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Acid-promoted Denitrogenative Pd-Catalyzed Addition of Arylhydrazines with Nitriles at Room Temperature

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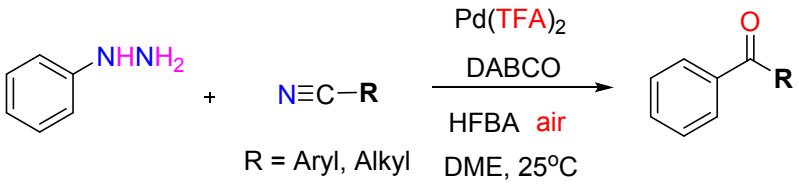
Supporting Materials

Content

General

Starting materials were purchased from common commercial sources and all solvents were purified and dried according to standard methods prior to use. Arylglyoxylic acids were prepared from corresponding aryl methyl ketone. ^{1}H NMR spectra were recorded on a 400 M Hz spectrometer using tetramethylsilane (TMS) as internal standard. Proton chemical shifts are reported in parts per million (ppm) relative to TMS. Multiplicities are reported as: singlet (s), doublet (d), triplet (t) and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. HRMS (EI) data were collected on High Resolution mass spectrometer (ion trap). Element analysis data were collected on elemental analyser (EuroVector, Italy, EA3000). Other substrates and catalysts were commercially available and used without additional purification.

Typical procedure for the product



A mixture of arylhydrazines (0.5 mmol), nitriles (0.5 mmol), $Pd(TFA)_2$ (5 mol%), DABCO (10 mol%), HFBA (0.5 mmol), was stirred at 25°C for 12 h in DME (1 mL). Afterward, the mixture was filtered through a pad of celite. The solvent was evaporated under reduced pressure, and the residue was subjected to flash column chromatography to obtain the desired product.

Characterization data of the product

(1) benzophenone (3a, 4a)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (82.8mg for 3a and 81.9mg for 4a). m.p. 47–49 ^{o}C (lit.[1] mp 47–48 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (d, J = 8.4 Hz, 4 H), 7.58 (t, J = 7.6 Hz, 2 H), 7.48 (t, J = 7.6 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.95, 137.60, 132.45, 130.09, 128.30. HRMS m/z (ESI) calcd for $C_{13}H_{11}O$ $[M+H]^+$ 183.0804, found 183.0800.

(2) 4-(dimethylamino)benzophenone (3b)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/10, v/v) afforded as a white solid (100.1mg). m.p. 92-93 ^{o}C (lit.[2] mp 93 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.80 (d, J = 7.2 Hz, 2 H), 7.72 (t, J = 6.8 Hz, 2 H), 7.52 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 6.67 (d, J = 7.6 Hz, 2 H), 3.06 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.17, 153.27, 139.30, 132.77, 131.15, 129.46, 128.04, 124.66, 110.53, 40.08. HRMS m/z (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1226, found 226.1223.

(3) 4-fluorobenzophenone (3c)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (90.0mg). m.p. 45–47 ^{o}C (lit.[4] mp 45–47 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (dd, J_1 = 8.4 Hz, J_2 = 5.2 Hz, 2 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.17 (t, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ195.31, 166.64 (d, J = 252 Hz), 137.48, 133.77, 132.74 (d, J = 9.0 Hz), 132.52, 129.90, 128.39, 115.57 (d, J = 21 Hz). HRMS m/z (ESI) calcd for $C_{13}H_{10}FO$ $[M+H]^+$ 201.0710, found 201.0703.

(4) 4-nitrobenzophenone (3d)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/3, v/v) afforded as a yellow solid (97.6mg). m.p. 141–142 ^{o}C (lit.[3] mp 140–142 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.35 (d, J = 7.6 Hz, 2 H), 7.94 (d, J = 7.6 Hz, 2

H), 7.82 (d, *J* = 7.6 Hz, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.79, 149.80, 142.88, 136.27, 133.48, 130.71, 130.11, 128.68, 123.54. HRMS (EI) Calcd for $C_{13}H_9NO_3$ (M^+) 227.0582, Found 227.0580. HRMS m/z (ESI) calcd for $C_{13}H_{10}NO_3$ $[M+H]^+$ 227.0582, found 227.0583.

(5) 4-benzoylbenzoic acid (3e)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 4/1/0.025, v/v/v) afforded as a white solid (83.8mg). m.p. 198–199 °C (lit.[7] mp 198–200 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.53 (br, 1 H), 8.24 (d, *J* = 8.4 Hz, 2 H), 7.88 (d *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 7.6 Hz, 2 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.01, 170.73, 142.15, 136.74, 133.12, 132.21, 130.16, 129.86, 128.52. HRMS m/z (ESI) calcd for $C_{14}H_{11}O_3$ $[M+H]^+$ 227.0703, found 227.0694.

(6) 3,4-dimethylbenzophenone (3f)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (92.4mg). m.p. 48–50 °C (lit.[8] mp 47–49 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, *J* = 8.0 Hz, 2 H), 7.64 (s, 1 H), 7.53-7.61 (m, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 2.36 (s, 3 H), 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.72, 141.99, 138.08, 136.75, 135.30, 132.11, 131.20, 129.94, 129.45, 128.19, 128.06, 20.05, 19.79. HRMS m/z (ESI) calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, found 211.1112.

(7) 3,4-dichlorobenzophenone (3g)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (100.4mg). m.p. 103–104 °C (lit.[9] mp 102–103 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (s, 1 H), 7.78 (d, *J* = 7.2 Hz, 2 H), 7.65 (t, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.22, 137.20, 137.01, 136.67, 133.01, 131.85, 130.46, 129.93, 129.08, 128.56. HRMS m/z (ESI) calcd for $C_{13}H_9Cl_2O$ $[M+H]^+$ 251.0025, found 251.0015.

(8) 4-methylbenzophenone (3h, 4c)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether =

1/20, v/v) afforded as a white solid (90.2mg for 3h and 88.2mg for 4c). m.p. 56–57 ^{o}C (lit.[3] mp 56–58 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 7.2 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.51, 143.26, 137.97, 134.89, 132.17, 130.34, 129.94, 128.99, 128.21, 21.67. HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961, found 197.0962.

(9) 3-methyl-benzophenone (3i)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as colorless oil (92.1mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.80 (d, *J* = 6.8 Hz, 2 H), 7.63 (s, 1 H) 7.58 (d, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.34-7.42 (m, 2 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.05, 138.18, 137.73, 137.60, 133.25, 132.39, 130.49, 130.08, 128.27, 128.11, 127.41, 21.40. HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961, found 197.0957.

(10) 2-methylbenzophenone (3j)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as colorless oil (82.3mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (d, *J* = 8.4 Hz, 2 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 1 H),7.23-7.34 (m, 3 H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.66, 138.63, 137.74, 136.77, 133.14, 131.00, 130.25, 130.14, 128.53, 128.47, 125.18, 20.01. HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961, found 197.0956.

(11) 2-benzoylthiophene (3k)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (78.0mg). m.p. 53–55 ^{o}C (lit.[6] mp 54–55 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.85 (t, *J* = 7.2 Hz, 2 H), 7.72 (d, *J* = 5.6 Hz, 1 H), 7.64 (d, *J* = 4.8 Hz, 1 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 7.16 (t, *J* = 4.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.25, 143.64, 138.16, 134.88, 134.23, 132.28, 129.18, 128.43, 127.98. HRMS m/z (ESI) calcd for $C_{11}H_9OS$ $[M+H]^+$ 189.0369, found 189.0363.

(12) 2-benzoylpyridine (3l)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a yellow solid (74.1mg). m.p. 42–43 ^{o}C (lit.[12] mp 42 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.73 (d, J = 4.8 Hz, 1 H), 8.02-8.08 (m, 3 H), 7.89 (t, J = 7.6 Hz, 1 H), 7.58 (d, J = 7.6 Hz, 1 H), 7.49 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.06, 155.07, 148.56, 137.08, 136.24, 132.94, 130.99, 128.19, 126.20, 124.63. HRMS m/z (ESI) calcd for $C_{12}H_{10}NO$ $[M+H]^+$ 184.0757, found 184.0749.

(13) 4-methoxy-benzophenone (4b)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (98.6mg). m.p. 57–58 ^{o}C (lit.[1] mp 58–59 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.83 (d, J = 8.4 Hz, 2 H), 7.75 (t, J = 7.6 Hz, 2 H), 7.56 (t, J = 7.6 Hz, 1 H), 7.47 (t, J = 7.6 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 3.88 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.60, 163.22, 138.25, 132.59, 131.94, 130.10, 129.75, 128.21, 113.56, 55.52. HRMS m/z (ESI) calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0910, found 213.0909.

(14) 4-bromo-benzophenone (4d)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (109.6mg). m.p. 78–80 ^{o}C (lit.[9] mp 79–80 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.77 (d, J = 8.4 Hz, 2 H), 7.58-7.69 (m, 5 H), 7.49 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.68, 137.13, 136.27, 132.72, 131.63, 131.60, 129.97, 128.44, 127.54. HRMS m/z (ESI) calcd for $C_{13}H_{10}{}^{79}BrO$ $[M+H]^+$ 260.9910, found 260.9907.

(15) 4-trifluoromethyl-benzophenone (4e)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/3, v/v) afforded as a yellow solid (107.5mg). m.p. 115–117 ^{o}C (lit.[3] mp 116–117 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (d, J = 8.0 Hz, 2 H), 7.81 (d, J = 7.2 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ195.56, 140.71, 136.71, 133.70 (dd, J_1 = 64.7 Hz, J_2 = 32.5 Hz), 133.12, 130.15 (d, J = 3.8 Hz), 128.55, 125.36(dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz), 123.70(d, J = 271.3 Hz). HRMS m/z (ESI) calcd for $C_{14}H_{10}F_3O$ $[M+H]^+$

251.0678, found 251.0674.

(16) 4-hydroxy-benzophenone (4f)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/15/0.08, v/v/v) afforded as a white solid (76.2mg). m.p. 133–135 ^{o}C (lit.[5] mp 133–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.81 (br, 1 H), 7.77 (d, *J* = 8.4 Hz, 4 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 6.93 (t, *J* = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.19, 161.05, 137.97, 133.24, 132.33, 129.94, 129.37, 128.32, 115.48. HRMS m/z (ESI) calcd for $C_{13}H_{11}O_2$ $[M+H]^+$ 199.0754, found 199.0749.

(17) 4-aminobenzophenone (4g)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether / acetic acid = 1/10/0.05, v/v/v) afforded as a yellow solid (71.9mg). m.p. 121–122 ^{o}C (lit.[6] mp 120–121 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.69-7.72 (m, 4 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 4.28 (br, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.47, 150.98, 138.86, 132.98, 131.49, 129.54, 128.13, 127.30, 112.78. HRMS m/z (ESI) calcd for $C_{13}H_{12}NO$ $[M+H]^+$ 198.0913, found 198.0910.

(18) 4-chloro-benzophenone (4h)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as colorless oil (92.1mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.67 (d, *J* = 6.4 Hz, 4 H), 7.60 (t, *J* = 7.2 Hz, 1 H), 7.56 (q, *J* = 8.0 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.58, 138.91, 137.20, 135.83, 132.69, 131.49, 129.95, 128.65, 128.42. HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $[M+H]^+$ 217.0415, found 217.0413.

(19) 3-chloro-benzophenone (4i)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (95.3mg). m.p. 85–86 ^{o}C (lit.[5] mp 85–87 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.79 (d, *J* = 7.6 Hz, 2 H), 7.78 (s, 1 H), 7.67 (d, *J* = 6.8 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.50 (t, *J* = 7.2 Hz, 2 H), 7.43 (t, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.31,

139.23, 136.92, 134.56, 132.88, 132.39, 130.05, 129.92, 129.66, 128.48, 128.14. HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $[M+H]^+$ 217.0415, found 217.0410.

(20) 2-chlorobenzophenone (4j)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (88.8mg). m.p. 44–46 ^oC (lit.[1] mp 43–45 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.41-7.49 (m, 4 H), 7.35-7.38 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.61, 138.61, 136.47, 133.72, 131.33, 131.15, 130.08, 129.13, 128.62, 126.70. HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $[M+H]^+$ 217.0415, found 217.0409.

(21) 2,3,4,5,6-pentamethyl-benzophenone (4k)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (61.7mg). m.p. 136–137 ^oC (lit.[10] mp 135–136 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 2.20 (s, 6 H), 2.02 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.98, 137.68, 135.56, 133.44, 132.91, 129.55, 129.03, 128.73, 17.57, 16.79, 15.98. HRMS m/z (ESI) calcd for $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found 253.1586.

(22) 2,3,4,5,6-perfluoro-benzophenone (4l)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (83.0mg). m.p. 34–35 ^oC (lit.[11] mp 33–34 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 7.6 Hz, 2 H), 7.70 (t, *J* = 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.33, 135.94, 135.04, 129.70, 129.11. HRMS m/z (ESI) calcd for $C_{13}H_5F_5O$ $[M+H]^+$ 273.0333, found 273.0331.

(23) 1-naphthyl-benzophenone (4m)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a white solid (95.1mg). m.p. 77–78 ^oC (lit.[3] mp 76–77 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.10 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 7.2 Hz, 1 H), 7.87 (d, *J* = 7.2 Hz, 2 H), 7.42-7.61 (m, 7 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.07, 138.30, 136.33, 133.73, 133.29, 131.32, 130.96,

130.45, 128.48, 128.44, 127.83, 127.30, 126.50, 125.70, 124.37. HRMS m/z (ESI) calcd for $C_{17}H_{13}O$ $[M+H]^+$ 233.0961, found 233.0961.

(24) 3-benzoylpyridine (4n)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) afforded as a yellow solid (76.9mg). m.p. 40–41 ^oC (lit.[12] mp 40-41 °C); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ8.99 (s, 1 H), 8.81 (d, *J* = 4.8 Hz, 1 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 7.44-7.83 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.85, 152.83, 150.91, 137.17, 136.63, 133.17, 133.10, 130.00, 128.60, 123.35. HRMS m/z (ESI) calcd for $C_{12}H_{10}NO$ $[M+H]^+$ 184.0757, found 184.0750.

(25) propiophenone (4o)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/50, v/v) afforded as colorless liquid (36.2mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.90 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 2.93 (q, *J* = 7.2 Hz, 2 H), 1.15 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.62, 136.86, 132.81, 128.48, 127.90, 31.69, 8.16. HRMS m/z (ESI) calcd for $C_9H_{11}O$ $[M+H]^+$ 135.0804, found 135.0802.

(26) pentanophenone (4p)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/50, v/v) afforded as colorless liquid (53.5mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.94 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 2.95 (t, *J* = 7.6 Hz, 2 H), 1.67-1.75 (m, 2 H), 1.37-1.43 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.47, 137.05, 132.84, 128.52, 128.01, 38.29, 26.45, 22.48, 13.94. HRMS m/z (ESI) calcd for $C_{11}H_{15}O$ $[M+H]^+$ 163.1117, found 163.1109.

(27) isobutyrophenone (4q)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/50, v/v) afforded as colorless liquid (55.5mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 7.6 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 3.55 (m, 1 H), 1.21 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.38, 136.16, 132.77, 128.58, 128.28, 35.29, 19.12. HRMS m/z (ESI) calcd for $C_{10}H_{13}O$ $[M+H]^+$

149.0961, found 149.0957.

(28) cyclopentyl(phenyl)methanone (4r)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/50, v/v) afforded as colorless liquid (69.6mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 3.66-3.75 (m, 1 H), 1.86-1.94 (m, 4 H), 1.60-1.77 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.75, 136.90, 132.69, 128.49, 128.44, 46.33, 29.96, 26.32. HRMS m/z (ESI) calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1117, found 175.1109.

(29) benzoylacetone (4s)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/30, v/v) afforded as colorless liquid (20.3mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.87 (d, *J* = 7.2 Hz, 2 H), 7.51 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 6.17 (s, 2 H), 2.19 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.78, 183.34, 134.88, 132.29, 128.83, 128.61, 127.00, 96.70, 25.84. HRMS m/z (ESI) calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0754, found 163.0749.

(30) 1,2-diphenylethanone (4t)

Purification by column chromatography (sila gel, ethyl acetate / petroleum ether = 1/20, v/v) afforded as a white solid (81.3mg). m.p. 55–56 ^{o}C (lit.[13] mp 55–56 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.01 (d, *J* = 7.8 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 7.22-7.34 (m, 5 H), 4.28 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.64, 136.62, 134.57, 133.19, 129.50, 128.70, 128.67, 128.64, 126.91, 45.52. HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961, found 197.0962.

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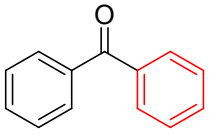
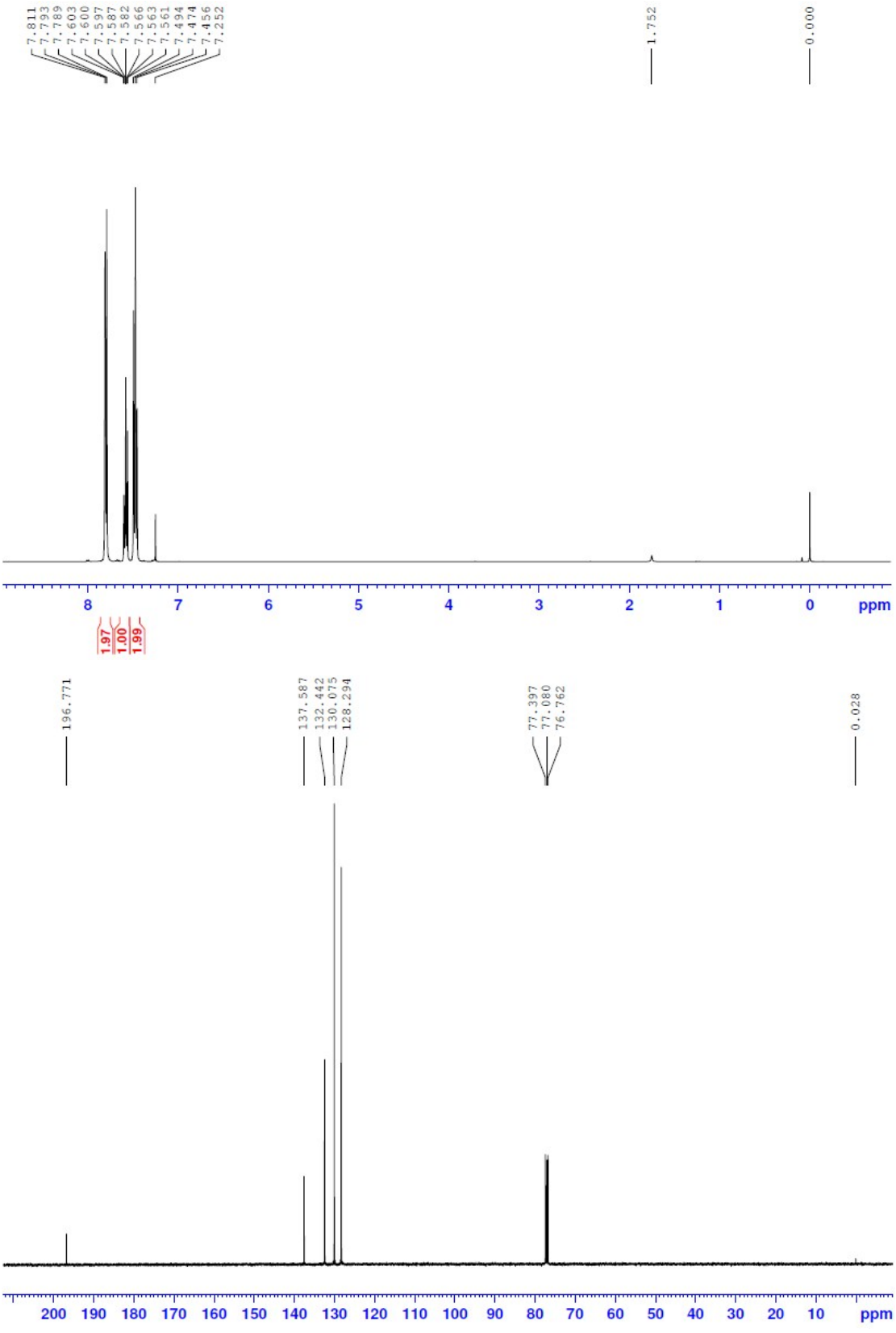
(1) benzophenone 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7.600
7.597
7.587
7.582
7.566
7.563
7.561
7.494
7.474
7.456
7.252
1.752
0.000
8
7
6
5
4
3
2
1
0
ppm
1.97
1.00
1.99
196.771
137.587
132.442
130.075
128.294
77.397
77.080
76.762
0.028
200
190
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150
140
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120
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90
80
70
60
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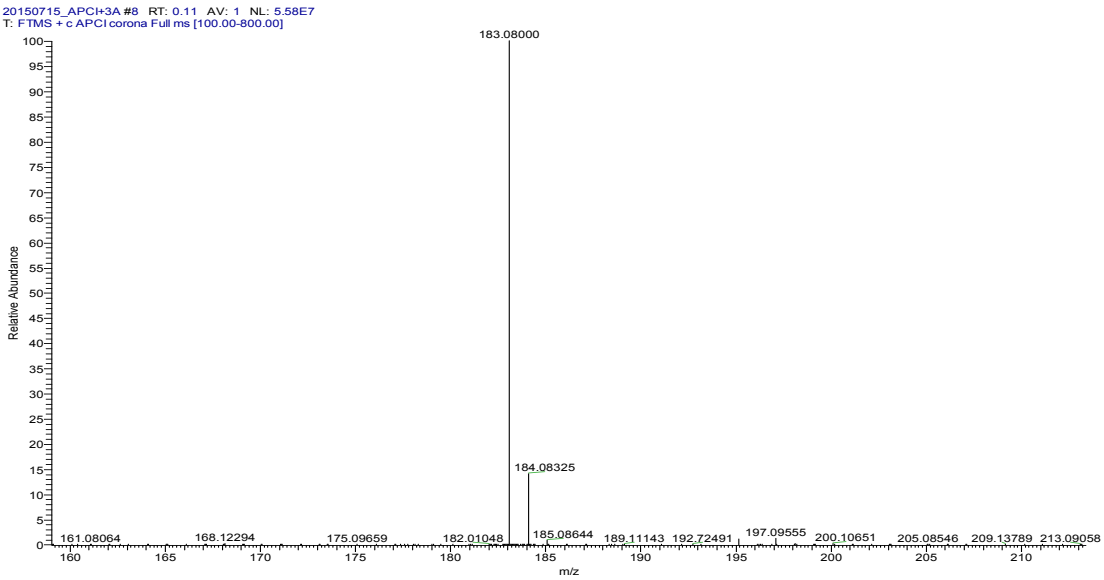
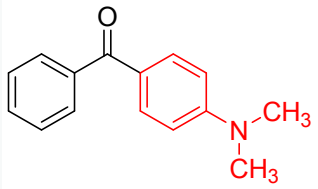
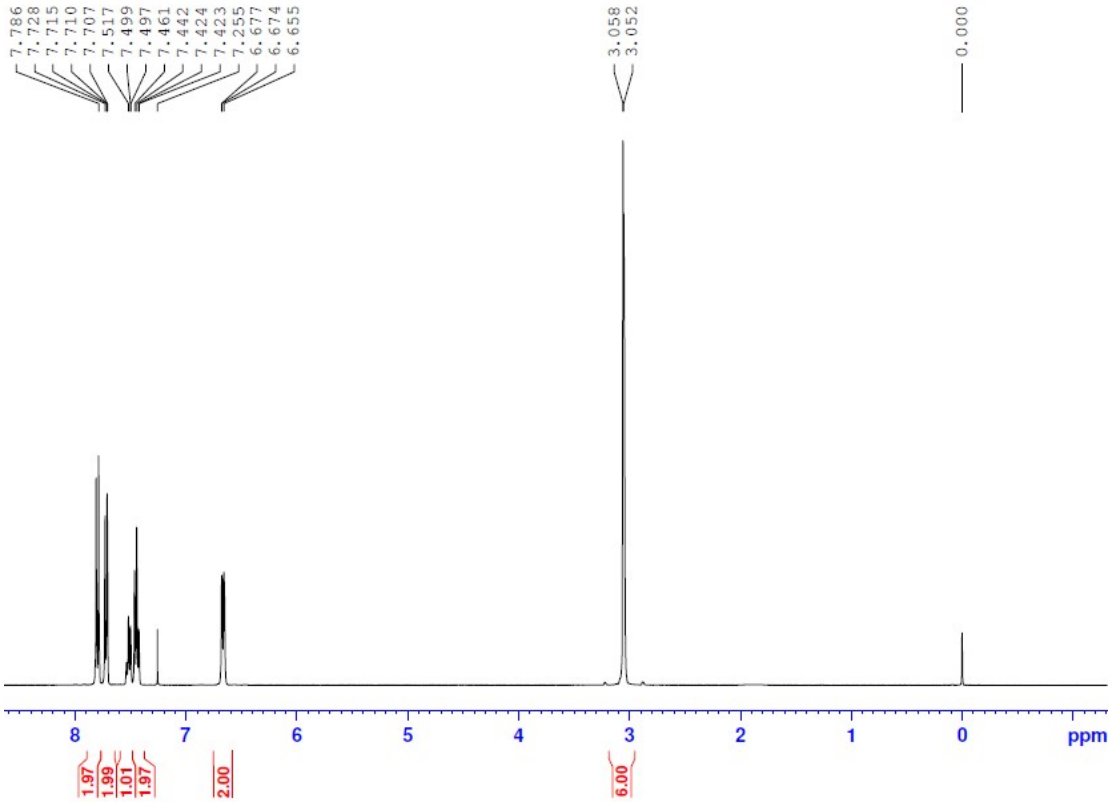
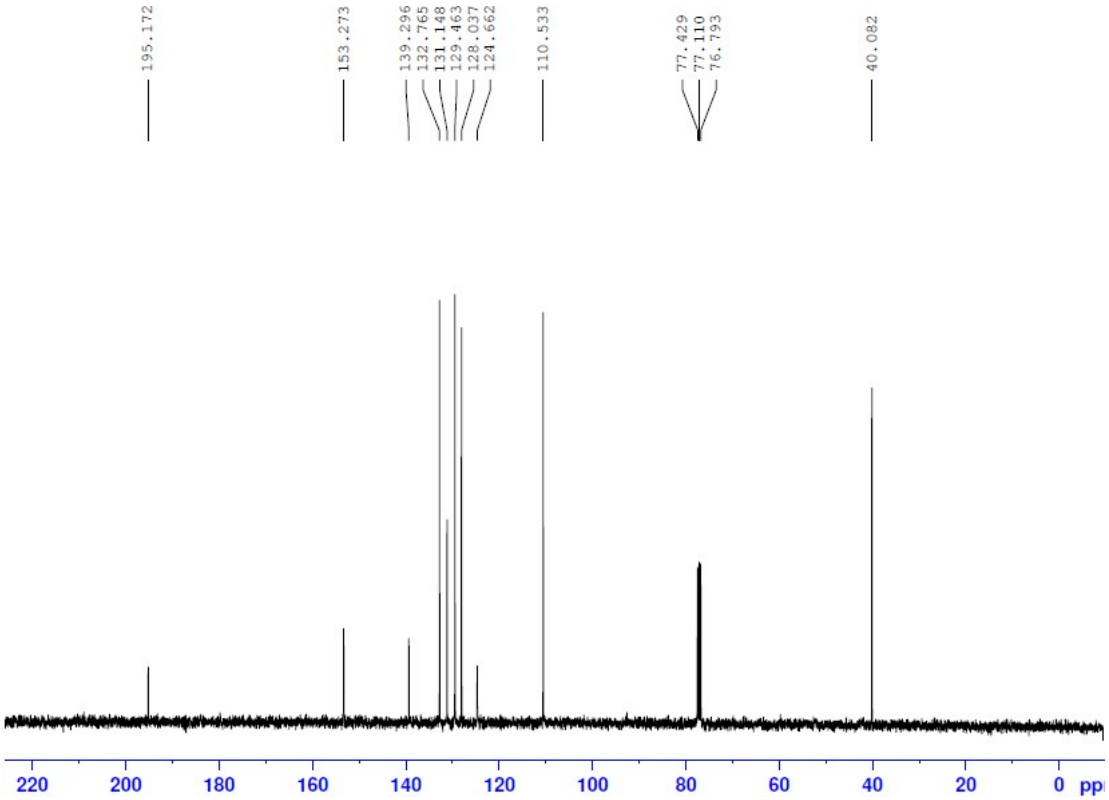
40
30
20
10
ppm

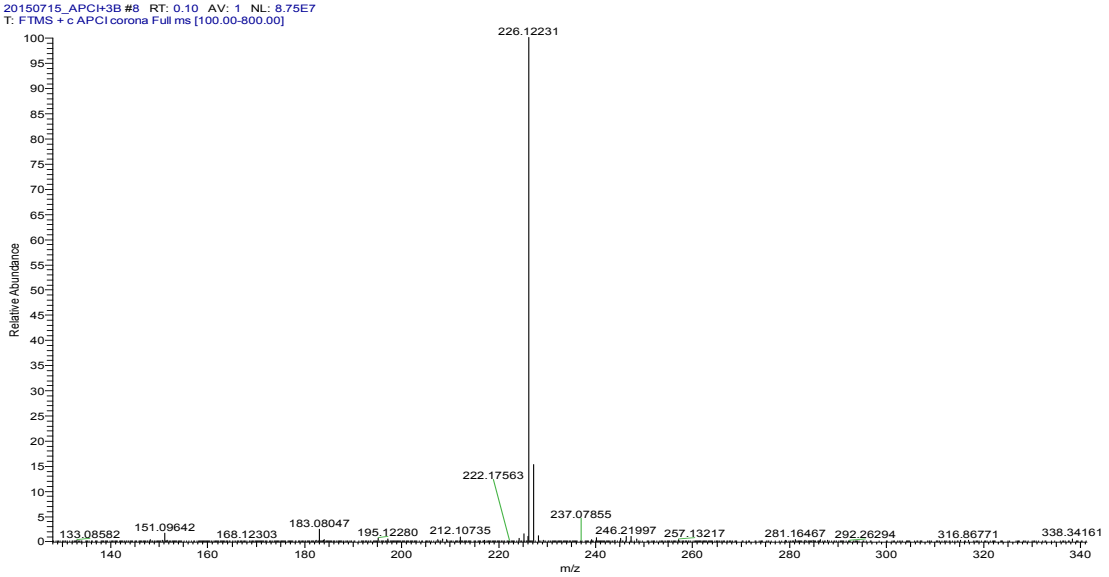




(2) 4-(dimethylamino)benzophenone







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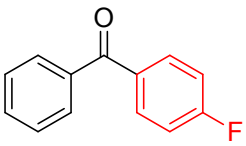

