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Cerium Photocatalyzed Radical Smiles Rearrangement of 2-Aryloxybenzoic acids

Alisha Rani tripathy,[a] Girish Suresh Yedase[a] and Veera Reddy Yatham[a]*

[a]Alisha Rani tripathy, Girish Suresh Yedase and Veera Reddy Yatham, School of Chemistry, Indian Institute of Science Education and Research, Thiruvananthapuram (IISER-TVM) 695551, India.

* Email: reddy@iisertvm.ac.in

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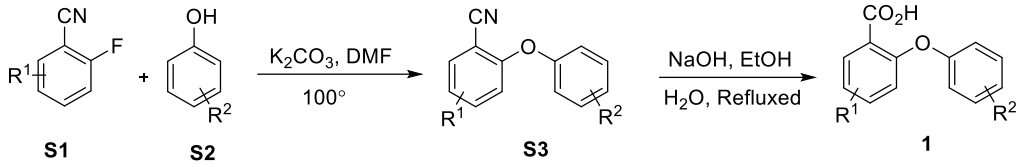
General Considerations:

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All reactions were conducted in 10 ml crimp glass vials. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization via TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (100-200 mesh) using a proper eluent system. NMR spectra were recorded in chloroform-d at 500 MHz for ^{1}H NMR spectra and 125 MHz for ^{13}C NMR spectra. ^{19}F NMR NMR spectra were recorded in chloroform-d at 471 MHz. Chemical shifts are quoted in parts per million referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; td, triplet of doublets; m, multiplet. Coupling constants, J, are reported in hertz. For ^{13}C NMR, chemical shifts are reported in parts per million referenced to the center of a triplet at 77.0 ppm of chloroform-d. FT-IR Alpha E (Bruker) spectrometer was used to record IR Spectra. Absorption were given in cm^{-1}. HRMS (Q-Exactive benchtop) was used for the high-resolution mass analysis. All 2-aryloxybenzoic acids was synthesized according to the literature procedure.[1]

Photochemical reactions were irradiated with 455 nm LEDs (OSRAM Oslon® SSL 80 royal-blue LEDs (λ_{max}= 455 nm (± 15 nm), 3.5 V, 700 mA), which were installed on a passive cooling system at the bottom (7 mm from the bottom-plane of the vials) of a custom-made 6-vials reactor (aluminium), which was equipped with a liquid cooling system (see **Figure 1**).

Synthesis and characterization of 2-aryloxy carboxylic acids:

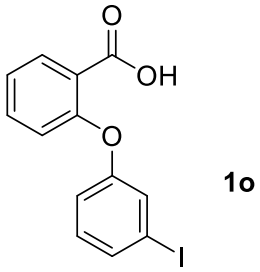
General procedure (A) for the synthesis of 2-aryloxy carboxylic acids (1)



S1 S2 S3 1

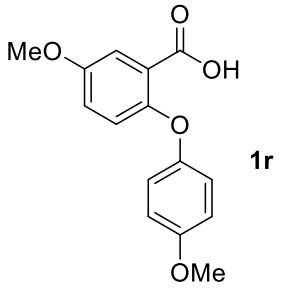
Step 1: A mixture of 2-fluorobenzonitrile **S1** (4.0 mmol, 1.0 equiv), phenol **S2** (4.8 mmol, 1.2 equiv), K_2CO_3 (12.0 mmol, 3.0 equiv) in DMF (5.0 ml) was stirred at 100 °C under Ar atmosphere for 14 h. Then the reaction mixture was cooled to room temperature. Then water (40 mL) and EtOAc (60 mL) was added to the reaction mixture. The organic layer was separated and washed with 5% NaOH (1 x 20 mL), H_2O (1x 20 mL), brine (10 mL x 3) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product **S3**.

Step 2: A mixture of NaOH (30.0 mmol, 7.5 equiv), H_2O (10 mL), EtOH (10 mL) and the crude product **S3** (4.0 mmol, 1.0 equiv) was stirred under reflux for 20 h. After cooling to room temperature, water (20 mL) was added and the mixture was extracted with Et_2O (10 mL). Then the aqueous phase was acidified with HCl and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The residue was purified by flash chromatography (silica gel, hexane:EtOAc=15:1-1:1) to afford compound **1**.



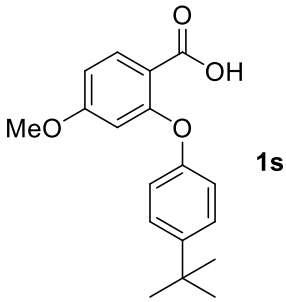
1o

2-(3-iodophenoxy) benzoic acid (1o) was prepared following the general procedure (**A**) described above, obtained as a white solid in 60% yield (816 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, J=1.6 Hz,7.85 Hz, 1H), 7.54-7.50 (m, 2H), 7.26-7.23 (m, 1H), 7.09 (t, J=8.1 Hz, 1H), 7.01 (dd, J=1.6 Hz, 8.2 Hz, 1H), 6.93 (d, 8.15 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.69, 156.44, 134.90, 133.52, 133.32, 131.33 (2C), 128.24, 124.23, 120.84, 119.52, 118.61, 94.36. IR (cm^{-1}): 3072, 2542, 1693, 1571, 1462, 1423, 1296, 1261, 1230, 1095, 889, 771. HRMS (ESI): m/z calcd for $C_{13}H_{10}O_3I$ $(M+H)^+$: 340.9669, found: 340.9662.



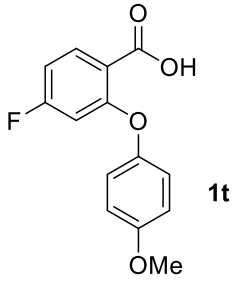
1r

5-methoxy-2-(4-methoxyphenoxy) benzoic acid (1r) was prepared following the general procedure (**A**) described above, obtained as a white solid in 90% yield (987 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J=3.2Hz, 1H), 7.04-7.00 (m, 3H), 6.93-6.91 (m, 2H), 6.76 (d, J=9.05 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.45, 157.29, 155.48, 151.78, 148.31, 122.39, 121.31(2C), 119.66, 118.74, 115.72, 115.40(2C), 56.07, 55.85. FT-IR (neat, cm^{-1}): 3303, 2414, 1710, 1699, 1490, 1413, 1271, 1213, 1031, 833, 756. HRMS (ESI): m/z calcd for $C_{15}H_{15}O_5$ $(M+H)^+$:275.0914, found: 275.0907.



1s

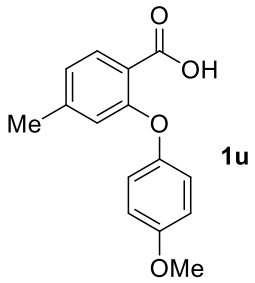
2-(4-(*tert*-butyl)phenoxy)-5-methoxybenzoic acid (1s) was prepared following the general procedure (**A**) described above, obtained as a white solid in 76% yield (913 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.40 (d, J=8.7 Hz, 2H), 7.04 (dd, J=3.2 Hz, 8.0 Hz, 1H), 7.02 (d, J=8.7 Hz, 2H), 6.85 (d, J=9.05, 1H), 3.85 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.59, 155.56, 152.86, 150.94, 148.26, 127.07 (2C), 122.26, 121.84, 119.69, 119.00, 115.51 (2C), 55.93, 34.50, 31.42 (3C). FT-IR (neat, cm^{-1}):3045, 2962, 1685, 1489, 1452, 1321, 1296, 1230, 1033, 831, 758. HRMS (ESI): m/z calcd for $C_{18}H_{21}O_4$ $(M+H)^+$:301.1434, found: 301.1427.



1t

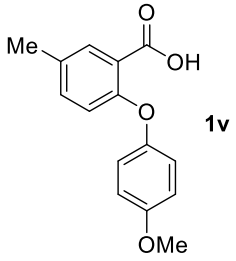
4-fluoro-2-(4-methoxyphenoxy) benzoic acid (1t) was prepared following the general procedure (**A**) described above, obtained as a white solid in 60% yield (629 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (t, J=8.6 Hz, 1H), 7.04-7.02 (m, 2H), 6.95-6.93 (m, 2H), 6.75 (dd, J=2.25 Hz, 8.8 Hz, 1H), 6.64-6.61 (m, 1H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.24, 165.02, 164.13 ($^{1}J_{C-F}$=244.3 Hz), 157.31, 147.85, 134.36, 122.06 (2C), 115.60 ($^{3}J_{C-F}$=3.1 Hz),

115.40 (2C), 112.43 ($^4J_{C-F}$=2.81Hz), 105.0 ($^2J_{C-F}$=25.93Hz), 55.82. ^{19}F NMR (471 MHz, $CDCl_3$) δ -104.34. FT-IR (neat, cm^{-1}): 3282, 2411, 1689, 1620, 1510, 1278, 1244, 1203, 1138, 981, 823, 765. HRMS (ESI): m/z calcd for $C_{14}H_{12}FO_4$ $(M+H)^+$:263.0714, found: 263.0710.



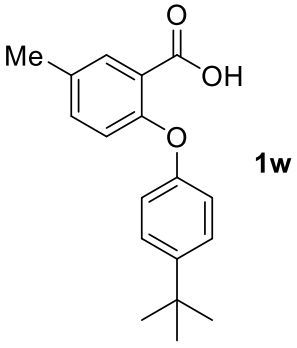
1u

2-(4-methoxyphenoxy)-4-methylbenzoic acid (1u) was prepared following the general procedure (**A**) described above, obtained as a white solid in 72% yield (743.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J= 8 Hz, 1H), 7.03-7.01 (m, 2H), 6.97-6.95 (m, 1H), 6.94-6.92 (m, 2H), 6.54 (s, 1H), 3.83 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.88, 157.23, 156.95, 148.41, 144.44, 132.53, 123.97, 121.63 (2C), 119.55, 117.42, 115.32 (2C), 55.82, 21.61. FT-IR (neat, cm^{-1}): 3462, 3159, 1668, 1602, 1500, 1417, 1244, 1195, 1029, 831, 761. HRMS (ESI): m/z calcd for $C_{15}H_{13}O_4$ $(M-H)^-$: 257.0819, found: 257.0819.



1v

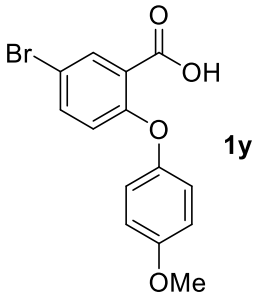
2-(4-methoxyphenoxy)-4-methylbenzoic acid (1v) was prepared following the general procedure (**A**) described above, obtained as a white solid in 78% yield (805.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.24 (dd, J=2.05 Hz, 8.5 Hz, 1H), 7.05 (d, J=9 Hz, 2H), 6.94 (d, J=9 Hz, 2H), 6.69 (d, J=8.5 Hz, 1H), 3.82 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.90, 157.41, 156.05, 147.74, 135.60, 133.69, 133.23, 121.75 (2C), 118.50, 116.73, 115.41 (2C), 55.84, 20.51. FT-IR (neat, cm^{-1}): 2958, 2835, 2601, 1703, 1496, 1452, 1317, 1240, 1029, 933, 840, 765. HRMS (ESI): m/z calcd for $C_{15}H_{15}O_4$ $(M+H)^+$:259.0961, found: 259.0965.



1w

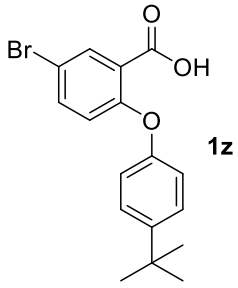
2-(4-(*tert*-butyl)phenoxy)-5-methylbenzoic acid (1w) was prepared following the general procedure (**A**) described above, obtained as a white solid in 55% yield (625 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.41 (d, J=8.65 Hz, 2H), 7.27-7.25 (m, 1H), 7.02 (d,

J=8.65 Hz, 2H), 6.77 (d, J=8.45 Hz, 1H), 2.36 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.98, 155.39, 152.37, 148.64, 135.58, 133.63, 133.53, 127.24 (2C), 119.67 (2C), 119.03, 117.67, 34.65, 31.55 (3C), 20.57. FT-IR (neat, cm^{-1}):3051, 2962, 2872, 1697, 1610, 1492, 1296, 1244, 1165, 837, 740. HRMS (ESI): m/z calcd for $C_{18}H_{21}O_3$ $(M+H)^+$:285.1485, found: 285.1481.



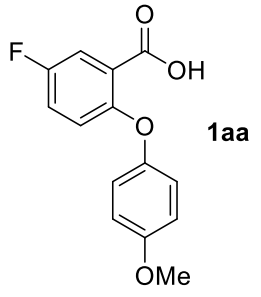
1y

5-bromo-2-(4-methoxyphenoxy) benzoic acid (1y) was prepared following the general 77procedure (**A**) described above, obtained as a white solid in 77% yield (995 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.51 (dd, J=2.5 Hz, 8.85 Hz, 1H), 7.04 (d, J=8.85 Hz, 2H), 6.93 (d, J=8.85 Hz, 2H), 6.67 (d, J=8.85 Hz, 1H), 3.83(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.34, 157.59, 157.42, 147.46, 137.45, 135.92, 121.79 (2C), 120.92, 118.59, 115.62, 115.54 (2C), 55.85. FT-IR (neat, cm^{-1}): 3005, 2839, 2615, 1699, 1509, 1417, 1232, 1101, 1635, 844, 783. HRMS (ESI): m/z calcd for $C_{14}H_{12}BrO_4$ $(M+H)^+$: 322.9913, found: 322.9908.



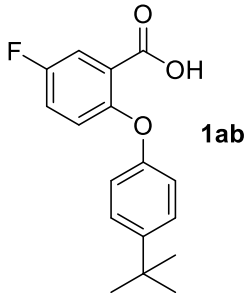
1z

5-bromo-2-(4-(*tert*-butyl) phenoxy) benzoic acid (1z): was prepared following the general procedure described above, obtained as a white solid in 83% yield (1.16 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.54 (dd, J=2.45 Hz, 8.85, 1H), 7.44-7.42 (m, 2H), 7.03-7.01 (m, 2H), 6.76 (d, J=8.85 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.18, 156.83, 151.98, 149.08, 137.53, 135.96, 127.42 (2C), 121.24, 119.80 (2C), 119.42, 115.99, 34.71, 31.54 (3C). FT-IR (neat, cm^{-1}): 3051, 2972, 1716, 1479, 1400, 1261, 1226, 1099, 813. HRMS (ESI): m/z calcd for $C_{17}H_{18}O_3Br$ $(M+H)^+$: 349.0434, found: 349.0429.



1aa

5-fluoro-2-(4-methoxyphenoxy) benzoic acid (1aa) was prepared following the general procedure (**A**) described above, obtained as a white solid in 78% yield (818 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.18-7.14 (m, 1H), 7.05-7.03 (m, 2H), 6.95-6.93 (m, 2H), 6.80 (dd, J=3.15 Hz, 9.1Hz, 1H), 3.83 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 165.02, 157.98 ($^{1}J_{C-F}$=242.51 Hz), 157.50 ($^{2}J_{C-F}$=61.03 Hz), 154.24 ($^{3}J_{C-F}$=16.83 Hz), 121.94, 121.75, 121.55 ($^{4}J_{C-F}$=7.56 Hz), 120.50, 119.54, 119.34, 118.84, 118.66, 115.53, 55.86. ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.96. FT-IR (neat, cm^{-1}): 1705, 1483, 1317, 1236, 1199, 1029, 835, 765. HRMS (ESI): m/z calcd for $C_{16}H_{18}O_4F$ $(M+H)^+$: 263.0714, found: 263.0709.



1ab

2-(4-(*tert*-butyl)phenoxy)-5-fluorobenzoic acid (1ab) was prepared following the general procedure (**A**) described above, obtained as a white solid in 68 % yield (783 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J=2.85 Hz, 8.6 Hz, 1H), 7.40 (d, J=8.45 Hz, 2H), 7.17-7.13 (m, 1H), 6.99 (d, J=8.5 Hz, 2H), 6.87-6.85 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.98, 158.13($^{1}J_{C-F}$=242.47 Hz), 153.54, 152.96, 148.40, 127.25 (2C), 121.6 ($^{2}J_{C-F}$=23.45 Hz), 119.99 ($^{3}J_{C-F}$=7.7Hz), 119.33, 119.27 (2C), 119.14, 34.62, 31.54 (3C). FT-IR (neat, cm^{-1}):2964 1711, 1683, 1485, 1450, 1249, 1211, 823, 752. HRMS (ESI): m/z calcd for $C_{17}H_{18}O_3F$ $(M+H)^+$: 289.1234, found: 289.1228. ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.46.

Optimization details:

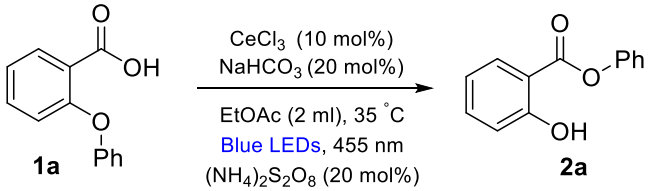
General procedure for screening reactions: A 10 mL glass vial was charged with 2-Phenoxybenzoic acid (0.2 mmol), Ce-photocatalyst (10 mol%), base (10 mol%), $(NH_4)_2S_2O_8$ (20 mol%) and a PTFE-coated stirring bar and the glass vial was sealed with a PTFE septum. Solvent (2 mL) was added. The reactions were placed in a pre-programed temperature (35 °C) controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED. After 24 hours, a sample of this solution was analyzed by ^{1}H NMR using trimethoxy benzene as the internal standard to determine the yield.

Figure 1: Blue LED reactor with magnetic stirring plate

Entry	Deviation from standard conditions	**2a**(%)[a]
1	***none***	***80****(75)*[b]
2	**$CeCl_3 \cdot 7H_2O$** instead of **$CeCl_3$**	68
3	**$(^nBu_4N)_2CeCl_6$** instead of **$CeCl_3$**	60
4	**$Ce(SO_4)_2.4H_2O$** instead of **$CeCl_3$**	35
5	**Cs_2CO_3** instead of **$NaHCO_3$**	40
6	**Na_2CO_3** instead of **$NaHCO_3$**	10
7	**K_3PO_4** instead of **$NaHCO_3$**	23
8	**with out $NaHCO_3$**	25
9	CH_3CN instead of EtOAc	75
10	THF instead of EtOAc	33
11	DCM instead of EtOAc	23
12	Dioxane instead of EtOAc	50
13	O_2 balloon instead of $(NH_4)_2S_2O_8$	68
14	Air instead of $(NH_4)_2S_2O_8$	55-70
15	Green Led's (530 nm)	0
16	without light	0
17	with out $CeCl_3$	trace

Table 1. Optimization of the reaction conditions. **1a** (0.2 mmol), $CeCl_3$ (10 mol%), EtOAc (2 ml) at 35 °C, 455 nm blue LED for 30 h. [a]NMR yields using trimethoxy benzene as internal standard. [b]Isolated yield.

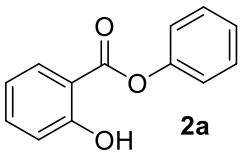
General procedure for cerium photocatalyzed radical Smiles rearrangement of 2-Aryloxybenzoic acids



General procedure (GP): A 10 mL glass vial equipped with a teflon-coated stirring bar was charged with 2-Aryloxybenzoic acid **1** (0.2 mmol), $CeCl_3$ (10 mol%), $NaHCO_3$ (20 mol%), $(NH_4)_2S_2O_8$ (20 mol%). And the glass vial was sealed with a PTFE septum. Solvent (2 mL) was added. The reaction was placed in a pre-programed temperature (35 °C) controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED. After 24-40 hours, the reaction mixture was concentrated under reduced pressure. Product **2** was purified by flash chromatography on silica using hexane and AcOEt.

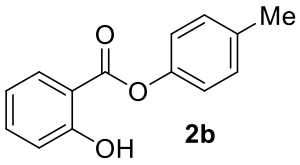
Note: At same time we run two independent reactions for each substrate and the obtained yield was the combined average yield of these two independent runs

Chacterization of products:



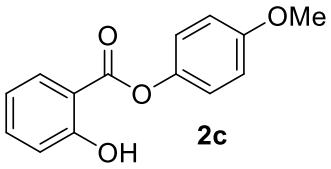
2a

Phenyl 2-hydroxybenzoate (2a): Following the general procedure **GP**, two parallel reactions of **1a** (0.2 mmol each one) afforded **2a** as an off-white solid in 75% yield (64.2 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.08 (dd, J= 1.6 Hz, 8 Hz, 1H), 7.56-7.53 (m, 1H), 7.46 (t, J=7.85 Hz, 2H), 7.31 (t, J=7.46 Hz, 1H), 7.21 (d, J=7.8 Hz, 2H), 7.04 (d, J=8.4 Hz, 1H) 6.98 (t, J=7.8 Hz, 1H), . ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.11, 162.37, 150.27, 136.63, 130.51, 129.80 (2C), 126.55, 121.80 (2C), 119.63, 118.00, 112.01. The analytical data are consistent with published ones.[2]



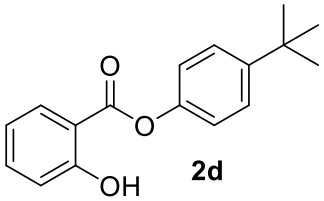
2b

***p*-tolyl 2-hydroxybenzoate (2b):** Following the general procedure **GP**, two parallel reactions of **1b** (0.2 mmol each one) afforded **2b** as a light-yellow solid in 80% yield (72.9 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ10.53 (s, 1H), 8.06 (d, J=7.9 Hz, 1H), 7.53 (dd, J=7.7, 1H), 7.24 (d, J=8.4 Hz, 2H), 7.08 (d, J=7.9 Hz, 2H), 7.03 (d, J=8.4 Hz, 1H), 6.96 (dd, J=7.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.29, 162.31, 148.00, 136.53, 136.27, 130.49, 130.28 (2C), 121.43 (2C), 119.57, 117.95, 112.08, 21.05. The analytical data are consistent with published ones.[2]



2c

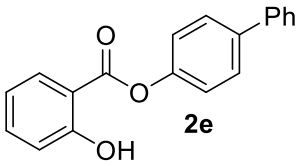
4-methoxyphenyl 2-hydroxybenzoate (**2c**): Following the general procedure **GP**, two parallel reactions of **1c** (0.2 mmol each one) afforded **2c** as an off-white solid in 80% yield (78.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ10.53 (s, 1H), 8.06 (d, J=7.95, 1H), 7.52 (t, J=7.55 Hz, 1H), 7.12 (d, J=8.4 Hz, 2H), 7.03 (d, J=8.4Hz, 1H), 6.95 (m, 3H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.40, 162.28, 157.80, 143.63, 136.51, 130.45, 122.52 (2C), 119.55, 117.93, 114.77 (2C), 112.03, 55.75. The analytical data are consistent with published ones. [2]



2d

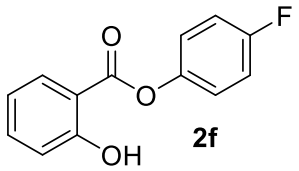
4-(*tert*-butyl) phenyl 2-hydroxybenzoate (**2d**): Following the general procedure **GP**, two parallel reactions of **1d** (0.2 mmol each one) afforded **2d** as an off-white solid in 79% yield (85.3 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.09 (d, J=9.4 Hz, 1H), 7.54 (m, 1H),

7.48 (d, J=8.65 Hz, 2H), 7.16 (d, J=8.7 Hz, 2H), 7.06 (d, J=8.4 Hz, 1H), 6.98 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.26, 162.32, 149.43, 147.86, 136.51, 130.47, 126.65 (2C), 121.06 (2C), 119.55, 117.93, 112.06, 34.68, 31.52 (3C). The analytical data are consistent with published ones. [1]



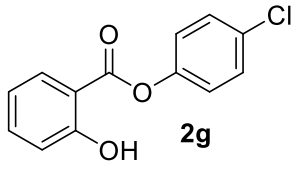
2e

[1,1'-biphenyl]-4-yl 2-hydroxybenzoate (**2e**): Following the general procedure **GP**, two parallel reactions of **1e** (0.2 mmol each one) afforded **2e** as a light-yellow solid in 85% yield (98.6 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.10 (dd, J=1.6 Hz, 8.0 Hz,1H), 7.65 (d, J=8.65 Hz, 2H), 7.60-7.59 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.39-7.35 (m, 1H), 7.30-7.28 (m, 2H), 7.05 (d, J=8.4 Hz, 1H), 7.0-6.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.15, 162.43, 149.68, 140.37, 139.79, 136.70, 130.54, 129.01(2C), 128.52 (2C), 127.67, 127.32 (2C), 122.07 (2C), 119.66, 118.05, 112.01. The analytical data are consistent with published ones. [2]



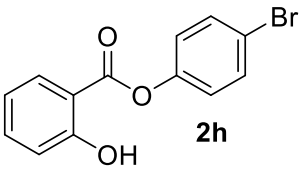
2f

4-fluorophenyl 2-hydroxybenzoate (2f): Following the general procedure **GP**, two parallel reactions of **1f** (0.2 mmol each one) afforded **2f** as a light-yellow semisolid in 67% yield (62.2 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.05 (dd, J=1.65 Hz, 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.20-7.12 (m, 4H), 7.04 (d, J=8.4 Hz, 1H), 6.99-6.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.89, 162.27, 160.58(d, $^{1}J_{C-F}$=243 Hz), 145.92 (d, $^{4}J_{C-F}$=2.85 Hz), 136.62, 130.31, 123.1(d, $^{3}J_{C-F}$=8.51Hz, 2C), 119.53, 117.92, 116.43(d, $^{2}J_{C-F}$=23.46 Hz, 2C), 111.66. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.07. The analytical data are consistent with published ones. [2]



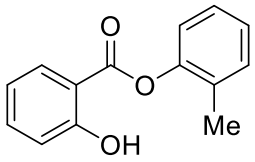
2g

4-chlorophenyl 2-hydroxybenzoate (**2g**): Following the general procedure **GP**, two parallel reactions of **1g** (0.2 mmol each one) afforded **2g** as a light-yellow solid in 81% yield (80.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.09 (dd, J =1.5 Hz, 8Hz, 1H), 7.60-7.56 (m, 1H),7.46-7.44 (m, 2H),7.20-7.19 (m, 2H), 7.08-7.07 (m, 1H),7.02-6.99 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.79, 162.40,148.70, 136.84, 132.01, 130.45, 129.85(2C), 123.19 (2C), 119.70, 118.07, 111.69. The analytical data are consistent with published ones. [2]



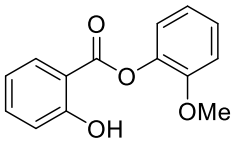
2h

4-bromophenyl 2-hydroxybenzoate (**2h**): Following the general procedure **GP**, two parallel reactions of **1h** (0.2 mmol each one) afforded **2h** as an off-white solid in 83% yield (97.3 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.05 (dd, J=1.65 Hz, 8.0 Hz, 1H), 7.58-7.53 (m, 3H), 7.12-7.10 (m, 2H), 7.04 (d, J=8.4Hz, 1H), 6.98(t, J=8.1Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.71, 162.40, 149.26, 136.86, 132.84 (2C), 130.45, 123.61 (2C), 121.51, 119.71, 118.07, 111.68. The analytical data are consistent with published ones. [2]



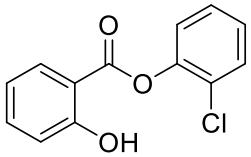
2i

o-tolyl 2-hydroxybenzoate (2i): Following the general procedure **GP**, two parallel reactions of **1**i (0.2 mmol each one) afforded **2i** as a light-yellow semisolid in 82% yield (74.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.13 (dd, J=8Hz, 1.65Hz,1H), 7.56-7.53 (m, 1H), 7.31-7.20 (m, 3H), 7.13(dd, J=8Hz, 1.15Hz, 1H), 7.05 (dd, J=8.4, 0.8 Hz, 1H), 6.98-6.97 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.84, 162.39, 148.90, 136.62, 131.49, 130.46, 130.44, 127.25, 126.70, 122.02, 119.65, 118.02, 111.91, 16.31. The analytical data are consistent with published ones. [2]



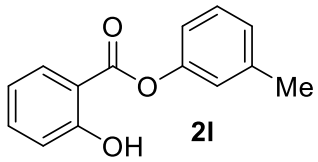
2j

2-methoxyphenyl 2-hydroxybenzoate (2j): Following the general procedure **GP**, two parallel reactions of **1j** (0.2 mmol each one) afforded **2j** as an off-white solid in 80% yield (78.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.14 (dd, J=1.5 Hz, 7.95 Hz, 1H), 7.55-7.51 (m, 1H), 7.29-7.26 (m, 1H), 7.16 (dd, J=1.45 Hz, 7.8Hz, 1H), 7.04-7.03 (m, 2H), 7.00-6.95 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.58, 162.20, 151.34, 139.25, 136.44, 130.78, 127.56, 122.96, 121.02, 119.57, 117.85, 112.75, 112.02, 56.06. The analytical data are consistent with published ones. [2]



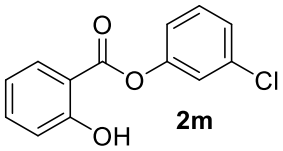
2k

2-chlorophenyl 2-hydroxybenzoate (**2k**): Following the general procedure **GP**, two parallel reactions of **1k** (0.2 mmol each one) afforded **2k** as light-yellow solid in 76% yield (75.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.06 (dd, J=1.5 Hz, 8.0 Hz,1H), 7.51-7.48 (m, 1H), 7.45-7.44 (m, 1H), 7.31-7.28 (m, 1H), 7.22-7.19 (m, 2H), 6.98 (d, J=8.5Hz, 1H), 6.94-6.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.10, 162.39, 146.57, 136.90, 130.71, 130.66, 128.03, 127.67, 127.18, 123.90, 119.78, 118.01, 111.48. The analytical data are consistent with published ones. [1]



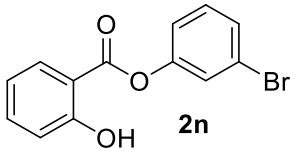
2l

***m*-tolyl 2-hydroxybenzoate** (**2l**): Following the general procedure **GP**, two parallel reactions of **1l** (0.2 mmol each one) afforded **2l** as an off-white solid in 74% yield (67.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.07 (dd, J=1.4 Hz, 7.9 Hz, 1H), 7.56-7.53 (m, 1H), 7.35 (t, J=7.8 Hz, 1H), 7.12 (d, J=7.6 Hz, 1H), 7.05-6.96 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.21, 162.34, 150.21, 140.10, 136.57, 130.50, 129.50, 127.34, 122.33, 119.60, 118.71, 117.97, 112.07, 21.49. The analytical data are consistent with published ones. [1]



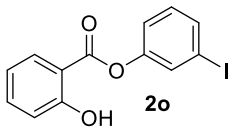
2m

3-chlorophenyl 2-hydroxybenzoate (**2m**): Following the general procedure **GP**, two parallel reactions of **1m** (0.2 mmol each one) afforded **2m** as an off-white solid in 71% yield (70.4 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.07 (d, J=7.95 Hz, 1H), 7.58 (t, J=7.95 Hz, 1H), 7.41 (t, J=8.1Hz, 1H), 7.33 (d, J=8.2 Hz, 1H), 7.30 (s, 1H), 7.16 (d, J=8.8 Hz, 1H), 7.08 (d, J=8.4 Hz, 1H), 7.01 (t, J=7.65 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.59, 162.44, 150.70, 136.86, 135.08, 130.46, 130.43, 126.80, 122.52, 120.20, 119.70, 118.07, 111.61. The analytical data are consistent with published ones. [3]



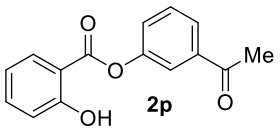
2n

3-bromophenyl 2-hydroxybenzoate (**2n**): Following the general procedure **GP**, two parallel reactions of **1n** (0.2 mmol each one) afforded **2n** as an off-white solid in 75% yield (87.3 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.03 (dd, J=1.4 Hz, 8.0 Hz,1H), 7.57-7.53 (m, 1H), 7.47-7.42 (m, 2H), 7.32 (t, J=8.05Hz, 1H), 7.18 (dd, J=1.45 Hz, 8.2 Hz, 1H), 7.04 (d, J=8.4 Hz, 1H), 6.96 (t, J=7.85, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.63, 162.46, 150.74, 136.90, 130.80, 130.45, 129.75, 125.38, 122.73, 120.71, 119.73, 118.10, 111.62. The analytical data are consistent with published ones. [1]



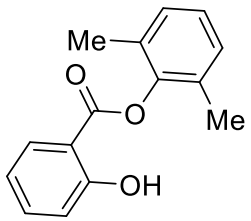
2o

3-iodophenyl 2-hydroxybenzoate (**2o**): Following the general procedure **GP**, two parallel reactions of **1o** (0.2 mmol each one) afforded **2o** as an off-white solid in 69% yield (93.8 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.37 (s, 1H), 8.03 (dd, J=1.6Hz, 8Hz, 1H), 7.66 (m, 1H), 7.61(dd, J=1.5 Hz, 1.85 Hz, 1H), 7.57-7.53 (m, 1H) 7.22-7.17 (m, 2H), 7.05 (d, J= 8.4Hz, 1H), 6.99-6.96 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 168.64, 162.46, 150.50, 136.89, 135.69, 131.05, 131.02, 130.45, 121.40, 119.73, 118.10, 111.63, 93.76. FT-IR (neat, cm^{-1}): 3192, 2922, 2856, 1695, 1581, 1467, 1301, 1253, 1193, 1062, 769, 680. HRMS (ESI): m/z calcd for $C_{13}H_8O_3I$ $(M-H)^-$: 338.9524, found: 338.9525.



