Supporting Information

Synthesis of 1,2,3-functionalized naphtols and phenols by decarboxylative cycloaddition/aromatization reactions of α-oxygenated lactones with allenoates or electron-deficient alkynes

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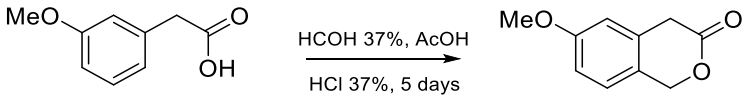
1. General Information

Unless otherwise noted, all chemicals, reagents and solvents for the performed reactions are commercially available. Isochroman-3-one was purchased from BLDpharm, substituted isochroman-3-ones were prepared according to literature procedures.[1,2] ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer with a broad band observe probe and a sample changer for 16 samples and on a Bruker Avance DRX 500 MHz spectrometer which are both property of the Austro Czech NMR Research Center "RERI uasb". The measurements were referenced on the solvent residual peak (δ_H 7.26 ppm, δ_C 77.16 ppm for $CDCl_3$ and δ_H 3.31 ppm, δ_C 49.5 ppm for MeOD). The ^{13}C NMR spectra were recorded under broad-band proton-decoupling. NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integrals. High resolution mass spectra were obtained using an Agilent QTOF 6520 with ESI source. EI-MS analysis was done with a Shimadzu GC-MS QP-2020 using He as carrier gas. Preparative column chromatography was carried out using Davisil LC 60A 70–200 MICRON silica gel. Thin layer chromatography was performed on Macherey-Nagel pre-coated TLC plates (silica gel, 60 F254, 0.20 mm, ALUGRAM® Xtra SIL). TLC plates were visualized under 254 nm UV lamp. The allenoates were synthesized in accordance with the literature.[3-5] Allenylsulfone was synthesized according to the literature.[6]

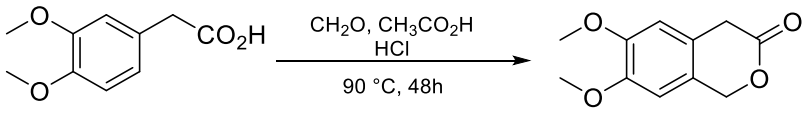
2. Syntheses of Starting Materials

6-Methoxyisochroman-3-one:



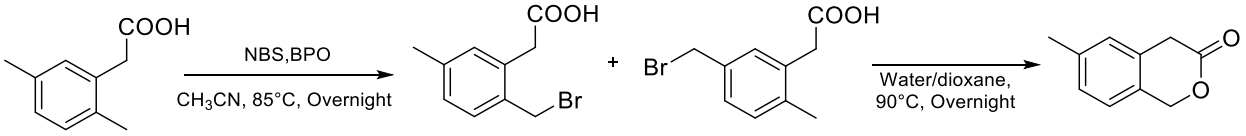
Prepared as reported in the literature.[1] White solid. Yield: 37% (150mg), m.p. and spectroscopic data were found in agreement with those reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.3 Hz, 1H), 6.83 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 5.26 (s, 2H), 3.83 (s, 3H), 3.68 (s, 2H).

6,7-dimethoxyisochroman-3-one:



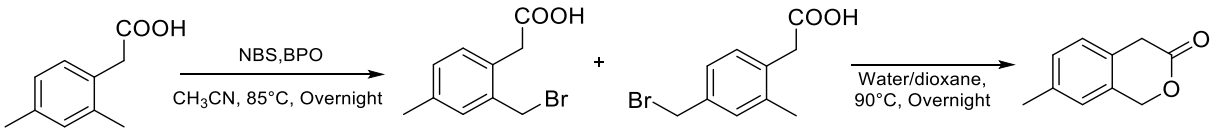
Prepared as reported in the literature.[1] White solid. Yield: 39% (170mg), m.p. and spectroscopic data were found in agreement with those reported in the literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.70 (s, 1H), 5.25 (s, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.63 (s, 2H).

6-methylisochroman-3-one:



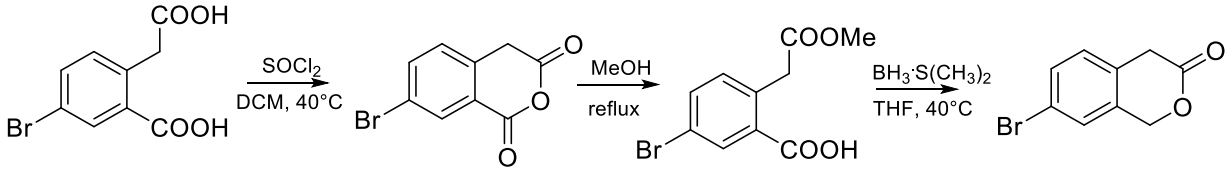
2-(2,5-dimethylphenyl)acetic acid (1.64 g, 10 mmol, 2.0 equiv.) was dissolved in CH_3CN (15 mL) and treated with N-Bromosuccinimide (NBS, 890 mg, 5 mmol, 1 equiv.) and Benzoyl peroxide (BPO, 120 mg, 0.5 mmol, 0.1 equiv.) at 85 °C for overnight. Then, the solvent was removed under reduced pressure, and the crude without any purification dissolved in 5 mL dioxane 5 mL of water and refluxed at 90 °C for overnight. Then, the solvent was removed under reduced pressure, and the crude was extracted with diethyl ether and 1M NaOH taken up ethyl acetate. Organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Purification by on silica gel (Petroleum ether/Ethyl acetate, 9:1) afforded the product as white solid. Overall yield of two steps: 34% (550 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 2H), 7.08 (s, 1H), 5.30 (s, 2H), 3.70 (s, 2H), 2.39 (s, 3H).

7-methylisochroman-3-one:



2-(2,4-dimethylphenyl)acetic acid (1.64 g, 10 mmol, 2.0 equiv.) was dissolved in CH_3CN (15 mL) and treated with *N*-Bromosuccinimide (NBS, 890 mg, 5 mmol, 1 equiv.) and Benzoyl peroxide (BPO, 120 mg, 0.5 mmol, 0.1 equiv.) at 85°C for overnight. Then, the solvent was removed under reduced pressure, and the crude without any purification dissolved in 5 mL dioxane 5 mL of water and refluxed at 90°C for overnight. Then, the solvent was removed under reduced pressure, and the crude was extracted with diethyl ether and 1M NaOH taken up ethyl acetate. Organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Purification by on silica gel (Petroleum ether/Ethyl acetate, 9:1) afforded the product as white solid. Overall yield of two steps: 38% (615 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 1H), 7.08 (d, *J* = 17.8 Hz, 1H), 7.02 (s, 1H), 5.24 (s, 2H), 3.63 (s, 2H), 2.32 (s, 3H).

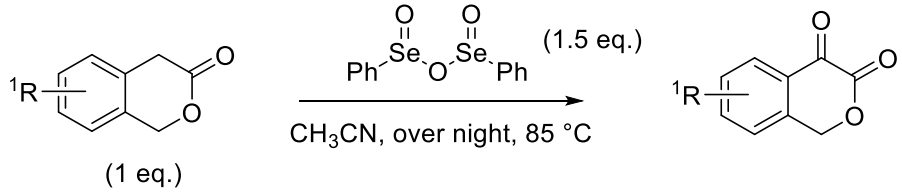
7-Bromo Isochroman-3-ones:



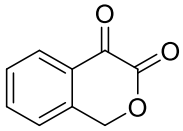
Prepared as reported in the literature.[1]

7-bromoisochroman-3-ones. White solid. Yield: 81% (100 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 1H), 7.47 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 5.34 (s, 2H), 3.73 (s, 2H).

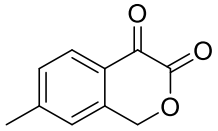
2.4 **General Procedure for synthesizing Isochromane-3,4-dione derivatives:**



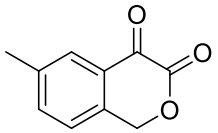
Benzeneseleninic acid anhydride (3 mmol, 1.5 equiv.) was added to a solution of isochromane-3-one derivatives (1.5 mmol, 1 equiv.) in 16 ml CH_3CN and stirred at 85°C for overnight. Then, solvent was removed under reduced pressure, and the crude was taken up ethyl acetate. Purification by chromatography on silica gel (Heptane/Ethyl acetate, 4:1). (Note that products are not very UV active.)



Isochromane-3,4-dione (1a): White solid. Yield: 72% (234 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.75 (td, *J* = 7.6, 1.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 5.72 (s, 2H).



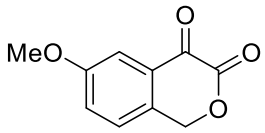
7-methylisochromane-3,4-dione (1b): White solid. Yield: 76% (268 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 5.66 (s, 2H), 2.48 (s, 3H).



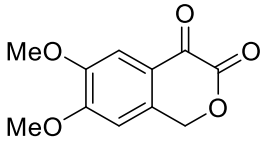
6-methylisochromane-3,4-dione (1c):

Purification by flash chromatography on silica gel (Heptane/Ethyl acetate, 7:3) afforded as a white solid (Yield 77%, 271 mg), m.p. 141.5-142.2°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.9 Hz, 0H), 7.49 (dd, *J* = 8.0, 2.2 Hz, 0H), 7.20 (d, *J* = 8.0 Hz, 0H), 5.62 (s, 1H), 2.36 (s, 1H). ^{13}C NMR (75 MHz,

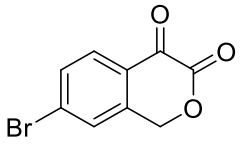
$CDCl_3$) δ 173.78, 157.16, 139.46, 137.14, 136.11, 129.80, 127.85, 124.38, 69.50, 21.06. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{10}H_9O_3]^+$:177.0547, found:177.0558.



Methoxyisochromane-3,4-dione (1d): White solid. Yield: 46% (177 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.6 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 5.67 (s, 2H), 3.89 (s, 3H).



6,7-dimethoxyisochromane-3,4-dione (1e): White solid. Yield: 41% (182 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.68 (s, 1H), 5.65 (s, 2H), 4.00 (s, 3H), 3.97 (s, 3H).

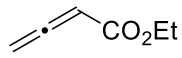


7-bromoisochromane-3,4-dione (1f): White solid. Yield: 58% (280 mg), m.p. and spectroscopic data were found in agreement with those reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.55 (s, 1H), 5.68 (s, 2H).

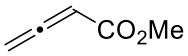
General Procedure for synthesizing 4-bromo-3-hydroxy-2H-pyran-2-one (2b):

To a solution of 3-hydroxy-2H-pyran-2-one **(2a)** (112 mg, 1 mmol) in DMF (1 mL) was added NBS (196 mg, 1.1 mmol, 1.1 eq.) portion wise. After the mixture was stirred overnight, the reaction mixture was diluted with H_2O and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtrated and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (Heptane/EtOAc=7/3), resulting in a yellow solid powder **(2b)** (118 mg, 62%). The spectra and physical data are identical to those reported in the literature.[9] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.04 (1H, d, *J* = 5.6 Hz), 6.45 (s, 1H), 6.42 (d, *J* = 5.6 Hz, 1H).

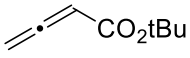
The following allenoates, but-3-ynoates, functionalized propynoates, and allenylsulfone have been used in this work:



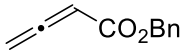
5a



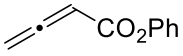
5b



5c



5d



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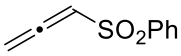
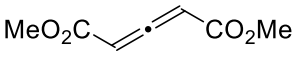


5f



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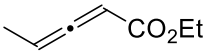
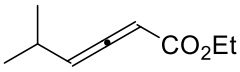


5h



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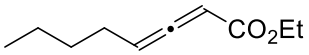
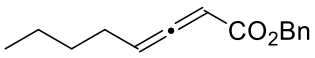
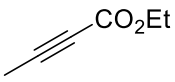


5j

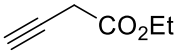


5k

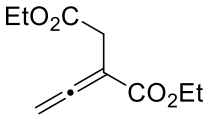


6a

6b



7a

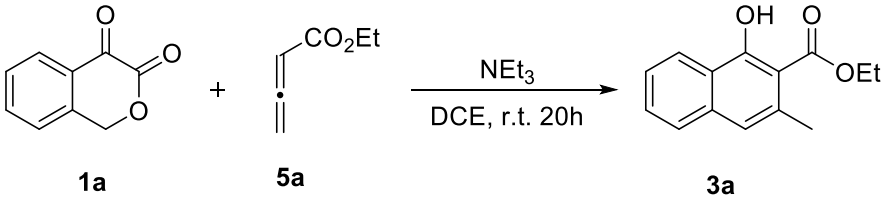


8

3. Detailed optimization of the reaction between 1a and 5a

No.	Dione 1a	Allenoate 5a	Base or additive	Solvent	Temp	Molarity	Time	Yield%
1	1 eq	2 eq	NEt_3(2eq.)	DCE	r.t	0.2	6 h	39%
2	2 eq	1 eq	NEt_3(2eq.)	DCE	r.t	0.2	4 h	48%
3	2 eq	1 eq	DABCO (3eq.)	DCE	r.t	0.2	15h	20%
4	2 eq	1 eq	NEt_3(2eq.)	DCM	50 °C	0.2	4h	32%
5	2 eq	1 eq	DIPEA(2eq.)	DCE	r.t	0.2	12 h	43%
6	2 eq	1 eq	NEt_3(2eq.)	DCM	r.t	0.2	12h	34%
7	2 eq	1 eq	NEt_3(2eq.)	ACN	r.t	0.2	12h	39%
8	2 eq	1 eq	NEt_3(2eq.)	MTBE	r.t	0.2	48%	12%
9	2 eq	1 eq	NEt_3(2eq.)	Toluene	r.t	0.2	48h	16%
10	2 eq	1 eq	K_2CO_3(2eq.)	DCE	r.t	0.2	24h	43%
11	2 eq	1 eq	NaOAc(3eq.)	DCE	r.t	0.2	12h	Decomp.
12	2 eq	1 eq	Cs_2CO_3(3eq.)	DCE	r.t	0.1	15 h	40%
13	2 eq	1 eq	NEt_3(3eq.)	DME	r.t	0.1	24 h	-
14	2 eq	1 eq	NEt_3(2eq.)	DCE	r.t	0.2	12 h	74%
15	2 eq	1 eq	NEt_3(2eq.)	DCE	r.t	0.5	4 h	70%
16	2 eq	1 eq	NEt_3(2eq.)	DCE	r.t	0.1	30 h	65%
17	2 eq	1 eq	NEt_3(1eq.)	DCE	r.t	0.1	40 h	40%
18	2 eq	1 eq	NEt_3(0.5eq.)	DCE	r.t	0.1	72 h	28%
19	2 eq	1 eq	$Sc(OTf)_3$ (20 mol%)	DCE	r.t	0.1	24h	-
20	2 eq	1 eq	$Cu(OTf)_2$ (20 mol%)	DCE	r.t	0.2	24h	-
21	**2 eq**	**1 eq**	**NEt_3(3eq.)**	**DCE**	**r.t**	**0.2**	**20 h**	**87%**
22	1.5 eq	1 eq	NEt_3(3eq.)	DCE	r.t	0.2	20 h	63%
23	1 eq	1 eq	NEt_3(3eq.)	DCE	r.t	0.2	20 h	42%
24	2 eq	1 eq	NEt_3(3eq.)	DCE	r.t	0.2	36 h	85%
25	2 eq	1 eq	NEt_3(3eq.)	DCE	r.t	0.1	24 h	62%
26	2 eq	1 eq	NEt_3(4eq.)	DCE	r.t	0.2	6 h	76%

4. General procedure for the syntheses of alpha naphthol and phenol derivatives 3 and 4:



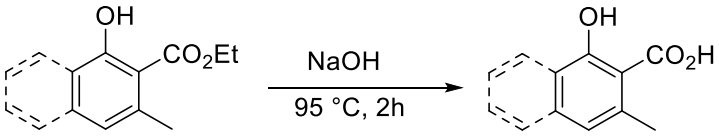
1a **5a** **3a**

In a round-bottomed flask equipped with a magnetic steer bar, isochromane-3,4-dione (**1a**) (64 mg, 0.4 mmol, 2 equiv.) and ethyl allenoate (**5a**) (23 µL, 0.2 mmol, 1 equiv.) were dissolved in 1,2-dichloroethane (1 mL) at room temperature. NEt_3 (84 µL, 0.6 mmol, 3 equiv.) was then added and the resulting reaction was stirred at room temperature and monitored by TLC. After 20 h, the homogeneous mixture was directly subjected to flash chromatography on silica gel (Heptane/Ethyl acetate 9:1) to afford **3a** (40 mg, 87% yield,) as a white solid.

Scale up reaction:

In a round-bottomed flask equipped with a magnetic steer bar, isochromane-3,4-dione (**1a**) (320 mg, 2 mmol, 2 equiv.) and ethyl allenoate (**5a**) (115 µL, 1 mmol, 1 equiv.) were dissolved in 1,2-dichloroethane (1 mL) at room temperature. NEt_3 (420 µL, 3 mmol, 3 equiv.) was then added and the resulting reaction was stirred at room temperature and monitored by TLC. After 20 h, the homogeneous mixture was directly subjected to flash chromatography on silica gel (Heptane/Ethyl acetate 9:1) to afford **3a** (184 mg, 80% yield,) as a white solid.

5. Saponification reactions:

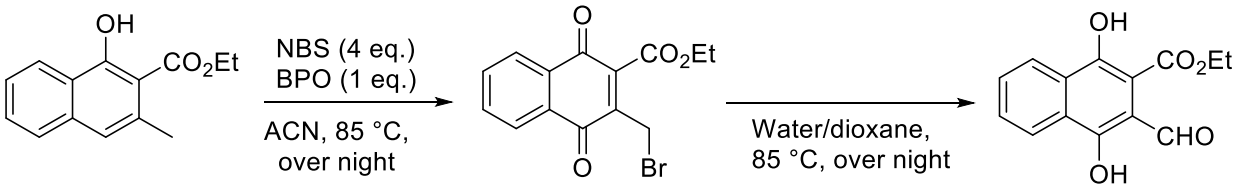


3a or 4a **10 or 11**

o-Cresotic acid analogous **10** or **11** was prepared by a modified procedure from Silverman et al.[10] **4a** (36 mg, 0.2 mmol) was dissolved in NaOH (2.35 M, 1.6 mL) and heated at 95 °C for 2 hours. The solution was cooled before acidifying with HCl (1 M). The white precipitate was filtered and dried to give **10** (37 mg, 96%). The spectroscopic data for 1 were in agreement with those reported in literature.[11]

3a (46 mg, 0.2 mmol) was dissolved in NaOH (2.35 M, 1.6 mL) and heated at 95 °C for 2 hours. The solution was cooled before acidifying with HCl (1 M). The white precipitate was filtered and dried to give **11** (29 mg, 92%). The spectroscopic data for 1 were in agreement with those reported in literature.[12]

6. Synthesis of ethyl 3-formyl-1,4-dioxo-1,4-dihydronaphthalene-2-carboxylate (13):

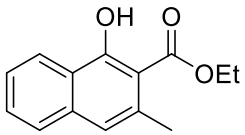


12 (56%) **13** (58%)

In a round-bottomed flask equipped with a magnetic steer bar, ethyl 1-hydroxy-3-methyl-2-naphthoate **(3a)** (46 mg, 0.2 mmol, 1 equiv.) were dissolved ACN (3 mL), then N-Bromosuccinimide (NBS, 142 mg, 0.8 mmol, 4 equiv.) and dibenzoyl peroxide (BPO, 48 mg, 0.2 mmol, 1 equiv.) were added and then resulting reaction was stirred at 85°C for overnight. After evaporation of the solvent, the crude was directly purified by chromatography on silica gel (Heptane/Ethyl acetate, 9:1 to Heptane/Ethyl acetate, 8:2) leading to the **12** (36 mg, 56% yield). The ethyl 3-(bromomethyl)-1,4-dioxo-1,4-dihydronaphthalene-2-carboxylate **12** (67 mg, 0.2 mmol) dissolved in 2 mL dioxane and 1 mL of water and refluxed at 85°C for overnight. Then solvent was removed under reduced pressure, and the crude was extracted with ethyl acetate. Organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. Purification on silica gel (Heptane/Ethyl acetate, 9:1 to Heptane/Ethyl acetate, 8:2)) afforded the product as white solid **13** (30 mg, 58% yield).

7. Full Analytical Details

Ethyl 1-hydroxy-3-methyl-2-naphthoate (3a):

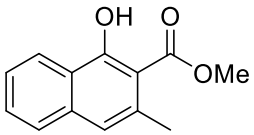


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). With **5a**) yield= 87%, 40 mg; with **6a**) yield= 37%, 17 mg; with (at 50 °C); **7a**) yield= 82%, 38 mg, afforded as a white solid. M.p. 60.7-61.6 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.59 (td, *J* = 7.7, 1.2 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.60 (dd, *J* = 8.2, 1.5 Hz, 2H), 5.56 (d, *J* = 3.4 Hz, 1H), 5.05 (d, *J* = 5.5 Hz, 1H), 4.30 (dd, *J* = 5.6, 3.4 Hz, 1H), 4.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 134.7, 133.4, 133.0, 130.5, 129.0, 128.9, 128.7, 127.6, 125.4, 122.7, 90.9, 79.6, 75.5, 51.7. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{13}O_3]^-$: 229.0870; found: 229.0878.

Analytical data are in accordance with those reported in the literature.[12]

Methyl 1-hydroxy-3-methyl-2-naphthoate (3b):

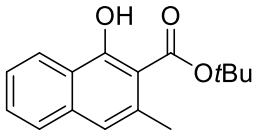


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 90%, 40 mg, afforded as a white solid. M.p. 81.2-82.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 1H), 7.59 (td, *J* = 7.7, 1.2 Hz, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.60 (dd, *J* = 8.2, 1.5 Hz, 2H), 5.56 (d, *J* = 3.4 Hz, 1H), 5.05 (d, *J* = 5.5 Hz, 1H), 4.30 (dd, *J* = 5.6, 3.4 Hz, 1H), 4.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 134.7, 133.4, 133.0, 130.5, 129.0, 128.9, 128.7, 127.6, 125.4, 122.7, 90.9, 79.6, 75.5, 51.7. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{13}H_{11}O_3]^-$: 215.0714; found: 215.0725.

Analytical data are in accordance with those reported in the literature.[13]

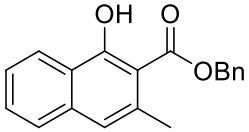
***Tert*-butyl 1-hydroxy-3-methyl-2-naphthoate (3c):**



Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 58%, 30 mg, afforded as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.95 (s, 1H), 8.37 (ddt, *J* = 8.3, 1.5, 0.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.7, 1.4 Hz, 1H), 7.10 (s, 1H), 2.66 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 162.3, 135.8, 135.1, 129.3, 126.4, 124.8, 123.9, 123.8, 120.5, 107.7, 83.6, 28.5, 24.9. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{16}H_{17}O_3]^-$: 257.1183; found: 257.1196.

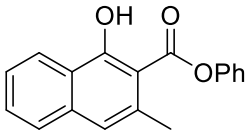
Benzyl 1-hydroxy-3-methyl-2-naphthoate (3d):



Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 83%, 46 mg, afforded as a white solid. M.p. 76.7-77.8°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.65 (s, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.40 – 7.25 (m, 6H), 6.96 (s, 1H), 5.34 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 162.8, 136.2, 135.3, 135.0, 129.7, 128.7, 128.6, 126.5, 125.0, 124.1, 123.7, 120.7, 106.2, 67.4, 24.9. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{19}H_{15}O_3]^-$: 291.1027; found: 291.1037.

Phenyl 1-hydroxy-3-methyl-2-naphthoate (3e):

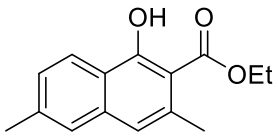


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 60%, 33 mg, afforded as a white solid. M.p. 102.8-103.5°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.50 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.55 – 7.49 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.21 (s, 1H), 2.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 163.6, 150.0, 136.4, 134.8, 130.1, 129.7, 126.6, 126.4,

125.2, 124.2, 123.7, 121.8, 121.1, 105.7, 24.8. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{18}H_{13}O_3]^-$: 277.0870; found: 27.0893.

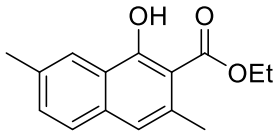
Ethyl 1-hydroxy-3,6-dimethyl-2-naphthoate (3f):



Purification by column chromatography (Heptane/Ethyl acetate, 95:5). yield= 92%, 45 mg, afforded as a white solid. M.p. 86.7-88.2°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.72 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.31 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 2.41 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 162.6, 139.8, 136.4, 135.2, 127.1, 125.6, 123.9, 121.8, 120.2, 105.7, 61.5, 24.7, 21.9, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{15}O_3]^-$: 243.1027; found: 243.1026.

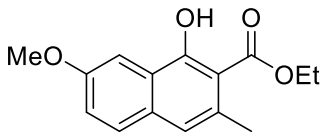
Ethyl 1-hydroxy-3,7-dimethyl-2-naphthoate (3g):



Purification by column chromatography (Heptane/Ethyl acetate, 95:5). Yield= 90%, 44 mg, afforded as a white solid. M.p. 79.8-81.3°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.80 (s, 1H), 8.14 (d, *J* = 0.9 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.04 (s, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 2.52 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 162.1, 134.7, 134.3, 134.0, 131.7, 126.3, 123.7, 122.9, 120.5, 106.4, 61.5, 24.6, 21.7, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{15}O_3]^-$: 243.1027; found: 243.1043.

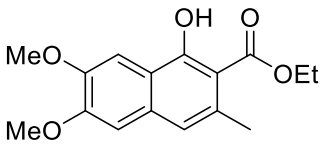
Ethyl 1-hydroxy-7-methoxy-3-methyl-2-naphthoate (3h):



Purification by column chromatography (Heptane/Ethyl acetate, 85:15). yield= 58%, 30 mg, afforded as a white solid. M.p. 104.5-105.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.75 (s, 1H), 7.64 (d, *J* = 2.8 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.21 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.04 (s, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.63 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 161.3, 157.2, 132.6, 131.4, 128.1, 124.4, 122.2, 120.5, 106.8, 102.0, 61.6, 55.4, 24.4, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{15}O_4]^-$: 259.0976; found: 259.0974.

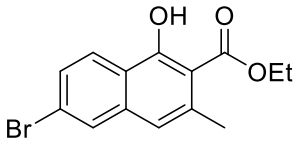
Ethyl 1-hydroxy-6,7-dimethoxy-3-methyl-2-naphthoate (3i):



Purification by column chromatography (Heptane/Ethyl acetate, 85:15). Yield= 52%, 30 mg, afforded as a white solid. M.p. 122.4-123.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.78 (s, 1H), 7.62 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 3.99 (s, 3H), 2.62 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 161.2, 152.3, 148.6, 133.8, 132.5, 119.5, 118.2, 105.4, 105.3, 102.7, 61.4, 56.0, 55.9, 24.5, 14.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{16}H_{17}O_5]^-$: 289.1081; found: 289.1071.

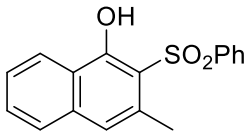
Ethyl 6-bromo-1-hydroxy-3-methyl-2-naphthoate (3j):



Purification by column chromatography (Heptane/Ethyl acetate, 9:1). Yield= 83%, 51 mg, afforded as a white solid. M.p. 88.7-90.2°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.83 (s, 1H), 8.21 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.50 (dd, *J* = 8.9, 2.0 Hz, 1H), 6.98 (s, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 2.65 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 172.4, 162.4, 136.9, 136.7, 128.4, 128.2, 125.8, 124.2, 122.1, 119.5, 106.6, 61.7, 24.6, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{14}{}^{79}BrO_3]^+$: 309.0121; found: 309.0137.

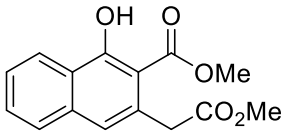
3-methyl-2-(phenylsulfonyl)naphthalen-1-ol (3k):



Purification by column chromatography (Pentane/Diethyl ether, 85:15). yield= 62%, 37 mg, afforded as a white solid. M.p. 121.4-122.8°C. (48 hours)

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.56 – 7.41 (m, 6H), 7.02 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 142.1, 136.4, 133.5, 132.4, 130.2, 129.2, 126.7, 126.6, 125.8, 124.3, 124.2, 121.8, 21.5. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{17}H_{13}O_3S]^-$: 297.0591; found: 297.0598.

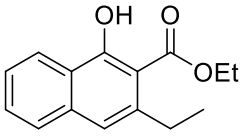
Methyl 1-hydroxy-3-(2-methoxy-2-oxoethyl)-2-naphthoate (3l):



Purification by column chromatography (Heptane/Ethyl acetate, 85:15). yield= 55%, 30 mg, afforded as a white solid. M.p. 105.4-107.2°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.33 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.53 (td, *J* = 7.4, 1.4 Hz, 1H), 7.43 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.05 (s, 1H), 3.93 (s, 2H), 3.86 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 172.1, 162.9, 135.8, 130.4, 129.9, 126.9, 125.9, 124.5, 124.1, 122.7, 105.5, 52.0, 51.9, 43.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{13}O_5]^-$: 273.0768; found: 273.0781.

Ethyl 3-ethyl-1-hydroxy-2-naphthoate (3m):

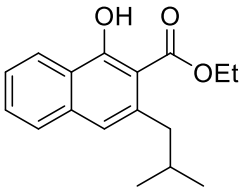


Purification by column chromatography (Heptane/Ethyl acetate, 95:5). yield= 28%, 14 mg, afforded as a yellow wax. (36 hours, 50 °C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.68 (s, 1H), 8.29 (d, *J* = 7.0 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.06 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 3.01 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 172.5, 162.5, 141.3, 136.2, 131.5, 129.5, 129.2, 126.6, 125.0, 124.0, 119.4, 61.7, 30.0, 16.3, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{15}O_5]^-$: 243.1027; found: 243.1046.

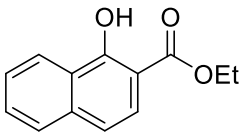
Ethyl 1-hydroxy-3-isobutyl-2-naphthoate (3n):



Purification by column chromatography (Heptane/Ethyl acetate, 95:5). yield= 26%, 14 mg, afforded as a yellow oil. (36 hours, 50 °C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.75 (s, 1H), 8.36 (ddt, *J* = 8.3, 1.5, 0.8 Hz, 1H), 7.66 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.04 (s, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 2.92 (d, *J* = 7.0 Hz, 2H), 1.85 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.47 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 162.6, 138.3, 135.8, 129.5, 126.7, 125.0, 124.0, 123.9, 121.5, 105.9, 61.7, 46.3, 29.8, 22.5, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{17}H_{19}O_3]^-$: 271.1340; found: 271.1331.

Ethyl 1-hydroxy-2-naphthoate (3o):

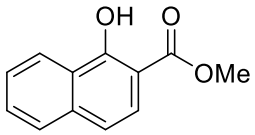


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 60%, 26 mg, afforded as a white solid. M.p. 41.1-42.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.08 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.60 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 161.0, 137.2, 129.3, 127.4, 125.7, 124.8, 124.3, 123.9, 118.5, 105.8, 61.4, 14.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{13}H_{11}O_3]^-$: 215.0714; found: 215.0737.

Analytical data are in accordance with those reported in the literature.[13]

Methyl 1-hydroxy-2-naphthoate (3p):

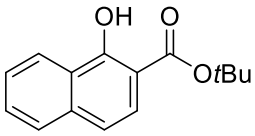


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 64%, 26 mg, afforded as a white solid. M.p. 76.8-78.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.61 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 7.53 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 160.9, 137.2, 129.4, 127.5, 125.8, 124.8, 124.2, 123.9, 118.6, 105.6, 52.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{12}H_9O_3]^-$: 201.0557; found: 201.0573.

Analytical data are in accordance with those reported in the literature.[13]

***Tert*-butyl 1-hydroxy-2-naphthoate (3q):**

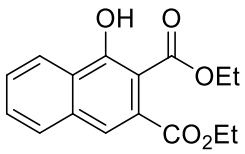


Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 54%, 26 mg, afforded as a pale yellow oil. (at 50 °C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.19 (s, 1H), 8.33 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 (t, *J* = 8.3 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.18 (s, 1H), 1.58 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 160.9, 137.0, 129.1, 127.4, 125.6, 124.9, 124.8, 123.8, 118.1, 107.0, 82.7, 28.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{15}O_3]^-$: 243.1027; found: 243.1053.

Analytical data are in accordance with those reported in the literature.[14]

Diethyl 1-hydroxynaphthalene-2,3-dicarboxylate (3r):



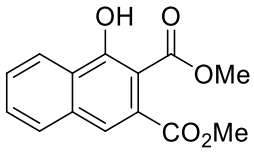
Purification by column chromatography (Heptane/Ethyl acetate, 85:15). yield= 81%, 47 mg, afforded as a white solid. M.p. 53.8-55.2°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.98 (s, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.33 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 4H), 1.31 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$)

δ 170.1, 169.2, 161.0, 135.2, 130.6, 130.1, 128.0, 127.2, 125.4, 124.0, 119.5, 103.2, 62.1, 61.5, 14.2, 14.0. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{16}H_{15}O_5]^-$: 287.0924; found: 215.0737.

Analytical data are in accordance with those reported in the literature.[15]

Dimethyl 1-hydroxynaphthalene-2,3-dicarboxylate (3s):

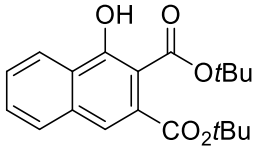


Purification by column chromatography (Heptane/Ethyl acetate, 85:15). yield= 84%, 44 mg, afforded as a white solid. M.p. 54.2-55.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.56 (td, *J* = 7.5, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.8, 1.6 Hz, 1H), 7.35 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 169.7, 160.9, 135.2, 130.2, 130.1, 128.0, 127.4, 125.4, 124.1, 119.7, 103.1, 52.8, 52.6. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{11}O_5]^-$: 259.0611; found: 259.0629.

Analytical data are in accordance with those reported in the literature.[15]

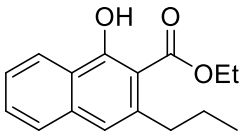
Di-tert-butyl 1-hydroxynaphthalene-2,3-dicarboxylate (3t):



Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 77%, 53 mg, afforded as a white solid. M.p. 72.1-73.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.29 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.56 – 7.50 (m, 1H), 7.51 – 7.44 (m, 1H), 7.40 (s, 1H), 1.56 (s, 9H), 1.55 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 167.3, 159.7, 134.6, 131.9, 129.6, 128.1, 127.2, 125.7, 123.9, 120.9, 105.8, 84.2, 81.7, 28.4, 28.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{20}H_{23}O_5]^-$: 343.1551; found: 343.1551.

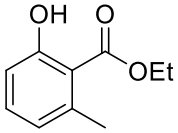
Ethyl 1-hydroxy-3-propyl-2-naphthoate (3u):



Purification by column chromatography (Heptane/Ethyl acetate, 95:05). yield 31%, 16 mg, afforded as a yellow wax. (at 50 °C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 12.78 (s, 1H), 8.38 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.13 (s, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 1.66 (td, *J* = 15.0, 7.6 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 162.6, 139.6, 136.0, 129.5, 126.6, 125.0, 124.0, 123.8, 120.4, 105.8, 61.6, 39.3, 25.2, 14.2, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{16}H_{17}O_3]^-$: 257.1183; found: 257.1204.

Ethyl 2-hydroxy-6-methylbenzoate (4a):

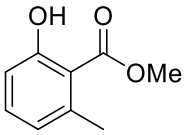


Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 92%, 33 mg, afforded as a white solid. M.p. 41.2-43.4°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 7.4 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 162.9, 141.4, 134.1, 122.9, 115.6, 112.4, 61.6, 24.1, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{10}H_{11}O_3]^-$: 179.0714; found: 179.0725.

Analytical data are in accordance with those reported in the literature.[16]

Methyl 2-hydroxy-6-methylbenzoate (4b):



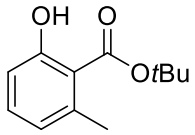
Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 94%, 31 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 3.96 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 162.8, 141.3, 134.2,

122.9, 115.6, 112.3, 52.1, 24.0. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_9H_9O_3]^-$: 165.0557; found: 165.0540. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_9H_9O_3]^-$: 165.0557; found: 165.0563.

Analytical data are in accordance with those reported in the literature.[17]

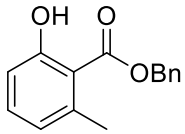
***Tert*-butyl 2-hydroxy-6-methylbenzoate (4c):**



Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 65%, 27 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 2.45 (s, 3H), 1.55 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 162.8, 141.0, 133.6, 122.8, 115.6, 113.7, 83.6, 28.4, 24.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{12}H_{15}O_3]^-$: 207.1027; found: 207.1023.

