Supporting Information

Transition-Metal-Free Aerobic Oxidation of Primary Alcohols to Carboxylic Acids

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General information

All reactions were performed in an air atmosphere with a balloon fitted on a Schlenk tube. All glassware was oven dried at 110 ^{o}C for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. ^{1}H and ^{13}C NMR data were recorded with Varian Mercury (300 or 400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks, respectively.

General Procedure for NaOH Promoted Oxidation of Primary Alcohols

A 10 mL Schlenk tube was charged with 1.0 mmol of NaOH. After the tube was backfilled with air balloon, 0.5 mmol of primary alcohol and 2 mL of THF were injected. The resulting solution was kept stirring for 12 h at 60 ^{o}C and then the suspended solution was quenched with water and extracted with ethyl acetate (3 × 10 mL). The aqueous layer was acidified with diluted hydrochloride (2 mL, 2M) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by removing the organic solvent.

General Procedure for ^{t}BuONa Promoted Oxidation of Primary Alcohols

A 10 mL schlenk flask was charged with 1.0 mmol of ^{t}BuONa. After the tube was backfilled with air balloon, 0.5 mmol of primary alcohol and 2 mL of THF were injected. The resulting solution was kept stirring for 1 h at 25 ^{o}C and then the suspended solution was quenched with water and extracted with ethyl acetate (3 × 10 mL). The aqueous layer was acidified with diluted hydrochloride (2 mL, 2M) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by removing the organic solvent.

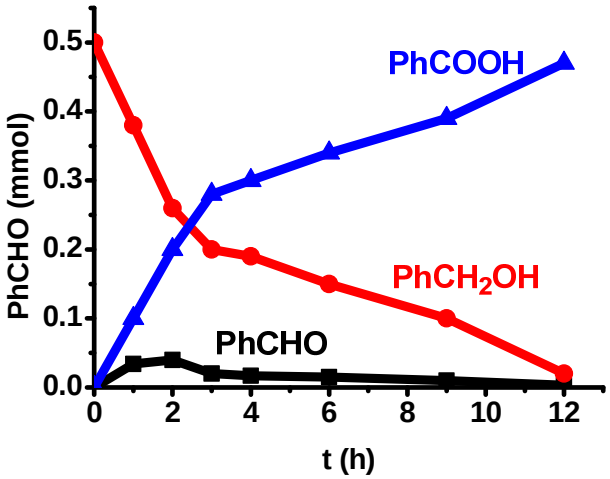
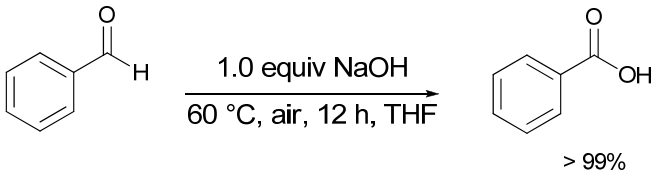
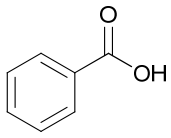


Figure 1. Distribution versus time in the oxidation of benzyl alcohol with 2.0 equiv NaOH at 60 ^{o}C.

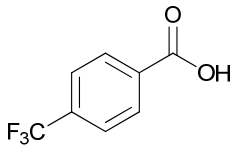
Procedure for NaOH Promoted Oxidation of benzaldehyde



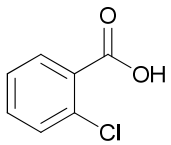
A 10 mL Schlenk tube was charged with NaOH (20.0 mg, 0.5 mmol). After the tube was backfilled with air balloon, benzaldehyde (53.1 mg, 0.5 mmol) and 2 mL of THF were injected. The resulting solution was kept stirring for 12 h at 60 ^{o}C and then the suspended solution was quenched with water and extracted with ethyl acetate (3 × 10 mL). The aqueous layer was acidified with diluted hydrochloride (2 mL, 2M) and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over sodium sulfate. The pure product was obtained by removing the organic solvent. The yield of the isolated product was >99%.



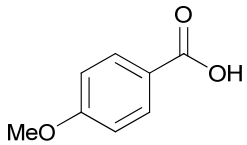
Benzoic acid (2a)[1]. Compound **2a** was prepared following the general procedure starting from benzyl alcohol (54.1 mg, 0.50 mmol). **2a** was isolated as a white solid (61 mg, > 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (b, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 133.8, 130.2, 129.3, 128.5 ppm.



4-Trifluoromethylbenzoic acid (2b)[2]. Compound **2b** was prepared following the general procedure starting from 4-Trifluoromethylbenzyl alcohol (88.1 mg, 0.50 mmol). **2b** was isolated as a white solid (85.5 mg, 90%).^{1}H NMR (300 MHz, DMSO) δ 9.48 (d, *J* = 8.1 Hz, 2H), 9.17 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (75 MHz, DMSO) δ 171.7, 140.1, 138.0, 135.5, 130.9 ppm.

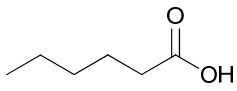


2-Chlorobenzoic acid (2c)[3]. Compound **2c** was prepared following the general procedure starting from 2-chlorobenzyl alcohol (71.3 mg, 0.50 mmol). **2c** was isolated as a brown solid (54.3 mg, 70%). ^{1}H NMR (400 MHz, DMSO) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.53 (m, 2H), 7.43 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 167.2, 133.0, 132.0, 131.9, 131.3, 131.1, 127.7 ppm.

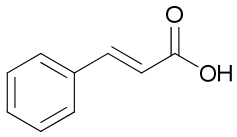


4-Methoxybenzoic acid (2d)[1]. Compound **2d** was prepared following the general procedure starting from 4-methoxybenzyl alcohol (69.1 mg, 0.50 mmol). **2d** was isolated as a white solid (52.4 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.26 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 144.8, 130.4,

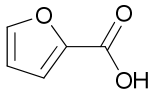
129.4, 126.7, 21.9 ppm.



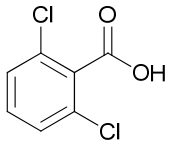
Hexanoic acid (2e)[4]. Compound **2e** was prepared following the general procedure starting from 1-hexanol (51.1 mg, 0.50 mmol). **2e** was isolated as as a colorless liquid (29.0 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.14 (b, 1H), 2.29 (s, 2H), 1.56 (s, 2H), 1.25 (s, 4H), 0.84 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.8, 34.3, 31.4, 24.6, 22.5, 14.1 ppm.



Cinnamic acid (2f)[1]. Compound **2f** was prepared following the general procedure starting from cinnamyl alcohol (67.1 mg, 0.50 mmol). **2f** was isolated as a brown solid (35.5 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 16.0 Hz, 1H), 7.56 (m, 2H), 7.41 (m, 3H), 6.46 (d, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 147.1, 134.0, 130.7, 129.0, 128.4, 117.3 ppm.

