# Supporting Information

## Aerobic oxidation at benzylic positions catalyzed by a simple $Pd(OAc)_2$/bis-triazole system

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### 1. General remarks.

Commercially available reagents were used throughout without purification unless otherwise stated. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz for $^1$H and 75.4 MHz for $^{13}$C) at 20 ºC. Chemical shifts (δ) are given in ppm downfield from $Me_4Si$ and are referenced as internal standard to the residual solvent (unless indicated) $CDCl_3$ (δ=7.26 for $^1$H and δ=77.00 for $^{13}$C). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on $SiO_2$ (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on $SiO_2$ (silica gel 60, Merck, 230–400 mesh ASTM). IR spectra were recorded on a Perkin–Elmer 1600 FT and JASCO FTIR-4100 infrared spectrophotometer as thin films, and only noteworthy absorptions are reported in $cm^{-1}$. Drying of organic extracts during work-up of reactions was performed over anhydrous $Na_2SO_4$. Evaporation of solvents was accomplished with a Büchi rotatory evaporator. MS and HR-MS were measured using a Waters GCT mass spectrometer.

**2. Synthesis of 2,6-dibromoisonicotinic acid.**[1] A mixture of citrazinic acid (500 mg, 3.22 mmol) and phosphorous(V) oxybromide (1.48 g, 5.16 mmol) were heated at 175 ºC under Ar for 5 h. After cooling, $H_2O$ (50 mL) was added, the aqueous layer was extracted with $CH_2Cl_2$ (4 x 20 mL). The combined organic extracts were dried with anhydrous $Na_2SO_4$ and the solvent was removed *in vacuo*, obtaining 2,6-dibromoisonicotinic acid as a reddish powder (683 mg, 76%). Mp: 176-178 ºC (EtOAc). $^1$H-NMR ($CDCl_3$) $\delta_H$ : 8.05 (s, 2H, H-3, H-5). $^{13}$C-NMR ($CDCl_3$) $\delta_C$ : 127.2 (C-3, C-5), 140.6 (C-2, C-6), 142.0 (C-4), 166.8 (COOH). IR (film) $\nu_{max}$: 3072, 2890, 2579, 1725, 1531. HRMS: calculated for $C_6H_4NO_2Br_2$: 279.8609, found 279.8617.

**3. Synthesis of 3,3'-(4-carboxy-2,6-pyridinediyl)-bis[1-butyl-1*H*-imidazolium] dibromide (L4).**[2] A solution of 2,6-dibromoisonicotinic acid (600 mg, 2.14 mmol) and 1-butylimidazole **L1** (665 mg, 5.36 mmol) was stirred at 150 ºC in a sealed tube for 24 h. After cooling, $CH_2Cl_2$ (15 mL) and $Et_2O$ (4 mL) were added to the mixture. The resultant precipitate was collected and purified by crystallization from MeOH:$Et_2O$ to afford 3,3'-(4-carboxy-2,6-pyridinediyl)-bis[1-butyl-1-H-imidazolium] dibromide as a brown powder (1,05 g, 93%). Mp: >300 ºC (EtOAc). $^1$H-NMR (MeOH-$d_4$) $\delta_H$: 0.93 (t, 6H, $J$ = 7.3, $CH_3$), 1.30-1.38 (m, 4H, $NCH_2CH_2\mathit{CH_2}CH_3$), 1.88-1.97 (m, 4H, $NCH_2\mathit{CH_2}CH_2CH_3$), 4.30 (t, 4H, $J$ = 7.3, $NCH_2$), 8.12 (s, 2H, H-4'), 8.47 (s, 2H, H-3, H-5), 8.87 (s, 2H, H-5'), 10.53 (s, 1H, H-2'). $^{13}$C-NMR (MeOH-$d_4$) $\delta_C$: 13.4 ($CH_3$), 18.9 ($NCH_2CH_2\mathit{CH_2}CH_3$), 31.1 ($NCH_2\mathit{CH_2}CH_2CH_3$), 49.5 ($NCH_2$), 113.6 (C-3, C-5), 119.5 (C-5'), 123.7 (C-4'), 136.3 (C-2'), 145.2 (C-4), 159.1 (C-2, C-6), 163.3 (COOH). IR (film) $\nu_{max}$: 2359, 1533, 1220. HRMS: Calculated for: $C_{20}H_{27}Br_2N_5O_2$ 527.0531, found: 527.0531.

**4. Synthesis of methyl 2,6-bis(bromomethyl)benzoate.**[3] NBS (13 g, 73.08 mmol) was added in four equal portions during 31 h to a solution of methyl 3,5-dimethylbenzoate (1.5 g, 9.13 mmol) in refluxing $CCl_4$ (55.5 mL), each addition being followed by a few milligrams of benzoyl peroxide. The reaction outcome was monitored by $^1$H-NMR. Upon completion, the mixture was cooled to room temperature and filtered. The filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), dried over anhydrous $Na_2SO_4$, and evaporated *in vacuo*. The residue was dissolved in anhydrous THF (20 mL), and diethyl phosphate (13.8 mL, 1.07 mmol) and *i*$Pr_2$NEt (18.6 mL, 1.07 mmol) were added at 0 ºC under Ar. The stirred mixture was allowed to warm to room temperature and stirred for 2 days (the reaction was monitored by $^1$H-NMR), and then poured onto ice/water and extracted with $Et_2O$ (4 x 30 mL). The organic layers were washed with 1M HCl (1 x 10 mL) and brine (1 x 10 mL), dried over anhydrous $Na_2SO_4$, and evaporated *in vacuo* to give a residue which was purified by flash chromatography on silicagel using $Et_2O$ as eluent. Methyl 3,5-bis(bromomethyl)benzoate was obtained as a yellow powder (1.46 g, 68%). Mp: 95-97 ºC (EtOAc). $^1$H-NMR ($CDCl_3$) $\delta_H$: 3.86 (s, 3H, $CH_3$), 4.44 (s, 4H, $CH_2$), 7.56 (s, 1H, H-1), 7.94 (d, 2H, $J$ = 1.6, H-3, H-5). $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 31.8 ($CH_3$), 52.4 ($CH_2$), 129.9 (C-3, C-5), 131.4 (C-4), 133.8 (C-1), 138.9 (C-2, C-6), 165.9 (CO). IR (film) $\nu_{max}$: 1728, 1604, 1436, 1318, 1231, 1108, 1026.

**5. Synthesis of methyl 2,6-bis(pyrazol-1-ylmethyl)benzoate (L5)**.[4] A mixture of methyl 2,6-bis(bromomethyl)benzoate (600 mg, 1.86 mmol), pyrazole **L2** (2.79 mg, 4.09 mmol), and $Cs_2CO_3$ (2.37 g, 7.27 mmol) was refluxed in dry acetonitrile (45 mL) under argon for 2 h. After cooling, the resultant solution was filtered and water (30 mL) was added. The aqueous layer was extracted with EtOAc (2 x 40 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and the solvent was removed *in vacuo* to give a residue which was purified by gradient flash chromatography on silicagel (Hexane:EtOAc 7:3 →EtOAc→EtOAc:MeOH 9.5:0.5). Methyl 2,6-bis(pyrazol-1-ylmethyl)benzoate was obtained as a white powder (570 mg, 99%). Mp: 62-63 ºC (Hexane: EtOAc). $^1$H-NMR ($CDCl_3$) $\delta_H$: 3.84 (s, 3H, $CH_3$), 5.29 (s, 4H, $CH_2$), 6.25 (s, 2H, H-4'), 7.17 (s, 1H, H-1), 7.36 (d, 2H, $J$ = 1.4, H-3'), 7.51 (d, 2H, $J$ = 2.0, H-3, H-5), 7.77 (s, 2H, H-5'). $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 52.3 ($CH_3$), 55.2 ($CH_2$), 106.3 (C-4'), 128.3 (C-3, C-5), 129.5 (C-5'), 131.1 (C-4), 131.3 (C-1), 137.9 (C-2, C-6), 139.9 (C-3'), 166.2 (CO). IR (film) $\nu_{max}$: 1720, 1428, 1303, 1213, 772 HRMS: Calculated for $C_{16}H_{16}N_4O_2$ 296.1273, found: 296.1275

**6. Synthesis of methyl 3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate (L6).**[5] A mixture of methyl 3,5-bis(bromomethyl)benzoate (600 mg, 1.86 mmol), 1*H*-1,2,4-triazole **L3** (283 mg, 4.09 mmol) and $Cs_2CO_3$ (2.37 mg, 7.27 mmol) was refluxed in dry acetonitrile (45 mL) under Ar for 3 h. After cooling, the resultant solution was filtered and water (30 mL) was added. The aqueous layer was extracted with EtOAc (3 X 40 mL). The combined organic extracts were dried with anhydrous $Na_2CO_3$ and the solvent was removed *in vacuo* to give a residue which was purified by silica gel chromatography eluting with hexane/EtOAc 7/3 → EtOAc → EtOAc/MeOH 9.5/0.5 to afford methyl 3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate **3** as a yellowish powder (510 mg, 92%). Mp: 105-107 ºC (EtOAc). $^1$H-NMR ($CDCl_3$) $\delta_H$ (ppm): 3.89 (3H, s, $CH_3$), 5.50 (4H, s, $CH_2$), 7.51 (1H, s, H-2), 7.92 (2H, s, H-4, H-6), 8.00 (2H, s, H-3'), 8.59 (2H, s, H-5'); $^{13}$C-NMR ($CDCl_3$) $\delta_C$ (ppm): 53.9 ($CH_2$), 123.9 (C-4'), 128.6 (C-5, C-2), 130.2 (C-4, C-6), 134.2 (C-5'), 135.7 (C-1, C-2); IR (film) $\nu_{max}$($cm^{-1}$) **:** 1716, 1508, 1428, 1314, 1213, 1142, 1020. HR-MS: Calculated for $C_{14}H_{14}N_6O_2$ 299.1256, found 299.1248.

**7. Aerobic oxidation of alcohols in the presence of $Pd(OAc)_2$ and L6. General procedure.** A round bottom flask equipped with a magnetic stirrer bar was charged with the alcohol (1 mmol), NaOAc (8.0 mg, 0.1 mmol), $Pd(OAc)_2$ (20 μL of a 5 x $10^{-6}$M solution in PEG-400, $10^{-7}$ mmol), L6 (20 μL of a 5 x $10^{-6}$M solution in PEG-400, $10^{-7}$ mmol) and PEG 400 (1 mL) at room temperature. The system was purged with molecular oxygen, and an oxygen-filled balloon (1-1.2 atm) was connected. The mixture was heated at 120 ºC under stirring for 48 h. The reaction outcome was monitored by $^1$H-NMR. Upon completion, the mixture was cooled to room temperature and water was added (50 mL aprox.). The resulting solution was acidified with HCl 1M (pH≈1-2) and extracted with $Et_2O$ (4 x 6 mL) and the combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to give a residue which was purified by flash column chromatography using hexane:ethyl acetate as eluent. By this procedure the following ketones and acids were prepared:

**Acetophenone.**[6] (119 mg, 99%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.61 (s, 3H, $CH_3$), 7.42-7.63 (m, 3H, $H_{arom}$), 7.96 (t, *J*= 8, 2H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 26.5 ($CH_3$), 128.2 ($C_{arom-H}$), 128.5 ($C_{arom-H}$), 133.0 ($C_{arom}$), 137.07 ($C_{q-arom}$), 198.1 (CO); LRMS (m/z): 120.1 ($M^+$).

**1-Phenyl-1-propanone.**[7] (122 mg, 91%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 1.22 (t, 3H, *J* = 7.2, $CH_3$), 3.0 (q, 2H, *J* = 7.3, $CH_2$), 7.45 (t, 2H, *J* = 6.9, $H_{arom}$), 7.54 (t, 1H, *J* = 6.6, $H_{arom}$), 7.96 (d, 2H, *J* = 8.3, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 8.2 ($CH_3$), 31.8 ($CH_2$), 127.9 ($C_{arom-H}$), 128.6 ($C_{arom-H}$), 132.9 ($C_{arom-H}$), 133.9 ($C_{q-arom}$), 200.8 (CO); LRMS (m/z): 134.1 ($M^+$).

**2,2-Dimethyl-1-phenylpropanone**.[7] (159 mg, 98%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 1.35 (s, 9H, $CH_3$), 7.30 (dd, 2H, *J* = 5.0, 2.3, $H_{arom}$), 7.44 (dd, 1H, *J* = 5.1, 1.5, $H_{arom}$), 7.66-7.72 (m, 2H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 28.0 ($CH_3$), 44.2 ($C_q$), 127.7 ($C_{arom-H}$), 127.8 ($C_{arom-H}$), 128.0 ($C_{arom-H}$), 130.8 ($C_{arom-H}$), 160.4 ($C_{q-arom}$), 209.3 (CO); LRMS (m/z): 162.1 ($M^+$).

**Benzoylcyanide.**[8] (71 mg, 54%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.47 (m, 2H, $H_{arom}$), 7.59 (m, 1H, $H_{arom}$), 8.13 (m, 2H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 115.2 (CN), 127.2 ($C_{arom-H}$), 128.5 ($C_{arom-H}$), 135.0 ($C_{arom-H}$), 140.1 ($C_{q-arom}$), 199.1 (CO); LRMS (m/z): 131.1 ($M^+$).

**2-Oxo-phenylacetic acid.**[9] (129 mg, 86%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.55 (t, 2H, *J* = 7.8, $H_{arom}$), 7.72 (d, 1H, *J* = 7.6, $H_{arom}$), 7.8.35 (d, 2H, *J* = 7.6, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 128.3 ($C_{arom-H}$), 129.2 ($C_{arom-H}$), 130.0 ($C_{arom-H}$), 133.6 ($C_{q-arom}$), 160.9 (COOH), 171.6 (CO); LRMS (m/z): 150.1 ($M^+$).

**1-(2-Methoxyphenyl)ethanone.**[10] (132 mg, 88%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.60 (s, 3H, $CH_3$), 3.89 (s, 3H, $OCH_3$), 6.91-7.03 (m, 2H, $H_{arom}$), 7.44 (t, 1H, *J* = 9.2, $H_{arom}$), 7.71 (d, 1H, *J* = 7.7, $CH_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 31.7 ($CH_3$), 55.4 ($OCH_3$), 111.5 ($C_{arom-H}$), 120.5 ($C_{arom-H}$), 126.3 ($C_{q-arom}$), 130.3 ($C_{arom-H}$), 133.6 ($C_{arom-H}$), 158.8 ($C_{q-arom}$), 199.8 (CO); LRMS (m/z): 150.1 ($M^+$).

**1-(*p*-Tolyl)ethanone .**[8] (114 mg, 85%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.39 (s, 3H, $CH_3$), 2.55 (s, 3H, $CH_3$), 7.24 (d, 2H, *J* = 8.2, $H_{arom}$), 7.84 (d, 2H, *J*= 8.2, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 21.6 ($CH_3$), 26.5 ($CH_3$), 128.5 ($C_{arom-H}$), 129.2 ($C_{arom-H}$), 134.7 ($C_{q-arom}$), 143.8 ($C_{q-arom}$), 197.8 (CO); LRMS (m/z): 134.1 ($M^+$).

**4-Chloroacetophenone.**[11] (129 mg, 84%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.58 (s, 3H, $CH_3$), 7.43 (d, 2H, *J* = 8.8, $H_{arom}$), 7.89 (d, 2H, *J* = 8.8, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$ (ppm): 26.5 ($CH_3$), 128.9 ($C_{arom-H}$), 129.7 ($C_{arom-H}$), 135.4 ($C_{q-arom}$), 139.6 ($C_{q-arom}$), 196.8 (CO); LRMS (m/z): 154.1 ($M^+$).

**Indanone.**[7] (128 mg, 97%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.67 (t, 2H, *J* = 5.8, $CH_2$), 3.13 (t, 2H, *J* = 5.3, $CH_2$), 7.37 (t, 1H, *J* = 7.5, $H_{arom}$), 7.48 (d, 1H, *J* = 7.5, $H_{arom}$), 7.59 (t, 1H, *J* = 7.5, $H_{arom}$), 7.76 (d, 1H, *J* = 7.5, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 25.8 ($CH_2$), 36.2 ($CH_2$), 123.7 ($C_{arom-H}$), 126.7 ($C_{arom-H}$), 127.3 ($C_{arom-H}$), 134.6 ($C_{arom-H}$), 137.1 ($C_{q-arom}$), 155.2 ($C_{q-arom}$), 207.1 (CO); LRMS (m/z): 132.1 ($M^+$).

**Fluorenone.**.[12] (169 mg, 94%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.20-7.25 (m, 2H, $H_{arom}$), 7.36-7.44 (m, 4H, $H_{arom}$), 7.59 (dd, 2H, *J* = 0.8, 7.4, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 120.1 (C), 124.0 ($C_{arom-H}$), 128.8 ($C_{arom-H}$), 133.9 ($C_{q-arom}$), 134.5 ($C_{arom-H}$), 144.18 ($C_{q-arom}$), 193.7 (CO); LRMS (m/z): 180.2 ($M^+$).

