Electronic Supplementary Information for:

A photoredox-neutral Smiles rearrangement of 2-aryloxybenzoic acids

Jose C. Gonzalez-Gomez,*[a] Nieves P. Ramirez,[a] Teresa Lana-Villarreal,[b] and Pedro Bonete[b]

[a] Instituto de Síntesis Orgánica (ISO) and Departamento de Química Orgánica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain.

[b] Instituto Universitario de Electroquímica and Departamento de Química Física, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain.

Table of Contents:

1. General Remarks

Commercially available reagents were purchased from different trading houses and were used without further purification. For prepared reagents, experimental procedures are described and original references are included herein. TLCs were performed on silica gel 60 F_{254}, using aluminium plates and visualized by exposure to ultraviolet light. Flash chromatographies (FC) were carried out on handpacked columns of silica gel 60 (230 – 400 mesh). Melting points are uncorrected and measured with a Reichert Thermovar apparatus. Infrared (IR) analysis was performed with a JASCO FT/IR 4100 spectrophotometer equipped with an ATR component; wavenumbers are given in cm^{-1}. LRMS were performed in an AGILENT 6890N mass spectrometer coupled with a gas chromatographer (GC); the mobile phase was helium (2 mL/min); HP-1 column of 12 m was used; temperature program starts at 80 ºC for 3 min, then up to 270 ºC with a rate of 15 ºC/min, and 10 min at 270 ºC, using the Electron Impact (EI) mode at 70 eV (unless otherwise indicated). HRMS analyses were carried out in an AGILENT 7200 using the Electron Impact (EI) mode at 70 eV by Q-TOF .^{1}H-NMR spectra were recorded at 300 or 400 MHz for ^{1}H-NMR and 75 or 101 MHz for ^{13}C NMR, using $CDCl_3$ as the solvent and TMS as an internal Standard (0.00 ppm) (unless otherwise indicated). The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad signal, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.16 ppm. Reactions were irradiated using ABI 12W 450 nm Blue LED Par38. The incident light intensity on the reactor was measured using an optical power meter (Thorlabs PM100D) equipped with a thermopile sensor (Thorlabs model S310C). UV-vis absorption spectra were obtained with a Shimadzu UV-2401 PC spectrophotometer. Time-resolved and steady state emission spectra were recorded using a Fluoromax-4 spectrometer equipped with FluoroHub single photon counting controller from Horiba Scientific. Steady state measurements were performed using 430 nm as excitation wavelength with a bandwidth of 2 nm. For time resolved emission measurements a 450 nm nanoled from Horiba Scientific with 1.5 ns pulses was employed.

2. Calibration Curve for Product 2a using Gas Chromatography

In this calibration, durene was used as internal standard to quantify the amount of **2a** formed in each one of the conditions tested. In two different volumetric flasks, were prepared EtOAc solutions of product **2a** (25 mL, 1.18 x 10^{-3} mM), and of durene (**IS**, 25 mL, 1.90 x 10^{-3}mM). From them, five diluted solutions were obtained containing different **2a:IS** molar ratios, as indicated in the table below. These solutions were prepared in various vials and 1 µL of each one was injected into the chromatographer to obtain the following data.

Table S1.

	IS (µL)	**2a** (µL)	**IS** (µmol)	**2a** (µmol)	%Area **IS**	%Area **2a**	%Area **2a** /%Area **IS**	µmol **2a** /µmol **IS**
1	100	100	0.19	0.12	67.0	33.0	0.492	0.623
2	100	95	0.19	0.11	68.9	31.1	0.451	0.592
3	100	70	0.19	0.08	75.5	24.5	0.324	0.436
4	100	60	0.19	0.07	77.9	22.1	0.284	0.374
5	100	40	0.19	0.05	83.0	17.1	0.206	0.249

As a result, we obtained the following calibration curve:

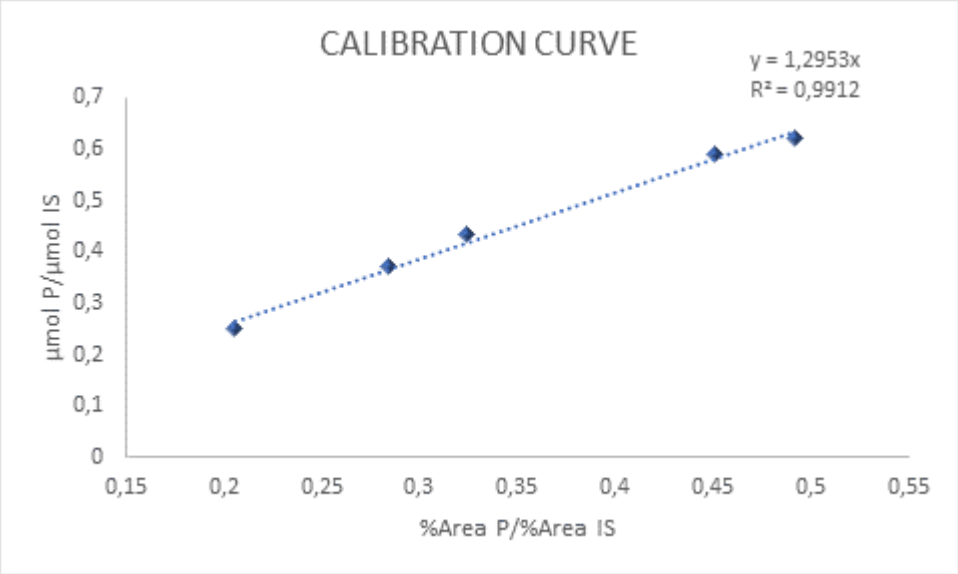
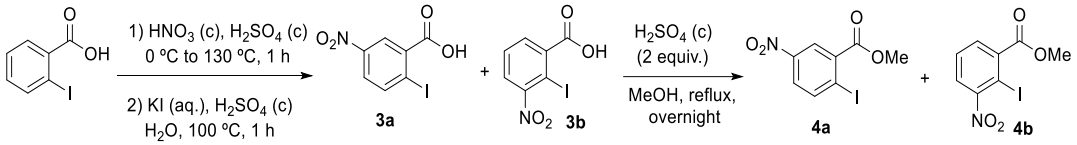


Figure S1. Calibration curve for 2a.