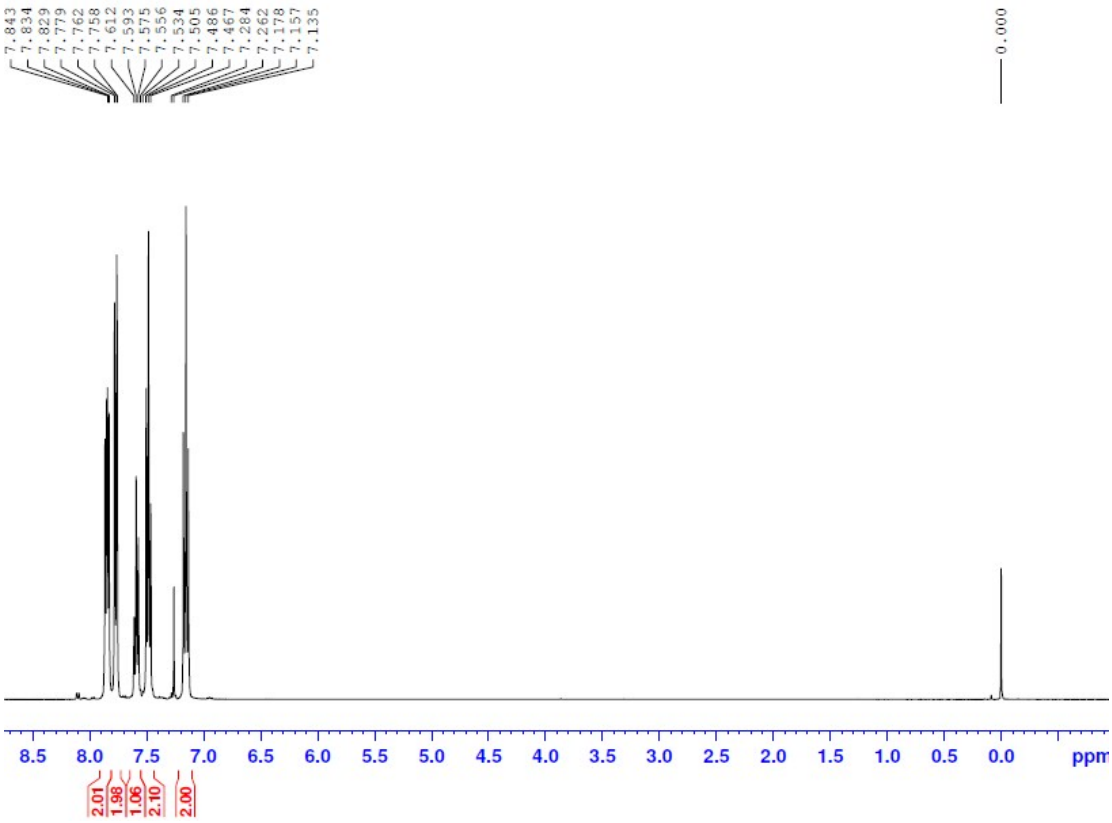
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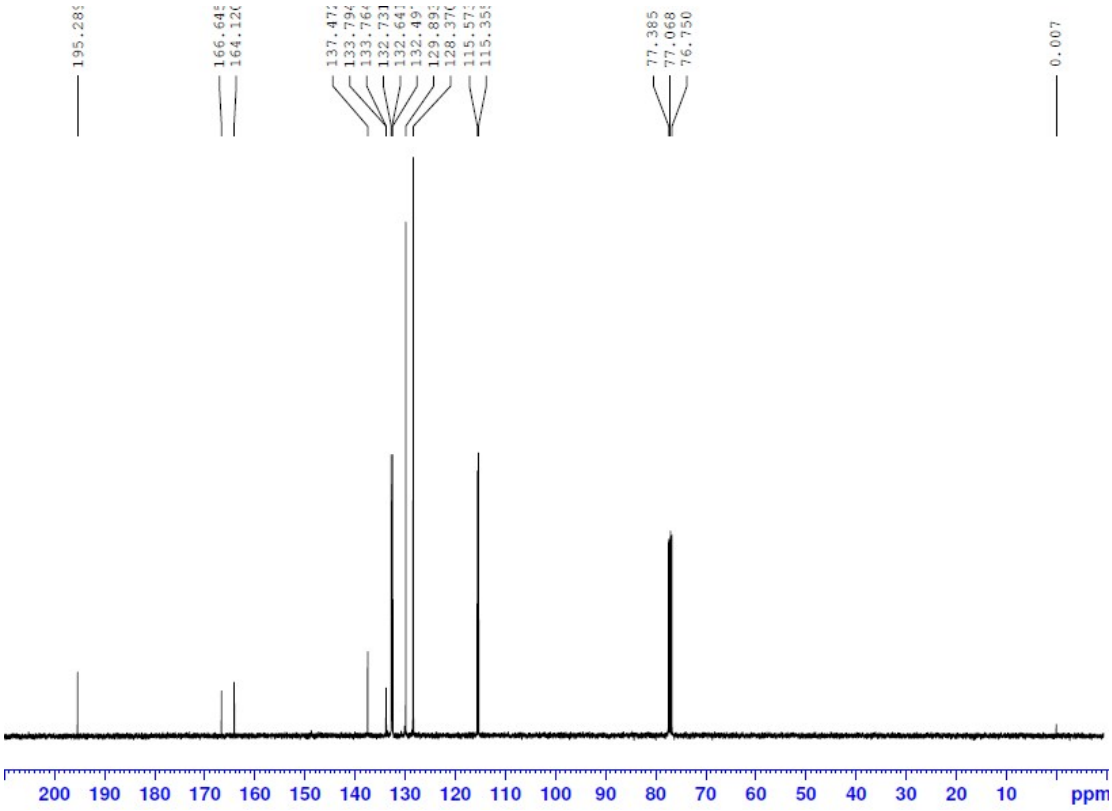
7.575
7.556
7.534
7.505
7.486
7.467
7.284
7.262
7.178
7.157
7.135
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
1.98
1.06
2.10
2.00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164.12
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133.79
133.76
132.73
132.64
132.49
129.89
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115.35
77.385
77.068
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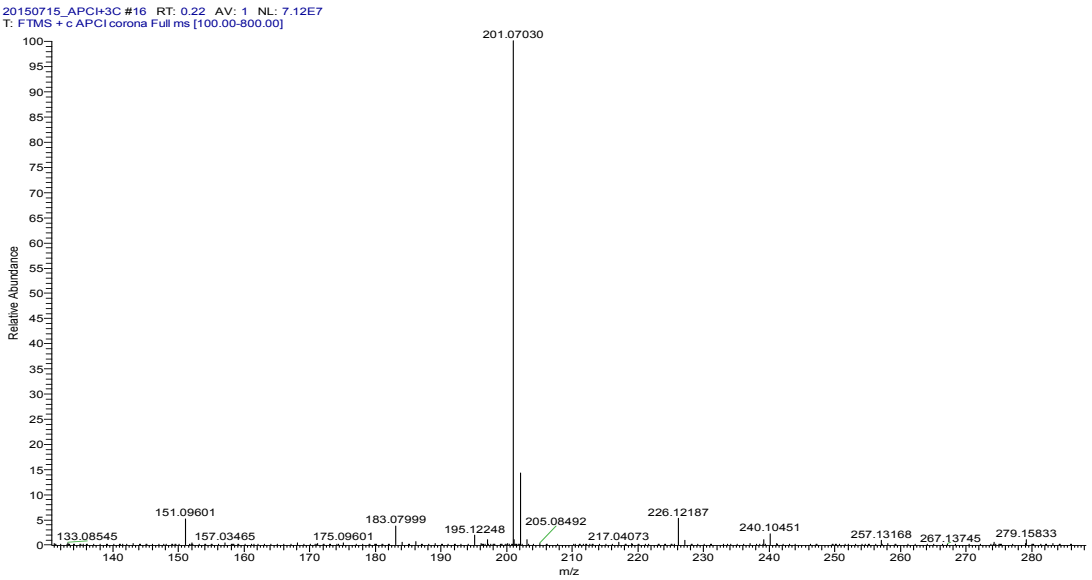
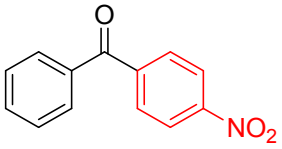
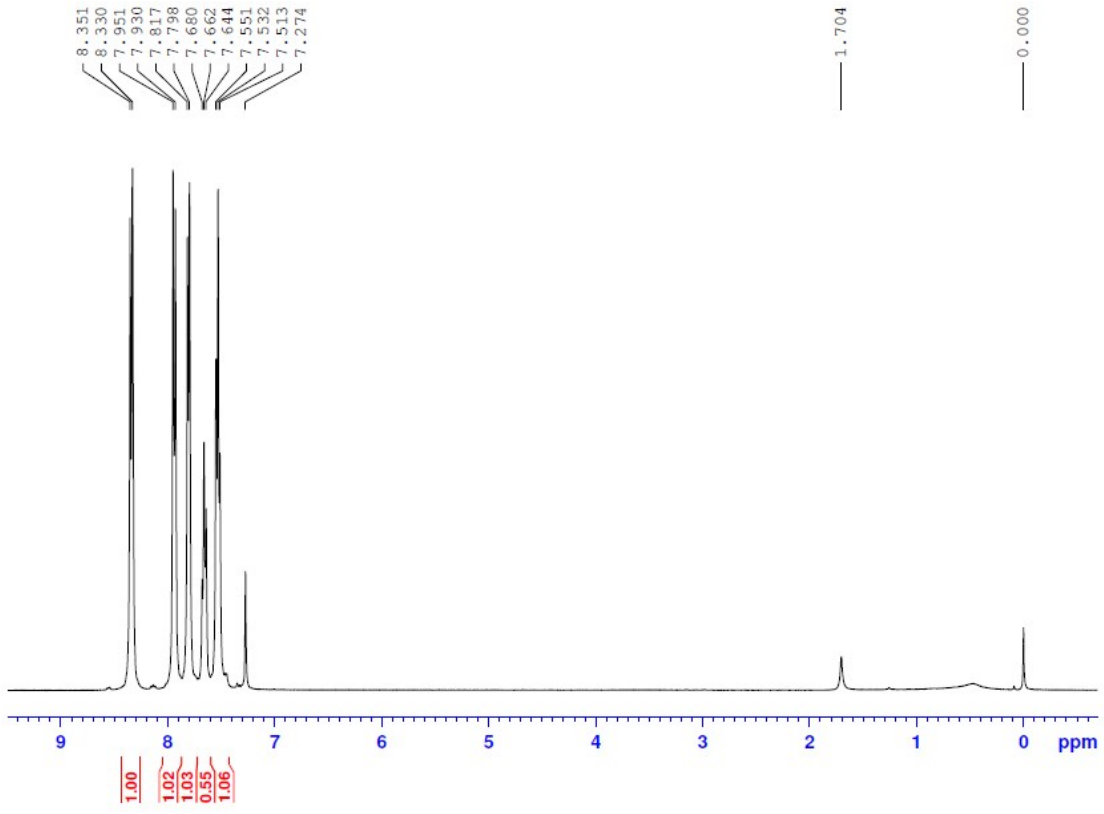
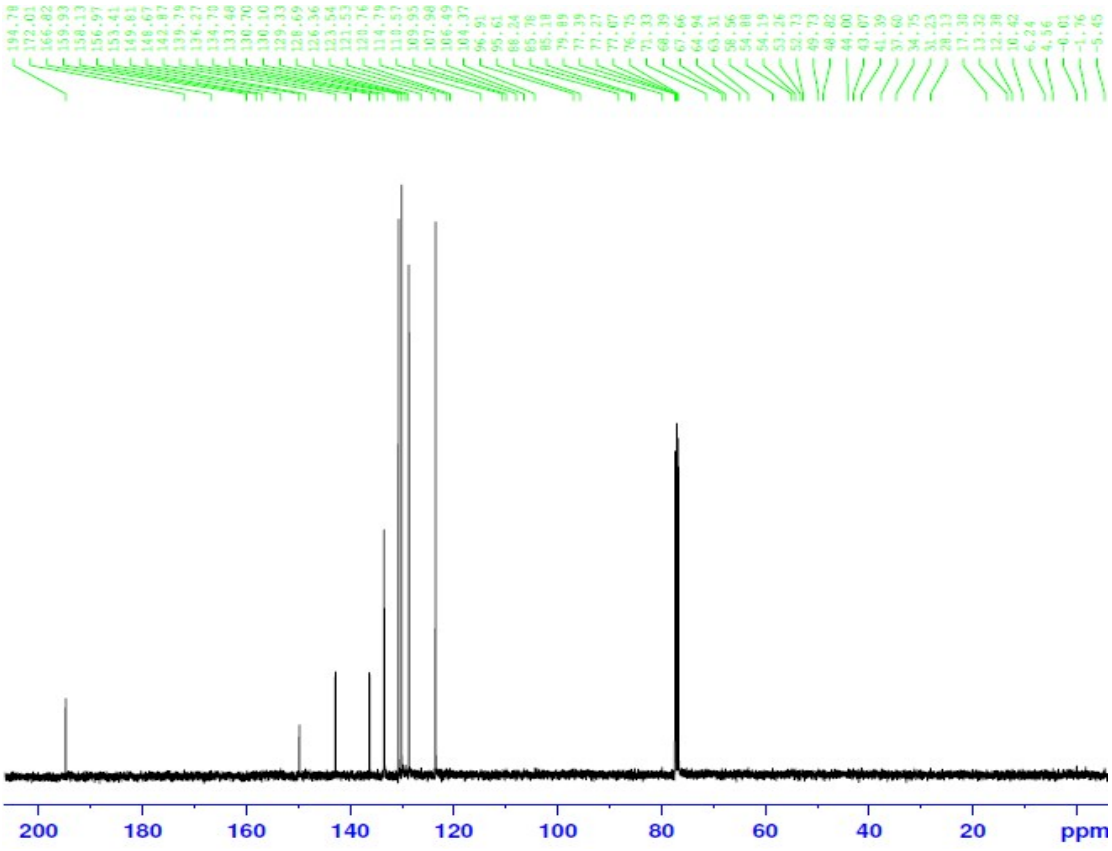
0.007
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

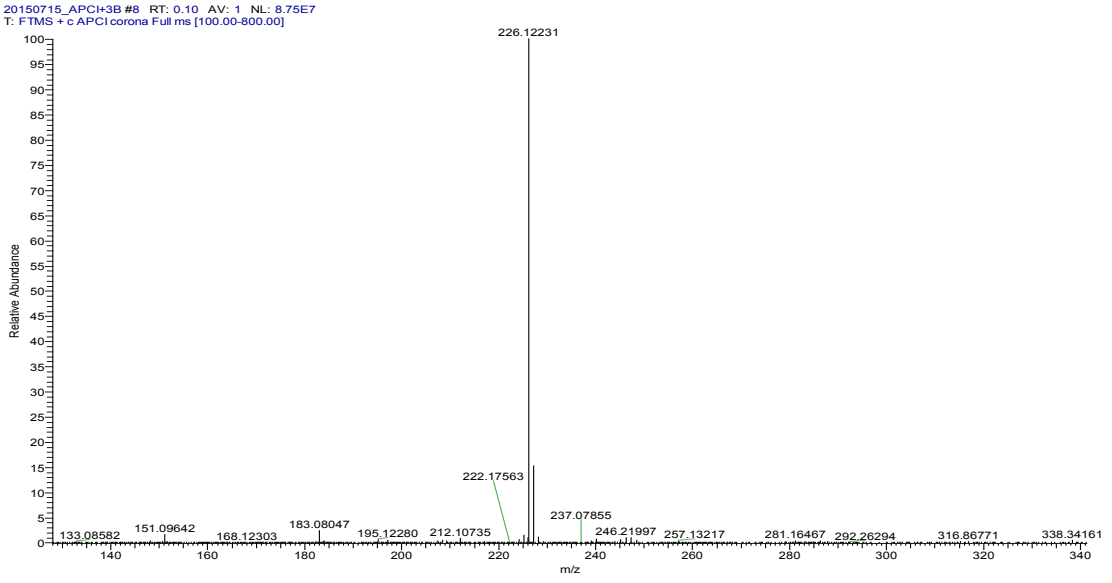




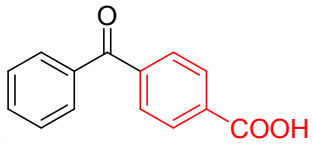
(4) 4-nitrobenzophenone

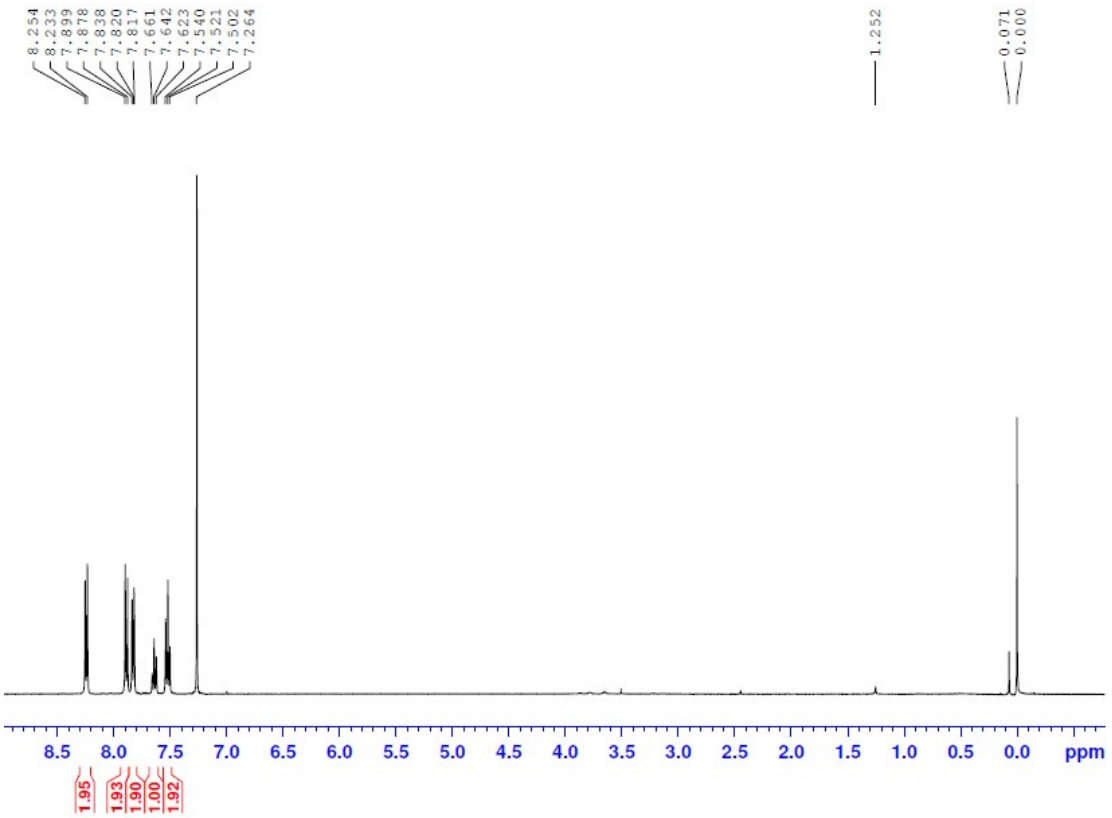






(5) 4-benzoylbenzoic acid

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7.540
7.521
7.502
7.264
1.252
0.071
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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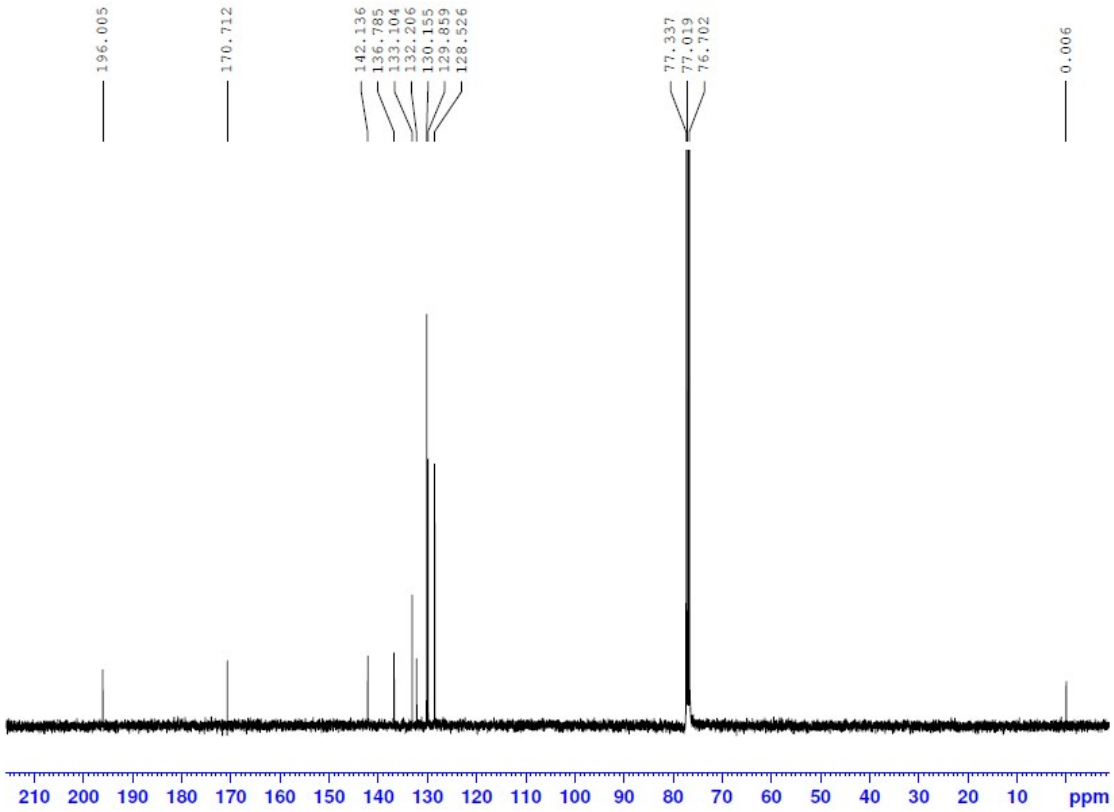
1.92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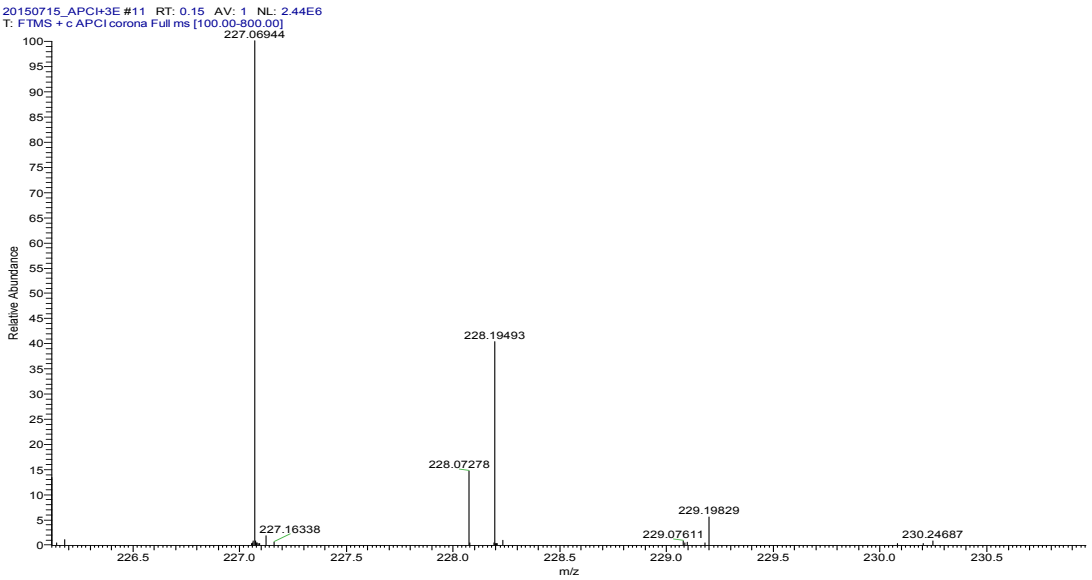
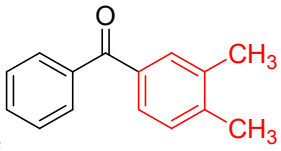
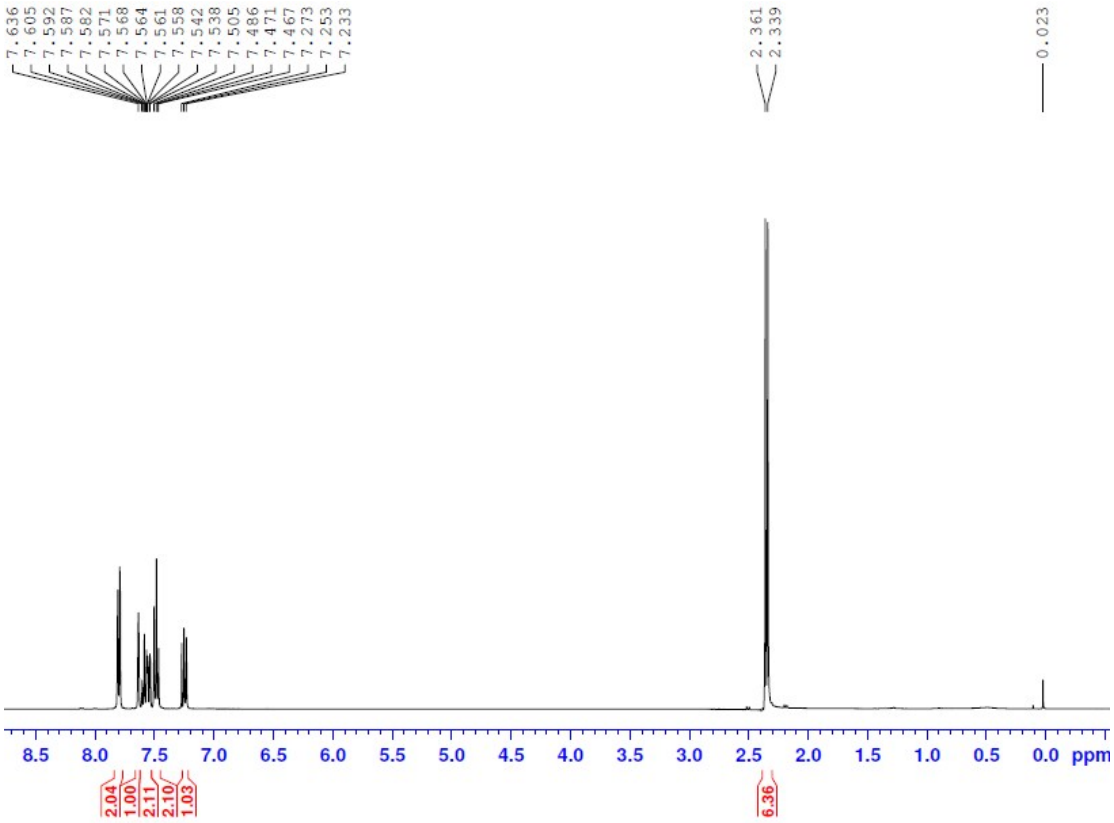
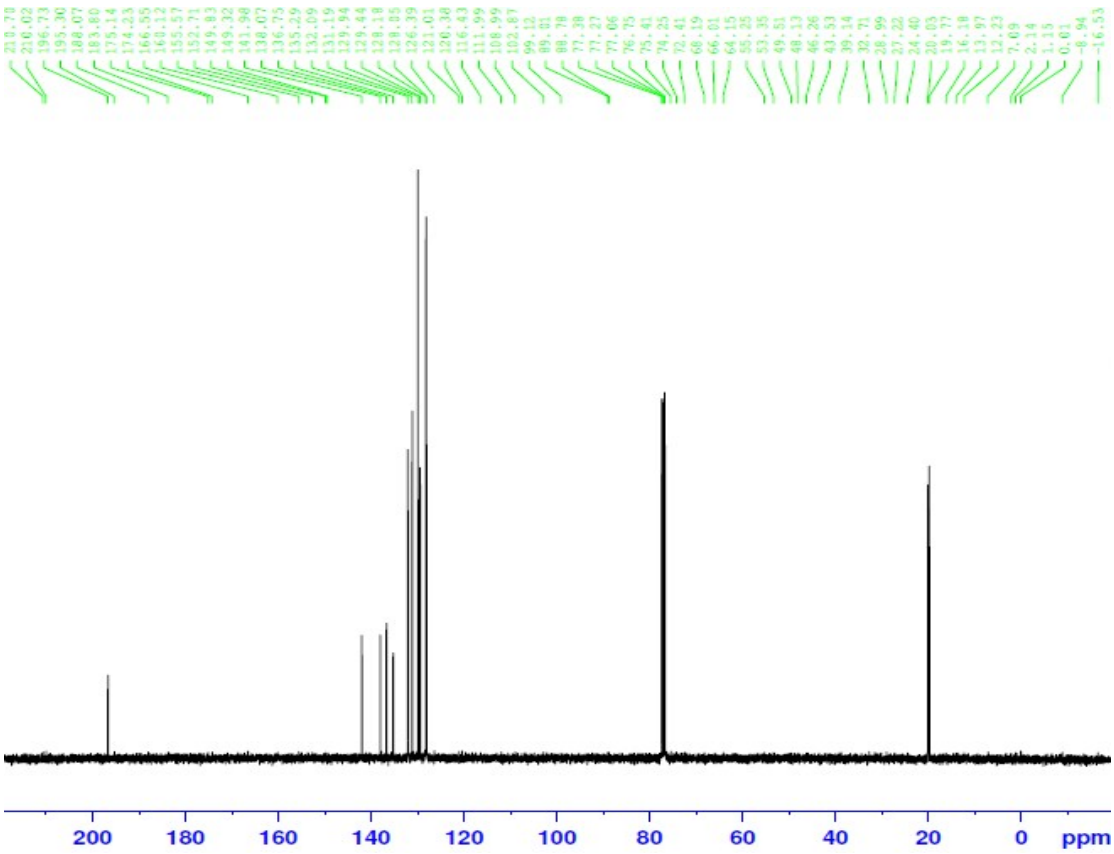
0.006
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