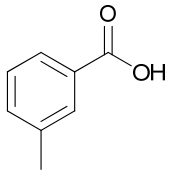


2-Furoic acid (2g)[2]. Compound **2g** was prepared following the general procedure starting from 2-furan methanol (49.1 mg, 0.50 mmol). **2g** was isolated as a colorless liquid (35.3 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (b, 1H), 7.68 – 7.62 (m, 1H), 7.34 (d, J = 3.5 Hz, 1H), 6.56 (dd, J = 3.5, 1.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 147.6, 143.9, 120.3, 112.4 ppm.

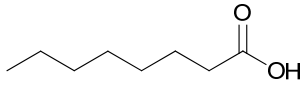


2,6-Dichlorobenzoic acid (2h)[1]. Compound **2h** was prepared following the general procedure starting from 2,6-dichlorobenzyl alcohol (88.5 mg, 0.50 mmol). **2h** was isolated as a brown solid (95.5 mg, > 99%). ^{1}H NMR (400 MHz, DMSO) δ 7.81 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 4.0 Hz, 1H), 7.50 (dd, J_1 = J_2 = 4.0 Hz 1H) ppm; ^{13}C

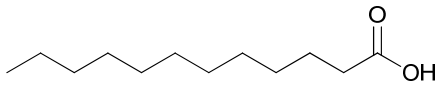
NMR (100 MHz, DMSO) δ 166.3, 137.0, 133.5, 132.8, 130.7, 130.5, 127.9 ppm.



3-Methylbenzoic acid (2i)[5]. Compound **2i** was prepared following the general procedure starting from 3-methylbenzyl alcohol (61.1 mg, 0.50 mmol). **2i**was isolated as a white solid(53.1 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.40 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 138.4, 134.7, 130.8, 129.3, 128.5, 127.5, 21.4 ppm.

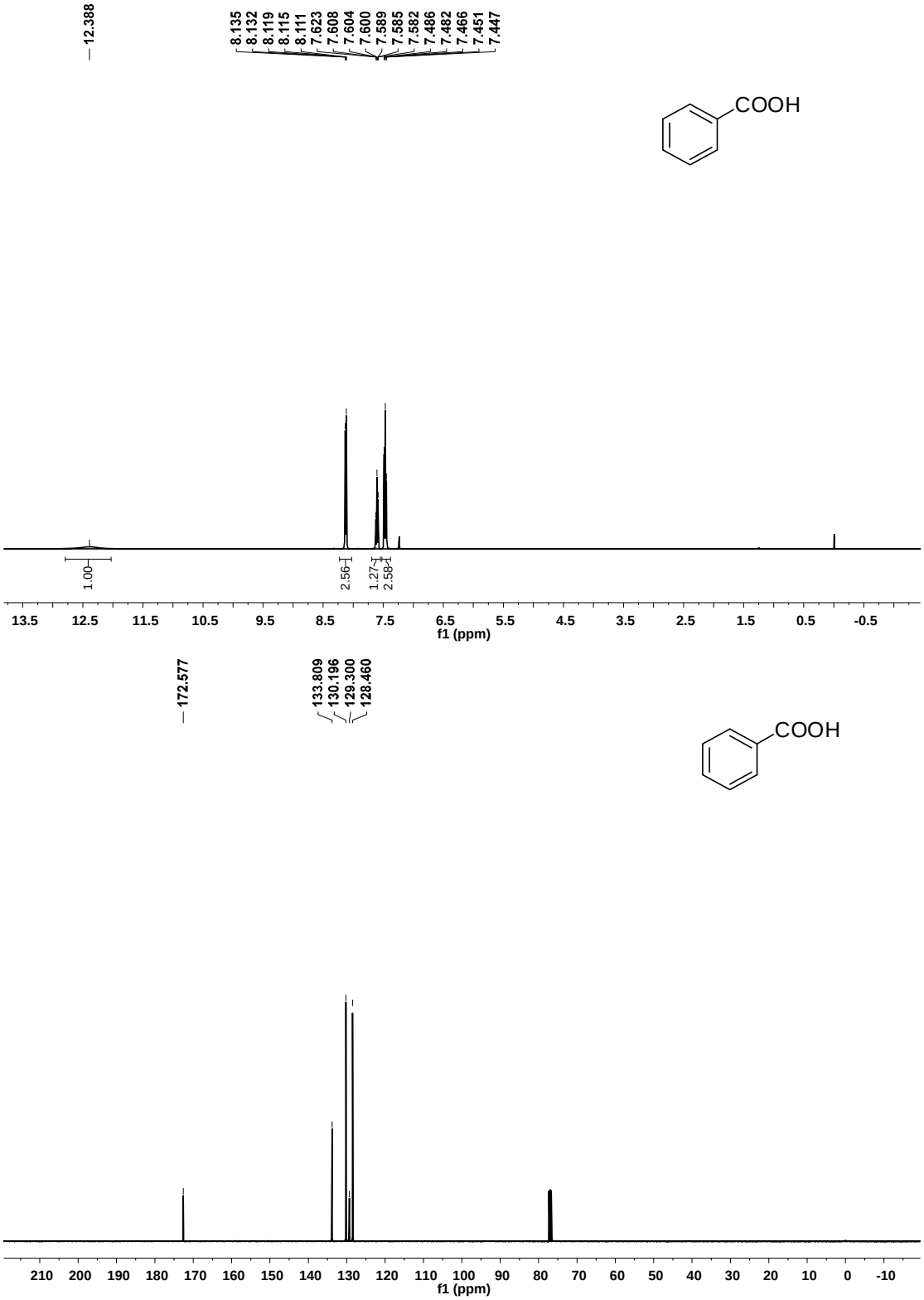


Octanoic acid (2j)[6]. Compound **2j** was prepared following the general procedure starting from 1-octanol (65.1 mg, 0.50 mmol). **2j** was isolated as a colorless liquid (39.6 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 8.0 Hz, 2H), 1.64 (t, *J* = 8.0 Hz, 2H), 1.35-1.28 (m, 8H), 0.88 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 34.1, 31.6, 29.0, 28.9, 24.7, 22.6, 14.1 ppm.

