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Supporting Information

An Easy Access of Tertiary Amides from Aldehydes and *N, N*-Dialkylchlorothiophosphoramidates

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1. General details

Aldehydes were obtained from commercial supplier, and used without further purification. Thin-layer chromatography (TLC) was conducted with E-Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized via UV and Iodine. Column chromatographic purification of products was performed on silica gel (60-120 mesh). ^{1}H NMR ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AVANCE II 400 MHz and 600 MHz. Chemical shifts were expressed in parts per millions (**δ**) downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra was obtained in Agilent 5975C GC-MS with DB5-MS (30.0 m x 0.25 mm) and Elemental analysis was performed on Elementar vario MICRO cube CHNS analyser.

2. Experimental procedures

A) Preparation of amides (Entry No. 1-10 & 14, 15):

Thiophosphoramidate (1.2 mmol) and Et_3N (5 mmol) were mixed together. The combined mixture was added in portions (1/10th part) to aldehyde (1 mmol) at 80-90 °C with continuous stirring, over a period of 1.5-2.5 hrs (as indicated in table 1) and each addition was followed by addition of 30 µL of 50% aqueous H_2O_2. Reaction was monitored by GC and TLC. Heating was continued, and after half an hour 50 µL of H_2O_2 and 150 µL of Et_3N were added. At this stage there was a near complete disappearance of aldehyde. Contents were heated further half an hour, then cooled and neutralized with 10% K_2CO_3 solution, extracted with hexane and further purified by column chromatography (Hexane : Ethyl acetate).

B) Preparation of amides (Entry No. 11-13, 16):

Thiophosphoramidate (2 mmol) and Et_3N (10 mmol) were mixed together. The combined mixture was added in portions (1/20th part) to aldehyde (1 mmol) at 80-90 °C with continuous stirring over a period of 4-6.5 hrs (as indicated in table 1) and each addition was followed by addition of 30 µL of 50% aqueous H_2O_2. The reaction was then followed similar to method A except for entry 16. For entry 16, after neutralization with 10% K_2CO_3, pH was adjusted to 2-3 with the help of dilute HCl and contents were extracted with diethyl ether. Ether layer was separated and washed with 10% $NaHCO_3$ solution. Further purification was achieved by column chromatography similar to other amides.

C) Preparation of amides from aliphatic aldehydes (entry 17, 18):

Aldehyde (1 mmol) and triethylamine (5 mmol) were mixed together. To this, thiophosphoramidate (1.2 m mol) was added in portions (1/10thpart) over a period of 3 hrs at 60-70 °C. Each addition of thiophosphoramidate was followed by addition of 30 µL of 50% aqueous H_2O_2. Further reaction monitoring and work up was done similar to method A.

D) Preparation of *N, N*-Dialkylchlorothiophosphoramidates:

$PSCl_3$ (20 mmol) was taken in 10 mL of DCM and dialkyl amine (20 mmol) was added drop wise with constant stirring at 0-5 °C. When the addition of secondary amine is over, triethylamine (22 mmol) was added slowly at the same temperature and reaction mixture was stirred for 30 min.

Temperature of the mixture then gradually increased to 60°C and reaction was continued further for half an hour. Contents were diluted with hexane and filter through a funnel having a bed of silica gel (2 cm). The organic layer was washed with dilute HCl, followed by 5% $NaHCO_3$ solution. After drying over sodium sulfate, solvent is removed under vacuum and pure *N, N*-dialkylchlorothiophosphoramidate is obtained as light yellow viscous liquid. It was used as such further reaction.

3. Spectroscopic characterization data

I) Amides (entry 1-18):

1) ***N, N*-Dibutyl-*p*-chlorobenzamide**: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 4H), 3.47 (br, s, 2H), 3.17 (br, s, 2H), 1.62 (br, s, 2H), 1.47 (br, s, 2H), 1.39 (br, s, 2H), 1.14 (br, s, 2H), 0.96 (br, s, 3H), 0.80 (br, s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.54, 135.77, 135.03, 128.61, 128.02, 48.84, 44.61, 30.84, 29.63, 20.27, 19.78, 13.84, 13.67; EIMS: 267 [M^+](5), 266[M^+-1](4), 224(11), 141(32), 139(100), 111(18), 75(5); Anal. Calcd for $C_{15}H_{22}ClNO$. C, 67.28; H, 8.28; N, 5.23. Found C, 67.37; H, 8.22; N, 5.18.

2) ***N, N*-Dihexyl-*p*-chlorobenzamide**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 4H), 3.46 (s, 2H), 3.16 (s, 2H), 1.63 (s, 2H), 1.47 (s, 2H), 1.34-0.84 (m, 18H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.54, 135.78, 135.06, 128.63, 128.03, 49.10, 44.92, 31.61, 31.29, 28.67, 27.49, 26.75, 26.22, 22.56, 13.98; EIMS: 323[M^+](6), 322[M^+-1](7), 252(17), 182(7), 141(33), 139(100), 111(13); Anal. Calcd for $C_{19}H_{30}ClNO$. C, 70.45; H, 9.34; N, 4.32. Found: C, 70.54; H, 9.27; N, 4.28.

3) **(4-Chloro-phenyl)-(2-methyl-piperidin-1-yl)-methanone**: colourless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.30 (m, 4H), 4.24 (br, 2H), 3.00 (br s, 1H), 1.67 (br s, 4H), 1.54 - 1.46 (br m, 2H), 1.23 (d, 3H, *J*=6.8); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 169.50, 135.26, 131.41, 128.75, 127.99, 30.32, 26.01, 18.84, 16.18; EIMS: 237[M^+](18), 236[M^+-1](20), 222(14), 141(33), 139 (100), 111(25), 75(8); Anal. Calcd for $C_{13}H_{16}ClNO$. C, 65.68; H, 6.78; N, 5.89. Found: C, 65.74; H, 6.81; N, 5.78.

4) ***N, N*-Dihexylbenzamide**: pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.36 (m, 5H), 3.50 (br, s, 2H), 3.20 (br, s, 2H), 1.68 (br, s, 2H), 1.50 (br, s, 2H), 1.37 (br, s, 6H), 1.24 (br, d, 2H, *J*=6 Hz), 1.13 (br, s, 4H), 0.93 (s, 3H), 0.86 (d, 3H, *J*=6.6 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 171.64, 137.42, 128.99, 128.34, 126.45, 49.00, 44.70, 31.67, 31.26, 29.72, 28.62, 27.50, 26.77, 26.19, 22.65, 22.45, 14.07, 13.94; EIMS: 289 [M^+](6), 288[M^+-1](7), 218(14), 148(6), 105(100), 77(17); Anal Calcd for $C_{15}H_{23}NO$. C, 78.84; H, 10.79; N, 4.84. Found: C, 78.75; H, 10.84, N, 4.86.

5) ***N, N*-Dibutyl-*o*-fluorobenzamide**: colourless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2H), 7.17 (dt, 1H, J_1=1.8 Hz, J_2=9.6 Hz), 7.07 (t, 1H, *J*=13.2 Hz), 3.51 (br, s, 2H), 3.13 (t, 2H, *J*=11.4 Hz), 1.68-1.61 (m, 2H), 1.48-1.35 (m, 4H), 1.12 (sext, 2H, *J*=10.6 Hz), 0.97 (t, 3H, *J*=11.4 Hz), 0.76 (t, 3H, *J*=10.8 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 166.57, 157.97 (d, J_{CF}=246.7 Hz), 130.65 (d, J_{CF}=7.69 Hz), 128.65 (d, J_{CF}=3.62 Hz), 125.49 (d, J_{CF}=18.40 Hz), 124.43 (d, J_{CF}=3.47 Hz), 115.74 (d, J_{CF}=21.72 Hz), 48.25, 44.34, 30.52, 29.54, 20.19, 19.69, 13.94, 13.55. EIMS: 251 [M^+](4), 208(14), 166(6),

123(100), 95(12), 75(2); Anal. Calcd for $C_{15}H_{22}FNO$. C, 71.68; H, 8.82; N, 5.57. Found: C, 71.79; H, 8.77; N, 5.50.

6) ***N, N*-Dibutyl-*o*-bromobenzamide**: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J*=5.6 Hz), 7.38-7.35 (m, 1H), 7.27-7.23 (m, 2H), 3.82-3.80 (m, 1H), 3.27-3.23 (m, 1H), 3.11-3.07 (m, 2H), 1.73-1.67 (m, 2H), 1.57-1.40 (m, 4H), 1.17-1.13 (m, 2H), 1.00 (t, 3H, *J*=4.8 Hz), 0.79 (t, 3H, *J*=5.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.85, 138.90, 132.71, 129.89, 127.86, 127.46, 119.27, 48.10, 44.34, 30.51, 29.27, 20.42, 19.80, 13.95, 13.59; EIMS: 312 [M^++2](7), 310 [M^+](7), 270(10), 268(10), 232(28), 185(96), 183(100), 157(15), 155(16), 105(11), 77(8); Anal. Calcd for $C_{15}H_{22}BrNO$. C, 57.70; H, 7.10; N, 4.49. Found: C, 57.56, H, 7.17; N, 4.54.

7) ***N, N*-Dibutyl-*p*-nitrobenzamide**: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, 2H, *J*=8.4 Hz), 7.54 (d, 2H, *J*=9H), 3.52 (t, 2H, *J*=7.2 Hz), 3.15 (t, 2H, *J*=7.2 Hz), 1.67 (t, 2H, *J*=7.2 Hz), 1.50 (t, 2H, *J*=7.2 Hz), 1.44-1.41 (m, 2H), 1.17-1.13 (m, 2H), 1.00 (t, 3H, *J*=7.2 Hz), 0.81 (t, 3H, *J*=7.2 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 169.27, 147.92, 143.52, 127.51, 123.82, 48.73, 44.62, 30.76, 29.55, 20.27, 19.73, 13.92, 13.61; EIMS: 278 [M^+](3), 277(4), 235(26), 193(9), 150(100), 120(11), 104(21), 76(8); Anal. Calcd for $C_{15}H_{22}N_2O_3$. C, 64.73; H, 7.97; N, 10.06. Found: C, 64.86; H, 7.91; N, 9.97.

8) ***N, N*-Dibutyl-*p*-ethylbenzamide**: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4H), 3.50 (br, s, 2H), 3.23 (br, s, 2H), 2.69 (q, 2H, *J*=7.2 Hz), 1.65 (s, 2H), 1.51 (br, s, 2H), 1.42 (br, s, 2H), 1.27-1.25 (m, 3H), 1.17 (br, s, 2H), 1.00 (br, s, 3H), 0.82 (br, s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.87, 145.29, 134.68, 127.76, 126.60, 48.82, 44.46, 30.85, 29.68, 28.92, 20.34, 19.78, 15.45, 13.97, 13.67; EIMS: 261 [M^+](18), 260(21), 218(18), 134(20), 133(100), 105(15), 79(12); Anal. Calcd for $C_{17}H_{27}NO$. C, 78.11; H, 10.41; N, 5.36. Found: C, 78.24; H, 10.34; 5.29.

9) ***N, N*-Diethyl-2-methyl-benzamide:** dark yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.14 (m, 4H), 3.75-3.35 (br, m, 2H), 3.12 (q, 2H), 2.28 (s, 3H), 1.26 (t, 3H, *J*=7.2 Hz), 1.02 (t, 3H, *J*=7.2 Hz) ; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 170.72, 137.05, 133.70, 130.16, 128.39, 125.64, 125.30, 42.47, 38.55, 18.66, 13.87, 12.76; EIMS: 191 [M^+](33), 190 [M^+-1](58), 176(49), 119(100), 118(24), 91(76), 65(24); Anal. Calcd for $C_{12}H_{17}NO$. C, 75.35; H, 8.96; N, 7.32. Found: C, 75.20, H, 9.02; N, 7.39.

10) **2-Methyl-*N, N*-dipropyl-benzamide**: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.13 (m, 4H), 3.67 (br, s, 1H), 3.28 (br, s, 1H), 3.02 (s, 2H), 2.28 (s, 3H), 1.70 (sext, 2H), 1.51-1.44 (m, 2H), 0.98 (t, 3H, *J*=7.2 Hz), 0.71 (t, 3H, 7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.31, 137.24, 133.85, 130.25, 128.46, 125.78, 125.68, 49.95, 45.87, 21.67, 20.67, 18.93, 11.56, 11.10; EIMS: 219[M^++1](5), 218(8), 204(18), 120(9), 119(100), 91(25), 65(6), Anal. Calcd for $C_{14}H_{21}NO$. C, 76.67; H, 9.65; N, 6.39. Found: C, 76.82; H, 9.59; N, 6.32.

11) ***N, N*-Dipropyl-*p*-methoxybenzamide**: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, 2H, *J*=8.4 Hz), 6.89 (d, 2H, *J*=8.4 Hz), 3.82 (s, 3H), 3.41 (br, s, 2H), 3.22 (br, s, 2H), 1.61 (br, s, 4H), 0.95 (br, s, 3H), 0.78 (br, s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 171.71, 160.19, 129.69, 128.35, 113.63, 55.30, 50.82, 46.54, 21.75, 20.86, 11.25; EIMS: 235(7), 234(10), 164(5), 136(9), 135(100), 92(7), 77(9) Anal. Calcd for $C_{14}H_{21}NO_2$. C, 71.46; H, 8.99; N, 5.95. Found: C, 71.33; H, 9.08; N, 5.97.

12) ***N, N*-Dibutylnaphthalene -1-carboxamide**: colourless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.40 (m, 7H), 3.83 (br, s, 1H), 3.47 (br, s, 1H), 3.07-3.02 (m, 2H), 1.82-1.79 (m, 2H), 1.53-1.49 (m, 2H), 1.46-1.43 (m, 2H), 1.08-1.04 (m, 5H), 0.67 (t, 3H, *J*=7.2 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 170.64, 135.24, 133.45, 129.66, 128.74, 128.34, 126.83, 126.31, 125.07, 124.88, 123.50, 48.50, 44.40,

30.81, 29.75, 20.50, 19.66, 14.01, 13.51; EIMS: 283 [M^+](48), 282 [M^+-1] (32), 240(27), 184(16), 155 (100), 127(87); Anal. Calcd for $C_{19}H_{25}NO$. C, 80.52, H, 8.89; N, 4.94. Found: C, 80.40; H, 8.94; N, 5.00.

13) ***N, N*-Dibutylnaphthalene -2-carboxamide**: colourless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.47 (m, 7H), 3.57 (br, s, 2H), 3.27 (br, s, 2H), 1.72-1.70 (d, 2H), 1.54 (br, s, 2H), 1.47 (br, s, 2H), 1.15 (br, s, 2H), 1.03 (br, s, 3H), 0.79 (br, s, 3H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 171.65, 134.73, 133.37, 132.79, 128.31, 128.21, 127.81, 126.74, 126.56, 125.97, 124.17, 48.90, 44.54, 30.90, 29.72, 20.38, 19.77, 14.00, 13.69; EIMS: 283 [M^+](20), 282(14), 240(12), 184(8), 156(14), 155(100), 127(49); Anal. Calcd for $C_{19}H_{25}NO$. C, 80.52, H, 8.89; N, 4.94. Found: C, 80.60; H, 8.85; N, 4.88.

14) ***N, N*-Dibutyl-thiophene-2-carboxamide**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.04 (m, 3H), 3.48 (t, 4H, *J*=7.6 Hz), 1.69-1.61 (m, 4H), 1.36-1.33 (m, 4H), 0.95 (t, 6H, *J*=6.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 164.12, 138.34, 128.22, 128.15, 126.67, 29.73, 20.14, 13.89; EIMS: 239 [M^+](4), 206(15), 196(13), 111(100), 83(5); Anal. Calcd for $C_{13}H_{21}NOS$. C, 65.23; H, 8.84, N, 5.85, S, 13.40. Found: C, 65.36; H, 8.76, N, 5.77; S, 13.42

15) ***N, N*-Dipropyl-isonicotinamide**: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, 2H, *J*=4.4 Hz), 7.25 (d, 2H, *J*=4.8 Hz), 3.46 (t, 2H, *J*=7.6 Hz), 3.10 (t, 2H, *J*=7.6 Hz), 1.67 (sext, 2H, *J*=7.6 Hz), 1.53 (sext, 2H, *J*=7.6 Hz), 0.98 (t, 3H, *J*=7.2 Hz), 0.756 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 169.14, 150.19, 144.94, 120.90, 50.50, 46.34, 29.69, 21.94, 20.69, 11.38, 10.98; EIMS: 206[M^+](14), 205[M^+-1] (14), 177(21), 135(7), 107(8), 106(100), 78(27), 51(8); Anal. Calcd for $C_{12}H_{18}N_2O$. C, 69.87; H, 8.80; N, 13.58. Found: C, 69.73; H, 8.86; N, 13.65

16) ***N, N*-Dibutyl-m-hydroxybenzamide:** colourless oil; 1H NMR (400 MHz, CDCl3) δ 7.13 (t, 1H, *J*=7.6 Hz)**,** 6.84 (s, 1H), 6.77-6.73 (m, 2H), 3.48 (t, 2H, J=7.6 Hz), 3.19 (t, 2H, J=7.6), 1.65-1.59 (m, 2H), 1.50-1.36 (m, 4H), 1.15-1.09 (m, 2H), 0.971 (t, 3H, J=7.2 Hz), 0.780 (t, 3H, J=7.2 Hz)**;** ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 172.54, 157.07, 137.10, 129.37, 117.09, 114.34, 48.98, 44.72, 30.69, 29.55, 20.28, 19.74, 13.94, 13.61; EIMS: 249(12), 206 (11), 122 (8), 121 (100), 93 (13); Anal. Calcd for $C_{15}H_{23}NO_2$. C, 72.25; H, 9.30; N, 5.62. Found: C, 72.14; H, 9.32; N, 5.63

17) ***N,N*-Diethyl dodecanamide:** light yellow oil; ^{1}H NMR (400 MHz, CDCl3) δ 3.36 (q, 2H, *J*=7.2 Hz), 3.30 (q, 2H, *J*=7.2 Hz), 2.28 (t, 2H, *J*=7.6 Hz), 1.63 (br m, 2H), 1.30-1.25 (m, 16H), 1.17 (t, 3H, *J*=7.2 Hz), 1.10 (t, 3H, *J*=7.2 Hz), 0.87 (t, 3H, *J*=6.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 172.38, 41.98, 40.03, 33.21, 31.93, 29.65, 29.64, 29.57, 29.55, 29.52, 29.35, 25.55, 22.70, 14.43, 14.12, 13.14; EIMS: Anal. Calcd for $C_{16}H_{33}NO$. C, 72.23; H, 13.02; N, 5.48; O, 6.26. Found: C, 72.37; H, 13.14; N, 5.45; O, 6.27

18) ***N,N*-Dibutyl dodecanamide:** light yellow oil; ^{1}H NMR (400 MHz, CDCl3) δ 3.29 (t, 2H, *J*=7.6 Hz), 3.20 (t, 2H, *J*=7.6 Hz), 2.27 (t, 2H, *J*=7.6 Hz), 1.64-1.61 (m, 4H), 1.57-1.46 (m, 4H), 1.37-1.25 (m, 18H), 0.96-0.86 (m, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 173.28, 47.81, 45.66, 33.20, 31.92, 31.28, 29.93, 29.64, 29.62, 29.54, 29.49, 29.34, 29.28, 29.13, 25.58, 24.85, 22.69, 20.27, 20.12, 14.11, 13.90, 13.83; EIMS: Anal. Calcd for $C_{20}H_{41}NO$. C, 77.10; H, 13.26; N, 4.50; O, 5.14. Found: C, 77.24; H, 13.29; N, 4.48; O, 5.15.

II) *N, N*-Dialkylchlorothiophosphoramidates:

1) ***N, N*-Diethylchlorothiophosphoramidates**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49 (dq, 4H, J_{PH}=21.2 Hz, J=8.0 Hz), 1.24 (t, 6H, J=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 42.22 (d, J_{PC}=3.7 Hz), 13.30 (d, J_{PC}=3.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.40. EIMS: 174(58), 172(100), 170(37), 162(22), 133(18), 56(53).

2) ***N, N*-Dipropylchlorothiophosphoramidates**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (dt, 4H, J_{PH}=18.4 Hz, J_{HH}=7.6 Hz), 1.66 (sext, 4H, J=7.6 Hz), 0.94 (t, 6H, J=7.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 49.29 (d, J_{PC}= 2.6 Hz), 20.92 (d, J_{PC}=3.7 Hz), 11.14; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.87; EIMS: 206(27), 204(50), 202(61), 200(100), 198(24), 164(59), 162(84), 70(62).

3) ***N, N*-Dibutylchlorothiophosphoramidates**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43-3.34 (m, 4H), 1.61 (quint, 4H, J=7.6 Hz), 1.35 (sext, 4H, J=7.6 Hz), 0.96 (t, 6H, J=7.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 47.35 (d, J_{PC}=2.8 Hz), 29.6 (d, J_{PC}=3.6 Hz), 19.83, 13.67; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.56; EIMS: 230(64), 228(100), 178(54), 176(79), 164(29), 162(42), 99(20), 84(81), 57(27).