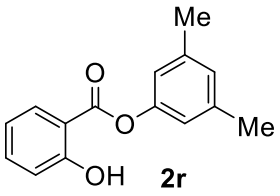
2p

3-acetylphenyl 2-hydroxybenzoate (2p): Following the general procedure **GP**, two parallel reactions of **1p** (0.2 mmol each one) afforded **2p** as a light-yellow semisolid in 70% yield (71.7 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.08 (dd, J=1.6 Hz, 8.0 Hz, 1H), 7.90 (d, J=7.75 Hz, 1H), 7.81-7.80 (m, 1H), 7.58-7.55 (m, 2H), 7.44 (dd, J=2.15 Hz, 8 Hz, 1H), 7.05 (d, J=8.35 Hz, 1H), 6.99 (t, J=8 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.95, 168.86, 162.45, 150.53, 138.91, 136.92, 130.48, 130.04, 126.60, 126.44, 121.66, 119.76, 118.10, 111.66, 26.85. The analytical data are consistent with published ones. [1]



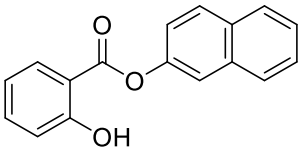
2q

2,6-dimethylphenyl 2-hydroxybenzoate (**2q**): Following the general procedure **GP**, two parallel reactions of **1q** (0.2 mmol each one) afforded **2q** as a light-yellow solid in 67% yield (64.8 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.16 (dd, J=8.2 Hz, 1.5 Hz, 1H), 7.57(t, J=8.6 Hz, 1H), 7.14 (s, 3H), 7.07 (d, J=8.4Hz, 1H), 7.01 (t, J=8.0 Hz, 1H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.44, 162.43, 147.74, 136.61, 130.43 (3C), 128.88 (2C), 126.48, 119.66, 118.04, 111.69, 16.45 (2C). The analytical data are consistent with published ones. [1]



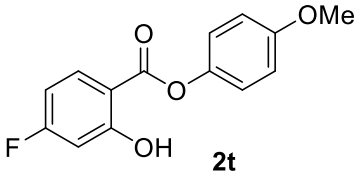
2r

3,5-dimethylphenyl 2-hydroxybenzoate (**2r**): Following the general procedure **GP**, two parallel reactions of **1r** (0.2 mmol each one) afforded **2r** as an off-white solid in 72% yield (69.7 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.06 (d, J=7.95 Hz,1H), 7.55-7.52 (m, 1H), 7.04 (d, J=8.35Hz, 1H), 6.99-6.96 (m, 2H), 6.84 (s, 2H), 2.37 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.27, 162.33, 150.18, 139.71(2C), 136.48, 130.47, 128.23, 119.55, 119.29 (2C), 117.94, 112.14, 21.38 (2C). The analytical data are consistent with published ones. [1]



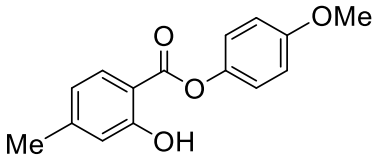
2s

Naphthalen-1-yl 2-hydroxybenzoate (2s): Following the general procedure **GP**, two parallel reactions of **1s** (0.2 mmol each one) afforded **2s** as light-yellow solid in 60% yield (63.3 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 8.14 (dd, J=1.6 Hz, 8.0 Hz, 1H), 7.92 (d, J=8.85 Hz, 1H), 7.89-7.87 (m, 1H), 7.85-7.83 (m, 1H), 7.68 (d, J=2.5Hz, 1H), 7.57-7.48 (m, 3H), 7.34 (dd, J=2.3, 8.85Hz, 1H), 7.05(d, J=8.4Hz, 1H), 7.01-6.98 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ 169.27, 162.43, 147.90, 136.70, 133.90, 131.86, 130.57, 129.83, 128.02, 127.88, 126.97, 126.20, 121.07, 119.68, 118.95, 118.05, 112.04. The analytical data are consistent with published ones.[3]



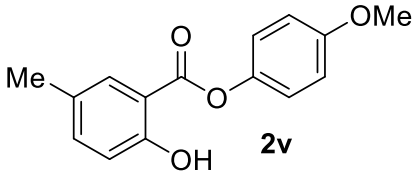
2t

4-methoxyphenyl 4-fluoro-2-hydroxybenzoate (**2t**): Following the general procedure **GP**, two parallel reactions of **1t** (0.2 mmol each one) afforded **2t** as an off-white solid in 65% yield (68.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.76 (dd, J=1.5Hz, 1H), 8.09-8.06 (m, 2H), 7.13-7.10 (m, 2H), 6.97-6.94 (m, 2H), 6.74-6.67 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 168.82, 167.84 ($^{1}J_{C-F}$=253Hz), 164.40 ($^{4}J_{C-F}$=14.28), 157.90, 143.50, 132.79 ($^{5}J_{C-F}$=11.68Hz), 122.49 (2C), 114.82 (2C), 108.82, 107.99 ($^{3}J_{C-F}$= 22.67Hz), 104.7 ($^{2}J_{C-F}$=24.1Hz), 55.80. ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.82. HRMS (ESI): m/z calcd for $C_{14}H_{10}O_4F$ $(M-H)^-$: 261.0569, found: 261.0569.



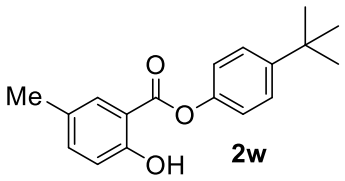
2u

4-methoxyphenyl 2-hydroxy-4-methylbenzoate (**2u**): Following the general procedure **GP**, two parallel reactions of **1u** (0.2 mmol each one) afforded **2u** as an off-white solid in 68% yield (70.1 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.93 (d, J=8.15 Hz, 1H), 7.11 (d, J=9Hz, 2H), 6.95 (d, J=9.05Hz, 2H), 6.85 (s, 1H), 6.77 (d, J=8.15Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.42, 162.29, 157.76, 148.06, 143.72, 130.25, 122.59(2C), 120.90, 118.05, 114.77(2C), 109.46, 55.79, 22.11. FT-IR (neat, cm^{-1}): 3184, 2926, 1680, 1506, 1336, 1249, 1193, 1066, 1028, 773, 704. HRMS (ESI): m/z calcd for $C_{15}H_{15}O_4$ $(M+H)^+$: 259.0965, found: 259.0962.



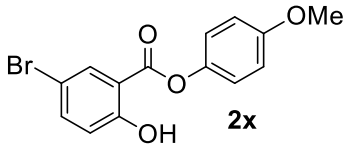
2v

4-methoxyphenyl 2-hydroxy-5-methylbenzoate (**2v**): Following the general procedure **GP**, two parallel reactions of **1v** (0.2 mmol each one) afforded **2v** as an off-white solid in 60% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.86 (s, 1H), 7.34 (dd, J=2.1 Hz, 8.5 Hz, 1H), 7.13-7.11 (m, 2H), 6.97-6.93 (m, 3H), 3.83 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.43, 160.26, 157.82, 143.74, 137.55, 130.09, 128.79, 122.56(2C), 117.73, 114.81(2C), 111.62, 55.79, 20.53. FT-IR (neat, cm^{-1}): 3230, 2945, 1689, 1505, 1296, 1190, 1068, 827. HRMS (ESI): m/z calcd for $C_{15}H_{15}O_4$ $(M+H)^+$: 259.0965, found: 259.0962.



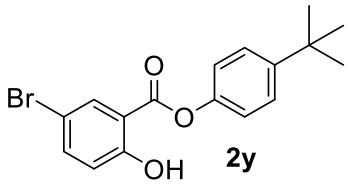
2w

4-(*tert*-butyl) phenyl 2-hydroxy-5-methylbenzoate (**2w**): Following the general procedure **GP**, two parallel reactions of **1b** (0.2 mmol each one) afforded **2b** as a light-yellow solid in 65% yield (60.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.89 (s, 1H), 7.50-7.45 (m, 2H), 7.37 (d, J=8.5 Hz, 1H), 7.18-7.14 (m, 2H), 6.96 (d, J=8.45 Hz, 1H), 2.37 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.32, 160.30, 149.44, 147.96, 137.57, 130.13, 128.80, 126.67 (2C), 126.51, 121.11 (2C), 117.75, 34.72, 31.57(3C), 29.85. FT-IR (neat, cm^{-1}): 3174, 2960, 2922, 2850, 1755, 1685, 1489, 1298, 1205, 1070, 809, 703. HRMS (ESI): m/z calcd for $C_{18}H_{21}O_3$ $(M+H)^+$: 285.1485, found: 285.1481.



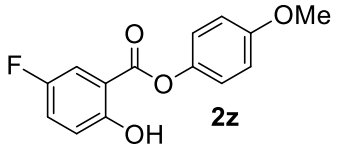
2x

4-methoxyphenyl 5-bromo-2-hydroxybenzoate (**2x**): Following the general procedure **GP**, two parallel reactions of **1x** (0.2 mmol each one) afforded **2x** as an off-white solid in 80% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.17 (d, J=2.5 Hz, 1H), 7.61 (dd, J=2.5 Hz, 8.9 Hz,1H), 7.11-7.13 (m, 2H), 6.97-6.93 (m, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.37, 161.27, 157.97, 143.40, 139.25, 132.68, 122.39 (2C), 119.95, 114.84 (2C), 113.56, 111.22, 55.79. FT-IR (neat, cm^{-1}): 3201, 2926, 1685, 1512, 1471, 1332, 1246, 1197, 1076, 821, 704. HRMS (ESI): m/z calcd for $C_{14}H_{10}O_4Br$ $(M-H)^-$: 320.9768, found: 320.9770.



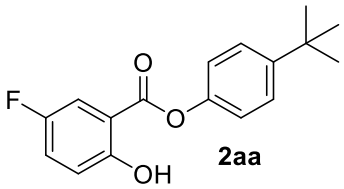
2y

4-(*tert*-butyl) phenyl 5-bromo-2-hydroxybenzoate (**2y**): Following the general procedure **GP**, two parallel reactions of **1y** (0.2 mmol each one) afforded **2y** as an off-white solid in 69% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.50 (s, 1H), 8.18 (d, J=2.4Hz, 1H), 7.61 (dd, J=2.4 Hz, 8.9Hz, 1H), 7.46 (d, J=8.6 Hz, 2H), 7.12 (d, J=8.6 Hz, 2H), 6.94 (d, J=8.9 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.24, 161.34, 149.76, 147.68, 139.26, 132.73, 126.75(2C), 120.93(2C), 119.97, 113.64, 111.23, 34.75, 31.55(3C). FT-IR (neat, cm^{-1}): 3441, 3190, 2962, 1689, 1465, 1327, 1210, 1064, 840, 705. HRMS (ESI): m/z calcd for $C_{17}H_{16}O_3Br$ $(M-H)^-$: 347.0288, found:347.0291.



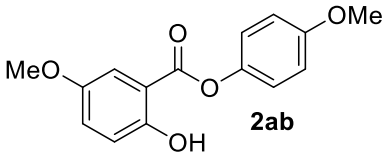
2z

4-methoxyphenyl 5-fluoro-2-hydroxybenzoate (**2z**): Following the general procedure **GP**, two parallel reactions of **1y** (0.2 mmol each one) afforded **2y** as an off-white solid in 53% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.74 (dd, J=3.15 Hz, 8.6 Hz, 1H), 7.29-7.25 (m, 1H), 7.12 (d, J= 9.05 Hz, 2H), 7.0 (dd, J=4.45 Hz, 9.15 Hz, 1H), 6.96 (d, J=9Hz, 2H), 3.83 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 168.62, 158.58, 157.95, 155.37 ($^{1}J_{C-F}$=237.33Hz), 143.45, 124.27 ($^{2}J_{C-F}$=23.57Hz), 124.08, 122.42 (2C), 119.30 ($^{3}J_{C-F}$=7.31Hz), 115.5 ($^{2}J_{C-F}$=30.33Hz), 114.84(2C), 112.02 ($^{3}J_{C-F}$=9.25 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -123.67. FT-IR (neat, cm^{-1}): 3213, 3082, 2922, 1695, 1512, 1485, 1340, 1257, 1193, 1062, 831, 783. HRMS (ESI): m/z calcd for $C_{14}H_{10}O_4F$ $(M-H)^-$:261.0569, found: 261.0569.



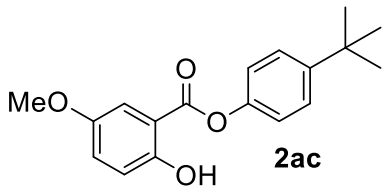
2aa

4-(*tert*-butyl)phenyl 5-fluoro-2-hydroxybenzoate (**2aa**): Following the general procedure **GP**, two parallel reactions of **1aa** (0.2 mmol each one) afforded **2aa** as an off-white solid in 57% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.66 (m, 1H), 7.38 (d, J=8.7 Hz, 2H), 7.21-7.17 (m, 1H), 7.04 (d, J=8.7 Hz, 2H), 6.94-6.91 (m, 1H), 1.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.48, 158.62, 155.37 ($^{1}J_{C-F}$=237.37), 149.71, 147.70, 126.74 (2C), 124.17 ($^{2}J_{C-F}$=23.5Hz), 120.95 (2C), 119.30 ($^{3}J_{C-F}$=7.33Hz), 115.6 ($^{2}J_{C-F}$=24Hz), 112.05 ($^{3}J_{C-F}$=7.35Hz), 34.73, 31.54 (3C). ^{19}F NMR (471 MHz, $CDCl_3$) δ -123.62. FT-IR (neat, cm^{-1}): 3201, 2964, 1693, 1489, 1344, 1195, 1055, 879, 788. HRMS (ESI): m/z calcd for $C_{17}H_{16}O_3F$ $(M-H)^-$:287.1089, found: 287.1092.



2ab

4-methoxyphenyl 2-hydroxy-5-methoxybenzoate (**2ab**): Following the general procedure **GP**, two parallel reactions of **1ab** (0.2 mmol each one) afforded **2ab** as a light-yellow solid in 63% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.50 (d, J=3.1 Hz, 1H), 7.16 (dd, J=3.1 Hz, 8.9Hz, 1H), 7.14-7.12 (m, 2H), 6.98-6.95 (m, 3H), 3.84 (s, 3H). 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.20, 157.83, 156.85, 152.32, 143.62, 125.06, 122.56(2C), 118.96, 114.79 (2C), 112.11, 111.45, 56.08, 55.78. FT-IR (neat, cm^{-1}): 3165, 2924, 2848, 1680, 1610, 1510, 1352, 1286, 1234, 1182, 1033, 813, 713. HRMS (ESI): m/z calcd for $C_{15}H_{15}O_5$ $(M+H)^+$: 275.0914, found: 275.0908.



2ac

4-(*tert*-butyl) phenyl 2-hydroxy-5-methoxybenzoate (**2ac**): Following the general procedure **GP**, two parallel reactions of **1ac** (0.2 mmol each one) afforded **2ac** as a light-yellow solid in 68% yield (60.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.51 (d, J=3.05Hz, 1H), 7.46 (d, J=8.65 Hz, 2H), 7.18-7.13 (m, 3H), 6.97 (d, J=9.05 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.06, 156.93, 152.37, 149.54, 147.91, 126.70 (2C), 125.04, 121.11 (2C), 118.98, 112.29, 111.56, 56.10, 34.72, 31.56 (3C). FT-IR (neat, cm^{-1}): 3448, 3248, 2958, 2927, 2858, 1693, 1492, 1282, 1220, 1195, 1058, 823, 779. HRMS (ESI): m/z calcd for $C_{18}H_{21}O_4$ $(M+H)^+$: 301.1434, found: 301.1426.

Set up for gram scale reaction

Following the general procedure **GP**, **1j** (4.1 mmol) and the reaction time was increased to 80 h yielded **2j** in 55% yield.

Set up for gram scale reaction

Mechanistic Studies

UV-Vis experiments:

In order to verify whether the interaction with the substituted benzyl alcohols and cerium (IV) could lead to the overall LMCT process, which reduced the Ce(IV) species to Ce(III), a similar approach to the one reported by Zuo et al. was used.[4] $(^{n}Bu_4N)_2Ce^{IV}Cl_6$ was chosen as a Ce(IV) source to ensure sufficient solubility in organic solvents and facilitate the detection of the species.

Synthesis of $(^{n}Bu_4N)_2Ce^{IV}Cl_6$

In a round-bottom flask equipped with a teflon-coated stirring bar, tetrabutylammonium chloride (3.24 g, 11.7 mmol, 2.0 equiv.) and $Ce(SO_4)_2{\cdot}(H_2O)_n$ (2.36 g, 5.8 mmol, 1.0 equiv.)

were charged, then HCl 37% (15 ml) was added at room temperature. After the formation of a yellow-orange precipitate, additional tetrabutylammonium chloride (324 mg, 1.2 mmol, 0.1 equiv.) was added and the reaction additionally stirred for 20 minutes. The suspension was cooled-down to 5°C using an ice-water bath, then the solid was collected by suction-filtration over a sintered funnel, then the yellow-orange solid was washed three times with the minimal amount of acetone (approx. 10 ml each time) and dried under high vacuum, to afford an intensely yellow powder (480 mg, 0.57 mmol, 10% yield).

Preparation of a basic solution of $(^nBu_4N)_2Ce^{IV}Cl_6$ in MeCN (solution A).

A glass vial charged with a teflon-coated stirring bar, $(^nBu_4N)_2Ce^{IV}Cl_6$ (2.2 mg, 2.6 μmol) and $NaHCO_3$ (1.7 mg, 21 μmol) and MeCN (4 ml, HPLC grade) and stirrer the reaction mixture under dark for 3 min.

Preparation of $Ce^{IV}(OCOAr)Cl_n$ in MeCN (solution B).

A vial equipped with a teflon-coated stirring bar, $(^nBu_4N)_2Ce^{IV}Cl_6$ (2.2 mg, 2.6 μmol), $NaHCO_3$ (0.8 mg, 10 μmol), 2-aryloxy carboxylic acid **1c** (3.6 mg, 0.015 mmol) and MeCN (4 ml, HPLC grade) and stirrer the reaction mixture under dark for 5 min.

Experimental procedure and sampling

The UV-Vis measurement where performed using Shimadzu UV-3600 Vis-NIR spectrophotometer using a fluorescence cuvette (1 cm optical pathway, both faces can transmit light). A single blue LED OSRAM Oslon® SSL 80 royal-blue LEDs (λmax= 455 nm (± 15 nm), 3.5 V, 700 mA), equipped with a metallic passive cooling element, was placed approx. 2 mm away from one transmitting side of the cuvette, at 90° from the measuring beam. The spectra were recorded in the 200-600 nm range.

In order to record the spectra, the corresponding previously prepared solution was withdrawn using a syringe, filtered-off using a syringe filter and transferred into the cuvette, closed with a PTFE stopper. The acquisition routine was started and after a certain time interval the illumination was started.

UV-Vis spectra of $(^nBu_4N)_2Ce^{IV}Cl_6$

Solution A was used to measure the UV-Vis spectra of $(^nBu_4N)_2Ce^{IV}Cl_6$ in absence of light

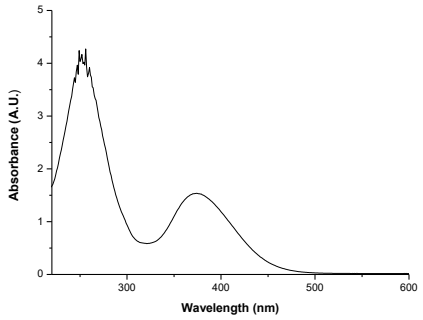


Figure 1: UV-Vis spectra of $(^nBu_4N)_2Ce^{IV}Cl_6$ in the absence of light

Spectra acquisition of $Ce^{IV}(OCOAr)Cl_n$ in the absence of light

Solution **B** was used, each spectrum was acquired after 1 min from the previous one. In the presence of 2-aryloxy carboxylic acid **1c**, the concentration of Ce(IV) species remained almost constant without blue light irradiation (Figure 2). The small modulation was most likely caused by the fact that, in order to operate the spectroscopic device, absolute darkness could not be reached.

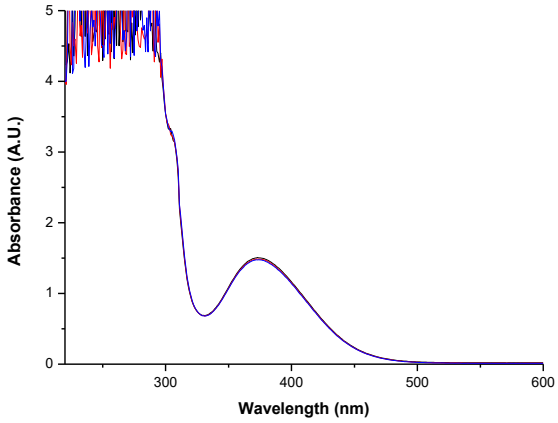


Figure 2: UV-Vis spectra of $Ce^{IV}(OCOAr)Cl_n$ in the absence of light

Spectra acquisition of $Ce^{IV}(OBn)Cl_n$ in the presence of light

Solution **B** was used, each spectrum was acquired in an appropriate time interval. Upon irradiation with 455 nm light with different time intervals the reduction of the Ce(IV) species ($\lambda max \approx 375$ nm) to Ce(III) species (broad and partially overlapped peak at lower wavelengths) (Figure 3) was observed.

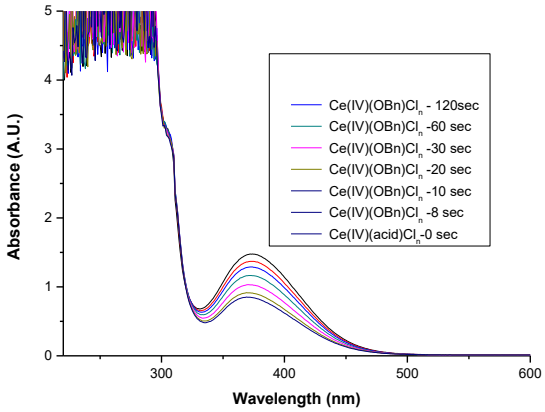
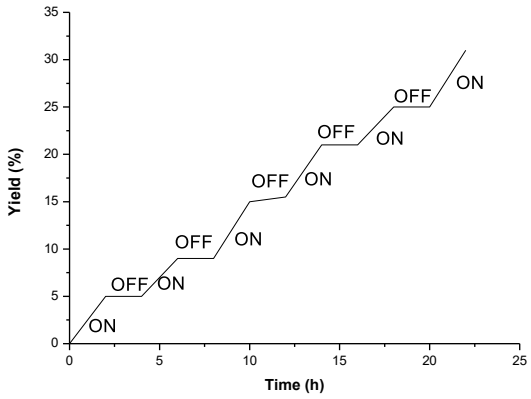


Figure 3: UV-Vis spectra of $Ce^{IV}(OCOAr)Cl_n$ in the presence of light with different time intervals.

ON/OFF experiment:

A 10 mL glass vial was charged with 2-Phenoxybenzoic acid (0.3 mmol), $CeCl_3$ (10 mol%), $(NH_4)_2S_2O_8$ (20 mol%), $NaHCO_3$ (20 mol%), trimethoxy benzene (0.1 mmol, internal standard) and stirring bar. Then the glass vial was sealed with a PTFE septum. EtOAc (3 mL) was added. The reaction vial was placed in a pre-programed temperature controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED at 35 °C. After the selected time has expired, a small aliquot was removed, concentrated under reduced pressure and then analyzed by ^1H NMR to determine the yield.

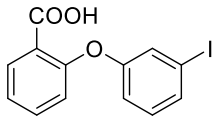


The reaction profile during alternating irradiation shows that the reaction does only proceed in the presence of light. This indicates that an essential reaction step requires light excitation. If radical chain processes are involved, the chain length is very short and does require constant initiation.

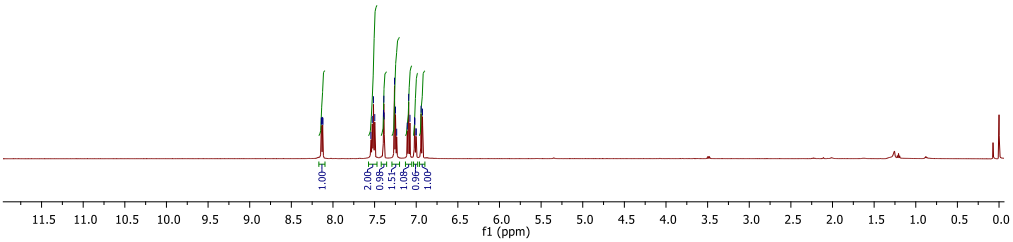
References:

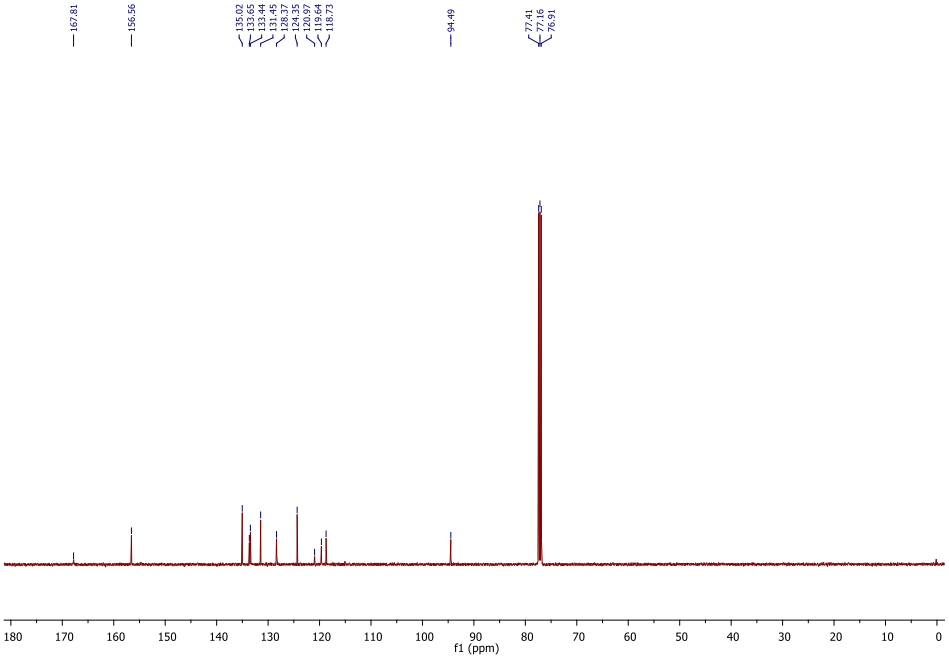
1. S.-F. Wang, X.-P. Cao, Y. Li, *Angew. Chem., Int. Ed*., **2017**, *56*, 13089.
2. A. Hossian, R. Jana, *Org. Biomol. Chem.* **2016**, *14*, 9768−9779.
3. J. C. Gonzalez-Gomez, N. P. Ramirez, T. Lana-Villarrealb, P. Boneteb *Org. Biomol. Chem*. **2017**, *15*, 9680−9684.

