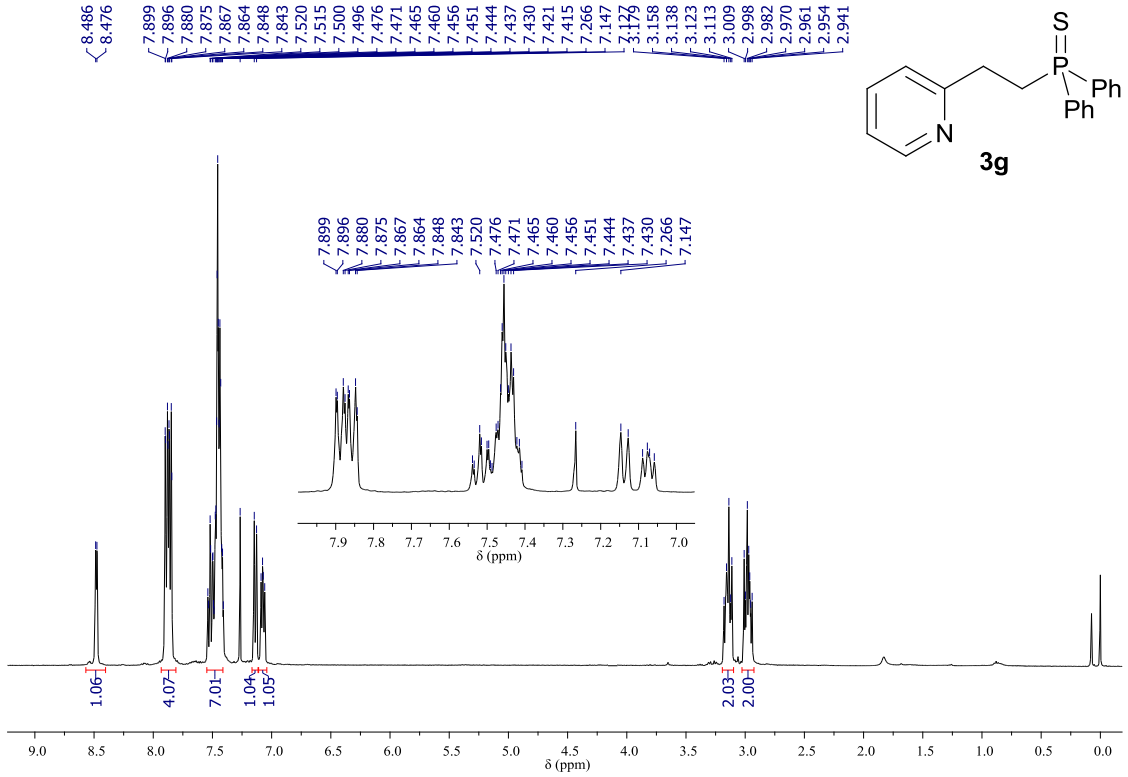

169.71
149.24
131.71
131.68
131.23
131.13
129.33
128.90
128.78
121.79
34.92
34.37
27.93
21.24
133.04
132.24
131.71
131.68
131.23
131.13
129.33
128.90
128.78
133
132
131
130
129
128
δ (ppm)
S
P
Ph
Ph
MeO2C
3ab
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

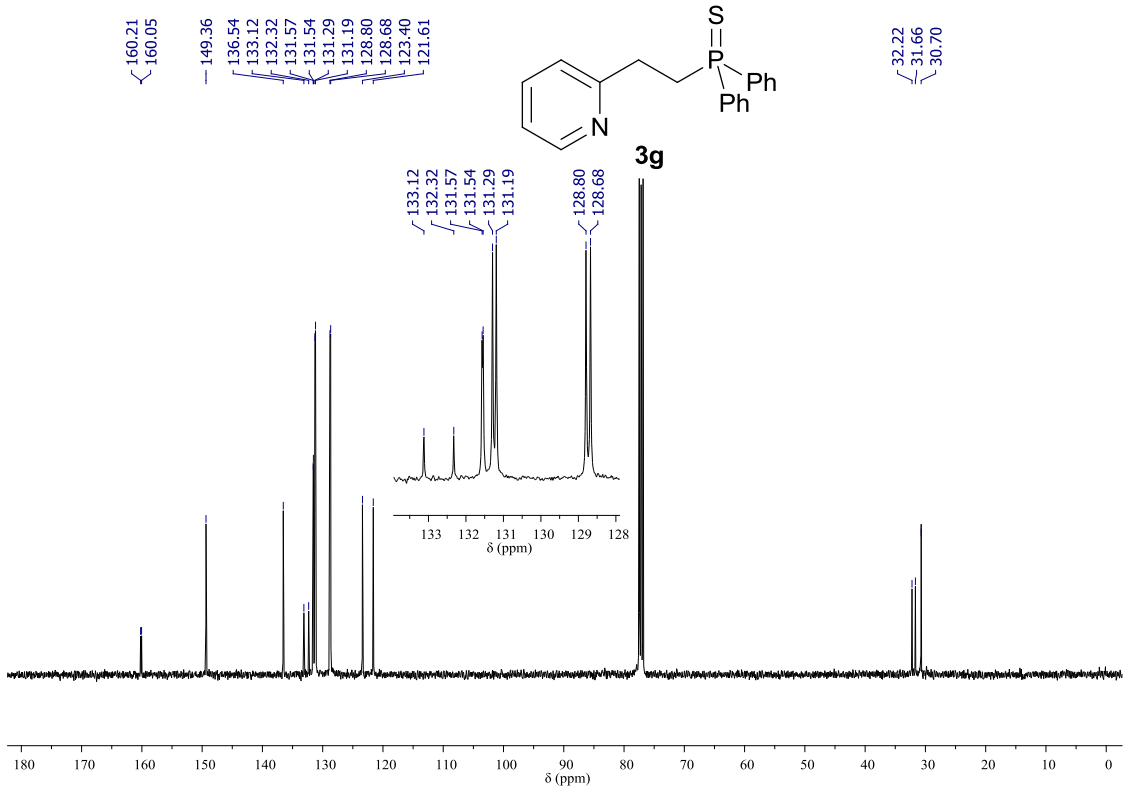

S
P
Ph
Ph
MeO2C
3ab
41.81
52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32
δ (ppm)

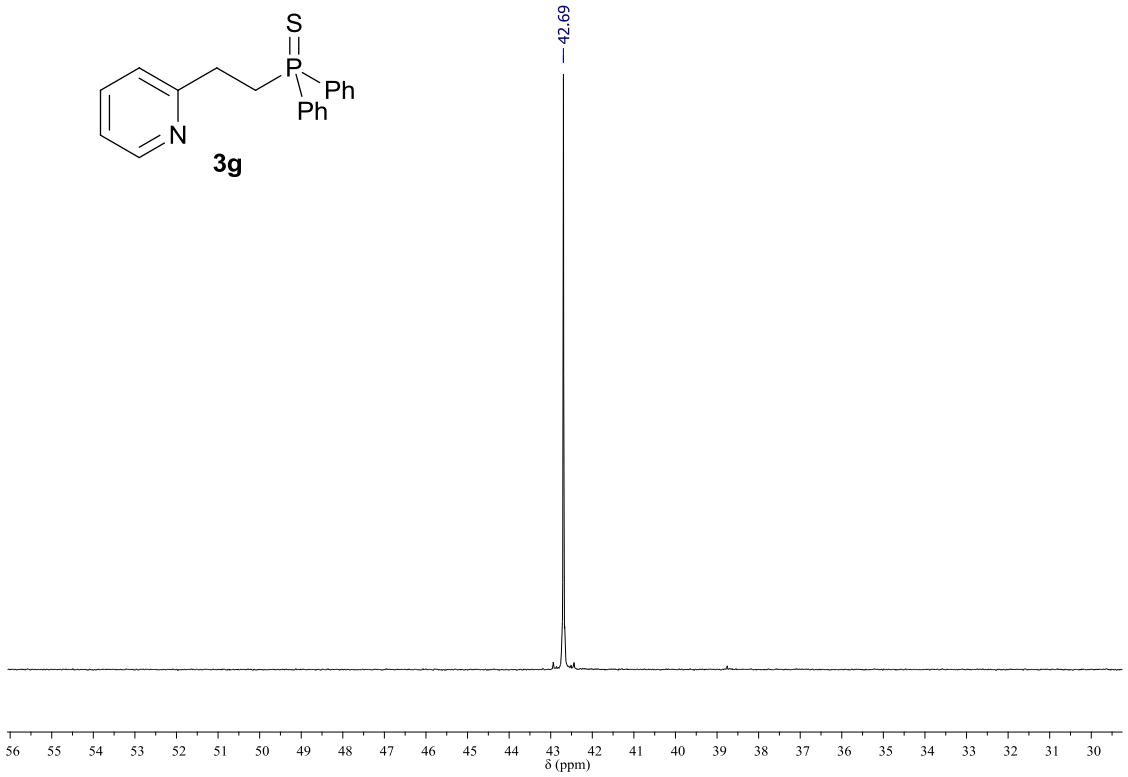

8.458
8.444
7.874
7.871
7.867
7.854
7.850
7.842
7.839
7.835
7.822
7.818
7.521
7.516
7.507
7.503
7.498
7.490
7.484
7.483
7.479
7.475
7.472
7.464
7.459
7.455
7.450
7.097
2.956
2.946
2.936
2.923
2.913
2.783
2.772
2.762
2.754
2.743
2.734
2.725
2.713
S
P
Ph
Ph
N
3f
2.05
3.99
6.13
2.13
2.00
2.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

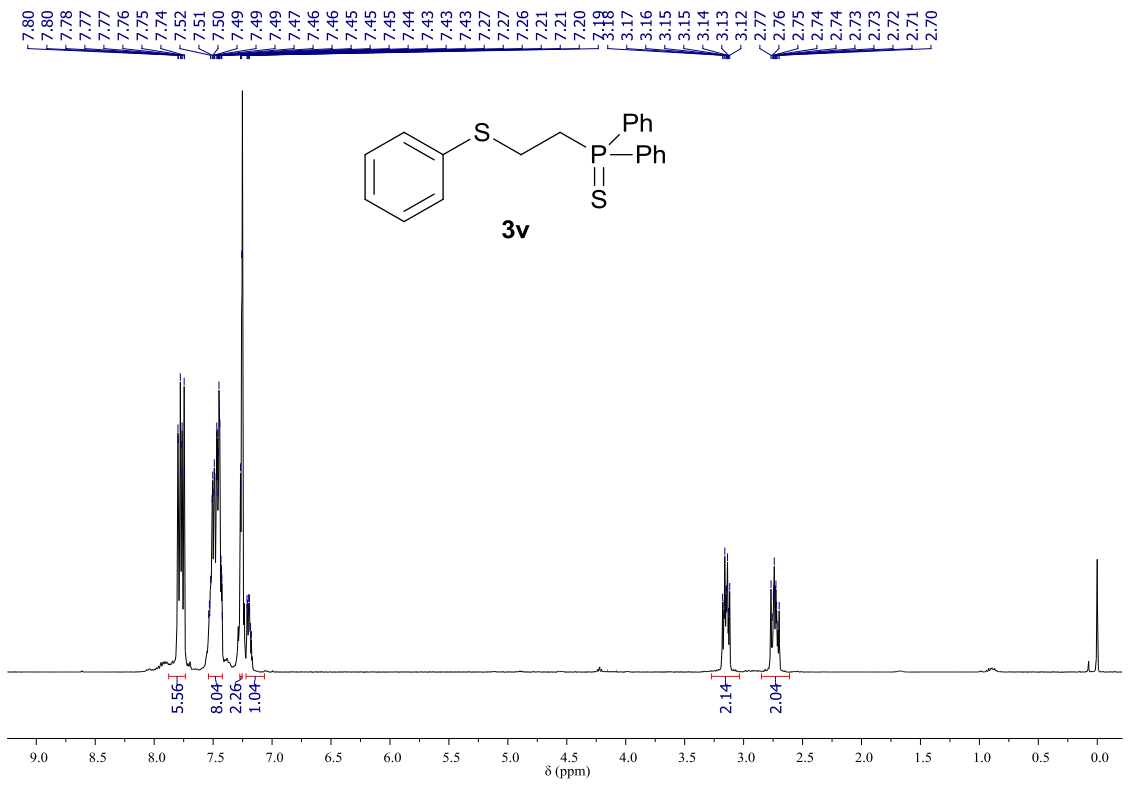

149.95
149.78
132.66
131.85
131.82
131.19
131.09
128.94
128.82
123.73
33.72
33.17
27.90
S
P
Ph
Ph
N
3f
δ (ppm)

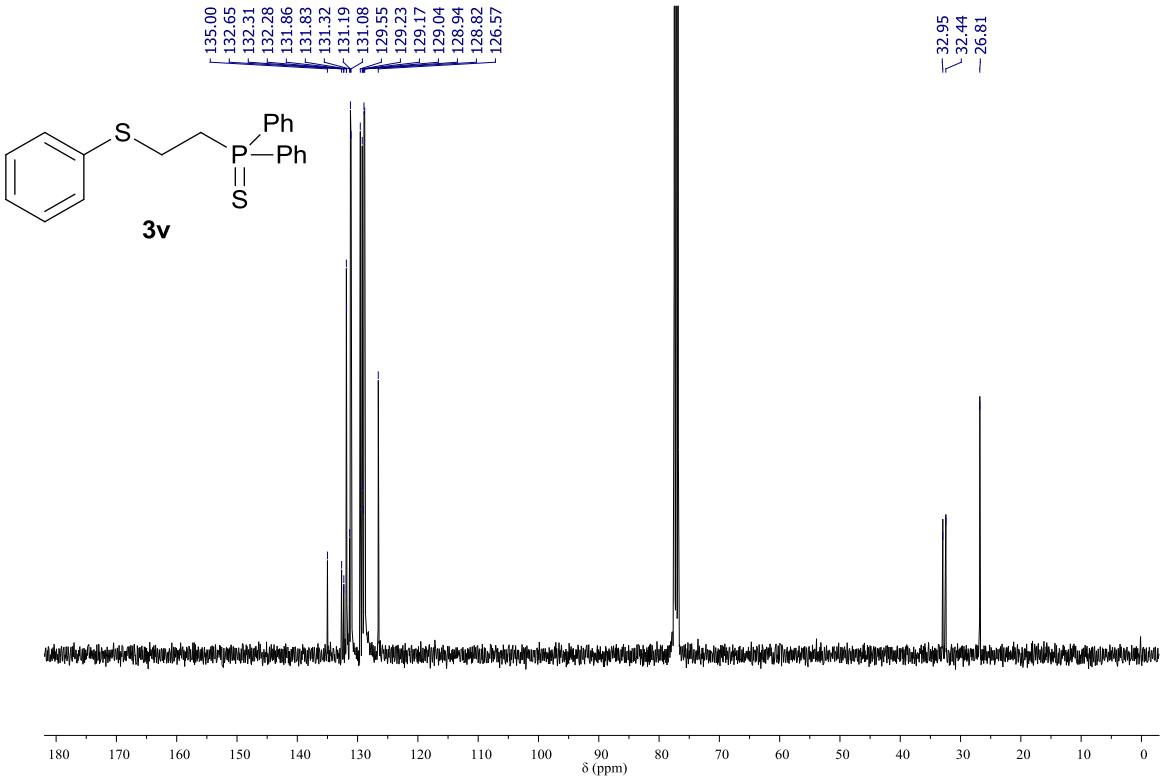

41.98
S
P
Ph
Ph
N
3f
δ (ppm)

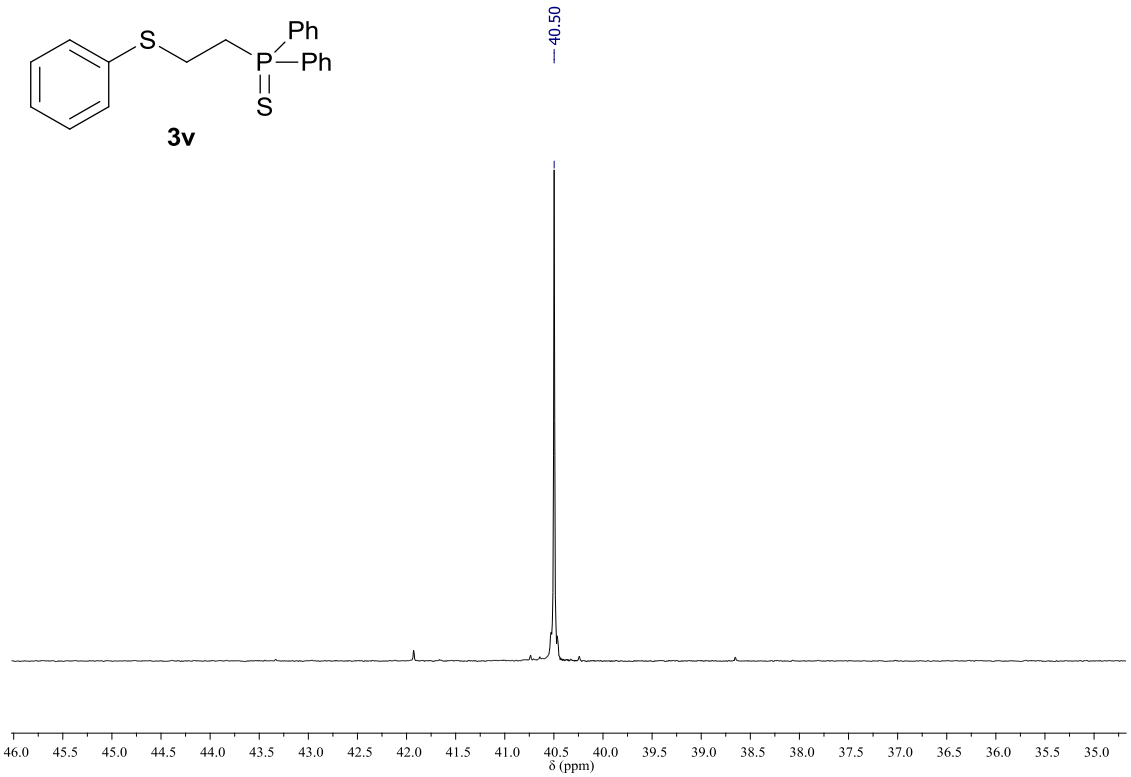

8.486
8.476
7.899
7.896
7.880
7.875
7.867
7.864
7.848
7.843
7.520
7.515
7.500
7.496
7.476
7.471
7.465
7.460
7.456
7.451
7.444
7.437
7.430
7.421
7.415
7.266
7.147
3.158
3.138
3.123
3.113
3.009
2.998
2.982
2.970
2.961
2.954
2.941
S
P
Ph
Ph
N
3g
1.06
4.07
7.01
1.04
1.05
2.03
2.00
δ (ppm)

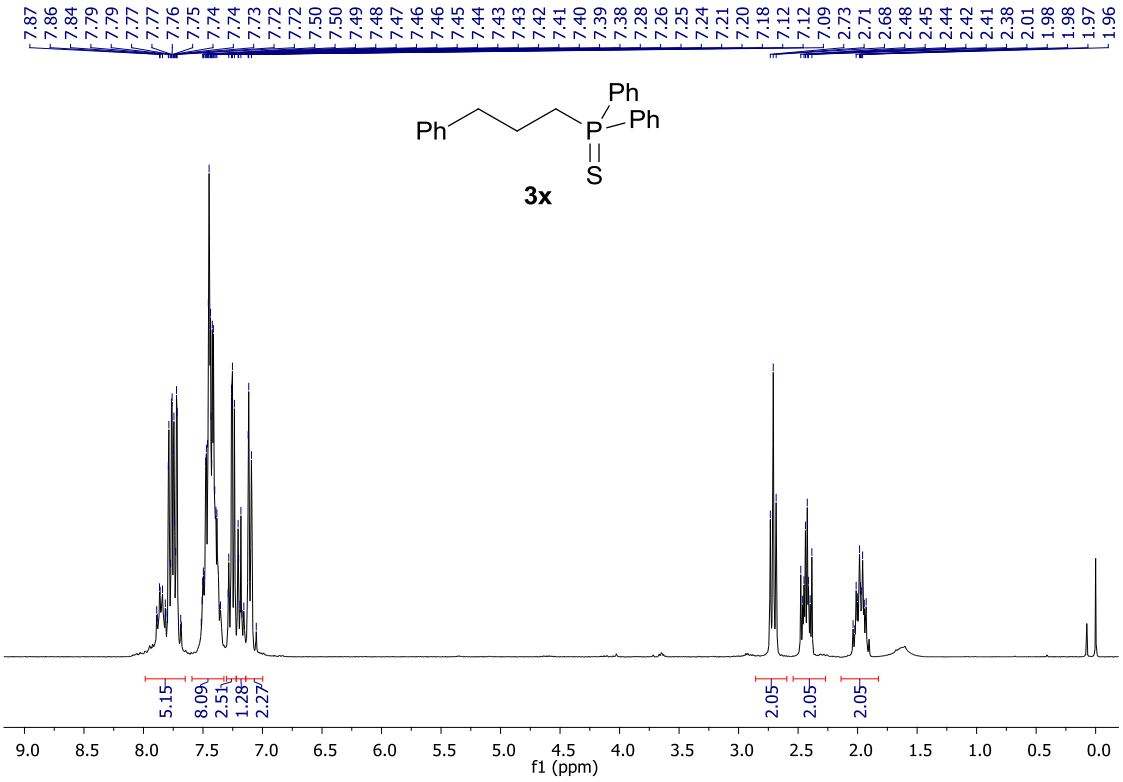

160.21
160.05
149.36
136.54
133.12
132.32
131.57
131.54
131.29
131.19
128.80
128.68
123.40
121.61
32.22
31.66
30.70
S
P
Ph
Ph
N
3g
δ (ppm)

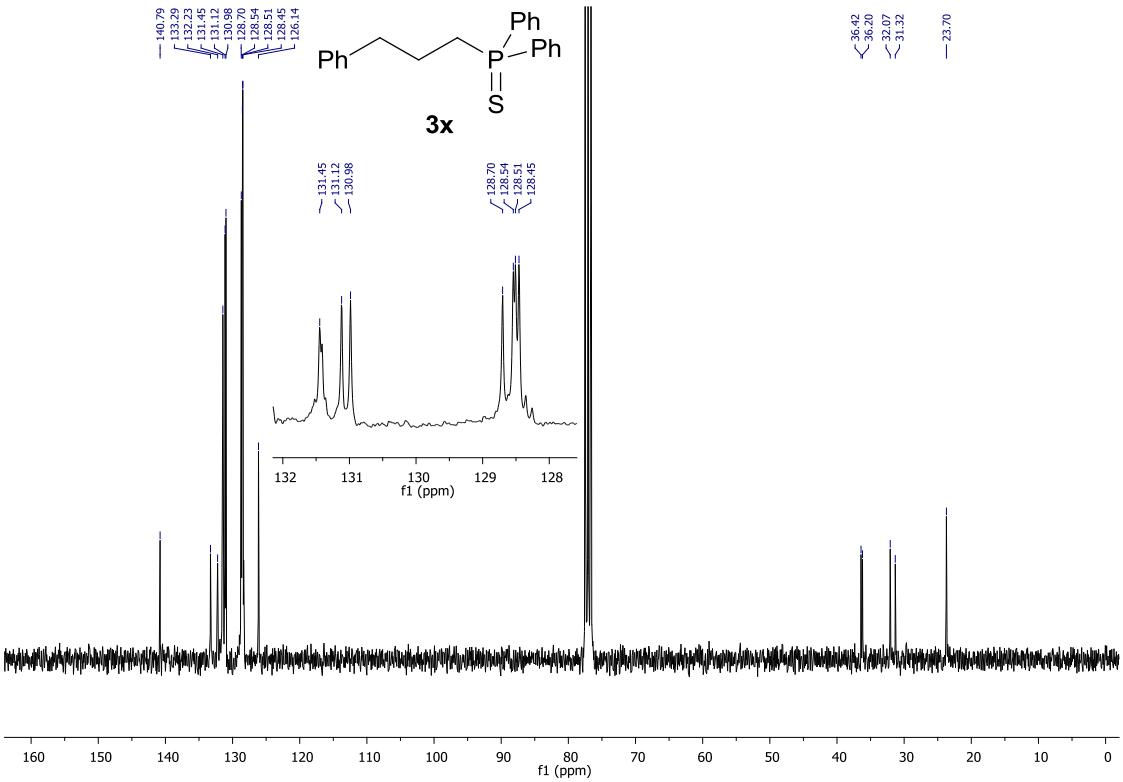

S
P
Ph
Ph
N
3g
42.69
56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30
δ (ppm)