**Xanthenone.**[8] (176 mg, 90%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.31 (t, 2H, *J* = 7.2, $H_{arom}$), 7.41 (d, 2H, *J* = 8.4, $H_{arom}$), 7.65 (t, 2H, *J* = 6.9, $H_{arom}$), 8.27 (d, 2H, *J* = 9.7, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 117.9 ($C_{arom-H}$, 121.7 ($C_{arom-H}$), 123.9 ($C_{arom-H}$), 126.6 ($C_{arom-H}$), 134.8 ($C_{arom-H}$), 156.1 ($C_{q-arom}$), 177.2 (CO); LRMS (m/z): 196.1 ($M^+$).

**Benzophenone7** (166 mg, 91%) $^1$H-NMR ($CDCl_3$) $\delta_H$ : 7.42-7.52 (m, 4H, $H_{arom}$), 7.54-7.62 (m, 2H, $H_{arom}$), 7.79-7.82 (m, 4H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$ : 128.2 ($C_{arom}$), 129.94 ($C_{arom}$), 132.3 ($C_{arom}$), 132.5 ($C_{q-arom}$), 196.6 (CO); LRMS (m/z): 182.1 ($M^+$).

**2-Methylbenzophenone**.[13] (145 mg, 74%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.34 (s, 3H, $CH_3$), 7.25-7.33 (m, 3H, $H_{arom}$), 7.38 (d, 1H, *J* = 7.5, $H_{arom}$), 7.45 (t, 2H, *J* = 7.5, $H_{arom}$), 7.58 (t, 1H, *J* = 8, $H_{arom}$), 7.81 (d, 2H, *J* = 8.3Hz, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 19.9 ($CH_3$); 125.2 ($C_{arom-H}$), 128.5 ($C_{arom-H}$), 130.1 ($C_{arom-H}$), 131.0 ($C_{arom-H}$), 133.1 ($C_{arom-H}$), 136.7 ($C_{q-arom}$), 137.8 ($C_{q-arom}$), 138.6 ($C_{q-arom}$), 198.6 (CO); LRMS (m/z): 196.2 ($M^+$).

**Benzil**.[14] (from benzoin 204 mg, 97%; from hydrobenzoin 199 mg, 95%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.50-7.56 (m, 4H, $H_{arom}$), 7.64-7.70 (m, 2H, $H_{arom}$), 7.94-8.01 (m, 4H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 129.0 ($C_{arom-H}$), 129.9 ($C_{arom-H}$), 133.0 ($C_{q-arom}$), 134.9 ($C_{arom-H}$), 194.6 (CO); LRMS (m/z): 210.1 ($M^+$).

**Desoxybenzoin.**[15] (184 mg, 94%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 4.30 (s, 2H, $CH_2$), 7.24-7.29 (m, 3H, $H_{arom}$), 7.32-7.36 (m, 2H, $H_{arom}$), 7.45-7.49 (m, 2H, $H_{arom}$), 7.55-7.59 (m, 2H, $H_{arom}$), 8.02-8.05 (m, 2H, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 45.5 ($CH_2$), 126.9 ($C_{arom-H}$), 126.9 ($C_{arom-H}$), 128.5 ($C_{q-arom}$), 128.6 ($C_{arom-H}$), 128.6 ($C_{arom-H}$), 128.7 ($C_{arom-H}$), 129.5 ($C_{arom-H}$), 133.17 ($C_{arom-H}$), 134.5 ($C_{q-arom}$), 136.6 ($C_{q-arom}$), 197.6 (CO); LRMS (m/z): 196.1 ($M^+$).

**Benzoic acid.**[16] (101 mg, 83%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.49 (t, 2H, *J* = 7.5, $H_{arom}$), 7.63 (t, 1H, *J* = 6.8, $H_{arom}$), 8.15 (d, 2H, *J* = 8.4, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 128.4 ($C_{arom-H}$), 129.6 ($C_{q-arom}$), 130.1 ($C_{arom-H}$), 133.7 ($C_{arom-H}$), 172.1 (COOH); LRMS (m/z): 122.1 ($M^+$).

**4-Isopropylbenzoic acid.**[17] (154 mg, 94%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 1.29 (d, 6H, *J* = 6.9, $CH_3$), 2.99 (q, 1H, *J* = 6.9, CH), 7.34 (d, 2H, *J* = 8.4, $H_{arom}$), 8.06 (d, 2H, *J* = 8.3, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$ : 23.7 ($CH_3$), 34.2 (CH), 126.6 ($C_{arom-H}$), 126.9 ($C_{q-arom}$), 130.4 ($C_{arom-H}$), 155.3 ($C_{q-arom}$), 172.4 (COOH); LRMS (m/z): 164.1 ($M^+$).

**4-Ethylbenzoic acid.**[16] (129 mg, 86%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 1.28 (t, 3H, *J* = 7.3, $CH_3$), 2.73 (q, 2H, *J* = 7.3, $CH_2$), 7.31 (d, 2H, *J* = 8.1, $H_{arom}$), 8.05 (d, 2H, *J* = 8.3, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 15.1 ($CH_3$), 29.0 ($CH_2$), 126.8 ($C_{q-arom}$), 128.0 ($C_{arom-H}$), 130.4 ($C_{arom-H}$), 150.8 ($C_{q-arom}$), 172.4 (COOH); LRMS (m/z): 150.1 ($M^+$).

**4-Methylbenzoic acid**.[16] (113 mg, 83%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 2.44 (s, 3H, $CH_3$), 7.28 (d, 2H, *J* = 8.4, $H_{arom}$), 8.02 (d, 2H, *J* = 8.2, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 21.7 ($CH_3$), 127.1 ($C_{q-arom}$), 129.1 ($C_{arom-H}$), 130.2 ($C_{arom-H}$), 144.6 ($C_{q-arom}$), 172.2 (COOH); LRMS (m/z): 136.1 ($M^+$).

**4-(Trifluoromethyl)benzoic acid.**[18] (144 mg, 76%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.70 (d, 2H, *J* = 7.7, $H_{arom}$), 8.16 (d, 2H, *J* = 7.3, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 123.2 (d, *J* = 272, $CF_3$), 127.4 (d, *J* = 3.7, $C_{arom-H}$), 132.1 ($C_{arom-H}$), 135.5 (d, *J* = 32.8, $C_{q-arom}$), 136.2 ($C_{q-arom}$), 168.6 (COOH); LRMS (m/z): 190.0 ($M^+$).

**3-Phenoxybenzoic acid.**[18] (175 mg, 82%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 7.03 (2H, d, *J* = 7.7, $H_{arom}$),. 7.15 (1H, t, *J* = 7.3, $H_{arom}$), 7.26 (1H, t, *J* = 3.8, $H_{arom}$;), 7.38 (3H, dd, J = 13.3, 5.6, $H_{arom}$), 7.44 (1H, d, *J* = 8, $H_{arom}$), 7.71 (1H, s, $H_{arom}$), 7.84 (1H, d, *J* = 7.7, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 119.2 ($C_{arom-H}$), 119.8 ($C_{arom-H}$), 123.9 ($C_{arom-H}$), 124.8 ($C_{arom-H}$), 129.9 ($C_{arom-H}$), 131.0 ($C_{q-arom}$), 156.5 ($C_{arom-H}$), 157.6 ($C_{arom-H}$), 160.5 ($C_{q-arom}$), 160.9 ($C_{q-arom}$), 171.0 (COOH); LRMS (m/z): 214.0 ($M^+$).

**3-Methoxybenzoic acid.**[19] (138 mg, 91%) $^1$H-NMR ($CDCl_3$) $\delta_H$: 3.86 (s, 3H, $OCH_3$), 7.15 (dd, 1H, *J* = 7.4, 1.8, $H_{arom}$), 7.37 (t, 1H, *J* = 8.0, $H_{arom}$), 7.62 (s, 1H, $H_{arom}$), 7.72 (d, 1H, *J* = 7.6, $H_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 55.4 ($OCH_3$), 114.4 ($C_{arom-H}$), 120.4 ($C_{arom-H}$), 122.7 ($C_{arom-H}$), 129.5 ($C_{arom-H}$), 130.6 ($C_{q-arom}$), 159.6 ($C_{q-arom}$), 172.1 (COOH); LRMS (m/z): 152.0 ($M^+$).

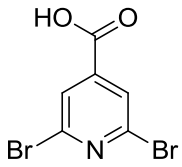
**8. Benzylic C-H oxidation in the presence of $Pd(OAc)_2$ and L6. General procedure.** A round bottom flask equipped with a magnetic stirrer bar was charged with the methylene compound (1 mmol), NaOAc (8.0 mg, 0.1 mmol), $Pd(OAc)_2$ (20 μL of a 5 x $10^{-6}$M solution in PEG-400, $10^{-7}$ mmol), **6** (20 μL of a 5 x $10^{-6}$M solution in PEG-400, $10^{-7}$ mmol) and PEG 400 (1 mL) at room temperature. The system was purged with molecular oxygen, and an oxygen-filled balloon (1-1.2 atm) was connected. The mixture was heated at 120 ºC under stirring for 48 h. The reaction outcome was monitored by $^1$H-NMR. Upon completion, the mixture was cooled to room temperature and water was added (50 mL aprox.). The resulting solution was acidified with HCl 1M (pH≈1-2) and extracted with $Et_2O$ (4 x 6 mL) and the combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to give a residue which was purified by flash column chromatography using hexane:ethyl acetate as eluent. By this procedure the following ketones were prepared:

**Acetophenone.**[6] (114 mg, 95%)
**Benzil.**[12] (204 mg, 97%)
**Xanthenone.**[8] (190 mg, 97%)

**Fluorenone**.[8] (175 mg, 97%)
**Anthraquinone.**[9] (185 mg, 89%) $^{1}$H-NMR ($CDCl_3$) $\delta_H$: 7.79-7.82 (m, 2H, $CH_{arom}$), 8.30-8.33 (m, 2H, $CH_{arom}$); $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 127.2 ($C_{arom-H}$), 133.5 ($C_{q-arom}$), 134.4 ($C_{arom-H}$), 183.2 (CO); LSMR (m/z): 208.1 ($M^+$).
**Benzophenone.**[7] (175 mg, 96%)

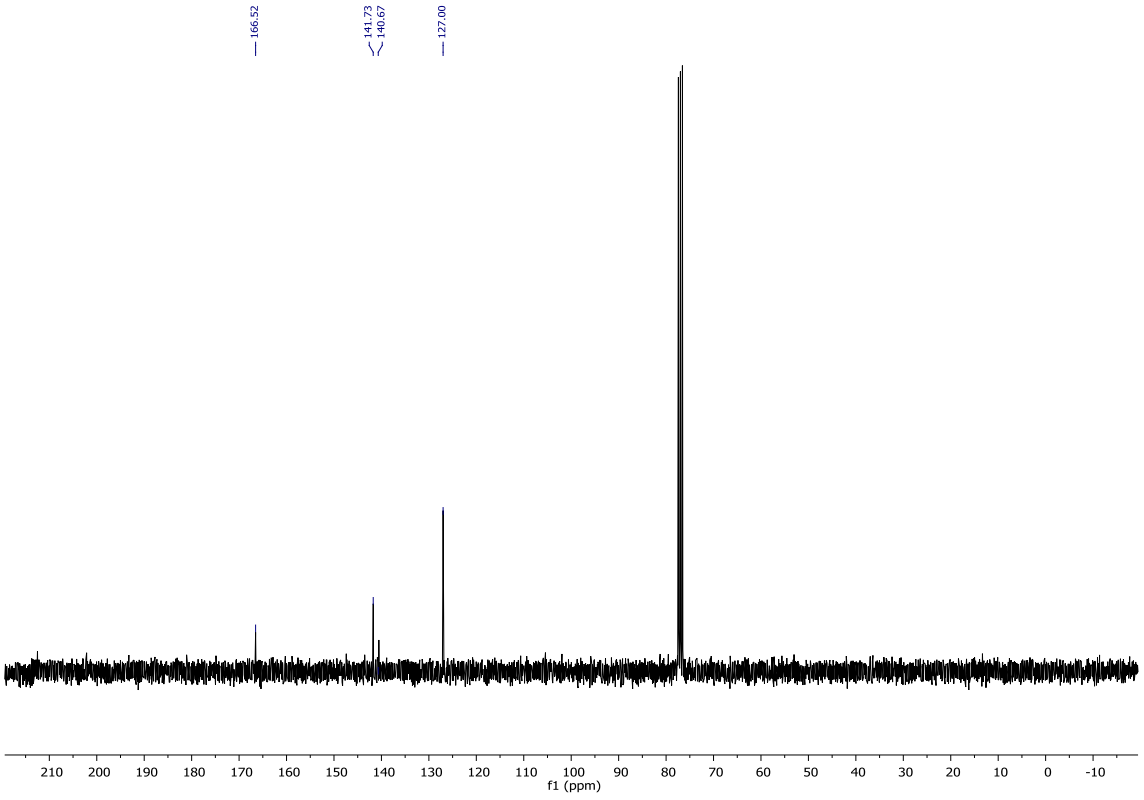
## 9. $^{1}$H-NMR and $^{13}$C-NMR spectra