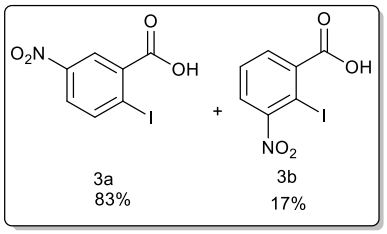
$$\frac{\mu mol\ \boldsymbol{2a}}{\mu mol\ \boldsymbol{IS}} = 1.2953\ x\ \frac{Area\ \boldsymbol{2a}}{Area\ \boldsymbol{IS}} \qquad \textbf{Eq S1}$$

3. Syntheses of 2-Halobenzoic Acids Derivatives

- *2-Iodobenzoic Acid Nitration*[1]



Step 1: A one neck round bottom flask was charged with 2-iodobenzoic acid (2 g, 8.06 mmol, 1 equiv.) and cooled to 0 ºC. Then, a mixture of HNO_3 (4 mL, 65%) and H_2SO_4 (9 mL, 98%) was added dropwise for 10 min, obtaining a dark mixture, which was stirred at 0 ºC for additional 15 min. The resulting mixture was then allowed to reach 23 ºC and stirred for 30 min. After this time, the reaction mixture was heated[2] at 130 ºC and stirred for 1 h (monitored by TLC). Subsequently, the reaction mixture was cooled down to reach room temperature and poured into ice-H_2O mixture (30 mL). The resulting pale-brown solid was filtered off under reduced pressure and washed with cold water until pH ~ 6. The white solid was suspended in H_2O (20 mL) and this mixture was treated carefully with an aqueous solution of KI (2 mL, 5.12 M). Finally, H_2SO_4 (5 drops, 98%) was added dropwise and the brown suspension was heated at 100 ºC whilst stirring for 1 h. The hot suspension was filtered and the resulting precipitate was washed with hot H_2O until pH ~ 6 to afford a white solid which was dried under reduced pressure to afford a regioisomeric mixture of **3a**:**3b** nitrated acids in a 83:17 ratio, respectively, according to ^{1}H-NMR.



2-Iodo-3-nitrobenzoic acid (**3b**) and 2-Iodo-5-ntrobenzoic acid (**3a**):[1b]

White solid (1.505 g); **^{1}H-NMR (300 MHz, DMSO-d_6)** *δ For major nitro isomer (**3a**):* 8.40 (d, *J* = 2.7 Hz, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.00 (*J* = 8.6, 2.8 Hz, 1H); *For minor nitro isomer (**3b**):* 7.92 (dd, *J* = 7.9, 1.5 Hz, 0.21 H), 7.79 (dd, *J* = 7.7, 1.5 Hz, 0.21H), 7.66 (t, *J* = 7.8 Hz, 0.21H) ppm.

Fischer Esterification: To a suspension of the above-mentioned mixture of carboxylic acids (1.600 g, 5.21 mmol) in MeOH (45 mL) was added H_2SO_4 (500 µL, 98%, 2 equiv.), and the obtained yellow mixture was heated at reflux whilst stirring overnight.

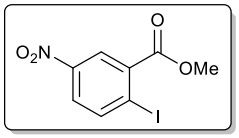
---

[1] (a) V. Subramanian, V. R. Batchu, D. Barange and M. Pal, *J. Org. Chem.*, 2005, **70**, 4778; (b) For the aqueous KI treatment see: N. Santschi, R. C. Sarott, E. Otth, R. Kissner and A. Togni, *Beilstein J. Org. Chem.*, 2014, **10**, 1.

[2] During this preparation, I_2 formation was observed. For this reason, this reaction must be conducted in a well-ventilated fume hood.

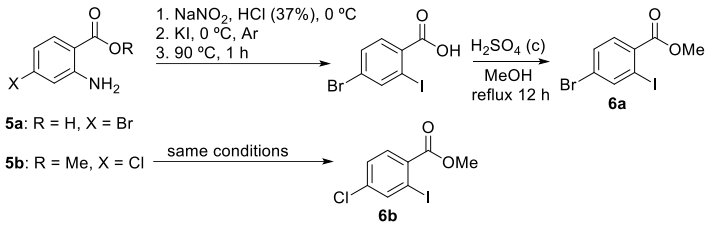
After this time, the reaction mixture was allowed to reach room temperature and MeOH was removed under reduced pressure. The solid residue obtained was suspended in H_2O (30 mL), verifying pH ~ 3, and treated with a saturated aqueous $NaHCO_3$ solution until pH ~ 5. Then, EtOAc (40 mL) was added and the two-layers mixture was stirred vigorously at room temperature for 15 min. Phases were separated and the aqueous layer was extracted with EtOAc (3 x 40 mL). Organic extracts were combined, washed with brine (1 x 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to give a solid residue which was purified by column chromatography (100% Hexane to 80:20 Hexane/EtOAc).

Methyl 2-iodo-5-nitrobenzoate (**4a**) [CAS 112239-00-6]:



Pale-yellow solid (1.075 g, 3.50 mmol, 43% over two steps): **TLC** R_f 0.19 (95:5 Hexane/EtOAc); **IR** ν 1686, 1669, 1603, 1469, 1441, 1260, 1236, 1084, 1060, 905, 722 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.64 (d, J = 2.7 Hz, 1H), 8.23 (d, J = 8.6 Hz, 1H), 7.99 (dd, J = 8.7, 2.7 Hz, 1H), 4.01 (s, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 165.1 (C), 147.8 (C), 143.0 (CH), 136.3 (C), 126.5 (CH), 125.7 (CH), 102.8 (C), 53.3 (CH_3) ppm; **GC** R_T 11.436 min; **LRMS (EI)** *m/z* (%) = 308 (M^+ + 1, 10), 307 (M^+, 99), 277 (18), 276 (100).

