First Reusable Ligand-Free Palladium Catalyzed C-P Bond Formation of Aryl Halides With Trialkylphosphites in Neat Water

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Supporting Information

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1. General considerations:

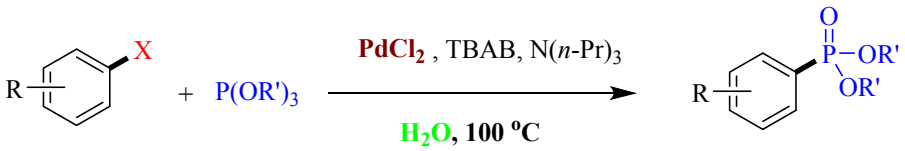
1.1 Reagents:

All the palladium catalysts have purity greater than 97% and arylhalides were reagent grade. All reagents and solvents were obtained from commercial suppliers and used without further purification.

1.2 Analytical methods:

^{1}H and ^{13}C spectra were recorded on a Brucker Avance DPX-250 spectrometer and ^{31}P NMR (on a Brucker UltraSheild-400 spectrometer) using tetramethylsilane (TMS) as internal standard in pure deuterated solvents. The reaction monitoring was carried out on silica gel analytical sheets or by GC analysis using a 1m length column packed with DC-200 stationary phase.Column chromatography was carried out on column of silica gel.

2 Palladium-catalyzed coupling of aryl halides with $P(OEt)_3$ and $P(OPr^i)_3$:

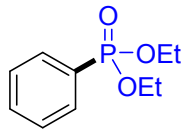


R: H, NO_2, CN, OCH_3, CH_3, CF_3, Br, Cl, OH, NH_2, Ph
R': Et, *i*-Pr, Ph
X: Cl, Br, I

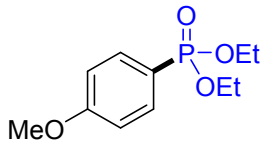
2.1 General Procedure for phosphonation of aryl halides with trialkylphosphites using $PdCl_2$ as catalyst in neat water:

A mixture of $PdCl_2$ (0.004 g, 0.022 mmol, 4.4 mol%), aryl halide (0.5 mmol), trialkylphosphite (2.0 mmol), *n*-Pr_3N (1.0 mmol, 0.18 mL), TBAB (0.5 mmol, 0.166 g,), in water (1.5 mL) was heated at 100 °C. After completion of the reaction monitored by GC or TLC analysis, the reaction mixture was cooled to room temperature. The organic compounds were extracted with ethyl acetate (3 × 10 mL) from the aqueous layer and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The crude organic mixture was then purified by silica gel column chromatography using petroleum ether/ethyl acetate 4:1 as eluent to obtain the desired product (Table 1).

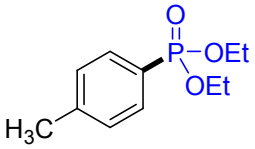
2.1 Characterization of the products:



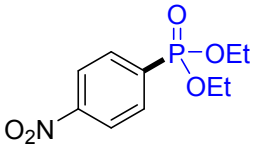
Diethyl-pheyl-posphonate[1,2,3,6]: (3a) [CAS No. 1754-49-0] oil, yield: 99%; 1H NMR (250 MHz, CDCl3/TMS): δ (ppm) = 1.22 (t, J = 7.0 Hz, 6H), 3.99-4.10 (m, 2H), 7.38–7.48 (m, 2H), 7.70-7.78 (m, 2H); 13C NMR (CDCl3, 62.5 MHz) δ 132.35, 131.69, 128.58, 128.34, 62.16, 16.37; ^{31}P NMR (CDCl3, 162 MHz) : δ(ppm) 18.35 ; HRMS: *m/z* 241.1



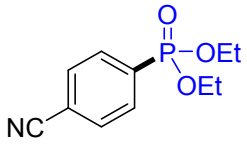
diethyl (4-methoxyphenyl)phosphonate[1,2,6]: (3b) [CAS No. 3762-33-2] oil yield 90% 1H NMR (250 MHz, CDCl3/TMS): δ (ppm) =1.18-1.23 (t, J = 7.1 Hz, 6H), 3.7-4.06 (m, 4H), 6.83-6.89 (m 2H), 7.59-7.68(m, 2H); 13C NMR (CDCl3, 62.5 MHz) δ 159.5, 129.4, 120.6, 113.8, 58.0, 55.0, 16.8; ^{31}P NMR(CDCl3, 162 MHz) δ 18.4; HRMS: *m/z* 244.1



diethyl p-tolylphosphonate[1,2,3,6] (3c) [CAS No. 3762-25-2] oil yield 83% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.18 (t, J = 6.9 Hz, 6H), 2.27(s), 3.93-4.01 (m, 4H), 7.12-7.16(m, 2H), 7.53-7.61(m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.4, 137.4, 133.0, 127.4, 64.0, 21.8, 16.4; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.8 HRMS: *m/z* 228.1

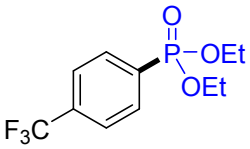


diethyl (4-nitrophenyl)phosphonate[1] (3d) [CAS No. 3762-25-2, 1754-42-3] oil yield 85% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.22 (t, J = 7.1 Hz, 3H), 3.77-3.89 (m, 4H), 7.50–7.54 (m, 2H), 8.16-8.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 149.60, 134.55, 129.26, 123.38, 57.81-58.00 (d, J = 2.2 Hz), 16.88-16.80 (d, J = 0.8 Hz),^{31}P NMR($CDCl_3$, 162 MHz) δ 14.91; HRMS: *m/z* 259.1

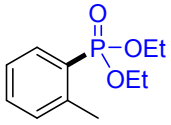


diethyl (4-cyanophenyl)phosphonate[1,6] (3e) [CAS No. 28255-72-3] oil yield 65% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.19-1.25 (t, J = 7.0 Hz, 6H), 3.80-3.86 (m,

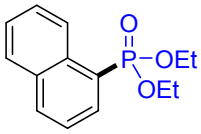
4H), 7.40–7.46 (m, 2H), 7.54-7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 140.1, 135.4, 131.2,118.2, 114.5, 66.5, 16.5; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.5; HRMS: *m/z* 239.1



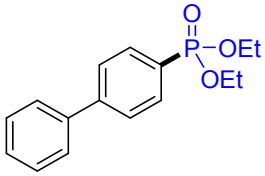
diethyl (4-(trifluoromethyl)phenyl)phosphonate[6] (3f) [CAS No. 99578-68-4] oil yield 83% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.24 (t, J = 6.9 Hz, 6H), 3.96-4.09 (m, 4H), 7.63-7.65(m, 2H), 7.81-7.79(m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 137.2, 135.6, 132.2, 125.0, 124.1, 59.1, 16.8 ; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.8, HRMS: *m/z* 282.1



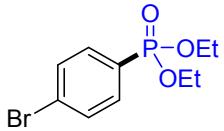
diethyl o-tolylphosphonate[6] (3g) [CAS No. 62778-16-9] oil yield 67% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.19 (t, J = 6.75 Hz, 6H), 2.45 (s), 3.96-4.02 (m, 4H), 7.11-7.31 (m, 2H), 7.77-7.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 141.7, 133.9, 132.4, 131.2, 131.0, 125.4, 61.9, 19.7, 16.2; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.0; HRMS: *m/z* 228.1



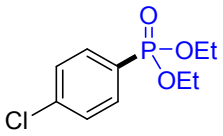
diethyl naphthalen-1-ylphosphonate[1,2,6] (3h) [CAS No. 25944-75-6] oil yield 99% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.13(t, J = 6.8 Hz, 6H), 3.78-3.88 (m, 4H), 7.11-7.31 (m, 2H), 7.02-8.23 (m, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 133.7,131.4, 127.3, 126.3, 59.1, 16.7; ^{31}P NMR($CDCl_3$, 162 MHz) δ 19.1; HRMS: *m/z* 264.1



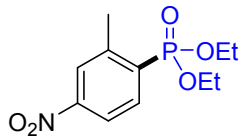
diethyl [1,1'-biphenyl]-4-ylphosphonate[2,6] (3i) oil yield 99% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.30-1.36 (t, J = 7.1, 6H), 4.08-4.17 (m, 4H), 7.42-7.91 (m, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 145.1, 141.1, 132.3, 128.8, 127.2, 118.2, 111.8 , 59.1, 16.2; ^{31}P NMR($CDCl_3$, 162 MHz) δ 17.8; HRMS: *m/z* 290.1



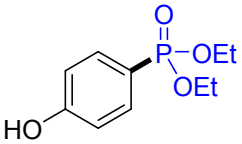
diethyl (4-bromophenyl)phosphonate (3j) [CAS No. 20677-12-7] oil yield 99% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.19-1.22 (t, J = 0.06 Hz, 6H), 3.97-4.02 (m, 4H), 7.49-7.59 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 137.0, 133.1, 128.8, 126.0, 58.9, 16.8; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.2 HRMS: *m/z* 292.1



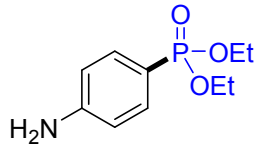
diethyl (4-chlorophenyl)phosphonate[1,2] (3k) [CAS No. 39225-17-7] oil yield 99% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.22(t, 6H), 3.95-4.04 (m, 4H), 7.33-7.38 (m, 2H), 7.61-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 138.5, 134.5, 129.2, 123.3, 58.0, 16.8; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.1; HRMS: *m/z* 248.0



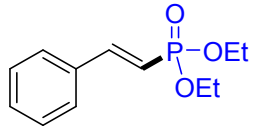
diethyl (2-methyl-4-nitrophenyl)phosphonate (3l) oil yield 85% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.17-1.20 (t, J=7.0, 6H), 2.45(s, 3H), 3.96-4.02 (m, 4H),7.29-7.32 (m, 1H); 7.77-7.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 153.4, 147.8, 135.6, 132.4, 126.6, 120.6, 61.0, 21.5, 16.9; ^{31}P NMR($CDCl_3$, 162 MHz) δ 17.9; HRMS: *m/z* 273.1



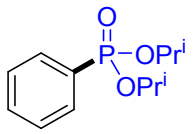
diethyl (4-hydroxyphenyl)phosphonate[1] (3m) [CAS No. 28255-39-2] oil yield 90% ; ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.26-1.27 (t, J= 7.0, 6H), 4.01-4.14(m, 4H), 6.92-7.62 (m, 4H); 9.42-9.44(1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.9, 138.6, 128.1, 127.9, 115.5, 68.6, 16.7; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.1; HRMS: *m/z* 230.1



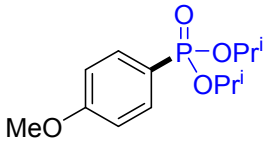
diethyl (4-aminophenyl)phosphonate (3n) [CAS No. 42822-57-1] oil yield 90% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.19-1.24 (t, J=6.9 6H), 3.93-4.08 (m, 4H), 6.64-6.66 (m, 2H); 7.44-7.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 150.5, 133.5, 121.1, 114.3, 61.7, 16.8; ^{31}P NMR($CDCl_3$, 162 MHz) δ 18.2; HRMS: *m/z* 229.1



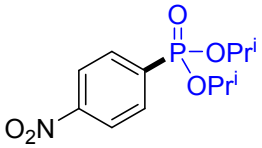
diethyl (E,Z)-styrylphosphonate[6] (3o) oil yield 90% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.26-1.33(t, J= 8.9, 6H), 4.02-4.11 (m, 4H), 6.13-6.28 (m, 2H), 7.25-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 148.7, 132.7, 130.2, 129.0 128.5, 127.6, 126.2, 112.1, 61.8, 16.2; ^{31}P NMR($CDCl_3$, 162 MHz) δ 17.4; HRMS: *m/z* 228.1



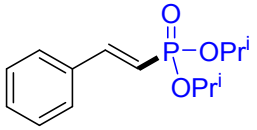
diisopropyl phenylphosphonate[1,3,4] (3p) [CAS No. 7237-16-3] oil yield 90% ^{1}H NMR (250 MHz, CDCl3/TMS): δ (ppm) =1.17-1.34(m, 12H), 4.53-4.71 (m, 2H), 7.39-7.46 (m, 2H), 7.73-7.82 (m, 2H); ^{13}C NMR (CDCl3, 62.5 MHz) δ 133.6, 124.1, 70.2, 24.0; ^{31}P NMR(CDCl3, 162 MHz) δ 16.0; HRMS: *m/z* 242.1



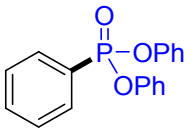
diisopropyl (4-methoxyphenyl)phosphonate[2] (3q) oil yield 90% ^{1}H NMR (250 MHz, CDCl3/TMS): δ (ppm) =1.09-1.26 (m, 12H), 3.72 (s, 3H), 4.50-4.58 (m, 2H), 6.81-6.86 (m, 2H) 7.59-7.68 (m, 2H); ^{13}C NMR (CDCl3, 62.5 MHz) δ 162.5, 133.6, 122.3, 113.8, 70.4, 55.1, 23.7; ^{31}P NMR($CDCl_3$, 162 MHz) δ 15.9 HRMS: *m/z* 272.1



diisopropyl (4-nitrophenyl)phosphonate[3] (3r) oil yield 90% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.20-1.37(m, 12H), 4.54-4.61 (m, 2H), 7.93-8.23 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 149.3, 139.4, 133.8, 121.2, 70.3, 25.8; ^{31}P NMR($CDCl_3$, 162 MHz) δ 16.5; HRMS: *m/z* 287.1



diisopropyl (E,Z)-styrylphosphonate[4] (3s) oil yield 90% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =1.22-1.30(m, 12H), 4.60-4.68 (m, 2H), 6.11-6.25 (m, 1H), 7.21-7.44(m, 6H), 7.50(s, 1H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 148.0, 134.7, 130.0, 128.7, 127.6, 116.8, 70.6, 23.0; ^{31}P NMR($CDCl_3$, 162 MHz) δ 19.5; HRMS: *m/z* 256.1

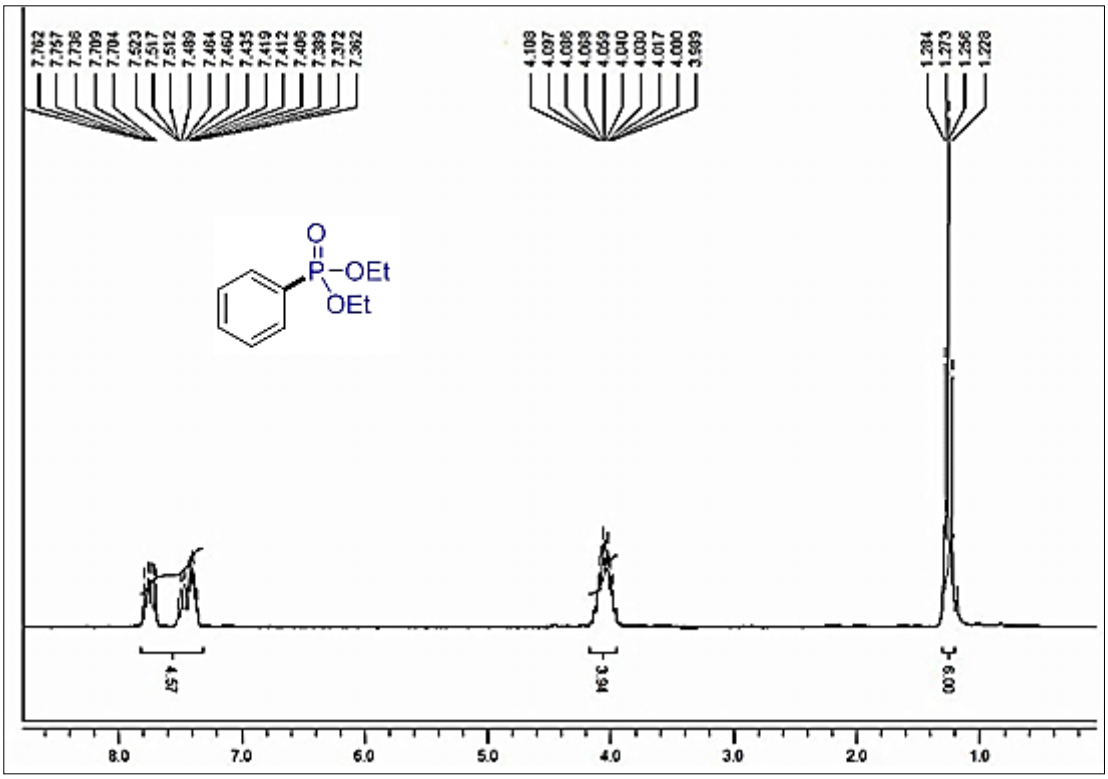


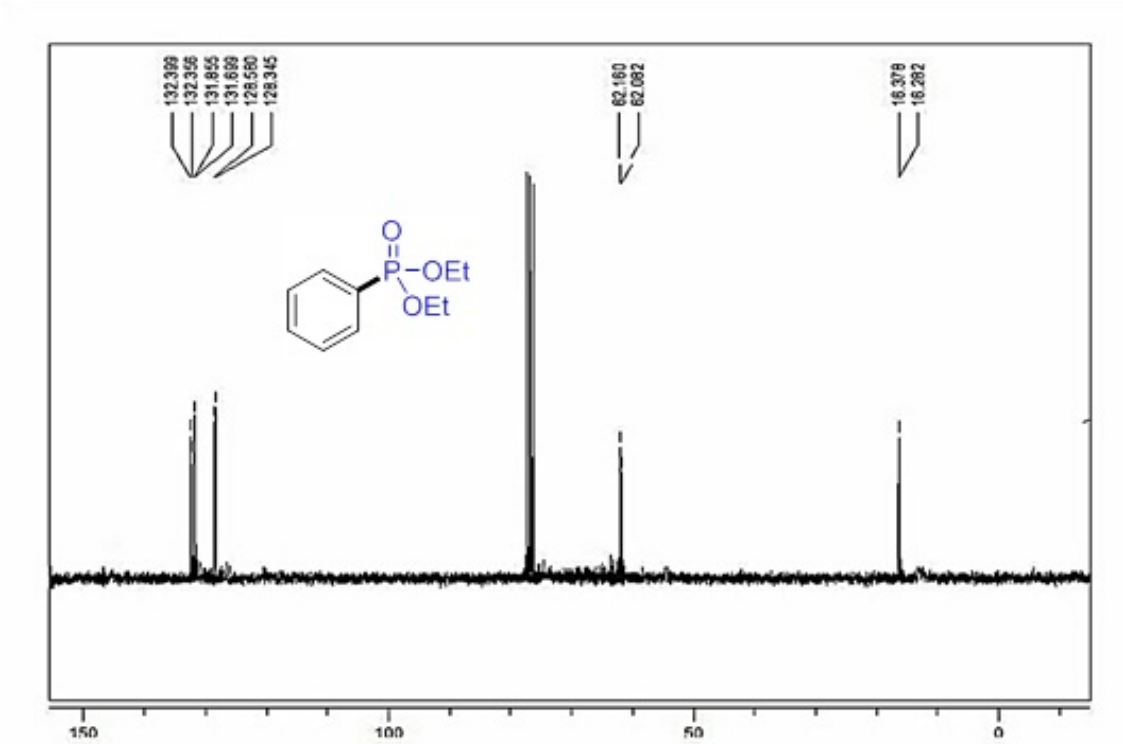
diphenyl phenylphosphonate (3t) [CAS No. 3049-24-9] oil yield 90% ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ (ppm) =6.88-6.93(m, 2H), 7.18-7.33 (m, 8H), 7.48-7.63 (m, 6H), 7.99-8.08(m, 2H), ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 150.2, 133.6, 132.3, 129.4, 129.0, 128.7, 125.5, 119.8; ^{31}P NMR($CDCl_3$, 162 MHz) δ 12.6; HRMS: *m/z* 310.1

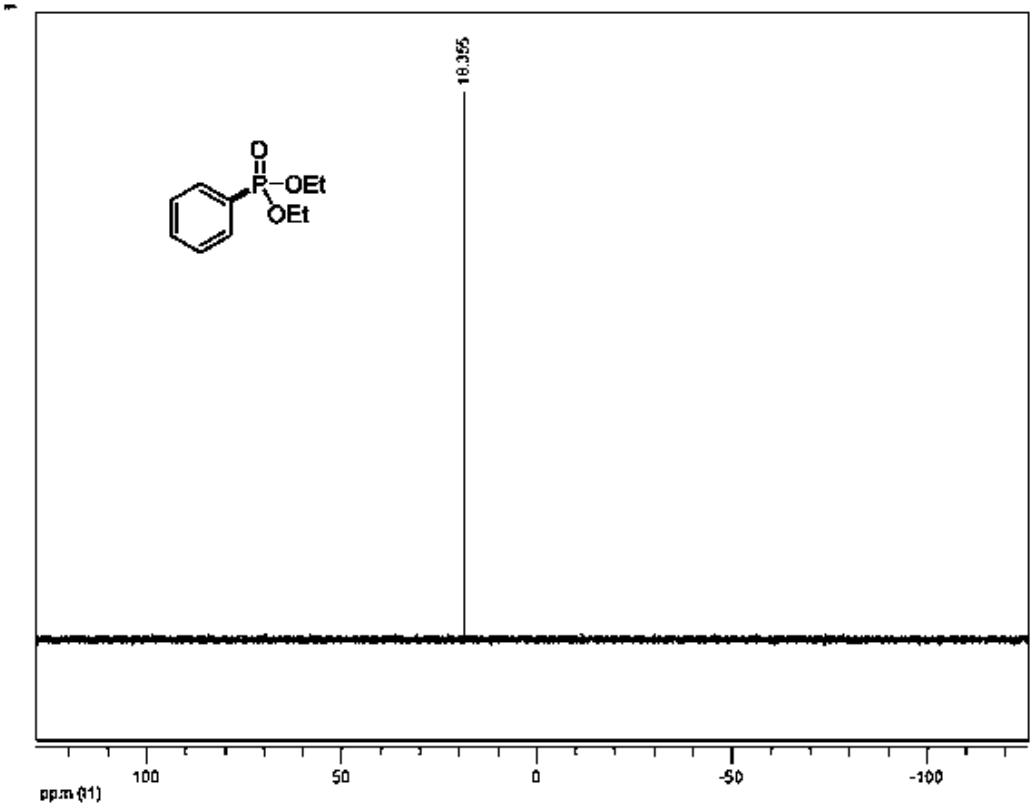
2.2 Synthesis of Diethyl-pheyl-posphonate in large scale:

