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Supporting Information

An outstanding catalyst for the oxygen-mediated oxidation of arylcarbinols, arylmethylene and arylacetylene compounds

Garazi Urgoitia, Raul SanMartin, Maria Teresa Herrero and Esther Dominguez**

Department of Organic Chemistry, University of Basque Country, 48080 Bilbao, Spain

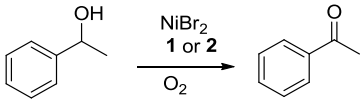
raul.sanmartin@ehu.es

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. High Res.

2. Table 1. Summary of assays for the oxidation of 1-phenylethanol



Entry	Reaction conditions[a]	**1**(%)[b]	**2**(%)[b]
1	DMSO:H_2O (1:1)	-	-
2	NaOAc, DMSO: H_2O (1:1)	-	-
3	NaOAc, H_2O	-	-
4	NaOAc, ETG	65	80
5	NaOAc, PEG-400	80	97
6	K_2CO_3, PEG-400	73	87
7	NaOAc, TBAB, PEG-400	35	40
8	NaOAc, PivOH, PEG-400	58	60
9	NaOAc, PEG-400: H_2O (1:1)	60	65
10[c]	$NiBr_2$, NaOAc, PEG-400	20	20
11[d]	Ligand (**1** or **2**), NaOAc, PEG-400	-	-
12[e]	NaOAc, PEG-400	94	97
13[f]	NaOAc, PEG-400	90	98
14[g]	NaOAc, PEG-400	80	97

[a] General reaction conditions: 1.0 eq. of 1-phenylethanol, 1 mL of solvent per mmol of substrate, molecular oxygen (1.0 atm.), 0.1 eq. of base and 0.1 eq. of additive (when appropriate), 0.01 mol% of $NiBr_2$, 0.01 mol% of triazole derivative **1** or **2**, 120ºC, 24h. [b] Isolated product. [c] Ligandless reaction. [d] No metal was added. [e] 0.001 mol% of $NiBr_2$, 0.001 mol% of **1** or **2**.[f] 10^{-4} mol% of $NiBr_2$, 10^{-4} mol% of **1** or **2**. [g] 10^{-5} mol% of $NiBr_2$, 10^{-5} mol% of **1** or **2**, 48h.

3. Synthesis of methyl 3,5-bis((1H-1,2,4-triazol-1-yl)methyl)benzoate (2). A mixture of methyl 3,5-bis(bromomethyl)benzoate (600 mg, 1.86 mmol), 1*H*-1,2,4-triazole **1** (283 mg, 4.09 mmol) and Cs_2CO_3 (2.37 gr, 7.27 mmol) was refluxed in dry acetonitrile (45 mL) under Ar for 3 h. After cooling, the resultant mixture 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 over anhydrous Na_2SO_4 and the solvent was removed *in vacuo* to give a residue which was purified by gradient flash chromatography (Hexane:EtOAc 7:3 → EtOAc → EtOAc:MeOH 9.5:0.5). Methyl 3,5-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzoate **2** was obtained as a yellowish solid (510 mg, 92%). Mp: 105-107 ºC (from EtOAc). ^{1}H-NMR ($CDCl_3$) δ_H: 3.89 (3H, s, CH_3), 5.50 (4H, s, CH_2), 7.35 (1H, s, H-4), 7.92 (2H, s, H-2, H-6), 8.00 (2H, s, H-3'), 8.59 (2H, s, H-5'). ^{13}C-NMR ($CDCl_3$) δ_C: 52.4 (CH_2), 52.6 (CH_3), 129.1 (C-3, C-5), 131.6 (C-1), 131.8 (C-2, C-6), 136.3 (C-5'), 143.3 (C-4), 152.6 (C-3'), 165.7 (CO). IR (film) ν_{max}: 1716, 1508, 1428, 1314, 1213, 1142, 1020. HRMS: Calculated for $C_{14}H_{14}N_6O_2$ 299.1256, found 299.1248.

4. Aerobic oxidation of alcohols in the presence of $NiBr_2$ and 1. 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), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **1** (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, 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), 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.[1] (96 mg, 80%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_C: 26.5 (CH_3), 128.2 (C_{arom-H}), 128.5 (C_{arom-H}), 133.0 (C_{arom}), 137.1 (C_{q-arom}), 198.1 (CO); LRMS (m/z): 120.1 (M^+).

Benzoylcyanide.[2] (125 mg, 96%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.47 (m, 2H, H_{arom}), 7.59 (m, 1H, H_{arom}), 8.13 (m, 2H, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 112.7 (CN), 129.5 (C_{arom-H}), 130.5 (C_{arom-H}), 133.4 (C_{arom-H}), 136.9 (C_{q-arom}), 167.9 (CO); LRMS (m/z): 131.1 (M^+).

Benzophenone.[2] (135 mg, 74%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_C : 128.2 (C_{arom}), 129.9 (C_{arom}), 132.3 (C_{arom}), 132.5 (C_{q-arom}), 196.6 (CO); LRMS (m/z): 182.1 (M^+).

1-(*p*-Tolyl)ethanone.[1] (115 mg, 86%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

1-Phenyl-1-propanone.[3] (115 mg, 86%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

1-(2-Methoxyphenyl)ethanone.[4] (112 mg, 75%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

2,2-Dimethyl-1-phenylpropanone.[5] (113 mg, 70%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

4-Chloroacetophenone.[7] (126 mg, 82%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

2-Methylbenzophenone.[6] (174 mg, 89%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

Indanone.[3] (99 mg, 75%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

1-Tetralone.[3] (131 mg, 90%). ^{1}H-NMR ($CDCl_3$) δ_H: 2.13 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 2.96 (t, 2H, *J* = 7.6, CH_2), 7.17-7.35 (m, 2H, H_{arom}), 7.46 (t, 1H, *J* = 6.7, H_{arom}), 8.03 (d, 1H, *J* = 7.8, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 23.3 (CH_2), 29.7 (CH_2), 39.2 (CH_2), 126.6 (C_{arom-H}), 127.1 (C_{arom-H}), 128.8 (C_{arom-H}), 132.6 (C_{q-arom}), 133.4 (C_{arom-H}), 144.5 (C_{q-arom}), 198.4 (CO); LRMS (m/z): 146.1 (M^+).

Fluorenone.[3] (169 mg, 94%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

Benzoic acid.[8] From benzyl alcohol (119 mg, 98%); from DL-mandelic acid (85 mg, 70%); from hydrobenzoin (170 mg, 70%); from benzoin (183 mg, 75%).^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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.[9] (115 mg, 70%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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.[8] (100 mg, 67%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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.[8] (95 mg, 70%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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.[10] (171 mg, 90%). ^{1}H-NMR (MeOD) δ_H: 7.77 (d, 2H, *J* = 7.7, H_{arom}), 8.18 (d, 2H, *J* = 7.3, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_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-Methoxybenzoic acid.[11] (114 mg, 75%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

4-Methoxybenzoic acid.[10] (102 mg, 67%). ^{1}H-NMR ($CDCl_3$) δ_H: 3.88 (3H, s, OCH_3), 6.95 (2H, d, *J* = 8.8, H_{arom}), 8.07 (2H, d, *J* = 8.9, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 55.4 (OCH_3), 126.6 (C_{q-arom}), 129.2 (C_{arom-H}), 130.2 (C_{arom-H}), 144.6 (C_{q-arom}), 172.3 (COOH); LRMS (m/z): 152.0 (M^+).

3-Phenoxybenzoic acid.[10] (128 mg, 60%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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^+).

3,4,5-Trimethoxybenzaldehyde.[12] (157 mg, 80%). ^{1}H-NMR ($CDCl_3$) δ_H: 3.91 (s, 9H, OCH_3), 7.11 (s, 2H, H_{arom}), 9.85 (s, 1H, CHO); ^{13}C-NMR ($CDCl_3$) δ_C: 56.2 (OCH_3), 60.9 (OCH_3), 106.6 (C_{arom-H}), 131.6 (C_{q-arom}), 143.5 (C_{q-arom}), 153.6. (C_{q-arom}), 190.9 (CHO); LRMS (m/z): 196.1 (M^+).

5. Aerobic oxidation of alcohols in the presence of $NiBr_2$ and 2. 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), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **2** (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, 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), 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. [1] (116 mg, 97%).

Benzoylcyanide. [2] (127 mg, 97%).

Benzophenone. [2] (169 mg, 93%).

1-(*p*-Tolyl)ethanone. [1] (131 mg, 98%).

1-Phenyl-1-propanone. [3] (126 mg, 94%).

1-(2-Methoxyphenyl)ethanone. [4] (147 mg, 98%).

2,2-Dimethyl-1-phenylpropanone. [5] (145 mg, 90%).

4-Chloroacetophenone. [7] (134 mg, 87%).

2-Methylbenzophenone. [6] (173 mg, 88%).

Indanone. [3] (123 mg, 93%).

1-Tetralone. [3] (131 mg, 90%).

Fluorenone. [3] (169 mg, 94%).

Cyclohexanone.[21] (20 mg, 20%). ^{1}H-NMR ($CDCl_3$) δ_H: 1.37-1.48 (m, 2H, CH_2), 1.49-1.62 (m, 4H, CH_2), 2.01 (t, 4H, *J* = 6.7, CH_2); ^{13}C-NMR ($CDCl_3$) δ_C: 24.7 (CH_2), 26.7 (CH_2), 41.6 (CH_2), 210.9 (CO).

Benzoic acid. [8] From benzyl alcohol (119mg, 98%); from DL-mandelic acid (119 mg, 98%); from hydrobenzoin (215 mg, 88%); from 1,2-diphenylethanol (237 mg, 97%); from benzoin (229 mg, 94%).

4-Isopropylbenzoic acid. [9] (154 mg, 94%).

4-Ethylbenzoic acid. [8] (141 mg, 94%).

4-Methylbenzoic acid. [8] (122 mg, 90%).

4-(Trifluoromethyl)benzoic acid. [10] (184 mg, 97%).

3-Methoxybenzoic acid. [11] (137 mg, 90%).

4-Methoxybenzoic acid. [10] (122 mg, 80%).

3-Phenoxybenzoic acid. [10] (188 mg, 88%).

3,4,5-Trimethoxybenzaldehyde. [12] (157 mg, 80%).

6. Aerobic oxidation of arylmethylene compounds in the presence of $NiBr_2$ and 1. 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), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **1** (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, 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), 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.[1] (108 mg, 90%).

Benzophenone.[2] (153 mg, 84%).

4-Benzoylpyridine.[14] (92 mg, 50%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.68-7.45 (m, 5H, H_{Ph}), 7.81 (d, 2H, J = 8.4, H_{arom}), 8.80 (d, 2H, J = 4.4, H_{py}); ^{13}C-NMR ($CDCl_3$) δ_C: 122.9 (C_{arom-H}), 128.6 (C_{arom-H}), 130.1 (C_{arom-H}), 133.5 (C_{q-arom}), 135.8 (C_{arom-H}), 144.3 (C_{q-arom}), 150.3 ($C_{q-arom(py)}$), 195.1 (CO); LRMS (m/z, %): 183.2 (M^+).

Benzoylcyanide .[2] (103 mg, 79%).

Fluorenone.[3] (175 mg, 97%).

Anthraquinone.[13] (104 mg, 50%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.79-7.82 (m, 2H, CH_{arom}), 8.30-8.33 (m, 2H, CH_{arom}); ^{13}C-NMR ($CDCl_3$) δ_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^+).

Xanthenone.[3] (153 mg, 78%). ^{1}H-NMR ($CDCl_3$) δ_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 ($CDCl_3$) δ_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): 196.10 (M^+).

Benzoic acid.[8] From phenylacetic acid (55 mg, 45%); from deoxybenzoin (166 mg, 68%).

7. Aerobic oxidation of arylmethylene compounds in the presence of $NiBr_2$ and 2. 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), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **2** (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol) and PEG 400 (1 mL per mmol of substrate) at room temperature. The system was purged with molecular oxygen, 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), 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.[1] (116 mg, 97%).

Benzophenone.[2] (176 mg, 97%).

4-Benzoylpyridine.[14] (128 mg, 70%).

Benzoylcyanide .[2] (107 mg, 82%).

Fluorenone.[3] (176 mg, 98%).

Anthraquinone.[13] (114 mg, 55%).

Xanthenone.[3] (190 mg, 97%).

Benzoic acid.[8] From phenylacetic acid (61 mg, 50%); from deoxybenzoin (220 mg, 90%).

8. Aerobic cleavage of C-C triple bond in the presence of $NiBr_2$ and 1. General procedure. A round bottom flask equipped with a magnetic stirrer bar was charged with the alkyne (1 mmol), NaOAc (8.0 mg, 0.1 mmol), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **1** (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), 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 acids were prepared:

Benzoic acid.[8] From phenylacetylene (110 mg, 90%); from 3-phenyl-2-propyn-1-ol (97 mg, 80%); from 3-phenyl-2-propynoic acid (88 mg, 72%); from ethyl phenylpropiolate (73 mg, 60%); from 1,3-diphenylprop-2-yn-1-one (200 mg, 82%); from 1-[4-(2-phenyleth-1-ynyl)phenyl]ethan-1-one (43 mg, 35%); from 1-phenyl-4-penten-1-yne (73 mg, 59%); from 1-phenyl-2-propyn-1-ol (113 mg, 93%); from 1,1,3-triphenyl-2-propyn-1-ol (61 mg, 50%).

4-Butylbenzoic acid. [16] (158 mg, 89%). ^{1}H-NMR ($CDCl_3$) δ_H: 0.95 (t, 3H, *J* = 7.3, CH_3), 1.29-1.44 (m, 2H, CH_2), 1.61-1.64 (CH_2), 2.69 (t, 2H, *J* = 7.7, CH_2), 7.28 (d, 2H, *J* = 9.7, H_{arom}), 8.04 (d, 1H, *J* = 8.1, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 13.8 (CH_3), 22.2 (CH_2), 33.1 (CH_2), 35.7 (CH_2), 126.7 ($C_{q\text{-}arom}$), 128.5 ($C_{arom\text{-}H}$), 130.2 ($C_{arom\text{-}H}$), 149.4 ($C_{q\text{-}arom}$), 172. 3 (COOH); LRMS (m/z): 178.1 (M^+).

2,4-Difluorobenzoic acid. [15] (107 mg, 68%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.05 (t, 2H, *J* = 9.3, H_{arom}), 8.01 (dd, 1H, *J* = 15.5, 8.2, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 103.0 (t, *J* = 26.2, $C_{arom\text{-}H}$), 109.6 (dd, *J* = 21.9, 3.9, $C_{arom\text{-}H}$), 132.4 (dd, *J* = 10.7, 2.4, $C_{arom\text{-}H}$), 159.8 ($C_{q\text{-}arom}$), 162.5 ($C_{q\text{-}arom}$), 163.4 (COOH); 165.8 ($C_{q\text{-}arom}$); LRMS (m/z): 158 (M^+).

4-Methoxy-2-methylbenzoic acid. [18] (146 mg, 88%). ^{1}H-NMR (MeOD) δ_H: 2.56 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.76-6.79 (m, 1H, H_{arom}), 7.90-7.94 (m, 2H, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 21.1 (CH_3), 54.4 (OCH_3), 110.5 ($C_{arom\text{-}H}$), 116.5 ($C_{arom\text{-}H}$), 121.7 ($C_{q\text{-}arom}$), 132.9 ($C_{arom\text{-}H}$), 142.5 ($C_{q\text{-}arom}$), 162.6 ($C_{q\text{-}arom}$), 169.3 (COOH); LRMS (m/z): 166.1 (M^+).

3,4-Dichlorobenzoic acid. [19] (161 mg, 85%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.56 (d, 1H, *J* = 8.4, H_{arom}), 7.92 (dd, 1H, *J* = 8.4, 2.0, H_{arom}), 8.18 (d, 1H, *J* = 1.9, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 127.8 ($C_{arom\text{-}H}$), 128.8 ($C_{arom\text{-}H}$), 129.4 ($C_{q\text{-}arom}$), 129.59 ($C_{arom\text{-}H}$), 130.7 ($C_{arom\text{-}H}$), 135.2 ($C_{q\text{-}arom}$), 164.5 (COOH); LRMS (m/z): 190 (M^+).

4-Acetylbenzoic acid. [20] (55 mg, 34%). ^{1}H-NMR ($CDCl_3$) δ_H: 2.64 (s, 3H, CH_3); 8.09 (d, 2H, *J* = 8.4, H_{arom}); 8.14 (d, 2H, *J* = 8.4, H_{arom}); ^{13}C-NMR (DMSO-d_6) δ_C: 26.9 (CH_3); 129.0 ($C_{arom\text{-}H}$); 130.6 ($C_{arom\text{-}H}$); 135.0 ($C_{q\text{-}arom}$); 141.3 ($C_{q\text{-}arom}$); 166.8 (COOH); 197.6 (CO); LRMS (m/z): 164 (M^+).

Benzophenone. [2] from 1,1,3-triphenyl-2-propyn-1-ol (55 mg, 30%).

