Electronic Supplementary Information

Magnetically Recyclable Cu-BTC@Fe_3O_4 Composite-Catalyzed $C_{(aryl)}$-S-P Bonds formation using aniline, P(O)H Compounds and Sulfur Powder

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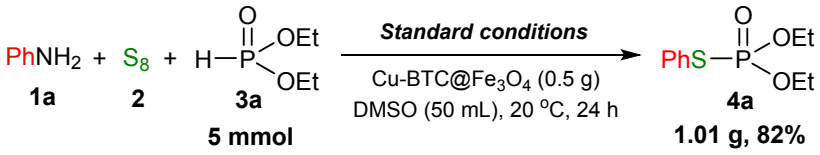
1. Experimental procedures

Polyvinylpyrrolidone K-30 (PVP, $(C_6H_9HO)_n$, MW: av. 40,000), $Cu(OAc)_2{\cdot}H_2O$ (98%), trimesic acid (H_3BTC, 99%), and carboxymethylcellulose (CMC, viscosity > 1900 mPa·s, surface density: 0.35 to 0.60 $g{\cdot}m^{-1}$), as well as carboxyl functionalized Fe_3O_4 (about 20 nm). All starting materials are commercially available and used directly without further purification.

Scale-up synthesis

The scale-up experiment was conducted in a two-neck 100 mL flask. The substrate amount was 5 mmol. The amounts of other reagents and the catalyst were increased to 25 times accordingly. The reaction method and purification were the same as the model reaction in Table 1.



Scheme S1 Gram-scale synthesis of **4a**.

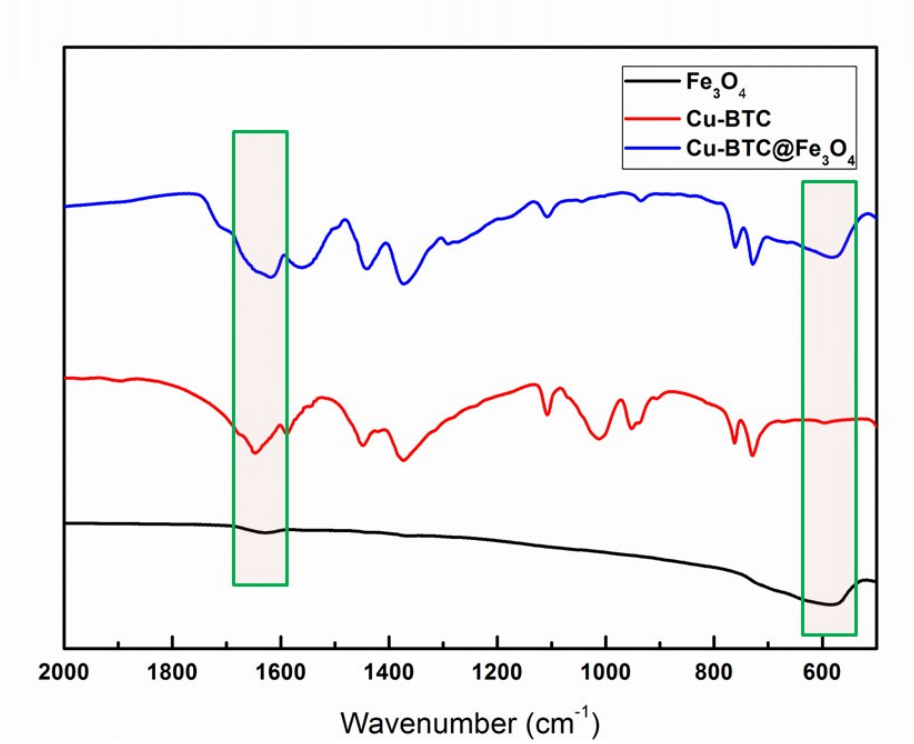
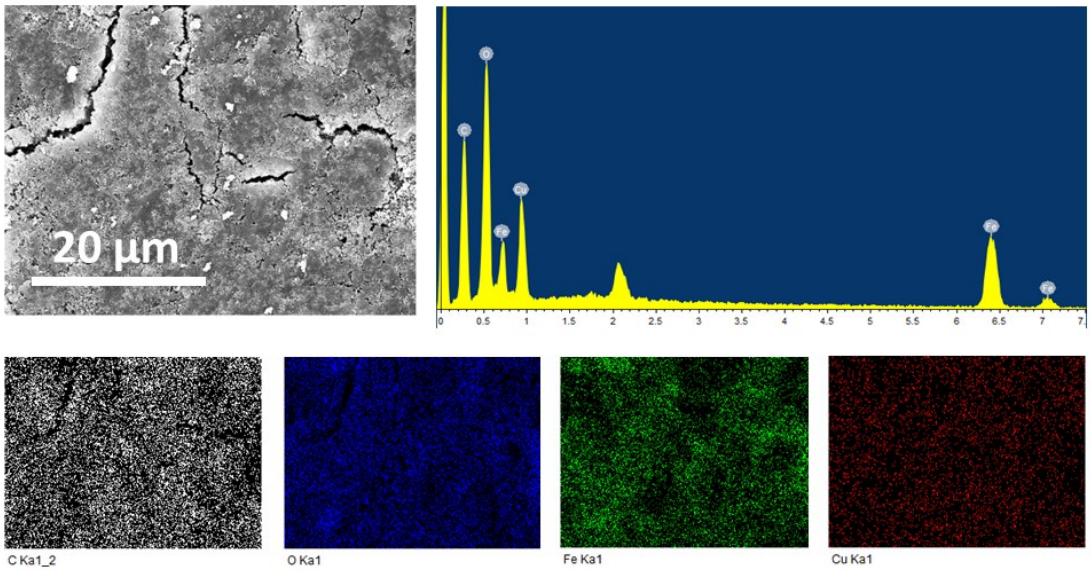


Fig. S1. IR spectra of carboxyl functionalized Fe_3O_4 (black), Cu-BTC (red) and Cu-BTC@Fe_3O_4 (blue).



Element	C	O	Fe	Cu
Weight Percentage (%)	39.51	35.42	12.89	12.18
Atomic Percentage (%)	55.51	37.36	3.90	3.24

Fig. S2. The EDS element analysis of Cu-BTC@Fe_3O_4, the scale bar is 20 µm.

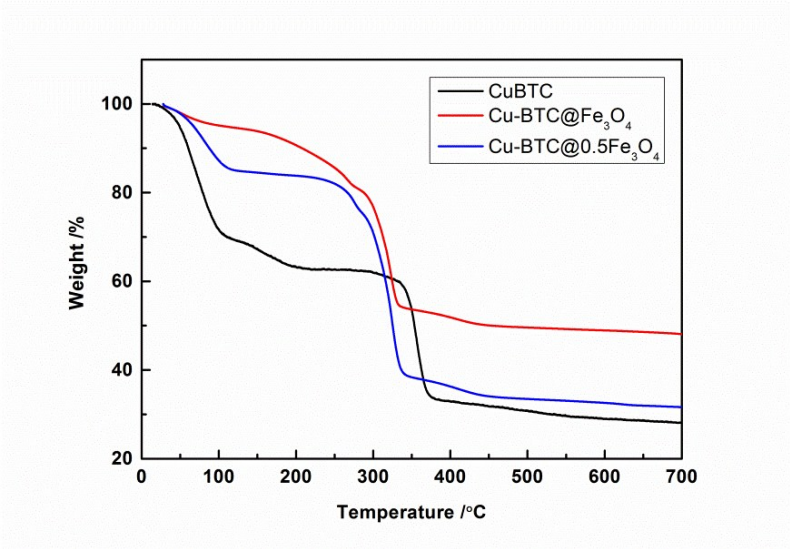


Fig. S3. The TG curves of Cu-BTC@ Fe_3O_4 with different ratios of starting materials.

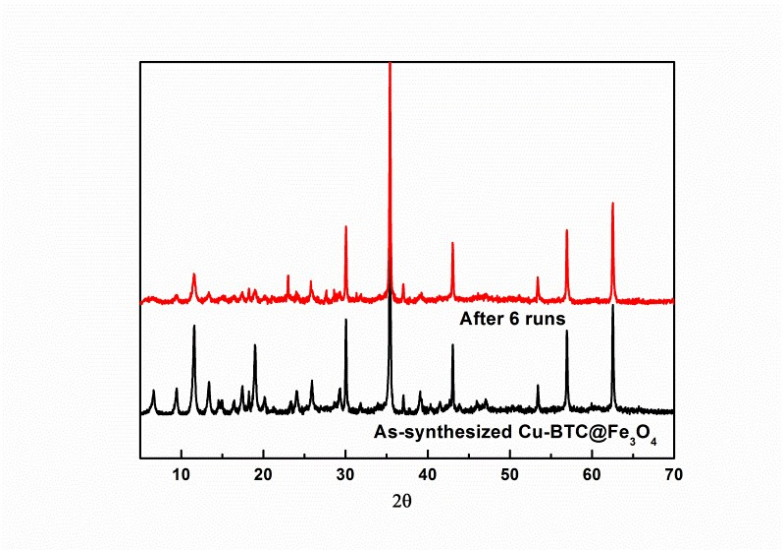
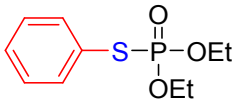
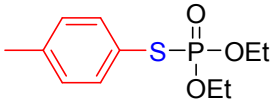


Fig. S4. The PXRD patterns of Cu-BTC@Fe_3O_4 before and after catalysis reaction.

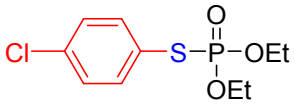
2 Characterization data



O,O-diethyl S-phenyl phosphorothioate ***(4a)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 2H), 7.43 – 7.27 (m, 3H), 4.28 – 4.06 (m, 4H), 1.28 (td, *J* = 7.1, 0.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5 (d, *J* = 5.2 Hz), 129.3 (d, *J* = 2.3 Hz), 129.0 (d, *J* = 2.8 Hz), 126.4 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 6.2 Hz), 15.9 (d, *J* = 7.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.8. MS-ESI: *m/z* = 268.8 $[M + Na]^+$.

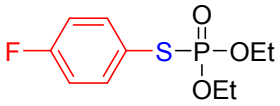


O,O-diethyl S-(p-tolyl) phosphorothioate ***(4b)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.26 – 4.08 (m, 4H), 2.33 (d, *J* = 2.0 Hz, 3H), 1.30 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2 (d, *J* = 3.2 Hz), 134.5 (d, *J* = 5.1 Hz), 130.1 (d, *J* = 2.4 Hz), 122.7 (d, *J* = 7.3 Hz), 63.9 (d, *J* = 6.1 Hz), 21.1 (d, *J* = 0.9 Hz), 16.0 (d, *J* = 7.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.3. MS-ESI: *m/z* = 282.9 $[M + Na]^+$.

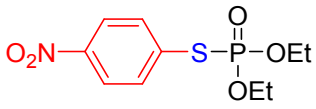


S-(4-chlorophenyl) O,O-diethyl phosphorothioate ***(4c)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.35 – 7.28 (m, 2H), 4.29 – 4.07 (m, 4H), 1.31 (td, *J* = 7.1, 0.8

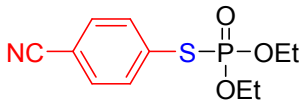
Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7 (d, J = 5.2 Hz), 135.5 (d, J = 3.5 Hz), 129.5 (d, J = 2.3 Hz), 125.1 (d, J = 7.2 Hz), 64.2 (d, J = 6.4 Hz), 16.0 (d, J = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.1. MS-ESI: m/z = 302.9 $[M + Na]^+$.



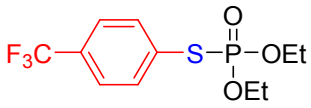
*S-(4-fluorophenyl) O,O-diethyl phosphorothioate (**4d**)*. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.03 (t, J = 8.6 Hz, 2H), 4.26 – 4.07 (m, 4H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (dd, J = 250, 3.2 Hz), 136.8 (dd, J = 6.3, 3.7 Hz), 121.6 (dd, J = 6.8, 2.6 Hz), 116.5 (dd, J = 37.3, 22.3 Hz), 64.1 (d, J = 6.4 Hz), 15.9 (d, J = 7.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.6. MS-ESI: m/z = 286.8 $[M + Na]^+$.



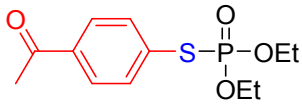
*O,O-diethyl S-(4-nitrophenyl) phosphorothioate (**4e**)*. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.79 – 7.74 (m, 2H), 4.34 – 4.14 (m, 4H), 1.35 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 136.1 (d, J = 6.6 Hz), 134.1 (d, J = 6.0 Hz), 124.1 (d, J = 1.5 Hz), 64.7 (d, J = 6.4 Hz), 16.0 (d, J = 7.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.8. MS-ESI: m/z = 314.0 $[M + Na]^+$.



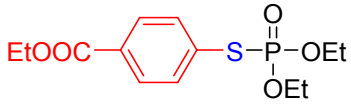
*S-(4-cyanophenyl) O,O-diethyl phosphorothioate (**4f**)*. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.61 – 7.58 (m, 2H), 4.29 – 4.09 (m, 4H), 1.30 (td, J = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2 (d, J = 6.0 Hz), 134.0 (d, J = 6.7 Hz), 132.6 (d, J = 1.6 Hz), 117.9 (d, J = 1.4 Hz), 112.4 (d, J = 2.4 Hz), 64.5 (d, J = 6.4 Hz), 15.9 (d, J = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.3. MS-ESI: m/z = 294.0 $[M + Na]^+$.



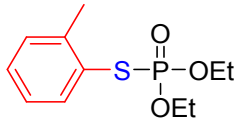
*O,O-diethyl S-(4-(trifluoromethyl)phenyl) phosphorothioate (**4g**)*. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.58 (d, J = 8.6 Hz, 2H), 4.30 – 4.10 (m, 4H), 1.31 (td, J = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2 (d, J = 5.6 Hz), 131.8 (d, J = 6.8 Hz), 130.8 (dd, J = 2.5, 32.7 Hz), 126.0 (dd, J = 3.7, 1.9 Hz), 123.6 (q, J = 270 Hz), 64.4 (d, J = 6.3 Hz), 15.9 (d, J = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.2. MS-ESI: m/z = 337.0 $[M + Na]^+$.



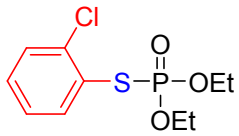
S-(4-acetylphenyl) O,O-diethyl phosphorothioate ***(4h)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz), 7.65 – 7.63 (m, 2H), 4.28 – 4.09 (m, 4H), 2.58 (s, 3H), 1.30 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 136.9 (d, J = 2.4 Hz), 133.8 (d, J = 5.7 Hz), 133.1 (d, J = 6.9 Hz), 128.9 (d, J = 1.8 Hz), 64.3 (d, J = 6.3 Hz), 26.6, 15.9 (d, J = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.2. MS-ESI: m/z = 310.8 $[M + Na]^+$.



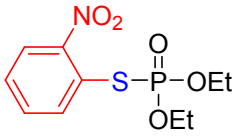
Ethyl 4-((diethoxyphosphoryl)thio)benzoate ***(4i)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.64 – 7.60 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.25 – 4.10 (m, 4H), 1.36 (t, J = 7.1 Hz, 3H), 1.29 (td, J = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 133.6 (d, J = 5.7 Hz), 132.7 (d, J = 6.9 Hz), 130.7 (d, J = 2.5 Hz), 130.2 (d, J = 1.8 Hz), 64.3 (d, J = 6.3 Hz), 61.2, 15.9 (d, J = 7.2 Hz), 14.2. ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.4. MS-ESI: m/z = 341.0 $[M + Na]^+$.



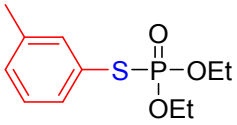
O,O-diethyl S-(o-tolyl) phosphorothioate ***(4j)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 1H), 7.30 – 7.23 (m, 2H), 7.22 – 7.13 (m, 1H), 4.22 – 4.07 (m, 4H), 2.52 (d, J = 1.4 Hz, 3H), 1.29 (td, J = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2 (d, J = 5.6 Hz), 136.1 (d, J = 4.2 Hz), 130.8 (d, J = 2.6 Hz), 129.4 (d, J = 3.1 Hz), 126.7 (d, J = 2.7 Hz), 125.7 (d, J = 7.4 Hz), 64.1 (d, J = 6.7 Hz), 21.4, 16.0 (d, J = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.0. MS-ESI: m/z = 283.0 $[M + Na]^+$.



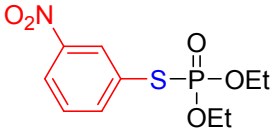
S-(2-chlorophenyl) O,O-diethyl phosphorothioate ***(4k)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 1H), 7.48 – 7.45 (m, 1H), 7.34 – 7.23 (m, 2H), 4.33 – 4.14 (m, 4H), 1.33 (td, J = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9 (d, J = 6.9 Hz), 136. 8 (d, J = 4.1 Hz), 130.3 (d, J = 6.7 Hz), 127.5 (d, J = 2.4 Hz), 64.4 (d, J = 6.2 Hz), 16.0 (d, J = 7.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.2. MS-ESI: m/z = 302.9 $[M + Na]^+$.