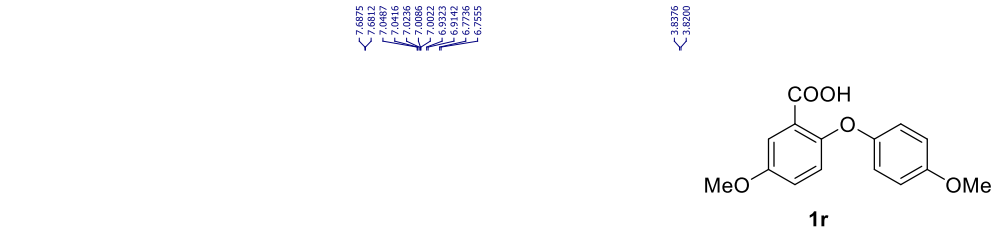
NMR Spectra



1o



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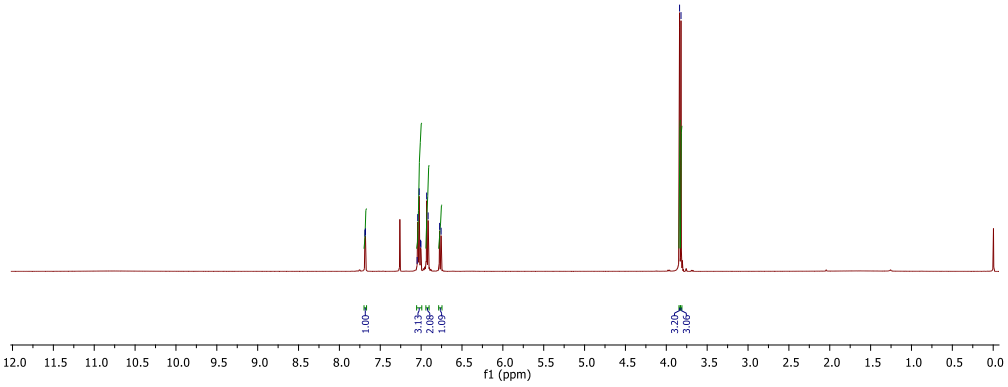
MeO
OMe

1r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1.09
3.39
3.00
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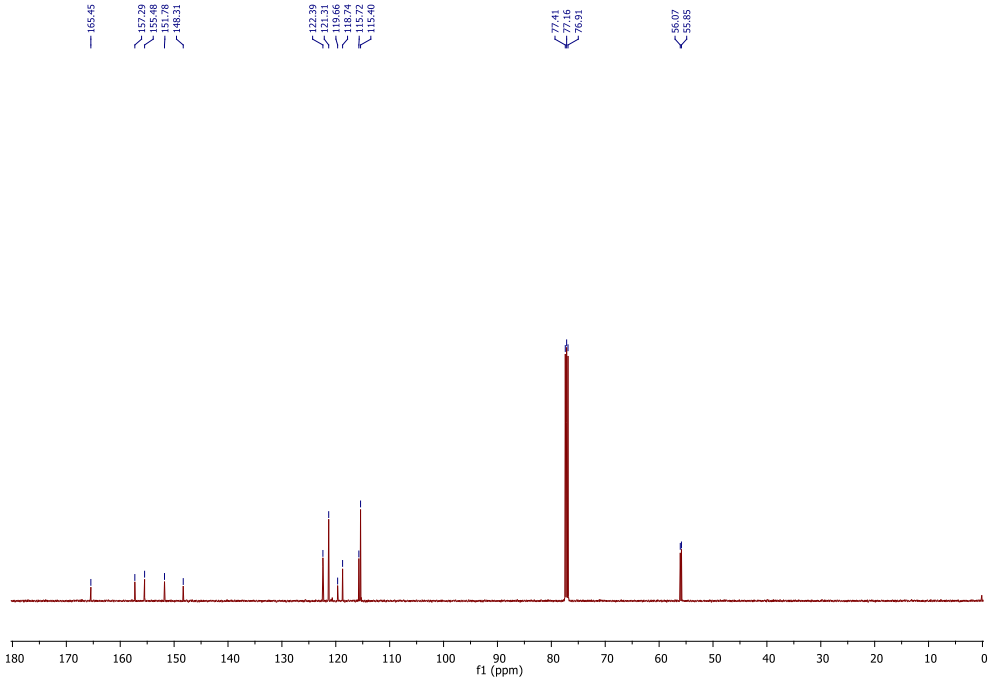
f1 (ppm)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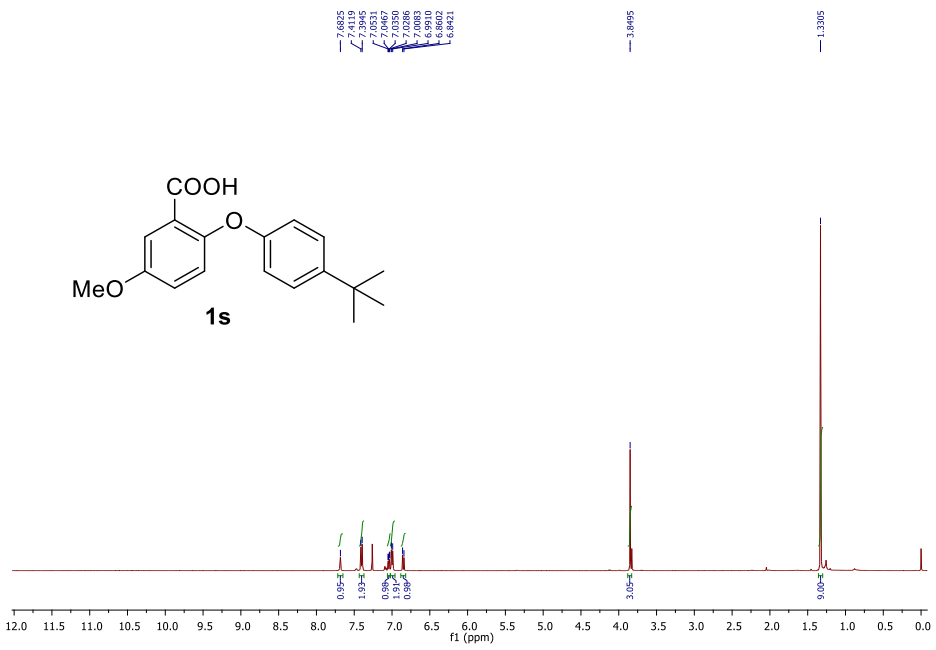
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1s
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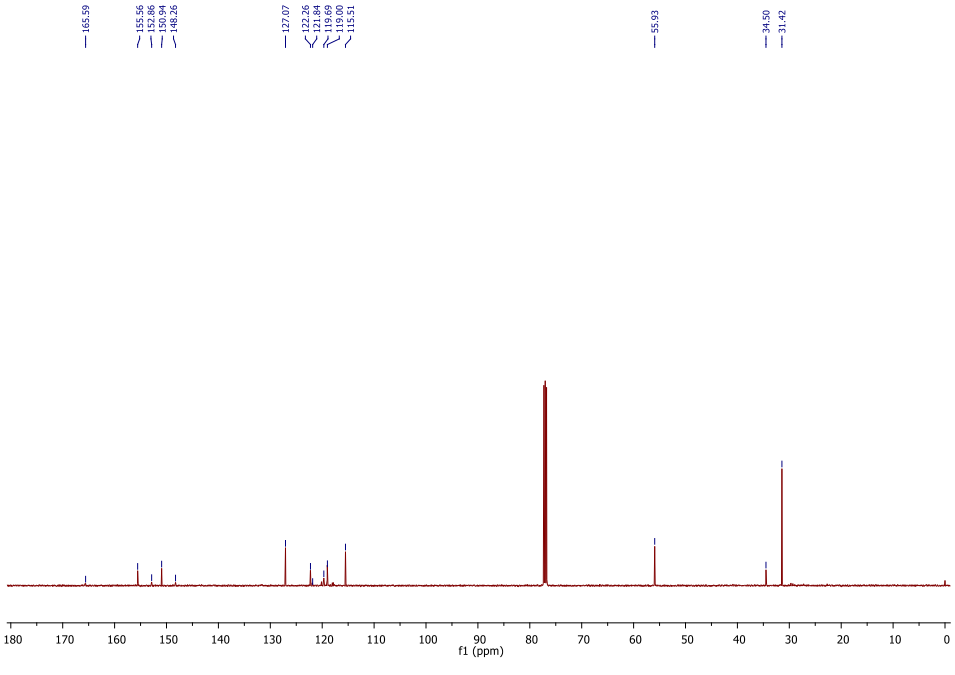
1.93
0.86
0.83
0.98
3.05
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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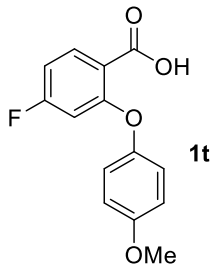
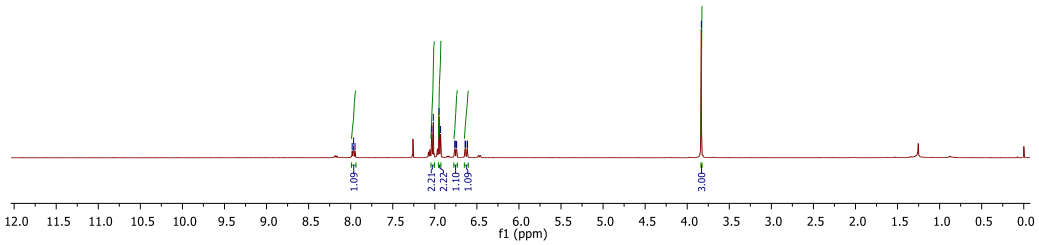
155.56
152.86
150.94
148.26
127.07
122.26
121.84
119.69
115.00
115.51
55.93
34.50
31.42
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.98
7.97
7.95
7.04
7.02
6.95
6.93
6.76
6.76
6.75
6.74
6.64
6.64
6.62
6.61
3.83


O
OH
F
O
OMe

1t


1.09
2.21
2.32
1.10
1.09
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.24
165.11
165.02
163.15
157.31
147.85
134.36
122.06
115.60
115.57
115.40
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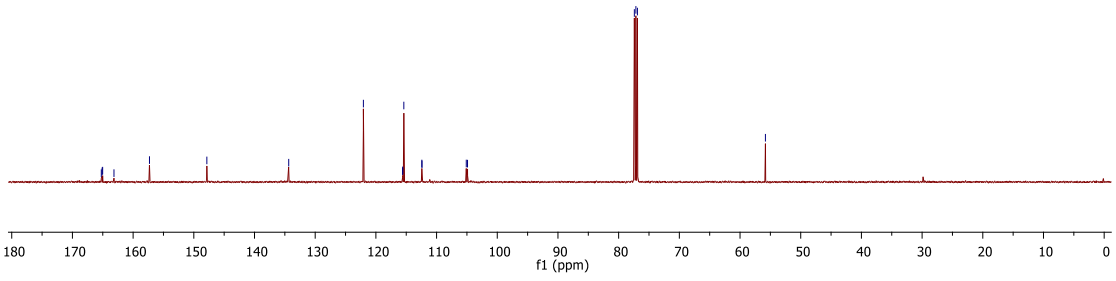
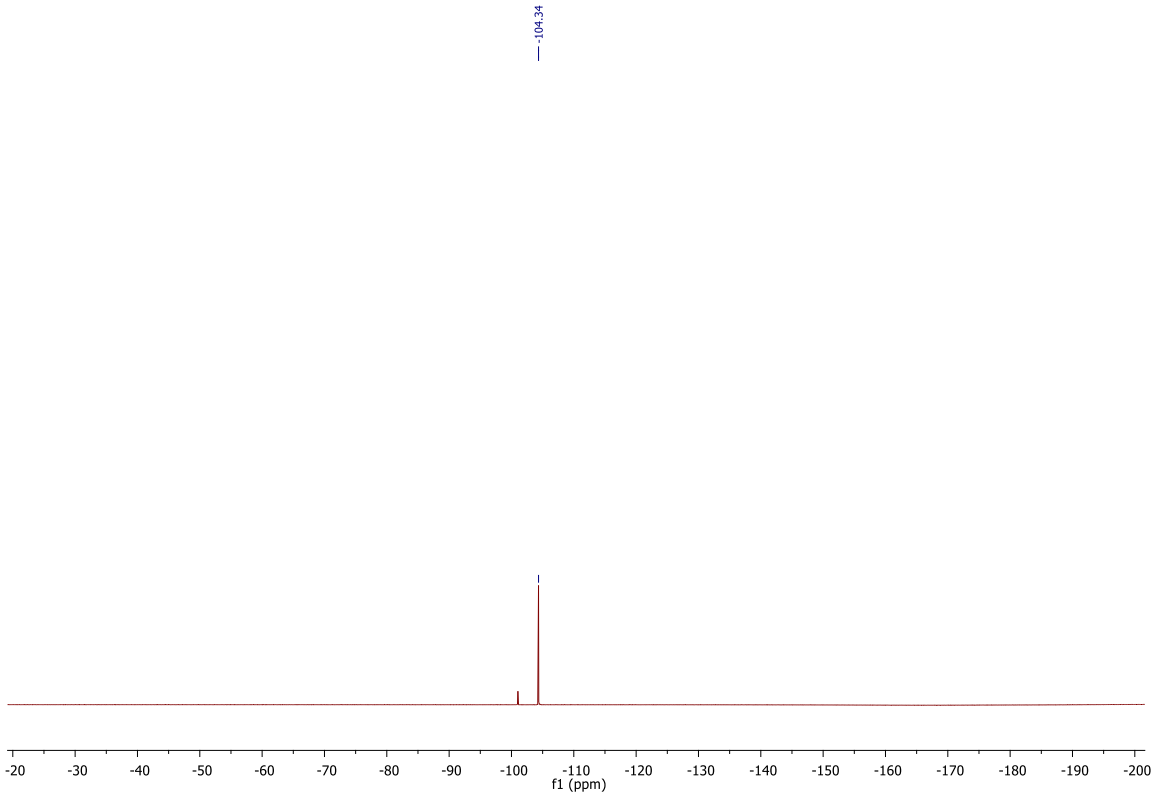
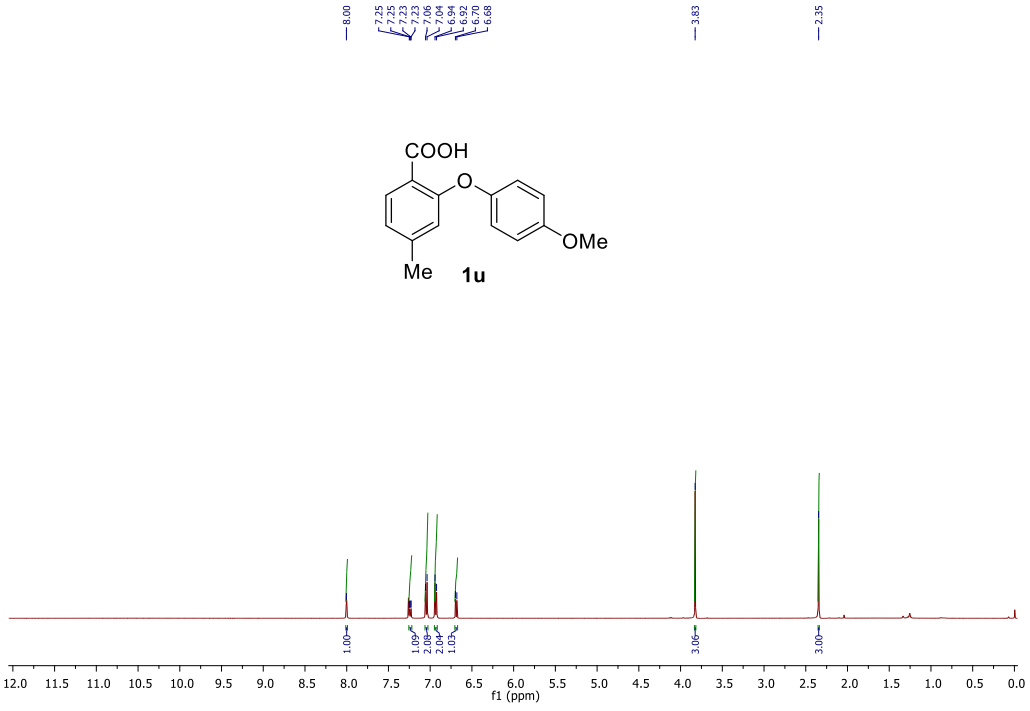
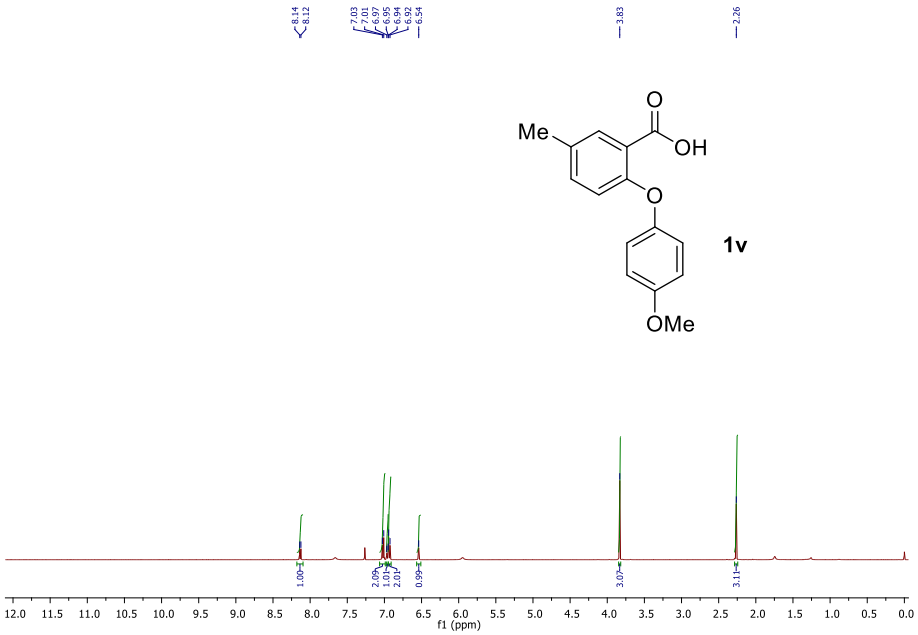
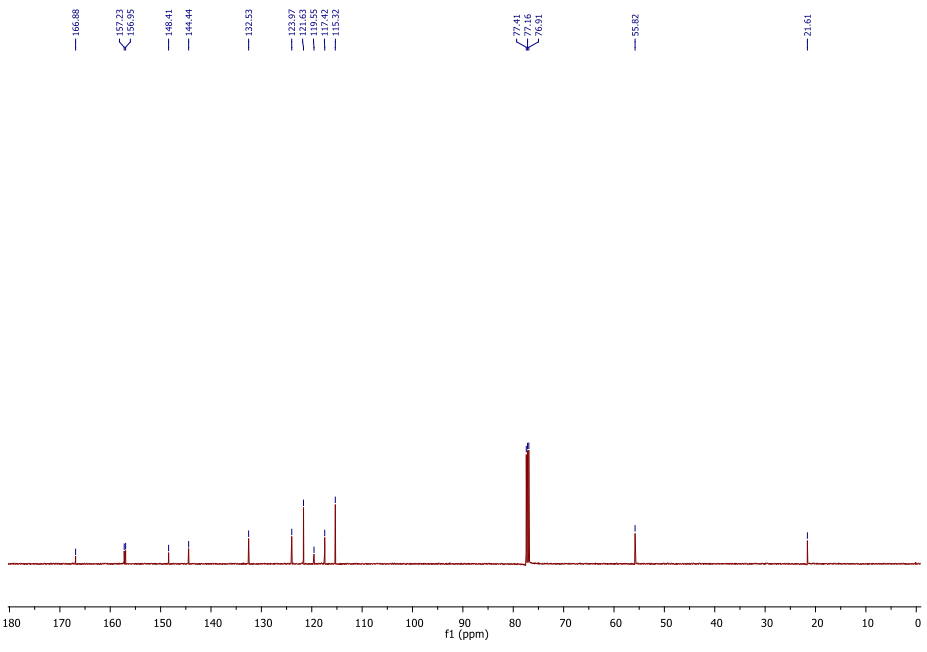
112.40
105.11
104.90
77.41
77.16
76.91
55.82

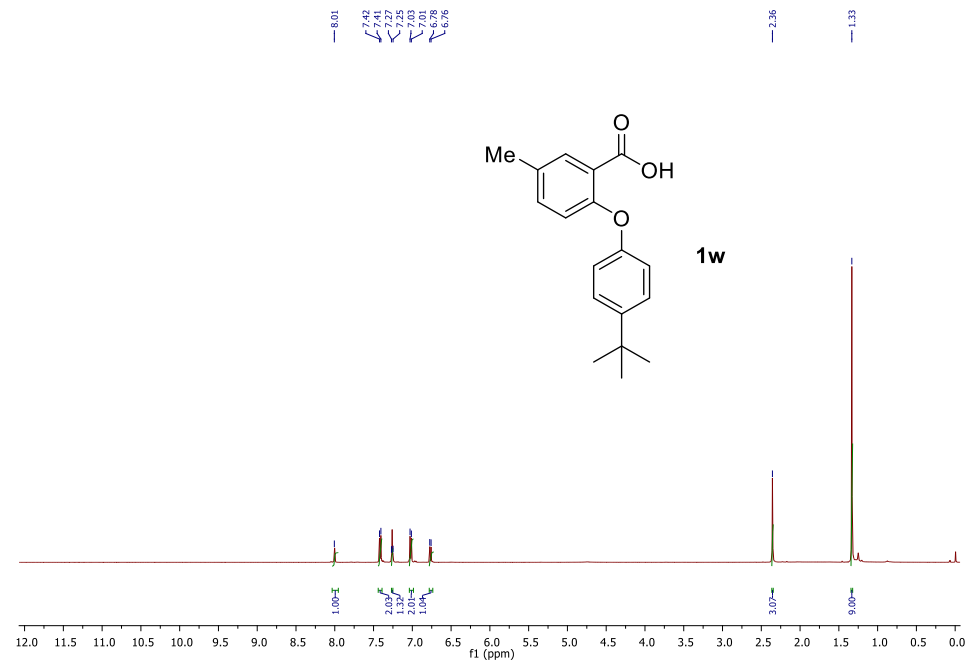

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

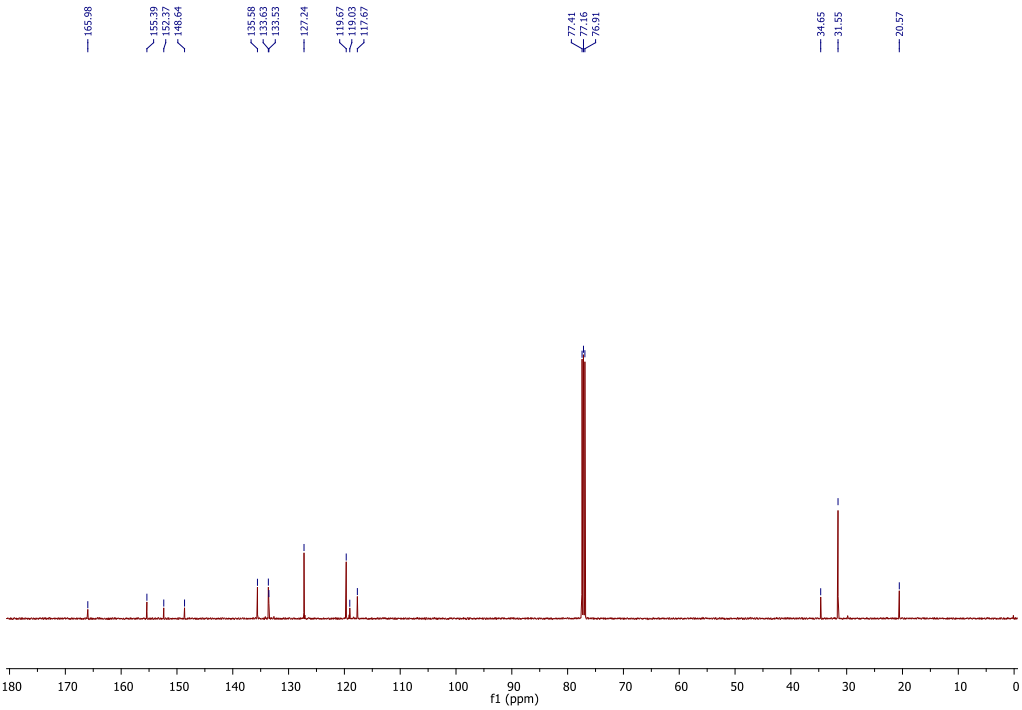

-104.34
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

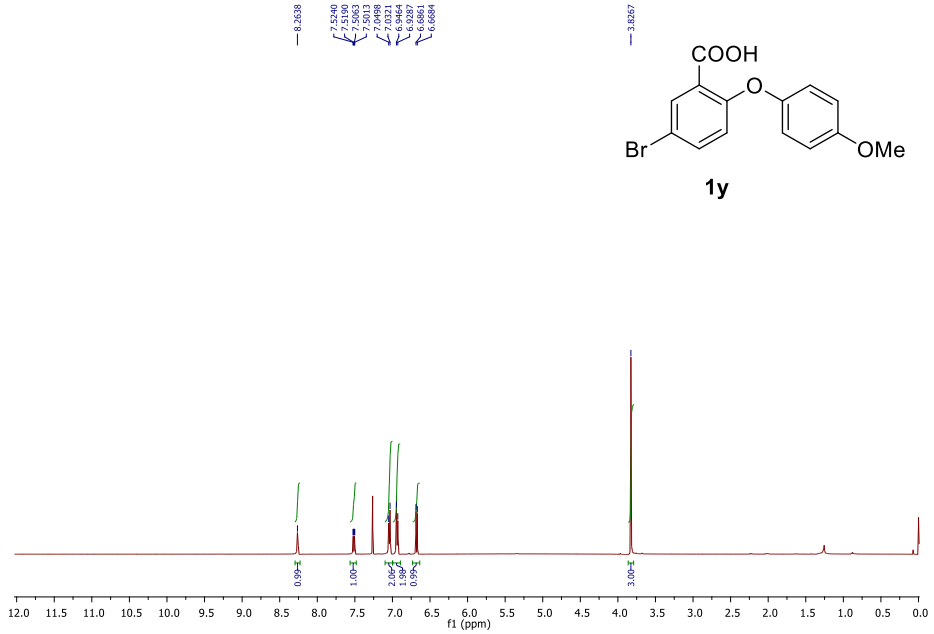

8.00
7.25
7.25
7.23
7.23
7.06
7.04
6.94
6.92
6.70
6.68
3.83
2.35
COOH
O
OMe
Me
1u
1.00
1.08
2.04
2.04
1.03
3.06
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.90
157.41
156.05
147.74
135.60
133.69
133.23
121.75
118.50
116.73
115.41
77.41
77.16
76.91
55.84
20.51
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

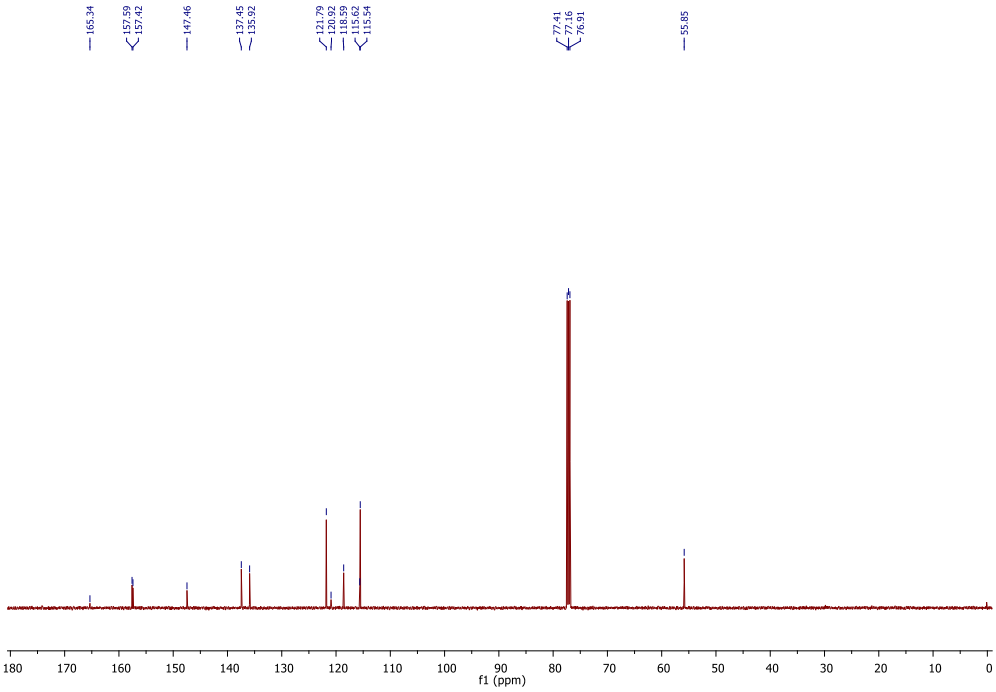

8.14
8.12
7.03
7.01
6.97
6.95
6.94
6.93
6.54
3.83
2.26
Me
O
OH
O
OMe
1v
1.00
2.09
1.01
2.01
0.99
3.07
3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

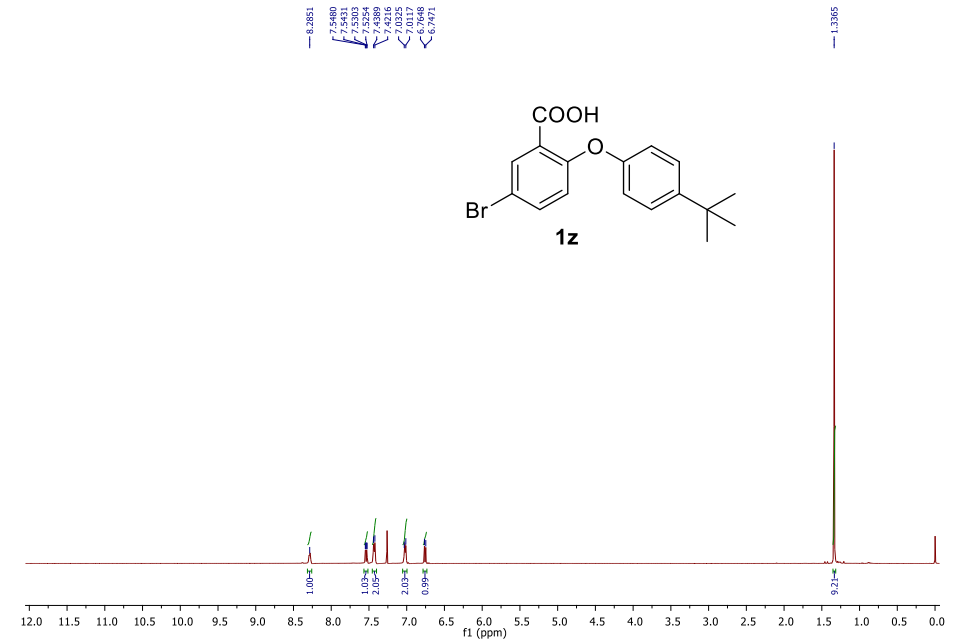

166.88
157.23
156.95
148.41
144.44
132.53
123.97
121.63
119.55
117.32
115.32
77.41
77.16
76.91
55.82
21.61
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

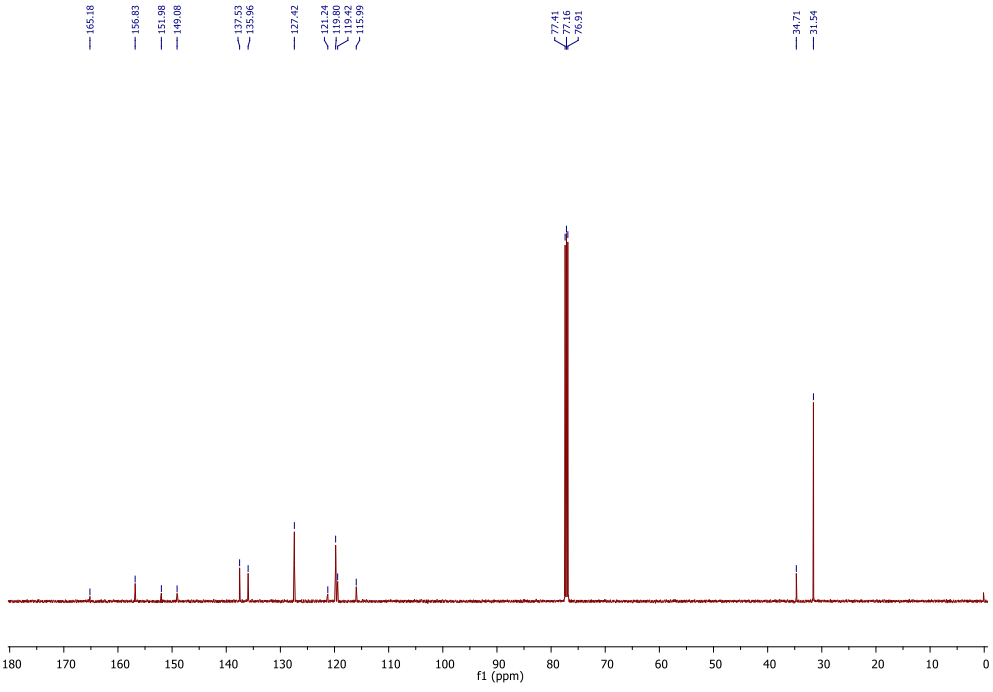

8.01
7.42
7.41
7.27
7.25
7.03
7.01
6.78
6.76
2.36
1.33
Me
O
OH
O
1w
1.00
2.03
1.12
2.01
1.04
3.07
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

