Supporting Information

Palladium-catalysed coupling of α-halo vinylphosphonate and α-phosphonovinyl sulfonate with alkylzincs: straightforward and versatile synthesis of α-alkyl vinylphosphonates

Li Zhang,[a] Yewen Fang,[*b,e], Xiaoping Jin,[*c] Ting Guo,[d] Ruifeng Li,[*a] Yan Li,[d] Xie Li,[b] Qilin Ye,[b] and Xiang Luo[b]

[a] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, No. 79 West Yingze Street, Taiyuan 030024, China

[b] School of Materials and Chemical Engineering, Ningbo University of Technology, No. 201 Fenghua Road, Ningbo 315211, China

[c] Department of Pharmaceutical Engineering, Zhejiang Pharmaceutical College, No. 888 Yinxian Avenue East, Ningbo 315100, China

[d] Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials and Ministry-of-Education Key Laboratory for Synthesis and Application of Organic Functional Molecules, Hubei University, No. 368 Youyi Dadao, Wuhan 430062, China

[e] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Table of contents

General information

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. DMA and toluene were distilled over CaH_2 prior to use. Zinc power was activated by washing with a dilute HCl solution.[1] Alkyl bromide, benzyl chloride, and dimethylzinc were obtained from commercial sources and used without further purification unless otherwise noted. Organozinc reagents,[2] α-halo vinylphosphonates,[3] and α-phosphonovinyl sulfonates[4] were synthesized according to the published procedures. The concentration of the resulting organozinc reagents were determined by iodiometric titration.[5]

NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ_H = 7.26, δ_C = 77.0). Spectra were reported as follow: chemical shift (δppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on ESI-Q-TOF spectrometer (Bruker microTOF-Q II).

Procedure for the preparation of alkylzinc bromide (2a-m, 5)

A dry 25 mL Schlenk-flask was heated with a heat gun (350 ^oC) for 10 min under high vacuum. After cooling to room temperature, the flask was flushed with nitrogen (repeated 3 times). Then, Zinc power (975 mg, 15 mmol), I_2 (127 mg, 0.5 mmol) and dry DMA (10 mL) was added. Stirring the mixture until the red color of I_2 disappeared, alkylic bromide (10 mmol) was added and stirred at 80 ^oC for 3-4 h.

Procedure for the preparation of benzylic zinc chloride (4a-l)

A dry 25 mL Schlenk-flask was heated with a heat gun (350 ^oC) for 10 min under high vacuum. After cooling to room temperature, the flask was flushed with nitrogen (repeated 3 times). Then, Zinc power (1.5-2.0 equiv), I_2 (127 mg, 0.5 mmol) and dry DMA (10 mL) was added. Stirring the mixture until the red color of I_2 disappeared, benzylic chloride (10 mmol) was added and stirred at the required temperature (40-80 ^oC) for 4 h.

General procedure for the synthesis of 3a-l, 3n, 6a-m, 7, 9, 11, 13, 15, 17 via Pd-catalysed Negishi cross-coupling

A Schlenk-flask was loaded with α-(pseudo)halo vinylphosphonate (0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), SPhos (16.4 mg, 0.04 mol). The flask was held under vacuum for 10 min and filled with nitrogen (repeated 3 times). DMA (1 mL) was introduced and the mixture was stirred. Alkylzinc bromide (1.2-1.4 equiv) or benzylic zinc chloride (1.1-1.2 equiv) was added dropwise at room temperature and stirred at 40 ^oC for 1-3 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH_4Cl (1 mL) and 1 N HCl (2 mL), and the mixture was extracted with EtOAc (4 × 4 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave the cross-coupling product α-substituted vinylphosphonate as a pale yellow oil.

The synthesis of 3m via Ni-catalysed Negishi cross-coupling of α-bromovinylphosphonate (1a)

with pent-4-en-1-ylzinc bromide (2m)

A Schlenk-flask was loaded with diethyl α-bromo vinylphosphonate (97.2 mg, 0.4 mmol), $NiCl_2$(dppp) (21.6 mg, 0.04 mol). The flask was held under vacuum for 10 min and filled with nitrogen (repeated 3 times). Then DMA (1 mL) was introduced and the mixture was stirred. The pent-4-en-1-ylzinc bromide (1.2 equiv) was added dropwise at room temperature and stirred at 40 °C for 3 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH_4Cl (1 mL) and 1 N HCl (2 mL), and the mixture was extracted with EtOAc (4 × 4 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave diethyl hepta-1,6-dien-2-ylphosphonate **3m** (68.7 mg, 74%) as a colorless oil.

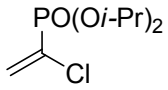
The synthesis of 19 via Pd-catalysed Negishi cross-coupling of diethyl α-bromo vinylphosphonate (1a) with dimethylzinc reagent

A Schlenk-flask was loaded with diethyl α-bromo vinylphosphonate (4.86 g, 20 mmol), $Pd(OAc)_2$ (224.5 mg, 1.0 mmol), SPhos (820 mg, 2.0 mmol). The flask was held under vacuum for 10 min and then filled with nitrogen (repeated 3 times). Then toluene (88 mL) was introduced and the mixture was stirred. The dimethylzinc (1 M in toluene, 12 mL, 1.2 equiv) was added dropwise at 0 °C and then stirred at 40 °C for 6 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH_4Cl (30 mL), and the mixture was extracted with EtOAc (4 × 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave the cross-coupling product α-methyl vinylphosphonate **19** (1.61g, 45%) as a pale yellow oil.

General procedure for the diimide reduction of alkenylphosphonates to access 1-alkylethylphosphonates (20a-f)

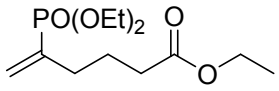
A Schlenk flask was loaded with diethyl α-substituted vinylphosphonate (82.2 mg, 0.3 mmol), NBSH (130.0 mg, 0.6 mmol), K_3PO_4 (63.6 mg, 0.3 mmol) and held under vacuum for 10 min and then filled with nitrogen. Then CH_3CN (2.0 mL) was introduced and the mixture was stirred at rt for 5-6 h. After completion of the reaction, the mixture was added water (3 mL), and extracted with EtOAc (4 × 3 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 overnight, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on a silica gel column using petroleum ether/EtOAc (1/1, v/v) as eluent to give 1-alkylethylphosphonates (**20a-f**) as an oil.

Characterizations of new compounds

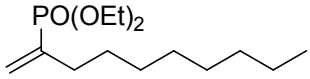


Diisopropyl (1-chlorovinyl)phosphonate (1f). Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (d, *J* = 6.2 Hz, 6H), 1.38 (d, *J* = 6.2 Hz, 6H), 4.67-4.76 (m, 2H), 6.12 (dd, *J* = 35.7 Hz, 1.3 Hz, 1H), 6.43 (dd, *J* = 13.3 Hz, 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.6 (d, *J* = 5.1 Hz), 24.0

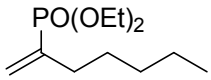
(d, J = 3.8 Hz), 72.3 (d, J = 5.7 Hz), 130.2 (d, J = 16.7 Hz), 131.8 (d, J = 206.3 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 5.7; IR (neat): ν (cm^{-1}) 3756, 3343, 2936, 2899, 2856, 1464, 1261, 991; GC-MS: *m*/*z* (rel intensity) 227 ($M+H^+$, 4), 185 (18), 169 (76), 144 (100), 124 (22), 107 (21), 98 (12), 81 (12); HRMS (ESI) $C_8H_{17}ClO_3P$ $[M+H]^+$ 227.0598, found 227.0611.



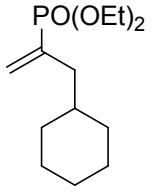
Ethyl 5-(diethoxyphosphoryl)hex-5-enoate (**3a**). Pale yellow oil (93.4 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24-1.27 (m, 3H), 1.32 (t, J = 7.1 Hz, 6H), 1.84-1.90 (m, 2H), 2.26-2.34 (m, 4H), 4.05-4.15 (m, 6H), 5.78 (d, J = 48.6 Hz, 1H), 6.06 (d, J = 22.9 Hz 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 16.3 (d, J = 6.3 Hz), 23.2 (d, J = 5.4 Hz), 31.5 (d, J = 11.1 Hz), 33.5, 60.3, 61.8 (d, J = 5.7 Hz), 129.6 (d, J = 9.5 Hz), 138.5 (d, J = 171.1 Hz), 173.2; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.3; IR (neat): ν (cm^{-1}) 3482, 2938, 2897, 2843, 1732, 1464, 1253, 1053, 1024, 966; LC-MS (ESI) $[M+H]^+$: 279.29; HRMS (ESI) $C_{12}H_{23}NaO_5P$ $[M+Na]^+$ 301.1175, found 301.1151.



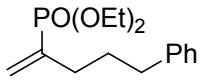
Diethyl dec-1-en-2-ylphosphonate (**3c**). Pale yellow oil (83.9 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, J = 7.1 Hz, 6.8 Hz, 3H), 1.25-1.34 (m, 16H), 1.48-1.54 (m, 2H), 2.20-2.26 (m, 2H), 4.02-4.13 (m, 4H), 5.75 (dd, J = 49.1 Hz, 1.6 Hz, 1H), 6.02(d, J = 23.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 16.3 (d, J = 6.3 Hz), 22.6, 27.9 (d, J = 5.7 Hz), 29.1, 29.2, 29.3, 31.8, 32.1 (d, J = 10.8 Hz), 61.7 (d, J = 5.8 Hz), 128.8 (d, J = 9.6 Hz), 139.4 (d, J = 169.6 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 20.0; IR (neat): ν (cm^{-1}) 3480, 2938, 2897, 2843, 1464, 1258, 1055, 1028, 962; LC-MS (ESI) $[M+H]^+$: 277.34; HRMS (ESI) calcd for $C_{14}H_{29}NaO_3P$ $[M+Na]^+$ 299.1747, found 299.1750.



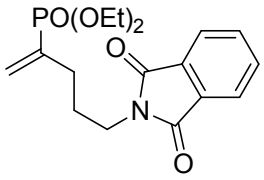
Diethyl hept-1-en-2-ylphosphonate (**3d**). Pale yellow oil (82.4 mg, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.29-1.35 (m, 10H), 1.49-1.55 (m, 2H), 2.20-2.26 (m, 2H), 4.02-4.13 (m, 4H), 5.75 (dd, J = 49.1 Hz, 1.0 Hz, 1H), 6.02 (d, J = 23.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 16.3 (d, J = 6.3 Hz), 22.4, 27.5 (d, J = 5.4 Hz), 31.3, 32.0 (d, J = 10.7 Hz), 61.6 (d, J = 5.6 Hz), 128.8 (d, J = 9.3 Hz), 139.4 (d, J = 169.6 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.9; IR (neat): ν (cm^{-1}) 3476, 2936, 2901, 2857, 1464, 1257, 1026, 960, 792; GC-MS: *m*/*z* (rel intensity) 235 ($M+H^+$, 10), 205 (44), 191 (29), 177 (74), 149 (100), 135 (53), 95 (44), 81 (44), 98 (12), 81 (12); HRMS (ESI) $C_{11}H_{23}NaO_3P$ $[M+Na]^+$ 257.1277, found 257.1288.



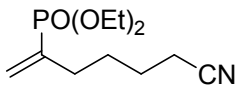
Diethyl (3-cyclohexylprop-1-en-2-yl)phosphonate (**3f**). Pale yellow oil (92.6 mg, 89% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80-0.89 (m, 2H), 1.09-1.27 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 6H), 1.56-1.74 (m, 6H), 2.12 (dd, *J* = 15.9 Hz, 7.1 Hz, 2H), 4.01-4.12 (m, 4H), 5.70 (dd, *J* = 48.9 Hz, 1.4 Hz, 1H), 6.05 (dd, *J* = 22.8 Hz, 1.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.4 Hz), 26.2, 26.5, 33.0, 35.7 (d, *J* = 3.5 Hz), 40.6 (d, *J* = 10.8 Hz), 61.6 (d, *J* = 5.9 Hz), 130.3 (d, *J* = 9.7 Hz), 137.6 (d, *J* = 169.2 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.9; IR (neat): ν (cm^{-1}) 3483, 2938, 2897, 2843, 1464, 1250, 1226, 1026, 961; GC-MS: *m*/*z* (rel intensity) 260 (M^+, 12), 178 (84), 150 (100), 122 (89), 96 (46), 82 (29); HRMS (ESI) calcd for $C_{13}H_{26}O_3P$ $[M+H]^+$ 261.1541, found 261.1545.



Diethyl (5-phenylpent-1-en-2-yl)phosphonate (**3h**). Pale yellow oil (86.9 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 6H), 1.83-1.89 (m, 2H), 2.26-2.32 (m, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 4.01-4.13 (m, 4H), 5.77 (d, *J* = 48.9 Hz, 1.5 Hz, 1H), 6.05 (d, *J* = 23.0 Hz, 1H), 7.17-7.20 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2 (d, *J* = 6.3 Hz), 29.6 (d, *J* = 5.4 Hz), 31.7 (d, *J* = 10.8 Hz), 35.2, 61.7 (d, *J* = 5.7 Hz), 125.8, 128.26, 128.32, 129.2 (d, *J* = 9.4 Hz), 138.9 (d, *J* = 170.3 Hz), 141.8; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.7; IR (neat): ν (cm^{-1}) 3502, 2938, 2895, 2843, 1463, 1254, 1053, 1026, 964; LC-MS (ESI) $[M+H]^+$: 283.19; HRMS (ESI) calcd for $C_{15}H_{24}O_3P$ $[M+H]^+$ 283.1458, found 283.1468.

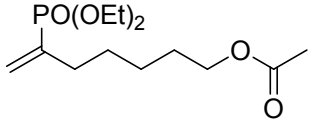


Diethyl (5-(1,3-dioxoisoindolin-2-yl)pent-1-en-2-yl)phosphonate (**3i**). Pale yellow oil (56.2 mg, 56% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 6H), 1.90-1.96 (m, 2H), 2.29-2.34 (m, 2H), 3.70-3.73 (m, 2H), 4.02-4.13 (m, 4H), 5.83 (dd, *J* = 48.6 Hz, 1.4 Hz, 1H), 6.07(dd, *J* = 23.0 Hz, 0.9 Hz, 1H), 7.71-7.73 (m, 2H), 7.84-7.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.3 Hz), 26.9 (d, *J* = 5.4 Hz), 29.4 (d, *J* = 11.1 Hz), 37.4, 61.9 (d, *J* = 5.7 Hz), 123.2, 129.7 (d, *J* = 9.3 Hz), 132.0, 134.0, 138.0 (d, *J* = 171.8 Hz), 168.3; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.2; IR (neat): ν (cm^{-1}) 3464, 2937, 2897, 2843, 1712, 1464, 917; LC-MS (ESI) $[M+H]^+$: 252.37; HRMS (ESI) calcd for $C_{17}H_{22}NNaO_5P$ $[M+Na]^+$ 374.1128, found 374.1152.

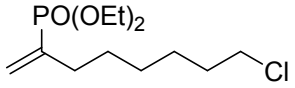


Diethyl (6-cyanohex-1-en-2-yl)phosphonate (**3j**). Pale yellow oil (86.2 mg, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.1 Hz, 6H), 1.70 (br, 4H), 2.28-2.31 (m, 2H), 2.37-2.38 (m, 2H), 4.05-4.12 (m, 4H), 5.76 (dd, *J* = 48.4 Hz, 1.2 Hz, 1H), 6.04 (d, *J* = 22.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.2 Hz), 16.9, 24.7, 26.9 (d, *J* = 5.2 Hz), 31.4 (d, *J* = 11.0 Hz), 61.8 (d, *J* = 5.8 Hz), 119.4, 129.4 (d, *J* = 9.2 Hz), 138.3 (d, *J* = 171.8 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.1; IR (neat): ν (cm^{-1}) 3447, 2936, 2899, 2843, 1464, 1223, 1051, 1024, 966;

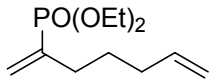
LC-MS (ESI) $[M+H]^+$: 246.26; HRMS (ESI) calcd for $C_{11}H_{21}O_3P$ $[M+H]^+$ 246.1254, found 246.1259.



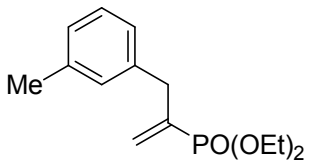
5-(Diethoxyphosphoryl)hex-5-en-1-yl acetate (**3k**). Pale yellow oil (93.4 mg, 80% yield); ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.1 Hz, 6H), 1.37-1.43(m, 2H), 1.53-1.59 (m, 2H), 1.62-1.68 (m, 2H), 2.04 (s, 3H), 2.22-2.28 (m, 2H), 4.01-4.13 (m, 6H), 5.75 (dd, *J* = 48.9 Hz, 1.4 Hz, 1H), 6.03 (d, *J* = 22.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.1 Hz), 20.9, 25.4, 27.5 (d, *J* = 5.2 Hz), 28.3, 31.9 (d, *J* = 10.8 Hz), 61.7 (d, *J* = 5.5 Hz), 64.3, 129.0 (d, *J* = 9.4 Hz), 139.0 (d, *J* = 170.5 Hz), 171.1; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.7; IR (neat): ν (cm^{-1}) 3495, 2938, 2897, 2843, 1738, 1464, 1240, 1026, 964; LC-MS (ESI) $[M+H]^+$: 293.31; HRMS (ESI) calcd for $C_{13}H_{26}O_5P$ $[M+H]^+$ 293.1512, found 293.1493.



Diethyl (8-chlorooct-1-en-2-yl)phosphonate (**3l**). Pale yellow oil (89.1 mg, 79% yield); ^1H NMR (500 MHz, $CDCl_3$): δ 1.30-1.35 (m, 8H), 1.41-1.48 (m, 2H), 1.50-1.56 (m, 2H), 1.73-1.79 (m, 2H), 2.20-2.26 (m, 2H), 3.50-3.53 (m, 2H), 4.03-4.11 (m, 4H), 5.74 (d, *J* = 49.0 Hz, 1H), 6.01 (dd, *J* = 23.0 Hz, 0.6 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.3 Hz), 26.5, 27.7 (d, *J* = 5.4 Hz), 28.3, 31.9 (d, *J* = 10.8 Hz), 32.4, 44.9, 61.7 (d, *J* = 5.6 Hz), 129.0 (d, *J* = 9.3 Hz), 139.1 (d, *J* = 170.3 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.8; IR (neat): ν (cm^{-1}) 3474, 2938, 2897, 2843, 1464, 1242, 1053, 1026, 964; GC-MS: *m*/*z* (rel intensity) 282 (M^+, 0.4), 247 (100), 219 (31), 205 (39), 177 (51), 163 (27), 149 (73), 109 (80), 81 (40); HRMS (ESI) calcd for $C_{12}H_{24}ClNaO_3P$ $[M+Na]^+$ 305.1044, found 305.1059.

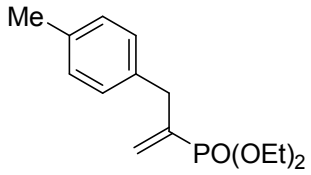


Diethyl hepta-1,6-dien-2-ylphosphonate (**3m**). Pale yellow oil (68.7 mg, 74% yield); ^1H NMR (500 MHz, $CDCl_3$): δ 1.30 (t, *J* = 7.1 Hz, 6H), 1.58-1.64 (m, 2H), 2.04-2.09 (m, 2H), 2.21-2.27 (m, 2H), 4.00-4.11 (m, 4H), 4.94-5.02 (m, 2H), 5.69-5.82 (m, 2H), 6.02 (d, *J* = 23.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.3 Hz), 27.1 (d, *J* = 5.4 Hz), 31.5 (d, *J* = 10.8 Hz), 33.1, 61.7 (d, *J* = 5.6 Hz), 114.9, 129.1 (d, *J* = 9.4 Hz), 138.1, 139.1 (d, *J* = 170.3 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.7; IR (neat): ν (cm^{-1}) 3464, 2938, 2897, 2843, 1464, 1253, 1055, 1026, 962; LC-MS (ESI) $[M+H]^+$: 233.26; HRMS (ESI) calcd for $C_{11}H_{21}NaO_3P$ $[M+Na]^+$ 255.1121, found 255.1123.

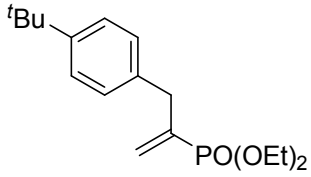


Diethyl (3-(m-tolyl)prop-1-en-2-yl)phosphonate (**6b**). Pale yellow oil (99.7 mg, 93% yield); ^1H

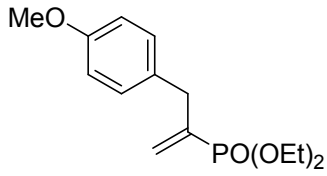
NMR (500 MHz, $CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 6H), 2.33 (s, 3H), 3.52 (d, J = 11.3 Hz, 2H), 3.93-4.09 (m, 4H), 5.58 (dd, J = 47.8 Hz, 1.6 Hz, 1H), 6.10 (dd, J = 22.3 Hz, 1.3 Hz, 1H), 6.98-7.05 (m, 3H), 7.18-7.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (d, J = 6.4 Hz), 21.3, 38.1 (d, J = 11.6 Hz), 61.7 (d, J = 5.5 Hz), 126.4, 127.2, 128.2, 130.1, 130.6 (d, J = 9.5 Hz), 137.5 (d, J = 7.6 Hz), 137.9, 139.0 (d, J = 171.8 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.1; IR (neat): ν (cm^{-1}) 3480, 2938, 2897, 2843, 1722, 1464, 1163, 1026, 966; LC-MS (ESI) $[M+H]^+$: 269.31; HRMS (ESI) calcd for $C_{14}H_{21}NaO_3P$ $[M+Na]^+$ 291.1121, found 291.1139.



Diethyl (3-(p-tolyl)prop-1-en-2-yl)phosphonate (**6c**). Pale yellow oil (96.5 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 6H), 2.33 (s, 3H), 3.51 (d, J = 11.1 Hz, 2H), 3.93-4.09 (m, 4H), 5.56 (dd, J = 47.9 Hz, 1.5 Hz, 1H), 6.09 (dd, J = 22.3 Hz, 1.1 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2 (d, J = 6.4 Hz), 21.0, 37.8 (d, J = 11.6 Hz), 61.7 (d, J = 5.7 Hz), 129.1, 129.2, 130.5 (d, J = 9.5 Hz), 134.5 (d, J = 7.6 Hz), 136.0, 139.2 (d, J = 171.2 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.2; IR (neat): ν (cm^{-1}) 3426, 2938, 2897, 2843, 1722, 1514, 1464, 1213, 1024, 968; LC-MS (ESI) $[M+H]^+$: 269.32; HRMS (ESI) calcd for $C_{14}H_{22}O_3P$ $[M+H]^+$ 269.1301, found 269.1293.

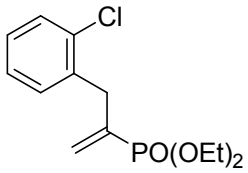


Diethyl (3-(4-(tert-butyl)phenyl)prop-1-en-2-yl)phosphonate (**6d**). Pale yellow oil (111.6 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (t, J = 7.1 Hz, 6H), 1.31 (s, 9H), 3.52 (d, J = 11.7 Hz, 2H), 3.90-4.08 (m, 4H), 5.61 (dd, J = 47.9 Hz, 1.6 Hz, 1H), 6.10 (dd, J = 22.3 Hz, 1.1 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2 (d, J = 6.6 Hz), 31.3, 34.4, 37.9 (d, J = 11.6 Hz), 61.7 (d, J = 5.5 Hz), 125.3, 129.0, 130.7 (d, J = 9.6 Hz), 134.5 (d, J = 7.3 Hz), 139.1 (d, J = 171.3 Hz), 149.4; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.1; IR (neat): ν (cm^{-1}) 3456, 2938, 2895, 2843, 1514, 1464, 1234, 1165, 1026, 966; LC-MS (ESI) $[M+H]^+$: 311.43; HRMS (ESI) calcd for $C_{17}H_{28}O_3P$ $[M+H]^+$ 311.1771, found 311.1779.

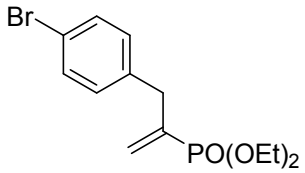


Diethyl (3-(4-methoxyphenyl)prop-1-en-2-yl)phosphonate (**6e**). Pale yellow oil (100.0 mg, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 6H), 3.49 (d, J = 11.7 Hz, 2H), 3.80 (s, 3H), 3.94-4.08 (m, 4H), 5.62 (dd, J = 48.9 Hz, 1.5 Hz, 1H), 6.10 (dd, J = 22.7 Hz, 1.1 Hz, 1H),

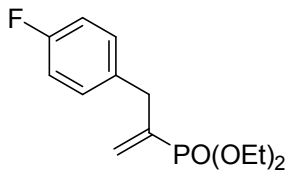
6.83-6.88 (m, 2H), 7.08-7.11 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.2 (d, J = 6.4 Hz), 37.4 (d, J = 11.8 Hz), 55.3, 62.4 (d, J = 5.6 Hz), 113.9, 129.3 (d, J = 7.9 Hz), 130.4, 131.3 (d, J = 9.8 Hz), 138.5 (d, J = 173.1 Hz), 158.4; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.1; IR (neat): ν (cm^{-1}) 3400, 2938, 2899, 2843, 1767, 1612, 1512, 1464, 1248, 1163, 1026, 968; LC-MS (ESI) $[M+H]^+$: 285.35; HRMS (ESI) calcd for $C_{14}H_{21}NaO_4P$ $[M+Na]^+$ 307.1070, found 307.1080.



Diethyl (3-(2-chlorophenyl)prop-1-en-2-yl)phosphonate (**6f**). Pale yellow oil (107.1 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (t, J = 7.1 Hz, 6H), 3.68 (dt, J = 9.0 Hz, 1.7Hz, 2H), 4.01-4.15 (m, 4H), 5.40 (dd, J = 47.8 Hz, 1.5 Hz, 1H), 6.10 (dd, J = 22.3 Hz, 1.1 Hz, 1H), 7.19-7.25 (m, 3H), 7.37-7.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, J = 6.4 Hz), 35.8 (d, J = 12.2 Hz), 61.9 (d, J = 5.5 Hz), 126.9, 128.4, 129.6, 130.4 (d, J = 9.4 Hz), 131.8, 134.5, 135.3 (d, J = 9.7 Hz), 136.9 (d, J = 173.1 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 18.6; IR (neat): ν (cm^{-1}) 3478, 2938, 2897, 2843, 1464, 1250, 1024, 966; LC-MS (ESI) $[M+H]^+$: 289.28; HRMS (ESI) calcd for $C_{13}H_{19}ClO_3P$ $[M+H]^+$ 289.0755, found 289.0777.

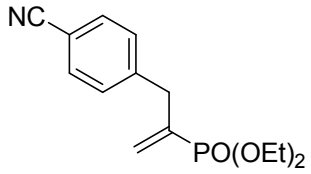


Diethyl (3-(4-bromophenyl)prop-1-en-2-yl)phosphonate (**6g**). Pale yellow oil (126.2 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H), 3.51 (d, J = 12.0 Hz, 2H), 3.94-4.10 (m, 4H), 5.62 (dd, J = 48.3 Hz, 1.4 Hz, 1H), 6.12 (dd, J = 22.5 Hz, 1.2 Hz, 1H), 7.05-7.08 (m, 2H), 7.42-7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (d, J = 6.3 Hz), 37.7 (d, J = 11.8 Hz), 62.3 (d, J = 6.0 Hz), 120.5, 131.0, 131.3 (d, J = 9.8 Hz), 131.5, 136.5 (d, J = 7.2 Hz), 138.0 (d, J = 174.2 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 18.5; IR (neat): ν (cm^{-1}) 3416, 2938, 2895, 2843, 1766, 1464, 1215, 1163, 1026, 968; LC-MS (ESI) $[M+H]^+$: 333.31; HRMS (ESI) calcd for $C_{13}H_{18}BrNaO_3P$ $[M+Na]^+$ 355.0069, found 355.0077.

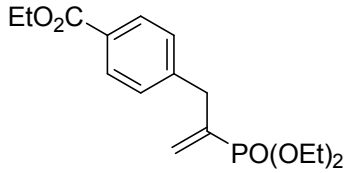


Diethyl (3-(4-fluorophenyl)prop-1-en-2-yl)phosphonate (**6h**). Pale yellow oil (103.4 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H), 3.53 (d, J = 11.7 Hz, 2H), 3.93-4.09 (m, 4H), 5.58 (dd, J = 47.6 Hz, 1.6 Hz, 1H), 6.10 (dd, J = 23.3 Hz, 1.1 Hz, 1H), 6.98-7.01 (m, 2H), 7.14-7.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (d, J = 6.4 Hz), 37.6 (d, J = 11.8 Hz), 62.3 (d, J = 5.8 Hz), 115.3 (d, J = 21.0 Hz), 130.8 (d, J = 7.9 Hz), 131.2 (d, J = 9.7 Hz), 133.1 (dd,

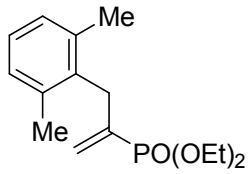
J = 7.2 Hz, 3.5 Hz), 138.3 (d, J = 174.0 Hz), 161.7 (d, J = 243.6 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 18.7; ^{19}F NMR (470 MHz, $CDCl_3$): δ -116.6; IR (neat): ν (cm^{-1}) 3422, 2938, 2897, 2843, 1464, 1223, 1026, 968; LC-MS (ESI) $[M+H]^+$: 273.32; HRMS (ESI) calcd for $C_{13}H_{18}FNaO_3P$ $[M+Na]^+$ 295.0870, found 295.0880.



Diethyl (3-(4-cyanophenyl)prop-1-en-2-yl)phosphonate (**6i**). Pale yellow oil (109.4 mg, 98% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (t, J = 7.1 Hz, 6H), 3.63 (d, J = 12.8 Hz, 2H), 3.95-4.10 (m, 4H), 5.67 (d, J = 48.2 Hz, 1H), 6.16 (d, J = 22.4 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.0 (d, J = 6.3 Hz), 38.4 (d, J = 11.9 Hz), 62.4 (d, J = 6.1 Hz), 110.5, 118.7, 130.0, 132.0 (d, J = 17.8 Hz), 132.2, 137.1 (d, J = 176.4 Hz), 143.2 (d, J = 6.3 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 18.5; IR (neat): ν (cm^{-1}) 3470, 2938, 2895, 2843, 2228, 1770, 1464, 1163, 1024, 972; LC-MS (ESI) $[M+H]^+$: 280.33; HRMS (ESI) calcd for $C_{14}H_{18}NNaO_3P$ $[M+Na]^+$ 302.0917, found 302.0928.

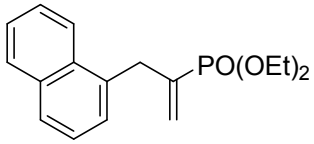


Ethyl 4-(2-(diethoxyphosphoryl)allyl)benzoate (**6j**). Pale yellow oil (125.2 mg, 96% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H), 1.39 (t, J = 7.1 Hz, 3H), 3.61 (d, J = 12.3 Hz, 2H), 3.95-4.11 (m, 4H), 4.37 (q, J = 7.1 Hz, 2H), 5.66 (dd, J = 48.8 Hz, 1.2 Hz, 1H), 6.16 (dd, J = 22.7 Hz, 0.9 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 16.1 (d, J = 6.4 Hz), 38.2 (d, J = 12.2 Hz), 61.0, 62.7 (d, J = 5.8 Hz), 129.0, 129.3, 129.8, 132.0 (d, J = 9.7 Hz), 137.3 (d, J = 175.9 Hz), 142.6 (d, J = 7.1 Hz), 166.5; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 18.3; IR (neat): ν (cm^{-1}) 3412, 2938, 2899, 2843, 1717, 1611, 1464, 1277, 1163, 1024, 970; LC-MS (ESI) $[M+H]^+$: 327.40; HRMS (ESI) calcd for $C_{16}H_{24}O_5P$ $[M+H]^+$ 327.1356, found 327.1356.

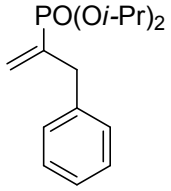


Diethyl (3-(2,6-dimethylphenyl)prop-1-en-2-yl)phosphonate (**6k**). Pale yellow oil (101.5 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38 (t, J = 7.1 Hz, 6H), 2.21 (s, 6H), 3.52 (d, J = 5.7 Hz, 2H), 4.10-4.21 (m, 4H), 5.10 (dd, J = 48.5 Hz, 1.7 Hz, 1H), 5.96 (dd, J = 22.7 Hz, 1.7 Hz, 1H), 7.03-7.09 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.4 (d, J = 6.2 Hz), 19.6, 31.4 (d, J = 11.7 Hz), 61.9 (d, J = 5.7 Hz), 126.6, 128.0, 128.2 (d, J = 9.8 Hz), 134.0 (d, J = 11.8 Hz), 136.7 (d, J =

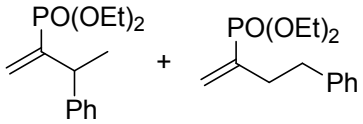
171.4 Hz), 137.1; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.4; IR (neat): ν (cm^{-1}) 3480, 2938, 2895, 2843, 1722, 1464, 1244, 1170, 1024, 964; LC-MS (ESI) $[M+H]^+$: 283.36; HRMS (ESI) calcd for $C_{15}H_{23}NaO_3P$ $[M+Na]^+$ 305.1277, found 305.1279.



Diethyl (3-(naphthalen-1-yl)prop-1-en-2-yl)phosphonate (**6l**). Pale yellow oil (119.2 mg, 98% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.1 Hz, 6H), 3.99 (d, *J* = 7.8 Hz, 2H), 4.09-4.20 (m, 4H), 5.26 (d, *J* = 48.4 Hz, 1H), 6.04 (d, *J* = 22.7 Hz, 1H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.42-7.49 (m, 3H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.85-7.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, *J* = 6.3 Hz), 35.2 (d, *J* = 12.0 Hz), 62.0 (d, *J* = 5.7 Hz), 124.2, 125.4, 125.6, 125.9, 127.6, 128.2, 128.6, 130.3 (d, *J* = 9.4 Hz), 131.9, 133.6 (d, *J* = 10.1 Hz), 133.8, 138.2 (d, *J* = 172.7 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.1; IR (neat): ν (cm^{-1}) 3474, 2936, 2900, 2857, 1464, 1242, 1024, 964; LC-MS (ESI) $[M+H]^+$: 305.14; HRMS (ESI) calcd for $C_{16}H_{19}NaO_3P$ $[M+Na]^+$ 327.1121, found 327.1138.

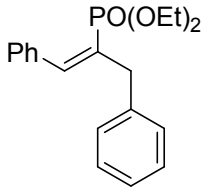


Dipropyl (3-phenylprop-1-en-2-yl)phosphonate (**6m**). Pale yellow oil (107.2 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.2 Hz, 6H), 1.32 (d, *J* = 6.2 Hz, 6H), 3.54 (d, *J* = 10.4 Hz, 2H), 4.61-4.70 (m, 2H), 5.46 (dd, *J* = 48.0 Hz, 1.7 Hz, 1H), 6.09 (dd, *J* = 22.5 Hz, 1.3 Hz, 1H), 7.17-7.31 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.7 (d, *J* = 4.8 Hz), 24.0 (d, *J* = 3.8 Hz), 38.2 (d, *J* = 11.4 Hz), 70.5 (d, *J* = 6.1 Hz), 126.4, 128.4, 129.5, 129.6 (d, *J* = 9.7 Hz), 137.8 (d, *J* = 8.2 Hz), 140.6 (d, *J* = 174.1 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 16.8; IR (neat): ν (cm^{-1}) 3462, 2936, 2901, 2845, 2359, 1464, 1385, 1252, 1107, 982; GC-MS: *m*/*z* (rel intensity) 282 (M^+, 10), 240 (21), 198 (100), 181 (26), 163 (25), 116 (94), 91 (21); HRMS (ESI) $C_{15}H_{23}O_3PNa$ $[M+Na]^+$ 305.1277, found 305.1290.