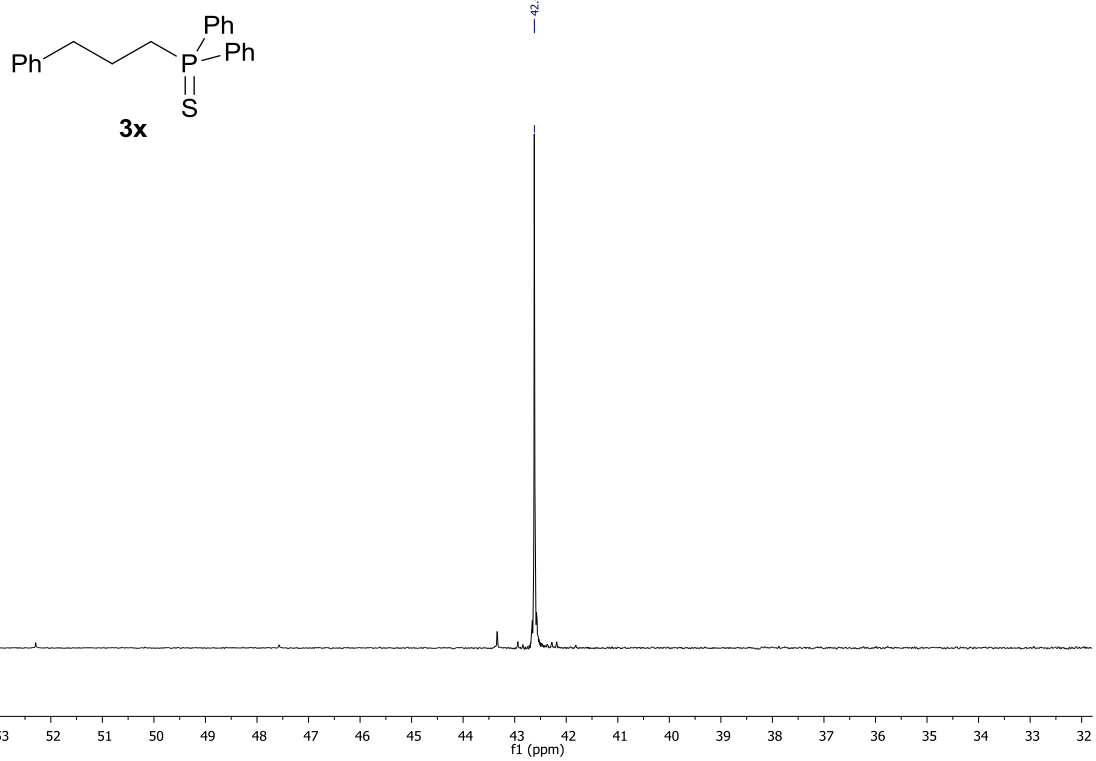

7.80 7.80 7.78 7.77 7.77 7.76 7.75 7.74 7.52 7.51 7.50 7.49 7.49 7.49 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.43 7.43 7.43 7.27 7.27 7.26 7.21 7.21 7.20 3.18 3.17 3.16 3.15 3.15 3.14 3.13 3.12 2.77 2.76 2.75 2.74 2.74 2.73 2.73 2.72 2.71 2.70
S
P
Ph
Ph
S
3v
5.56
8.04
2.26
1.04
2.14
2.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

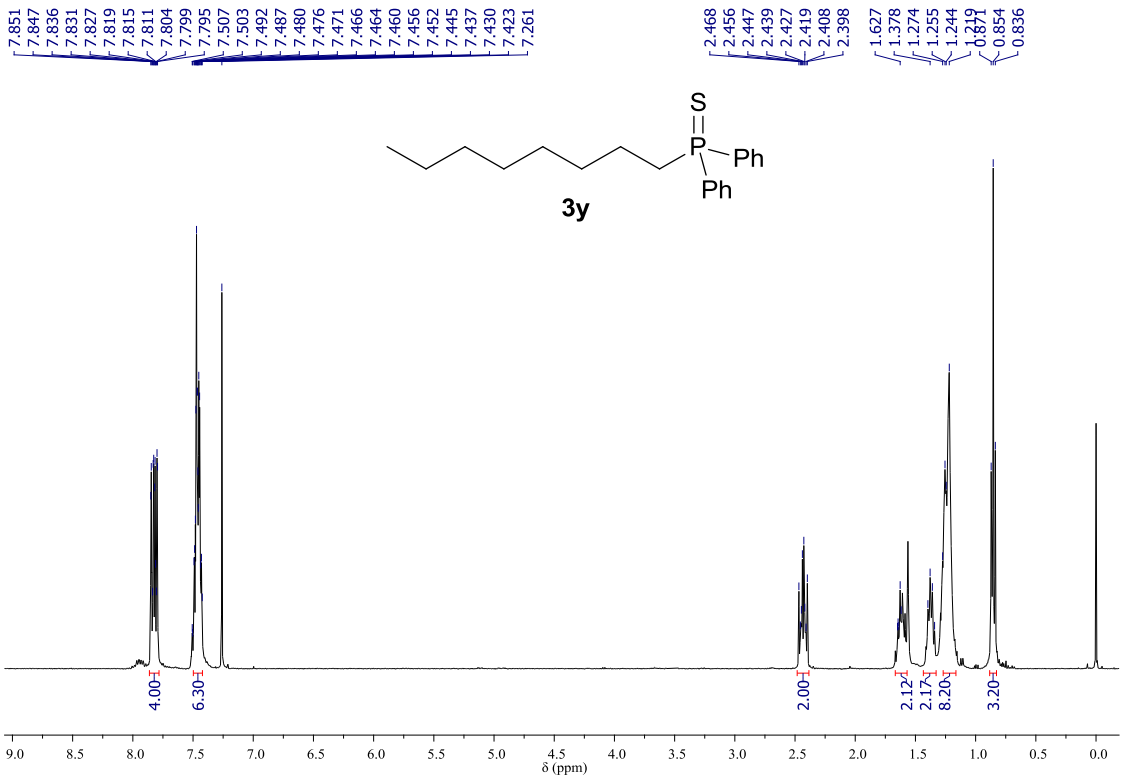

135.00
132.65
132.31
132.28
131.86
131.83
131.32
131.19
131.08
129.55
129.23
129.17
129.04
128.94
128.82
126.57
32.95
32.44
26.81
S
P
Ph
Ph
S
3v
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

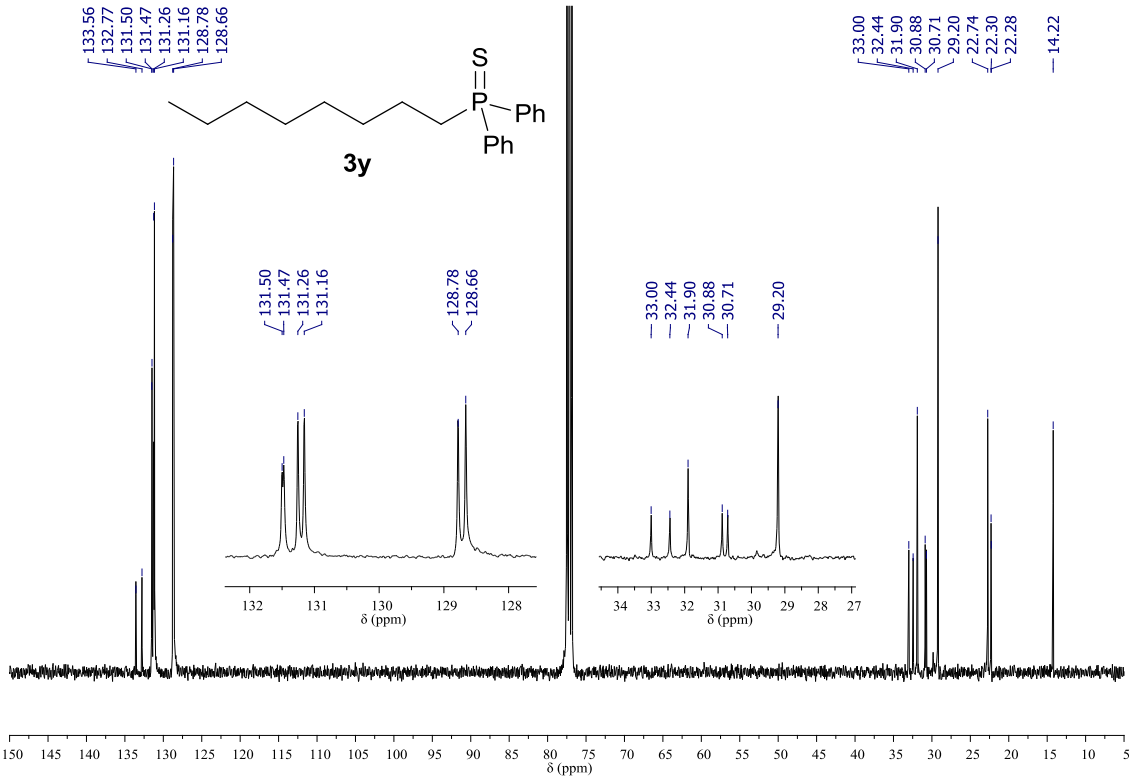

40.50
S
P
Ph
Ph
S
3v
46.0 45.5 45.0 44.5 44.0 43.5 43.0 42.5 42.0 41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 36.0 35.5 35.0
δ (ppm)

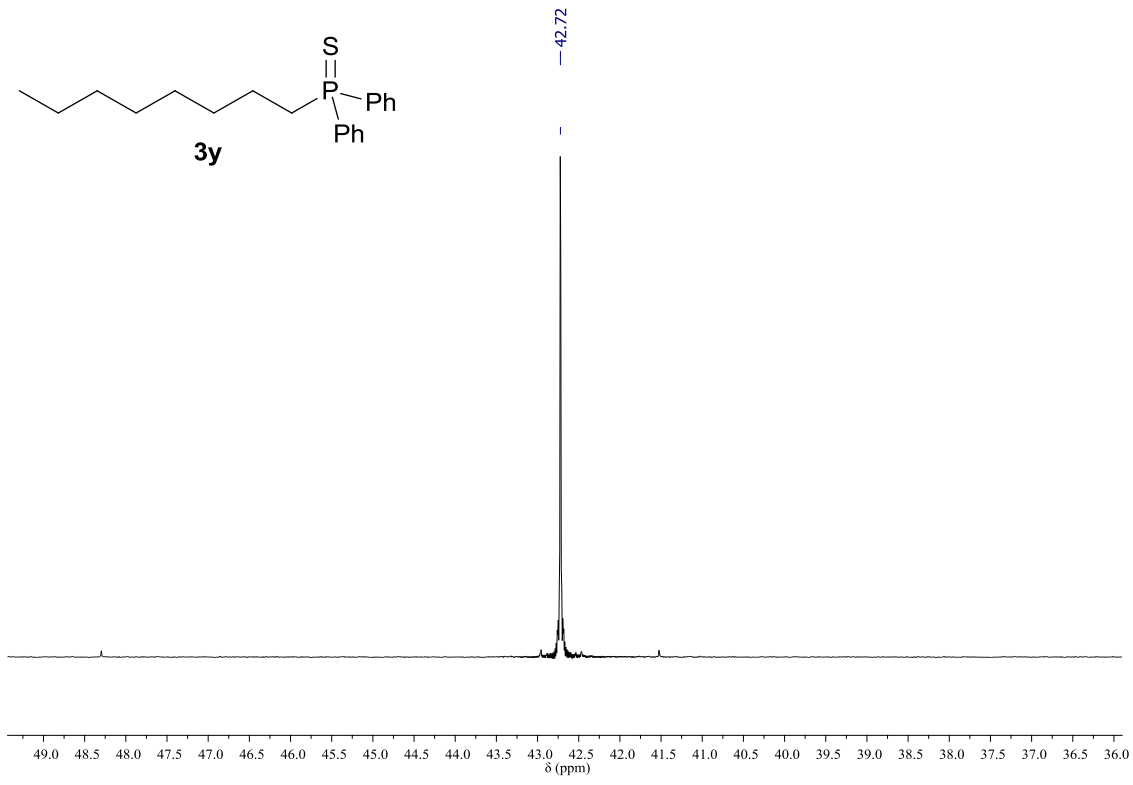

7.87 7.86 7.84 7.79 7.79 7.77 7.77 7.76 7.75 7.74 7.74 7.73 7.72 7.72 7.50 7.50 7.49 7.48 7.47 7.46 7.46 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.39 7.38 7.28 7.26 7.25 7.24 7.21 7.20 7.18 7.12 7.12 7.09 2.73 2.71 2.68 2.48 2.45 2.44 2.42 2.41 2.38 2.01 1.98 1.98 1.97 1.96
Ph
Ph
P
Ph
S
3x
5.15
8.09
2.51
1.28
2.27
2.05
2.05
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

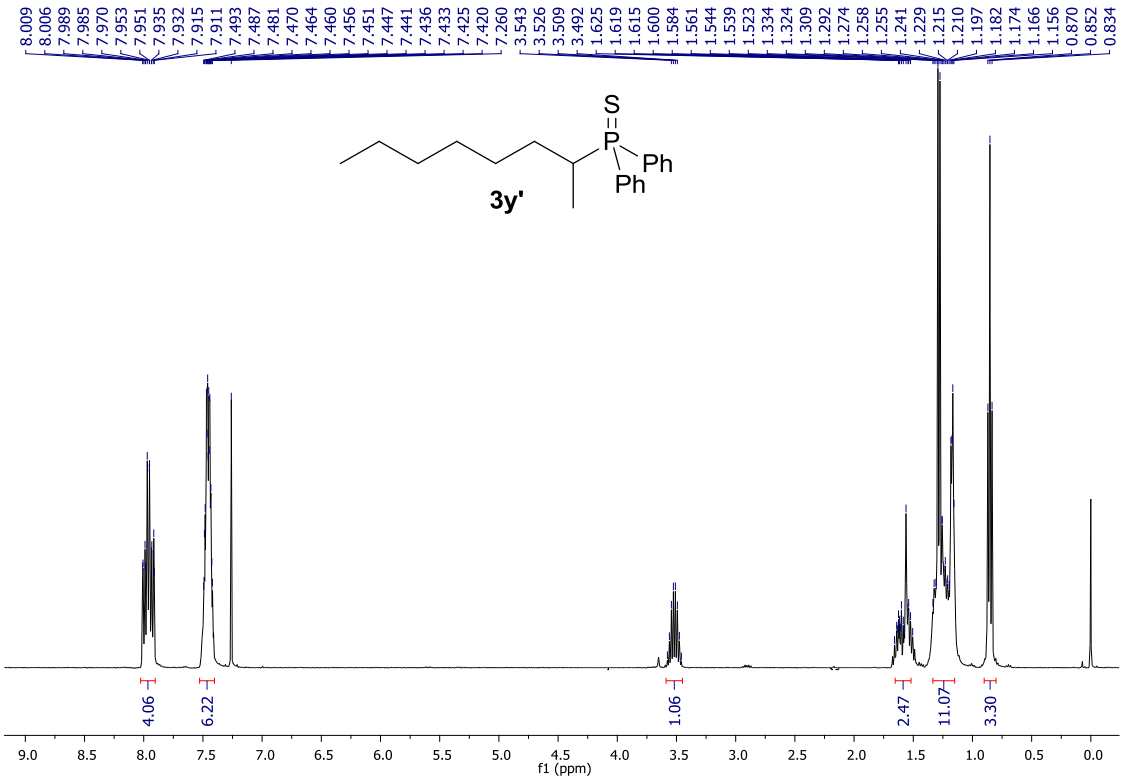

140.79 133.29 132.23 131.45 131.12 130.98 128.70 128.54 128.51 128.45 126.14
Ph
Ph
P
Ph
S
3x
131.45 131.12 130.98
128.70 128.54 128.51 128.45
132 131 130 129 128
f1 (ppm)
36.42 36.20 32.07 31.32 23.70
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

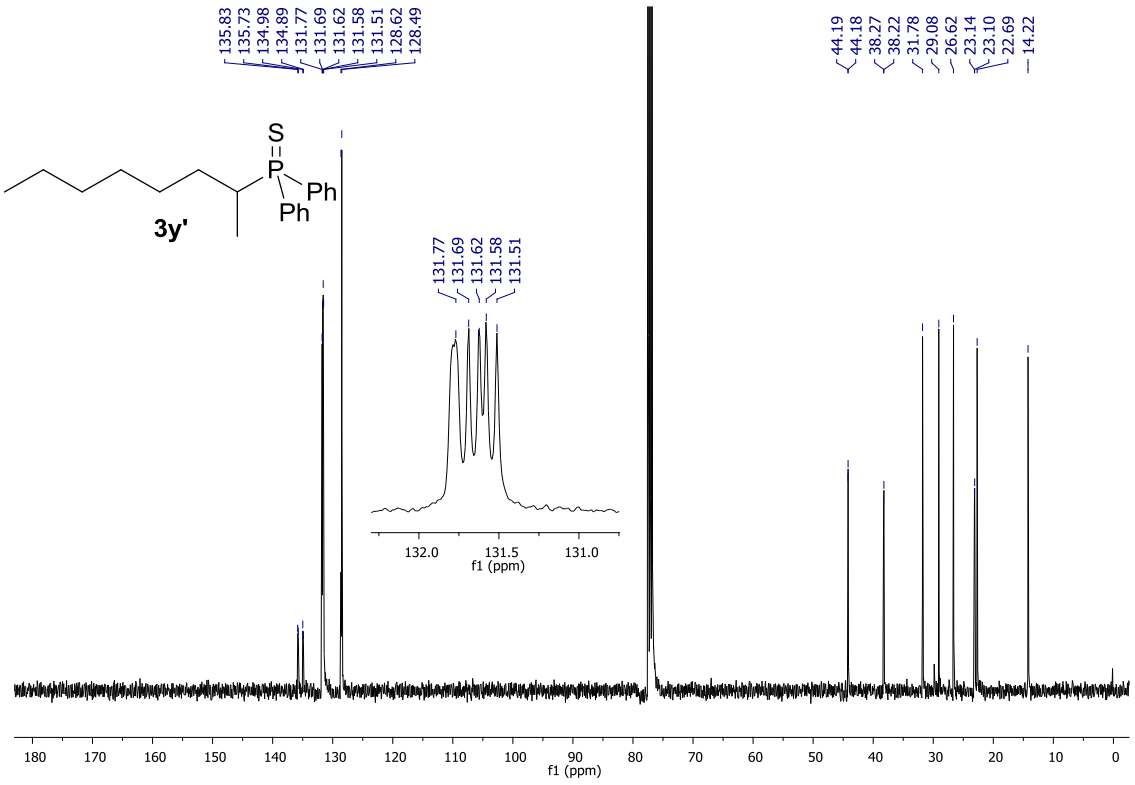

Ph
Ph
Ph
P
S
3x
42.62
53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35 34 33 32
f1 (ppm)

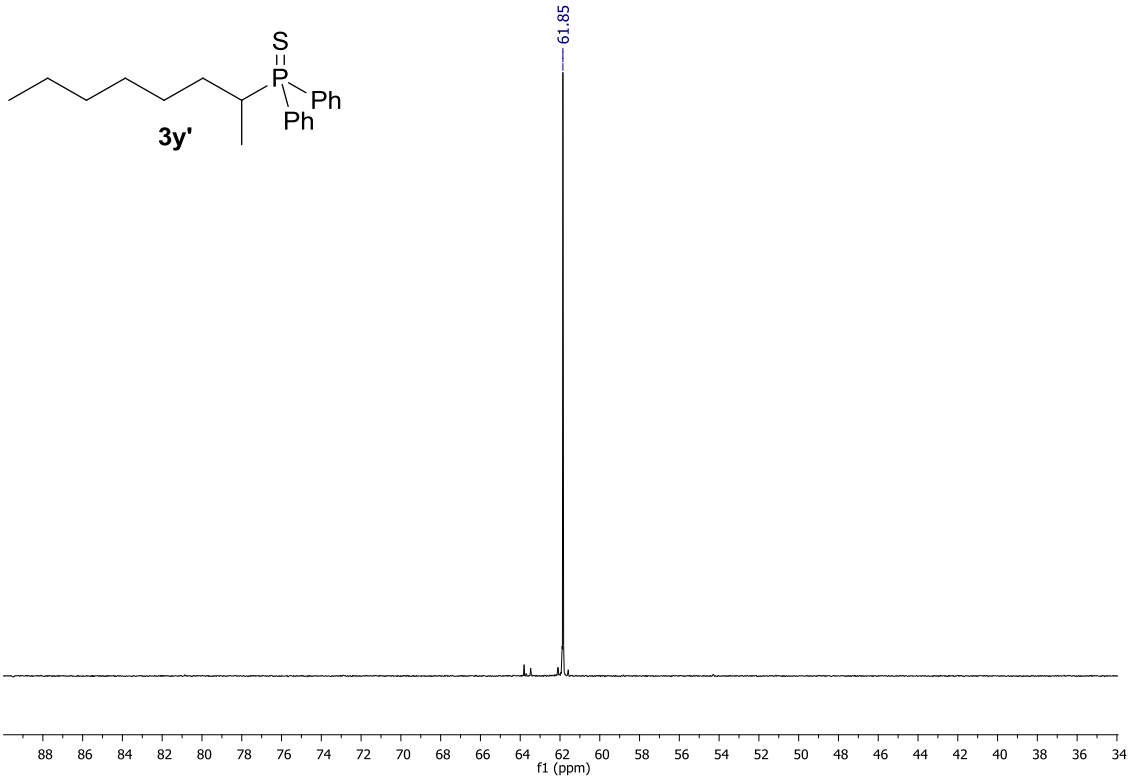

7.851 7.847 7.836 7.831 7.827 7.819 7.815 7.811 7.804 7.799 7.795 7.507 7.503 7.492 7.487 7.480 7.476 7.471 7.466 7.464 7.460 7.456 7.452 7.445 7.437 7.430 7.423 7.261
2.468 2.456 2.447 2.439 2.427 2.419 2.408 2.398
1.627 1.378 1.274 1.255 1.244 1.219 0.871 0.854 0.836
S
P
Ph
Ph
3y
4.00 6.30 2.00 2.12 2.17 8.20 3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

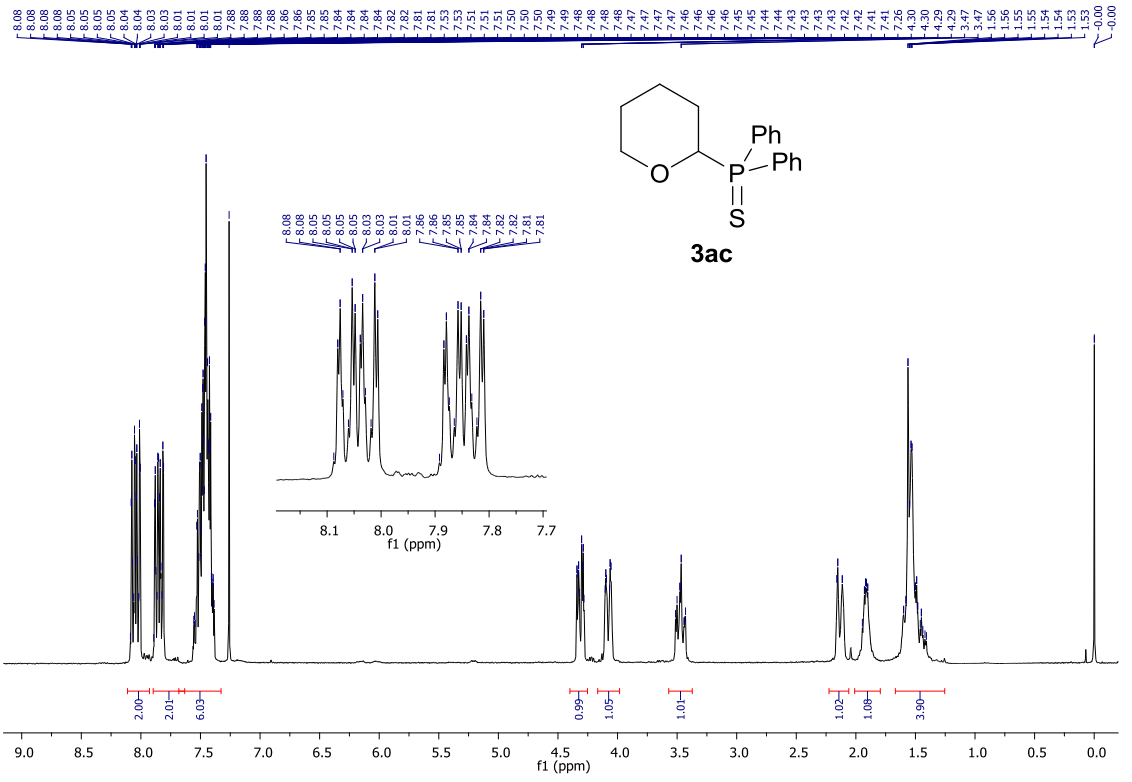

133.56
132.77
131.50
131.47
131.26
131.16
128.78
128.66
33.00
32.44
31.90
30.88
30.71
29.20
22.74
22.30
22.28
14.22
S
P
Ph
Ph
3y
δ (ppm)