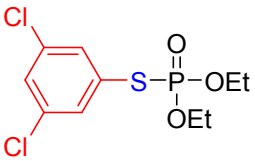
O,O-diethyl S-(2-nitrophenyl) phosphorothioate ***(4l)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 2H), 7.60 – 7.45 (m, 2H), 4.32 – 4.09 (m, 4H), 1.31 (td, *J* = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6 (d, *J* = 7.8 Hz), 136.1 (d, *J* = 4.9 Hz), 132.8 (d, *J* = 1.7 Hz), 129.2 (d, *J* = 2.0 Hz), 125.2 (d, *J* = 1.6 Hz), 123.0 (d, *J* = 6.3 Hz), 64.8 (d, *J* = 6.7 Hz), 15.9 (d, *J* = 7.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.9. MS-ESI: *m/z* = 314.0 $[M + Na]^+$.



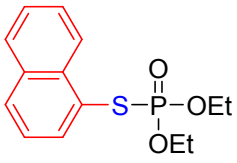
O,O-diethyl S-(m-tolyl) phosphorothioate ***(4m)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.27– 7.15 (m, 2H), 4.29 – 4.10 (m, 4H), 2.35 (s, 3H), 1.31 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1 (d, *J* = 2.3 Hz), 135.1 (d, *J* = 5.2 Hz), 131.5 (d, *J* = 5.2 Hz), 129.8 (d, *J* = 2.9 Hz), 129.1 (d, *J* = 2.3 Hz), 126.0 (d, *J* = 7.2 Hz), 63.9 (d, *J* = 6.2 Hz), 21.2 (s), 15.9 (d, *J* = 7.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.1. MS-ESI: *m/z* = 282.9 $[M + Na]^+$.



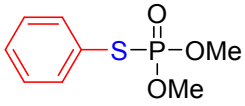
O,O-diethyl S-(3-nitrophenyl) phosphorothioate ***(4n)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 3.9, 1.9 Hz, 1H), 8.20 (ddd, *J* = 8.3, 2.8, 2.1 Hz, 1H), 7.90 (ddd, *J* = 7.8, 2.8, 1.8 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 4.31 – 4.12 (m, 4H), 1.32 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 140.4 (d, *J* = 5.4 Hz), 130.4, 129.5 (dd, *J* = 13.5, 9.8 Hz), 129.0 (dd, *J* = 15.2, 5.3 Hz), 123.9, 64.5 (d, *J* = 6.5 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.9. MS-ESI: *m/z* = 314.0 $[M + Na]^+$.



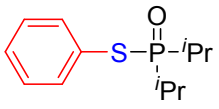
S-(3,5-dichlorophenyl) O,O-diethyl phosphorothioate ***(4o)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (t, *J* = 1.9 Hz, 2H), 7.35 (q, *J* = 1.8 Hz, 1H), 4.30 – 4.11 (m, 4H), 1.34 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3 (d, *J* = 2.4 Hz), 132.3 (d, *J* = 5.4 Hz), 129.9 (d, *J* = 7.1 Hz), 129.2 (d, *J* = 2.7 Hz), 64.5 (d, *J* = 6.4 Hz), 15.9 (d, *J* = 7.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.5. MS-ESI: *m/z* = 336.9 $[M + Na]^+$.



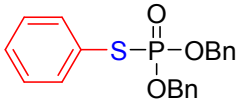
O,O-diethyl S-(naphthalen-1-yl) phosphorothioate ***(4p)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 8.4 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.63 – 7.43 (m, 3H), 4.22 – 4.02 (m, 4H), 1.18 (td, J = 7.1, 0.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2 (d, J = 5.6 Hz), 134.6 (d, J = 4.1 Hz), 134.2 (d, J = 2.3 Hz), 130.2 (d, J = 3.5 Hz), 128.5, 127.0, 126.4, 125.7 (dd, J = 17.5, 2.1 Hz), 123.6 (d, J = 8.1 Hz), 64.2 (d, J = 6.5 Hz), 15.9 (d, J = 7.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 22.6. MS-ESI: *m/z* = 319.0 $[M + Na]^+$.



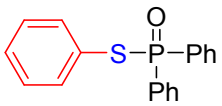
O,O-dimethyl S-phenyl phosphorothioate ***(4q)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.37 – 7.31 (m, 3H), 3.82 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5 (d, J = 5.2 Hz), 129.4 (d, J = 2.3 Hz), 129.1 (d, J = 2.9 Hz), 125.9 (d, J = 7.3 Hz), 54.2 (d, J = 6.1 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 26.2. MS-ESI: *m/z* = 240.8 $[M + Na]^+$.



S-phenyl diisopropylphosphinothioate ***(4r)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.34 – 7.29 (m, 3H), 4.80 – 4.69 (m, 2H), 1.31 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5 (d, J = 5.5 Hz), 129.3 (d, J = 5.2 Hz), 128.7 (d, J = 1.8 Hz), 127.3 (d, J = 5.2 Hz), 73.3 (d, J = 5.5 Hz), 23.8 (d, J = 4.1 Hz), 23.5 (d, J = 6.0 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.4. MS-ESI: *m/z* = 297.0 $[M + Na]^+$.



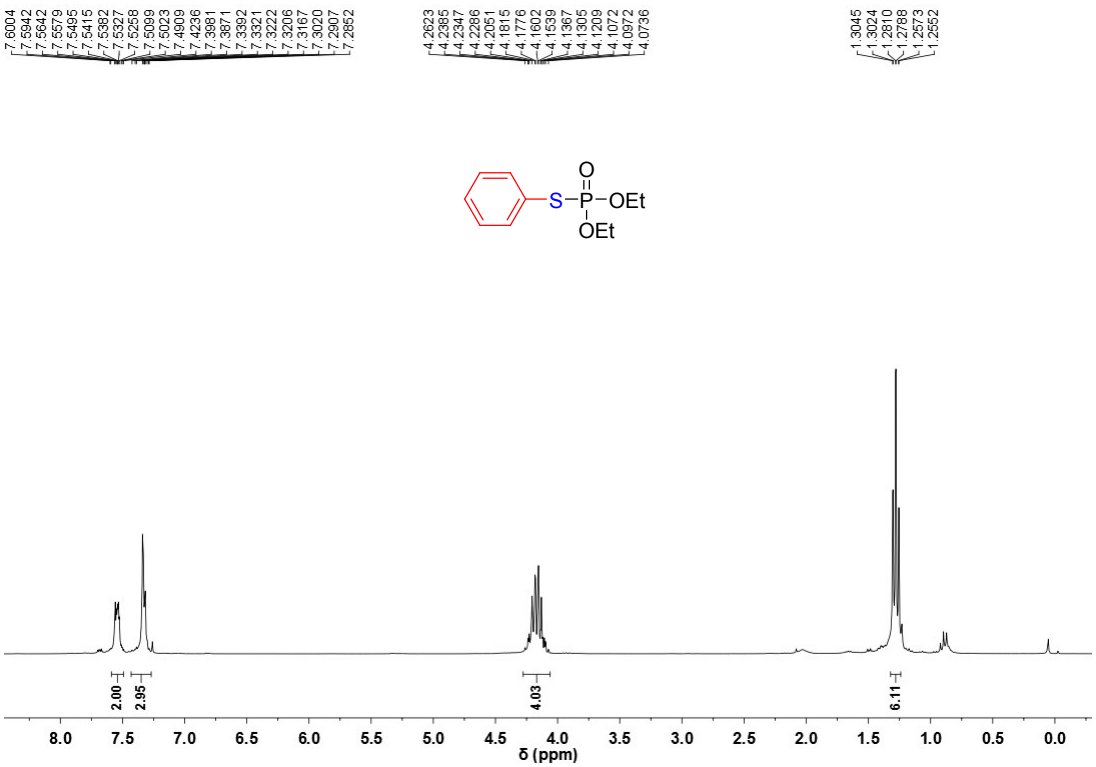
O,O-dibenzyl S-phenyl phosphorothioate ***(4s)***. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.33 – 7.24 (m, 13H), 5.17 – 5.05 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3 (d, J = 7.6 Hz), 134.7 (d, J = 5.3 Hz), 129.3 (d, J = 2.4 Hz), 129.0 (d, J = 3.0 Hz), 128.5, 128.4, 128.0, 125.8 (d, J = 7.3 Hz), 69.3 (d, J = 6.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 23.9. MS-ESI: *m/z* = 370.9 $[M + H]^+$.

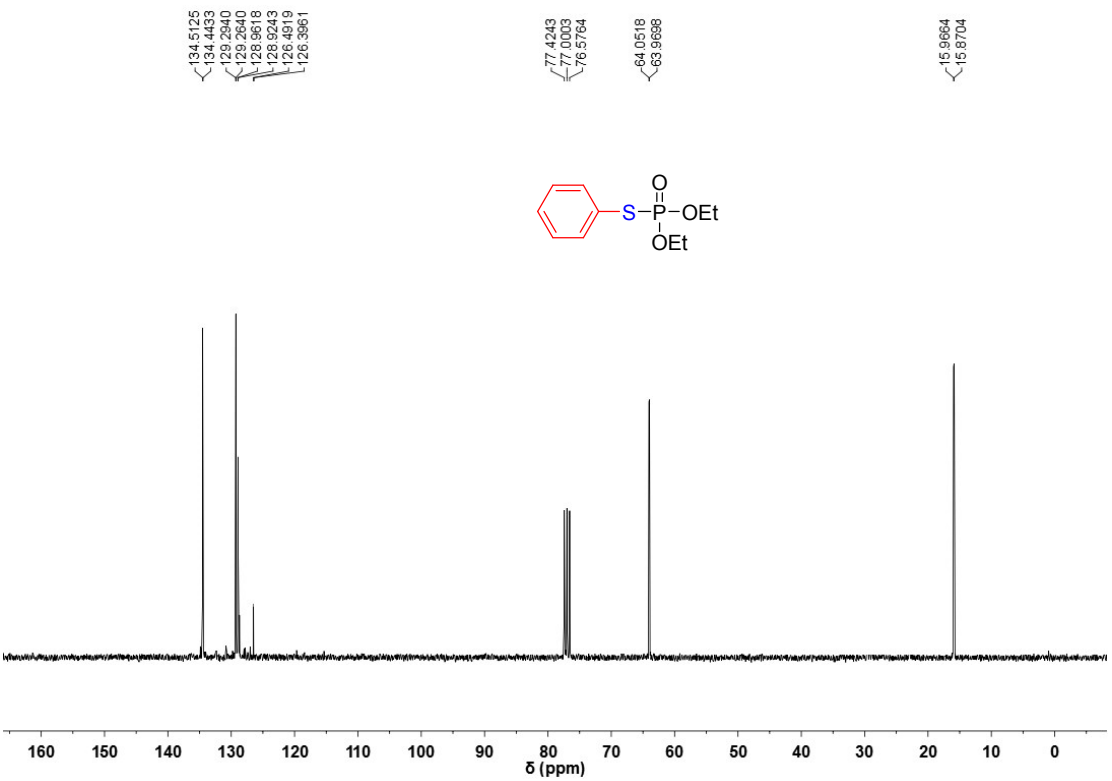


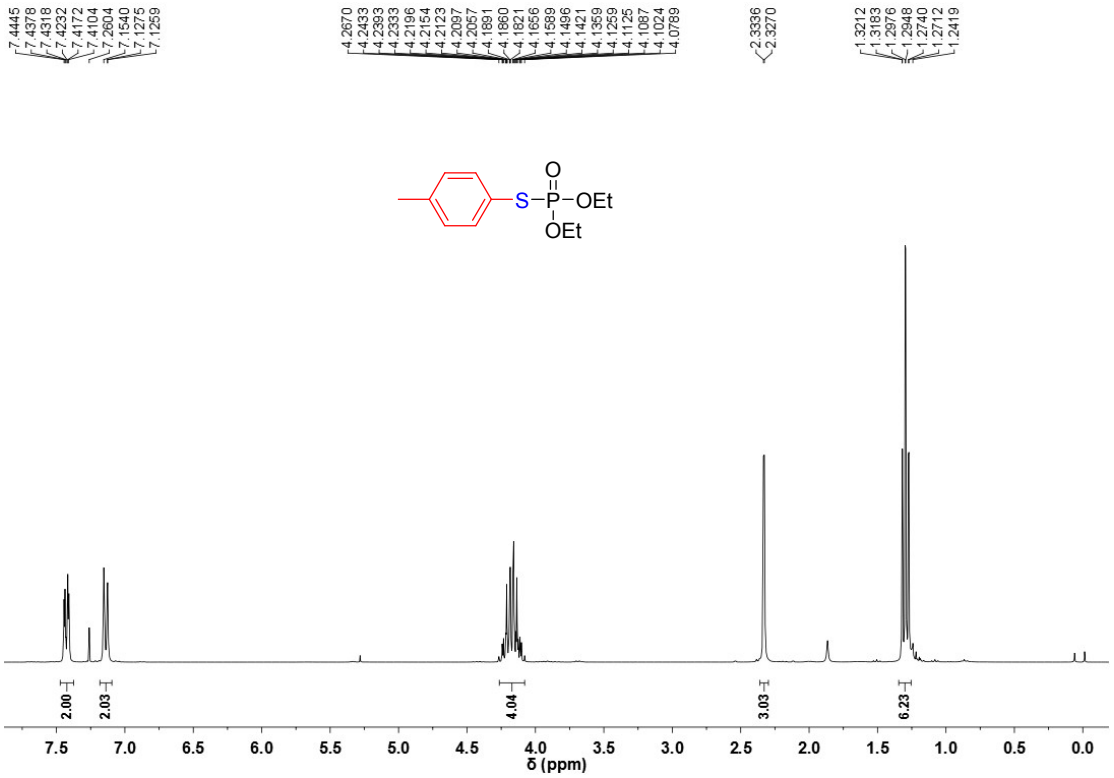
S-phenyl diphenylphosphinothioate ***(4u)***. White solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.50 – 7.39 (m, 8H), 7.24 – 7.15 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.3 (d, J = 3.9 Hz), 133.2, 132.2 (d, J = 3.0 Hz), 131.5 (d, J = 10.2 Hz), 129.0 (d, J = 1.7 Hz), 128.9 (d, J = 2.2 Hz),

128.5 (d, J = 13.2 Hz), 126.1 (d, J = 5.2 Hz). ^{31}P NMR (121 MHz, $CDCl_3$): δ 41.4. MS-ESI: m/z = 333.1 $[M + Na]^+$.

