K_2CO_3-promoted aerobic oxidative cross-coupling of trialkyl phosphites with thiophenols

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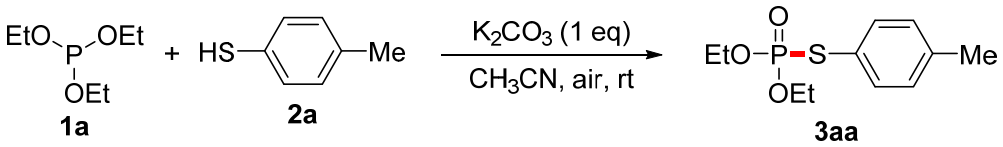
SUPPORTING INFORMATION

Content:

1. General Information

All reactions were carried out under an atmosphere of air using oven-dried glassware and standard syringe/septa techniques. Petroleum ether refers to the petroleum fraction bp 40~60 °C. Commercial reagents were used without purification unless otherwise noted. Flash chromatography was performed using the indicated solvent system on silica gel standard grade 60 (230–400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. ^{31}P NMR spectra were recorded on a 162 MHz spectrometer. ^{19}F NMR spectra were recorded on a 376 MHz spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF. Melting points (mp) were uncorrected and measured on micro melting point apparatus.

2. General Procedure for the Cross-Coupling Reactions

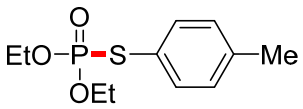


To a solution of triethyl phosphite **1a** (66 mg, 0.40 mmol) and *p*-toluenethiol **2a** (114 mg, 0.92 mmol) in CH_3CN (2 mL) was added K_2CO_3 (55 mg, 0.40 mmol). The mixture was stirred at room temperature under air atmosphere for 5 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1, v/v) to give the desired product **3aa** (96 mg, 92%) as a colorless oil.

3. Characterizations of Compounds 3

The known compounds **3aa**–**3au**, **3aw**, **3ax**, **3ba**, **3bg**, **3ca**, **3cg**, **3da**, **3dg**, and **3ga** showed characterization data in full agreement with previously reported data.

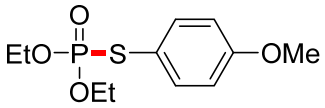
O,O-Diethyl *S*-(*p*-tolyl) phosphorothioate (3aa)[1]



3aa

Colorless oil (96 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.2, 1.9 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.25–4.10 (m, 4H), 2.33 (d, J = 1.7 Hz, 3H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 (d, J = 3.1 Hz), 134.7 (d, J = 5.1 Hz), 130.3 (d, J = 2.4 Hz), 122.9 (d, J = 7.3 Hz), 64.1 (d, J = 6.2 Hz), 21.3 (d, J = 0.8 Hz), 16.1 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.4.

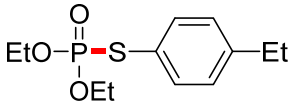
O,O-Diethyl *S*-(4-methoxyphenyl) phosphorothioate (3ab)[1]



3ab

Colorless oil (77 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.8, 2.1 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.24–4.08 (m, 2H), 3.79 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 2.9 Hz), 136.5 (d, J = 4.8 Hz), 116.8 (d, J = 7.4 Hz), 115.1 (d, J = 2.4 Hz), 64.1 (d, J = 6.3 Hz), 55.5, 16.2 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.6.

O,O-Diethyl *S*-(4-ethylphenyl) phosphorothioate (3ac)[2]

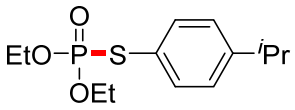


3ac

Colorless oil (71 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.2, 2.0 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.25–4.12 (m, 2H), 2.63 (q, J = 7.4 Hz, 1H), 1.30 (t, J =

7.1 Hz, 6H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6 (d, J = 3.1 Hz), 134.8 (d, J = 5.1 Hz), 129.1 (d, J = 2.4 Hz), 123.1 (d, J = 7.3 Hz), 64.1 (d, J = 6.2 Hz), 28.6, 16.10 (d, J = 7.2 Hz), 15.4 (d, J = 1.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.4.

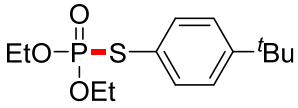
_O,O_-Diethyl _S_-(4-isopropylphenyl) phosphorothioate (3ad)[3]



3ad

Colorless oil (106 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.3, 2.0 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 4.25–4.11 (m, 2H), 2.94–2.83 (m, 1H), 1.30 (t, J = 7.1 Hz, 6H), 1.22 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, J = 3.1 Hz), 134.8 (d, J = 5.1 Hz), 127.7 (d, J = 2.3 Hz), 123.2 (d, J = 7.2 Hz), 64.1 (d, J = 6.2 Hz), 33.9, 23.9, 16.1 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.4.

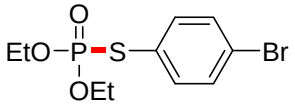
_S_-(4-(_tert_-Butyl)phenyl) _O,O_-diethyl phosphorothioate (3ae)[4]



3ae

Colorless oil (94 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.5, 2.0 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.26–4.11 (m, 4H), 1.30 (t, J = 7.1 Hz, 9H), 1.29 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4 (d, J = 3.1 Hz), 134.3 (d, J = 5.1 Hz), 126.5 (d, J = 2.3 Hz), 122.9 (d, J = 7.2 Hz), 64.0 (d, J = 6.2 Hz), 34.7, 31.2, 15.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.4.

_S_-(4-Bromophenyl) _O,O_-diethyl phosphorothioate (3af)[1]

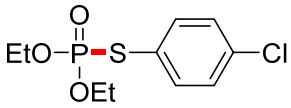


3af

Colorless oil (65 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.7 Hz, 2H), 7.43 (dd, J = 8.6, 1.9 Hz, 2H), 4.26–3.0 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1 (d, J = 5.2 Hz), 132.6 (d, J = 2.2 Hz), 126.0 (d, J = 7.2

Hz), 123.8 (d, J = 3.6 Hz), 64.4 (d, J = 6.4 Hz), 16.2 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.9.

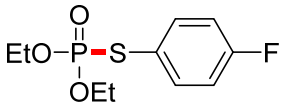
_S_-(4-Chlorophenyl) _O,O_-diethyl phosphorothioate (3ag)[1]



3ag

Colorless oil (101 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.5, 1.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 4.26–4.10 (m, 2H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9 (d, J = 5.2 Hz), 135.6 (d, J = 3.4 Hz), 129.7 (d, J = 2.2 Hz), 125.3 (d, J = 7.2 Hz), 64.4 (d, J = 6.4 Hz), 16.1 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.2.

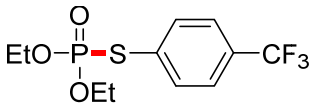
_O,O_-Diethyl _S_-(4-fluorophenyl) phosphorothioate (3ah)[1]



3ah

Colorless oil (99 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.06–7.02 (m, 2H), 4.25–4.09 (m, 4H), 1.30 (td, J = 7.1, 0.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (dd, $J_{C\text{-}F}$ = 250 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 136.8 (dd, $J_{C\text{-}F}$ = 8.5 Hz, $J_{C\text{-}P}$ = 5.0 Hz), 121.9 (dd, $J_{C\text{-}F}$ = 7.3 Hz, $J_{C\text{-}P}$ = 3.4 Hz), 116.7 (dd, $J_{C\text{-}F}$ = 22.2 Hz, $J_{C\text{-}P}$ = 2.4 Hz), 64.3 (d, $J_{C\text{-}P}$ = 6.4 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7 (d, J = 5.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6 (d, J = 5.3 Hz).

_O,O_-Diethyl _S_-(4-(trifluoromethyl)phenyl) phosphorothioate (3ai)[5]

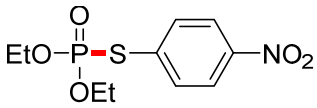


3ai

Colorless oil (79 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 4.29–4.13 (m, 4H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (d, $J_{C\text{-}P}$ = 5.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 7.8 Hz), 131.1 (dd, $J_{C\text{-}F}$ = 32.4 Hz, $J_{C\text{-}P}$ = 2.8 Hz), 126.3 (dd, $J_{C\text{-}F}$ = 3.7 Hz, $J_{C\text{-}P}$ = 1.8 Hz), 123.9 (d, $J_{C\text{-}F}$ = 274

Hz), 64.6 (d, J = 6.3 Hz), 16.2 (d, J = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (d, J = 1.3 Hz).

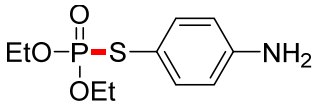
_O,O_-Diethyl _S_-(4-nitrophenyl) phosphorothioate (3aj)[6]



3aj

Colorless oil (99 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 4.30–4.14 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (d, J = 2.2 Hz), 136.4 (d, J = 6.6 Hz), 134.2 (d, J = 6.0 Hz), 124.2 (d, J = 1.3 Hz), 64.9 (d, J = 6.4 Hz), 16.1 (d, J = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1.

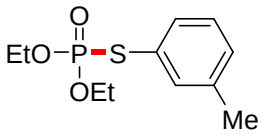
_S_-(4-Aminophenyl) _O,O_-diethyl phosphorothioate (3ak)[1]



3ak

Colorless oil (52 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.5, 1.9 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 4.21–4.11 (m, 4H), 3.23 (s, 2H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 (d, J = 2.7 Hz), 136.4 (d, J = 4.6 Hz), 115.8 (d, J = 2.4 Hz), 113.1 (d, J = 7.5 Hz), 63.9 (d, J = 6.3 Hz), 16.1 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.1.

_O,O_-Diethyl _S_-(_m_-tolyl) phosphorothioate (3al)[2]

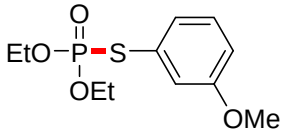


3al

Colorless oil (74 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 10.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 4.24–4.12 (m, 4H), 2.34 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J = 2.3 Hz), 135.3 (d, J = 5.3 Hz), 131.7 (d, J = 5.2 Hz), 129.9 (d, J = 2.9 Hz), 129.2 (d, J = 2.3 Hz),

126.3 (d, J = 7.2 Hz), 64.2 (d, J = 6.2 Hz), 21.4, 16.1 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.1.

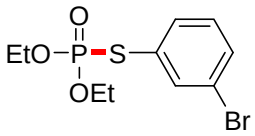
_O,O_-Diethyl _S_-(3-methoxyphenyl) phosphorothioate (3am)[1]



3am

Colorless oil (88 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 4.0 Hz, 2H), 6.91 (d, J = 8.3 Hz, 1H), 4.28–4.13 (m, 4H), 3.81 (s, 3H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J = 2.1 Hz), 130.1 (d, J = 2.2 Hz), 127.6 (d, J = 7.1 Hz), 126.7 (d, J = 5.5 Hz), 119.8 (d, J = 5.2 Hz), 115.2 (d, J = 2.8 Hz), 64.2 (d, J = 6.2 Hz), 55.5, 16.1 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9.

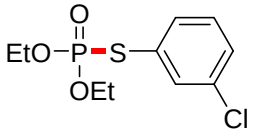
_S_-(3-Bromophenyl) _O,O_-diethyl phosphorothioate (3an)[2]



3an

Colorless oil (67 mg, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 1.8 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 7.9 Hz, 1H), 4.25–4.12 (m, 4H), 1.32 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1 (d, J = 5.4 Hz), 133.1 (d, J = 5.2 Hz), 132.3 (d, J = 2.7 Hz), 130.7 (d, J = 2.2 Hz), 128.9 (d, J = 7.1 Hz), 122.9 (d, J = 2.6 Hz), 64.5 (d, J = 6.3 Hz), 16.1 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.9.

_S_-(3-Chlorophenyl) _O,O_-diethyl phosphorothioate (3ao)[2]

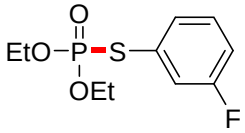


3ao

Colorless oil (45 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 1.8 Hz, 1H), 7.46 (dd, J = 7.6, 1.3 Hz, 1H), 7.33 (dd, J = 8.1, 1.3 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H),

4.25–4.14 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9 (d, J = 2.4 Hz), 134.3 (d, J = 5.4 Hz), 132.7 (d, J = 5.3 Hz), 130.4 (d, J = 2.2 Hz), 129.4 (d, J = 2.8 Hz), 128.7 (d, J = 7.1 Hz), 64.5 (d, J = 6.3 Hz), 16.1 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.9.

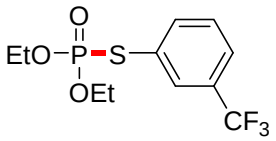
_O,O_-Diethyl _S_-(3-fluorophenyl) phosphorothioate (3ap)[2]



3ap

Colorless oil (98 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 3H), 7.07 (m, 1H), 4.28–4.12 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (dd, $J_{C\text{-}F}$ = 250 Hz, $J_{C\text{-}P}$ = 2.2 Hz), 130.6 (dd, $J_{C\text{-}F}$ = 8.3 Hz, $J_{C\text{-}P}$ = 2.1 Hz), 130.2 (dd, $J_{C\text{-}F}$ = 5.6 Hz, $J_{C\text{-}P}$ = 3.2 Hz), 128.8 (dd, $J_{C\text{-}F}$ = 8.0 Hz, $J_{C\text{-}P}$ = 7.3 Hz), 121.4 (dd, $J_{C\text{-}F}$ = 22.9 Hz, $J_{C\text{-}P}$ = 5.3 Hz), 116.3 (dd, $J_{C\text{-}F}$ = 21.0 Hz, $J_{C\text{-}P}$ = 2.7 Hz), 64.4 (d, $J_{C\text{-}P}$ = 6.3 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.2 (d, J = 1.5 Hz).

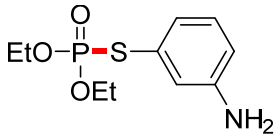
_O,O_-Diethyl _S_-(3-(trifluoromethyl)phenyl) phosphorothioate (3aq)[5]



3aq

Colorless oil (60 mg, 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.48 (dd, J = 8.0, 7.6 Hz, 1H), 4.28–4.13 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.9 (dd, $J_{C\text{-}F}$ = 32.7 Hz, $J_{C\text{-}P}$ = 2.1 Hz), 131.4 (dd, $J_{C\text{-}F}$ = 5.3 Hz, $J_{C\text{-}P}$ = 3.8 Hz), 129.9 (d, $J_{C\text{-}P}$ = 2.1 Hz), 128.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 125.9 (dd, $J_{C\text{-}F}$ = 6.8 Hz, $J_{C\text{-}P}$ = 3.3 Hz), 123.6 (d, $J_{C\text{-}F}$ = 273 Hz), 64.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.

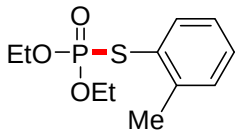
_S_-(3-Aminophenyl) _O,O_-diethyl phosphorothioate (3ar)[5]



3ar

Brown solid (70 mg, 67%): mp 155–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 7.8 Hz, 1H), 6.91 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 8.8 Hz, 1H), 4.19–4.16 (m, 4H), 3.14 (s, 2H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4 (d, J = 2.0 Hz), 130.1 (d, J = 2.1 Hz), 127.1 (d, J = 7.0 Hz), 124.3 (d, J = 5.6 Hz), 120.6 (d, J = 5.3 Hz), 115.8 (d, J = 2.8 Hz), 64.2 (d, J = 6.3 Hz), 16.1 (d, J = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.2.

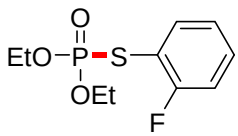
***O,O*-Diethyl *S*-(*o*-tolyl) phosphorothioate (3as)**[5]



3as

Colorless oil (80 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.1 Hz, 1H), 7.29–7.26 (m, 2H), 7.22–7.13 (m, 1H), 4.25–4.08 (m, 4H), 2.53 (d, J = 1.0 Hz, 3H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (d, J = 5.6 Hz), 136.3 (d, J = 4.2 Hz), 130.9 (d, J = 2.6 Hz), 129.6 (d, J = 3.0 Hz), 126.9 (d, J = 2.7 Hz), 125.9 (d, J = 7.4 Hz), 64.3 (d, J = 6.7 Hz), 21.5, 16.2 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.1 .

***O,O*-Diethyl S-(2-fluorophenyl) phosphorothioate (3at)**[5]

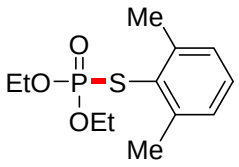


3at

Colorless oil (63 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.59 (m, 1H), 7.41–7.34 (m, 1H), 7.13 (dd, J = 14.2, 7.6 Hz, 2H), 4.30–4.16 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (dd, $J_{C\text{-}F}$ = 249 Hz, $J_{C\text{-}P}$ = 5.4 Hz), 137.5 (d, $J_{C\text{-}P}$ = 4.2 Hz), 131.6 (dd, $J_{C\text{-}F}$ = 8.0 Hz, $J_{C\text{-}P}$ = 3.0 Hz), 124.9 (dd, $J_{C\text{-}F}$ = 3.8

Hz, $J_{C\text{-}P}$ = 2.7 Hz), 116.3 (dd, $J_{C\text{-}F}$ = 22.9 Hz, $J_{C\text{-}P}$ = 2.5 Hz), 113.8 (dd, $J_{C\text{-}F}$ = 18.4 Hz, $J_{C\text{-}P}$ = 7.4 Hz), 64.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.4 (d, J = 3.7 Hz). ^{19}F NMR (376 MHz, CDCl3) δ -106.2 (d, J = 3.9 Hz).

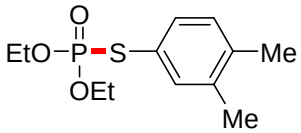
_S_-(2,6-Dimethylphenyl) _O,O_-diethyl phosphorothioate (3au)[2]



3au

Colorless oil (98 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.10 (m, 3H), 4.14–3.09 (m, 4H), 2.58 (d, J = 1.2 Hz, 6H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4 (d, J = 4.7 Hz), 129.5 (d, J = 3.7 Hz), 128.6 (d, J = 3.3 Hz), 124.9 (d, J = 8.0 Hz), 64.3 (d, J = 7.4 Hz), 22.7 (d, J = 1.2 Hz), 16.2 (d, J = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.2.

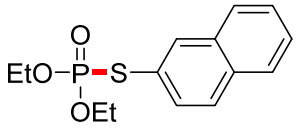
_S_-(3,4-Dimethylphenyl) _O,O_-diethyl phosphorothioate (3av)



3av

Colorless oil (95 mg, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 7.09 (d, J = 7.8 Hz, 1H), 4.26–4.11 (m, 4H), 2.24 (s, 6H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (d, J = 3.2 Hz), 137.9 (d, J = 2.4 Hz), 135.9 (d, J = 5.0 Hz), 132.3 (d, J = 5.1 Hz), 130.7 (d, J = 2.4 Hz), 122.9 (d, J = 7.3 Hz), 64.1 (d, J = 6.2 Hz), 19.8, 19.6, 16.1 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{20}O_3PS$ 275.0865, found 275.0866.

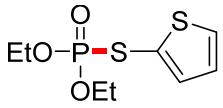
***O,O*-Diethyl *S*-(naphthalen-2-yl) phosphorothioate (3aw)**[1]



3aw

Colorless oil (65 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.84–7.79 (m, 3H), 7.61 (d, J = 8.6 Hz, 1H), 7.51 (dd, J = 6.3, 3.2 Hz, 2H), 4.29–4.14 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5 (d, J = 6.8 Hz), 133.7 (d, J = 2.3 Hz), 133.2 (d, J = 2.0 Hz), 131.1 (d, J = 4.1 Hz), 129.1 (d, J = 1.6 Hz), 127.9 (dd, J = 3.5, 1.1 Hz), 127.2 (d, J = 1.0 Hz), 126.9 (d, J = 0.7 Hz), 123.9 (d, J = 7.4 Hz), 64.3 (d, J = 6.3 Hz), 16.2 (d, J = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9.

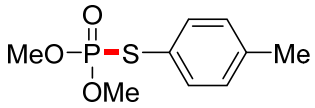
***O,O*-Diethyl *S*-(thiophen-2-yl) phosphorothioate (3ax)**[3]



3ax

Colorless oil (65 mg, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 1H), 7.23 (dd, J = 3.3, 2.6 Hz, 1H), 7.02 (dd, J = 5.1, 3.8 Hz, 1H), 4.29–4.15 (m, 4H), 1.34 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (d, J = 6.6 Hz), 131.2 (d, J = 4.2 Hz), 127.9 (d, J = 3.4 Hz), 123.3 (d, J = 8.9 Hz), 64.5 (d, J = 6.0 Hz), 16.1 (d, J = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.8.

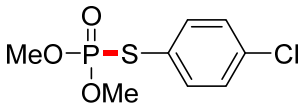
***O,O*-Dimethyl *S*-(*p*-tolyl) phosphorothioate (3ba)**[7]



3ba

Colorless oil (37 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.2, 2.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 3.81 (d, J = 12.6 Hz, 6H), 2.35 (d, J = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7 (d, J = 3.2 Hz), 134.8 (d, J = 5.0 Hz), 130.4 (d, J = 2.5 Hz), 122.4 (d, J = 7.5 Hz), 54.4 (d, J = 6.0 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.7.

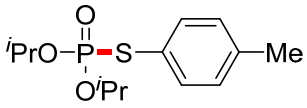
_S_-(4-Chlorophenyl) _O,O_-dimethyl phosphorothioate (3bg)[8]



3bg

Colorless oil (15 mg, 15%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.5, 2.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 3.82 (d, J = 12.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0 (d, J = 5.2 Hz), 135.9 (d, J = 3.5 Hz), 129.9 (d, J = 2.3 Hz), 124.7 (d, J = 7.4 Hz), 54.5 (d, J = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.5.

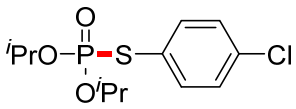
_O,O_-Diisopropyl _S_-(_p_-tolyl) phosphorothioate (3ca)[7]



3ca

Colorless oil (105 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.2, 1.8 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.80–4.67 (m, 2H), 2.32 (d, J = 1.4 Hz, 3H), 1.31 (d, J = 6.2 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (d, J = 3.0 Hz), 134.5 (d, J = 5.3 Hz), 130.1 (d, J = 2.2 Hz), 123.6 (d, J = 7.2 Hz), 73.3 (d, J = 6.8 Hz), 23.8 (dd, J = 33.4, 4.9 Hz), 21.3 (d, J = 0.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.9.

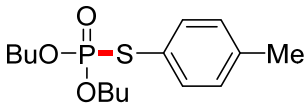
_S_-(4-Chlorophenyl) _O,O_-diisopropyl phosphorothioate (3cg)[3]



3cg

Colorless oil (108 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.5, 1.8 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 4.79–4.68 (m, 2H), 1.28 (dd, J = 23.8, 6.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6 (d, J = 5.5 Hz), 135.2 (d, J = 3.2 Hz), 129.5 (d, J = 2.1 Hz), 126.0 (d, J = 7.1 Hz), 73.7 (d, J = 7.0 Hz), 23.8 (dd, J = 30.0, 4.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7.

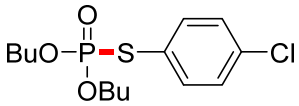
***O,O*-Dibutyl *S*-(*p*-tolyl) phosphorothioate (3da)**[1]



3da

Colorless oil (111 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.2, 1.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.16–4.03 (m, 4H), 2.33 (d, J = 1.6 Hz, 3H), 1.65–1.58 (m, 4H), 1.39–1.29 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J = 3.1 Hz), 134.7 (d, J = 5.1 Hz), 130.2 (d, J = 2.3 Hz), 122.9 (d, J = 7.2 Hz), 67.8 (d, J = 6.6 Hz), 32.2 (d, J = 7.1 Hz), 21.3, 18.8, 13.65. ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.4.

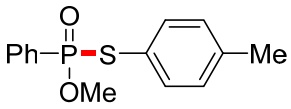
***O,O*-Dibutyl *S*-(4-chlorophenyl) phosphorothioate (3dg)**[1]



3dg

Colorless oil (108 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.5, 1.9 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 4.17–4.03 (m, 4H), 1.66–1.59 (m, 4H), 1.39–1.30 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (d, J = 5.3 Hz), 135.6 (d, J = 3.4 Hz), 129.6 (d, J = 2.2 Hz), 125.4 (d, J = 7.1 Hz), 68.1 (d, J = 6.8 Hz), 32.3 (d, J = 7.0 Hz), 18.8, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.2.

***O*-Methyl *S*-(*p*-tolyl) phenylphosphonothioate (3fa)**

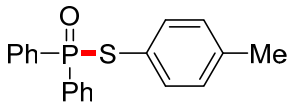


3fa

Colorless oil (50 mg, 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 13.6, 7.2 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (dt, J = 12.2, 6.1 Hz, 2H), 7.16 (dd, J = 8.1, 1.8 Hz, 2H), 7.02 (d, J = 7.9 Hz, 2H), 3.94 (d, J = 12.3 Hz, 3H), 2.30 (d, J = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J = 3.0 Hz), 135.4 (d, J = 4.1 Hz), 132.5 (d, J = 3.3 Hz), 131.5 (d, J = 10.6 Hz), 130.0 (d, J = 2.4 Hz), 128.2 (d, J = 14.9 Hz), 122.7 (d,

J = 5.7 Hz), 52.4 (d, J = 7.0 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}O_2PS$ 279.0603, found 279.0606.

_S_-(_p_-Tolyl) diphenylphosphinothioate (3ga)[7]



3ga

White solid (71 mg, 55%): mp 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 12.8, 7.2 Hz, 4H), 7.51 (t, J = 7.9 Hz, 2H), 7.44 (td, J = 7.5, 3.0 Hz, 4H), 7.32 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J = 2.5 Hz), 135.5 (d, J = 3.8 Hz), 133.4, 132.4 (d, J = 2.9 Hz), 131.8 (d, J = 10.2 Hz), 130.1 (d, J = 1.8 Hz), 128.6 (d, J = 13.1 Hz), 122.4 (d, J = 5.2 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.4.

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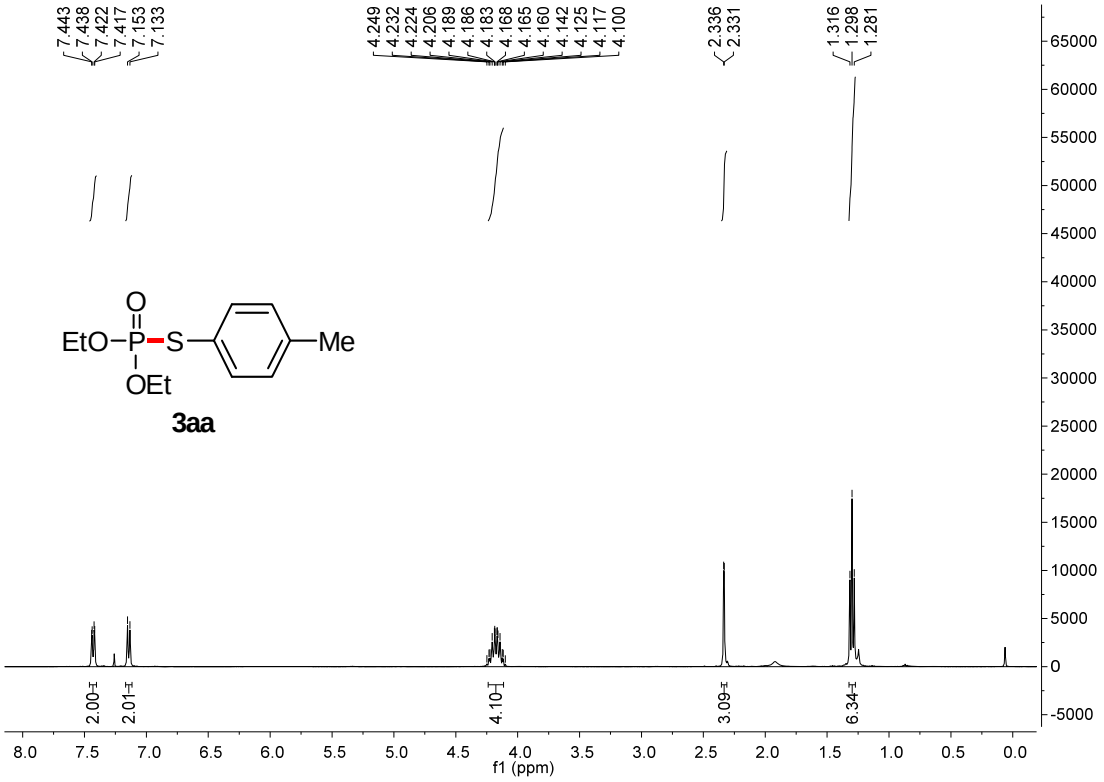
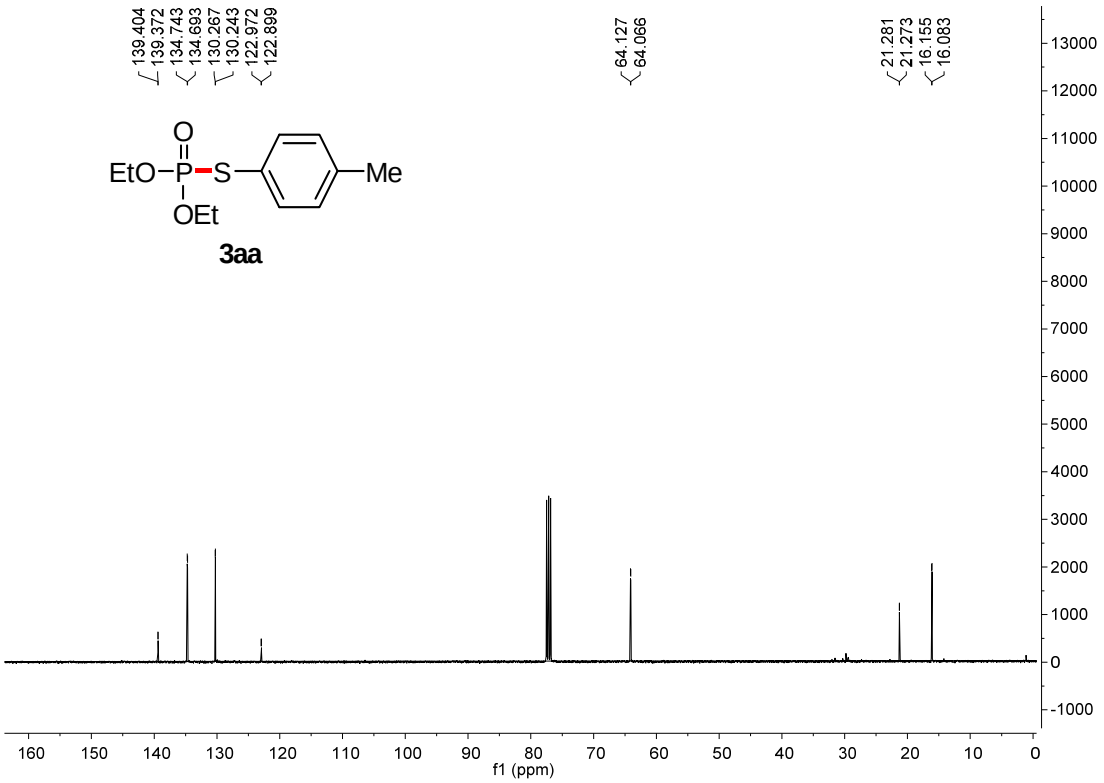
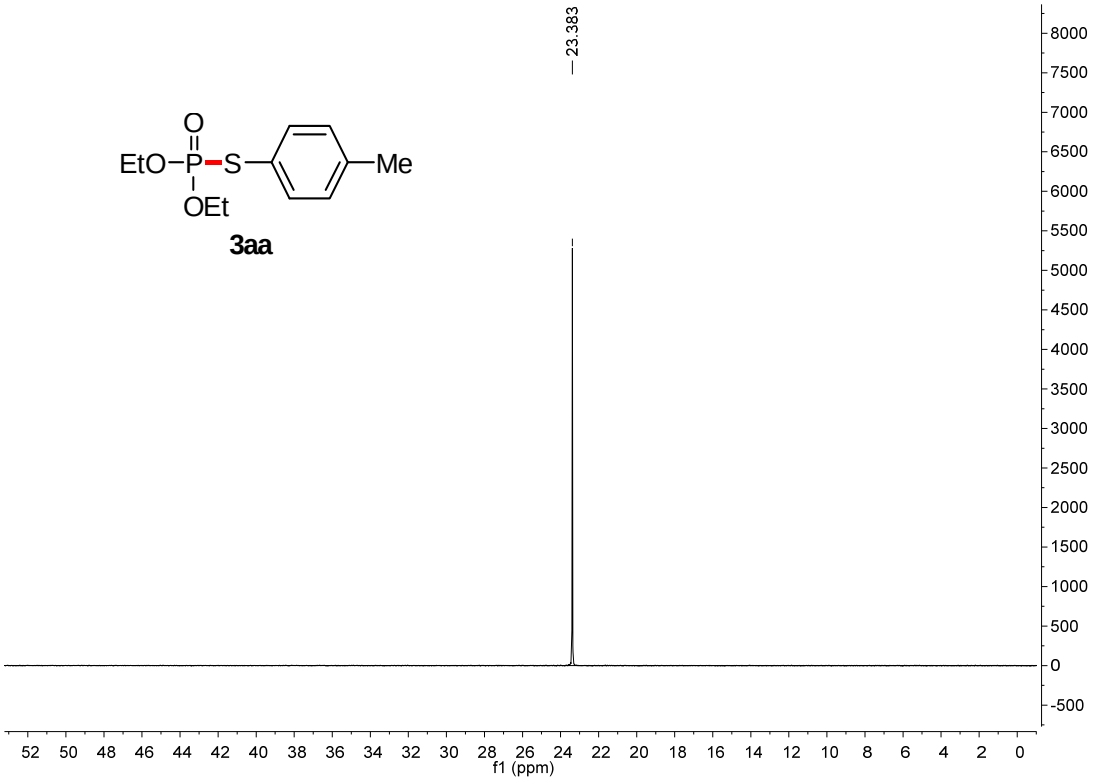
4. Copies of NMR Spectra for 3



