Electronic Supplementary Information

Catalyst-Free Phosphorylation of Aryl Halides with Trialkyl Phosphites through Electrochemical Reduction

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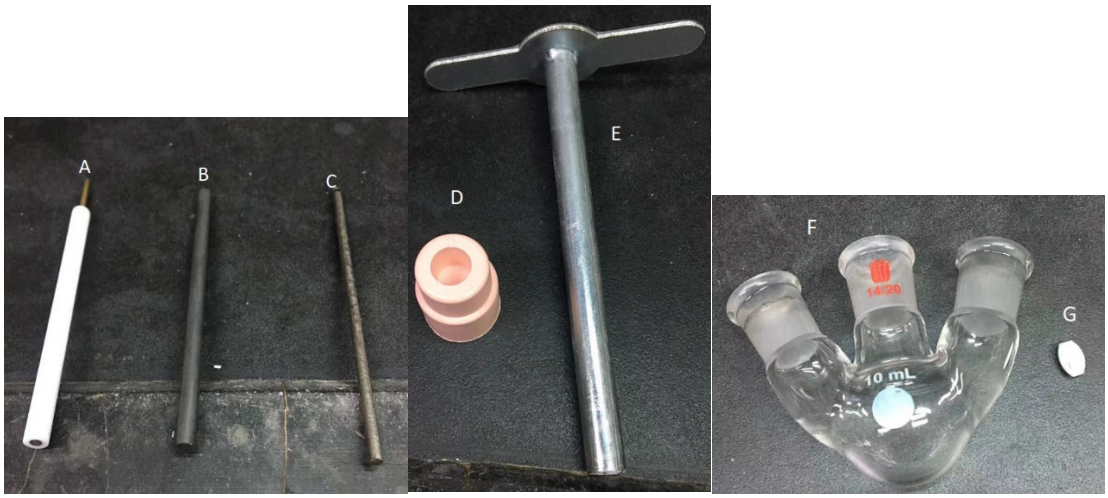
1) General information

The electrodes were purchased from AIDAHENGSHENG, Tianjin. Potentiostats (ITECH IT6720) were purchased on JD.COM. All necessary reagents were purchased from commercial suppliers and be used without further purification. The solvents were all distilled prior to use. 200-300 mesh silica gels for the chromatography were used. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Brucker ARX 400 spectrometer. ^{31}P NMR was recorded at 162 MHz with Brucker ARX 400 spectrometer. ^{19}F NMR was recorded at 376 MHz with Brucker ARX 400 spectrometer. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) are reported relative to the chemical shift of tetramethylsilane (TMS): chemical shifts (δ) were reported in ppm, and coupling constants (J) are in Hertz (Hz). For ^{31}P NMR (162 MHz) spectra 85% phosphoric acid (δ = 0) was served as external standard. IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. All of the substrates were purchased from commercial suppliers.

2) Preparation of the electrochemical cell

2.1 Materials used

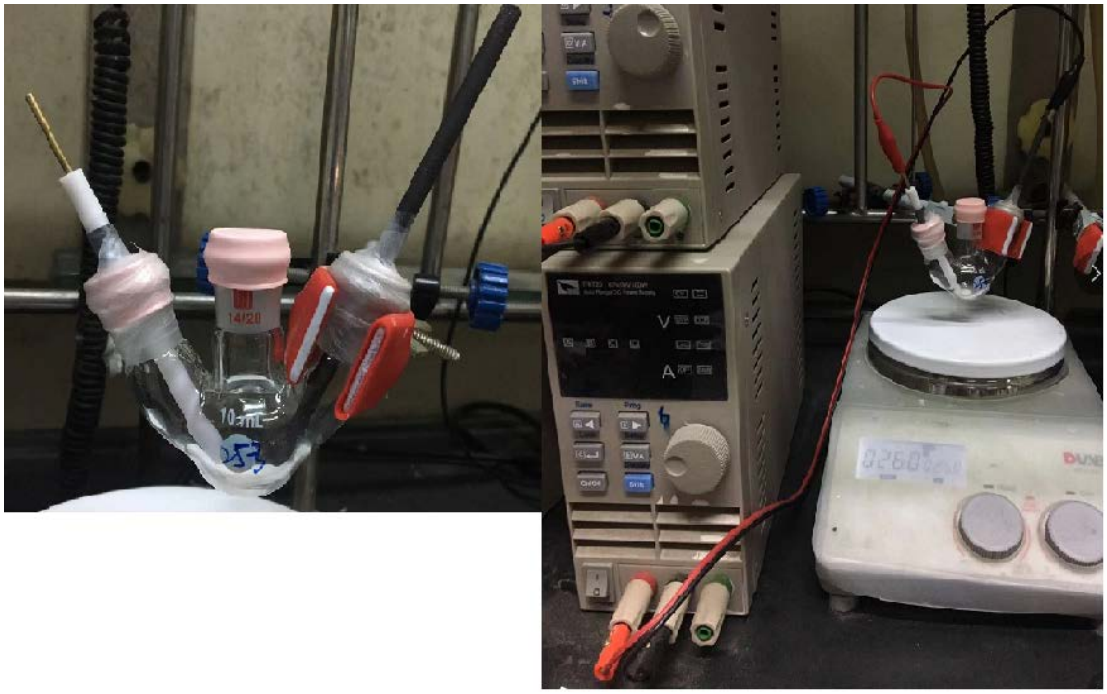


A: Ni plate electrode; B: graphite electrode; C: Ni rob; D: rubber plug (#14); E: hole puncher; F: three-necked round bottom bottle (10 mL); G: stirring bar

2.2 Preparation of the electrode

A hole was taken on the rubber plug with the hole puncher, and then the electrode was inserted.

2.3 Preparation of the undivided cell



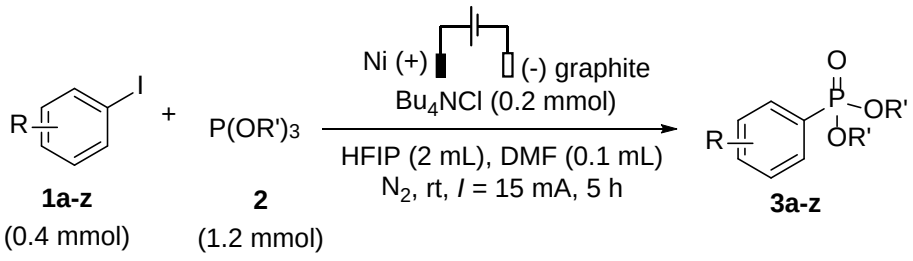
Left to right: 1) the undivided cell, parafilm was used to enhance the sealing property. 2) linkage of the undivided cell to the potentiostats.

2.4 Undivided cell for the gram-scale synthesis

From left to right: 1) the Ni rob was inserted into a #19 rubber plug as the anode. 2) a 100 mL three-necked round bottom bottle was used for the undivided cell.

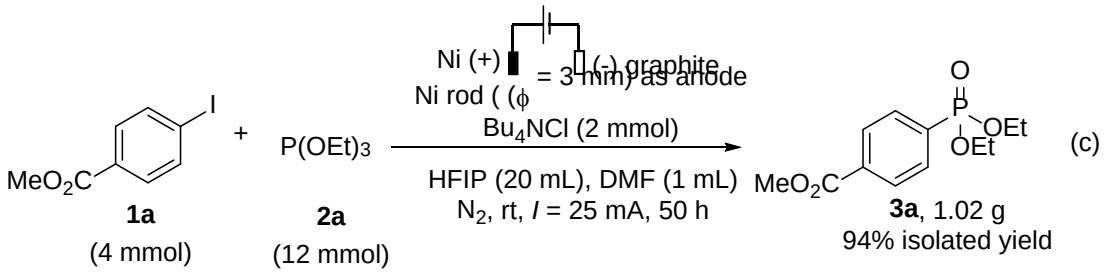
3) Experimental procedure

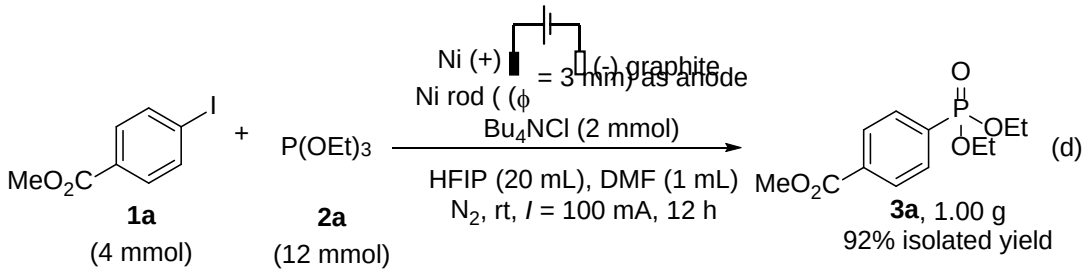
3.1 General procedure for the phosphorylation of aryl iodides (0.4 mmol scale)



Aryl iodide (0.4 mmol) and TBAC (56 mg, 0.2 mmol) were added into a 10 mL undivided cell (see section 2.3). After the reaction system was degassed for three times, 2 mL HFIP and 0.1 mL DMF were then added. After the addition of trialkyl phosphite (1.2 mmol), the reaction mixture was electrolyzed under a constant current of 15 mA for 5 h under stirring. Solvent was evaporated under reduced pressure, and the residue was purified by preparation thin-layer chromatography (PE:EA = 1:2) to afford crude product (mixed with 0-0.4 equivalent of trialkyl phosphate). The crude product was then purified by reduced-pressure distillation to remove trialkyl phosphate and afford the pure product.

3.2 Procedure for the gram-scale phosphorylation of methyl 4-iodobenzoate (**1a**)

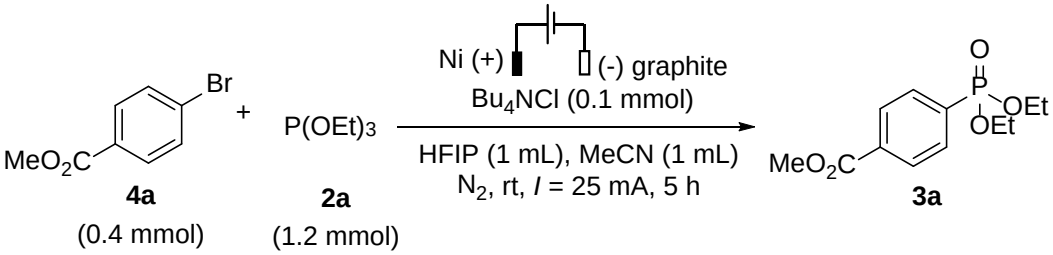




4-Iodobenzoate (**1a**) (1.048 g, 4 mmol) and TBAC (555 mg, 2 mmol) were added into a 100 mL undivided cell (see section 2.4). After the reaction system was degassed for three times, 20 mL HFIP and 1 mL DMF were then added. After the addition of $P(OEt)_3$ (1.992 g, 12 mmol), the reaction mixture was electrolyzed under a constant current of 25 mA for 50 h (or 100 mA for 12 h) under stirring. Solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (PE:EA = 2:1) to afford crude product (mixed with triethyl phosphate). The crude product was then purified by reduced-pressure distillation to remove triethyl phosphate and afford the pure product.

3.3 Optimization of the reaction conditions for the phosphorylation of aryl bromides

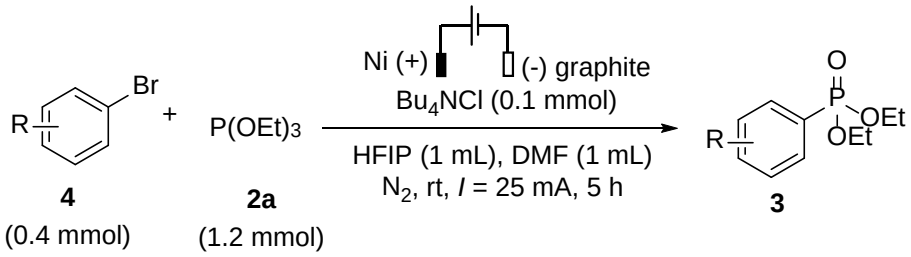
Table 1. Optimization of the Reaction Conditions[a]



Entry	Variation from standard conditions	Yield (%)[b]
1	none	77
2	HFIP (2 mL) and DMF (0.1 mL) as solvent	45
3	HFIP (2 mL) and DMF (1 mL) as solvent	35
4	TBAC (0.05 mmol)	56
5	TBAC (0.3 mmol)	73
6	I = 20 mA, 8 h	71
7	I = 50 mA, 2.5 h	73
8	60 °C	72

[a]Standard conditions: Ni plate anode, graphite cathode, **4a** (0.4 mmol), **2a** (1.2 mmol), TBAC (0.1 mmol), HFIP (1 mL), MeCN (1 mL), undivided cell, rt, 25 mA, 5 h. [b]Isolated yield.

3.4 General procedure for the phosphorylation of aryl bromides (0.4 mmol scale)

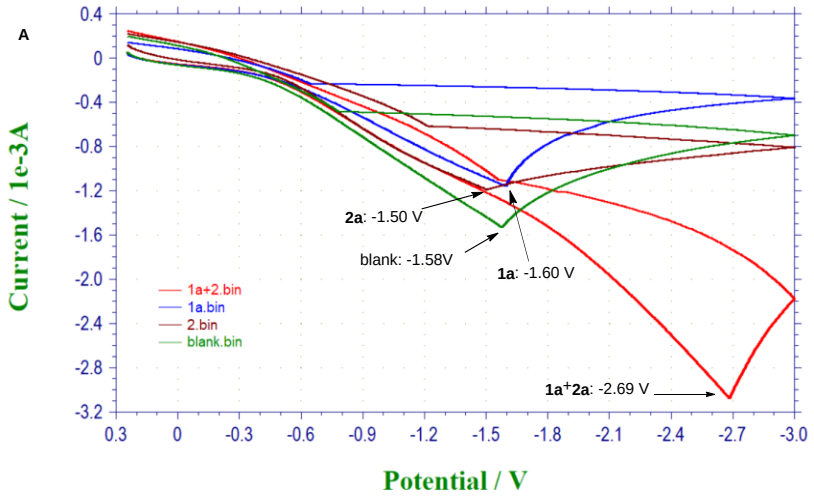


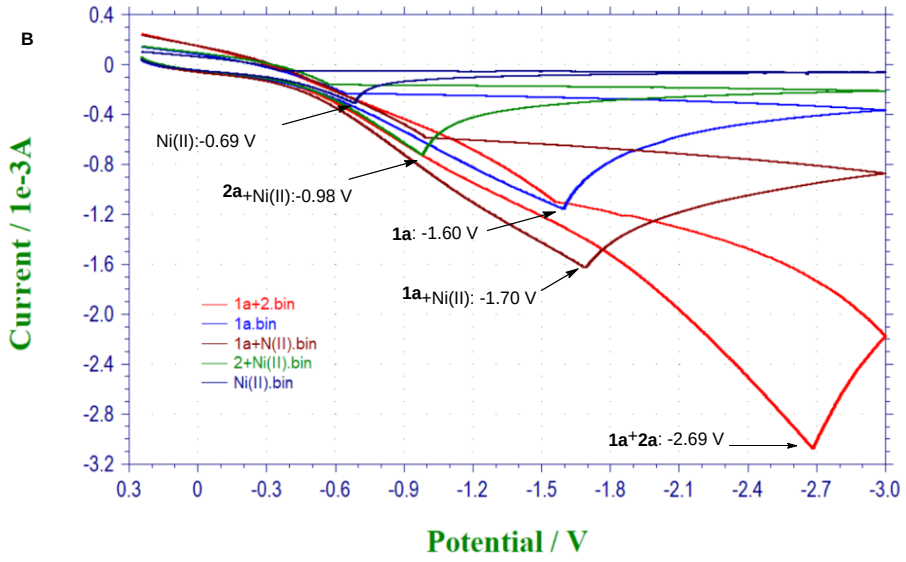
Aryl bromide (0.4 mmol) and TBAC (56 mg, 0.2 mmol) were added into a 10 mL undivided cell (see section 2.3). After the reaction system was degassed for three times, 1 mL HFIP and 1 mL MeCN were then added. After the addition of $P(OEt)_3$ (199 mg, 1.2 mmol), the reaction mixture was electrolyzed under a constant current of 25 mA for 5 h under stirring. Solvent was evaporated under reduced pressure, and the residue was purified by preparation thin-layer chromatography (PE:EA = 1:2) to afford crude product (mixed with 0-0.5 equivalent of triethyl phosphate). The crude product was then purified by reduced-pressure distillation to remove triethyl phosphate and afford the pure product.

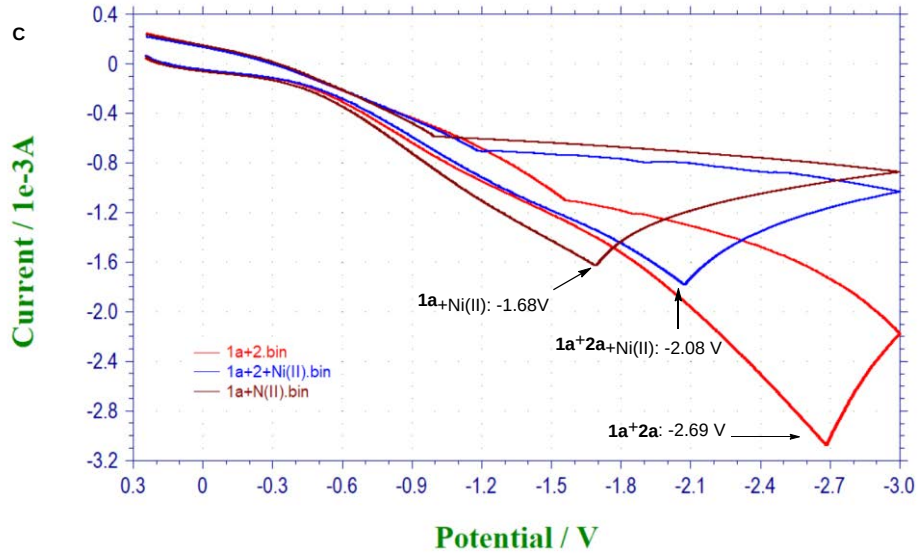
4) Cyclic voltammetry (CV) experiments

Cyclic voltammetry experiments were carried out with a CHI660E work station at room temperature. A mixture solvent of HFIP and DMF (20:1 v/v) was used, with Bu_4NCl (0.1 M) as electrolyte. The experiments used a graphite electrode as the working electrode, a Ni plate electrode (ϕ = 0.3 mm) as the counter electrode and a saturated calomel electrode (SCE) (0.244 V at 25 °C) as the reference electrode. The electric potential was between +0.25 and -3.0 V vs SCE, with 0.1 V/s scan rate. The concentration was 10 mM (for **1a** and $NiCl_2$) or 30 mM (for **2a**).

Figure S1. Cyclic voltammetry curves



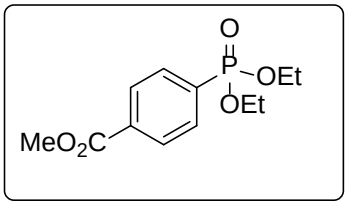




Discussion: As shown in *Figure S1A,* the reduction wave of HFIP was observed in the blank curve (green curve in *Figure S1A*). The separate addition of **1a** and **2a** gave no significant influence, but the combined addition of **1a** and **2a** gave a new reduction wave at -2.69 V and the reduction of HFIP was inhibited under this condition. Results shown in *Figure. S1B* reflected the influence of $NiCl_2$ in several reaction systems. Neither the activation of **1a** or a new reduction wave of Ni(II) was observed in the combination of **1a** and $NiCl_2$ (brown curve in *Figure S2B*, compared to the curve of **1a**, blue line), which indicated that Ni(II)/Ni(0) cycle was not likely to be involved in the reaction. On the other hand, the reduction of HFIP was obviously inhibited in the presence of Ni(II) (deep blue curve and green curve in *Figure S1B*). As shown in Figure S1C, the CV curves of **1a** in the presence of **2a** give only one reduction peak, indicating that after the reduction-generated aryl radical reacts with **2a**, a further reduction process on the cathode was not likely to exist.

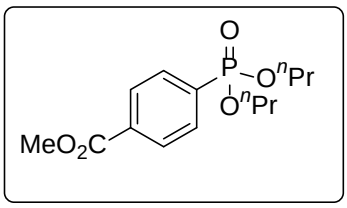
5) Spectra data for the products

Methyl 4-(diethoxyphosphoryl)benzoate (**3a**)[1]



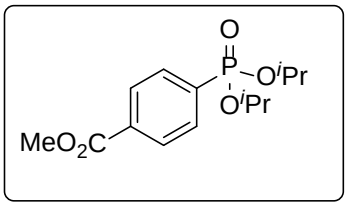
Yield 94% (103.0 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.2, 3.6 Hz, 2H), 7.90 (dd, J = 12.9, 8.0 Hz, 2H), 4.23-4.06 (m, 4H), 3.95 (s, 3H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 133.5 (d, J = 3.1 Hz), 133.2 (d, J = 186.6 Hz), 131.7 (d, J = 10.1 Hz), 129.4 (d, J = 15.1 Hz), 62.4 (d, J = 5.6 Hz), 52.4, 16.3 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.58; IR (film): 2982, 1731, 1278, 1106, 1020, 967 cm^{-1}.

Methyl 4-(dipropoxyphosphoryl)benzoate (**3ac**)



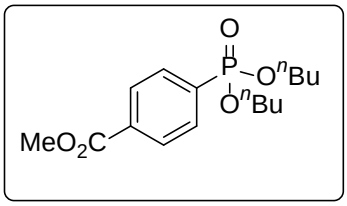
Yield 99% (119 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.1, 3.8 Hz, 2H), 7.90 (dd, J = 12.9, 8.0 Hz, 2H), 4.10-3.97 (m, 4H), 3.95 (s, 3H), 1.75-1.66 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 133.4 (d, J = 3.1 Hz), 133.2 (d, J = 187.0), 131.7 (d, J = 10.0 Hz), 129.3 (d, J = 15.0 Hz), 67.8 (d, J = 5.8 Hz), 52.4, 23.7 (d, J = 6.4 Hz), 10.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.36; IR (film): 2969, 1730, 1279, 1106, 999, 730 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{22}O_5P$ $[M+H]^+$ 301.1199 (301.119937), found 301.1199 (301.119888).

Methyl 4-(diisopropoxyphosphoryl)benzoate (**3ad**)[10]



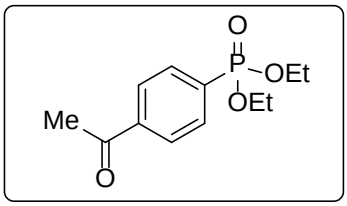
Yield 99% (119 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.10 (m, 2H), 7.90 (dd, J = 12.9, 8.2 Hz, 2H), 4.76-4.68 (m, 2H), 3.95 (s, 3H), 1.38 (d, J = 6.2 Hz, 6H), 1.23 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 134.8 (d, J = 187.1 Hz), 133.1 (d, J = 3.1 Hz), 131.7 (d, J = 10.1 Hz), 129.2 (d, J = 14.9 Hz), 71.1 (d, J = 5.7 Hz), 52.4, 24.0 (d, J = 3.9 Hz), 23.8 (d, J = 4.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 15.14; IR (film): 2982, 1730, 1278, 1252, 1102, 980 cm^{-1}.

Methyl 4-(dibutoxyphosphoryl)benzoate (**3ae**)



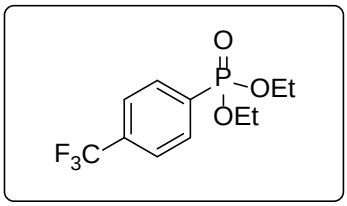
Yield 75% (98 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.1, 3.8 Hz, 2H), 7.88 (dd, J = 12.9, 8.1 Hz, 2H), 4.12-4.00 (m, 4H), 3.95 (s, 3H), 1.69-1.62 (m, 4H), 1.42-1.36 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 133.4 (d, J = 3.4 Hz), 133.2 (d, J = 186.5 Hz), 131.7 (d, J = 9.9 Hz), 129.4 (d, J = 14.9 Hz), 66.0 (d, J = 5.8 Hz), 52.4, 32.4 (d, J = 6.3 Hz), 18.7, 13.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.40; IR (film): 2959, 1731, 1278, 1105, 1019, 978 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_5P$ $[M+H]^+$ 329.1512 (329.151237), found 329.1512 (329.151201).

Diethyl (4-acetylphenyl)phosphonate (**3b**)[1]



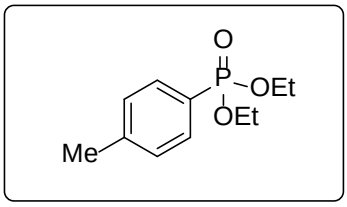
Yield 72% (74.0 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.02 (m, 2H), 7.92 (ddd, J = 12.7, 8.1, 1.3 Hz, 2H), 4.23-4.06 (m, 4H), 2.64 (d, J = 1.8 Hz, 3H), 1.34 (td, J = 7.0, 1.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 139.7 (d, J = 3.0 Hz), 133.3 (d, J = 186.5 Hz), 132.0 (d, J = 10.1 Hz), 128.0 (d, J = 15.0 Hz), 62.3 (d, J = 5.4 Hz), 26.7, 16.3 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.41; IR (film): 2984, 1691, 1396, 1253, 1018, 962 cm^{-1}.