3 Copies of ^{1}H NMR and ^{13}C NMR spectra



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7.4172
7.4104
7.2604
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7.1275
7.1259
4.2670
4.2433
4.2393
4.2333
4.2196
4.2154
4.2123
4.2097
4.2057
4.1891
4.1860
4.1821
4.1656
4.1589
4.1496
4.1421
4.1359
4.1259
4.1125
4.1087
4.1024
4.0789
2.3336
2.3270
1.3212
1.3183
1.2976
1.2948
1.2740
1.2712
1.2419
O
S
P
OEt
OEt
2.00
2.03
4.04
3.03
6.23
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
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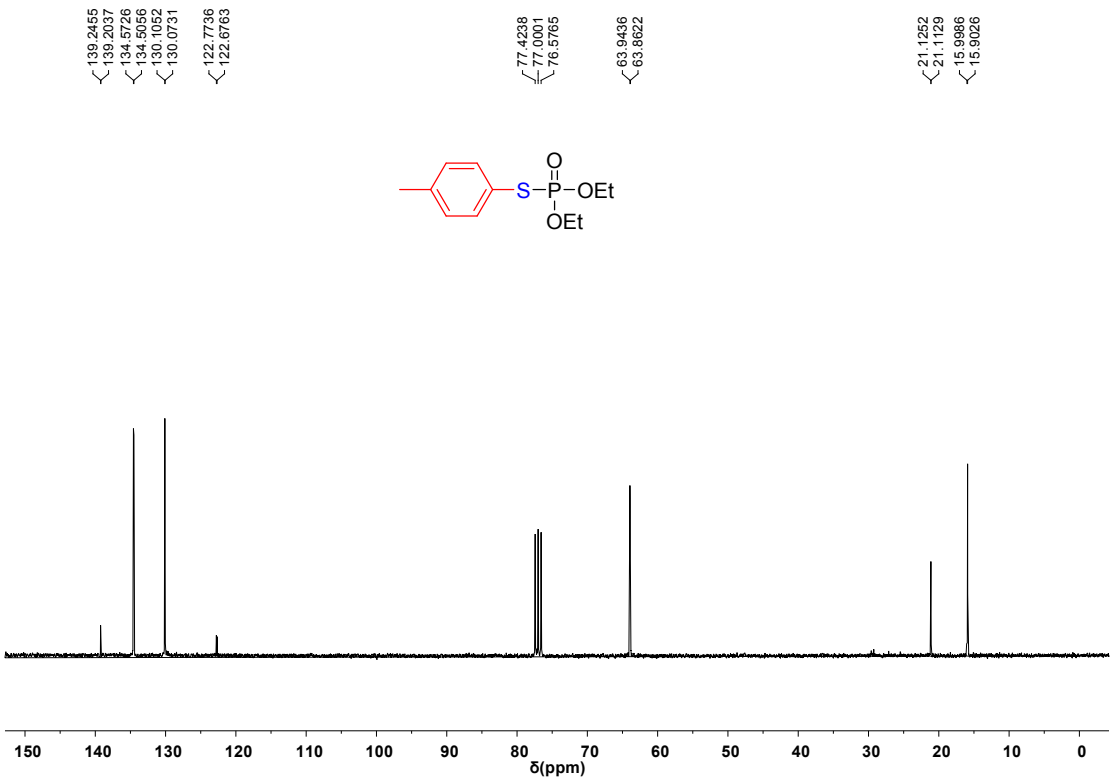
0.5
0.0
δ (ppm)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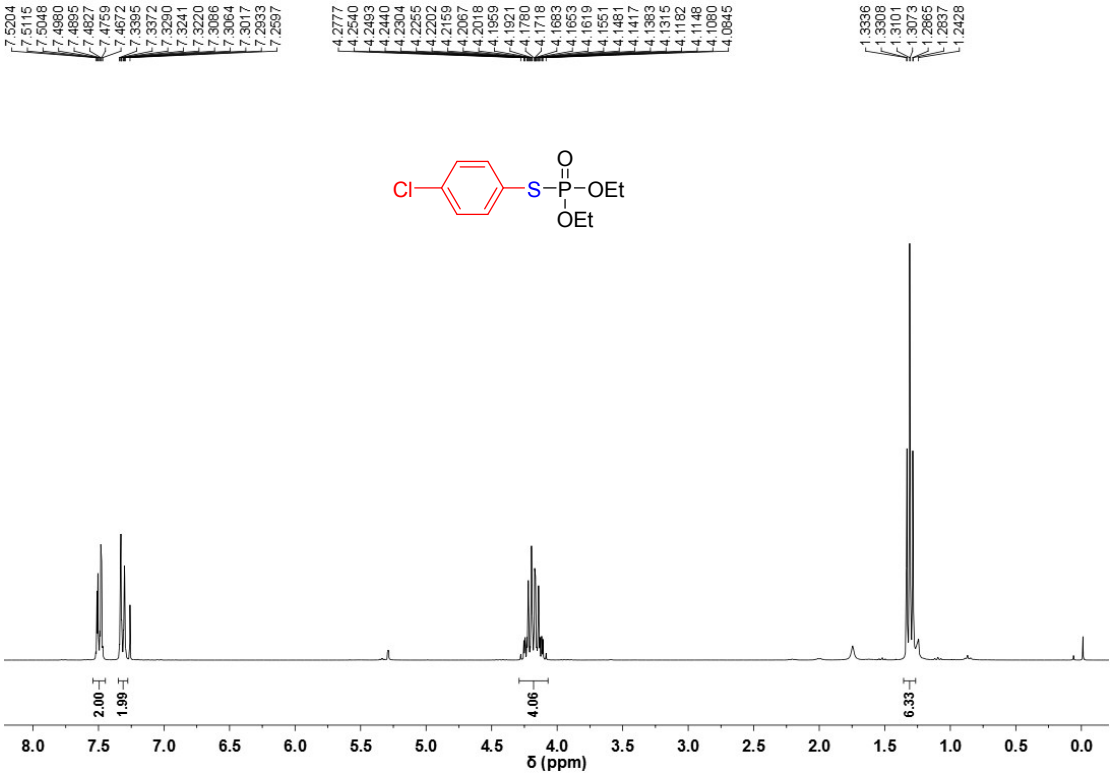
139.2037
134.5726
134.5056
130.1052
130.0731
122.7736
122.6763
77.4238
77.0001
76.5765
63.9436
63.8622
21.1252
21.1129
15.9986
15.9026
O
S
P
OEt
OEt
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ(ppm)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7.4895
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7.3395
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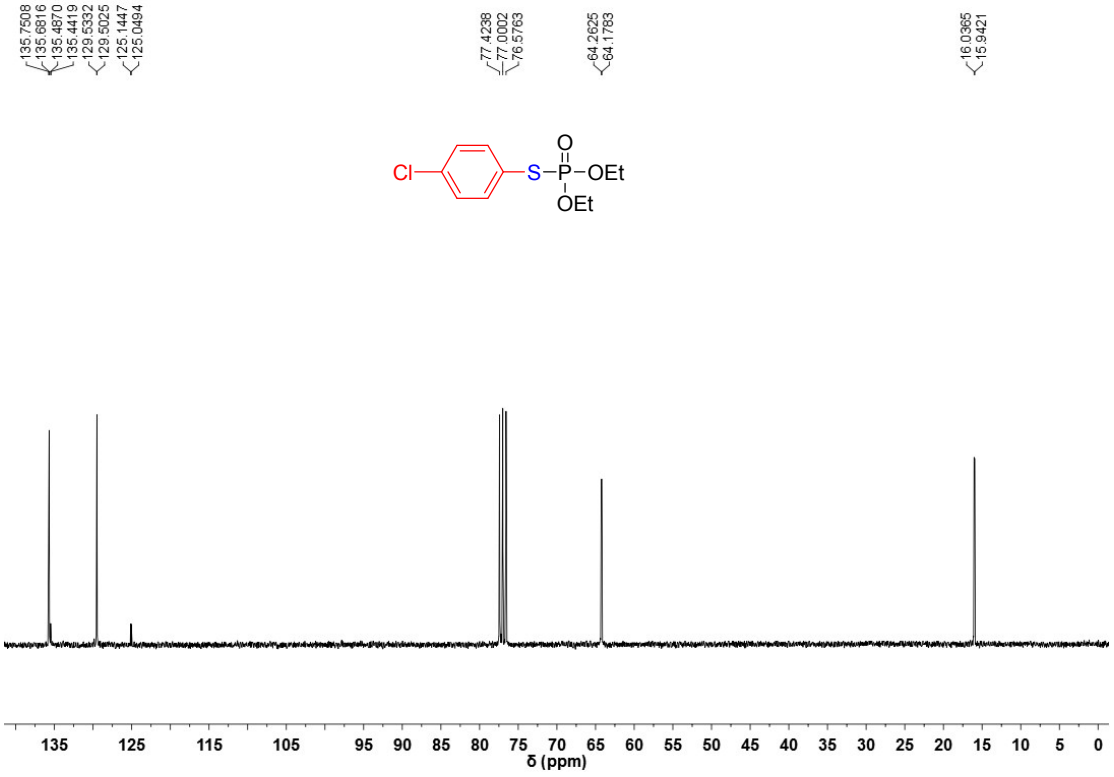
7.3290
7.3241
7.3220
7.3086
7.3064
7.3017
7.2933
7.2597
4.2777
4.2540
4.2493
4.2440
4.2304
4.2255
4.2202
4.2159
4.2067
4.2018
4.1959
4.1921
4.1760
4.1718
4.1683
4.1653
4.1619
4.1551
4.1481
4.1417
4.1383
4.1315
4.1182
4.1148
4.1080
4.0845
1.3336
1.3308
1.3101
1.3073
1.2865
1.2837
1.2428
Cl
S
P
O
OEt
OEt
2.00
1.99
4.06
6.33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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76.5763
64.2625
64.1783
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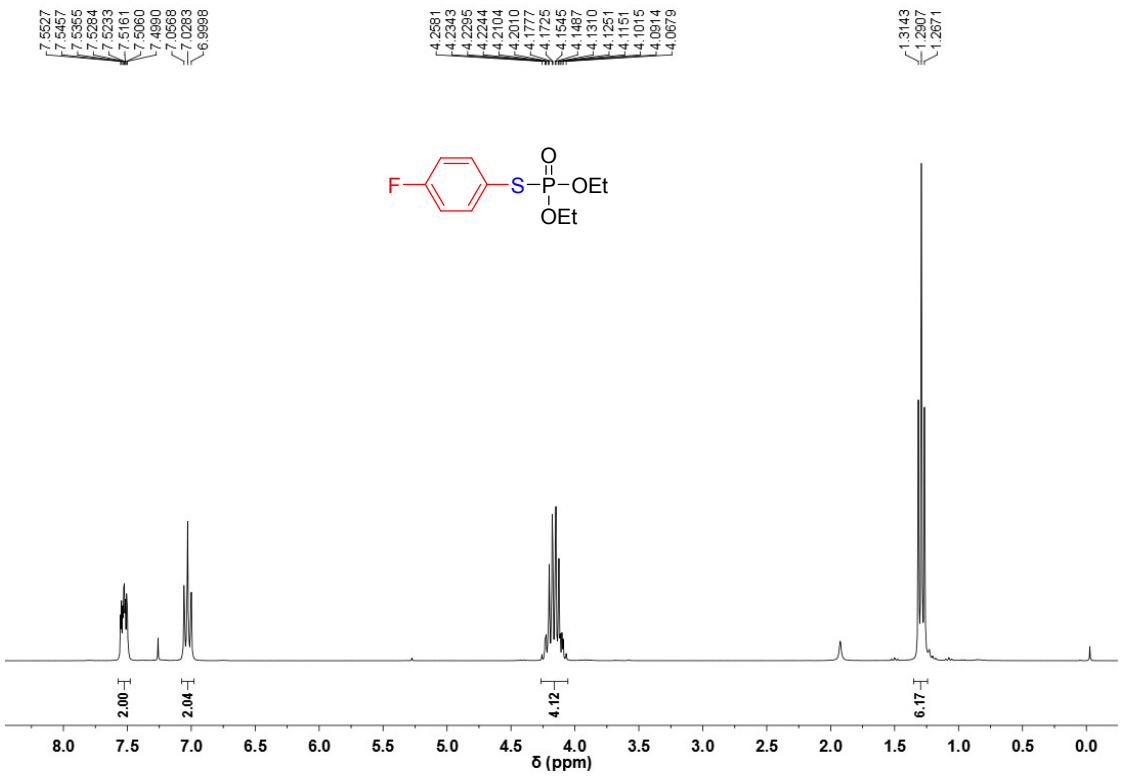
15.9421
Cl
S
P
O
OEt
OEt
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
δ (ppm)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7.5060
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7.0283
6.9998
4.2581
4.2343
4.2295
4.2244
4.2104
4.2010
4.1777
4.1725
4.1545
4.1487
4.1310
4.1251
4.1151
4.1015
4.0914
4.0679
1.3143
1.2907
1.2671
F
S
P
O
OEt
OEt
2.00
2.04
4.12
6.17
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
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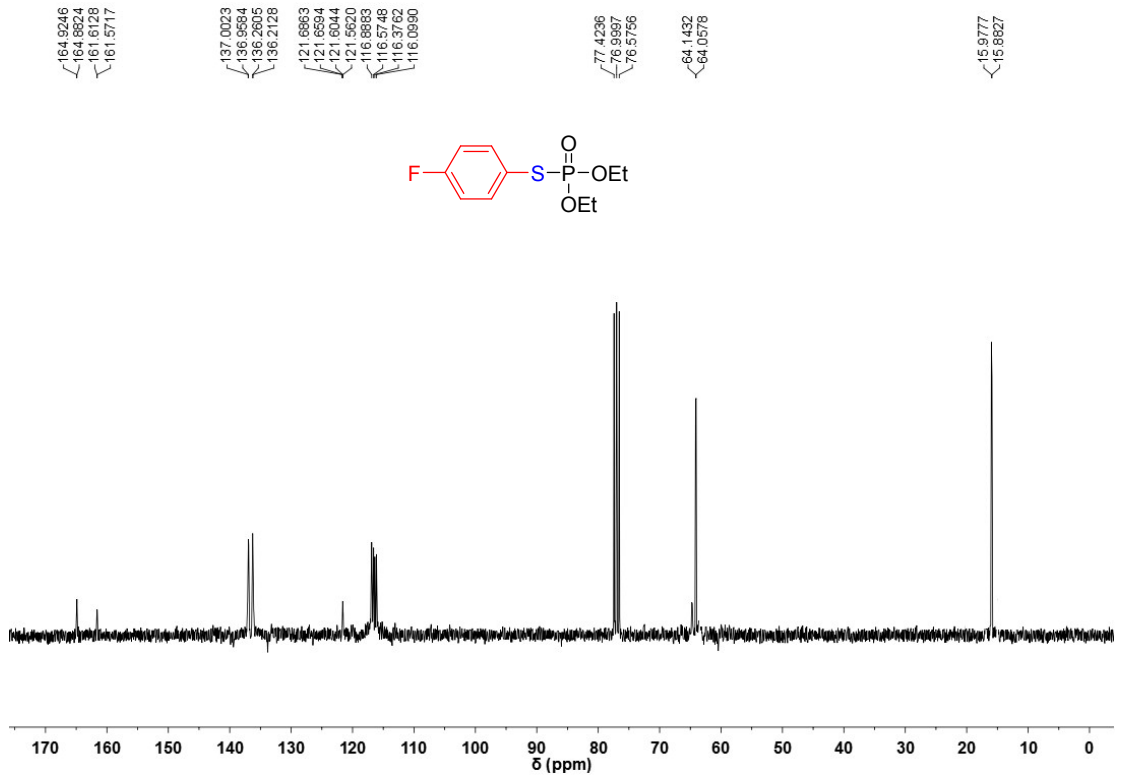
0.0
δ (ppm)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136.2605
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121.6044
121.5620
116.8883
116.5748
116.3762
116.0990
77.4236
76.9997
76.5756
64.1432
64.0578
15.9777
15.8827
F
S
P
O
OEt
OEt
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140
130
120
110
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90
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50
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20
10
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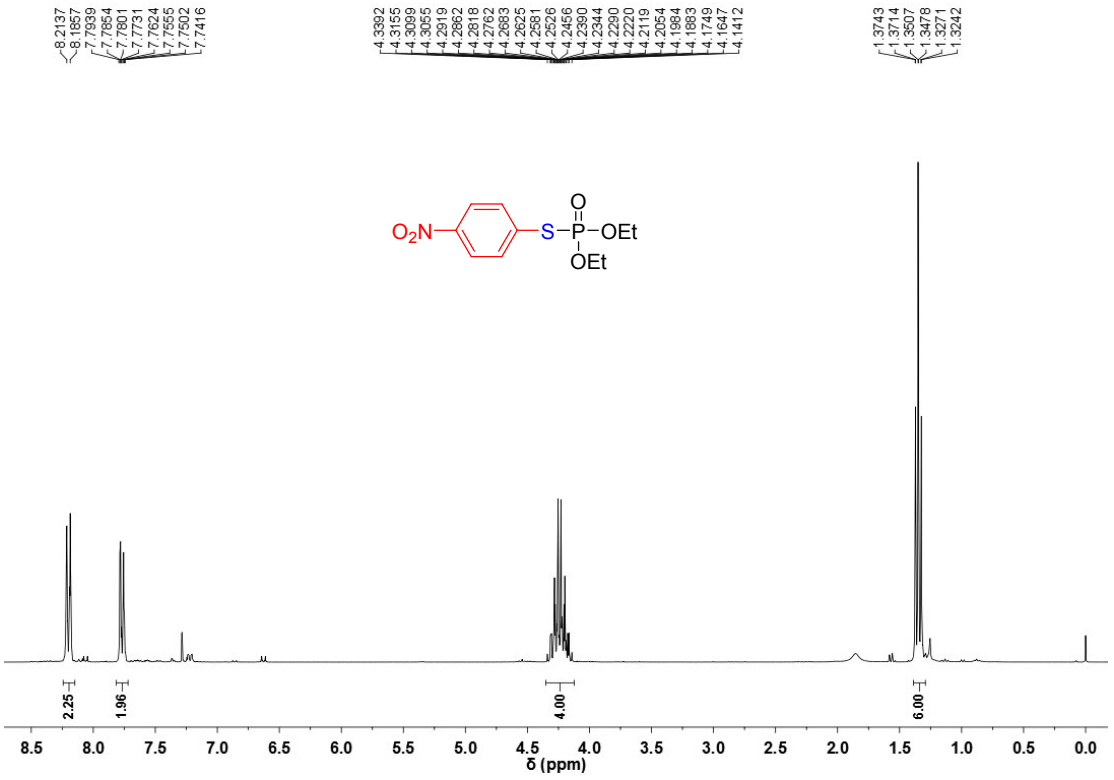
δ (ppm)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7.7801
7.7731
7.7624
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7.7502
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4.3392
4.3155
4.3099
4.3055
4.2919
4.2862
4.2818
4.2762
4.2683
4.2625
4.2581
4.2526
4.2456
4.2390
4.2344
4.2290
4.2220
4.2119
4.2054
4.1984
4.1883
4.1749
4.1647
4.1412
1.3743
1.3714
1.3507
1.3478
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S
P
O
OEt
OEt
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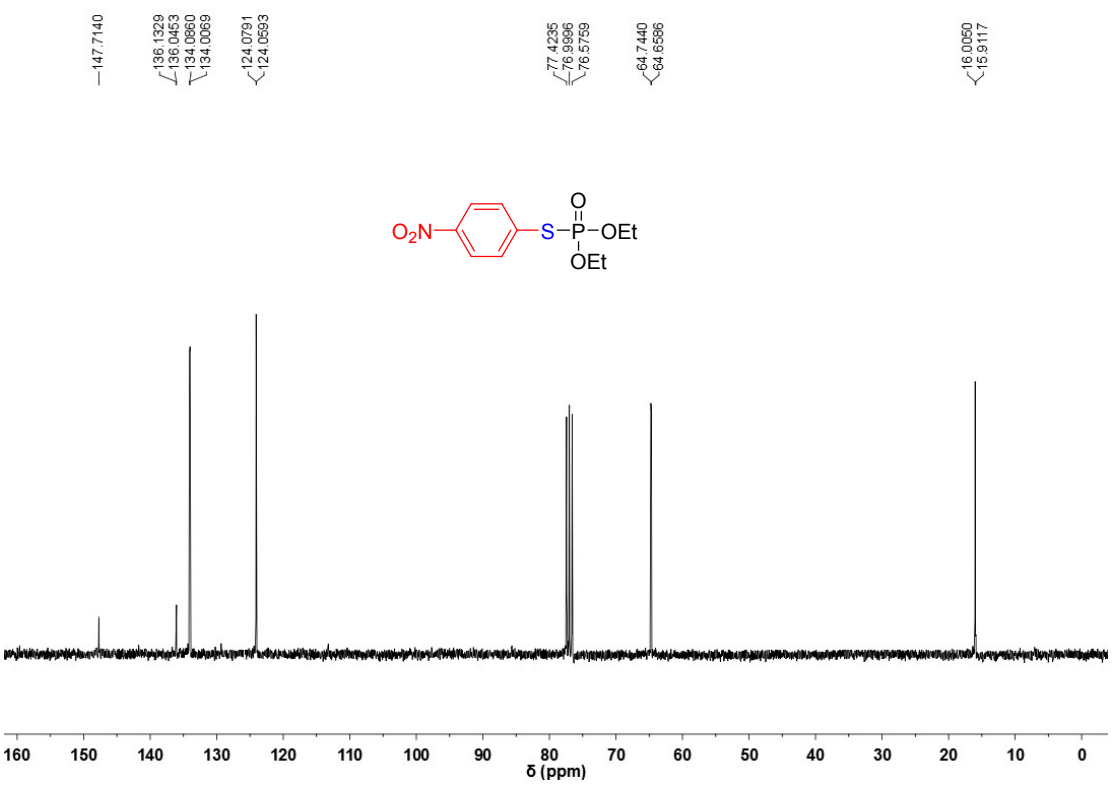
4.00
6.00
δ (ppm)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134.0860
134.0069
124.0791
124.0693
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64.6586
16.0050
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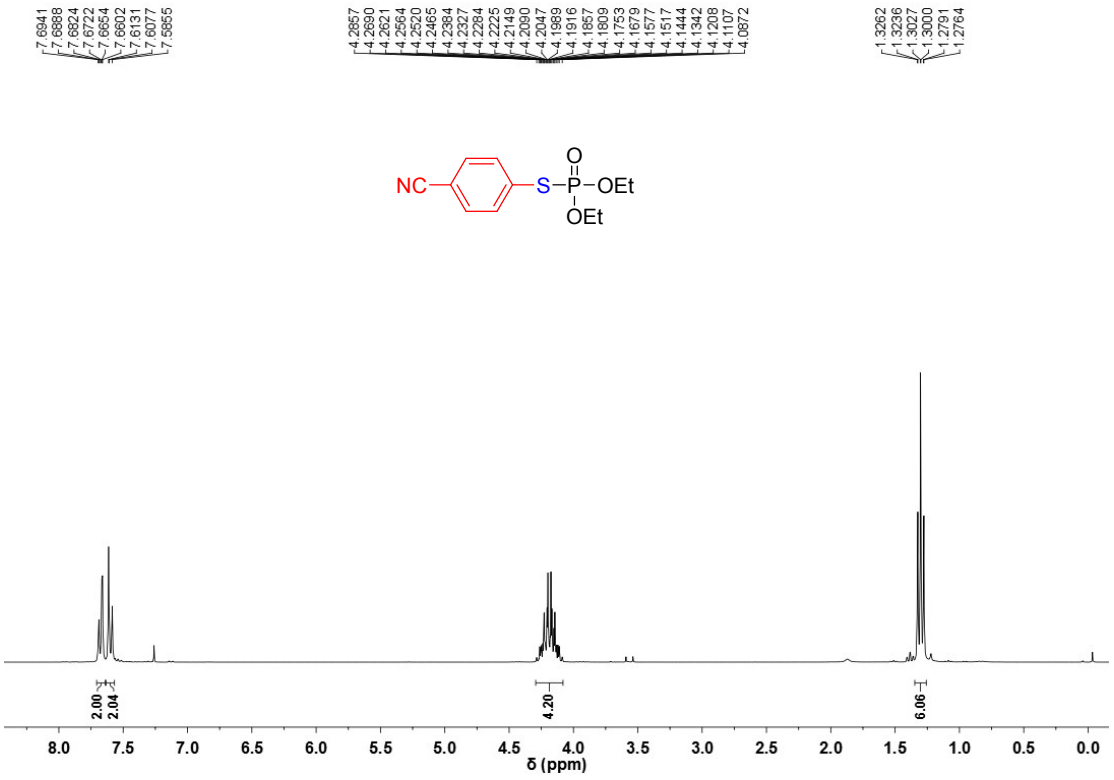
O2N
S
P
O
OEt
OEt
δ (ppm)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7.5855
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4.2690
4.2621
4.2564
4.2520
4.2465
4.2384
4.2327
4.2284
4.2225
4.2149
4.2090
4.2047
4.1989
4.1916
4.1857
4.1809
4.1753
4.1679
4.1577
4.1517
4.1444
4.1342
4.1208
4.1107
4.0872
1.3262
1.3236
1.3027
1.3000
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NC
S
P
O
OEt
OEt
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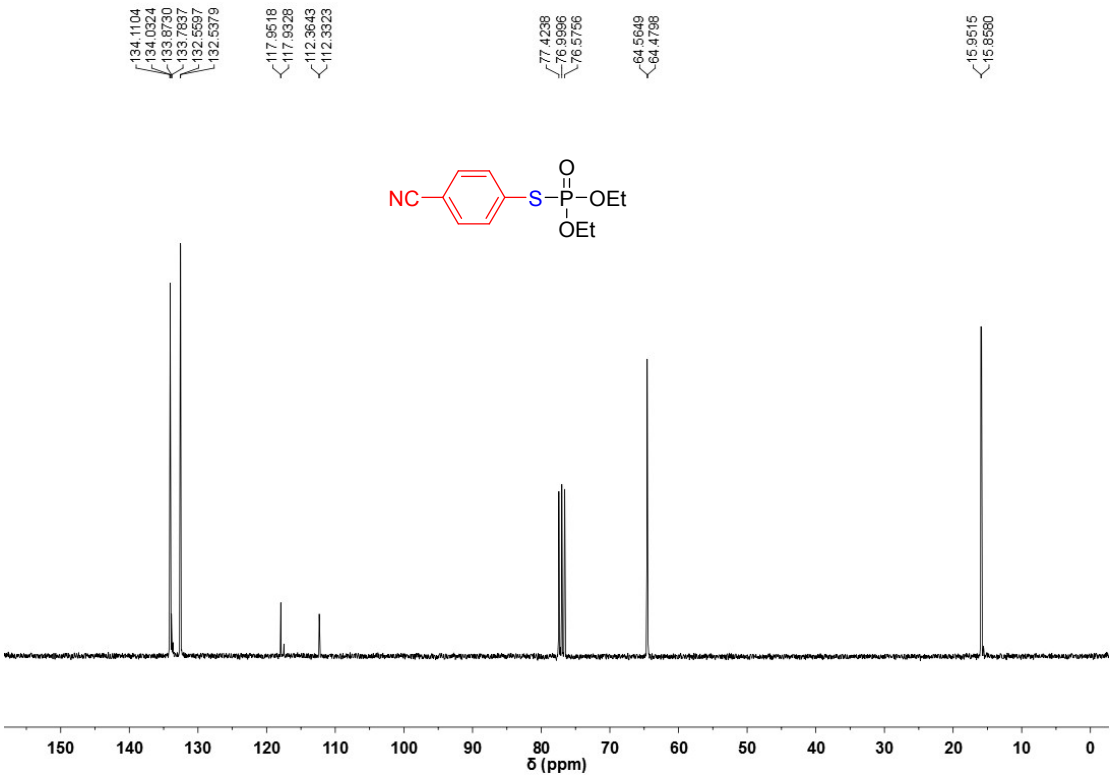
4.20
6.06
δ (ppm)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117.9328
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112.3323
77.4238
76.9996
76.5756
64.5649
64.4798
15.9515
15.8580
NC
S
P
O
OEt
OEt
δ (ppm)


