Supplementary Material (ESI) for Chemical Communications

– Electronic Supplementary Material (ESI) –

Iron catalyzed dehydrogenative phosphonation of *N*,*N*-dimethylanilines

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General. All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were recorded on 300 and 400 MHz NMR spectrometers. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (δ_H 7.24 and δ_C 77.0 ppm). Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS was performed on a Finnigan MAT 95Q mass spectrometer. Infrared spectra of neat substances were recorded on a Perkin-Elmer Spectrum BX II FT-IR spectrometer equipped with an ATR probe (diamond).

Materials. Commercially available tertiary amines were used as received. *N*,*N*-Dimethyl-p-anisidine was prepared according to a literature procedure.[S1]

The following iron and copper salts were used: Iron(II) acetate (anhydrous, 97 %, Strem), iron(III) bromide (99 %, ABCR), iron(II) chloride (98 %, Aldrich), iron(II) fluoride (99 %, Strem), iron(II) perchlorate hydrate (98 %, Aldrich), iron(III) chloride (anhydrous, 97 %, Acros), copper(I) bromide (98 %, Acros), and copper(I) chloride (98 %, Merck).

Dialkyl phosphonates (Aldrich) and *tert*.-butyl hydroperoxide (TBHP, 5.5 M solution in decane, purum, Aldrich) were purchased.

Typical Procedure for the Iron Catalyzed Phosphonation of Tertiary Amines. Under an atmosphere of dry N_2, a 25 mL Schlenk flask was charged with iron(II) chloride (10 mol-%, 13 mg). The tertiary amine (1.0 mmol), dialkyl phosphonate (2.0 mmol), and MeOH (2.0 mL) were added successively by syringe. To the mixture was added dropwise *tert*.-butyl hydroperoxide (2.5 mmol, 0.470 mL, 5.5 M solution in decane) over a period of 5 min. The mixture was stirred at room temperature for the indicated time. At the end of the reaction, the reaction mixture was poured into a saturated aqueous NaCl solution (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic phases were combined, and the volatile components were evaporated in a rotary evaporator. The crude product was purified by column chromatography on silica gel (n-pentane/ethyl acetate/triethylamine).

(S1) J. A. Hodges and R. T. Raines, *Org. Lett*., 2006, **8**, 4695–4697.

Dimethyl [(4-methoxyphenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2954, 2835, 1511, 1464, 1409, 1358, 1299, 1242, 1180, 1106, 1019, 869, 813, 790 and 687; δ_H($CDCl_3$, 400 MHz) 2.95 (s, 3 H), 3.62 (d, $^2J_{H,P}$ 7.6 Hz, 2 H), 3.69 (d, $J_{H,P}$ 10.4 Hz, 6 H), 3.72 (s, 3 H), 6.76–6.81 ppm (m, 4 H); δ_C($CDCl_3$, 100 MHz) 39.9, 50.7 (d, $^1J_{C,P}$ 162 Hz), 52.7 (d, $J_{C,P}$ 7.0 Hz), 55.6, 114.6, 115.0, 144.0 (d, $J_{C,P}$ 3.7 Hz), 152.5 ppm; δ_P($CDCl_3$, 162 MHz) 26.30 ppm; HRMS *m/z* (EI) 259.0970, $C_{11}H_{18}NO_4P$ requires 259.0973.

Diethyl [(4-methoxyphenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2982, 2934, 2907, 2834, 1512, 1466, 1443, 1408, 1391, 1366, 1296, 1242, 1182, 1164, 1099, 1019, 956, 861, 815, 773 and 687; δ_H($CDCl_3$, 400 MHz) 1.24 (t, *J* 7.2 Hz, 6 H), 2.95 (s, 3 H), 3.59 (d, $^2J_{H,P}$ 8.0 Hz, 2 H), 3.72 (s, 3 H), 4.01–4.11 (m, 4 H), 6.76–6.81 ppm (m, 4 H); δ_C($CDCl_3$, 100 MHz) 16.4 (d, $J_{C,P}$ 5.6 Hz), 39.7, 51.2 (d, $^1J_{C,P}$ 162 Hz), 55.7, 62.1 (d, $J_{C,P}$ 7.0 Hz), 114.5, 114.9 (d, $J_{C,P}$ 0.9 Hz), 144.3 (d, $J_{C,P}$ 3.8 Hz), 152.3 ppm; δ_P($CDCl_3$, 162 MHz) 23.92 ppm; HRMS *m/z* (ESI+) 288.1351, $[C_{13}H_{23}NO_4P]^+$ requires 288.1359.

Di-*iso*-propyl [(4-methoxyphenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2978, 2934, 2834, 1512, 1466, 1385, 1374, 1297, 1242, 1180, 1141, 1104, 1037, 978, 898, 887, 853, 815, 754 and 687; δ_H($CDCl_3$, 400 MHz) 1.21 (d, *J* 6.4 Hz, 6 H), 1.29 (d, *J* 6.0 Hz, 6 H), 2.96 (s, 3 H), 3.52 (d, $^2J_{H,P}$ 8.0 Hz, 2 H), 3.72 (s, 3 H), 4.66–4.74 (m, 2 H), 6.79 ppm (s, 4 H); δ_C($CDCl_3$, 100 MHz) 24.0 (d, $J_{C,P}$ 4.9 Hz), 24.2 (d, $J_{C,P}$ 3.6 Hz), 39.9, 52.0 (d, $^1J_{C,P}$ 166 Hz), 55.7, 70.7 (d, $J_{C,P}$ 7.3 Hz), 114.4, 115.0, 144.6 (d, $J_{C,P}$ 4.2 Hz), 152.2 ppm; δ_P($CDCl_3$, 162 MHz) 22.06 ppm; HRMS *m/z* (EI) 315.1580, $C_{15}H_{28}NO_4P$ requires 315.1599.

Dimethyl [methyl(p-tolyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2954, 2919, 2853, 1676, 1616, 1520, 1450, 1360, 1230, 1184, 1107, 1022, 869, 800, 714 and 692; δ_H($CDCl_3$, 400 MHz) 2.22 (s, 3 H), 2.97 (s, 3 H), 3.66 (d, $^2J_{H,P}$ 7.6 Hz, 2 H), 3.69 (d, $J_{H,P}$ 10.4 Hz, 6 H), 6.71 (d, J 8.6 Hz, 2 H), 7.02 ppm (d, J 8.6 Hz, 2 H); δ_C($CDCl_3$, 100 MHz) 20.1, 39.3, 49.8 (d, $^1J_{C,P}$ 162 Hz), 52.6 (d, $J_{C,P}$ 7.0 Hz), 113.2 (d, $J_{C,P}$ 1 Hz), 126.9 (d, $J_{C,P}$ 0.9 Hz), 129.6 (d, $J_{C,P}$ 0.4 Hz), 147.2 ppm (d, $J_{C,P}$ 2.8 Hz); δ_P($CDCl_3$, 162 MHz) 26.08 ppm; HRMS *m/z* (ESI+) 244.1091, $[C_{11}H_{19}NO_3P]^+$ requires 244.1097.

Diethyl [methyl(p-tolyl)amino]methylphosphonate

Known compound; the ^{1}H NMR spectroscopic data agree with those given in lit.[S2]. Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2981, 2907, 2868, 2819, 1678, 1616, 1520, 1477, 1443, 1391, 1360, 1244, 1230, 1188, 1164, 1100, 1046, 1019, 957, 861, 801, 774, 715 and 692; δ_H($CDCl_3$, 300 MHz) 1.24 (t, J 7.0 Hz, 6 H), 2.22 (s, 3 H), 2.97 (s, 3 H), 3.63 (d, $^2J_{H,P}$ 7.8 Hz, 2 H), 4.00–4.10 (m, 4 H), 6.71 (d, J 8.4 Hz, 2 H), 7.01 ppm (d, J 8.4 Hz, 2 H); δ_C($CDCl_3$, 75.5 MHz) 16.4 (d, $J_{C,P}$ 5.7 Hz), 20.1, 39.3, 50.3 (d, $^1J_{C,P}$ 162 Hz) , 62.0 (d, $J_{C,P}$ 7.0 Hz), 113.2 (d, $J_{C,P}$ 1.1 Hz), 126.7 (d, $J_{C,P}$ 0.8 Hz), 129.5, 147.4 ppm (d, $J_{C,P}$ 2.9 Hz); δ_P($CDCl_3$, 162 MHz) 23.83 ppm.

Di-*iso*-propyl [methyl(p-tolyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2978, 2930, 2873, 1680, 1617, 1520, 1467, 1453, 1384, 1374, 1359, 1247, 1230, 1179, 1142, 1104, 978, 898, 886, 853, 801, 755, 718 and 690; δ_H($CDCl_3$, 400 MHz) 1.21 (d, J 6.0 Hz, 6 H), 1.29 (d, J 6.0 Hz, 6 H), 2.22 (s, 3 H), 2.98 (s, 3 H), 3.56 (d, $^2J_{H,P}$ 8.4 Hz, 2 H), 4.66–4.74 (m, 2 H), 6.72 (d, J 8.2 Hz, 2 H), 7.00 ppm (d, J 8.0 Hz, 2 H); δ_C($CDCl_3$, 100 MHz) 20.2, 23.9 (d, $J_{C,P}$ 4.9 Hz), 24.1(d, $J_{C,P}$ 3.6 Hz), 39.3, 51.2 (d, $^1J_{C,P}$ 166 Hz), 70.8 (d, $J_{C,P}$ 7.3 Hz), 113.4(d, $J_{C,P}$ 1.0 Hz), 126.6, 129.4, 147.7 ppm (d, $J_{C,P}$ 3.6

(S2) G. Bidan and M. Genies, *Tetrahedron*, 1981, **37**, 2297–2301.

Hz); δ_P($CDCl_3$, 162 MHz) 22.11 ppm; HRMS *m/z* (EI) 299.1643, $C_{15}H_{26}NO_3P$ requires 299.1650.

