Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Metal-Free Oxidative Cleavage of C-C bond in *α*-Hydroxy-*β*-oxophosphonates

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1. General Information.

All chemicals were obtained from Sigma-Aldrich Company and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical shifts of protons reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvents (CDCl3: 7.26 ppm). ^{13}C-NMR spectra were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) down field from tetra methyl silane and are referenced to the carbon resonance of the solvent (CDCl3:77.0 ppm). Mass spectra of compounds were recorded with ESI-MS.

2. Experimental procedures

Synthesis of *α*-Hydroxy-*β*-oxo phosphonates (HOP).[1]

α-Hydroxy-*β*-oxo phosphonates were synthesized by the standard reported protocol.

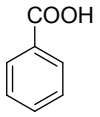
Synthesis of Diethyl (2-oxo-2-phenylethyl)phosphonate (4).[2]

Diethyl (2-oxo-2-phenylethyl)phosphonate (**4**) was synthesized by the reported protocol

Procedure for oxidative C-C bond cleavage in HOP to acids. Reaction vessel charged with 1 mmol of *α*-hydroxy-*β*-oxo phosphonate **1** and was added 2 mL of toluene, 2 mmol of TBHP. The reaction mixture allowed stirring for 4 days at room temperature. After completion of the reaction, crude mass was extracted with ethyl acetate. Then it was purified by column chromatography using silica gel (# 100-200 mesh size) and eluted with ethyl acetate and hexane (1:4) to produced desire product **2** in good yields (68-95 %).

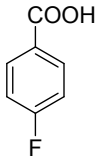
3. Spectral data of acid compounds.

Benzoicacid (**2a**).[3]



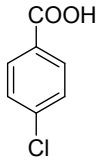
^{1}H NMR (400 MHz, MeOD) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, MeOD) δ 170.06, 134.11, 131.86, 130.80, 129.50; ESI-MS: 145.1 (M^+ + Na).

4-Fluorobenzoicacid (**2b**).[4]



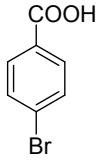
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.2, 5.8 Hz, 2H), 7.15 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, MeOD) δ 168.77, 168.45, 165.94, 133.53, 133.43, 128.42, 116.51, 116.29; ESI-MS: 139.0 (M^+ -1).

4-Chlorobenzoicacid (**2c**).**[4]**



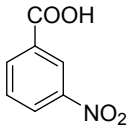
^{1}H NMR (400 MHz, CDCl3) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, MeOD) δ 168.76, 140.29, 132.35, 130.73, 129.76; ESI-MS: 155.2 (M^+ -1).

4-Bromobenzoicacid (**2d**).[3]



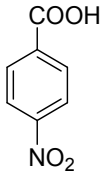
^{1}H NMR (400 MHz, MeOD) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, MeOD) δ 168.89, 132.84, 132.50, 131.15, 128.81; ESI-MS: 199.2 (M^+ -1).

3-Nitrobenzoicacid (**2e**).[3]



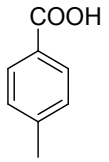
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.53 – 8.43 (m, 2H), 7.73 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, MeOD) δ 165.95, 148.25, 135.02, 132.47, 129.67, 126.89, 123.89; ESI-MS: 166.1 (M^+ -1).

4-Nitrobenzoicacid (**2f**).[3]



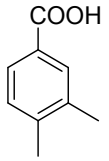
^{1}H NMR (400 MHz, MeOD) δ 8.23 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (126 MHz, MeOD) δ 167.63, 151.96, 137.63, 131.97, 124.57; ESI-MS: 166.2 (M^+ -1).

4-Methylbenzoicacid (**2g**).[3]



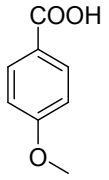
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.22, 144.64, 130.27, 129.22, 126.60, 21.76; ESI-MS: 137.4 (M^+ + 1).

3,4-Dimethylbenzoicacid (**2h**).[5]



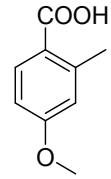
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.57, 143.41, 136.92, 131.22, 129.81, 127.87, 126.85, 20.18, 19.74; ESI-MS: 148.8 (M^+ -1).

4-Methoxybenzoicacid (**2i**).[3]



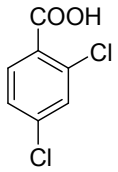
^{1}H NMR (500 MHz, MeOD) δ 7.87 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (126 MHz, MeOD) δ 169.83, 165.09, 132.85, 124.01, 114.69, 55.98; ESI-MS: 151.2 (M^+-1).

4-Methoxy-2-methylbenzoic acid (**2j**).[6]



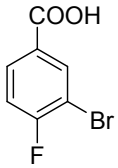
^{1}H NMR (400 MHz, DMSO) δ 7.84 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 168.00, 161.71, 142.15, 132.78, 122.02, 116.69, 111.11, 55.22, 21.86; ESI-MS: 167.1 (M^++1).

2,4-Dichlorobenzoic acid (**2k**).[4]



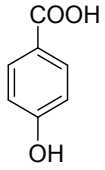
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 1.9 Hz, 1H), 7.35 (dd, J = 8.5, 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27, 139.56, 136.01, 133.50, 131.46, 127.18, 126.64; ESI-MS: 189.2 (M^+ -1).

3-Bromo-4-Fluorobenzoicacid (**2l**).[7]



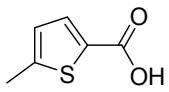
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 6.6, 2.1 Hz, 1H), 8.07 (ddd, *J* = 8.6, 4.7, 2.1 Hz, 1H), 7.23 (dd, *J* = 16.5, 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.20, 163.97, 161.43, 136.11, 136.09, 131.55, 131.46, 126.77, 126.73, 116.82, 116.59, 109.68, 109.47; ESI-MS: 216.8 (M^+-1).

4-Hydroxybenzoic acid (**2m**).[8]



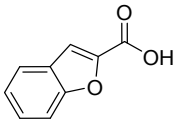
^{1}H NMR (400 MHz, DMSO) δ 10.28 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO) δ 167.66, 162.05, 132.01, 121.79, 115.59; ESI-MS: 137.0 (M^+-1).

5-Methylthiophene-2-carboxylic acid (**2n**).[9]



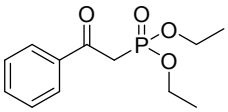
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 3.6 Hz, 1H), 6.81 (d, *J* = 3.1 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.61, 147.76, 133.41, 128.01, 124.63, 13.78; ESI-MS: 141.0 (M^+-1).

Benzofuran-2-carboxylic acid (**2o**).[9]



1H NMR (500 MHz, MeOD) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 4.2 Hz, 2H), 7.50 – 7.43 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, MeOD) δ 161.09, 155.74, 146.02, 127.33, 127.10, 123.50, 122.64, 113.45, 111.56; ESI-MS: 163.1 (M^++1).

Diethyl (2-oxo-2-phenylethyl)phosphonate (**4**)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.62 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 4.20 – 4.08 (m, 4H), 3.64 (d, *J* = 22.7 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H); ESI-MS: 257.0 (M^++1).

4. References:

1. Battula, S.; Battini, N.; Singh, D.; Ahmed, Q. N. *Org. Biomol. Chem.* **2015**, DOI: 10.1039/c5ob01310k.
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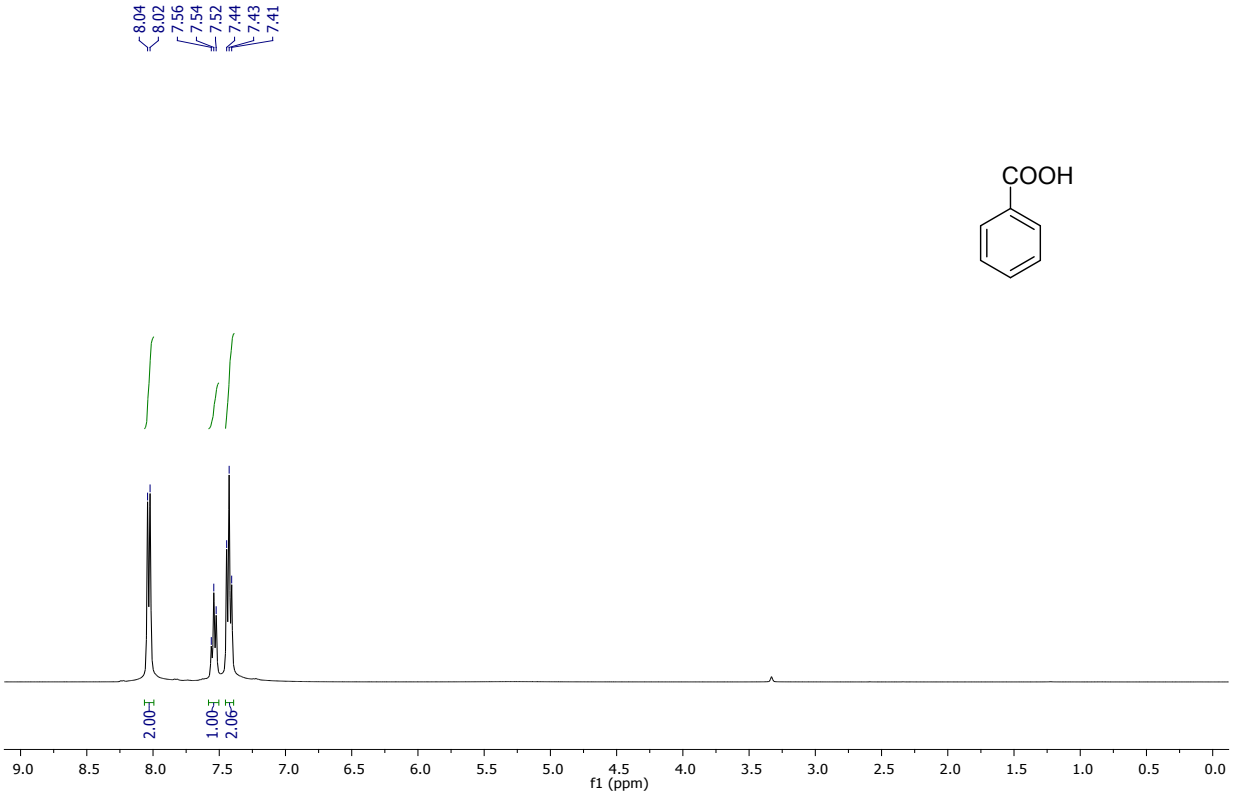
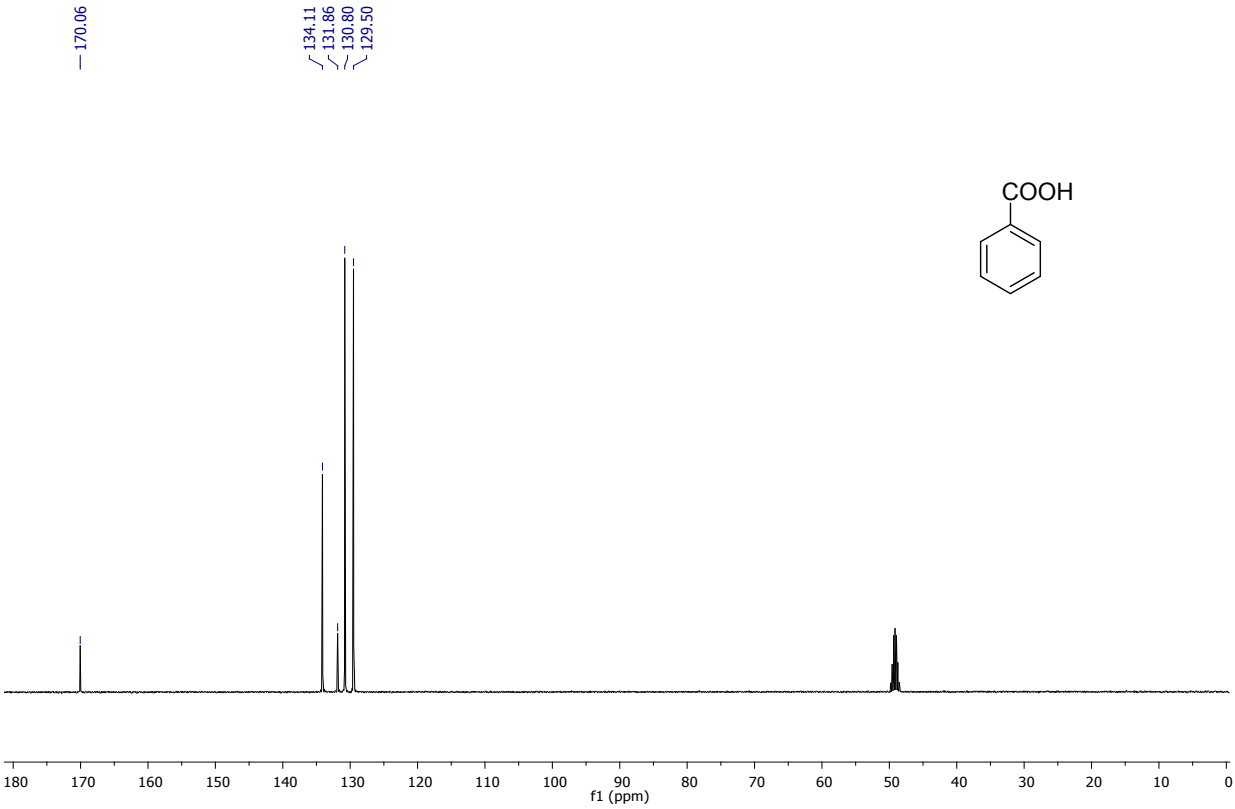
9. Kumar, K. A. A.; Venkateswarlu, V.; Vishwakarma, R. A.; Sawant, S. D., *Synthesis* **2015,** *47*, A–H.