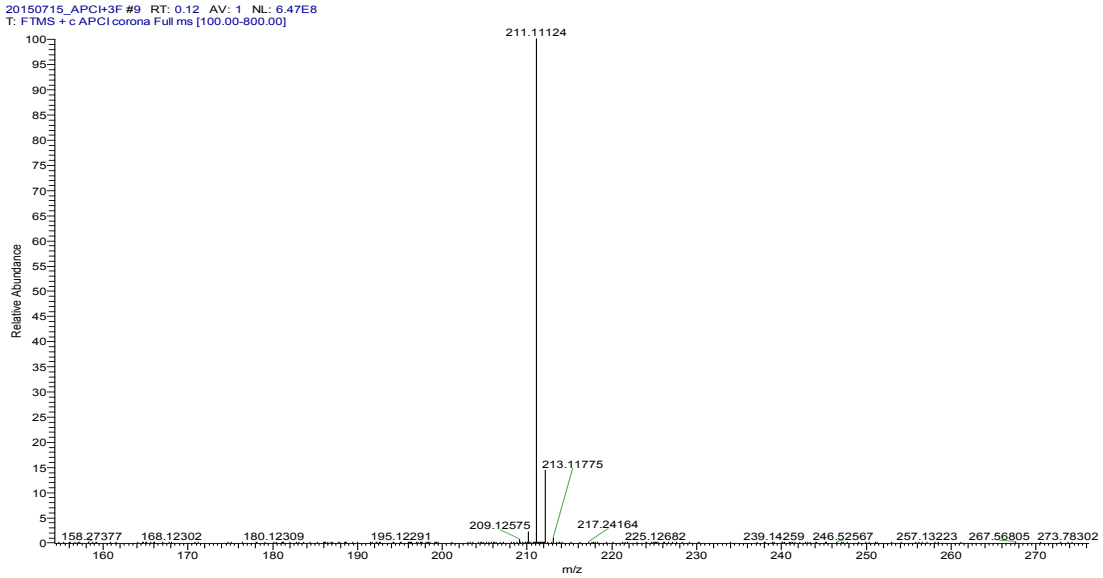




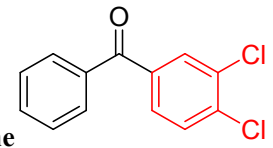
(6) 3,4-dimethylbenzophenone

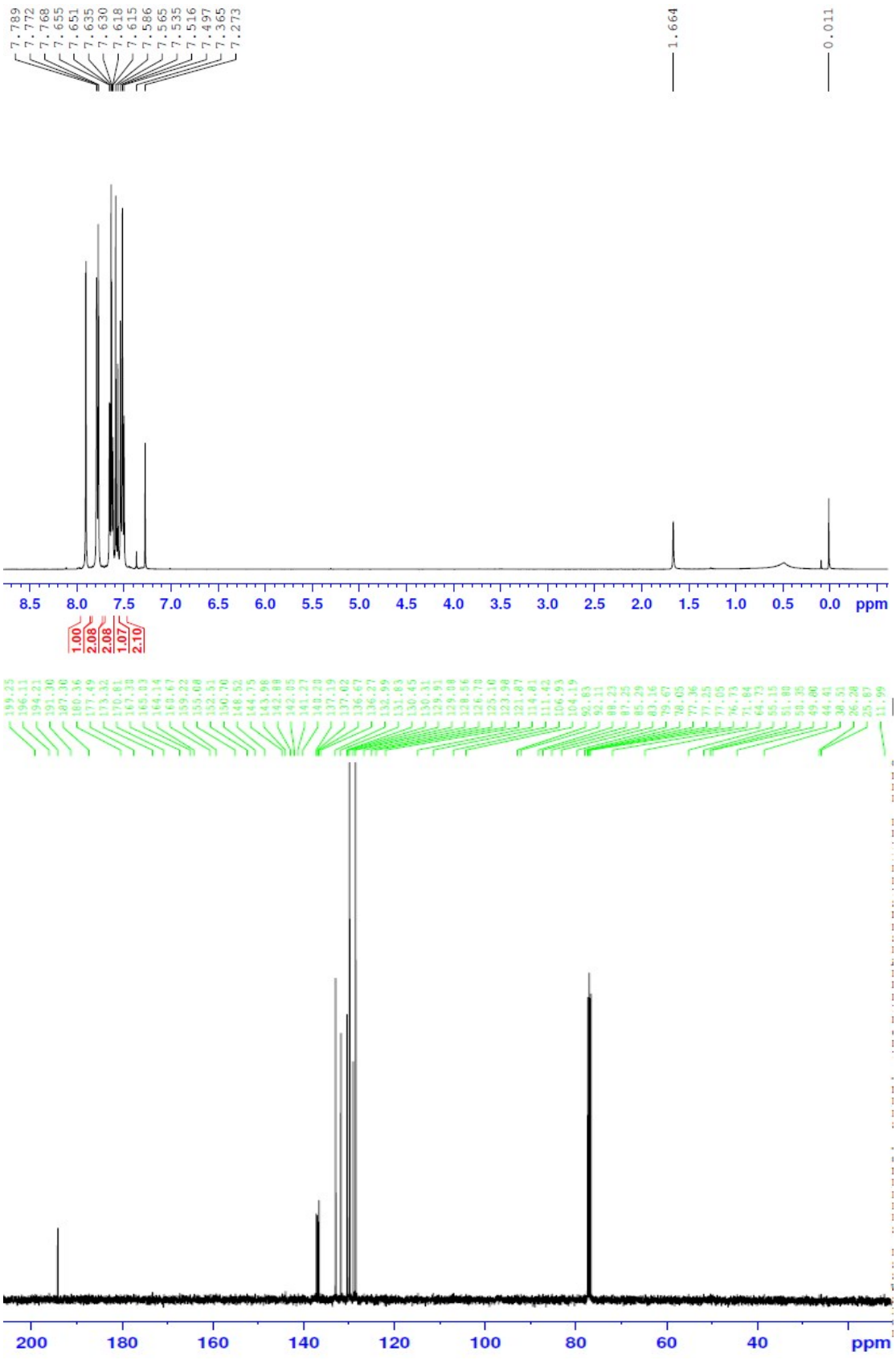






(7) 3,4-dichlorobenzophenone

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7.516
7.497
7.365
7.273
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0.011
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8.0
7.5
7.0
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6.0
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3.0
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1.5
1.0
0.5
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ppm
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140
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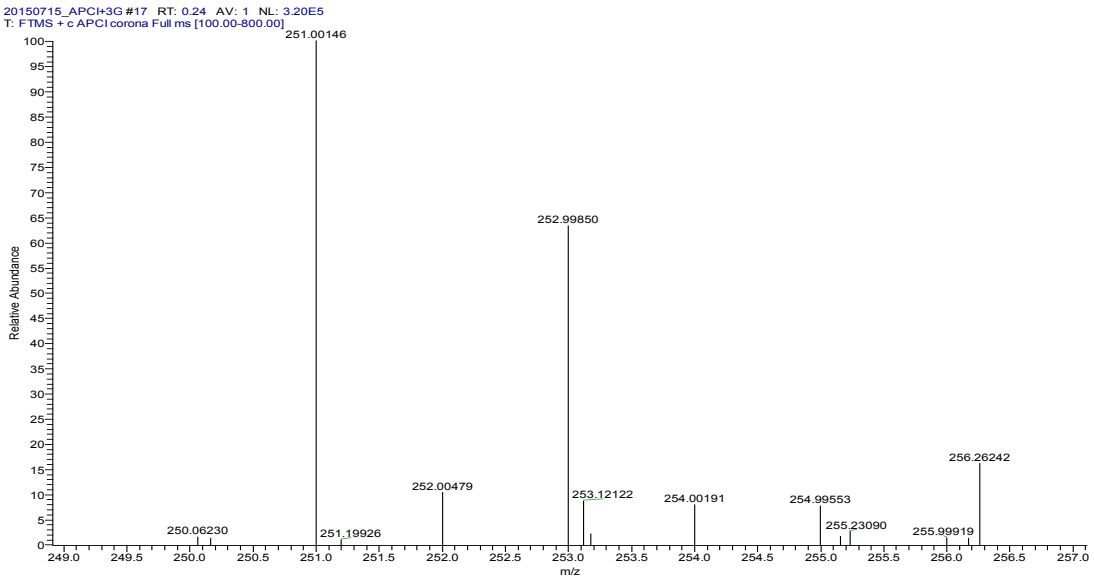
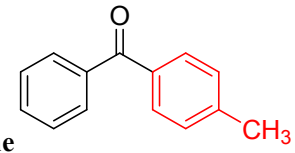
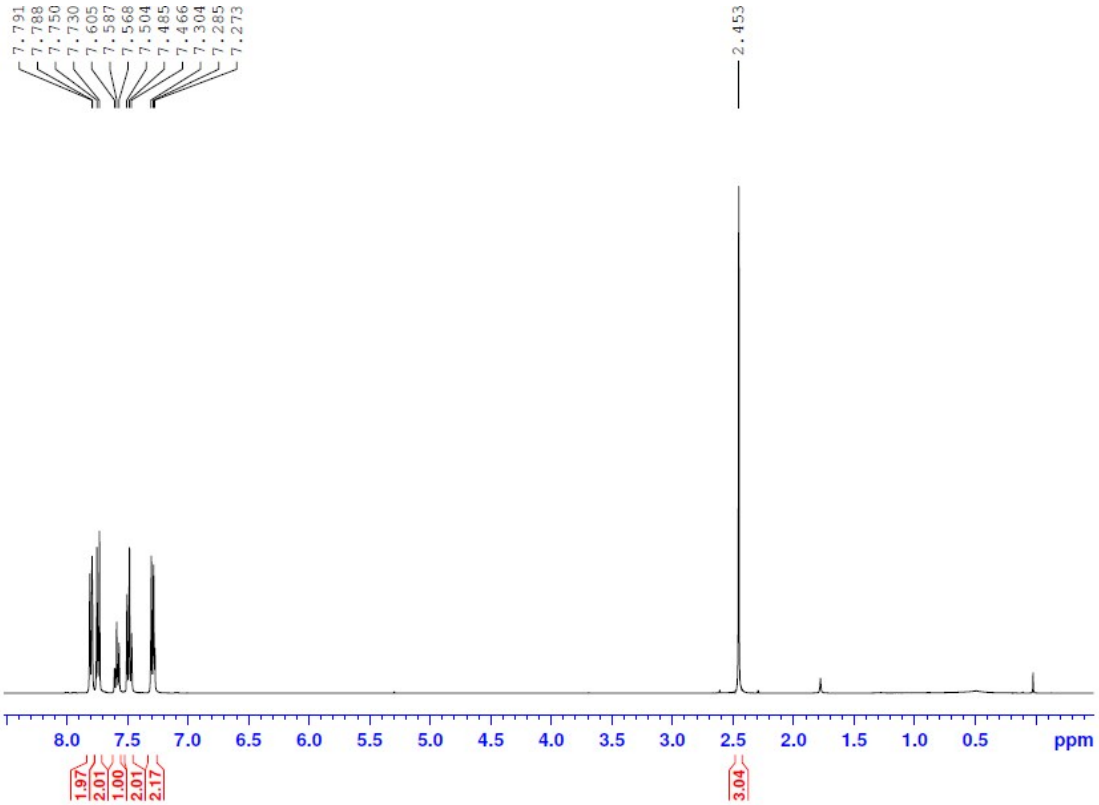
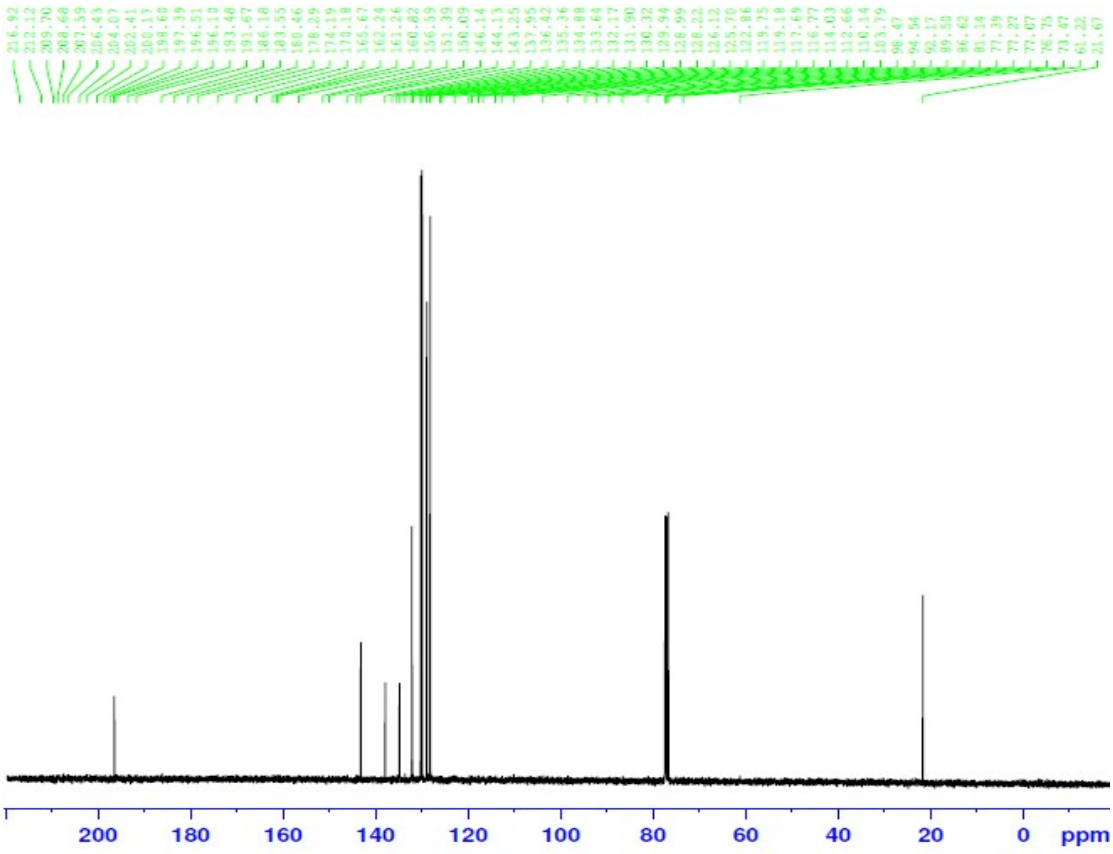
80
60
40
ppm

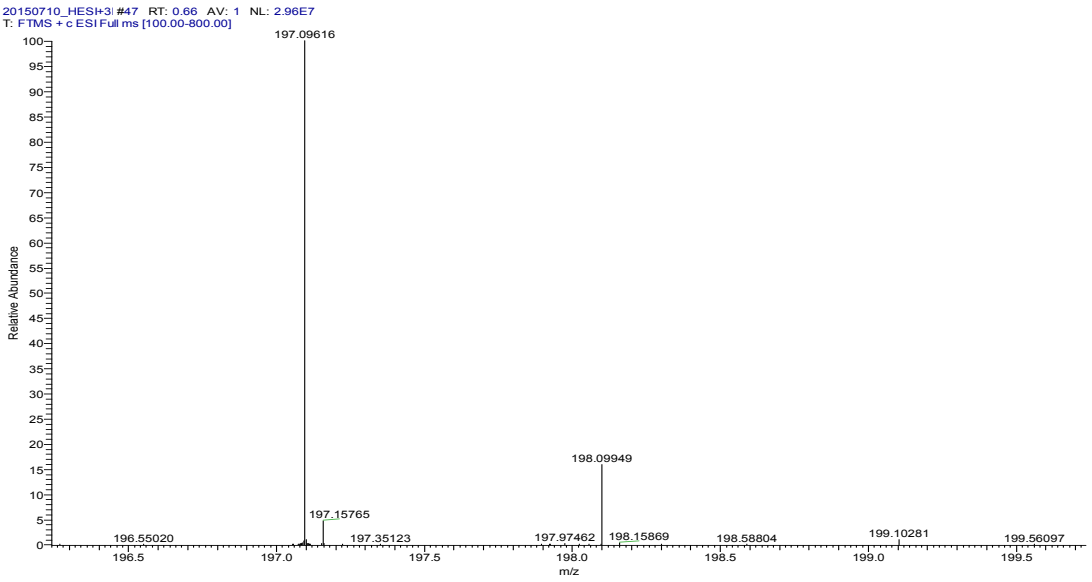




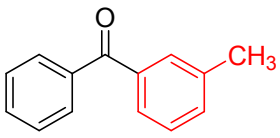
(8) 4-methylbenzophenone

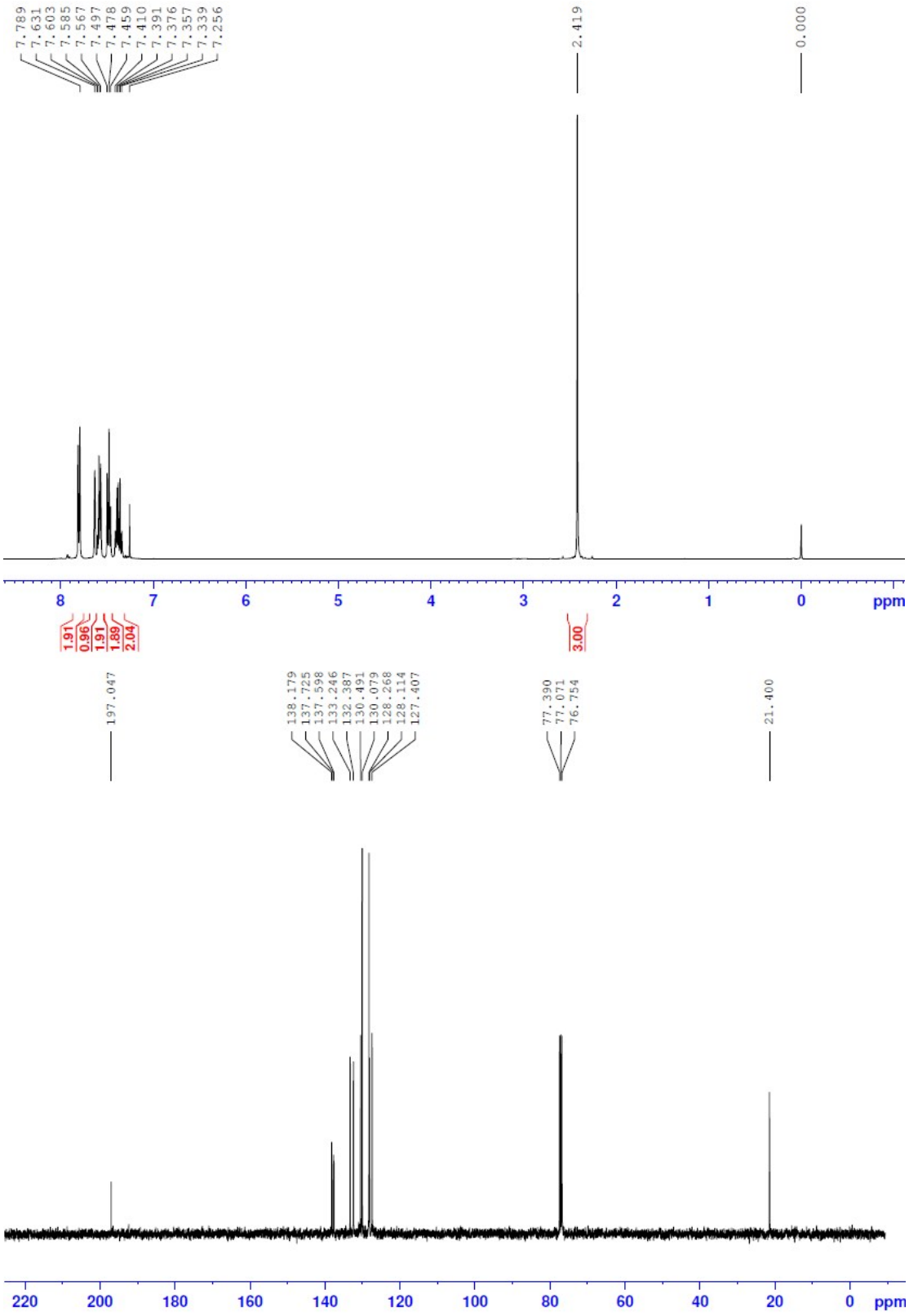






(9) 3-methyl-benzophenone

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7.339
7.256
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8
7
6
5
4
3
2
1
0
ppm
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0.96
1.91
1.89
2.04
3.00
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130.079
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128.114
127.407
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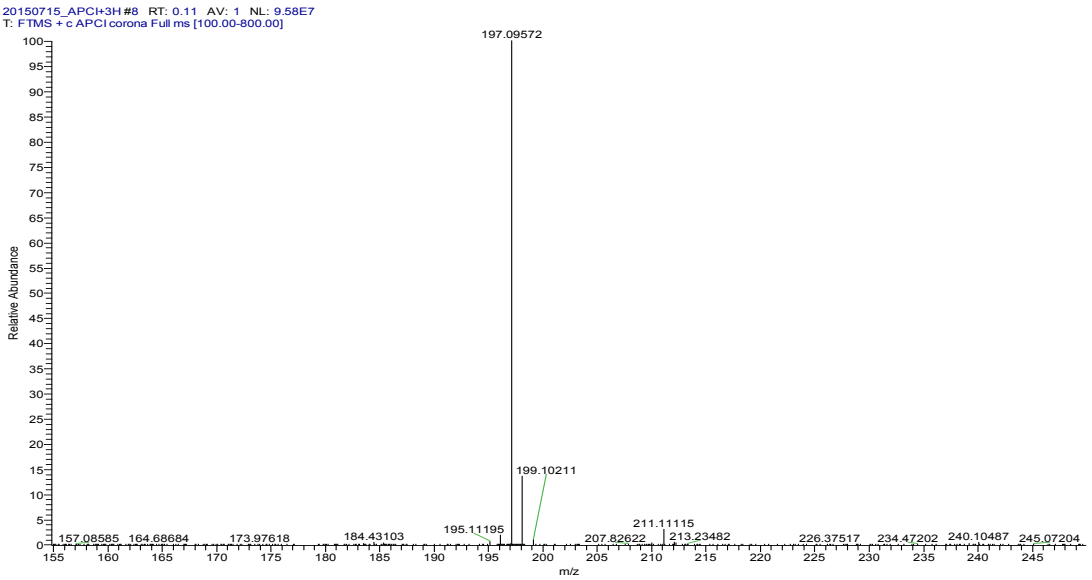
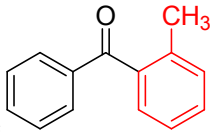
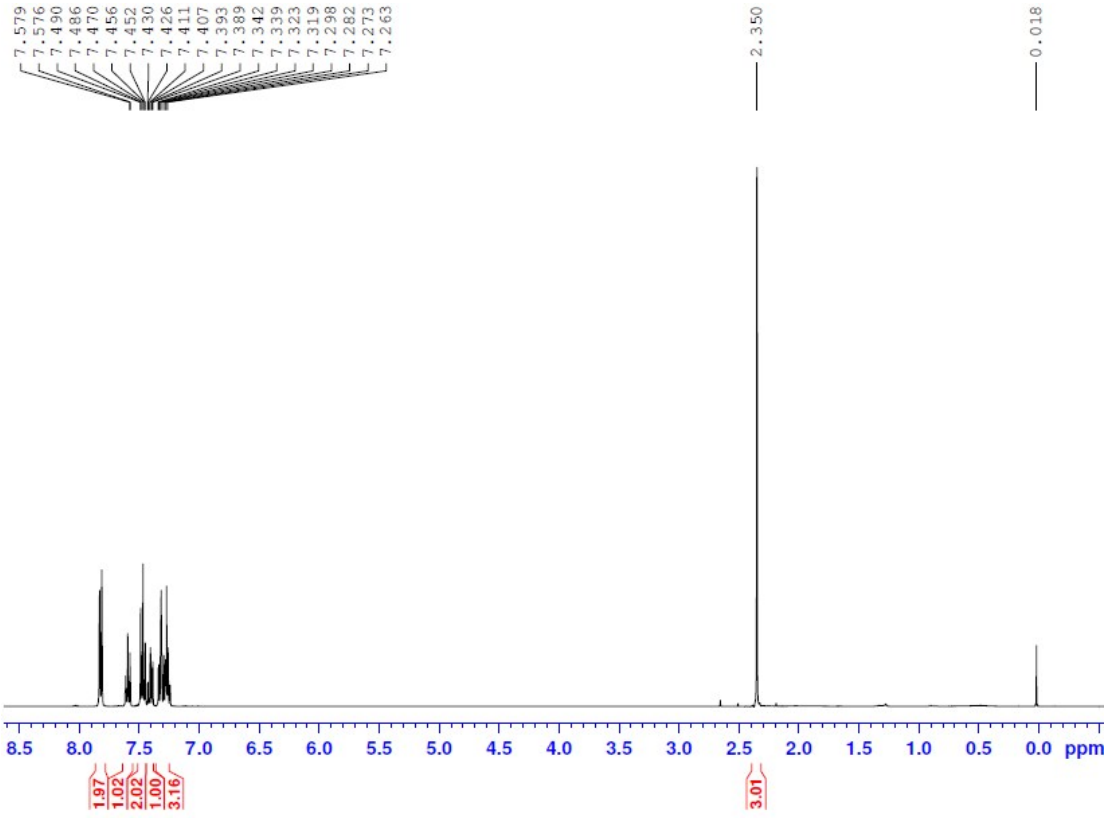
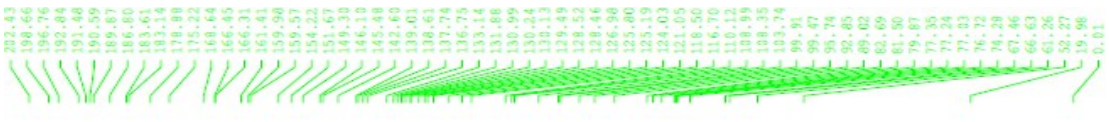
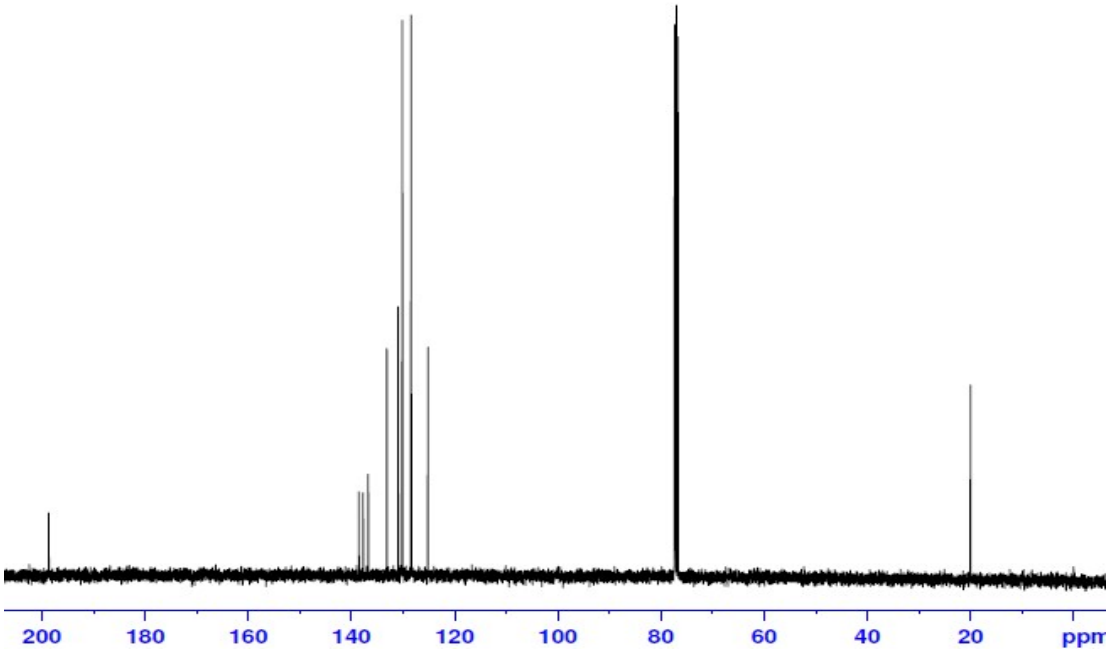