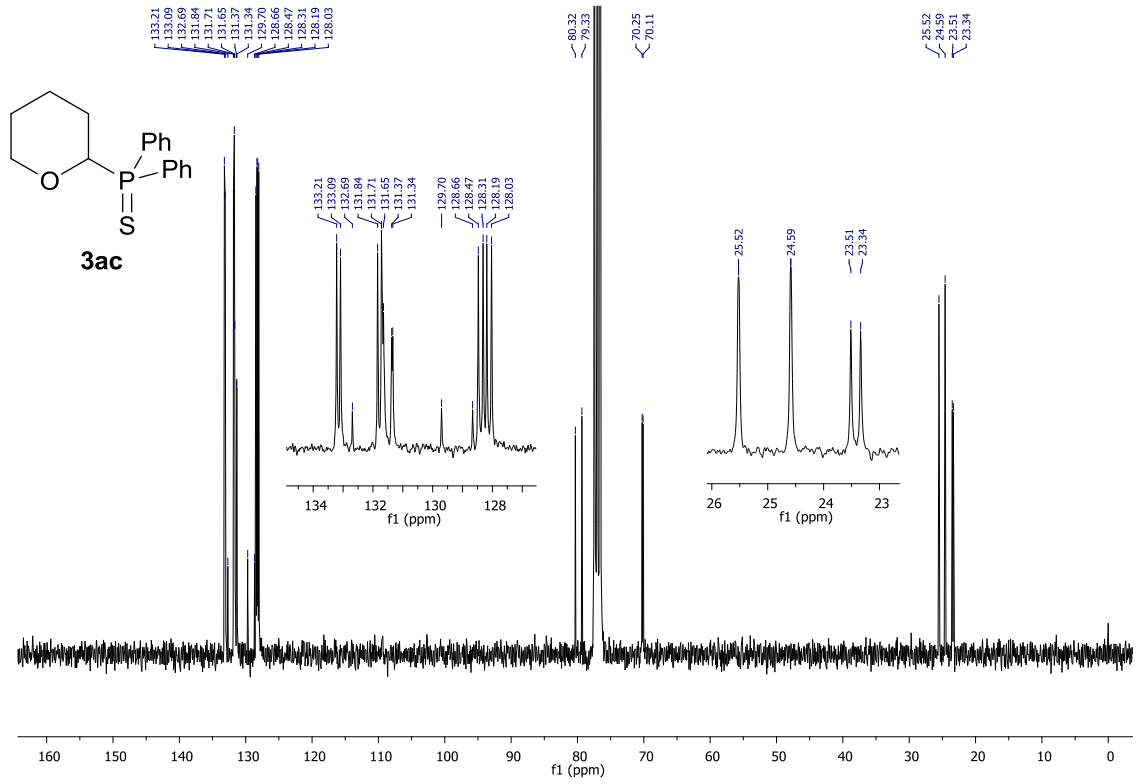

42.72
S
P
Ph
Ph
3y
δ (ppm)

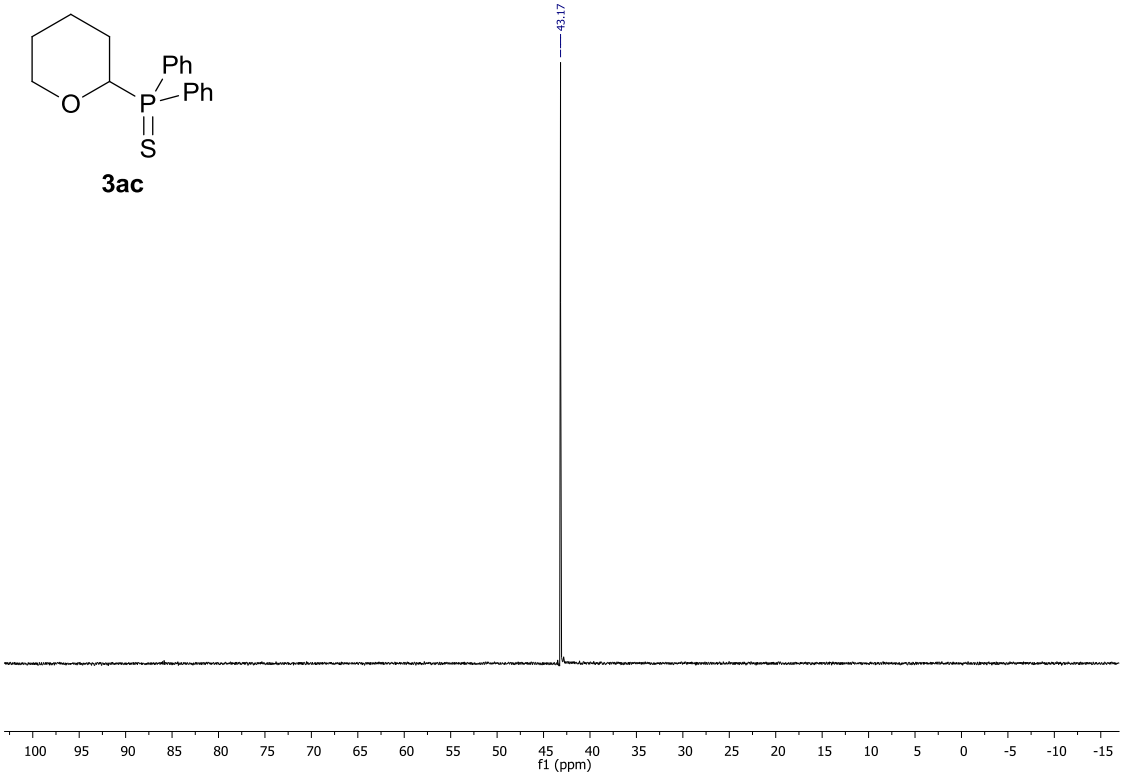

8.009
8.006
7.989
7.985
7.970
7.953
7.951
7.935
7.932
7.915
7.911
7.493
7.487
7.481
7.470
7.464
7.460
7.456
7.451
7.447
7.441
7.436
7.433
7.425
7.420
7.260
3.543
3.526
3.509
3.492
1.625
1.619
1.615
1.600
1.584
1.561
1.544
1.539
1.523
1.334
1.324
1.309
1.292
1.274
1.258
1.255
1.241
1.229
1.215
1.210
1.197
1.182
1.174
1.166
1.156
0.870
0.852
0.834
S
P
Ph
Ph
3y'
4.06
6.22
1.06
2.47
11.07
3.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


135.83
135.73
134.98
134.89
131.77
131.69
131.62
131.58
131.51
128.62
128.49
44.19
44.18
38.27
38.22
31.78
29.08
26.62
23.14
23.10
22.69
14.22
S
P
Ph
Ph
3y'
131.77
131.69
131.62
131.58
131.51
132.0
131.5
131.0
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

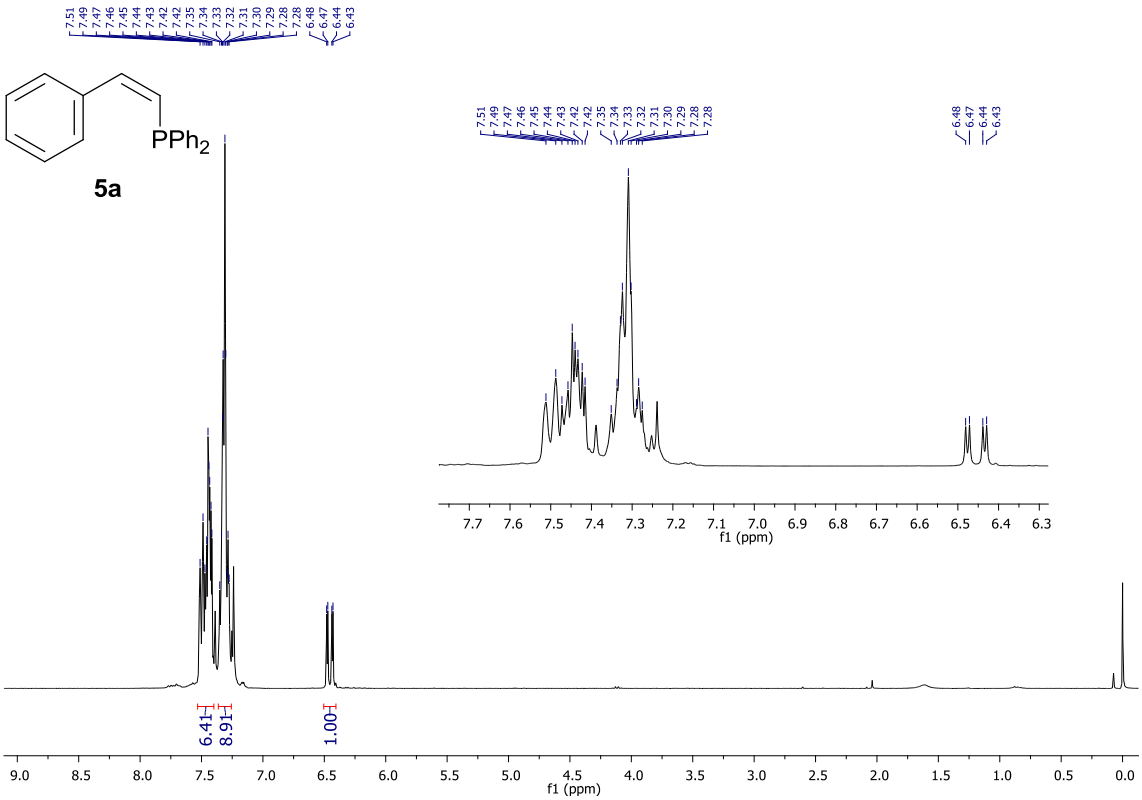

S
P
Ph
Ph
3y'
61.85
f1 (ppm)

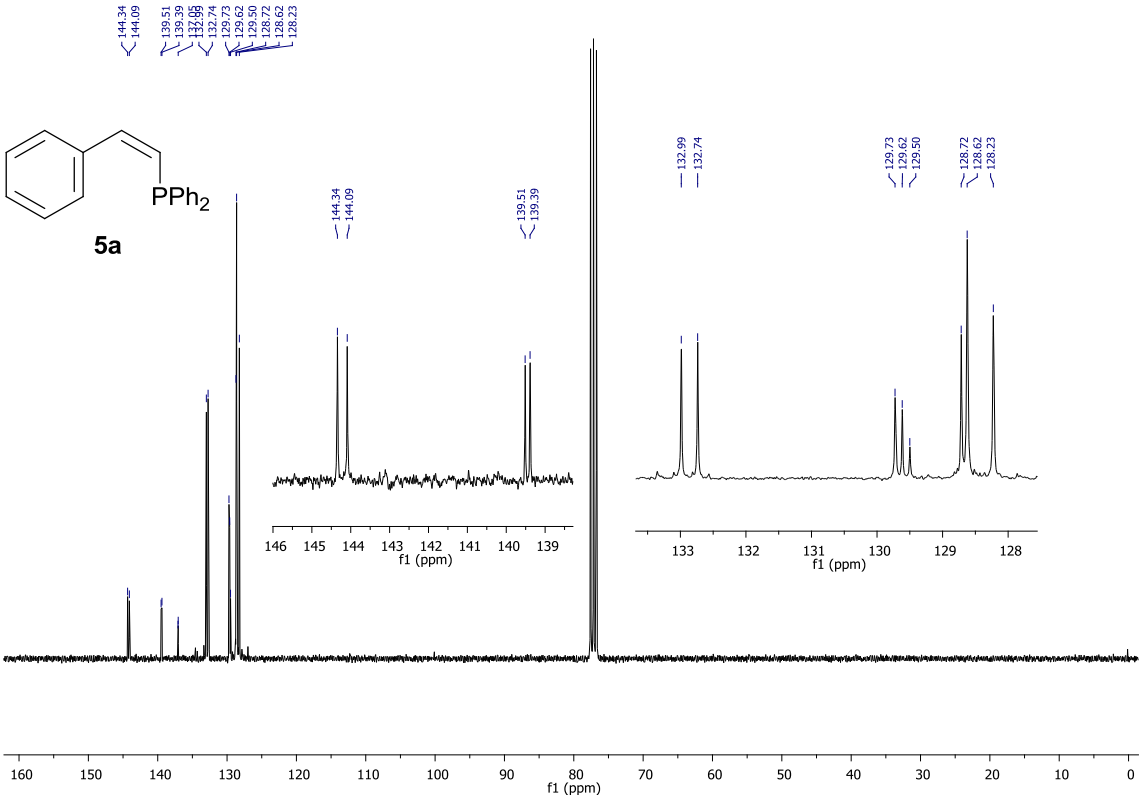

O
P
Ph
Ph
S
3ac
f1 (ppm)

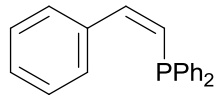

133.21
133.09
132.69
131.84
131.71
131.65
131.37
131.34
129.70
128.66
128.47
128.31
128.19
128.03
80.32
79.33
70.25
70.11
25.52
24.59
23.51
23.34
Ph
Ph
O
P
S
3ac
f1 (ppm)
f1 (ppm)
f1 (ppm)


43.17
Ph
Ph
O
P
S
3ac
f1 (ppm)

NMR spectra of compounds 5






PPh2

5a

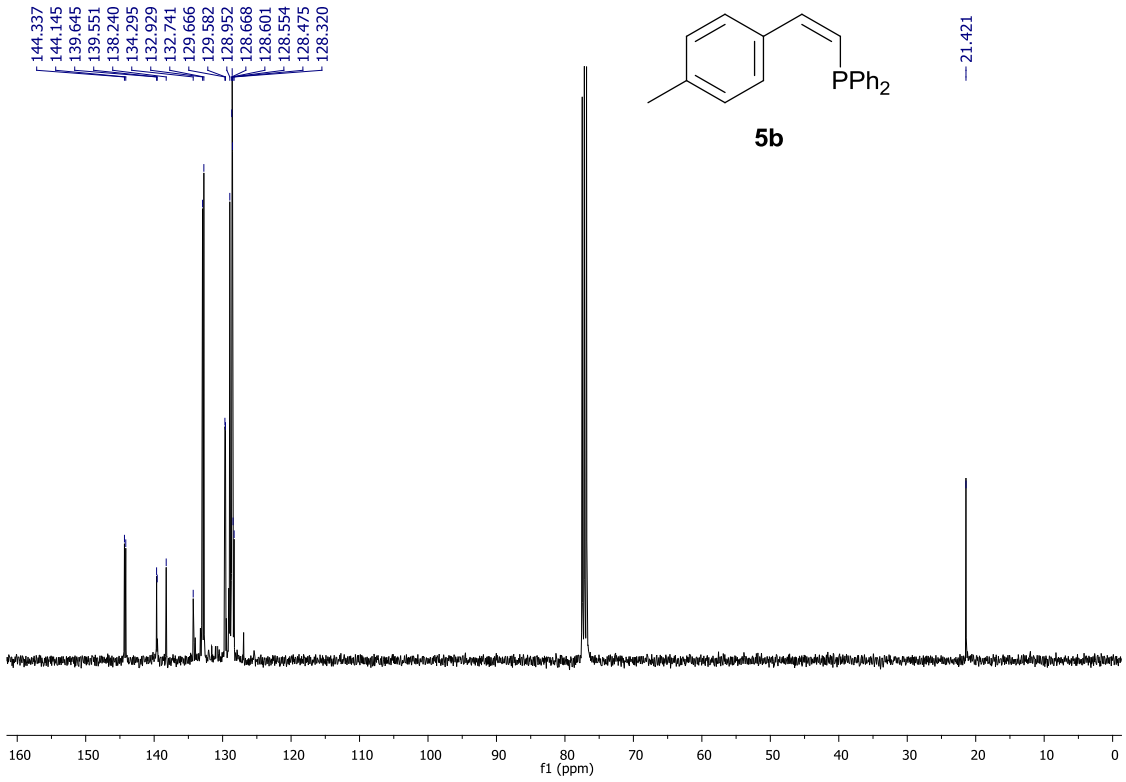
24.81
2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36 -38 -40 -42 -44 -46 -48 -50 -52
f1 (ppm)

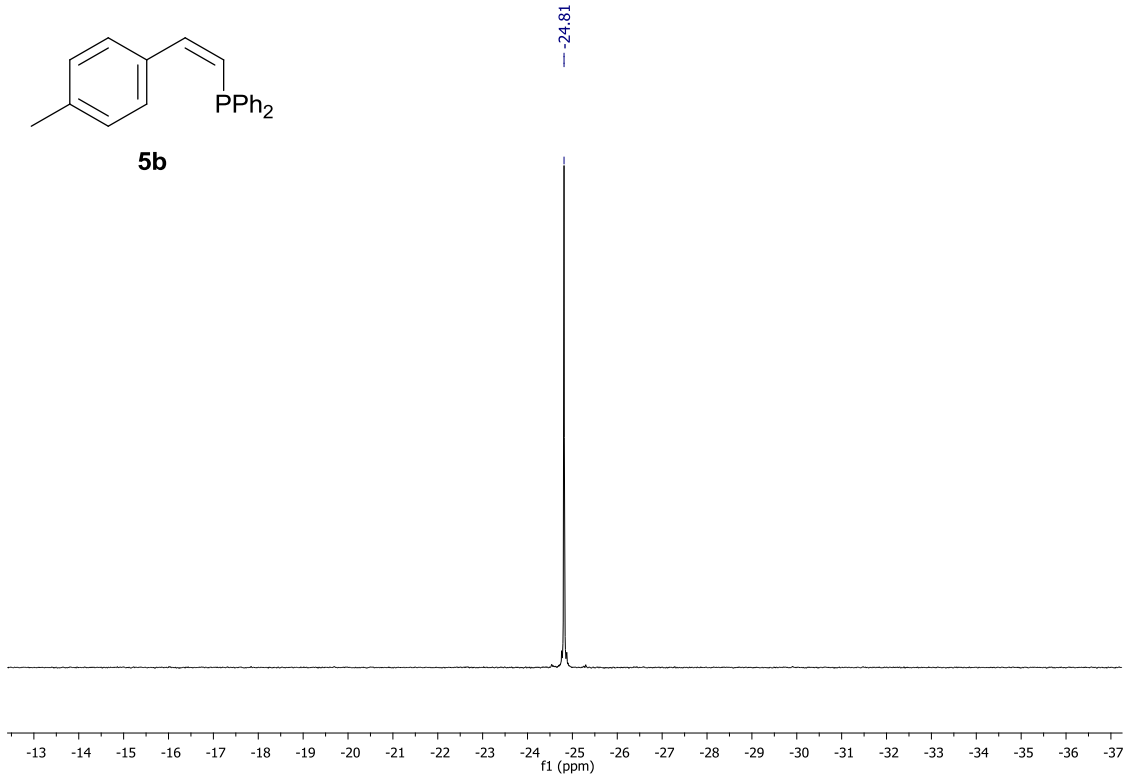

7.444
7.439
7.393
7.331
7.323
7.321
7.320
7.318
7.316
7.314
7.310
7.307
7.302
7.298
7.129
6.404
6.397
6.373
6.366

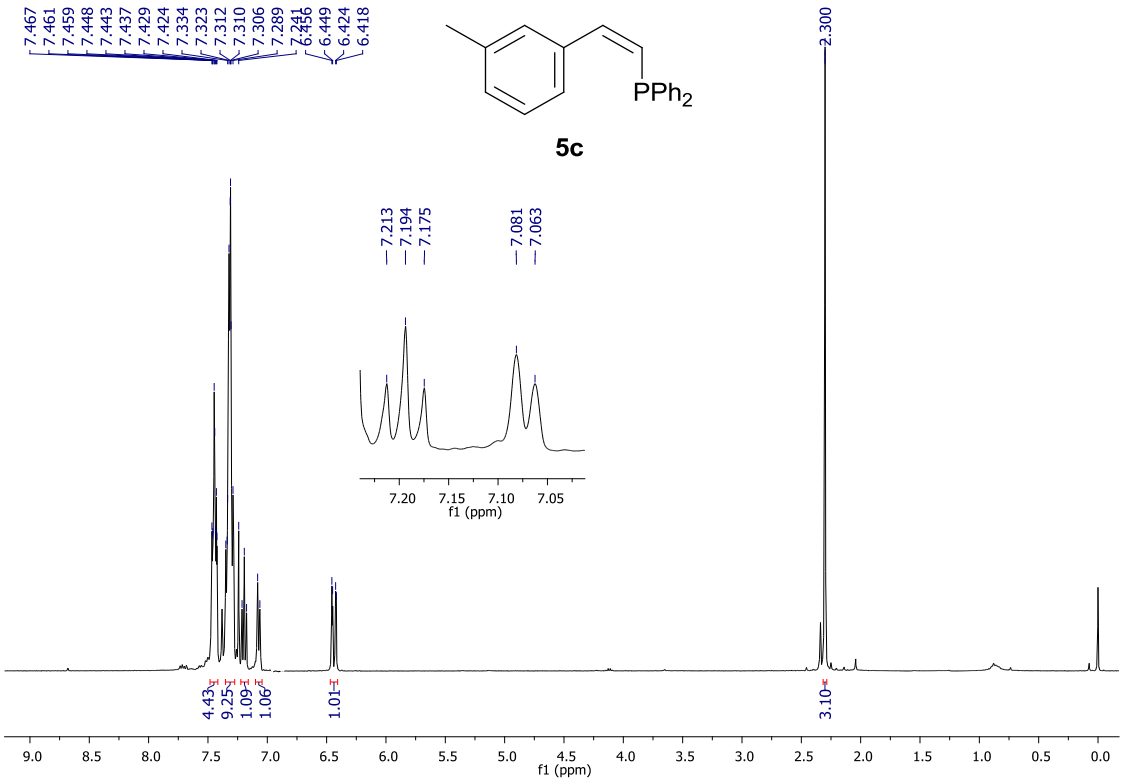
PPh2

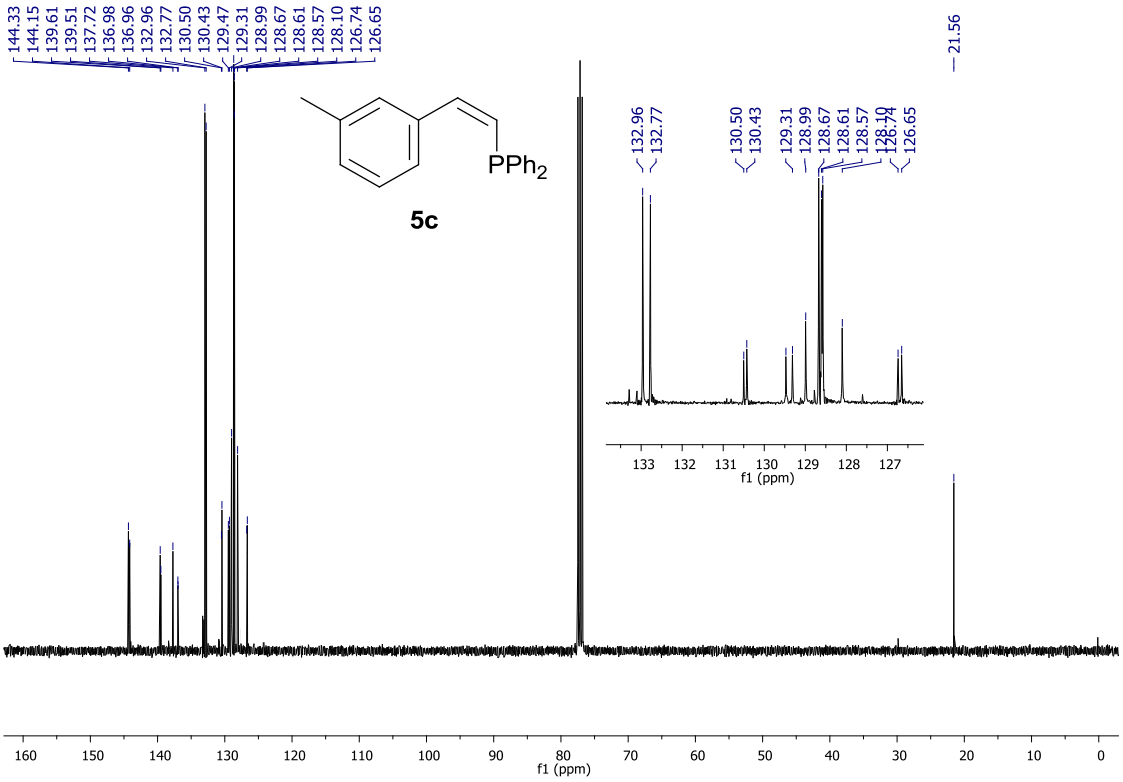
5b

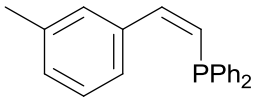
2.321
5.54
7.36
2.22
1.03
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.337
144.145
139.645
139.551
138.240
134.295
132.929
132.741
129.666
129.582
128.952
128.668
128.601
128.554
128.475
128.320
21.421
PPh2
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-24.81
PPh2
5b
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
-26
-27
-28
-29
-30
-31
-32
-33
-34
-35
-36
-37
f1 (ppm)

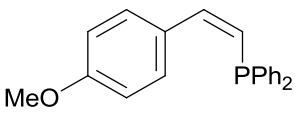

7.467
7.461
7.459
7.448
7.443
7.437
7.429
7.424
7.334
7.323
7.312
7.310
7.306
7.289
7.241
6.456
6.449
6.424
6.418
2.300
PPh2
5c
7.213
7.194
7.175
7.081
7.063
7.20
7.15
7.10
7.05
f1 (ppm)
4.43
9.25
1.09
1.06
1.01
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.33
144.15
139.61
139.51
137.72
136.98
136.96
132.96
132.77
130.50
130.43
129.47
129.31
128.99
128.67
128.61
128.57
128.10
126.74
126.65
21.56
PPh2
5c
132.96
132.77
130.50
130.43
129.31
128.99
128.67
128.61
128.57
128.10
126.74
126.65
133
132
131
130
129
128
127
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PPh2

