Electronic Supplementary Information (ESI)

Construction of Ar-P bond by Pd-catalyzed oxidative cross-coupling of arylsilanes with H-phosphonates via C-Si bond cleavage

Haiqing Luo,* Haidong Liu, Xingwei Chen, Keke Wang, Xuzhong Luo and Kejun Wang*

Department of Chemistry & Chemical Engineering, Gannan Normal University, Ganzhou341000, China

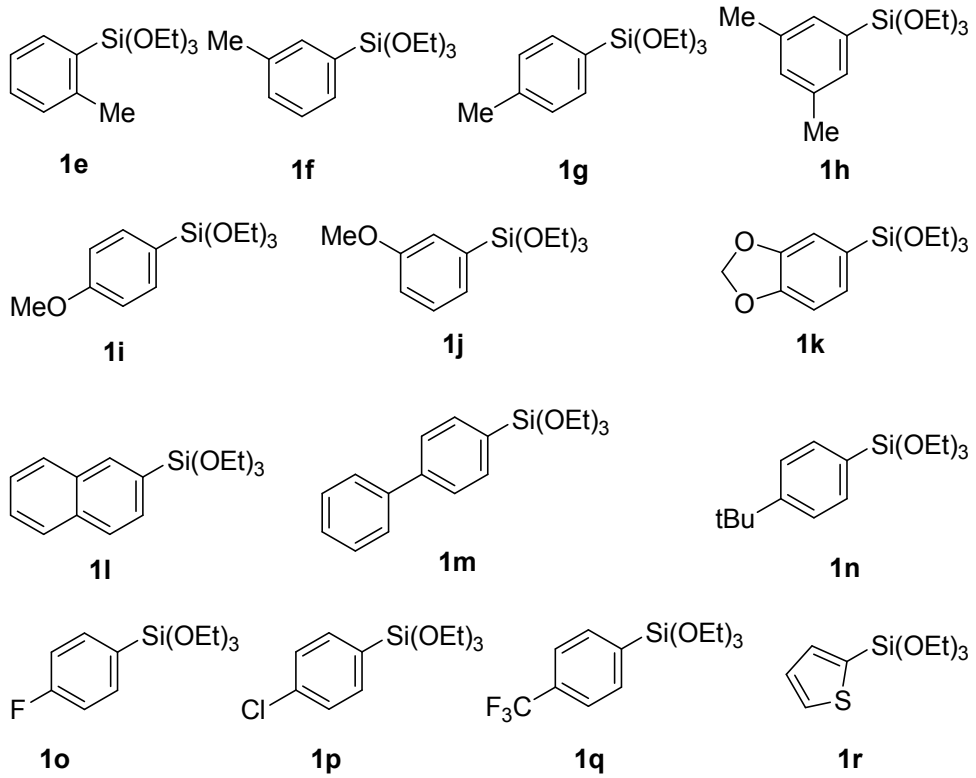
Email: luohq@gnnu.cn; wangkejun@sina.com

Table of Contents

1. General Information:

All the palladium-catalyzed oxidative cross-coupling reactions were carried out in oven-dried glassware sealed with rubber septa under air condition. All the compounds were known and characterized by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR with 400 MHz Bruker AVANCE spectrometers (400 MHz, 100 MHz and 162 MHz, respectively). Chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.0 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. Mass spectra were recorded on a GC-MS spectrometer (Agilent 5973N-GC/MSD) at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). In addition, column chromatography was performed on silica gel 200 - 300 mesh.

Materials: Unless otherwise noted, all reagents were purchased energy chemistry, Ouhe and J&K and used without further purification. DMF, DMSO, 1,4-Dioxane and DCE were extra dry bought from energy chemistry. THF was distilled over sodium. The arylsilanes(1e-r) were prepared in accordance with references[1].

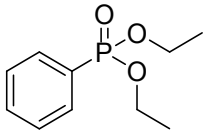


2. General procedure for Pd-catalyzed oxidative cross-coupling of arylsilanes with H-phosphonates.

To a 10 mL of seal tube equipped with a magnetic bar were added $Pd(PPh_3)_2Cl_2$ (0.0125 mmol, 5 mol%), Ag_2CO_3 (0.5 mmol, 2.0 equiv), and KF (1 mmol, 4.0 equiv). The DMF (4 mL) and arylsilane **1** (0.5 mmol, 2.0 equiv) were added subsequently. The reaction mixture was allowed to stir at room temperature for 15 min. Followed by addition of H-phosphonate diester **2** (0.25 mmol, 1 equiv) by microsyringe. Then, the sealed tube was screw capped and put into a preheated oil bath at 80 ^oC for 12 h. After completed, the reaction was cooled to room temperature, and then the mixture was diluted with 10 mL EtOAc. The mixture was filtered with a pad of cellite and extracted with EtOAc (3*10mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica gel chromatography (petroleum ether/ethyl acetate) to provide pure product **3**.

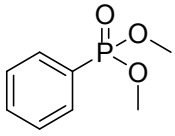
3. Characterization data for the products.

Diethyl phenylphosphonate (3a).



Colorless oil (phenyltriethyloxysilane, 44.9 mg, 84 % yield), (phenyltrimethoxysilane, 38.5 mg, 72 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 2H), 7.60 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 4.21 – 4.02 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.3 (d, *J* = 3.1 Hz), 131.6 (d, *J* = 9.9 Hz), 128.4 (d, *J* = 15.0 Hz), 128.2 (d, *J* = 188.7), 62.0 (d, *J* = 5.4 Hz), 16.2 (d, *J* = 6.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.6 . **MS (EI)** m/z: 214, 186, 158, 141, 105, 77. This compound is known[2].

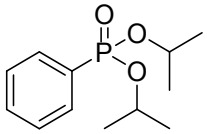
Dimethyl phenylphosphonate (3b).



Colorless oil (25.1 mg, 54 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 13.4, 6.5 Hz, 2H), 7.58 (t, *J* = 7.4Hz, 1H), 7.53 – 7.43 (m, 2H), 3.77 (d, *J* = 11.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.6 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 9.9 Hz), 128.5 (d,

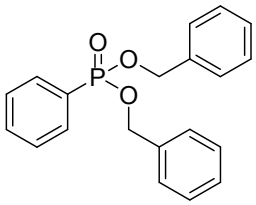
J = 15.1 Hz), 126.8 (d, *J* = 188.9 Hz), 52.7 (d, *J* = 5.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.5 . **MS (EI)** m/z: 185, 156, 141, 91, 77. This compound is known[2].

Diisopropyl phenylphosphonate (3c).



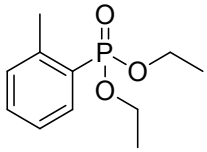
Colorless oil (56.3 mg, 93 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.42 (m, 2H), 4.73 – 4.65 (m, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.23 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.0 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 9.9 Hz), 129.9 (d, *J* = 188.2 Hz), 128.3 (d, *J* = 15.0 Hz), 70.7 (d, *J* = 5.5 Hz), 24.1 (d, *J* = 4.0 Hz), 23.8 (d, *J* = 4.8 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.5. **MS (EI)** m/z: 242, 201, 183, 159, 141, 77. This compound is known[2].

Dibenzyl phenylphosphonate (3d).



Colorless oil (55.8 mg, 66 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$)δ 7.81 (dd, *J* = 13.5, 6.8 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.35 – 7.26 (m, 10H), 5.15 – 4.99 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.0 (d, *J* = 6.9 Hz), 132.5 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 10.0 Hz), 128.4, 128.37 (d, *J* = 15.2 Hz) 128.2, 127.8, 127.7 (d, *J* = 181.09 Hz), 67.5 (d, *J* = 5.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.7. **HRMS (ESI)** calcd for $C_{20}H_{19}O_3PNa$ $[M + Na]^+$ 361.0964, found 361.0961. This compound is known[2].

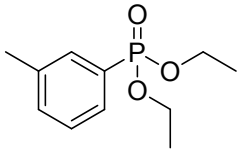
Diethyl o-tolylphosphonate (3e).



Colorless oil (28.5 mg, 50 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.81 (m, 1H), 7.44 – 7.40 (m, 1H), 7.33 – 7.20 (m, 2H), 4.24 – 3.99 (m, 4H), 2.58 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7 (d, *J* = 10.1 Hz), 133.8 (d, *J* = 10.3 Hz), 132.4 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 14.9 Hz), 126.8 (d, *J* = 184.0 Hz), 125.3 (d, *J* = 14.9 Hz), 61.8 (d, *J* = 5.5 Hz), 21.2 (d, *J* = 3.6 Hz), 16.3 (d, *J* = 6.5 Hz).

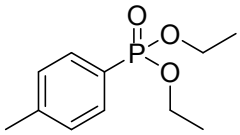
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5 . **MS (EI)** m/z: 228, 213, 200, 185, 172, 154, 119, 91, 65. This compound is known[2].

Diethyl m-tolylphosphonate (3f).



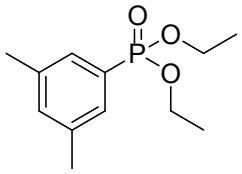
Colorless oil (53.6 mg, 94 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.38 – 7.33 (m, 2H), 4.21 – 4.00 (m, 4H), 2.40 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2 (d, *J* = 15.0 Hz), 133.1 (d, *J* = 3.2 Hz), 132.2 (d, *J* = 9.9 Hz), 128.0 (d, *J* = 187.6 Hz), 128.7 (d, *J* = 9.7 Hz), 128.3 (d, *J* = 15.7 Hz), 62.0 (d, *J* = 5.3 Hz), 21.2, 16.2 (d, *J* = 6.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.2 . **MS (EI)** m/z: 228, 200, 172, 155, 119, 91, 65. This compound is known[2].

Diethyl p-tolylphosphonate (3g).



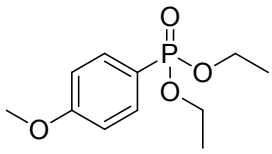
Colorless oil (42.8 mg, 75 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.51 (m, 2H), 7.30 – 7.26 (m, 2H), 4.21 – 3.92 (m, 4H), 2.40 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 10.2 Hz), 129.1 (d, *J* = 15.4 Hz), 124.9 (d, *J* = 190.2 Hz), 61.9 (d, *J* = 5.4 Hz), 21.5 (d, *J* = 1.4 Hz), 16.2 (d, *J* = 6.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.5 . **MS (EI)** m/z: 228, 200, 172, 155, 119, 108, 91, 65. This compound is known[2].

Diethyl (3,5-dimethylphenyl)phosphonate (3h).



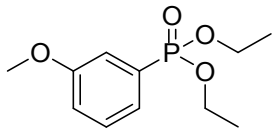
Colorless oil (41.2 mg, 68 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 12.1 Hz, 2H), 7.18 (s, 1H), 4.21 – 4.00 (m, 4H), 2.35 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9 (d, *J* = 3.1 Hz), 131.6 (d, *J* = 10.3 Hz), 125.4 (d, *J* = 15.2 Hz), δ 124.9 (d, *J* = 191.0 Hz), 62.0 (d, *J* = 5.4 Hz), 35.0 , 31.0 , 16.3 (d, *J* = 6.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.5 . **MS (EI)** m/z: 242, 214, 186, 133, 107, 91, 77. This compound is known[3].

Diethyl (4-methoxyphenyl)phosphonate (3i)



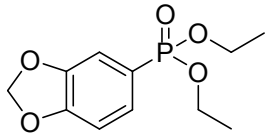
Colorless oil (51.2 mg, 84 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.01 – 6.93 (m, 2H), 4.19 – 3.99 (m, 4H), 3.85 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 3.4 Hz), 133.7 (d, *J* = 11.3 Hz), 119.4 (d, *J* = 195.1 Hz), 113.9 (d, *J* = 16.1 Hz), 61.8 (d, *J* = 5.3 Hz), 55.2, 16.2 (d, *J* = 6.5 Hz).**^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.6. **MS (EI)** m/z: 244, 216, 188, 171, 135, 108, 92, 77. This compound is known[2].

Diethyl (3-methoxyphenyl)phosphonate (3j).



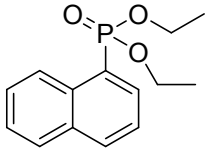
Colorless oil (53.7 mg, 88 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 3H), 7.12 – 7.03 (m, 1H), 4.26 – 3.98 (m, 4H), 3.85 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 19.0 Hz), 129.7 (d, *J* = 17.6 Hz), 129.5 (d, *J* = 187.6 Hz), 123.9 (d, *J* = 9.3 Hz), 118.7 (d, *J* = 3.2 Hz), 116.3 (d, *J* = 11.4 Hz), 62.1 (d, *J* = 5.4 Hz), 55.3 , 16.2 (d, *J* = 6.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.6 . **MS (EI)** m/z: 244, 216, 201, 188, 172, 158, 135, 108, 92, 77. This compound is known[2].

Diethyl benzo[d][1,3]dioxol-5-ylphosphonate (3k).



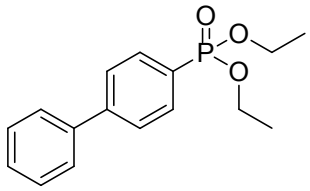
Colorless oil (51.6 mg, 80 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 14.0, 7.9, 1.5 Hz, 1H), 7.21 (dd, *J* = 12.9, 1.4 Hz, 1H), 6.89 (dd, *J* = 7.9, 3.6 Hz, 1H), 6.03 (s, 2H), 4.18 – 3.99 (m, 4H), 1.32 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1 (d, *J* = 3.6 Hz), 147.7 (d, *J* = 22.7 Hz), 127.3 (d, *J* = 11.2 Hz), 121.1 (d, *J* = 193.3 Hz), 111.1 (d, *J* = 12.3 Hz), 108.5 (d, *J* = 18.7 Hz), 101.5 , 61.9 (d, *J* = 5.3 Hz), 16.2 (d, *J* = 6.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.9 . **MS (EI)** m/z: 258, 230, 202, 186, 149, 122, 65. This compound is known[4].

Diethyl naphthalen-1-ylphosphonate (3l)



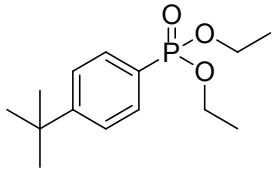
Colorless oil (43.6 mg, 66 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 9.6 Hz, 1H), 8.25 (ddd, *J* = 16.3, 7.0, 1.3 Hz, 1H), 8.04 (d, *J* = 9.6 Hz, 1H), 7.90 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.50 (m, 2H), 4.26 – 4.16 (m, 2H), 4.13 – 1.03 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl3) δ 134.6 (d, *J* = 9.2 Hz), δ 133.6 (d, *J* = 3.2 Hz), δ 133.5 (d, *J* = 13.2 Hz), 132.6 (d, *J* = 11.0 Hz), 128.7 (d, *J* = 1.9 Hz), 127.4 , 126.6 (d, *J* = 4.2 Hz), 126.3 , 124.5 (d, *J* = 16.6 Hz), 124.5 (d, *J* = 183.3 Hz), 62.1 (d, *J* = 5.2 Hz), 16.3 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.1 . **MS (EI)** m/z: 264, 235, 221, 208, 192, 173, 155, 128, 115. This compound is known[2].

Diethyl [1,1'-biphenyl]-4-ylphosphonate (3m).



Colorless oil (60.9 mg, 84 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.73 – 7.65 (m, 2H), 7.62 – 7.58 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.35 (m, 1H), 4.24 – 4.05 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.1 (d, *J* = 3.2 Hz), 139.8 , 132.2 (d, *J* = 10.2 Hz), 128.8 , 128.06 , 127.2 , 127.0 , δ 126.7 (d, *J* = 190.4 Hz), 62.1 (d, *J* = 5.4 Hz), 16.3 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.9 . **MS (EI)** m/z: 290, 262, 234, 218, 181, 169, 152. This compound is known[2].

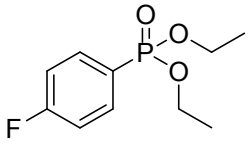
Diethyl (4-(tert-butyl)phenyl)phosphonate (3n).



Colorless oil (42.5 mg, 63 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.52 – 7.44 (m, 2H), 4.20 – 4.00 (m, 4H), 1.36 – 1.30 (m, 15H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9 (d, *J* = 3.1 Hz), 131.6 (d, *J* = 10.3 Hz), 125.4 (d, *J* = 15.2 Hz), 124.90 (d, *J* = 191.0 Hz), 62.0 (d, *J* = 5.4 Hz), 35.0 , 31.0 , 16.3 (d, *J* = 6.6 Hz). **^{31}P**

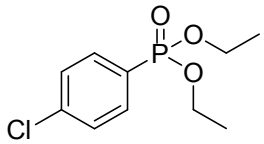
NMR (162 MHz, $CDCl_3$) δ 19.5 . **MS (EI)** m/z: 270, 255, 277, 199. This compound is known[5].

Diethyl (4-fluorophenyl)phosphonate (3o).



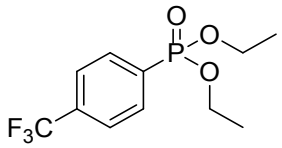
Colorless oil (23.8 mg, 41 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 2H), 7.18– 7.13 (m, 2H), 4.22 – 4.01 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3 (dd, J =254.5 , 13.0 Hz), 134.3 (dd, *J* = 11.4, 9.0 Hz), 124.4 (dd, *J* = 192.5, 3.5 Hz), 115.8 (dd, *J* = 21.4, 16.3 Hz), 62.2 (d, *J* = 5.4 Hz), 16.3 (d, *J* = 6.5 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.7 . **MS (EI)** m/z: 232, 176, 159, 123, 112, 96, 75. This compound is known[2].

Diethyl (4-chlorophenyl)phosphonate (3p).



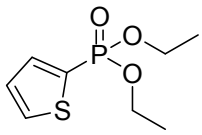
Colorless oil (32.9 mg, 53 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.50 – 7.41 (m, 2H), 4.22 – 4.01 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8 (d, *J* = 4.0 Hz), 133.0 (d, *J* = 10.8 Hz), 128.7 (d, *J* = 15.6 Hz), 126.7 (d, *J* = 191.0 Hz), 62.1 (d, *J* = 5.5 Hz), 16.1 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.5 . **MS (EI)** m/z: 247, 107, 91, 77. This compound is known[5].

Diethyl (4-(trifluoromethyl)phenyl)phosphonate (3q).



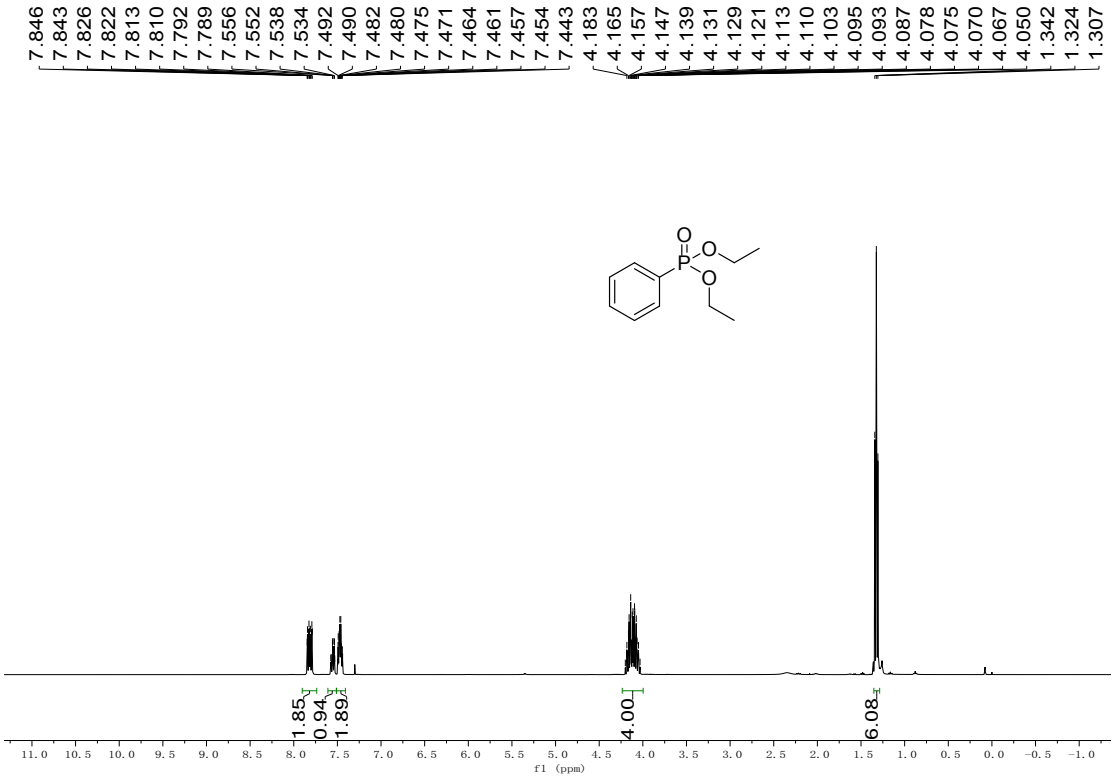
Colorless oil (21.9 mg, 31 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 13.0, 7.8 Hz, 2H), 7.77 – 7.70 (m, 2H), 4.25 – 4.05 (m, 4H), 1.34 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 134.0 (dd, *J* = 32.8, 3.4 Hz), δ 132.8 (d, *J* = 188.1Hz), δ 132.2 (d, *J* = 10.1 Hz), 123.5 (d, *J* = 273.9 Hz), 62.5 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.2 . **MS (EI)** m/z: 282, 255, 227, 209, 173, 162, 145, 126, 95. This compound is known[2].