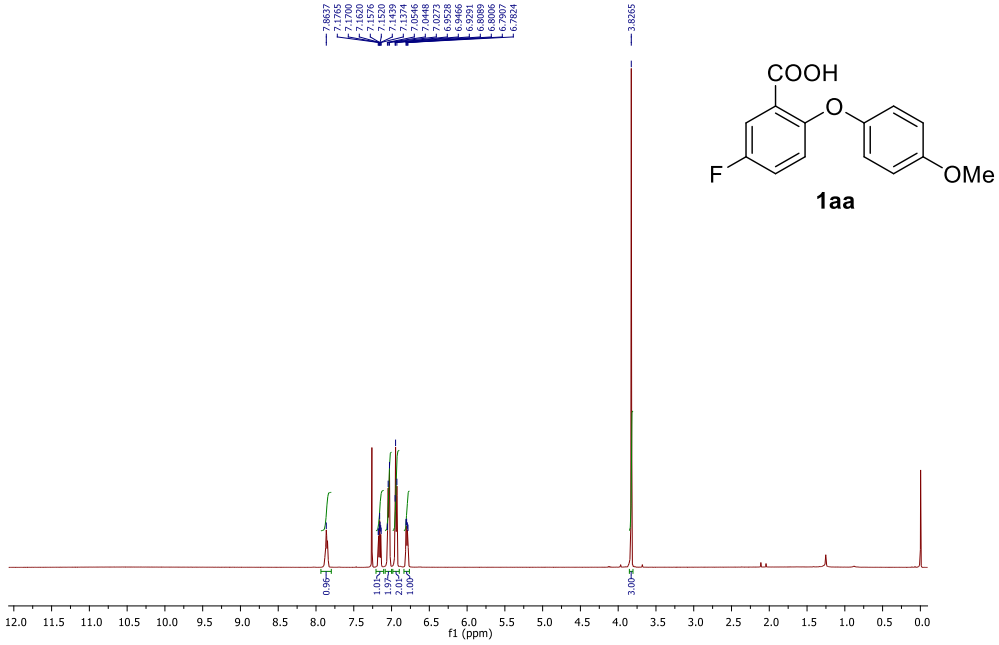

165.98
155.39
152.37
148.64
135.58
133.63
133.53
127.24
119.67
119.03
117.67
77.41
77.16
76.91
34.65
31.55
20.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.2638
7.5240
7.5190
7.5063
7.3693
7.3498
7.0321
6.9464
6.9287
6.6661
6.6604
3.8267
COOH
O
Br
OMe
1y
0.99
1.00
2.06
1.99
0.99
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


165.34
157.59
157.42
147.46
137.45
135.92
121.79
120.92
118.59
115.62
115.54
77.41
77.16
76.91
55.85
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

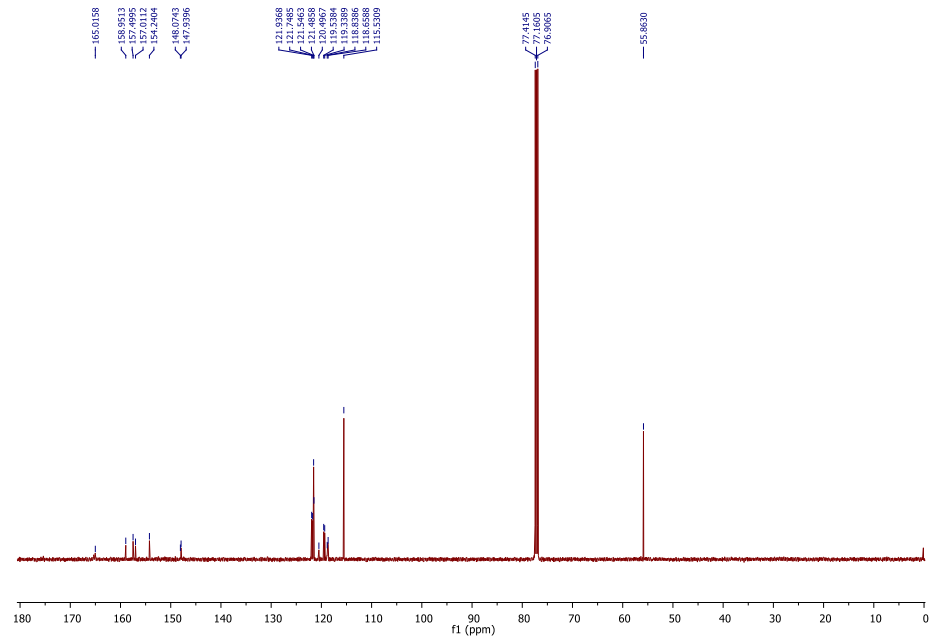

8.2851
7.5480
7.5431
7.5303
7.5254
7.4389
7.4216
7.0325
7.0177
6.7648
6.7471
1.3365
COOH
O
Br
1z
1.00
1.03
2.05
2.03
0.99
9.21
f1 (ppm)

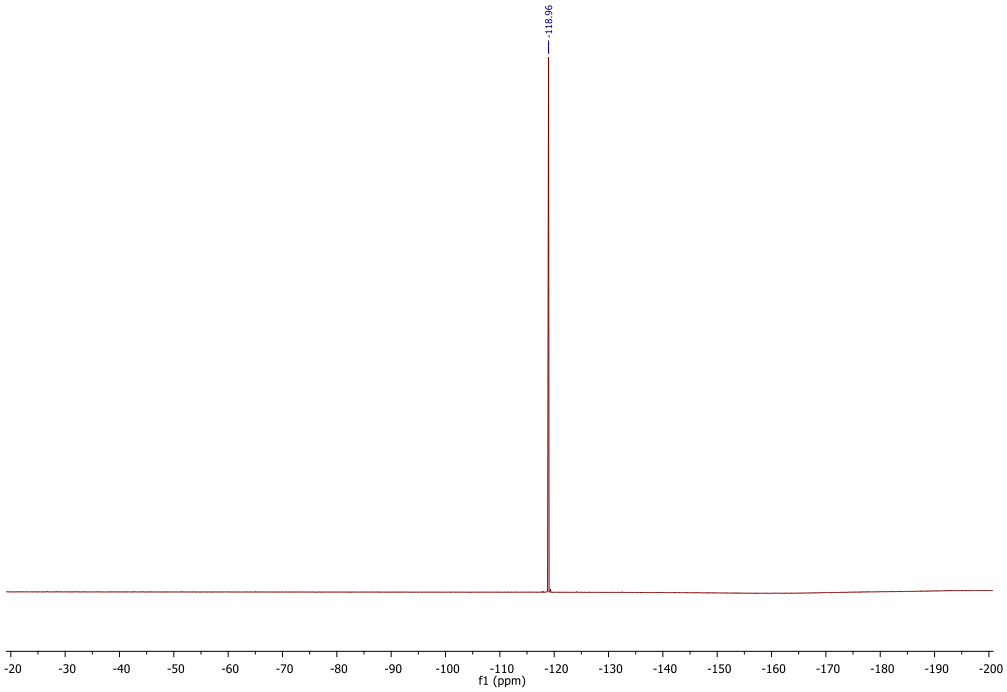

165.18
156.83
151.98
149.08
137.53
135.96
127.42
121.24
119.80
119.42
115.99
77.41
77.16
76.91
34.71
31.54
f1 (ppm)

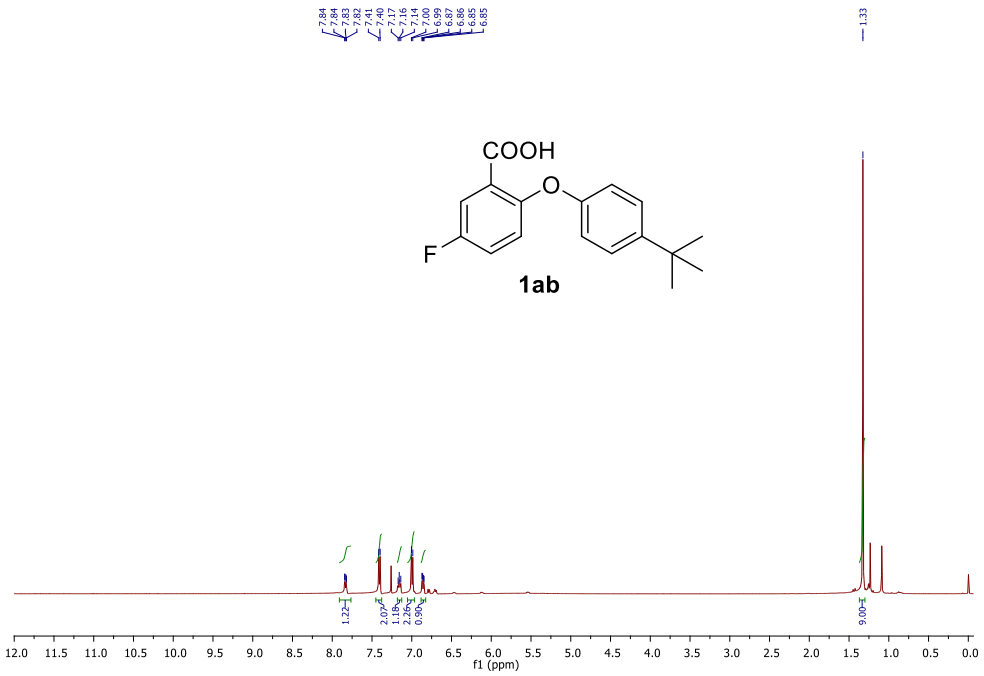

7.8637
7.1765
7.1700
7.1600
7.1576
7.1520
7.1439
7.1374
7.1294
7.1046
7.0448
7.0273
6.9528
6.9466
6.9291
6.8089
6.8006
6.7907
6.7824
3.8265
0.96
1.01
1.97
2.01
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

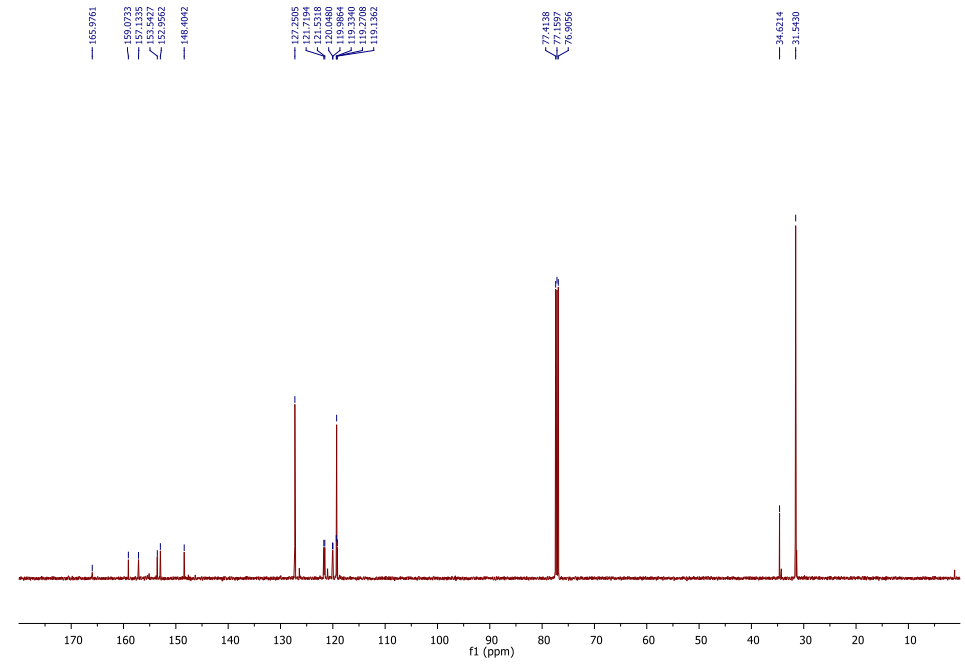
COOH
O
F
OMe

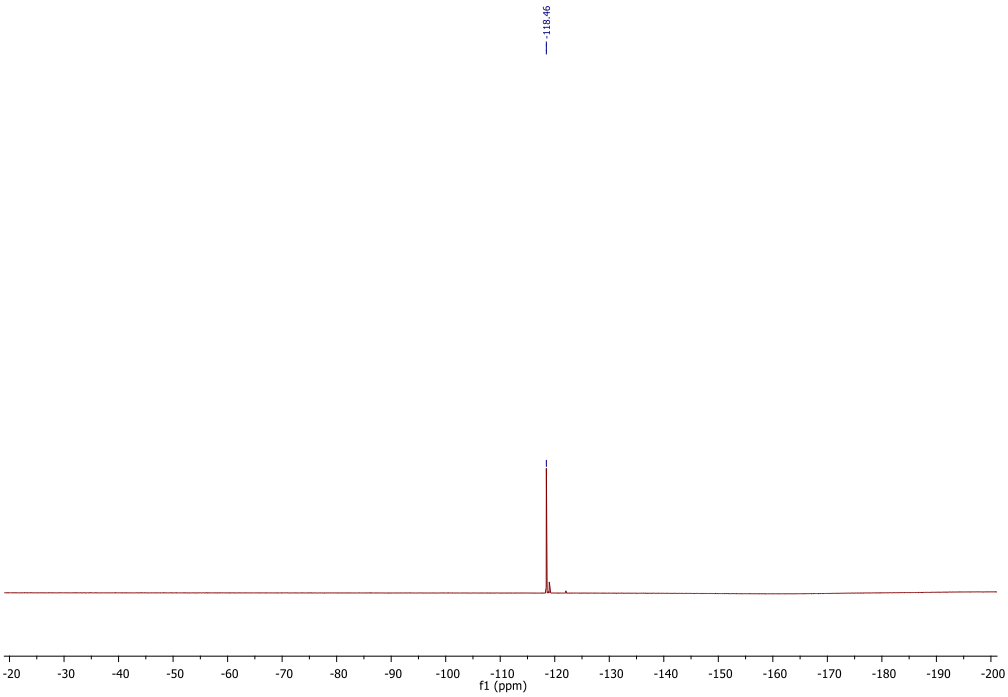
1aa


165.0158
158.9513
157.4995
157.0112
154.2404
148.0743
147.9396
121.9368
121.7965
121.5463
121.4858
120.4967
119.5764
119.3389
118.8386
118.6588
115.5309
77.4145
77.1605
76.9065
55.8630
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

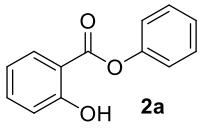

-118.96
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


7.84
7.84
7.83
7.82
7.41
7.40
7.17
7.16
7.14
7.00
6.99
6.87
6.86
6.85
6.85
1.33
COOH
O
F
1ab
1.22
2.07
1.19
2.16
0.99
9.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

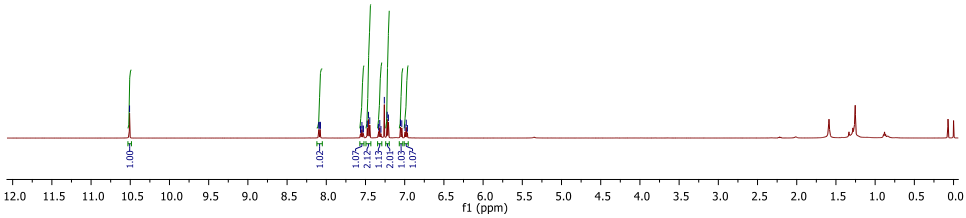

165.9761
150.0723
157.1335
153.5427
152.9562
148.4042
127.2505
121.7194
121.5318
120.0480
119.9864
119.9246
119.2708
119.1362
77.4138
77.1597
76.9056
34.6214
31.5430
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-118.46
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

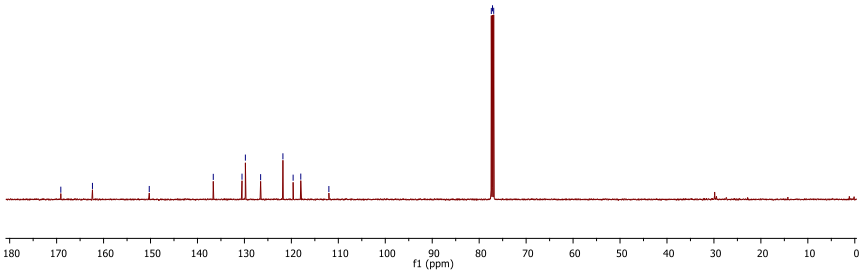

10.5092
8.0946
8.0914
8.0786
8.0754
7.5828
7.5686
7.5455
7.5315
7.5283
7.4770
7.4653
7.4453
7.3328
7.3179
7.3031
7.2997
7.2397
7.2335
7.2079
7.0538
7.0370
6.9957
6.9801
6.9654

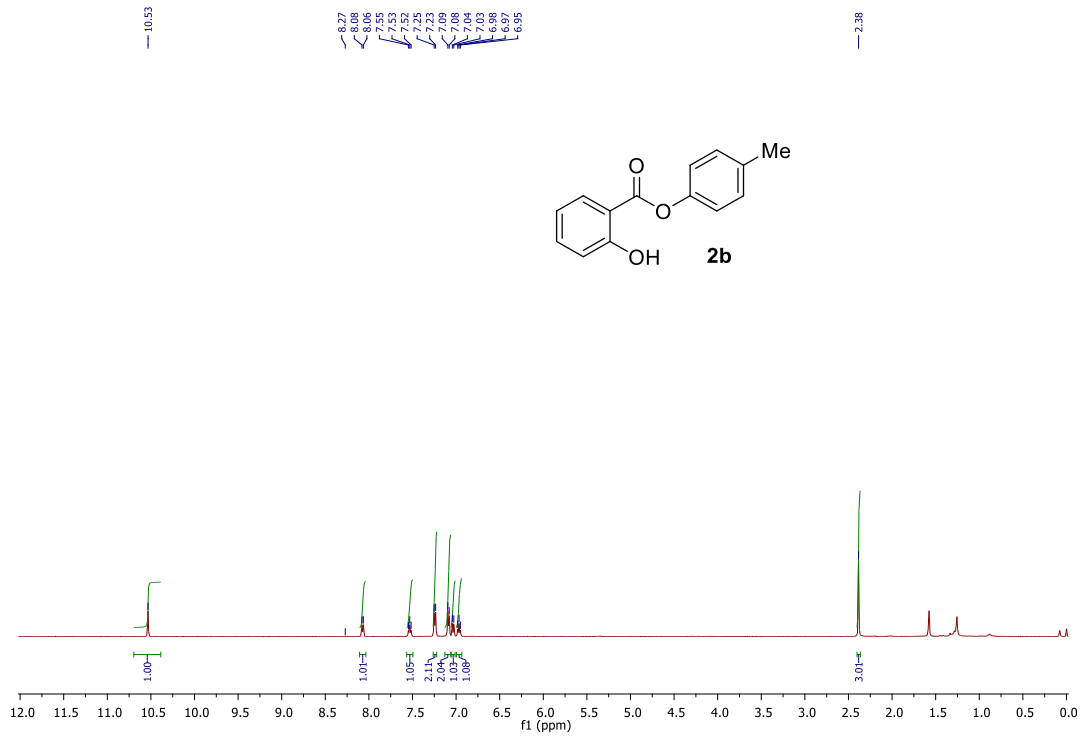

O
O
OH

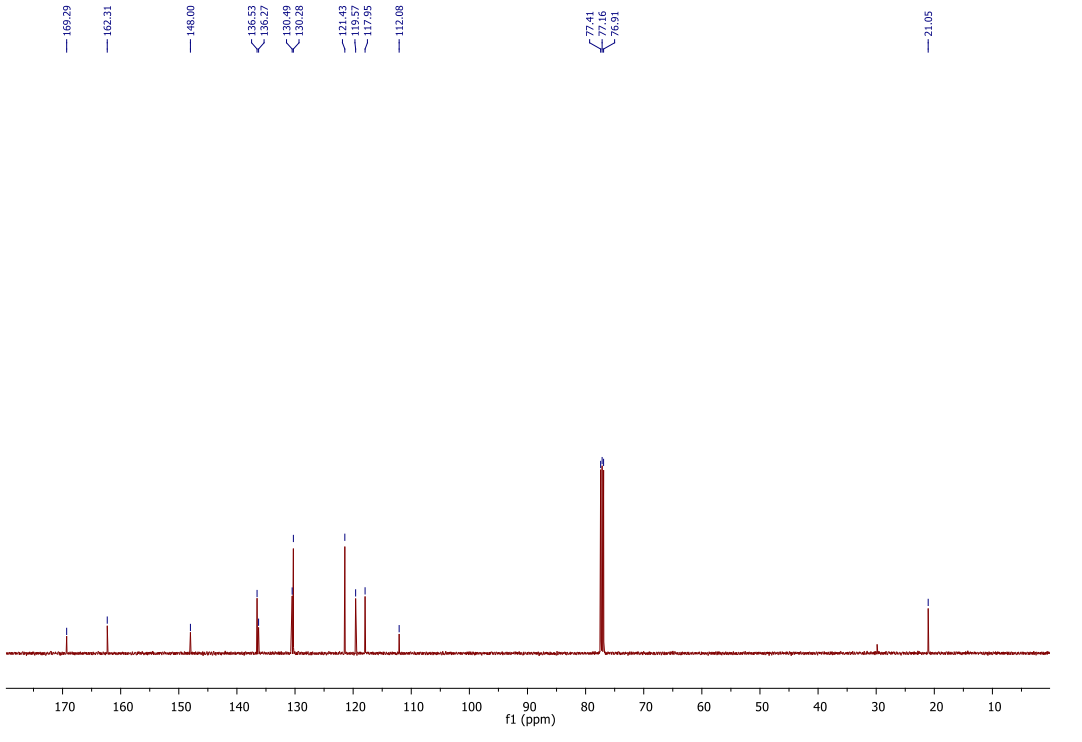
2a

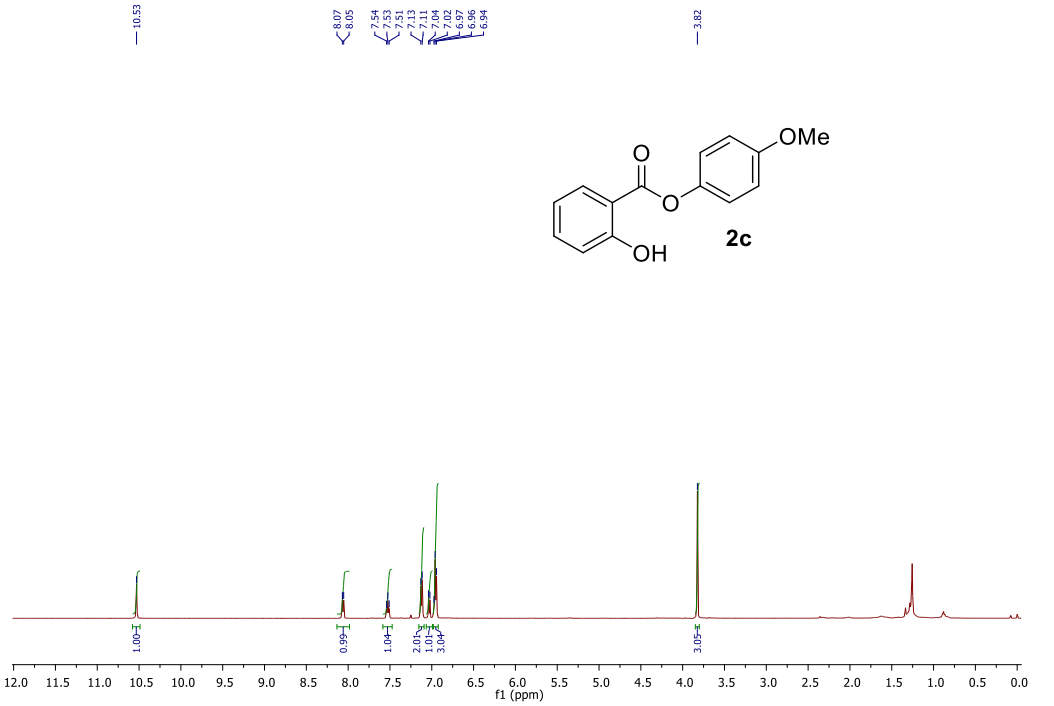

1.00
1.02
1.07
2.12
1.13
2.03
1.03
1.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

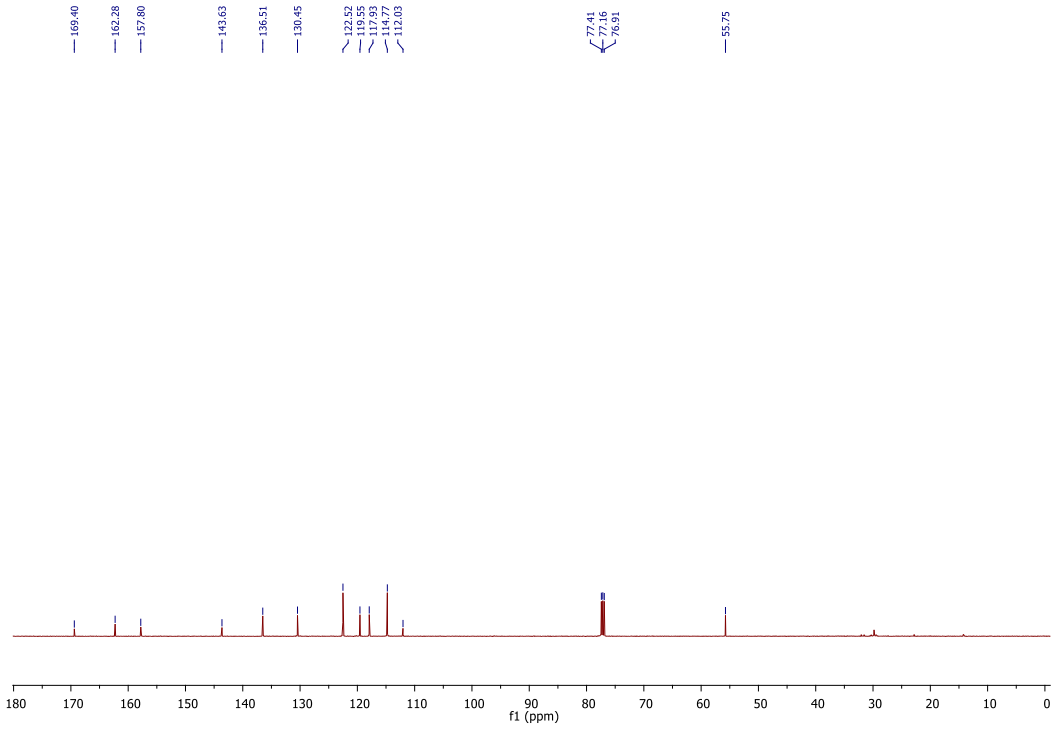

169.11
162.37
150.27
136.63
130.51
129.80
126.55
121.80
119.63
118.00
112.01
77.41
77.16
76.91


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


10.53
8.27
8.08
8.06
7.55
7.53
7.52
7.35
7.33
7.09
7.08
7.04
7.03
6.98
6.97
6.95
2.38
Me
O
O
OH
2b
1.00
1.01
1.05
2.11
2.04
1.03
1.00
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.29
162.31
148.00
136.53
136.27
130.49
130.28
121.43
119.57
117.95
112.08
77.41
77.16
76.91
21.05
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


10.53
8.07
8.05
7.54
7.53
7.51
7.13
7.11
7.04
7.02
6.97
6.96
6.94
3.82
OMe
O
O
OH
2c
1.00
0.99
1.04
2.01
1.01
3.04
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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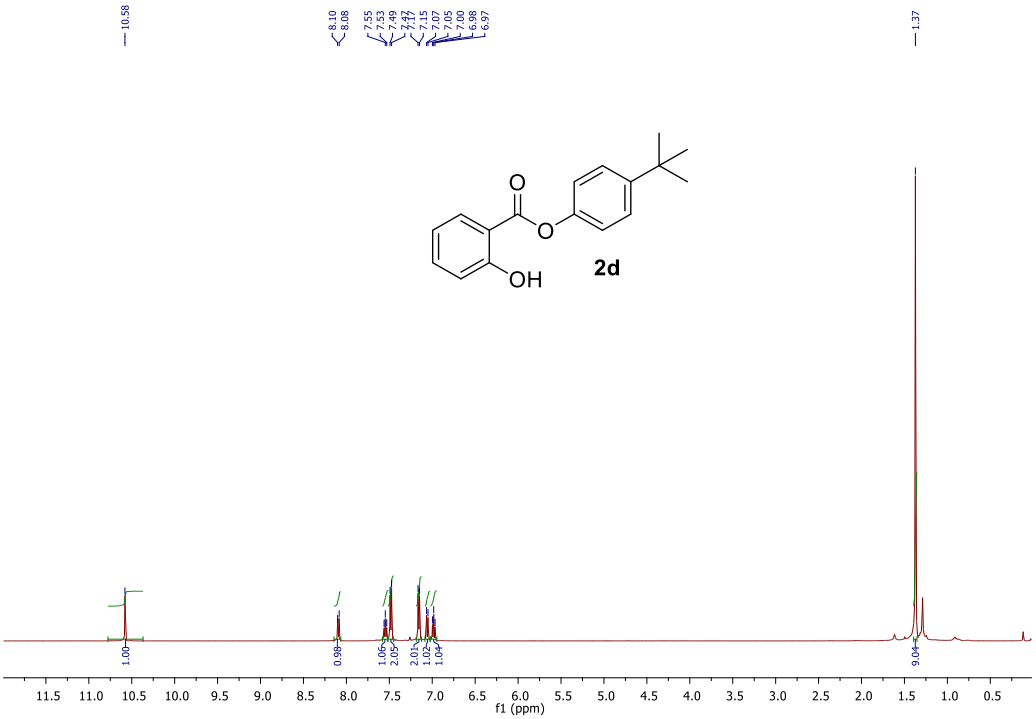
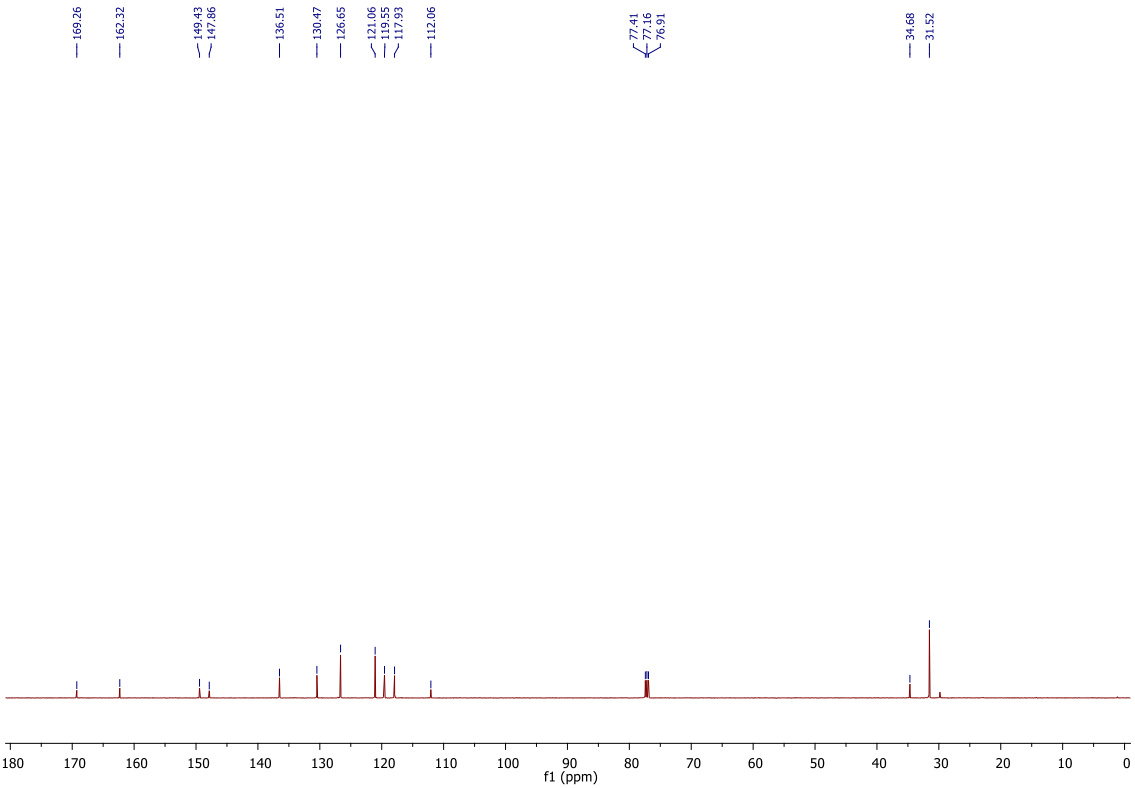
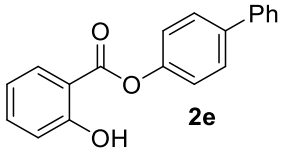
162.28
157.80
143.63
136.51
130.45
122.52
119.55
117.93
114.77
112.03
77.41
77.16
76.91
55.75
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