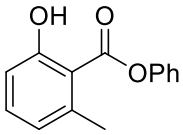
Benzyl 2-hydroxy-6-methylbenzoate (4d):



Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 84%, 41 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.33 (s, 1H), 7.51 – 7.39 (m, 5H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 5.45 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 163.0, 141.4, 135.2, 134.3, 128.7, 128.6, 128.6, 123.0, 115.7, 112.3, 67.4, 24.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{15}H_{13}O_3]^-$: 241.0870; found: 241.0894.

Phenyl 2-hydroxy-6-methylbenzoate (4e):

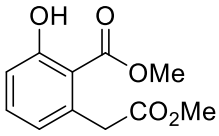


Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 77%, 35 mg, afforded as a white solid. M.p. 49.1-50.2°C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.93 (s, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.23 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 7.4 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 163.5, 149.8, 141.7, 135.0, 129.7, 126.5, 123.3, 121.7, 115.9, 111.7, 24.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{11}O_3]^-$: 227.0714; found: 227.0719.

Analytical data are in accordance with those reported in the literature.[18]

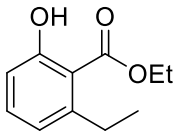
Methyl 2-hydroxy-6-(2-methoxy-2-oxoethyl)benzoate (4f):



Purification by column chromatography (Pentane/Diethyl ether, 9:1). yield= 86%, 39 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.18 (s, 1H), 7.36 (dd, *J* = 8.5, 7.3 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 3.89 (s, 3H), 3.89 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 171.1, 163.0, 136.4, 134.6, 123.9, 117.6, 112.1, 52.1, 51.9, 42.6. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{11}H_{11}O_5]^-$: 223.0612; found: 223.0629.

Ethyl 2-ethyl-6-hydroxybenzoate (4g):



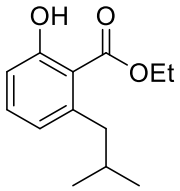
Purification by column chromatography (Pentane/Diethyl ether, 95:05). yield= 85%, 33 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.74 (dd, *J* = 7.5, 1.3 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.95 (q, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 162.6, 147.5, 134.3, 121.7, 115.6,

111.9, 61.6, 29.6, 16.3, 14.0. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{11}H_{13}O_5]^-$: 193.0870; found: 193.0894.

Analytical data are in accordance with those reported in the literature.[19]

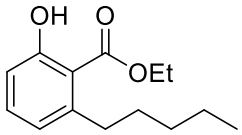
Ethyl 2-hydroxy-6-isobutylbenzoate (4h):



Purification by column chromatography (Pentane/Diethyl ether, 95:05). yield= 82%, 36 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, CDCl3) δ 11.25 (s, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.85 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.66 (dd, *J* = 7.5, 1.4 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.81 (d, *J* = 7.1 Hz, 2H), 1.81 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.44 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 162.8, 144.6, 133.7, 123.7, 115.8, 112.2, 61.7, 45.6, 30.2, 22.5, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{13}H_{17}O_3]^-$:221.1183; found:221.1166.

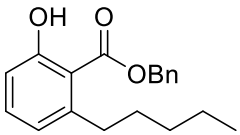
Ethyl 2-hydroxy-6-pentylbenzoate (4i):



Purification by column chromatography (Pentane/Diethyl ether, 95:05). yield= 59%, 28 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.23 (s, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.5, 1.4 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.96 – 2.85 (m, 2H), 1.64 – 1.51 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.38 – 1.31 (m, 4H), 0.98 – 0.84 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 162.7, 146.2, 134.1, 122.5, 115.6, 112.0, 61.6, 36.7, 32.1, 31.9, 22.6, 14.1, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{19}O_3]^-$: 235.1319; found: 235.1340.

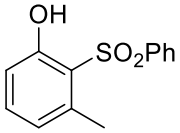
Benzyl 2-hydroxy-6-pentylbenzoate (4j):



Purification by column chromatography (Pentane/Diethyl ether, 95:05). yield= 58%, 35 mg, afforded as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.49 – 7.38 (m, 5H), 7.29 (t, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.71 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.39 (s, 2H), 2.88 – 2.77 (m, 2H), 1.48 – 1.36 (m, 2H), 1.24 – 1.11 (m, 2H), 1.11 – 1.02 (m, 2H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 162.8, 146.4, 134.8, 134.3, 129.1, 128.8, 128.7, 122.5, 115.6, 111.8, 67.7, 36.8, 32.2, 31.9, 22.6, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{19}H_{21}O_3]^-$: 297.1496; found: 297.1477.

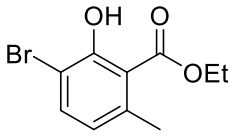
3-methyl-2-(phenylsulfonyl)phenol (4k):



Purification by column chromatography (Pentane/Diethyl ether, 85:15). yield= 52%, 26 mg, afforded as a white solid. M.p. 72.3-73.6 °C. (20 hours)

. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.89 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.56 – 7.49 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 141.8, 139.4, 135.4, 133.6, 129.2, 126.7, 123.8, 120.4, 117.5, 21.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{13}H_{11}O_3S]^-$: 247.0434; found: 247.0431.

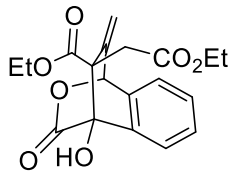
Ethyl 3-bromo-2-hydroxy-6-methylbenzoate (4l):



Purification by column chromatography (Pentane/Diethyl ether, 95:05). yield= 83%, 43 mg, afforded as a white solid. M.p. 57.2-58.4 °C.

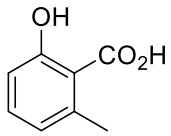
^{1}H NMR (300 MHz, $CDCl_3$) δ 12.04 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 159.0, 140.9, 137.2, 123.5, 113.6, 108.9, 62.2, 23.9, 14.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{10}H_{10}{}^{79}BrO_3]^-$: 256.9818; found: 256.9837.

Ethyl (1S,3S,4S)-3-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylene-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalene-3-carboxylate: (mix of diastereomers) (9)



Purification by column chromatography (Heptane/Ethyl acetate, 7:3). yield= 38%, 27 mg, afforded as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.60 $^{major+minor}$ (m, 1.6H), 7.52 – 7.31 $^{major+minor}$ (m, 4.6H), 5.77^{major} (s, 1H), 5.71^{minor} (s, 0.6H), 5.55^{major} (s, 1H), 5.52^{major} (s, 1H), 5.48^{major} (s, 1H), 5.20^{minor} (s, 0.6H), 4.83^{minor} (s, 0.6H), 4.32 – 4.25^{minor} (m, 1H), 4.18^{major} (q, *J* = 7.1 Hz, 2H), 4.14 – 4.07^{minor} (m, 1H), 3.91^{major} (q, *J* = 7.1 Hz, 2H), 3.59^{minor} (s, 0.6H), 3.23^{major} (d, *J* = 16.9 Hz, 1H), 2.84^{major} (d, *J* = 17.0 Hz, 1H), 2.51^{minor} (d, *J* = 16.1 Hz, 0.6H), 2.21^{minor} (d, *J* = 16.1 Hz, 0.6H), 1.36 – 1.19 $^{major+minor}$ (m, 7H), 0.91^{major} (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 172.0, 171.6, 171.0, 170.4, 169.4, 143.1, 142.9, 135.4, 135.1, 134.0, 133.6, 129.7, 129.4, 128.8, 128.5, 124.0, 123.7, 122.9, 122.5, 117.0, 116.9, 82.1, 80.6, 78.8, 78.3, 62.6, 61.9, 61.5, 61.2, 54.2, 52.9, 41.7, 40.8, 14.1, 14.0, 13.8, 13.6. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{19}H_{21}O_7]^+$: 361.1282; found: 361.1299.

2-Hydroxy-6-methylbenzoic acid (10):

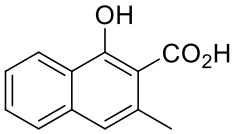


yield= 96%, 29 mg, afforded as a white solid. M.p. 166.2-168.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 163.7, 142.9, 135.5, 123.3, 115.9, 111.0, 24.1. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_8H_7O_3]^-$: 151.0401; found: 151.0423.

Analytical data are in accordance with those reported in the literature.[20]

1-Hydroxy-3-methyl-2-naphthoic acid (11):

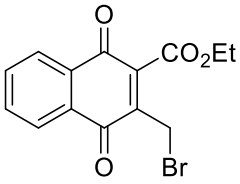


yield= 92%, 37 mg, afforded as a white solid. M.p. 191.4-193.7 °C.

^{1}H NMR (300 MHz, MeOD) δ 8.25 (d, *J* = 9.7 Hz, 0H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.37 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.06 (s, 1H), 2.73 (s, 3H). ^{13}C NMR (75 MHz, MeOD) δ 161.1, 136.8, 135.5, 127.8, 126.0, 123.9, 123.6, 123.1, 118.8, 23.0. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{12}H_9O_3]^-$: 201.0557; found: 201.0570.

Analytical data are in accordance with those reported in the literature.[21]

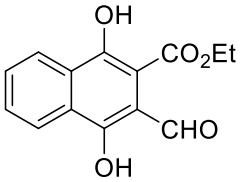
Ethyl 3-(bromomethyl)-1,4-dioxo-1,4-dihydronaphthalene-2-carboxylate (12):



Purification by column chromatography (Heptane/Ethyl acetate, 7:3). yield= 56%, 36 mg, afforded as a white wax.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.1, 3.0 Hz, 1H), 8.10 (dd, *J* = 5.5, 3.6 Hz, 1H), 7.80 (d, *J* = 3.4 Hz, 1H), 7.78 (d, *J* = 3.2 Hz, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 4.38 (s, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.2, 181.6, 163.3, 141.6, 139.6, 134.6, 134.6, 131.4, 127.0, 126.7, 62.7, 20.7, 14.2. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{10}{}^{79}BrO_3]^-$: 320.9767; found: 320.9740.

Ethyl 3-formyl-1,4-dihydroxy-2-naphthoate (13):



Purification by column chromatography (Heptane/Ethyl acetate, 9:1). yield= 58%, 30 mg, afforded as a white solid. M.p. 104.2-105.4 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 13.99 (s, 1H), 12.16 (s, 1H), 10.49 (s, 1H), 8.42 – 8.34 (m, 2H), 7.76 – 7.64 (m, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4,

170.8, 158.4, 155.9, 130.9, 130.1, 129.3, 128.2, 124.6, 124.4, 109.7, 101.4, 62.5, 14.3. HRMS (MALDI-FT ICR): *m/z* calcd. for $[C_{14}H_{11}O_5]^-$: 259.0612; found: 259.0603.

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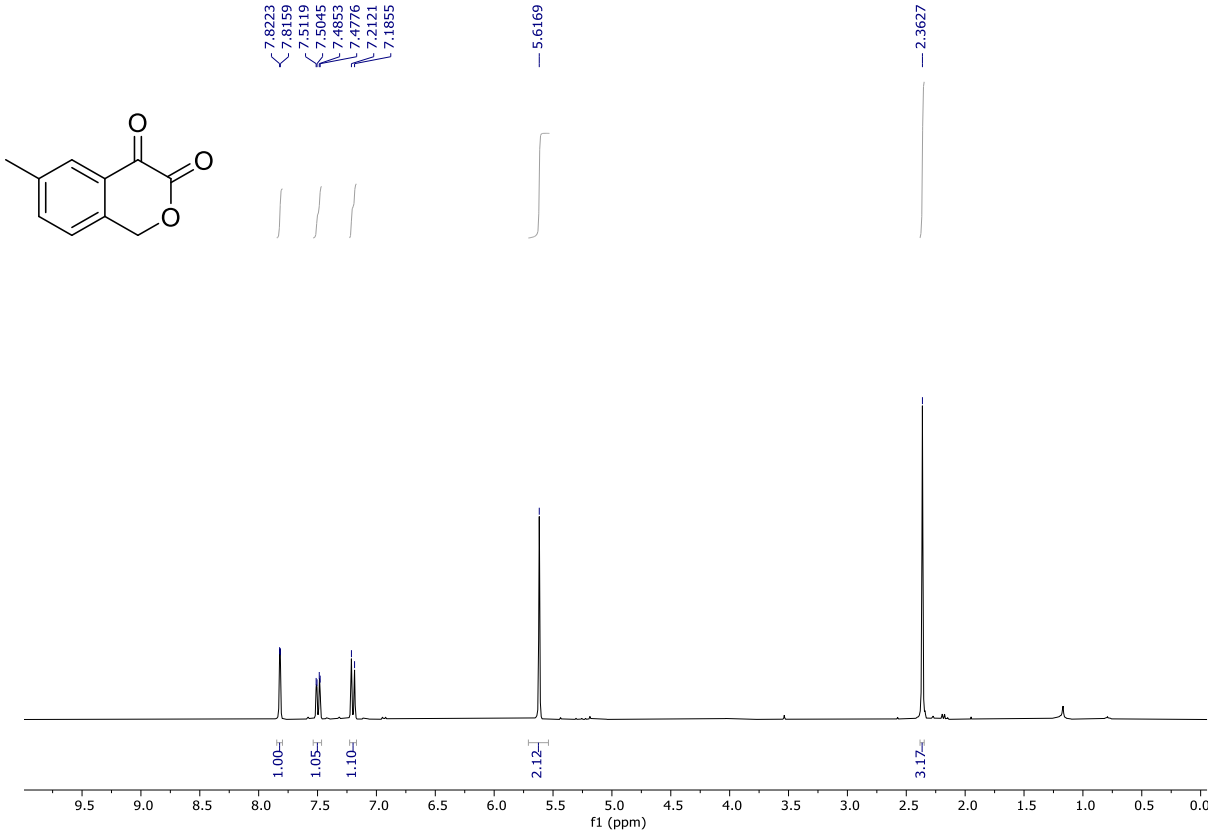
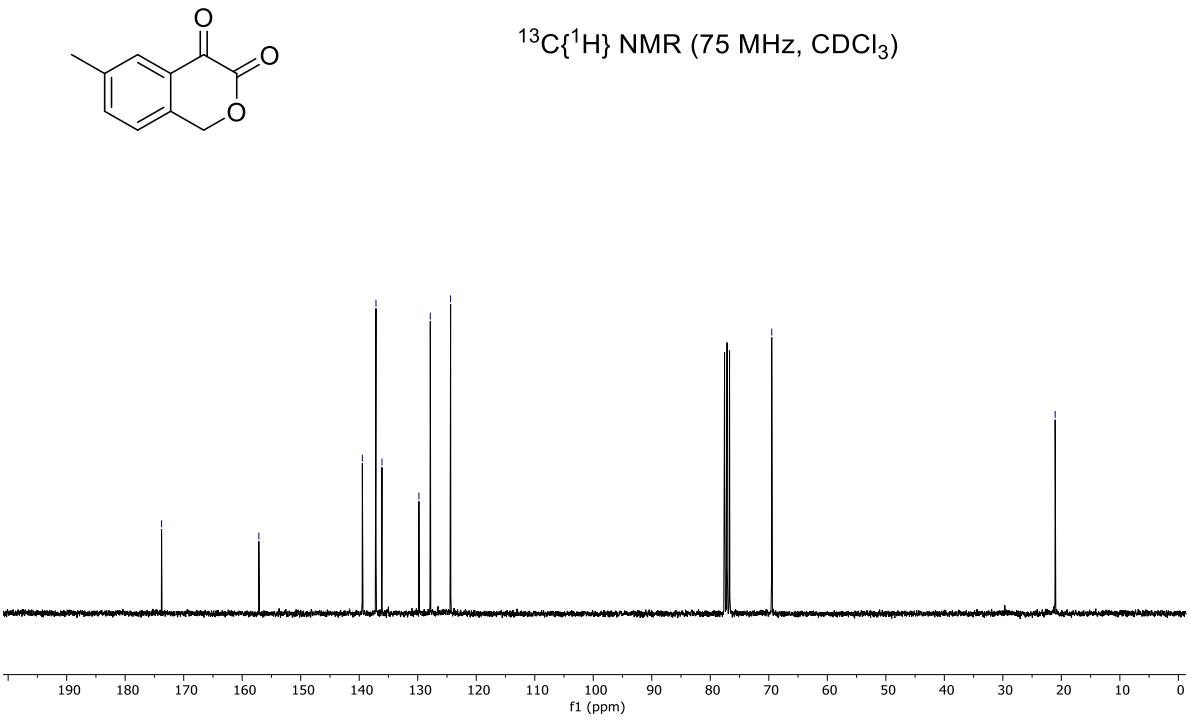
9. NMR Spectra

6-methylisochromane-3,4-dione (1c):

^{1}H NMR (300 MHz, $CDCl_3$)

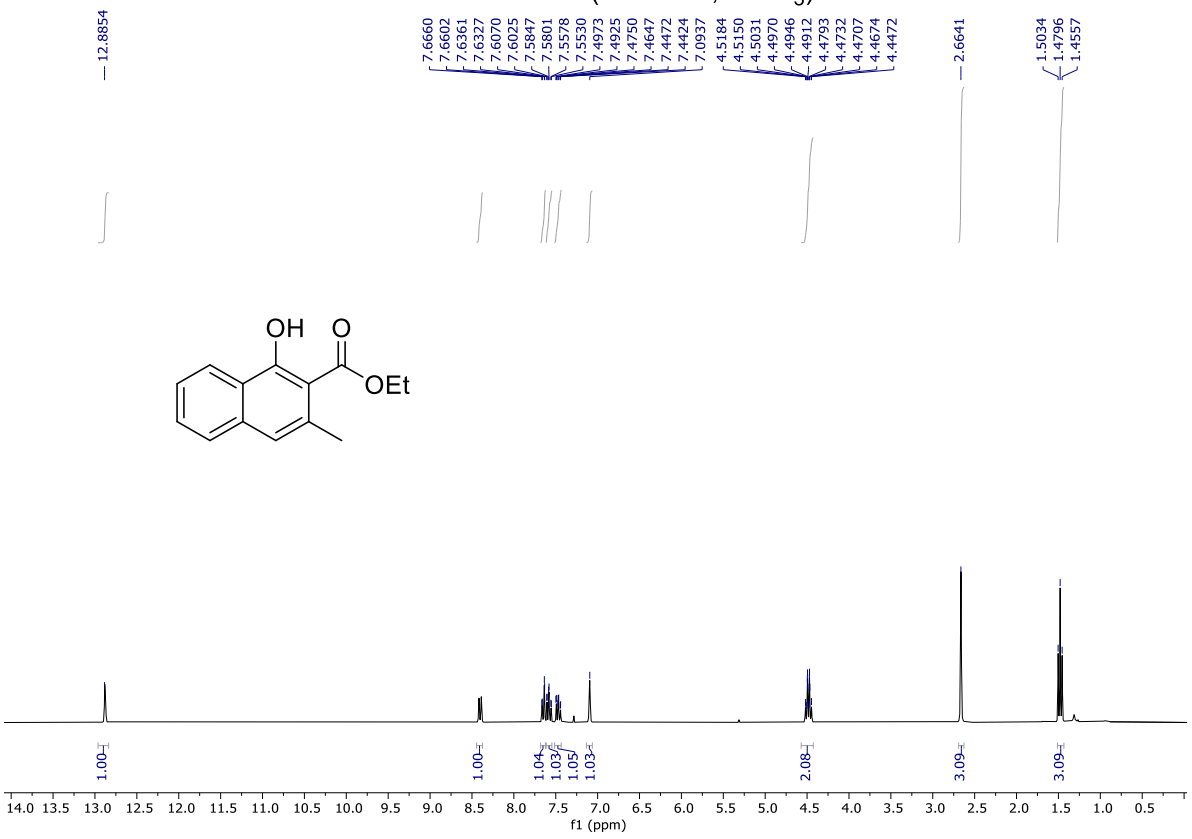


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

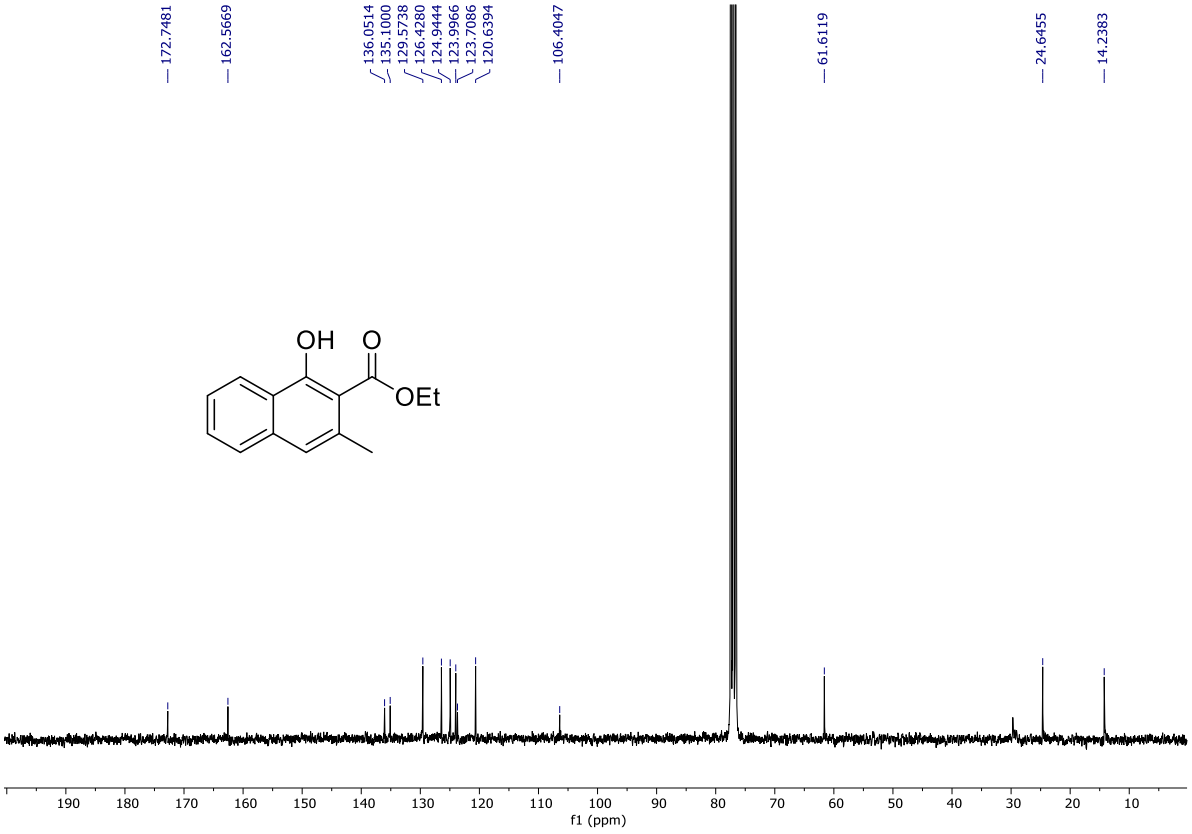


Ethyl 1-hydroxy-3-methyl-2-naphthoate (3a):

^{1}H NMR (300 MHz, $CDCl_3$)

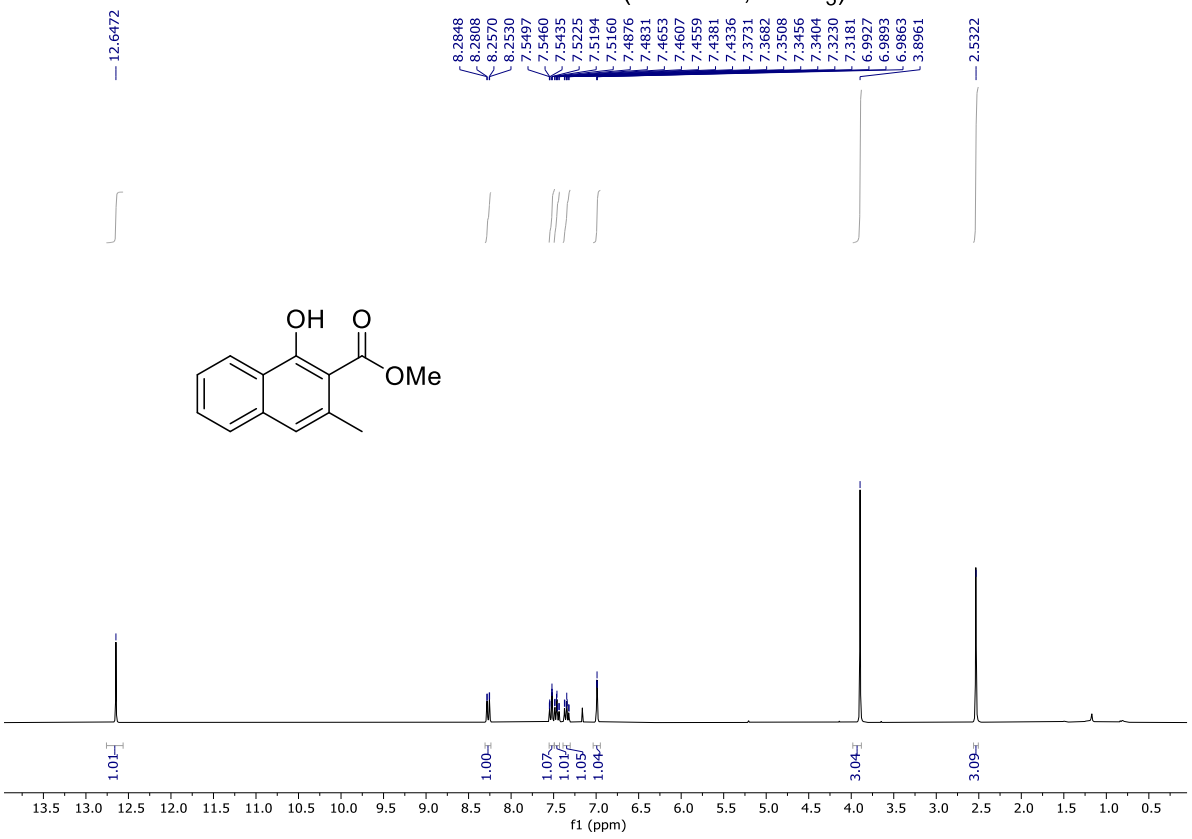


^{1}H NMR (300 MHz, $CDCl_3$)

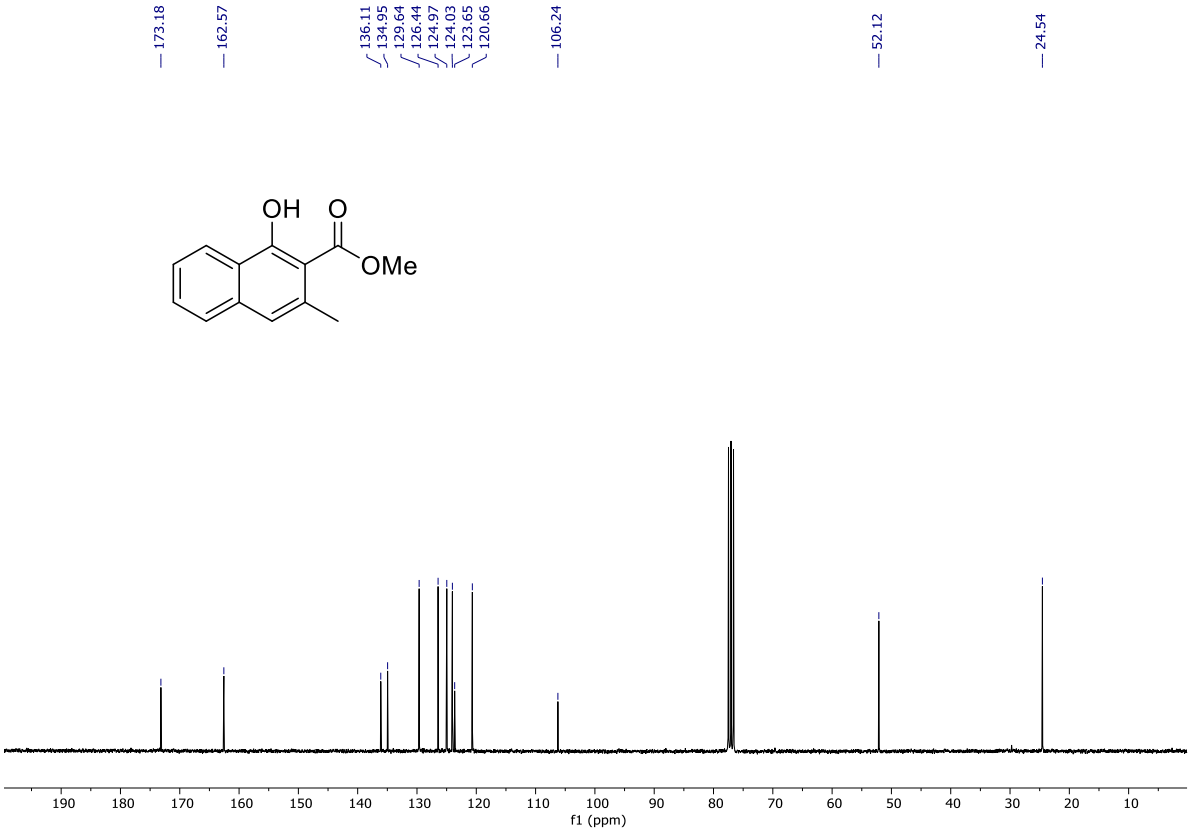


Methyl 1-hydroxy-3-methyl-2-naphthoate (3b):

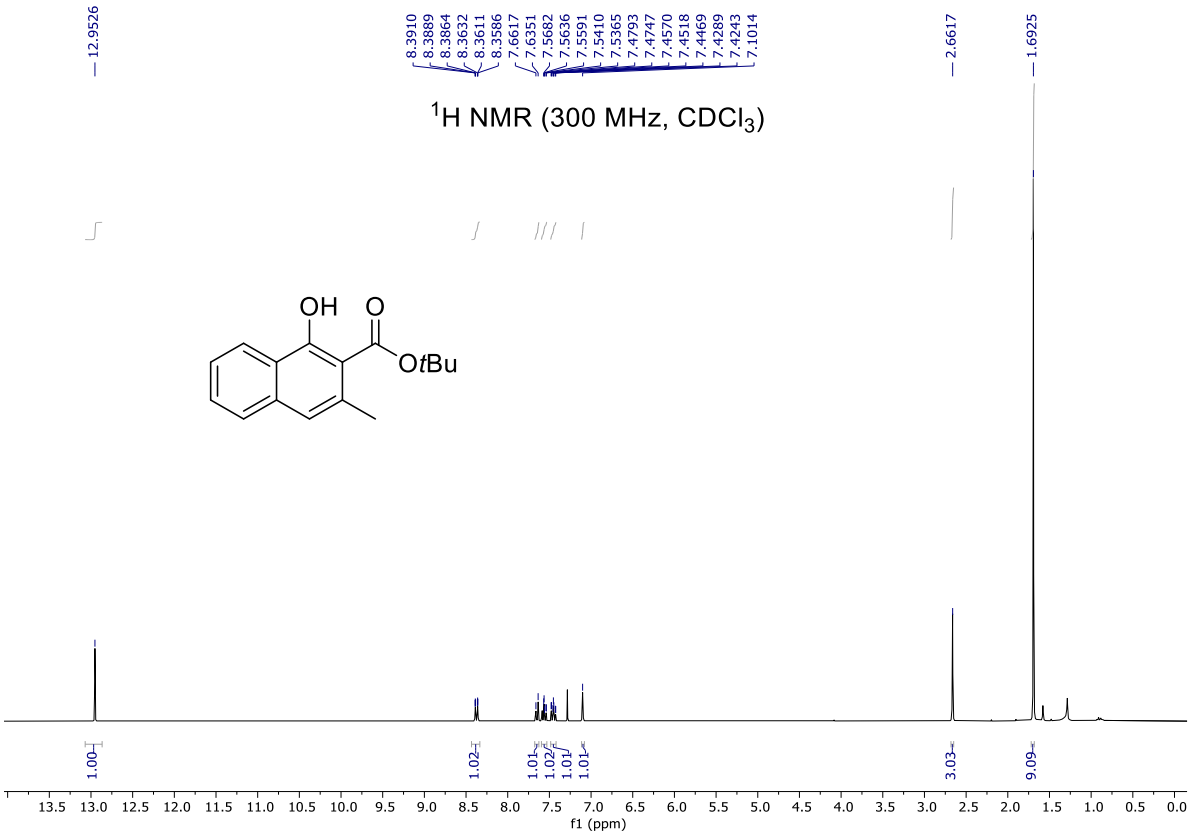
^{1}H NMR (300 MHz, $CDCl_3$)

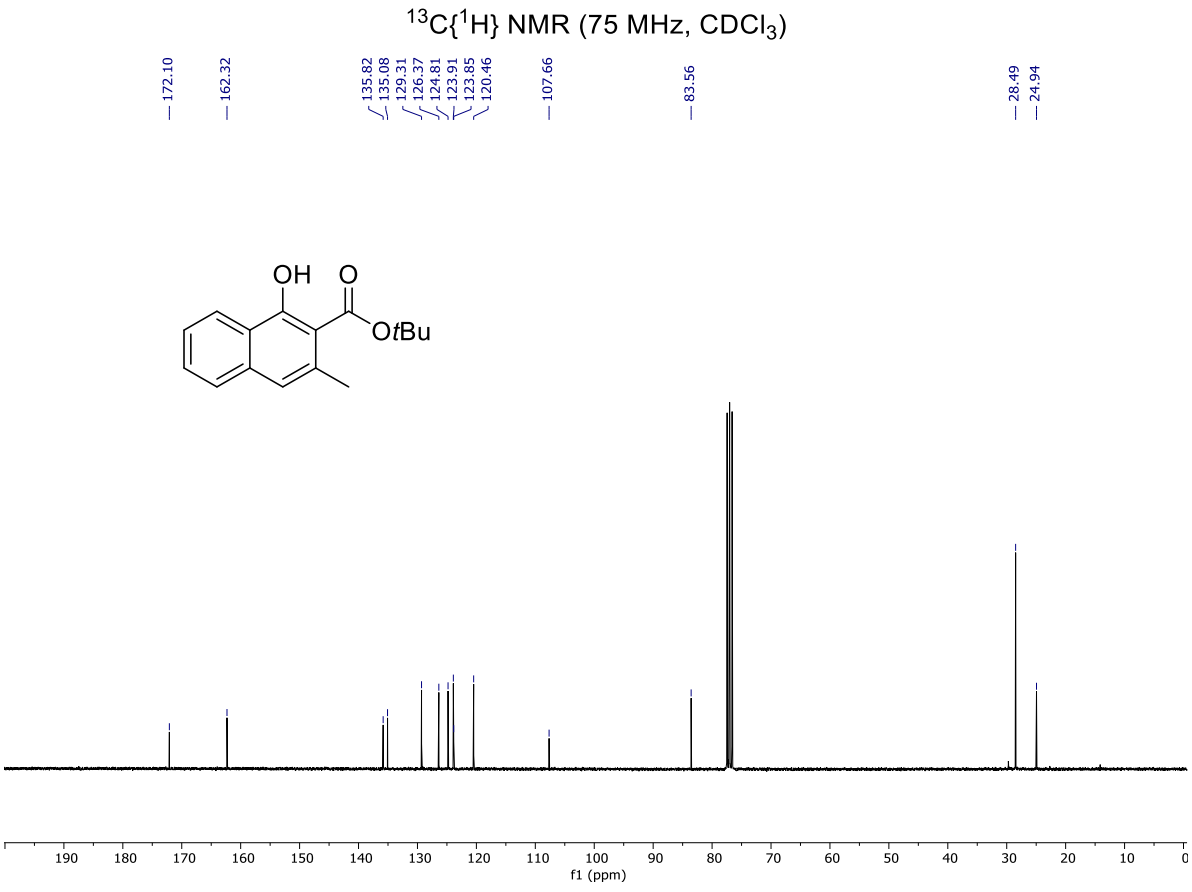


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



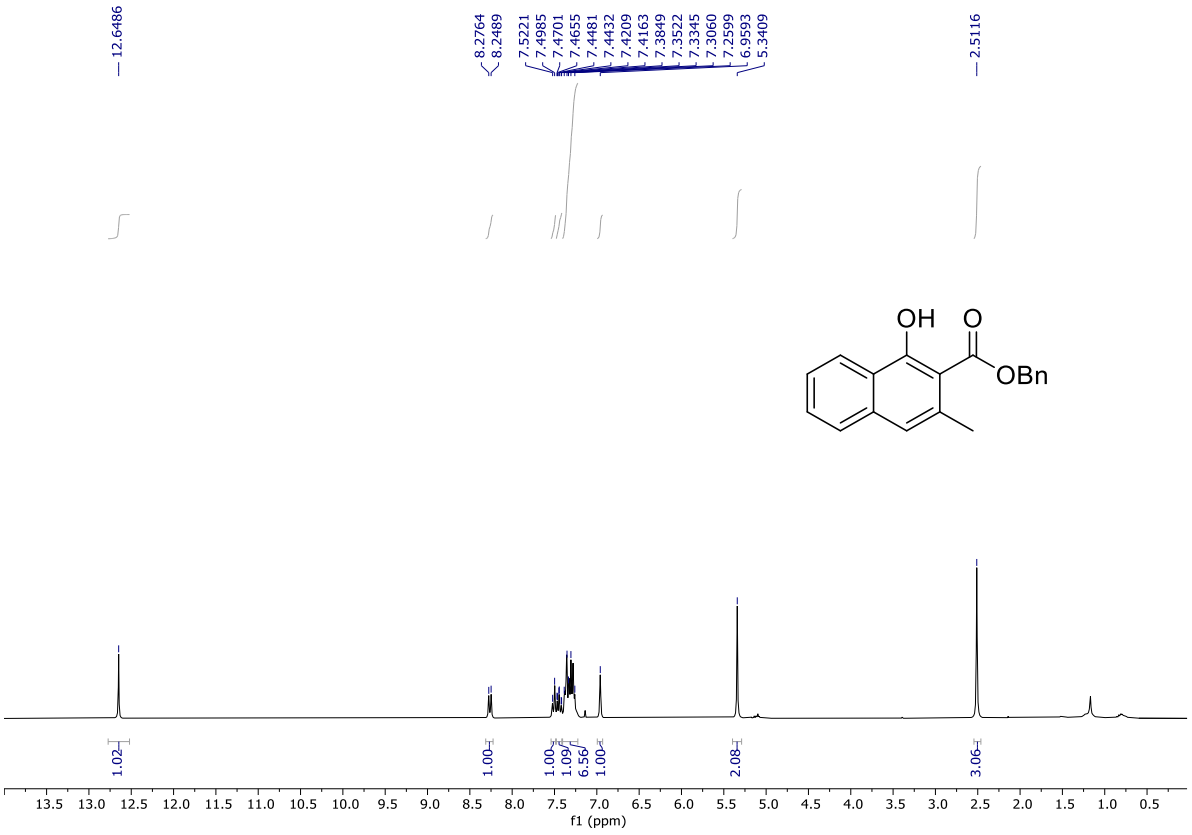
***Tert*-butyl 1-hydroxy-3-methyl-2-naphthoate (3c):**