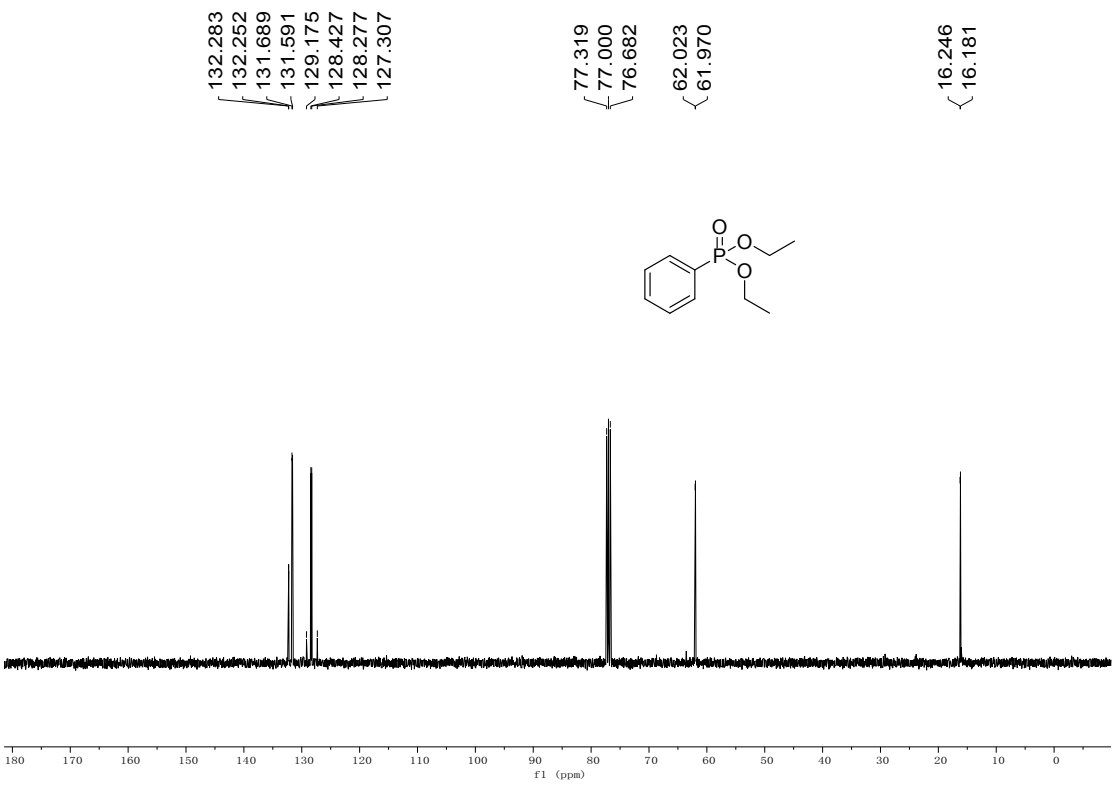
Diethyl thiophen-2-ylphosphonate (3r).

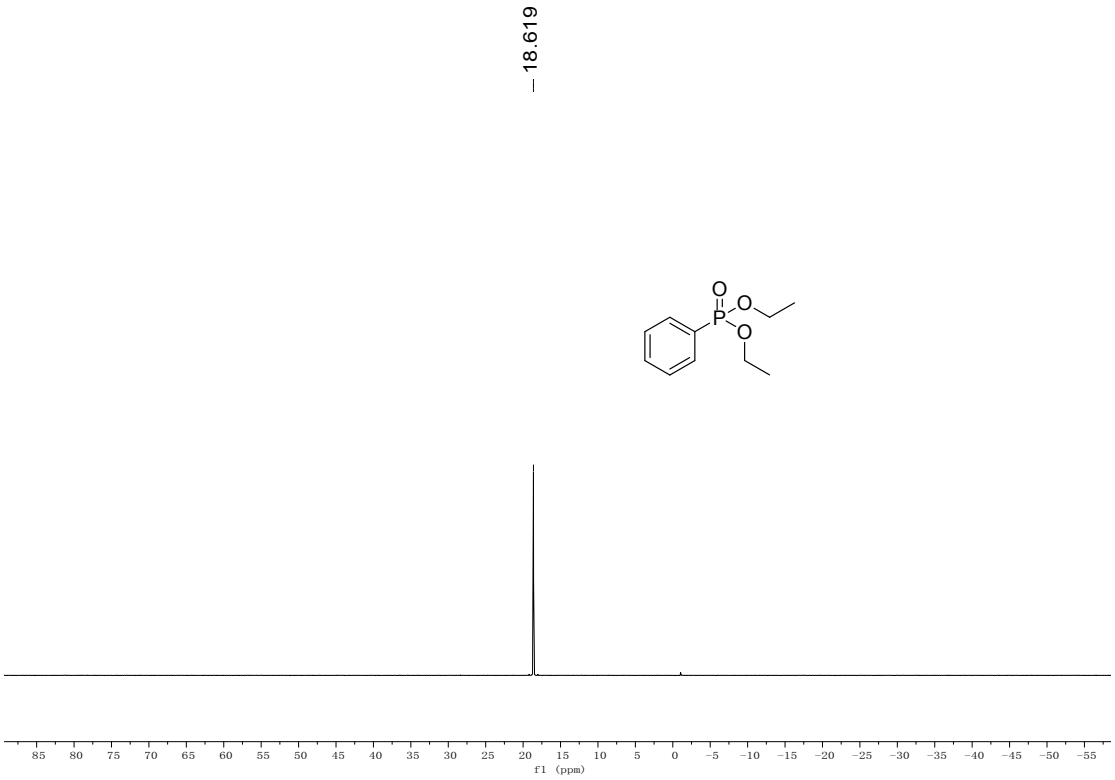


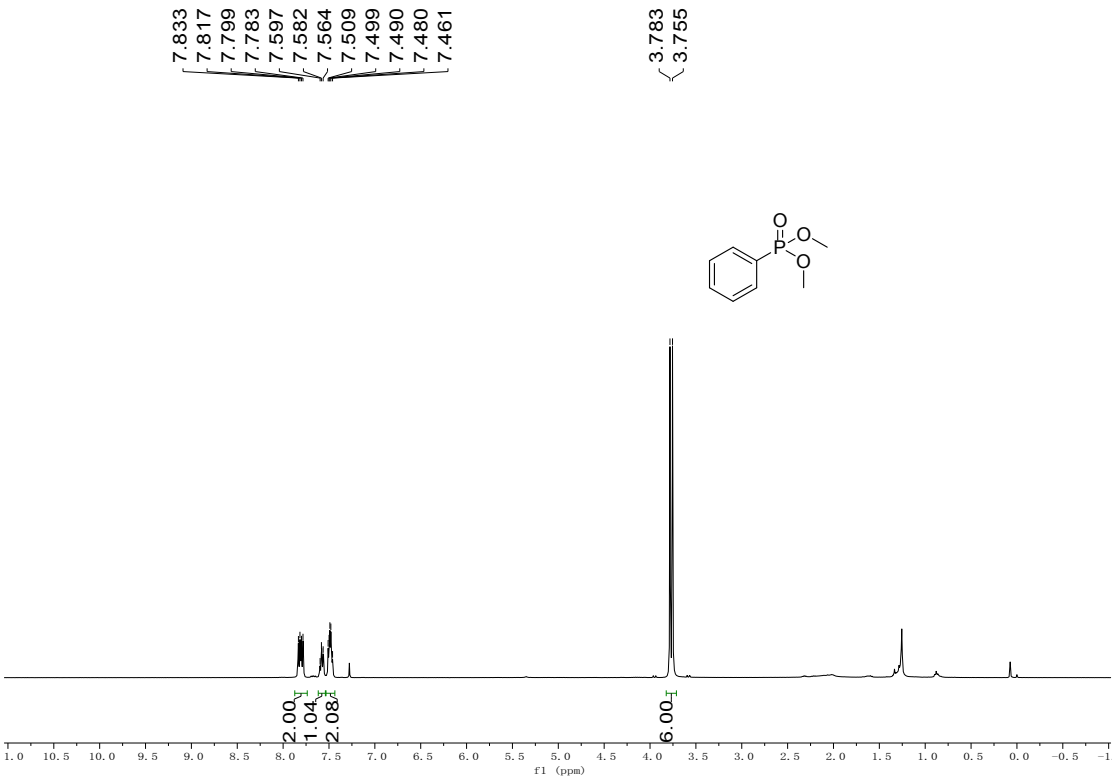
Colorless oil (19.4 mg, 35 % yield): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 2H), 7.20 – 7.17 (m, 1H), 4.23 – 4.05 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7 (d, *J* = 12.4 Hz), 133.4 (d, *J* = 7.5 Hz), 128.0 (d, *J* = 18.4 Hz), δ 127.8 (d, *J* = 210.9 Hz), 62.6 (d, *J* = 5.4 Hz), 16.2 (d, *J* = 6.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 11.9 . **MS (EI)** m/z: 220, 192, 164, 147, 111, 84. This compound is known[6].

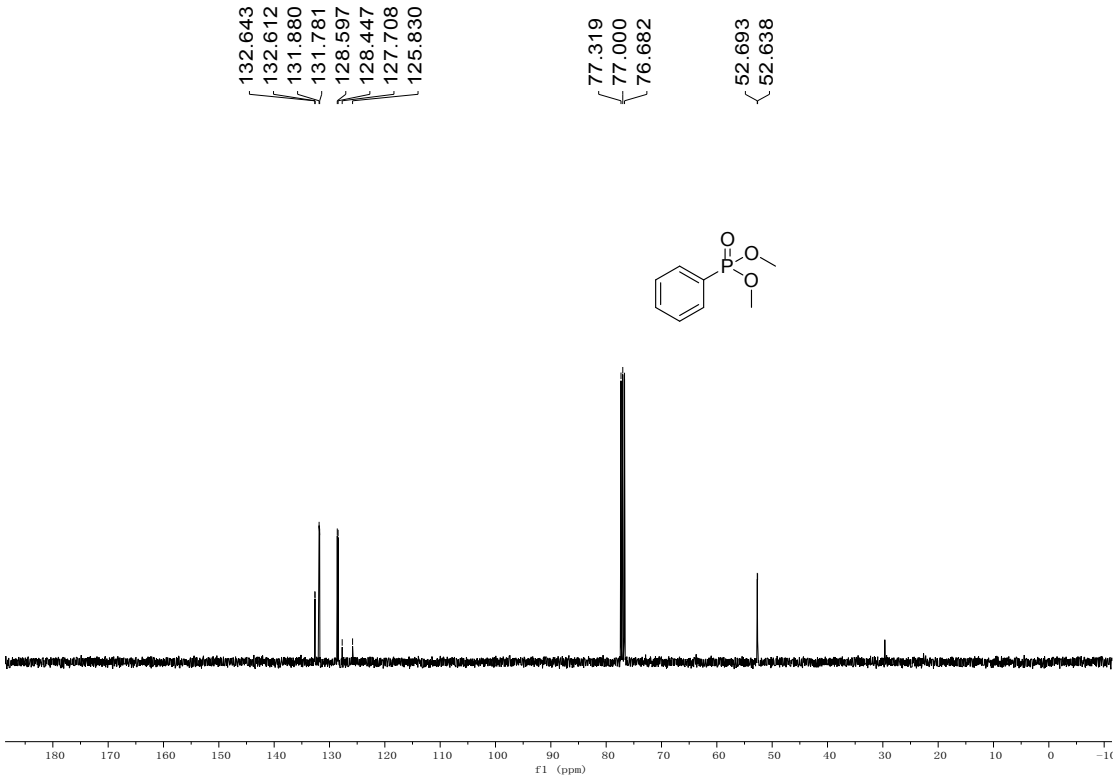
4. ^{1}H, ^{13}C and ^{31}P NMR spectra of the products.

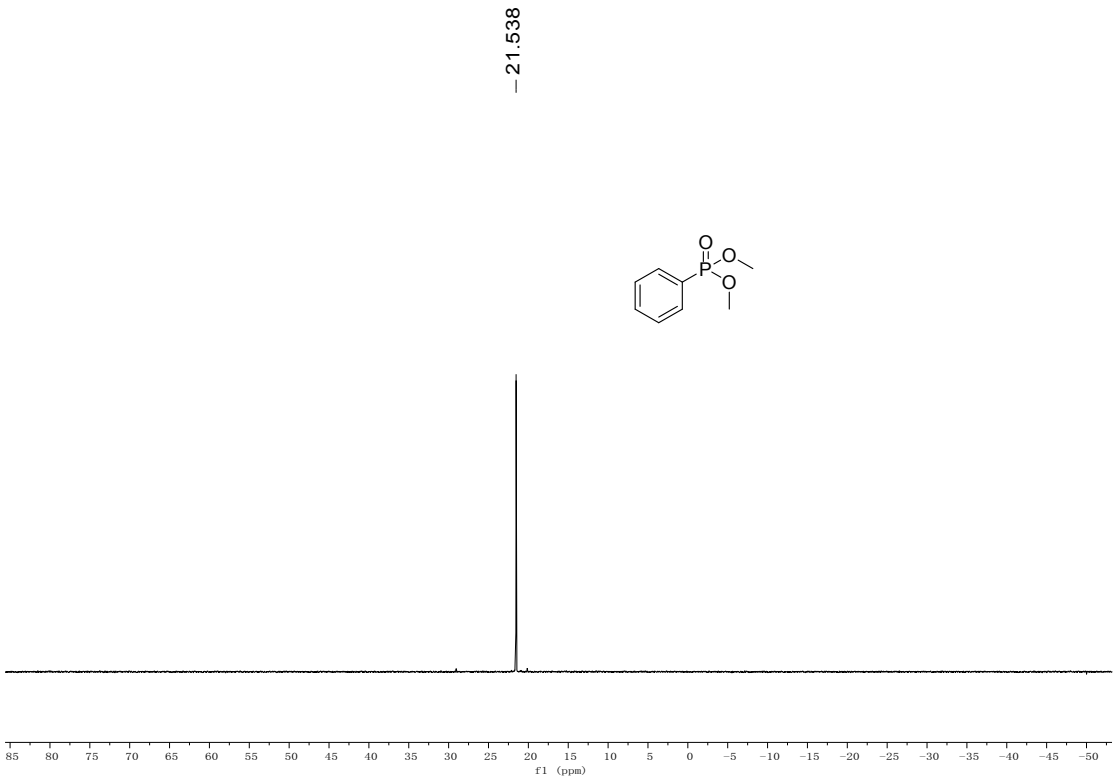


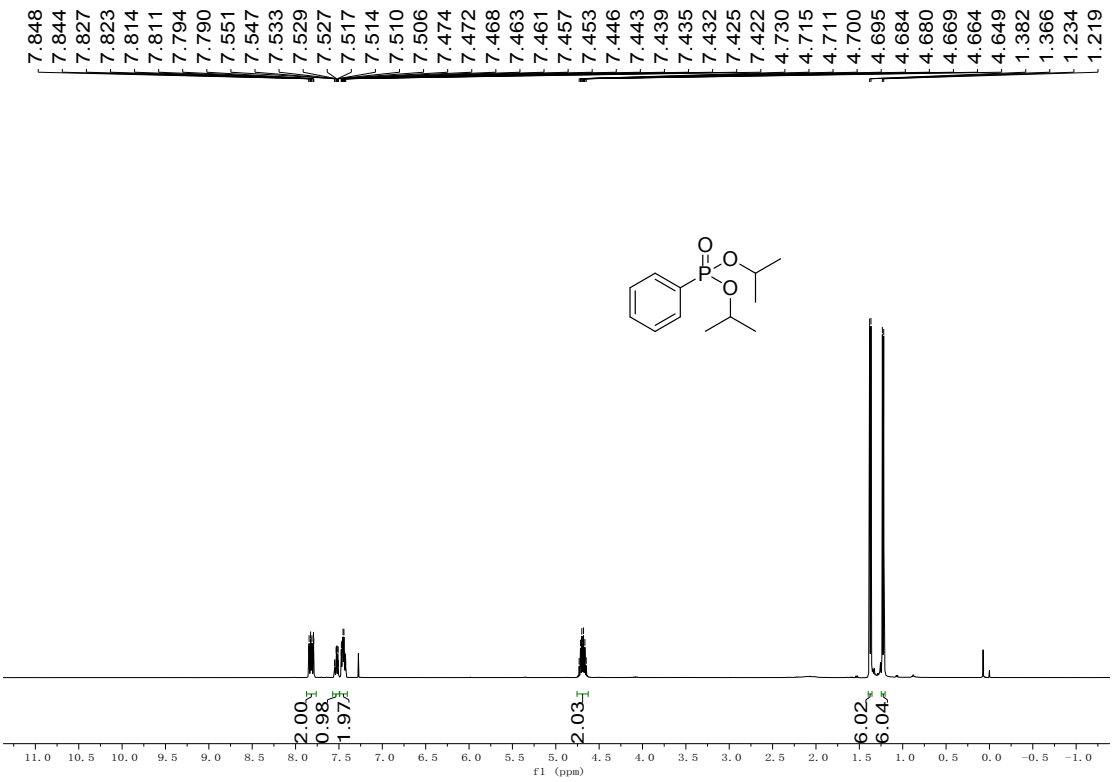


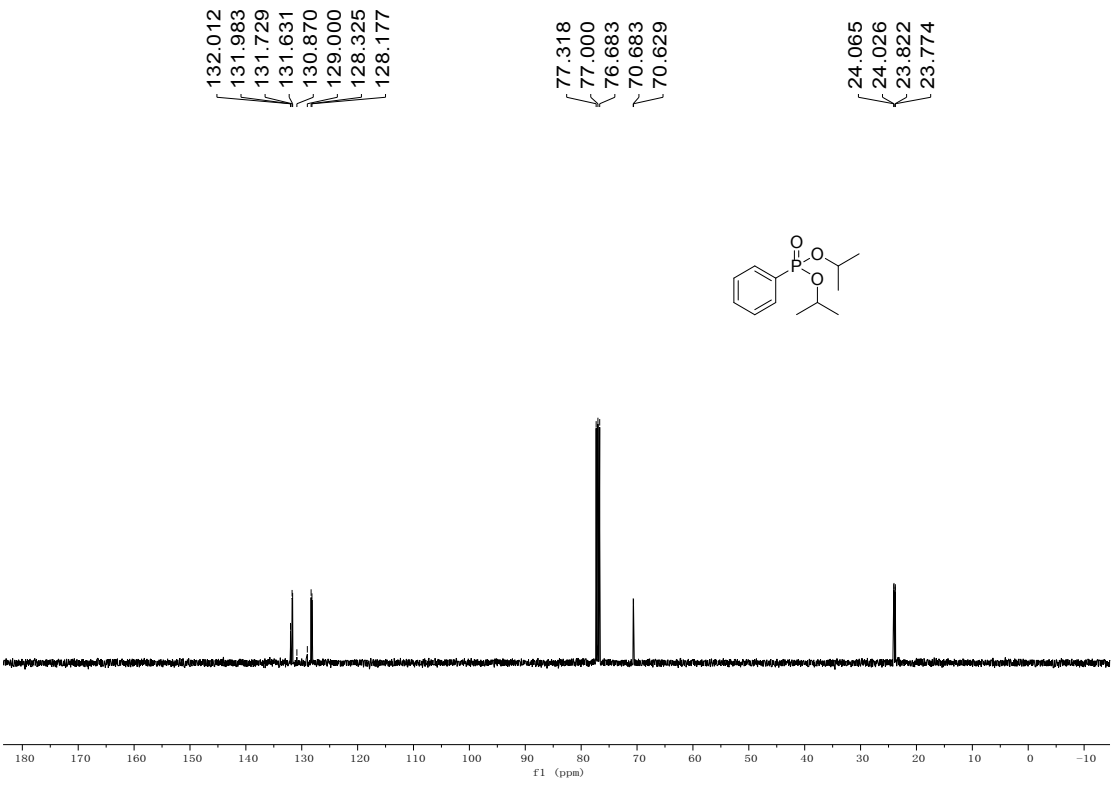

18.619
f1 (ppm)

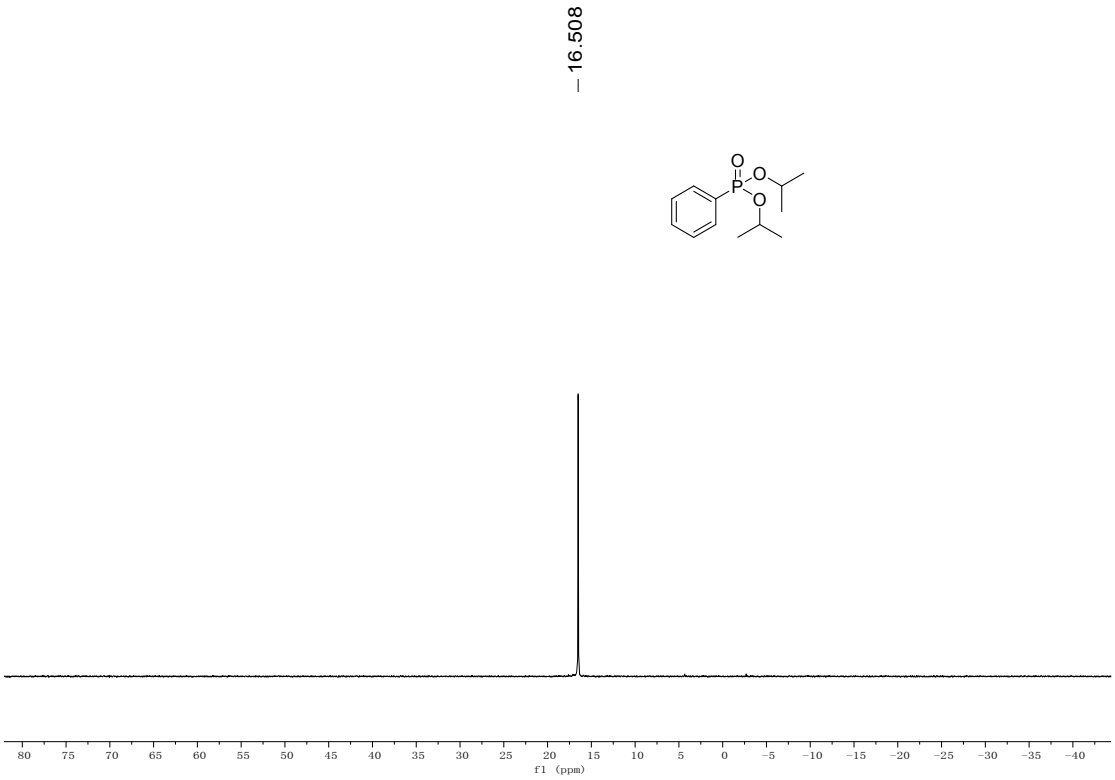

7.833
7.817
7.799
7.783
7.597
7.582
7.564
7.509
7.499
7.490
7.480
7.461
3.783
3.755
2.00
1.04
2.08
6.00
f1 (ppm)