Diethyl [methyl-phenyl-amino]methylphosphonate

Known compound (lit.[S3]). Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2981, 2930, 2907, 1677, 1599, 1506, 1365, 1296, 1244, 1197, 1162, 1099, 1048, 1019, 956, 860, 778, 747 and 691; δ_H($CDCl_3$, 400 MHz) 1.24 (t, *J* 7.2 Hz, 6 H), 3.01 (s, 3 H), 3.68 (d, $^2J_{H,P}$ 8.0 Hz, 2 H), 4.01–4.11 (m, 4 H), 6.73 (t, *J* 7.4 Hz, 1 H), 6.80 (d, *J* 8.4 Hz, 2 H), 7.19–7.23 ppm (m, 2 H); δ_C($CDCl_3$, 100 MHz) 16.4 (d, $J_{C,P}$ 5.7 Hz), 39.2, 49.9 (d, $^1J_{C,P}$ 162 Hz), 62.1 (d, $J_{C,P}$ 7.0 Hz), 112.9 (d, $J_{C,P}$ 1.1 Hz), 117.5, 129.0, 149.3 ppm (d, $J_{C,P}$ 2.2 Hz); δ_P($CDCl_3$, 162 MHz) 23.46 ppm; HRMS *m/z* (EI) 257.1170, $C_{12}H_{20}NO_3P$ requires 257.1181.

Dimethyl [(4-bromophenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2953, 2903, 2851, 1591, 1496, 1367, 1310, 1238, 1194, 1107, 1080, 1020, 869, 801, 754, 713 and 692; δ_H($CDCl_3$, 400 MHz) 2.96 (s, 3 H), 3.64 (d, $^2J_{H,P}$ 8.0 Hz, 2 H), 3.67 (dd, $J_{H,P}$ 10.8 Hz, *J* 0.4 Hz, 6 H), 6.62 (d, *J* 9.0 Hz, 2 H), 7.25 ppm (d, *J* 9.0 Hz, 2 H); δ_C($CDCl_3$, 100 MHz) 39.2, 49.1 (d, $^1J_{C,P}$ 161 Hz), 52.6 (d, $J_{C,P}$ 6.9 Hz), 109.5 (d, $J_{C,P}$ 1.2 Hz), 114.3 (d, $J_{C,P}$ 1.2 Hz), 131.7, 147.9 ppm (d, $J_{C,P}$ 1.6 Hz); δ_P($CDCl_3$, 162 MHz) 25.43 ppm; HRMS *m/z* (EI) 306.9972, $C_{10}H_{15}NO_3{}^{79}BrP$ requires 306.9973.

Diethyl [(4-bromophenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2982, 2906, 2821, 1679, 1591, 1496, 1368, 1239, 1196, 1163, 1099, 1046, 1018, 956, 860, 806, 750 and 694; δ_H($CDCl_3$, 400 MHz) 1.24 (t, *J* 7.0 Hz, 6 H), 2.99 (s, 3 H), 3.64 (d, $^2J_{H,P}$ 7.6 Hz, 2 H), 3.99–4.11 (m, 4 H), 6.66 (d, *J* 9.0 Hz, 2

(S3) (*a*) B. E. Ivanov and S. S. Krokhina, *Russ. Chem. Bull.*, 1967, 405–407 (*Izv. Akad. Nauk SSSR, Ser. Khim.* 1971, 424–426); (*b*) B. E. Ivanov and S. S. Krokhina, *Russ. Chem. Bull.*, 1971, 2629–2632 (*Izv. Akad.Nauk SSSR, Ser. Khim.* 1971, 2773–2776). (*c*) F. Effenberger and H. Kottmann, *Tetrahedron,* 1985, **41**, 4171–4182.

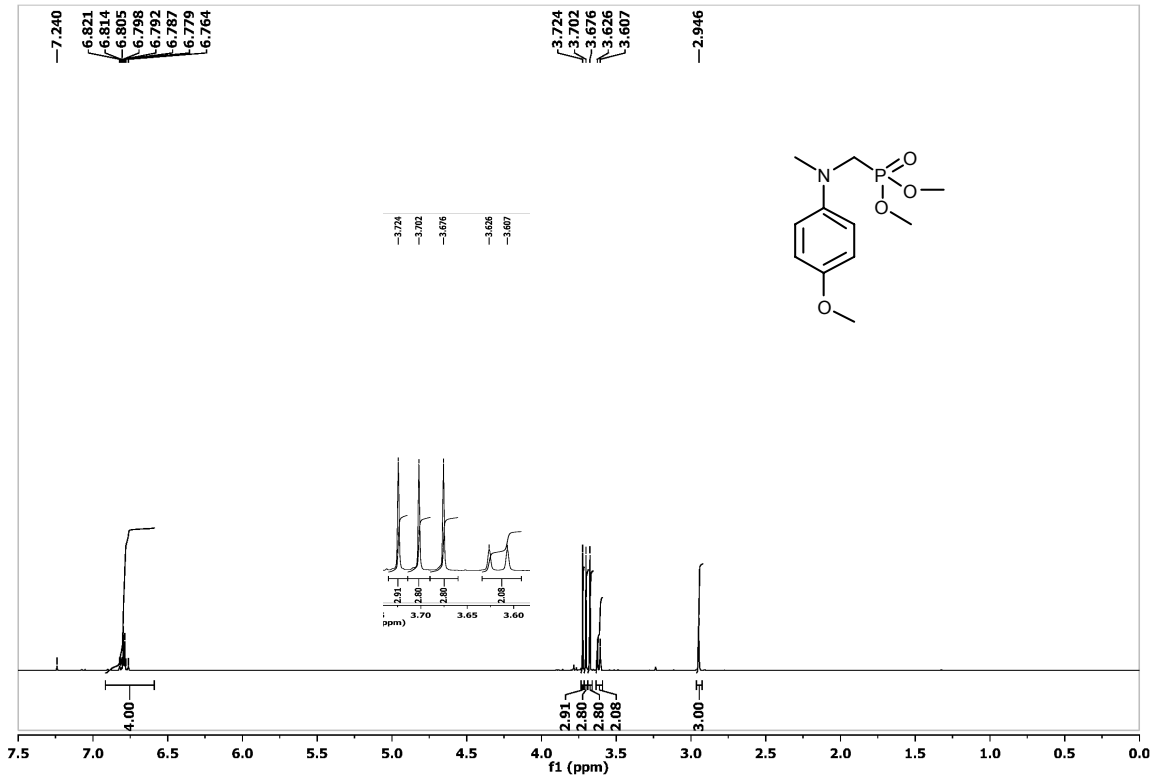
H), 7.27 ppm (d, *J* 9.0 Hz, 2 H); δ_C($CDCl_3$, 100 MHz) 16.4 (d, $J_{C,P}$ 5.6 Hz), 39.3, 49.8 (d, $^1J_{C,P}$ 162 Hz), 62.2 (d, $J_{C,P}$ 7.0 Hz), 109.5(d, $J_{C,P}$ 1.2 Hz), 144.5 (d, $J_{C,P}$ 1.1 Hz), 131.6, 148.1 (d, $J_{C,P}$ 1.6 Hz) ppm; δ_P($CDCl_3$, 162 MHz) 22.97 ppm; HRMS *m/z* (EI) 335.0277, $C_{12}H_{19}NO_3{}^{79}BrP$ requires 335.0286.

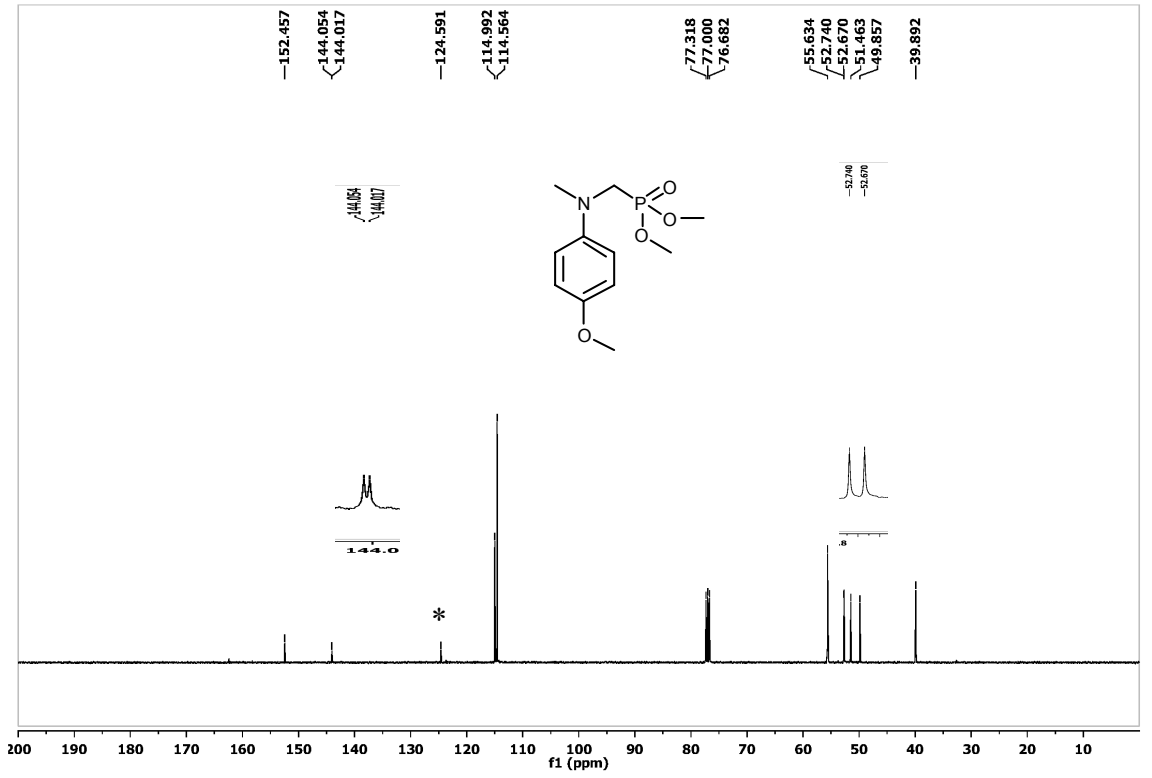
Diisopropyl [(4-bromophenyl)(methyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2978, 2933, 2822, 1681, 1592, 1496, 1385, 1372, 1245, 1195, 1179, 1142, 1104, 1080, 978, 899, 887, 853, 806, 735 and 718; δ_H($CDCl_3$, 400 MHz) 1.18 (d, *J* 6.0 Hz, 6 H), 1.27 (d, *J* 6.4 Hz, 6 H), 2.97 (s, 3 H), 3.56 (d, $^2J_{H,P}$ 8.4 Hz, 2 H), 4.63–4.71 (m, 2 H), 6.64 (d, *J* 9.0 Hz, 2 H), 7.24 ppm (d, *J* 9.0 Hz, 2 H); δ_C($CDCl_3$, 100 MHz) 23.9 (d, $J_{C,P}$ 4.8 Hz), 24.1 (d, $J_{C,P}$ 3.6 Hz), 39.3, 50.5 (d, $^1J_{C,P}$ 164 Hz), 70.9 (d, $J_{C,P}$ 7.4 Hz), 109.1 (d, $J_{C,P}$ 1.1 Hz), 114.5(d, $J_{C,P}$ 1.2 Hz), 131.5, 148.3 ppm (d, $J_{C,P}$ 1.9 Hz); δ_P($CDCl_3$, 162 MHz) 21.21 ppm; HRMS *m/z* (EI) 363.0586, $C_{14}H_{23}NO_3{}^{79}BrP$ requires 363.0599.