4) ***N, N*-Dihexylchlorothiophosphoramidates**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.41-3.33 (m, 4H), 1.62 (t, 4H, J=6.8 Hz), 1.31 (s, 12H), 0.89 (t, 6H, J=6.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 47.75 (d, J_{PC}=2.7 Hz), 31.44, 27.62 (d, J_{PC}=3.6 Hz), 26.38, 22.56, 13.98; ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.55; EIMS: 284(100), 286(66), 178(56), 176(79), 162(22), 127(20), 112(88).

5) **(2-methylpiperidin-1-yl)phosphonothioic dichloride**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60-4.53 (m, 1H), 3.99-3.91 (m, 1H), 3.12-3.01 (m, 1H), 1.82-1.48 (m, 6H), 1.29 (d, 3H, J=6.8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 50.28, 41.57, 30.26 (d, J_{PC}=6.1 Hz), 25.60 (d, J_{PC}=4.7 Hz), 18.33 (d, J_{PC}=1.0 Hz), 15.88 (d, J_{PC}=3.0 Hz); ^{31}P NMR (162 MHz, CDCl3) δ 59.44**;** EIMS: 200(61), 198(100), 97(83), 83(23), 69(30).

4. Copies of ^{1}H NMR and ^{13}C NMR

1. ^{1}H NMR spectra of *N*, *N*-Dibutyl-*p*-chlorobenzamide

2. ^{13}C NMR spectra of *N*, *N*-Dibutyl-*p*-chlorobenzamide

3. ^{1}H NMR spectra of *N*, *N*-Dihexyl-*p*-chlorobenzamide

4. ^{13}C NMR spectra of *N*, *N*-Dihexyl-*p*-chlorobenzamide

5. ^{1}H NMR spectra of (4-Chloro-phenyl)-(2-methyl-piperidin-1-yl)-methanone

6. ^{13}C NMR of (4-Chloro-phenyl)-(2-methyl-piperidin-1-yl)-methanone

7. ^{1}H NMR spectra of *N*, *N*-Dihexylbenzamide

8. ^{13}C NMR spectra of *N*, *N*-Dihexylbenzamide

9. ^{1}H NMR spectra of *N*, *N*-Dibutyl-*o*-fluorobenzamide

10. ^{13}C NMR spectra of *N*, *N*-Dibutyl-*o*-fluorobenzamide

11. ^{1}H NMR spectra of *N*, *N*-Dibutyl-*o*-bromobenzamide

12. ^{13}C NMR spectra of *N*, *N*-Dibutyl-*o*-bromobenzamide

13. ^{1}H NMR spectra of *N*, *N*-Dibutyl-*p*-nitrobenzamide

14. ^{13}C NMR spectra of *N*, *N*-Dibutyl-*p*-nitrobenzamide

15. ^{1}H NMR spectra of *N*, *N*-Dibutyl-*p*-ethylbenzamide

16. ^{13}C NMR spectra of *N*, *N*-Dibutyl-*p*-ethylbenzamide

17. ^{1}H NMR spectra of *N*, *N*-Diethyl-2-methyl-benzamide

18. ^{13}C NMR spectra of *N*, *N*-Diethyl-2-methyl-benzamide

19. ^{1}H spectra of 2-Methyl-*N, N*-dipropyl-benzamide

20. ^{13}C NMR spectra of 2-Methyl-*N, N*-dipropyl-benzamide

21. ^{1}H NMR spectra of *N*, *N*-Dipropyl-*p*-methoxybenzamide

22. ^{13}C NMR of *N*, *N*-Dipropyl-*p*-methoxybenzamide

23. ^{1}H NMR spectra of *N*, *N*-Dibutylnaphthalene -1-carboxamide

24. ^{13}C NMR of *N*, *N*-Dibutylnaphthalene -1-carboxamide

25. ^{1}H NMR of *N*, *N*-Dibutylnaphthalene -2-carboxamide

26. ^{13}C NMR of *N*, *N*-Dibutylnaphthalene -2-carboxamide

27. ^{1}H NMR spectra of *N*, *N*-Dibutyl-thiophene-2-carboxamide

28. ^{13}C NMR spectra of *N*, *N*-Dibutyl-thiophene-2-carboxamide

29. ^{1}H NMR spectra of *N, N*-Dipropyl-isonicotinamide

30. ^{13}C NMR spectra of *N, N*-Dipropyl-isonicotinamide

31. ^{1}H NMR spectra of *N*, *N*-Dibuty-m-hydroxybenzamide

32. ^{13}C NMR spectra of *N*, *N*-Dibuty-m-hydroxybenzamide

33. ^{1}H NMR spectra of *N,N*-Diethyl dodecanamide

34. ^{13}C NMR spectra of *N,N*-Diethyl dodecanamide

35. ^{1}H NMR spectra of *N,N*-butyl dodecanamide

36. ^{13}C NMR spectra of *N,N*-butyl dodecanamide

37. ^{1}H NMR of Diethylphosphoramidothioic dichloride

38. ^{13}C NMR of Diethylphosphoramidothioic dichloride

39. ^{31}P NMR spectra of Diethylphosphoramidothioic dichloride

40. ^{1}H NMR spectra of Dipropylphosphoramidothioic dichloride

41. ^{13}C NMR of Dipropylphosphoramidothioic dichloride

42. ^{31}P NMR spectra of Dipropylphosphoramidothioic dichloride

43. ^{1}H NMR spectra of Dibutylphosphoramidothioic dichloride

44. ^{13}C NMR spectra of Dibutylphosphoramidothioic dichloride

45. ^{31}P NMR spectra of Dibutylphosphoramidothioic dichloride

46. ^{1}H NMR spectra of Dihexylphosphoramidothioic dichloride

47. ^{13}C NMR spectra of Dihexylphosphoramidothioic dichloride

48. ^{31}P NMR spectra of Dihexylphosphoramidothioic dichloride

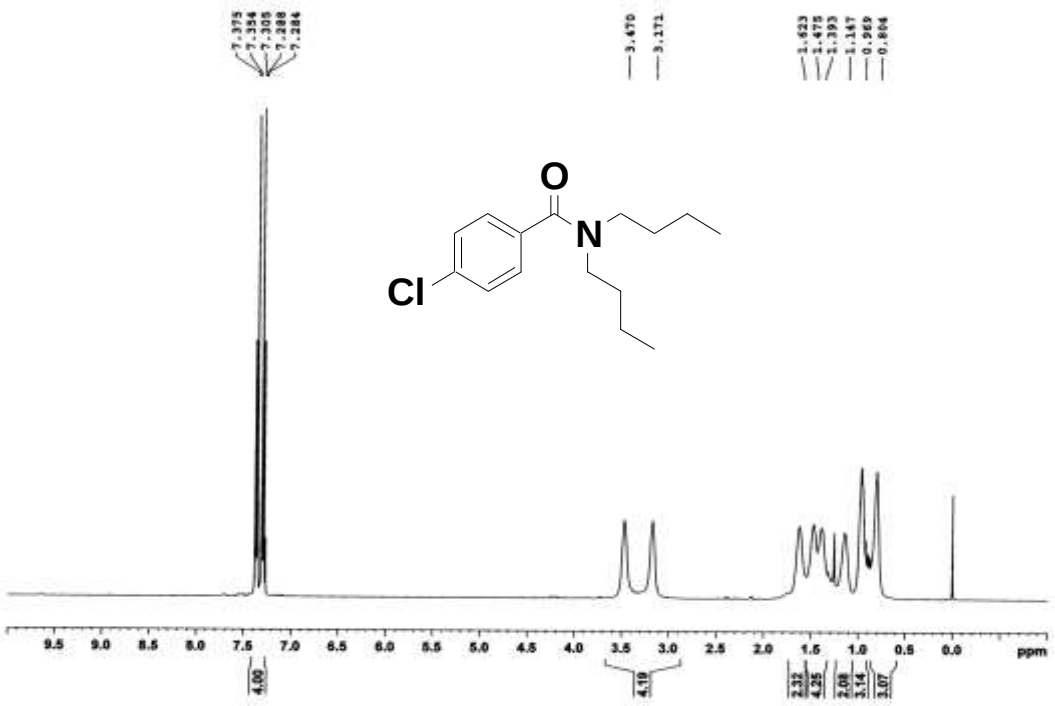
49. ^{1}H NMR spectra of (2-methylpiperidin-1-yl)phosphonothioic dichloride

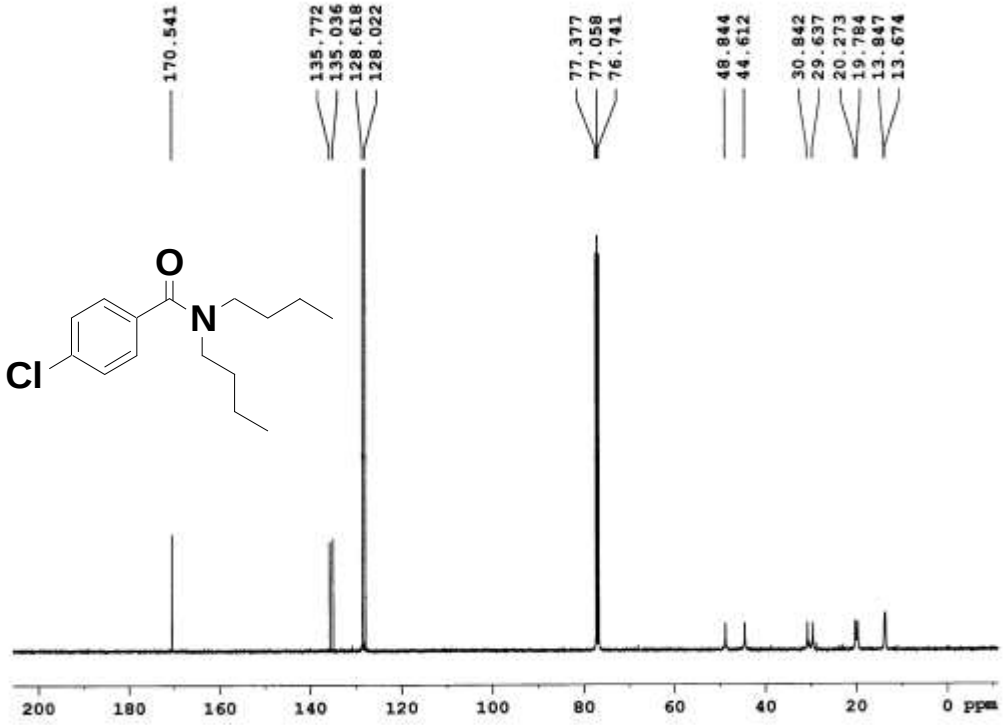
50. ^{13}C NMR spectra of (2-methylpiperidin-1-yl)phosphonothioic dichloride

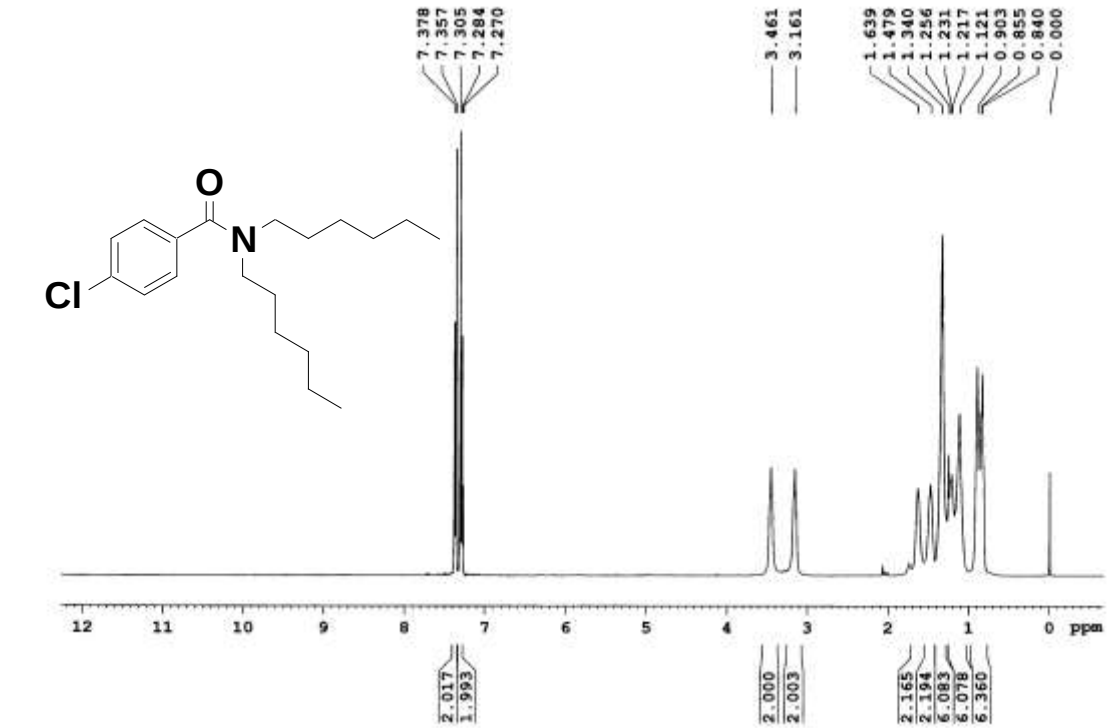
51. ^{31}P NMR spectra of (2-methylpiperidin-1-yl)phosphonothioic dichloride

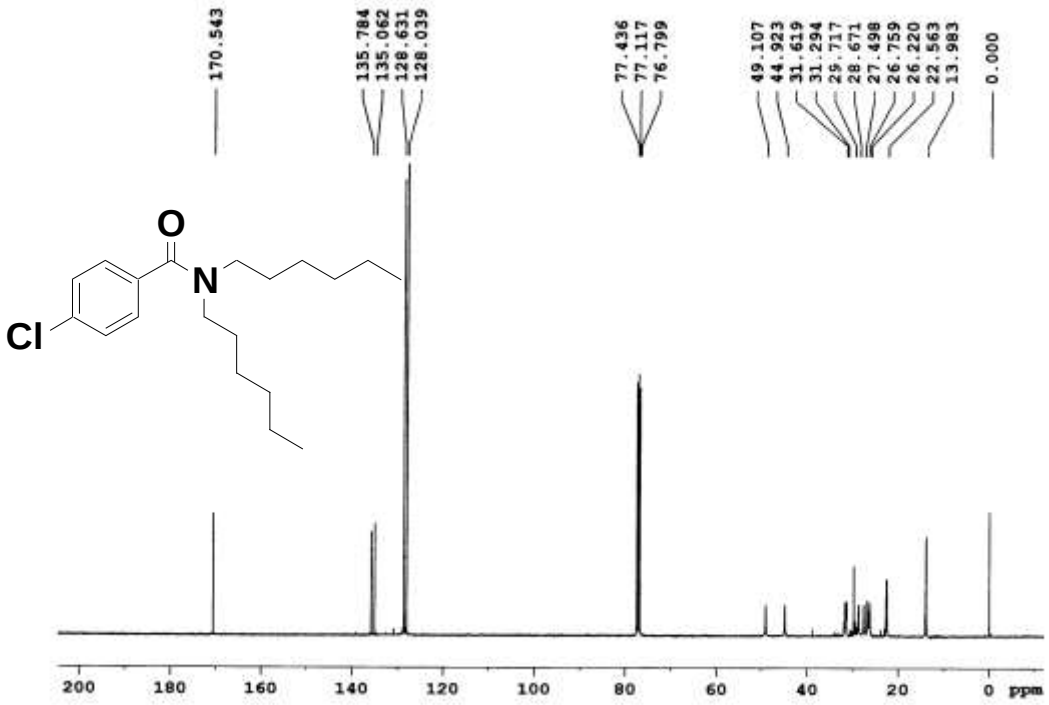
52. ^{31}P NMR spectra of *N*, *N*-dibutylchlorothiophosphoramidate/4-chlorobenzoic acid reaction

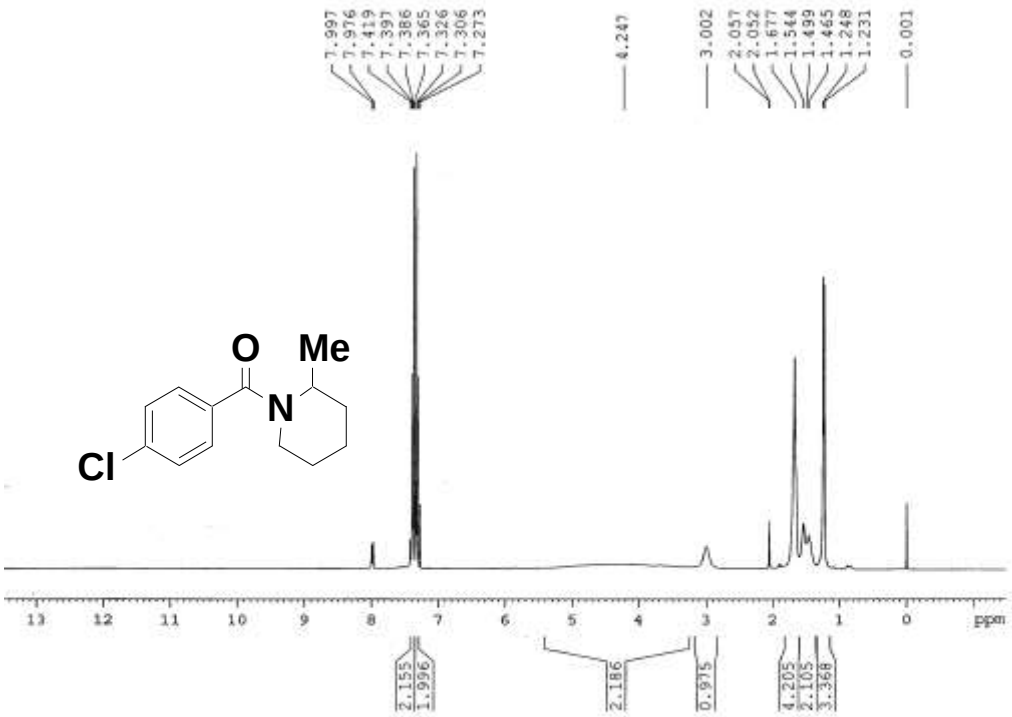
53. ^{31}P NMR spectra of N, N-dibutylchlorothiophosphoramidate/4-chlorobenzaldehyde reaction