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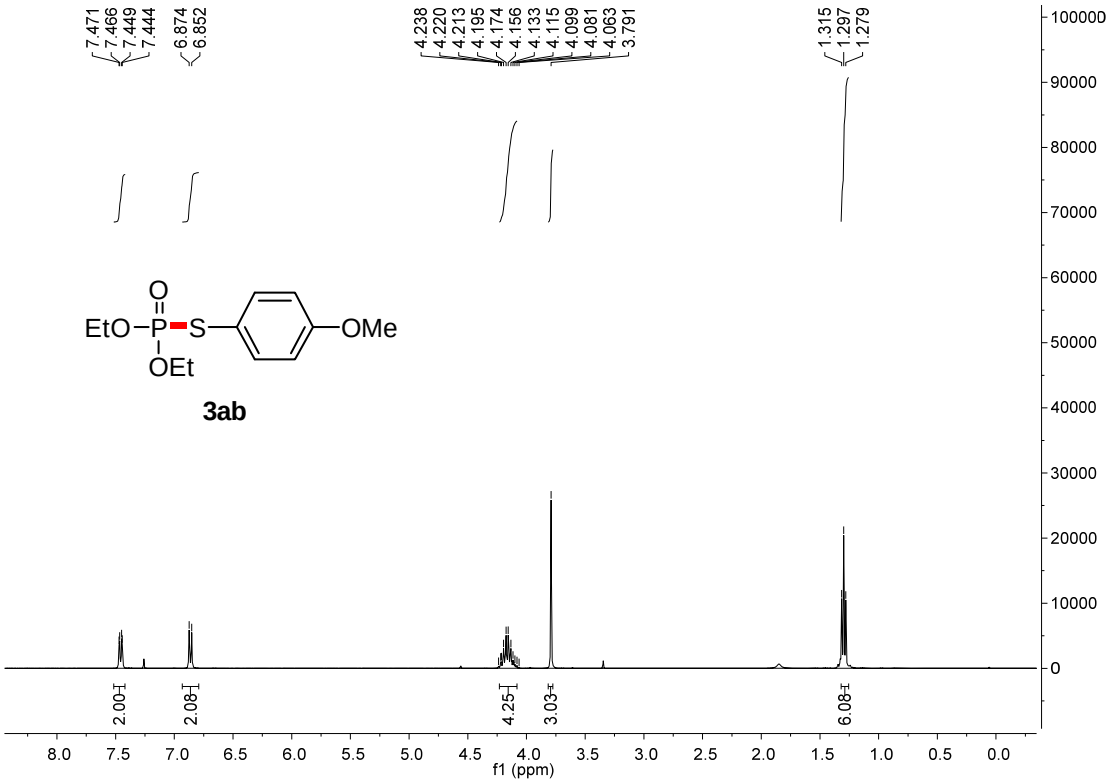
OEt
O
3aa
f1 (ppm)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4.115
4.099
4.081
4.063
3.791
1.315
1.297
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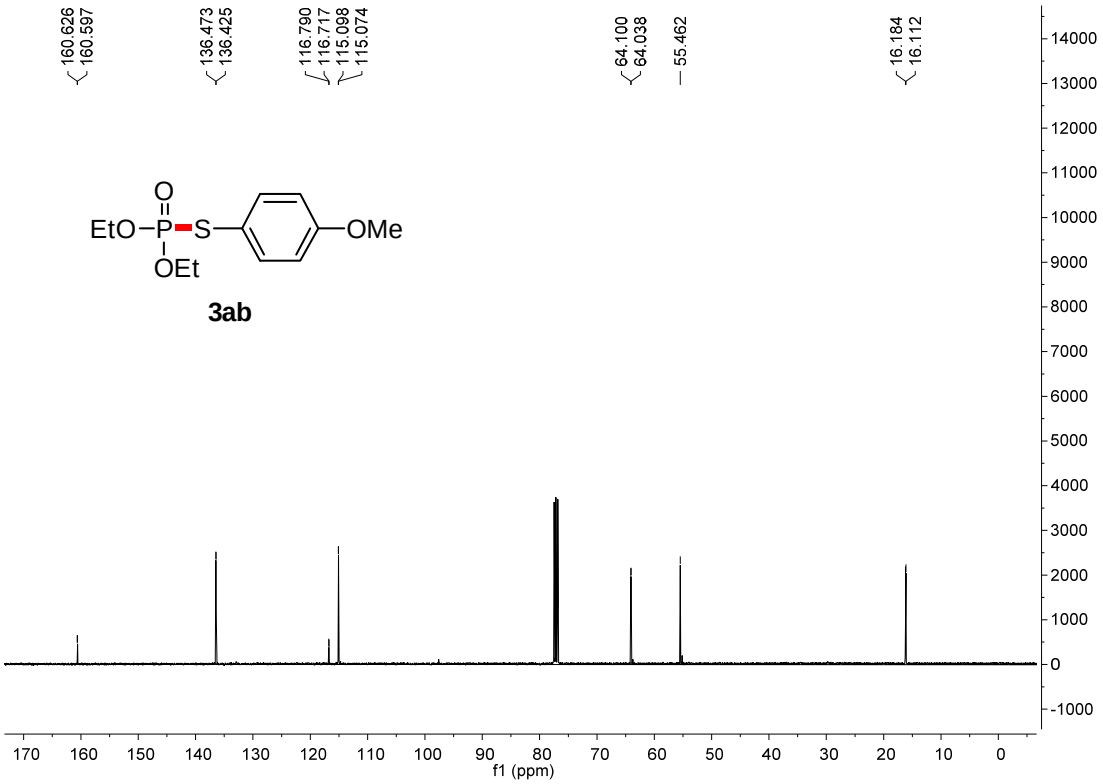
OMe
OEt
O
3ab
2.00
2.08
4.25
3.03
6.08
f1 (ppm)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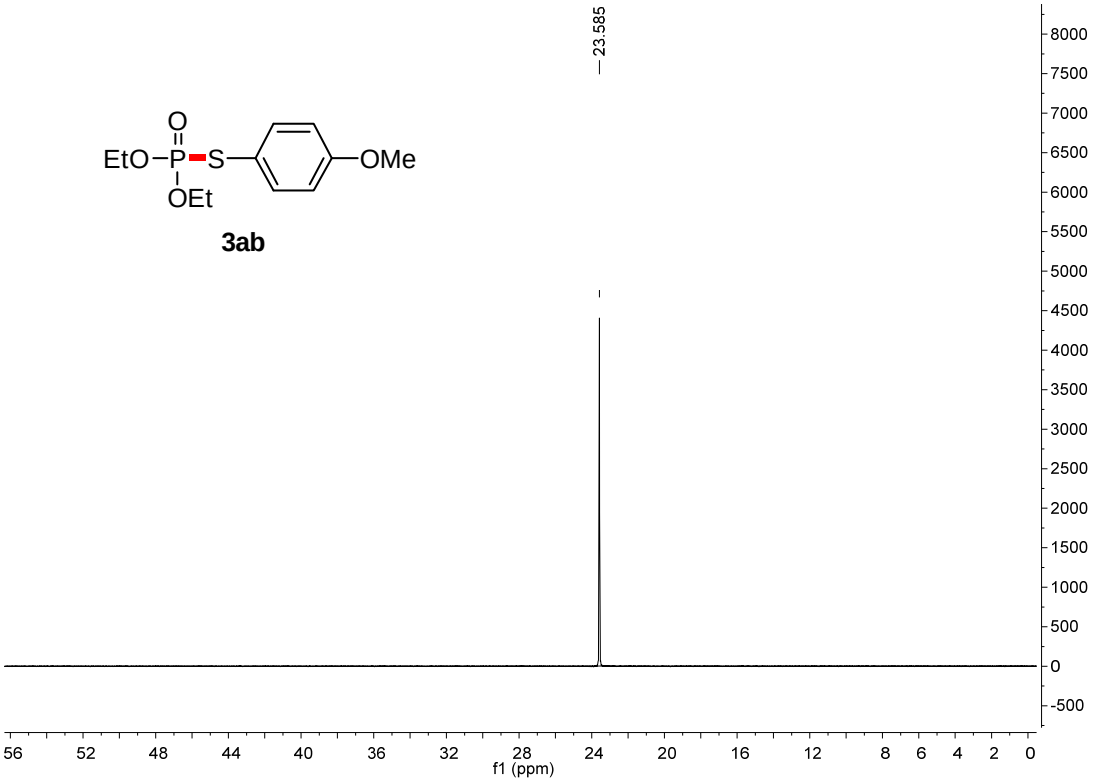
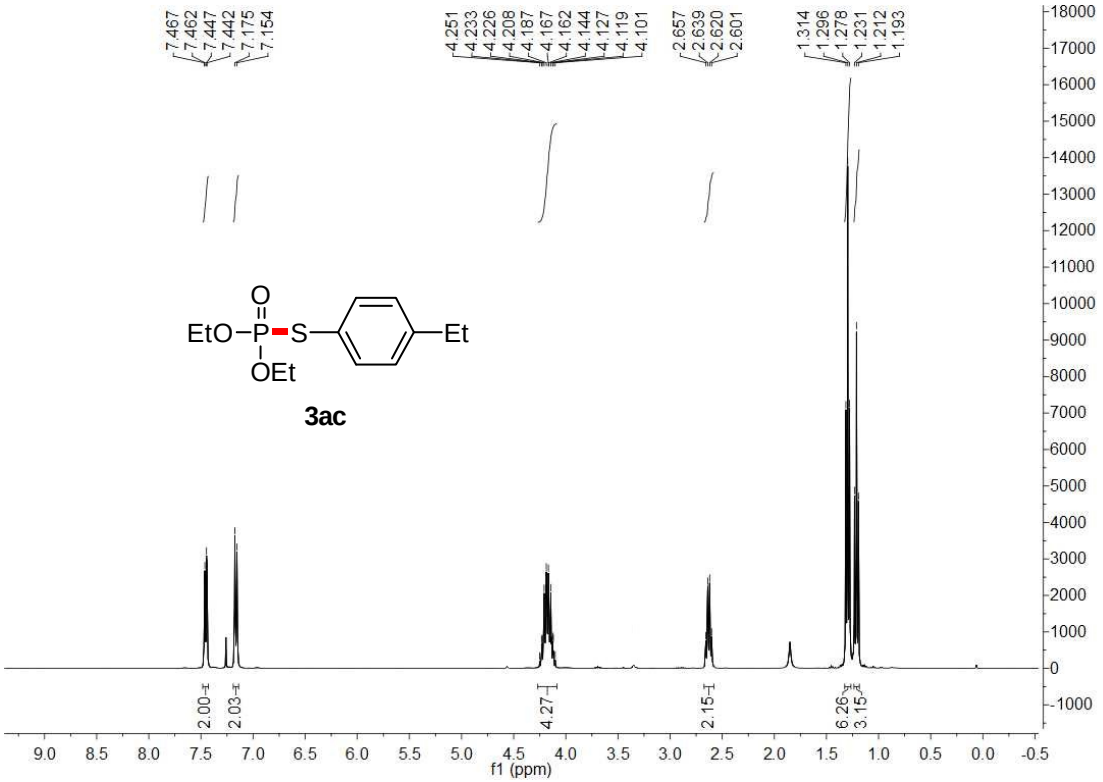
EtO
P
S
OMe
OEt
O
3ab
f1 (ppm)


23.585
EtO
P
S
OMe
OEt
O
3ab
f1 (ppm)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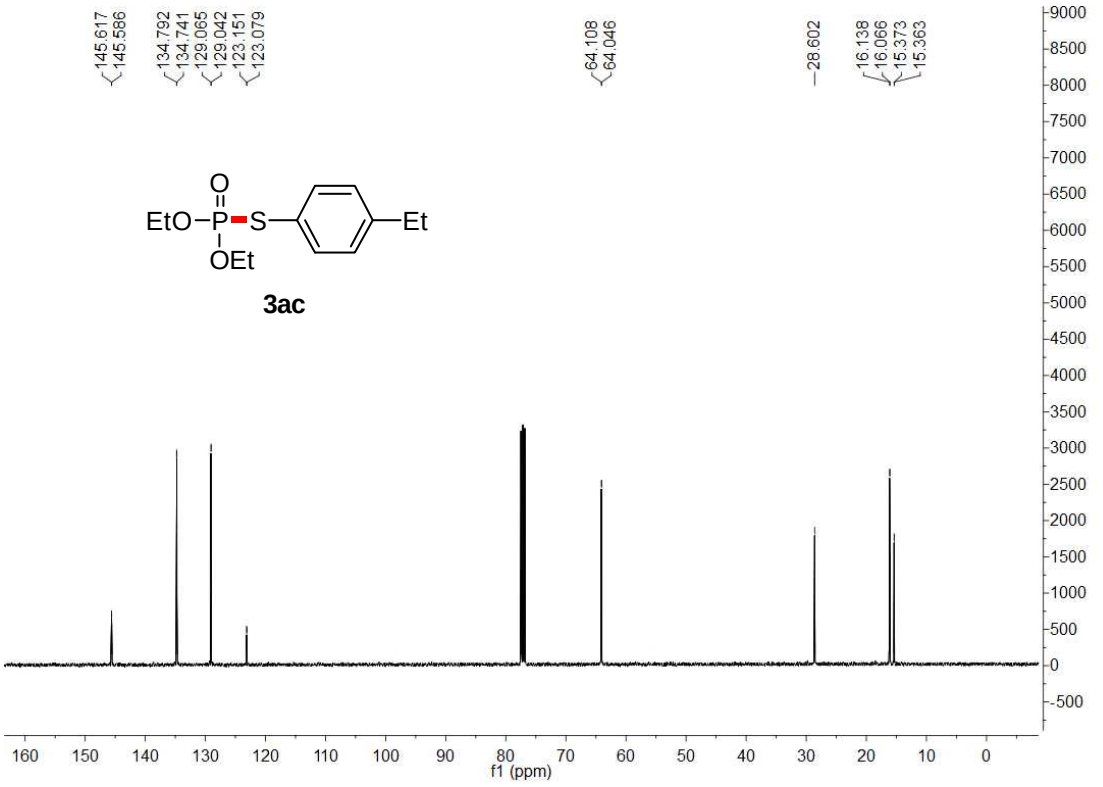
7.462
7.447
7.442
7.175
7.154
4.251
4.233
4.226
4.208
4.187
4.167
4.162
4.144
4.127
4.119
4.101
2.657
2.639
2.620
2.601
1.314
1.296
1.278
1.231
1.212
1.193
EtO
P
S
OEt
Et
3ac
2.00
2.03
4.27
2.15
6.26
3.15
f1 (ppm)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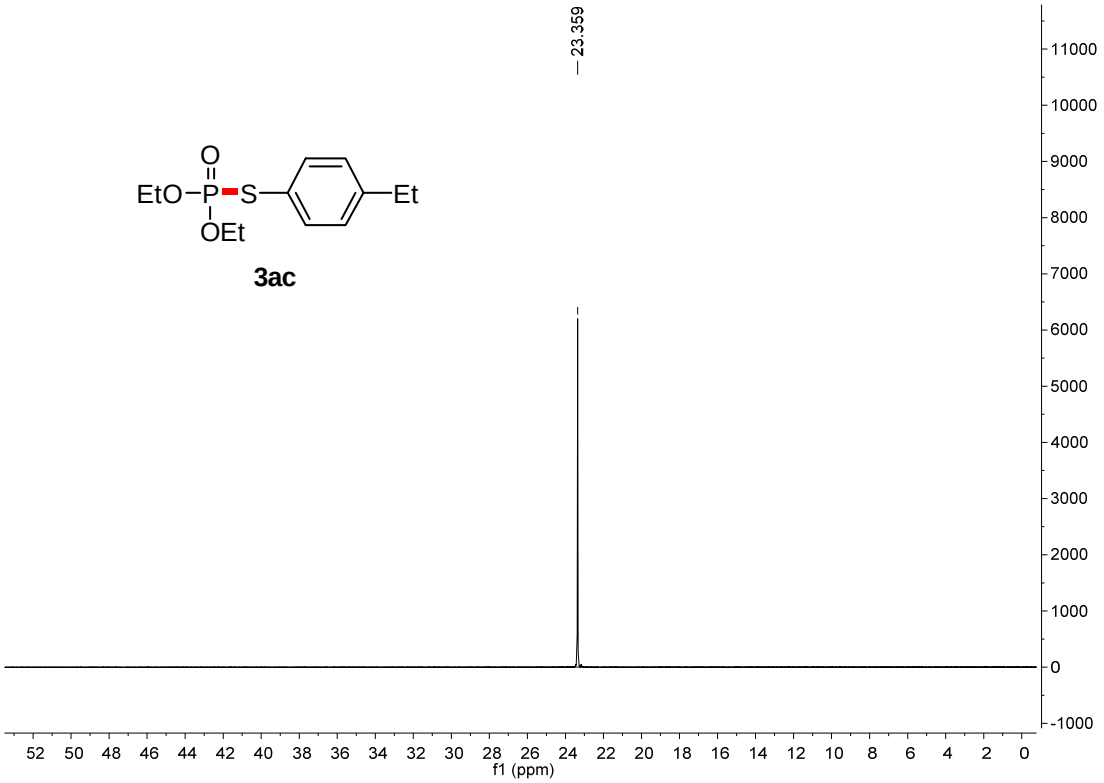
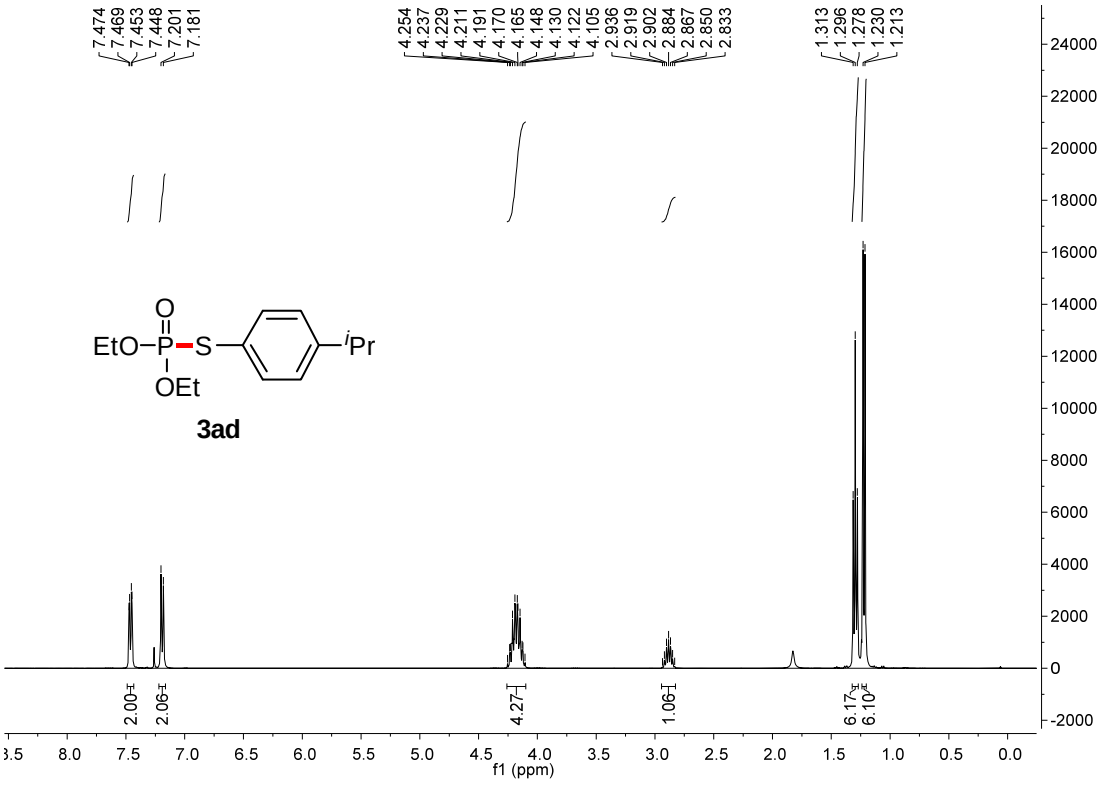
145.586
134.792
134.741
129.065
129.042
123.151
123.079
64.108
64.046
28.602
16.138
16.066
15.373
15.363
EtO
P
S
OEt
Et
3ac
f1 (ppm)


23.359
EtO
P
S
OEt
Et
O
3ac
f1 (ppm)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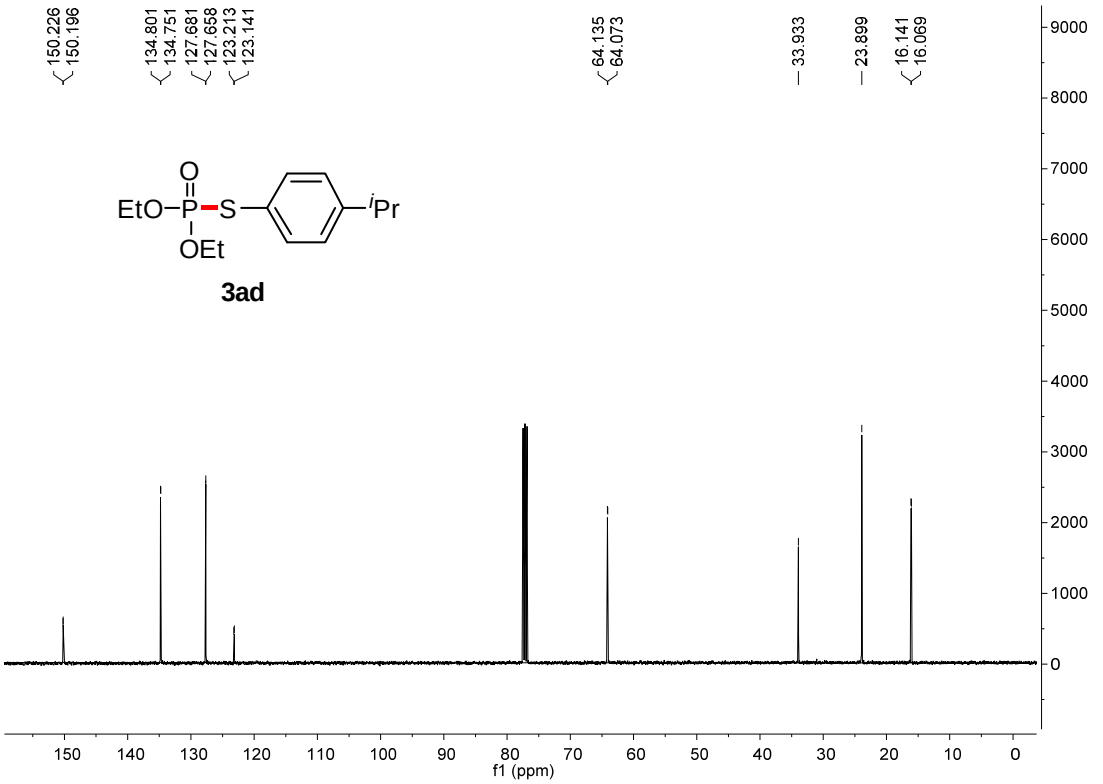
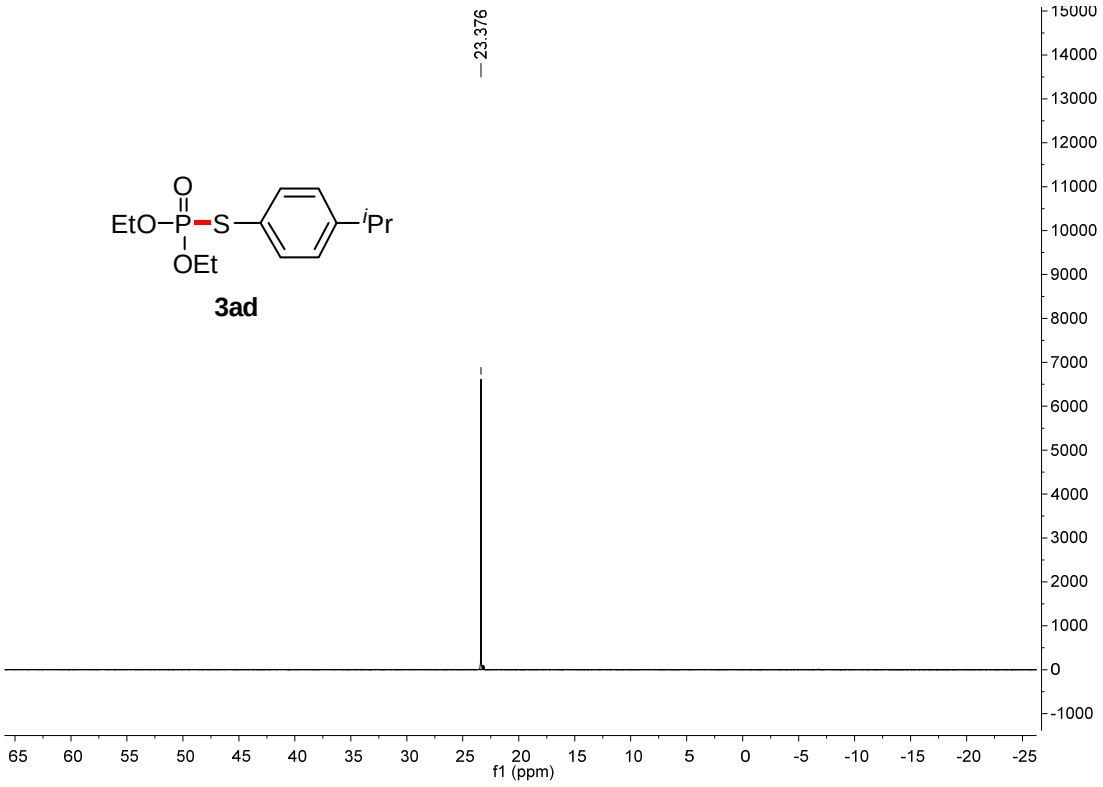
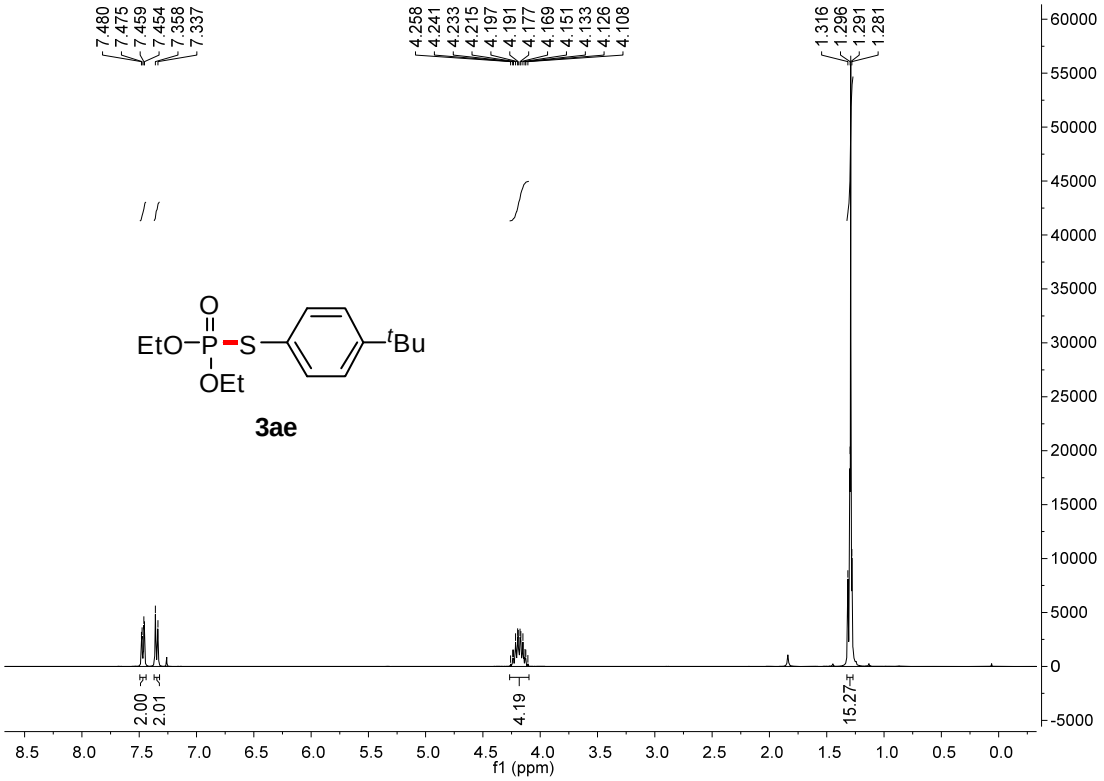
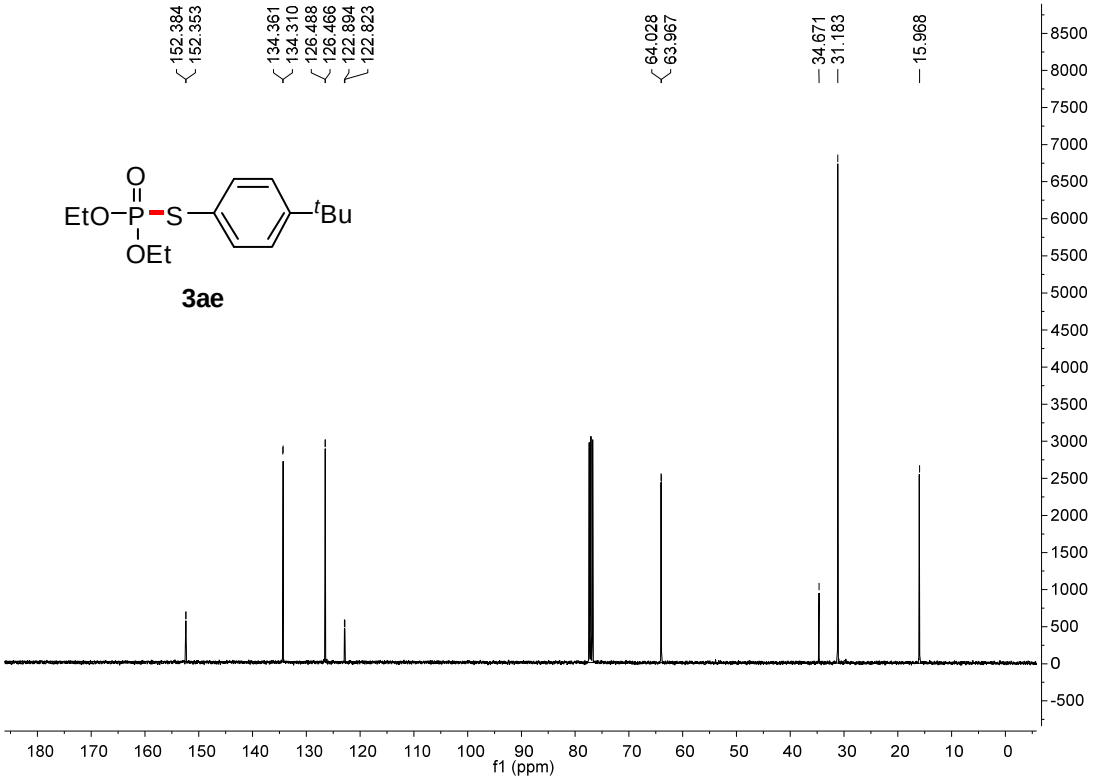
7.469
7.453
7.448
7.201
7.181
4.254
4.237
4.229
4.211
4.191
4.170
4.165
4.148
4.130
4.122
4.105
2.936
2.919
2.902
2.884
2.867
2.850
2.833
1.313
1.296
1.278
1.230
1.213
EtO
P
S
OEt
iPr
O
3ad
2.00
2.06
4.27
1.06
6.17
6.10
f1 (ppm)


150.226
150.196
134.801
134.751
127.681
127.658
123.213
123.141
64.135
64.073
33.933
23.899
16.141
16.069
EtO–P(=O)(OEt)–S–C6H4–iPr
3ad
f1 (ppm)


23.376
EtO–P(=O)(OEt)–S–C6H4–iPr
3ad
f1 (ppm)


7.480
7.475
7.459
7.454
7.358
7.337
4.258
4.241
4.233
4.215
4.197
4.191
4.177
4.169
4.151
4.133
4.126
4.108
1.316
1.296
1.291
1.281
EtO
P
S
OEt
tBu
3ae
2.00
2.01
4.19
15.27
f1 (ppm)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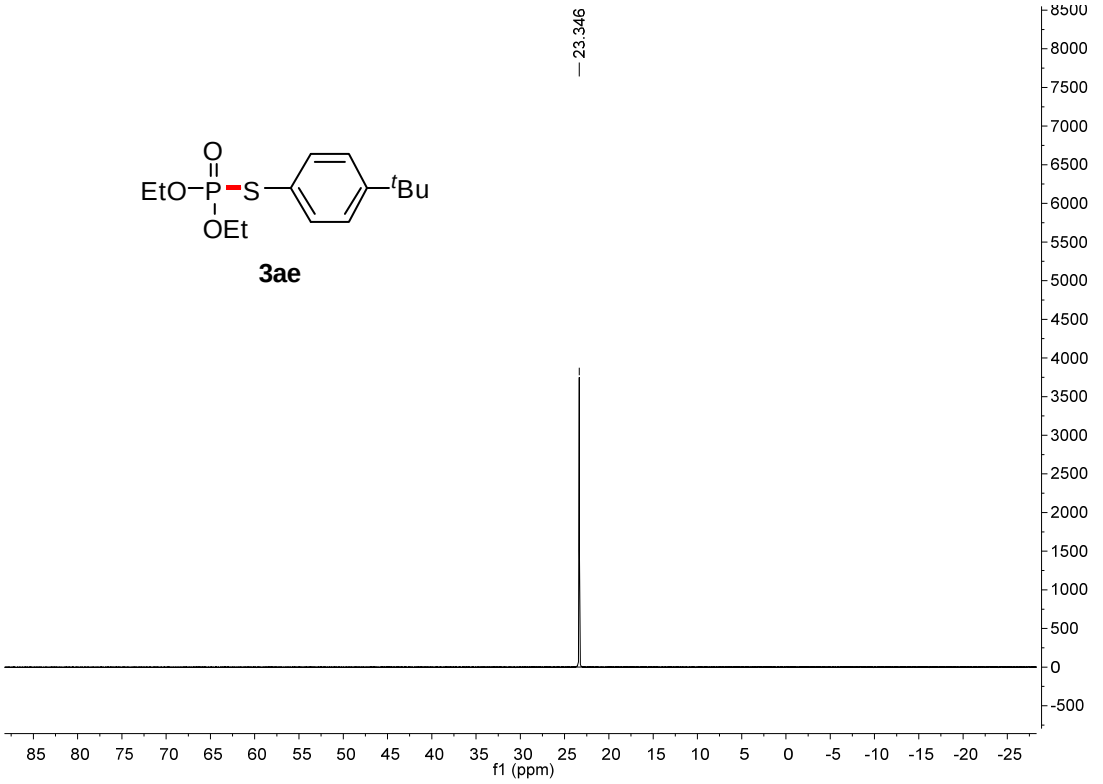
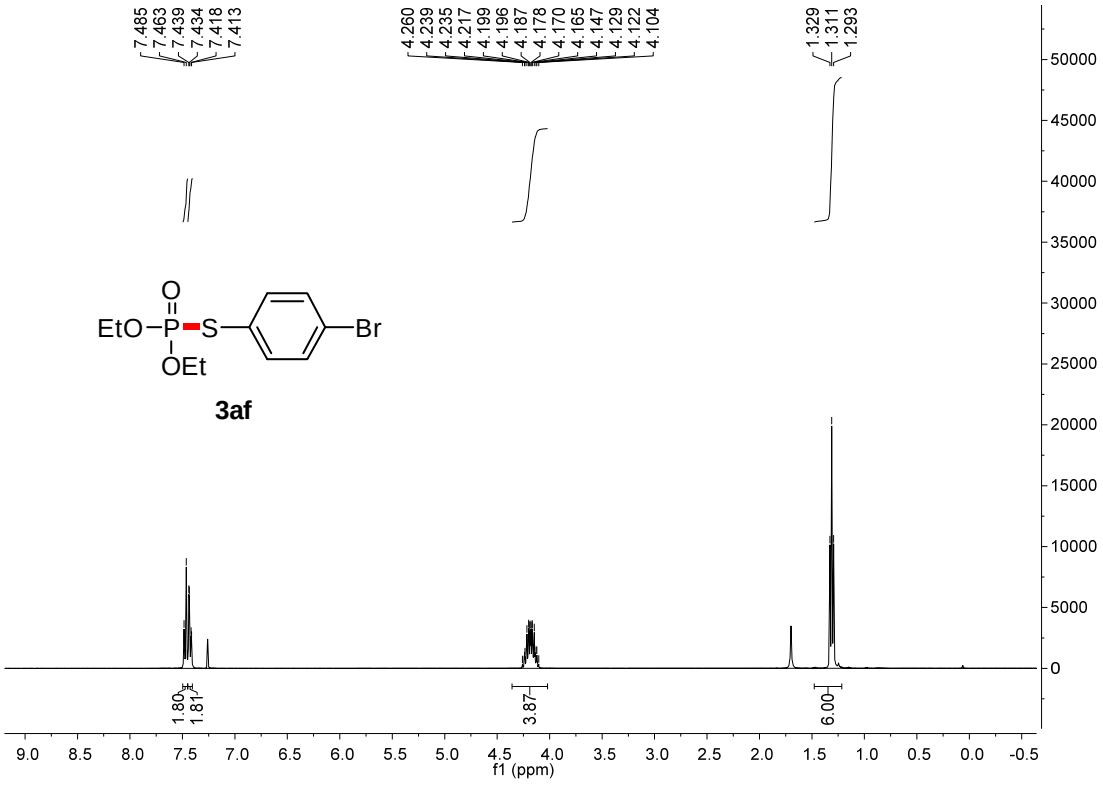
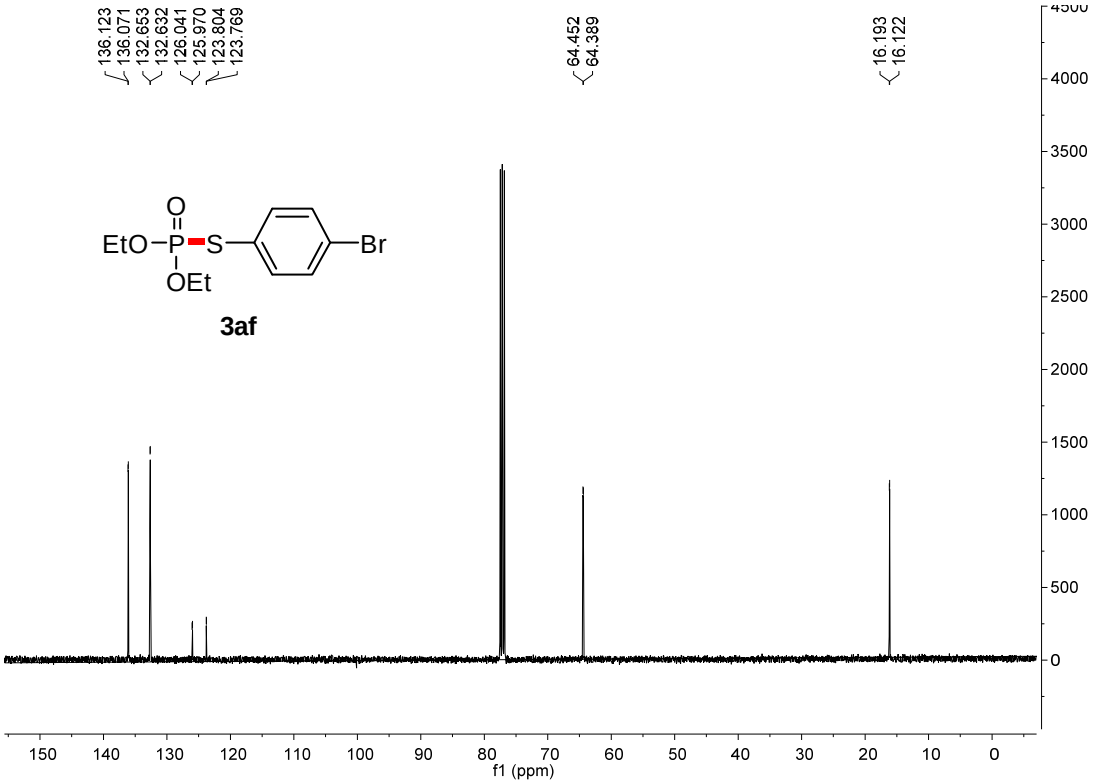
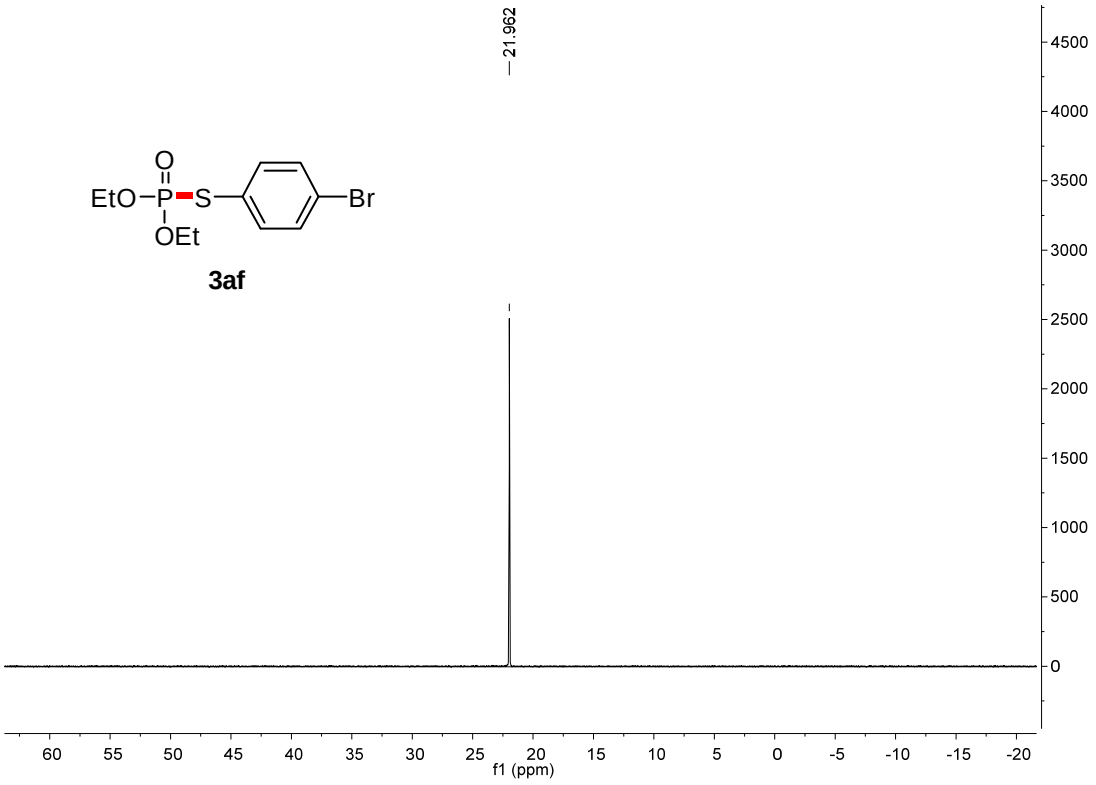
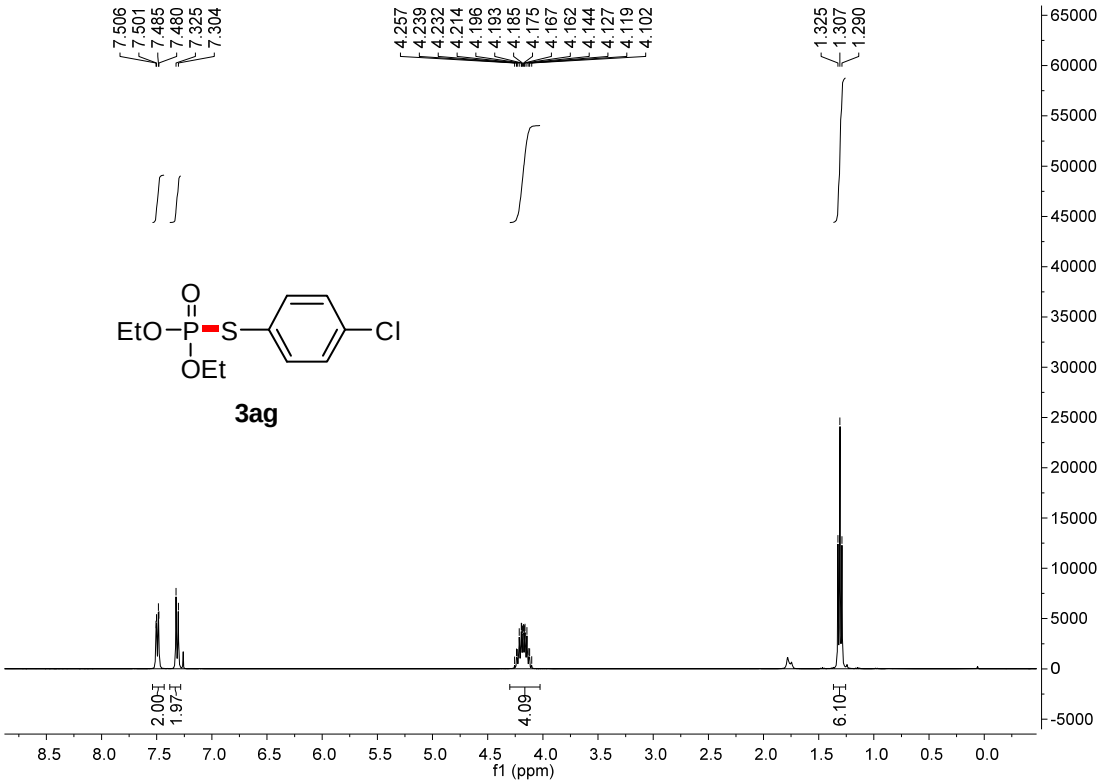
152.353
134.361
134.310
126.488
126.466
122.894
122.823
64.028
63.967
34.671
31.183
15.968
EtO
P
S
OEt
tBu
3ae
f1 (ppm)