Diethyl [methyl(3-nitrophenyl)amino]methylphosphonate

Viscous oil; ν_{max}(neat/ATR probe)/cm^{-1} 2983, 2908, 1618, 1571, 1524, 1497, 1444, 1415, 1371, 1344, 1297, 1232, 1204, 1163, 1099, 1047, 1018, 958, 882, 860, 783, 734 and 669; δ_H($CDCl_3$, 400 MHz) 1.22 (t, *J* 7.0 Hz, 6 H); 3.08 (s, 3 H), 3.71 (d, $^2J_{H,P}$ 8.0 Hz, 2 H), 4.02–4.10 (m, 4 H), 7.03–7.06 (m, 1 H), 7.29 (t, *J* 8.2 Hz, 1 H), 7.49–7.55 ppm (m, 2 H); δ_C($CDCl_3$, 100 MHz) 16.4 (d, $J_{C,P}$ 5.6 Hz), 39.4, 49.3 (d, $^1J_{C,P}$ 161 Hz), 62.2 (d, $J_{C,P}$ 7.0 Hz), 106.6 (d, $J_{C,P}$ 1.0 Hz), 111.6, 118.1 (d, $J_{C,P}$ 1.1 Hz), 129.5 (d, $J_{C,P}$ 0.7 Hz), 149.1, 149.4 ppm; δ_P($CDCl_3$, 162 MHz) 22.37 ppm; HRMS *m/z* (EI) 302.1019, $C_{12}H_{19}N_2O_5P$ requires 302.1032.





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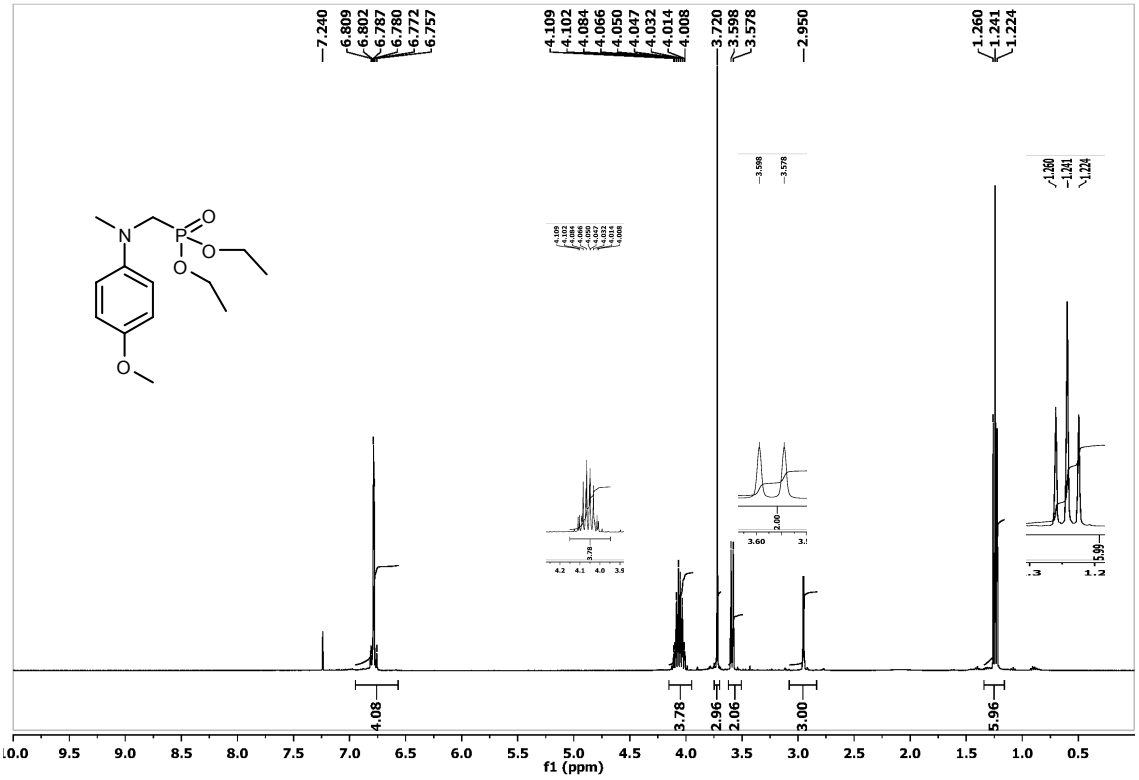
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4.047
4.032
4.014
4.008
3.720
3.598
3.578
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1.241
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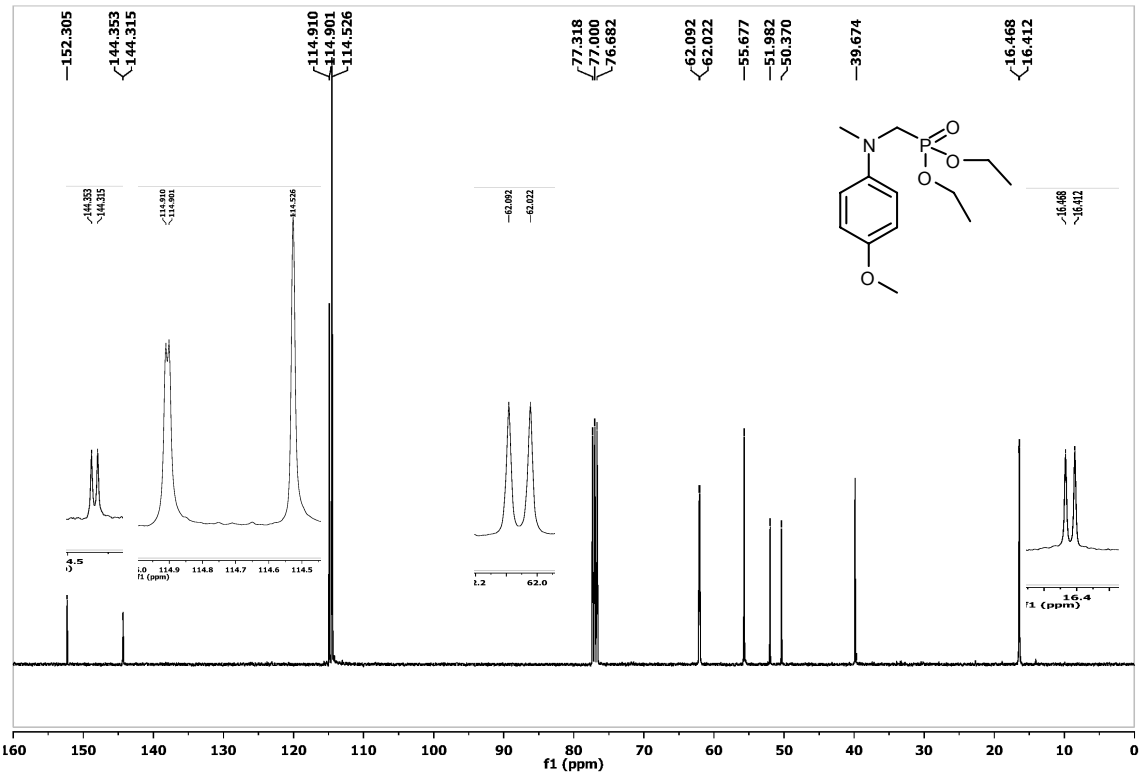
2.06
3.00
5.96
f1 (ppm)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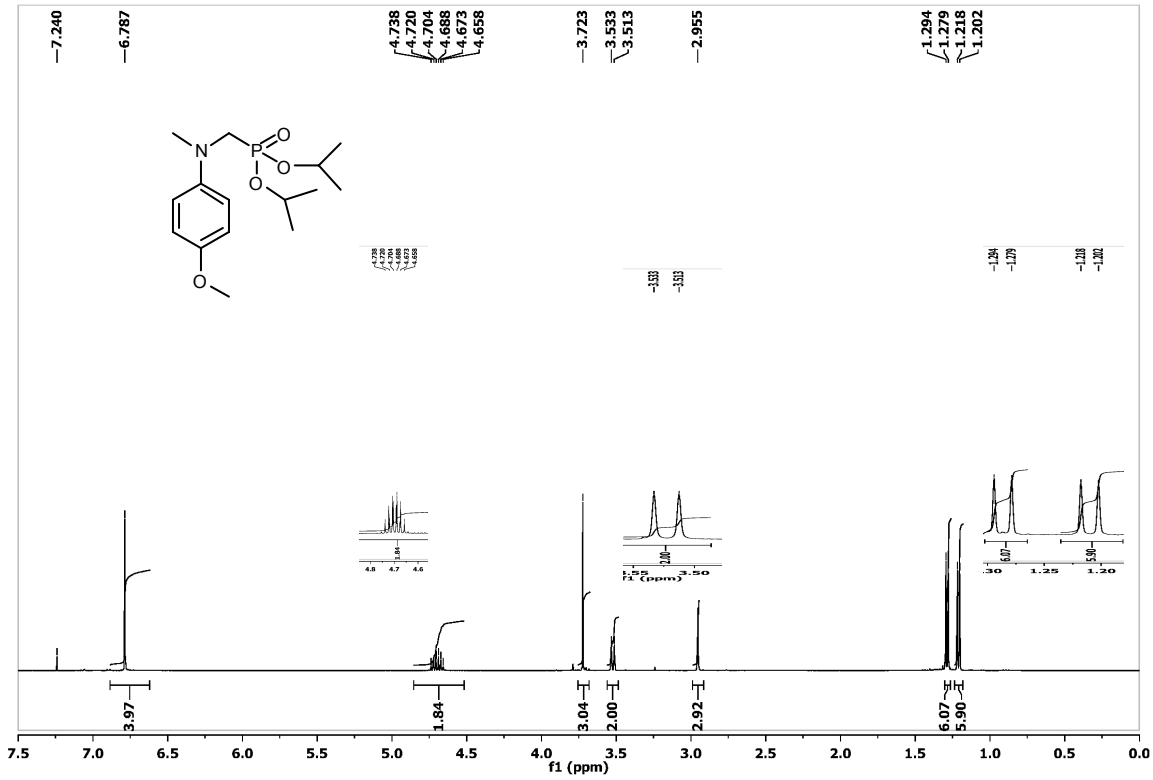
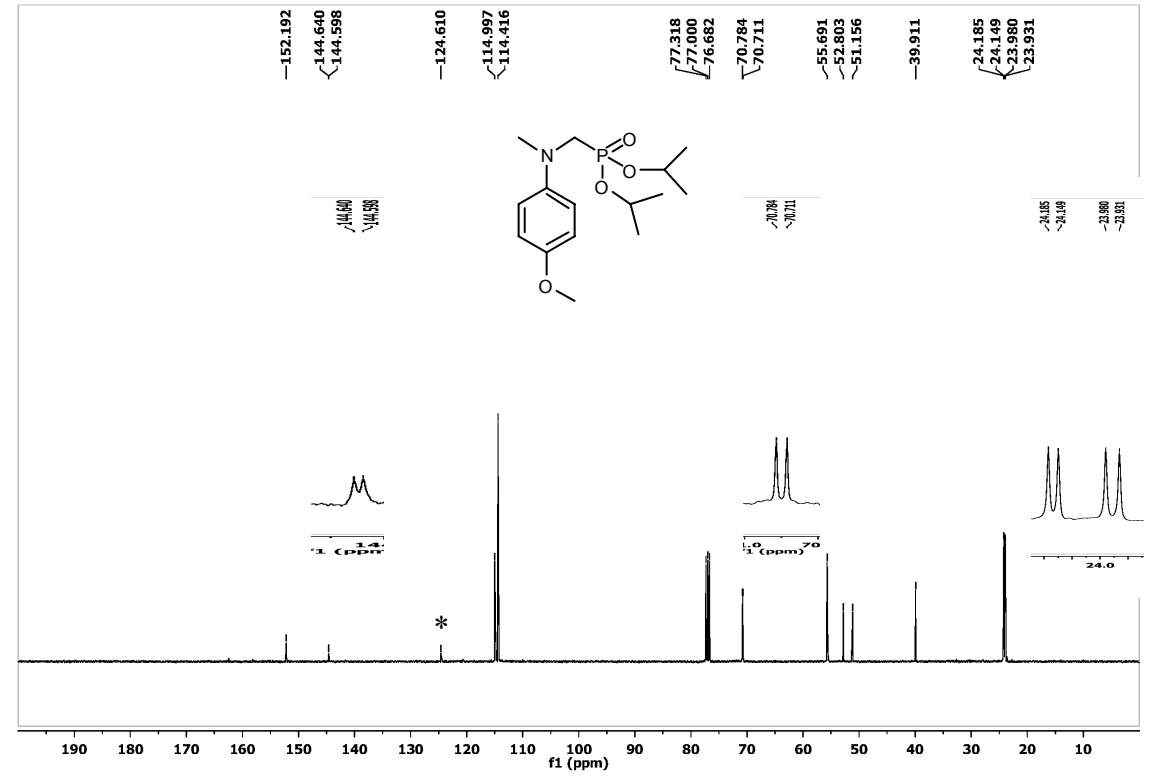
f1 (ppm)





