Electronic Supplementary Information

Arenediazonium tetrafluoroborates in palladium-catalyzed C-P bond–forming reactions. Synthesis of arylphosphonates, -phosphine oxides and -phosphines.

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GENERAL INFORMATION

Melting points are uncorrected. All of the reagents, catalysts, and solvents are commercially available and were used as purchased, without further purification. Reaction products were purified by flash column cromathography using SiO_2 25-40 μm and eluting with *n*-hexane/EtOAc or *n*-hexane/EtOAc/methanol mixtures.

GENERAL PROCEDURES

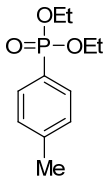
Typical Procedure for the Preparation of (2): Diethyl 4-Methoxyphenylphosphonate (2a). To a stirred mixture of **1a** (110.9 mg, 0.50 mmol) and KI (249.0 mg, 1.50 mmol) in 1.0 mL of anhydrous MeCN, $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), $P(OEt)_3$ (0.75 mmol, 128 μL), and Cs_2CO_3 (1.0 mmol, 325.8 mg) were added at room temperature and under argon with 2.0 mL of MeCN (the reactor was protected from light with aluminium film). Then, the reaction mixture was stirred for 18 h at 80 °C under argon. After this time, the reaction mixture was cooled to room temperature, diluted with EtOAc, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc 15/85 v/v) to afford 102.8 mg (84% yield) of **2a**: oil;[1] IR (neat) 2895, 2917, 1444, 1234, 1024, 966 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.74 (dd, J_1 = 12.7 Hz, J_2 = 8.7 Hz, 2 H), 6.96 (dd, J_1 = 8.7 Hz, J_2 = 3.3 Hz, 2 H), 4.16-3.95 (m, 4 H), 3.84 (s, 3 H), 1.31 (t, J = 7.0 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 163.0 (d, J = 3.0 Hz), 133.7 (d, J = 11.1 Hz), 119.0 (d, J = 195.0 Hz), 114.0 (d, J = 16.2 Hz), 61.9 (d, J = 5.4 Hz), 55.3, 16.3 (d, J = 6.2 Hz); ^{31}P NMR (161.9 MHz) δ -7.46. MS (m/z): 244 (29%) M^+, 188 (95 %), 108 (100%), 77 (37%); Anal Calcd for $C_{11}H_{17}O_4P$ C, 54.10; H, 7.02; found C, 54.21; H, 7.00.

Typical Procedure for the Preparation of (6): (4-Methoxyphenyl)diphenylphosphine oxide (6a). To a stirred solution of **1a** (110.9 mg, 0.50 mmol) and KI (249.0 mg, 1.50 mmol) in 1.0 mL of anhydrous MeCN, $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), $H(O)PPh_2$ (0.75 mmol, 151.6 mg), and Cs_2CO_3 (1.00 mmol, 325.8 mg) were added at room temperature and under argon with 2.0 mL of MeCN (the reactor was protected from light with aluminium film). Then, the mixture was stirred for 4 h at 80 °C under argon. After this time, the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, *n*-hexane/EtOAc/methanol 10/85/5 v/v) to afford 138.9 mg (90% yield) of **6a**: mp: 106-108 °C (lit.[2] mp: 113-115°C). IR (KBr) 1598, 1191, 1120 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.66-7.37 (m,

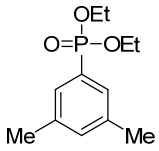
12 H), 6.93 (dd, J_1 = 8.8 Hz, J_2 = 2.0, 2 H), 3.76 (s, 3H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 162.5 (d, J = 2.8 Hz), 133.9 (d, J = 11.2 Hz), 132.8 (d, J = 103.6 Hz), 131.9 (d, J = 20.3 Hz), 131.8 (d, J = 52.7 Hz), 128.4 (d, J = 12.1 Hz), 123.4 (d, J = 111.1 Hz), 114.1 (d, J = 13.1 Hz), 55.3; ^{31}P NMR (161.9 MHz) δ 1.98. MS (m/z): 308 (67%) M^+, 307 (100%), 231 (23%), 215 (26%), 77 (30%). Anal Calcd for $C_{19}H_{17}O_2P$, C, 74.02; H, 5.56; found C, 74.21; H, 5.54.

Typical Procedure for the One-pot Preparation of (2) from Anilines: Diethyl 4-Methoxyphenylphosphonate (2a). A solution of $Et_2O{\cdot}BF_3$ (0.55 mmol, 56 μL) in 1.0 mL of anhydrous THF was cooled at -15°C and 4-methoxyaniline (61.5 mg, 0.50 mmol) was added. Then, *tert*-butyl nitrite (0.65 mmol, 77 μL) was added dropwise to the rapidly stirred reaction mixture. Following complete addition, the temperature was maintained at -15°C for 10 min and subsequently allowed to warm to 5 °C in an ice-water bath over a 20-min period. Then, the reaction mixture was warmed to room temperature and stirred at the same temperature till the starting aniline was converted into 4-methoxybenzenediazonium tetrafluoroborate **1a**. The reaction mixture was then concentrated under reduced pressure. The residue was diluited with 3 mL of anhydrous MeCN, KI (249.0 mg, 1.50 mmol), $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), $P(OEt)_3$ (0.75 mmol, 128 μL), and Cs_2CO_3 (1.00 mmol, 325.8 mg) were added and the resultant reaction mixture was stirred at 80 °C for 4h (the reactor was protected from light with aluminium film). After this time, the usual workup afforded 69.0 mg (56% yield) of **2a.**

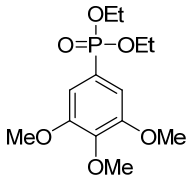
CHARACTERIZATION DATA



Diethyl Tolylphosphonate (2b): oil.[3] IR (neat) 2983, 1606, 1444, 1247, 1130, 968 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.62 (dd, J_1 = 12.8 Hz, J_2 = 8.0 Hz, 2 H), 7.19 (dd, J_1 = 7.6 Hz, J_2 = 4.0 Hz, 2 H), 4.07-3.95 (m, 4 H), 1.95 (s, 1 H), 1.28-1.18 (m, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 142.8 (d, J = 3.2 Hz), 131.7 (d, J = 10.2 Hz), 129.1 (d, J = 15.4 Hz), 125.0 (d, J = 189.2 Hz), 63.5 (d, J = 5.8 Hz), 21.5, 15.9 (d, J = 6.5 Hz); ^{31}P NMR (161.9 MHz) δ -7.64. MS (m/z): 228 (21%) M^+, 172 (100%), 155 (48%), 91 (95%), 77 (6%). Anal Calcd for $C_{11}H_{17}O_3P$, C, 57.89; H, 7.51; found C, 57.93; H, 7.48.

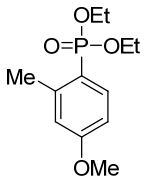


Diethyl 3,5-Dimethylphenylphosphonate (2c): oil. IR (neat) 2981, 1444, 1245, 1054, 1024, 964, 586 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.42 (s, 1 H), 7.38 (s, 1 H), 7.15 (s, 1 H), 4.15-4.02 (m, 4 H), 2.33 (s, 6 H), 1.31 (t, J = 6.8 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 138.1 (d, J = 15.7 Hz), 133.9 (d, J = 3.0 Hz), 129.3 (d, J = 9.7 Hz), 128.0 (d, J = 186.3 Hz), 61.9 (d, J = 5.4 Hz), 21.1, 16.3 (d, J = 6.3 Hz); ^{31}P NMR (161.9 MHz) δ -7.44. MS (m/z): 242 (36%) M^+, 214 (26%), 186 (100%), 106 (95%), 77 (45%). Anal Calcd for $C_{12}H_{19}O_3P$, C, 59.50; H, 7.91; found C, 59.63; H, 7.90.

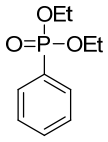


Diethyl 3,4,5-Trimethoxyphenylphosphonate (2d): oil. IR (neat) 2981, 1579, 1502, 1461, 1405, 1319, 1247, 1126,1052, 1022, 966 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.01 (s, 1 H), 6.97 (s, 1 H), 4.14-4.02 (m, 4 H), 3.87 (s, 6 H), 3.86 (s, 3 H), 1.31 (t, J = 7.0 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 153.3 (d, J = 22.0 Hz), 141.6 (d, J =3.7 Hz), 122.8 (d, J =191.5 Hz), 108.8 (d, J = 11.3 Hz), 62.2 (d, J = 5.3 Hz), 60.7, 56.3(d, J = 0.5 Hz), 16.3 (d, J = 6.4 Hz); ^{31}P NMR (161.9 MHz) δ -

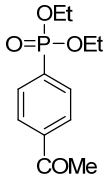
7.84. MS (m/z): 304 (100%) M^+, 232 (40%), 168 (59%), 93 (28%). Anal Calcd for $C_{13}H_{21}O_6P$, C, 51.31; H, 6.96; found C, 51.42; H, 6.95.



Diethyl 2-Methyl-4-Methoxyphenylphosphonate (2e): oil. IR (neat) 2981, 1600, 1444, 1243, 1087, 1024, 962 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.85 (dd, J_1 = 13.6 Hz, J_2 = 8.4 Hz, 1 H), 6.79-6.75 (m, 2 H), 4.16-4.02 (m, 4 H), 3.82 (s, 3 H), 2.53 (s, 3 H), 1.31 (t, J = 6.8 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 162.8 (d, J = 3.3 Hz), 143.9 (d, J =11.7 Hz), 136.1 (d, J =11.9 Hz), 118.2 (d, J = 191.3 Hz), 117.1 (d, J = 15.6 Hz), 110.3 (d, J = 15.9 Hz), 61.7 (d, J = 4.5 Hz), 55.2, 21.3 (d, J = 3.2 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR (161.9 MHz) δ -6.87. MS (m/z): 258 (64%) M^+, 230 (57%), 202 (100%), 186 (72%), 149 (70%), 121 (67%), 91 (55%), 77 (48%). Anal Calcd for $C_{12}H_{19}O_4P$, C, 55.81; H, 7.42; found C, 55.73; H, 7.45.

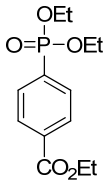


Diethyl Phenylphosphonate (2f): oil.[1] IR (neat) 2983, 1440, 1247, 1132, 1024, 966 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.88-7.80 (m, 2 H), 7.60-7.53 (m, 1 H), 7.50-7.40 (m, 2 H), 4.25-3.99 (m, 4 H), 1.34(t, J = 6.8 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 132.3 (d, J = 2.8 Hz), 131.8 (d, J = 9.9 Hz), 128.4 (d, J = 188.0 Hz), 128.5 (d, J = 14.9 Hz), 62.1 (d, J = 5.4 Hz), 16.3 (d, J = 6.4 Hz); ^{31}P NMR (161.9 MHz) δ -8.39. MS (m/z): 214 (22%) M^+, 186 (12%), 158 (88%), 141 (84%), 77 (100%). Anal Calcd for $C_{10}H_{15}O_3P$, C, 56.07; H, 7.06; found C, 56.22; H, 7.04.

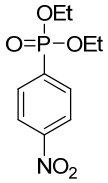


Diethyl 4-Acetylphenylphosphonate (2g): oil.[1] IR (neat) 2983, 1691, 1442, 1261, 1022, 968 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 8.05-8.02 (m, 2 H), 7.98-7.91(m, 2 H), 4.19-4.10 (m, 4 H), 2.66 (s, 3 H), 1.35 (t, J = 6.8 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 197.5, 139.8 (d, J = 3.5 Hz), 133.4 (d, J = 185.8 Hz), 132.1 (d, J = 10.1 Hz), 128.0 (d, J = 15 Hz), 62.4 (d, J = 5.6 Hz), 26.8, 16.3 (d, J = 6.3 Hz); ^{31}P NMR (161.9 MHz) δ -10.3 H MS (m/z): 256 (26%) M^+, 241(59%), 213 (100%),

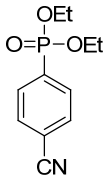
185 (57%), 167 (33%), 77 (24%). Anal Calcd for $C_{12}H_{17}O_4P$, C, 54.25; H, 6.69; found C, 54.33; H, 6.70.



Diethyl 4-Ethoxycarbonylphenylphosphonate (2h): oil.[1] IR (neat) 2983, 2933, 2908, 1722, 1274, 1022, 970 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 8.02-7.99 (m, 2 H), 7.82-7.74 (m, 2 H), 4.25 (q, J = 7.2 Hz, 2H), 4.06-3.94 (m, 4 H), 1.29 (t, J = 7.2 Hz, 3 H), 1.26-1.19 (m, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 165.6, 133.8 (d, J = 3.3 Hz), 132.9 (d, J = 186 Hz), 131.6 (d, J = 10.1 Hz), 129.3 (d, J = 15.1 Hz), 62.3 (d, J = 5.5 Hz), 61.3, 16.3 (d, J = 5.6 Hz), 14.1; ^{31}P NMR (161.9 MHz) δ -10.2 . MS (m/z): 286 (32%) M^+; 213 (100%); 202 (99%), 185 (72%), 177 (70%), 149 (42%), 77 (51%). Anal Calcd for $C_{13}H_{19}O_5P$, C, 54.54; H, 6.69; found C, 54.63; H, 6.68.

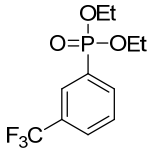


Diethyl 4-Nitrophenylphosphonate (2i): oil.[4] IR (neat) 2985, 1527, 1351, 1255, 1128, 1024, 973 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 8.26 (dd, J_1 = 8.7 Hz, J_2 = 3.1 Hz, 2 H), 7.96 (dd, J_1 = 12.6 Hz, J_2 = 8.7 Hz, 2 H), 4.18-4.02 (m, 4 H), 1.28 (t, J = 7.0 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 150.2 (d, J = 4.2 Hz), 135.7 (d, J = 186.3 Hz), 132.9 (d, J = 10.5 Hz), 123.3 (d, J = 15.2 Hz), 64.6 (d, J = 5.6 Hz), 16.2 (d, J = 6.2 Hz); ^{31}P NMR (161.9 MHz) δ -12.3 . MS (m/z): 258 (7%) M^+, 214 (17%), 204 (100%), 186 (37%), 123 (32%), 77 (39%). Anal Calcd for $C_{10}H_{14}NO_5P$, C, 46.34; H, 5.44; found C, 46.25; H, 5.47.

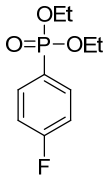


Diethyl 4-Cyanophenylphosphonate (2j): oil. IR (neat) 2985, 2233, 1444, 1255, 1124, 1022, 971 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 7.87 (dd, J_1 = 13.2 Hz, J_2 = 8.0 Hz, 2 H), 7.72-7.69 (m, 2 H), 4.15-4.01 (m, 4 H), 1.27 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 133.9 (d, J = 187.0 Hz), 132.2 (d, J = 9.8 Hz), 131.9 (d, J = 14.9 Hz), 117.8, 115.9 (d, J = 3.4 Hz), 62.7 (d, J = 5.6 Hz),

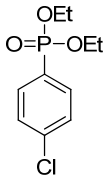
16.3 (d, J = 6.2 Hz); ^{31}P NMR (161.9 MHz) δ -11.9. MS (m/z): 239 (7%) M^+, 212(22%), 184 (100%), 166 (90%), 130 (46%), 102 (64%), 75 (26%). Anal Calcd for $C_{11}H_{14}NO_3P$, C, 55.23; H, 5.90; found C, 55.32; H, 5.87.



Diethyl 3-Trifluoromethylphenylphosphonate (2k): oil. IR (neat) 2987, 1427, 1330, 1255, 1132, 1052, 1024, 970 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 8.06-7.94 (m, 2 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.58-7.57 (m, 1 H), 4.17-4.07 (m, 4 H), 1.30 (t, J= 7.6 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 134.9 (d, J_{C-P} = 9.3 Hz), 131.15 (dq, J_{C-P} =15.7 Hz, J_{C-F} =32.0 Hz), 130.2 (d, J_{C-P} =188.3 Hz), 129.0 (d, J_{C-P} = 14.9 Hz), 128.9 (q, J_{C-F} = 3.7 Hz), 128.6 (dq, J_{C-P} =11.0 Hz, J_{C-F} =3.8 Hz), 123.7 (dq, J_{C-P} = 11.0 Hz, J_{C-F} = 262.0 Hz,), 62.5 (d, J_{C-P} = 5.9 Hz), 16.3 (d, J_{C-P} = 6.2 Hz); ^{31}P NMR (161.9 MHz) δ -10.87; ^{19}F NMR (376.5 MHz) δ -62.8. MS (m/z): 282 (8%) M^+, 255 (24%), 227 (100%), 209 (43%), 145 (58%), 75 (16%). Anal Calcd for $C_{11}H_{14}F_3O_3P$, C, 46.82; H, 5.00; found C, 46.89; H, 5.01.

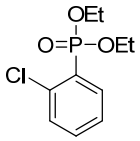


Diethyl 4-Fluorophenylphosphonate (2l): oil. IR (neat) 2985, 1594, 1502, 1247, 1130, 1024, 968 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.87-7.80 (m, 2 H), 7.19-7.14 (m, 2 H), 4.21-4.03 (m, 4 H), 1.33 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 166.4 (dd, J_{C-P} = 3.8 Hz, J_{C-F} = 251.5 Hz), 134.3 (dd, J_1 =11.1 Hz, J_2 = 9.1 Hz), 125.5 (d, J_{C-P} =194.3 Hz), 115.4 (dd, J_{C-P} =16.4 Hz, J_{C-F} = 21.5 Hz), 62.1 (d, J_{C-P} = 5.4 Hz), 16.2 (d, J_{C-P} = 6.2 Hz); ^{31}P NMR (161.9 MHz) δ -9.39; ^{19}F NMR (376.5 MHz) δ -106.0. MS (m/z): 232 (17%) M^+, 176 (100%), 159 (83%), 112 (40%), 95 (52%), 75 (33%). Anal Calcd for $C_{10}H_{14}FO_3P$, C, 51.73; H, 6.08; found C, 51.80; H, 6.04.

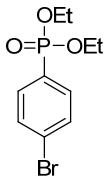


Diethyl 4-Chlorophenylphosphonate (2m): oil.[1] IR (neat) 2983, 1444, 1251, 1024, 970, 775 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.73 (dd, J_1 = 12.9 Hz, J_2 = 8.4 Hz, 2 H), 7.43 (dd, J_1 = 8.4 Hz, J_2 =

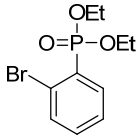
3.2 Hz, 2 H), 4.19-4.01 (m, 4 H), 1.38-1.23 (m, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 139.8 (d, *J* = 4.0 Hz), 134.0 (d, *J* = 10.7 Hz), 129.6 (d, *J* = 15.7 Hz), 127.8 (d, *J* = 191.9 Hz), 62.7 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 6.4 Hz); ^{31}P NMR (161.9 MHz) δ -9.62 . MS (m/z): 250 (6%) M^{+2}, 248 (18%) M^{+}, 192 (100%), 175 (52%), 139 (43%), 75 (42%). Anal Calcd for $C_{10}H_{14}ClO_3P$, C, 48.30; H, 5.68; found C, 48.45; H, 5.66.



Diethyl 2-Chlorophenylphosphonate (2n): oil. IR (neat) 2983, 1583, 1427, 1247, 1022, 971, 567 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 8.02 (dd, J_1 = 14.0 Hz, J_2 = 7.6 Hz, 2 H),), 7.49-7.48 (m, 2 H), 7.39-7.35 (m, 1 H), 4.28-4.11 (m, 4 H), 1.37 (t, *J* = 7.2Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 136.8 (d, *J* = 3.0 Hz), 135.9 (d, *J* = 7.9 Hz), 133.7 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 10.3 Hz), 127.2 (d, *J* = 192.1 Hz), 126.5 (d, *J* = 13.8 Hz), 62.7 (d, *J* = 5.6 Hz), 16.2 (d, *J* = 6.5 Hz); ^{31}P NMR (161.9 MHz) δ -12.7. MS (m/z): 248 (9%) M^{+}, 213 (100%), 185 (93%), 139 (85%), 75 (68%). Anal Calcd for $C_{10}H_{14}ClO_3P$, C, 48.30; H, 5.68; found C, 48.25; H, 5.71.