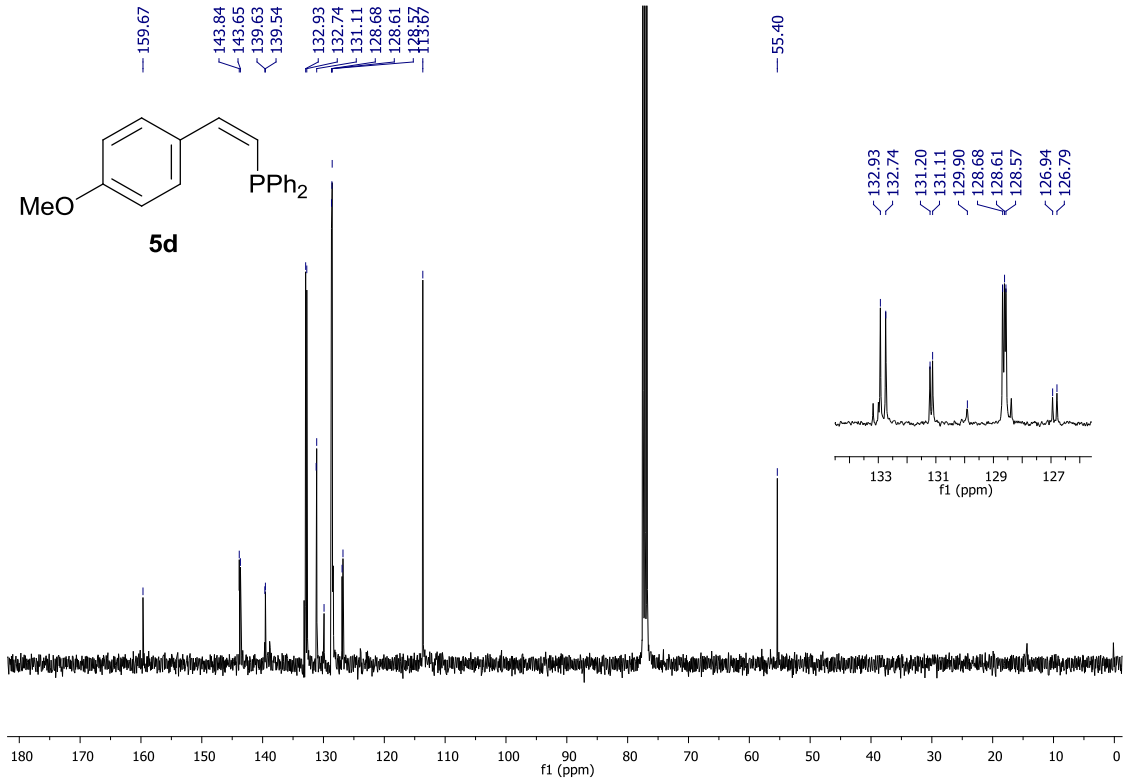
5c

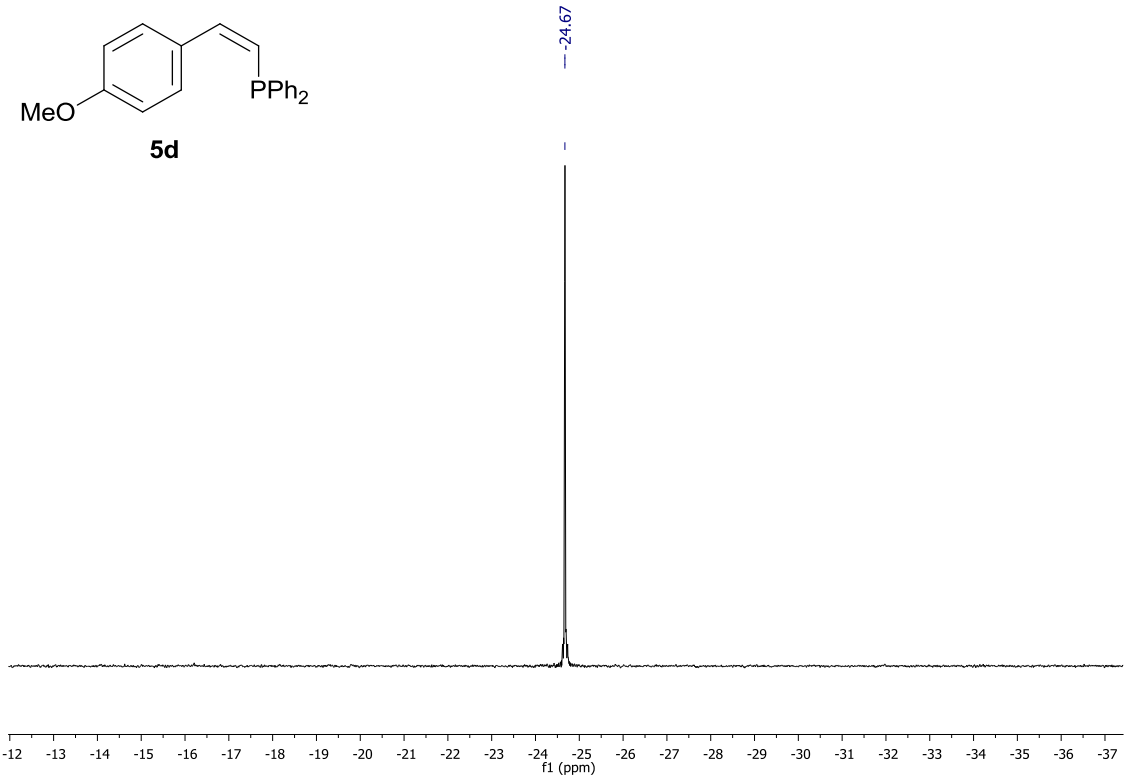
-24.53
-13 -14 -15 -16 -17 -18 -19 -20 -21 -22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35 -36
f1 (ppm)

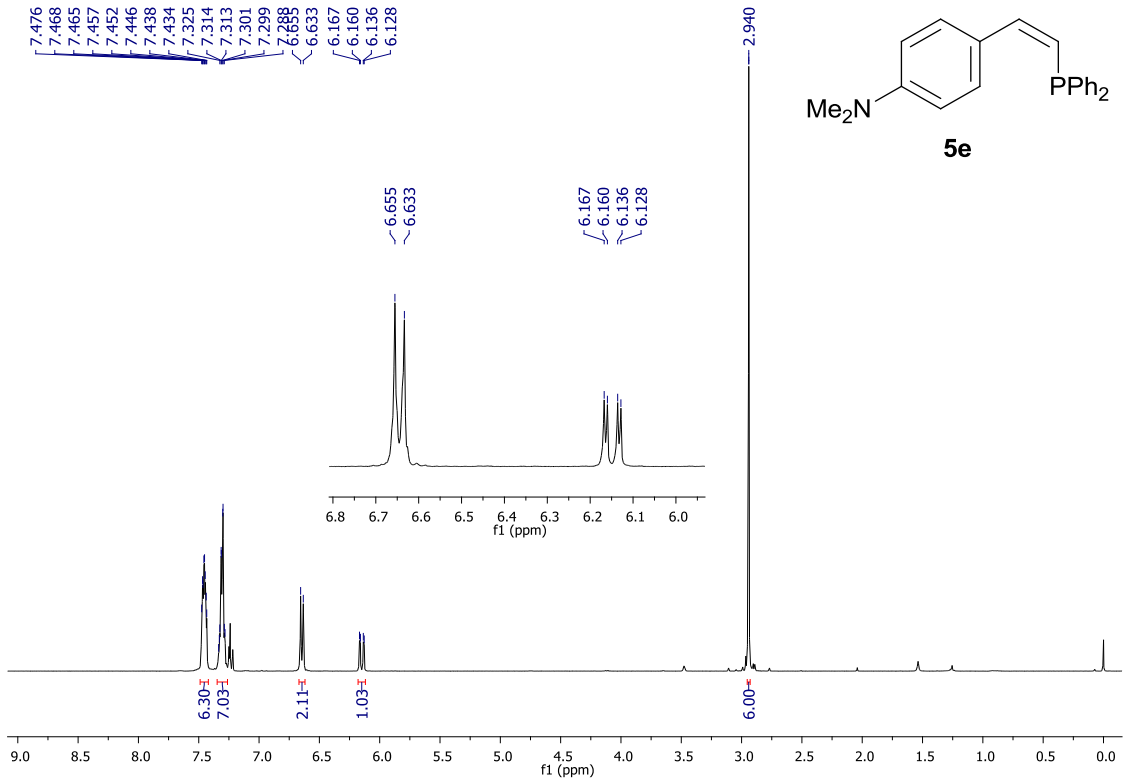

MeO
PPh2

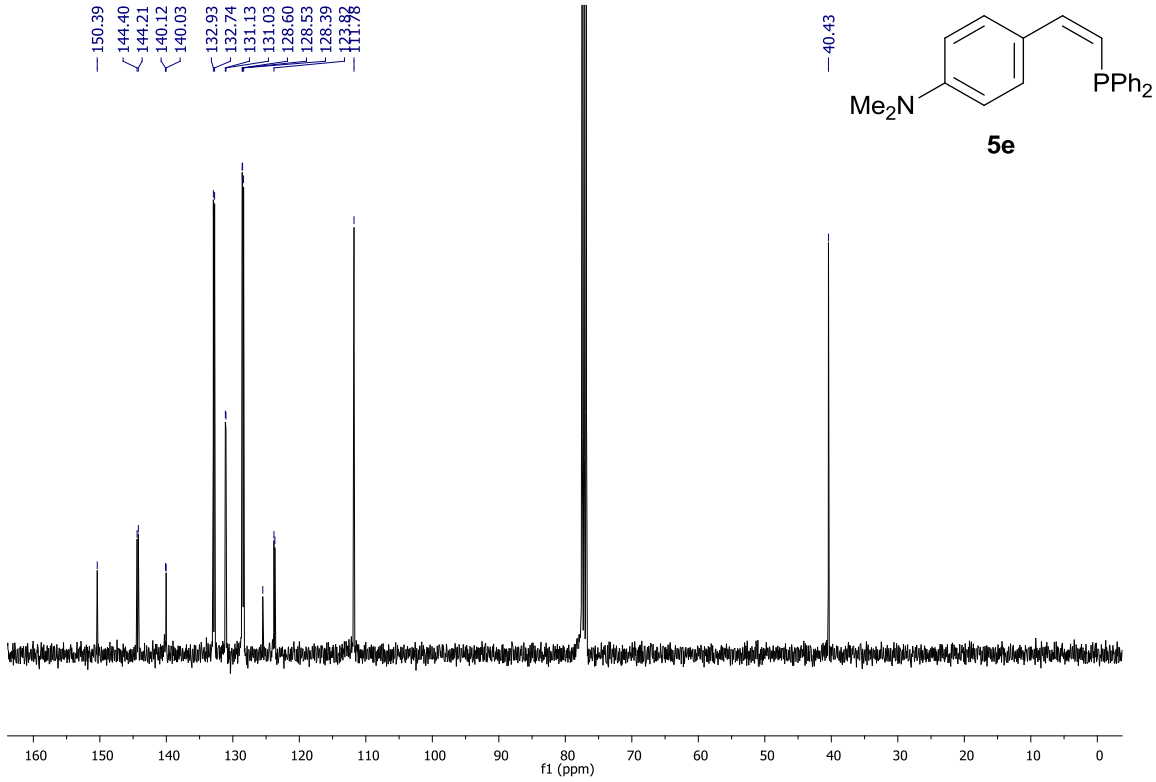
5d

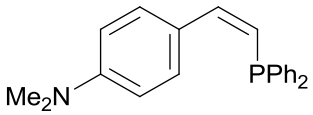
7.48
7.47
7.46
7.45
7.44
7.43
7.33
7.33
7.32
7.32
7.31
7.31
7.25
6.86
6.83
6.33
6.32
6.30
6.29
3.79
6.38
7.32
2.28
1.07
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2
f1 (ppm)


159.67
143.84
143.65
139.63
139.54
132.93
132.74
131.11
128.68
128.61
128.57
113.67
55.40
MeO
PPh2
5d
132.93
132.74
131.20
131.11
129.90
128.68
128.61
128.57
126.94
126.79
133
131
129
127
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-24.67
MeO
PPh2
5d
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
-24
-25
-26
-27
-28
-29
-30
-31
-32
-33
-34
-35
-36
-37
f1 (ppm)


7.476
7.468
7.465
7.457
7.452
7.446
7.438
7.434
7.325
7.314
7.313
7.301
7.299
7.288
6.655
6.633
6.167
6.160
6.136
6.128
2.940
6.655
6.633
6.167
6.160
6.136
6.128
6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0
f1 (ppm)
6.30
7.03
2.11
1.03
6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Me2N
PPh2
5e

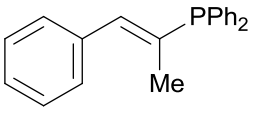

150.39
144.40
144.21
140.12
140.03
132.93
132.74
131.13
131.03
128.60
128.53
128.39
123.82
111.78
40.43
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Me2N
PPh2
5e

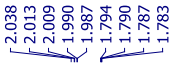

Me2N
PPh2

5e

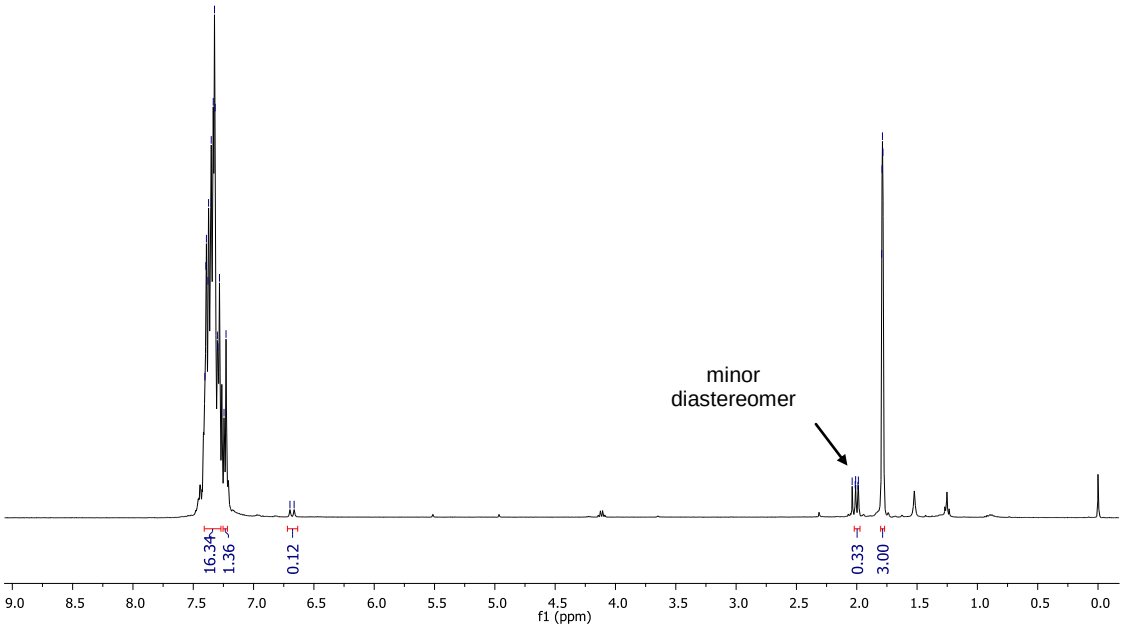
-23.95
-13 -14 -15 -16 -17 -18 -19 -20 -21 -22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35
f1 (ppm)

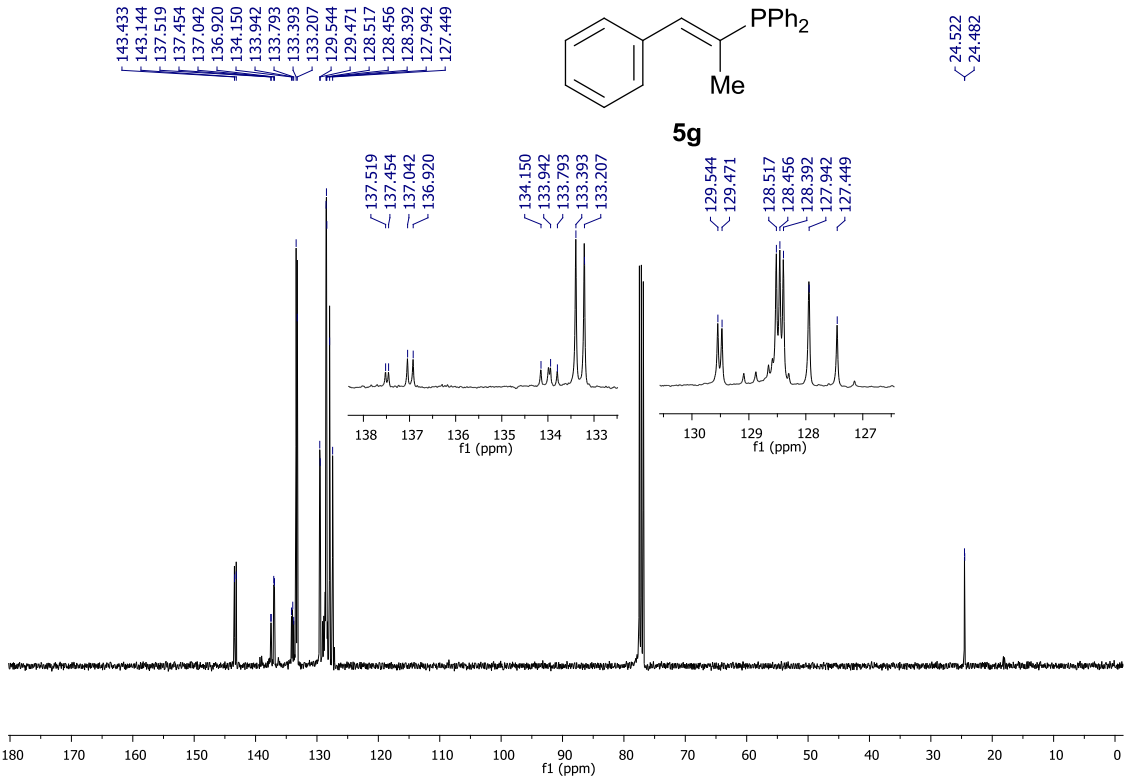

7.403
7.396
7.391
7.378
7.373
7.351
7.334
7.324
7.319
7.300
7.296
7.283
7.245
7.228
6.699
6.664

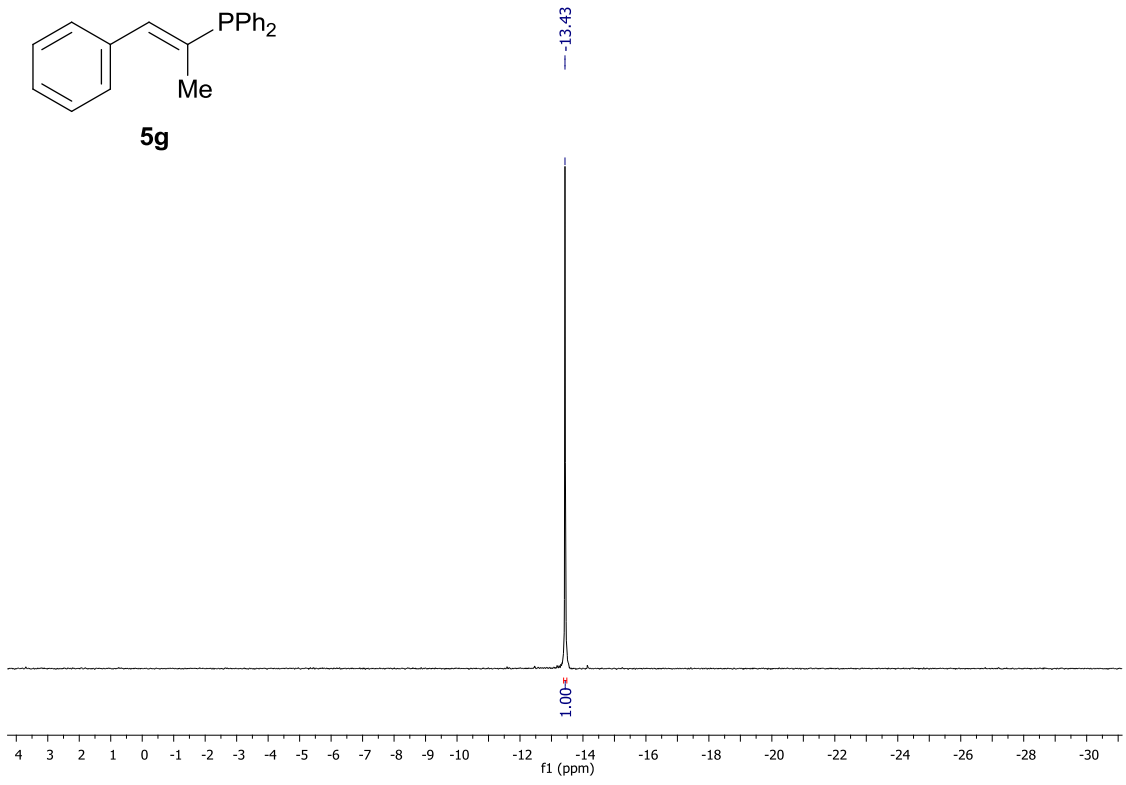

PPh2
Me

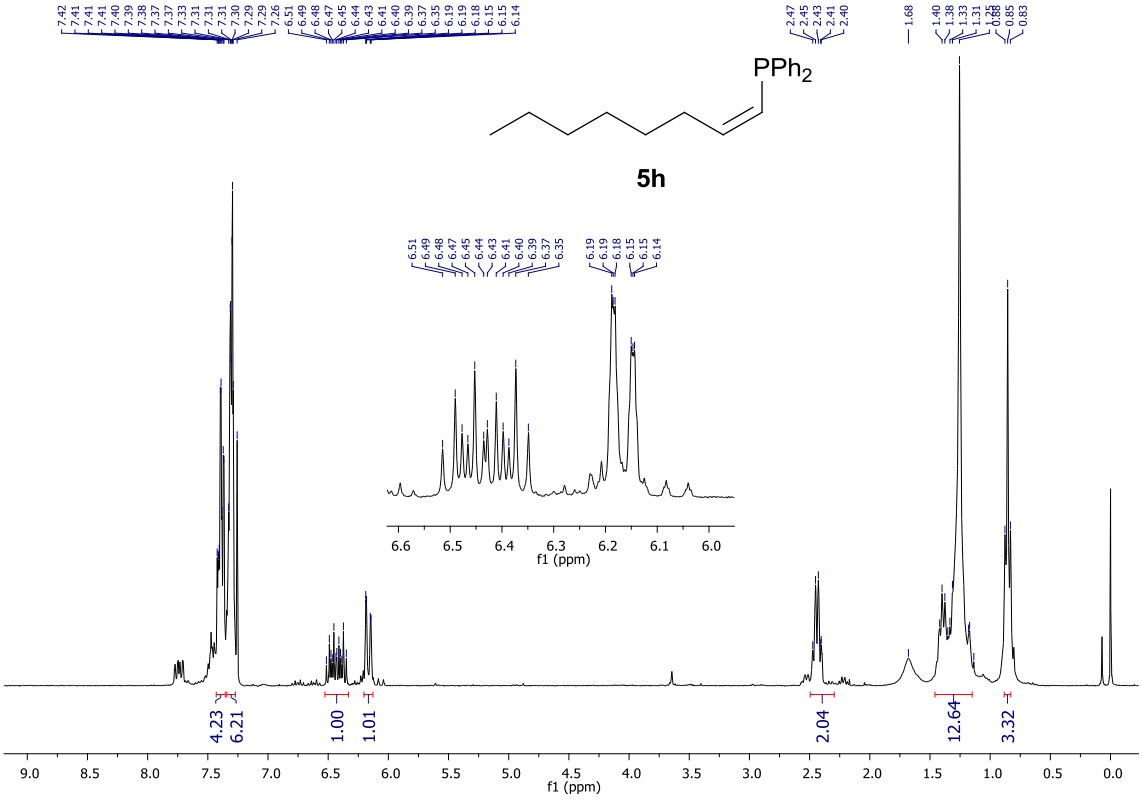

2.038
2.013
2.009
1.990
1.987
1.794
1.790
1.787
1.783

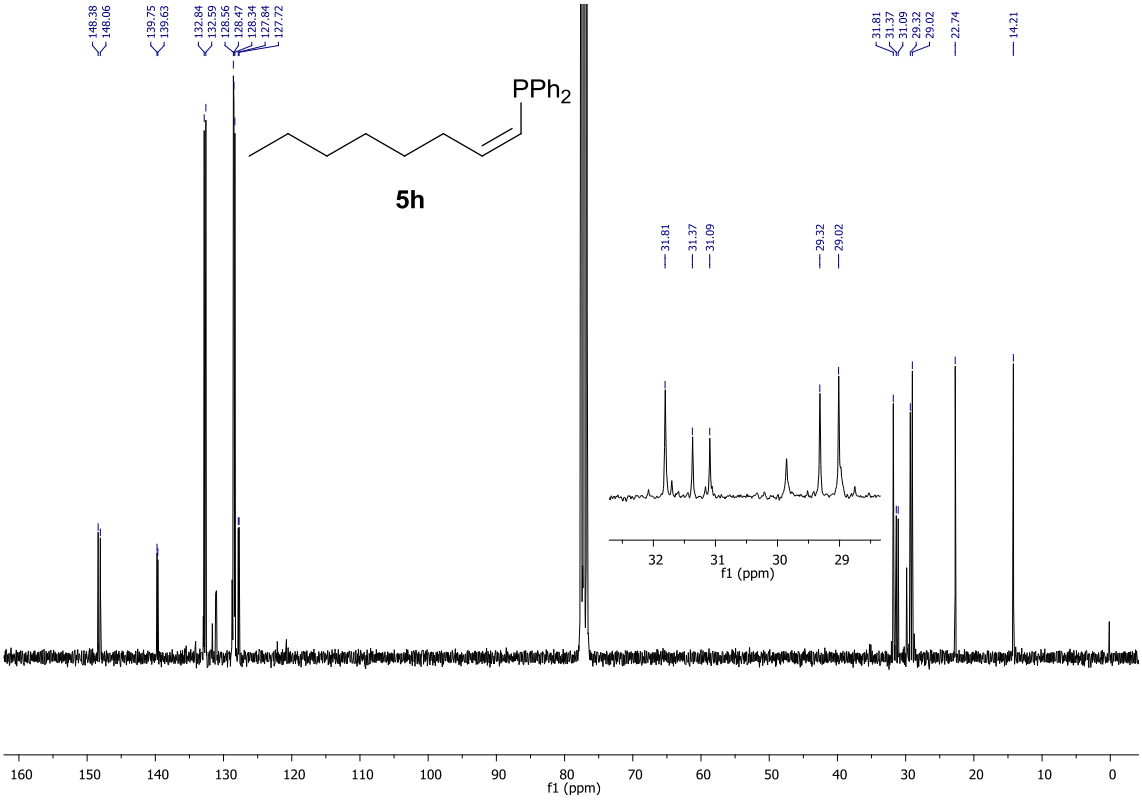
5g

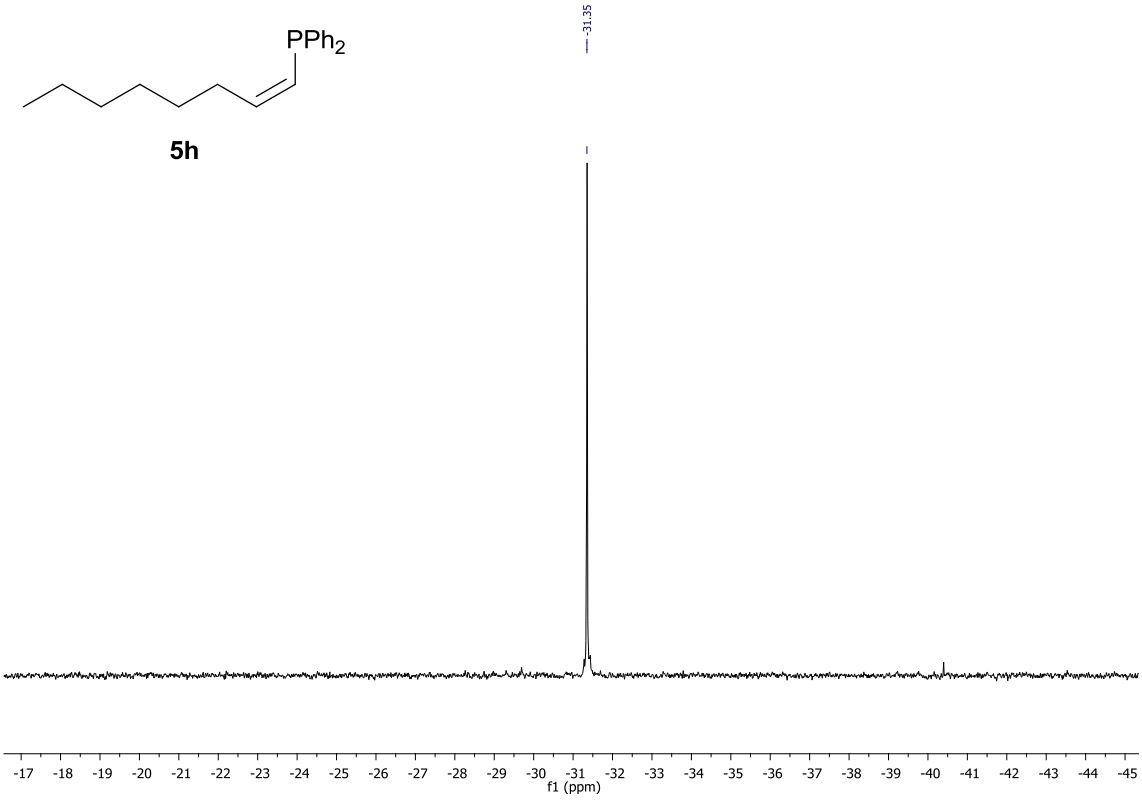

minor
diastereomer
16.34
1.36
0.12
0.33
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