Iodobenzene (0.1 mol, 11.1mL), $PdCl_2$ (0.05 g, 0.22 mmol), triethylphosphite (0.4 mol, 67.2 mL), *n*-Pr_3N (0.2 mol, 37.7 mL) and TBAB (0.1 mol, 32.23 g,), in water (150 mL) was heated at 100 ^oC. After completion, the reaction mixture was cooled to room temperature and extracted with ethyl acetate from the aqueous layer, and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The crude organic mixture was then purified by silica gel column chromatography using petroleum ether/ethyl acetate 4:1 to obtain the desired product. (Yield 78%)

2.3 Copies of 1H, 13C, and 13P NMR spectra



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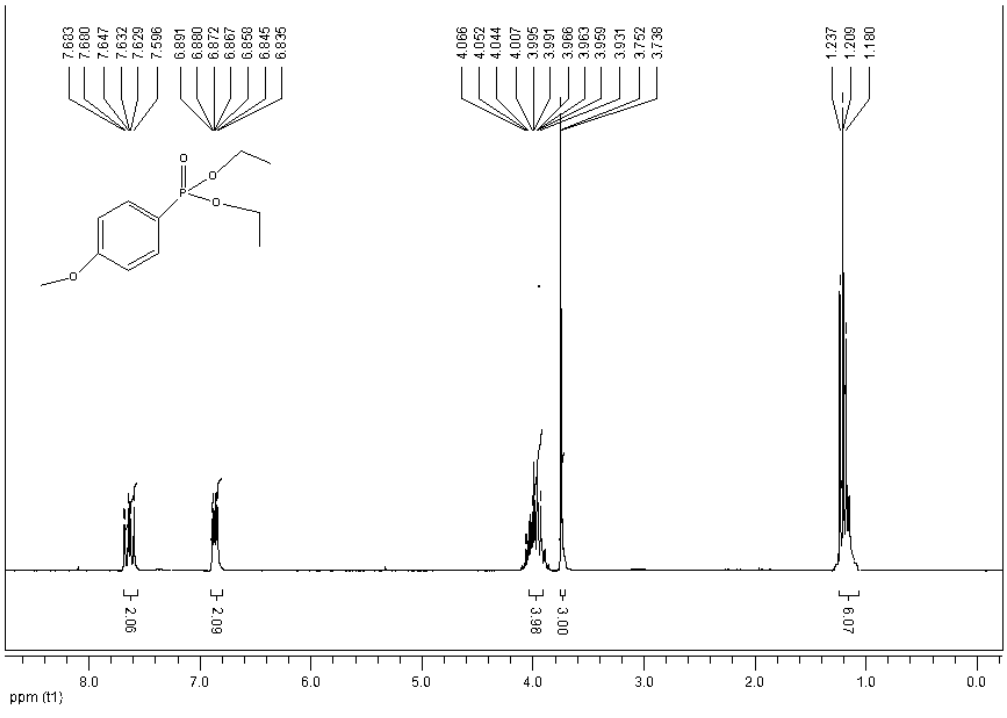
ppm (t1)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3.991
3.986
3.963
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3.931
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3.98
3.00
6.07
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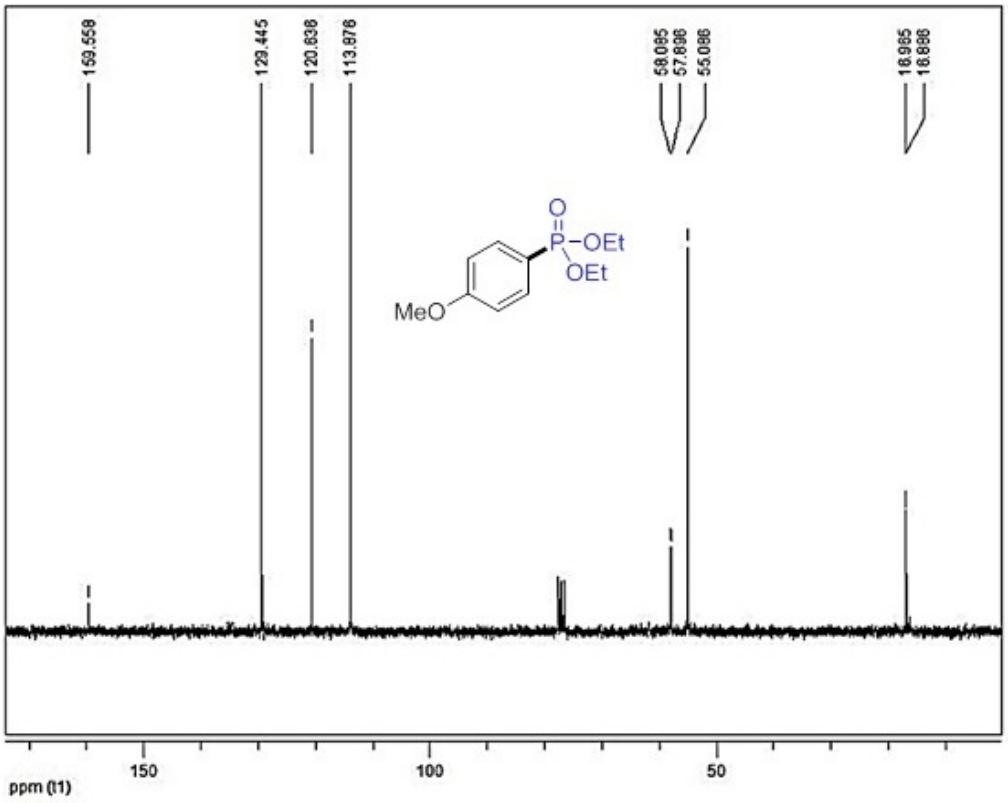
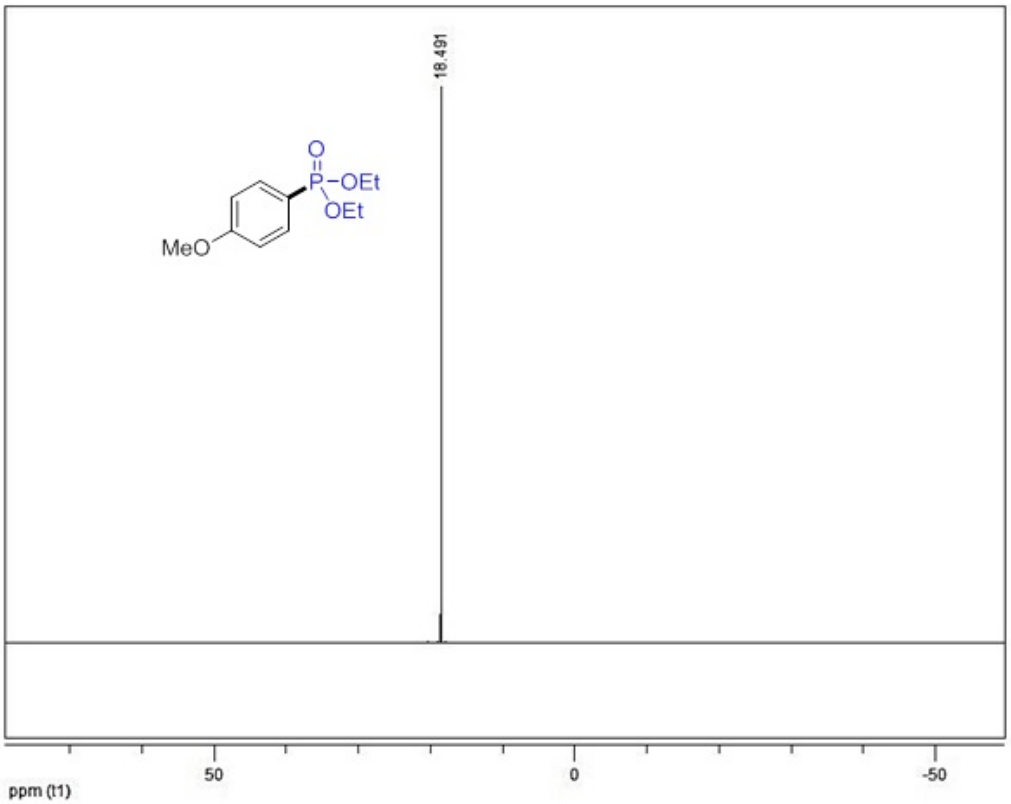
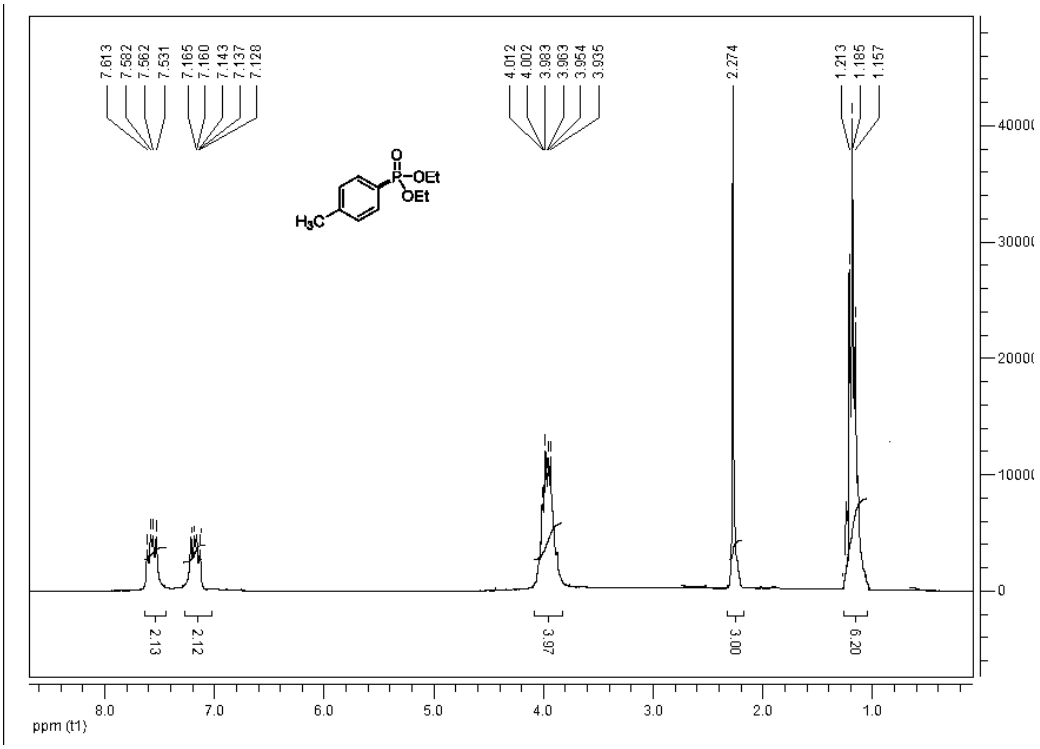
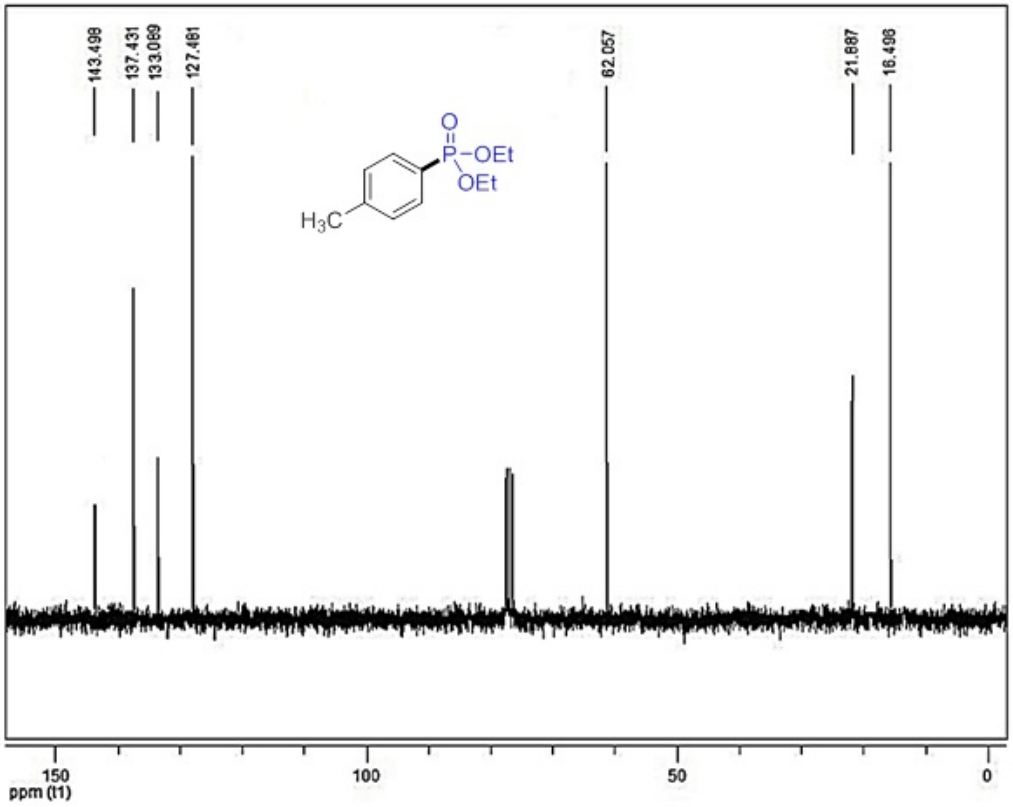
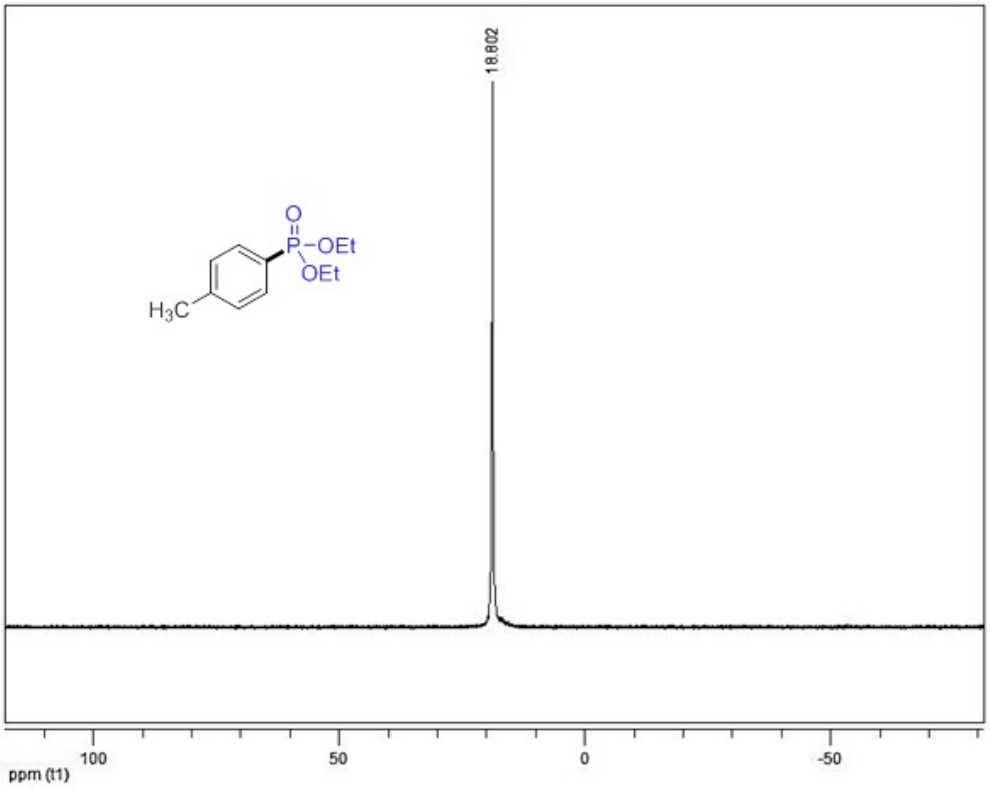
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

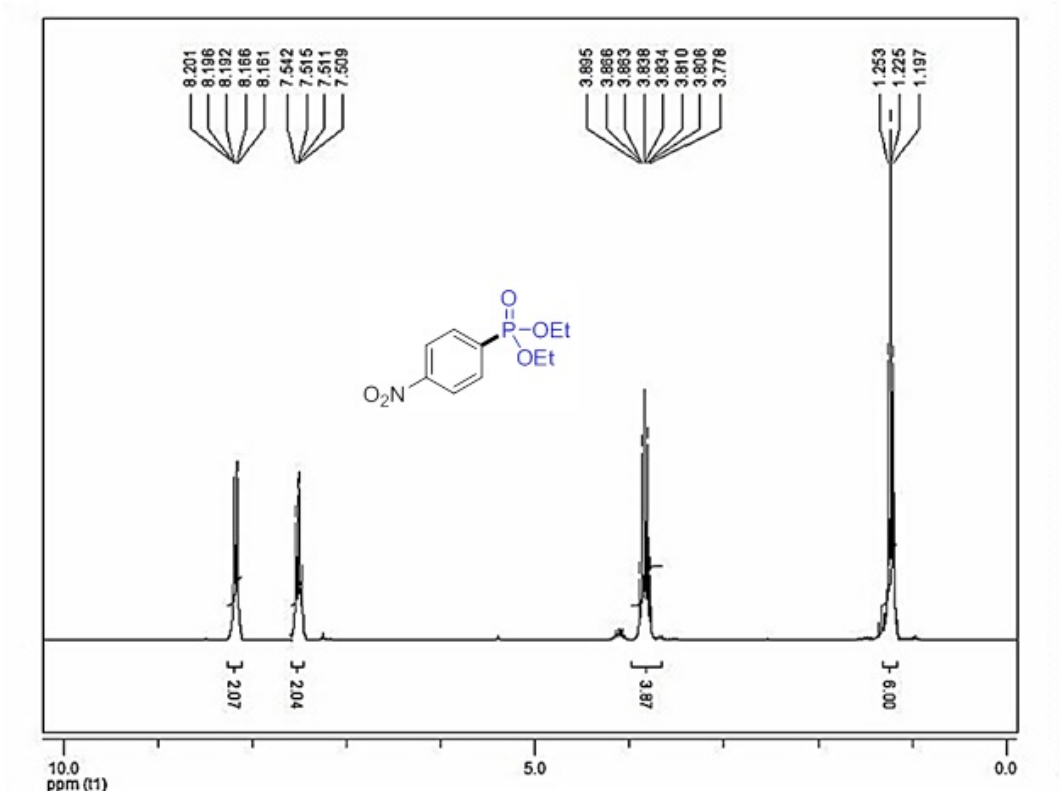

159.558
129.445
120.636
113.876
58.085
57.696
55.086
16.985
16.886
O
P–OEt
OEt
MeO
150
100
50
ppm (t1)

