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Diazaphosphinyl Radical-catalyzed Deoxygenation of α-Carboxy Ketones: A New Protocol for Chemo-selective C-O Bond Scission via Mechanism Regulation

Jingjing Zhang,[1] Jin-Dong Yang,[1]* Jin-Pei Cheng[1,2]*

[1]Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing 100084, China.

[2]State Key Laboratory of Elemento-organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

Content

1. General information.

Chemical: Unless otherwise noted, all commercially available compounds were used as received without further purification. Toluene was purchased from J&K Chemical (99.9%, extra dry, water < 30 ppm, J&K seal) and used without further purification. Other solvents were distilled by standard solvent treatment methods. Flash chromatography was performed to purify the products. Reaction temperature refers to temperature of an aluminum heating block or a silicon oil bath, which was controlled by an electronic temperature modulator from IKA.

Analysis: NMR spectra were acquired on NMR spectrometer with 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal. Data for ^{1}H NMR spectra were reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations were as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

2. General procedure for synthesis of substrates.

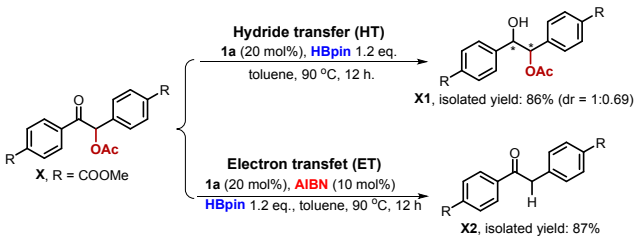
General procedure A: A mixture of benzoin (1.0 equiv) and pyridine (2.0 equiv) was heated up to 100 °C and stirred for 5 minutes to give a clear solution. The reaction mixture was then cooled to 0 °C and acetylchloride (or pivaloyl chloride, 2.0 equiv) was added slowly. The resulting mixture was stirred again at 100 °C for 5 minutes and then cooled to room temperature. After stirring for another 30 minutes the reaction mixture was dissolved in DCM and washed with 2 M H_2SO_4, a saturated aqueous solution of $NaHCO_3$ and brine. The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/EtOAc = 10 : 1) to afford the corresponding acetylated benzoin.

General procedure B: To a mixture of the carboxylic acid (1.0 equiv) and 2-bromo acetophenone (1.1 equiv) in acetone, DIPEA (5.0 equiv) was added. The mixture was stirred at room temperature overnight. The mixture was poured into ethyl acetate (20 mL) and washed with water (3 × 30 mL). The organic layer was dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/EtOAc = 3 : 1) to afford the protected carboxylic acids.

General procedure C (C-O bond activation): **2** (0.4 mmol), AIBN (0.04 mmol), **1a** (0.08 mmol), HBpin (0.48 mmol) and toluene (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 ^{o}C. After 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum and the crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20 : 1) to afford the corresponding products **3** of C-O bond activation.

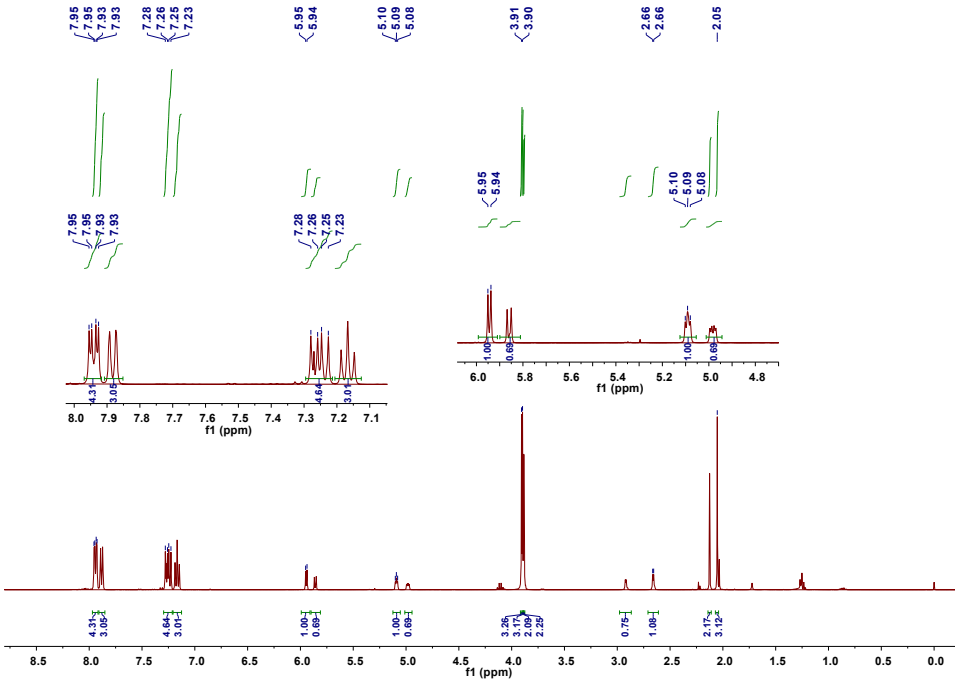
General procedure D (deprotection): **4** (0.4 mmol), AIBN (0.04 mmol), **1a** (0.08 mmol), HBpin (0.48 mmol) and toluene (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 ^{o}C. After 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum. The crude product was dissolved in CH_3CN (5 mL) and 0.1 M HCl aqueous solution (1 mL) was added. After stirring 30 minutes, the resulting mixture was concentrated under vacuum and purified by flash column chromatography (petroleum ether/EtOAc = 2 : 1) to afford the corresponding deprotected products **5**.

3. Procedure for chemo-selective reduction.



(1) ***Hydride reduction:*** **X** (0.4 mmol), **1a** (0.08 mmol), HBpin (0.48 mmol) and toluene (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 °C. After 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum and the crude product was hydrolyzed with 1 M NaOH aqueous solution (2 mL) about 30 min, and the mixture was extracted with diethylether and purified by flash column chromatography (petroleum ether/EtOAc = 10 : 1) to afford the corresponding product **X1** of carbonyl reduction. The NMR data of **X1** were shown below.
(2) ***Electron reduction:*** **X** (0.4 mmol), AIBN (0.04 mmol), **1a** (0.08 mmol), HBpin (0.48 mmol) and toluene (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 °C. After 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum and the crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20 : 1) to afford the corresponding product **X2** of C-O bond activation.

X1: **^{1}H NMR** (400 MHz, $CDCl_3$) **Major isomer**: δ 7.94 (dd, *J* = 8.3, 3.3 Hz, 4H), 7.25 (dd, *J* = 13.0, 8.3 Hz, 4H), 5.94 (d, *J* = 5.3 Hz, 1H), 5.12 – 5.05 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.66 (d, *J* = 3.7 Hz, 1H), 2.05 (s, 3H). **Minor isomer:** δ 7.88 (d, *J* = 7.4 Hz, 4H), 7.17 (t, *J* = 8.0 Hz, 4H), 5.86 (d, *J* = 7.1 Hz, 1H), 4.98 (dd, *J* = 7.0, 3.2 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.91 (t, *J* = 4.1 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.96, 169.73, 166.82, 166.72, 166.70, 166.60, 144.18, 143.73, 141.44, 140.92, 130.12, 130.08, 129.97, 129.90, 129.53, 129.46, 129.40, 127.61, 127.21, 127.01, 126.84, 79.33, 78.27, 76.42, 75.70, 52.20, 52.18, 21.05, 20.98.



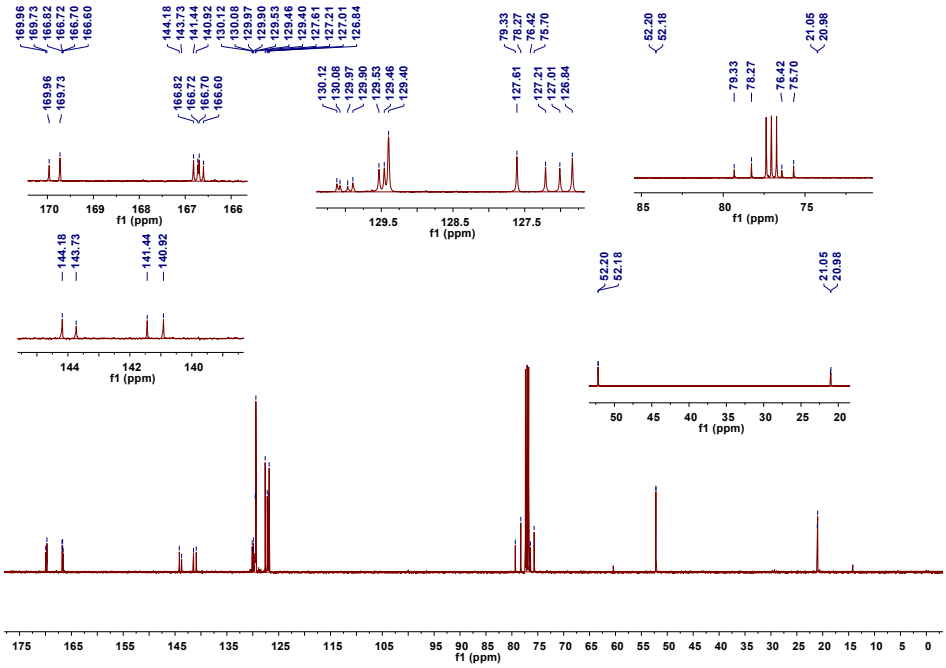
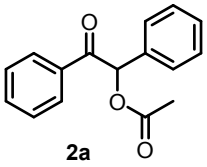


Figure S1: The ^{1}H NMR and ^{13}C NMR spectra of **X1**.

4. Representative experimental data for acetylated benzoin derivatives.[1]

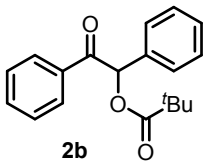
2-Oxo-1,2-diphenylethyl acetate (**2a**):



2a

According to ***General Procedure A*** using benzoin (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 11.4 g (44.8 mmol, 90%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.52 (dd, *J* = 16.0, 7.7 Hz, 3H), 7.39 (ddd, *J* = 19.1, 11.8, 7.1 Hz, 5H), 6.90 (s, 1H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.73, 170.46, 134.64, 133.64, 133.48, 129.35, 129.15, 128.81, 128.72, 128.65, 77.68, 20.79. **HRMS** calculated for $C_{16}H_{14}O_3Na$ (M+Na): 277.0835, found: 277.0837.

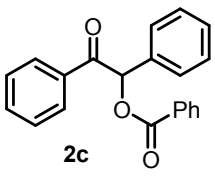
2-Oxo-1,2-diphenylethyl pivalate (**2b**):



2b

According to ***General Procedure B*** using benzoin (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 14.2 g (48.0 mmol, 96%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.43 (m, 3H), 7.43 – 7.30 (m, 5H), 6.79 (s, 1H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.31, 178.03, 134.92, 133.87, 133.33, 129.02, 128.96, 128.77, 128.58, 128.28, 77.30, 38.74, 27.09. **HRMS** calculated for $C_{19}H_{20}O_3Na$ (M+Na): 319.1305, found: 319.1309.

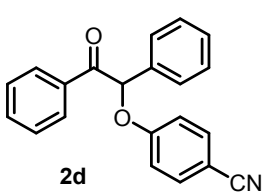
2-Oxo-1,2-diphenylethyl benzoate (**2c**):



2c

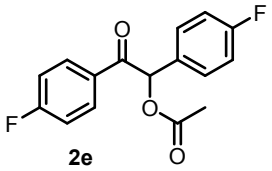
According to ***General Procedure B*** using benzoin (50 mmol, 1.0 equiv) and benzoic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 14.2 g (48.0 mmol, 96%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.11 – 7.99 (m, 2H), 7.66 – 7.52 (m, 4H), 7.51 – 7.38 (m, 7H), 7.13 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.71, 166.03, 134.79, 133.82, 133.48, 133.36, 130.01, 129.45, 129.32, 129.14, 128.87, 128.68, 128.41,

77.95. **HRMS** calculated for $C_{21}H_{16}O_3Na$ (M+Na): 339.0992, found: 339.0991.


2d

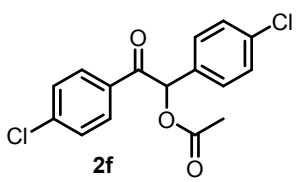
According to ***General Procedure A*** using benzoin (50 mmol, 1.0 equiv) and 4-hydroxybenzonitrile (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 15.2 g (48.5 mmol, 97%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.64 – 7.51 (m, 5H), 7.51 – 7.36 (m, 5H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.50 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.40, 160.70, 134.18, 134.09, 133.97, 129.33, 129.26, 129.11, 128.84, 127.67, 118.88, 116.22, 105.06, 82.44.

1,2-Bis(4-fluorophenyl)-2-oxoethyl acetate (**2e**):


2e

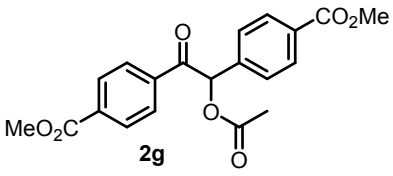
According to ***General Procedure A*** using 1,2-bis(4-fluorophenyl)-2-hydroxyethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 10.5 g (45.5 mmol, 91%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.91 (m, 2H), 7.53 – 7.39 (m, 2H), 7.18 – 6.96 (m, 4H), 6.83 (s, 1H), 2.20 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.65, -111.33. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.11, 170.36, 165.86 (d, *J* = 256.1 Hz), 163.23 (d, *J* = 249.4 Hz), 131.46 (d, *J* = 9.5 Hz), 130.87 (d, *J* = 2.9 Hz), 130.57 (d, *J* = 8.5 Hz), 129.42 (d, *J* = 3.2 Hz), 116.26 (d, *J* = 21.8 Hz), 115.94 (d, *J* = 22.0 Hz), 76.61, 20.64.

1,2-Bis(4-chlorophenyl)-2-oxoethyl acetate (**2f**):


2f

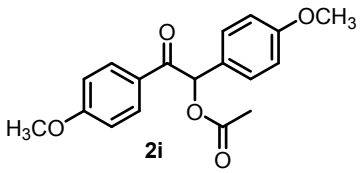
According to ***General Procedure A*** using 1,2-bis(4-fluorophenyl)-2-hydroxyethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 10.2 g (45.5 mmol, 77%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.31 (m, 6H), 6.80 (s, 1H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.39, 170.27, 140.19, 135.61, 132.74, 131.86, 130.12, 129.92, 129.45, 129.11, 76.65, 20.68. **HRMS** calculated for $C_{16}H_{12}Cl_2O_3Na$ (M+Na): 345.0056, found: 345.0059.

Dimethyl 4,4'-(1-acetoxy-2-oxoethane-1,2-diyl)dibenzoate (**2g**):


2g

According to ***General Procedure A*** using 2-hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 12.2 g (39.1 mmol, 78%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 6.88 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.20, 170.28, 166.26, 165.88, 137.71, 137.70, 134.33, 131.11, 130.36, 129.89, 128.64, 128.47, 77.22, 52.53, 52.32, 20.68. **HRMS** calculated for $C_{20}H_{17}O_7$ (M-H): 369.0980, found: 369.0975.

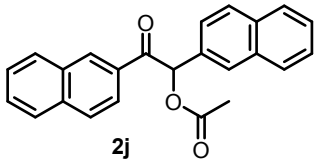
1,2-Bis(4-methoxyphenyl)-2-oxoethyl acetate (**2i**):


2i

According to ***General Procedure A*** using 2-hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 7.8 g

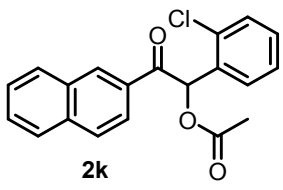
(30.4 mmol, 61%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.93 – 6.87 (m, 3H), 6.85 (d, *J* = 9.8 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.12, 170.51, 163.69, 160.30, 131.11, 130.15, 127.50, 126.12, 114.55, 113.86, 77.02, 55.42, 55.25, 20.83. **HRMS** calculated for $C_{18}H_{18}O_5$ (M+Na): 337.1046, found: 337.1043.

1,2-Di(naphthalen-2-yl)-2-oxoethyl acetate (**2j**):


2j

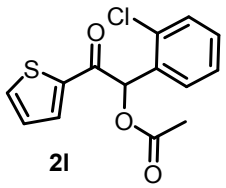
According to ***General Procedure A*** using 2-hydroxy-1,2-di(naphthalen-2-yl)ethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 9.3 g (31.4 mmol, 63%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.13 – 8.03 (m, 2H), 7.96 – 7.78 (m, 6H), 7.70 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.63 – 7.47 (m, 4H), 7.29 (d, *J* = 4.5 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.81, 170.58, 135.69, 133.54, 133.31, 132.35, 132.08, 131.22, 130.80, 129.69, 129.18, 128.78, 128.68, 128.63, 128.25, 127.76, 127.75, 126.97, 126.87, 126.63, 125.58, 124.25, 77.89, 20.91. **HRMS** calculated for $C_{24}H_{18}O_3Na$ (M+Na): 377.1148, found: 377.1144.

1-(2-Chlorophenyl)-2-(naphthalen-2-yl)-2-oxoethyl acetate (**2k**):


2k

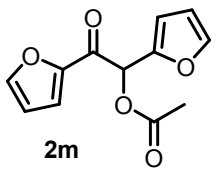
According to ***General Procedure A*** using 2-(2-chlorophenyl)-2-hydroxy-1-(naphthalen-2-yl)ethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 10.1 g (36.1 mmol, 72%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.01 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.82 (m, 2H), 7.65 – 7.52 (m, 3H), 7.48 (ddd, *J* = 12.6, 7.8, 1.4 Hz, 2H), 7.28 (dtd, *J* = 22.6, 7.5, 1.4 Hz, 2H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.33, 170.20, 135.83, 134.06, 132.36, 131.89, 131.63, 130.81, 130.71, 130.42, 130.21, 129.81, 128.88, 128.64, 127.74, 127.60, 126.88, 123.99, 73.80, 20.68.

1-(2-Chlorophenyl)-2-oxo-2-(thiophen-2-yl)ethyl acetate (**2l**):


2l

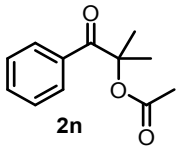
According to ***General Procedure A*** using 2-(2-chlorophenyl)-2-hydroxy-1-(naphthalen-2-yl)ethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 9.5 g (40.3 mmol, 81%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.9, 1.0 Hz, 1H), 7.66 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.49 (ddd, *J* = 7.6, 5.7, 1.6 Hz, 2H), 7.37 – 7.26 (m, 2H), 7.22 (s, 1H), 7.10 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.15, 170.04, 140.87, 134.80, 134.05, 133.04, 131.97, 130.87, 130.42, 130.11, 128.37, 127.59, 73.90, 20.61.

1,2-Di(furan-2-yl)-2-oxoethyl acetate (**2m**):


2m

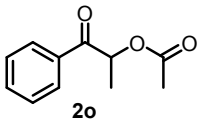
According to ***General Procedure A*** using 1,2-di(furan-2-yl)-2-hydroxyethan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 7.5 g (42.6 mmol, 85%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.46 (dd, *J* = 1.8, 0.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.78 (s, 1H), 6.55 – 6.50 (m, 2H), 6.40 (dd, *J* = 3.3, 1.9 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.65, 170.03, 150.23, 147.18, 146.55, 144.20, 119.17, 112.50, 111.70, 111.05, 70.39, 20.55.

2-Methyl-1-oxo-1-phenylpropan-2-yl acetate (**2n**):


2n

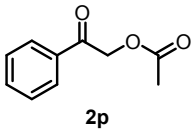
According to ***General Procedure A*** using 2-hydroxy-2-methyl-1-phenylpropan-1-one (50 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 10:1): 7.3 g (49.3 mmol, 99%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.57 – 7.48 (m, 1H), 7.47 – 7.38 (m, 2H), 1.95 (s, 3H), 1.74 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.10, 170.05, 134.63, 132.42, 128.43, 128.36, 84.26, 25.36, 21.38.

1-oxo-1-phenylpropan-2-yl acetate (**2o**):


2o

The substrate was synthesized according to the reference.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.98 (q, *J* = 7.0 Hz, 1H), 2.15 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.84, 170.36, 134.41, 133.54, 128.76, 128.43, 71.41, 20.71, 17.13.

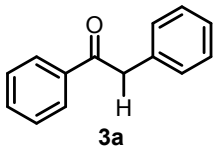
2-oxo-2-phenylethyl acetate (**2p**):


2p

The substrate was synthesized according to the reference.[3] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 5.35 (s, 2H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.15, 170.38, 134.23, 133.87, 128.85, 127.74, 66.02, 20.55.

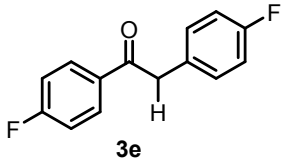
5. Experimental data for deoxygenation of acetylated benzoin derivatives.[1]

1,2-Diphenylethan-1-one (**3a**):


3a

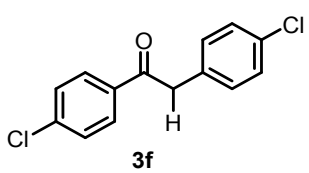
According to ***General Procedure C*** using 102 mg **2a** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 73 mg (0.37 mmol, 92%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.62 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 7.42 – 7.24 (m, 5H), 4.33 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.65, 136.64, 134.58, 133.18, 129.49, 128.70, 128.66, 128.64, 126.91, 45.53.

1,2-Bis(4-fluorophenyl)ethan-1-one (**3e**):


3e

According to ***General Procedure C*** using 116 mg **2e** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 90.5 mg (0.39 mmol, 99%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 7.97 (m, 2H), 7.24 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 4.26 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.74, -115.79. ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.77, 165.82 (d, *J* = 255.2 Hz), 161.94 (d, *J* = 245.4 Hz), 132.88 (d, *J* = 2.9 Hz), 131.22, 131.13, 131.05, 130.97, 129.98 (d, *J* = 3.3 Hz), 44.46. **HRMS** calculated for $C_{14}H_9F_2O$ (M-H): 231.0627, found: 231.0630.

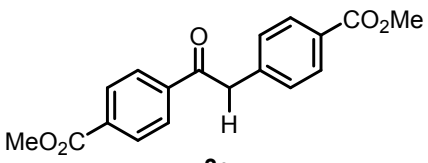
1,2-Bis(4-chlorophenyl)ethan-1-one (**3f**):


3f

According to ***General Procedure C*** using 129 mg **2f** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 103 mg (0.39 mmol, 99%) colorless crystals. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 4.25 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.89, 139.88, 134.65, 133.05, 132.54, 130.82, 129.93, 129.07, 128.89, 44.71.

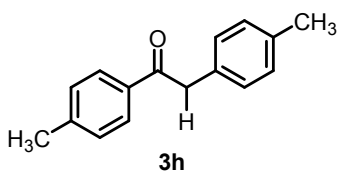
Dimethyl 4,4'-(1-oxoethane-1,2-diyl)dibenzoate (**3g**):



3g

According to ***General Procedure C*** using 148 mg **2g** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 109 mg (0.35 mmol, 87%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 8.02 (dd, *J* = 12.3, 8.3 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.37 (s, 2H), 3.95 (s, 3H), 3.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.30, 166.80, 166.07, 139.60, 139.19, 134.18, 130.01, 129.95, 129.61, 129.10, 128.42, 52.49, 52.09, 45.69. **HRMS** calculated for $C_{18}H_{16}O_5Na$ (M+Na): 335.0890, found: 335.0897.

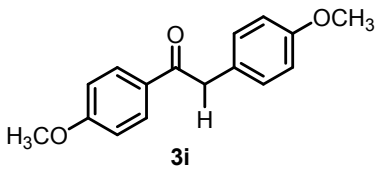
1,2-Di-p-tolylethan-1-one (**3h**):



3h

According to ***General Procedure C*** using 113 mg **2h** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 65 mg (0.29 mmol, 72%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.20 – 7.15 (m, 4H), 4.25 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.53, 143.93, 136.41, 134.12, 131.68, 129.39, 129.32, 129.30, 128.79, 45.09, 21.69, 21.11. **HRMS** calculated for $C_{16}H_{16}ONa$ (M+Na): 247.1093, found: 247.1096.

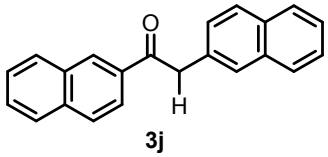
1,2-Bis(4-methoxyphenyl)ethan-1-one (**3i**):



3i

According to ***General Procedure C*** using 126 mg **2i** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 77 mg (0.30 mmol, 75%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.19 (s, 2H), 3.88 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.52, 163.47, 158.47, 130.92, 130.36, 129.68, 126.97, 114.13, 113.77, 55.46, 55.25, 44.39.

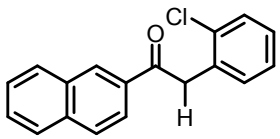
1,2-Di(naphthalen-2-yl)ethan-1-one (**3j**):



3j

According to ***General Procedure C*** using 142 mg **2j** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 95 mg (0.32 mmol, 80%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.09 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.72 (m, 6H), 7.61 – 7.52 (m, 2H), 7.50 – 7.40 (m, 3H), 4.57 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.68, 135.63, 133.96, 133.59, 132.52, 132.40, 132.26, 130.48, 129.66, 128.61, 128.59, 128.37, 128.15, 127.80, 127.69, 127.66, 127.63, 126.83, 126.14, 125.77, 124.30, 45.77.

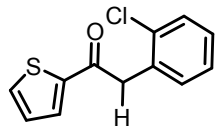
2-(2-Chlorophenyl)-1-(naphthalen-2-yl)ethan-1-one (**3k**):



3k

According to ***General Procedure C*** using 135 mg **2k** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 70 mg (0.25 mmol, 62%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.12 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.98 – 7.89 (m, 2H), 7.70 – 7.56 (m, 2H), 7.46 (dd, *J* = 5.3, 3.9 Hz, 1H), 7.38 – 7.22 (m, 3H), 4.61 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.38, 135.70, 134.47, 133.90, 133.24, 132.53, 131.70, 130.15, 129.67, 129.57, 128.62, 128.60, 127.82, 126.97, 126.86, 124.05, 43.31.

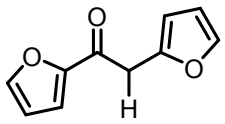
2-(2-Chlorophenyl)-1-(thiophen-2-yl)ethan-1-one (**3l**):



3l

According to ***General Procedure C*** using 118 mg **2l** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 61 mg (0.26 mmol, 65%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.8 Hz, 1H), 7.68 (d, *J* = 4.9 Hz, 1H), 7.43 (dd, *J* = 5.6, 3.7 Hz, 1H), 7.34 (dd, *J* = 5.9, 3.4 Hz, 1H), 7.27 (dt, *J* = 4.8, 3.7 Hz, 2H), 7.21 – 7.13 (m, 1H), 4.40 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.22, 143.76, 134.42, 134.02, 132.69, 132.43, 131.66, 129.54, 128.67, 128.20, 126.96, 43.72.

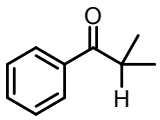
1,2-Di(furan-2-yl)ethan-1-one (**3m**):



3m

According to ***General Procedure C*** using 118 mg **2m** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 61 mg (0.26 mmol, 65%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.41 – 7.34 (m, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.34 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.26 (dd, *J* = 3.2, 0.6 Hz, 1H), 4.16 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.81, 152.01, 147.74, 146.81, 142.13, 118.23, 112.47, 110.69, 108.38, 38.21. **HRMS** calculated for $C_{10}H_8O_3Na$ (M+Na): 199.0366, found:199.0370.

2-Methyl-1-phenylpropan-1-one (**3n**):

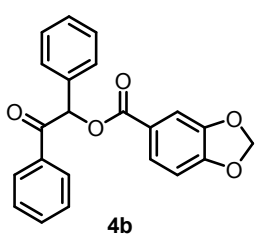


3n

According to ***General Procedure C*** using 82 mg **2n** (0.40 mmol, 1.0 equiv) and equivalent **1a** (0.4 mmol): yield after column chromatography (silica gel, petroleum ether/EtOAc = 20:1): 31 mg (0.21 mmol, 52%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.62 – 7.53 (m, 1H), 7.53 – 7.42 (m, 2H), 3.58 (hept, *J* = 6.8 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.48, 136.24, 132.77, 128.60, 128.31, 35.36, 19.15.

6. Experimental data for desyl protected carboxylic acids.[4]

2-Oxo-1,2-diphenylethyl benzo[d][1,3]dioxole-5-carboxylate (**4b**):



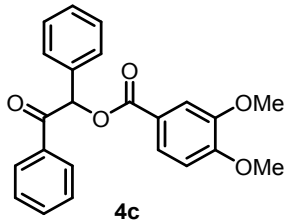
4b

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and benzo[*d*][1,3]dioxole-5-carboxylic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 16.6 g (46 mmol, 92%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 2H), 7.78 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.70 – 7.50 (m, 4H), 7.50 – 7.34 (m, 5H), 7.10 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.82, 165.35, 152.03, 147.77, 134.79, 133.86, 133.48, 129.30, 129.14, 128.86, 128.67, 126.01, 123.37, 109.84, 108.06, 101.86, 77.89. **HRMS** calculated for

$C_{22}H_{16}O_5Na$ (M+Na): 383.0890, found:383.0892.

The NMR spectroscopic data are in good agreement with those in the literature.[5]

2-Oxo-1,2-diphenylethyl 3,4-dimethoxybenzoate (**4c**):

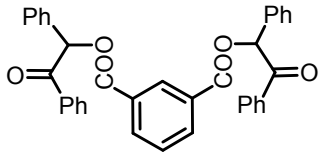


4c

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and 3,4-dimethoxybenzoic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 18.4 g (49 mmol, 98%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 3H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.42 (dt, *J* = 15.6, 7.9 Hz, 5H), 7.10 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.97, 165.88, 153.39, 148.65, 134.76, 133.86, 133.52, 129.30, 129.15, 128.87, 128.69, 124.25, 121.79, 112.23, 110.27, 77.83, 56.07, 56.01.

The NMR spectroscopic data are in good agreement with those in the literature.[5]

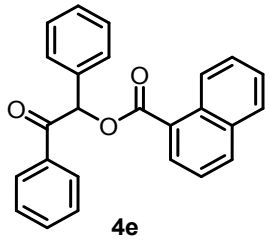
Bis(2-oxo-1,2-diphenylethyl) isophthalate (**4d**):



4d

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and isophthalic acid (30 mmol, 0.6 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 13.1 g (24 mmol, 96%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 1.4 Hz, 1H), 8.36 (dd, *J* = 7.8, 1.7 Hz, 2H), 8.07 – 7.99 (m, 4H), 7.65 – 7.50 (m, 7H), 7.48 – 7.36 (m, 10H), 7.14 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.41, 165.12, 134.64, 134.60, 133.58, 133.49, 133.48, 131.61, 129.99, 129.43, 129.22, 128.87, 128.79, 128.72, 78.42.

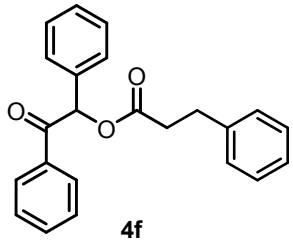
2-Oxo-1,2-diphenylethyl 1-naphthoate (**4e**):



4e

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and 1-naphthoic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 17.6 g (48 mmol, 96%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.7 Hz, 1H), 8.39 (dd, *J* = 7.3, 0.9 Hz, 1H), 8.05 (t, *J* = 8.0 Hz, 3H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.34 (m, 11H), 7.23 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.96, 166.97, 134.76, 133.84, 133.79, 133.70, 133.59, 131.49, 130.95, 129.39, 129.22, 128.92, 128.81, 128.76, 128.53, 127.92, 126.28, 125.83, 124.58, 78.14. **HRMS** calculated for $C_{25}H_{18}O_3Na$ (M+Na): 389.1148, found:389.1150.

2-Oxo-1,2-diphenylethyl 3-phenylpropanoate (**4f**):



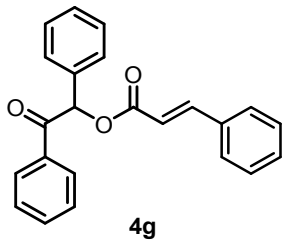
4f

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and 3-phenylpropanoic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 16.9 g (49 mmol, 98%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 3H), 6.92 (s, 1H), 3.06 (dd, *J* = 11.9, 4.4 Hz, 2H), 2.95 – 2.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.79, 172.37, 140.35, 134.70, 133.65, 133.49, 129.32, 129.13, 128.83, 128.69, 128.67,

128.52, 128.33, 126.28, 77.66, 35.56, 30.79.

The NMR spectroscopic data are in good agreement with those in the literature.[4]

2-Oxo-1,2-diphenylethyl cinnamate (**4g**):

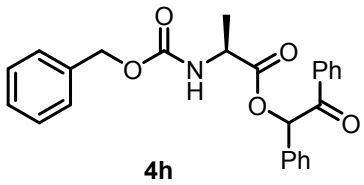


4g

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and cinnamic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 16.8 g (49 mmol, 98%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.82 (d, *J* = 16.0 Hz, 1H), 7.56 (ddd, *J* = 9.1, 7.7, 1.3 Hz, 5H), 7.51 – 7.32 (m, 8H), 7.05 (s, 1H), 6.63 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.82, 166.28, 146.17, 134.76, 134.29, 133.83, 133.48, 130.51, 129.35, 129.17, 128.90, 128.87, 128.77, 128.67, 128.26, 117.18, 77.65. **HRMS** calculated for $C_{23}H_{18}O_3Na$ (M+Na): 365.1148, found: 365.1145.

The NMR spectroscopic data are in good agreement with those in the literature.[4]

2-Oxo-1,2-diphenylethyl ((benzyloxy)carbonyl)-L-alaninate (**4h**):

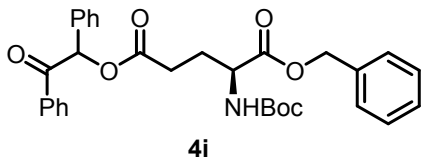


4h

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and ((benzyloxy)carbonyl)-L-alanine (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 20.4 g (49 mmol, 98%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 4.9 Hz, 2H), 7.60 – 7.29 (m, 13H), 6.91 (s, 1H), 5.50 – 5.26 (m, 1H), 5.24 – 5.03 (m, 2H), 4.71 – 4.43 (m, 1H), 1.56 (dd, *J* = 53.3, 6.9 Hz, 3H).

The NMR spectroscopic data are in good agreement with those in the literature.[4]

1-Benzyl 5-(2-oxo-1,2-diphenylethyl) (tert-butoxycarbonyl)-L-glutamate (**4i**):



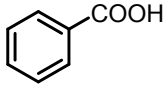
4i

According to ***General Procedure B*** using 2-bromo-1,2-diphenylethan-1-one (50 mmol, 1.0 equiv) and (S)-5-(benzyloxy)-4-((tert-butoxycarbonyl)amino)-5-oxopentanoic acid (55 mmol, 1.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 5:1): 26.0 g (49 mmol, 98%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.43 – 7.27 (m, 10H), 6.85 (d, *J* = 4.1 Hz, 1H), 5.31 – 5.06 (m, 3H), 4.47 – 4.32 (m, 1H), 2.68 – 2.42 (m, 2H), 2.37 – 2.19 (m, 1H), 2.12 – 1.93 (m, 1H), 1.42 – 1.40 (m, 9H).

The NMR spectroscopic data are in good agreement with those in the literature.[4]

7. Experimental data for deprotected carboxylic acids.[4]

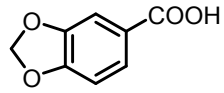
Benzoic acid (**5a**):



5a

According to ***General Procedure D*** using 126 mg **4a** (or **2c**) (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 48 mg (0.40 mmol, 99%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 8.21 – 8.12 (m, 2H), 7.70 – 7.61 (m, 1H), 7.57 – 7.44 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.58, 133.85, 130.24, 129.36, 128.50.

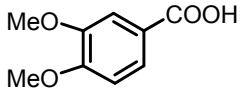
Benzo[*d*][1,3]dioxole-5-carboxylic acid (**5b**):



5b

According to ***General Procedure D*** using 114 mg **4b** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 56 mg (0.34 mmol, 84%) colorless crystals. **^{1}H NMR** (400 MHz, DMSO) δ 12.66 (s, 1H), 7.55 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.37 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.13 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 167.06, 151.58, 147.92, 125.41, 125.12, 109.24, 108.52, 102.39.

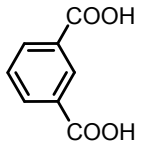
3,4-Dimethoxybenzoic acid (**5c**):



5c

According to ***General Procedure D*** using 150 mg **4c** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 55 mg (0.30 mmol, 74%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.97 (s, 3H), 3.97 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.11, 153.77, 148.70, 124.61, 121.74, 112.35, 110.35, 56.06, 56.01.

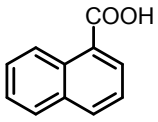
Isophthalic acid (**5d**):



5d

According to ***General Procedure D*** using 222 mg **4d** (0.40 mmol, 1.0 equiv) and HBpin (0.84 mmol, 2.1 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 61 mg (0.37 mmol, 92%) colorless crystals. **^{1}H NMR** (400 MHz, DMSO) δ 13.31 (s, 2H), 8.50 (s, 1H), 8.18 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 167.06, 133.82, 131.72, 130.42, 129.58.