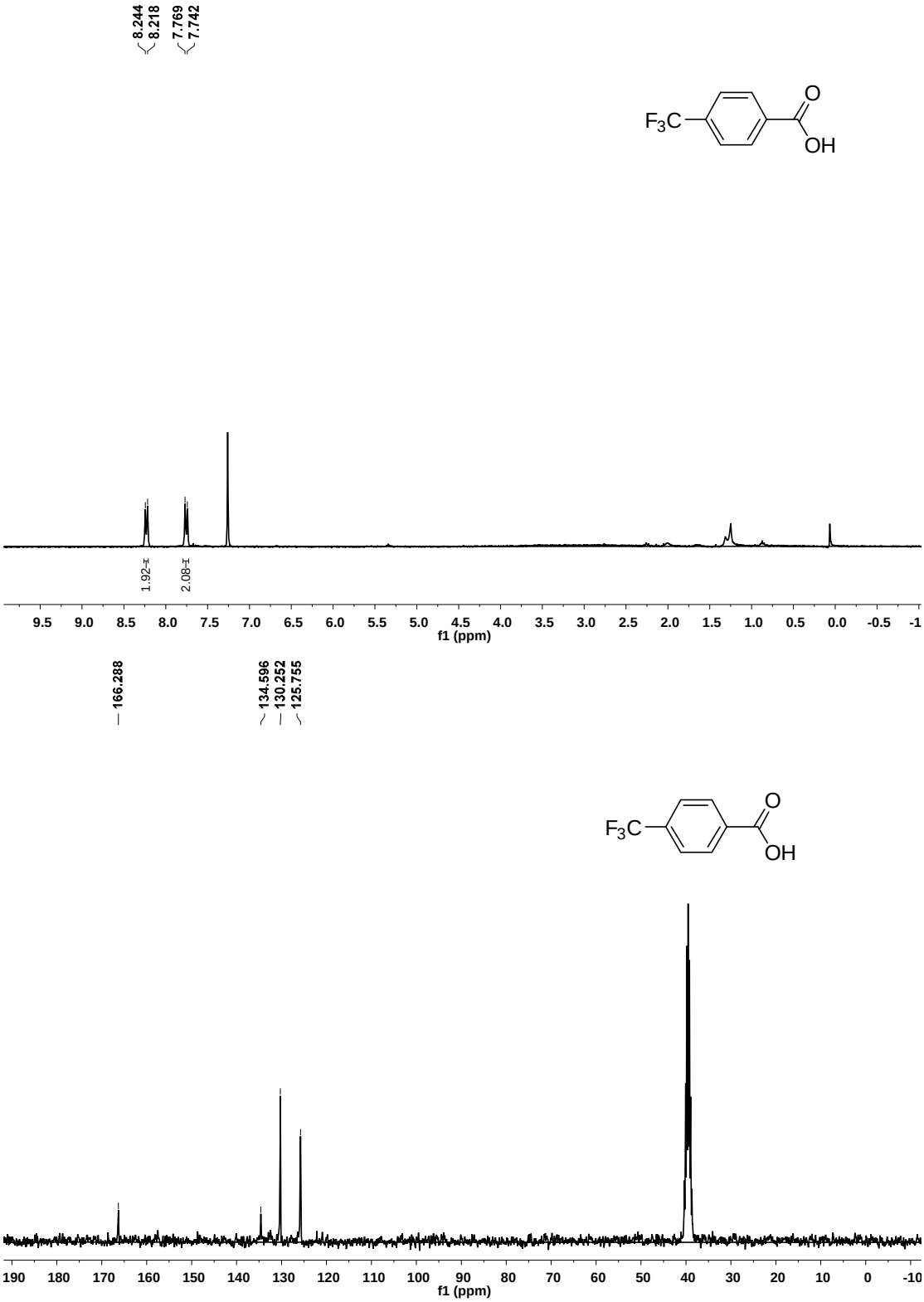


Dodecanoic acid (2k)[7]. Compound **2k** was prepared following the general procedure starting from 1-dodecanol (93.2 mg, 0.50 mmol). **2k** was isolated as a white solid (55.0 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (b, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.62 (t, *J* = 6.6 Hz, 2H), 1.25 (s, 16H), 0.87 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.7, 34.3, 32.1, 29.8, 29.6, 29.5, 29.3, 24.9, 22.9, 14.3 ppm.