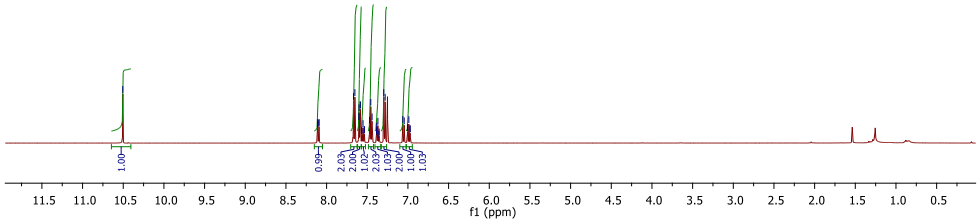

10.58
8.10
8.08
7.55
7.53
7.49
7.47
7.17
7.15
7.07
7.05
7.00
6.98
6.97
1.37
O
O
OH
2d
1.00
0.98
1.06
2.05
2.01
1.02
1.04
9.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


169.26
162.32
149.43
147.86
136.51
130.47
126.65
121.06
119.55
117.93
112.06
77.41
77.16
76.91
34.68
31.52
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

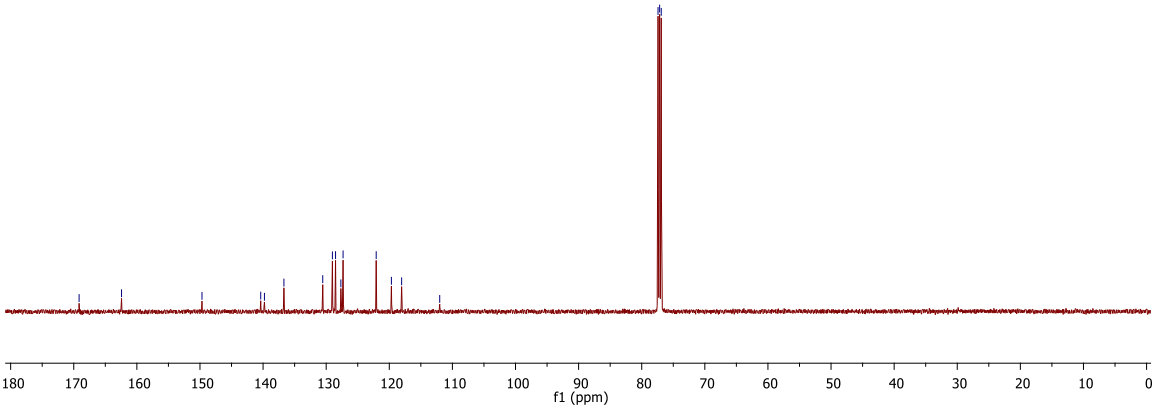

10.51
8.11
8.11
8.10
8.09
7.67
7.65
7.60
7.60
7.59
7.59
7.57
7.57
7.55
7.54
7.54
7.47
7.46
7.44
7.39
7.38
7.38
7.37
7.36
7.35
7.30
7.28
7.06
7.05
7.00
7.00
6.99
6.97
6.97


Ph
O
O
OH

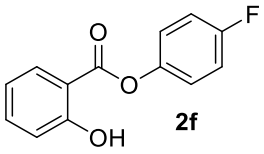
2e


1.00
0.99
2.03
2.00
1.02
2.05
1.03
2.00
1.00
1.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

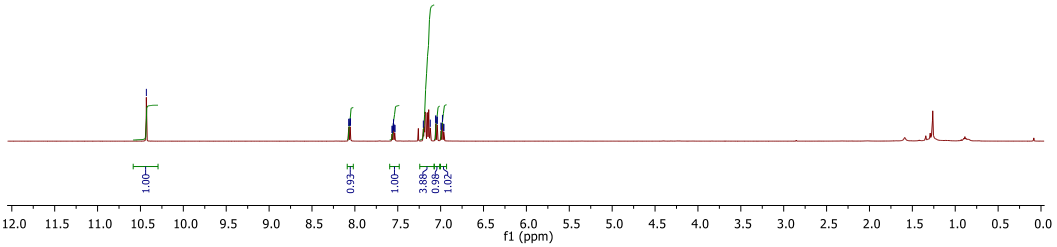

169.15
162.43
149.68
140.37
139.79
136.70
130.54
129.01
128.52
127.67
127.32
122.07
119.66
118.05
112.01
77.41
77.16
76.91


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

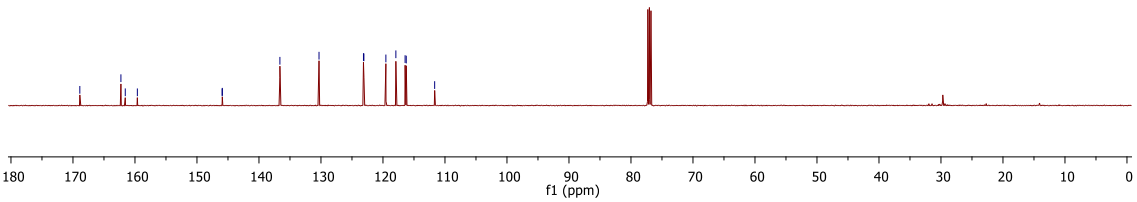

10.43
8.07
8.07
8.05
8.05
7.55
7.55
7.12
7.06
7.06
7.04
7.04
7.00
6.99
6.98
6.96
6.96

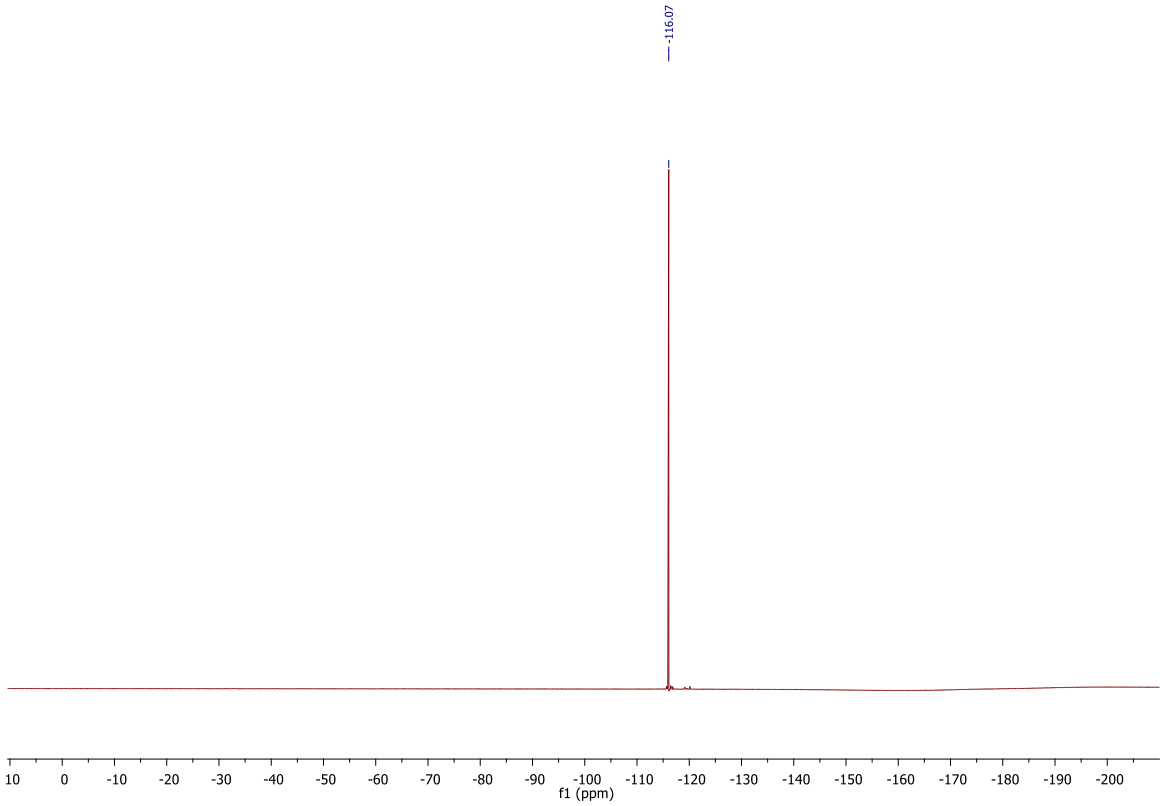

O
O
F
OH

2f

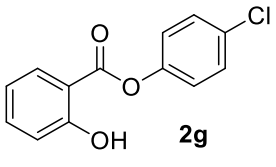

1.00
0.93
1.00
3.88
0.98
1.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.8933
162.2669
161.5638
159.6146
145.9347
145.9119
136.6232
130.3139
123.1443
123.0762
119.5301
117.9191
116.4309
116.2432
111.6620

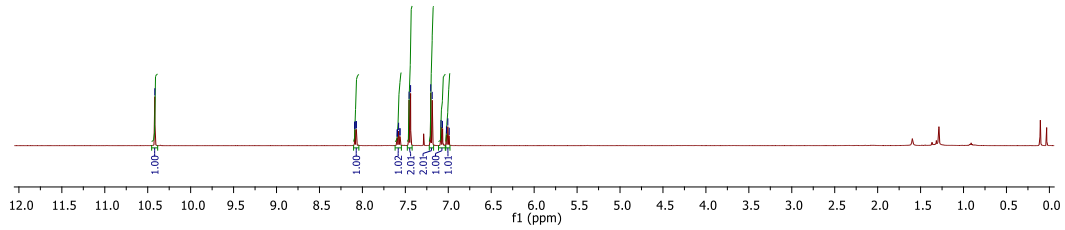

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-116.07
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

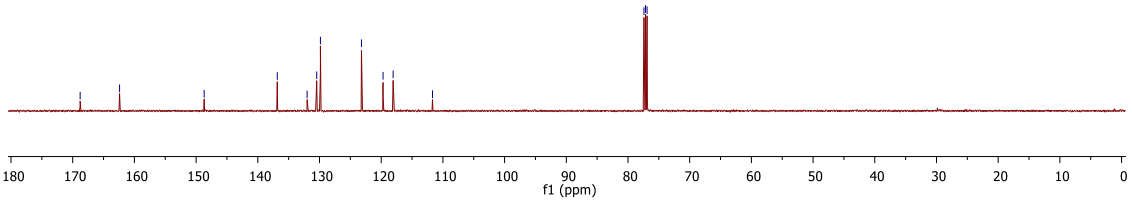

10.42
8.09
8.09
8.07
8.07
7.60
7.59
7.58
7.56
7.56
7.46
7.44
7.20
7.19
7.08
7.07
7.02
7.01
6.99

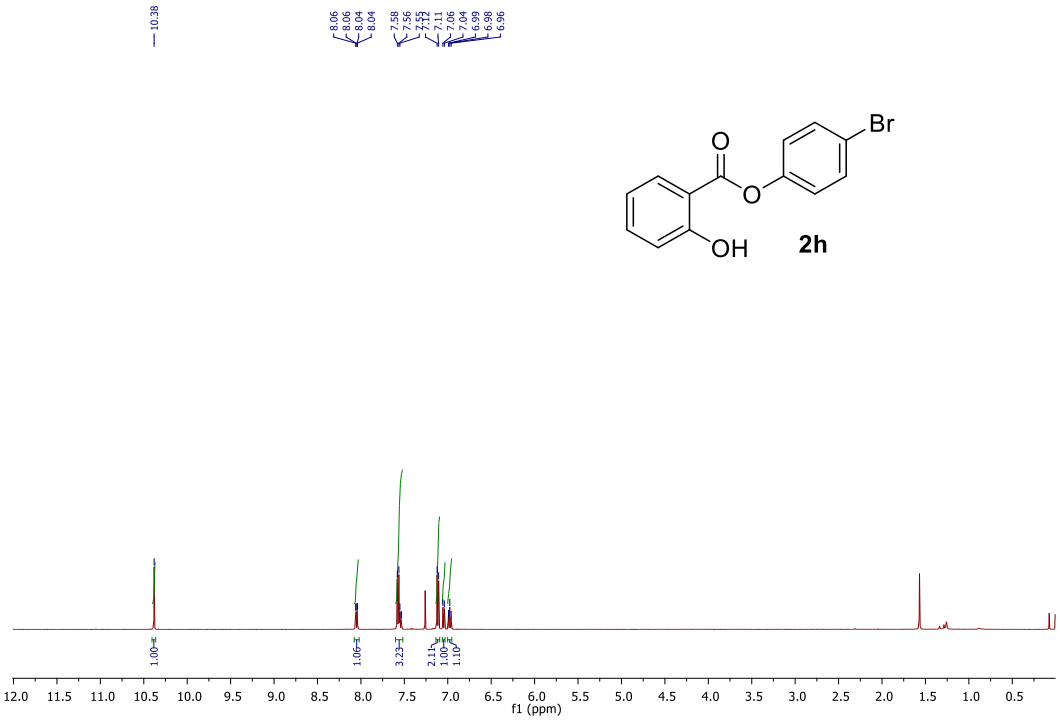

Cl
O
O
OH

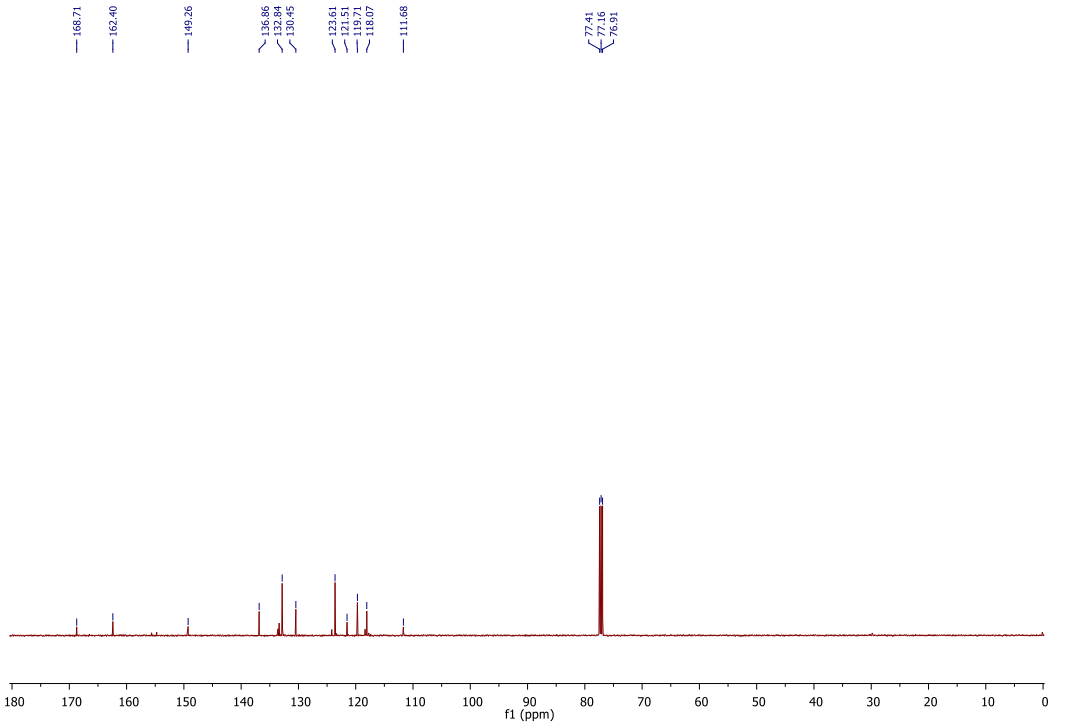
2g


1.00
1.00
1.02
2.01
2.01
1.00
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

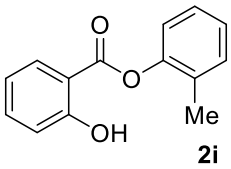

168.79
162.40
148.70
136.84
132.01
130.45
129.85
123.19
119.70
118.07
111.69
77.41
77.16
76.91


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

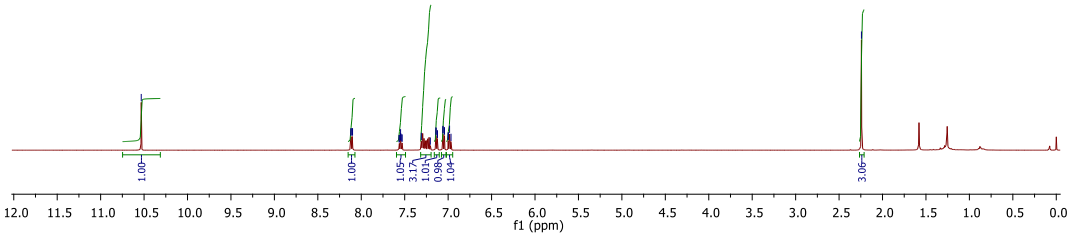

10.38
8.06
8.06
8.04
8.04
7.58
7.56
7.55
7.12
7.11
7.06
7.04
6.99
6.98
6.96
Br
O
O
OH
2h
1.00
1.06
3.23
2.11
1.00
1.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


168.71
162.40
149.26
136.86
132.84
130.45
123.61
121.51
119.71
118.07
111.68
77.41
77.16
76.91
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

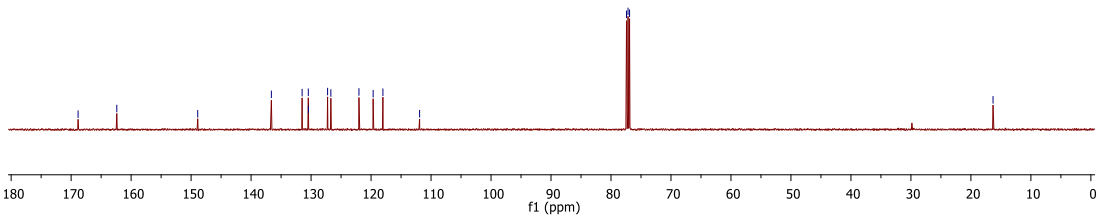

10.53
8.12
8.12
8.10
8.10
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.31
7.20
7.14
7.14
7.12
7.12
7.06
7.06
7.04
7.04
7.00
7.00
6.98
6.97
2.24

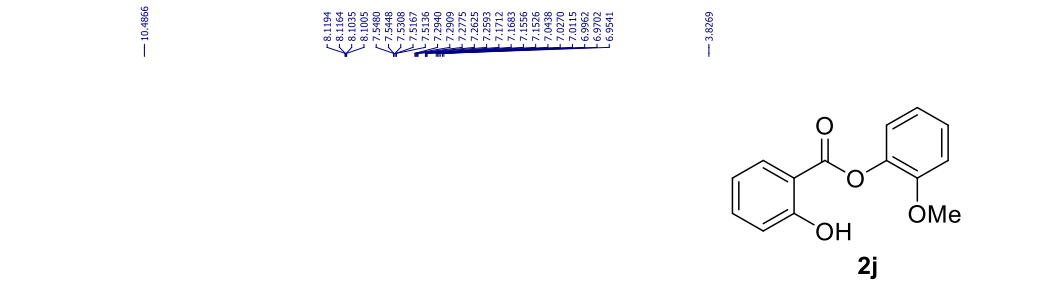

O
O
Me
OH

2i


1.00
1.00
1.05
3.17
1.01
0.98
1.04
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

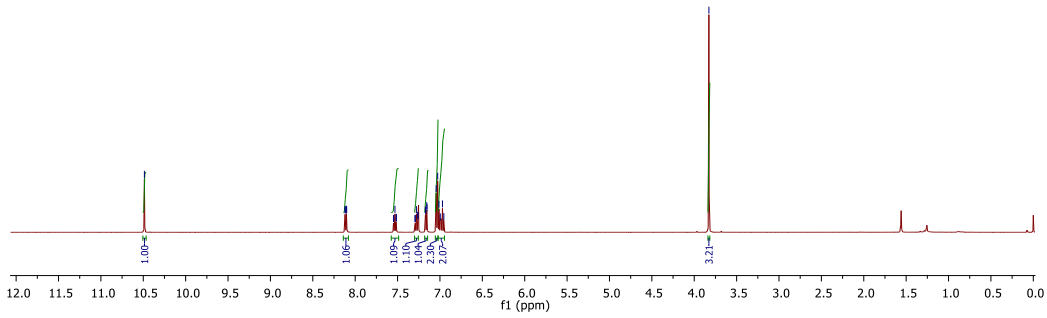

168.84
162.39
148.90
136.62
131.49
130.46
130.44
127.25
126.70
122.02
119.65
118.02
111.91
77.41
77.16
76.91
16.31


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

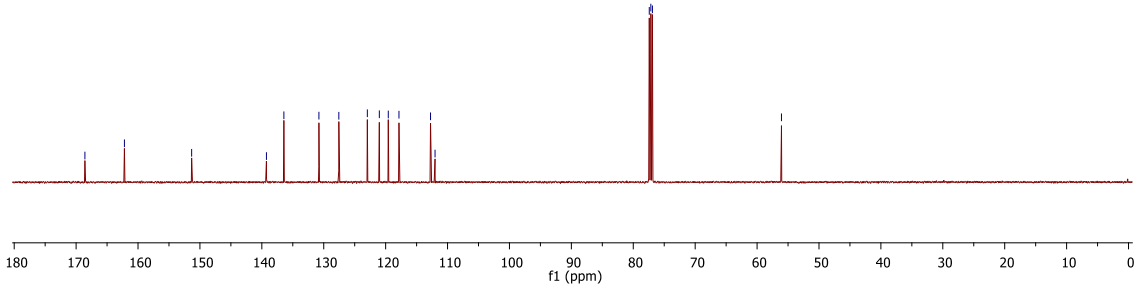

10.4866
8.1194
8.1164
8.1035
8.1005
7.5480
7.5448
7.5308
7.5167
7.5136
7.2940
7.2909
7.2775
7.2625
7.2593
7.1712
7.1683
7.1556
7.1526
7.0438
7.0270
7.0115
6.9952
6.9702
6.9541
3.8269

O
O
OMe
OH

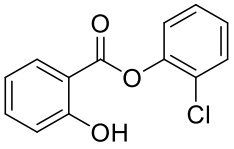
2j


1.00
1.06
1.09
1.10
1.04
2.36
2.07
3.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

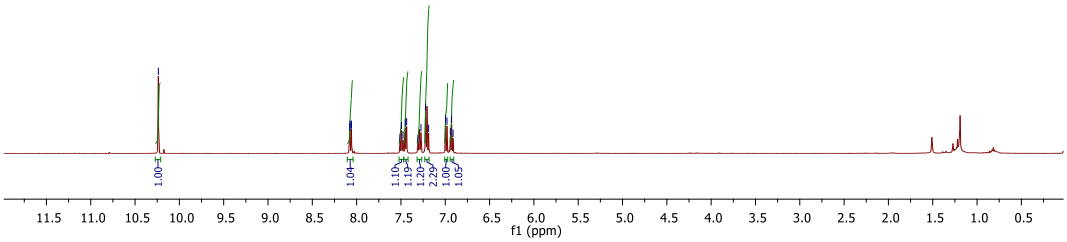

168.58
162.20
151.34
139.25
136.44
130.78
127.56
122.96
121.02
119.57
117.85
112.75
112.02
77.41
77.16
76.91
56.06


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

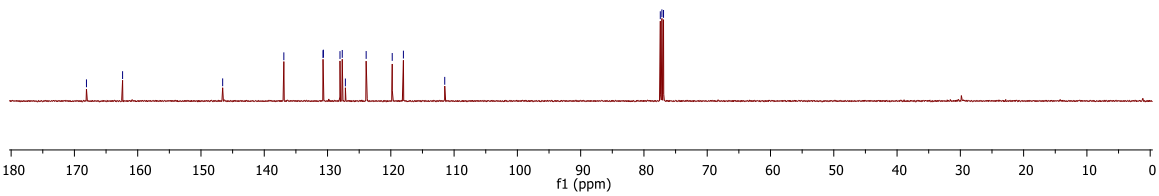

10.24
8.08
8.07
8.06
8.06
7.51
7.49
7.48
7.45
7.44
7.31
7.27
7.22
7.19
7.00
6.98
6.94
6.93
6.91

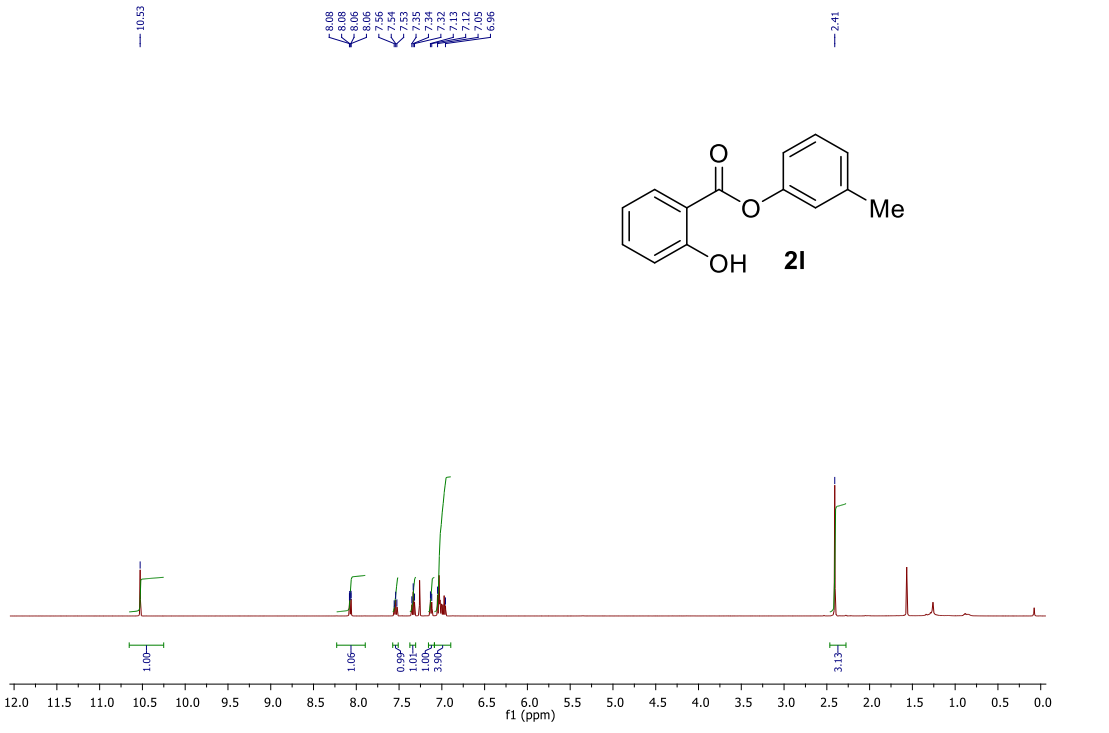

O
O
Cl
OH

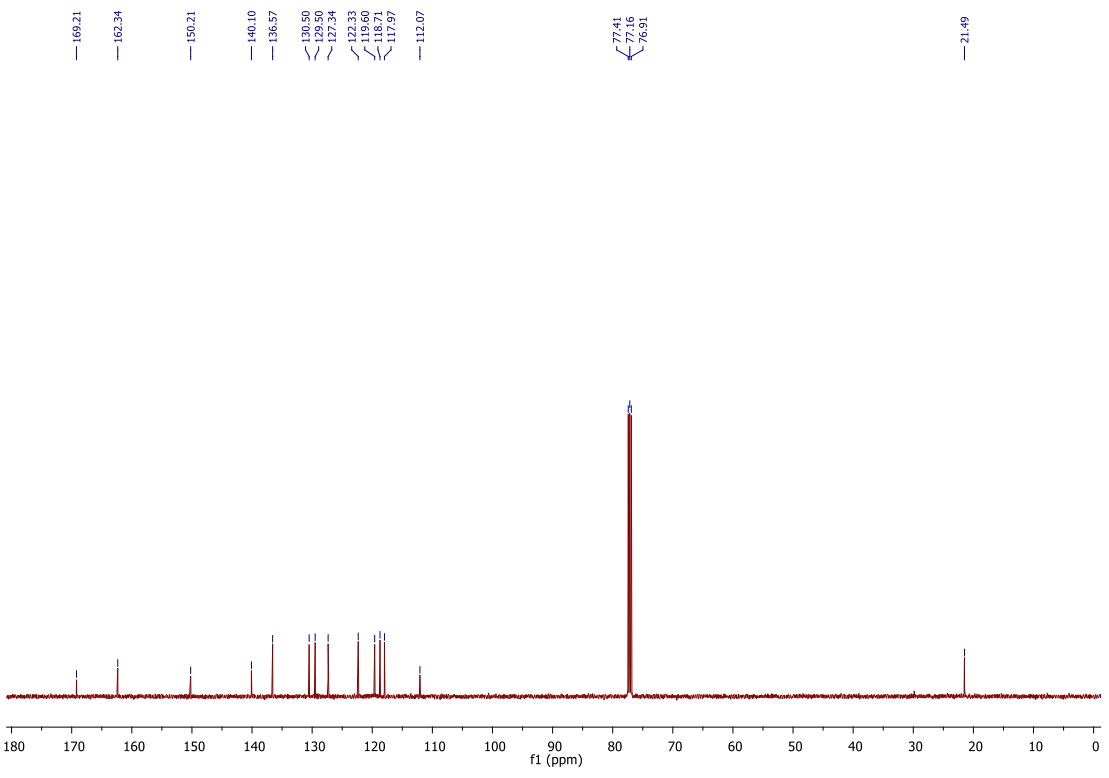
2k


1.00
1.04
1.10
1.19
1.20
2.29
1.00
1.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