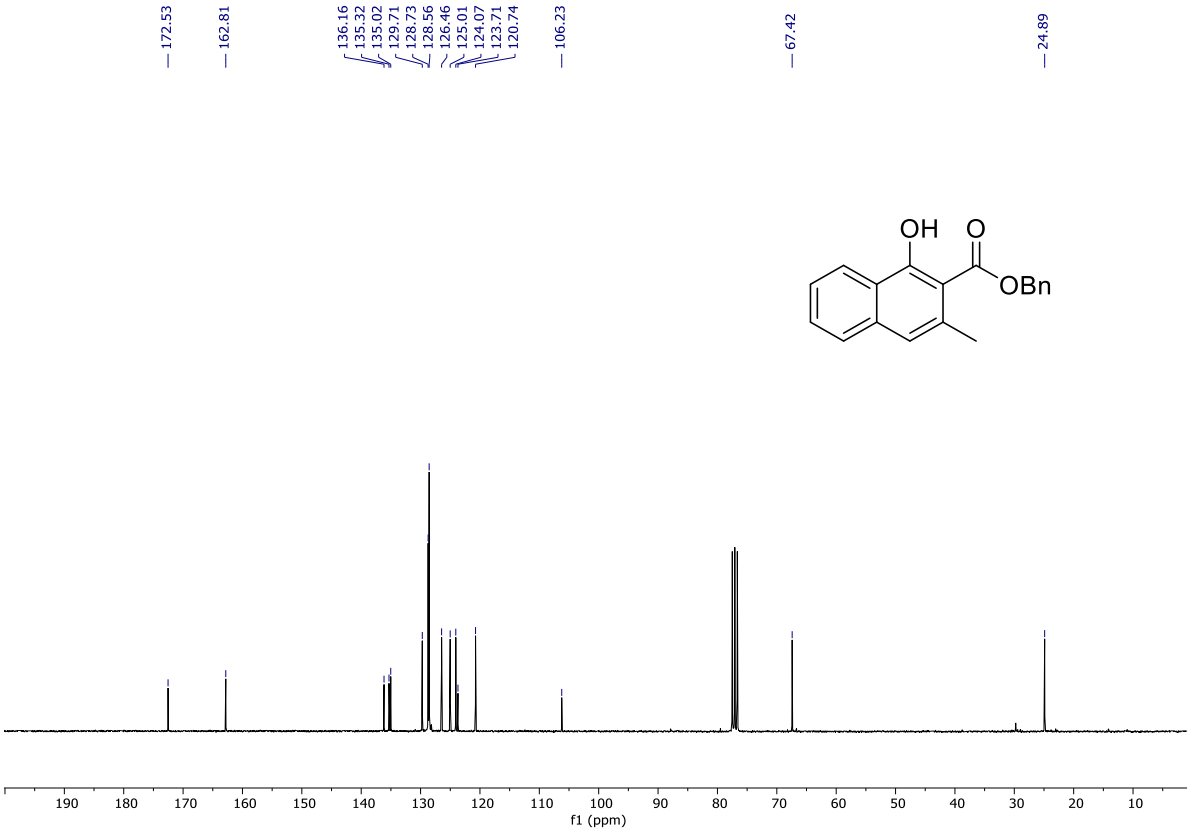


Benzyl 1-hydroxy-3-methyl-2-naphthoate (3d):

^{1}H NMR (300 MHz, $CDCl_3$)

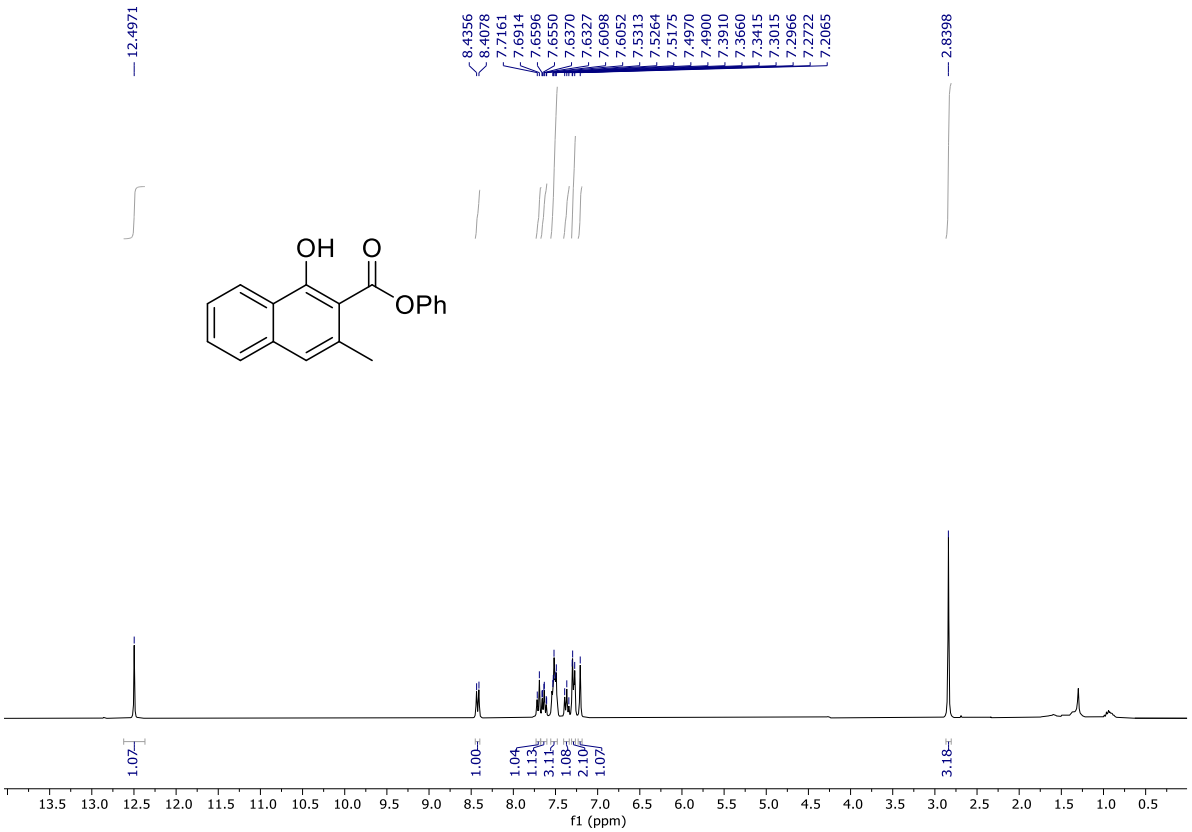


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

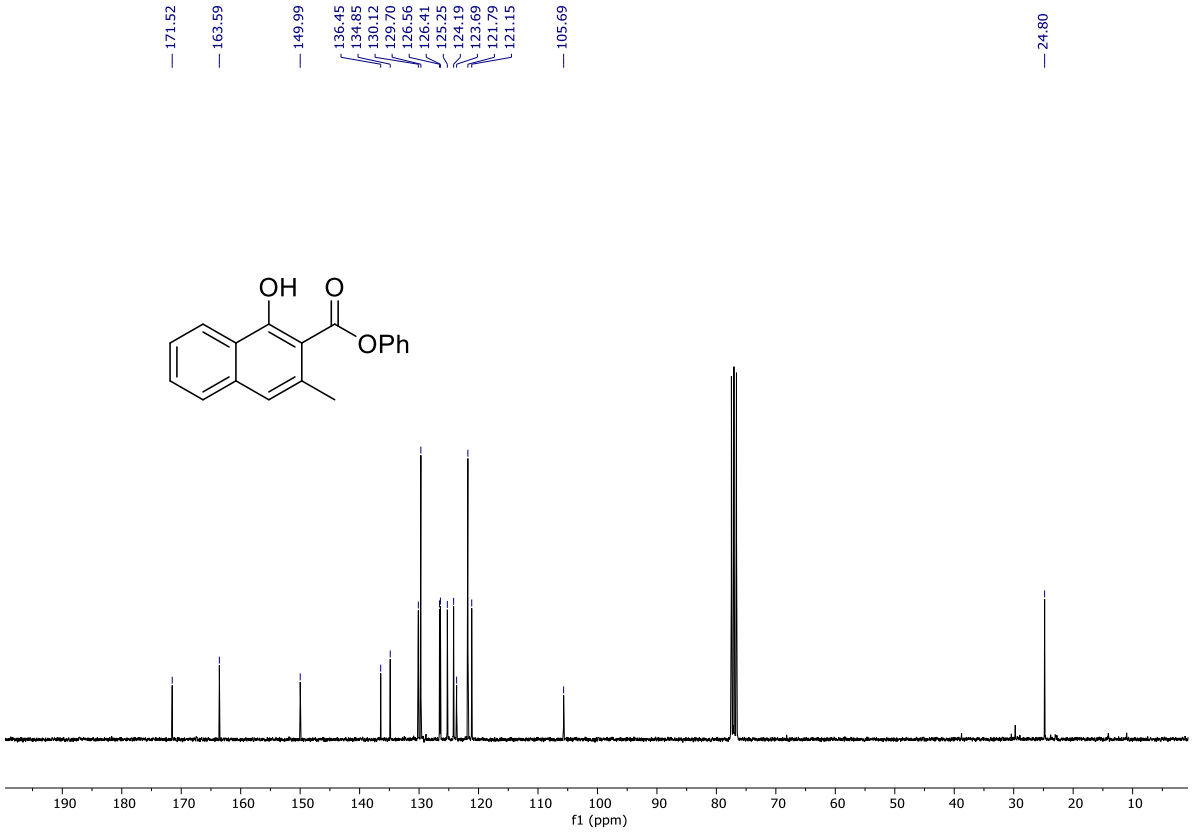


Phenyl 1-hydroxy-3-methyl-2-naphthoate (3e):

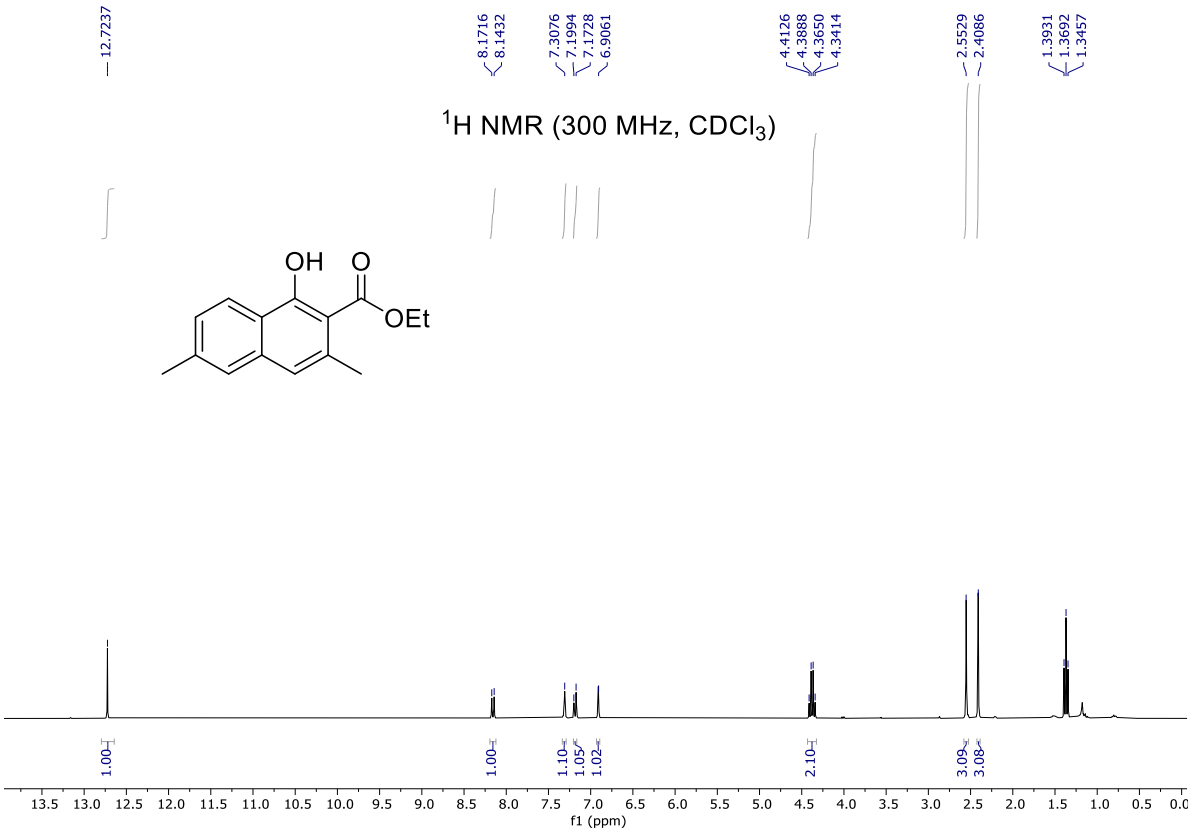
^{1}H NMR (300 MHz, $CDCl_3$)

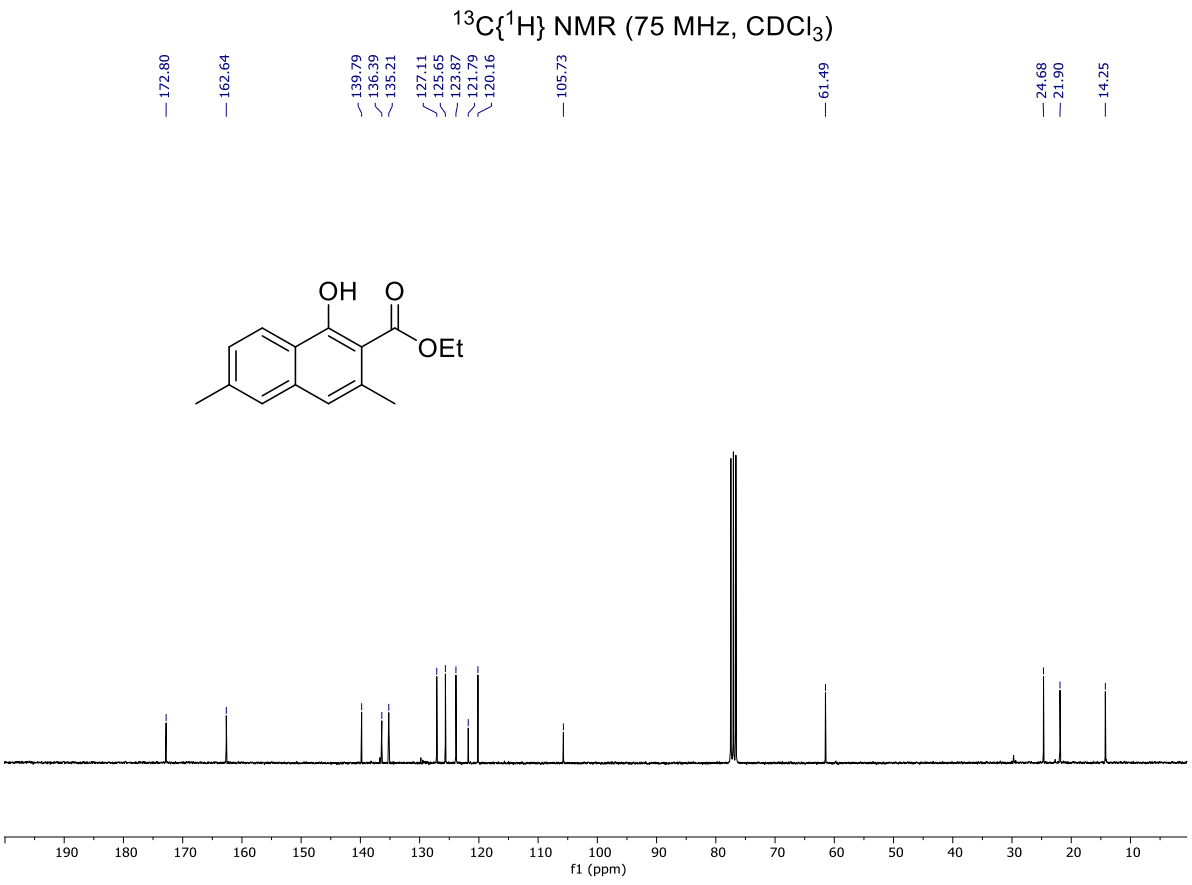


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

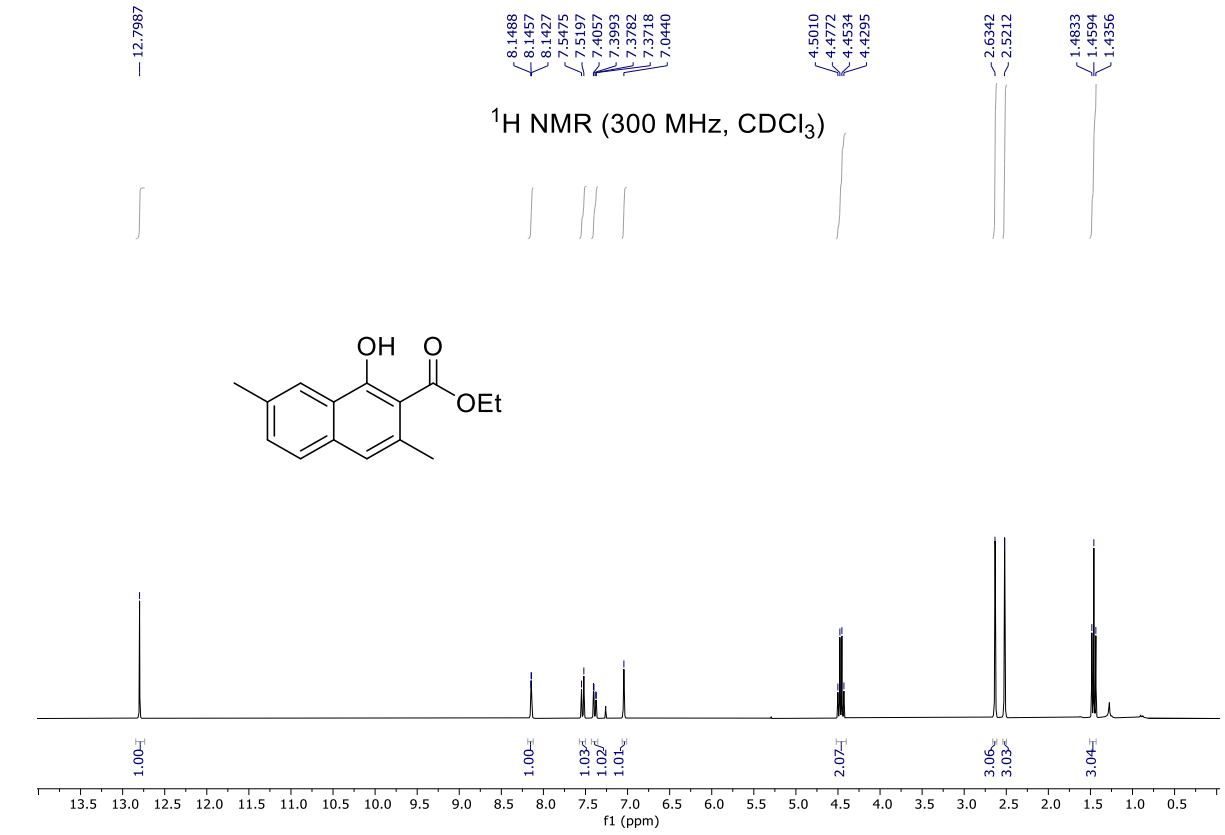


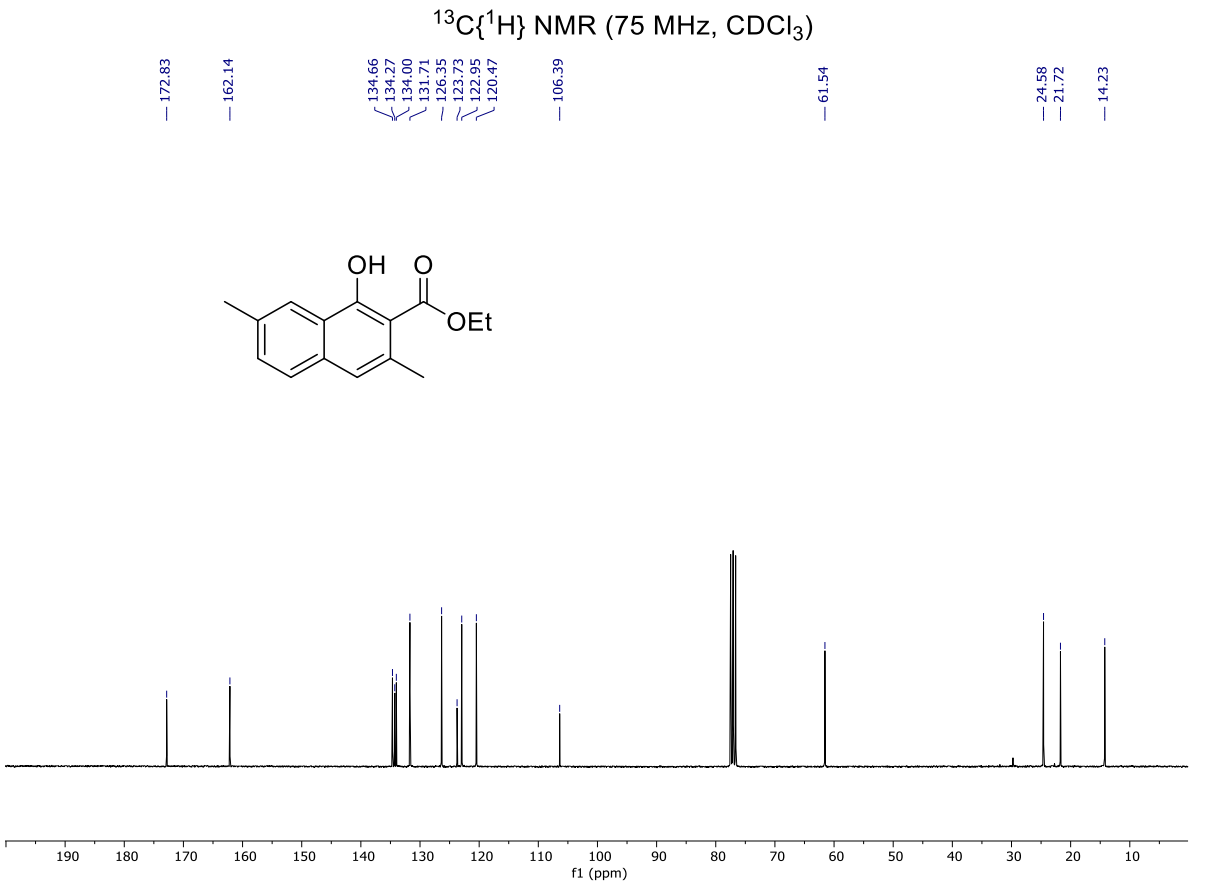
Ethyl 1-hydroxy-3,6-dimethyl-2-naphthoate (3f):



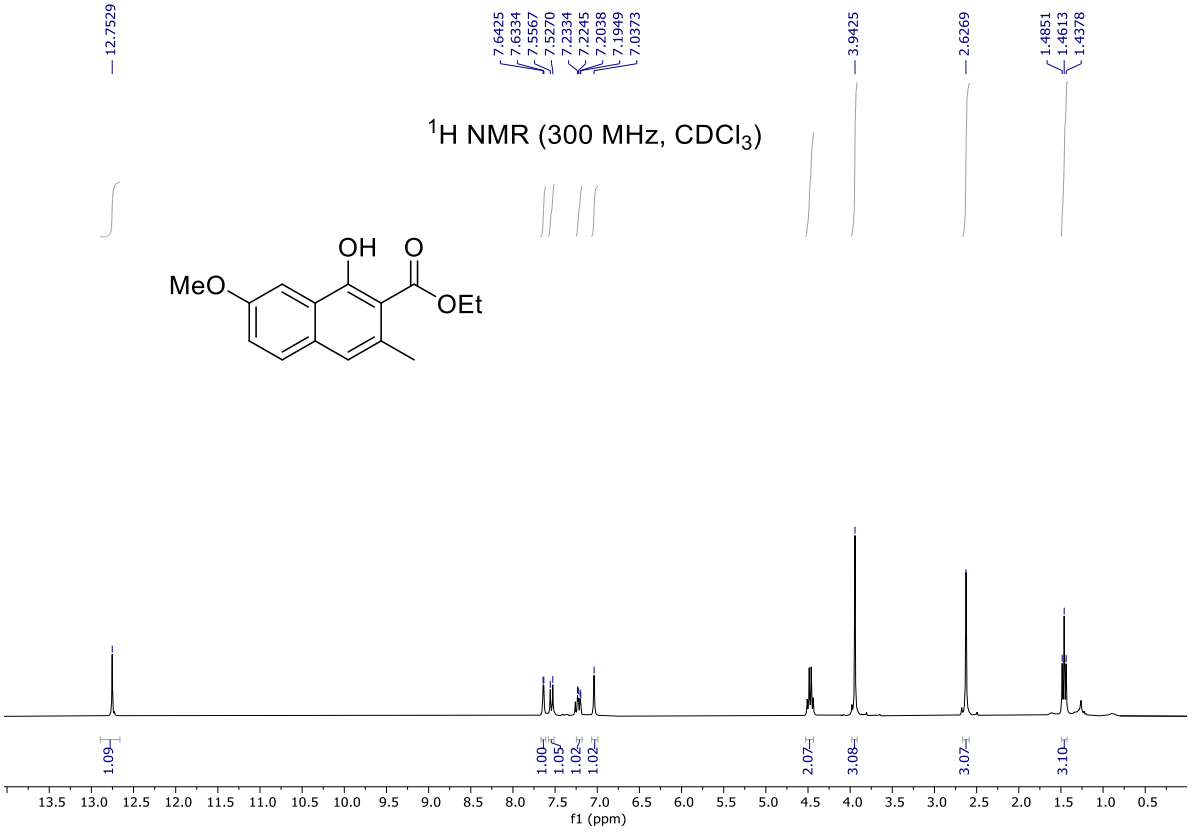


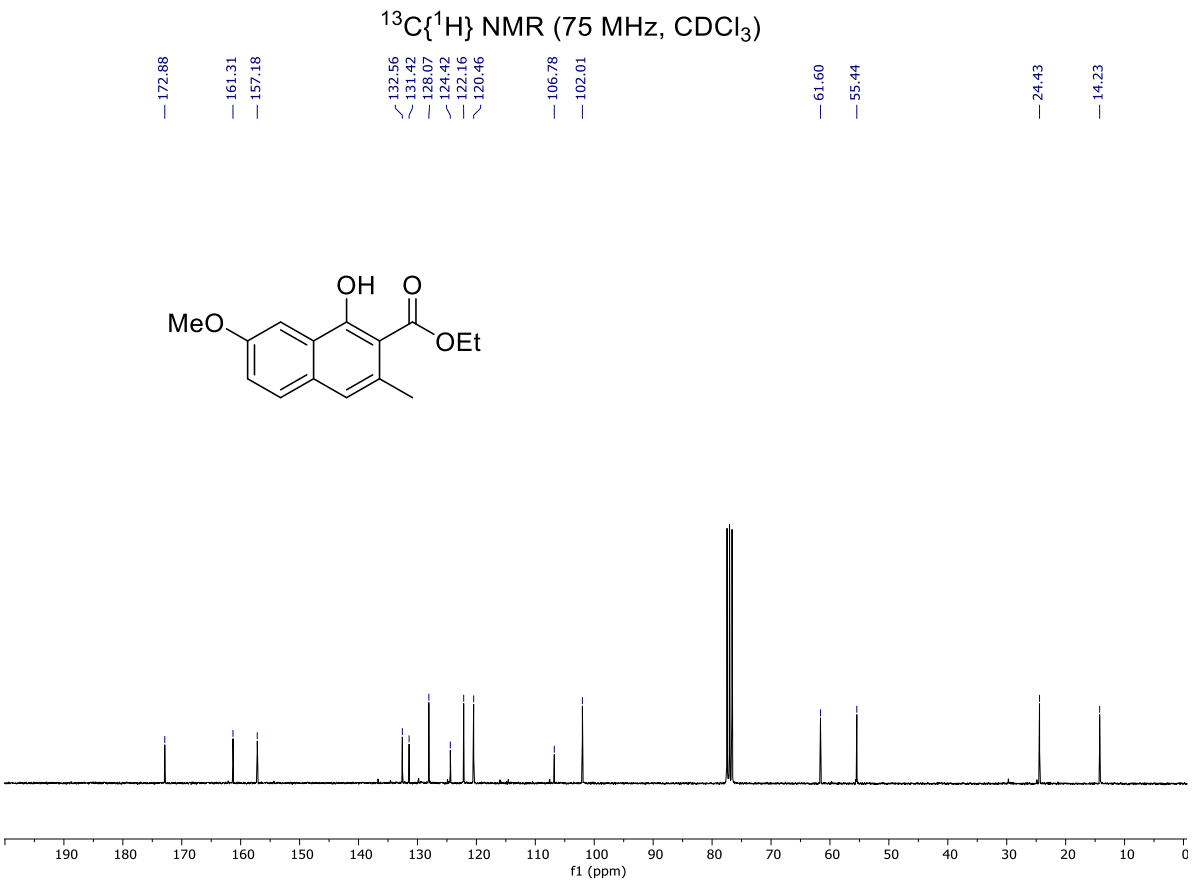
Ethyl 1-hydroxy-3,7-dimethyl-2-naphthoate (3g):



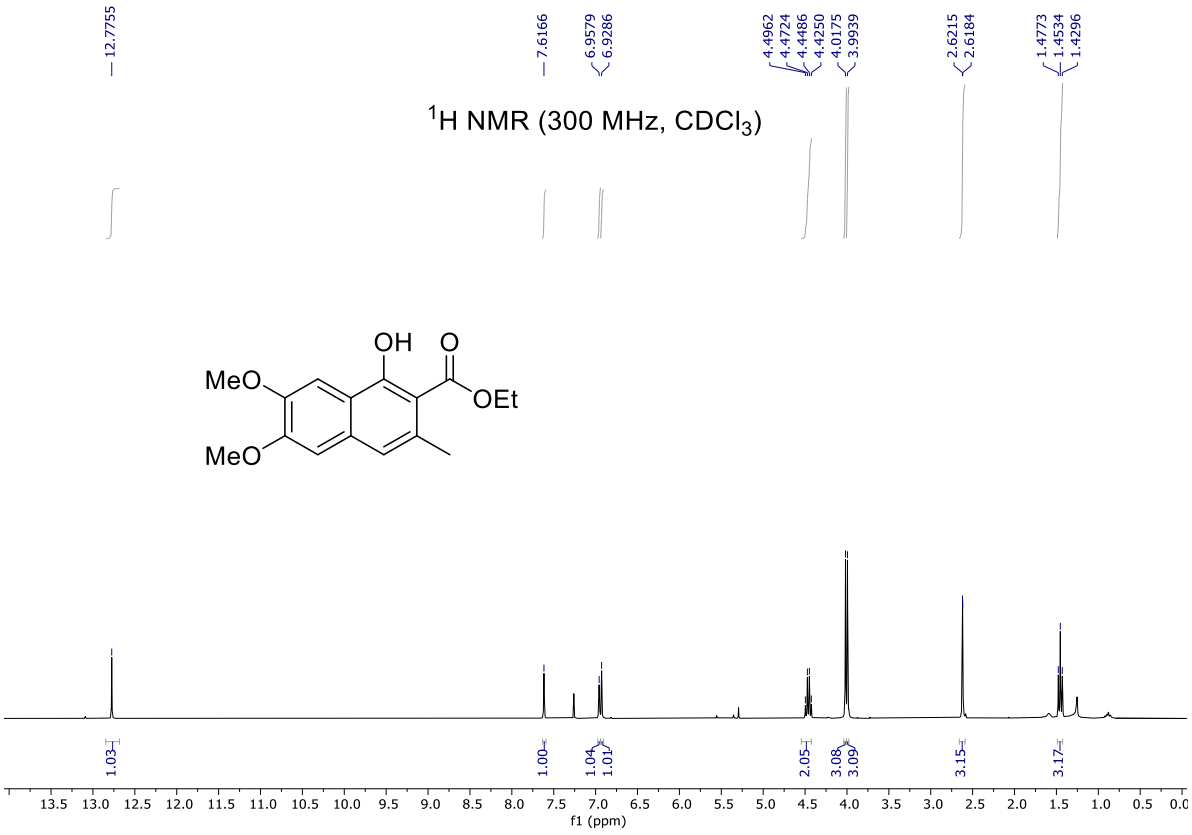


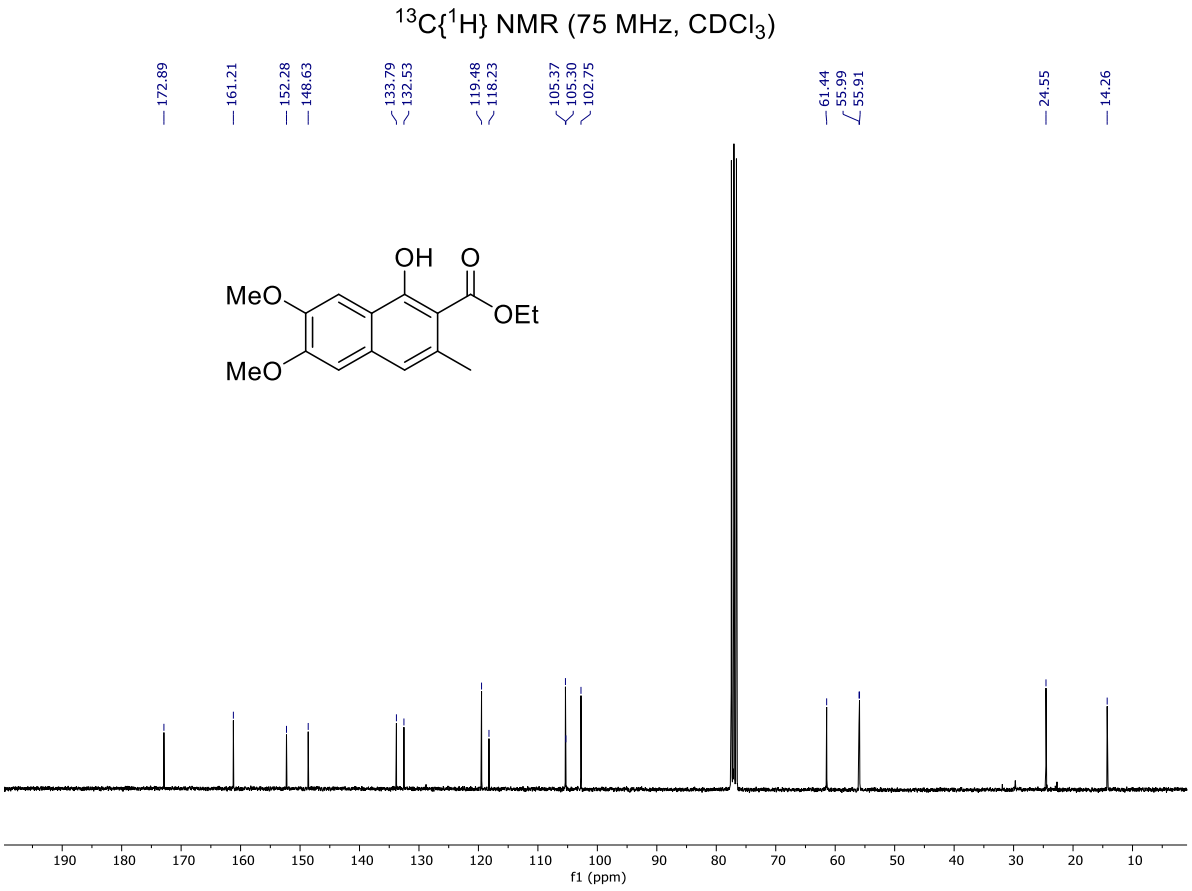
Ethyl 1-hydroxy-7-methoxy-3-methyl-2-naphthoate (3h):