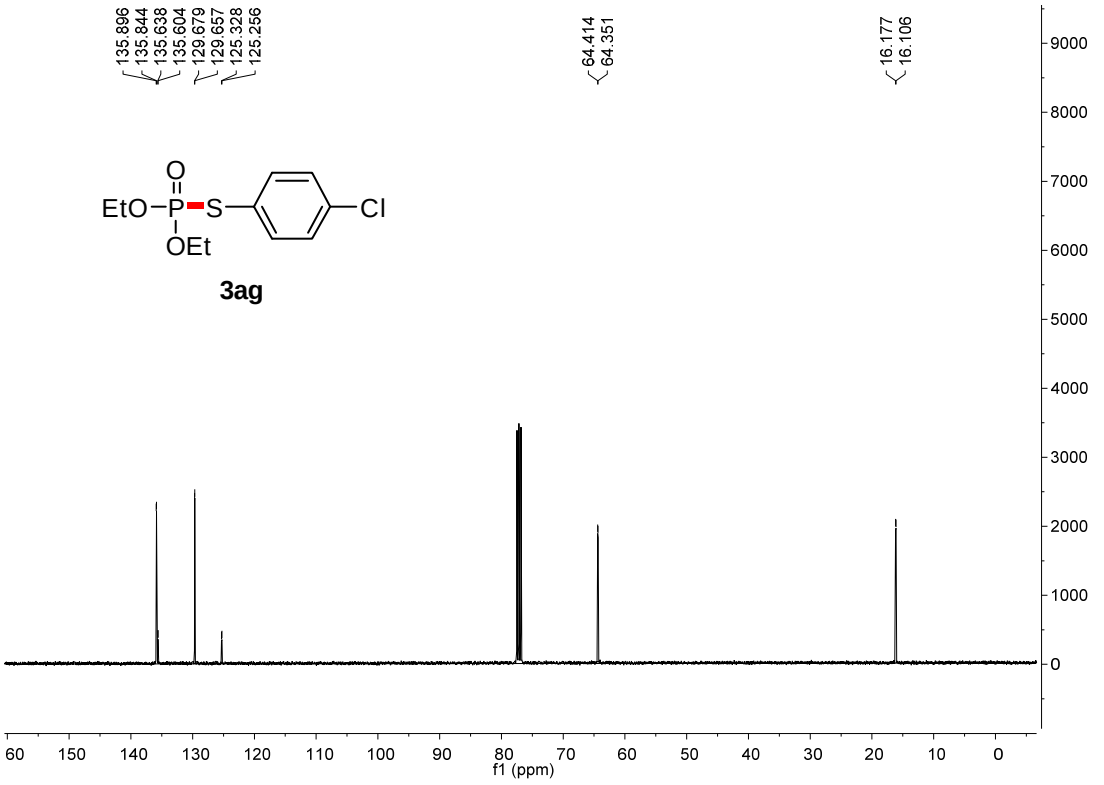

23.346
EtO
P
S
OEt
tBu
3ae
f1 (ppm)


7.485
7.463
7.439
7.434
7.418
7.413
4.260
4.239
4.235
4.217
4.199
4.196
4.187
4.178
4.170
4.165
4.147
4.129
4.122
4.104
1.329
1.311
1.293
EtO
P
S
OEt
Br
3af
1.80
1.81
3.87
6.00
f1 (ppm)


136.123
136.071
132.653
132.632
126.041
125.970
123.804
123.769
64.452
64.389
16.193
16.122
EtO
P
S
Br
OEt
O
3af
f1 (ppm)


21.962
EtO
P
S
Br
OEt
O
3af
f1 (ppm)


7.506
7.501
7.485
7.480
7.325
7.304
4.257
4.239
4.232
4.214
4.196
4.193
4.185
4.175
4.167
4.162
4.144
4.127
4.119
4.102
1.325
1.307
1.290
EtO
P
S
Cl
OEt
3ag
2.00
1.97
4.09
6.10
f1 (ppm)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135.844
135.638
135.604
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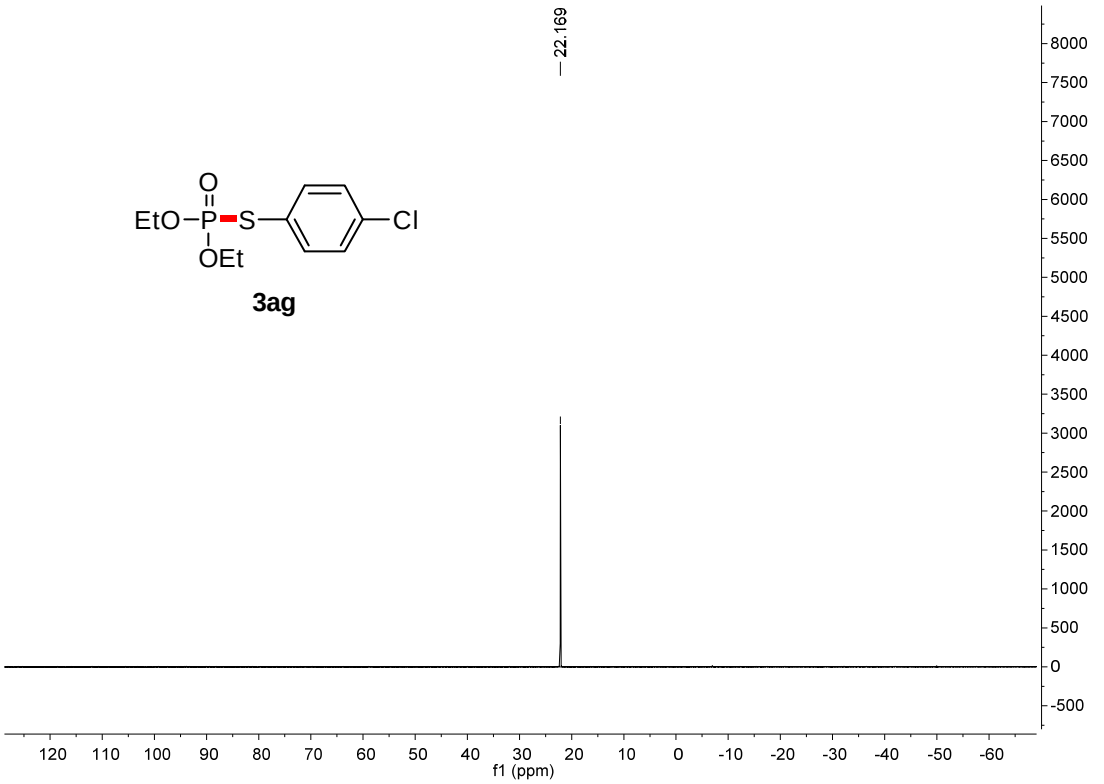
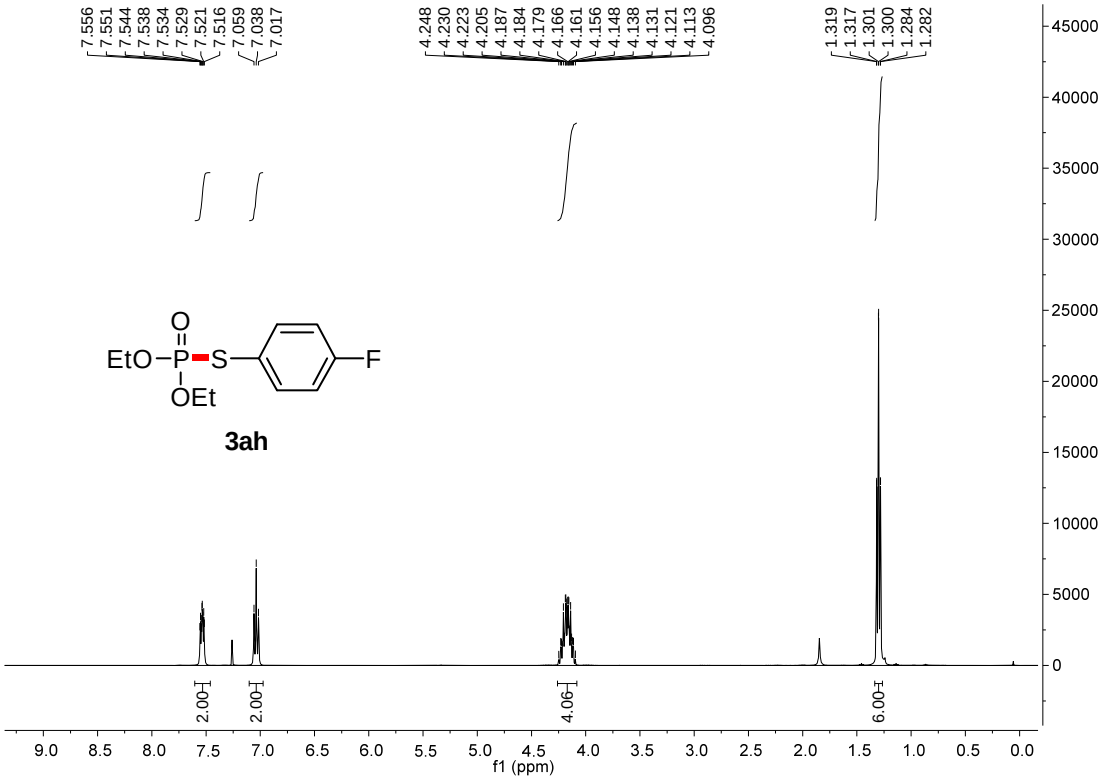
129.657
125.328
125.256
64.414
64.351
16.177
16.106
EtO
P
S
Cl
OEt
3ag
f1 (ppm)


22.169
EtO
P
S
Cl
OEt
O
3ag
f1 (ppm)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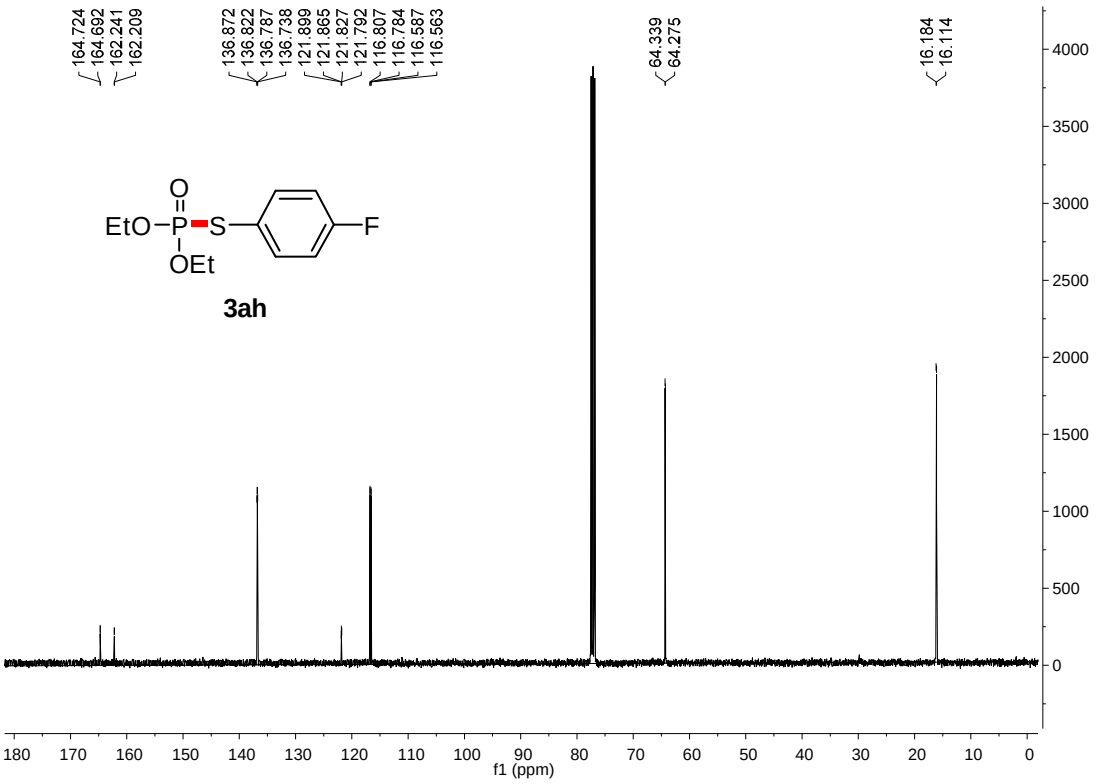
7.551
7.544
7.538
7.534
7.529
7.521
7.516
7.059
7.038
7.017
4.248
4.230
4.223
4.205
4.187
4.184
4.179
4.166
4.161
4.156
4.148
4.138
4.131
4.121
4.113
4.096
1.319
1.317
1.301
1.300
1.284
1.282
EtO
P
S
F
OEt
O
3ah
2.00
2.00
4.06
6.00
f1 (ppm)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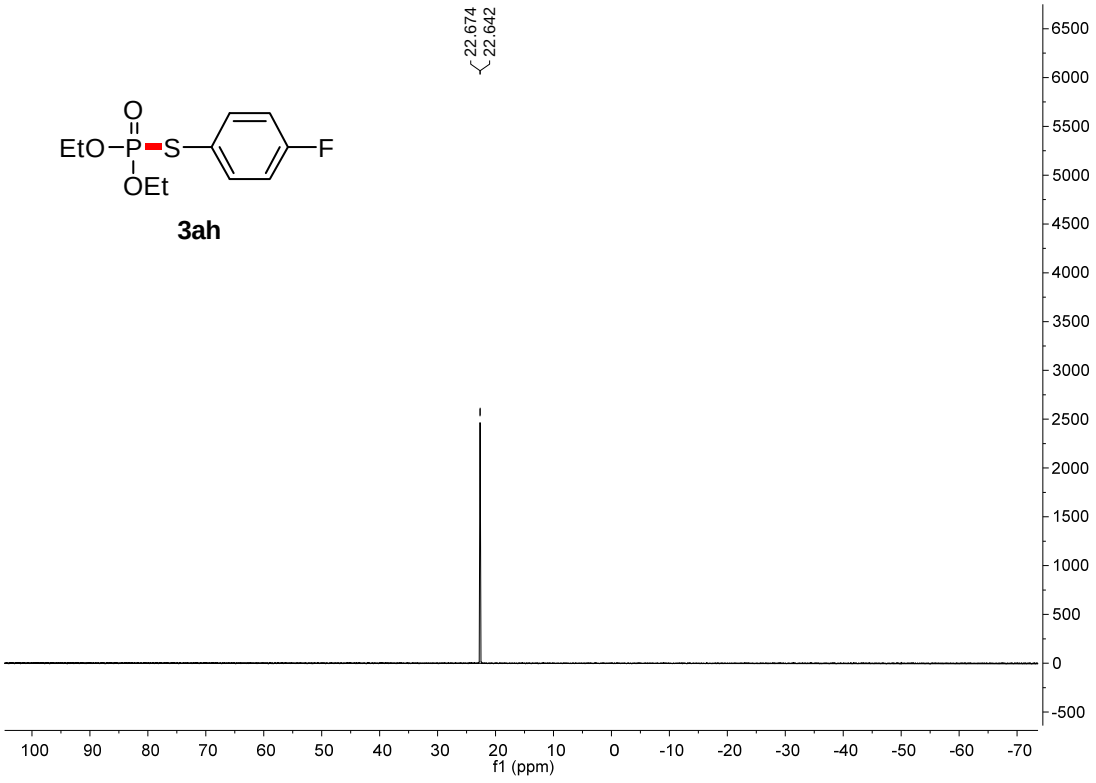
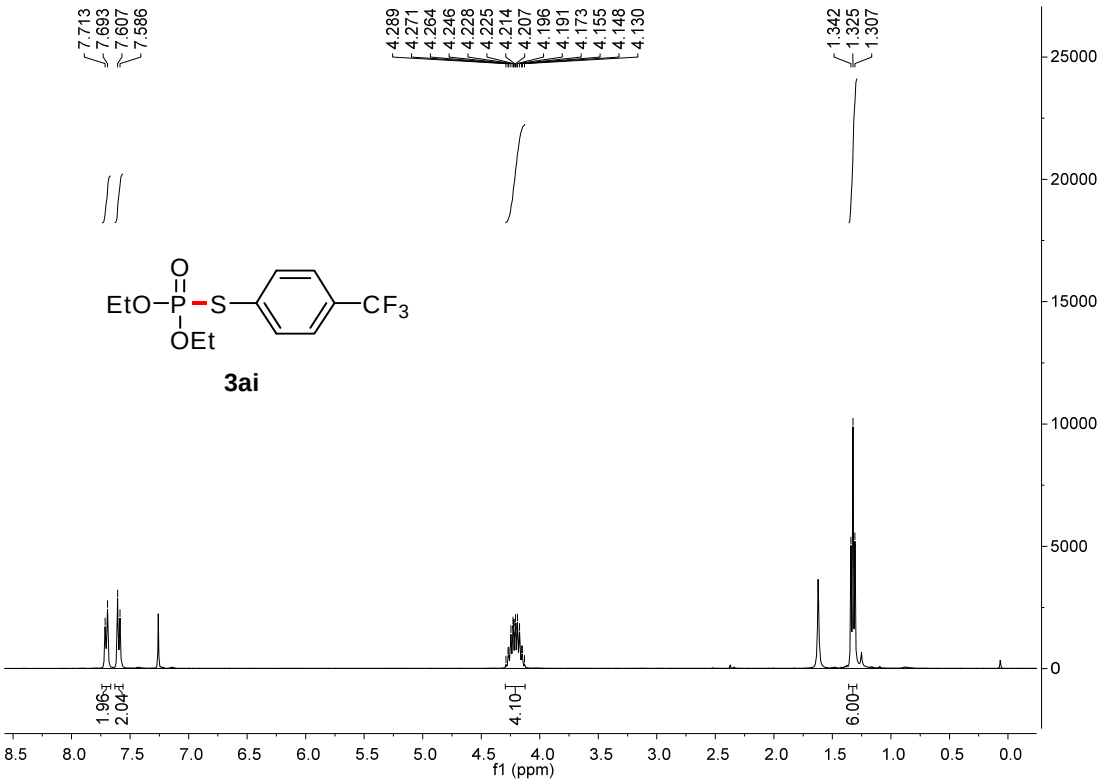
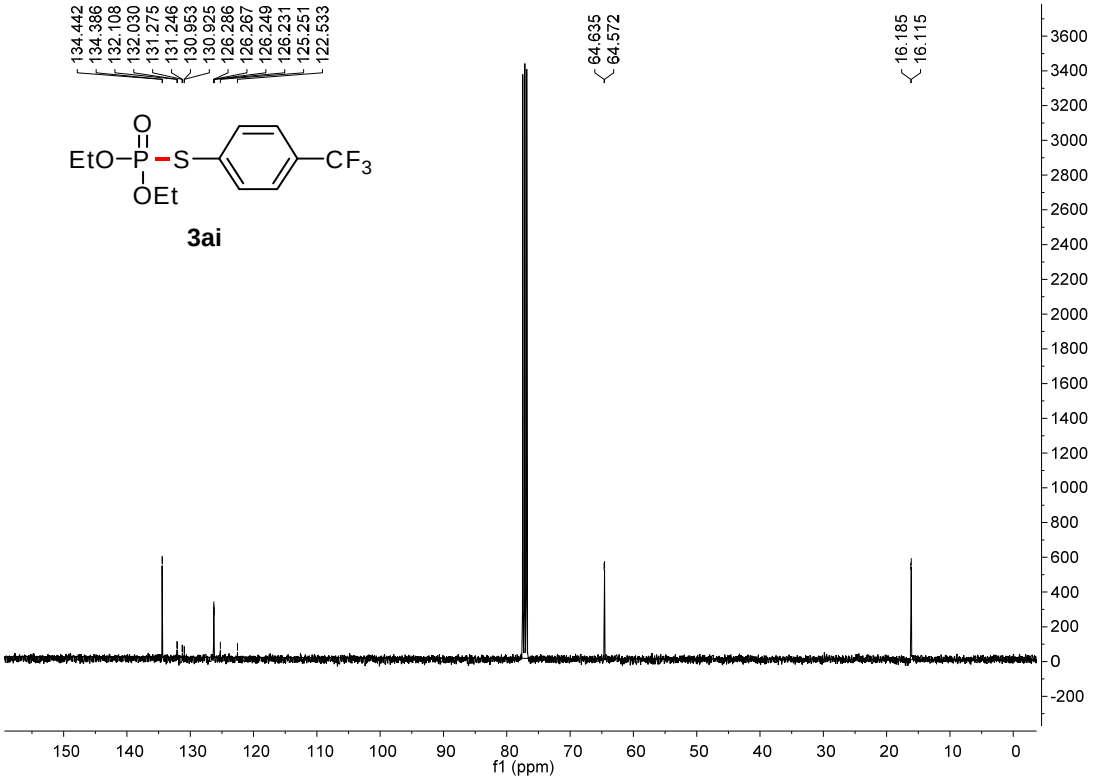
164.692
162.241
162.209
136.872
136.822
136.787
136.738
121.899
121.865
121.827
121.792
116.807
116.784
116.587
116.563
64.339
64.275
16.184
16.114
O
EtO
P
S
F
OEt
3ah
f1 (ppm)


22.674
22.642
O
EtO
P
S
F
OEt
3ah
f1 (ppm)


7.713
7.693
7.607
7.586
4.289
4.271
4.264
4.246
4.228
4.225
4.214
4.207
4.196
4.191
4.173
4.155
4.148
4.130
1.342
1.325
1.307
EtO–P(=O)(OEt)–S–C6H4–CF3
3ai
1.96
2.04
4.10
6.00
f1 (ppm)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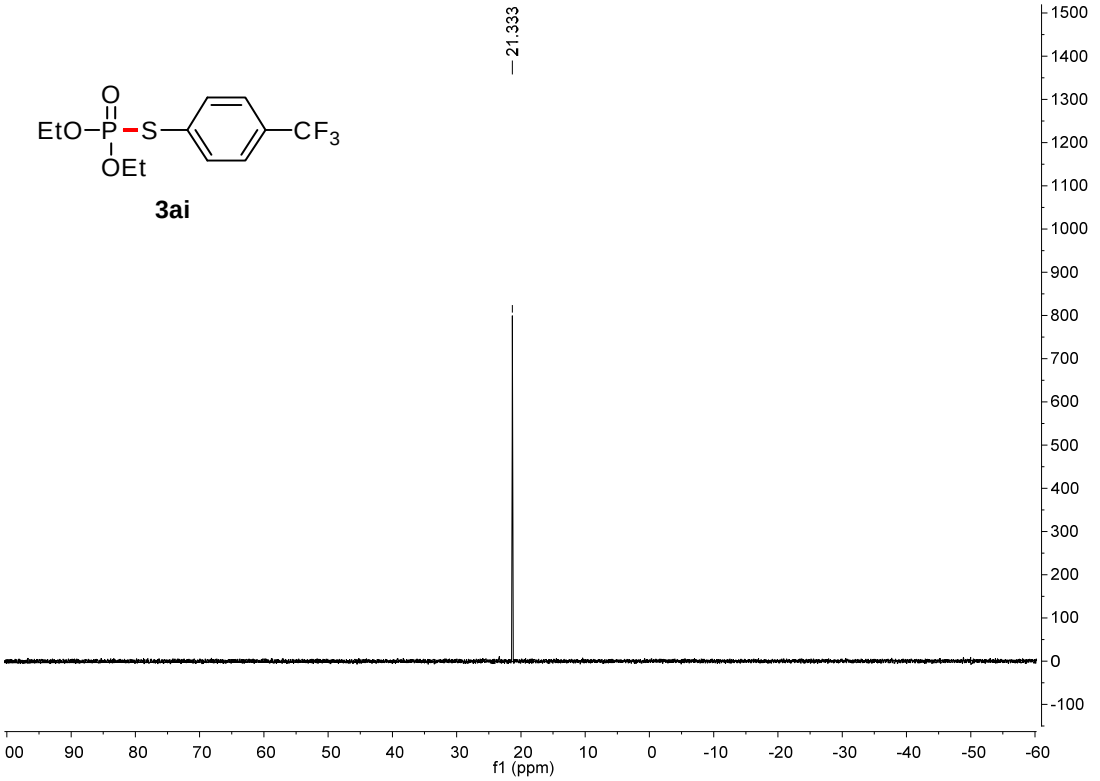
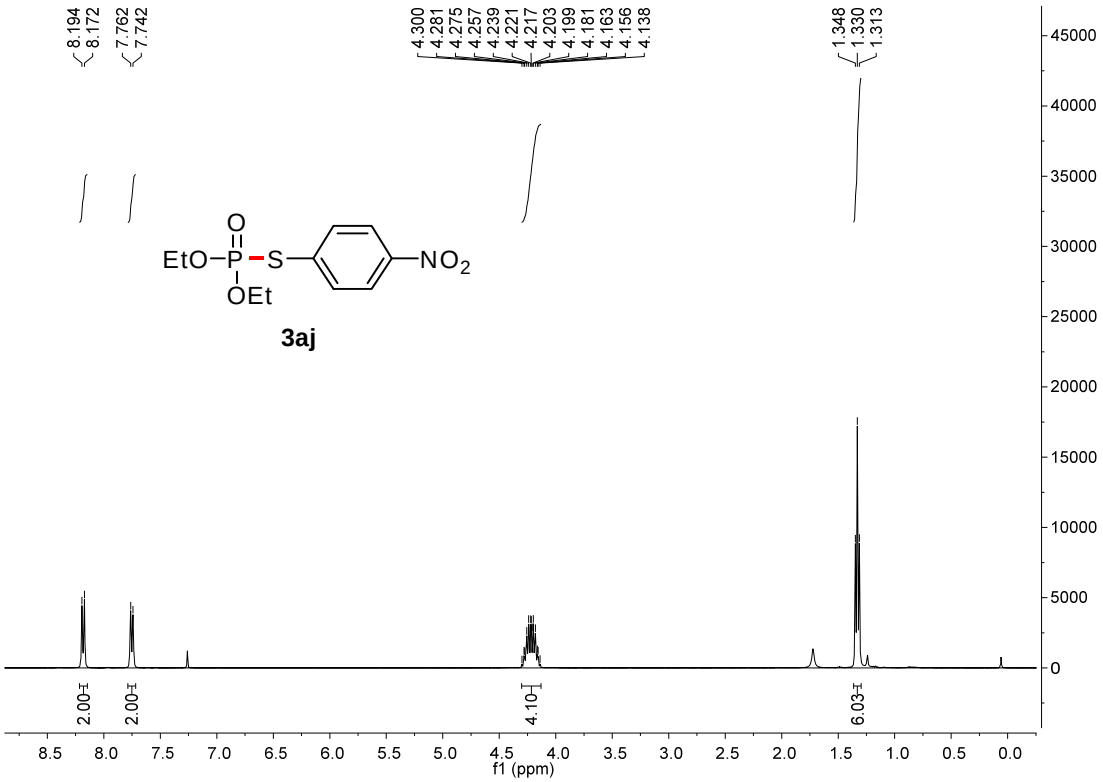
132.108
132.030
131.275
131.246
130.953
130.925
126.286
126.267
126.249
126.231
125.251
122.533
64.635
64.572
16.185
16.115
EtO–P(=O)(OEt)–S–C6H4–CF3
3ai
f1 (ppm)


21.333
EtO
P
S
OEt
CF3
3ai
f1 (ppm)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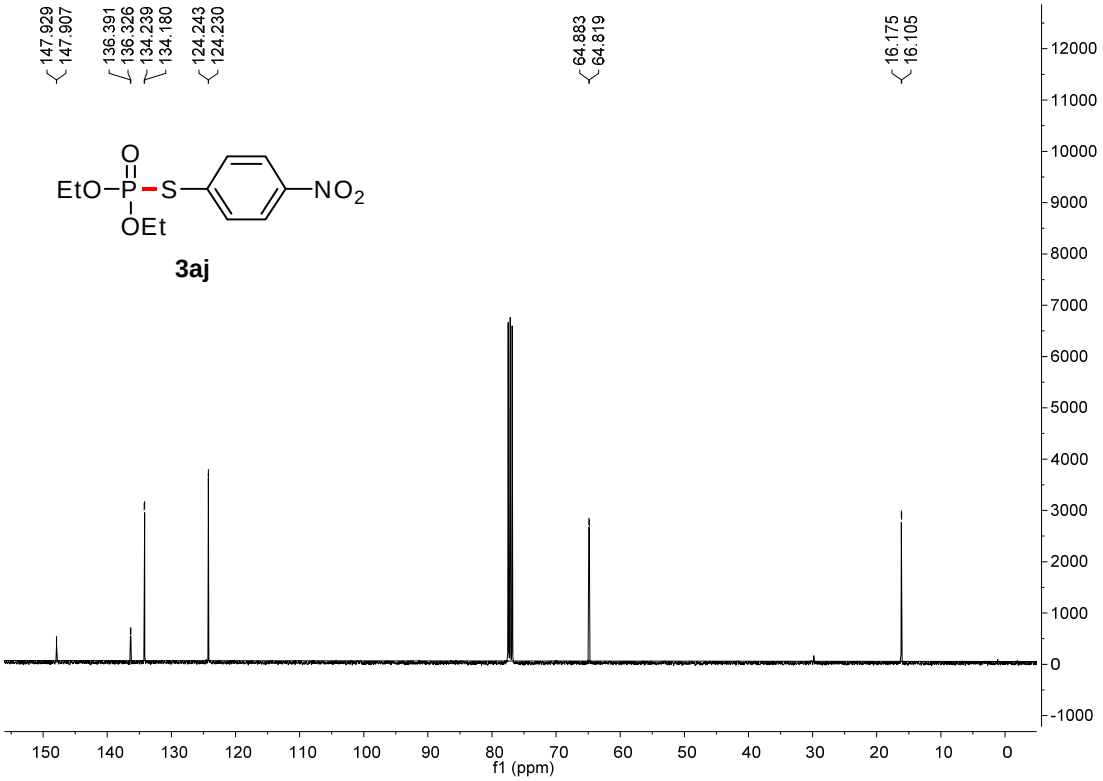
8.172
7.762
7.742
4.300
4.281
4.275
4.257
4.239
4.221
4.217
4.203
4.199
4.181
4.163
4.156
4.138
1.348
1.330
1.313
EtO
P
S
OEt
NO2
3aj
2.00
2.00
4.10
6.03
f1 (ppm)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136.391
136.326
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134.180
124.243
124.230
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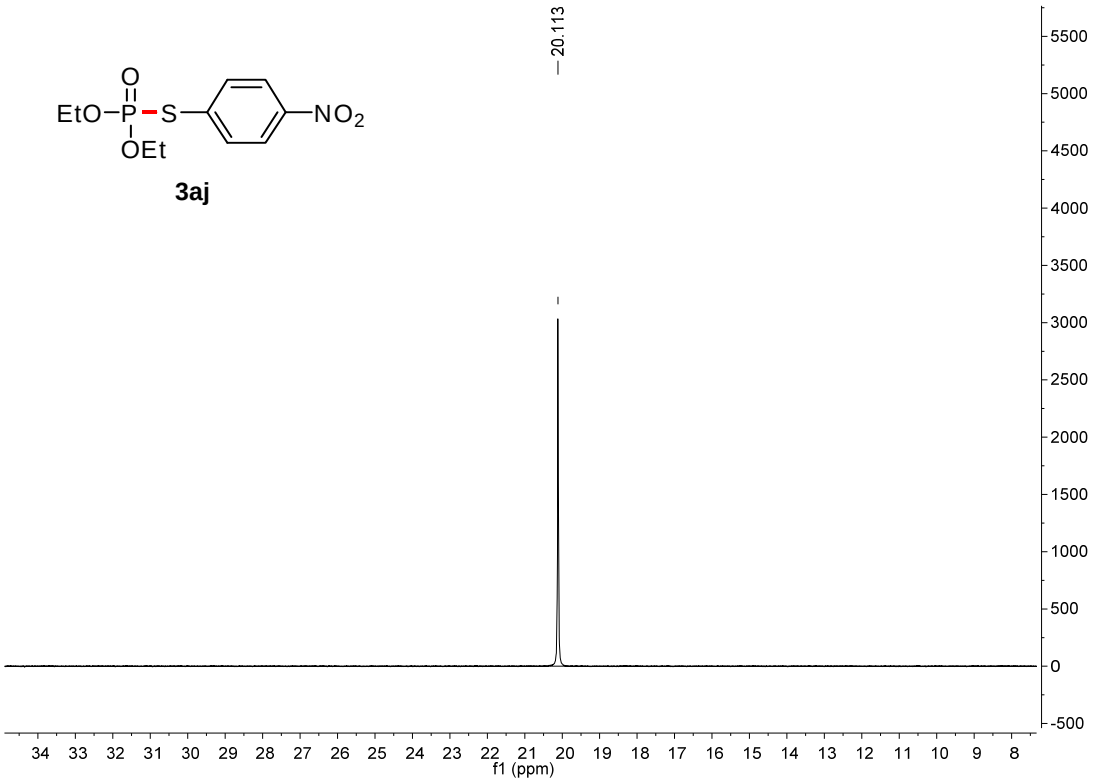
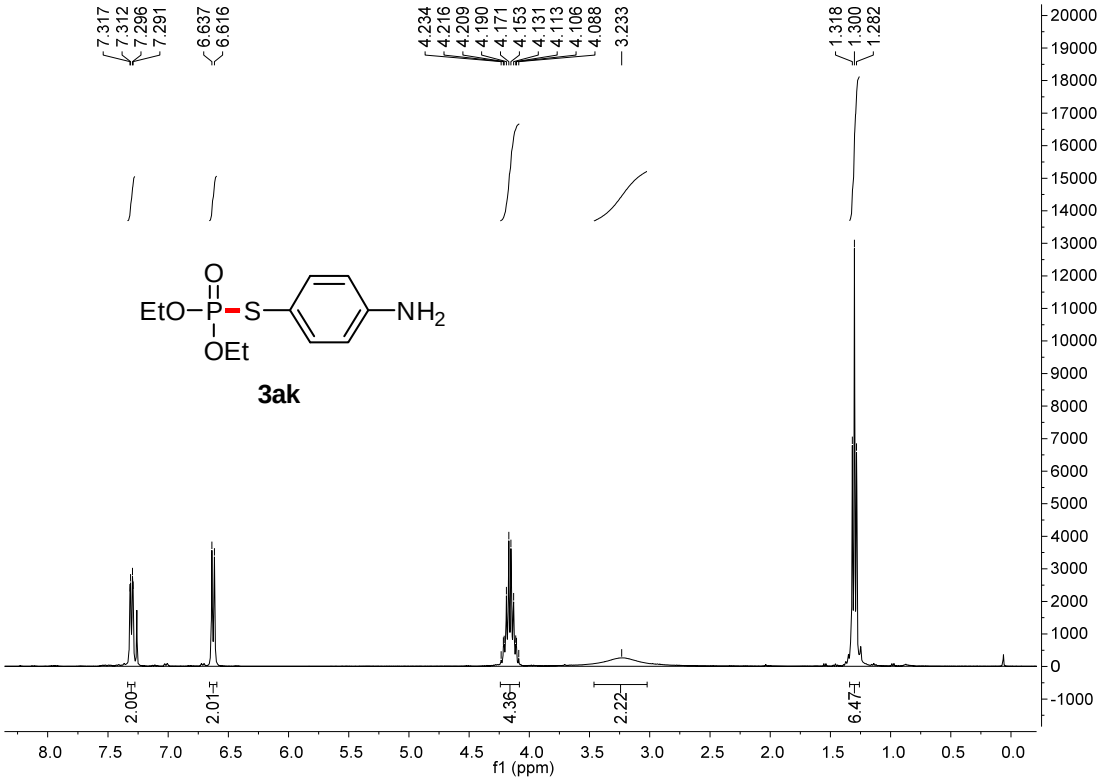
64.819
16.175
16.105
EtO
P
S
NO2
OEt
3aj
f1 (ppm)