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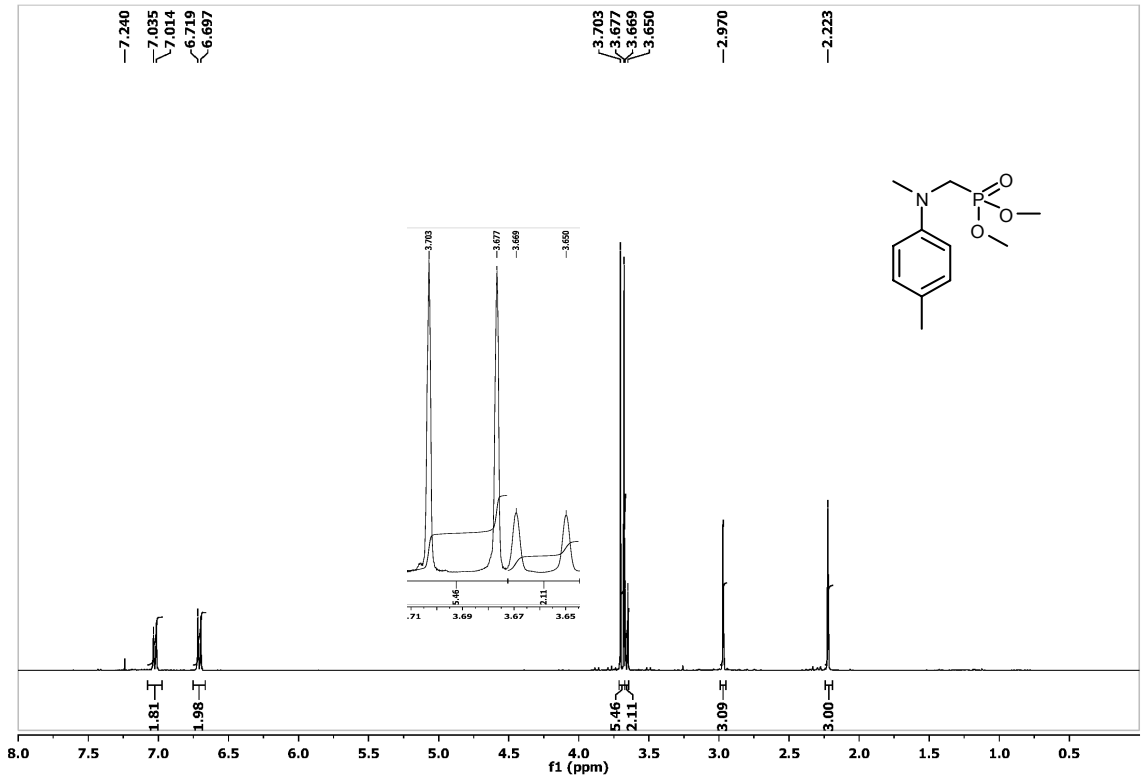
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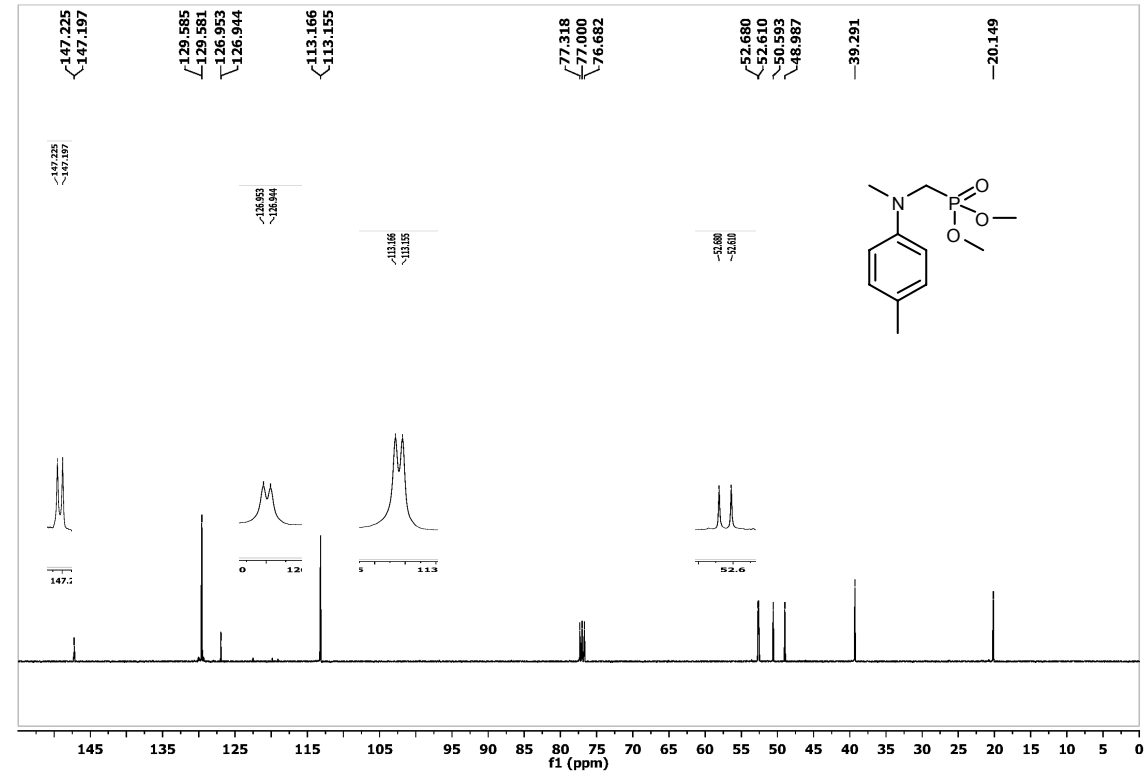
f1 (ppm)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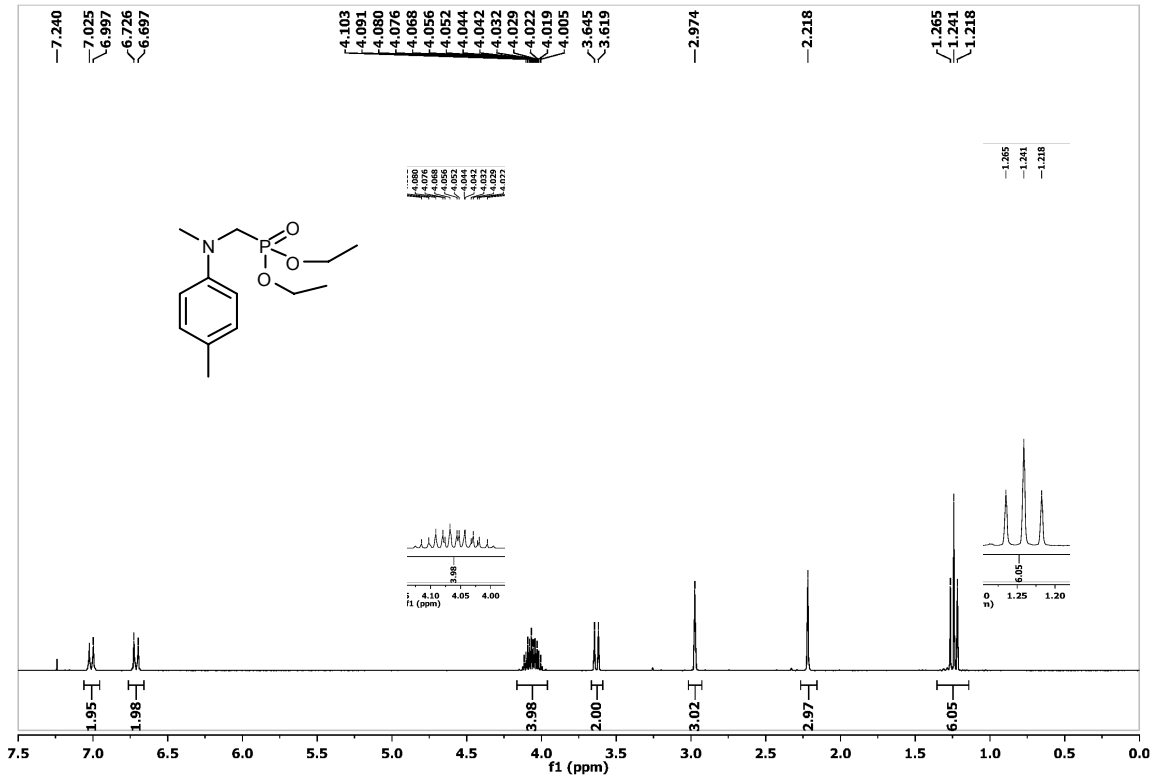
f1 (ppm)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4.042
4.032
4.029
4.022
4.019
4.005
3.645