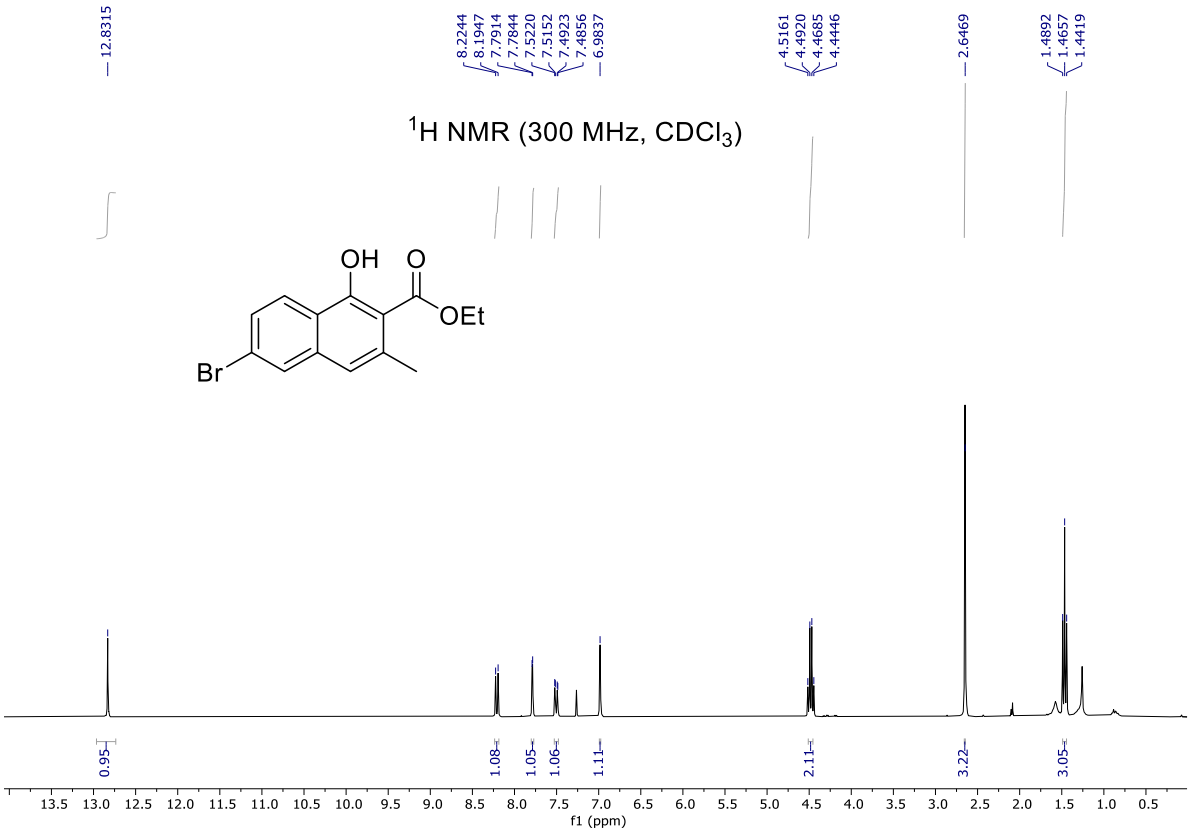


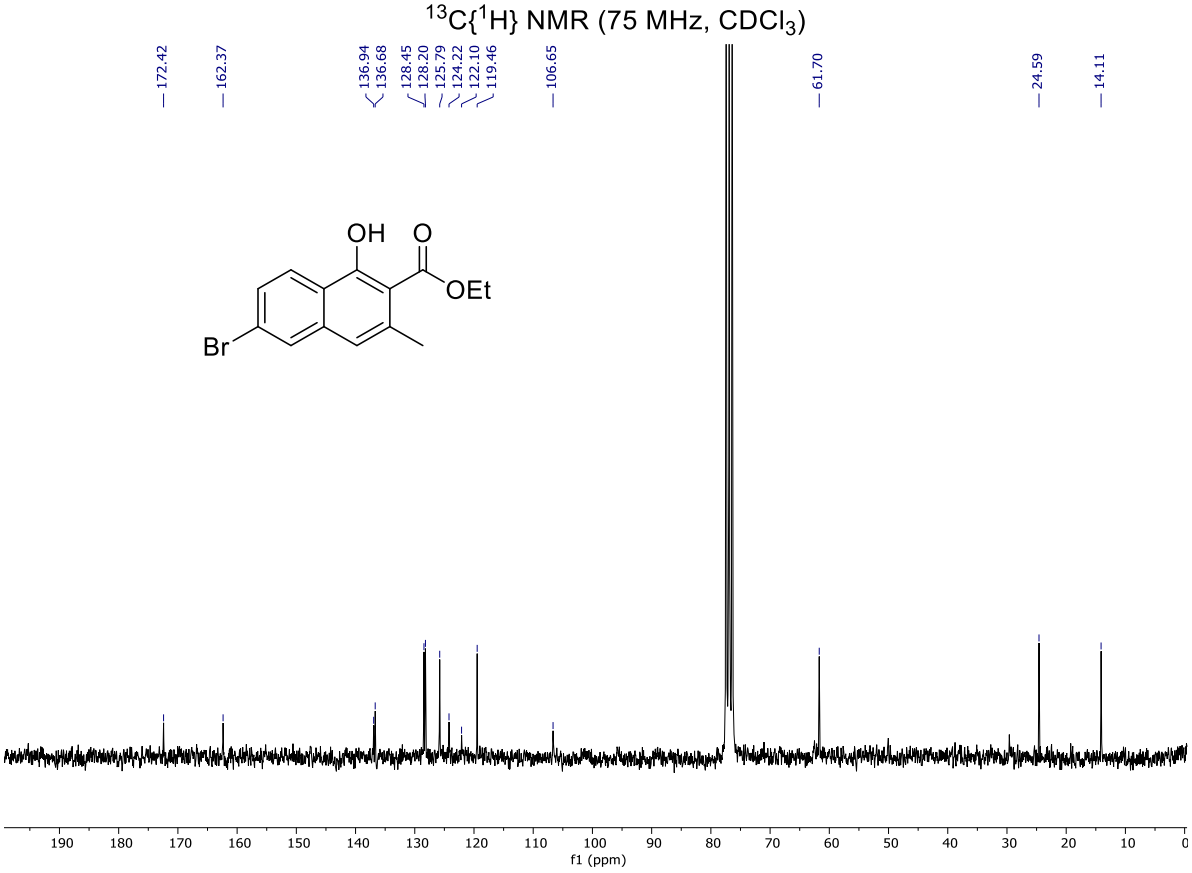
Ethyl 1-hydroxy-6,7-dimethoxy-3-methyl-2-naphthoate (3i):





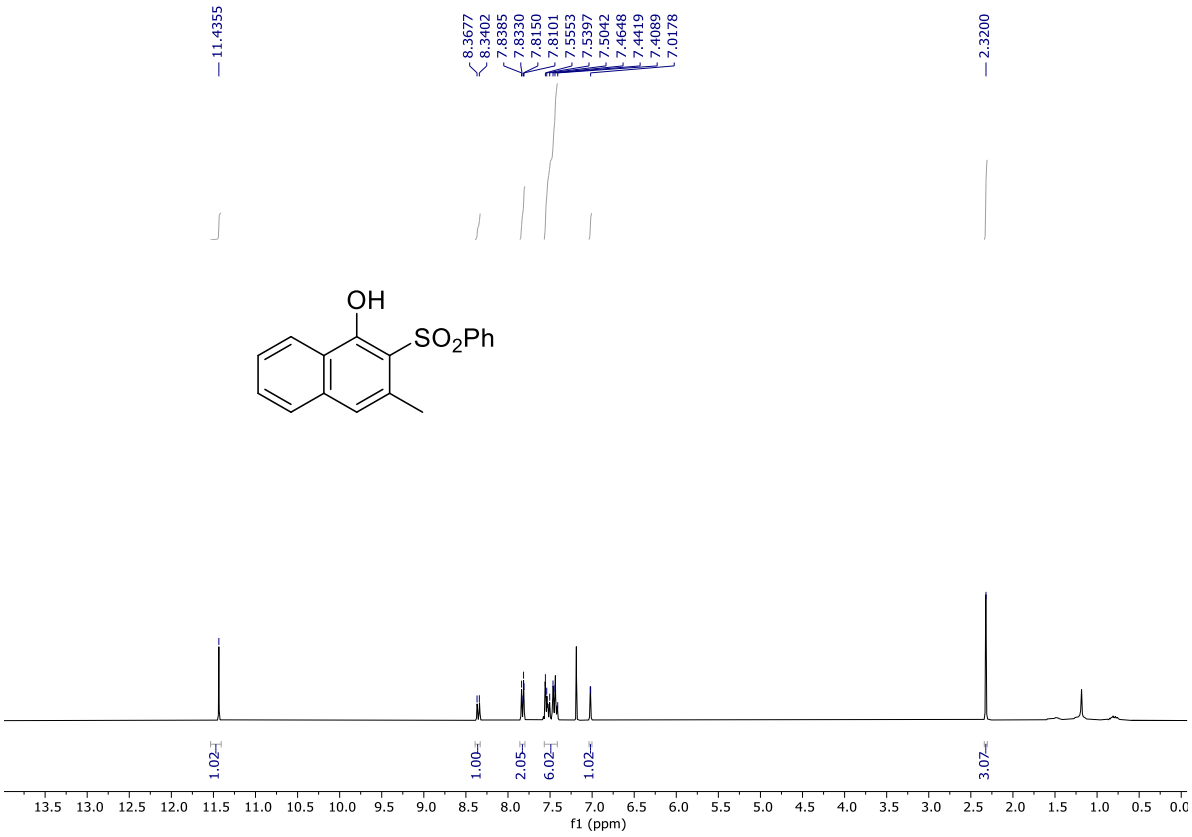
Ethyl 6-bromo-1-hydroxy-3-methyl-2-naphthoate (3j):



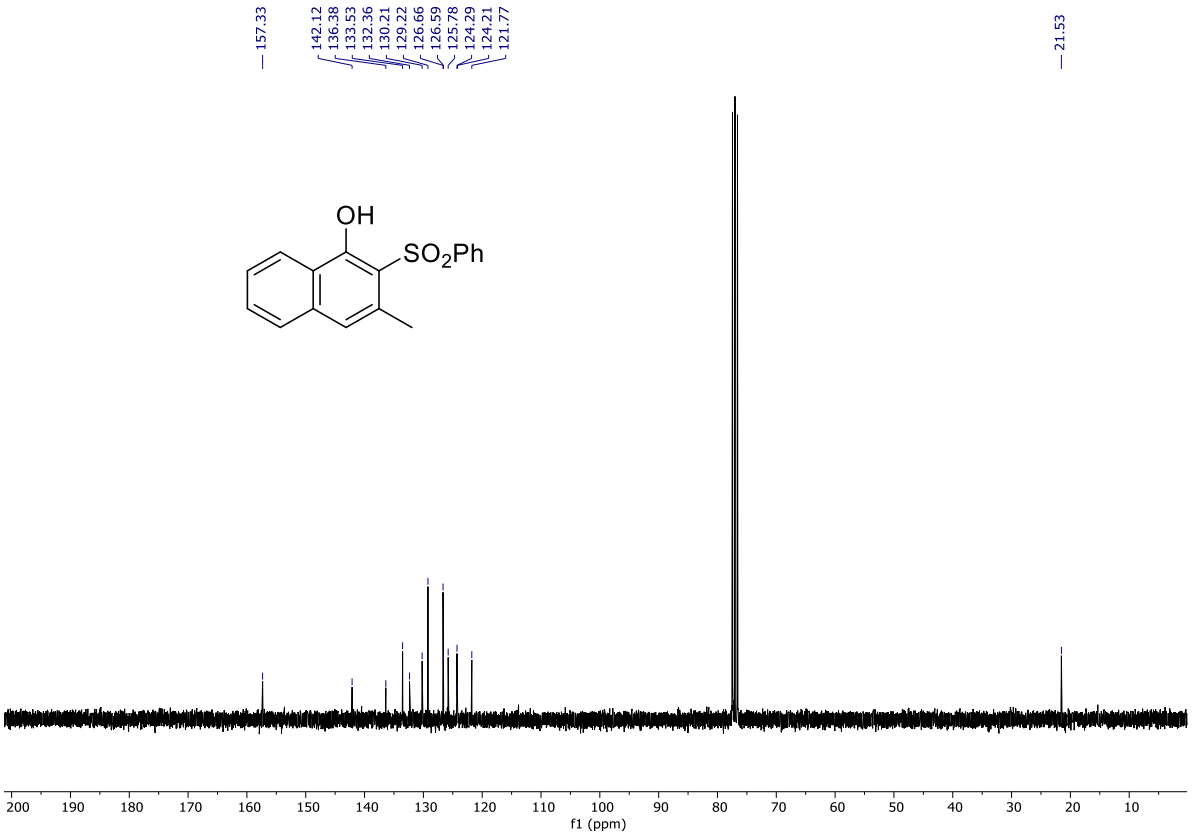


3-methyl-2-(phenylsulfonyl)naphthalen-1-ol (3k):

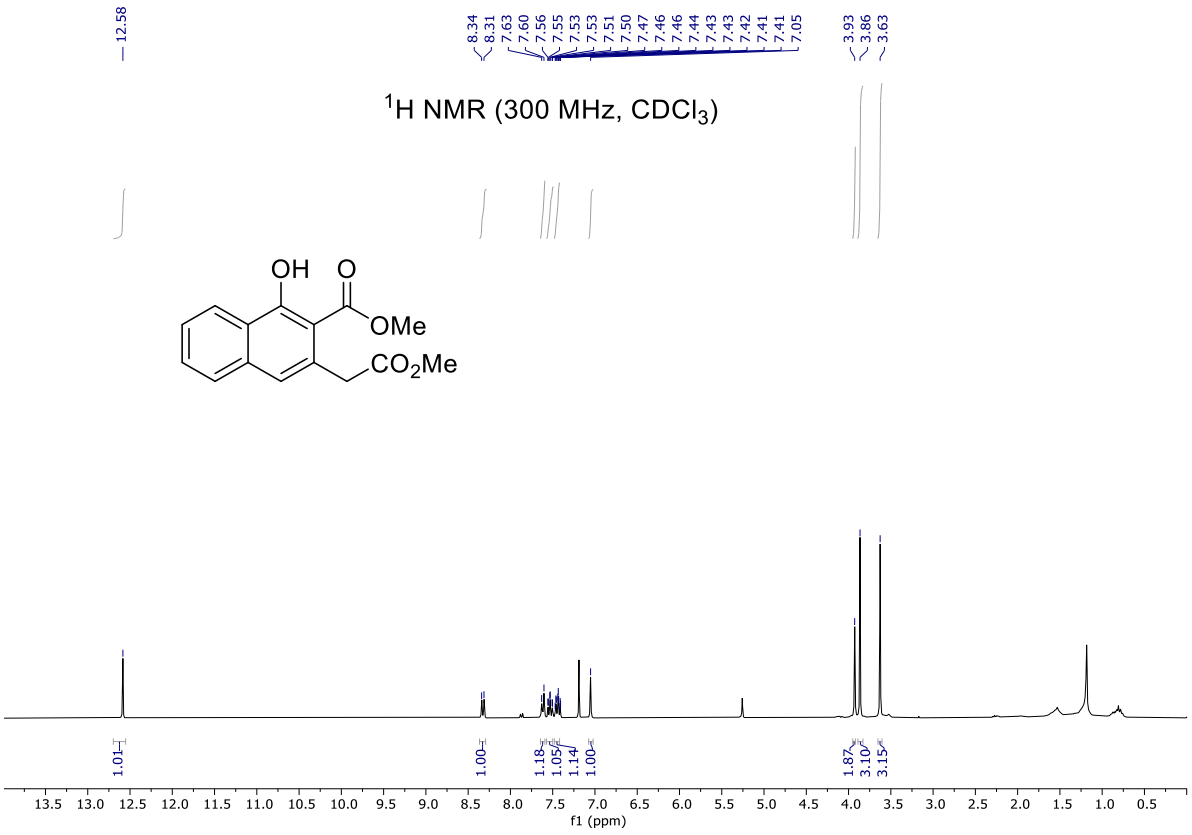
^{1}H NMR (300 MHz, $CDCl_3$)

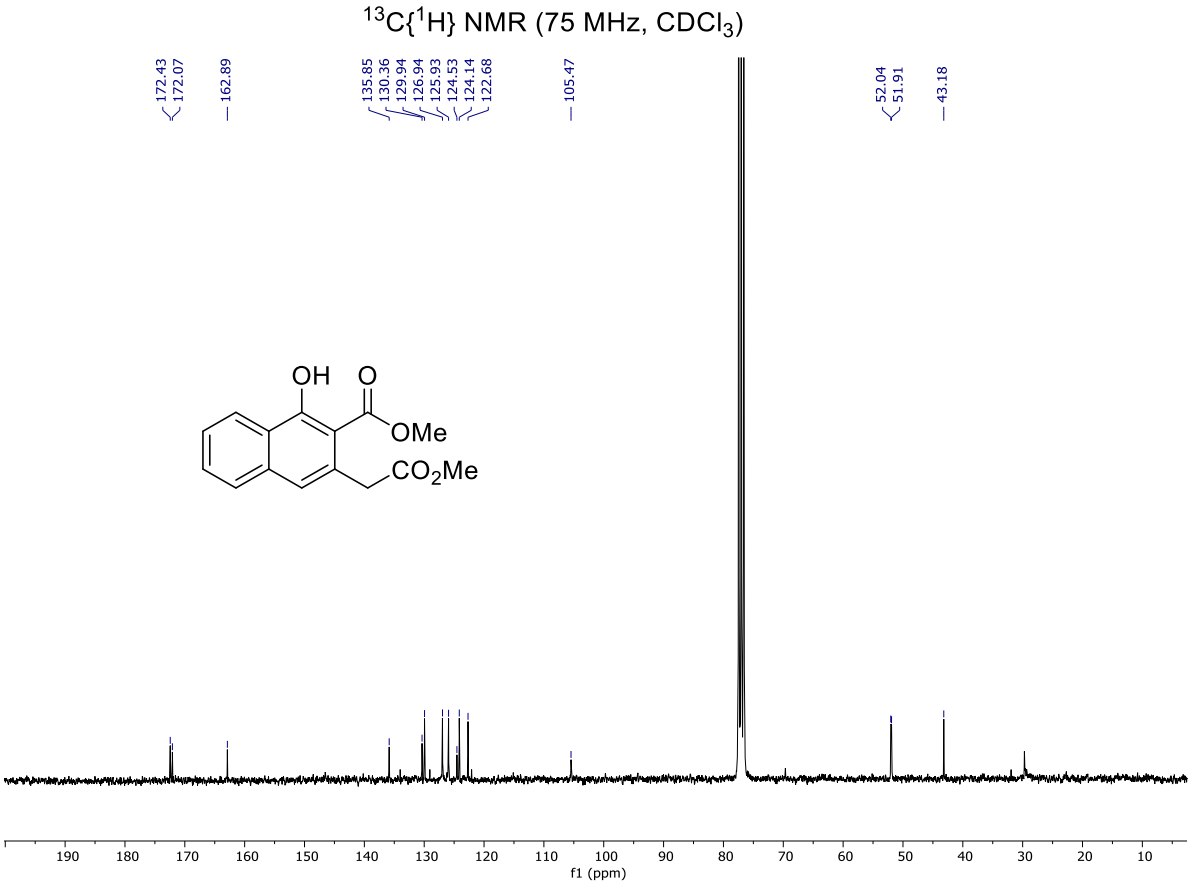


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

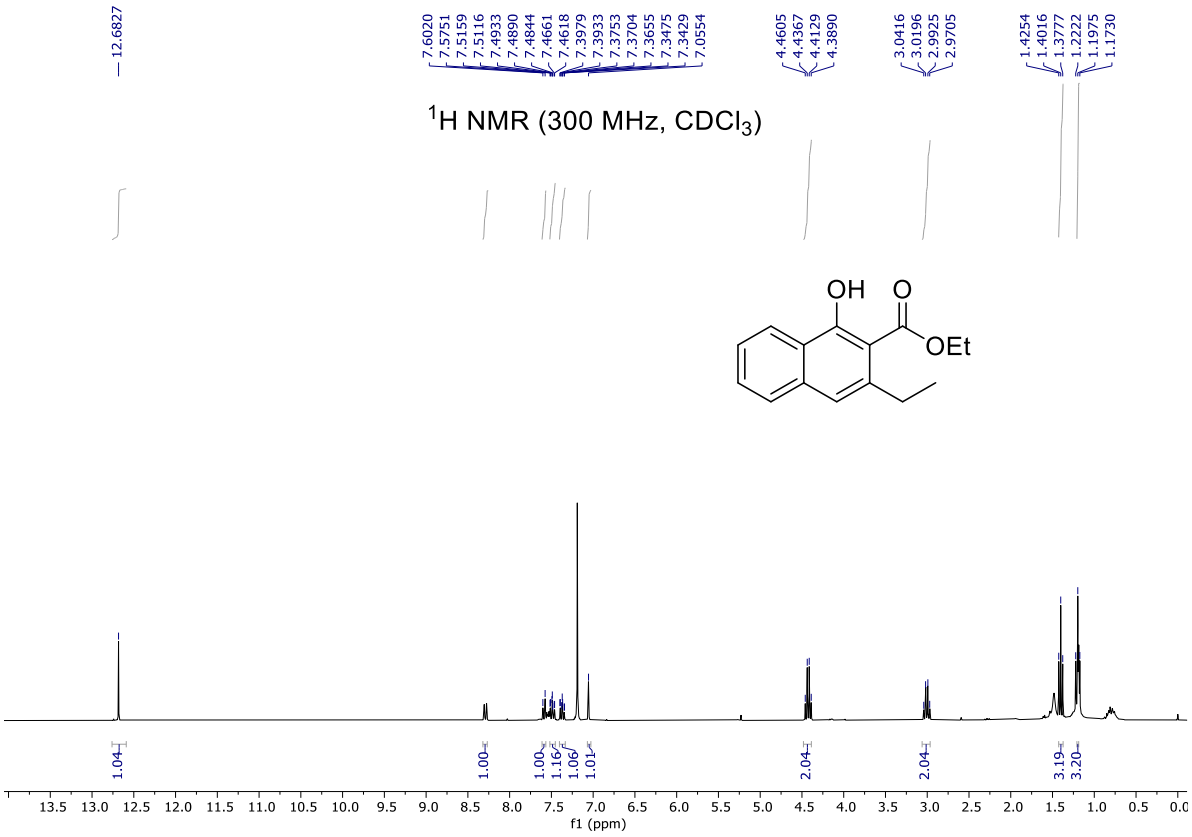


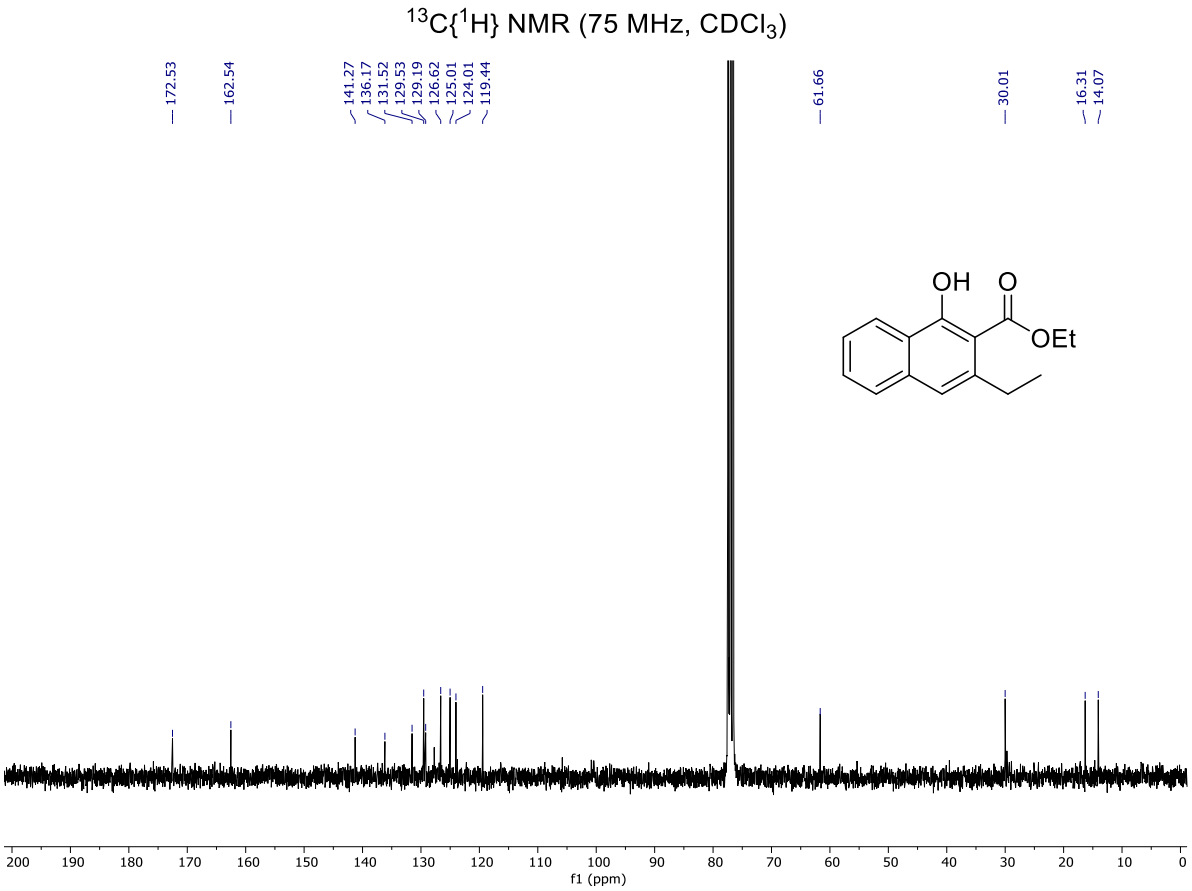
Methyl 1-hydroxy-3-(2-methoxy-2-oxoethyl)-2-naphthoate (3l):



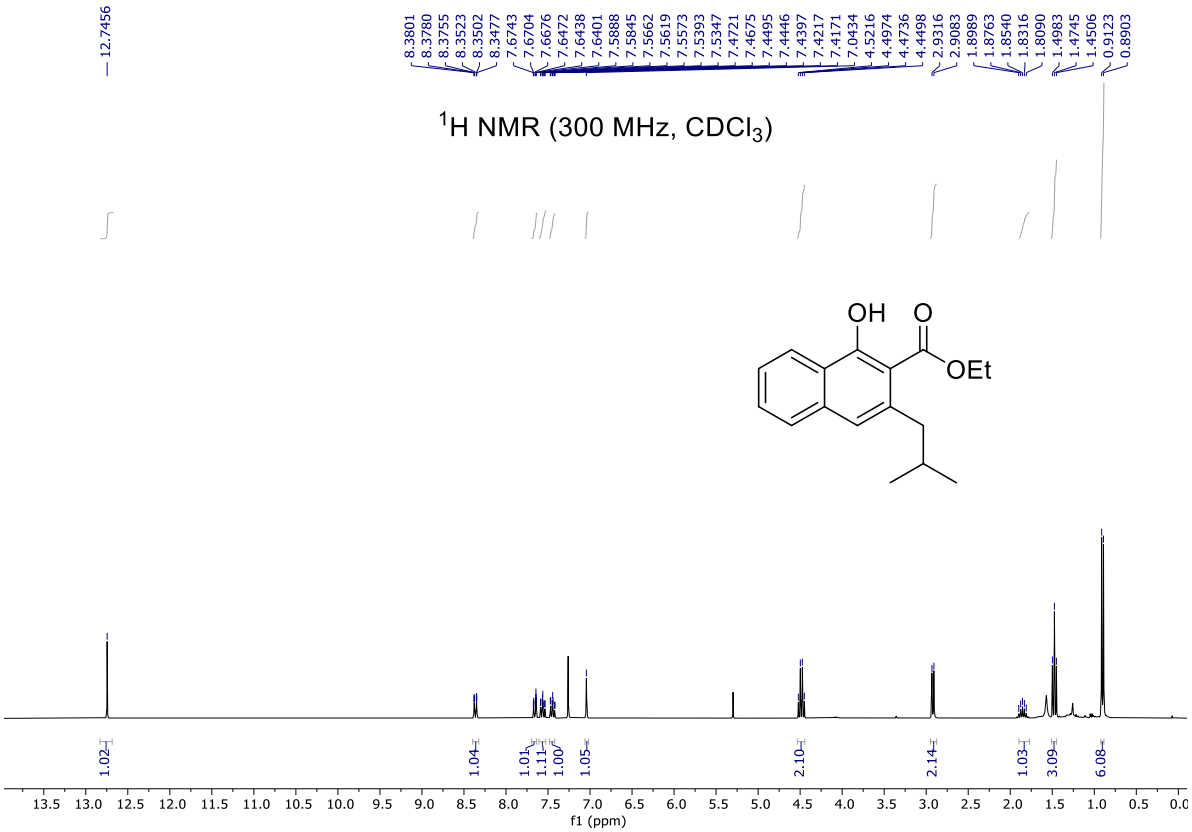


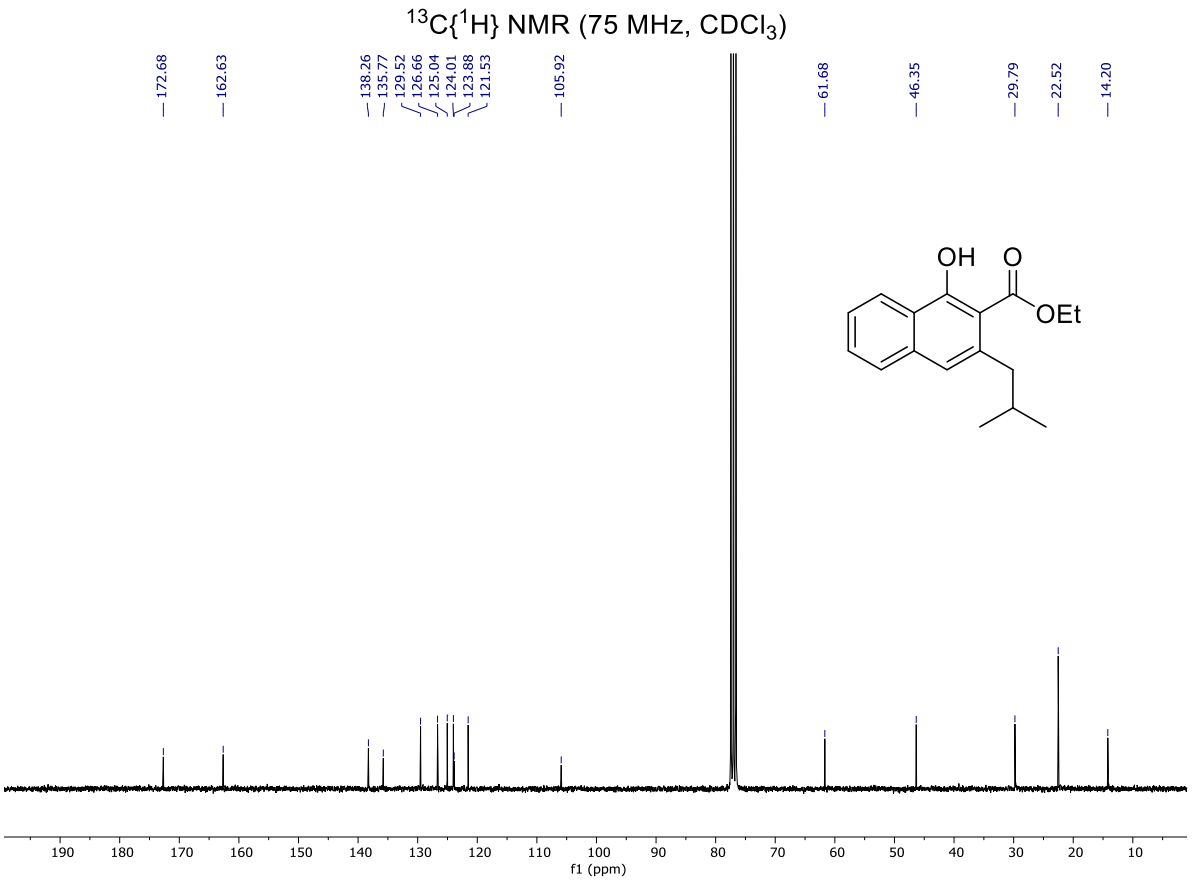
Ethyl 3-ethyl-1-hydroxy-2-naphthoate (3m):





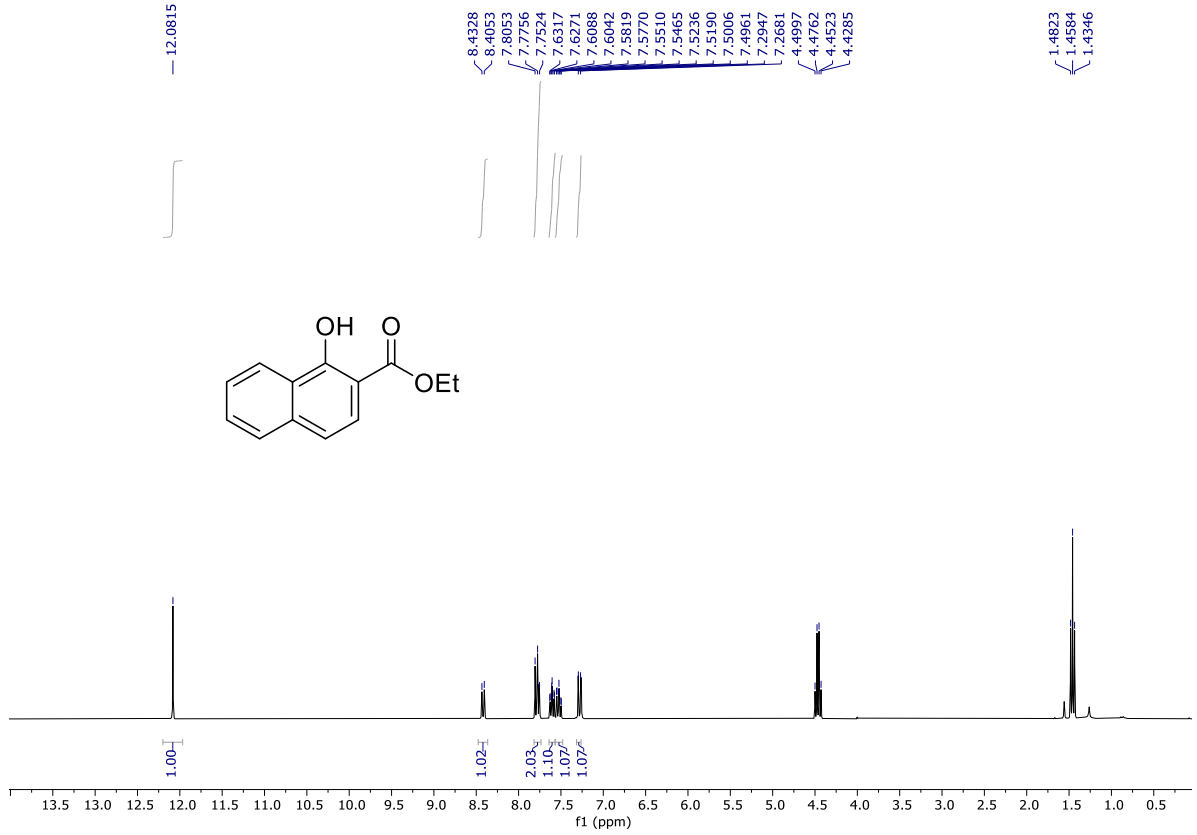
Ethyl 1-hydroxy-3-isobutyl-2-naphthoate (3n):