20.113
EtO
P
S
NO2
OEt
3aj
f1 (ppm)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7.312
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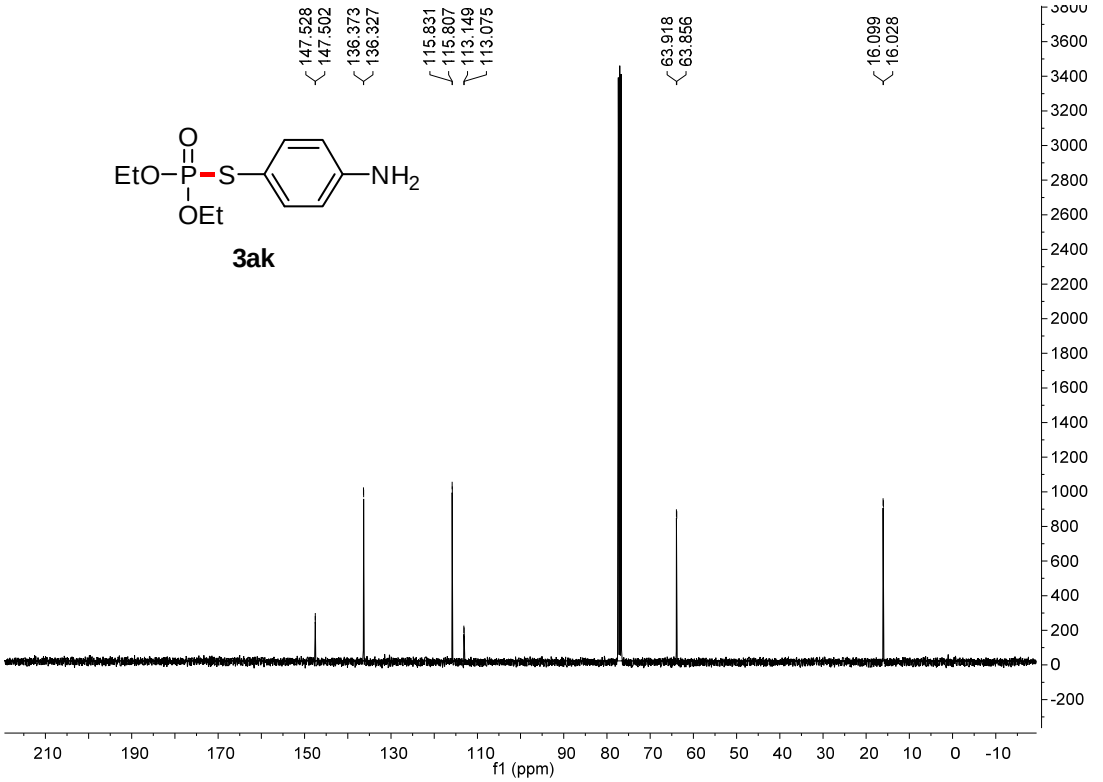
7.291
6.637
6.616
4.234
4.216
4.209
4.190
4.171
4.153
4.131
4.113
4.106
4.088
3.233
1.318
1.300
1.282
EtO
P
S
NH2
OEt
3ak
2.00
2.01
4.36
2.22
6.47
f1 (ppm)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115.807
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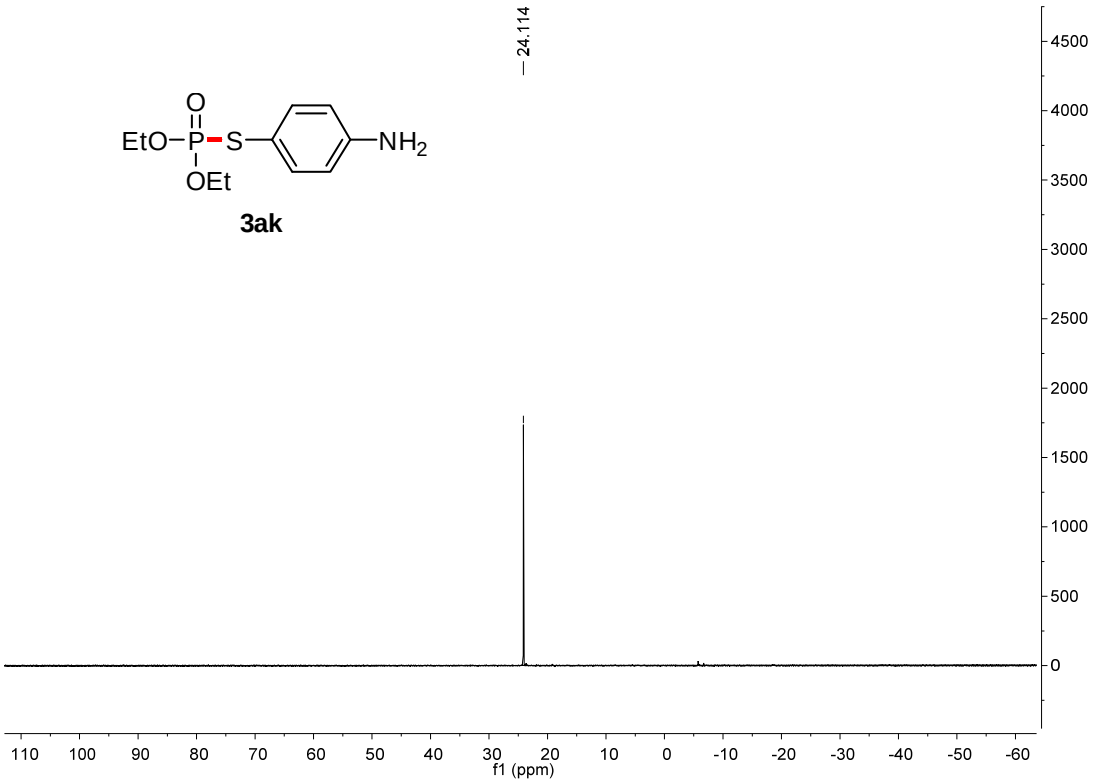
63.856
16.099
16.028
EtO
P
S
NH2
OEt
3ak
f1 (ppm)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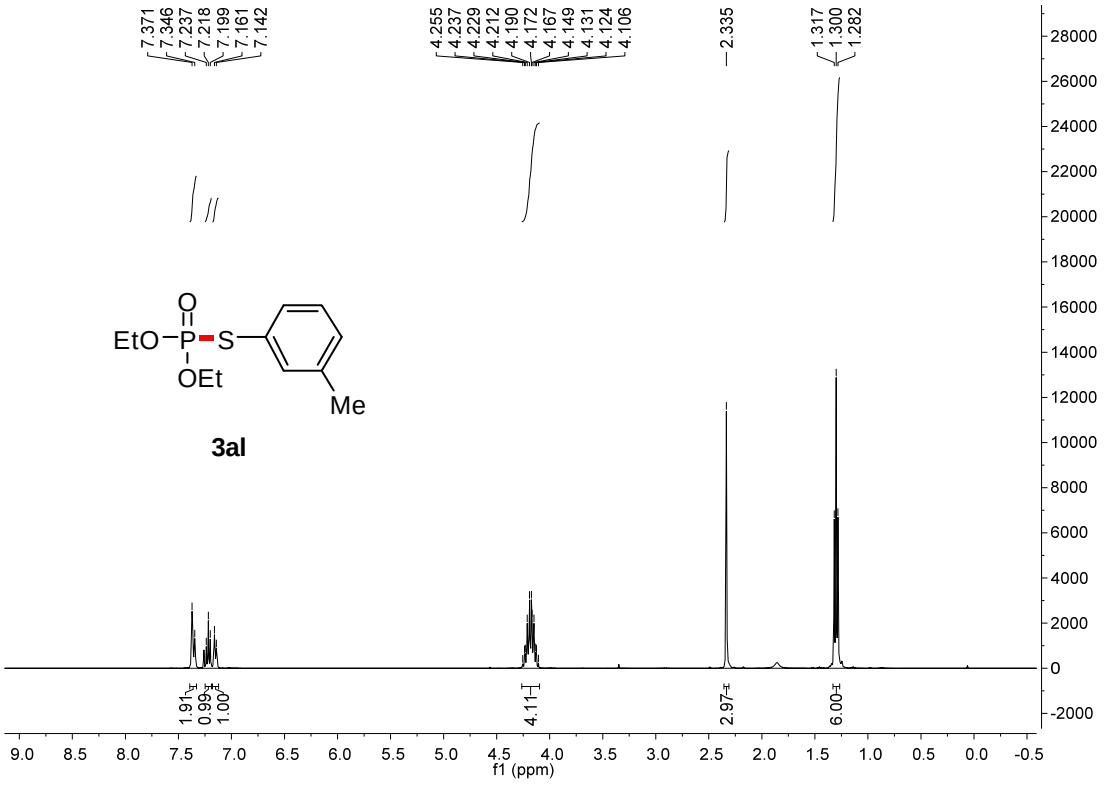
P
S
NH2
OEt
O
3ak
f1 (ppm)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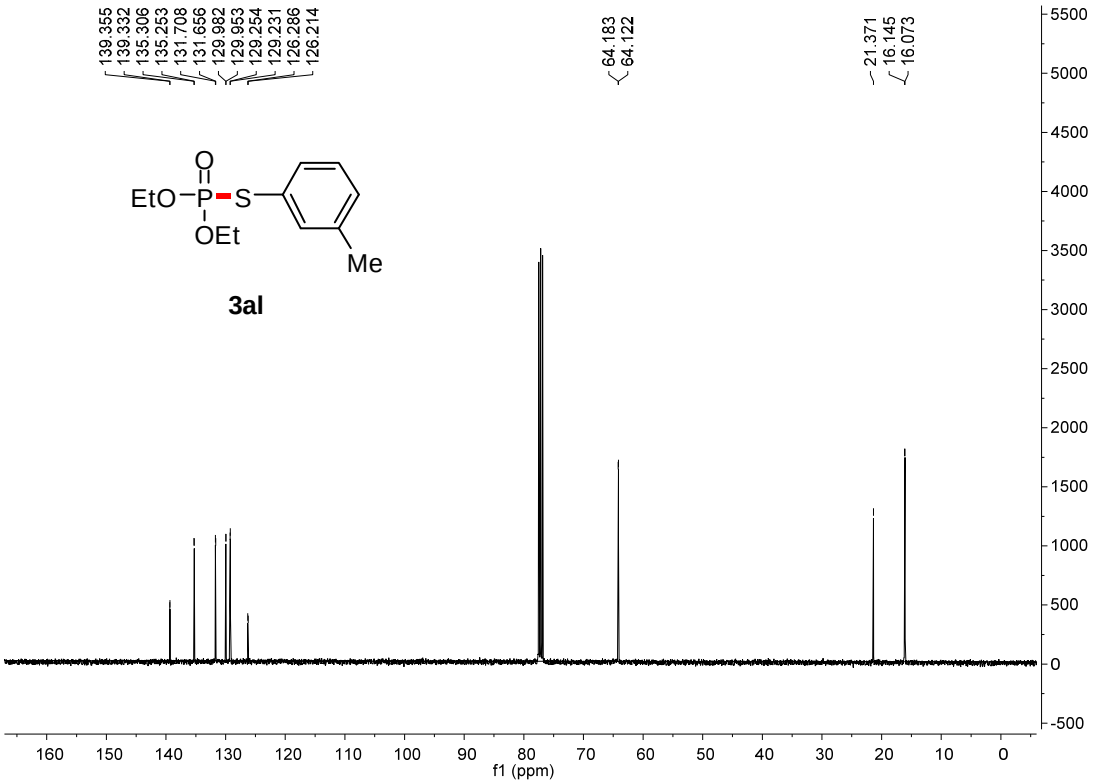
7.199
7.161
7.142
4.255
4.237
4.229
4.212
4.190
4.172
4.167
4.149
4.131
4.124
4.106
2.335
1.317
1.300
1.282
EtO
P
S
OEt
Me
3al
1.91
0.99
1.00
4.11
2.97
6.00
f1 (ppm)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129.231
126.286
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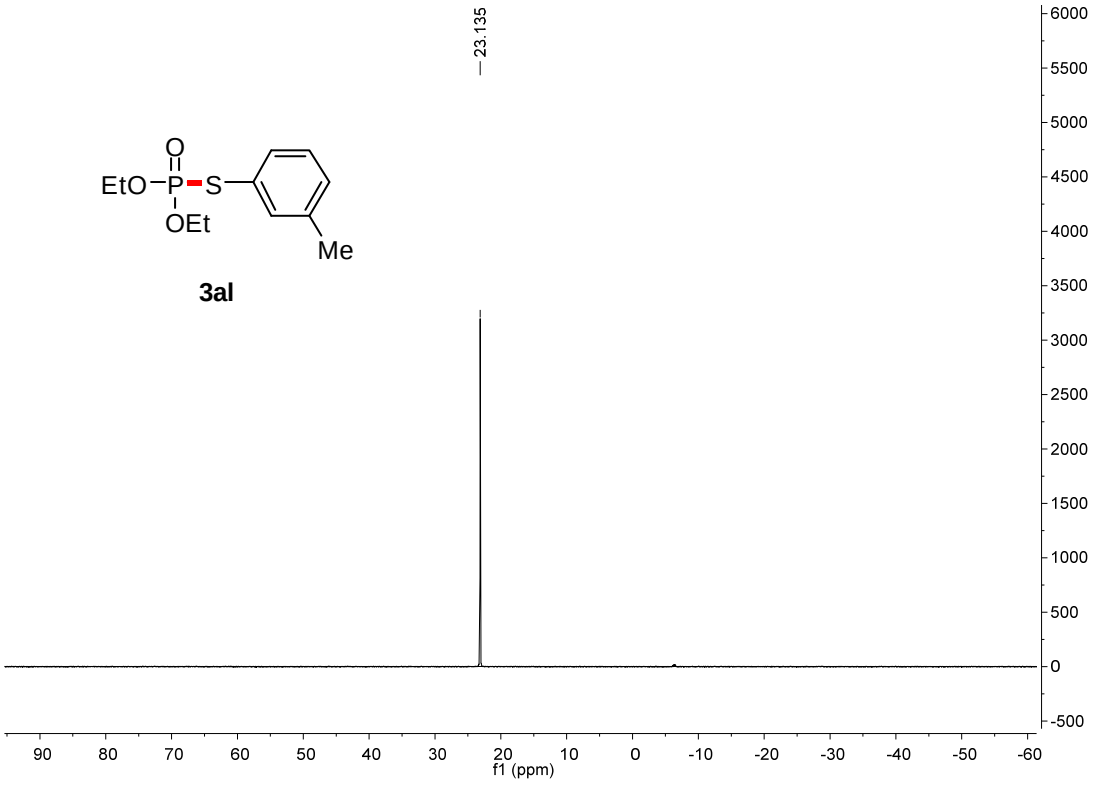
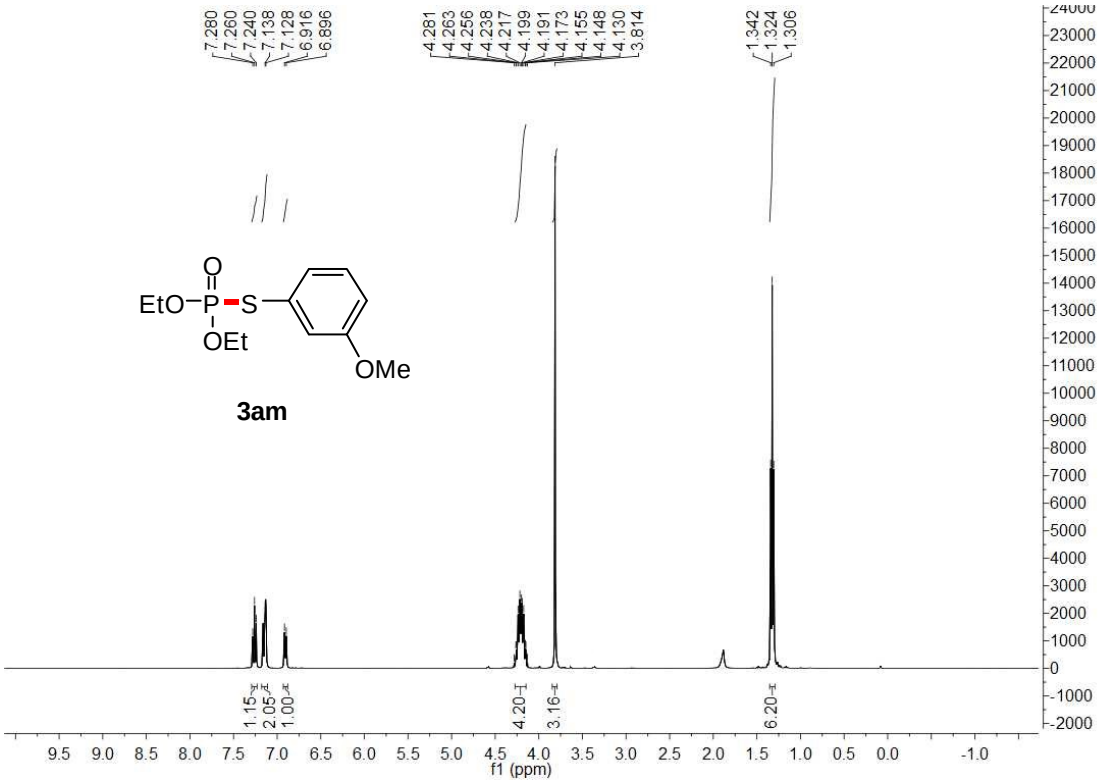
64.183
64.122
21.371
16.145
16.073
EtO
P
S
OEt
O
Me
3al
f1 (ppm)


23.135
EtO
P
S
OEt
O
Me
3al
f1 (ppm)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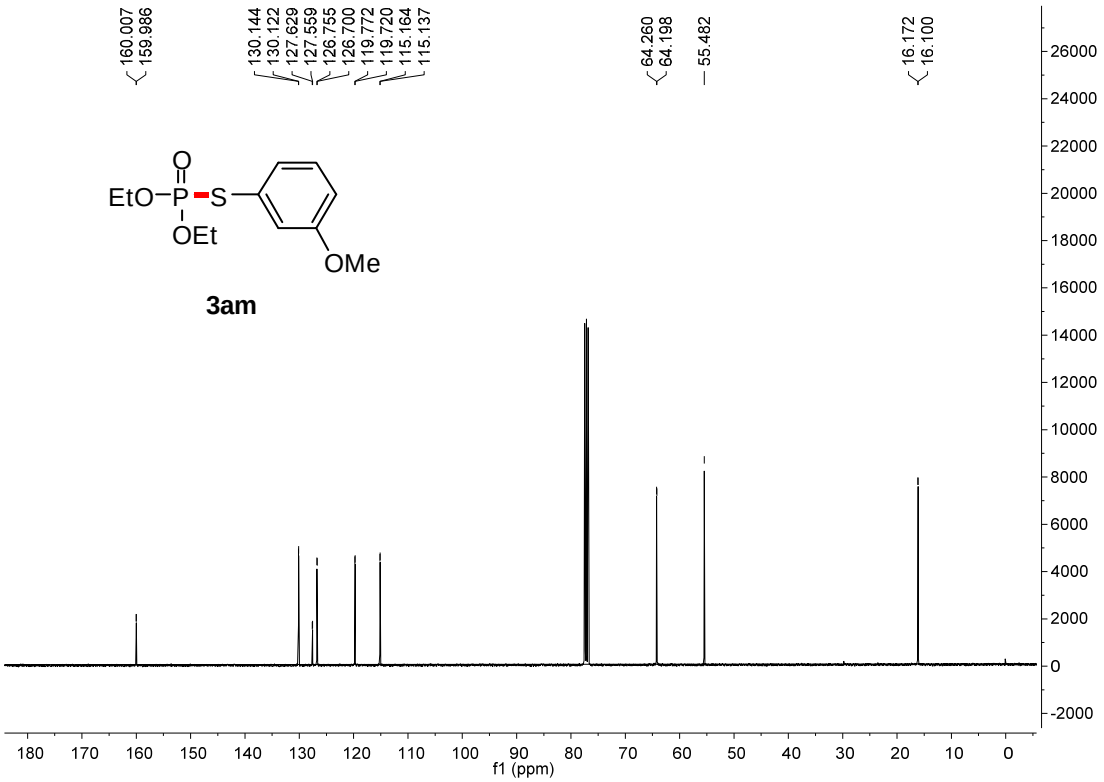
7.260
7.240
7.138
7.128
6.916
6.896
4.281
4.263
4.256
4.238
4.217
4.199
4.191
4.173
4.155
4.148
4.130
3.814
1.342
1.324
1.306
EtO
P
S
O
OEt
OMe
3am
1.15
2.05
1.00
4.20
3.16
6.20
f1 (ppm)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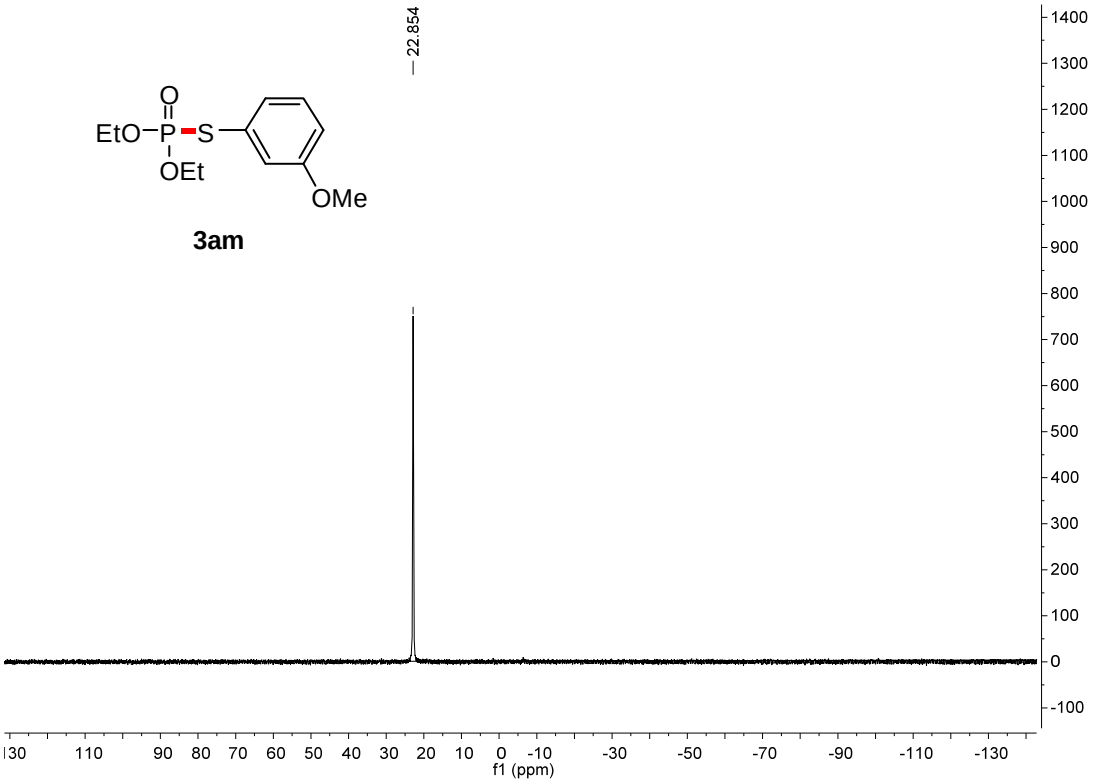
126.755
126.700
119.772
119.720
115.164
115.137
64.260
64.198
55.482
16.172
16.100
EtO
P
S
O
OEt
OMe
3am
f1 (ppm)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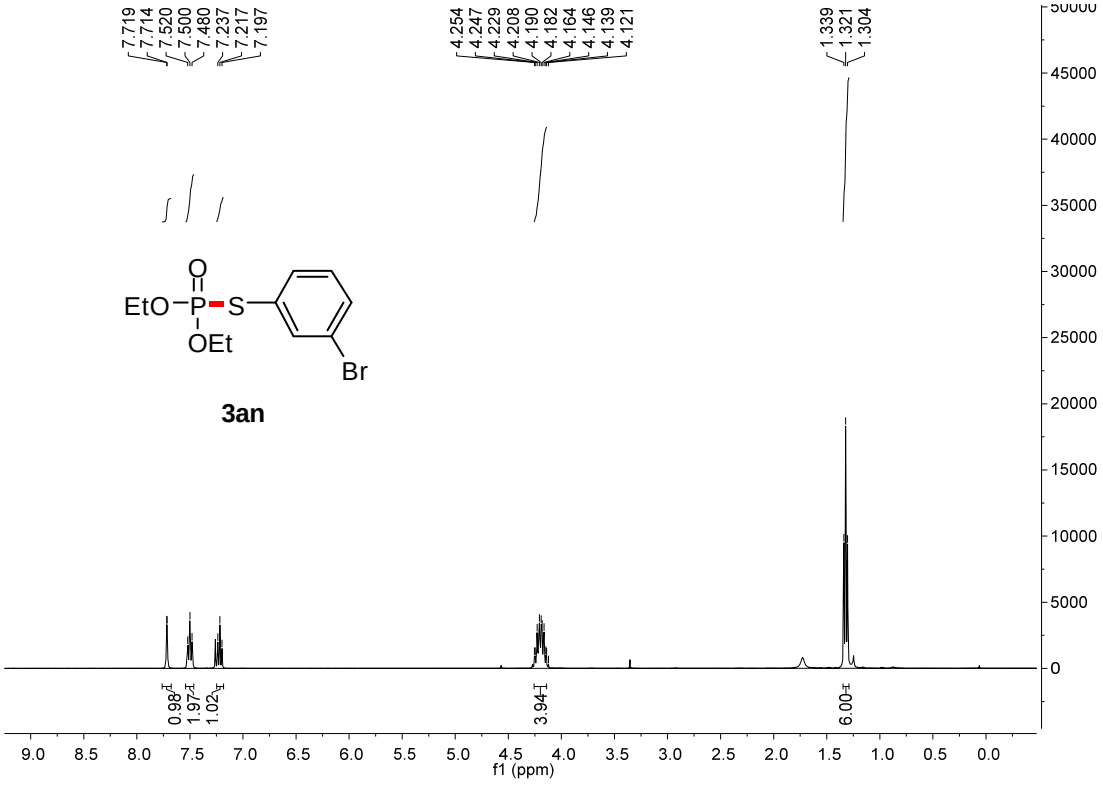
OMe
3am
f1 (ppm)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7.480
7.237
7.217
7.197
4.254
4.247
4.229
4.208
4.190
4.182
4.164
4.146
4.139
4.121
1.339
1.321
1.304
EtO
P
S
OEt
Br
3an
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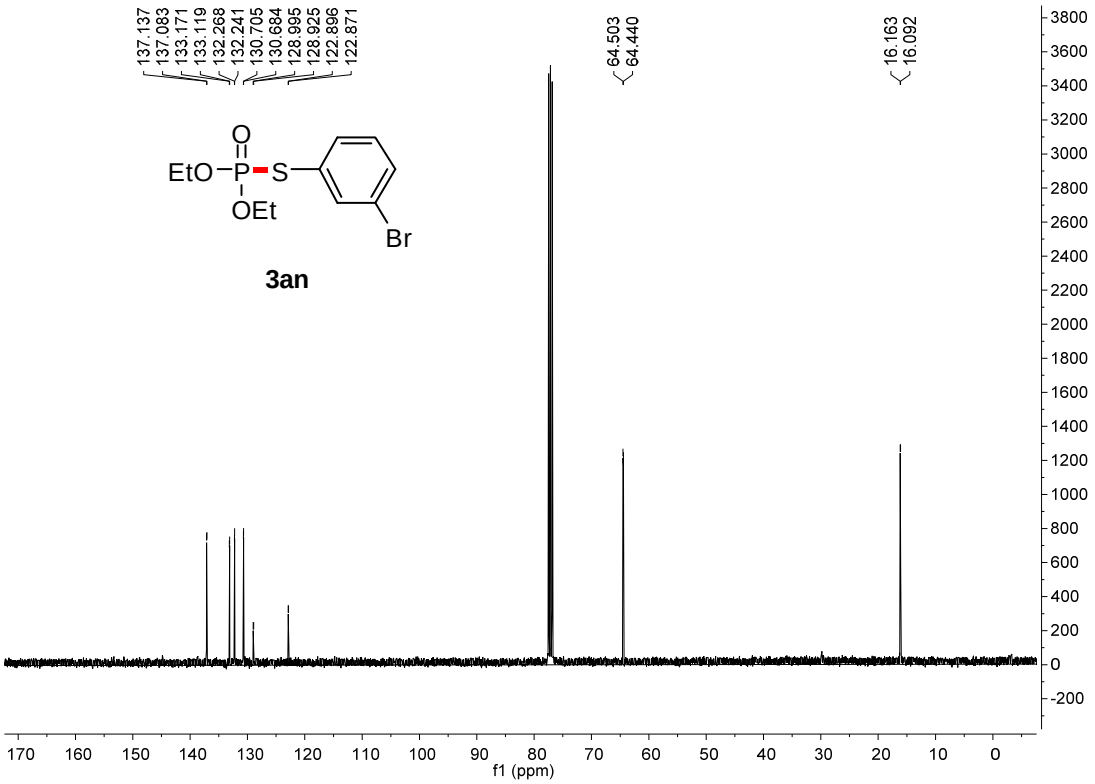
1.02
3.94
6.00
f1 (ppm)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132.268
132.241
130.705
130.684
128.995
128.925
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122.871
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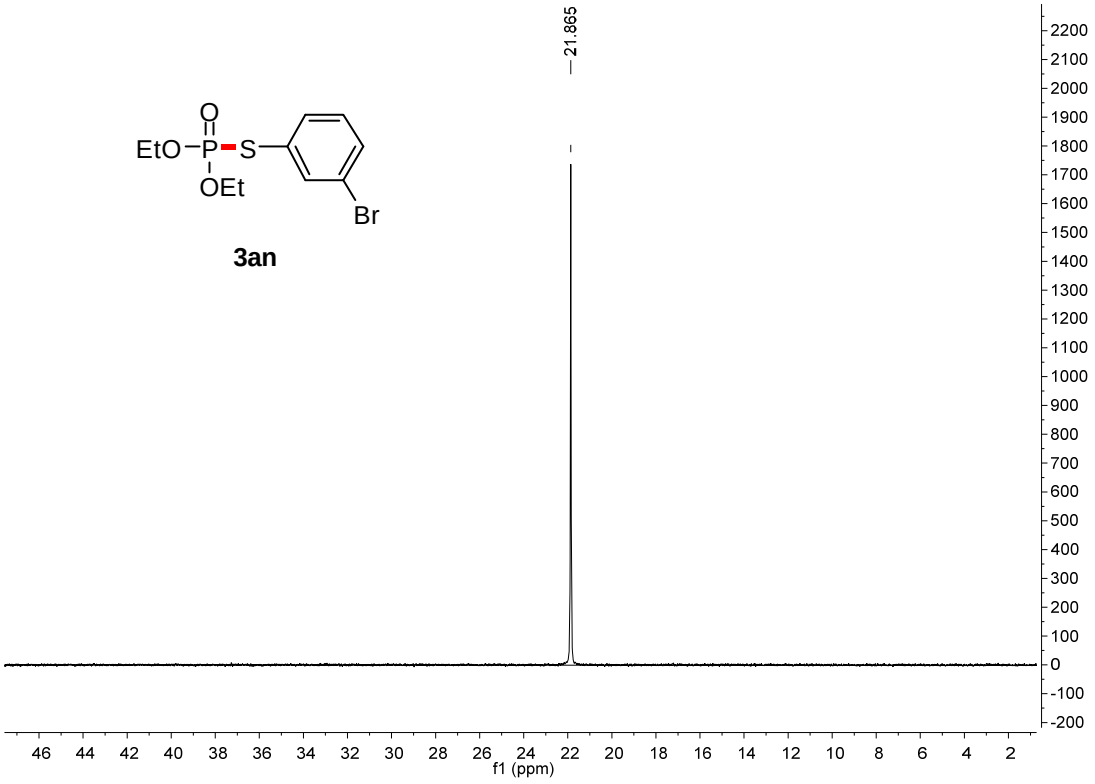
64.440
16.163
16.092
EtO
P
S
OEt
O
Br
3an
f1 (ppm)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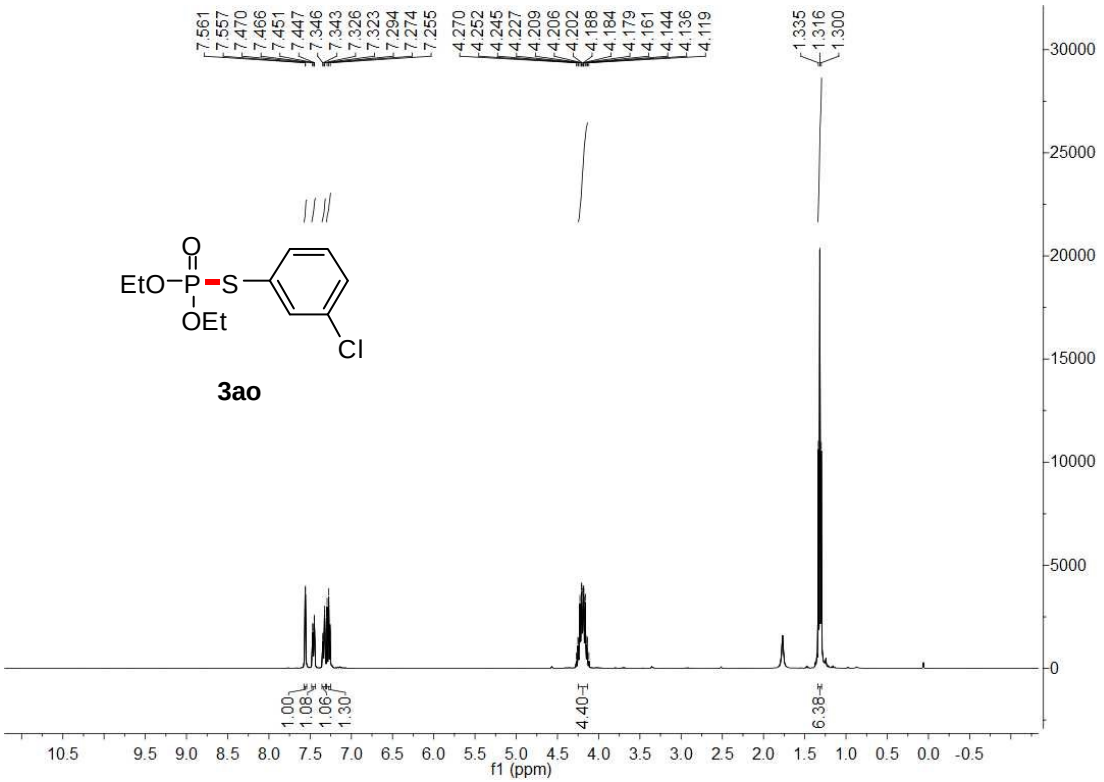
S
OEt
O
Br
3an
f1 (ppm)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7.343
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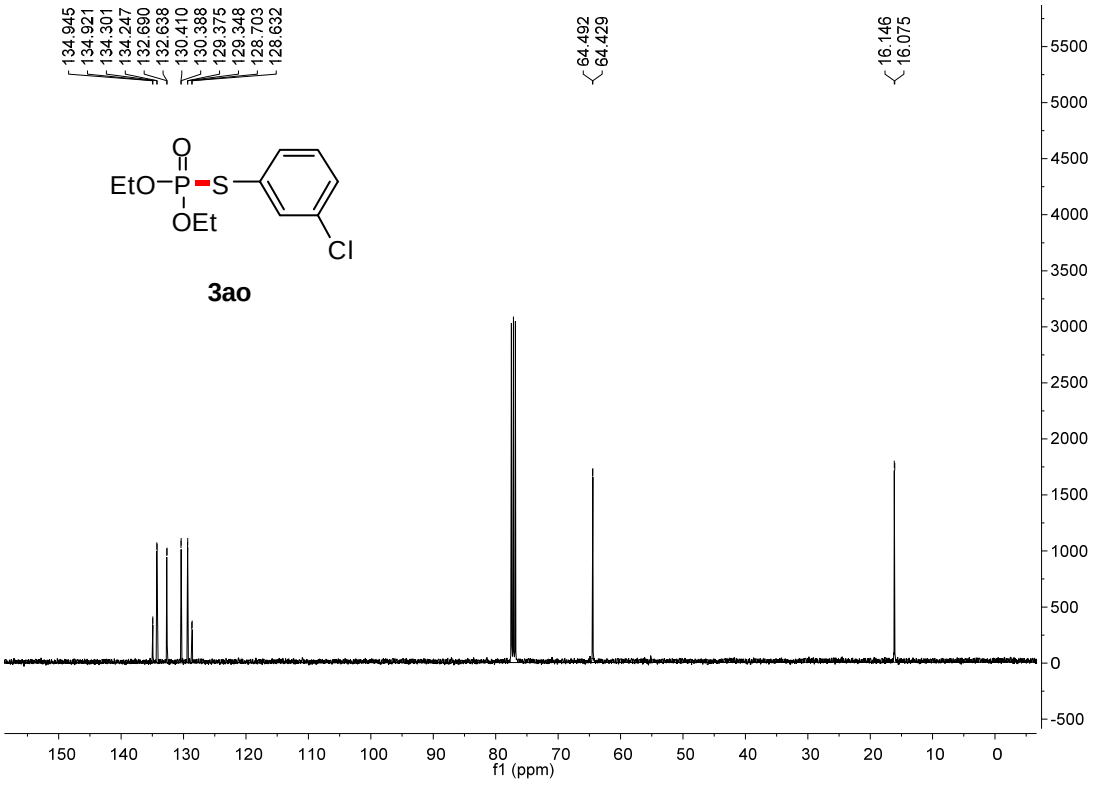
7.323
7.294
7.274
7.255
4.270
4.252
4.245
4.227
4.209
4.206
4.202
4.188
4.184
4.179
4.161
4.144
4.136
4.119
1.335
1.316
1.300
EtO
P
S
OEt
Cl
3ao
1.00
1.08
1.06
1.30
4.40
6.38
f1 (ppm)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134.247
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132.638
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130.388
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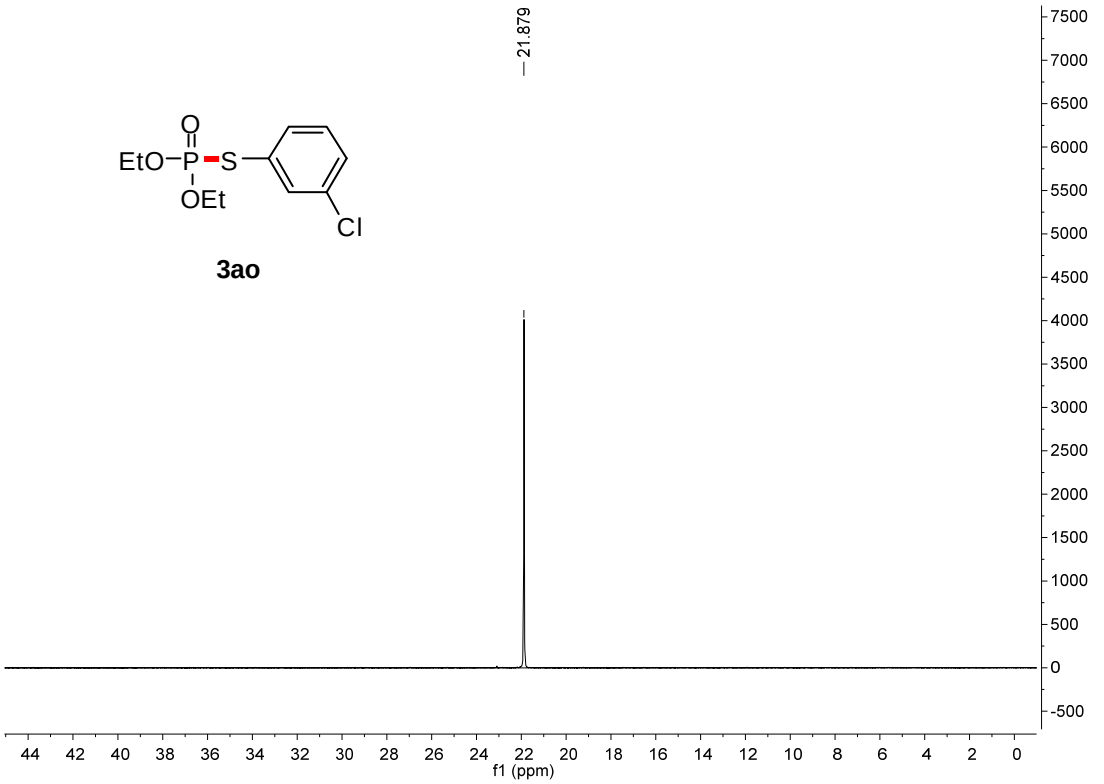
64.492
64.429
16.146
16.075
EtO
P
S
OEt
Cl
3ao
f1 (ppm)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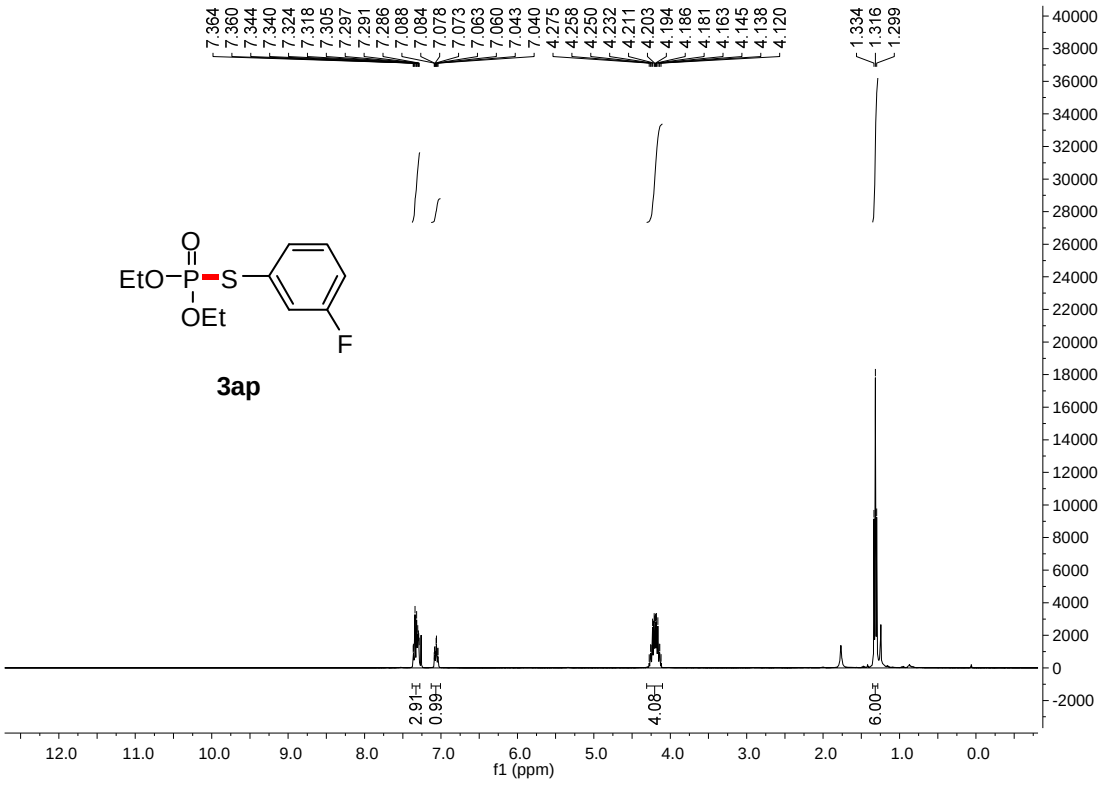
EtO
P
S
OEt
Cl
f1 (ppm)