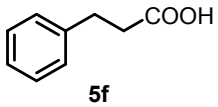
1-Naphthoic acid (**5e**):



5e

According to ***General Procedure D*** using 146 mg **4e** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 58 mg (0.34 mmol, 85%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 8.7 Hz, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.60 (dt, *J* = 13.7, 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.43, 134.71, 133.95, 131.93, 131.66, 128.75, 128.15, 126.36, 125.94, 125.59, 124.57.

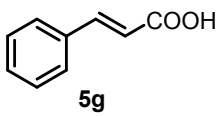
3-Phenylpropanoic acid (**5f**):



5f

According to ***General Procedure D*** using 138 mg **4f** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 60 mg (0.40 mmol, 99%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.29 (dd, *J* = 9.5, 5.5 Hz, 2H), 7.21 (t, *J* = 6.3 Hz, 3H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.61, 140.17, 128.61, 128.31, 126.43, 35.71, 30.60.

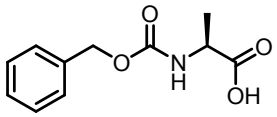
Cinnamic acid (**5g**):



5g

According to ***General Procedure D*** using 137 mg **4g** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 41 mg (0.28 mmol, 71%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.0 Hz, 1H), 7.57 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.42 (dd, *J* = 4.9, 1.6 Hz, 3H), 6.48 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.73, 147.16, 134.03, 130.80, 128.99, 128.42, 117.35.

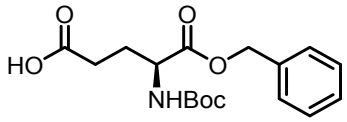
((Benzyloxy)carbonyl)-L-alanine (**5h**):



5h

According to ***General Procedure D*** using 167 mg **4h** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 80 mg (0.36 mmol, 90%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.37 (t, *J* = 4.1 Hz, 5H), 5.44 (d, *J* = 7.5 Hz, 1H), 5.23 – 5.06 (m, 2H), 4.63 – 4.10 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H).

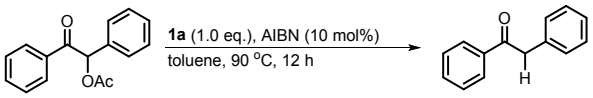
(S)-5-(Benzyloxy)-4-((tert-butoxycarbonyl)amino)-5-oxopentanoic acid (**5i**):



5i

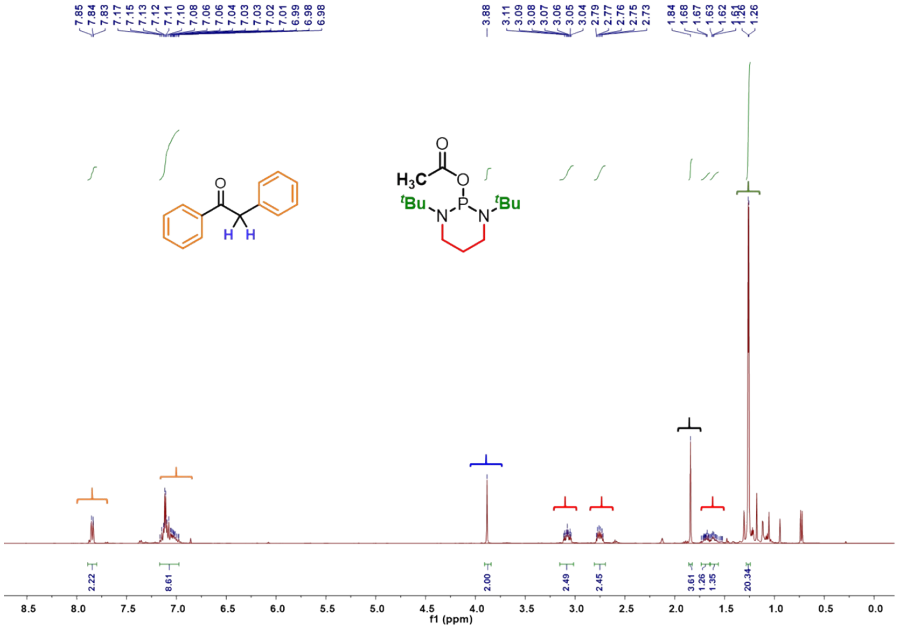
According to ***General Procedure D*** using 212 mg **4i** (0.40 mmol, 1.0 equiv): yield after column chromatography (silica gel, petroleum ether/EtOAc = 2:1): 121 mg (0.36 mmol, 91%) colorless crystals. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.37 (s, 5H), 5.32 – 5.13 (m, 3H), 4.36 (t, *J* = 39.5 Hz, 1H), 2.62 – 2.36 (m, 2H), 2.22 (dd, *J* = 13.1, 6.0 Hz, 1H), 2.09 – 1.85 (m, 1H), 1.45 (s, 9H).

8. Noncatalytic C-O bond activation of 2a using equivalent 1a as the reductant.



2a **3a**, isolated yield: 99%

2a (0.4 mmol), AIBN (0.04 mmol), **1a** (0.4 mmol) and toluene (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 °C. After 3 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum and the crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20 : 1) to afford the corresponding products **3a** (78 mg, 0.4 mmol). The ^{1}H NMR and ^{31}P NMR spectra were shown below:



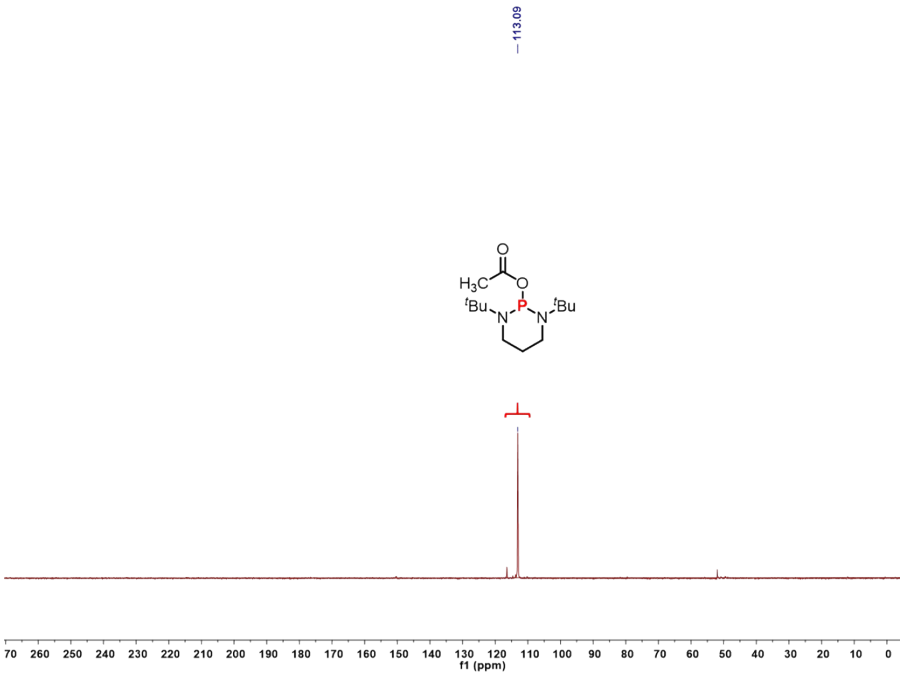
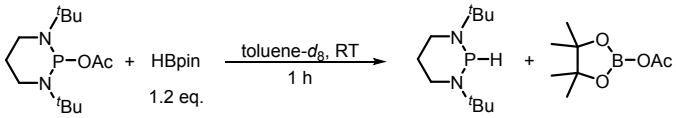


Figure S2: The ^{1}H NMR and ^{31}P NMR spectra of the reaction mixture of **2a** with equivalent **1a**.

9. Verification of mechanism of the catalyst regeneration process.



1a-OAc **1a,** NMR yield: 91%

Step A: **2a** (0.1 mmol), AIBN (0.01 mmol), **1a** (0.1 mmol) and toluene-d_8 (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 ° for 3 hours. **2a** was completely consumed to generate **3a** and a new phosphorus specie was generated and assigned to **1a-OAc** through the analysis of ^{1}H NMR and ^{31}P NMR spectra.

Step B: HBpin (0.12 mmol, 1.2 equiv) was added to the reaction mixture of ***Step A***, and the reaction was monitored by ^{1}H NMR and ^{31}P NMR spectra at room temperature.

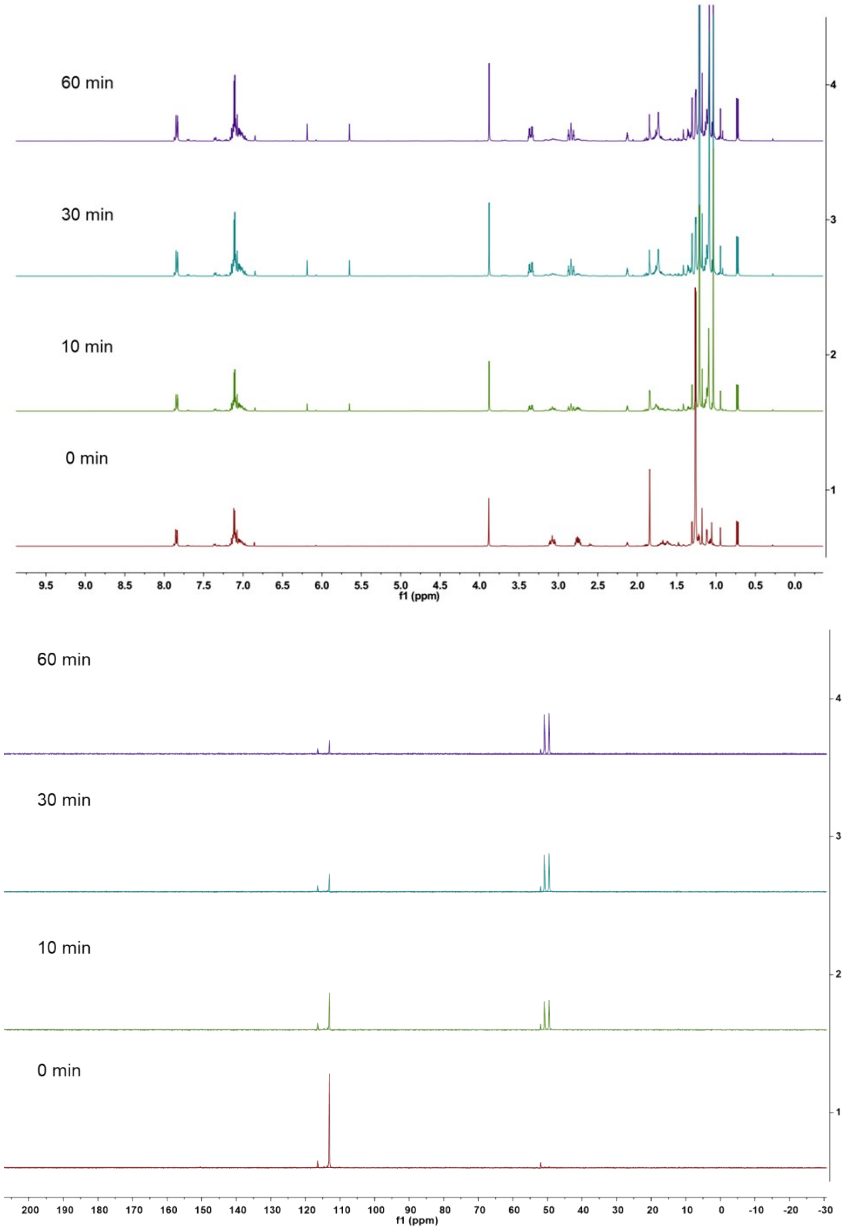
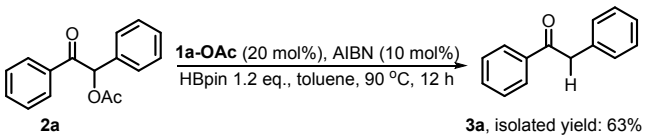


Figure S3: The monitored ^{1}H NMR and ^{31}P NMR spectra of the reaction of HBpin with **1a-OAc**.

10. Catalytic C-O bond activation of 2a using 1a-OAc as the catalyst.



2a **3a**, isolated yield: 63%

Step A: **2a** (0.02 mmol), AIBN (0.002 mmol), **1a** (0.02 mmol) and toluene-d_8 (1.0 mL) were taken in a Schlenk tube under argon. The mixture was stirred at 90 ° for 3 hours. **2a** was completely consumed to generate **3a** and a new phosphorus specie was generated and assigned to **1a-OAc** through the analysis of ^{1}H NMR and ^{31}P NMR spectra.

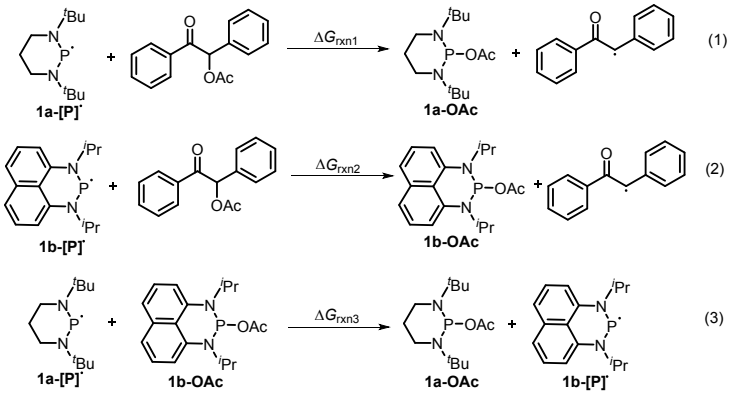
Step B: **2a** (0.1 mmol), AIBN (0.01 mmol) and HBpin (0.12 mmol) was added to the resulted mixture of ***Step A*** in the a Schlenk tube under argon. The mixture was stirred at 90 °C. After 12 hours, the reaction mixture was cooled to room temperature. The resulting mixture was concentrated under vacuum and the

crude product was purified by flash column chromatography (petroleum ether/EtOAc = 20 : 1) to afford the corresponding products **3a** (12.4 mg, 0.063 mmol).

11. DFT calculations.

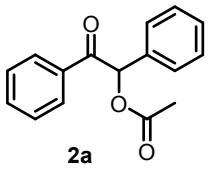
Quantum chemistry calculations were conducted by using Gaussian 09[6]. Geometry optimizations and frequency computations were performed using the M06-2X[7] density functional in conjunction with the 6-31+G(d) basis set and an ultrafine integration grid. The SMD[8] model was used to account for the solvation effects of toluene, the solvent used experimentally. All of the optimized geometries were characterized as minima or transition state structures by frequency calculations. Thermal free energy corrections were obtained at 293.15 K. To obtain more accurate electronic energies, single-point energy calculations were performed at the (SMD)-M06-2X/6-311++G(2df,2p) level with the (SMD)-M06-2X/6-31+G(d) optimized structure.

The differences of bond dissociation free energies of P-O bonds of **1a-OAc** and **1b-OAc** were calculated on the basic of reaction Gibbs free energy changes of Eq. S1-4 through DFT calculations. The P-O bond of **1b-OAc** is 0.78 kcal/mol larger than that of **1a-OAc**, however, the reaction did not work at all when **1b** was as the reductant. Therefore, the mechanism that the phosphinyl radicals abstract the oxygen atom of *O*-acetylated benzoin to perform the C-O bond activation was excluded.

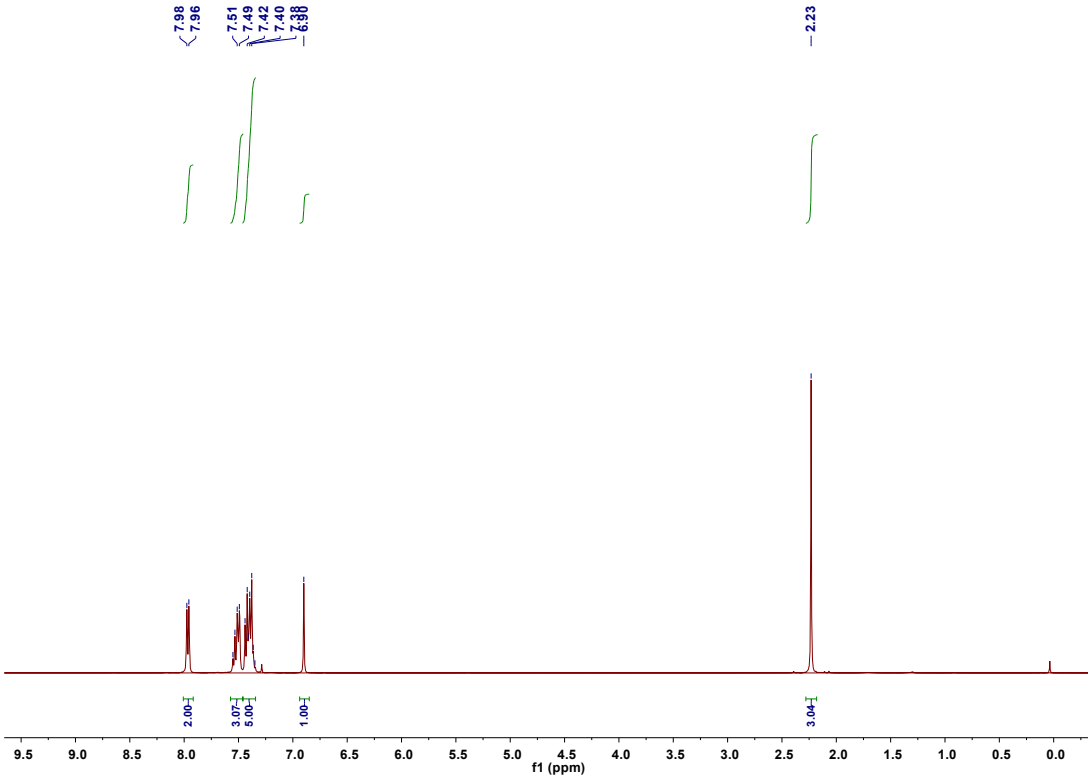


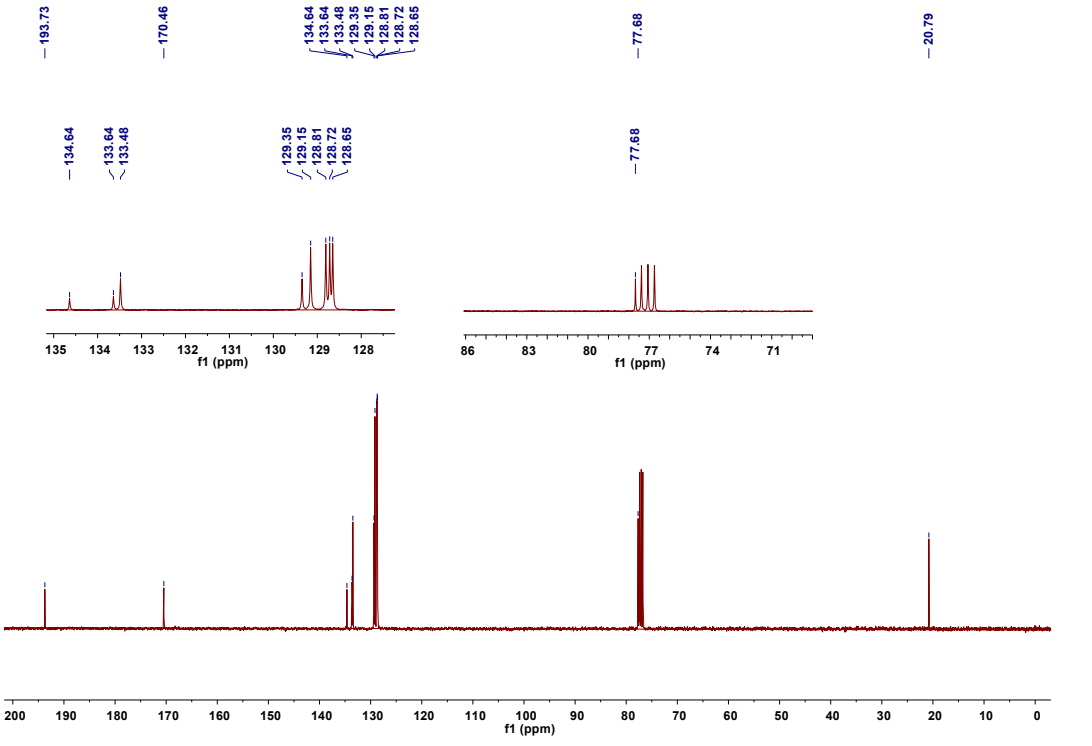
$$\Delta G_{rxn3} = \Delta G_{rxn1} - \Delta G_{rxn2} = BDFE_{\mathbf{1b\text{-}OAc}}(P\text{-}O) - BDFE_{\mathbf{1a\text{-}OAc}}(P\text{-}O) = 0.78\ kcal/mol \quad (4)$$

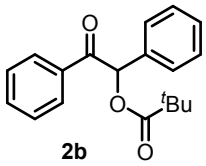
12. NMR spectra.



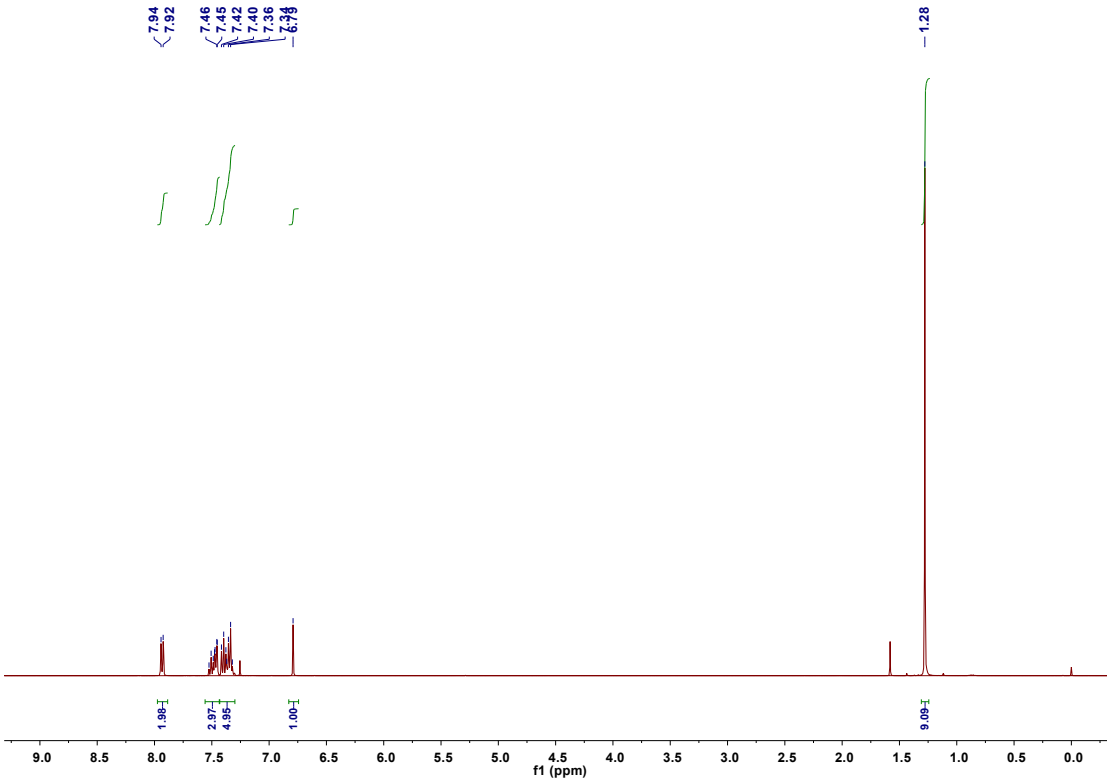
2a






O
O
tBu
O

2b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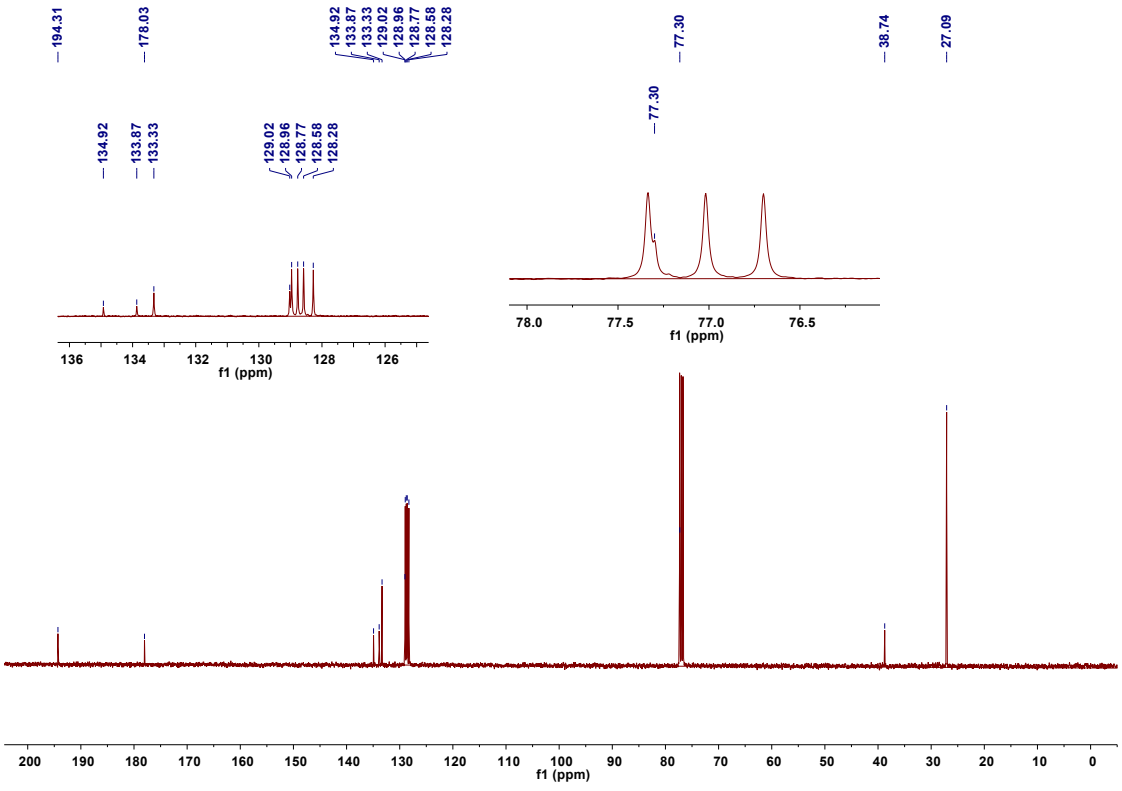
7.92
7.46
7.45
7.42
7.40
7.36
1.28
1.98
2.97
4.95
1.00
9.09
f1 (ppm)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133.33
129.02
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128.77
128.58
128.28
77.30
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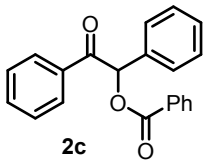
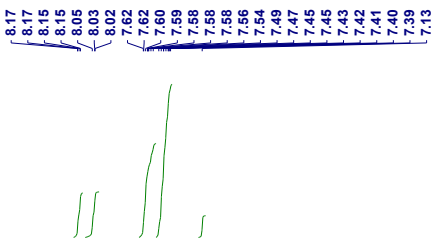
27.09
f1 (ppm)


O
O
Ph
O

2c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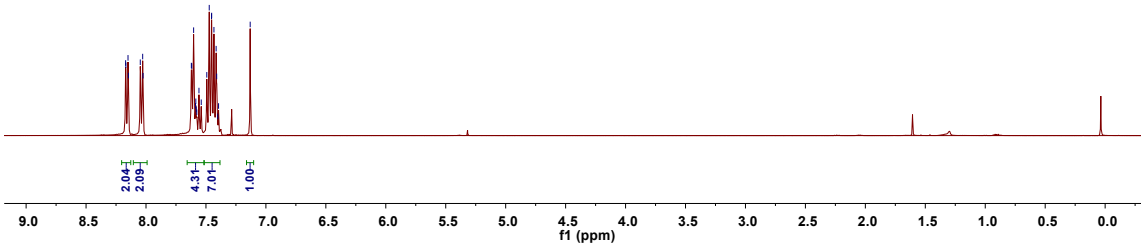
7.13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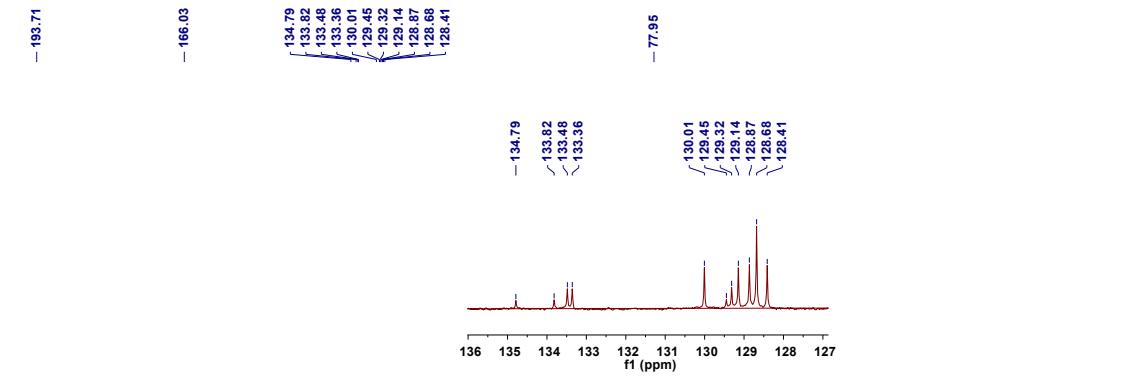
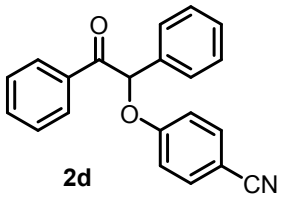
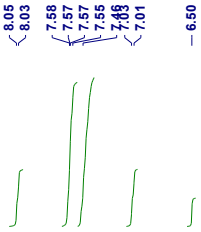
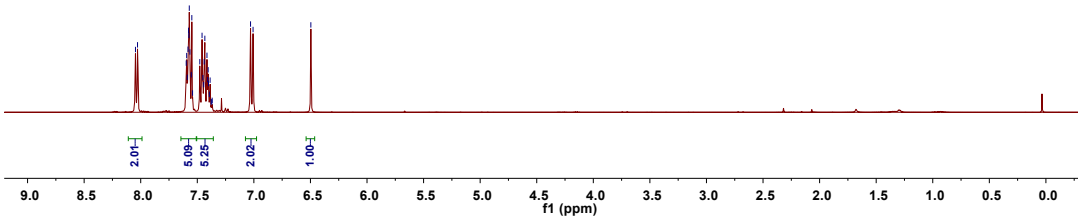
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

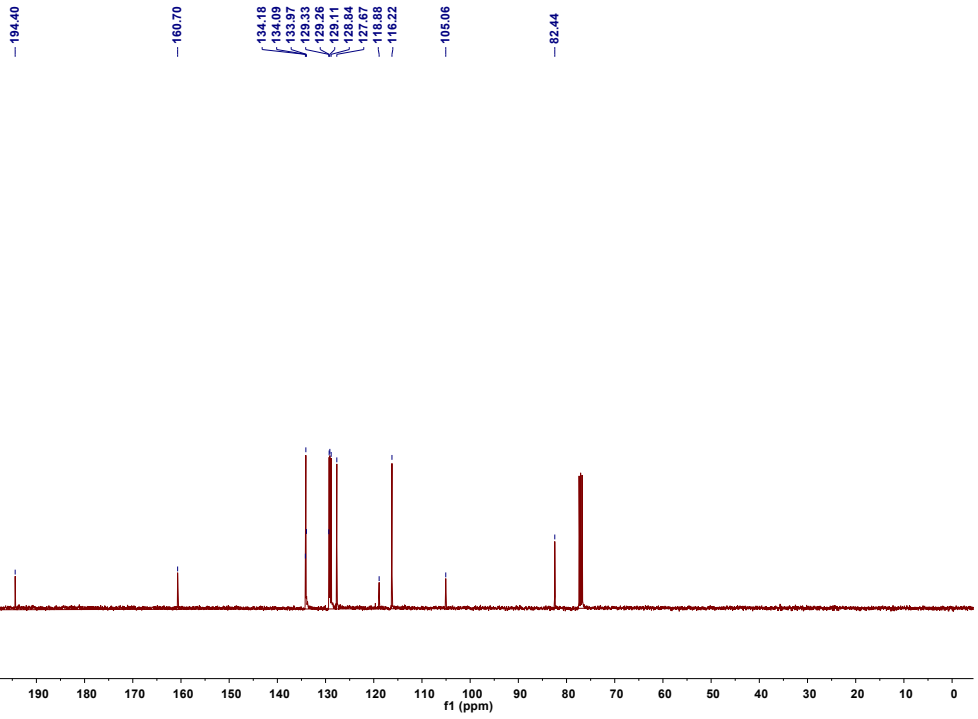

193.71
166.03
134.79
133.82
133.48
133.36
130.01
129.45
129.32
129.14
128.87
128.68
128.41
77.95
134.79
133.82
133.48
133.36
130.01
129.45
129.32
129.14
128.87
128.68
128.41
136
135
134
133
132
131
130
129
128
127
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

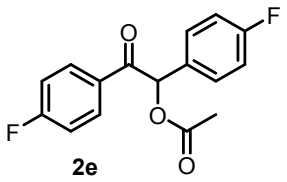

O
O
CN

2d

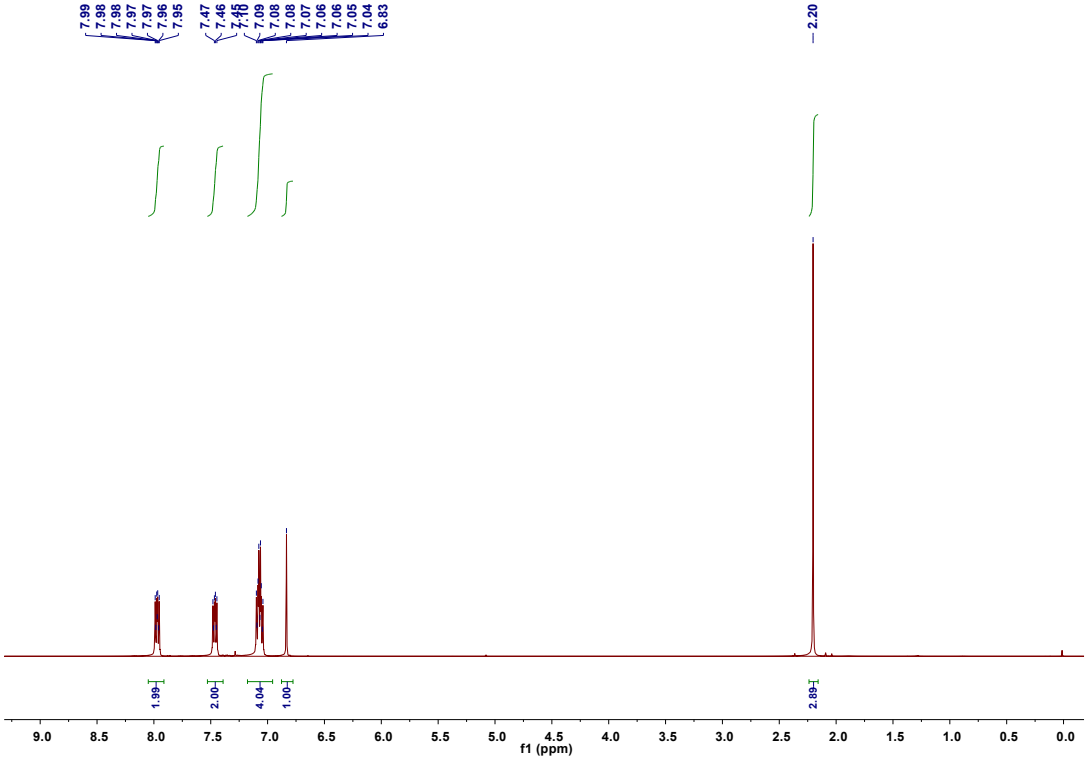

8.05
8.03
7.58
7.57
7.57
7.57
7.55
7.46
7.03
7.01
6.50

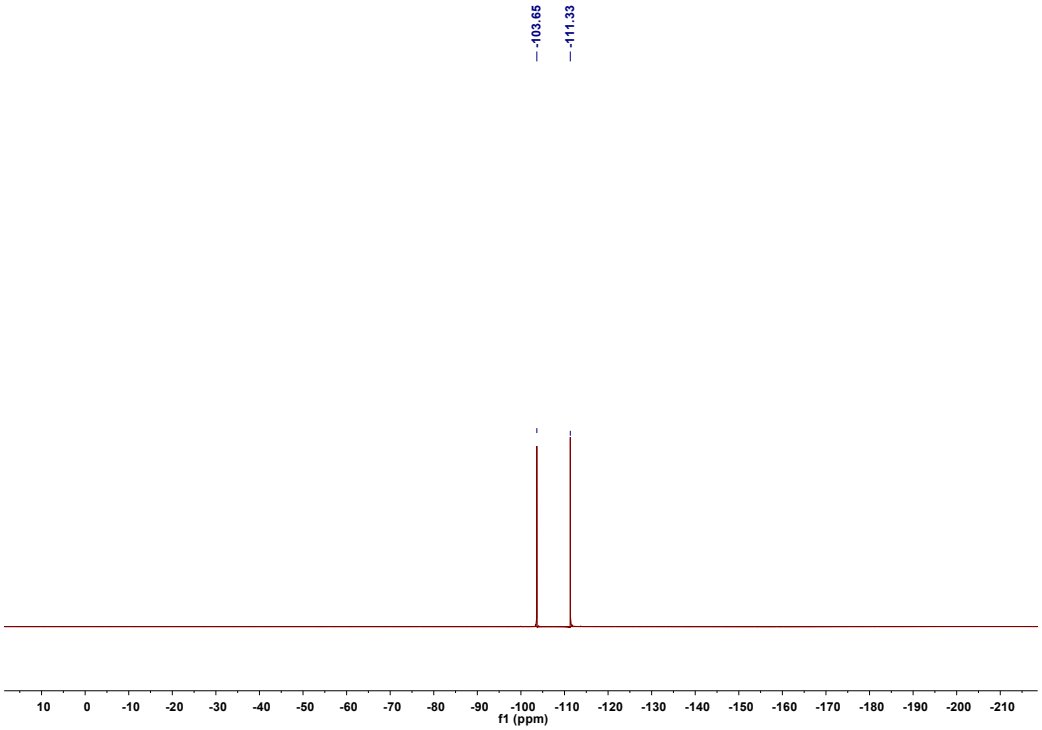

2.01
5.09
5.25
2.02
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

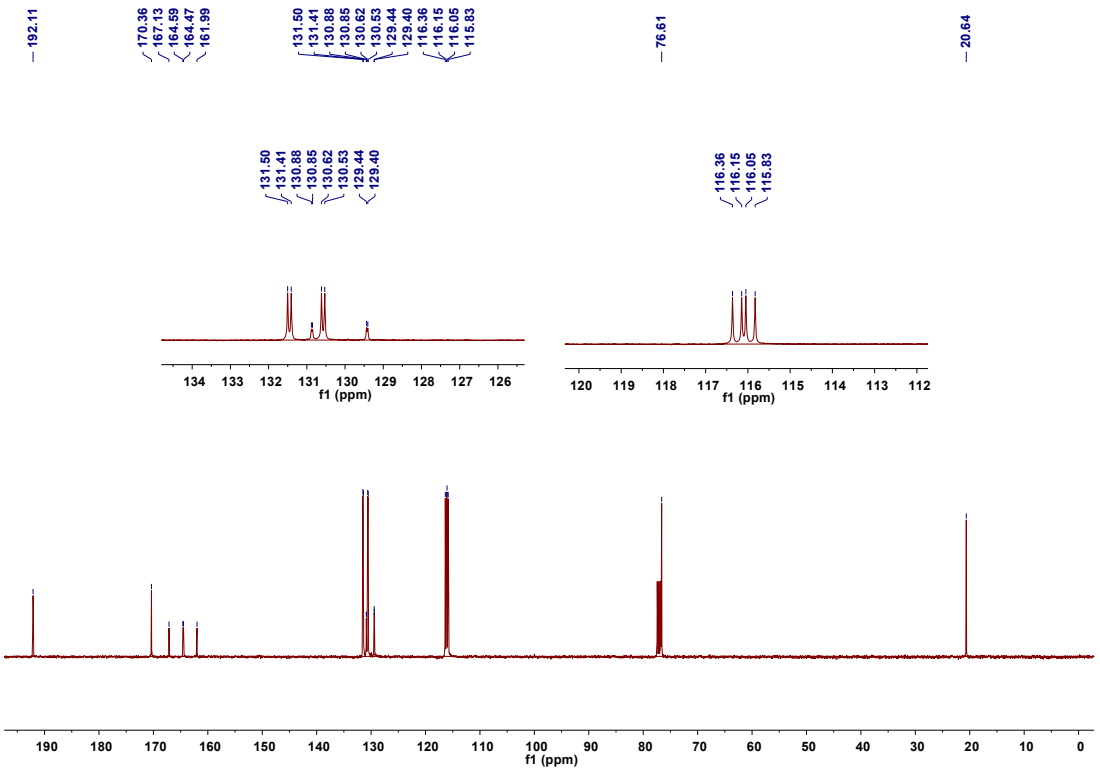

194.40
160.70
134.18
134.09
133.97
129.33
129.26
129.11
128.84
127.67
118.88
116.22
105.06
82.44
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
F
O
F
O