7.7060
7.7032
7.7012
7.6770
7.6743
7.5952
7.5664
7.2597
4.2959
4.2722
4.2671
4.2622
4.2485
4.2434
4.2385
4.2338
4.2249
4.2197
4.2148
4.2102
4.2039
4.1961
4.1909
4.1866
4.1803
4.1773
4.1701
4.1630
4.1567
4.1537
4.1465
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1.3109
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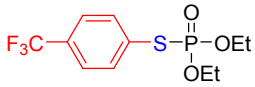
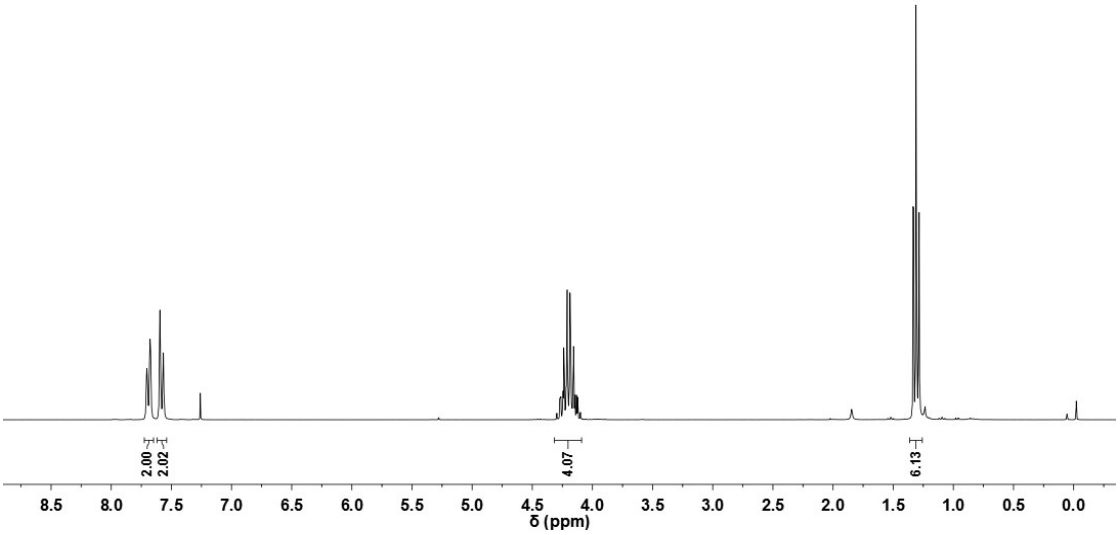
1.2873
1.2845


F3C
S
P
O
OEt
OEt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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