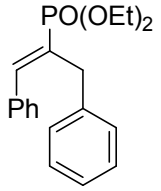


Diethyl (3-phenylbut-1-en-2-yl)phosphonate (**7**). Pale yellow oil (30.0 mg, 28% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.47 (d, *J* = 7.2 Hz, 3H), 3.63-3.71 (m, 1H), 3.81-3.87 (m, 1H), 3.88-4.01 (m, 3H), 5.88 (dd, *J* = 48.5 Hz, 1.2 Hz, 1H), 6.21 (d, *J* = 23.1 Hz, 1H), 7.18-7.23 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.0 (d, *J* = 7.0 Hz), 16.2 (d, *J* = 6.5 Hz), 21.3 (d, *J* = 6.8 Hz), 41.1 (d, *J* = 11.6 Hz), 61.6 (d, *J* = 5.5 Hz), 126.4, 127.6, 128.3, 129.1 (d, *J* = 9.2 Hz), 143.68 (d, *J* = 4.4 Hz), 143.70 (d, *J* = 169.7 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.2; **Diethyl (4-phenylbut-1-en-2-yl)phosphonate** (**3g**). Pale yellow oil (17.2 mg, 16% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (t, *J* = 7.1 Hz, 6H),

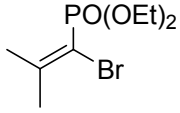
2.53-2.59 (m, 2H), 2.83-2.86 (m, 2H), 4.03-4.15 (m, 4H), 5.75 (dd, J = 48.8 Hz, 1.5 Hz, 1H), 6.06 (dd, J = 23.0 Hz, 1.1 Hz, 1H), 7.18-7.23 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.3 (d, J = 6.3 Hz), 33.9 (d, J = 11.1 Hz), 34.3 (d, J = 5.4 Hz), 61.8 (d, J = 5.9 Hz), 126.0, 128.3, 128.4, 129.6 (d, J = 9.5 Hz), 138.5 (d, J = 171.0 Hz), 141.1; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.5; LC-MS (ESI) $[M+H]^+$: 269.31; IR (neat): ν (cm^{-1}) 3431, 2938, 2897, 2843, 1463, 1247, 1055, 1028, 962; HRMS (ESI) calcd for $C_{14}H_{21}NaO_3P$ $[M+Na]^+$ 291.1121, found 291.1128.



(*Z*)-diethyl (1,3-diphenylprop-1-en-2-yl)phosphonate (**11**). Pale yellow oil (128.0 mg, 97% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, J = 7.1 Hz, 6H), 3.69-3.89 (m, 6H), 7.05 (d, J = 47.9 Hz, 1H), 7.21-7.34 (m, 8H), 7.48 (d, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.9 (d, J = 6.8 Hz), 42.0 (d, J = 12.1 Hz), 61.5 (d, J = 5.8 Hz), 126.4, 127.7, 128.1, 128.4, 129.1 (d, J = 1.5 Hz), 129.4, 130.5 (d, J = 173.6 Hz), 136.2 (d, J = 7.4 Hz), 138.8 (d, J = 5.3 Hz), 145.0 (d, J = 9.3 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 17.4; IR (neat): ν (cm^{-1}) 3420, 2936, 2899, 2843, 2359, 1464, 1240, 1026, 966; GC-MS: *m*/*z* (rel intensity) 330 (M^+, 31), 301 (10), 273 (17), 239 (10), 191 (100), 165 (22), 129 (12), 115 (59), 91 (41); HRMS (ESI) $C_{19}H_{24}O_3P$ $[M+H]^+$ 331.1458, found 331.1446.

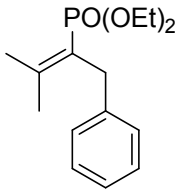


(*E*)-diethyl (1,3-diphenylprop-1-en-2-yl)phosphonate (**15**). Pale yellow oil (88.4 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (t, J = 7.1 Hz, 6H), 3.83-3.92 (m, 4H), 3.98-4.05 (m, 2H), 7.18-7.42 (m, 10H), 7.75 (d, J = 24.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.0 (d, J = 6.5 Hz), 33.6 (d, J = 9.2 Hz), 61.7 (d, J = 5.6 Hz), 126.2, 128.2, 128.4, 128.55, 128.6 (d, J = 176.9 Hz), 128.7, 129.0, 135.1 (d, J = 23.2 Hz), 138.2 (d, J = 1.6 Hz), 144.9 (d, J = 12.1 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.3; IR (neat): ν (cm^{-1}) 3462, 2936, 2902, 2845, 2359, 1464, 1250, 1024, 962; GC-MS: *m*/*z* (rel intensity) 330 (M^+, 50), 301 (10), 273 (16), 239 (12), 191 (100), 165 (25), 129 (11), 115 (59), 91 (44); HRMS (ESI) $C_{19}H_{24}O_3P$ $[M+H]^+$ 331.1458, found 331.1433.

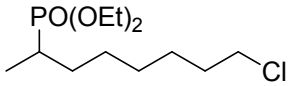


Diethyl (1-bromo-2-methylprop-1-en-1-yl)phosphonate (**16a**). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (t, J = 7.1 Hz, 6H), 2.09 (d, J = 2.2 Hz, 3H), 2.30 (d, J = 2.9 Hz, 3H), 4.06-4.18 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (d, J = 6.6 Hz), 23.3 (d, J = 3.9 Hz), 28.0 (d, J = 13.9 Hz), 62.5 (d, J = 5.4 Hz), 106.5 (d, J = 207.5 Hz), 156.0 (d, J = 17.0 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 9.7; IR (neat): ν (cm^{-1}) 3462, 2934, 2903, 2845, 1602, 1464, 1253, 1024, 970;

LC-MS (ESI) $[M+H]^+$: 271.04; HRMS (ESI) $C_8H_{17}BrO_3P$ $[M+H]^+$ 271.0093, found 271.0075.



Diethyl (3-methyl-1-phenylbut-2-en-2-yl)phosphonate (**17**). Pale yellow oil (104.9 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.1 Hz, 6H), 1.89 (d, *J* = 2.5 Hz, 3H), 2.23 (d, *J* = 3.3 Hz, 3H), 3.69 (d, *J* = 17.7 Hz, 2H), 3.82-3.99 (m, 4H), 7.14-7.27 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.1 (d, *J* = 6.4 Hz), 23.2 (d, *J* = 19.2 Hz), 23.9 (d, *J* = 7.7 Hz), 35.8 (d, *J* = 12.0 Hz), 61.1 (d, *J* = 5.6 Hz), 122.2 (d, *J* = 178.8 Hz), 125.8, 128.07, 128.14, 139.7 (d, *J* = 1.8 Hz), 153.3 (d, *J* = 12.0 Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 20.8; IR (neat): ν (cm^{-1}) 3462, 2936, 2899, 2845, 2359, 1464, 1229, 1026, 959; GC-MS: *m*/*z* (rel intensity) 282 (M^+, 63), 253 (10), 225 (15), 191 (13), 157 (10), 143 (88), 129 (100), 115 (18), 91 (34); HRMS (ESI) $C_{15}H_{24}O_3P$ $[M+H]^+$ 283.1458, found 283.1448.



Diethyl (8-chlorooctan-2-yl)phosphonate (**20f**). Colorless oil (62.2 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (dd, *J* = 18.7 Hz, 7.1Hz, 3H), 1.29-1.37 (m, 9H), 1.40-1.48 (m, 3H), 1.72-1.81 (m, 5H), 3.52 (t, *J* = 6.7 Hz, 2H), 4.05-4.14 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.1 (d, *J* = 5.0 Hz), 16.5 (d, *J* = 5.8 Hz), 26.6, 27.1 (d, *J* = 13.4 Hz), 28.6, 29.7 (d, *J* = 3.7 Hz), 30.6 (d, *J* = 139.9 Hz), 32.5, 45.0, 61.4 (dd, *J* = 6.7 Hz, 4.5Hz); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 35.0; IR (neat): ν (cm^{-1}) 3462, 2938, 2899, 2843, 1464, 1230, 1056, 1028, 960; LC-MS (ESI) $[M+H]^+$: 285.23; HRMS (ESI) $C_{12}H_{26}ClNaO_3P$ $[M+Na]^+$ 307.1200, found 307.1202.

References of known compounds

3b, **3g**	Y. Fang, L. Zhang, X. Jin, J. Li, M. Yuan, R. Li, T. Wang, T. Wang, H. Hu and J. Gu, *Eur. J. Org. Chem.*, 2016, 1577-1587.
3e	I. Maciagiewicz, P. Dybowski and A. Skowronska, *Polish J. Chem.*, 1998, **72**, 2389-2393.
3n	P. L. Bailey and R. F. W. Jackson, *Tetrahedron Lett.*, 1991, **32**, 3119-3122.
6a	H. Krawczyk, J. Koszuk and R. Bodalski, *Polish J. Chem.*, 2000, **74**, 1123-1128.

9, **13**	Y. Kobayashi and A. D. William, *Adv. Synth. Catal.*, 2004, **346**, 1749-1757.
19	M. Kalek, A. Ziadi and J. Stawinski, *Org. Lett.*, 2008, **10**, 4637-4640.
20a	M. P. Teulade and P. Savignac, *Tetrahedron Lett.*, 1987, **28**, 405-408.
20b, **20c**, **20d**	Y. Fang, M. Yuan, X. Jin, L. Zhang, R. Li, S. Yang and M. Fang, *Tetrahedron Lett.*, 2016, **57**, 1368-1371.
20e	A. Norder, P. Herrmann, E. Herdtweck and T. Bach, *Org. Lett.*, 2010, **12**, 3690-3692.

References

1 M. Yuguchi, M. Tokuda and K. Orito, *J. Org. Chem.,* 2004, **69**, 908-914.

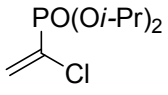
2 S. Huo, *Org. Lett.,* 2003, **5**, 423-425.

3 (*a*) L. Zhang, Y. Fang, X. Jin, H. Xu, R. Li, H. Wu, B. Chen, Y. Zhu, Y. Yang and Z. Tian, *Org. Biomol. Chem.,* 2017, **15**, 8985-8989; (*b*) S. K. Mandal, A.K. Ghosh, R. Kumar and B. Zajc, *Org. Biomol. Chem.,* 2012, **10**, 3164-3167; (*c*) C. E. Mckenna, L. A. Khawli, W.-Y. Ahmad, P. Pham and J.-P. Bongartz, *Phosphorus and Sulfur*, 1988, **37**, 1-12; (*d*) Y. Kobayashi and A. D. William, *Adv. Synth. Catal.,* 2004, **346**, 1749-1757; (*e*) H. Lahrache, S. Robin and G. Rousseau, *Tetrahedron Lett.,* 2005, **46**, 1635-1637.

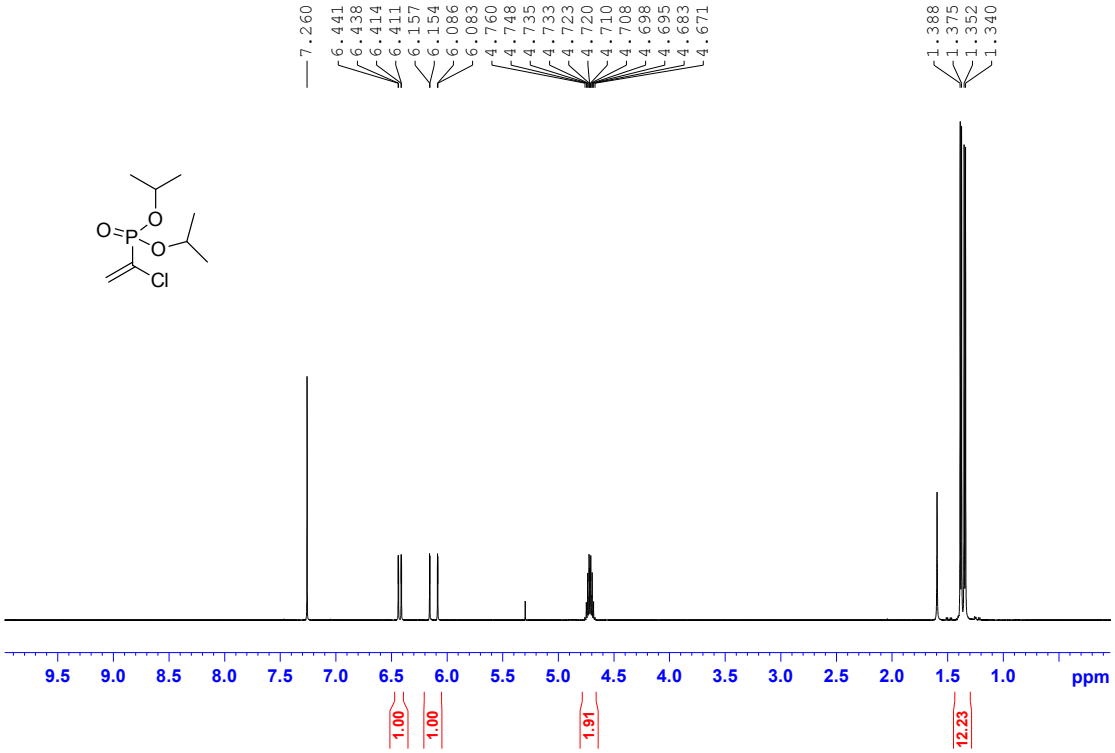
4 (*a*)Y. Fang, L. Zhang, X. Jin, J. Li, M. Yuan, R. Li, T. Wang, T. Wang, H. Hu and J. Gu, *Eur. J. Org. Chem.,* 2016, 1577-1587; (*b*) T. Okauchi, T. Yano, T. Fukamachi, J. Ichikawa and T. Minami, *Tetrahedron Lett.*, 1999, **40**, 5337-5340.

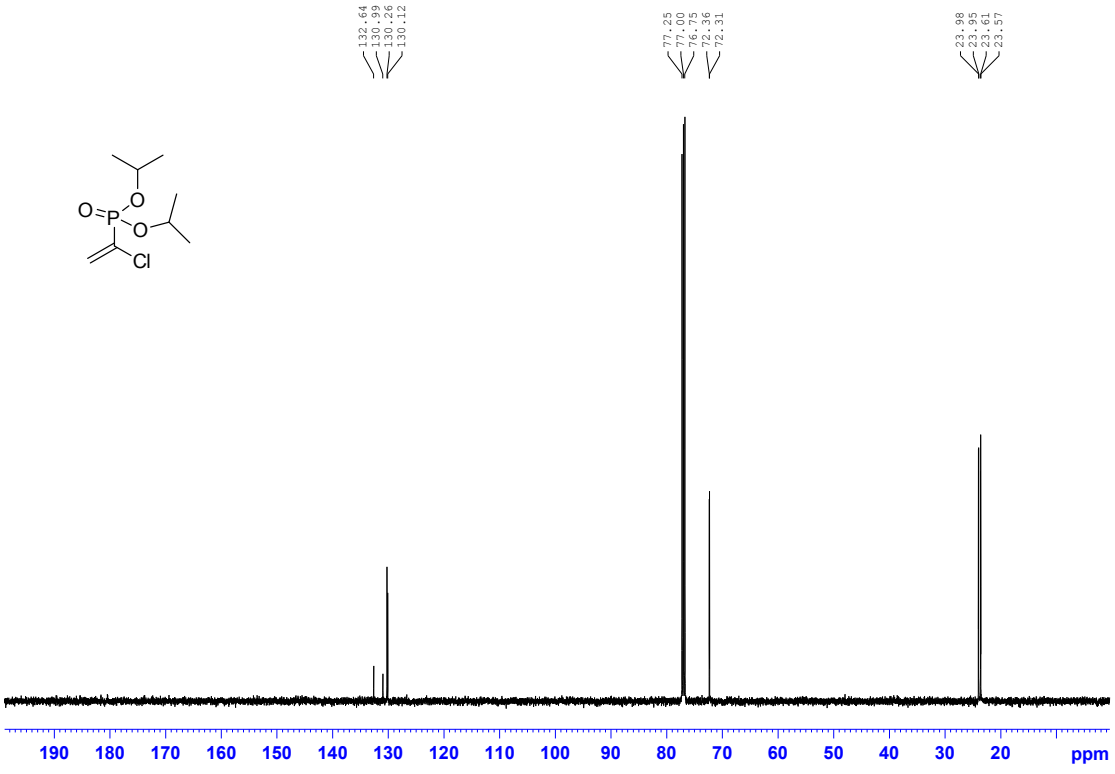
5 A. Krasovskiy, and P. Knochel, *Synthesis,* 2006, **5**, 890-891.

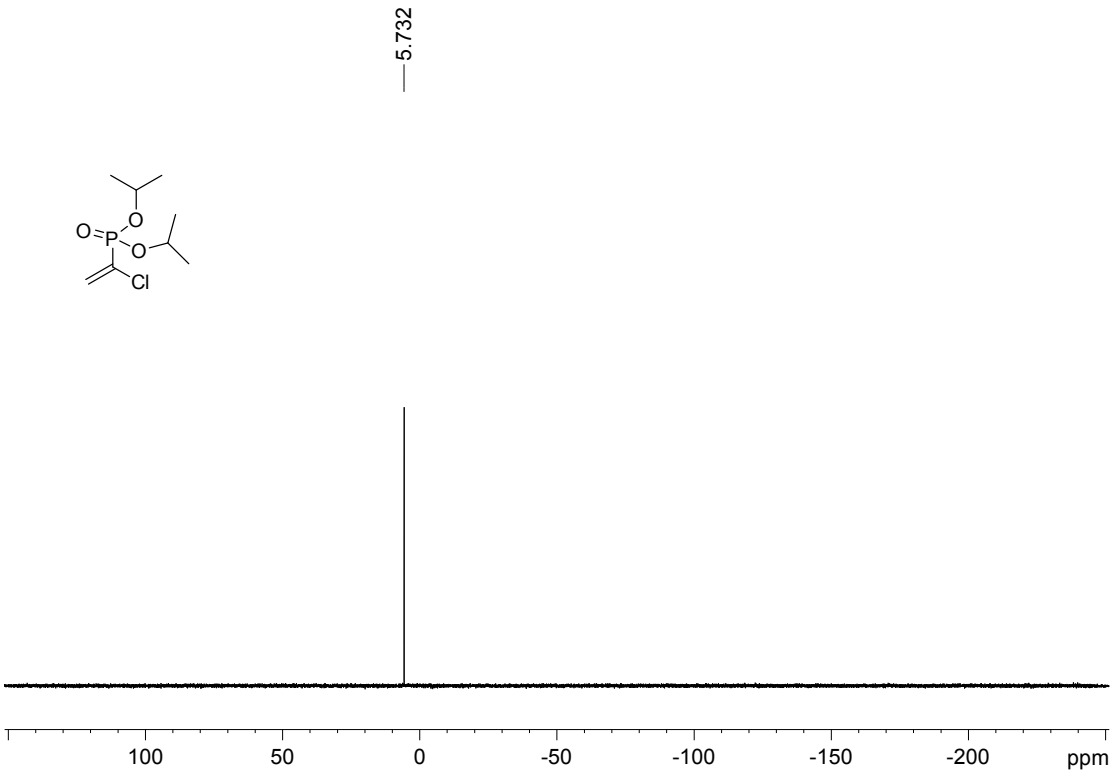
^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectra of new compounds

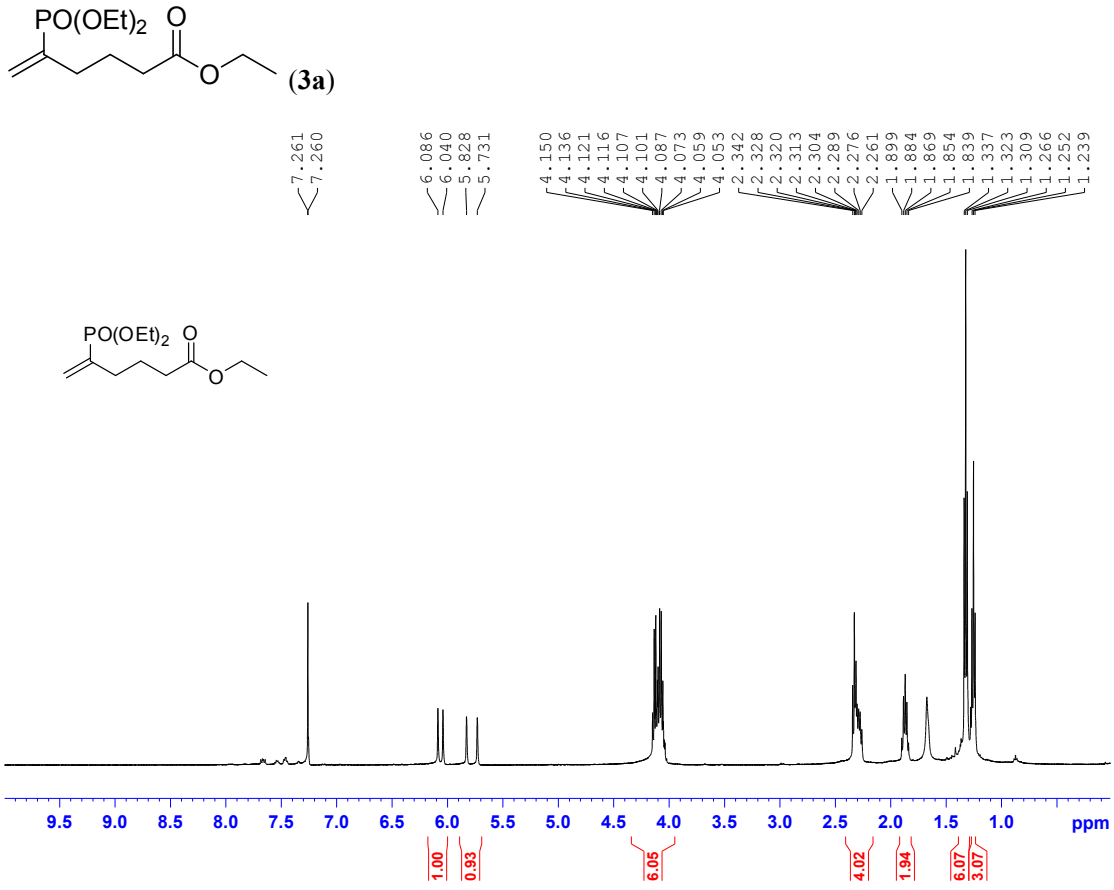


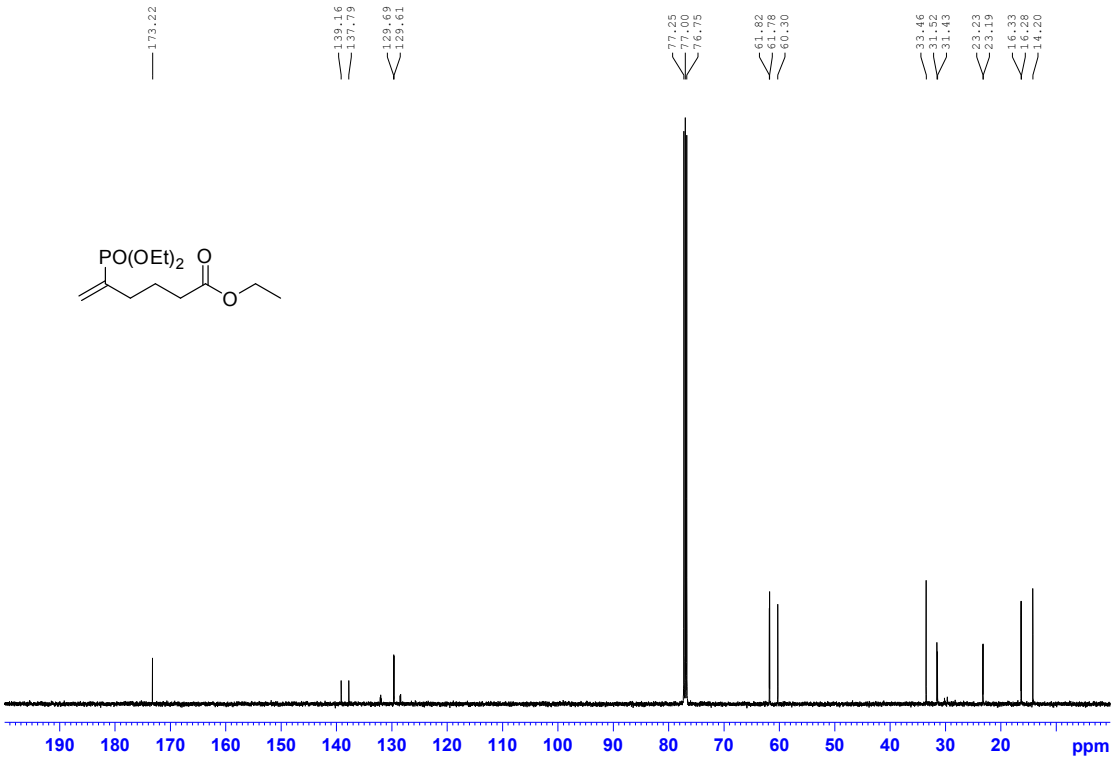
(**1f**)

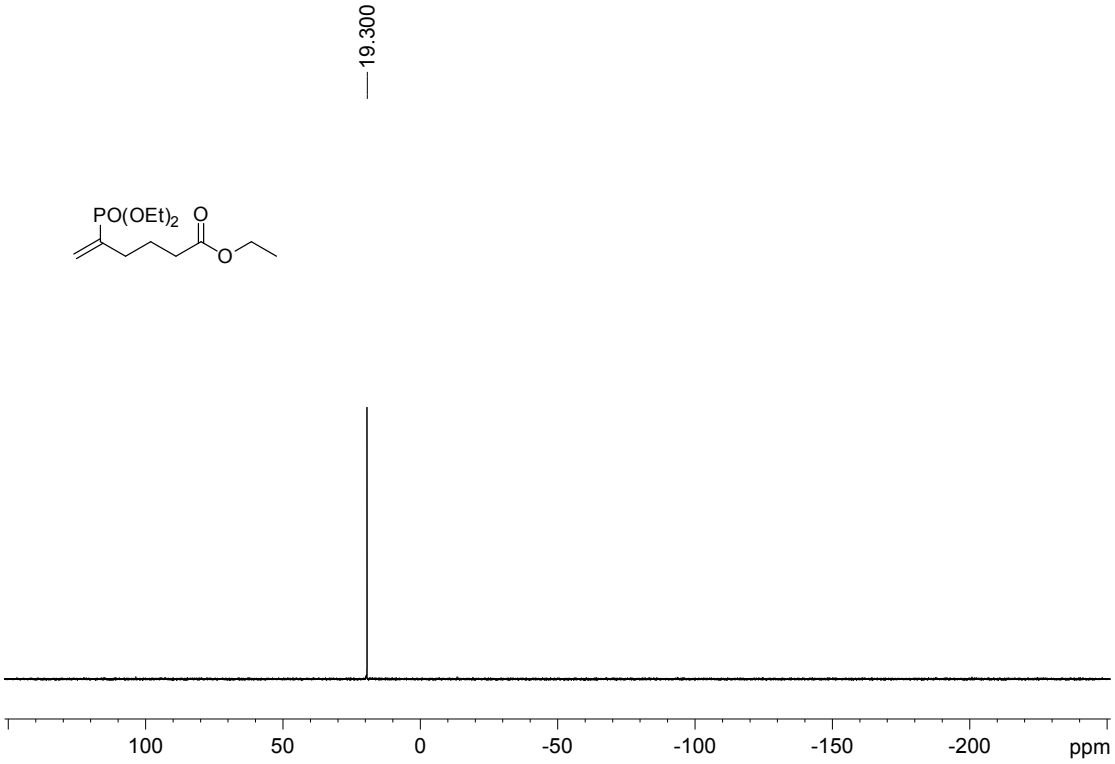

7.260
6.441
6.438
6.414
6.411
6.157
6.154
6.086
6.083
4.760
4.748
4.735
4.733
4.723
4.720
4.710
4.708
4.698
4.695
4.683
4.671
1.388
1.375
1.352
1.340
O
P
O
O
Cl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
1.91
12.23

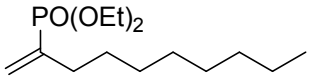

132.64
130.99
130.26
130.12
77.25
77.00
76.75
72.36
72.31
23.98
23.95
23.61
23.57
O
P
O
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


5.732
O
P
O
O
Cl
100
50
0
-50
-100
-150
-200
ppm

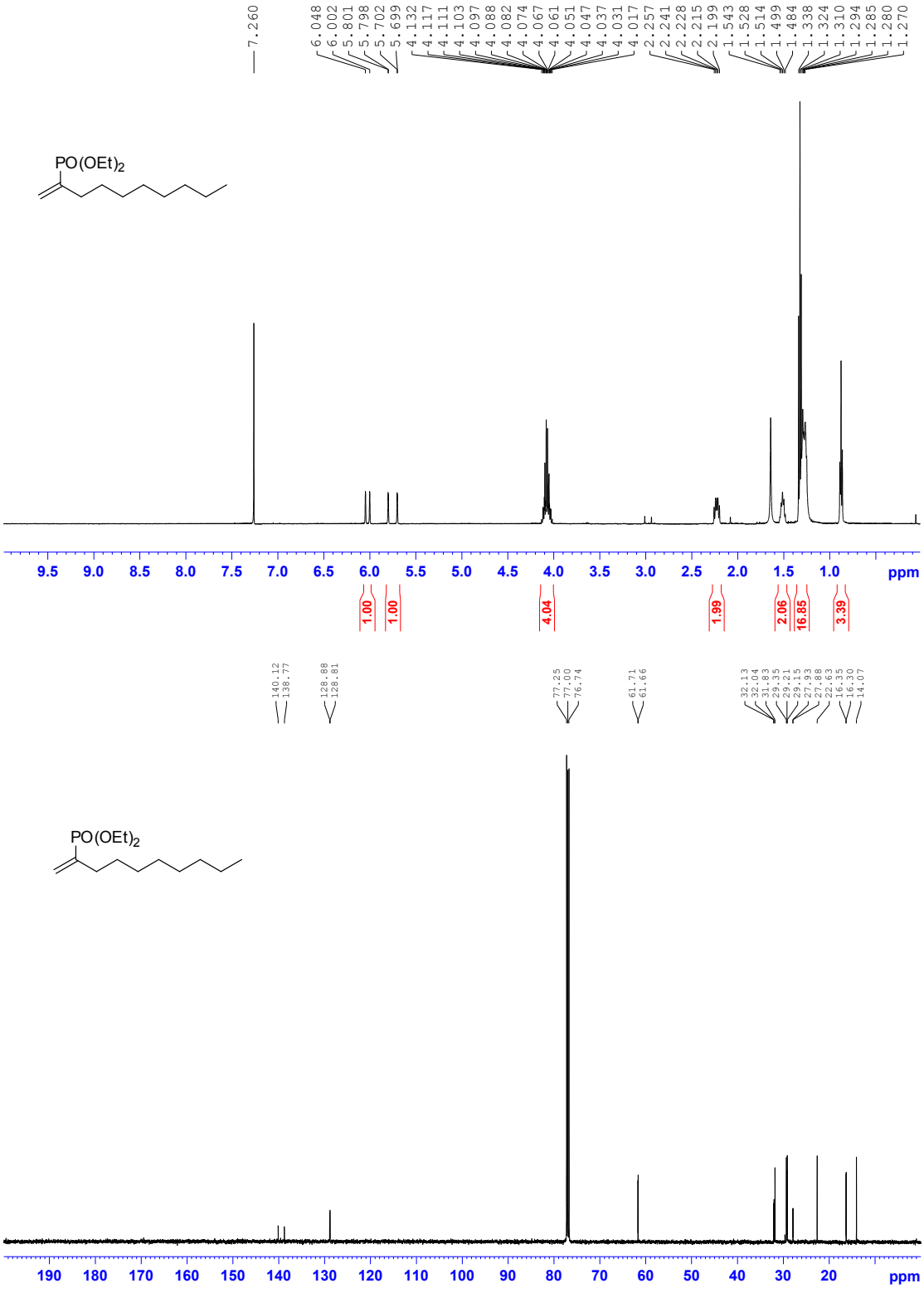

PO(OEt)2
O
O
(3a)
7.261
7.260
6.086
6.040
5.828
5.731
4.150
4.136
4.121
4.116
4.107
4.101
4.087
4.073
4.059
4.053
2.342
2.328
2.320
2.313
2.304
2.289
2.276
2.261
1.899
1.884
1.869
1.854
1.839
1.337
1.323
1.309
1.266
1.252
1.239
PO(OEt)2
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.93
6.05
4.02
1.94
6.07
3.07

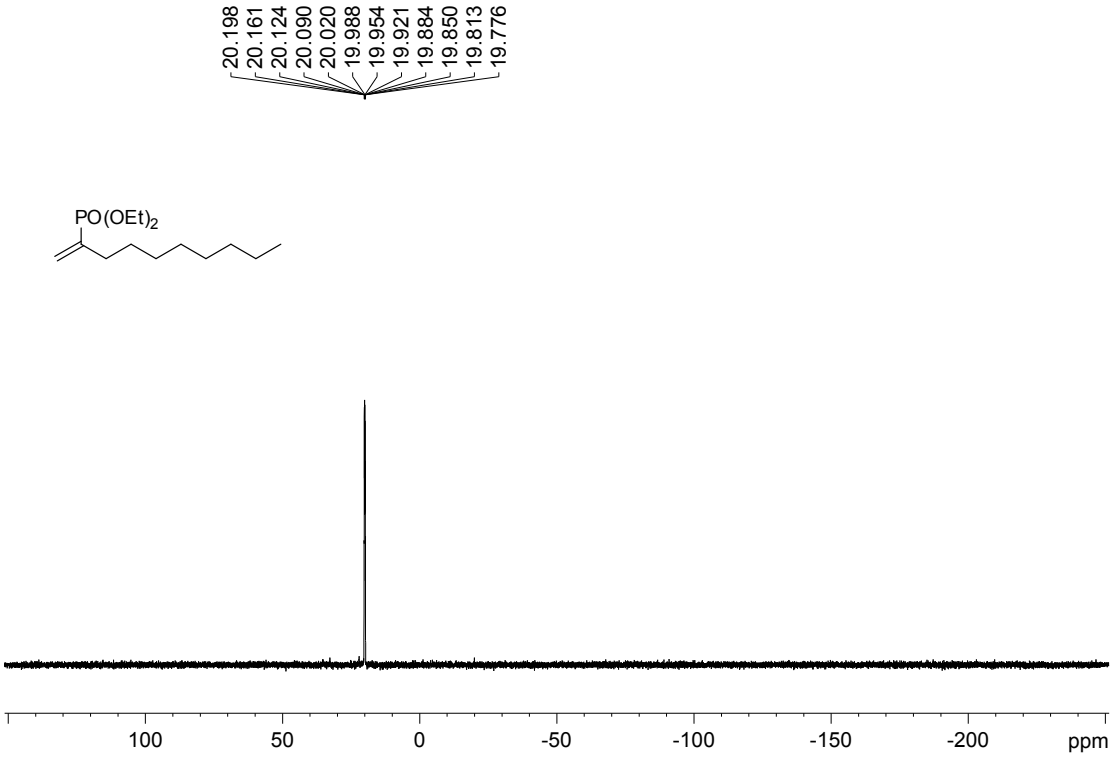

173.22
139.16
137.79
129.69
129.61
77.25
77.00
76.75
61.82
61.78
60.30
33.46
31.52
31.43
23.23
23.19
16.33
16.28
14.20
PO(OEt)2
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