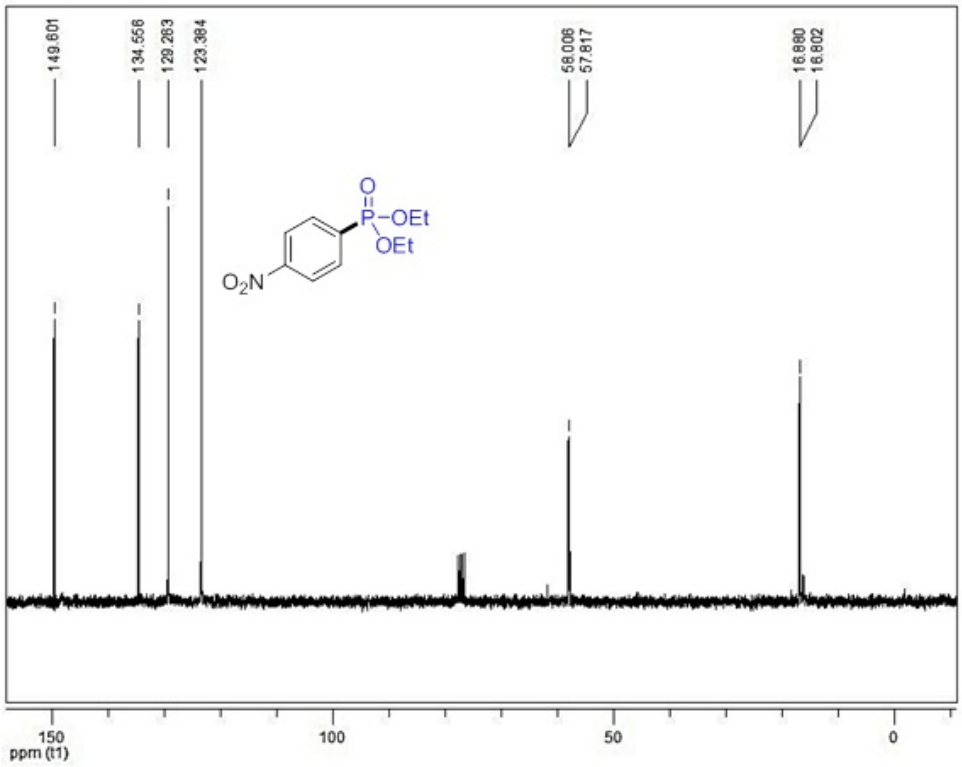

18.491
O
P–OEt
OEt
MeO
50
0
-50
ppm (t1)

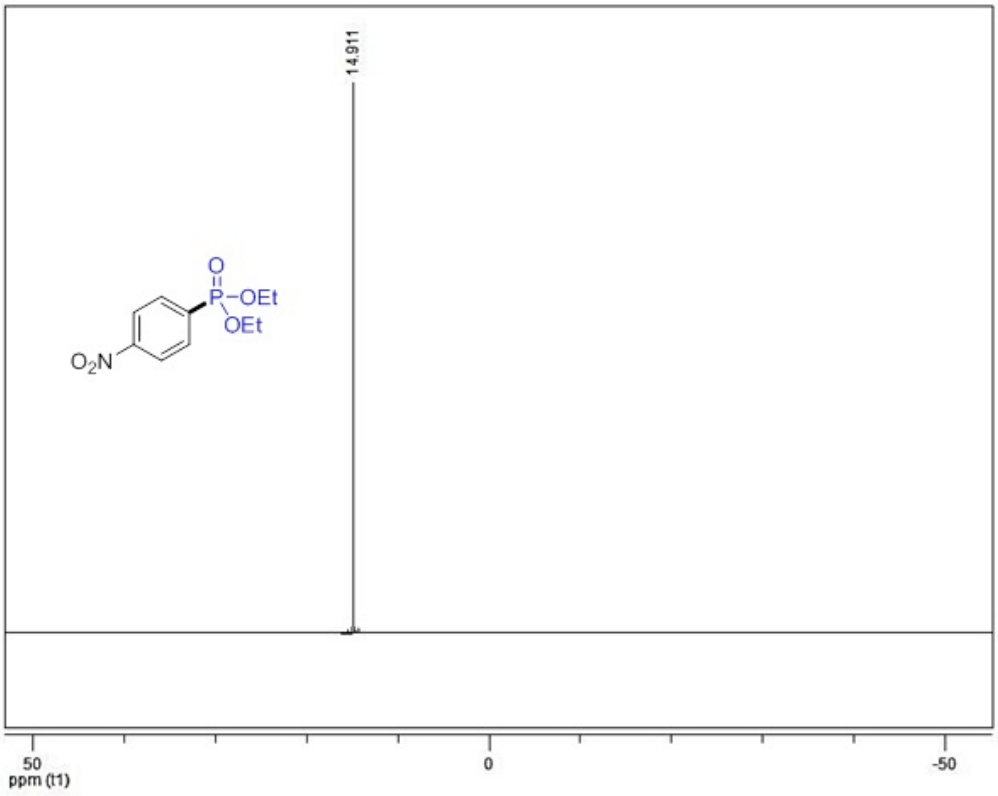

7.613
7.582
7.562
7.531
7.165
7.160
7.143
7.137
7.128
4.012
4.002
3.983
3.963
3.954
3.935
2.274
1.213
1.185
1.157
O
P–OEt
OEt
H3C
2.13
2.12
3.97
3.00
6.20
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

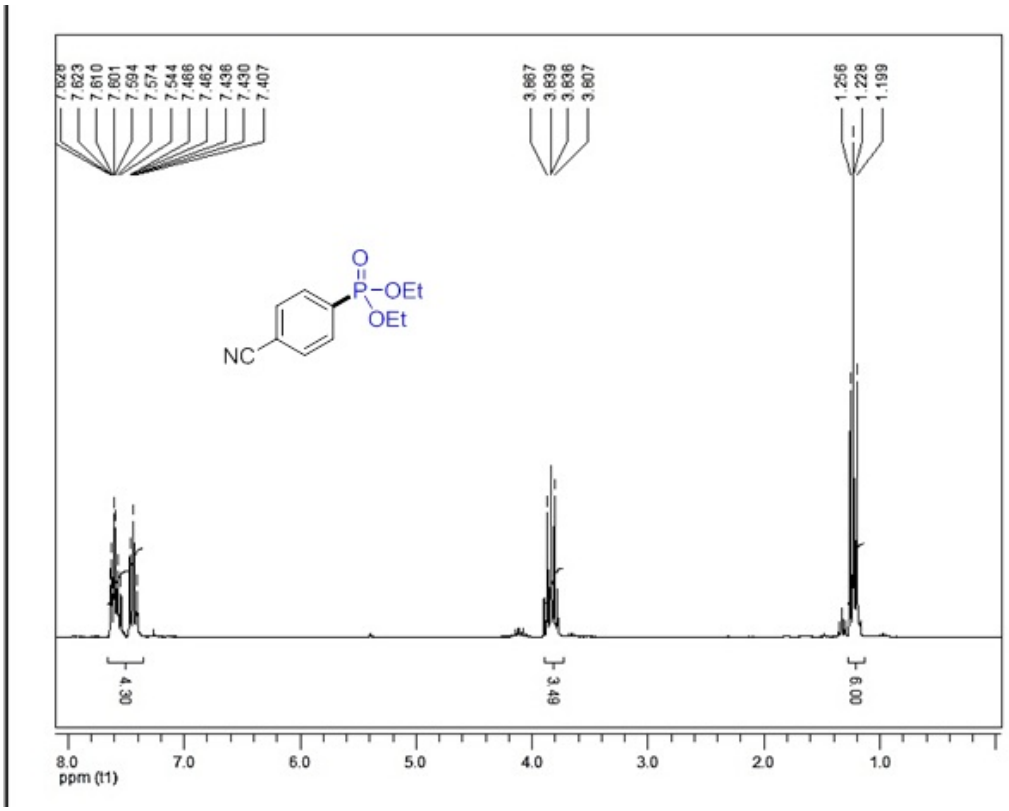

143.498
137.431
133.069
127.461
62.057
21.887
16.496
O
P–OEt
OEt
H3C
150
100
50
0
ppm (t1)

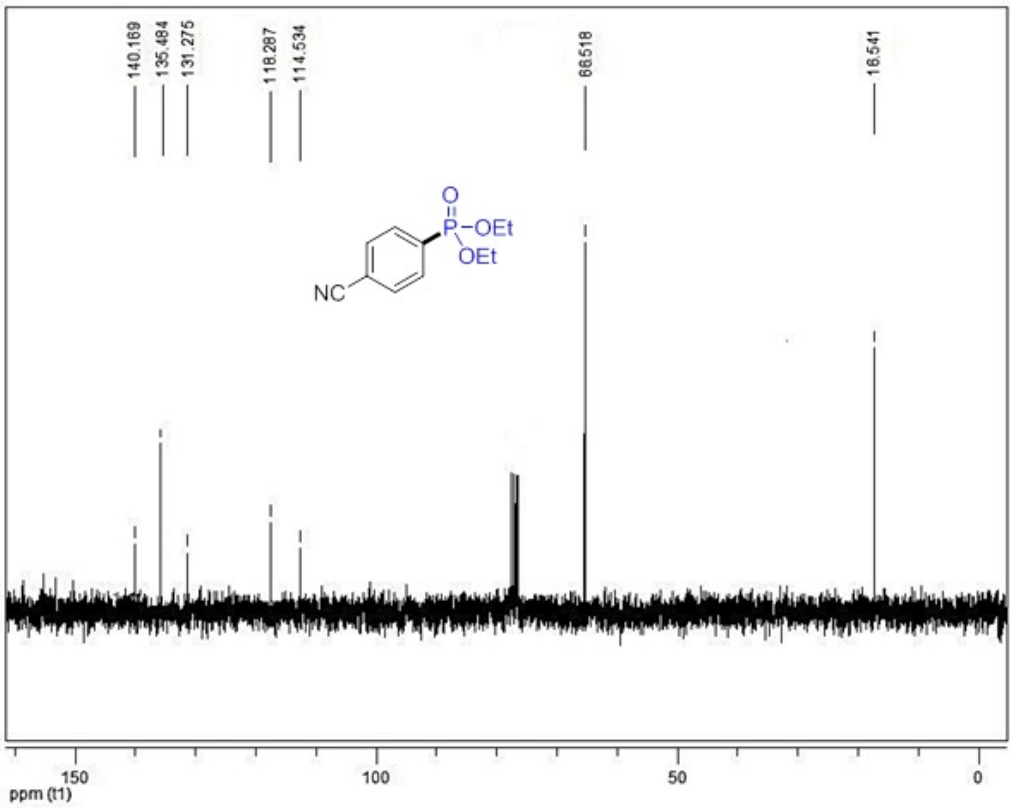

18.802
O
P–OEt
OEt
H3C
100
50
0
-50
ppm (t1)

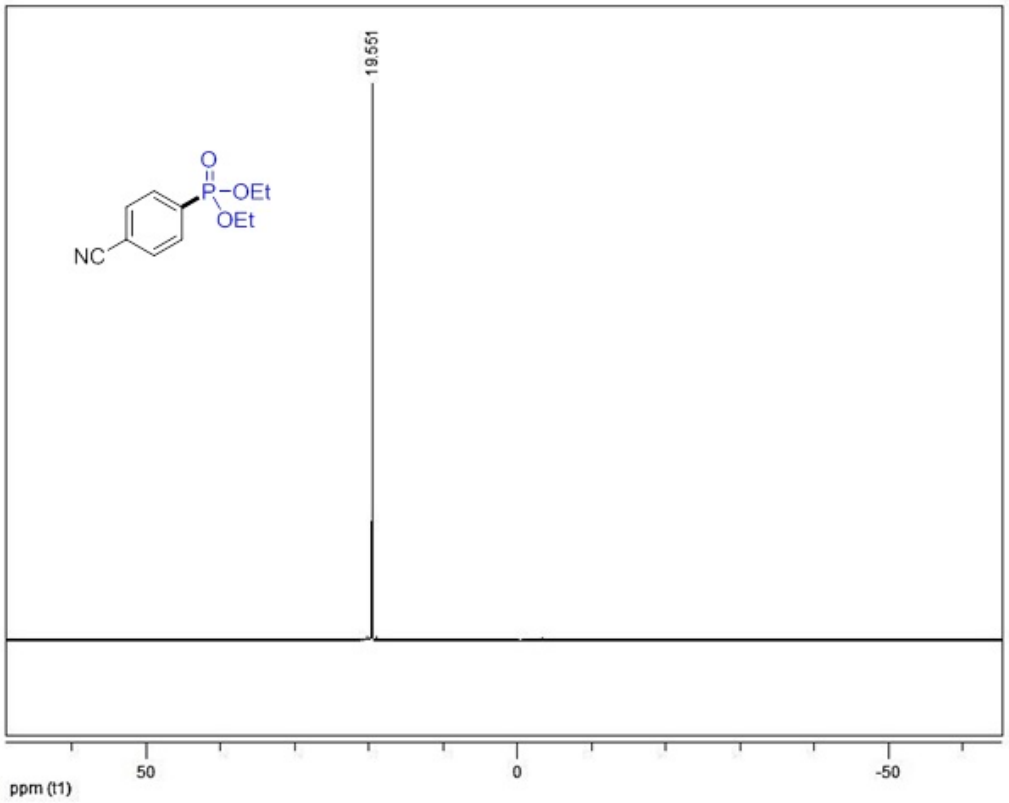

8.201
8.196
8.192
8.166
8.161
7.542
7.515
7.511
7.509
3.895
3.886
3.863
3.838
3.834
3.810
3.806
3.778
1.253
1.225
1.197
O
P–OEt
OEt
O2N
2.07
2.04
3.87
6.00
10.0
ppm (t1)
5.0
0.0

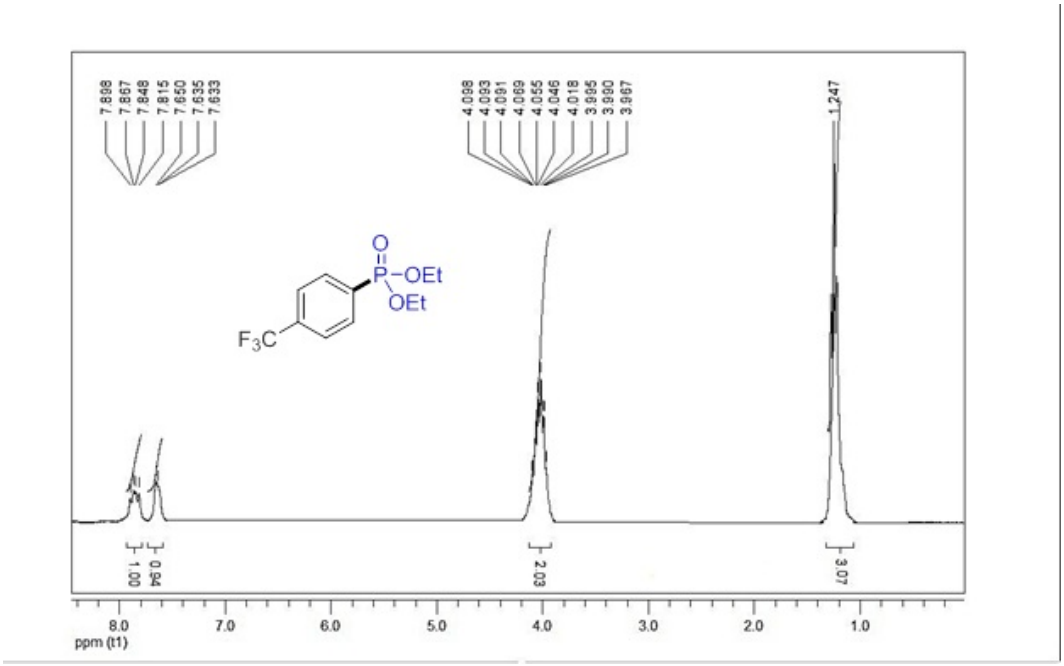

149.601
134.556
129.263
123.384
58.006
57.817
16.880
16.802
O
P–OEt
OEt
O2N
150
ppm (t1)
100
50
0

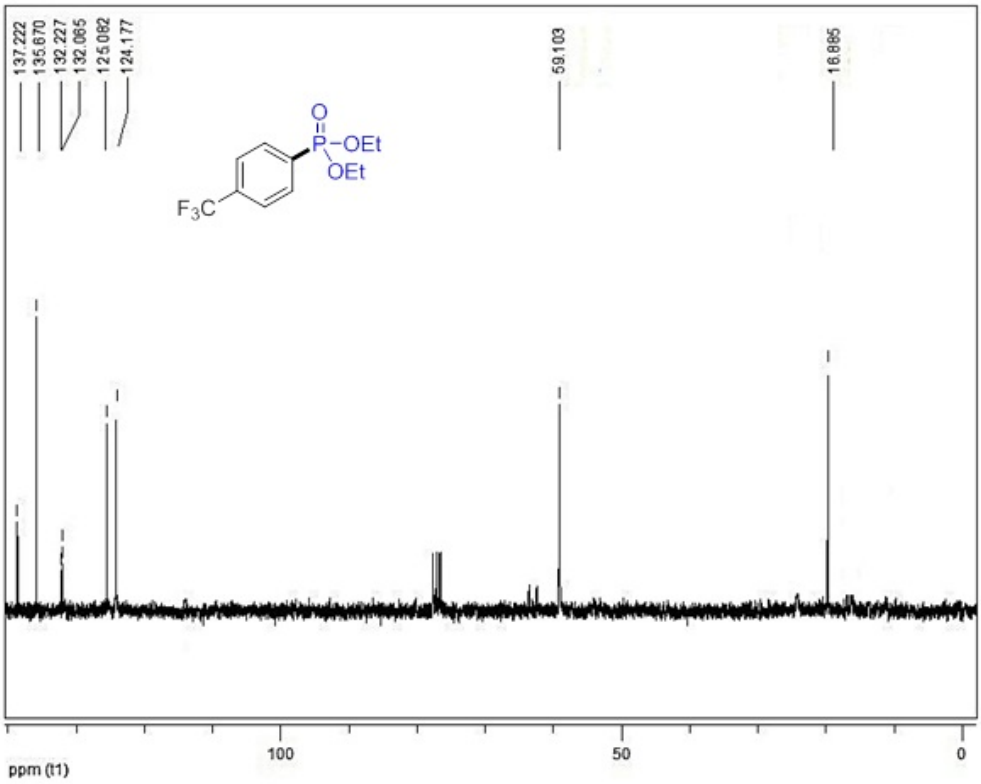

14.911
O
P–OEt
OEt
O2N
50
ppm (t1)
0
-50

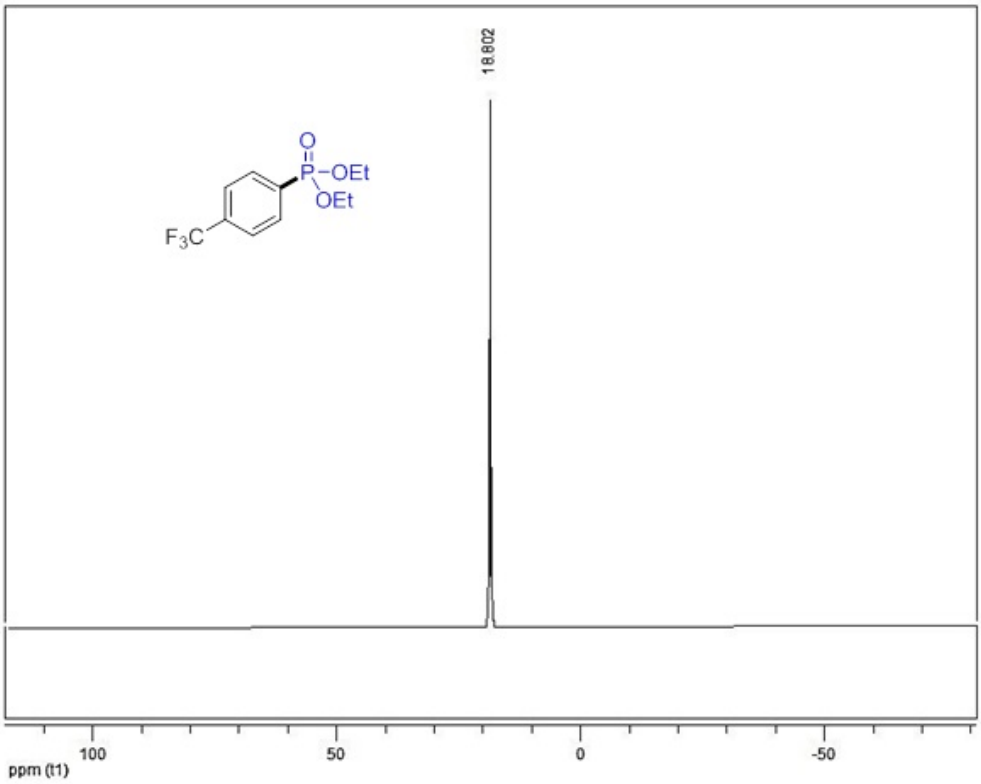

7.628
7.623
7.610
7.601
7.594
7.574
7.544
7.466
7.462
7.436
7.430
7.407
3.867
3.839
3.836
3.807
1.256
1.228
1.199
O
P
OEt
OEt
NC
4.30
3.49
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

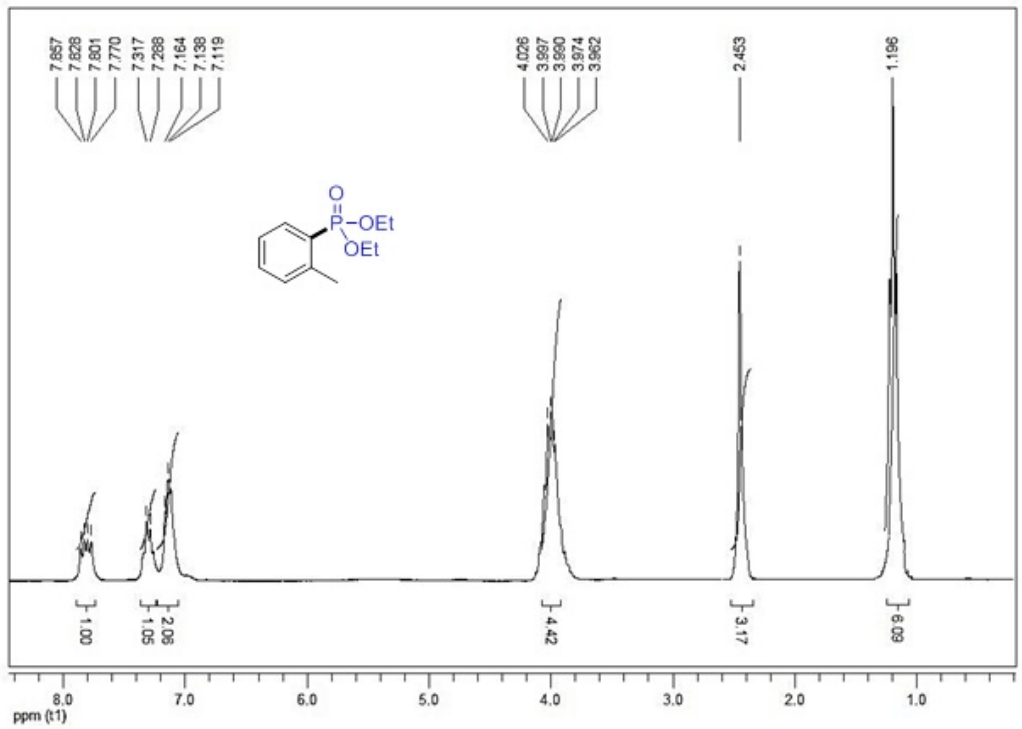

140.169
135.484
131.275
118.287
114.534
66.518
16.541
O
P
OEt
OEt
NC
150
100
50
0
ppm (t1)