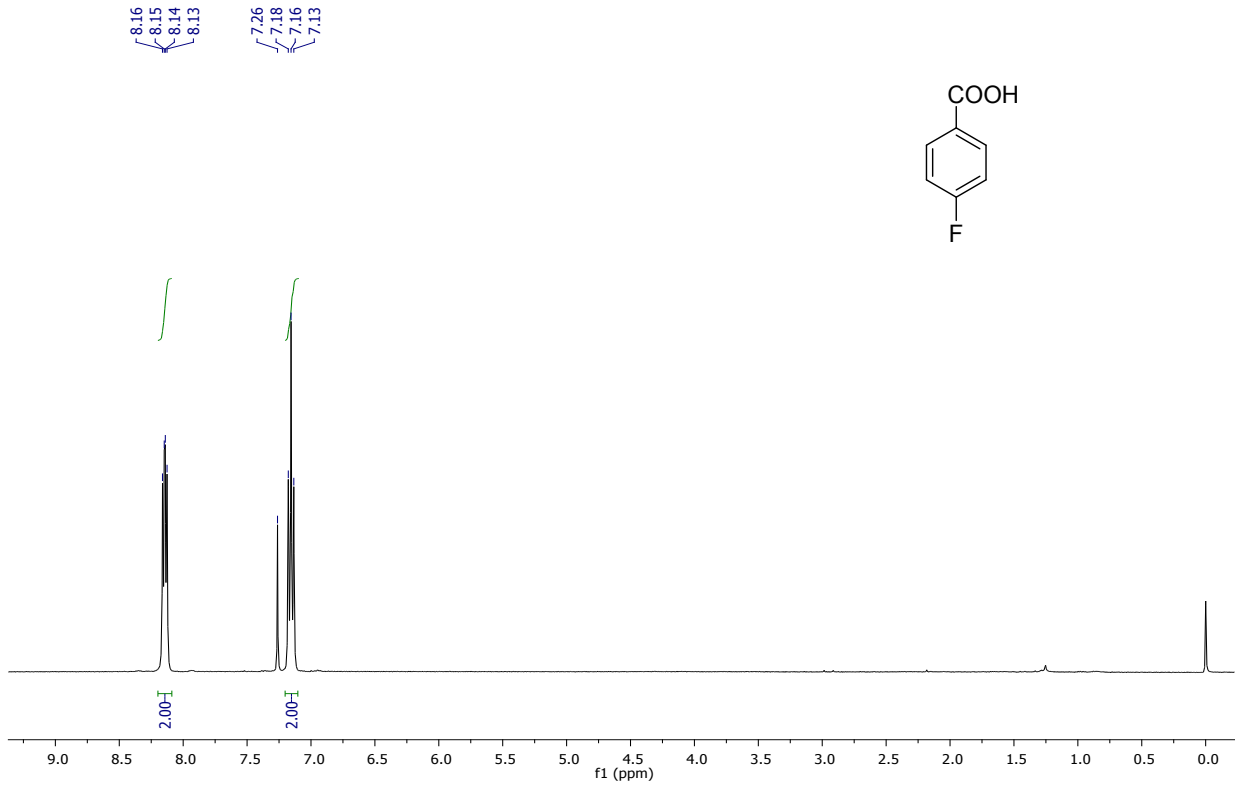
5. NMR spectra of products (2a-2l)