Diethyl (4-(trifluoromethyl)phenyl)phosphonate (**3c**)[2]



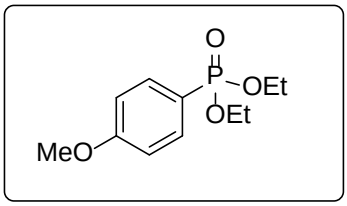
Yield 99% (112.6 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 12.9, 8.1 Hz, 2H), 7.74 (dd, J = 7.8, 2.9 Hz, 2H), 4.24-4.07 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0 (qd, J = 32.7, 3.2 Hz), 132.7 (d, J = 187.8 Hz), 132.1 (d, J = 10.0 Hz), 125.2 (dq, J = 15.1, 3.7 Hz), 123.5 (q, J = 272.7 Hz), 62.4 (d, J = 5.5 Hz), 16.2 (d, J = 6.4 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz) δ -63.4; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 16.79; IR (film): 2992, 1400, 1324, 1133, 1019, 970 cm^{-1}.

Diethyl *p*-tolylphosphonate (**3d**)[1]



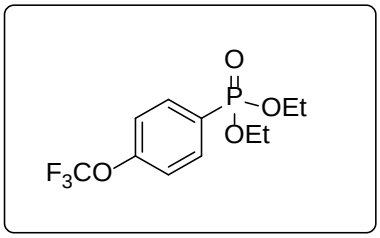
Yield 66% (60.1 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 13.1, 8.0 Hz, 2H), 7.29 (dd, J = 7.9, 4.0 Hz, 2H), 4.18-4.01 (m, 4H), 2.40 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, J = 3.1 Hz), 131.7 (d, J = 10.3 Hz), 129.1 (d, J = 15.4 Hz), 124.9 (d, J = 190.0 Hz), 61.8 (d, J = 5.3 Hz), 21.5, 16.2 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 20.08; IR (film): 2980, 1606, 1250, 1130, 1024, 964 cm^{-1}.

Diethyl (4-methoxyphenyl)phosphonate (**3e**)[1]



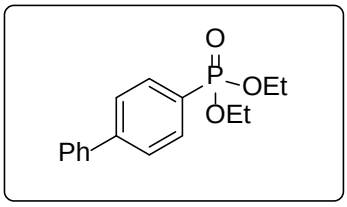
Yield 54% (52.8 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 6.97 (dd, J = 12.2, 8.8 Hz, 2H), 4.15-4.02 (m, 4H), 3.85 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 3.5 Hz), 133.7 (d, J = 11.2 Hz), 119.4 (d, J = 195.0 Hz), 113.9 (d, J = 16.0 Hz), 61.8 (d, J = 5.2 Hz), 55.3, 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 20.26; IR (film): 2982, 1601, 1241, 1133, 1026, 964, 730 cm^{-1}.

Diethyl (4-(trifluoromethoxy)phenyl)phosphonate (**3f**)[3]



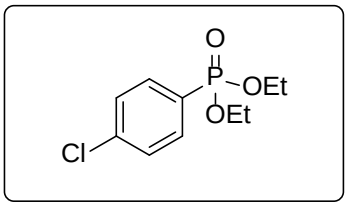
Yield 99% (118.7 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 12.9, 8.7 Hz, 2H), 7.32-7.29 (m, 2H), 4.20-4.07 (m, 4H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 133.8 (d, J = 10.9 Hz), 127.1 (d, J = 191.5 Hz), 120.4 (d, J = 16.2 Hz), 120.2 (q, J = 258.8 Hz), 62.3 (d, J = 5.6 Hz), 16.3 (d, J = 6.5 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz) δ -57.7; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.52; IR (film): 2987, 1598, 1487, 1253, 1023, 965 cm^{-1}.

Diethyl [1,1'-biphenyl]-4-ylphosphonate (**3g**)



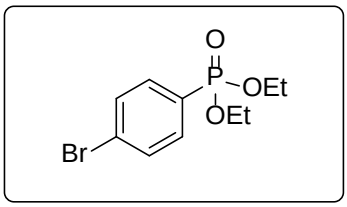
Yield 65% (75.6 mg). Colorless oil. Purified by preparation thin-layer chromatography (PE:EA:DCM = 1:1:0.15) to afford crude product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 13.0, 8.2 Hz, 2H), 7.68 (dd, J = 8.1, 3.8 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.1 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 4.23-4.06 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (d, J = 3.4 Hz), 139.8, 132.2 (d, J = 10.2 Hz), 128.8, 127.7, 127.2, 127.0, 126.8 (d, J = 189.7 Hz), 62.0 (d, J = 5.4 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.54; IR (film): 2978, 1601, 1392, 1250, 1134, 1023, 964 cm^{-1}.

Diethyl (4-chlorophenyl)phosphonate (**3h**)[4]



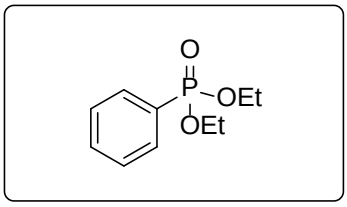
Yield 43% (43.0 mg). Colorless oil. Purified by preparation thin-layer chromatography (PE:EA:DCM = 1:1:0.05) to afford crude product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 12.9, 8.3 Hz, 2H), 7.45 (dd, J = 8.3, 3.4 Hz, 2H), 4.18-4.05 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9 (d, J = 3.9 Hz), 133.1 (d, J = 10.7 Hz), 128.8 (d, J = 15.5 Hz), 126.9 (d, J = 190.8 Hz), 62.2 (d, J = 5.5 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 18.19; IR (film): 2983, 1586, 1392, 1249, 1132, 1024, 969 cm^{-1}.

Diethyl (4-bromophenyl)phosphonate (**3i**)[5]



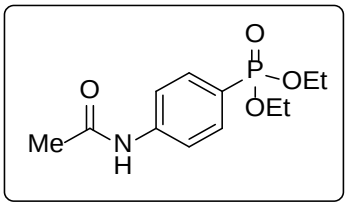
Yield 51% (59.9 mg). Colorless oil. Purified by preparation thin-layer chromatography (PE:EA:DCM = 1:1:0.05) to afford crude product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.65 (m, 2H), 7.63-7.60 (m, 2H), 4.20-4.03 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2 (d, J = 10.5 Hz), 131.7 (d, J = 15.5 Hz), 127.5 (d, J = 4.1 Hz), 127.4 (d, J = 190.2 Hz), 62.2 (d, J = 5.4 Hz), 16.3 (d, J = 6.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 18.31; IR (film):2982, 1581, 1388, 1250, 1023, 966 cm^{-1}.

Diethyl phenylphosphonate (**3j**)[1]



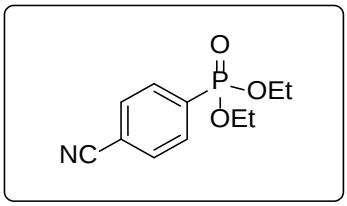
Yield 56% (48.5 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.56 (td, J = 7.4, 1.2 Hz, 1H), 7.49 – 7.44 (m, 4H), 4.20-4.03 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (d, J = 3.1 Hz), 131.7 (d, J = 10.0 Hz), 128.4 (d, J = 15.1 Hz), 128.3 (d, J = 187.7 Hz), 62.0 (d, J = 5.3 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.36; IR (film): 2986, 1245, 1132, 1026, 967, 731 cm^{-1}.

Diethyl (4-acetamidophenyl)phosphonate (**3k**)[6]



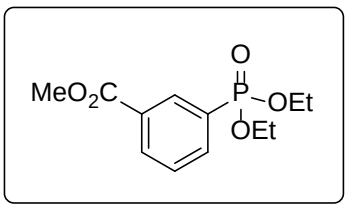
Yield 82% (89.0 mg). White solid, m.p. 137-139 ^{o}C. Purified by silica gel column chromatography (EA) to afford pure product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.74-7.70 (m, 4H), 4.11-4.05 (m, 4H), 2.20 (s, 3H), 1.31 (t, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 142.7, 132.6 (d, J = 10.7 Hz), 121.8 (d, J = 192.7 Hz), 119.2 (d, J = 15.2 Hz), 62.2 (d, J = 5.4 Hz), 24.4, 16.2 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.37; IR (film): 1072, 1595, 1531, 1227, 1024, 963 cm^{-1}.

Diethyl (4-cyanophenyl)phosphonate (**3l**)[1]



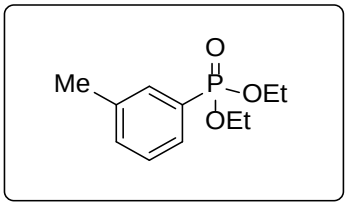
Yield 65% (62.2 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 13.1, 7.9 Hz, 2H), 7.77 (dd, J = 7.9, 3.3 Hz, 2H), 4.22-4.09 (m, 4H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8 (d, J = 187.8), 132.2 (d, J = 10.0 Hz), 131.9 (d, J = 14.9 Hz), 117.8, 115.9(d, J = 3.4 Hz), 62.6 (d, J = 5.7 Hz), 16.2 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 15.81; IR (film): 2984, 2233, 1394, 1254, 1019, 971, 803 cm^{-1}.

Methyl 3-(diethoxyphosphoryl)benzoate (**3m**)[7]



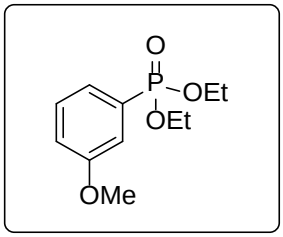
Yield 90% (97.9 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 13.8 Hz, 1H), 8.23 (dd, J = 7.8, 1.3 Hz, 1H), 8.02 (dd, J = 12.9, 7.6 Hz, 1H), 7.58 (td, J = 7.7, 4.0 Hz, 1H), 4.23-4.06 (m, 4H), 3.95 (s, 3H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.9 (d, J= 10.0 Hz), 133.2 (d, J = 2.9 Hz), 132.7 (d, J = 10.9 Hz), 130.4 (d, J = 14.9 Hz), 129.2 (d, J = 189.7 Hz), 128.6 (d, J = 15.1 Hz), 62.3 (d, J = 5.4 Hz), 52.3, 16.2 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 17.73; IR (film): 2992, 1728, 1439, 1252, 1140, 1021, 966 cm^{-1}.

Diethyl m-tolylphosphonate (**3n**)[1]



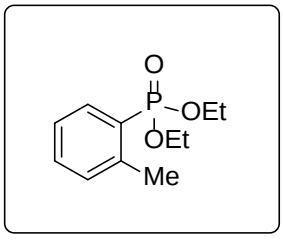
Yield 76% (69.5 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.58 (m, 2H), 7.37-7.35 (m, 2H), 4.18-4.04 (m, 4H), 2.40 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2 (d, J = 14.9 Hz), 133.1 (d, J = 3.1 Hz), 132.2 (d, J = 9.9 Hz), 128.7 (d, J = 9.8 Hz), 128.3 (d, J = 15.6 Hz), 128.0 (d, J = 186.8 Hz), 62.0 (d, J = 5.5 Hz), 21.3, 16.3 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.80; IR (film): 2962, 1444, 1392, 1249, 1023, 964, 785, 696 cm^{-1}.

Diethyl (3-methoxyphenyl)phosphonate (**3o**)[8]



Yield 69% (67.6 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 3H), 7.10-7.07 (m, 1H), 4.18-4.10 (m, 4H), 3.85 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, J = 18.7 Hz), 129.7 (d, J = 17.6 Hz), 129.5 (d, J = 186.6 Hz), 123.9 (d, J = 9.3 Hz), 118.7 (d, J = 3.3 Hz), 116.3 (d, J = 11.2 Hz), 62.1 (d, J = 5.4 Hz), 55.4, 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.15; IR (film): 2987, 1598, 1487, 1253, 1023, 965 cm^{-1}.

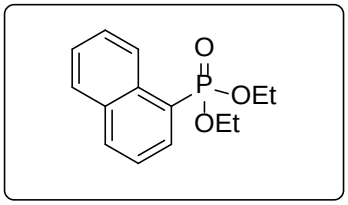
Diethyl *o*-tolylphosphonate (**3p**)[1]



Yield 91% (82.7 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 1H), 7.42-7.41 (m, 1H), 7.28-7.24 (m, 2H), 4.19-4.05 (m, 4H), 2.58 (s, 3H), 1.33 (t, J = 7.1

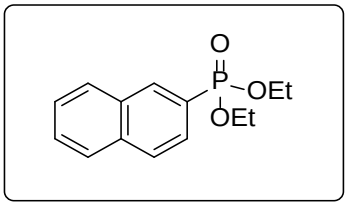
Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, J = 10.2 Hz), 133.8 (d, J = 10.3 Hz), 132.4 (d, J = 2.9 Hz), 131.1 (d, J = 14.8 Hz), 126.7 (d. J = 184.0 Hz), 125.3 (d, J = 15.1 Hz), 61.8 (d, J = 5.4 Hz), 21.1 (d, J = 3.6 Hz), 16.2 (d, J = 6.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.95; IR (film): 2981, 1597, 1453, 1392, 1245, 1022, 963, 754 cm^{-1}.

Diethyl naphthalen-1-ylphosphonate (**3q**)[1]



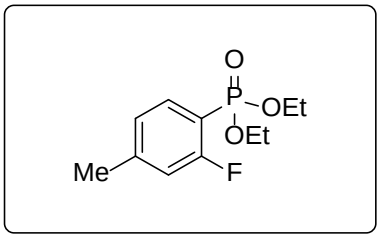
Yield 74% (78.4 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 8.5 Hz, 1H), 8.25 (ddd, J = 16.3, 7.0, 1.0 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1 H), 7.63-7.59 (m, 1H), 7.57-7.51 (m, 2H), 4.26-4.16 (m, 2H), 4.13-4.03 (m, 2H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6 (d, J = 9.3 Hz), 133.6 (d, J = 3.1 Hz), 133.5, 132.6 (d, J = 10.8 Hz), 128.7 (d, J = 1.5 Hz), 127.4, 126.6 (d, J = 4.2 Hz), 126.3, 124.5 (d, J = 182.5 Hz), 124.5 (d, J = 16.7 Hz), 62.1 (d, J = 5.2 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.77; IR (film): 2989, 1508, 1243, 1050, 1021, 967 cm^{-1}.

Diethyl naphthalen-2-ylphosphonate (**3r**)[1]



Yield 77% (82.1 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 15.5 Hz. 1H), 7.95-7.87 (m, 3H), 7.80-7.74 (m, 1H), 7.62-7.54 (m, 2H), 4.23-4.08 (m, 4H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 134.0 (d, J = 10.2 Hz), 132.3 (d, J = 16.6 Hz), 128.8, 128.3 (d, J = 14.1 Hz), 128.2, 127.7, 126.8, 126.3 (d, J = 9.9 Hz), 125.3 (d, J = 187.9 Hz), 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 19.57; IR (film): 2984, 1593, 1392, 1252, 1022, 965, 748, 651 cm^{-1}.

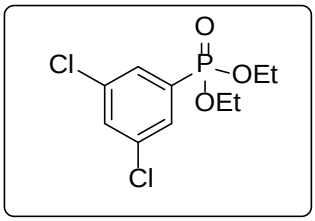
Diethyl (2-fluoro-4-methylphenyl)phosphonate (**3s**)



Yield 63% (61.6 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.70 (m, 1H), 7.06-7.04 (m, 1H), 6.94 (dd, J = 10.3, 5.9 Hz, 1H), 4.22-4.09 (m, 4H), 2.40 (s, 3H),

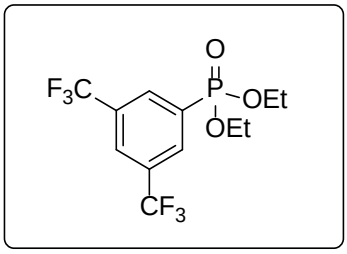
1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.1, 146.3 (dd, J = 8.4, 2.4 Hz), 134.7 (dd, J = 6.5, 4.4 Hz), 124.9 (dd, J = 14.0, 2.9 Hz), 116.6 (dd, J = 22.3, 8.3 Hz), 112.9 (dd, J = 190.6, 18.4 Hz), 62.3 (d, J = 5.6 Hz), 21.5, 16.2 (d, J = 6.6 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz) δ -105.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 14.84; IR (film): 2989, 1620, 1410, 1250, 1023, 969 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{17}O_3FP$ $[M+H]^+$ 247.0894, found 247.0888.

Diethyl (3,5-dichlorophenyl)phosphonate (**3t**)



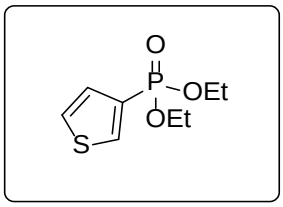
Yield 56% (63.3 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 13.6, 1.9 Hz, 2H), 7.53 (t, J = 1.8 Hz, 1H), 4.23-4.06 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5 (d, J = 22.1 Hz), 132.3 (d, J = 187.9 Hz), 132.3 (d, J = 2.9 Hz), 129.8 (d, J = 10.0 Hz), 62.7 (d, J = 5.6 Hz), 16.3 (d, J = 6.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 15.17; IR (film): 2986, 1560, 1258, 1159, 1020, 971, 796 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{14}O_3Cl_2P$ $[M+H]^+$; 283.0052, found 283.0044.

Diethyl (3,5-bis(trifluoromethyl)phenyl)phosphonate (**3u**)



Yield 87% (121.4 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 13.3 Hz, 2H), 8.05 (s, 1H), 4.27-4,13 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (d, J = 192.3 Hz), 132.0 (dd, J = 34.1, 15.4 Hz), 132.1, 131.9 (d, J = 8.1 Hz), 125.9 (q, J = 3.5 Hz), 120.1 (qd, J = 270.9, 2.1 Hz), 63.0 (d, J = 5.7 Hz), 16.2 (d, J = 6.2 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz) δ -63.2; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 14.25; IR (film): 2988, 1616, 1368, 1281, 1136, 1021, 972, 682 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}O_3F_6P$ $[M+H]^+$ 351.0579, found 351.0572.

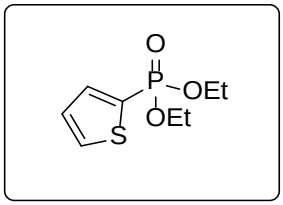
Diethyl thiophen-3-ylphosphonate (**3v**)[9]



Yield 58% (51.1 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, J = 8.2,

2.8, 1.1 Hz, 1H), 7.45-7.42 (m, 1H), 7.35-7.32 (m, 1H), 4.18-1.06 (m, 4H), 1.32 (t, J = 1.32 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (d, J = 18.2 Hz), 129.4 (d, J = 196.7 Hz), 128.9 (d, J = 16.7 Hz), 127.1 (d, 20.0 Hz), 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 13.71; IR (film): 2987, 1501, 1392, 1246, 1021, 966, 793, 657 cm^{-1}.

Diethyl thiophen-2-ylphosphonate (**3w**)[3]



Yield 46% (40.7 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 2H), 7.20-7.17 (m, 2H), 7.21-4.08 (m, 4H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6 (d, J = 12.4 Hz), 133.3 (d, J = 7.5 Hz), 128.0 (d, J = 18.4 Hz), 127.8 (d, J = 210.0), 62.6 (d, J = 5.4 Hz), 16.2 (d, J = 6.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.40; IR (film): 2984, 1410, 1251, 1019, 970, 749, 653 cm^{-1}.

6) Reference

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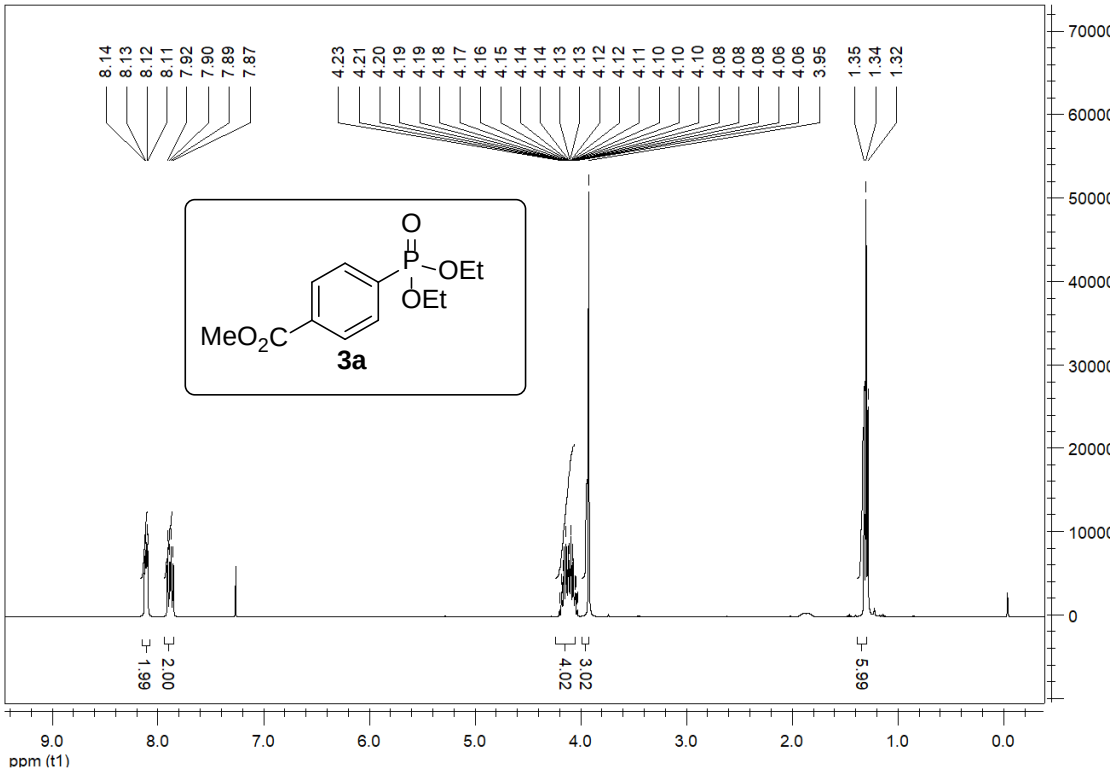
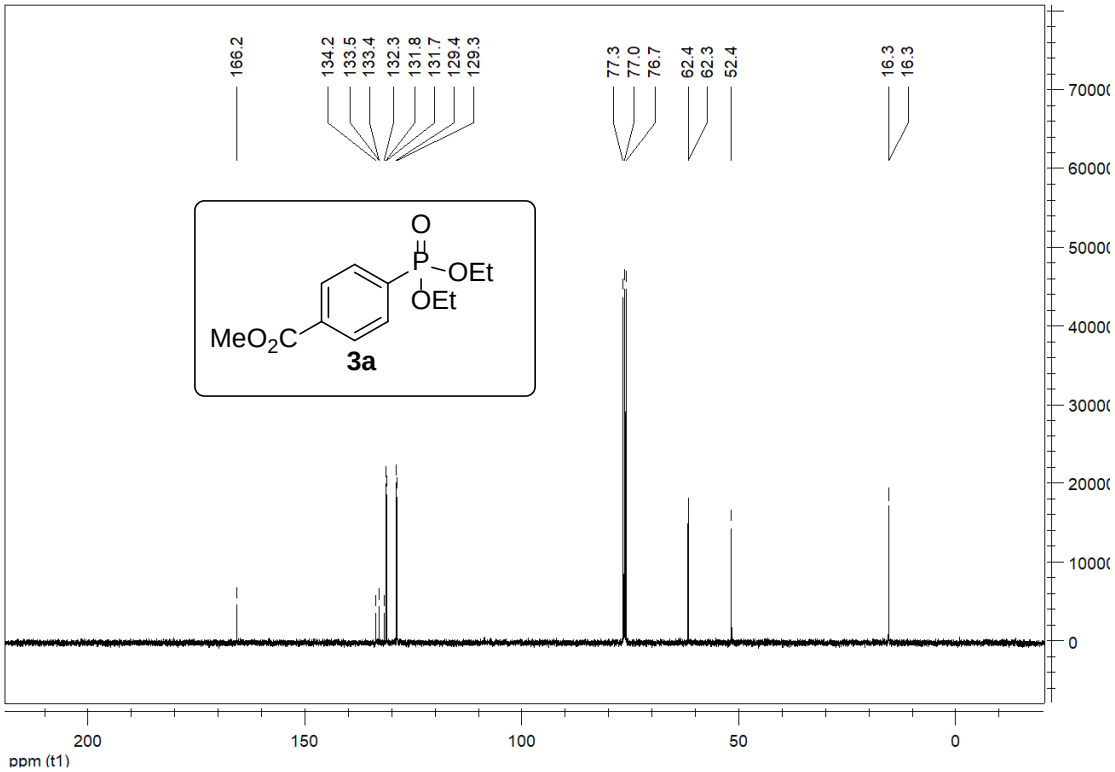
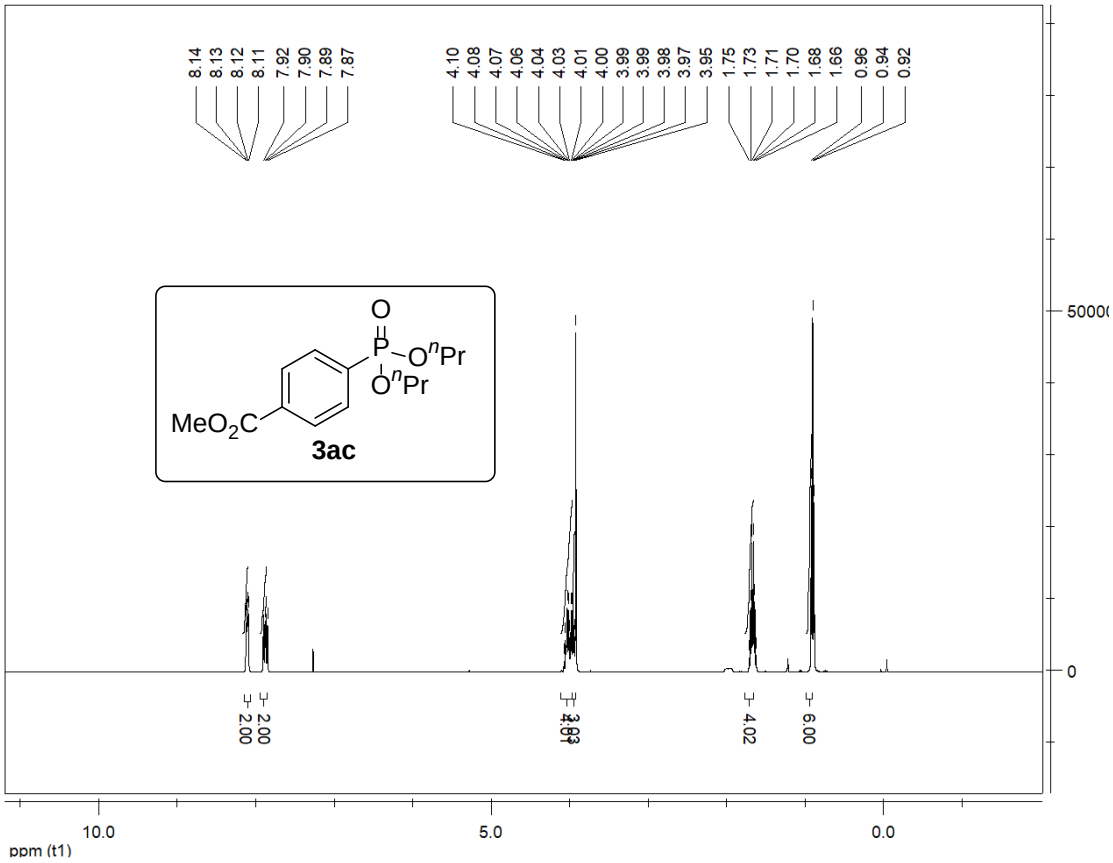
7) ^{1}H and ^{13}C NMR spectra