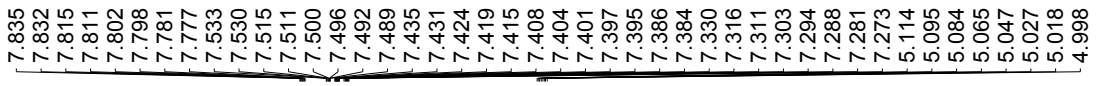

132.643
132.612
131.880
131.781
128.597
128.447
127.708
125.830
77.319
77.000
76.682
52.693
52.638
O
P
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

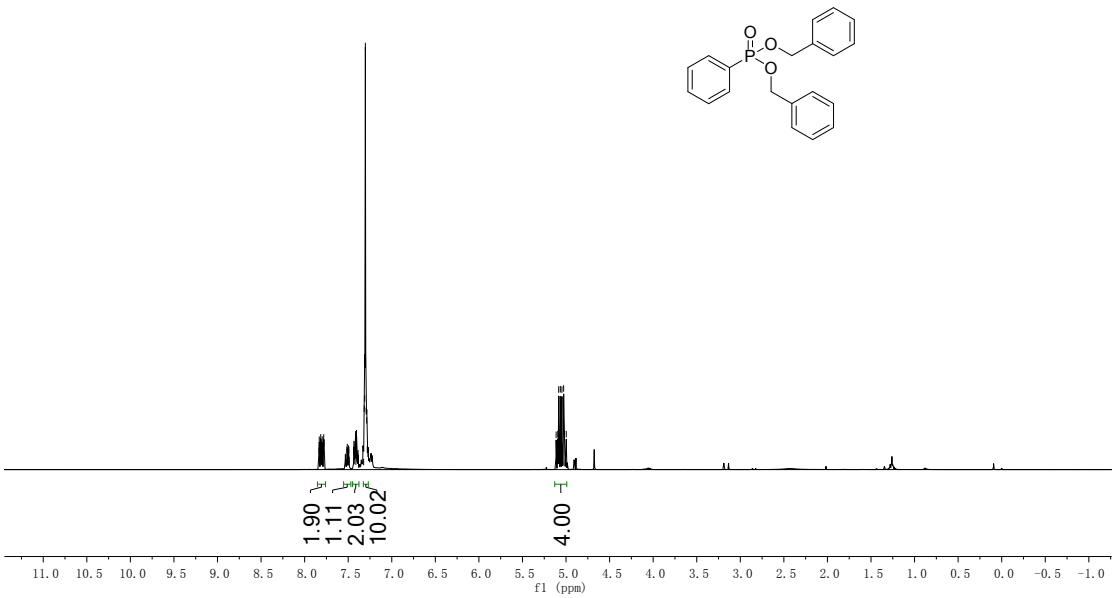

21.538
O
P
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)


7.848
7.844
7.827
7.823
7.814
7.811
7.794
7.790
7.551
7.547
7.533
7.529
7.527
7.517
7.514
7.510
7.506
7.474
7.472
7.468
7.463
7.461
7.457
7.453
7.446
7.443
7.439
7.435
7.432
7.425
7.422
4.730
4.715
4.711
4.700
4.695
4.684
4.680
4.669
4.664
4.649
1.382
1.366
1.234
1.219
O
P
O
O
2.00
0.98
1.97
2.03
6.02
6.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


132.012
131.983
131.729
131.631
130.870
129.000
128.325
128.177
77.318
77.000
76.683
70.683
70.629
24.065
24.026
23.822
23.774
O
P
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

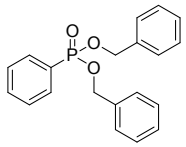

16.508
f1 (ppm)

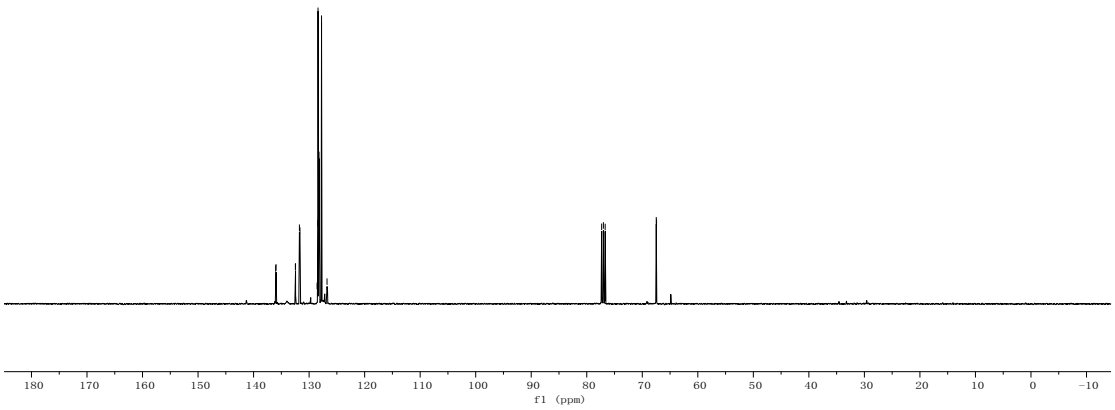

7.835
7.832
7.815
7.811
7.802
7.798
7.781
7.777
7.533
7.530
7.515
7.511
7.500
7.496
7.492
7.489
7.435
7.431
7.424
7.419
7.415
7.408
7.404
7.401
7.397
7.395
7.386
7.384
7.330
7.316
7.311
7.303
7.294
7.288
7.281
7.273
5.114
5.095
5.084
5.065
5.047
5.027
5.018
4.998


1.90
1.11
2.03
10.02
4.00
f1 (ppm)

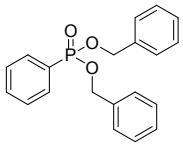
136.026
135.957
132.477
132.446
131.747
131.647
128.564
128.444
128.394
128.294
128.216
127.762
126.771

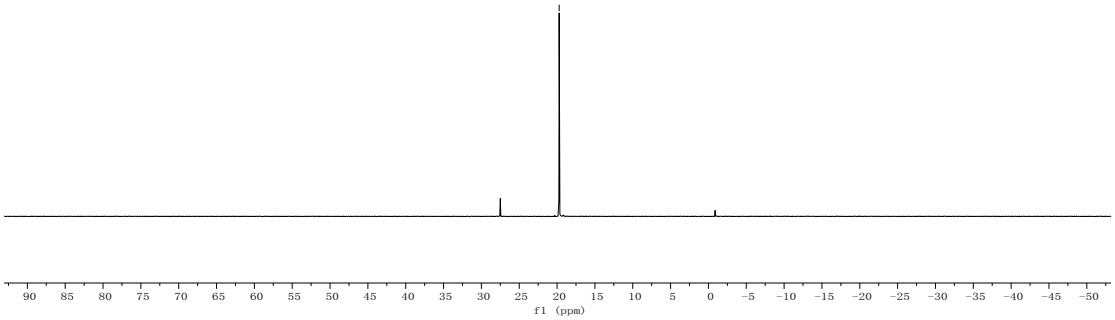
77.319
77.001
76.682
67.483
67.429

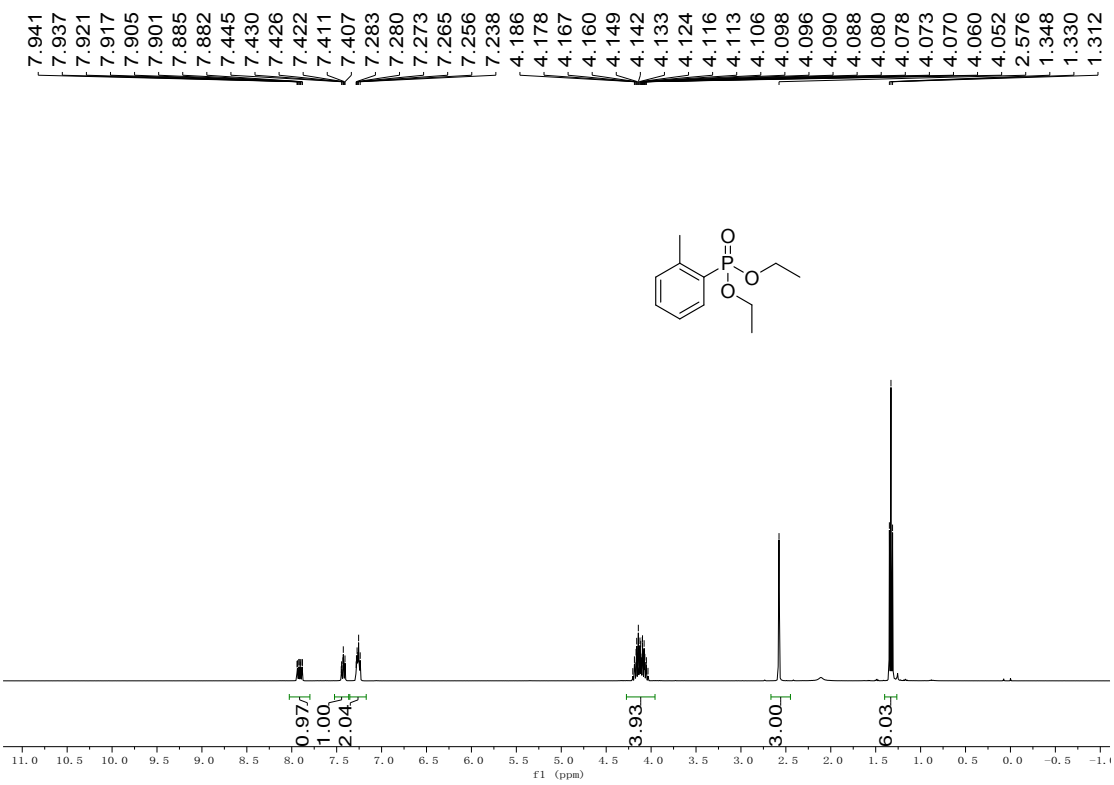


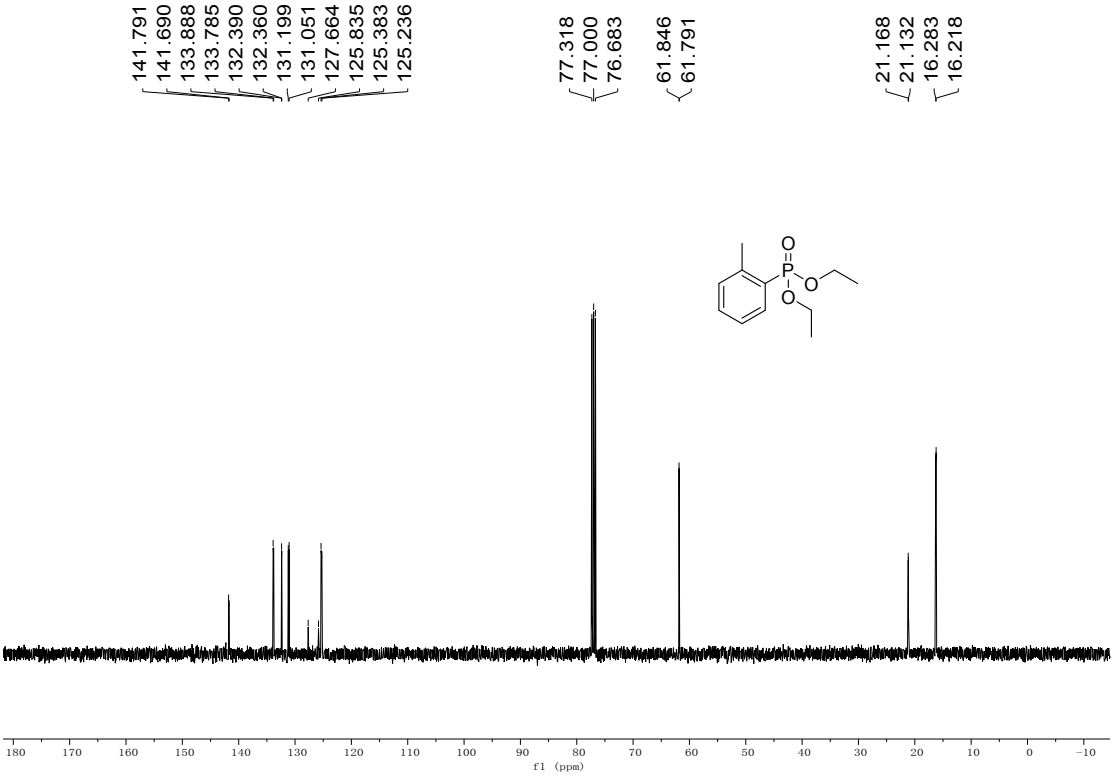


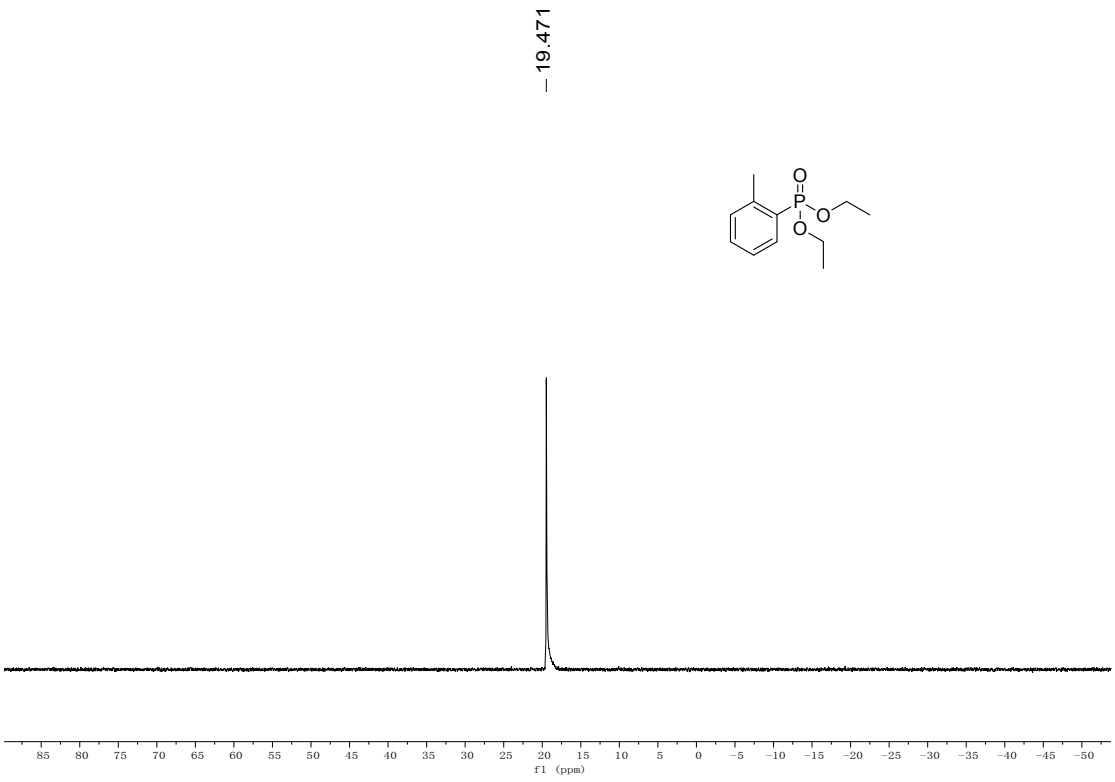
19.724

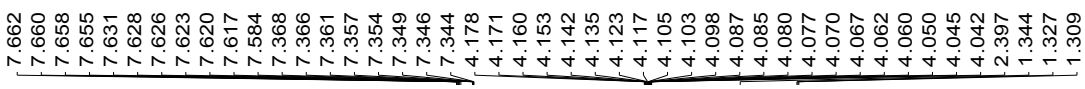


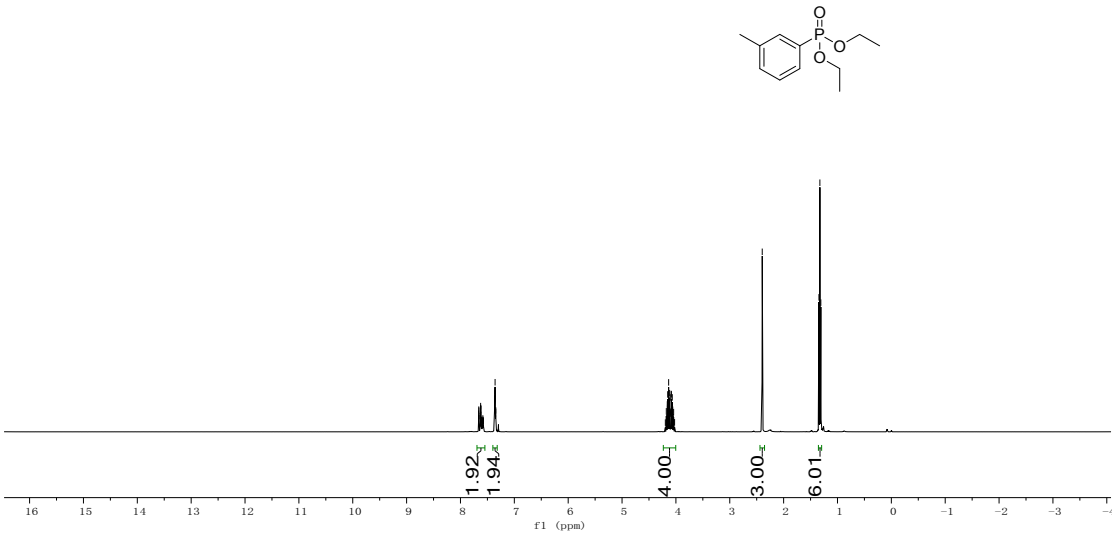


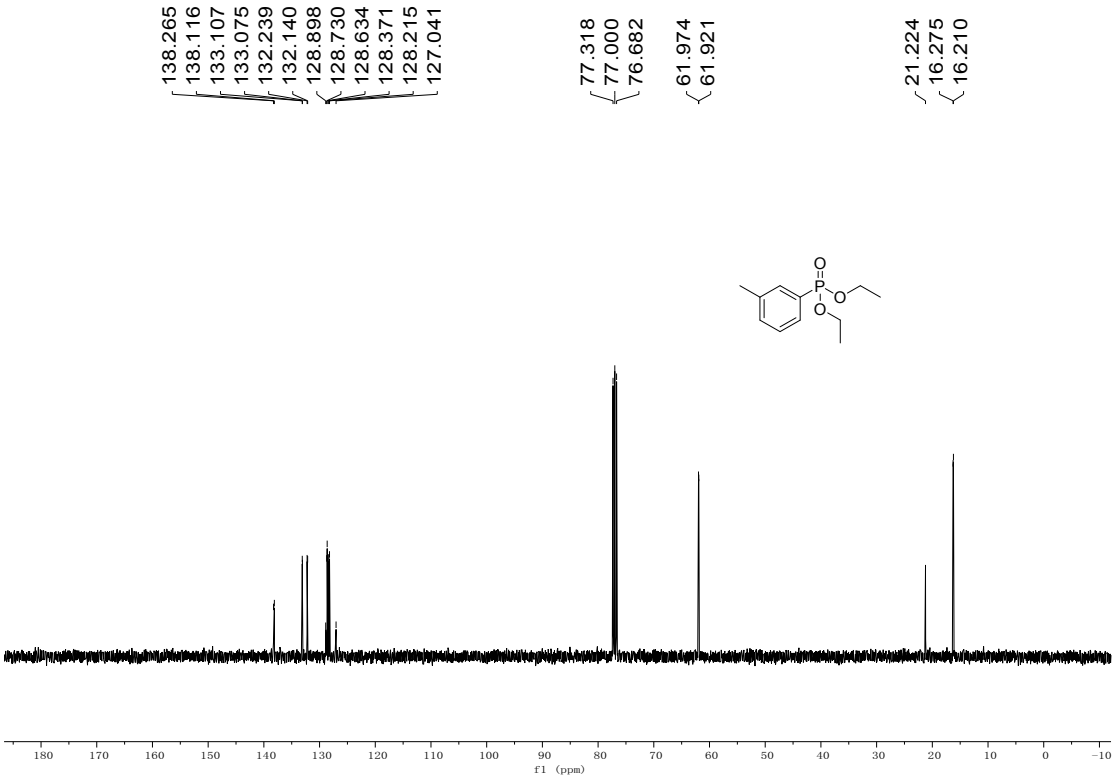

7.941
7.937
7.921
7.917
7.905
7.901
7.885
7.882
7.445
7.430
7.426
7.422
7.411
7.407
7.283
7.280
7.273
7.265
7.256
7.238
4.186
4.178
4.167
4.160
4.149
4.142
4.133
4.124
4.116
4.113
4.106
4.098
4.096
4.090
4.088
4.080
4.078
4.073
4.070
4.060
4.052
2.576
1.348
1.330
1.312
O
P
O
O
0.97
1.00
2.04
3.93
3.00
6.03
f1 (ppm)