- *Methyl 2-Iodobenzoate Derivatives Syntheses*[1a,3]



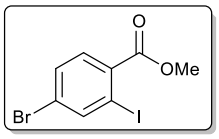
To a one neck round bottom flask equipped with a stirring magnetic bar, a suspension of the desired aniline (**5a** or **5b**, 6 mmol, 1 equiv.) in H_2O (12 mL) was added, followed by HCl (6 mL, 60 mmol, 10 equiv., 37%). The resulting suspension was cooled down to 0 ºC whilst stirring under Ar atmosphere. When the mixture reached this temperature, an aqueous solution of $NaNO_2$ (414 mg, 7.20 mmol, 1.20 equiv.) was added dropwise for 10 min and then, the orange mixture was stirred for 30 min under the same conditions. At this time, a cold aqueous solution of KI (1.495 g, 9 mmol, 1.50 equiv.) was added slowly during 10 min at 0 ºC, while stirring under Ar atmosphere, and the resulting red-brown mixture was stirred for another 1 h. The cooling bath was removed and the reaction was heated to 90 ºC for 1 h whilst stirring under Ar atmosphere. Finally, the

[3] W. Ma, J. Fang, J. Ren and Z. Wang, *Org. Lett.*, 2005, **17**, 4180.

mixture was allowed to reach room temperature and it was quenched with an aqueous saturated solution of $Na_2S_2O_3$ (15 mL). EtOAc (15 mL) was added, the two-layer mixture was stirred vigorously at room temperature for 15 min, phases were separated and the aqueous layer was extracted with EtOAc (3 x 15 mL). Organic extracts were successively washed with saturated $Na_2S_2O_3$ solution (2 x 10 mL) and brine (1 x 5 mL), dried over anhydrous Mg_2SO_4, filtered and concentrated under reduced pressure to give the desired crude product which was purified by column chromatography.

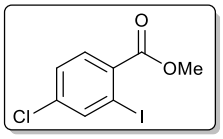
The following procedure to the preparation of the ester **6a** is like the previously describes method to the Fischer esterification method that appears in the previous page.

Methyl 4-bromo-2-iodobenzoate (**6a**):[4]



Compound **6a**[5] was purified by column chromatography (100% Hexane to 97:3 Hexane/EtOAc) and obtained as a yellow oil (201 mg, 0.59 mmol, 40%): **TLC** R_f 0.42 (95:5 Hexane/EtOAc); visualized by exposure to UV light; **IR** ν 2888, 1731, 1564, 1433, 1282, 1245, 1109, 1030, 768, 728 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 8.17 (d, J = 1.9 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.54 (dd, J = 8.4, 1.9 Hz, 1H), 3.93 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 166.2 (C), 143.7 (CH), 133.7 (C), 132.1 (CH), 131.3 (CH), 126.8 (C), 95.0 (C), 52.8 (CH_3) ppm; **GC** R_T 10.749 min; **LRMS (EI)** *m/z* (%) = 342 (M^+, ^{81}Br, 74), 340 (M^+, ^{79}Br, 74), 311 (^{81}Br, 100), 309 (^{79}Br, 100).

Methyl 4-chloro-2-iodobenzoate (**6b**):[6]



Compound **6b** was purified by column chromatography (100% Hexane to 99:1 Hexane/EtOAc) and obtained as a yellow oil (992 mg, 3.36 mmol, 56%): **TLC** R_f 0.42 (95:5 Hexane/EtOAc); visualized by exposure to UV light; **IR** *v* 2989, 1728, 1571, 1276, 1248, 1041, 899, 717 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 8.01 (*d*, J = 2.0 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.39 (dd, J = 8.4, 2.1 Hz, 1H), 3.93 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 166.1 (C), 141.1 (CH), 138.3 (C), 133.2 (C), 131.9 (CH), 128.3 (CH), 94.7 (C), 52.7 (CH_3) ppm; **GC** R_T 10.095 min; **LRMS (EI)** *m/z* (%) = 298 (M^+ ^{37}Cl, 29), 296 (M^+ ^{35}Cl, 84), 267 (^{37}Cl, 40), 266 (^{35}Cl, 10), 265 (^{35}Cl, 100).

---

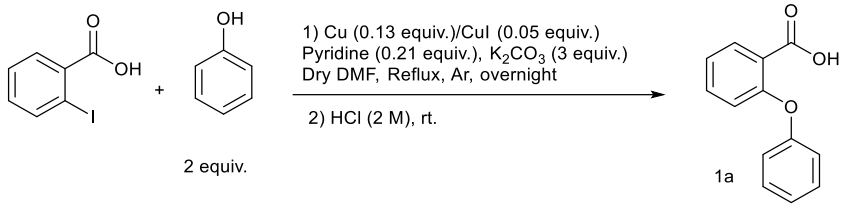
[4] J. M. L'Helgoual'ch, G. Bentabed-Ababsa, G. Chevallier, M. Yonehara, M. Uchiyama, A. Derdour and F. Mongin, *Chem. Commun.*, 2008, 5375.

[5] Before purification, the crude of the Sandsmeyer reaction was esterified using the method describe above for compound **4a**.

[6] A. J. Kennedy, A. M. Bruce, C. Gineste, T. E. Ballard, I. N. Olekhnovich, T. L. Macdonald and P. S. Hoffman, *Antimicrob. Agents Chemother.*, 2016, **60**, 3980.

4. Syntheses of 2-Aryloxybenzoic acids.

Method A: Ullmann coupling using carboxylic acids as starting materials



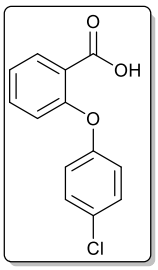
To a flamed dried two neck round bottom flask was added 2-iodobenzoic acid (2.532 g, 10 mmol) and dry DMF (80 mL), under Ar atmosphere. To this solution, were added phenol (1.900 g, 20 mmol, 2 equiv.), followed by K_2CO_3 (4.190 g, 30 mmol, 3 equiv.) and pyridine (166 μL, 2.10 mmol, 0.21 equiv.). The mixture was purged with Ar at room temperature for 5 min. Then, Cu (85 mg, 1.30 mmol, 0.13 equiv.) and CuI (95.6 mg, 0.50 mmol, 0.05 equiv.) were added. Finally, the blue reaction mixture was heated to reflux, while stirring under Ar atmosphere overnight. After this time, the reaction mixture was cooled down to room temperature, poured into H_2O (400 mL) (pH ~ 8) and quenched with HCl (2M) until pH ~ 3. At this point, the formed precipitated was filtered out, washed with cold H_2O until pH ~ 6, and dried under vacuum. The resulting pale-brown solid was purified by column chromatography to obtain the desired compound **1a**[7] as a white-solid (1.032 g, 4.82 mmol, 48%).