134.2502
134.1760
131.8805
131.7905
131.0814
131.0477
130.6461
130.6117
126.0822
126.0569
126.0328
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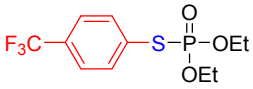
15.8837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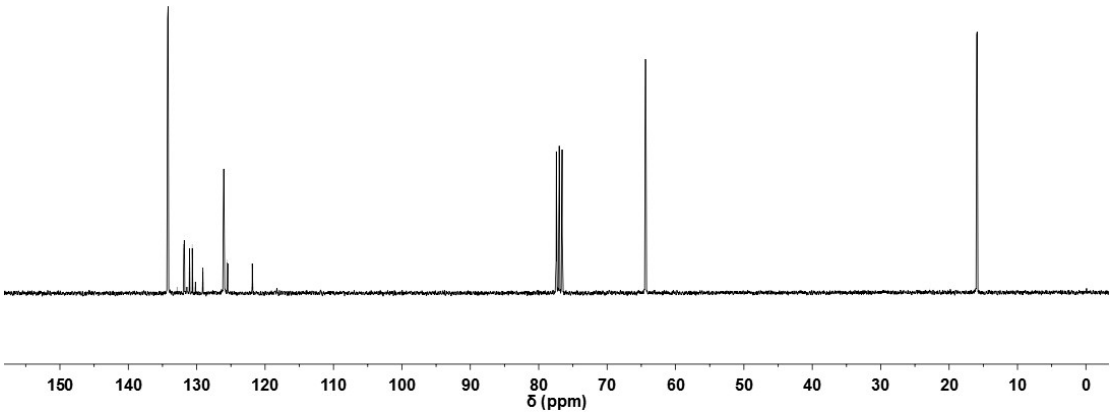
S
P
O
OEt
OEt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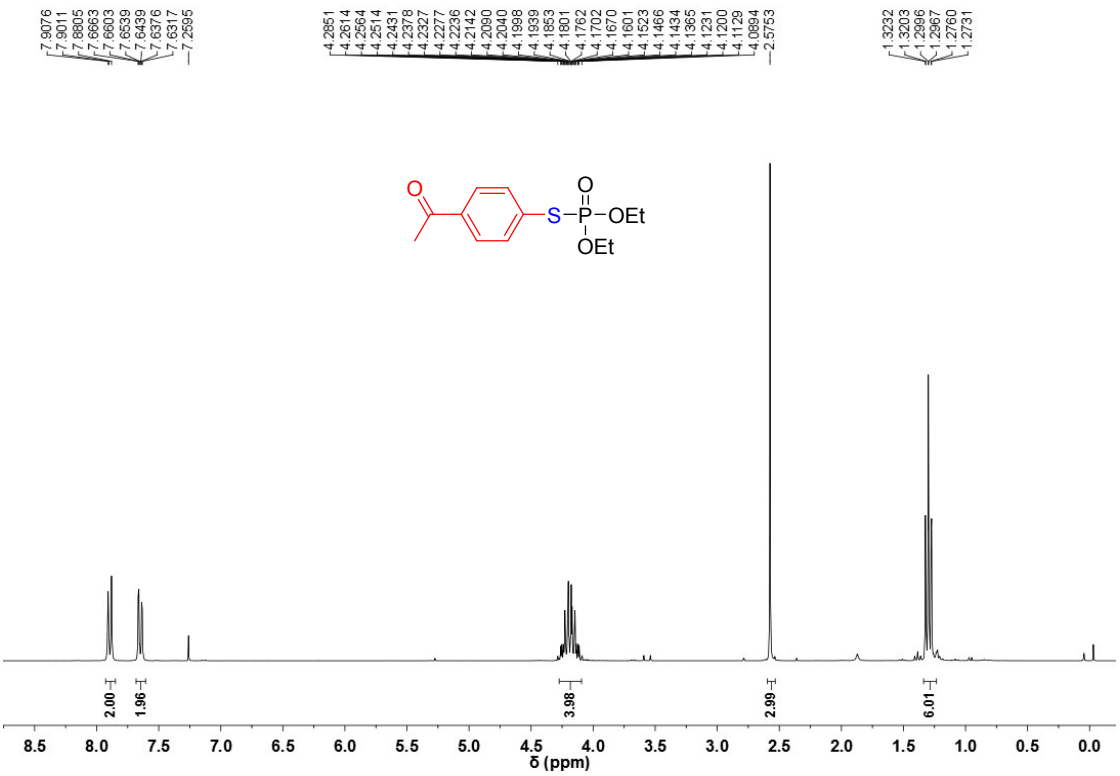
90
80
70
60
50
40
30
20
10
0
δ (ppm)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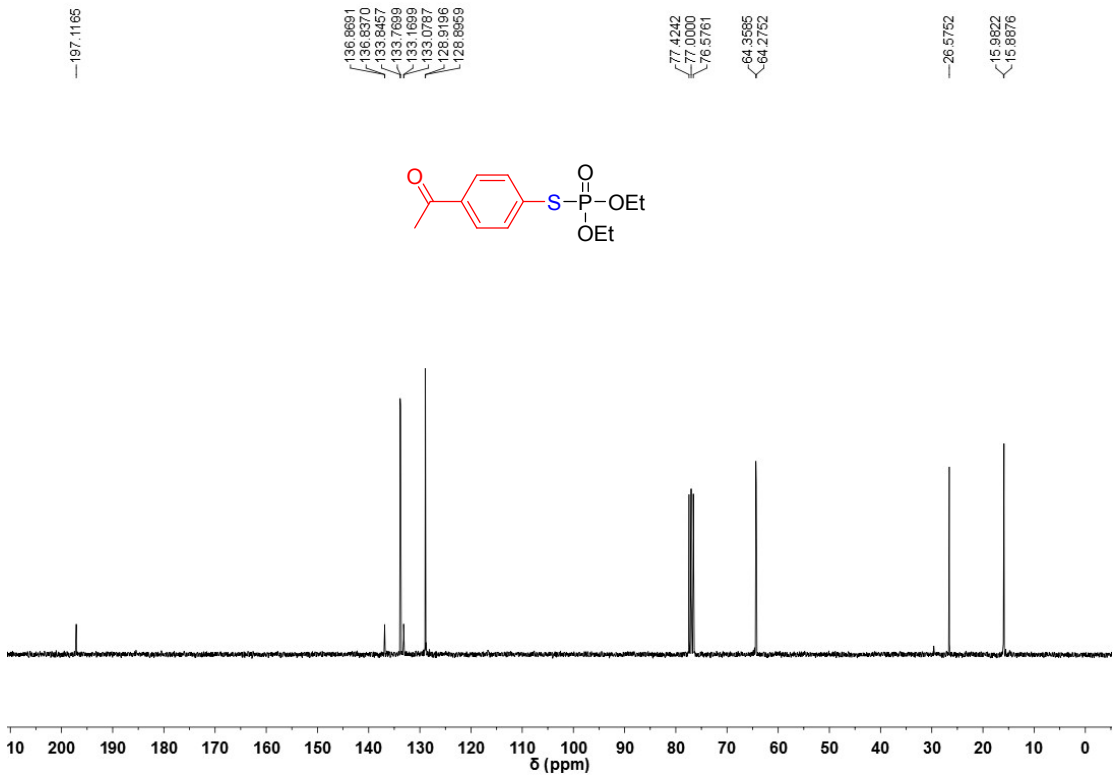
4.2614
4.2564
4.2514
4.2431
4.2378
4.2327
4.2277
4.2236
4.2142
4.2090
4.2040
4.1998
4.1939
4.1853
4.1801
4.1762
4.1702
4.1670
4.1601
4.1523
4.1466
4.1434
4.1365
4.1231
4.1200
4.1129
4.0894
2.5753
1.3232
1.3203
1.2896
1.2867
1.2760
1.2731
O
O
S
P
OEt
OEt
2.00
1.96
3.98
2.99
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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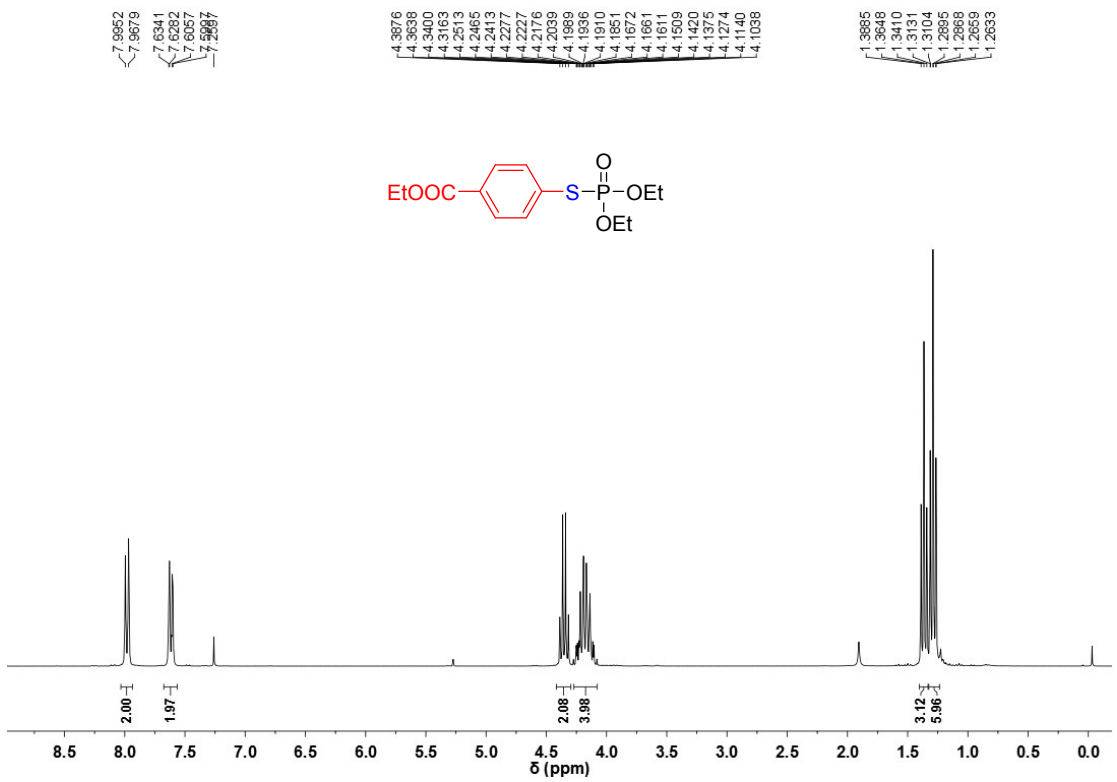
77.0000
76.5761
64.3585
64.2752
26.5752
15.9822
15.8876
O
O
S
P
OEt
OEt
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)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4.2277
4.2227
4.2176
4.2039
4.1989
4.1936
4.1910
4.1851
4.1672
4.1661
4.1611
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4.1420
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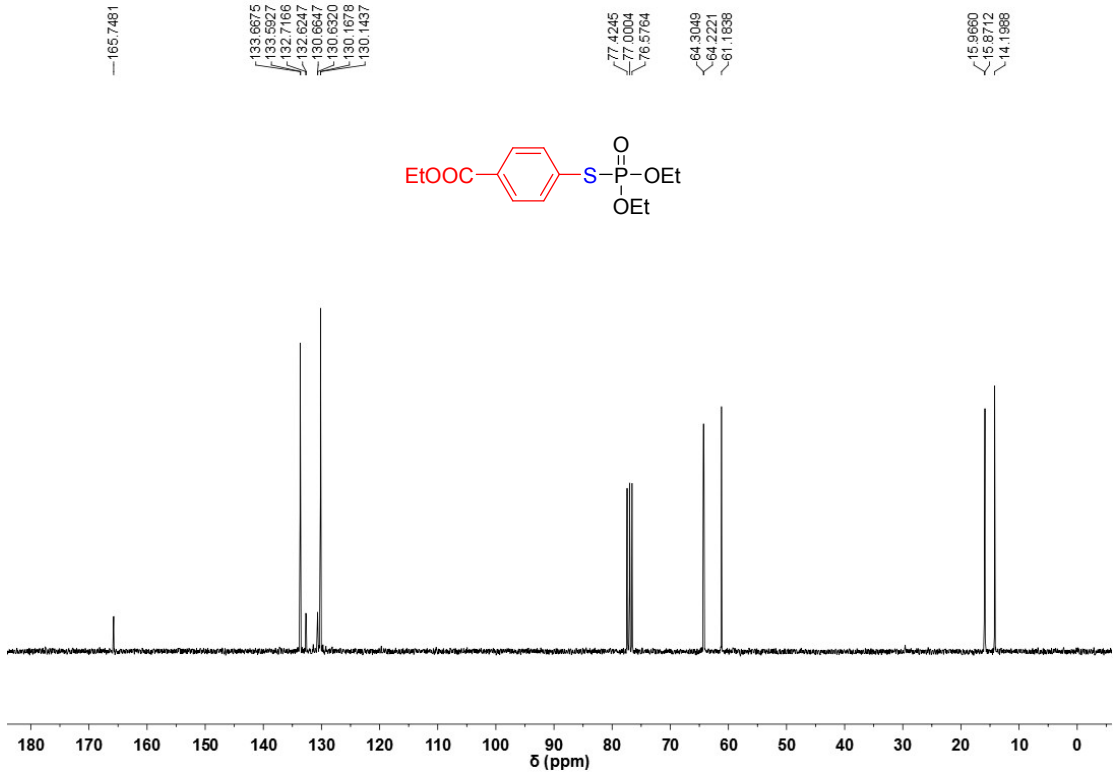
4.1140
4.1038
1.3885
1.3648
1.3410
1.3131
1.3104
1.2895
1.2868
1.2659
1.2633
EtOOC
S
P
O
OEt
OEt
2.00
1.97
2.08
3.98
3.12
5.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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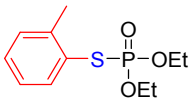
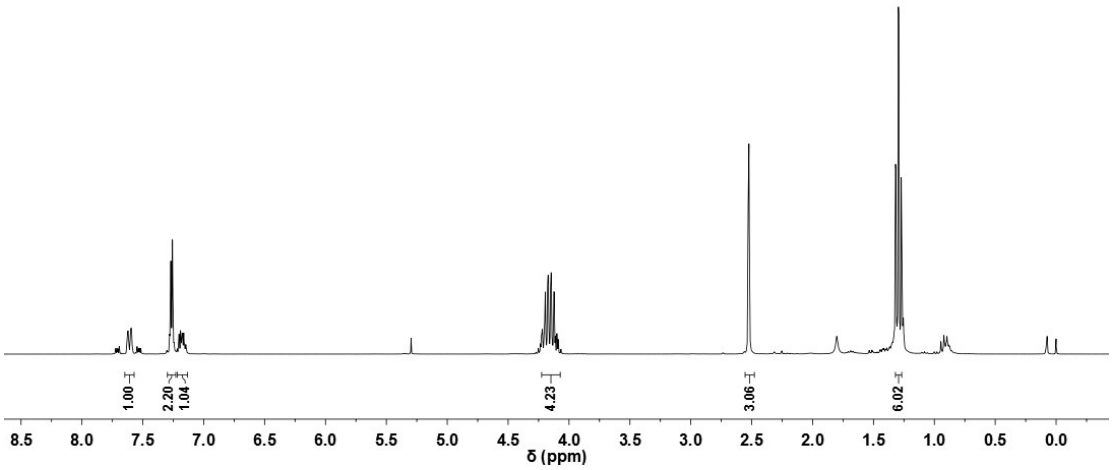
76.5764
64.3049
64.2221
61.1838
15.9660
15.8712
14.1988
EtOOC
S
P
O
OEt
OEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.6935
7.6221
7.6181
7.5996
7.5964
7.5931
7.5468
7.2795
7.2749
7.2702
7.2569
7.2445
7.2025
7.1904
7.1854
7.1768
7.1750
7.1639
7.1469
4.2525
4.2352
4.2288
4.2240
4.2188
4.2049
4.1995
4.1952
4.1912
4.1758
4.1714
4.1674
4.1523
4.1465
4.1438
4.1367
4.1288
4.1229
4.1204
4.1129
4.0995
4.0953
4.0894
4.0659
2.5272
2.5226
1.3190
1.3162
1.2955
1.2927
1.2718
1.2691


O
S
P
OEt
OEt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2.20
1.04
4.23
3.06
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


142.2251
142.1513
136.1707
136.1147
130.8248
130.7899
129.4152
129.3742
126.7159
126.6798
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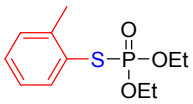
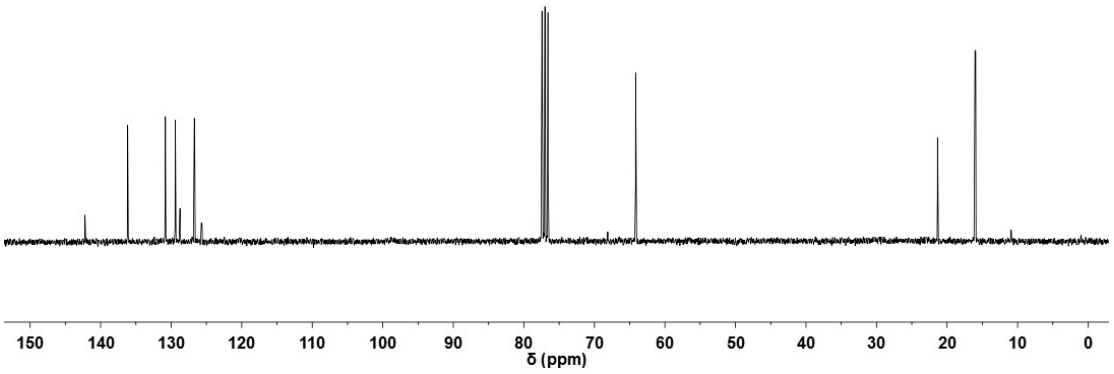
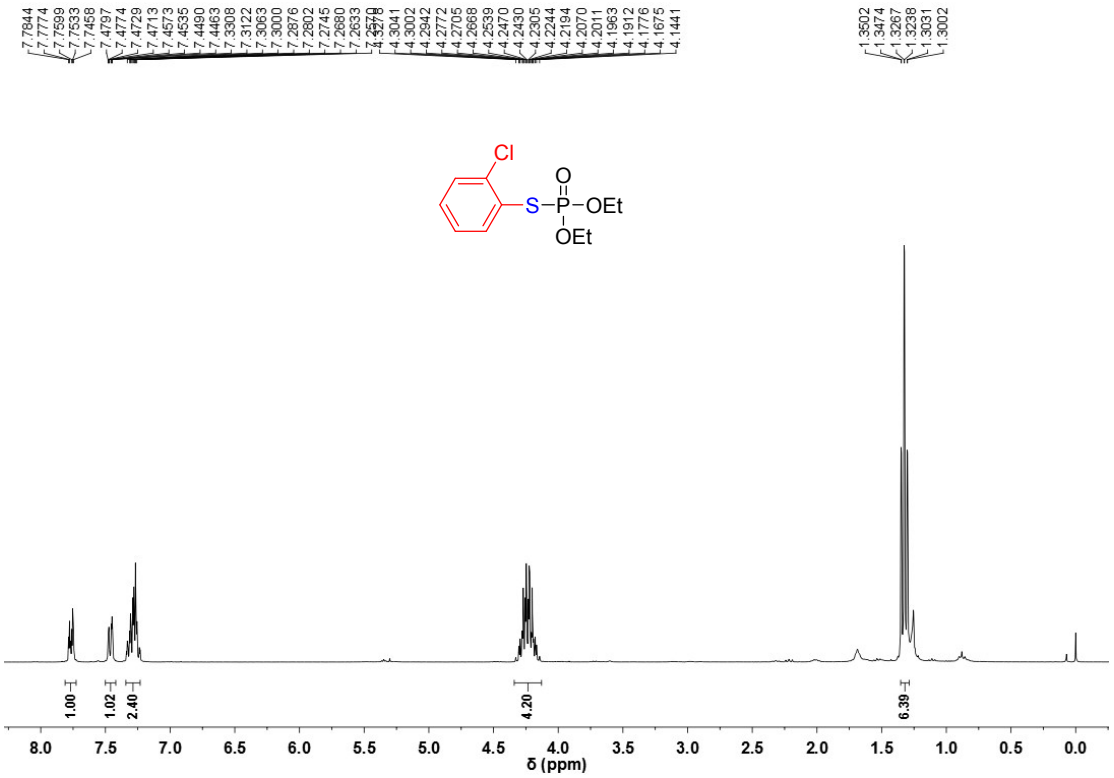
125.6191
77.4237
76.9999
76.5762
64.1469
64.0579
21.3483
16.0375
15.9432