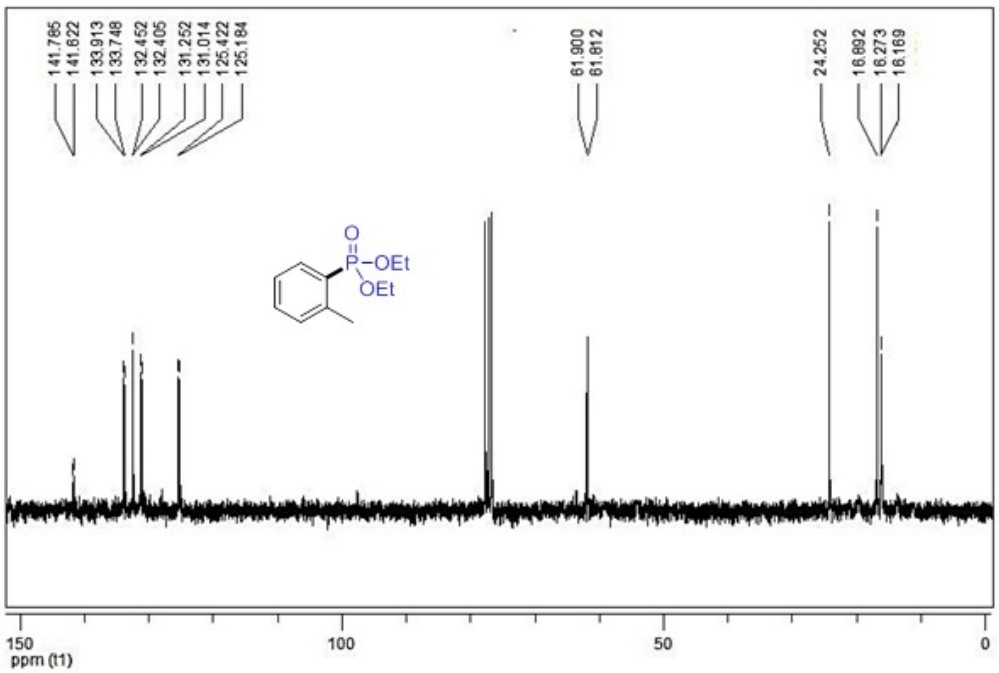

19.551
O
P–OEt
OEt
NC
50
0
-50
ppm (t1)

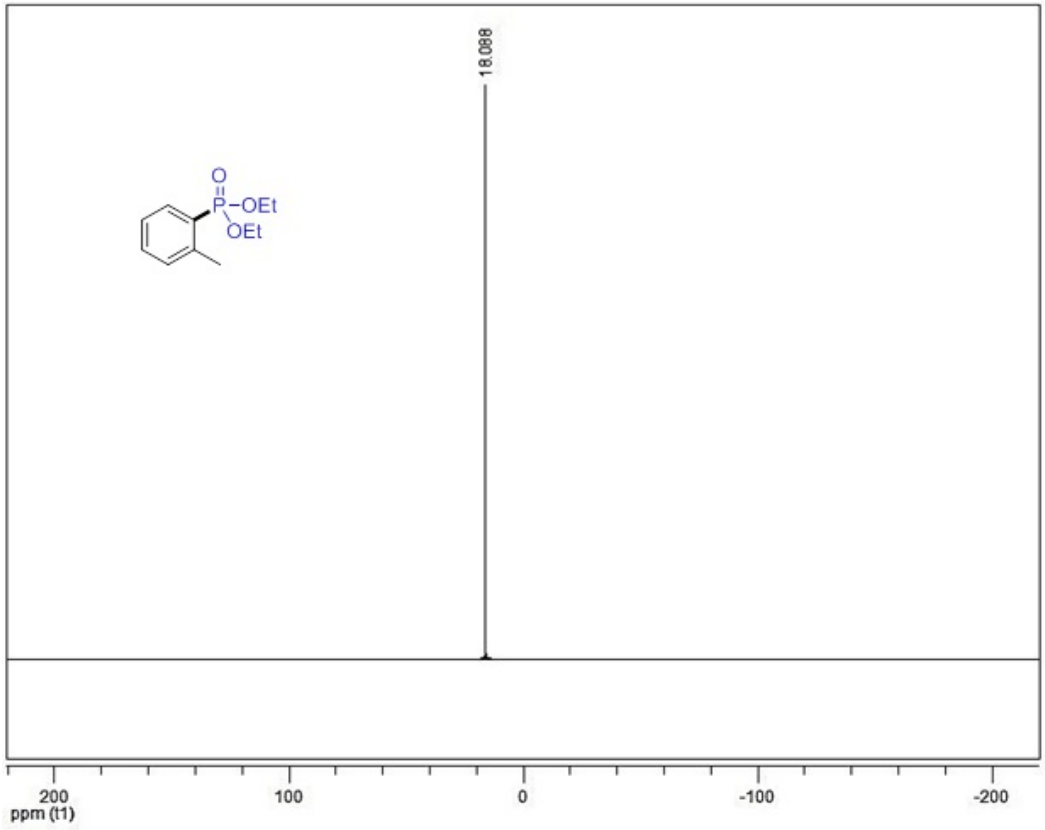

7.898
7.867
7.848
7.815
7.650
7.635
7.633
4.098
4.093
4.091
4.069
4.055
4.046
4.018
3.995
3.990
3.967
1.247
O
P–OEt
OEt
F3C
1.00
0.94
2.03
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

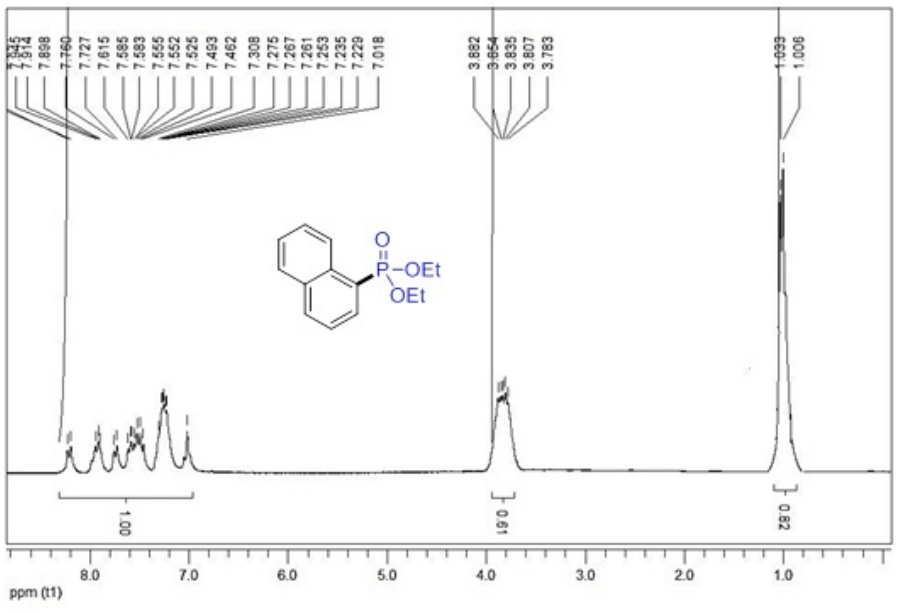

137.222
135.670
132.227
132.065
125.082
124.177
59.103
16.885
O
P–OEt
OEt
F3C
100
50
0
ppm (t1)

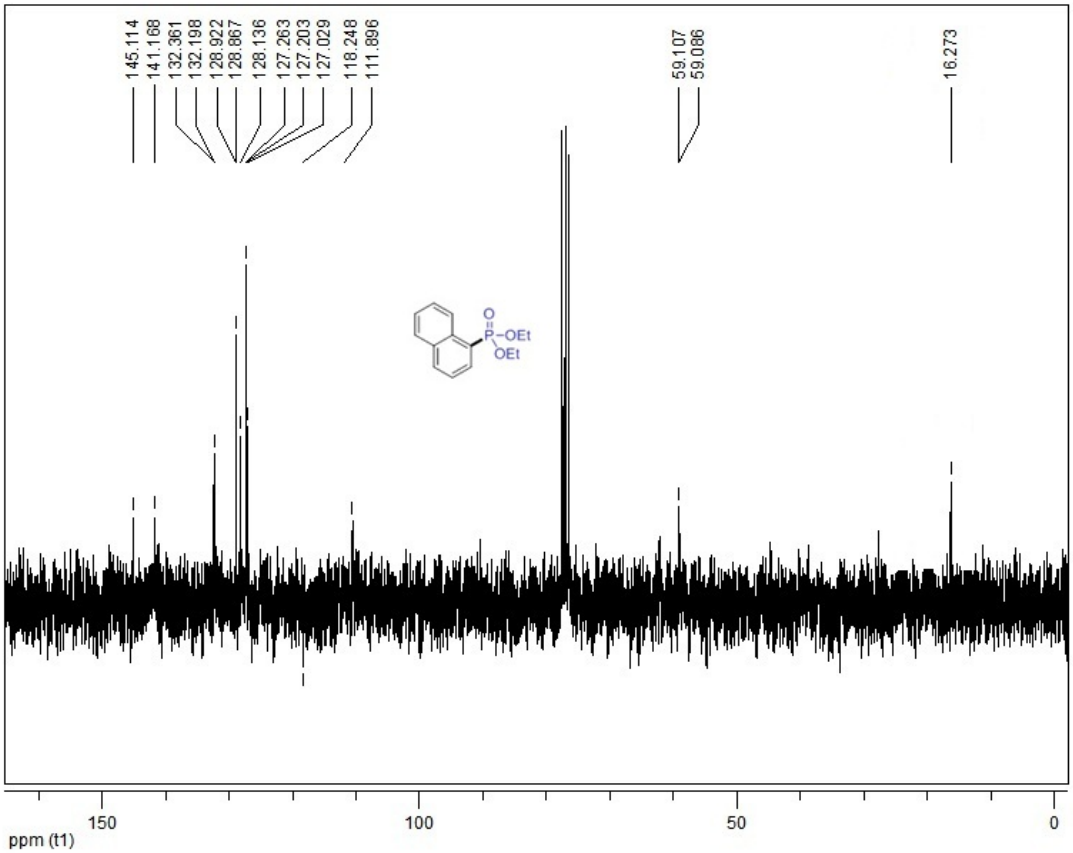

18.602
O
P–OEt
OEt
F3C
100
50
0
-50
ppm (t1)

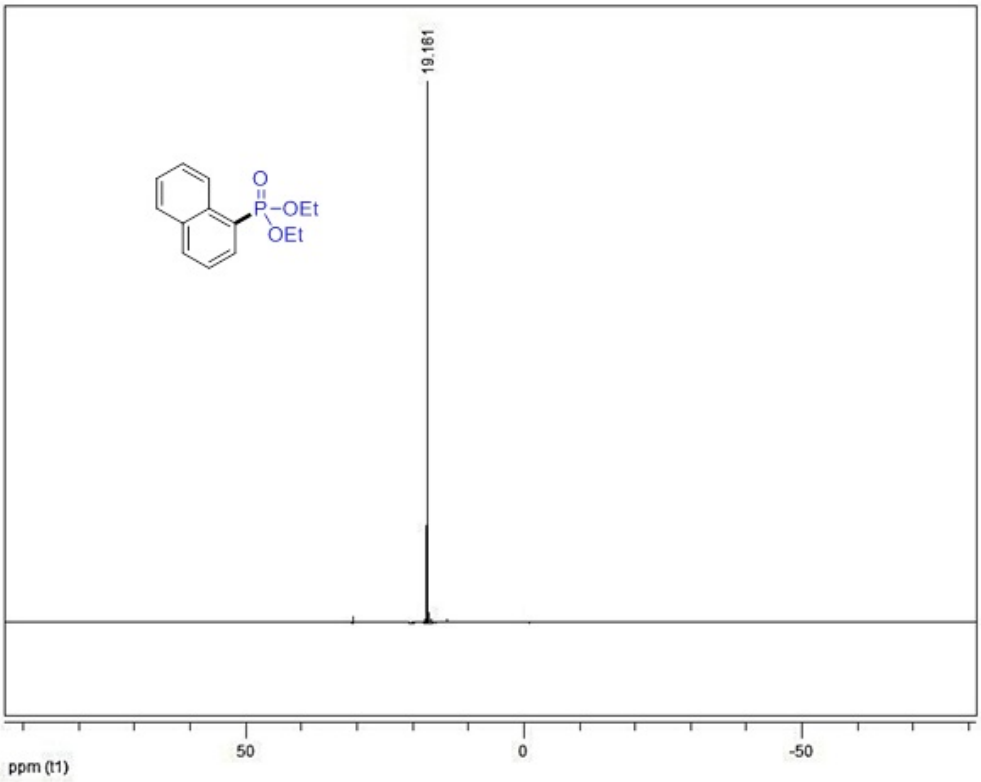

7.857
7.828
7.801
7.770
7.317
7.288
7.164
7.138
7.119
4.026
3.997
3.990
3.974
3.962
2.453
1.196
O
P–OEt
OEt
1.00
1.05
2.06
4.42
3.17
6.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

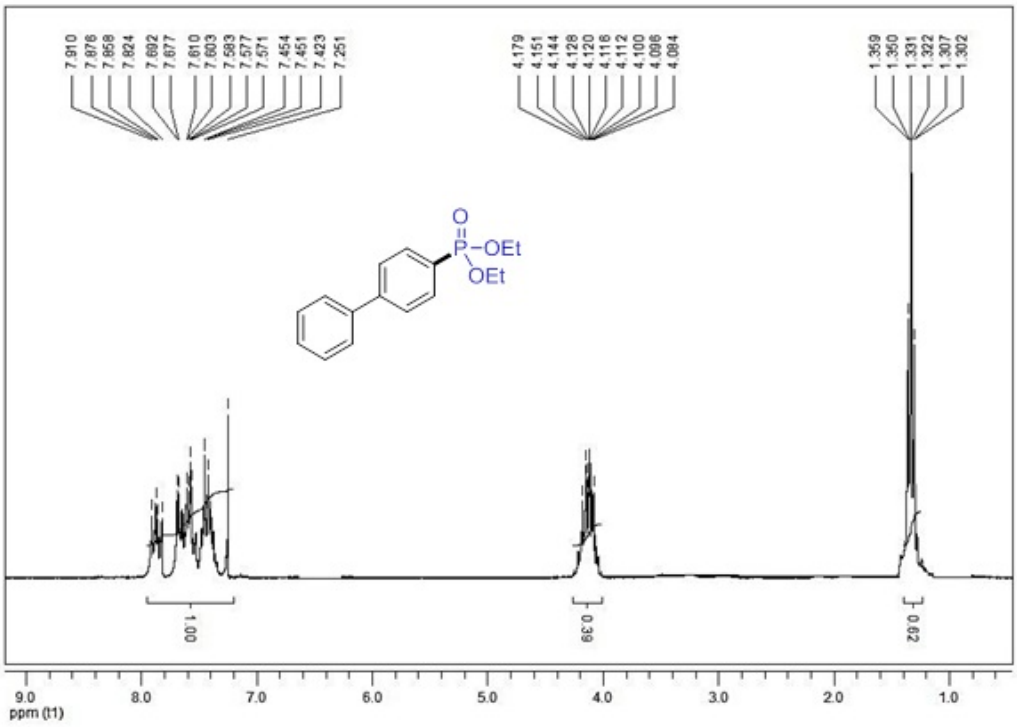

141.765
141.622
133.913
133.748
132.452
132.405
131.252
131.014
125.422
125.184
61.900
61.812
24.252
16.892
16.273
16.169
O
P–OEt
OEt
150
100
50
0
ppm (t1)

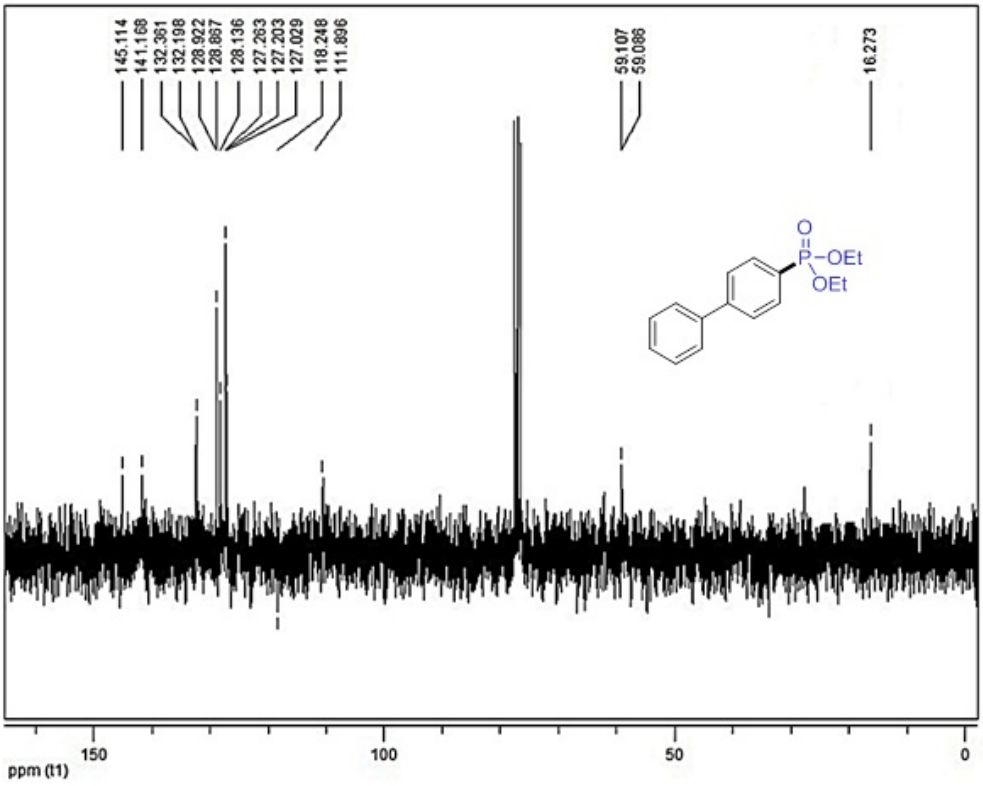

18.088
O
P–OEt
OEt
200
100
0
-100
-200
ppm (t1)

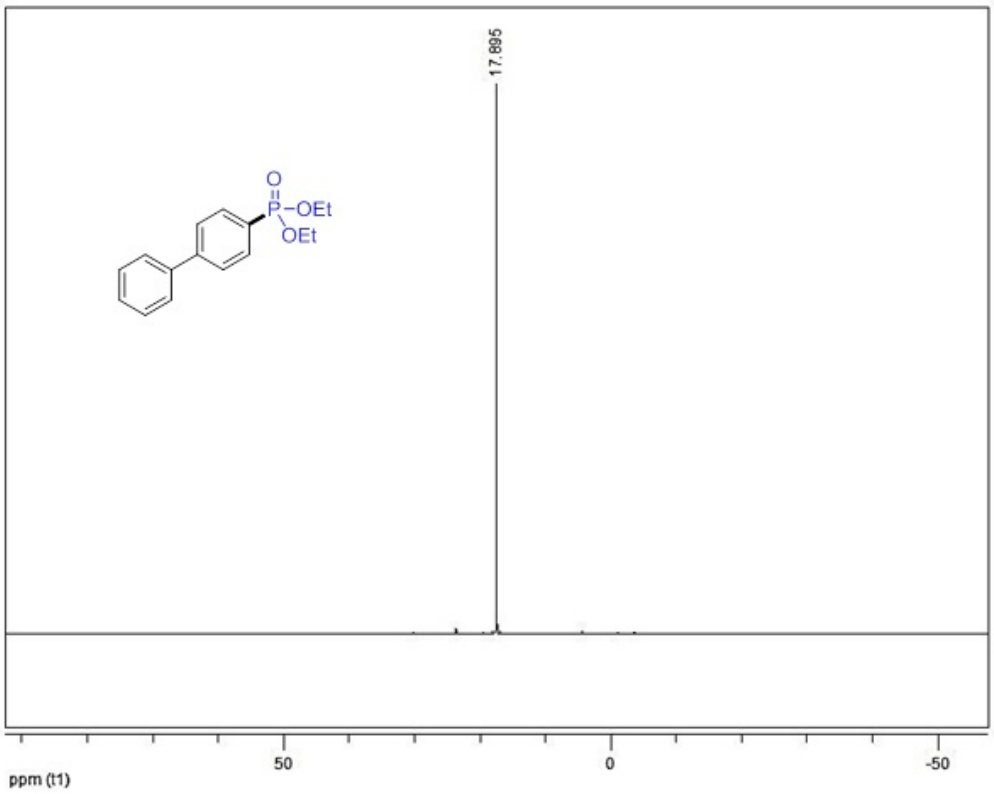

7.945
7.914
7.898
7.760
7.727
7.615
7.585
7.583
7.555
7.552
7.525
7.493
7.462
7.308
7.275
7.267
7.261
7.253
7.235
7.229
7.018
3.882
3.854
3.835
3.807
3.783
1.033
1.006
O
P–OEt
OEt
1.00
0.61
0.82
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