2,6-Dibromoisonicotinic acid

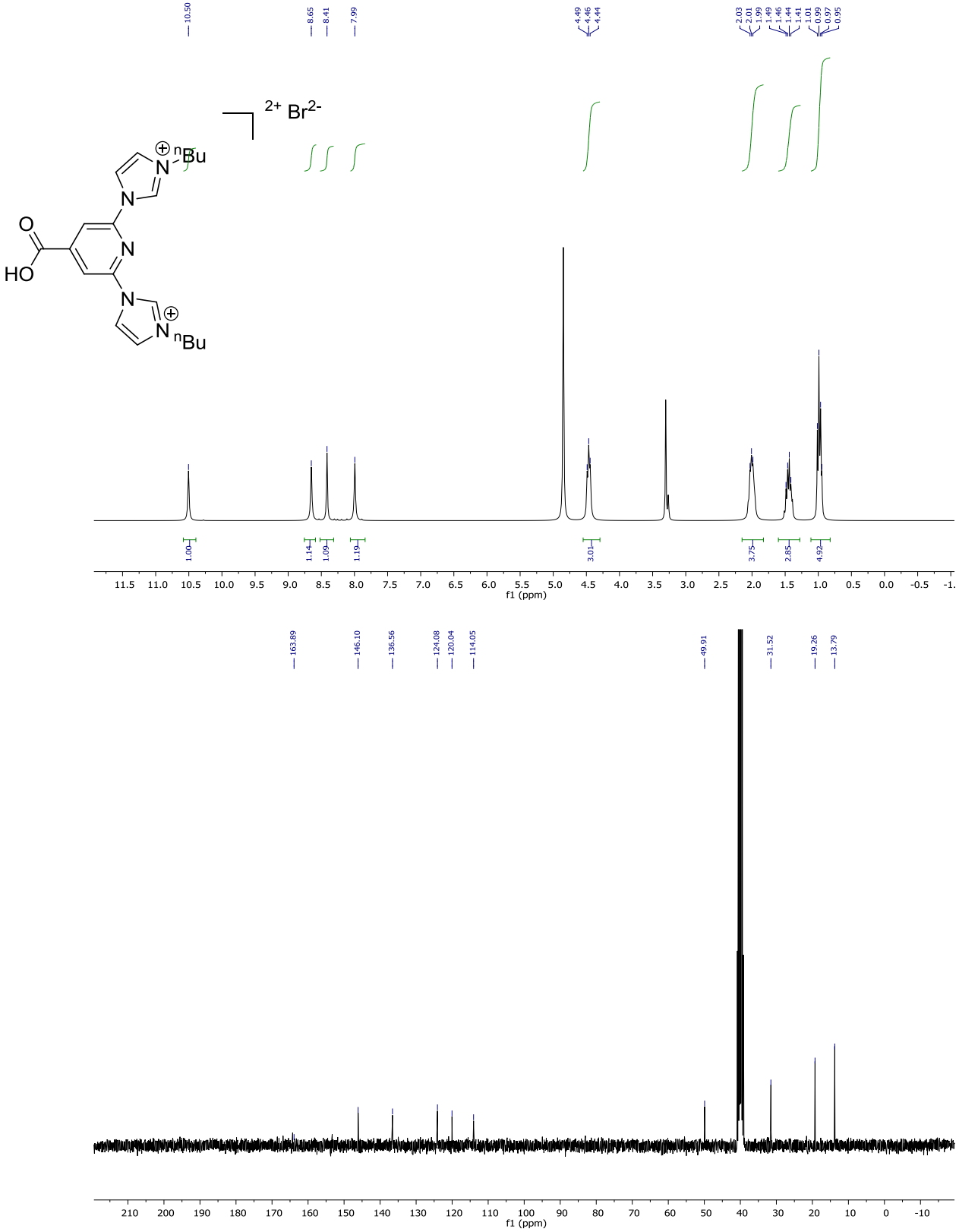




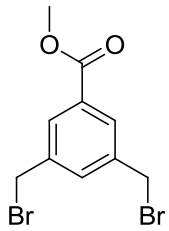


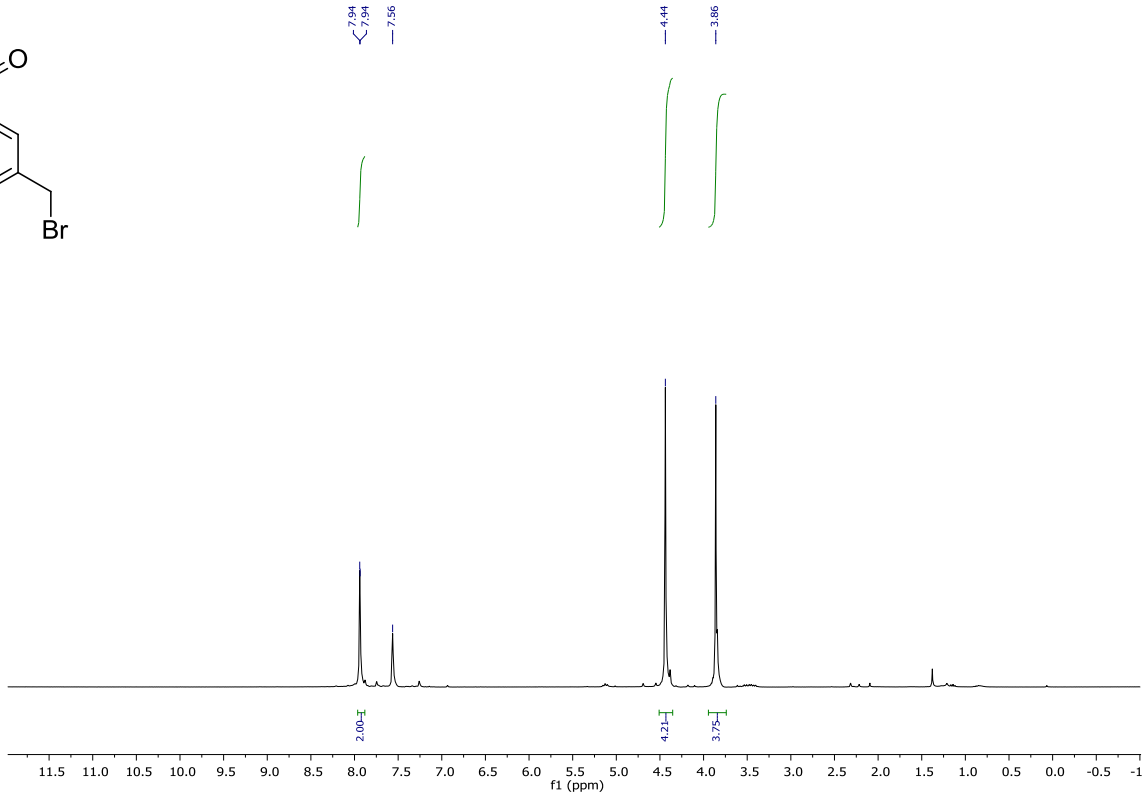


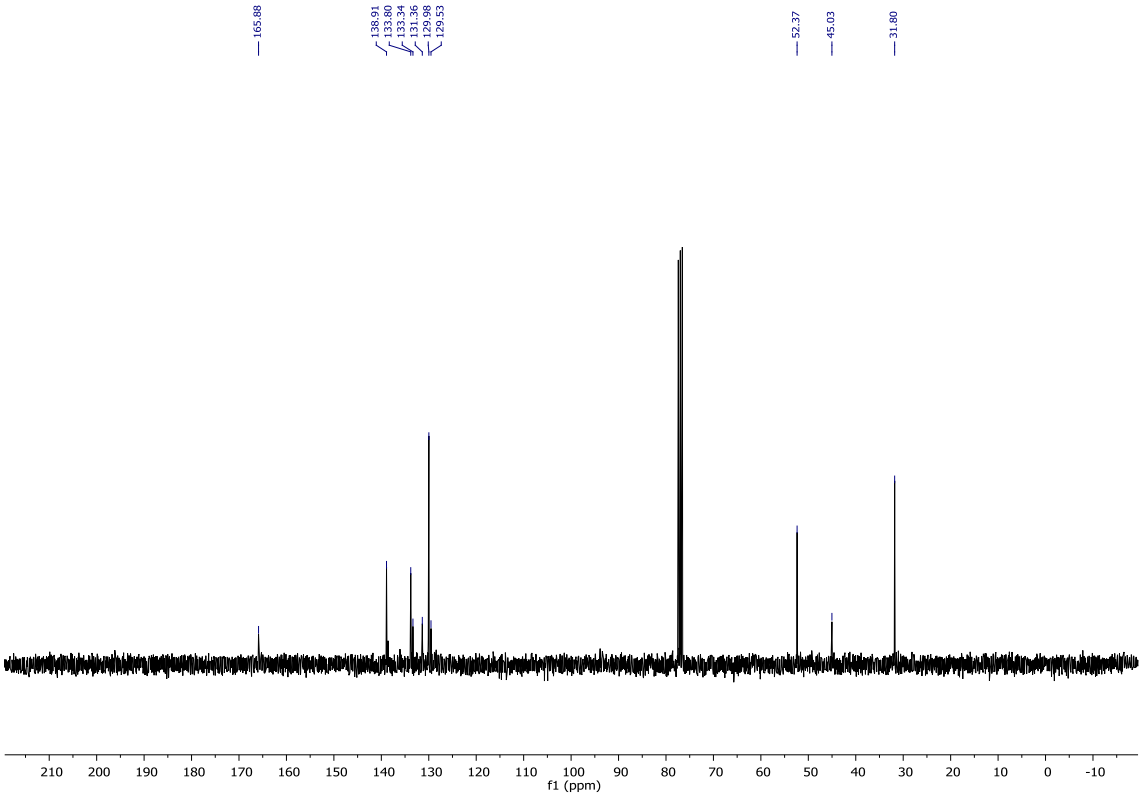
3,3’-(4-Carboxy-2,6-pyridinediyl)-bis[1-butyl-1*H*-imidazolium] dibromide (**L4**)



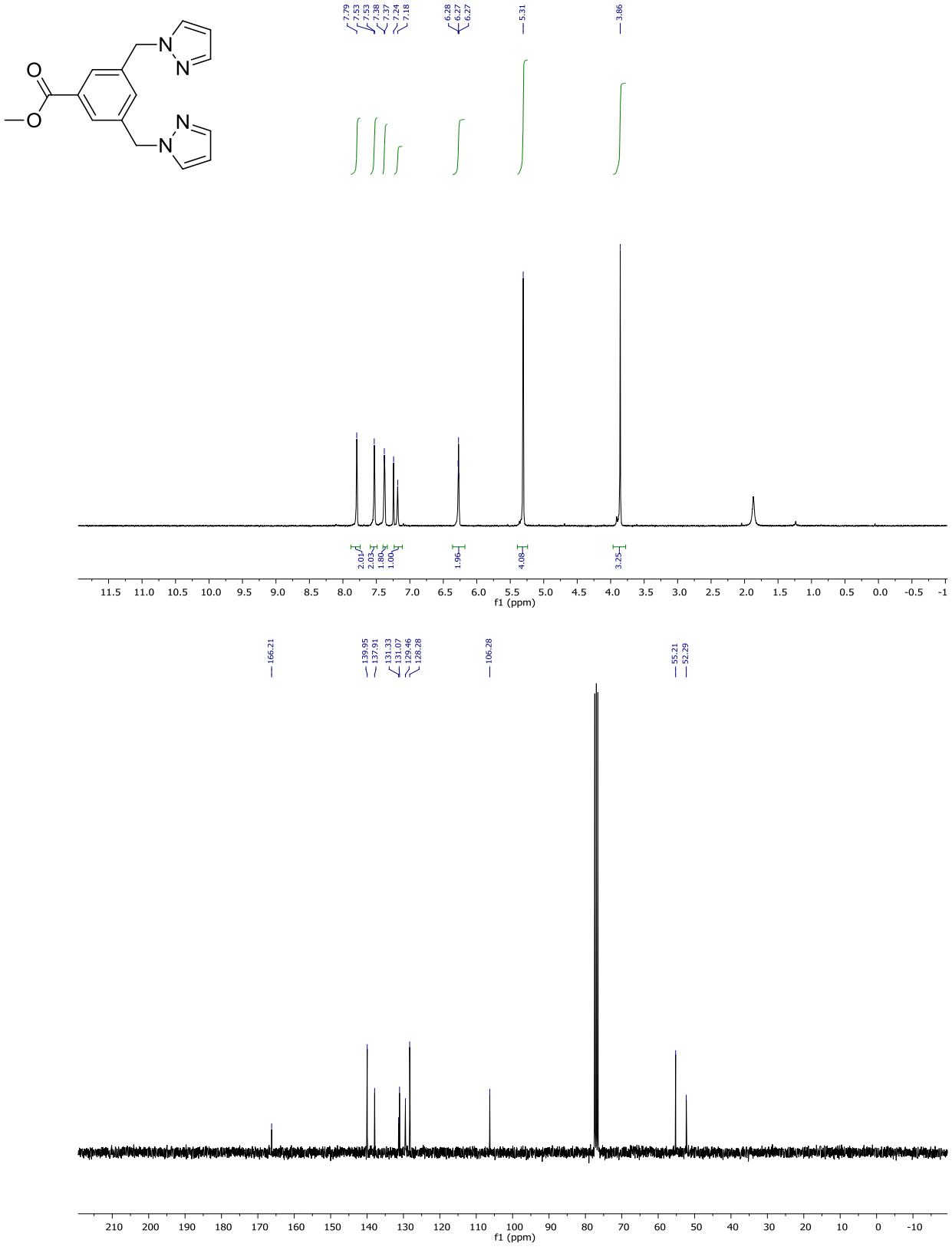
- Methyl 2,6-bis(bromomethyl)benzoate.



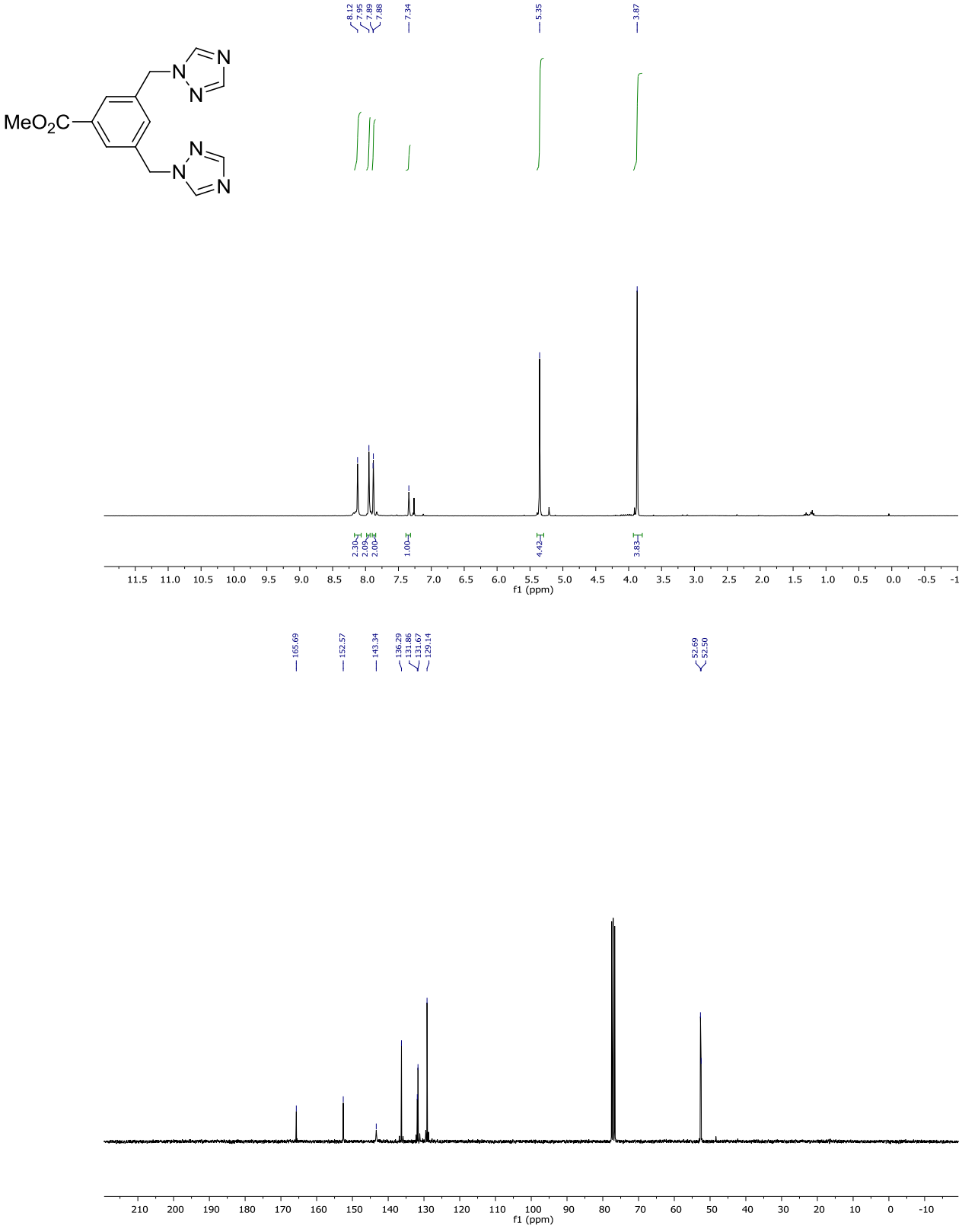



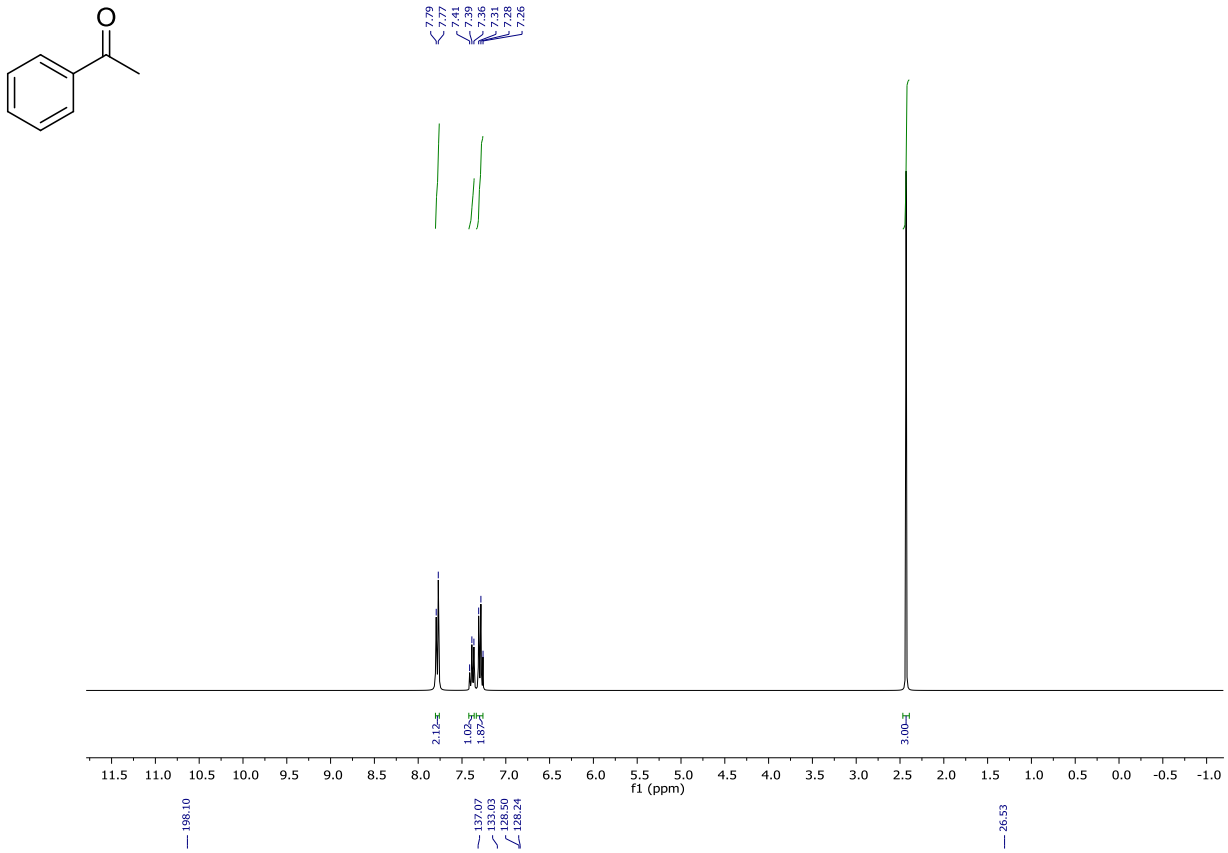
- Methyl 2,6-bis(pyrazol-1-ylmethyl)benzoate (**L5**).