3ao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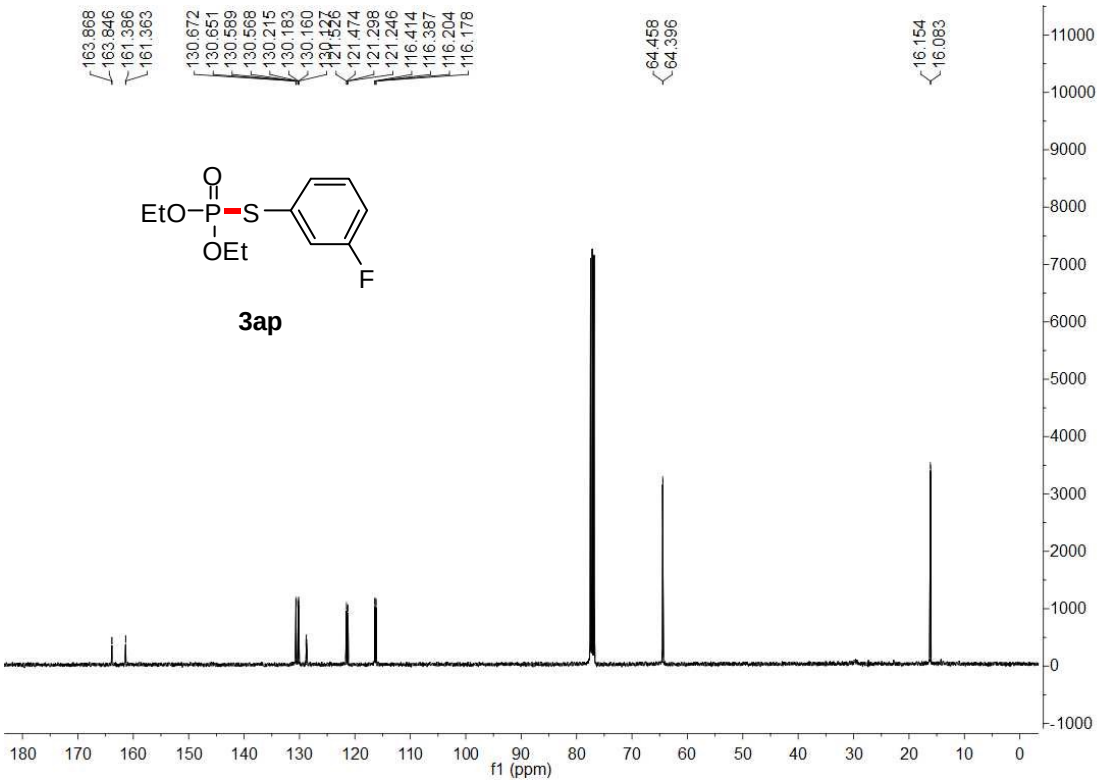
7.318
7.305
7.297
7.291
7.286
7.088
7.084
7.078
7.073
7.063
7.060
7.043
7.040
4.275
4.258
4.250
4.232
4.211
4.203
4.194
4.186
4.181
4.163
4.145
4.138
4.120
1.334
1.316
1.299
EtO
P
S
OEt
F
2.91
0.99
4.08
6.00
f1 (ppm)