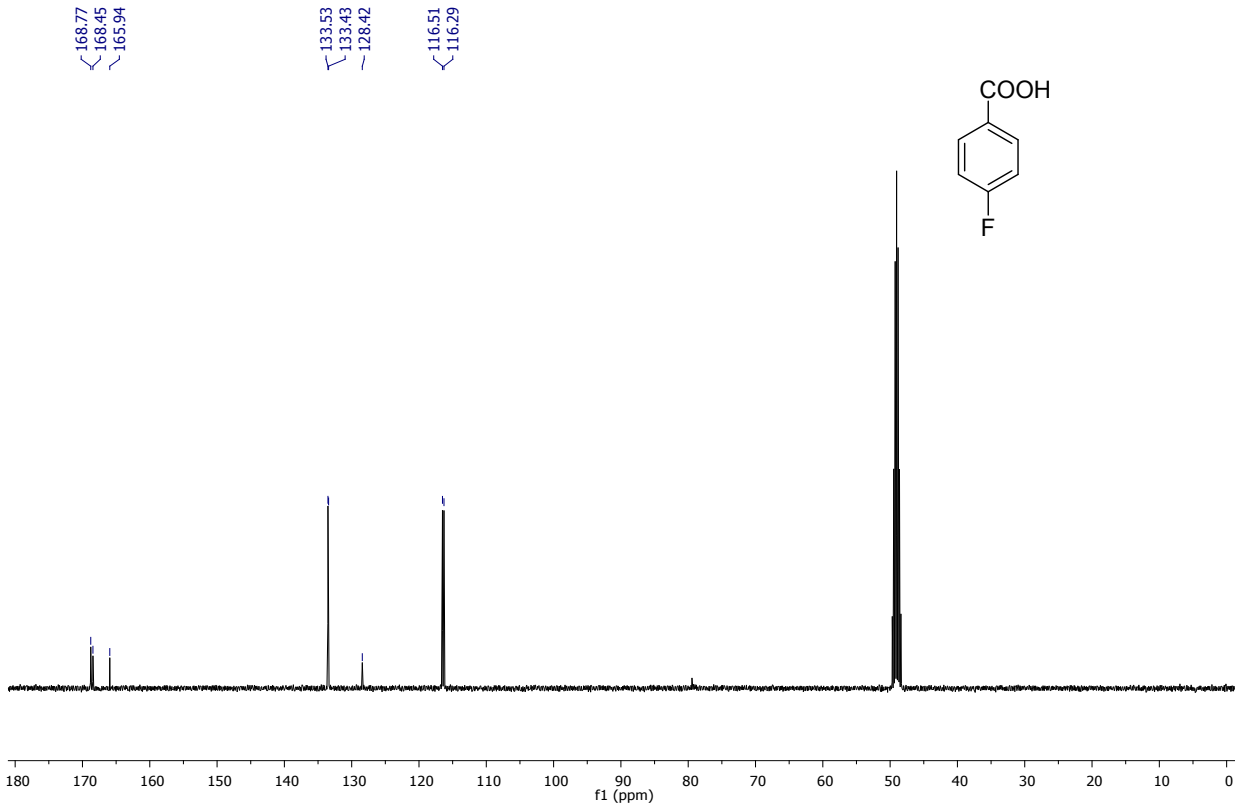
2a. Benzoic acid



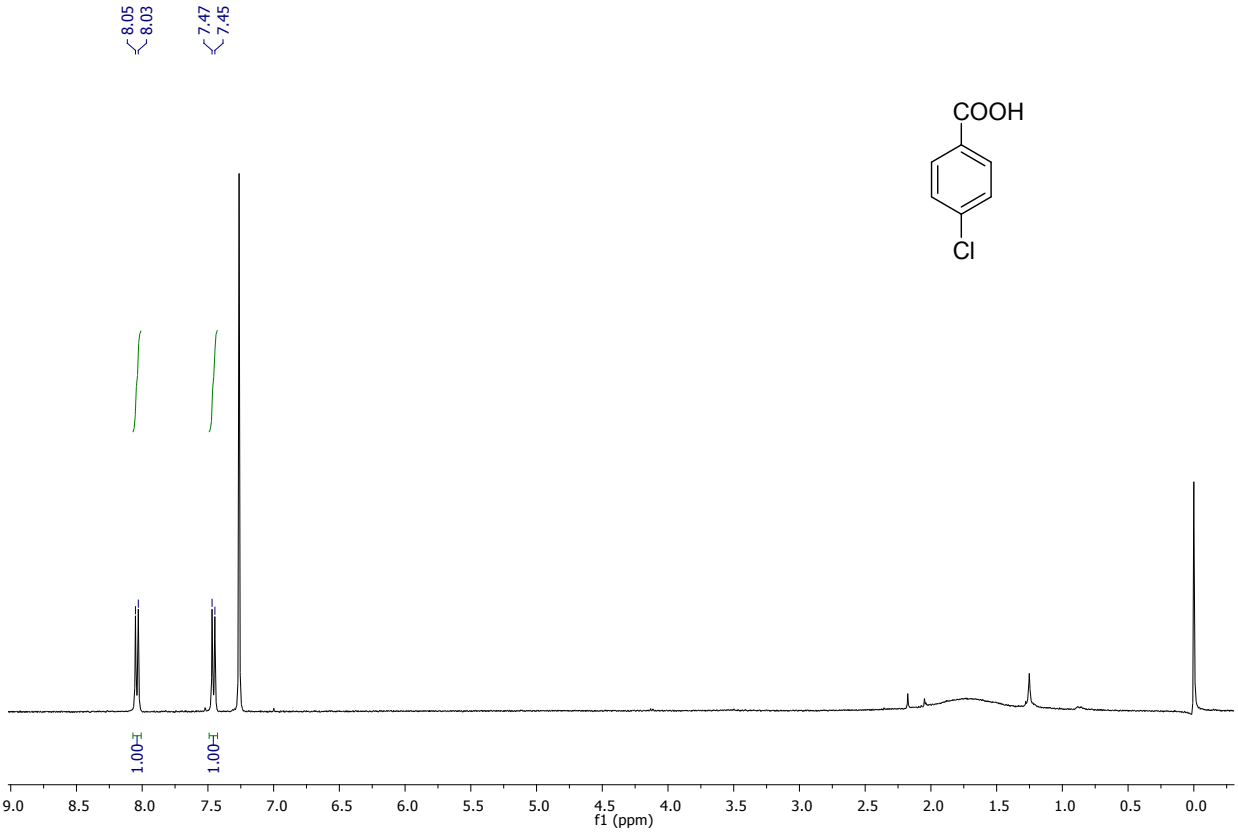


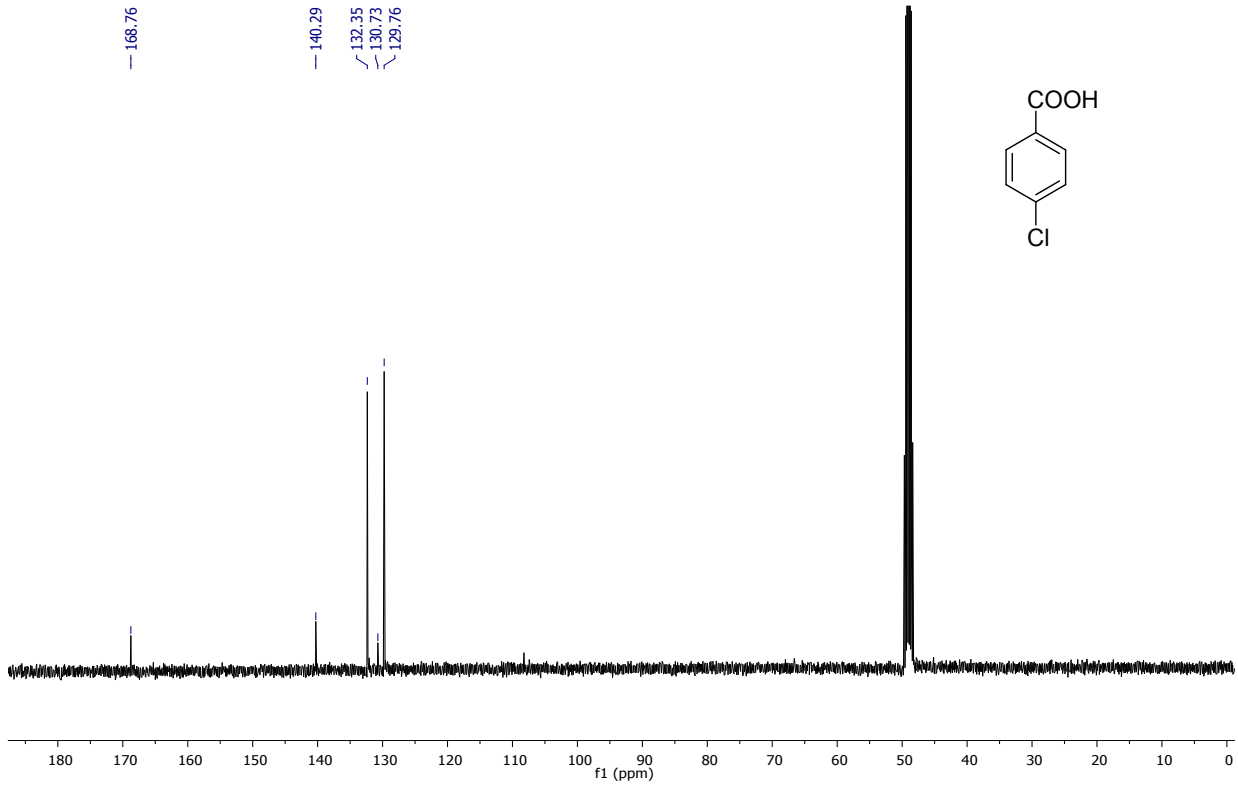
2b. 4-Fluorobenzoic acid



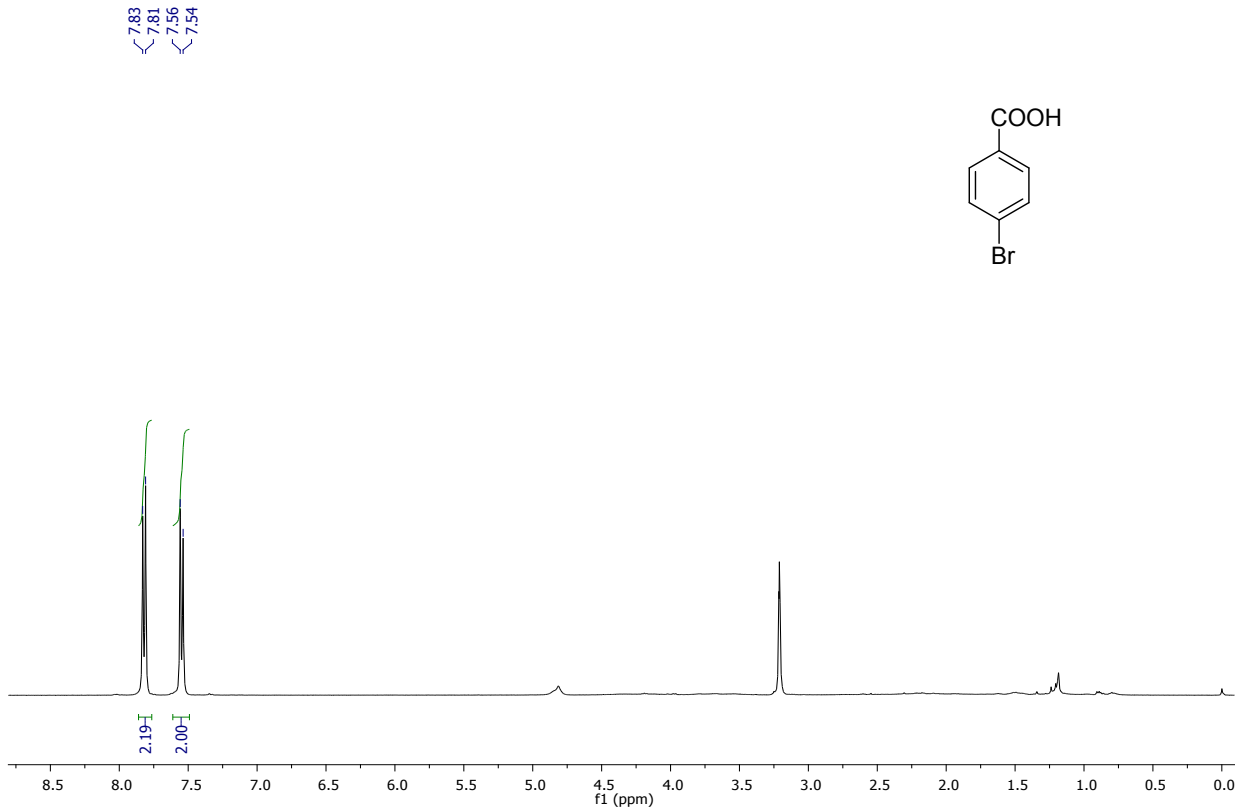


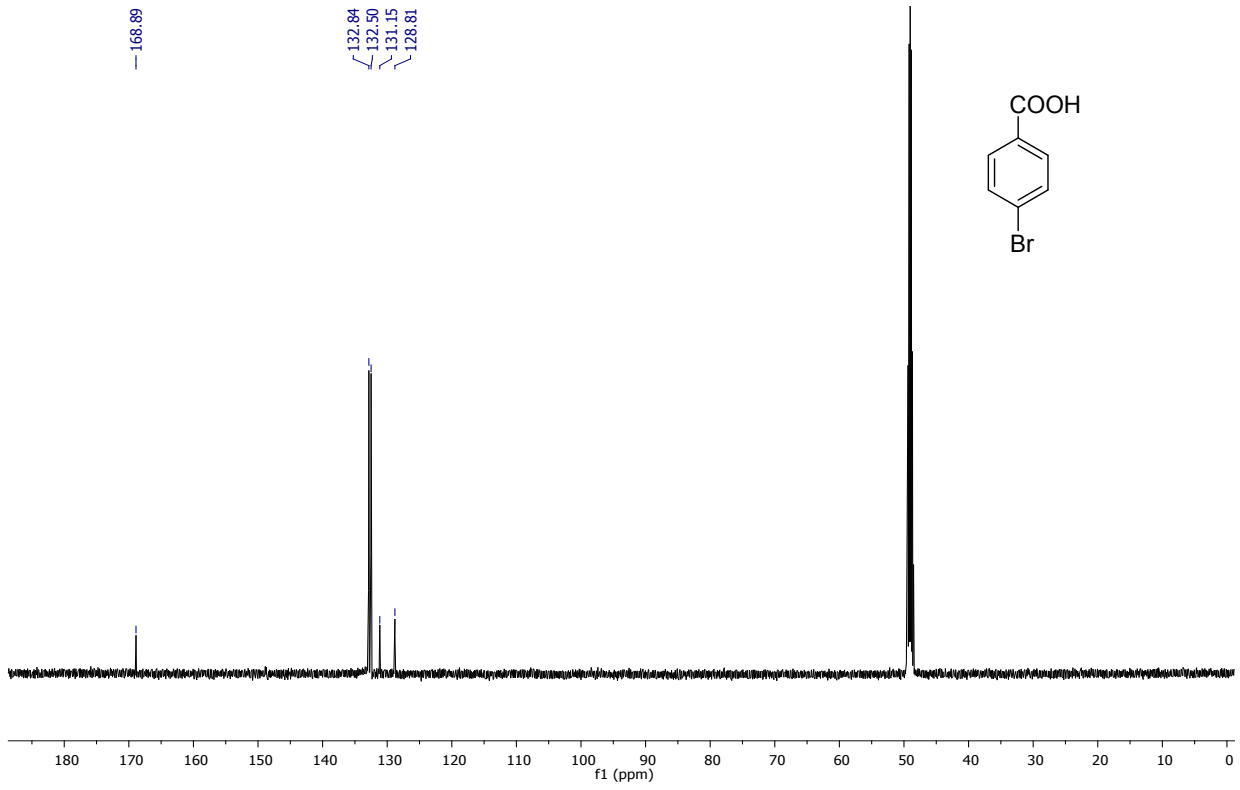
2c. 4-Chlorobenzoic acid