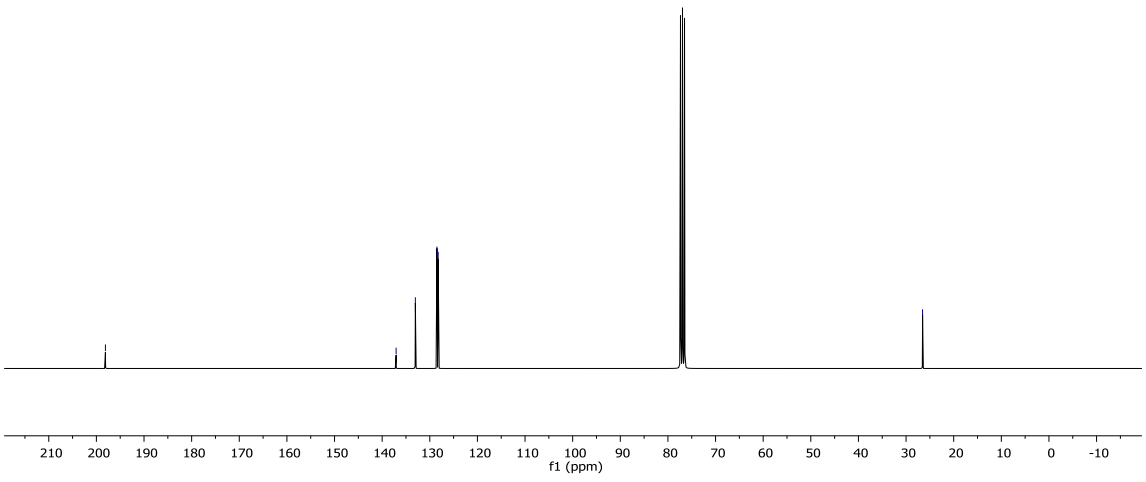


- Methyl 3,5-bis((1H-1,2,4-triazol-1-yl)methyl)benzoate (**L6**)