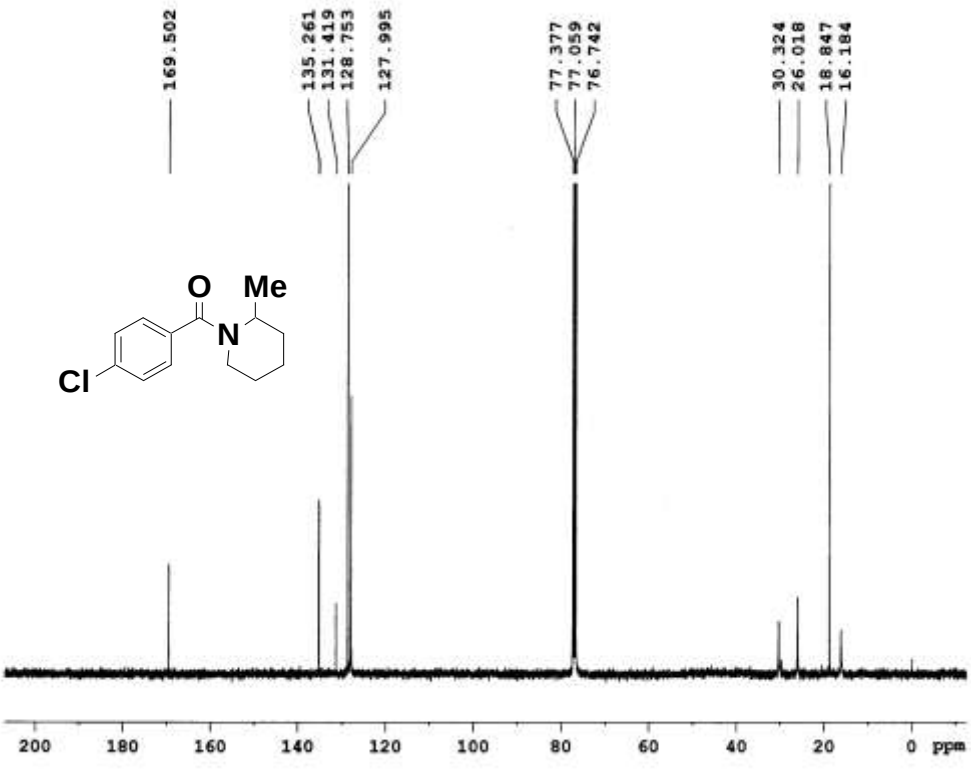


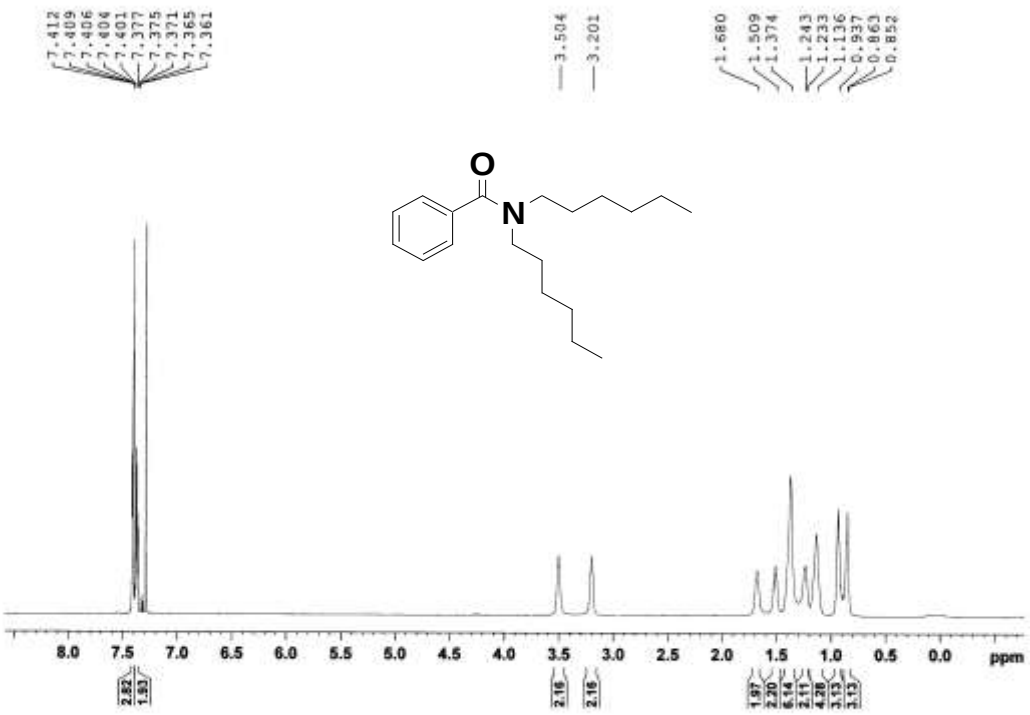


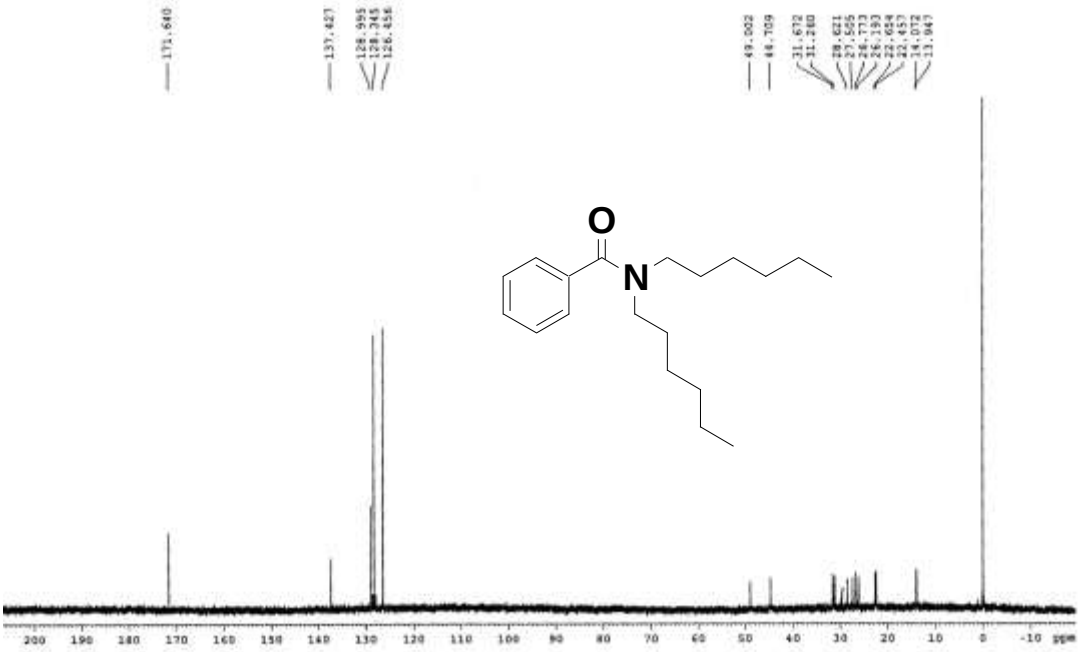


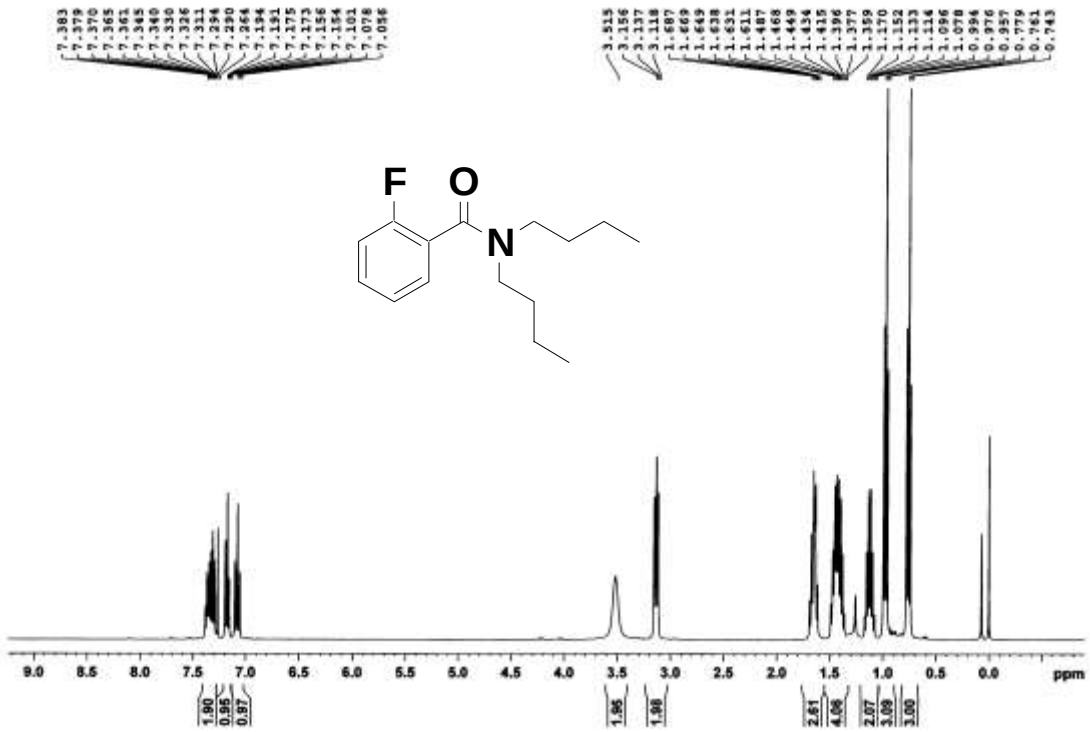


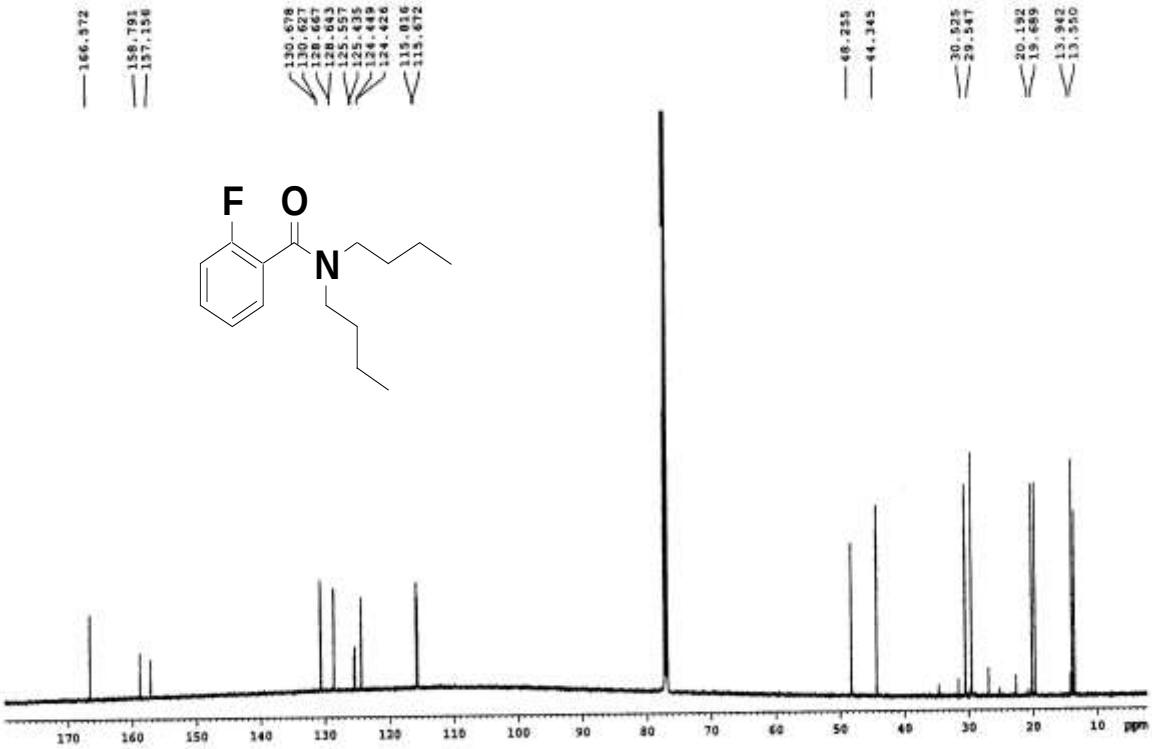


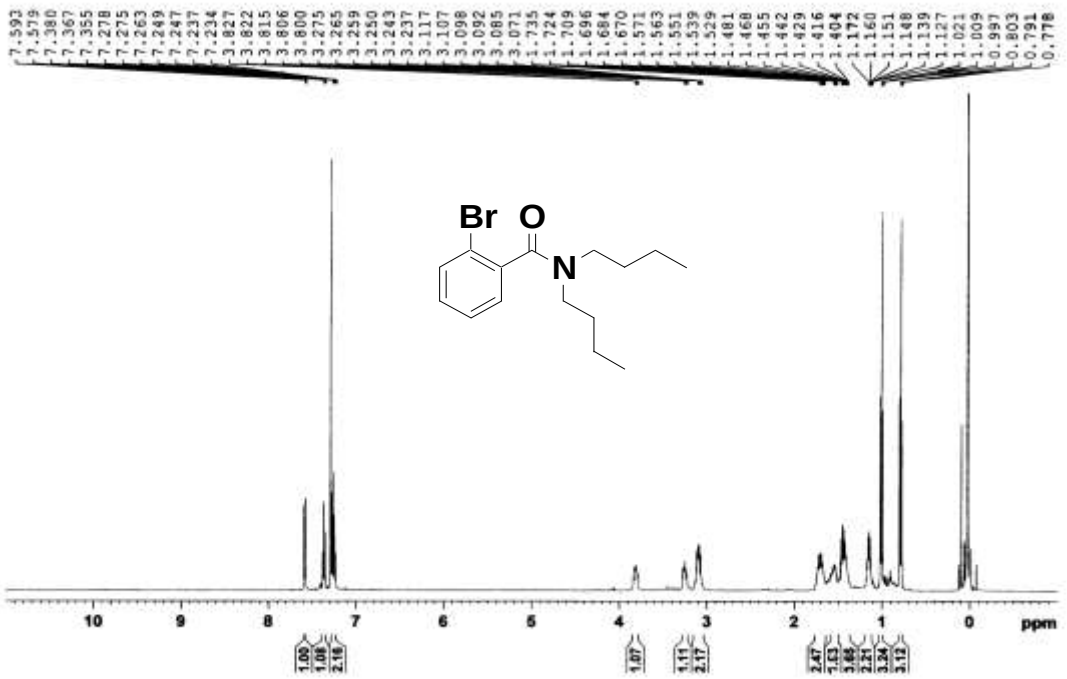


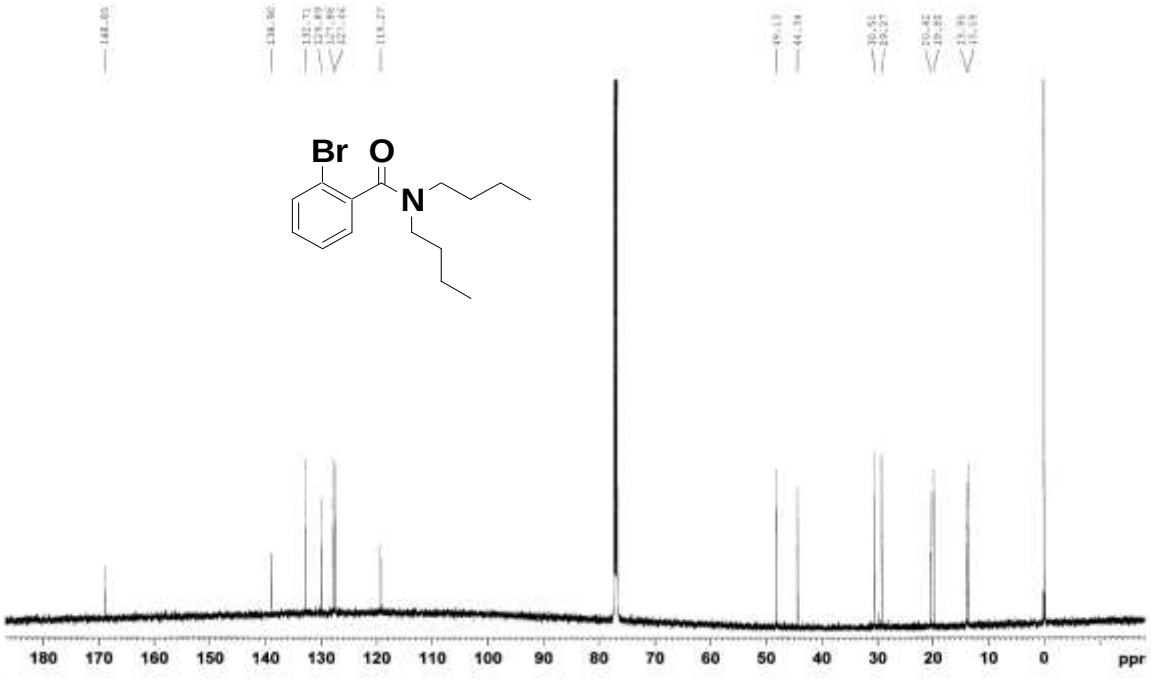


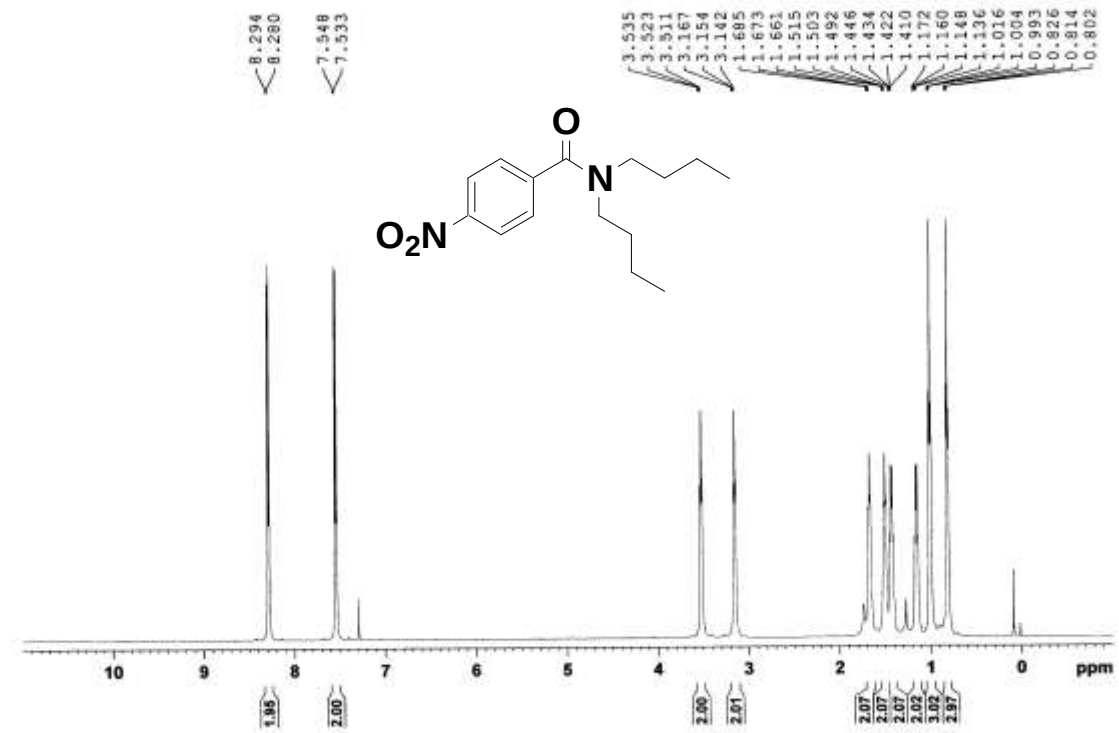








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8.280
7.548
7.533
3.535
3.523
3.511
3.167
3.154
3.142
1.685
1.673
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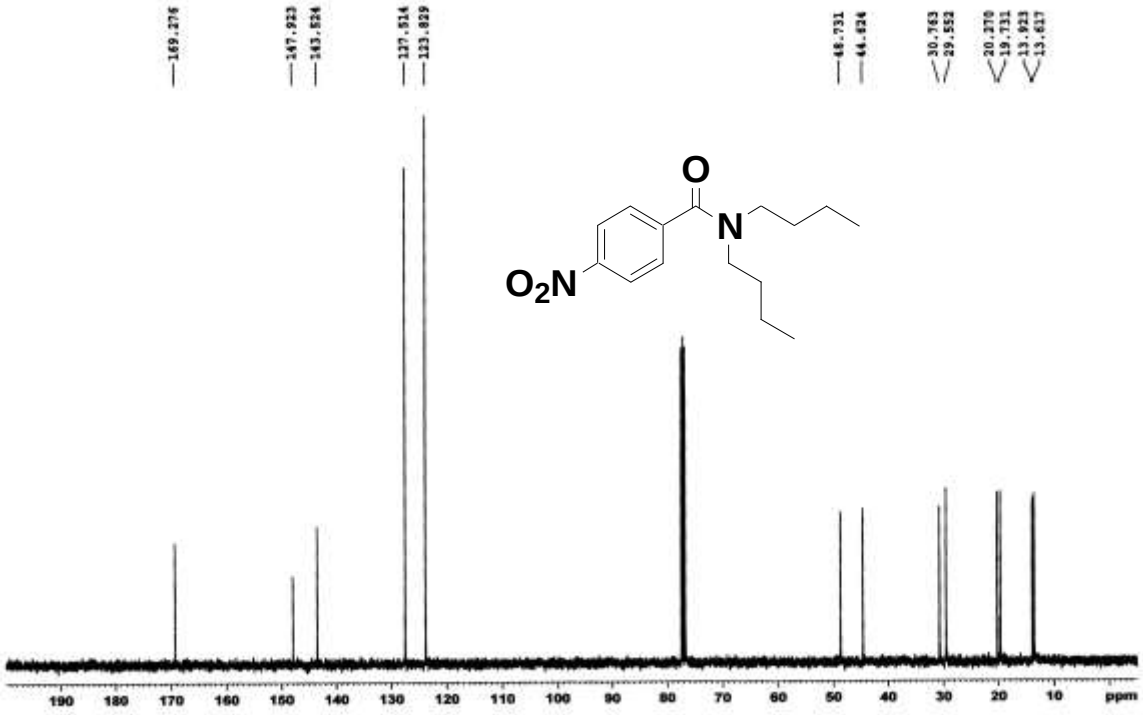
1.515
1.503
1.492
1.446
1.434
1.422
1.410
1.172
1.160
1.148
1.136
1.016
1.004
0.993
0.826
0.814
0.802
O
N
O2N
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
2.00
2.00
2.01
2.07
2.07
2.07
2.02
3.02
2.97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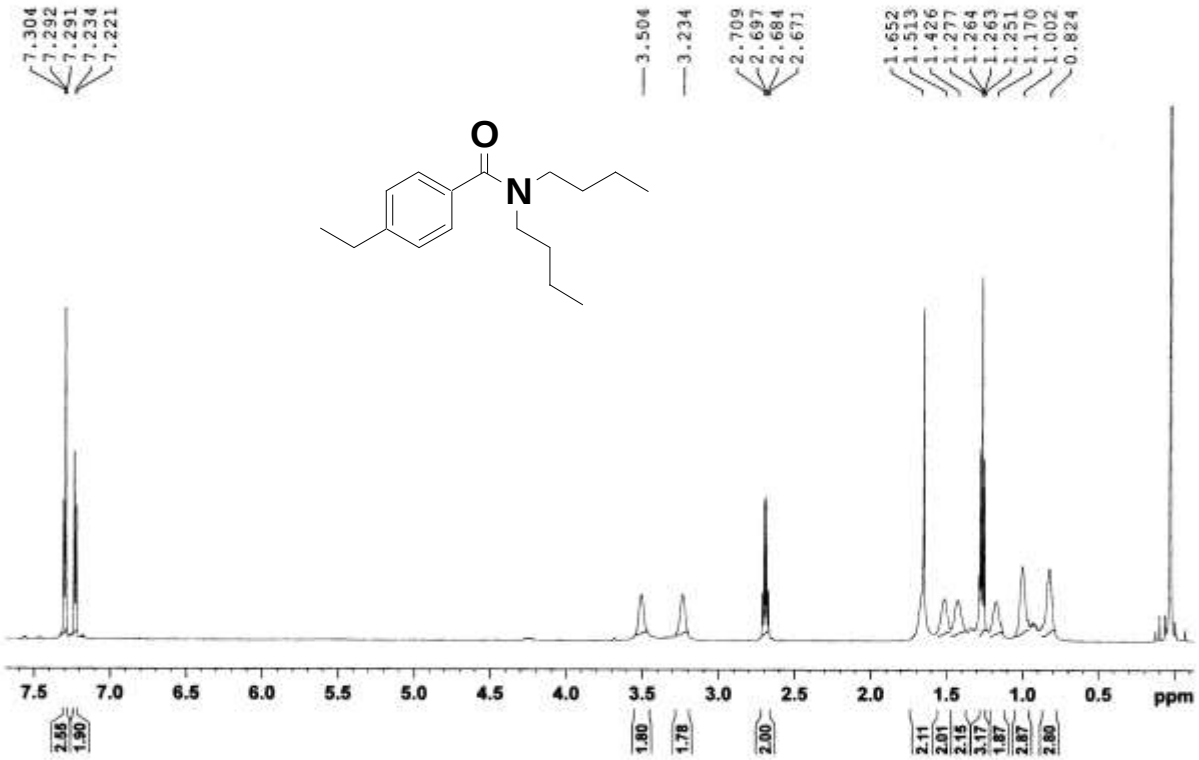