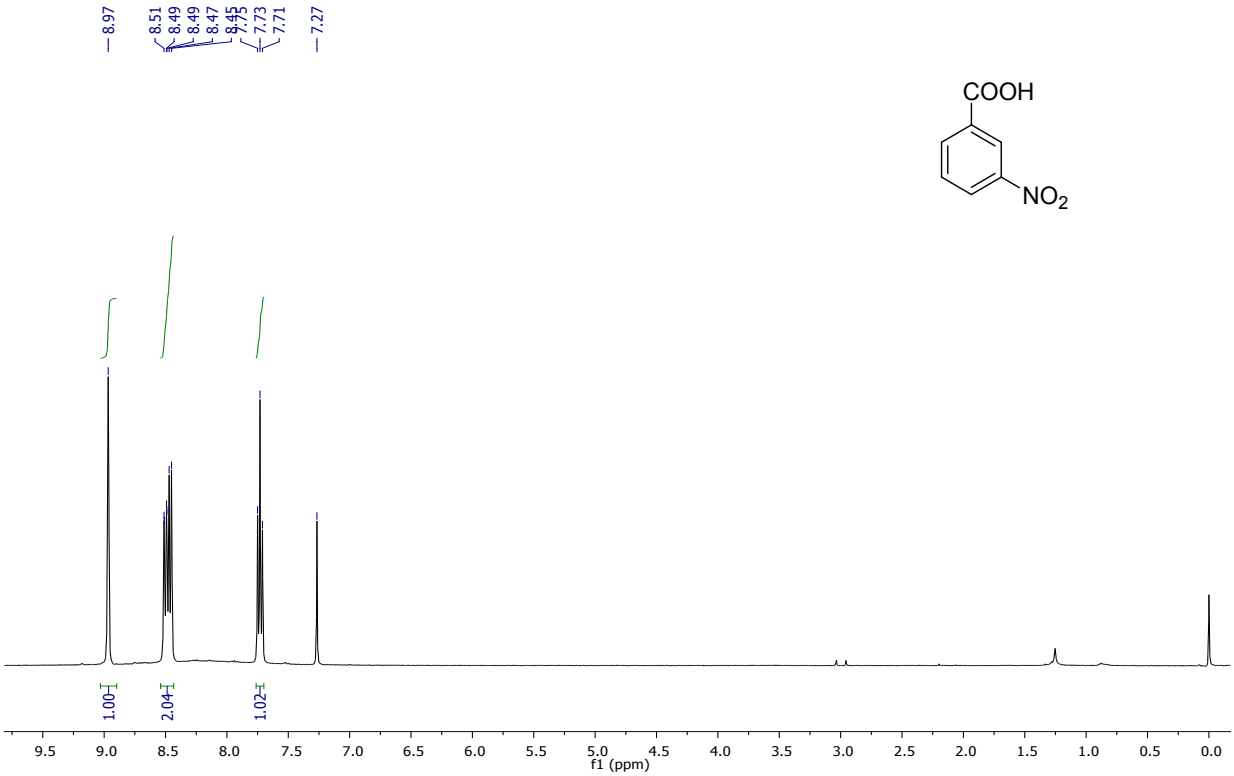


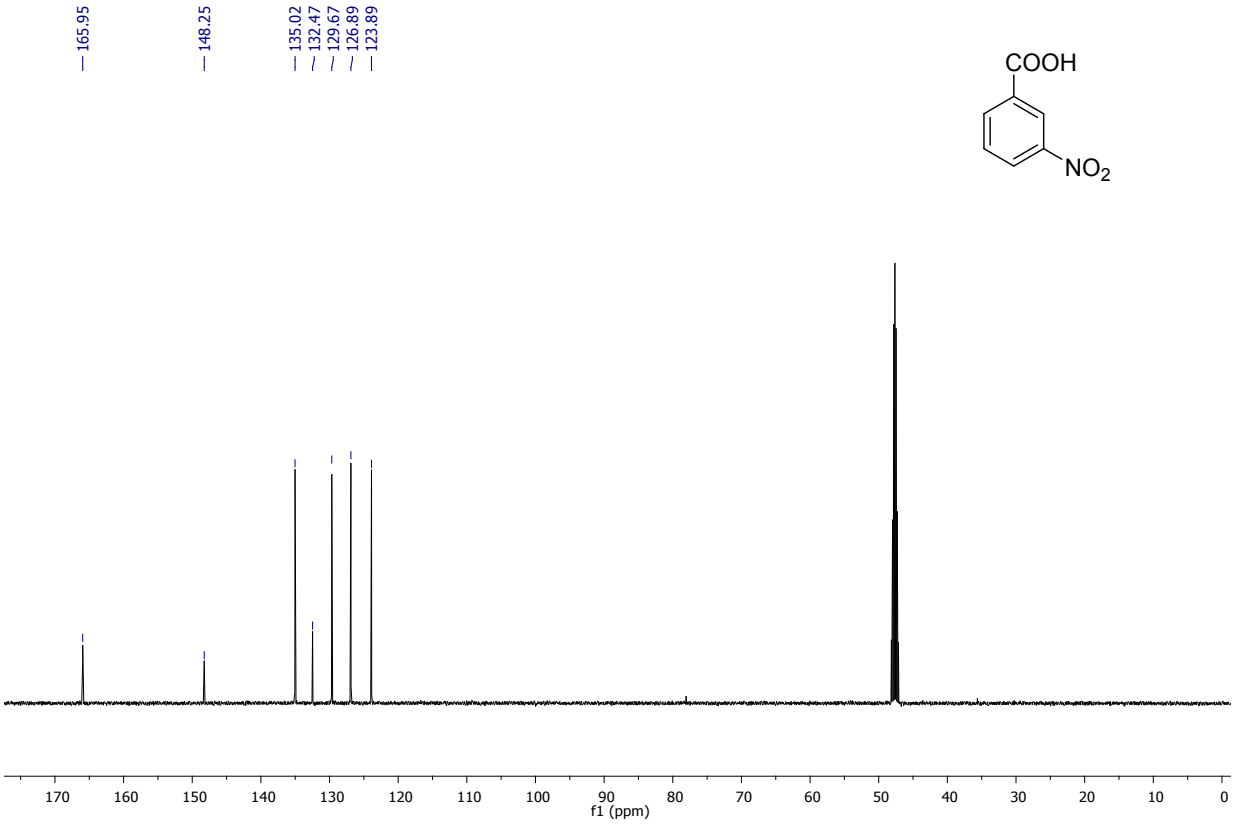
2d. 4-Bromobenzoic acid



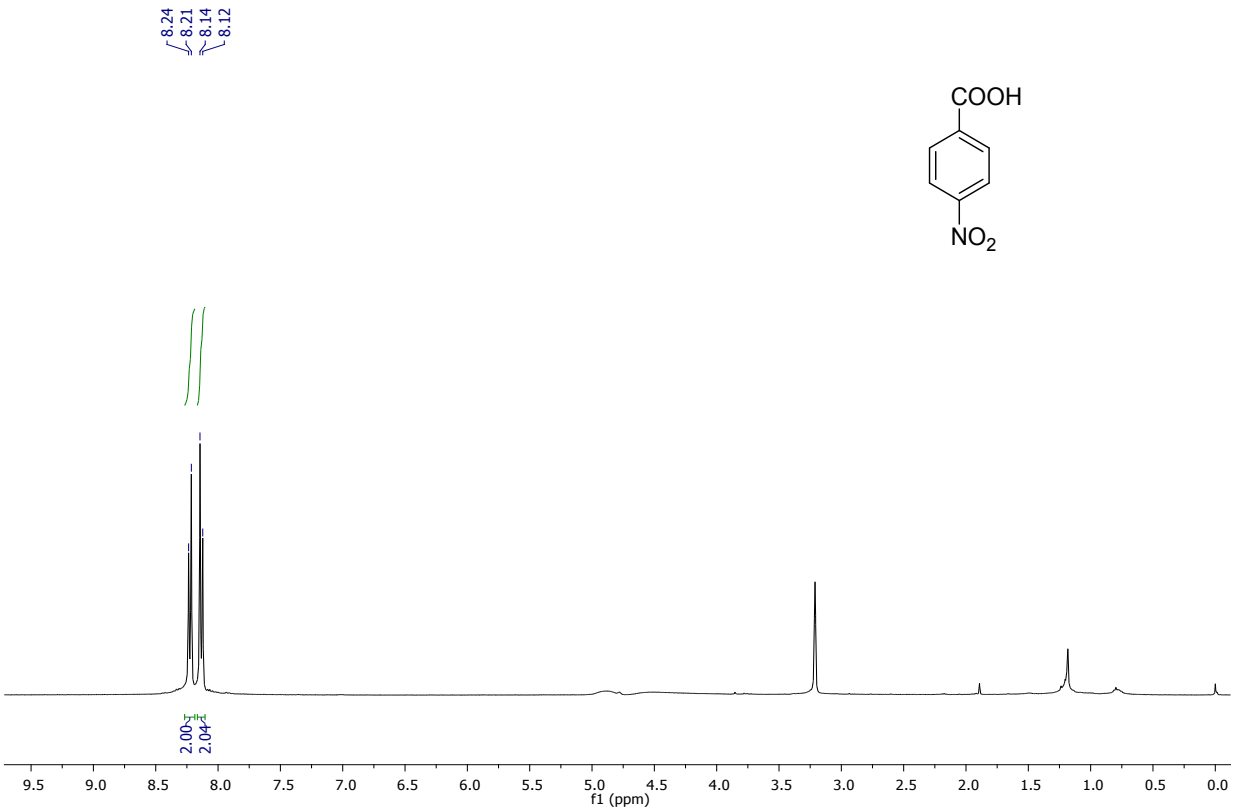


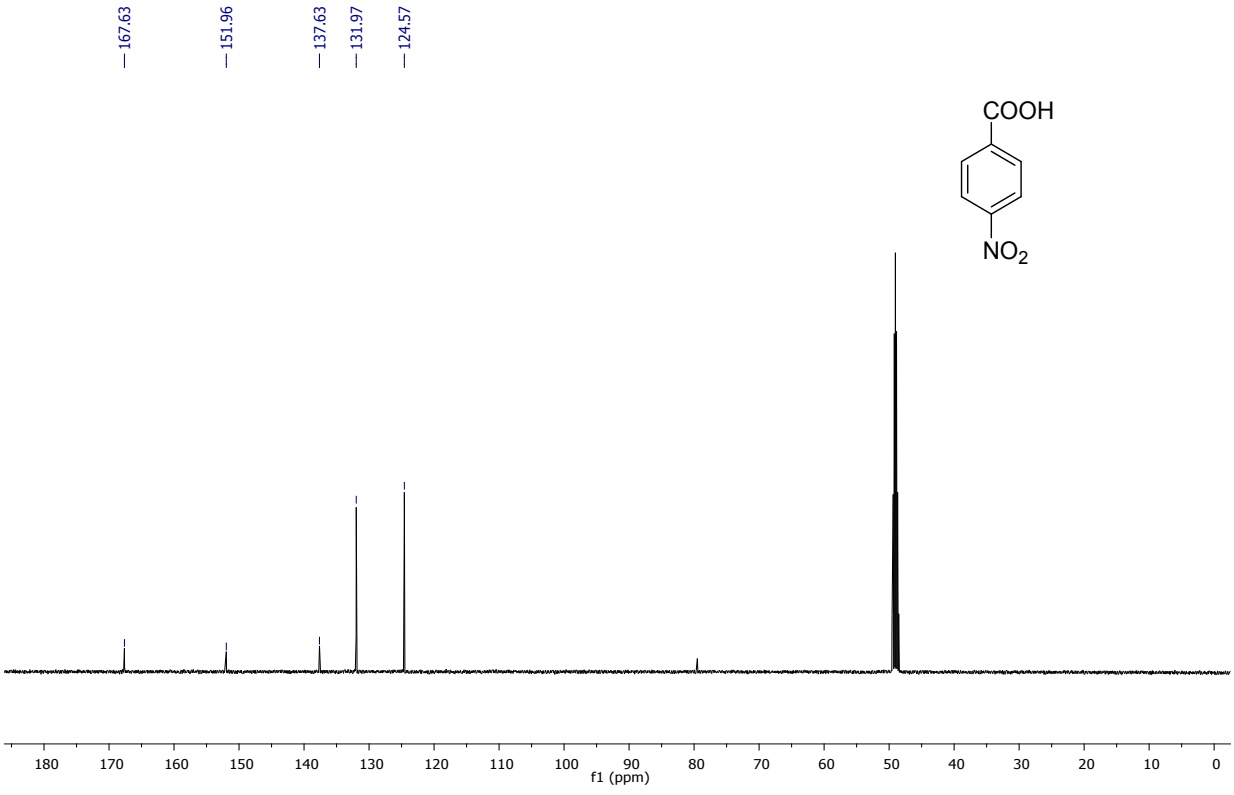
2e. 3-Nitrobenzoic acid



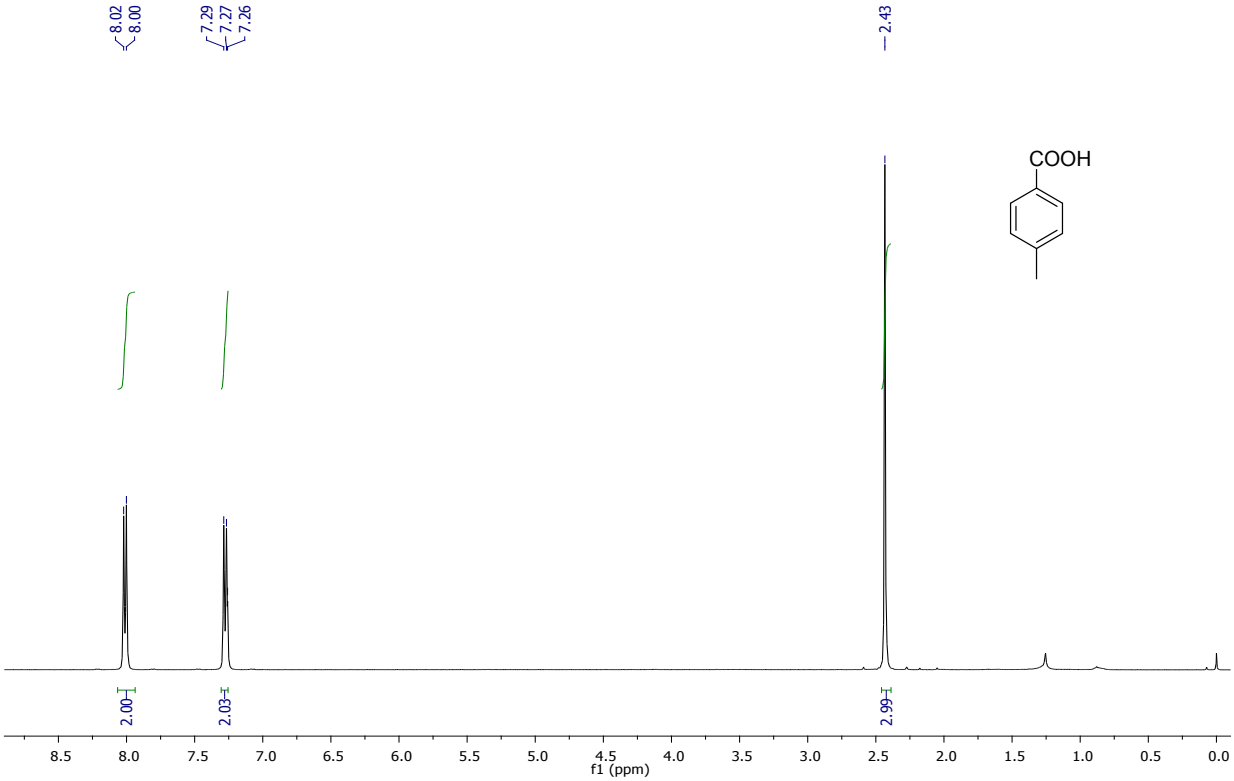