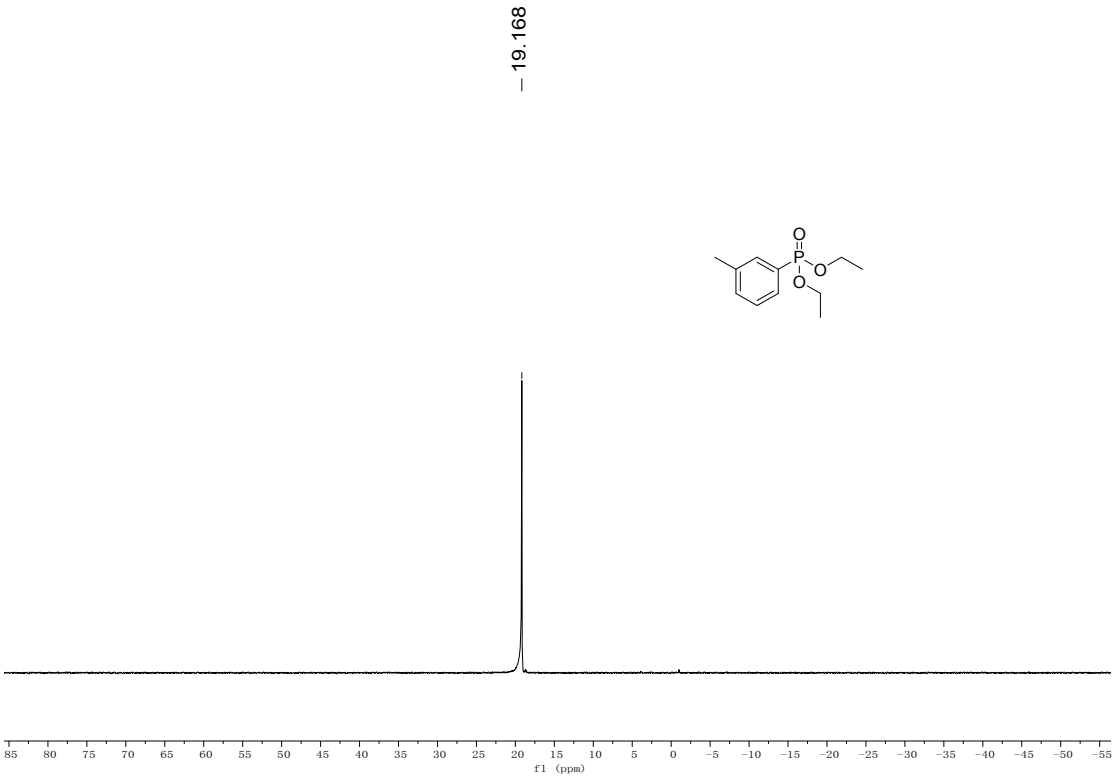

141.791
141.690
133.888
133.785
132.390
132.360
131.199
131.051
127.664
125.835
125.383
125.236
77.318
77.000
76.683
61.846
61.791
21.168
21.132
16.283
16.218
O
P
O
O
f1 (ppm)

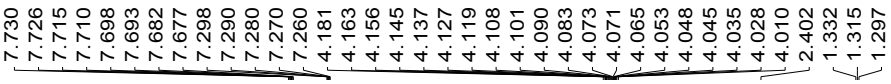

19.471
O
P
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

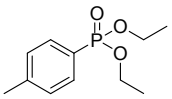

7.662
7.660
7.658
7.655
7.631
7.628
7.626
7.623
7.620
7.617
7.584
7.368
7.366
7.361
7.357
7.354
7.349
7.346
7.344
4.178
4.171
4.160
4.153
4.142
4.135
4.123
4.117
4.105
4.103
4.098
4.087
4.085
4.080
4.077
4.070
4.067
4.062
4.060
4.050
4.045
4.042
2.397
1.344
1.327
1.309

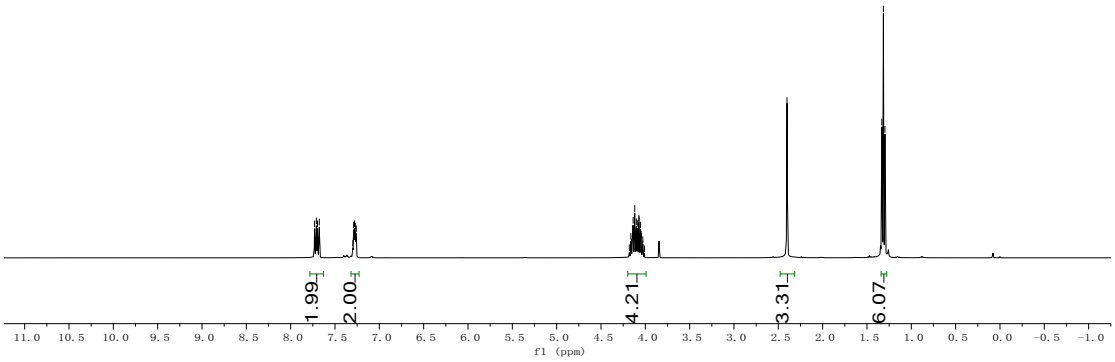

O
P
O
O
1.92
1.94
4.00
3.00
6.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

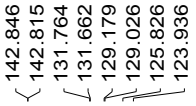

138.265
138.116
133.107
133.075
132.239
132.140
128.898
128.730
128.634
128.371
128.215
127.041
77.318
77.000
76.682
61.974
61.921
21.224
16.275
16.210
O
P
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

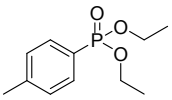

19.168
O
P
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50 −55
f1 (ppm)

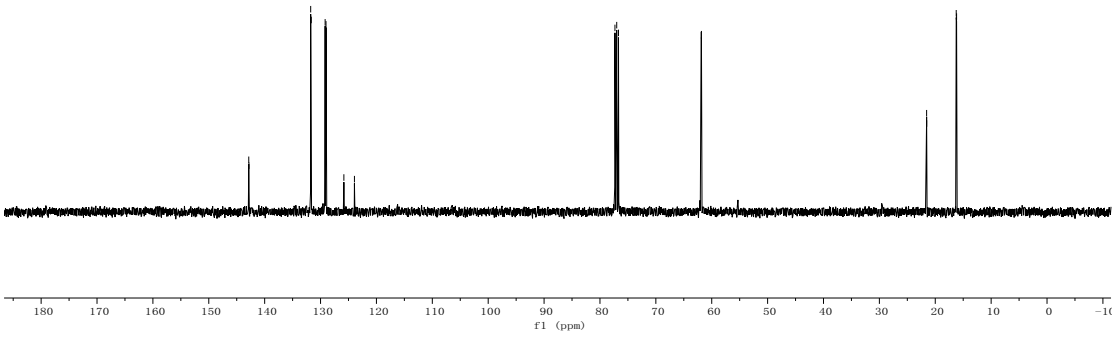

7.730
7.726
7.715
7.710
7.698
7.693
7.682
7.677
7.298
7.290
7.280
7.270
7.260
4.181
4.163
4.156
4.145
4.137
4.127
4.119
4.108
4.101
4.090
4.083
4.073
4.071
4.065
4.053
4.048
4.045
4.035
4.028
4.010
2.402
1.332
1.315
1.297

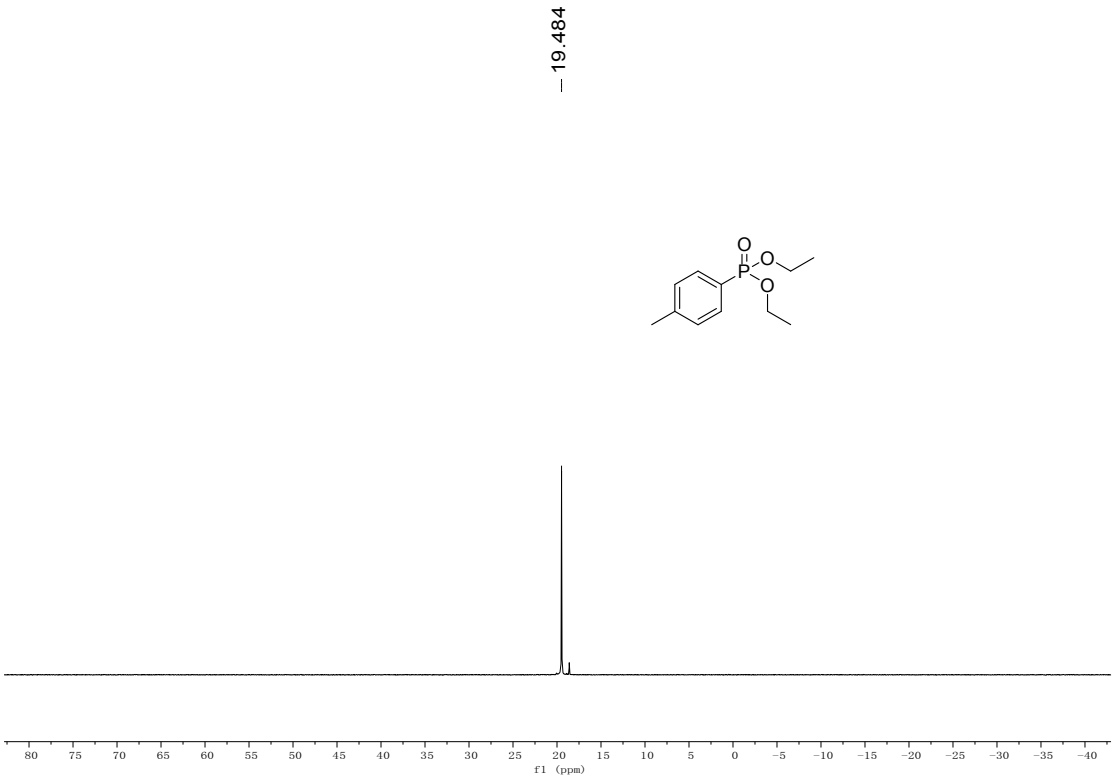


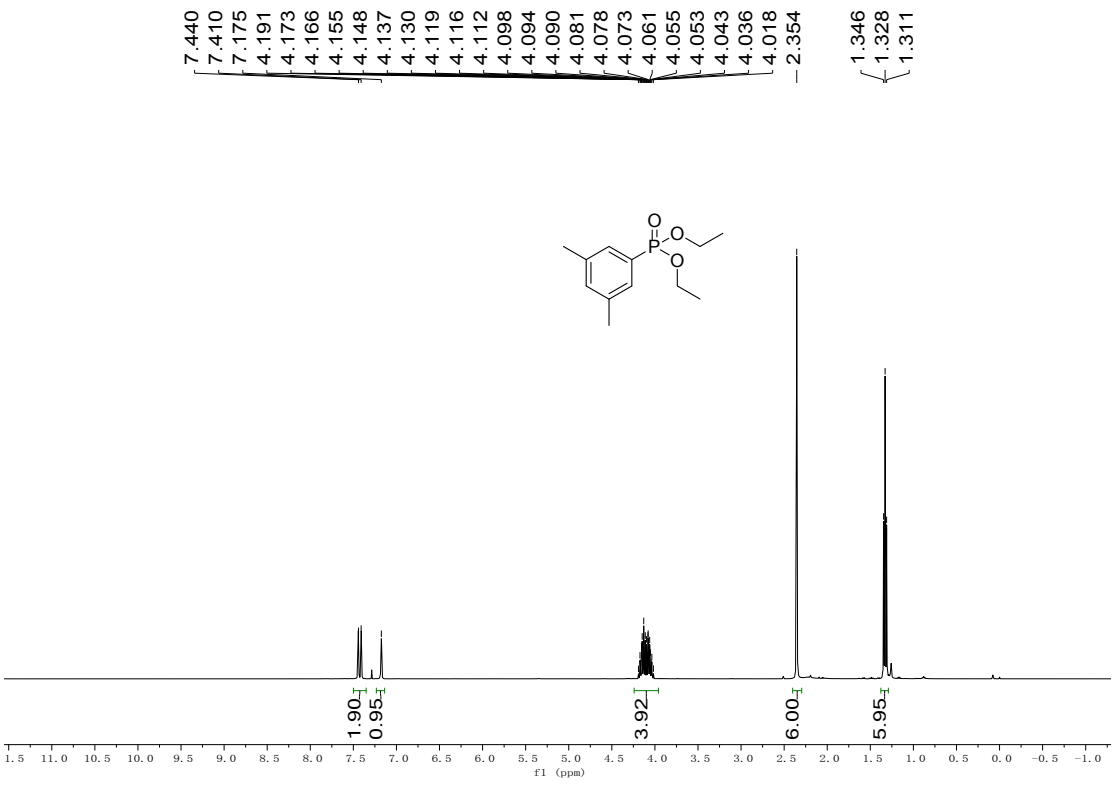

1.99
2.00
4.21
3.31
6.07
f1 (ppm)

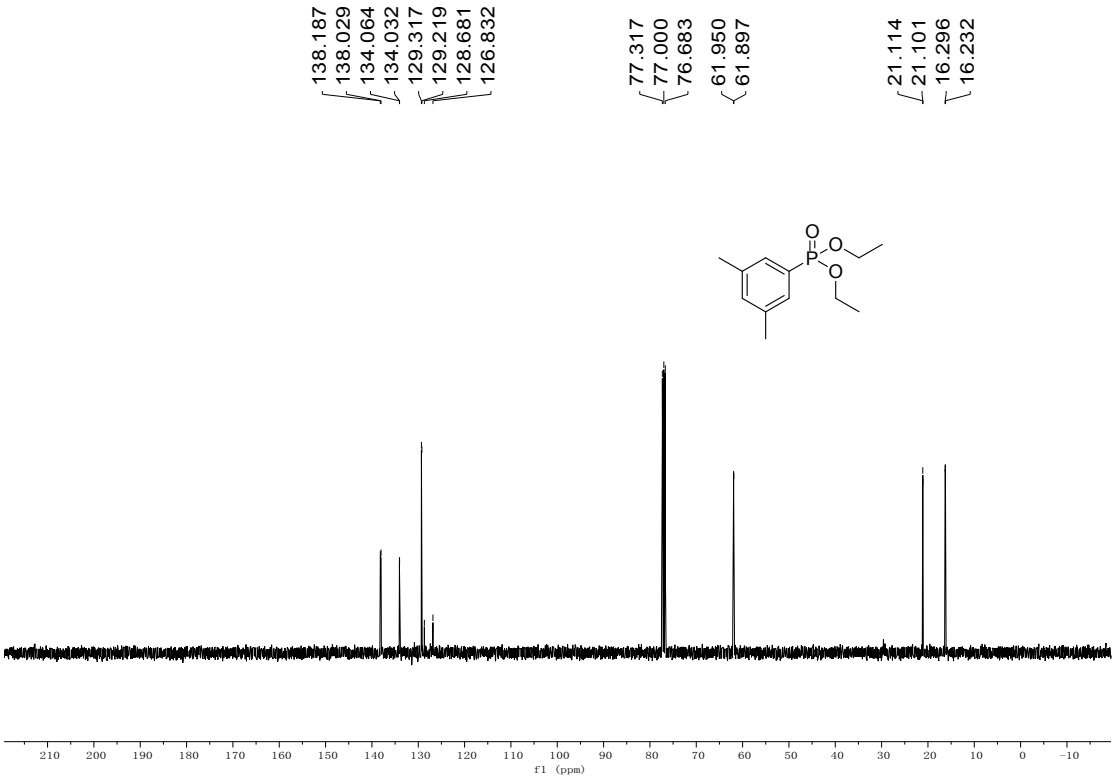

142.846
142.815
131.764
131.662
129.179
129.026
125.826
123.936
77.318
77.001
76.683
61.894
61.841
21.546
21.532
16.249
16.183

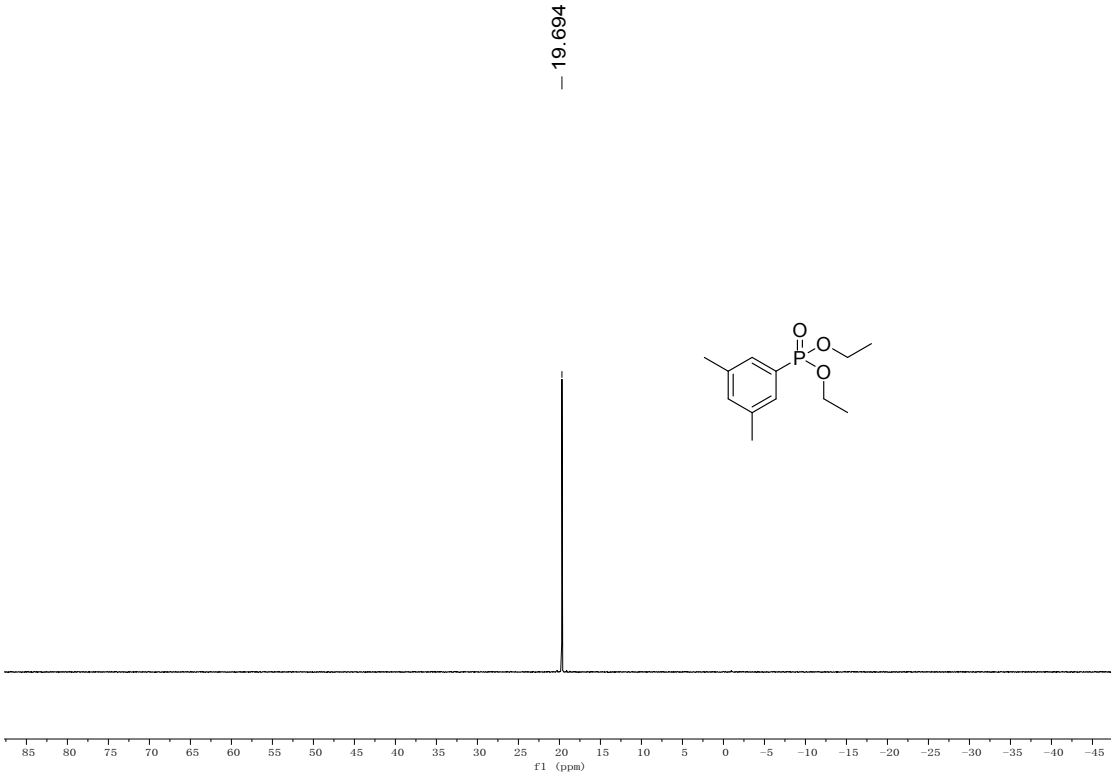


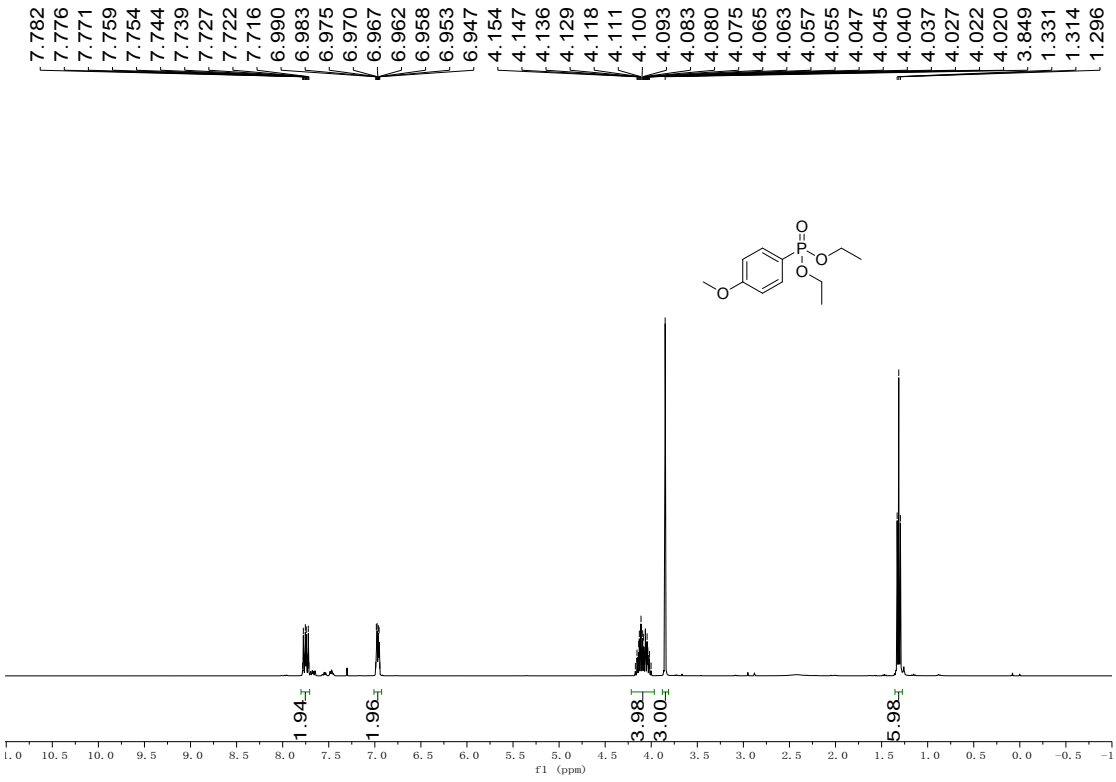

f1 (ppm)