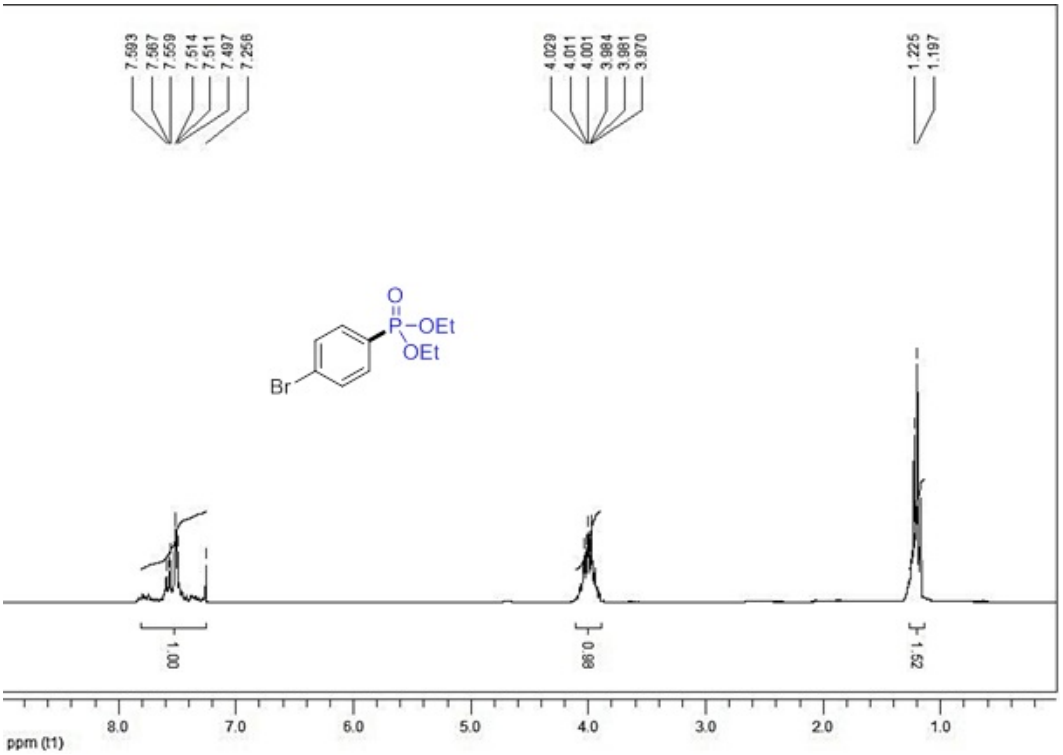

145.114
141.168
132.361
132.198
128.922
128.867
128.136
127.263
127.203
127.029
118.248
111.896
59.107
59.086
16.273
O
P–OEt
OEt
150
100
50
0
ppm (t1)

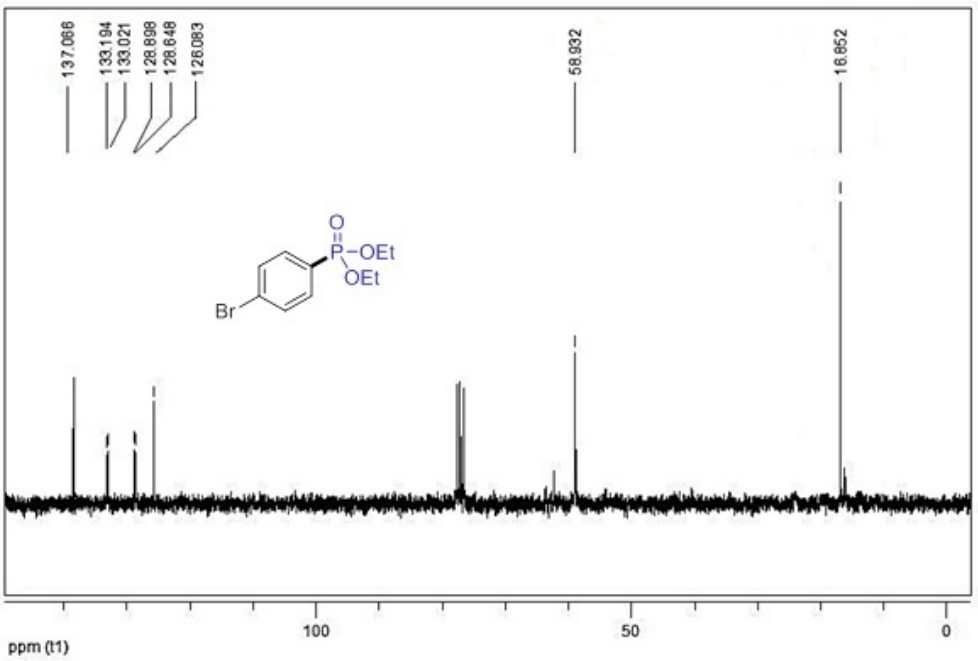

19.161
O
P–OEt
OEt
50
0
-50
ppm (t1)

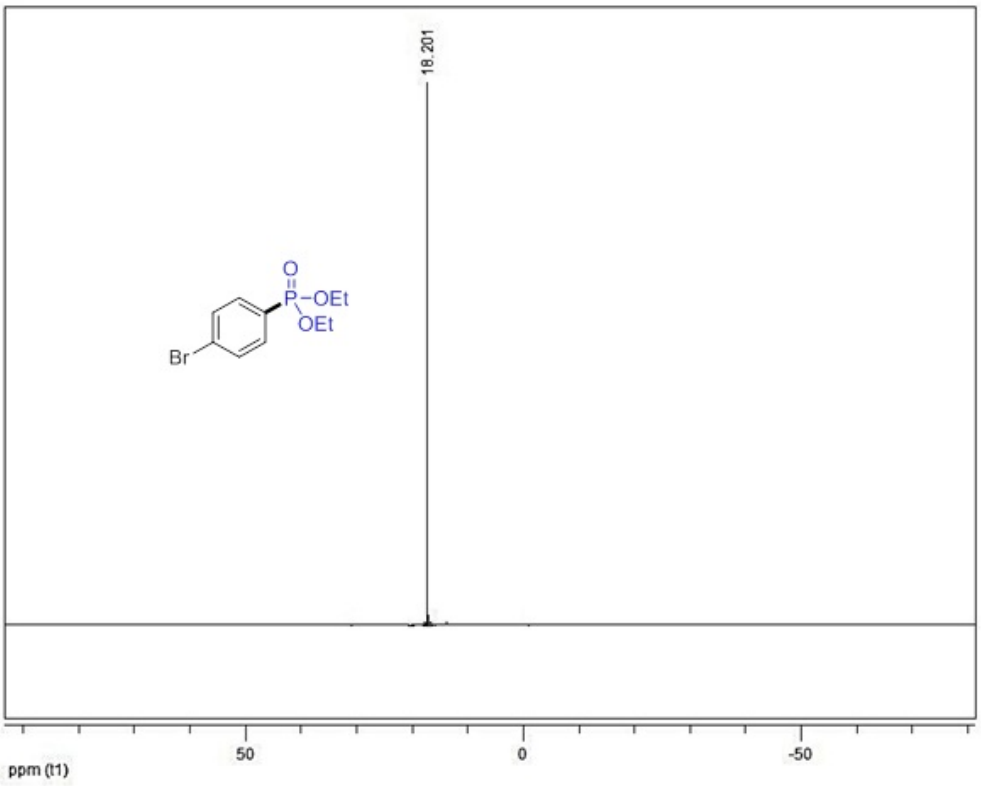

7.910
7.876
7.858
7.824
7.692
7.677
7.610
7.603
7.583
7.577
7.571
7.454
7.451
7.423
7.251
4.179
4.151
4.144
4.128
4.120
4.116
4.112
4.100
4.096
4.084
1.359
1.350
1.331
1.322
1.307
1.302
O
P–OEt
OEt
1.00
0.33
0.62
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

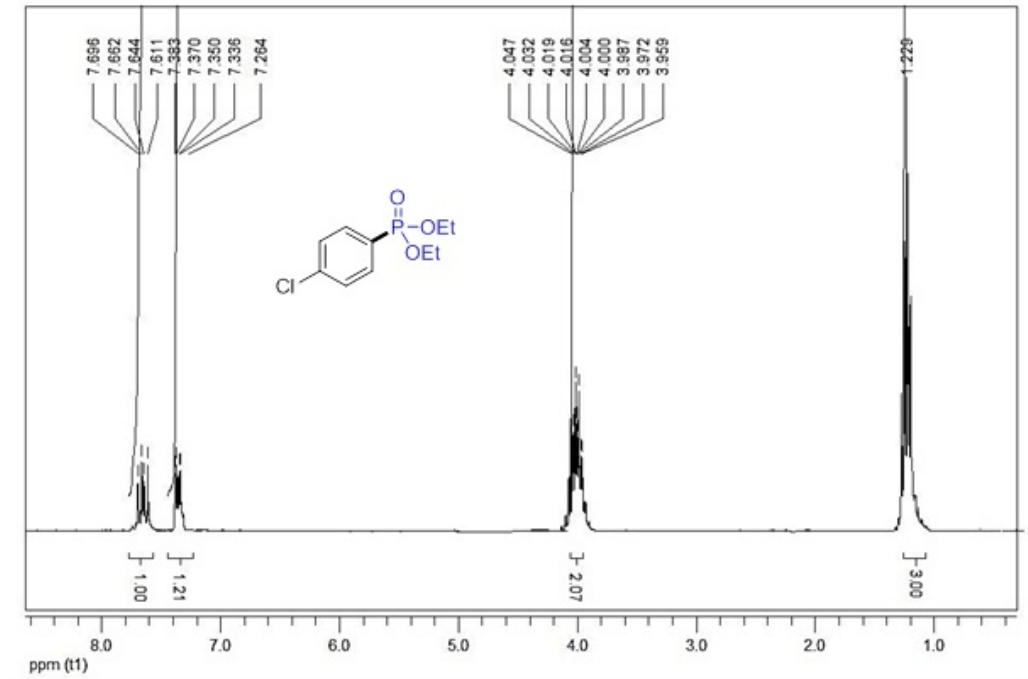

145.114
141.168
132.361
132.198
128.922
128.867
128.136
127.263
127.203
127.029
118.248
111.896
59.107
59.086
16.273
O
P–OEt
OEt
150
100
50
0
ppm (t1)

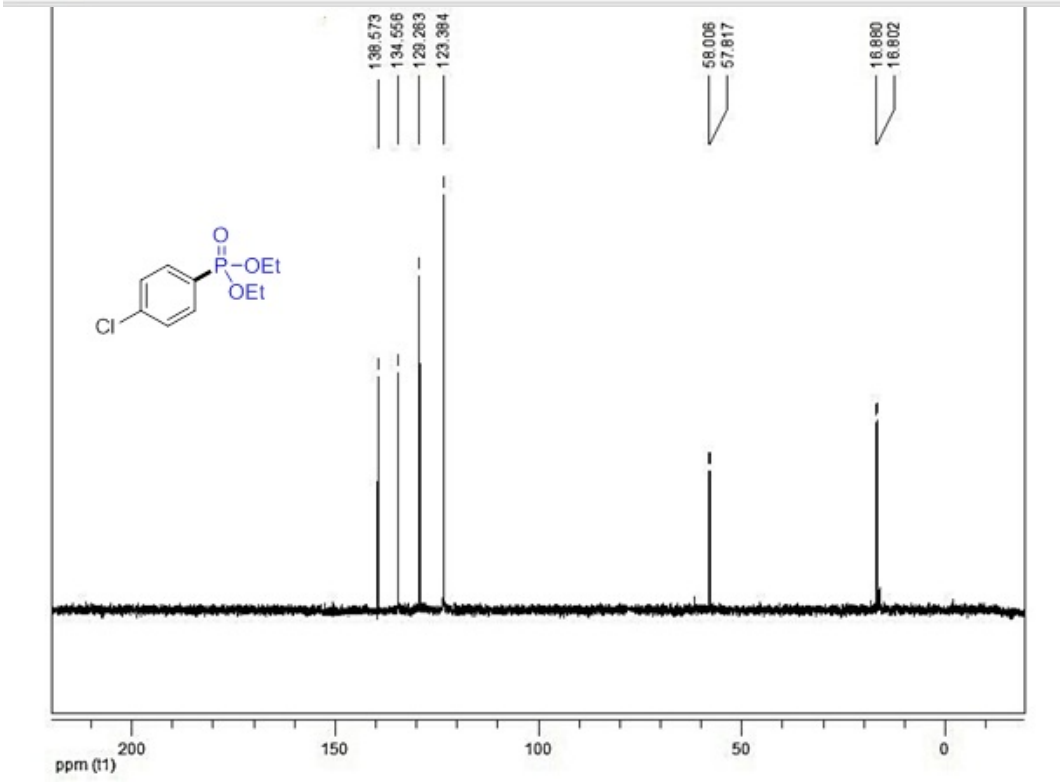

17.895
O
P
OEt
OEt
ppm (t1)
50
0
-50

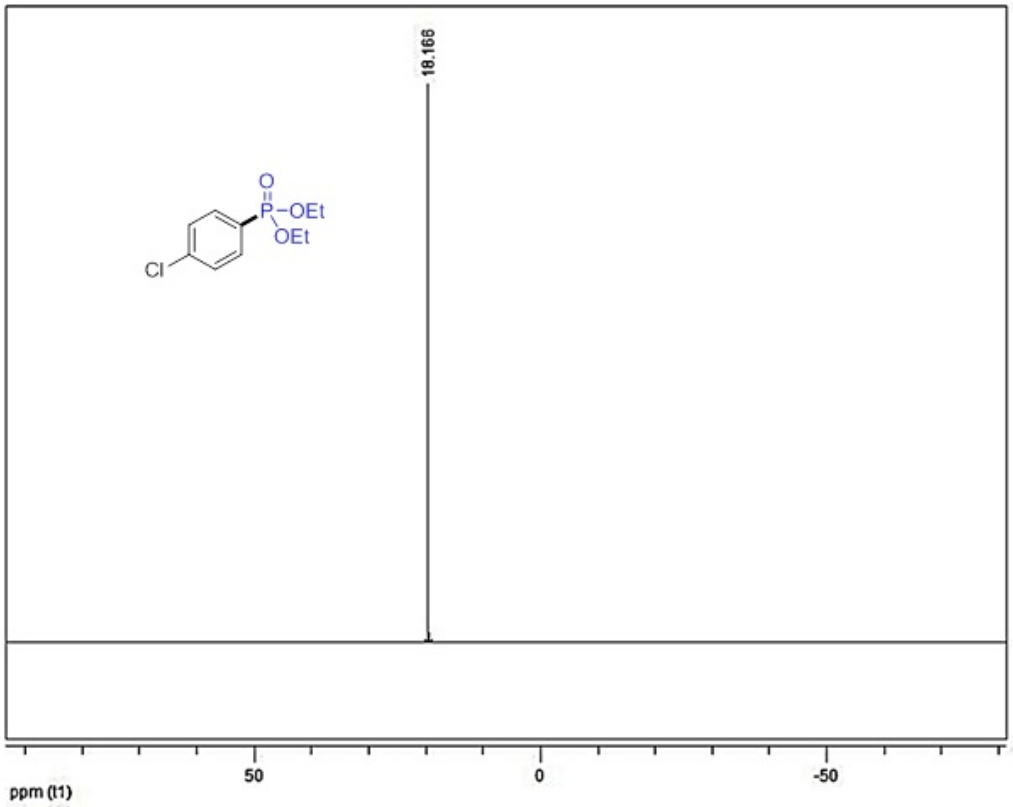

7.593
7.587
7.559
7.514
7.511
7.497
7.266
4.029
4.011
4.001
3.984
3.981
3.970
1.225
1.197
O
P
OEt
OEt
Br
1.00
0.98
1.52
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

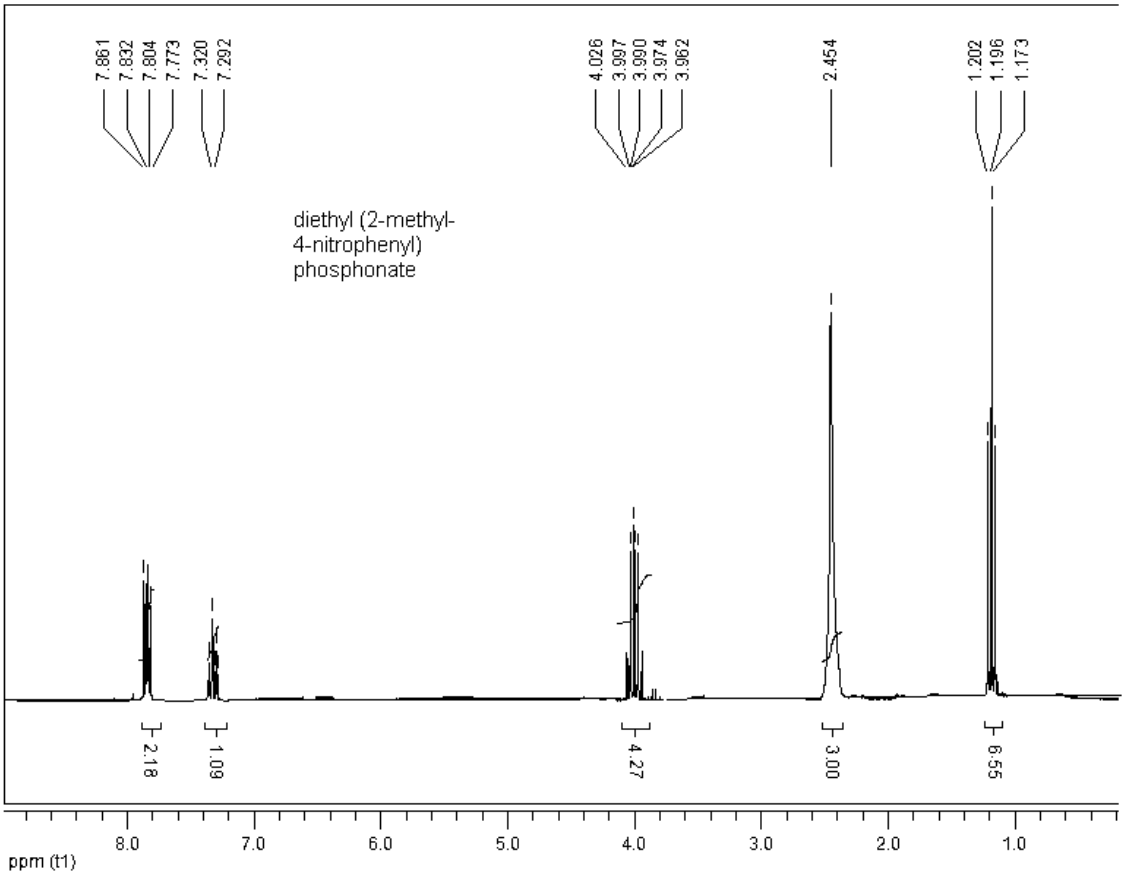

137.066
133.194
133.021
128.898
128.648
126.083
58.932
16.852
O
P
OEt
OEt
Br
100
50
0
ppm (t1)