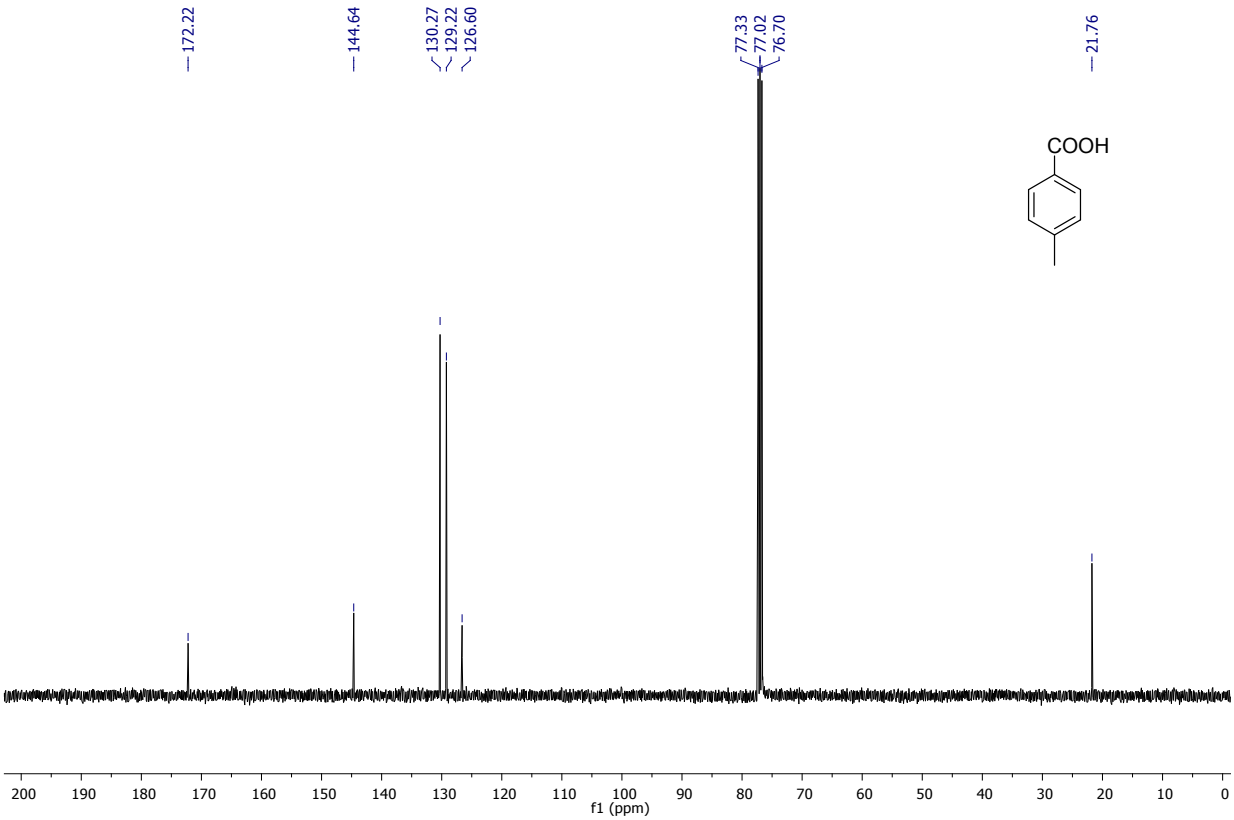
2f. 4-Nitrobenzoic acid



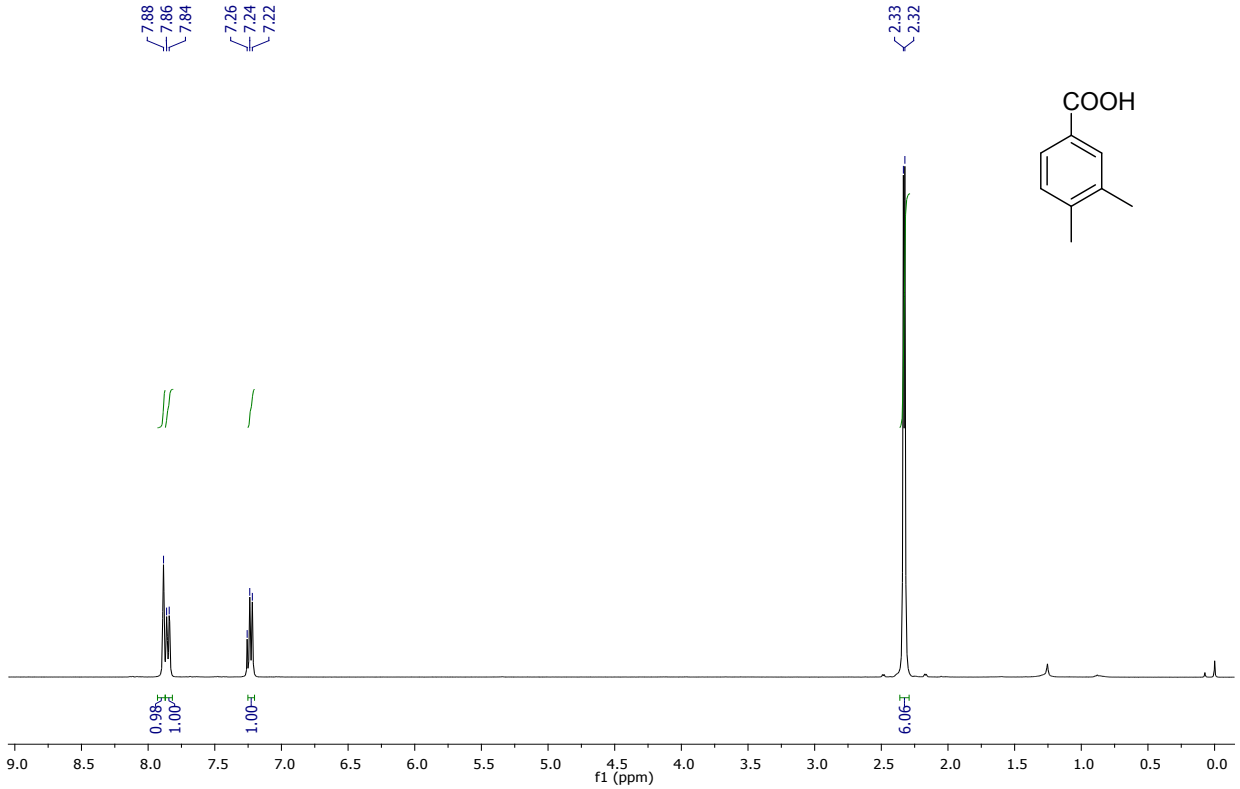


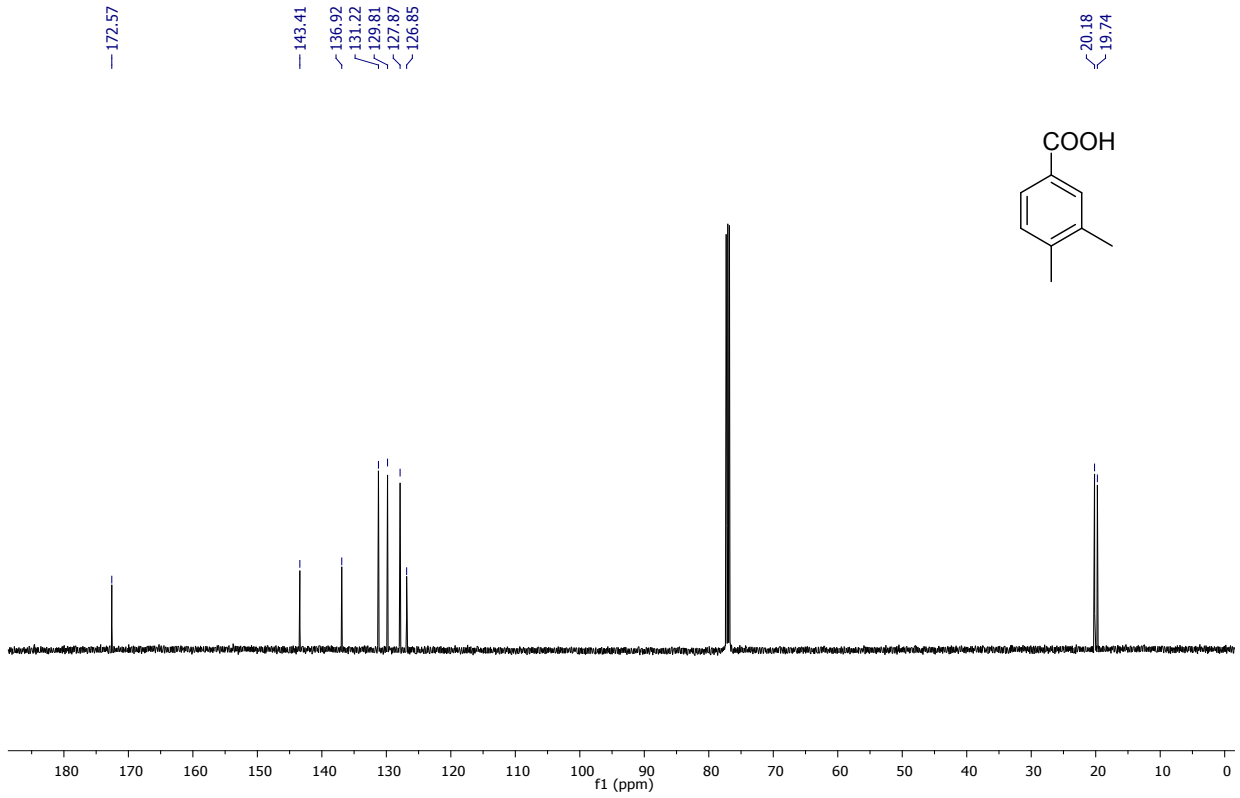
2g. 4-Methylbenzoic acid



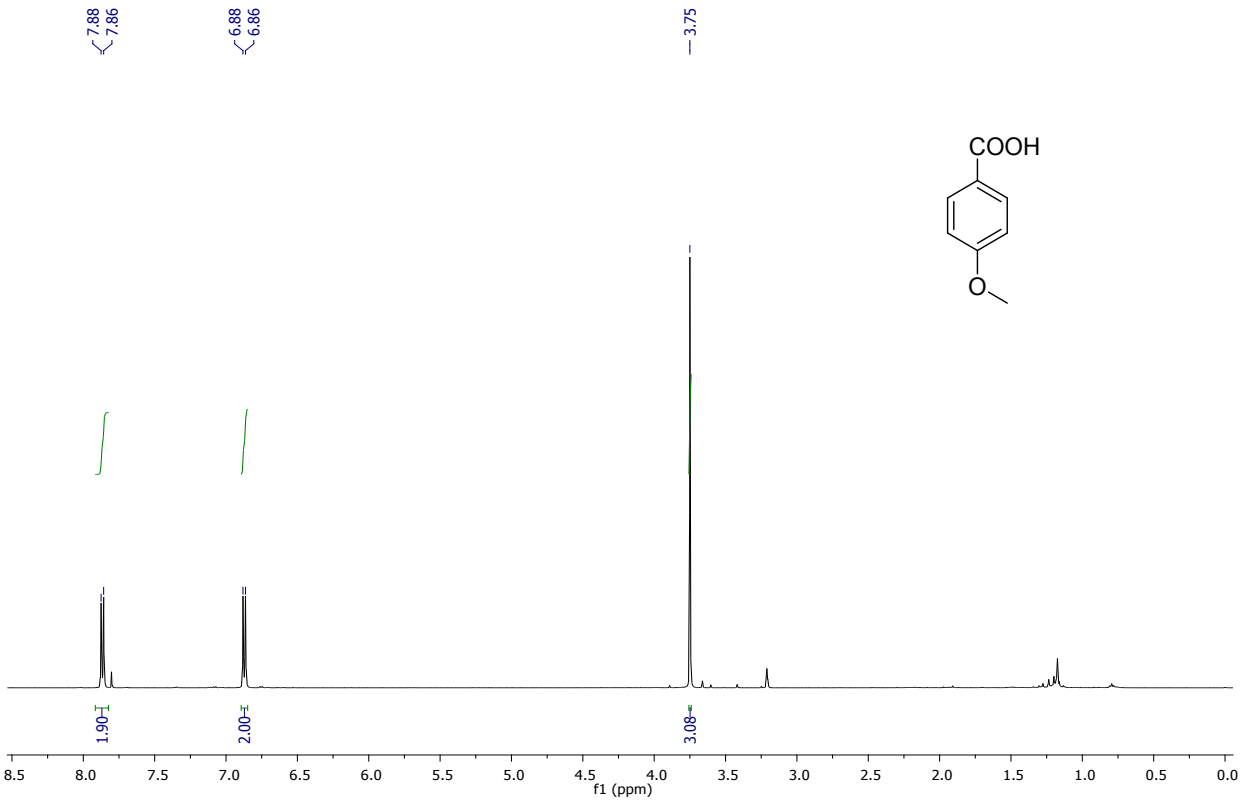


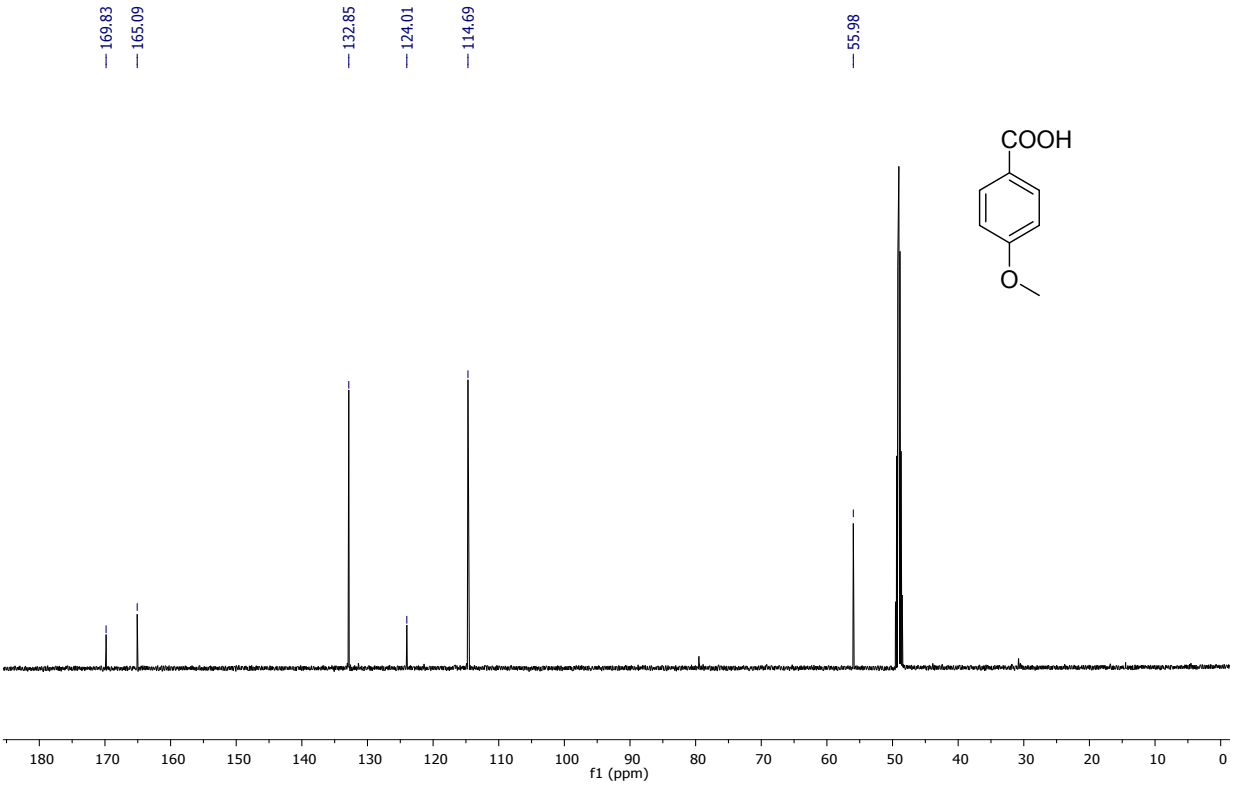
2h. 3,4-Dimethylbenzoic acid