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8.13
8.12
8.11
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7.90
7.89
7.87
4.10
4.08
4.07
4.06
4.04
4.03
4.01
4.00
3.99
3.99
3.98
3.97
3.95
1.75
1.73
1.71
1.70
1.68
1.66
0.96
0.94
0.92
O
P
O^{n}Pr
O^{n}Pr
MeO$_2$C
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2.00
2.00
4.02
6.00
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10.0
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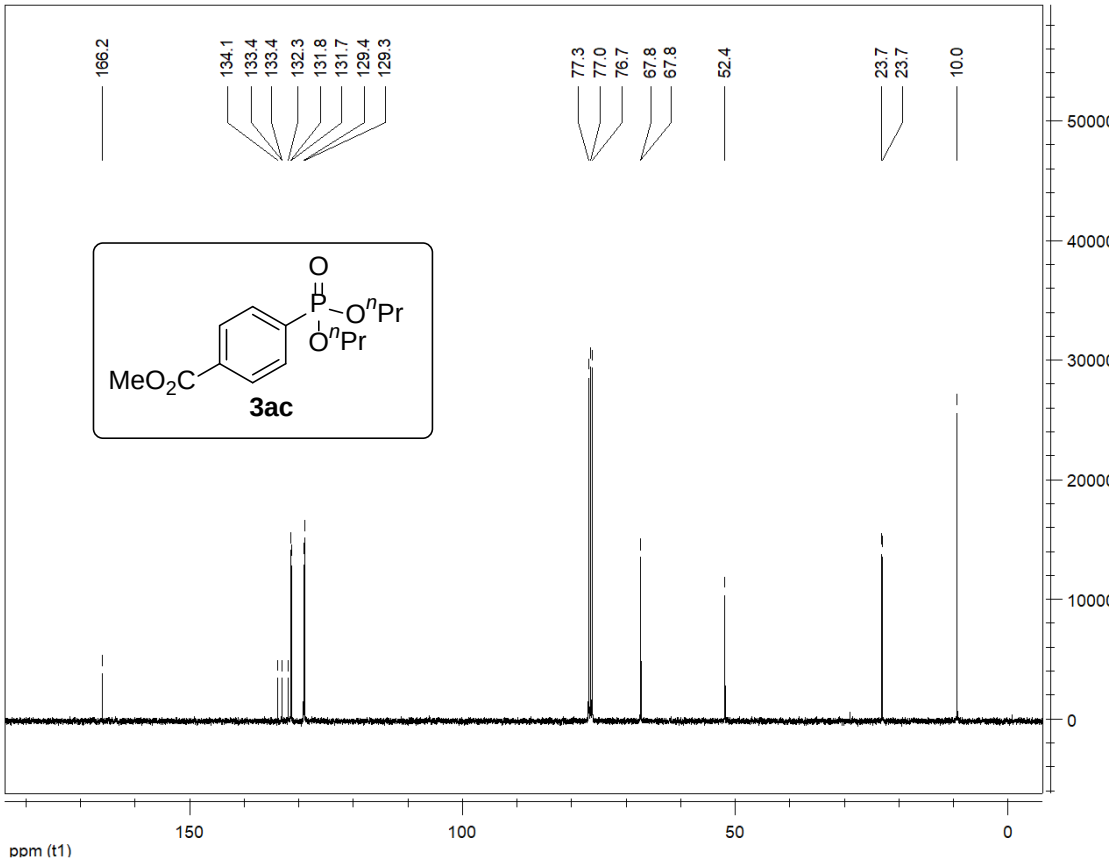
ppm (t1)


166.2
134.1
133.4
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77.0
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67.8
67.8
52.4
23.7
23.7
10.0
O
P
O^{n}Pr
O^{n}Pr
MeO$_2$C
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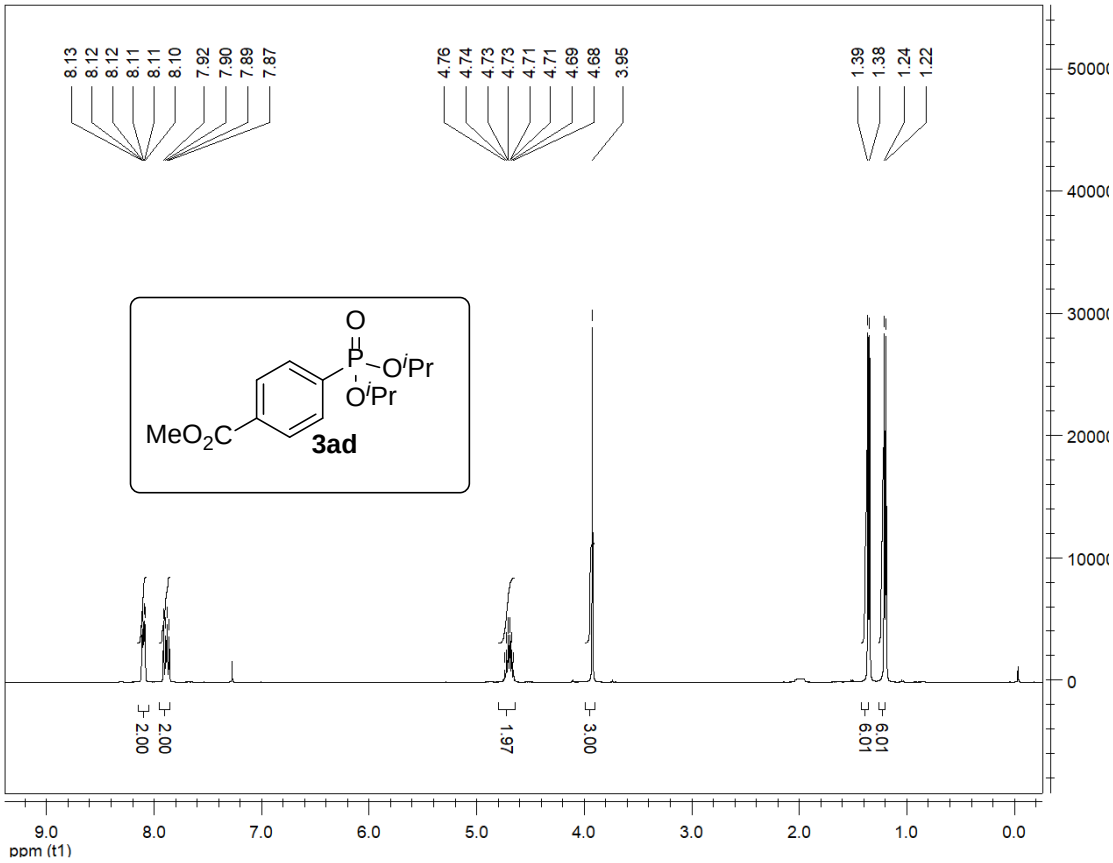
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)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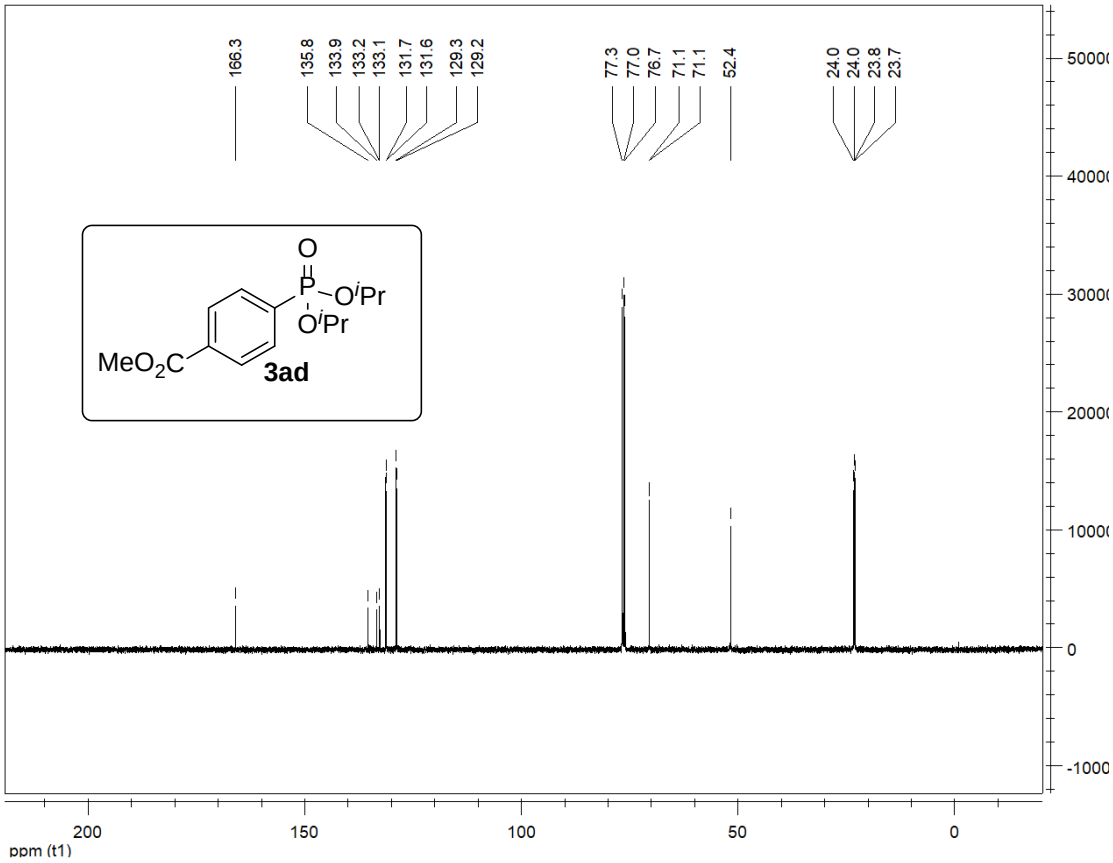
8.12
8.12
8.11
8.11
8.10
7.92
7.90
7.89
7.87
4.76
4.74
4.73
4.73
4.71
4.71
4.69
4.68
3.95
1.39
1.38
1.24
1.22
O
P
O^{i}Pr
O^{i}Pr
MeO$_2$C
3ad
2.00
2.00
1.97
3.00
6.01
6.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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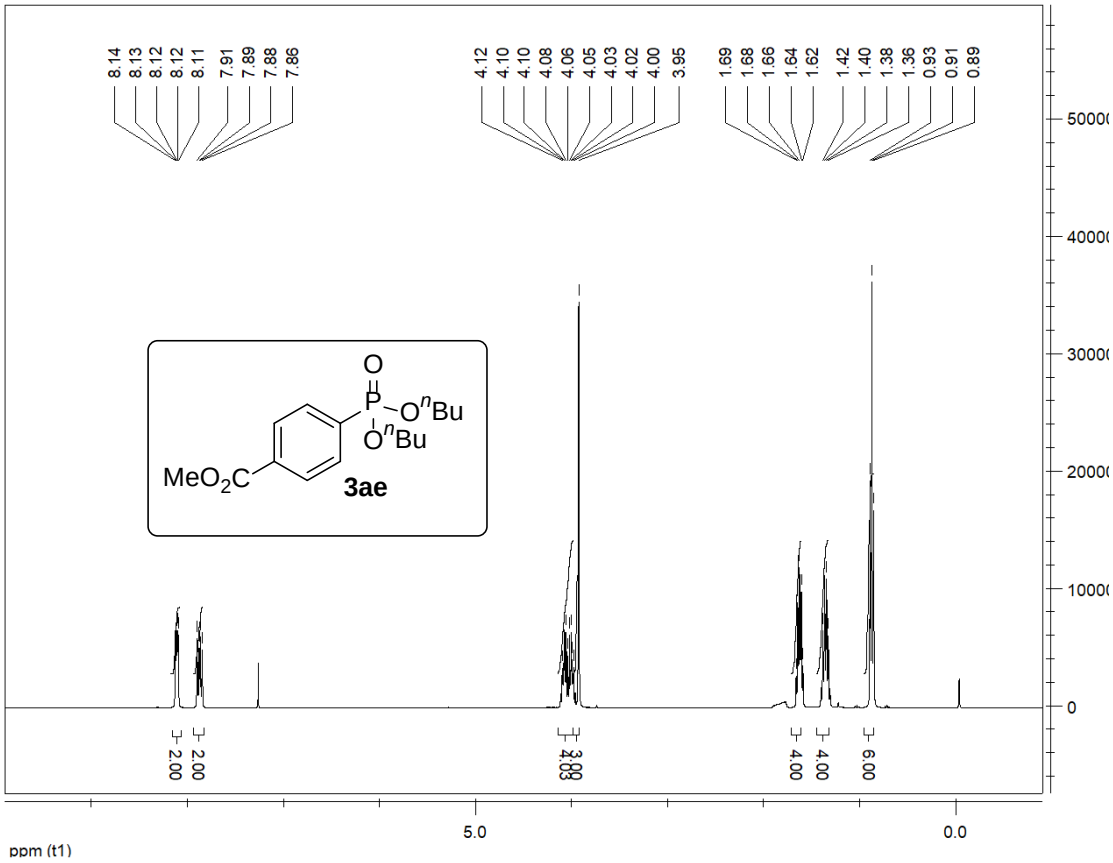
133.9
133.2
133.1
131.7
131.6
129.3
129.2
77.3
77.0
76.7
71.1
71.1
52.4
24.0
24.0
23.8
23.7
O
P
O^{i}Pr
O^{i}Pr
MeO$_2$C
3ad
200
150
100
50
0
ppm (t1)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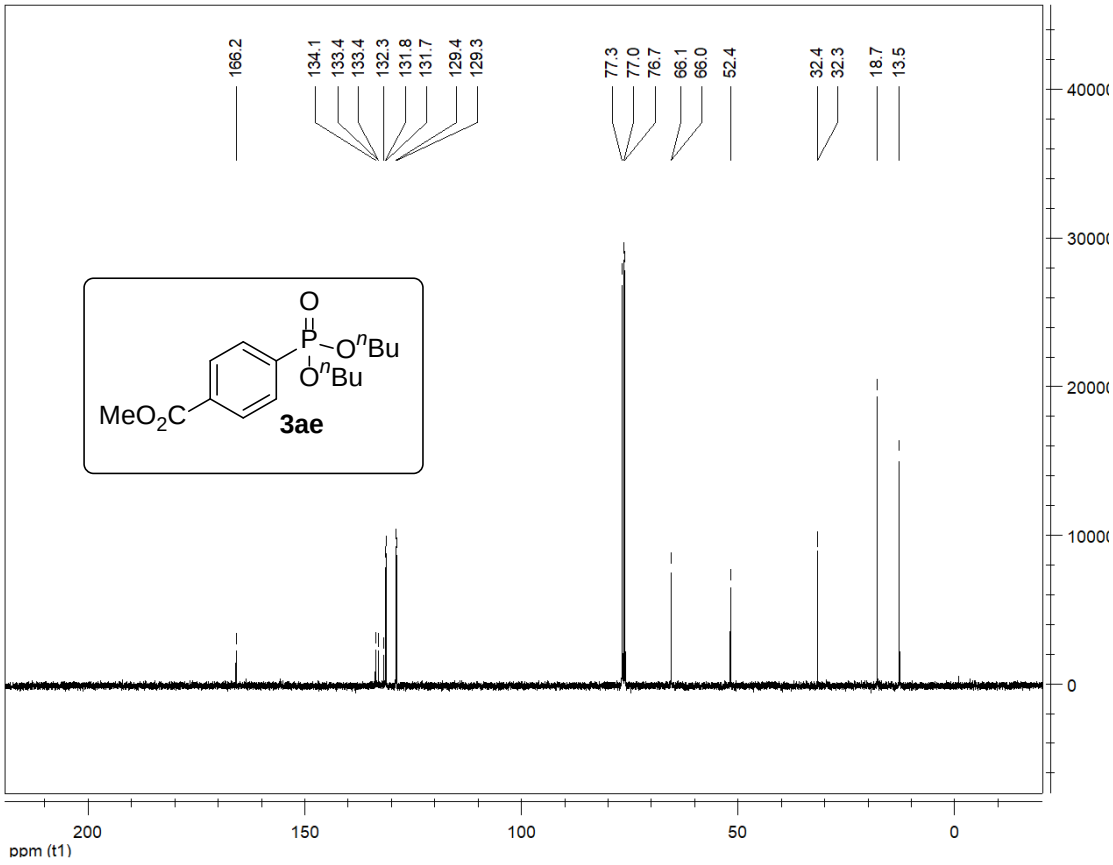
8.13
8.12
8.12
8.11
7.91
7.89
7.88
7.86
4.12
4.10
4.10
4.08
4.06
4.05
4.03
4.02
4.00
3.95
1.69
1.68
1.66
1.64
1.62
1.42
1.40
1.38
1.36
0.93
0.91
0.89
O
P
O^{n}Bu
O^{n}Bu
MeO$_2$C
3ae
2.00
2.00
3.08
4.00
4.00
6.00
5.0
0.0
ppm (t1)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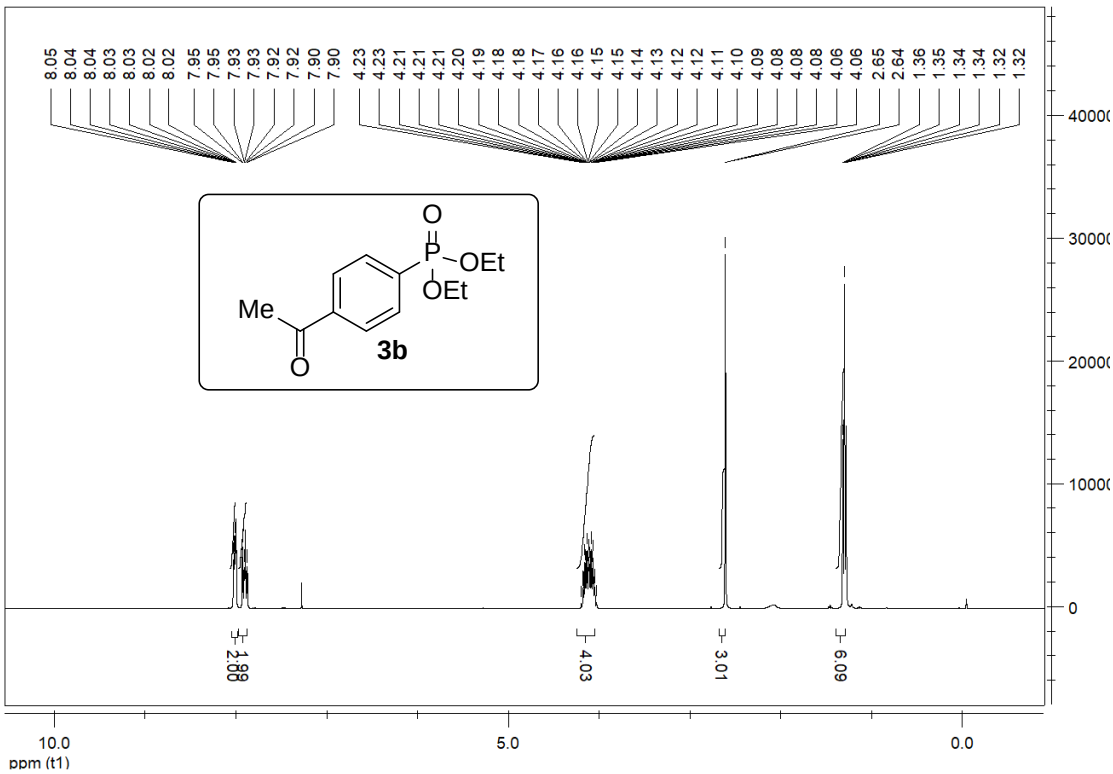
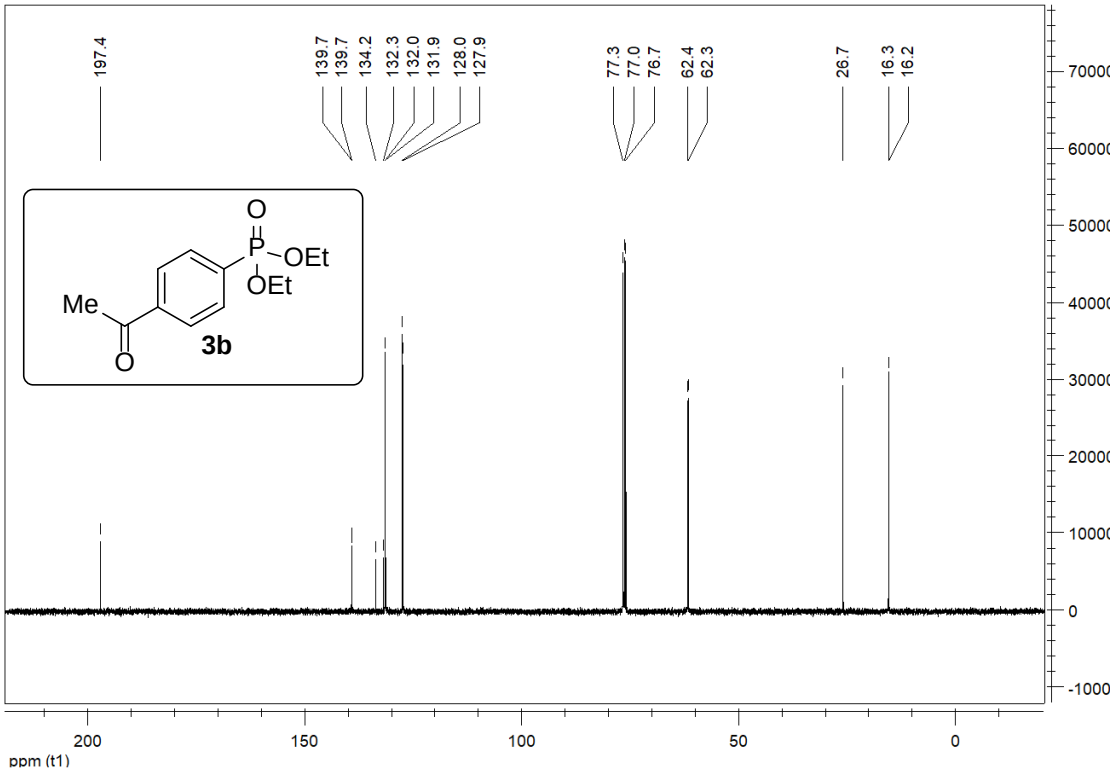
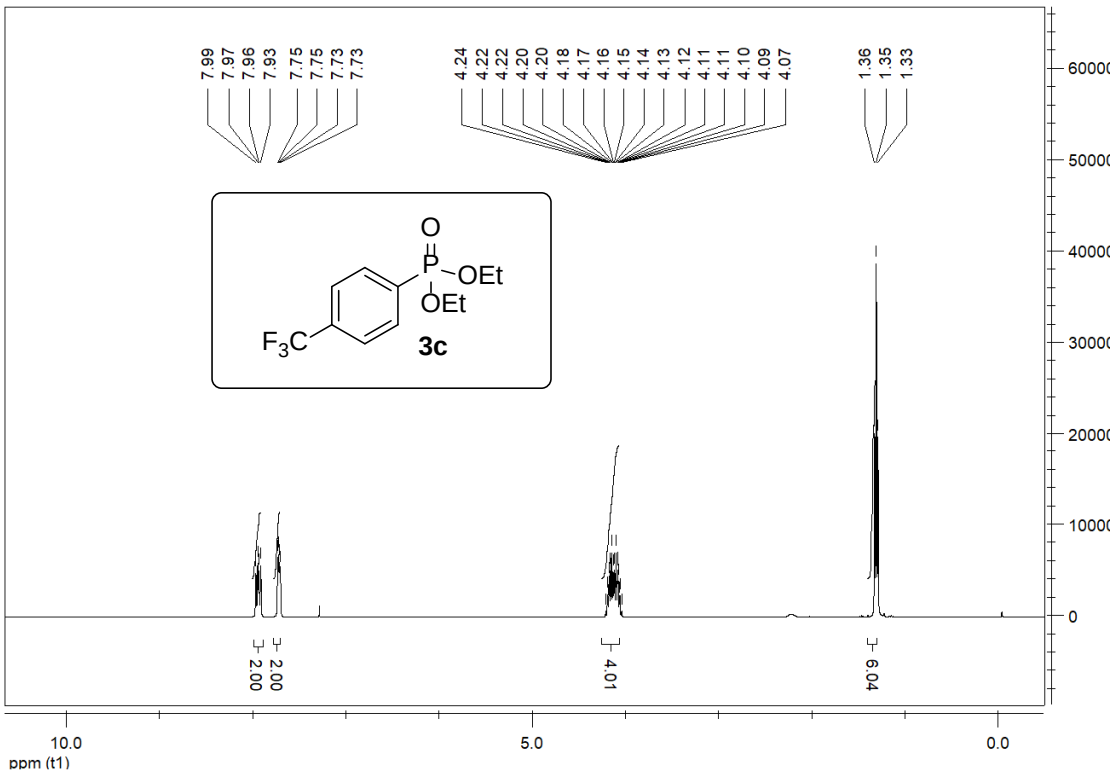
131.8
131.7
129.4
129.3
77.3
77.0
76.7
66.1
66.0
52.4
32.4
32.3
18.7
13.5
O
P
O^{n}Bu
O^{n}Bu
MeO$_2$C
3ae
200
150
100
50
0
ppm (t1)