2e


7.99
7.98
7.98
7.97
7.97
7.96
7.95
7.47
7.46
7.45
7.10
7.09
7.08
7.08
7.07
7.06
7.06
7.05
7.04
6.83
2.20
1.99
2.00
4.04
1.00
2.89
f1 (ppm)


-103.65
-111.33
f1 (ppm)


192.11
170.36
167.13
164.59
164.47
161.99
131.50
131.41
130.88
130.85
130.62
130.53
129.44
129.40
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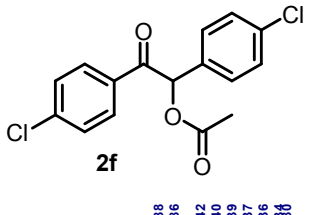
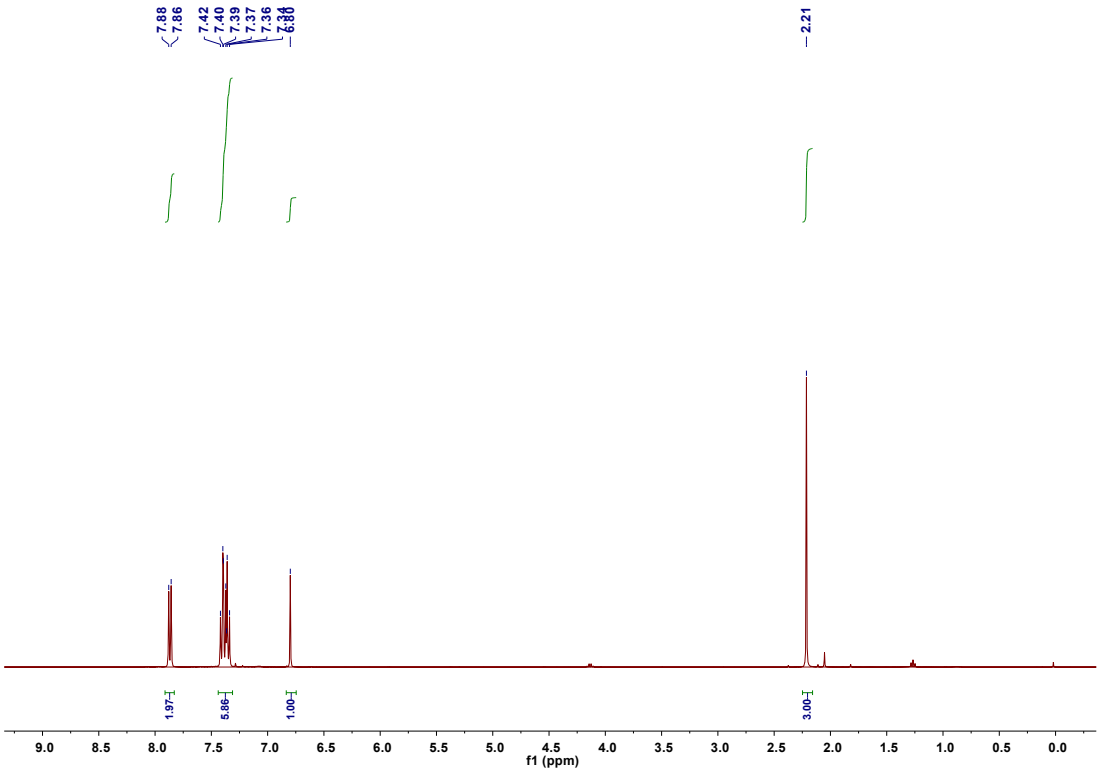
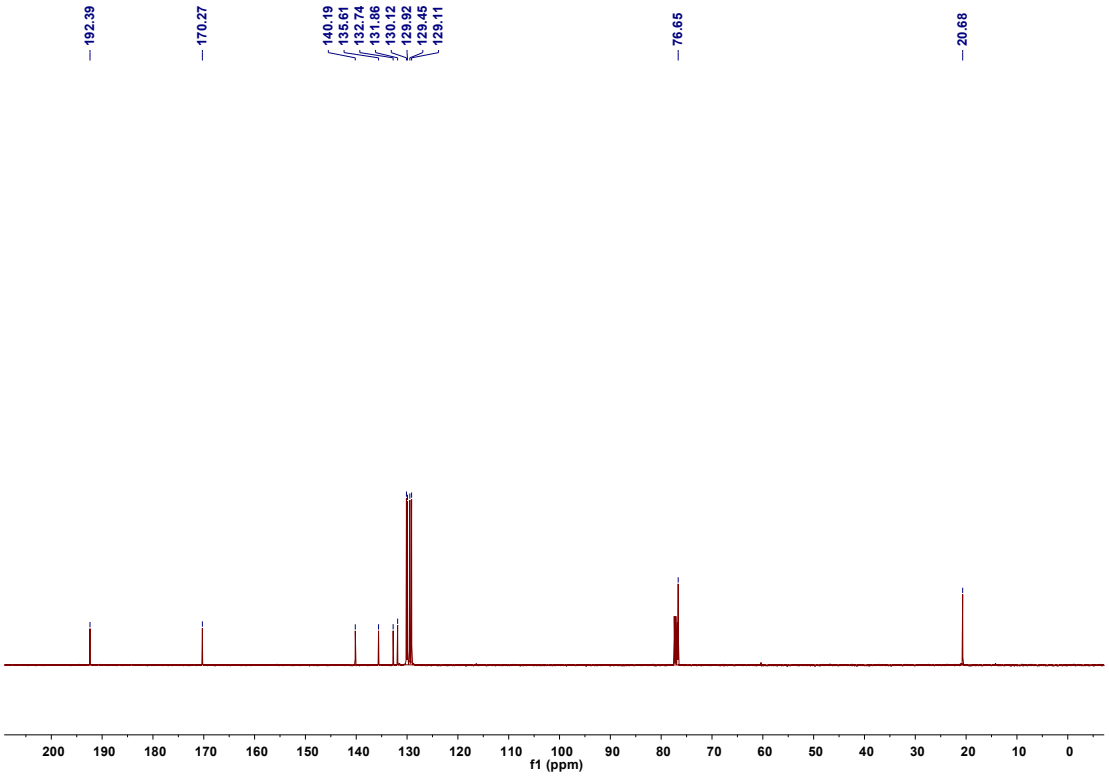
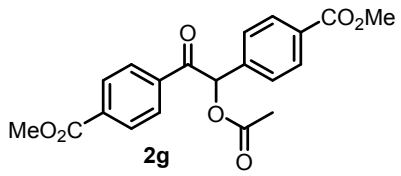
116.15
116.05
115.83
76.61
20.64
f1 (ppm)

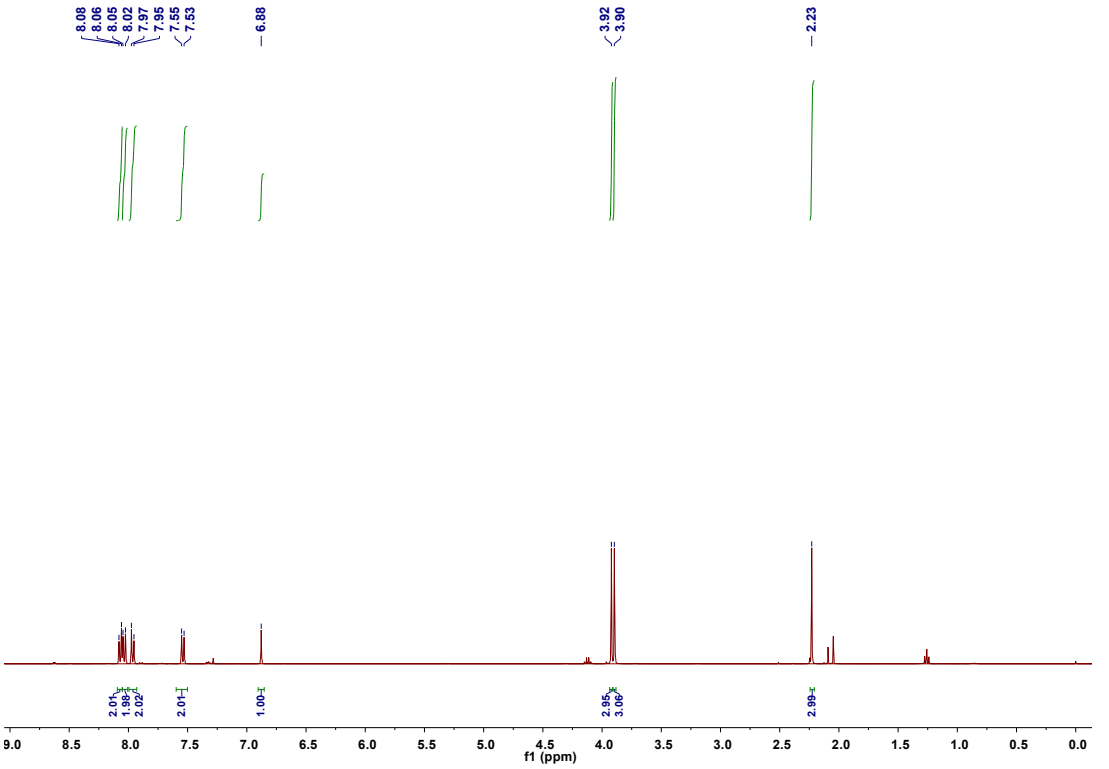

Cl
O
O
Cl
O
2f

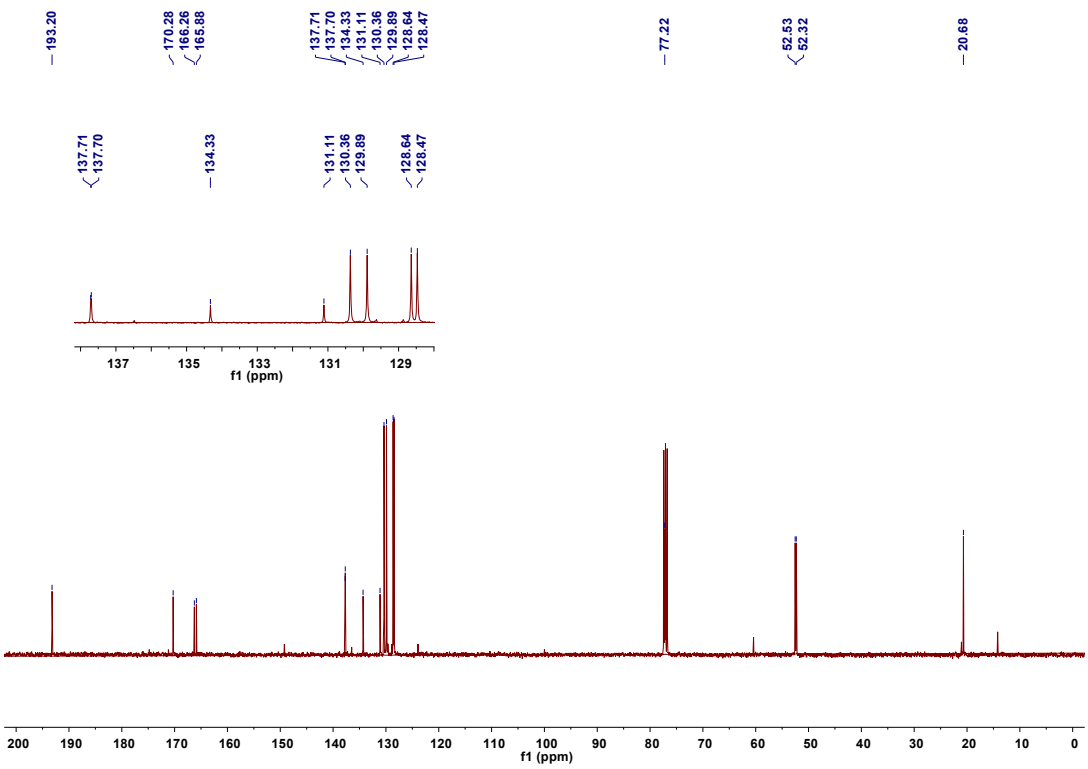

7.88
7.86
7.42
7.40
7.39
7.37
7.36
2.21
1.97
5.86
1.00
3.00
f1 (ppm)

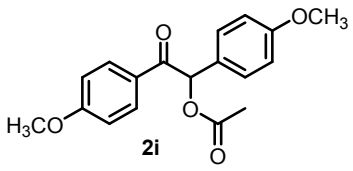

192.39
170.27
140.19
135.61
132.74
131.86
130.12
129.92
129.45
129.11
76.65
20.68
f1 (ppm)


CO2Me
O
O
O
MeO2C

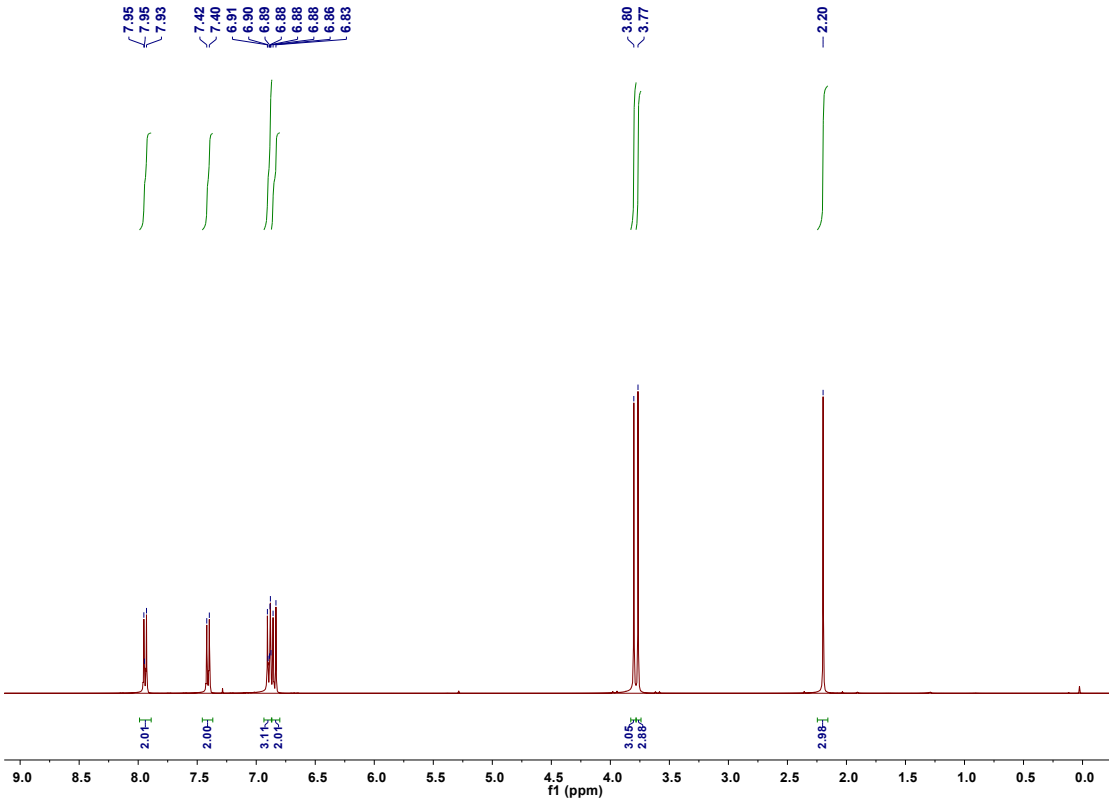
2g

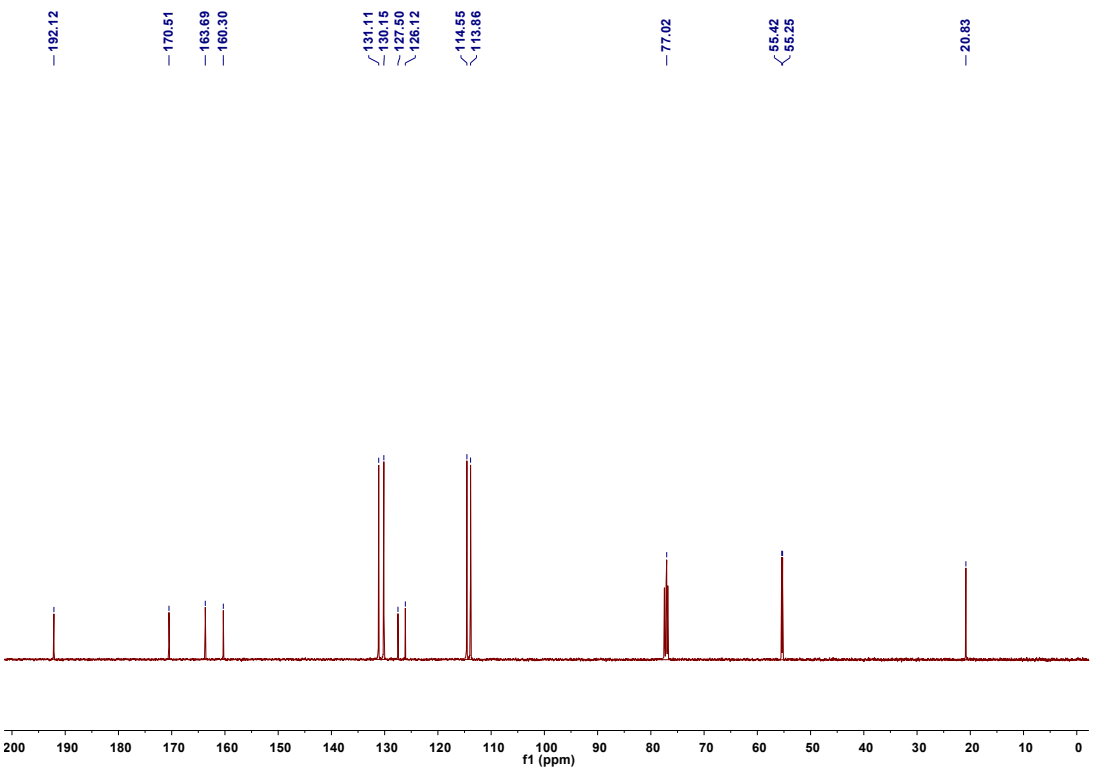

8.08
8.06
8.05
8.02
7.97
7.95
7.55
7.53
6.88
3.92
3.90
2.23
2.01
1.98
2.02
2.01
1.00
2.95
3.06
2.99
f1 (ppm)

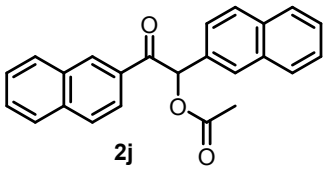

193.20
170.28
166.26
165.88
137.71
137.70
134.33
131.11
130.36
129.89
128.64
128.47
77.22
52.53
52.32
20.68
f1 (ppm)


OCH3
O
O
O
H3CO

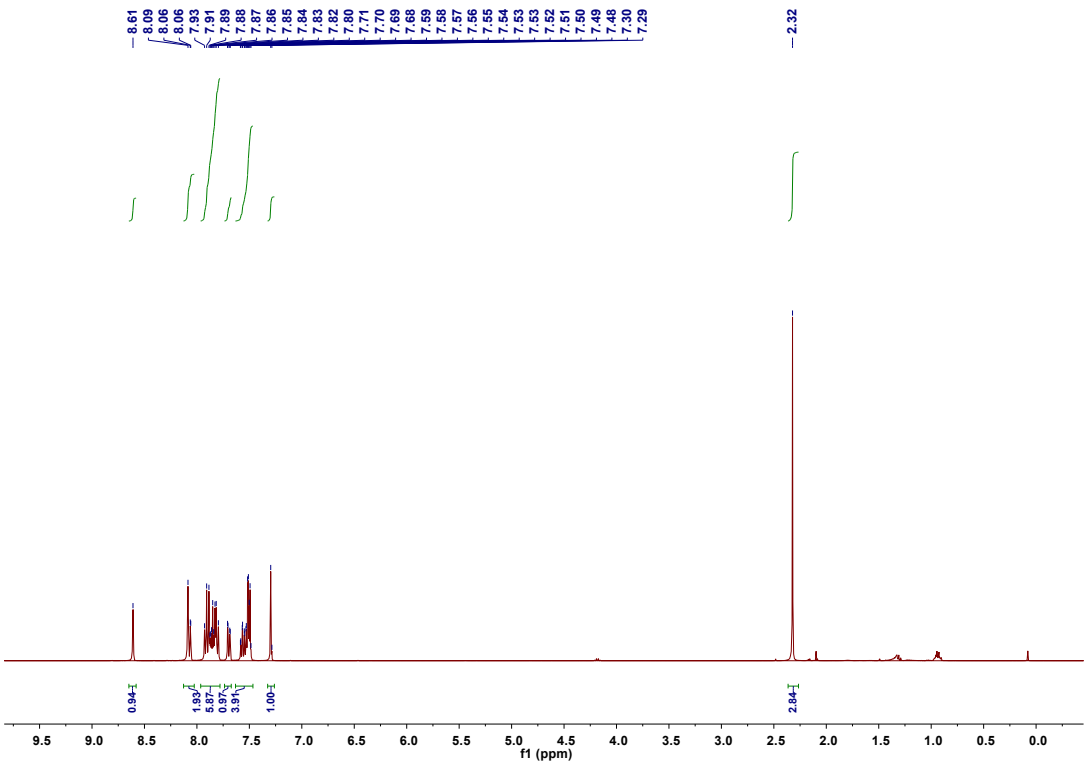
2i

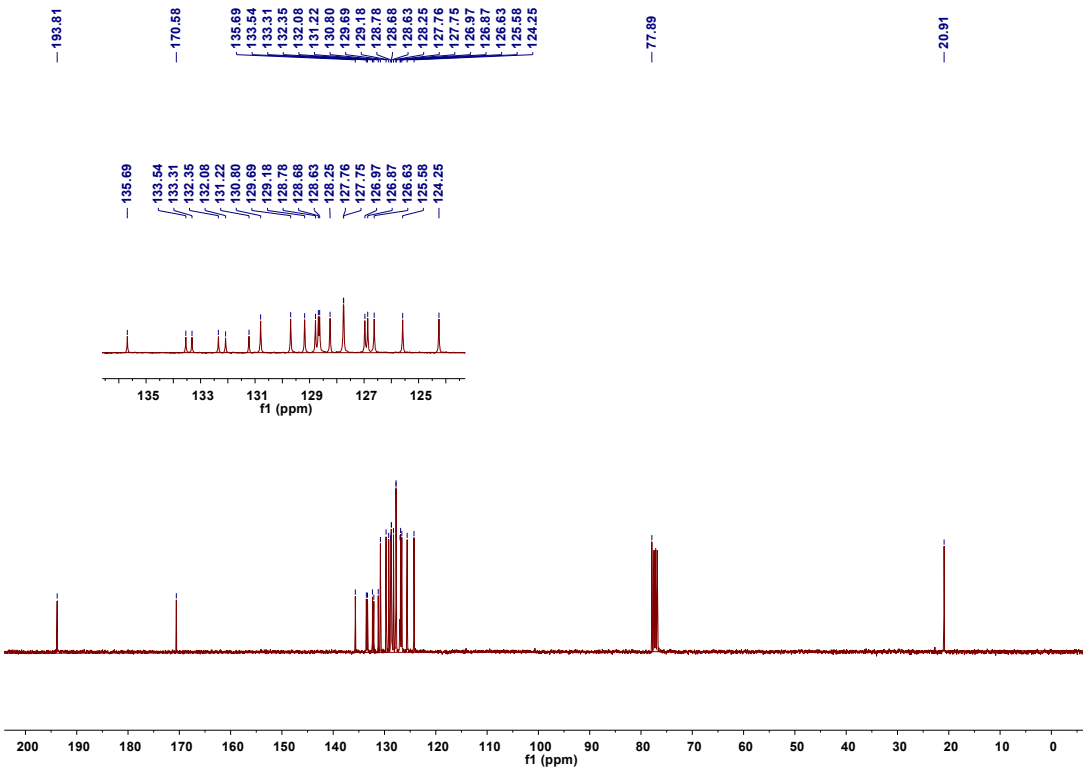

7.95
7.95
7.93
7.42
7.40
6.91
6.90
6.89
6.88
6.88
6.88
6.86
6.83
3.80
3.77
2.20
2.01
2.00
3.11
2.01
3.05
2.88
2.98
f1 (ppm)

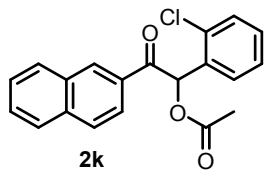

192.12
170.51
163.69
160.30
131.11
130.15
127.50
126.12
114.55
113.86
77.02
55.42
55.25
20.83
f1 (ppm)



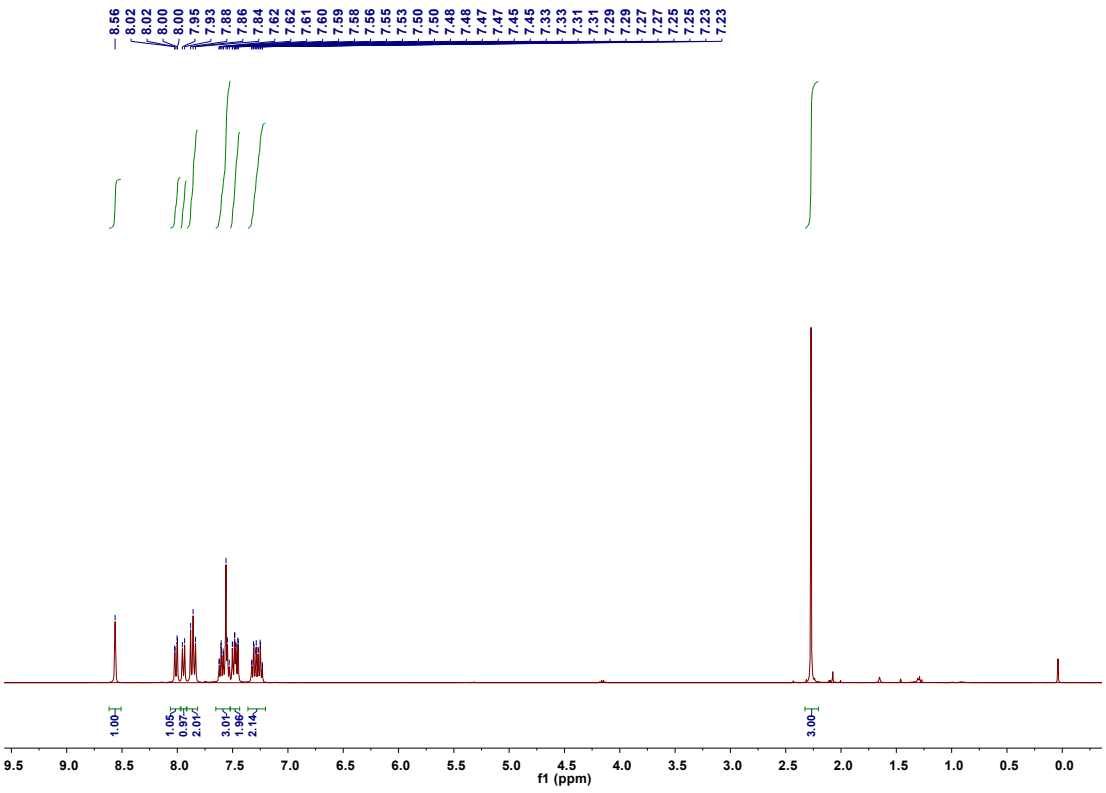
2j

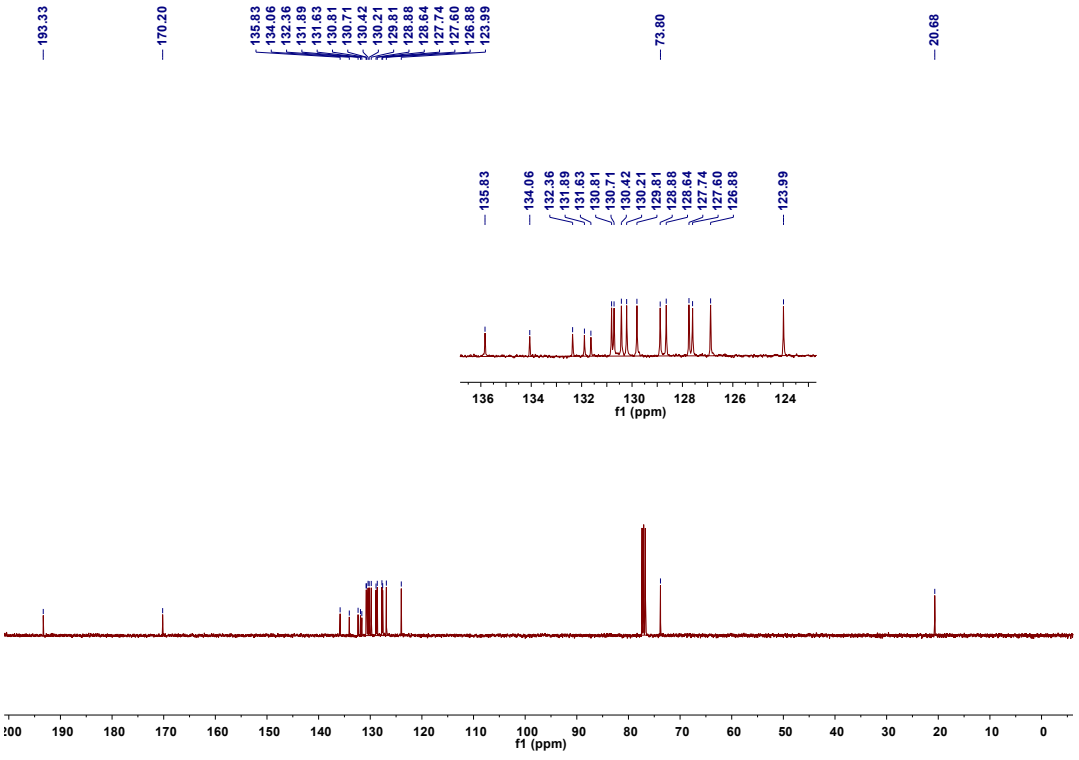

8.61
8.09
8.06
8.06
7.93
7.91
7.89
7.88
7.87
7.86
7.85
7.84
7.83
7.82
7.80
7.71
7.70
7.69
7.68
7.59
7.58
7.57
7.56
7.55
7.54
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.30
7.29
2.32
0.94
1.93
5.87
0.97
3.91
1.00
2.84
f1 (ppm)

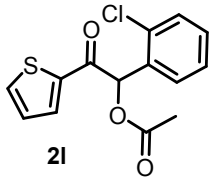

193.81
170.58
135.69
133.54
133.31
132.35
132.08
131.22
130.80
129.69
129.18
128.78
128.68
128.63
128.25
127.76
127.75
126.97
126.87
126.63
125.58
124.25
77.89
20.91
f1 (ppm)