19.300
PO(OEt)2
O
O
100 50 0 -50 -100 -150 -200 ppm


PO(OEt)2

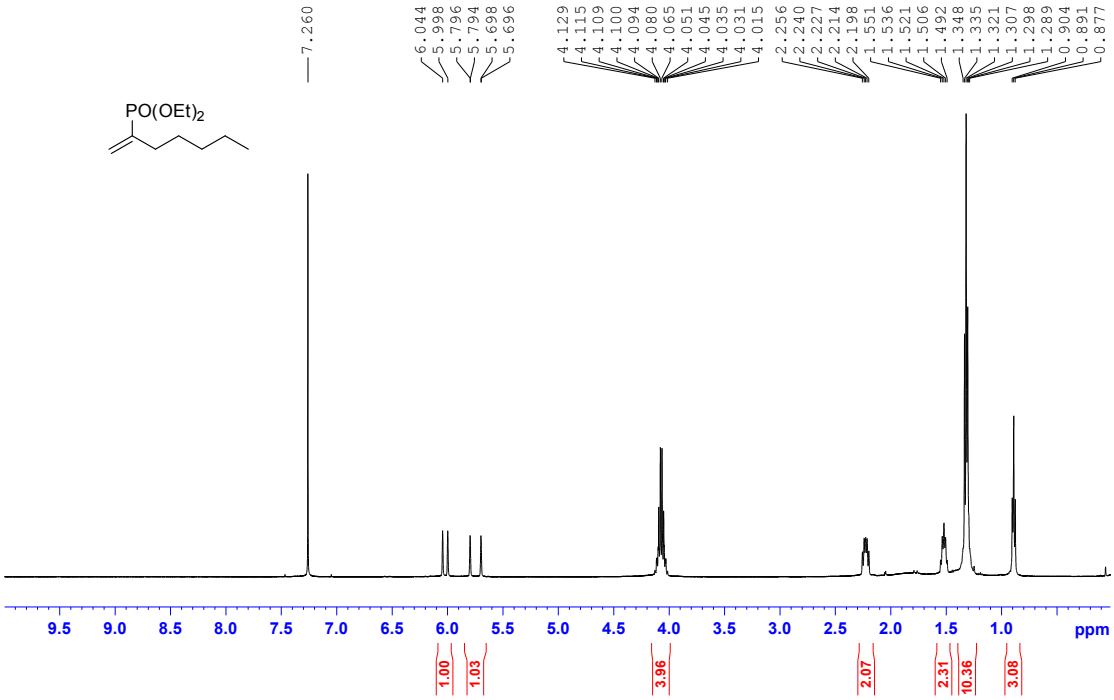
(**3c**)

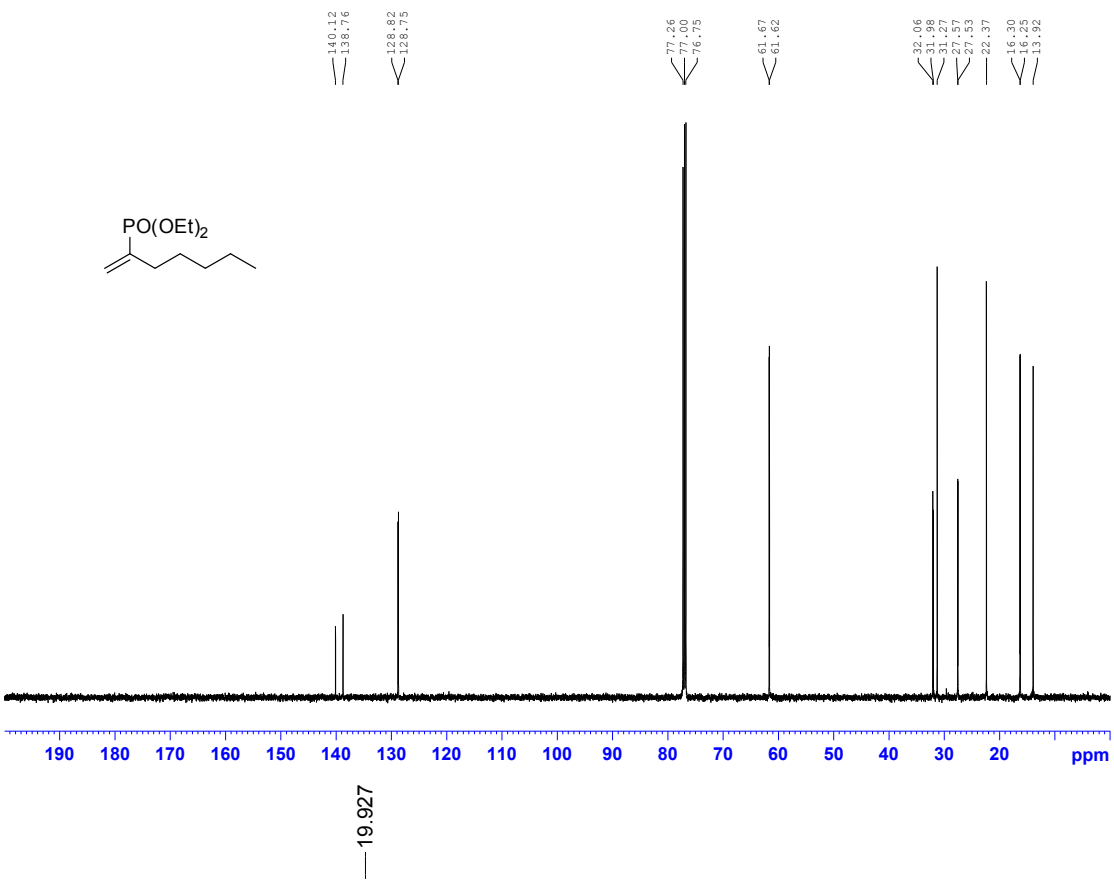

7.260
6.048
6.002
5.801
5.798
5.702
5.699
4.132
4.117
4.111
4.103
4.097
4.088
4.082
4.074
4.067
4.061
4.051
4.047
4.037
4.031
4.017
2.257
2.241
2.228
2.215
2.199
1.543
1.528
1.514
1.499
1.484
1.338
1.324
1.310
1.294
1.285
1.280
1.270
PO(OEt)2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.00
4.04
1.99
2.06
16.85
3.39
140.12
138.77
128.88
128.81
77.25
77.00
76.74
61.71
61.66
32.13
32.04
31.83
29.35
29.21
29.15
27.93
27.88
22.63
16.35
16.30
14.07
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

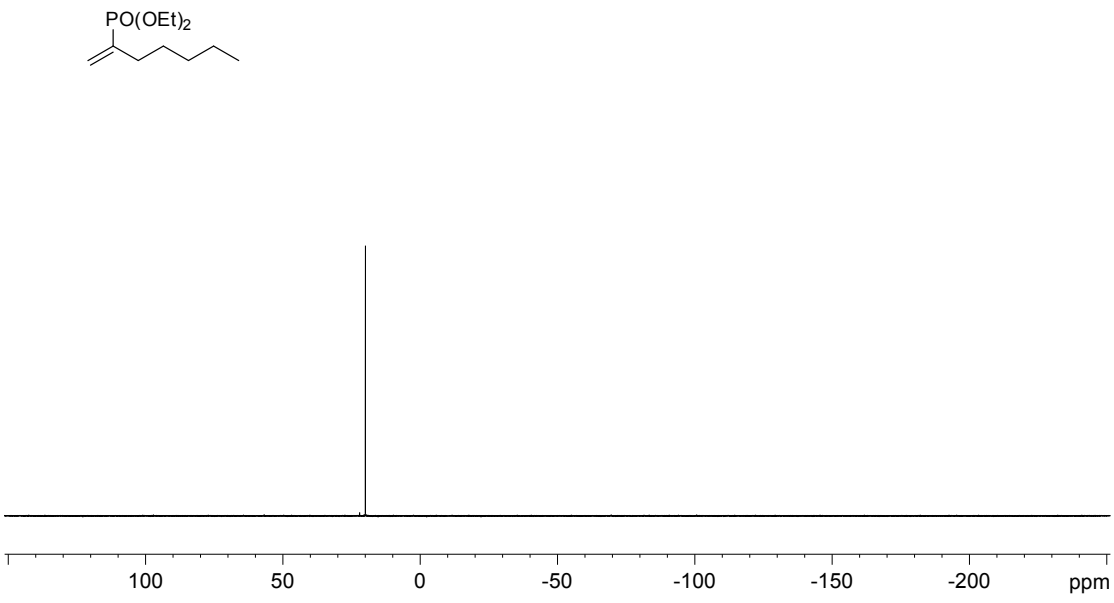

20.198
20.161
20.124
20.090
20.020
19.988
19.954
19.921
19.884
19.850
19.813
19.776
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm

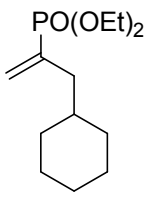
PO(OEt)$_2$

(**3d**)

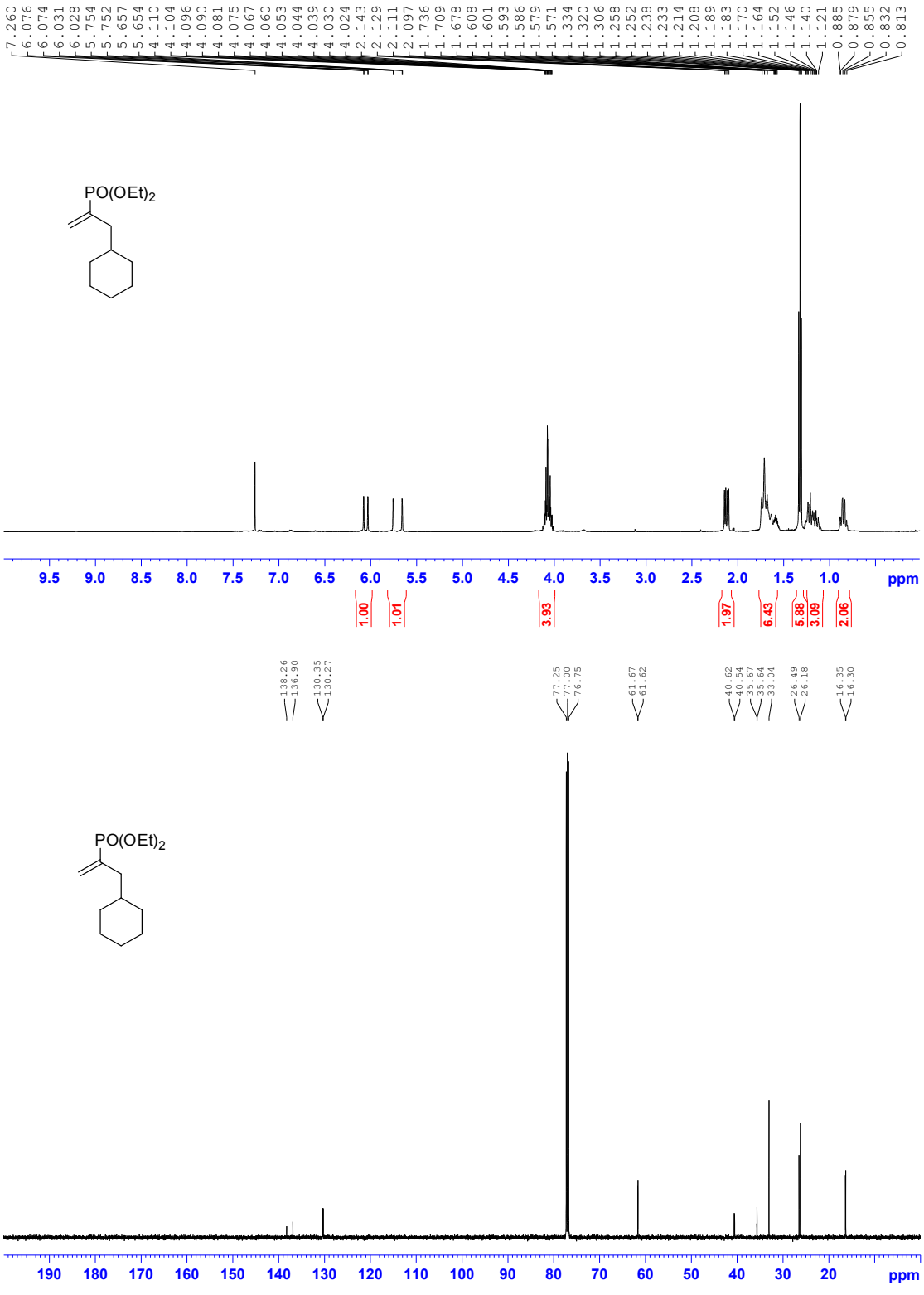

7.260
6.044
5.998
5.796
5.794
5.698
5.696
4.129
4.115
4.109
4.100
4.094
4.080
4.065
4.051
4.045
4.035
4.031
4.015
2.256
2.240
2.227
2.214
2.198
1.551
1.536
1.521
1.506
1.492
1.348
1.335
1.321
1.307
1.298
1.289
0.904
0.891
0.877
PO(OEt)2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.03
3.96
2.07
2.31
10.36
3.08

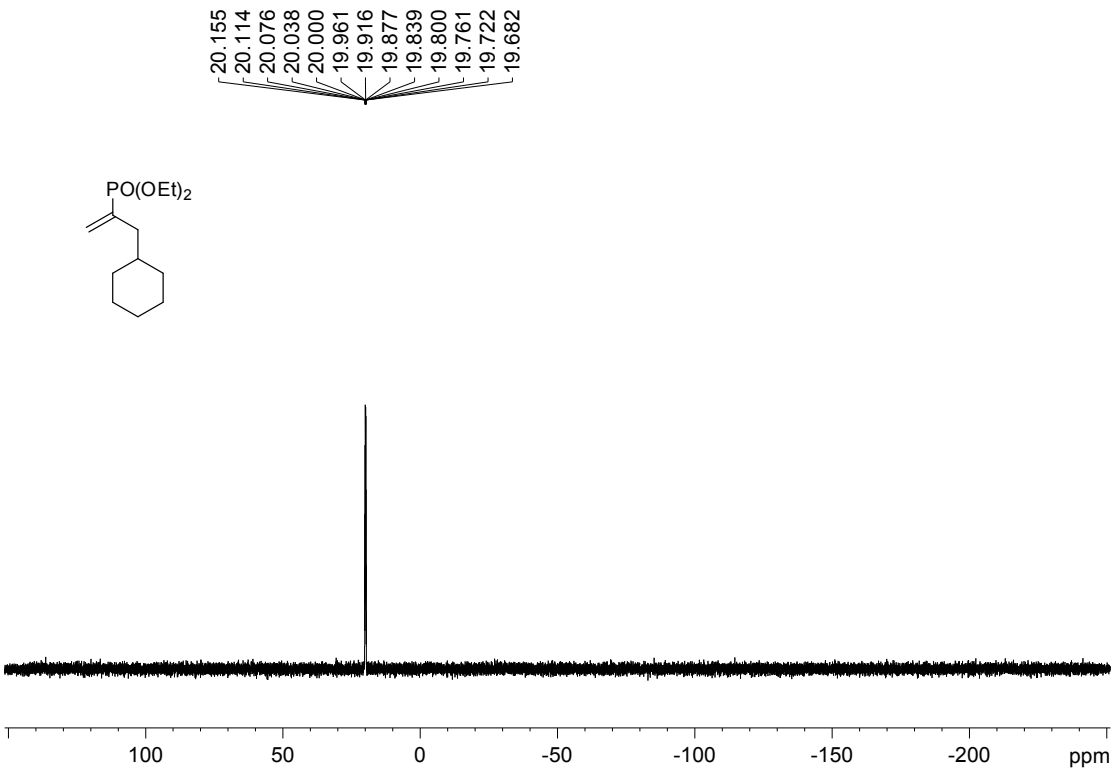

140.12
138.76
128.82
128.75
77.26
77.00
76.75
61.67
61.62
32.06
31.98
31.27
27.57
27.53
22.37
16.30
16.25
13.92
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

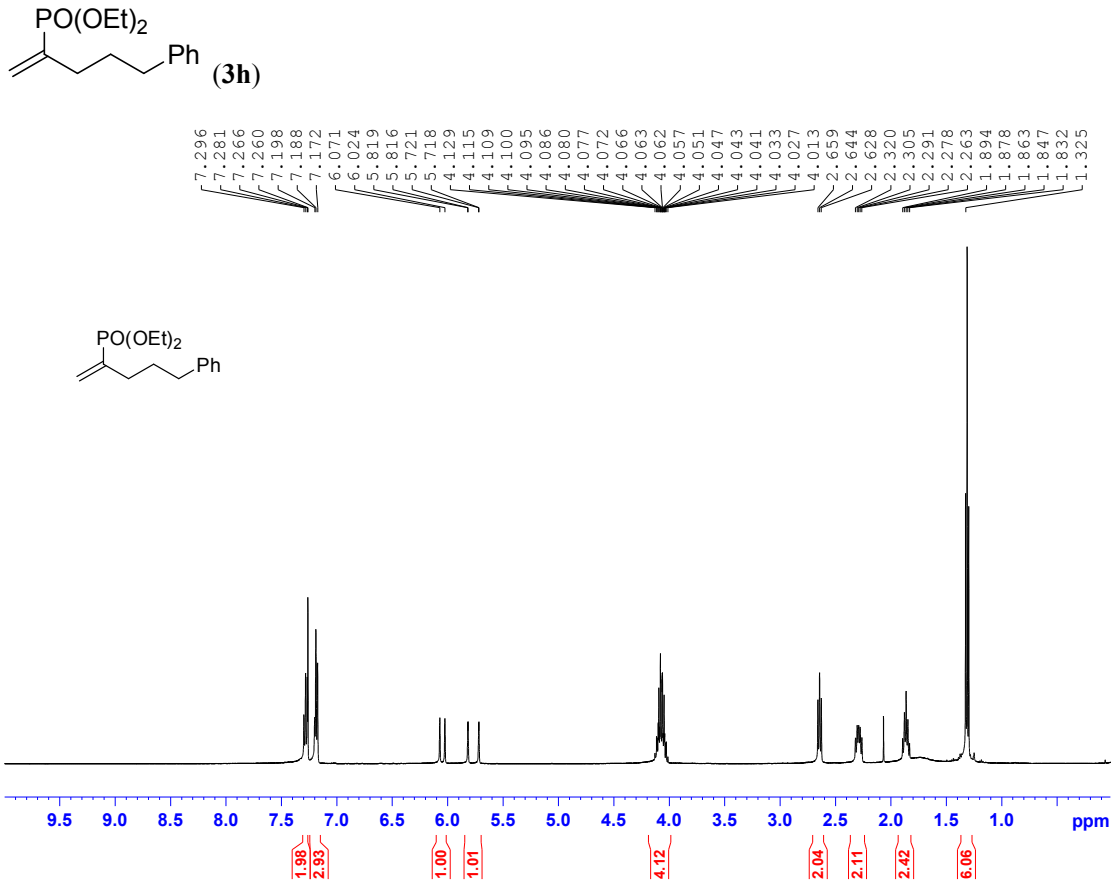

19.927
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm

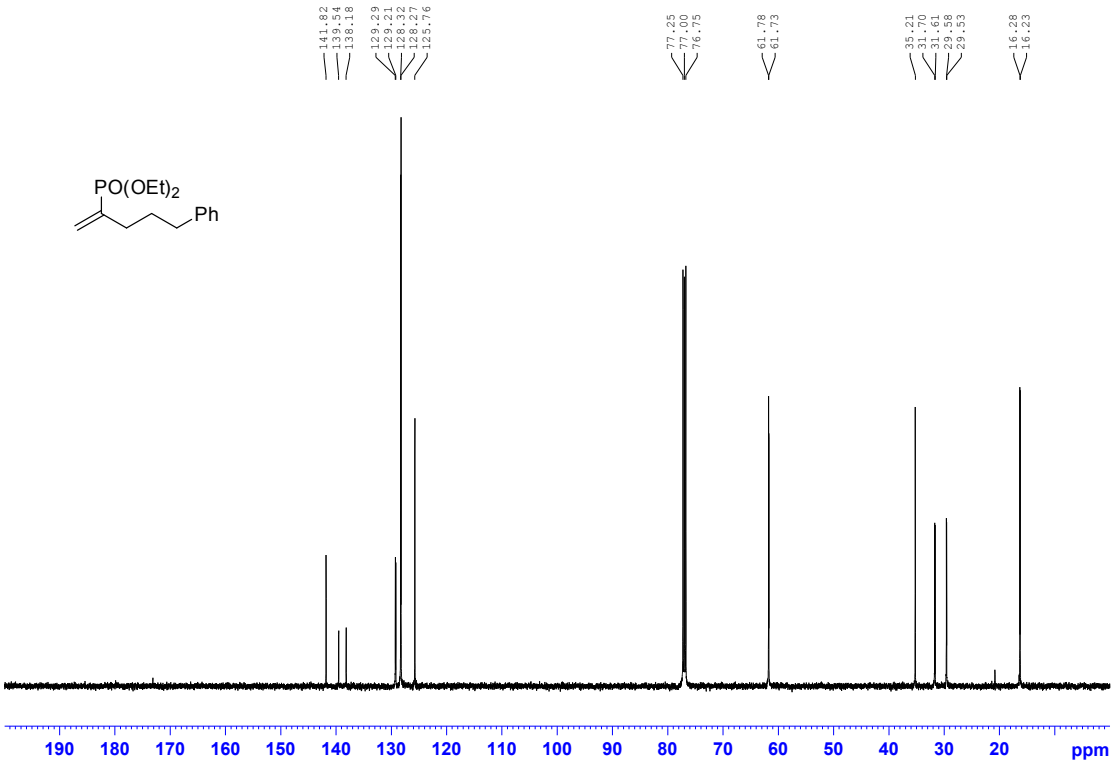

PO(OEt)2

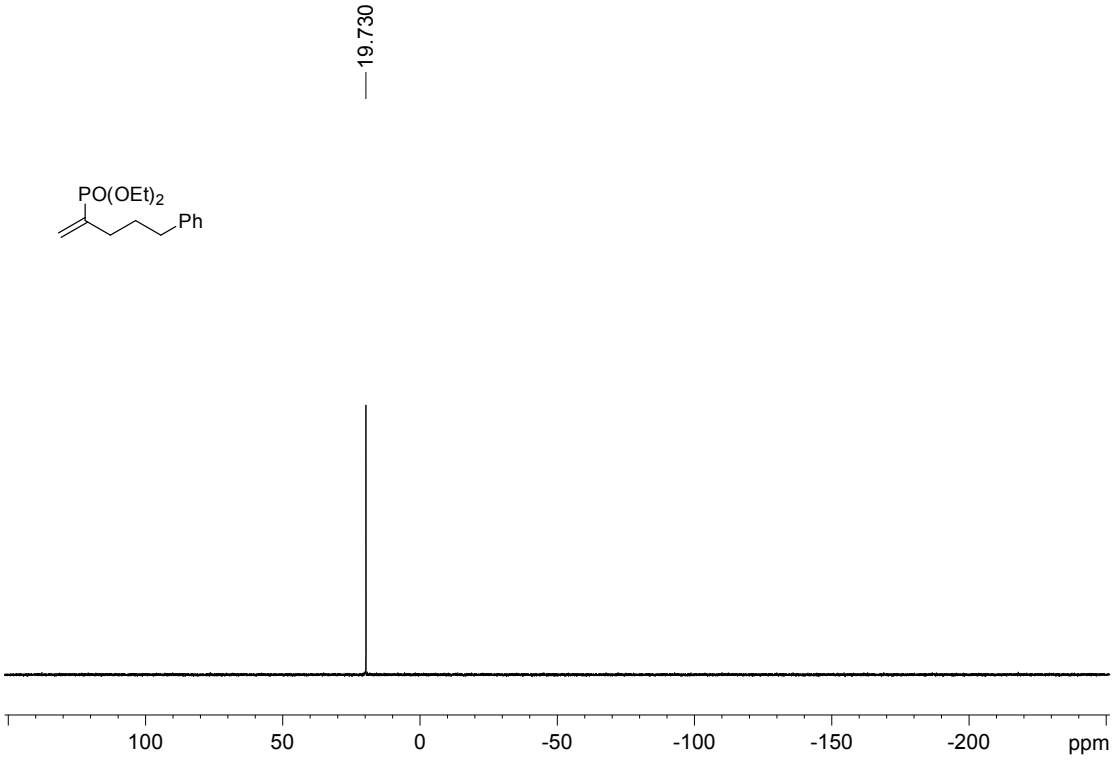
(**3f**)

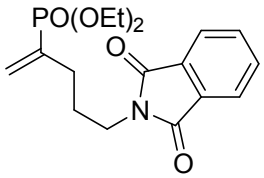

7.260
6.076
6.074
6.031
6.028
5.754
5.752
5.657
5.654
4.110
4.104
4.096
4.090
4.081
4.075
4.067
4.060
4.053
4.044
4.039
4.030
4.024
2.143
2.129
2.111
2.097
1.736
1.709
1.678
1.608
1.601
1.593
1.586
1.579
1.571
1.334
1.320
1.306
1.258
1.252
1.238
1.233
1.214
1.208
1.189
1.183
1.170
1.164
1.152
1.146
1.140
1.121
0.885
0.879
0.855
0.832
0.813
PO(OEt)2
9.5 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 ppm
1.00
1.01
3.93
1.97
6.43
5.88
3.09
2.06
138.26
136.90
130.35
130.27
77.25
77.00
76.75
61.67
61.62
40.62
40.54
35.67
35.64
33.04
26.49
26.18
16.35
16.30
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


20.155
20.114
20.076
20.038
20.000
19.961
19.916
19.877
19.839
19.800
19.761
19.722
19.682
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm

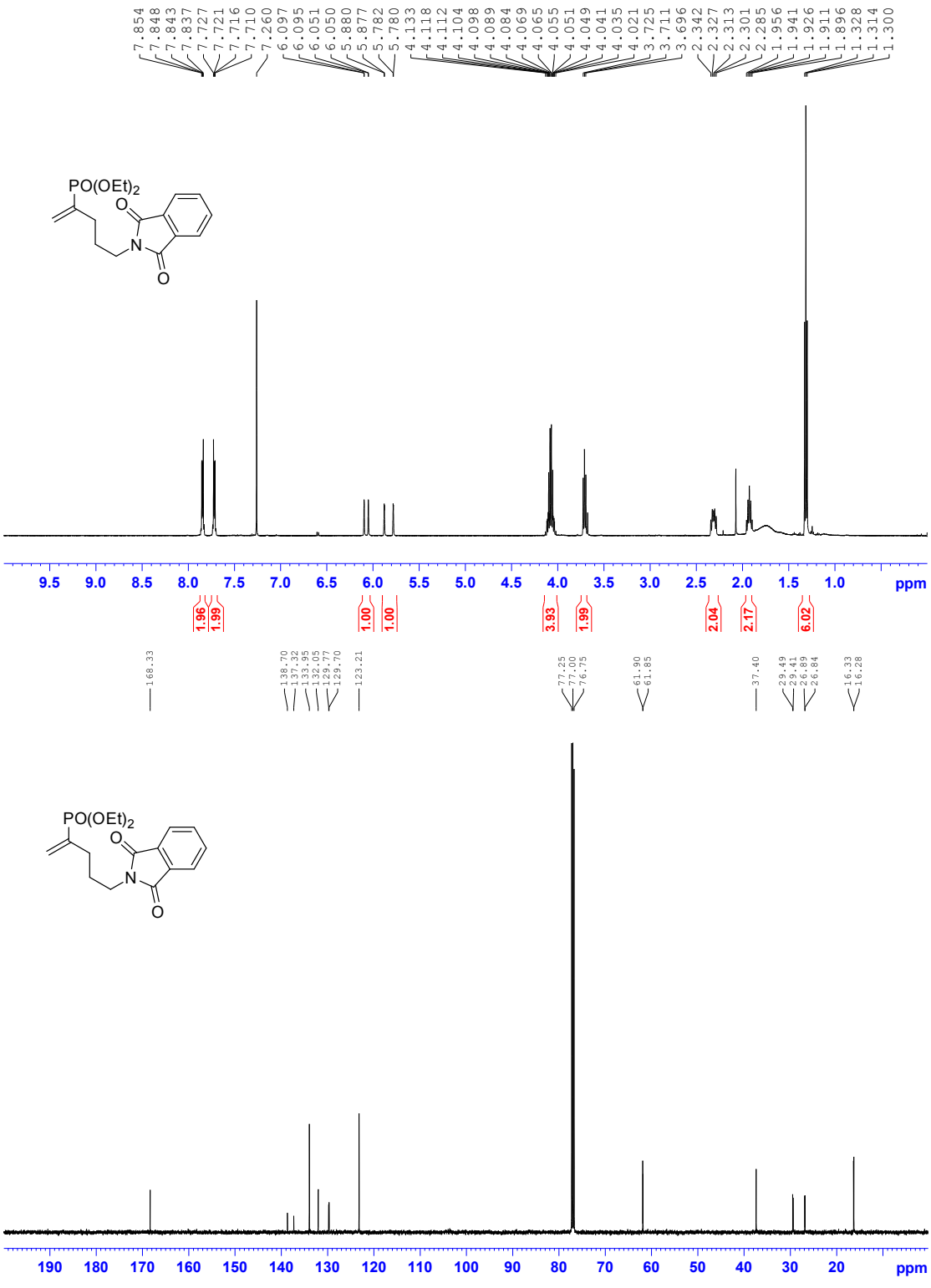

PO(OEt)2
Ph
(3h)
7.296
7.281
7.266
7.260
7.198
7.188
7.172
6.071
6.024
5.819
5.816
5.721
5.718
4.129
4.115
4.109
4.100
4.095
4.086
4.080
4.077
4.072
4.066
4.063
4.062
4.057
4.051
4.047
4.043
4.041
4.033
4.027
4.013
2.659
2.644
2.628
2.320
2.305
2.291
2.278
2.263
1.894
1.878
1.863
1.847
1.832
1.325
PO(OEt)2
Ph
9.5
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
ppm
1.98
2.93
1.00
1.01
4.12
2.04
2.11
2.42
6.06

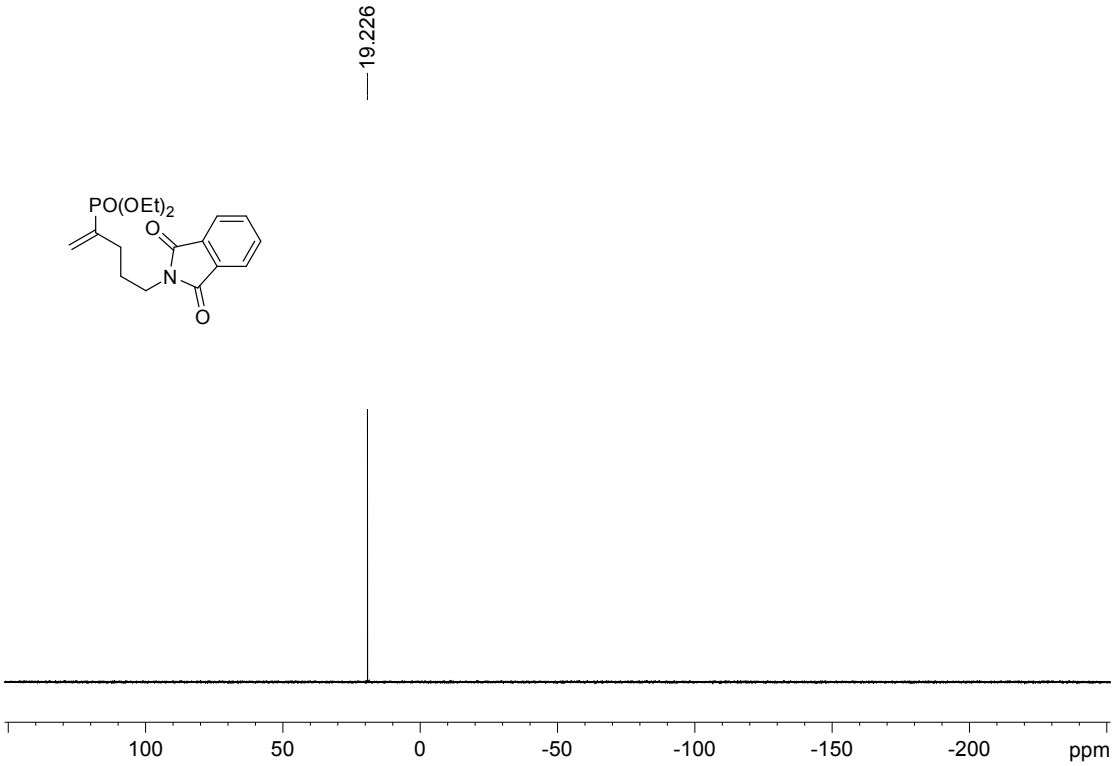

141.82
139.54
138.18
129.29
129.21
128.32
128.27
125.76
77.25
77.00
76.75
61.78
61.73
35.21
31.70
31.61
29.58
29.53
16.28
16.23
PO(OEt)2
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

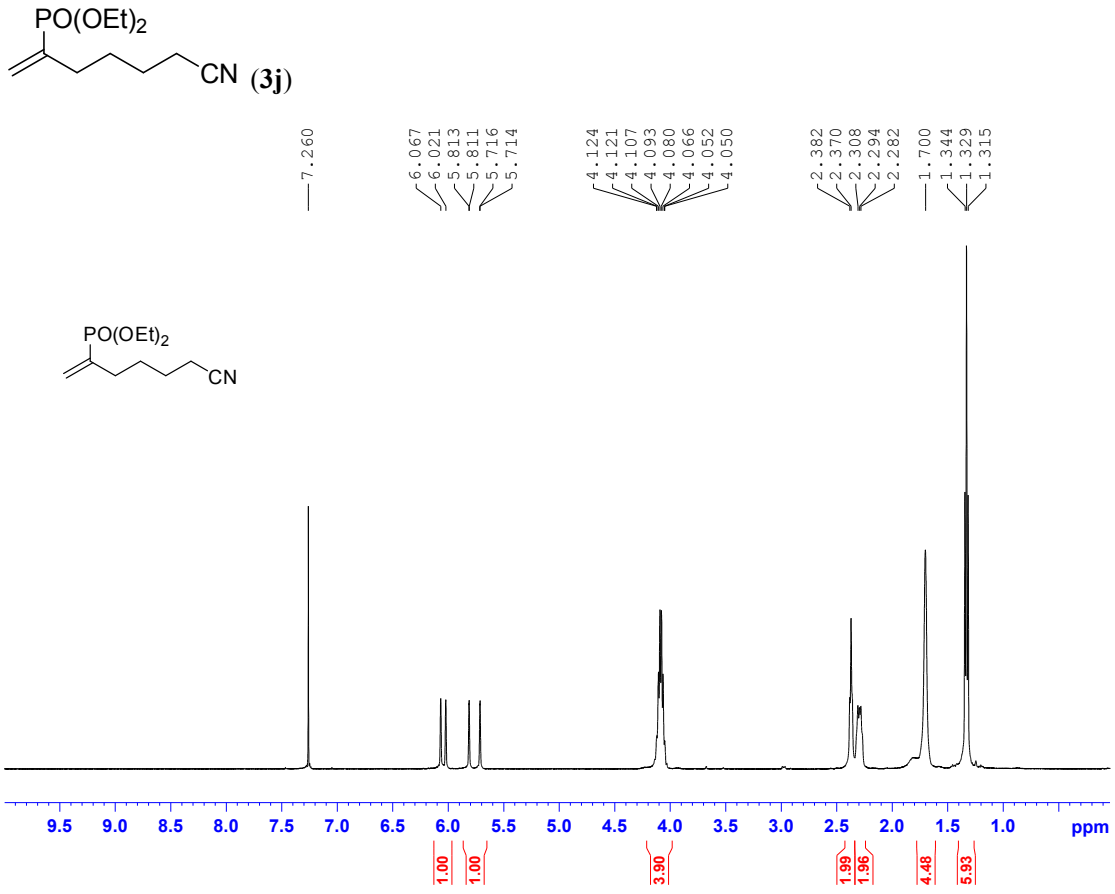

19.730
PO(OEt)2
Ph
100 50 0 -50 -100 -150 -200 ppm


PO(OEt)2
O
N
O

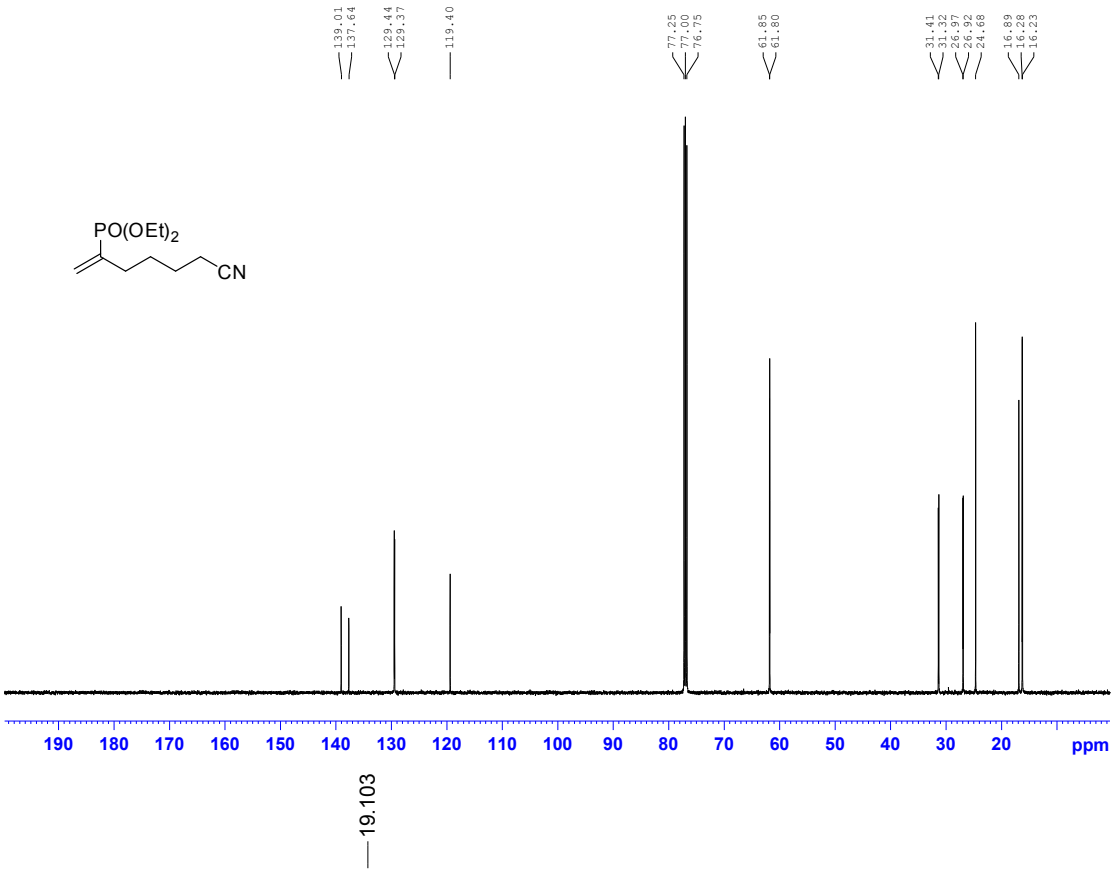
(**3i**)