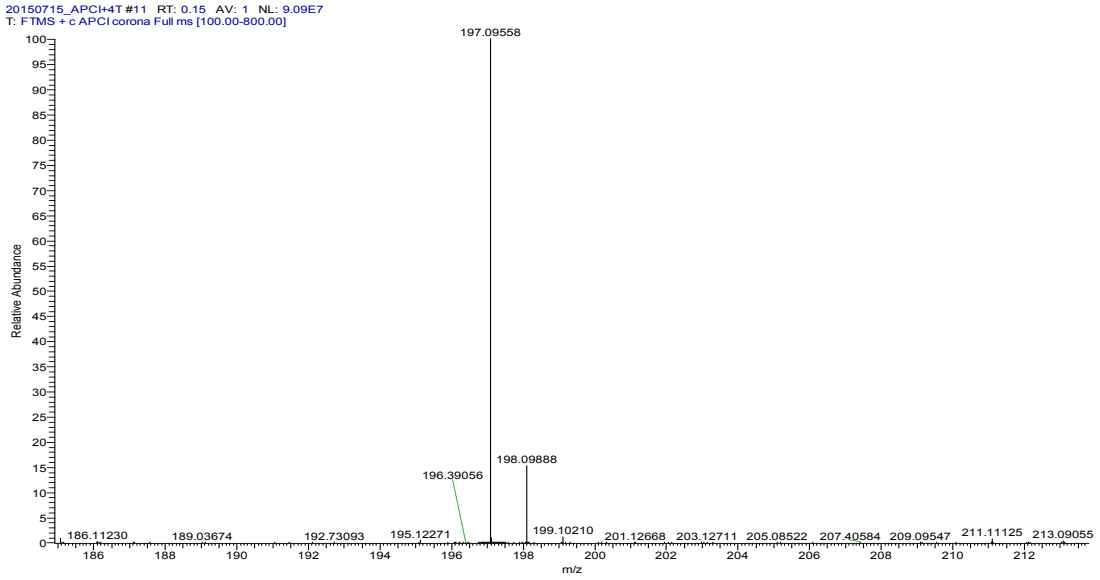


(10) 2-methylbenzophenone

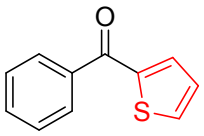


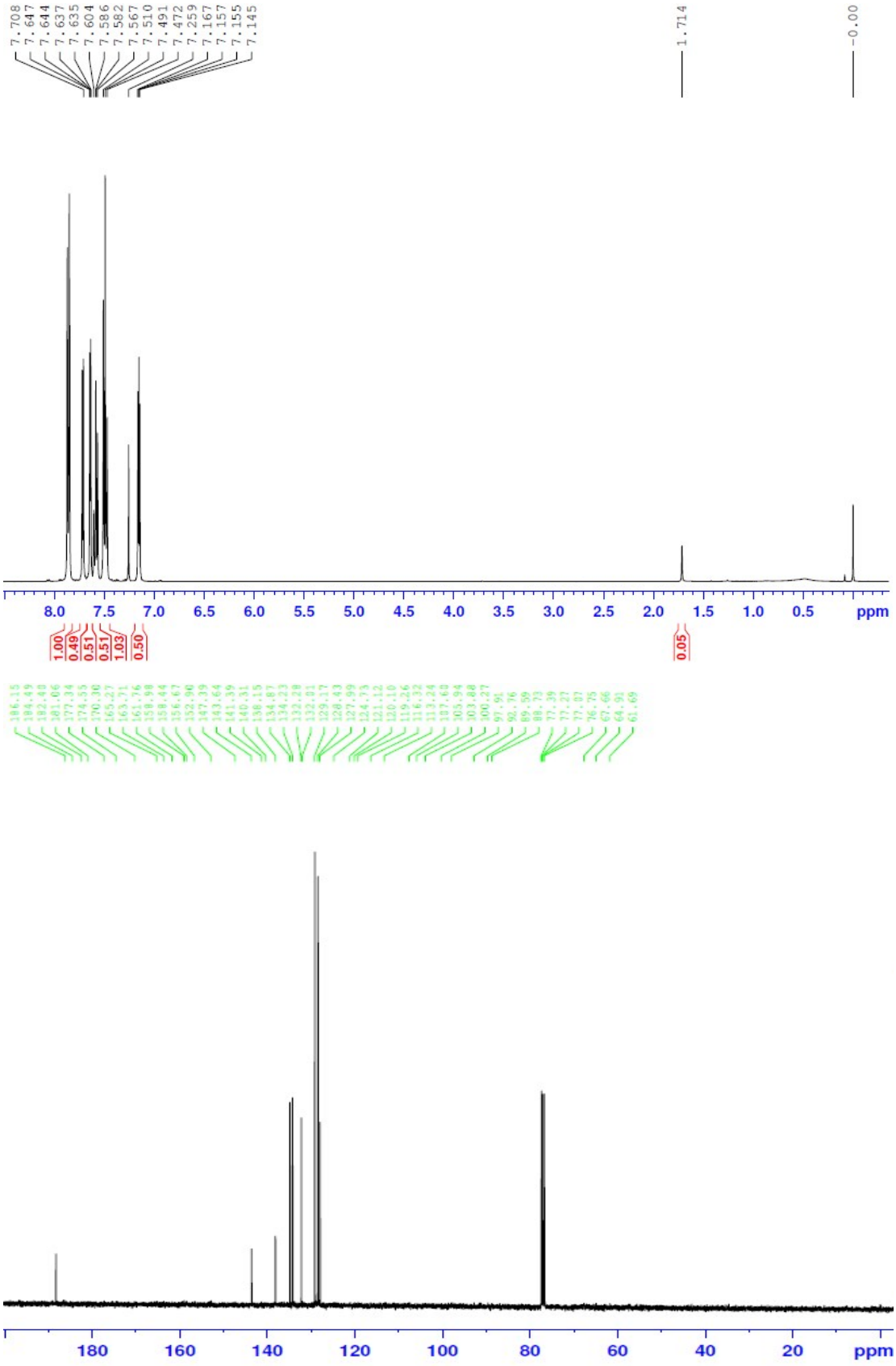






(11) 2-benzoylthiophene

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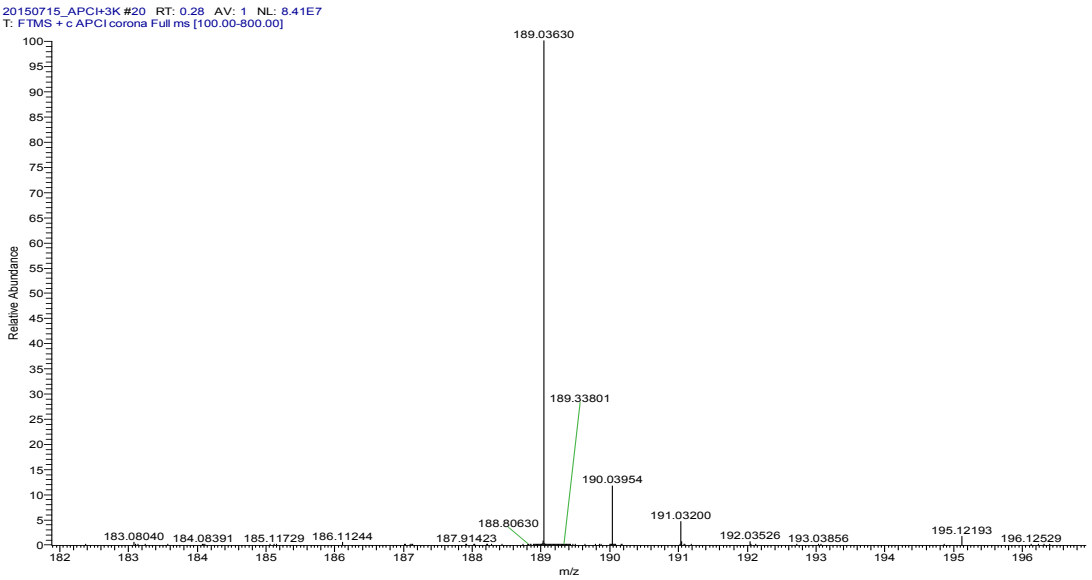
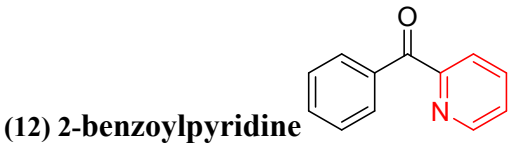
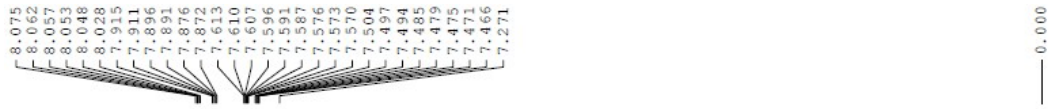
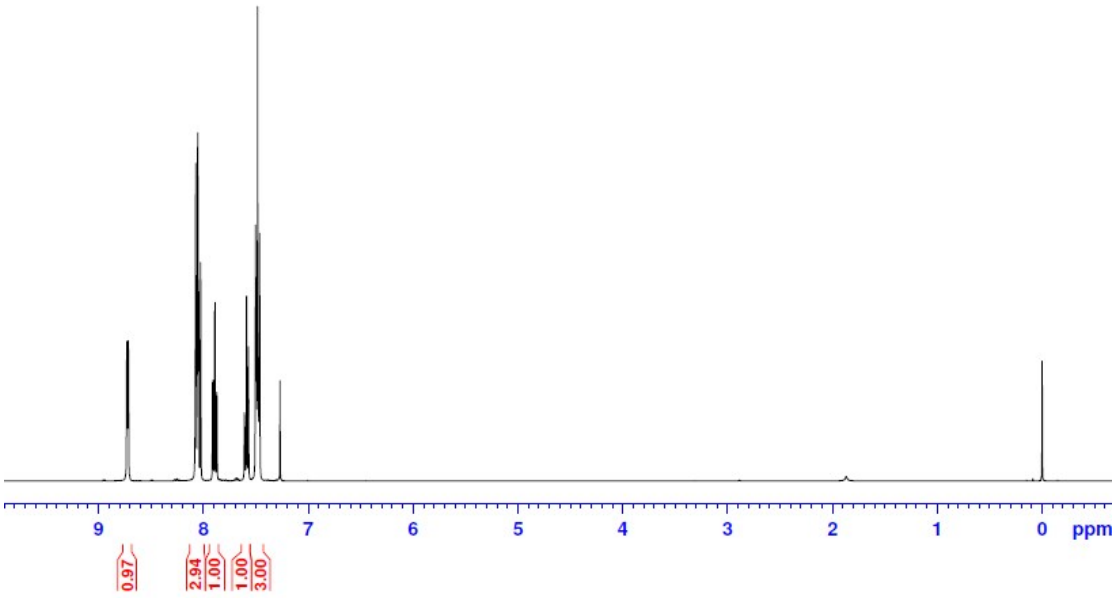
7.259
7.167
7.157
7.155
7.145
1.714
-0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.49
0.51
0.51
1.03
0.50
0.05
180
160
140
120
100
80
60
40
20
ppm

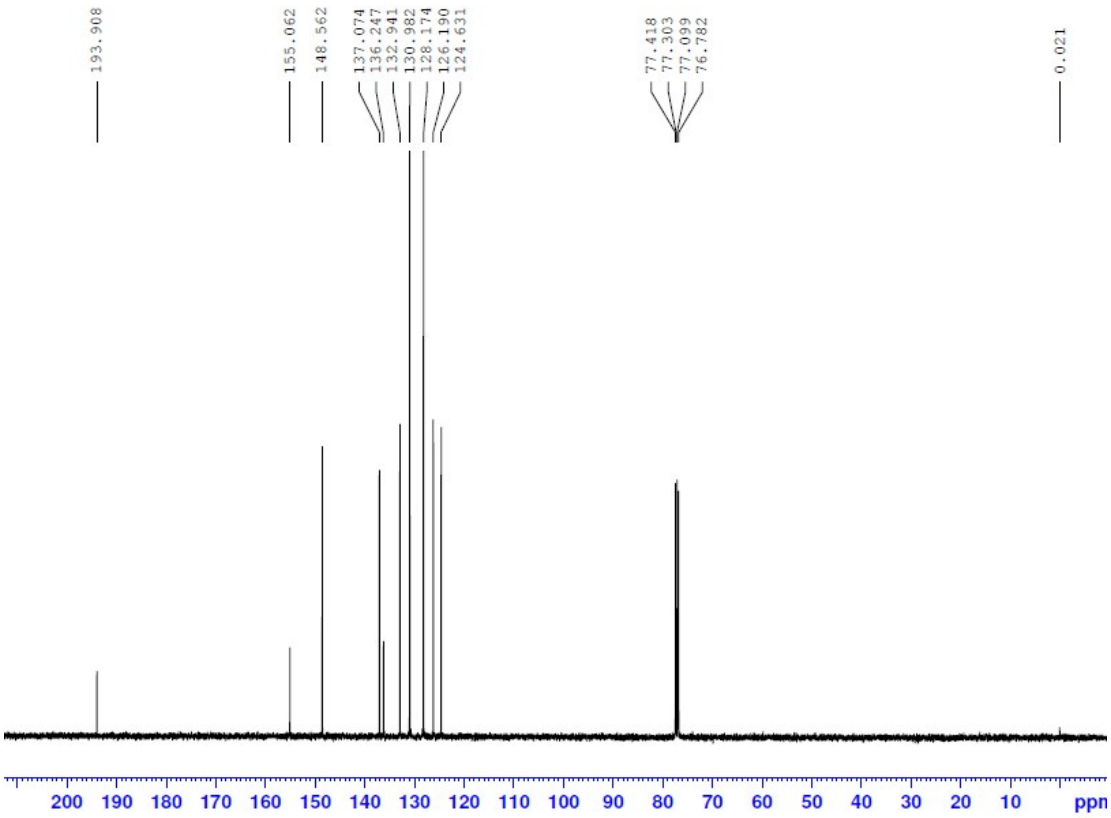


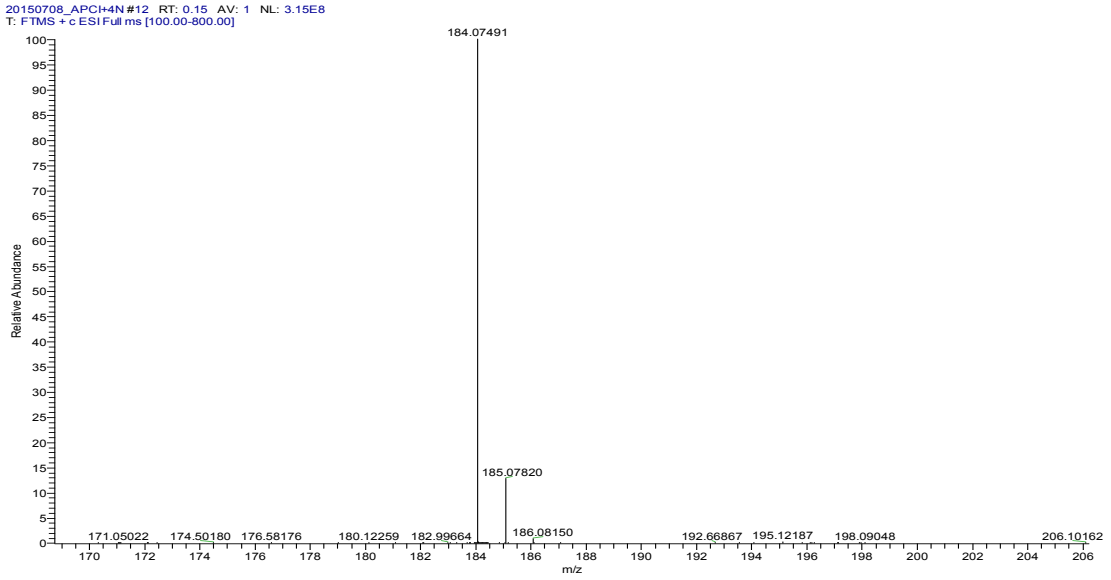
(12) 2-benzoylpyridine



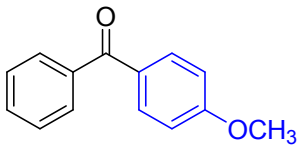


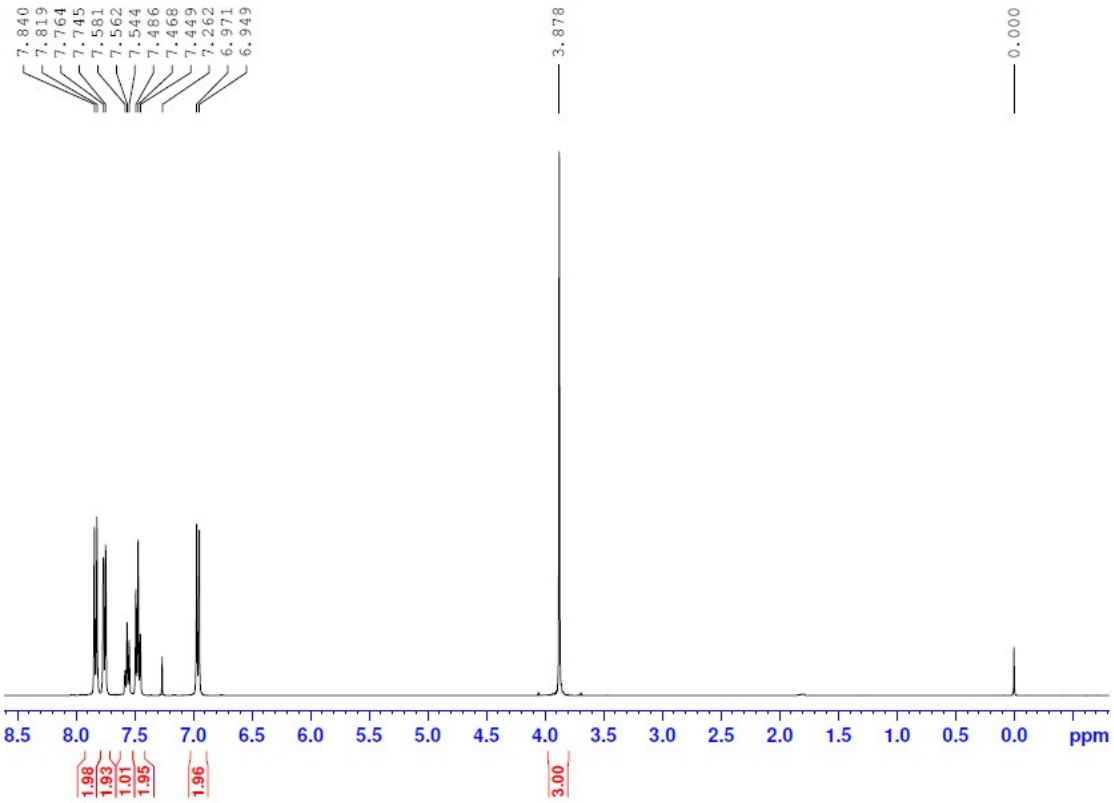


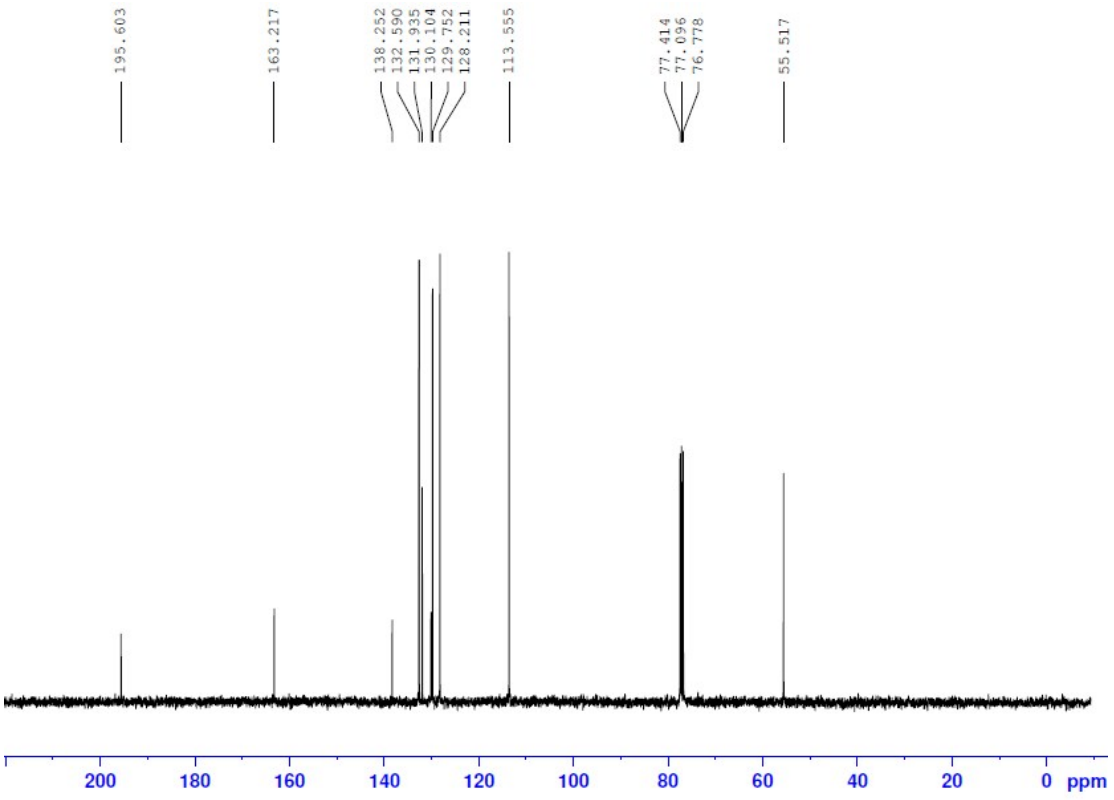


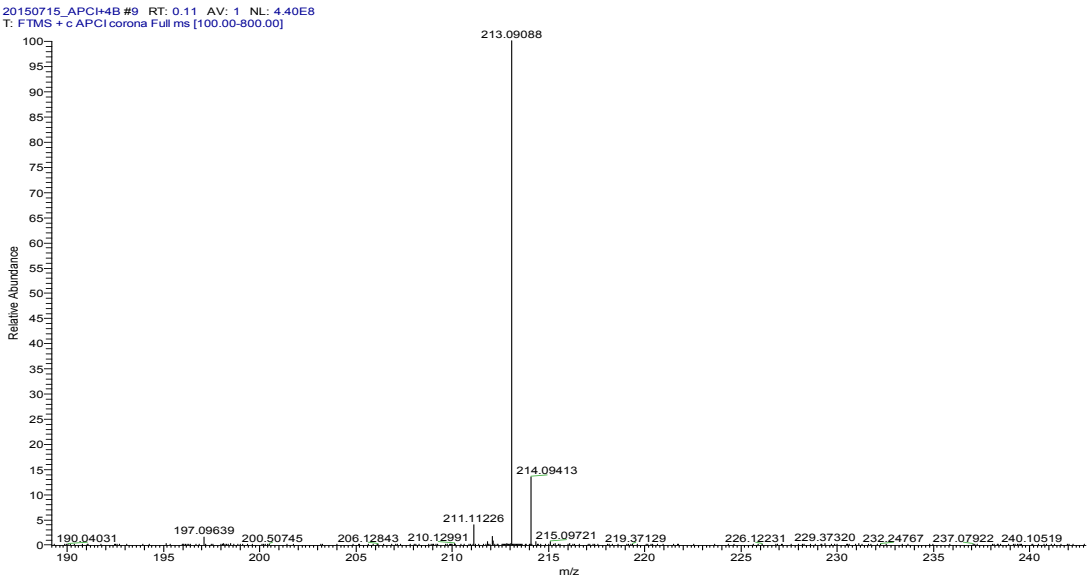


(13) 4-methoxy-benzophenone

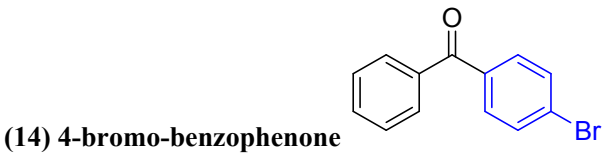


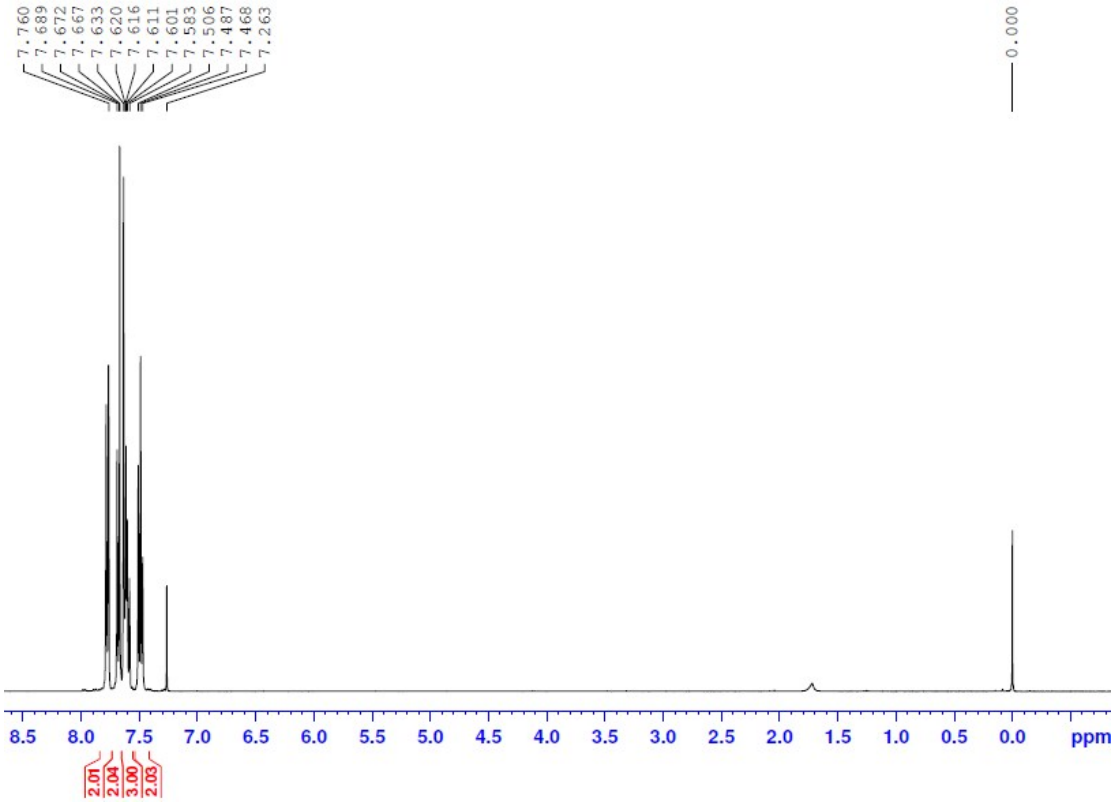

7.840
7.819
7.764
7.745
7.581
7.562
7.544
7.486
7.468
7.449
7.262
6.971
6.949
3.878
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.98
1.93
1.01
1.95
1.96
3.00

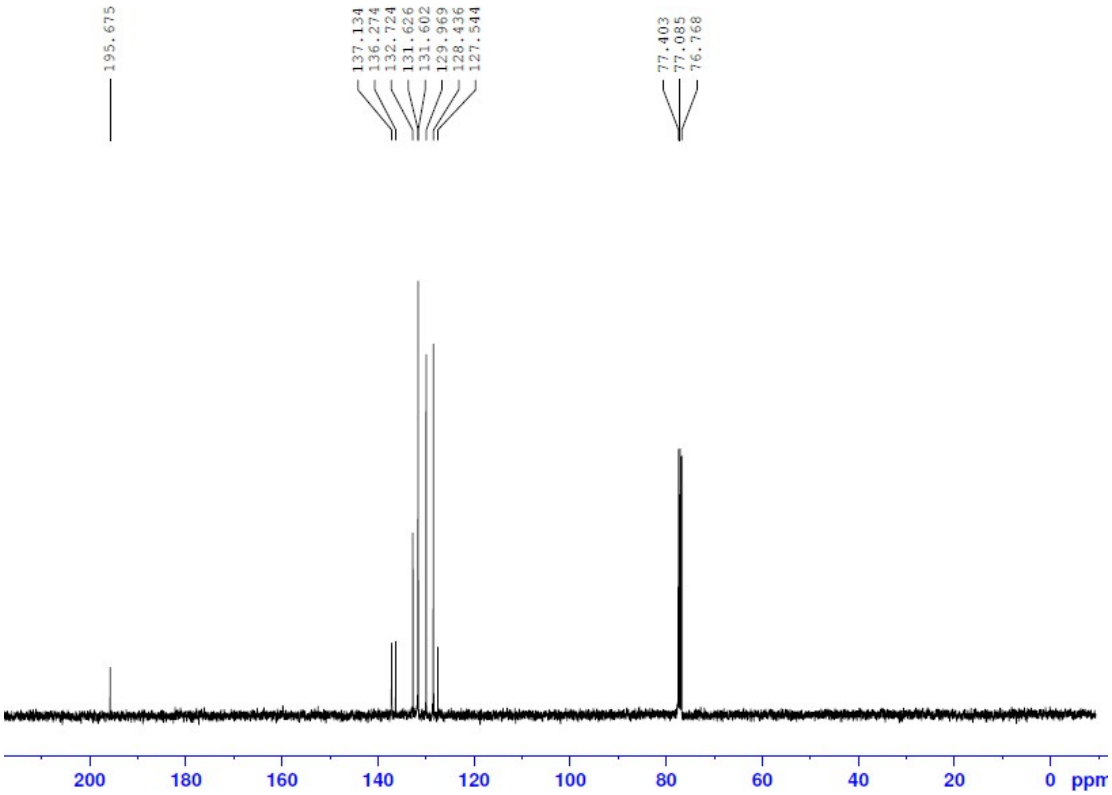

195.603
163.217
138.252
132.590
131.935
130.104
129.752
128.211
113.555
77.414
77.096
76.778
55.517
200 180 160 140 120 100 80 60 40 20 0 ppm