8.05 8.04 8.04 8.03 8.03 8.02 8.02 7.95 7.95 7.93 7.93 7.92 7.92 7.90 7.90
4.23 4.23 4.21 4.21 4.21 4.20 4.19 4.18 4.18 4.17 4.16 4.16 4.15 4.15 4.14 4.13 4.12 4.12 4.11 4.10 4.09 4.08 4.08 4.06 4.06
2.65 2.64 1.36 1.35 1.34 1.34 1.32 1.32
O
P
OEt
OEt
Me
O
3b
2.00
4.03
3.01
6.09
10.0
5.0
0.0
ppm (t1)


197.4
139.7 139.7 134.2 132.3 132.0 131.9 128.0 127.9
77.3 77.0 76.7 62.4 62.3
26.7
16.3 16.2
O
P
OEt
OEt
Me
O
3b
200
150
100
50
0
ppm (t1)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7.75
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7.73
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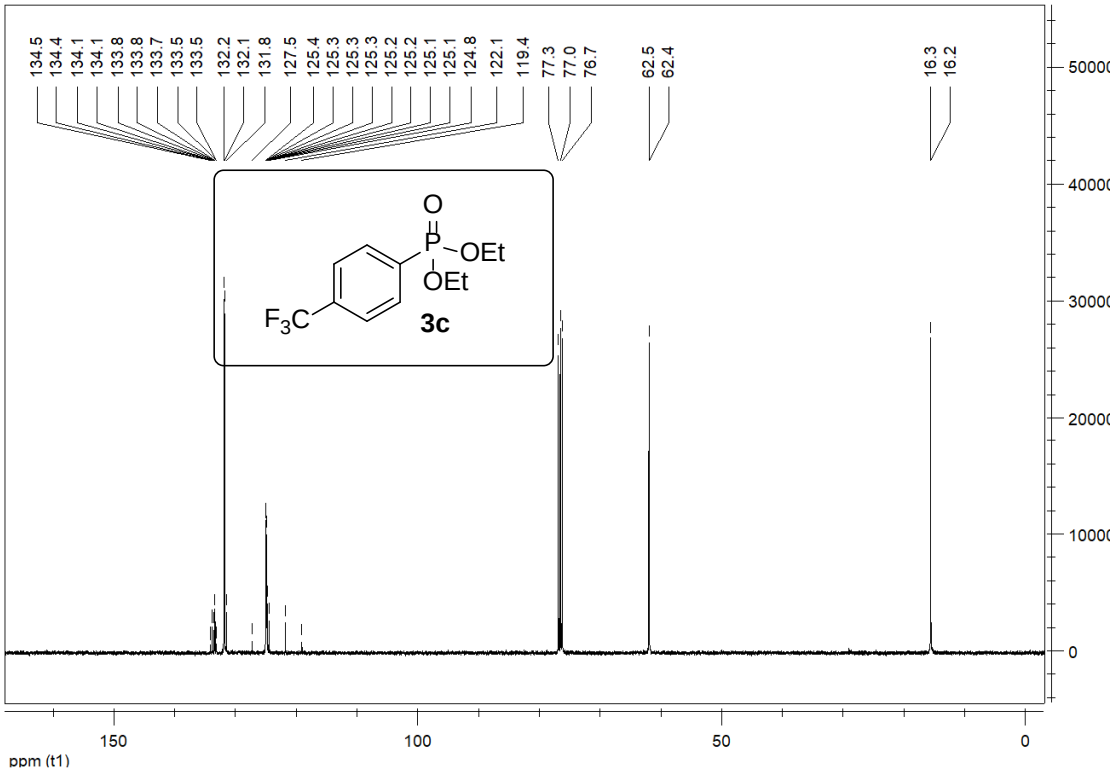
4.22
4.22
4.20
4.20
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.10
4.09
4.07
1.36
1.35
1.33
O
P
OEt
OEt
F3C
3c
2.00
2.00
4.01
9.04
10.0
5.0
0.0
ppm (t1)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134.1
134.1
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133.8
133.7
133.5
133.5
132.2
132.1
131.8
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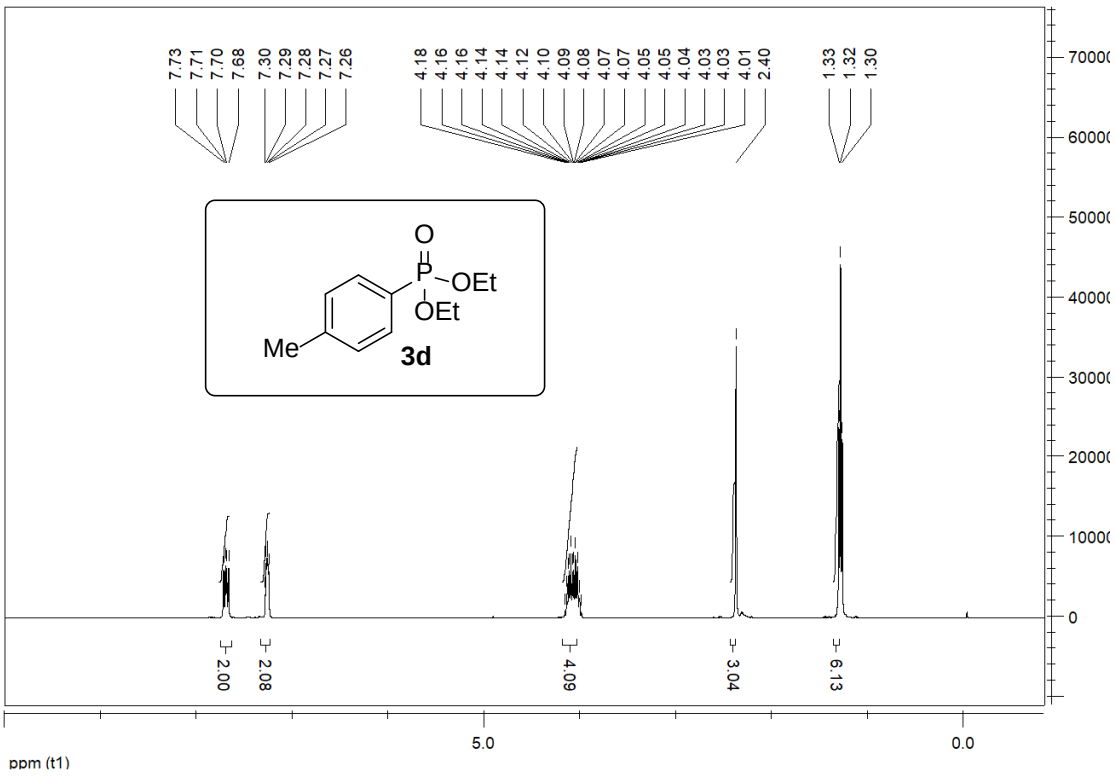
125.4
125.3
125.3
125.3
125.2
125.2
125.1
125.1
124.8
122.1
119.4
77.3
77.0
76.7
62.5
62.4
16.3
16.2
O
P
OEt
OEt
F3C
3c
150
100
50
0
ppm (t1)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7.68
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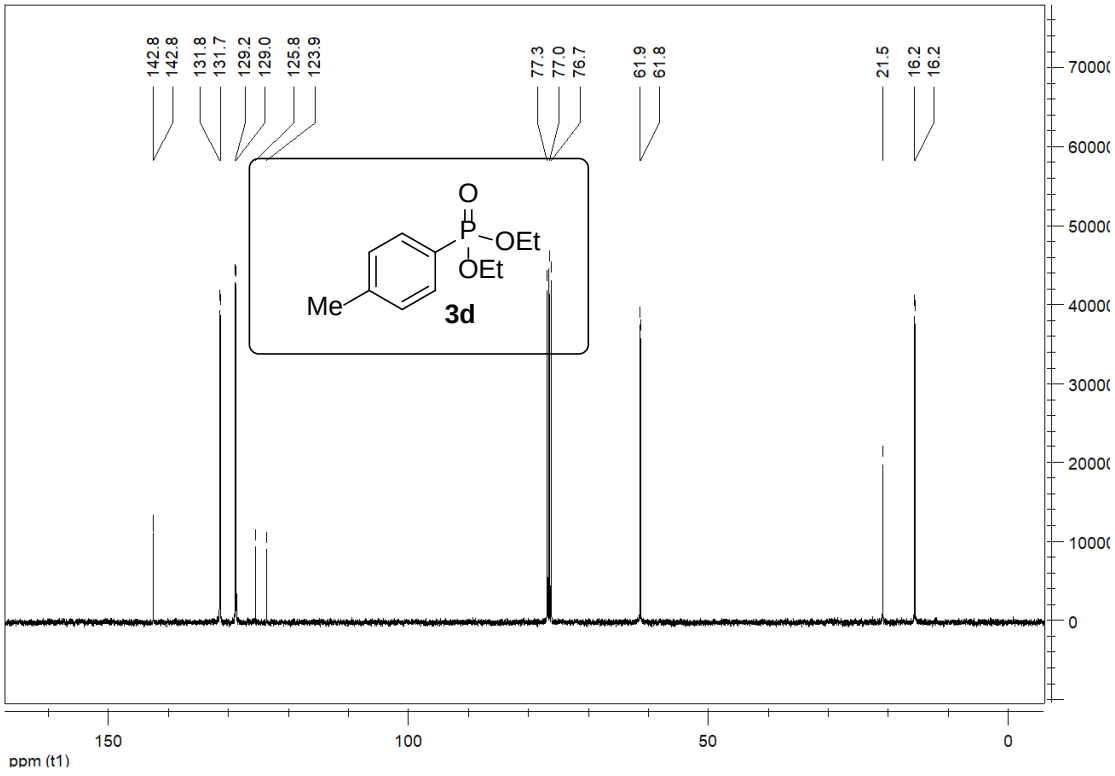
7.27
7.26
4.18
4.16
4.16
4.14
4.14
4.12
4.10
4.09
4.08
4.07
4.07
4.05
4.05
4.04
4.03
4.03
4.01
2.40
1.33
1.32
1.30
O
P
OEt
OEt
Me
3d
2.00
2.08
4.09
3.04
6.13
5.0
0.0
ppm (t1)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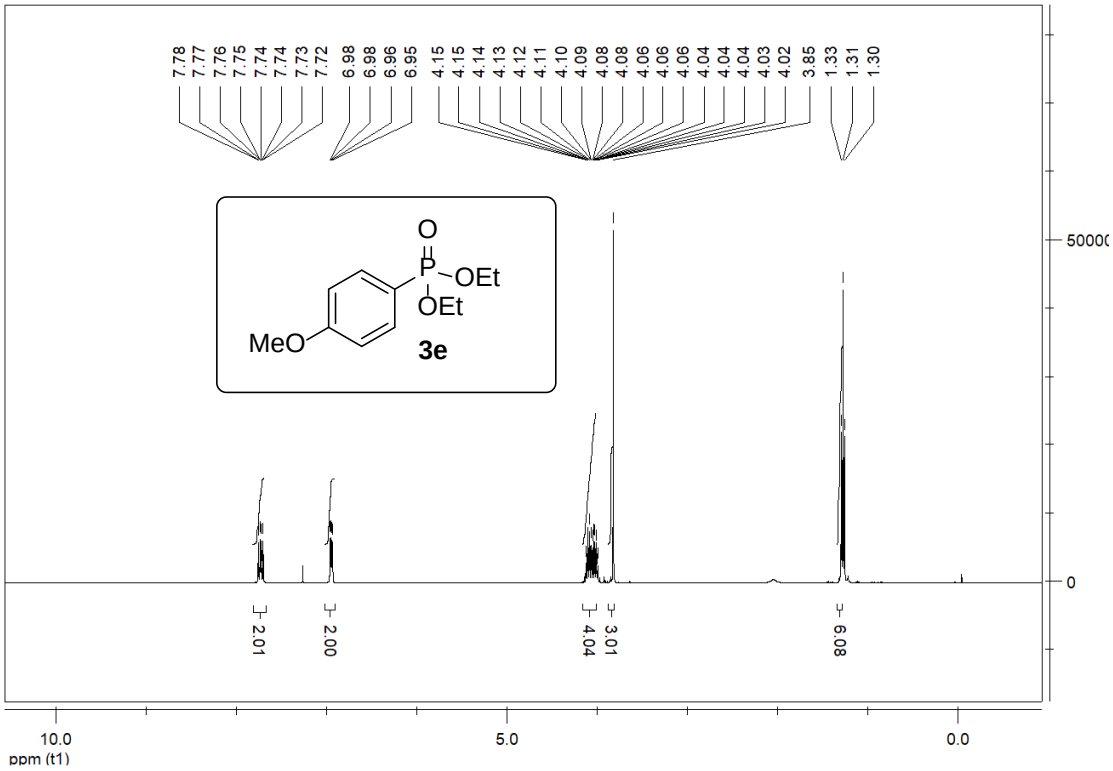
142.8
131.8
131.7
129.2
129.0
125.8
123.9
77.3
77.0
76.7
61.9
61.8
21.5
16.2
16.2
O
P
OEt
OEt
Me
3d
150
100
50
0
ppm (t1)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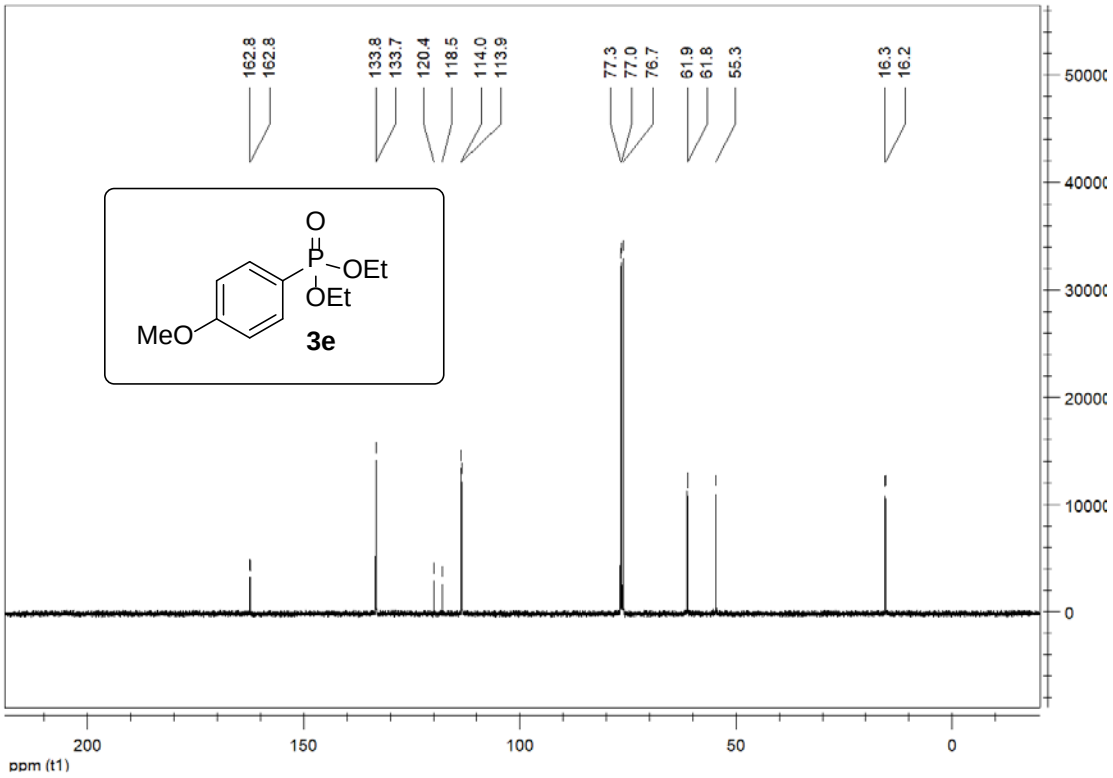
7.77
7.76
7.75
7.74
7.74
7.73
7.72
6.98
6.98
6.96
6.95
4.15
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.08
4.06
4.06
4.06
4.04
4.04
4.04
4.03
4.02
3.85
1.33
1.31
1.30
O
P
OEt
OEt
MeO
3e
2.01
2.00
4.04
3.01
6.08
50000
0
10.0
5.0
0.0
ppm (t1)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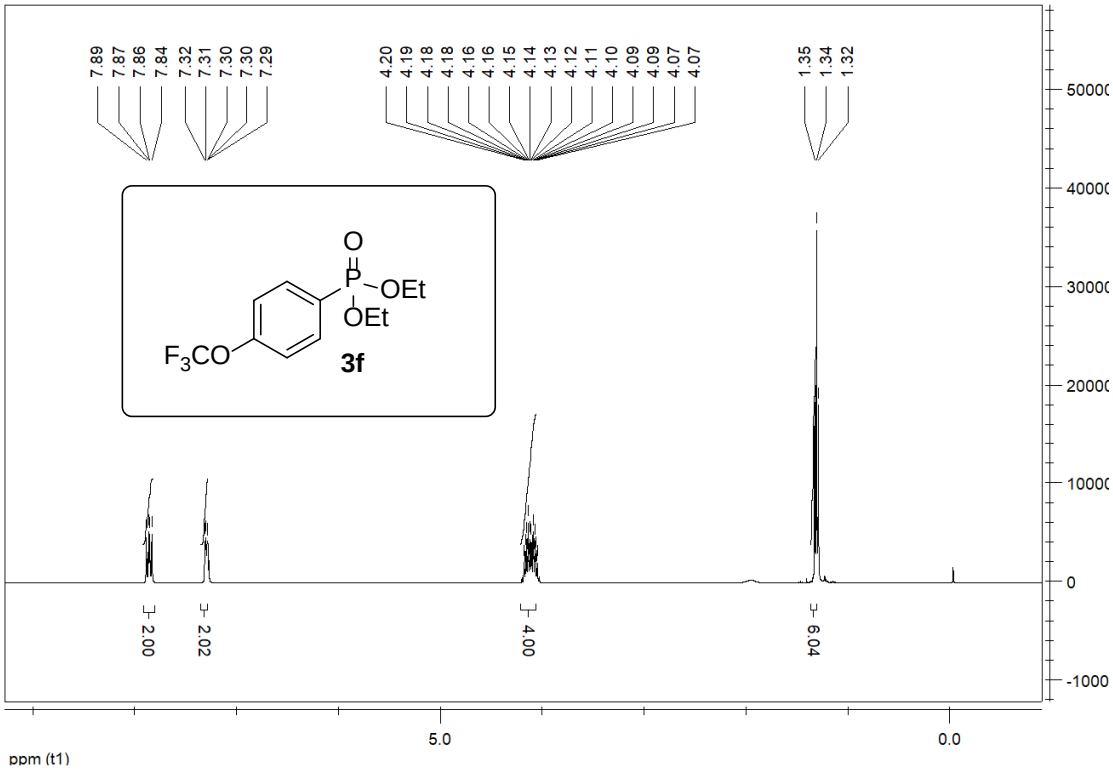
162.8
133.8
133.7
120.4
118.5
114.0
113.9
77.3
77.0
76.7
61.9
61.8
55.3
16.3
16.2
O
P
OEt
OEt
MeO
3e
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)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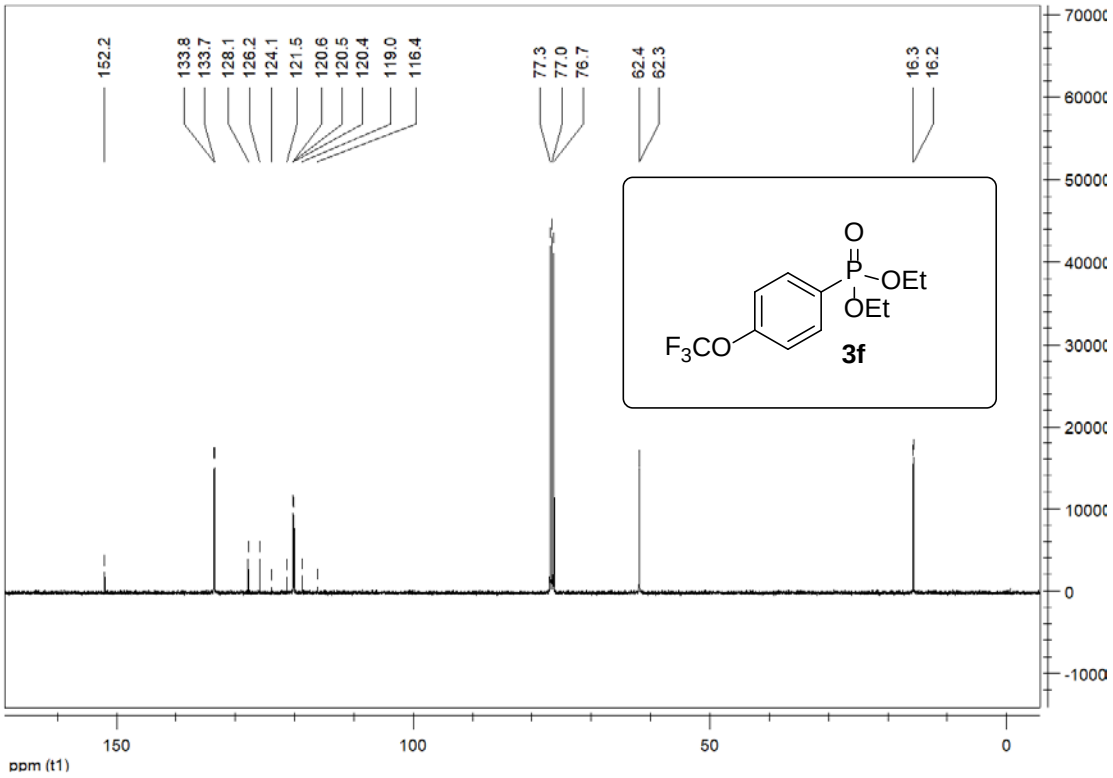
7.31
7.30
7.30
7.29
4.20
4.19
4.18
4.18
4.16
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.09
4.07
4.07
1.35
1.34
1.32
O
P
OEt
OEt
F3CO
3f
2.00
2.02
4.00
9.04
5.0
0.0
ppm (t1)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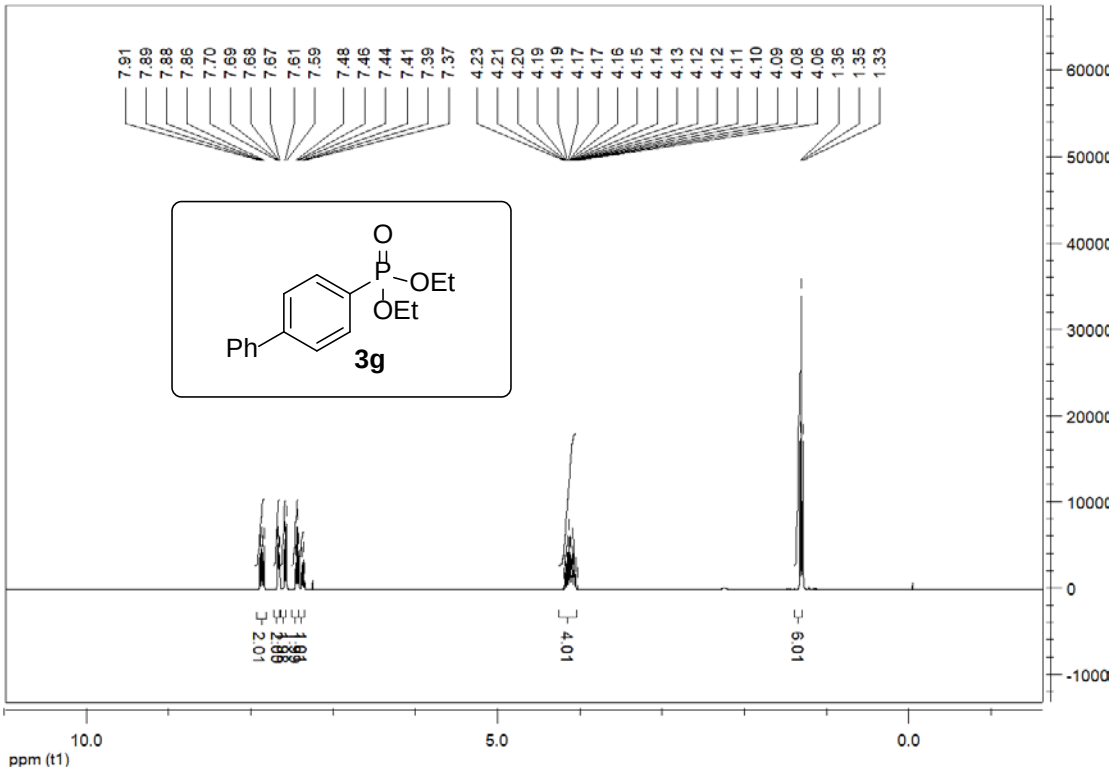
133.8
133.7
128.1
126.2
124.1
121.5
120.6
120.5
120.4
119.0
116.4
77.3
77.0
76.7
62.4
62.3
16.3
16.2
O
P
OEt
OEt
F3CO
3f
150
100
50
0
ppm (t1)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7.69
7.68
7.67
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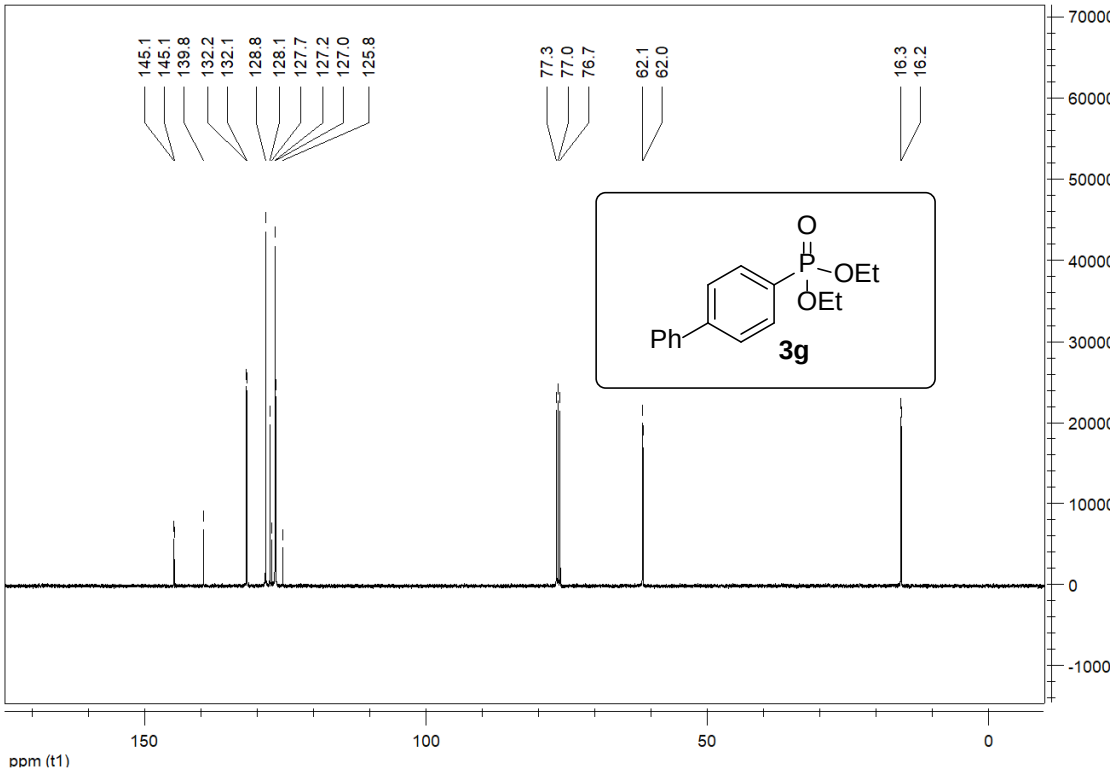
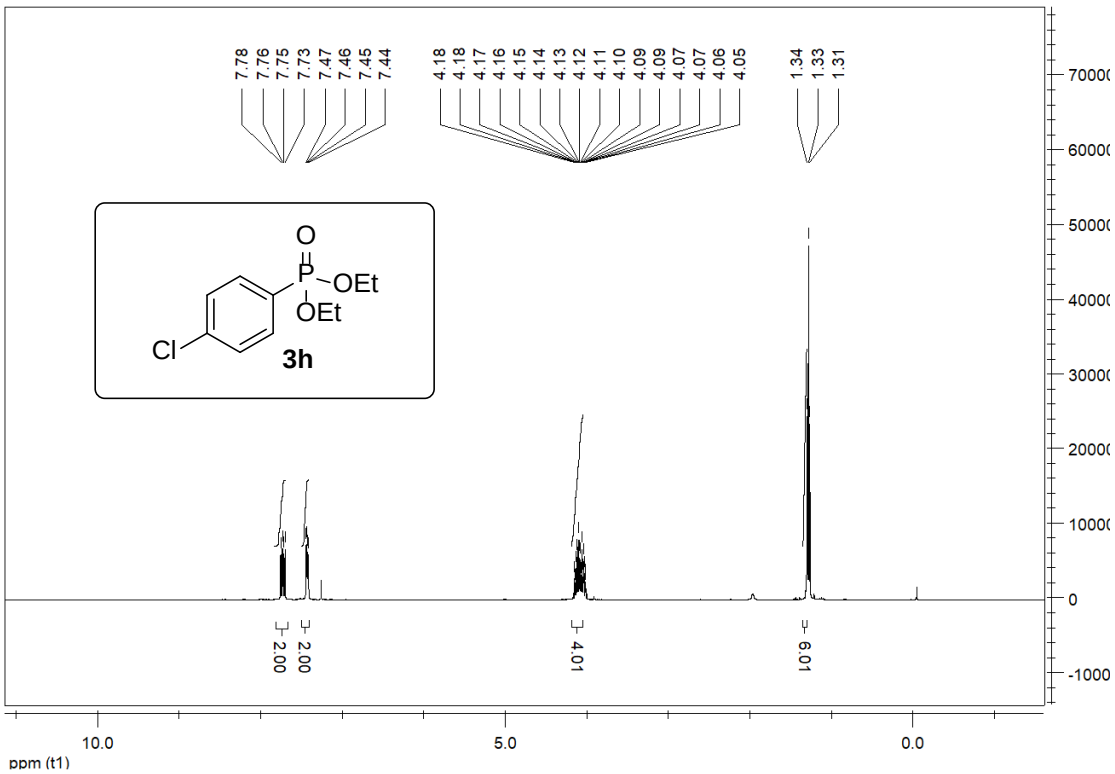
7.59
7.48
7.46
7.44
7.41
7.39
7.37
4.23
4.21
4.20
4.19
4.19
4.17
4.17
4.16
4.15
4.14
4.13
4.12
4.12
4.11
4.10
4.09
4.08
4.06
1.36
1.35
1.33
O
P
OEt
OEt
Ph
3g
2.01
4.01
6.01
10.0
5.0
0.0
ppm (t1)