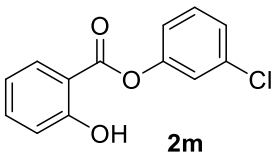

168.10
162.39
146.57
136.90
130.71
130.66
128.03
127.67
127.18
123.90
119.78
118.01
111.48
77.41
77.16
76.91


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

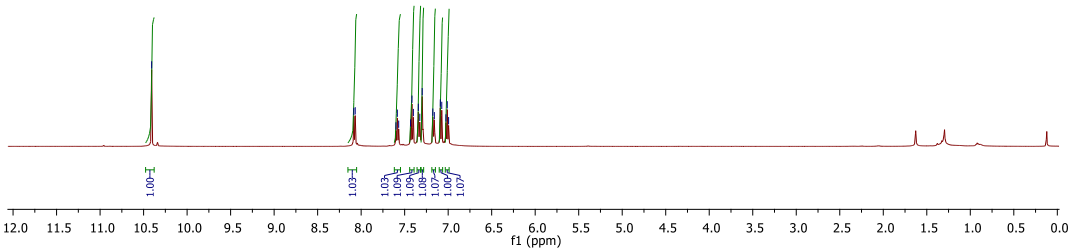

10.53
8.08
8.08
8.06
8.06
7.56
7.54
7.53
7.35
7.34
7.32
7.13
7.12
7.05
6.96
2.41
O
O
Me
OH
2l
1.00
1.06
0.99
1.01
1.06
3.90
3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.21
162.34
150.21
140.10
136.57
130.50
129.50
127.34
122.33
119.60
118.71
117.97
112.07
77.41
77.16
76.91
21.49
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

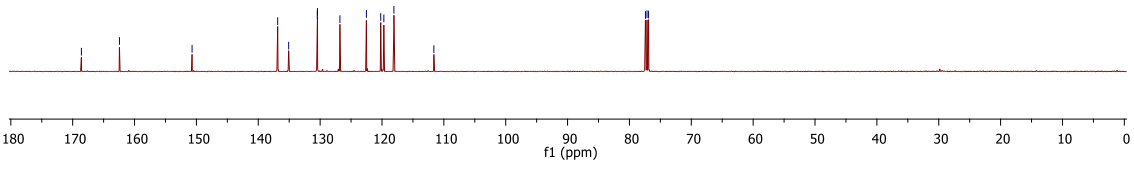

10.41
8.08
8.07
7.60
7.58
7.57
7.43
7.42
7.40
7.34
7.33
7.30
7.18
7.16
7.09
7.07
7.03
7.01
7.00


O
O
Cl
OH

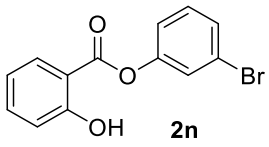
2m


1.00
1.03
1.03
1.09
1.09
1.08
1.07
1.00
1.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

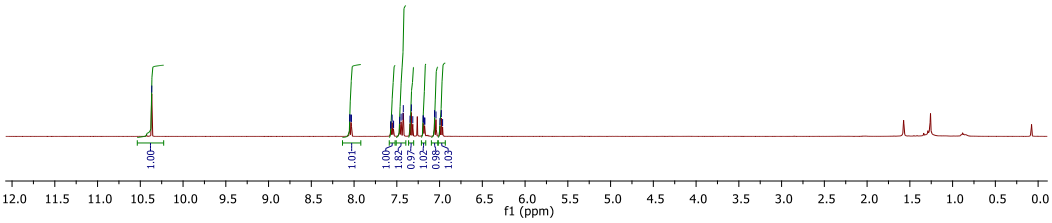

168.59
162.44
150.70
136.86
135.08
130.46
130.43
126.80
122.52
120.20
119.70
118.07
111.61
77.41
77.16
76.91


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

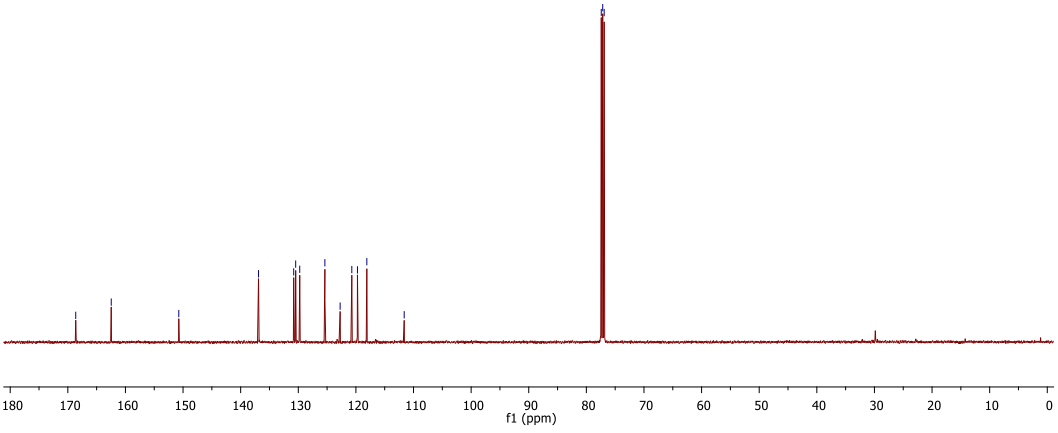

10.37
8.05
8.05
8.03
8.03
7.57
7.57
7.55
7.54
7.54
7.47
7.45
7.43
7.42
7.35
7.33
7.31
7.19
7.19
7.18
7.17
7.06
7.04
7.00
6.98
6.96

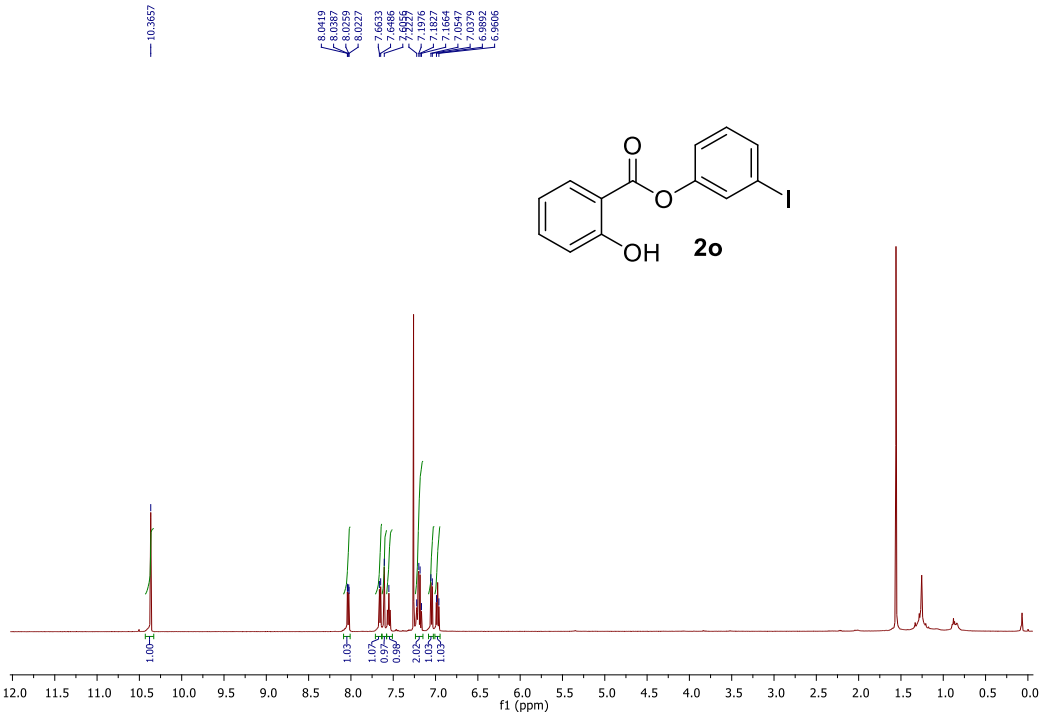

O
O
Br
OH

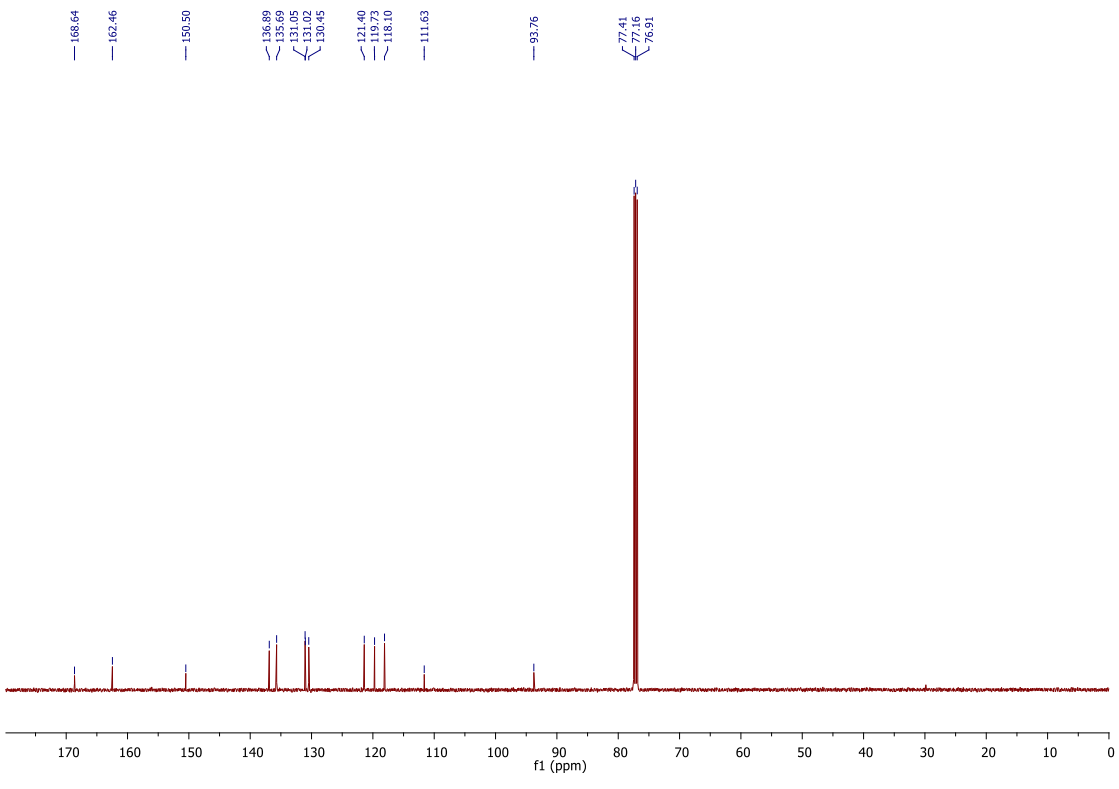
2n


1.00
1.01
1.00
1.82
0.97
1.02
0.98
1.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

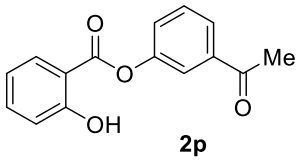

168.63
162.46
150.74
136.90
130.80
130.45
129.75
125.38
122.73
120.71
119.73
118.10
111.62
77.41
77.16
76.91


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

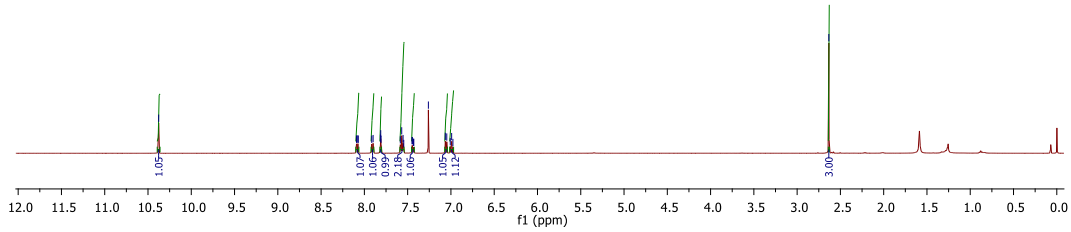

10.3657
8.0419
8.0387
8.0259
8.0227
7.6633
7.6486
7.6055
7.5907
7.2227
7.1976
7.1827
7.1664
7.0547
7.0379
6.9892
6.9606
O
O
I
OH
2o
1.00
1.03
1.07
0.97
0.98
2.02
1.03
1.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

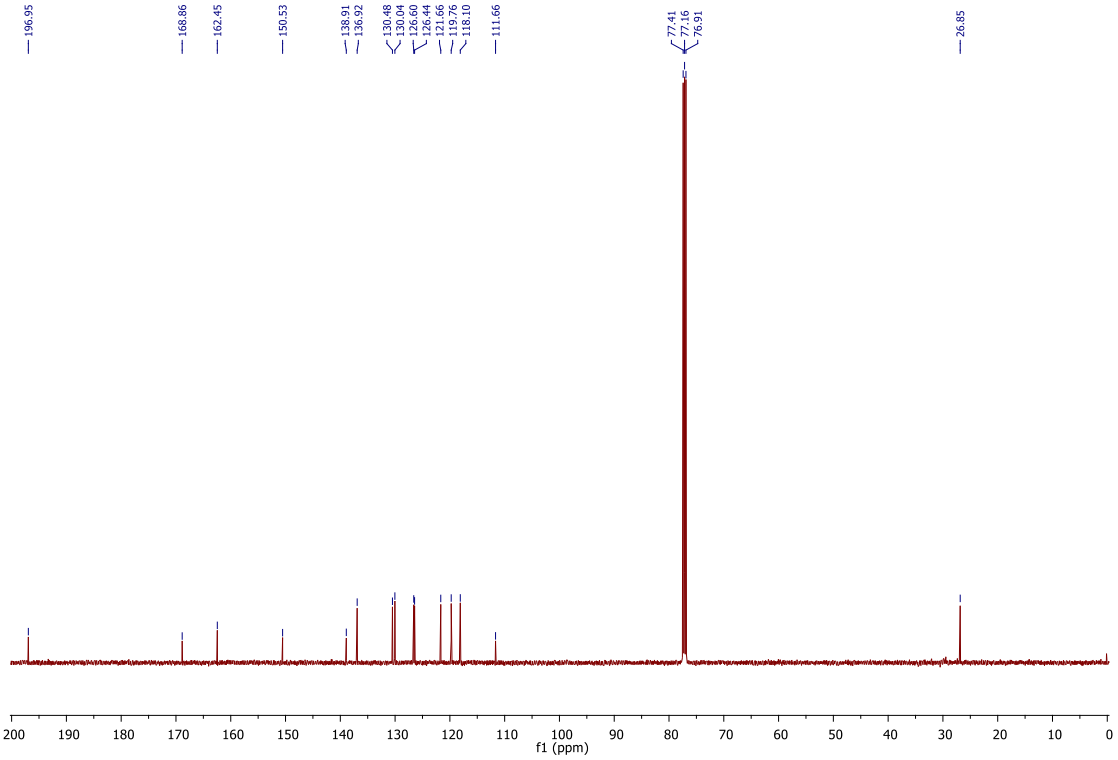

168.64
162.46
150.50
136.89
135.69
131.05
131.02
130.45
121.40
119.73
118.10
111.63
93.76
77.41
77.16
76.91
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

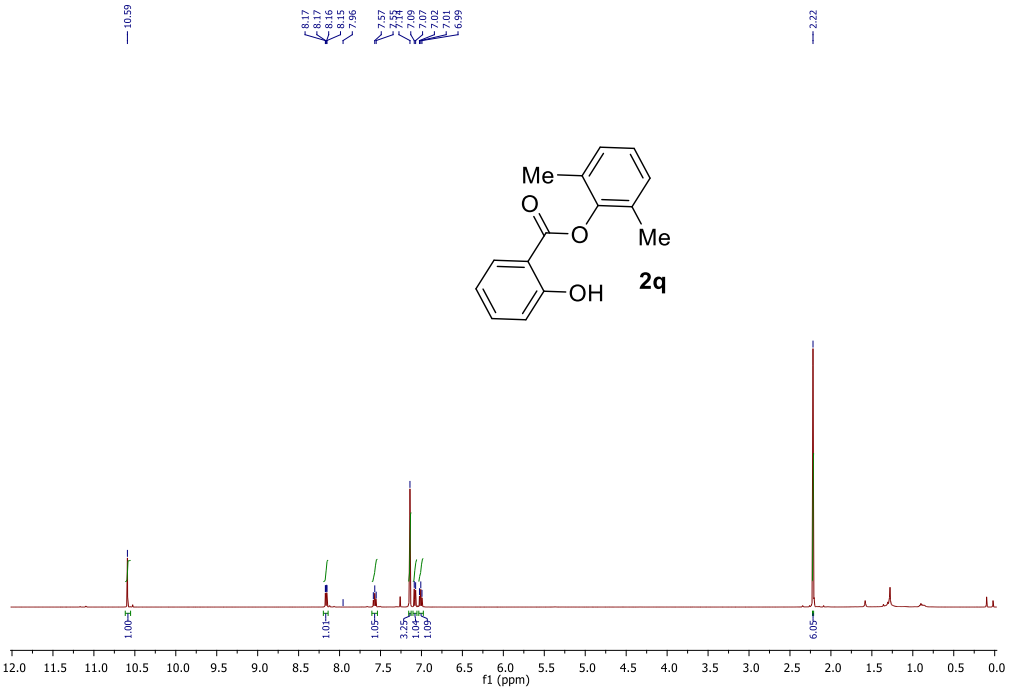

10.3769
8.0906
8.0874
8.0746
8.0714
7.9147
7.8992
7.8148
7.8111
7.8074
7.5846
7.5686
7.5529
7.5490
7.4494
7.4451
7.4334
7.4289
7.2604
7.0647
7.0480
7.0076
6.9917
6.9771
2.6338

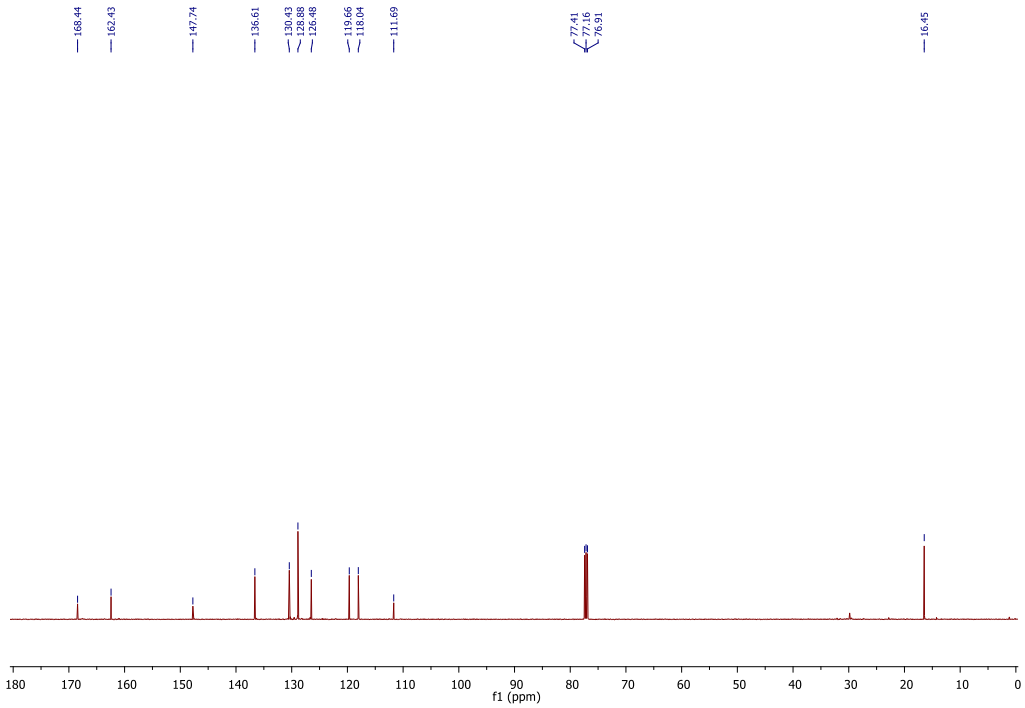

O
O
Me
O
OH

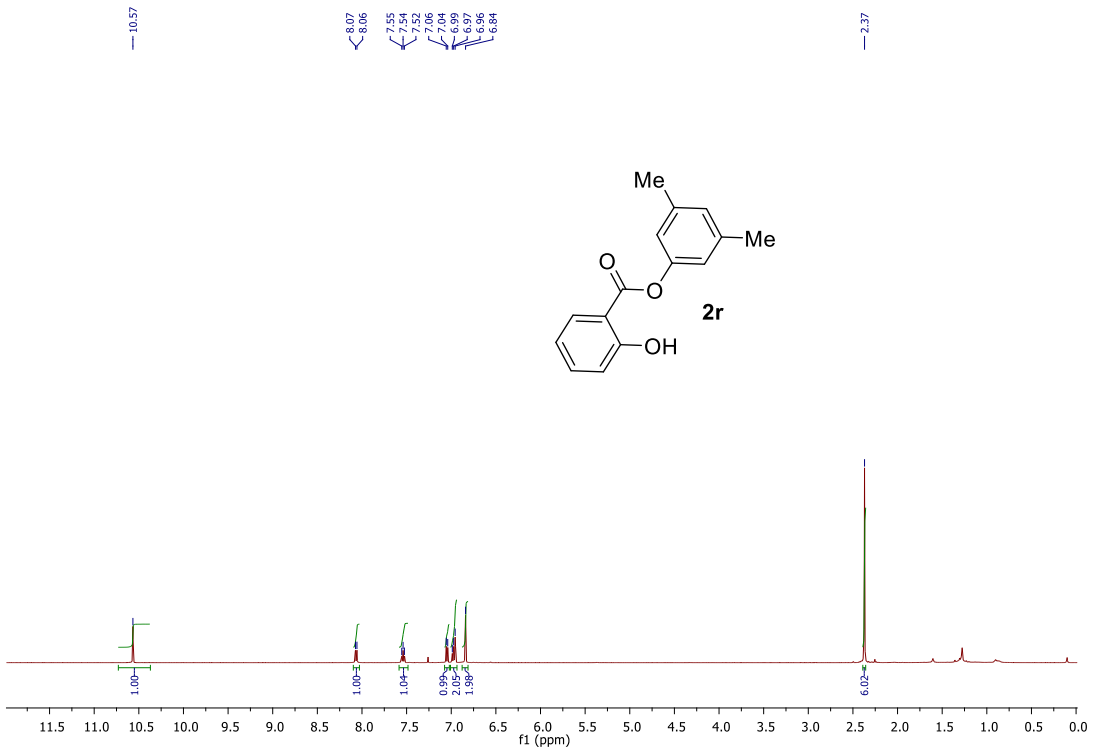
2p

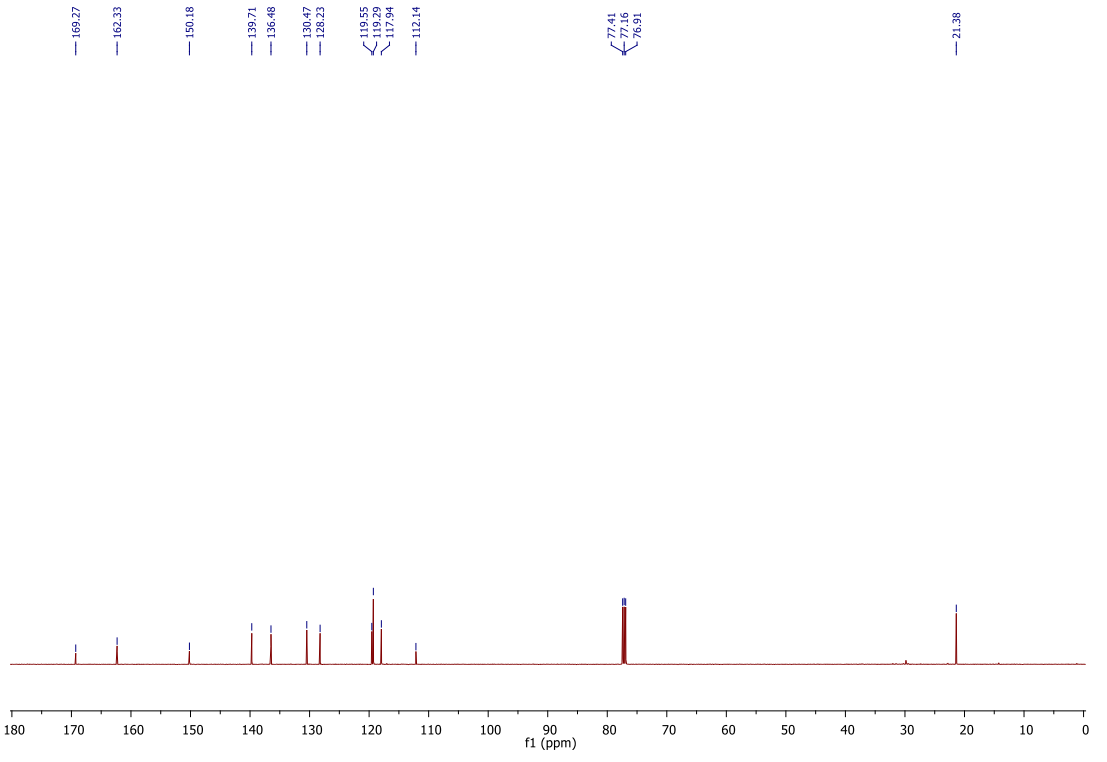

1.05
1.07
1.06
0.99
2.18
1.06
1.05
1.12
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.95
168.86
162.45
150.53
138.91
136.92
130.48
130.04
126.60
126.44
121.66
119.76
118.10
111.66
77.41
77.16
76.91
26.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.59
8.17
8.17
8.16
8.15
7.96
7.57
7.55
7.14
7.09
7.07
7.03
7.01
6.99
2.22
Me
O
O
Me
OH
2q
1.00
1.01
1.05
3.25
1.04
1.09
6.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.44
162.43
147.74
136.61
130.43
128.88
126.48
119.66
118.04
111.69
77.41
77.16
76.91
16.45
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.57
8.07
8.06
7.55
7.54
7.52
7.06
7.04
6.99
6.97
6.96
6.84
2.37
Me
Me
O
O
OH
2r
1.00
1.00
1.04
0.99
2.05
1.98
6.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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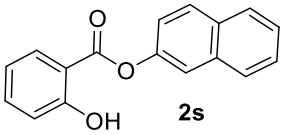
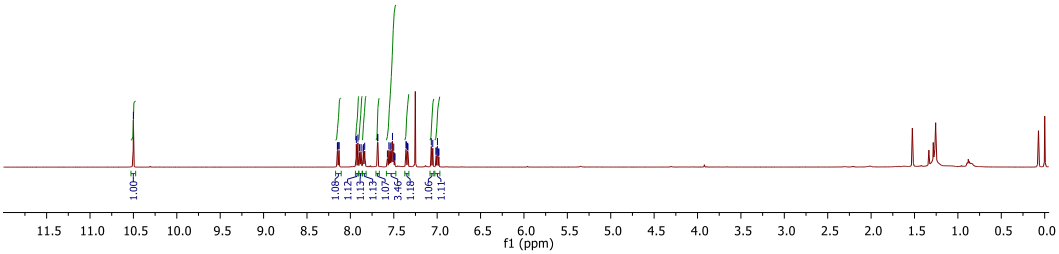
162.33
150.18
139.71
136.48
130.47
128.23
119.55
119.29
117.94
112.14
77.41
77.16
76.91
21.38
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

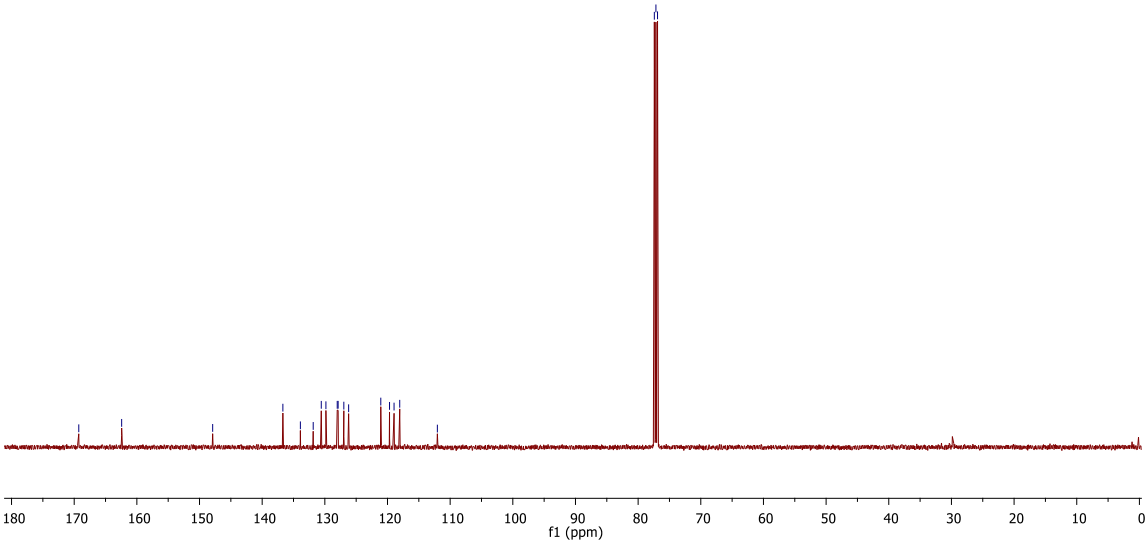

10.50
8.15
8.15
8.13
8.13
7.93
7.91
7.89
7.88
7.85
7.85
7.84
7.69
7.68
7.57
7.56
7.54
7.53
7.51
7.50
7.49
7.49
7.36
7.35
7.34
7.34
7.07
7.05
7.01
7.01
7.00
6.98
6.98


O
O
OH

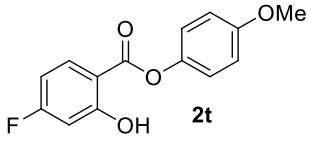
2s


1.00
1.08
1.12
1.13
1.13
1.07
3.46
1.18
1.06
1.11
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

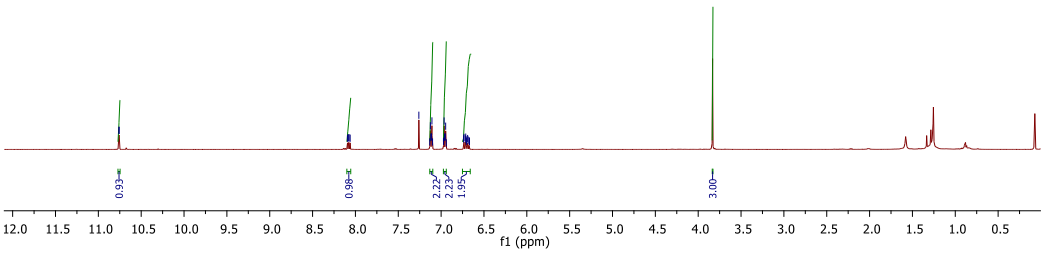

169.27
162.43
147.90
136.70
133.90
131.86
130.57
129.83
128.02
127.88
126.97
126.20
121.07
119.68
118.95
118.05
112.04
77.41
77.16
76.91