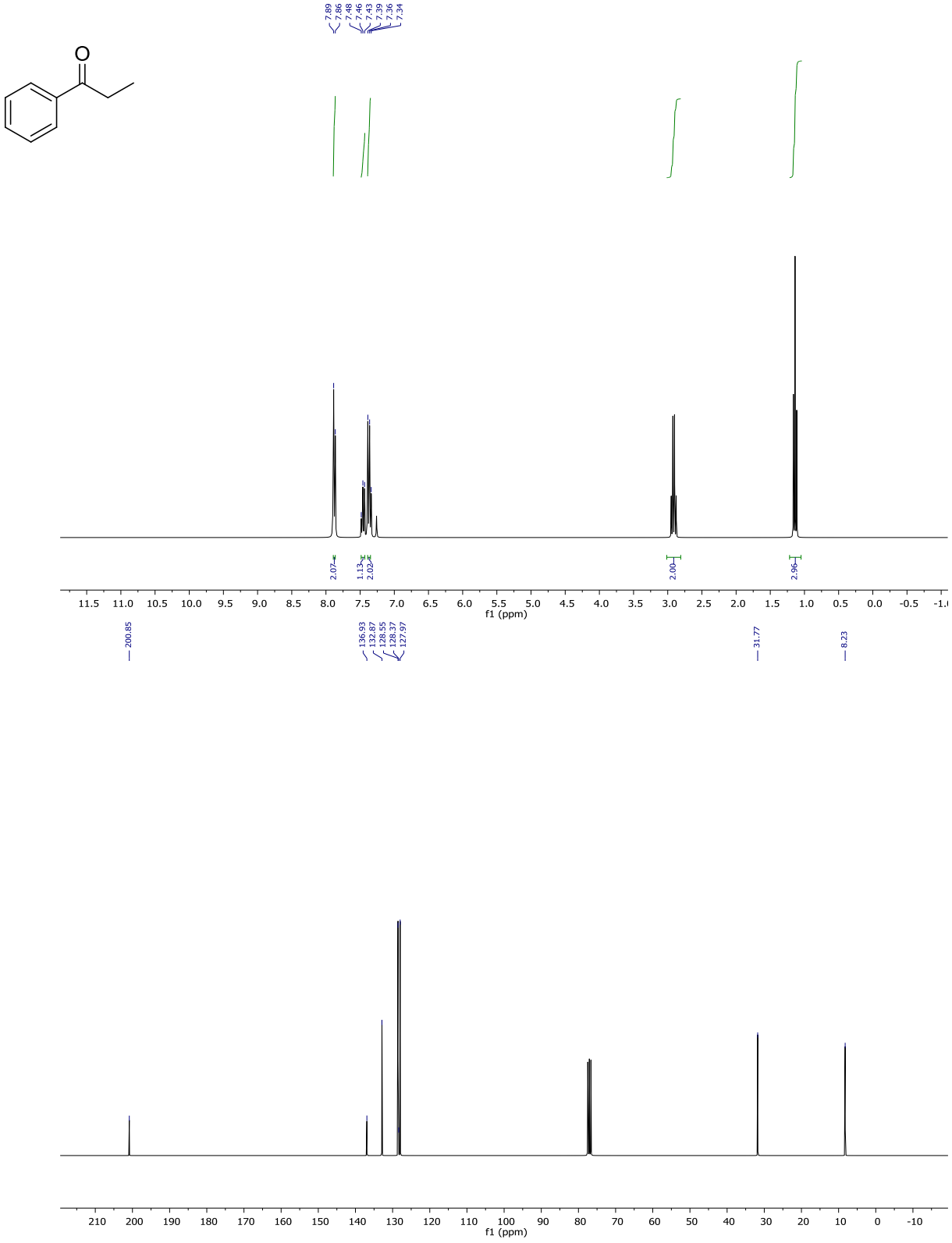


- Acetophenone

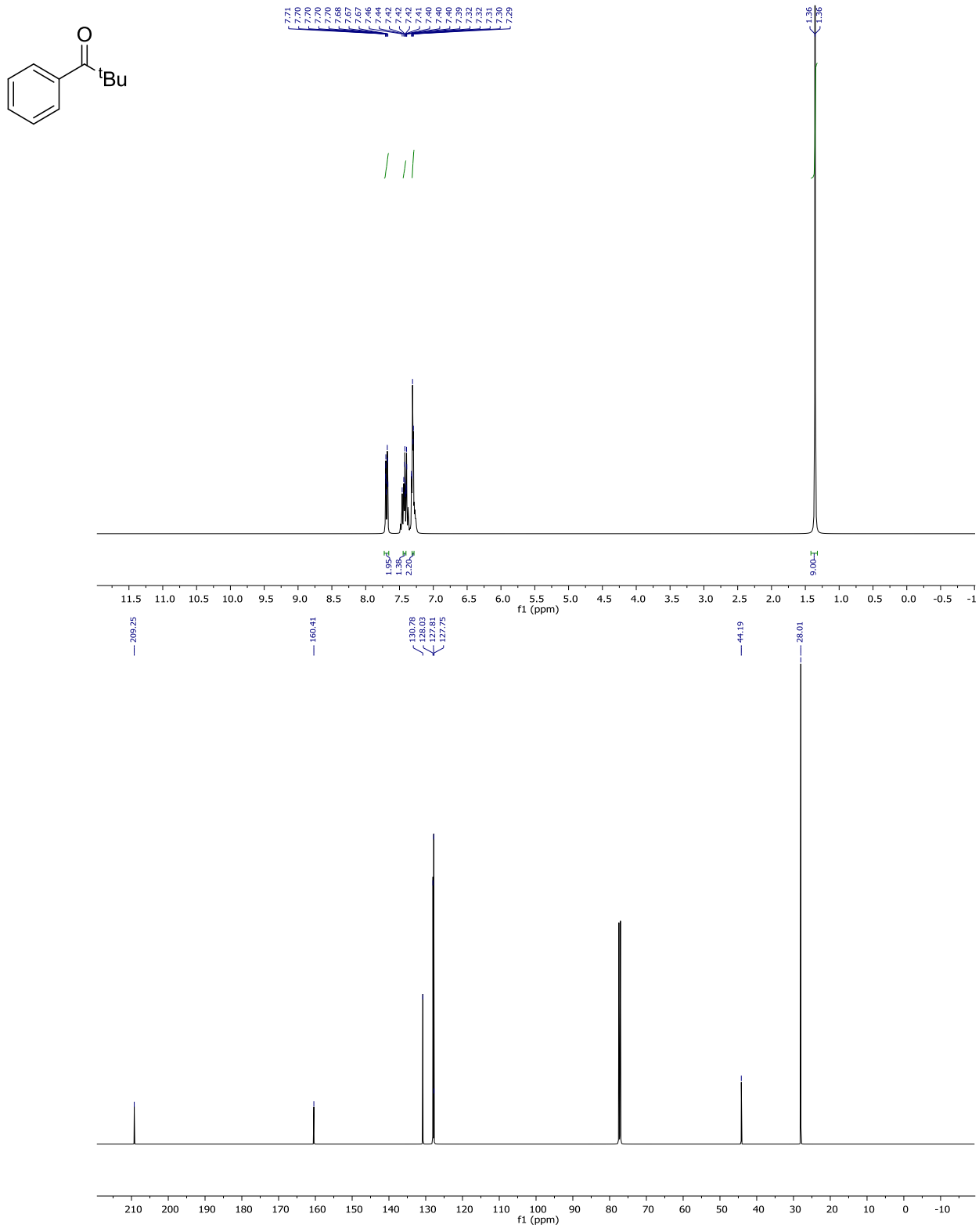


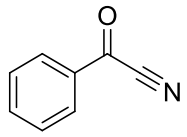
- 1-Phenyl-1-propanone

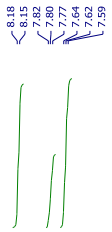


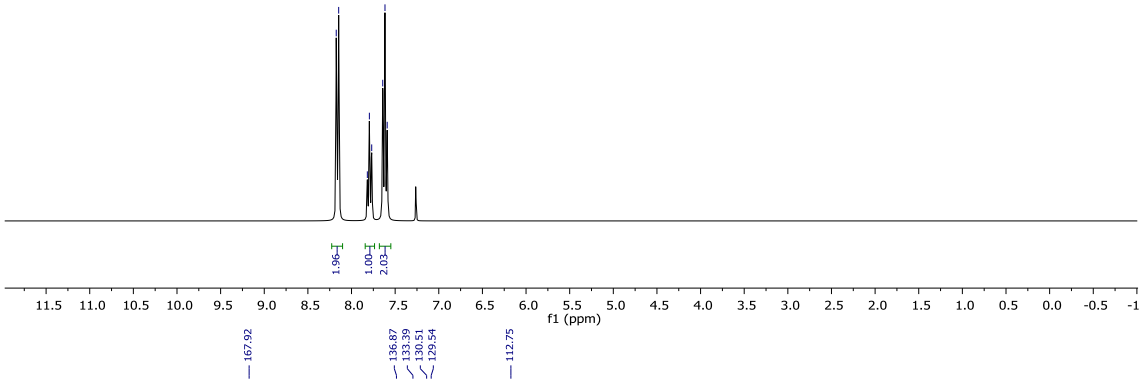
- 2,2-Dimethyl-1-phenylpropanone

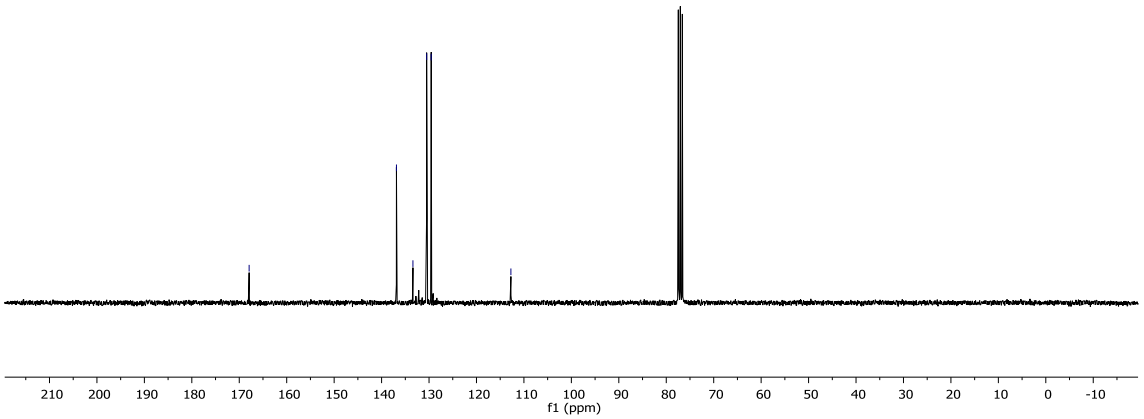


- Benzoylcyanide

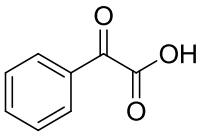


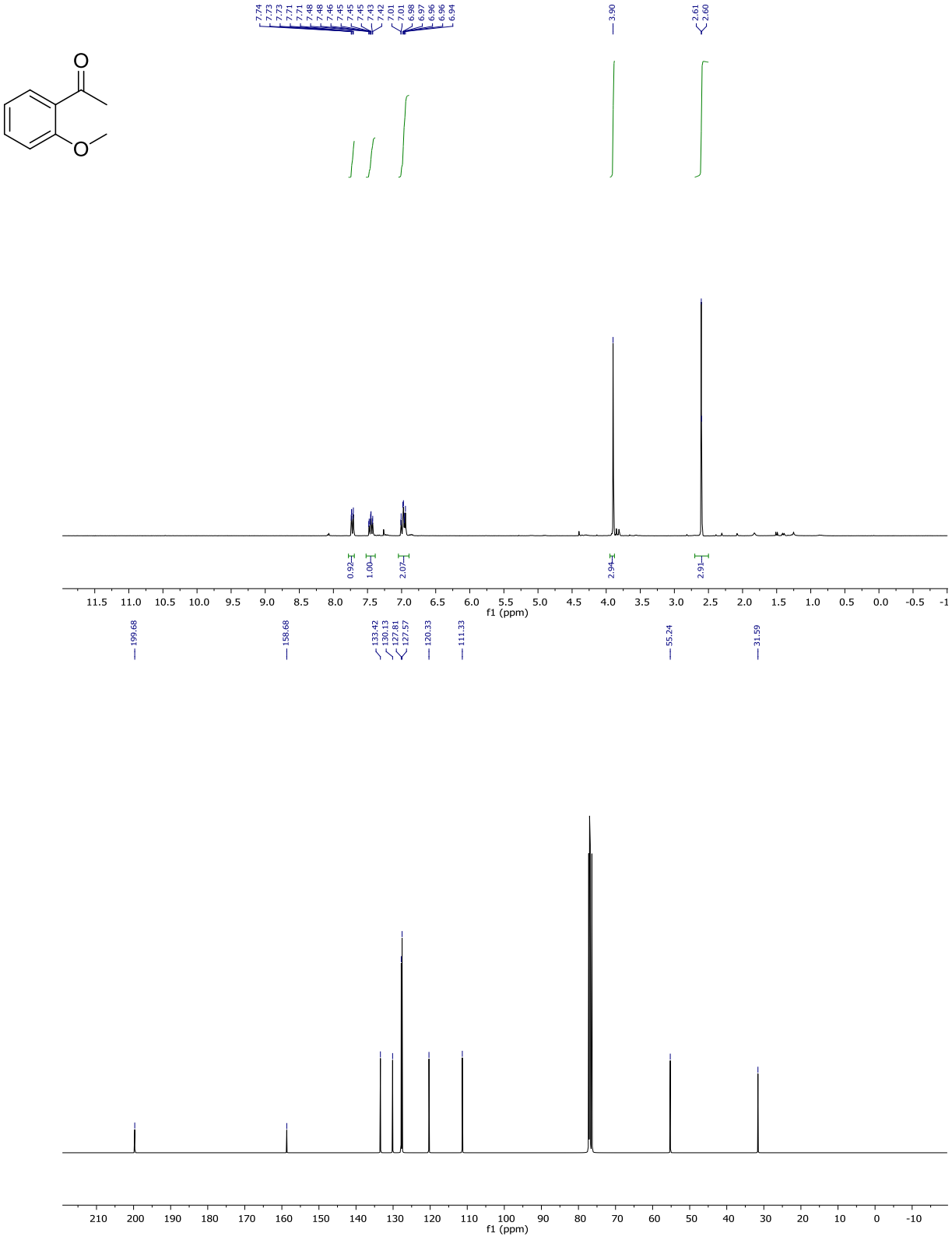



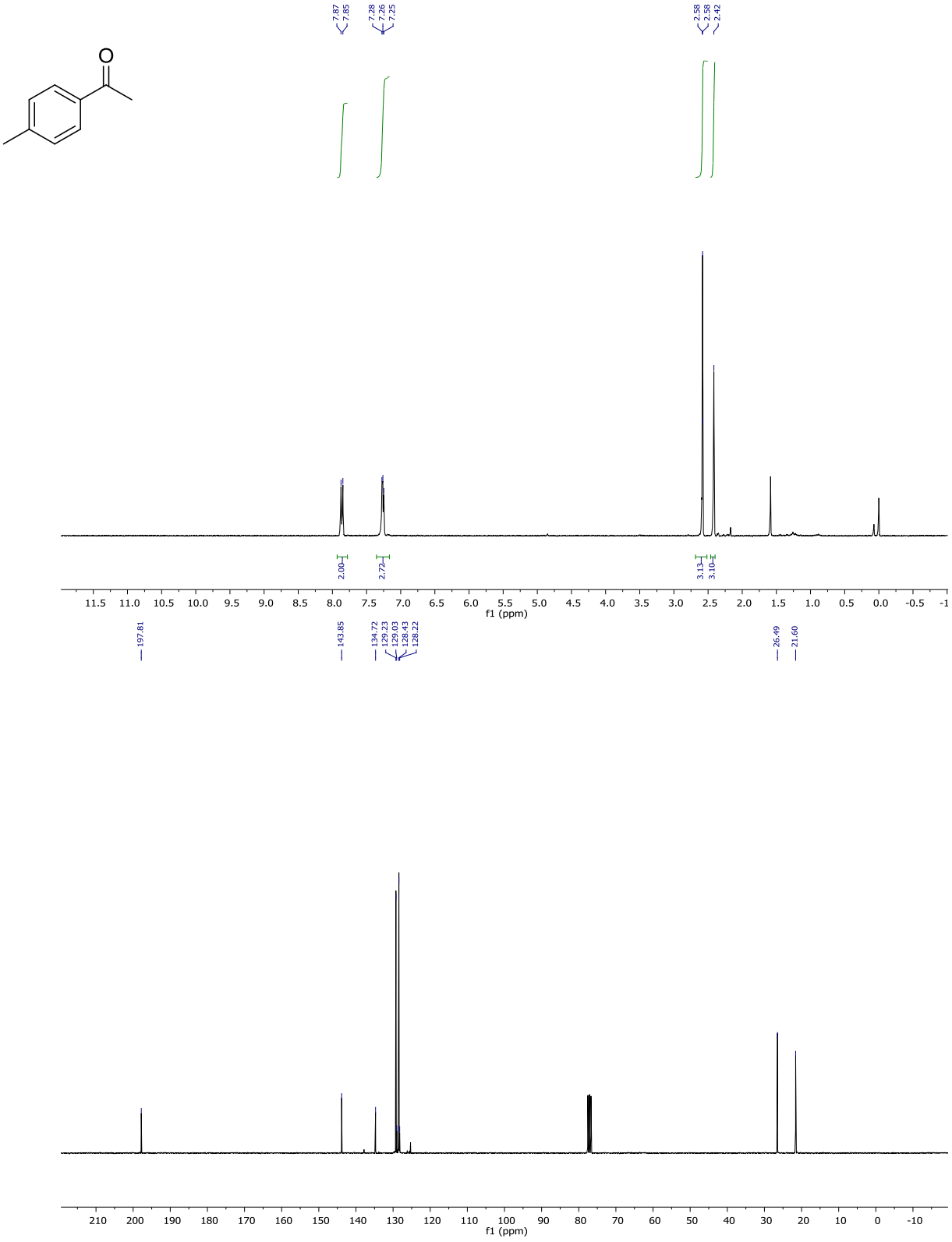
-2-Oxo-phenylacetic acid



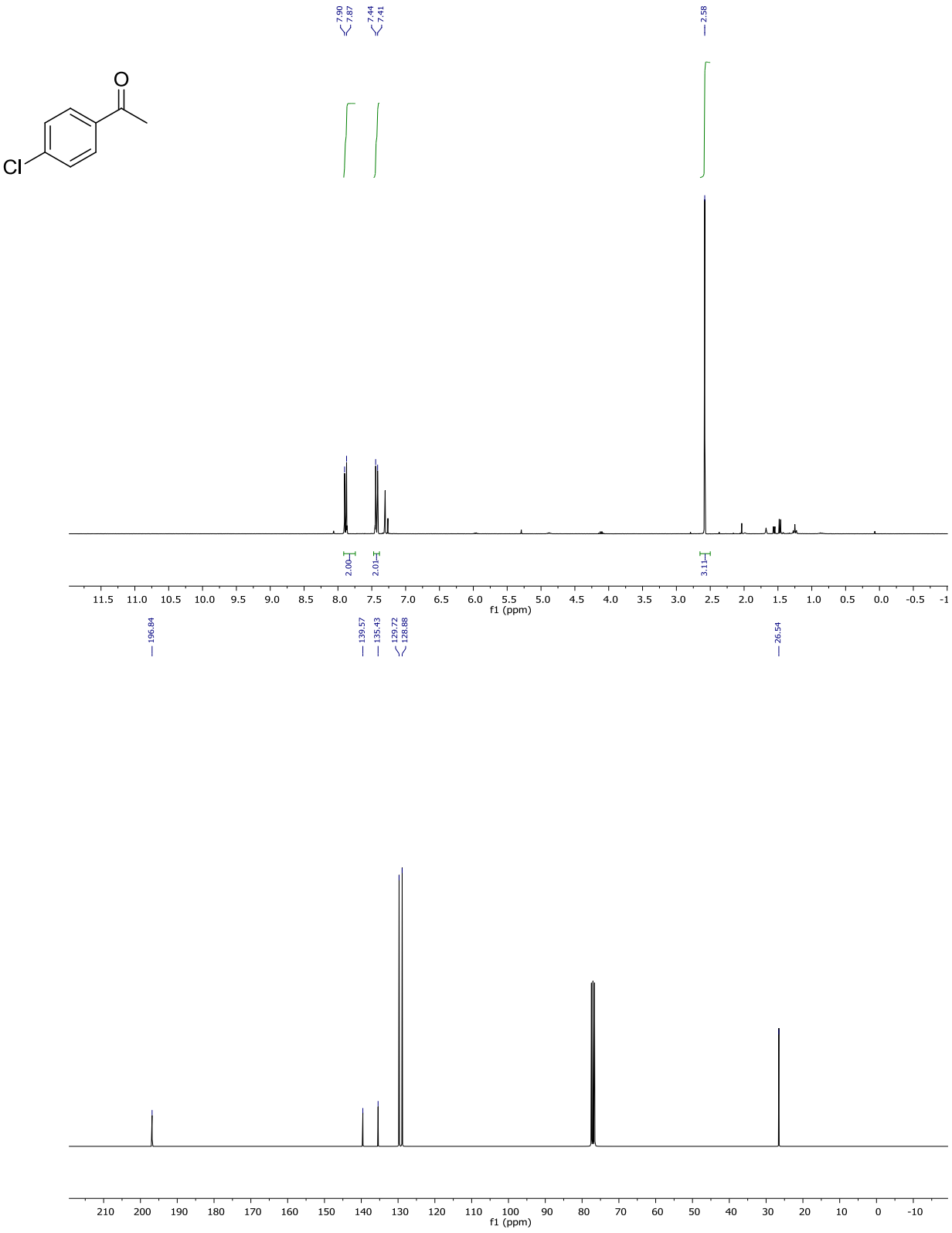
- 1-(2-Methoxyphenyl)ethanone



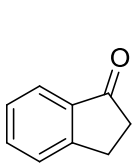
- 1-(*p*-Tolyl)ethanone

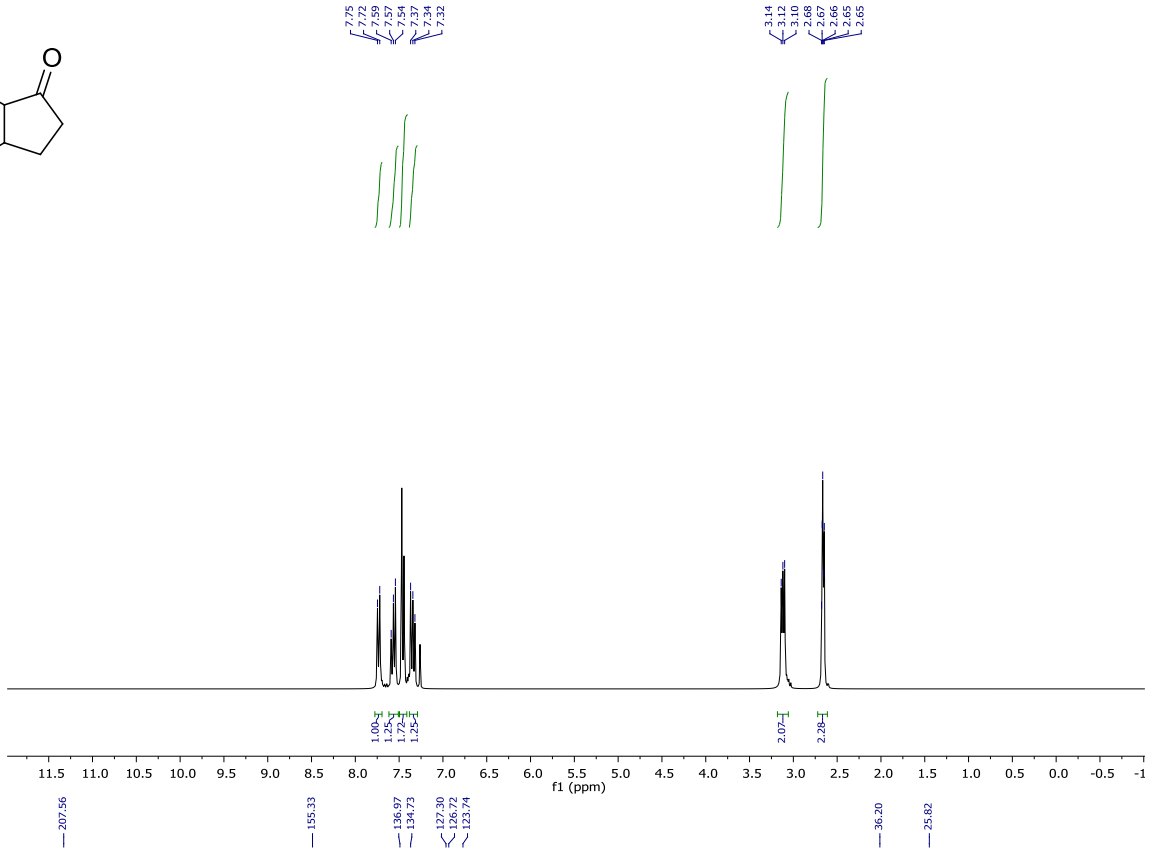


- 4-Chloroacetophenone



- Indanone

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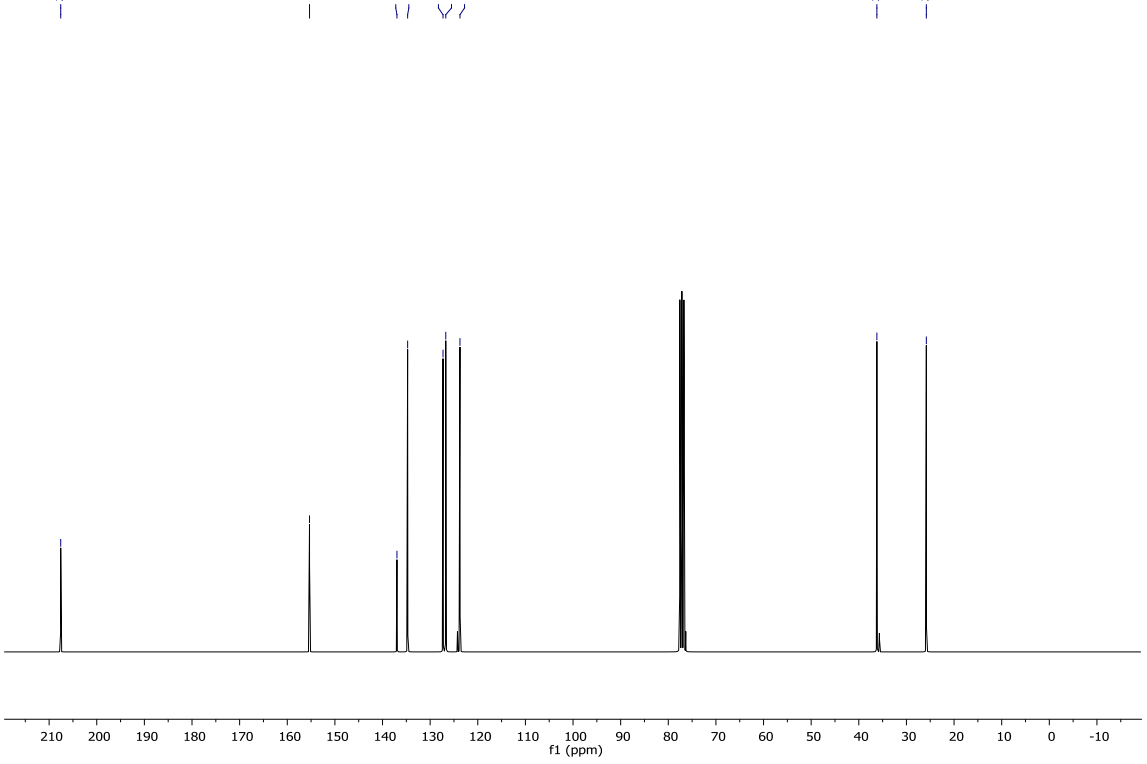
7.57
7.54
7.37
7.34
7.32
3.14
3.12
3.10
2.68
2.67
2.66
2.65
2.65
1.00
1.25
1.72
1.25
2.07
2.28
f1 (ppm)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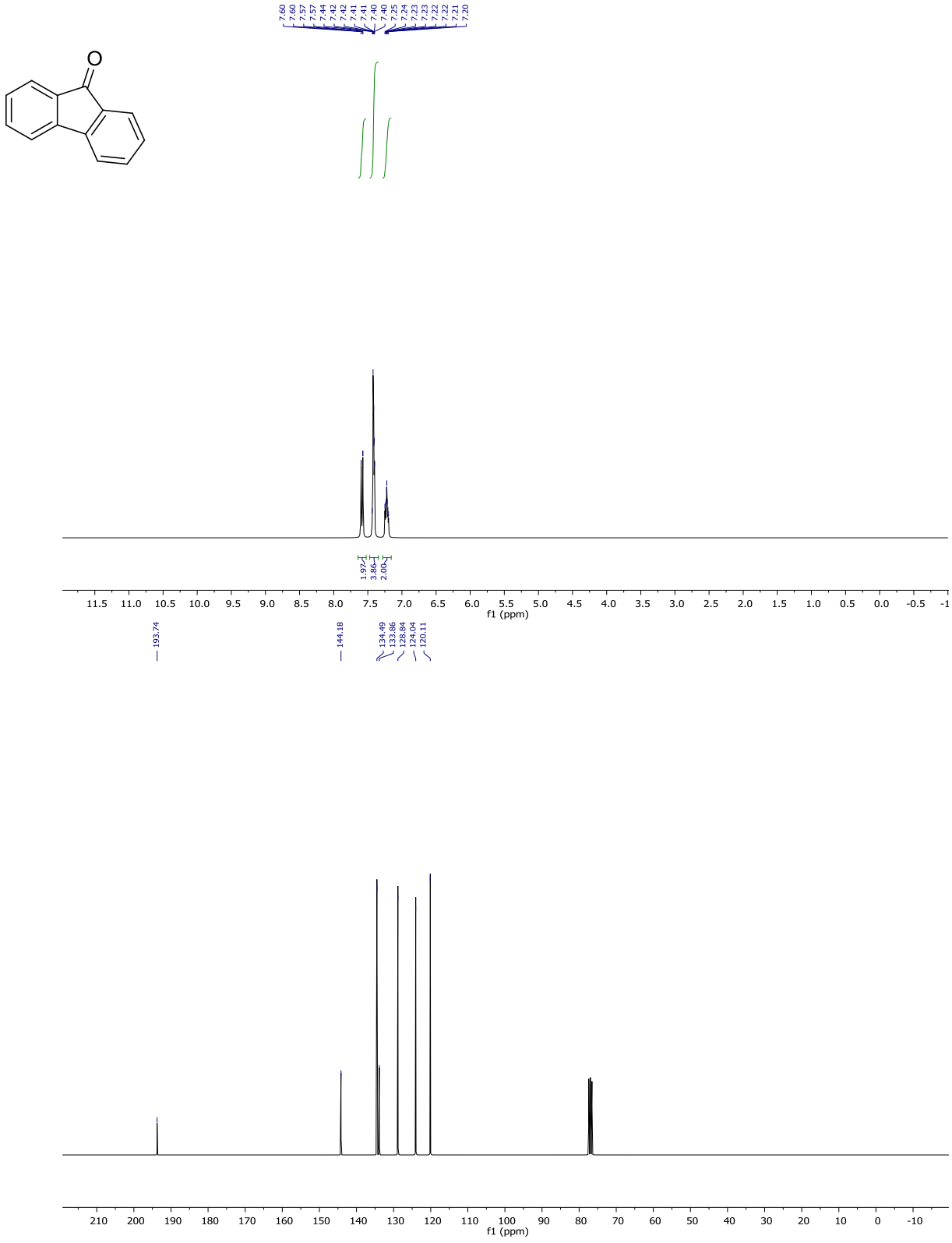
155.33
136.97
134.73
127.30
126.72
123.74
36.20
25.82
f1 (ppm)