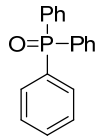


Diethyl 4-Bromophenylphosphonate (2o): oil.[3] IR (neat) 2983, 1581, 1479, 1444, 1249, 1024, 968 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.65-7.55 (m, 4 H), 4.18-3.98(m, 4 H), 1.27 (t, *J* = 6.4 Hz, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 133.3 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 15.4 Hz), 127.4 (d, *J* = 189.3 Hz), 127.5 (d, *J* = 3.9 Hz), 62.3 (d, *J* = 5.4 Hz), 16.3 (d, *J* = 6.4 Hz); ^{31}P NMR (161.9 MHz) δ -9.5 Hz. MS (m/z): 294 (18%) M^{+2}, 292 (19%) M^{+}, 236 (100%), 221 (38%), 185 (26%), 156 (25%), 76 (51%). Anal Calcd for $C_{10}H_{14}BrO_3P$, C, 40.98; H, 4.81; found C, 40.76; H, 4.83.

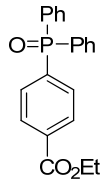


Diethyl 2-Bromophenylphosphonate (2p): oil.[5] IR (neat) 2983, 1452, 1247, 1022, 970 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.99-7.96 (m, 1 H), 7.95-7.61(m, 1 H), 7.39-7.33 (m, 2 H), 4.22-4.05 (m, 4 H), 1.36-1.30 (m, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 136.3 (d, *J* = 8.2 Hz), 134.3 (d, *J* =

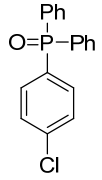
11.1 Hz), 133.5 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 191.4 Hz), 126.9 (d, *J* = 13.6 Hz), 125.2 (d, *J* = 3.9 Hz), 63.6 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 6.5 Hz); ^{31}P NMR (161.9 MHz) δ -12.5. MS (m/z): 294 (5%) M^{+2}, 292 (5%) M^{+}, , 213 (51%), 185 (100%), 157 (86%), 141 (77%), 77 (54%). Anal Calcd for $C_{10}H_{14}BrO_3P$, C, 40.98; H, 4.81; found C, 40,69; H, 4.78.



Triphenyl Phosphine oxide (6b): mp: 148-149°C (Lit.[3] mp: 119-123°C). IR (KBr) 1436, 1118, 723 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.68-7.61 (m, 6 H), 7.52-7.38 (m, 9 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 132.5 (d, *J* = 105.0 Hz), 132.0 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 2.7 Hz), 128.5 (d, *J* = 12.2 Hz); ^{31}P NMR (161.9 MHz) δ 1.86 . MS (m/z): 278 (42%) M^{+}, 277 (100%), 201 (17%), 183 (19%), 77 (41%). Anal Calcd for $C_{18}H_{15}OP$, C, 77.69; H, 5.43; found C, 77.54; H, 5.46.

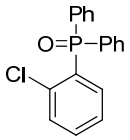


(4-Ethoxycarbonylphenyl)Diphenylphosphine oxide (6c): oil. IR (neat) 3056, 2983, 1718, 1436, 1274, 1195, 1103, 728, 696 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 8.11 (dd, J_1 = 8.4 Hz, J_2 = 2.7 2 H), 7.75(dd, J_1 = 11.0 Hz, J_2 = 8.4, 2 H), 7.71-7.59 (m, 2 H), 7.57-7.50 (m, 4 H), 7.49-7.42 (m, 4 H), 4.40 (q, *J* = 7.3 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 165.7, 137.5 (d, *J* = 100.8 Hz), 133.6 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 9.9 Hz), 131.9 (d, *J* = 104.8 Hz), 129.4 (d, *J* = 12.1 Hz), 128.6 (d, *J* = 12.1 Hz), 61.4, 14.2; ^{31}P NMR (161.9 MHz) δ 1.27. MS (m/z): 350 (11%) M^{+}, 349 (100%), 321 (25%), 305 (10%), 277 (8%), 201 (11%), 183 (23%), 77 (30%). Anal Calcd for $C_{21}H_{19}O_3P$, C, 71.99; H, 5.47; found C, 71.85; H, 5.49.

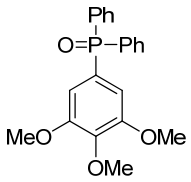


(4-Chlorophenyl)Diphenylphosphine oxide (6d): mp: 135-138 °C (Lit.[3] mp: 143-145 °C). IR (KBr) 2921, 1597, 1438, 1191, 1116, 696 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.68-7.41 (m, 14 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 138.6 (d, *J* = 3.3 Hz), 133.5 (d, *J* = 10.7 Hz), 132.1.9 (d, *J* =

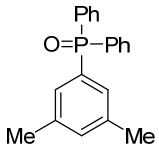
104.5 Hz), 132.2 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 9.9 Hz), 131.2 (d, *J* = 105.1 Hz), 128.9 (d, *J* = 12.7 Hz), 128.6 (d, *J* = 12.2 Hz); ^{31}P NMR (161.9 MHz) δ 1.13. MS (m/z): 314 (13%) M^{+2}, 312 (42%) M^{+}, 311 (100%), 277 (8%), 201 (10%), 183 (20%), 152 (22%), 77 (50%). Anal Calcd for $C_{18}H_{14}ClOP$, C, 69.13; H, 4.51; found C, 69.26; H, 4.47.



(2-Chlorophenyl)diphenylphosphine oxide (6f): mp 99-102 °C. IR (KBr) 1434, 1187, 1120, 545 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.76-7.61 (m, 4 H), 7.60-7.47 (m, 9 H); 7.37-7.33 (m, 1 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 137.9 (d, *J* = 4.1 Hz), 135.6 (d, *J* = 9.5 Hz), 135.2, 133.4 (d, *J* = 1.7 Hz), 132.0 (d, *J* = 7.7 Hz), 131.8 (d, *J* = 106.8 Hz), 131.2 (d, *J* = 103.5 Hz), 131.1 (d, *J* = 6.8 Hz), 128.5 (d, *J* = 12.5 Hz), 126.6 (d, *J* = 10.9 Hz); ^{31}P NMR (161.9 MHz) δ 1.52. MS (m/z): 312 (77%) M^{+}, 282 (100%), 208 (97%), 152 (90%), 78 (67%). Anal Calcd for $C_{18}H_{14}ClOP$, C, 69.13; H, 4.51; found C, 69.21; H, 4.53.



(3,4,5-Trimethoxyphenyl)Diphenylphosphine oxide (6g): oil. IR (neat) 2938, 2221, 1577, 1502, 1436, 1403, 1313, 1122, 698 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.69-7.64 (m, 4 H), 7.56-7.52 (m, 2 H), 7.48-7.44 (m, 4 H), 6.87 (s, 1 H), 6.84 (s, 1 H), 3.88 (s, 3 H), 3.76 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 153.3 (d, *J* = 17.6 Hz), 141.2 (d, *J* = 5.4 Hz), 132.4 (d, *J* = 104.5 Hz), 132.5 (d, *J* = 9.8 Hz), 132.0 (d, *J* = 2.8 Hz), 128.5 (d, *J* = 12.2 Hz), 126.9 (d, *J* = 106.3 Hz), 60.8, 56.3(d, *J* = 0.9 Hz); ^{31}P NMR (161.9 MHz) δ 2.78. MS (m/z): 368 (100%) M^{+}, 367 (94%), 337 (13%), 199 (61%), 77 (26%). Anal Calcd for $C_{21}H_{21}O_4P$, C, 68.47; H, 5.75; found C, 68.53; H, 5.76.



(3,5-Dimethylphenyl)Diphenylphosphine oxide (6h): oil. IR (neat) 2217, 1598, 1436, 1187, 1118, 698 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 7.70-7.65 (m, 4 H), 7.54-7.53 (m, 2 H), 7.48-7.45 (m, 4 H), 7.30 (s, 1 H), 7.27 (s, 1 H), 7.17 (s,1 H), 2.31 (s, 6 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ 138.2

(d, J = 12.9 Hz), 133.8 (d, J = 2.7 Hz), 132.6 (d, J = 104.5 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 103.9 Hz), 131.8 (d, J =2.6 Hz), 129.7 (d, J = 9.9 Hz), 128.5 (d, J = 12.2 Hz); ^{31}P NMR (161.9 MHz) δ 2.76. MS (m/z): 306 (51%) M^+, 305 (100%), 227 (9%), 199 (11%), 77 (24%). Anal Calcd for $C_{20}H_{19}OP$, C, 78.41; H, 6.25; found C, 78.57; H, 6.23.

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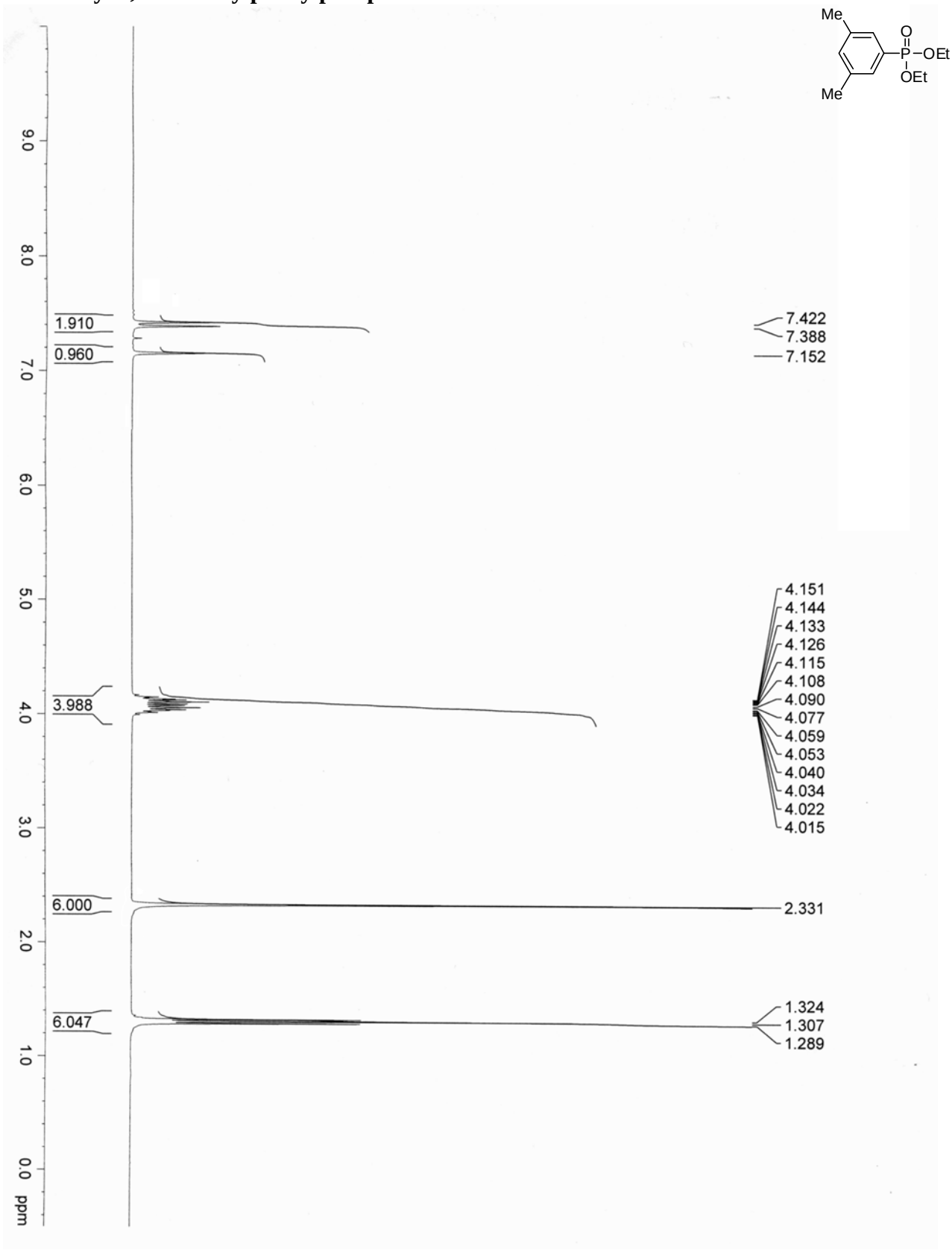
(1) Yong Luo, Jie Wu, *Organometallics*, **2009**, *28*, 6823-6826.
(2) Vaillard S. E., Muck-Lichtenfeld C., Grimme S., Studer A., *Angewandte Chemie Int. Ed.*, **2007**, *46*, 6533-6536.
(3) Huang. C, Tang X., Fu H., Jiang Y., Zhao Y., *J. Org. Chem.*, **2006**, *71*, 5020-5022.
(4) Kalec M., Ziadi A., Stawinski J., *Org. Lett*, **2008**, *10*, 4637-4640.
(5) Bonnaventure I., Charette A. B., *J. Org. Chem.*, **2008**, *73 (16)*, 6330-6340.

NMR Spectra

2c: Diethyl 3,5-Dimethylphenylphosphonate



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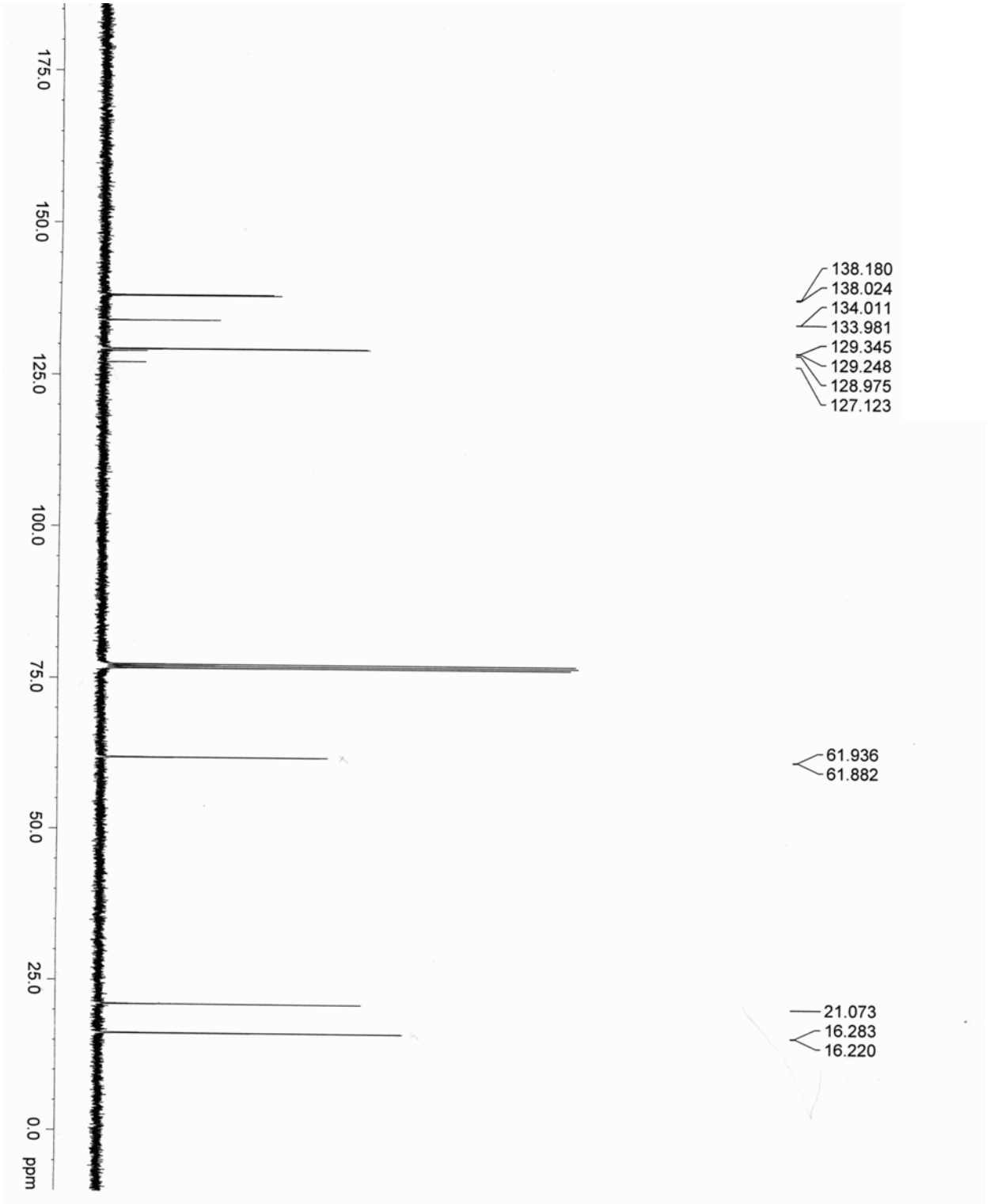

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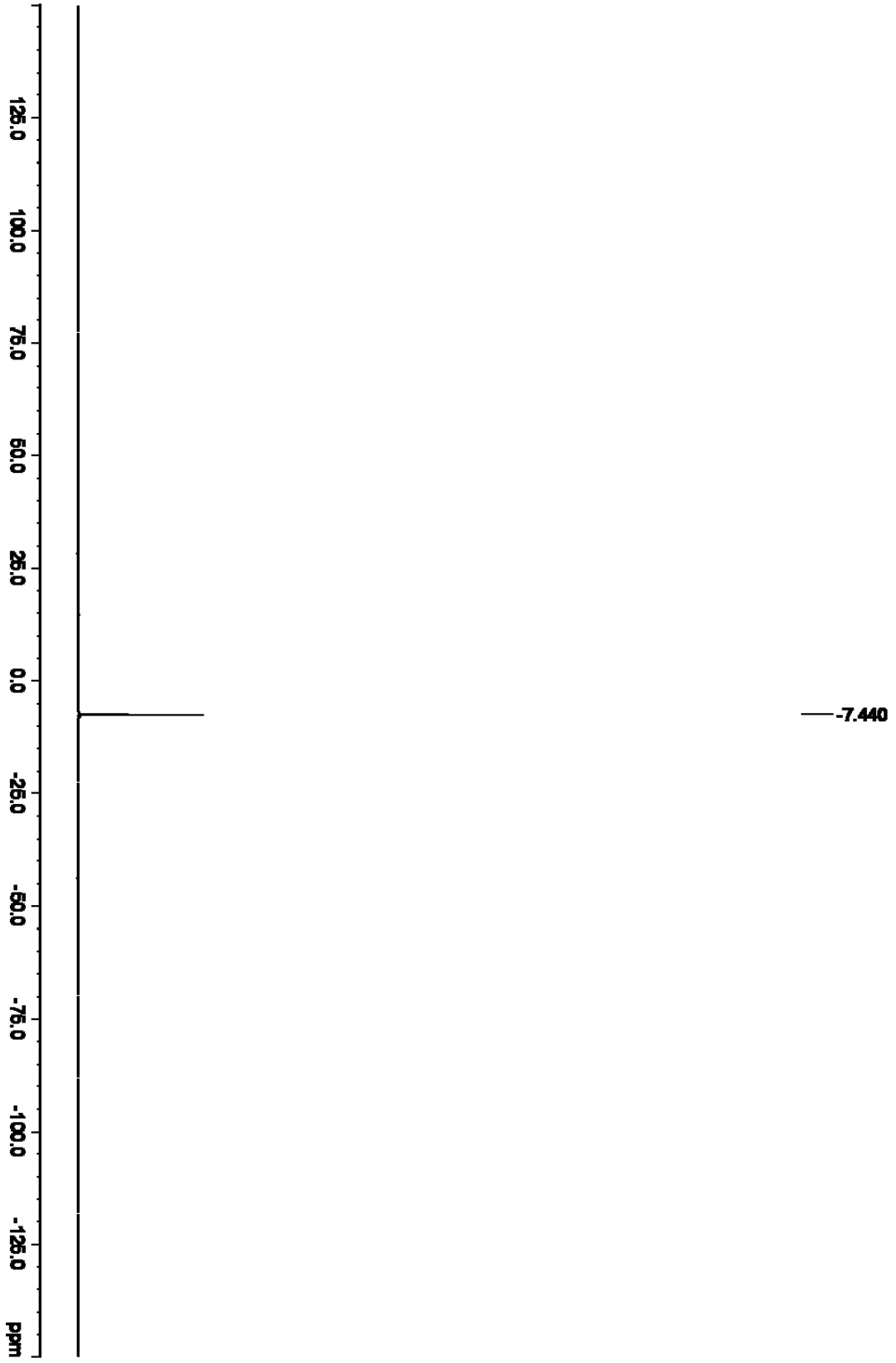
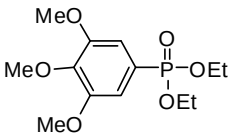
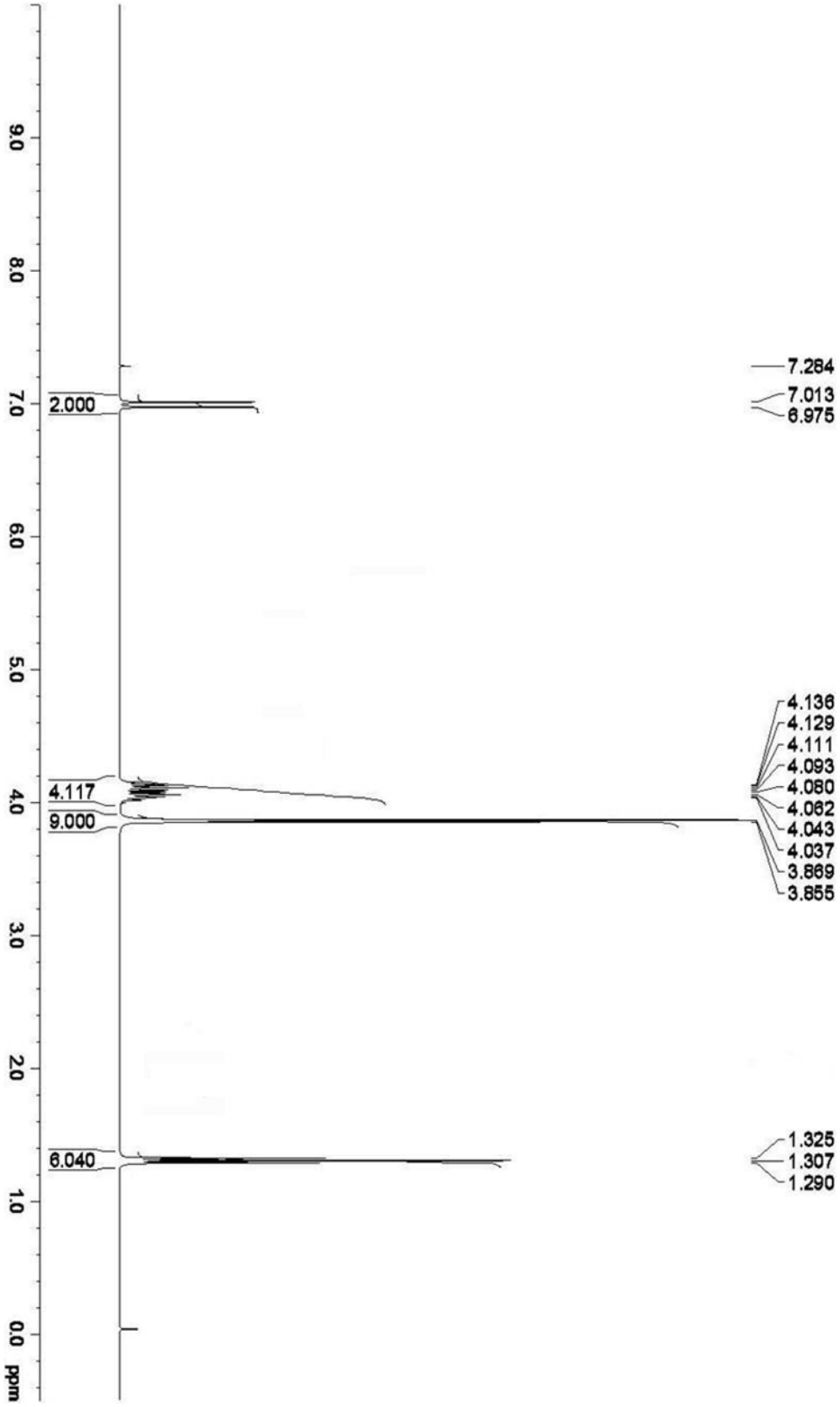