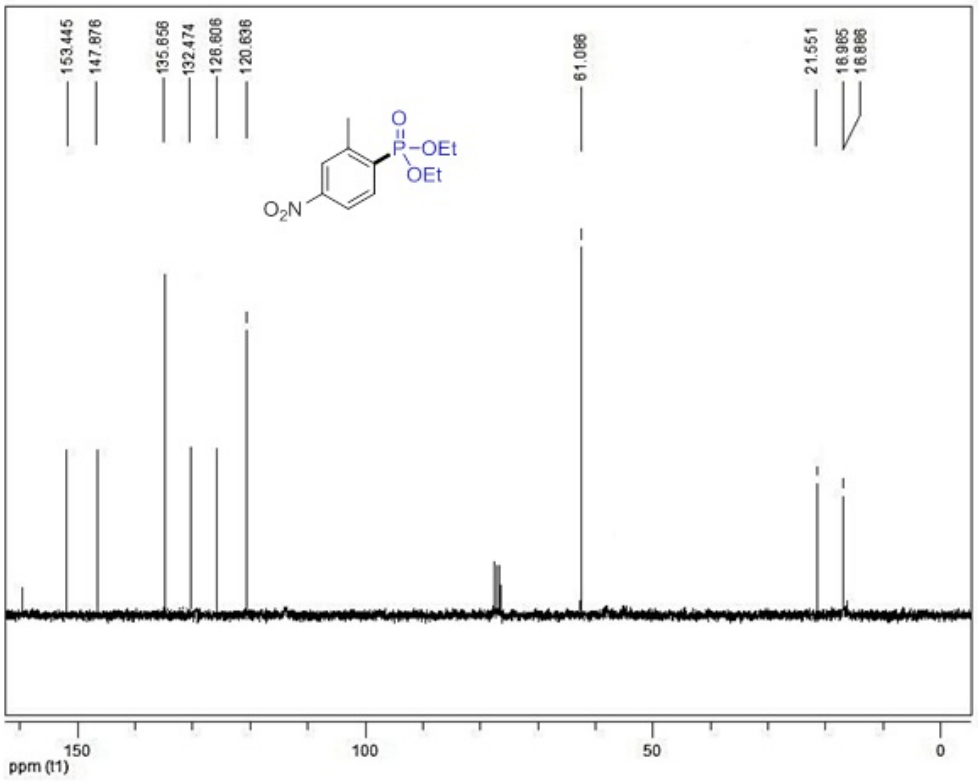

18.201
O
P
OEt
OEt
Br
50
0
-50
ppm (t1)

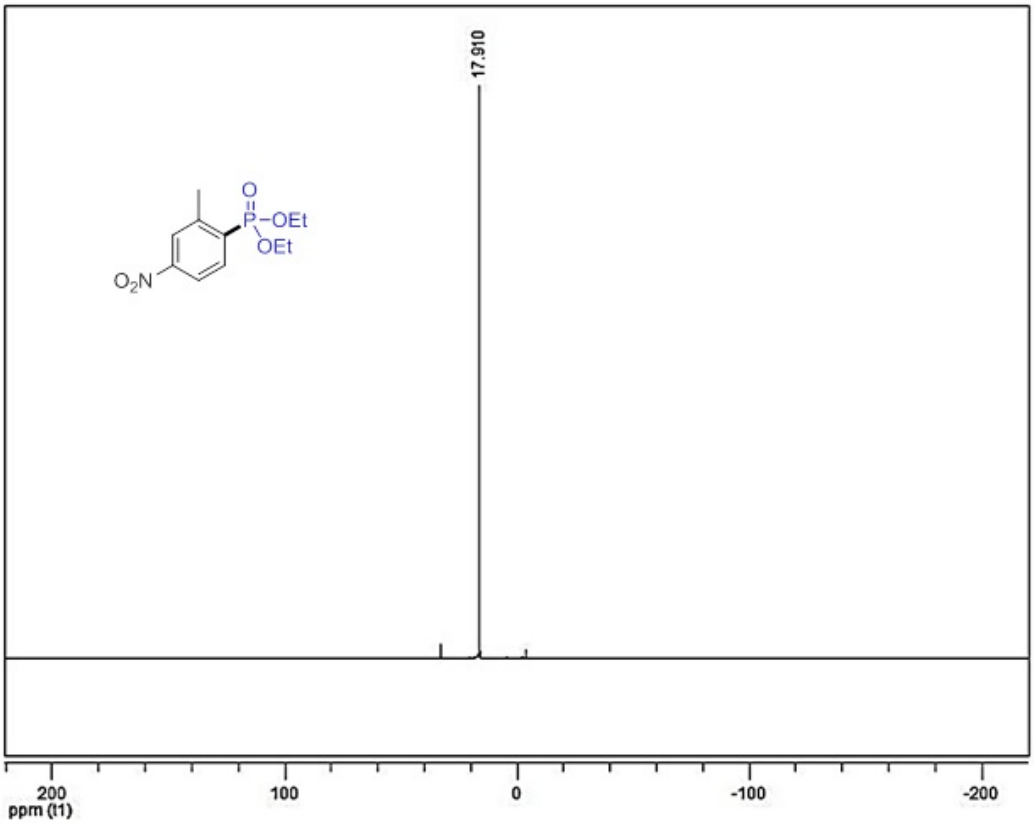

7.696
7.662
7.644
7.611
7.383
7.370
7.350
7.336
7.264
4.047
4.032
4.019
4.016
4.004
4.000
3.987
3.972
3.959
1.229
O
P–OEt
OEt
Cl
1.00
1.21
2.07
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

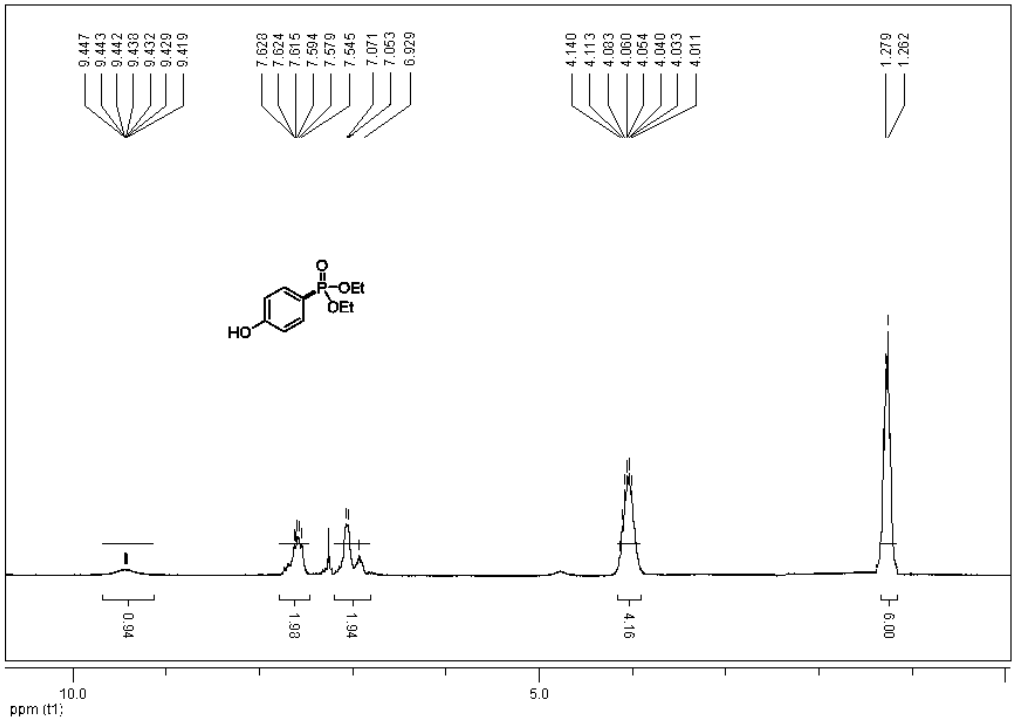

138.573
134.556
129.263
123.384
58.006
57.817
16.880
16.802
O
P–OEt
OEt
Cl
200
150
100
50
0
ppm (t1)

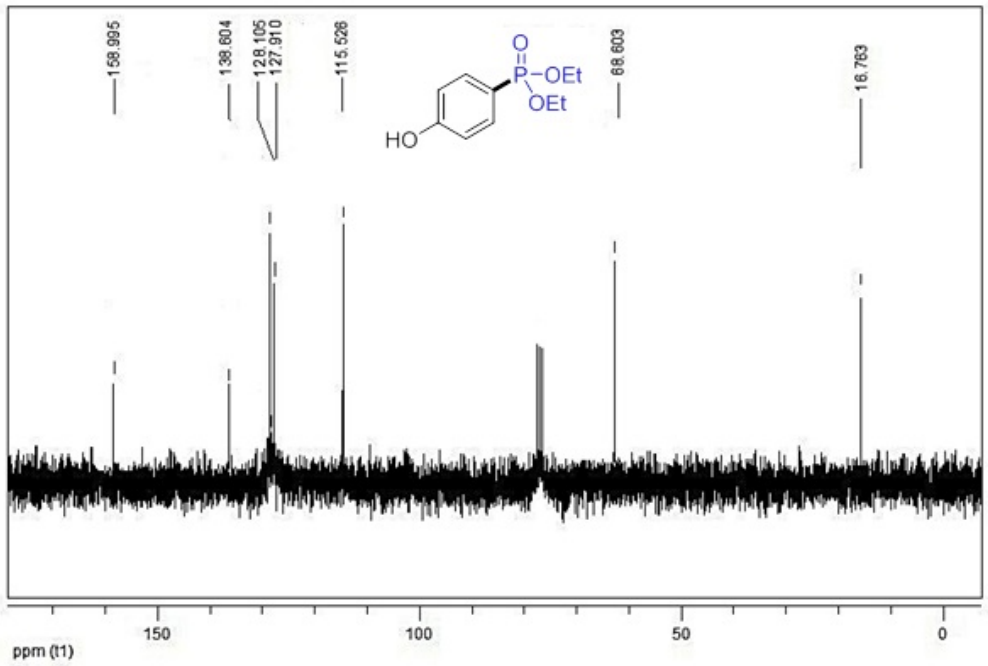

18.166
O
P–OEt
OEt
Cl
50
0
-50
ppm (t1)

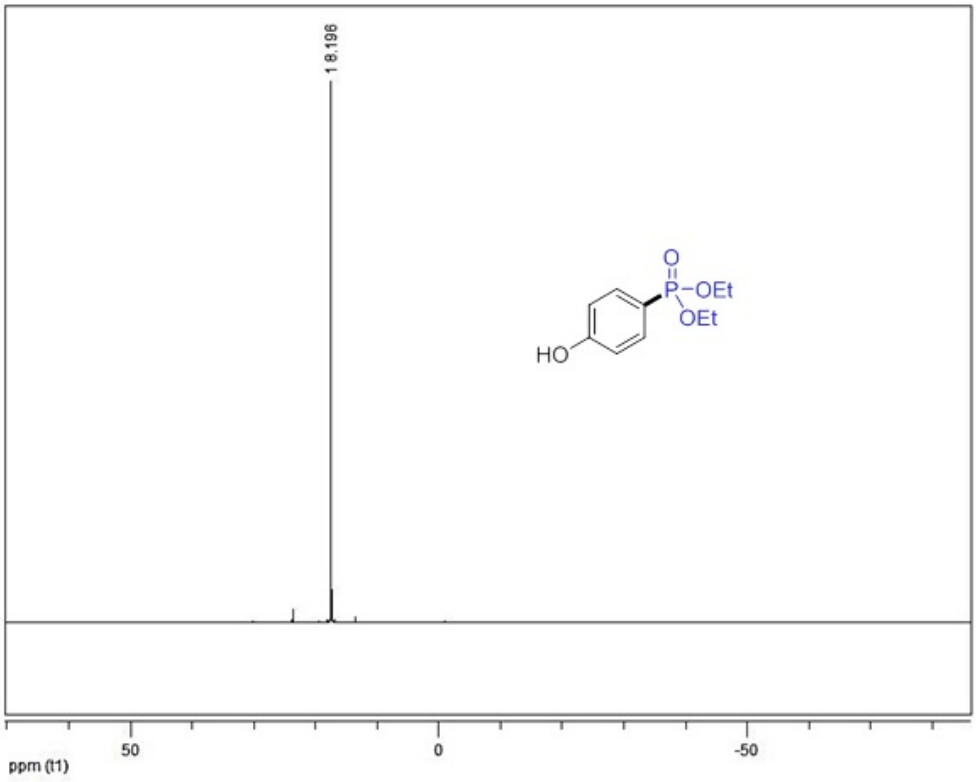

7.861
7.832
7.804
7.773
7.320
7.292
4.026
3.997
3.990
3.974
3.962
2.454
1.202
1.196
1.173
diethyl (2-methyl-
4-nitrophenyl)
phosphonate
2.18
1.09
4.27
3.00
6.55
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

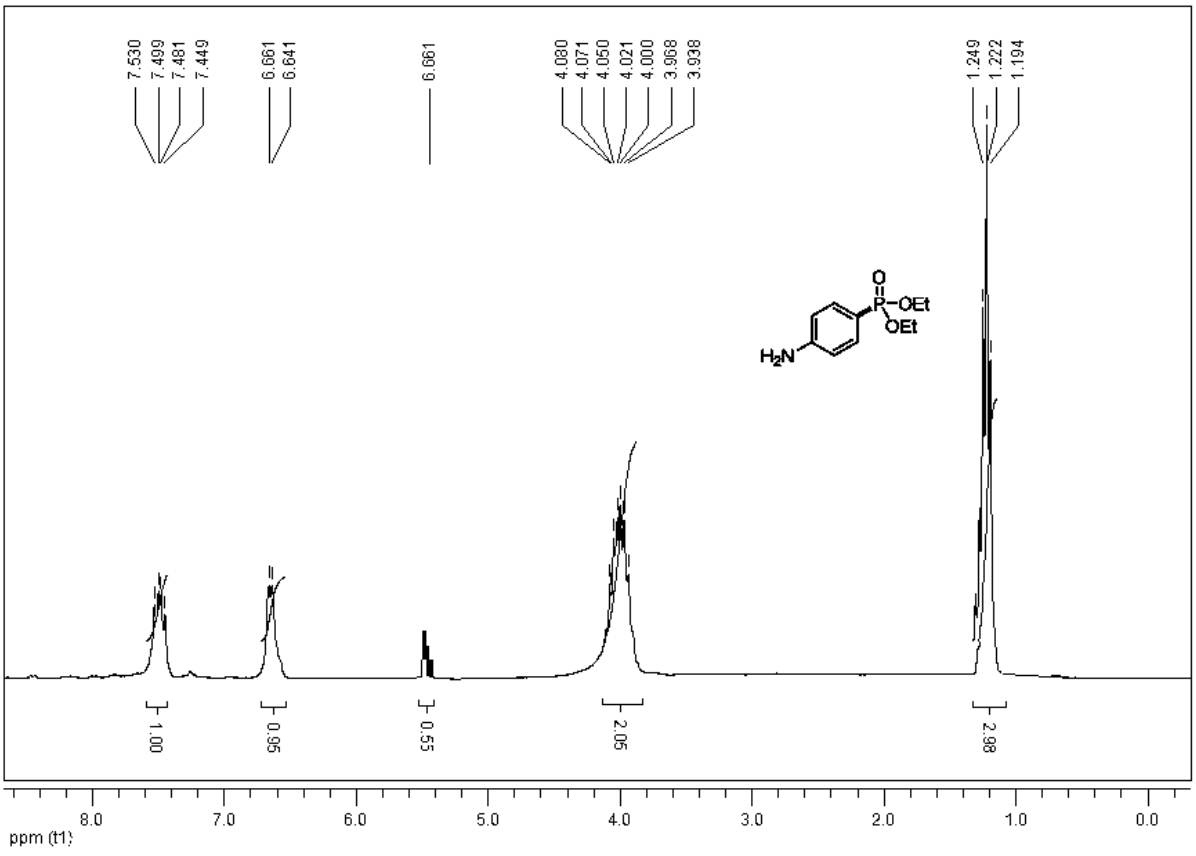

153.445
147.876
135.658
132.474
128.606
120.636
61.086
21.551
16.965
16.886
O
P–OEt
OEt
O2N
150
100
50
0
ppm (t1)

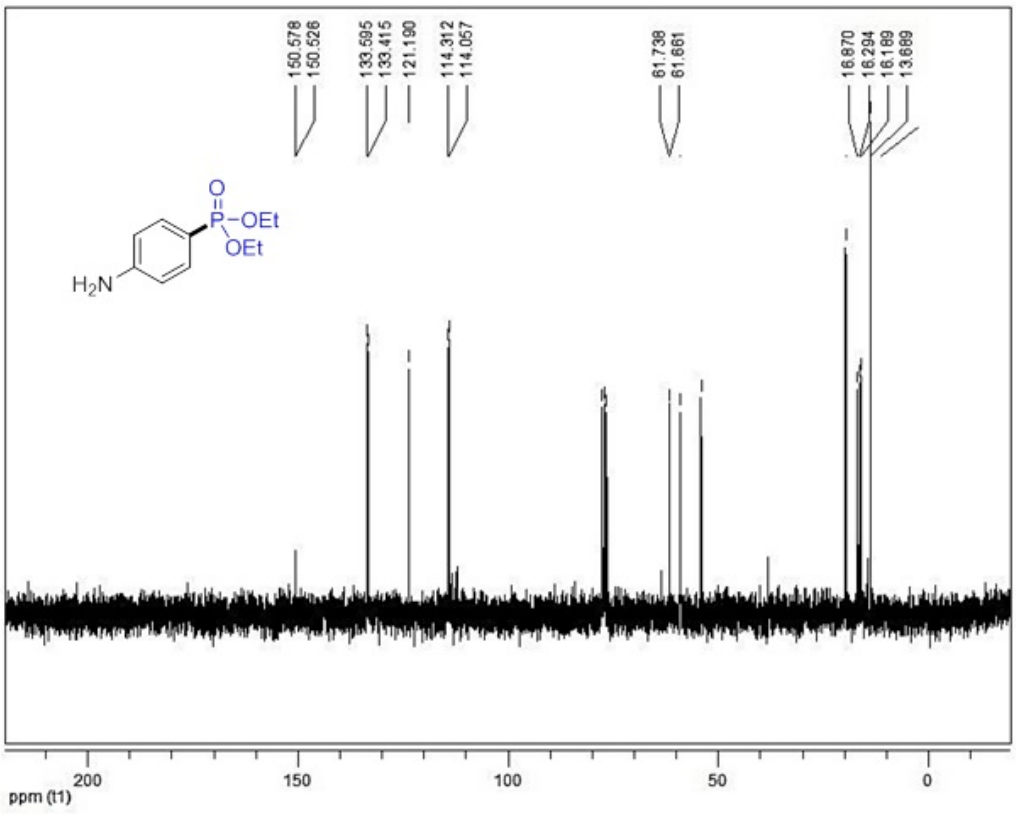

17.910
O
P–OEt
OEt
O2N
200
100
0
-100
-200
ppm (t1)

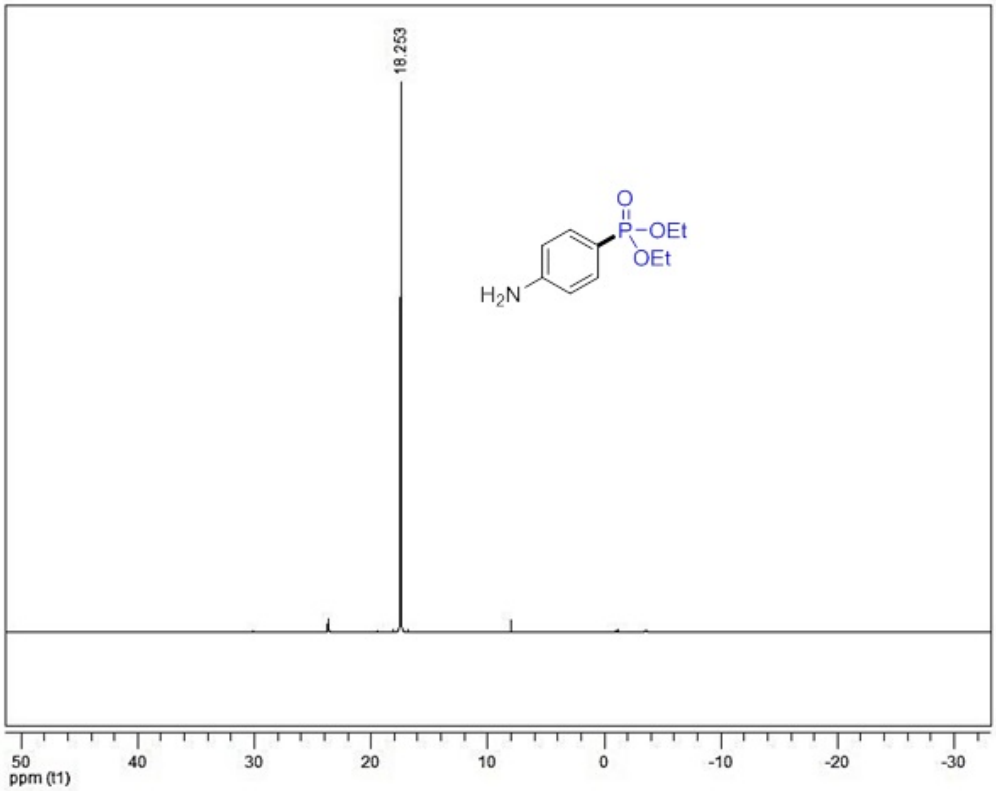

9.447
9.443
9.442
9.438
9.432
9.429
9.419
7.628
7.624
7.615
7.594
7.579
7.545
7.071
7.053
6.929
4.140
4.113
4.083
4.060
4.054
4.040
4.033
4.011
1.279
1.262
HO
O
P
OEt
OEt
0.94
1.93
1.94
4.16
6.00
10.0
5.0
ppm (t1)