3ap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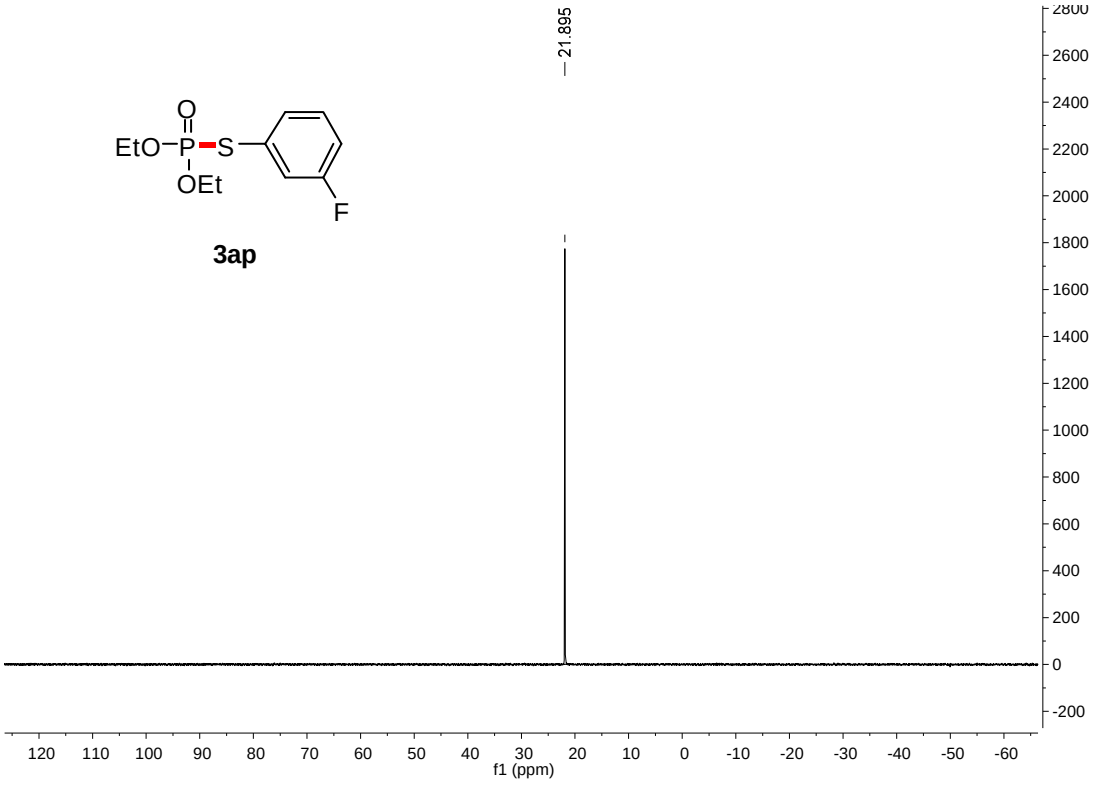
121.474
121.298
121.246
116.414
116.387
116.204
116.178
64.458
64.396
16.154
16.083
EtO
P
S
OEt
F
3ap
f1 (ppm)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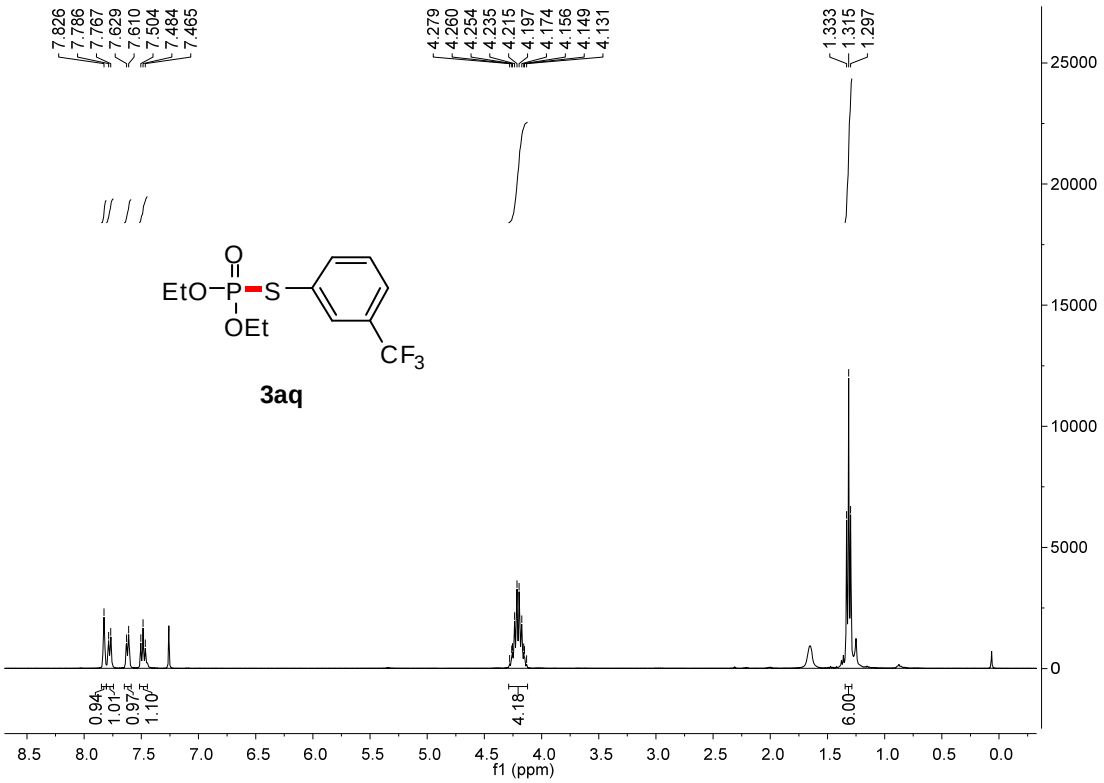
S
OEt
F
3ap
f1 (ppm)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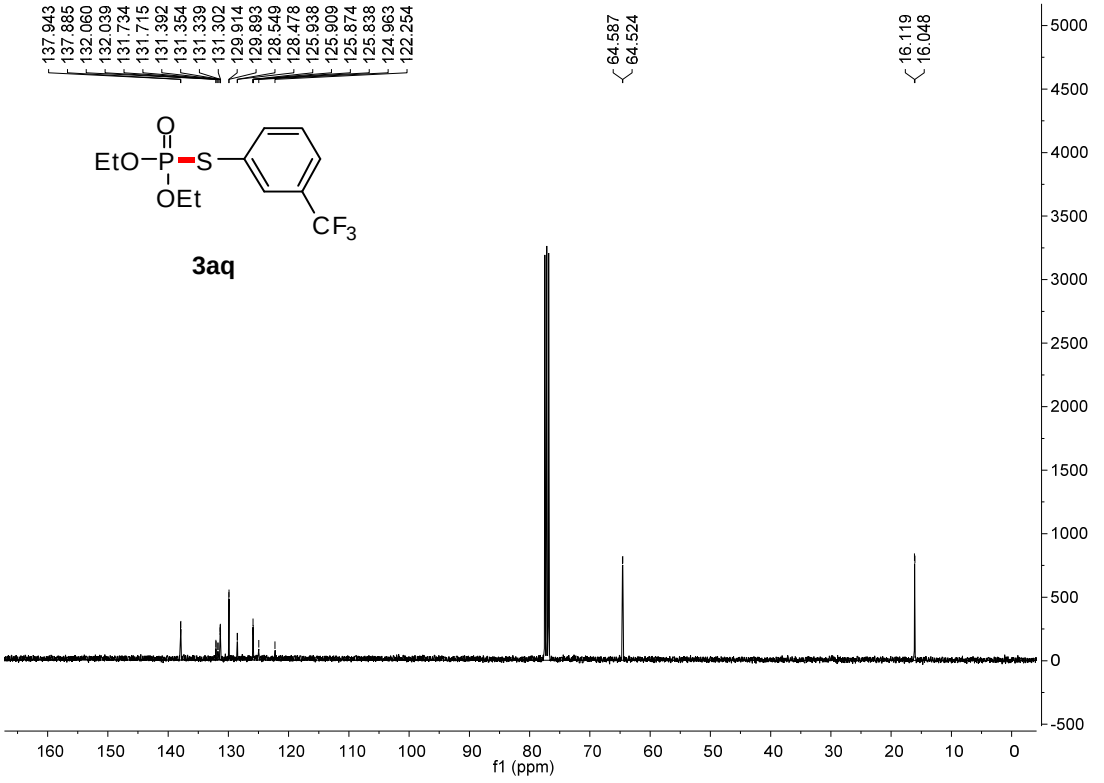
7.767
7.629
7.610
7.504
7.484
7.465
4.279
4.260
4.254
4.235
4.215
4.197
4.174
4.156
4.149
4.131
1.333
1.315
1.297
EtO
P
S
OEt
CF3
3aq
0.94
1.01
0.97
1.10
4.18
6.00
f1 (ppm)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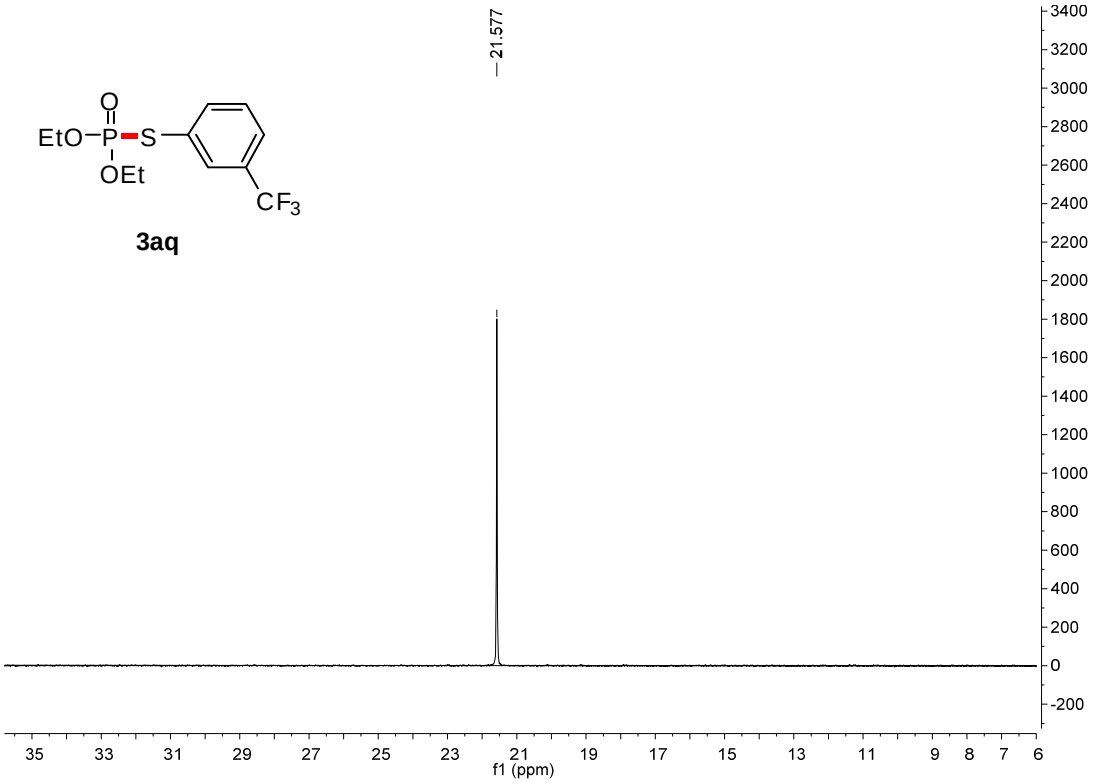
132.039
131.734
131.715
131.392
131.354
131.339
131.302
129.914
129.893
128.549
128.478
125.938
125.909
125.874
125.838
124.963
122.254
64.587
64.524
16.119
16.048
EtO
P
S
OEt
CF3
3aq
f1 (ppm)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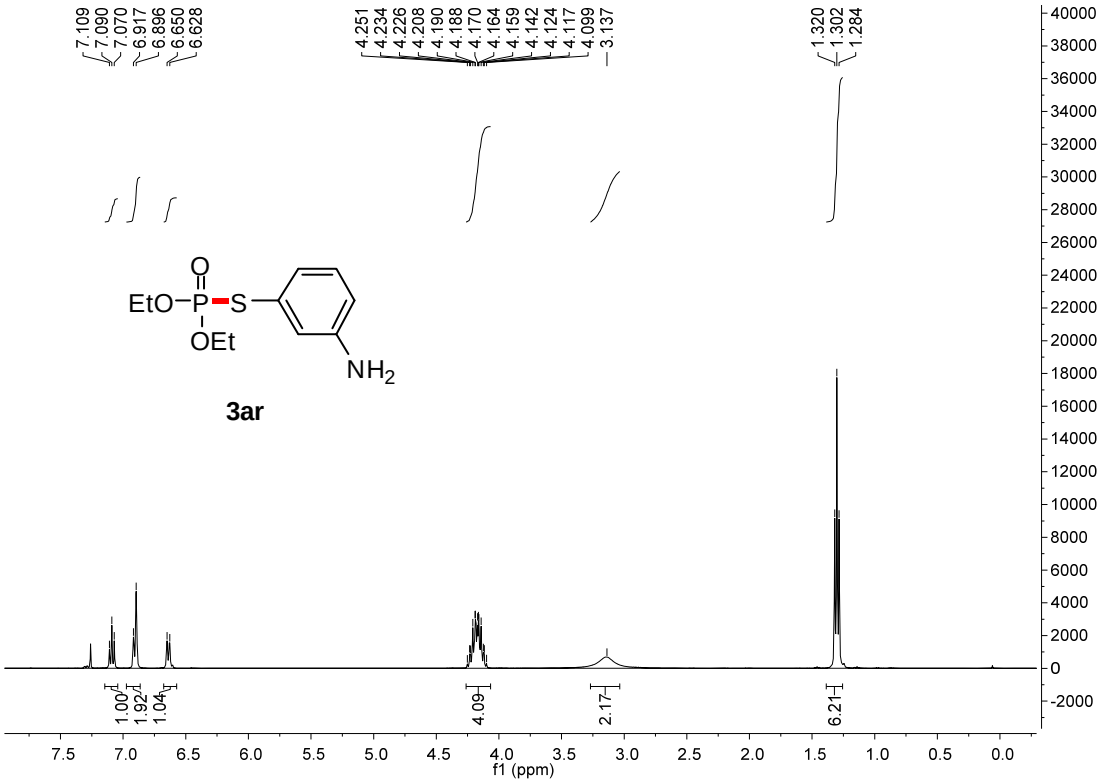
P
S
O
OEt
CF3
3aq
f1 (ppm)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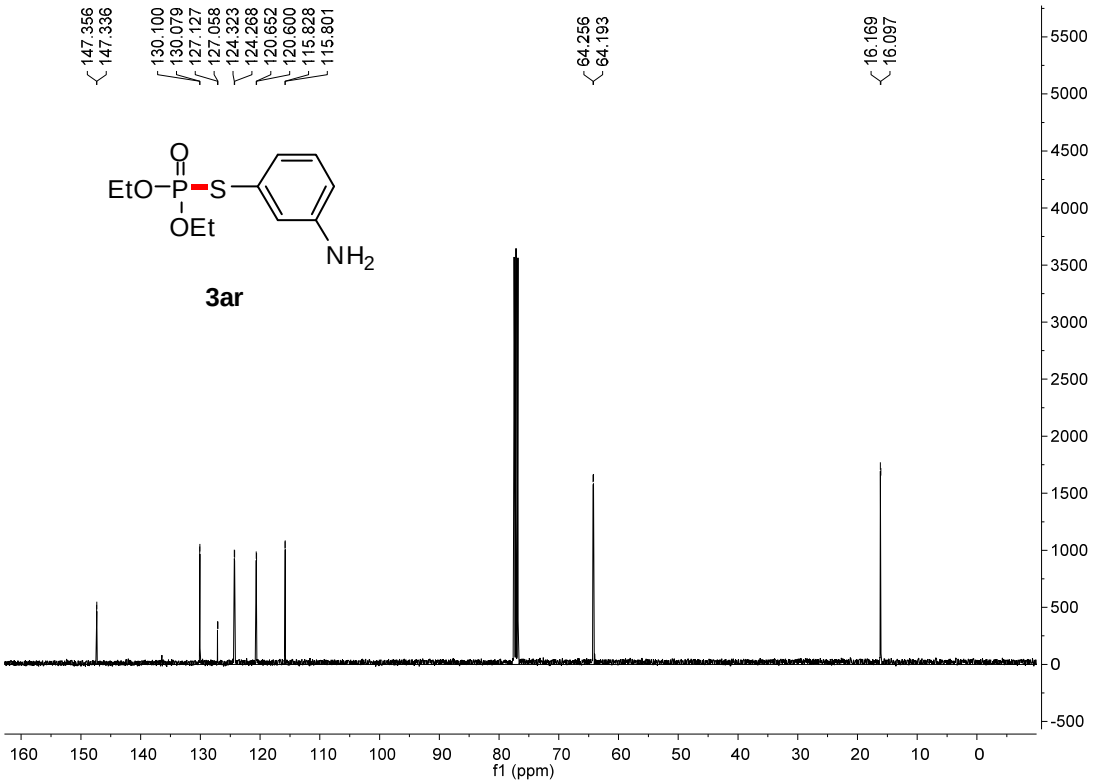
7.090
7.070
6.917
6.896
6.650
6.628
4.251
4.234
4.226
4.208
4.190
4.188
4.170
4.164
4.159
4.142
4.124
4.117
4.099
3.137
1.320
1.302
1.284
EtO
P
S
O
OEt
NH2
3ar
1.00
1.92
1.04
4.09
2.17
6.21
f1 (ppm)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147.336
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130.079
127.127
127.058
124.323
124.268
120.652
120.600
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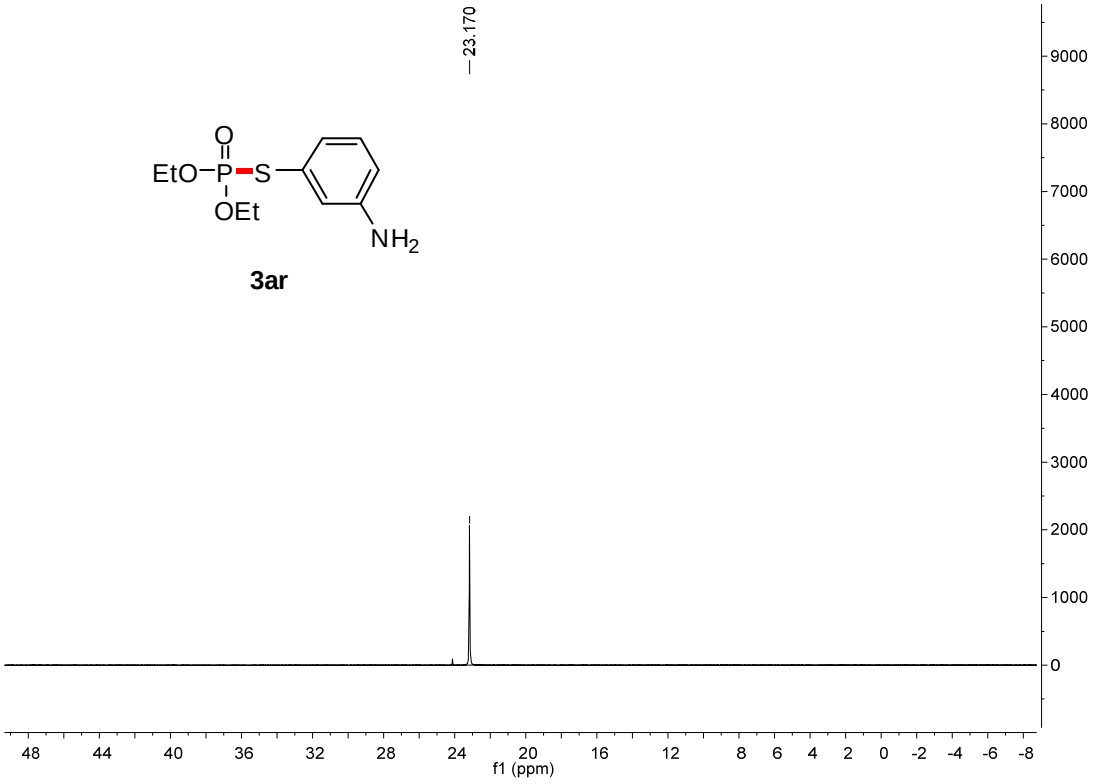
64.256
64.193
16.169
16.097
EtO
P
S
OEt
NH2
3ar
f1 (ppm)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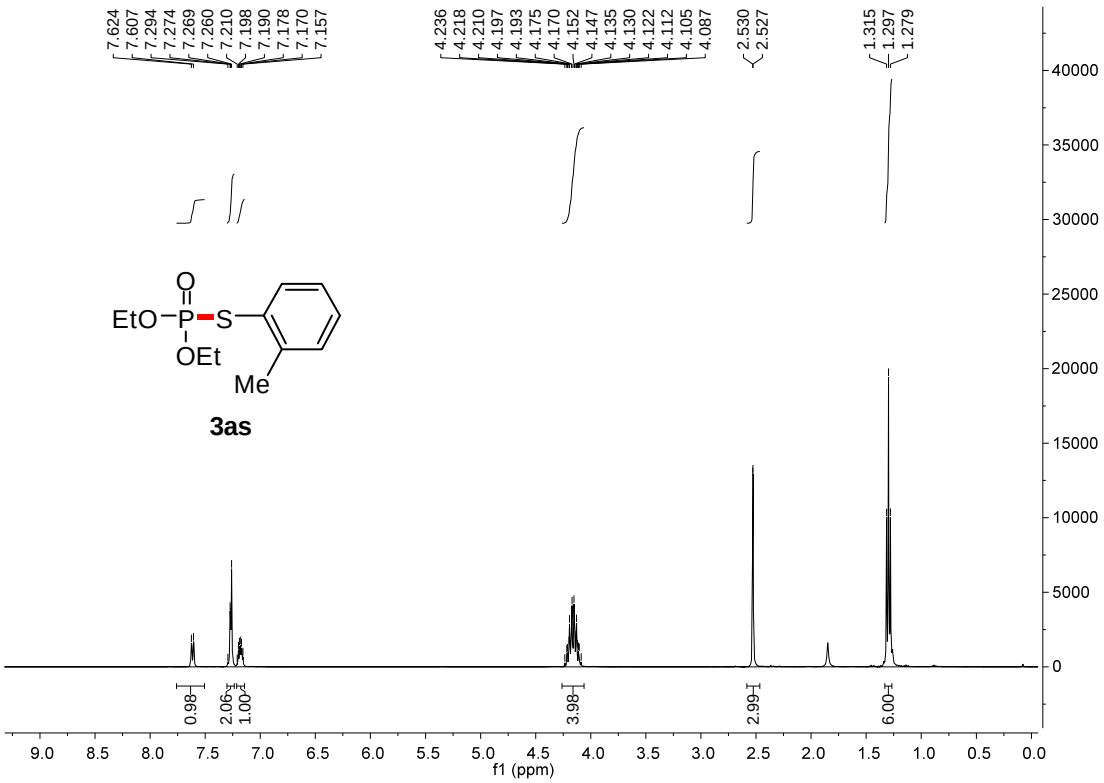
EtO
P
S
OEt
NH2
3ar
f1 (ppm)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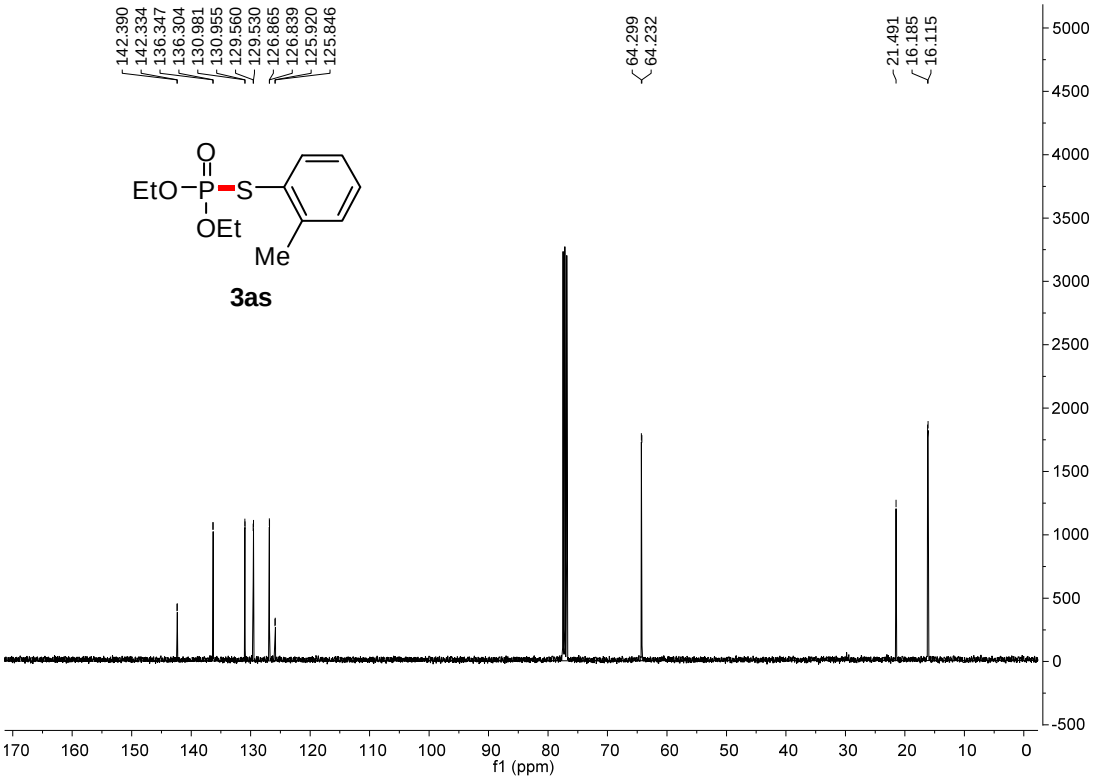
7.607
7.294
7.274
7.269
7.260
7.210
7.198
7.190
7.178
7.170
7.157
4.236
4.218
4.210
4.197
4.193
4.175
4.170
4.152
4.147
4.135
4.130
4.122
4.112
4.105
4.087
2.530
2.527
1.315
1.297
1.279
EtO
P
S
OEt
Me
3as
0.98
2.06
1.00
3.98
2.99
6.00
f1 (ppm)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126.839
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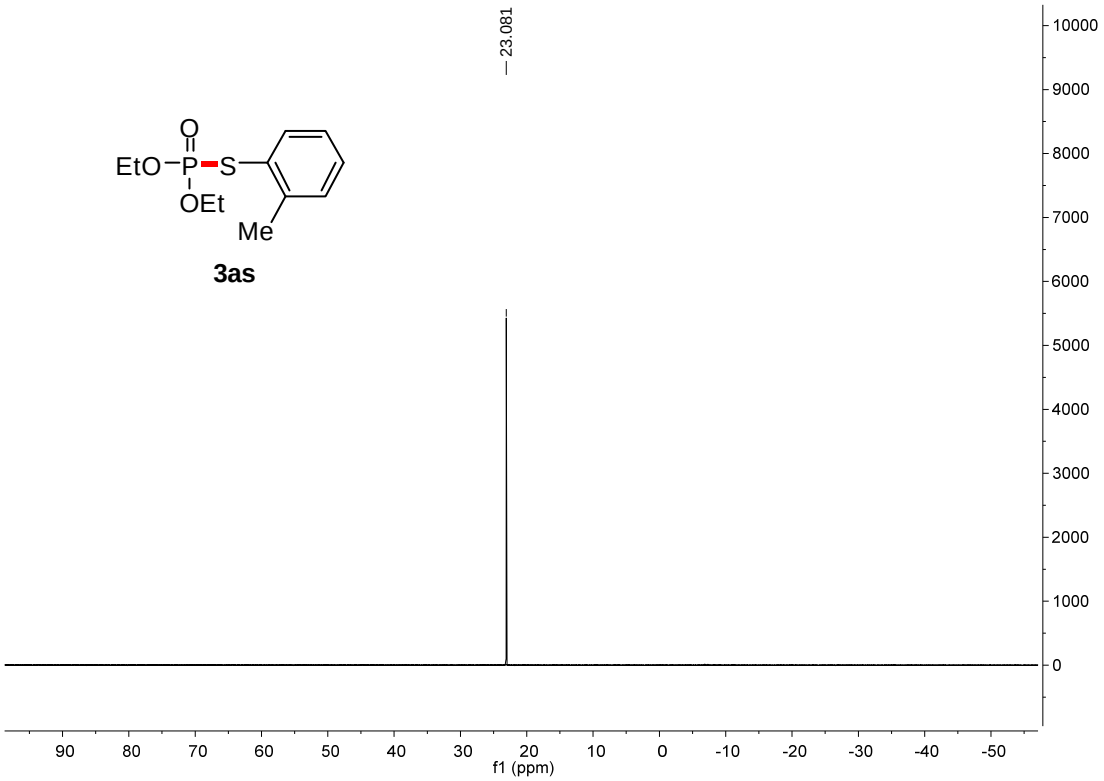
64.232
21.491
16.185
16.115
EtO
P
S
OEt
Me
3as
f1 (ppm)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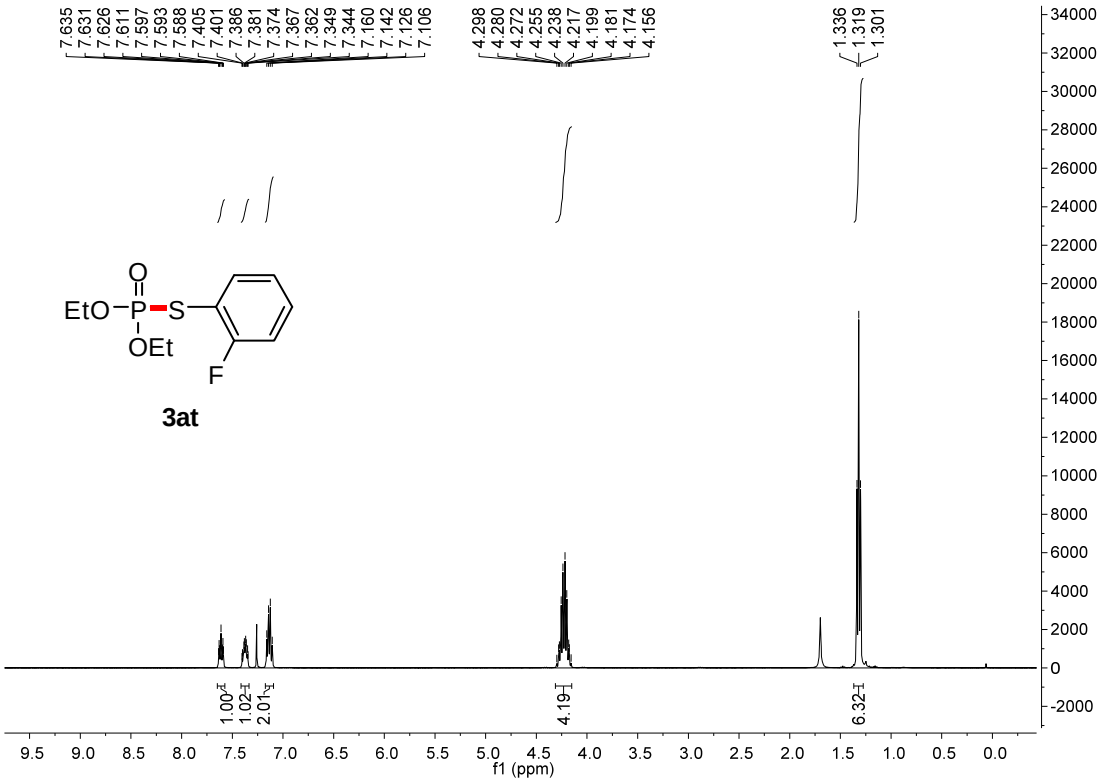
P
S
OEt
Me
3as
f1 (ppm)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7.593
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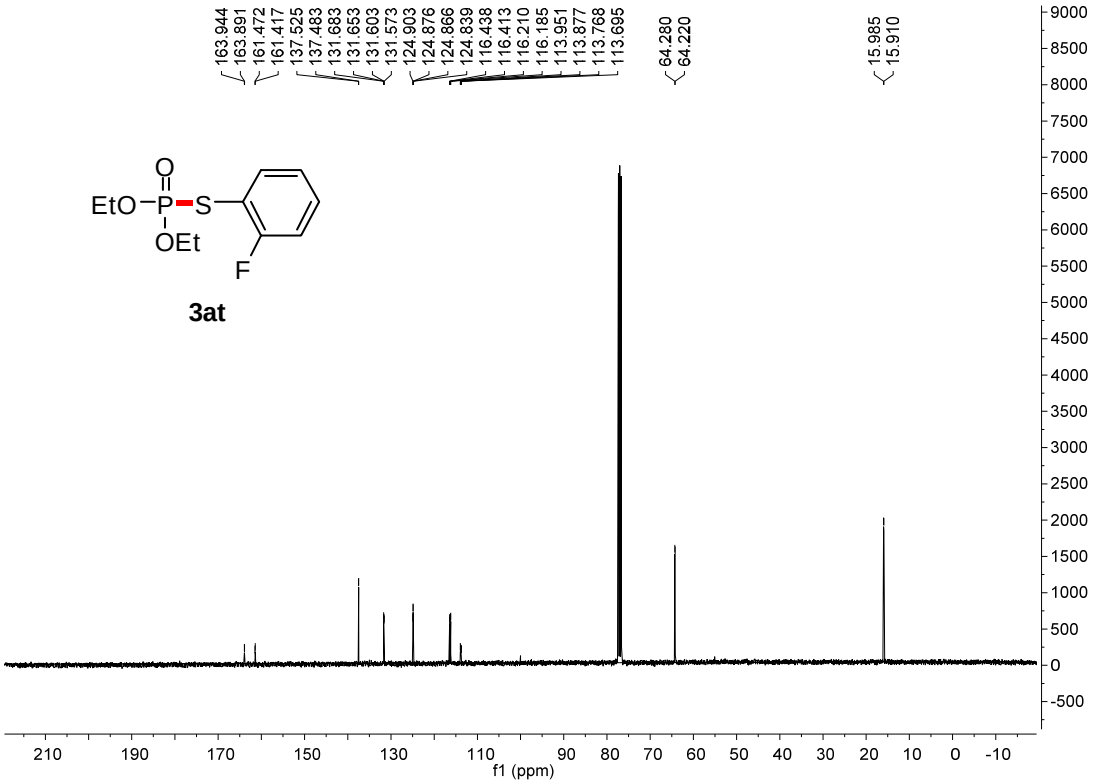
7.405
7.401
7.386
7.381
7.374
7.367
7.362
7.349
7.344
7.160
7.142
7.126
7.106
4.298
4.280
4.272
4.255
4.238
4.217
4.199
4.181
4.174
4.156
1.336
1.319
1.301
EtO
P
S
OEt
F
3at
1.00
1.02
2.01
4.19
6.32
f1 (ppm)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131.653
131.603
131.573
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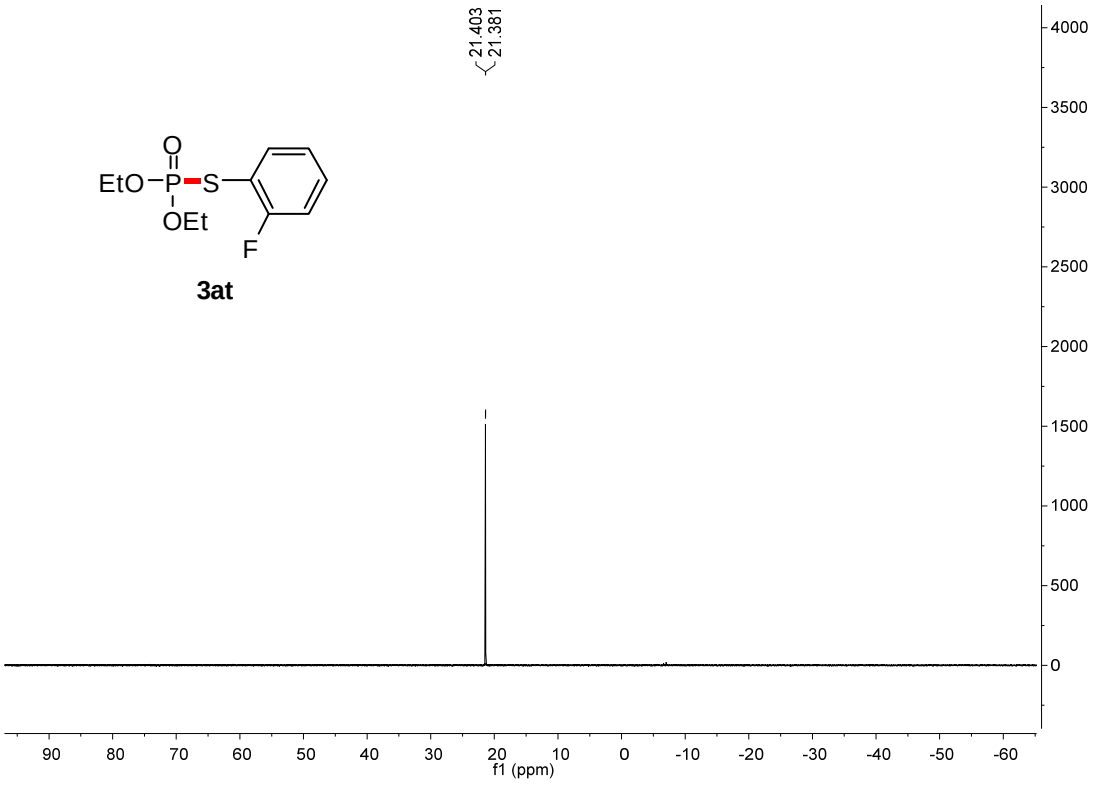
124.876
124.866
124.839
116.438
116.413
116.210
116.185
113.951
113.877
113.768
113.695
64.280
64.220
15.985
15.910
EtO
P
S
OEt
F
3at
f1 (ppm)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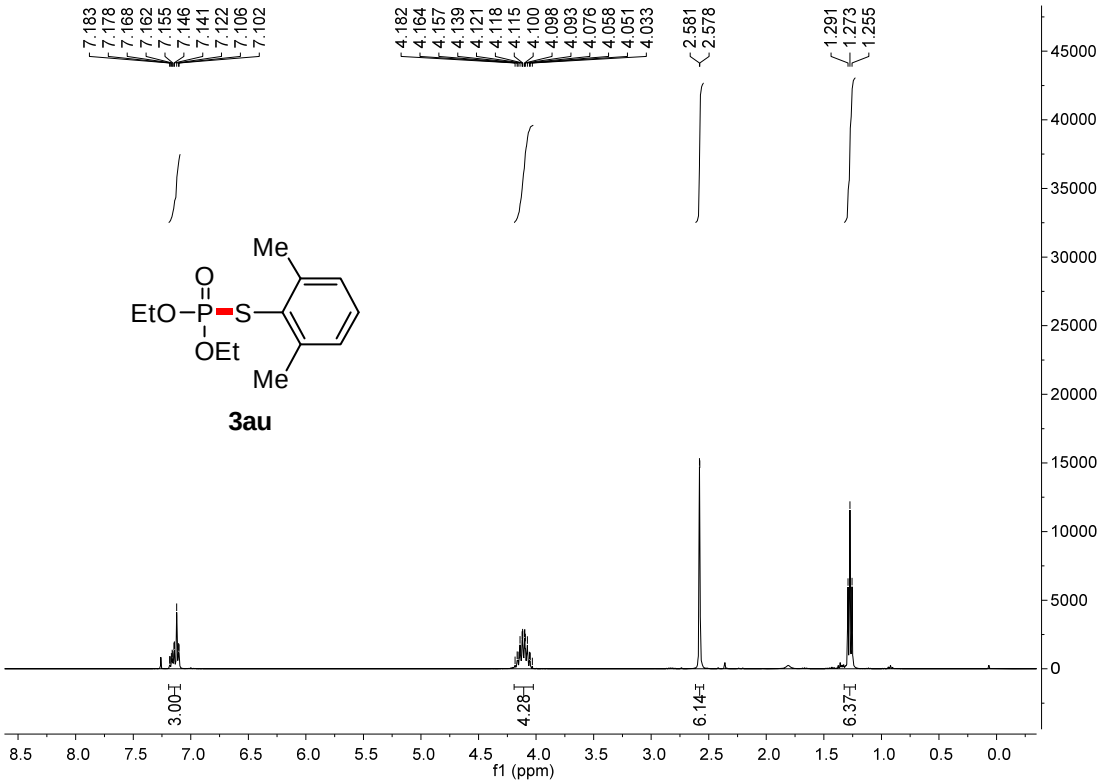
21.381
EtO
P
S
OEt
F
3at
f1 (ppm)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7.155
7.146
7.141
7.122
7.106
7.102
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4.164
4.157
4.139
4.121
4.118
4.115
4.100
4.098
4.093
4.076
4.058
4.051
4.033
2.581
2.578
1.291
1.273
1.255
Me
O
EtO
P
S
OEt
Me
3au
3.00
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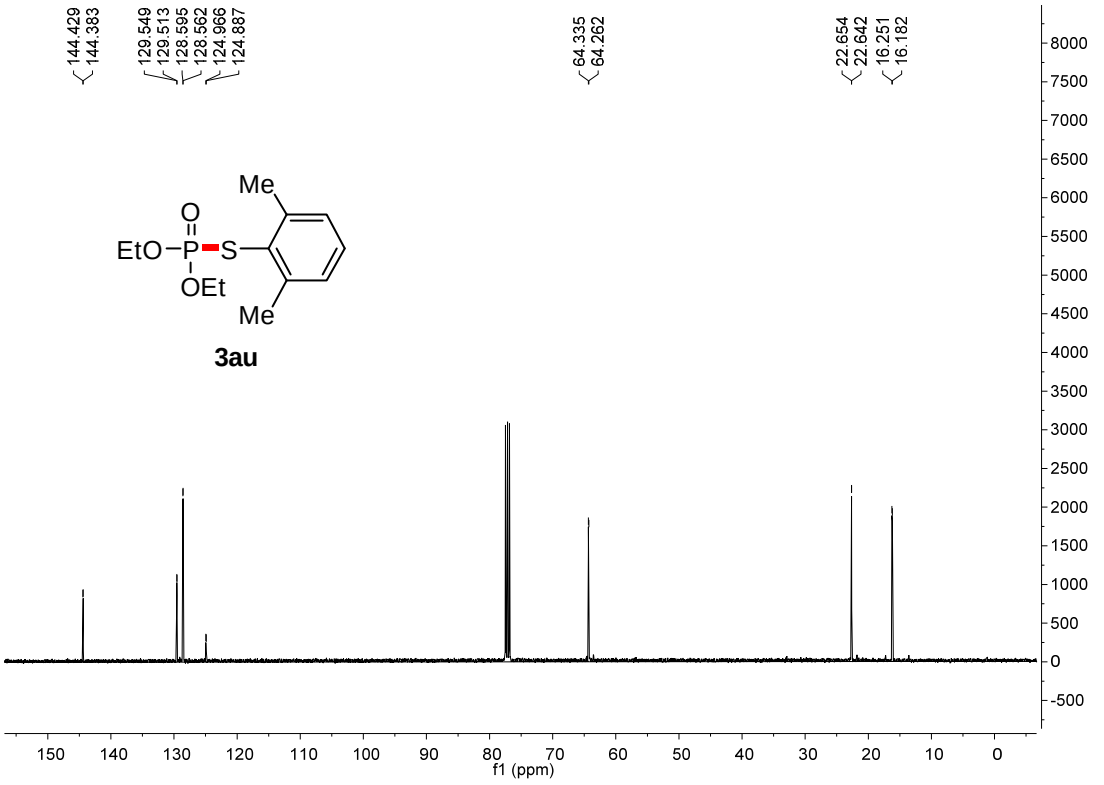
6.14
6.37
f1 (ppm)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128.562
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124.887
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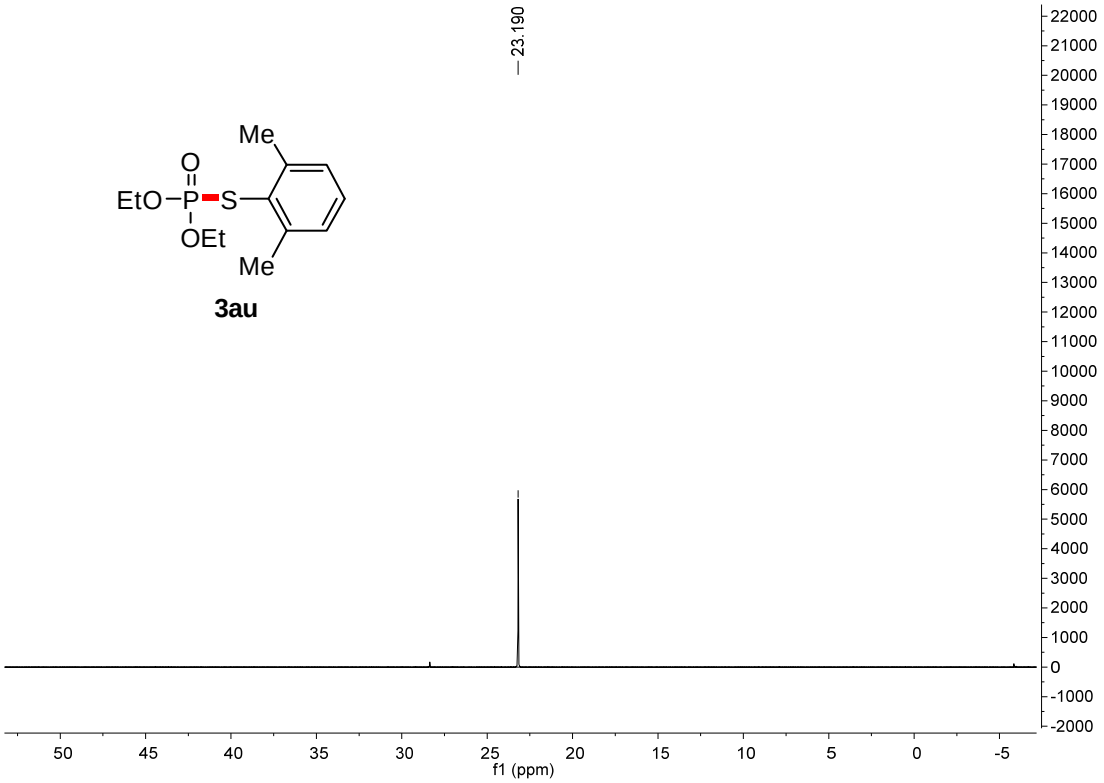
22.642
16.251
16.182
Me
O
EtO
P
S
OEt
Me
3au
f1 (ppm)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EtO
P
S
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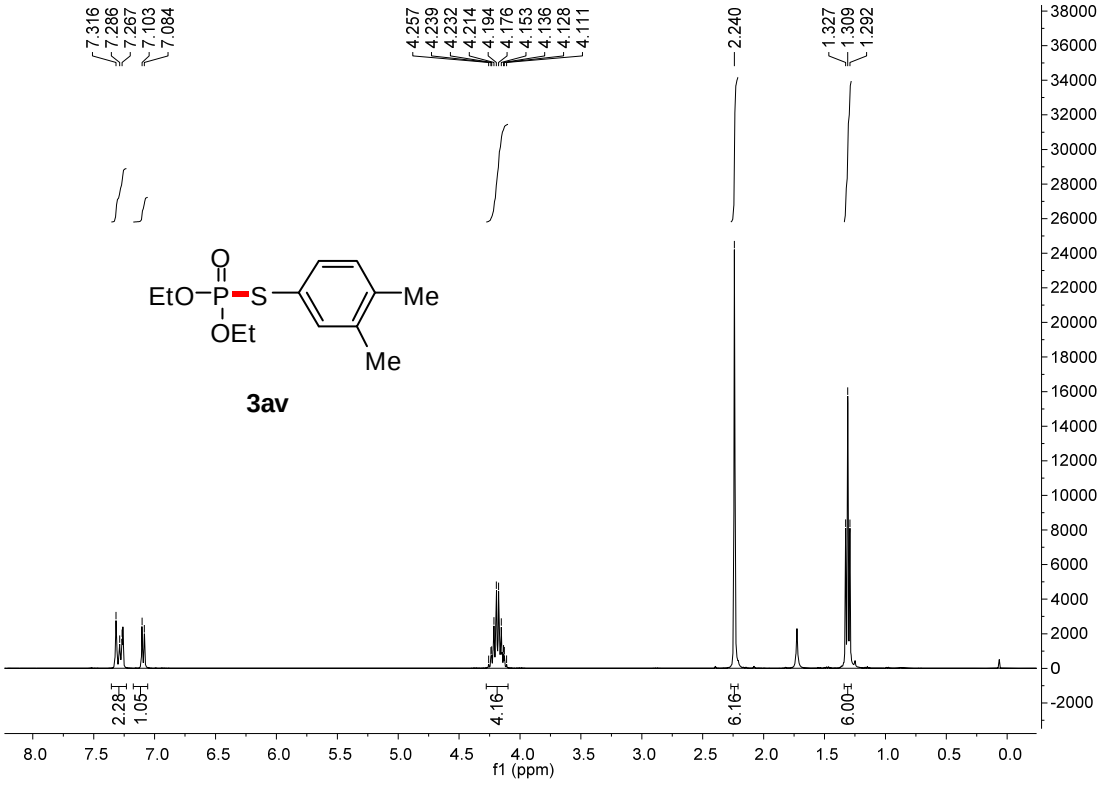
Me
3au
f1 (ppm)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7.084
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4.239
4.232
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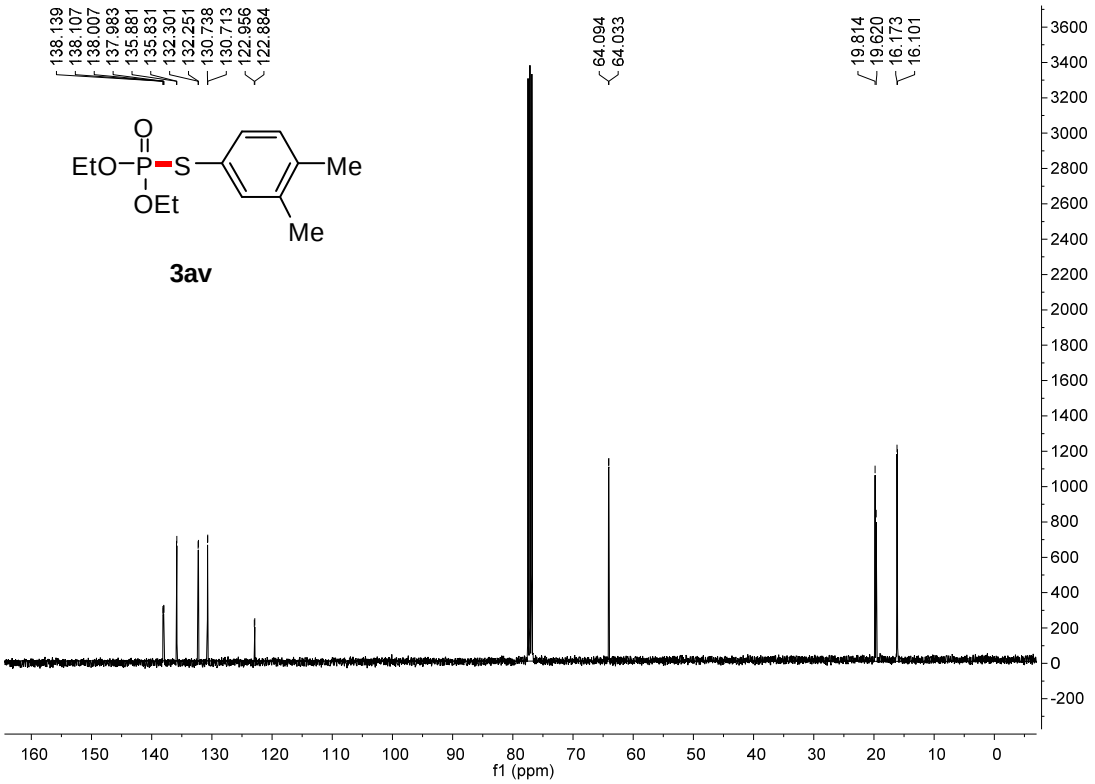
4.194
4.176
4.153
4.136
4.128
4.111
2.240
1.327
1.309
1.292
O
EtO
P
S
Me
OEt
Me
3av
2.28
1.05
4.16
6.16
6.00
f1 (ppm)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132.251
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130.713
122.956
122.884
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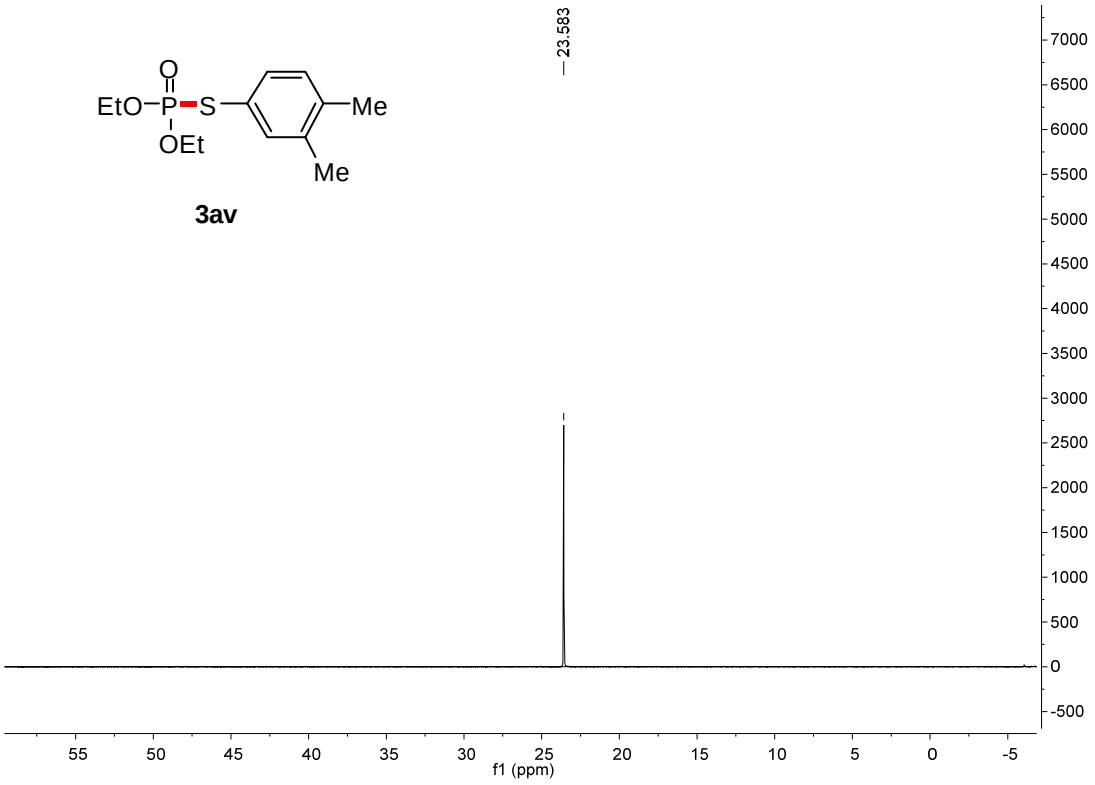
64.033
19.814
19.620
16.173
16.101
EtO
P
S
OEt
Me
Me
3av
f1 (ppm)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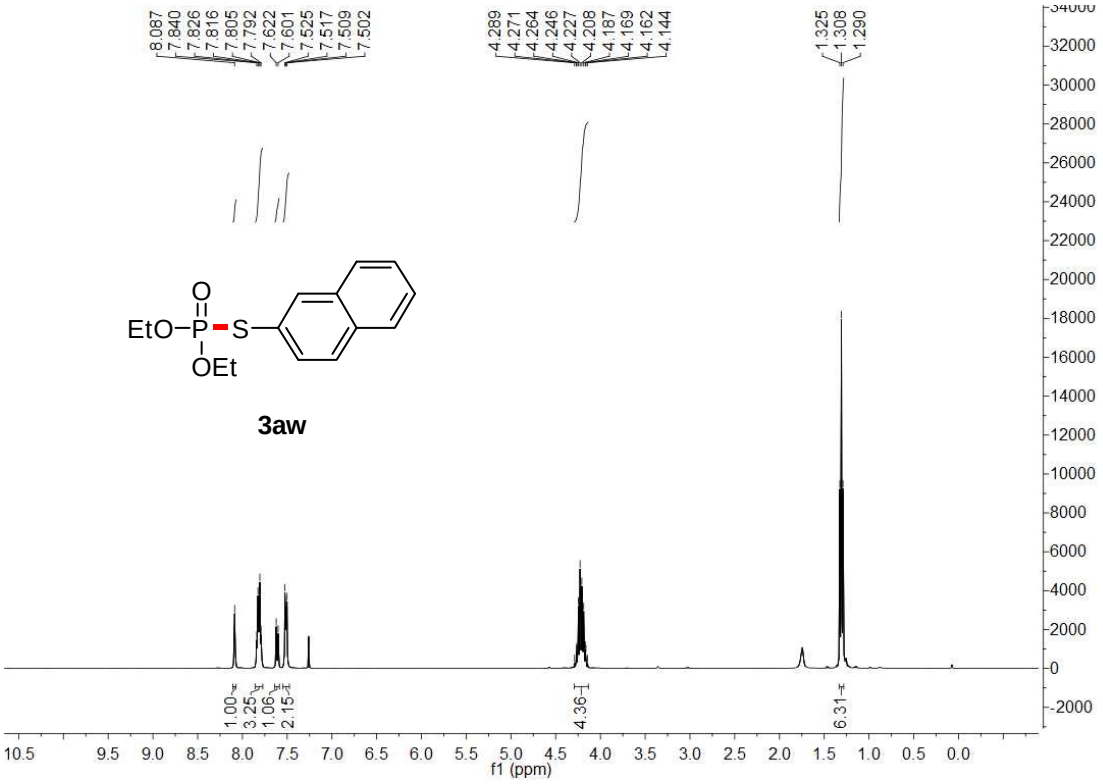
P
S
OEt
Me
Me
3av
f1 (ppm)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7.601
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7.517
7.509
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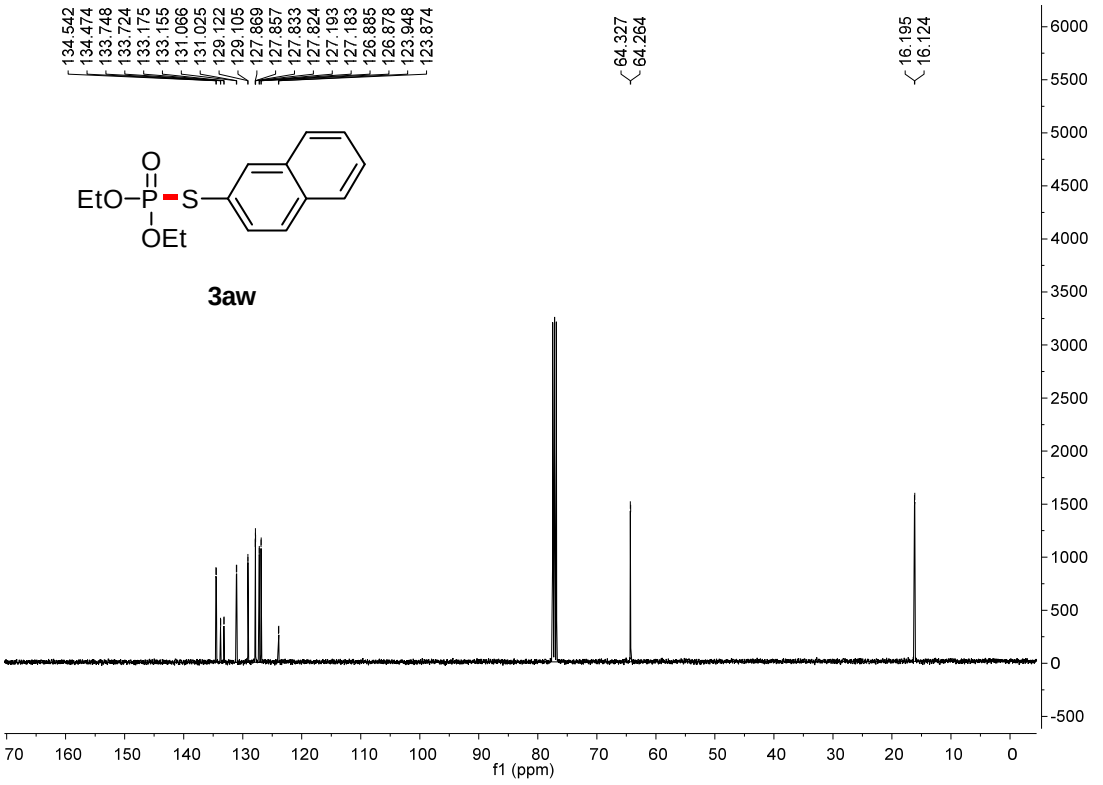
4.289
4.271
4.264
4.246
4.227
4.208
4.187
4.169
4.162
4.144
1.325
1.308
1.290
EtO
P
S
OEt
1.00
3.25
1.06
2.15
4.36
6.31
f1 (ppm)

3aw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131.066
131.025
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129.105
127.869
127.857
127.833
127.824
127.193
127.183
126.885
126.878
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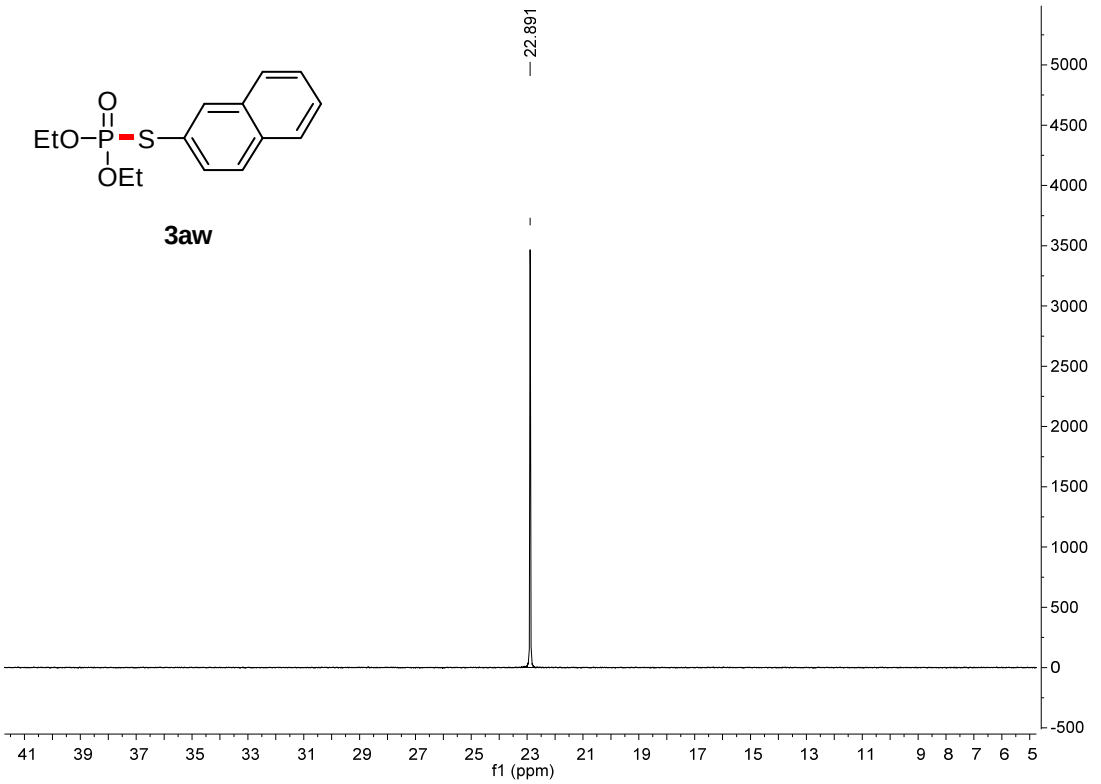
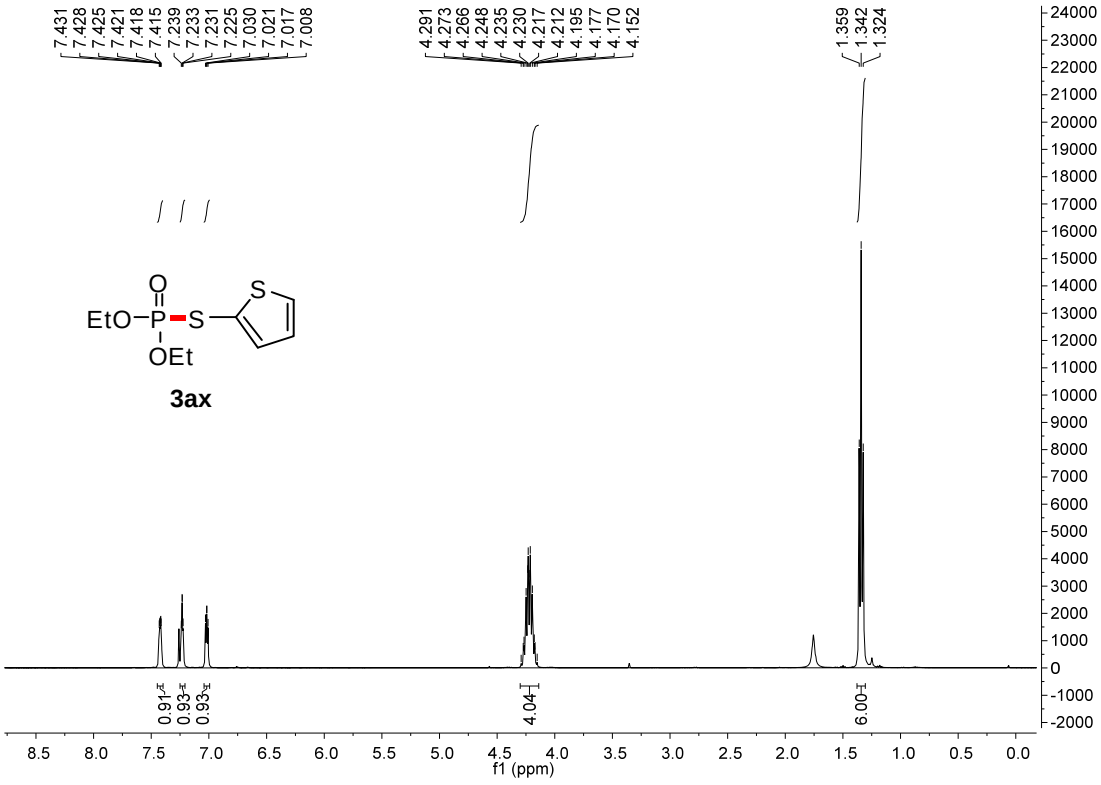
64.327
64.264
16.195
16.124
EtO
P
S
OEt
f1 (ppm)