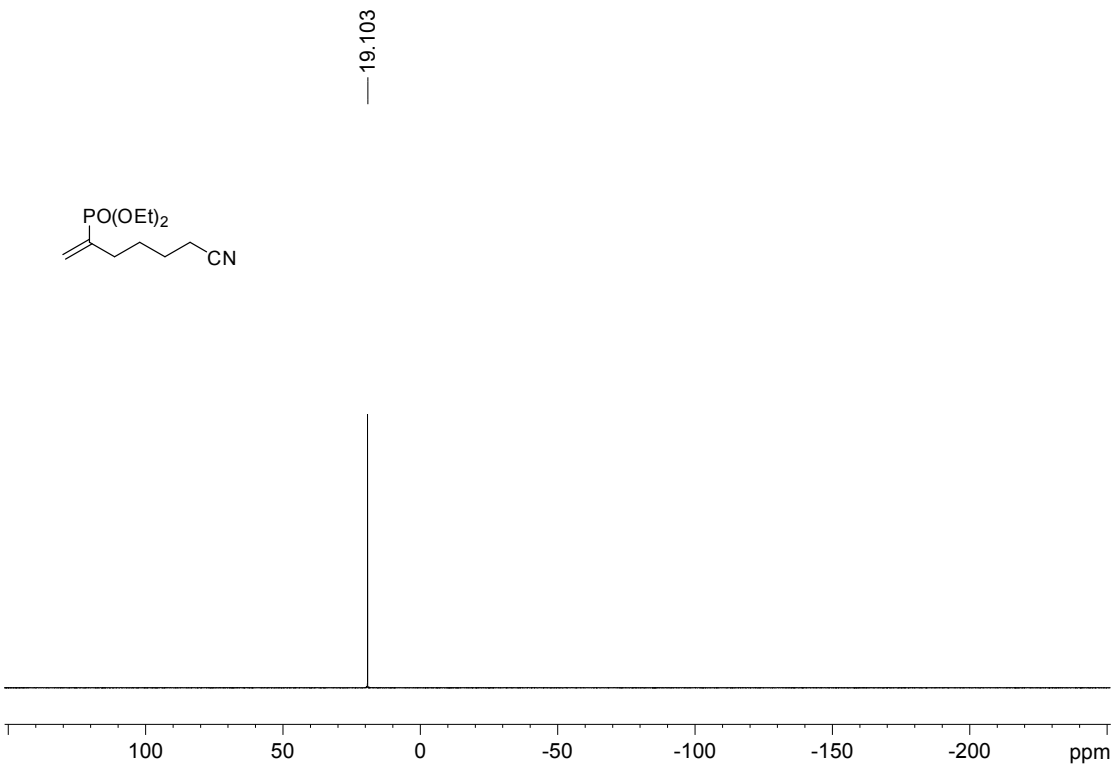

7.854
7.848
7.843
7.837
7.727
7.721
7.716
7.710
7.260
6.097
6.095
6.051
6.050
5.880
5.877
5.782
5.780
4.133
4.118
4.112
4.104
4.098
4.089
4.084
4.069
4.065
4.055
4.051
4.049
4.041
4.035
4.021
3.725
3.711
3.696
2.342
2.327
2.313
2.301
2.285
1.956
1.941
1.926
1.911
1.896
1.328
1.314
1.300
PO(OEt)2
O
N
O
9.5 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 ppm
1.96
1.99
1.00
1.00
3.93
1.99
2.04
2.17
6.02
168.33
138.70
137.32
133.95
132.05
129.77
129.70
123.21
77.25
77.00
76.75
61.90
61.85
37.40
29.49
29.41
26.89
26.84
16.33
16.28
PO(OEt)2
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

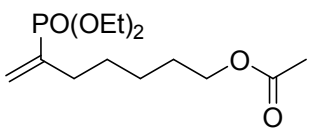

19.226
PO(OEt)2
O
N
O
100
50
0
-50
-100
-150
-200
ppm


PO(OEt)2
CN
7.260
6.067
6.021
5.813
5.811
5.716
5.714
4.124
4.121
4.107
4.093
4.080
4.066
4.052
4.050
2.382
2.370
2.308
2.294
2.282
1.700
1.344
1.329
1.315
PO(OEt)2
CN
9.5
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
ppm
1.00
1.00
3.90
1.99
1.96
4.48
5.93

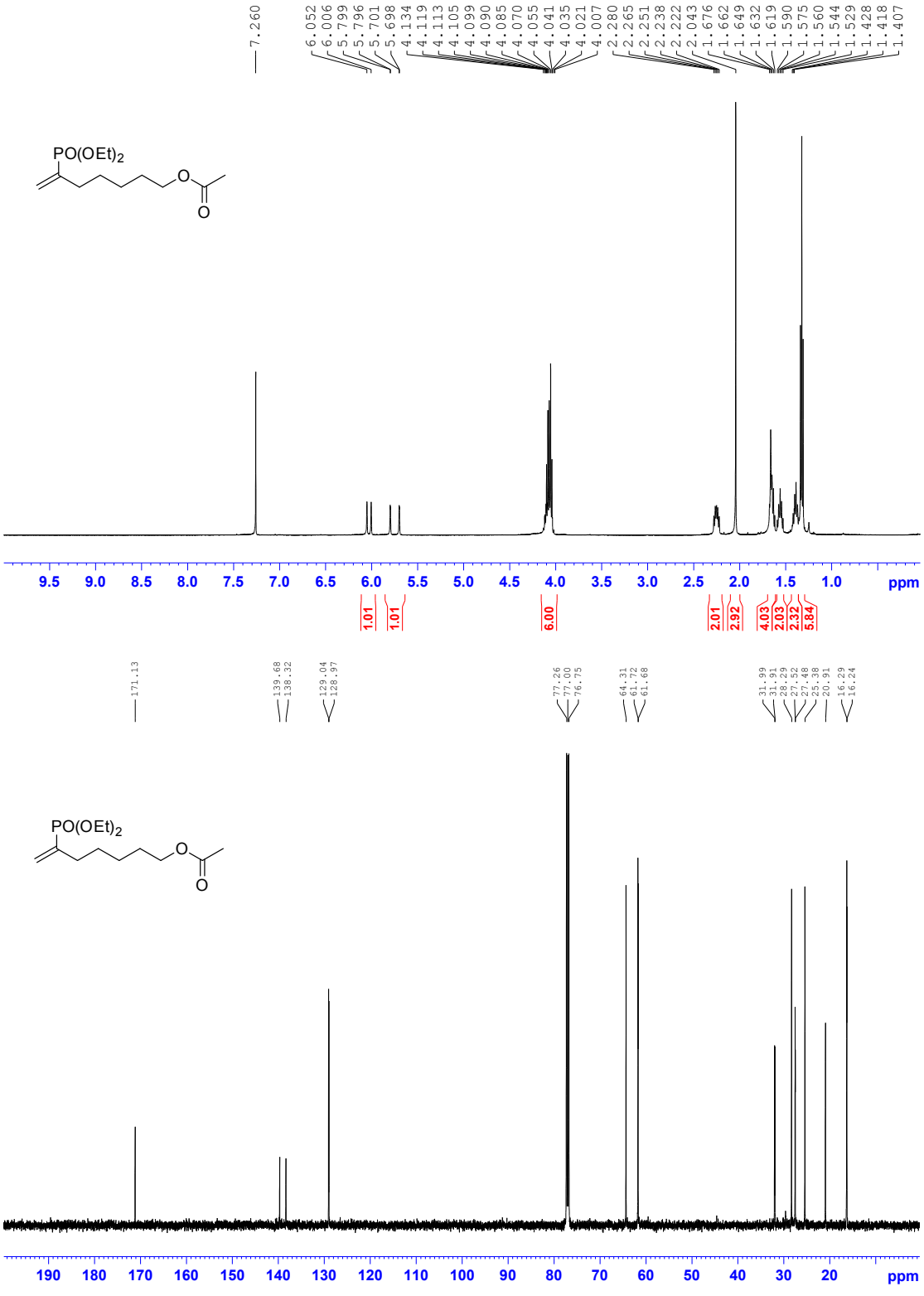
(**3j**)

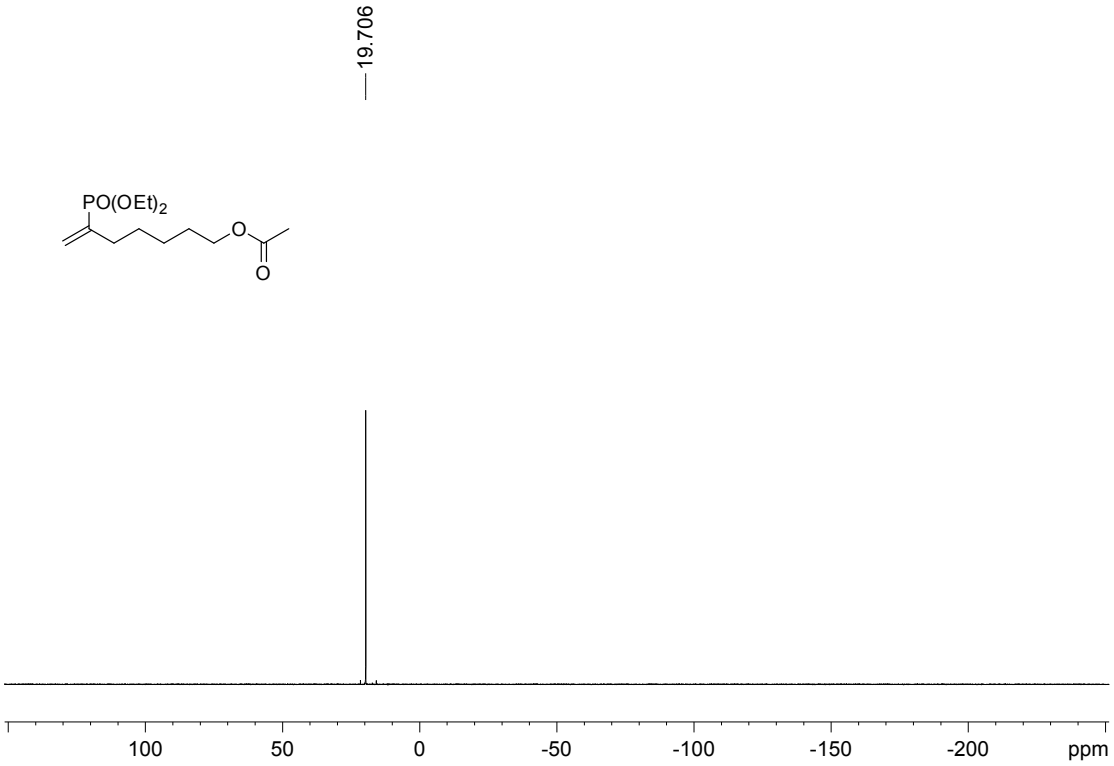

139.01
137.64
129.44
129.37
119.40
77.25
77.00
76.75
61.85
61.80
31.41
31.32
26.97
26.92
24.68
16.89
16.28
16.23
PO(OEt)2
CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

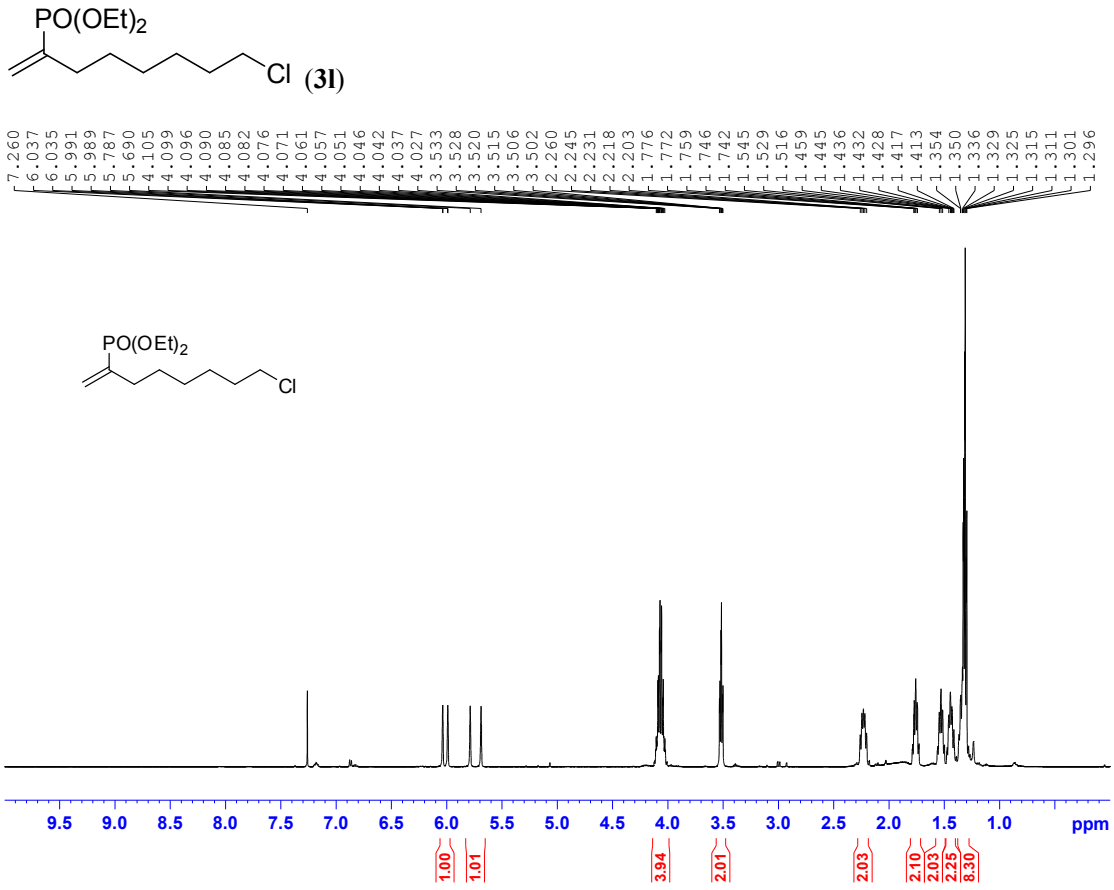

19.103
PO(OEt)2
CN
100 50 0 -50 -100 -150 -200 ppm

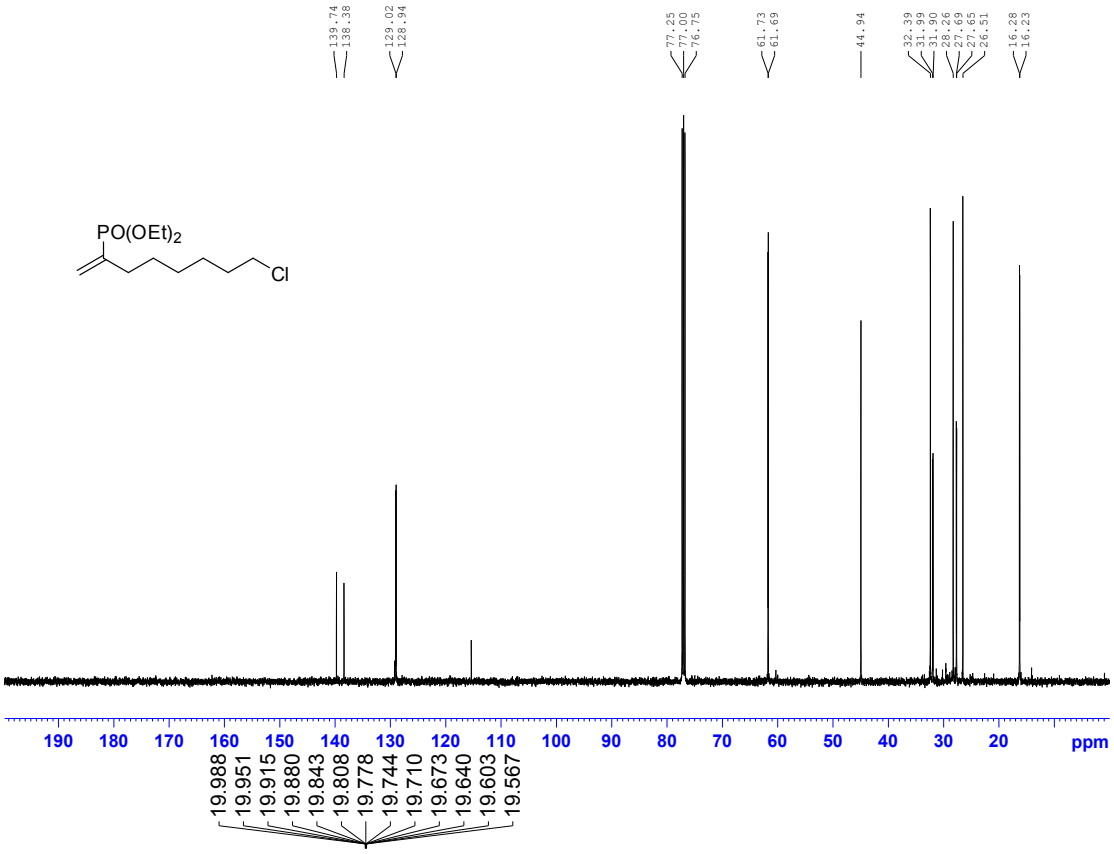

PO(OEt)2
O
O

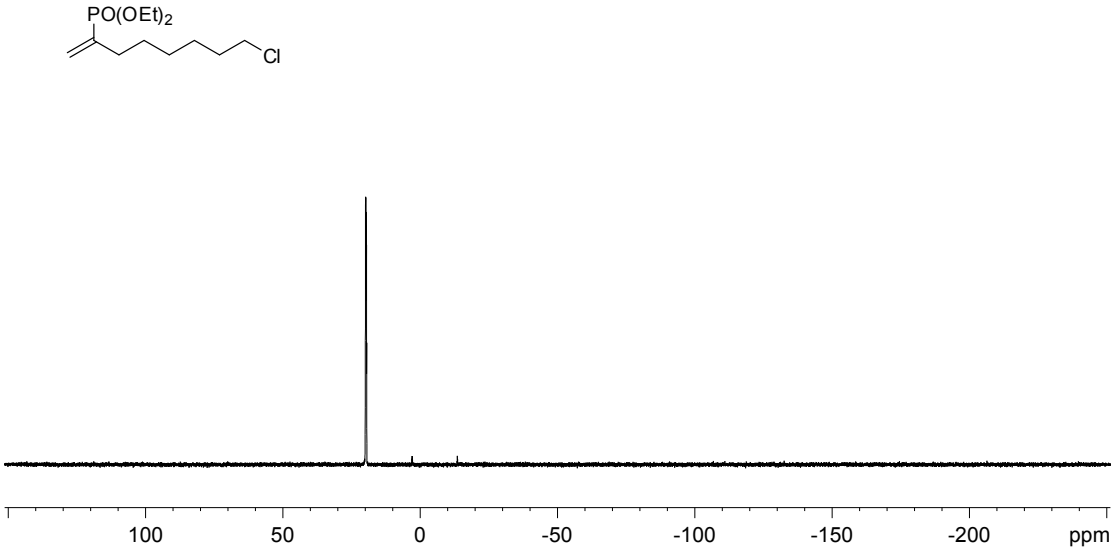
(3k)

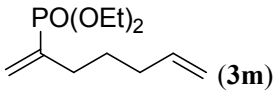

7.260
6.052
6.006
5.799
5.796
5.701
5.698
4.134
4.119
4.113
4.105
4.099
4.090
4.085
4.070
4.055
4.041
4.035
4.021
4.007
2.280
2.265
2.251
2.238
2.222
2.043
1.676
1.662
1.649
1.632
1.619
1.590
1.575
1.560
1.544
1.529
1.428
1.418
1.407
PO(OEt)2
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.01
1.01
6.00
2.01
2.92
4.03
2.03
2.32
5.84
171.13
139.68
138.32
129.04
128.97
77.26
77.00
76.75
64.31
61.72
61.68
31.99
31.91
28.29
27.52
27.48
25.38
20.91
16.29
16.24
PO(OEt)2
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


19.706
PO(OEt)2
O
O
100
50
0
-50
-100
-150
-200
ppm

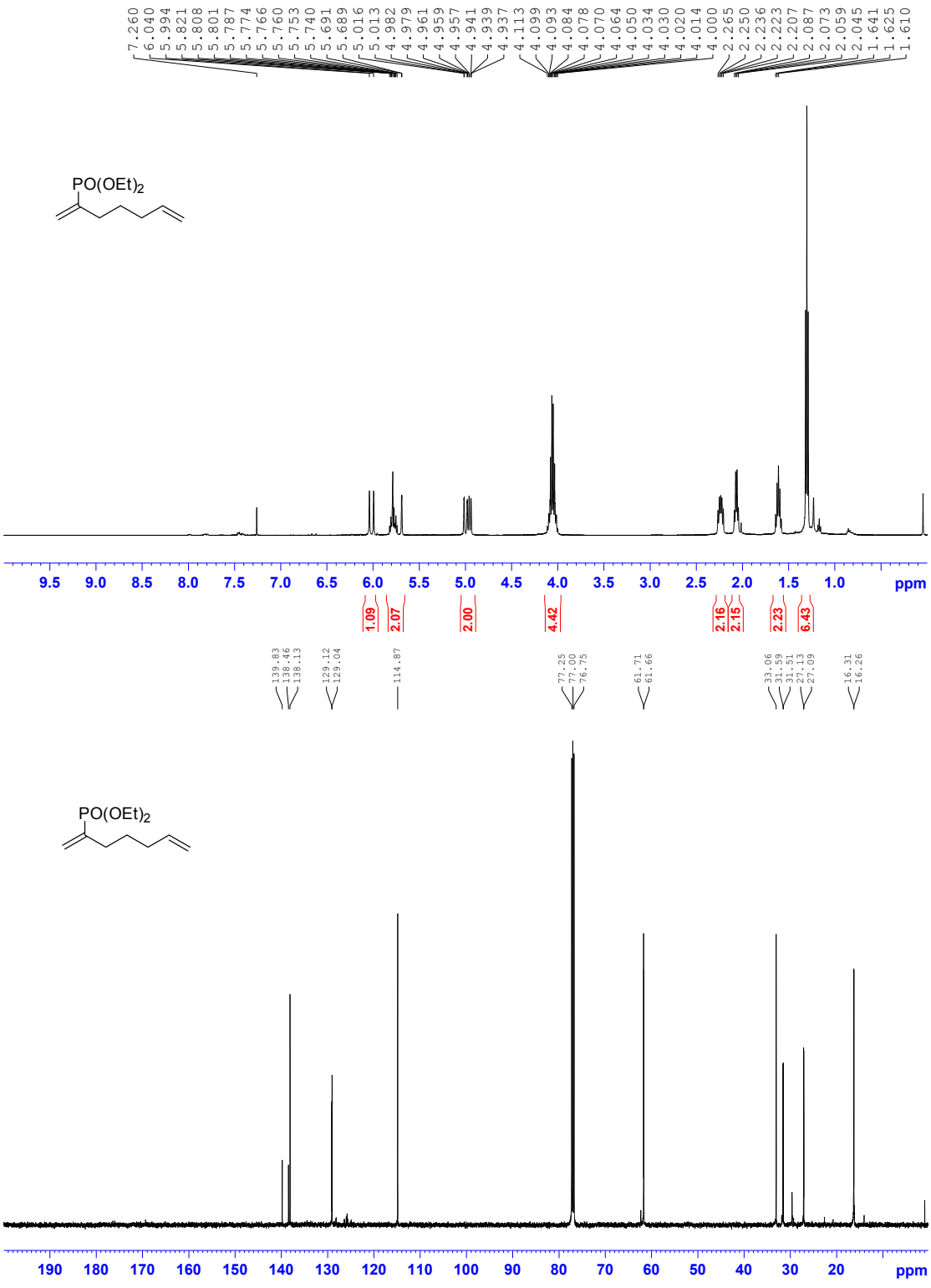

PO(OEt)2
Cl
(3l)
7.260
6.037
6.035
5.991
5.989
5.787
5.690
4.105
4.099
4.096
4.090
4.085
4.082
4.076
4.071
4.061
4.057
4.051
4.046
4.042
4.037
4.027
3.533
3.528
3.520
3.515
3.506
3.502
2.260
2.245
2.231
2.218
2.203
1.776
1.772
1.759
1.746
1.742
1.545
1.529
1.516
1.459
1.445
1.436
1.432
1.428
1.417
1.413
1.354
1.350
1.336
1.329
1.325
1.315
1.311
1.301
1.296
PO(OEt)2
Cl
9.5
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
ppm
1.00
1.01
3.94
2.01
2.03
2.10
2.03
2.25
8.30

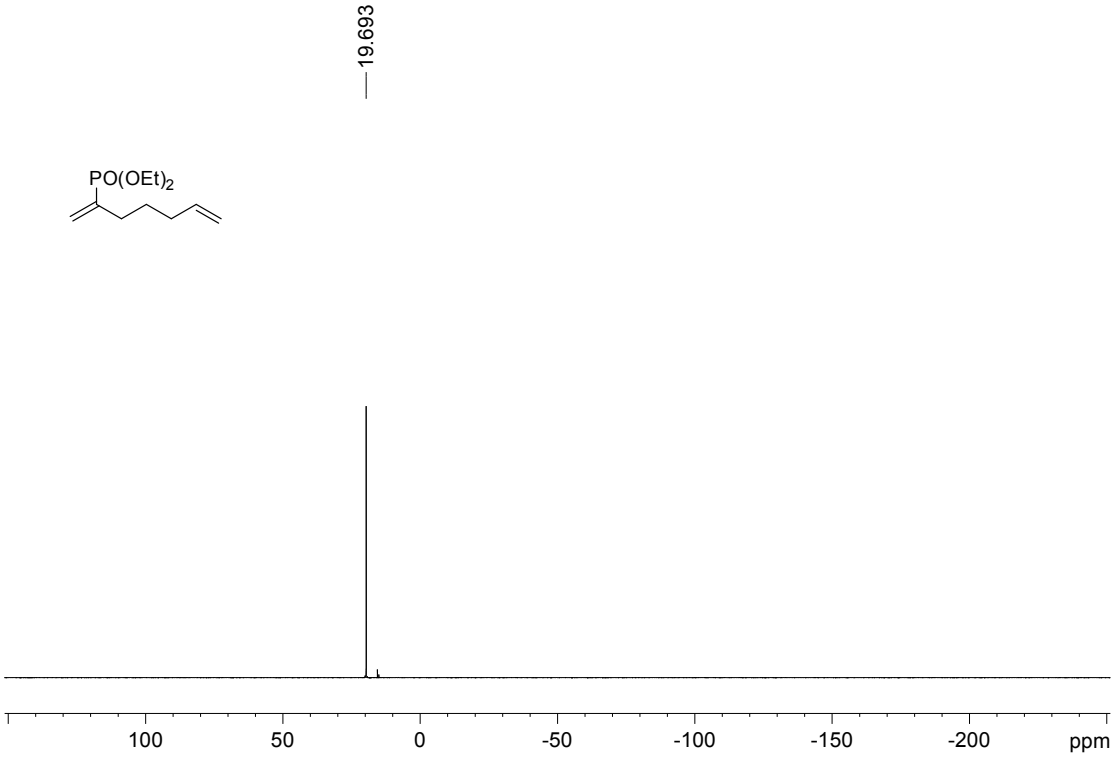

139.74
138.38
129.02
128.94
77.25
77.00
76.75
61.73
61.69
44.94
32.39
31.99
31.90
28.26
27.69
27.65
26.51
16.28
16.23
PO(OEt)2
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
19.988
19.951
19.915
19.880
19.843
19.808
19.778
19.744
19.710
19.673
19.640
19.603
19.567

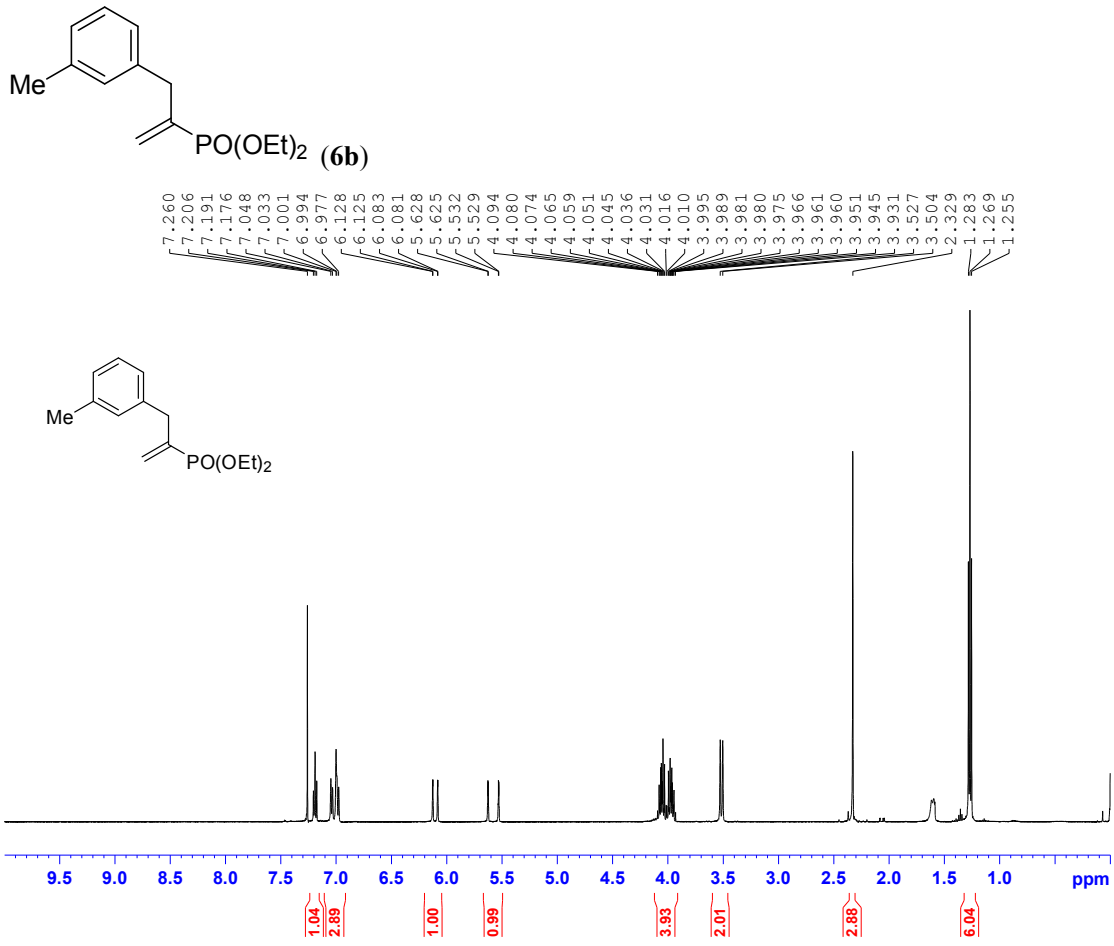

PO(OEt)2
Cl
100 50 0 -50 -100 -150 -200 ppm

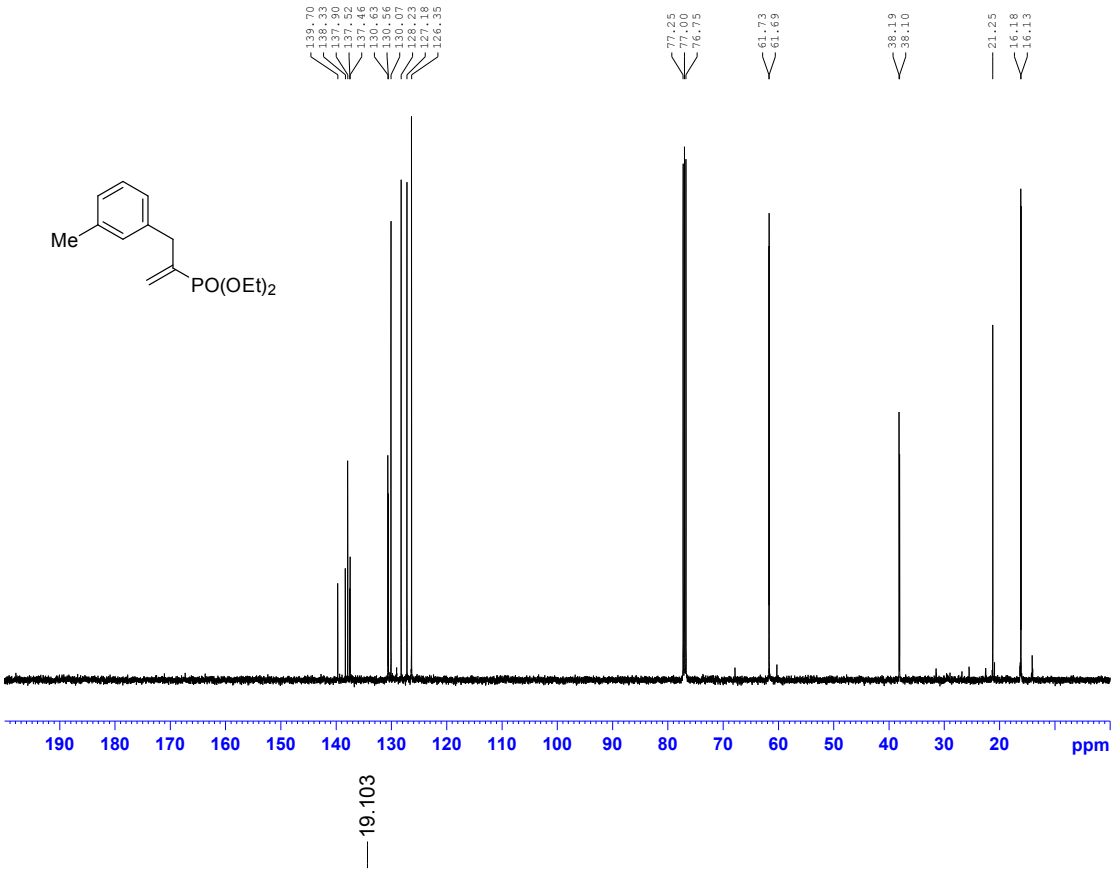

PO(OEt)2

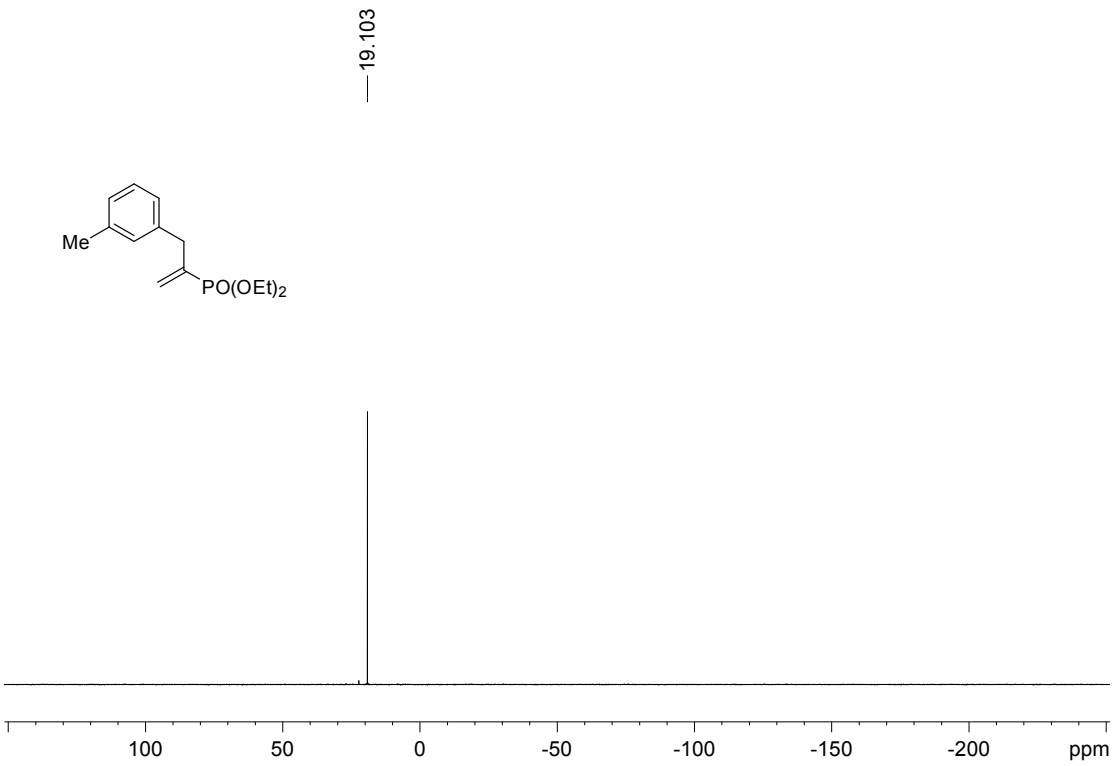
(3m)