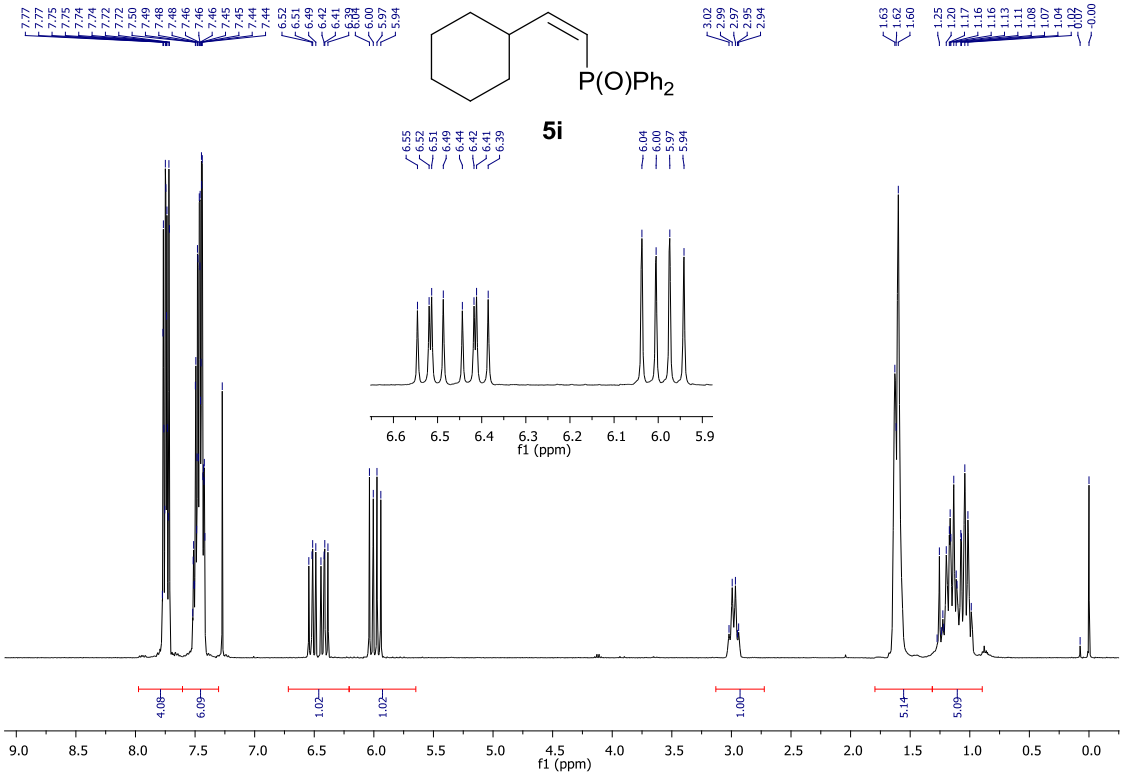

143.433
143.144
137.519
137.454
137.042
136.920
134.150
133.942
133.793
133.393
133.207
129.544
129.471
128.517
128.456
128.392
127.942
127.449
PPh2
Me
24.522
24.482
5g
137.519
137.454
137.042
136.920
134.150
133.942
133.793
133.393
133.207
129.544
129.471
128.517
128.456
128.392
127.942
127.449
138 137 136 135 134 133
f1 (ppm)
130 129 128 127
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

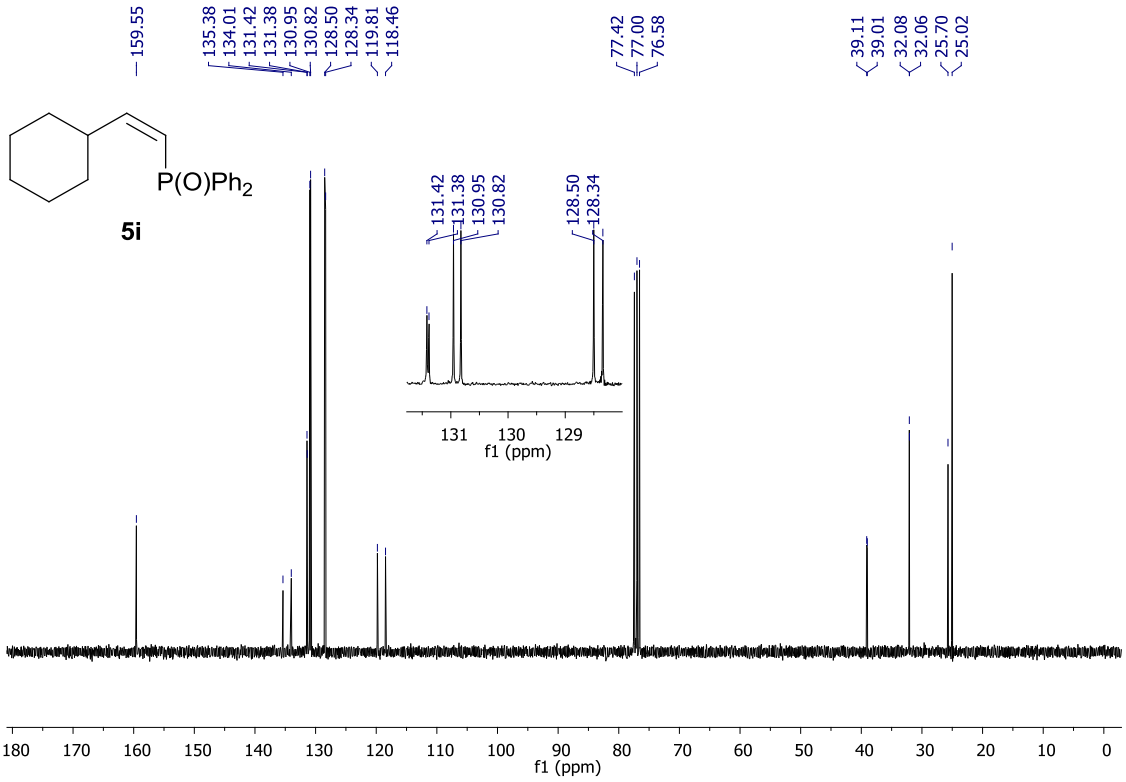

PPh2
Me
5g
-13.43
1.00
4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30
f1 (ppm)

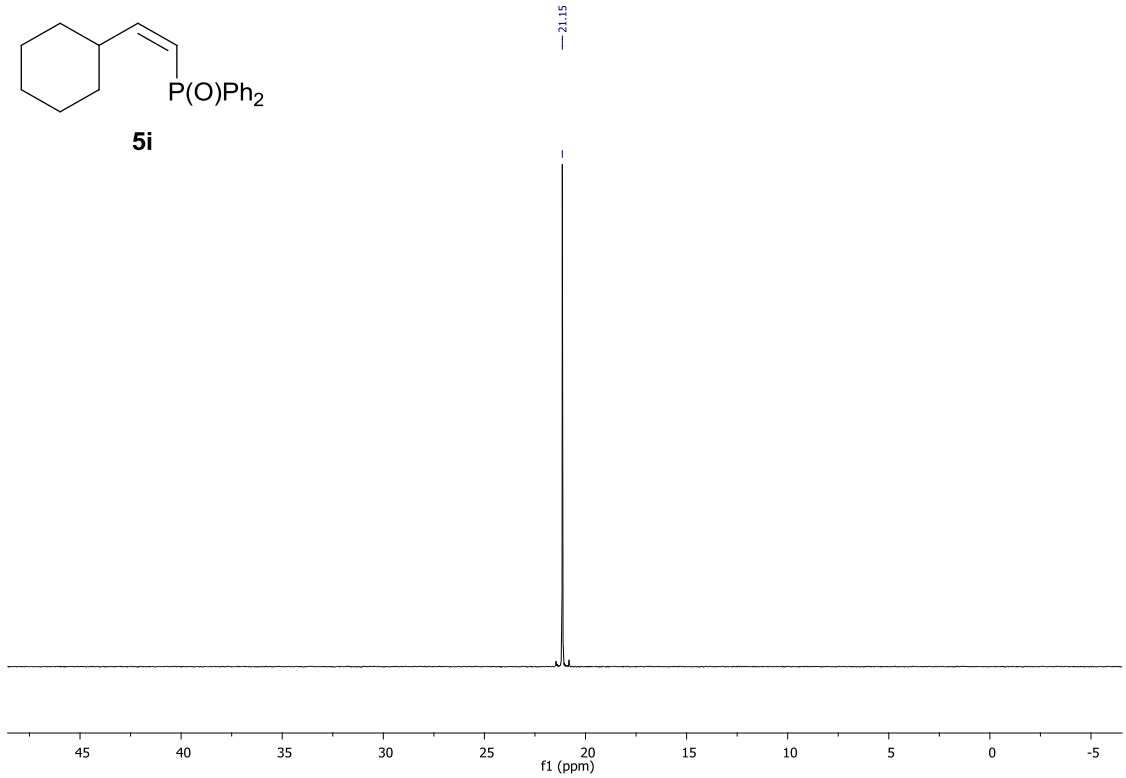

PPh2
5h
4.23
6.21
1.00
1.01
2.04
12.64
3.32
f1 (ppm)

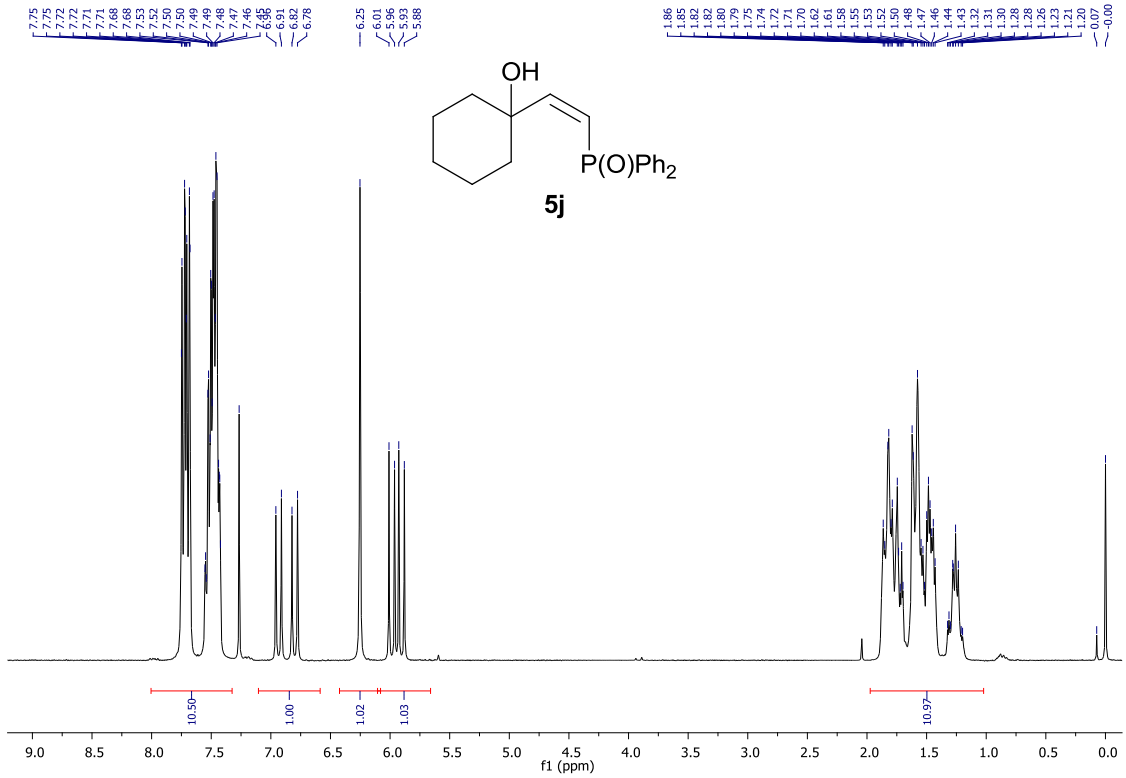

PPh2
5h
f1 (ppm)

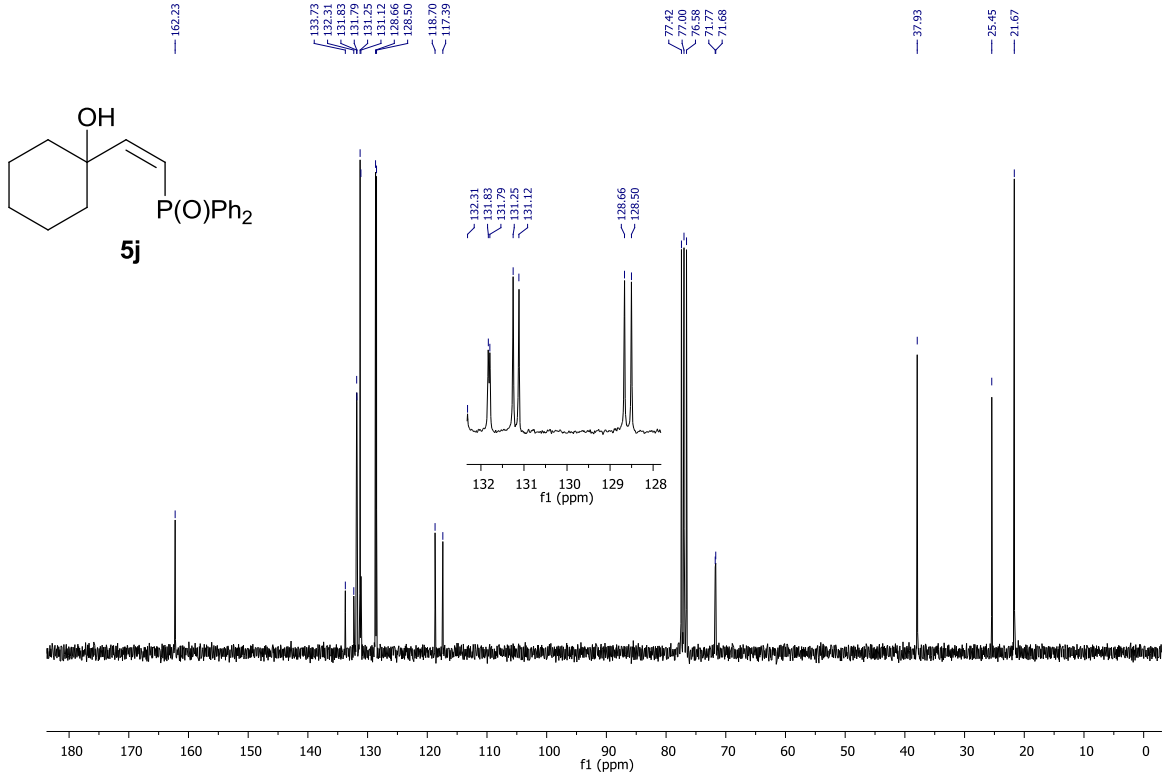

PPh2
5h
31.35
-17 -18 -19 -20 -21 -22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35 -36 -37 -38 -39 -40 -41 -42 -43 -44 -45
f1 (ppm)

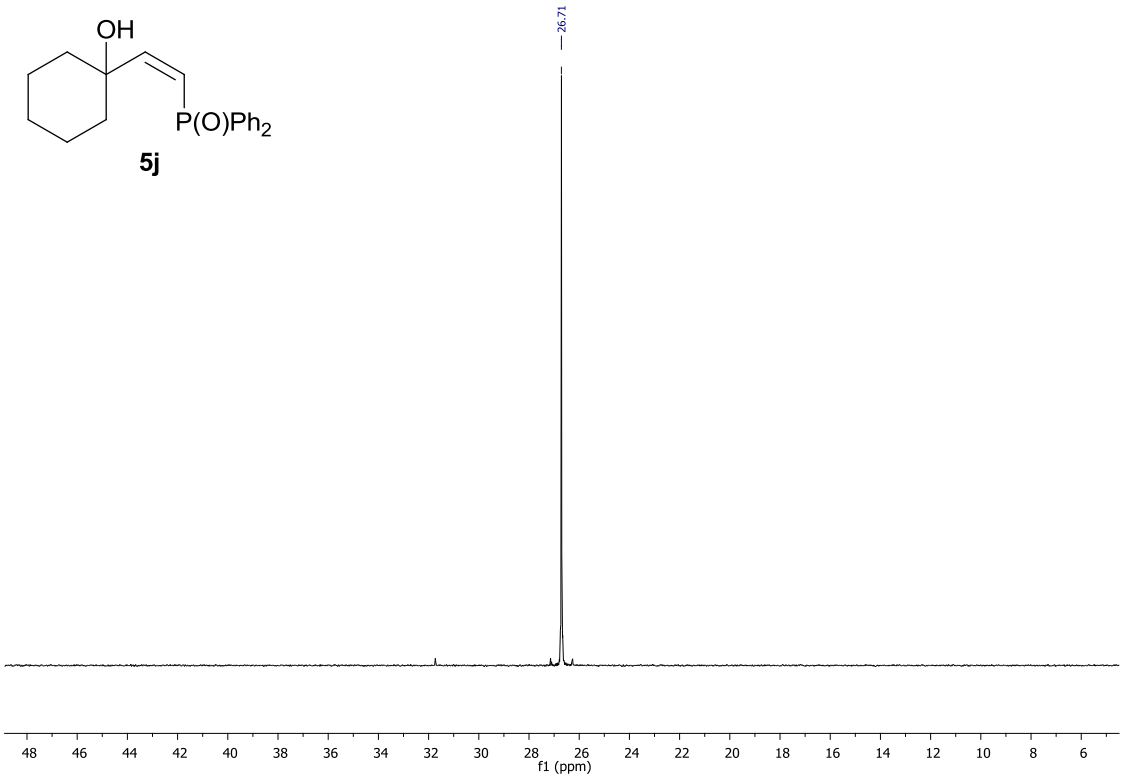

P(O)Ph2
5i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9
f1 (ppm)


159.55
135.38
134.01
131.42
131.38
130.95
130.82
128.50
128.34
119.81
118.46
77.42
77.00
76.58
39.11
39.01
32.08
32.06
25.70
25.02
P(O)Ph2
5i
131.42
131.38
130.95
130.82
128.50
128.34
131 130 129
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

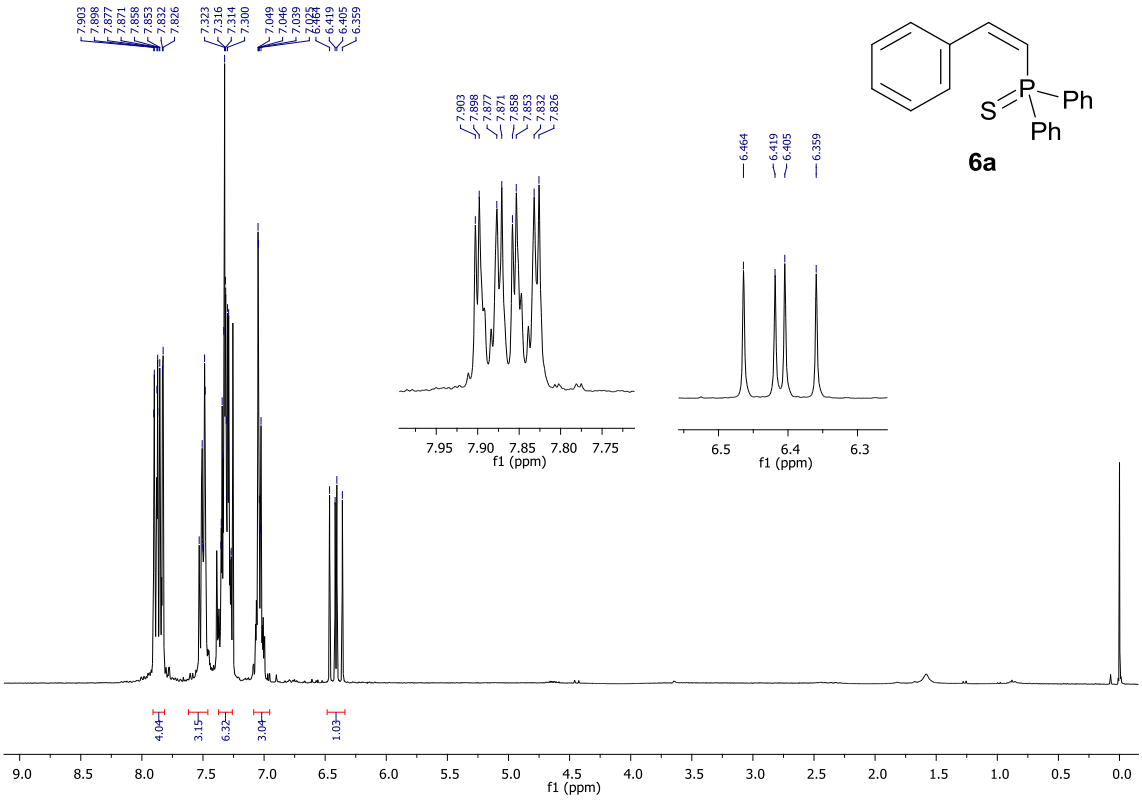

21.15
P(O)Ph2
5i
45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

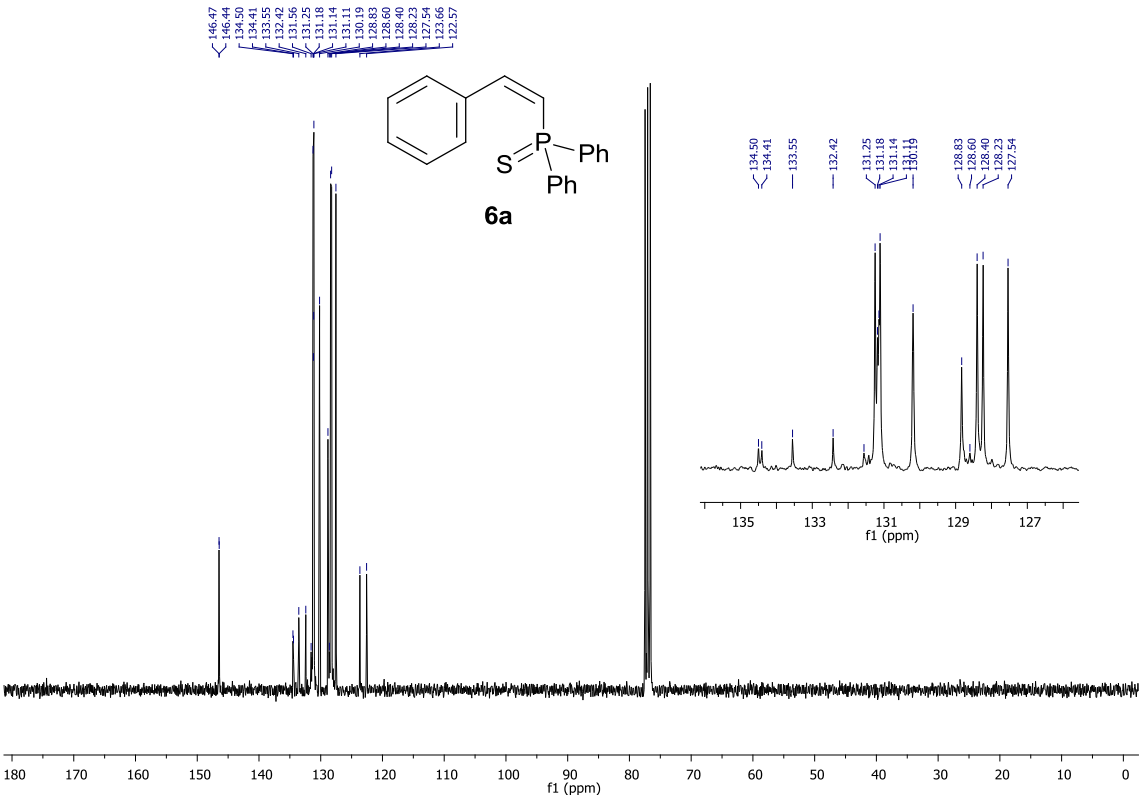

OH
P(O)Ph2
5j
f1 (ppm)

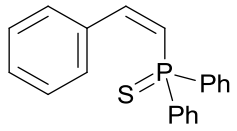

OH
P(O)Ph2
5j
f1 (ppm)


OH
P(O)Ph2
5j
26.71
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
f1 (ppm)