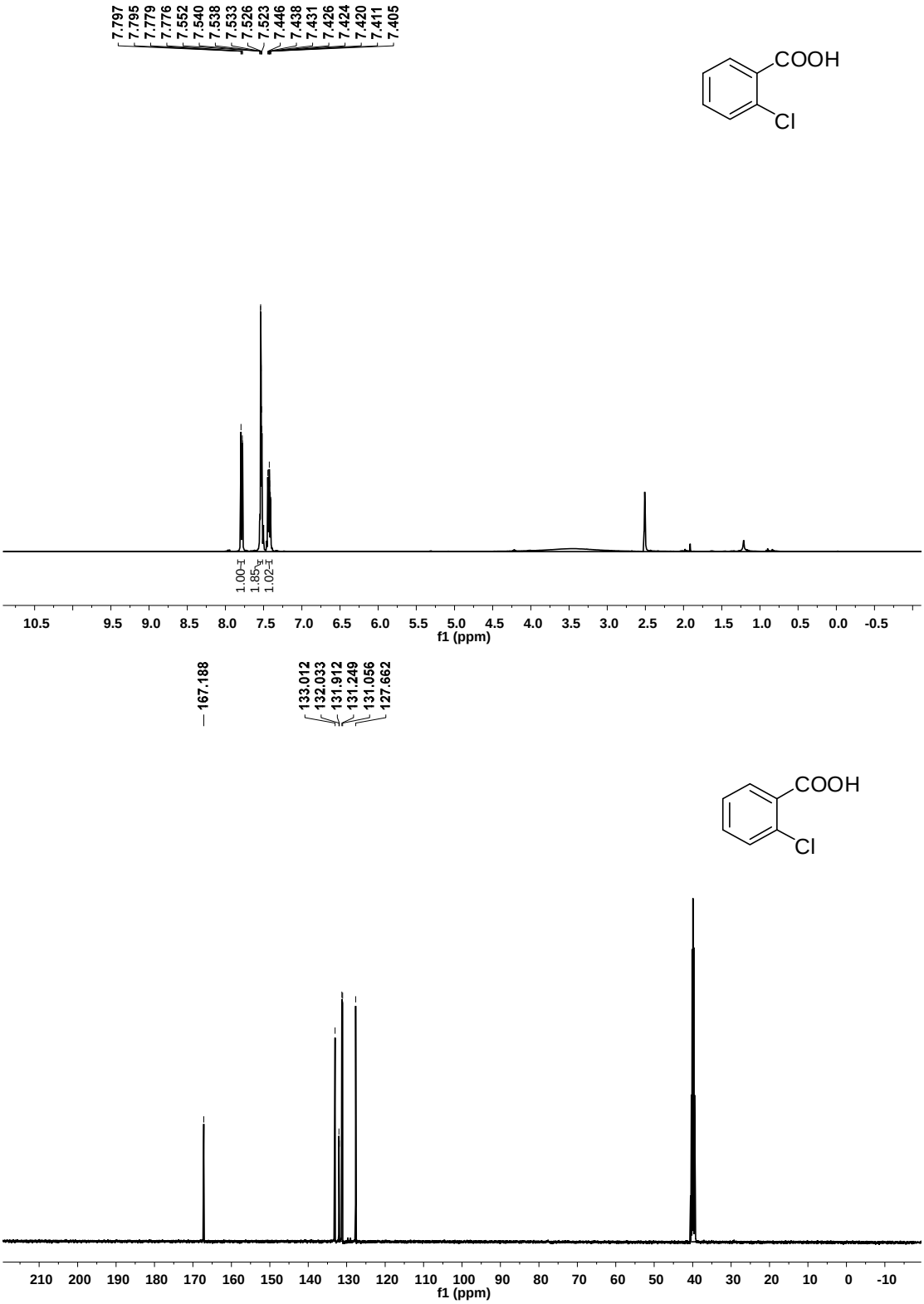
2a



2b

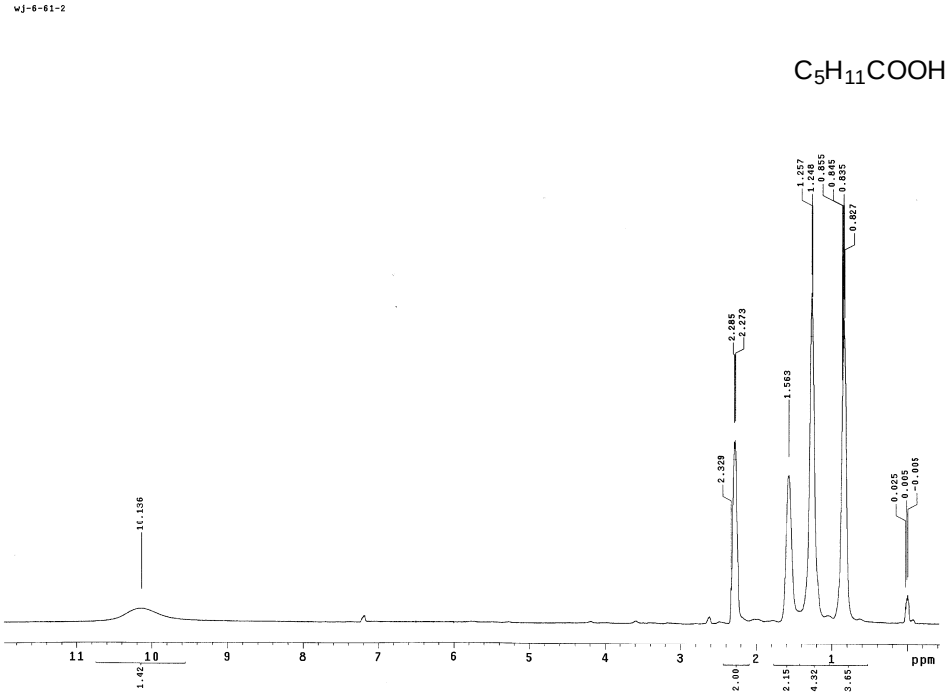


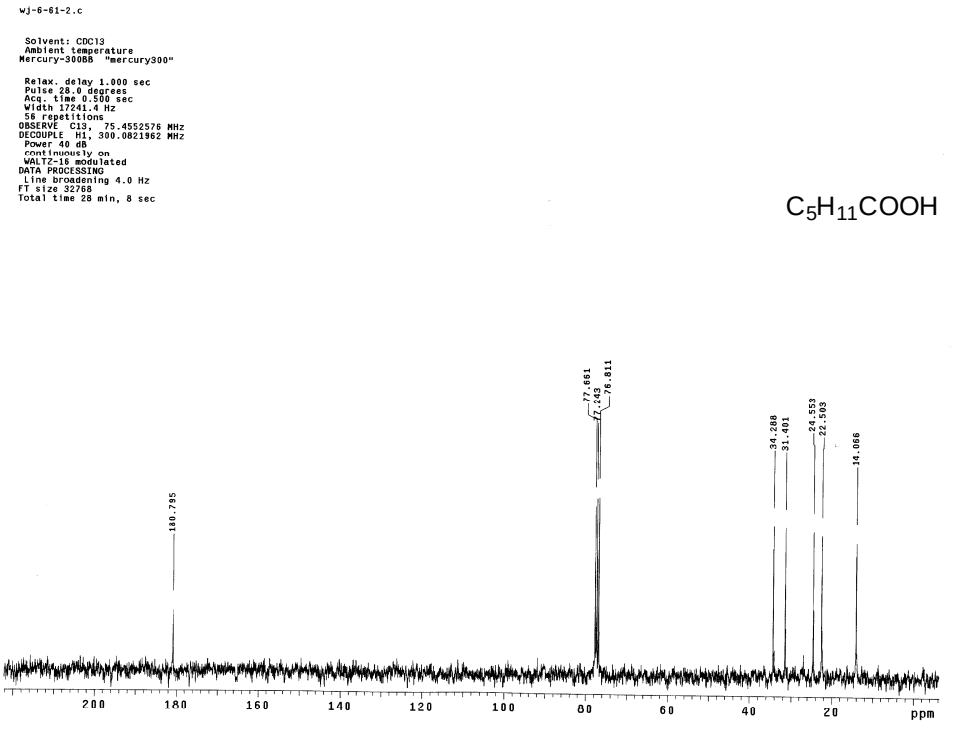
2c