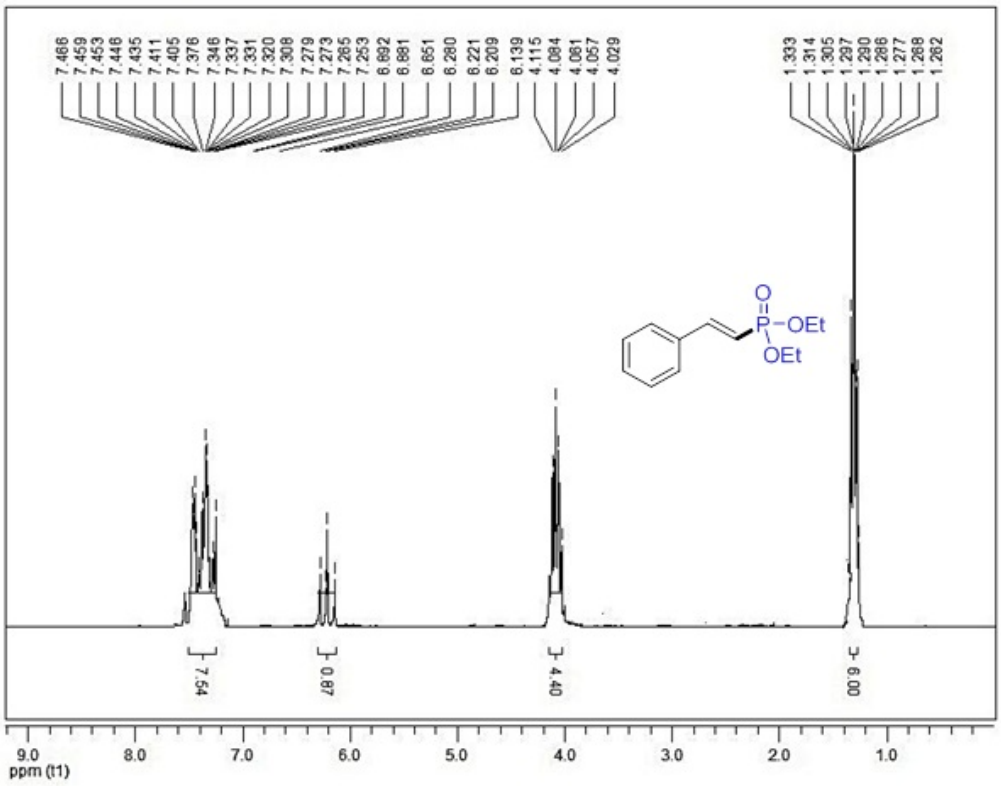

158.995
138.604
128.105
127.910
115.526
68.603
16.763
HO
O
P
OEt
OEt
150
100
50
0
ppm (t1)

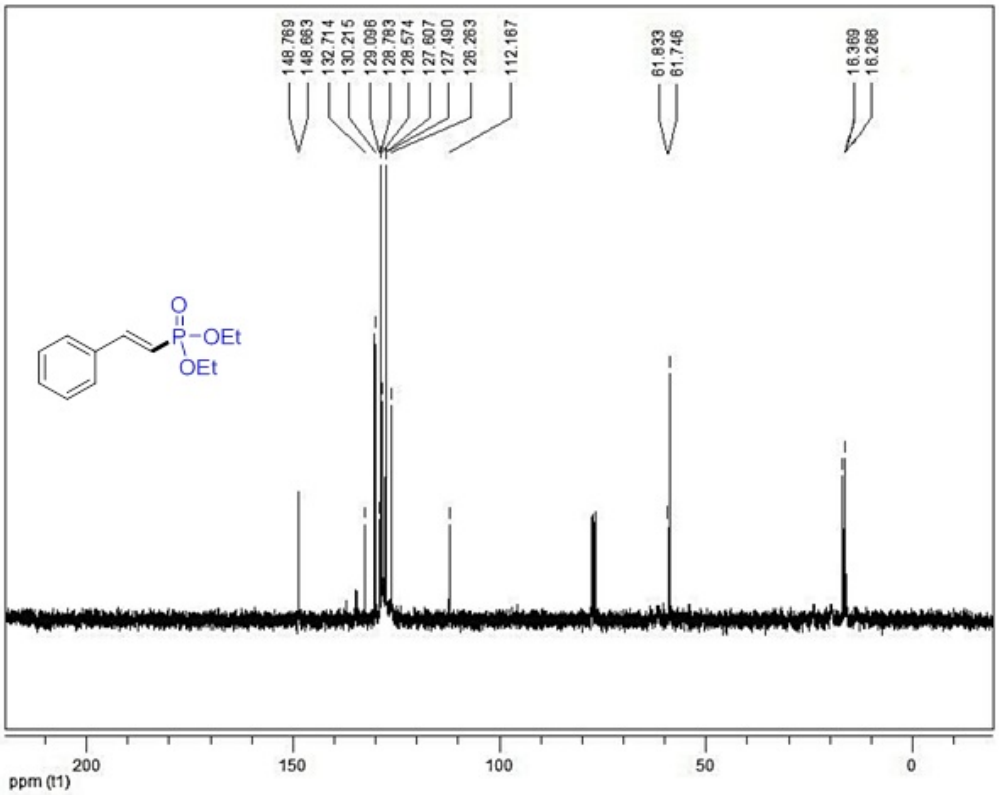

18.196
O
P–OEt
OEt
HO
50
0
-50
ppm (t1)

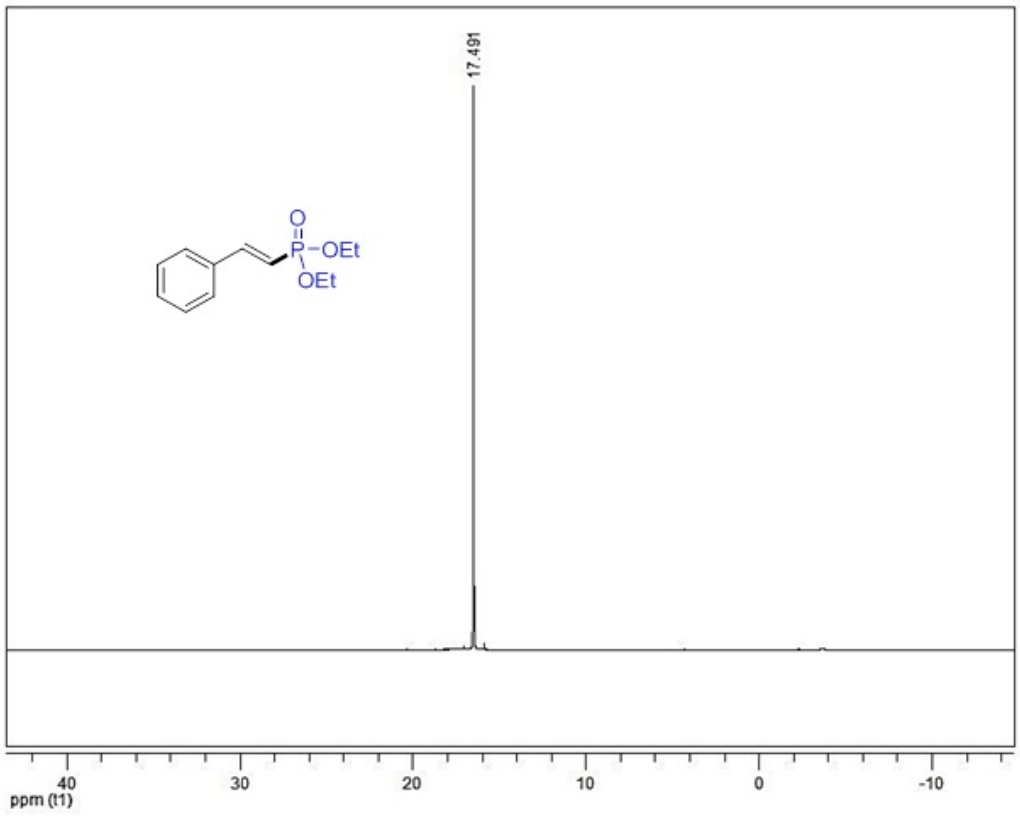

7.530
7.499
7.481
7.449
6.661
6.641
6.661
4.080
4.071
4.050
4.021
4.000
3.968
3.938
1.249
1.222
1.194
O
P–OEt
OEt
H2N
1.00
0.96
0.55
2.05
2.98
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

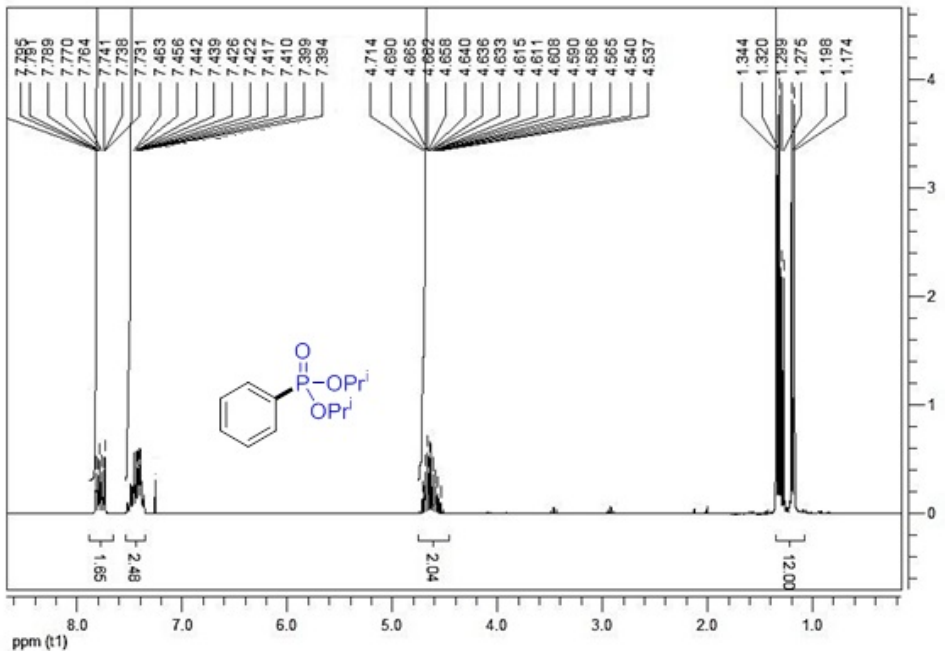

150.578
150.526
133.595
133.415
121.190
114.312
114.057
61.738
61.661
16.870
16.294
16.189
13.669
O
P–OEt
OEt
H2N
200
150
100
50
0
ppm (t1)

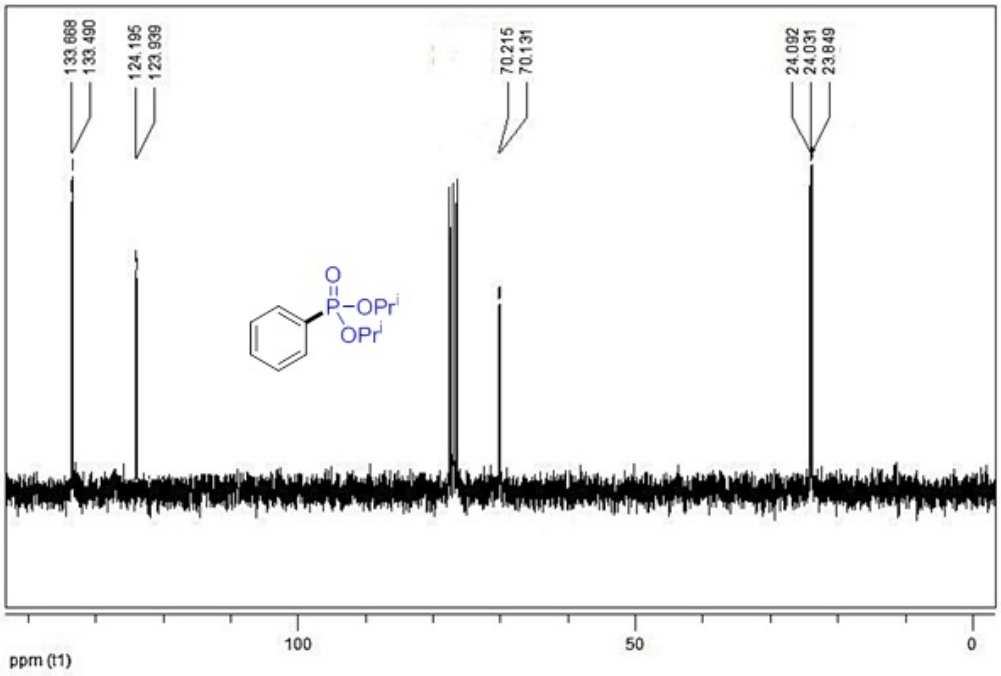

18.253
O
P–OEt
OEt
H2N
50
40
30
20
10
0
-10
-20
-30
ppm (t1)

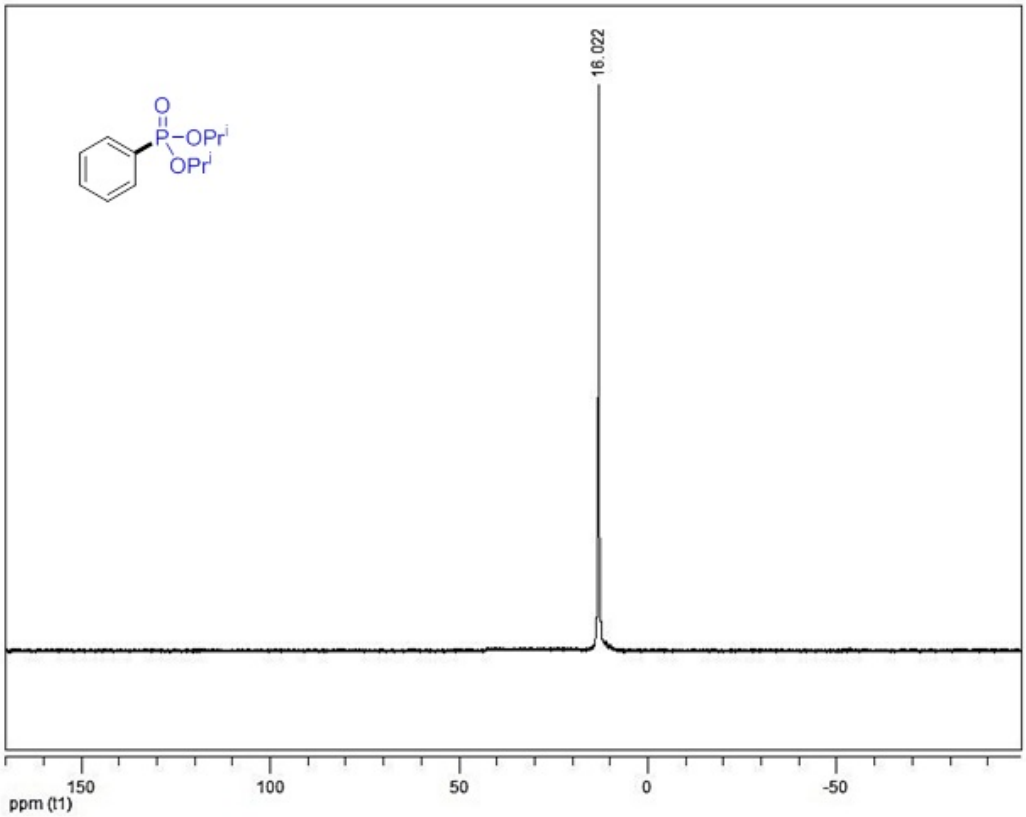

7.466
7.459
7.453
7.446
7.435
7.411
7.405
7.376
7.346
7.337
7.331
7.320
7.308
7.279
7.273
7.265
7.253
6.892
6.881
6.651
6.280
6.221
6.209
6.139
4.115
4.084
4.061
4.057
4.029
1.333
1.314
1.305
1.297
1.290
1.286
1.277
1.268
1.262
O
P–OEt
OEt
7.54
0.87
4.40
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

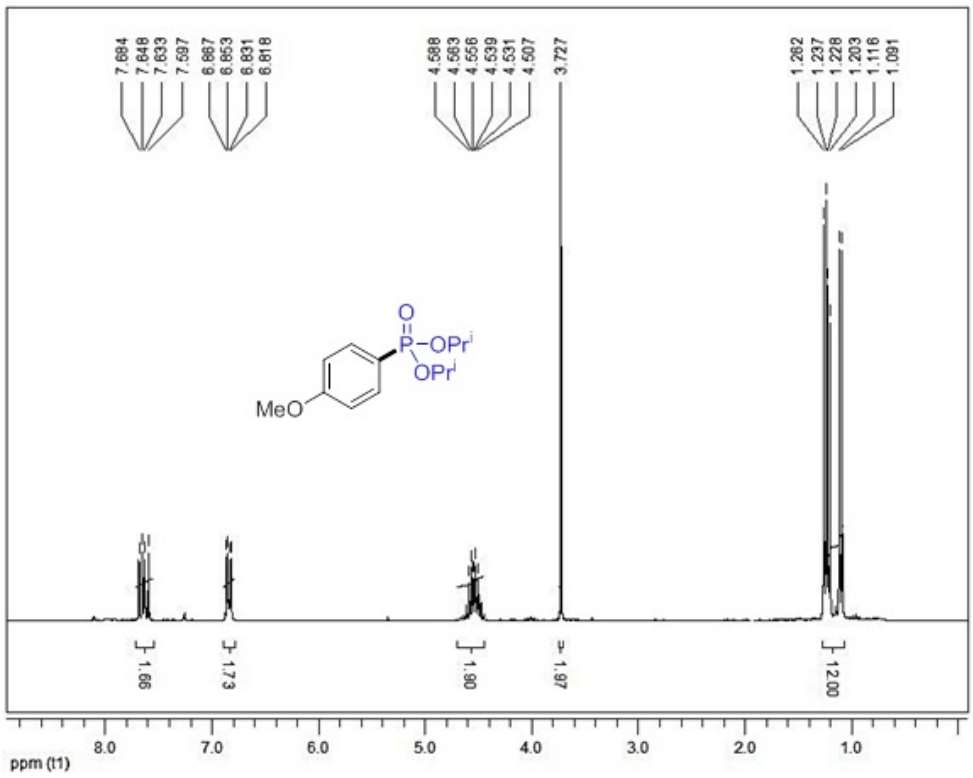

148.769
148.663
132.714
130.215
129.096
128.783
128.574
127.607
127.490
126.263
112.167
61.833
61.746
16.369
16.266
O
P–OEt
OEt
200
150
100
50
0
ppm (t1)

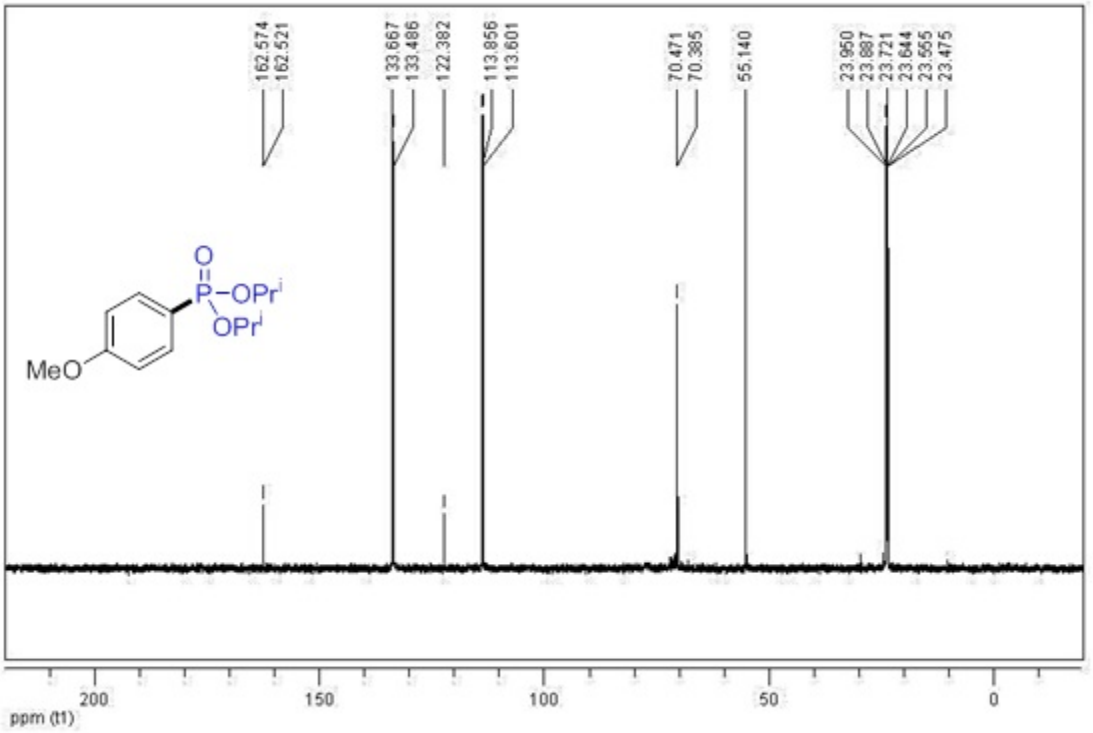

17.491
O
P–OEt
OEt
40
30
20
10
0
-10
ppm (t1)

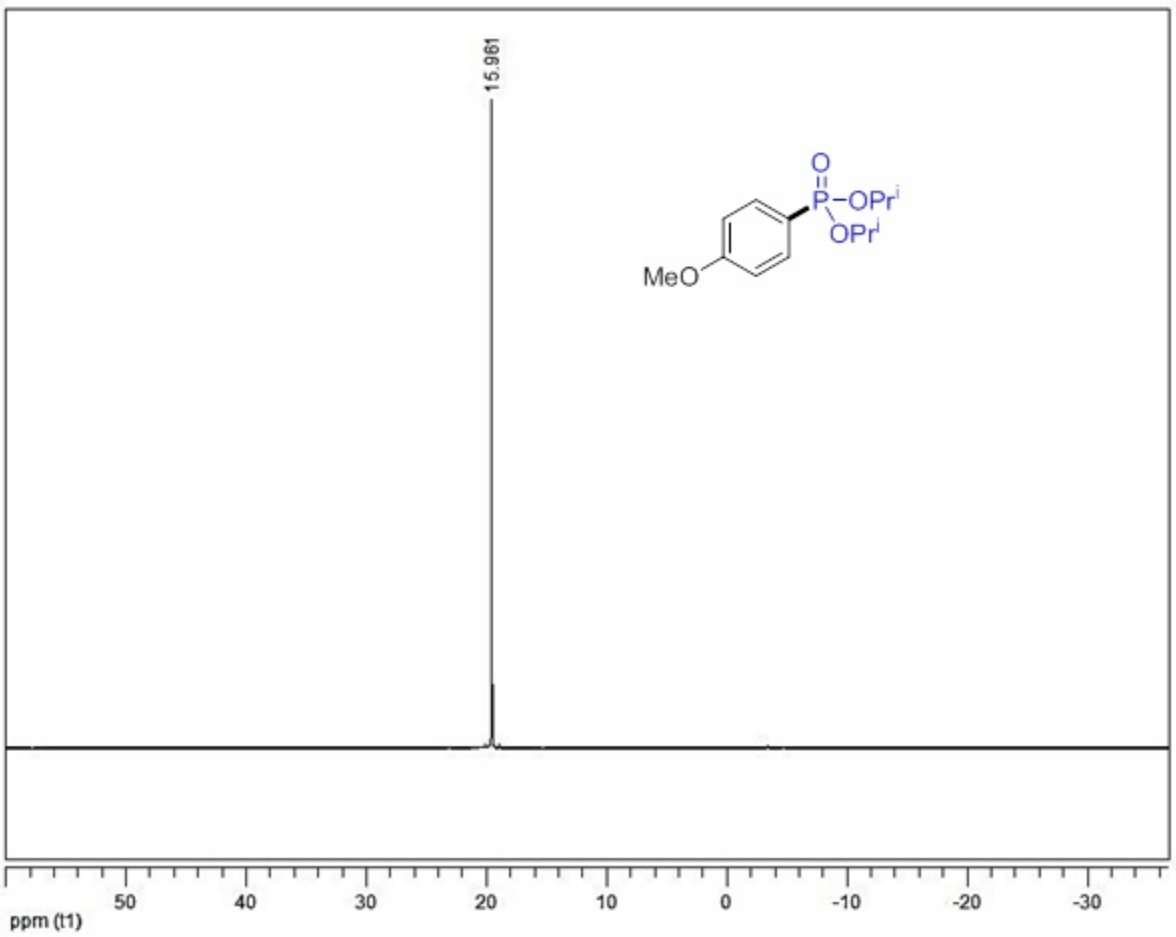

7.795
7.791
7.789
7.770
7.764
7.741
7.738
7.731
7.463
7.456
7.442
7.439
7.426
7.422
7.417
7.410
7.399
7.394
4.714
4.690
4.685
4.658
4.640
4.636
4.633
4.615
4.611
4.608
4.590
4.586
4.565
4.540
4.537
1.344
1.320
1.275
1.198
1.174
O
P–OPr^i
OPr^i
1.65
2.48
2.04
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