NMR spectra of compounds 6

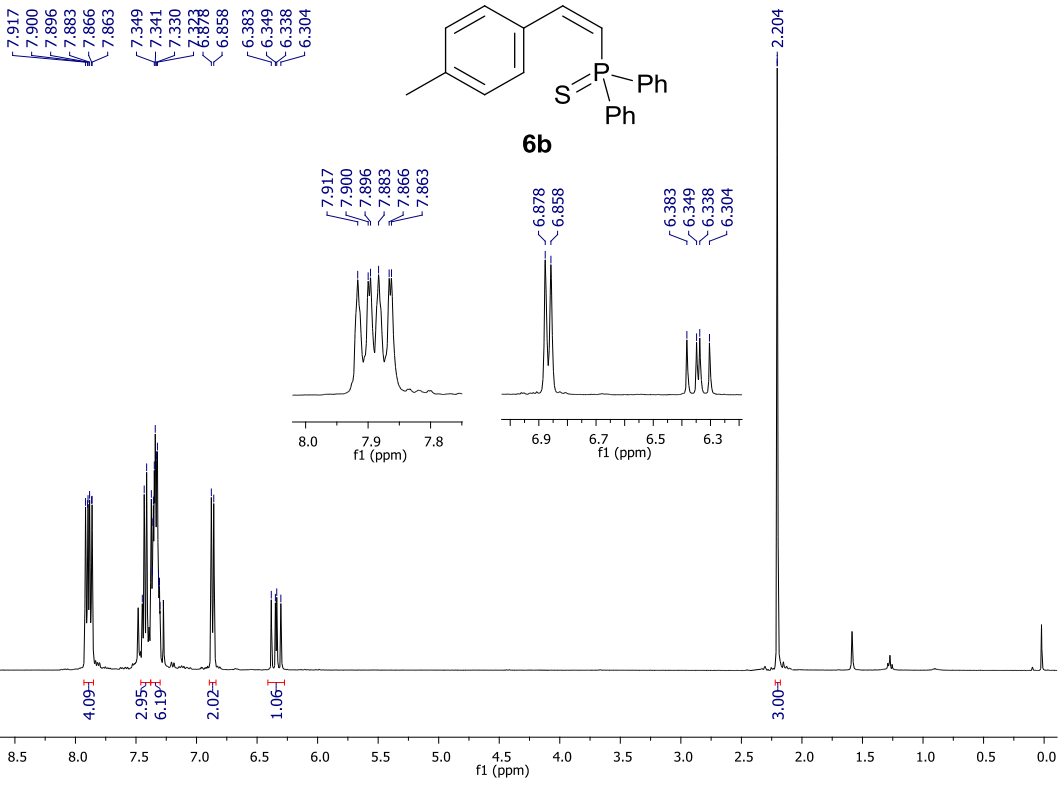




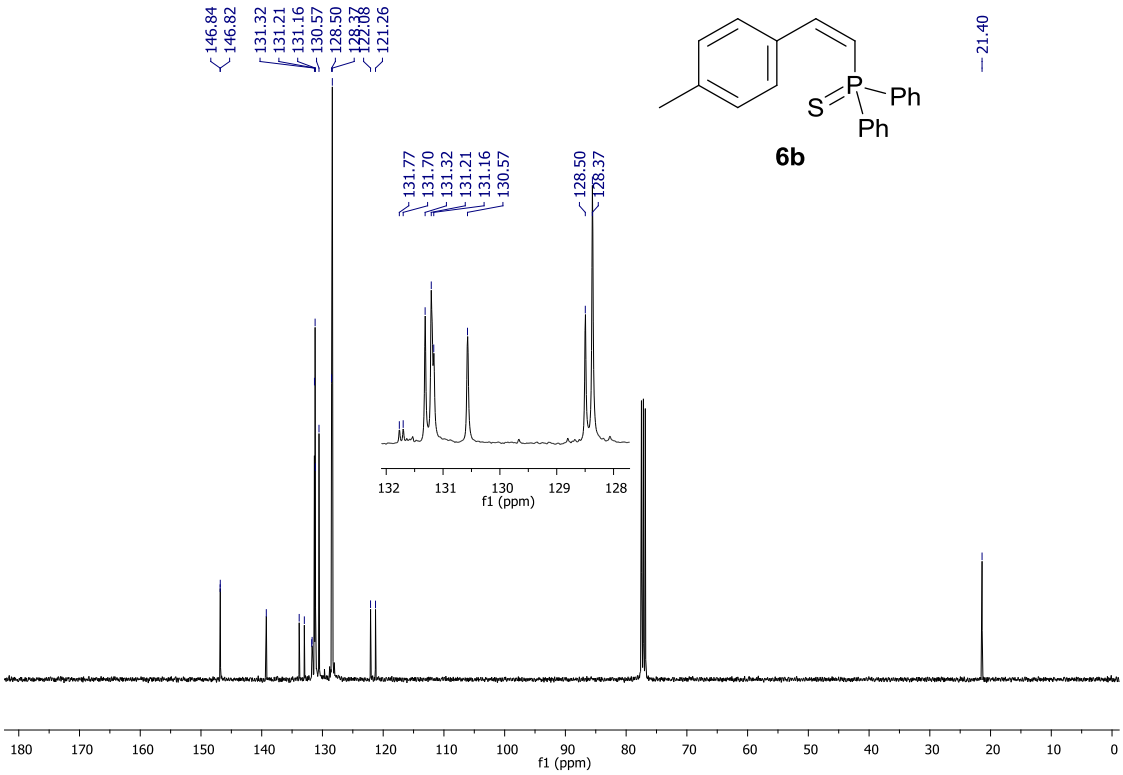

P
S
Ph
Ph

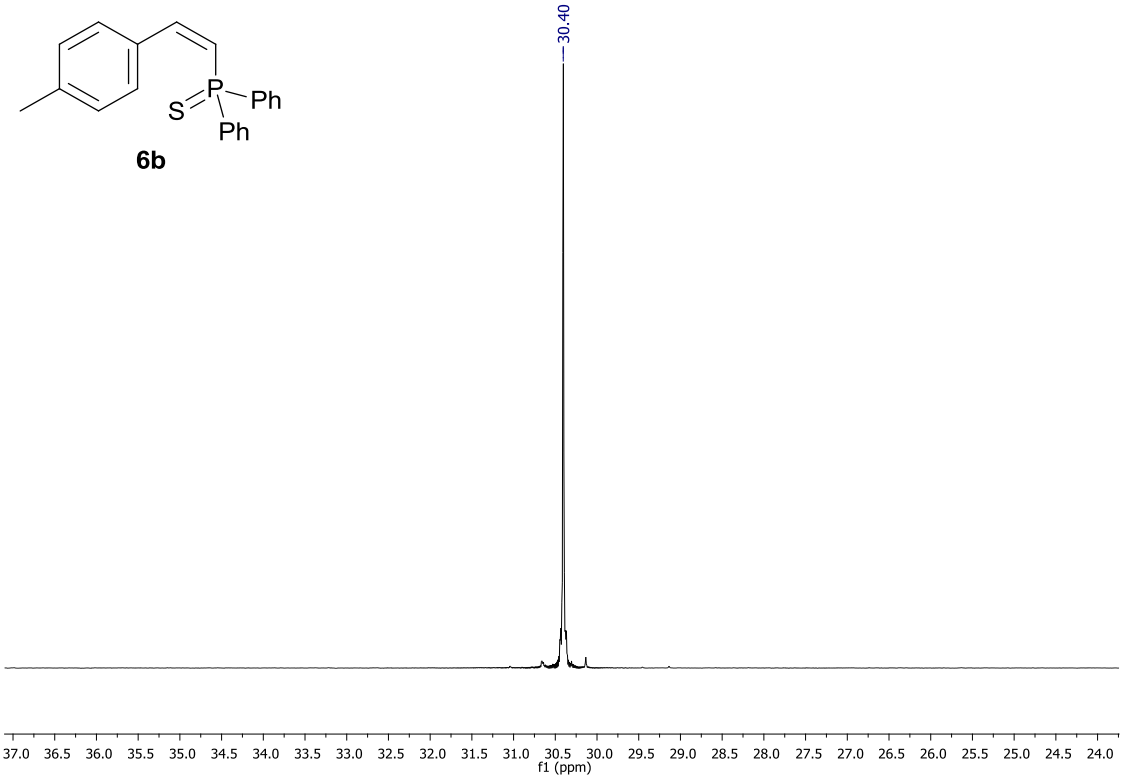
6a

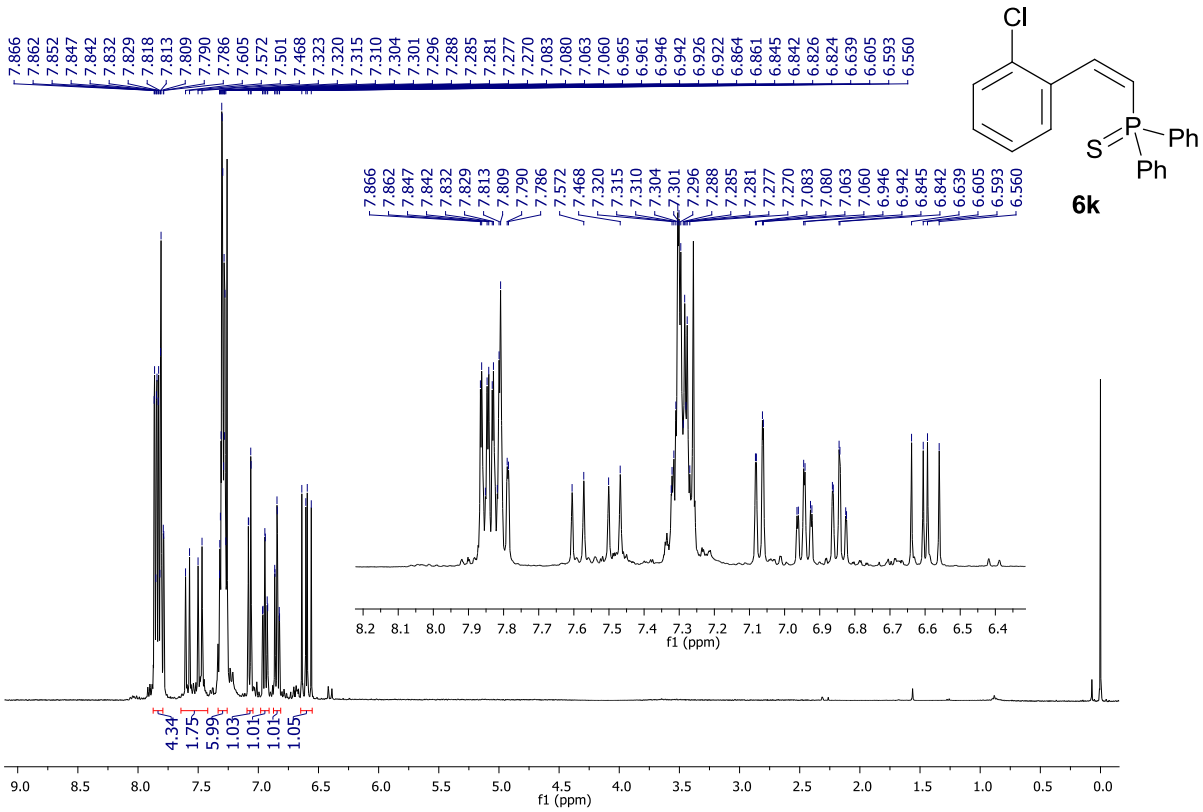
30.26
35.5 35.0 34.5 34.0 33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0 25.5 25.0
f1 (ppm)

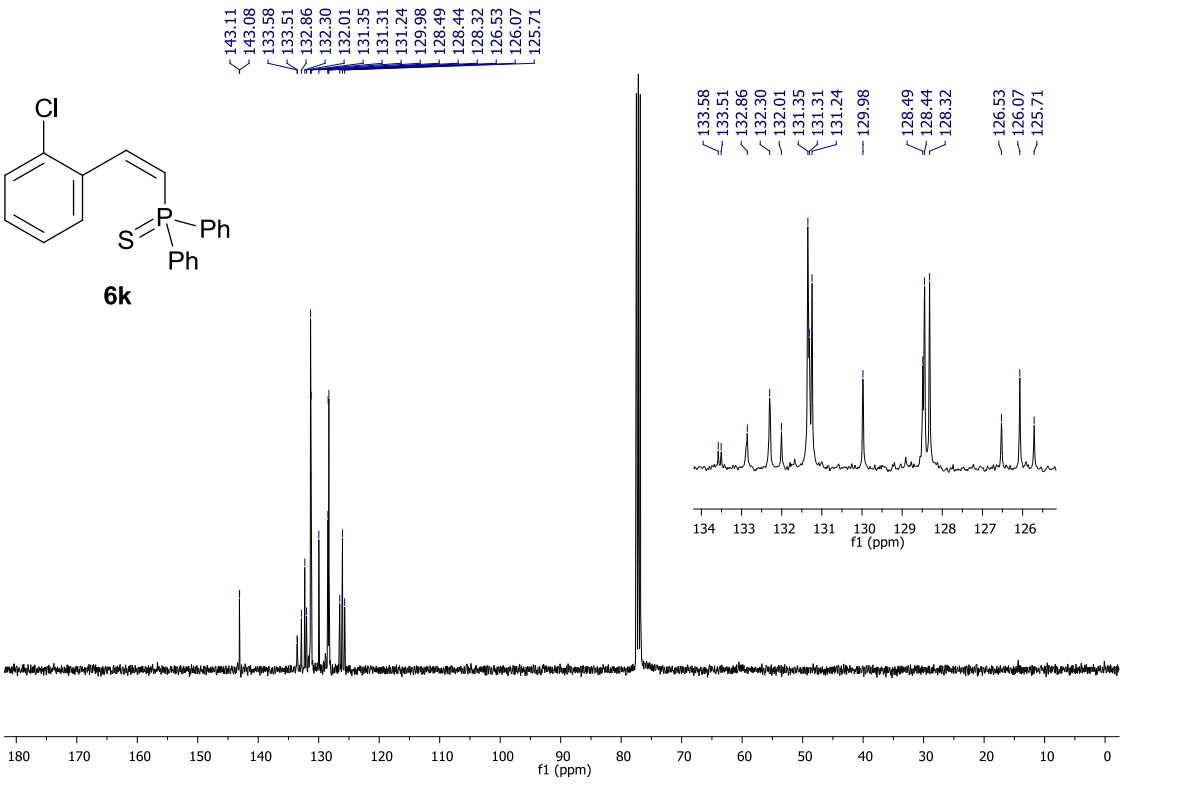

7.917
7.900
7.896
7.883
7.866
7.863
7.349
7.341
7.330
7.323
6.878
6.858
6.383
6.349
6.338
6.304
2.204
P
S
Ph
Ph
8.0 7.9 7.8
f1 (ppm)
6.9 6.7 6.5 6.3
f1 (ppm)
4.09
2.95
6.19
2.02
1.06
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

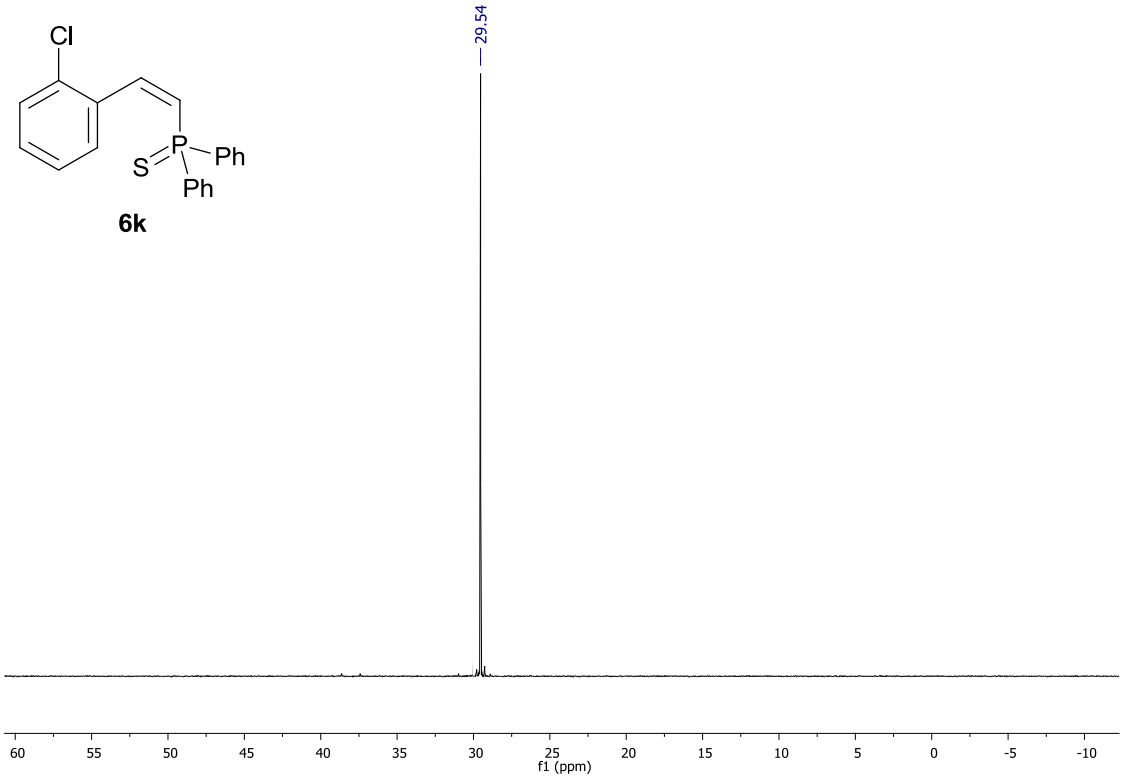
6b


146.84
146.82
131.32
131.21
131.16
130.57
128.50
128.37
121.26
21.40
131.77
131.70
131.32
131.21
131.16
130.57
128.50
128.37
132
131
130
129
128
f1 (ppm)
S
P
Ph
Ph
6b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

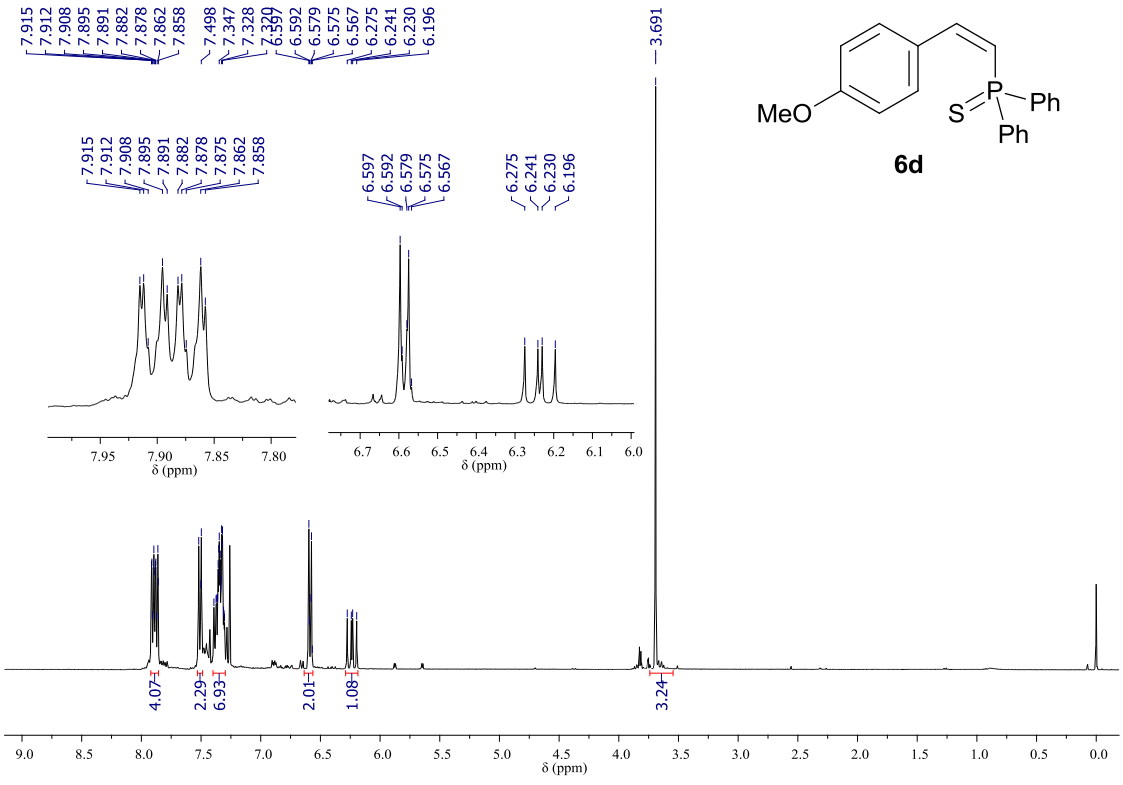

30.40
S
P
Ph
Ph
6b
37.0
36.5
36.0
35.5
35.0
34.5
34.0
33.5
33.0
32.5
32.0
31.5
31.0
30.5
30.0
29.5
29.0
28.5
28.0
27.5
27.0
26.5
26.0
25.5
25.0
24.5
24.0
f1 (ppm)


7.866
7.862
7.852
7.847
7.842
7.832
7.829
7.818
7.813
7.809
7.790
7.786
7.605
7.572
7.501
7.468
7.323
7.320
7.315
7.310
7.304
7.301
7.296
7.288
7.285
7.281
7.277
7.270
7.083
7.080
7.063
7.060
6.965
6.961
6.946
6.942
6.926
6.922
6.864
6.861
6.845
6.842
6.826
6.824
6.639
6.605
6.593
6.560
Cl
P
S
Ph
Ph
6k
4.34
1.75
5.99
1.03
1.01
1.01
1.05
f1 (ppm)


143.11
143.08
133.58
133.51
132.86
132.30
132.01
131.35
131.31
131.24
129.98
128.49
128.44
128.32
126.53
126.07
125.71
Cl
P
S
Ph
Ph
6k
f1 (ppm)

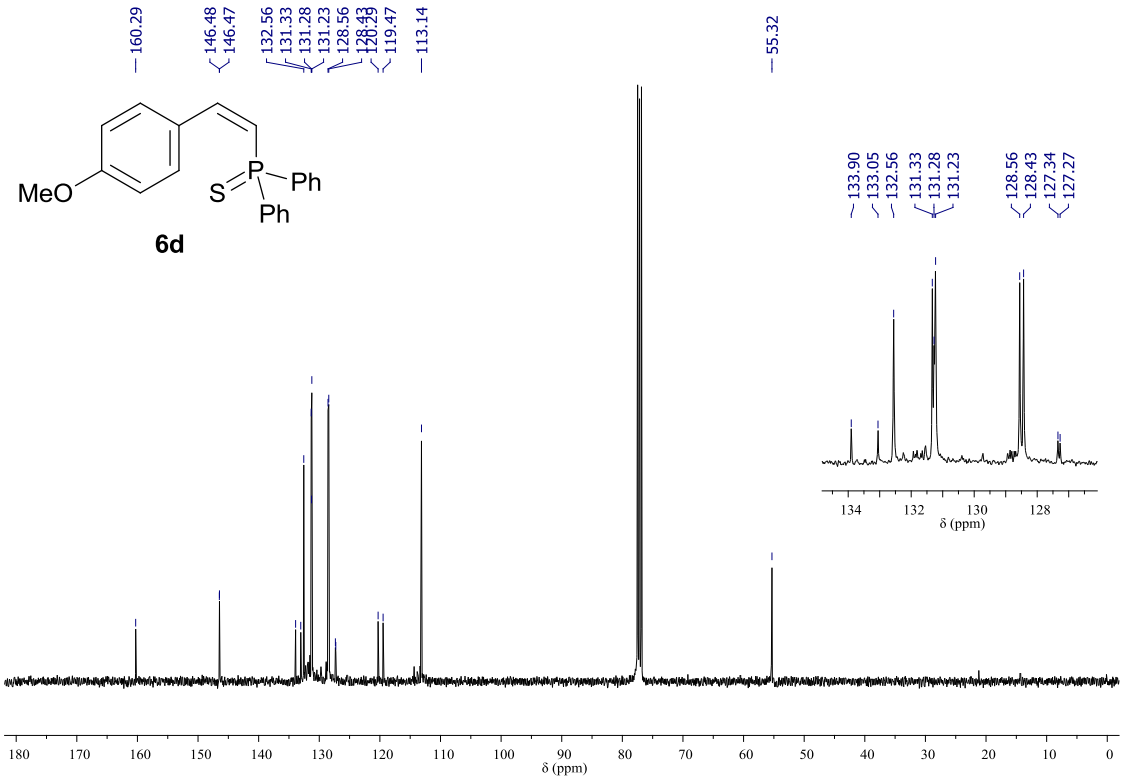

Cl
P
S
Ph
Ph
29.54
f1 (ppm)