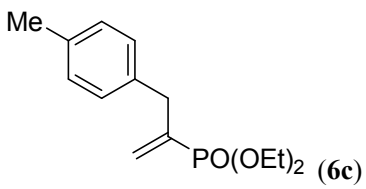

7.260
6.040
5.994
5.821
5.808
5.801
5.787
5.774
5.766
5.760
5.753
5.740
5.691
5.689
5.016
5.013
4.982
4.979
4.961
4.959
4.957
4.941
4.939
4.937
4.113
4.099
4.093
4.084
4.078
4.070
4.064
4.050
4.034
4.030
4.020
4.014
4.000
2.265
2.250
2.236
2.223
2.207
2.087
2.073
2.059
2.045
1.641
1.625
1.610
PO(OEt)2
9.5 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 ppm
1.09
2.07
2.00
4.42
2.16
2.15
2.23
6.43
139.83
138.46
138.13
129.12
129.04
114.87
77.25
77.00
76.75
61.71
61.66
33.06
31.59
31.51
27.13
27.09
16.31
16.26
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


19.693
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm

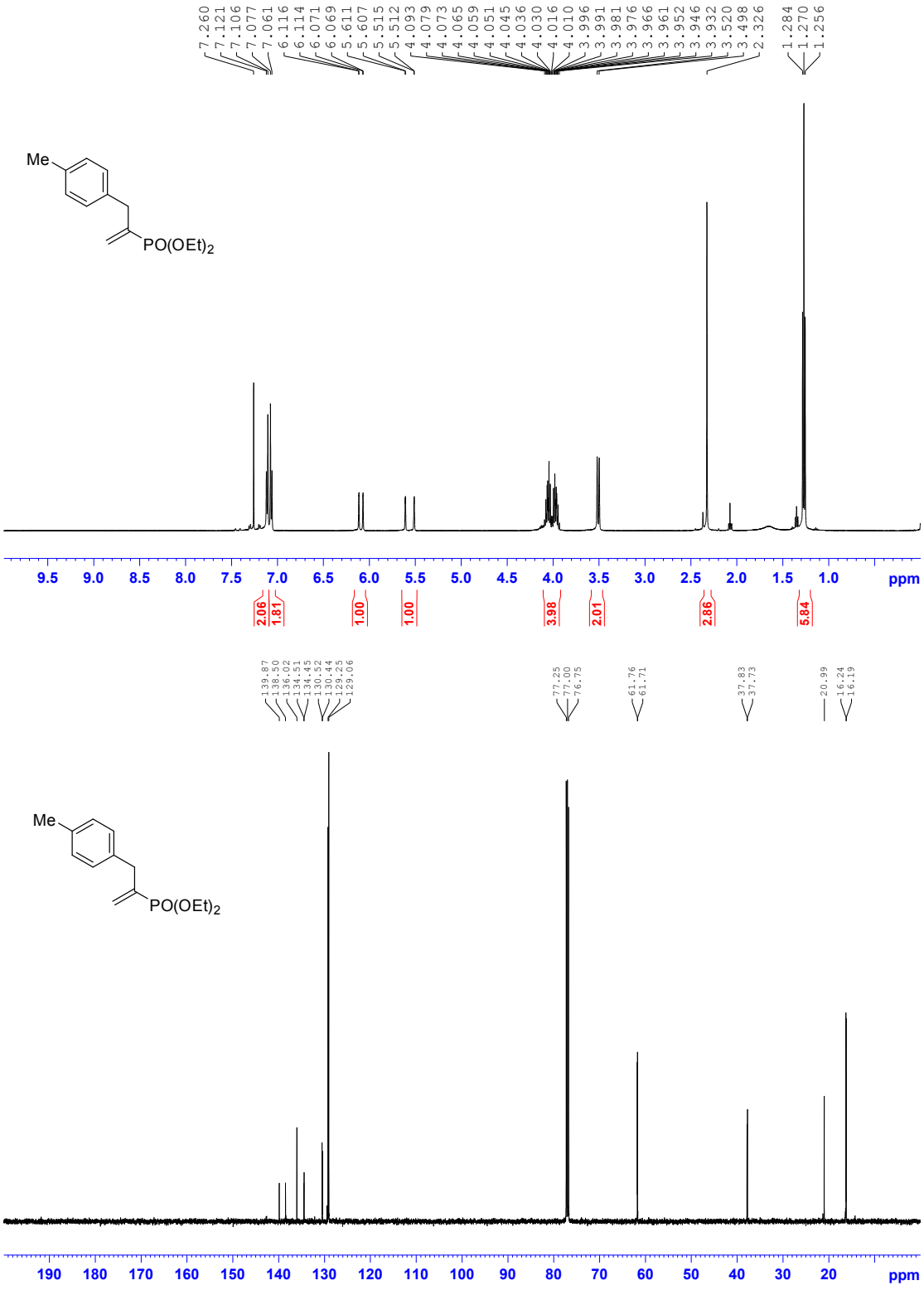

Me
PO(OEt)2
(6b)
7.260
7.206
7.191
7.176
7.048
7.033
7.001
6.994
6.977
6.128
6.125
6.083
6.081
5.628
5.625
5.532
5.529
4.094
4.080
4.074
4.065
4.059
4.051
4.045
4.036
4.031
4.016
4.010
3.995
3.989
3.981
3.980
3.975
3.966
3.961
3.960
3.951
3.945
3.931
3.527
3.504
2.329
1.283
1.269
1.255
Me
PO(OEt)2
9.5
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
ppm
1.04
2.89
1.00
0.99
3.93
2.01
2.88
6.04

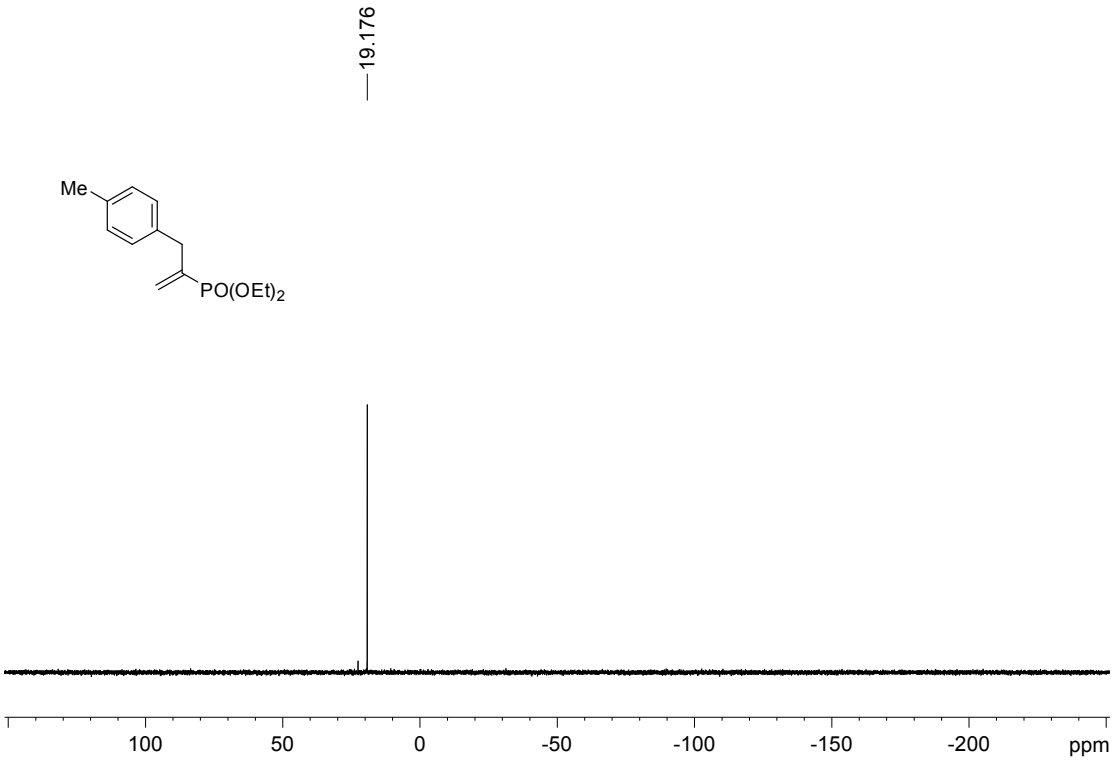

139.70
138.33
137.90
137.52
137.46
130.63
130.56
130.07
128.23
127.18
126.35
77.25
77.00
76.75
61.73
61.69
38.19
38.10
21.25
16.18
16.13
Me
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

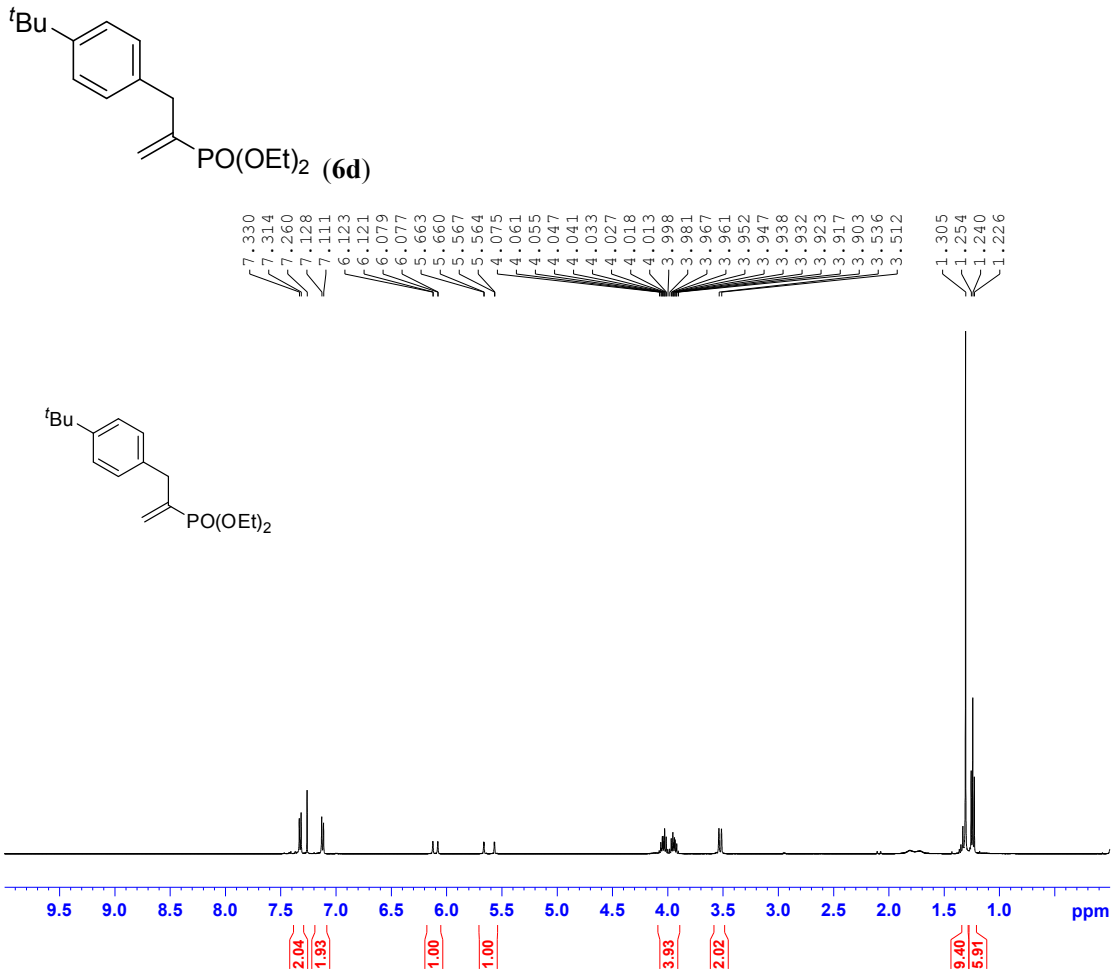

19.103
Me
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm

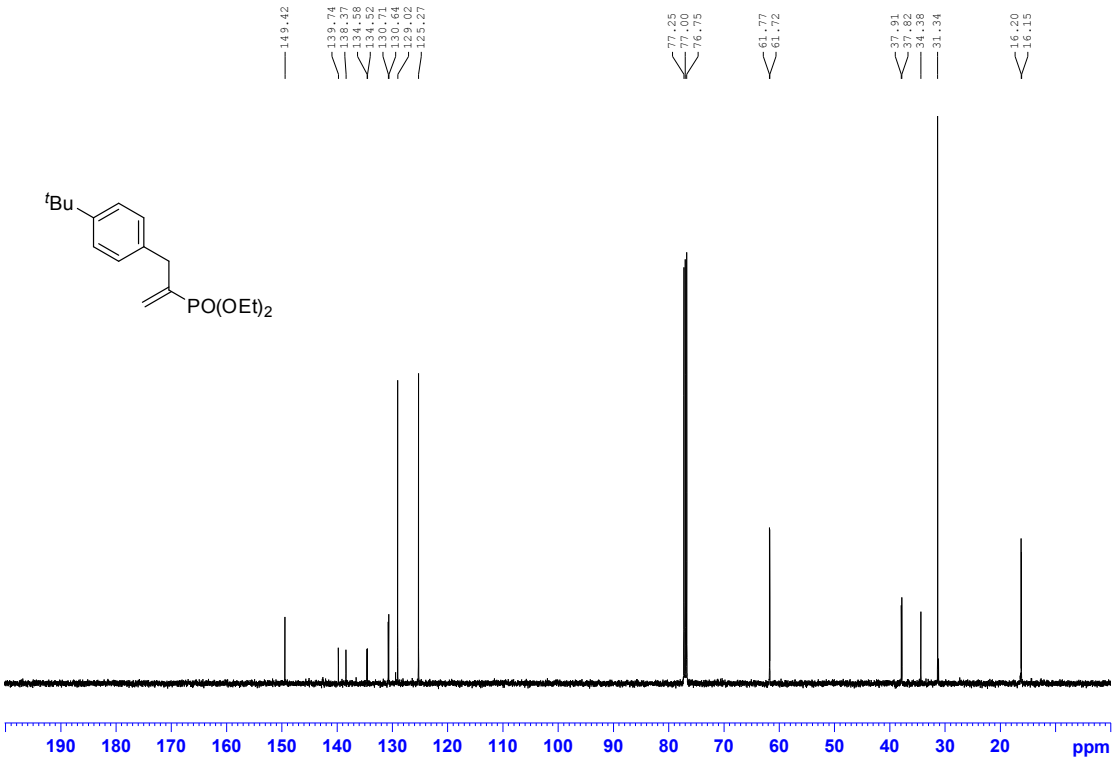

Me
PO(OEt)2

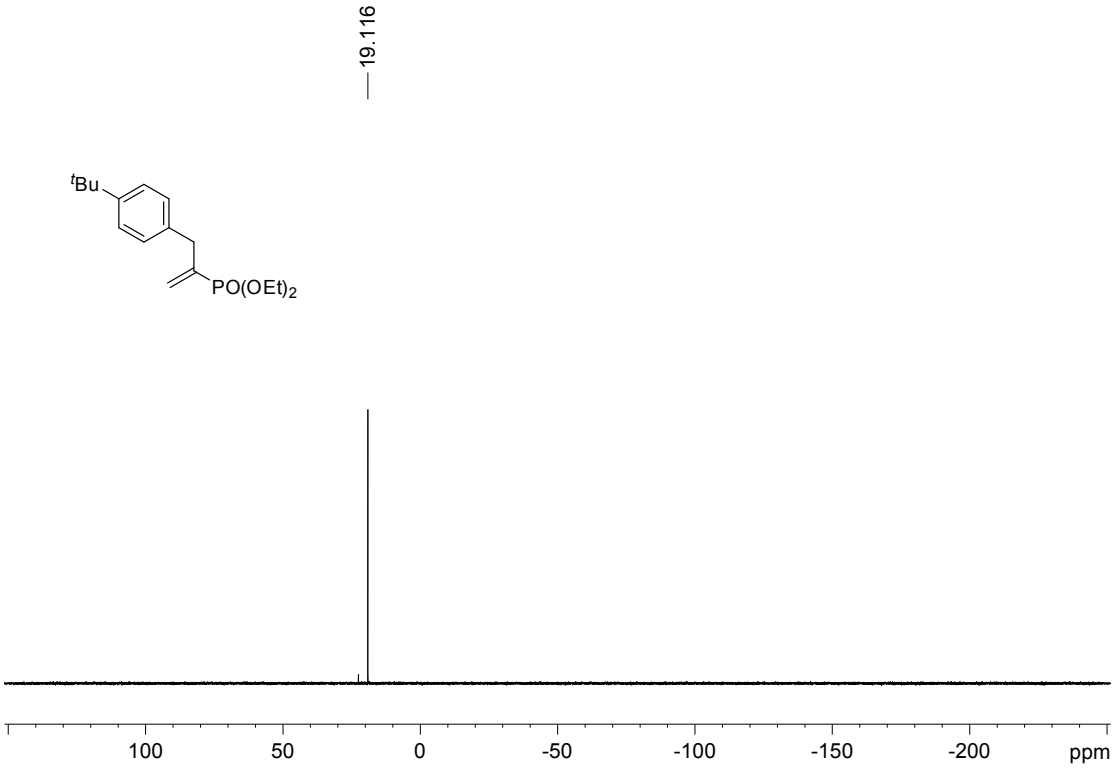
(6c)

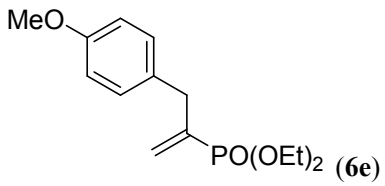

7.260
7.121
7.106
7.077
7.061
6.116
6.114
6.071
6.069
5.611
5.607
5.515
5.512
4.093
4.079
4.073
4.065
4.059
4.051
4.045
4.036
4.030
4.016
4.010
3.996
3.991
3.981
3.976
3.966
3.961
3.952
3.946
3.932
3.520
3.498
2.326
1.284
1.270
1.256
Me
PO(OEt)2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
1.81
1.00
1.00
3.98
2.01
2.86
5.84
139.87
138.50
136.02
134.51
134.45
130.52
130.44
129.25
129.06
77.25
77.00
76.75
61.76
61.71
37.83
37.73
20.99
16.24
16.19
Me
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


19.176
Me
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm

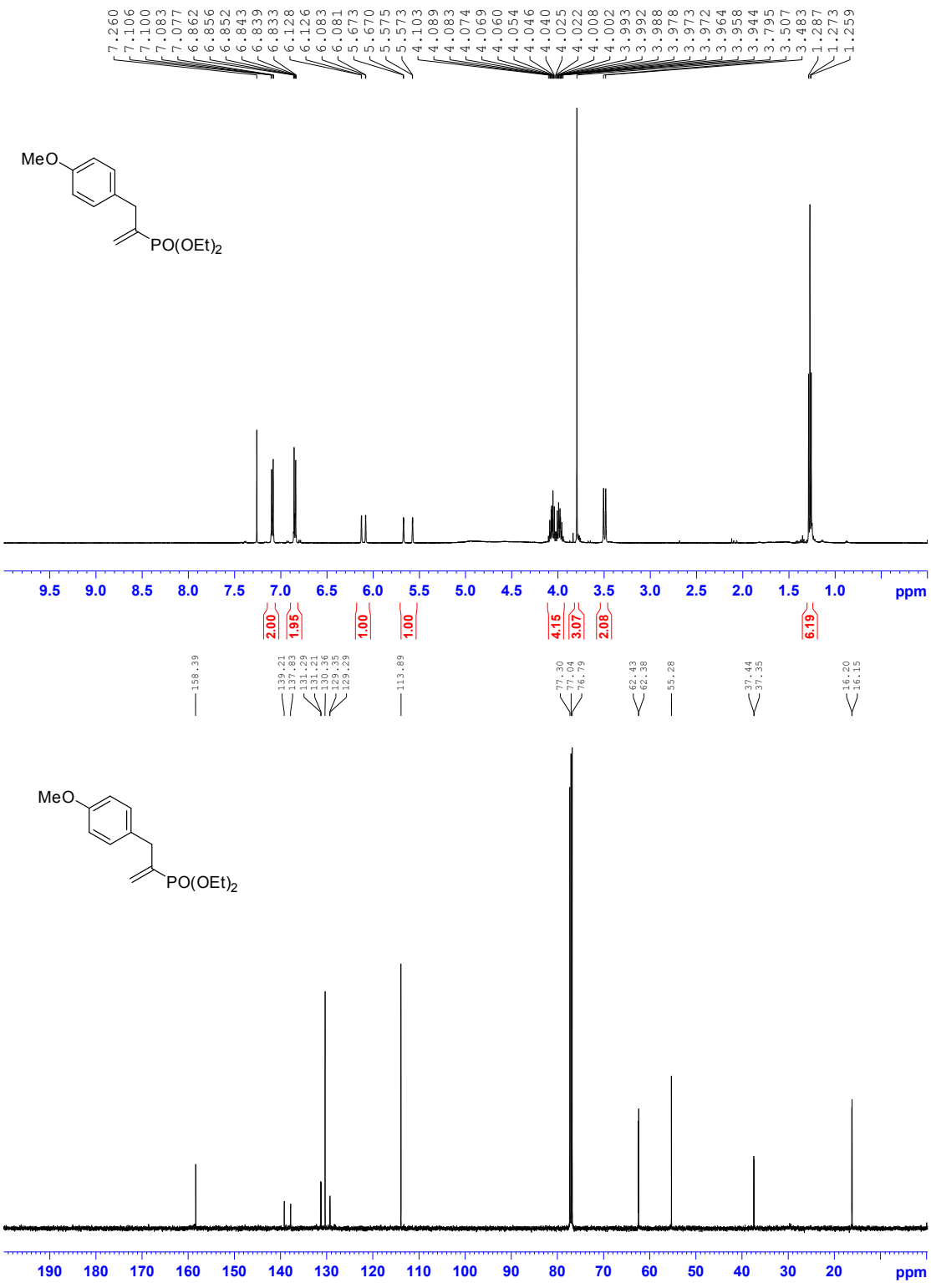

tBu
PO(OEt)2
(6d)
7.330
7.314
7.260
7.128
7.111
6.123
6.121
6.079
6.077
5.663
5.660
5.567
5.564
4.075
4.061
4.055
4.047
4.041
4.033
4.027
4.018
4.013
3.998
3.981
3.967
3.961
3.952
3.947
3.938
3.932
3.923
3.917
3.903
3.536
3.512
1.305
1.254
1.240
1.226
tBu
PO(OEt)2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.04
1.93
1.00
1.00
3.93
2.02
9.40
5.91

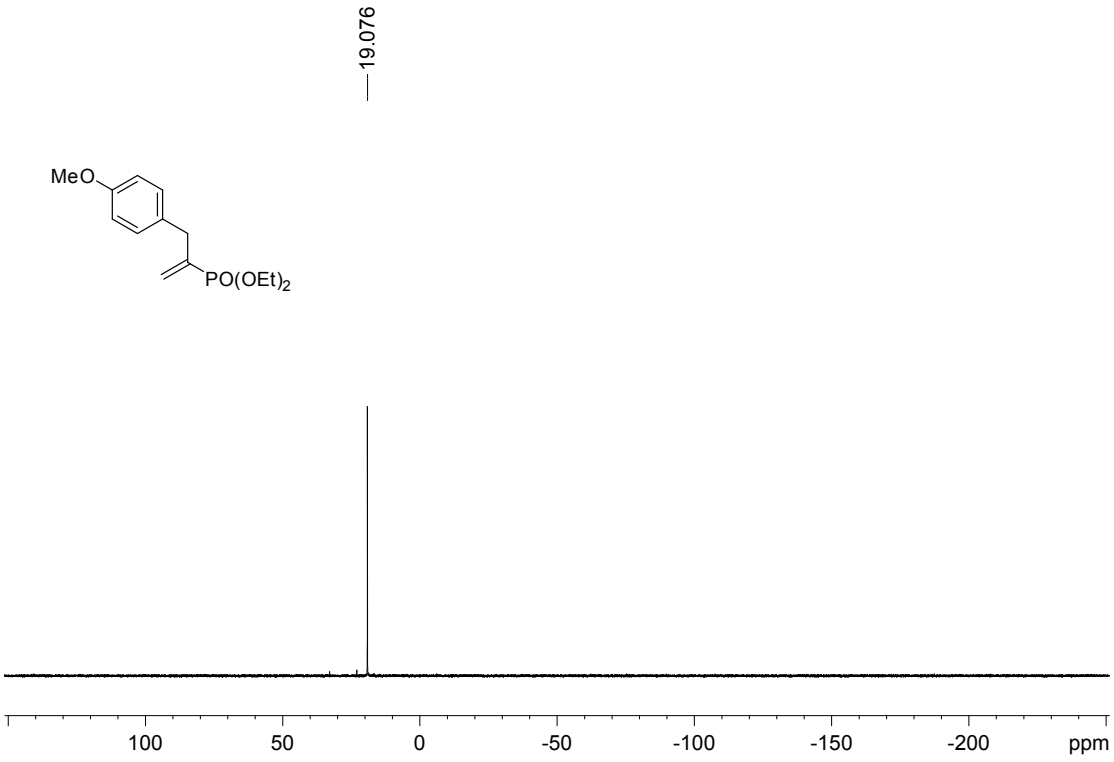

149.42
139.74
138.37
134.58
134.52
130.71
130.64
129.22
125.27
77.25
77.00
76.75
61.77
61.72
37.91
37.82
34.38
31.34
16.20
16.15
tBu
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

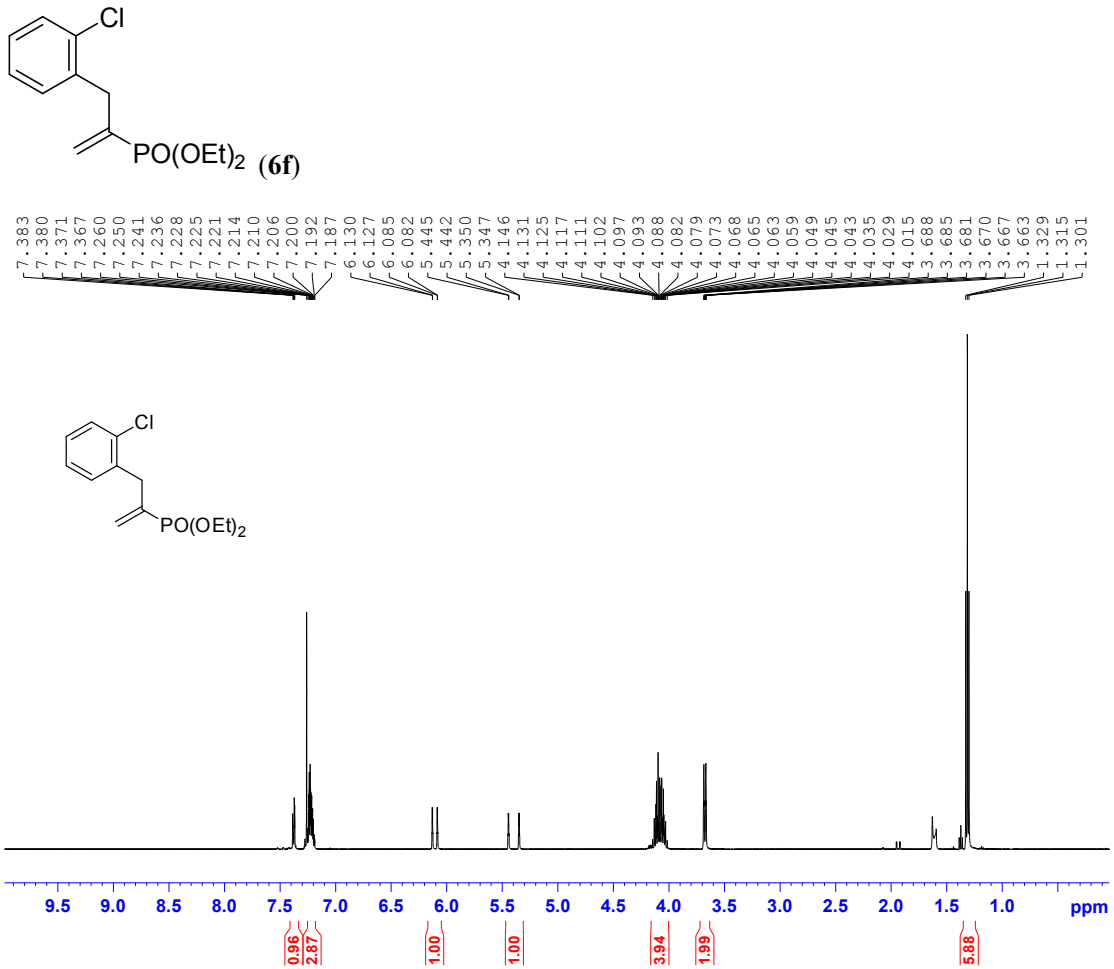

19.116
tBu
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm


MeO
PO(OEt)2

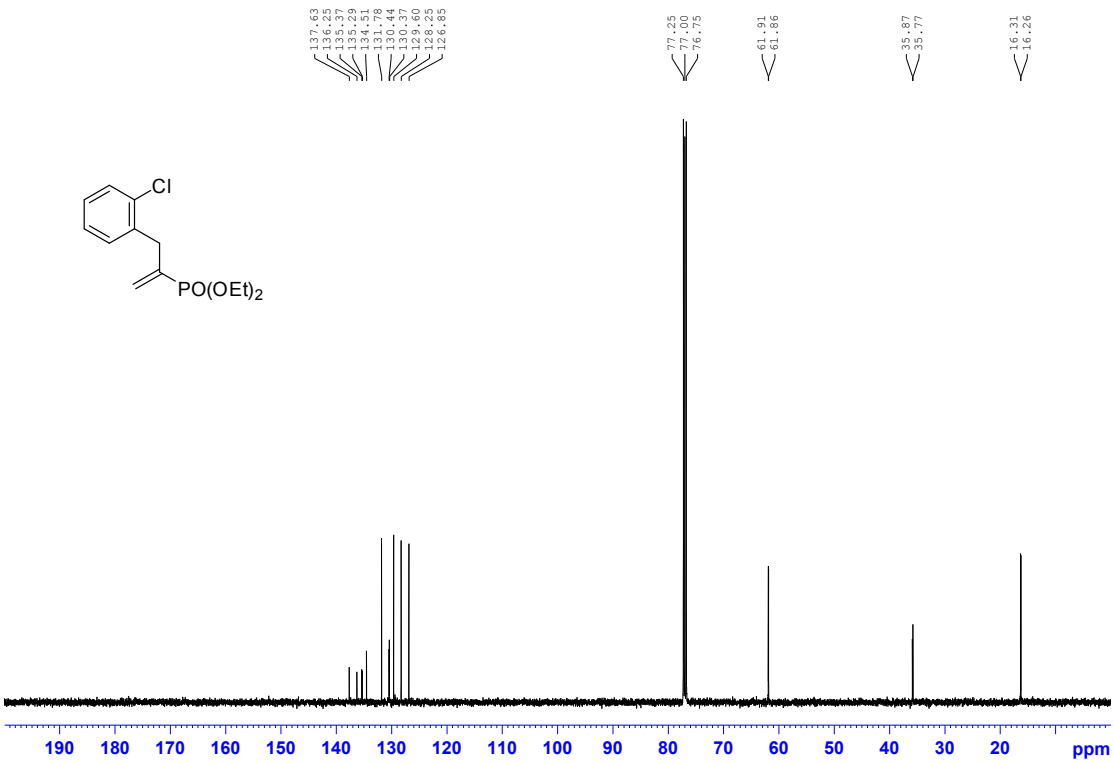
(6e)

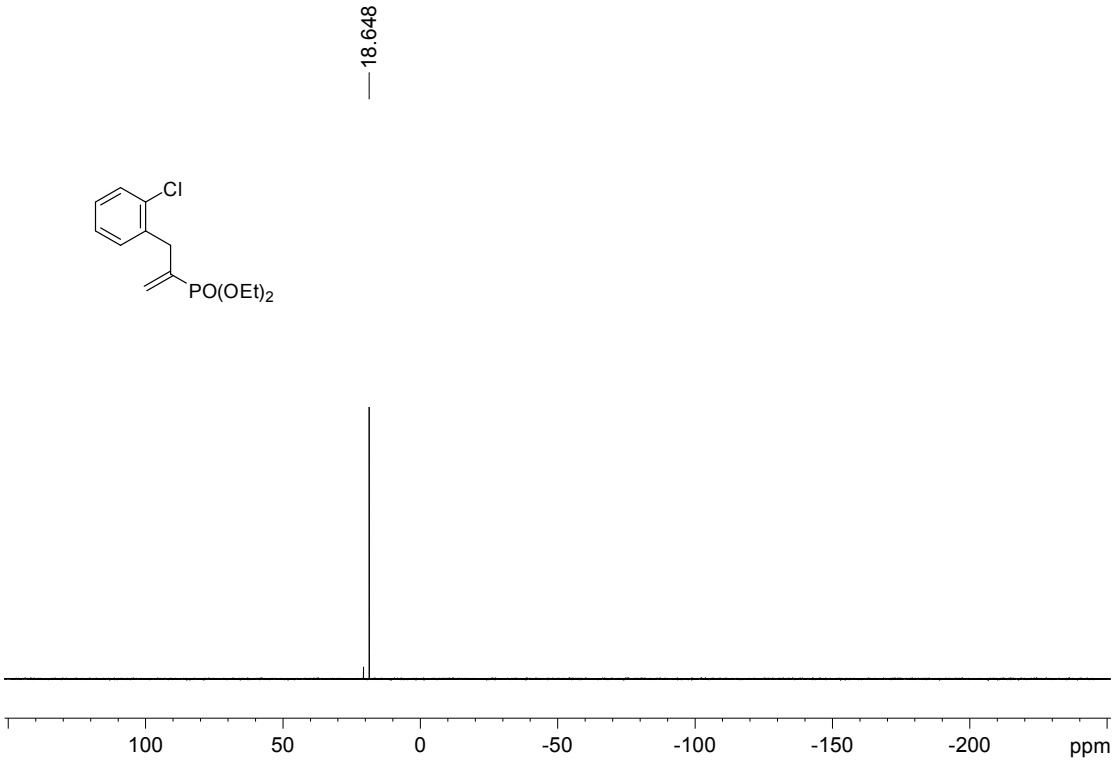

7.260
7.106
7.100
7.083
7.077
6.862
6.856
6.852
6.843
6.839
6.833
6.128
6.126
6.083
6.081
5.673
5.670
5.575
5.573
4.103
4.089
4.083
4.074
4.069
4.060
4.054
4.046
4.040
4.025
4.022
4.008
4.002
3.993
3.992
3.988
3.978
3.973
3.972
3.964
3.958
3.944
3.795
3.507
3.483
1.287
1.273
1.259
MeO
PO(OEt)2
9.5 9.0 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 ppm
2.00
1.95
1.00
1.00
4.15
3.07
2.08
6.19
158.39
139.21
137.83
131.29
131.21
130.36
129.35
129.29
113.89
77.30
77.04
76.79
62.43
62.38
55.28
37.44
37.35
16.20
16.15
MeO
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