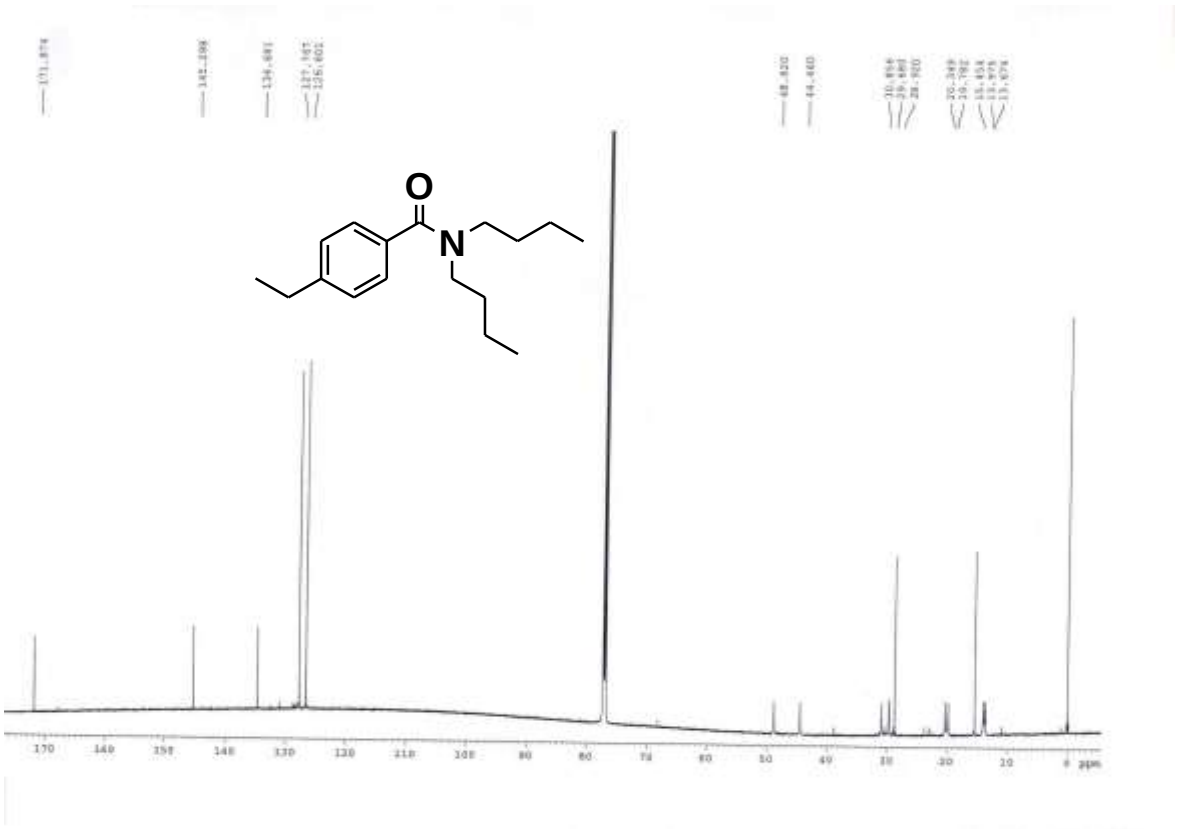
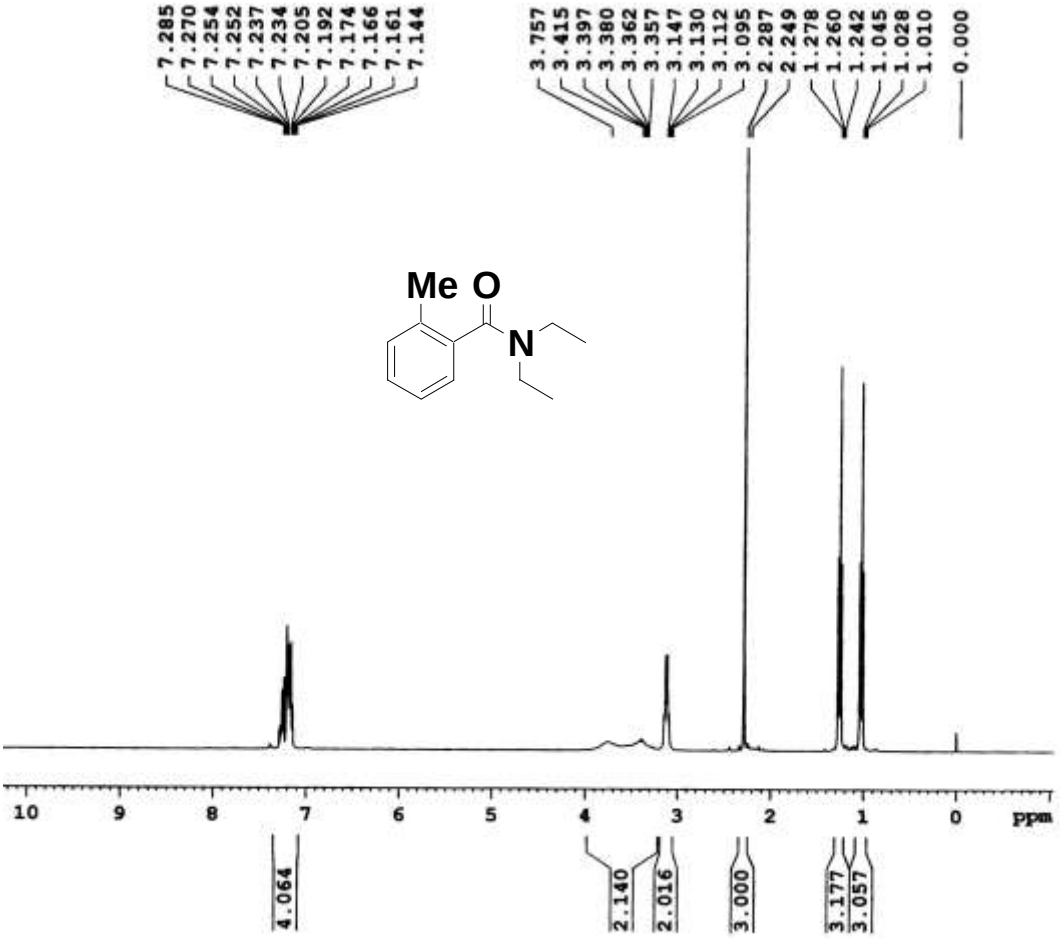
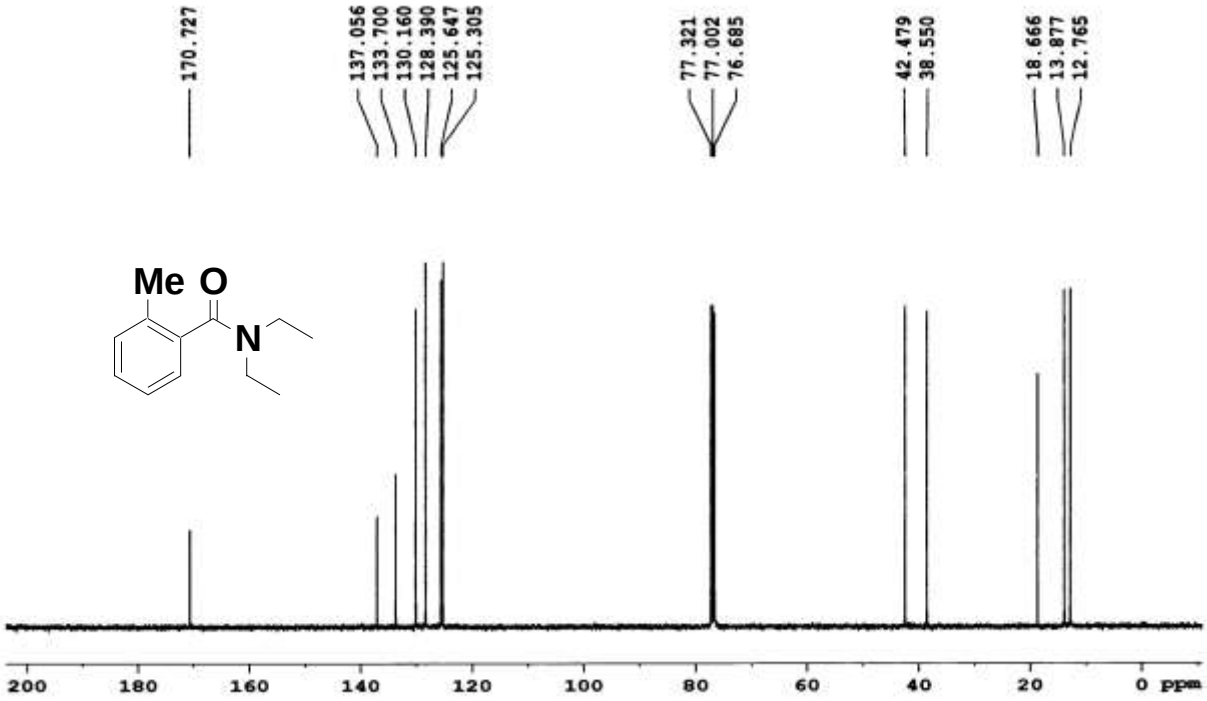
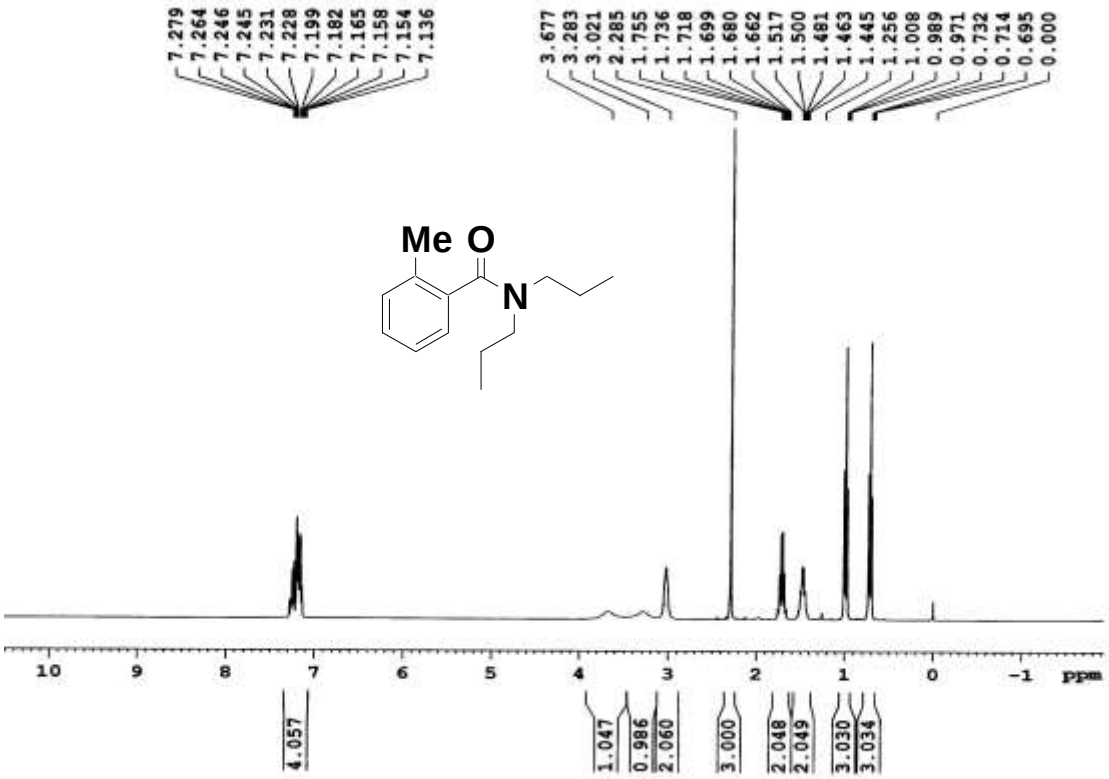
147.923
143.624
127.514
123.829
68.731
44.624
30.763
29.553
20.270
19.731
13.923
13.617
O
N
O2N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm







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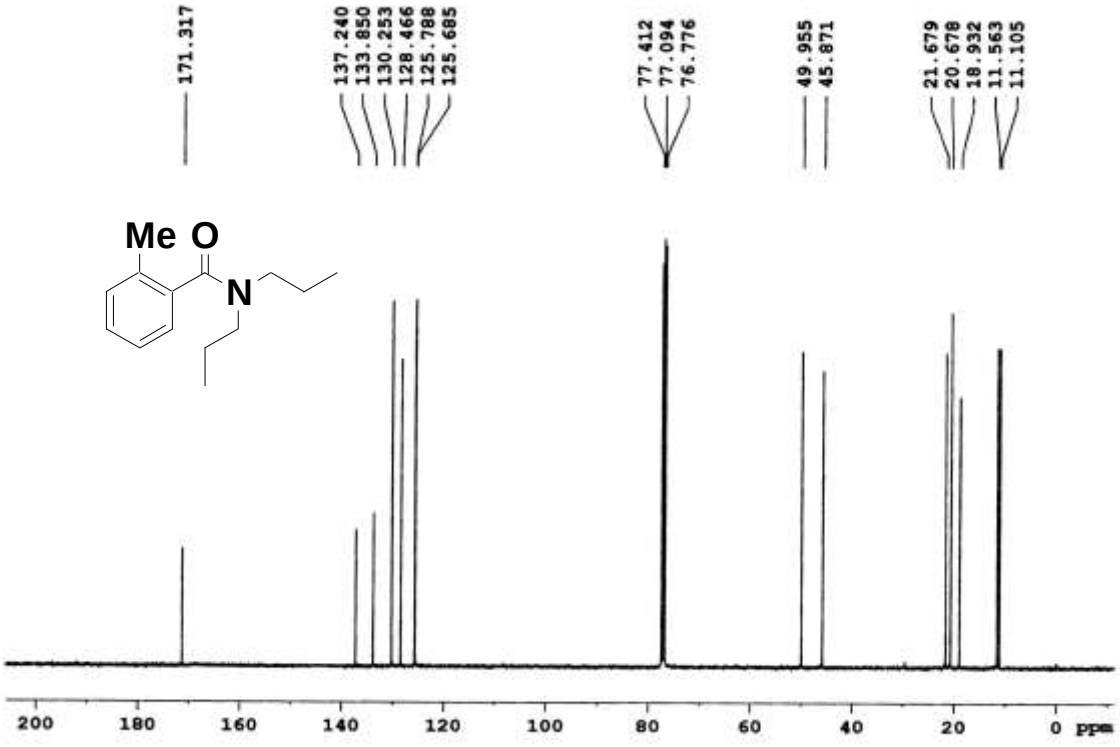
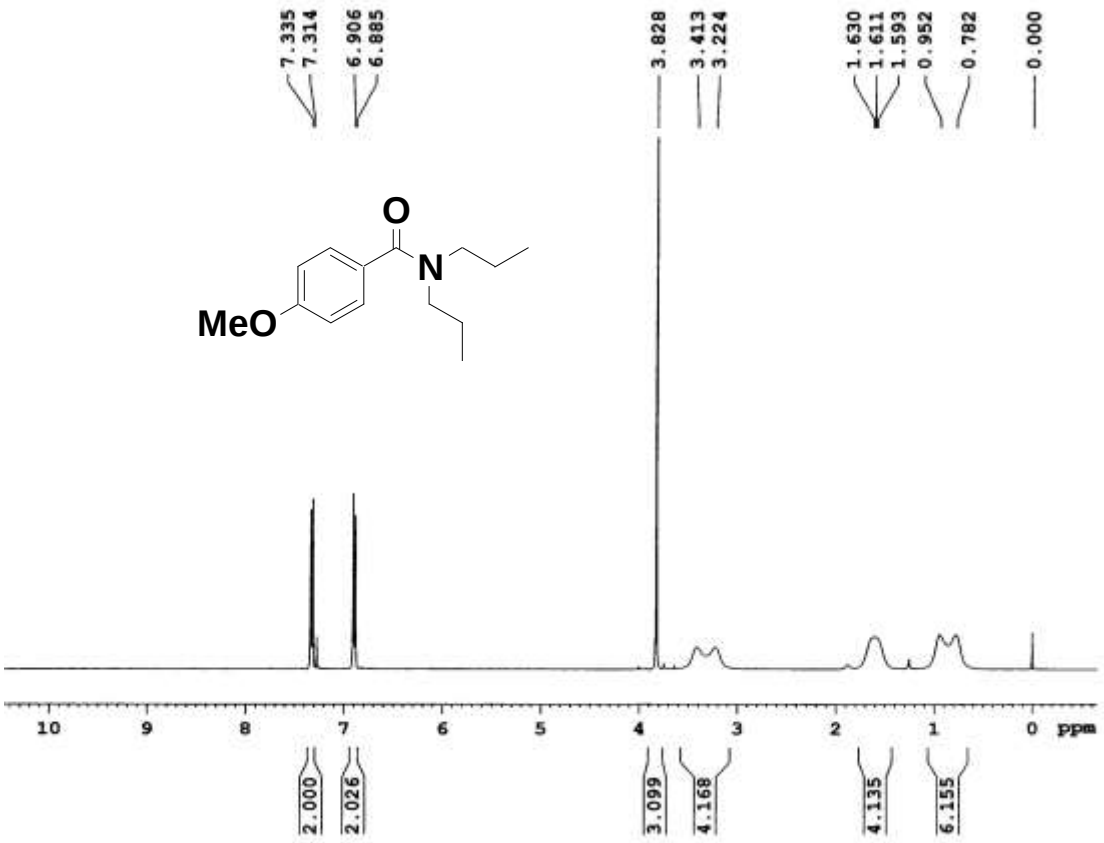
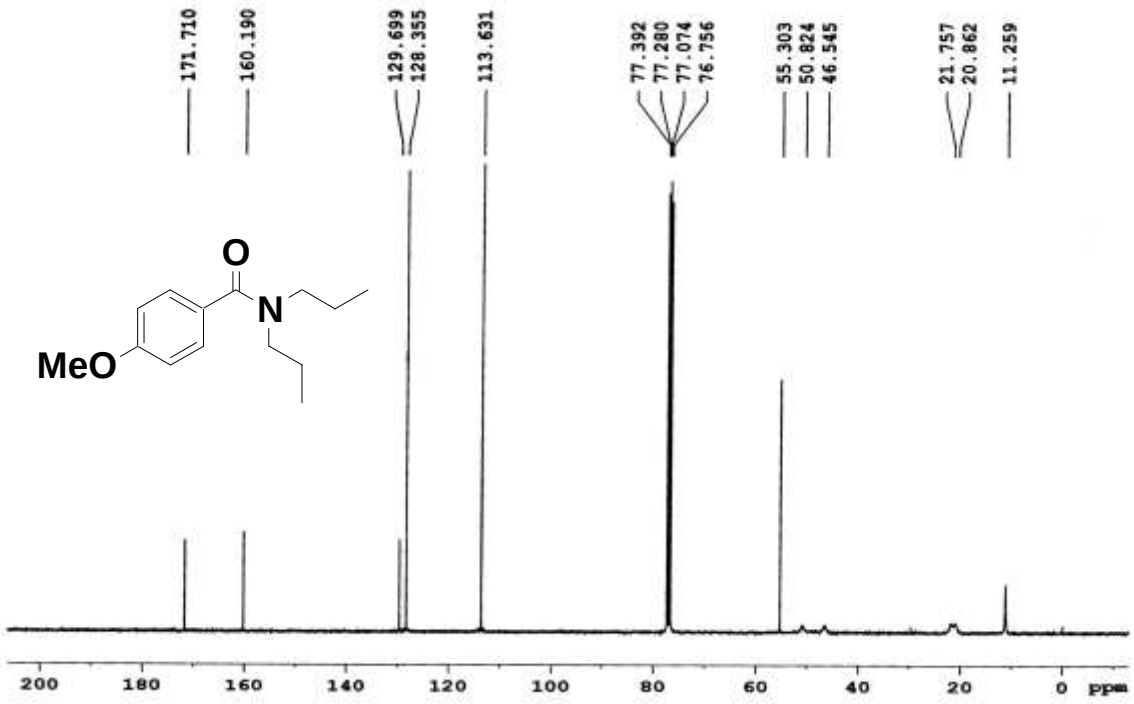
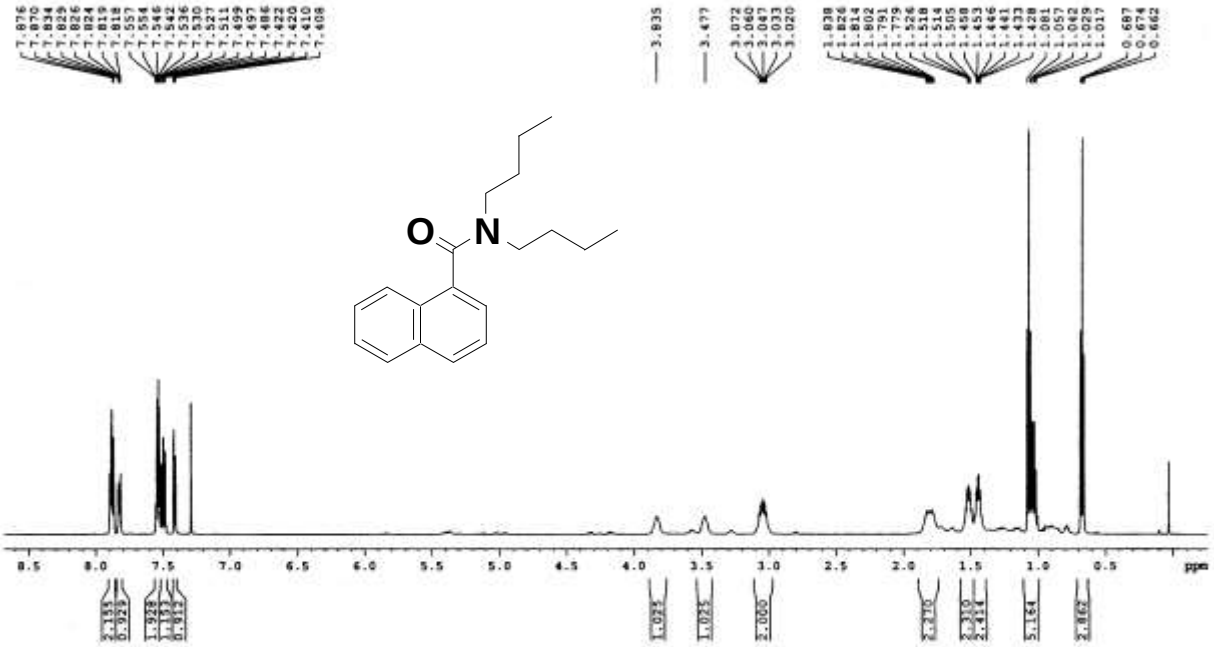
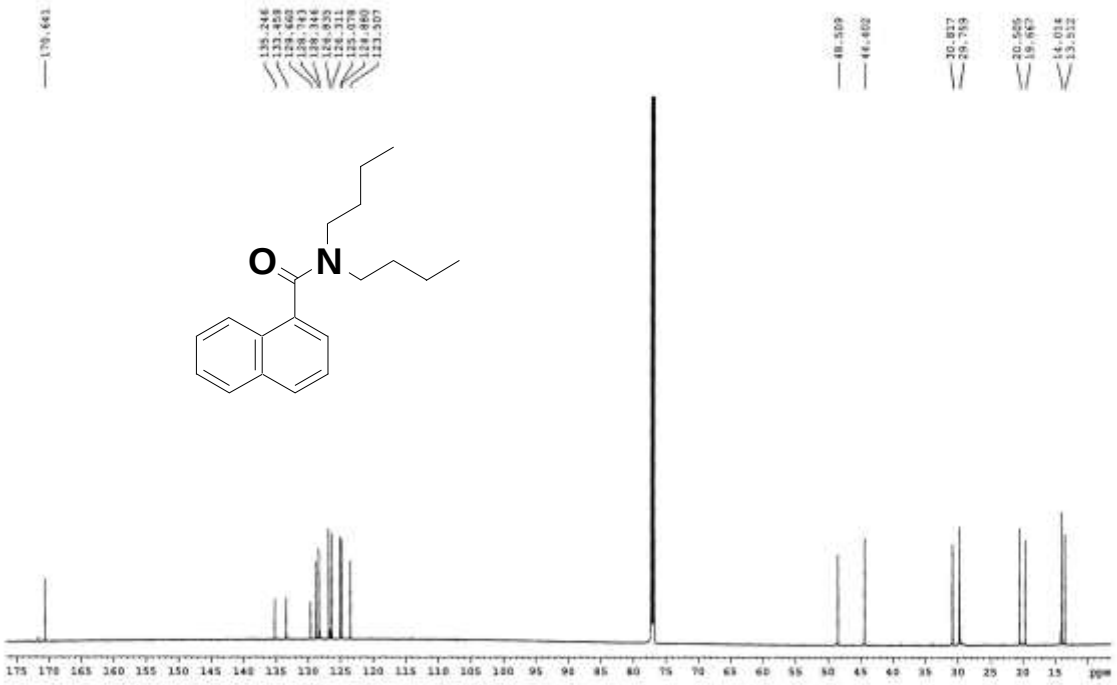
7.246
7.245
7.231
7.228
7.199
7.182
7.165
7.158
7.154
7.136
3.677
3.283
3.021
2.285
1.755
1.736
1.718
1.699
1.680
1.662
1.517
1.500
1.481
1.463
1.445
1.256
1.008
0.989
0.971
0.732
0.714
0.695
0.000
Me O
N
10 9 8 7 6 5 4 3 2 1 0 -1 ppm
4.057
1.047
0.986
2.060
3.000
2.048
2.049
3.030
3.034