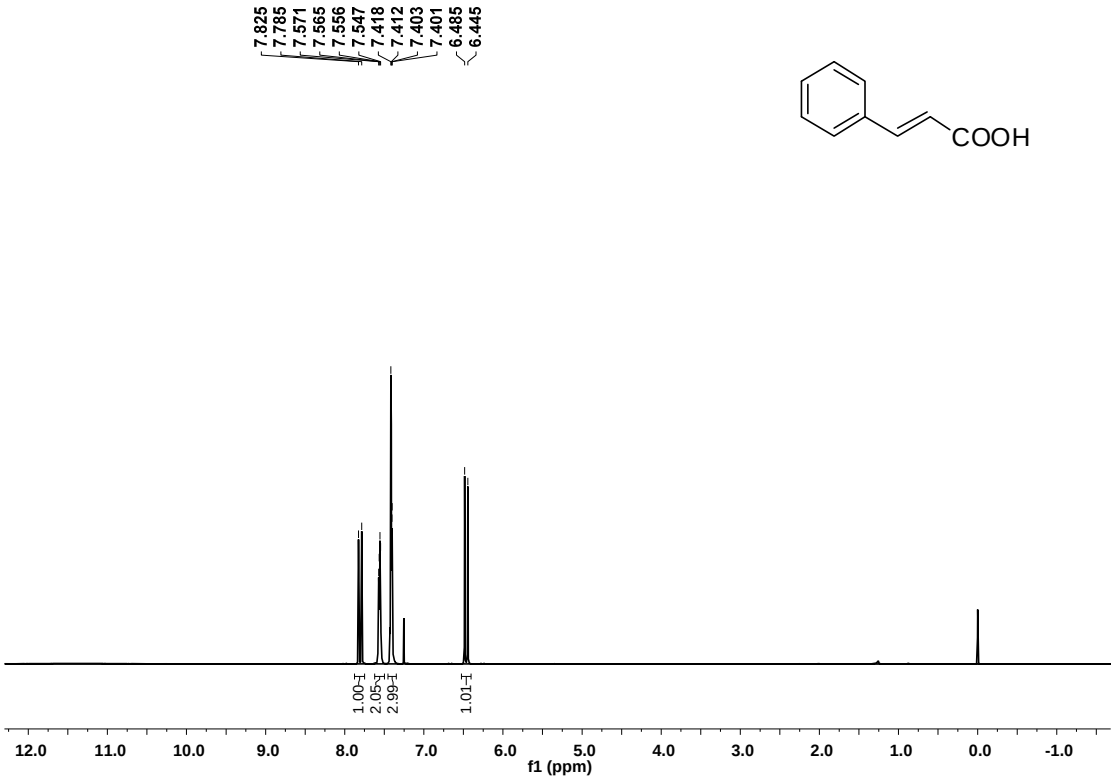
2d

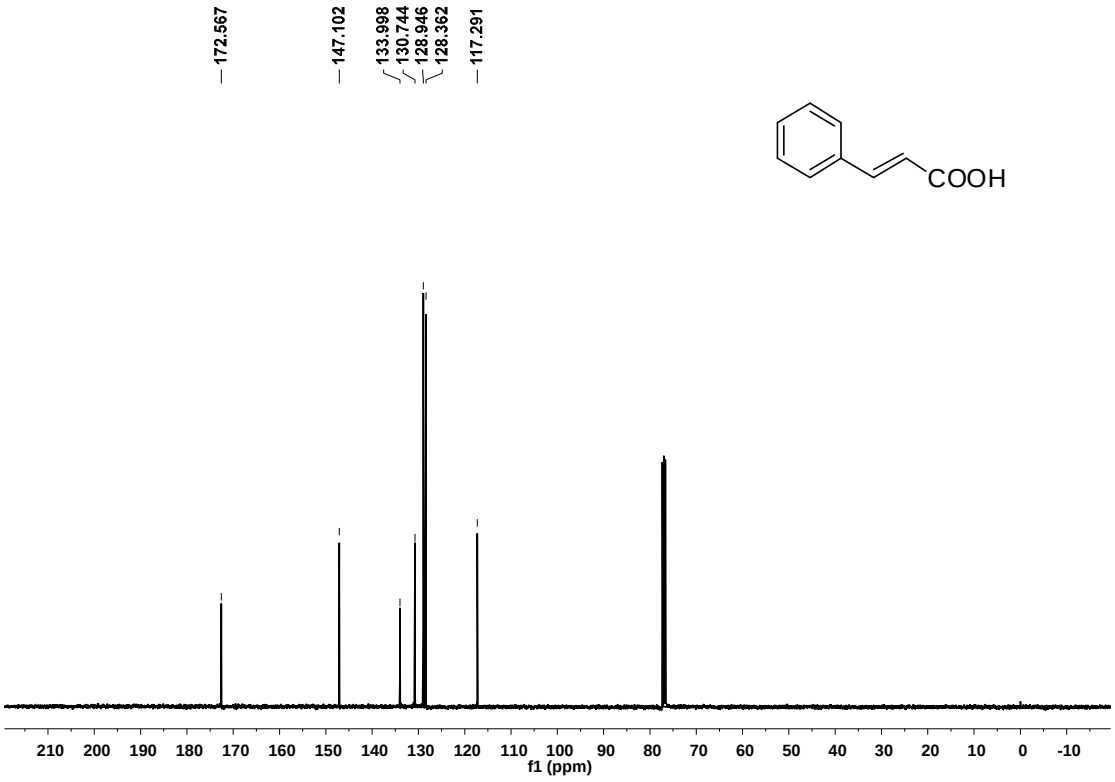
2e



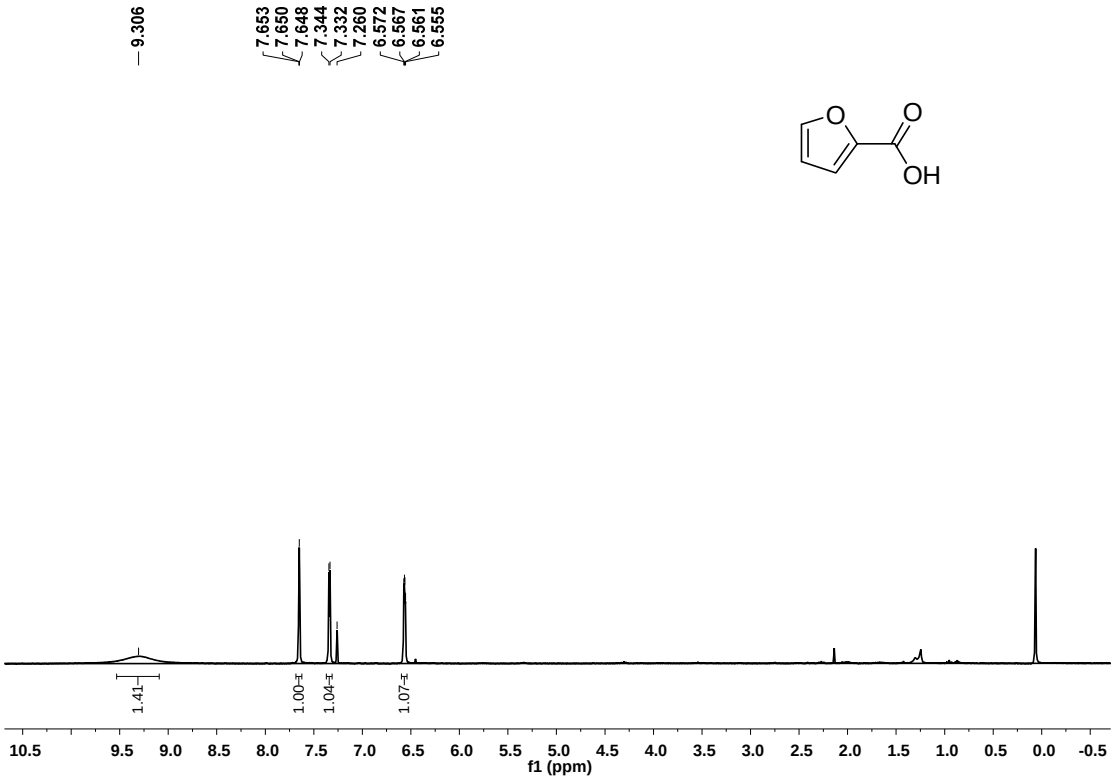