TLC R_f 0.15 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** (EtOH/H_2O 1:1) 110 - 113 ºC/lit.[9]110 - 112 ºC; **IR** *ν* 2750, 1681, 1597, 1576, 1485, 1447, 1415, 1237, 919, 753, 694, 654 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** *δ* 8.18 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.45 - 7.38 (m, 2H), 7.28 - 7.16 (m, 2H), 7.10 (dd, *J* = 8.5, 0.9 Hz, 2H), 6.87 (dd, *J* = 8.4, 0.7 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** *δ* 166.8 (C), 157.4 (C), 155.0 (C), 134.9 (CH), 133.6 (CH), 130.4 (2 x CH), 125.4 (CH), 123.8 (CH), 120.2 (2 x CH), 119.9 (C), 118.1 (CH) ppm; **GC** R_T 12.050 min; **LRMS (EI)** *m/z* (%) = 214 (M^+, 45), 197 (8), 168 (7), 139 (6), 122 (8), 121 (100), 120 (9), 94 (6), 93 (7), 92 (7), 77 (10), 65 (8), 51 (9).

2-(4-Chlorophenoxy)benzoic acid (**1b**):[7]

Compound **1b** was prepared from 2-iodobenzoic acid (1.735 g, 6 mmol, 1 equiv.) and *p*-chlorophenol (1.518 g, 12 mmol, 2 equiv.) following the general *method A* described above for **1a.**

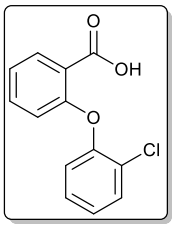
[7] A. Hossian and R. Jana, *Org. Biomol. Chem.*, 2016, **14**, 9768.
[8] J. P. Taygerly, L. M. Miller, A. Yee and E. A. Peterson, *Green Chem.* 2012, **14**, 3020.
[9] R. F. Pellón, A. Martín, M. Mesa, M. L. Docampo and V. Gomez, *J. Chem. Res.*, 2006, **8**, 527.



Compound **1b** was obtained as a white solid (656 mg, 2.64 mmol, 44%): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 115 – 116 ºC/lit.[7] 115 – 117 ºC; **IR** *v* 2836, 1687, 1601, 1480, 1309, 1240, 1165, 1087, 927, 820, 754, 702 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.12 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.33 (dd, *J* = 5.4, 4.4 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.23 (td, J = 7.8, 1.1 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.98 (dd, *J* = 5.4, 4.4 Hz, 1H), 6.91 (dd, *J* = 8.3, 0.9 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.8 (C), 157.0 (C), 154.8 (C), 135.0 (CH), 133.3 (CH), 130.0 (2 x CH), 129.6 (C), 124.1 (CH), 120.9 (C), 120.6 (2 x CH), 119.5 (CH) ppm; **GC** R_T 13.438 min; **LRMS (EI)** *m/z* (%) = 250 (M^+ ^{37}Cl, 11), 248 (M^+ ^{35}Cl, 31), 139 (10), 122 (12), 121 (100), 120 (8), 93 (9), 75 (8), 66 (7).

2 - (2 - Chlorophenoxy)benzoic acid (**1g**):[10]

Compound **1g** was prepared from 2-iodobenzoic acid (506 mg, 2 mmol, 1 equiv.) and *o*-chlorophenol (423 µL, 4 mmol, 2 equiv,) following the general *method A* described above for **1a.**



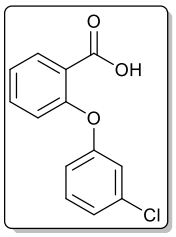
Compound **1g** was obtained as a pale - brown solid (203 mg, 0.82 mmol, 41%): **TLC** R_f 0.12 ([9:1 Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 119 - 121 ºC/lit.[10] 114 - 115 ºC; **IR** *v* 2980, 1668, 1471, 1444, 1262, 1237, 939, 754 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.18 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.30 (td, *J* = 7.8, 1.7 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.75 (dd, *J* = 8.3, 0.7 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.6 (C), 156.8 (C), 150.7 (C), 134.9 (CH), 133.7 (CH), 131.3 (CH), 128.4 (CH), 126.6 (C), 126.4 (CH), 123.8 (CH), 122.0 (CH), 119.7 (C), 117.2 (CH) ppm; **GC** R_T 12.744 min; **LRMS (EI)** *m/z* (%) = 250 (M^+ ^{37}Cl, 6), 248.(M^+ ^{35}Cl, 19), 213 (10), 168 (11), 139 (16), 121 (100), 120 (14), 92 (15), 65 (16), 63 (14), 50 (11).

2 - (3 - Chlorophenoxy)benzoic acid (**1k**):[7]

Compound **1k** was prepared from 2-iodobenzoic acid (506 mg, 2 mmol, 1 equiv.) and *m*-chlorophenol (430 µL, 4 mmol, 2 equvi.) following the general *method A* described above for **1a.**

Compound **1k** was obtained as a pale-brown solid (233 mg, 0.94 mmol, 47%): **TLC** R_f 0.12 ([9:1 Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 94 - 96 ºC/lit.[7] 98 -

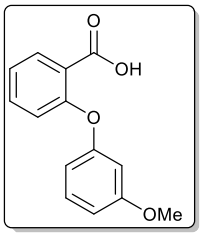
[10] R. F. Pellón and M. L. Docampo, *Synth. Commun.*, 2003, **33**, 921.