171.317
137.240
133.850
130.253
128.466
125.788
125.685
77.412
77.094
76.776
49.955
45.871
21.679
20.678
18.932
11.563
11.105
Me O
N
200 180 160 140 120 100 80 60 40 20 0 ppm






O
N
ppm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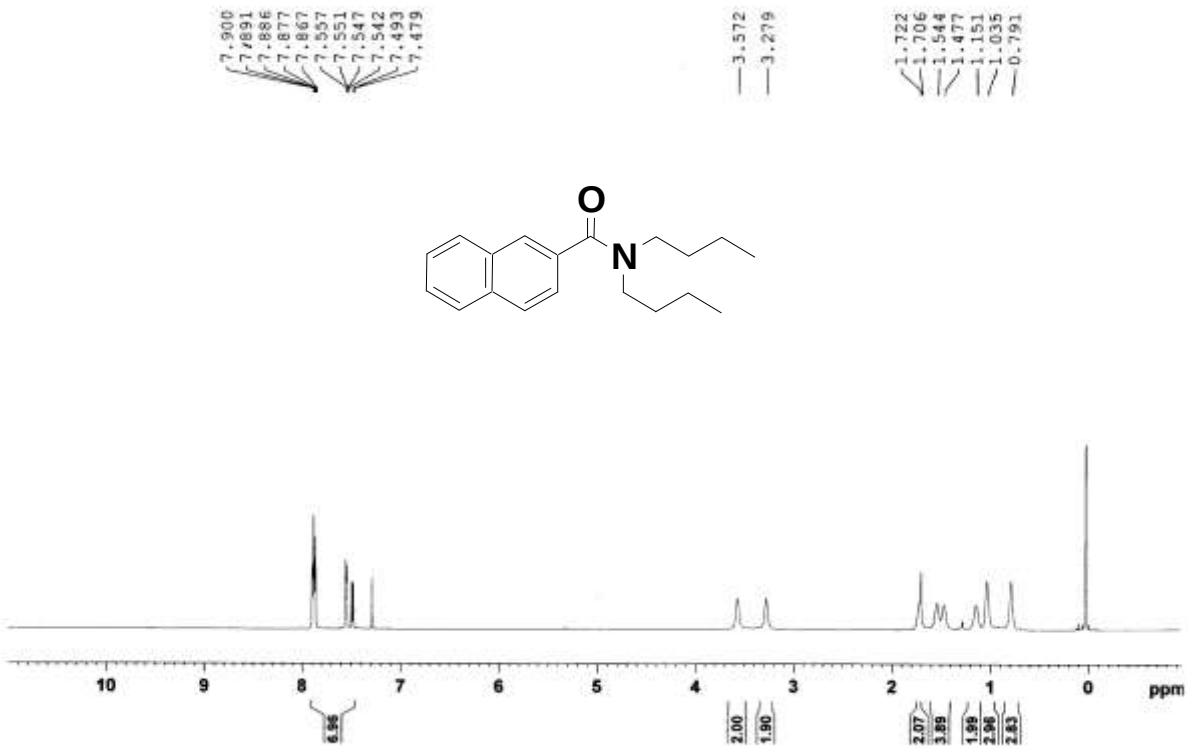
N
ppm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7.877
7.867
7.557
7.551
7.547
7.542
7.493
7.479
3.572
3.279
1.722
1.706
1.544
1.477
1.151
1.035
0.791
O
N
10
9
8
7
6
5
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2.07
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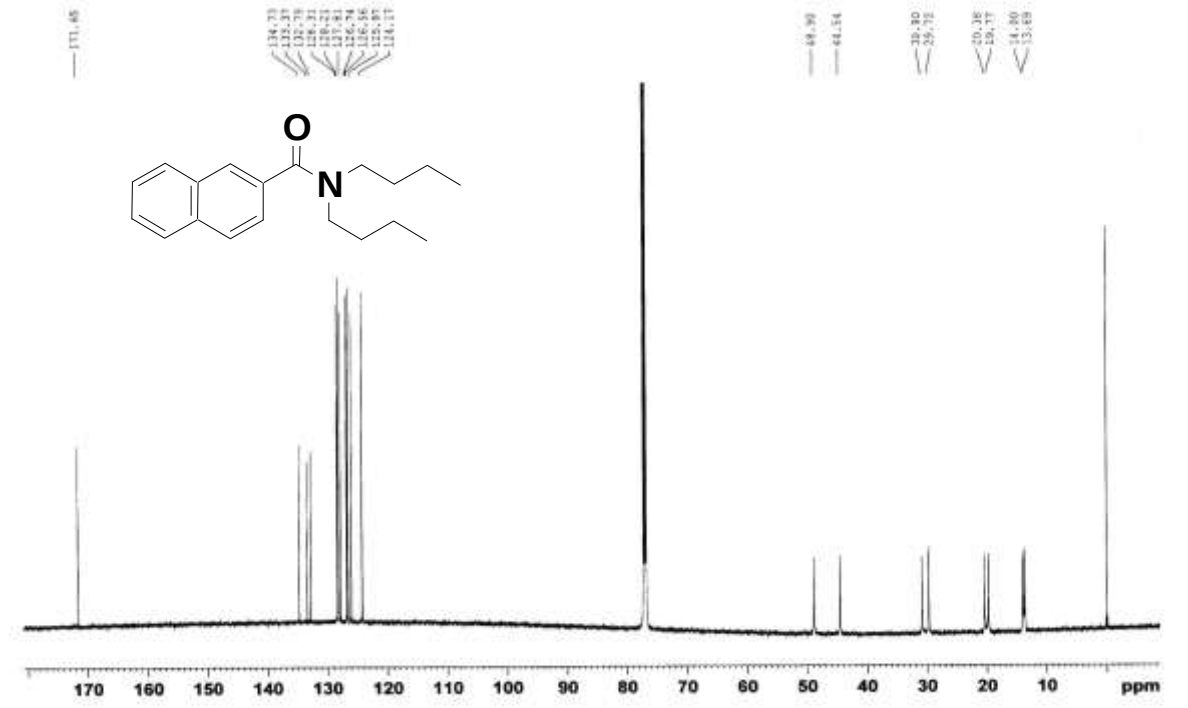
2.96
2.83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128.21
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126.74
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124.17
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13.69
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150
140
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110
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70
60
50
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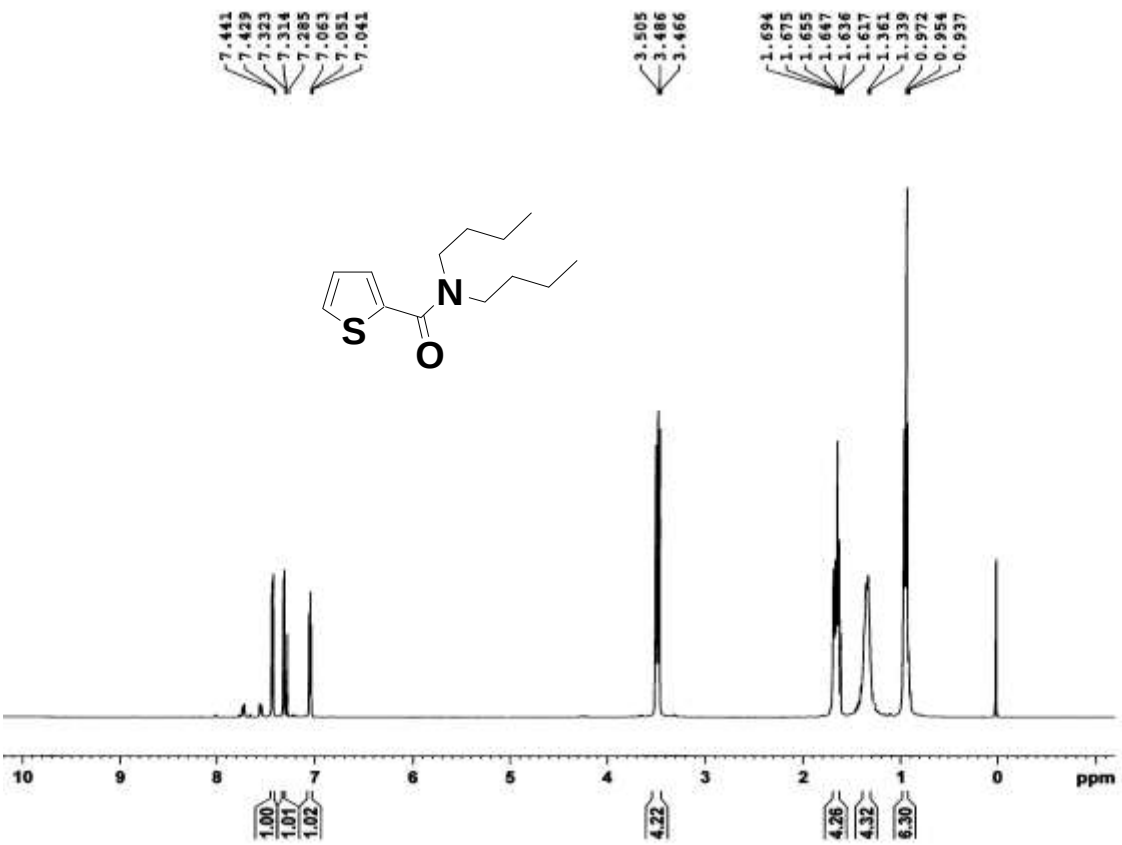
30
20
10
ppm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1.655
1.647
1.636
1.617
1.361
1.339
0.972
0.954
0.937
S
N
O
10
9
8
7
6
5
4
3
2
1
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ppm
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1.02
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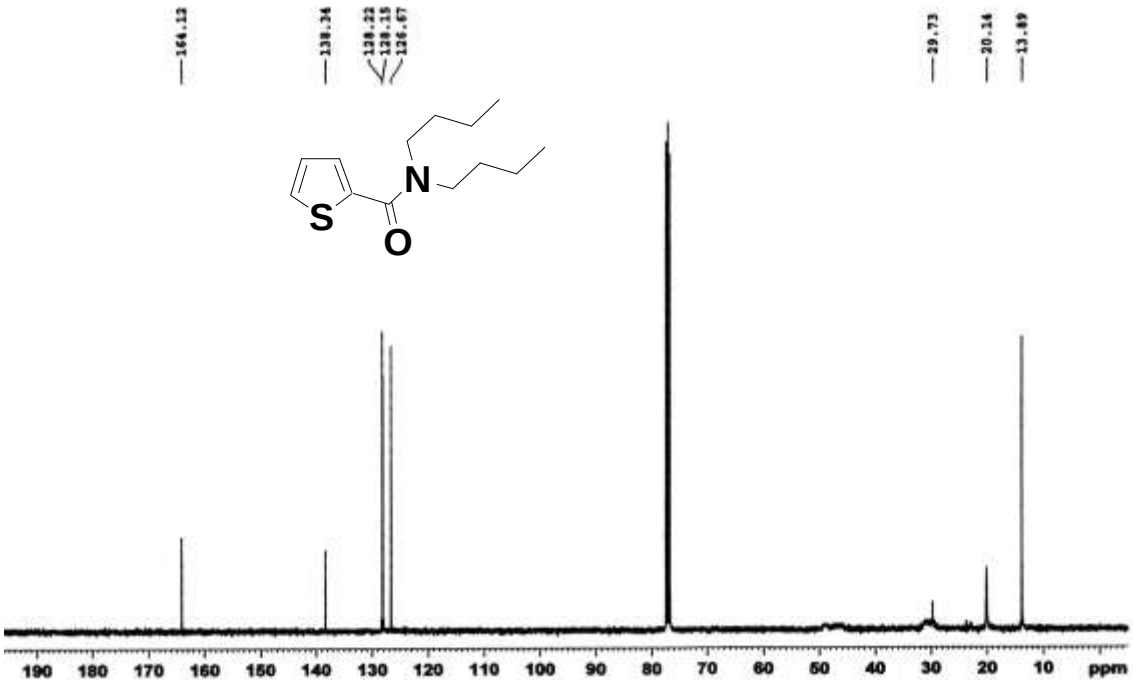
4.26
4.32
6.30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128.15
126.67
39.73
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13.89
S
N
O
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150
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120
110
100
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70
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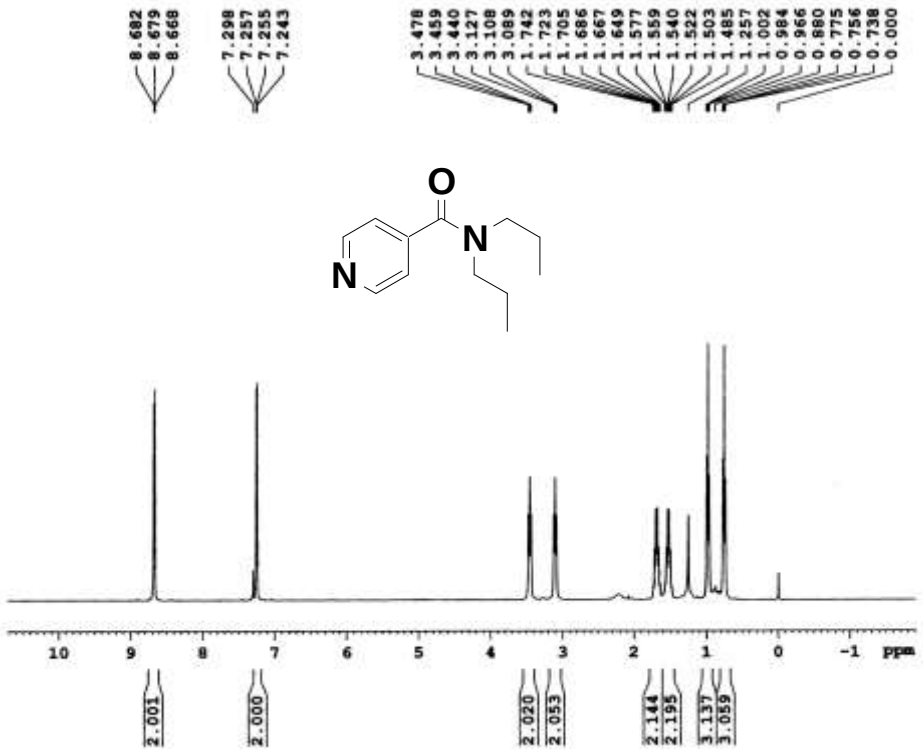
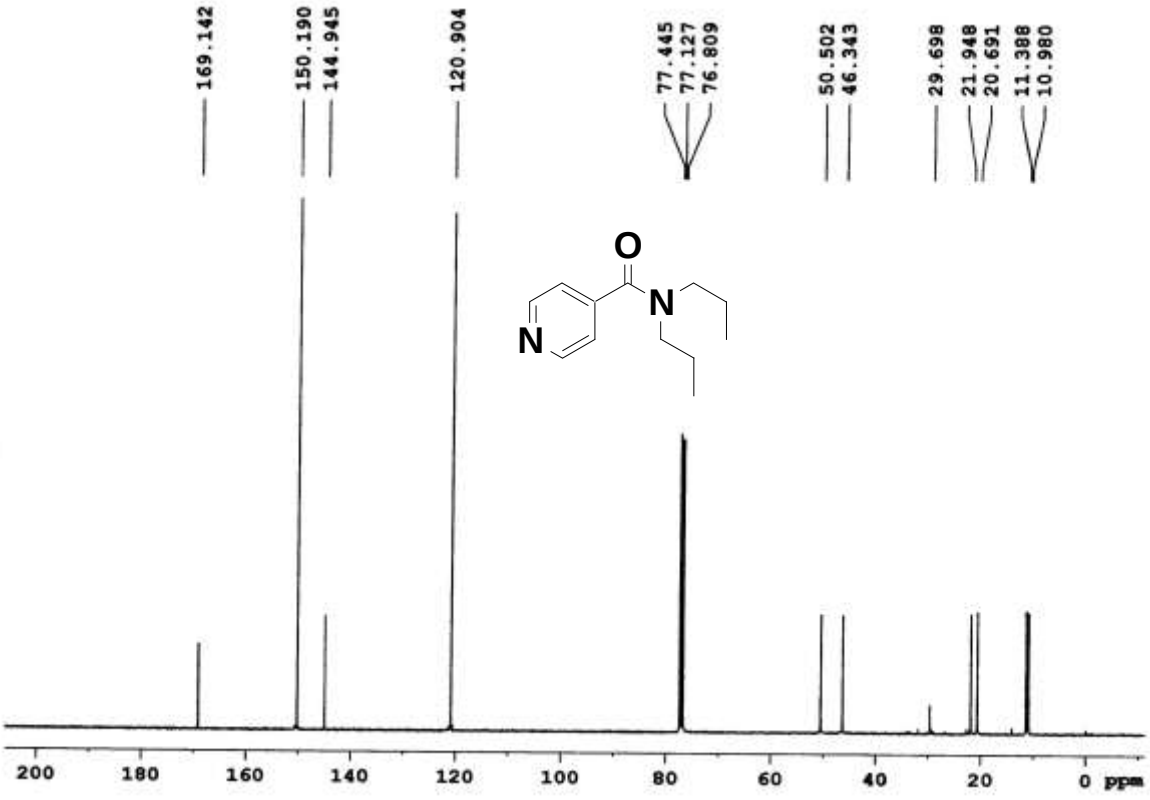
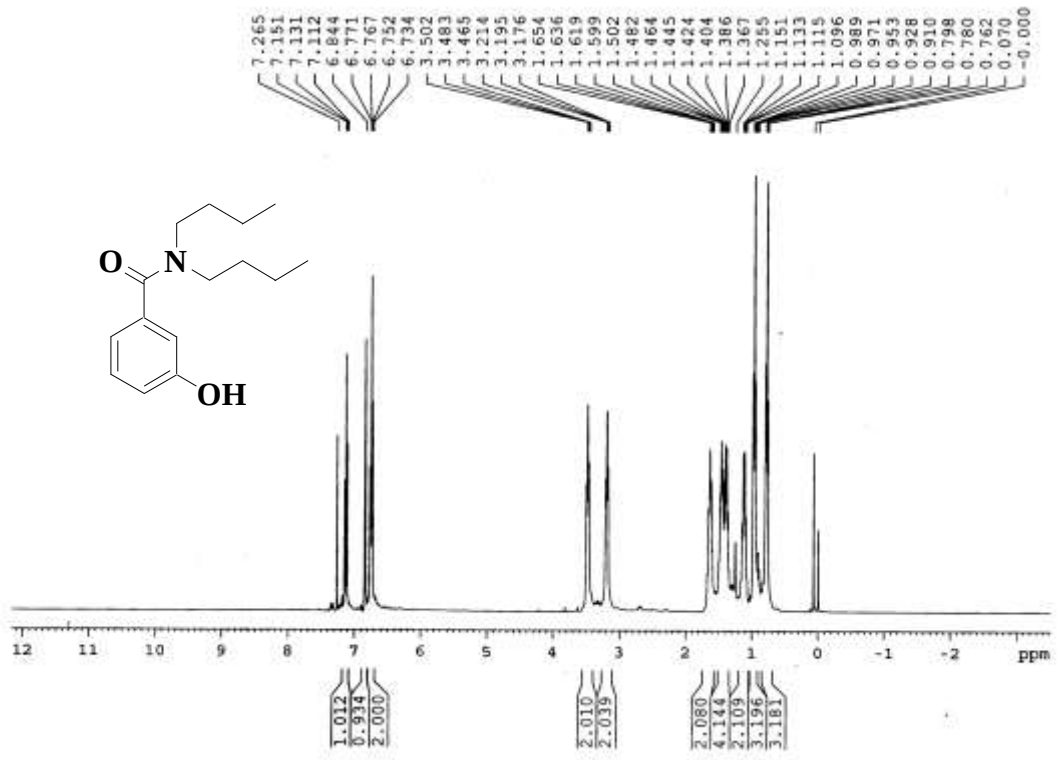
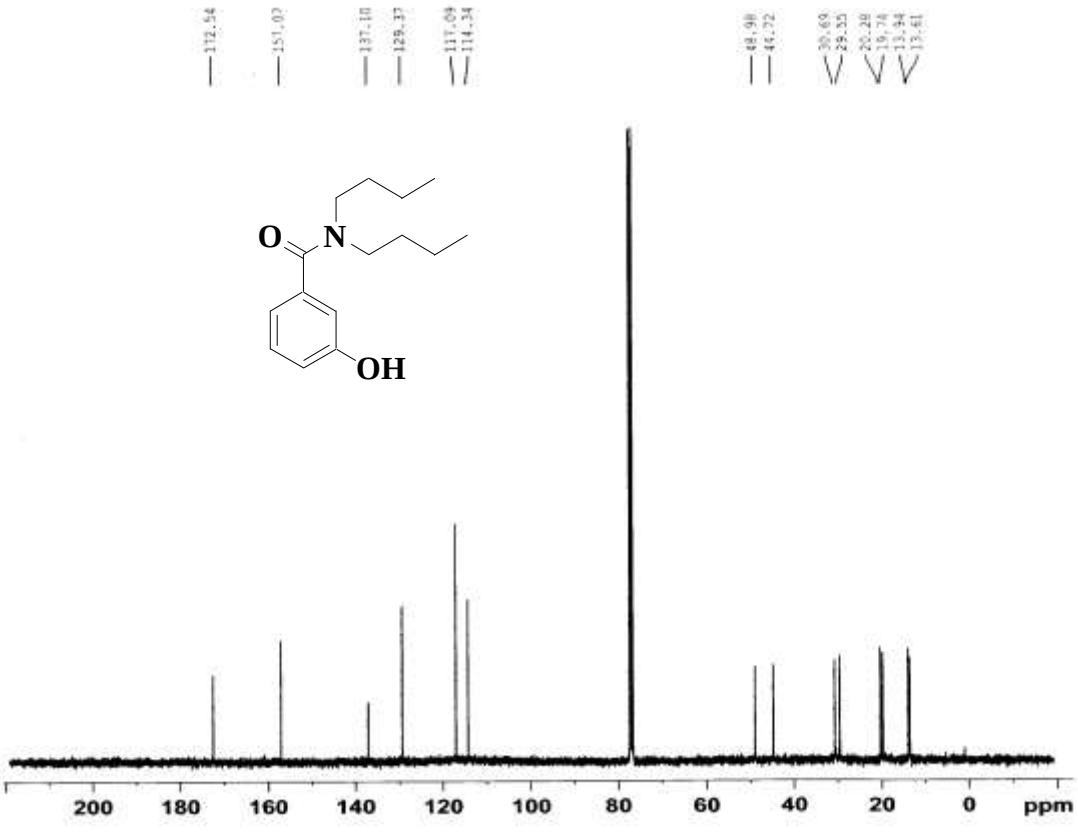
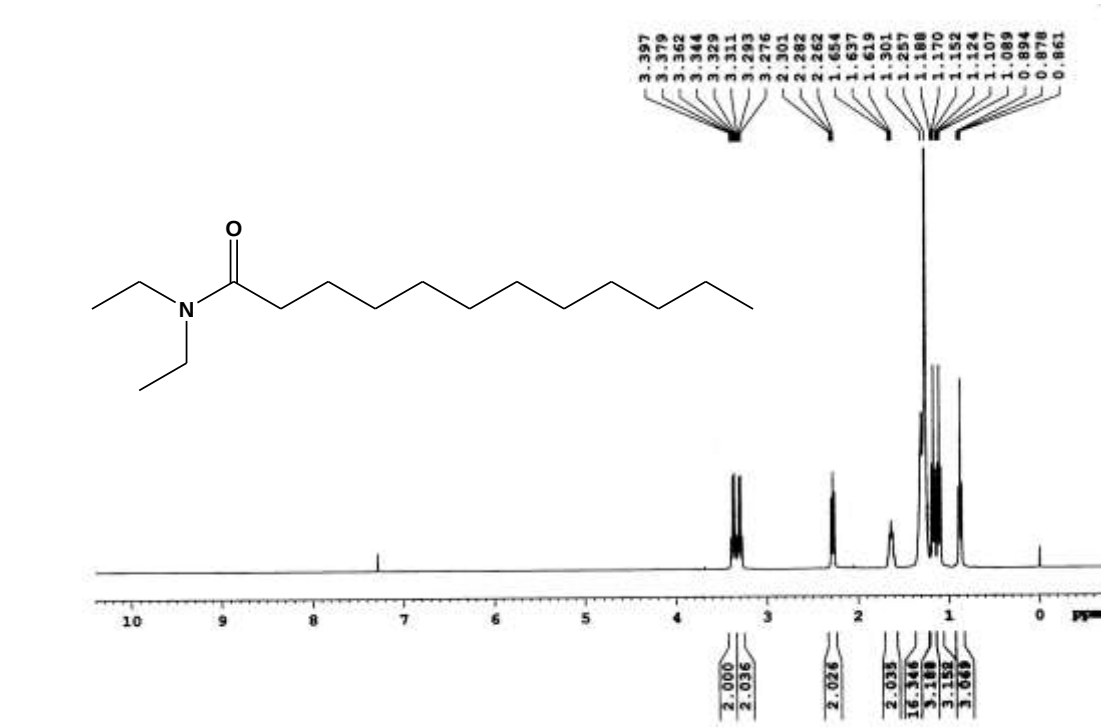
30
20
10
ppm