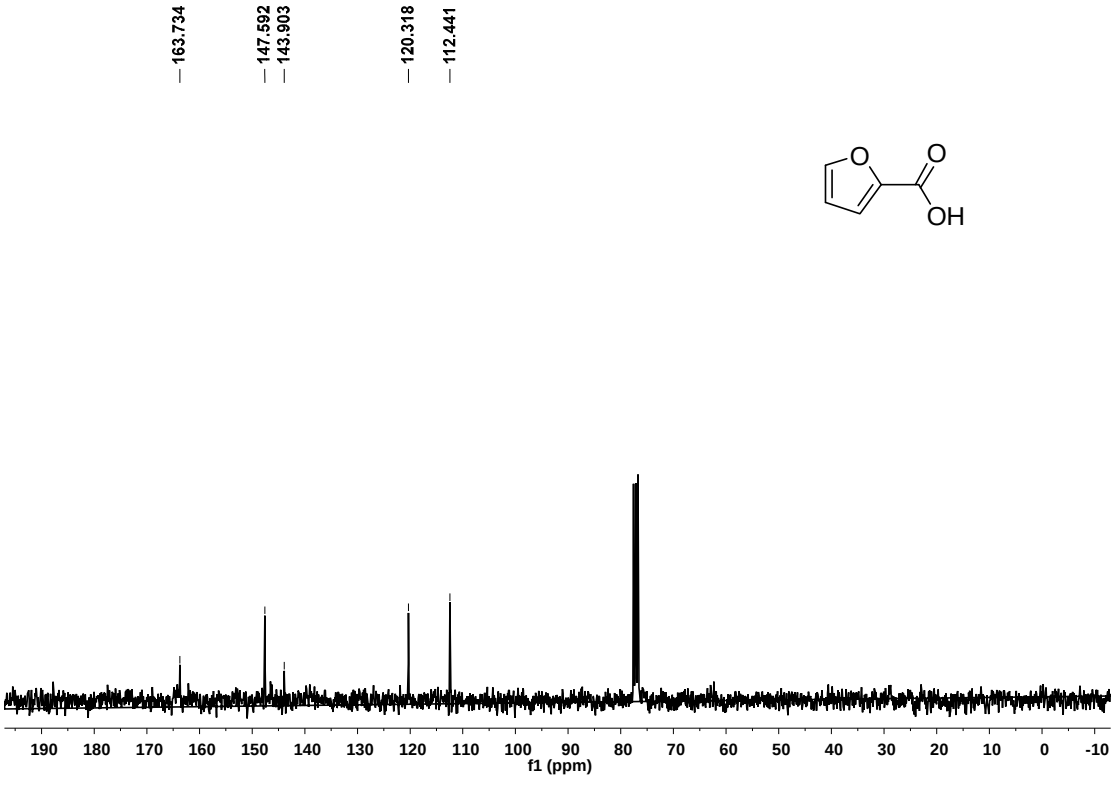
2f



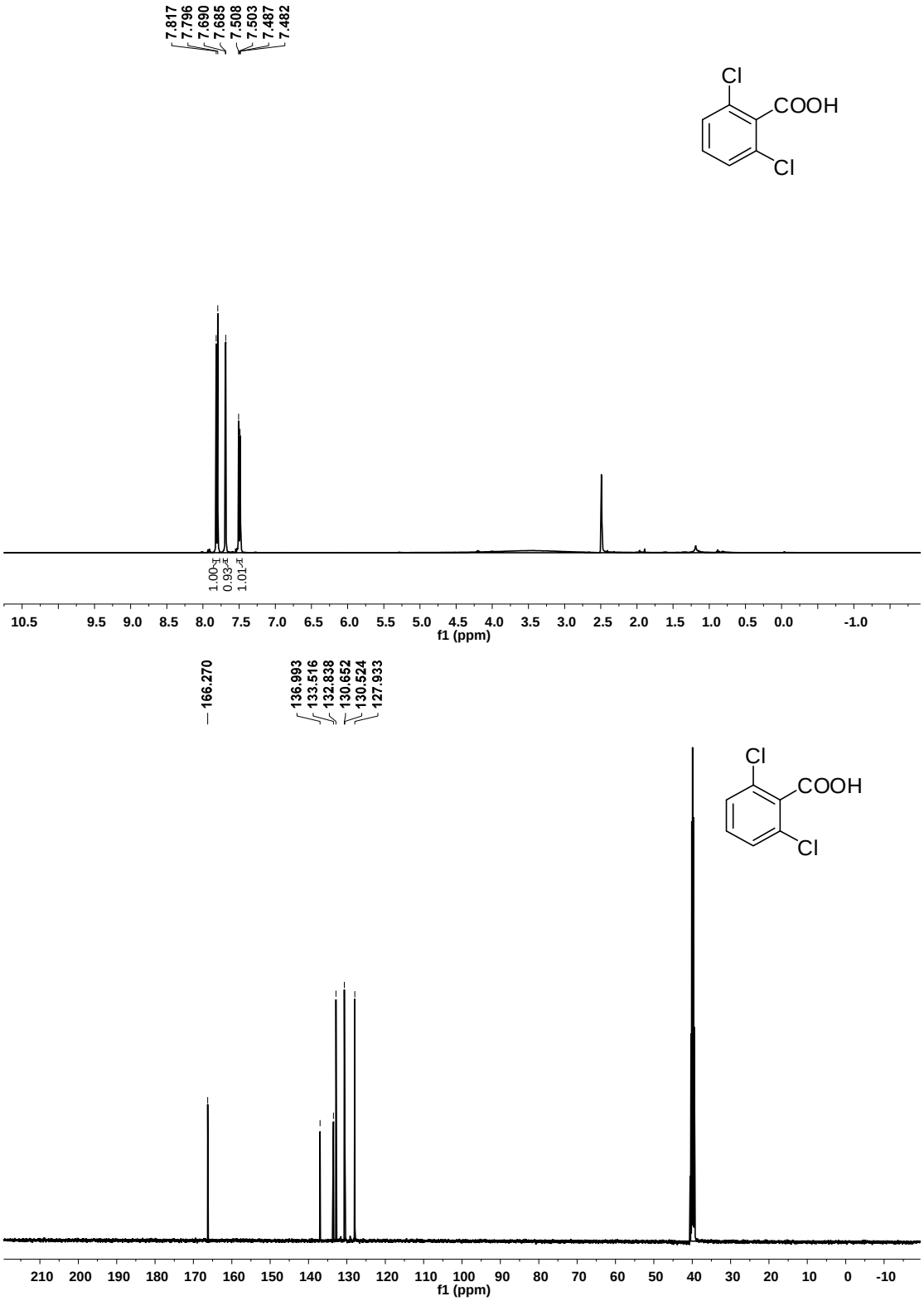


2g

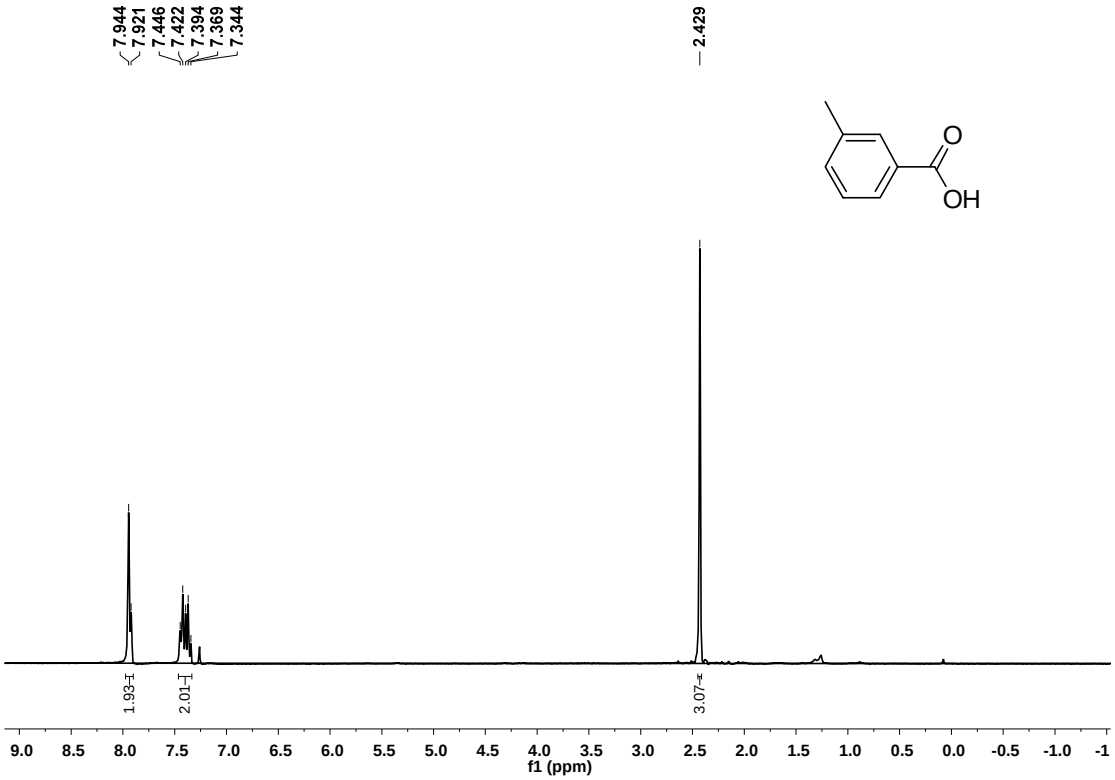