9. Aerobic cleavage of C-C triple bond in the presence of $NiBr_2$ and 2. General procedure. A round bottom flask equipped with a magnetic stirrer bar was charged with the alkyne (1 mmol), NaOAc (8.0 mg, 0.1 mmol), $NiBr_2$ (20 μL of a 5 x 10^{-6}M solution in PEG-400, 10^{-7} mmol), **2** (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, 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), 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 acids were prepared:

Benzoic acid.[8] From phenylacetylene (112 mg, 92%); from diphenylacetylene (234 mg, 96%); from 3-phenyl-2-propyn-1-ol (115 mg, 94%); from 1-phenyl-1propyne (107 mg, 88%); from 3-phenyl-2-propynoic acid (91 mg, 75%); from ethyl phenylpropiolate (110 mg, 90%); from 1,3-diphenylprop-2-yn-1-one (210 mg, 86%); from 1-[4-(2-phenyleth-1-ynyl)phenyl]ethan-1-one (57 mg, 47%); from 1-phenyl-

4-penten-1-yne (110 mg, 90%); from 1-phenyl-2-propyn-1-ol (115 mg, 94%); from 1,1,3-triphenyl-2-propyn-1-ol (73 mg, 60%).

4-Butylbenzoic acid. [17] (162 mg, 91%).

4-Bromobenzoic acid. [8] (158 mg, 79%). ^{1}H-NMR ($CDCl_3$) δ_H: 7.63 (d, 2H, J = 8.7, H_{arom}), 7.91(d, 2H, J = 8.7, H_{arom}); ^{13}C-NMR ($CDCl_3$) δ_C: 125.8 ($C_{q\text{-}arom}$), 128.2 ($C_{q\text{-}arom}$), 129.5 ($C_{arom\text{-}H}$), 129.9 ($C_{arom\text{-}H}$), 165.9 (COOH); LRMS (m/z): 199.9 (M^+).

2,4-Difluorobenzoic acid. [15] (112 mg, 71%).

4-Methoxy-2-methylbenzoic acid. [18] (161 mg, 97%).

3,4-Dichlorobenzoic acid.[19] (170 mg, 90%).

4-Acetylbenzoic acid. [20] (75 mg, 46%).

Benzophenone. [2] from 1,1,3-triphenyl-2-propyn-1-ol (36 mg, 20%).

10. Large-scale aerobic oxidation of 1-phenylethanol. A round bottom flask equipped with a magnetic stirrer bar was charged with 1-phenylethanol (1.5 gr, 12.28 mmol), NaOAc (100 mg, 1.23 mmol), $NiBr_2$ (245 μL of a 5 x 10^{-6}M solution in PEG-400, 1.23 x 10^{-6} mmol), **2** (245 μL of a 5 x 10^{-6}M solution in PEG-400, 1.23 x 10^{-6} mmol) and PEG 400 (12.3 mL) at room temperature. The system was purged with molecular oxygen an oxygen-filled balloon (1-1.2 atm) was connected. The mixture was heated at 120ºC under stirring for 120 h. The reaction outcome was monitored by ^{1}H-NMR. Upon completion, the mixture was cooled to room temperature and water was added (100 mL aprox.). The resulting solution was acidified with HCl 1M (pH≈1-2), extracted with Et_2O (4 x 30 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. Acetophenone was obtained as a yellowish oil (1.41 g, 96%).

11. Large-scale oxidative cleavage of phenylacetylene. A round bottom flask equipped with a magnetic stirrer bar was charged with phenylacetylene (1.5 gr, 14.68 mmol), NaOAc (120 mg, 1.46 mmol), $NiBr_2$ (294 μL of a 5 x 10^{-6}M solution in PEG-400, 1.47 x 10^{-6} mmol), **2** (294 μL of a 5 x 10^{-6}M solution in PEG-400, 1.47 x 10^{-6} mmol) and PEG 400 (14.7 mL) at room temperature. The system was purged with molecular oxygen, an oxygen-filled balloon (1-1.2 atm) was connected. The mixture was heated at 120ºC 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 (100 mL aprox.). The resulting solution was acidified with HCl 1M (pH≈1-2), extracted with Et_2O (4 x 30 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 (7:3) as eluent. Benzoic acid was obtained as a white solid (1.2 g, 67%).

When the reaction time (heating at 120ºC) was prolonged to 120h, the same procedure applied to phenylacetylene provided benzoic acid (1.73 g, 96%) as a white powder.

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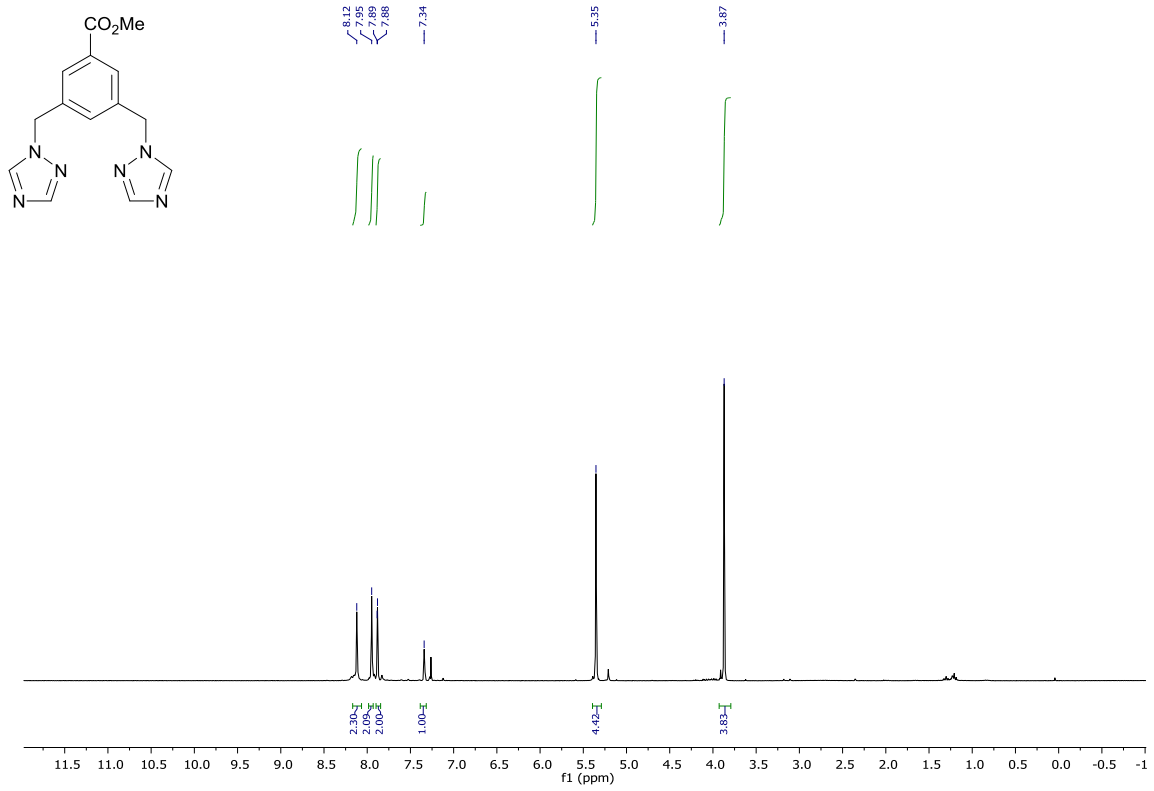
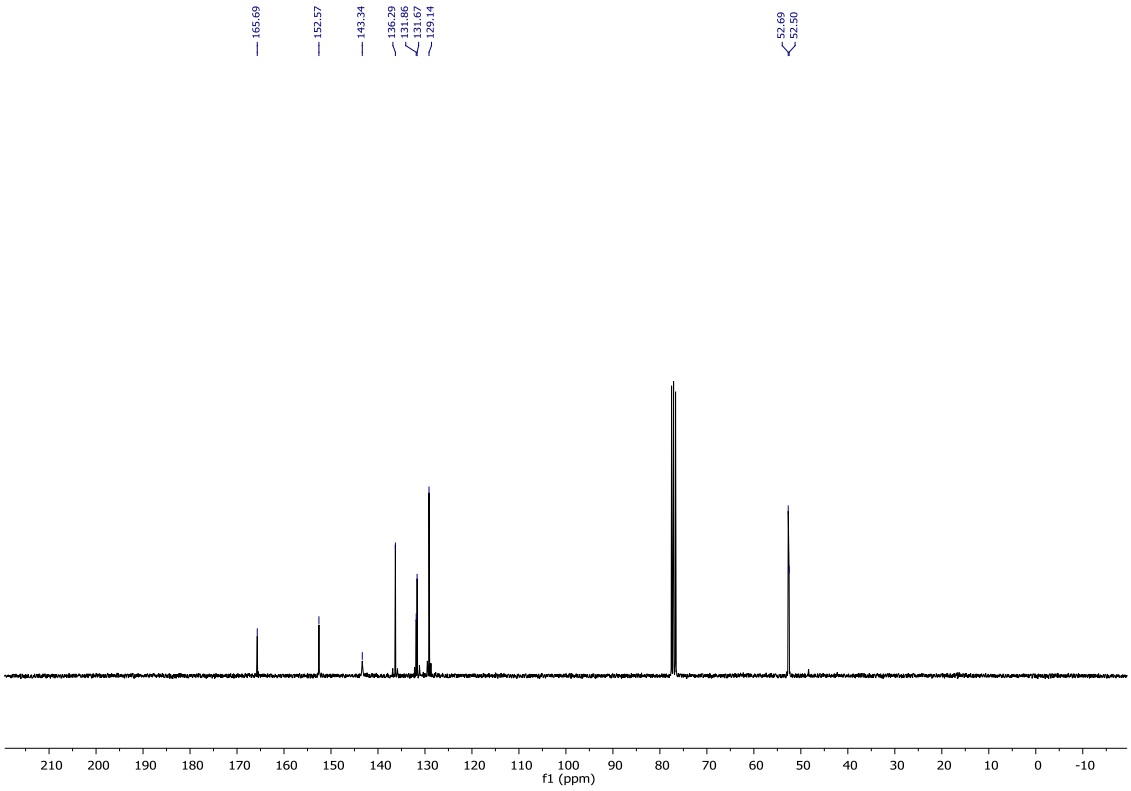
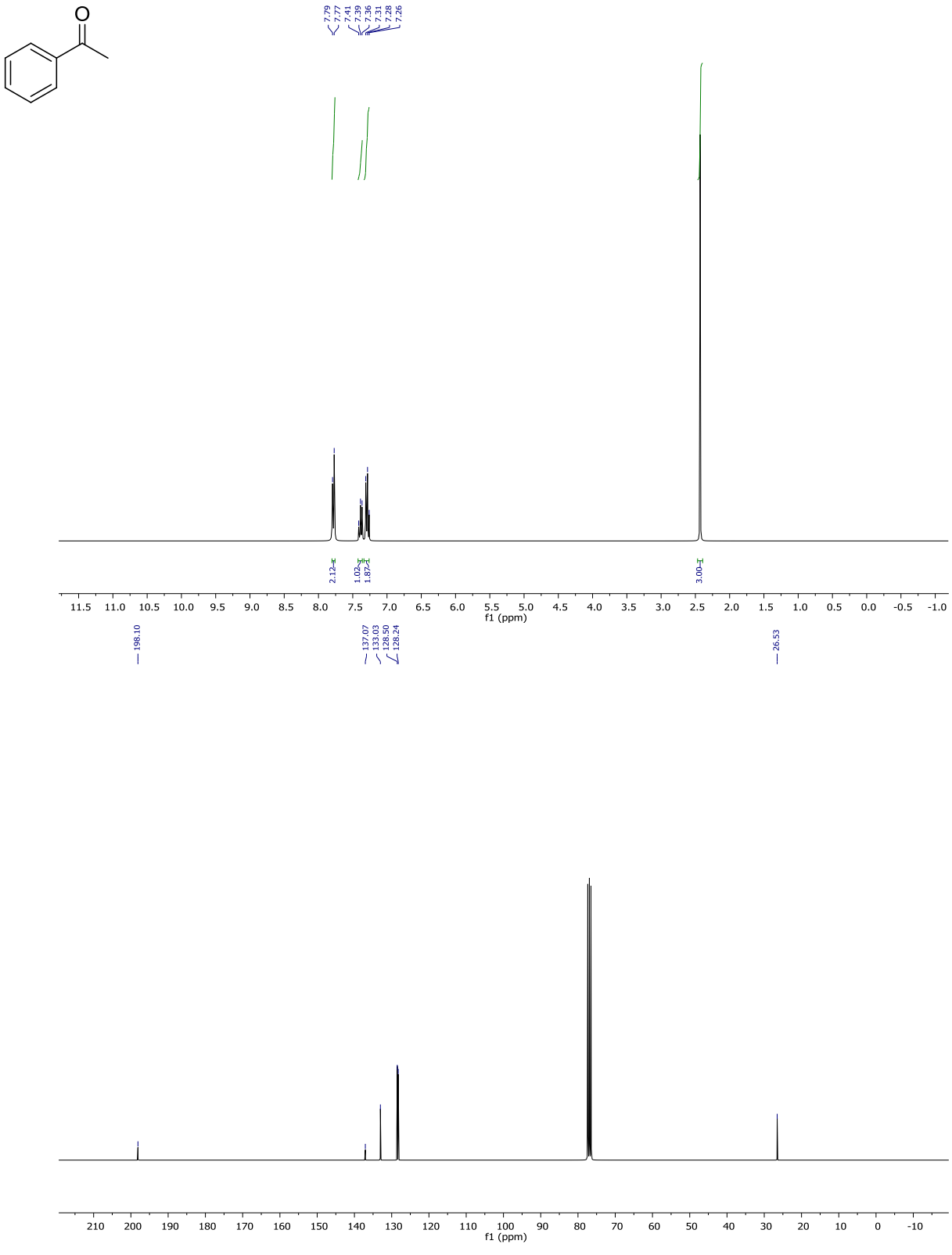
12. ^{1}H NMR and ^{13}C NMR spectra