3.619
2.974
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3.02
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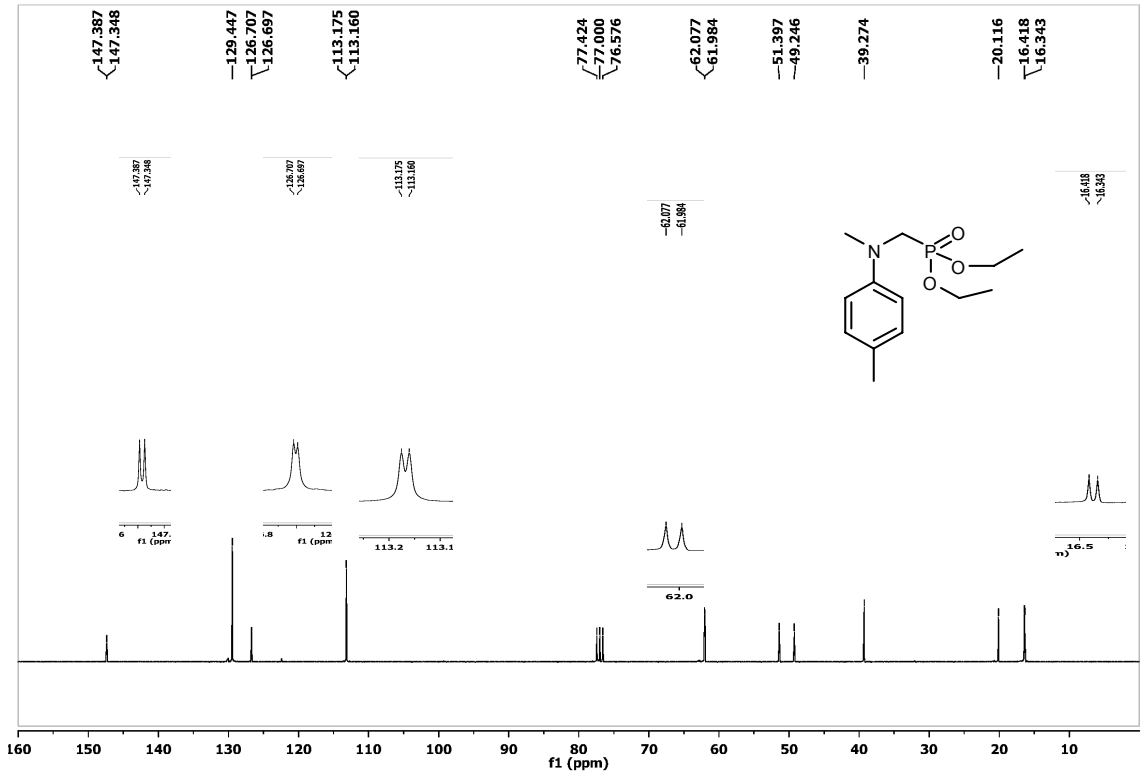
f1 (ppm)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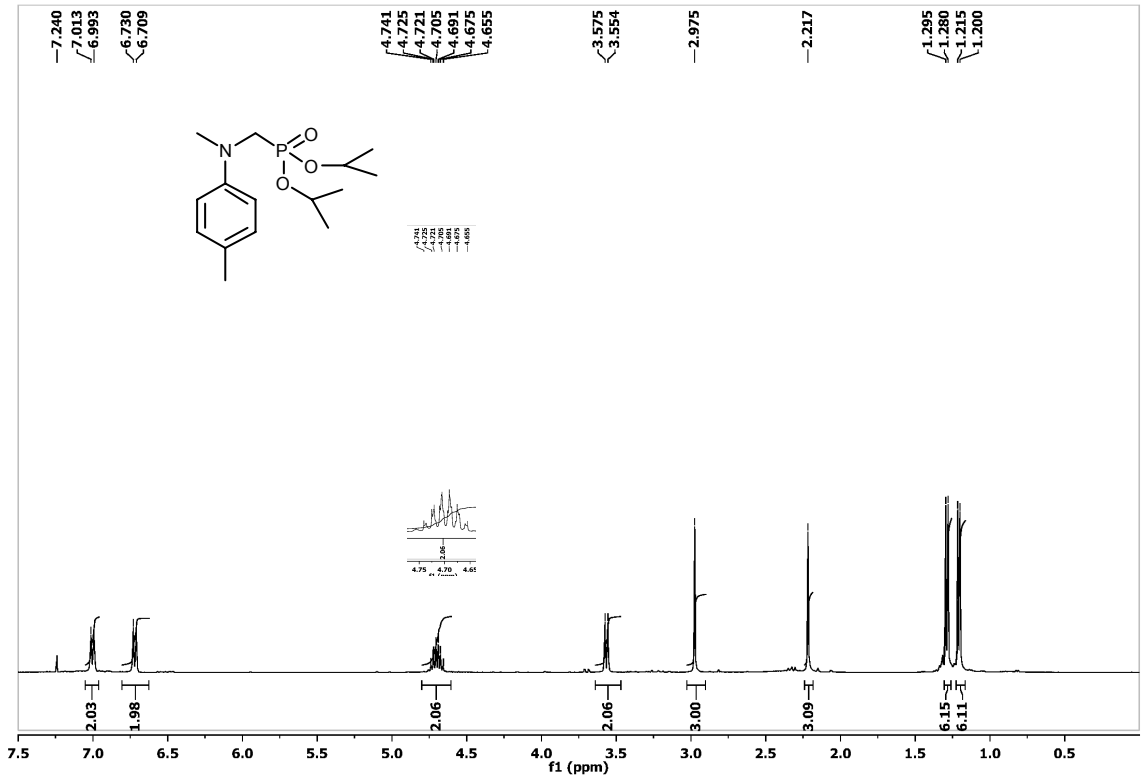
f1 (ppm)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3.554
2.975
2.217
1.295