O
S
P
OEt
OEt


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.7844
7.7774
7.7599
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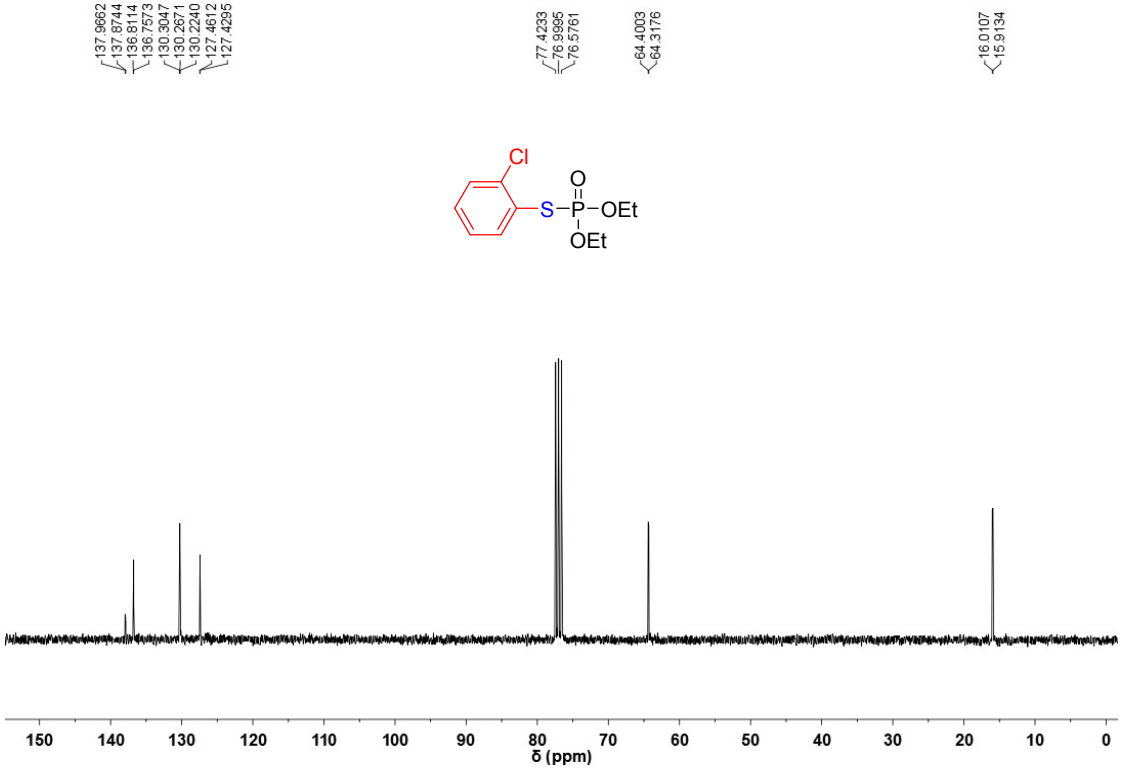
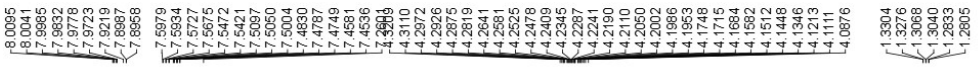
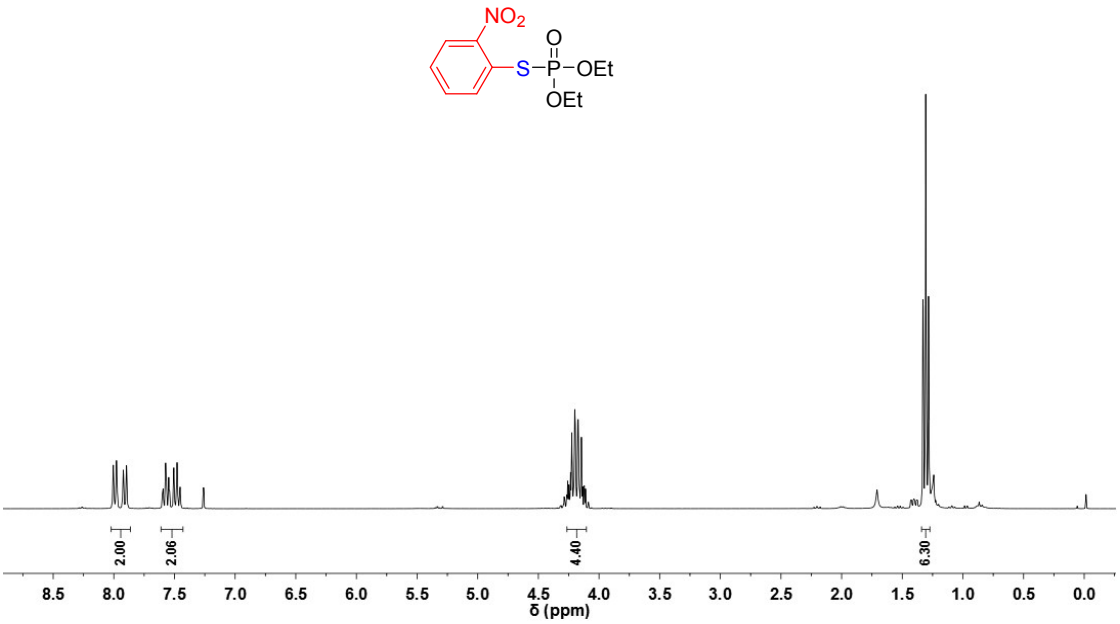
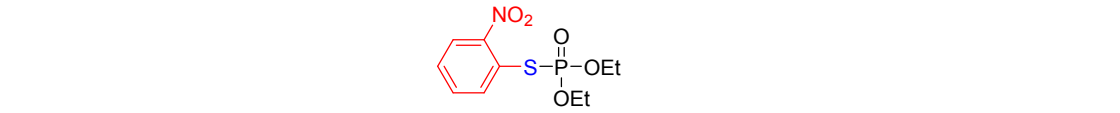
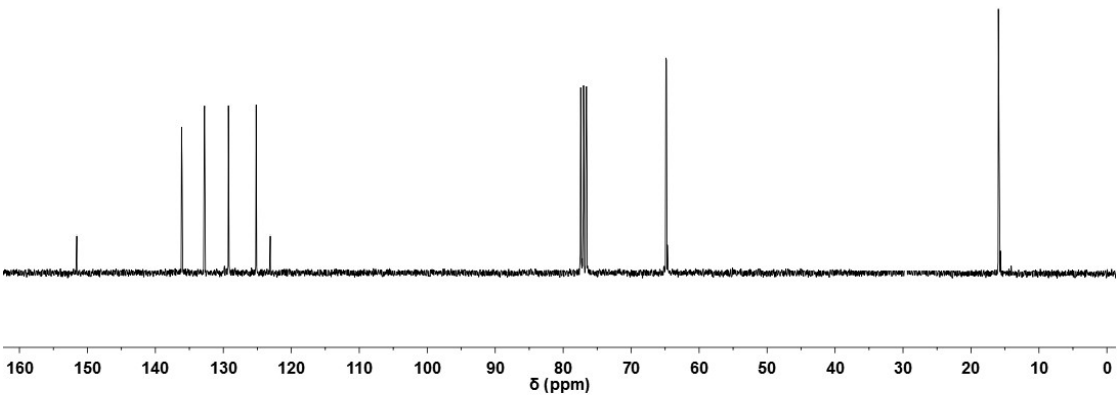
7.4774
7.4729
7.4713
7.4573
7.4535
7.4490
7.4463
7.3308
7.3122
7.3063
7.3000
7.2876
7.2802
7.2745
7.2680
7.2633
4.3041
4.3002
4.2942
4.2772
4.2705
4.2668
4.2539
4.2470
4.2430
4.2305
4.2244
4.2194
4.2070
4.2011
4.1963
4.1912
4.1776
4.1675
4.1441
1.3502
1.3474
1.3267
1.3238
1.3031
1.3002
Cl
O
S
P
OEt
OEt
1.00
1.02
2.40
4.20
6.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

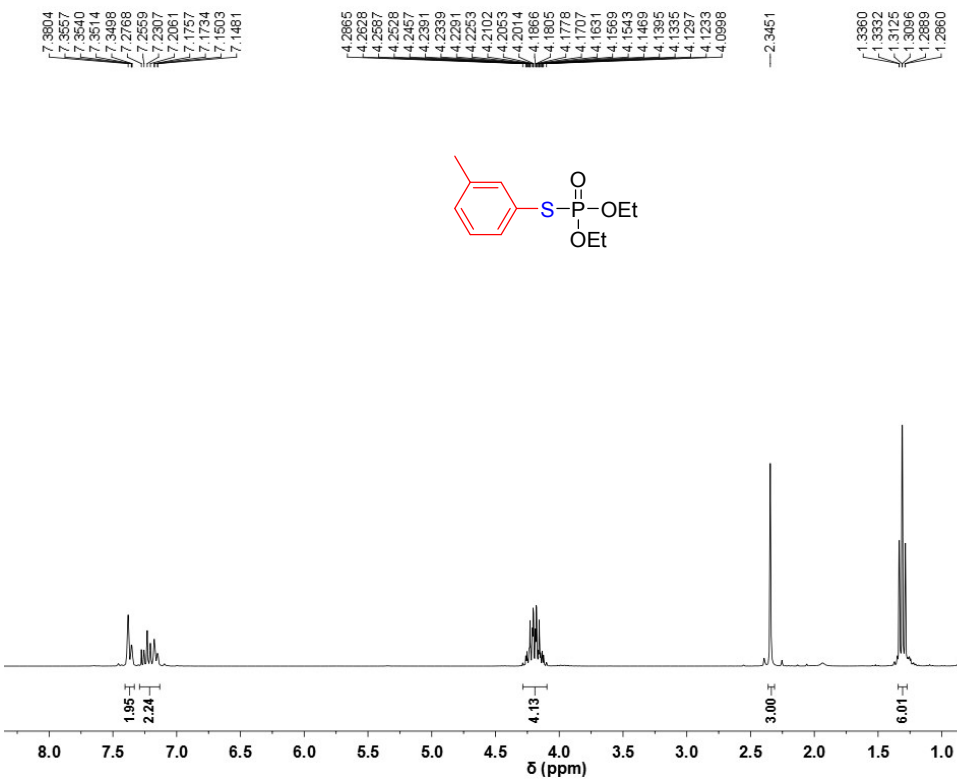

137.9662
137.8744
136.8114
136.7573
130.3047
130.2671
130.2240
127.4612
127.4295
77.4233
76.9995
76.5761
64.4003
64.3176
16.0107
15.9134
Cl
O
S
P
OEt
OEt
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

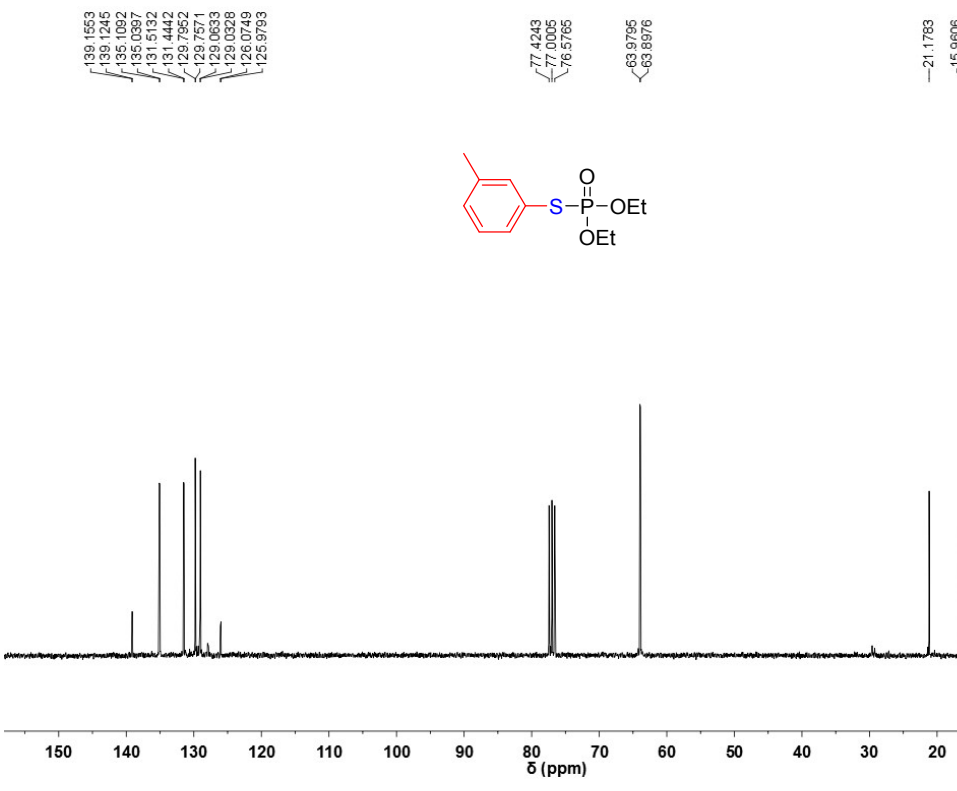


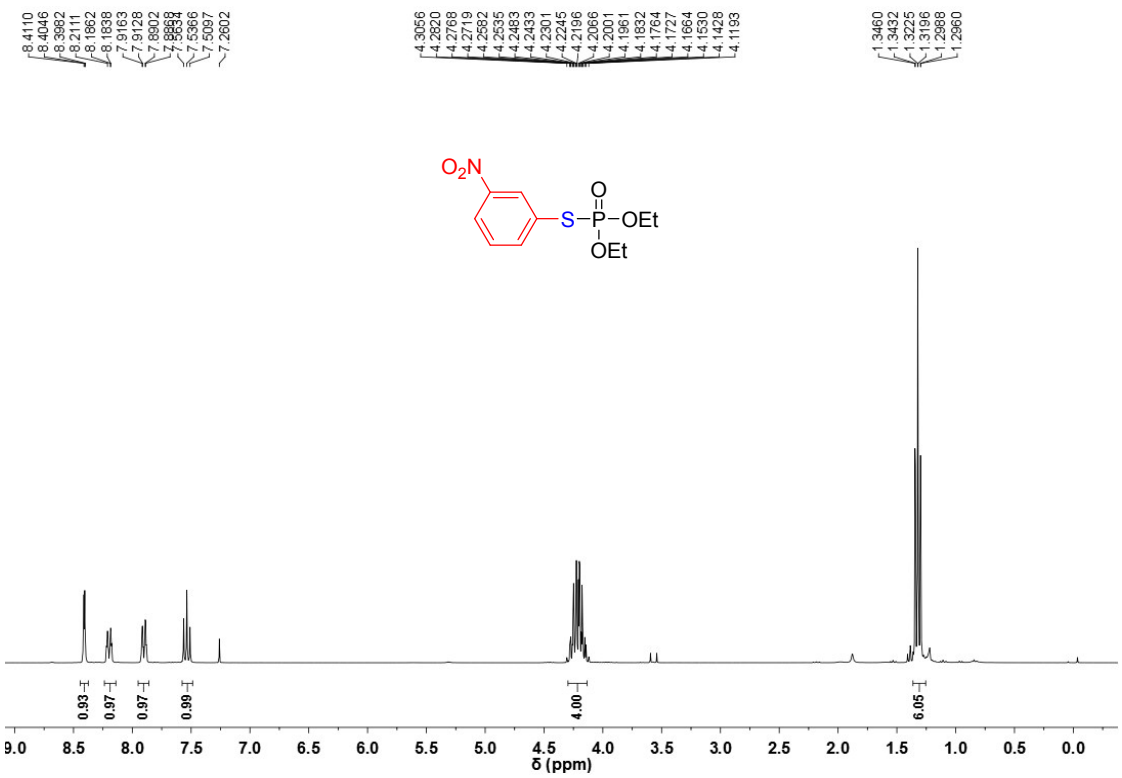

NO2
O
S
P
OEt
OEt
2.00
2.06
4.40
6.30
δ (ppm)

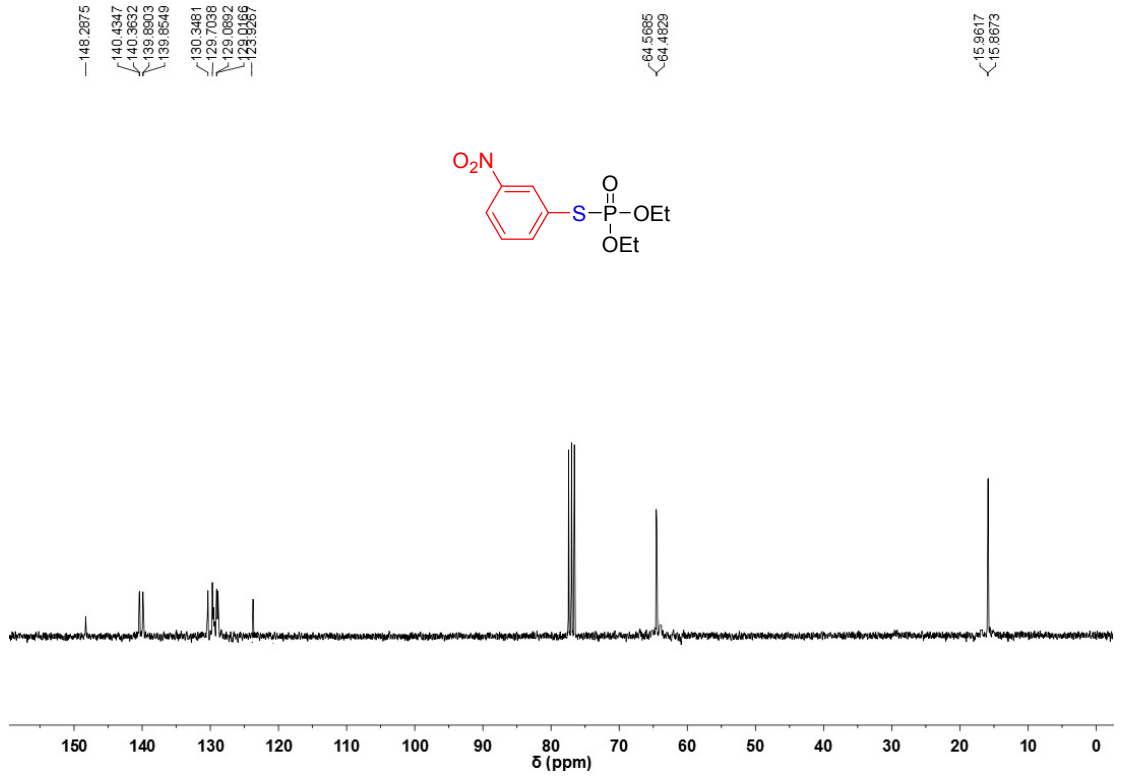

NO2
O
S
P
OEt
OEt

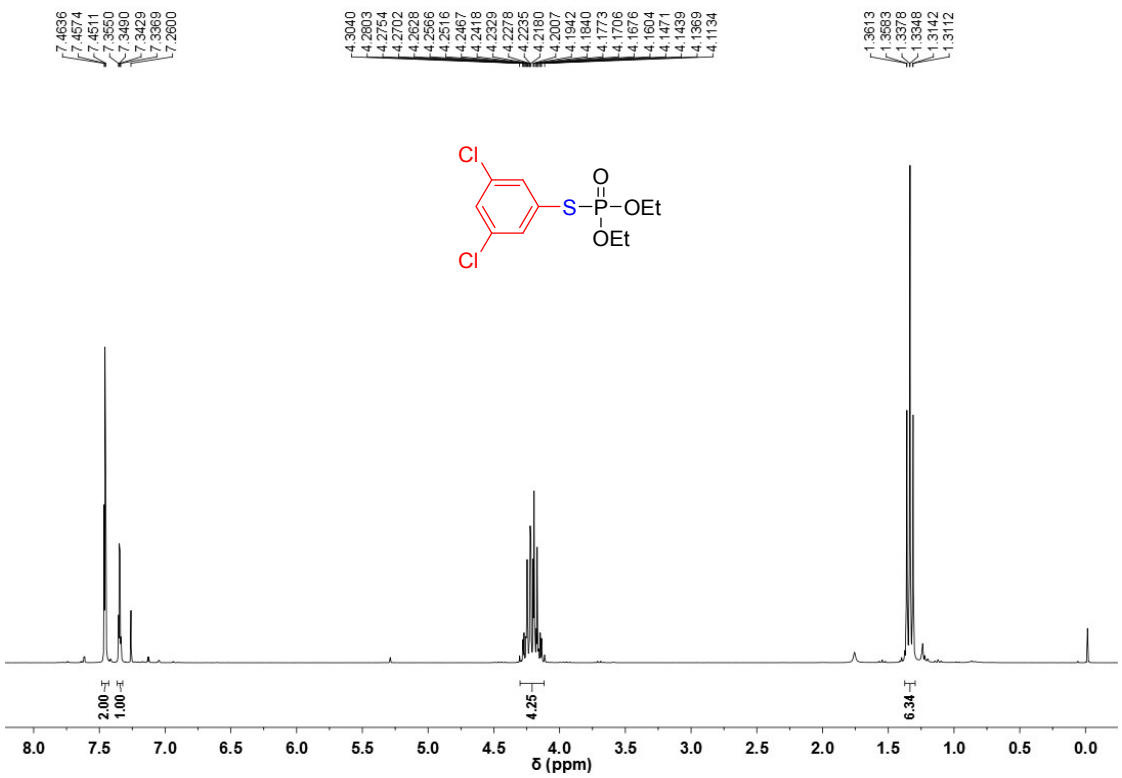

δ (ppm)