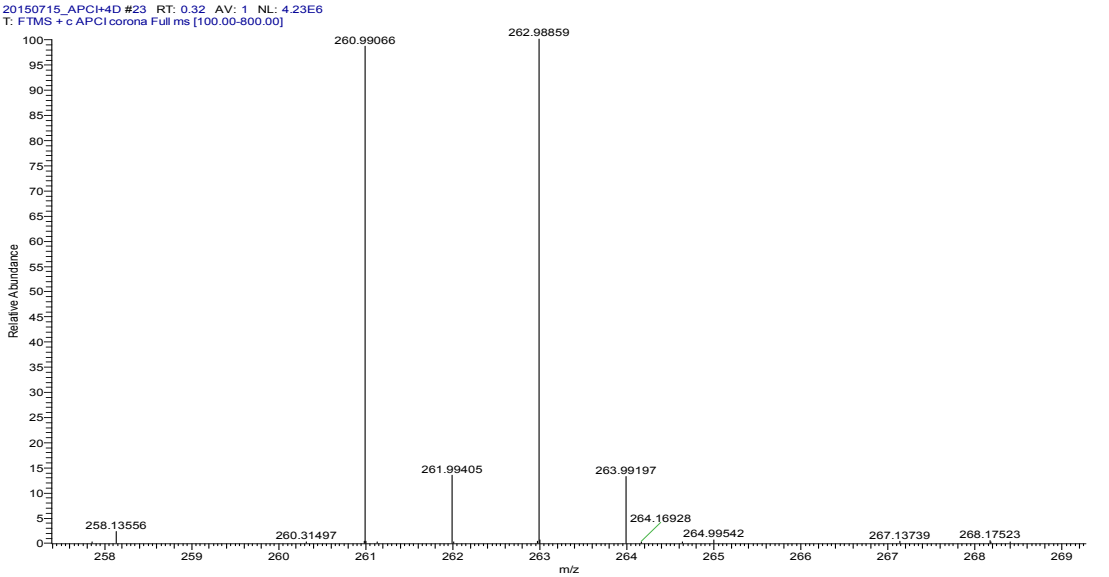


(14) 4-bromo-benzophenone

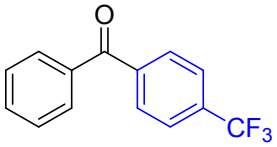


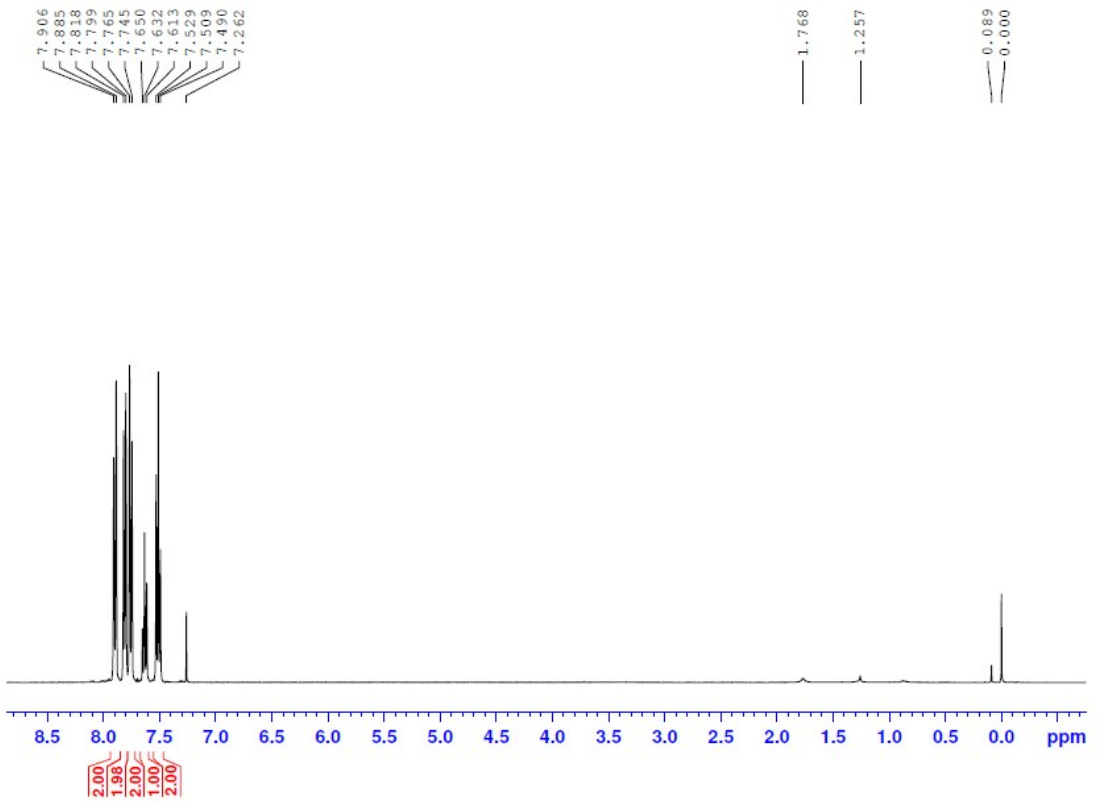


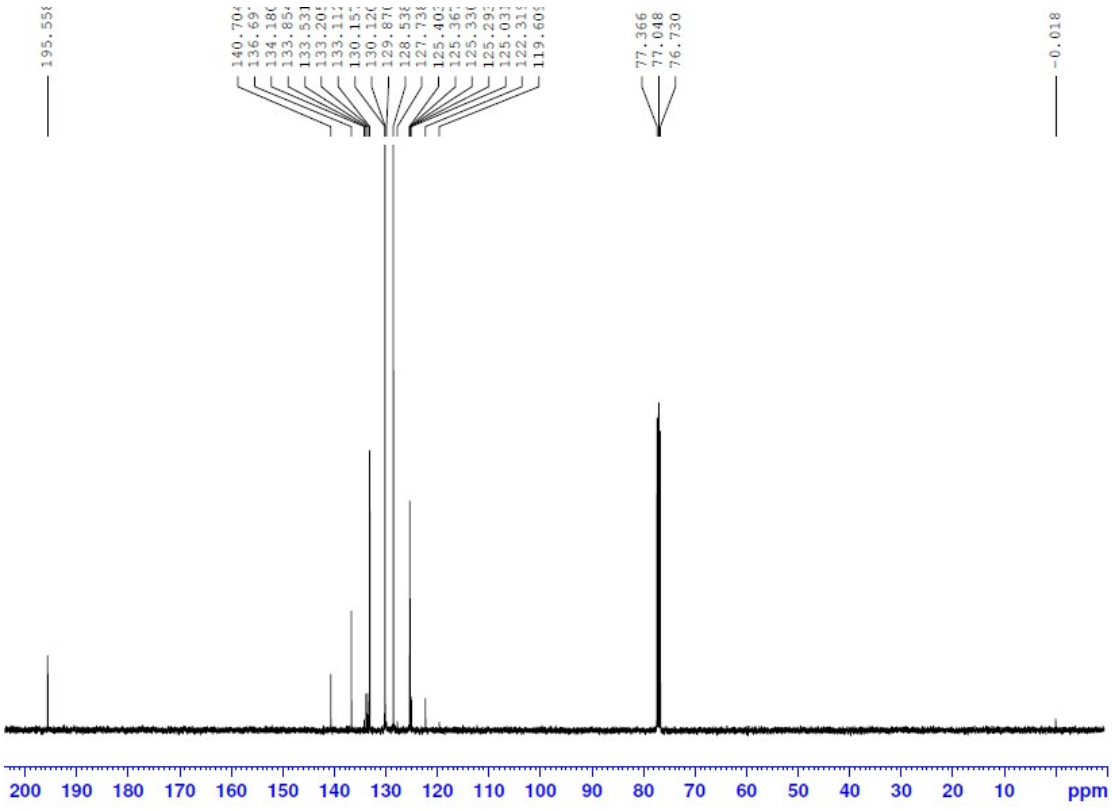


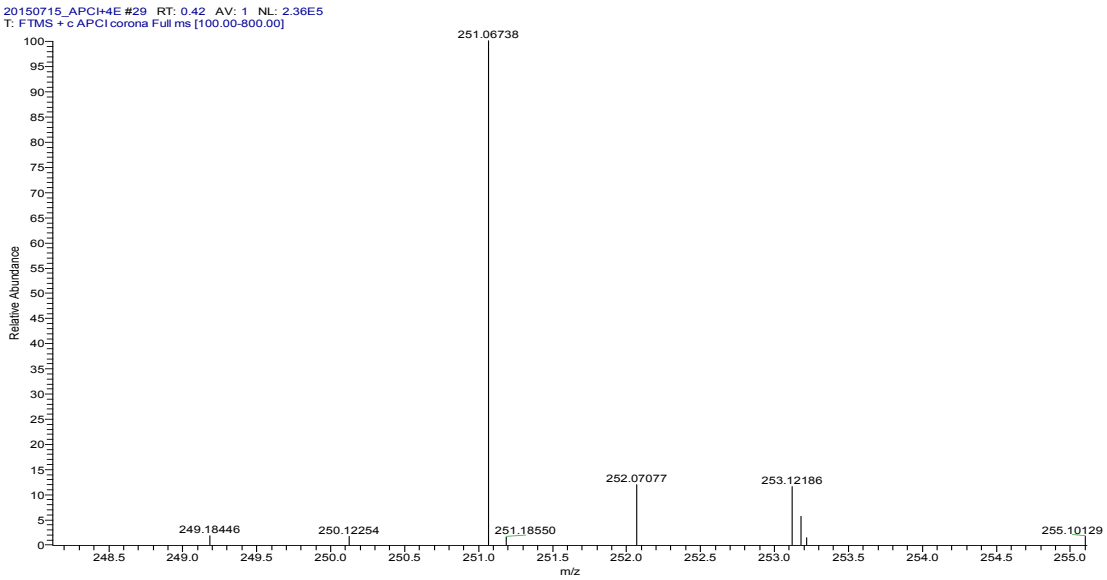


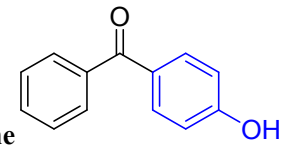
(15) 4-trifluoromethyl-benzophenone



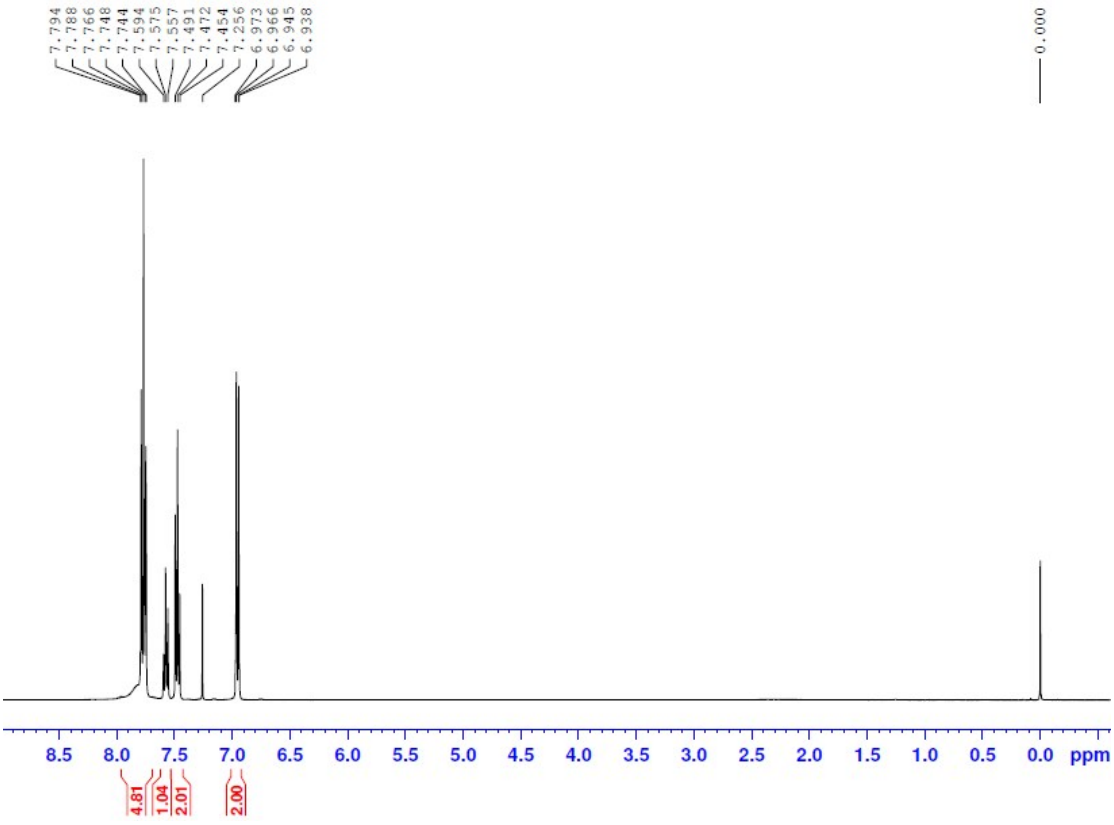

7.906
7.885
7.818
7.799
7.765
7.745
7.650
7.632
7.613
7.529
7.509
7.490
7.262
1.768
1.257
0.089
0.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.98
2.00
1.00
2.00

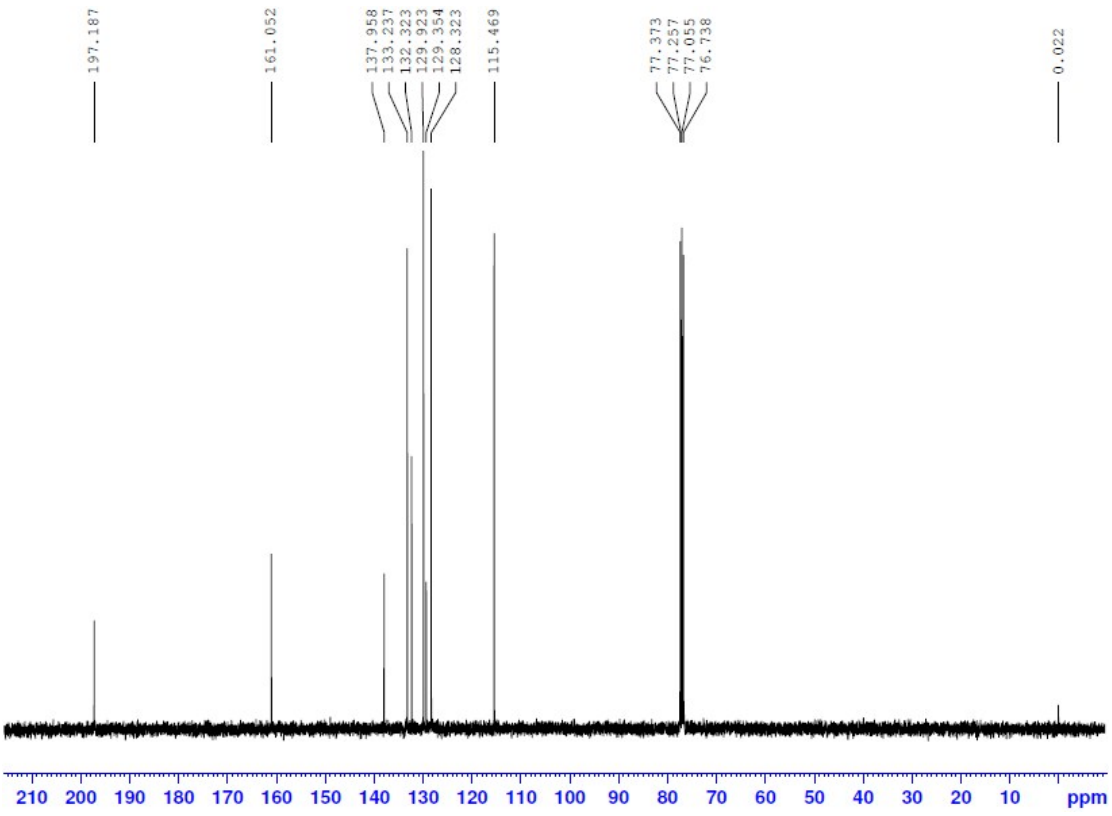

195.55
140.70
136.69
134.18
133.85
133.53
133.20
133.11
130.15
130.12
129.87
128.53
127.73
125.40
125.36
125.33
125.29
125.03
122.31
119.60
77.366
77.048
76.730
-0.018
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

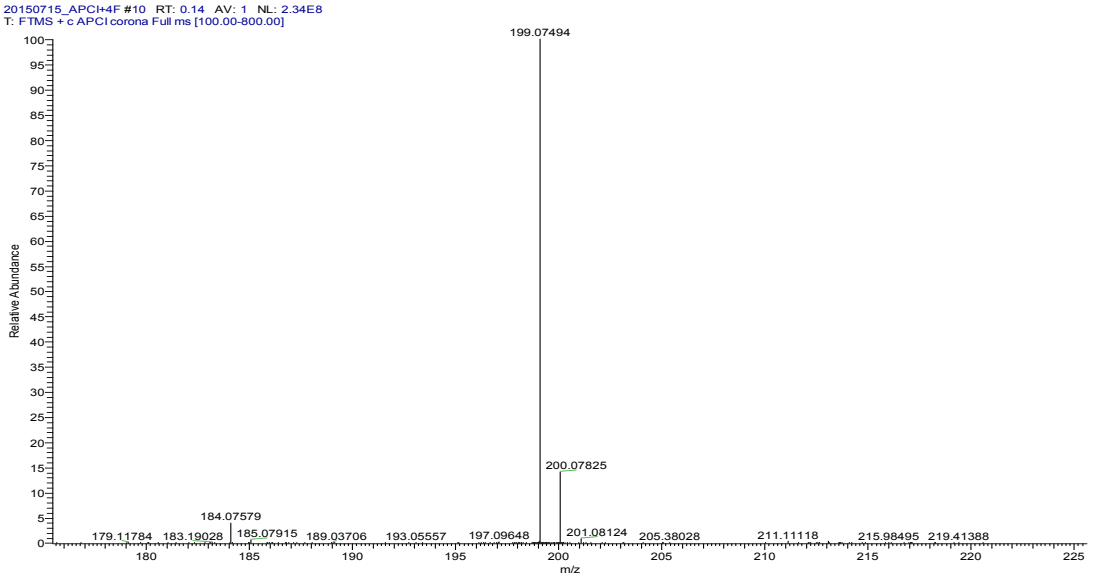




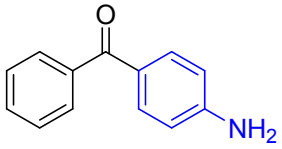
(16) 4-hydroxy-benzophenone

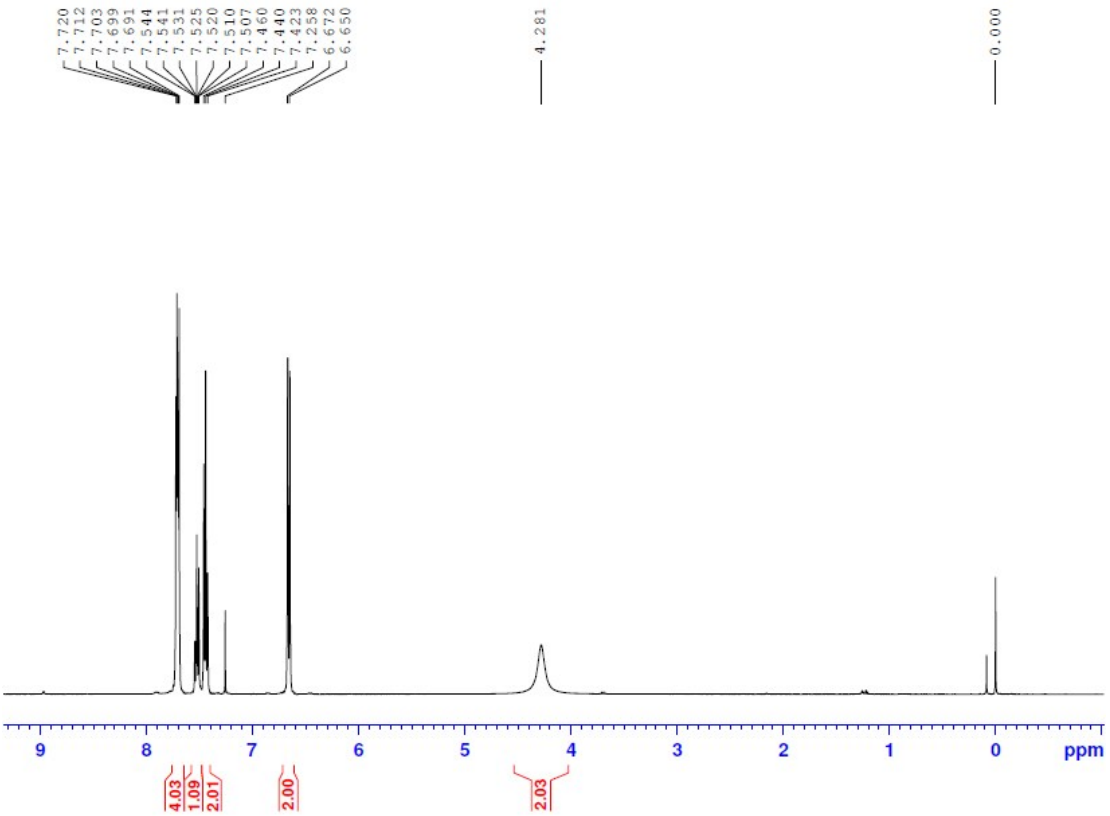


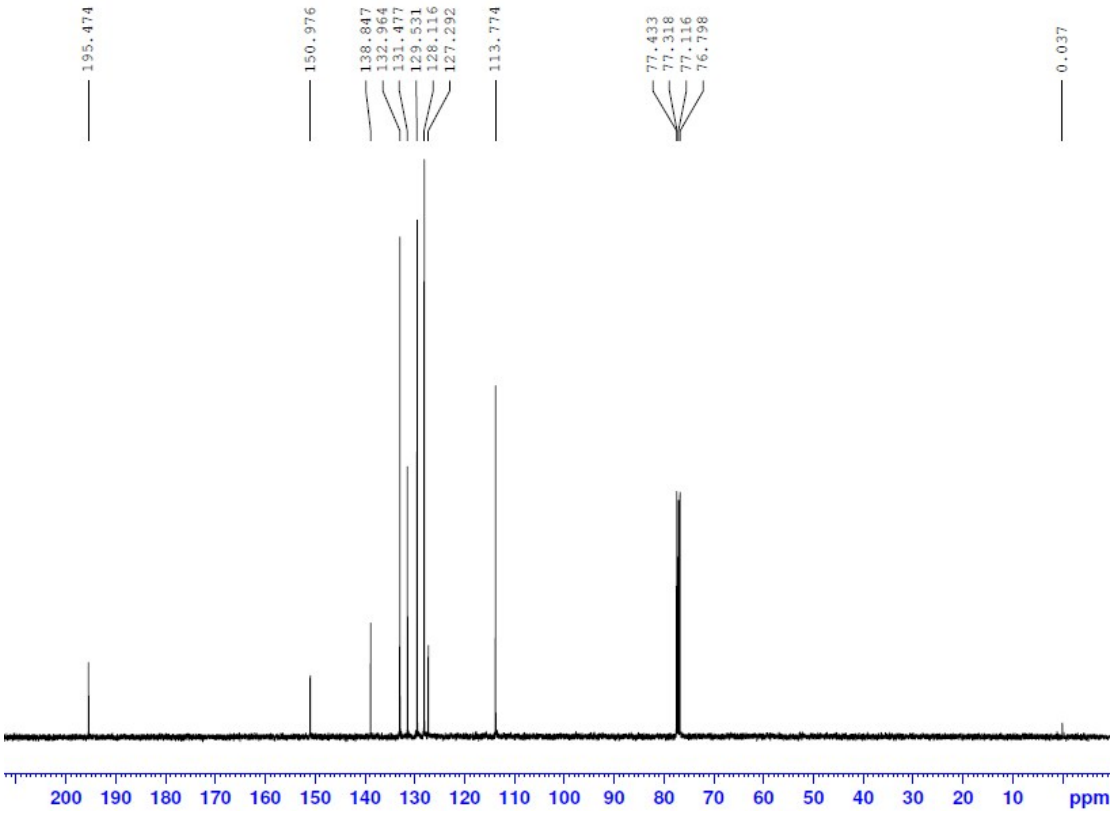


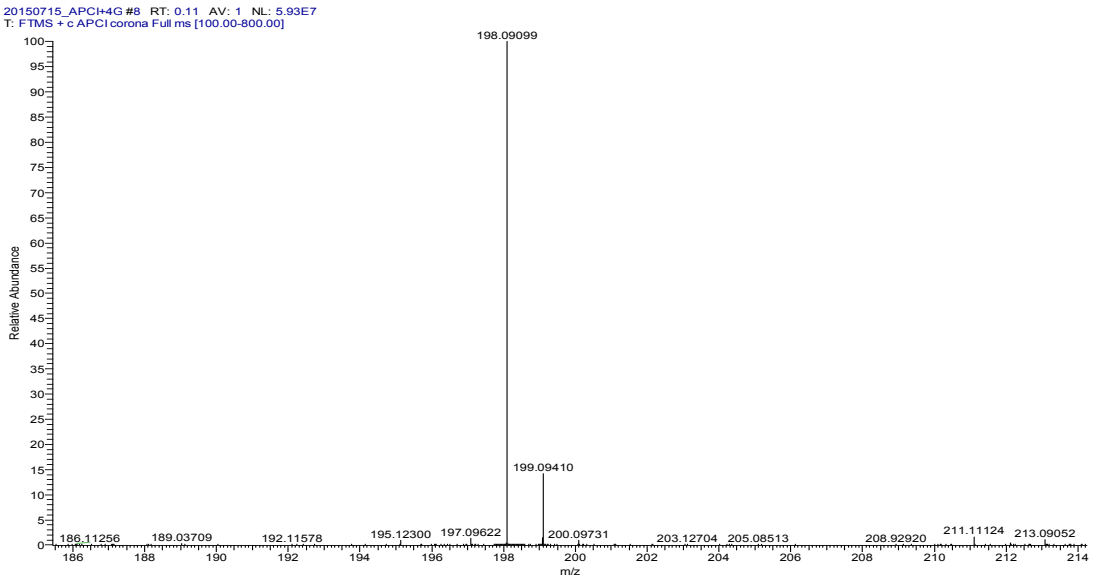


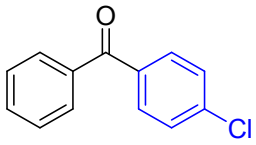
(17) 4-aminobenzophenone



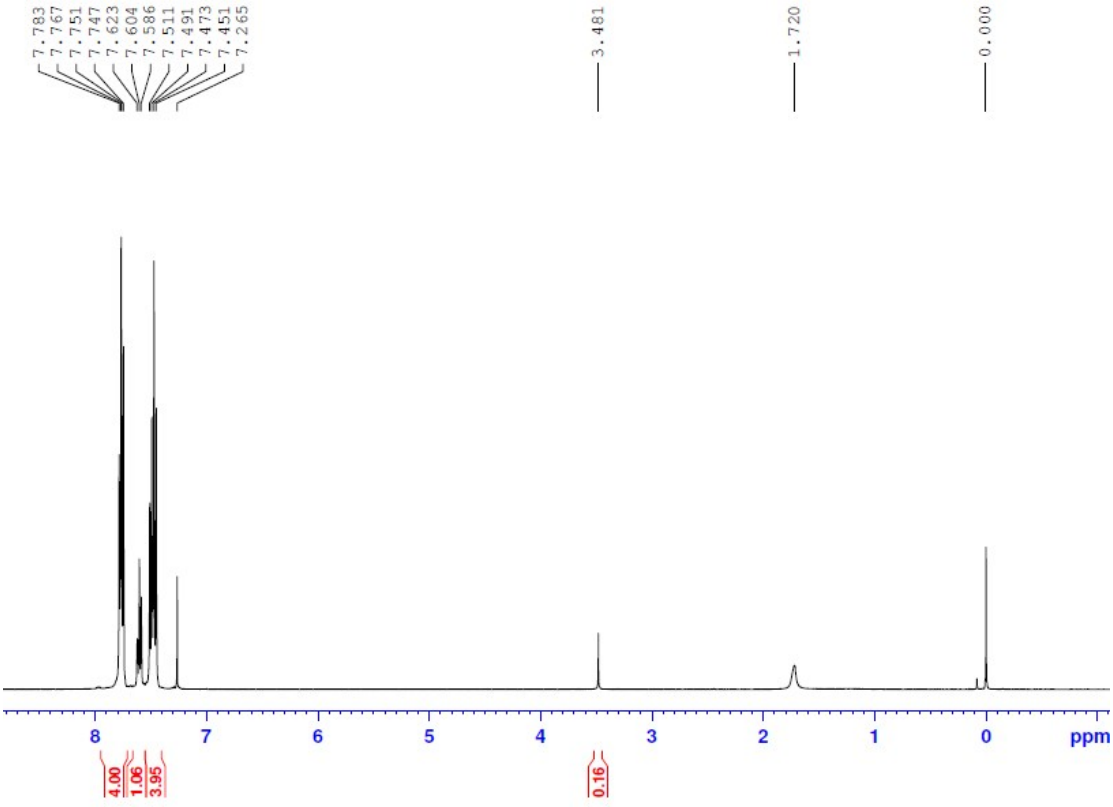

7.720
7.712
7.703
7.699
7.691
7.544
7.541
7.531
7.525
7.520
7.510
7.507
7.460
7.440
7.423
7.258
6.672
6.650
4.281
0.000
9
8
7
6
5
4
3
2
1
0
ppm
4.03
1.09
2.01
2.00
2.03

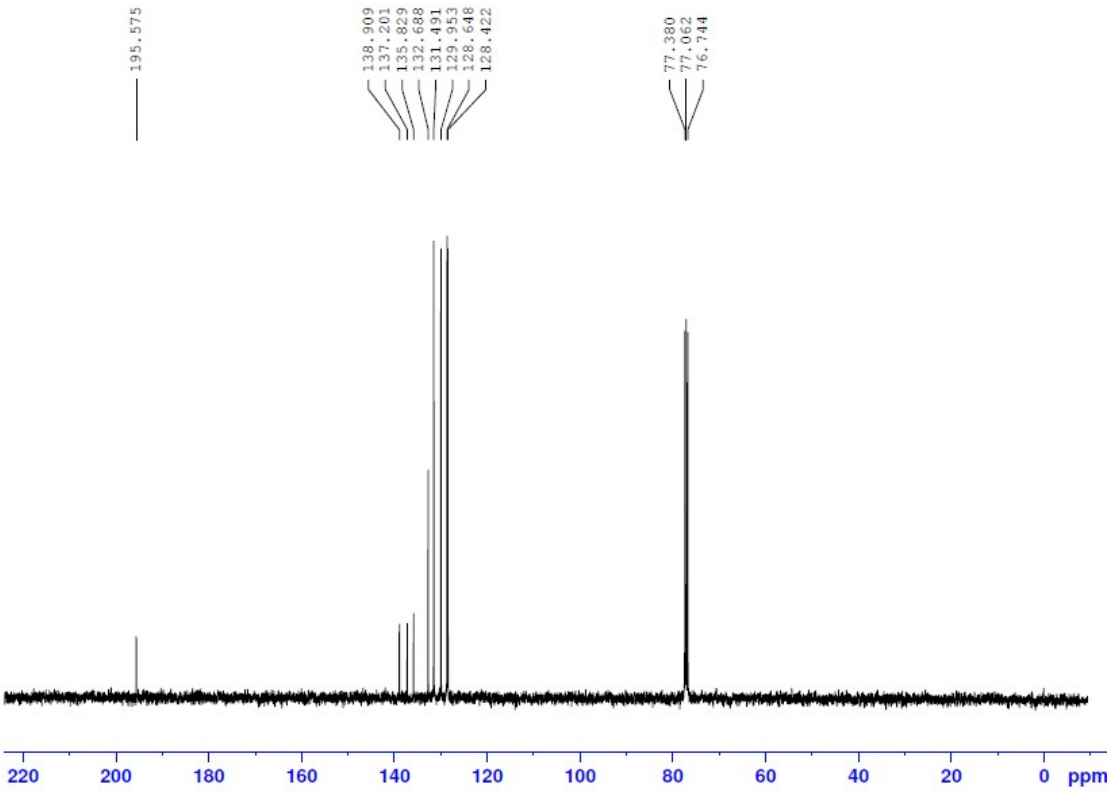

195.474
150.976
138.847
132.964
131.477
129.531
128.116
127.292
113.774
77.433
77.318
77.116
76.798
0.037
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