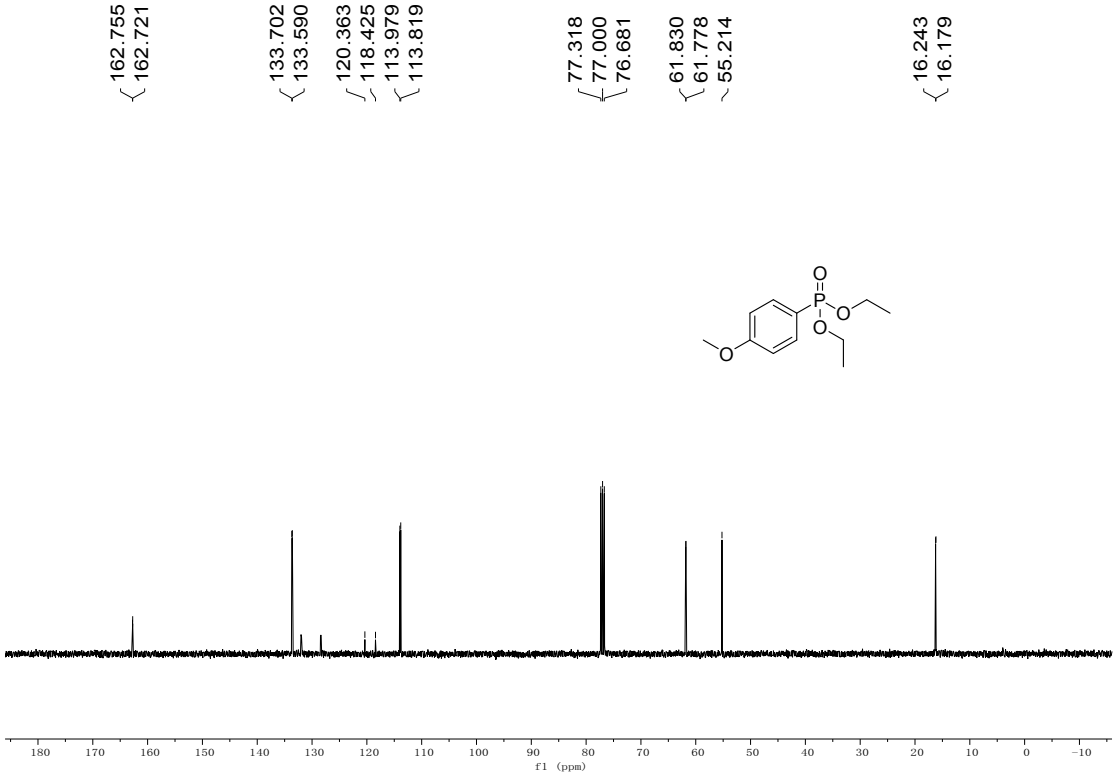

19.484
f1 (ppm)

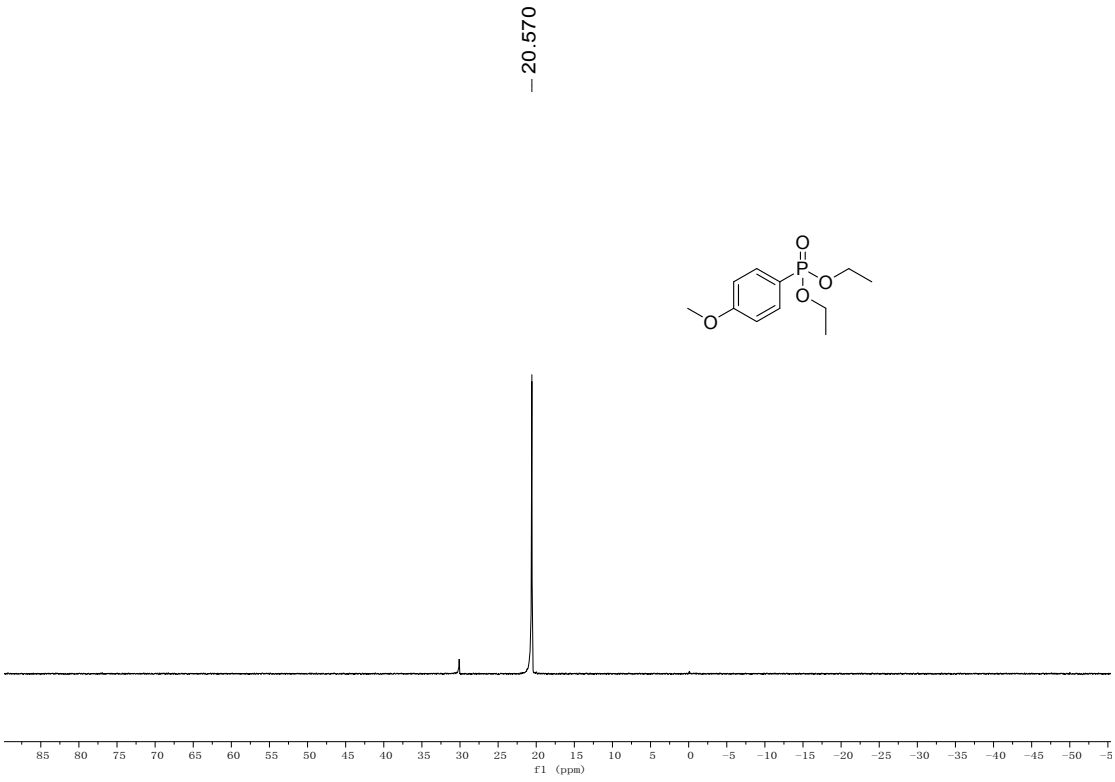

7.440
7.410
7.175
4.191
4.173
4.166
4.155
4.148
4.137
4.130
4.119
4.116
4.112
4.098
4.094
4.090
4.081
4.078
4.073
4.061
4.055
4.053
4.043
4.036
4.018
2.354
1.346
1.328
1.311
1.90
0.95
3.92
6.00
5.95
f1 (ppm)

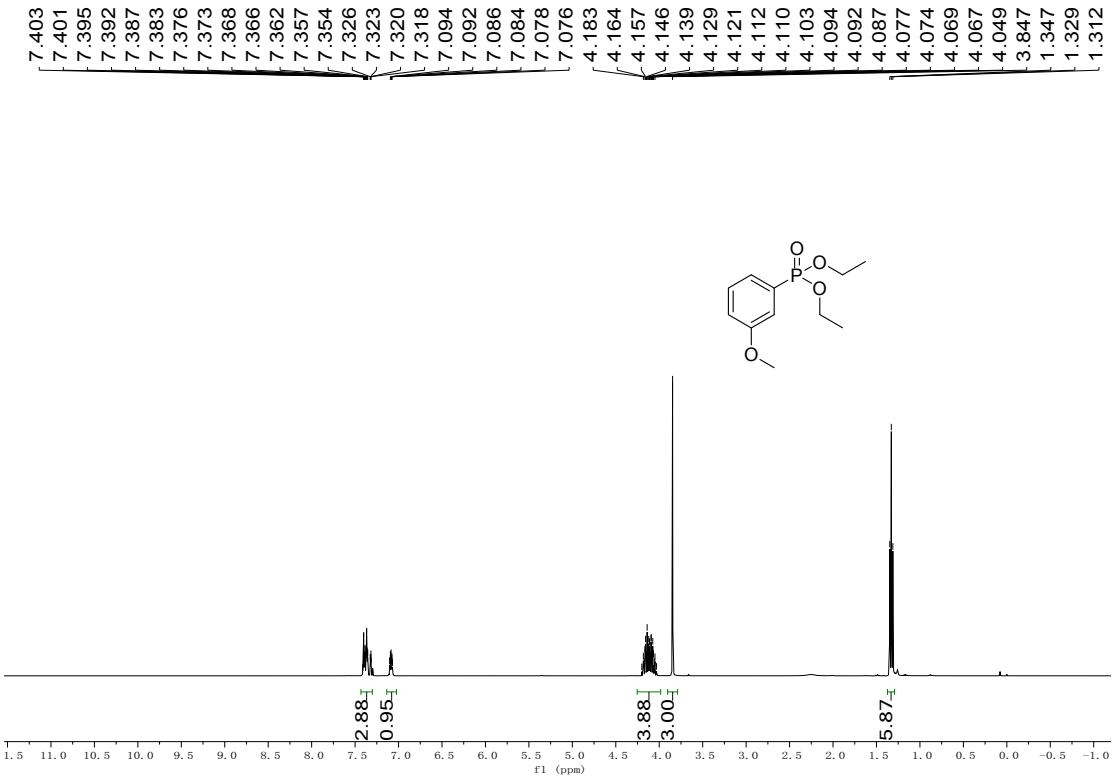

138.187
138.029
134.064
134.032
129.317
129.219
128.681
126.832
77.317
77.000
76.683
61.950
61.897
21.114
21.101
16.296
16.232
O
P
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

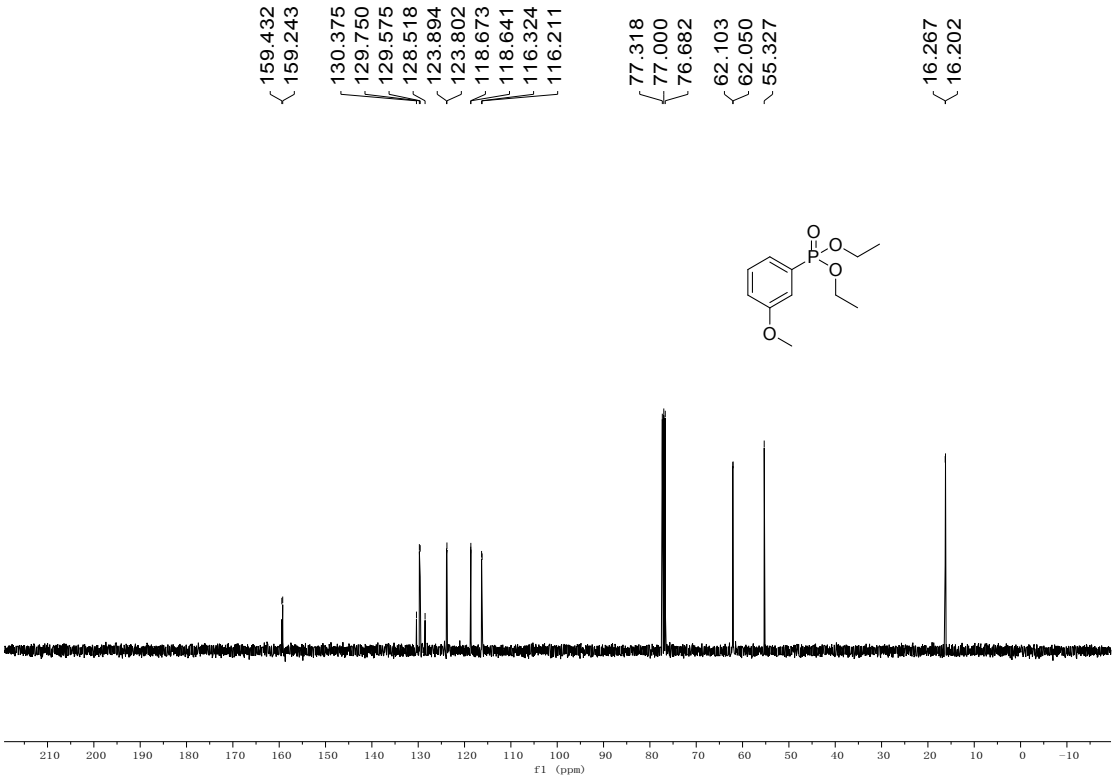

19.694
O
P
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45
f1 (ppm)

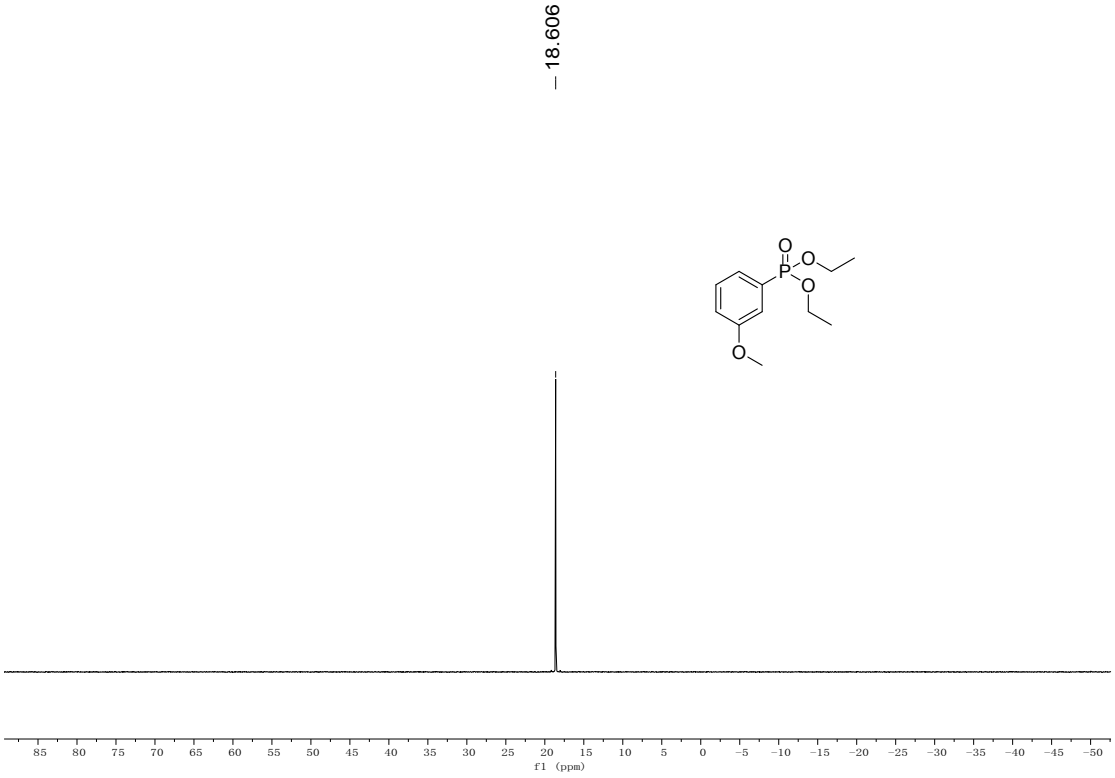

7.782
7.776
7.771
7.759
7.754
7.744
7.739
7.727
7.722
7.716
6.990
6.983
6.975
6.970
6.967
6.962
6.958
6.953
6.947
4.154
4.147
4.136
4.129
4.118
4.111
4.100
4.093
4.083
4.080
4.075
4.065
4.063
4.057
4.055
4.047
4.045
4.040
4.037
4.027
4.022
4.020
3.849
1.331
1.314
1.296
O
P
O
O
O
1.94
1.96
3.98
3.00
5.98
f1 (ppm)

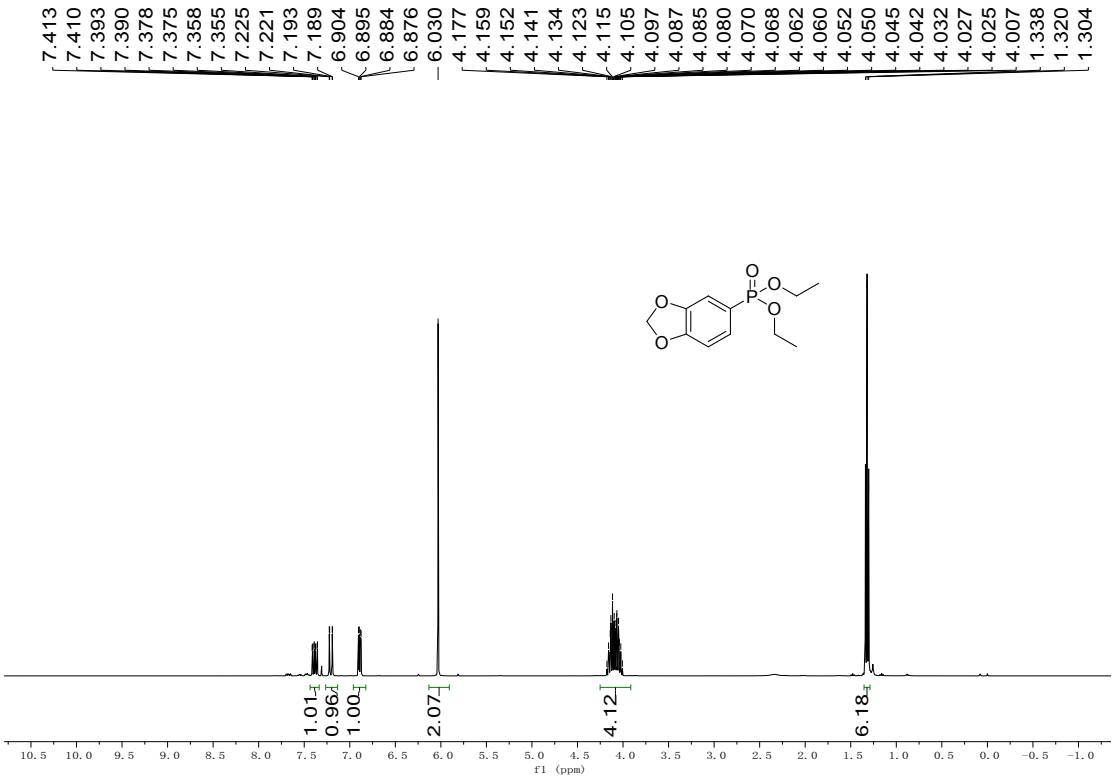

162.755
162.721
133.702
133.590
120.363
118.425
113.979
113.819
77.318
77.000
76.681
61.830
61.778
55.214
16.243
16.179
O
P
O
O
O
f1 (ppm)

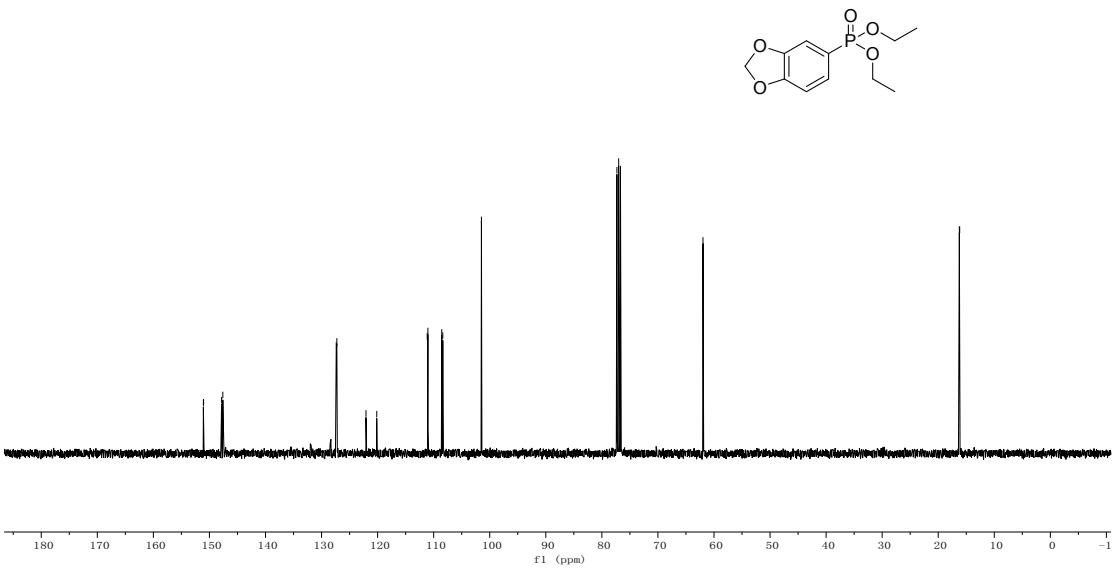

20.570
f1 (ppm)

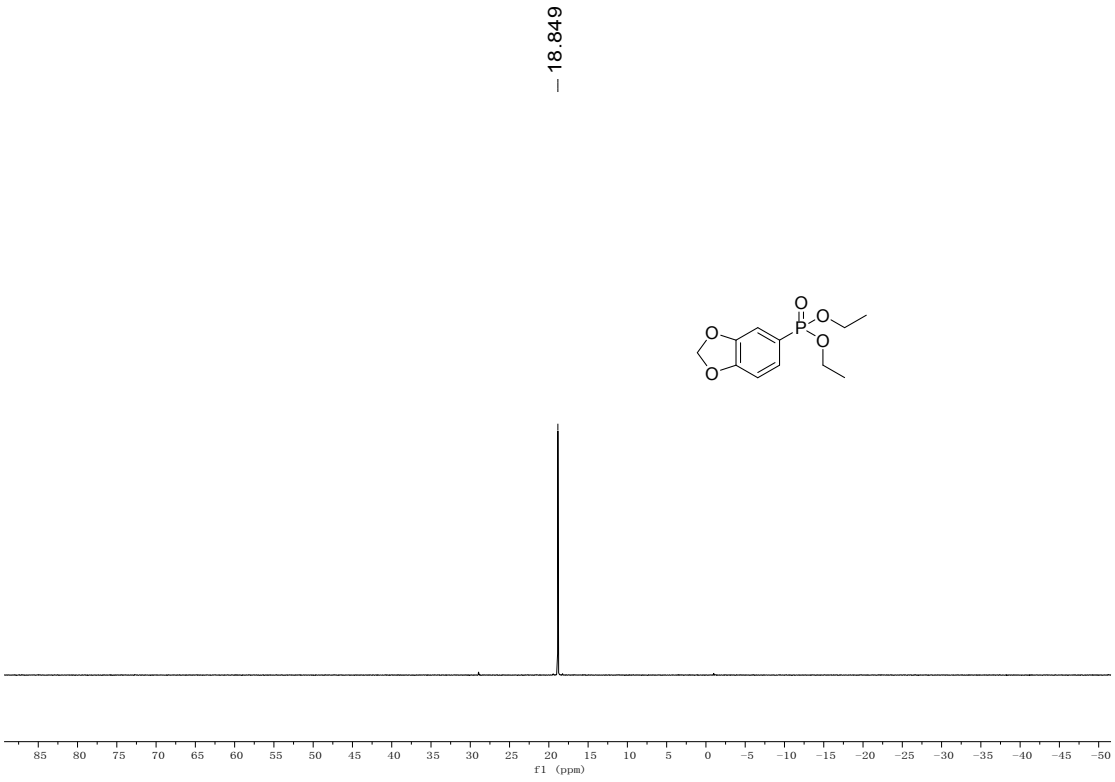

7.403
7.401
7.395
7.392
7.387
7.383
7.376
7.373
7.368
7.366
7.362
7.357
7.354
7.326
7.323
7.320
7.318
7.094
7.092
7.086
7.084
7.078
7.076
4.183
4.164
4.157
4.146
4.139
4.129
4.121
4.112
4.110
4.103
4.094
4.092
4.087
4.077
4.074
4.069
4.067
4.049
3.847
1.347
1.329
1.312
2.88
0.95
3.88
3.00
5.87
f1 (ppm)