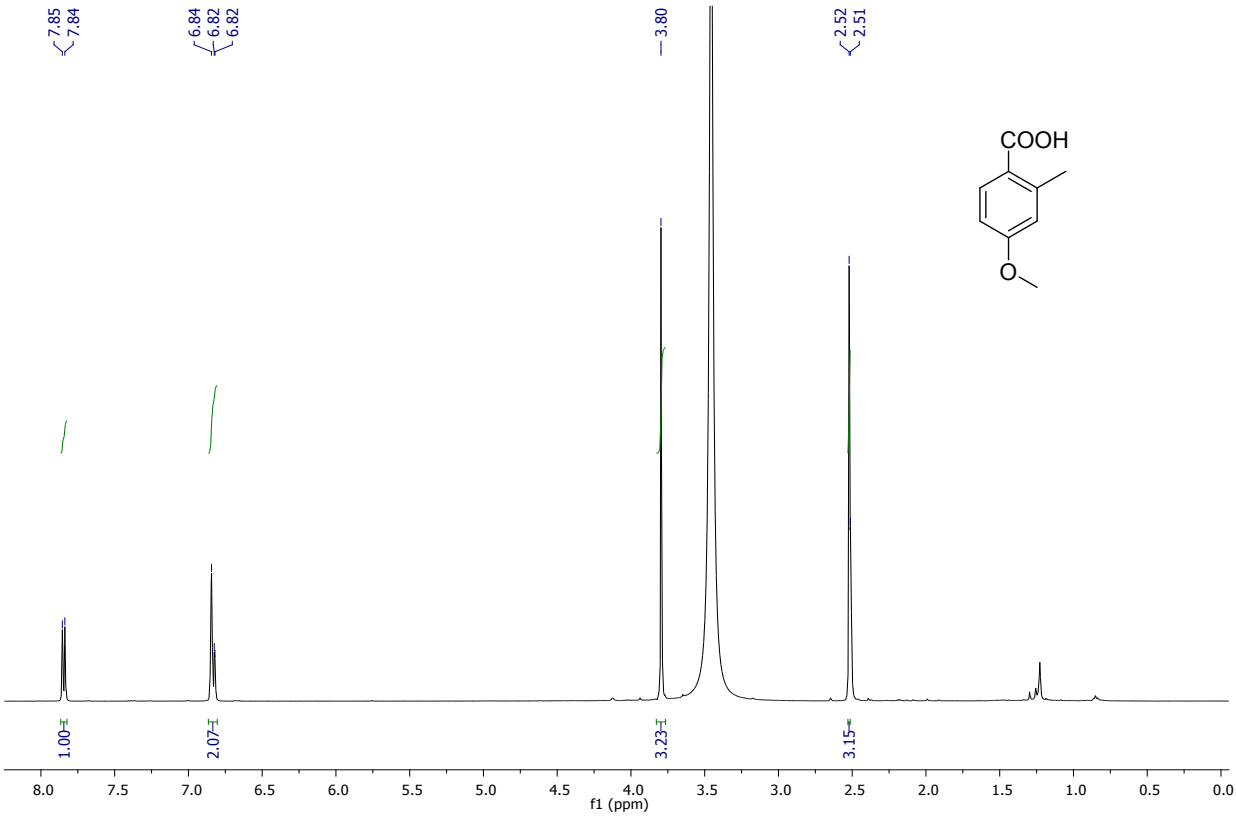


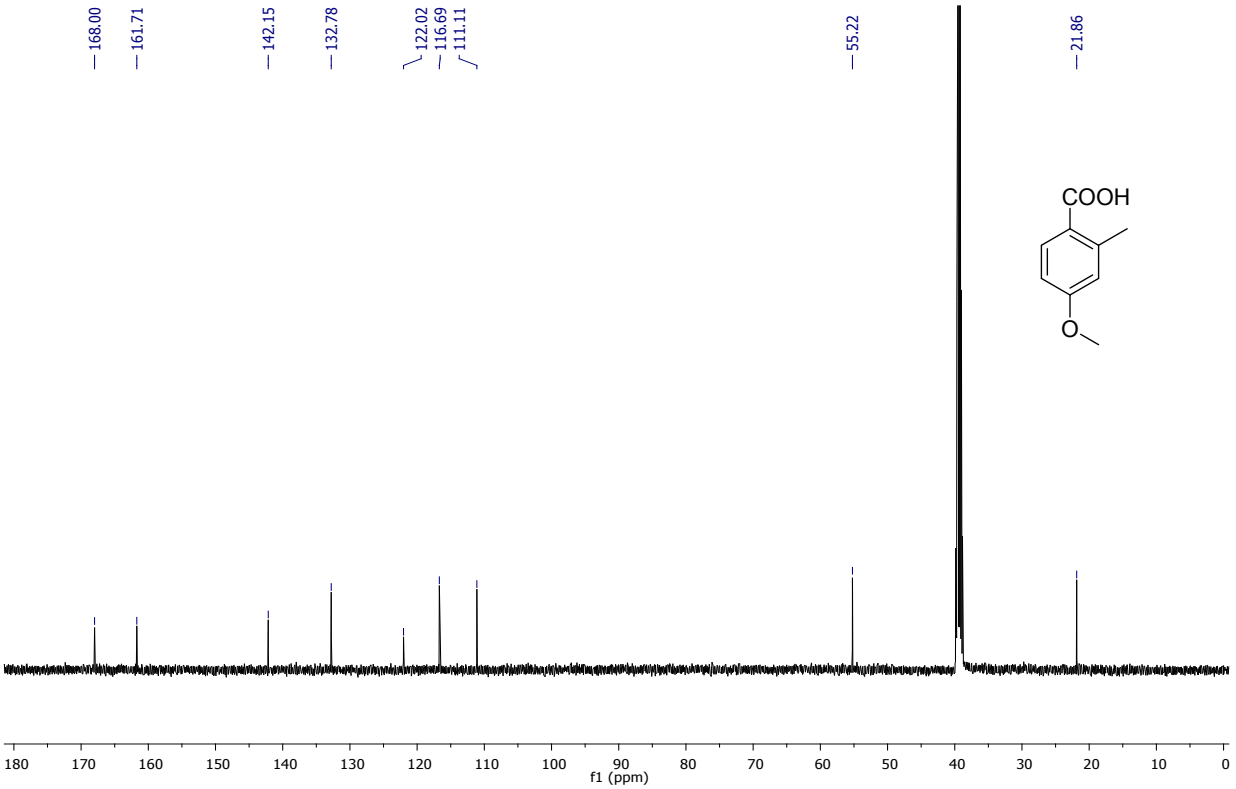
2i. 4-Methoxybenzoic acid



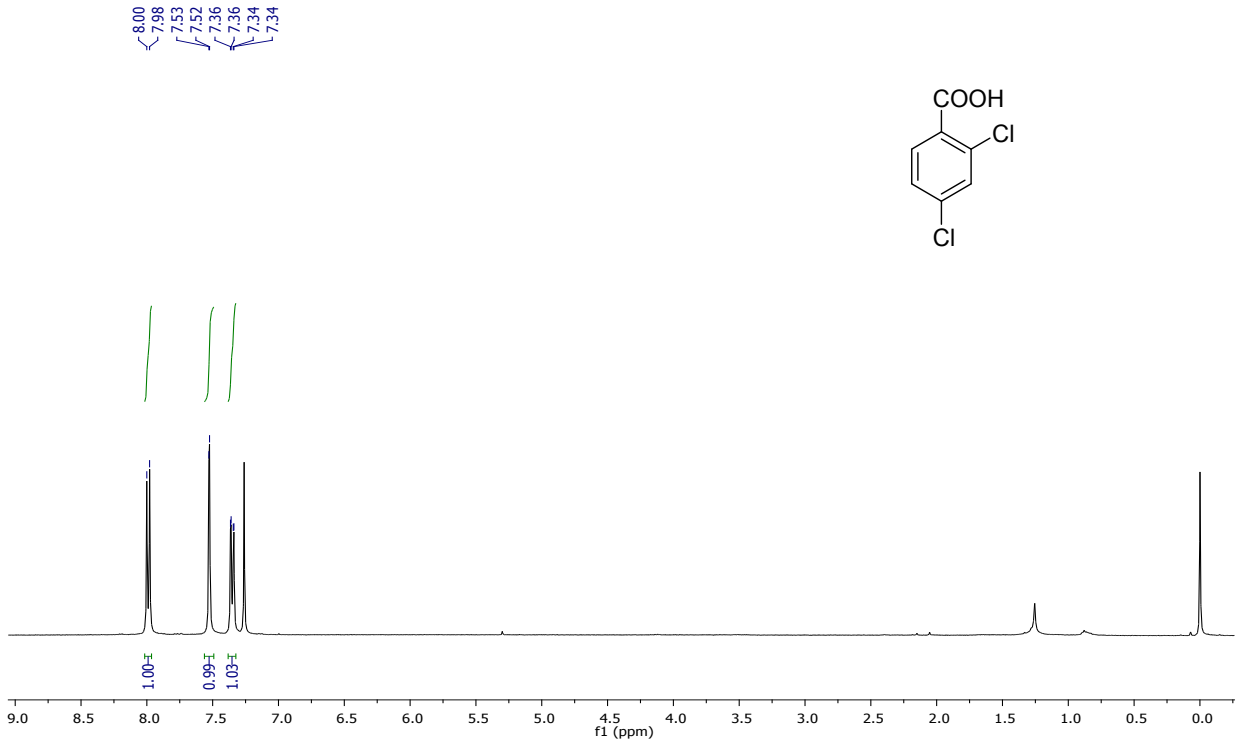


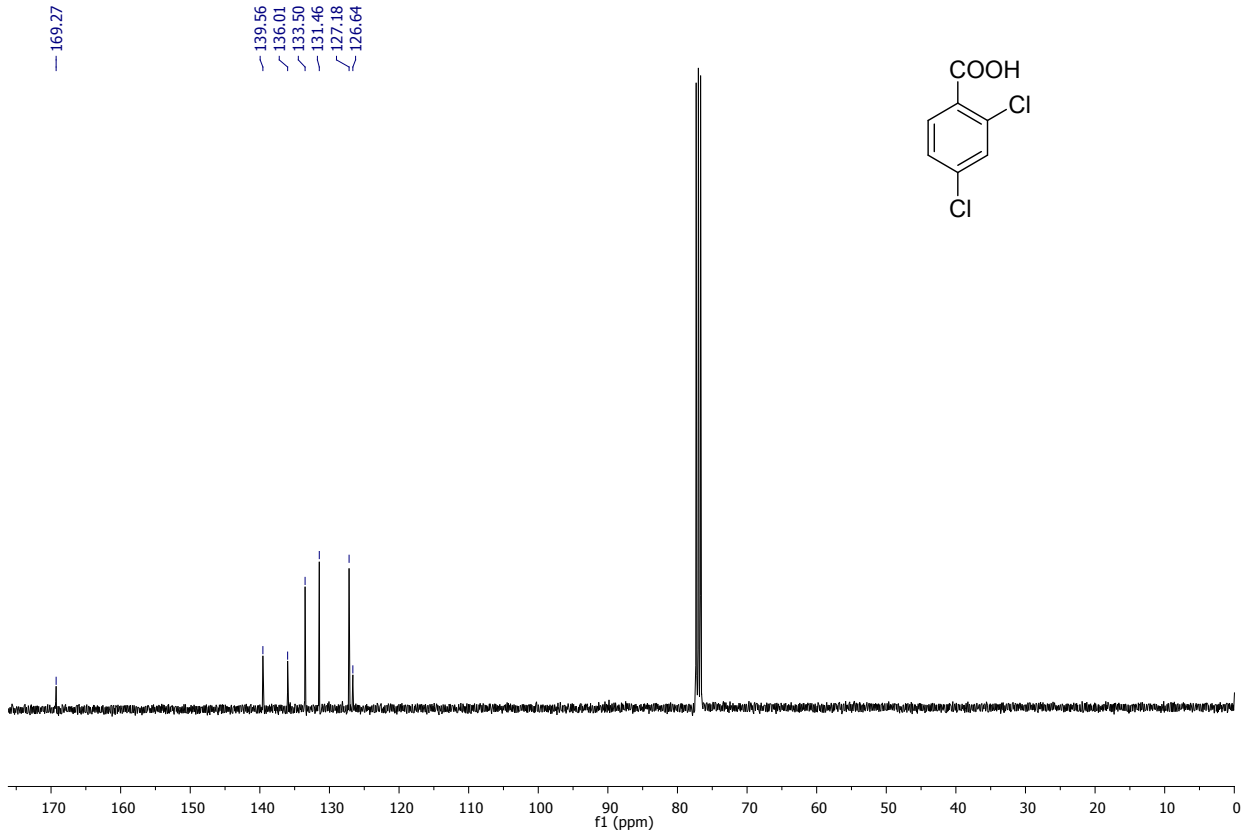
2j. 4-Methoxy-2-methylbenzoic acid



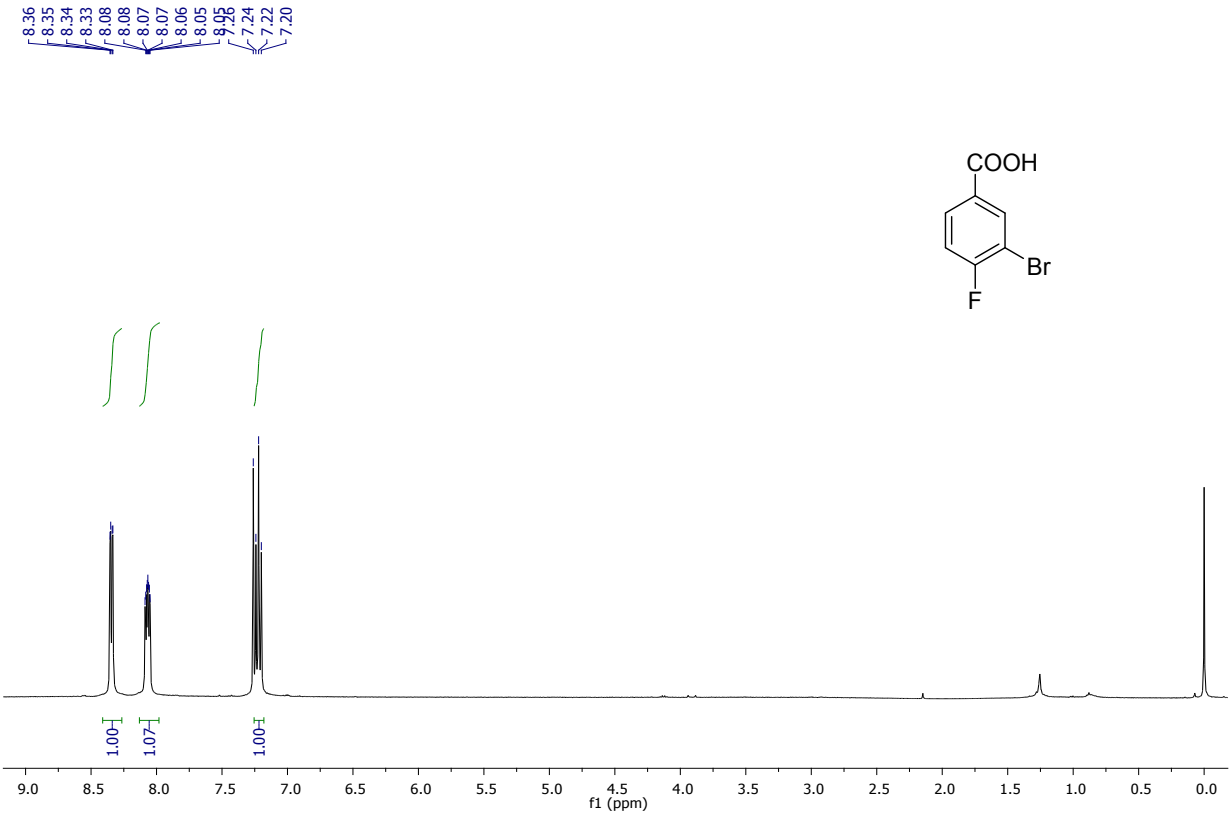