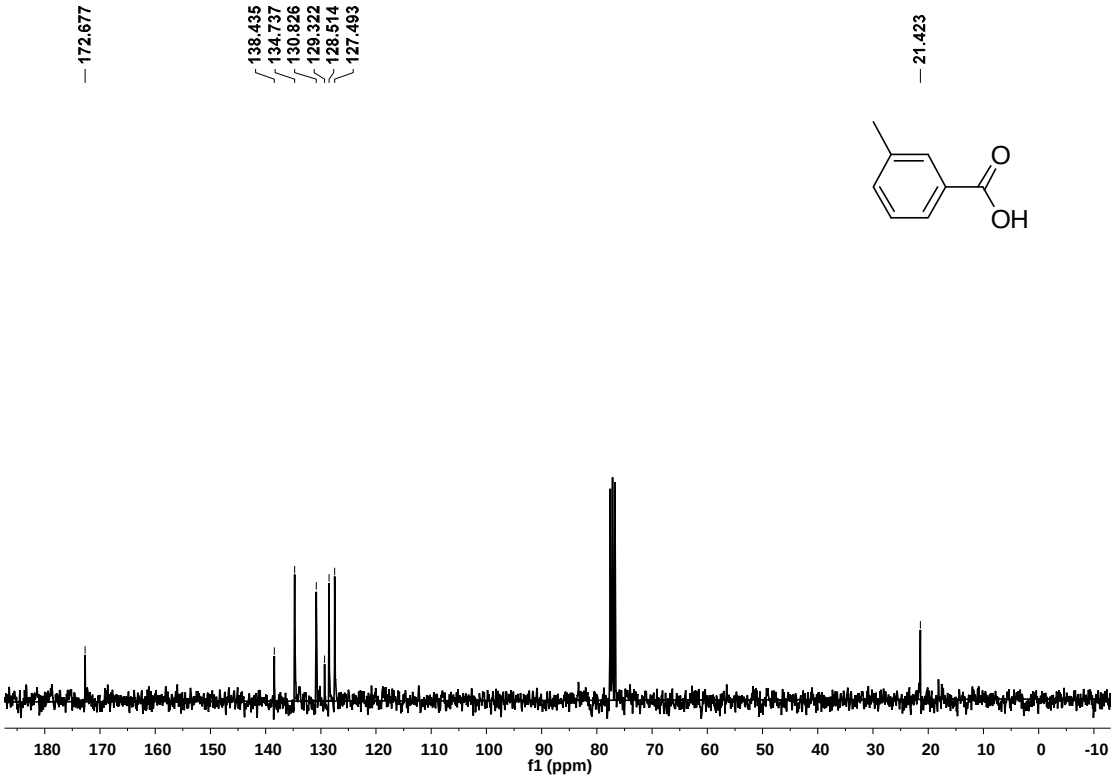


2h



2i





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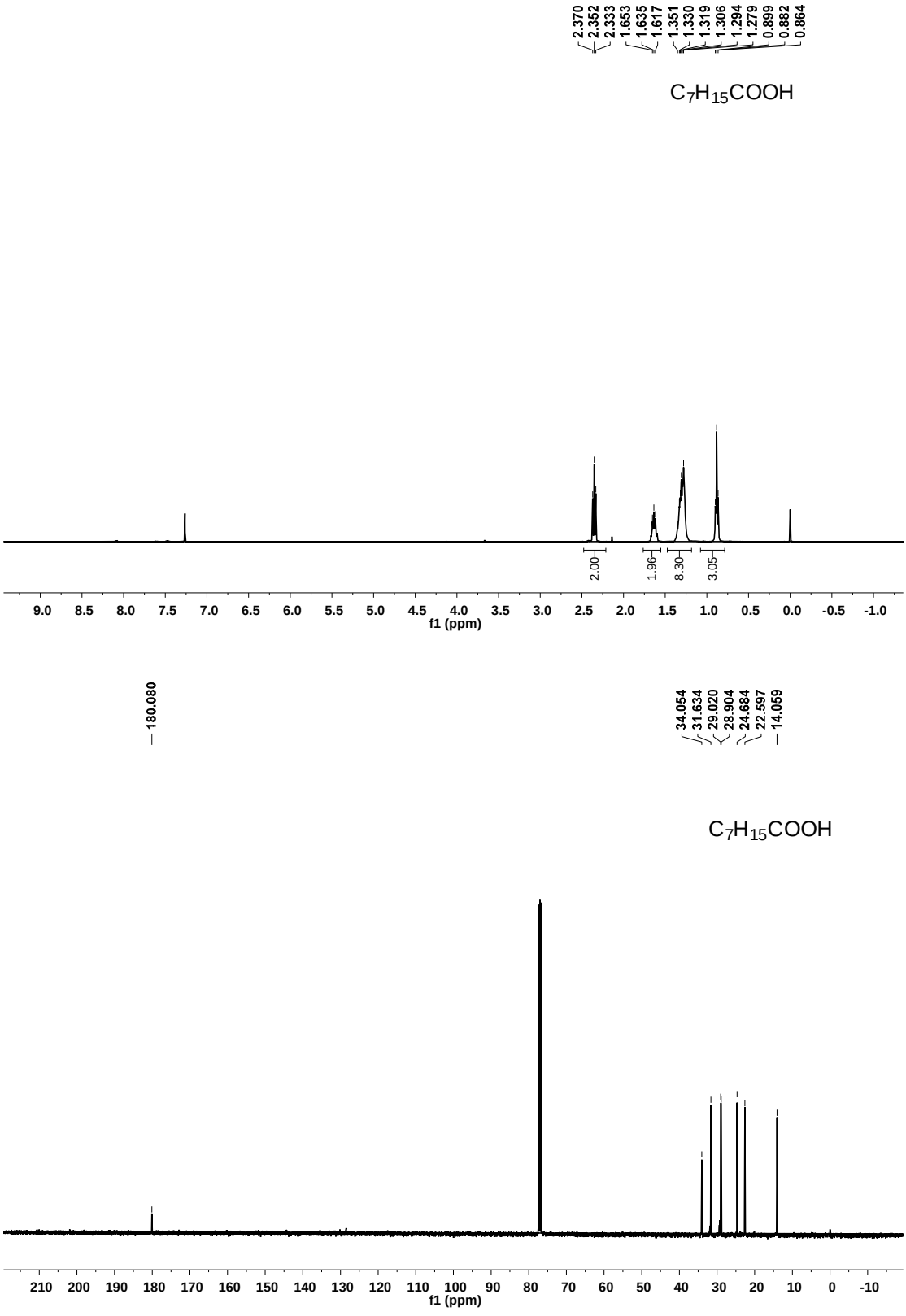