- Fluorenone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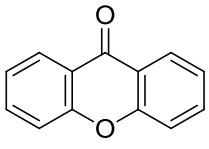
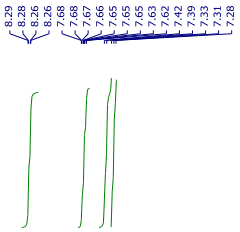
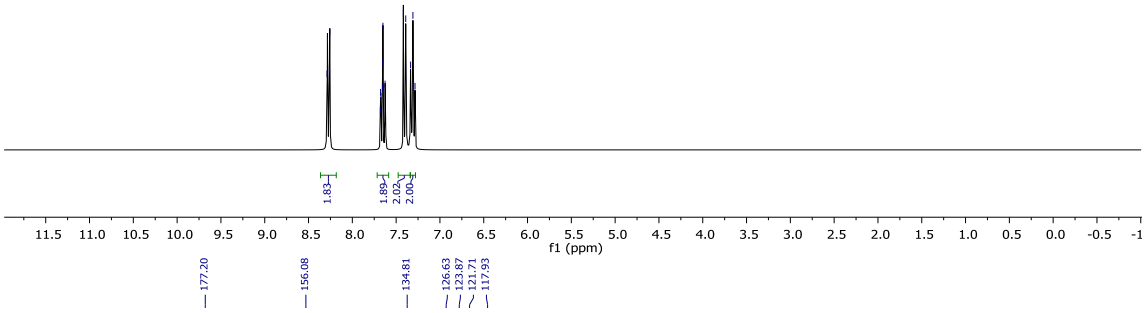
7.60
7.57
7.57
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.25
7.24
7.23
7.22
7.22
7.21
7.20
O
1.97
3.86
2.00
f1 (ppm)
193.74
144.18
134.49
133.86
128.84
124.04
120.11
f1 (ppm)

- Xanthenone


O
O


8.29
8.28
8.26
8.26
7.68
7.68
7.67
7.66
7.65
7.65
7.65
7.63
7.62
7.42
7.39
7.33
7.31
7.28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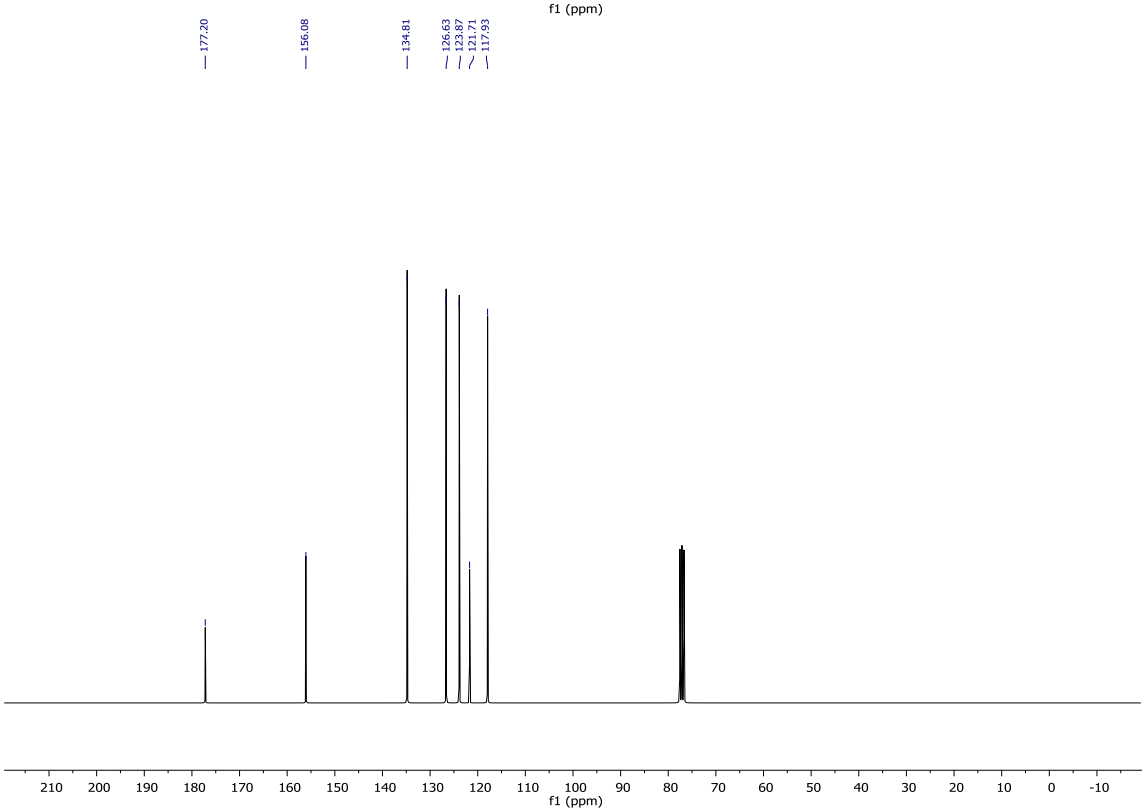
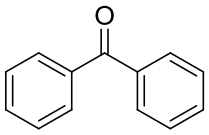
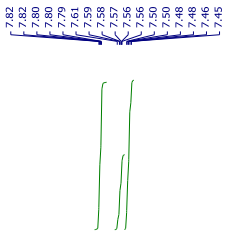
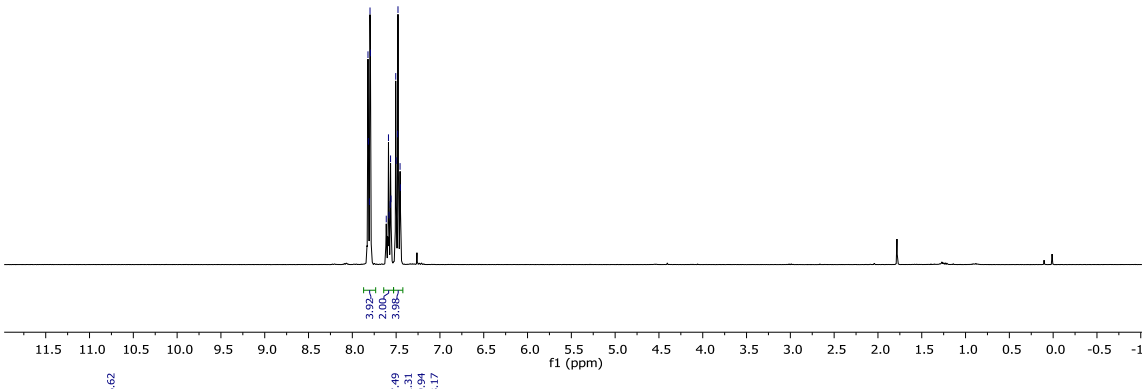
1.89
2.02
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

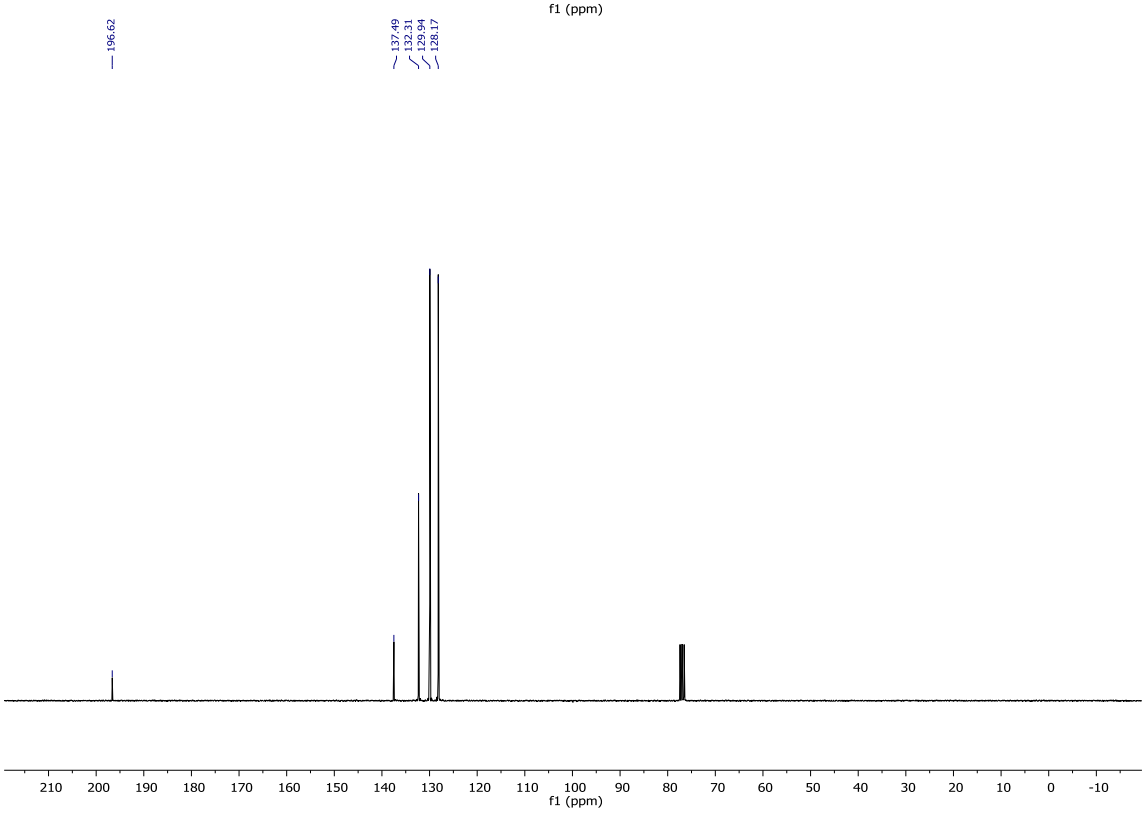

177.20
156.08
134.81
126.63
123.87
121.71
117.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