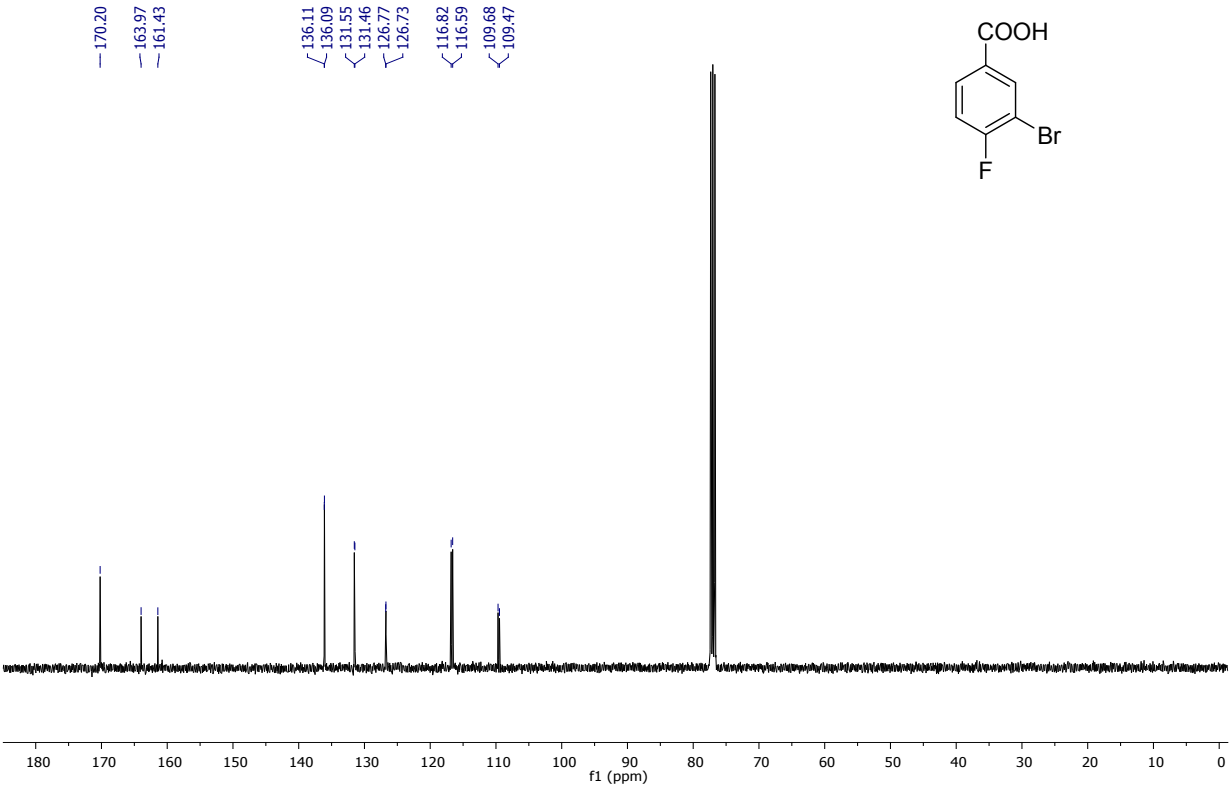
2k. 2,4-Dichlorobenzoic acid



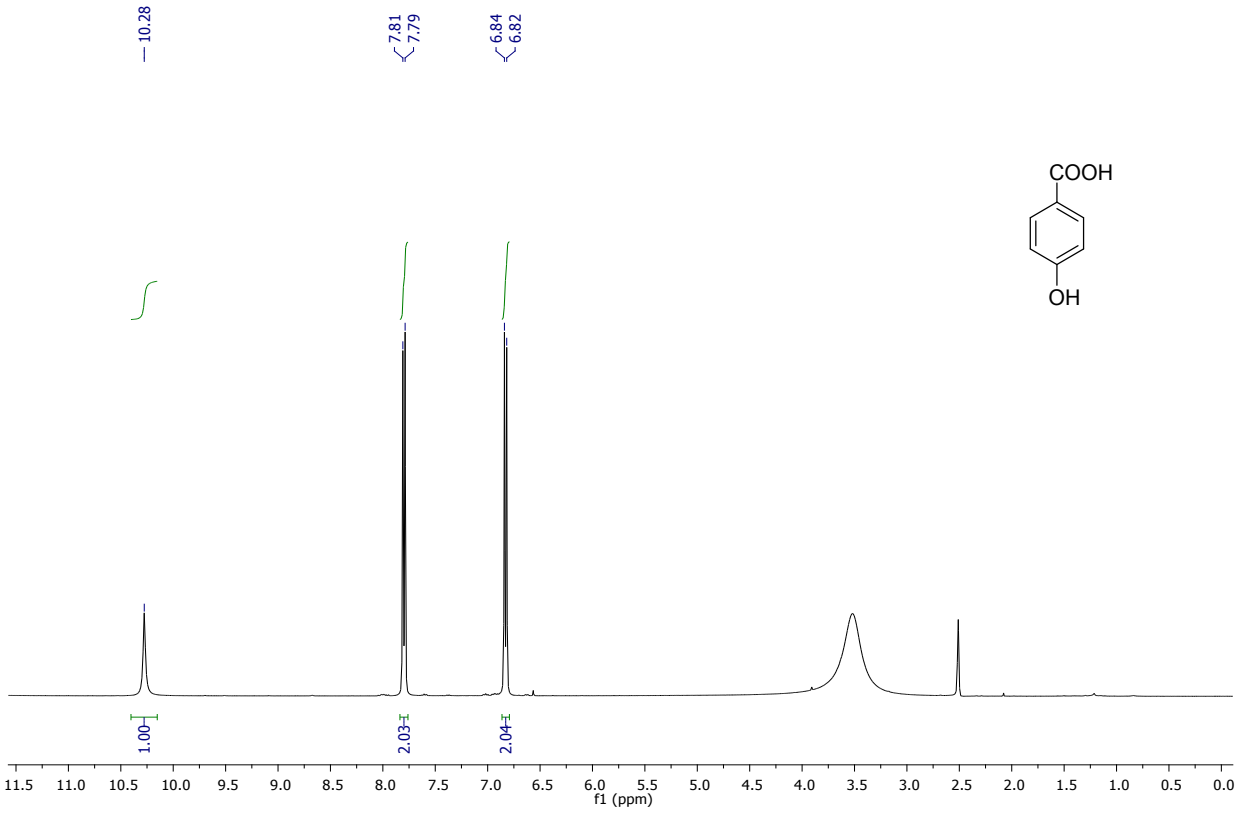


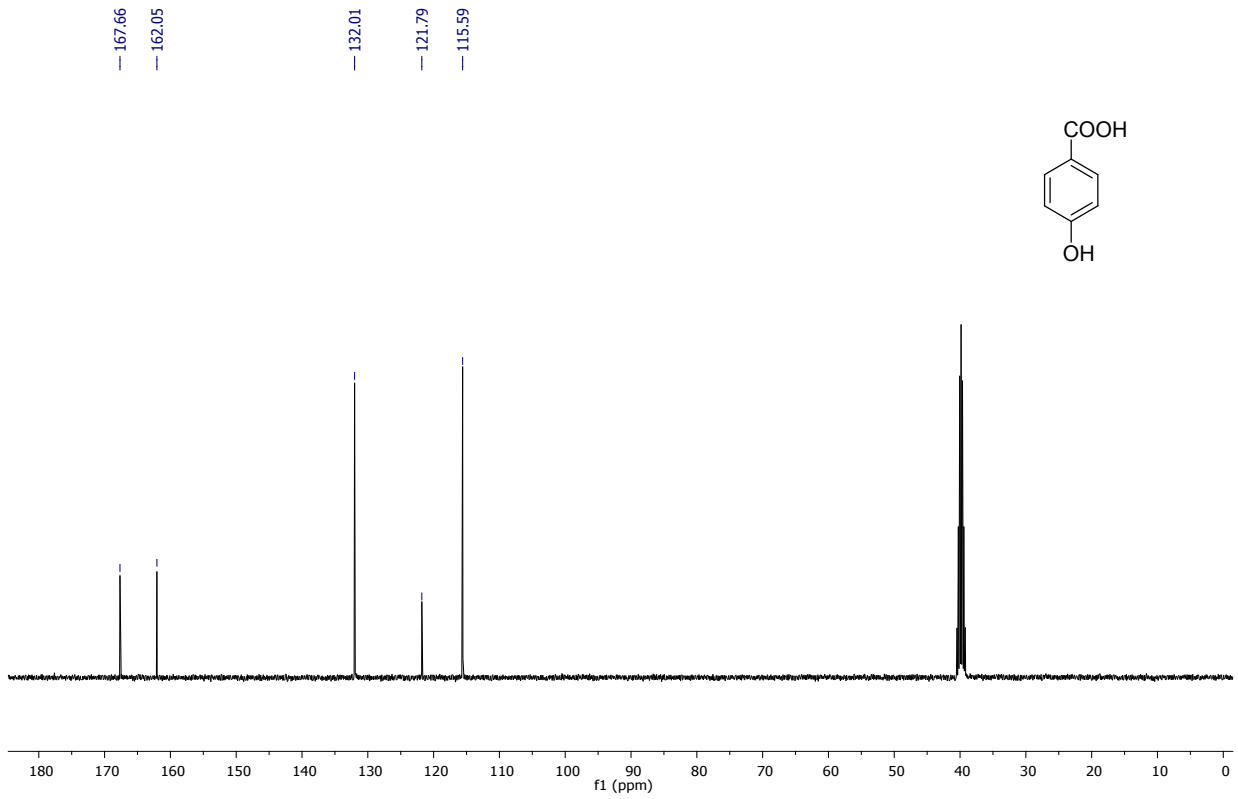
2l. 3-Bromo-4-Fluorobenzoicacid



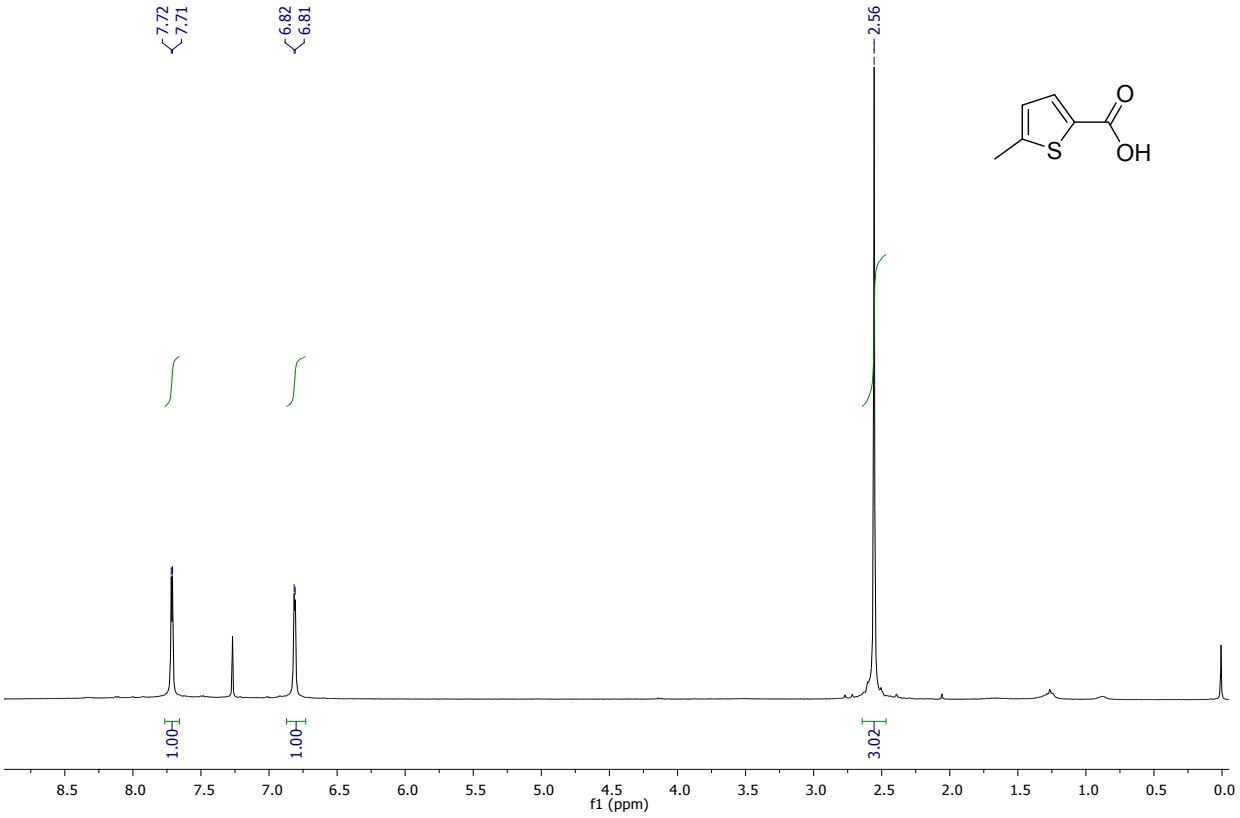


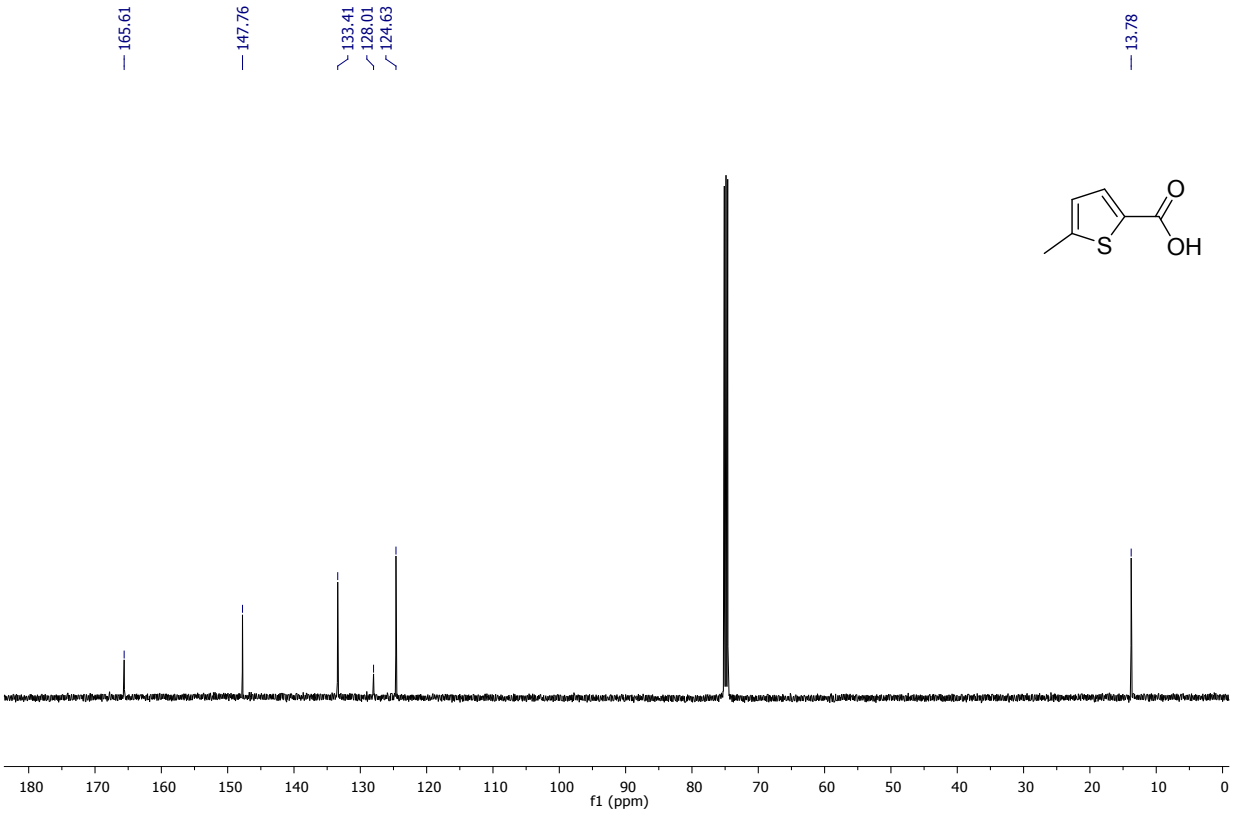