2d: Diethyl 3,4,5-Trimethoxyphenylphosphonate





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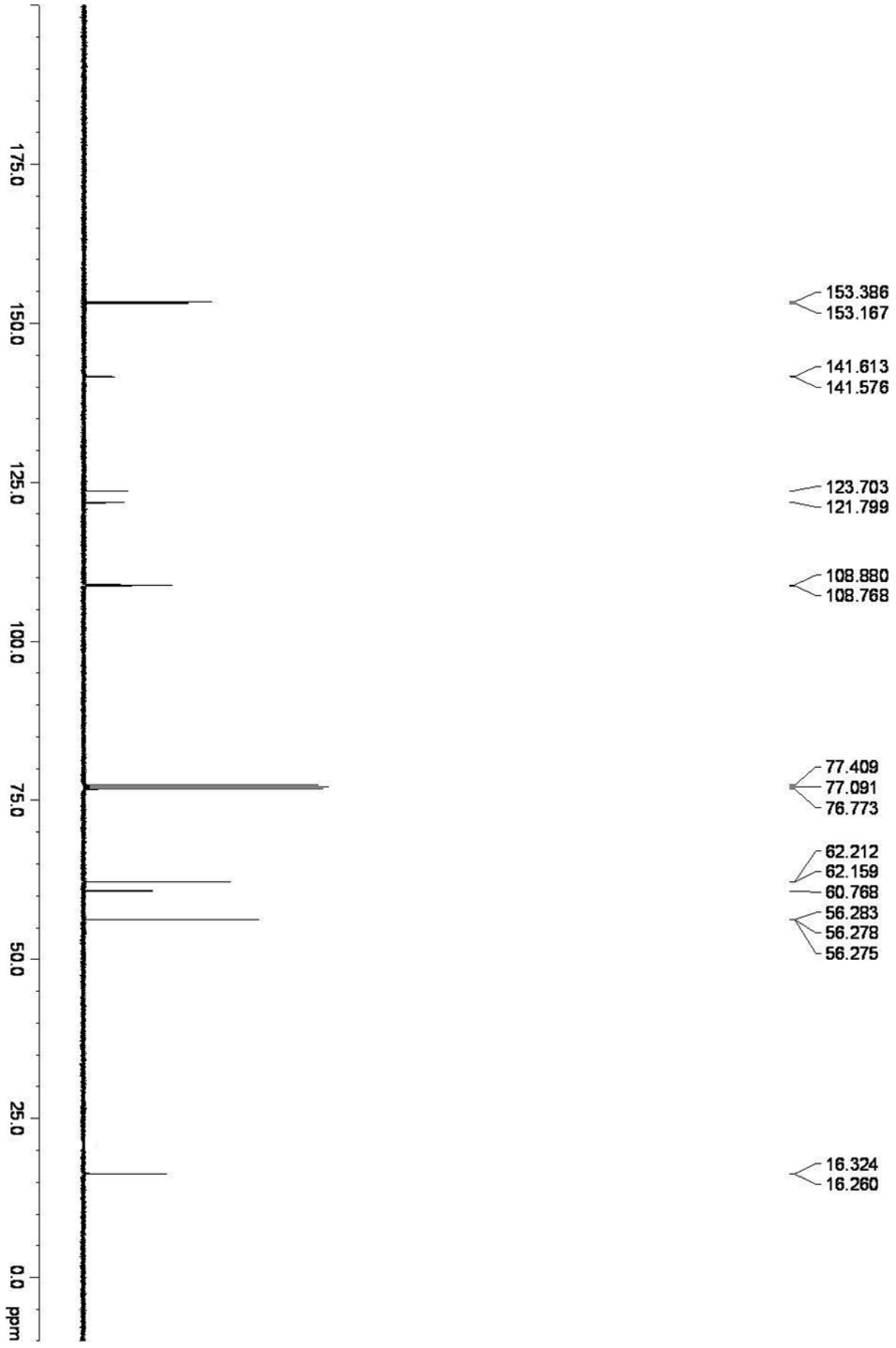

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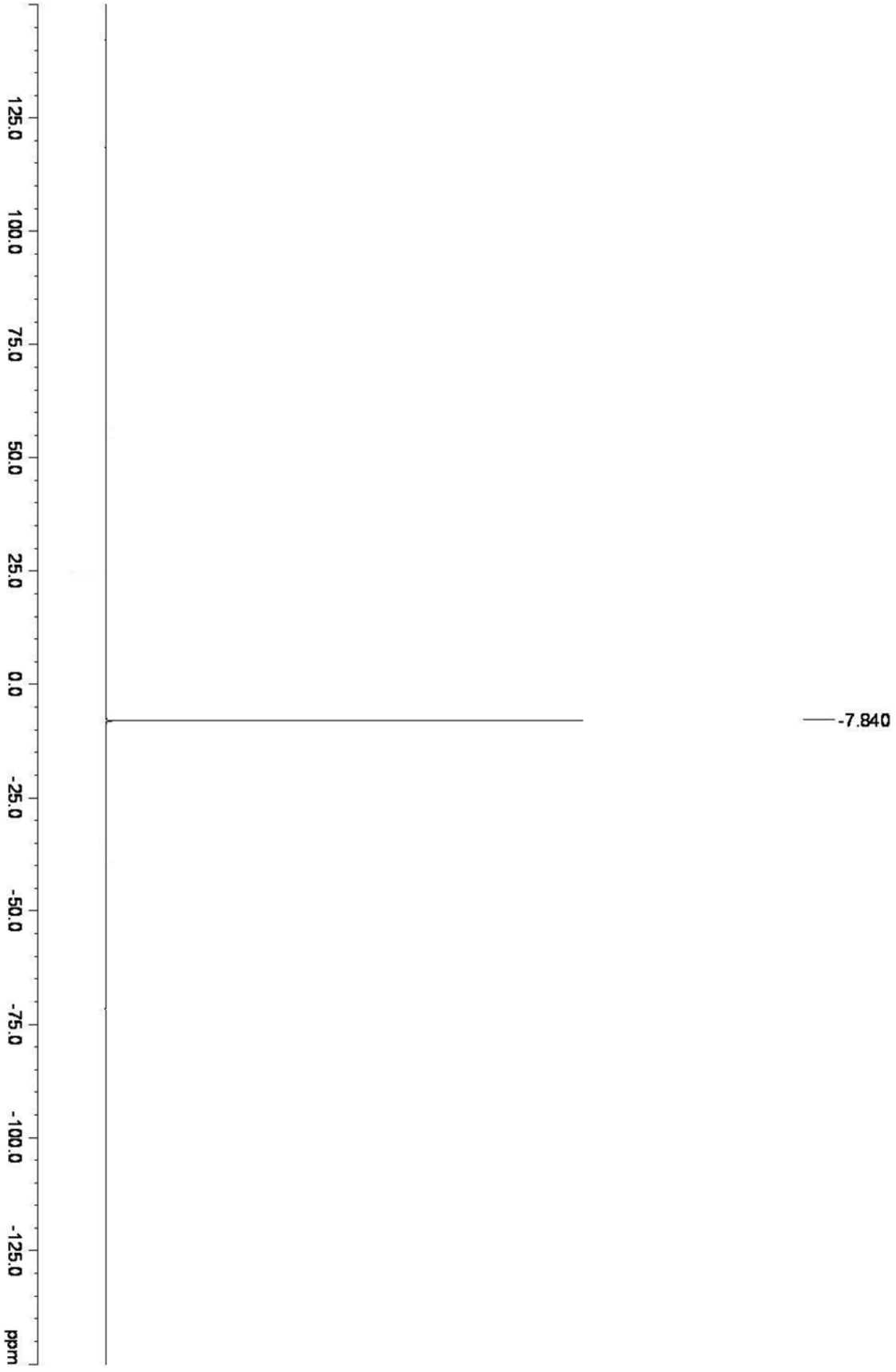
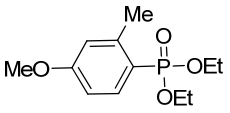
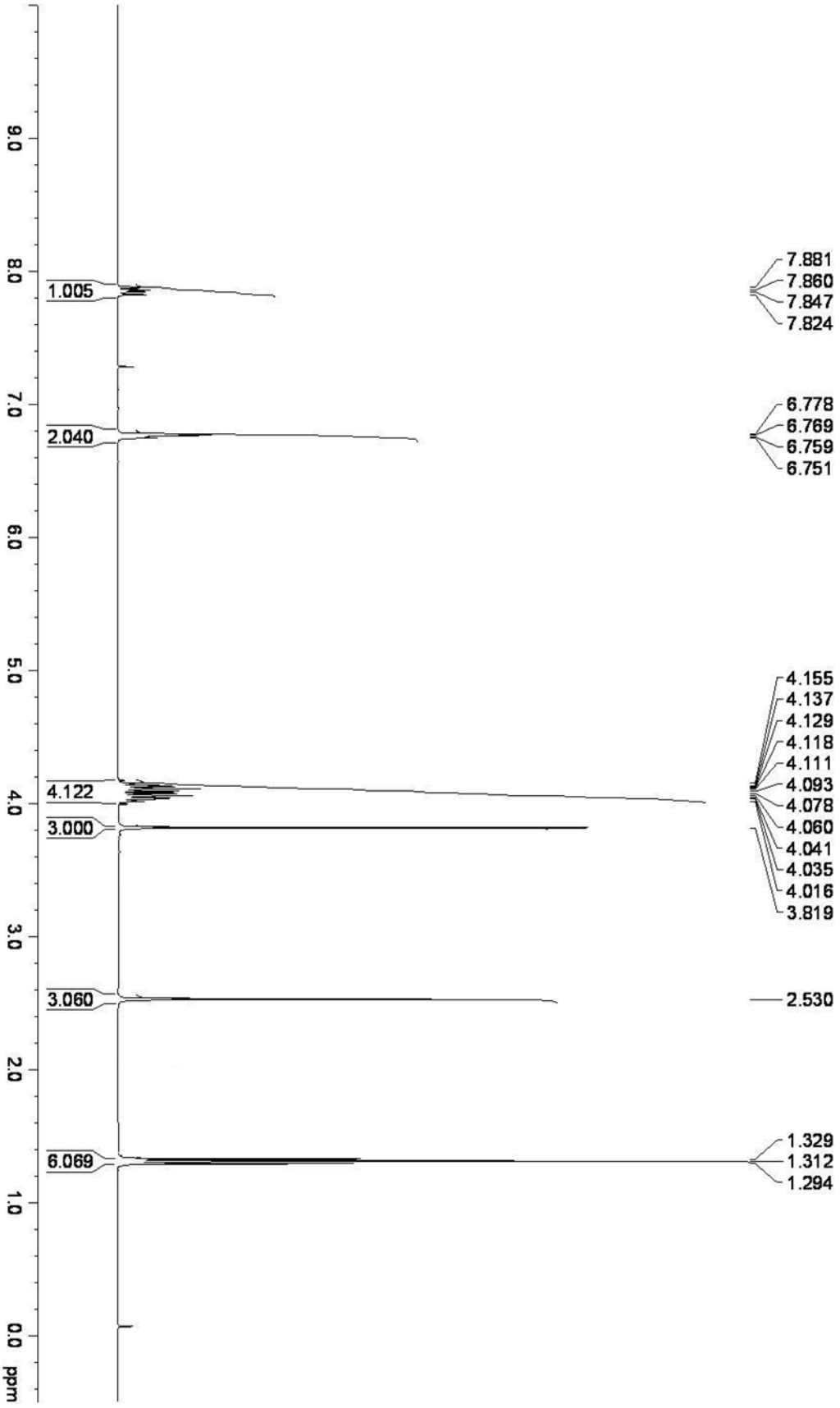


2e: Diethyl 2-Methyl-4-Methyoxyphenylphosphonate





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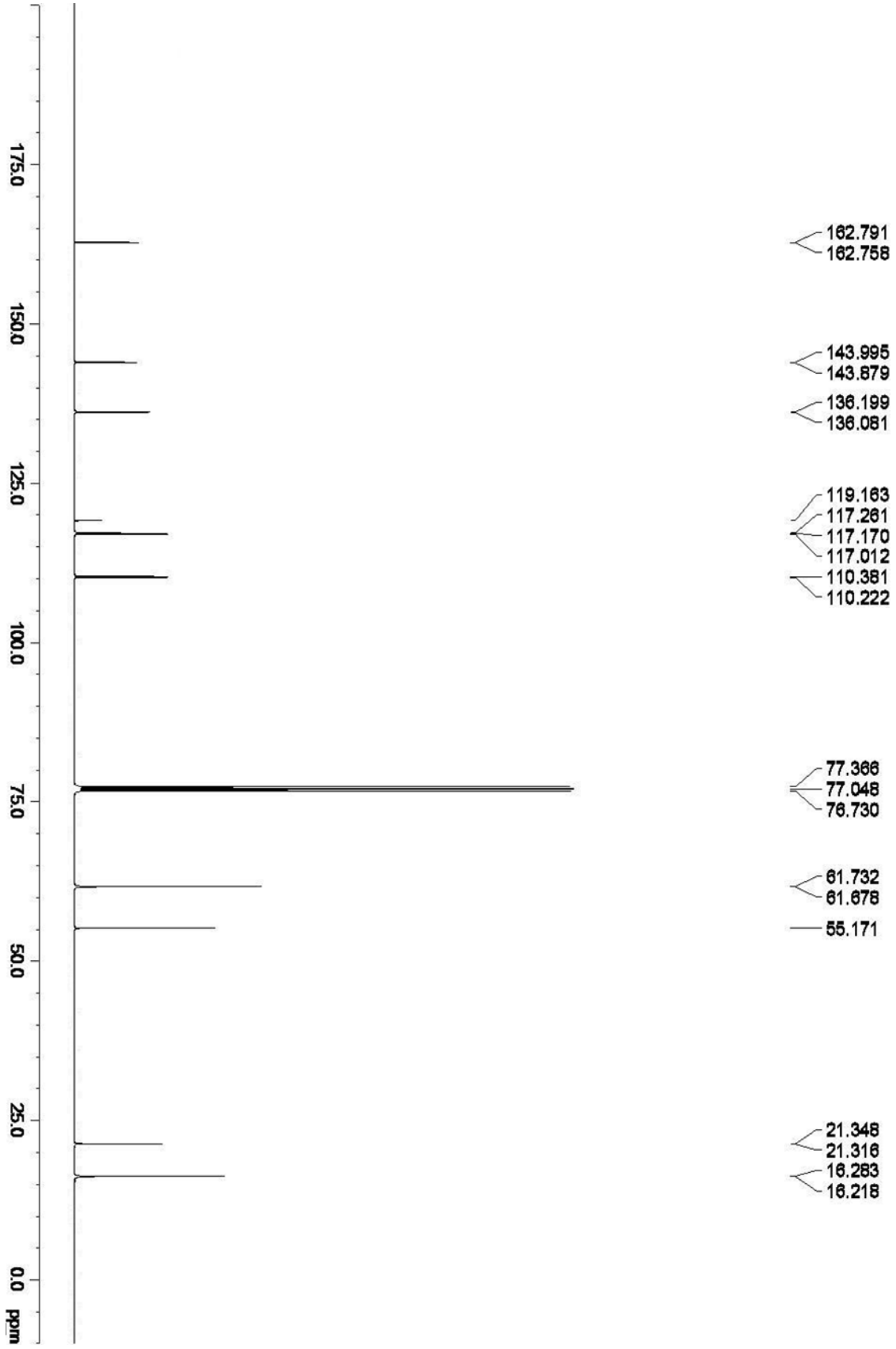