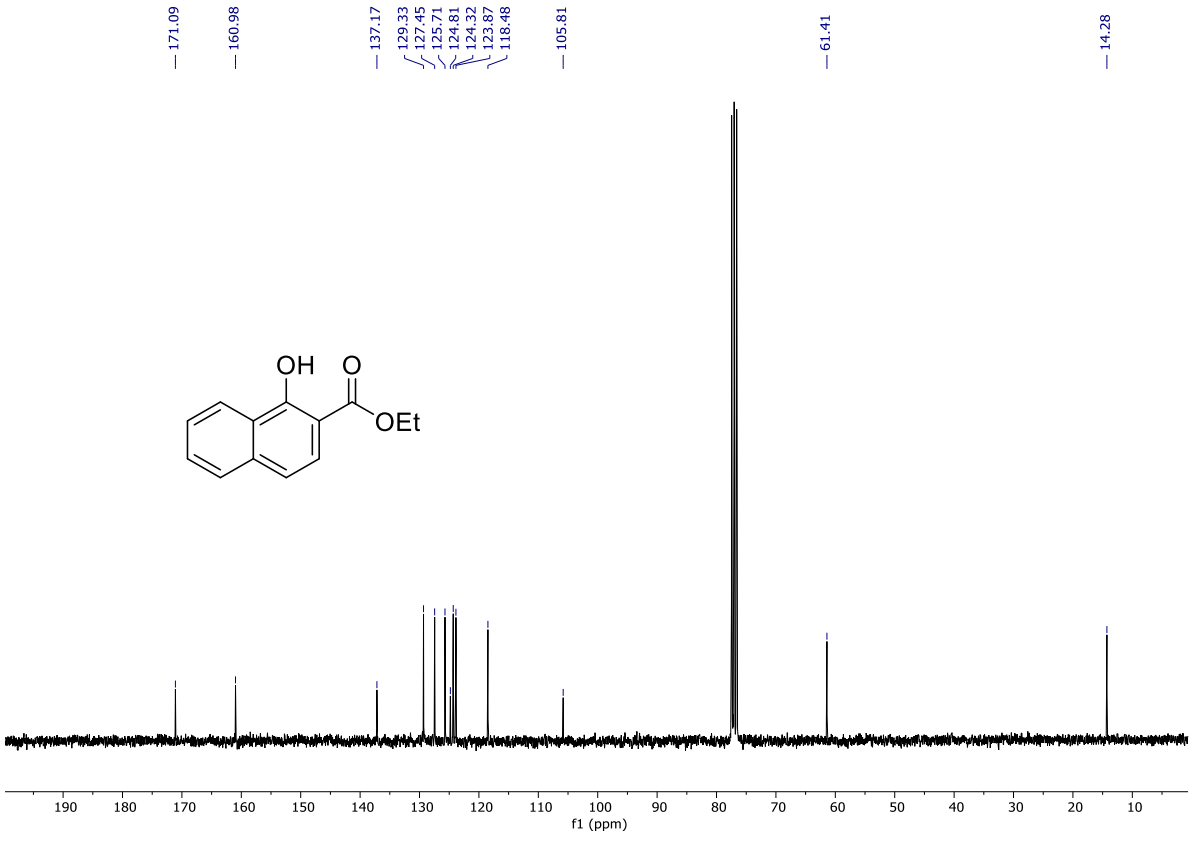


Ethyl 1-hydroxy-2-naphthoate (3o):

^{1}H NMR (300 MHz, $CDCl_3$)

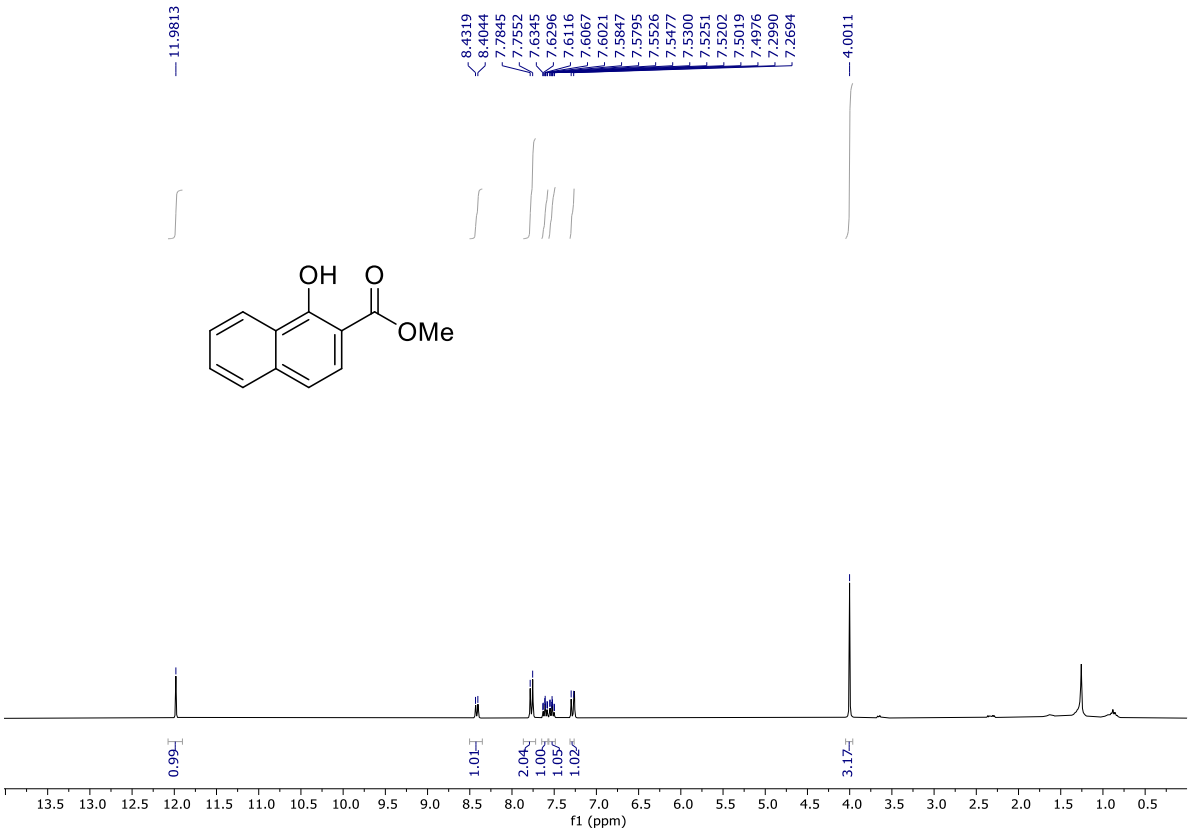


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

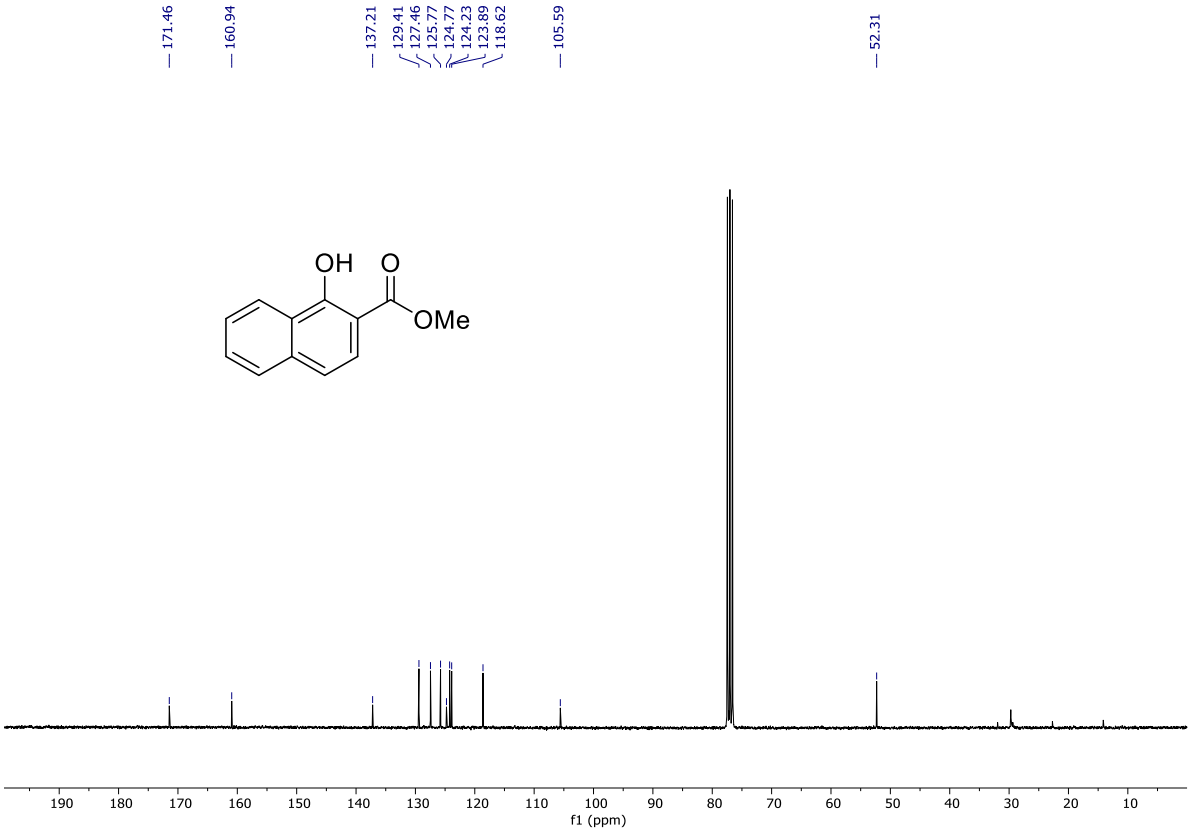


Methyl 1-hydroxy-2-naphthoate (3p):

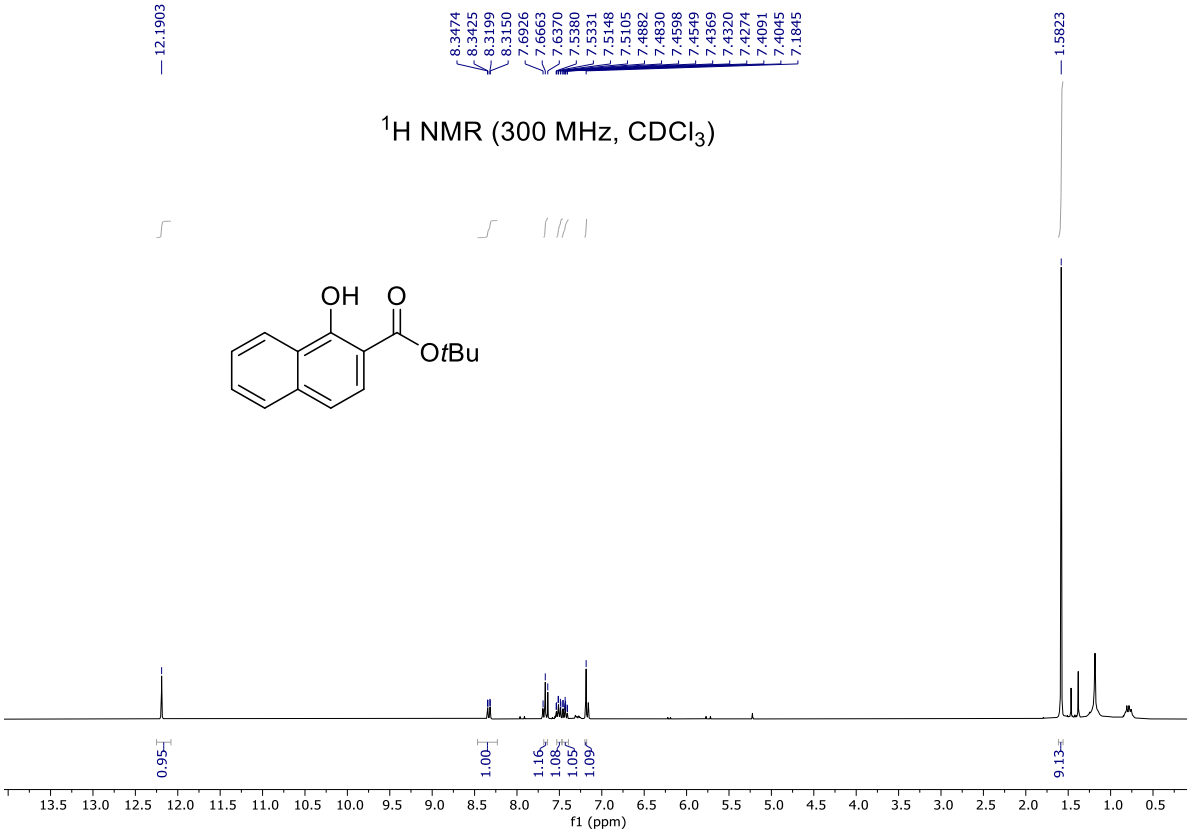
^{1}H NMR (300 MHz, $CDCl_3$)

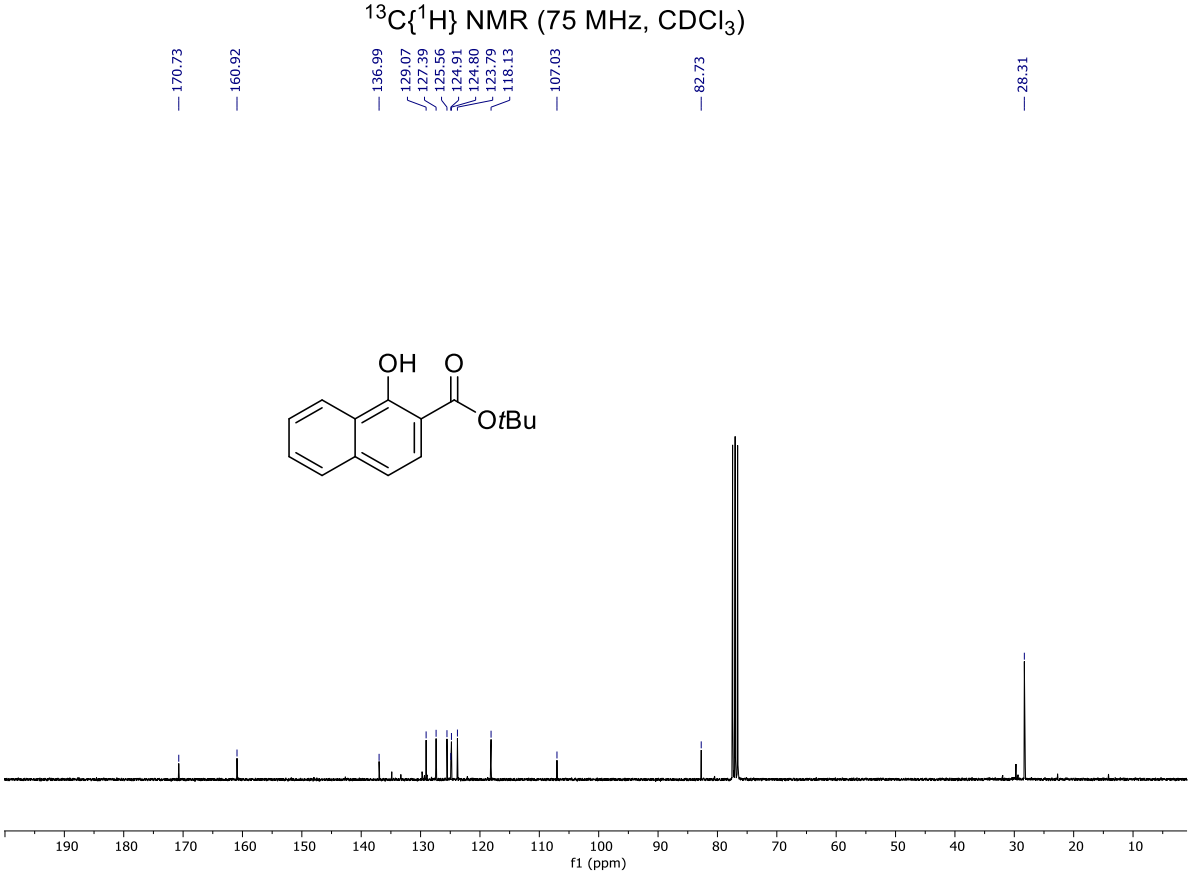


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

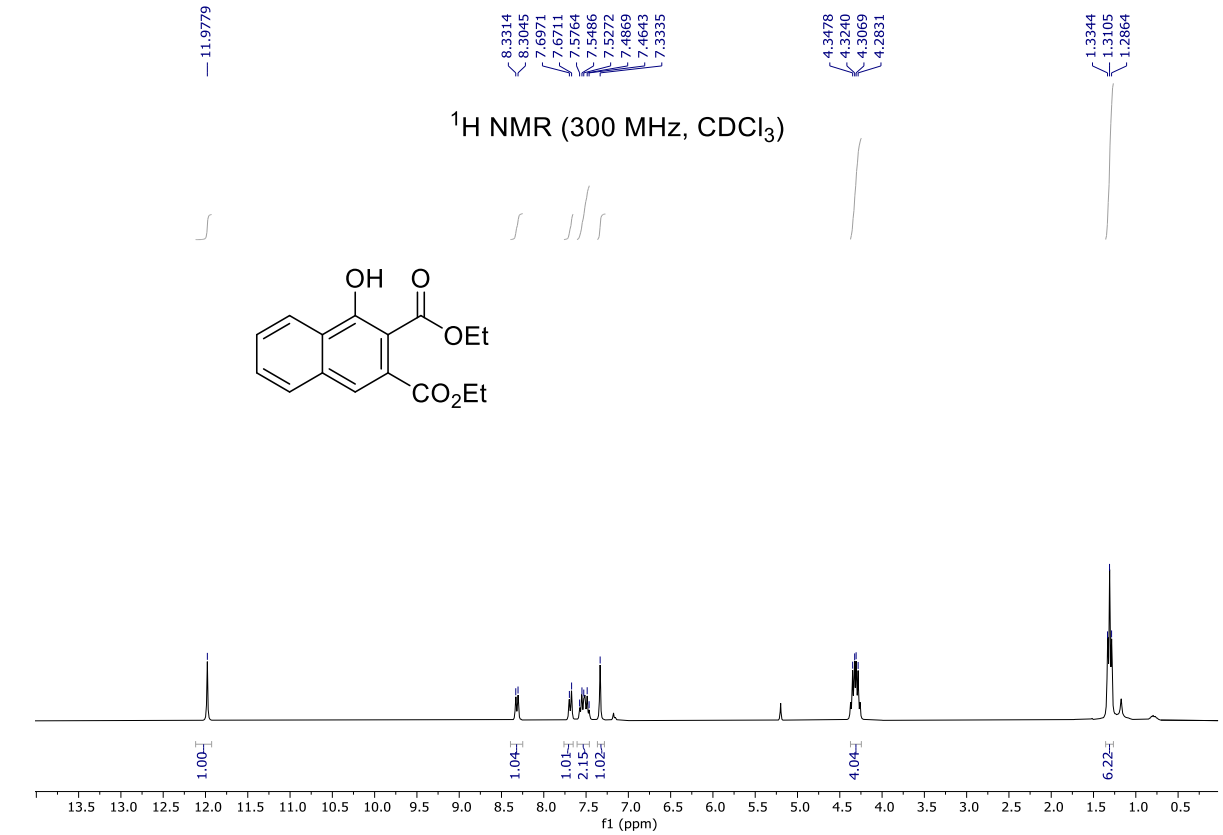


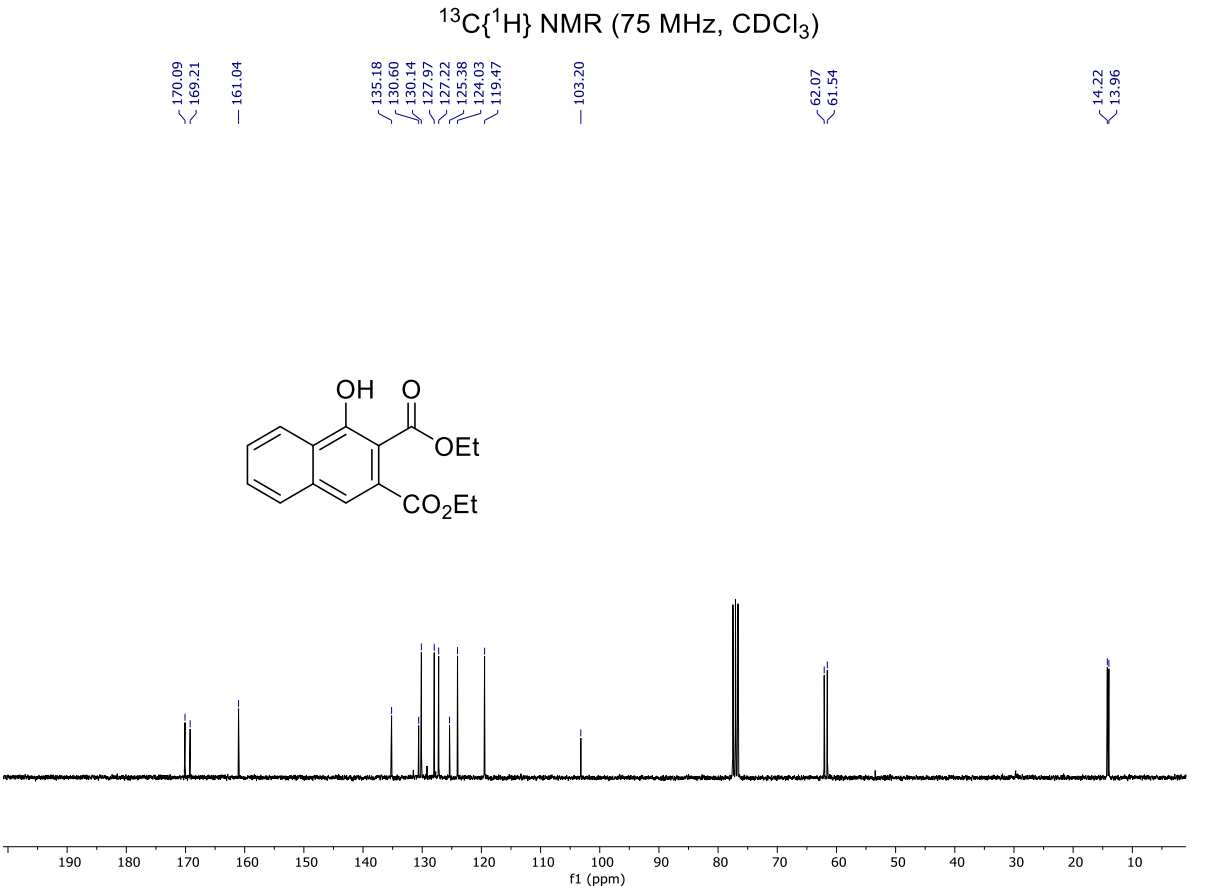
***Tert*-butyl 1-hydroxy-2-naphthoate (3q):**



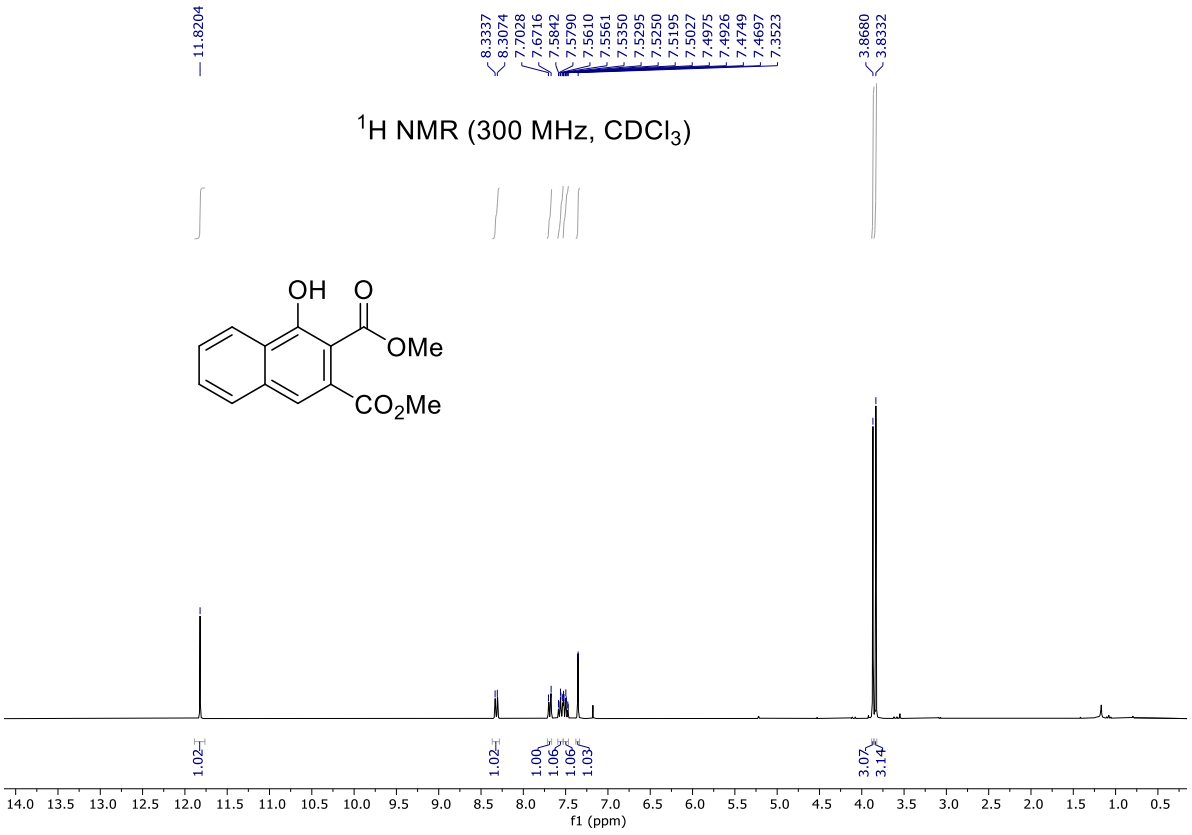


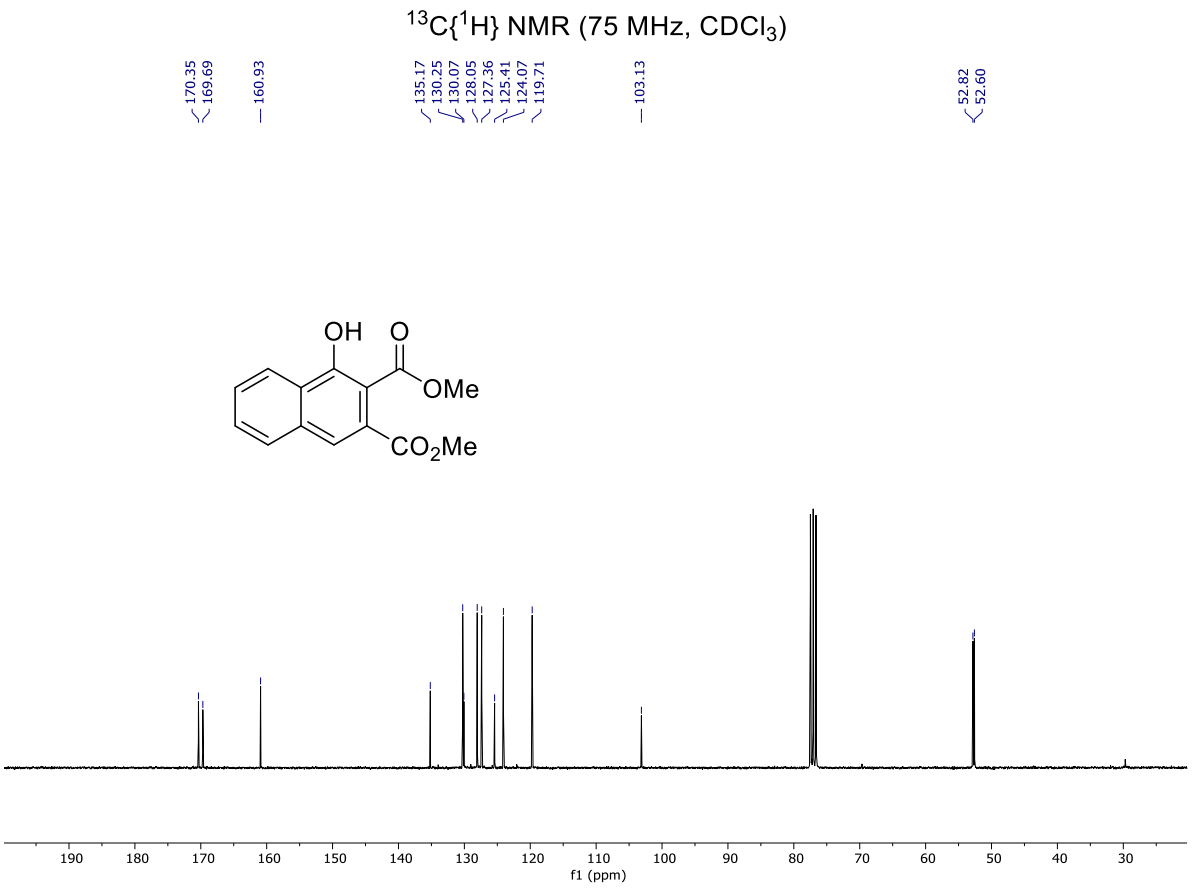
Diethyl 1-hydroxynaphthalene-2,3-dicarboxylate (3r):



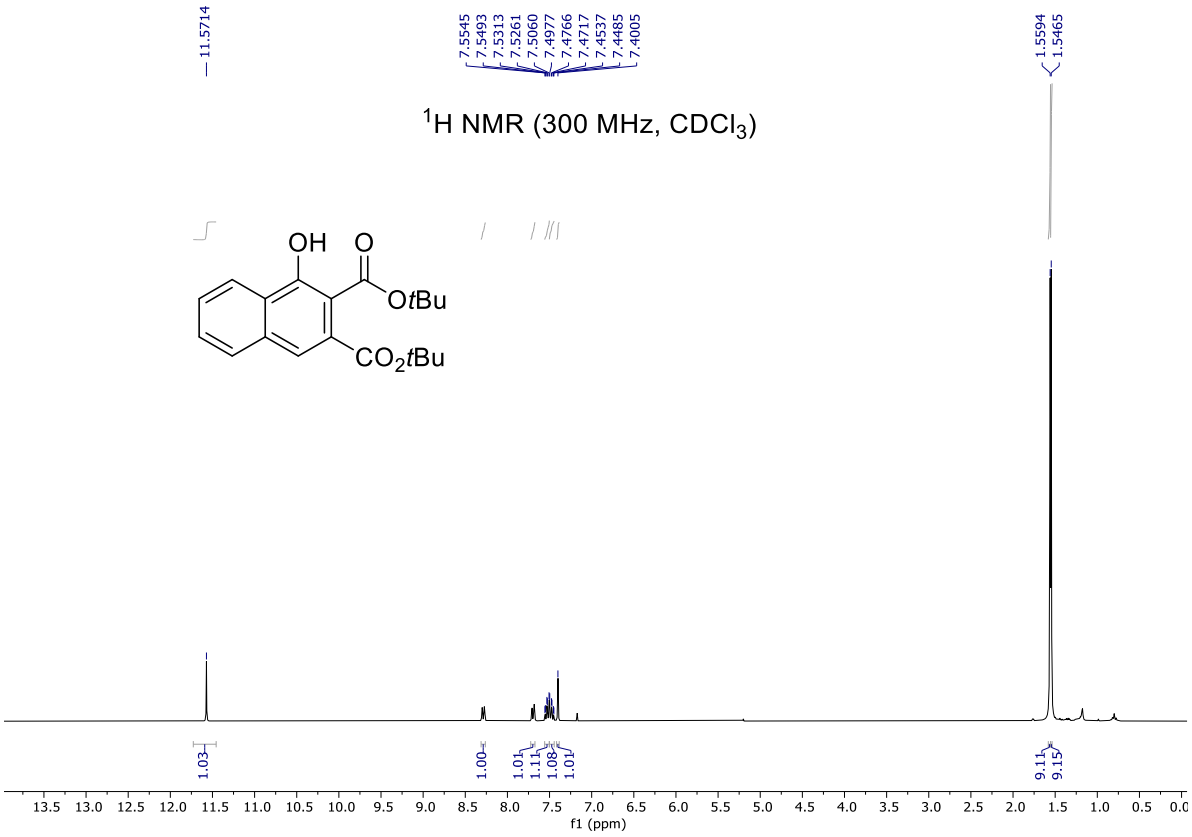


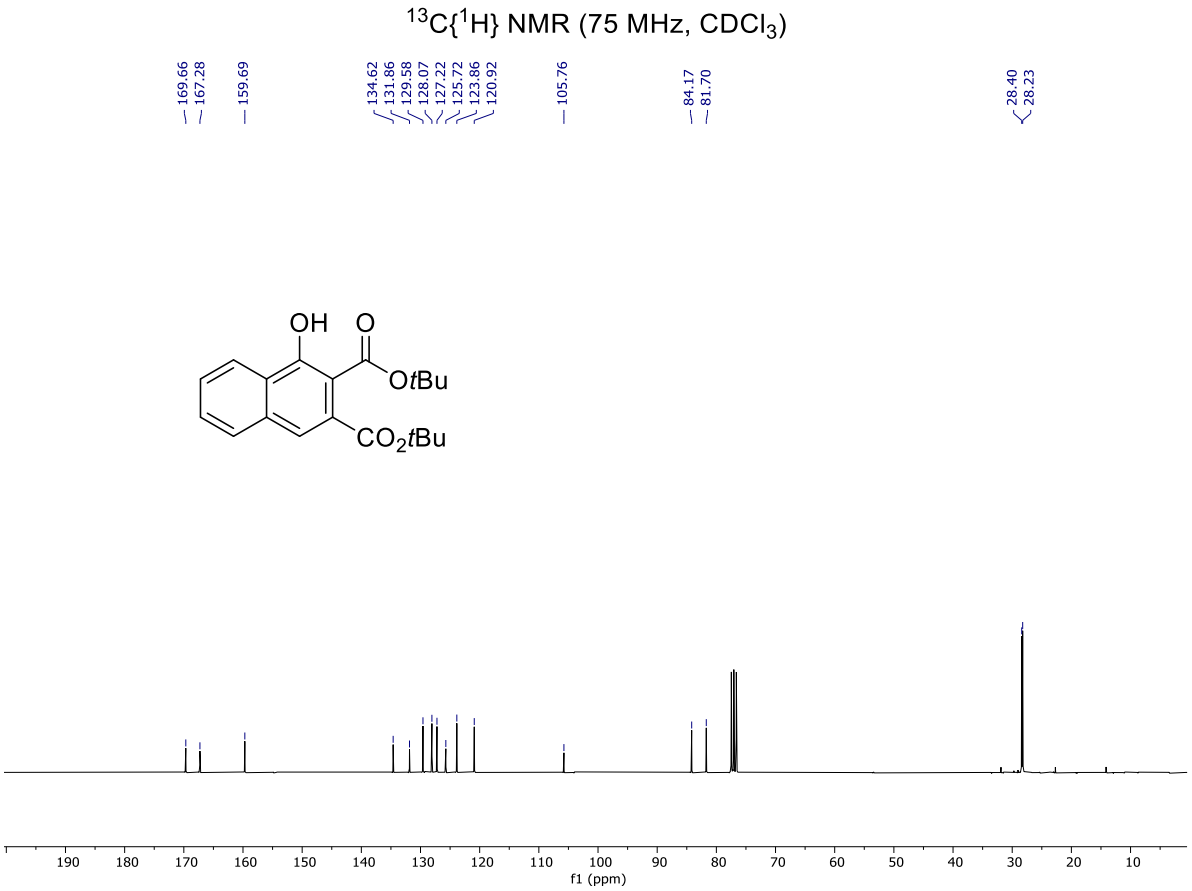
Dimethyl 1-hydroxynaphthalene-2,3-dicarboxylate (3s):