100ºC; **IR** *v* 3060, 1697, 1592, 1471, 1264, 1232, 911, 734, 704 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.12 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.30 - 7.23 (m, 2H), 7.13 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.01 (t, *J* = 2.1 Hz, 1H), 6.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.91 (ddd, *J* = 8.3, 2.4, 0.9 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.9 (C), 157.3 (C), 156.5 (C), 135.4 (C), 135.0 (CH), 133.3 (CH), 130.8 (CH), 124.4 (CH), 124.3 (CH), 121.4 (C), 120.3 (CH), 119.4 (CH), 117.2 (CH) ppm; **GC** R_T 13.295 min; **LRMS (EI)** *m/z* (%) = 250 (M^+ ^{37}Cl, 12), 248 (M^+ ^{35}Cl, 38), 168 (11), 139 (11), 121 (100), 120 (13), 92 (7), 75 (8).

2-(3-Methoxyphenoxy)benzoic acid (**1l**):[7]

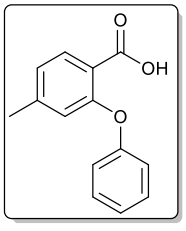
Compound **1l** was prepared from 2-iodobenzoic acid (506 mg, 2 mmol, 1 equiv.) and 3-methoxyphenol (449 µL, 4 mmol, 2 equiv.) following the general *method A* described above for **1a.**



Compound **1l** was obtained as a pale-brown solid (209 mg, 0.86 mmol, 43% over two steps): **TLC** R_f 0.13 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 119 - 120 ºC/lit.[7] 118 - 120 ºC; **IR** *v* 2967, 2655, 2580, 1604, 1487, 1445, 1264, 1228, 1147, 1086, 955, 844, 773, 687 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.31 - 7.26 (m, 1H), 7.21 (td, *J* = 7.9, 1.1 Hz, 1H), 6.92 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.76 (ddd, *J* = 8.4, 2.3, 0.9 Hz, 1H), 6.66 (dd, *J* = 2.2, 0.9 Hz, 1H), 6.64 (dd, *J* = 4.2, 2.0 Hz, 1H), 3.79 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.7 (C), 161.3 (C), 157.2 (C), 156.5 (C), 134.9 (CH), 133.4 (CH), 130.7 (CH), 123.8 (CH), 120.2 (C), 118.8 (CH), 111.9 (CH), 110.7 (CH), 105.9 (CH), 55.6 (CH_3) ppm; **GC** R_T 13.707 min; **LRMS (EI)** *m/z* (%) = 245 (M^+ + 1, 14), 244 (M+, 90), 199 (18), 184 (16), 124 (25), 121 (100), 92 (13), 77 (10), 64 (11).

4-Methyl-2-phenoxybenzoic acid (**1o**):

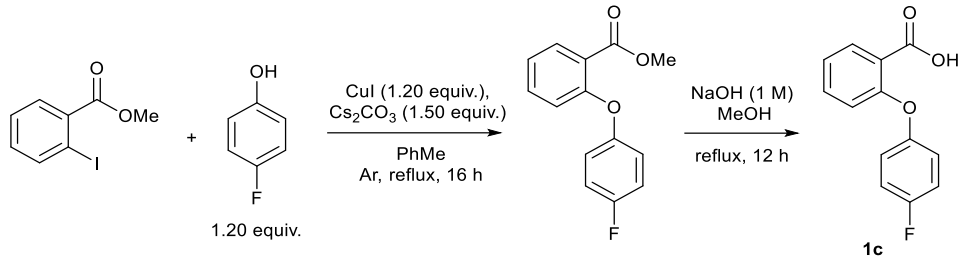
Compound **1o** was prepared from 2-bromo-4-methylbenzoic acid (1.317 g, 6 mmol, 1 equiv.) and phenol (1.140 g, 12 mmol, 2 equiv.) following the general *method A* described above for **1a**.



Compound **1o** was obtained as a white solid (625 mg, 2.74 mmol, 46%): **TLC** R_f 0.15 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 138 - 140 ºC; **IR** *v* 2594, 1686, 1665, 1610, 1488, 1412, 1310, 1243, 1203, 1155, 1088, 953, 827, 766, 692 cm^{-1}; **^{1}H-NMR (300**

MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.44 - 7.37 (m, 2H), 7.25 -7.19 (m, 1H), 7.11 - 7.05 (m, 2H), 7.01 (dd, J = 8.0, 0.8 Hz, 1H), 6.66 (br s, 1H), 2.30 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.2 (C), 157.3 (C), 155.2 (C), 146.4 (C), 133.4 (CH), 130.3 (2 x CH), 125.1 (CH), 124.8 (CH), 120.1 (2 x CH), 118.8 (CH), 117.2 (C). 22.0 (CH_3) ppm; **GC** R_T 12.291 min; **LRMS (EI)** *m/z* (%) = 228 (M^+, 35) , 211 (7), 136 (11), 135 (100), 134 (9), 77 (14), 51 (8); **HRMS (EI)** *Calcd.* for $C_{14}H_{12}O_3$ 228.0786, found 228.0783.

Method B: Ullmann coupling using methyl 2-iodobenzoate derivatives and subsequent hydrolysis.



Ullmann coupling: Into a flamed dried Pyrex tube, equipped with a stirring magnetic bar and under Ar atmosphere, was added a solution of 4-fluorophenol (272 mg, 2.40 mmol, 1.20 equiv.) in dry PhMe (4 mL). To this solution were added the methyl 2-iodobenzoate derivative (297 µL, 2 mmol, 1 equiv.) and Cs_2CO_3 (681 mg, 2.07 mmol, 1.50 equiv.). Then, Ar was flushed for 5 min and CuI (190 mg, 1 mmol, 0.5 equiv.) was added. Finally, the reaction mixture was heated at 130 º C, while stirring under Ar atmosphere overnight. After full conversion (monitored by TLC and/or GC), the reaction mixture was diluted with EtOAc (7 mL), filtered through a short pad of celite and washed with EtOAc (8 mL). The filtrate was concentrated under reduced pressure and the resulting brown residue was purified by column chromatography to provide the corresponding methyl esters as oils.