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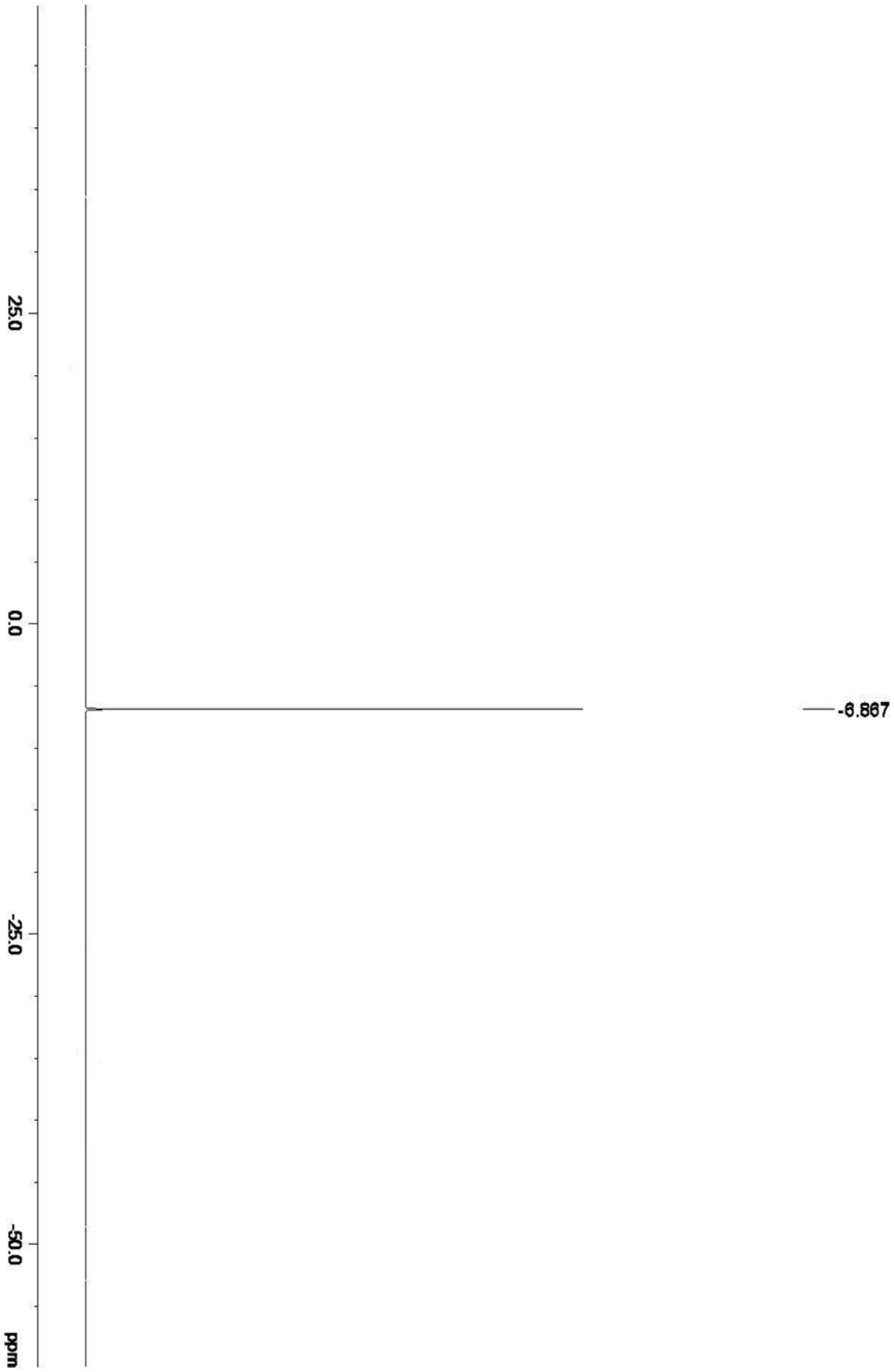
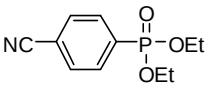
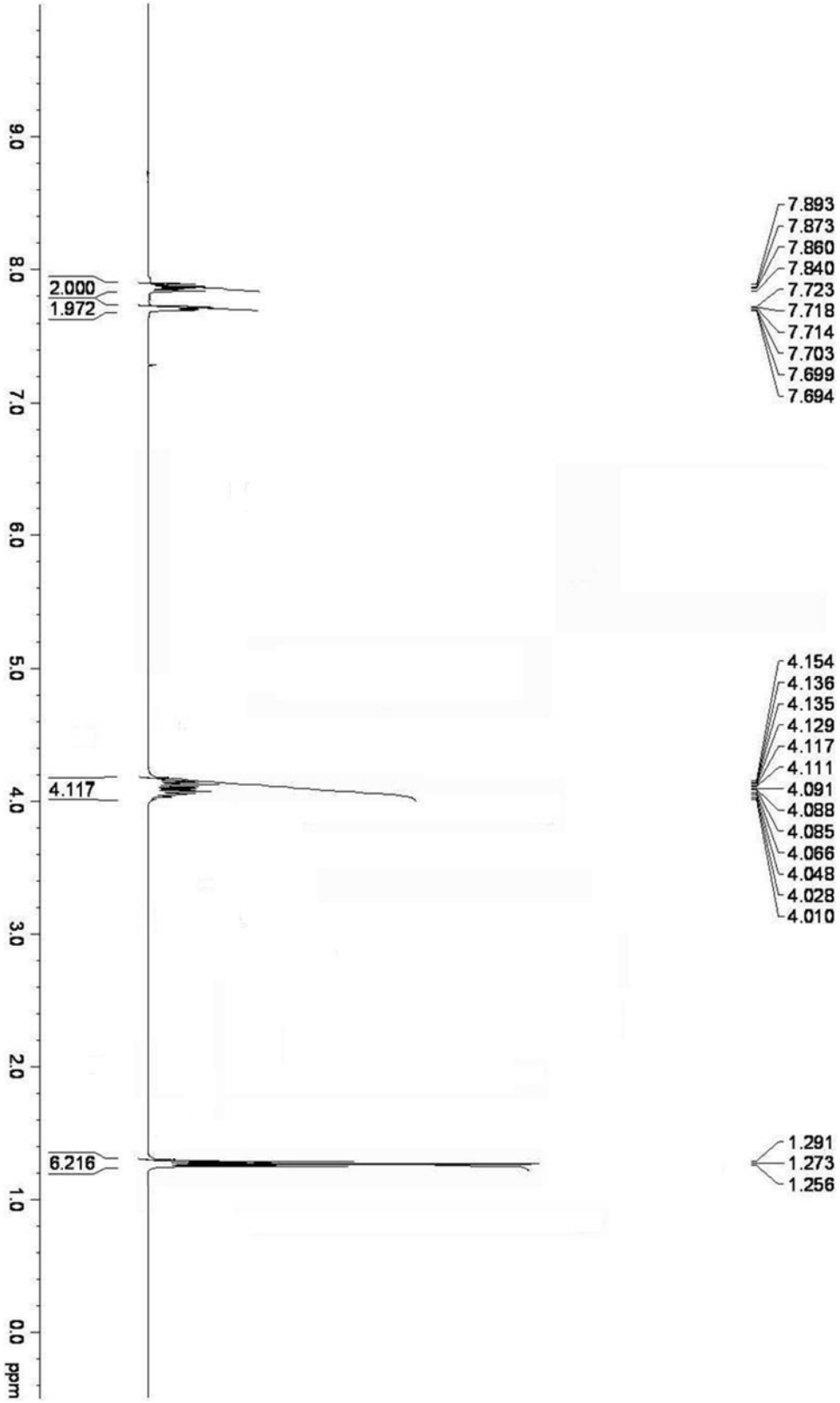


2j: Diethyl 4-Cyanophenylphosphonate





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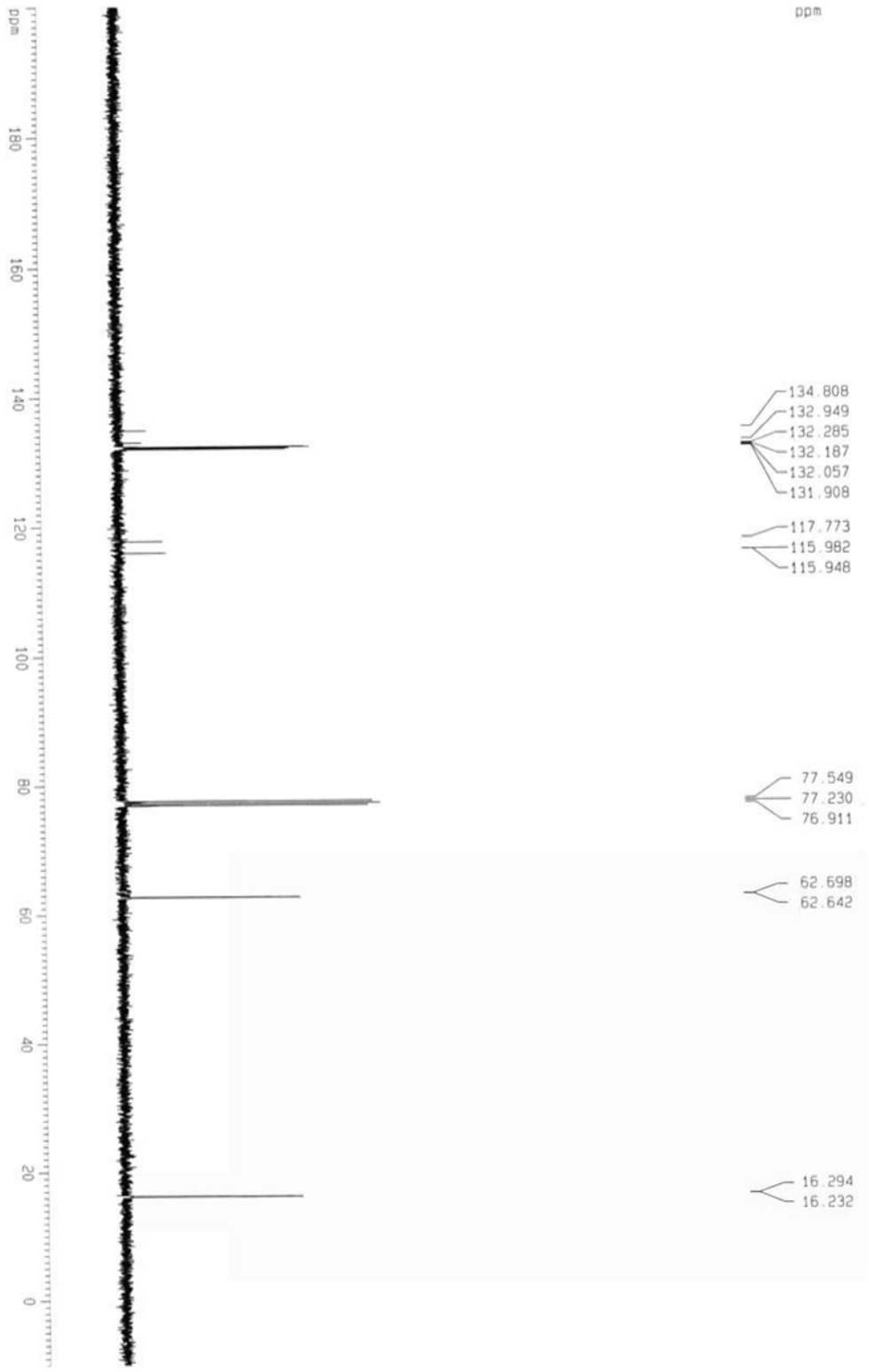

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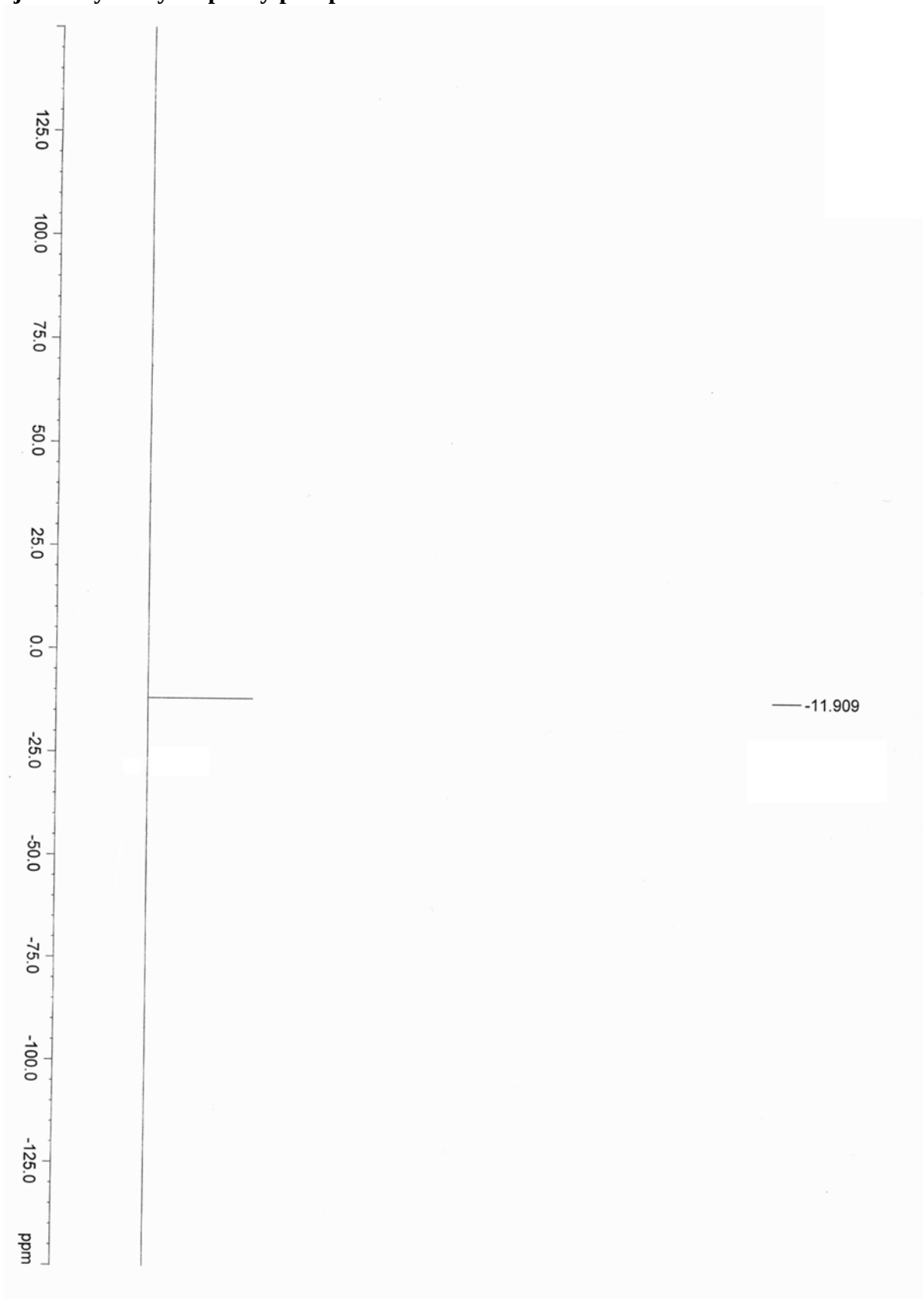
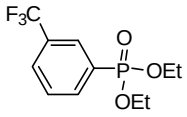
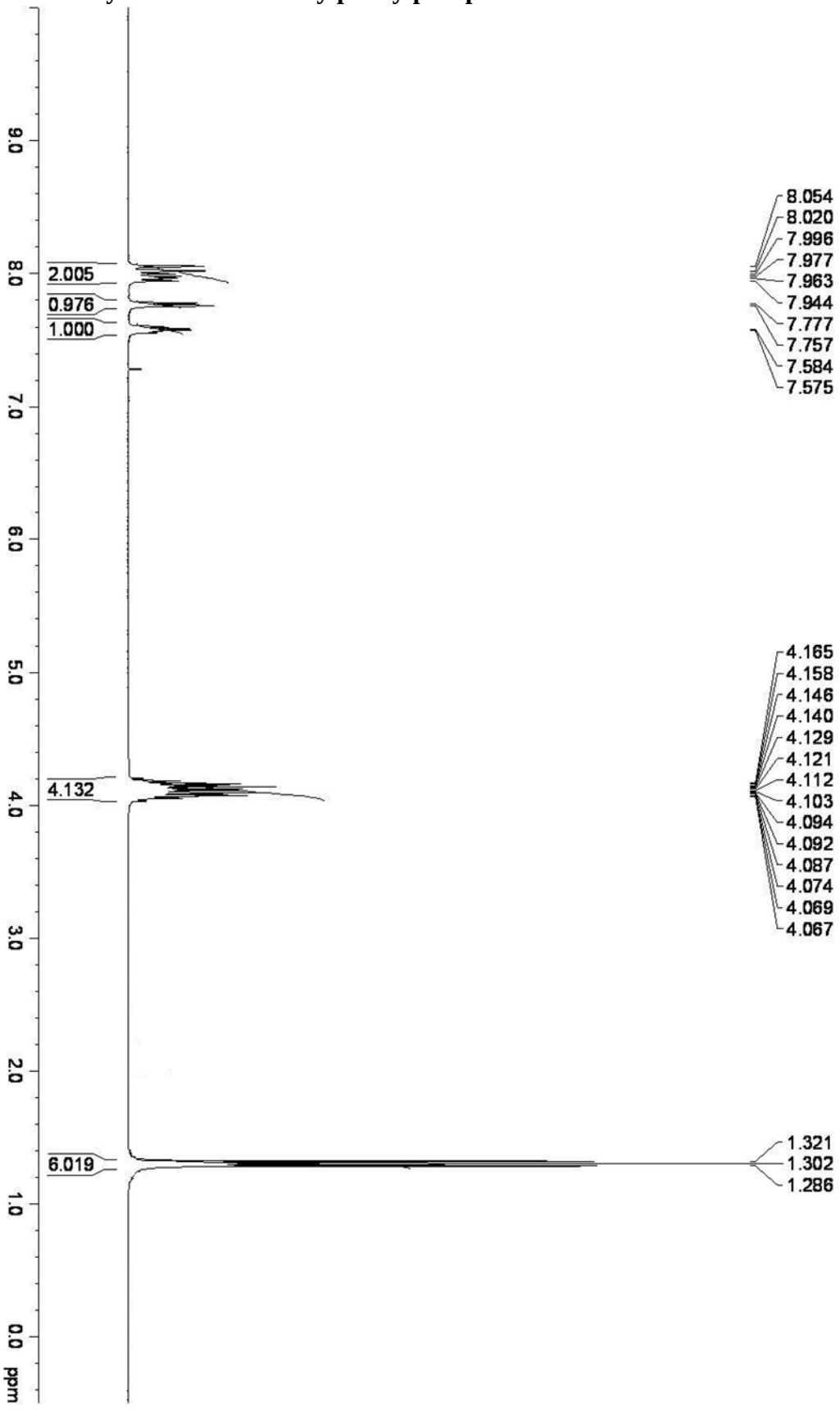


2k: Diethyl 3-Trifluoromethylphenylphosphonate





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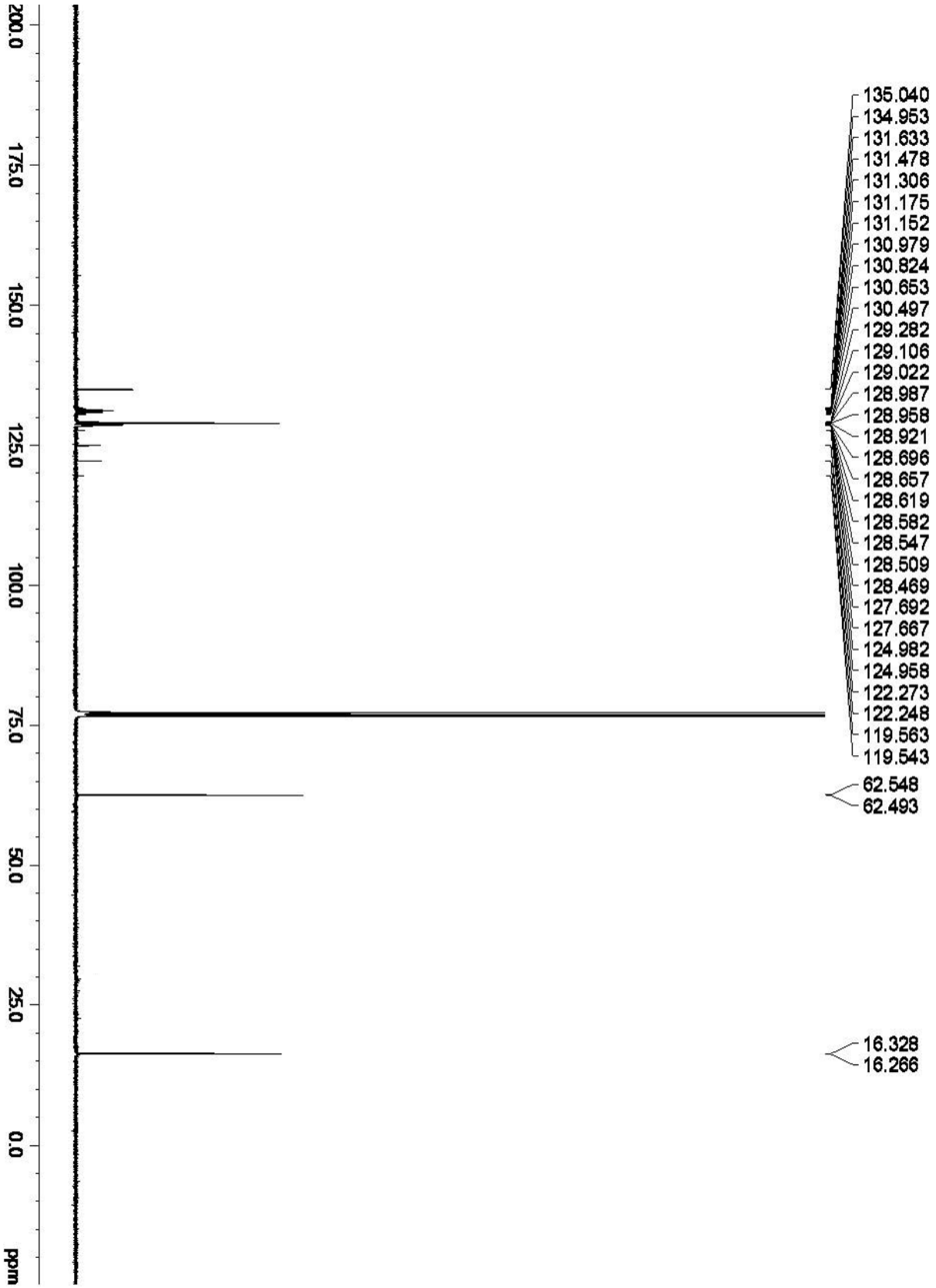