Cl
O
O
O

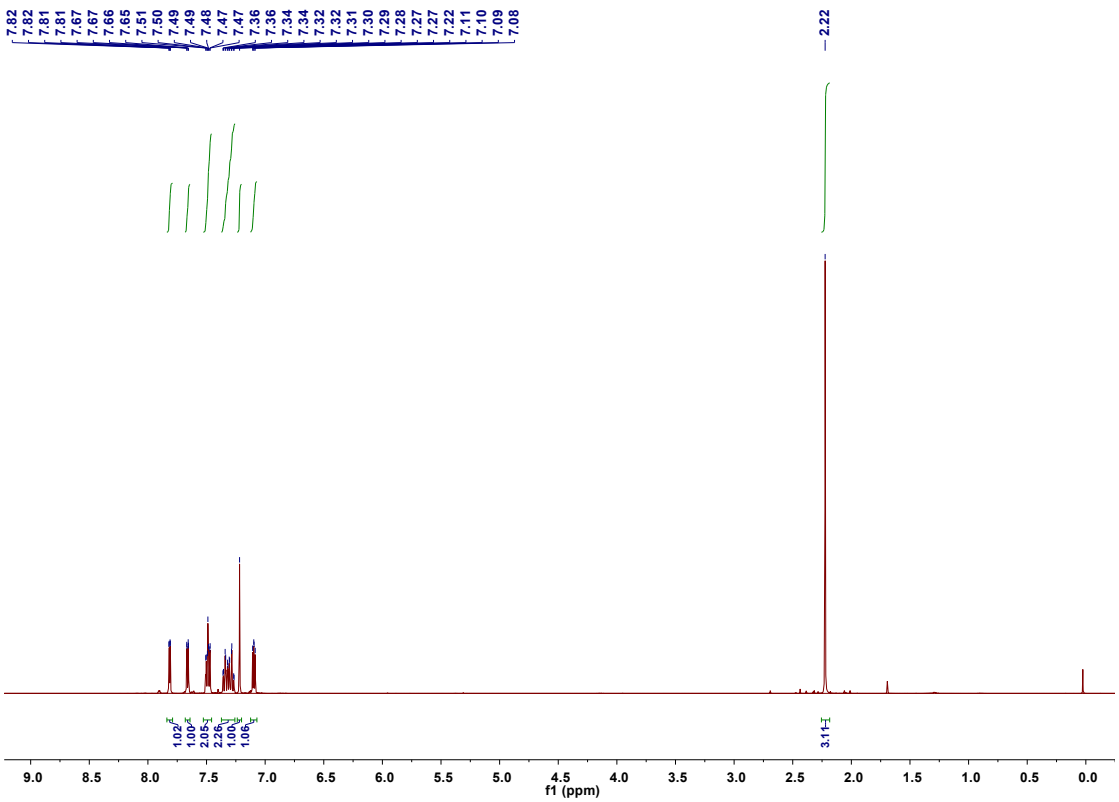
2k

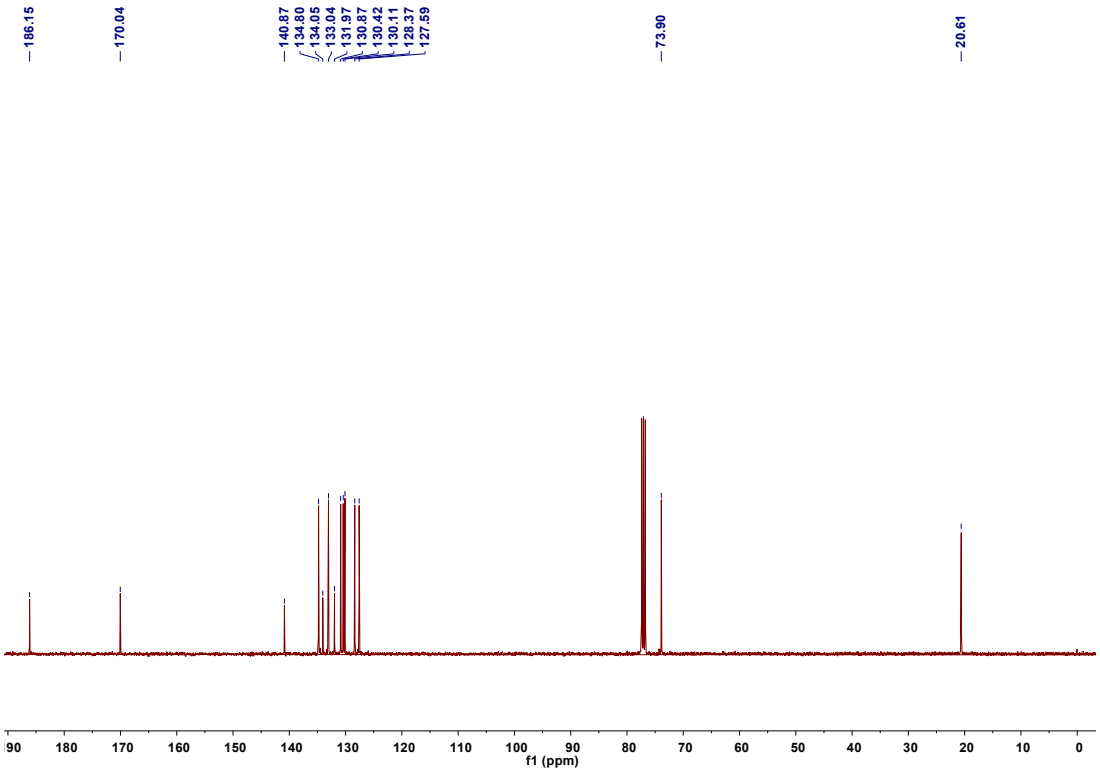

8.56
8.02
8.02
8.00
8.00
7.95
7.93
7.88
7.86
7.84
7.62
7.62
7.61
7.60
7.59
7.58
7.56
7.55
7.53
7.50
7.50
7.48
7.48
7.47
7.47
7.45
7.45
7.33
7.33
7.31
7.31
7.29
7.29
7.27
7.27
7.25
7.25
7.23
7.23
1.00
1.05
0.97
2.01
3.01
1.96
2.14
3.00
f1 (ppm)

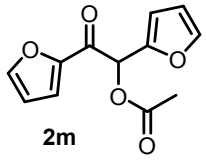

193.33
170.20
135.83
134.06
132.36
131.89
131.63
130.81
130.71
130.42
130.21
129.81
128.88
128.64
127.74
127.60
126.88
123.99
73.80
20.68
f1 (ppm)
f1 (ppm)


Cl
O
S
O
O

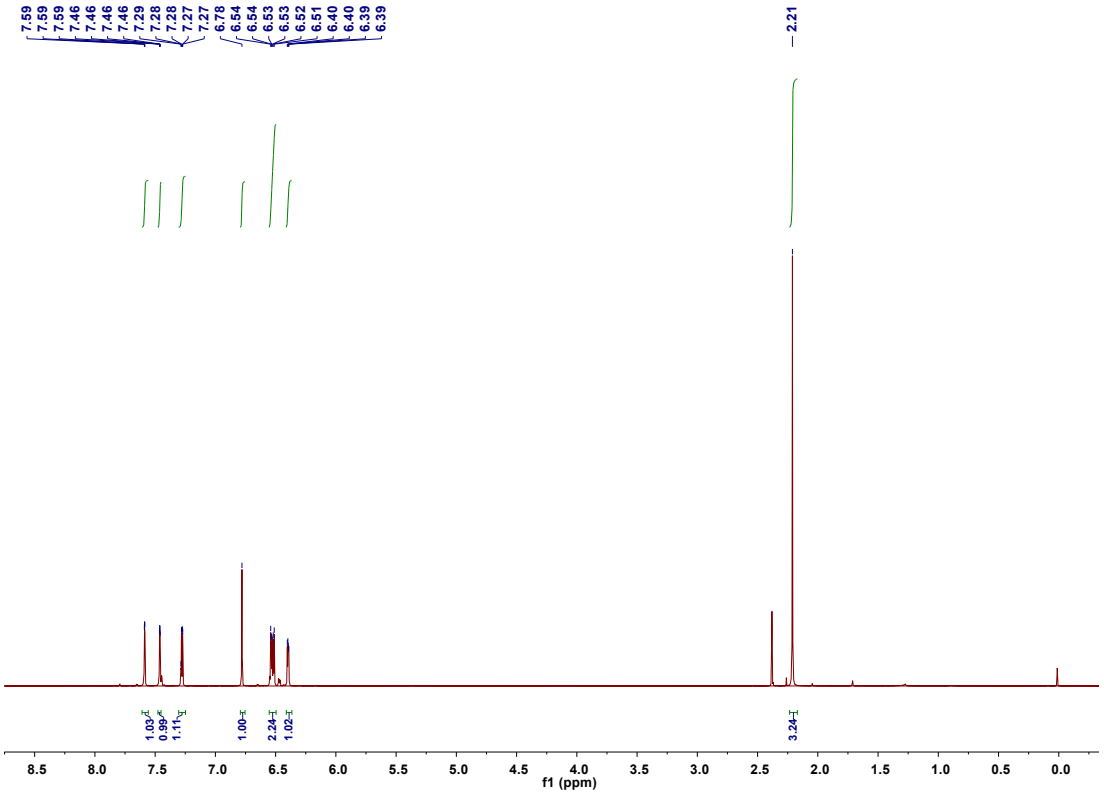
2l

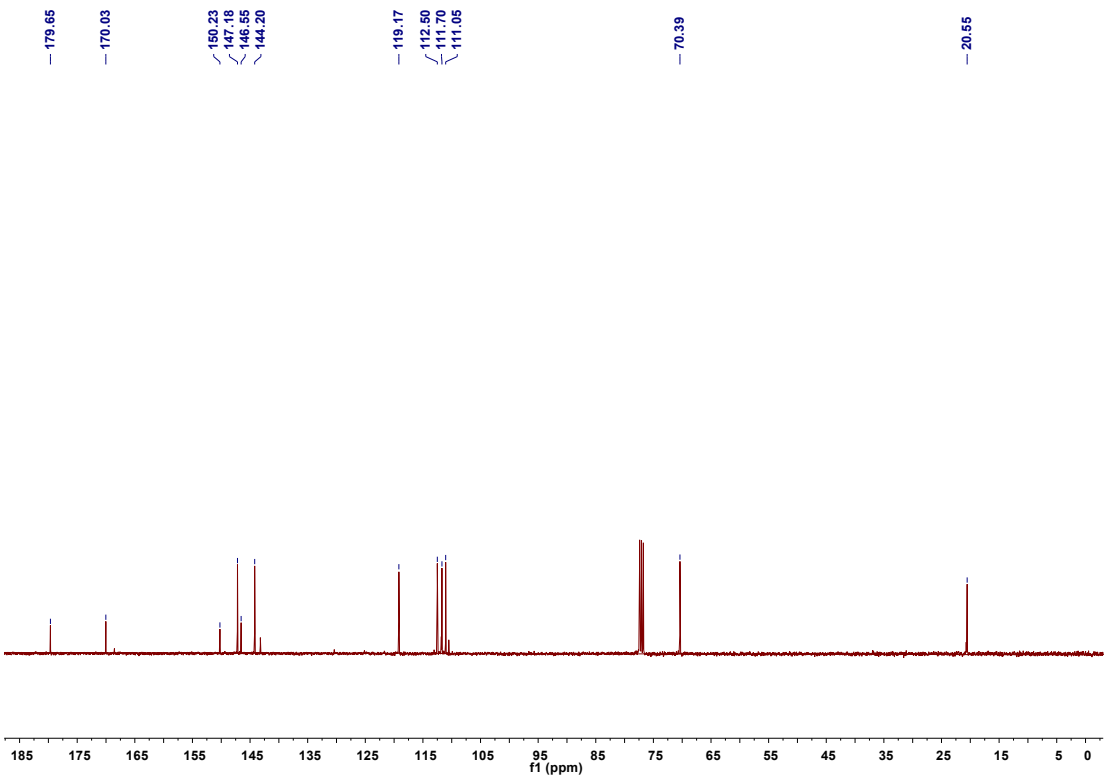

7.82
7.82
7.81
7.81
7.67
7.67
7.66
7.65
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.22
7.11
7.10
7.09
7.08
2.22
1.02
1.00
2.05
2.26
1.00
1.06
3.11
f1 (ppm)

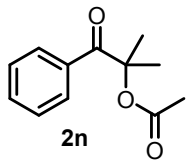

186.15
170.04
140.87
134.80
134.05
133.04
131.97
130.87
130.42
130.11
128.37
127.59
73.90
20.61
f1 (ppm)



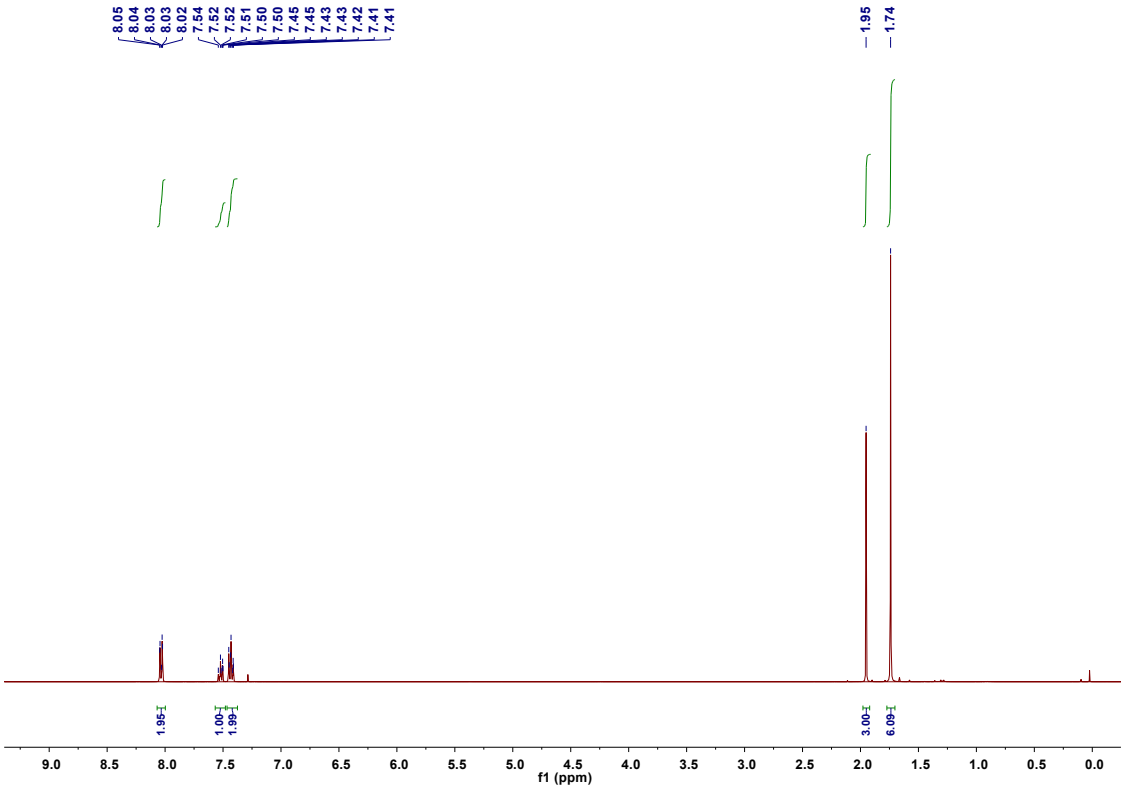
2m

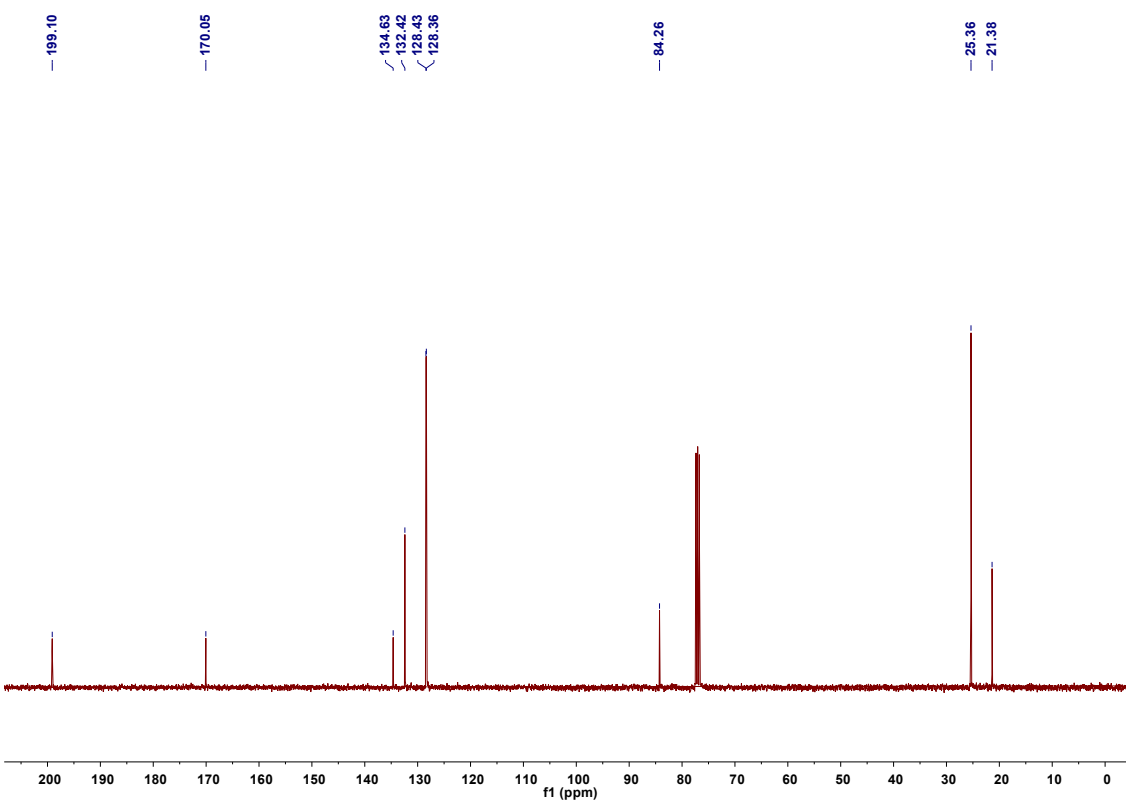

7.59
7.59
7.59
7.46
7.46
7.46
7.46
7.29
7.28
7.28
7.27
7.27
6.78
6.54
6.54
6.53
6.53
6.52
6.51
6.40
6.40
6.39
6.39
2.21
1.03
0.99
1.11
1.00
2.24
1.02
3.24
f1 (ppm)

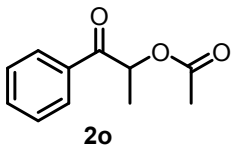

179.65
170.03
150.23
147.18
146.55
144.20
119.17
112.50
111.70
111.05
70.39
20.55
185 175 165 155 145 135 125 115 105 95 85 75 65 55 45 35 25 15 5 0
f1 (ppm)



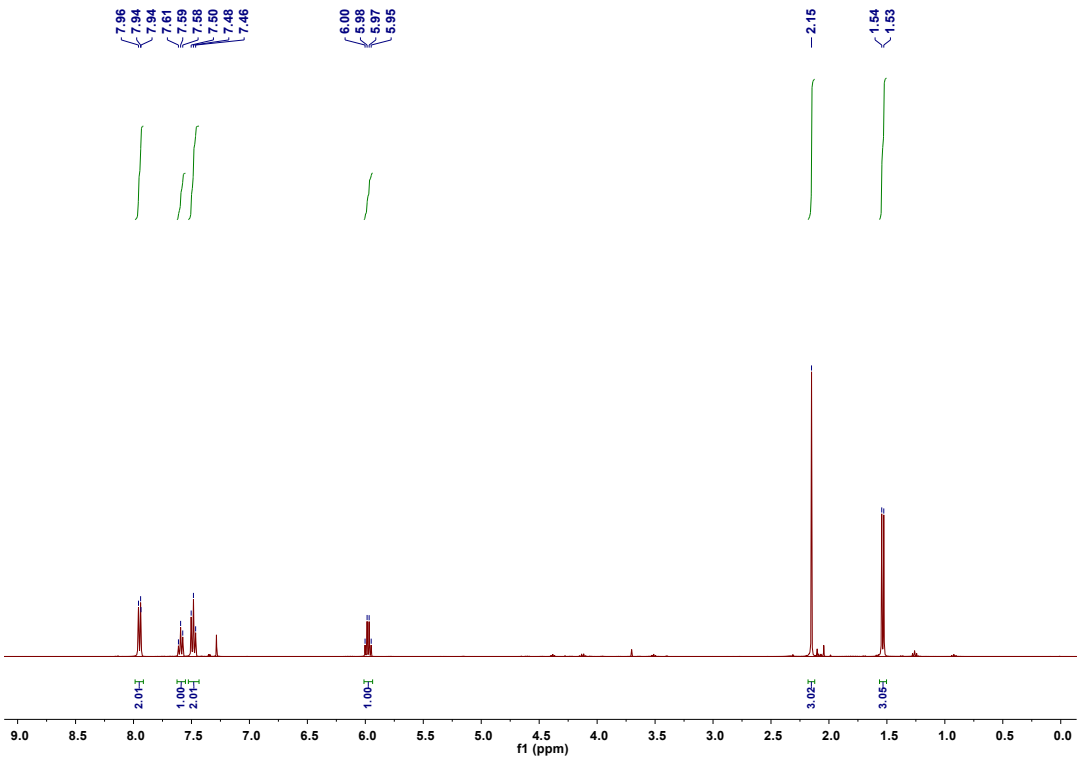
2n

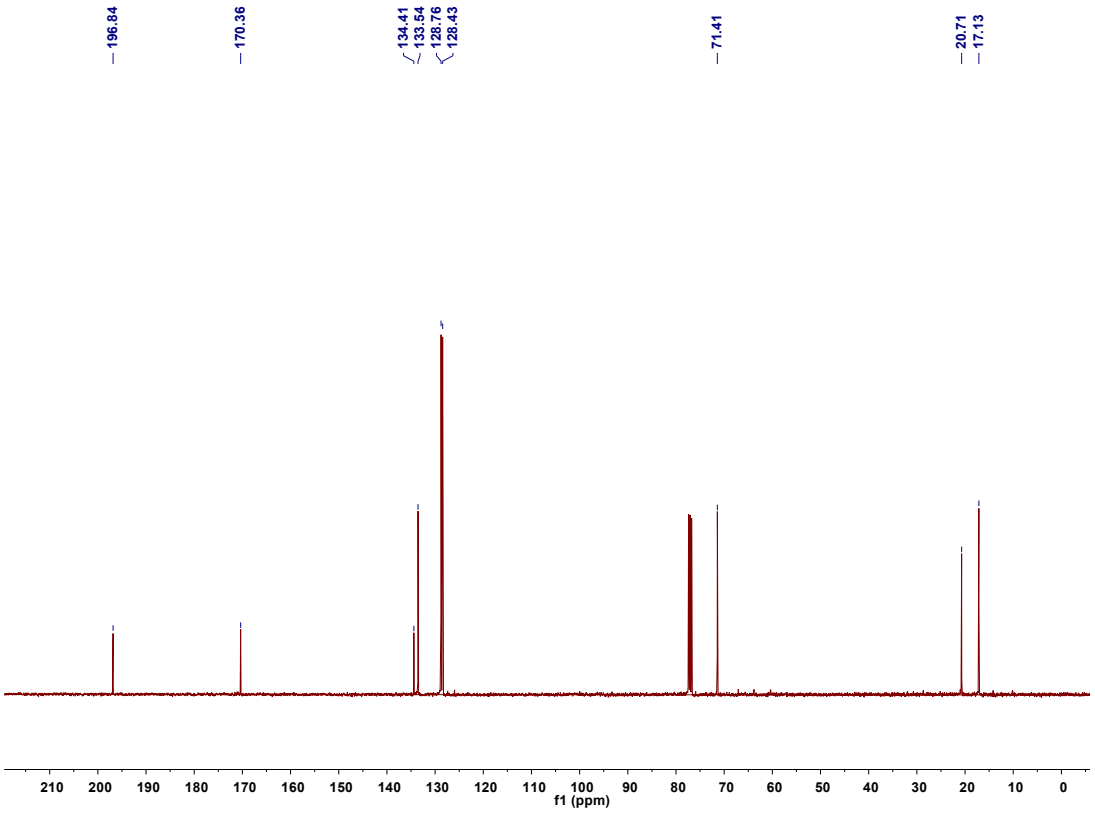

8.05
8.04
8.03
8.03
8.02
7.54
7.52
7.52
7.51
7.50
7.50
7.45
7.45
7.43
7.43
7.42
7.41
7.41
1.95
1.74
1.95
1.00
1.99
3.00
6.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

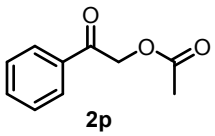

199.10
170.05
134.63
132.42
128.43
128.36
84.26
25.36
21.38
f1 (ppm)



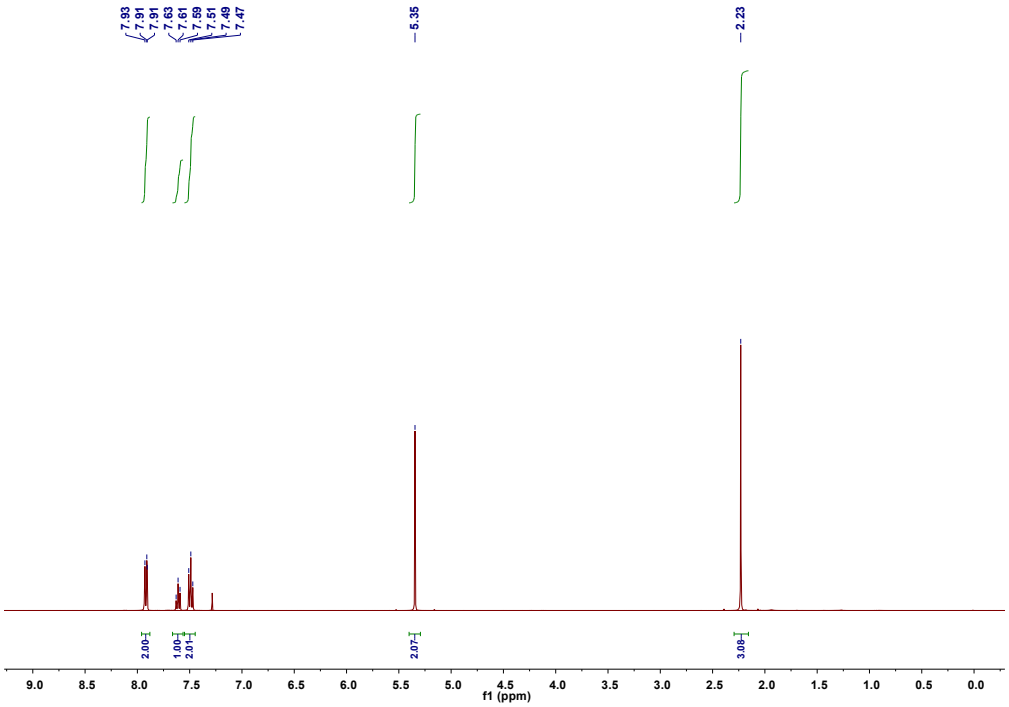
2o

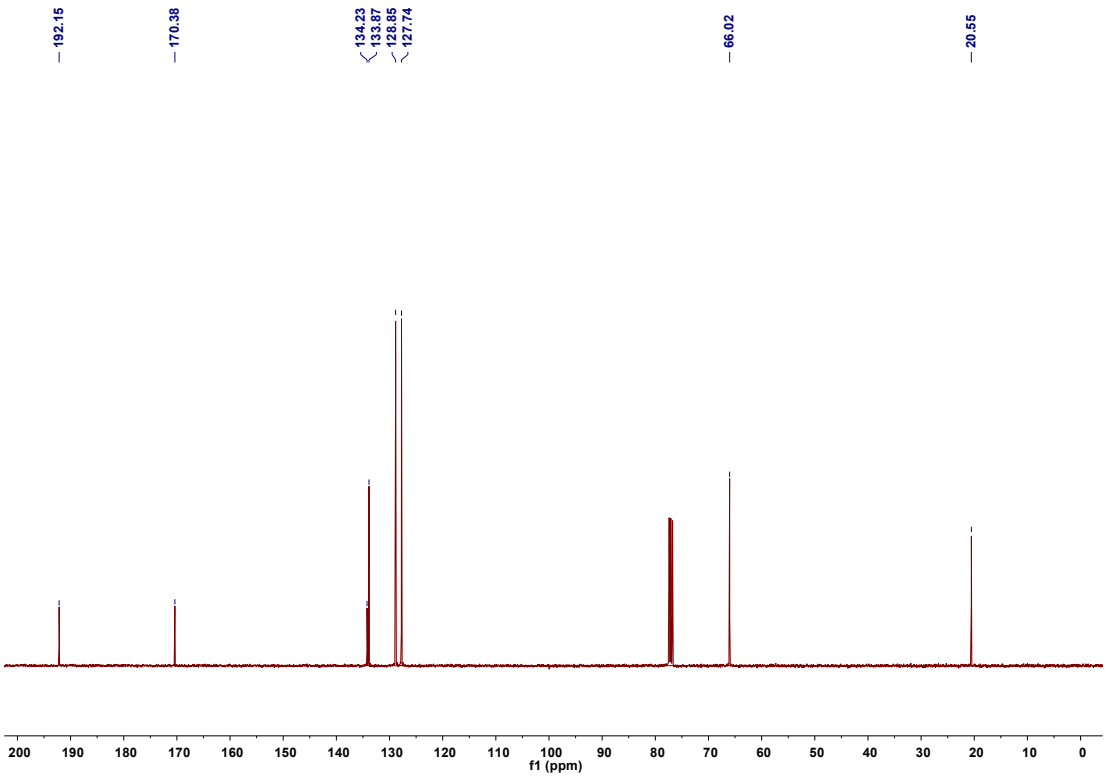

7.96
7.94
7.94
7.61
7.59
7.58
7.50
7.48
7.46
6.00
5.98
5.97
5.95
2.15
1.54
1.53
2.01
1.00
2.01
1.00
3.02
3.05
f1 (ppm)

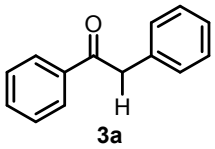

196.84
170.36
134.41
133.54
128.76
128.43
71.41
20.71
17.13
f1 (ppm)



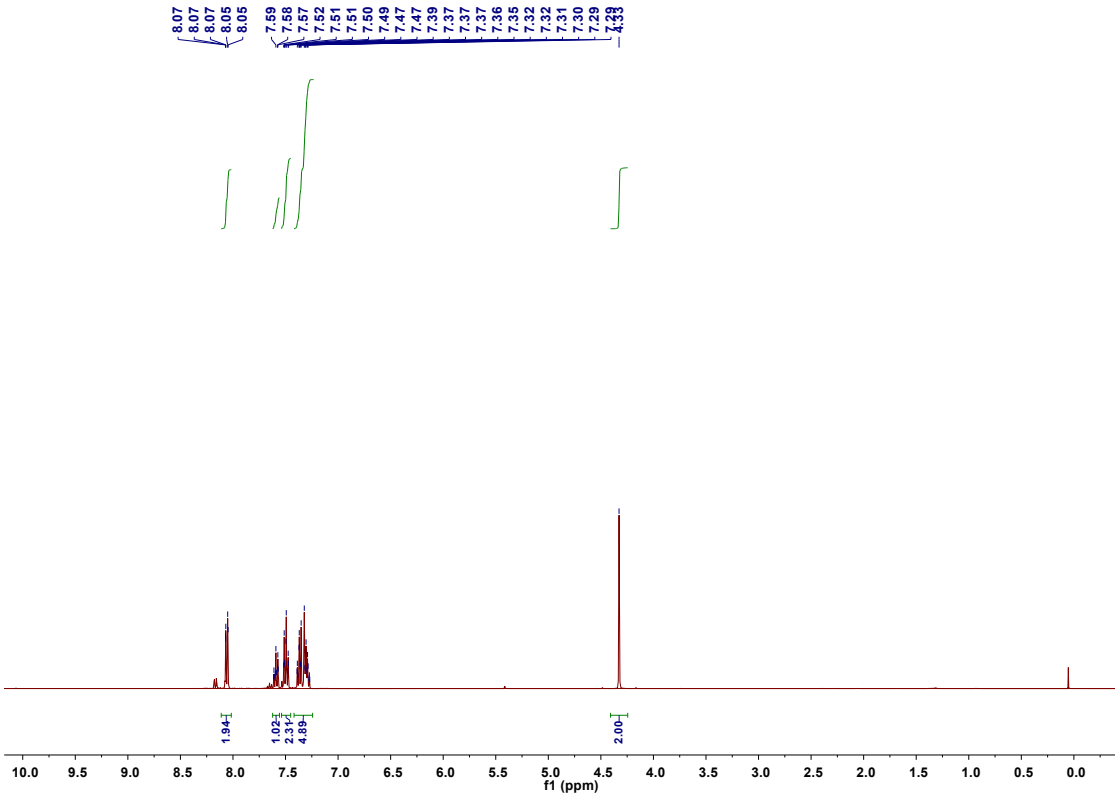
2p


7.93
7.91
7.91
7.63
7.61
7.59
7.51
7.49
7.47
5.35
2.23
2.00
1.00
2.01
2.07
3.08
f1 (ppm)


192.15
170.38
134.23
133.87
128.85
127.74
66.02
20.55
f1 (ppm)


O
H

3a


8.07
8.07
8.07
8.05
8.05
7.59
7.58
7.57
7.52
7.51
7.51
7.50
7.49
7.47
7.47
7.39
7.37
7.37
7.37
7.36
7.35
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7.29
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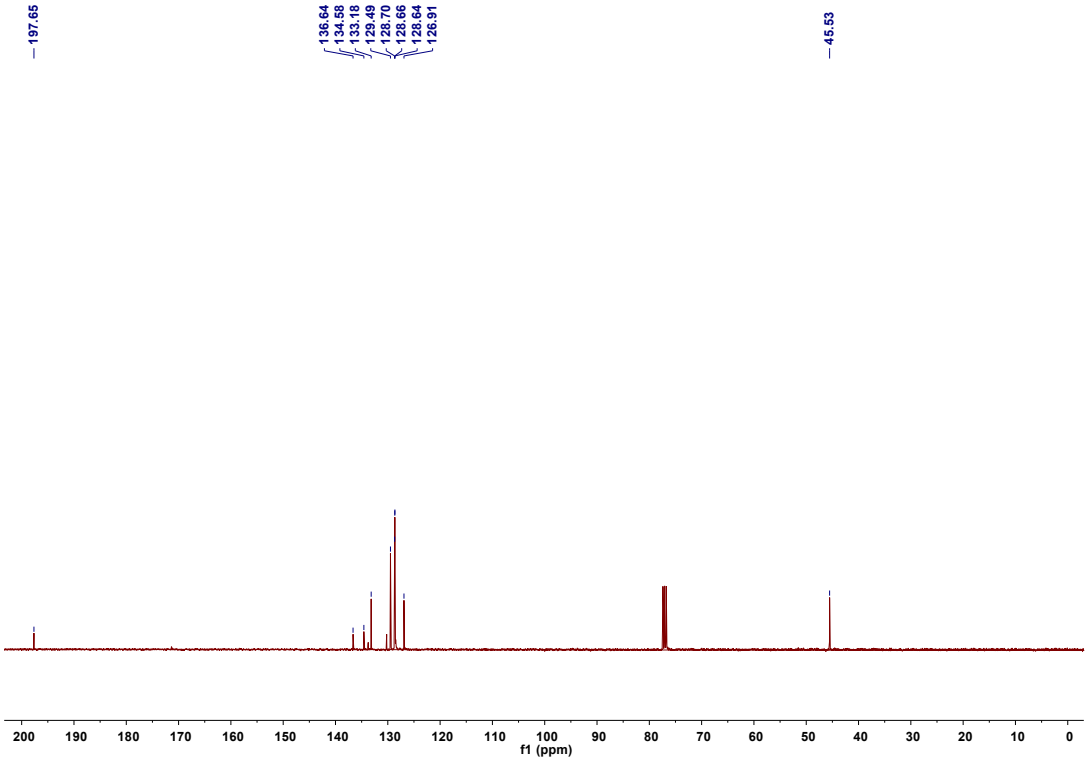
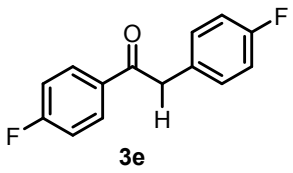
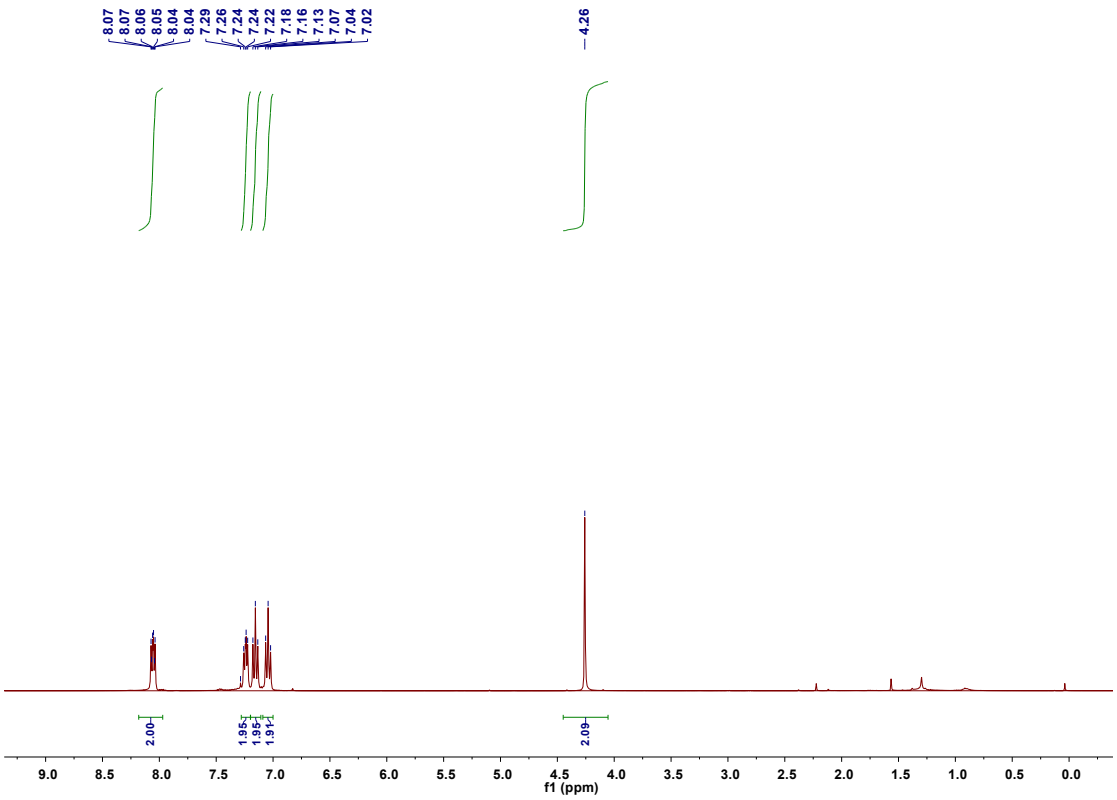
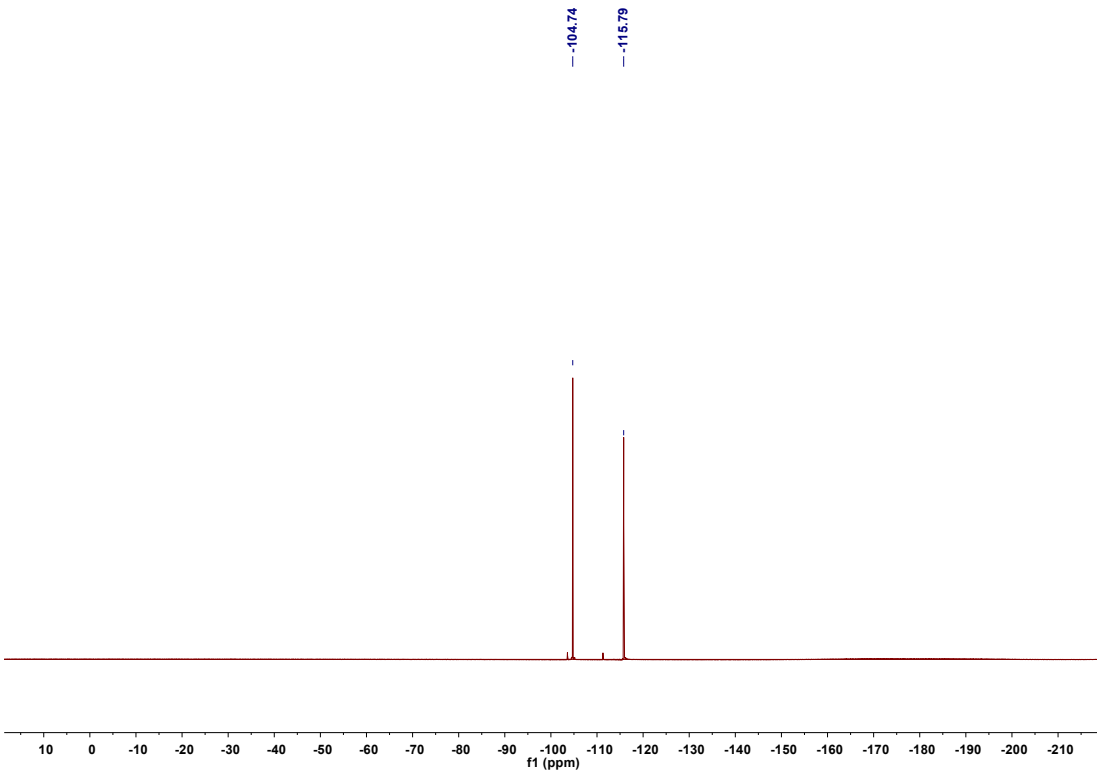
1.94
1.02
2.31
4.89
2.00
f1 (ppm)