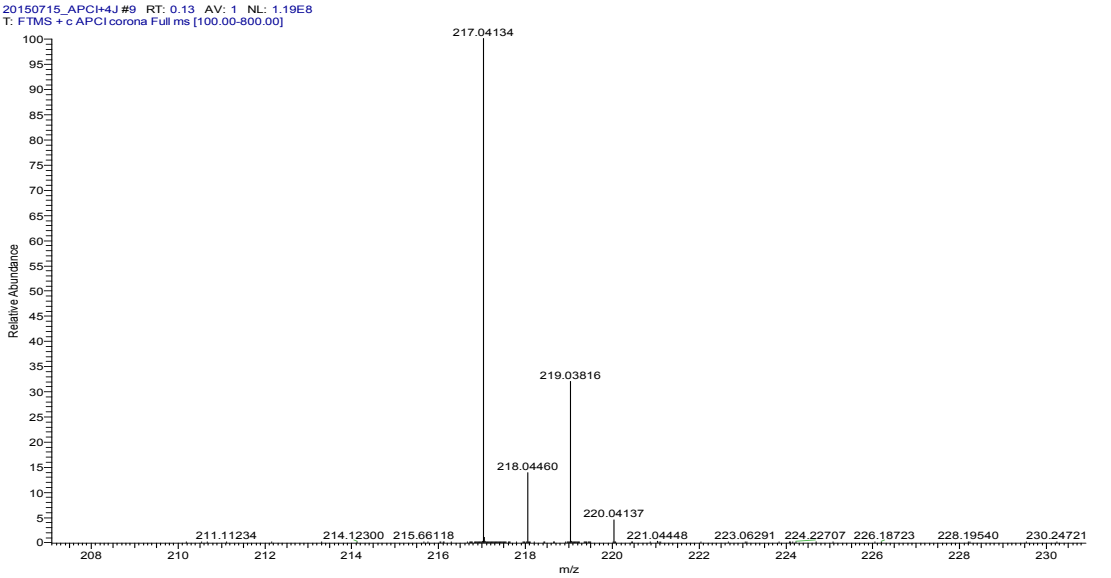




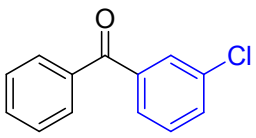
(18) 4-chloro-benzophenone

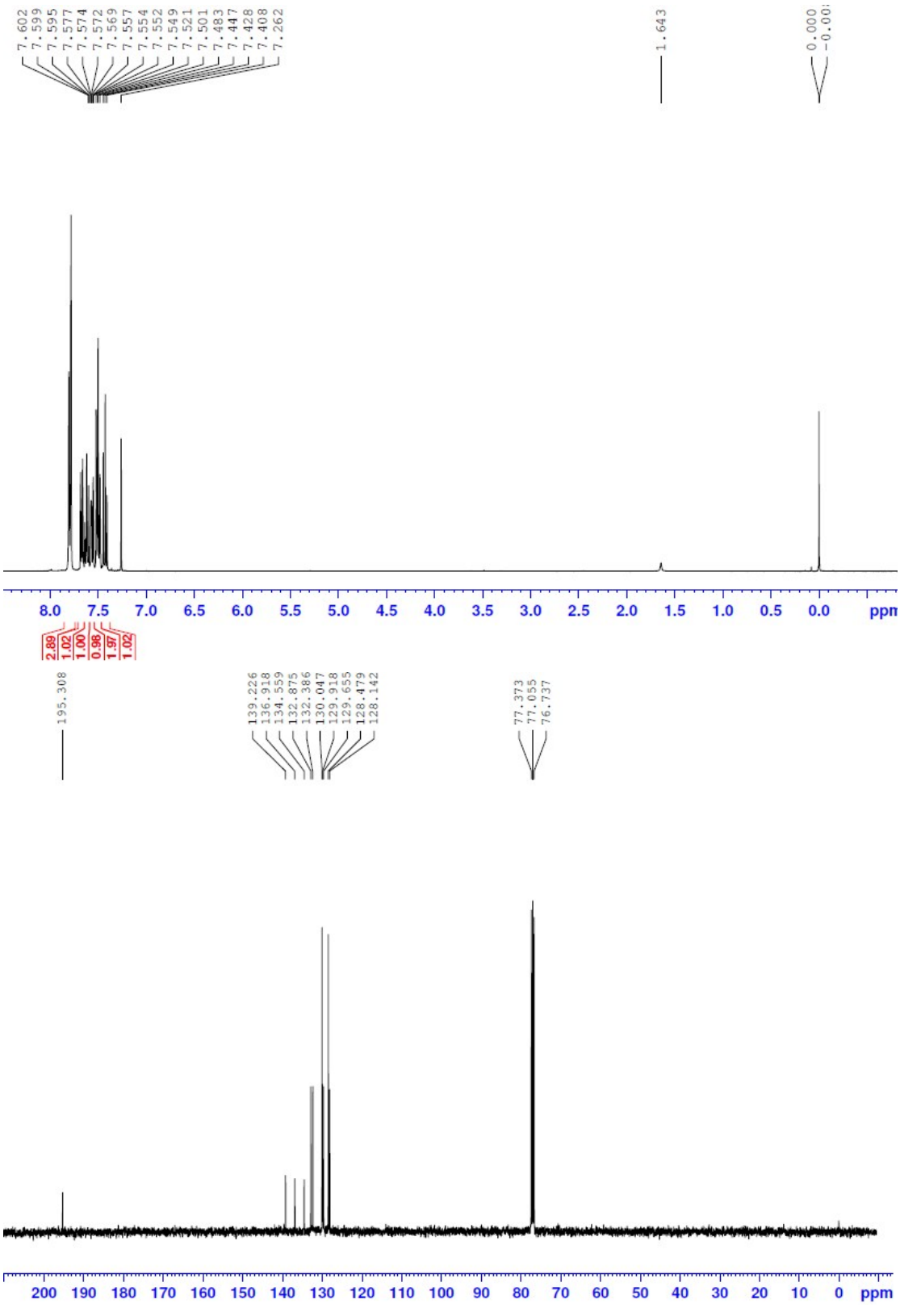


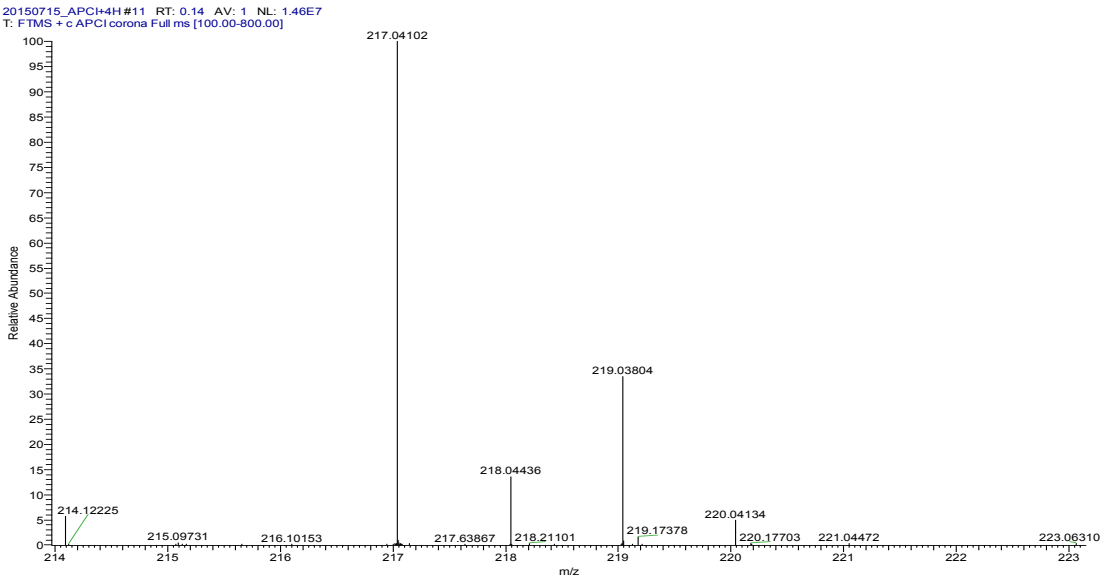


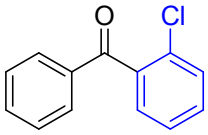


(19) 3-chloro-benzophenone

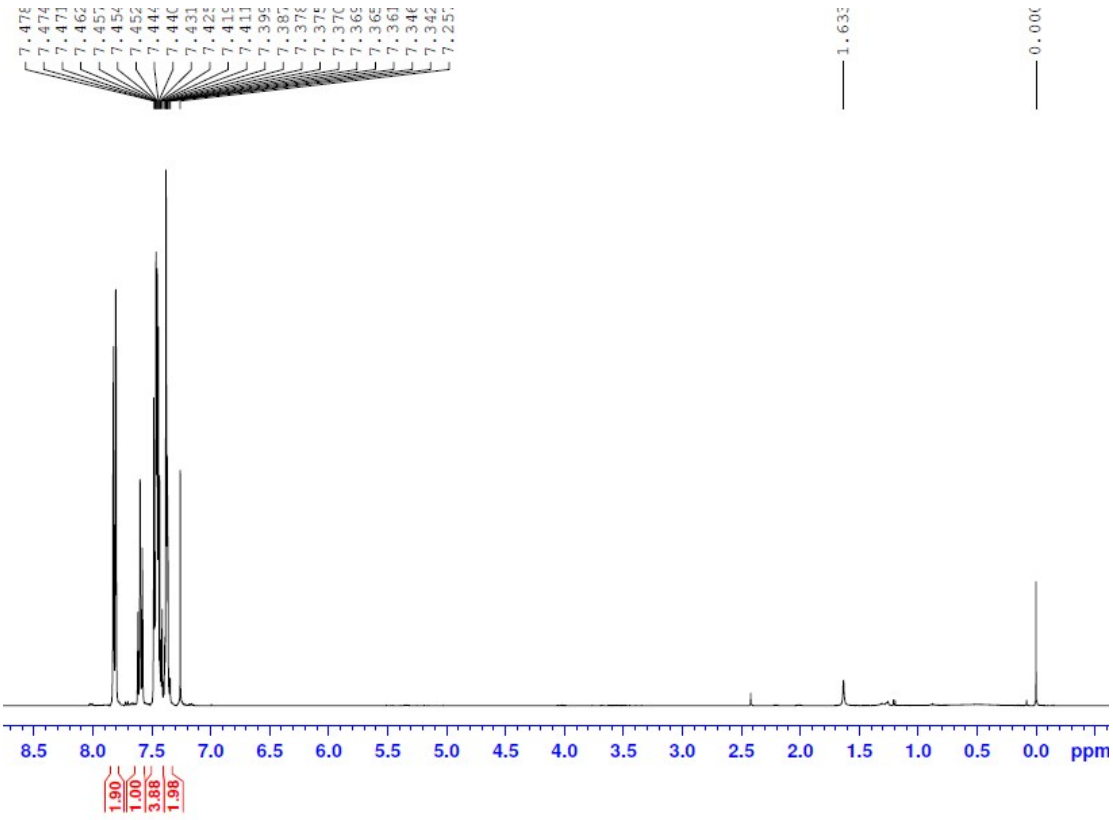


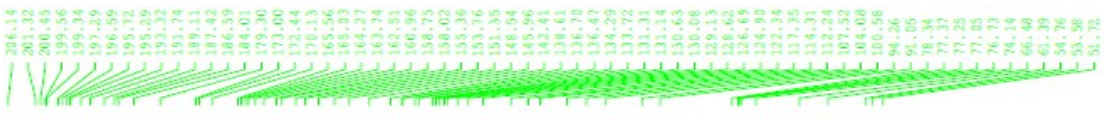

7.602
7.599
7.595
7.577
7.574
7.572
7.569
7.557
7.554
7.552
7.549
7.521
7.501
7.483
7.447
7.428
7.408
7.262
1.643
0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.89
1.02
1.00
0.96
1.97
1.02
195.308
139.226
136.918
134.559
132.875
132.386
130.047
129.918
129.655
128.479
128.142
77.373
77.055
76.737
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

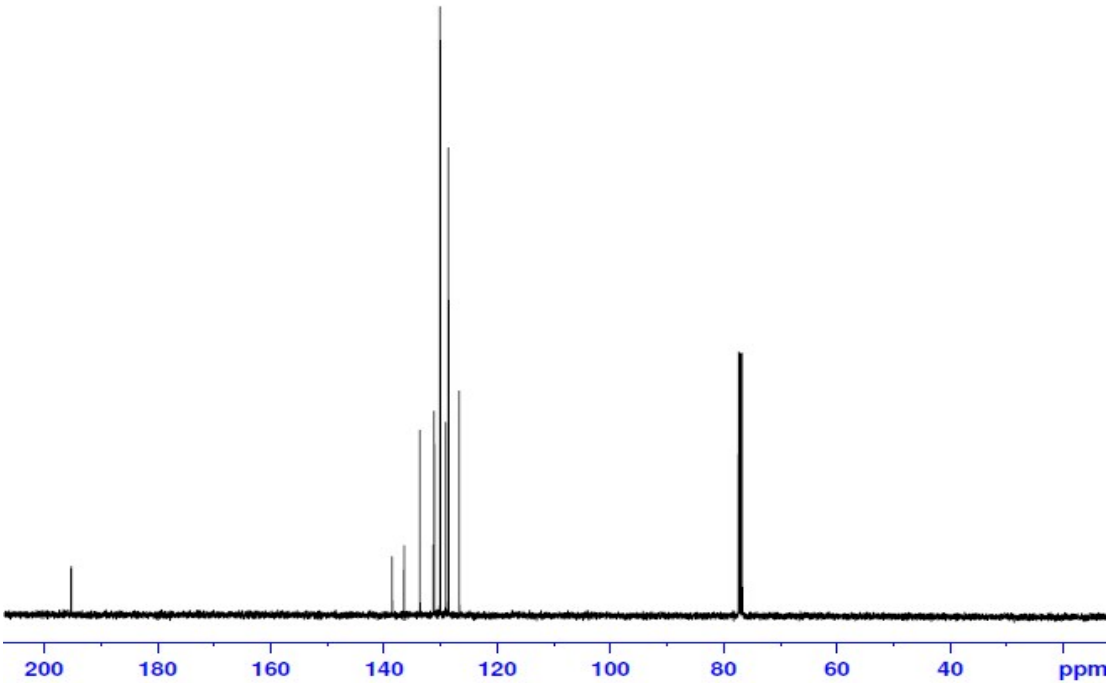


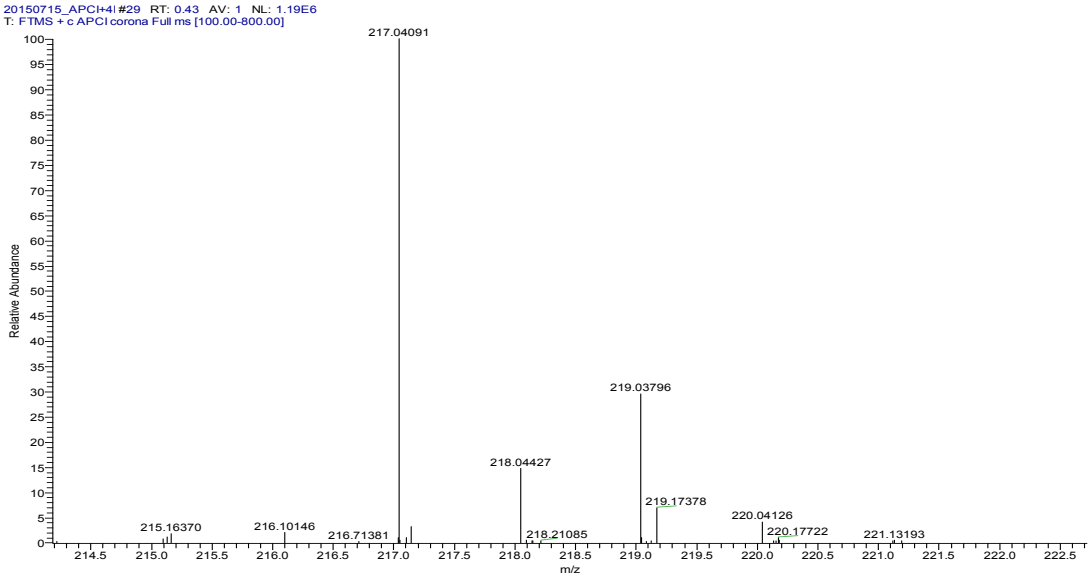


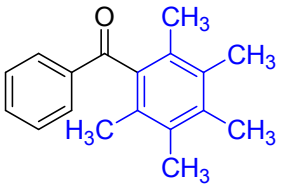
(20) 2-chlorobenzophenone



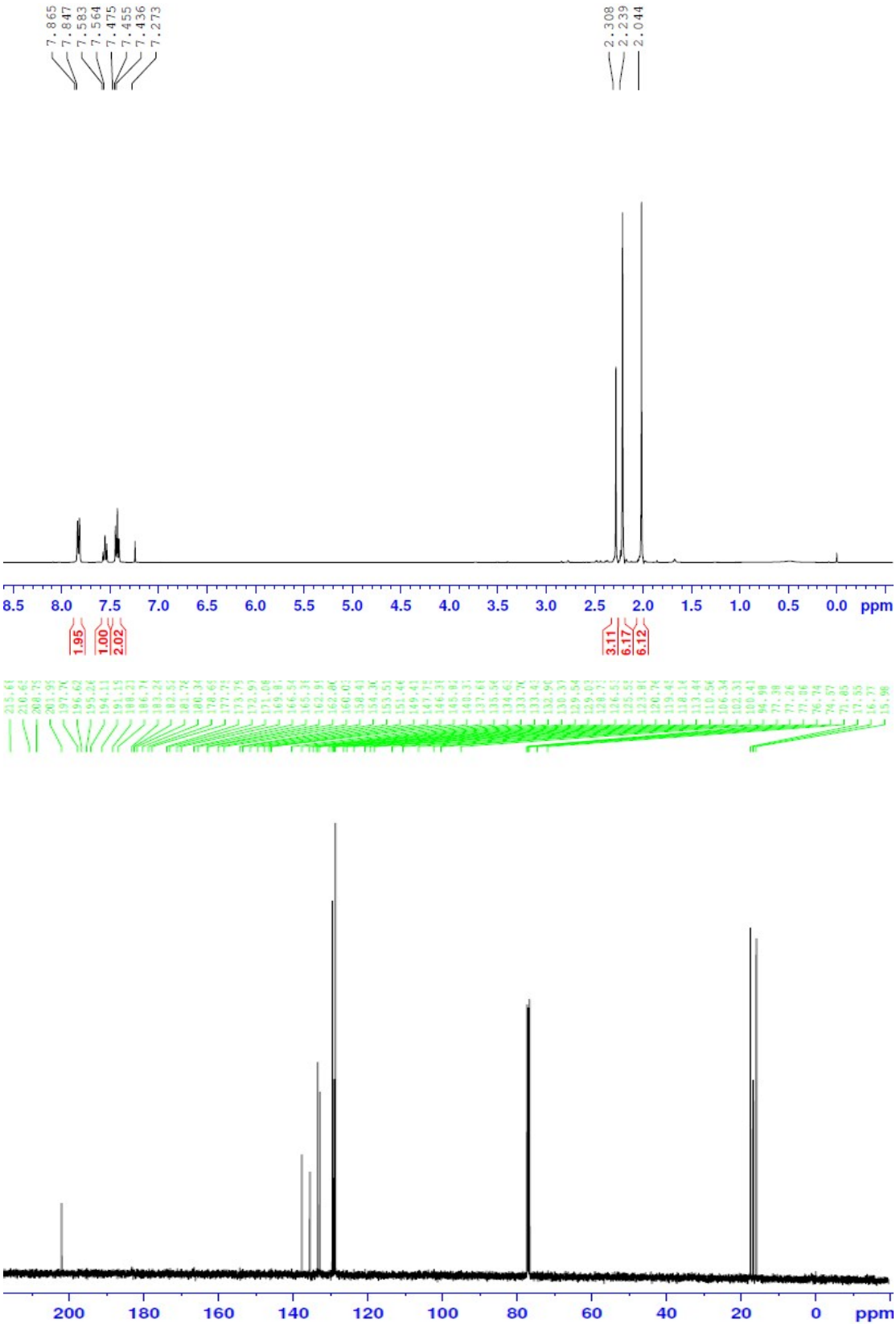


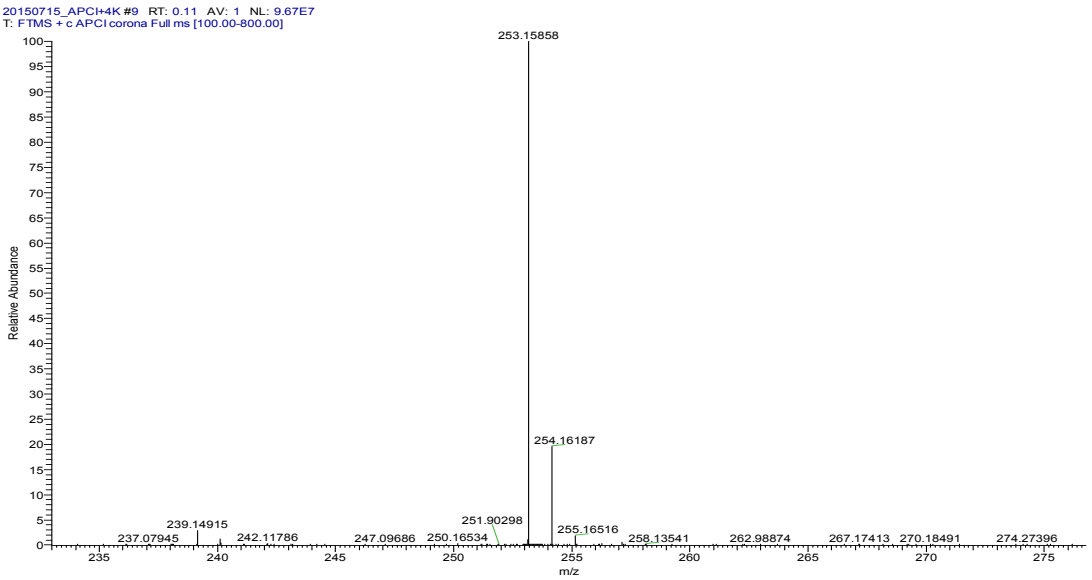


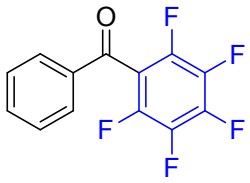




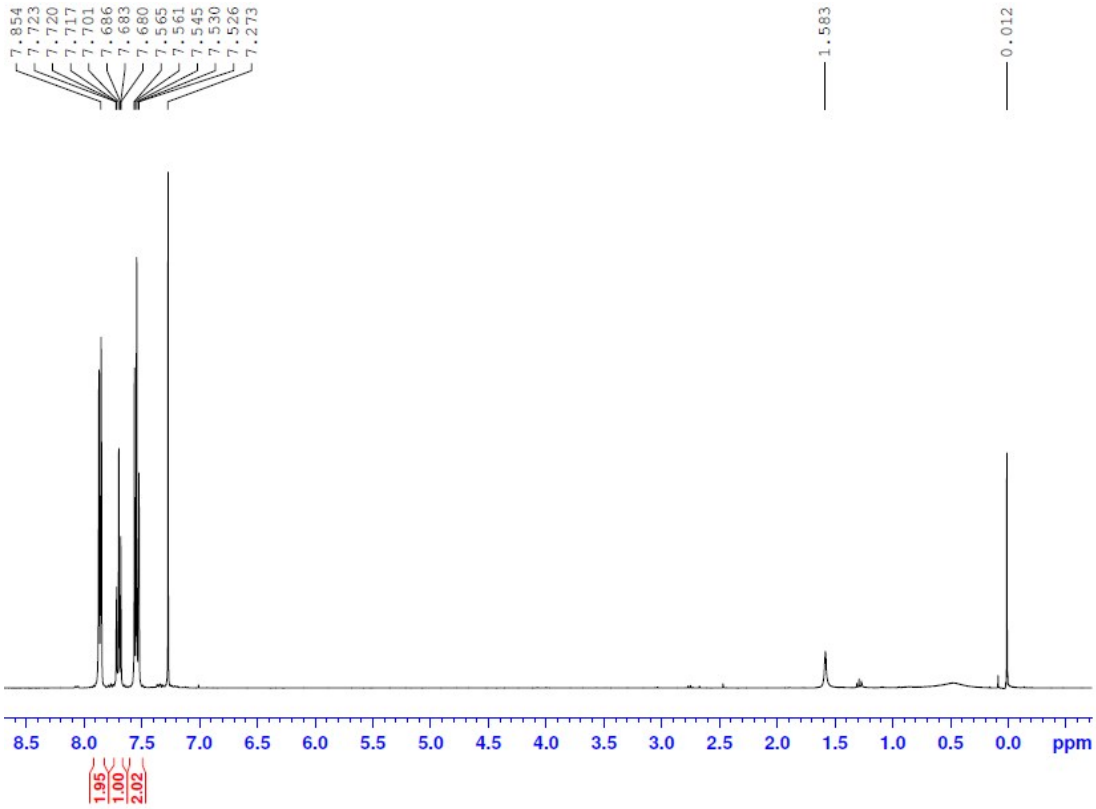
(21) 2,3,4,5,6-pentamethyl-benzophenone

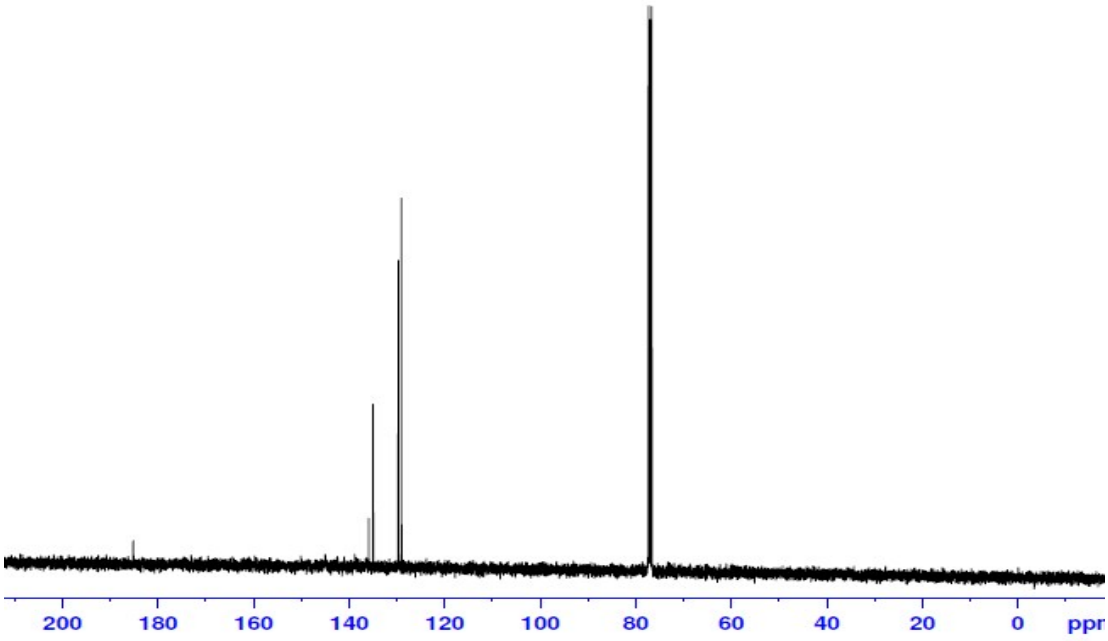

7.865
7.847
7.583
7.564
7.475
7.455
7.436
7.273
2.308
2.239
2.044
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.95
1.00
2.02
3.11
6.17
6.12
200 180 160 140 120 100 80 60 40 20 0 ppm