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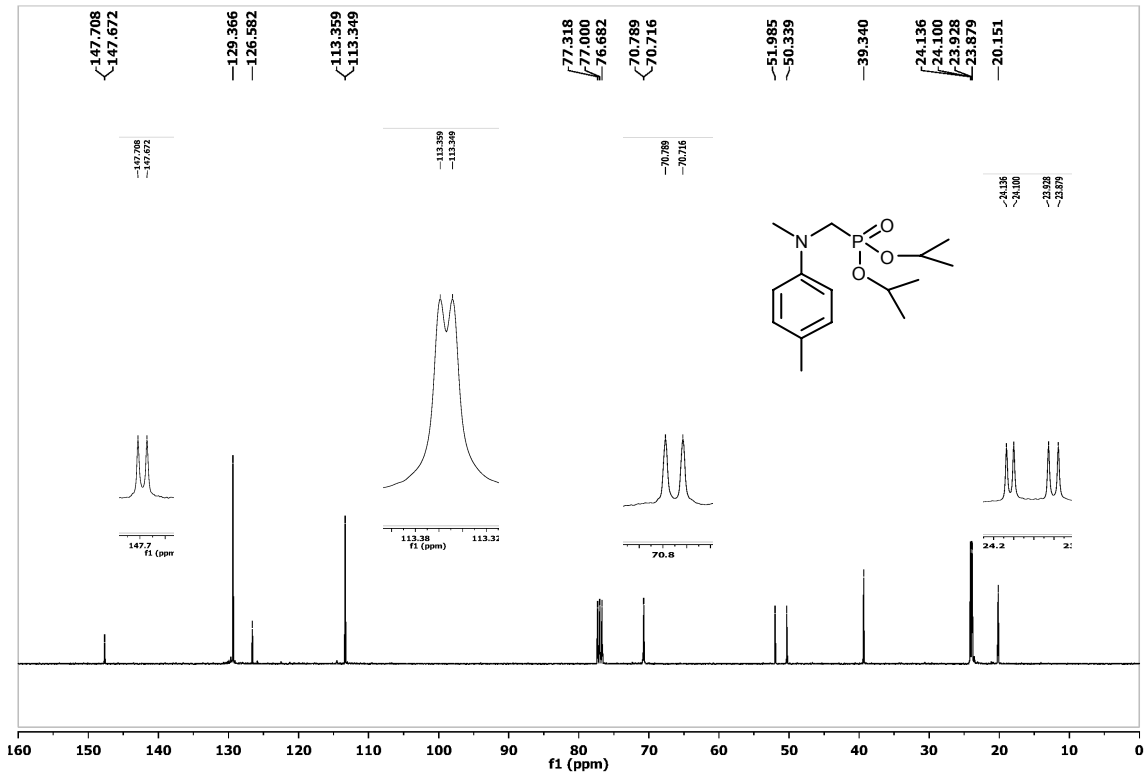
3.00
3.09
6.15
6.11
f1 (ppm)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23.928
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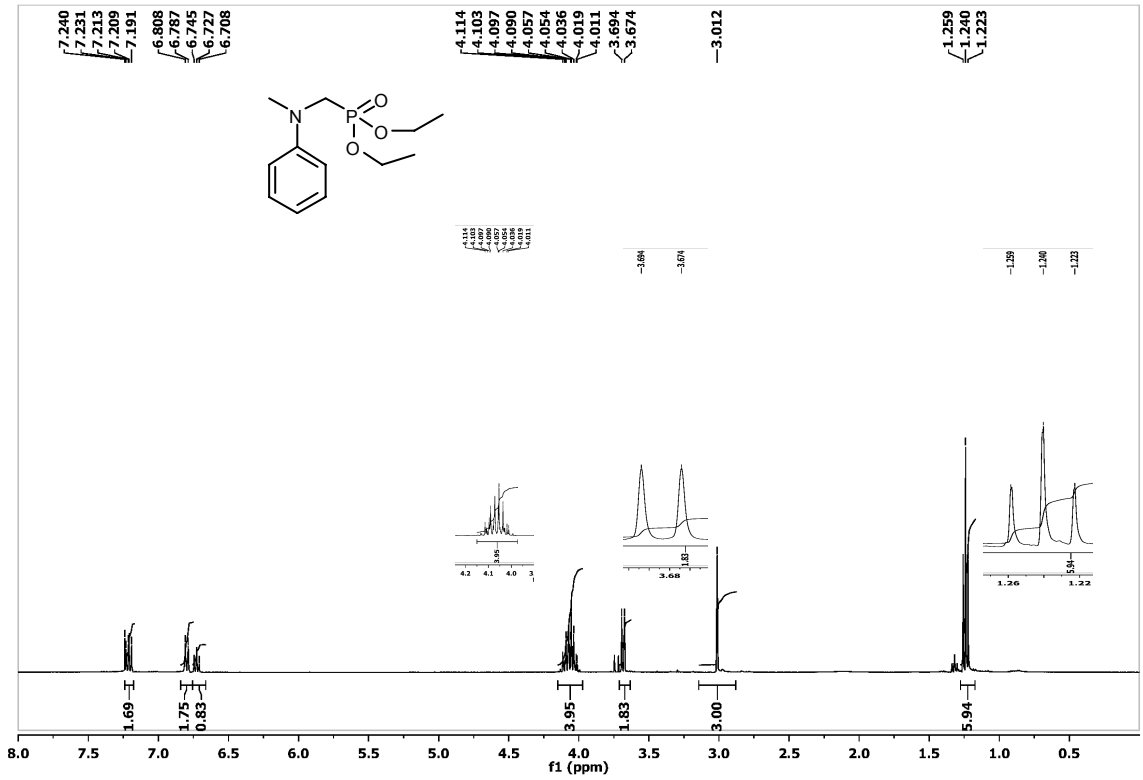
20.151
f1 (ppm)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4.054
4.036
4.019
4.011
3.694
3.674
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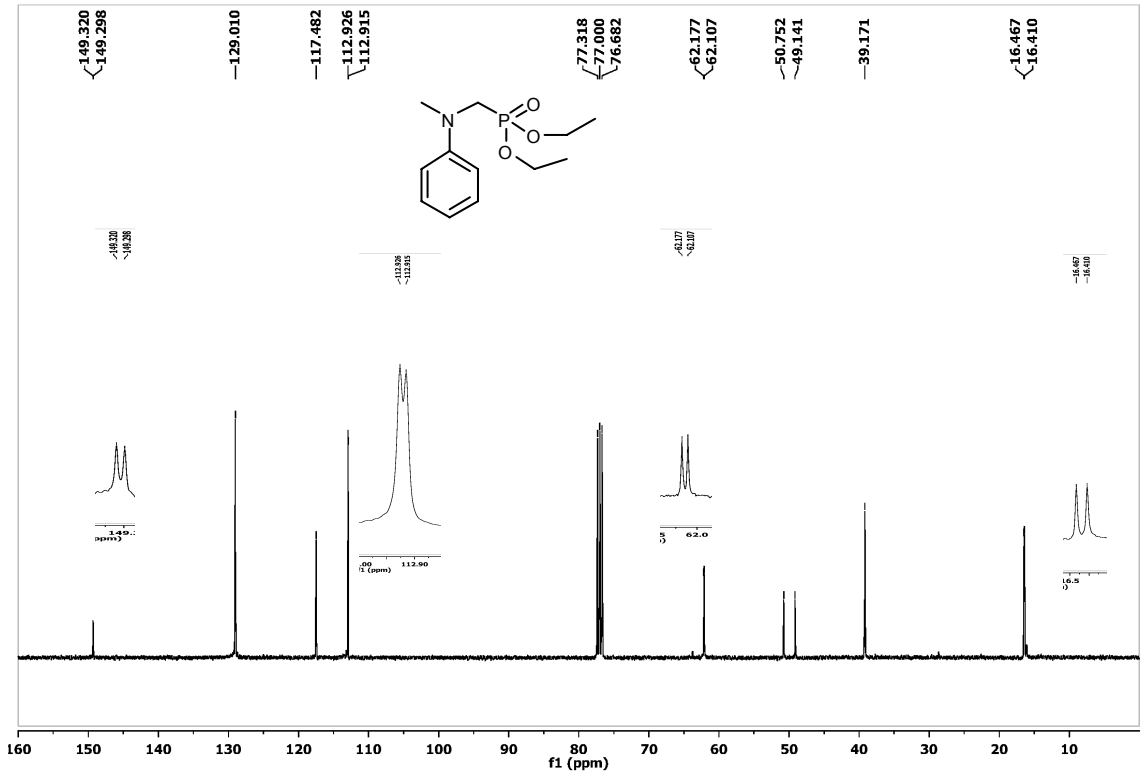