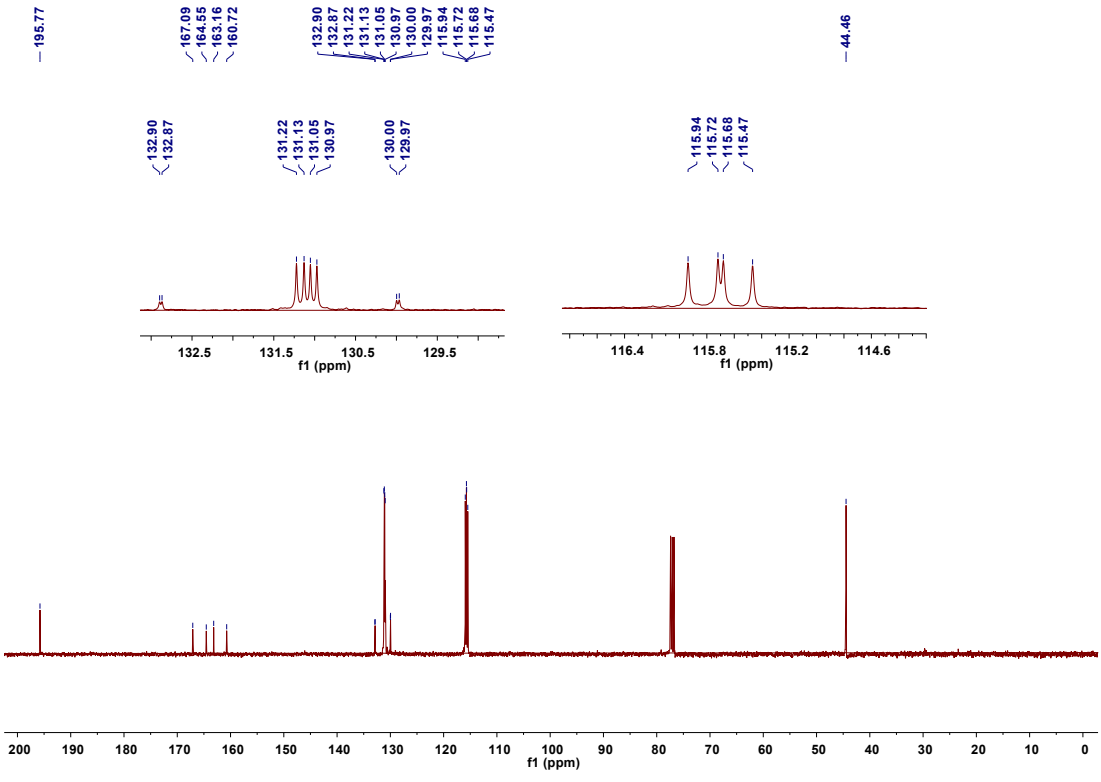

197.65
136.64
134.58
133.18
129.49
128.70
128.66
128.64
126.91
45.53
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

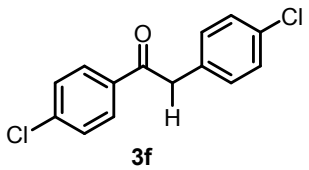

O
F
F
H

3e


8.07
8.07
8.06
8.05
8.04
8.04
7.29
7.26
7.24
7.24
7.22
7.18
7.16
7.13
7.07
7.04
7.02
4.26
2.00
1.95
1.95
1.91
2.09
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
f1 (ppm)

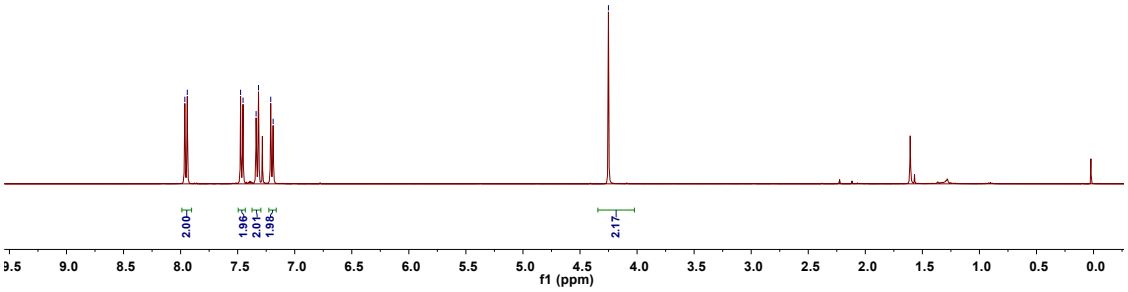

-104.74
-115.79
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

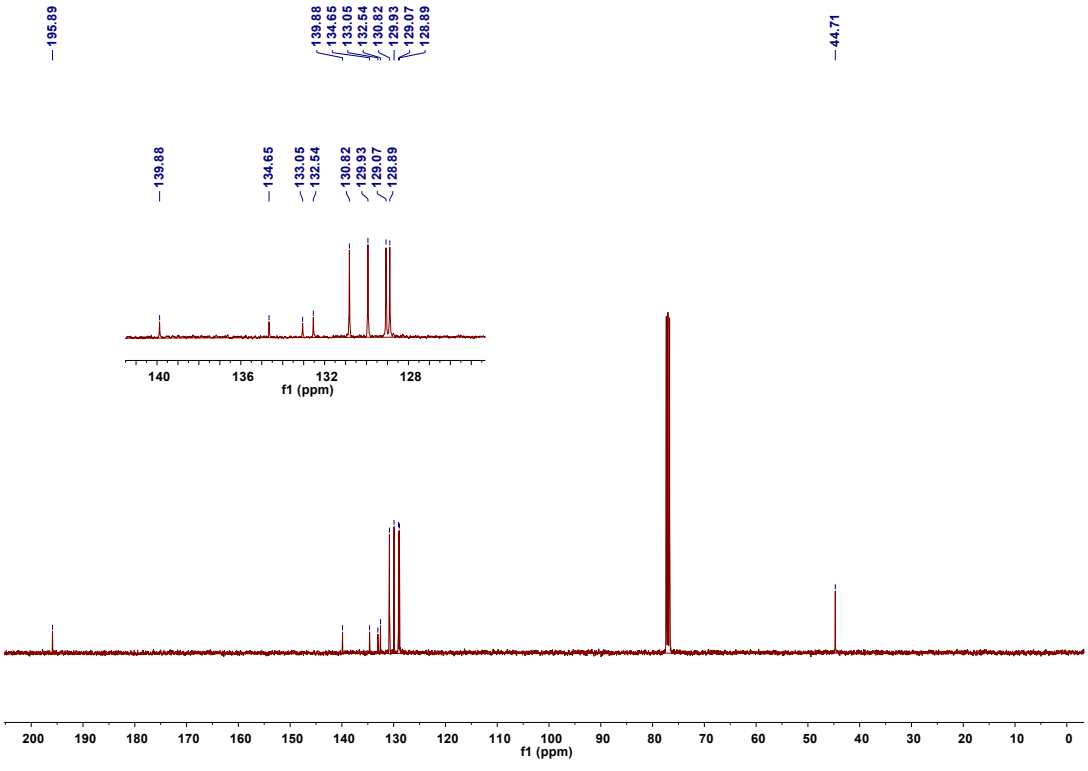

195.77
167.09
164.55
163.16
160.72
132.90
132.87
131.22
131.13
131.05
130.97
130.00
129.97
115.94
115.72
115.68
115.47
44.46
132.5 131.5 130.5 129.5
f1 (ppm)
116.4 115.8 115.2 114.6
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

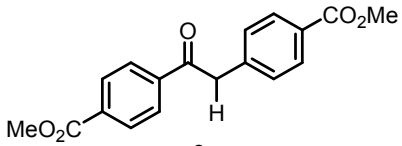

O
Cl
H
Cl

3f

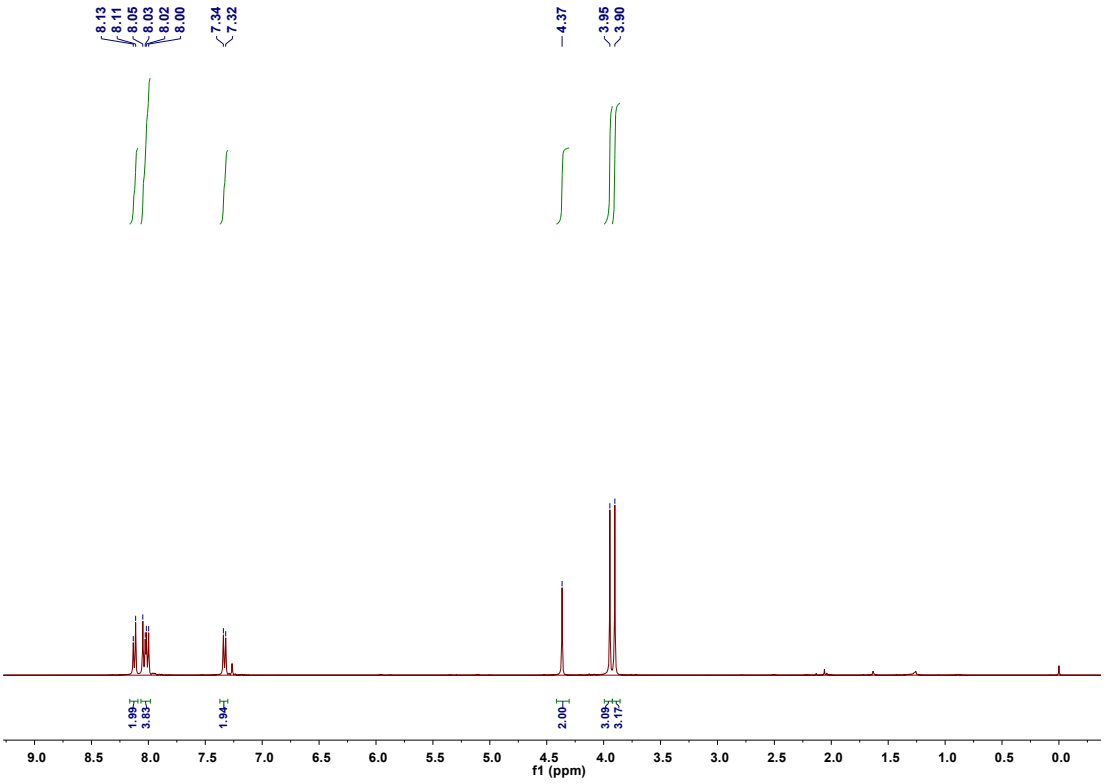

7.96
7.94
7.47
7.45
7.34
7.32
7.21
7.19
4.25

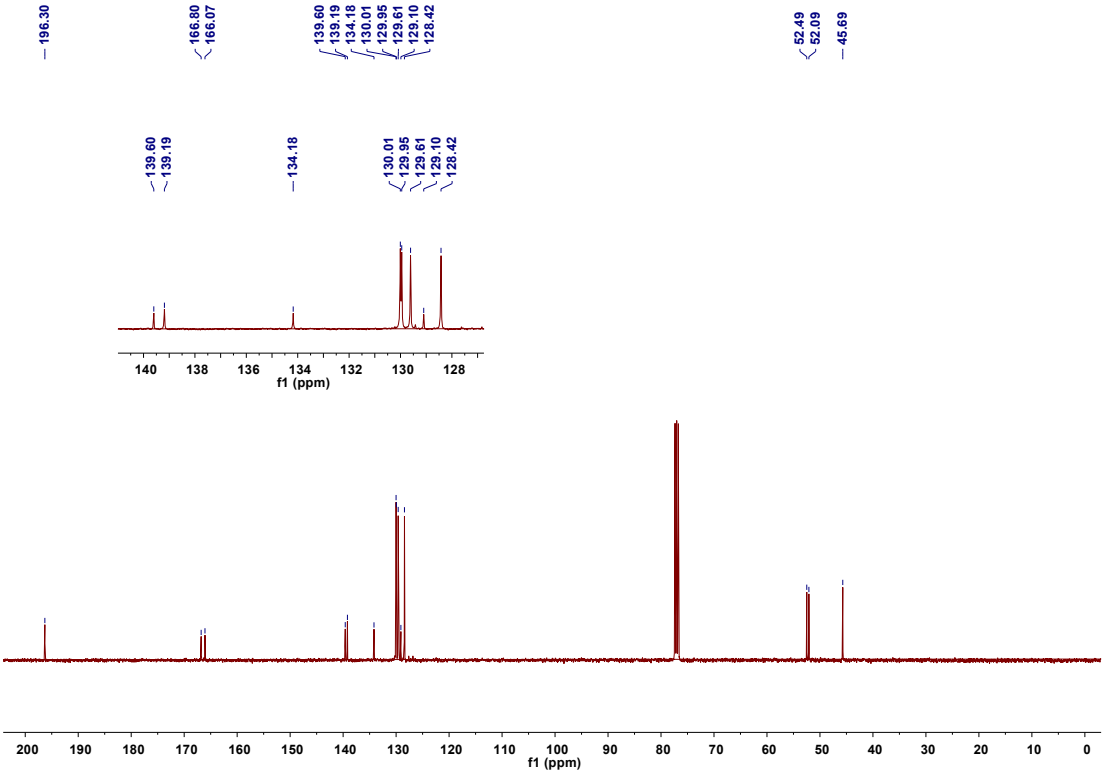

2.00
1.96
2.01
1.98
2.17
f1 (ppm)

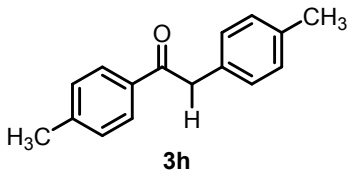

195.89
139.88
134.65
133.05
132.54
130.82
129.93
129.07
128.89
44.71
f1 (ppm)


O
CO_2Me
H
MeO_2C

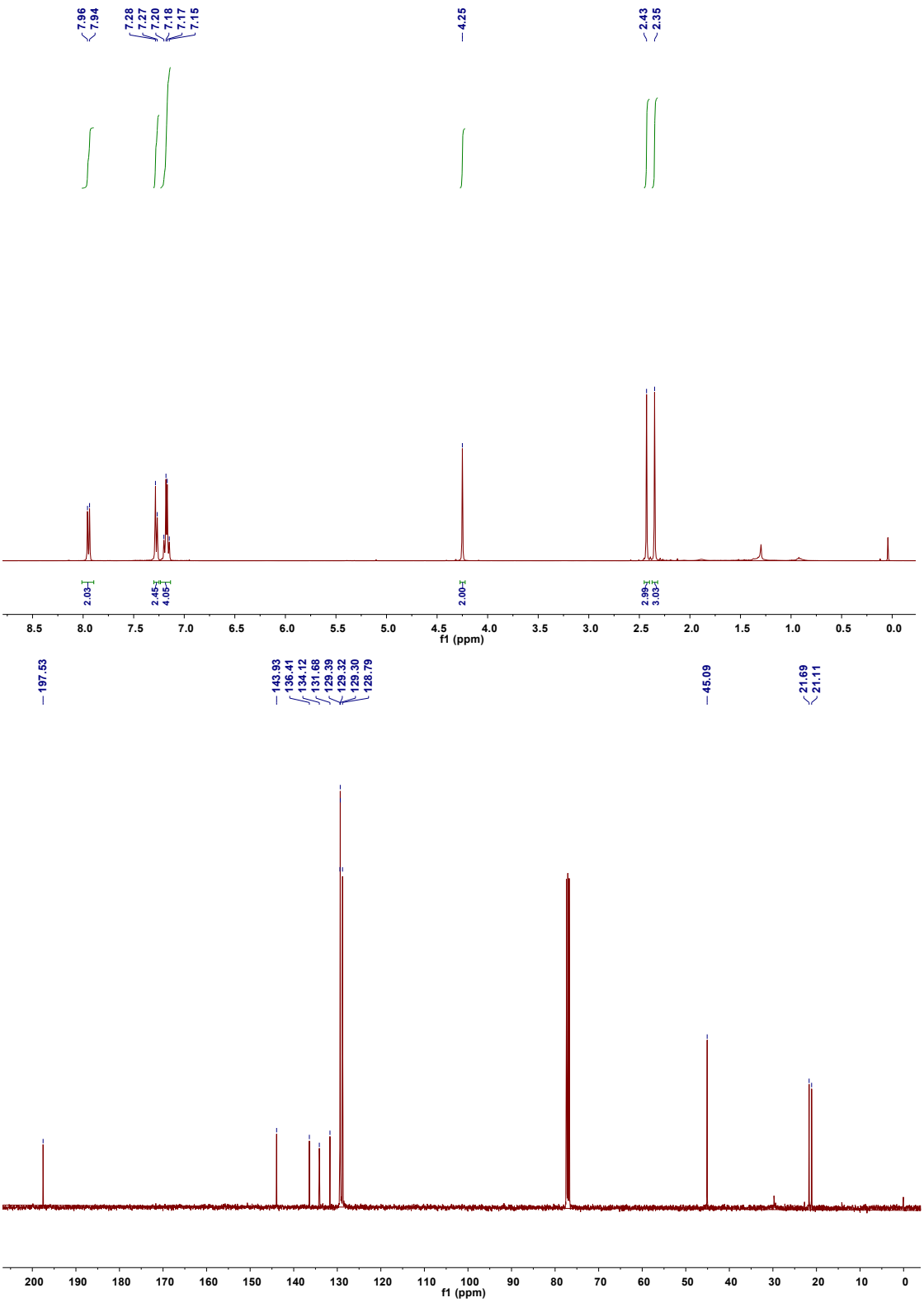
3g

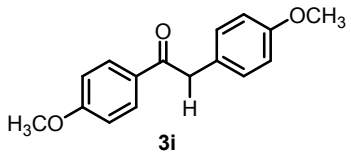

8.13
8.11
8.05
8.03
8.02
8.00
7.34
7.32
4.37
3.95
3.90
1.99
3.83
1.94
2.00
3.09
3.17
f1 (ppm)


196.30
166.80
166.07
139.60
139.19
134.18
130.01
129.95
129.61
129.10
128.42
52.49
52.09
45.69
f1 (ppm)

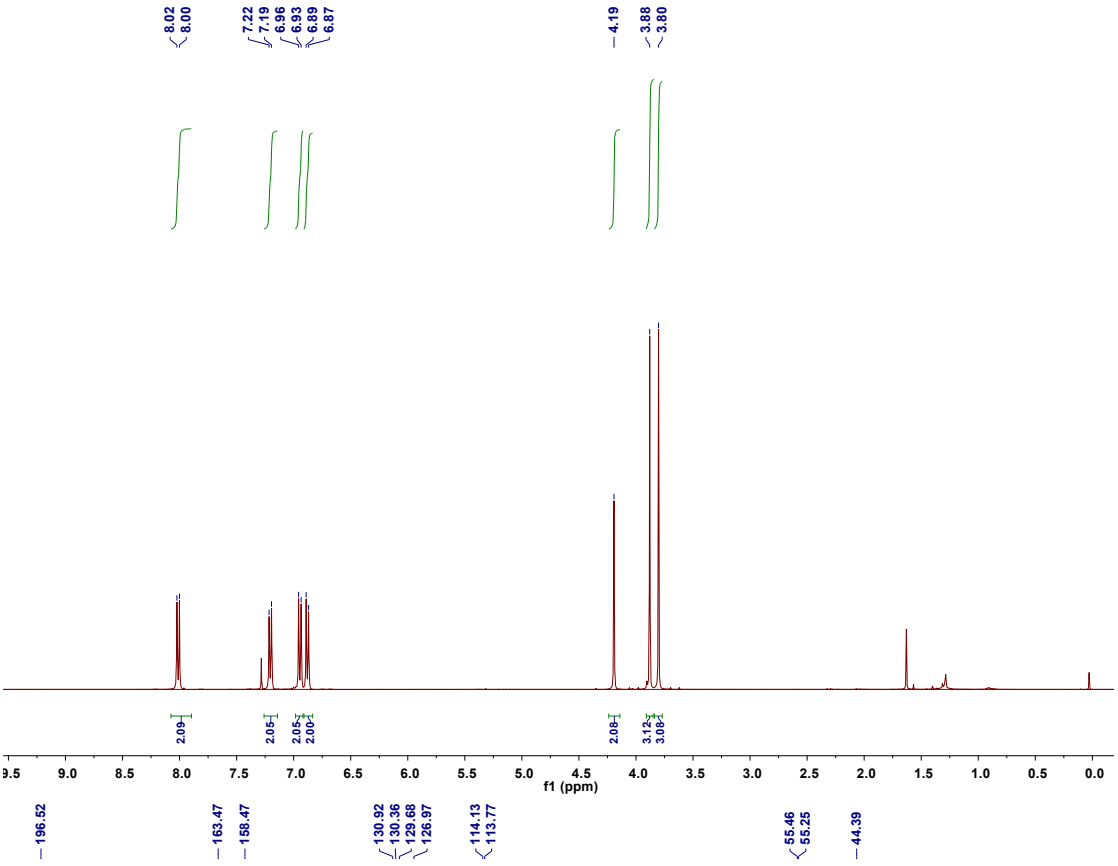

O
CH3
H
H3C

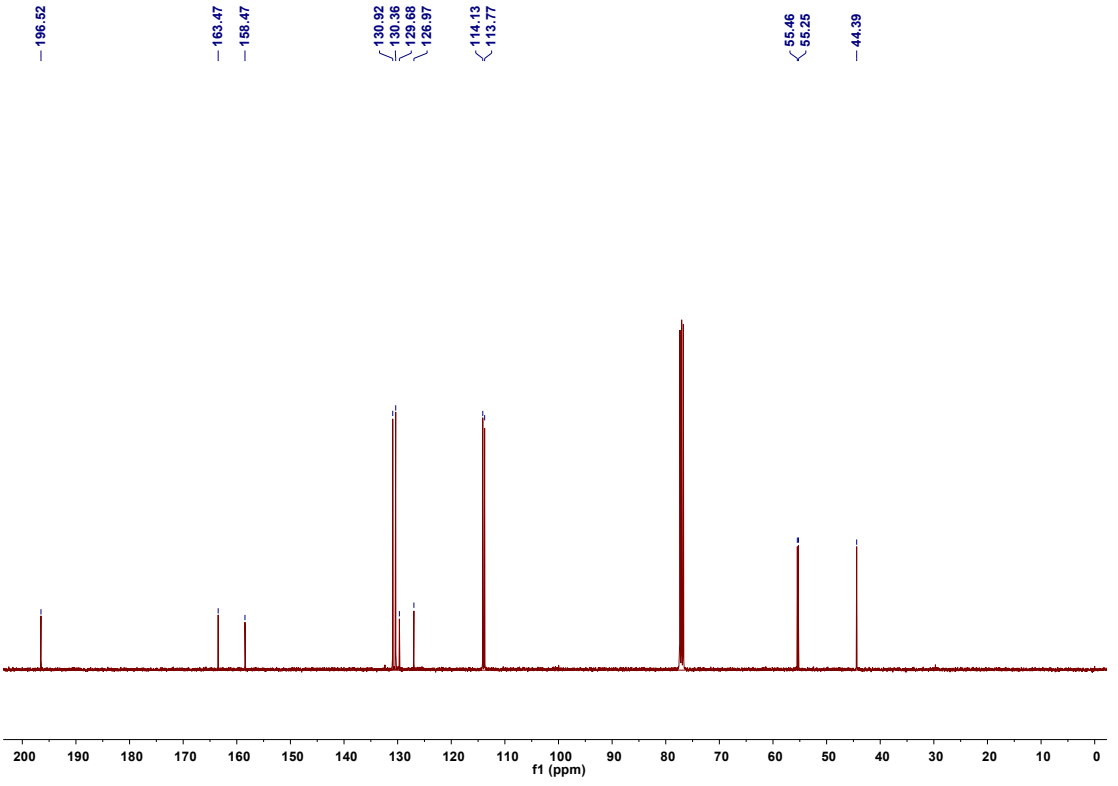
3h

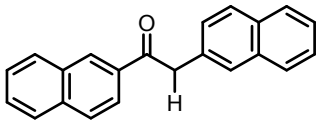

7.96
7.94
7.28
7.27
7.20
7.18
7.17
7.15
4.25
2.43
2.35
2.03
2.45
4.05
2.00
2.99
3.03
f1 (ppm)
197.53
143.93
136.41
134.12
131.68
129.39
129.32
129.30
128.79
45.09
21.69
21.11
f1 (ppm)


O
OCH3
H
H3CO

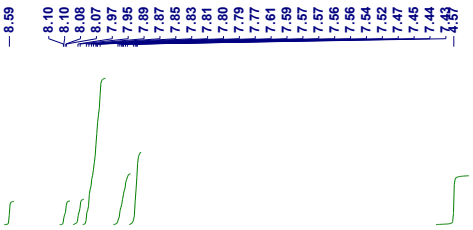
3i

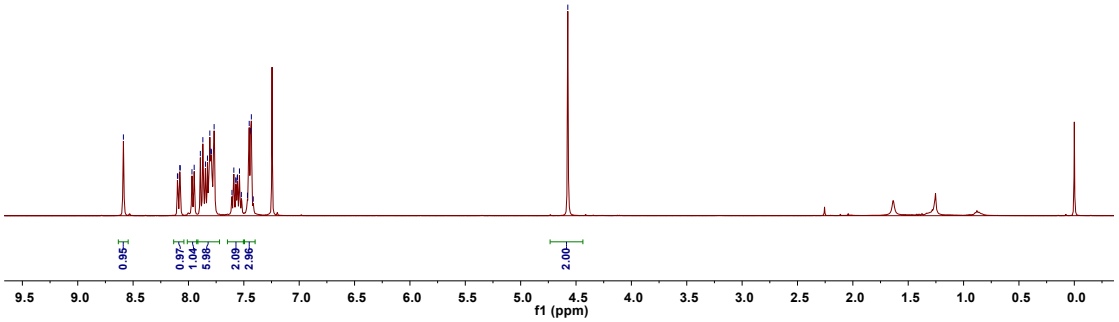

8.02
8.00
7.22
7.19
6.96
6.93
6.89
6.87
4.19
3.88
3.80
2.09
2.05
2.05
2.00
2.08
3.12
3.08
f1 (ppm)


196.52
163.47
158.47
130.92
130.36
129.68
126.97
114.13
113.77
55.46
55.25
44.39
f1 (ppm)


O
H

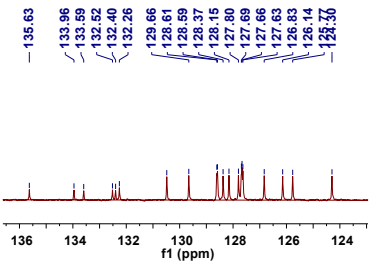
3j

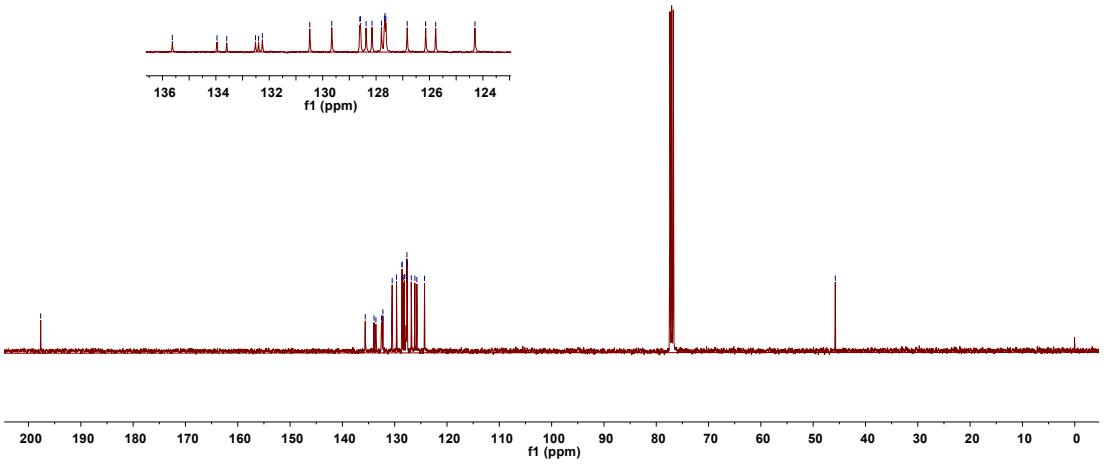

8.59
8.10
8.10
8.08
8.07
7.97
7.95
7.89
7.87
7.85
7.83
7.81
7.80
7.79
7.77
7.61
7.59
7.57
7.57
7.56
7.55
7.54
7.52
7.47
7.45
7.44
7.43
7.43

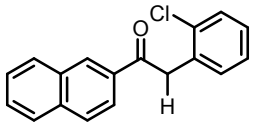

0.95
0.97
1.04
5.98
2.09
2.96
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.68
135.63
133.96
133.59
132.52
132.40
132.26
130.48
129.66
128.61
128.59
128.37
128.15
127.80
127.69
127.66
127.63
126.83
126.14
125.77
124.30

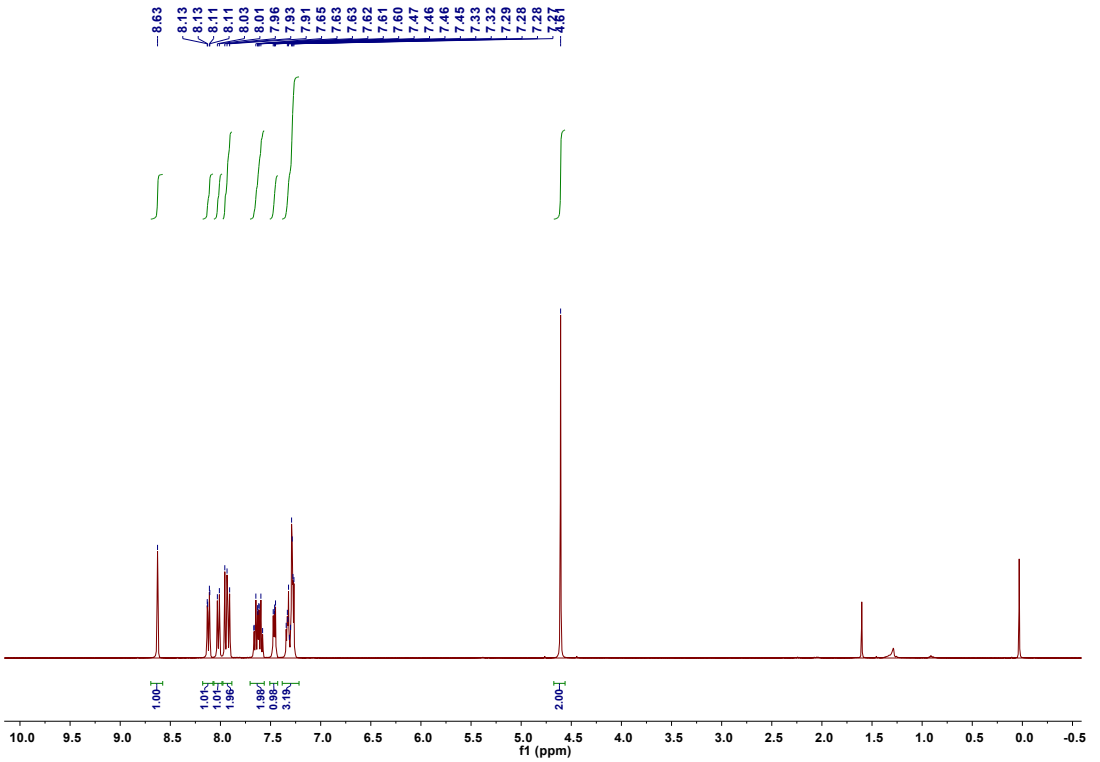

45.77

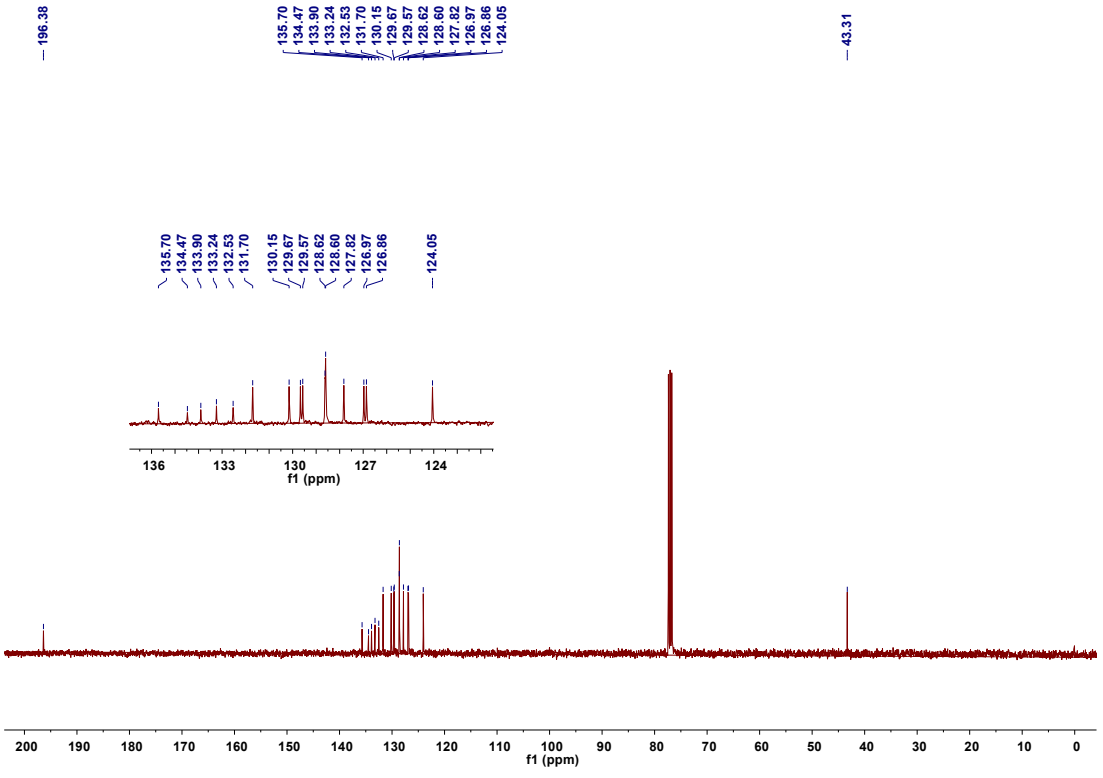

135.63
133.96
133.59
132.52
132.40
132.26
129.66
128.61
128.59
128.37
128.15
127.80
127.69
127.66
127.63
126.83
126.14
136 134 132 130 128 126 124
f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
O
H