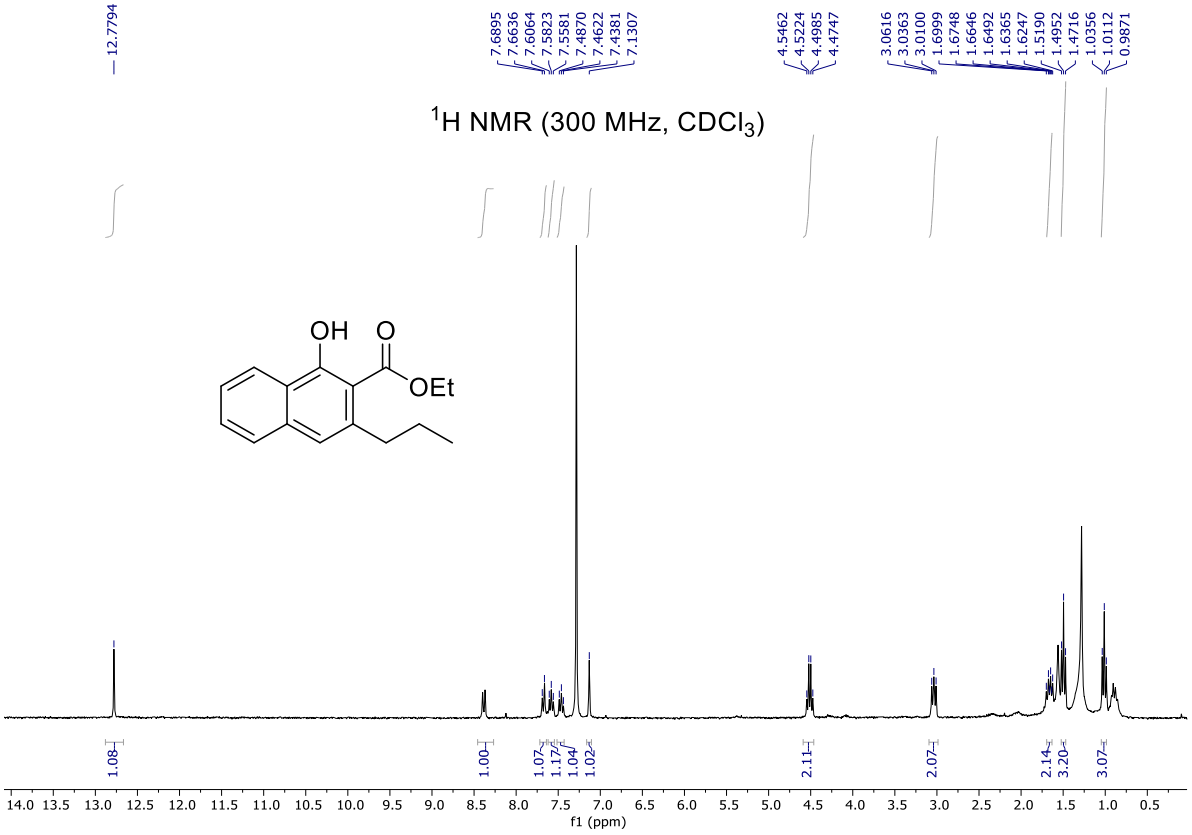


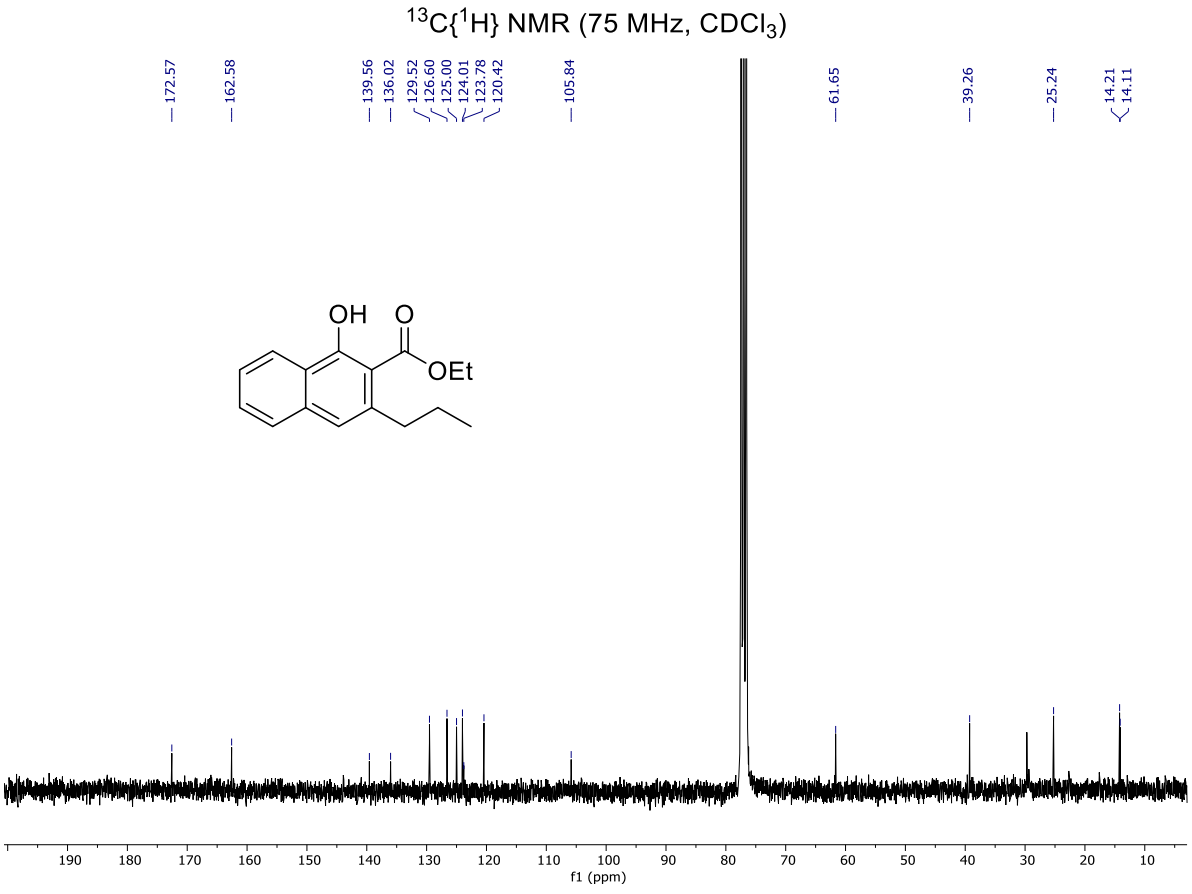
Di-tert-butyl 1-hydroxynaphthalene-2,3-dicarboxylate (3t):





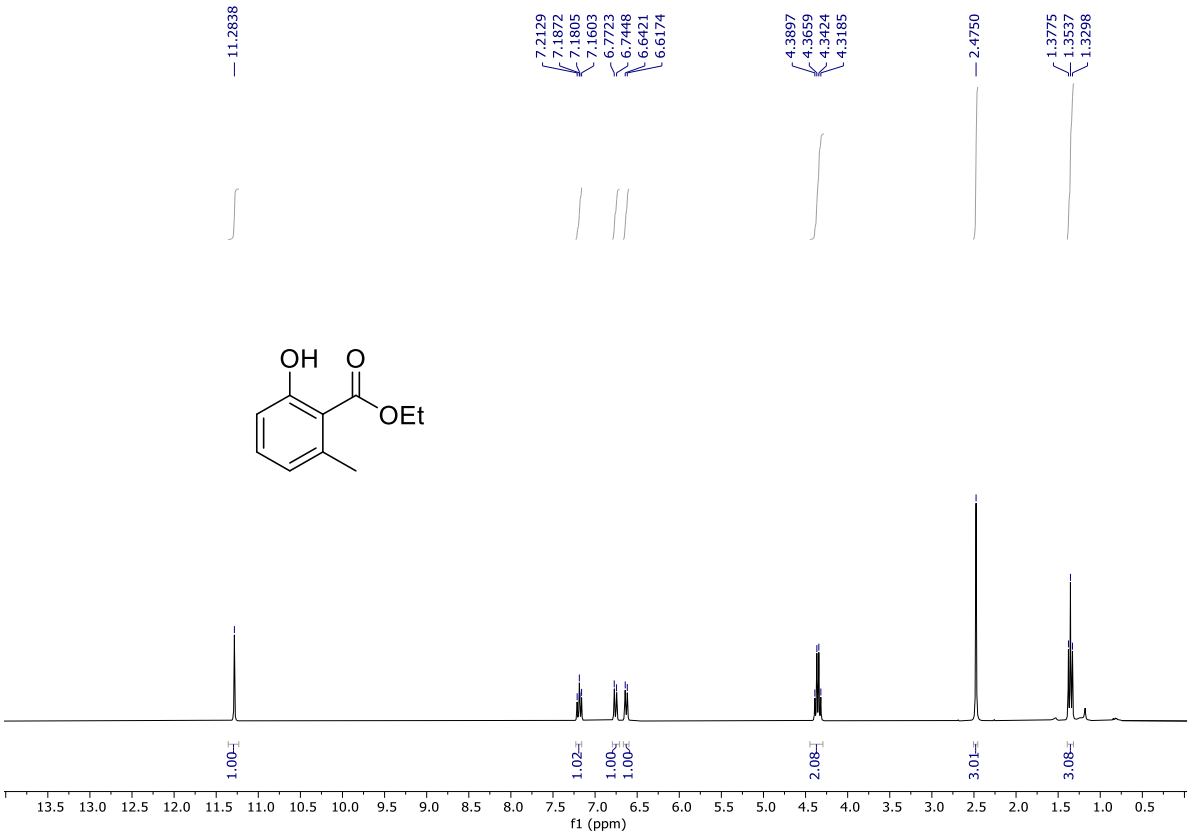
Ethyl 1-hydroxy-3-propyl-2-naphthoate (3u):



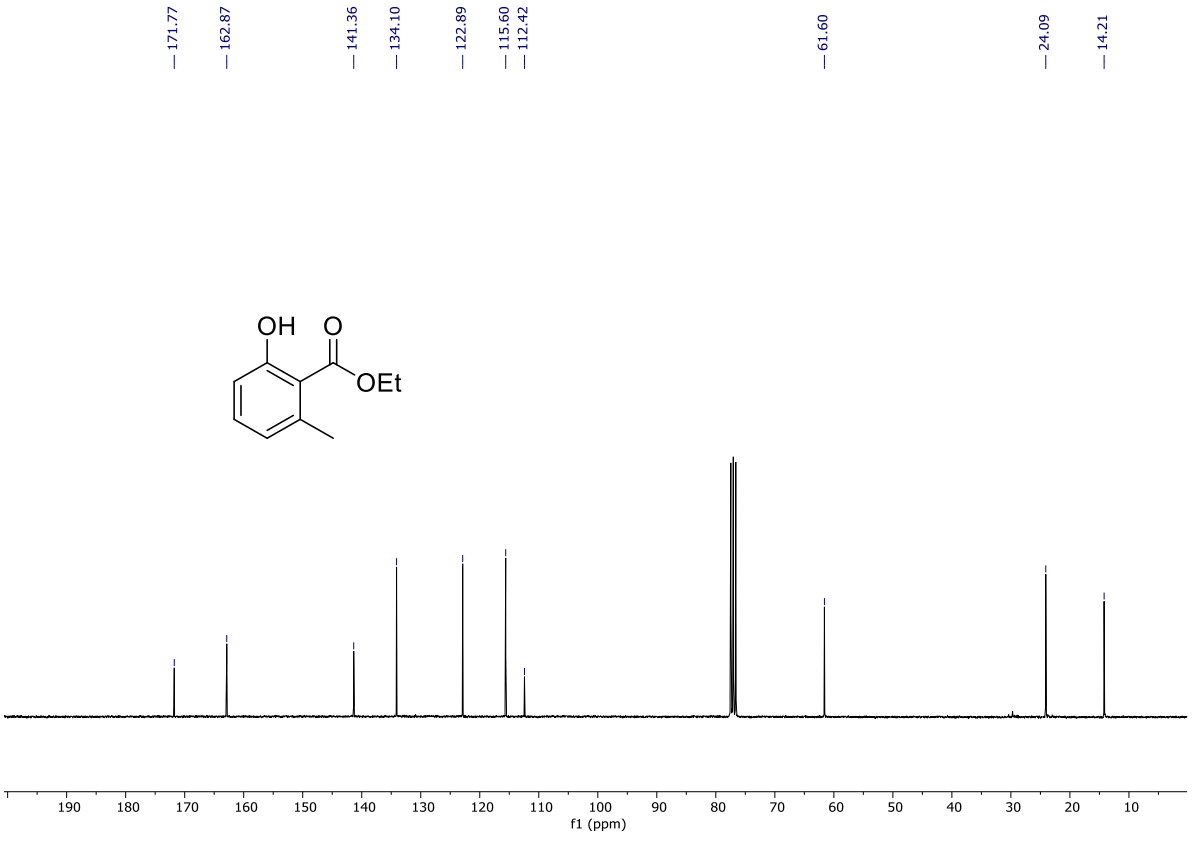


Ethyl 2-hydroxy-6-methylbenzoate (4a):

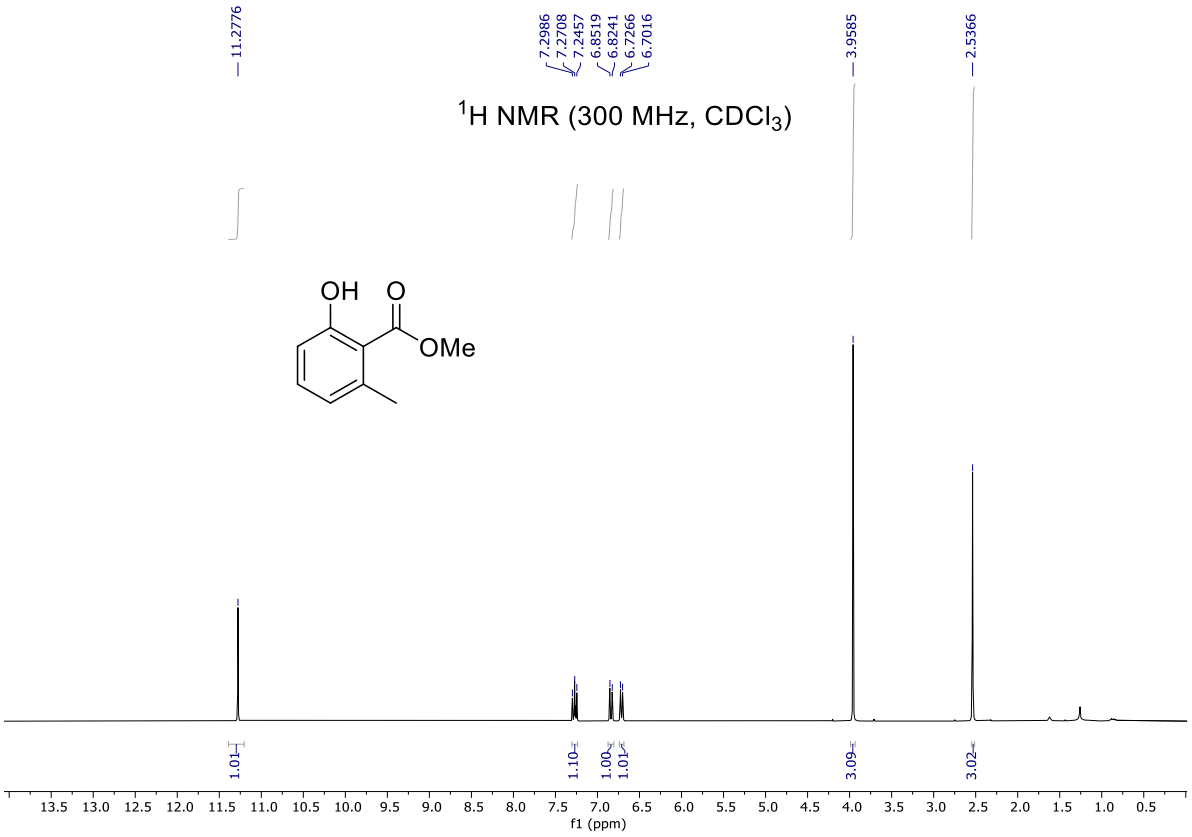
^{1}H NMR (300 MHz, $CDCl_3$)

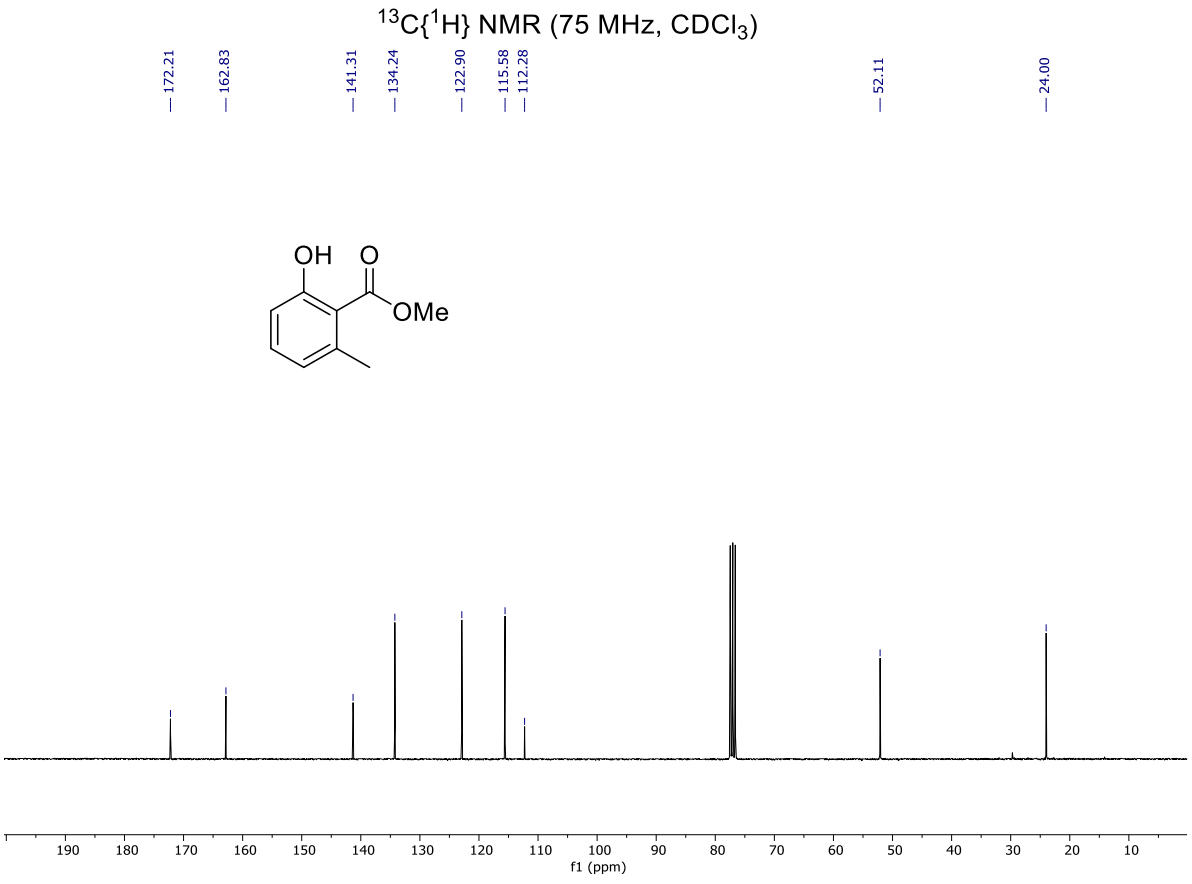


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

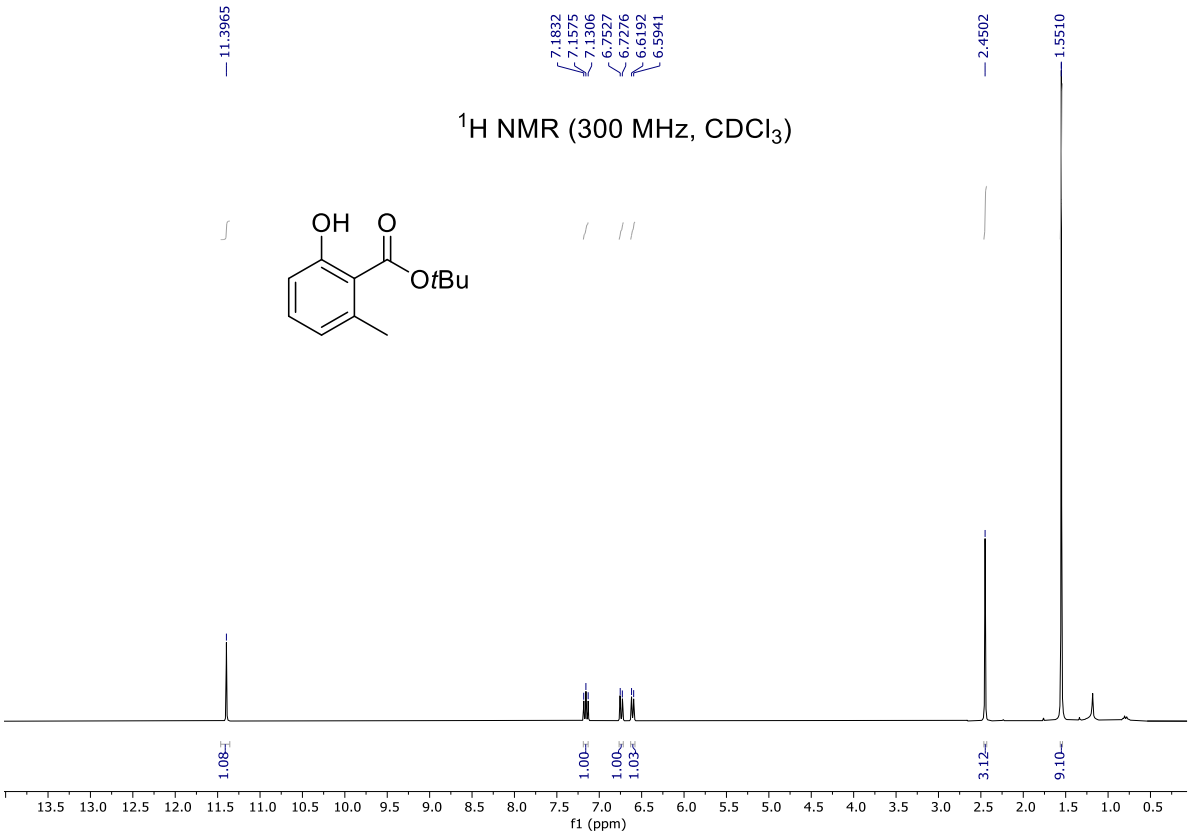


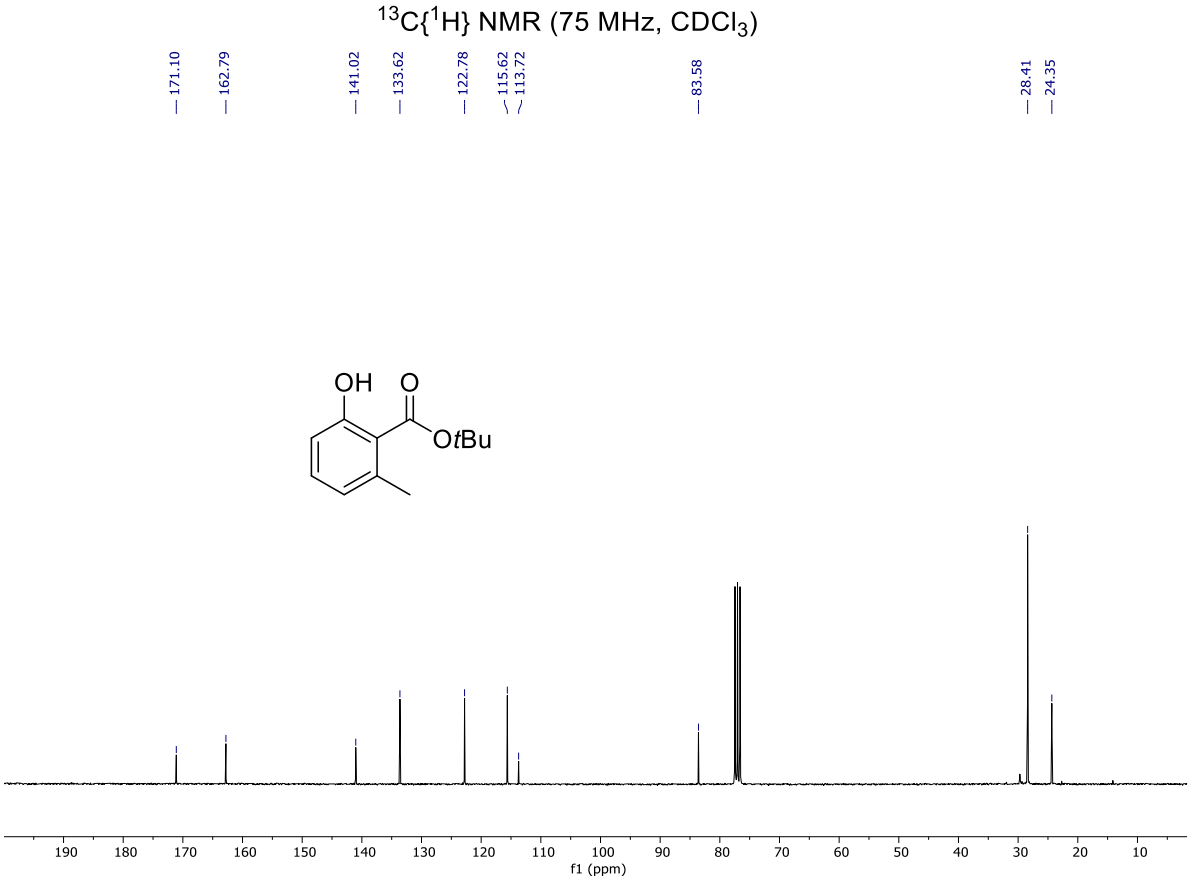
Methyl 2-hydroxy-6-methylbenzoate (4b):





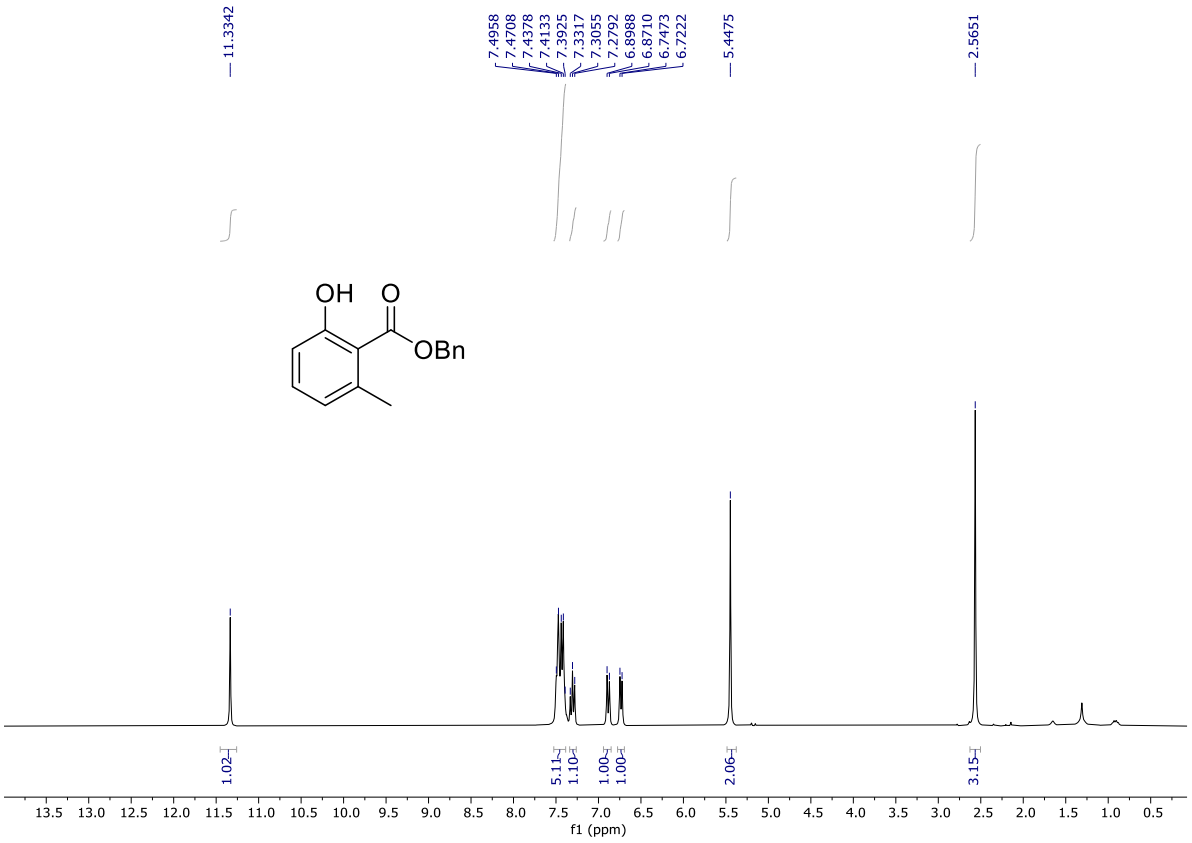
***Tert*-butyl 2-hydroxy-6-methylbenzoate (4c):**



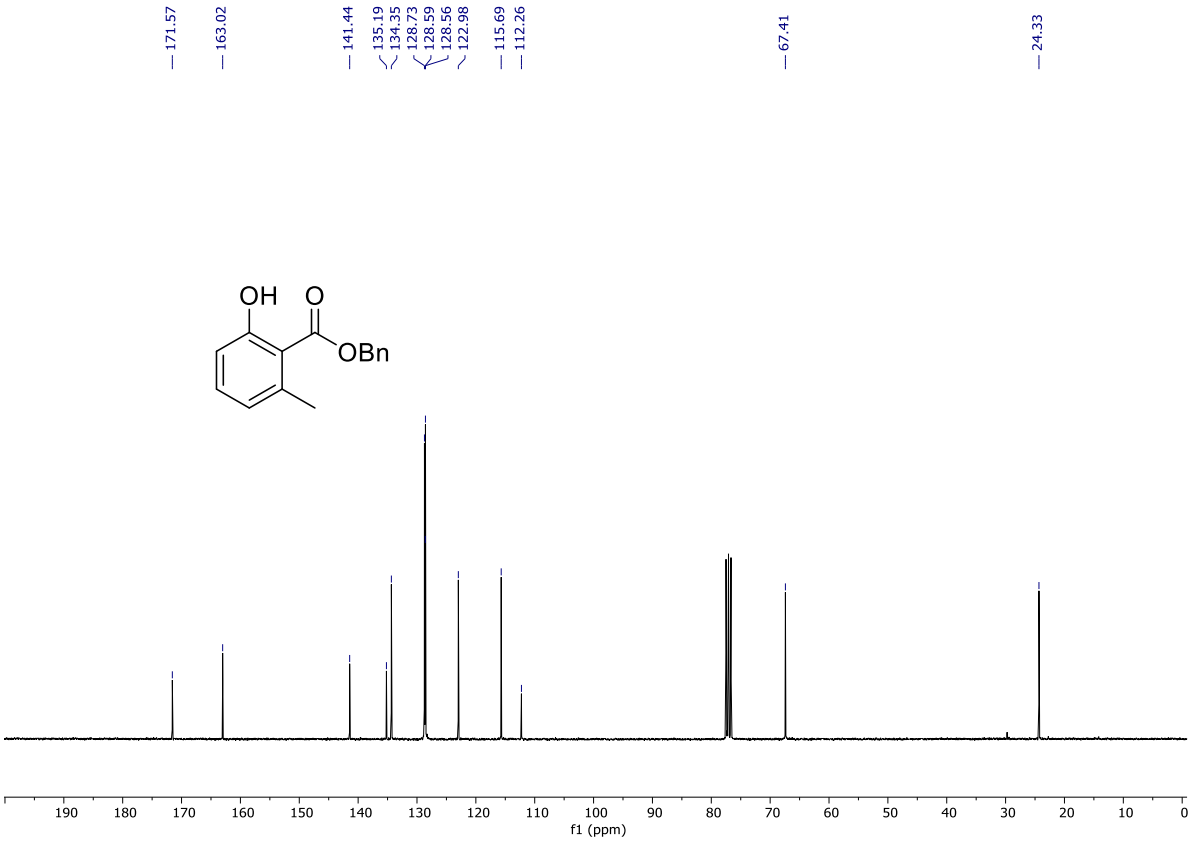


Benzyl 2-hydroxy-6-methylbenzoate (4d):

^{1}H NMR (300 MHz, $CDCl_3$)

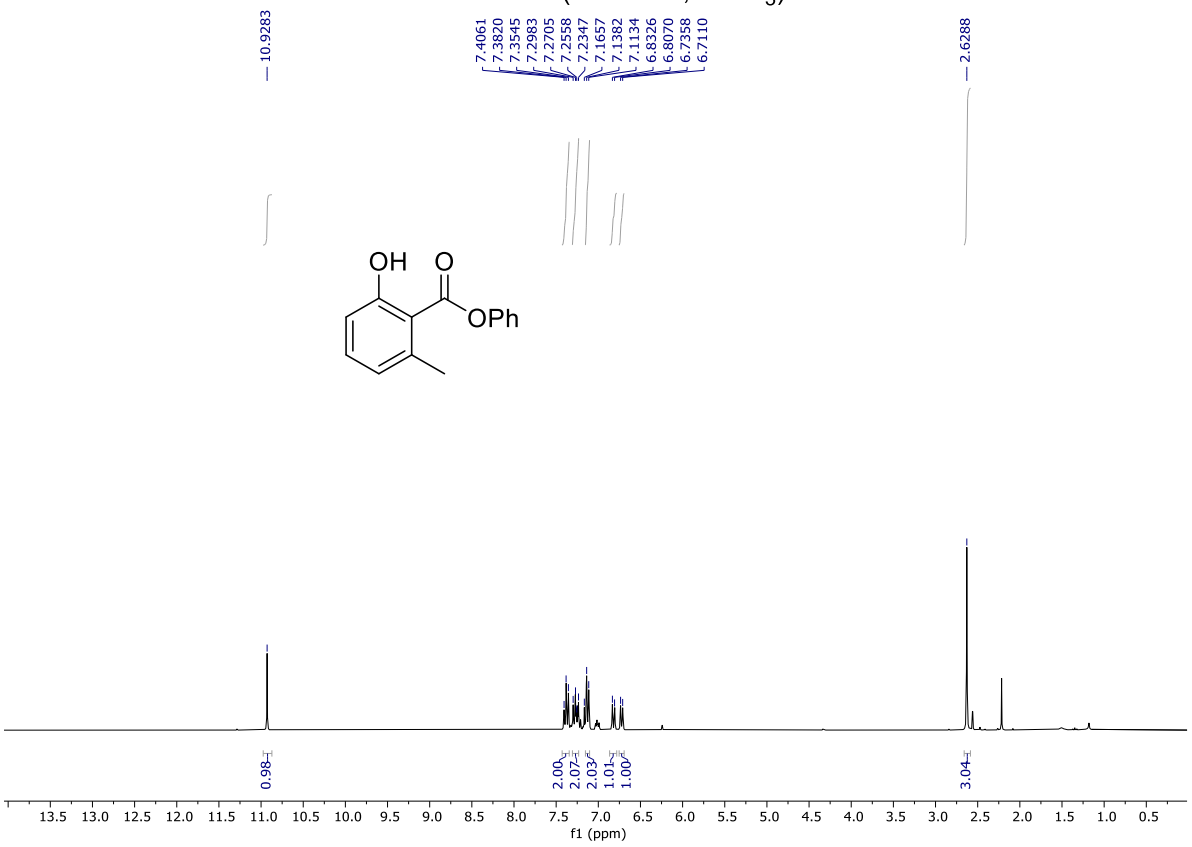


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

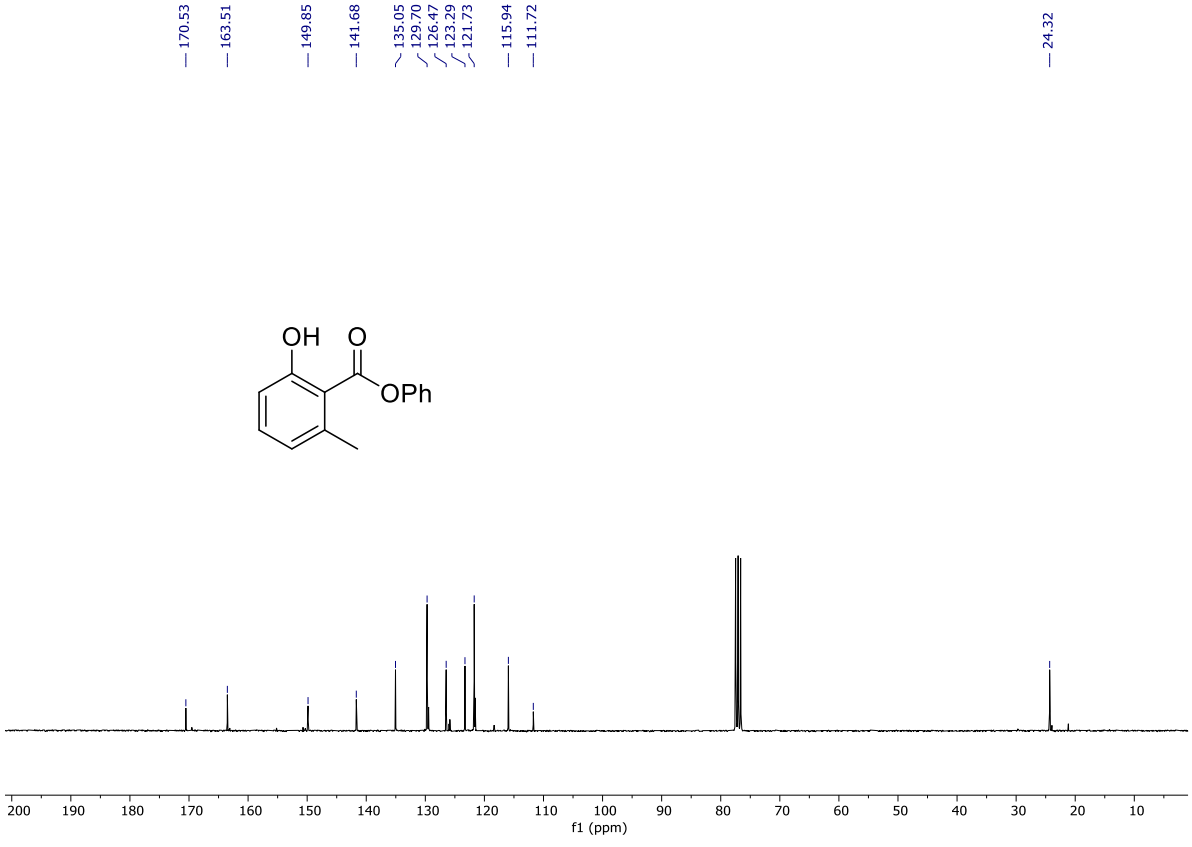


Phenyl 2-hydroxy-6-methylbenzoate (4e):