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

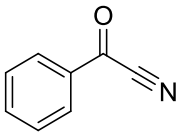


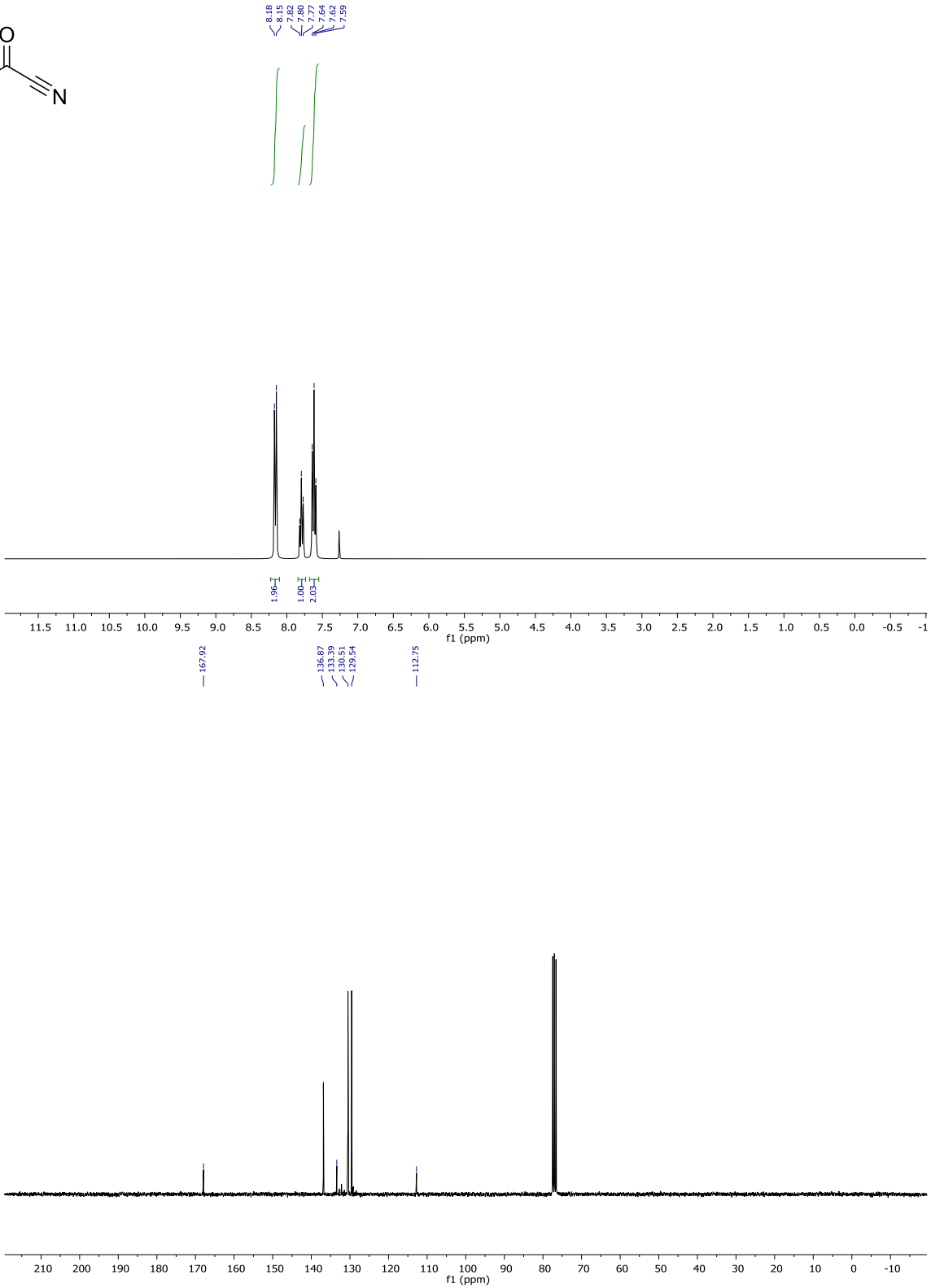


- Acetophenone

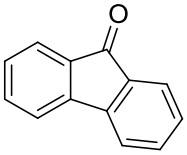


- Benzoylcyanide





- Fluorenone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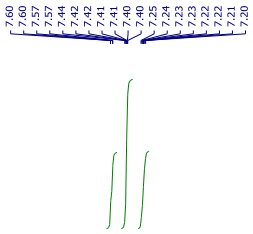
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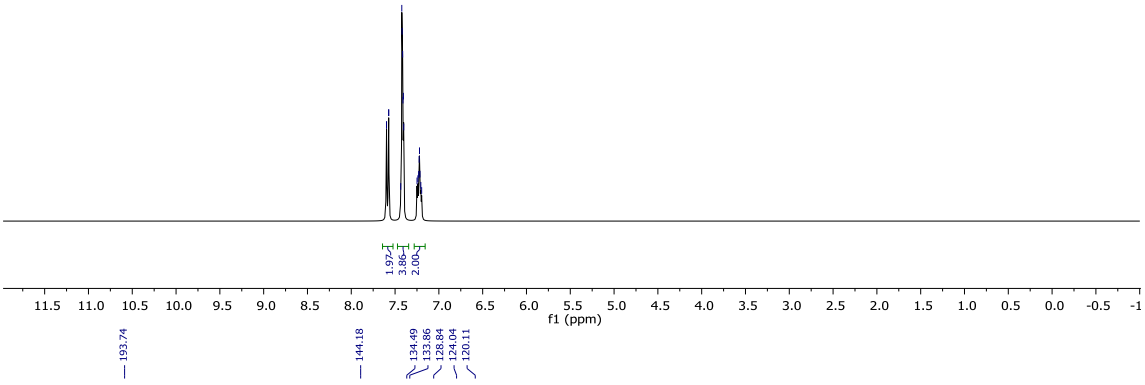
7.20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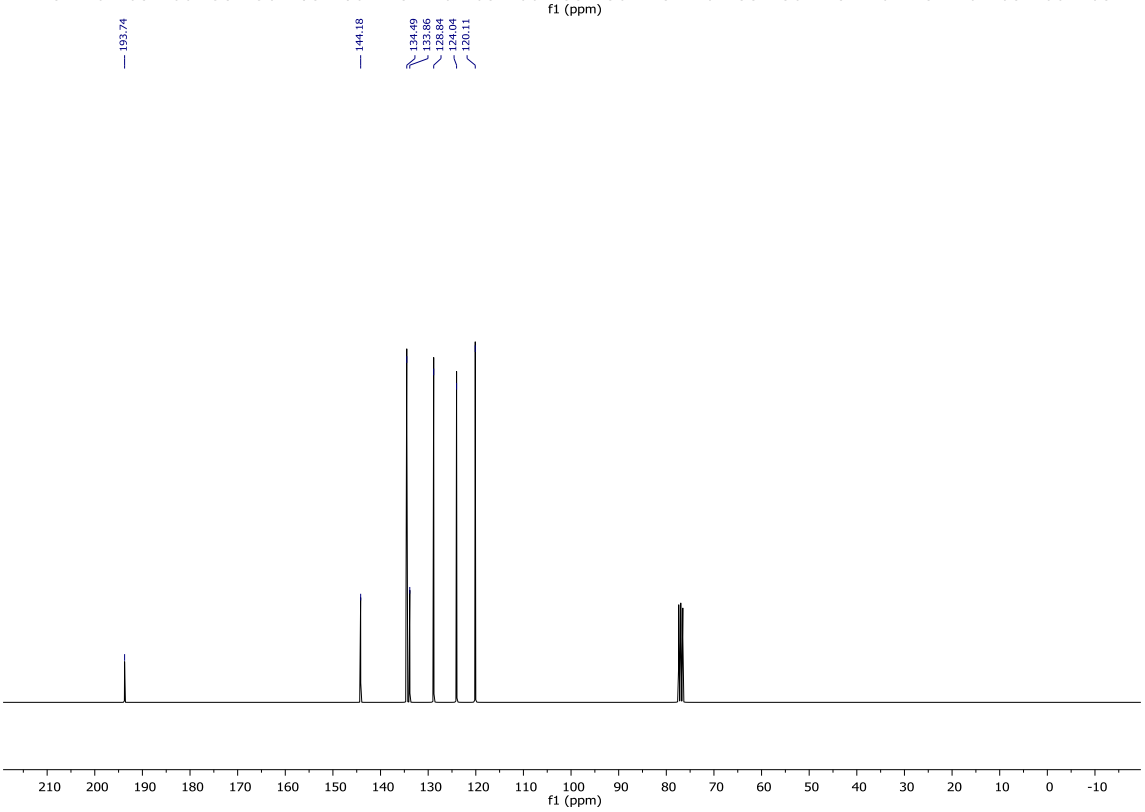
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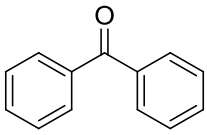
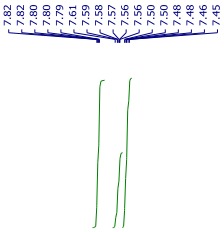
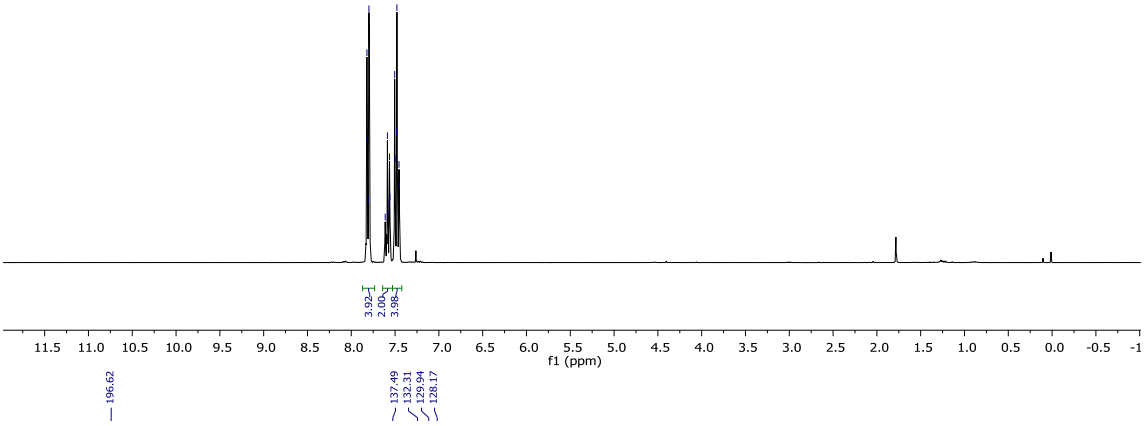
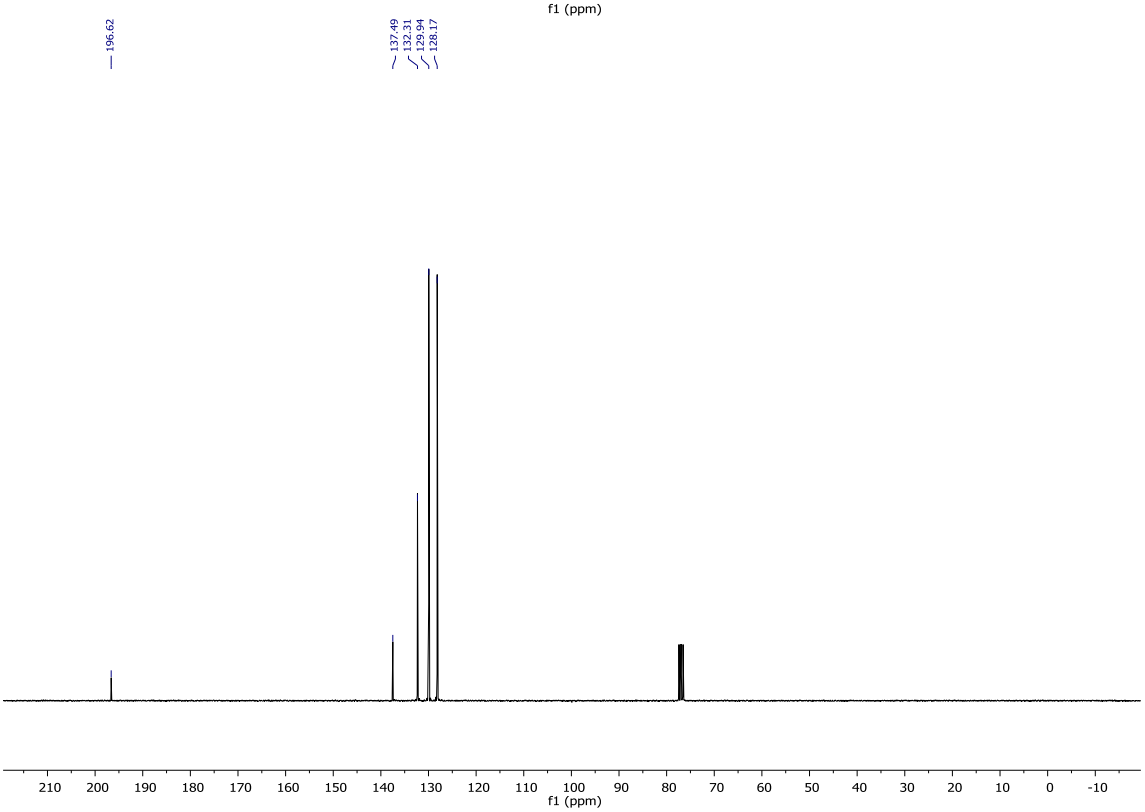
f1 (ppm)

- Benzophenone

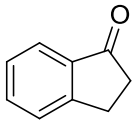








- Indanone



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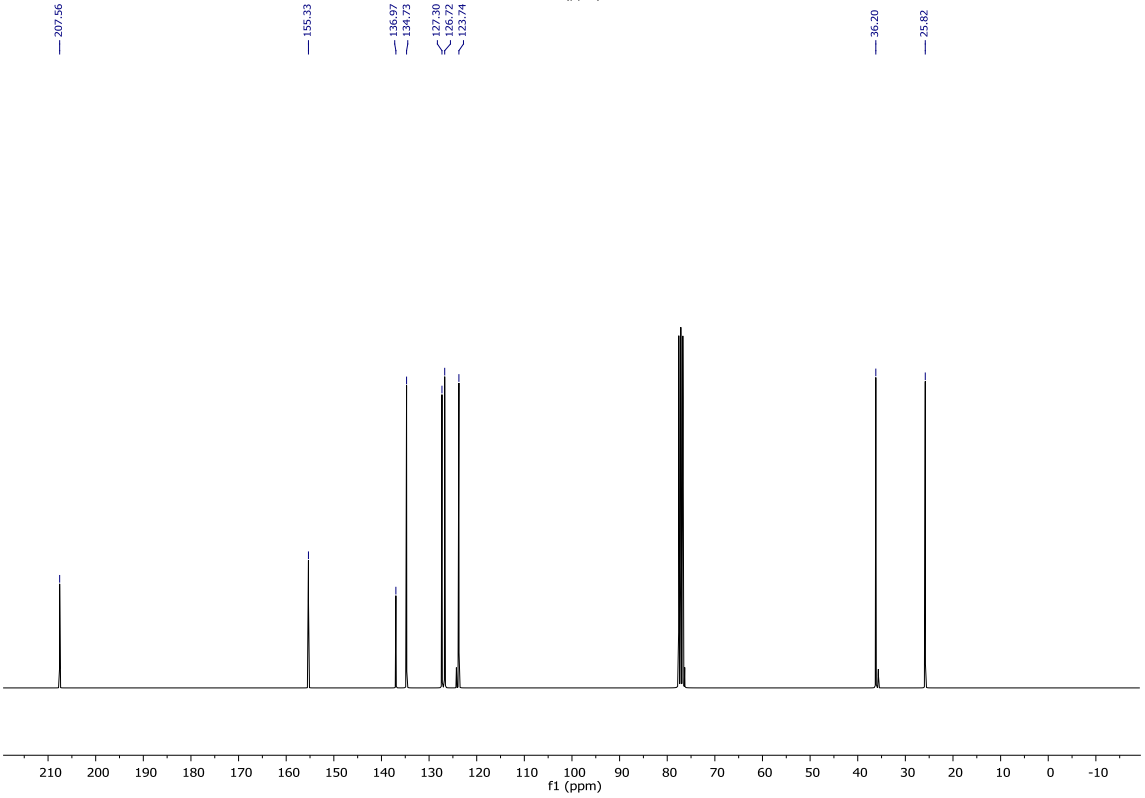
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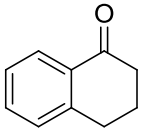
- 1-Tetralone