- Benzophenone

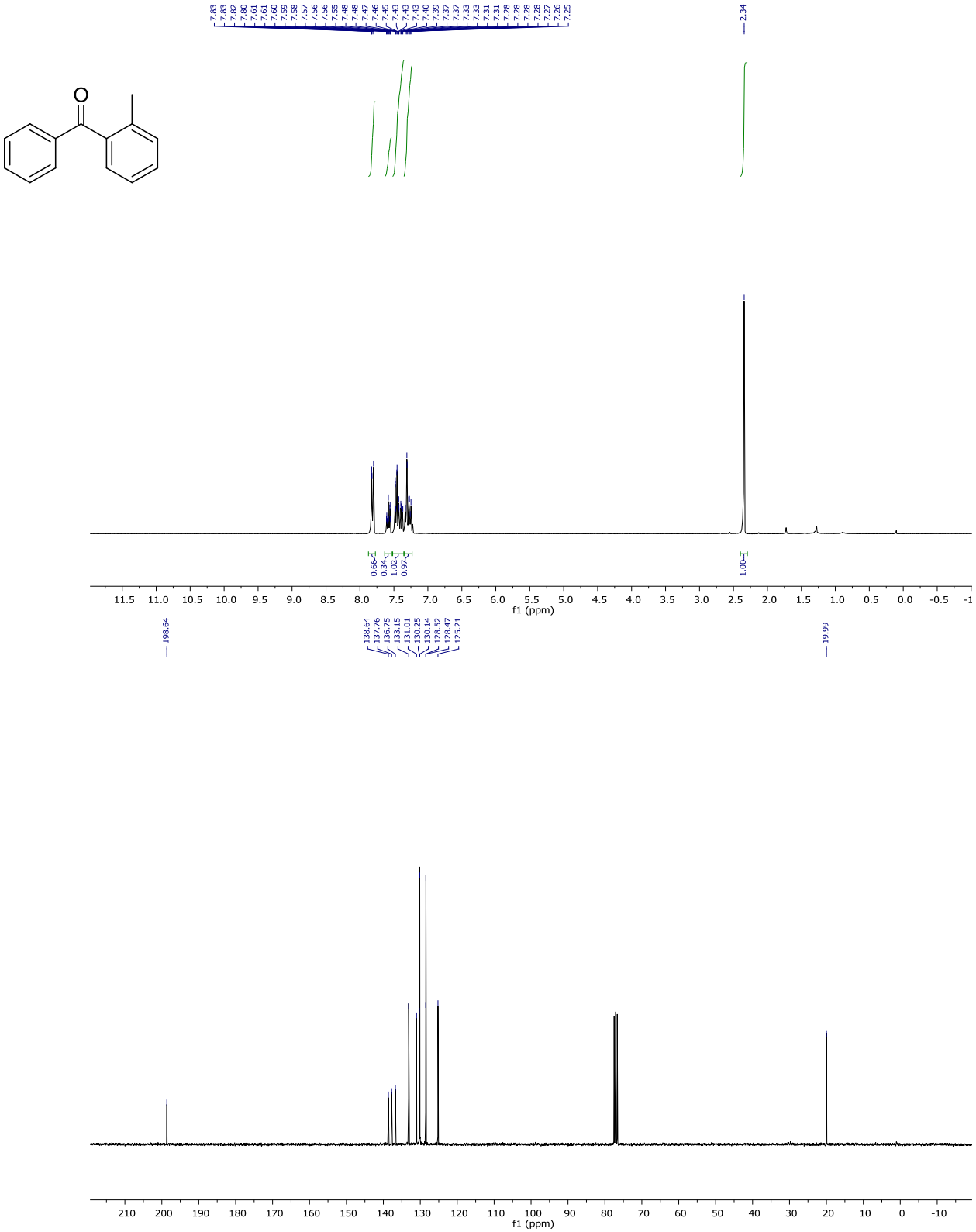




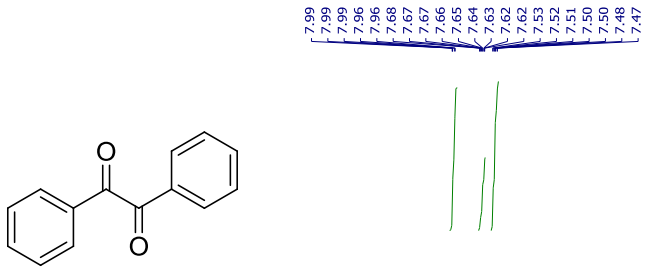



- 2-Methylbenzophenone



-Benzil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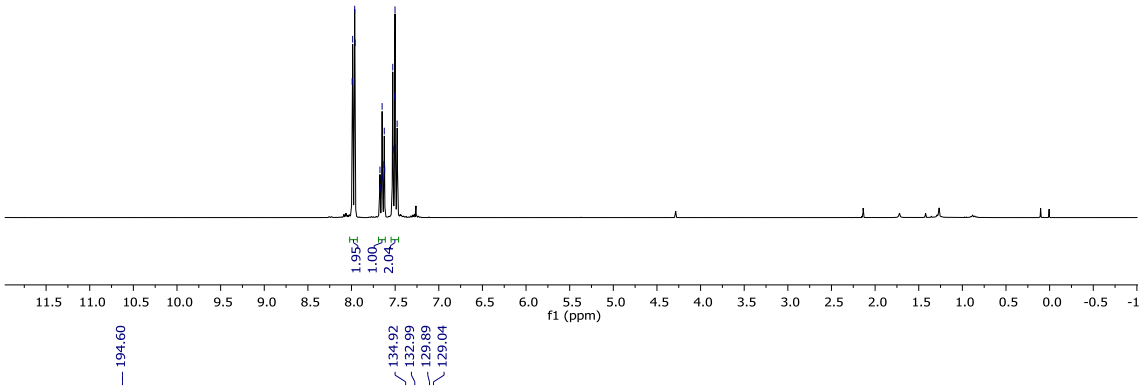
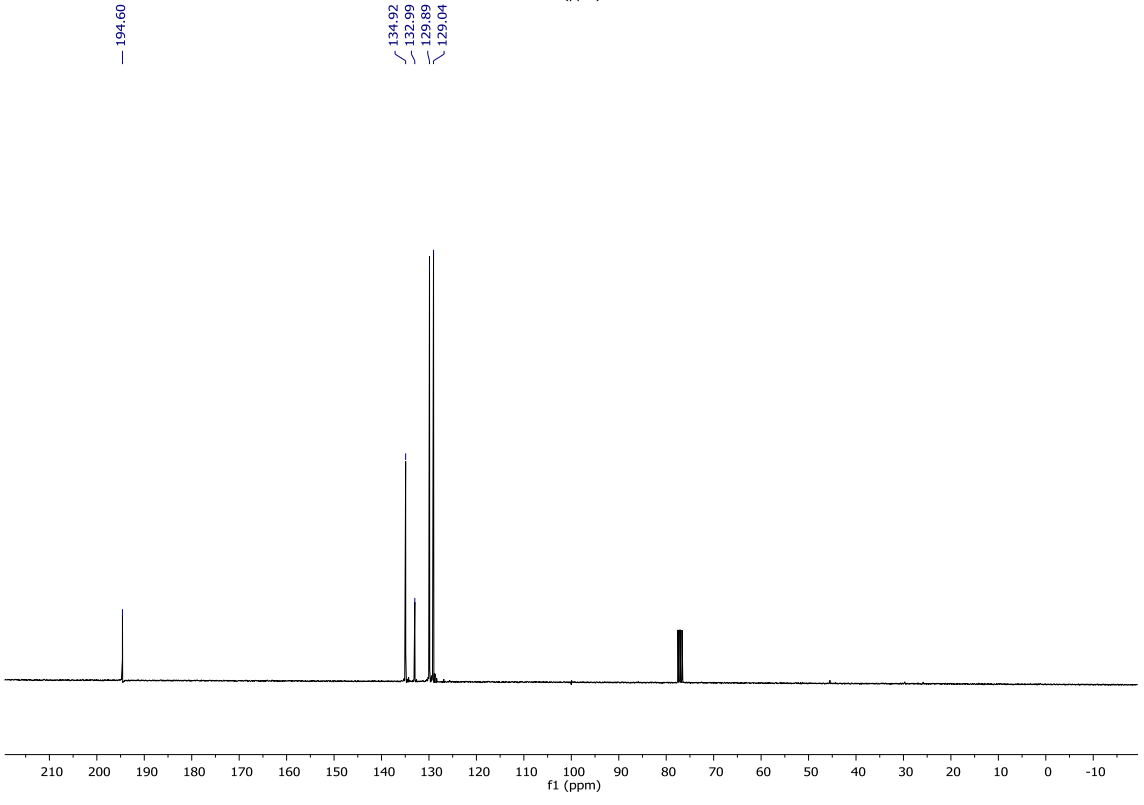
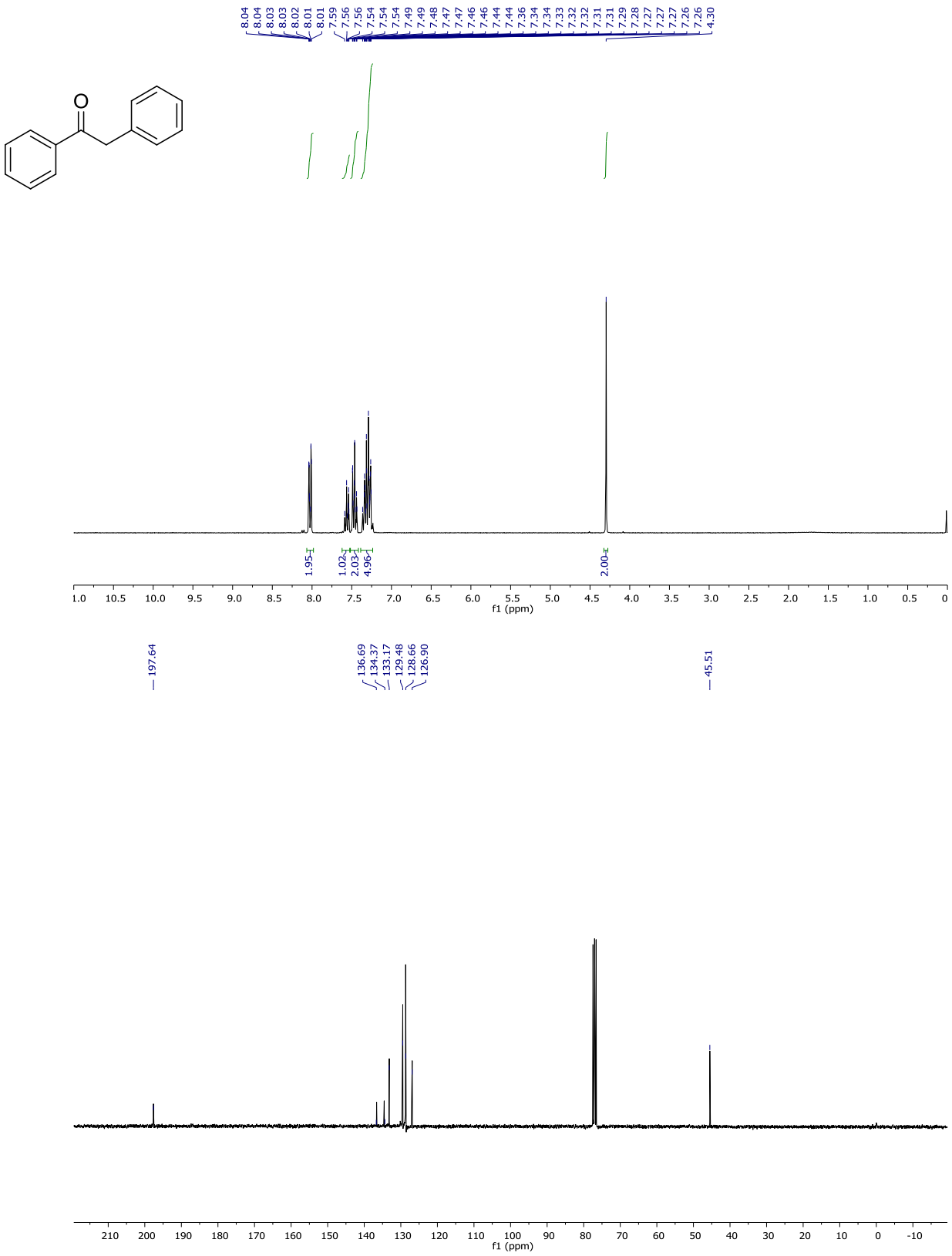
7.67
7.66
7.65
7.64
7.63
7.62
7.62
7.53
7.52
7.51
7.50
7.50
7.48
7.47
O
O

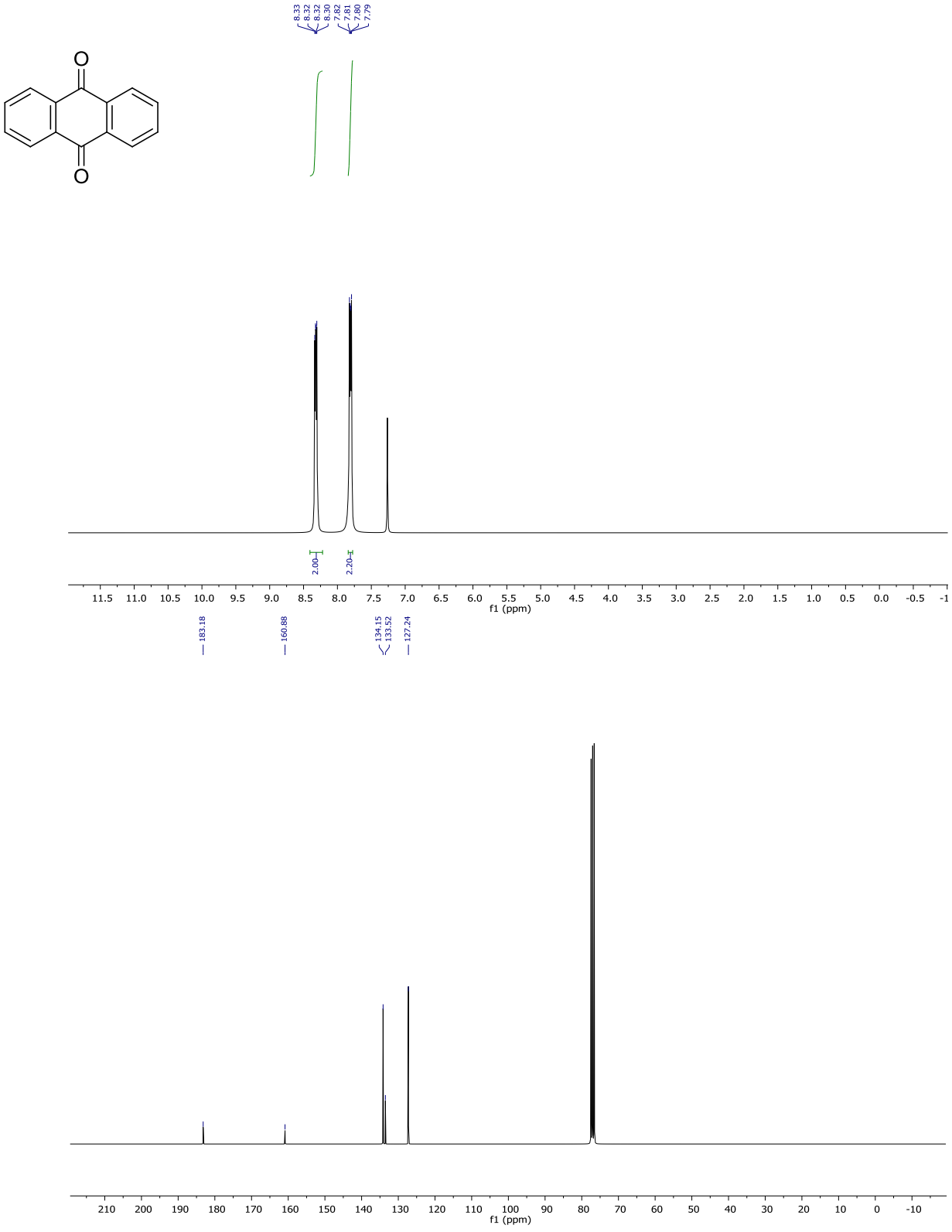

1.95
1.00
2.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


194.60
134.92
132.99
129.89
129.04
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