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1.619
1.301
1.257
1.188
1.170
1.152
1.124
1.107
1.089
0.894
0.878
0.861
O
N
10
9
8
7
6
5
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2.035
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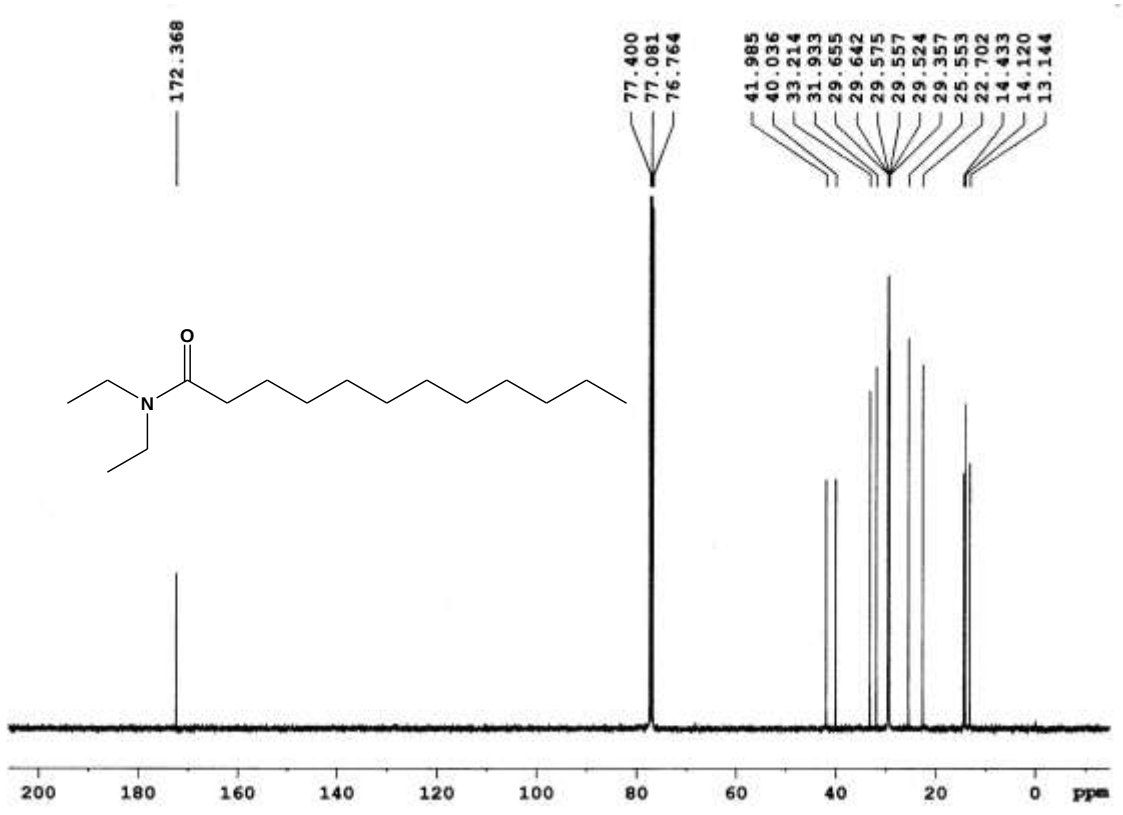
3.158
3.069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31.933
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29.642
29.575
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29.524
29.357
25.553
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13.144
O
N
200
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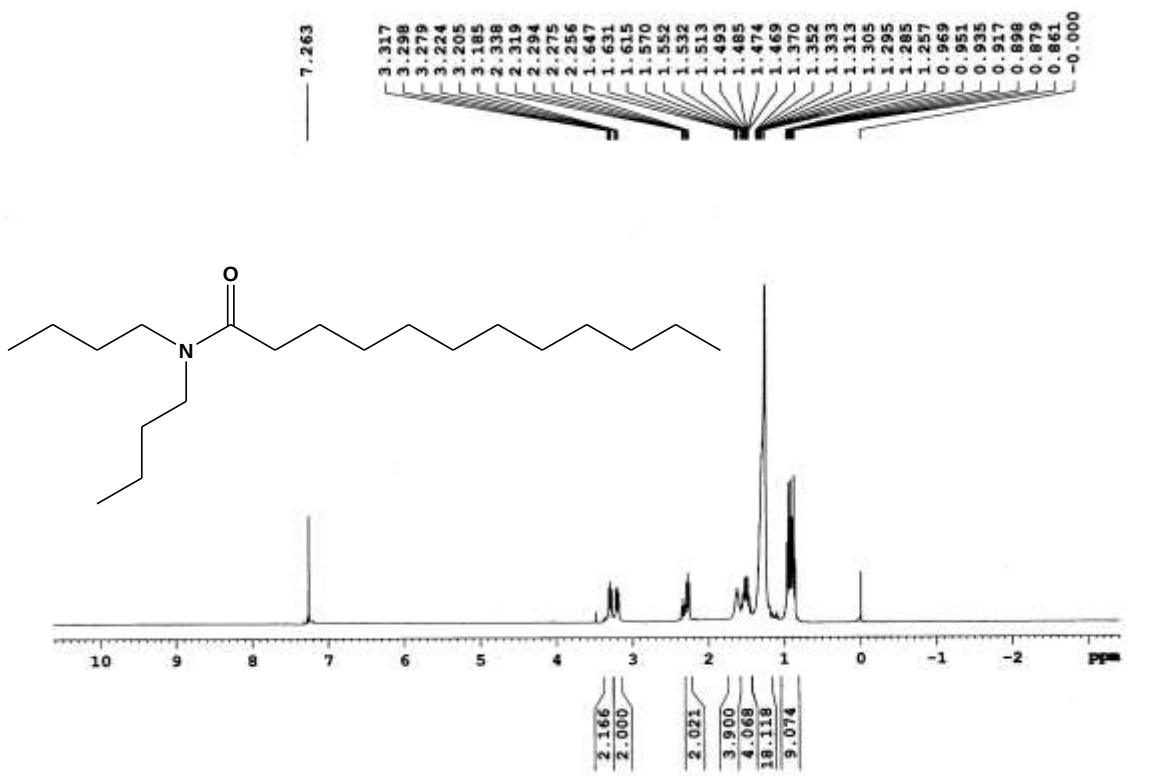
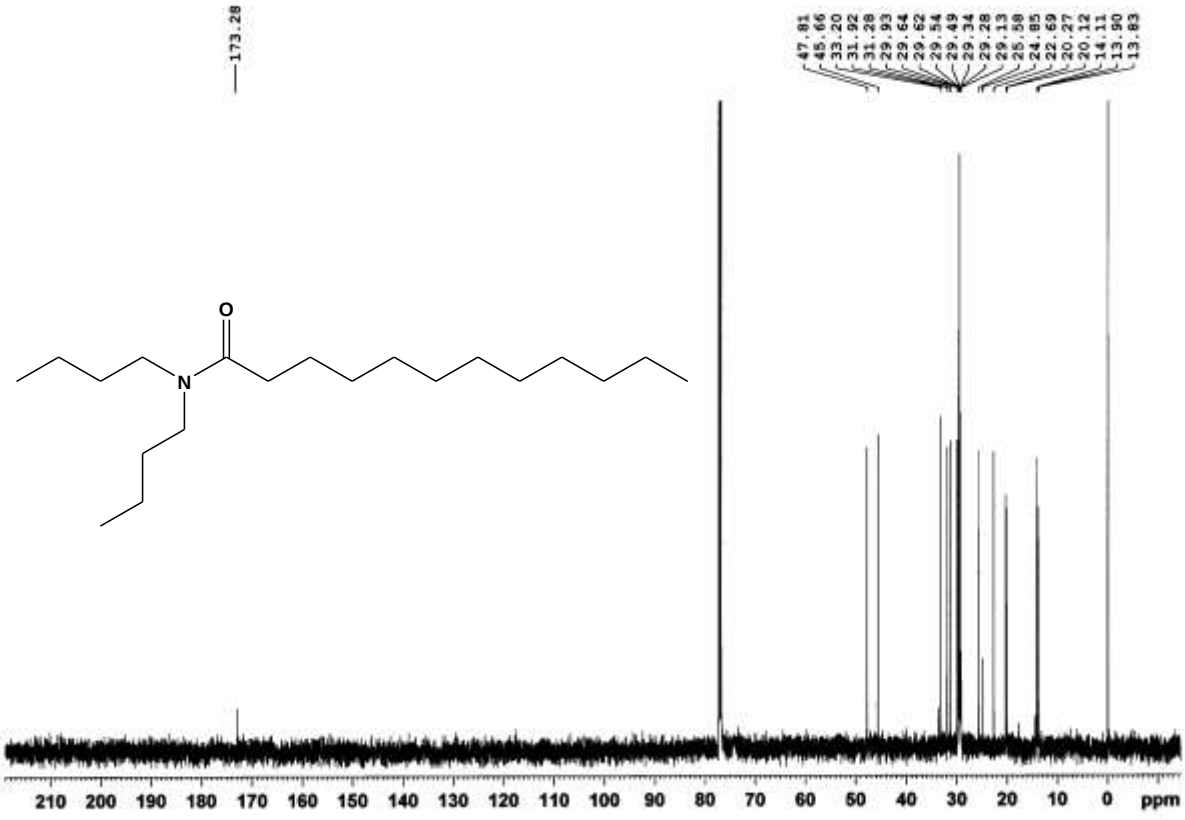
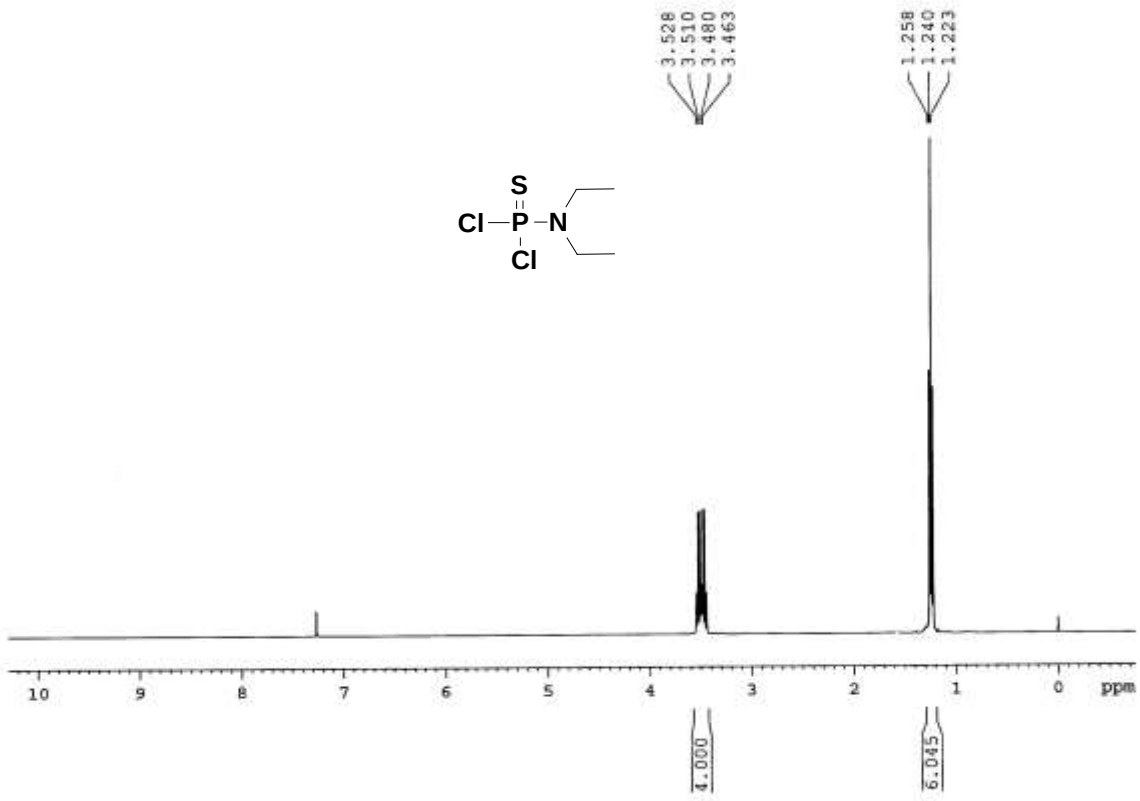
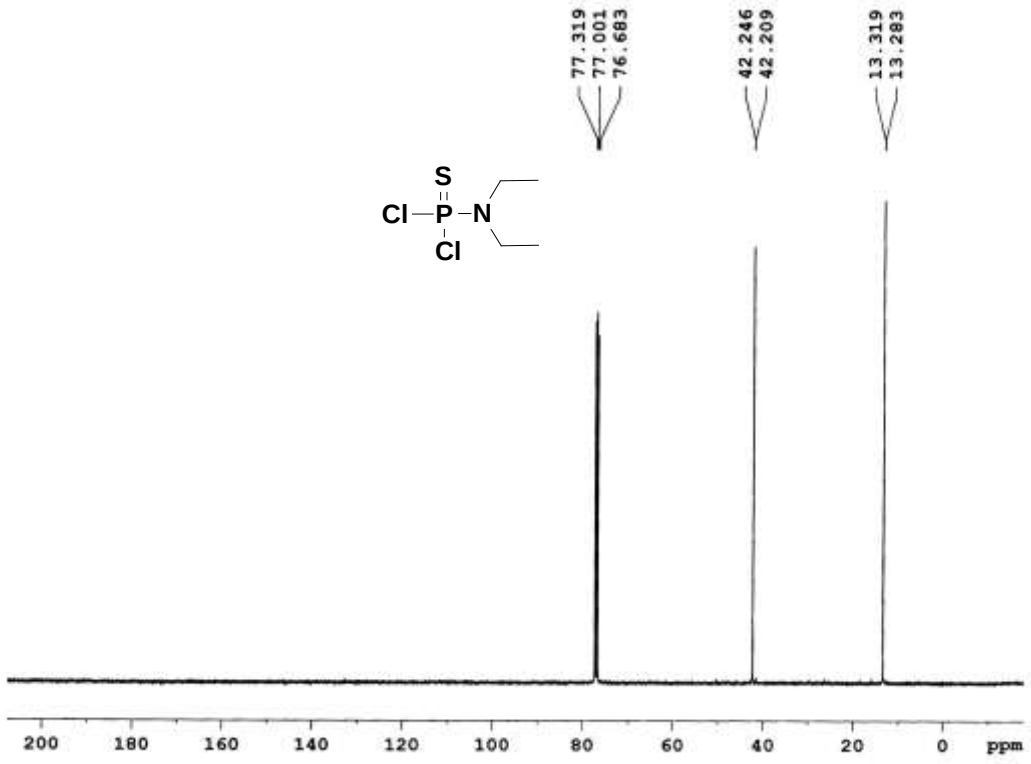
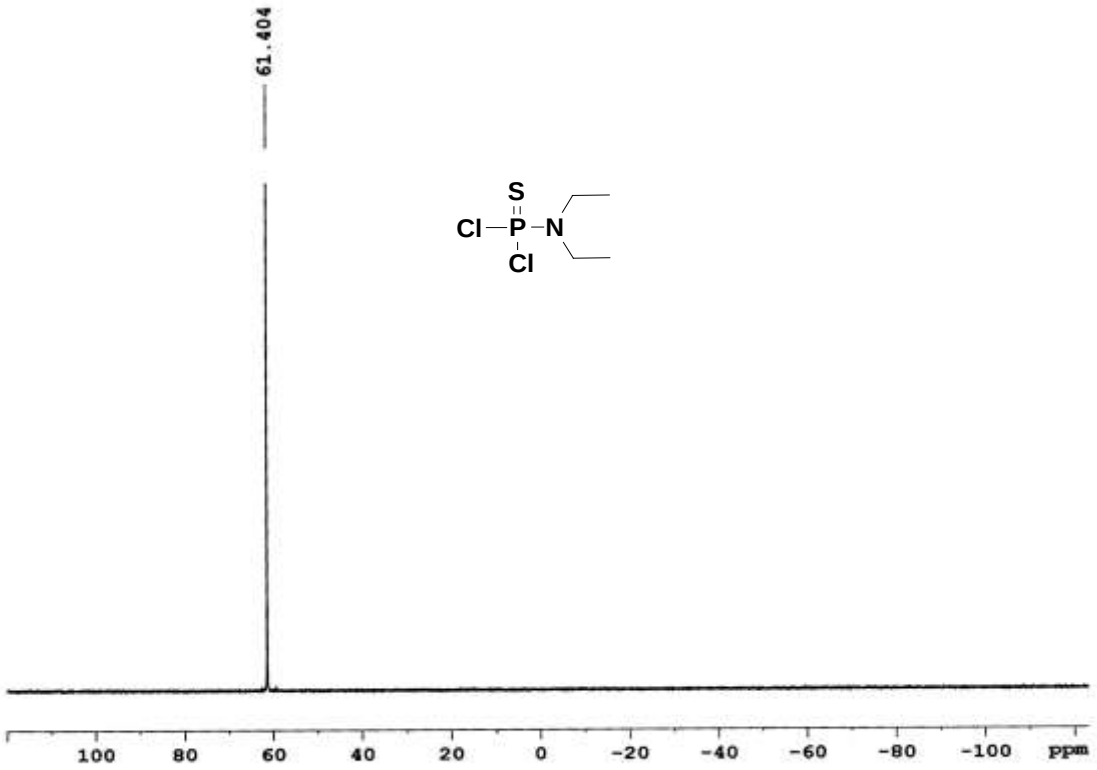
160
140
120
100
80
60
40
20
0
ppm