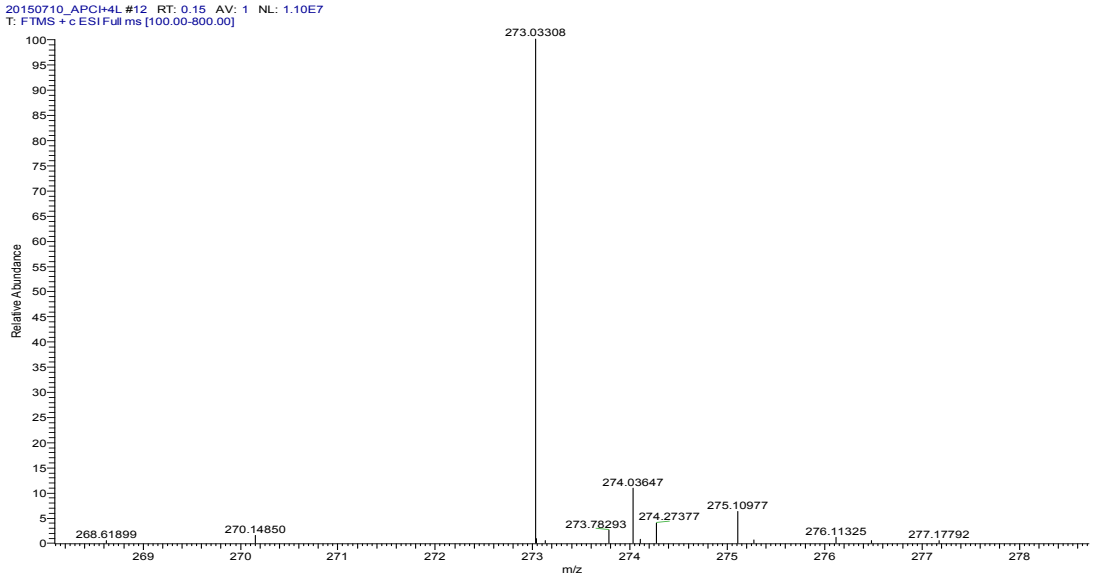




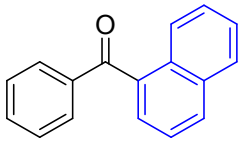
(22) 2,3,4,5,6-perfluoro-benzophenone

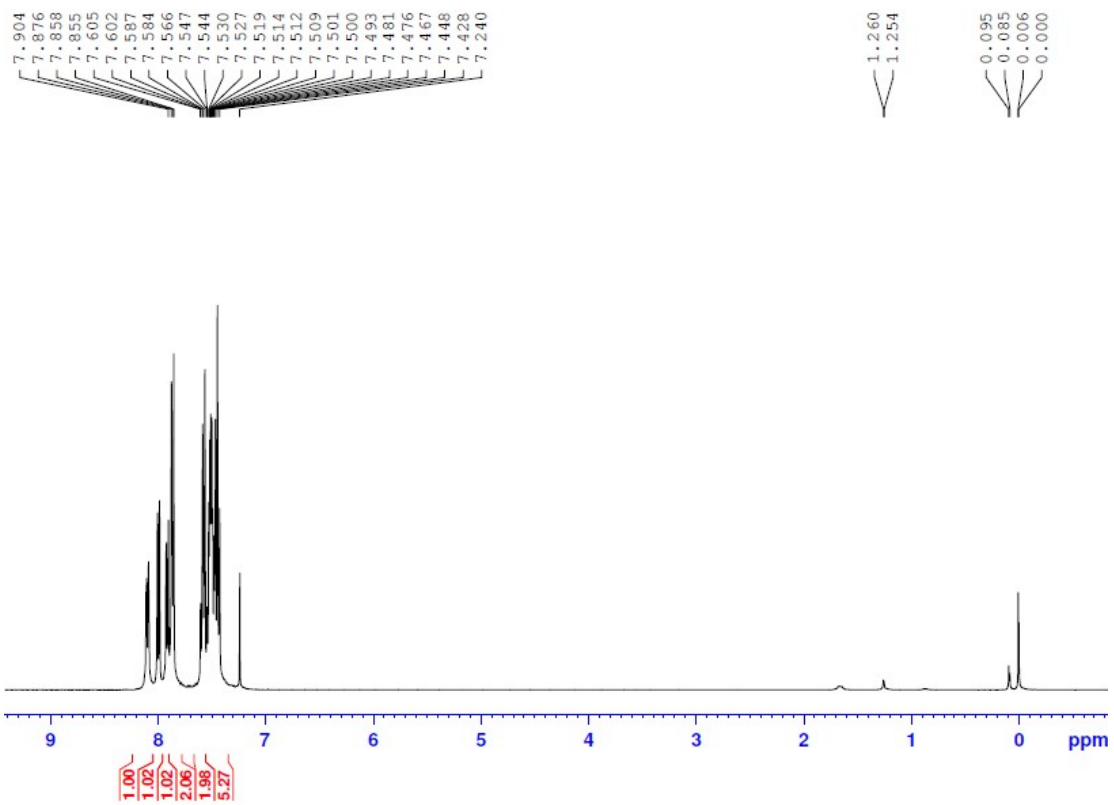


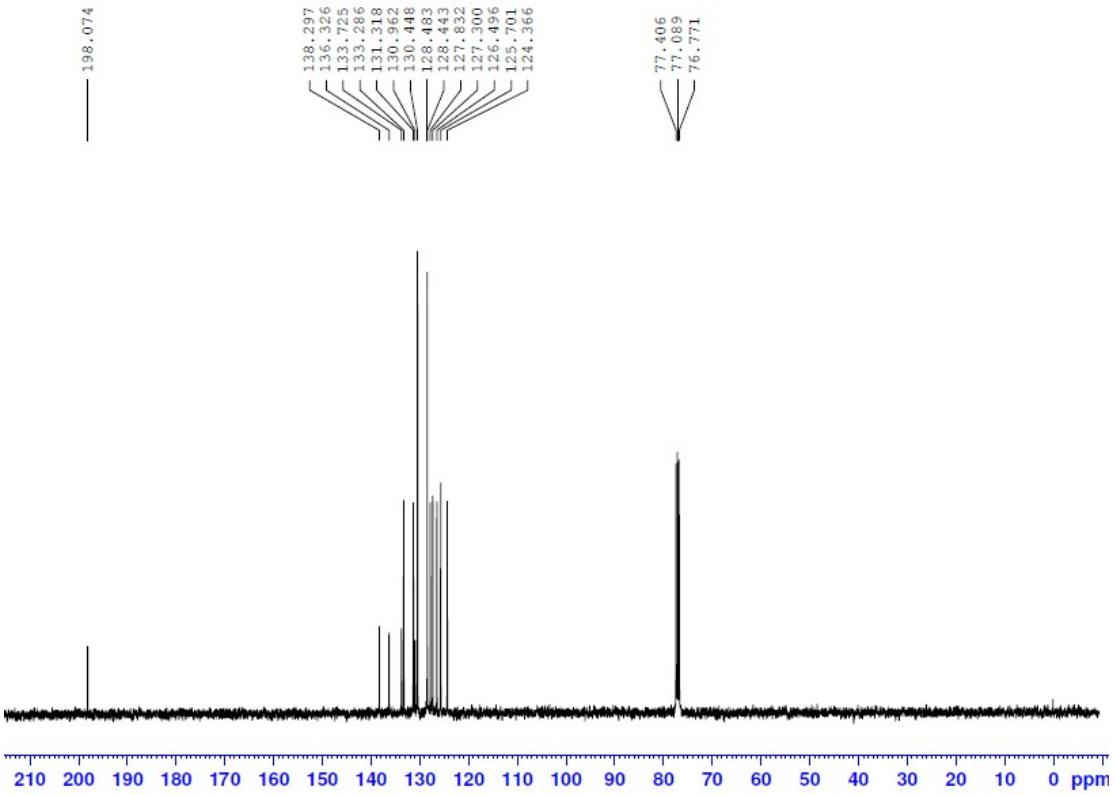


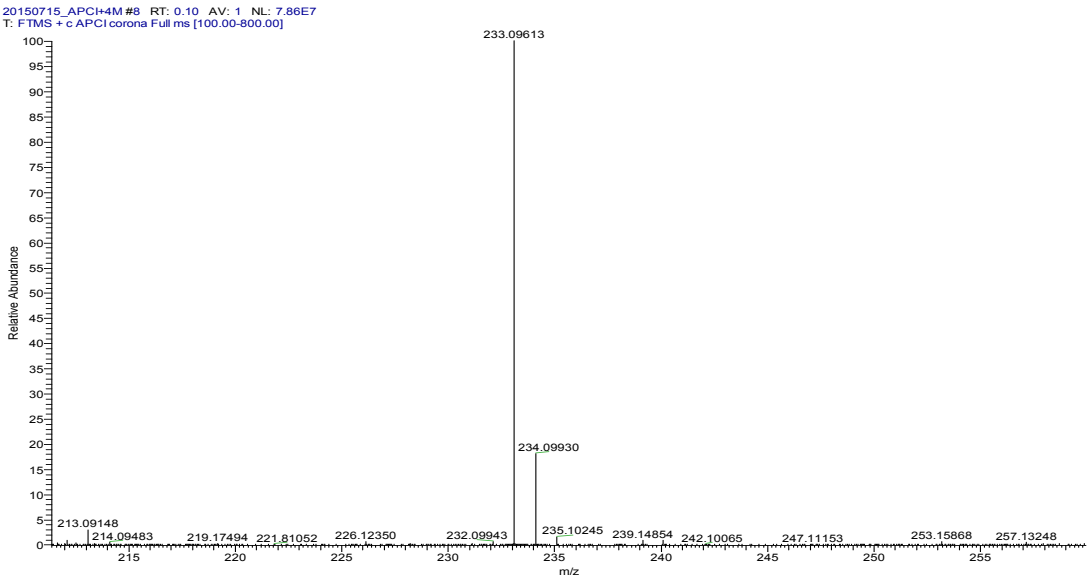


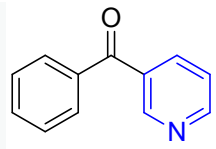
(23) 1-naphthyl-benzophenone



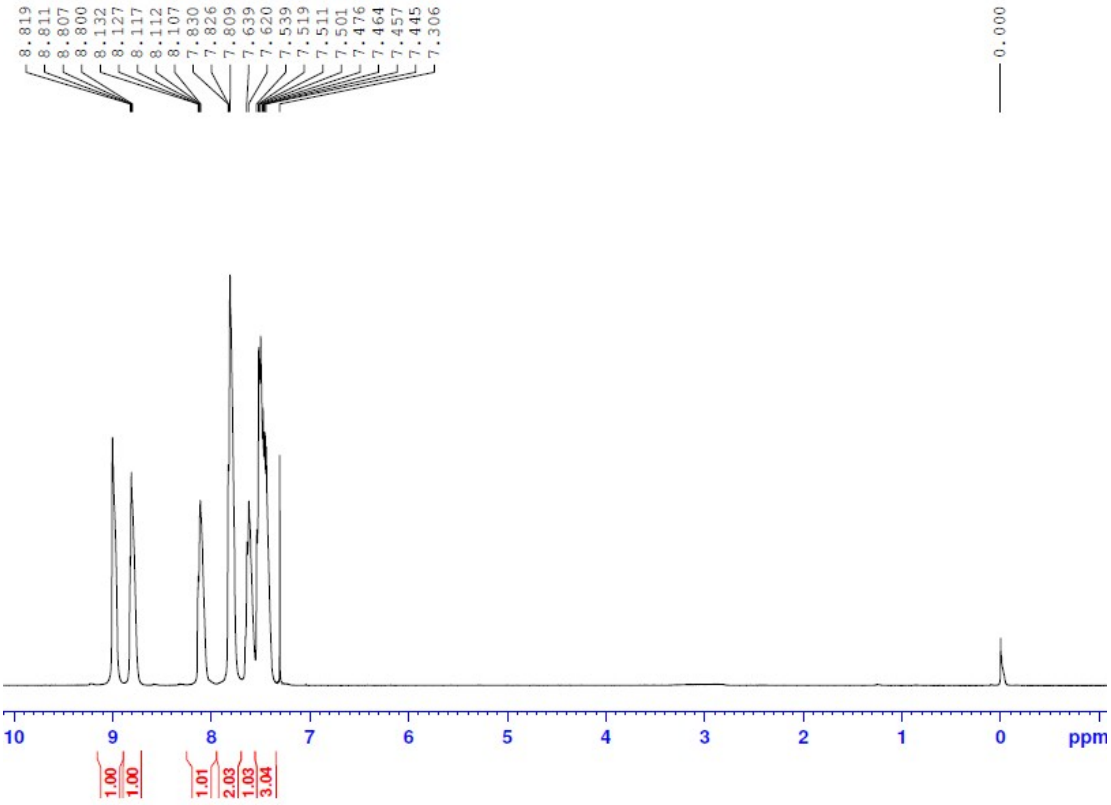

7.904
7.876
7.858
7.855
7.605
7.602
7.587
7.584
7.566
7.547
7.544
7.530
7.527
7.519
7.514
7.512
7.509
7.501
7.500
7.493
7.481
7.476
7.467
7.448
7.428
7.240
1.260
1.254
0.095
0.085
0.006
0.000
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.02
2.06
1.98
5.27

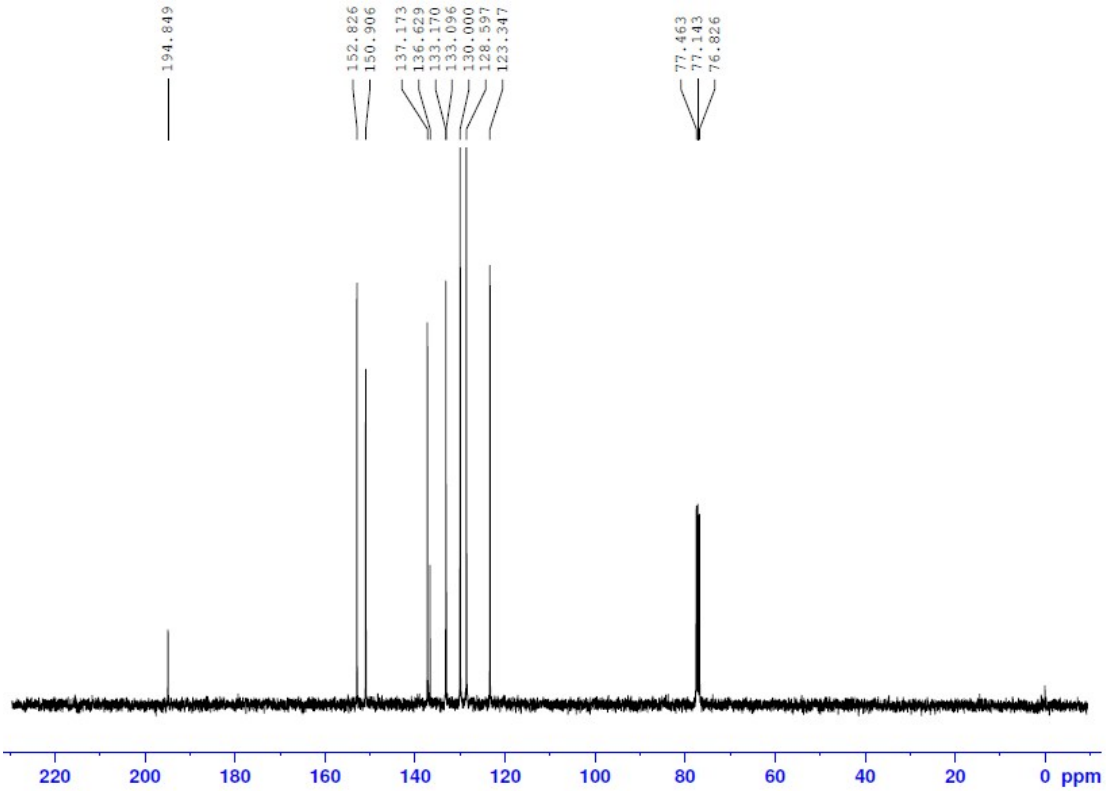

198.074
138.297
136.326
133.725
133.286
131.318
130.962
130.448
128.483
128.443
127.832
127.300
126.496
125.701
124.366
77.406
77.089
76.771
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

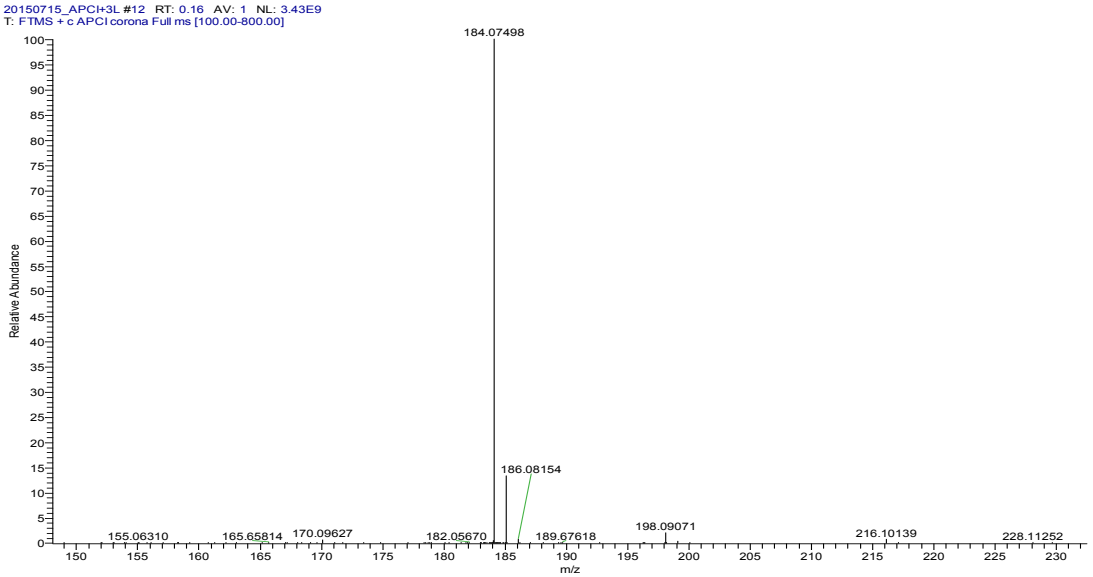




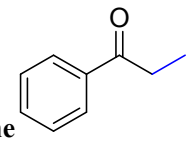
(24) 3-Benzoylpyridine

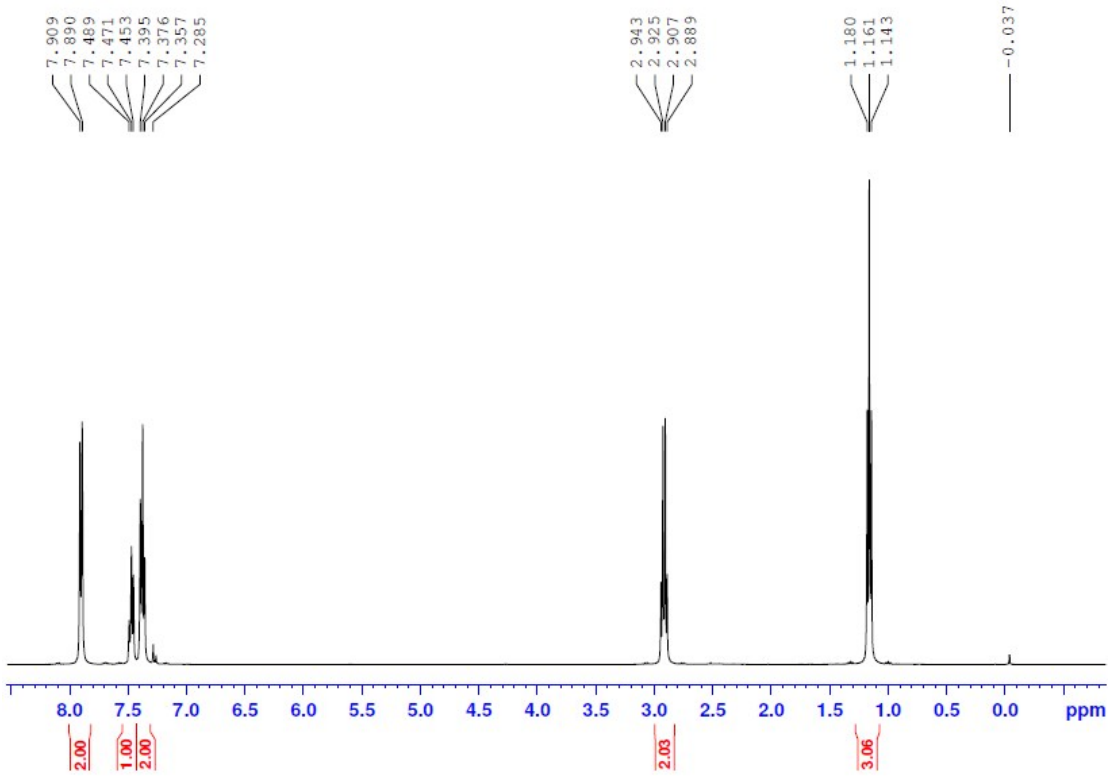


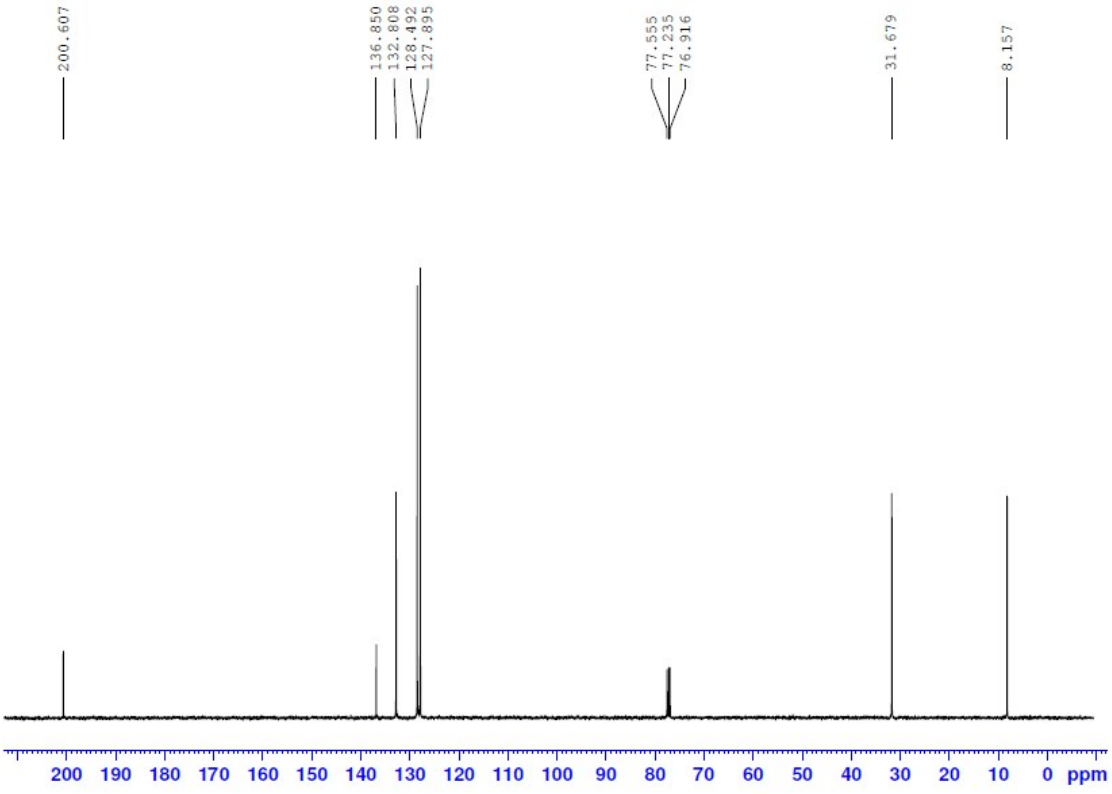


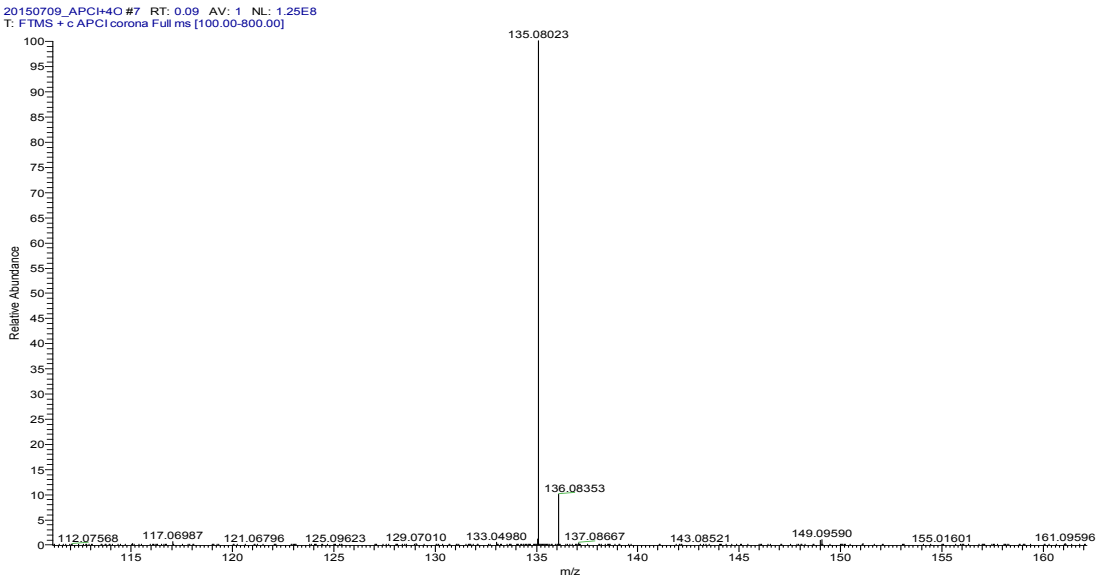


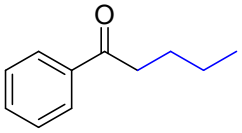
(25) propiophenone



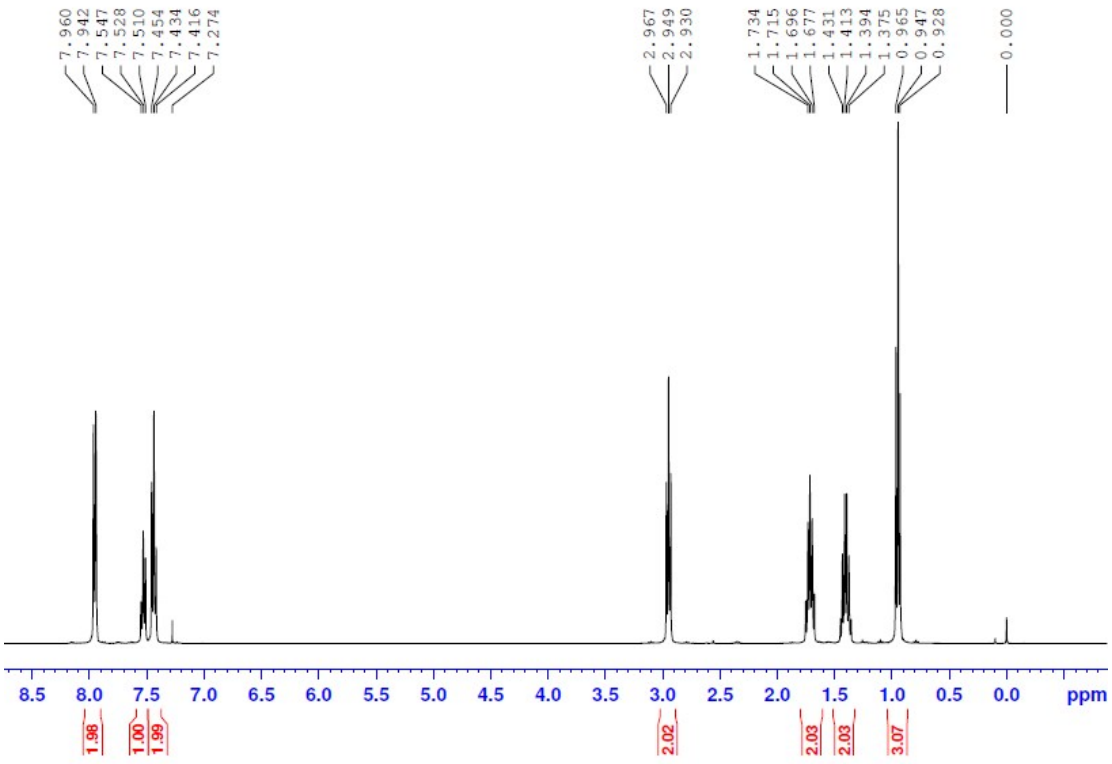

7.909
7.890
7.489
7.471
7.453
7.395
7.376
7.357
7.285
2.943
2.925
2.907
2.889
1.180
1.161
1.143
0.037
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.00
2.00
2.03
3.06

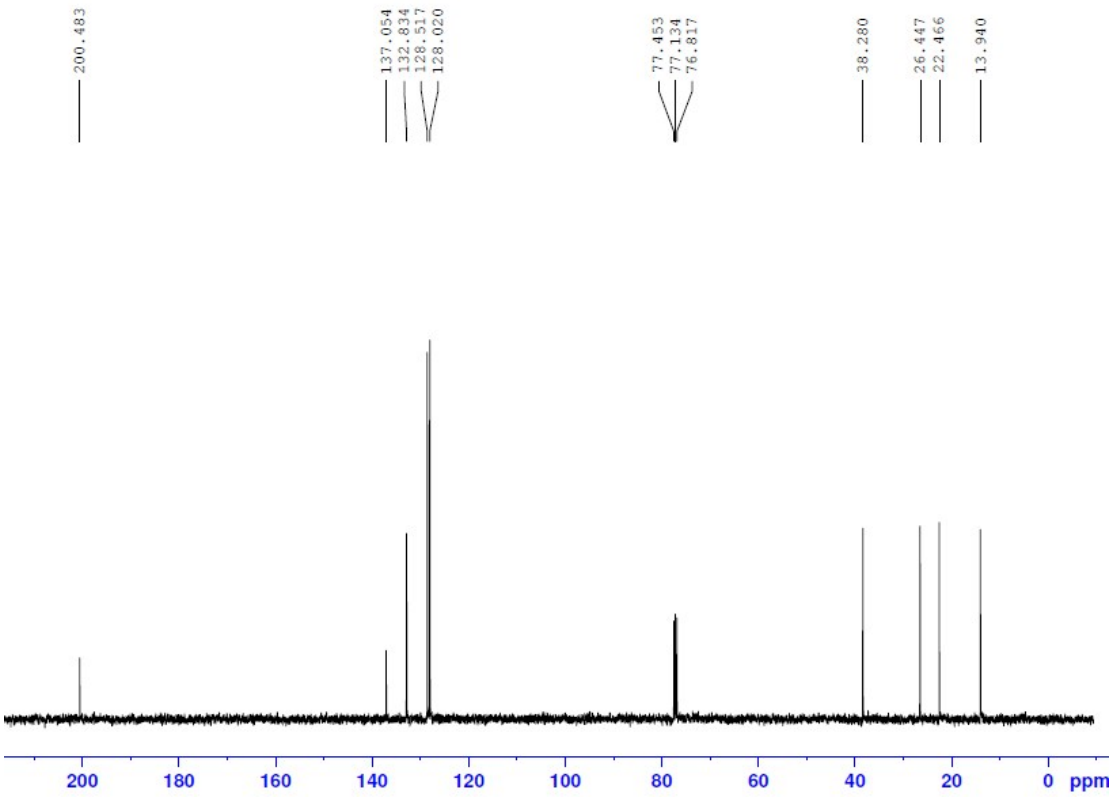

200.607
136.850
132.808
128.492
127.895
77.555
77.235
76.916
31.679
8.157
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