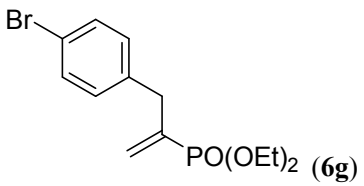

19.076
MeO
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm


Cl
PO(OEt)2
7.383
7.380
7.371
7.367
7.260
7.250
7.241
7.236
7.228
7.225
7.221
7.214
7.210
7.206
7.200
7.192
7.187
6.130
6.127
6.085
6.082
5.445
5.442
5.350
5.347
4.146
4.131
4.125
4.117
4.111
4.102
4.097
4.093
4.088
4.082
4.079
4.073
4.068
4.065
4.063
4.059
4.049
4.045
4.043
4.035
4.029
4.015
3.688
3.685
3.681
3.670
3.667
3.663
1.329
1.315
1.301
Cl
PO(OEt)2
9.5
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
ppm
0.96
2.87
1.00
1.00
3.94
1.99
5.88

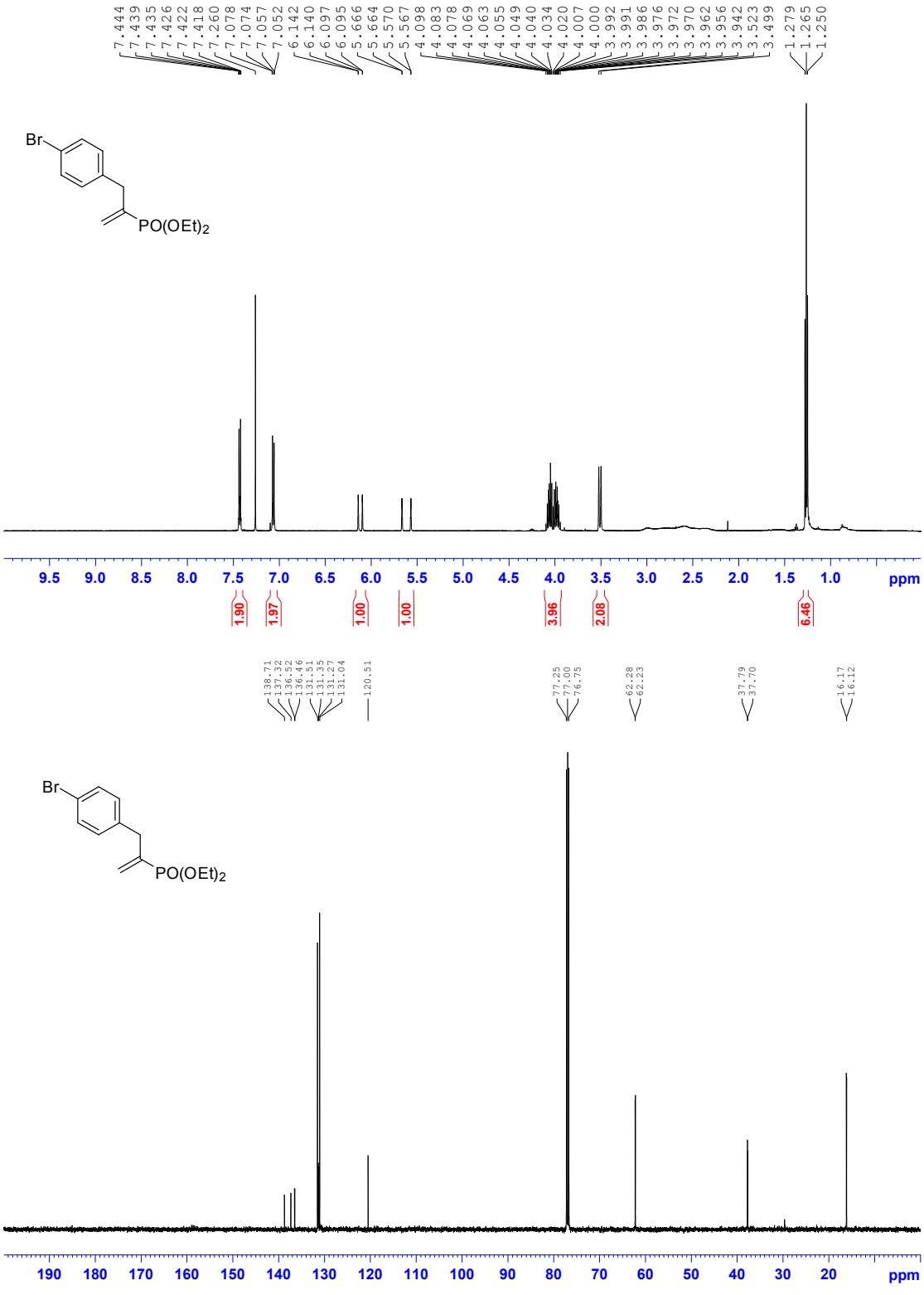
(6f)

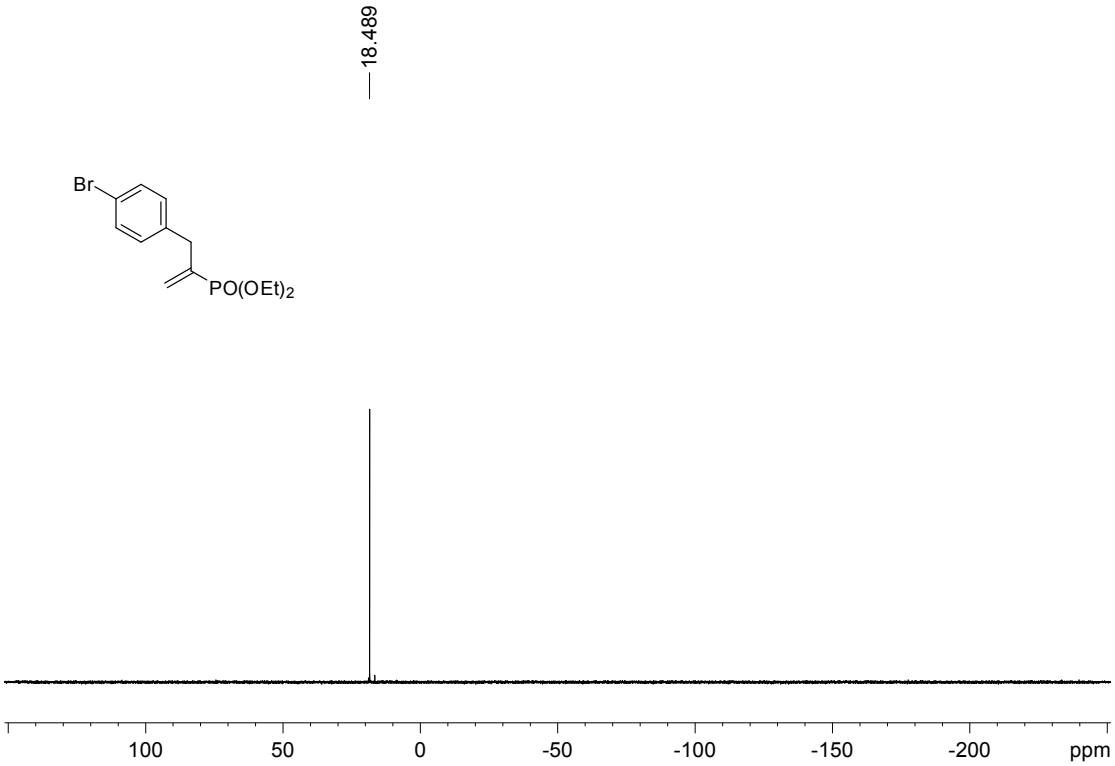

137.63
136.25
135.37
135.09
134.51
131.78
130.44
130.37
129.60
128.25
126.85
77.25
77.00
76.75
61.91
61.86
35.87
35.77
16.31
16.26
Cl
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

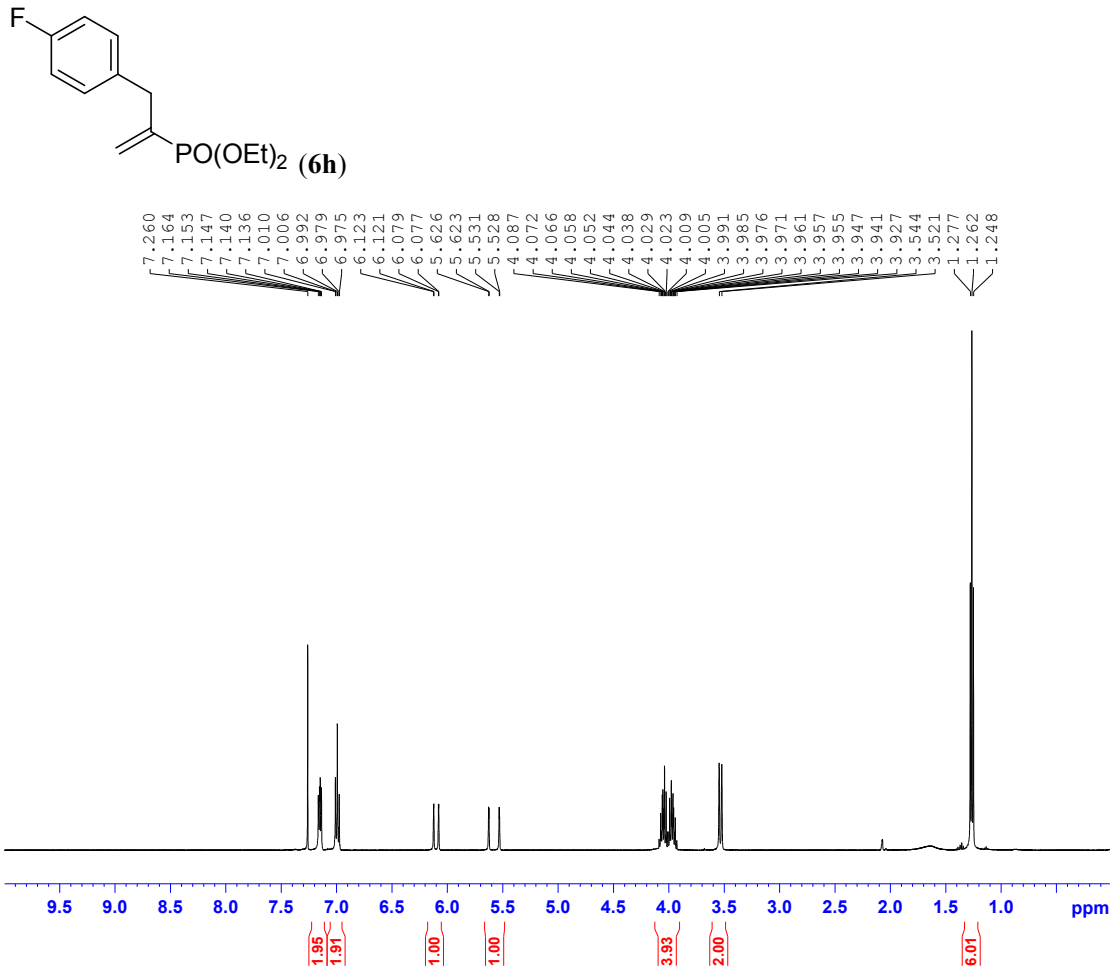

18.648
Cl
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm


Br
PO(OEt)2

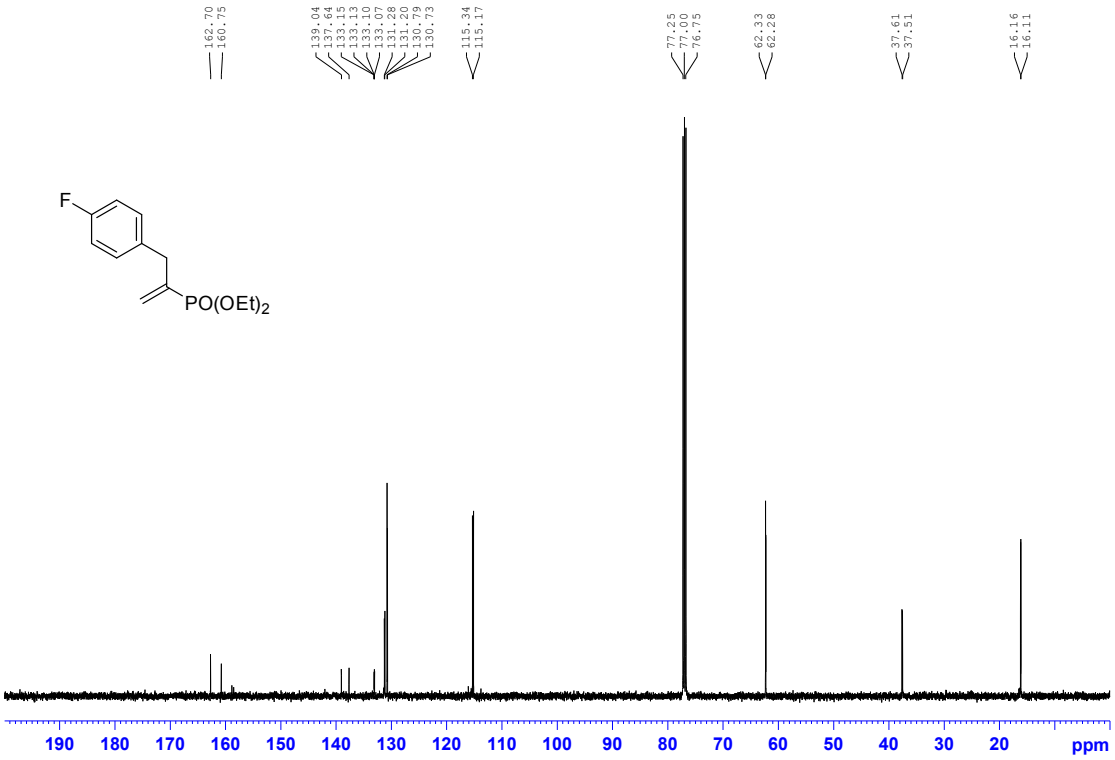
(6g)

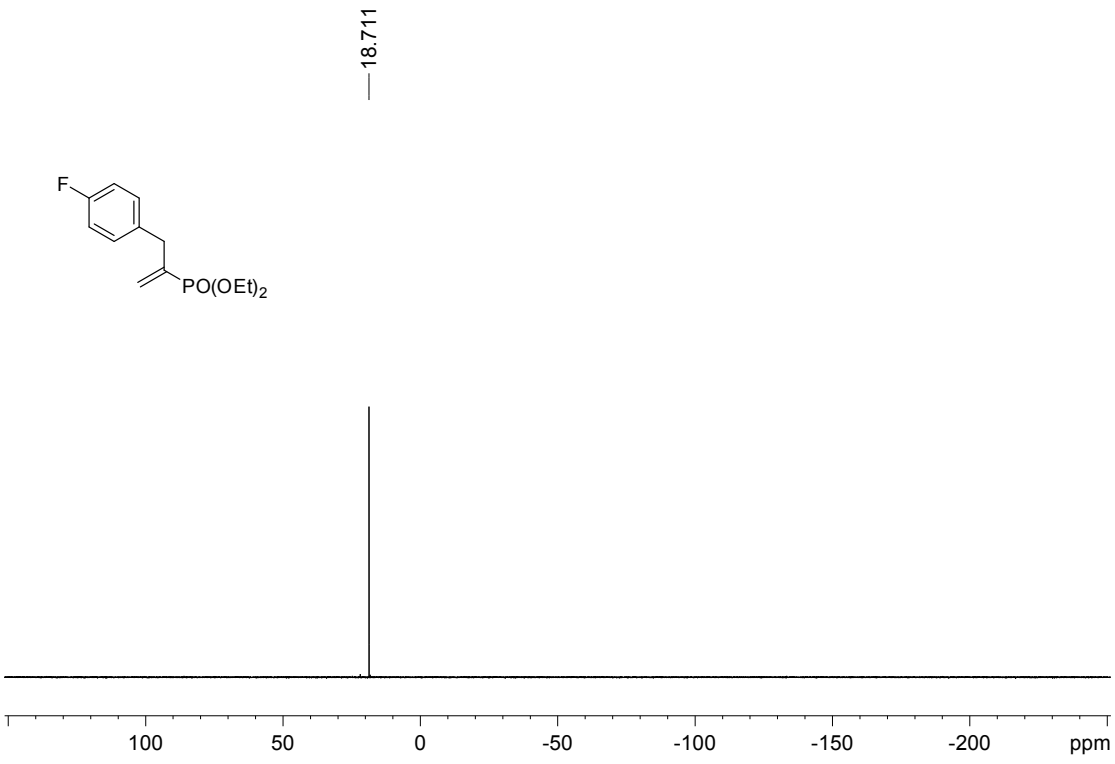

7.444
7.439
7.435
7.426
7.422
7.418
7.260
7.078
7.074
7.057
7.052
6.142
6.140
6.097
6.095
5.666
5.664
5.570
5.567
4.098
4.083
4.078
4.069
4.063
4.055
4.049
4.040
4.034
4.020
4.007
4.000
3.992
3.991
3.986
3.976
3.972
3.970
3.962
3.956
3.942
3.523
3.499
1.279
1.265
1.250
Br
PO(OEt)2
9.5 9.0 8.5 8.0 7.5 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 ppm
1.90
1.97
1.00
1.00
3.96
2.08
6.46
138.71
137.32
136.52
136.46
131.51
131.35
131.27
131.04
120.51
77.25
77.00
76.75
62.28
62.23
37.79
37.70
16.17
16.12
Br
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

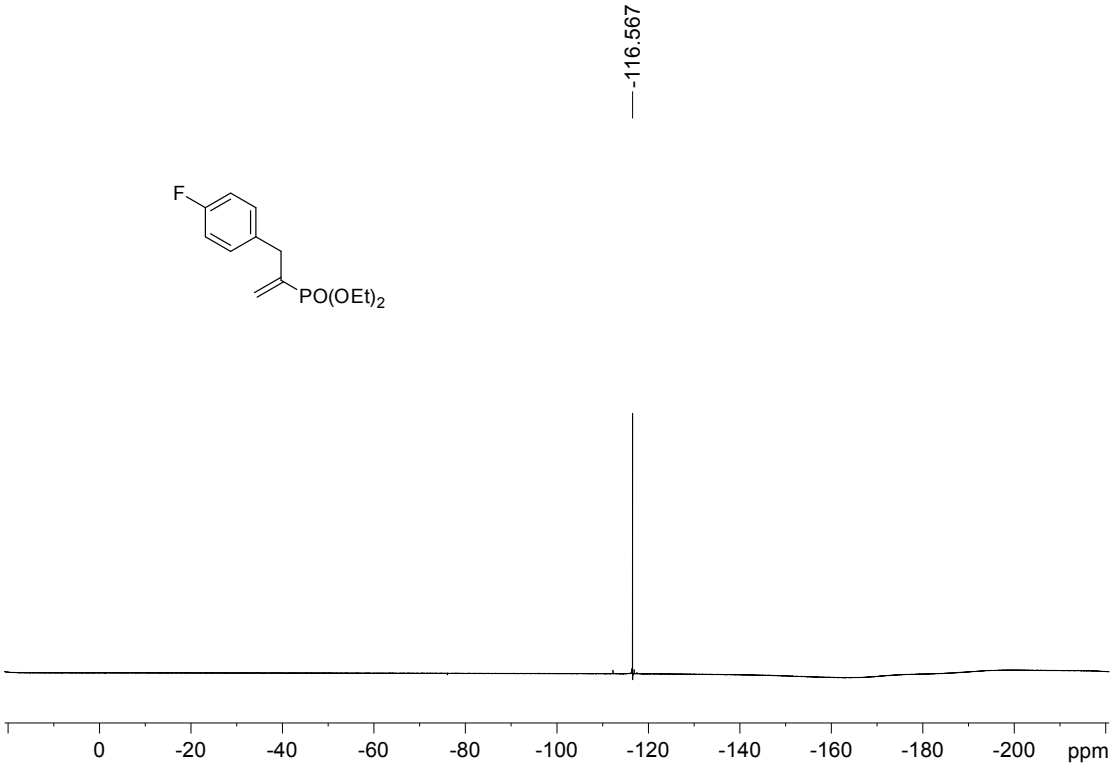

18.489
Br
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm

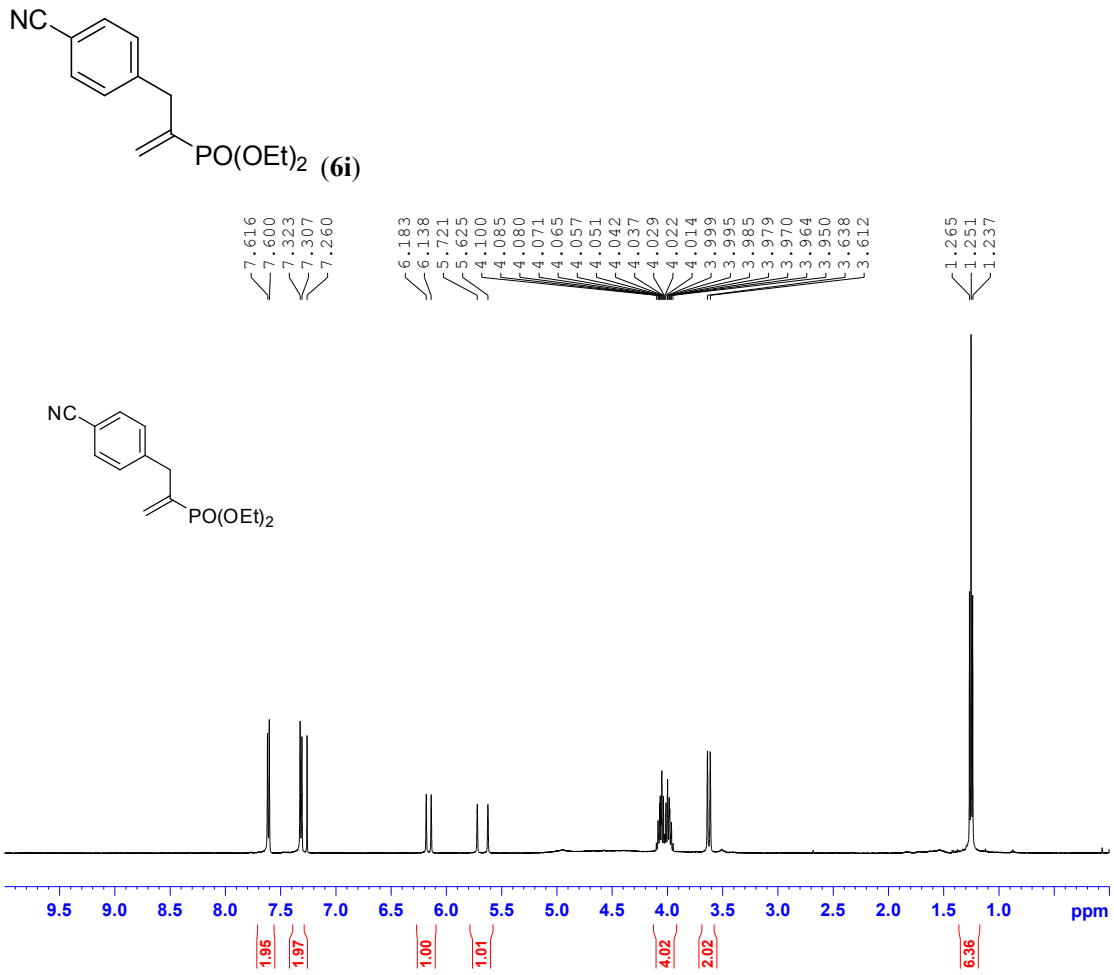

F
PO(OEt)2
7.260
7.164
7.153
7.147
7.140
7.136
7.010
7.006
6.992
6.979
6.975
6.123
6.121
6.079
6.077
5.626
5.623
5.531
5.528
4.087
4.072
4.066
4.058
4.052
4.044
4.038
4.029
4.023
4.009
4.005
3.991
3.985
3.976
3.971
3.961
3.957
3.955
3.947
3.941
3.927
3.544
3.521
1.277
1.262
1.248
9.5
9.0
8.5
8.0
7.5
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
ppm
1.95
1.91
1.00
1.00
3.93
2.00
6.01

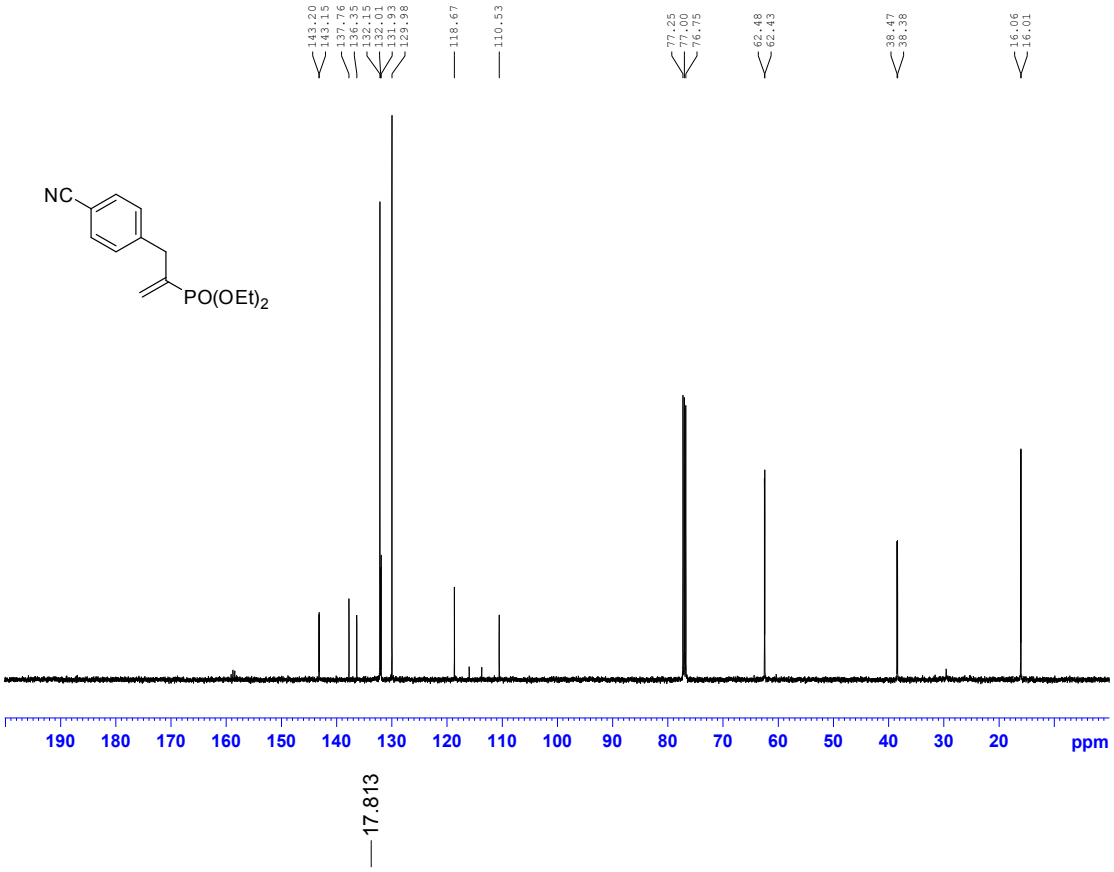
(6h)

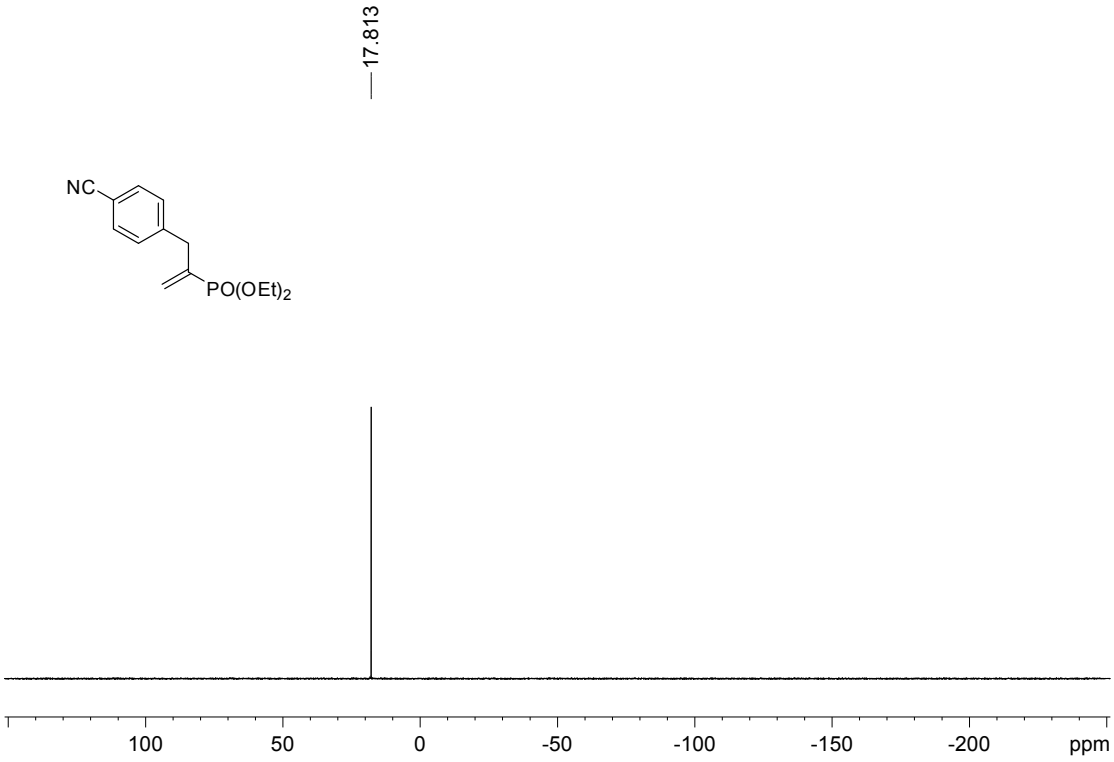

162.70
160.75
139.04
137.64
133.15
133.13
133.10
133.07
131.28
131.20
130.79
130.73
115.34
115.17
77.25
77.00
76.75
62.33
62.28
37.61
37.51
16.16
16.11
F
PO(OEt)2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

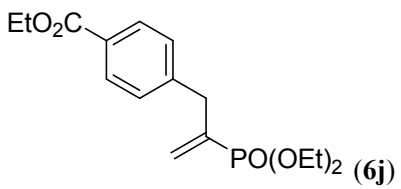

18.711
F
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm


-116.567
F
PO(OEt)2
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

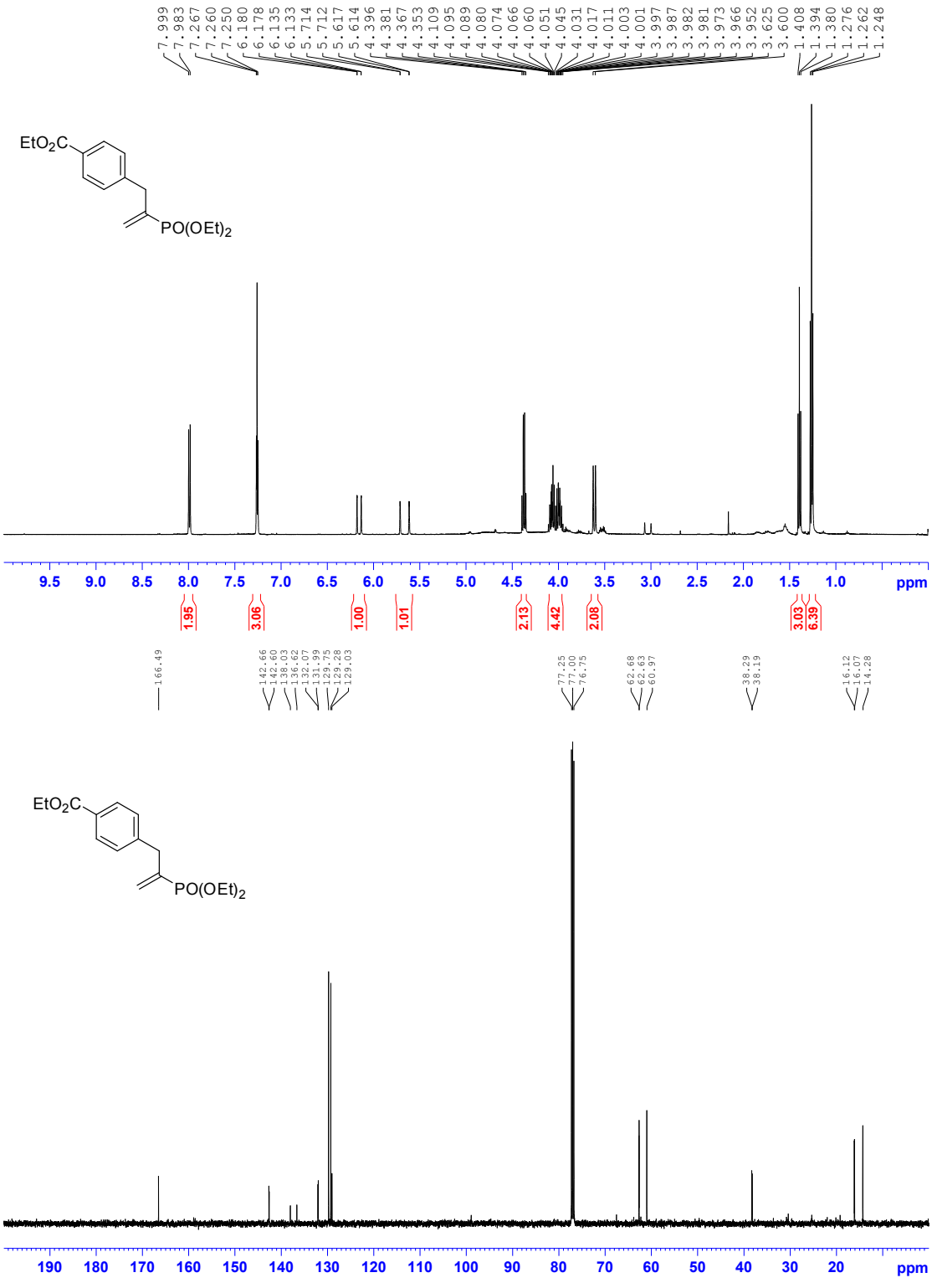

NC
PO(OEt)2
(6i)
7.616
7.600
7.323
7.307
7.260
6.183
6.138
5.721
5.625
4.100
4.085
4.080
4.071
4.065
4.057
4.051
4.042
4.037
4.029
4.022
4.014
3.999
3.995
3.985
3.979
3.970
3.964
3.950
3.638
3.612
1.265
1.251
1.237
NC
PO(OEt)2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.95
1.97
1.00
1.01
4.02
2.02
6.36