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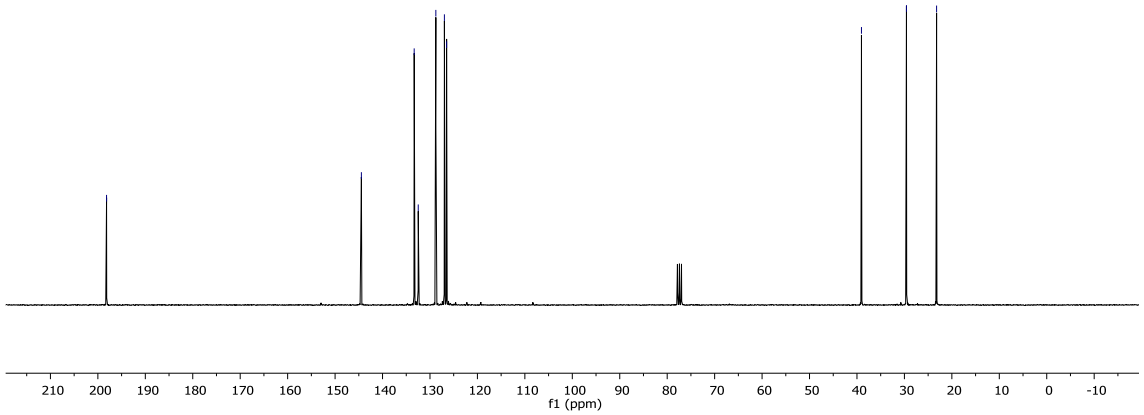
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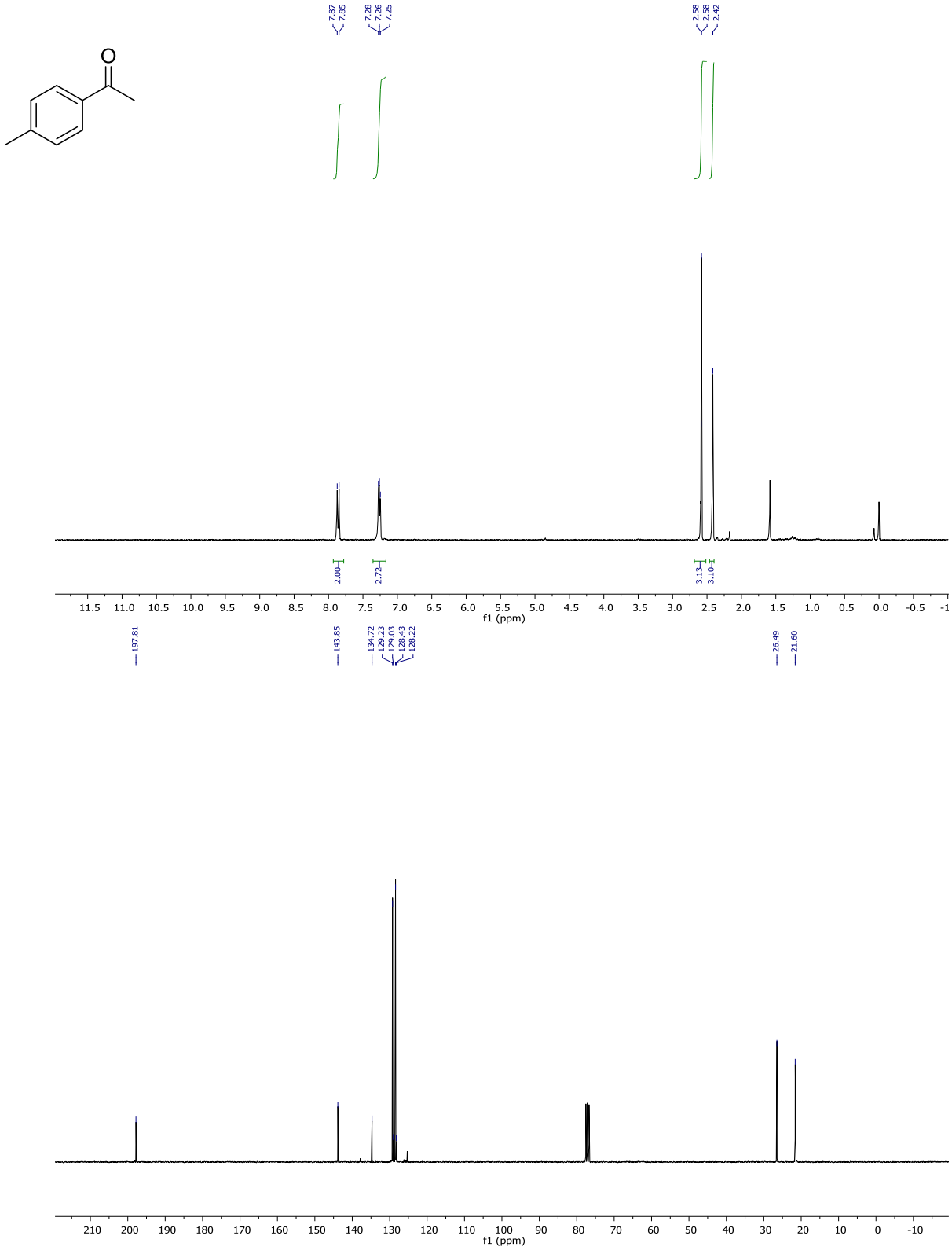
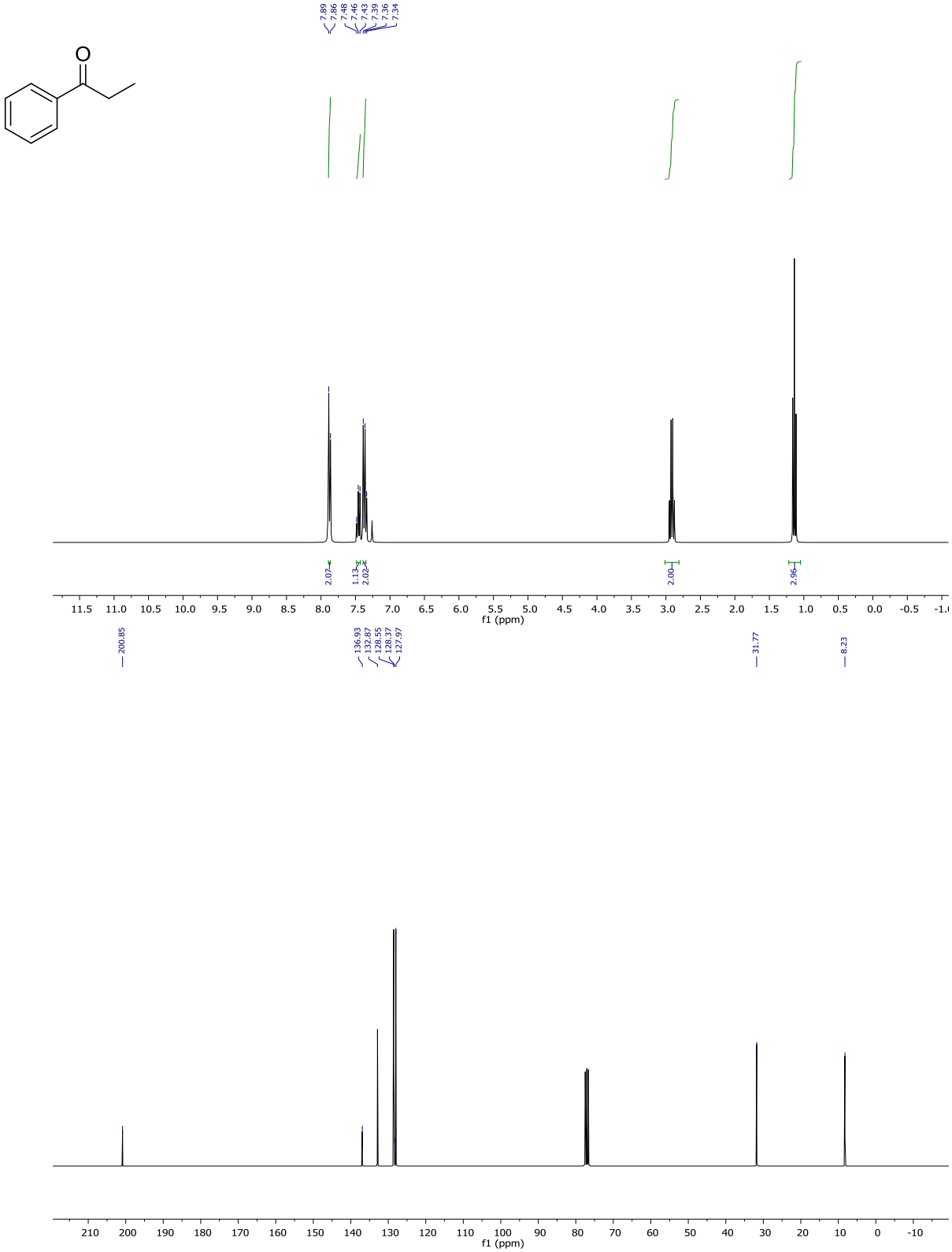
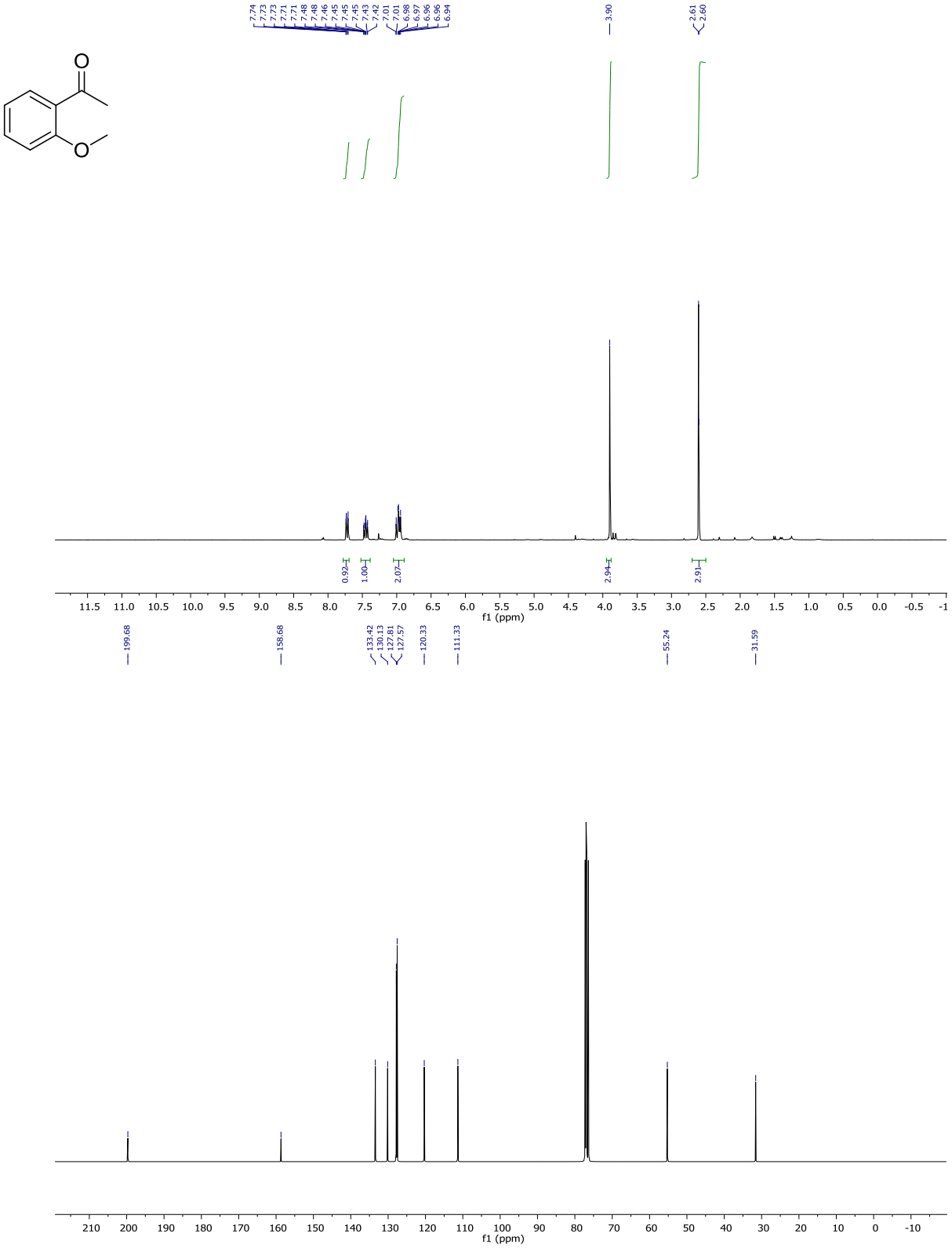
- 1-(*p*-Tolyl)ethanone



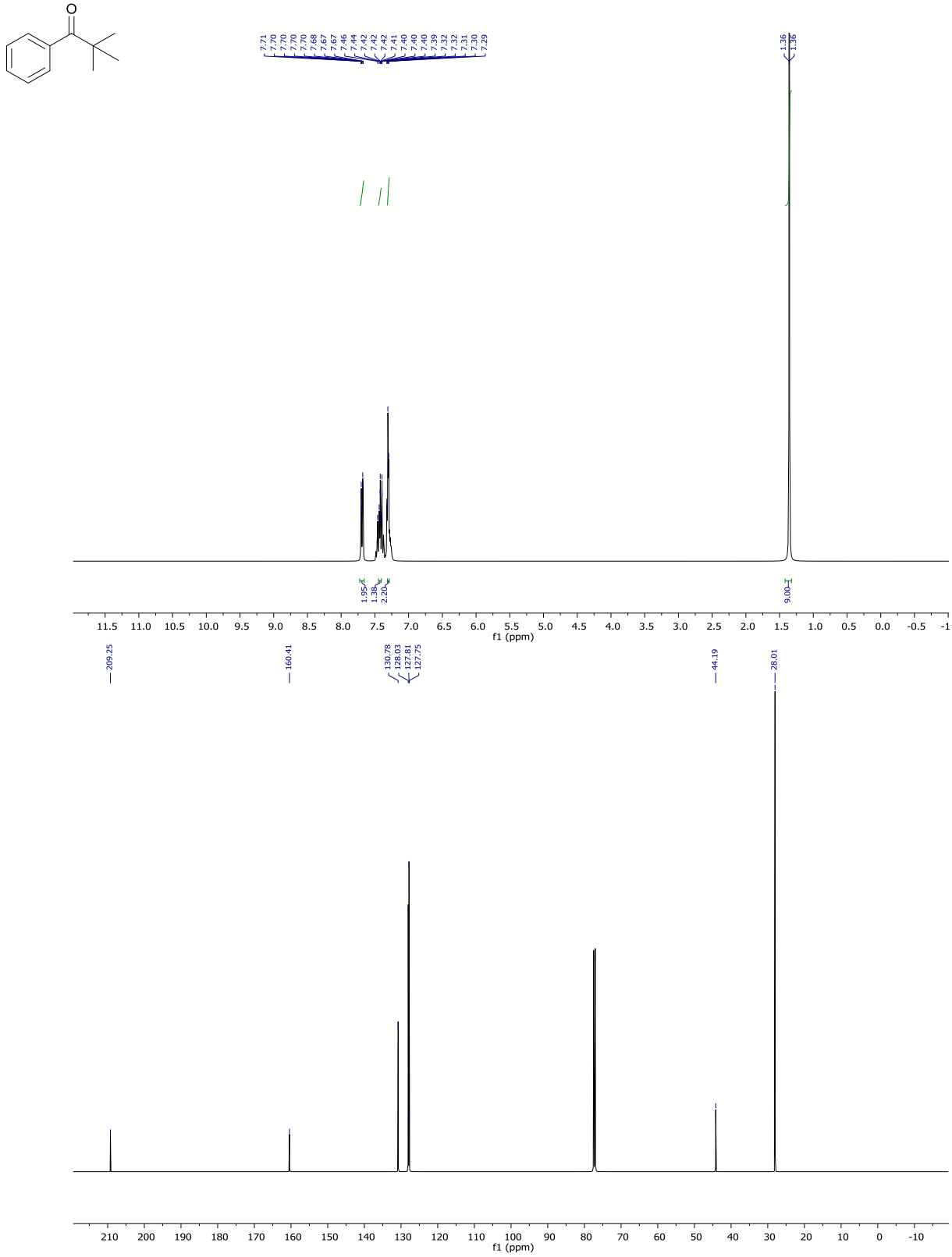
- 1-Phenyl-1-propanone



- 1-(2-methoxyphenyl)ethanone



- 2,2-Dimethyl-1-phenylpropanone



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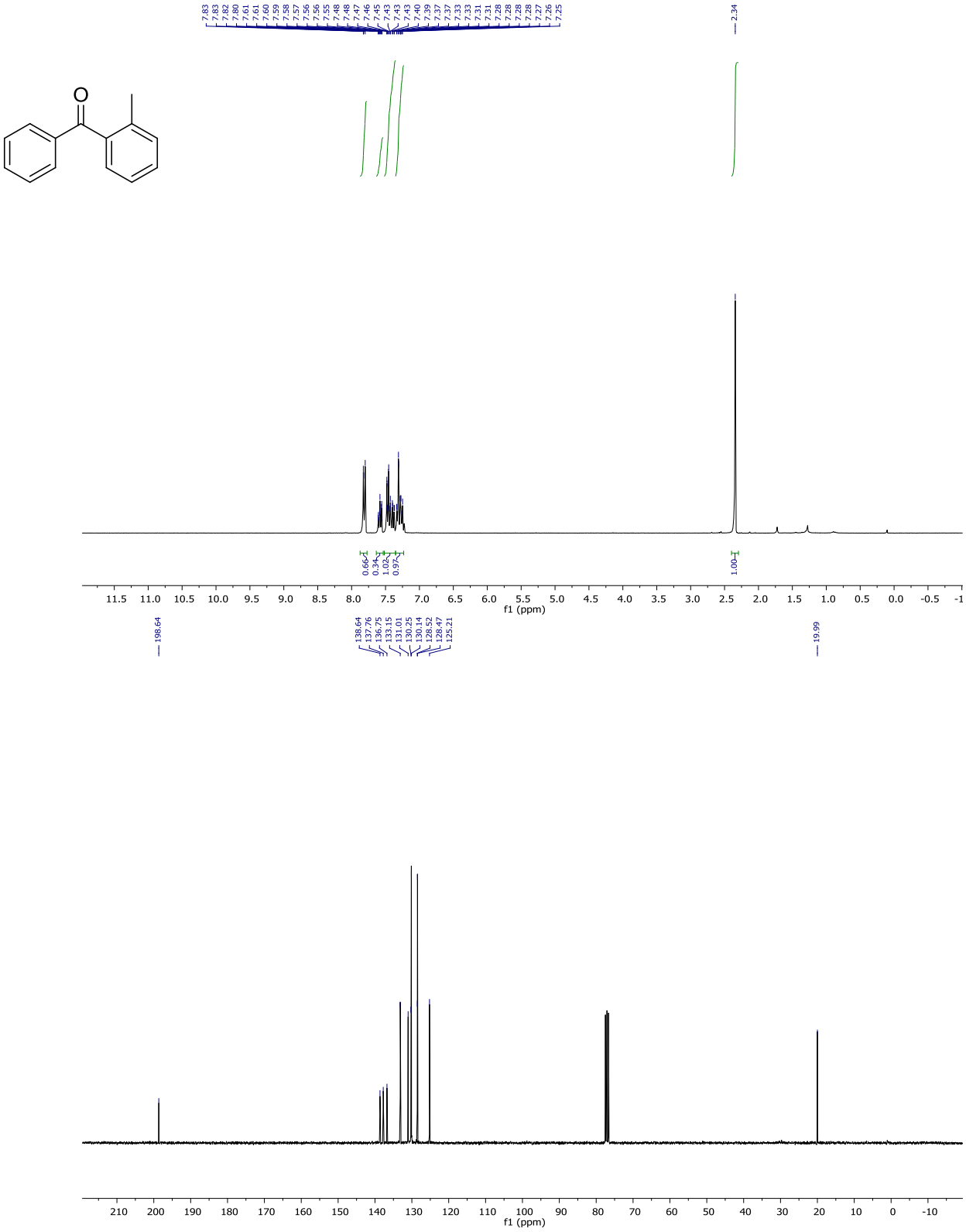