145.1
145.1
139.8
132.2
132.1
128.8
128.1
127.7
127.2
127.0
125.8
77.3
77.0
76.7
62.1
62.0
16.3
16.2
O
P
OEt
OEt
Ph
3g
150
100
50
0
ppm (t1)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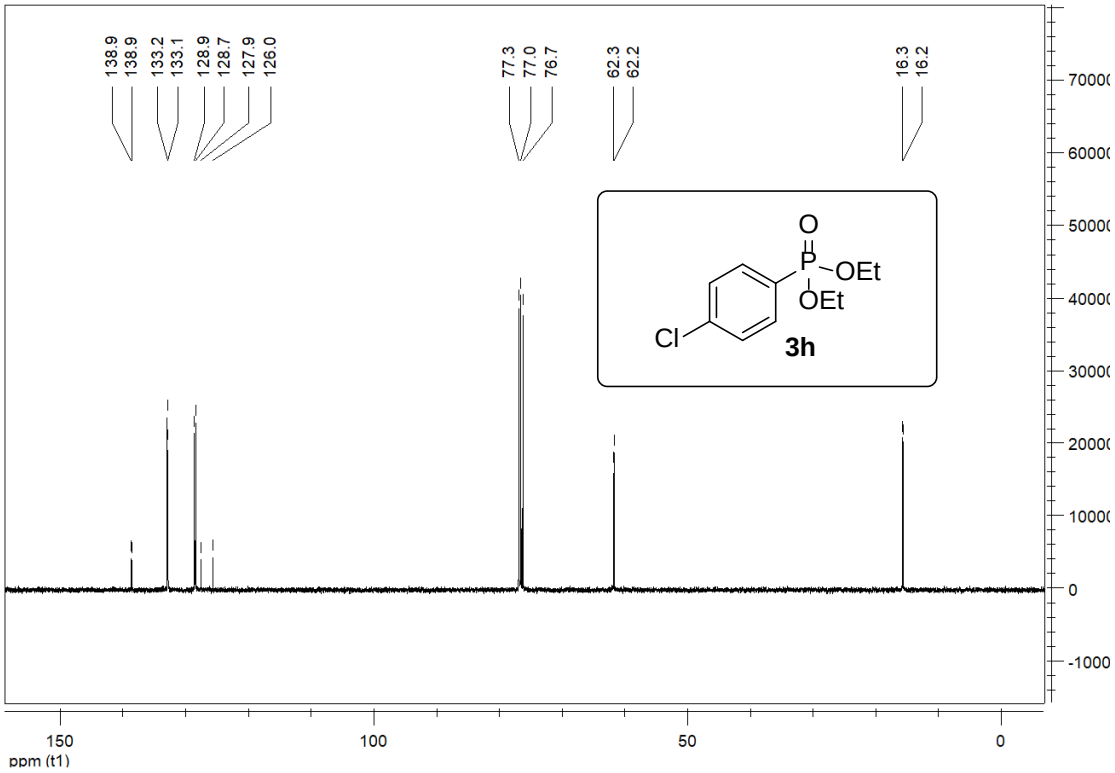
7.46
7.45
7.44
4.18
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.09
4.07
4.07
4.06
4.05
1.34
1.33
1.31
O
P
OEt
OEt
Cl
3h
2.00
2.00
4.01
6.01
10.0
5.0
0.0
ppm (t1)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138.9
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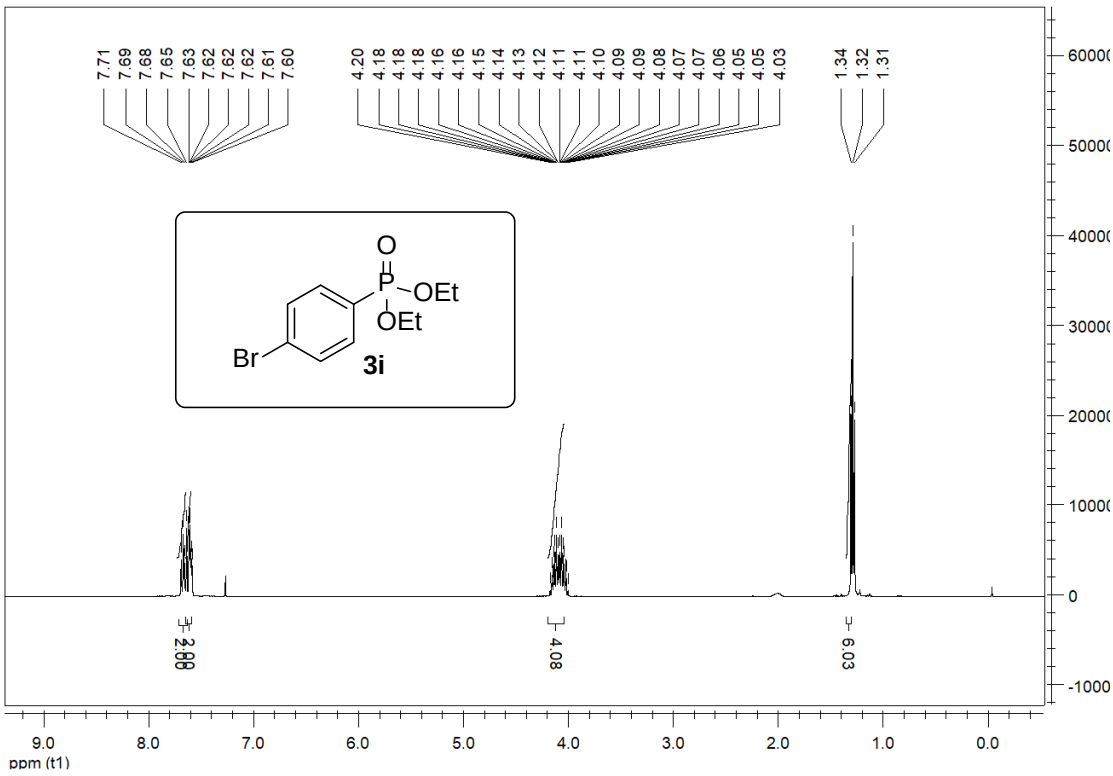
128.7
127.9
126.0
77.3
77.0
76.7
62.3
62.2
16.3
16.2
O
P
OEt
OEt
Cl
3h
150
100
50
0
ppm (t1)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7.62
7.62
7.62
7.61
7.60
4.20
4.18
4.18
4.18
4.16
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.10
4.09
4.09
4.08
4.07
4.07
4.06
4.05
4.05
4.03
1.34
1.32
1.31
O
P
OEt
OEt
Br
3i
2.00
4.08
6.03
9.0
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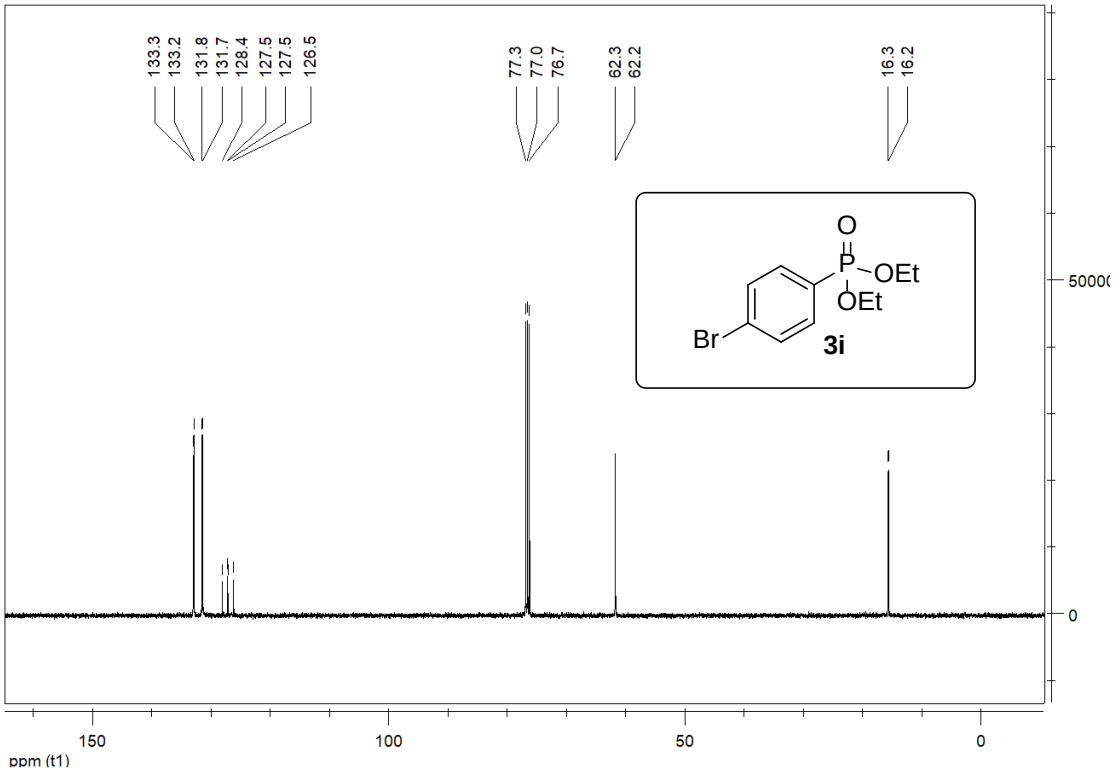
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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133.2
131.8
131.7
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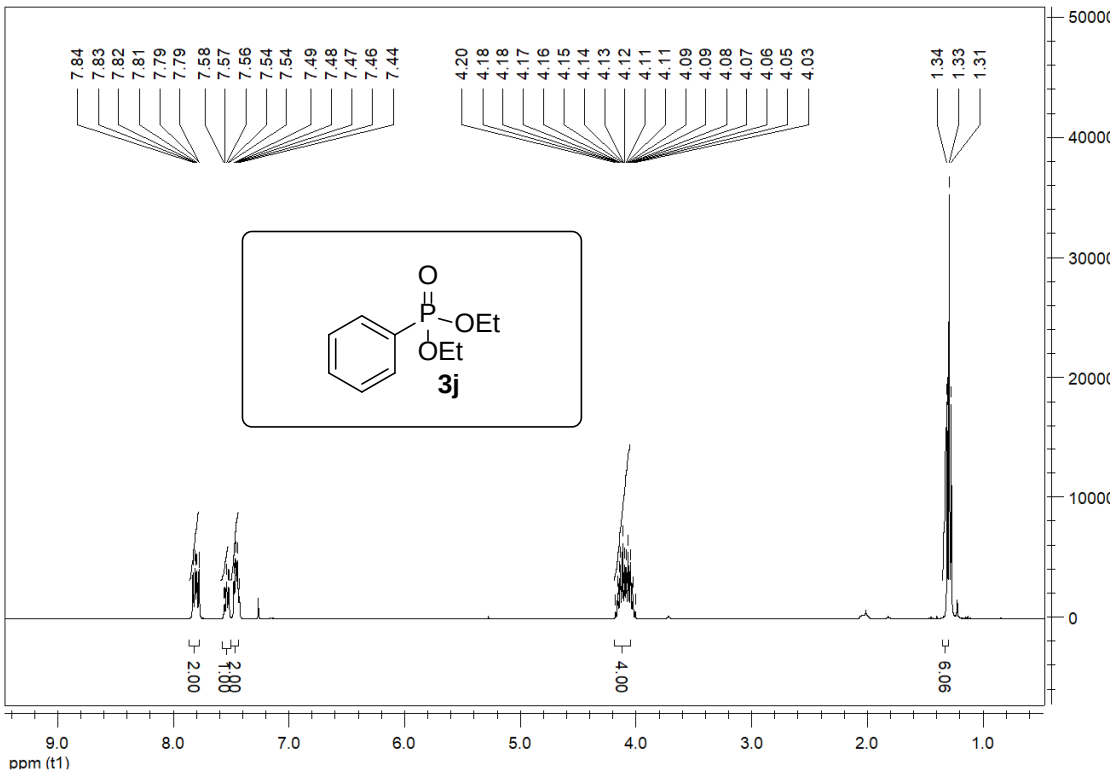
127.5
127.5
126.5
77.3
77.0
76.7
62.3
62.2
16.3
16.2
O
P
OEt
OEt
Br
3i
150
100
50
0
ppm (t1)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7.48
7.47
7.46
7.44
4.20
4.18
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.09
4.09
4.08
4.07
4.06
4.05
4.03
1.34
1.33
1.31
O
P
OEt
OEt
3j
2.00
2.08
4.00
6.06
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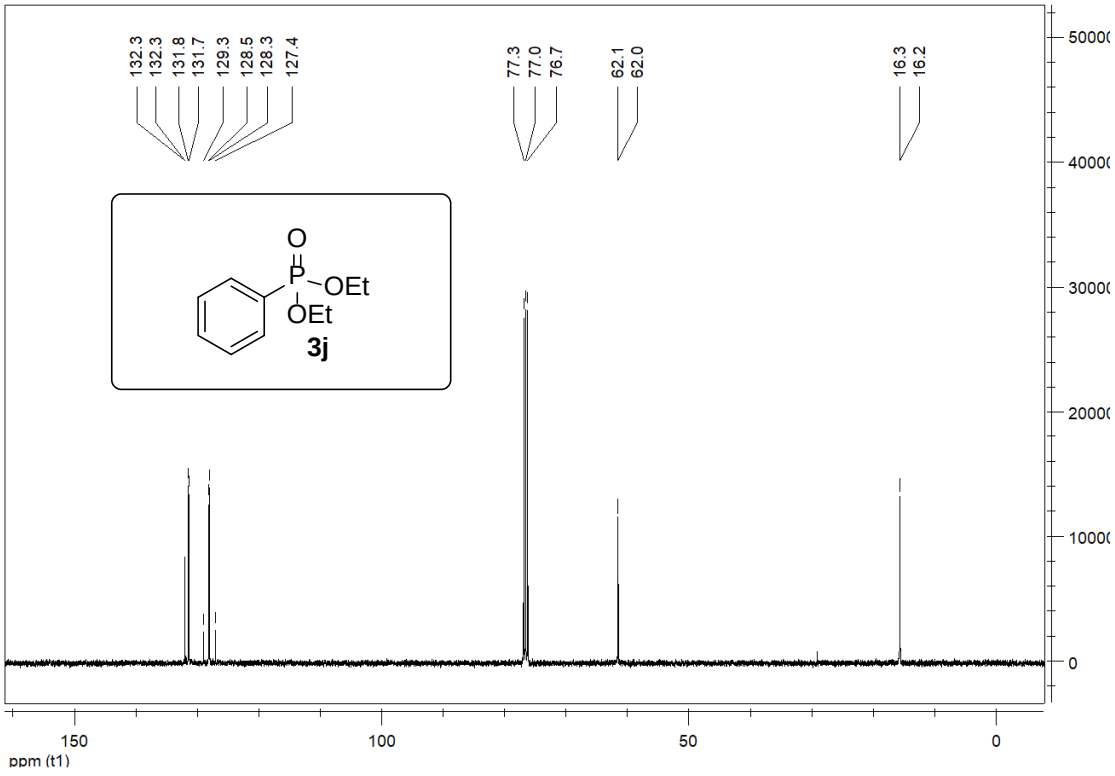
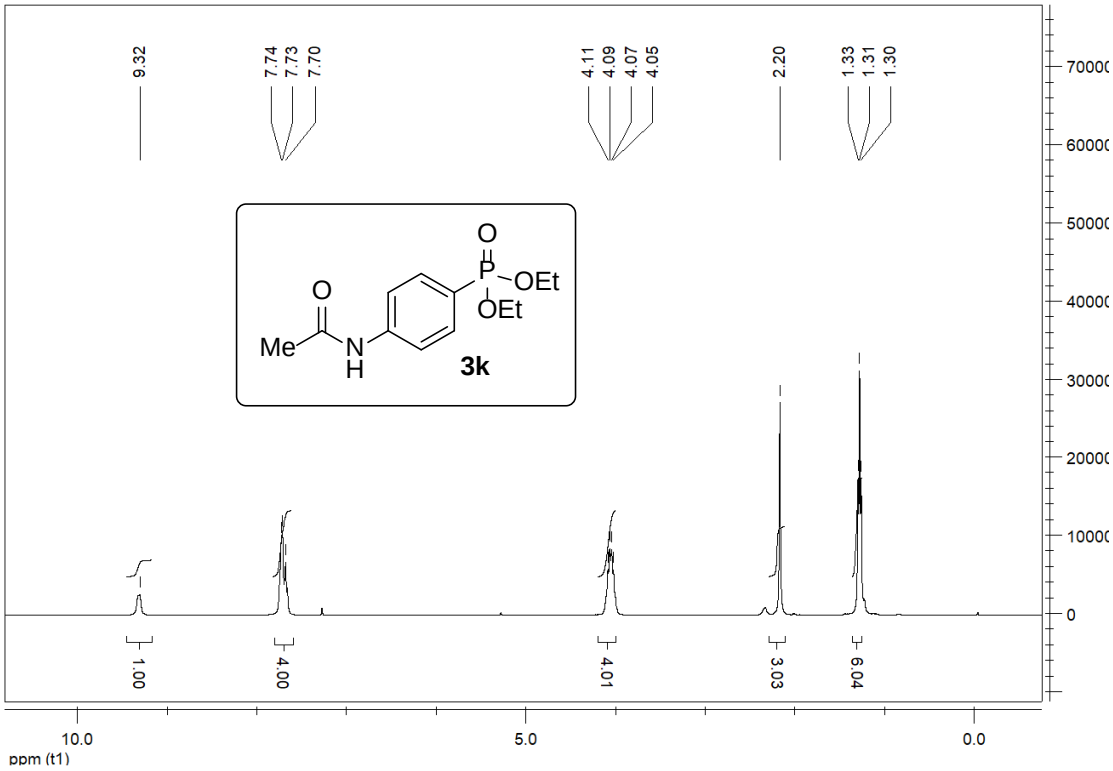
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