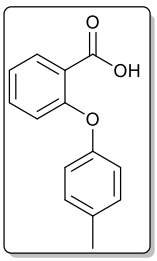
Hydrolysis: To a stirred solution of the desired methyl ester (1 mmol) in MeOH (4 mL) was added an aqueous solution of NaOH (1 M, 4 mL) at room temperature. The reaction mixture was heated to reflux, observing complete hydrolysis by TLC after 12 h. The reaction mixture was concentrated under reduced pressure. The residue was quenched with 2 M HCl until pH < 3 and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (1 × 5 mL), dried over anhydrous $MgSO_4$,

filtered, and concentrated under reduced pressure to afford the desired pure compound **1c.**[7]

Compound **1c** was obtained as a pale-brown solid (202, 0.87 mmol, 44% over two steps): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 142 - 143 ºC/lit.[7] 142 - 144 ºC; **IR** *v* 2924, 1685, 1592, 1502, 1483, 1249, 1209, 1192, 1084, 849, 768 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.21 (td, *J* = 7.9, 1.0, Hz, 1H), 7.14 - 7.02 (m, 4H), 6.84 (dd, *J* = 8.4, 0.8 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.0 (C), 159.9 (d, *J* = 244.4 Hz, C), 157.6 (C), 151.0 (d, *J* = 3.0 Hz, C), 135.0 (CH), 133.6 (CH), 123.8 (CH), 121.7 (d, *J* = 8.1 Hz, 2 × CH), 119.9 (C), 117.9 (CH), 117.0 (d, *J* = 24.2 Hz, 2 × CH) ppm; **GC** R_T 11.958 min; **LRMS (EI)** *m/z* (%) = 233 (M^+ + 1, 7), 232 (M^+, 42), 215 (6), 186 (9), 157 (6), 133 (6), 122 (8), 121 (100), 120 (8), 112 (7), 93 (9), 92 (8), 75 (7), 65 (8).

2-(*p*-Tolyloxy)benzoic acid (**1d**):[7]

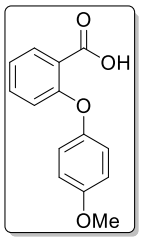
Compound **1d** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol, 1 equiv.) and *p*-cresol (259.2 mg, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1d** was obtained as a pale-brown solid (221 mg, 0.97 mmol, 49% over to steps): **TLC** R_f 0.11 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 117 - 119 ºC/lit.[7] 117 - 119 ºC; **IR** *v* 2987, 2592, 1669, 1600, 1481, 1460, 1303, 1234, 1164, 933, 878, 835, 756 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.18 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 7.23 - 7.16 (m, 3H), 7.04 - 6.96 (m, 2H), 6.83 (dd, *J* = 8.4, 0.8 Hz, 1H), 2.37 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 166.9 (C), 157.9 (C), 152.4 (C), 135.3 (C), 134.9 (CH). 133.5 (CH), 130.9 (2 x CH), 123.4 (CH), 120.3 (2 x CH), 119.4 (C), 117.5 (CH), 20.9 (CH_3) ppm; **GC** R_T 12.884 min; **LRMS (EI)** *m/z* (%) = 229 (M^+ + 1, 7), 228 (M^+, 47), 181 (8), 122 (8), 121 (100), 108 (11), 107 (8), 65 (11).

2-(4-Methoxyphenoxy)benzoic acid (**1e**):[7]

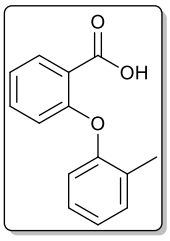
Compound **1e** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol, 1 equiv.) and *p*-methoxyphenol (301 mg, 2.4 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1e** was obtained as a white solid (215 mg, 0.88 mmol, 44% over two steps): **TLC** R_f 0.13 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 133 - 136 ºC/lit.[7] 143 - 145 ºC; **IR** *v* 2890, 1686, 1596, 1504, 1270, 1220, 1193, 1032, 838, 764 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.19 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.20 - 7.14 (m, 1H), 7.07 (d, *J* = 9.1 Hz, 1H), 7.07 (dd, *J* = 5.9, 4.6 Hz, 1H), 6.95 (dd, *J* = 5.9, 4.6 Hz, 1H), 6.79 (dd, *J* = 8.4, 0.5 Hz, 1H), 3.83 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 165.7 (C), 158.3 (C), 157.3 (C), 147.3 (C), 135.0 (CH), 133.8 (CH), 123.4 (CH), 122.0 (2 x CH), 118.8 (C), 116.5 (CH), 115.5 (2 x CH), 55.9 (CH_3) ppm; **GC** R_T 13.247 min; **LRMS (EI)** *m/z* (%) = 244 (M+, 36), 124 (36), 121 (100), 65 (23).

2-(*o*-Tolyloxy)benzoic acid (**1h**):[7]

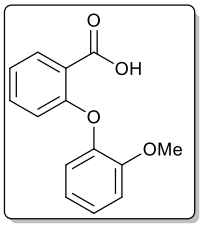
Compound **1h** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol, 1 equiv.) and *o*-cresol (250 µL, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1h** was obtained as a pale-yellow solid (182 mg, 0.80 mmol, 40% over two steps): **TLC** R_f 0.13 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 122 ºC/lit.[7] 122 - 124 ºC; **IR** *v* 2820, 1670, 1602, 1460, 1388, 1308, 1232, 1088, 907, 756 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.33 - 7.14 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 2.22 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 157.6 (C), 152.1 (C), 134.9 (C), 133.8 (C), 132.2 (2 x CH), 130.7 (C), 127.9 (2 x CH), 126.2 (CH), 123.1 (CH), 121.2 (CH), 115.9 (CH), 16.2 (CH_3) ppm; **GC** R_T 12.518 min; **LRMS (EI)** *m/z* (%) = 229 (M^+ + 1, 12), 228 (M+, 82), 211 (10), 209 (14), 182 (17), 181 (58), 153 (10), 121 (100), 91 (23), 77 (11), 65 (20).