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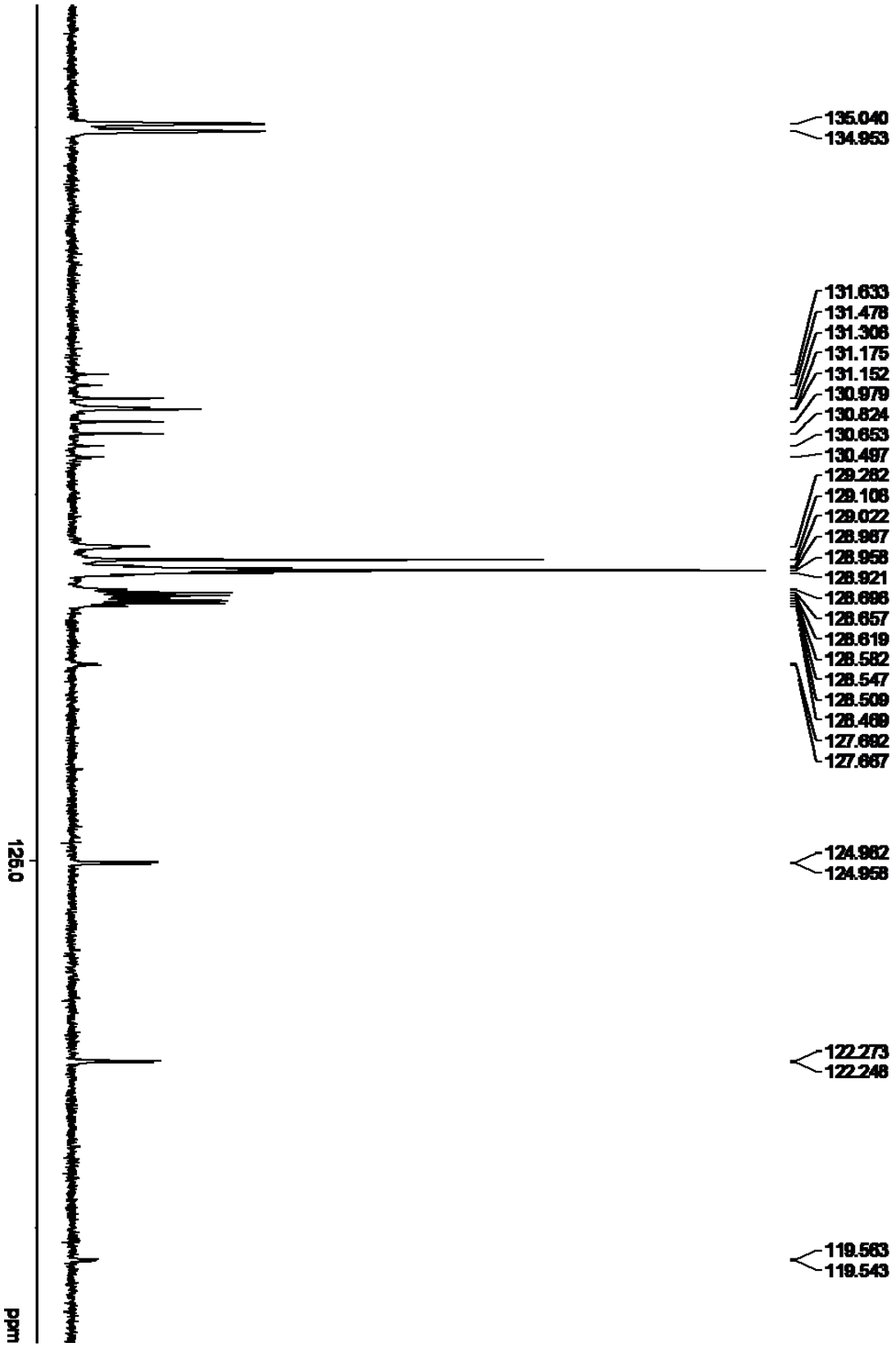

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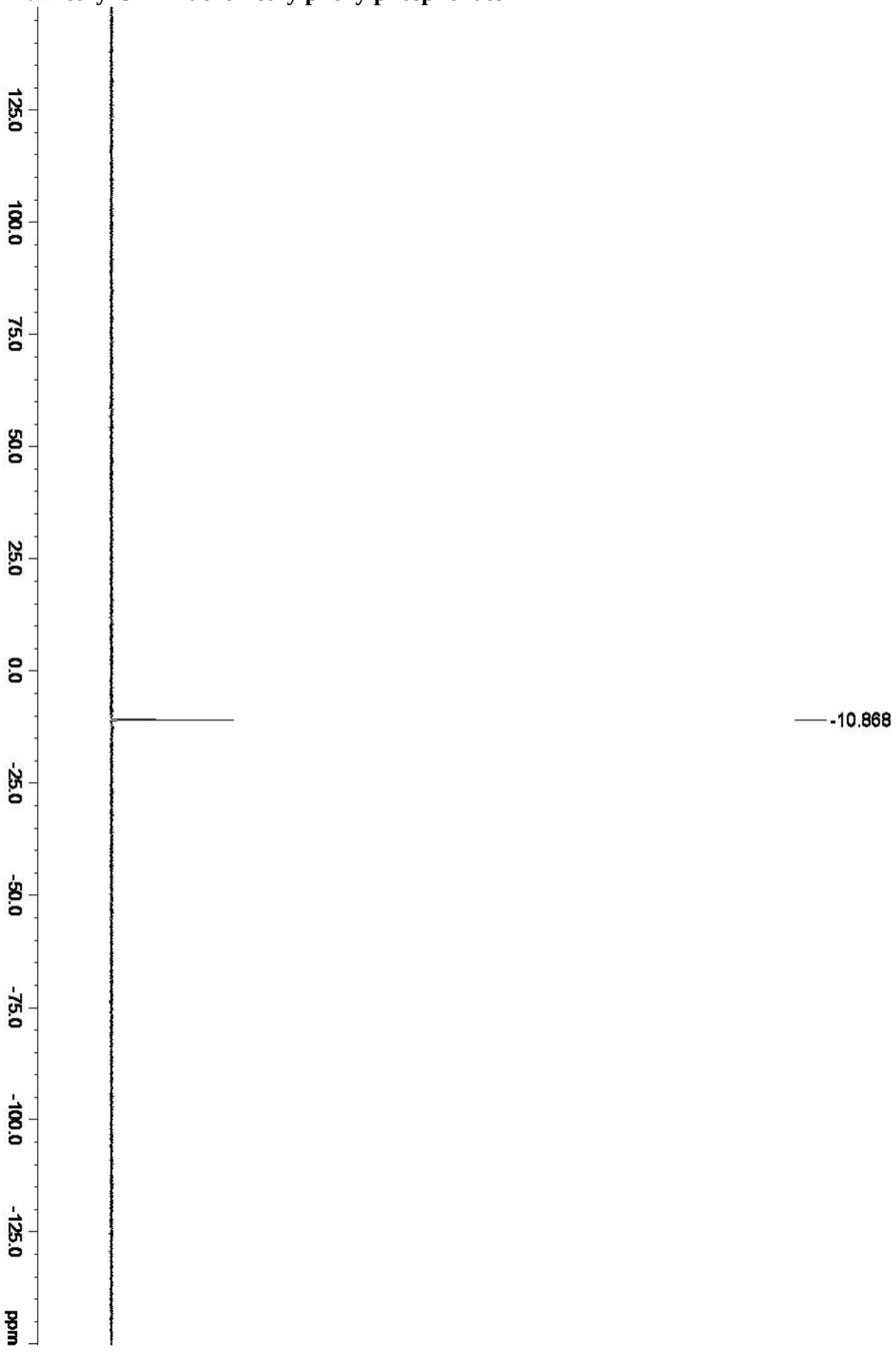

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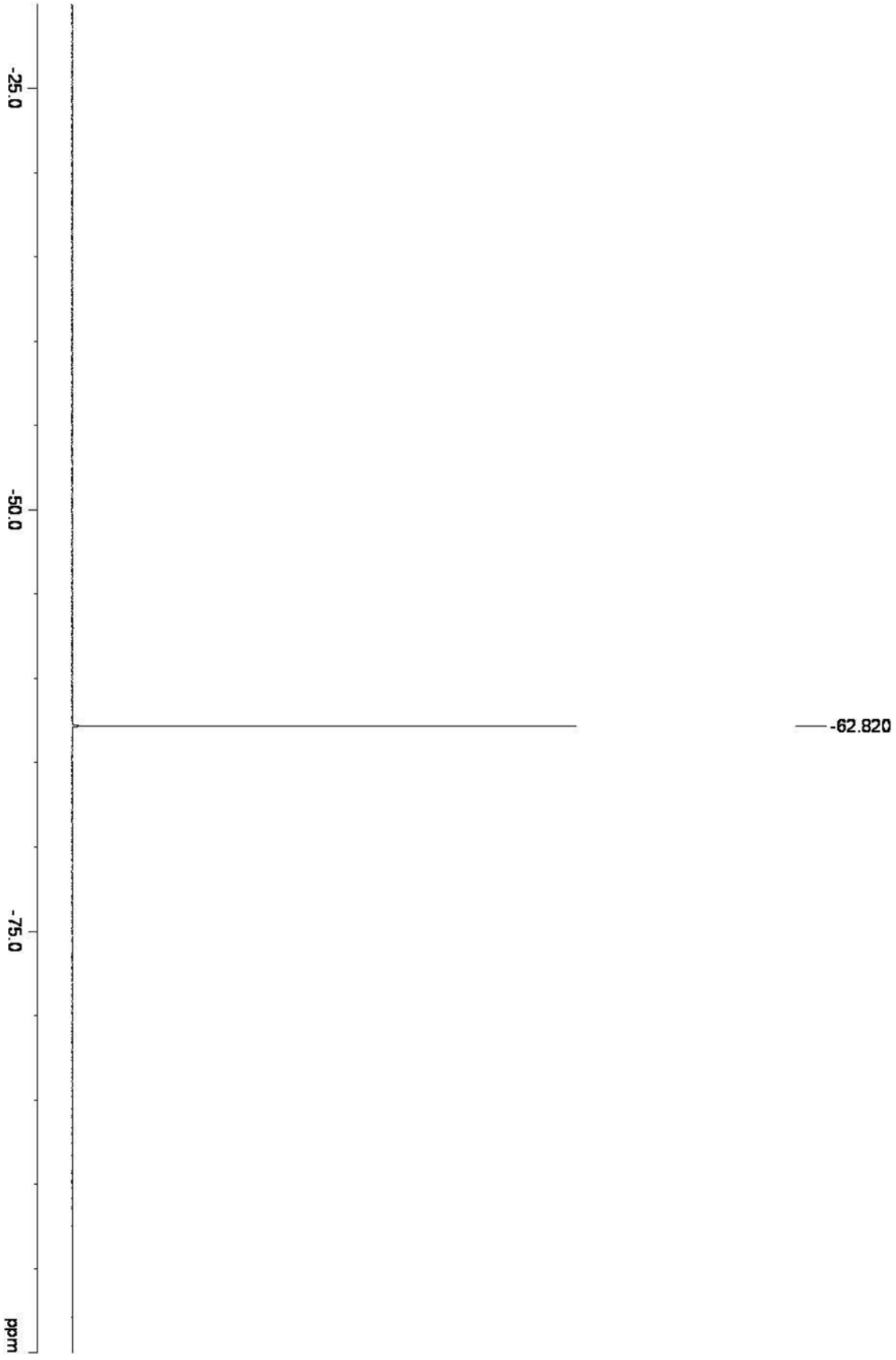
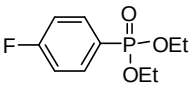
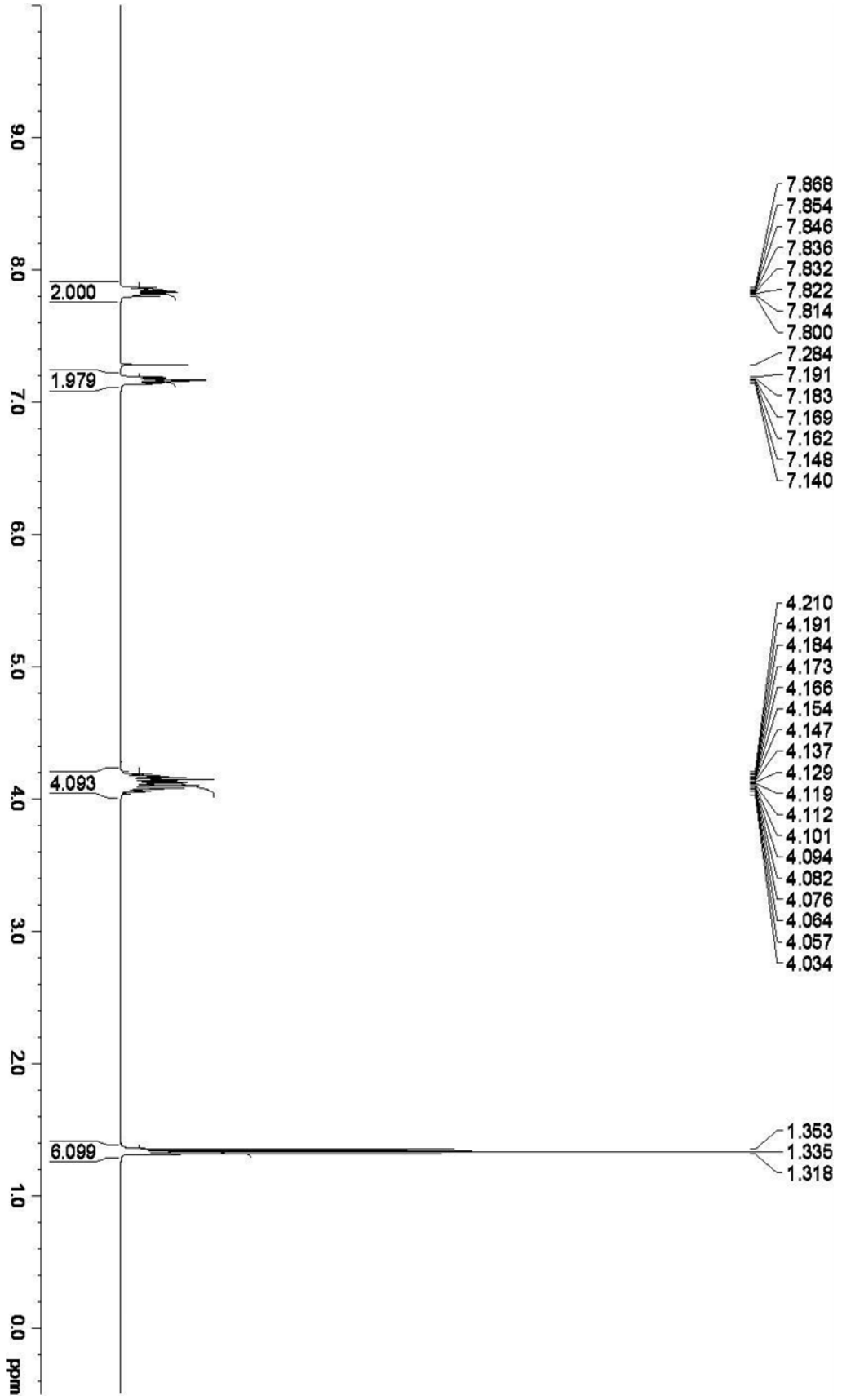


2l: Diethyl 4-Fluorophenylphosphonate





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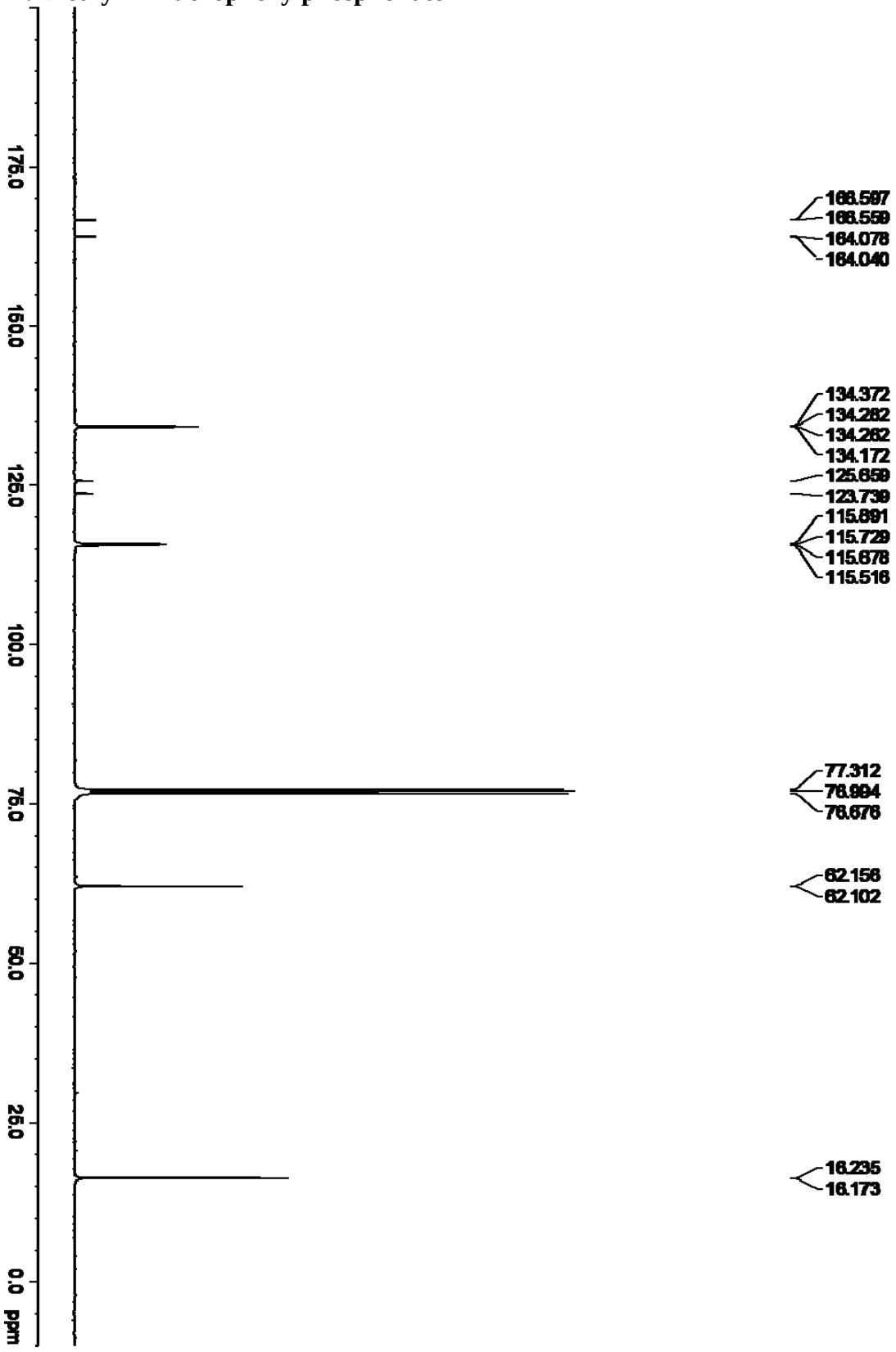