5.94
f1 (ppm)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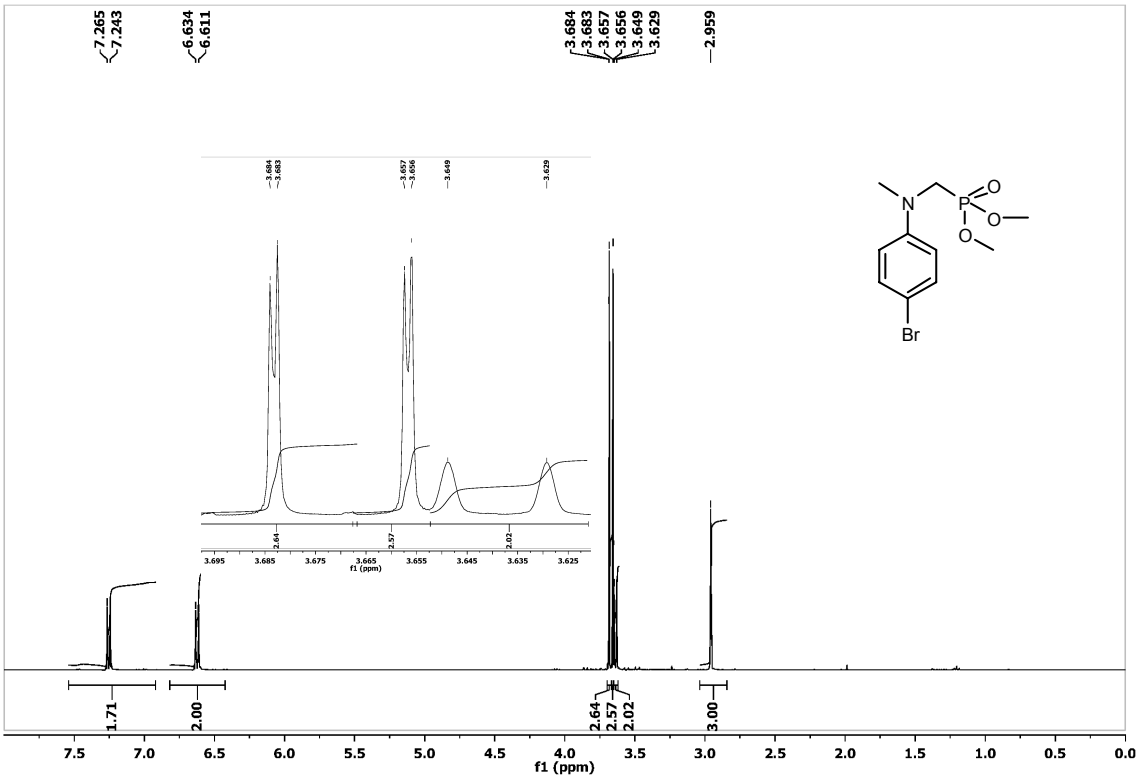
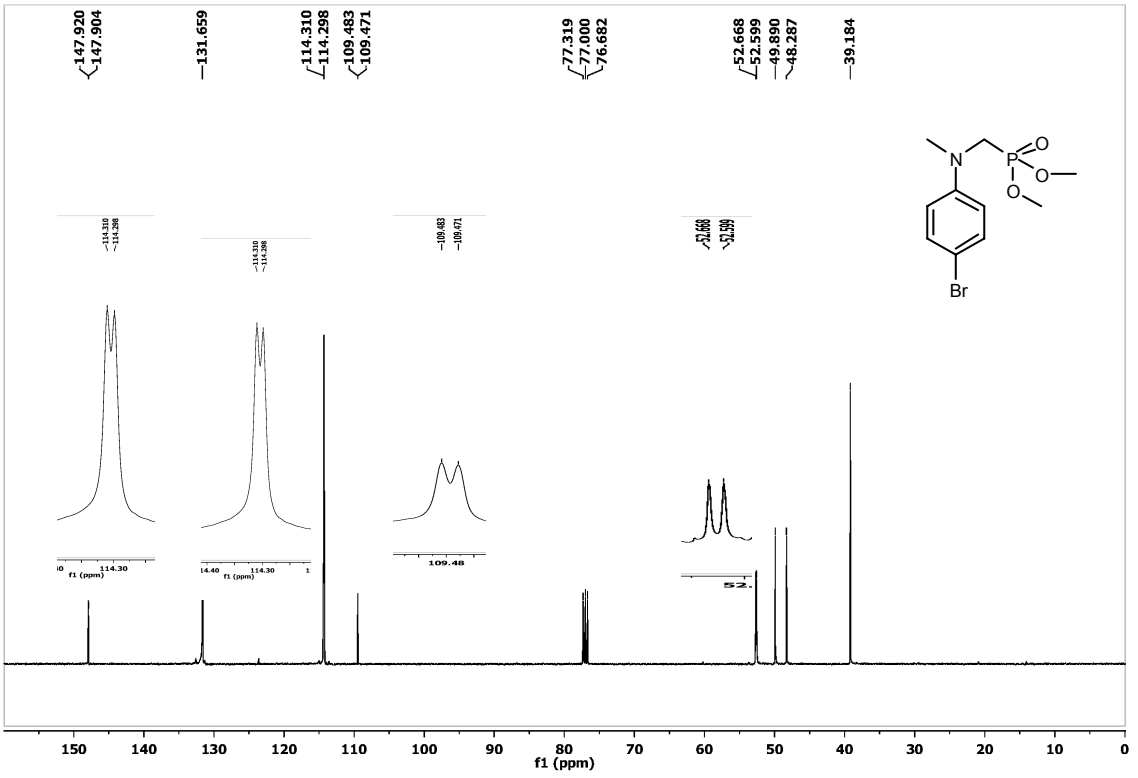
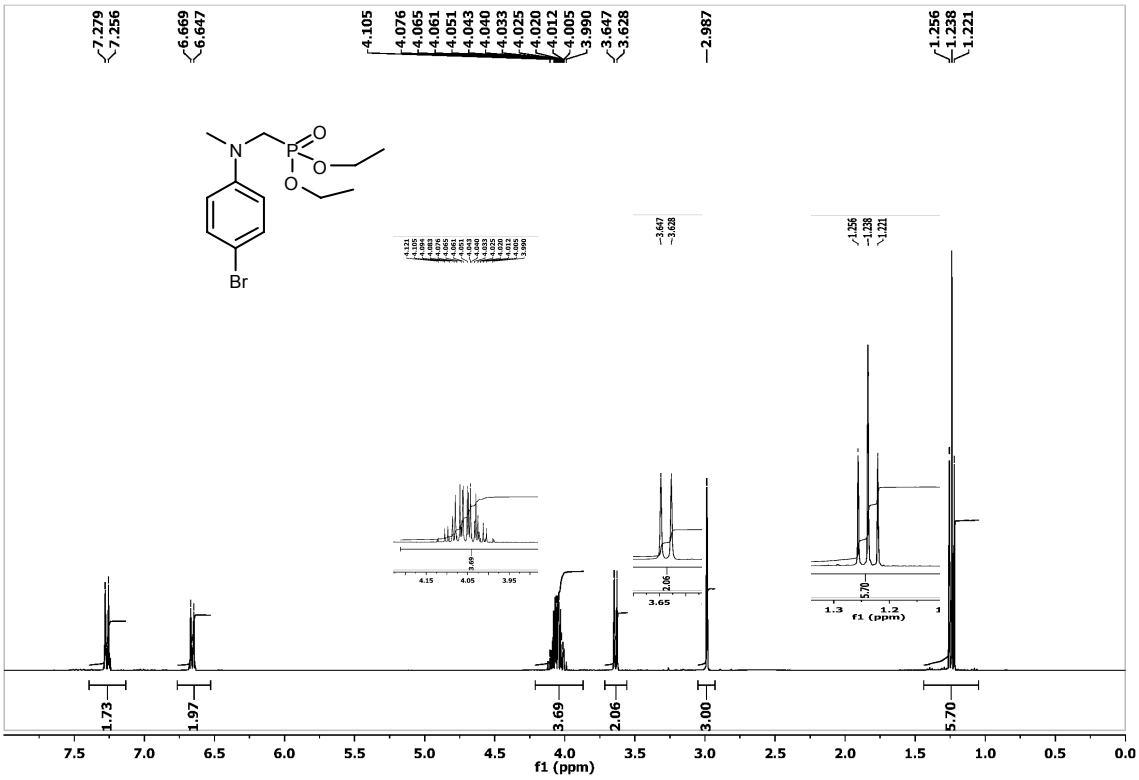
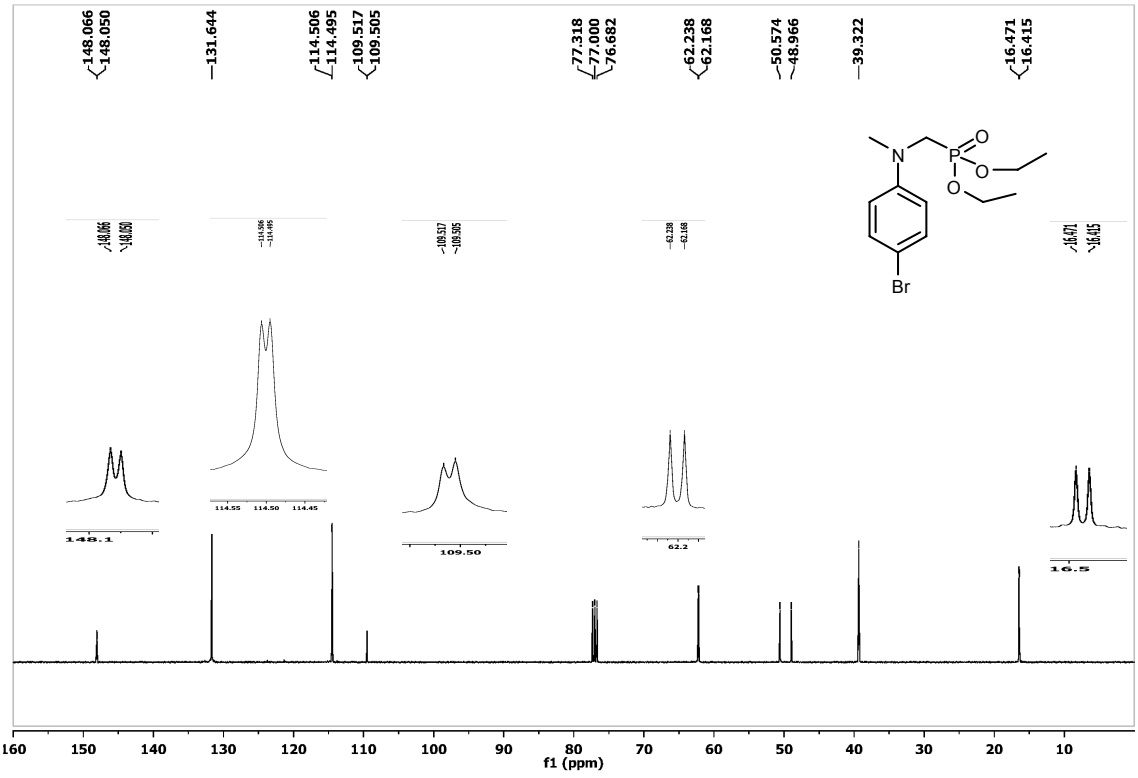
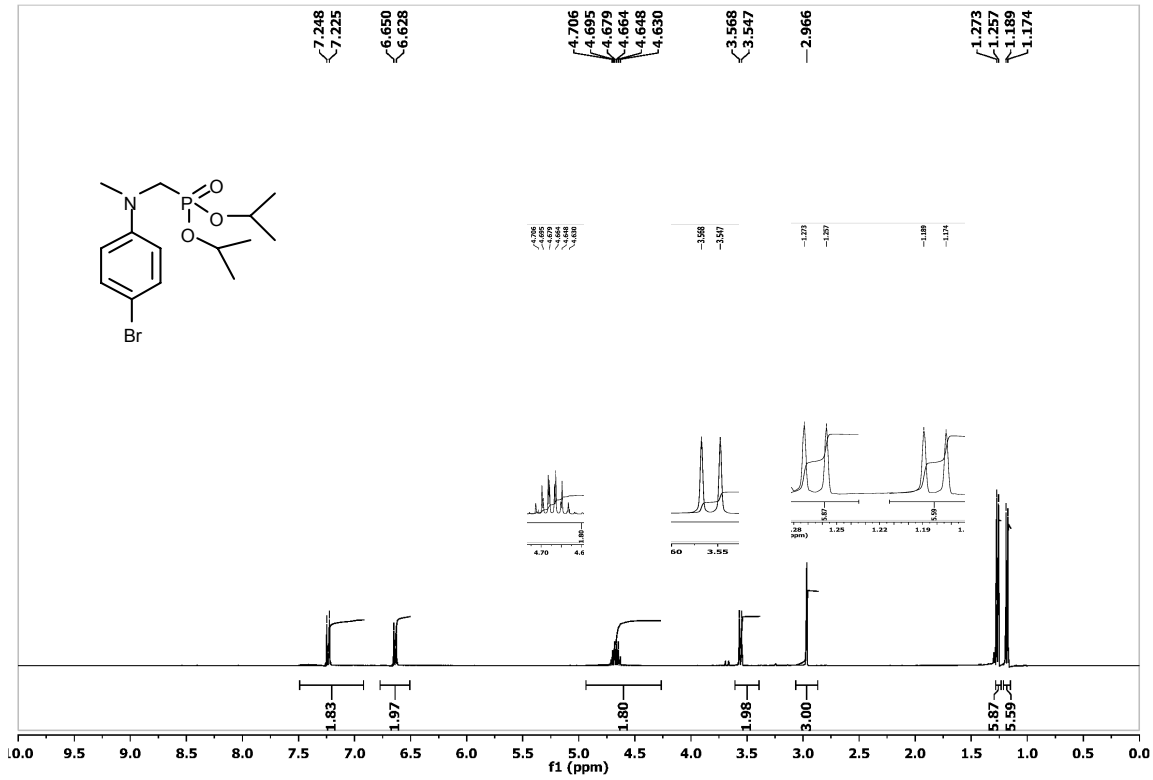
77.000
76.682
62.177
62.107
50.752
49.141
39.171
16.467
16.410
f1 (ppm)