2-(2-Methoxyphenoxy)benzoic acid (**1i**):[7]

Compound **1i** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol, 1 equiv.) and guaiacol (301 mg, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

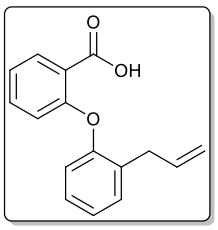


Compound **1i** was obtained as a pale - yellow solid (217 mg, 0.89 mmol, 45% over two steps): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 115 - 116 ºC/lit.[7] 114 - 116 ºC;

IR *v* 2837, 1662, 1602, 1460, 1304, 1257, 1220, 742 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.18 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 7.31 - 7.26 (m, 1H), 7.22 - 7.14 (m, 2H), 7.05 - 7.00 (m, 2H), 6.77 (dd, *J* = 8.4, 0.9 Hz, 1H), 3.78 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 166.1 (C), 157.7 (C), 151.5 (C), 142.2 (C), 134.6 (CH), 133.5 (CH), 127.3 (CH), 123.2 (CH), 123.1 (CH), 121.3 (CH), 118.8 (C), 115.6 (CH), 113.2 (CH), 56.0 (CH_3) ppm; **GC** R_T 12.886 min; **LRMS (EI)** *m/z* (%) = 244 (M+, 48), 207 (9), 124 (18), 121 (100), 65 (10).

2-(2-Allylphenoxy)benzoic acid (**1j**):

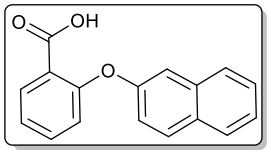
Compound **1j** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol) and 2-allylphenol (319 µL, 2.40 mmol, 2 equiv.) following the general *method B* described above for **1c**.



Compound **1j** was obtained after re-crystallization (EtOH/H_2O 1:1) as a pale-brown crystalline solid (216 mg, 0.85 mmol, 43% over two steps): **TLC** R_f 0.15 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 142 ºC; **IR** *v* cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.21 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.44 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 7.37 - 7.30 (m, 1H), 7.26 (ddd, *J* = 8.7, 7.2, 1.9 Hz, 2H), 7.22 - 7.15 (m, 1H), 7.00 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.71 (dd, *J* = 8.4, 0.9 Hz, 1H), 5.91 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.02 (ddq, *J* = 20.3, 17.0, 1.5 Hz, 2H), 3.37 (d, *J* = 6.5 Hz, 2H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 166.5 (C), 157.5 (C), 152.1 (C), 135.8 (CH), 134.9 (CH), 133.8 (CH), 132.4 (C), 131.5 (CH), 128.4 (CH), 126.2 (CH), 123.3 (CH), 120.9 (CH), 119.0 (C), 116.7 (CH_2), 116.5 (CH), 34.5 (CH_2) ppm; **GC** R_T 12.819 min; **LRMS (EI)** *m/z* (%) = 255 (M^+ + 1, 10), 254 (M^+, 60), 248 (10), 236 (52), 235 (88), 221 (32), 219 (22), 218 (31), 209 (13), 208 (22), 207 (49), 181 (33), 179 (10), 178 (14), 165 (20), 152 (14), 147 (43), 139 (12), 132 (15), 131 (17), 121 (79), 117 (50), 116 (26), 115 (100), 105 (11), 91 (22), 89 (15), 77 (23), 63 (14), 51 (14); **HRMS (EI)** *Calcd.* for $C_{16}H_{14}O_3$ 254.0943, found 254.0945.

2-(Naphthalen-2-yloxy) acid (**1m**):[7]

Compound **1m** was prepared from methyl 2-iodobenzoate (297 µl, 2 mmol, 1 equiv.) and 2-naphtol (353.1 mg, 2.4 mmol, 1.2 equiv.) following the general *method B* described above for **1c**.

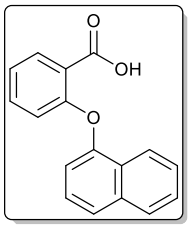


Compound **1m** was obtained as a pale - brown solid (239 mg, 0.91 mmol, 46% over two steps): **TLC** R_f 0.12 (9:1

[Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 119 - 120 ºC/lit.[7] 118 - 120 ºC; **IR** *v* 2962, 1675, 1595, 1455, 1309, 1246, 1217, 1159, 1084, 860, 773 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.19 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.90 – 7.73 (m, 3H), 7.53 - 7.42 (m, 4H), 7.30 - 7.20 (m, 2H), 6.92 (dd, *J* = 8.3, 0.9 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.8 (C), 157.4 (C), 153.1 (C), 135.0 (CH), 134.2 (C), 133.5 (CH), 131.0 (C), 130.6 (CH), 128.0 (CH), 127.5 (CH), 127.1 (CH), 125.7 (CH), 123.8 (CH), 120.3 (C), 120.0 (CH), 118.9 (CH), 116.0 (CH) ppm; **LRMS (DIP)** *m/z* (%) = 265 (M^+ + 1, 18), 264 (M^+, 100), 218 (13), 189 (21), 145 (10), 144 (96), 127 (15), 126 (10), 121 (94), 115 (28).

2-(Naphthalen-1-yloxy)benzoic acid (**1n**):[11]

Compound **1n** was prepared from methyl 2-iodobenzoate (297 µL, 2 mmol, 1 equiv.) and 1-naphtol (350 mg, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

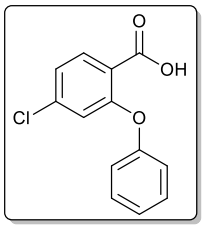


Compound **1n** was obtained as a pale-brown solid (225 mg, 0.86 mmol, 43% over two steps): **TLC** R_f 0.15 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 114 - 117 ºC; **IR** *v* 2987, 2659, 1675, 1601, 1390, 1231, 1090, 937, 761, 712 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.21 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.11 - 8.06 (m, 2H), 7.91 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.64 - 7.38 (m, 5H), 7.19 (td, *J* = 7.9, 1.0 Hz, 1H), 7.09 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.76 (dd, *J* = 8.4, 0.9 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.8 (C), 158.1 (C), 150.9 (C), 135.0 (CH), 133.5 (CH), 130.3 (CH), 128.6 (C), 128.2 (CH), 127.1 (CH), 126.9 (CH), 125.9 (CH), 125.5 (CH), 123.5 (CH), 121.8 (CH), 119.6 (C), 117.8 (CH), 115.8 (CH) ppm; **LRMS (DIP)** *m/z* (%) = 265 (M^+ + 1, 16), 264 (M^+, 87), 218 (14), 189 (17), 144 (51), 127 (11), 121 (100), 115 (33).