3aw


22.891
EtO
P
S
OEt
O
3aw
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
41 39 37 35 33 31 29 27 25 23 21 19 17 15 13 11 9 8 7 6 5
f1 (ppm)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7.017
7.008
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4.273
4.266
4.248
4.235
4.230
4.217
4.212
4.195
4.177
4.170
4.152
1.359
1.342
1.324
EtO
P
S
OEt
O
S
3ax
0.91
0.93
0.93
4.04
6.00
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
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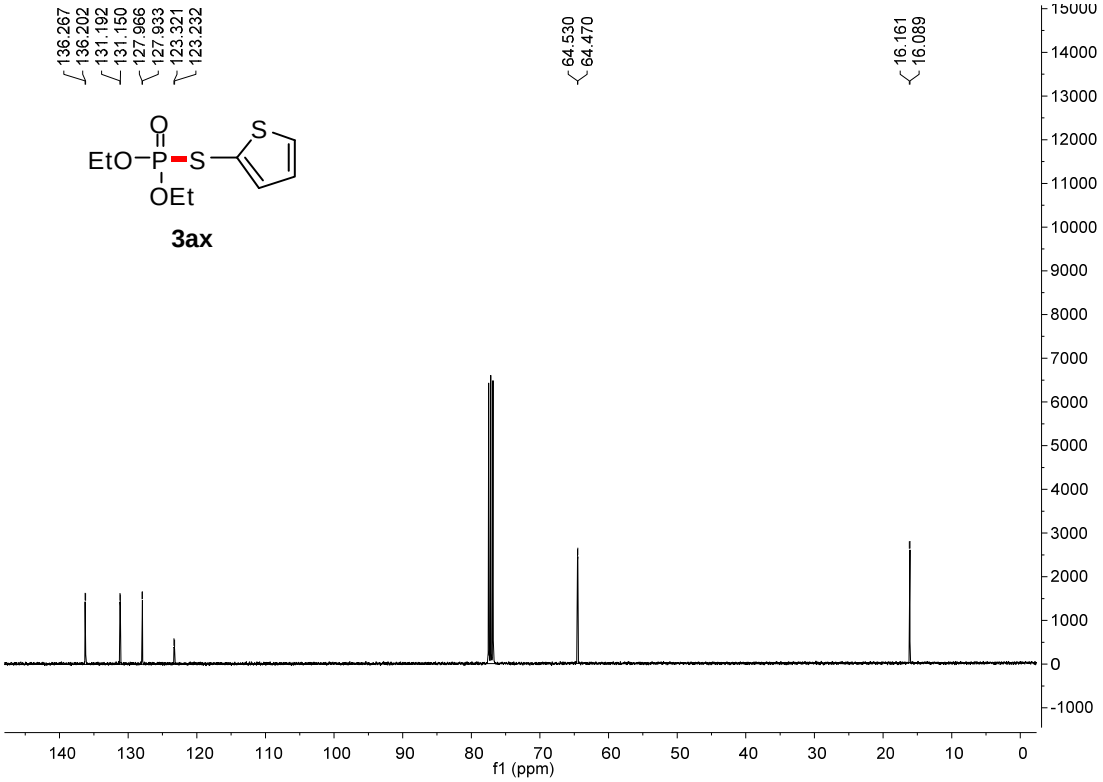
f1 (ppm)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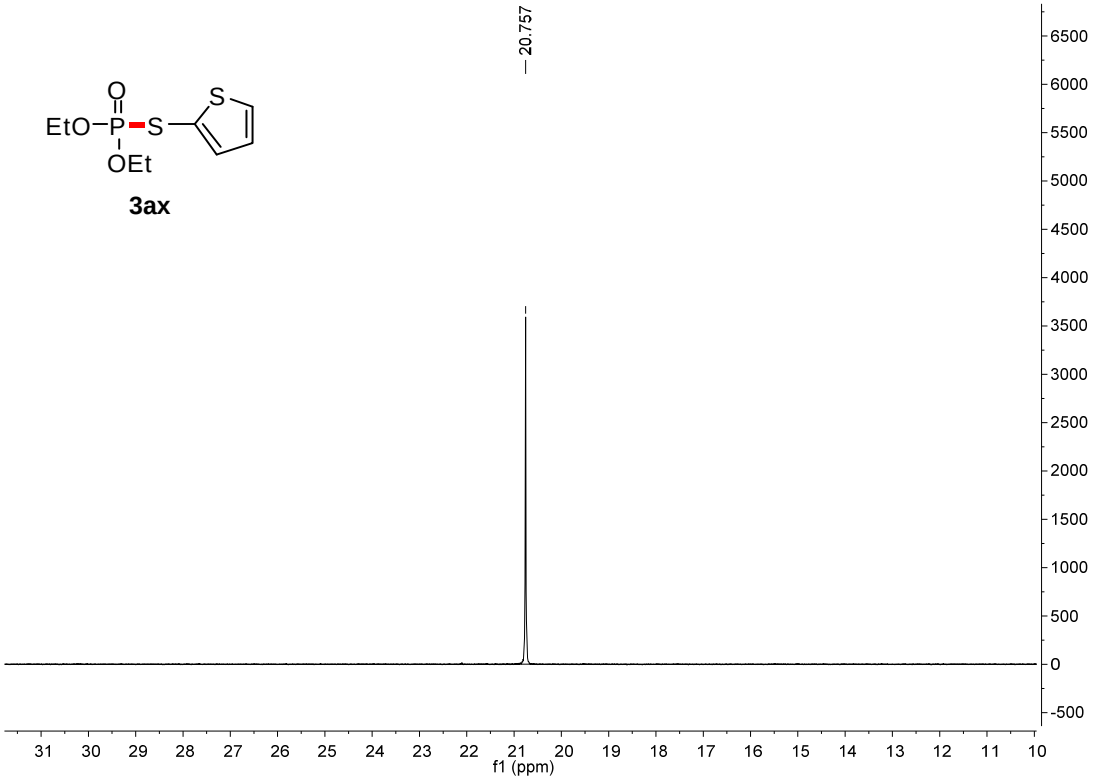
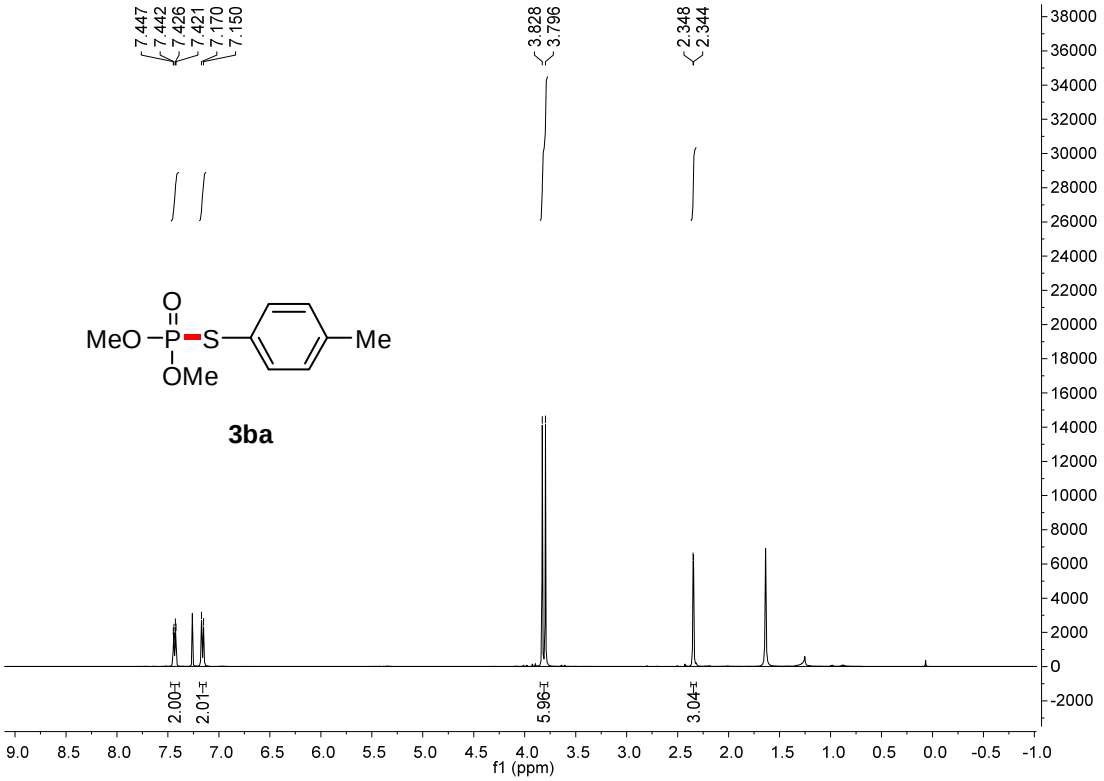
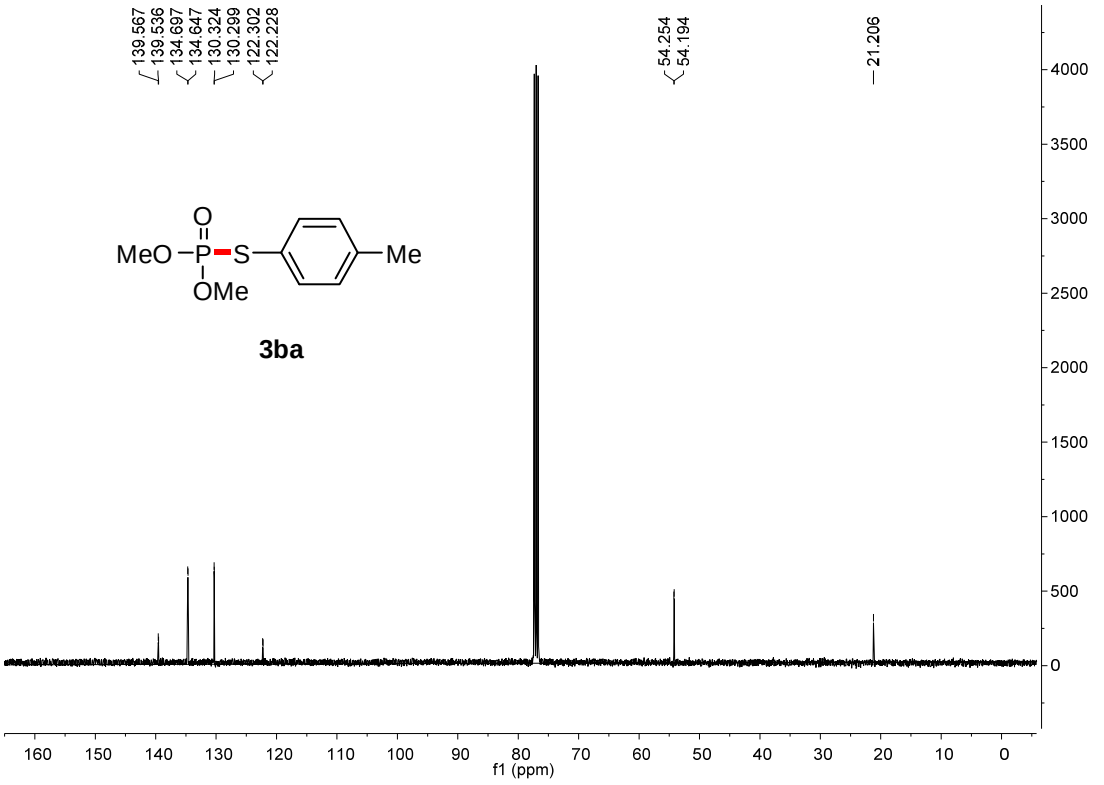
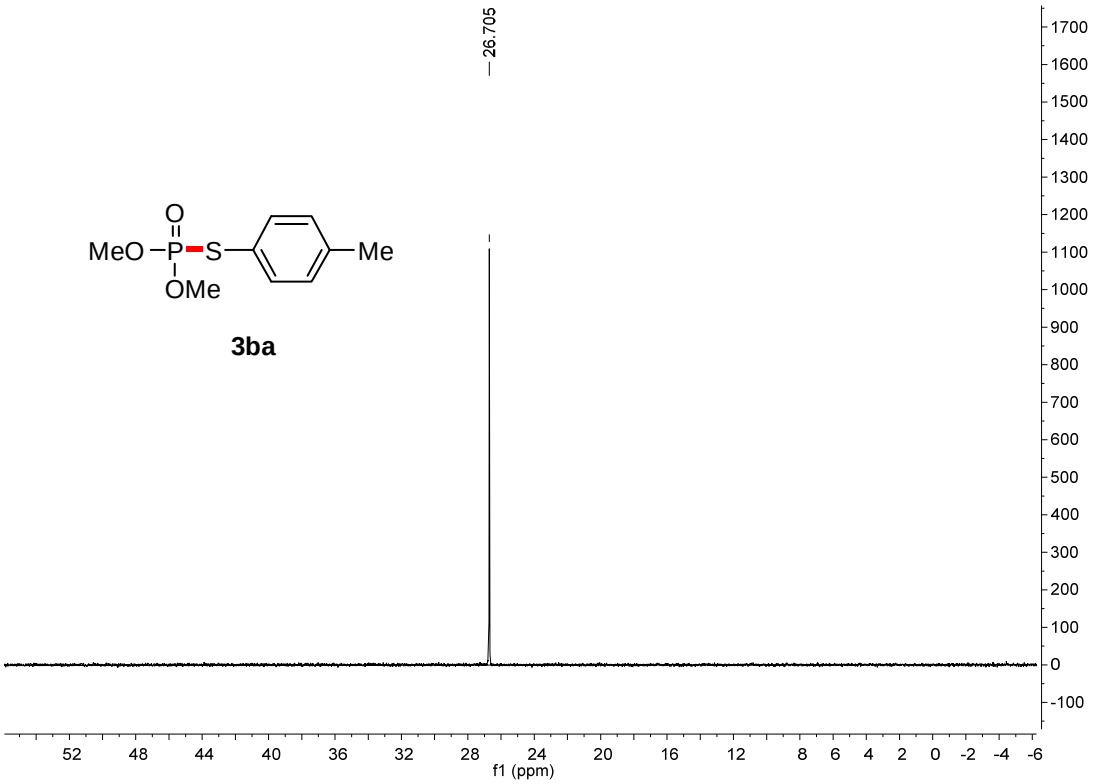
136.202
131.192
131.150
127.966
127.933
123.321
123.232
64.530
64.470
16.161
16.089
EtO
P
S
O
OEt
S
3ax
f1 (ppm)

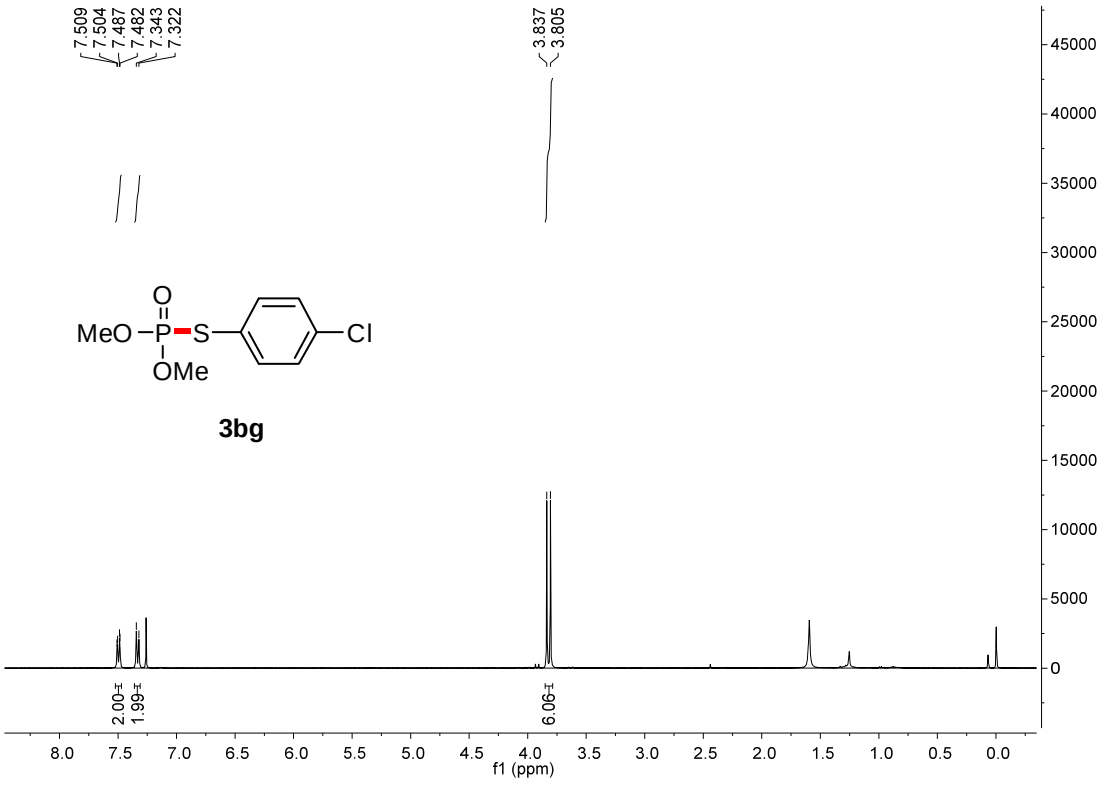

20.757
EtO
P
S
O
OEt
S
3ax
f1 (ppm)


7.447
7.442
7.426
7.421
7.170
7.150
3.828
3.796
2.348
2.344
MeO
P
S
OMe
Me
O
3ba
2.00
2.01
5.96
3.04
f1 (ppm)

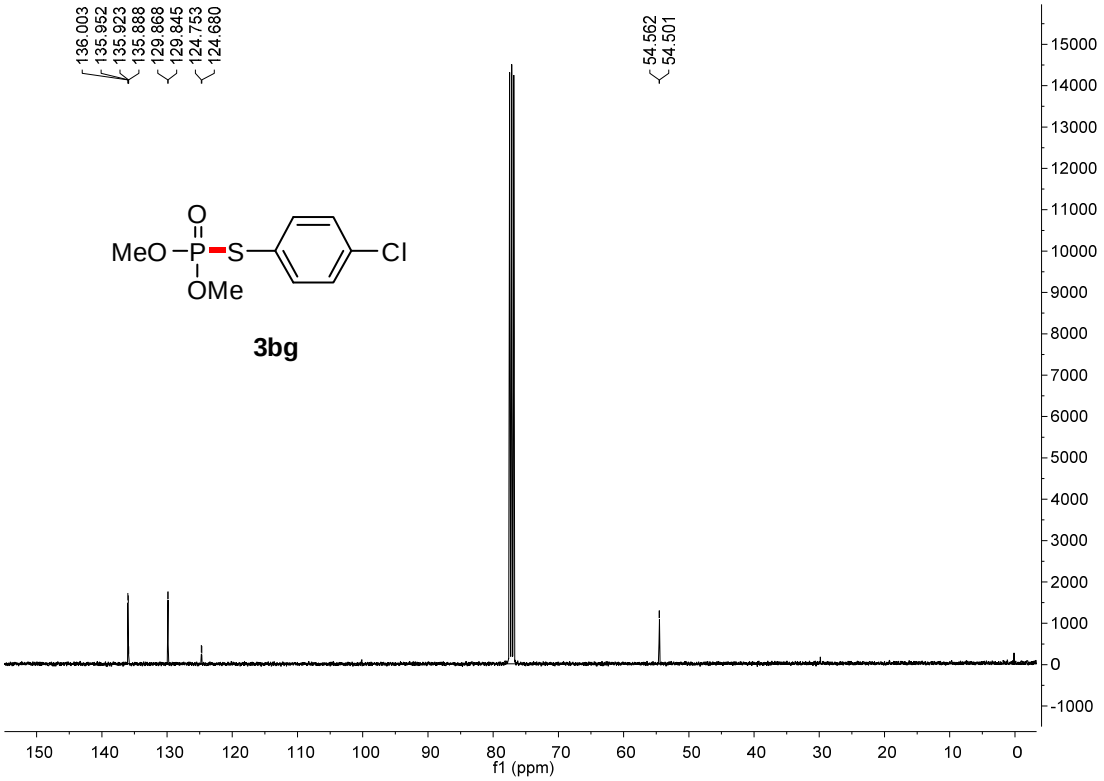

139.567
139.536
134.697
134.647
130.324
130.299
122.302
122.228
54.254
54.194
21.206
MeO
P
S
OMe
Me
O
3ba
f1 (ppm)

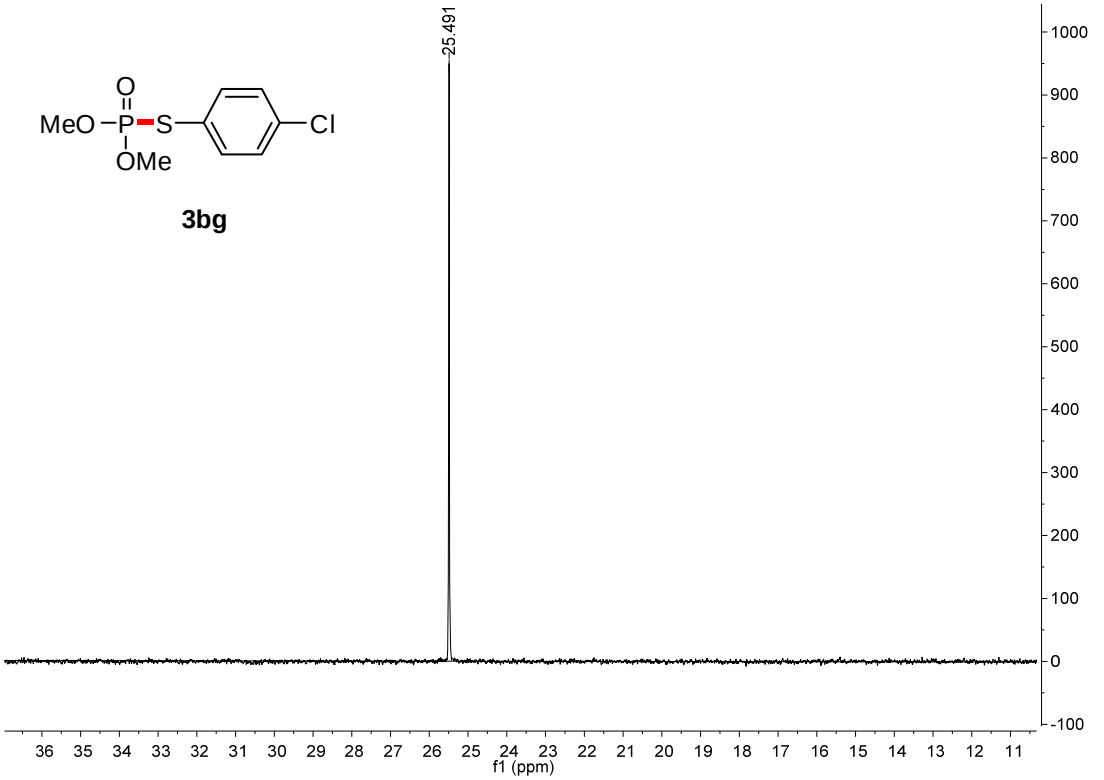

26.705
MeO
P
S
Me
OMe
O
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
52
48
44
40
36
32
28
24
20
16
12
8
6
4
2
0
-2
-4
-6
f1 (ppm)

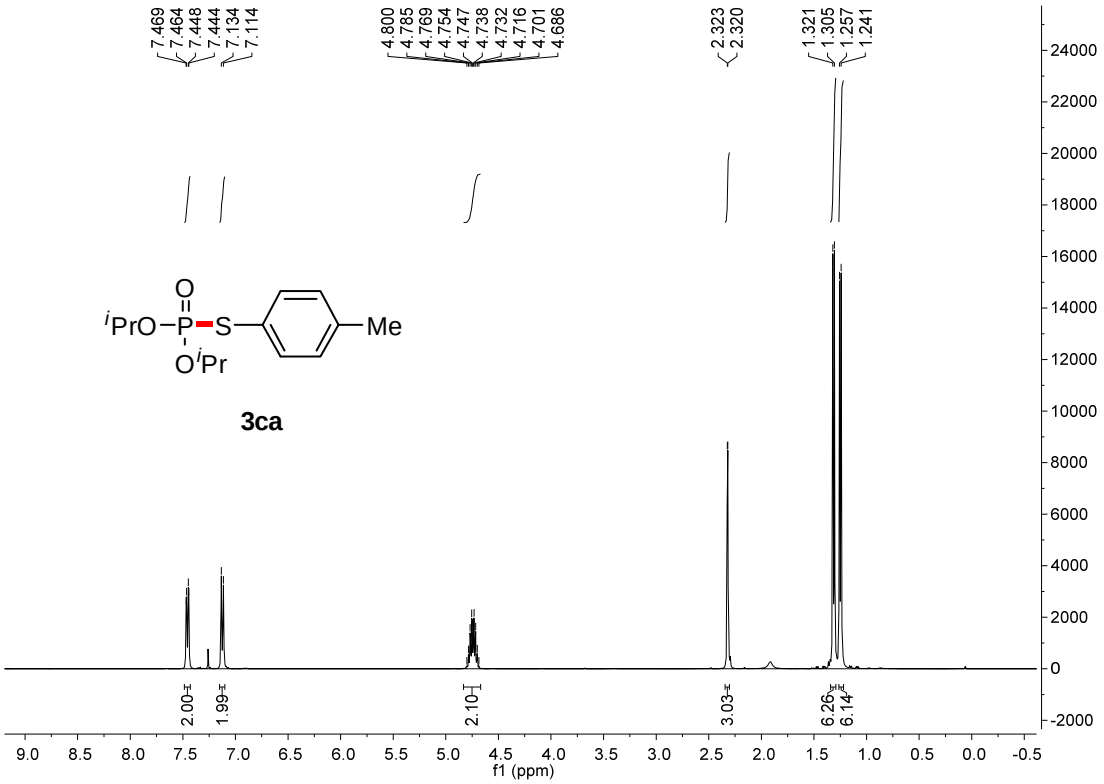
3ba


7.509
7.504
7.487
7.482
7.343
7.322
3.837
3.805
MeO
P
S
Cl
OMe
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
1.99
6.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3bg

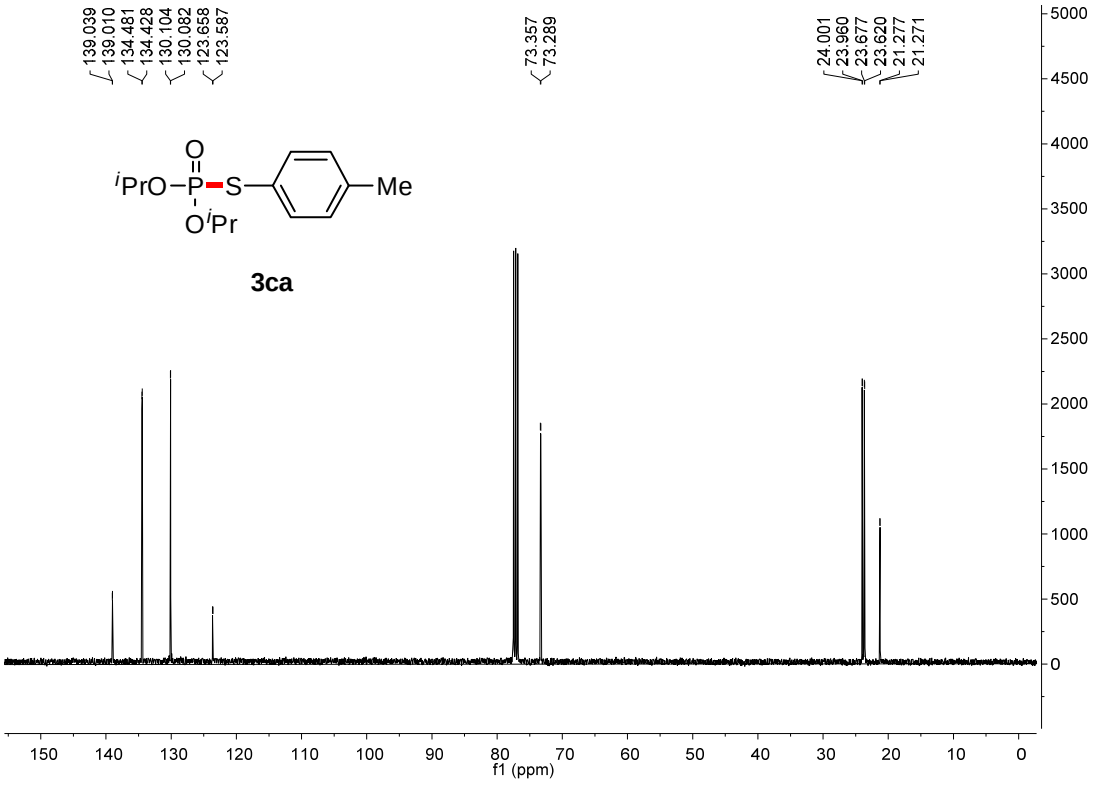

136.003
135.952
135.923
135.888
129.868
129.845
124.753
124.680
54.562
54.501
MeO
P
S
Cl
OMe
O
3bg
f1 (ppm)


25.491
MeO
P
S
Cl
OMe
O
3bg
f1 (ppm)


7.469
7.464
7.448
7.444
7.134
7.114
4.800
4.785
4.769
4.754
4.747
4.738
4.732
4.716
4.701
4.686
2.323
2.320
1.321
1.305
1.257
1.241
2.00
1.99
2.10
3.03
6.26
6.14
f1 (ppm)

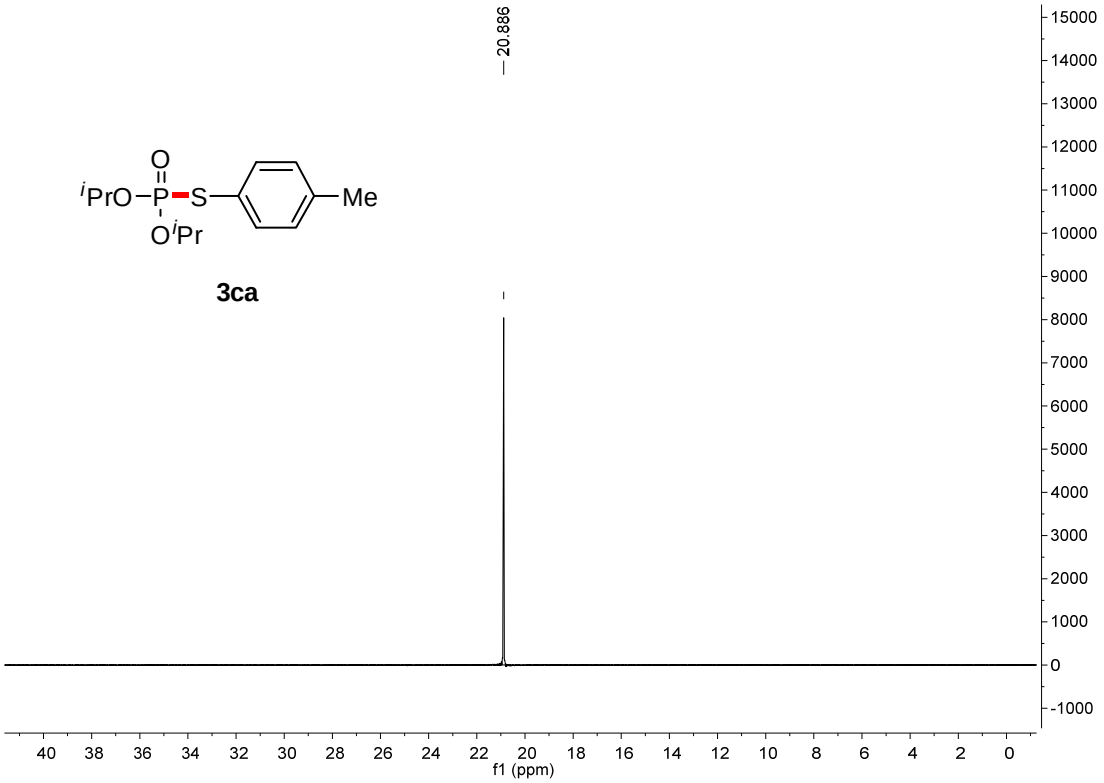
iPrO
P
S
Me
OiPr

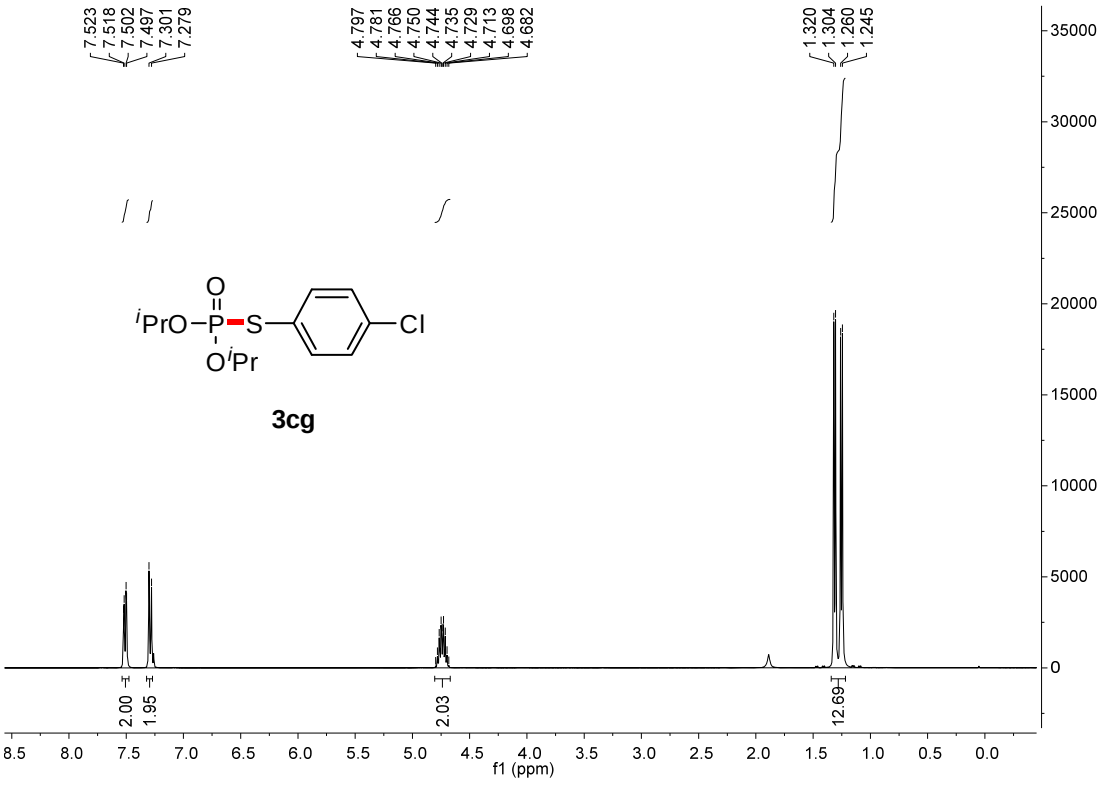
3ca

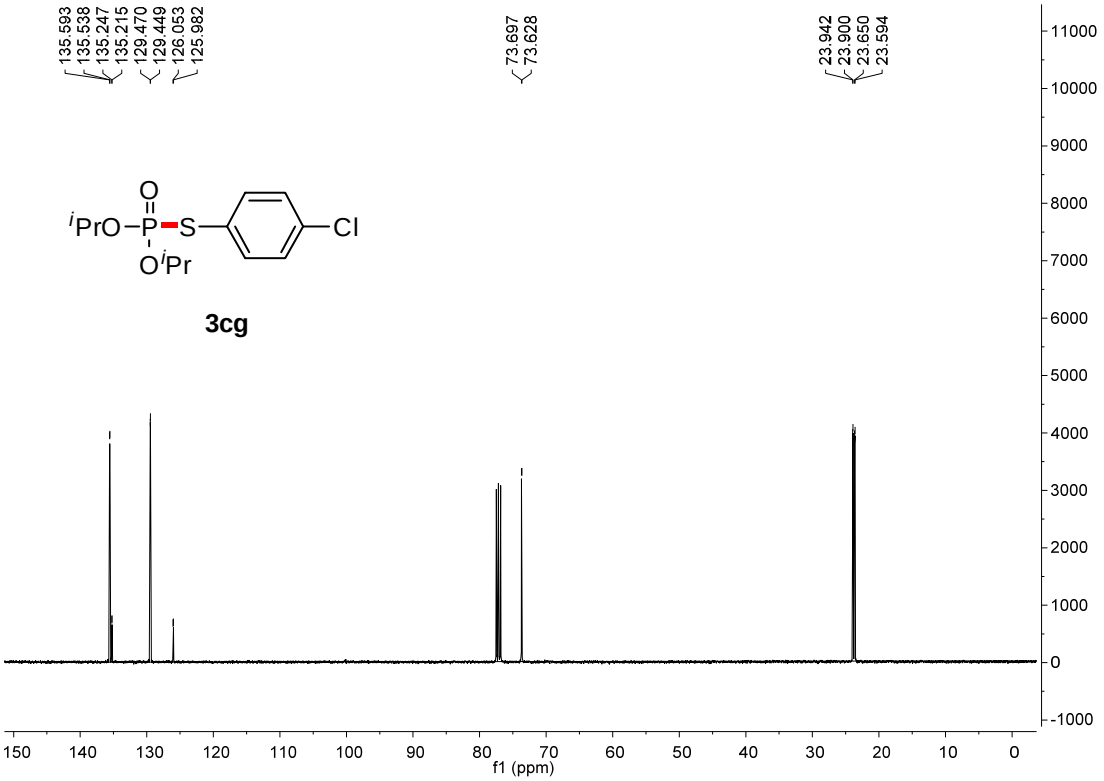

139.039
139.010
134.481
134.428
130.104
130.082
123.658
123.587
73.357
73.289
24.001
23.960
23.677
23.620
21.277
21.271
f1 (ppm)