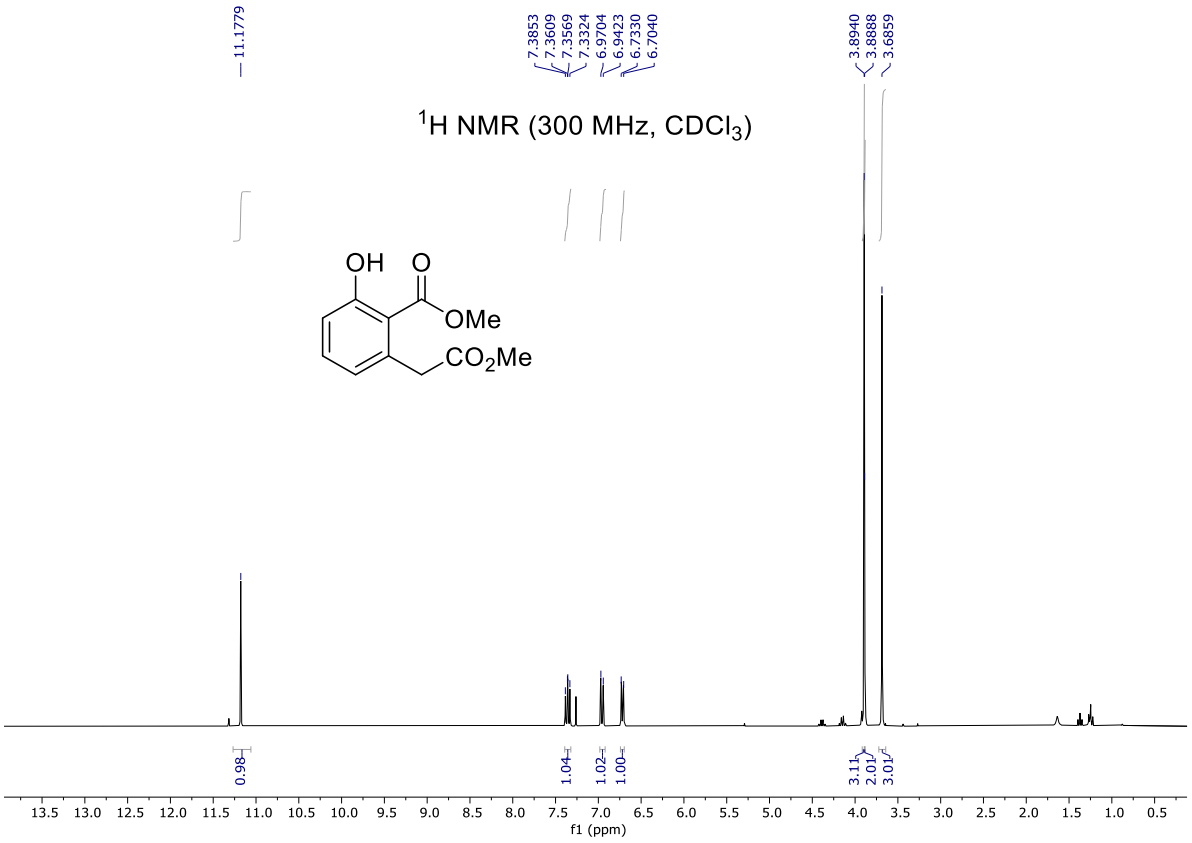
^{1}H NMR (300 MHz, $CDCl_3$)

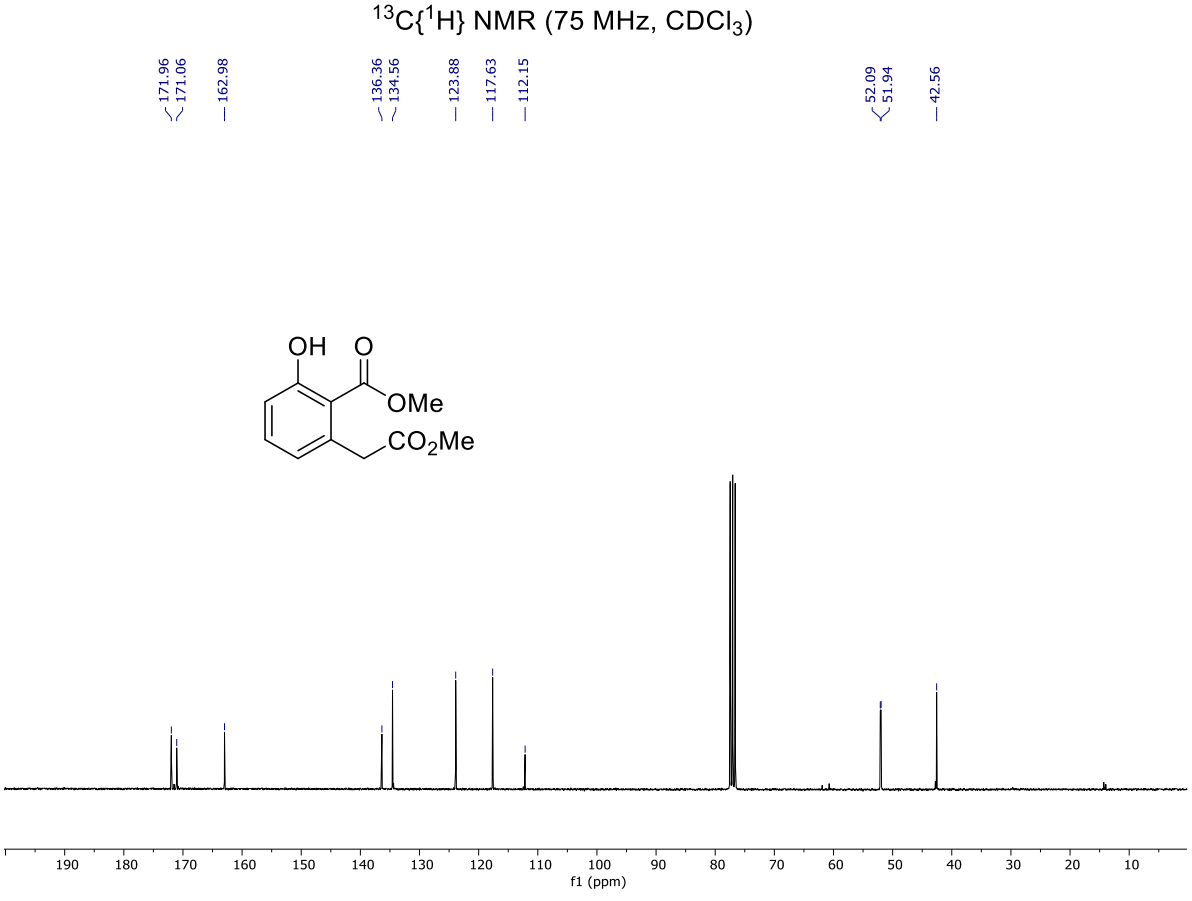


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

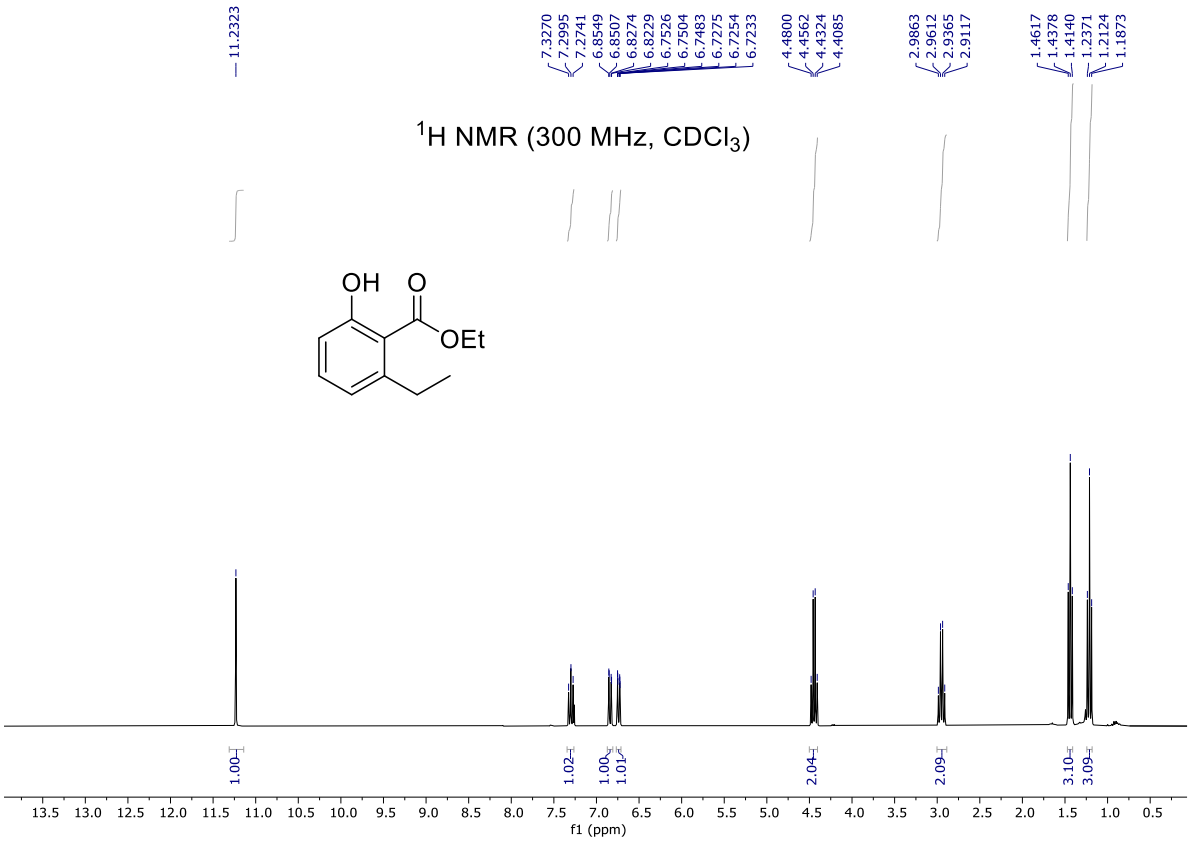


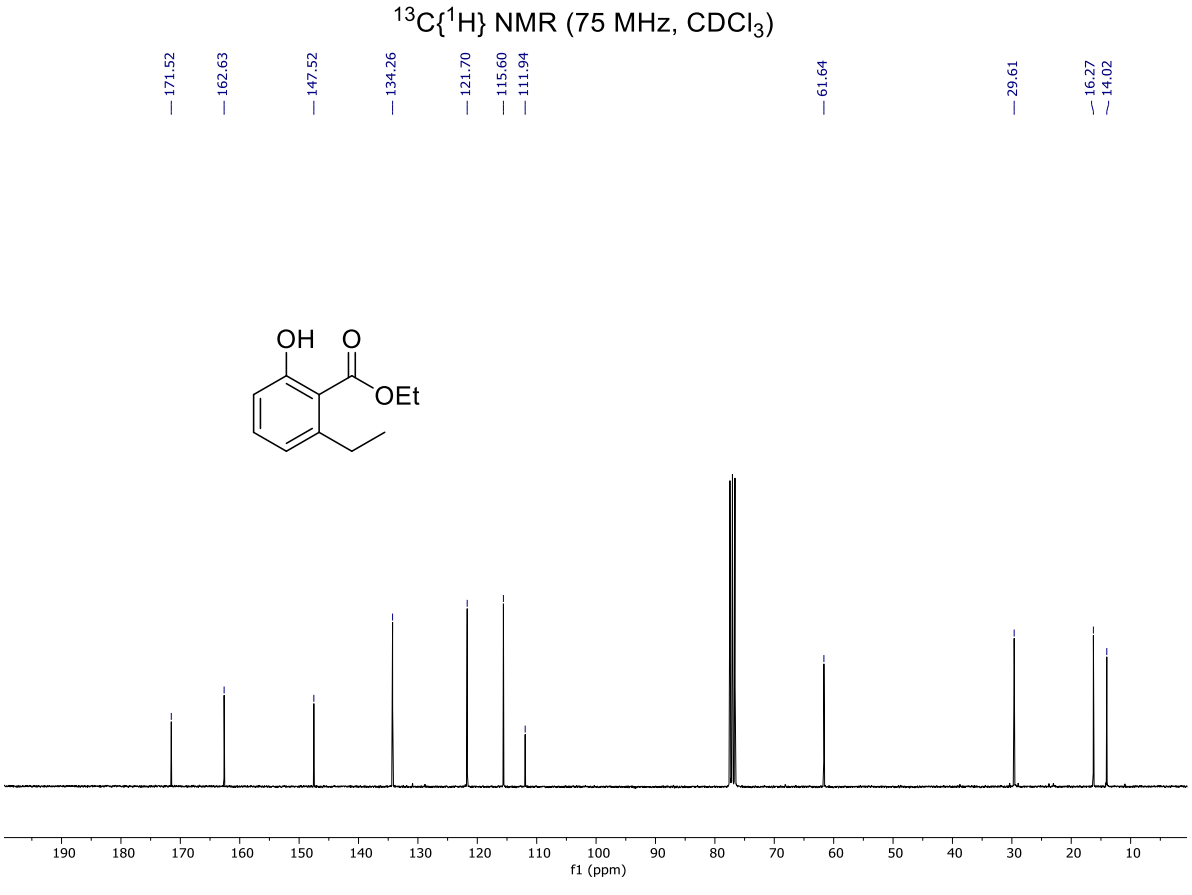
Methyl 2-hydroxy-6-(2-methoxy-2-oxoethyl)benzoate (4f):



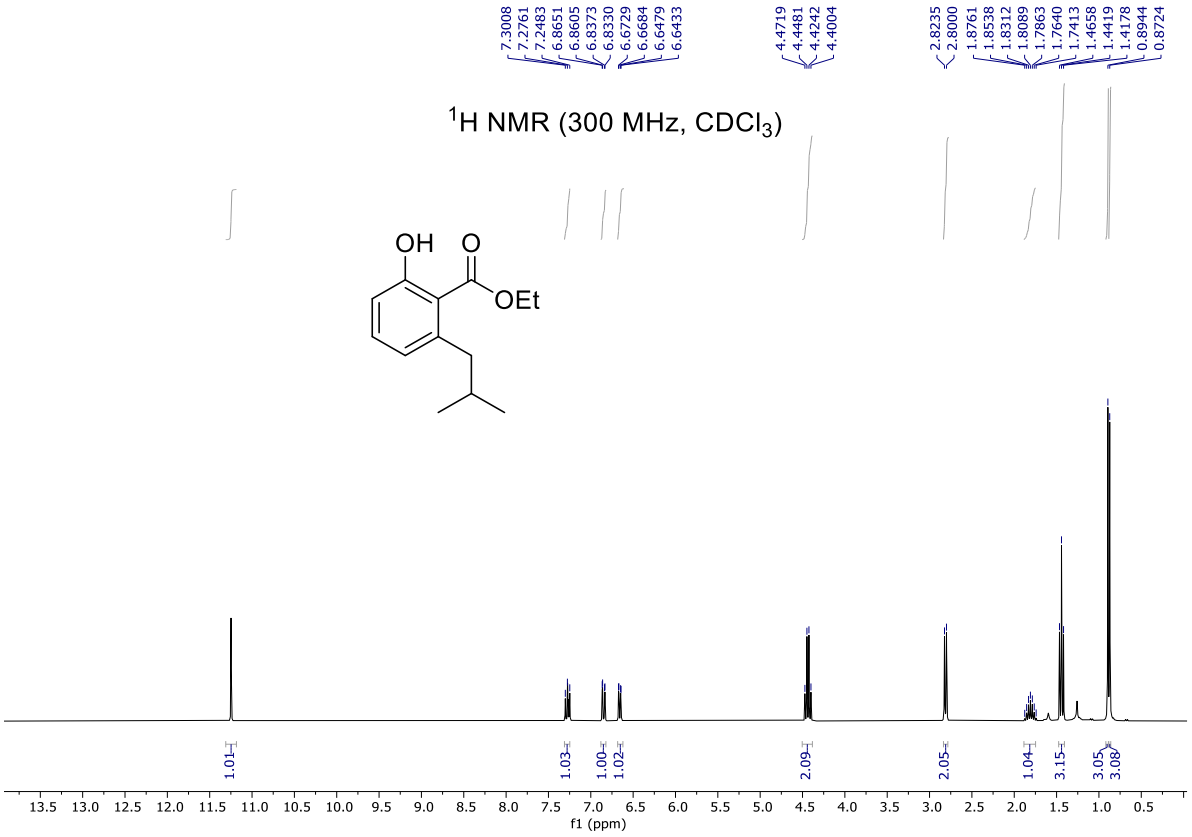


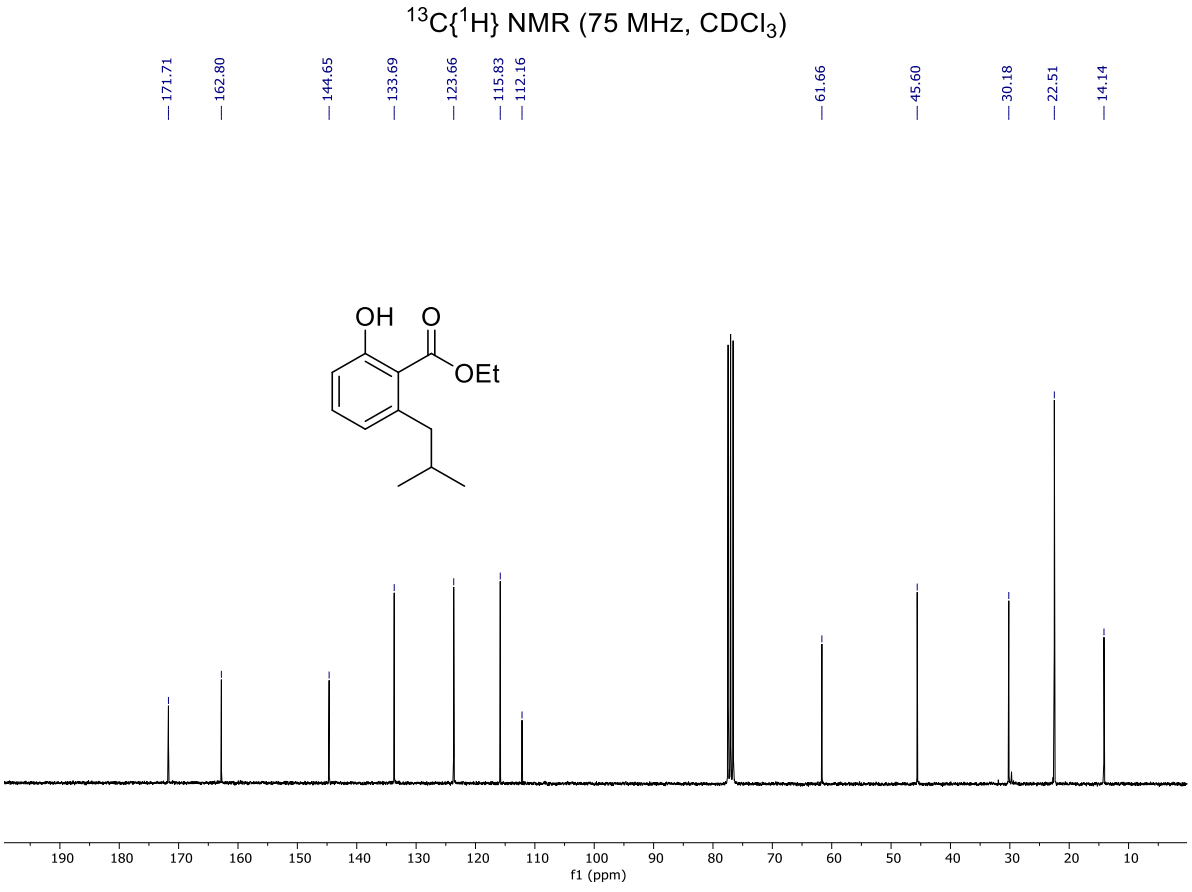
Ethyl 2-ethyl-6-hydroxybenzoate (4g):



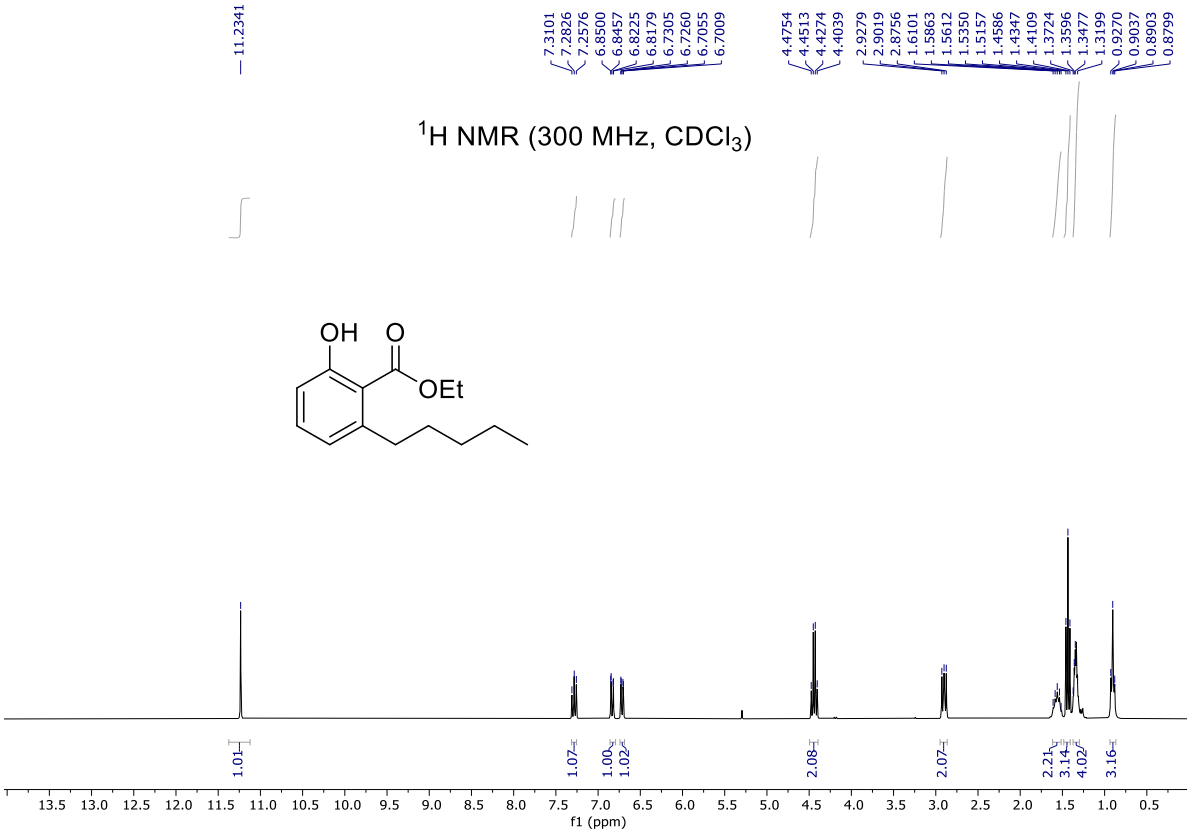


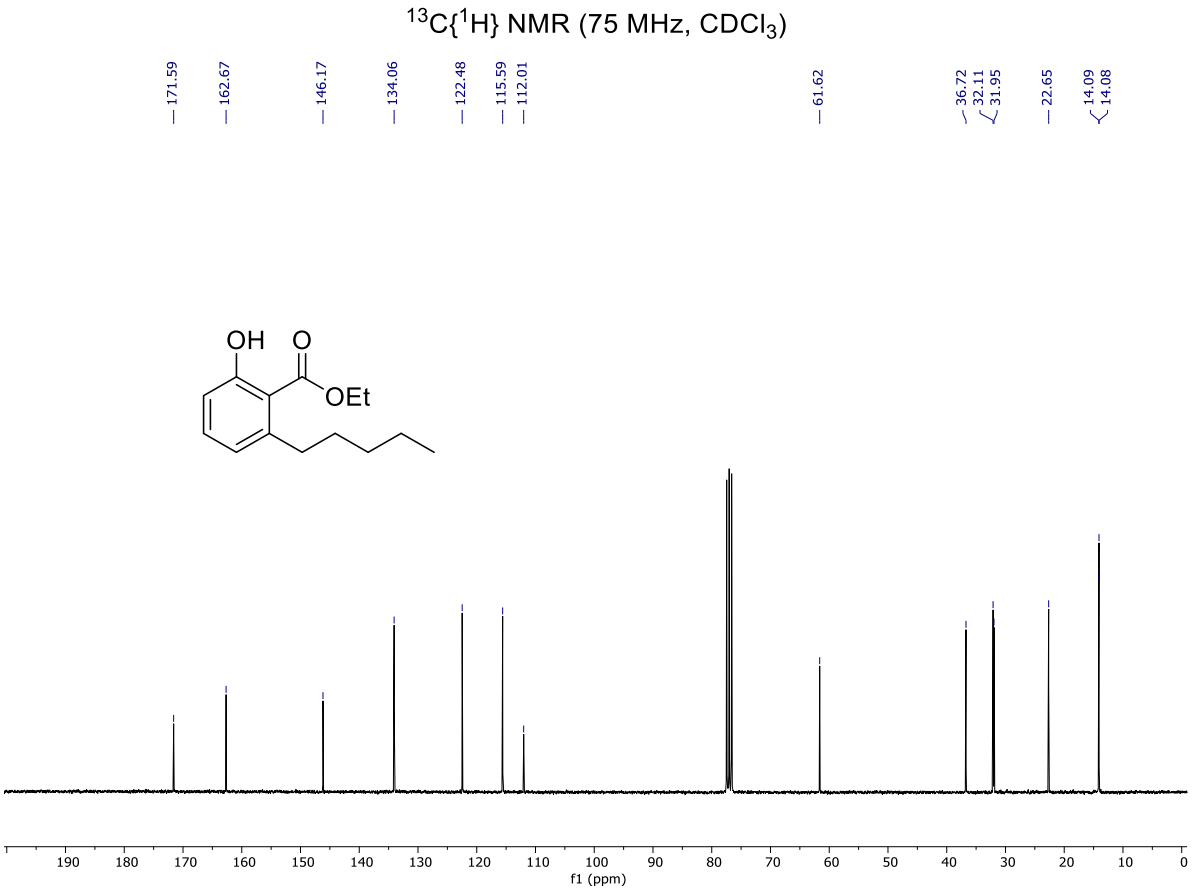
Ethyl 2-hydroxy-6-isobutylbenzoate (4h):





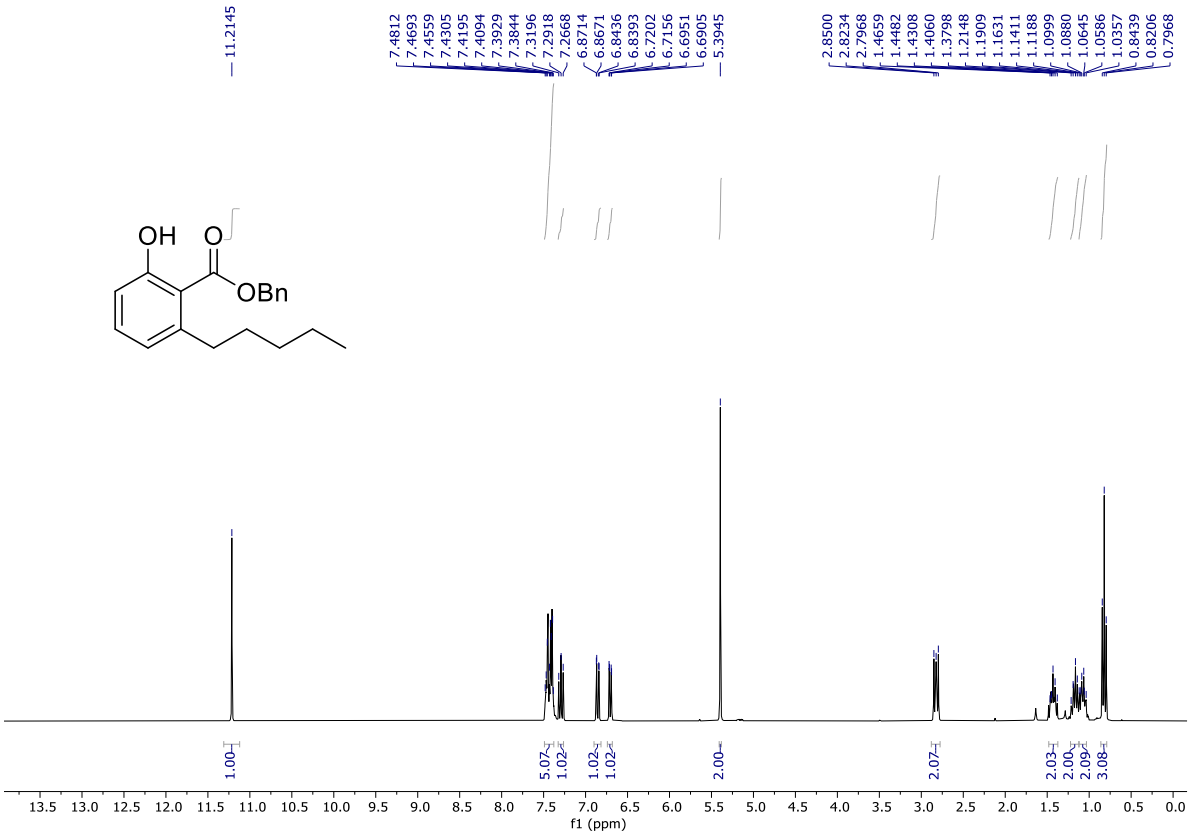
Ethyl 2-hydroxy-6-pentylbenzoate (4i):



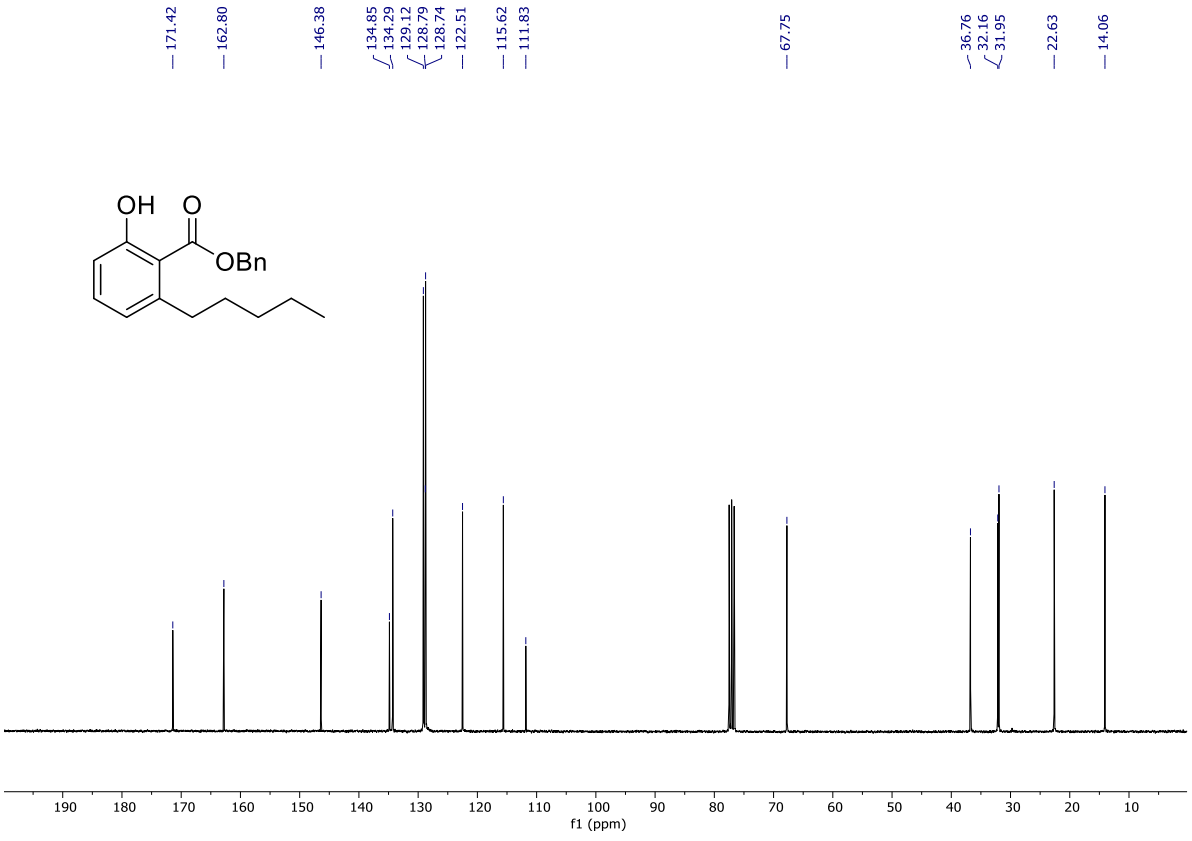


Benzyl 2-hydroxy-6-pentylbenzoate (4j):

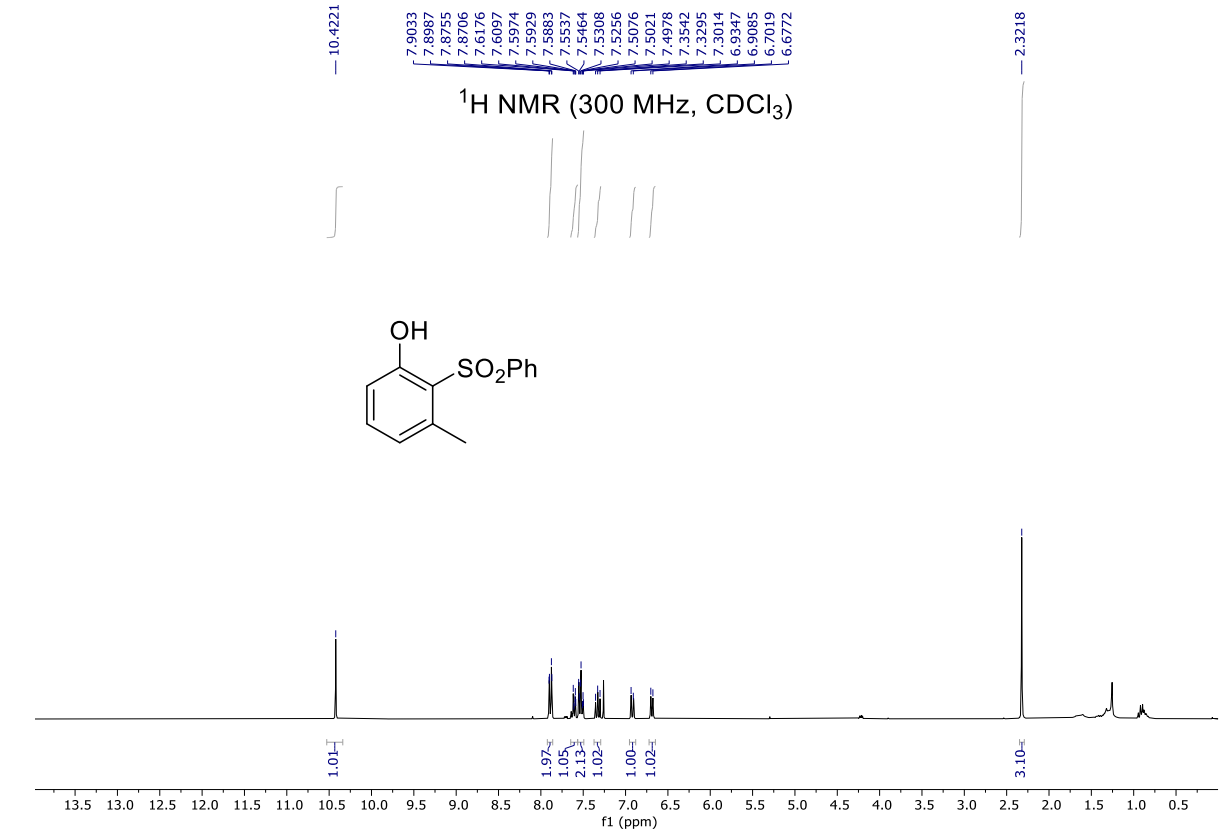
^{1}H NMR (300 MHz, $CDCl_3$)