2m. 4-Hydroxybenzoic acid



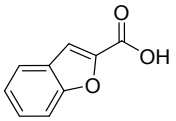


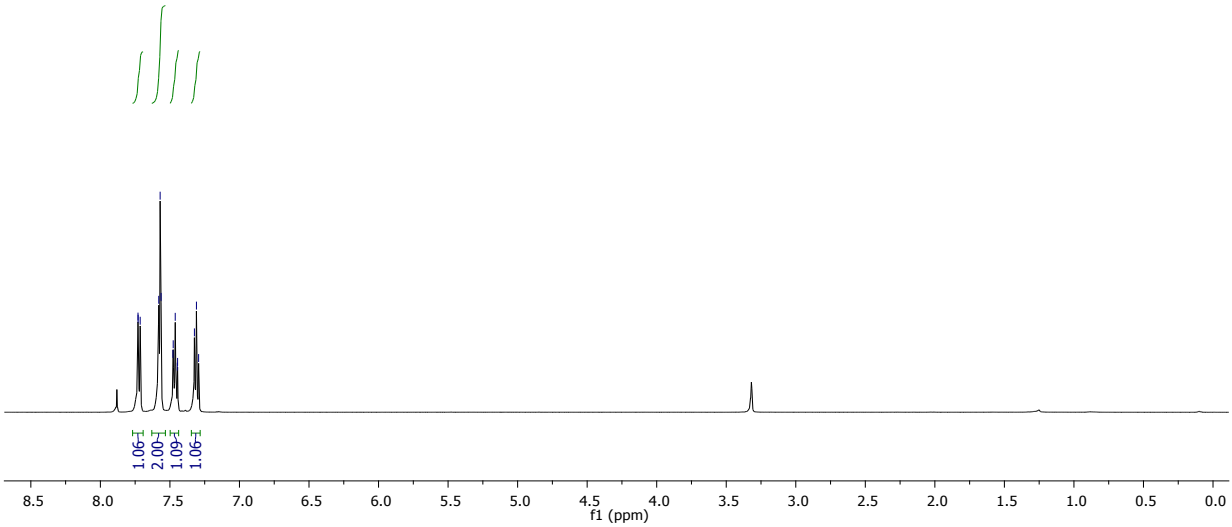
2n. 5-Methylthiophene-2-carboxylic acid

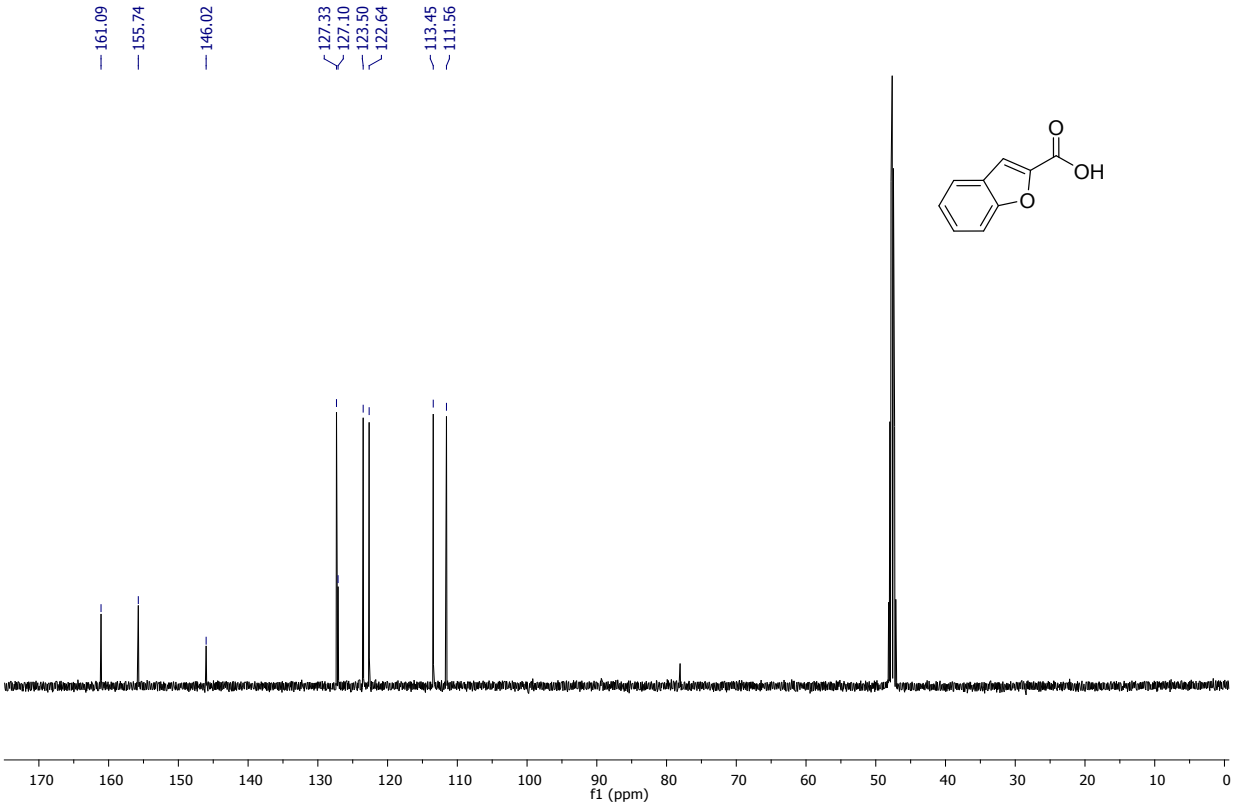




2o. Benzofuran-2-carboxylic acid







Diethyl (2-oxo-2-phenylethyl)phosphonate (4)