3k


8.63
8.13
8.13
8.11
8.11
8.03
8.01
7.96
7.93
7.91
7.65
7.63
7.63
7.62
7.61
7.60
7.47
7.46
7.45
7.33
7.32
7.29
7.28
7.28
7.27
7.27
1.00
1.01
1.01
1.96
1.98
0.98
3.15
2.00
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
f1 (ppm)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135.70
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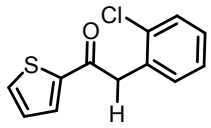
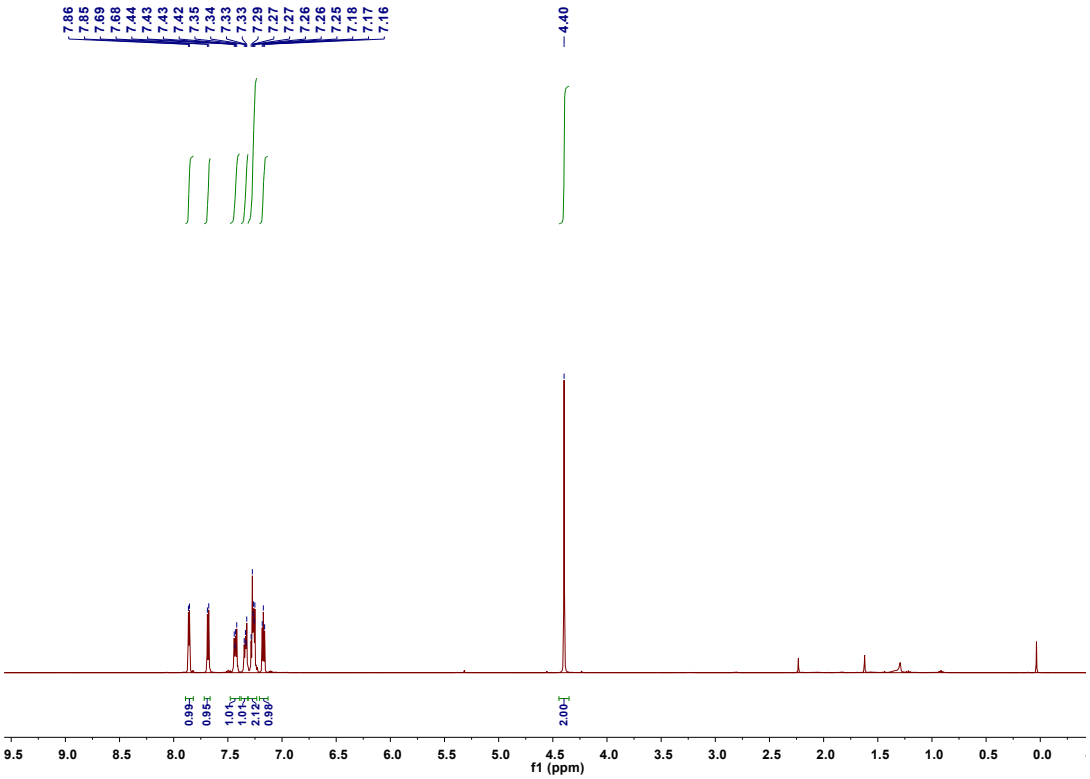
133.90
133.24
132.53
131.70
130.15
129.67
129.57
128.62
128.60
127.82
126.97
126.86
124.05
43.31
136 133 130 127 124
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
O
S
H

3l


7.86
7.85
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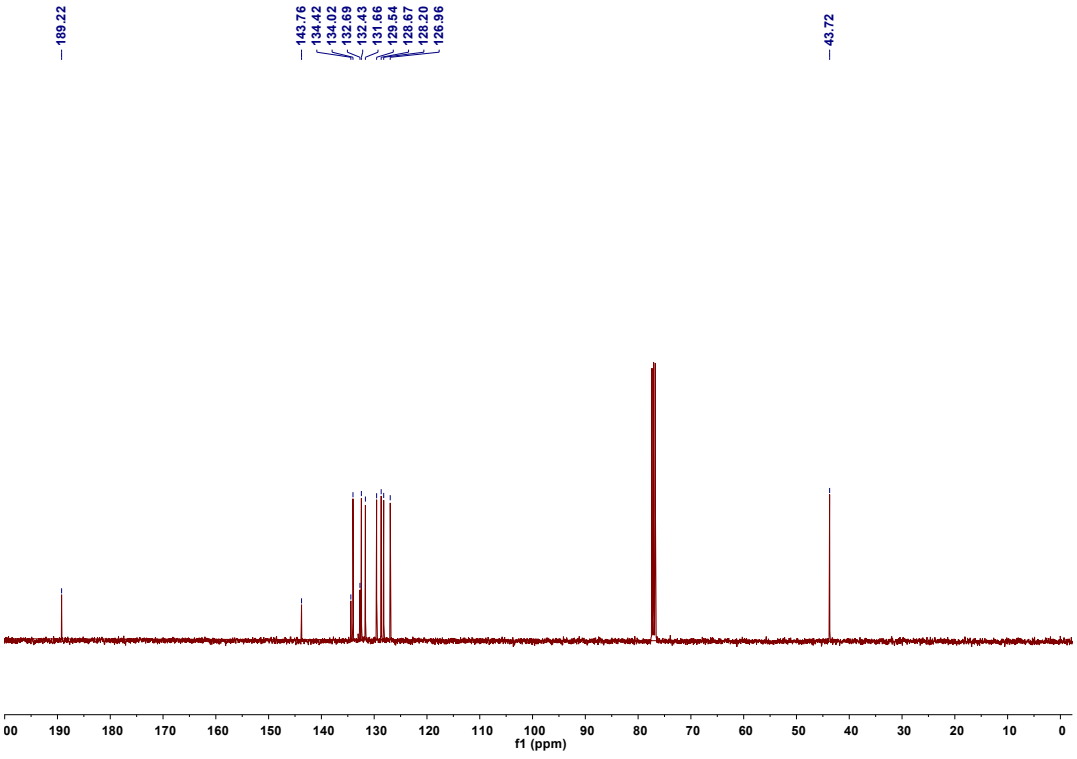
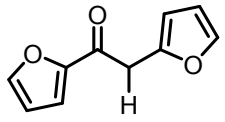
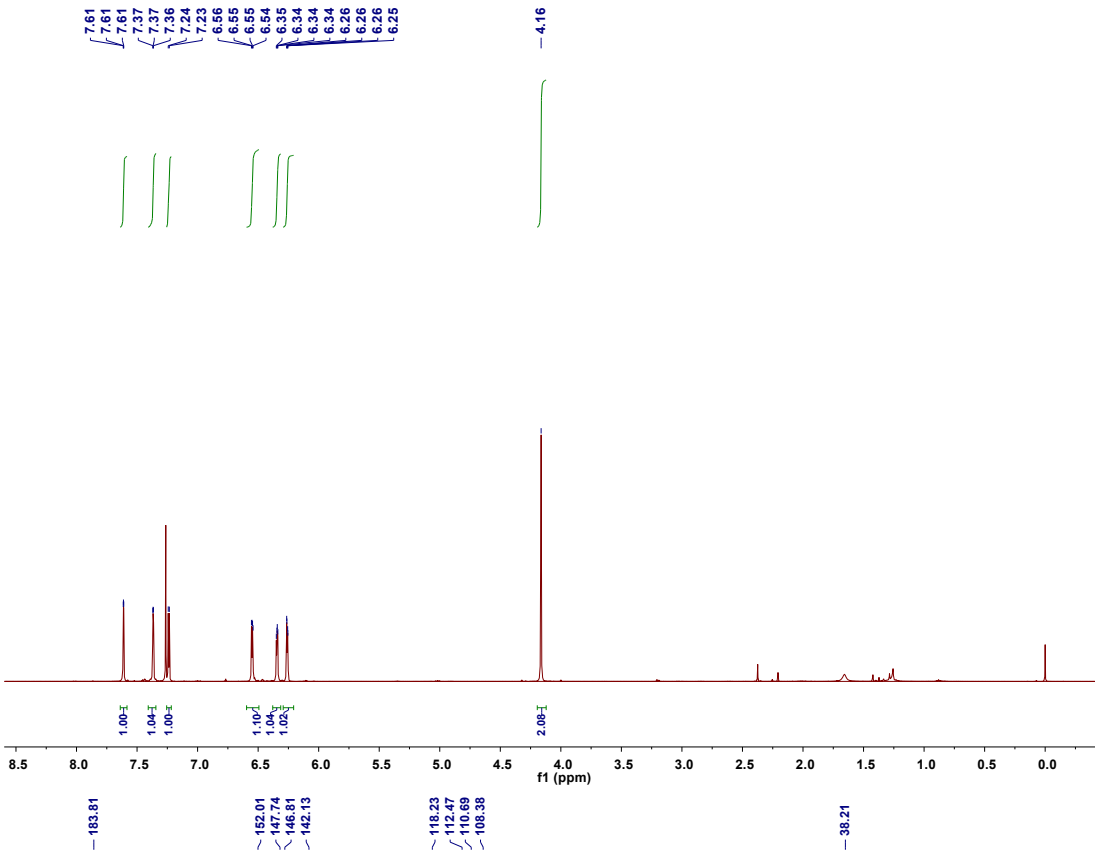
7.68
7.44
7.43
7.43
7.42
7.35
7.34
7.33
7.33
7.29
7.27
7.27
7.26
7.26
7.25
7.18
7.17
7.16
4.40
0.99
0.95
1.01
1.01
2.12
0.98
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


189.22
143.76
134.42
134.02
132.69
132.43
131.66
129.54
128.67
128.20
126.96
43.72
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
H

3m


7.61
7.61
7.61
7.37
7.37
7.36
7.24
7.23
6.56
6.55
6.55
6.54
6.35
6.34
6.34
6.34
6.26
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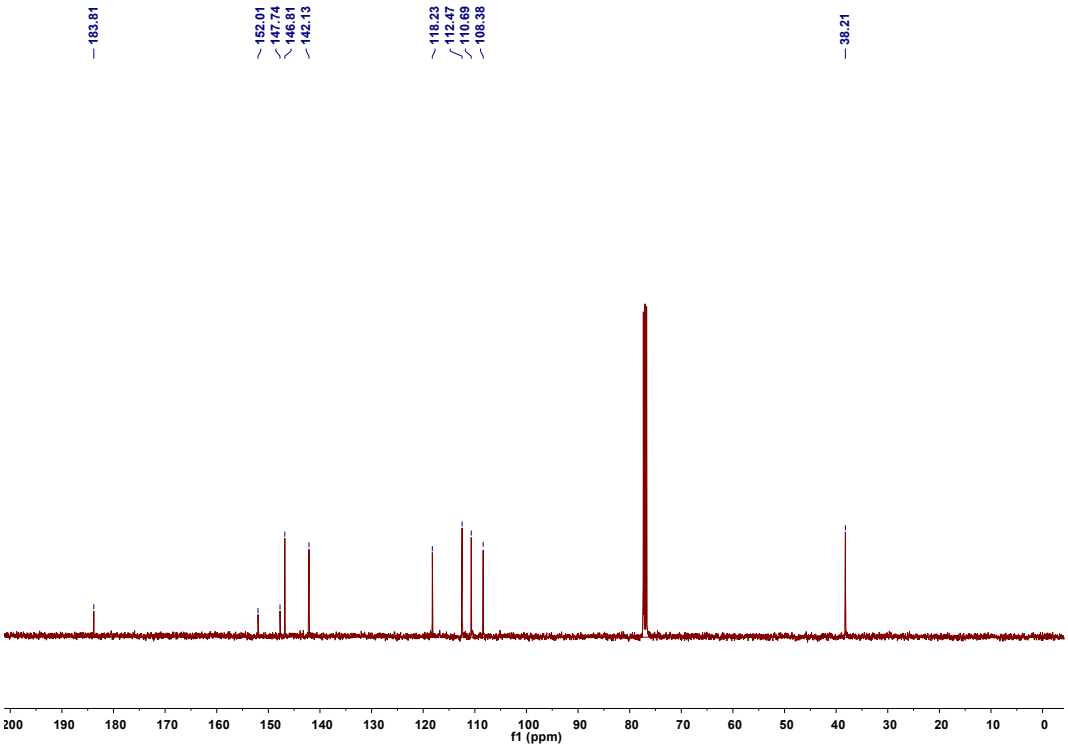
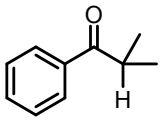
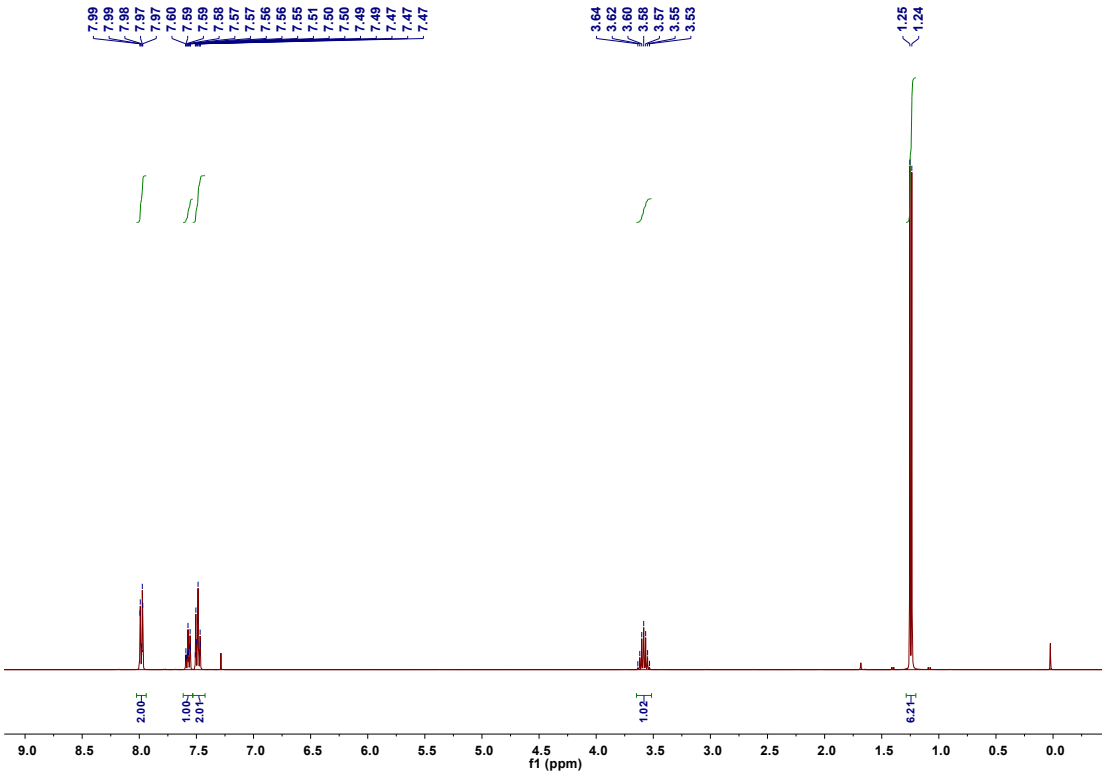
1.10
1.04
1.02
2.08
f1 (ppm)


183.81
152.01
147.74
146.81
142.13
118.23
112.47
110.69
108.38
38.21
f1 (ppm)


O
H

3n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7.97
7.60
7.59
7.59
7.58
7.57
7.57
7.56
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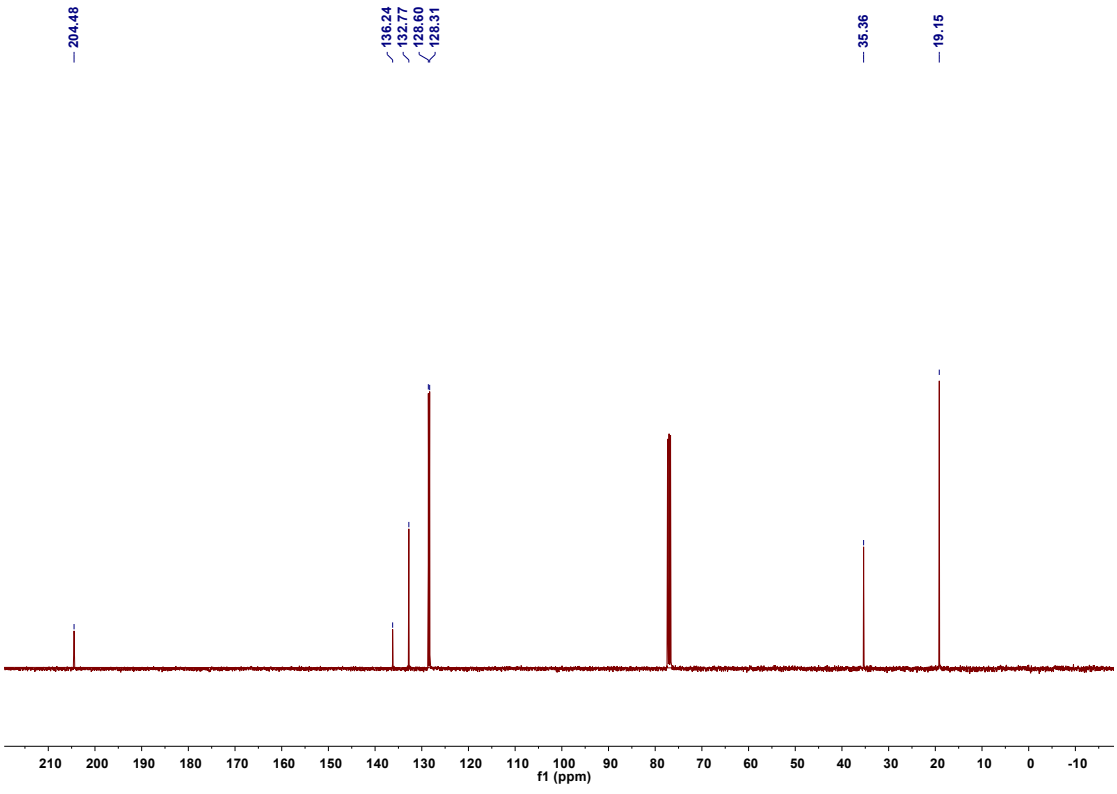
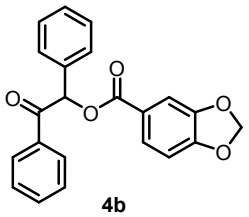
7.55
7.51
7.50
7.50
7.49
7.49
7.47
7.47
7.47
3.64
3.62
3.60
3.58
3.57
3.55
3.53
1.25
1.24
2.00
1.00
2.01
1.02
6.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.48
136.24
132.77
128.60
128.31
35.36
19.15
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)



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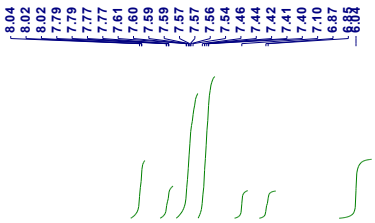
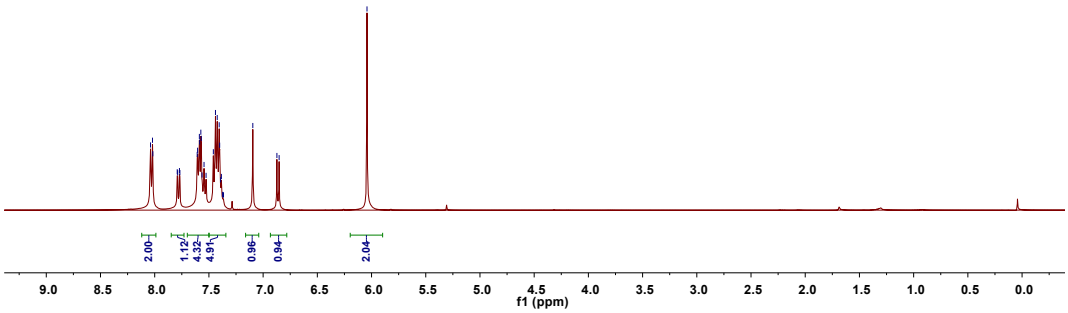
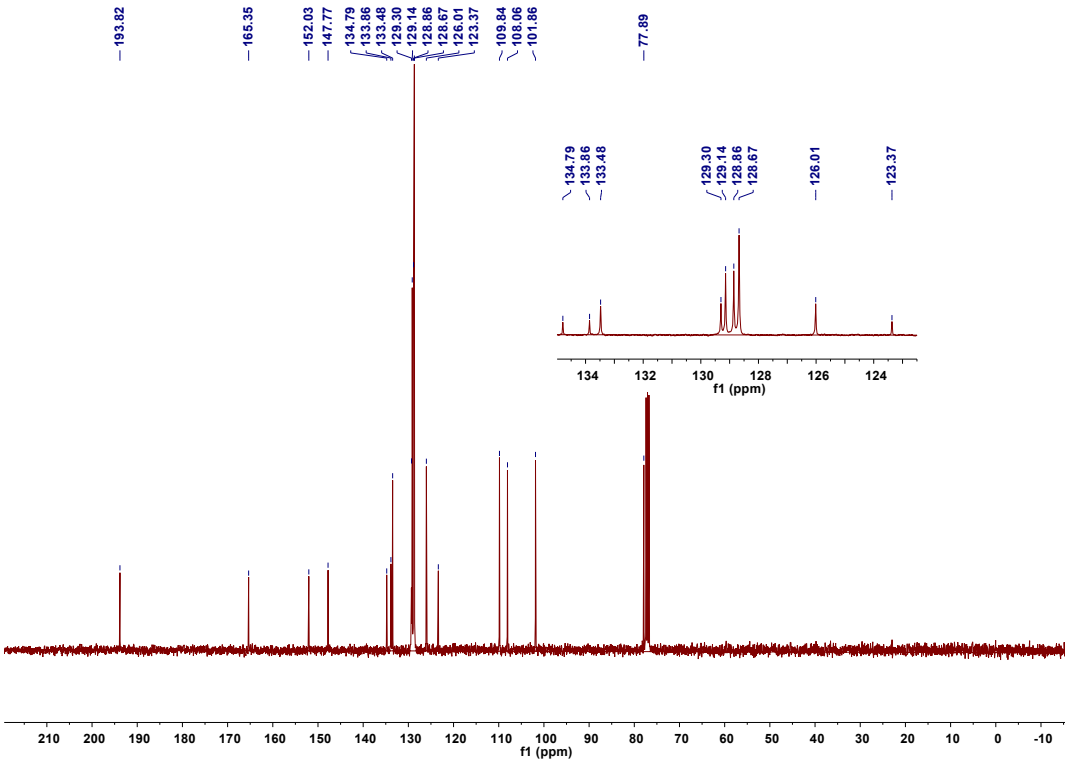

8.04
8.02
8.02
7.79
7.79
7.77
7.77
7.61
7.60
7.59
7.59
7.57
7.57
7.56
7.54
7.46
7.44
7.42
7.41
7.40
7.10
6.87
6.85
6.84


2.00
1.12
4.32
4.91
0.96
0.94
2.04
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
f1 (ppm)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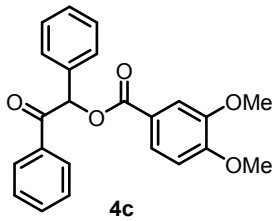
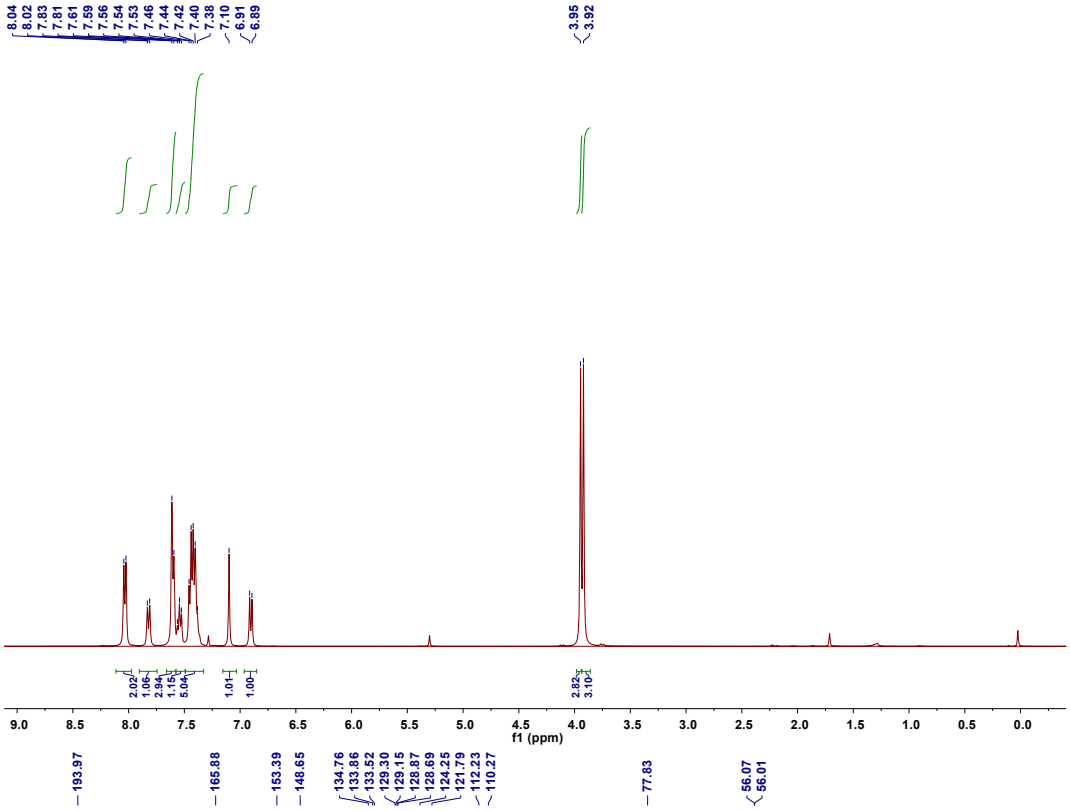
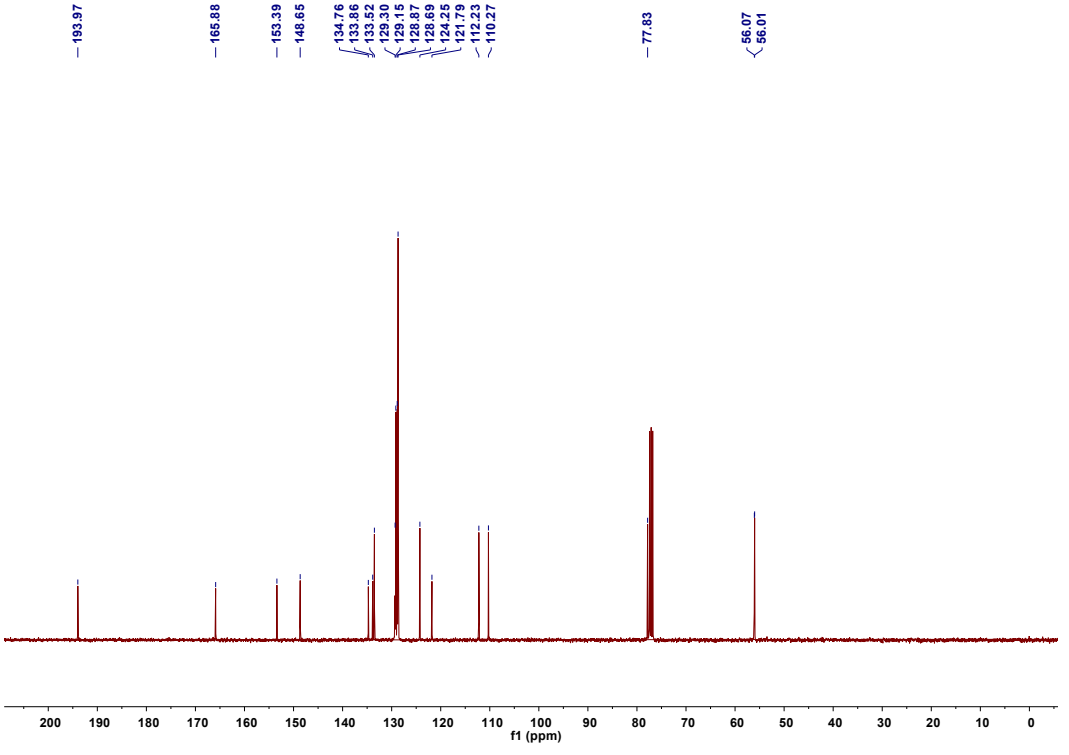
165.35
152.03
147.77
134.79
133.86
133.48
129.30
129.14
128.86
128.67
126.01
123.37
109.84
108.06
101.86
77.89
134
132
130
128
126
124
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
O
OMe
OMe

4c


8.04
8.02
7.83
7.81
7.61
7.59
7.56
7.54
7.53
7.46
7.44
7.42
7.40
7.38
7.10
6.91
6.89
3.95
3.92
2.02
1.06
2.94
1.15
5.04
1.01
1.00
2.83
3.10
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
f1 (ppm)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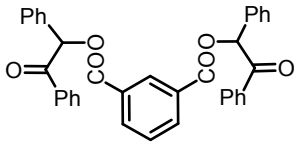
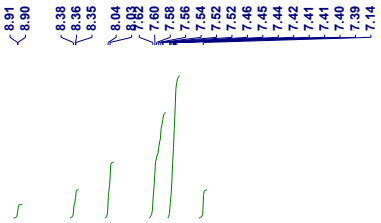
165.88
153.39
148.65
134.76
133.86
133.52
129.30
129.15
128.87
128.69
124.25
121.79
112.23
110.27
77.83
56.07
56.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
O
O
O
Ph
Ph
O
O
O
O
Ph

4d


8.91
8.90
8.38
8.36
8.35
8.04
8.03
8.02
7.60
7.58
7.56
7.54
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7.46
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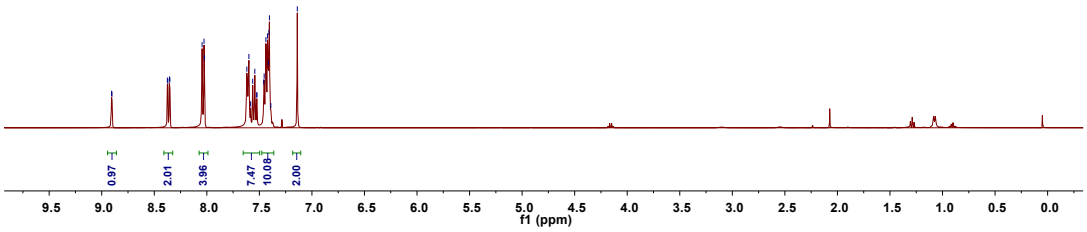
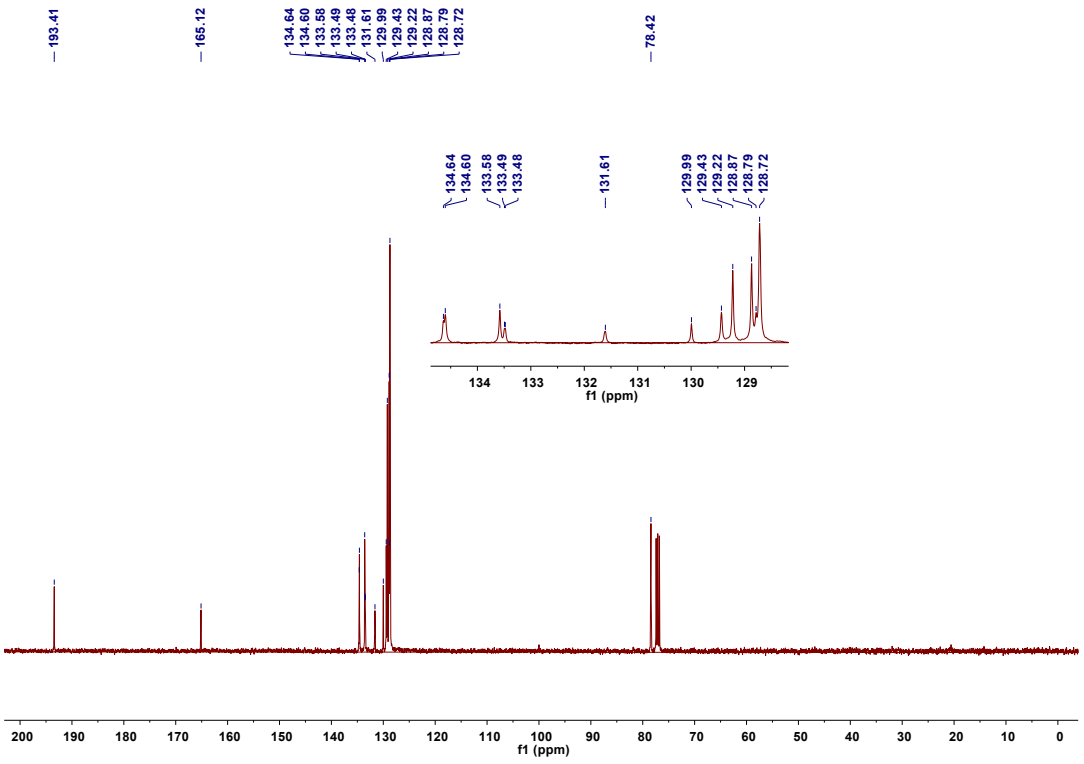
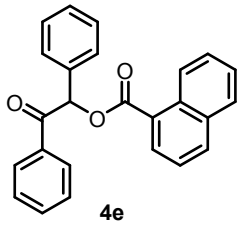
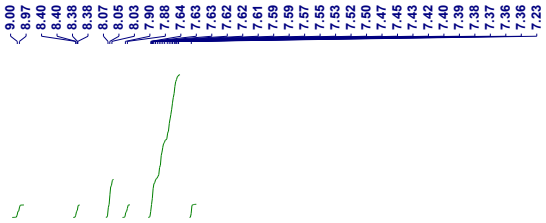
7.42
7.41
7.41
7.40
7.39
7.14


0.97
2.01
3.96
7.47
10.08
2.00
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
f1 (ppm)


193.41
165.12
134.64
134.60
133.58
133.49
133.48
131.61
129.99
129.43
129.22
128.87
128.79
128.72
78.42
134
133
132
131
130
129
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4e


9.00
8.97
8.40
8.40
8.38
8.38
8.07
8.05
8.03
7.90
7.88
7.64
7.63
7.63
7.62
7.62
7.61
7.59
7.59
7.57
7.55
7.53
7.52
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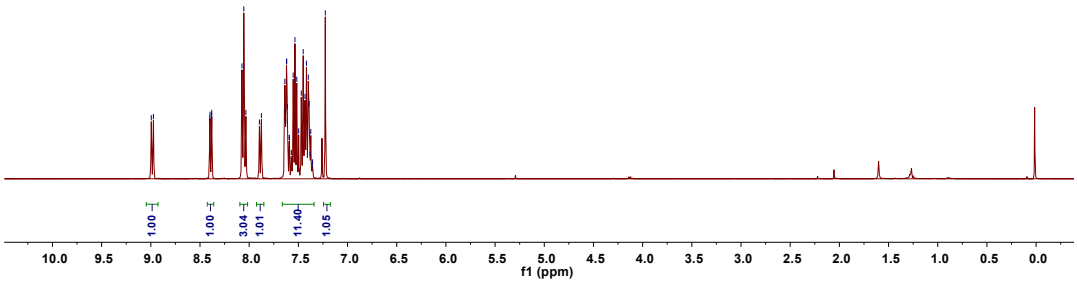
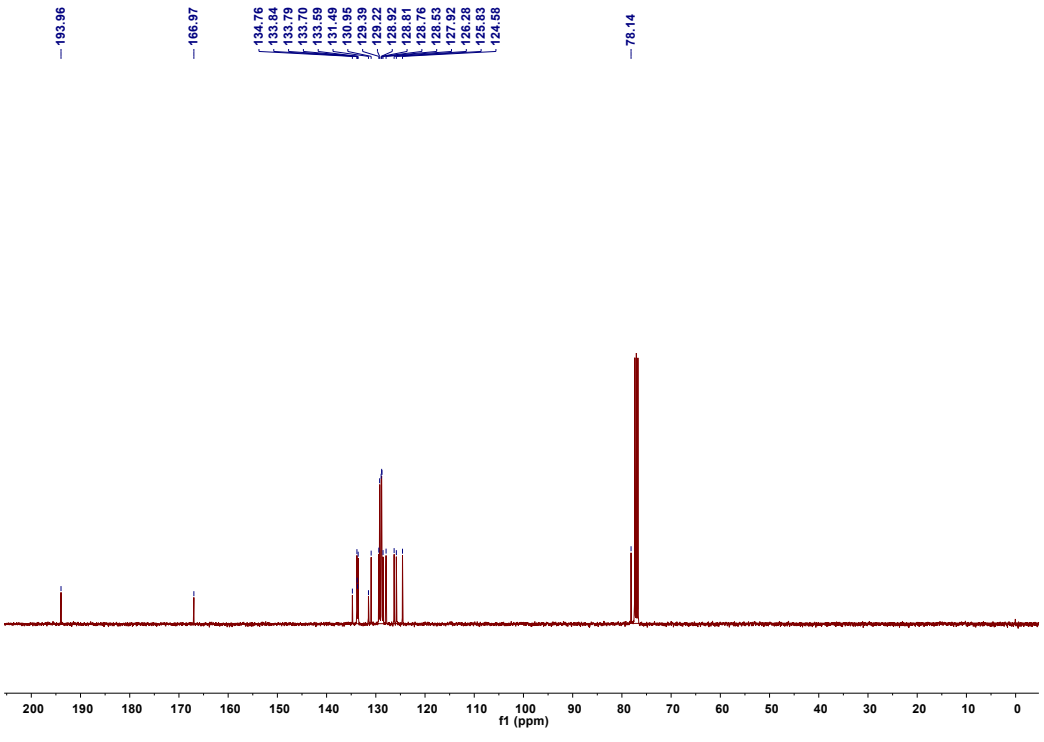
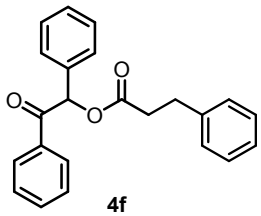
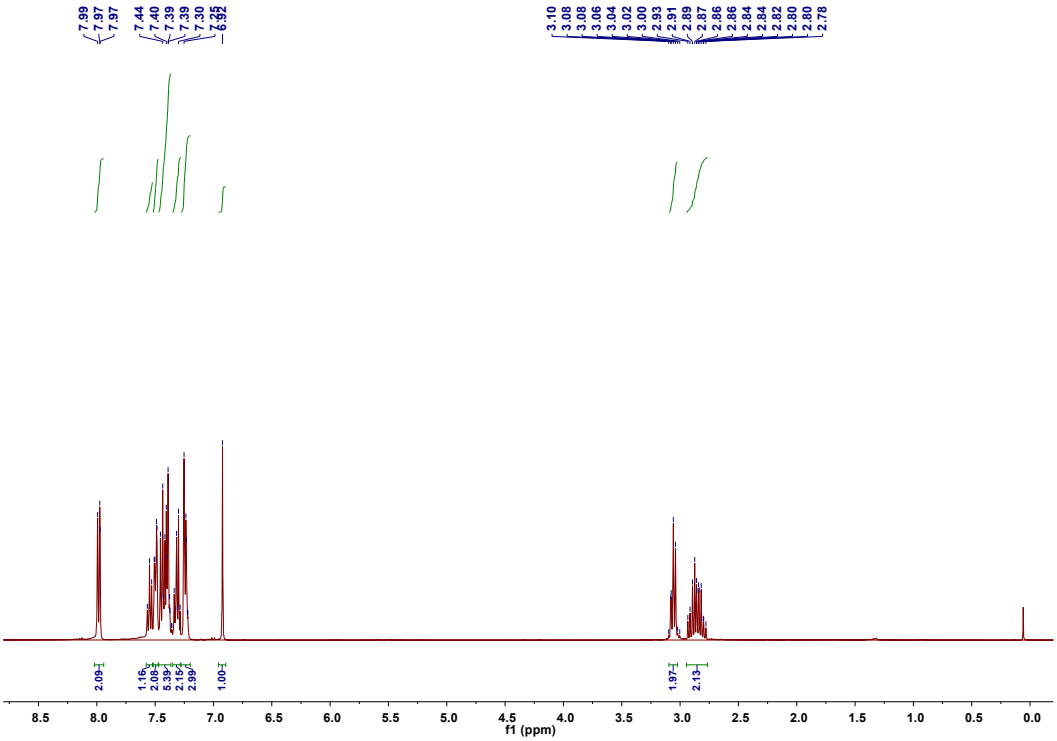
7.39
7.38
7.37
7.36
7.36
7.23