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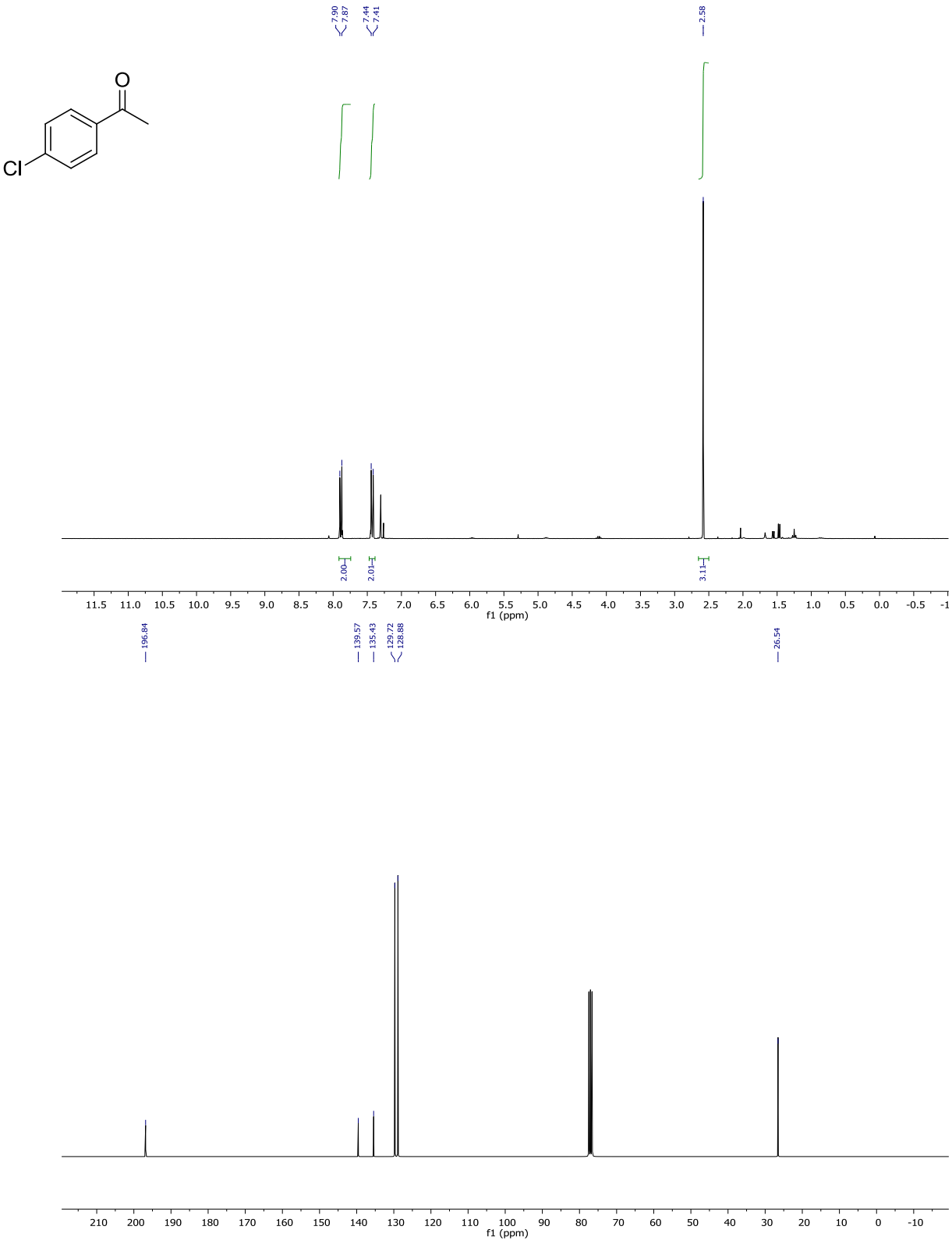
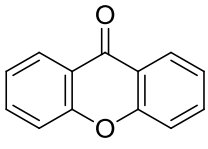
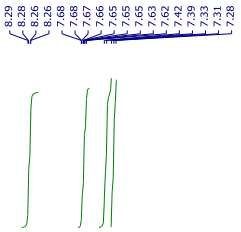
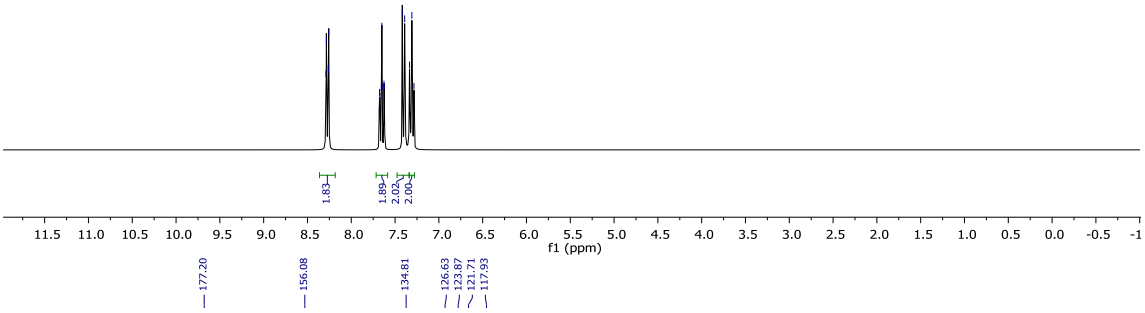
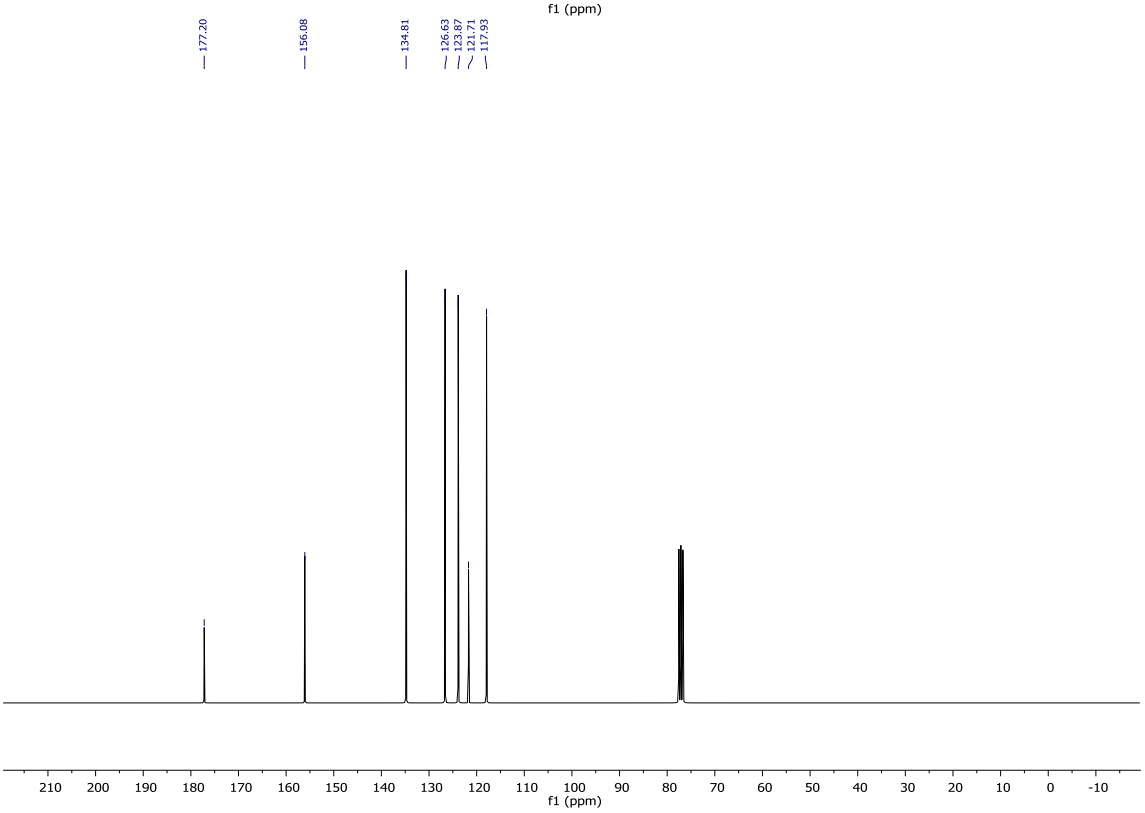


- Xanthenone

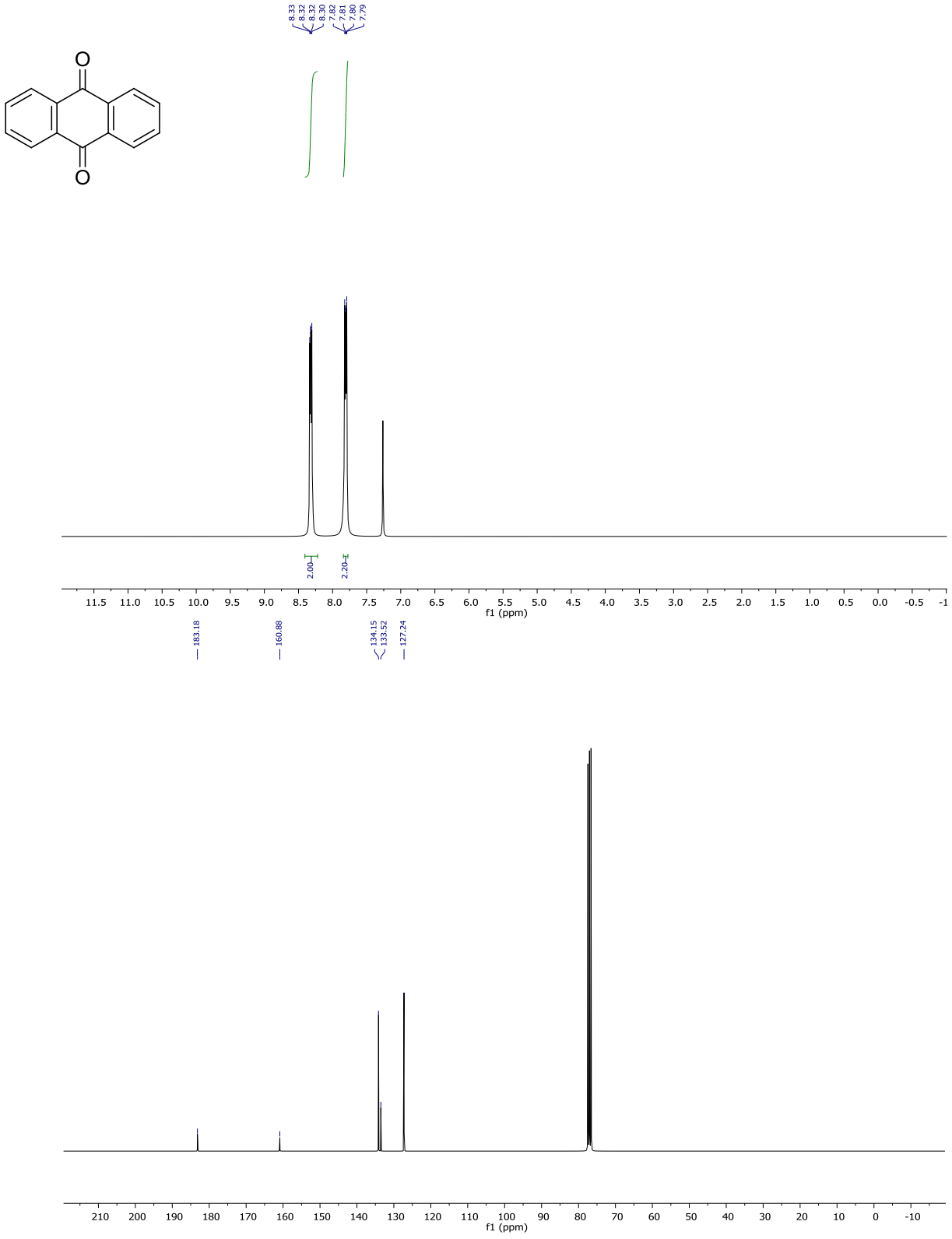

O
O


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

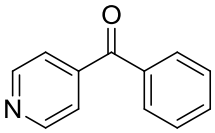

1.83
1.89
2.02
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

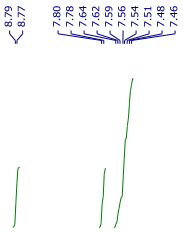

177.20
156.08
134.81
126.63
123.87
121.71
117.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