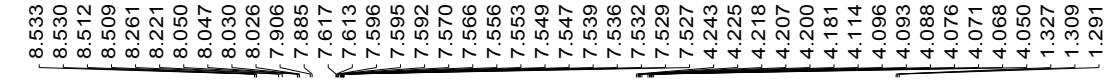

159.432
159.243
130.375
129.750
129.575
128.518
123.894
123.802
118.673
118.641
116.324
116.211
77.318
77.000
76.682
62.103
62.050
55.327
16.267
16.202
O
P
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

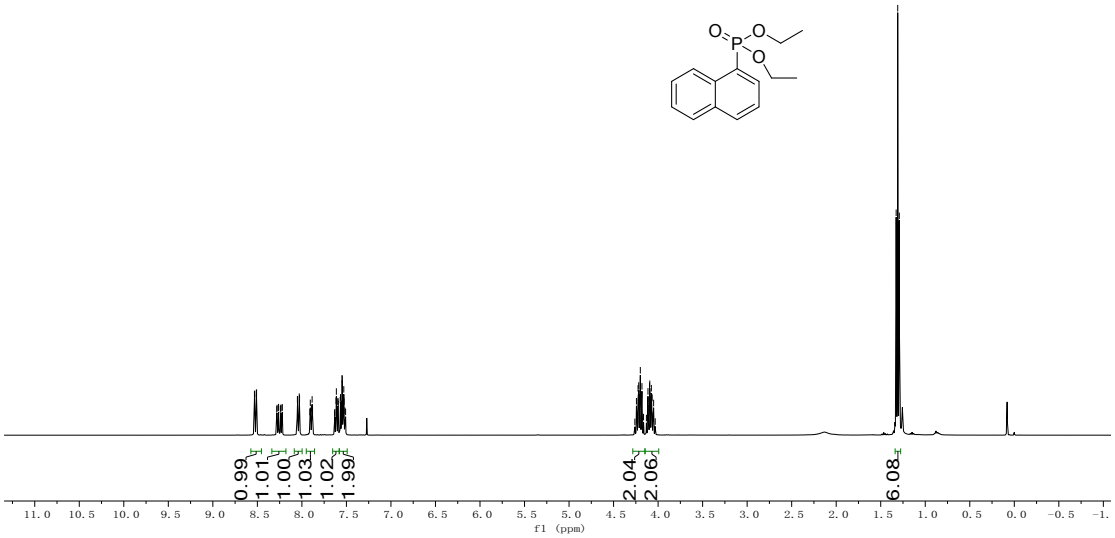

18.606
O
P
O
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

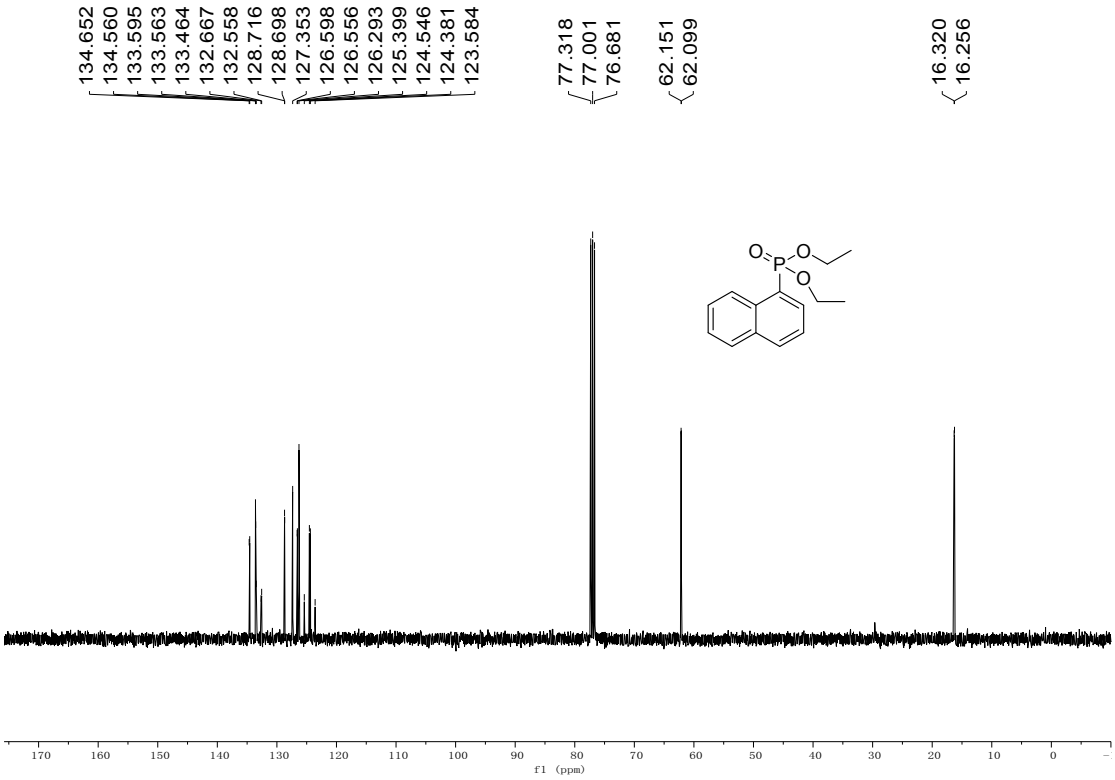

7.413
7.410
7.393
7.390
7.378
7.375
7.358
7.355
7.225
7.221
7.193
7.189
6.904
6.895
6.884
6.876
6.030
4.177
4.159
4.152
4.141
4.134
4.123
4.115
4.105
4.097
4.087
4.085
4.080
4.070
4.068
4.062
4.060
4.052
4.050
4.045
4.042
4.032
4.027
4.025
4.007
1.338
1.320
1.304
1.01
0.96
1.00
2.07
4.12
6.18
f1 (ppm)

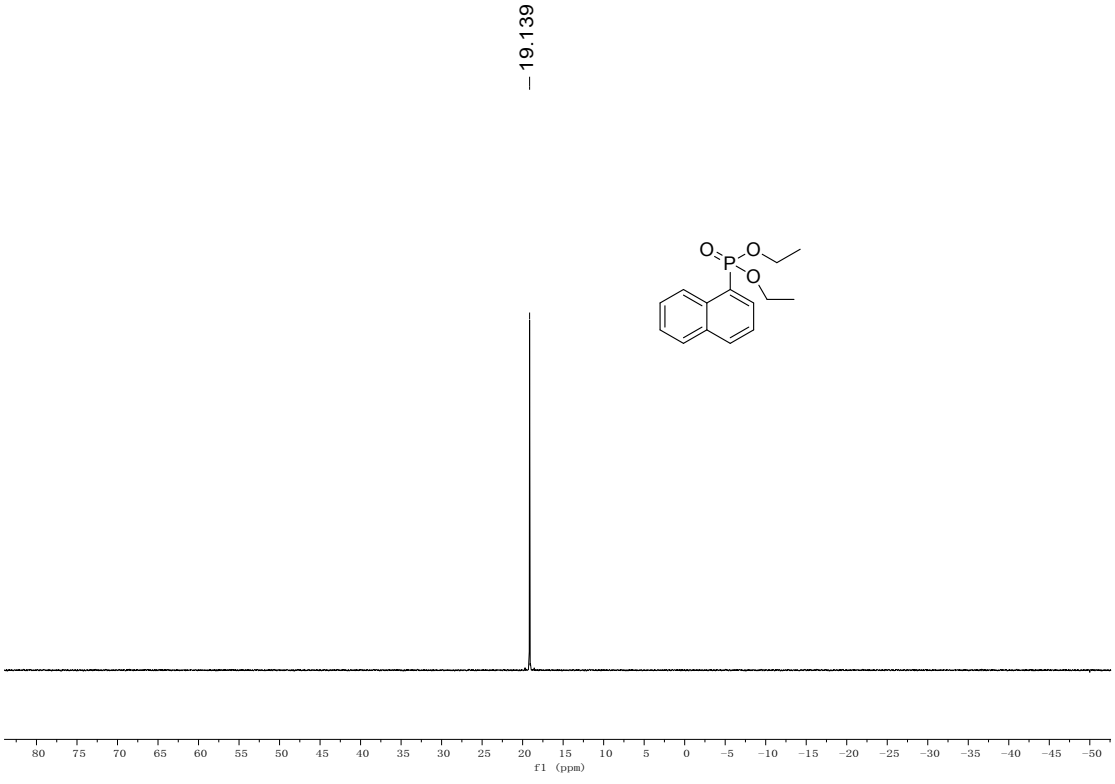

151.078
151.042
147.833
147.608
127.383
127.272
122.075
120.153
111.153
111.031
108.560
108.374
101.482
77.317
76.999
76.681
61.963
61.910
16.236
16.170
f1 (ppm)

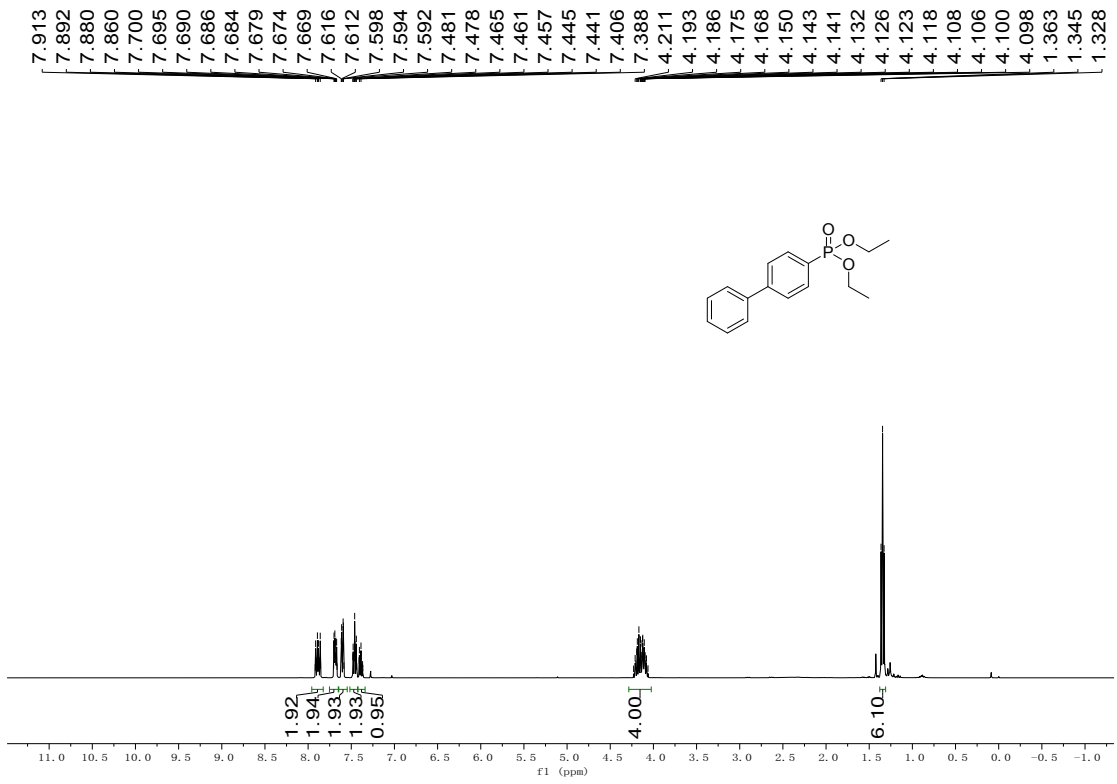

18.849
O
O
O
P
O
O
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

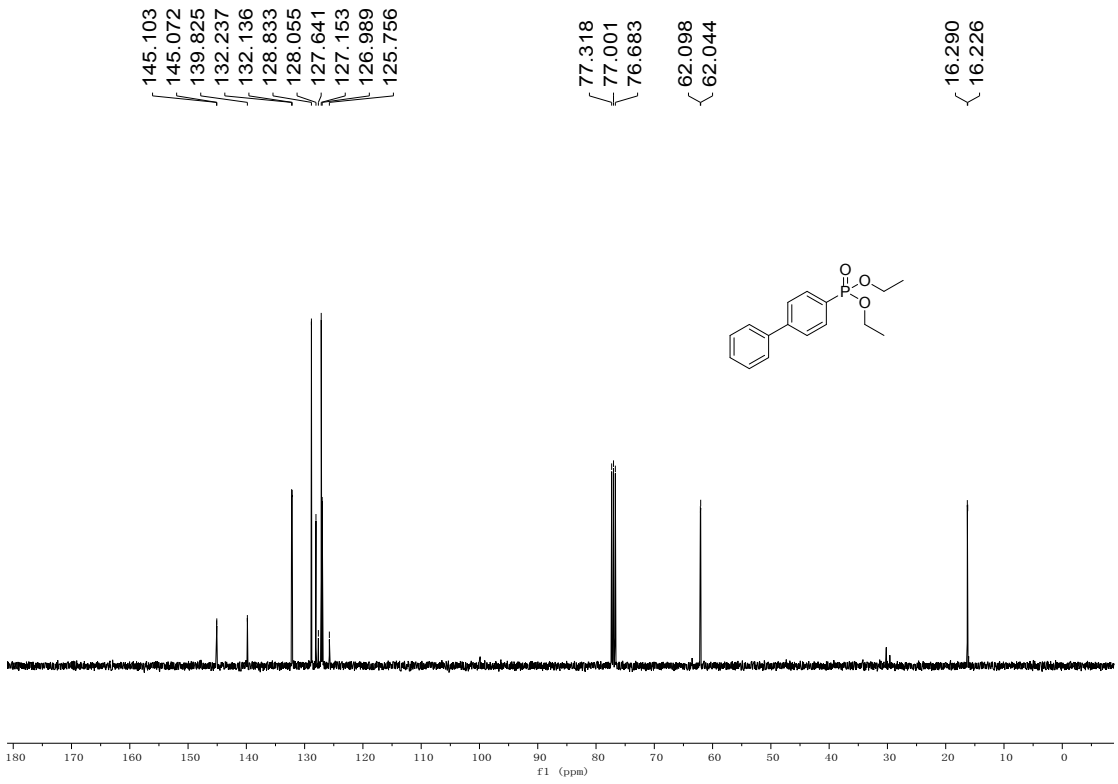

8.533
8.530
8.512
8.509
8.261
8.221
8.050
8.047
8.030
8.026
7.906
7.885
7.617
7.613
7.596
7.595
7.592
7.570
7.566
7.556
7.553
7.549
7.547
7.539
7.536
7.532
7.529
7.527
4.243
4.225
4.218
4.207
4.200
4.181
4.114
4.096
4.093
4.088
4.076
4.071
4.068
4.050
1.327
1.309
1.291

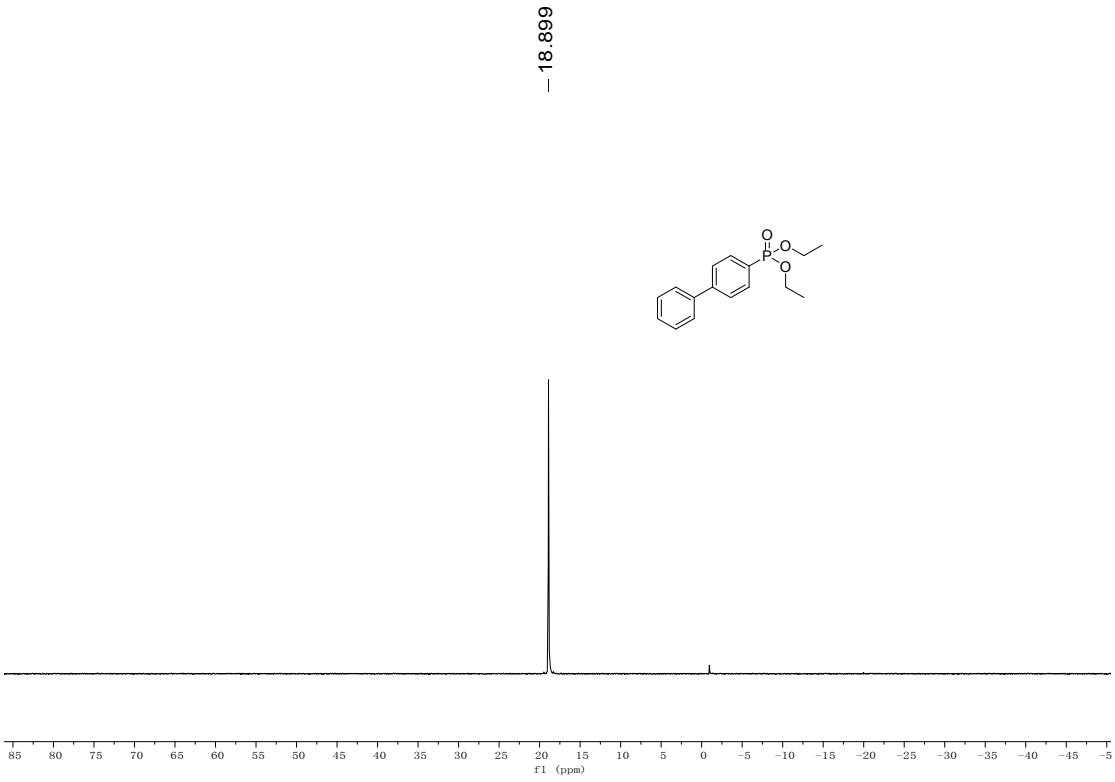

O
P
O
O
0.99
1.01
1.00
1.03
1.02
1.99
2.04
2.06
6.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

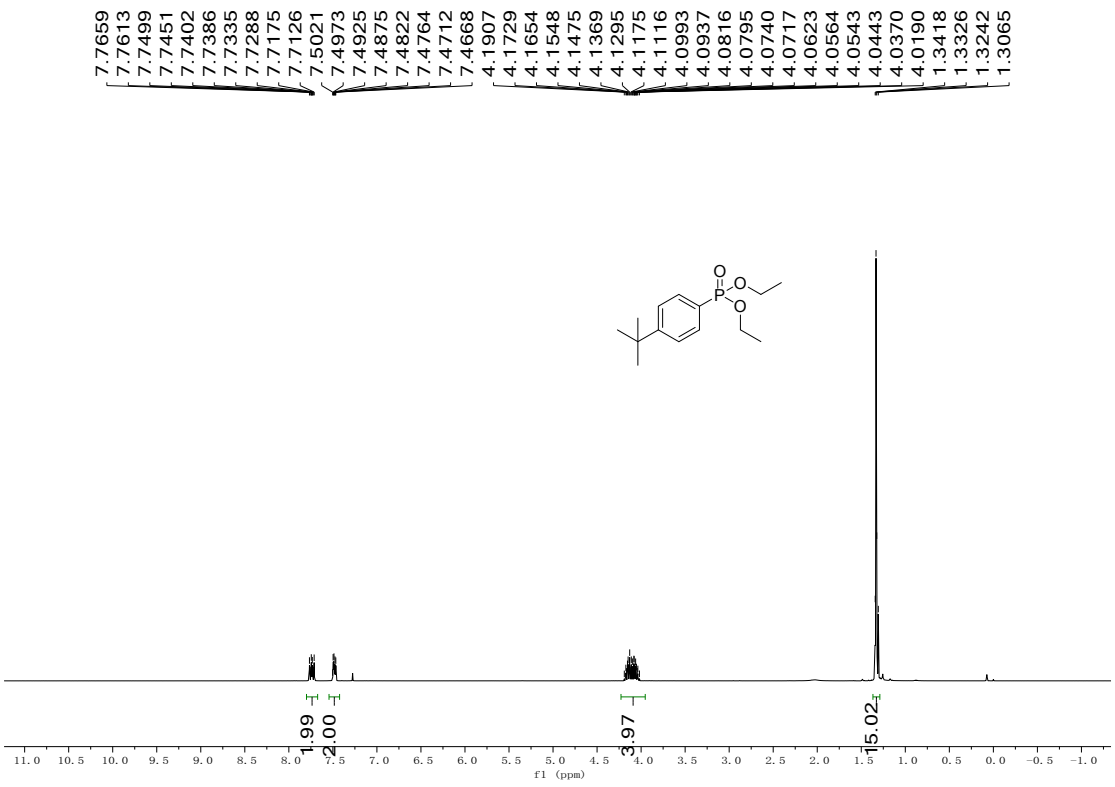

134.652
134.560
133.595
133.563
133.464
132.667
132.558
128.716
128.698
127.353
126.598
126.556
126.293
125.399
124.546
124.381
123.584
77.318
77.001
76.681
62.151
62.099
16.320
16.256
O
P
O
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