1.00
1.00
3.04
1.01
11.40
1.05
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
f1 (ppm)


193.96
166.97
134.76
133.84
133.79
133.70
133.59
131.49
130.95
129.39
129.22
128.92
128.81
128.76
128.53
127.92
126.28
125.83
124.58
78.14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4f


7.99
7.97
7.97
7.44
7.40
7.39
7.39
7.30
3.10
3.08
3.08
3.06
3.04
3.02
3.00
2.93
2.91
2.89
2.87
2.86
2.86
2.84
2.84
2.82
2.80
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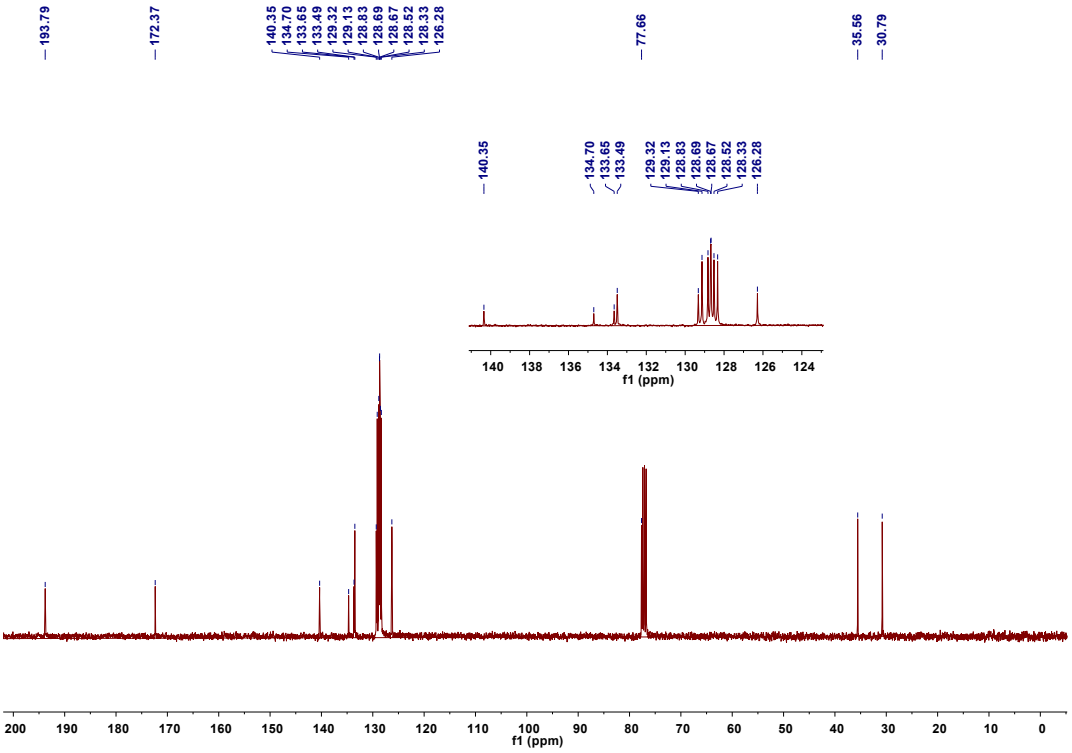
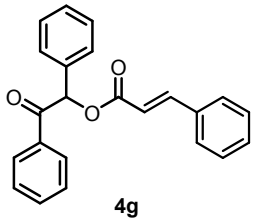
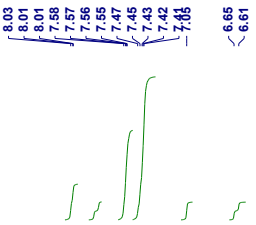
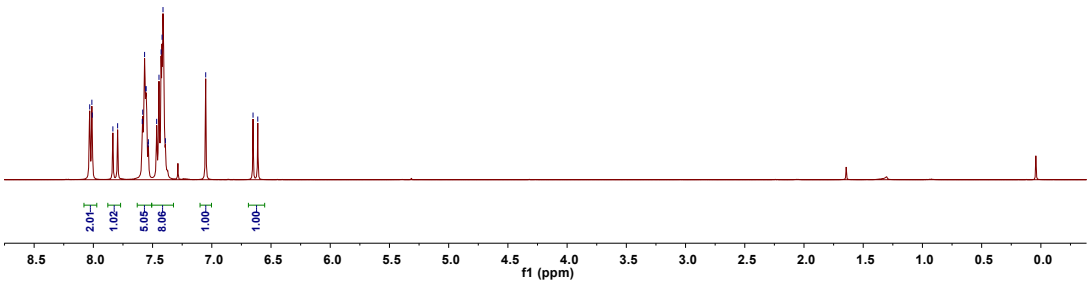
2.99
1.00
1.97
2.13
f1 (ppm)

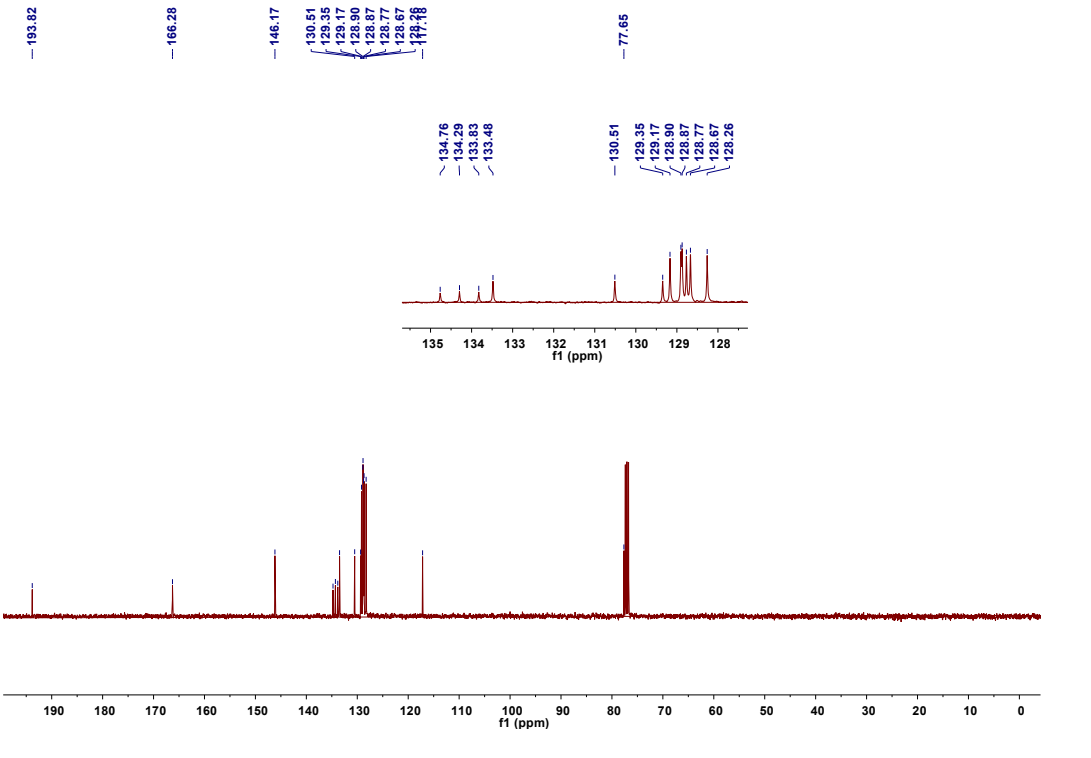

193.79
172.37
140.35
134.70
133.65
133.49
129.32
129.13
128.83
128.69
128.67
128.52
128.33
126.28
77.66
35.56
30.79
f1 (ppm)

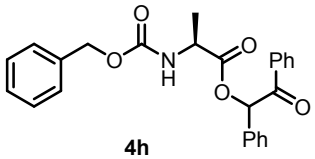


4g

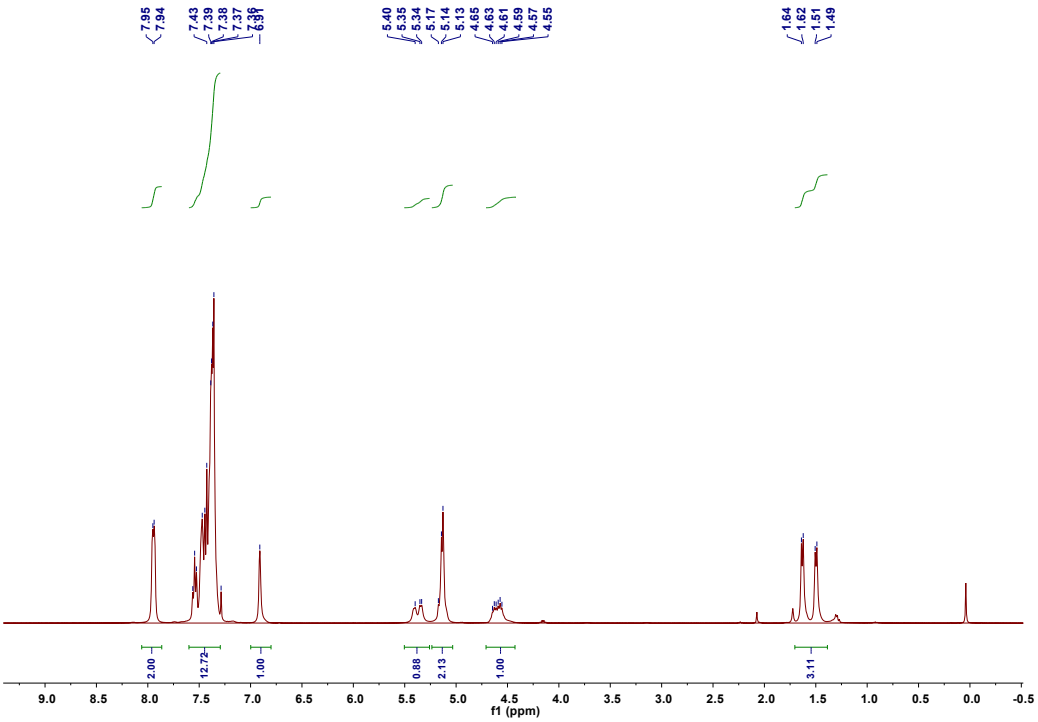

8.03
8.01
8.01
7.58
7.57
7.56
7.55
7.47
7.45
7.43
7.42
6.65
6.61


2.01
1.02
5.05
8.06
1.00
1.00
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
f1 (ppm)


193.82
166.28
146.17
130.51
129.35
129.17
128.90
128.87
128.77
128.67
77.65
134.76
134.29
133.83
133.48
130.51
129.35
129.17
128.90
128.87
128.77
128.67
128.26
135
134
133
132
131
130
129
128
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4h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7.94
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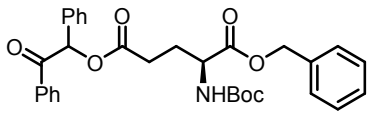
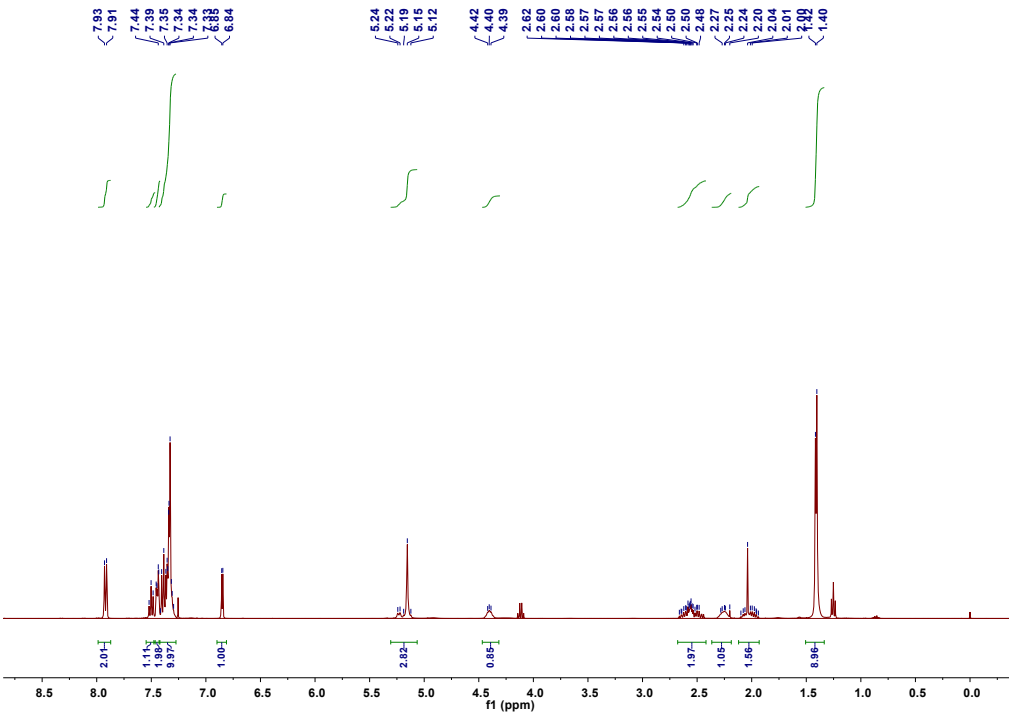
7.39
7.38
7.37
5.40
5.35
5.34
5.17
5.14
5.13
4.65
4.63
4.61
4.59
4.57
4.55
1.64
1.62
1.51
1.49
2.00
12.72
1.00
0.88
2.13
1.00
3.11
f1 (ppm)



4i


7.93
7.91
7.44
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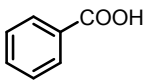
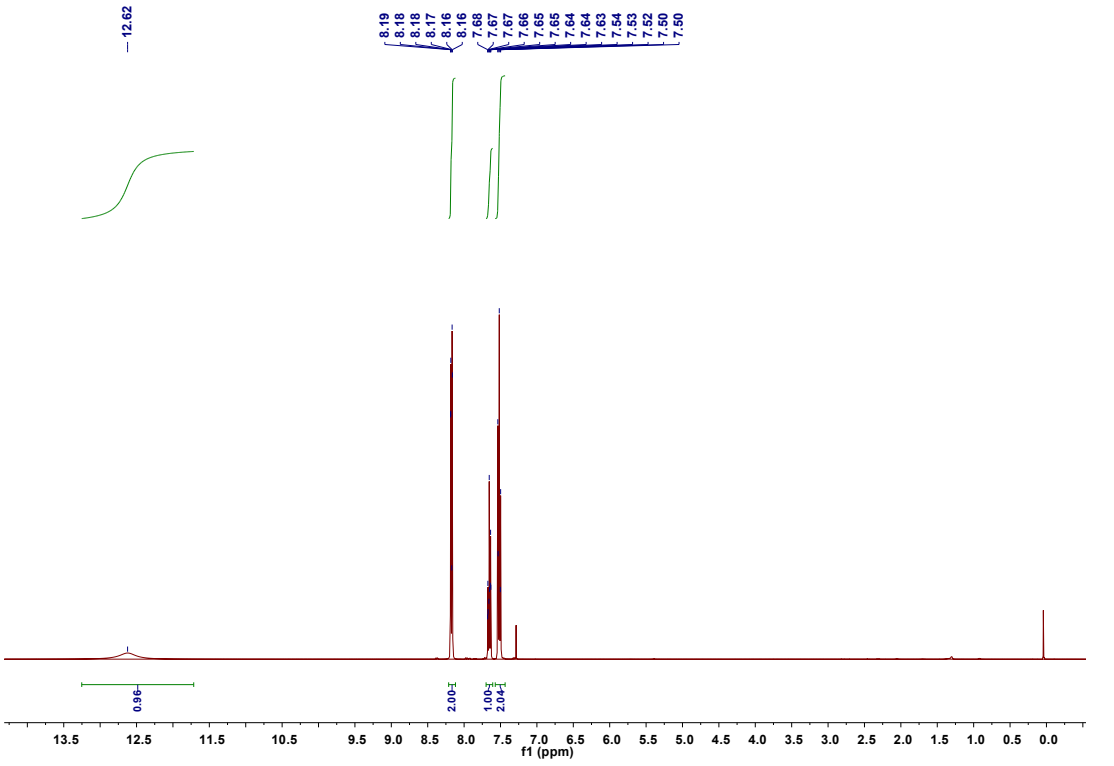
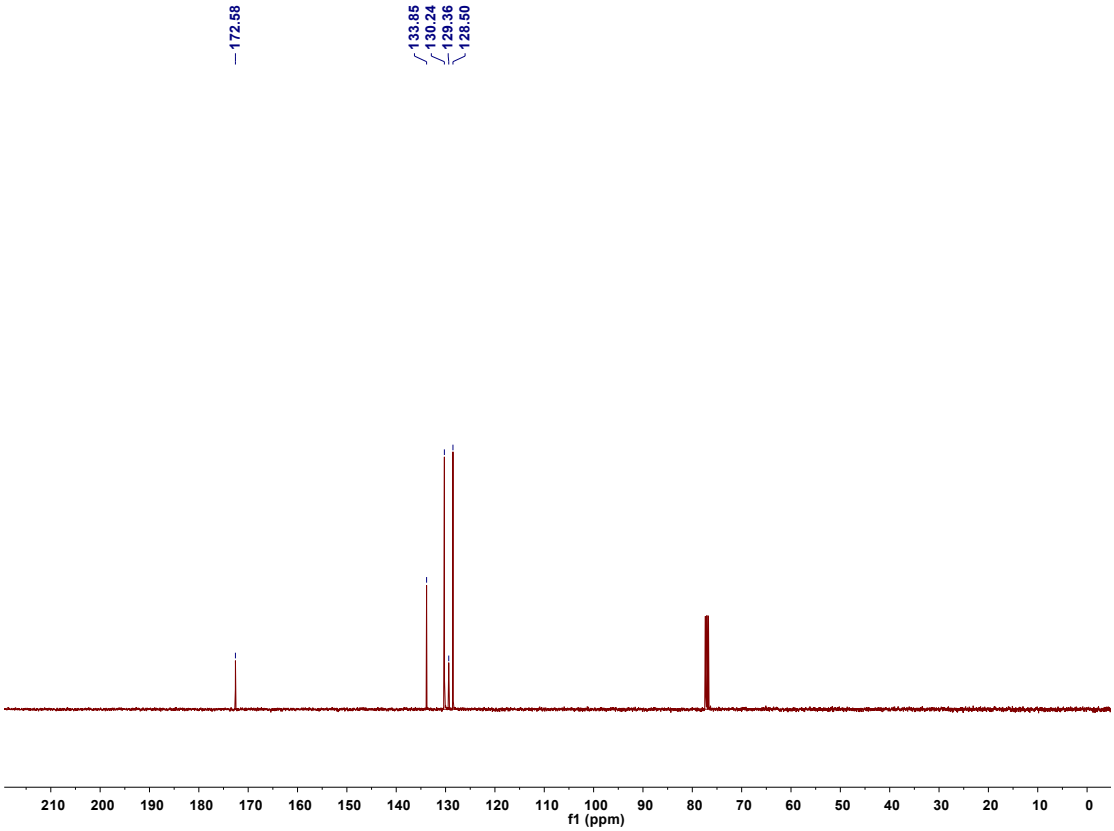
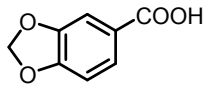
7.35
7.34
7.34
6.84
5.24
5.22
5.19
5.15
5.12
4.42
4.40
4.39
2.62
2.60
2.60
2.58
2.57
2.57
2.56
2.56
2.55
2.54
2.50
2.50
2.48
2.27
2.25
2.24
2.20
2.04
2.01
1.40
2.01
1.11
1.98
9.97
1.00
2.82
0.85
1.97
1.05
1.56
8.96
f1 (ppm)


COOH

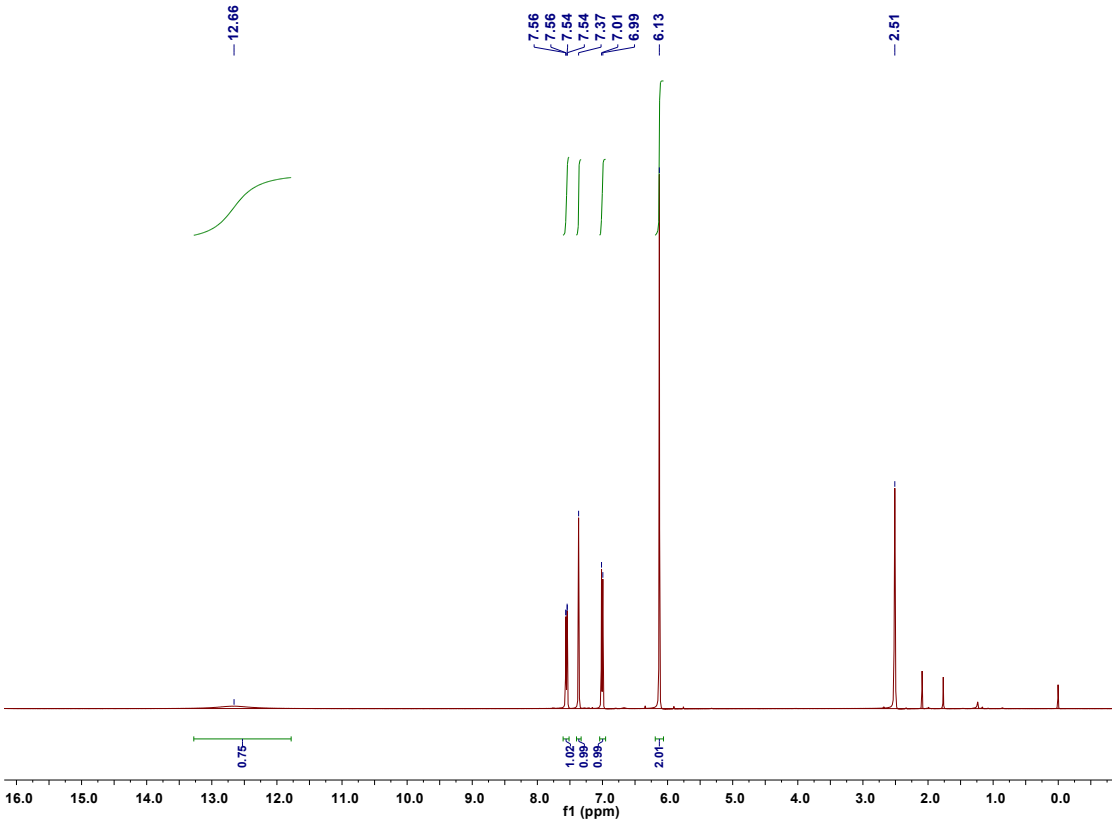
5a

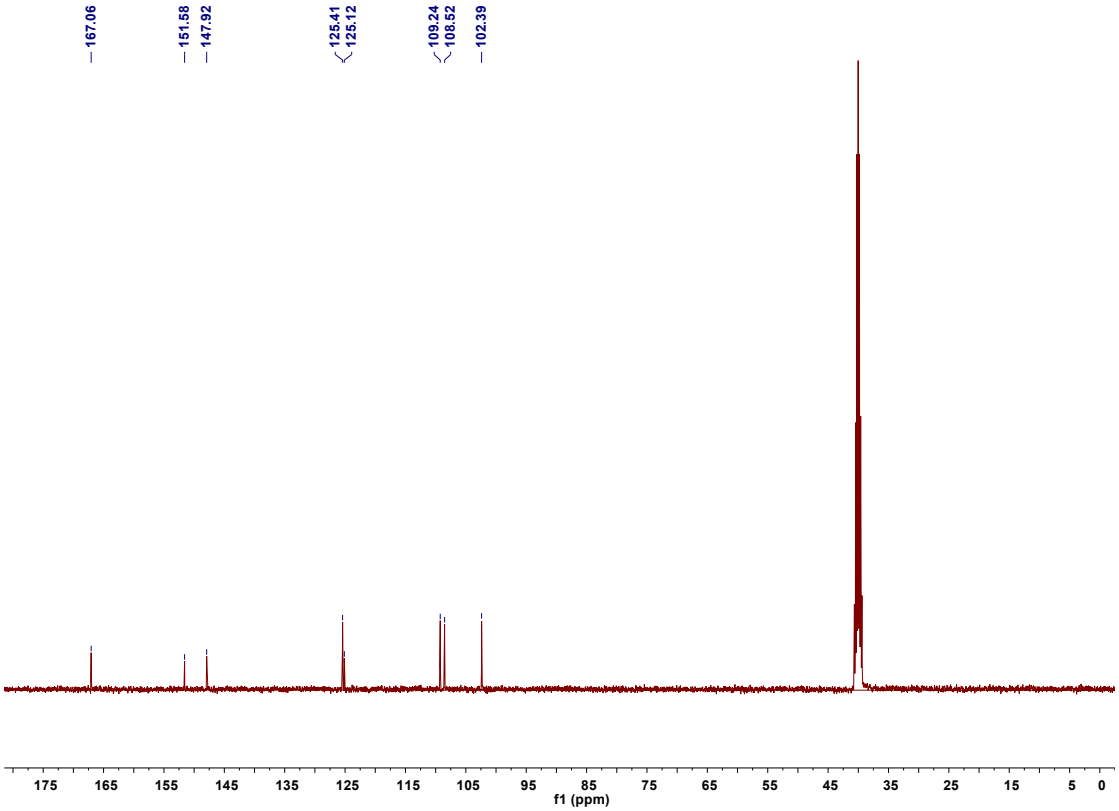

12.62
8.19
8.18
8.18
8.17
8.16
8.16
7.68
7.67
7.67
7.66
7.65
7.65
7.64
7.64
7.63
7.54
7.53
7.52
7.50
7.50
0.96
2.00
1.00
2.04
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

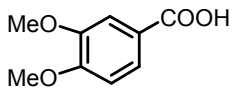

172.58
133.85
130.24
129.36
128.50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


COOH
O
O

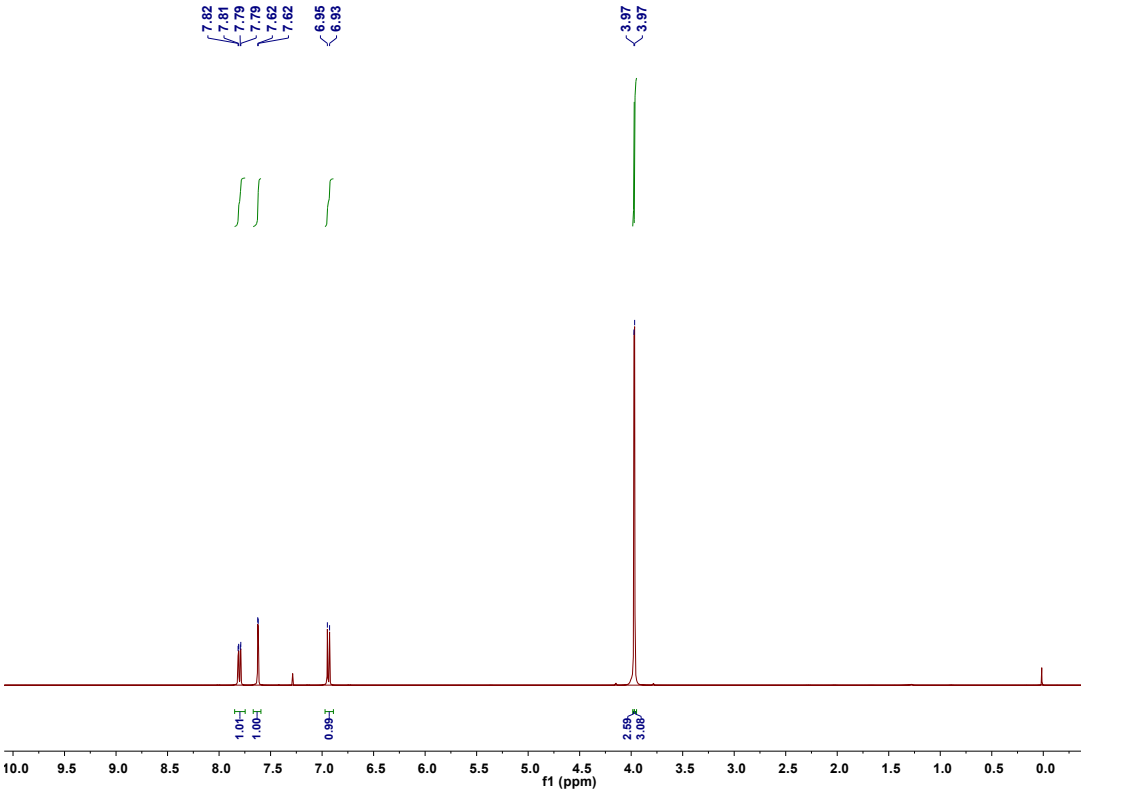
5b

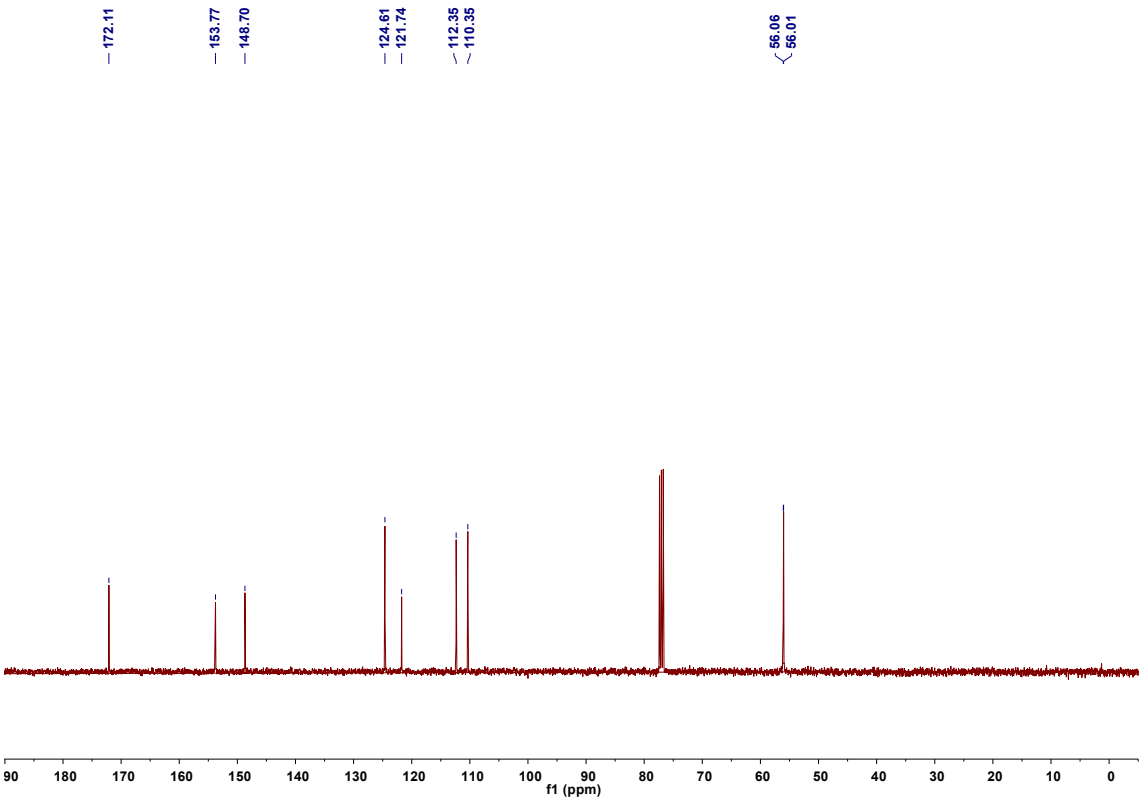

12.66
7.56
7.56
7.54
7.54
7.37
7.01
6.99
6.13
2.51
0.75
1.02
0.99
0.99
2.01
f1 (ppm)

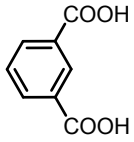

167.06
151.58
147.92
125.41
125.12
109.24
108.52
102.39
f1 (ppm)


MeO
COOH
MeO

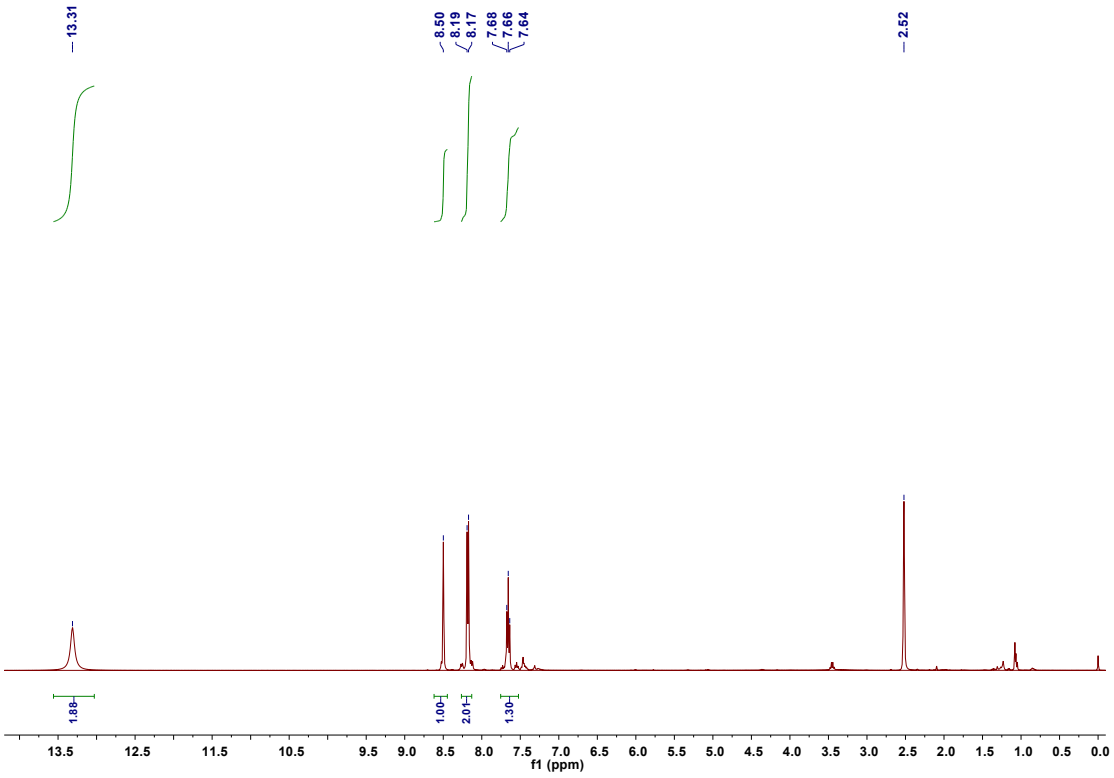
5c

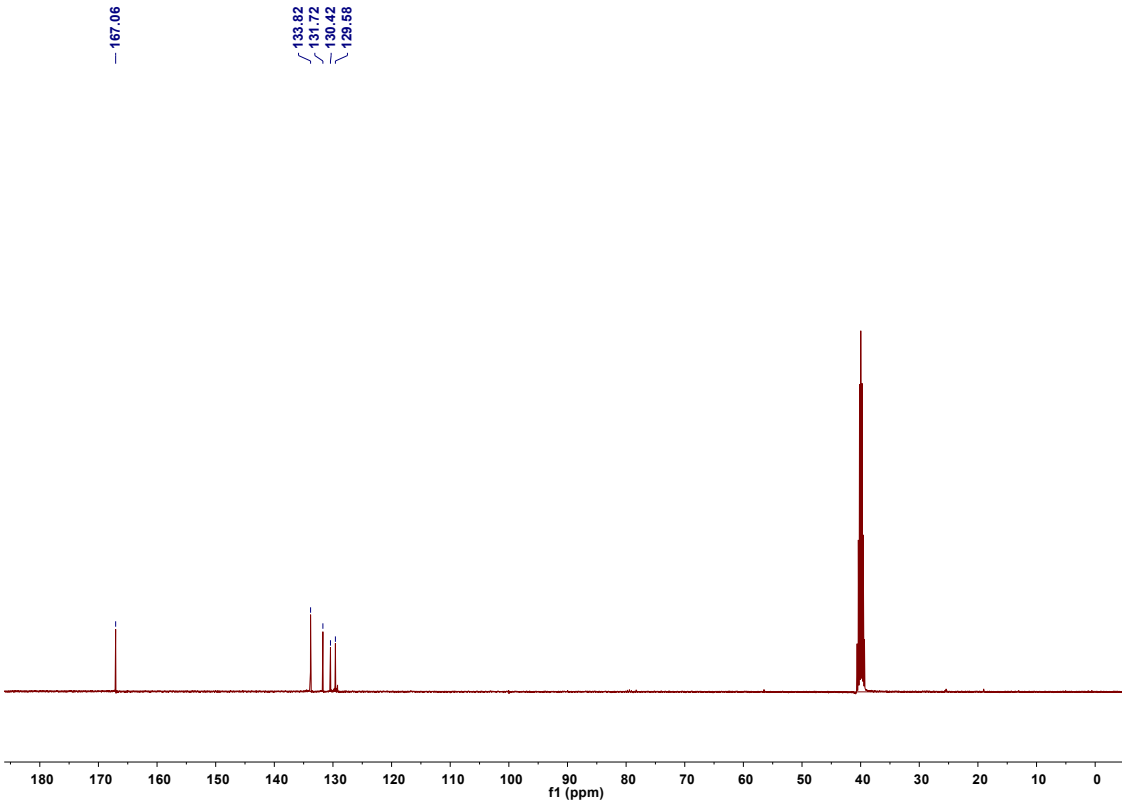

7.82
7.81
7.79
7.79
7.62
7.62
6.95
6.93
3.97
3.97
1.01
1.00
0.99
2.59
3.08
f1 (ppm)