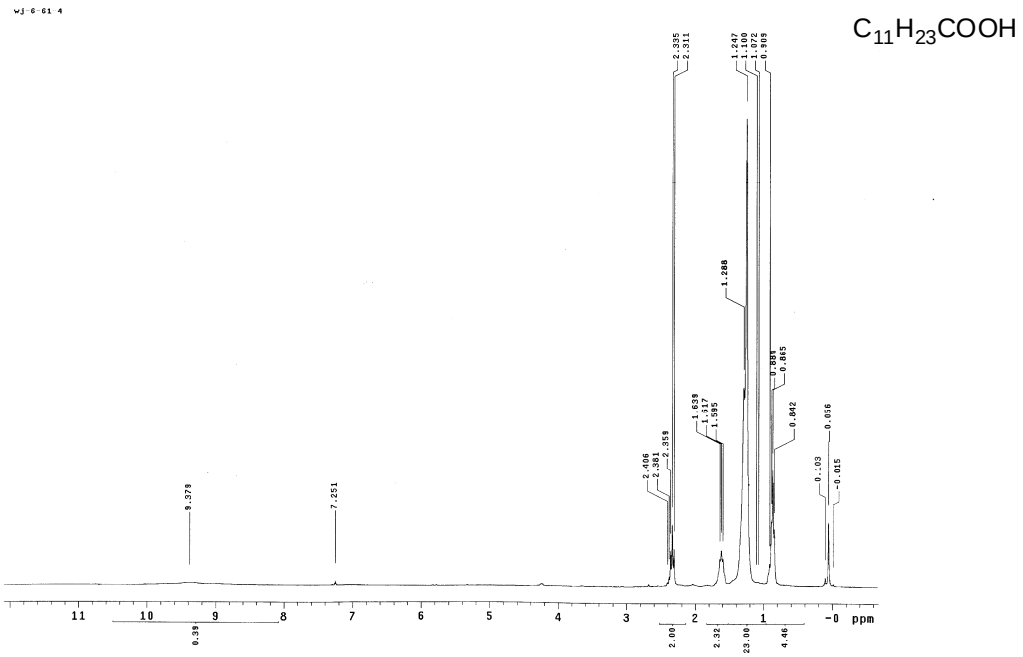
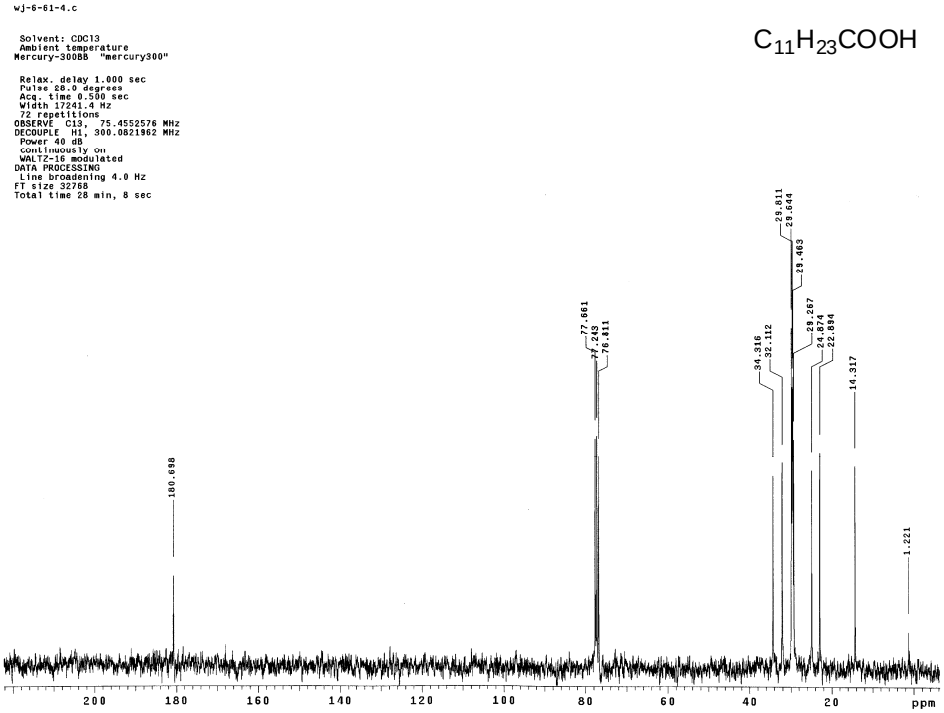


2k





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