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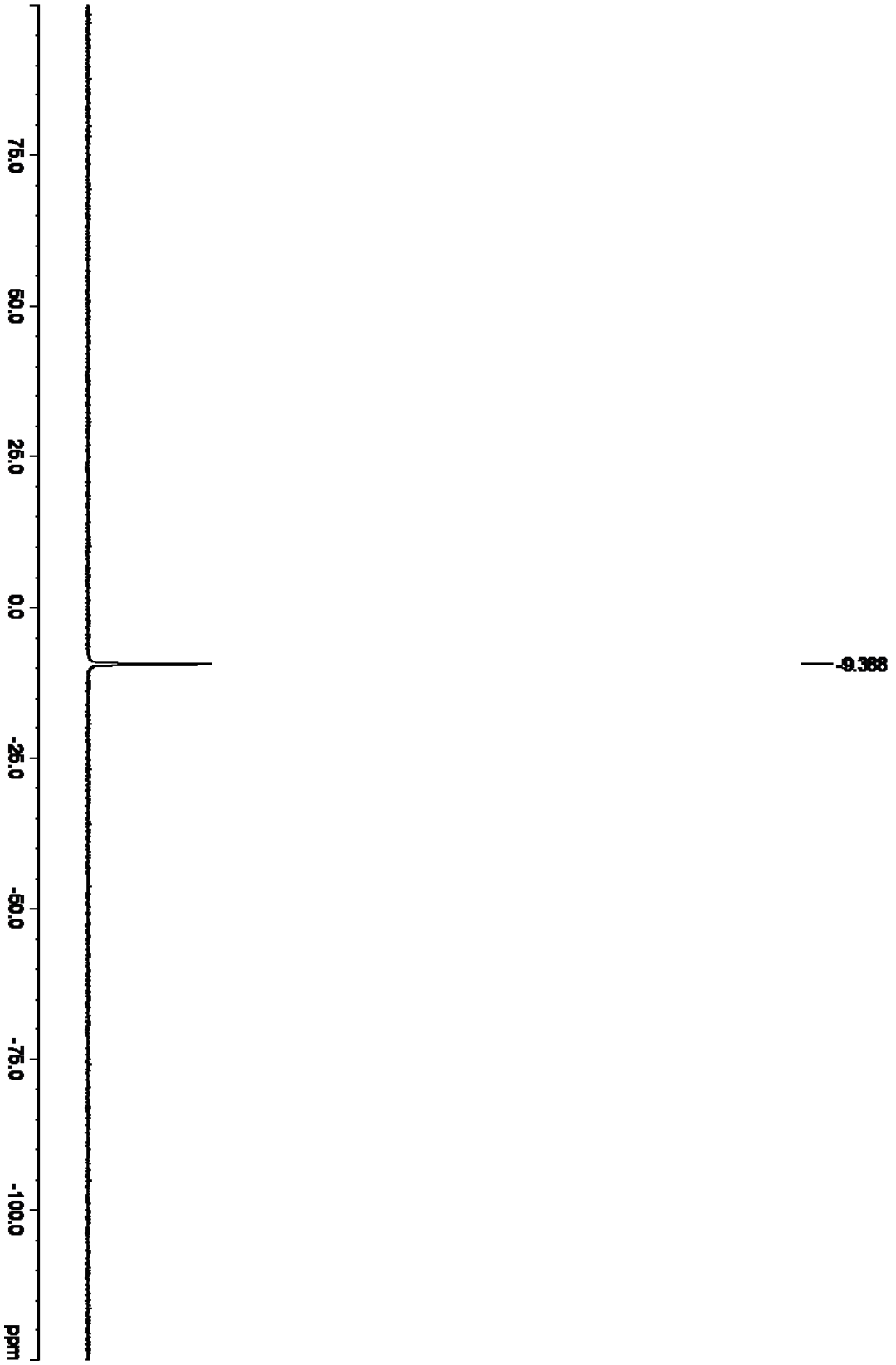
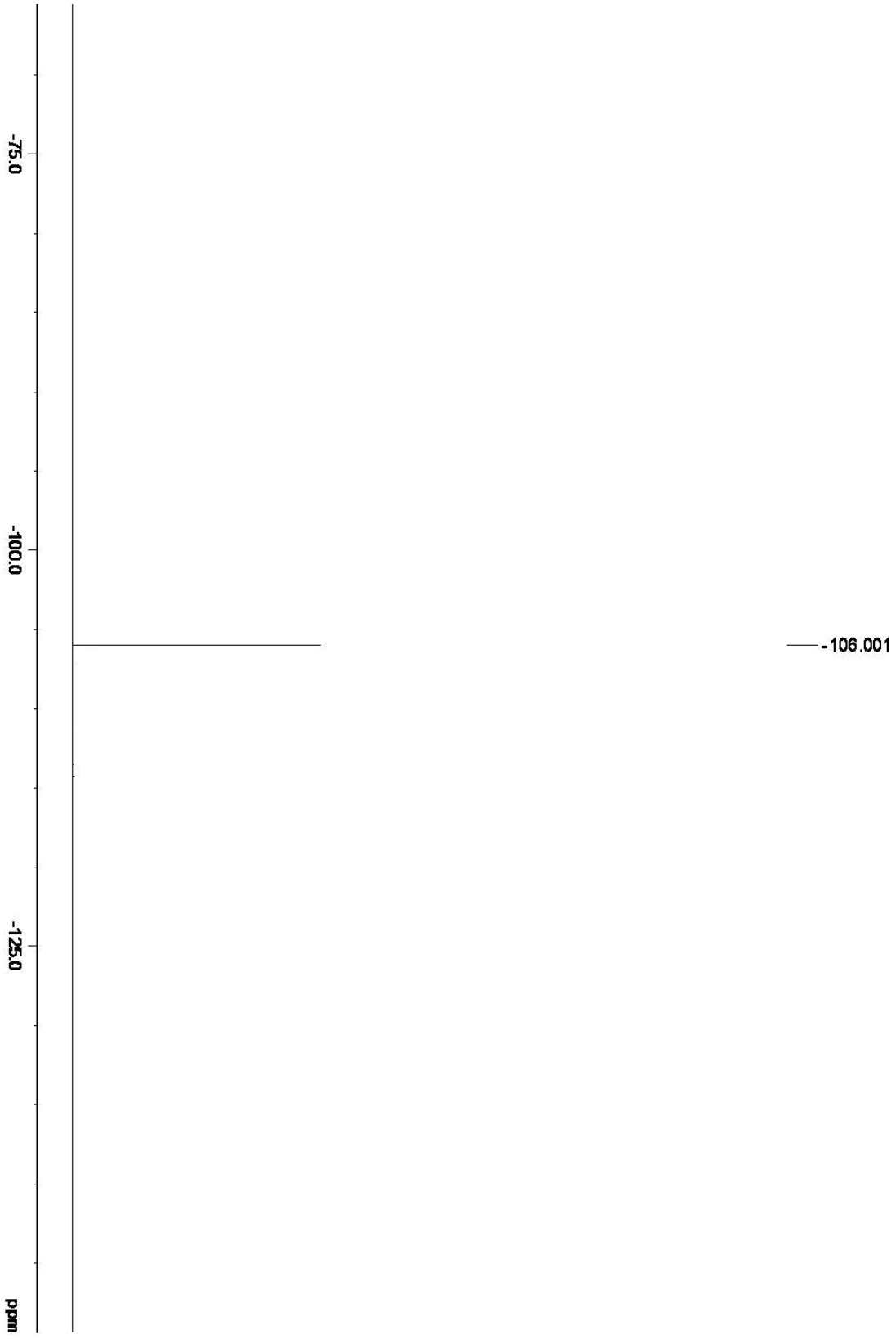
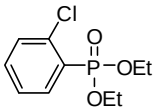
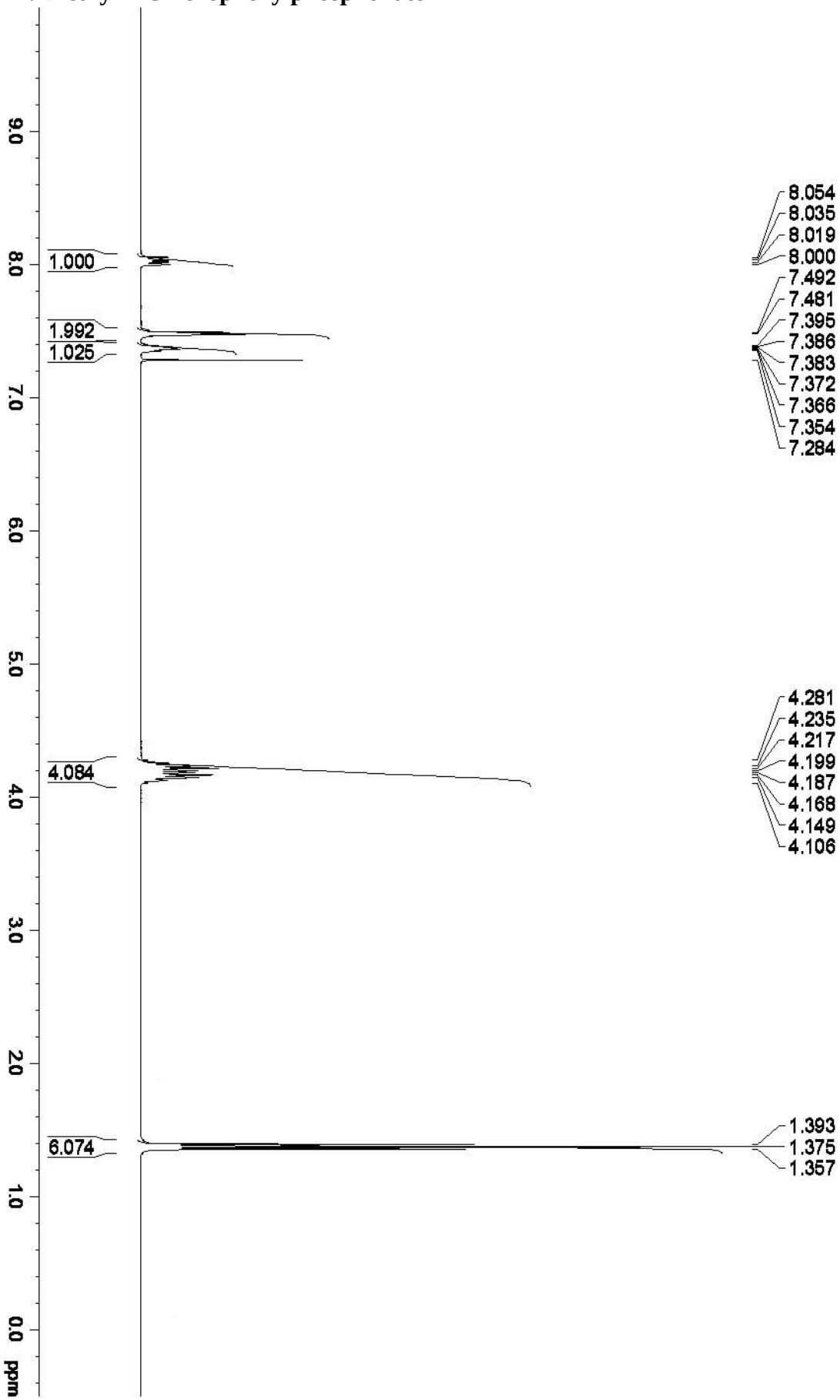