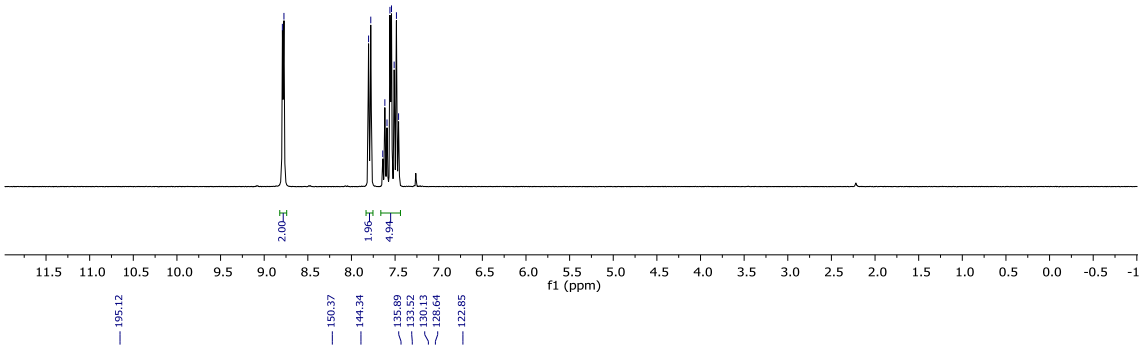
- Anthraquinone

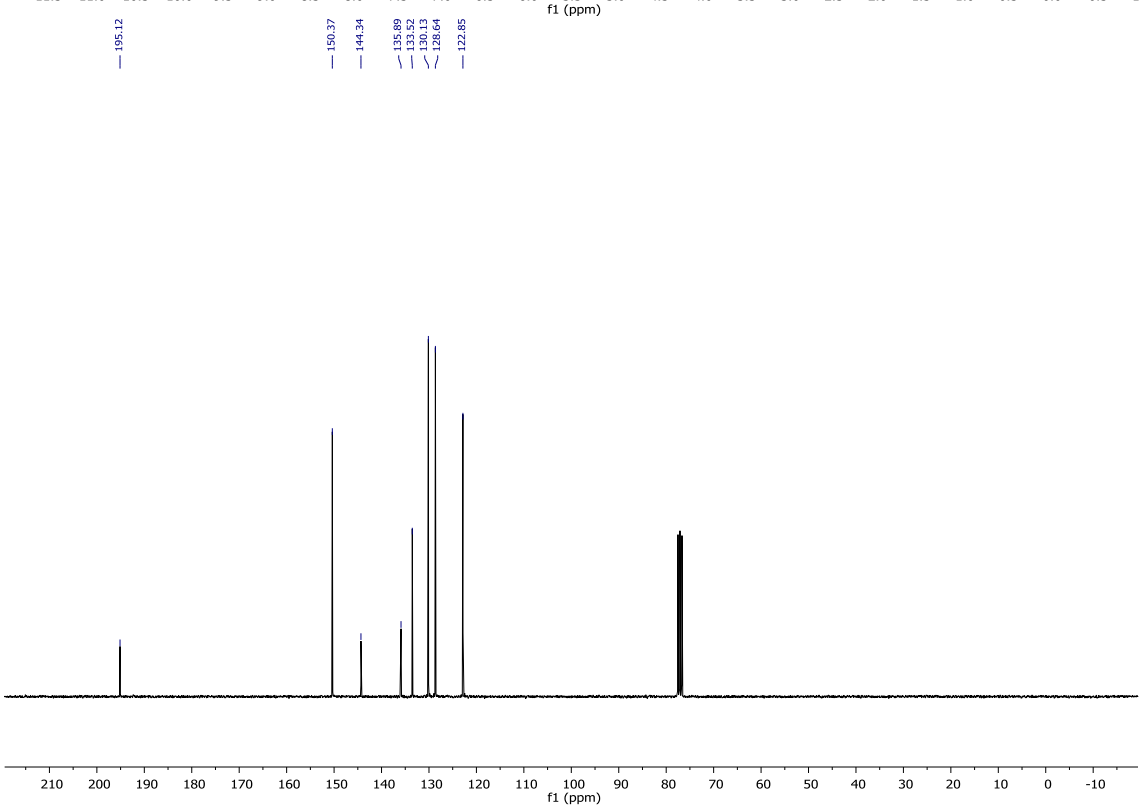


- 4-Benzoylpyridine

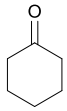




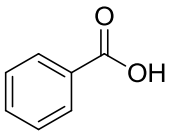




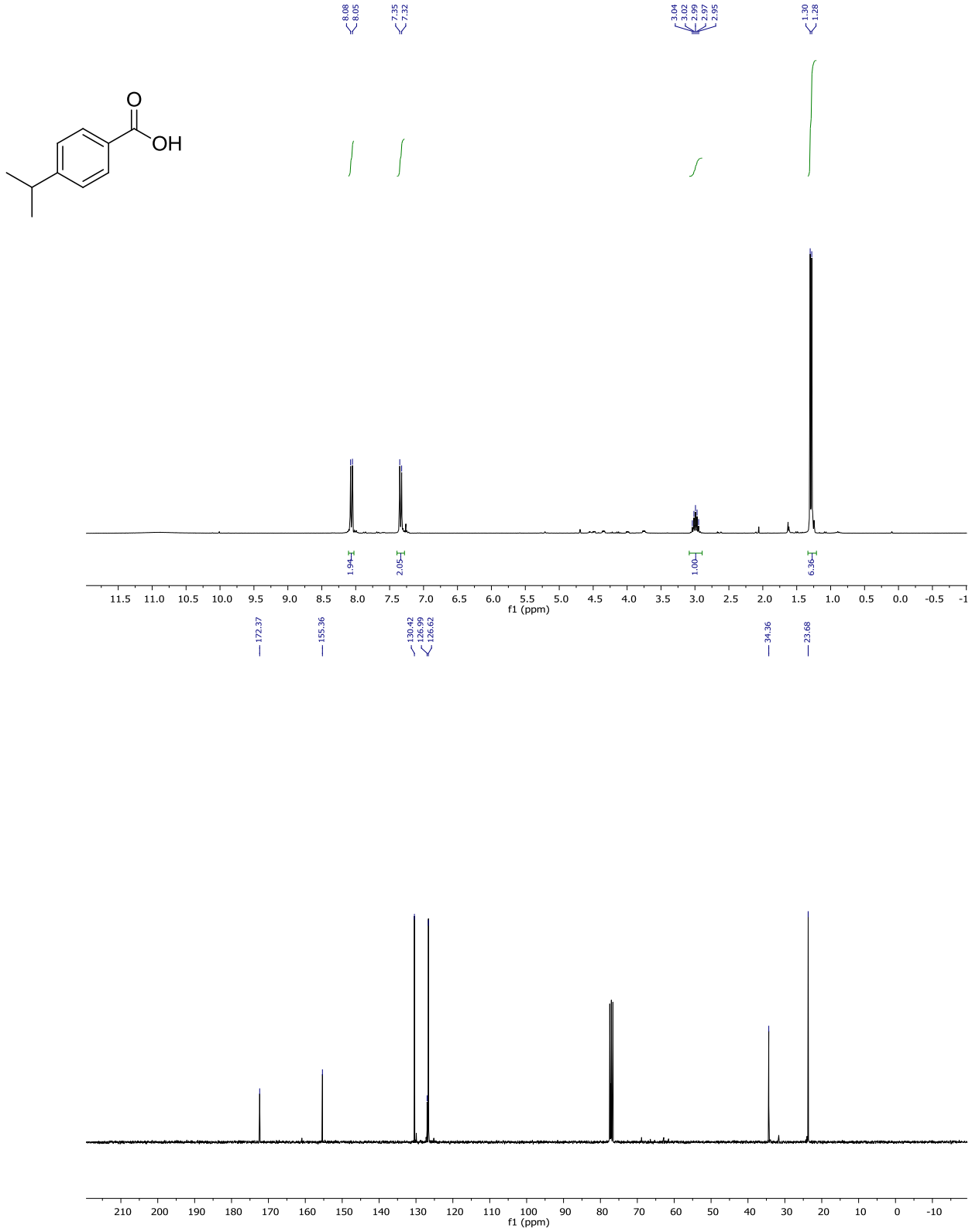
- Cyclohexanone



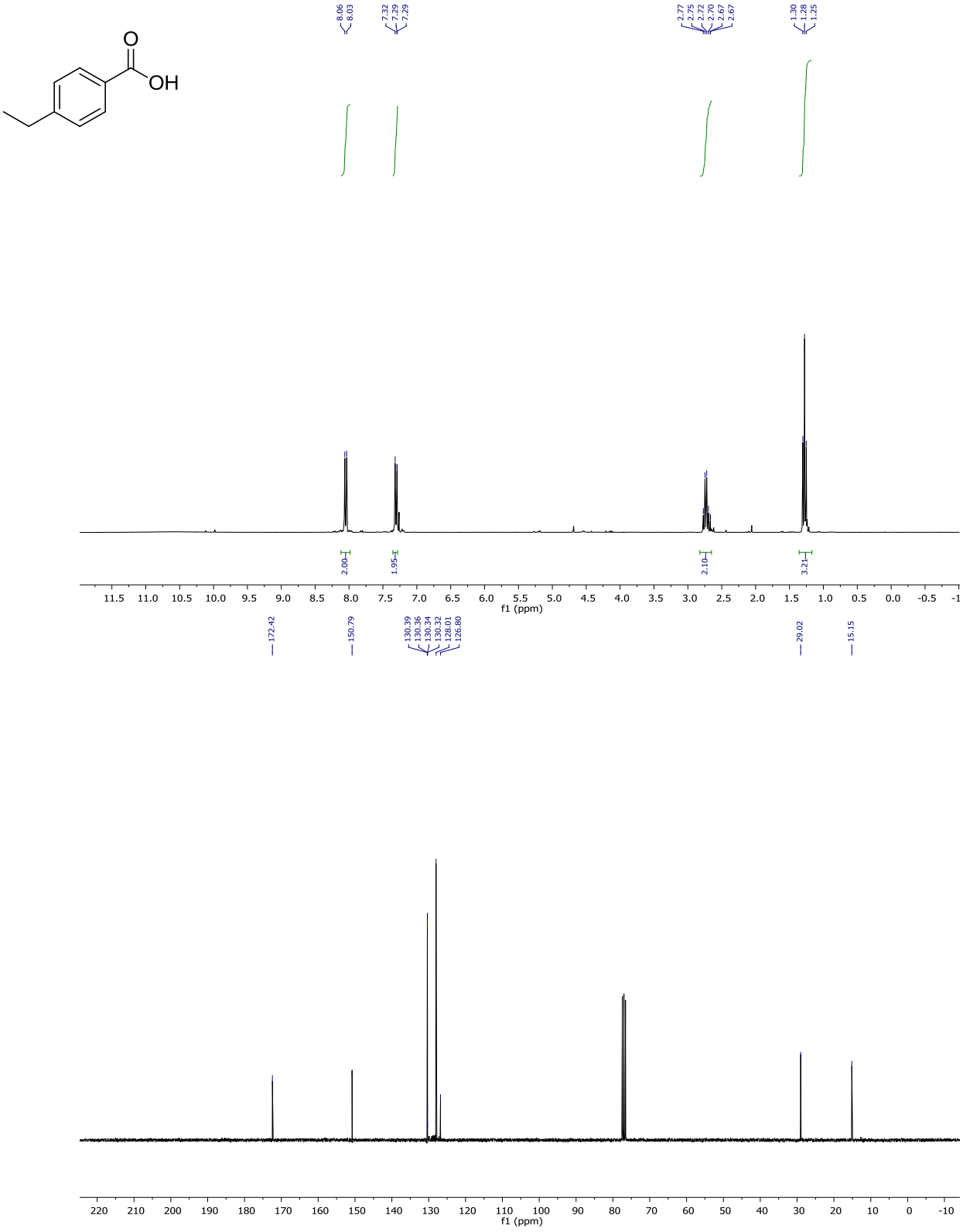
- Benzoic acid



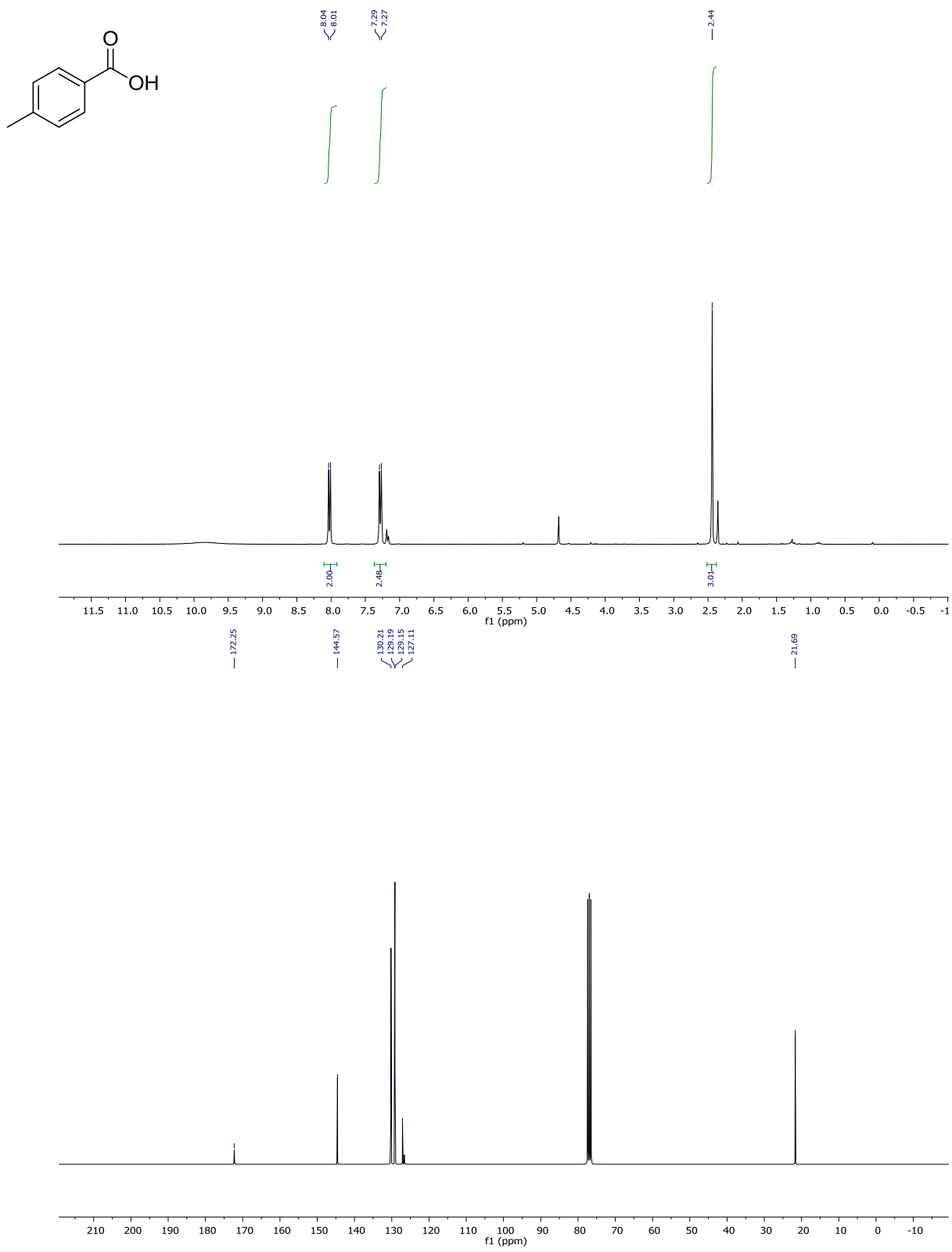
- 4-Isopropylbenzoic acid



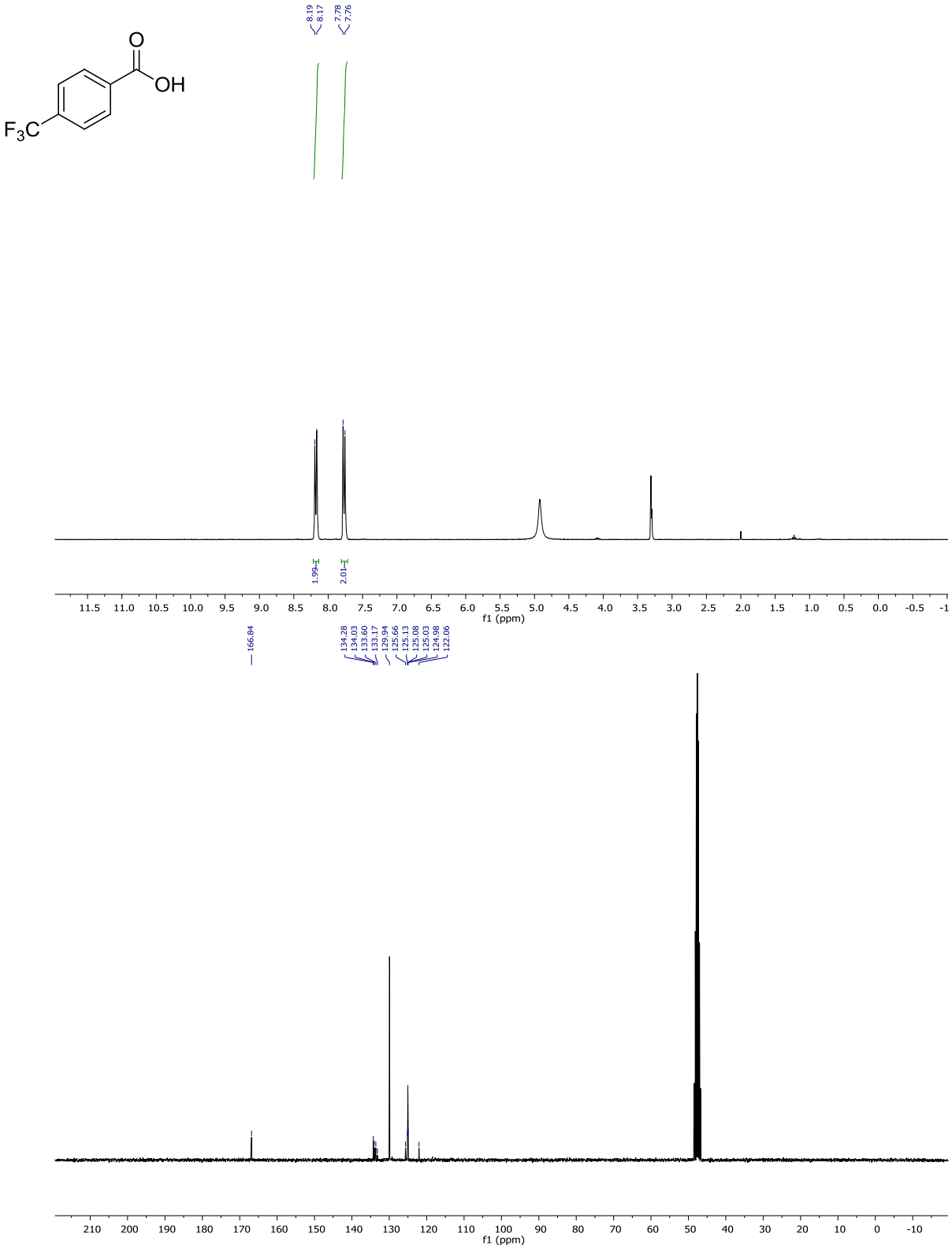
- 4-Ethylbenzoic acid



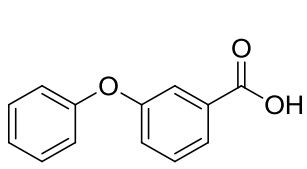
- 4-Methylbenzoic acid

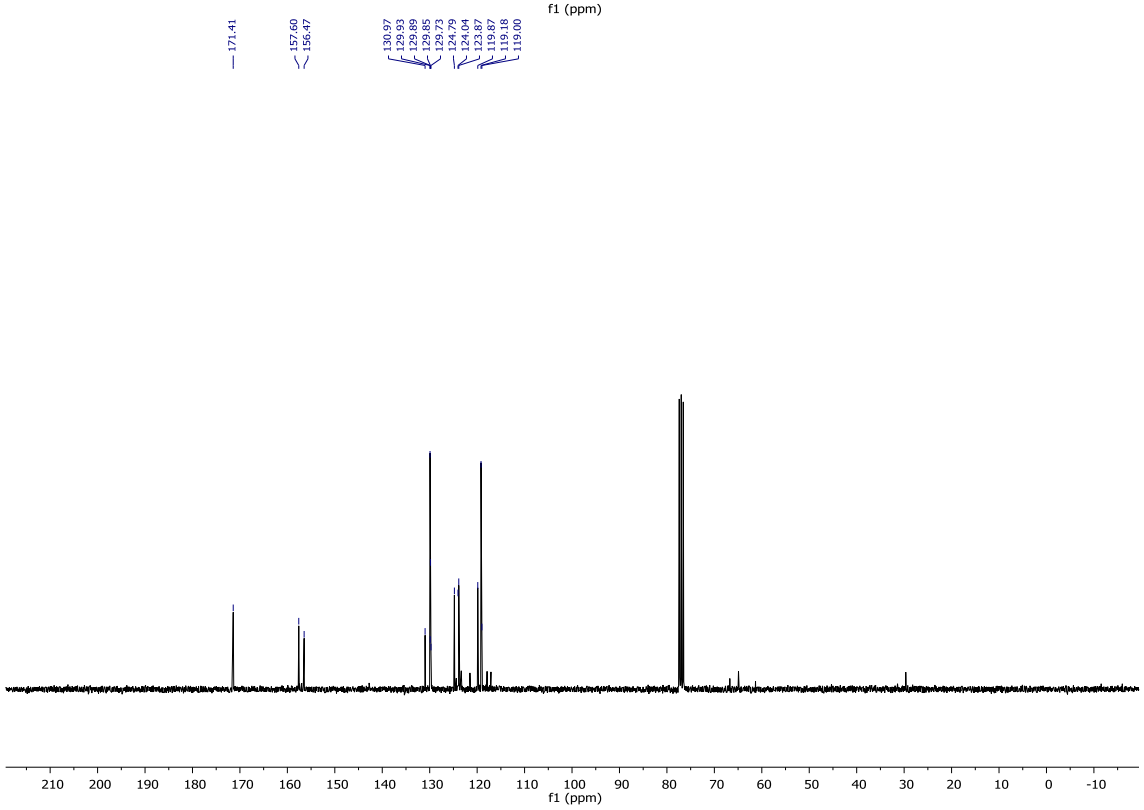


- 4-(Trifluoromethyl)benzoic acid

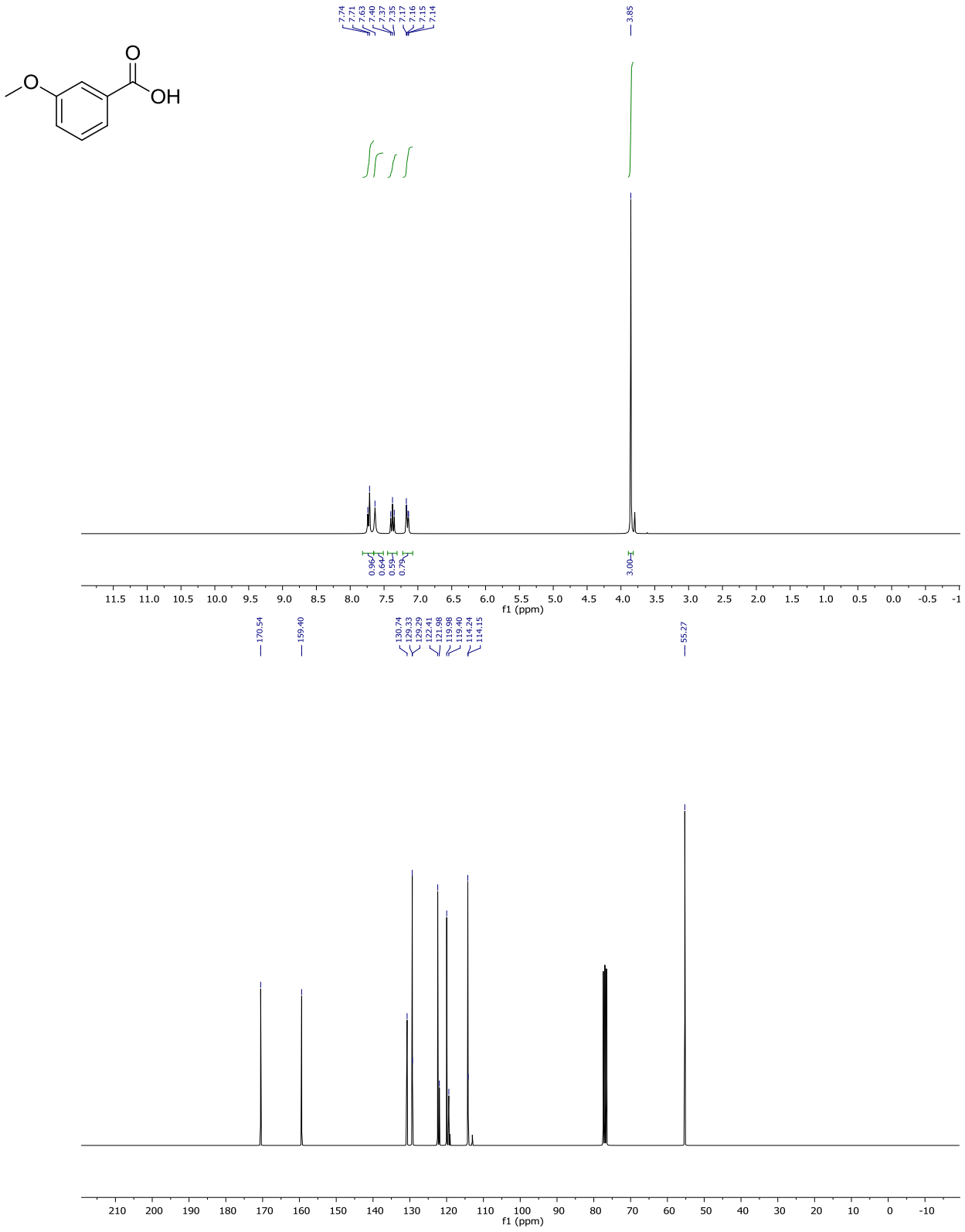


- 3-Phenoxybenzoic acid