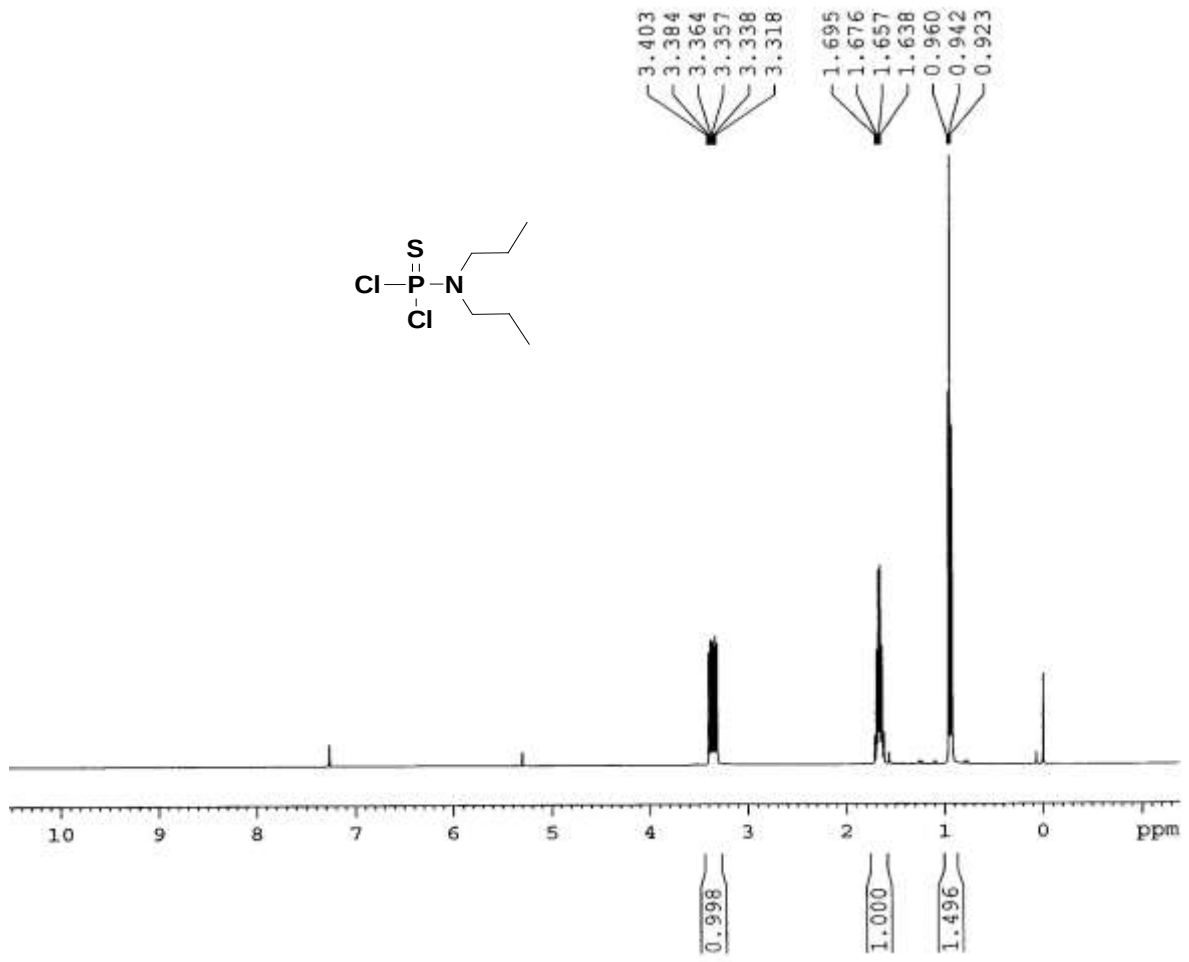


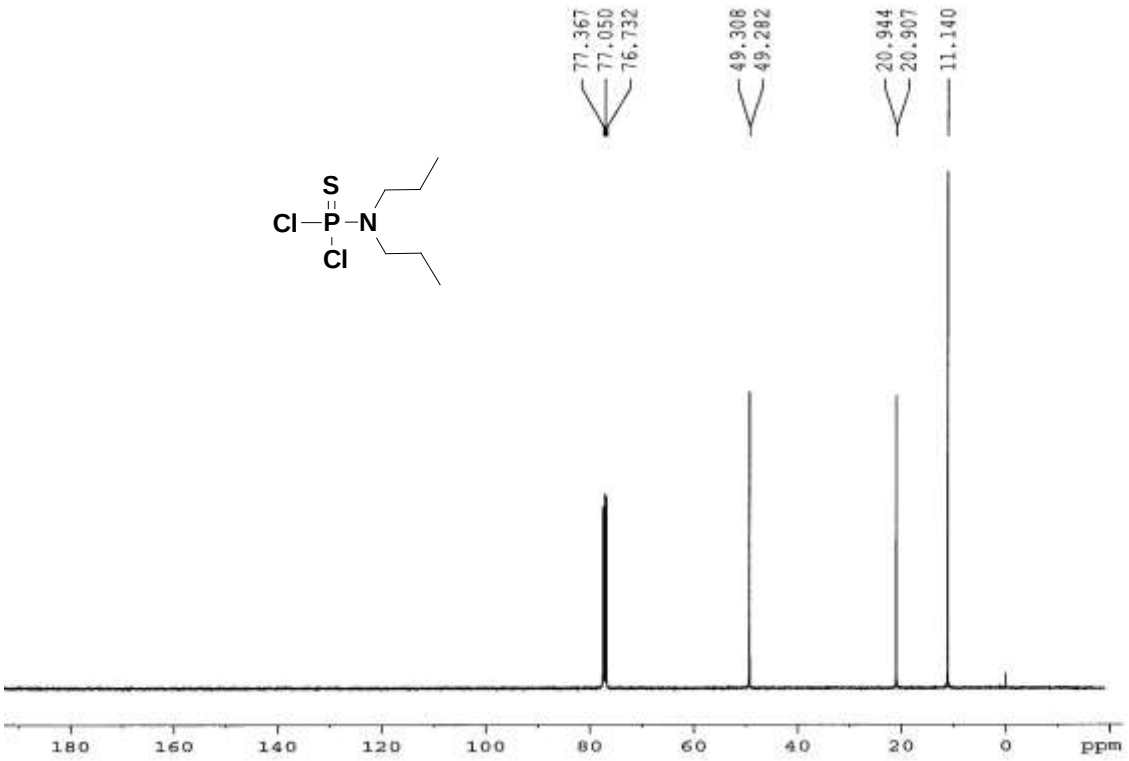


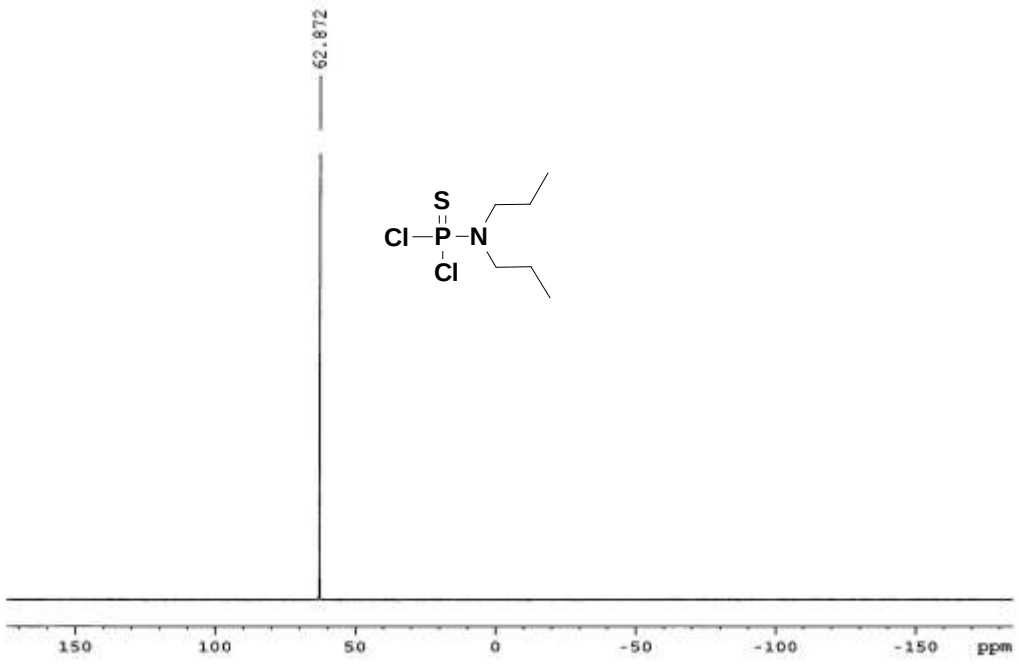


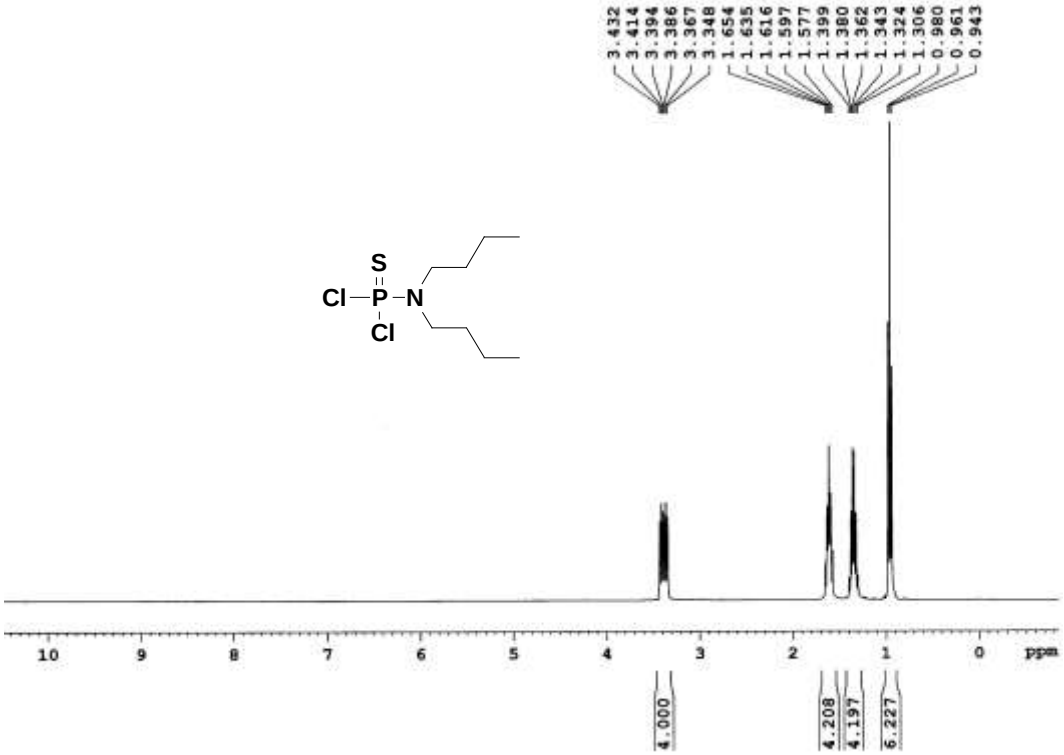


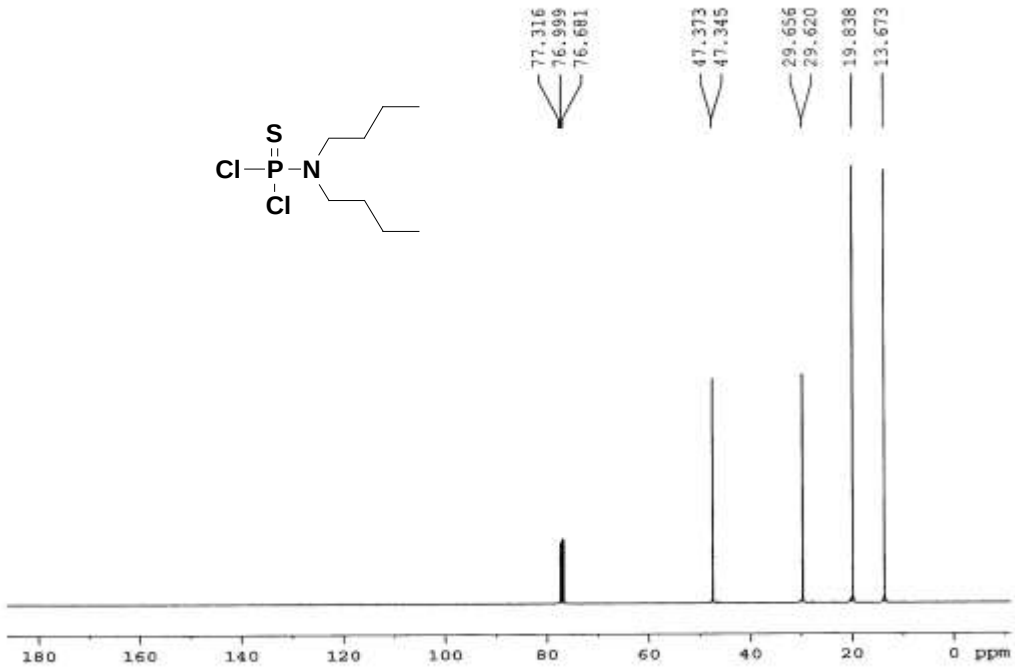


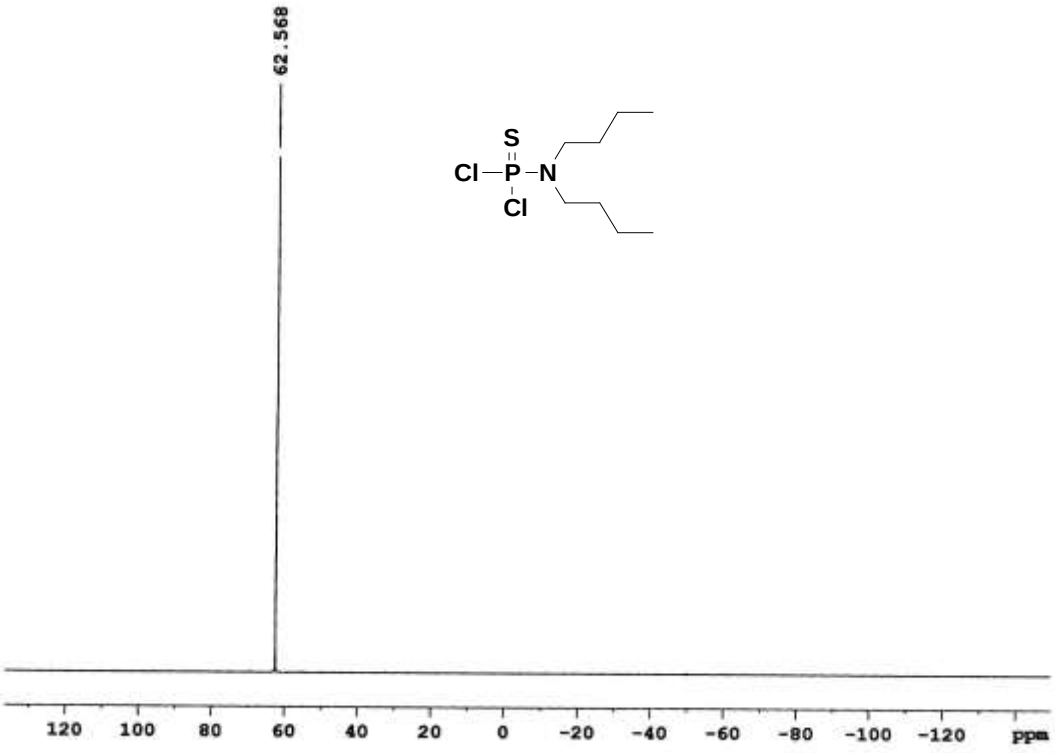


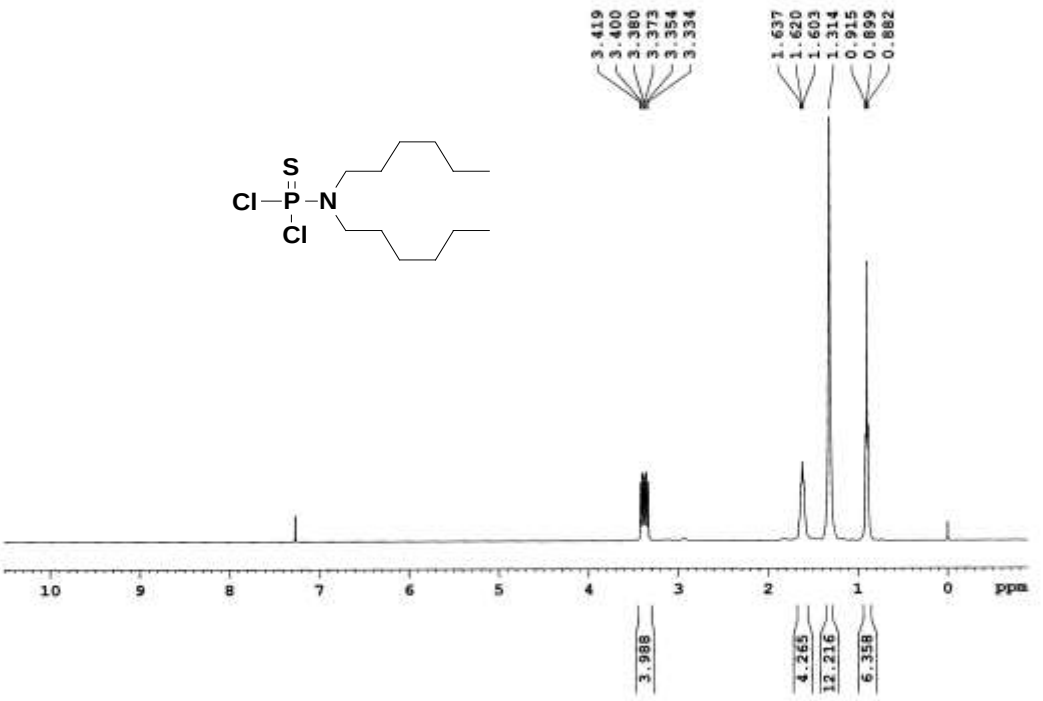


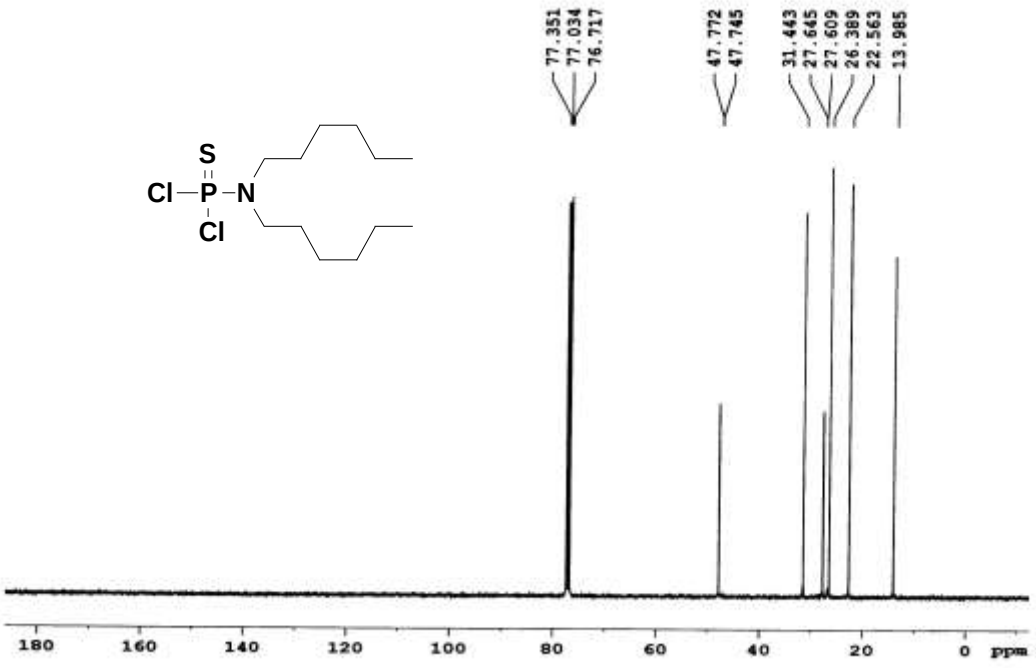


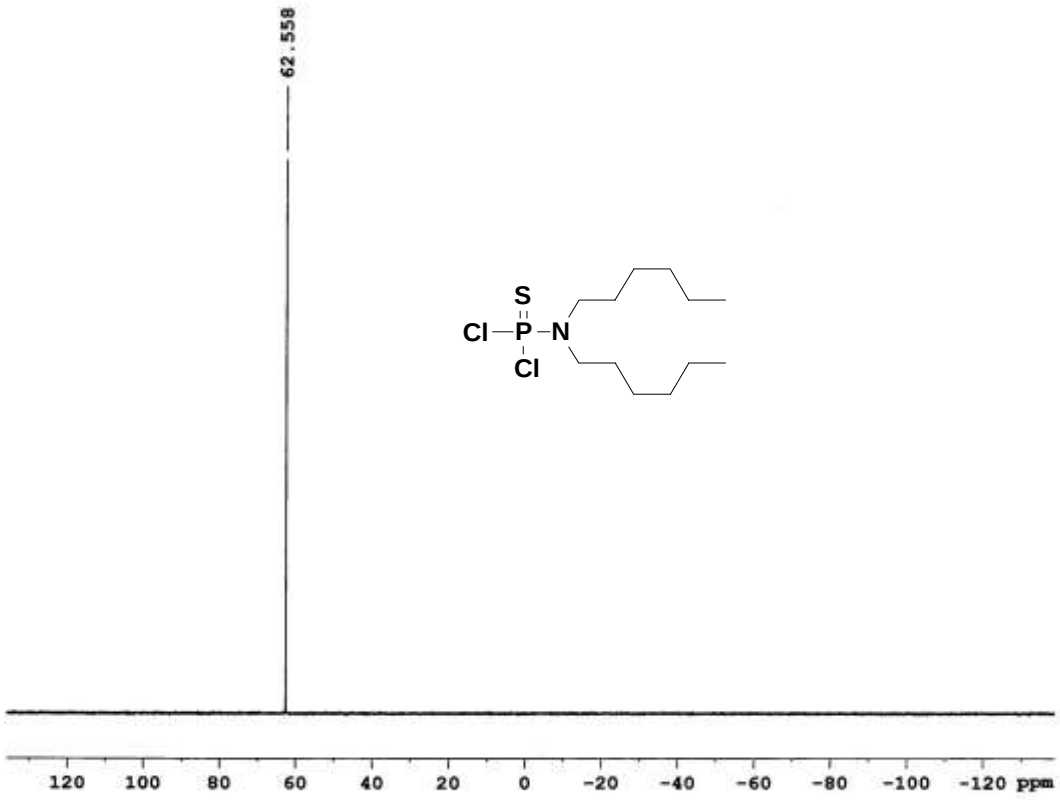