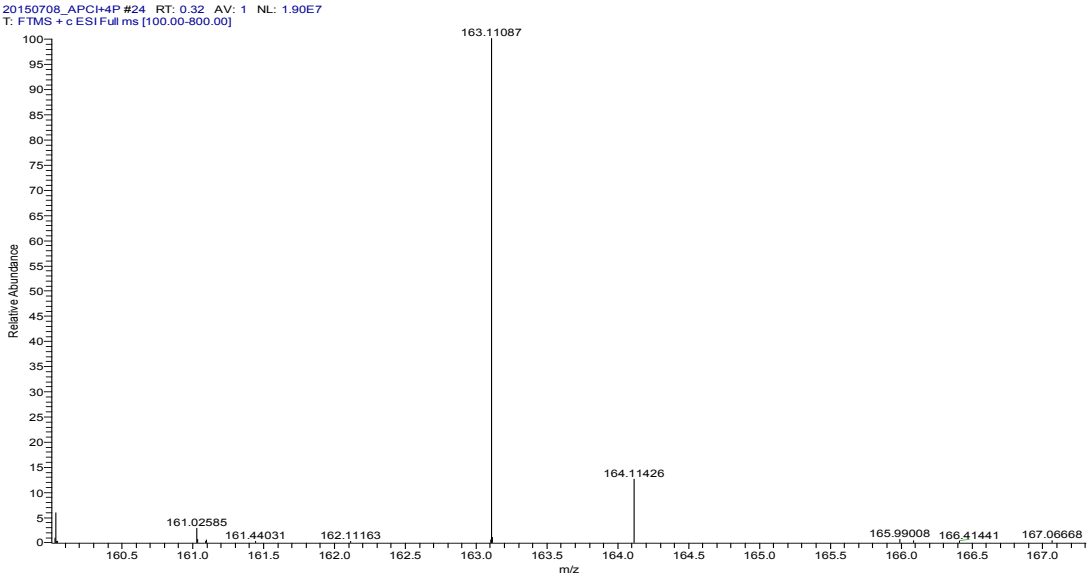


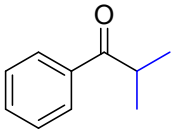


(26) pentanophenone

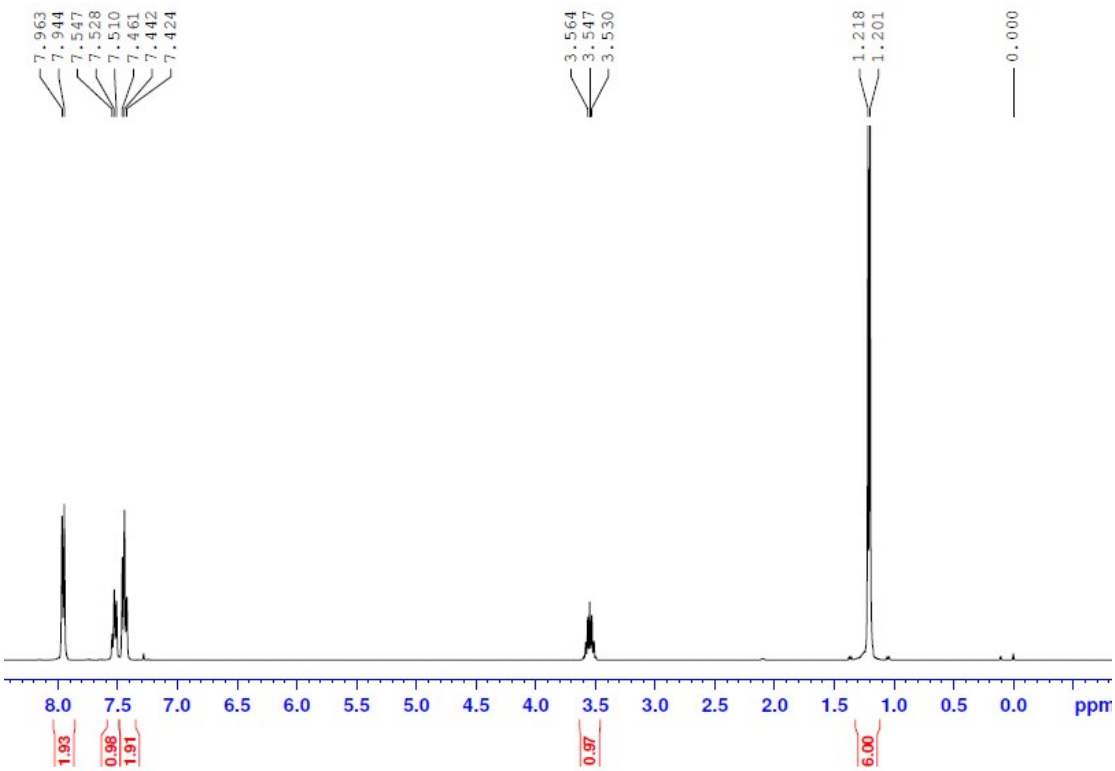


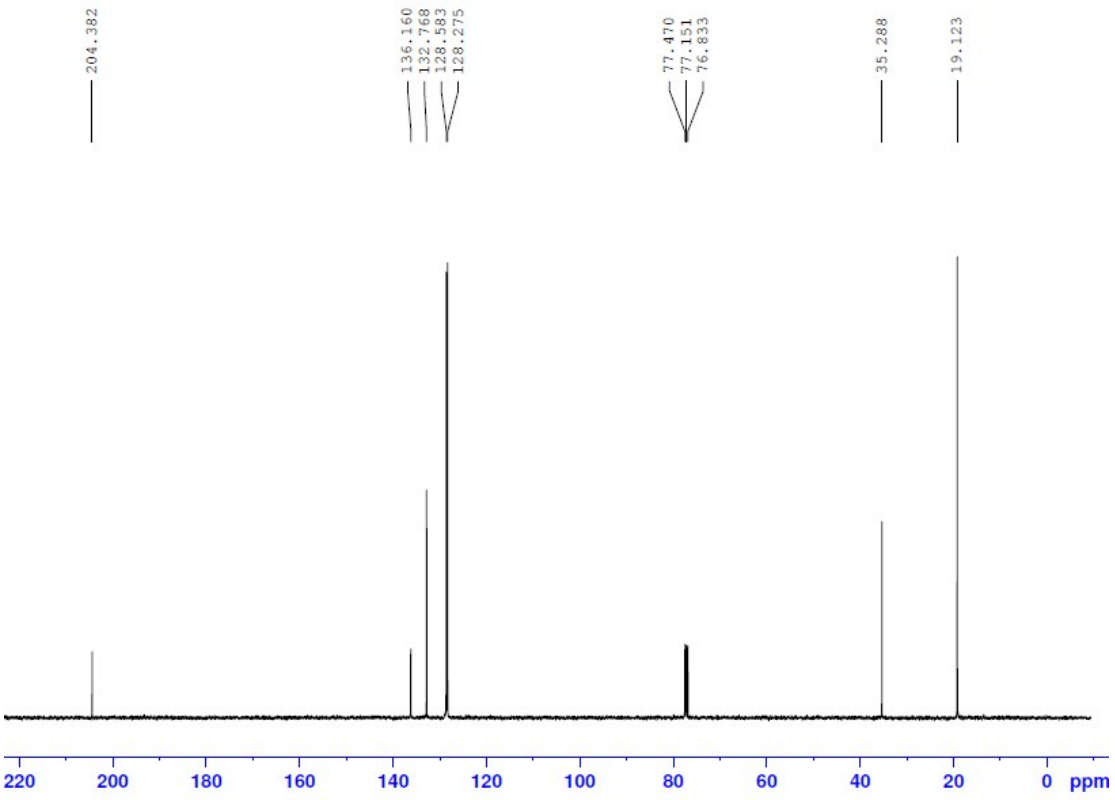


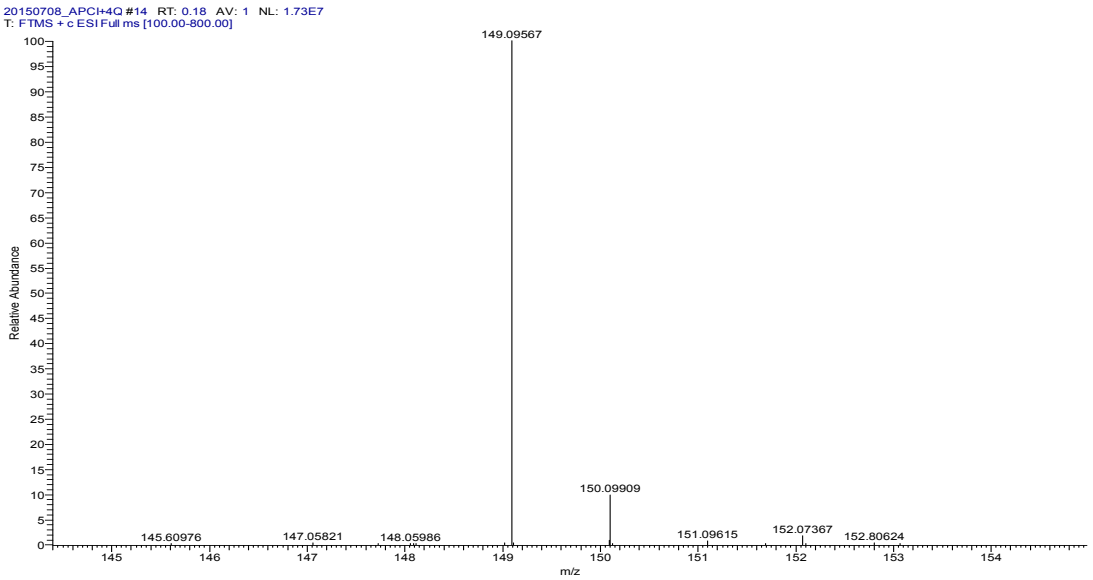


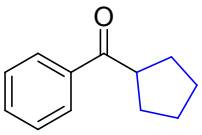


(27) isobutyrophenone

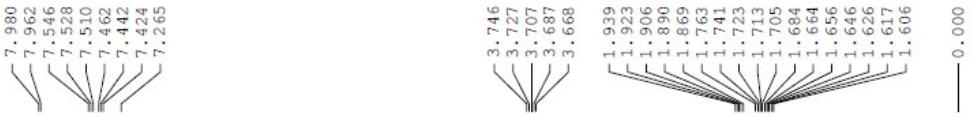

7.963
7.944
7.547
7.528
7.510
7.461
7.442
7.424
3.564
3.547
3.530
1.218
1.201
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.93
0.98
1.91
0.97
6.00

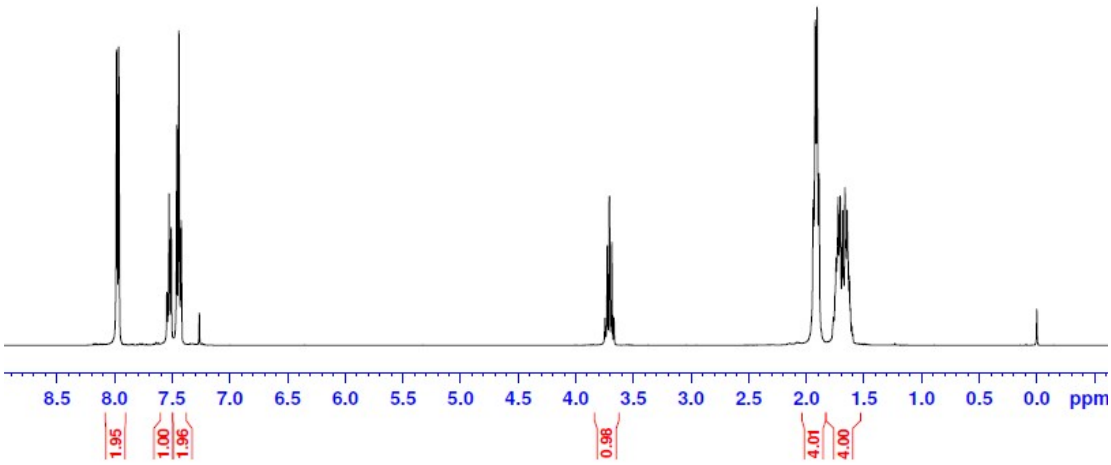

204.382
136.160
132.768
128.583
128.275
77.470
77.151
76.833
35.288
19.123
220
200
180
160
140
120
100
80
60
40
20
0
ppm

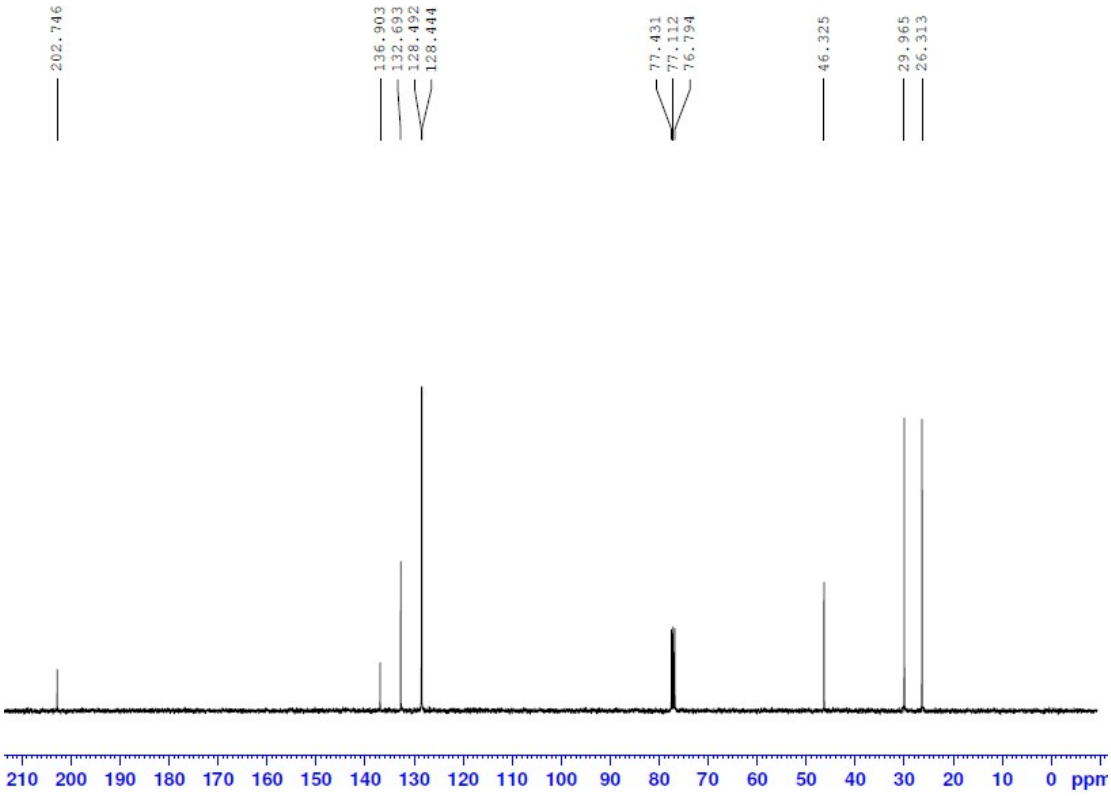


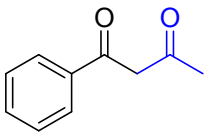


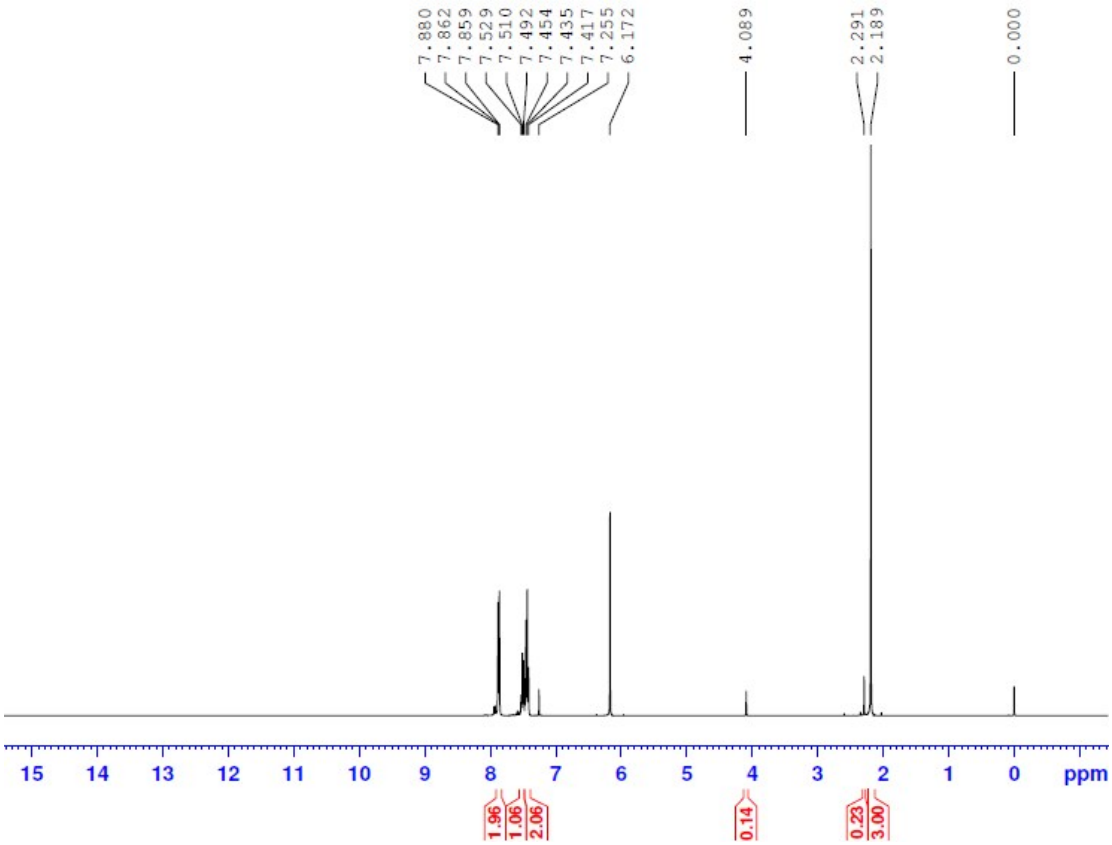
(28) cyclopentyl(phenyl)methanone

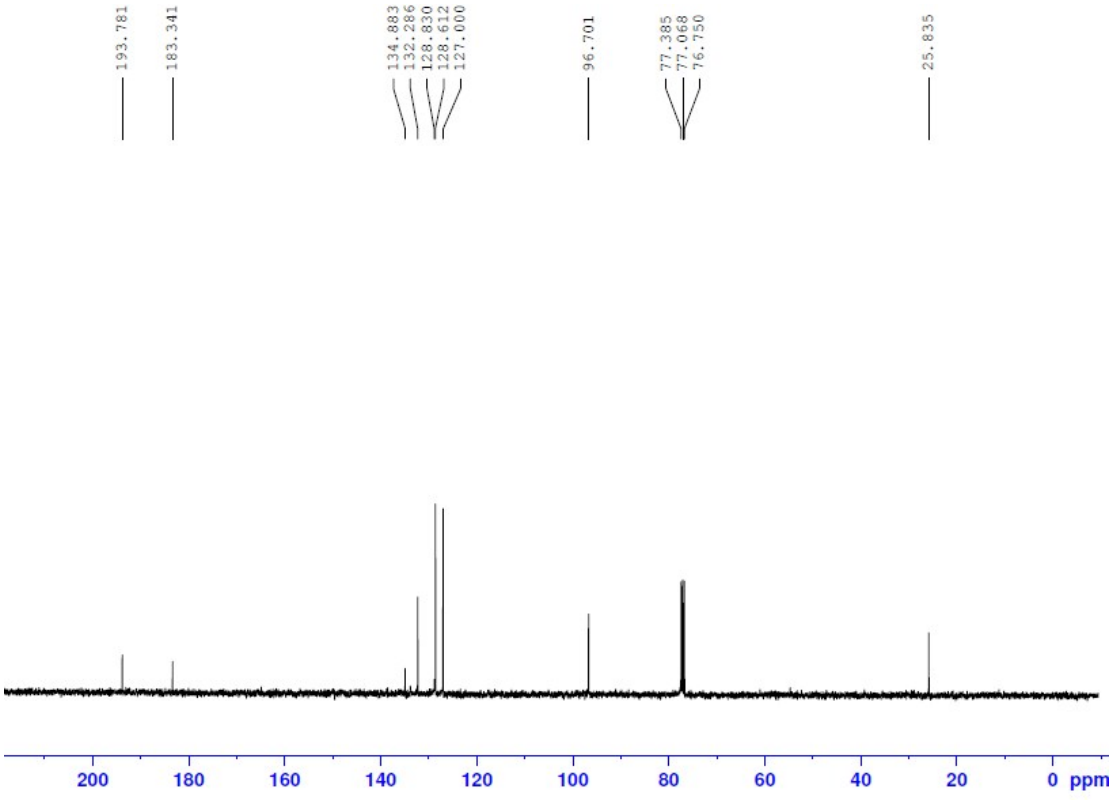


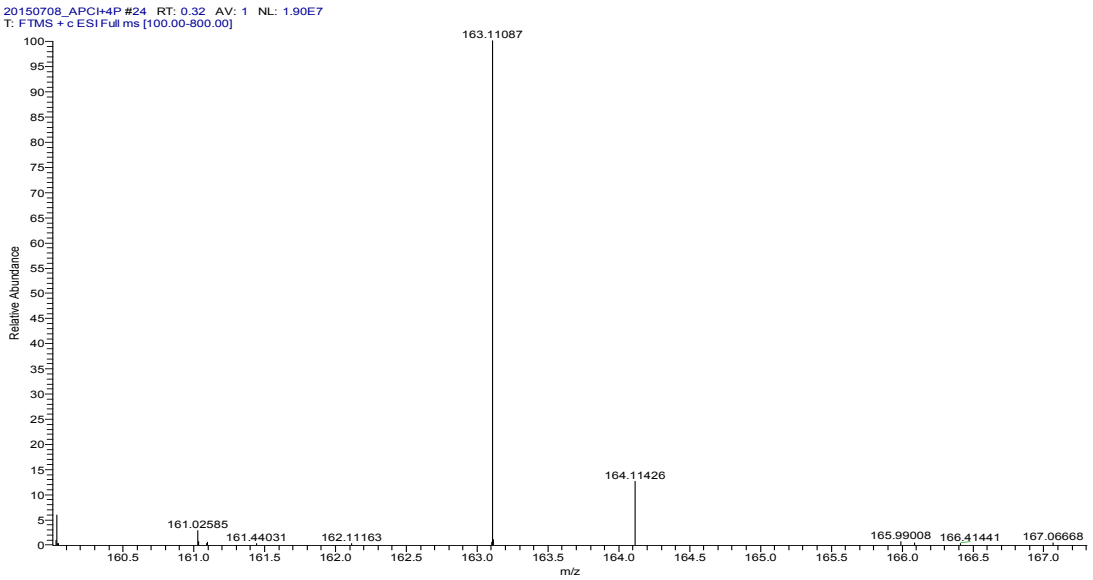


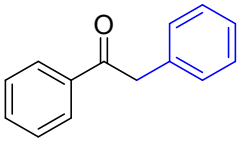


(29) benzoylacetone 

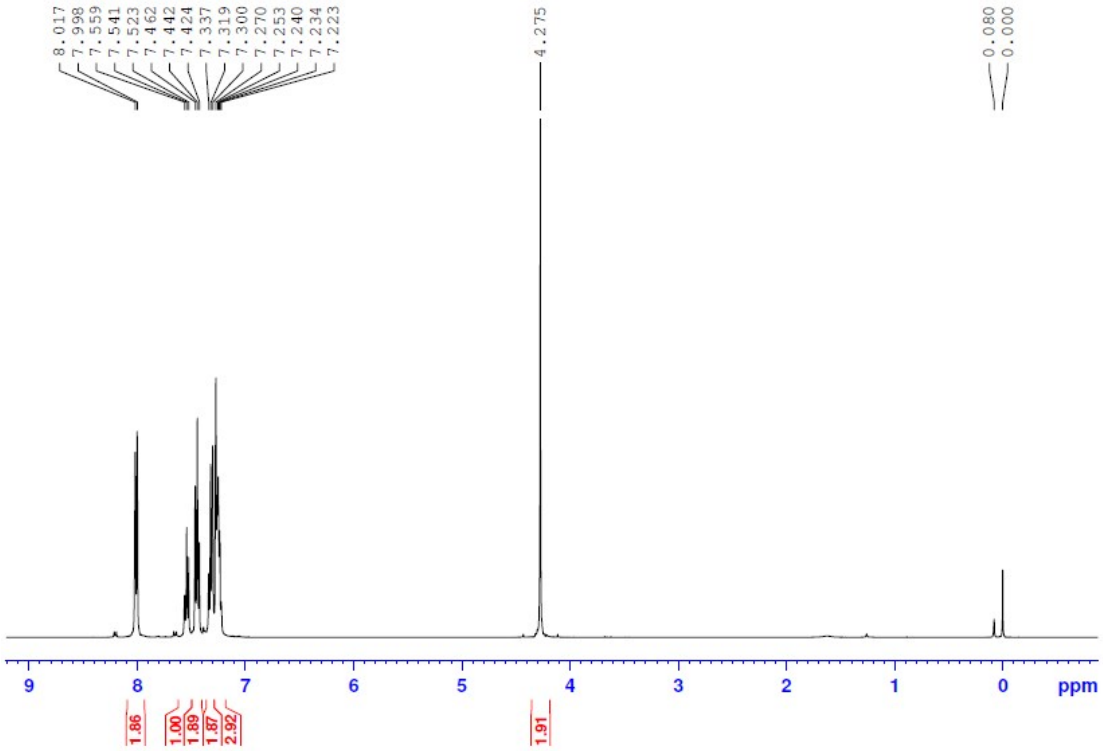

7.880
7.862
7.859
7.529
7.510
7.492
7.454
7.435
7.417
7.255
6.172
4.089
2.291
2.189
0.000
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.96
1.06
2.06
0.14
0.23
3.00

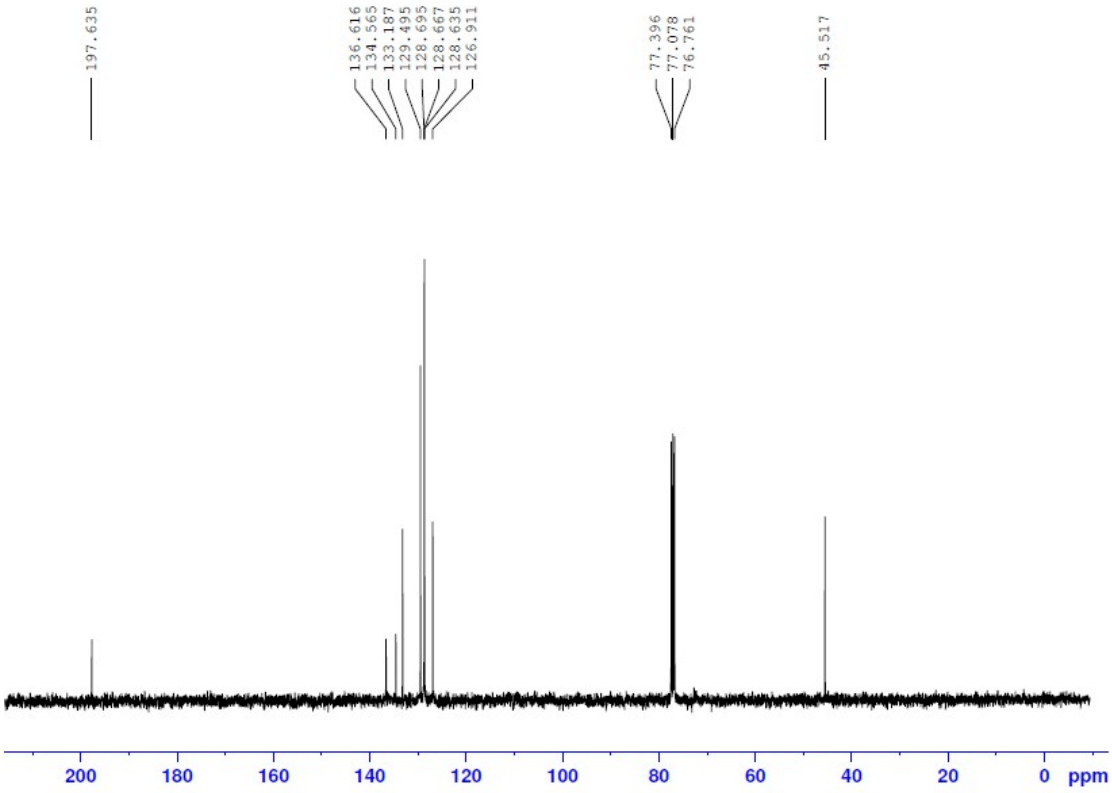

193.781
183.341
134.883
132.286
128.830
128.612
127.000
96.701
77.385
77.068
76.750
25.835
200 180 160 140 120 100 80 60 40 20 0 ppm

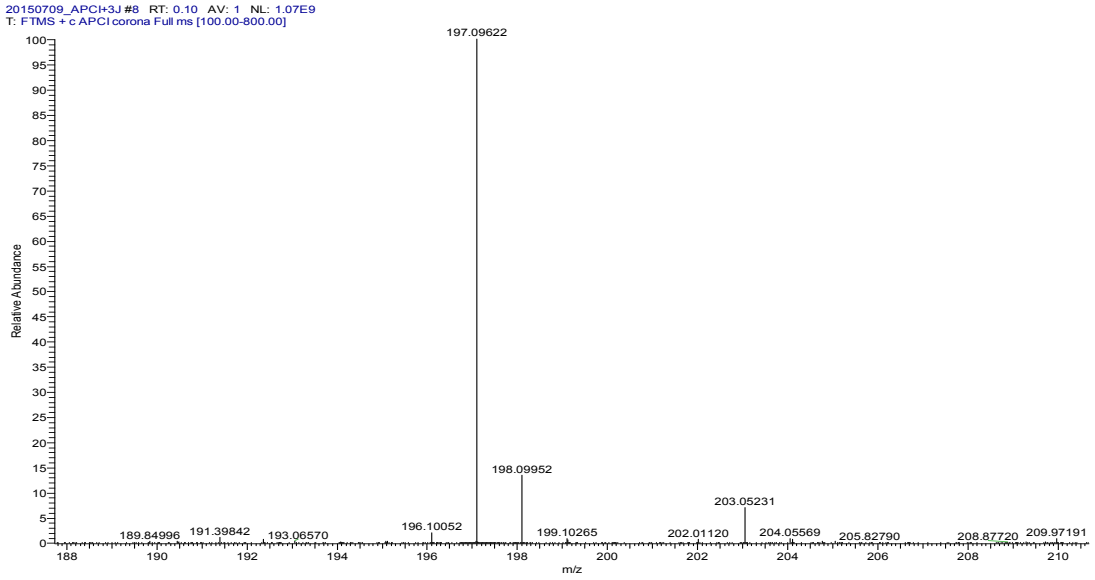




(30) 1,2-diphenylethanone




197.635
136.616
134.565
133.187
129.495
128.695
128.667
128.635
126.911
77.396
77.078
76.761
45.517
200
180
160
140
120
100
80
60
40
20
0
ppm


20150709_APCI+3J #8 RT: 0.10 AV: 1 NL: 1.07E9
T: FTMS + c APCI corona Full ms [100.00-800.00]
Relative Abundance
m/z
197.09622
198.09952
203.05231
189.84996
191.39842
193.06570
196.10052
199.10265
202.01120
204.05569
205.82790
208.87720
209.97191