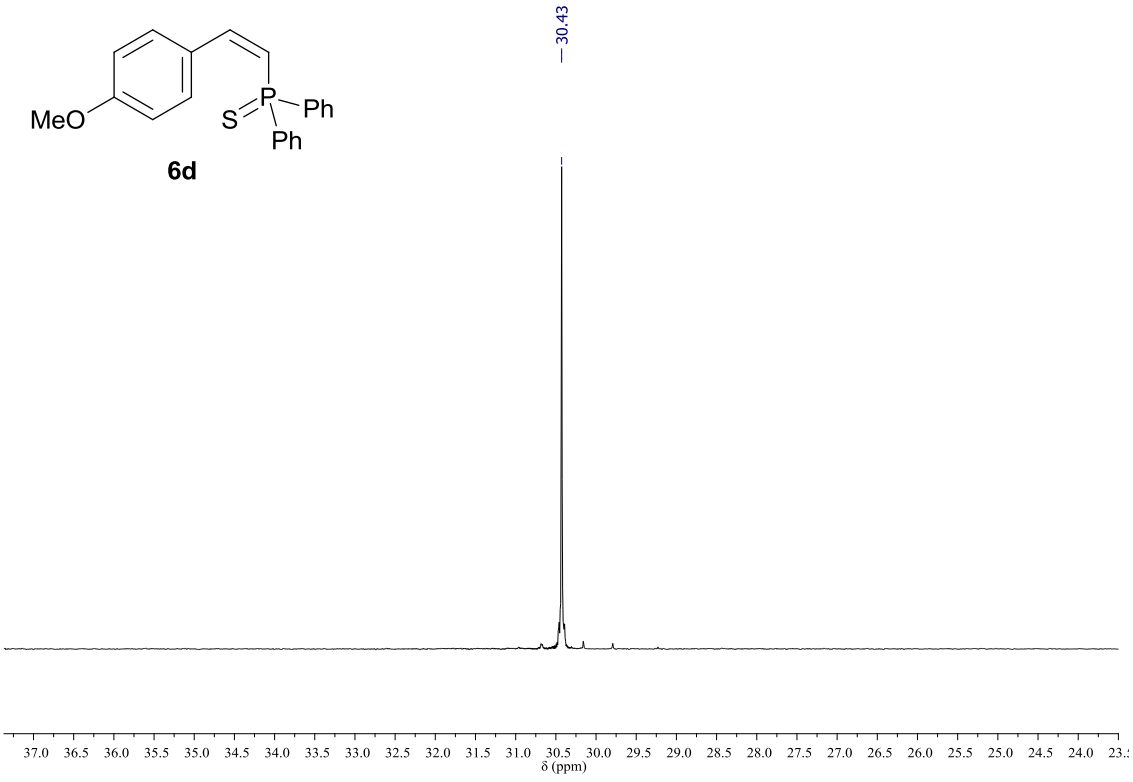
6k

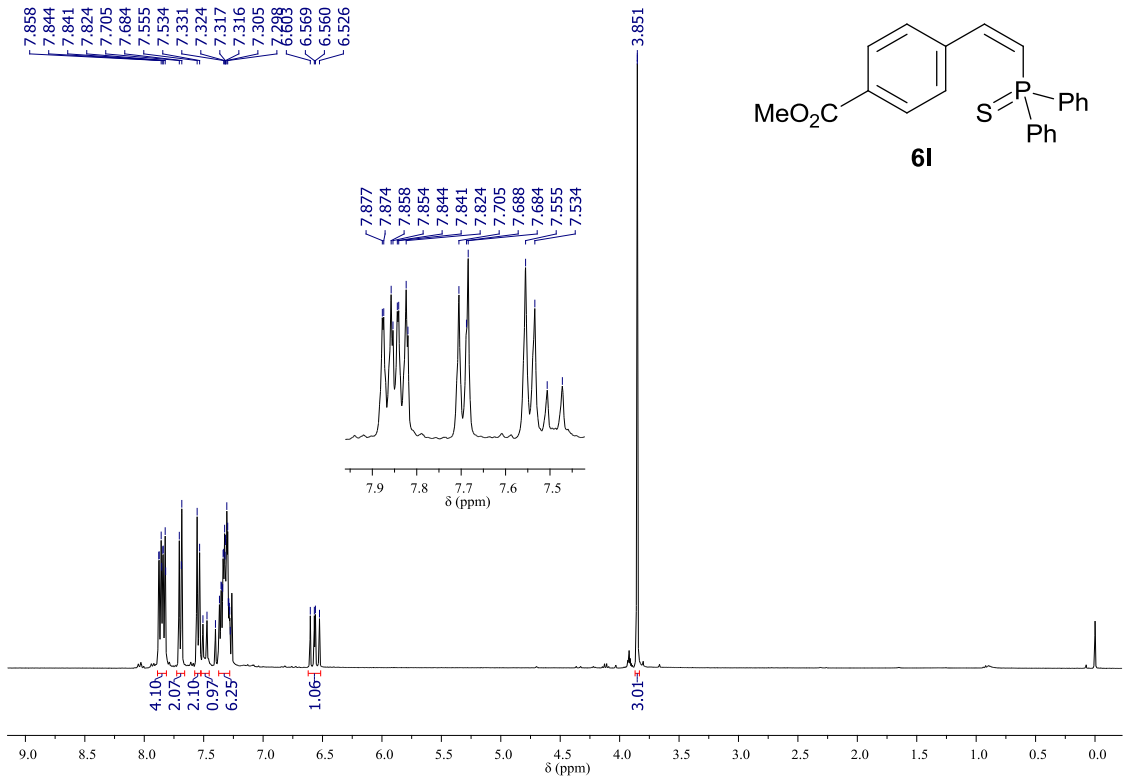

7.915
7.912
7.908
7.895
7.891
7.882
7.878
7.862
7.858
7.498
7.347
7.328
6.592
6.579
6.575
6.567
6.275
6.241
6.230
6.196
3.691
δ (ppm)
4.07
2.29
6.93
2.01
1.08
3.24

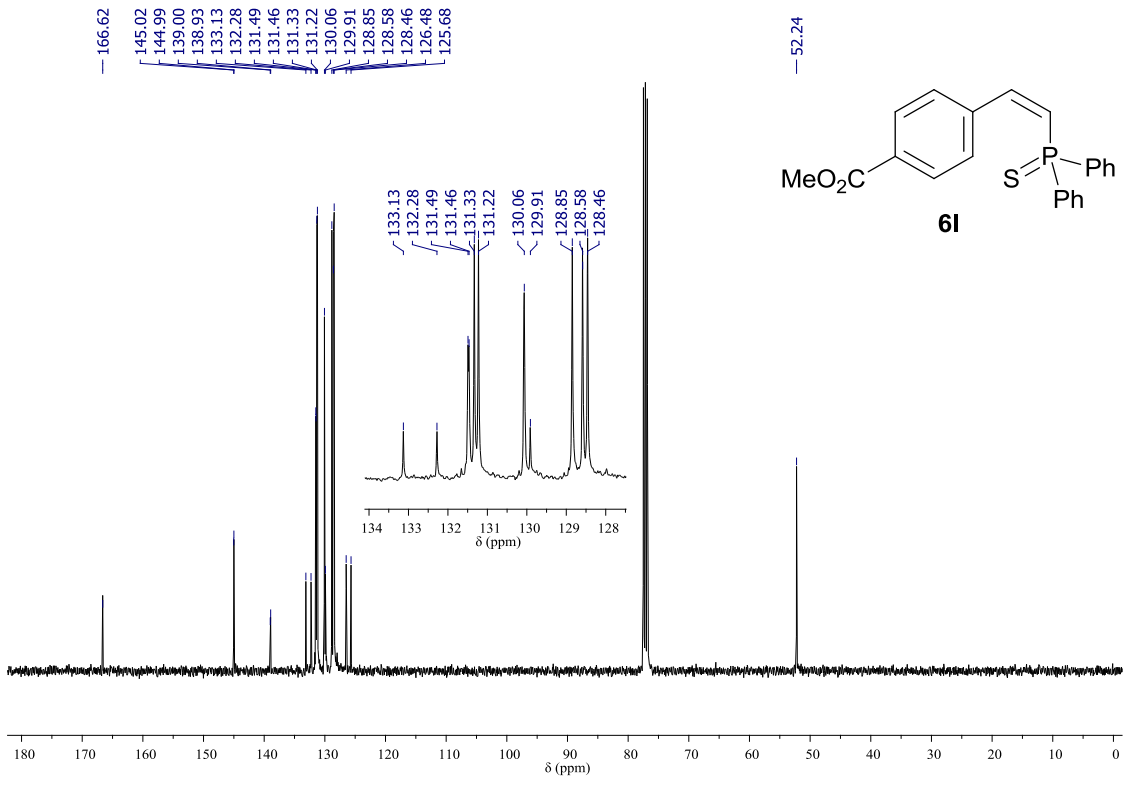
MeO
P
S
Ph
Ph

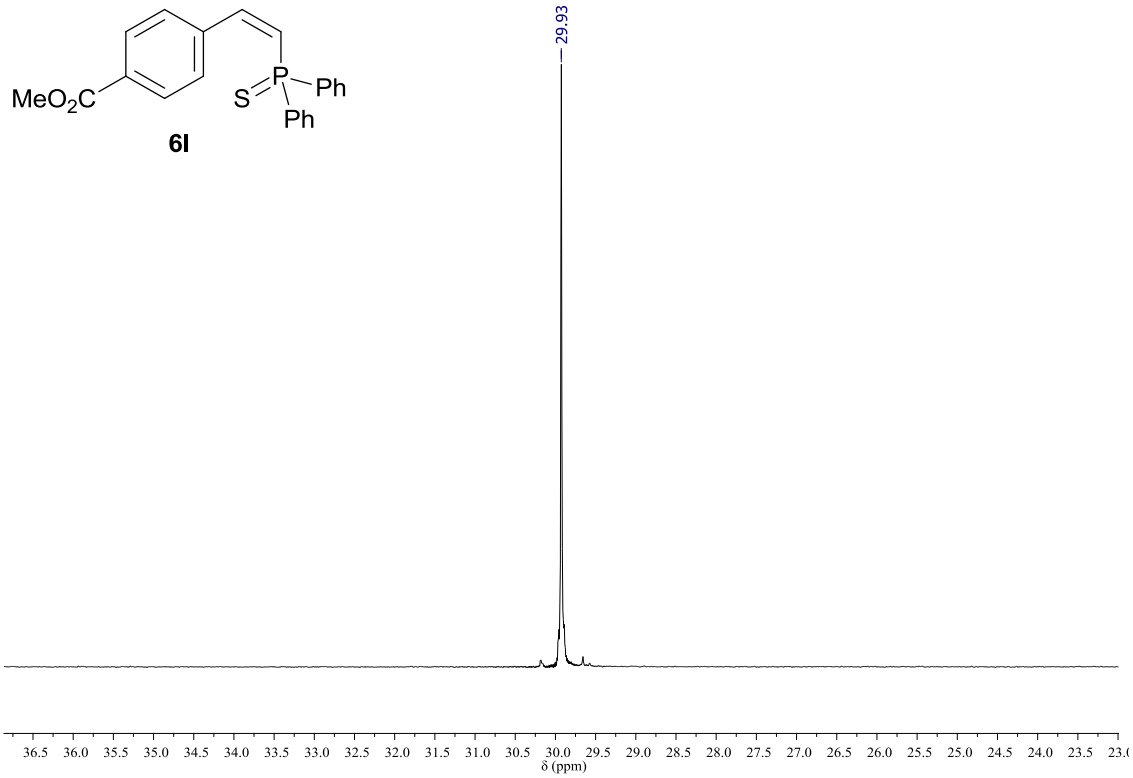
6d

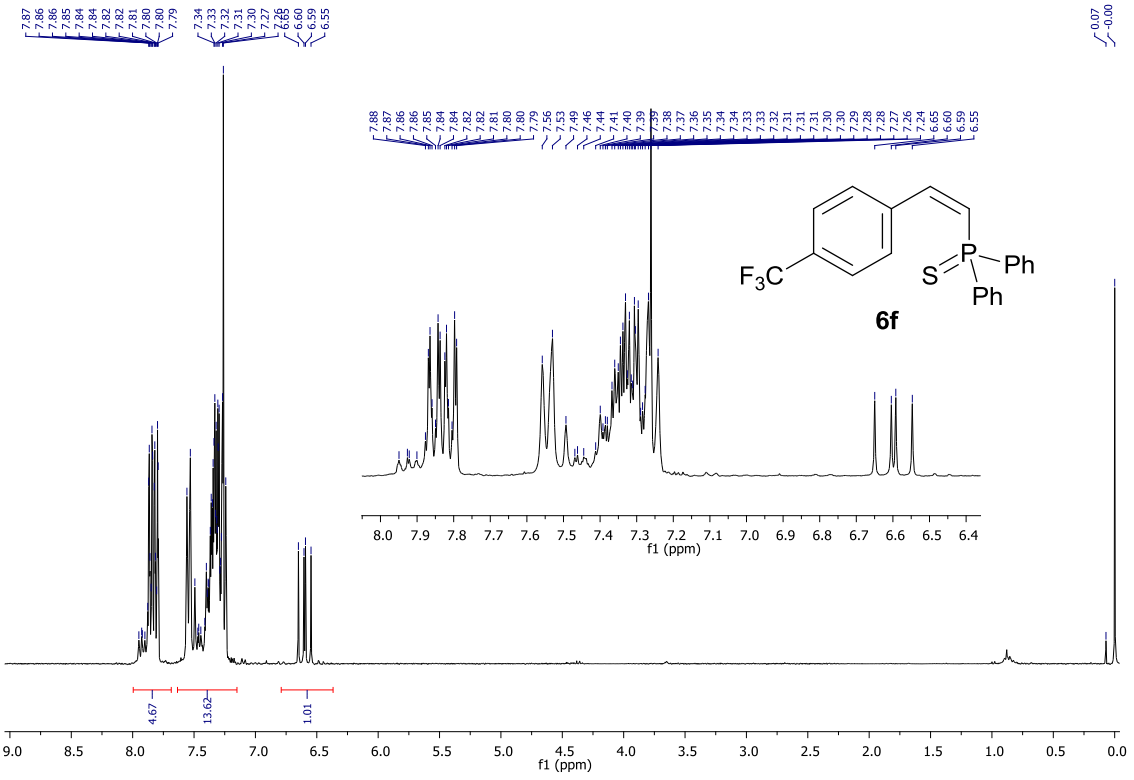

160.29
146.48
146.47
132.56
131.33
131.28
131.23
128.56
128.43
128.29
119.47
113.14
55.32
MeO
P
S
Ph
Ph
6d
133.90
133.05
132.56
131.33
131.28
131.23
128.56
128.43
127.34
127.27
134
132
130
128
δ (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

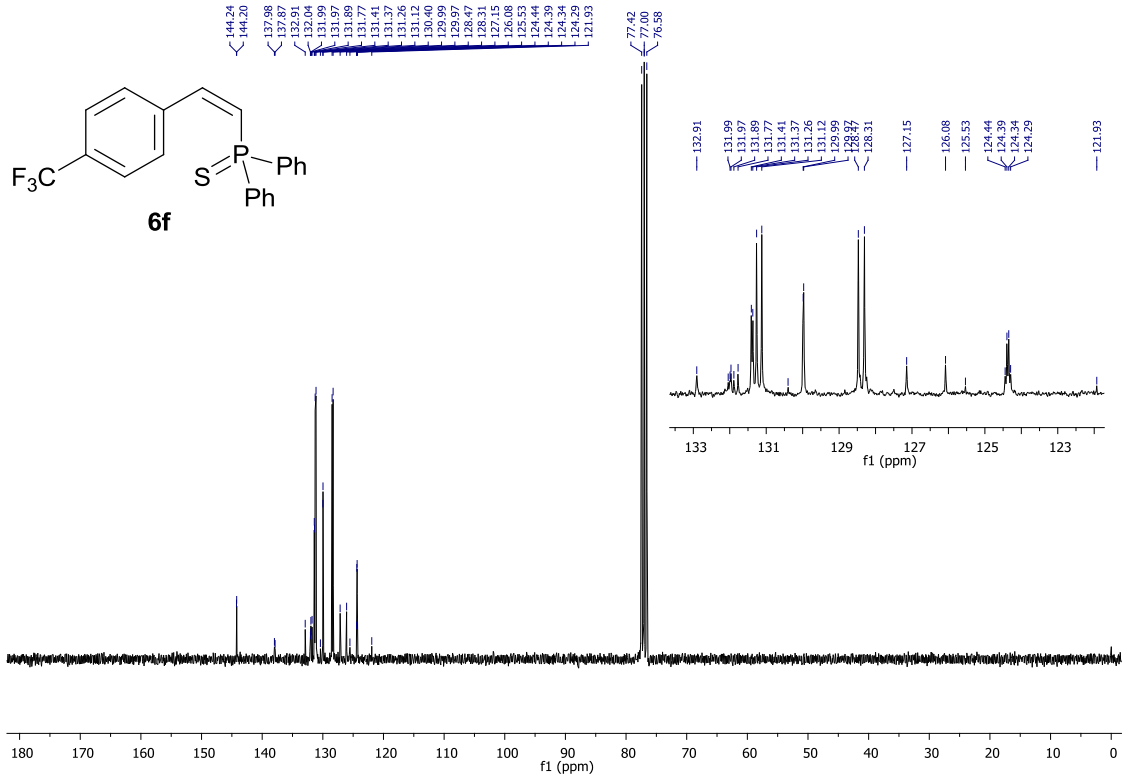

30.43
MeO
P
S
Ph
Ph
6d
37.0
36.5
36.0
35.5
35.0
34.5
34.0
33.5
33.0
32.5
32.0
31.5
31.0
30.5
30.0
29.5
29.0
28.5
28.0
27.5
27.0
26.5
26.0
25.5
25.0
24.5
24.0
δ (ppm)

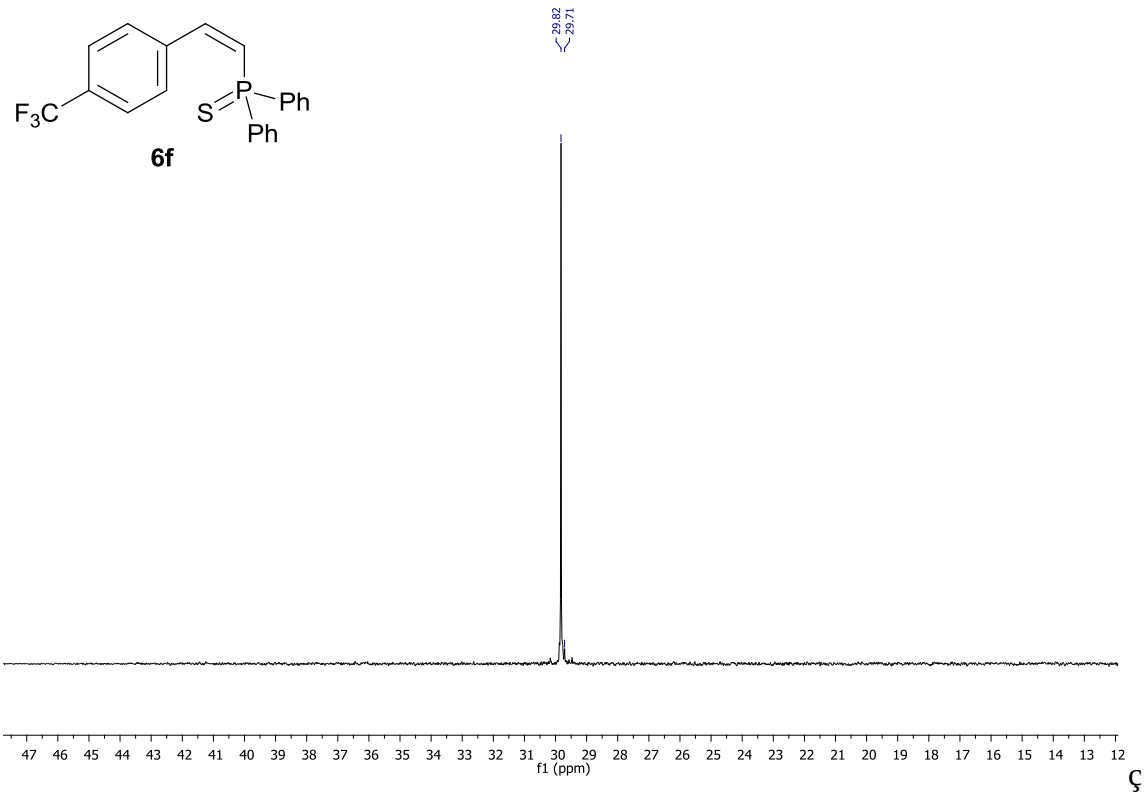

7.858
7.844
7.841
7.824
7.705
7.684
7.555
7.534
7.331
7.324
7.317
7.316
7.305
6.569
6.560
6.526
3.851
7.877
7.874
7.858
7.854
7.844
7.841
7.824
7.705
7.688
7.684
7.555
7.534
7.9 7.8 7.7 7.6 7.5
δ (ppm)
4.10
2.07
2.10
0.97
6.25
1.06
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)
MeO2C
S
P
Ph
Ph
6l


166.62
145.02
144.99
139.00
138.93
133.13
132.28
131.49
131.46
131.33
131.22
130.06
129.91
128.85
128.58
128.46
126.48
125.68
52.24
133.13
132.28
131.49
131.46
131.33
131.22
130.06
129.91
128.85
128.58
128.46
134 133 132 131 130 129 128
δ (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)
MeO2C
S
P
Ph
Ph
6l

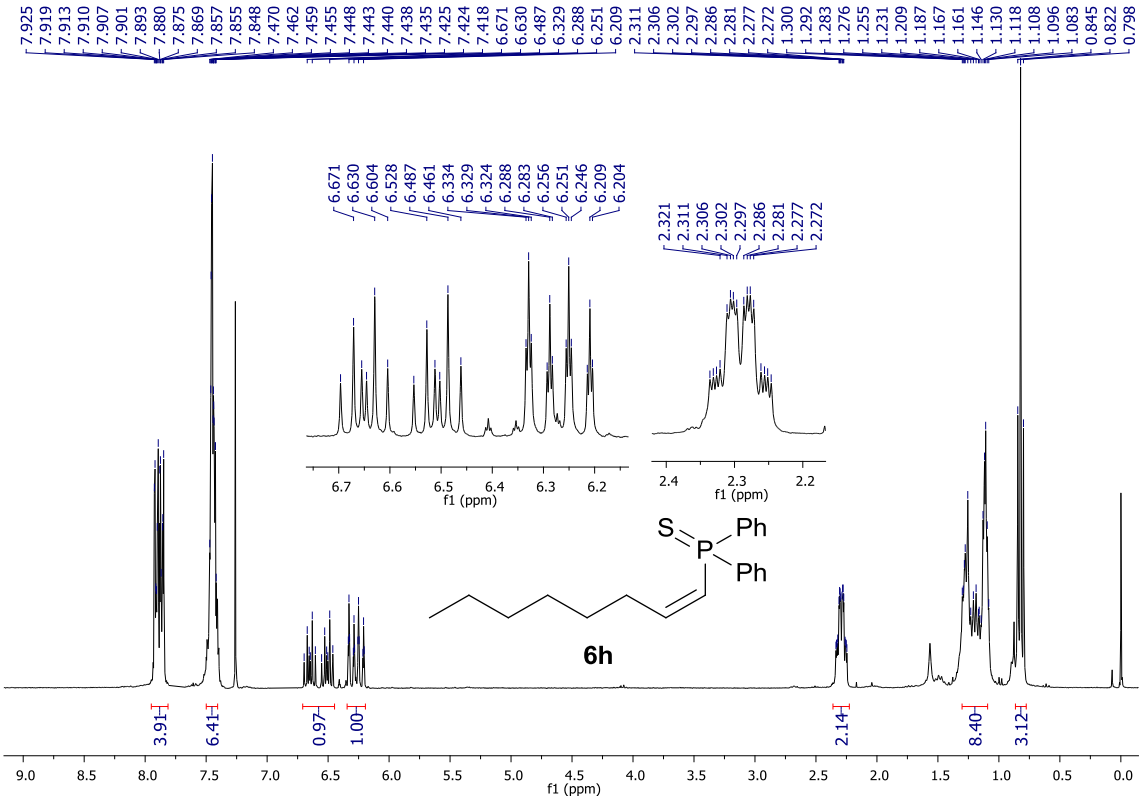

MeO2C
P
S
Ph
Ph
6l
29.93
δ (ppm)


F3C
P
S
Ph
Ph
6f
f1 (ppm)
4.67
13.62
1.01


144.24
144.20
137.98
137.87
132.91
132.04
131.99
131.97
131.89
131.77
131.41
131.37
131.26
131.12
130.40
129.99
129.97
128.47
128.31
127.15
126.08
125.53
124.44
124.39
124.34
124.29
121.93
77.42
77.00
76.58
F3C
S
P
Ph
Ph
6f
132.91
131.99
131.97
131.89
131.77
131.41
131.37
131.26
131.12
129.99
129.97
128.47
128.31
127.15
126.08
125.53
124.44
124.39
124.34
124.29
121.93
133
131
129
127
125
123
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


29.82
29.71
F3C
S
P
Ph
Ph
6f
47
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
f1 (ppm)