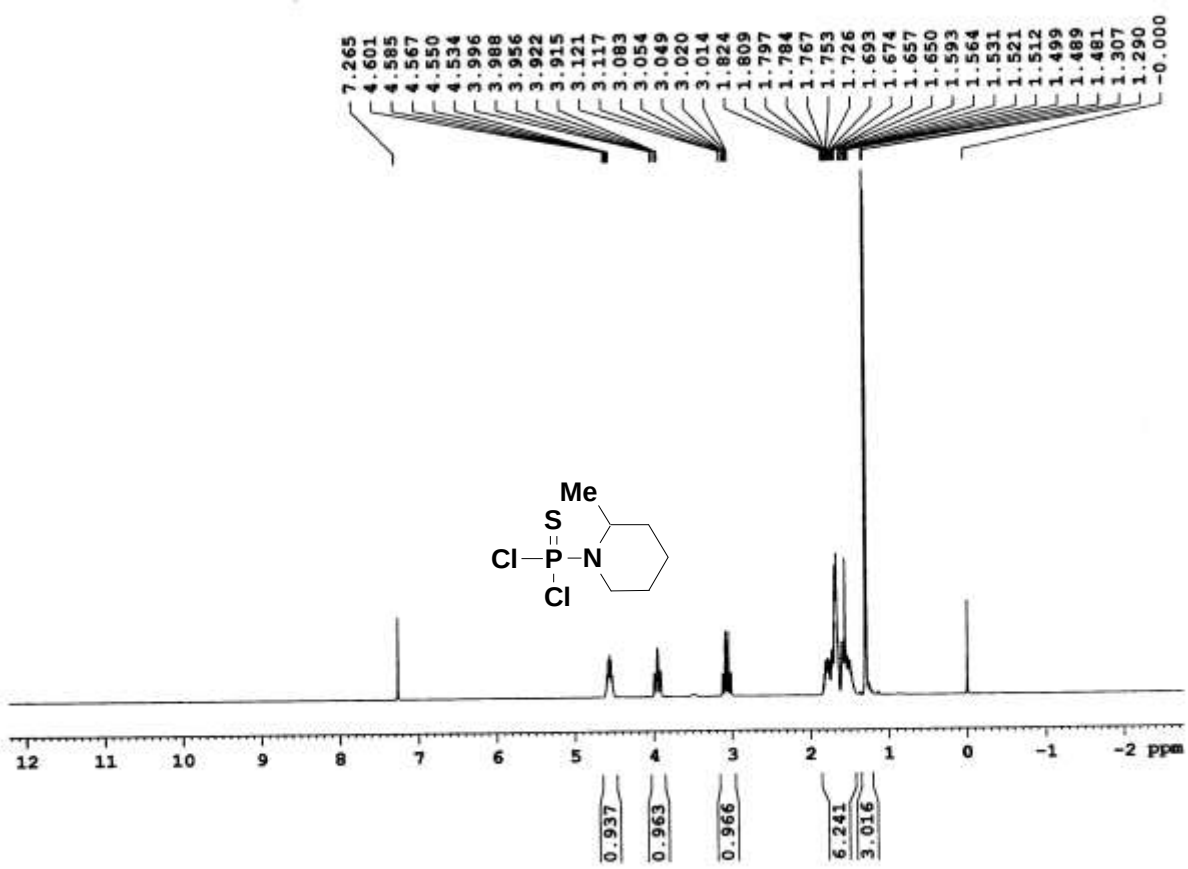


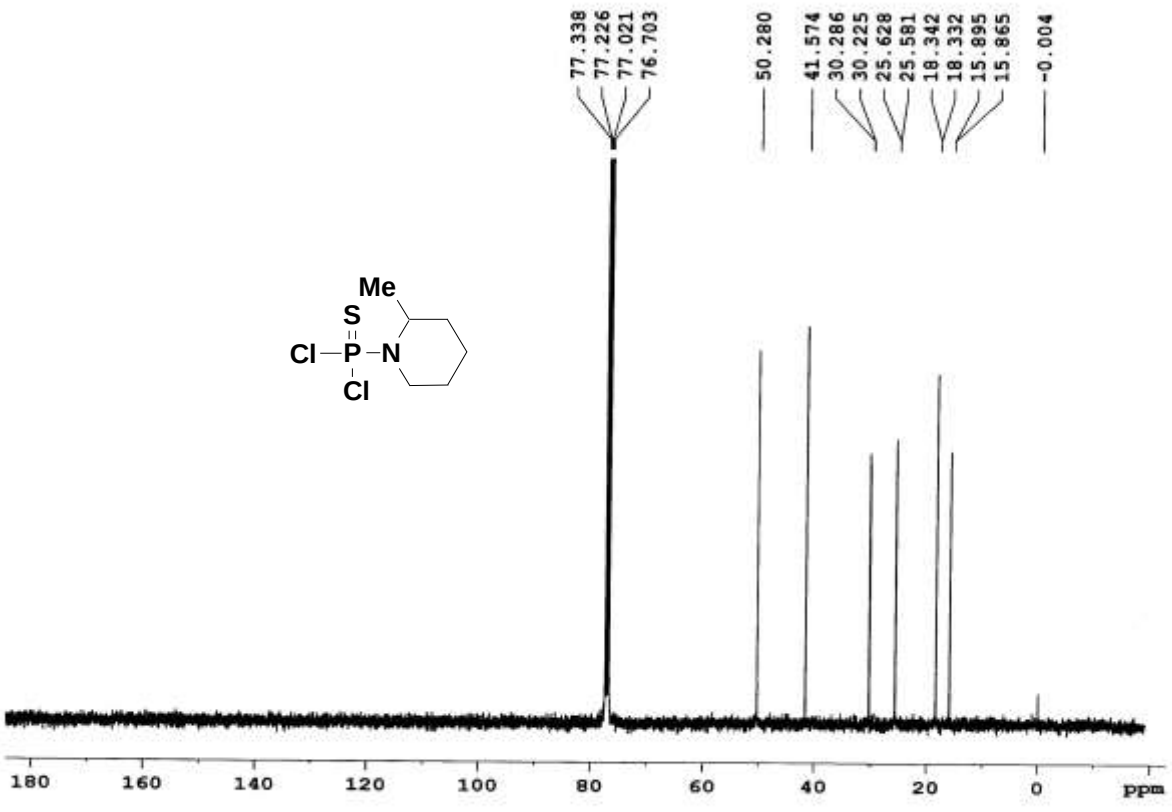


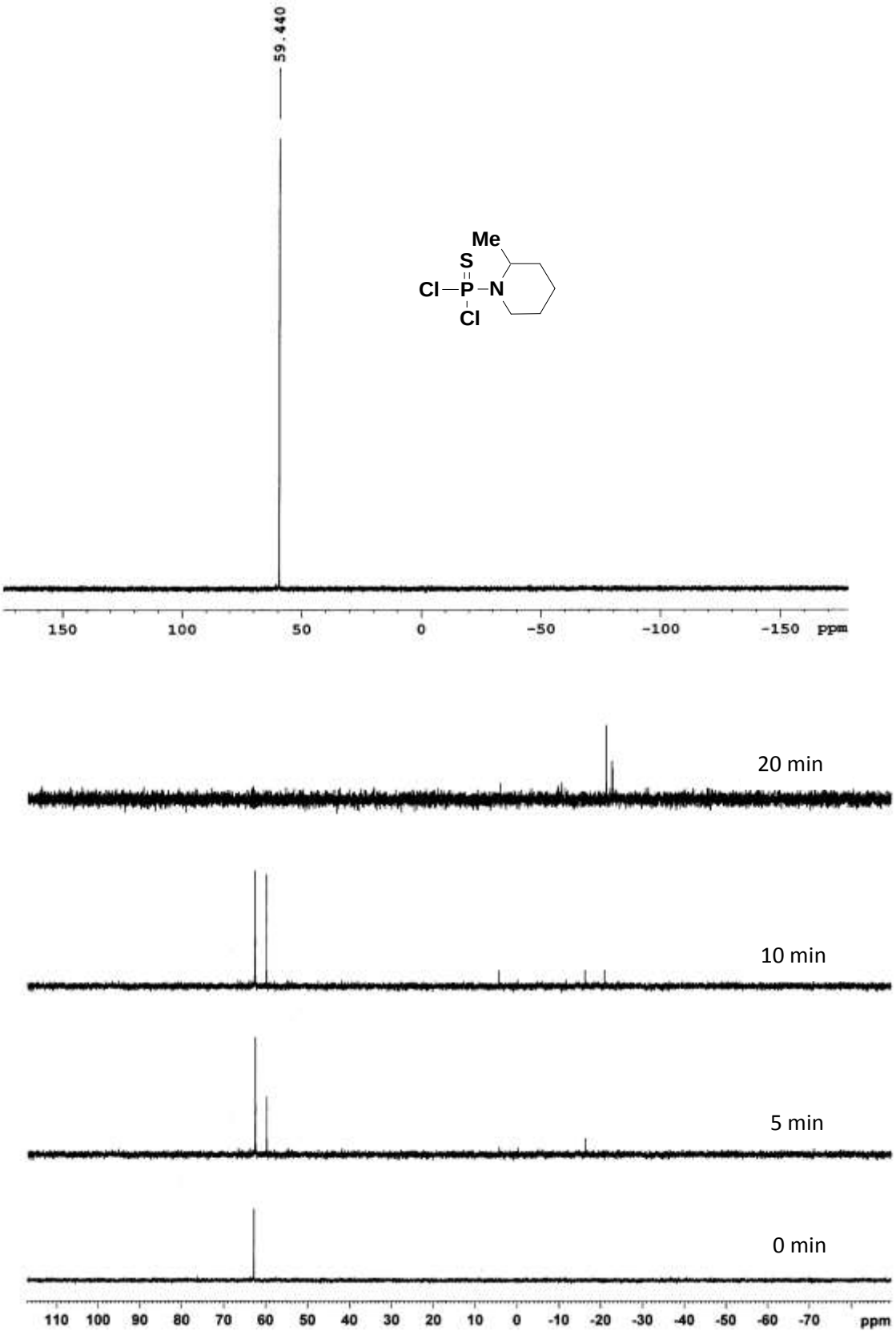




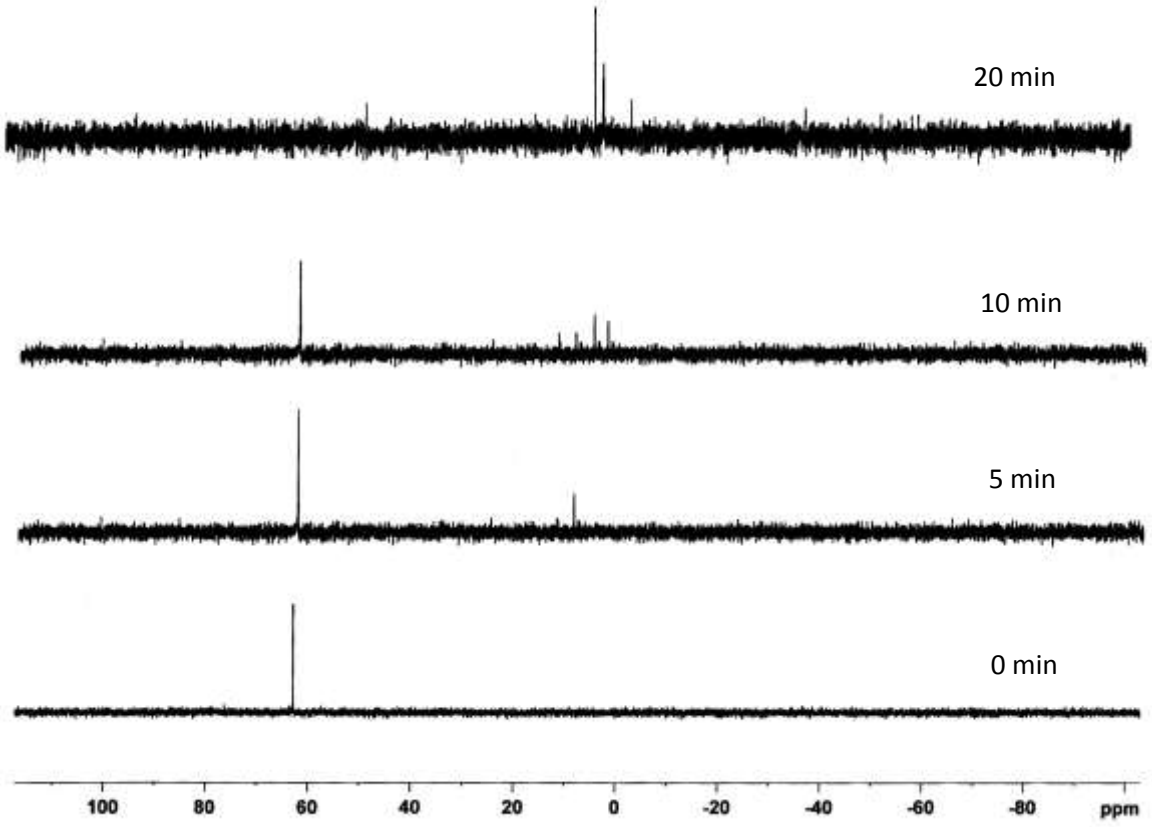








^{31}P NMR of *N*, *N*-dibutylchlorothiophosphoramidate/4-chlorobenzoic acid reaction



^{31}P NMR of *N*, *N*-dibutylchlorothiophosphoramidate/4-chlorobenzaldehyde reaction