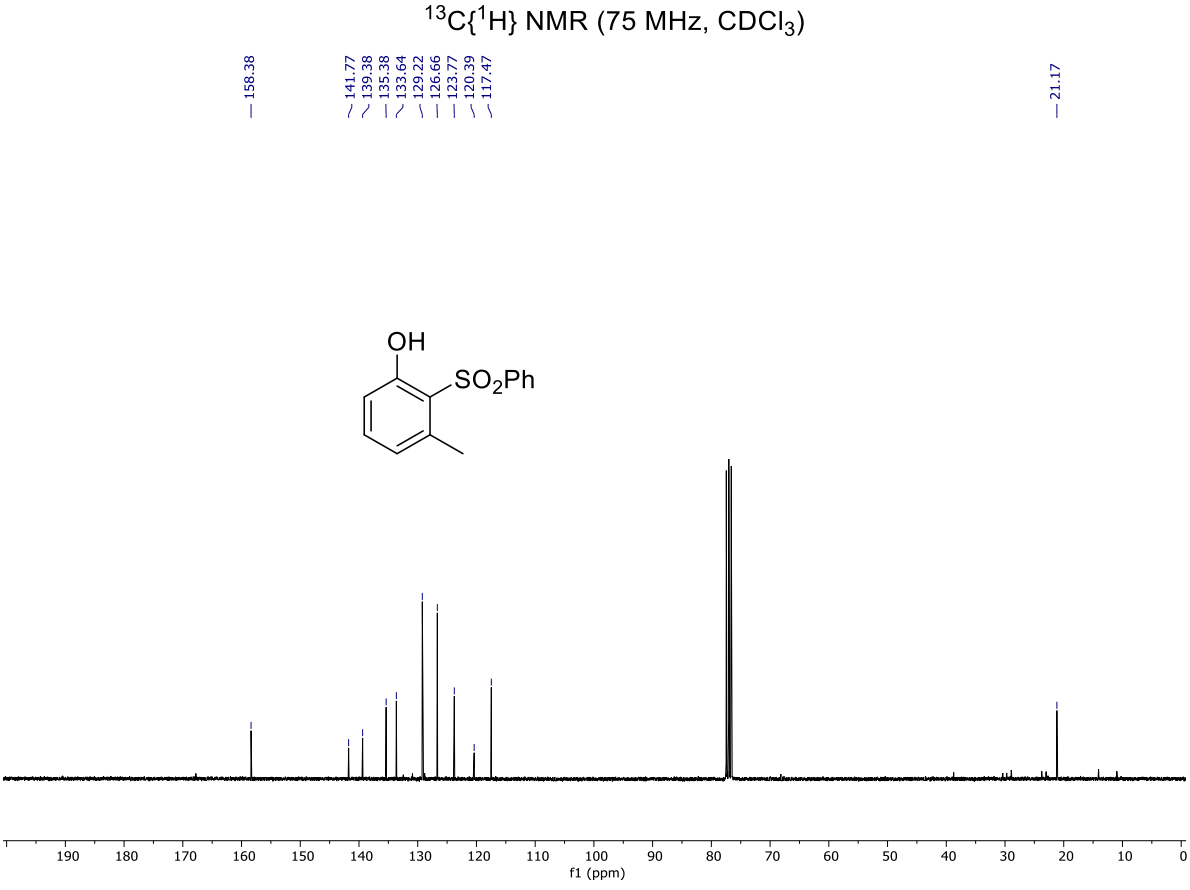


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

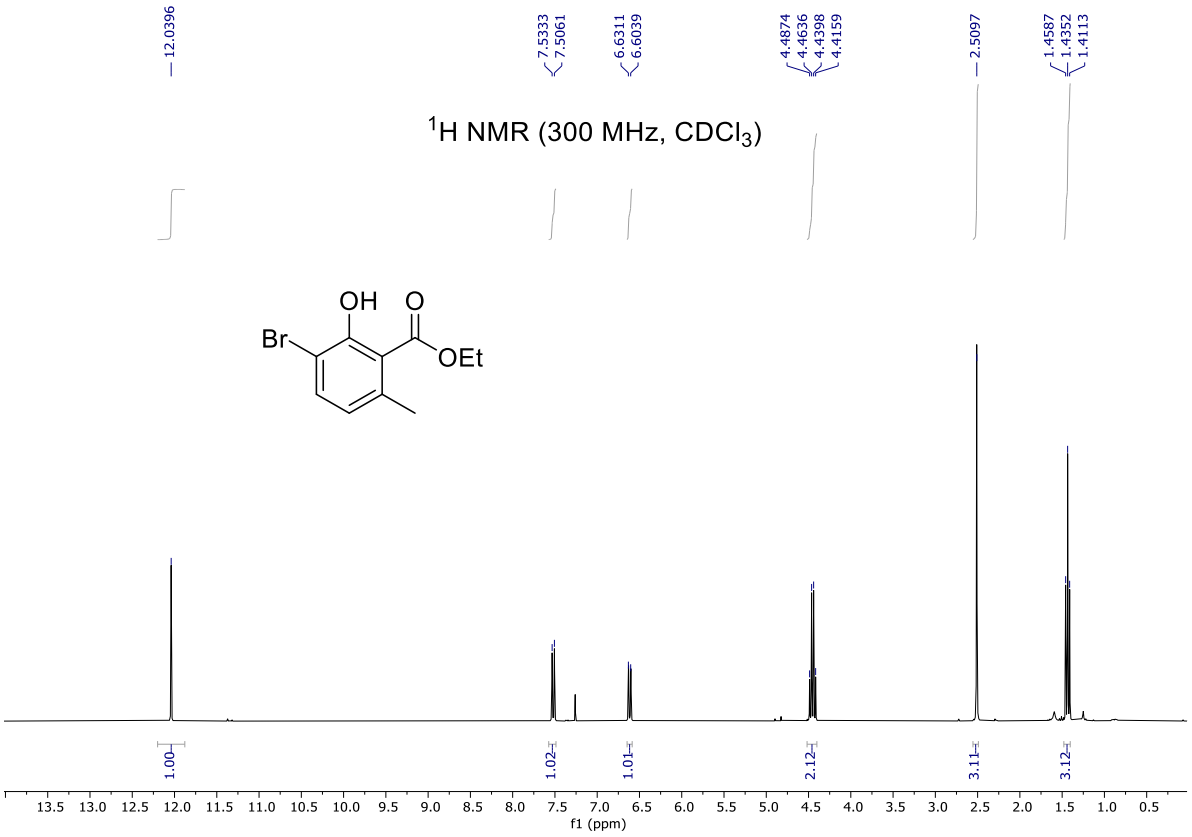


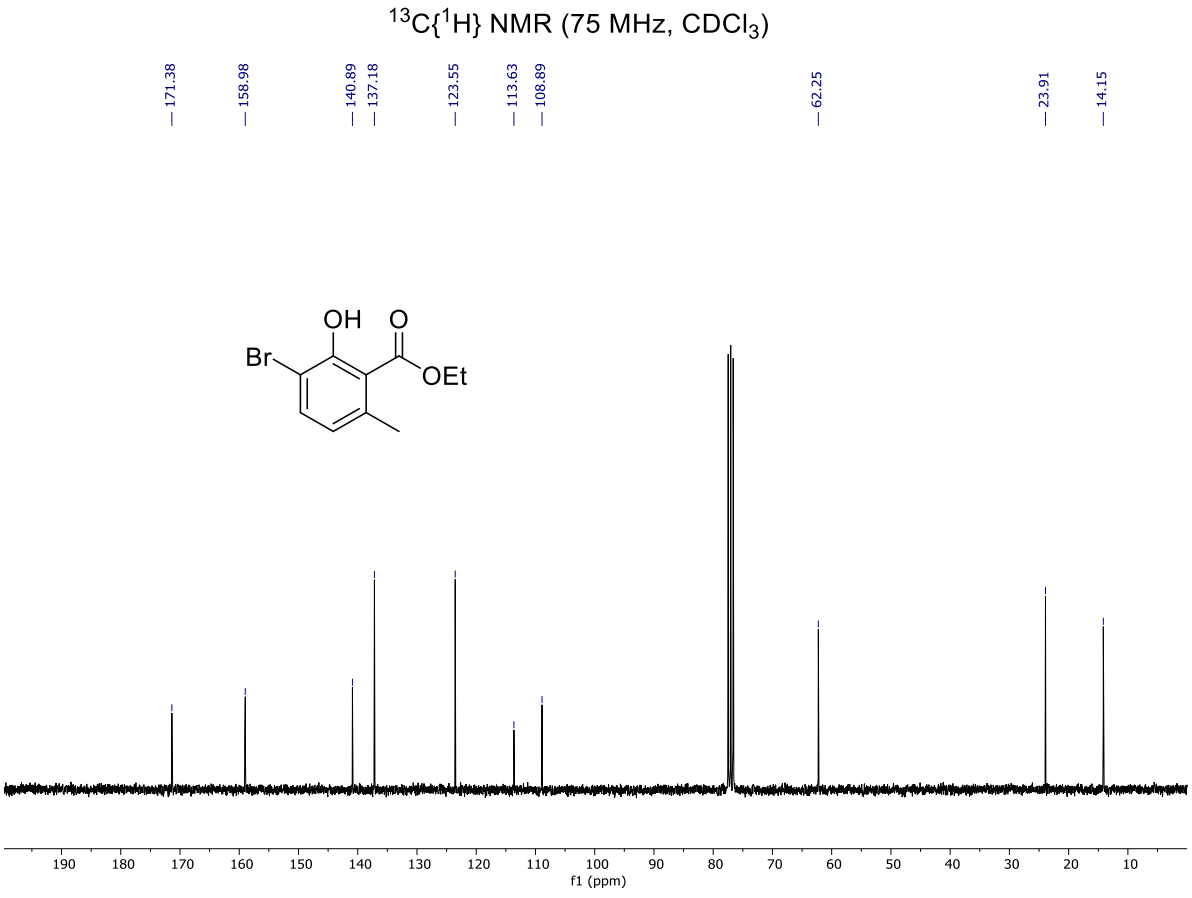
3-methyl-2-(phenylsulfonyl)phenol (4k):



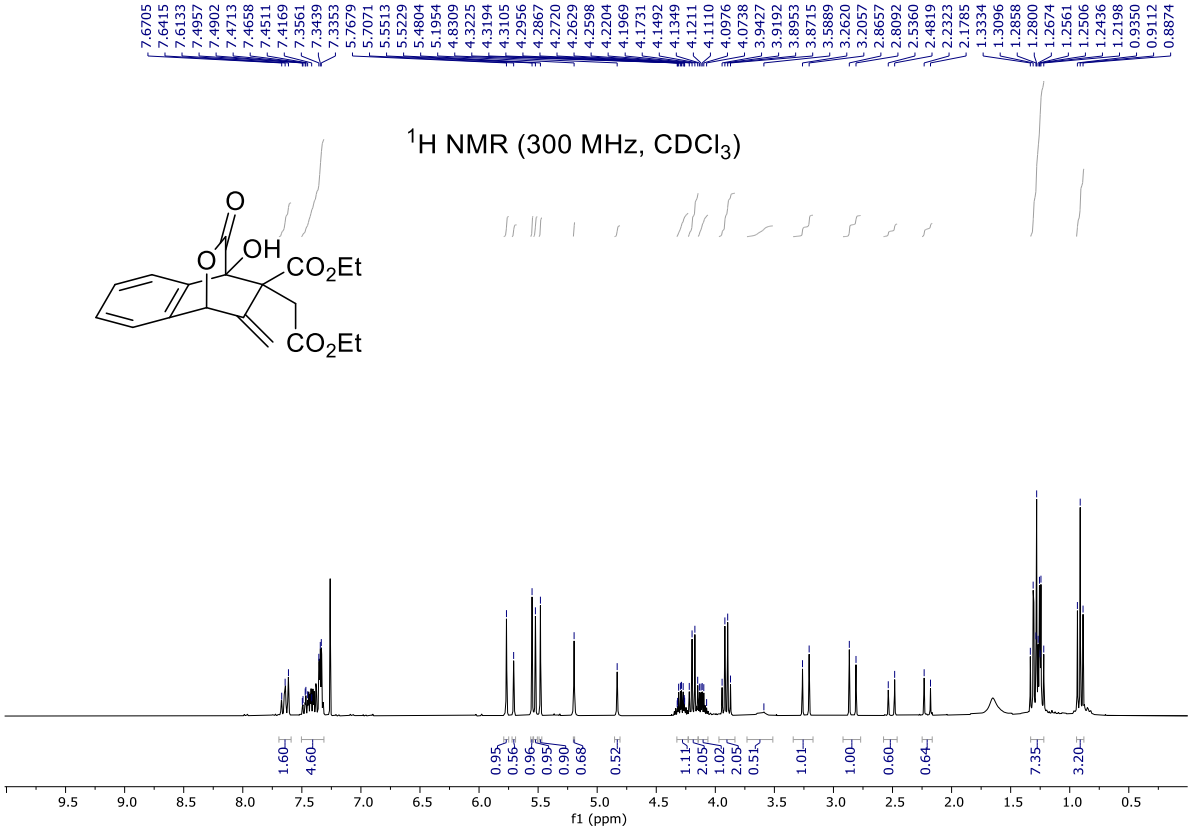


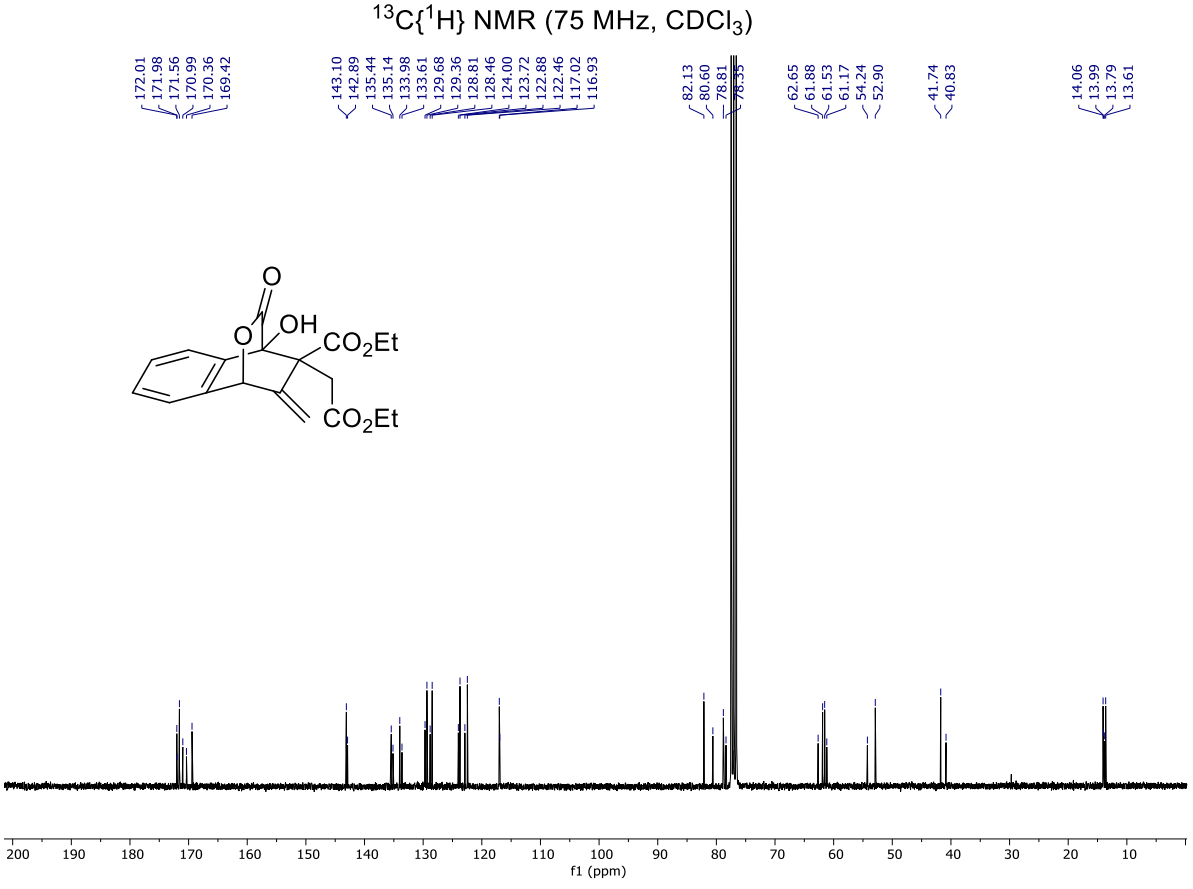
Ethyl 3-bromo-2-hydroxy-6-methylbenzoate (4l):



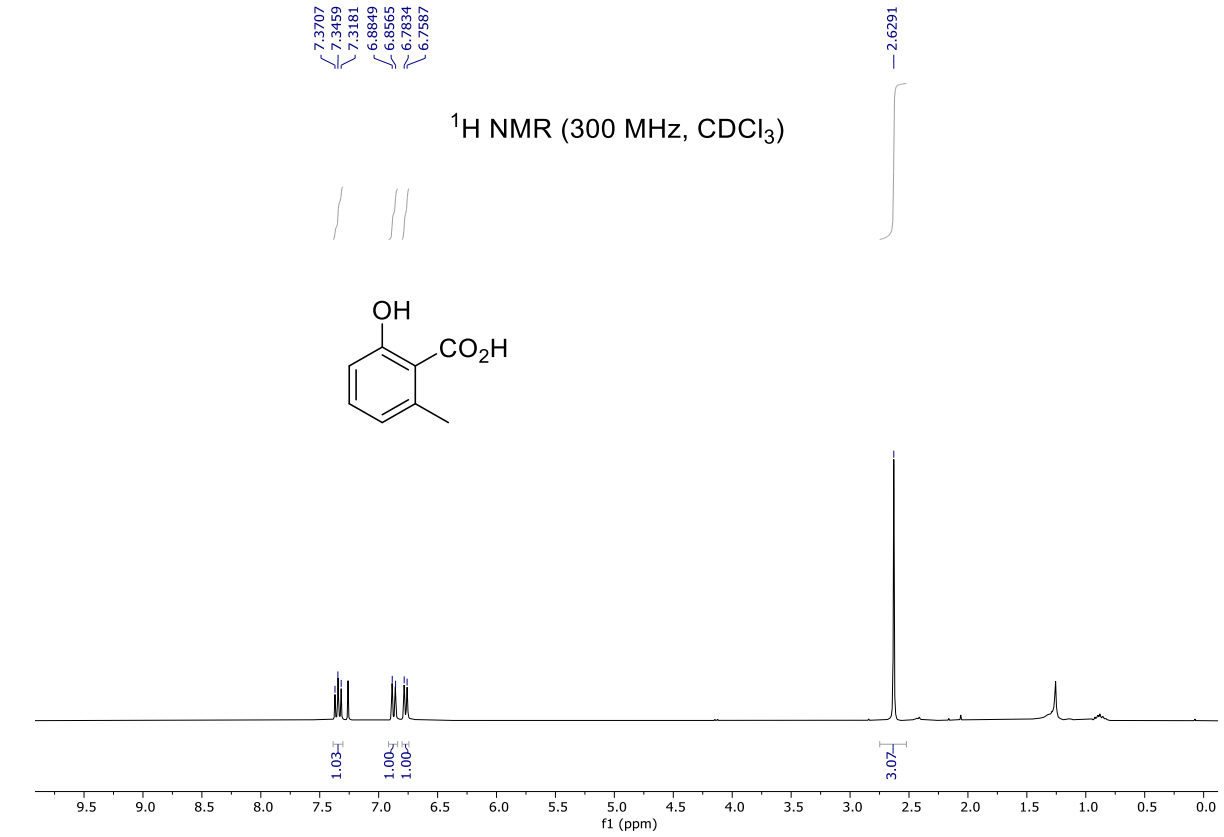


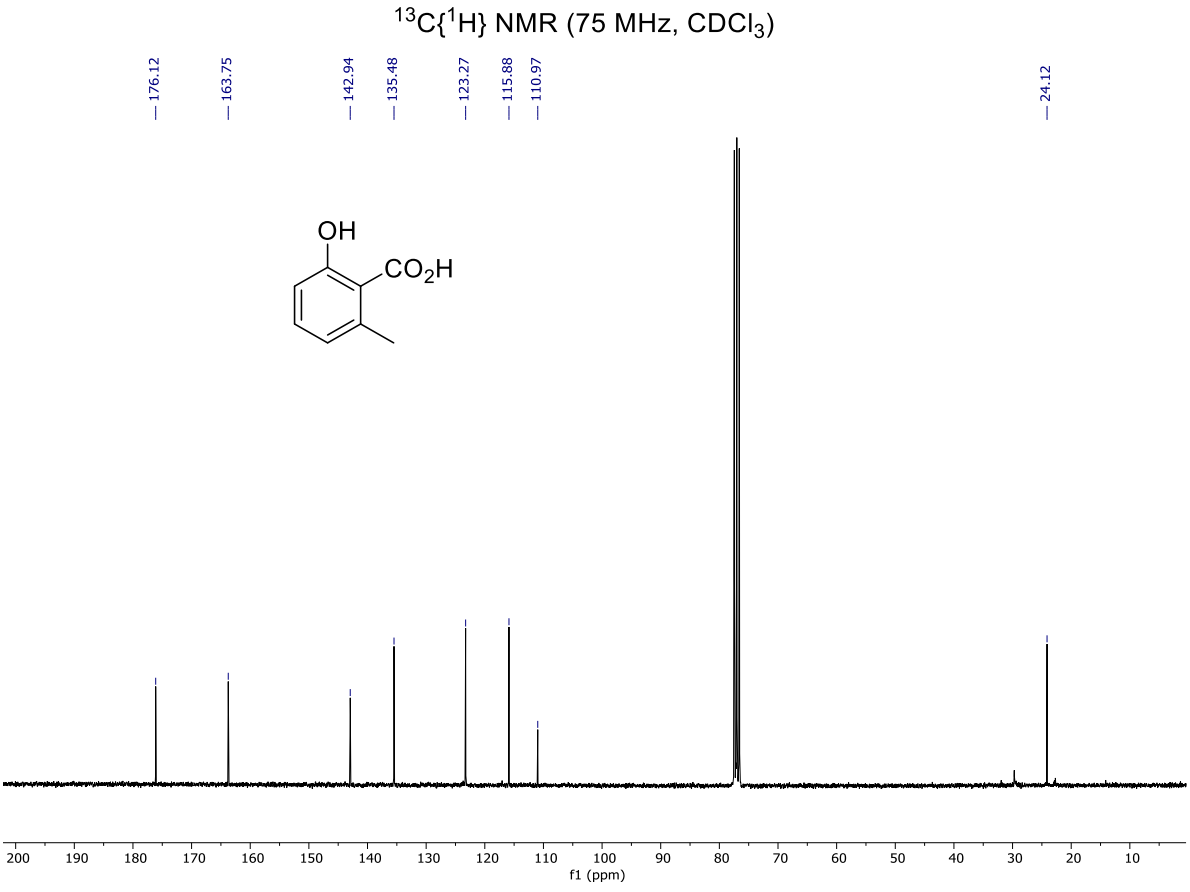
Ethyl-3-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylene-9-oxo-1,2,3,4-tetrahydro-1,4-(epoxymethano)naphthalene-3-carboxylate (9):



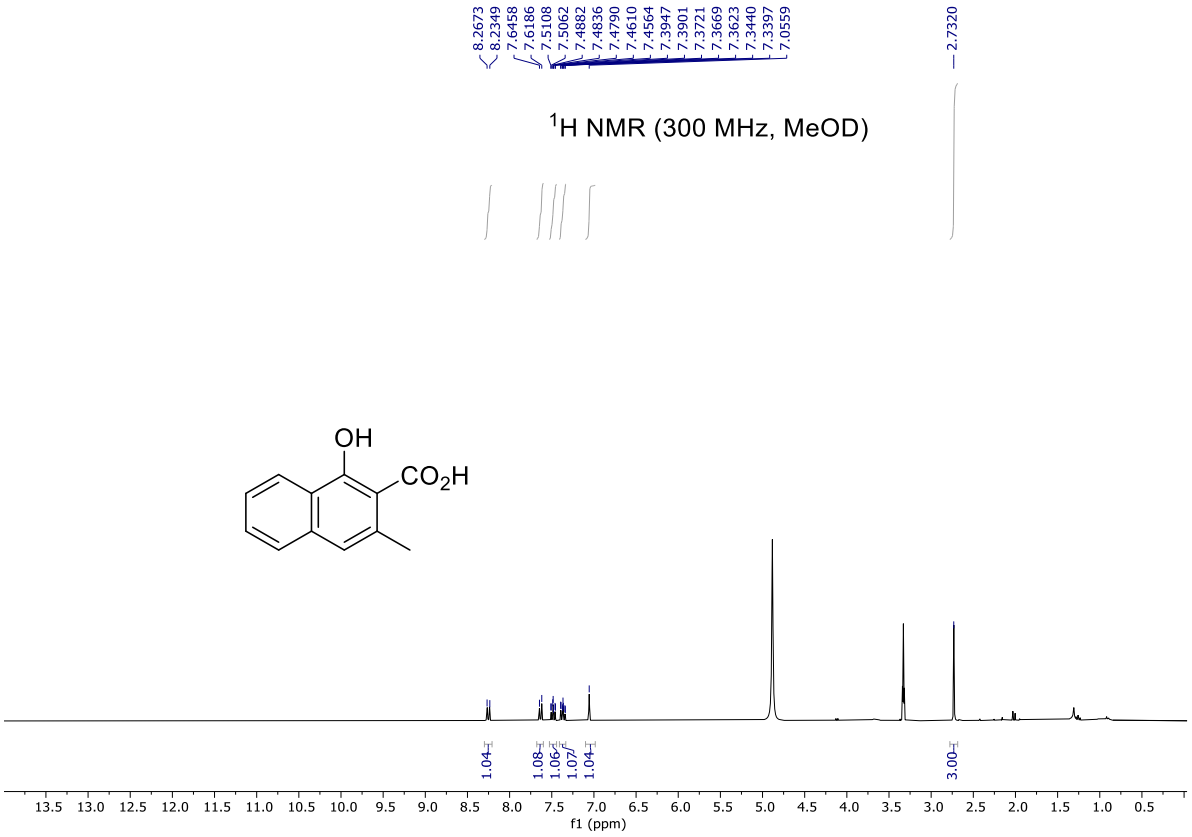


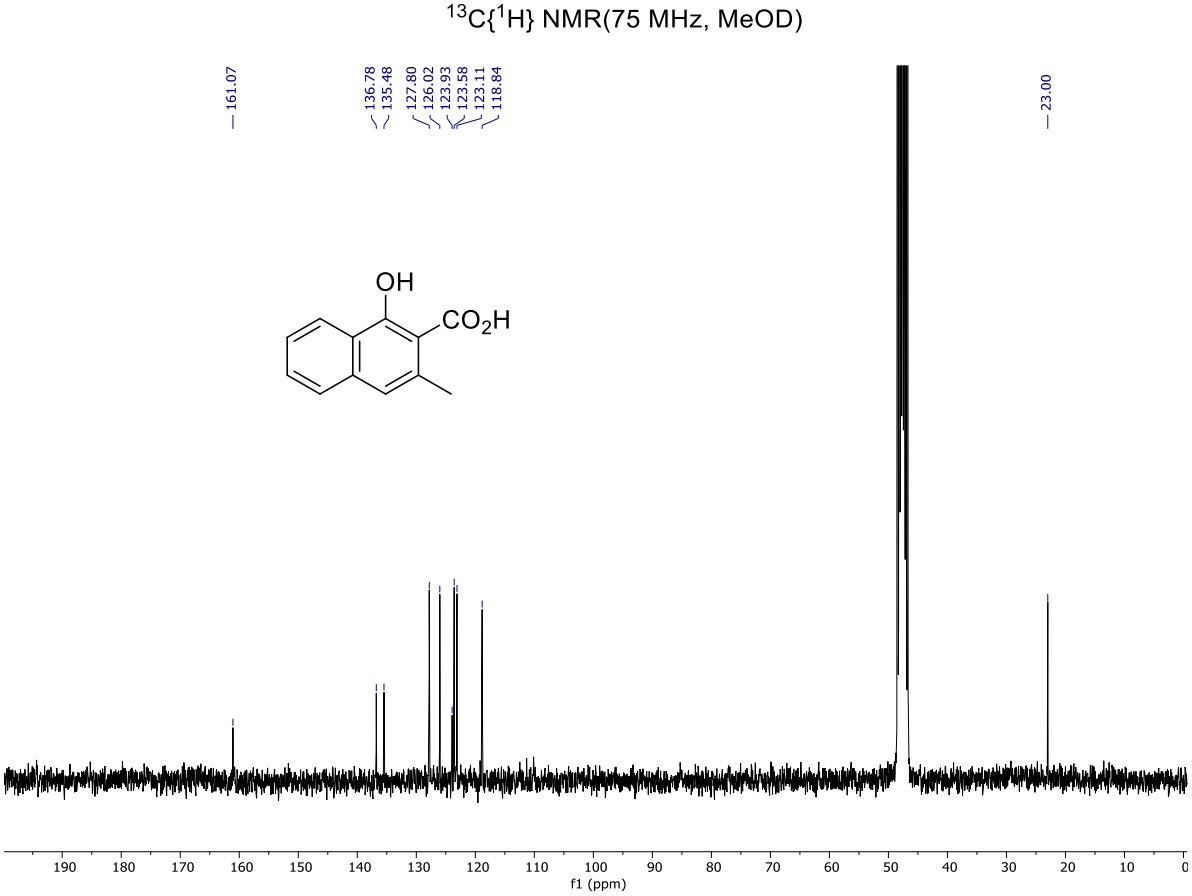
2-hydroxy-6-methylbenzoic acid (10):



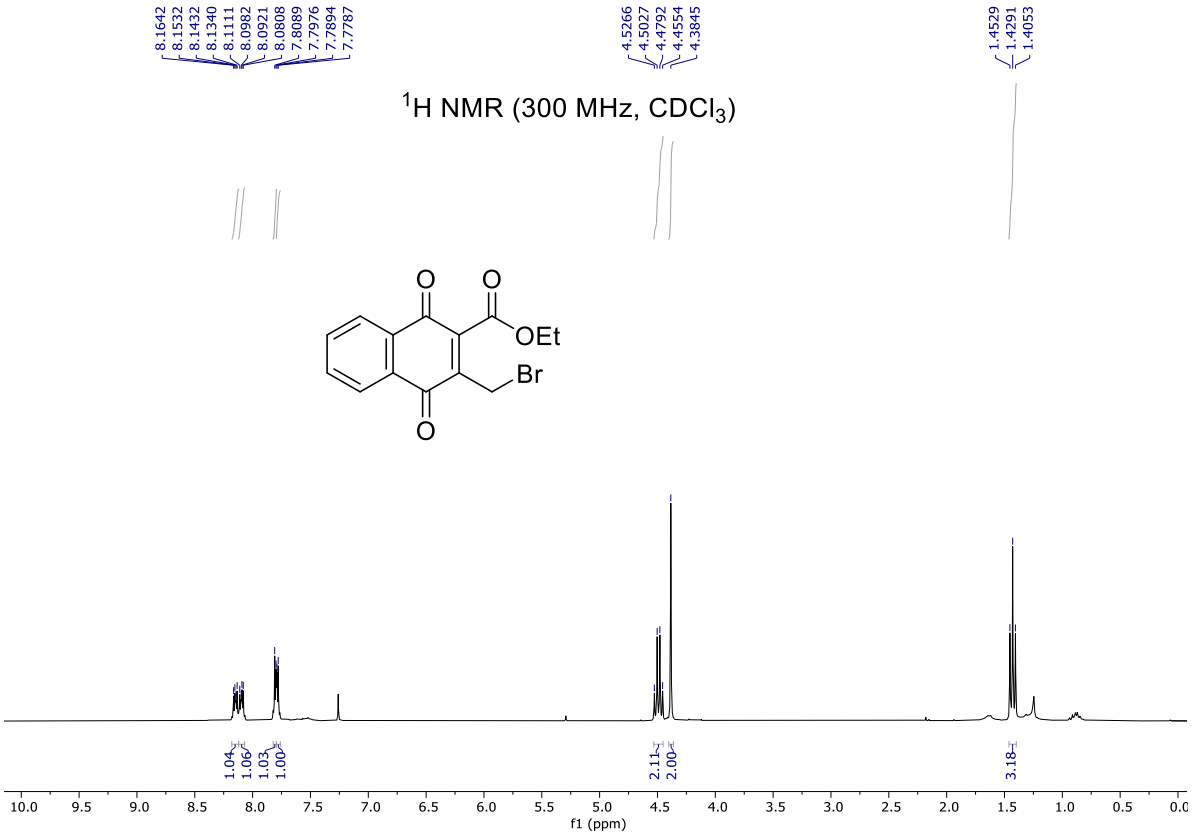


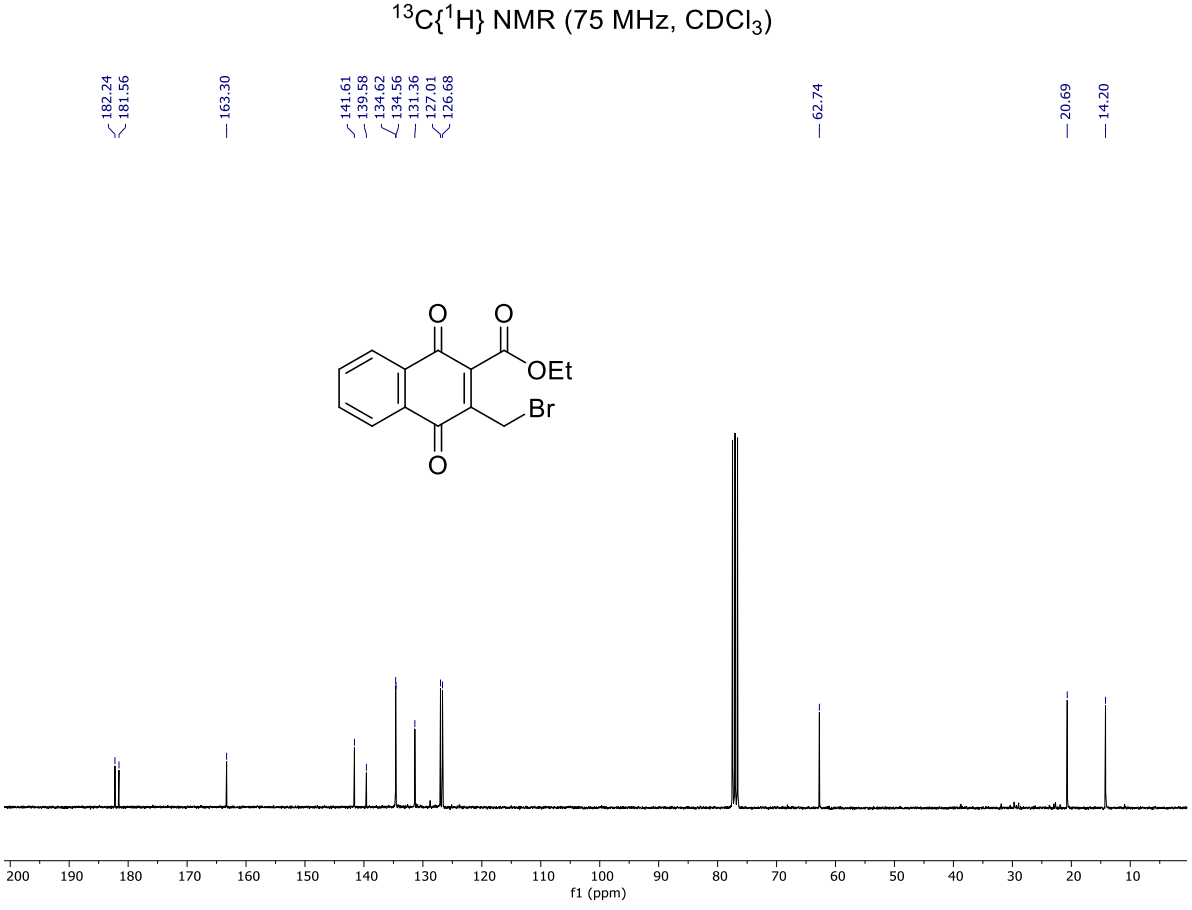
1-hydroxy-3-methyl-2-naphthoic acid (11):





Ethyl 3-(bromomethyl)-1,4-dioxo-1,4-dihydronaphthalene-2-carboxylate (12):





Ethyl 3-formyl-1,4-dihydroxy-2-naphthoate (13):