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

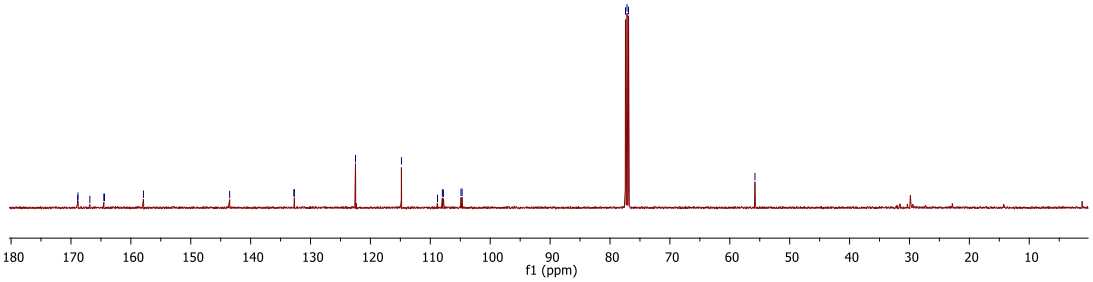

10.7603
10.7573
8.0921
8.0790
8.0744
8.0613
7.2598
7.1326
7.1252
7.1208
7.1117
7.1071
7.0999
6.9723
6.9650
6.9605
6.9512
6.9466
6.9395
6.7380
6.7331
6.7175
6.7126
6.7077
6.7026
6.6985
6.6944
6.6737
6.6688

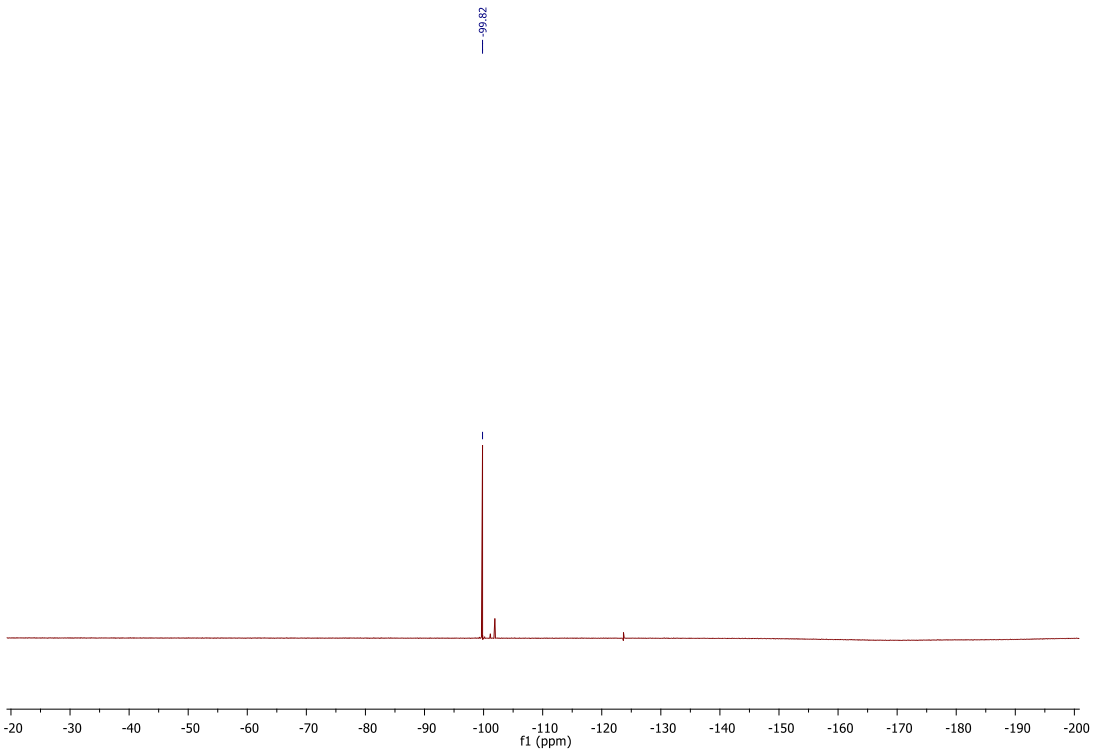

OMe
O
O
F
OH

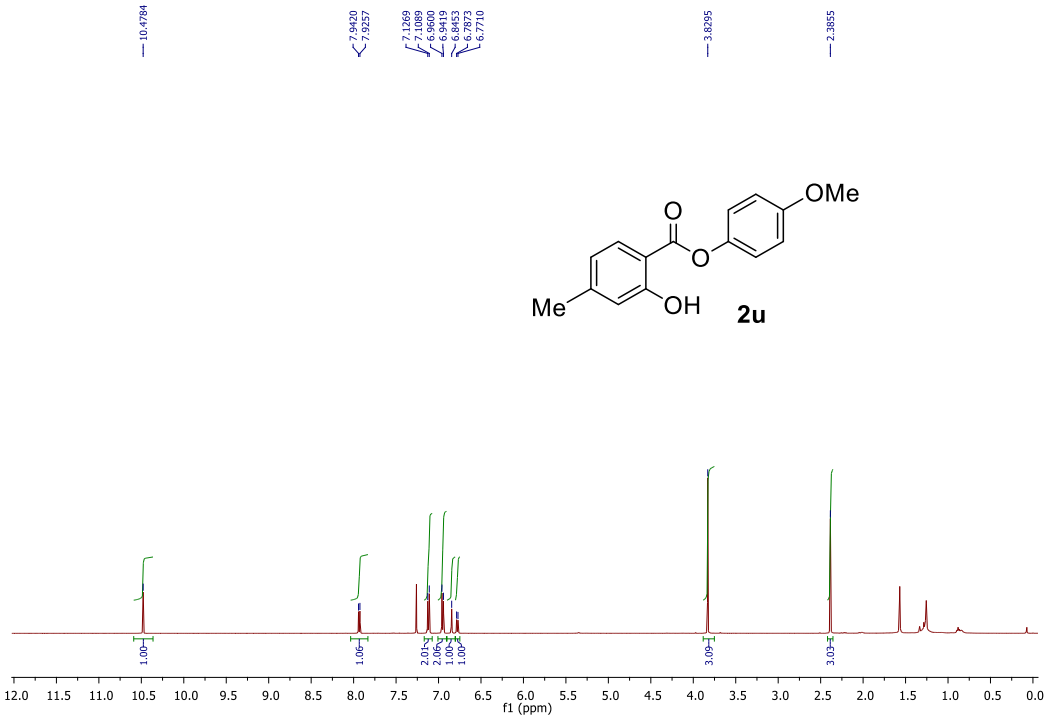
2t

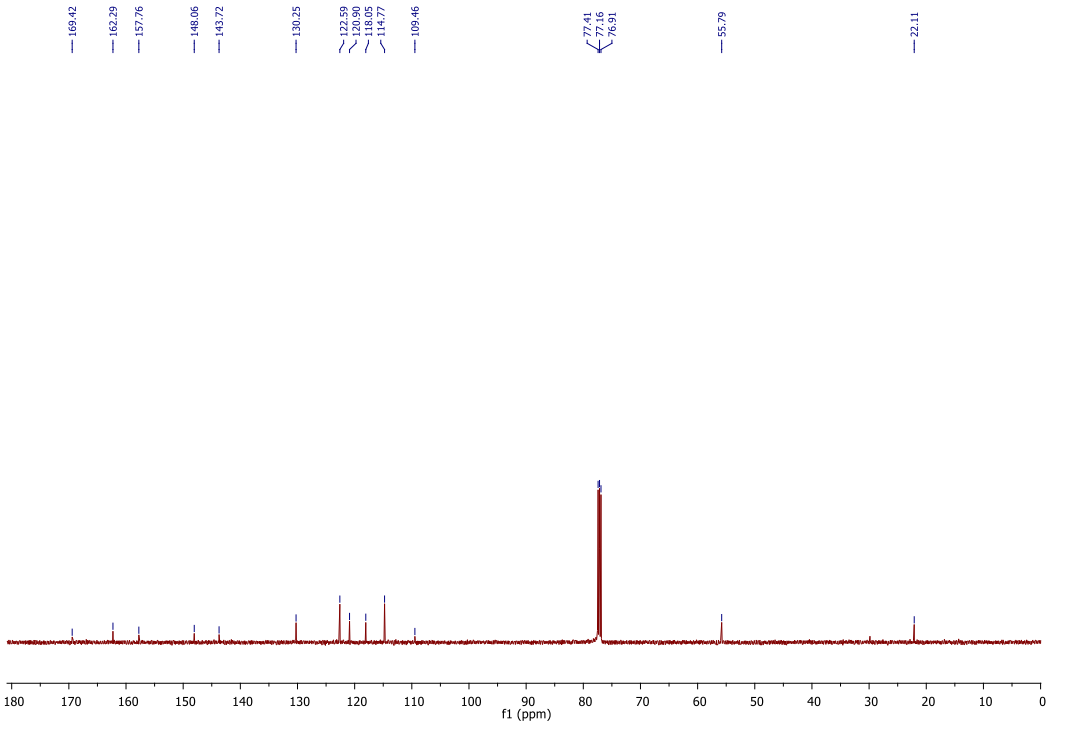

0.93
0.98
2.22
2.23
1.95
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

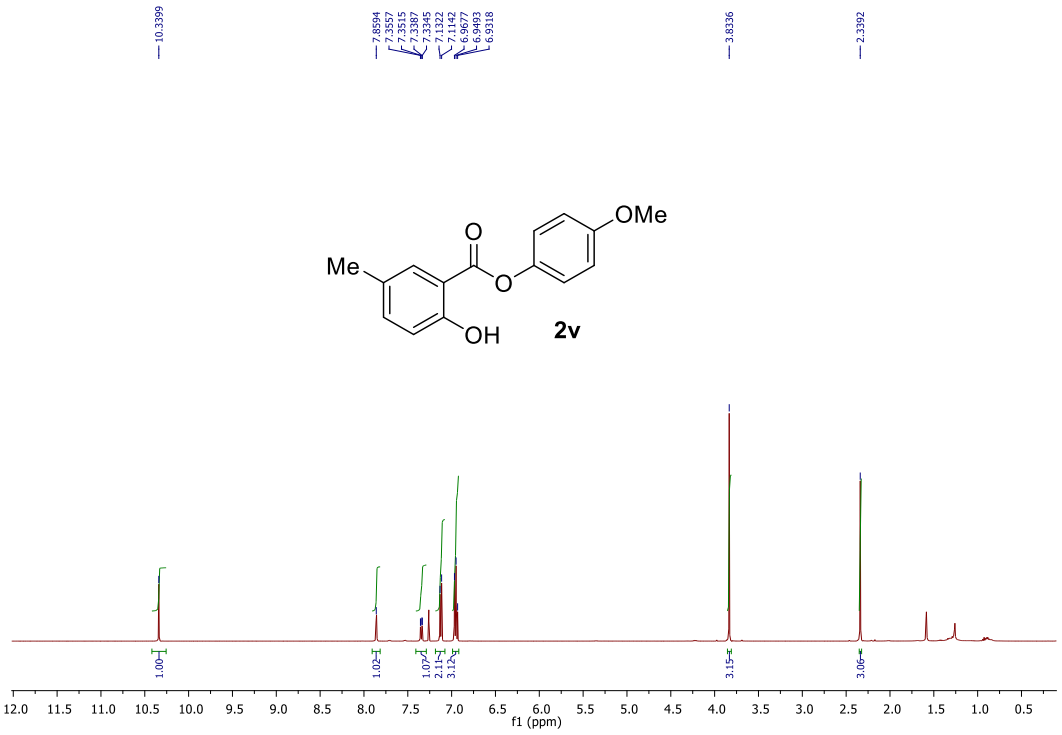

168.8773
168.8049
168.8421
164.5098
164.3955
157.8996
143.4988
132.7868
132.6953
122.4932
114.8241
108.8047
107.9912
107.8098
104.8812
104.6884
77.4137
77.1597
76.9058
55.7981

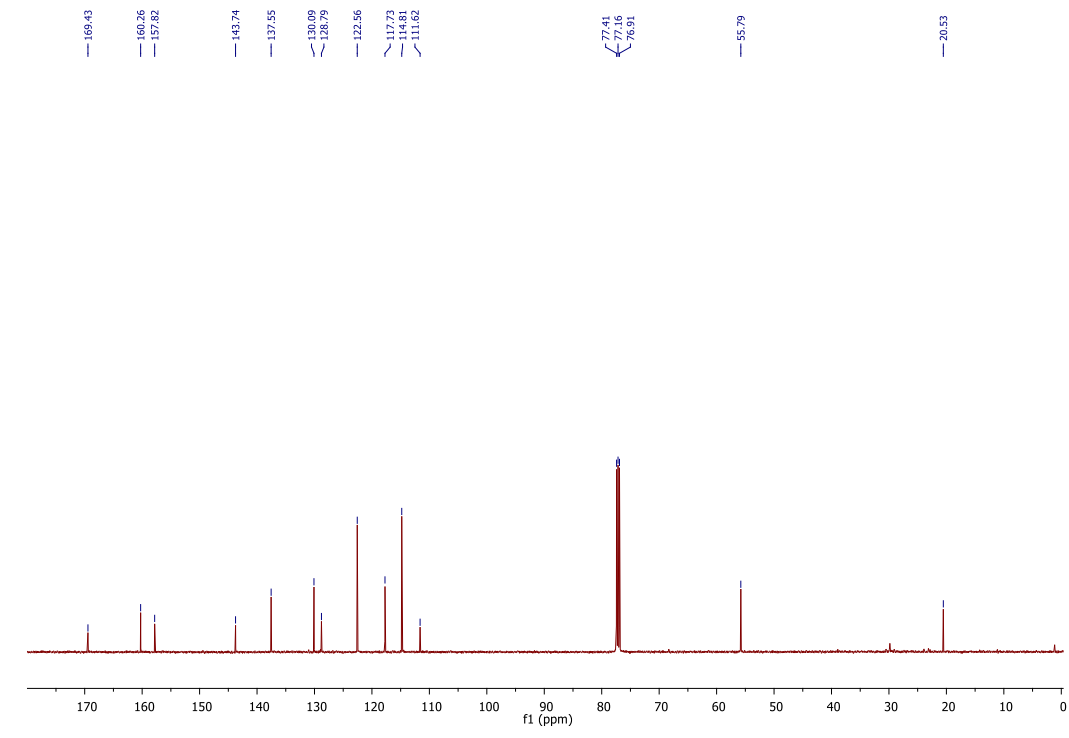

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

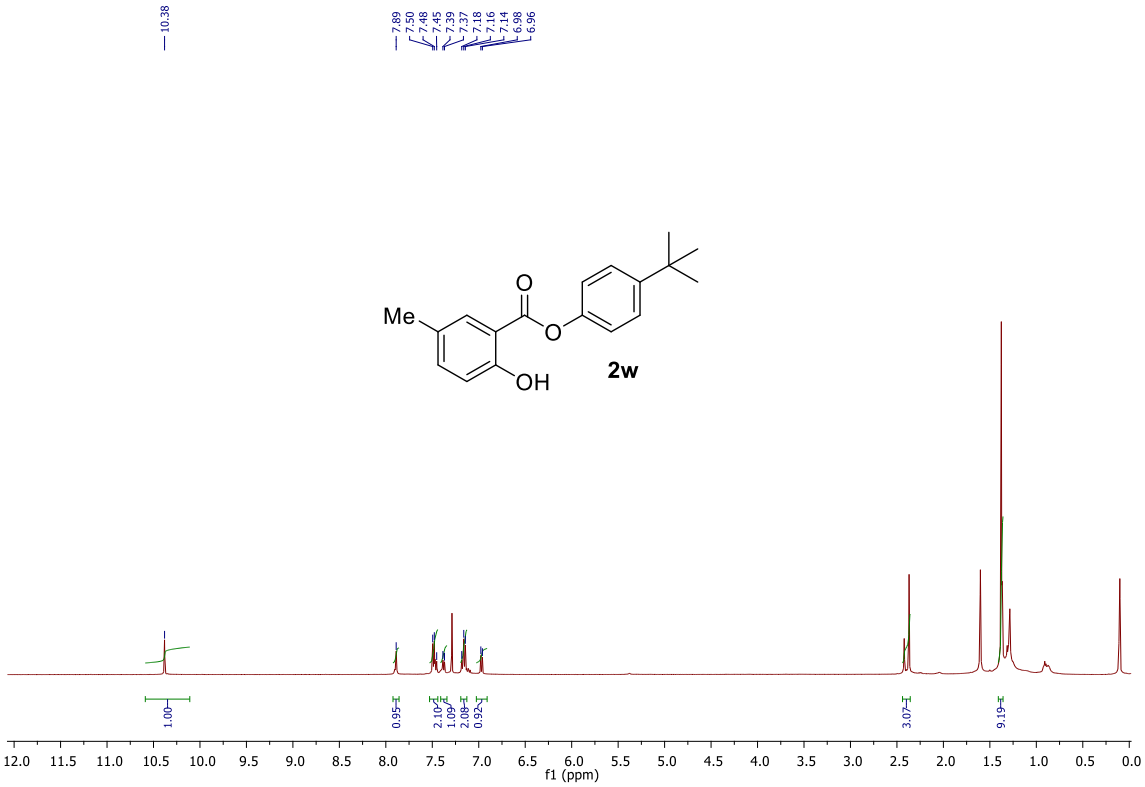

-99.82
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

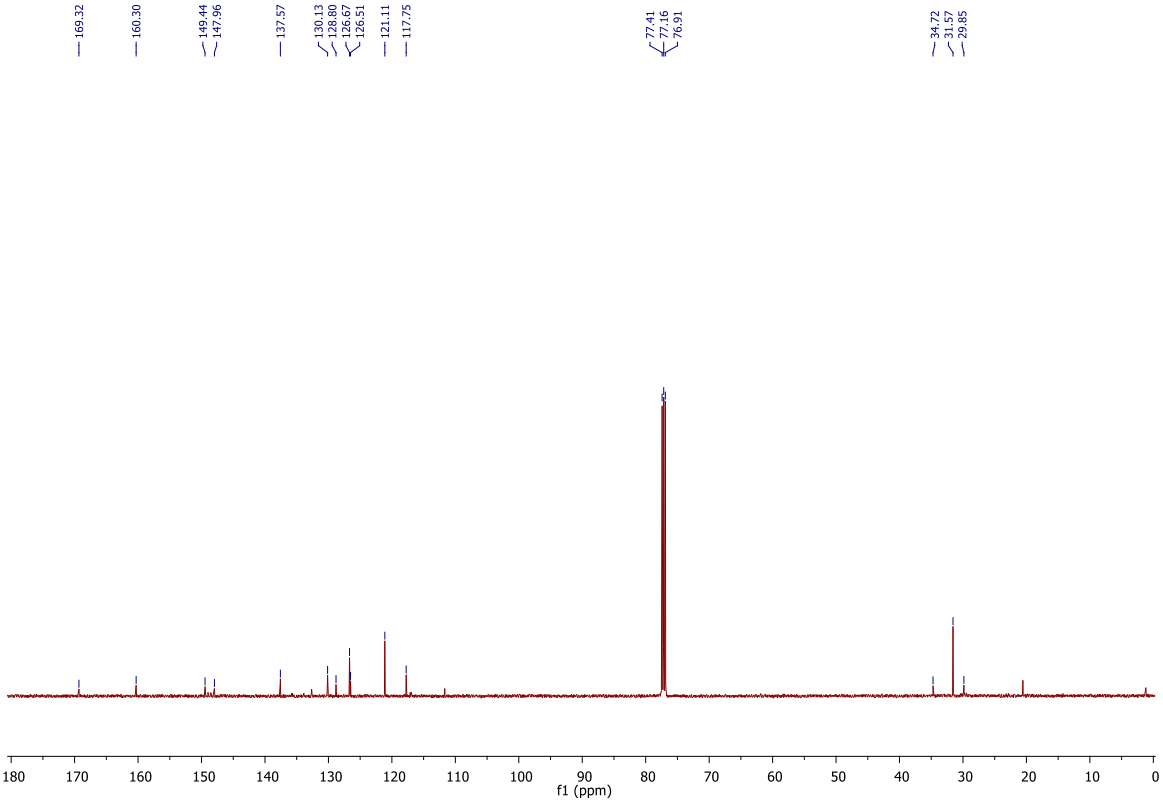

10.4784
7.9420
7.9257
7.1269
7.1089
6.9600
6.9419
6.8453
6.7873
6.7710
3.8295
2.3855
OMe
O
O
Me
OH
2u
1.00
1.06
2.01
2.06
1.08
1.08
3.09
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

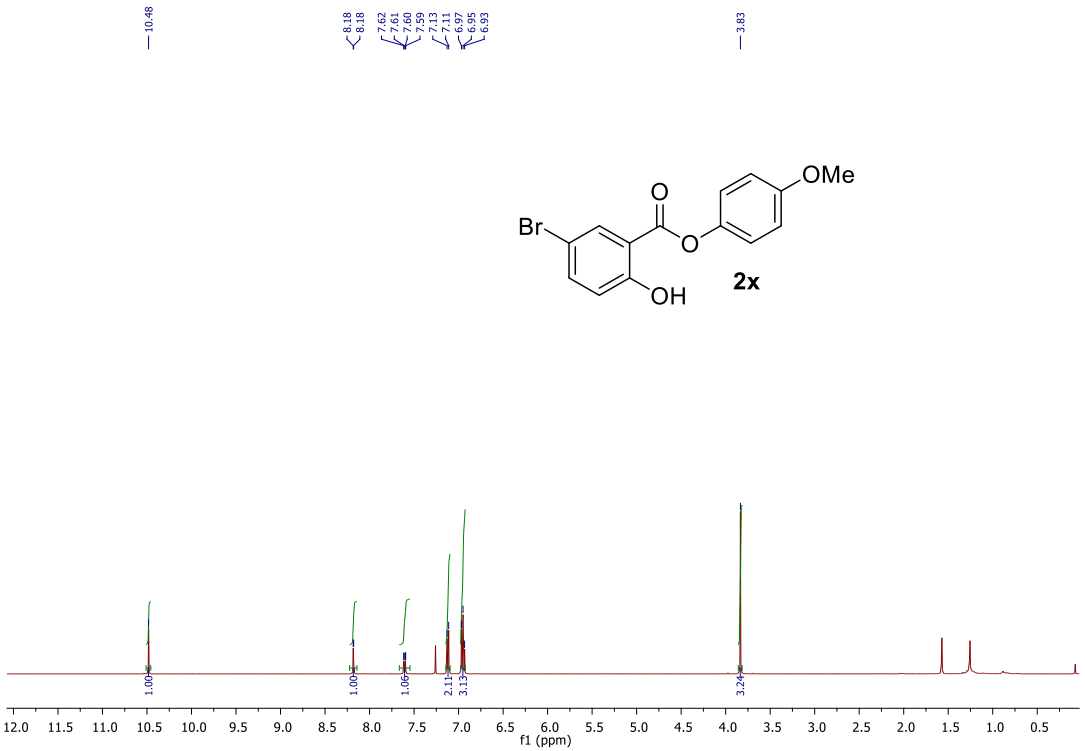

169.42
162.29
157.76
148.06
143.72
130.25
122.59
120.90
118.05
114.77
109.46
77.41
77.16
76.91
55.79
22.11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

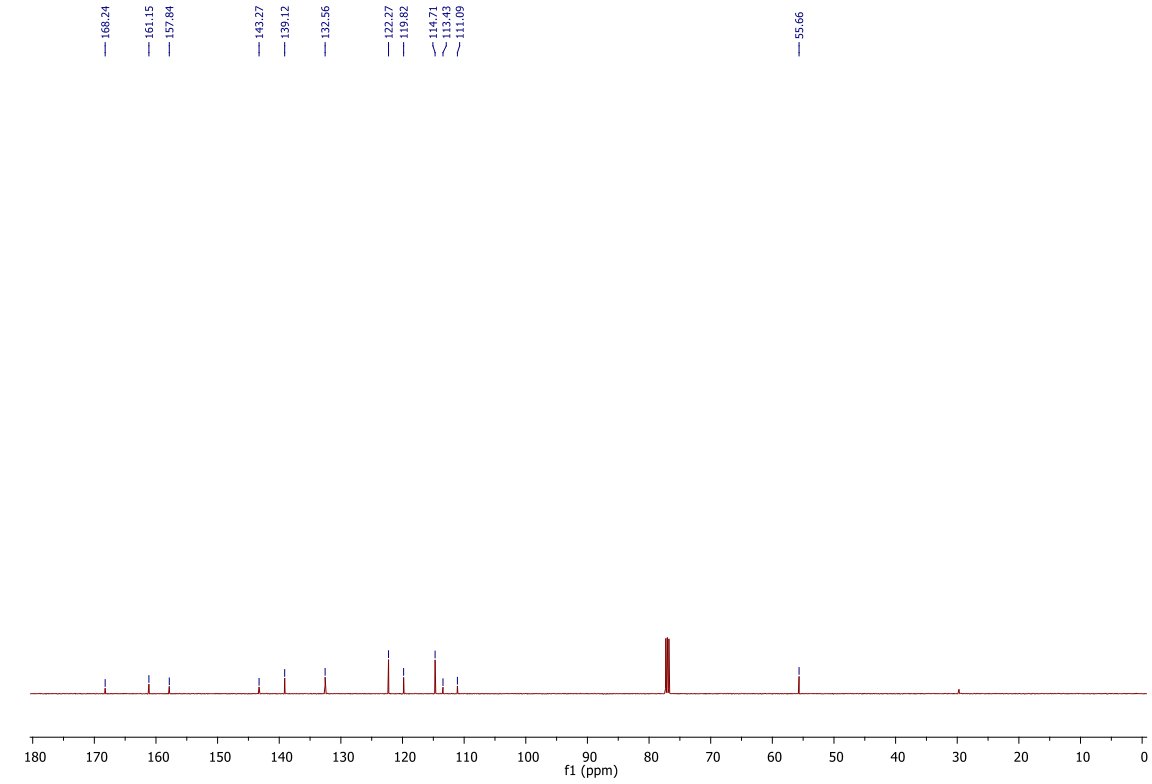

10.3399
7.8594
7.3557
7.3515
7.3387
7.3345
7.1322
7.1148
6.9677
6.9493
6.9318
3.8336
2.3392
OMe
O
Me
O
OH
2v
1.00
1.02
1.07
2.11
3.12
3.15
3.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

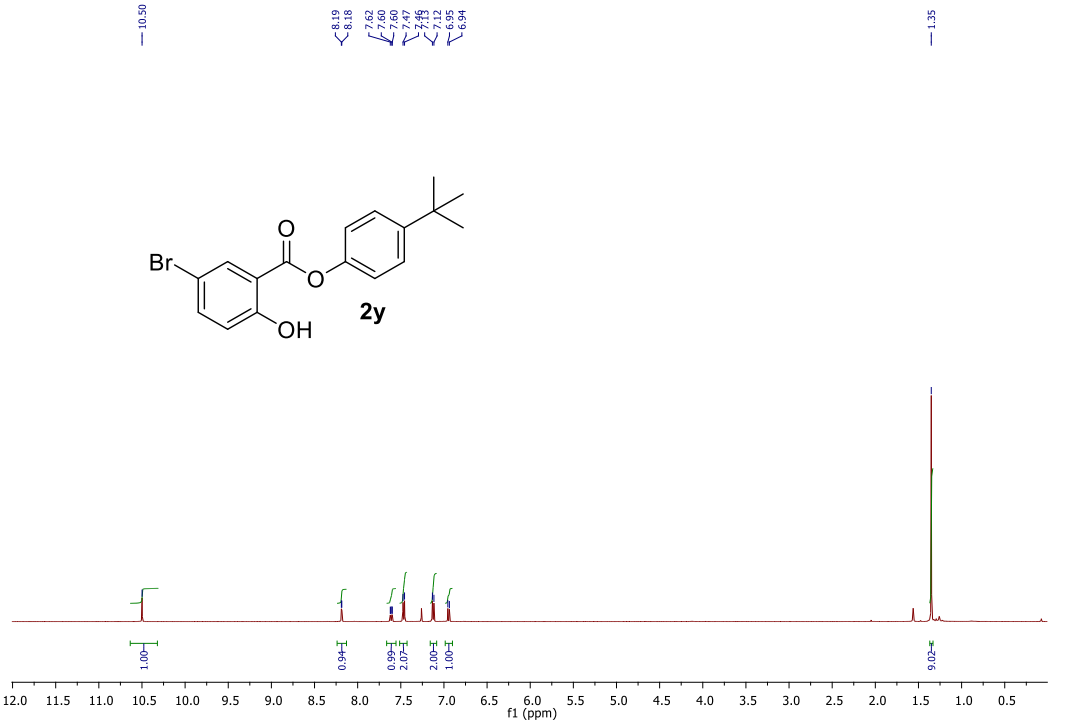

169.43
160.26
157.82
143.74
137.55
130.09
128.79
122.56
117.73
114.81
111.62
77.41
77.16
76.91
55.79
20.53
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

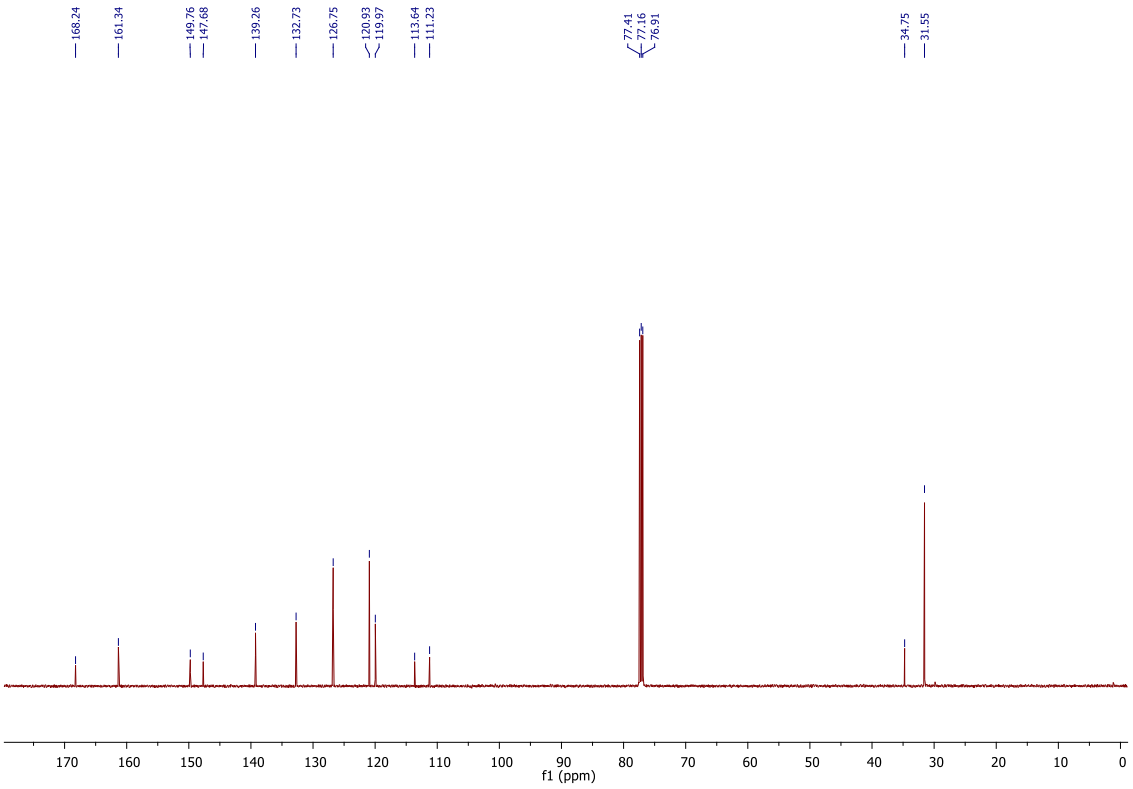

10.38
7.89
7.50
7.48
7.45
7.39
7.37
7.18
7.16
7.14
6.98
6.96
Me
O
O
OH
2w
1.00
0.95
2.10
1.09
2.08
0.92
3.07
9.19
f1 (ppm)