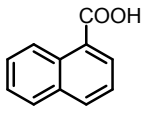

172.11
153.77
148.70
124.61
121.74
112.35
110.35
56.06
56.01
f1 (ppm)


COOH
COOH

5d

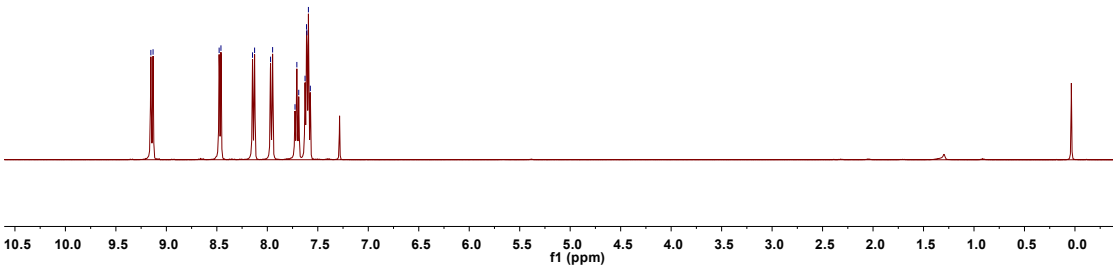

13.31
8.50
8.19
8.17
7.68
7.66
7.64
2.52
1.88
1.00
2.01
1.30
f1 (ppm)


167.06
133.82
131.72
130.42
129.58
f1 (ppm)

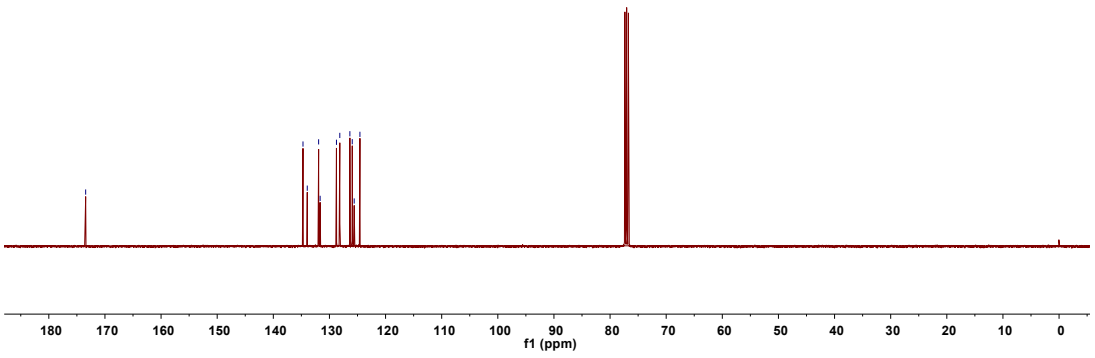

COOH

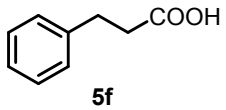
5e


9.15
9.13
8.48
8.46
8.15
8.13
7.97
7.95
7.73
7.71
7.69
7.63
7.61
7.61
7.59
7.57

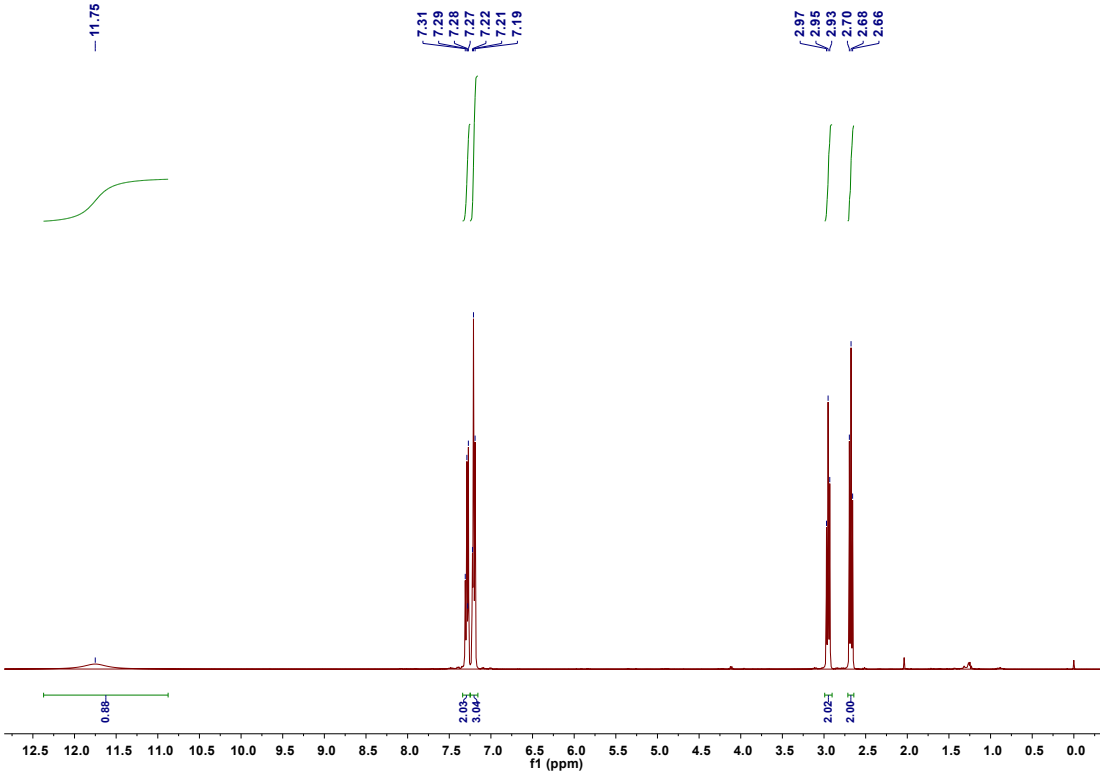

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

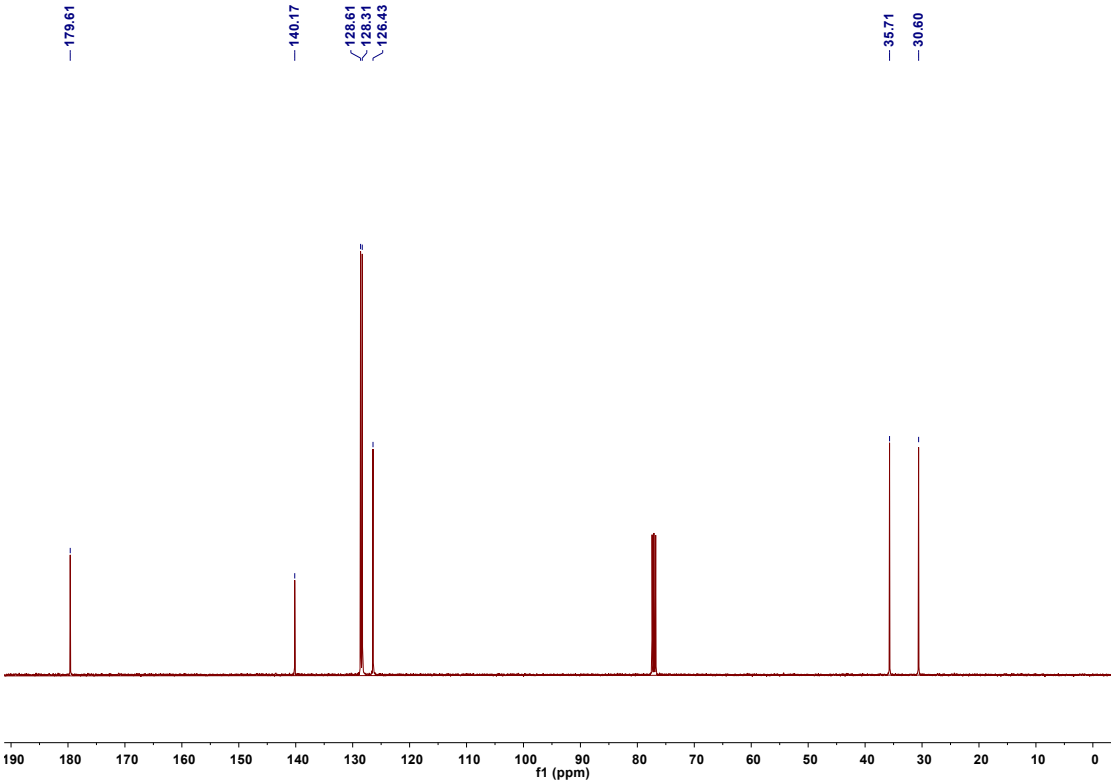

173.43
134.71
133.95
131.93
131.66
128.75
128.15
126.36
125.94
125.59
124.57

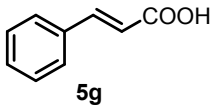

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


COOH

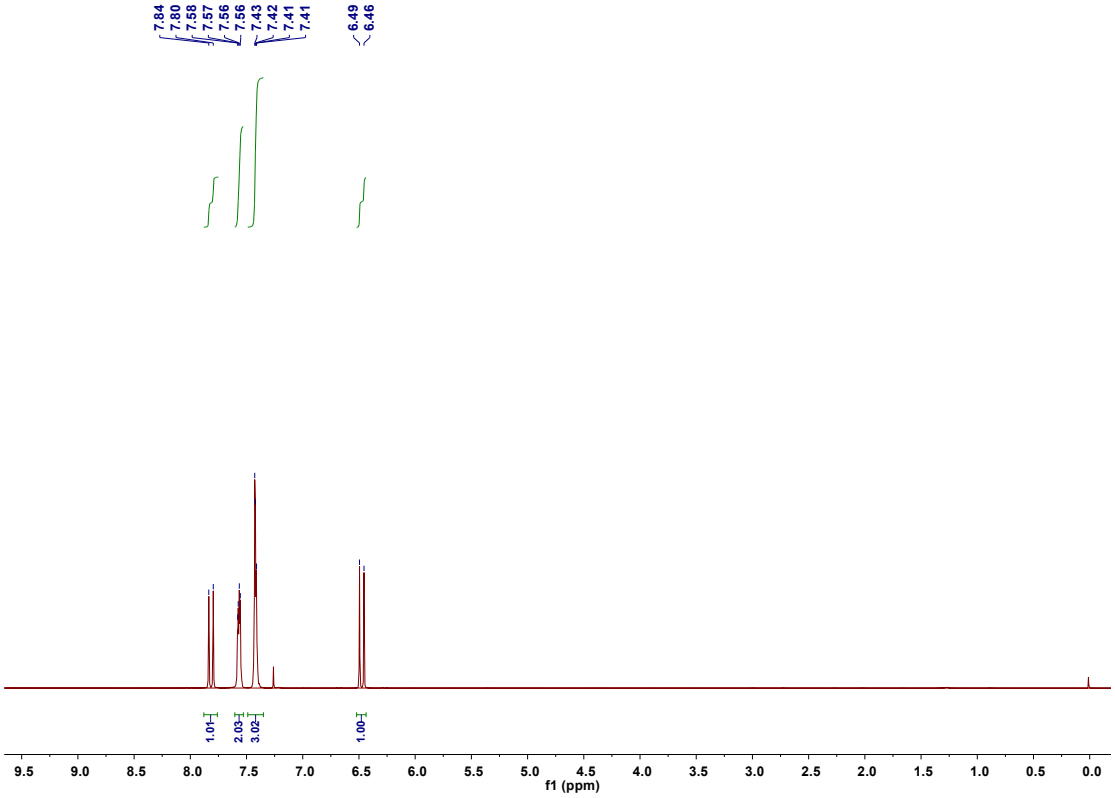
5f

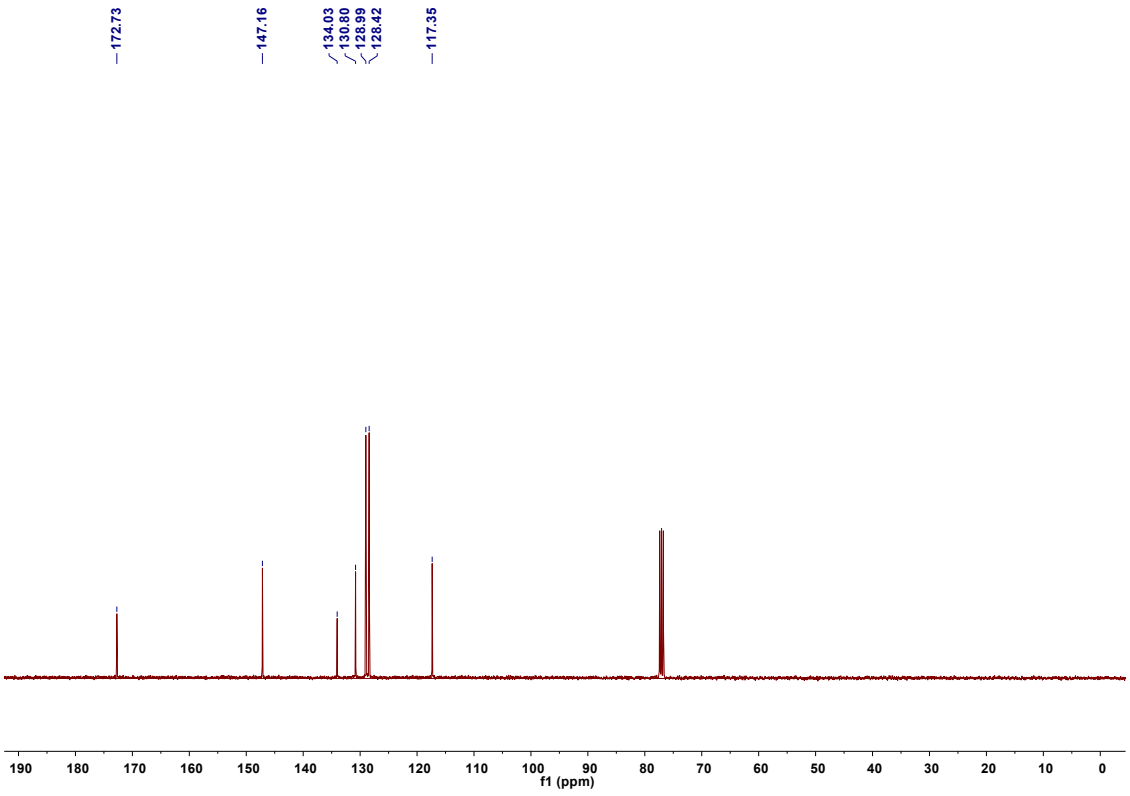

11.75
7.31
7.29
7.28
7.27
7.22
7.21
7.19
2.97
2.95
2.93
2.70
2.68
2.66
0.88
2.03
3.04
2.02
2.00
f1 (ppm)

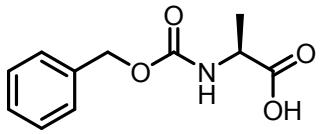

179.61
140.17
128.61
128.31
126.43
35.71
30.60
f1 (ppm)


COOH

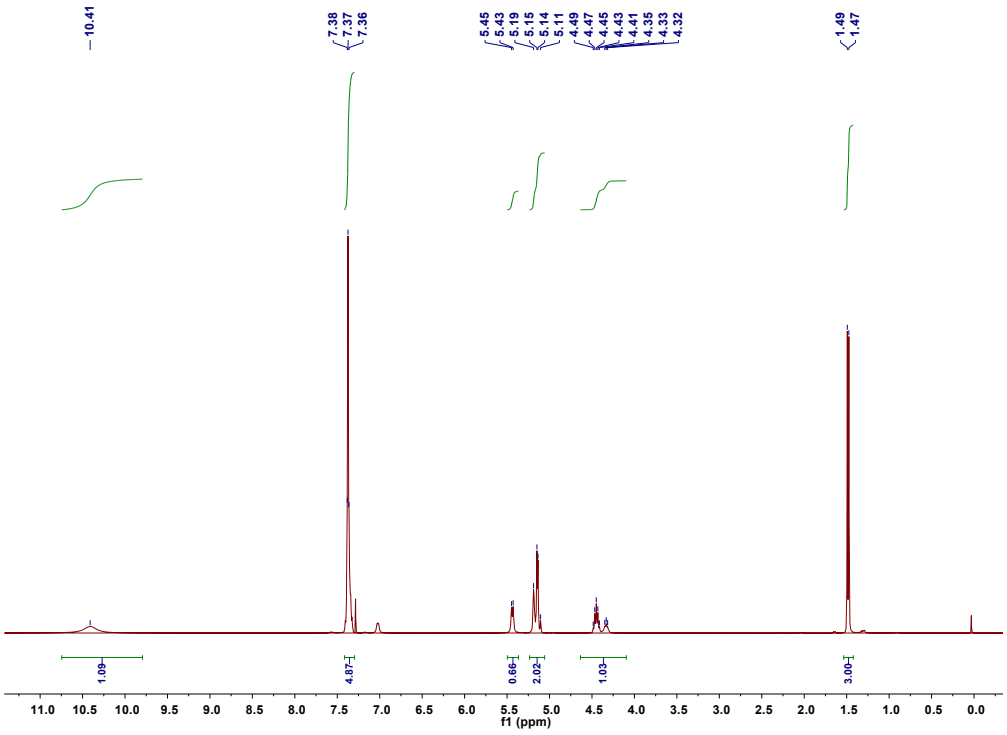
5g

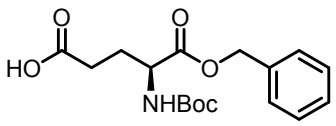

7.84
7.80
7.58
7.57
7.56
7.56
7.43
7.42
7.41
7.41
6.49
6.46
1.01
2.03
3.02
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.73
147.16
134.03
130.80
128.99
128.42
117.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

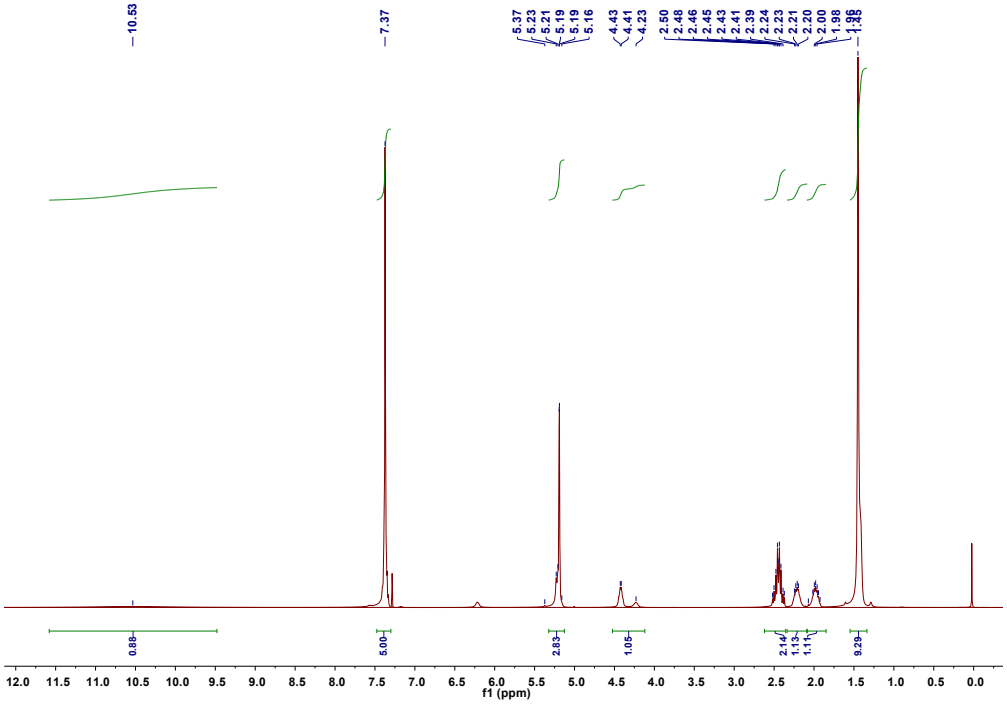

O
O
N
H
O
OH

5h

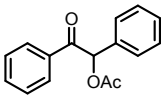

10.41
7.38
7.37
7.36
5.45
5.43
5.19
5.15
5.14
5.11
4.49
4.47
4.45
4.43
4.41
4.35
4.33
4.32
1.49
1.47
1.09
4.87
0.66
2.02
1.03
3.00
f1 (ppm)


O
O
HO
O
NHBoc

5i

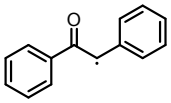

10.53
7.37
5.37
5.23
5.21
5.19
5.19
5.16
4.43
4.41
4.23
2.50
2.48
2.46
2.45
2.43
2.41
2.39
2.24
2.23
2.21
2.20
2.00
1.98
1.96
1.45
0.88
5.00
2.83
1.05
2.14
1.13
1.11
9.29
f1 (ppm)

13. SMD-M06-2X/6-31+G(d) calculated cartesian coordinates and energies.



C	-2.49426600	0.34218500	0.66918000
C	-1.97402400	-0.81638200	0.07990100
C	-2.84758300	-1.77526100	-0.44636400
C	-4.22250800	-1.57583600	-0.39254800
C	-4.73616800	-0.41965500	0.19670500
C	-3.87209600	0.53556300	0.73118900
H	-1.83528300	1.09431700	1.09481100
H	-2.43115500	-2.67225500	-0.89509700
H	-4.89546900	-2.32059200	-0.80718800
H	-5.81043200	-0.26370100	0.24107900
H	-4.27070900	1.43270100	1.19557900
C	-0.50439300	-1.09423100	0.00450700
O	-0.08249300	-2.19217100	-0.28855800
C	0.46007800	0.06088700	0.32577500
C	1.91477100	-0.30607700	0.19966100
C	2.46551400	-0.58521200	-1.05442100
C	2.72264500	-0.36188900	1.33438400
C	3.81159400	-0.91728700	-1.16816900
H	1.83610500	-0.54506300	-1.93993700
C	4.07142800	-0.70110200	1.22235200
H	2.29809400	-0.13129100	2.30905200
C	4.61692500	-0.97754400	-0.02858400
H	4.23423700	-1.13411000	-2.14525900
H	4.69421000	-0.73924700	2.11147400
H	5.66771300	-1.23863600	-0.11864700
H	0.25725300	0.41065000	1.34487500
O	0.11907700	1.10254800	-0.60548800
C	0.18782100	2.37722600	-0.15953900
O	0.44447200	2.66191700	0.98576700
C	-0.10892800	3.34757100	-1.26381000
H	-0.10842100	4.36324500	-0.86895800
H	0.65059500	3.25211900	-2.04586200
H	-1.08004800	3.11577200	-1.71101100

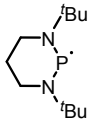
Zero-point correction=	0.264802 (Hartree/Particle)
Thermal correction to Energy=	0.280661
Thermal correction to Enthalpy=	0.281605
Thermal correction to Gibbs Free Energy=	0.218671
Sum of electronic and zero-point Energies=	-843.247339
Sum of electronic and thermal Energies=	-843.231480
Sum of electronic and thermal Enthalpies=	-843.230536
Sum of electronic and thermal Free Energies=	-843.293470



C	-2.34470600	-1.11693900	-0.41270800
C	-1.94613000	0.16567900	-0.01979600
C	-2.91730000	1.09487400	0.36941400
C	-4.26271100	0.74167200	0.38678900
C	-4.65386800	-0.54037000	-0.00281200
C	-3.69395300	-1.46565600	-0.40932400

H	-1.60953800	-1.84255500	-0.75006000
H	-2.60059400	2.09233900	0.65955300
H	-5.00802600	1.46600000	0.70330800
H	-5.70490000	-0.81545400	0.00652700
H	-3.99491000	-2.45977600	-0.72726200
C	-0.50909300	0.60639700	-0.02512200
O	-0.24277800	1.80799600	-0.12398000
C	0.51236800	-0.41341600	0.13280200
C	1.92901200	-0.23520700	0.06484700
C	2.74490500	-1.36090500	0.34460000
C	2.56810800	0.98522300	-0.26891200
C	4.12692500	-1.27500400	0.30168600
H	2.26657300	-2.30374700	0.59999300
C	3.95322100	1.05872200	-0.31319600
H	1.96403700	1.85668400	-0.48742100
C	4.73859900	-0.06177900	-0.02715900
H	4.73141500	-2.14928300	0.52508900
H	4.43007200	1.99997500	-0.57151900
H	5.82195600	0.00958400	-0.06249000
H	0.17388700	-1.41748100	0.36946400

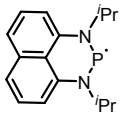
Zero-point correction= 0.209171 (Hartree/Particle)
Thermal correction to Energy= 0.221054
Thermal correction to Enthalpy= 0.221998
Thermal correction to Gibbs Free Energy= 0.168991
Sum of electronic and zero-point Energies= -614.862999
Sum of electronic and thermal Energies= -614.851116
Sum of electronic and thermal Enthalpies= -614.850172
Sum of electronic and thermal Free Energies= -614.903180



C	-0.16571600	2.17598100	0.37143100
C	1.26903400	1.66958100	0.24320100
H	1.75889000	2.22174500	-0.56696600
H	1.82293600	1.88199200	1.17255500
H	-0.17388200	3.26044400	0.21644100
C	-1.06969400	1.48343700	-0.64697500
H	-0.61711100	1.54868400	-1.64747100
H	-2.03292900	1.99594100	-0.69307500
H	-0.56186600	1.98193900	1.37562300
P	0.01527400	-0.77561000	0.44613700
N	-1.28622700	0.07923000	-0.29164800
N	1.30911800	0.23848600	-0.09014100
C	2.66635100	-0.37546000	-0.10623000
C	3.64467200	0.56401600	-0.82335600
C	3.17567400	-0.64581300	1.31863000
C	2.62706300	-1.69038300	-0.89481000
H	3.27228100	0.82694600	-1.82034400
H	3.82970800	1.48604400	-0.26348100
H	4.60785200	0.05696600	-0.94170400
H	2.53510200	-1.37274500	1.83147600
H	4.19451000	-1.05000900	1.29453800
H	3.19315300	0.27255500	1.91628500
H	3.64515000	-2.07617100	-1.01732500

H	2.03859700	-2.46140900	-0.38981400
H	2.19278300	-1.52717000	-1.88733800
C	-2.68135600	-0.35637700	-0.04606700
C	-2.72075400	-1.86177200	0.24094400
C	-3.28704500	0.39190500	1.15187700
C	-3.51385900	-0.10375200	-1.31123500
H	-2.24903600	-2.43045500	-0.56759700
H	-2.22459400	-2.11926100	1.18268000
H	-3.76488800	-2.18169300	0.32187900
H	-3.31235500	1.47481000	0.98578400
H	-4.31709100	0.06201200	1.33111700
H	-2.70063800	0.19598500	2.05705600
H	-4.53134200	-0.48559000	-1.17120000
H	-3.59574600	0.95966600	-1.55590500
H	-3.06505900	-0.61927700	-2.16718800

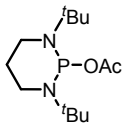
Zero-point correction= 0.346785 (Hartree/Particle)
Thermal correction to Energy= 0.363505
Thermal correction to Enthalpy= 0.364449
Thermal correction to Gibbs Free Energy= 0.303085
Sum of electronic and zero-point Energies= -883.837231
Sum of electronic and thermal Energies= -883.820511
Sum of electronic and thermal Enthalpies= -883.819567
Sum of electronic and thermal Free Energies= -883.880931



C	2.88137500	2.27275800	-0.08881800
C	3.49766900	1.05090900	-0.07218600
C	2.71999600	-0.13693100	-0.06054600
C	1.29293600	-0.06567000	-0.05911000
C	0.67201100	1.23715500	-0.08094500
C	1.47670300	2.36952800	-0.08887100
H	4.46162800	-1.41907400	-0.06776700
H	3.46897200	3.18678800	-0.09255800
H	4.58078700	0.96550600	-0.07012900
C	3.37532800	-1.39616400	-0.06943100
C	0.54515100	-1.30014500	-0.07951500
H	1.03878900	3.35847500	-0.07328400
C	1.23283500	-2.50702600	-0.08310600
C	2.64038000	-2.55051600	-0.08282000
H	0.69922300	-3.44796200	-0.06498200
H	3.13402900	-3.51866700	-0.08411600
N	-0.72621400	1.33880000	-0.10992100
N	-0.85635400	-1.26036200	-0.11263000
P	-1.73070800	0.08567600	0.50285100
C	-1.35525300	2.67125400	-0.24728900
C	-1.46008600	3.39294200	1.09823900
C	-2.71809700	2.58750100	-0.93430600
H	-0.70587100	3.23866300	-0.91995000
H	-0.49665100	3.43111300	1.61540800
H	-1.81855700	4.41875400	0.95768200
H	-2.17158000	2.87320400	1.75101200
H	-2.65937500	1.99728200	-1.85439400
H	-3.48549100	2.14840900	-0.28922500
H	-3.04325200	3.60040300	-1.19455500
C	-1.61703500	-2.52286300	-0.24814000

C	-2.95962400	-2.30323800	-0.94484500
C	-1.80210700	-3.22175800	1.10128400
H	-1.02509200	-3.15706200	-0.91390500
H	-2.83251200	-1.72775200	-1.86730400
H	-3.38673700	-3.27837300	-1.20212900
H	-3.68168100	-1.78291200	-0.30774500
H	-0.85015100	-3.34813600	1.62588700
H	-2.46431000	-2.63002000	1.74443900
H	-2.25666100	-4.20926500	0.96515000

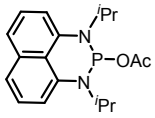
Zero-point correction= 0.333028 (Hartree/Particle)
Thermal correction to Energy= 0.350802
Thermal correction to Enthalpy= 0.351746
Thermal correction to Gibbs Free Energy= 0.287505
Sum of electronic and zero-point Energies= -1071.950951
Sum of electronic and thermal Energies= -1071.933178
Sum of electronic and thermal Enthalpies= -1071.932233
Sum of electronic and thermal Free Energies= -1071.996475



C	-0.20131800	-1.04954500	-2.20724700
C	1.18208400	-1.22357100	-1.58842000
H	1.48944900	-2.26855000	-1.71503900
H	1.90541100	-0.59890500	-2.13172800
H	-0.22674900	-1.60322800	-3.15213700
C	-1.29135900	-1.57369300	-1.28237100
H	-1.10147500	-2.63063100	-1.04067800
H	-2.25117500	-1.52618000	-1.80386700
H	-0.40041800	0.00278400	-2.42911800
P	-0.02115500	0.00696300	0.56861100
N	-1.37331700	-0.78666100	-0.04730100
N	1.20667800	-0.91179600	-0.15027000
C	2.56812700	-0.82915500	0.46085500
C	3.41424600	-2.00499800	-0.04254200
C	3.25468000	0.49633900	0.10212200
C	2.46888500	-0.94764200	1.98669000
H	2.90478400	-2.95844900	0.13828700
H	3.64832000	-1.92925000	-1.10899500
H	4.36533400	-2.01832100	0.49938000
H	2.72143500	1.34096000	0.55276200
H	4.28421000	0.50883300	0.47874300
H	3.29469100	0.64922700	-0.98241400
H	3.47737100	-1.01826600	2.40827400
H	1.98157200	-0.08178400	2.44297200
H	1.91197300	-1.84828600	2.26934700
C	-2.73162700	-0.49355500	0.47785200
C	-2.65277600	0.17667400	1.85333200
C	-3.47977600	0.44957200	-0.47662600
C	-3.49703300	-1.81354300	0.63599000
H	-2.10276800	-0.43988800	2.57201200
H	-2.17522500	1.16212700	1.81202800
H	-3.67005500	0.31959400	2.23223200
H	-3.59837600	0.01641000	-1.47535300
H	-4.48288800	0.66697200	-0.09169000

H	-2.93510300	1.39468500	-0.57842600
H	-4.48858000	-1.62503900	1.06171600
H	-3.64325300	-2.32510800	-0.32065800
H	-2.95417100	-2.48873400	1.30688000
O	-0.01002700	1.42429600	-0.54628400
C	0.32803800	2.62838100	-0.08454700
O	0.71105300	2.84862500	1.04776300
C	0.20246200	3.69456700	-1.14468400
H	-0.77972800	3.64173700	-1.62248100
H	0.35646200	4.67971300	-0.70317500
H	0.95674400	3.51999200	-1.91928900

Zero-point correction= 0.401021 (Hartree/Particle)
Thermal correction to Energy= 0.422552
Thermal correction to Enthalpy= 0.423496
Thermal correction to Gibbs Free Energy= 0.350753
Sum of electronic and zero-point Energies= -1112.246391
Sum of electronic and thermal Energies= -1112.224860
Sum of electronic and thermal Enthalpies= -1112.223916
Sum of electronic and thermal Free Energies= -1112.296659



C	-2.11249900	-3.22380900	-0.14981100
C	-3.12129900	-2.34133800	0.12920000
C	-2.87380700	-0.94376000	0.09960800
C	-1.57029100	-0.45279700	-0.21301700
C	-0.52524000	-1.40600200	-0.48501900
C	-0.81556300	-2.76158800	-0.45045200
H	-4.91850900	-0.43531800	0.59129000
H	-2.29694300	-4.29447100	-0.13191400
H	-4.12267800	-2.68881400	0.36873500
C	-3.93617400	-0.03580900	0.35410500
C	-1.37298400	0.97253600	-0.28295300
H	-0.04164300	-3.49484700	-0.63789500
C	-2.43672900	1.82020300	-0.01626100
C	-3.71493900	1.31351300	0.29554900
H	-2.30042500	2.89421000	-0.02920100
H	-4.52177100	2.01343700	0.49525300
N	0.76559200	-0.94593900	-0.80423900
N	-0.10842100	1.47060200	-0.64480100
P	1.29006800	0.57882500	-0.27451700
C	1.74940700	-1.87752500	-1.40499700
C	2.52848600	-2.66646000	-0.35145600
C	2.70088300	-1.15337200	-2.35651500
H	1.15198000	-2.56239400	-2.01511900
H	1.86563600	-3.09759900	0.40553600
H	3.08824100	-3.48145700	-0.82465700
H	3.23661700	-2.01068600	0.16481400
H	2.14815700	-0.54455900	-3.08026700
H	3.40688100	-0.50993400	-1.82219200
H	3.28444800	-1.89767300	-2.90835500
C	0.06564800	2.91219400	-0.92754100
C	1.14531900	3.14490300	-1.98409800
C	0.34937300	3.71439300	0.34317000
H	-0.87958400	3.24053100	-1.36776500
H	0.96375800	2.52563800	-2.86875500

H	1.12778500	4.19631400	-2.28991100
H	2.14911100	2.92735100	-1.60588400
H	-0.38315600	3.50193400	1.12809700
H	1.34400200	3.46444600	0.73347200
H	0.33316000	4.78947100	0.13247100
O	0.93145800	0.44714800	1.42192300
C	1.88526900	0.00592000	2.25791000
O	2.98102700	-0.35221200	1.88385500
C	1.42430800	0.02135300	3.68818600
H	0.51874800	-0.58420500	3.78833600
H	2.21031600	-0.36640100	4.33616500
H	1.16977600	1.04519900	3.97890700

Zero-point correction= 0.386615 (Hartree/Particle)
Thermal correction to Energy= 0.409138
Thermal correction to Enthalpy= 0.410082
Thermal correction to Gibbs Free Energy= 0.334861
Sum of electronic and zero-point Energies= -1300.361430
Sum of electronic and thermal Energies= -1300.338907
Sum of electronic and thermal Enthalpies= -1300.337962
Sum of electronic and thermal Free Energies= -1300.413184

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