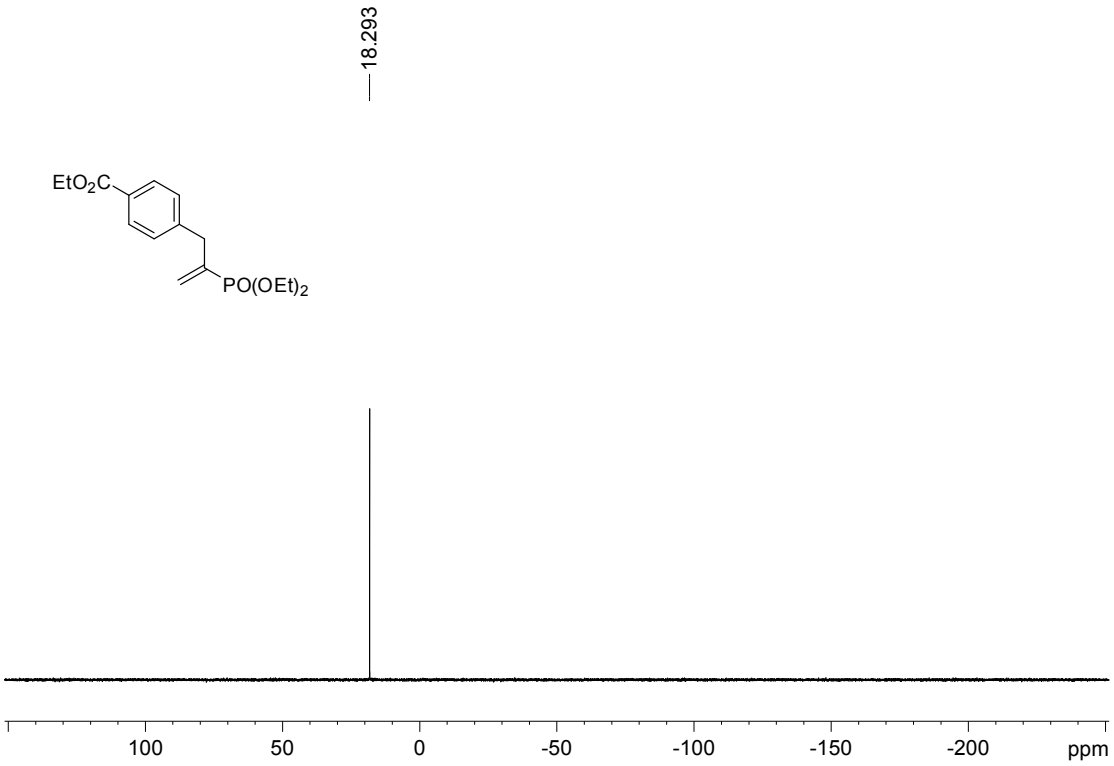

143.20
143.15
137.76
136.35
132.15
132.01
131.93
129.98
118.67
110.53
77.25
77.00
76.75
62.48
62.43
38.47
38.38
16.06
16.01
NC
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

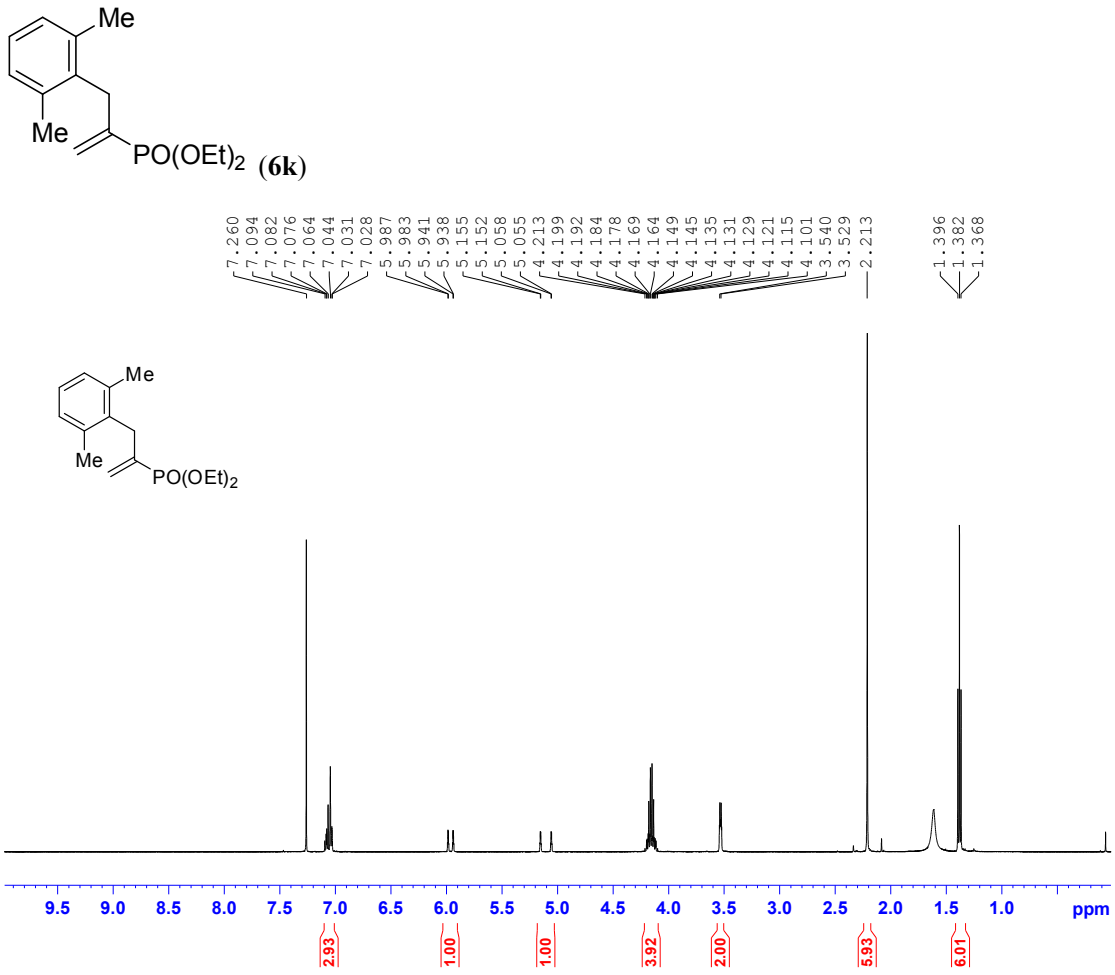

17.813
NC
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm


EtO2C
PO(OEt)2

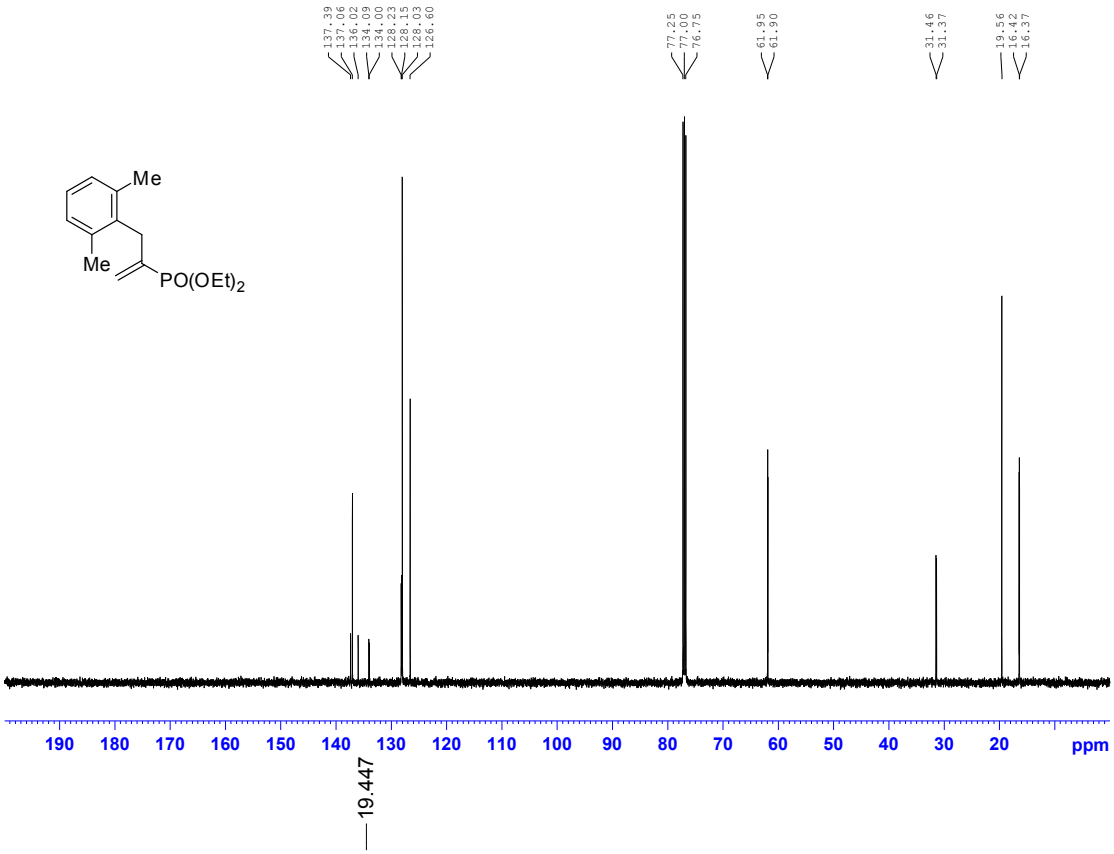
(6j)

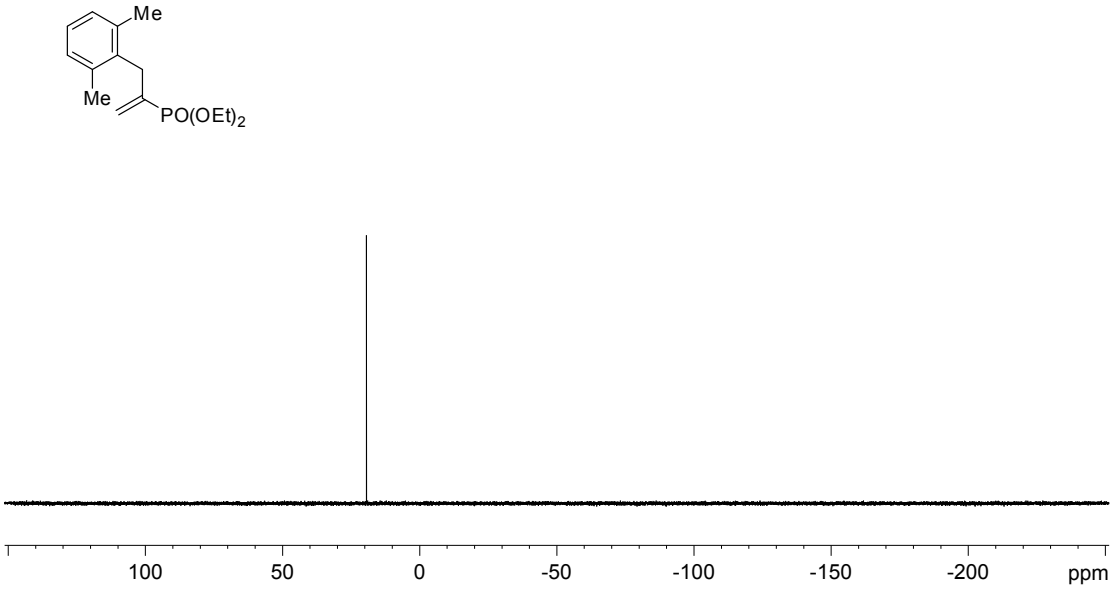

7.999
7.983
7.267
7.260
7.250
6.180
6.178
6.135
6.133
5.714
5.712
5.617
5.614
4.396
4.381
4.367
4.353
4.109
4.095
4.089
4.080
4.074
4.066
4.060
4.051
4.045
4.031
4.017
4.011
4.003
4.001
3.997
3.987
3.982
3.981
3.973
3.966
3.952
3.625
3.600
1.408
1.394
1.380
1.276
1.262
1.248
EtO2C
PO(OEt)2
9.5 9.0 8.5 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 ppm
1.95
3.06
1.00
1.01
2.13
4.42
2.08
3.03
6.39
166.49
142.66
142.60
138.03
136.62
132.07
131.99
129.75
129.28
129.03
77.25
77.00
76.75
62.68
62.63
60.97
38.29
38.19
16.12
16.07
14.28
EtO2C
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

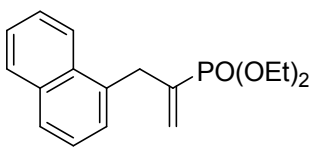

18.293
EtO2C
PO(OEt)2
100
50
0
-50
-100
-150
-200
ppm


Me
Me
PO(OEt)2
7.260
7.094
7.082
7.076
7.064
7.044
7.031
7.028
5.987
5.983
5.941
5.938
5.155
5.152
5.058
5.055
4.213
4.199
4.192
4.184
4.178
4.169
4.164
4.149
4.145
4.135
4.131
4.129
4.121
4.115
4.101
3.540
3.529
2.213
1.396
1.382
1.368
9.5
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
ppm
2.93
1.00
1.00
3.92
2.00
5.93
6.01

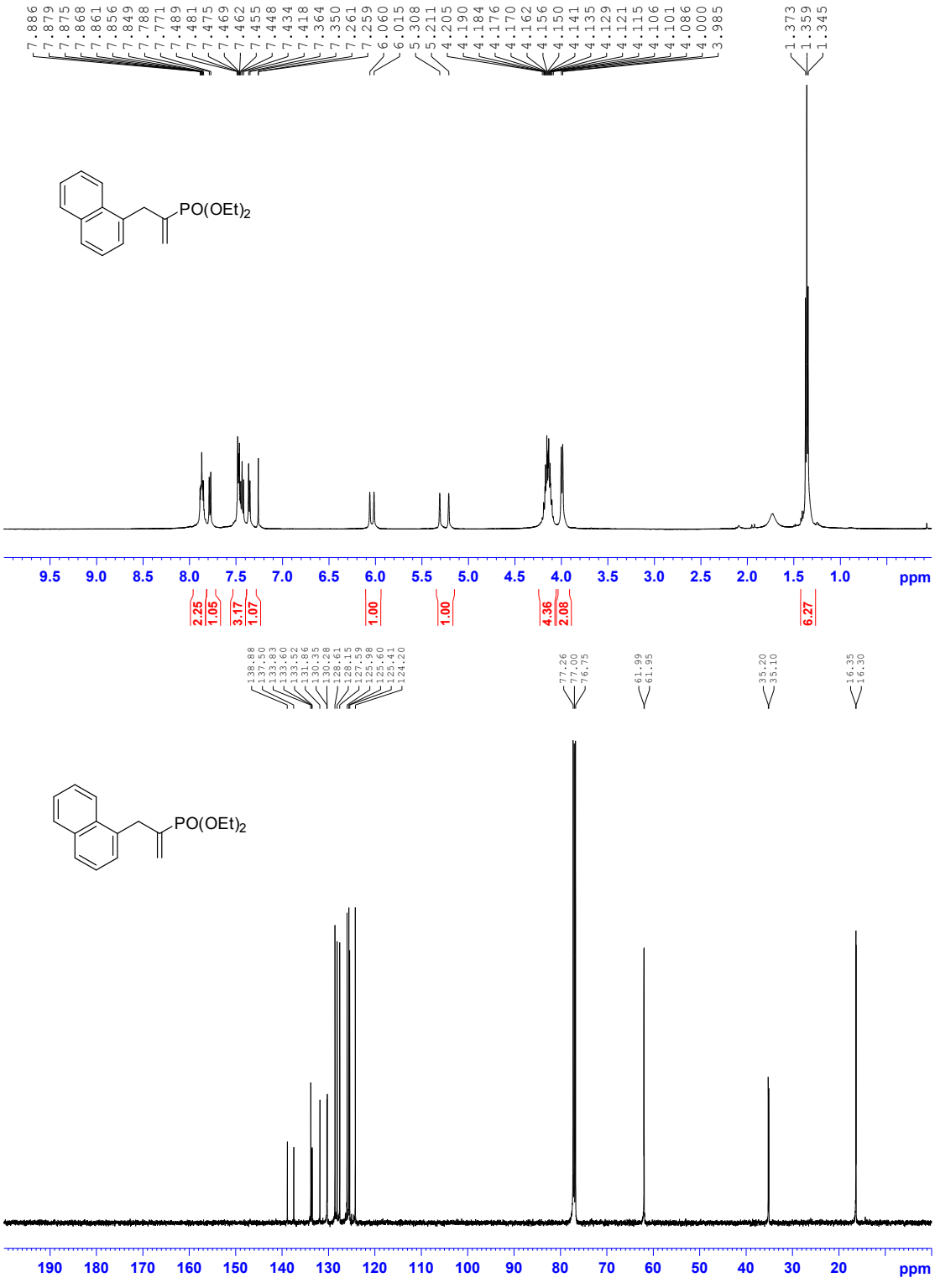
(6k)

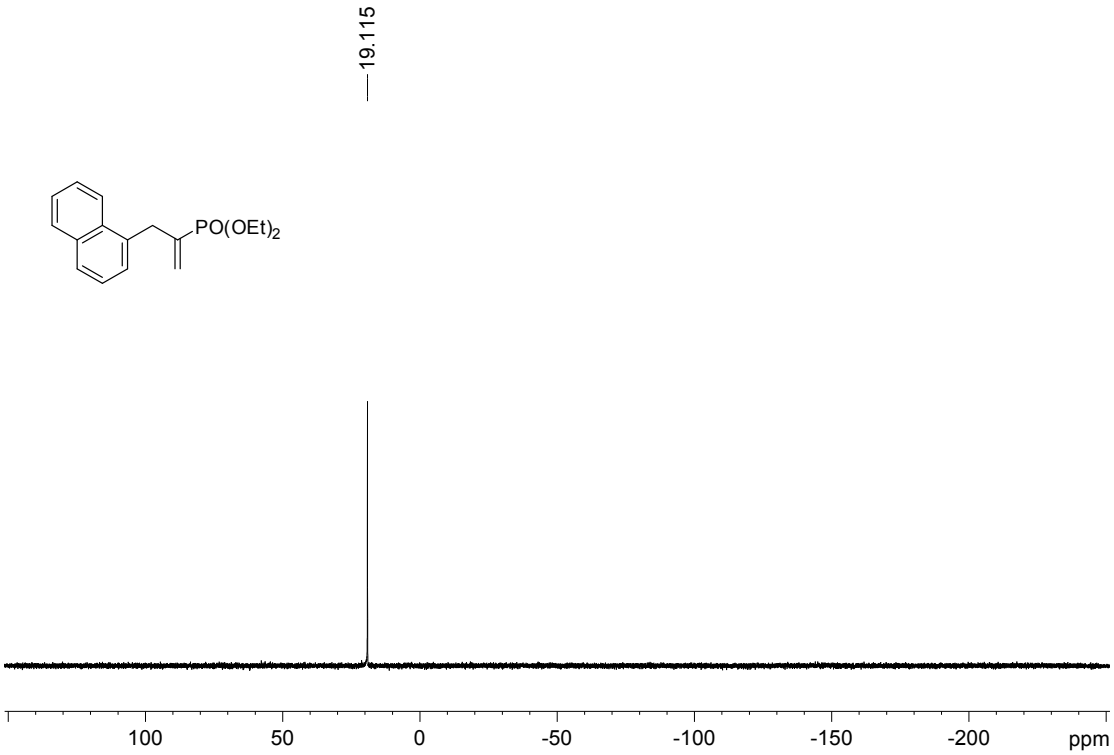

137.39
137.06
136.02
134.09
134.00
128.23
128.15
128.03
126.60
77.25
77.00
76.75
61.95
61.90
31.46
31.37
19.56
16.42
16.37
Me
Me
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
19.447


Me
Me
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm


PO(OEt)2

(**6l**)

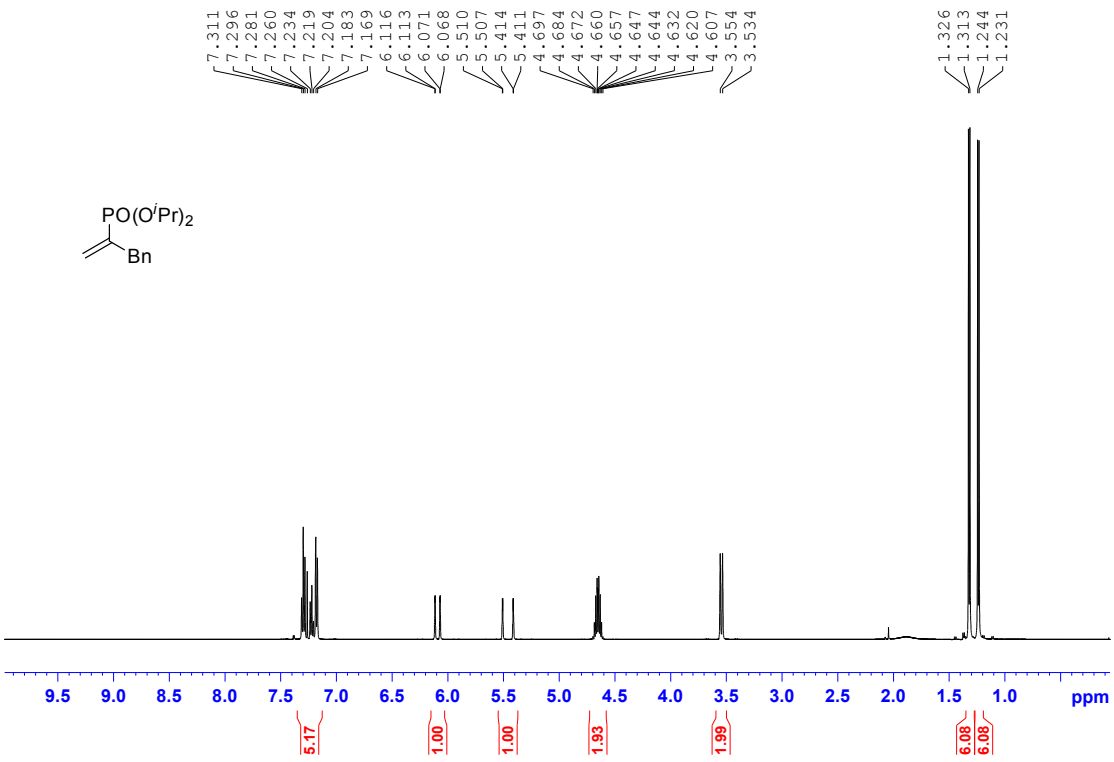

7.886
7.879
7.875
7.868
7.861
7.856
7.849
7.788
7.771
7.489
7.481
7.475
7.469
7.462
7.455
7.448
7.434
7.418
7.364
7.350
7.261
7.259
6.060
6.015
5.308
5.211
4.205
4.190
4.184
4.176
4.170
4.162
4.156
4.150
4.141
4.135
4.129
4.121
4.115
4.106
4.101
4.086
4.000
3.985
1.373
1.359
1.345
PO(OEt)2
9.5 9.0 8.5 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 ppm
2.25
1.05
3.17
1.07
1.00
1.00
4.36
2.08
6.27
138.88
137.50
133.83
133.60
133.52
131.86
130.35
130.28
128.61
128.15
127.59
125.98
125.60
125.41
124.20
77.26
77.00
76.75
61.99
61.95
35.20
35.10
16.35
16.30
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

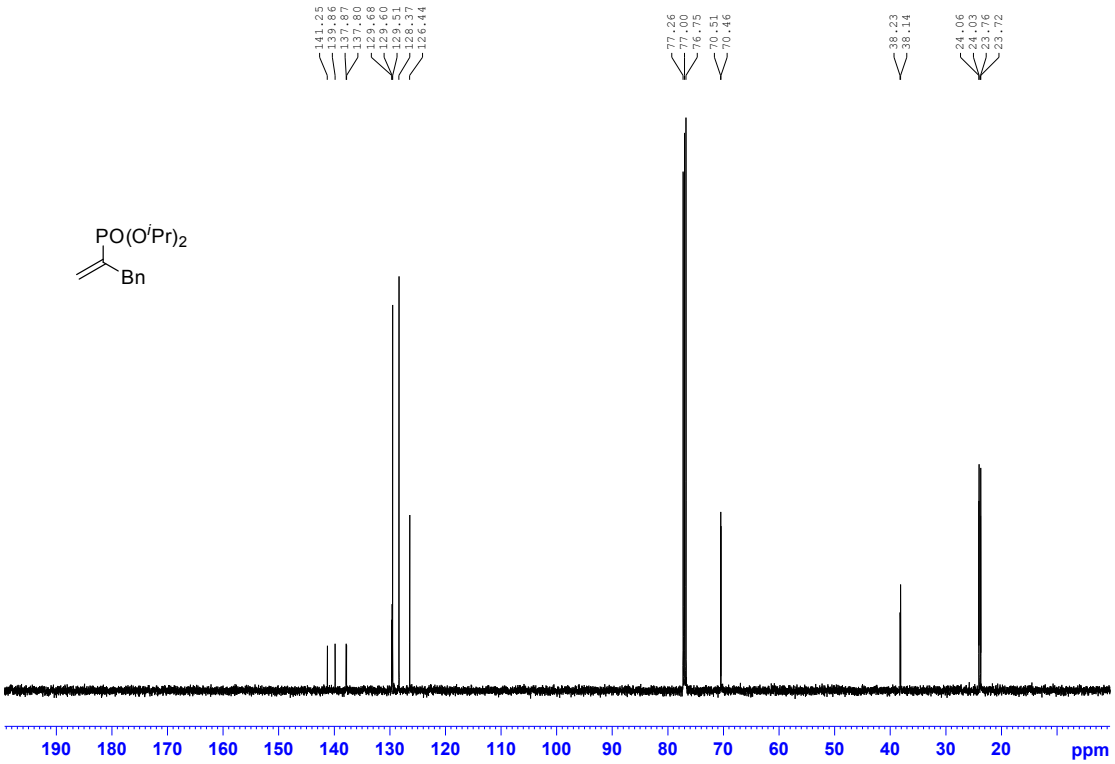


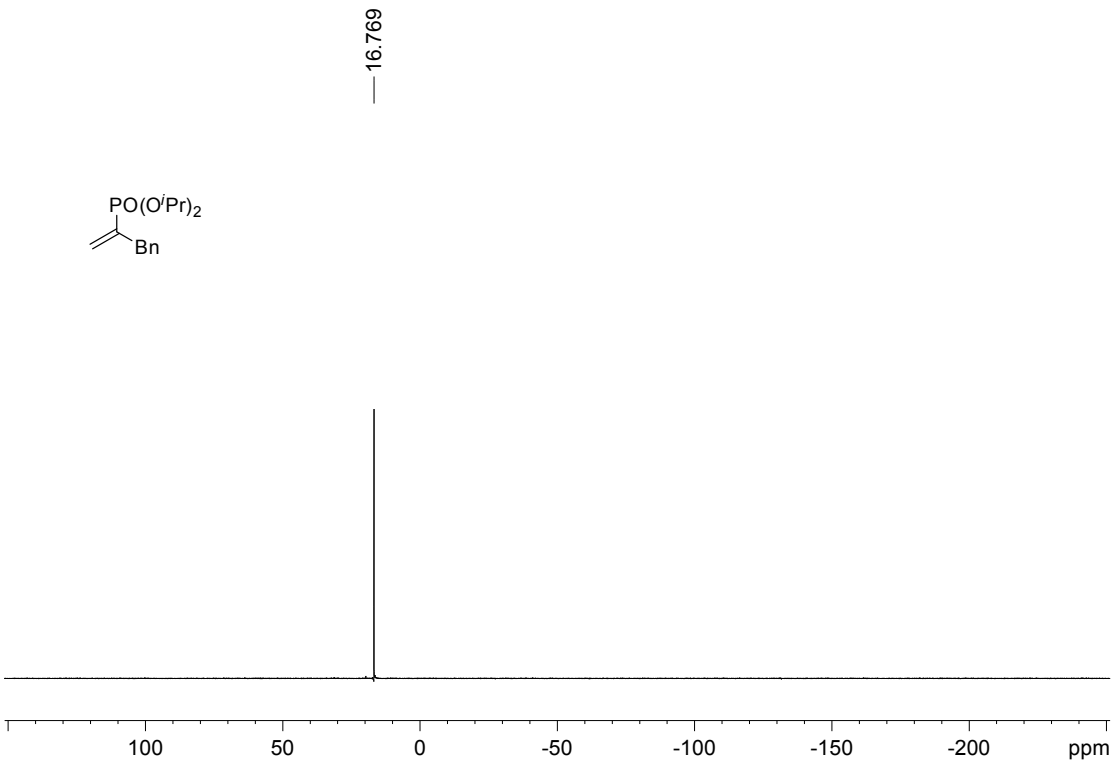
PO(O*i*-Pr)$_2$

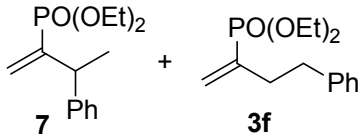
Bn

(6m)

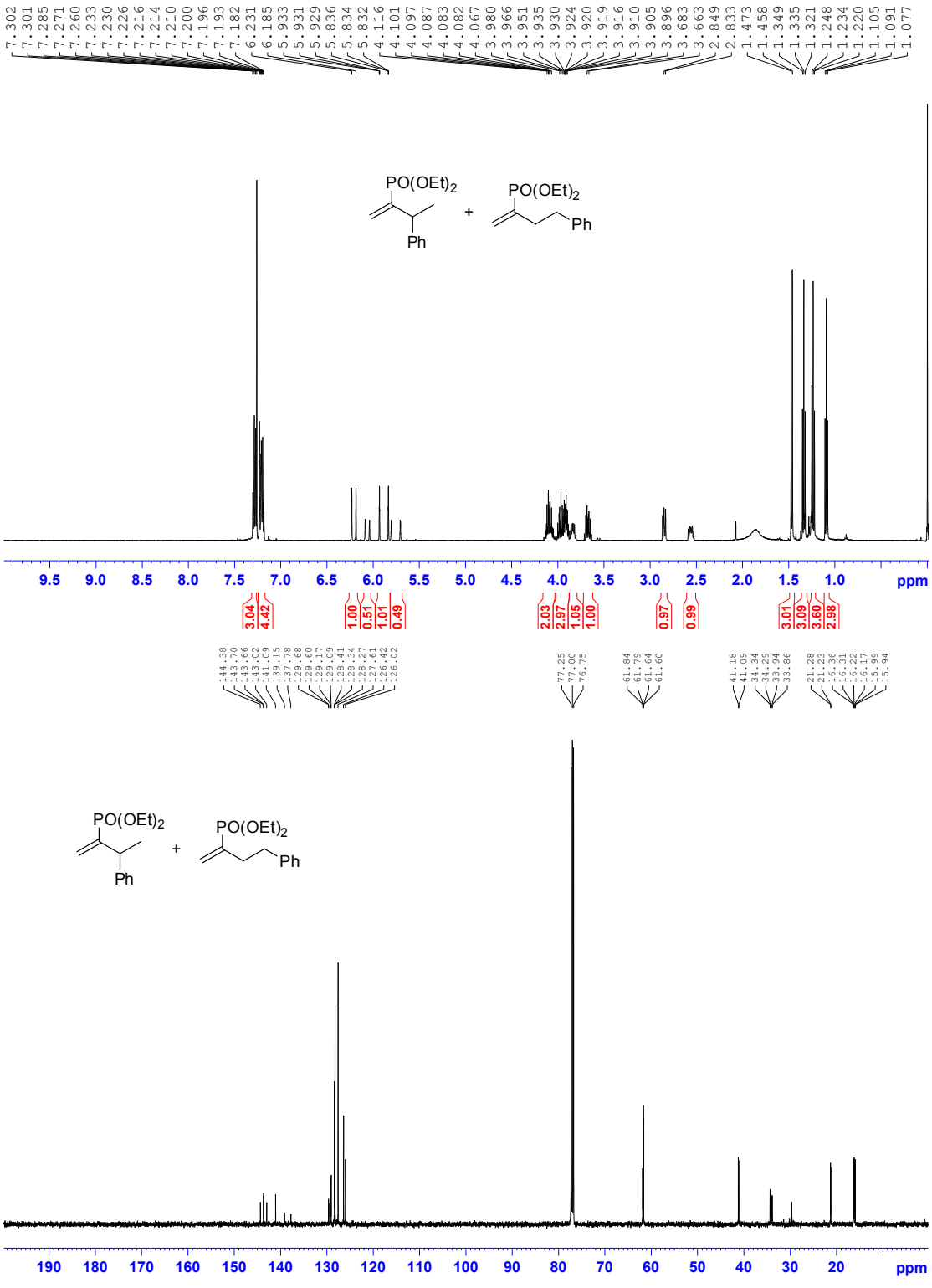


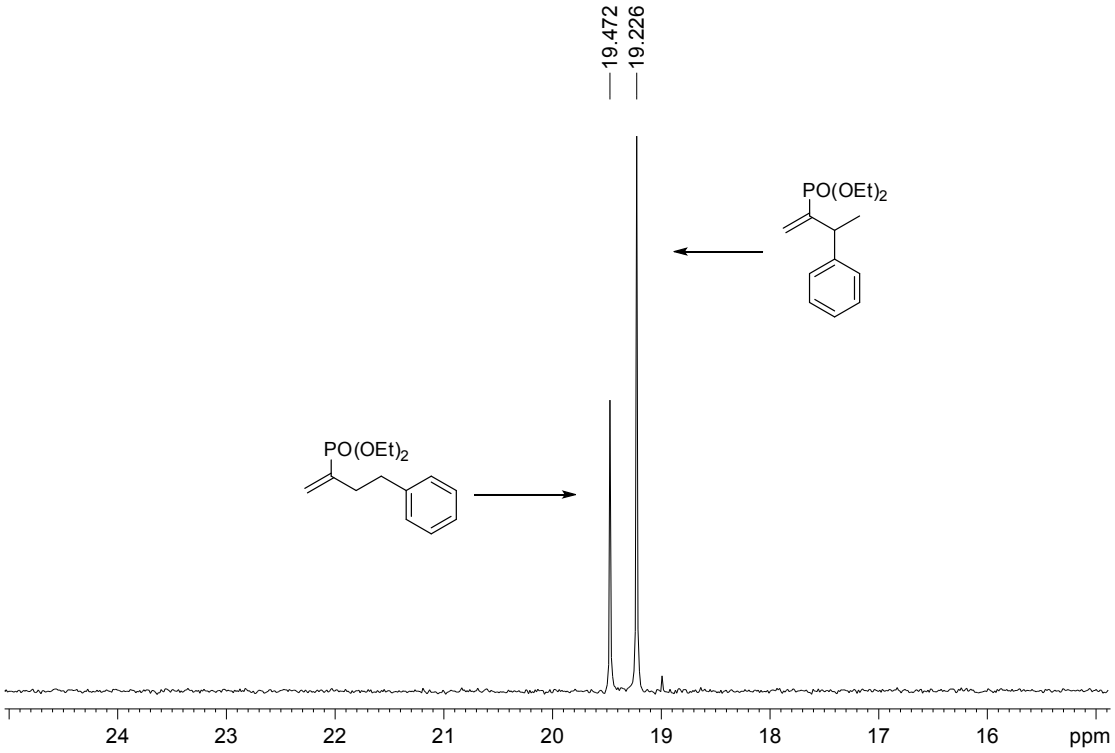

141.25
139.86
137.87
137.80
129.68
129.60
129.51
128.37
126.44
77.26
77.00
76.75
70.51
70.46
38.23
38.14
24.06
24.03
23.76
23.72
PO(O^{i}Pr)$_2$
Bn
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