132.3
132.3
131.8
131.7
129.3
128.5
128.3
127.4
77.3
77.0
76.7
62.1
62.0
16.3
16.2
O
P
OEt
OEt
3j
150
100
50
0
ppm (t1)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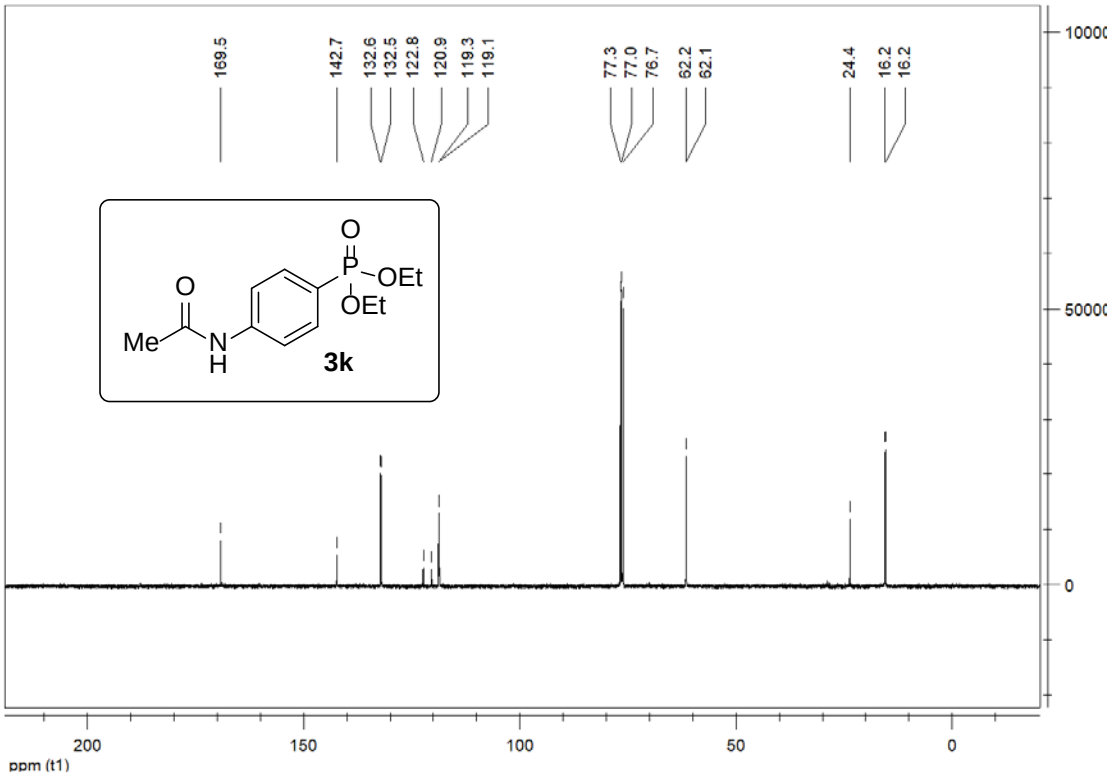
7.73
7.70
4.11
4.09
4.07
4.05
2.20
1.33
1.31
1.30
O
P
OEt
OEt
O
Me
N
H
3k
1.00
4.00
4.01
3.03
6.04
10.0
5.0
0.0
ppm (t1)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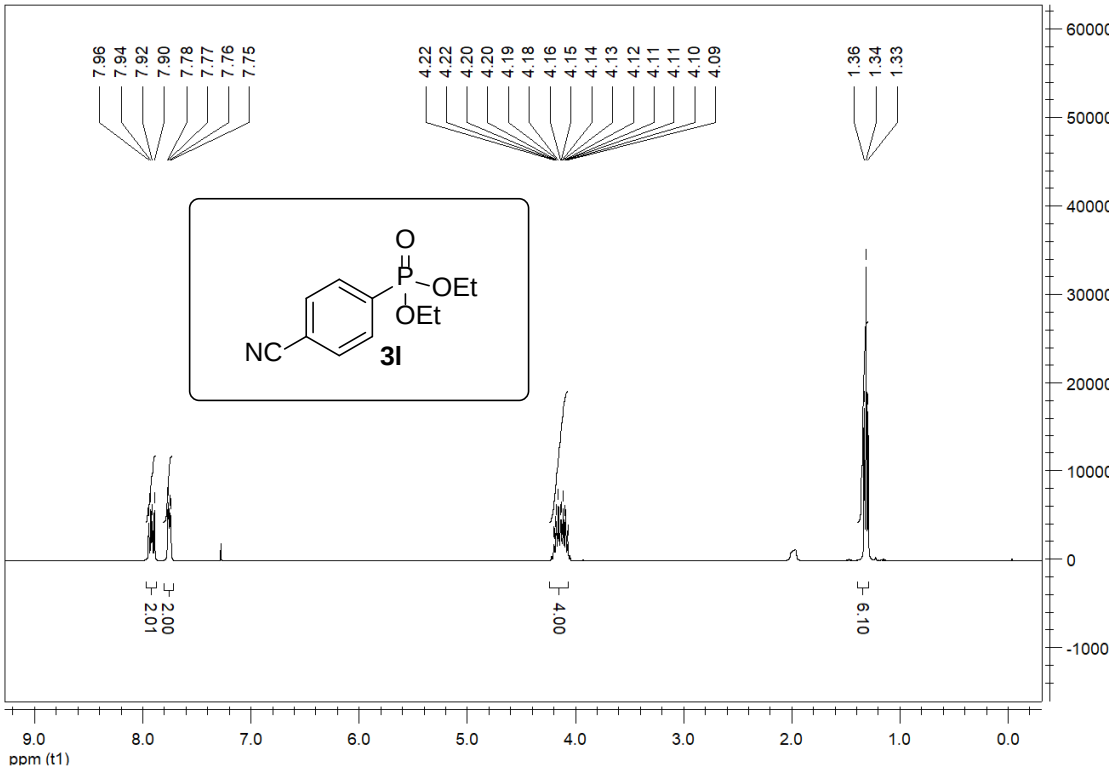
142.7
132.6
132.5
122.8
120.9
119.3
119.1
77.3
77.0
76.7
62.2
62.1
24.4
16.2
16.2
O
P
OEt
OEt
O
Me
N
H
3k
200
150
100
50
0
ppm (t1)


7.96
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7.92
7.90
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7.77
7.76
7.75
4.22
4.22
4.20
4.20
4.19
4.18
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.10
4.09
1.36
1.34
1.33
O
P
OEt
OEt
NC
3l
2.01
2.00
4.00
6.10
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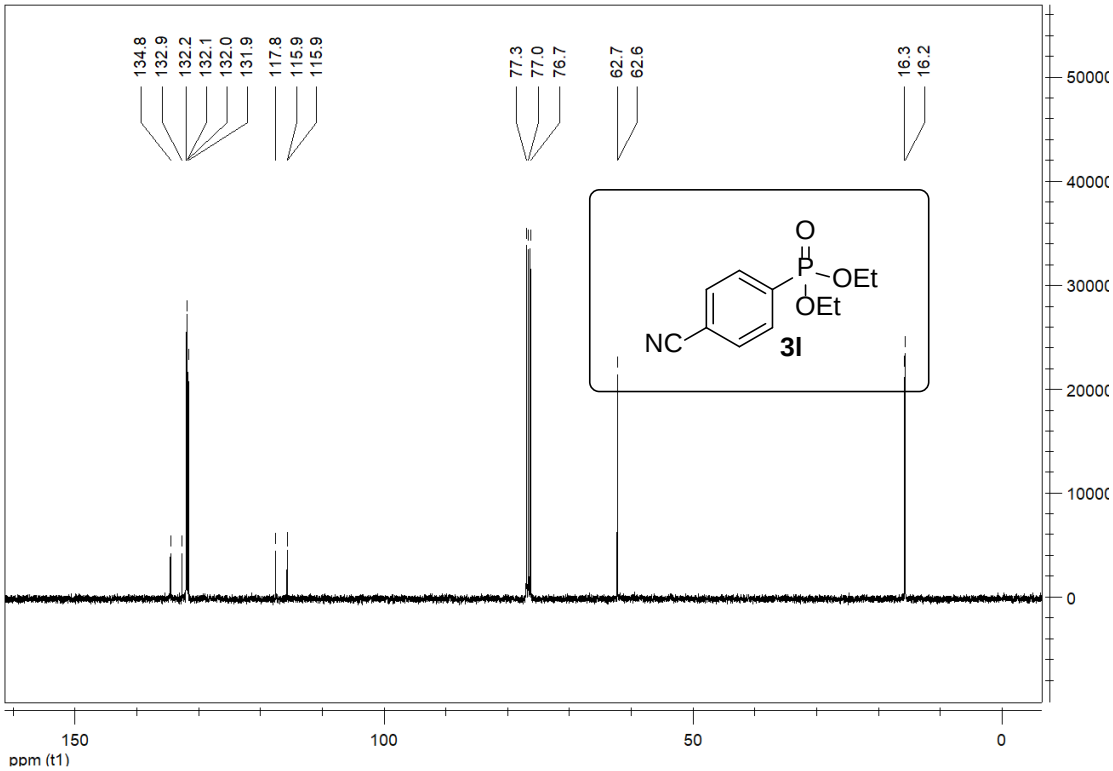
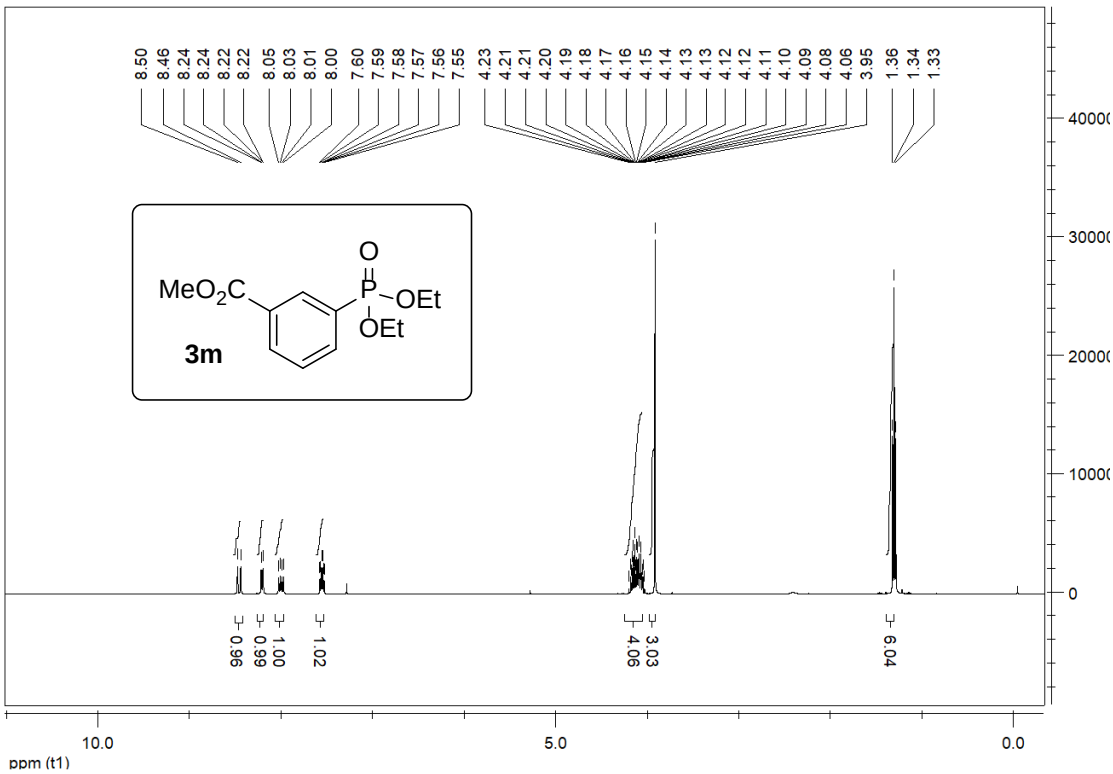
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