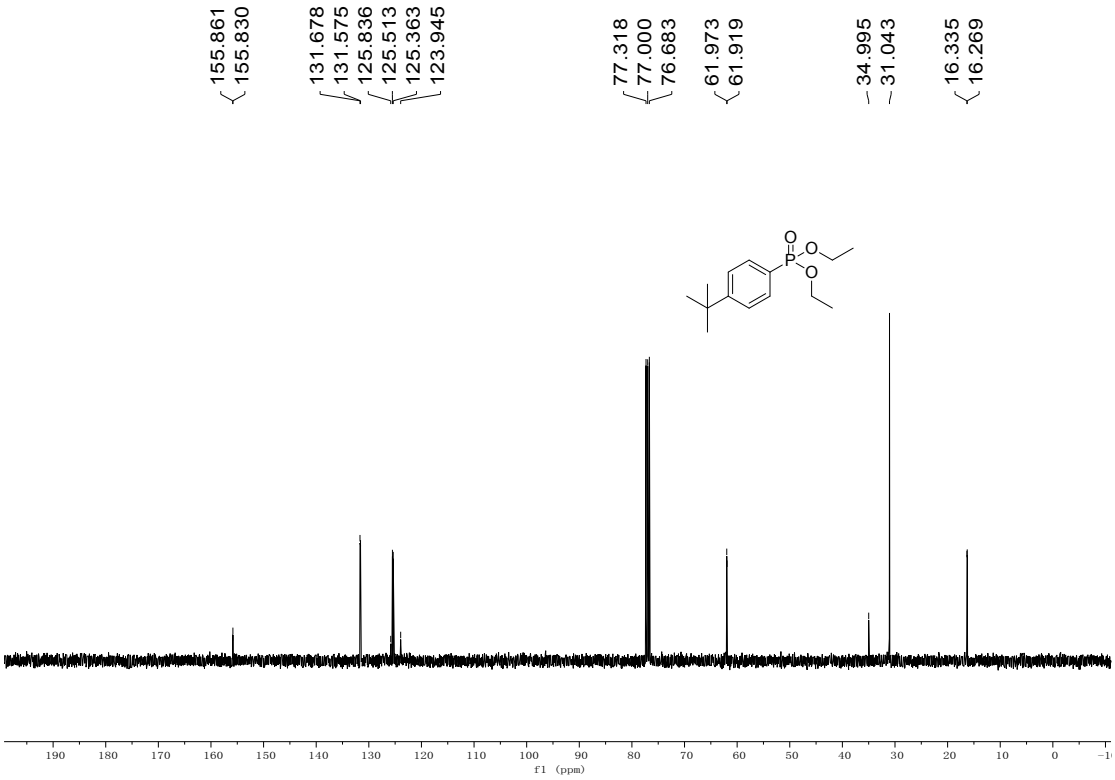

19.139
O
P
O
O
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

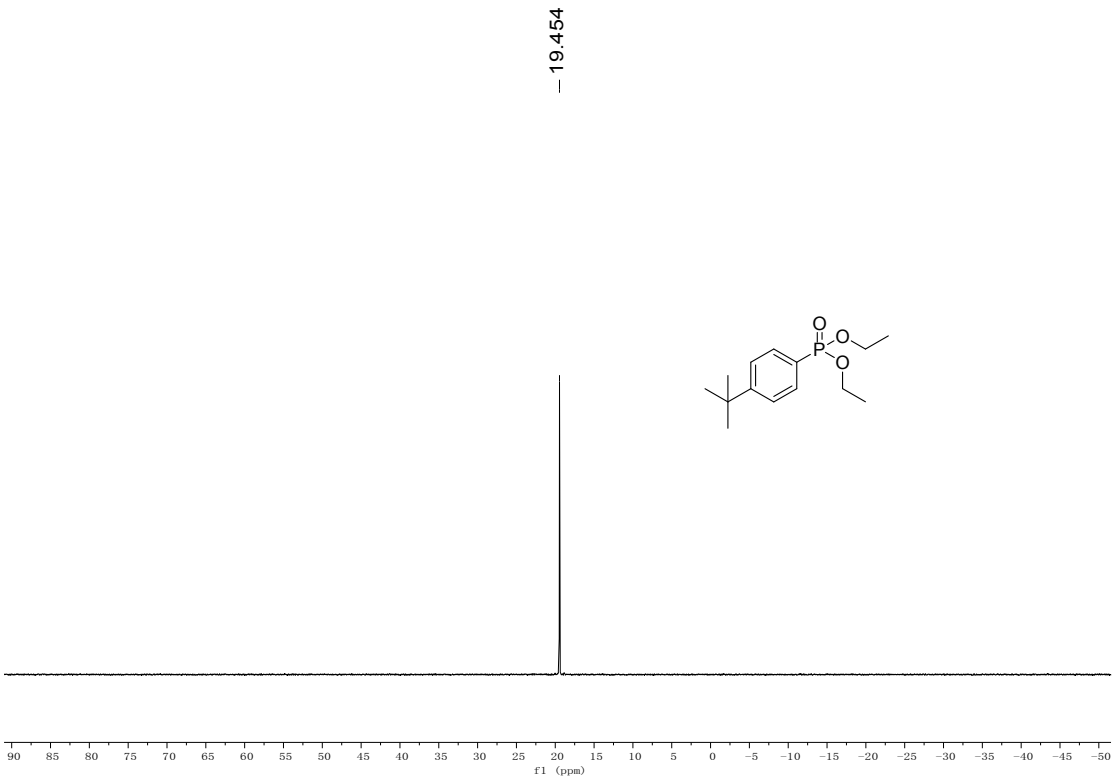

7.913
7.892
7.880
7.860
7.700
7.695
7.690
7.686
7.684
7.679
7.674
7.669
7.616
7.612
7.598
7.594
7.592
7.481
7.478
7.465
7.461
7.457
7.445
7.441
7.406
7.388
4.211
4.193
4.186
4.175
4.168
4.150
4.143
4.141
4.132
4.126
4.123
4.118
4.108
4.106
4.100
4.098
1.363
1.345
1.328
O
P
O
O
1.92
1.94
1.93
1.93
0.95
4.00
6.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

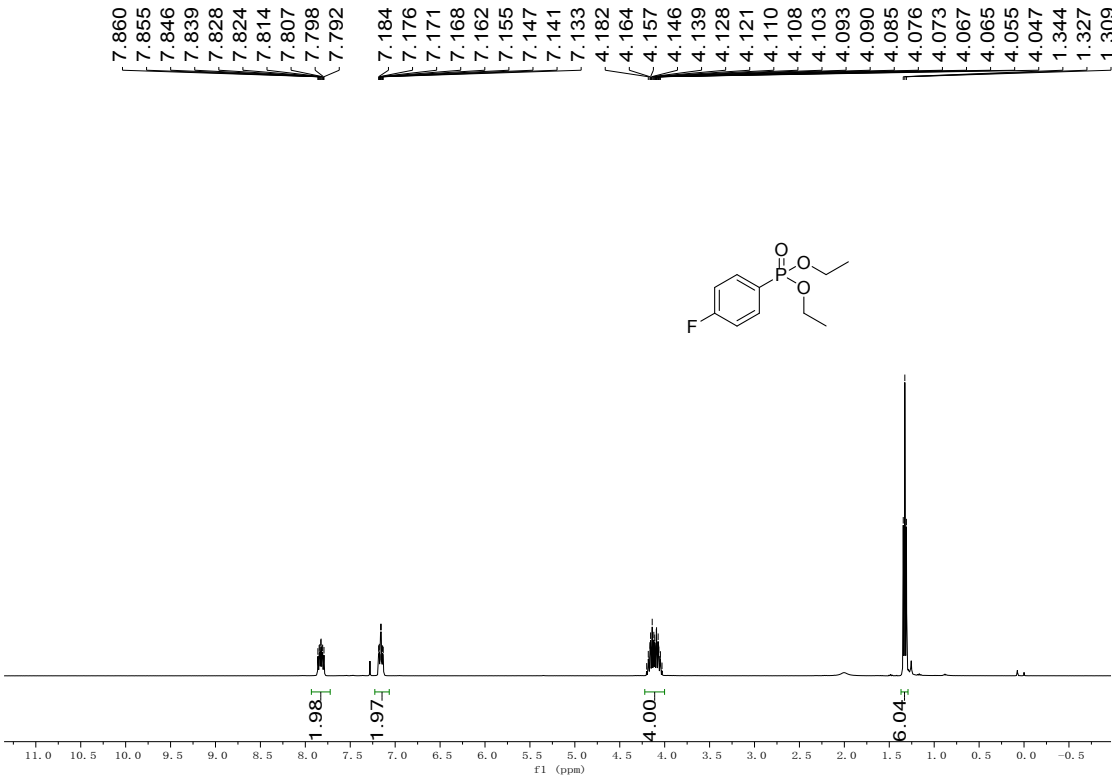

145.103
145.072
139.825
132.237
132.136
128.833
128.055
127.641
127.153
126.989
125.756
77.318
77.001
76.683
62.098
62.044
16.290
16.226
O
P
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

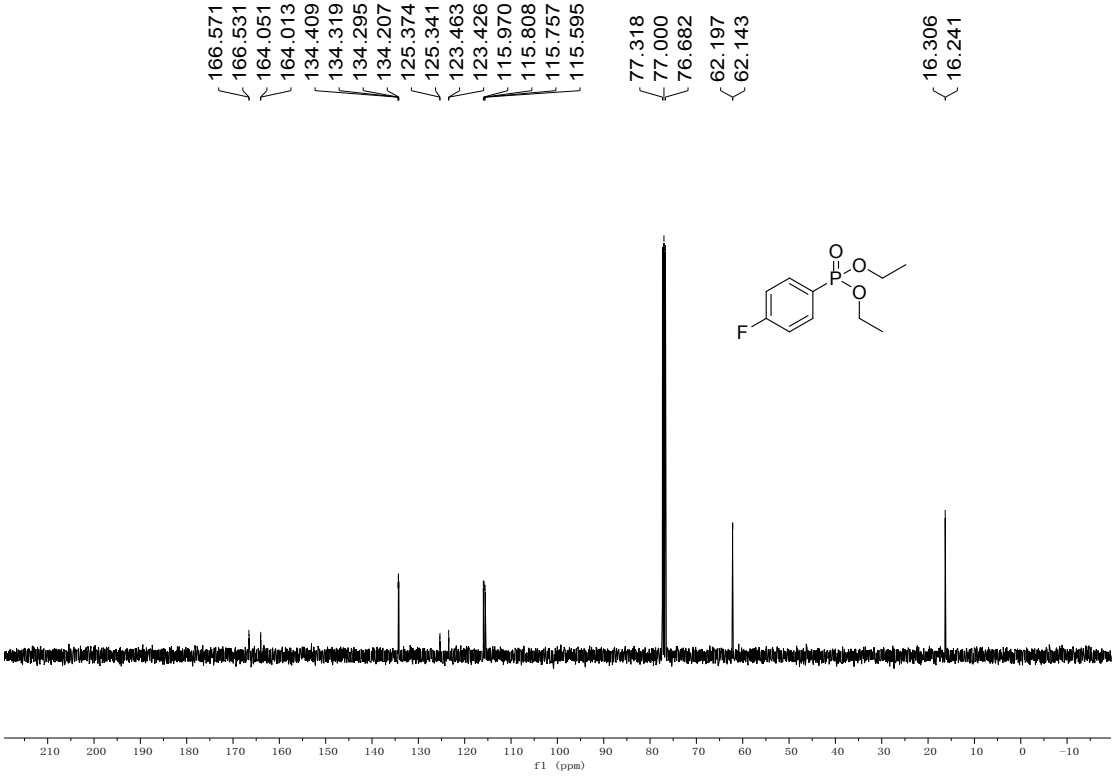

18.899
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -5
f1 (ppm)

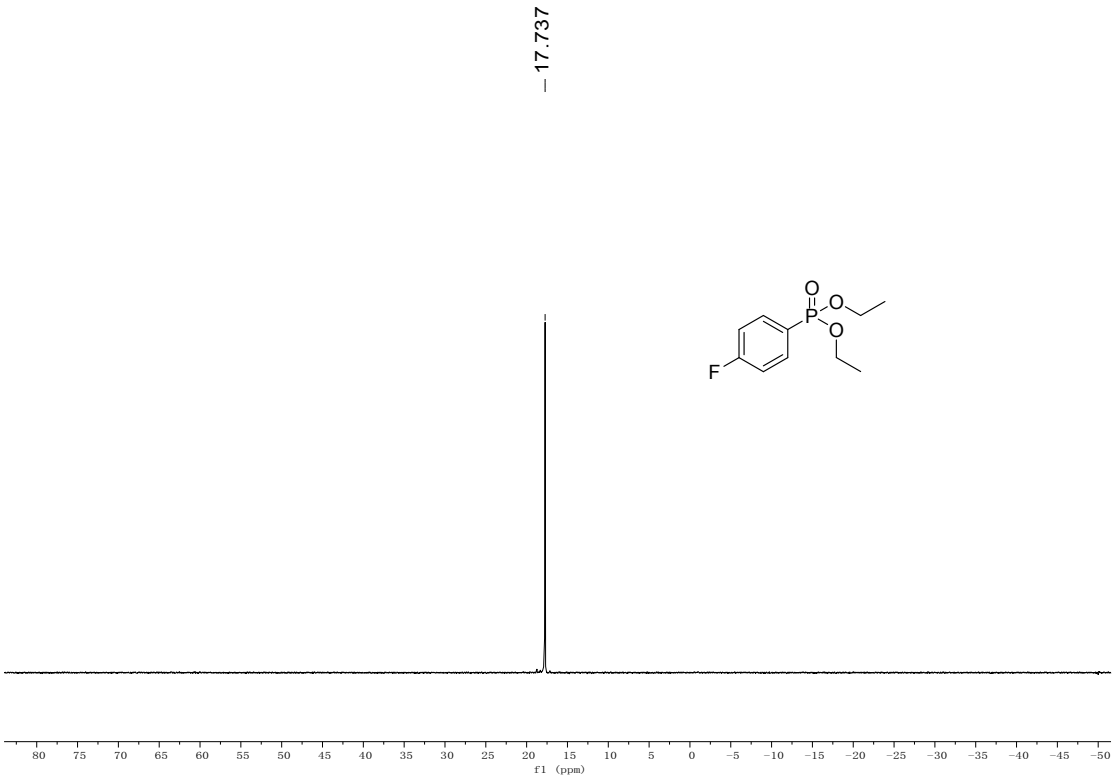

7.7659
7.7613
7.7499
7.7451
7.7402
7.7386
7.7335
7.7288
7.7175
7.7126
7.5021
7.4973
7.4925
7.4875
7.4822
7.4764
7.4712
7.4668
4.1907
4.1729
4.1654
4.1548
4.1475
4.1369
4.1295
4.1175
4.1116
4.0993
4.0937
4.0816
4.0795
4.0740
4.0717
4.0623
4.0564
4.0543
4.0443
4.0370
4.0190
1.3418
1.3326
1.3242
1.3065
1.99
2.00
3.97
15.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

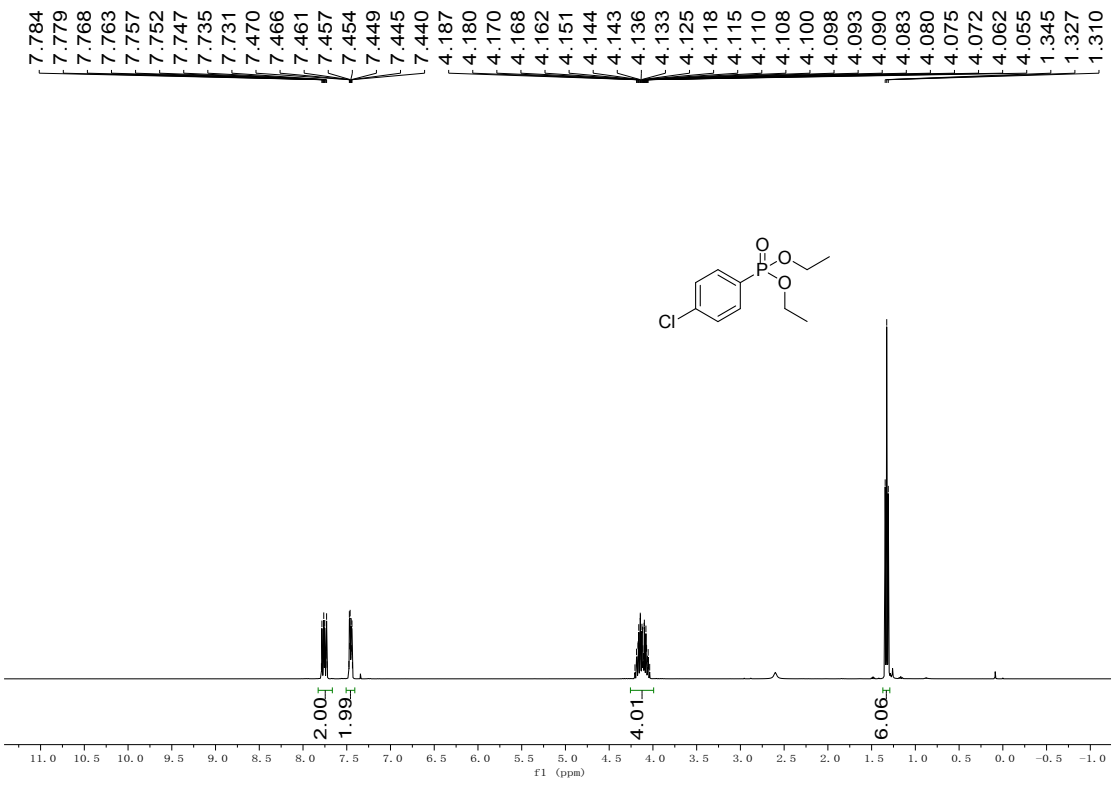

155.861
155.830
131.678
131.575
125.836
125.513
125.363
123.945
77.318
77.000
76.683
61.973
61.919
34.995
31.043
16.335
16.269
f1 (ppm)

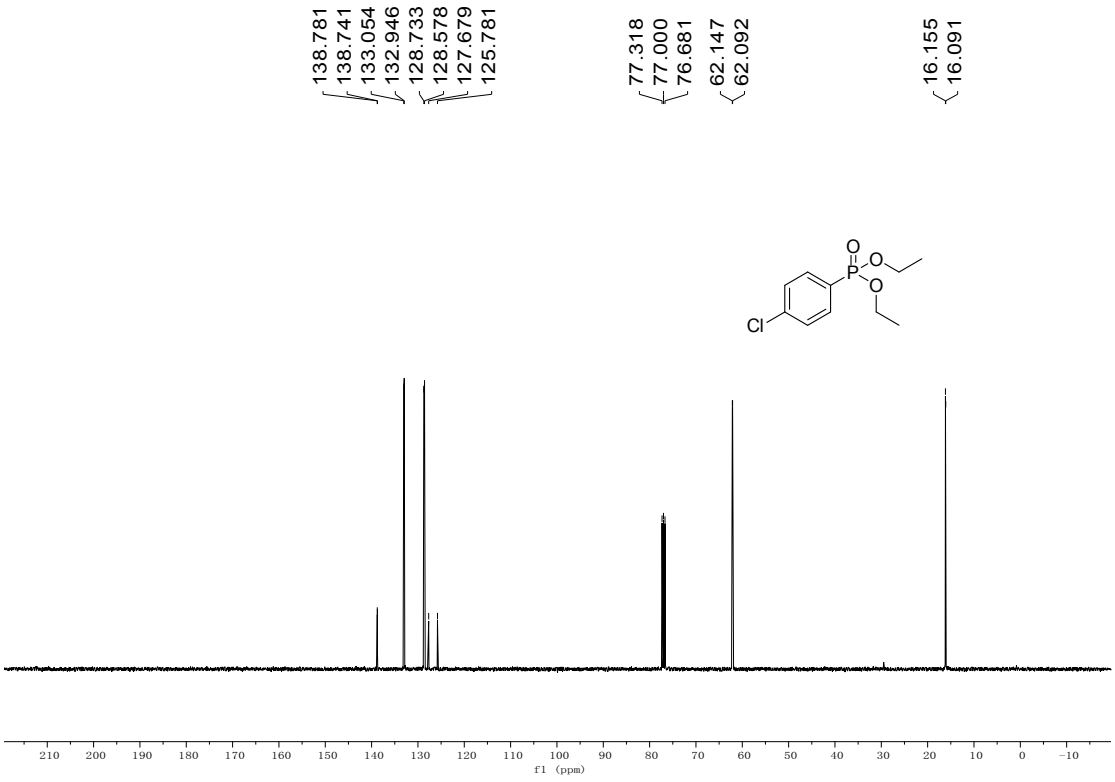

19.454
f1 (ppm)