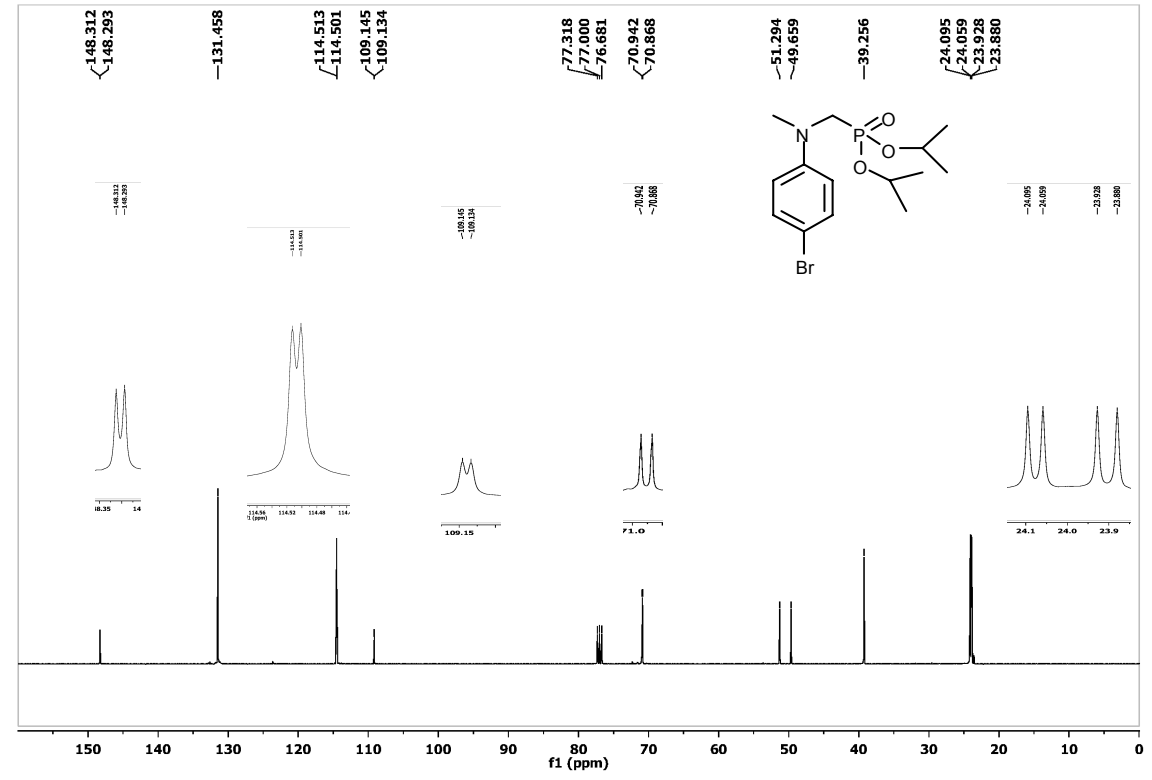

7.265
7.243
6.634
6.611
3.684
3.683
3.657
3.656
3.649
3.629
2.959
1.71
2.00
2.64
2.57
2.02
3.00
f1 (ppm)
Br

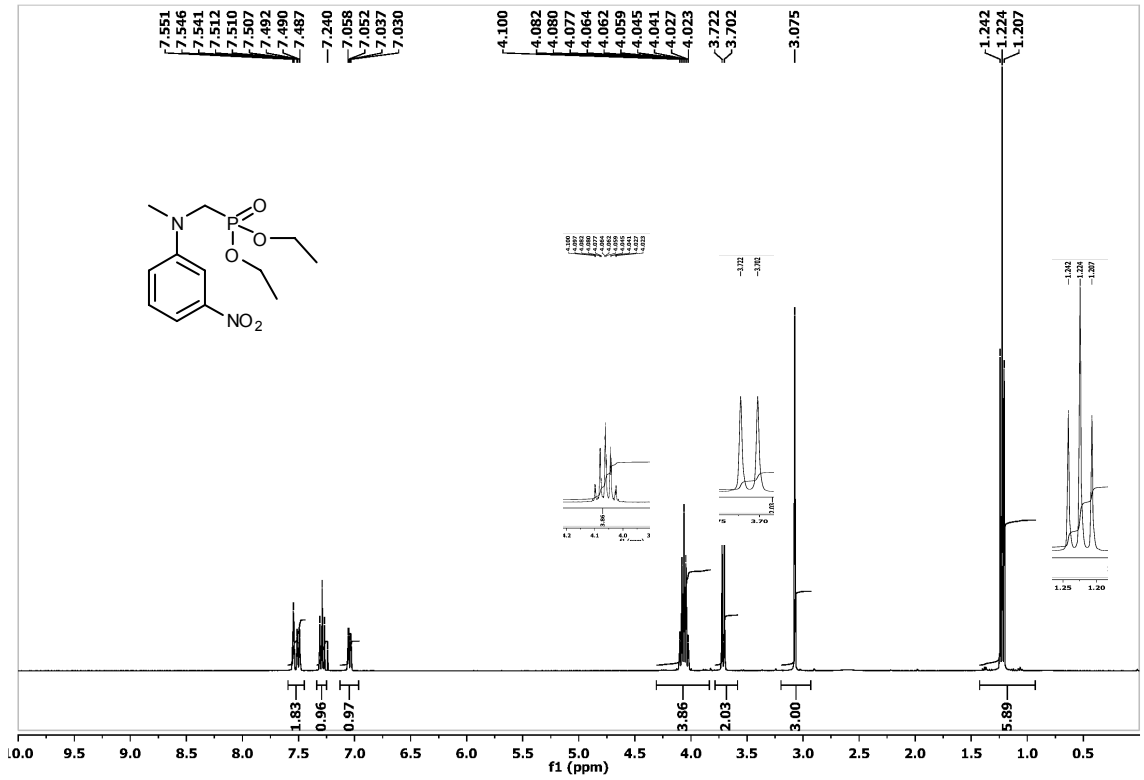

147.920
147.904
131.659
114.310
114.298
109.483
109.471
77.319
77.000
76.682
52.668
52.599
49.890
48.287
39.184
f1 (ppm)
Br

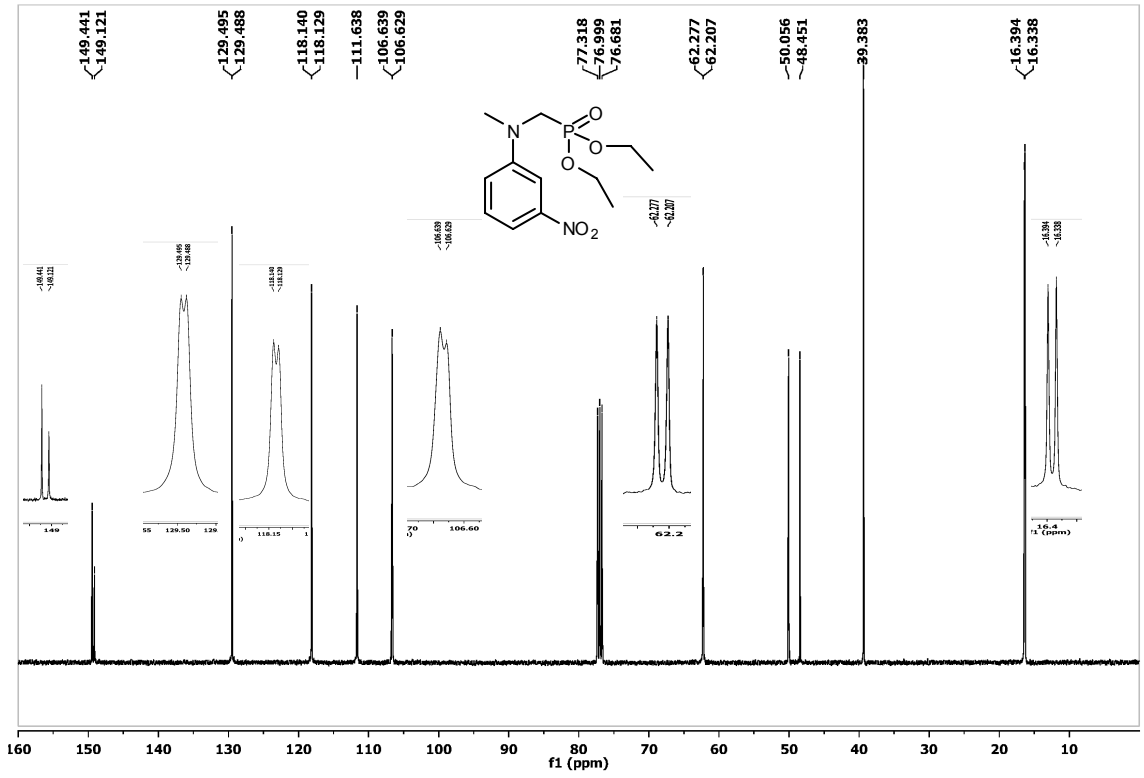

7.279
7.256
6.669
6.647
4.105
4.076
4.065
4.061
4.051
4.043
4.040
4.033
4.025
4.020
4.012
4.005
3.990
3.647
3.628
2.987
1.256
1.238
1.221
N
P
O
O
O
Br
1.73
1.97
3.69
2.06
3.00
5.70
f1 (ppm)


148.066
148.050
131.644
114.506
114.495
109.517
109.505
77.318
77.000
76.682
62.238
62.168
50.574
48.966
39.322
16.471
16.415
N
P
O
O
O
Br
148.1
109.50
62.2
16.5
f1 (ppm)


7.248
7.225
6.650
6.628
4.706
4.695
4.679
4.664
4.648
4.630
3.568
3.547
2.966
1.273
1.257
1.189
1.174
Br
1.83
1.97
1.80
1.98
3.00
5.87
5.59
f1 (ppm)


148.312
148.293
131.458
114.513
114.501
109.145
109.134
77.318
77.000
76.681
70.942
70.868
51.294
49.659
39.256
24.095
24.059
23.928
23.880
Br
f1 (ppm)


7.551
7.546
7.541
7.512
7.510
7.507
7.492
7.490
7.487
7.240
7.058
7.052
7.037
7.030
4.100
4.082
4.080
4.077
4.064
4.062
4.059
4.045
4.041
4.027
4.023
3.722
3.702
3.075
1.242
1.224
1.207
1.83
0.96
0.97
3.86
2.03
3.00
5.89
f1 (ppm)


149.441
149.121
129.495
129.488
118.140
118.129
111.638
106.639
106.629
77.318
76.999
76.681
62.277
62.207
50.056
48.451
39.383
16.394
16.338
f1 (ppm)