134.8
132.9
132.2
132.1
132.0
131.9
117.8
115.9
115.9
77.3
77.0
76.7
62.7
62.6
16.3
16.2
O
P
OEt
OEt
NC
3l
150
100
50
0
ppm (t1)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7.57
7.56
7.55
4.23
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.13
4.12
4.12
4.11
4.10
4.09
4.08
4.06
3.95
1.36
1.34
1.33
MeO2C
O
P
OEt
OEt
3m
0.96
0.99
1.00
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6.04
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30000
20000
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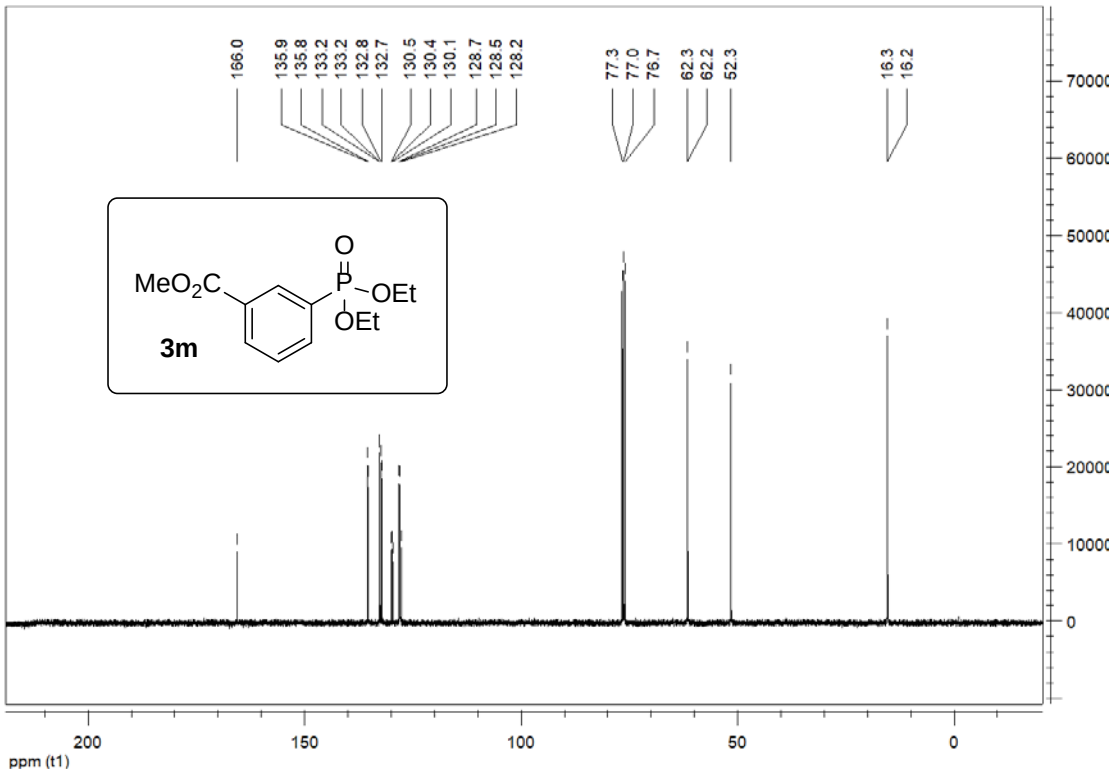
0.0
ppm (t1)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128.7
128.5
128.2
77.3
77.0
76.7
62.3
62.2
52.3
16.3
16.2
MeO2C
O
P
OEt
OEt
3m
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60000
50000
40000
30000
20000
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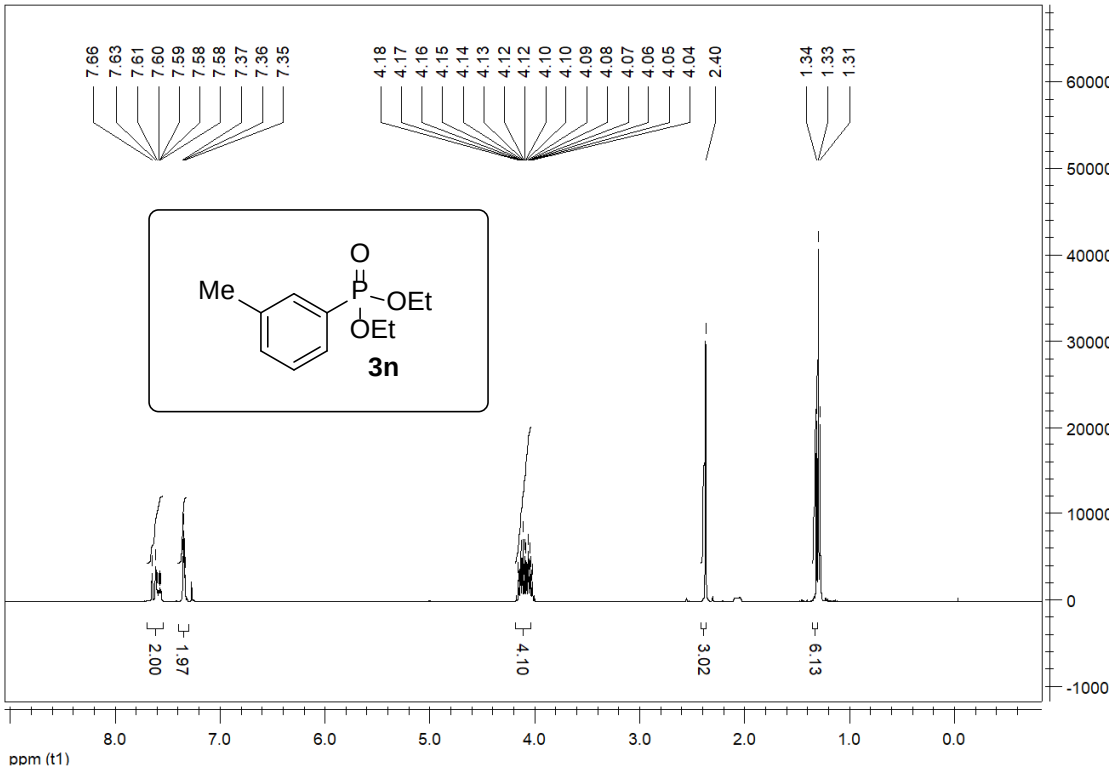
100
50
0
ppm (t1)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4.13
4.12
4.12
4.10
4.10
4.09
4.08
4.07
4.06
4.05
4.04
2.40
1.34
1.33
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P
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OEt
3n
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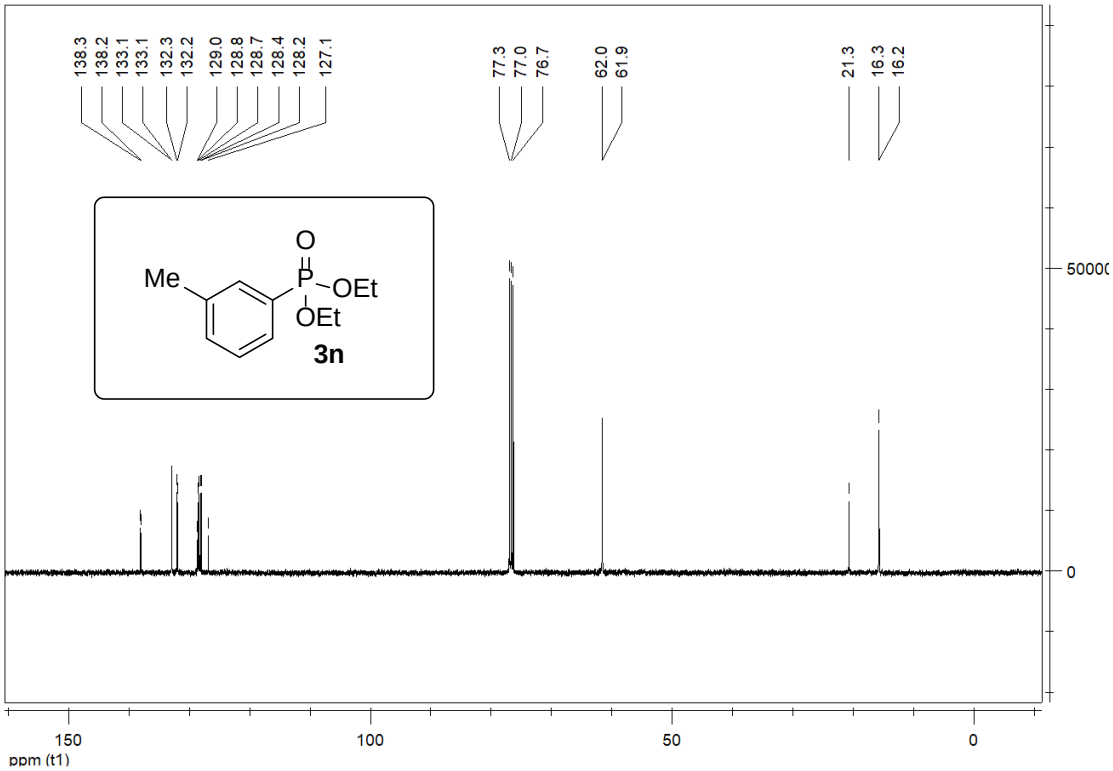
4.10
3.02
6.13
ppm (t1)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128.4
128.2
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77.3
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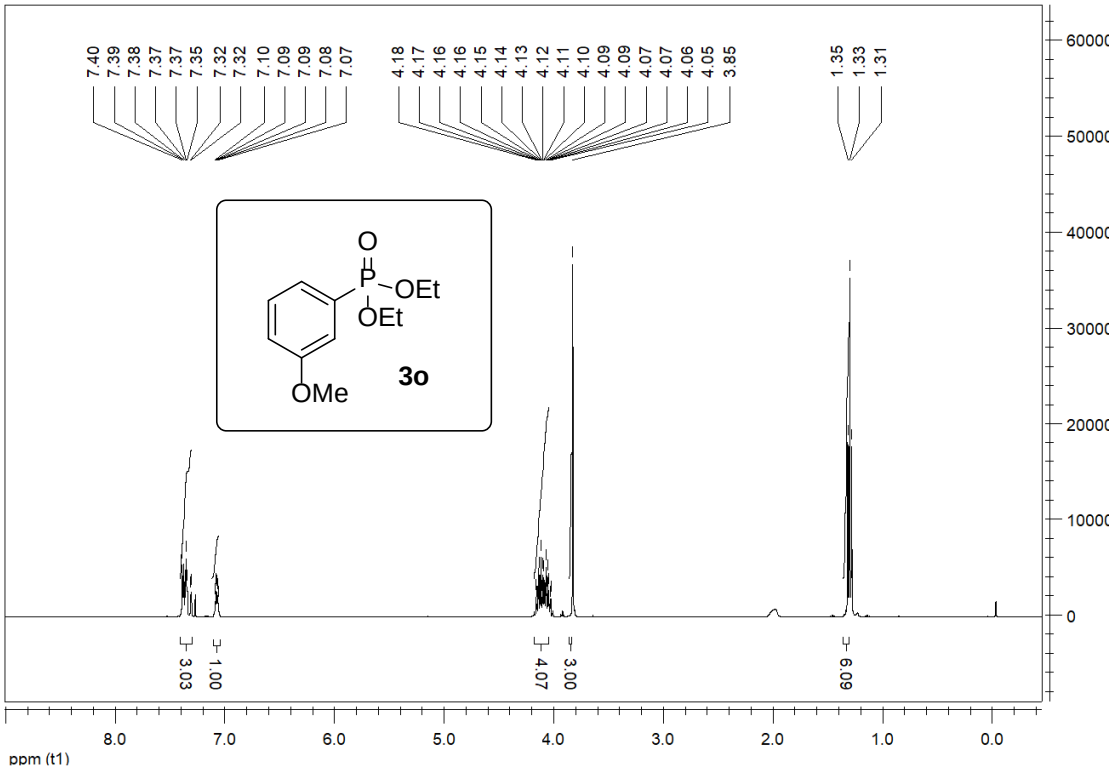
16.3
16.2
Me
O
P
OEt
OEt
3n
ppm (t1)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7.32
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7.08
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4.16
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4.11
4.10
4.09
4.09
4.07
4.07
4.06
4.05
3.85
1.35
1.33
1.31
O
P
OEt
OEt
OMe
3o
3.03
1.00
4.07
3.00
6.09
8.0
7.0
6.0
5.0
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2.0
1.0
0.0
ppm (t1)
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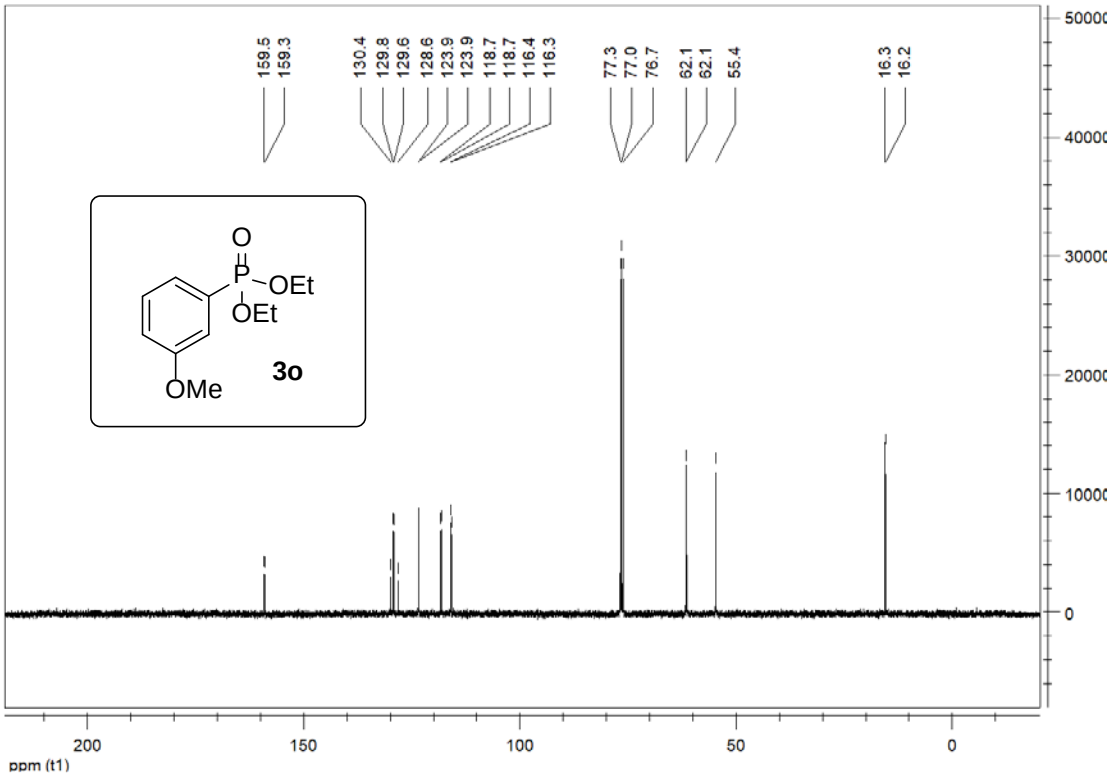
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123.9
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118.7
116.4
116.3
77.3
77.0
76.7
62.1
62.1
55.4
16.3
16.2
O
P
OEt
OEt
OMe
3o
200
150
100
50
0
ppm (t1)
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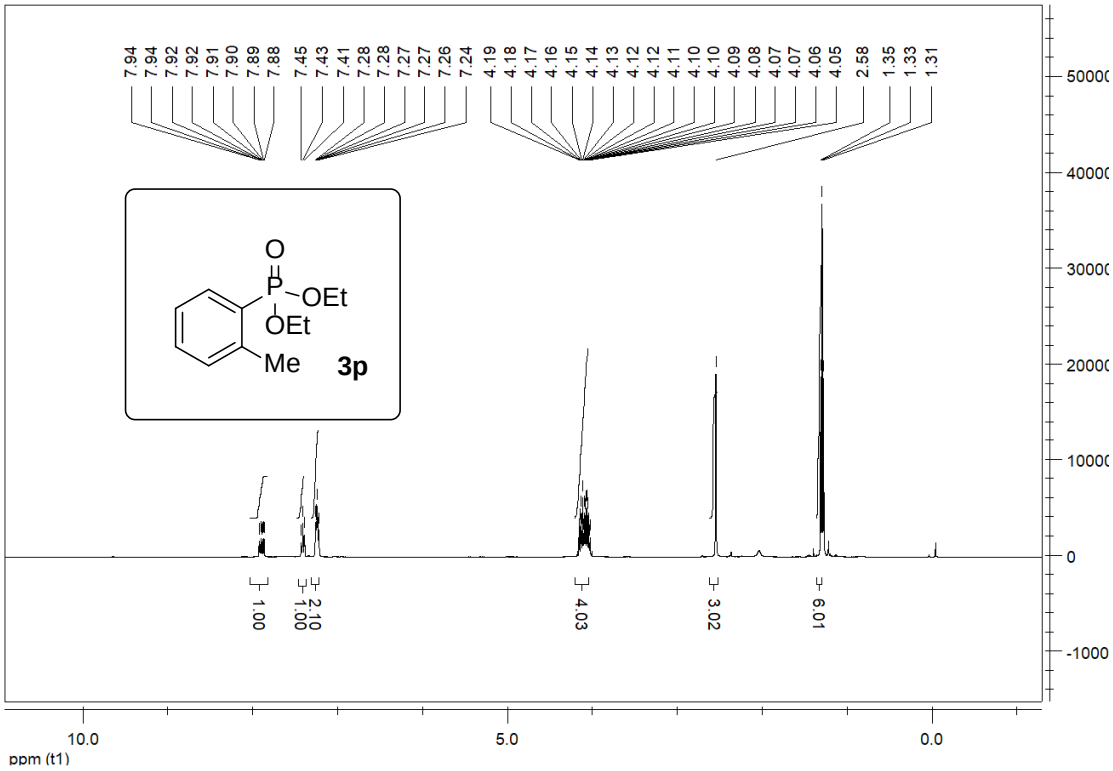
30000
20000
10000
0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7.43
7.41
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7.28
7.27
7.27
7.26
7.24
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.12
4.11
4.10
4.10
4.09
4.08
4.07
4.07
4.06
4.05
2.58
1.35
1.33
1.31
O
P
OEt
OEt
Me
3p
1.00
2.10
1.00
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20000
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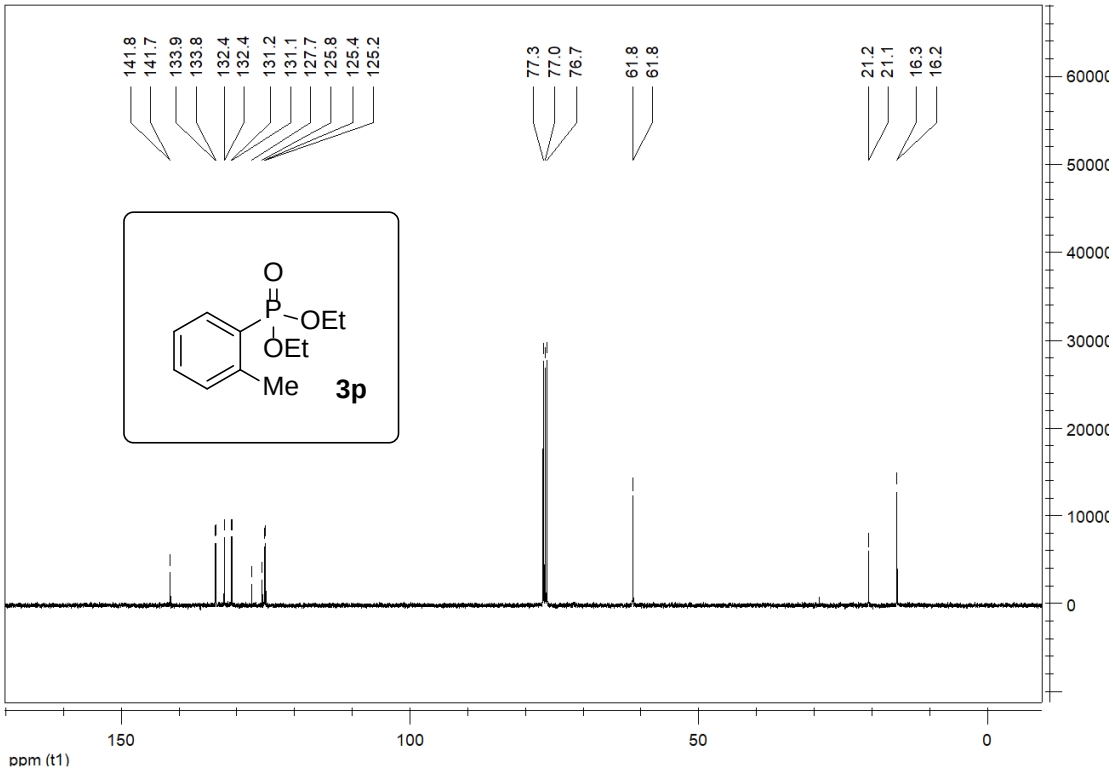
ppm (t1)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132.4
131.2
131.1
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125.8
125.4
125.2
77.3
77.0
76.7
61.8
61.8
21.2
21.1
16.3
16.2
O
P
OEt
OEt
Me
3p
60000
50000
40000
30000
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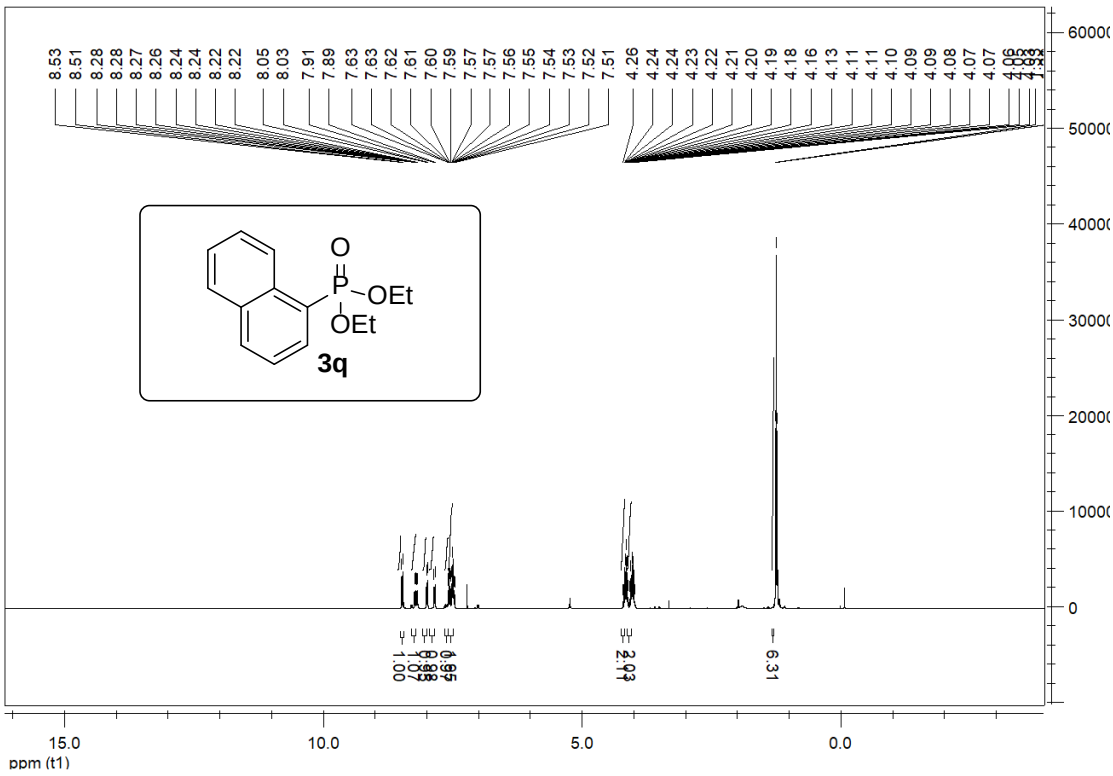
100
50
0
ppm (t1)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8.22
8.05
8.03
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7.89
7.63
7.63
7.62
7.61
7.60
7.59
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.51
4.26
4.24
4.24
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4.22
4.21
4.20
4.19
4.18
4.16
4.13
4.11
4.11
4.10
4.09
4.09
4.08
4.07
4.07
4.06
O
P
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OEt
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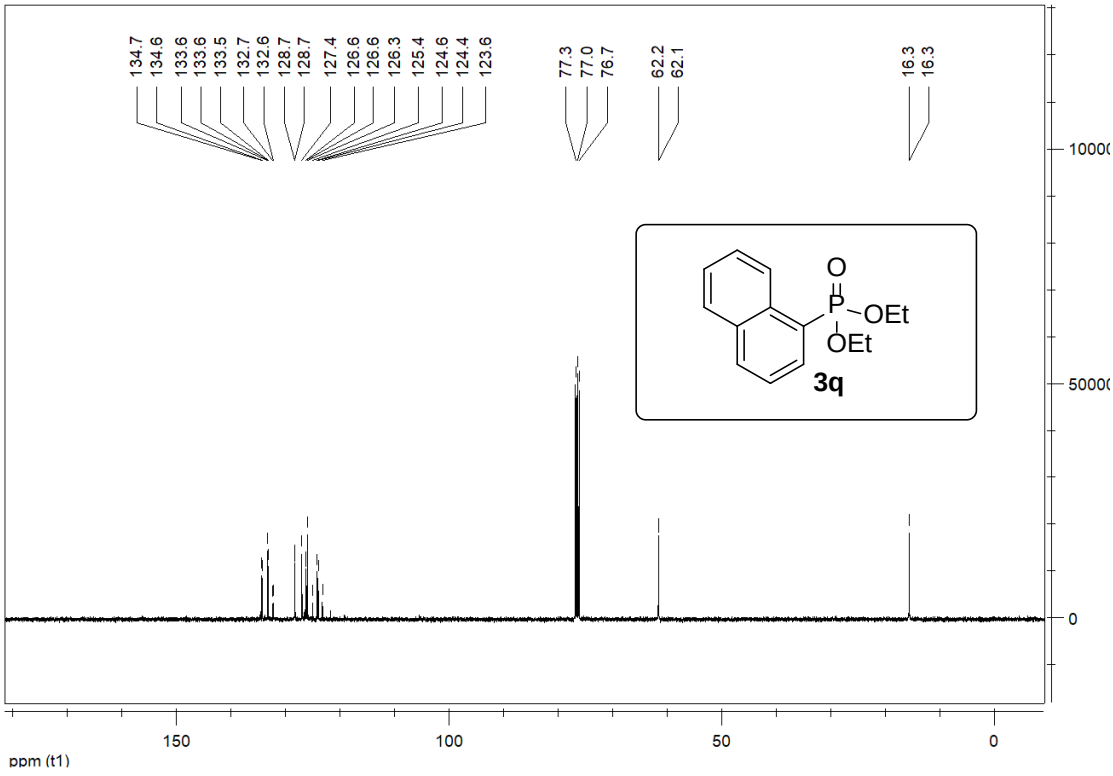
ppm (t1)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126.3
125.4
124.6
124.4
123.6
77.3
77.0
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16.3
16.3
O
P
OEt
OEt
3q
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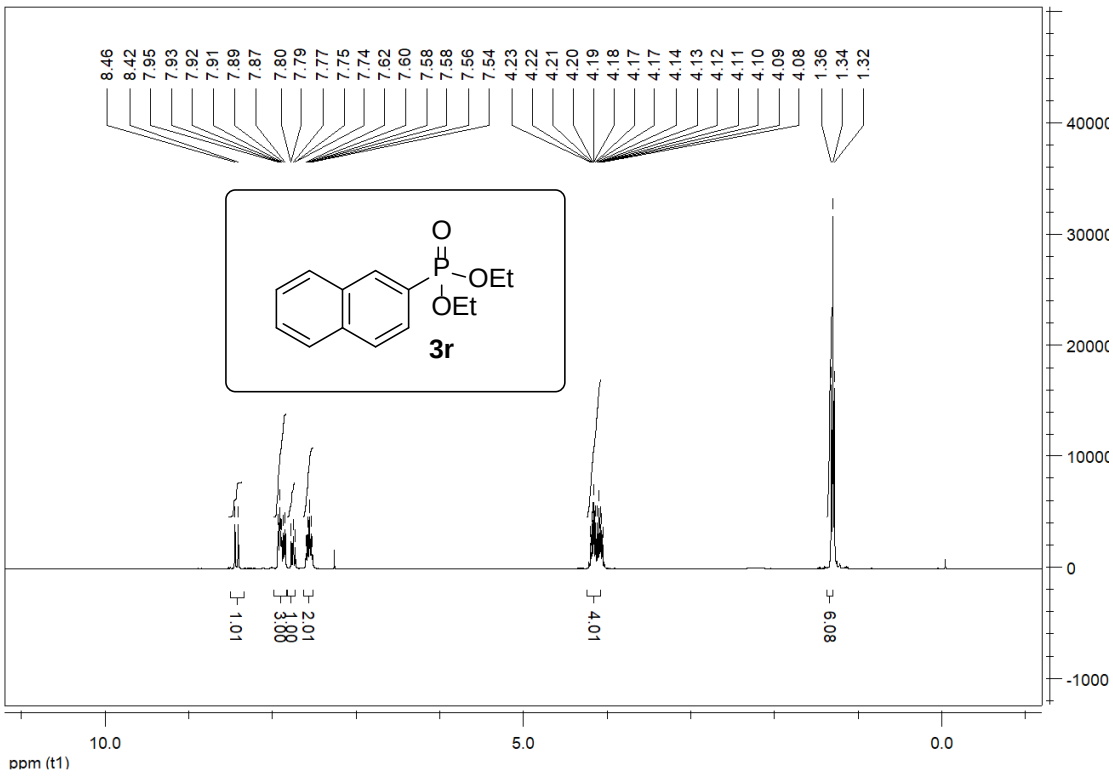
100
50
0
ppm (t1)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7.74
7.62
7.60
7.58
7.58
7.56
7.54
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.17
4.14
4.13
4.12
4.11
4.10