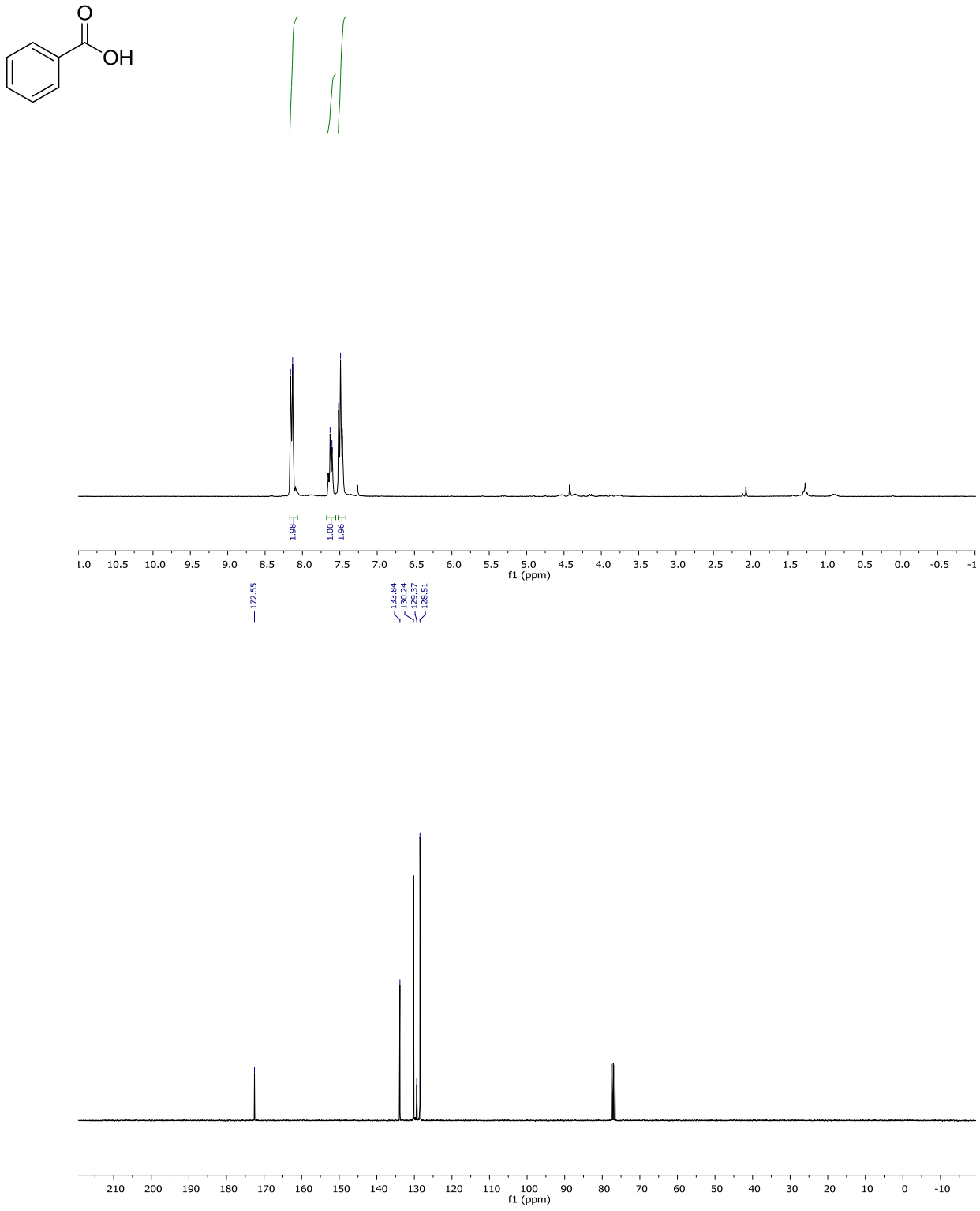
-Deoxybenzoin



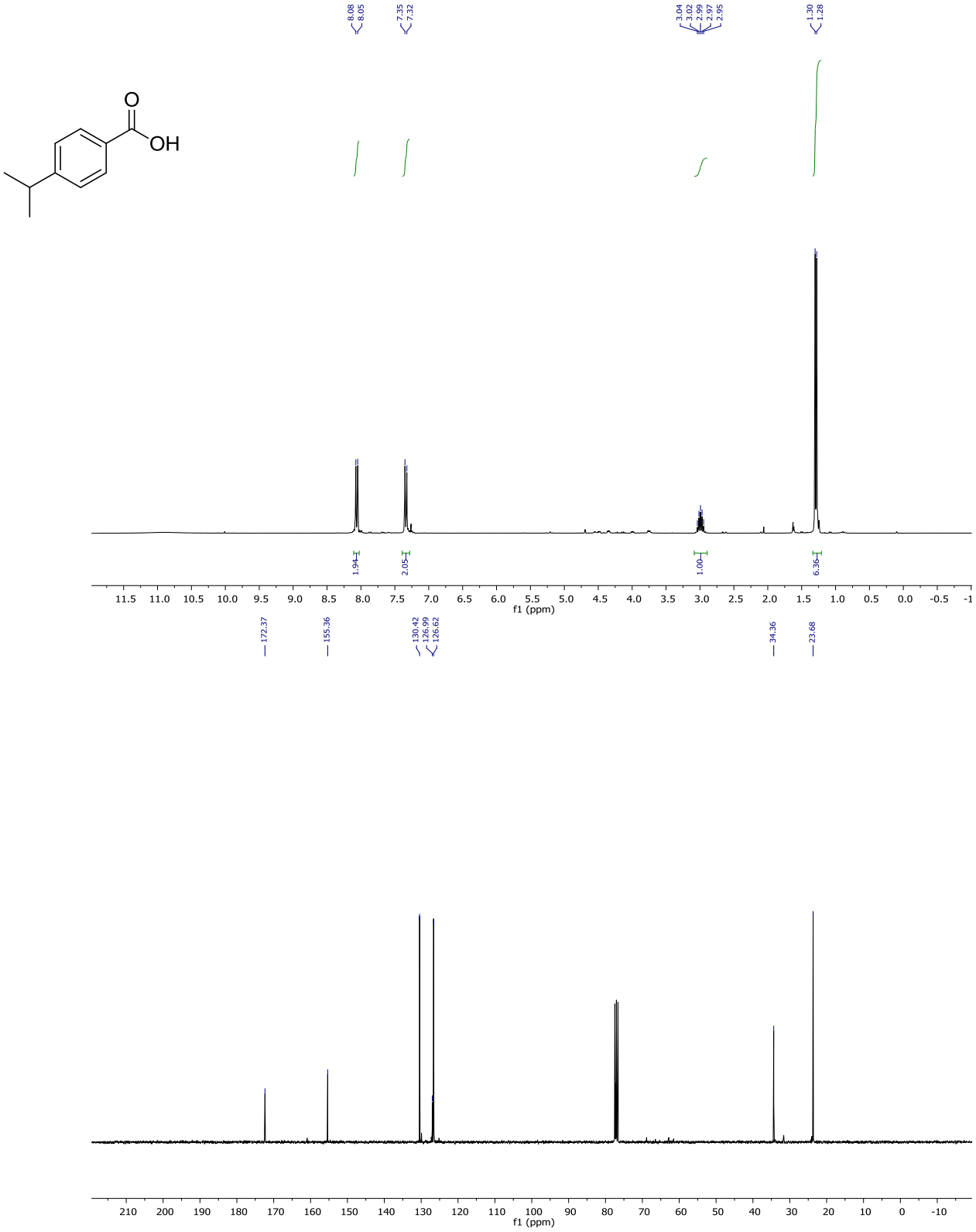
- Anthraquinone



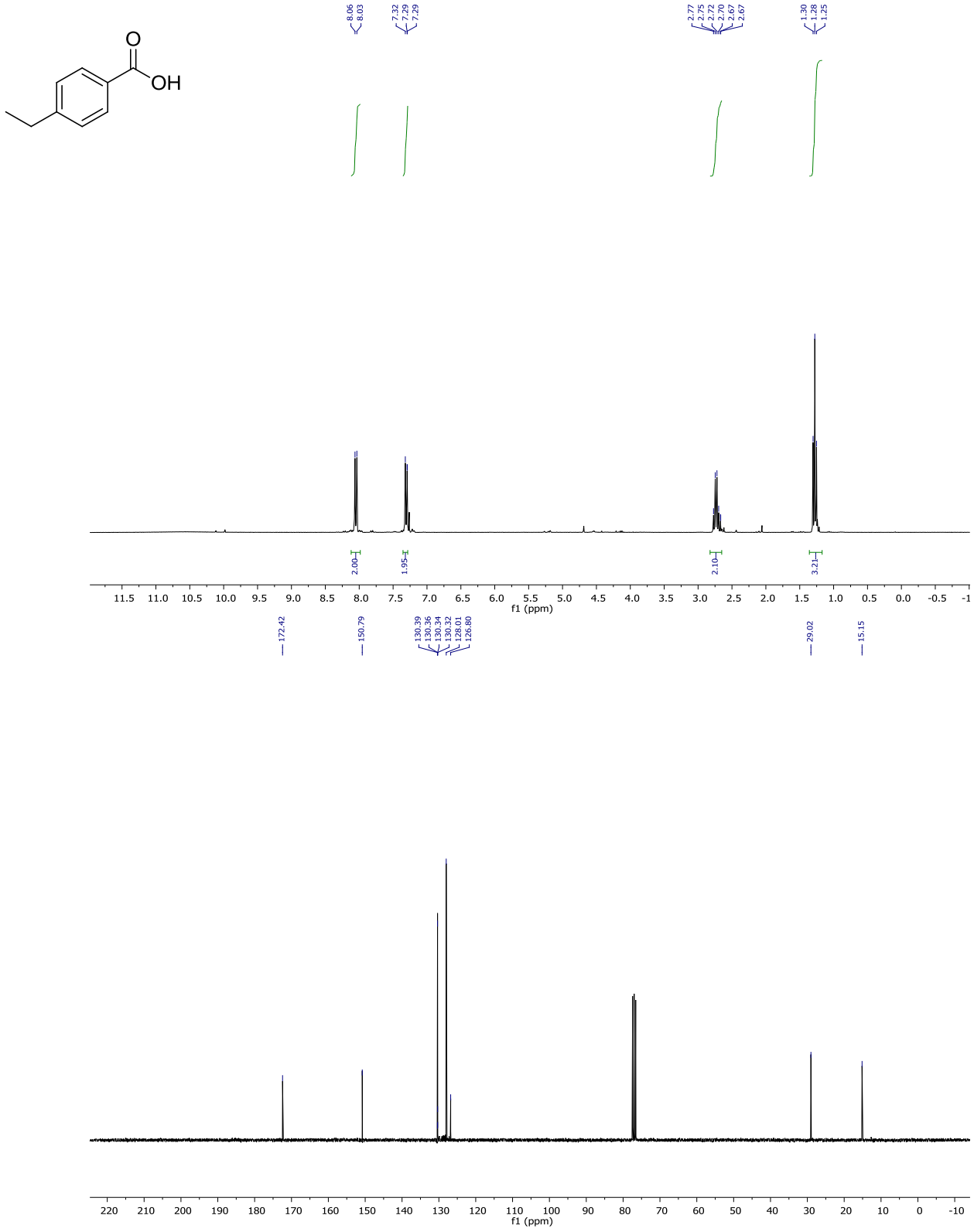
- Benzoic acid



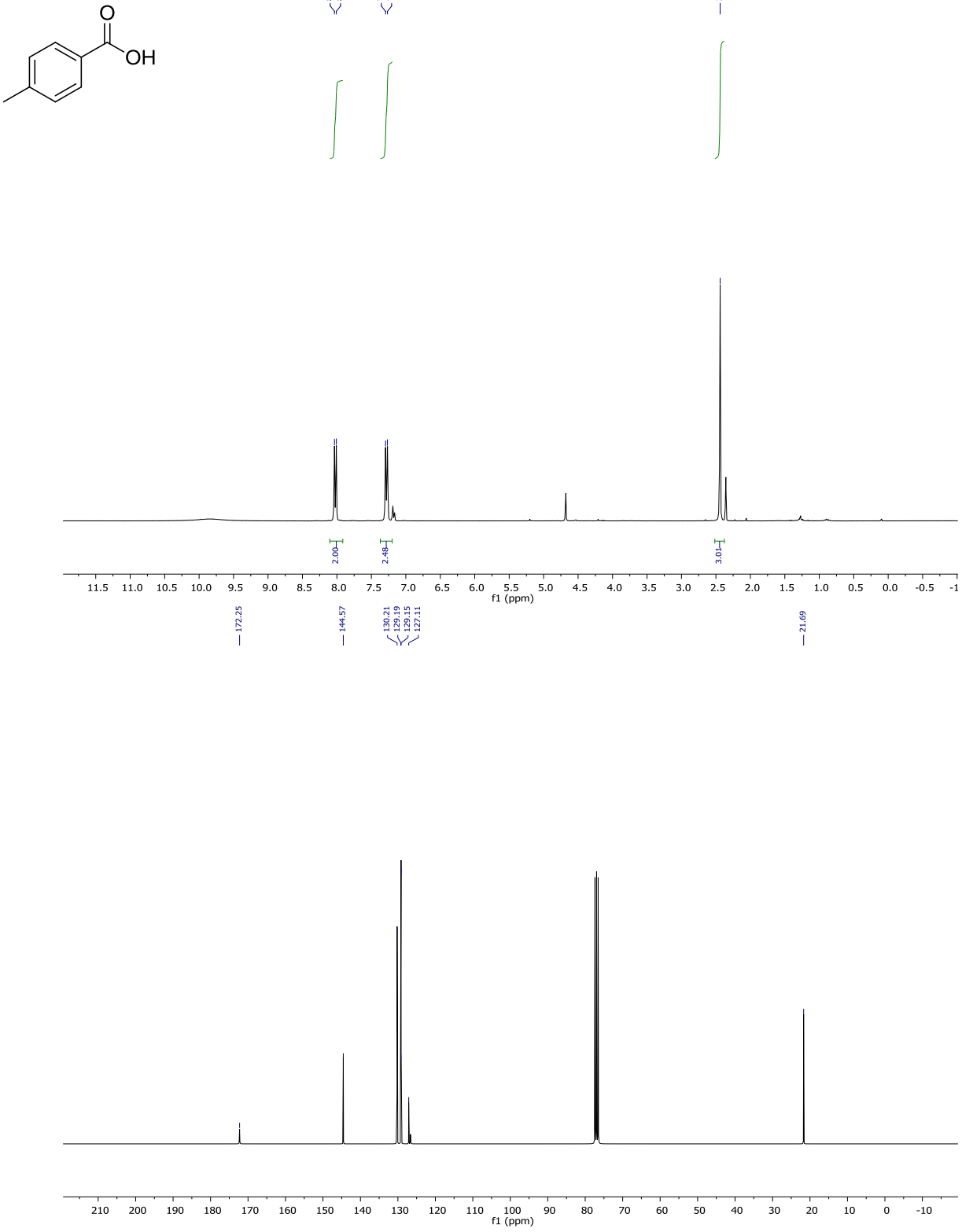
- 4-Isopropylbenzoic acid



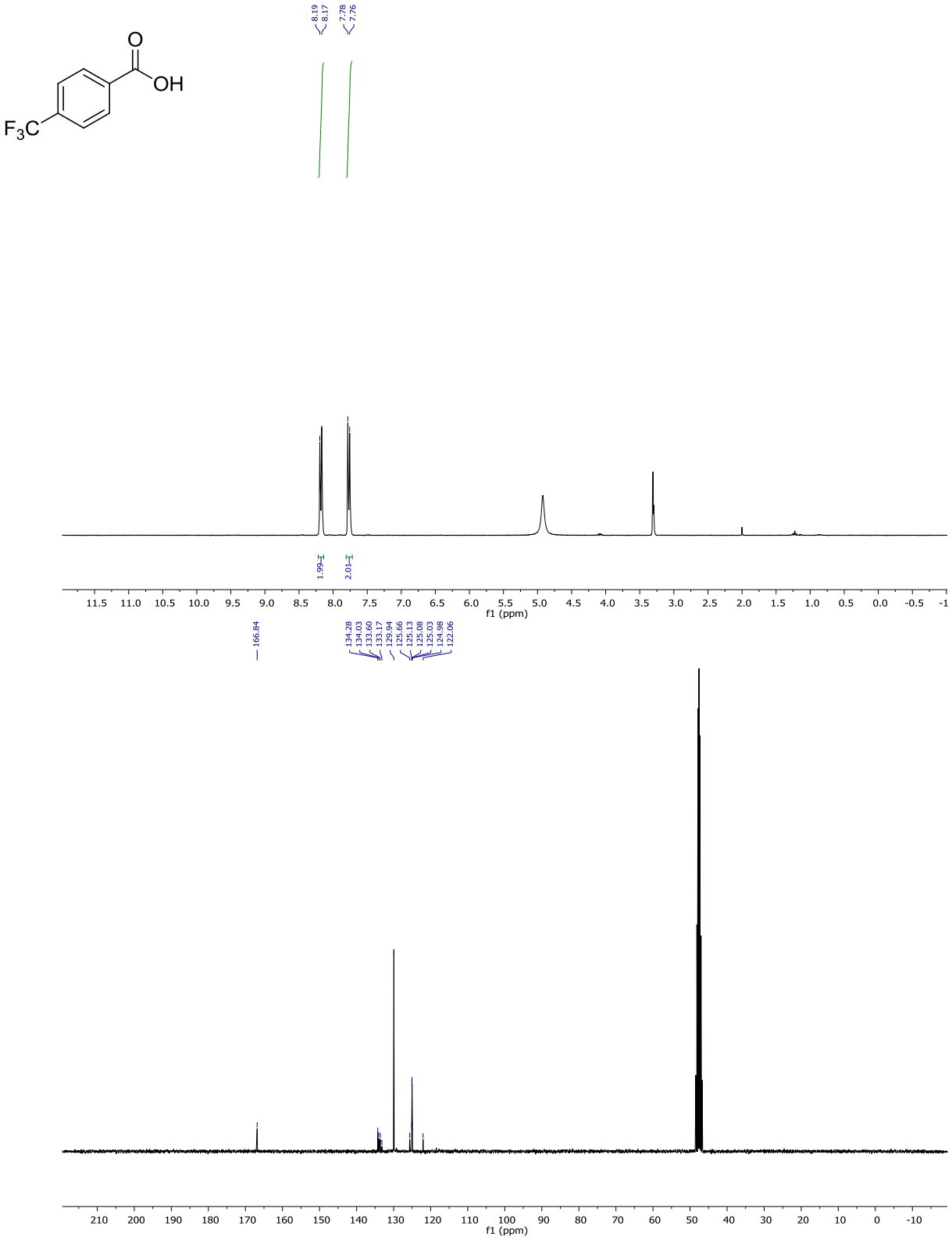
- 4-Ethylbenzoic acid



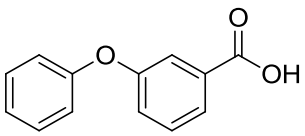
- 4-Methylbenzoic acid

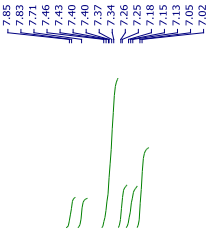


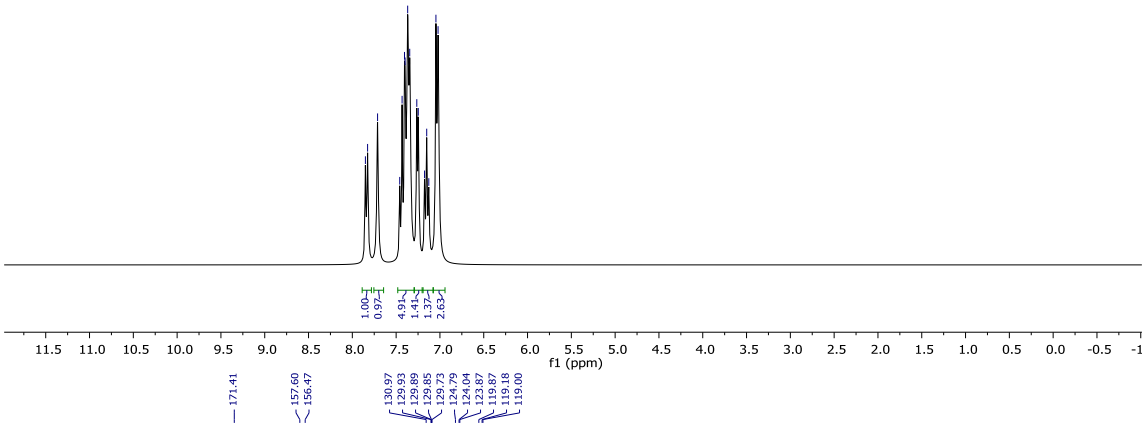
- 4-(Trifluoromethyl)benzoic acid



- 3-Phenoxybenzoic acid

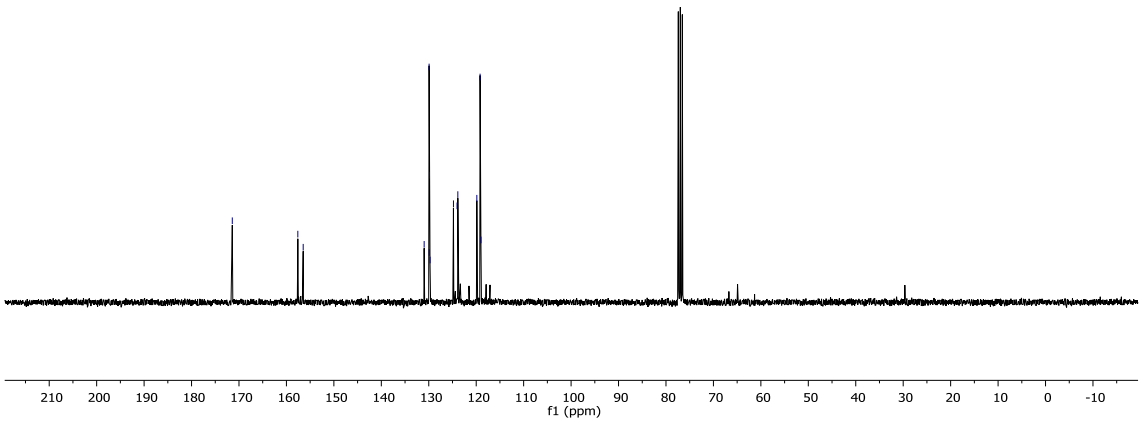


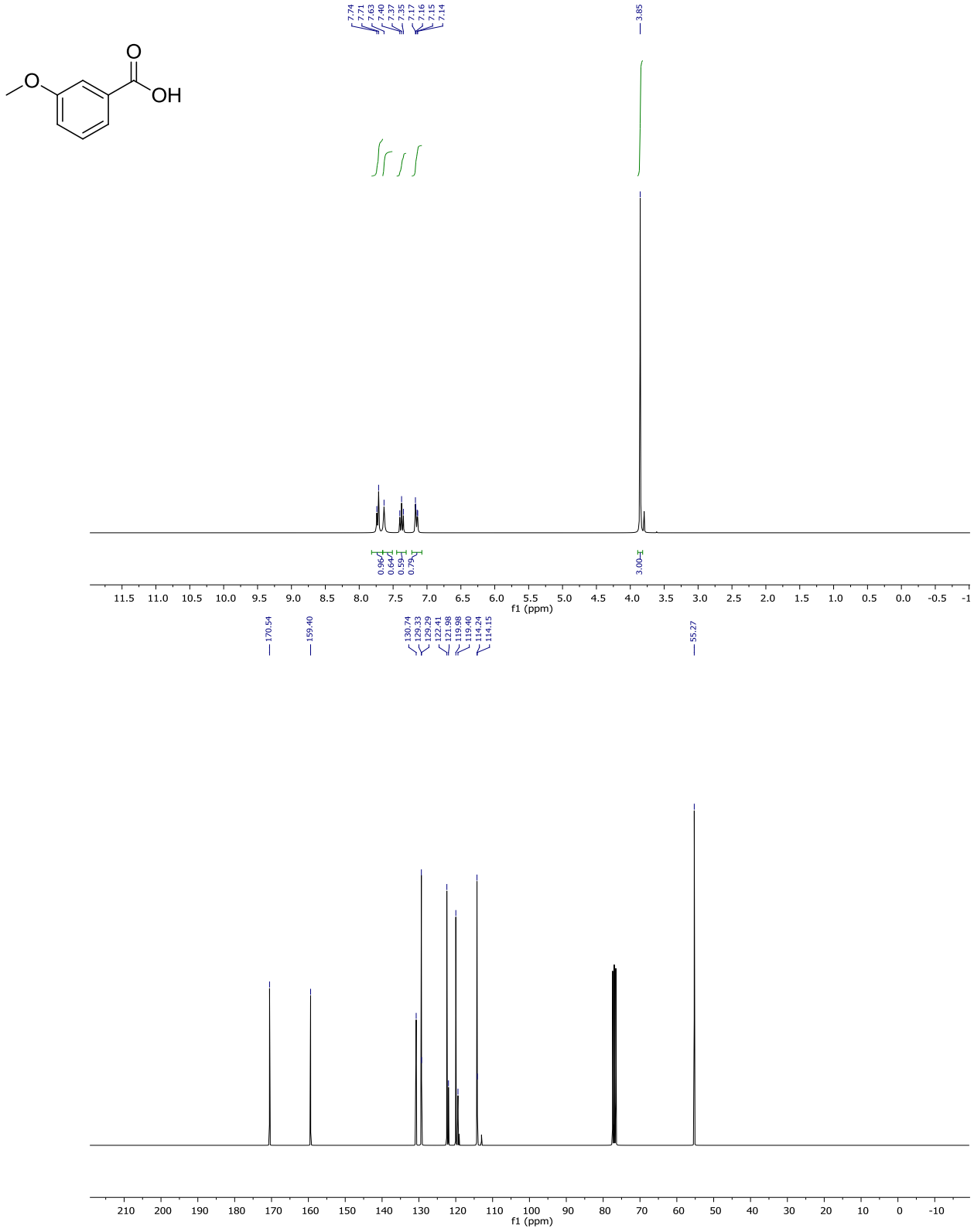









- 3-Methoxybenzoic acid



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