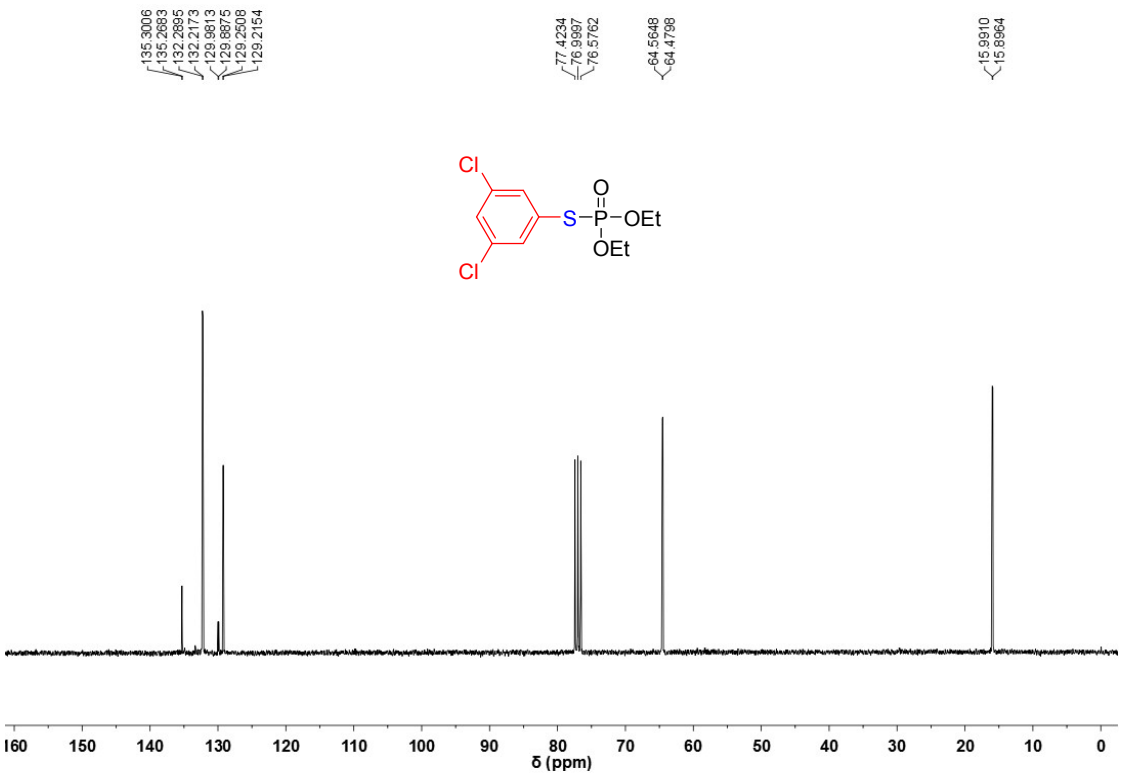

7.3804
7.3557
7.3540
7.3514
7.3498
7.2768
7.2559
7.2307
7.2061
7.1757
7.1734
7.1503
7.1481
4.2865
4.2628
4.2587
4.2528
4.2457
4.2391
4.2339
4.2291
4.2253
4.2102
4.2053
4.2014
4.1866
4.1805
4.1778
4.1707
4.1631
4.1569
4.1543
4.1469
4.1395
4.1335
4.1297
4.1233
4.0998
2.3451
1.3360
1.3332
1.3125
1.3096
1.2889
1.2860
O
S
P
OEt
OEt
1.95
2.24
4.13
3.00
6.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

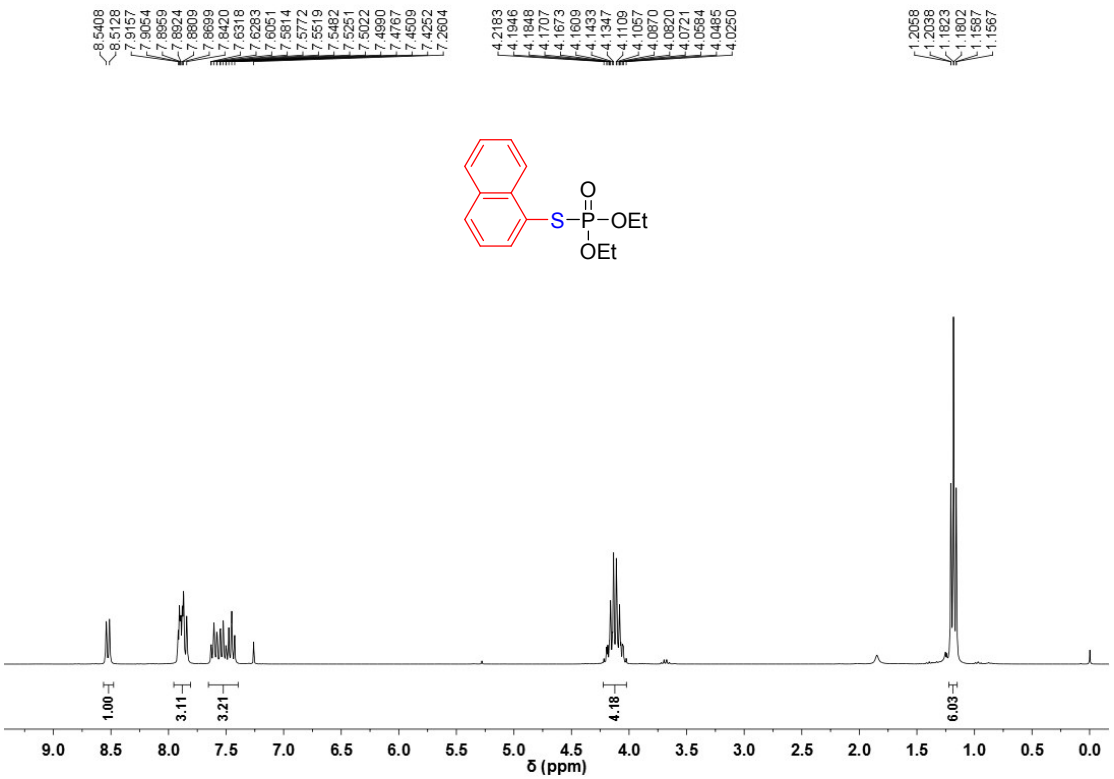

139.1553
139.1245
135.1092
135.0397
131.5132
131.4442
129.7952
129.7571
129.0633
129.0328
126.0749
125.9793
77.4243
77.0005
76.5765
63.9795
63.8976
21.1783
15.9606
15.8641
O
S
P
OEt
OEt
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

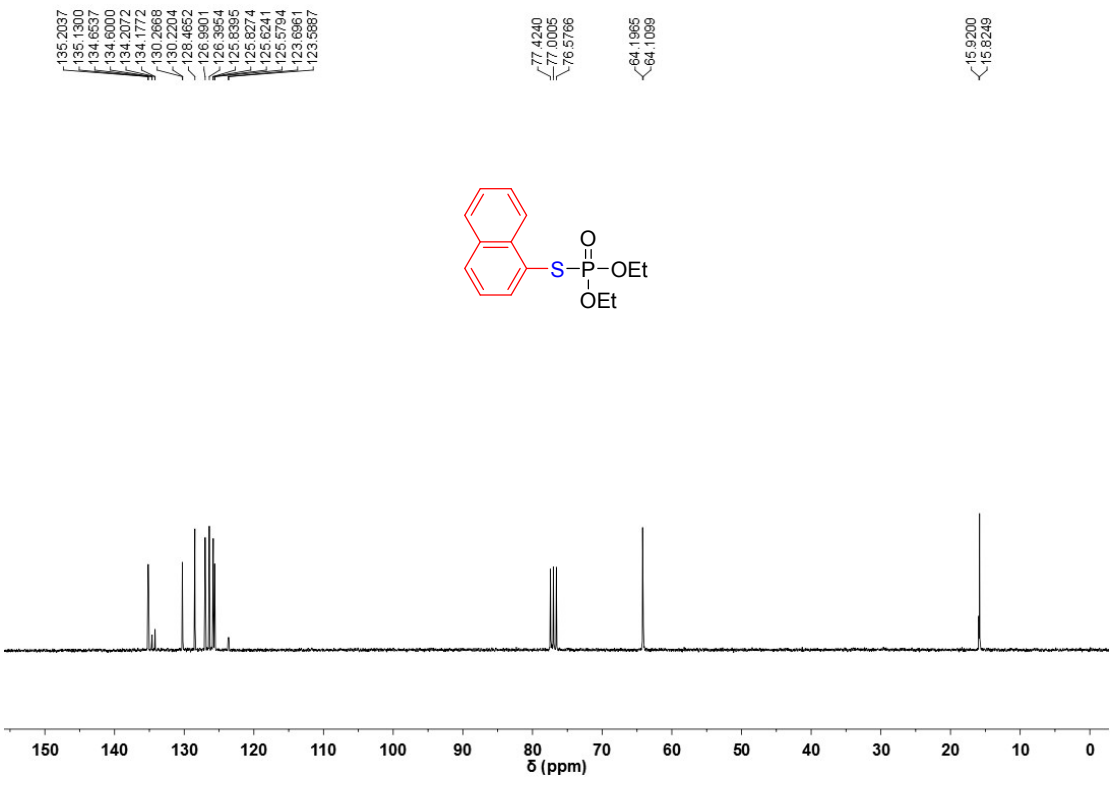

8.4110
8.4046
8.3982
8.2111
8.1862
8.1838
7.9163
7.9128
7.8902
7.5386
7.5097
7.2602
4.3056
4.2820
4.2768
4.2719
4.2582
4.2535
4.2483
4.2433
4.2301
4.2245
4.2196
4.2066
4.2001
4.1961
4.1832
4.1764
4.1727
4.1664
4.1530
4.1428
4.1193
1.3460
1.3432
1.3225
1.3196
1.2988
1.2960
O2N
O
S
P
OEt
OEt
0.93
0.97
0.97
0.99
4.00
6.05
δ (ppm)


148.2875
140.4347
140.3632
139.8903
139.8549
130.3481
129.7038
129.0892
123.9267
64.5685
64.4829
15.9617
15.8673
O2N
O
S
P
OEt
OEt
δ (ppm)


7.4636
7.4574
7.4511
7.3650
7.3490
7.3429
7.3369
7.2600
4.3040
4.2803
4.2754
4.2702
4.2628
4.2566
4.2516
4.2467
4.2418
4.2329
4.2278
4.2235
4.2180
4.2007
4.1942
4.1840
4.1773
4.1706
4.1676
4.1604
4.1471
4.1439
4.1369
4.1134
1.3613
1.3583
1.3378
1.3348
1.3142
1.3112
Cl
Cl
S
P
O
OEt
OEt
2.00
1.00
4.25
6.34
δ (ppm)


135.3006
135.2683
132.2895
132.2173
129.9813
129.8875
129.2508
129.2154
77.4234
76.9997
76.5762
64.5648
64.4798
15.9910
15.8964
Cl
Cl
S
P
O
OEt
OEt
δ (ppm)