4.09
4.08
1.36
1.34
1.32
O
P
OEt
OEt
3r
1.01
3.88
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20000
10000
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-1000
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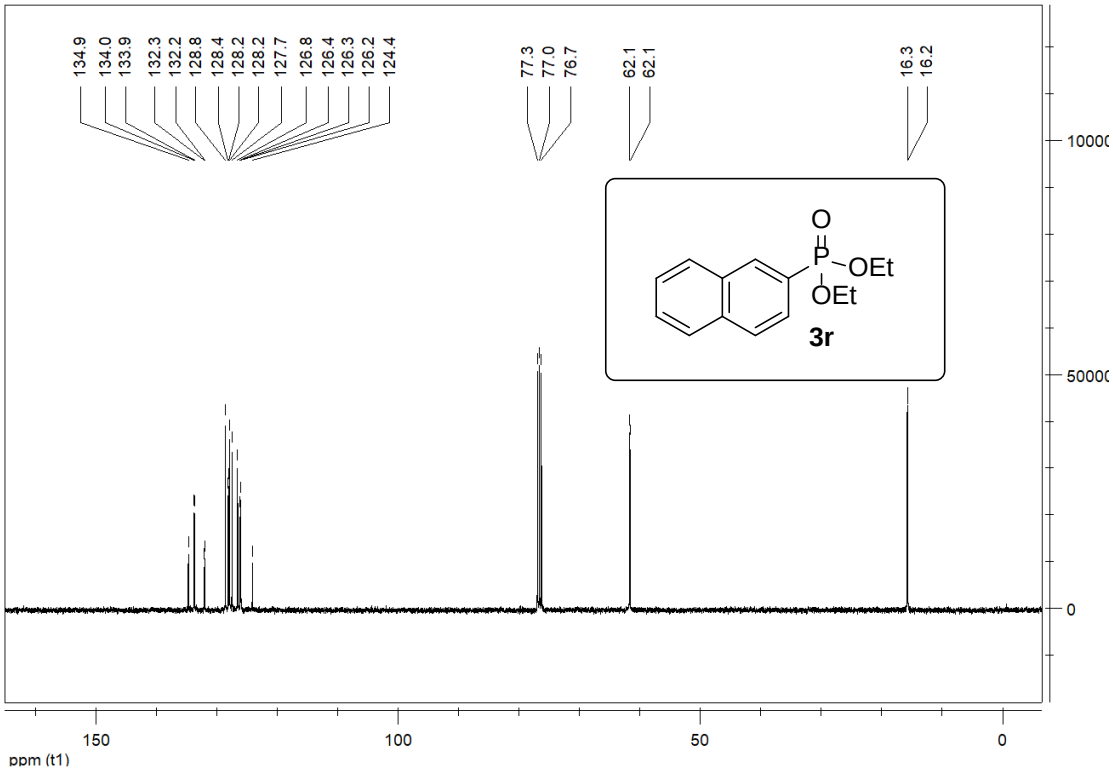
ppm (t1)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126.8
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126.3
126.2
124.4
77.3
77.0
76.7
62.1
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O
P
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OEt
3r
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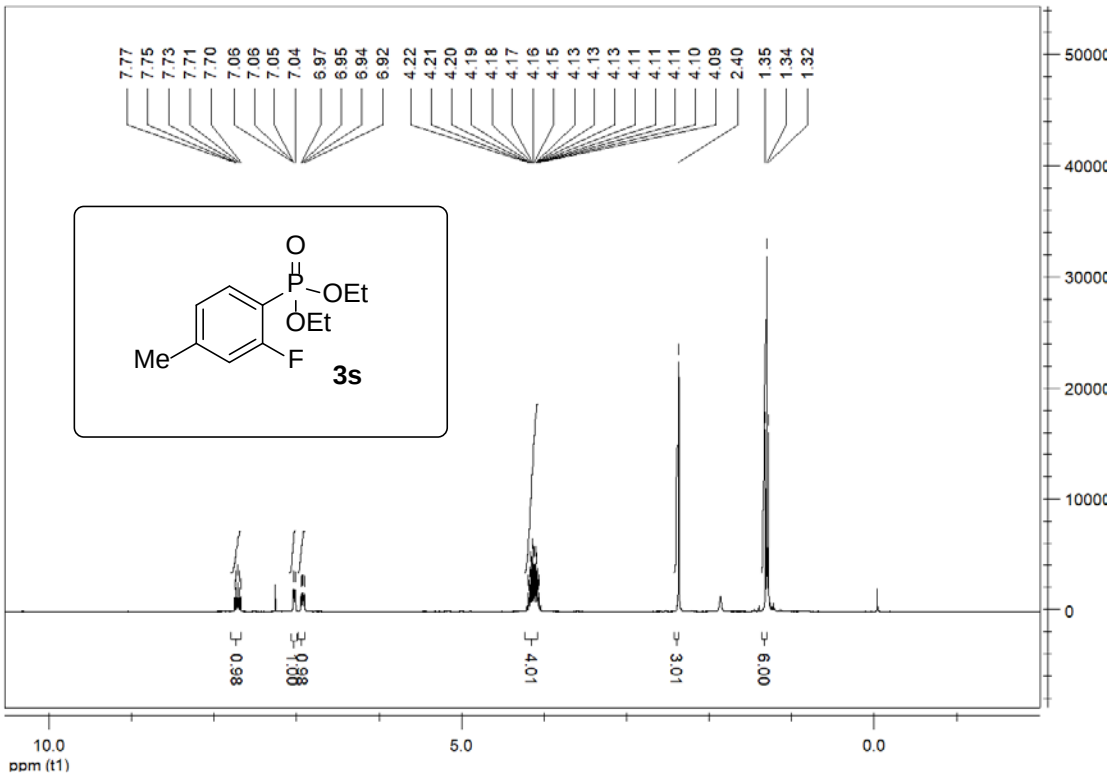
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6.95
6.94
6.92
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4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.13
4.13
4.13
4.11
4.11
4.11
4.10
4.09
2.40
1.35
1.34
1.32
O
P
OEt
OEt
Me
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3.01
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10.0
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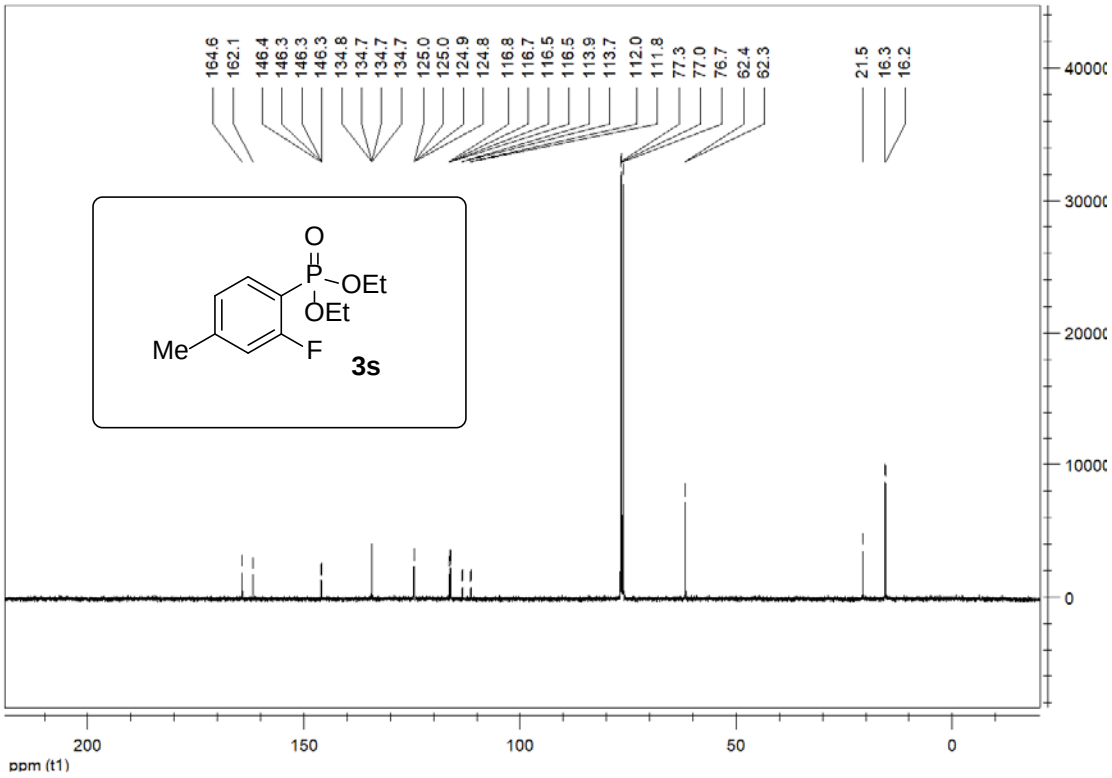
ppm (t1)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124.8
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116.7
116.5
116.5
113.9
113.7
112.0
111.8
77.3
77.0
76.7
62.4
62.3
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P
OEt
OEt
Me
F
3s
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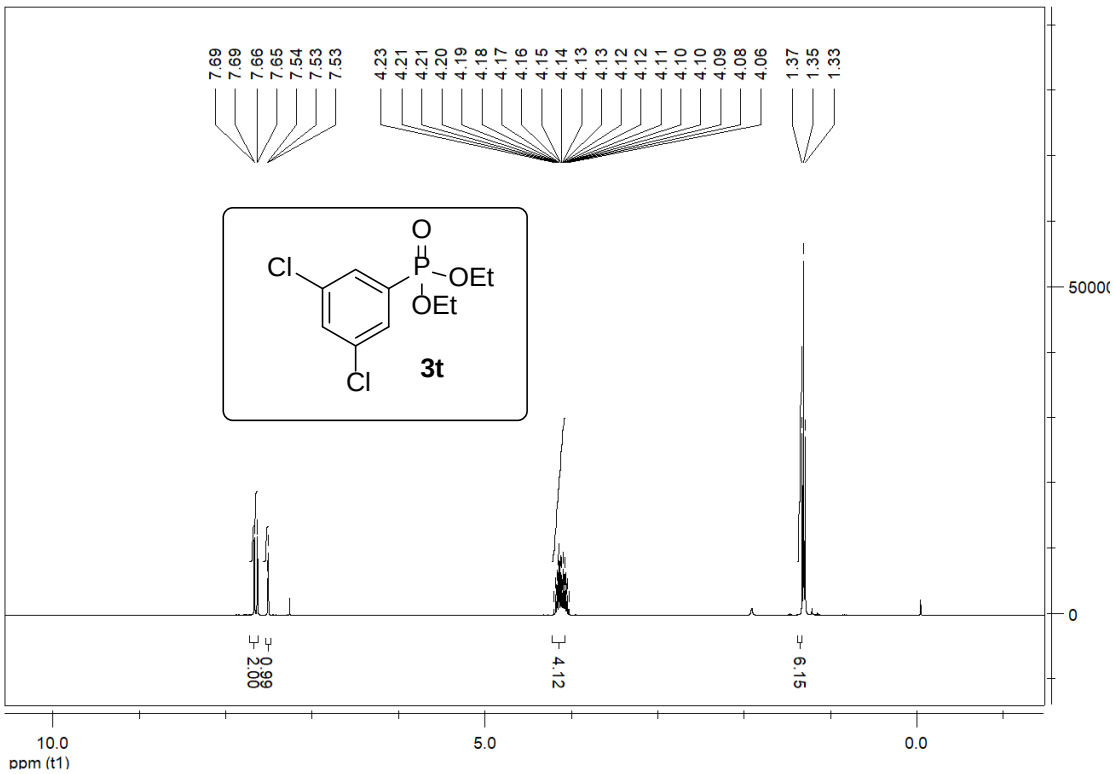
100
50
0
ppm (t1)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4.17
4.16
4.15
4.14
4.13
4.13
4.12
4.12
4.11
4.10
4.10
4.09
4.08
4.06
1.37
1.35
1.33
Cl
O
P
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Cl
3t
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0
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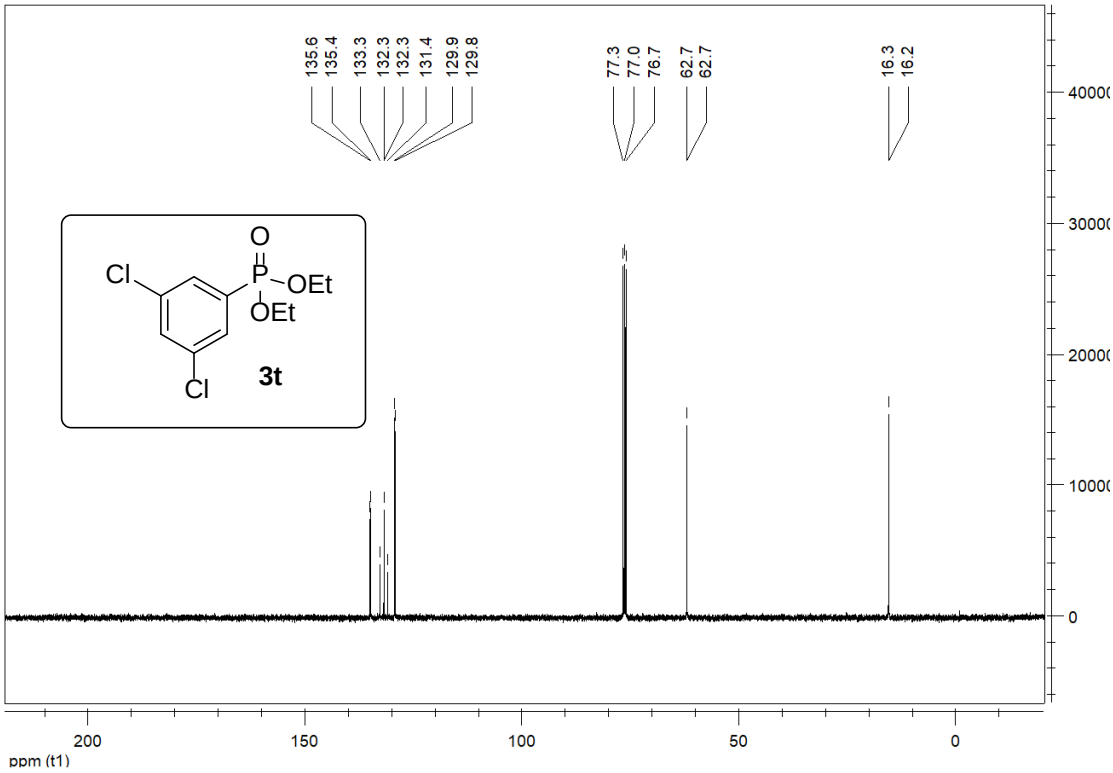
0.0
ppm (t1)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76.7
62.7
62.7
16.3
16.2
Cl
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P
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Cl
3t
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30000
20000
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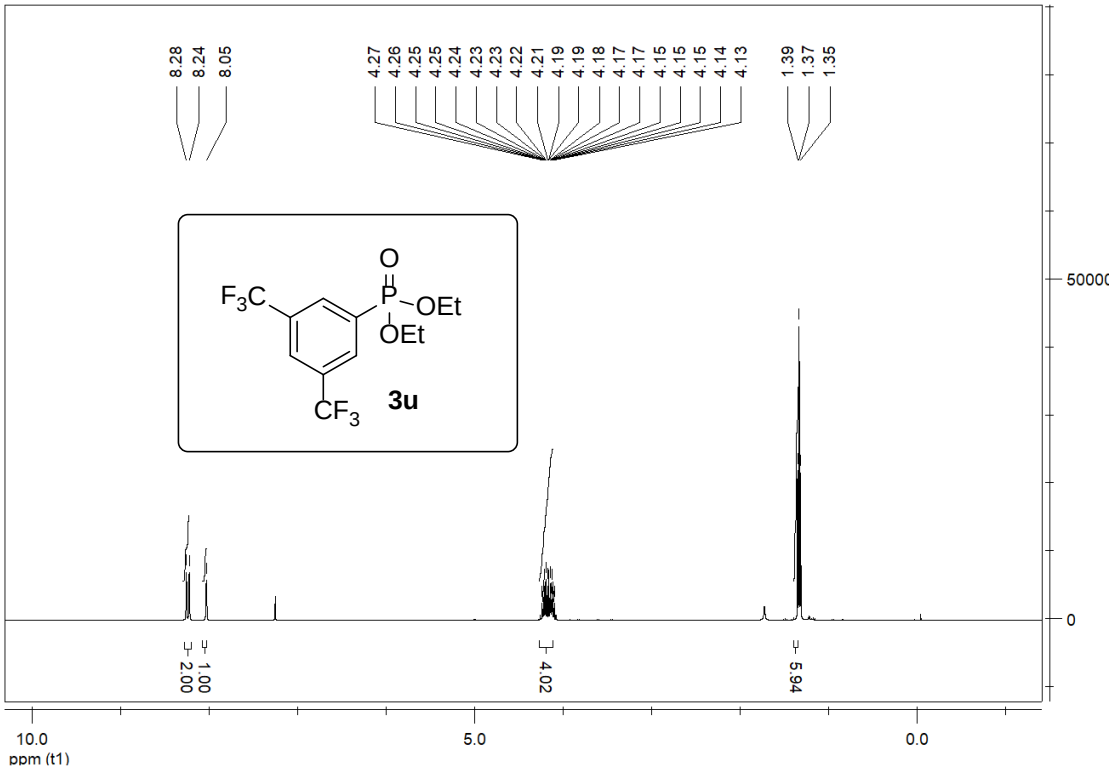
50
0
ppm (t1)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4.18
4.17
4.17
4.15
4.15
4.15
4.14
4.13
1.39
1.37
1.35
O
P
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OEt
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CF3
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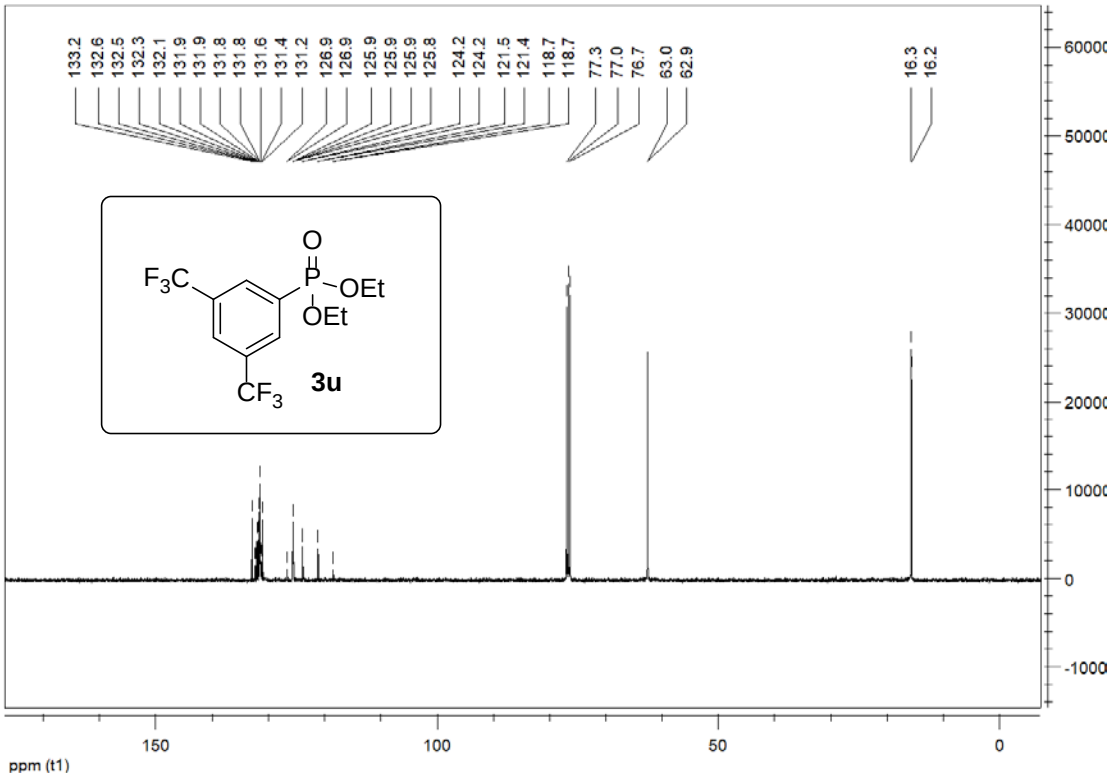
ppm (t1)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121.4
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118.7
77.3
77.0
76.7
63.0
62.9
16.3
16.2
O
P
OEt
OEt
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30000
20000
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0
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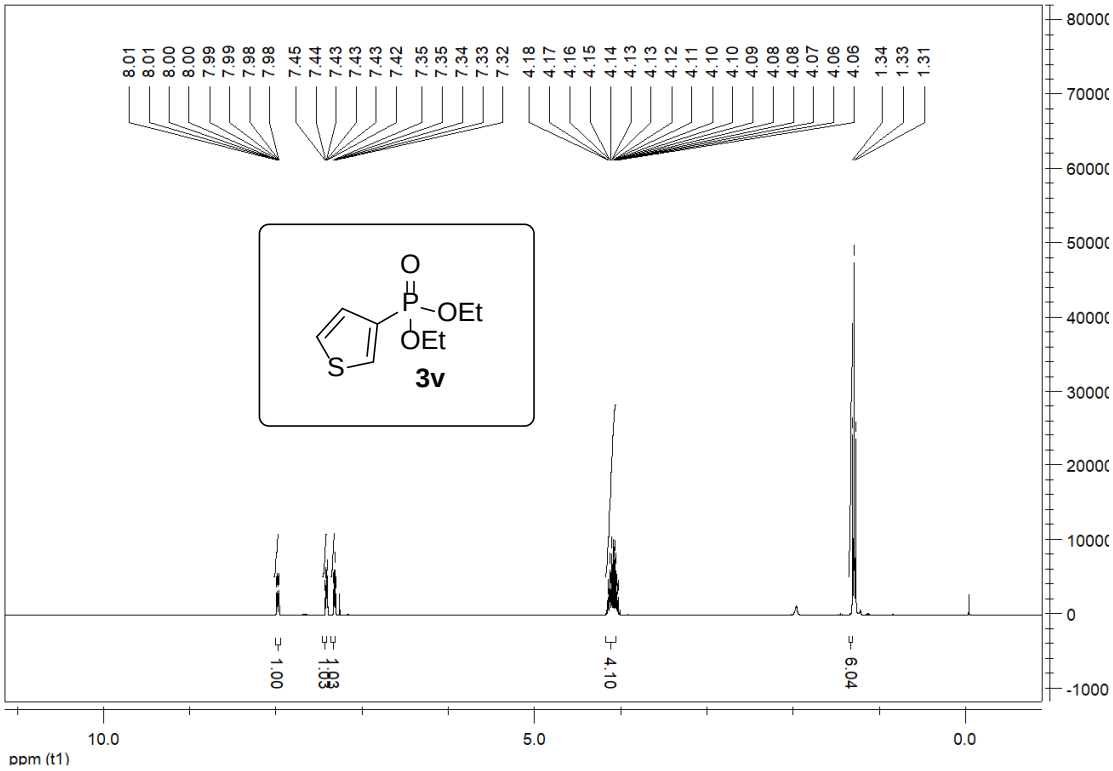
50
0
ppm (t1)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7.33
7.32
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4.17
4.16
4.15
4.14
4.13
4.13
4.12
4.11
4.10
4.10
4.09
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1.33
1.31
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S
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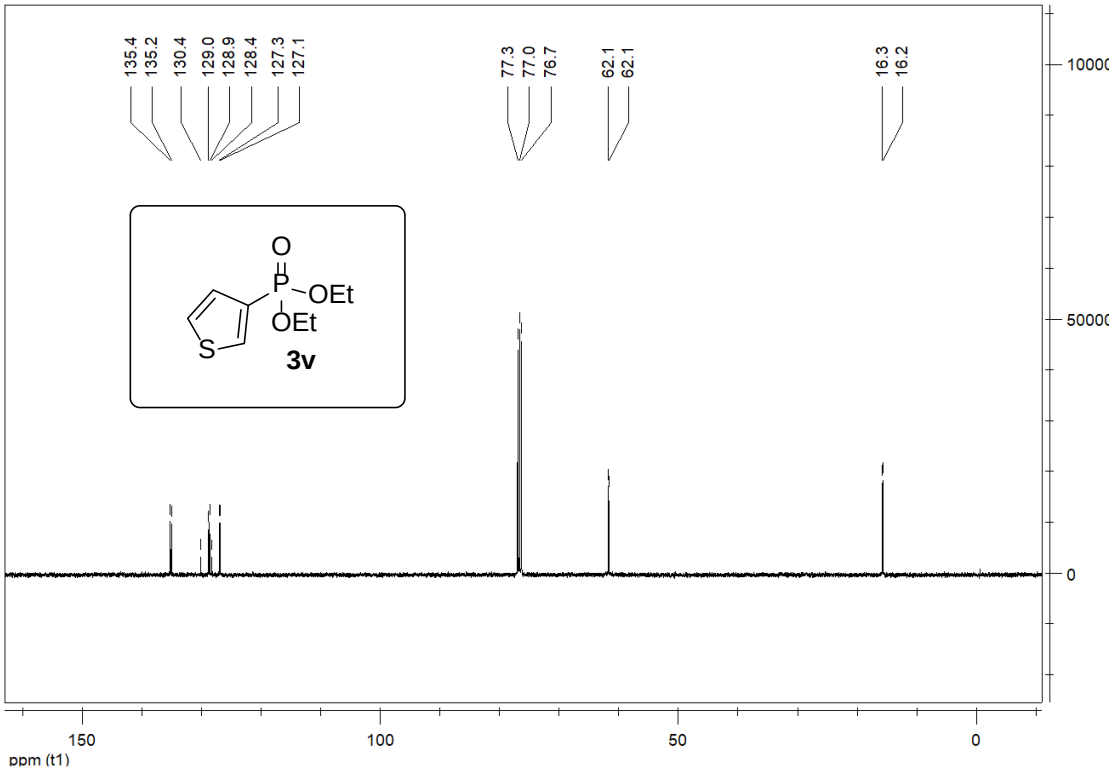
ppm (t1)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127.1
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77.0
76.7
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16.2
O
P
OEt
OEt
S
3v
150
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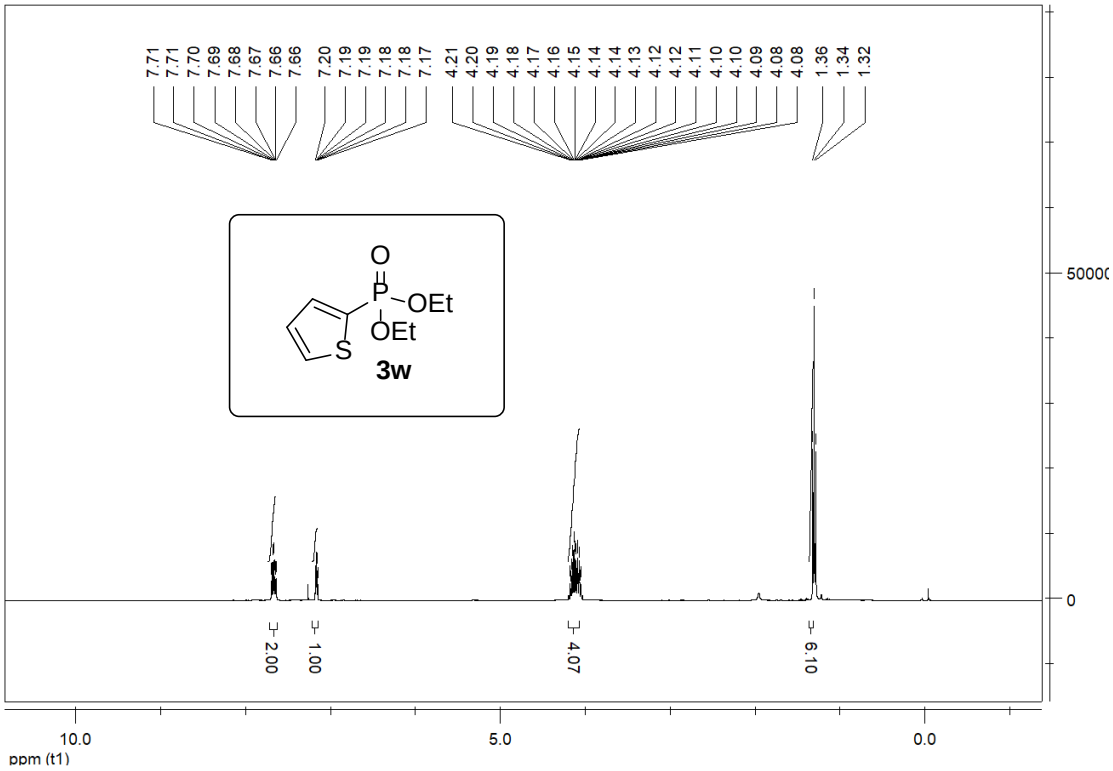
ppm (t1)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4.12
4.12
4.11
4.10
4.10
4.09
4.08
4.08
1.36
1.34
1.32
O
P
OEt
OEt
S
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1.00
4.07
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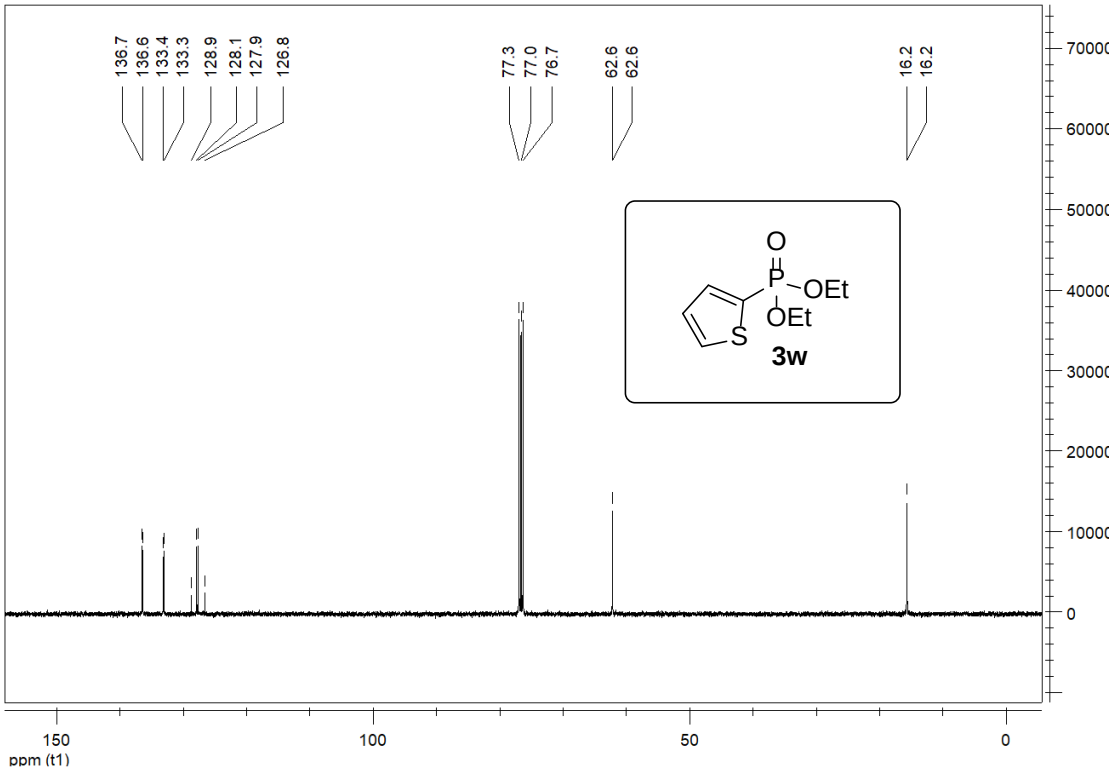
0.0
ppm (t1)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127.9
126.8
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77.0
76.7
62.6
62.6
16.2
16.2
O
P
OEt
OEt
S
3w
70000
60000
50000
40000
30000
20000
10000
0
150
100
50
0
ppm (t1)