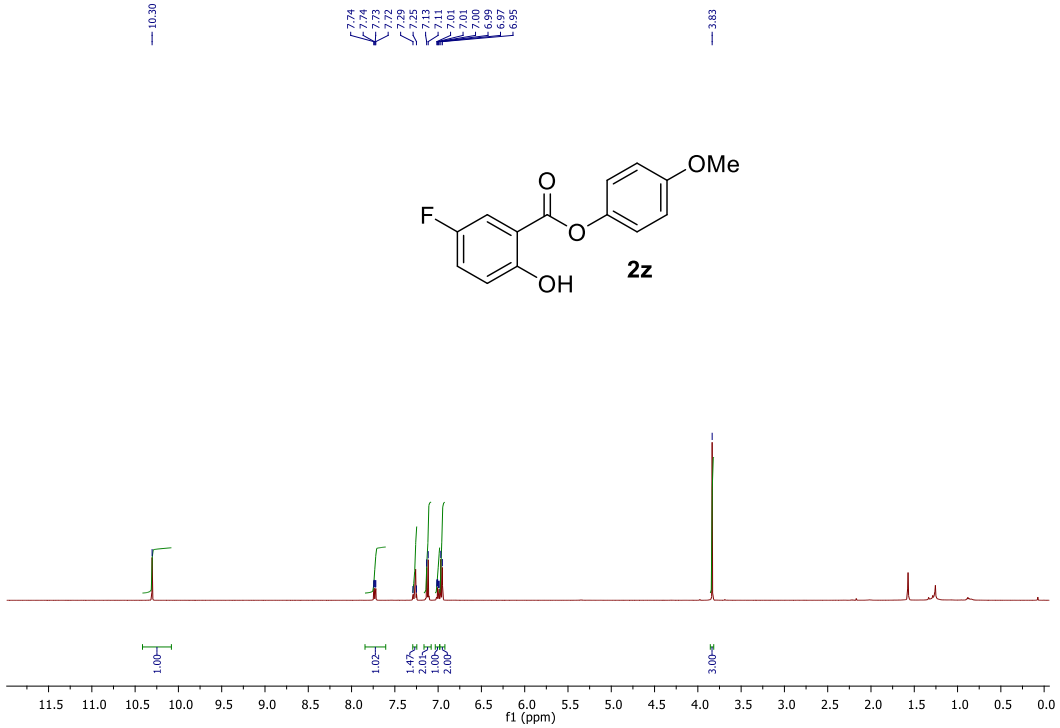

169.32
160.30
149.44
147.96
137.57
130.13
128.80
126.67
126.51
121.11
117.75
77.41
77.16
76.91
34.72
31.57
29.85
f1 (ppm)

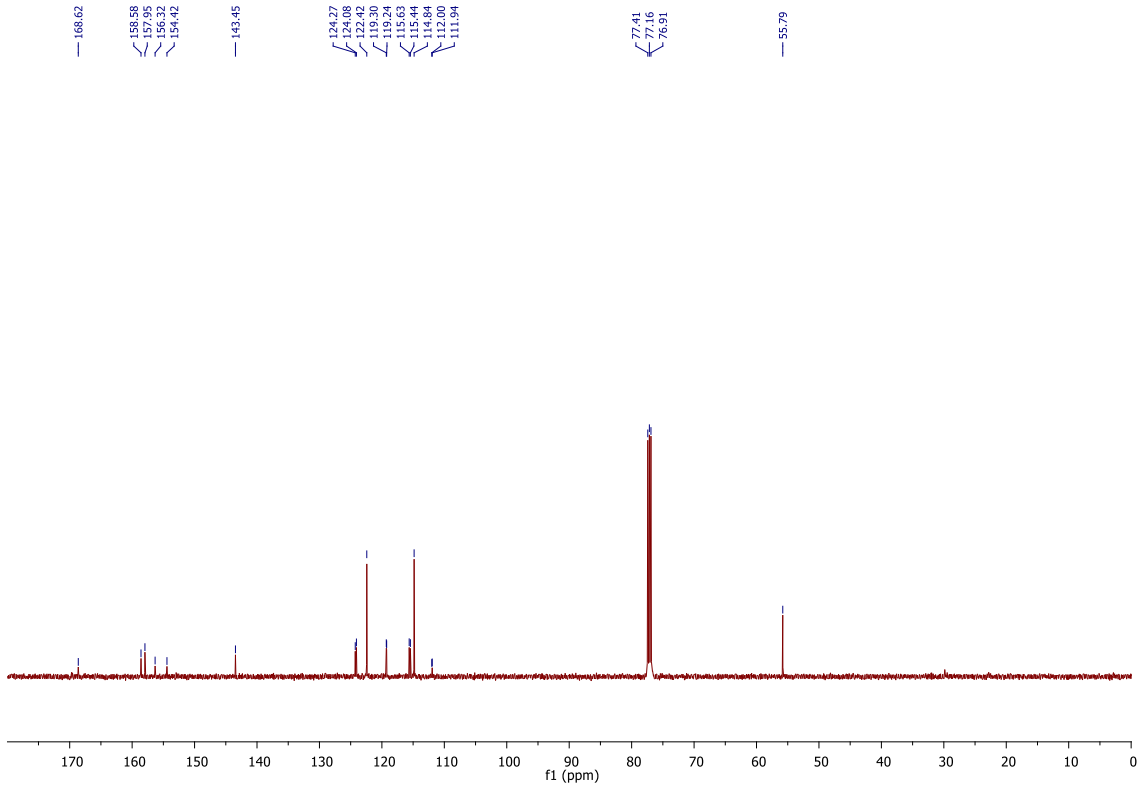

10.48
8.18
8.18
7.62
7.61
7.60
7.59
7.13
7.11
6.97
6.95
6.93
3.83
OMe
O
Br
O
OH
2x
1.00
1.00
1.06
2.11
3.13
3.24
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

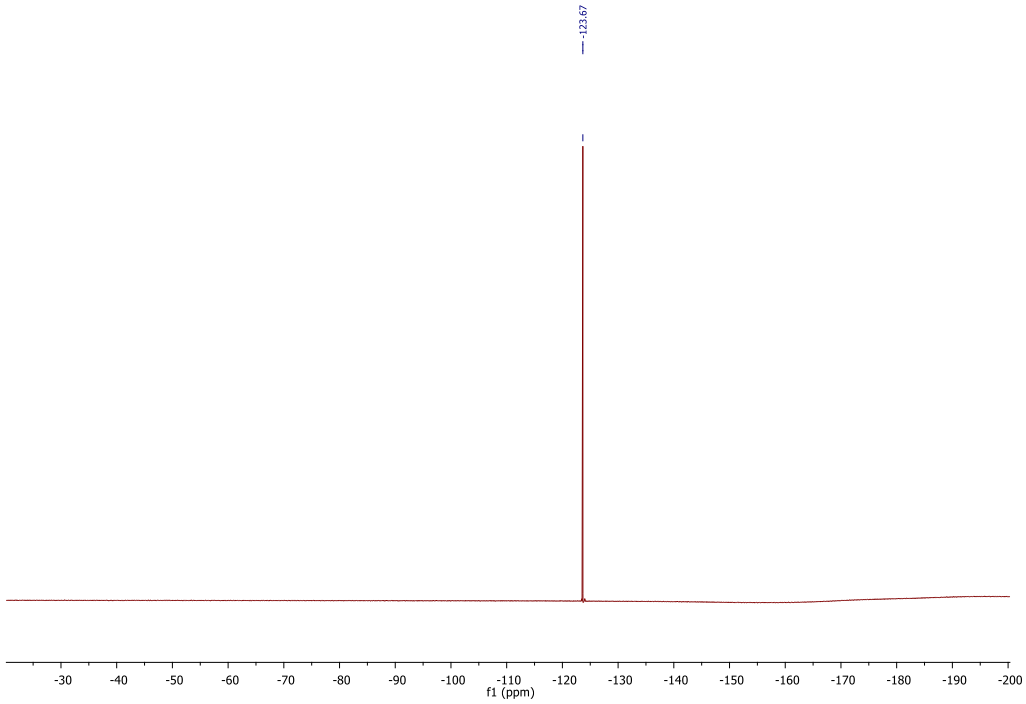

168.24
161.15
157.84
143.27
139.12
132.56
122.27
119.82
114.71
113.43
111.09
55.66
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

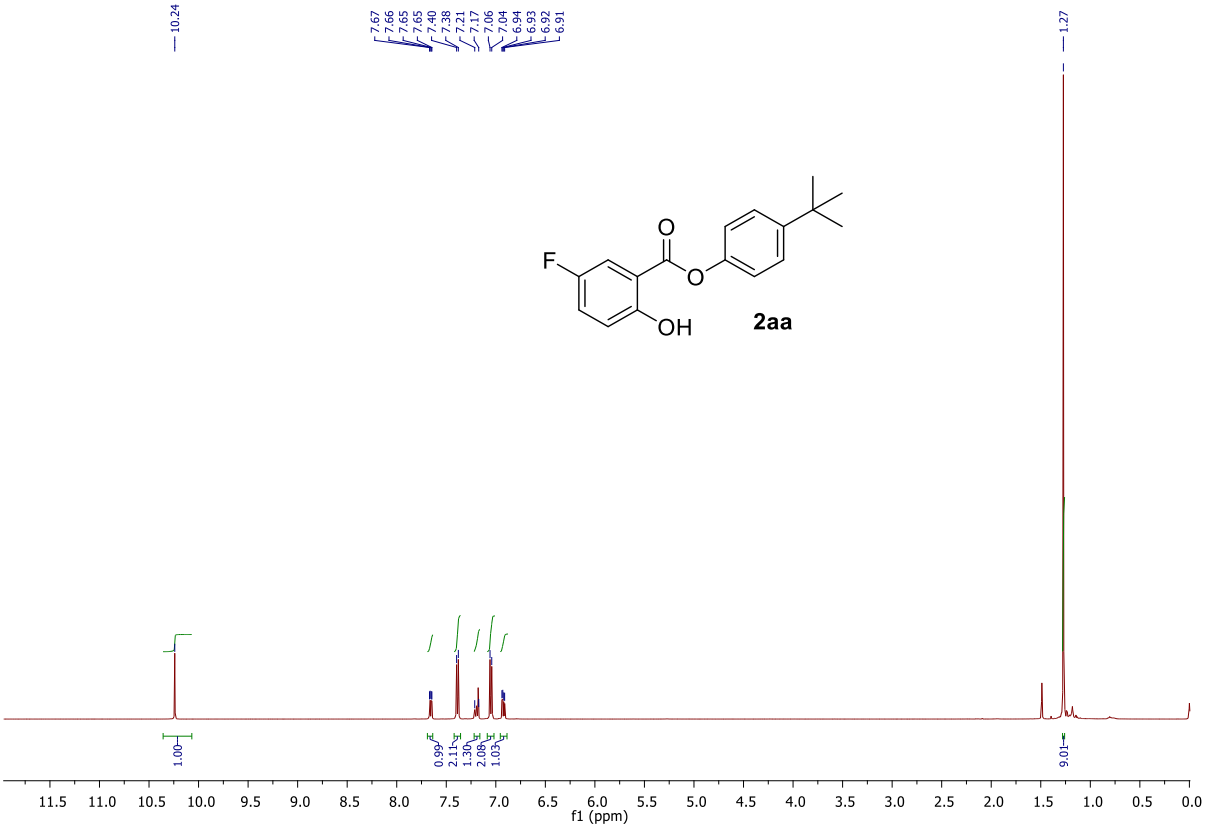

10.50
8.19
8.18
7.62
7.60
7.60
7.47
7.45
7.12
6.95
6.94
1.35
Br
O
O
OH
2y
1.00
0.94
0.99
2.07
2.00
1.00
9.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

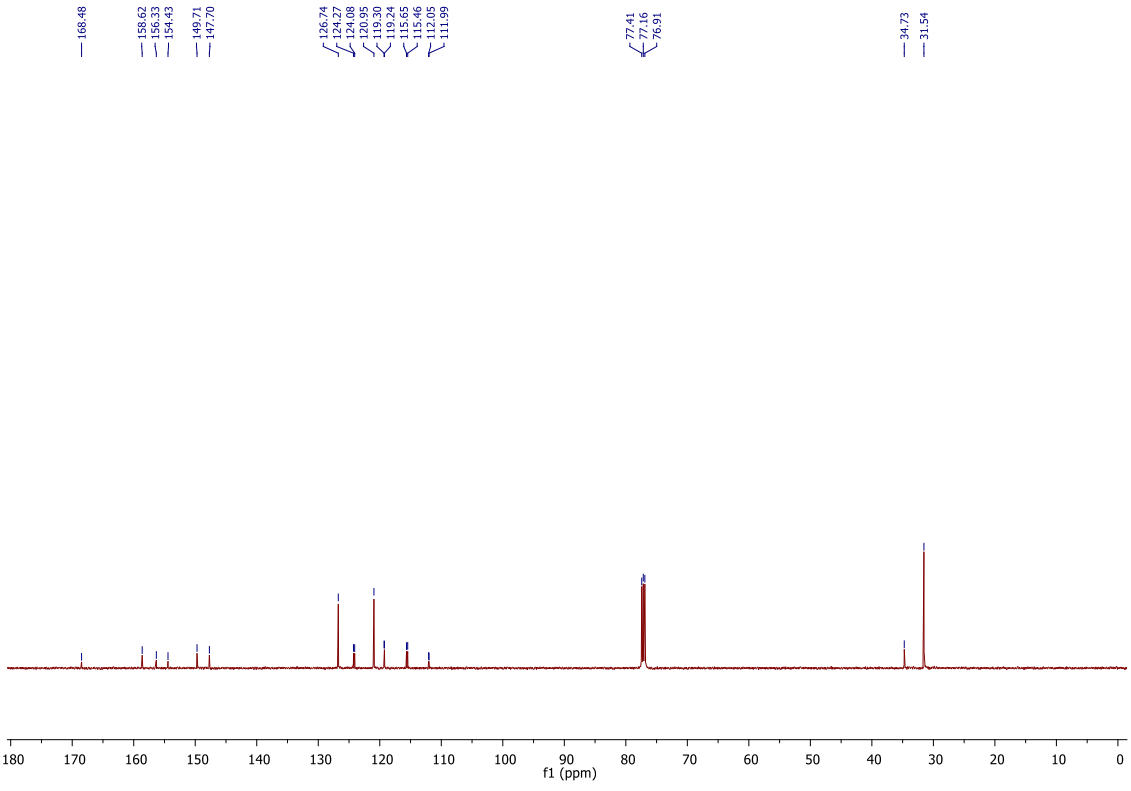

168.24
161.34
149.76
147.68
139.26
132.73
126.75
120.93
119.97
113.64
111.23
77.41
77.16
76.91
34.75
31.55
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

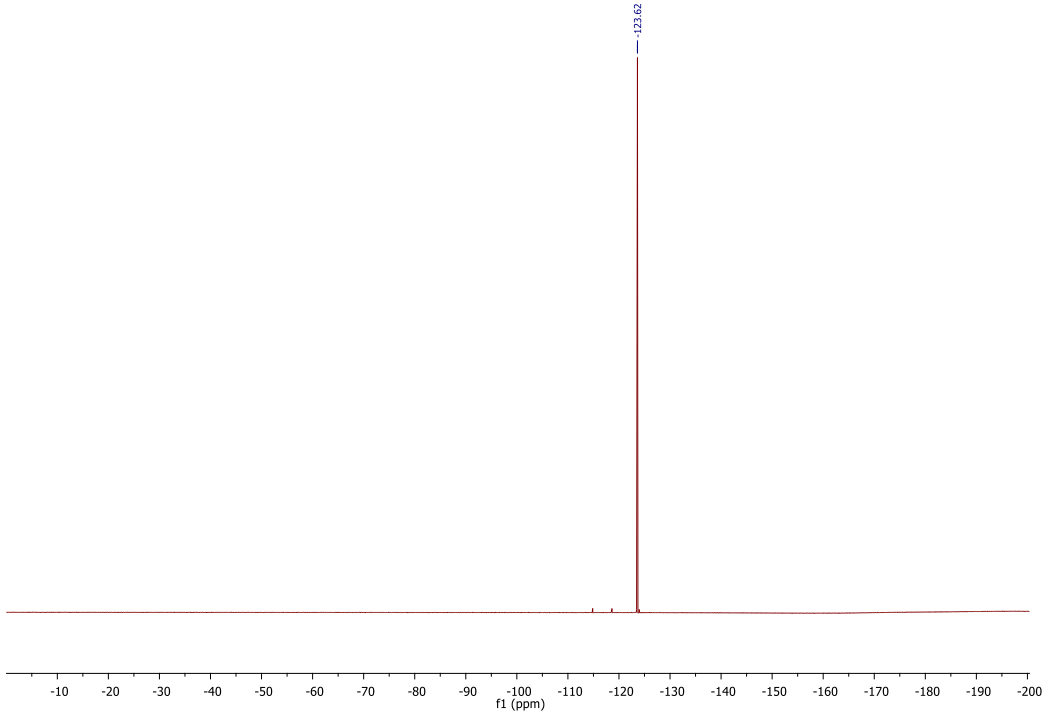

10.30
7.74
7.74
7.73
7.72
7.29
7.25
7.13
7.11
7.01
7.01
7.00
6.99
6.97
6.95
3.83
OMe
O
F
O
OH
2z
1.00
1.02
1.47
2.01
1.05
2.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.62
158.58
157.95
156.32
154.42
143.45
124.27
124.08
122.42
119.30
119.24
115.63
115.44
114.84
112.00
111.94
77.41
77.16
76.91
55.79
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-123.67
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


10.24
7.67
7.66
7.65
7.65
7.40
7.38
7.21
7.17
7.06
7.04
6.94
6.93
6.92
6.91
1.27
F
O
O
OH
2aa
1.00
0.99
2.11
1.30
2.08
1.03
9.01
f1 (ppm)


168.48
158.62
156.33
154.43
149.71
147.70
126.74
124.27
124.08
120.95
119.30
119.24
115.65
115.46
112.05
111.99
77.41
77.16
76.91
34.73
31.54
f1 (ppm)


-123.62
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
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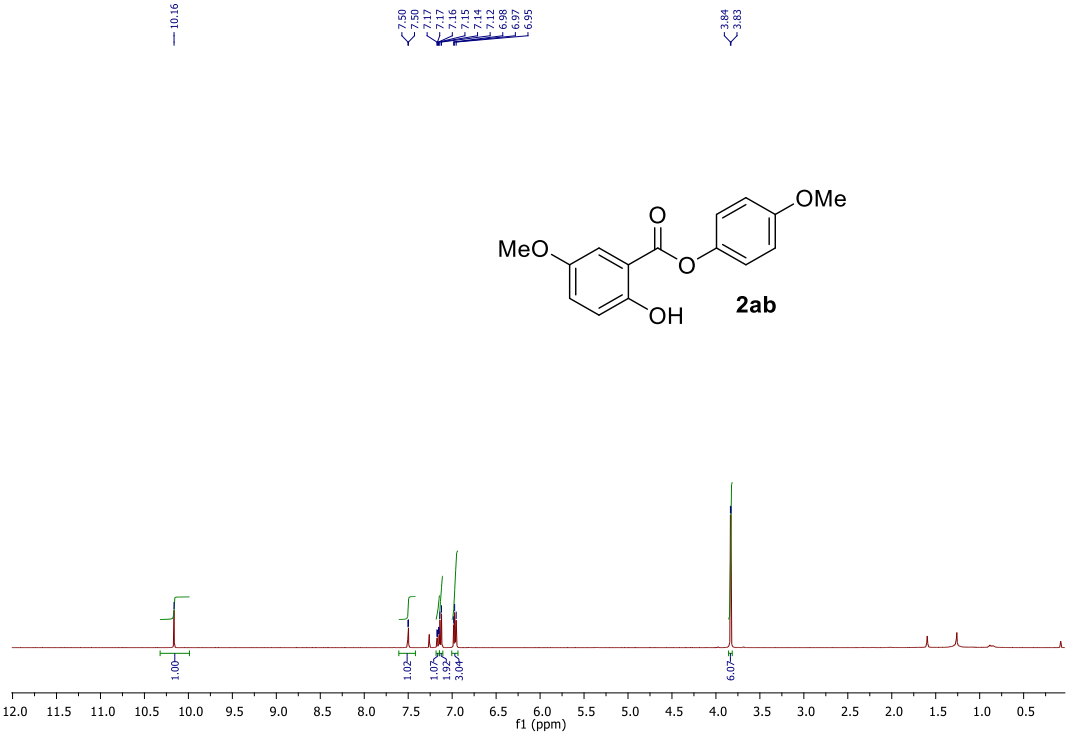
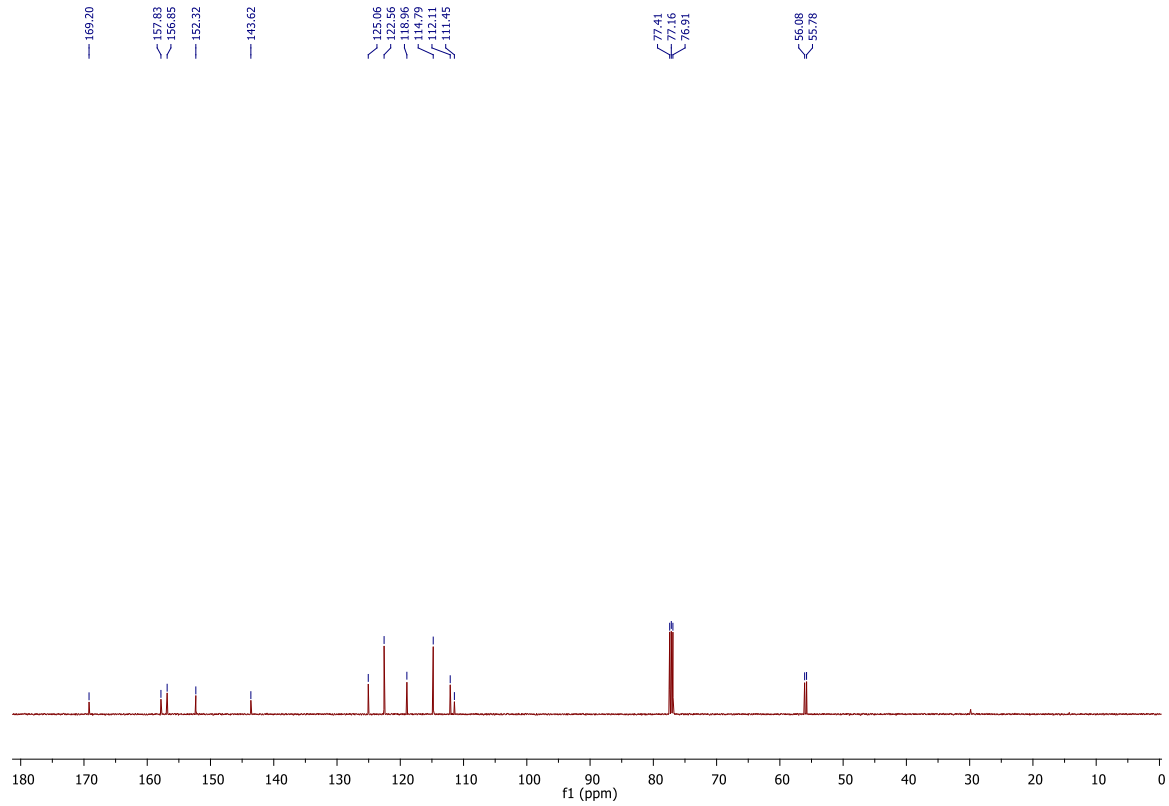
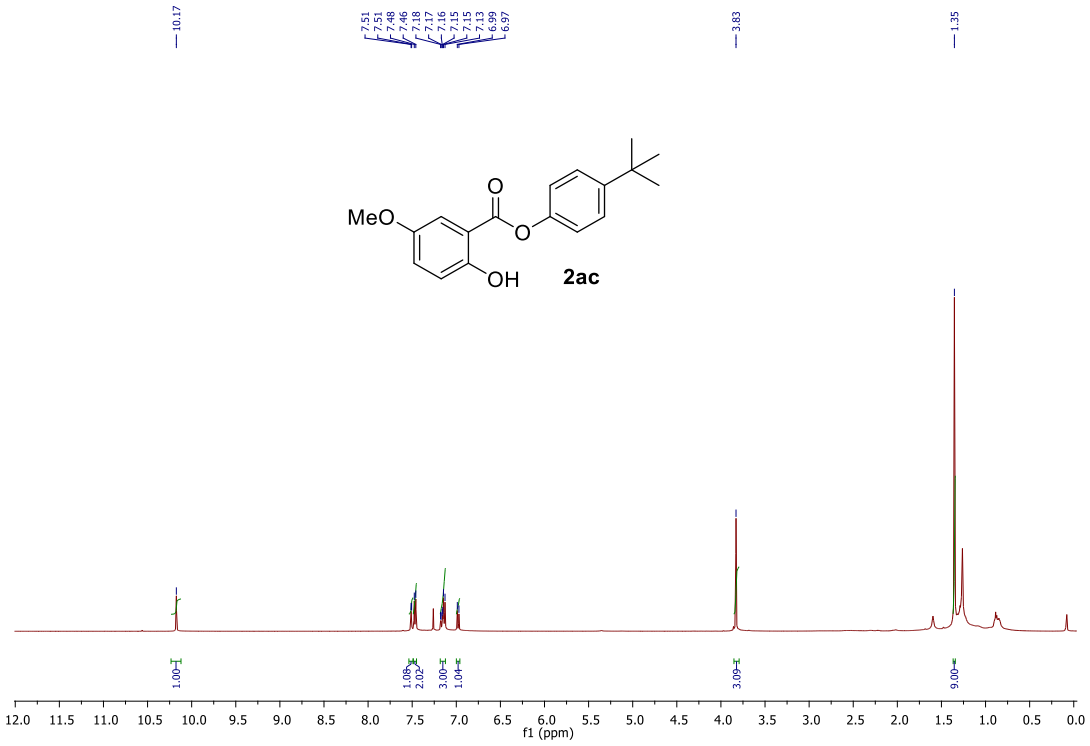
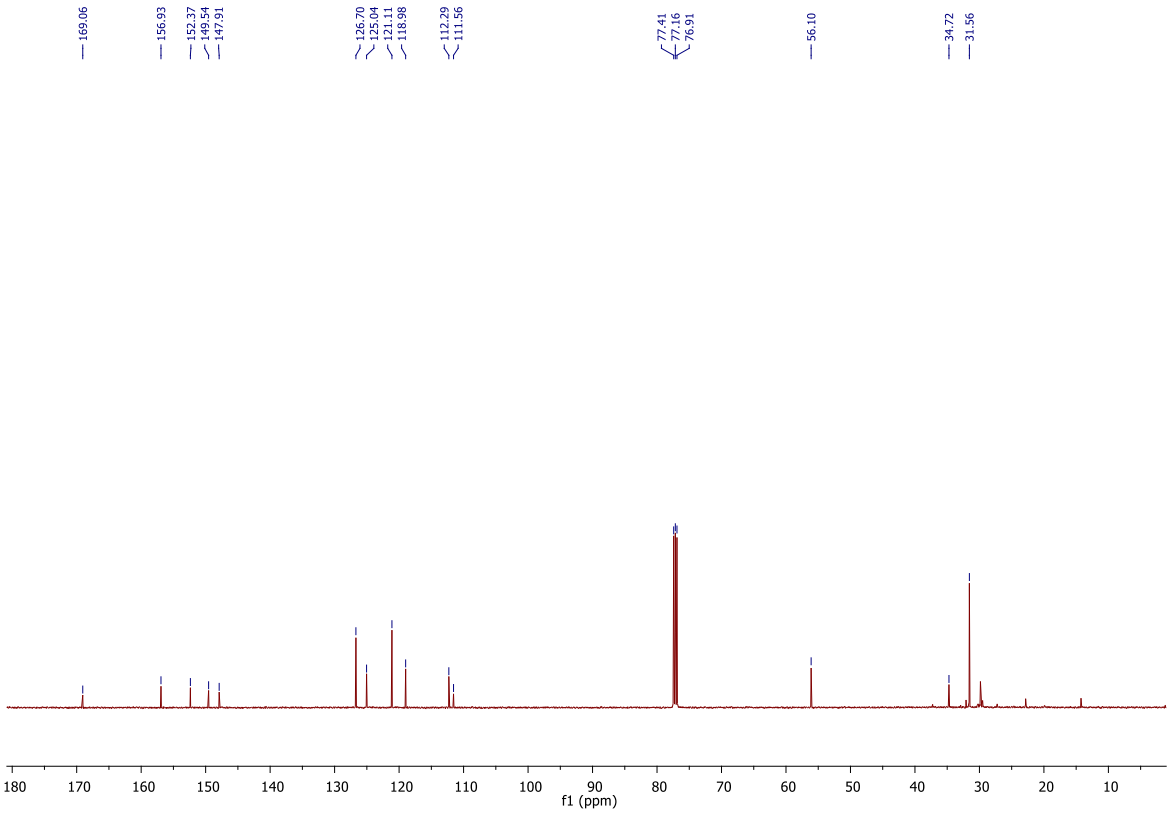
-150
-160
-170
-180
-190
-200
f1 (ppm)


10.16
7.50
7.50
7.17
7.17
7.16
7.15
7.14
7.12
6.98
6.97
6.95
3.84
3.83
MeO
O
O
OMe
OH
2ab
1.00
1.02
1.07
1.92
3.04
6.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


169.20
157.83
156.85
152.32
143.62
125.06
122.56
118.96
114.79
112.11
111.45
77.41
77.16
76.91
56.08
55.78
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.17
7.51
7.51
7.48
7.46
7.18
7.17
7.16
7.15
7.15
7.13
6.99
6.97
3.83
1.35
MeO
O
O
OH
2ac
1.00
1.08
2.02
3.00
1.04
3.09
9.00
f1 (ppm)


169.06
156.93
152.37
149.54
147.91
126.70
125.04
121.11
118.98
112.29
111.56
77.41
77.16
76.91
56.10
34.72
31.56
f1 (ppm)