8.5408
8.5128
7.9157
7.9054
7.8959
7.8924
7.8809
7.8699
7.8420
7.6318
7.6283
7.6051
7.5814
7.5772
7.5519
7.5482
7.5251
7.5022
7.4990
7.4767
7.4509
7.4252
7.2604
4.2183
4.1946
4.1848
4.1707
4.1673
4.1609
4.1433
4.1347
4.1109
4.1057
4.0870
4.0820
4.0721
4.0584
4.0485
4.0250
1.2058
1.2038
1.1823
1.1802
1.1587
1.1567
O
S
P
OEt
OEt
1.00
3.11
3.21
4.18
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)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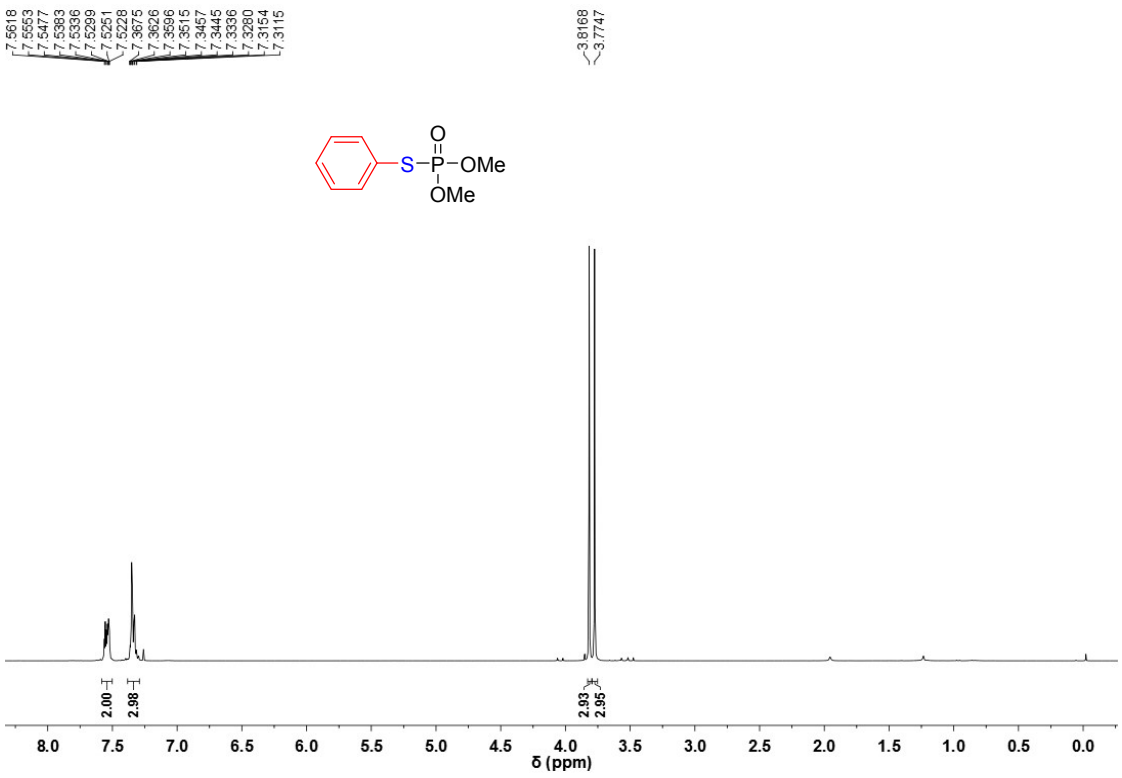
134.6537
134.6000
134.2072
134.1772
130.2668
130.2204
128.4652
126.9901
126.3954
125.8395
125.8274
125.6241
125.5794
123.6961
123.5887
77.4240
77.0005
76.5766
64.1965
64.1099
15.9200
15.8249
O
S
P
OEt
OEt
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)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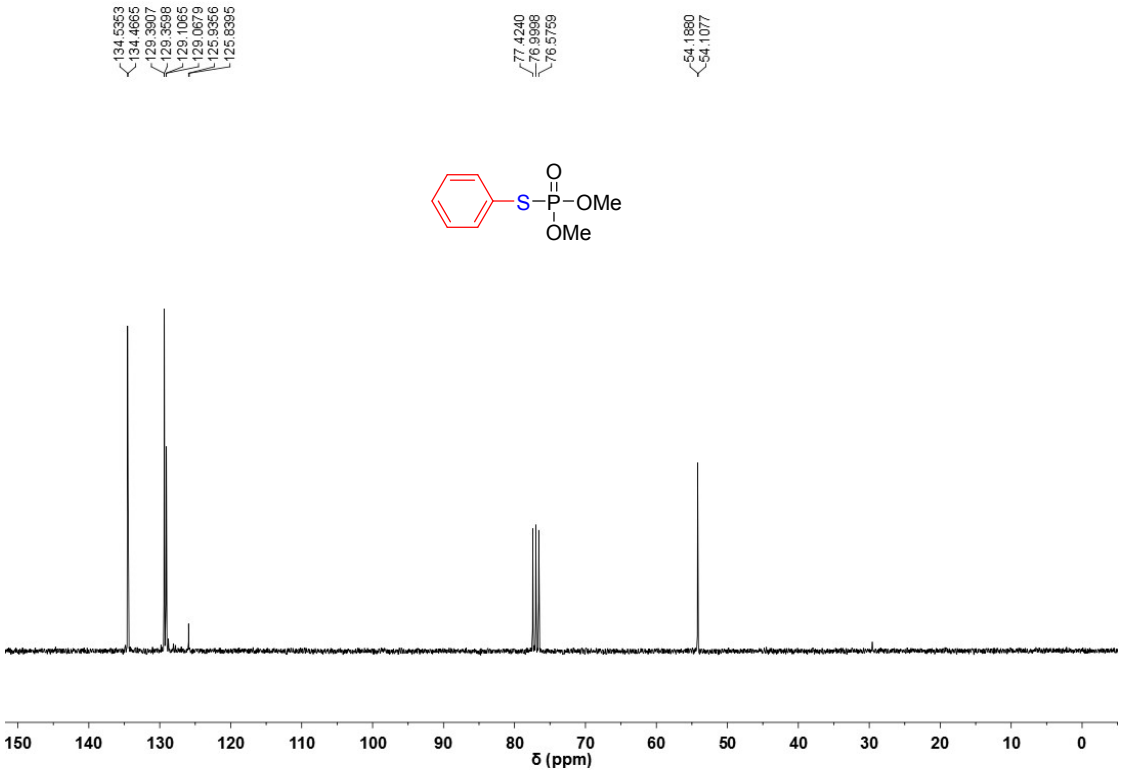
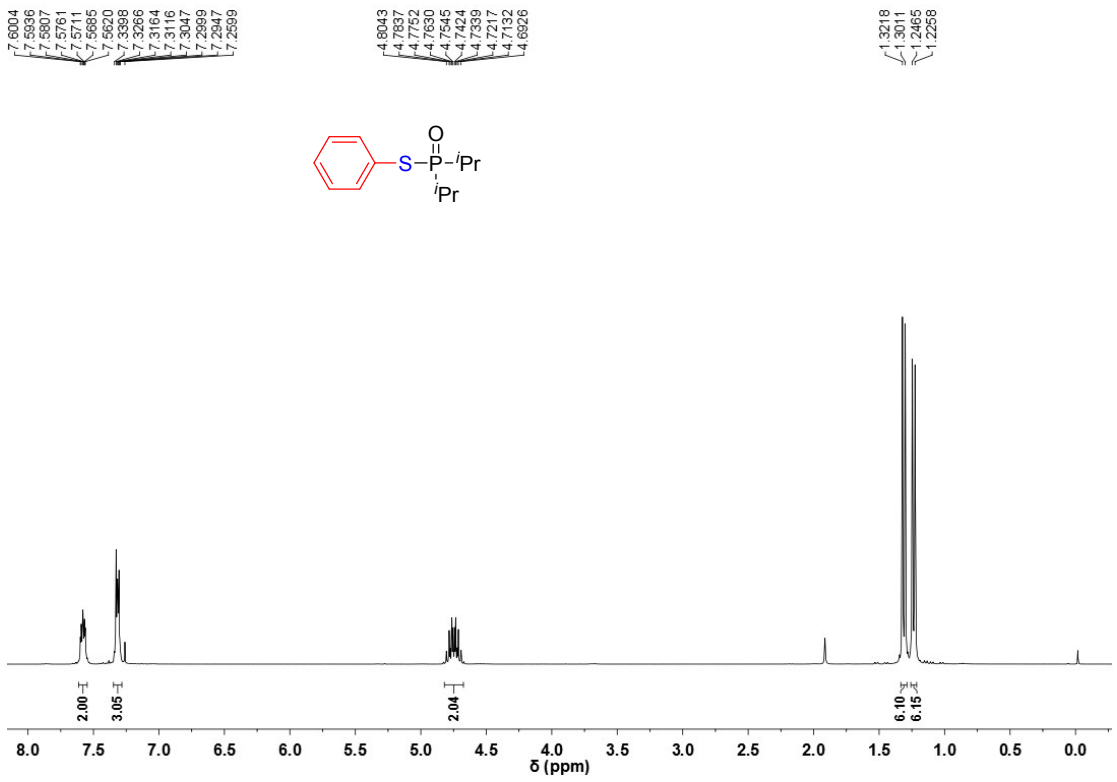
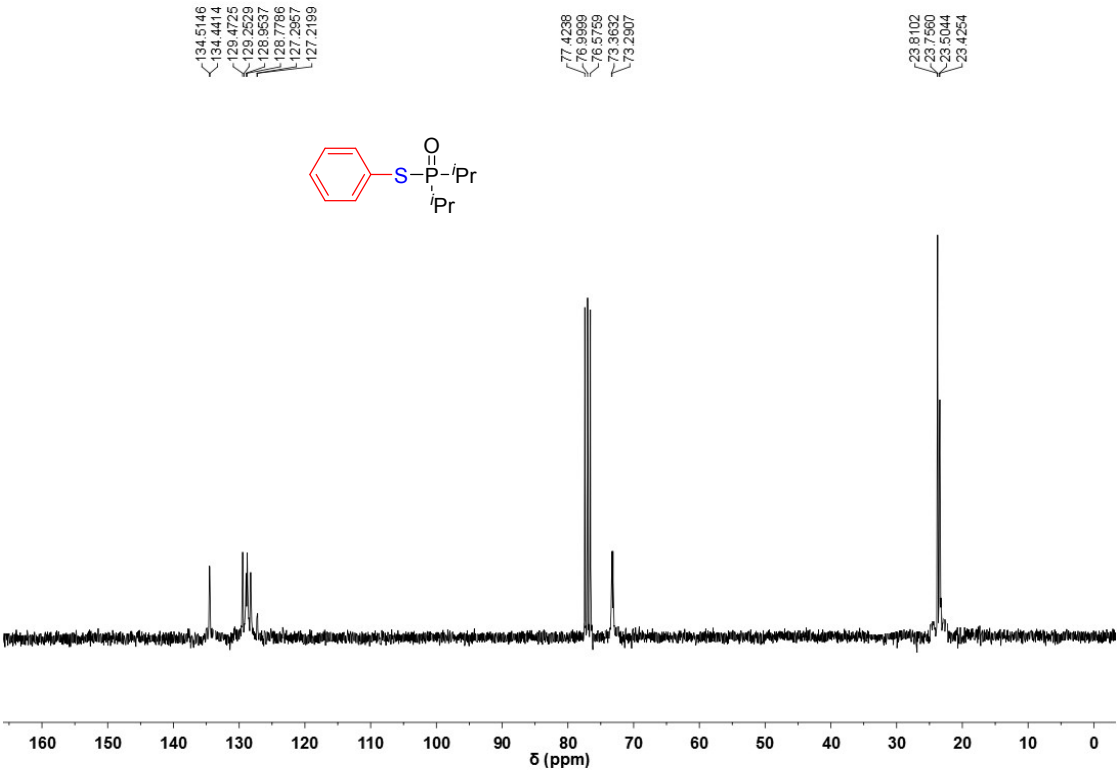
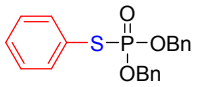
7.5336
7.5299
7.5251
7.5228
7.3675
7.3626
7.3596
7.3515
7.3457
7.3445
7.3336
7.3280
7.3154
7.3115
3.8168
3.7747
O
S
P
OMe
OMe
2.00
2.98
2.93
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

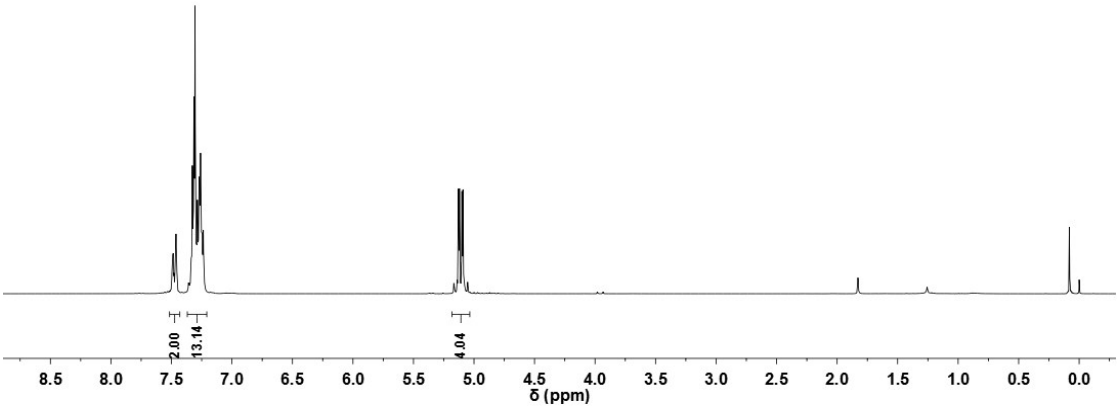

134.5353
134.4665
129.3907
129.3598
129.1065
129.0679
125.9356
125.8395
77.4240
76.9998
76.5759
54.1880
54.1077
O
S
P
OMe
OMe
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.6004
7.5936
7.5807
7.5761
7.5711
7.5685
7.5620
7.3398
7.3266
7.3164
7.3116
7.3047
7.2999
7.2947
7.2599
4.8043
4.7837
4.7752
4.7630
4.7545
4.7424
4.7339
4.7217
4.7132
4.6926
1.3218
1.3011
1.2465
1.2258
O
S
P
iPr
iPr
2.00
3.05
2.04
6.10
6.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

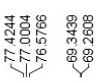

134.5146
134.4414
129.4725
129.2529
128.9537
128.7786
127.2957
127.2199
77.4238
76.9999
76.5759
73.3632
73.2907
23.8102
23.7560
23.5044
23.4254
O
S
P
iPr
iPr
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

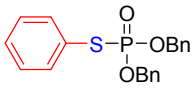

7.4957
7.4914
7.4889
7.4848
7.4790
7.4688
7.4623
7.4569
7.3348
7.3271
7.3200
7.3140
7.3100
7.3050
7.2930
7.2852
7.2789
7.2712
7.2591
7.2478
7.2462
7.2363
5.1671
5.1389
5.1281
5.1200
5.1000
5.0913
5.0811
5.0522

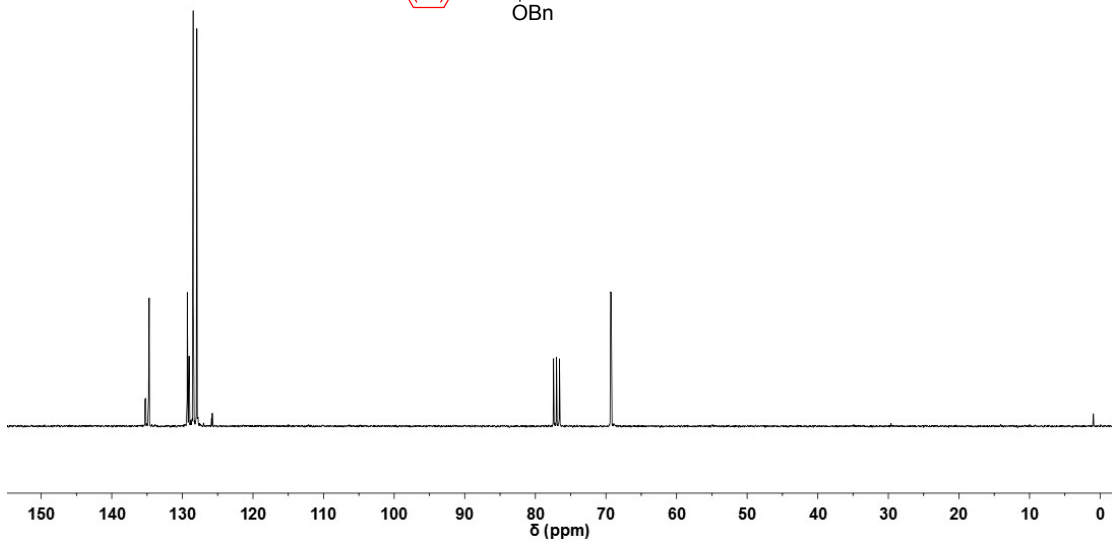

O
S
P
OBn
OBn


2.00
13.14
4.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


135.3017
135.2012
134.7756
134.7056
129.3033
129.2721
129.0688
129.0296
128.4929
128.4667
127.9508
125.8595
125.7632


77.4244
77.0004
76.5766
69.3439
69.2608


O
S
P
OBn
OBn


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.8848
7.8803
7.8752
7.8650
7.8581
7.8526
7.8418
7.8375
7.8324
7.8218
7.8149
7.8097
7.5291
7.5235
7.5182
7.5158
7.5047
7.4986
7.4900
7.4861
7.4807
7.4748
7.4691
7.4639
7.4583
7.4531
7.4454
7.4376
7.4336
7.4266
7.4212
7.4157
7.4104
7.4043
7.3980
7.3927
7.2624
7.2427
7.2380
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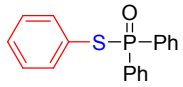
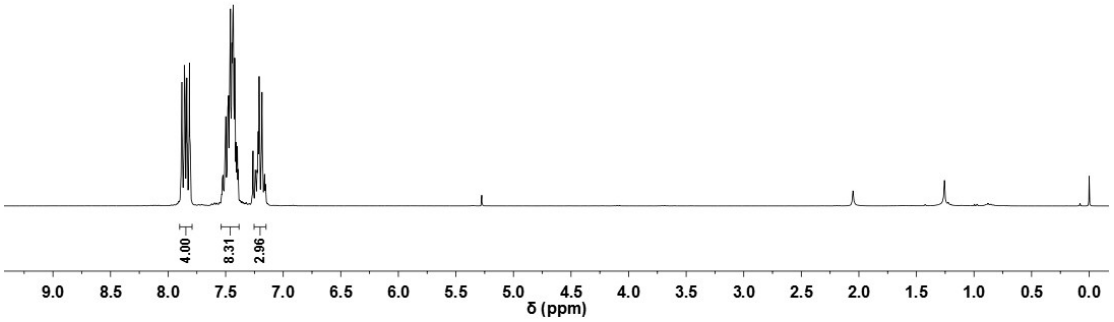
7.1552


O
S
P
Ph
Ph


4.00
8.31
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


135.3277
135.2759
133.1586
132.2541
132.2139
131.6049
131.4692
129.0519
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128.8317
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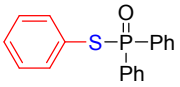
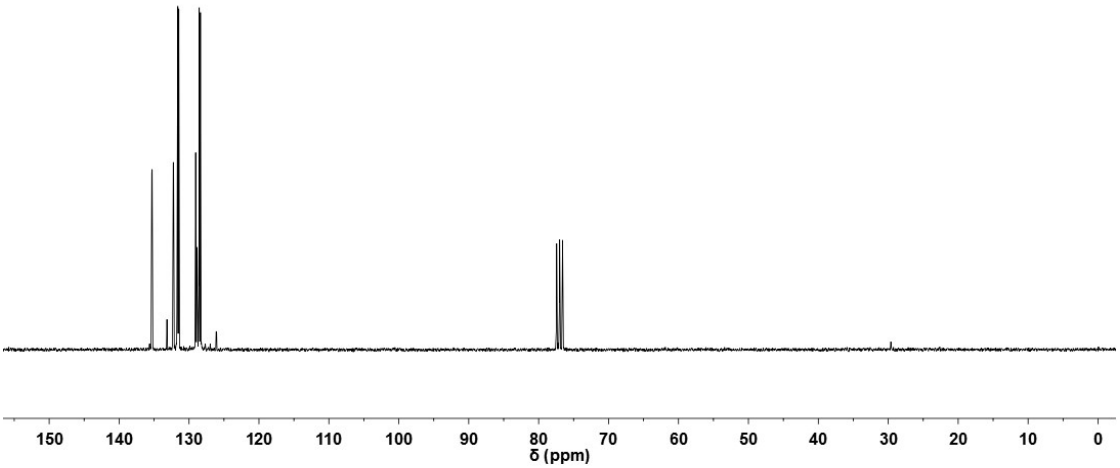
128.3683
126.1231
126.0546


77.4235
76.9996
76.5759


O
S
P
Ph
Ph


150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)