2l: Diethyl 4-Fluorophenylphosphonate

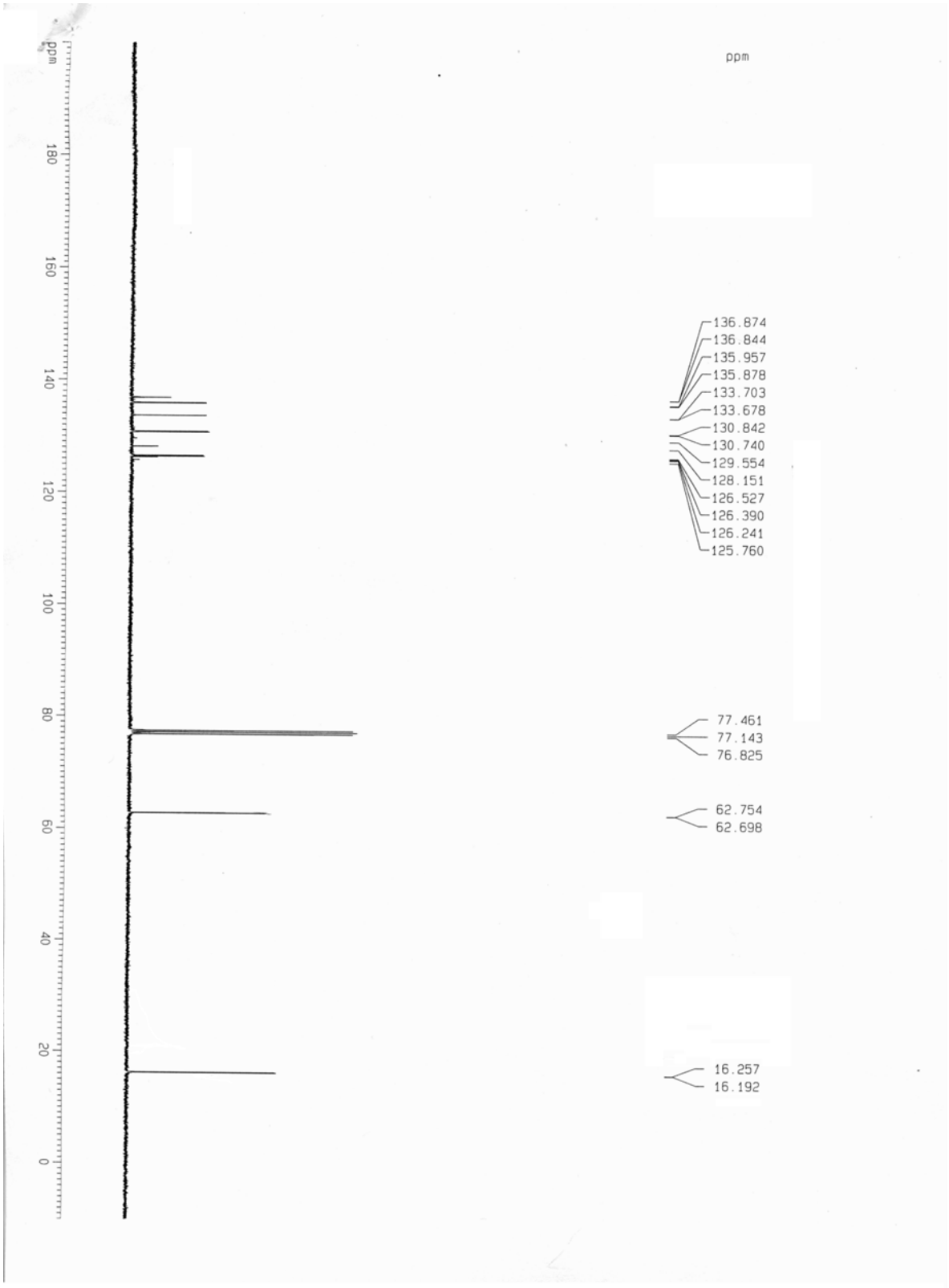


2n: Diethyl 2-Chlorophenylphosphonate

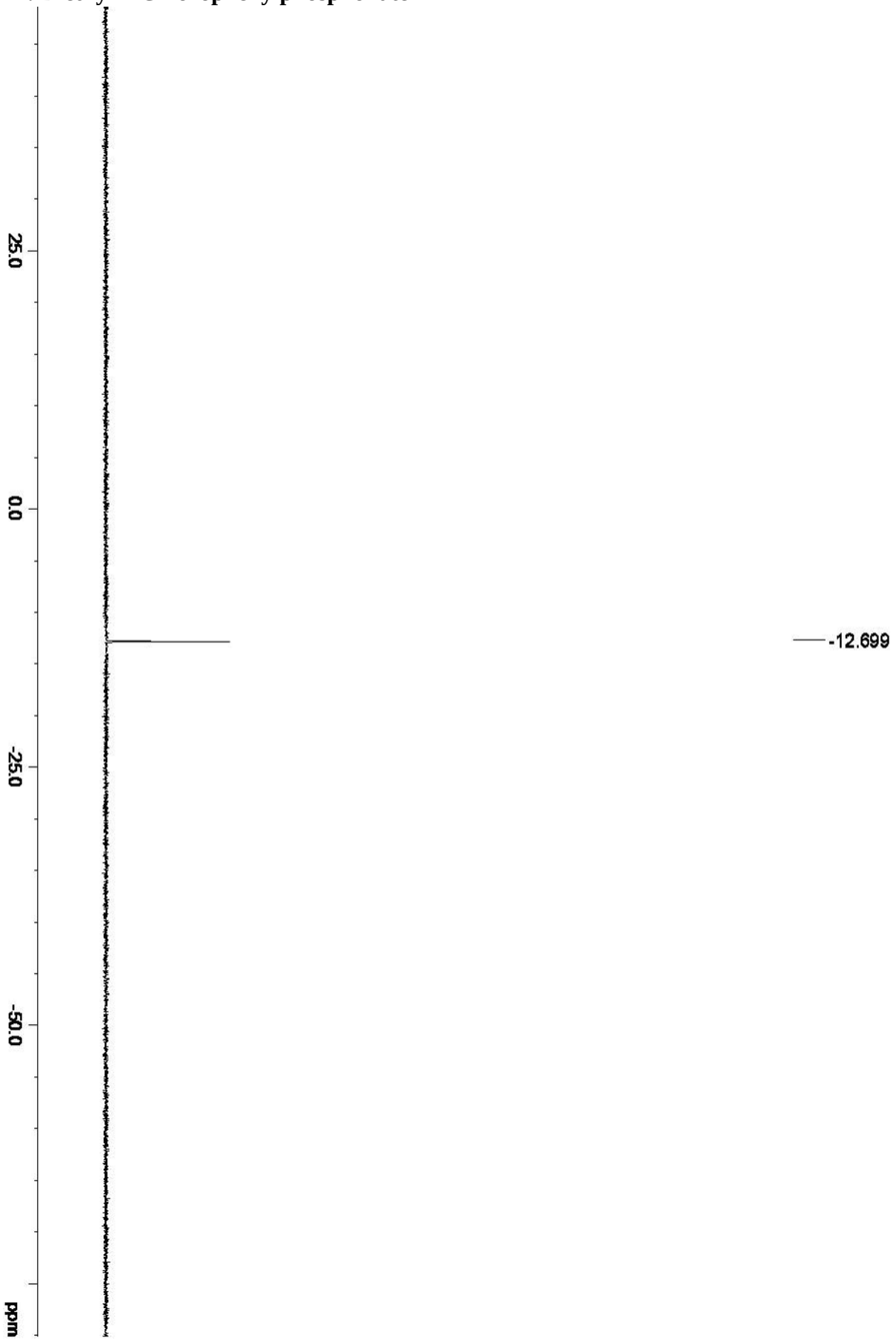




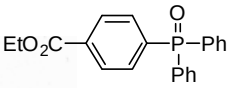
2n: Diethyl 2-Chlorophenylphosphonate

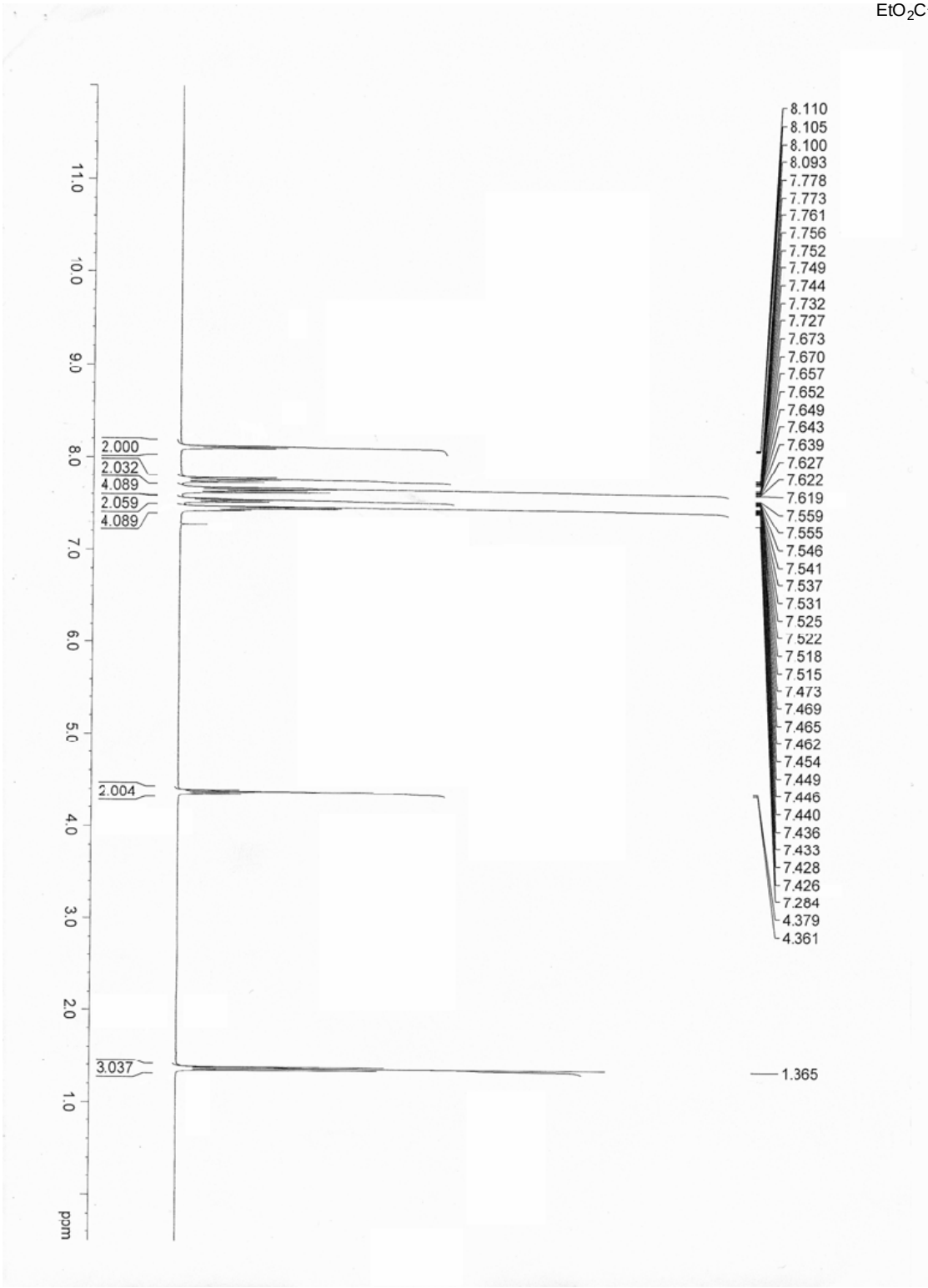


2n: Diethyl 2-Chlorophenylphosphonate

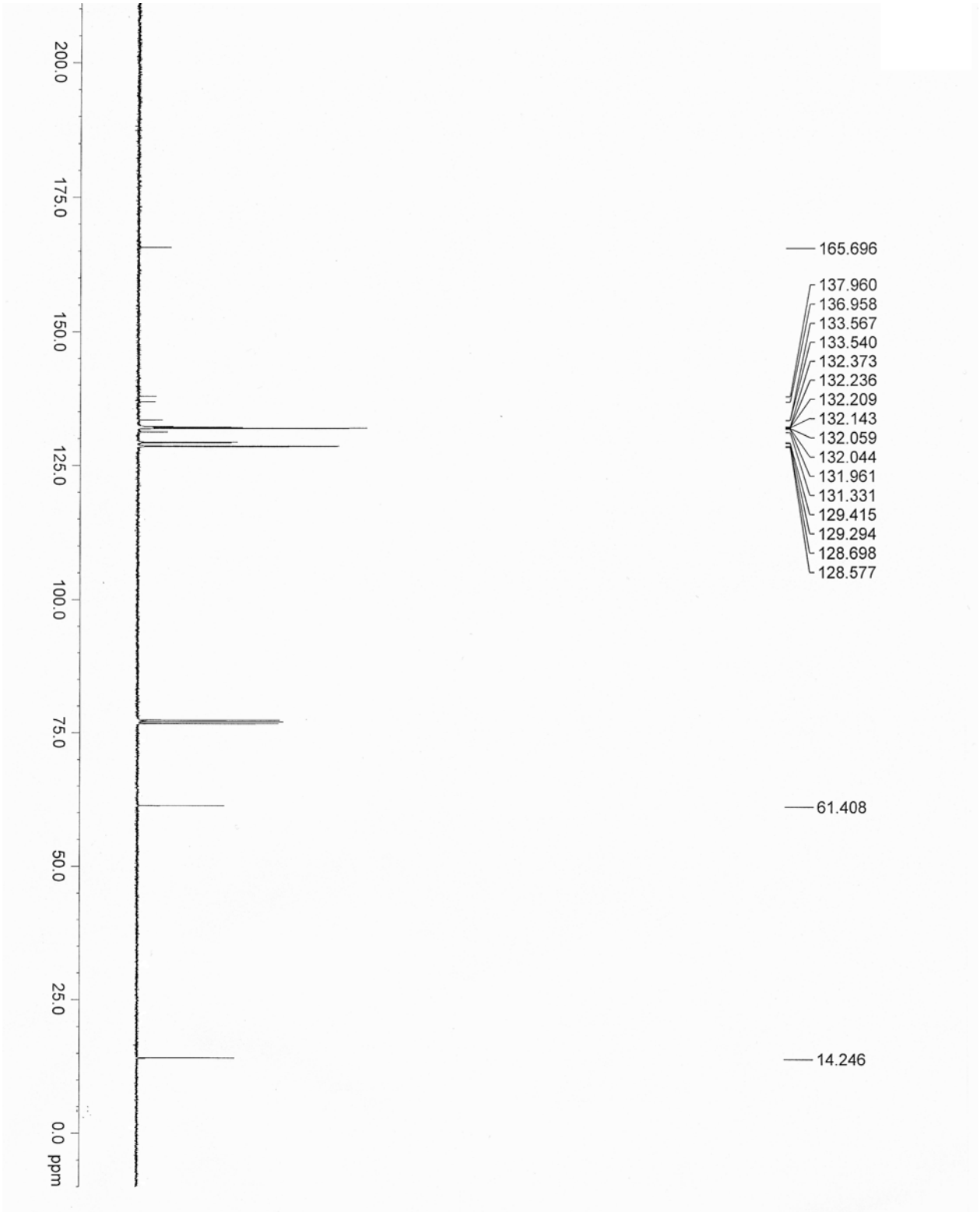


6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide

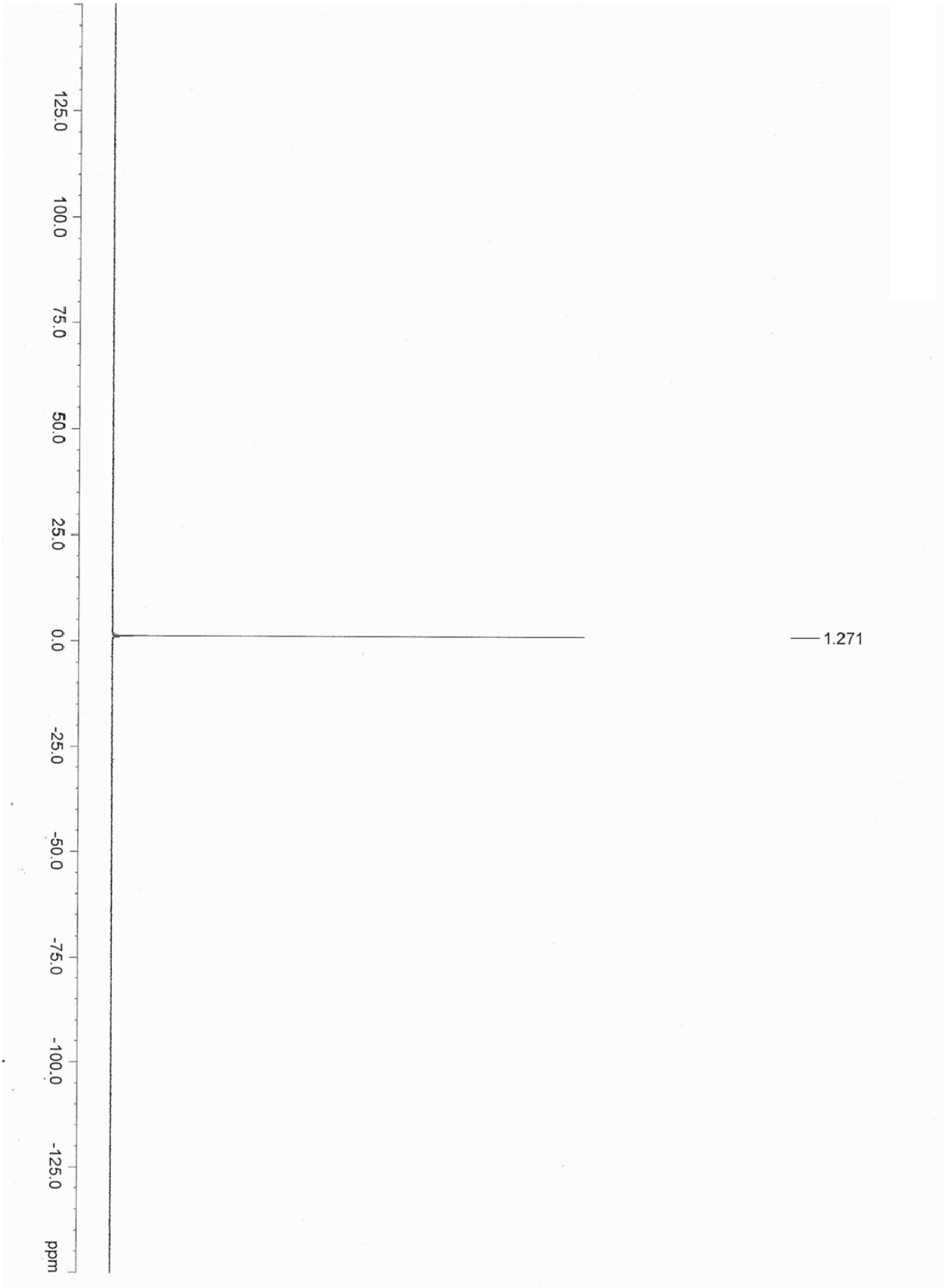




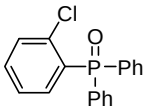
6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide

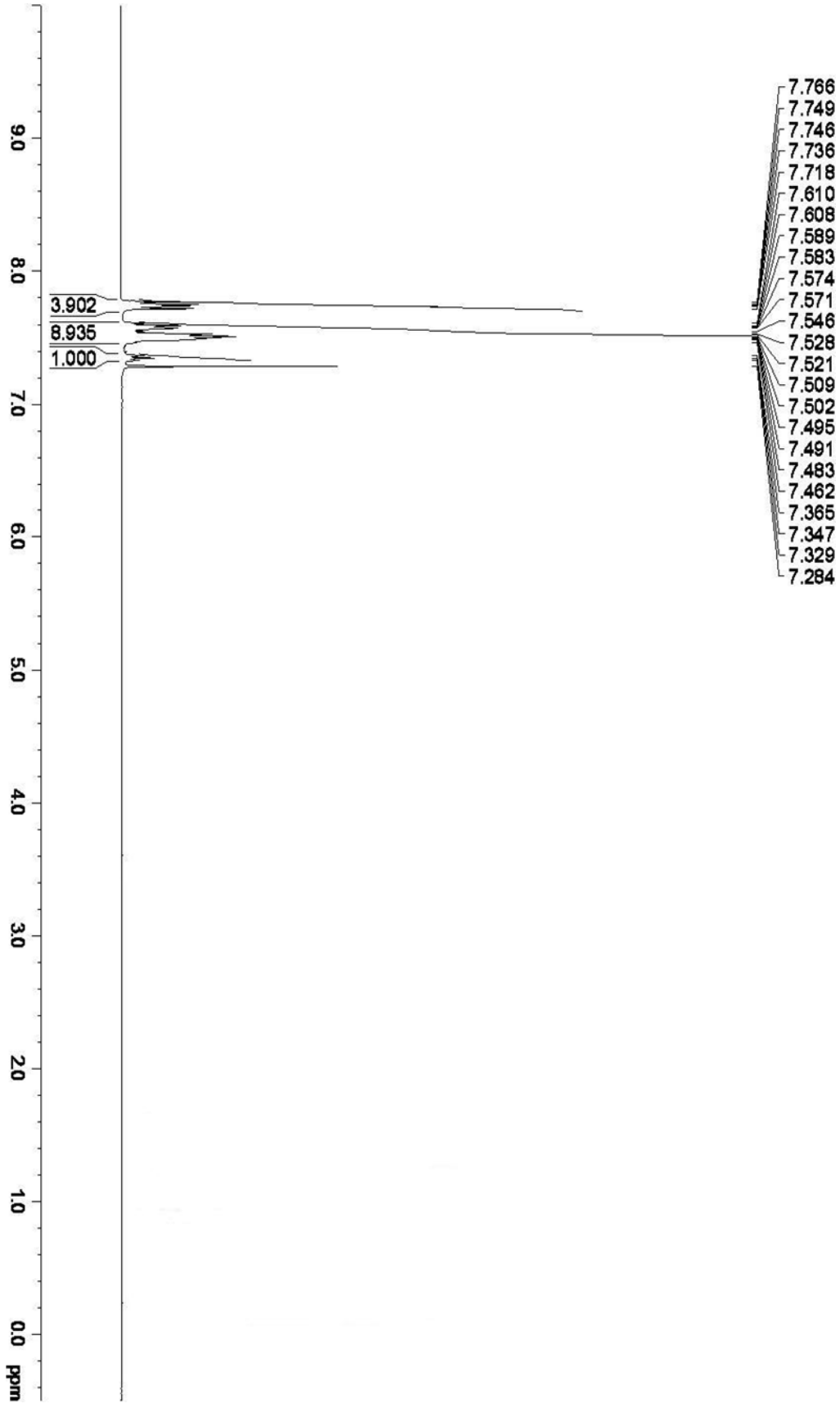


6c: (4-Ethoxycarbonylphenyl) Diphenylphosphine oxide

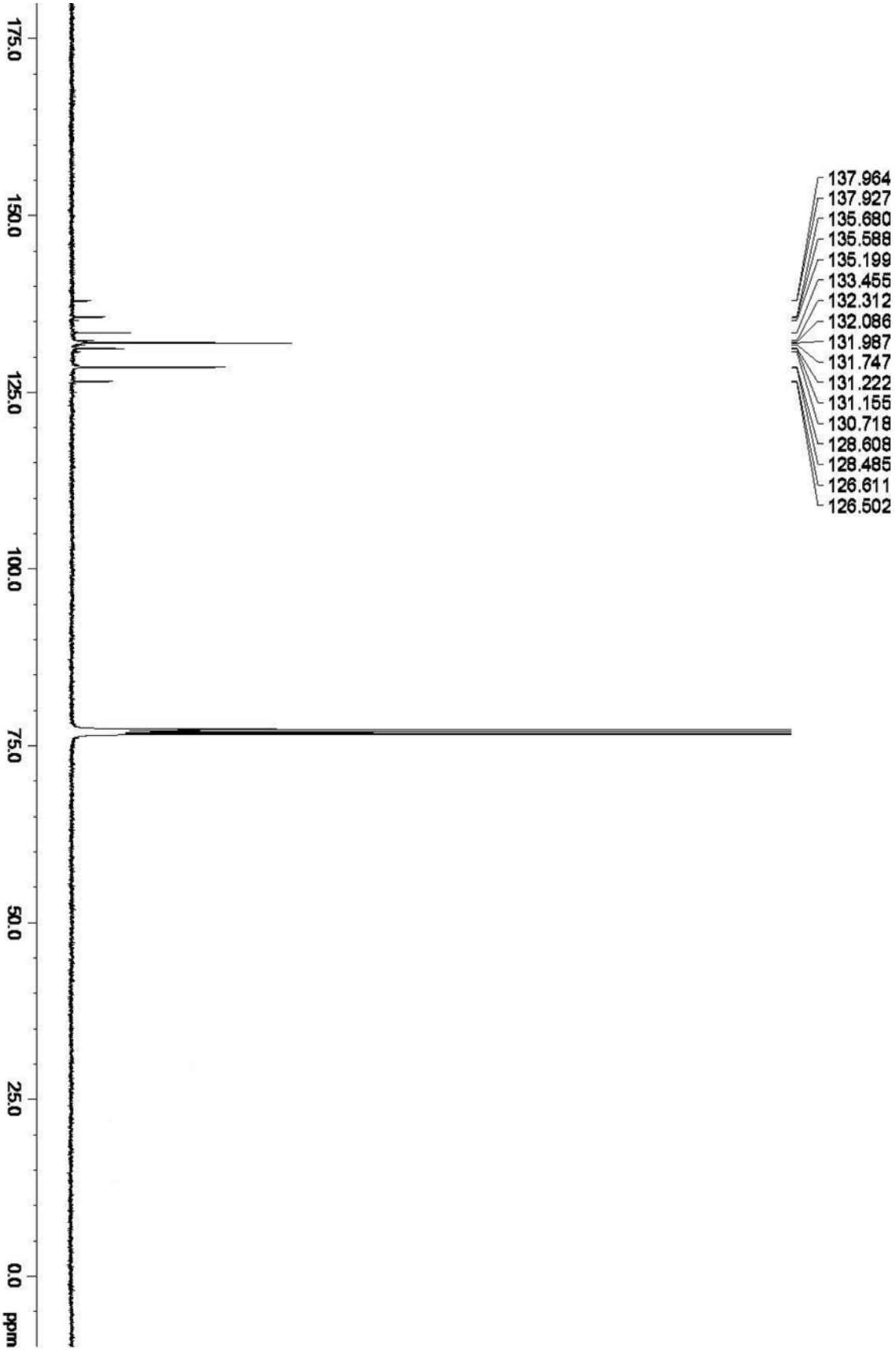


6f: 2-Chlorophenyl Diphenylphosphine oxide

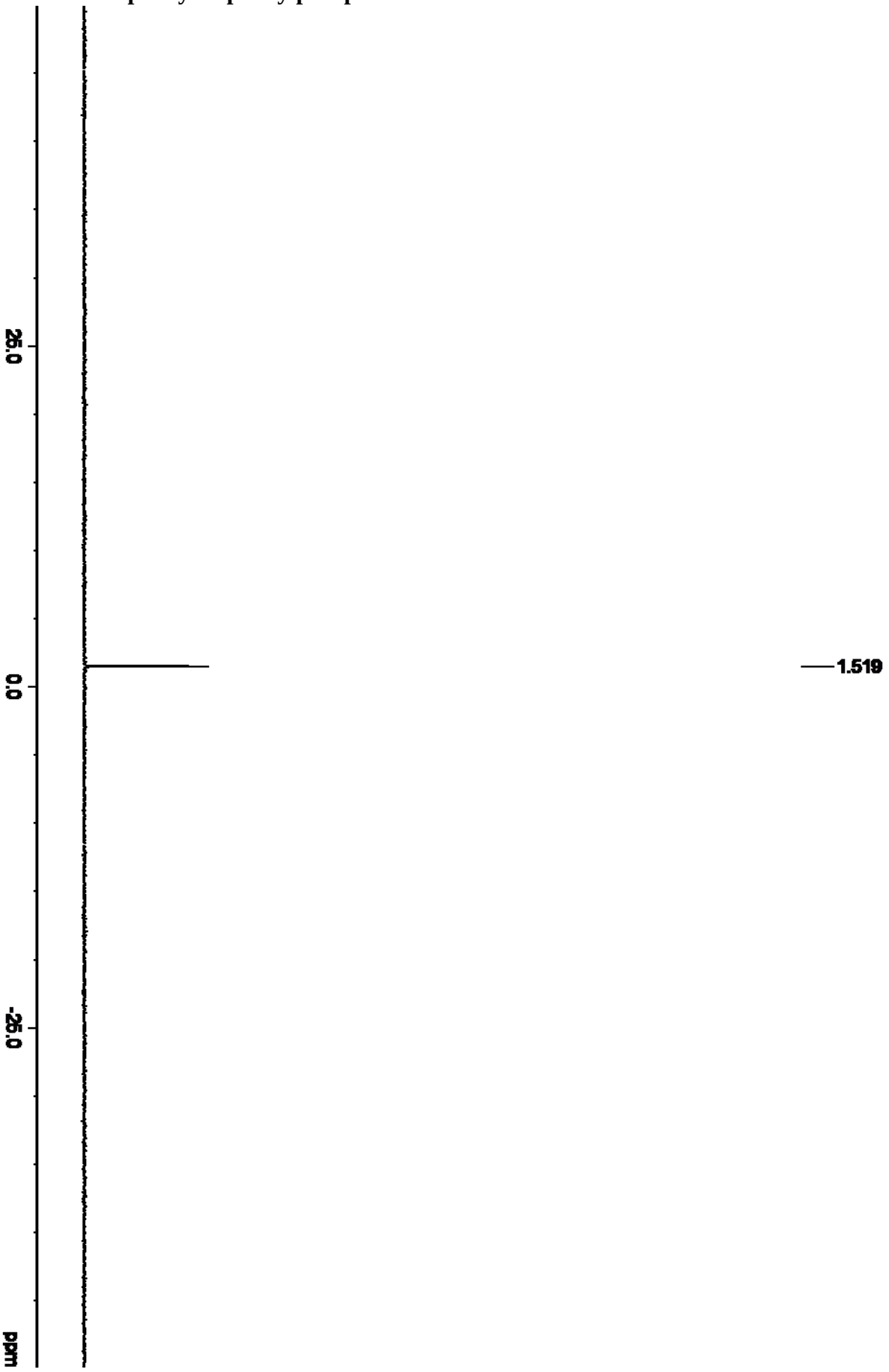




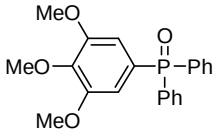
6f: 2-Chlorophenyl Diphenylphosphine oxide