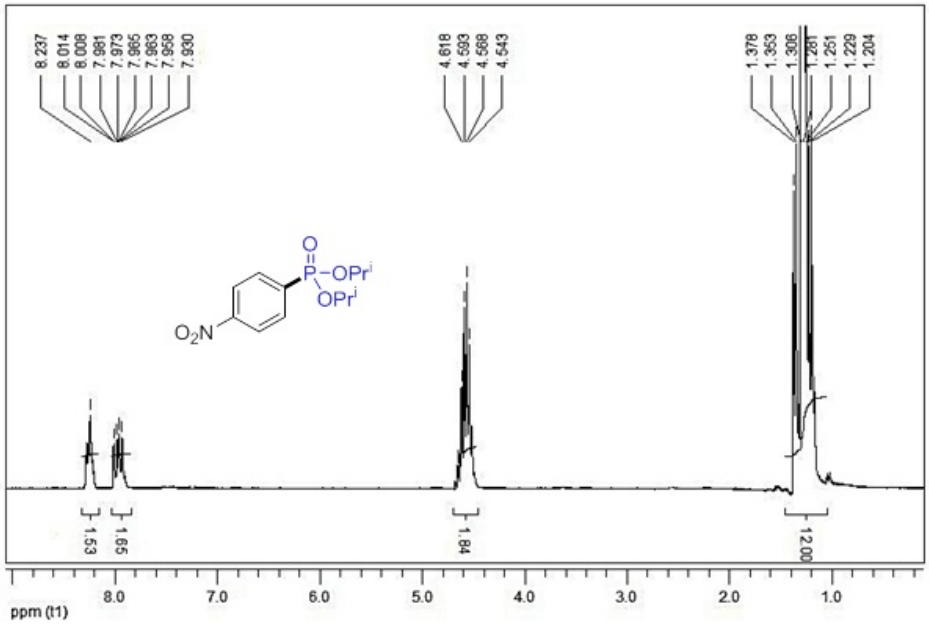

133.668
133.490
124.195
123.939
70.215
70.131
24.092
24.031
23.849
O
P–OPr^i
OPr^i
100
50
0
ppm (t1)

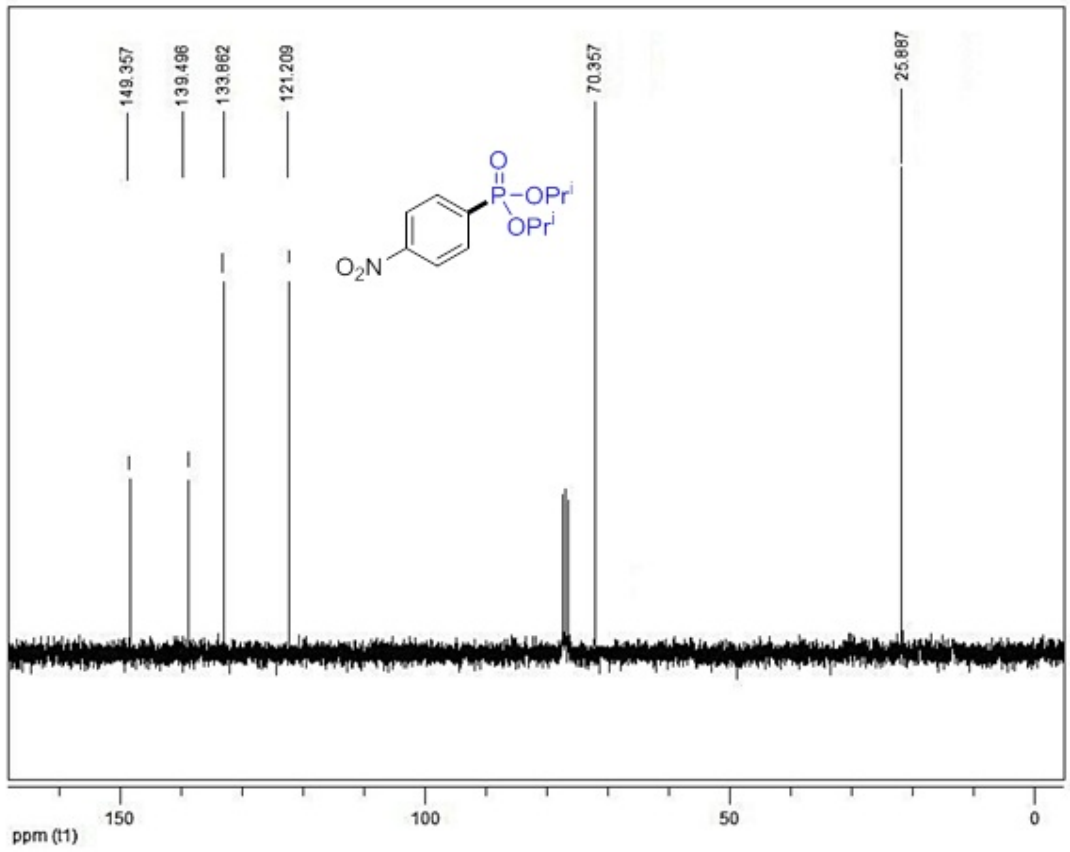

16.022
O
P–OPr^i
OPr^i
150
100
50
0
-50
ppm (t1)

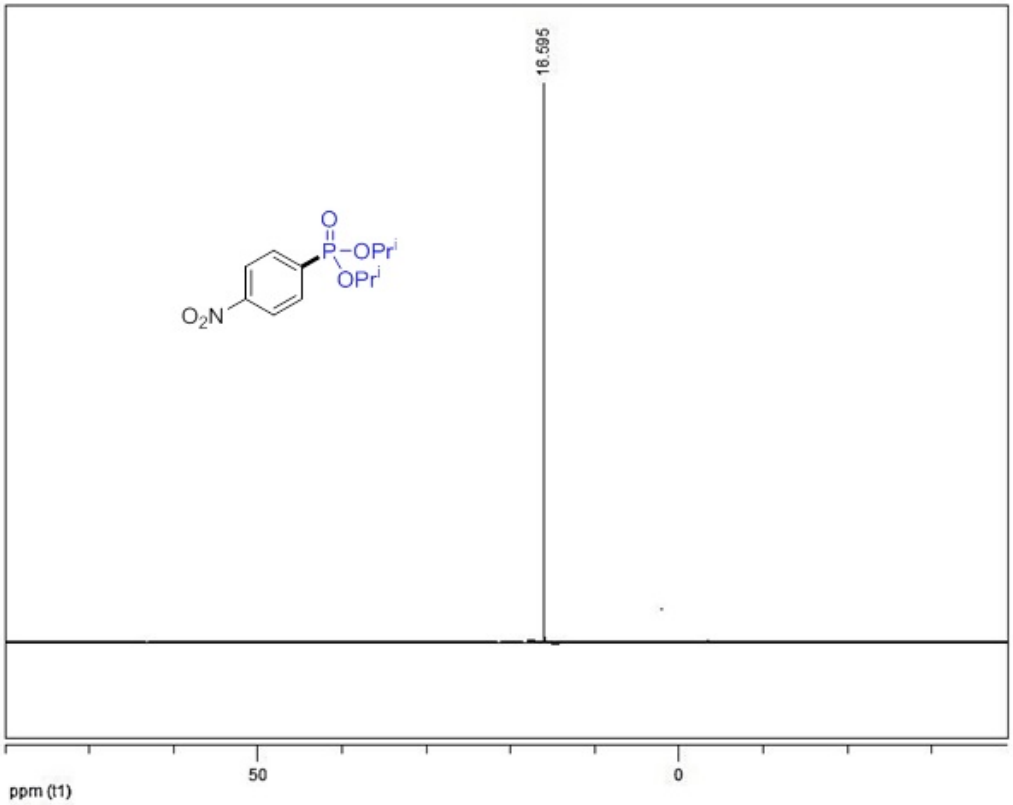

7.684
7.648
7.633
7.597
6.867
6.853
6.831
6.818
4.588
4.563
4.556
4.539
4.531
4.507
3.727
1.262
1.237
1.228
1.203
1.116
1.091
O
P–OPr^i
OPr^i
MeO
1.66
1.73
1.80
1.97
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

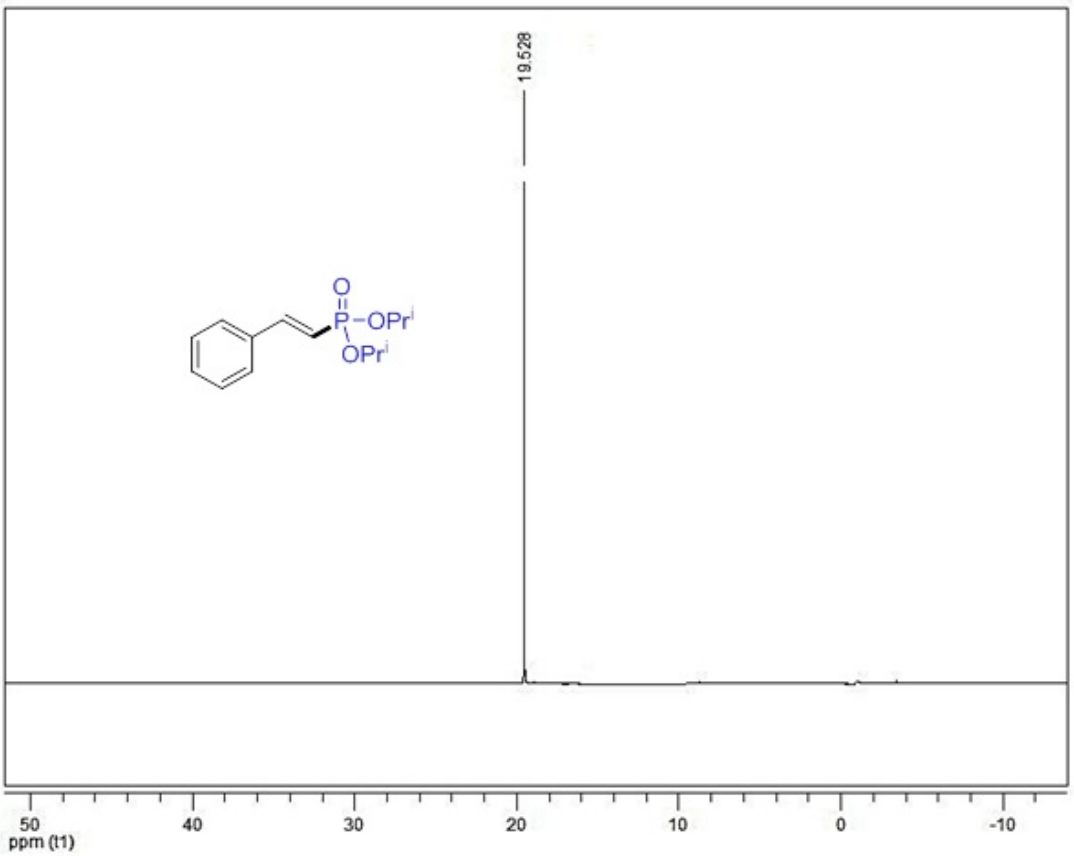

162.574
162.521
133.667
133.486
122.382
113.856
113.601
70.471
70.385
55.140
23.950
23.887
23.721
23.644
23.555
23.475
O
P–OPr^i
OPr^i
MeO
200
150
100
50
0
ppm (t1)

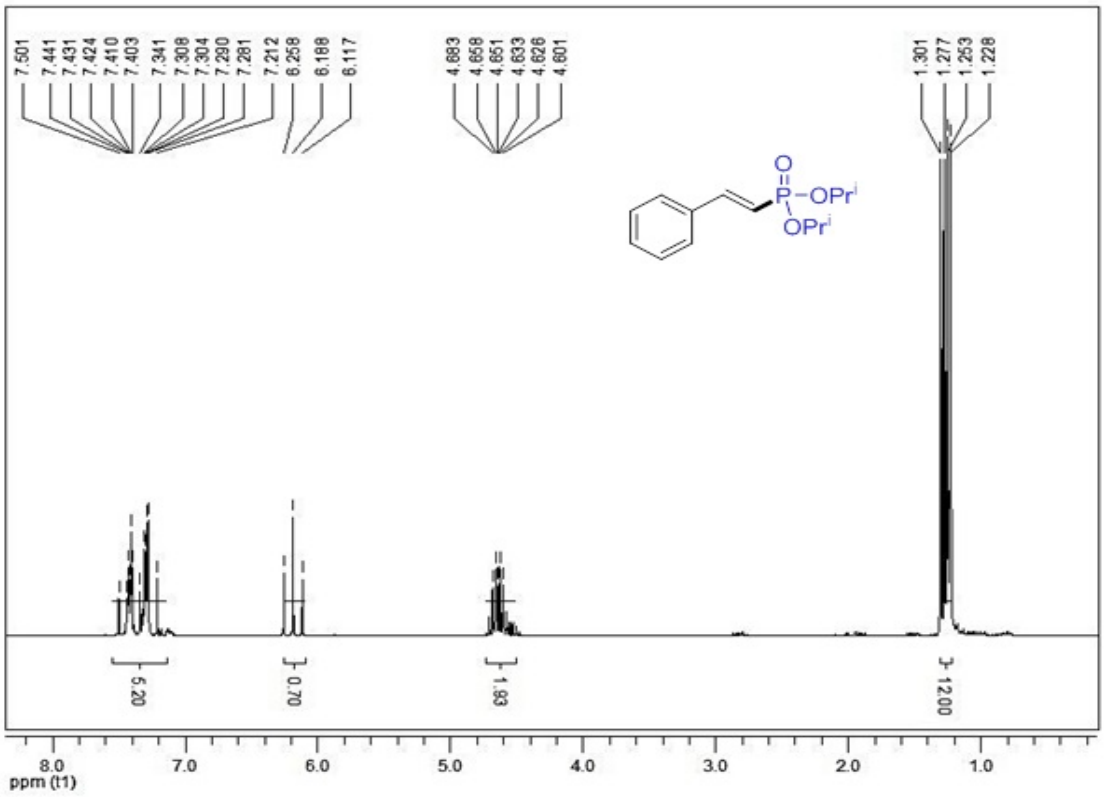

15.961
MeO
O
P–OPr^i
OPr^i
50
40
30
20
10
0
-10
-20
-30
ppm (t1)

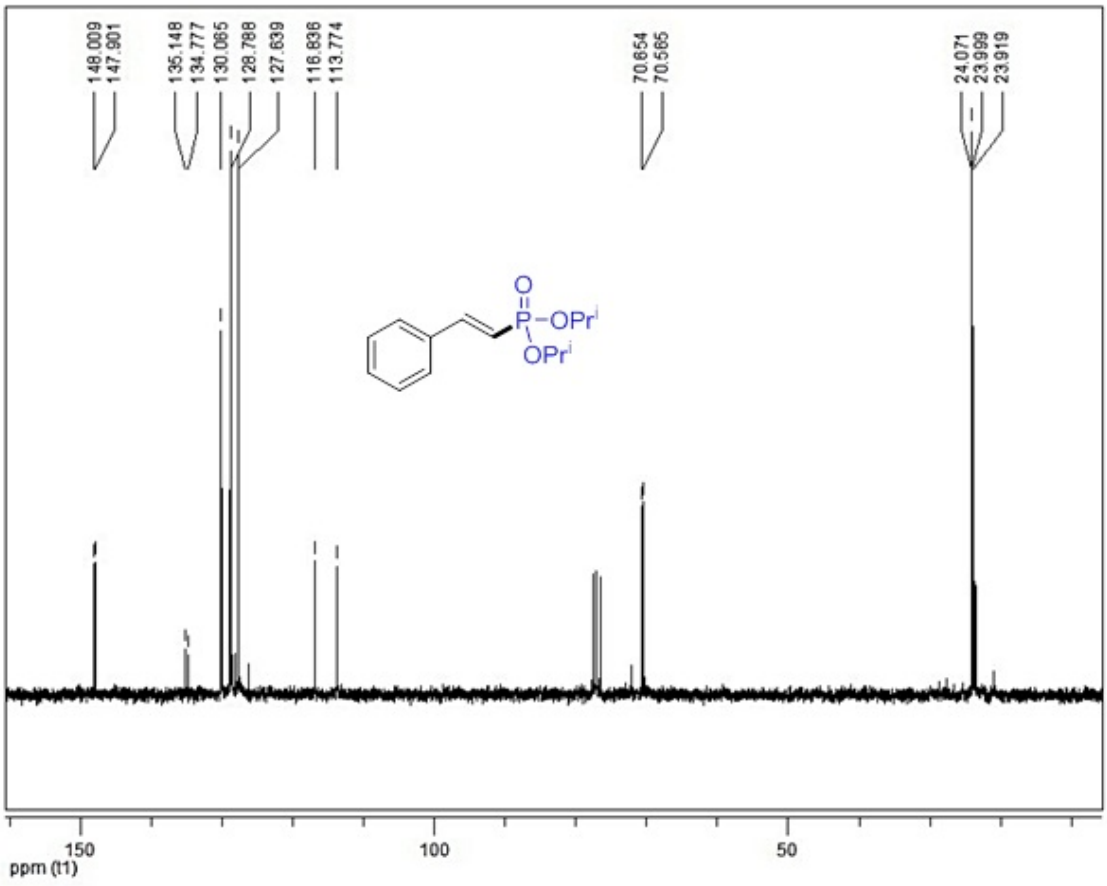

8.237
8.014
8.008
7.981
7.973
7.965
7.963
7.958
7.930
4.618
4.593
4.568
4.543
1.378
1.353
1.306
1.281
1.251
1.229
1.204
O
P–OPr^i
OPr^i
O_2N
1.53
1.65
1.84
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


149.357
139.496
133.862
121.209
70.357
25.887
O
P–OPr^i
OPr^i
O_2N
150
100
50
0
ppm (t1)


16.595
O
P–OPr^i
OPr^i
O_2N
50
0
ppm (t1)


19.528
O
P–OPr^i
OPr^i
50
40
30
20
10
0
-10
ppm (t1)


7.501
7.441
7.431
7.424
7.410
7.403
7.341
7.308
7.304
7.290
7.281
7.212
6.258
6.188
6.117
4.683
4.658
4.651
4.633
4.626
4.601
1.301
1.277
1.253
1.228
O
P–OPr^i
OPr^i
6.20
0.70
1.93
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



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