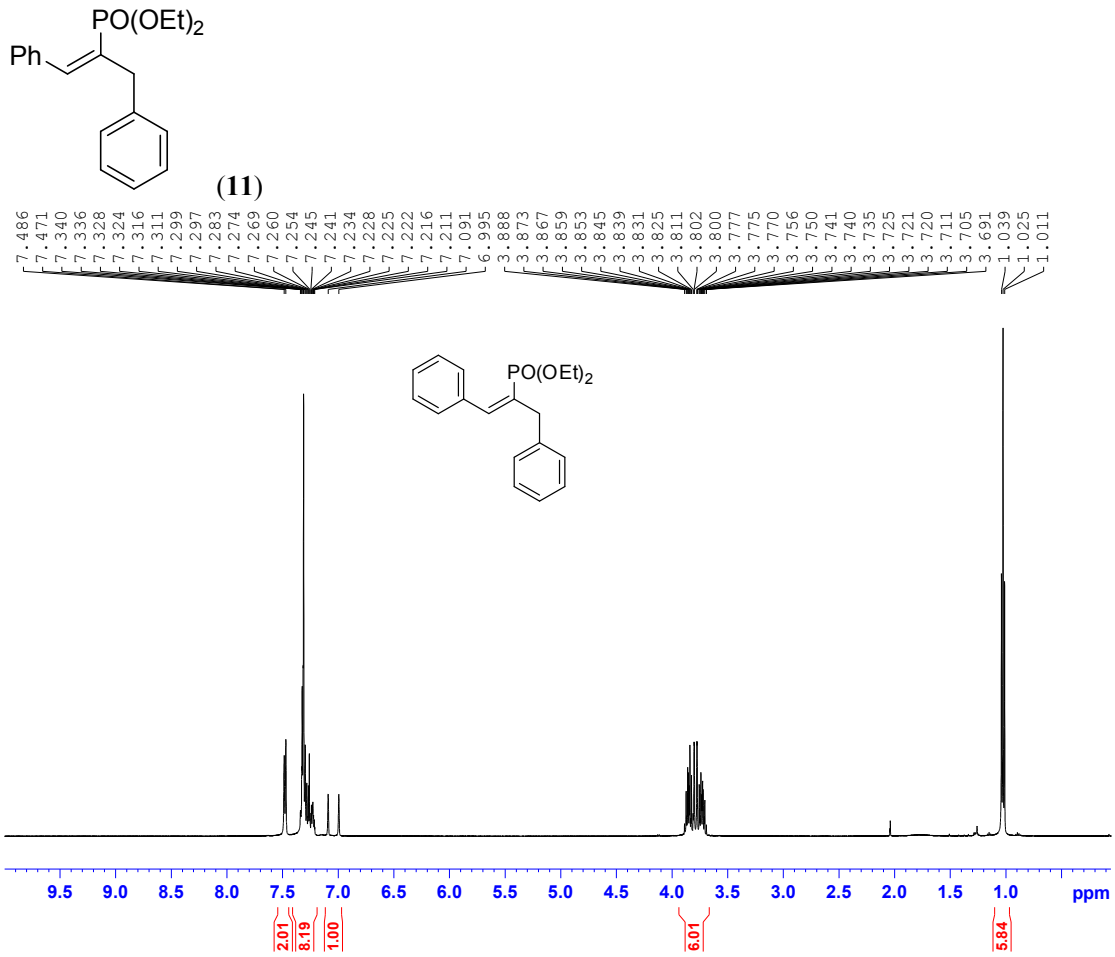

16.769
PO(O^{i}Pr)$_2$
Bn
100 50 0 -50 -100 -150 -200 ppm

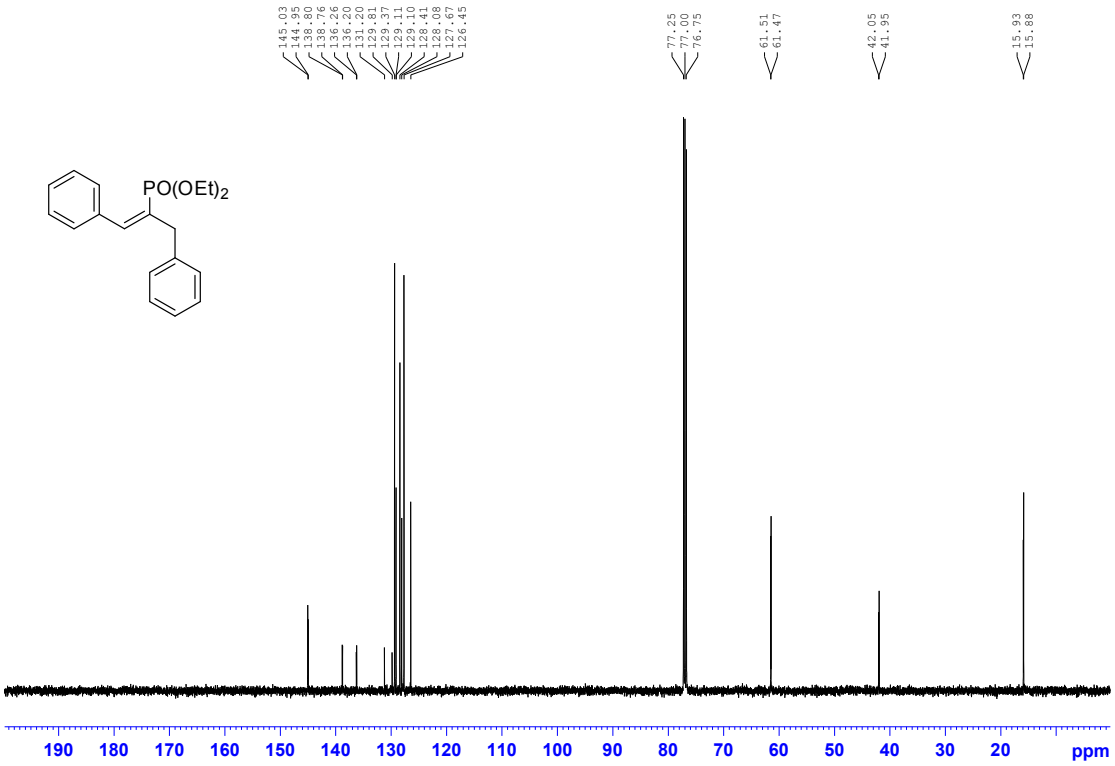

PO(OEt)$_2$
Ph
+
PO(OEt)$_2$
Ph

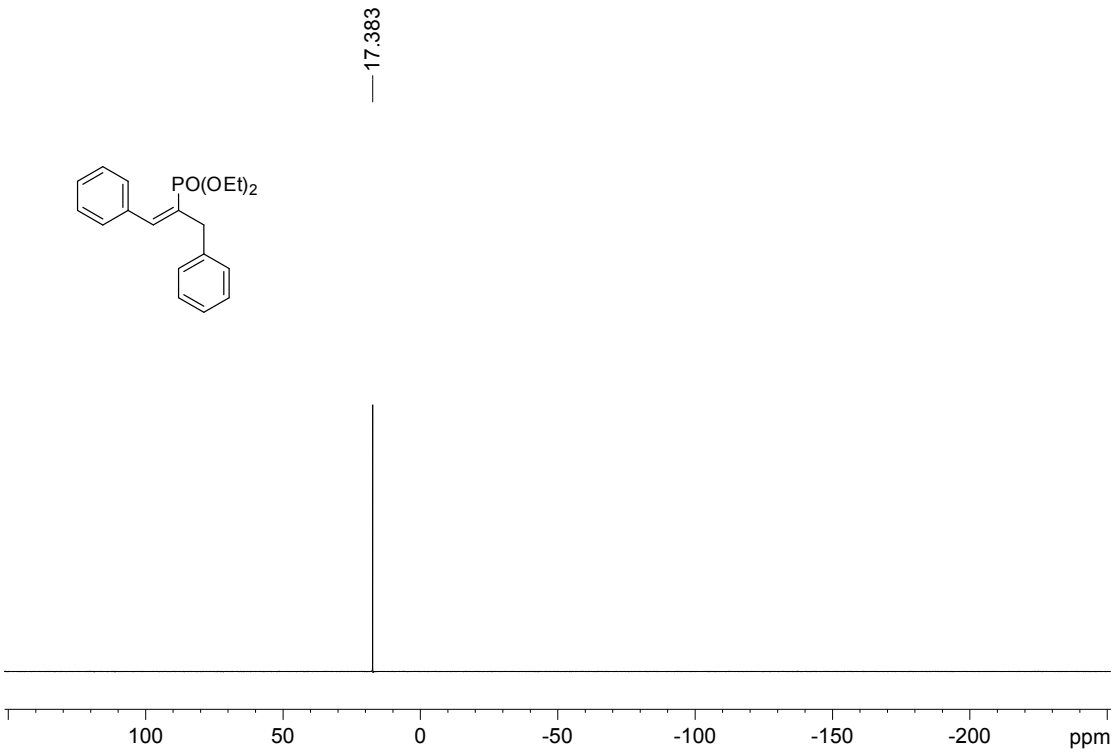
7 **3f**

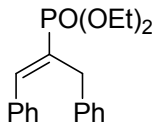

7.302
7.301
7.285
7.271
7.260
7.233
7.230
7.226
7.216
7.214
7.210
7.200
7.196
7.193
7.182
6.231
6.185
5.933
5.931
5.929
5.836
5.834
5.832
4.116
4.101
4.097
4.087
4.083
4.082
4.067
3.980
3.966
3.951
3.935
3.930
3.924
3.920
3.919
3.916
3.910
3.905
3.896
3.683
3.663
2.849
2.833
1.473
1.458
1.349
1.335
1.321
1.248
1.234
1.220
1.105
1.091
1.077
PO(OEt)2
Ph
+
PO(OEt)2
Ph
9.5 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 ppm
3.04 4.42 1.00 0.51 1.01 0.49 2.03 2.97 1.05 1.00 0.97 0.99 3.01 3.09 3.60 2.98
144.38
143.70
143.66
143.02
141.09
139.15
137.78
129.68
129.60
129.17
128.41
128.34
128.27
127.61
126.42
126.02
77.25
77.00
76.75
61.84
61.79
61.64
61.60
41.18
41.09
34.34
34.29
33.94
33.86
21.28
21.23
16.36
16.31
16.22
16.17
15.99
15.94
PO(OEt)2
Ph
+
PO(OEt)2
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


19.472
19.226
PO(OEt)2
PO(OEt)2
24
23
22
21
20
19
18
17
16
ppm

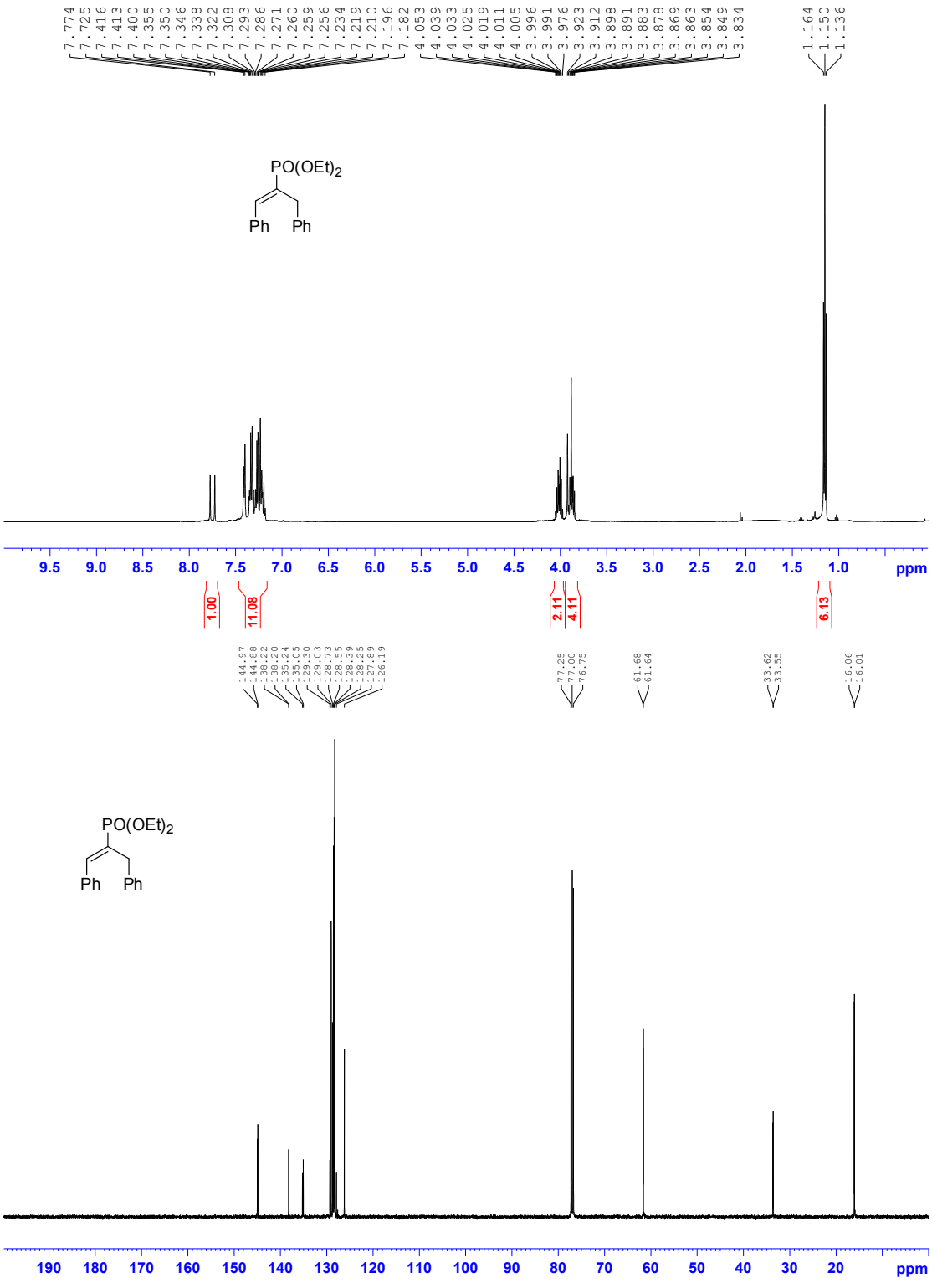

PO(OEt)2
Ph
(11)
7.486
7.471
7.340
7.336
7.328
7.324
7.316
7.311
7.299
7.297
7.283
7.274
7.269
7.260
7.254
7.245
7.241
7.234
7.228
7.225
7.222
7.216
7.211
7.091
6.995
3.888
3.873
3.867
3.859
3.853
3.845
3.839
3.831
3.825
3.811
3.802
3.800
3.777
3.775
3.770
3.756
3.750
3.741
3.740
3.735
3.725
3.721
3.720
3.711
3.705
3.691
1.039
1.025
1.011
PO(OEt)2
9.5
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
ppm
2.01
8.19
1.00
6.01
5.84

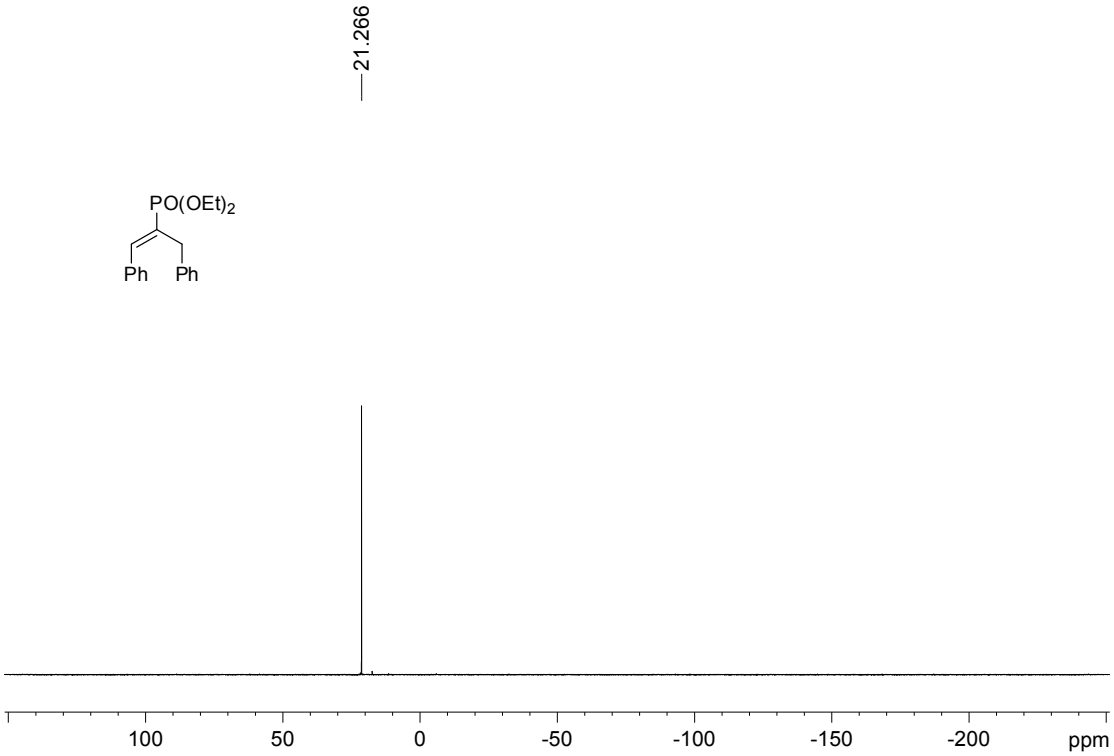

145.03
144.55
138.80
138.76
136.26
136.20
131.20
129.81
129.37
129.11
129.10
128.41
128.08
127.67
126.45
77.25
77.00
76.75
61.51
61.47
42.05
41.95
15.93
15.88
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

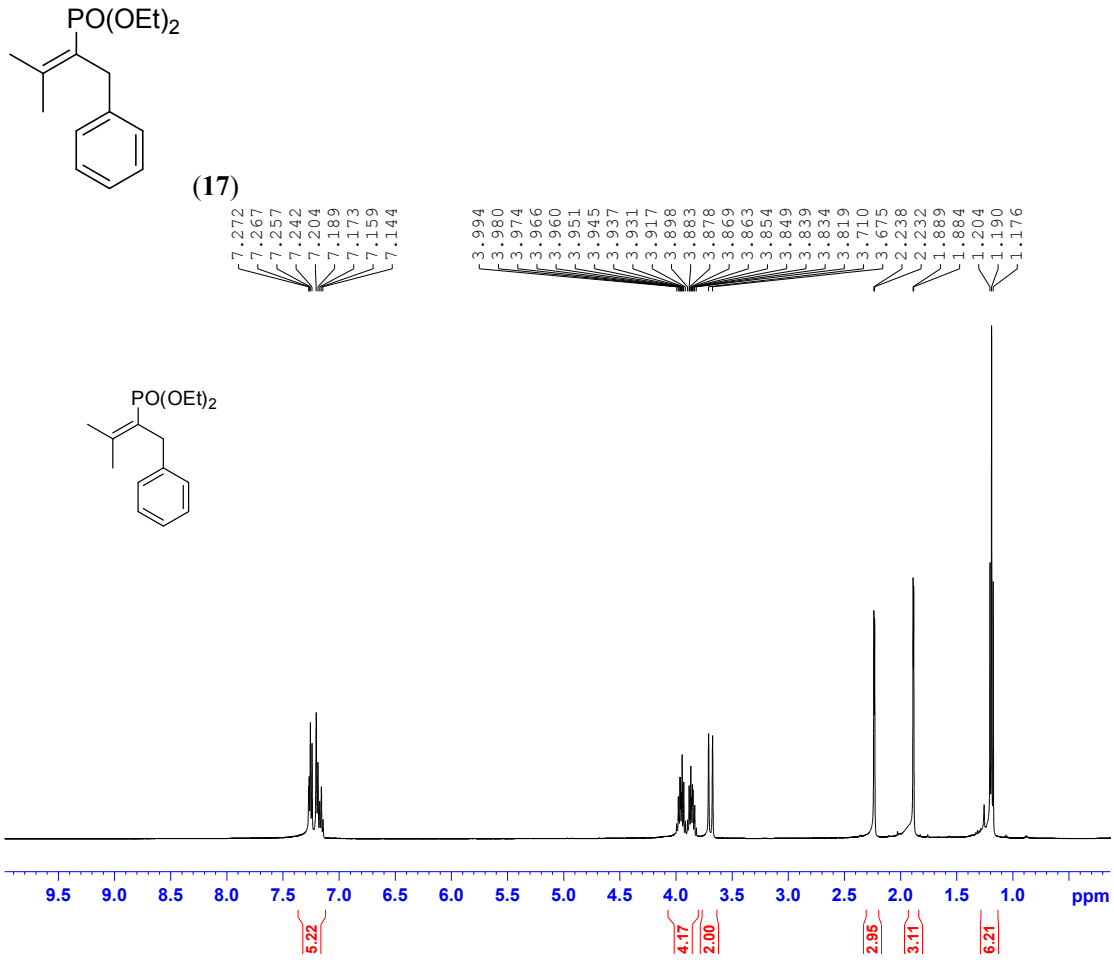

17.383
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm

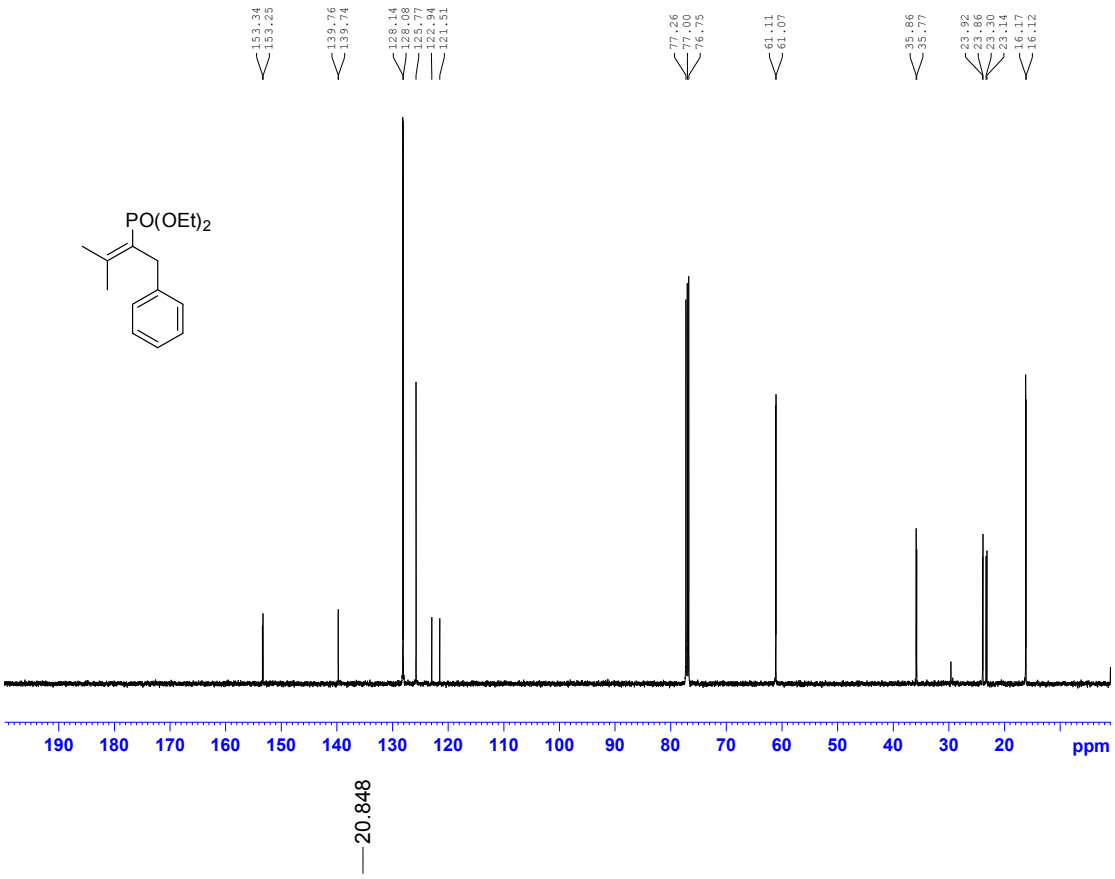

PO(OEt)2
Ph
Ph

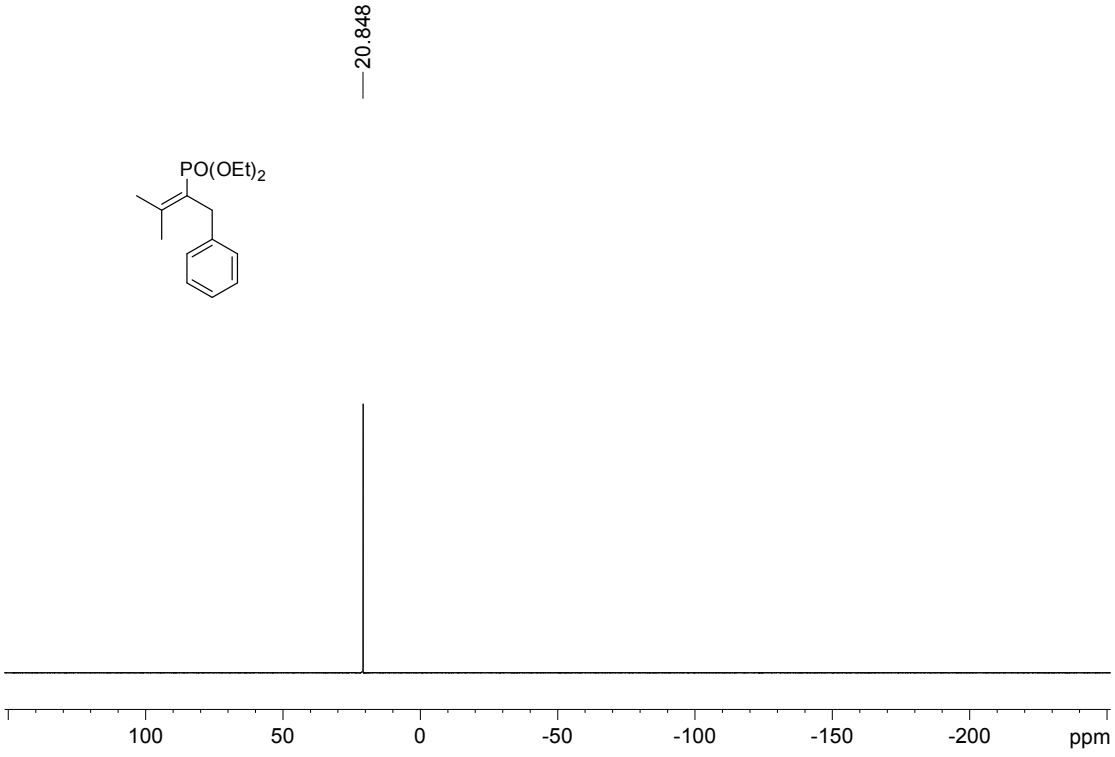
(**15**)

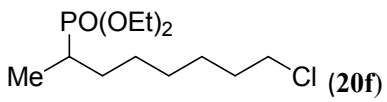

7.774
7.725
7.416
7.413
7.400
7.355
7.350
7.346
7.338
7.322
7.308
7.293
7.286
7.271
7.260
7.259
7.256
7.234
7.219
7.210
7.196
7.182
4.053
4.039
4.033
4.025
4.019
4.011
4.005
3.996
3.991
3.976
3.923
3.912
3.898
3.891
3.883
3.878
3.869
3.863
3.854
3.849
3.834
1.164
1.150
1.136
PO(OEt)2
Ph
Ph
9.5 9.0 8.5 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 ppm
1.00
11.08
2.11
4.11
6.13
144.97
144.88
138.22
138.20
135.24
135.05
129.30
129.03
128.73
128.55
128.39
128.25
127.89
126.19
77.25
77.00
76.75
61.68
61.64
33.62
33.55
16.06
16.01
PO(OEt)2
Ph
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


21.266
PO(OEt)2
Ph
Ph
100
50
0
-50
-100
-150
-200
ppm

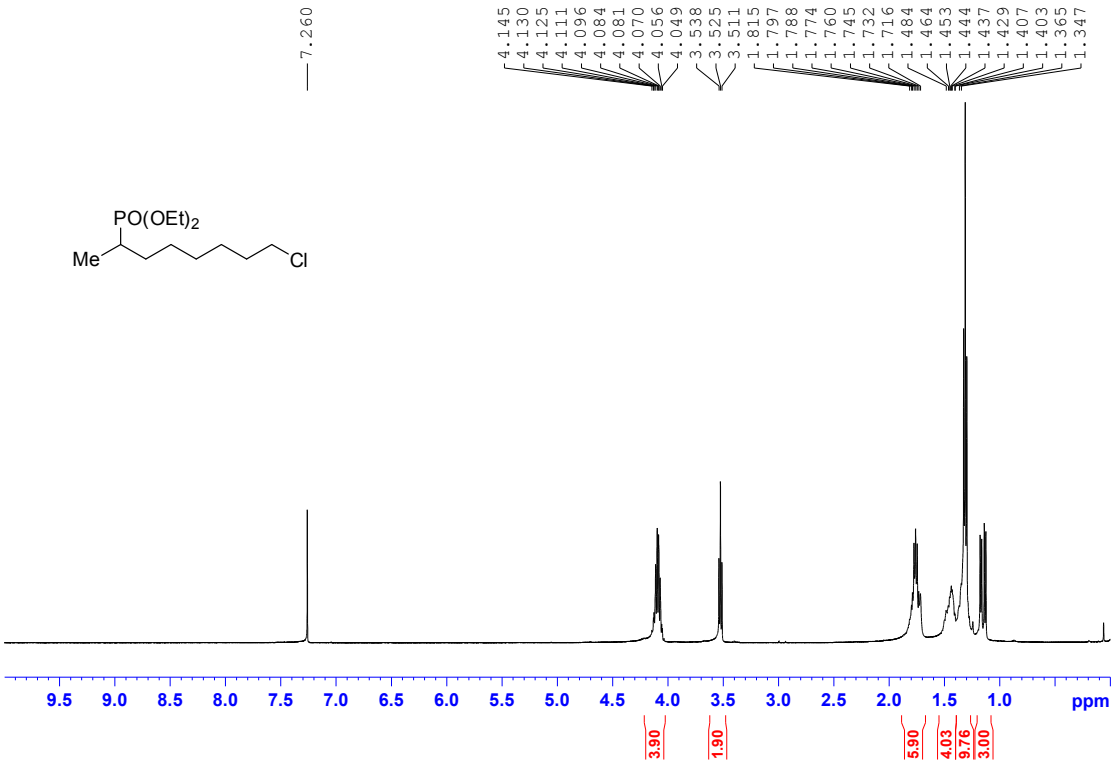

PO(OEt)2
(17)
7.272
7.267
7.257
7.242
7.204
7.189
7.173
7.159
7.144
3.994
3.980
3.974
3.966
3.960
3.951
3.945
3.937
3.931
3.917
3.898
3.883
3.878
3.869
3.863
3.854
3.849
3.839
3.834
3.819
3.710
3.675
2.238
2.232
1.889
1.884
1.204
1.190
1.176
PO(OEt)2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.22
4.17
2.00
2.95
3.11
6.21

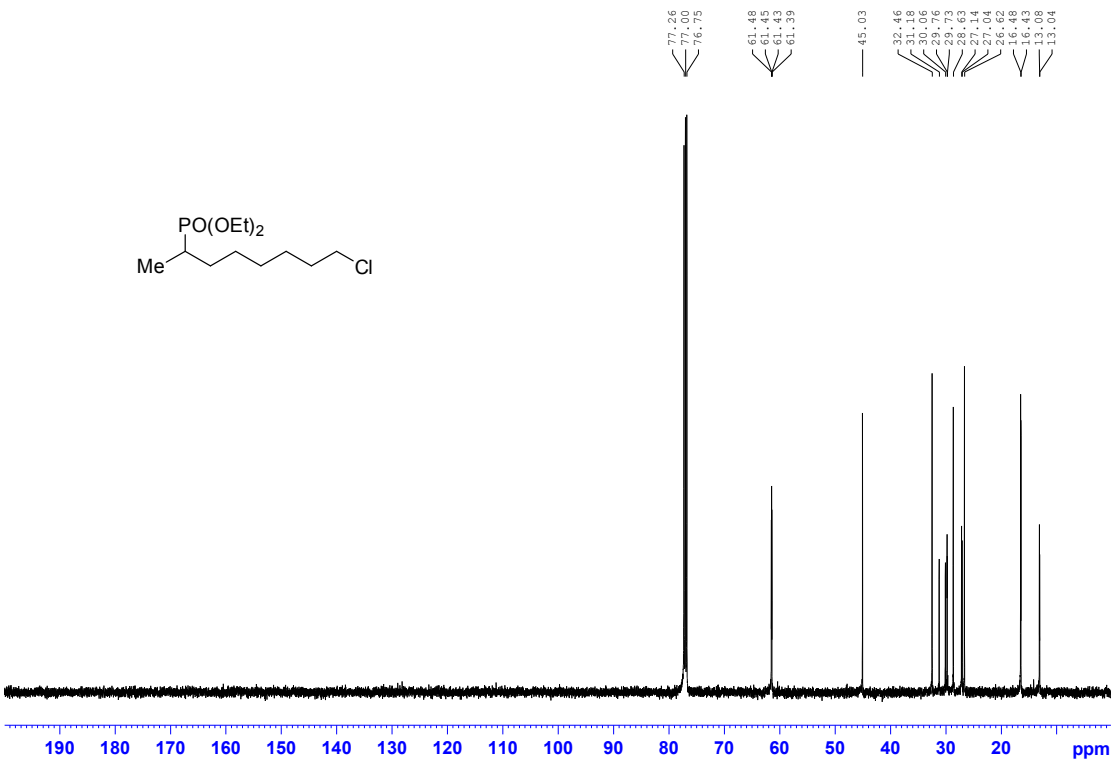

153.34
153.25
139.76
139.74
128.14
128.08
125.77
122.94
121.51
77.26
77.00
76.75
61.11
61.07
35.86
35.77
23.92
23.86
23.30
23.14
16.17
16.12
PO(OEt)2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

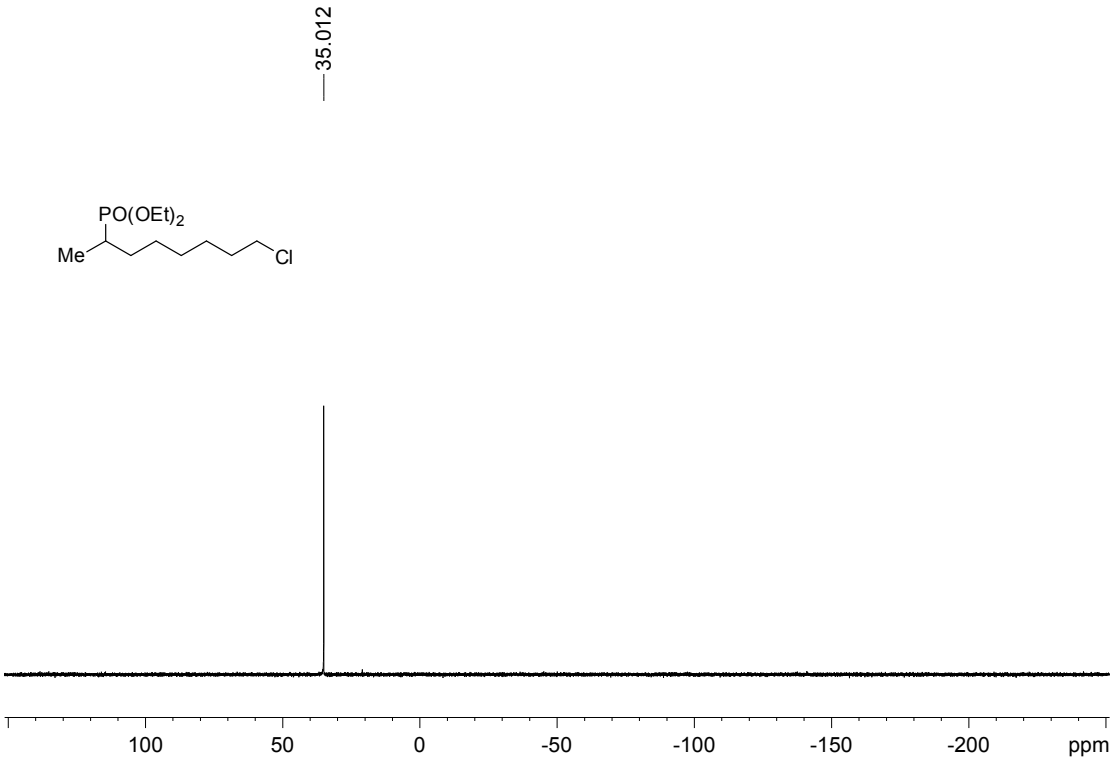

20.848
PO(OEt)2
100 50 0 -50 -100 -150 -200 ppm


PO(OEt)2
Me
Cl

(20f)


7.260
4.145
4.130
4.125
4.111
4.096
4.084
4.081
4.070
4.056
4.049
3.538
3.525
3.511
1.815
1.797
1.788
1.774
1.760
1.745
1.732
1.716
1.484
1.464
1.453
1.444
1.437
1.429
1.407
1.403
1.365
1.347
PO(OEt)2
Me
Cl
9.5 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 ppm
3.90
1.90
5.90
4.03
9.76
3.00


77.26
77.00
76.75
61.48
61.45
61.43
61.39
45.03
32.46
31.18
30.06
29.76
29.73
28.63
27.14
27.04
26.62
16.48
16.43
13.08
13.04
PO(OEt)2
Me
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


35.012
PO(OEt)2
Me
Cl
100
50
0
-50
-100
-150
-200
ppm