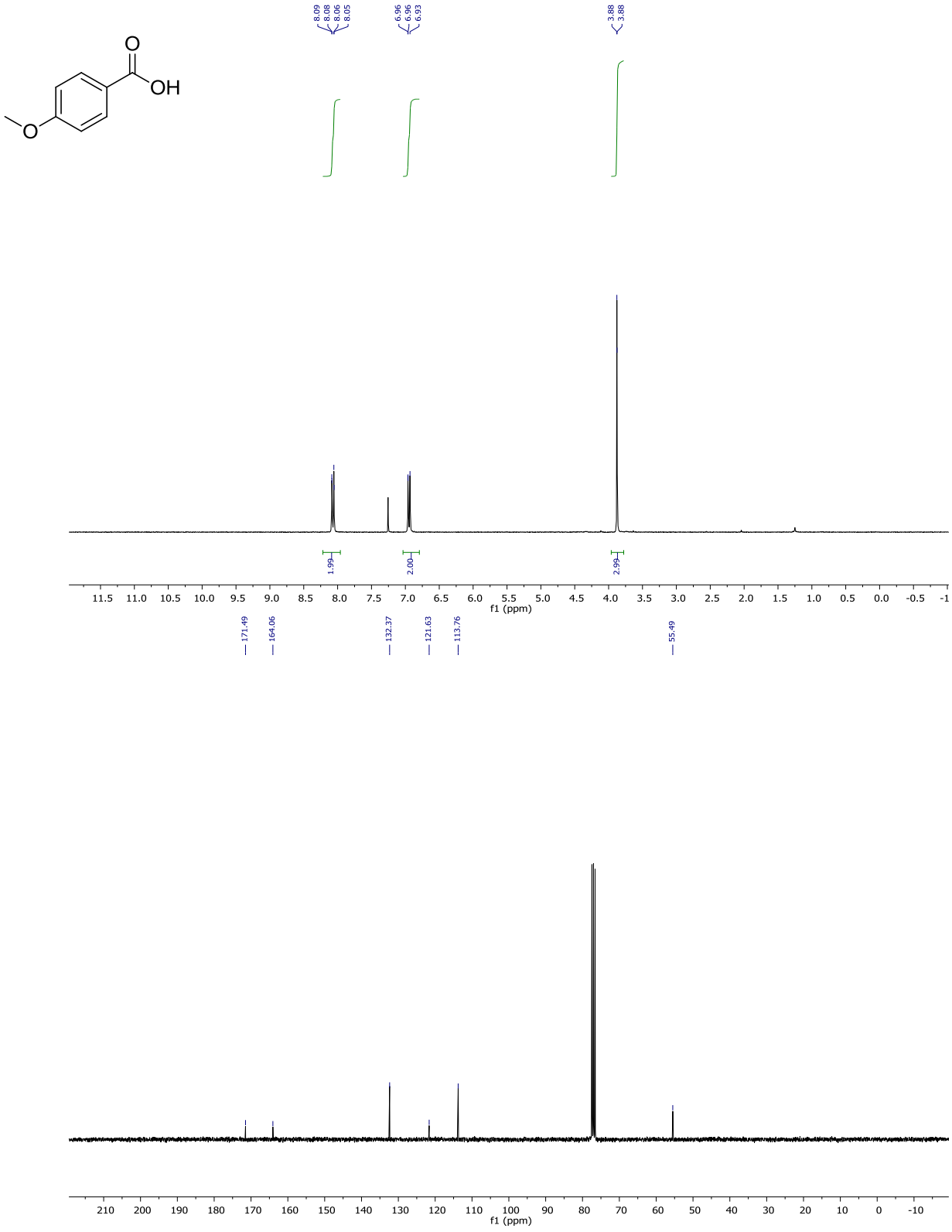




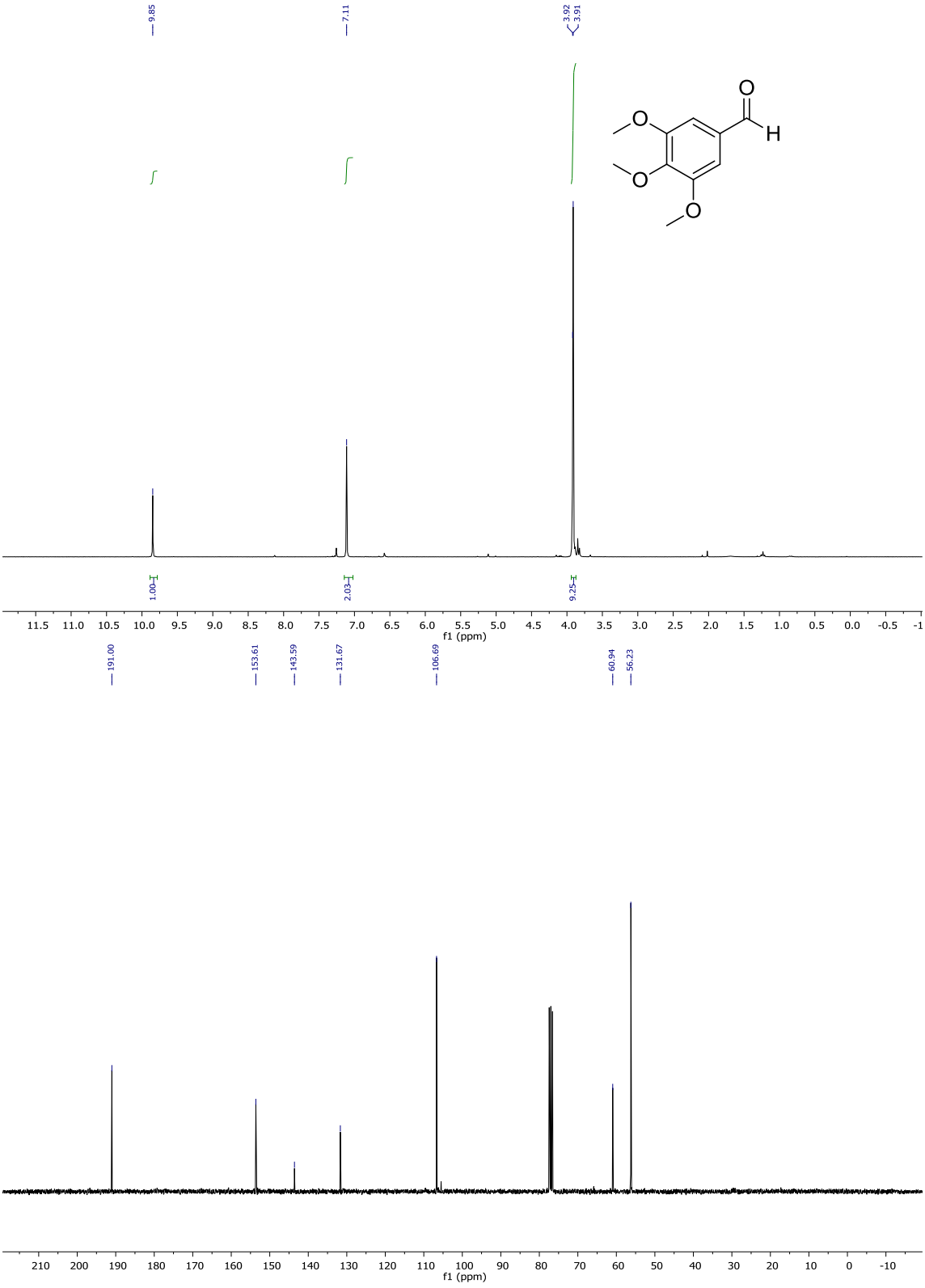
- 3-Methoxybenzoic acid



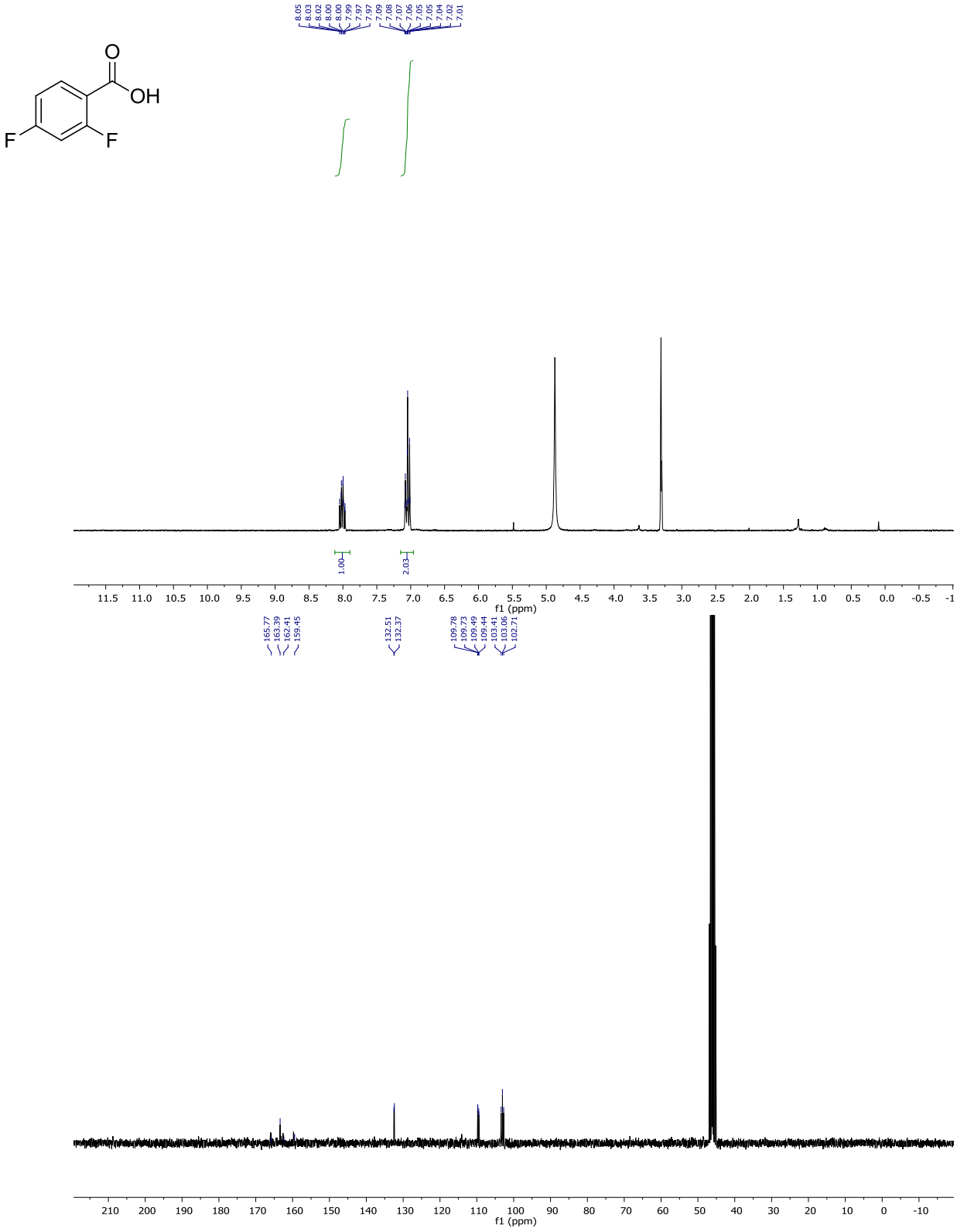
- 4-Methoxybenzoic acid



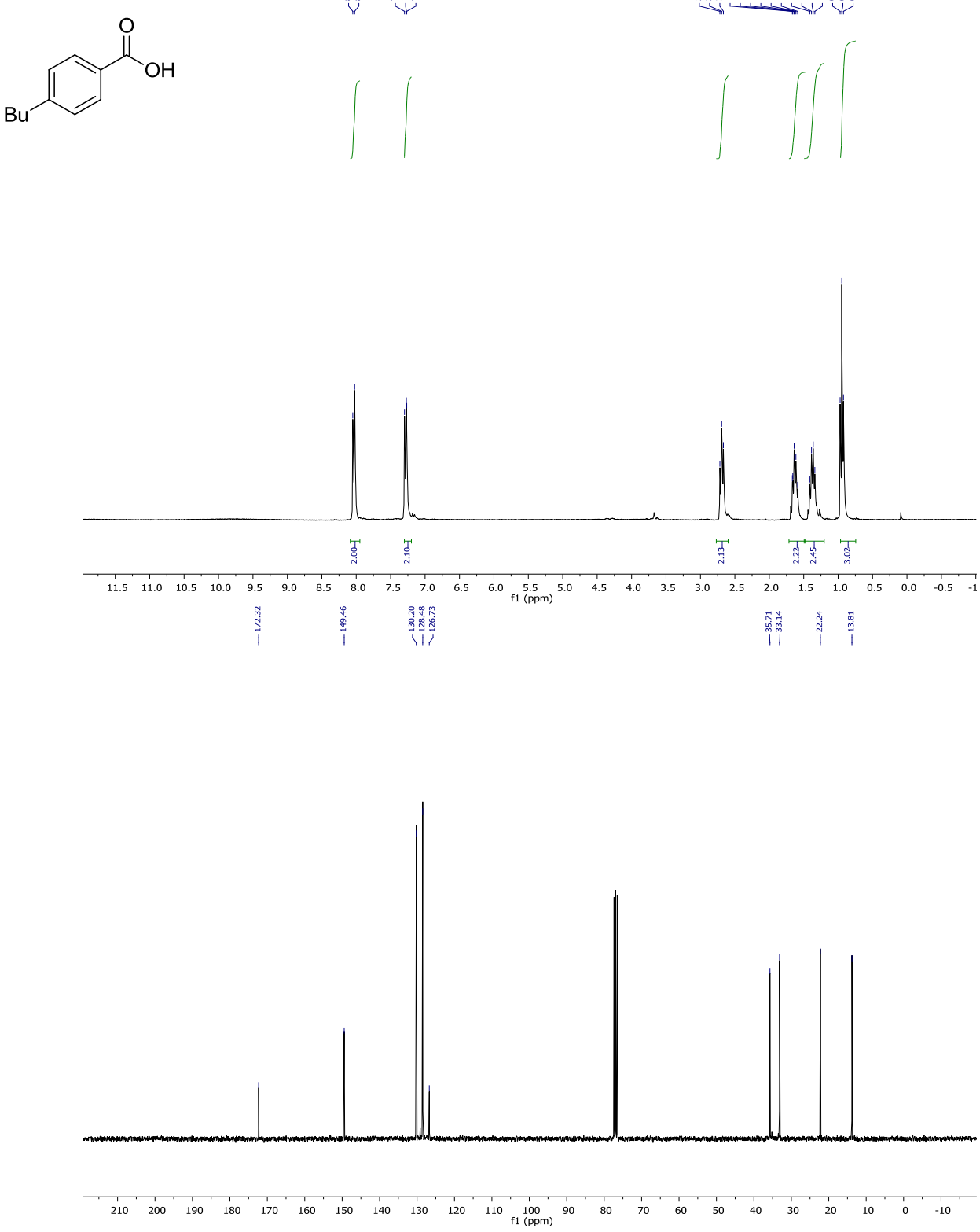
- 3,4,5-Trimethoxybenzaldehyde



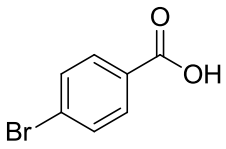
- 2,4-Difluorobenzoic acid



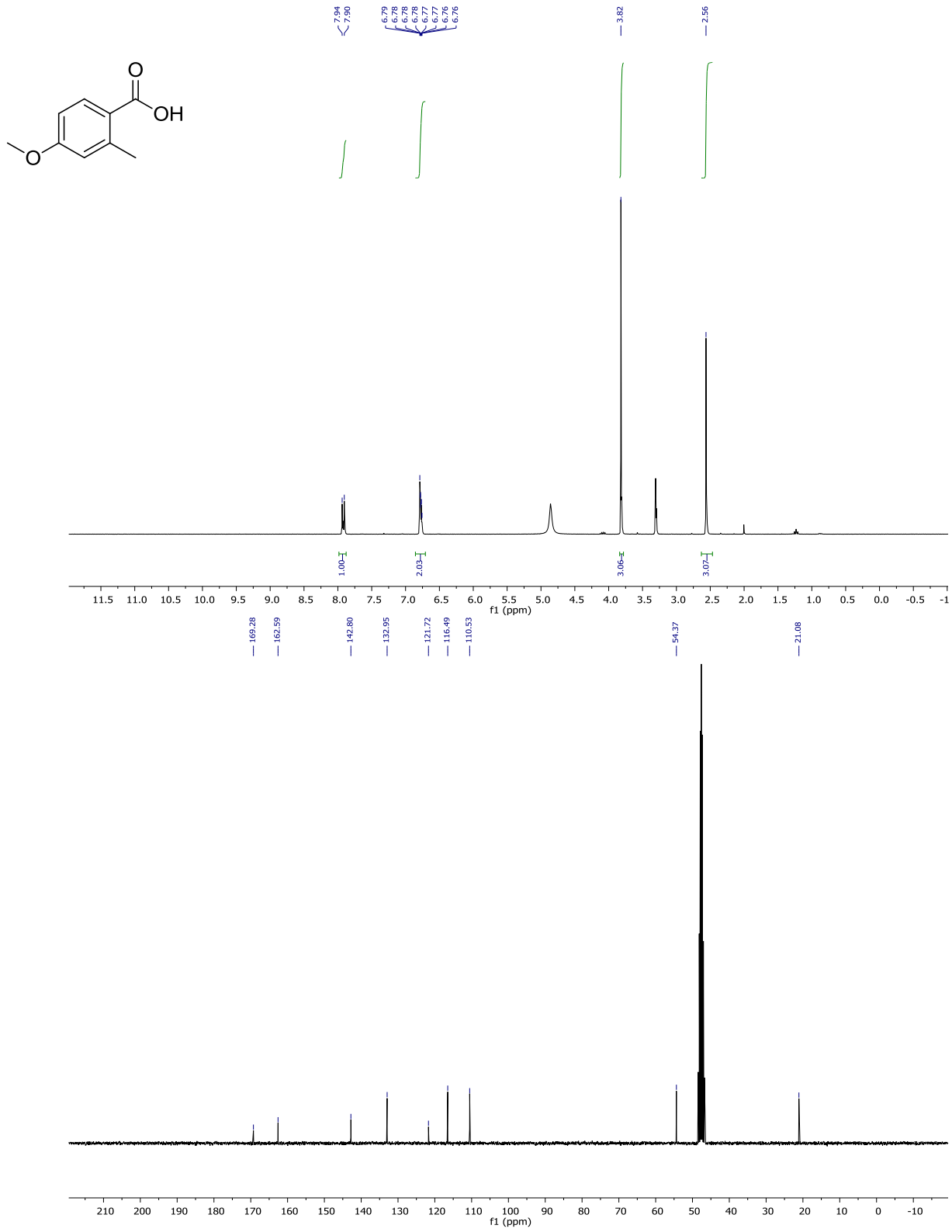
- 4-Butylbenzoic acid



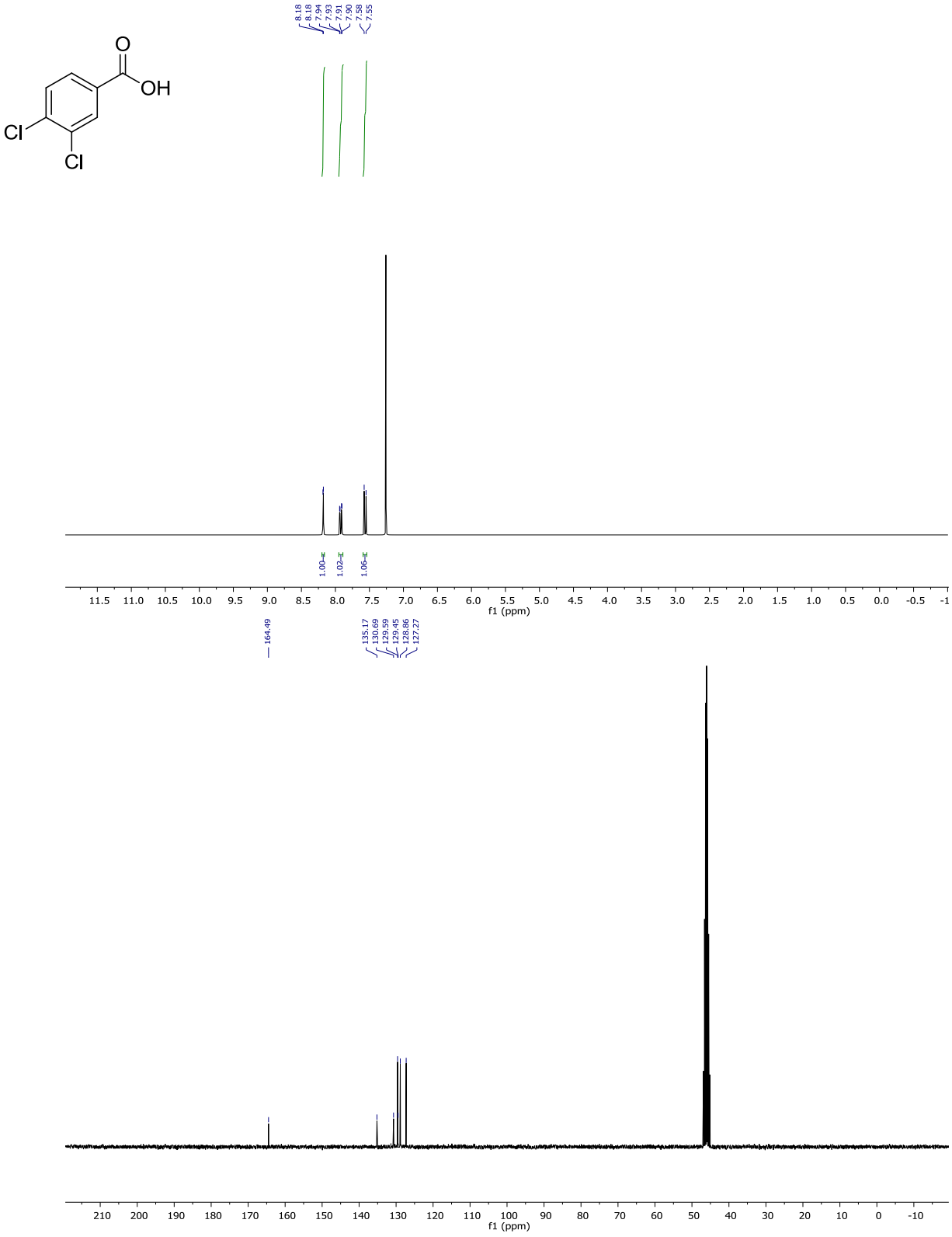
- 4-Bromobenzoic acid



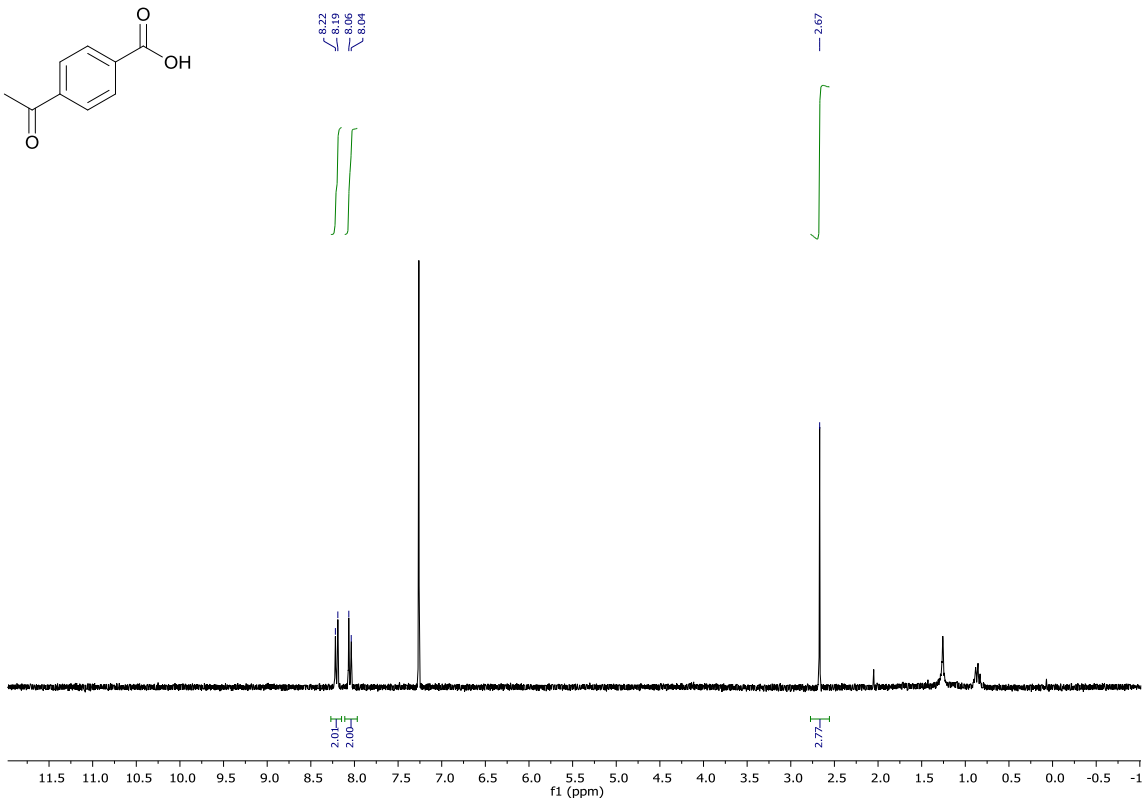
- 4-Methoxy-2-methylbenzoic acid

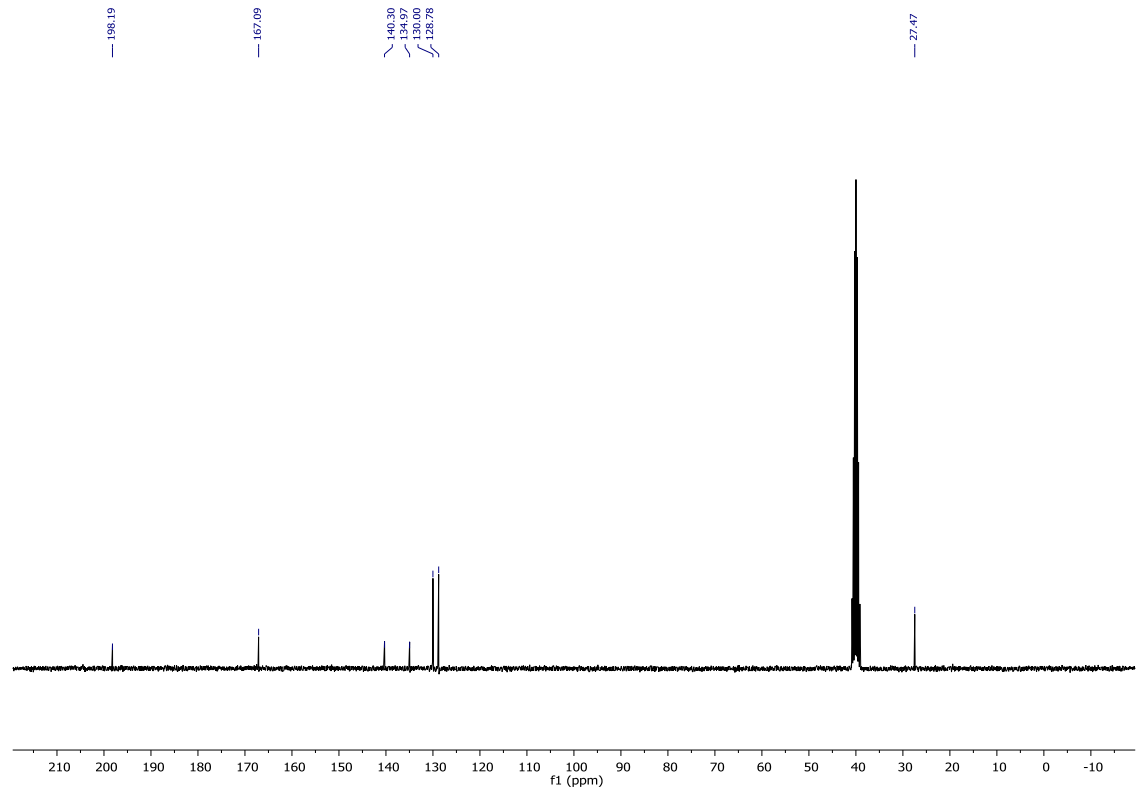


- 3,4-Dichlorobenzoic acid

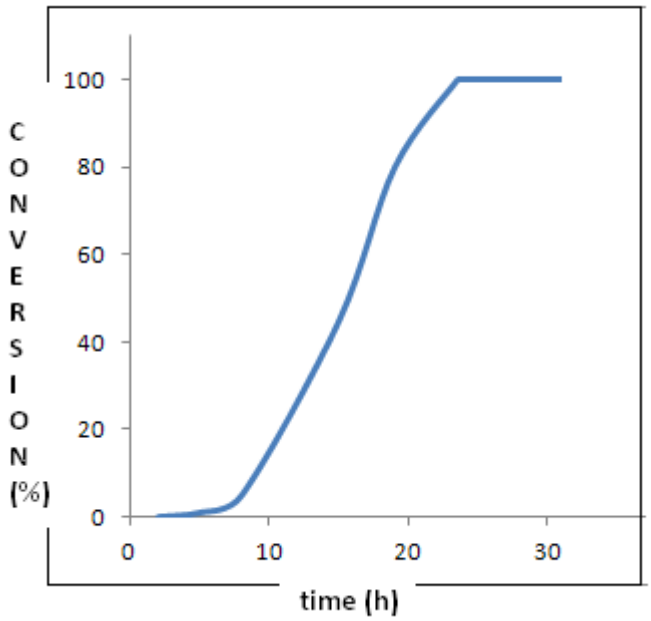


- 4-Acetylbenzoic acid





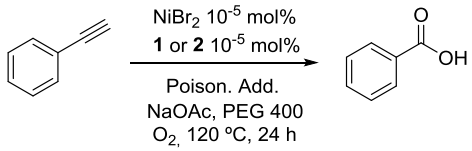
12. Kinetic Plot



Conversion rate (%) *vs* time (h) in the oxidative cleavage of phenylacetylene

13. Summary of poisoning experiments

Table S2. Summary of poisoning experiments



Entry	Poisoning additive	Conv. **1** (%)[a]	Conv. **2** (%)[a]
1	Hg(0)	99	99
2	CS_2 (0.5eqv)	89	87
3	CS_2 (2eqv)	88	85
4	PPh_3 (0.03eqv)	90	89
5	PPh_3 (0.3eqv)	90	89
6	PPh_3 (4eqv)	90	88
7	py (150equiv)[b]	96	95
8	PVPy (300equiv)[c]	98	99

[a] Conversion rate measured by ^{1}H-NMR. 4-Chloroanisole was used as internal standard. [b] py: Pyridine [c] PVPy: Polyvinylpyridine.

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