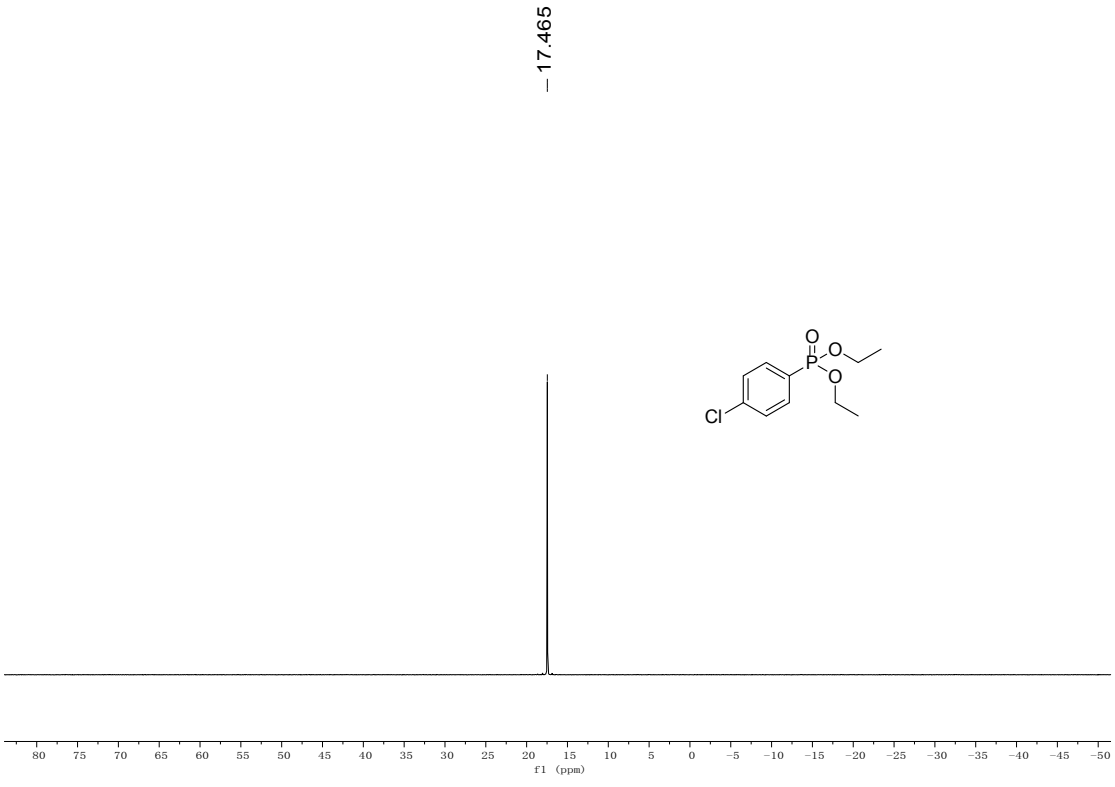

7.860
7.855
7.846
7.839
7.828
7.824
7.814
7.807
7.798
7.792
7.184
7.176
7.171
7.168
7.162
7.155
7.147
7.141
7.133
4.182
4.164
4.157
4.146
4.139
4.128
4.121
4.110
4.108
4.103
4.093
4.090
4.085
4.076
4.073
4.067
4.065
4.055
4.047
1.344
1.327
1.309
O
P
O
O
F
1.98
1.97
4.00
6.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

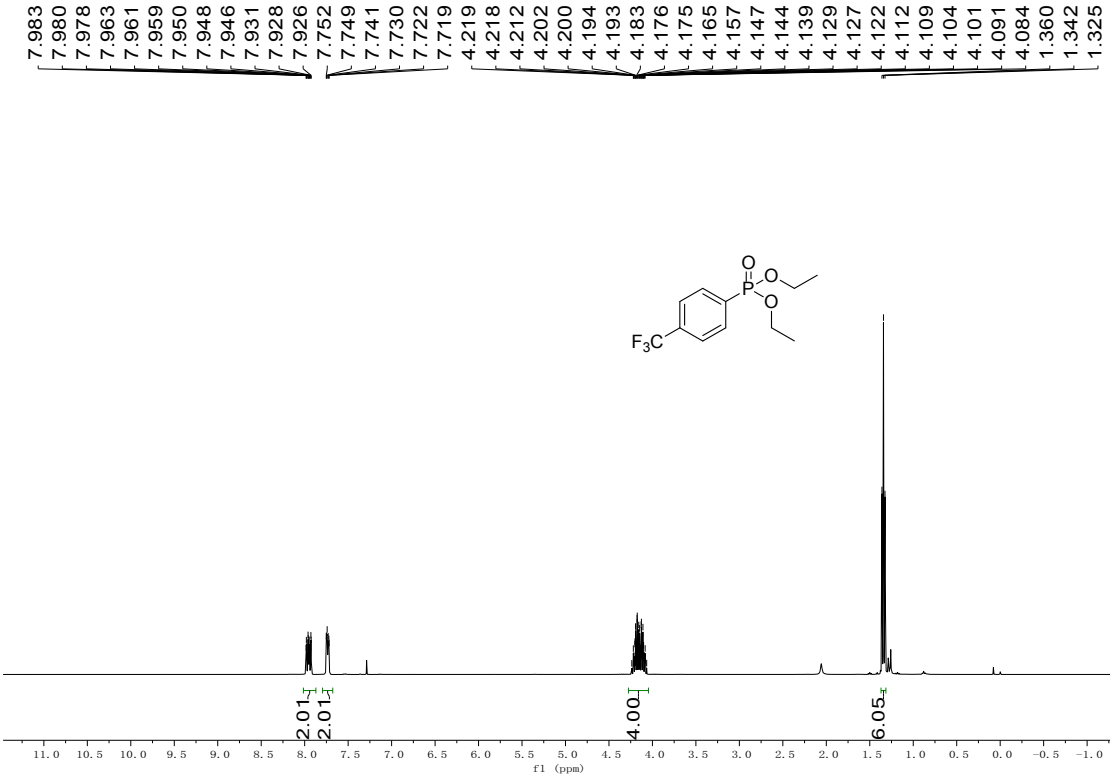

166.571
166.531
164.051
164.013
134.409
134.319
134.295
134.207
125.374
125.341
123.463
123.426
115.970
115.808
115.757
115.595
77.318
77.000
76.682
62.197
62.143
16.306
16.241
O
P
O
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

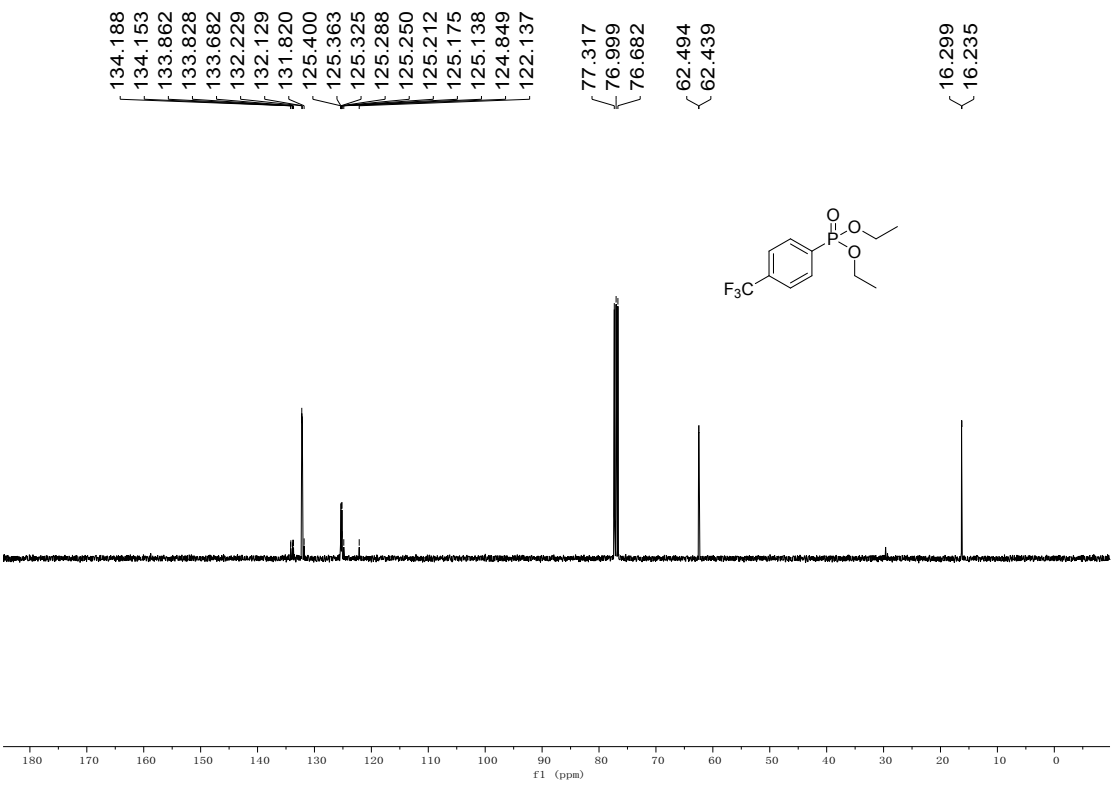

17.737
F
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

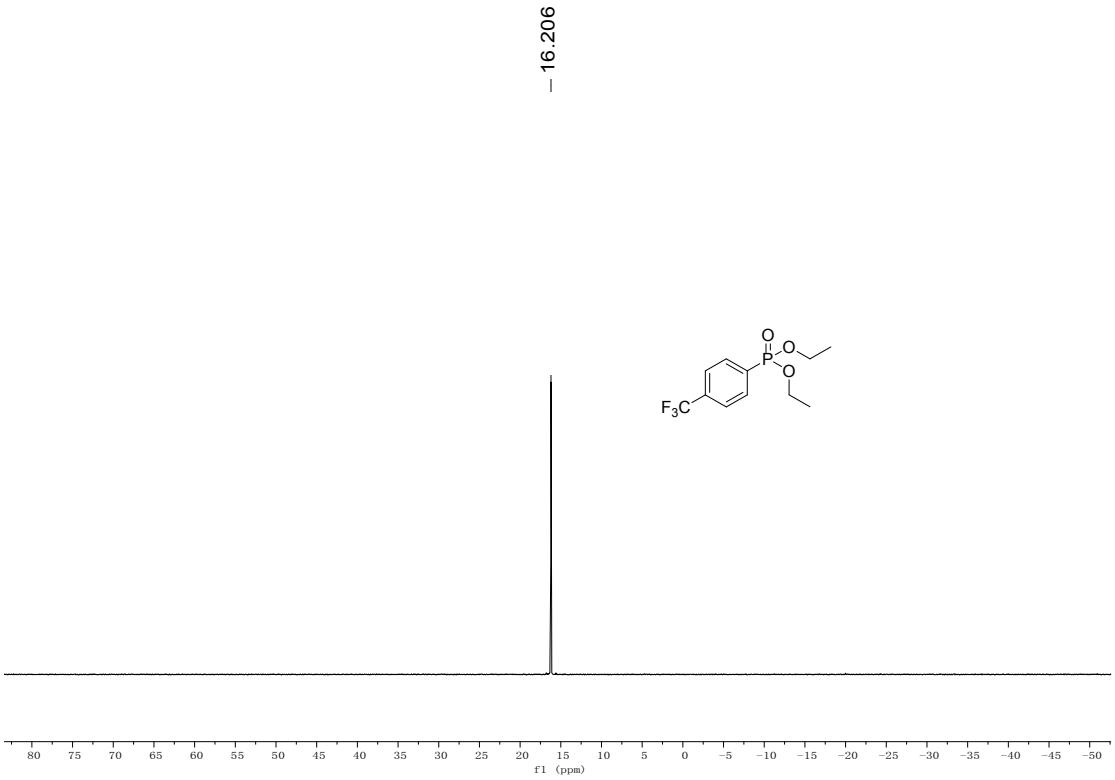

7.784
7.779
7.768
7.763
7.757
7.752
7.747
7.735
7.731
7.470
7.466
7.461
7.457
7.454
7.449
7.445
7.440
4.187
4.180
4.170
4.168
4.162
4.151
4.144
4.143
4.136
4.133
4.125
4.118
4.115
4.110
4.108
4.100
4.098
4.093
4.090
4.083
4.080
4.075
4.072
4.062
4.055
1.345
1.327
1.310
Cl
2.00
1.99
4.01
6.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

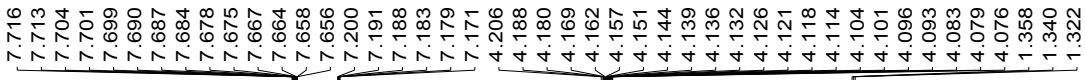

138.781
138.741
133.054
132.946
128.733
128.578
127.679
125.781
77.318
77.000
76.681
62.147
62.092
16.155
16.091
O
P
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

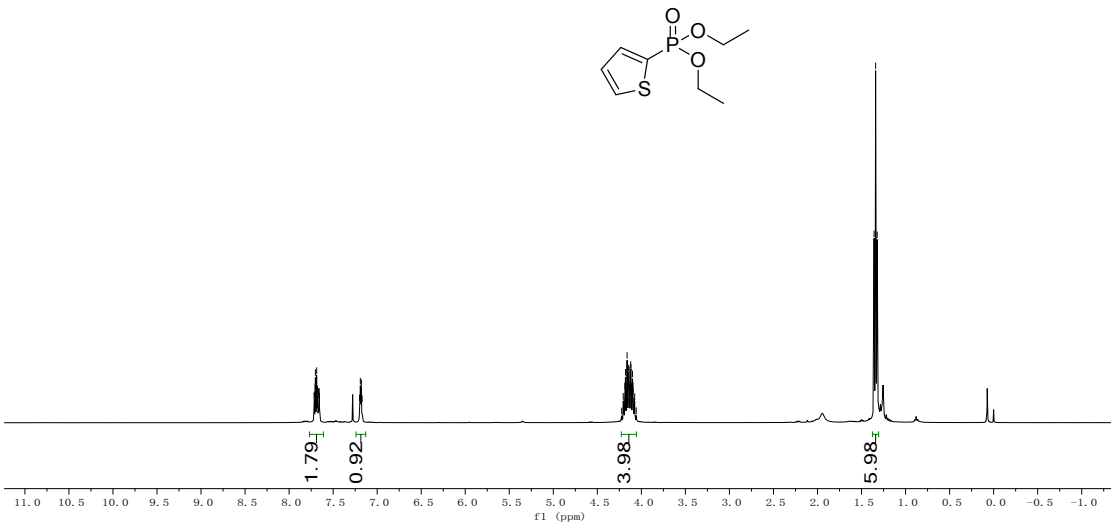

17.465
O
P
O
O
Cl
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

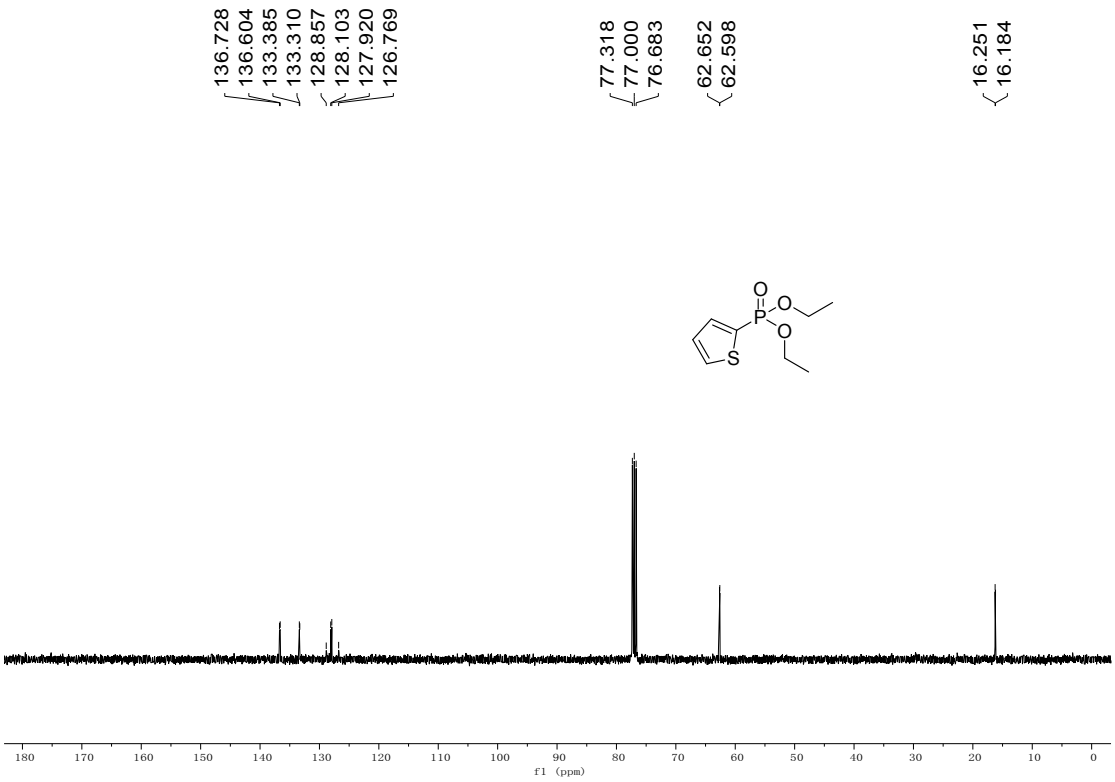

7.983
7.980
7.978
7.963
7.961
7.959
7.950
7.948
7.946
7.931
7.928
7.926
7.752
7.749
7.741
7.730
7.722
7.719
4.219
4.218
4.212
4.202
4.200
4.194
4.193
4.183
4.176
4.175
4.165
4.157
4.147
4.144
4.139
4.129
4.127
4.122
4.112
4.109
4.104
4.101
4.091
4.084
1.360
1.342
1.325
O
P
O
O
F3C
2.01
2.01
4.00
6.05
f1 (ppm)

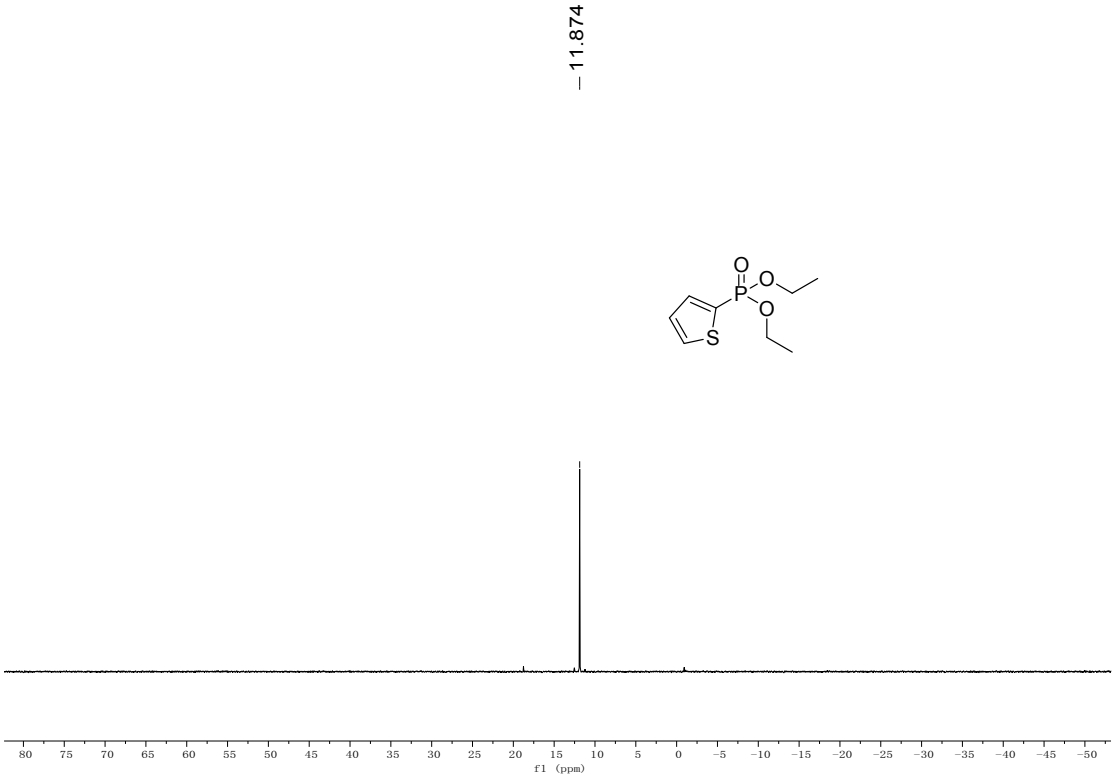

134.188
134.153
133.862
133.828
133.682
132.229
132.129
131.820
125.400
125.363
125.325
125.288
125.250
125.212
125.175
125.138
124.849
122.137
77.317
76.999
76.682
62.494
62.439
16.299
16.235
O
P
O
O
F3C
f1 (ppm)


16.206
O
P
O
O
F3C
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)


7.716
7.713
7.704
7.701
7.699
7.690
7.687
7.684
7.678
7.675
7.667
7.664
7.658
7.656
7.200
7.191
7.188
7.183
7.179
7.171
4.206
4.188
4.180
4.169
4.162
4.157
4.151
4.144
4.139
4.136
4.132
4.126
4.121
4.118
4.114
4.104
4.101
4.096
4.093
4.083
4.079
4.076
1.358
1.340
1.322


O
P
O
O
S
1.79
0.92
3.98
5.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


136.728
136.604
133.385
133.310
128.857
128.103
127.920
126.769
77.318
77.000
76.683
62.652
62.598
16.251
16.184
O
P
O
O
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.874
O
P
O
O
S
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40 −45 −50
f1 (ppm)

5. References.

[1] A. S. Manoso, C. Ahn, A. Soheili, C. J. Handy, R. Correia, W. M. Seganish, P. DeShong, *J. Org. Chem.*, 2004, **69**, 8305.

[2] R. Zhuang, J. Xu, Z. Cai, G. Tang, M. Fang, Y. Zhao, *Org. Lett*., 2011, **13**, 2110.

[3] W. Xu, G. Hu, P. Xu, Y. Gao, Y. Yin, Y. Zhao, *Adv. Synth. Catal* , 2014, **356**, 2948.

[4] R. A. Dhokale, S. B. Mhaske, *Org. Lett*., 2013, **15**, 2218.

[5] T. Miao, L. Wang, *Adv. Synth. Catal* , 2014, **356**, 967.

[6] C-B. Xiang, Y-J. Bian, X-R. Mao, Z-Z. Huang. *J. Org. Chem* , 2012, **77**, 7706.