Ç


7.925 7.919 7.913 7.910 7.907 7.901 7.893 7.880 7.875 7.869 7.857 7.855 7.848 7.470 7.462 7.459 7.455 7.448 7.443 7.440 7.438 7.435 7.425 7.424 7.418 6.671 6.630 6.487 6.329 6.288 6.251 6.209
2.311 2.306 2.302 2.297 2.286 2.281 2.277 2.272 1.300 1.292 1.283 1.276 1.255 1.231 1.209 1.187 1.167 1.161 1.146 1.130 1.118 1.108 1.096 1.083 0.845 0.822 0.798
6.671 6.630 6.604 6.528 6.487 6.461 6.334 6.329 6.324 6.288 6.283 6.256 6.251 6.246 6.209 6.204
2.321 2.311 2.306 2.302 2.297 2.286 2.281 2.277 2.272
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S
P
Ph
Ph
6h
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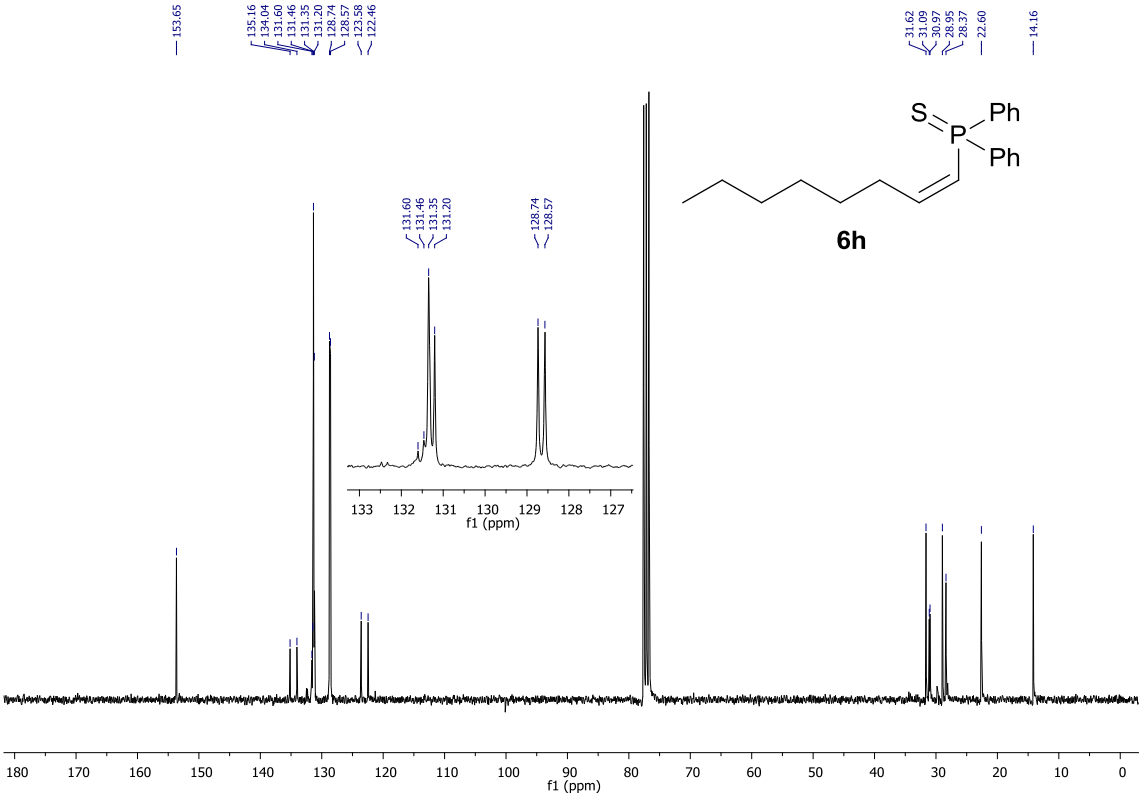
f1 (ppm)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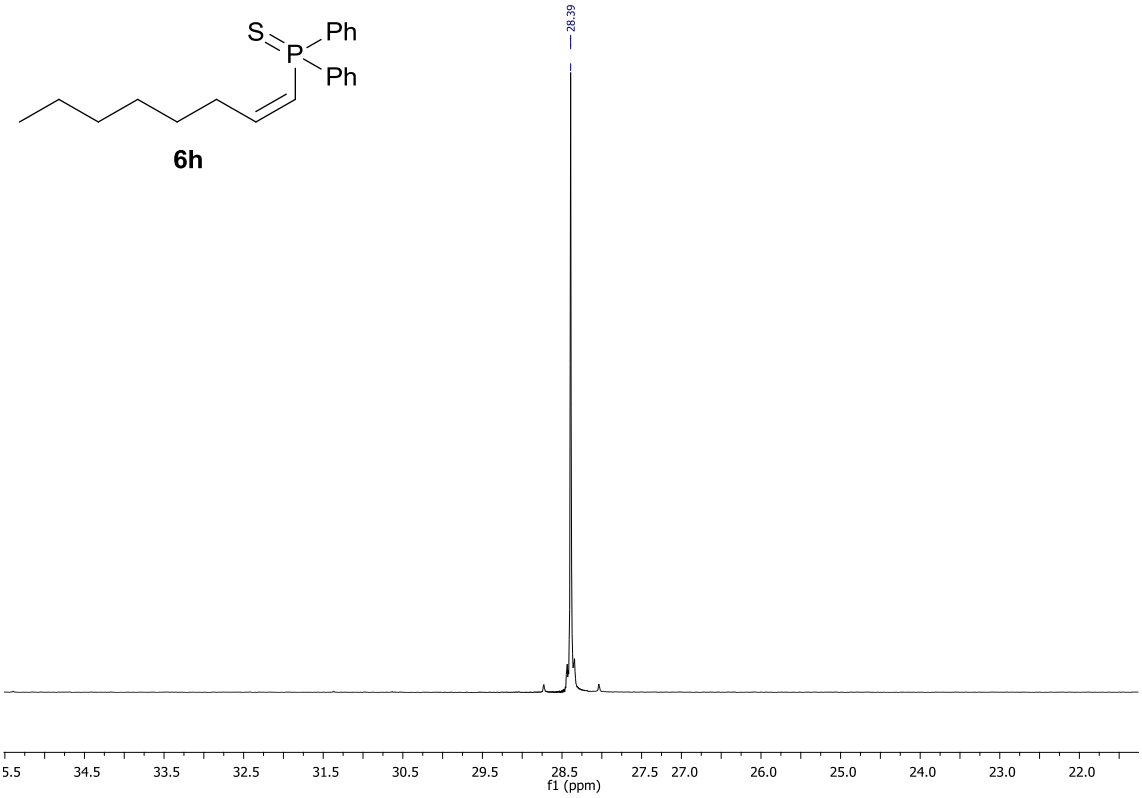
135.16 134.04 131.60 131.46 131.35 131.20 128.74 128.57 123.58 122.46
31.62 31.09 30.97 28.95 28.37 22.60 14.16
131.60 131.46 131.35 131.20 128.74 128.57
f1 (ppm)
S
P
Ph
Ph
6h
f1 (ppm)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P
Ph
Ph
6h
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5.5
34.5
33.5
32.5
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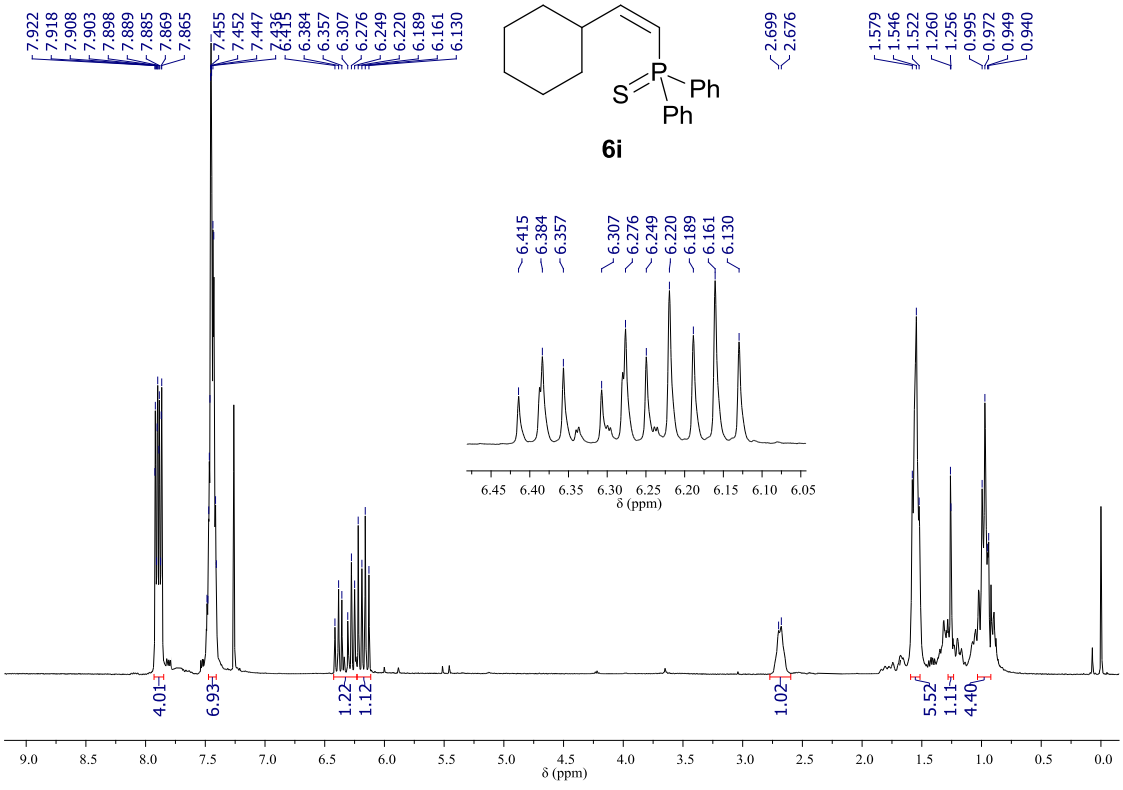
22.0
f1 (ppm)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6.249
6.220
6.189
6.161
6.130
2.699
2.676
1.579
1.546
1.522
1.260
1.256
0.995
0.972
0.949
0.940
S
P
Ph
Ph
6i
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
6.05
δ (ppm)
4.01
6.93
1.22
1.12
1.02
5.52
1.11
4.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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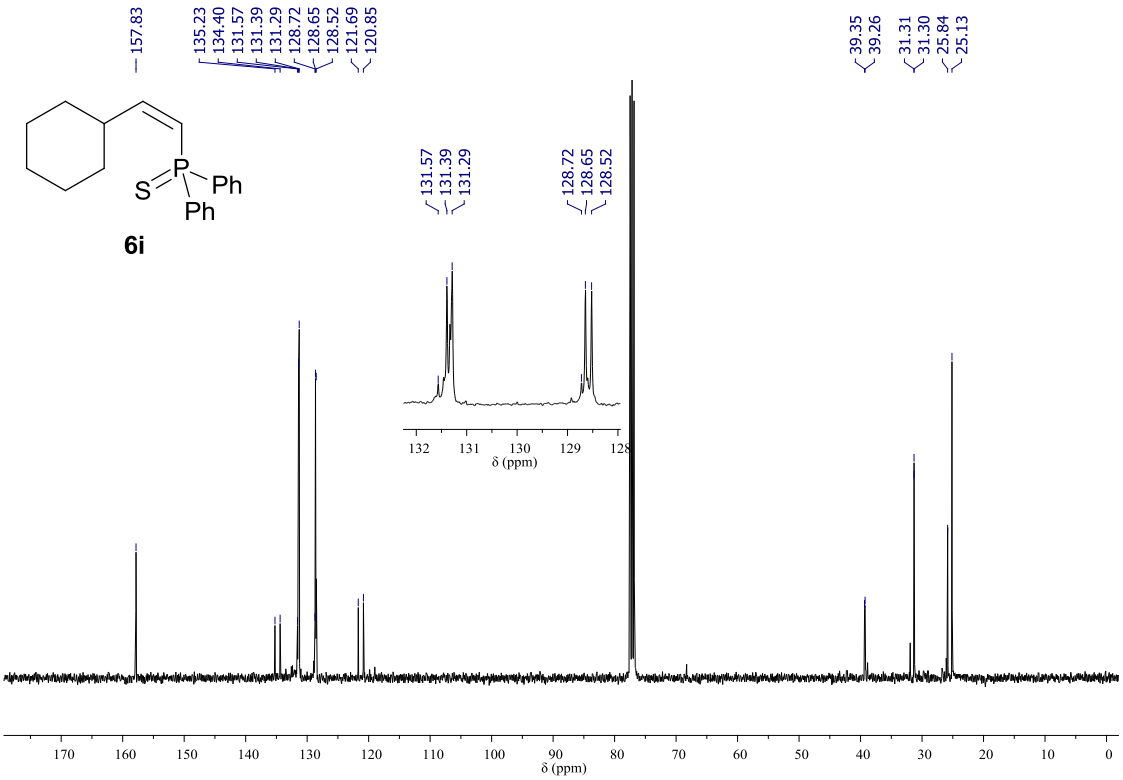
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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31.30
25.84
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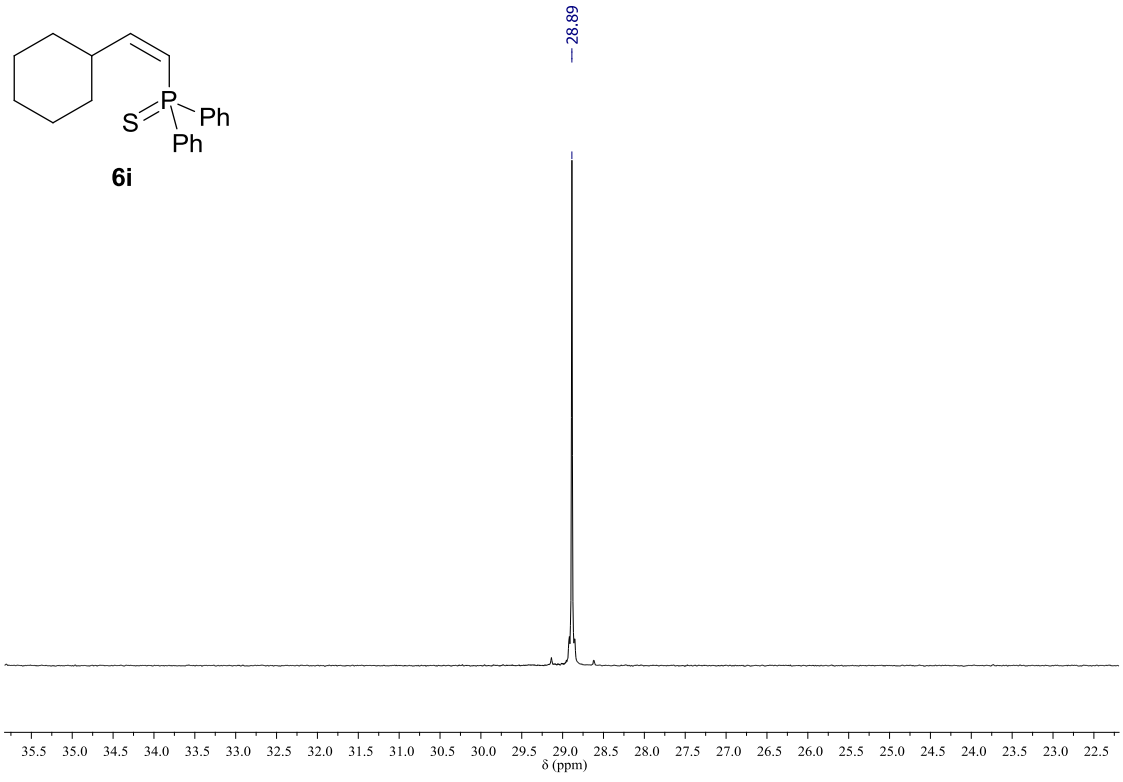
P
S
Ph
Ph
6i
δ (ppm)
δ (ppm)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P
S
Ph
Ph
6i
δ (ppm)

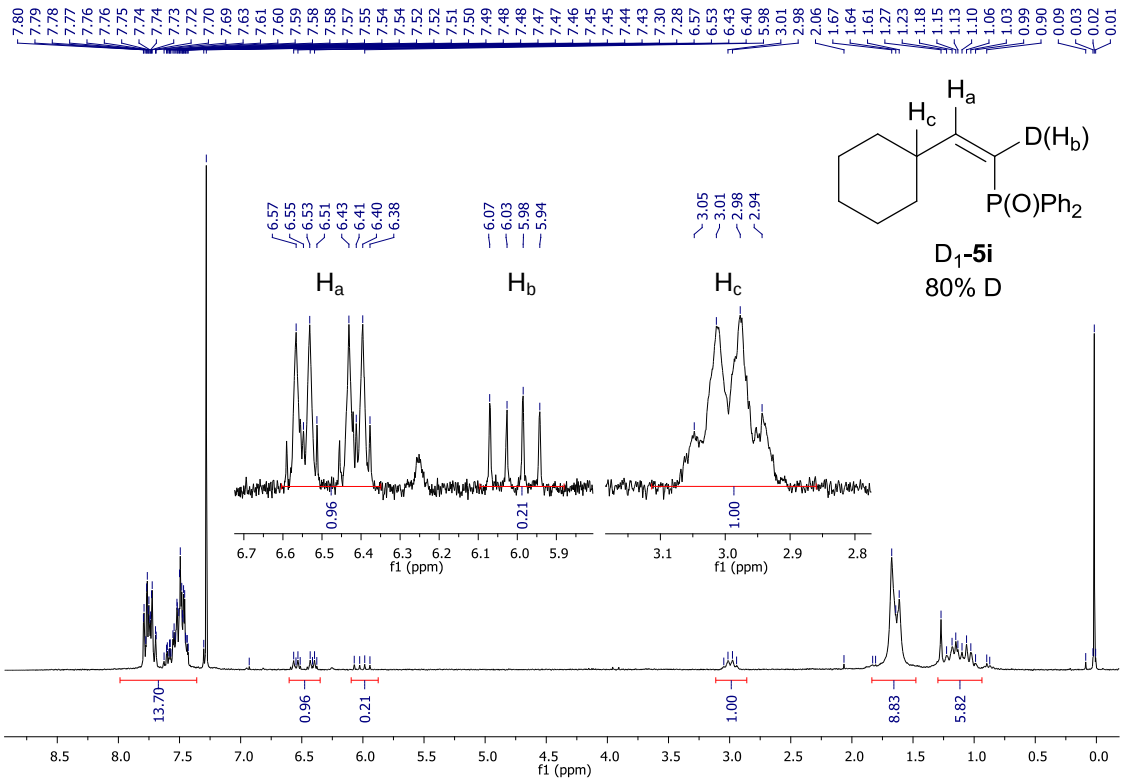

Figure S1. ^{1}H NMR spectrum of α-D_1-**5i**.

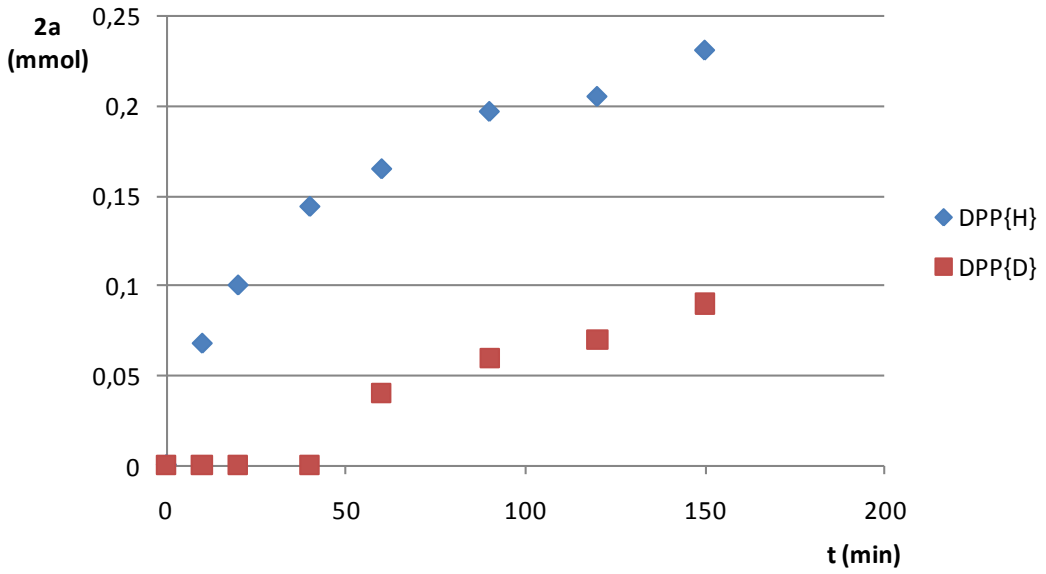

Figure S2. Kinetic isotope effect graphic for the synthesis of **2a**.

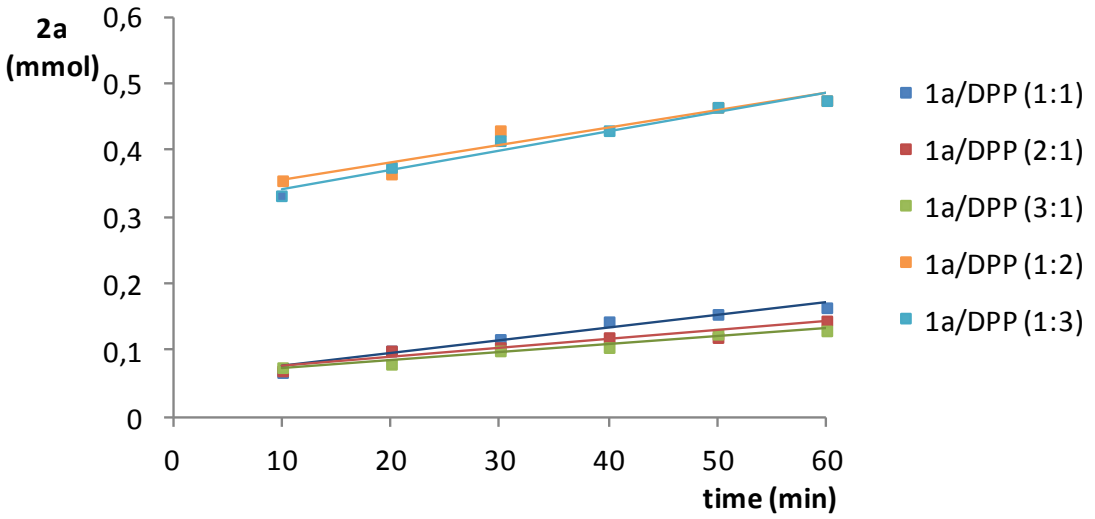

Figure S3. Effect of the styrene (**1a**)/diphenylphosphine (DPP) ratio on the formation of **2a**.

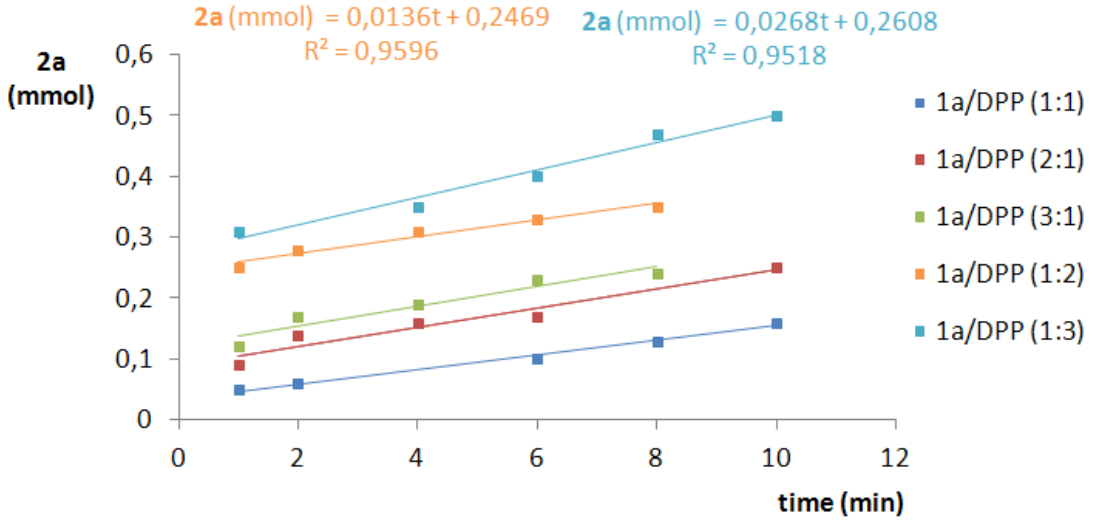

Figure S4. Initial rates determined for the reaction of styrene (**1a**) and diphenylphosphine (DPP).

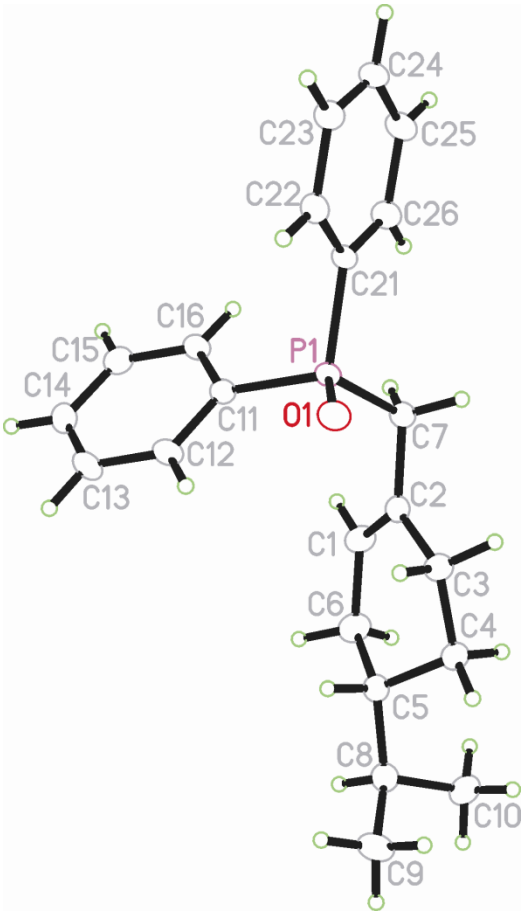

Figure S5. Plot showing the X-ray structure and atomic numbering for compound **2z**.

• Chemical formula: $C_{22}H_{27}OP$
• Formula weight: M = 338.40
• Crystal system: monoclinic
• Unit-cell dimensions: a = 5.7190(3), b = 17.9432(10), c = 9.0209(5) Å
• Unit cell volume: U = 914.22(9) $Å^3$
• Temperature: T = 100(2)
• Space group symbol: $P2_1$
• No. of formula units in unit cell: Z = 2
• Number of reflections measured: 19038
• Number of independent reflections: 3750
• R_{int} = 0.0271
• wR_2 = 0.0741

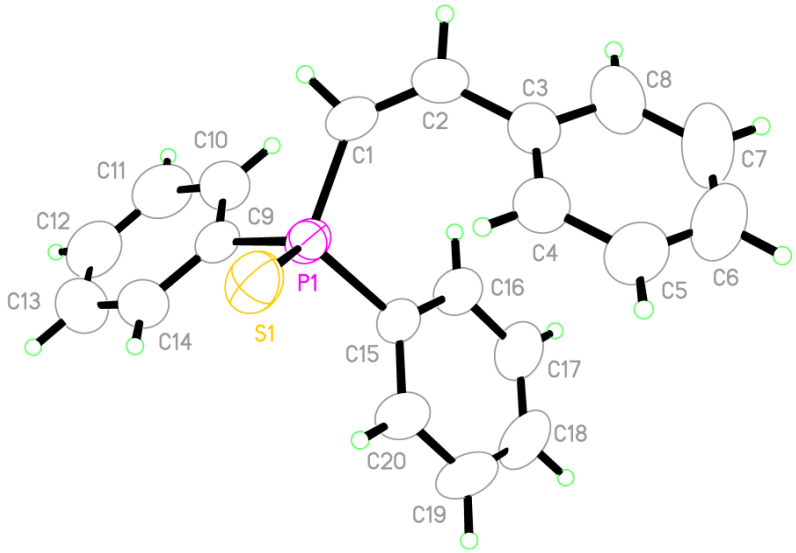

Figure S6. Plot showing the X-ray structure and atomic numbering for compound **6a**.

- Chemical formula: $C_{20}H_{17}PS$
- Formula weight: M = 320.37
- Crystal system: monoclinic
- Unit-cell dimensions: a = 14.697(3), b = 6.6112(11), c = 17.826(3) Å
- Unit cell volume: U = 1719.3(5) $Å^3$
- Temperature: T = 298(1)
- Space group symbol: P 21/n
- No. of formula units in unit cell: Z = 4
- Number of reflections measured: 3025
- Number of independent reflections: 2399
- R_{int} = 0.0538
- wR_2 = 0.1062