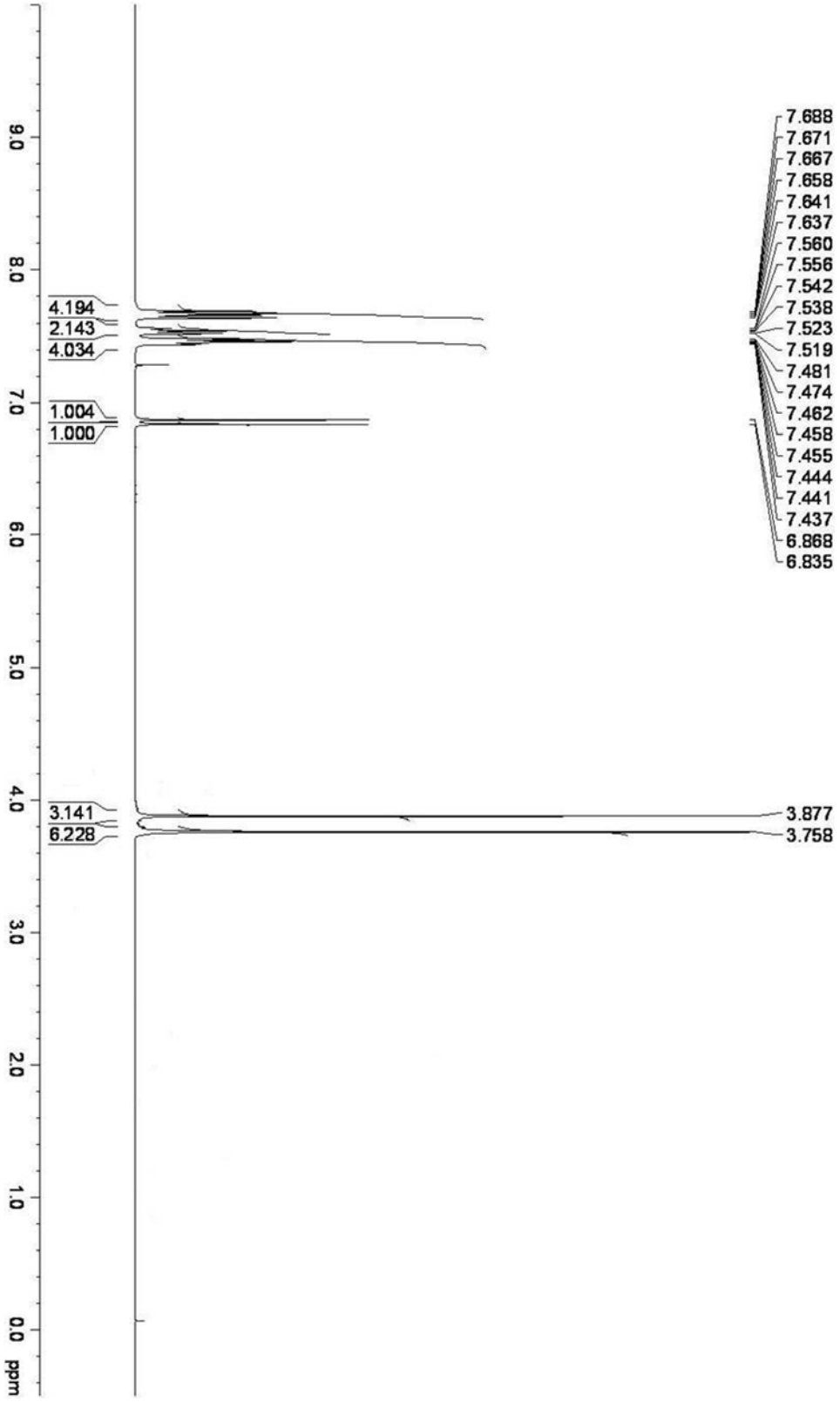


6f: 2-Chlorophenyl Diphenylphosphine oxide

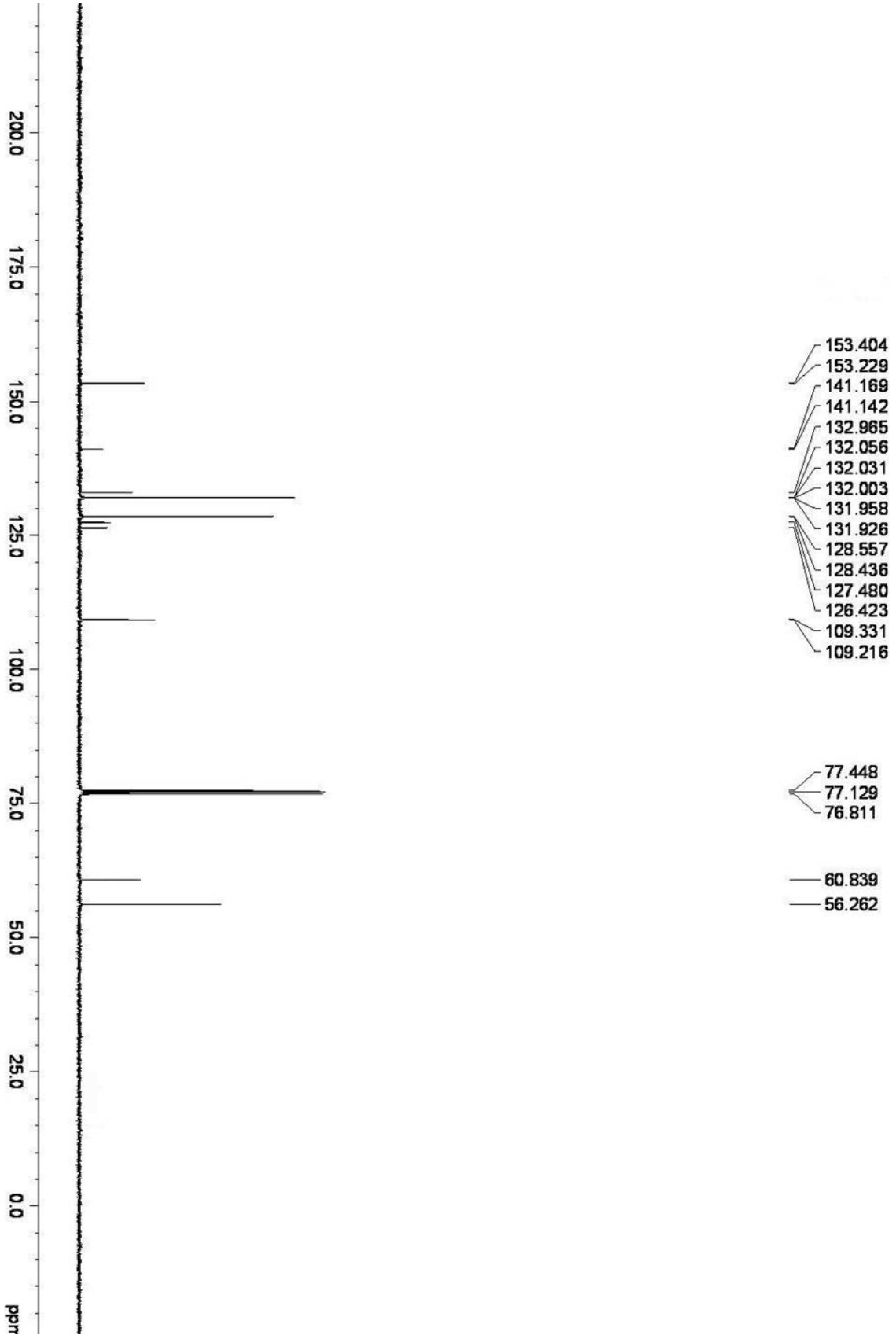


6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide

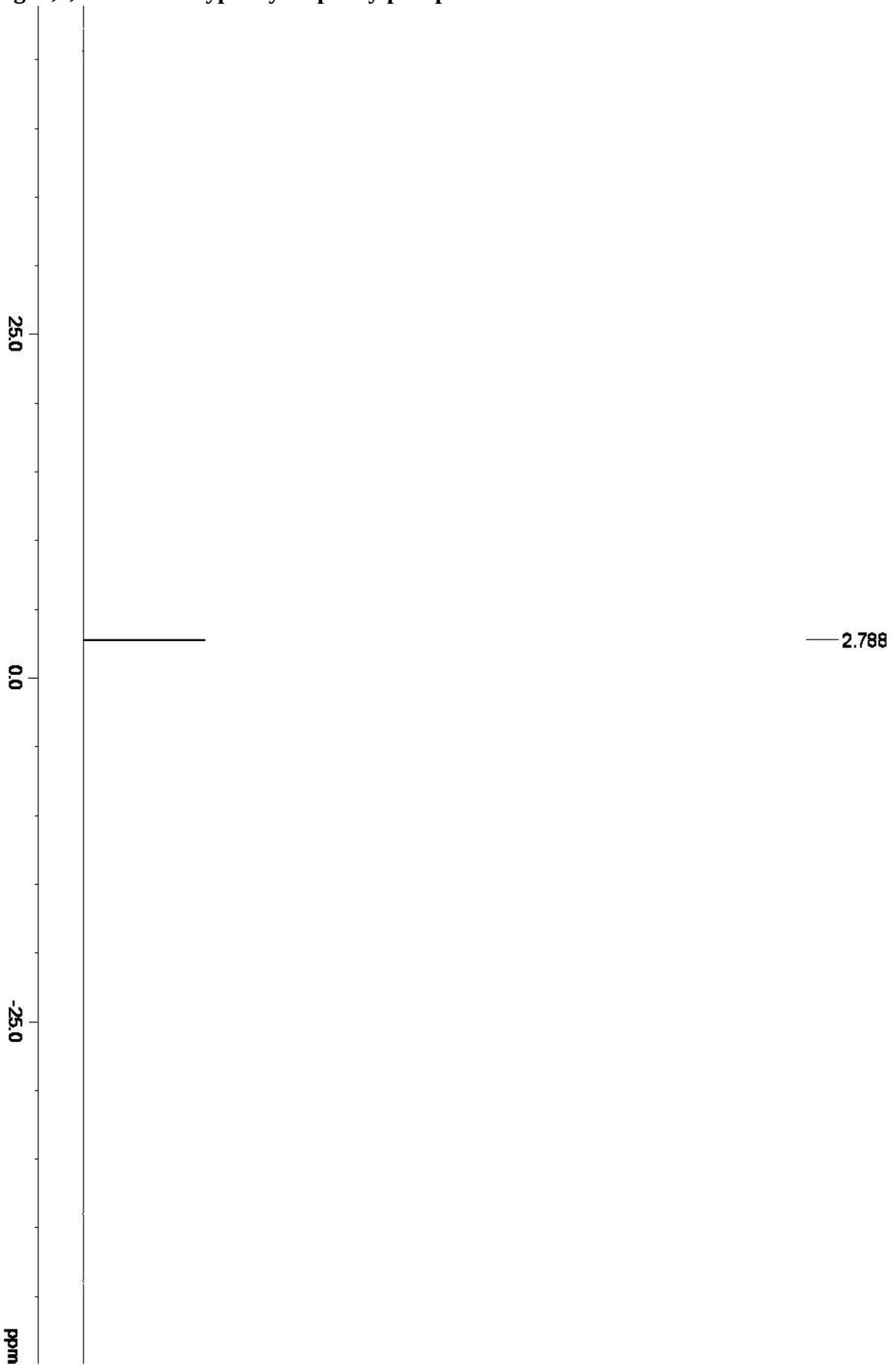




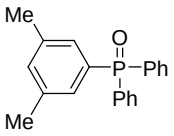
6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide

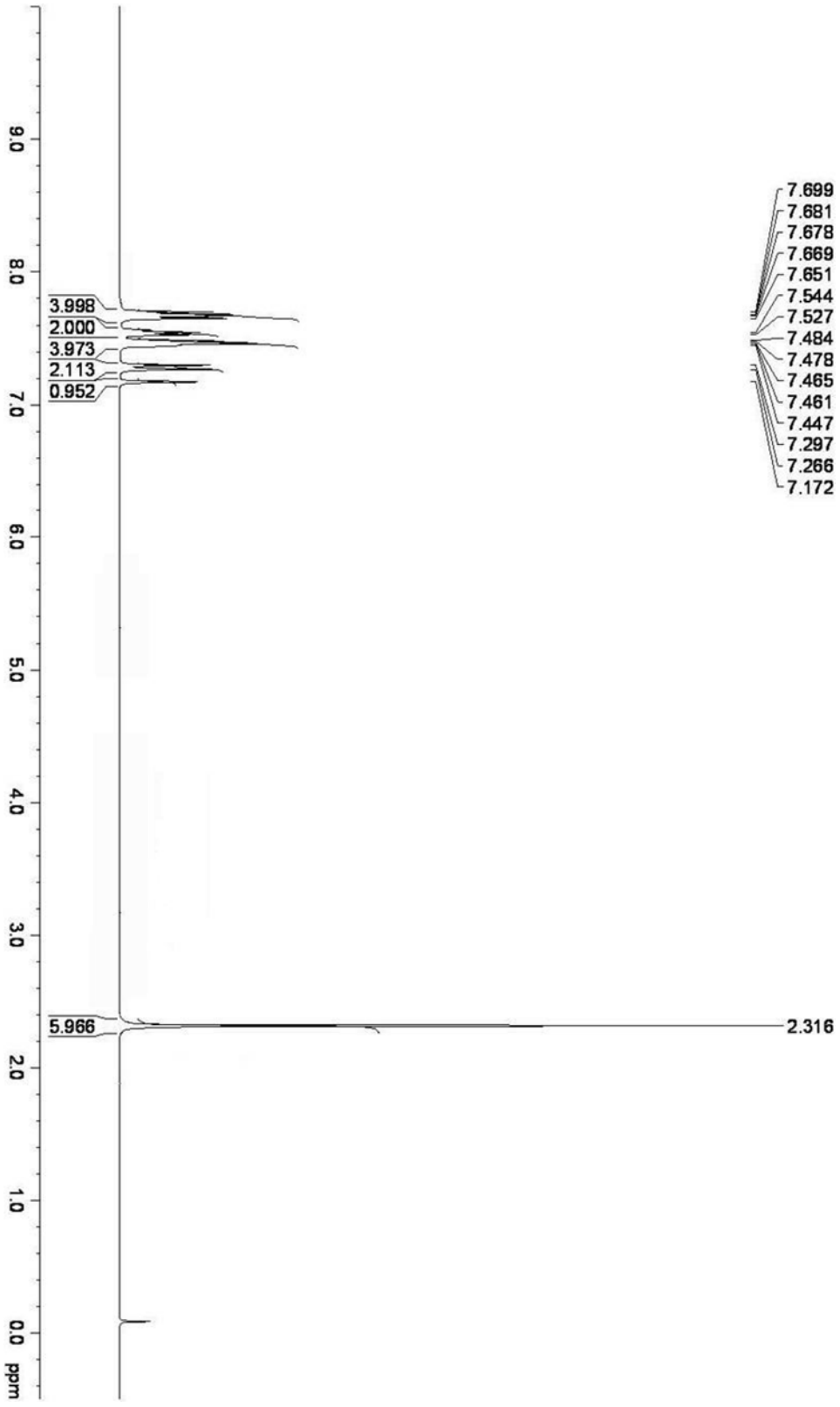


6g: 3,4,5-Trimethoxyphenyl Diphenylphosphine oxide

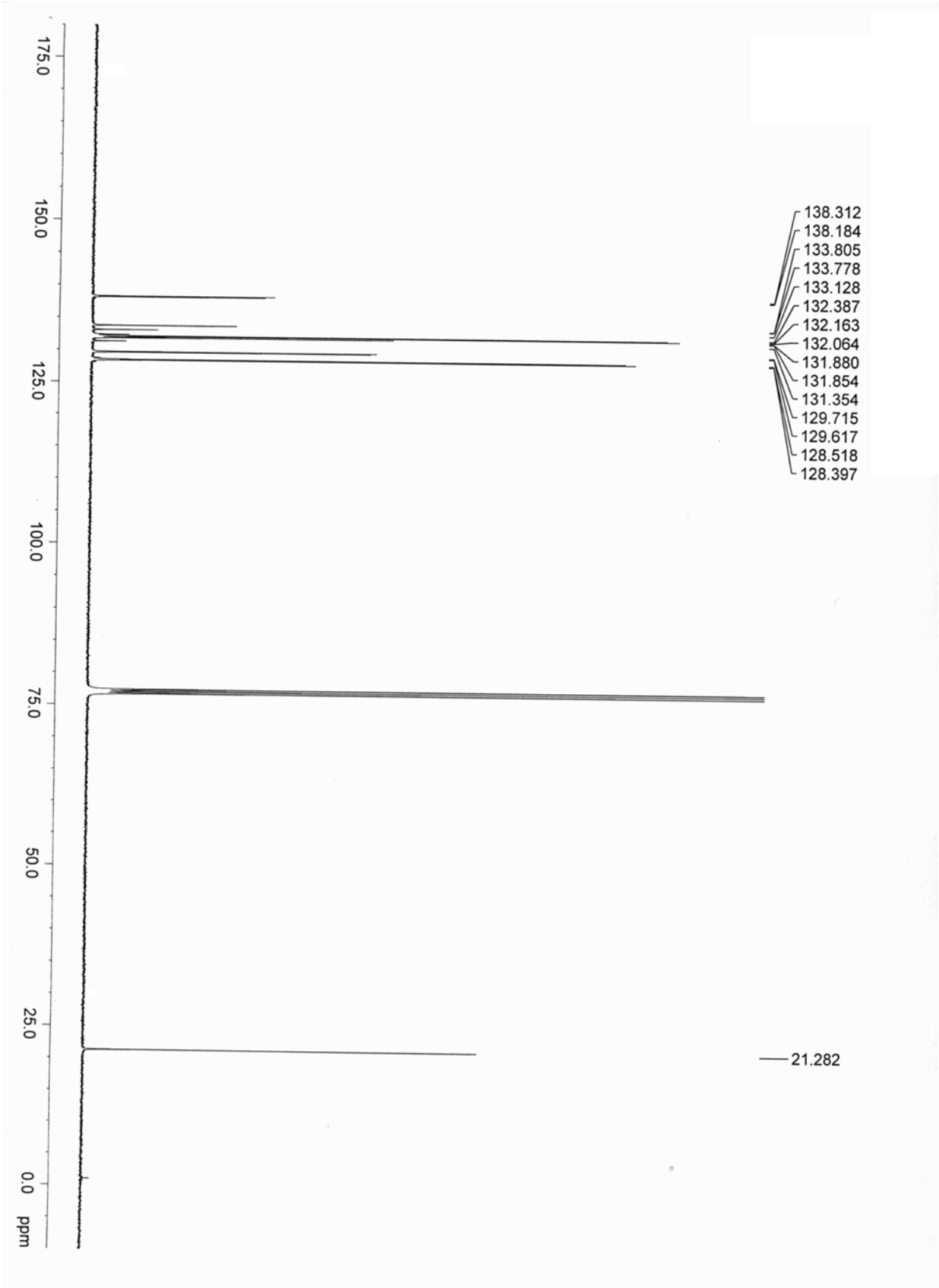


6h: 3,5-Dimethylphenyl Diphenylphosphine oxide





6h: 3,5-Dimethylphenyl Diphenylphosphine oxide



6h: 3,5-Dimethylphenyl Diphenylphosphine oxide