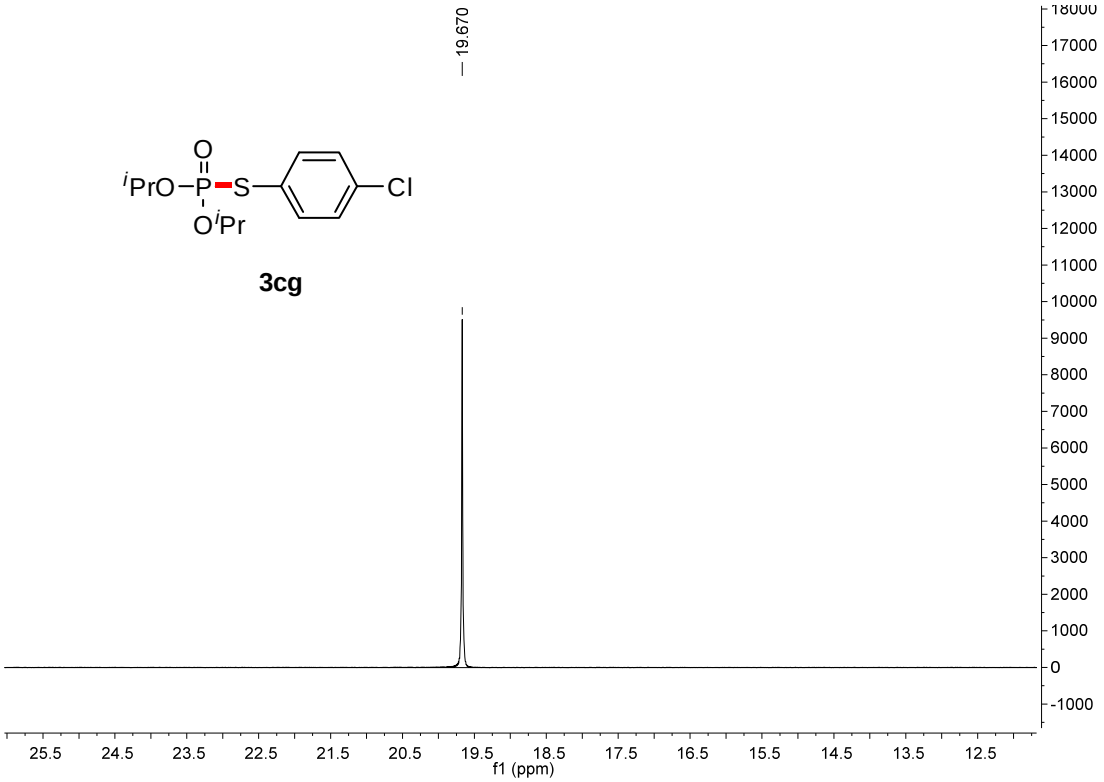
iPrO
P
S
Me
OiPr

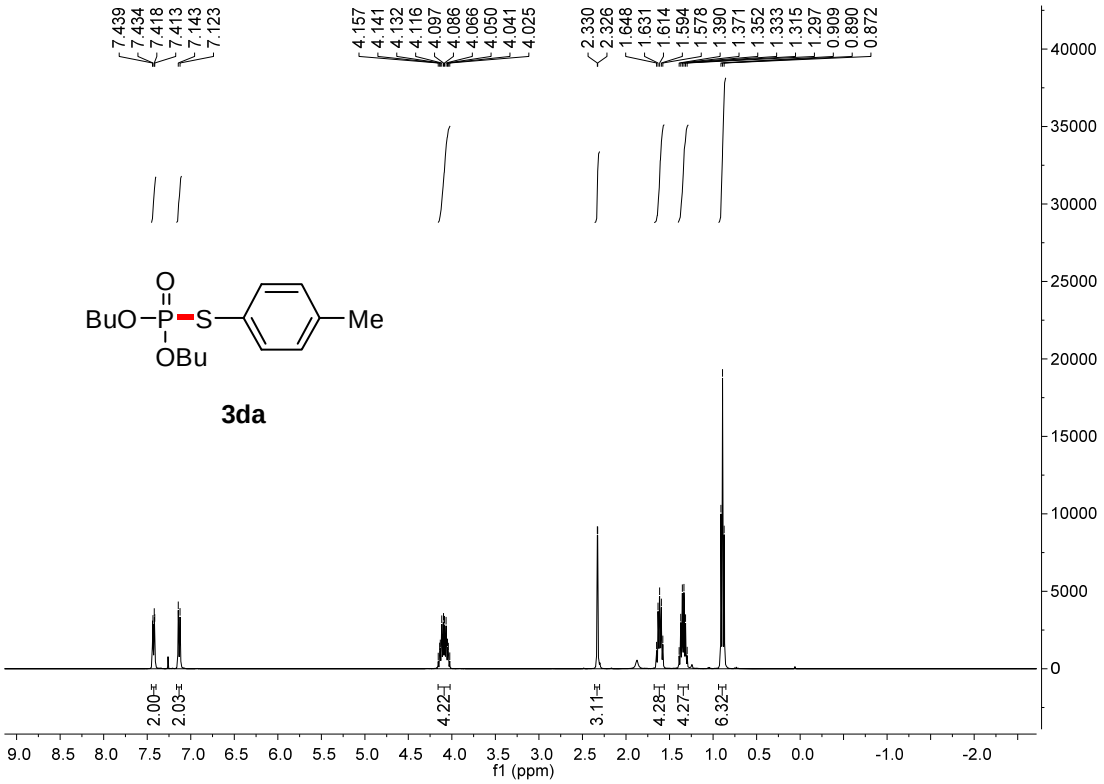
3ca

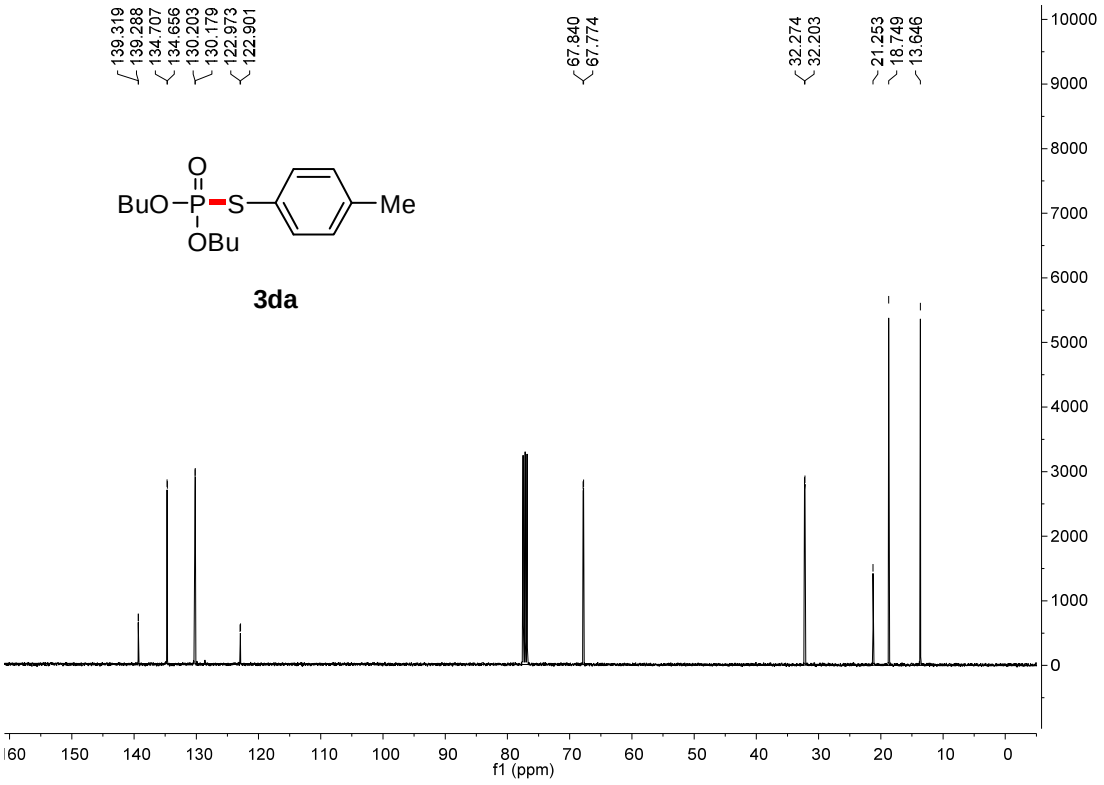

20.886
iPrO–P(=O)(OiPr)–S–Me
3ca
f1 (ppm)

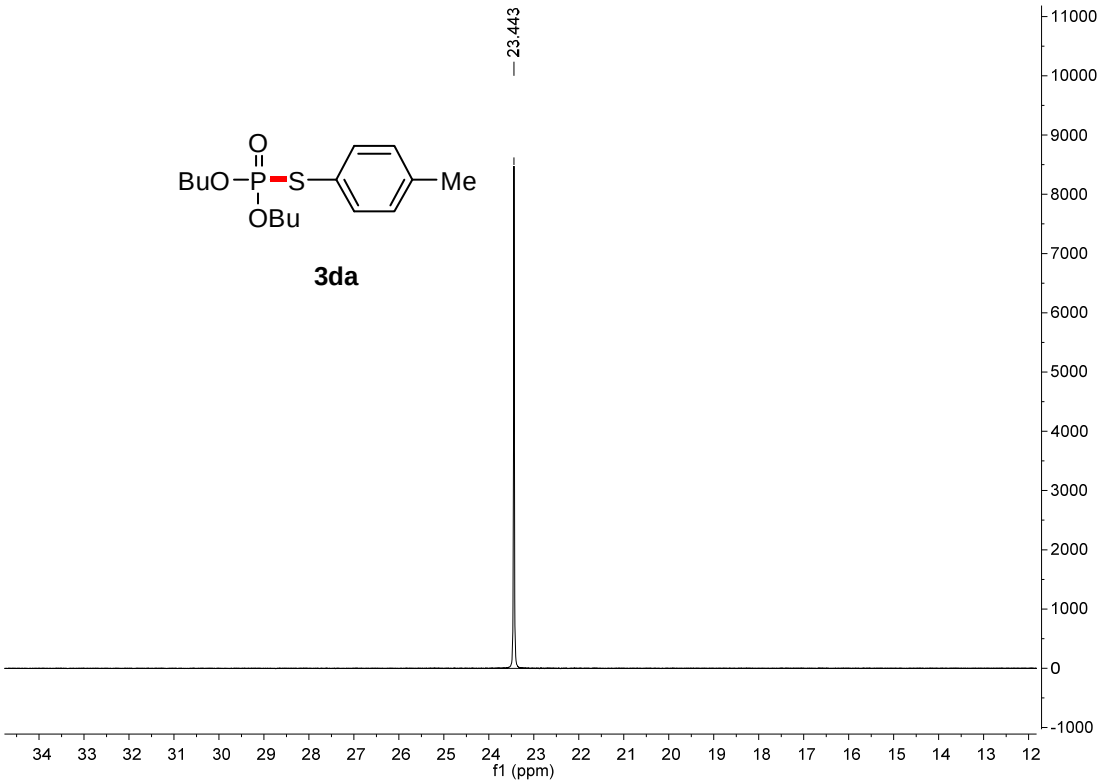

7.523
7.518
7.502
7.497
7.301
7.279
4.797
4.781
4.766
4.750
4.744
4.735
4.729
4.713
4.698
4.682
1.320
1.304
1.260
1.245
iPrO–P(=O)(OiPr)–S–Cl
3cg
2.00
1.95
2.03
12.69
f1 (ppm)


135.593
135.538
135.247
135.215
129.470
129.449
126.053
125.982
73.697
73.628
23.942
23.900
23.650
23.594
O
iPrO–P–S
Cl
OiPr
3cg
f1 (ppm)

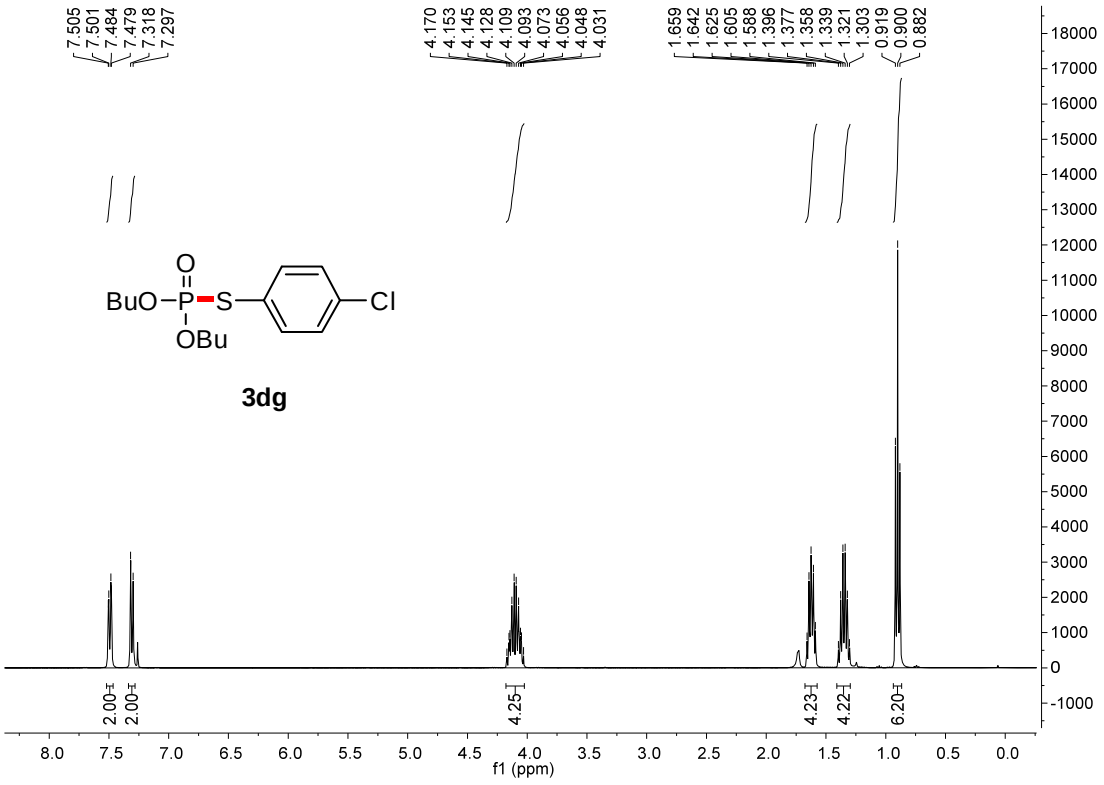

19.670
O
iPrO–P–S
Cl
OiPr
3cg
f1 (ppm)


7.439
7.434
7.418
7.413
7.143
7.123
4.157
4.141
4.132
4.116
4.097
4.086
4.066
4.050
4.041
4.025
2.330
2.326
1.648
1.631
1.614
1.594
1.578
1.390
1.371
1.352
1.333
1.315
1.297
0.909
0.890
0.872
BuO
P
S
Me
OBu
3da
2.00
2.03
4.22
3.11
4.28
4.27
6.32
f1 (ppm)

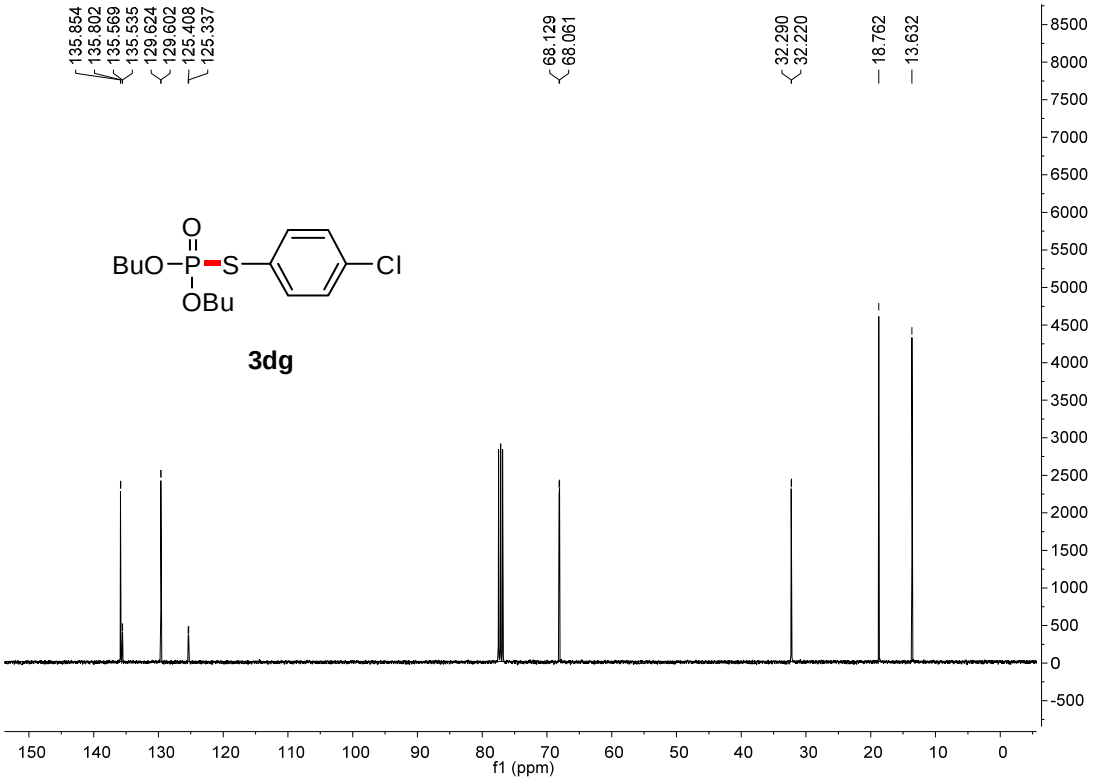

139.319
139.288
134.707
134.656
130.203
130.179
122.973
122.901
67.840
67.774
32.274
32.203
21.253
18.749
13.646
BuO
P
S
Me
OBu
3da
f1 (ppm)

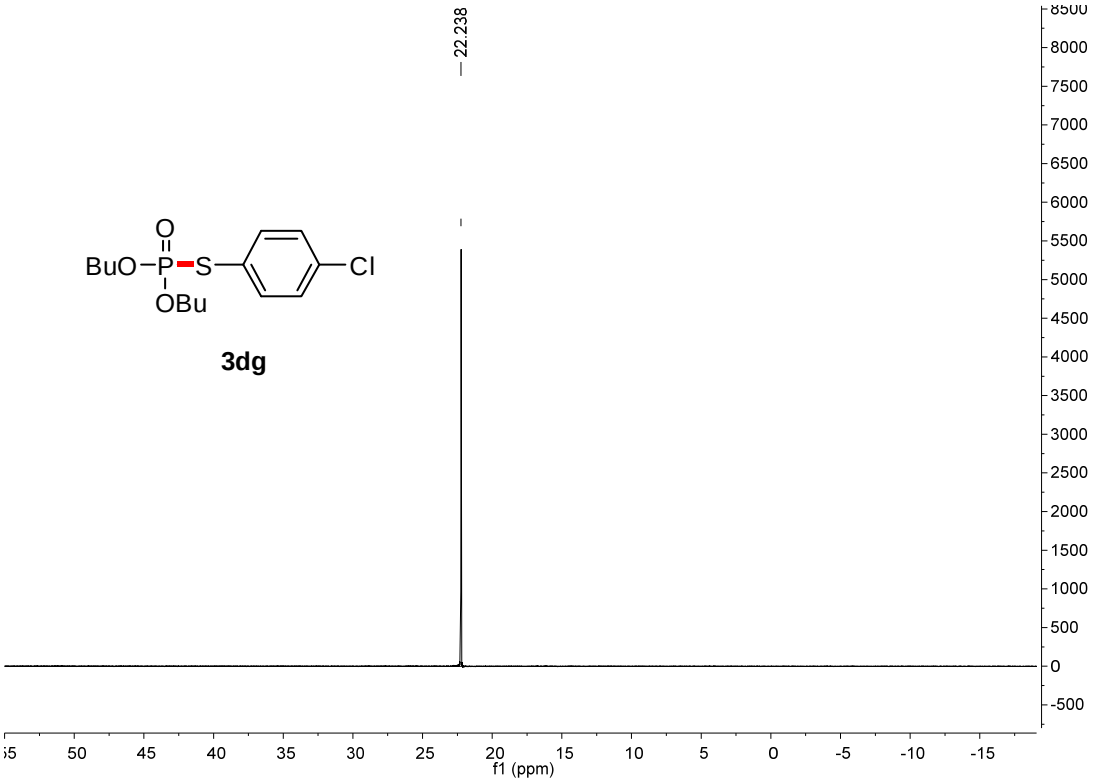

23.443
BuO
P
S
OBu
Me
f1 (ppm)

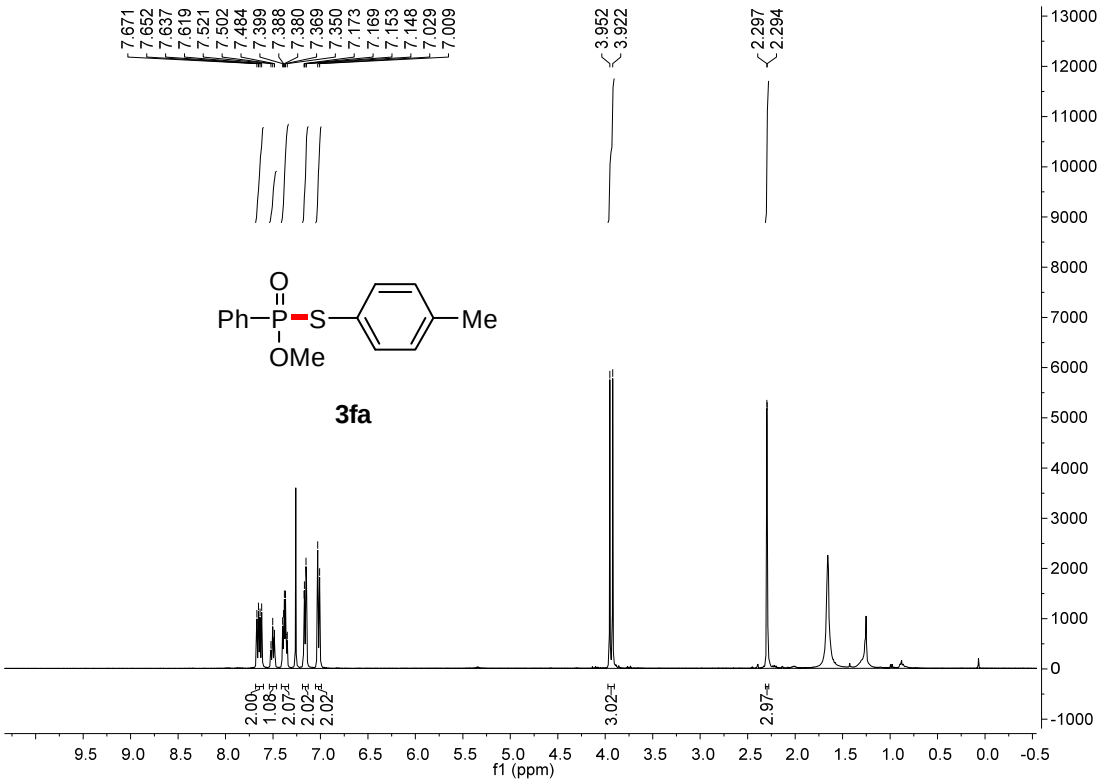
3da

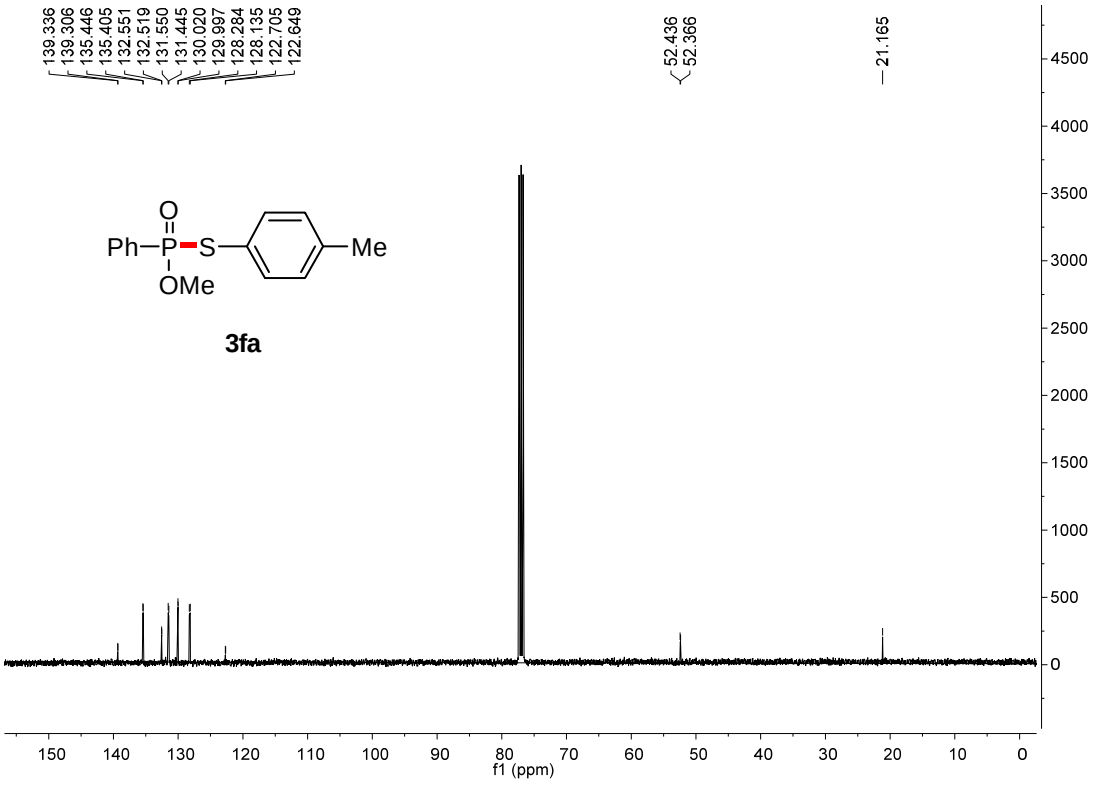

7.505
7.501
7.484
7.479
7.318
7.297
4.170
4.153
4.145
4.128
4.109
4.093
4.073
4.056
4.048
4.031
1.659
1.642
1.625
1.605
1.588
1.396
1.377
1.358
1.339
1.321
1.303
0.919
0.900
0.882
BuO
P
S
OBu
Cl
2.00
2.00
4.25
4.23
4.22
6.20
f1 (ppm)

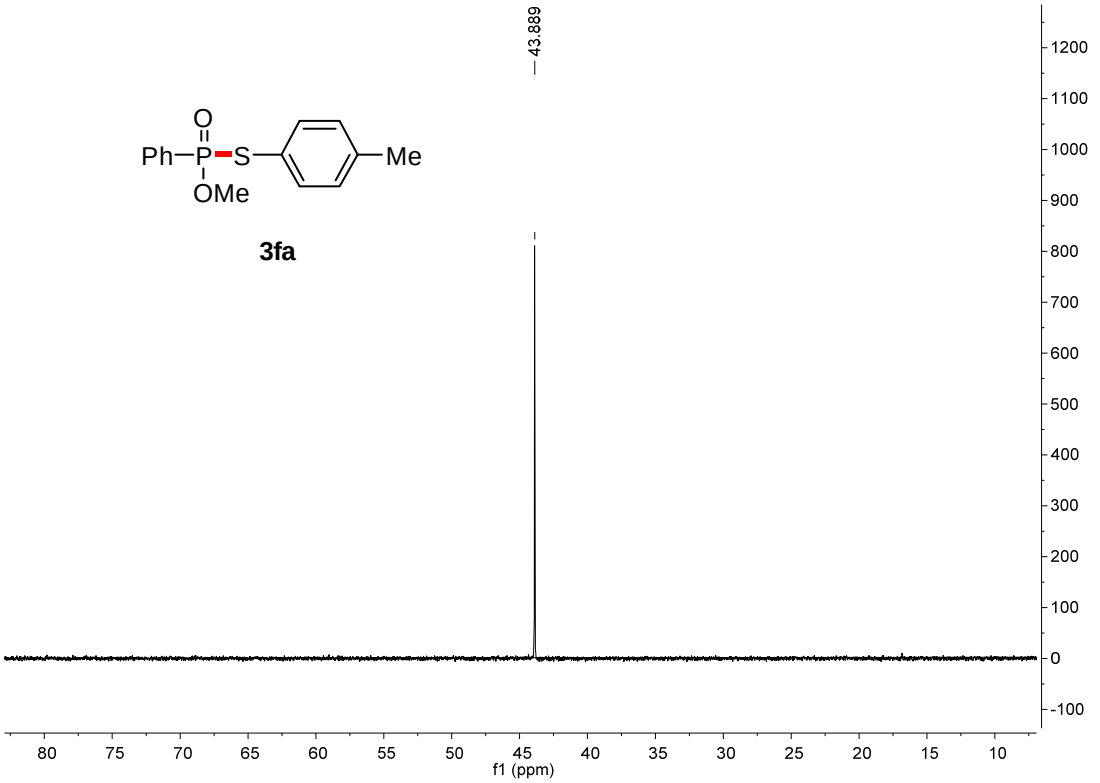
3dg

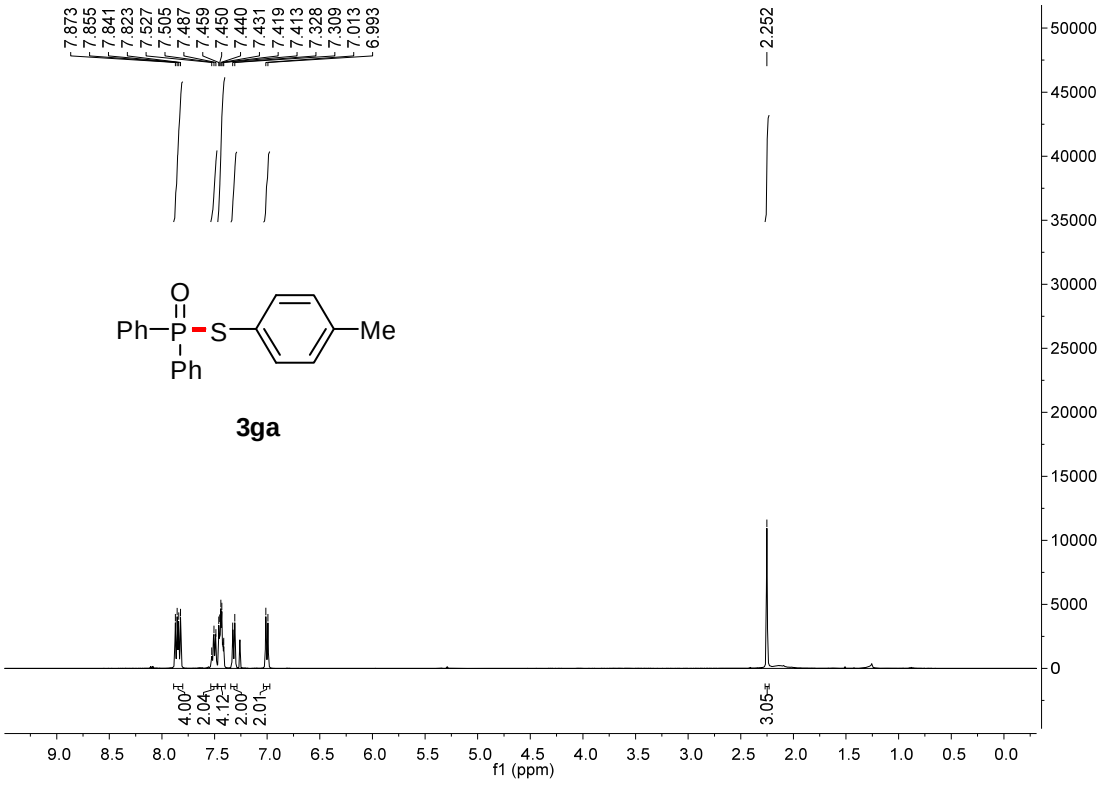

135.854
135.802
135.569
135.535
129.624
129.602
125.408
125.337
68.129
68.061
32.290
32.220
18.762
13.632
BuO
P
S
Cl
OBu
O
3dg
f1 (ppm)

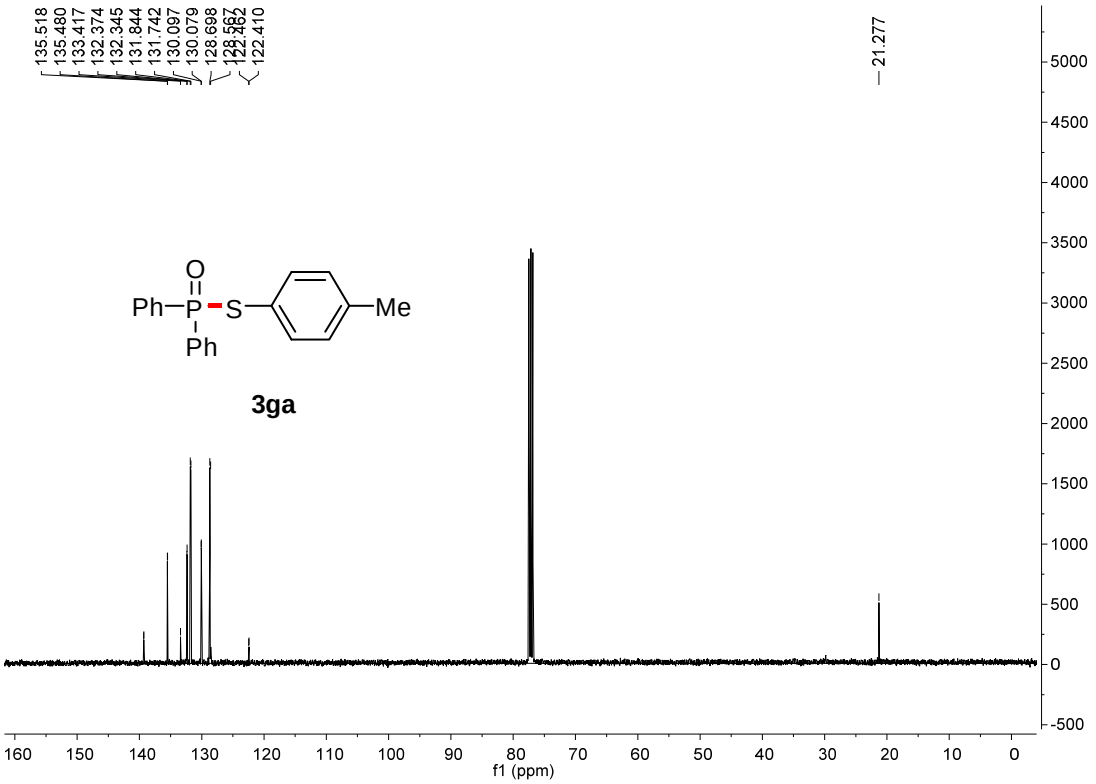

22.238
BuO
P
S
Cl
OBu
O
3dg
f1 (ppm)

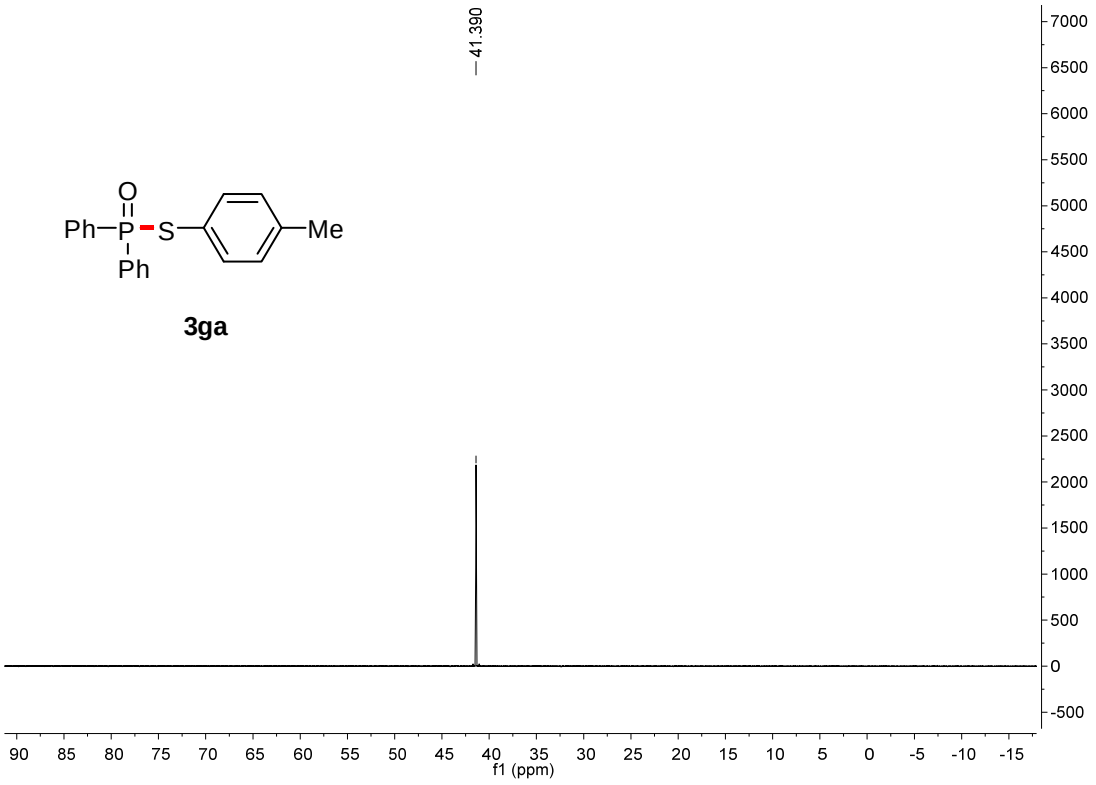

7.671
7.652
7.637
7.619
7.521
7.502
7.484
7.399
7.388
7.380
7.369
7.350
7.173
7.169
7.153
7.148
7.029
7.009
3.952
3.922
2.297
2.294
Ph
P
S
Me
OMe
O
3fa
2.00
1.08
2.07
2.02
2.02
3.02
2.97
f1 (ppm)


139.336
139.306
135.446
135.405
132.551
132.519
131.550
131.445
130.020
129.997
128.284
128.135
122.705
122.649
52.436
52.366
21.165
Ph
P
S
Me
OMe
O
3fa
f1 (ppm)


43.889
Ph
P
O
S
OMe
Me
3fa
f1 (ppm)


7.873
7.855
7.841
7.823
7.527
7.505
7.487
7.459
7.450
7.440
7.431
7.419
7.413
7.328
7.309
7.013
6.993
2.252
Ph
P
O
S
Ph
Me
3ga
4.00
2.04
4.12
2.00
2.01
3.05
f1 (ppm)


135.518
135.480
133.417
132.374
132.345
131.844
131.742
130.097
130.079
128.698
122.462
122.410
21.277
Ph
P
O
S
Me
Ph
3ga
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


41.390
Ph
P
O
S
Me
Ph
3ga
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)
7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500