4-Chloro-2-phenoxybenzoic acid (**1p**):[7]

Compound **1p** was prepared from methyl 4-chloro-2-iodobenzoate (**6a**) (592 mg, 2 mmol 1 equiv.) and phenol (226 mg, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

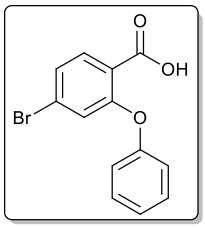
[11] C. Wang, I. Piel and F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 4194.



Compound **1p** was obtained as a pale - yellow solid (219 mg, 0.88 mmol, 44% over two steps): **TLC** R_f 0.13 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 160 - 161 ºC/lit.[7] 155 - 157 ºC; **IR** ν 2577, 1672, 1595, 1479, 1438, 1390, 1306, 1227, 1189, 1142, 920, 862, 758, 693 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 8.08 (d, J = 8.5 Hz, 1H), 7.43 7.46 - 7.41 (m, 2H), 7.28 - 7.24 (m, 1H), 7.16 (dd, J = 8.5, 1.9 Hz, 1H), 7.10 - 7.08 (m, 2H), 6.84 (d, J = 1.9 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.5 (C), 158.3 (C), 154.8 (C), 140.8 (C), 134.4 (CH), 130.5 (2 x CH), 125.6 (CH), 123.8 (CH), 120.2 (2 x CH), 118.54 (C), 118.50 (C) ppm; **GC** R_T 12.501 min; **LRMS (EI)** *m/z* (%) = 250 (M^+ ^{37}Cl, 7), 248 (M^+ ^{35}Cl, 22), 168 (11), 157 (31), 155 (100), 139 (15), 94 (13), 77 (25), 63 (17), 51 (29).

4-Bromo-2-phenoxybenzoic acid (**1q**):

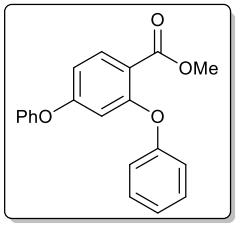
Compound **1q** was prepared from methyl 4-bromo-2-iodobenzoate (**6b**) (350 mg, 1.02 mmol, 1 equiv.) and phenol (115 mg, 1.224 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1q** was obtained as a white solid (224 mg, 0.79 mmol, 40% over two steps): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 179 - 180 ºC; **IR** ν 2887, 1696, 1585, 1479, 1390, 1264, 1046, 732 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.9 Hz, 2H), 7.33 (dd, J = 8.4, 1.5 Hz, 1H), 7.28 - 7.24 (m, 1H), 7.09 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 1.6 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.0 (C), 158.0 (C), 154.7 (C), 134.5 (CH), 130.6 (2 x CH), 129.1 (C), 126.9 (CH), 125.7 (CH), 121.4 (CH), 120.2 (2 x CH), 118.9 (C) ppm; **LRMS (DIP)** *m/z* (%) = 294 (M^+ ^{81}Br, 32), 292 (M^+ ^{79}Br, 32), 201 (^{81}Br, 98), 200 (^{79}Br, 11), 199 (^{79}Br, 100), 168 (19), 139 (15), 94 (12), 77 (15), 51 (12); **HRMS (DIP)** *Calcd.* for $C_{13}H_9BrO_3$ 291.9735, found 291.9739.

2,4-diphenoxybenzoic acid methyl ester (**1r-methyl ester**):

Compound **1r** was prepared from methyl 4-bromo-2-iodobenzoate (350 mg, 1.02 mmol, 1 equiv.) and phenol (115.1 mg, 1.224 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

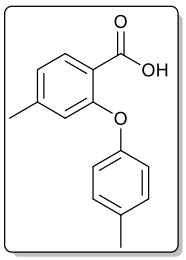


Compound **1r** was obtained as a colorless oil (105 mg, 0.33 mmol, 33%): **TLC** R_f 0.38 (9:1 Hexane/EtOAc); **IR** ν 1689, 1593, 1500, 1481, 1433, 1267, 1213, 1087, 877, 842, 766, 734 cm^{-1}; **^{1}H-NMR**

(400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 1H), 7.41 - 7.28 (m, 4H), 7.21 - 7.16 (m, 1H), 7.13 - 7.10 (m, 1H), 7.08 - 7.03 (m, 2H), 7.02 - 6.97 (m, 2H), 6.73 (dd, J = 8.7, 2.4 Hz, 1H), 6.61 (d, J = 2.4 Hz, 1H), 3.81 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 165.7 (C), 162.4 (C), 158.3 (C), 157.3 (C), 155.4 (C), 133.8 (CH), 130.1 (2 x CH), 129.9 (2 x CH), 124.8 (CH), 123.5 (CH), 120.2 (2 x CH), 118.4 (2 x CH), 117.1 (C), 112.4 (CH), 110.0 (CH), 52.1 (CH_3) ppm; **GC** R_T 12.380 min; **LRMS (EI)** *m/z* (%) = 321 (M^+ + 1, 21), 320 (M^+, 94), 290 (20), 289 (100), 168 (10); **HRMS (EI)** *Calcd.* for $C_{20}H_{16}O_4$ 320.1049, found 320.1048.

4-Methyl-2-(*p*-tolyloxy)benzoic acid (**1s**) [CAS 97214-15-8]:

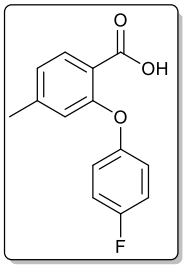
Compound **1s** was prepared from methyl 2-bromo-4-methylbenzoate (456 mg, 2 mmol, 1 equiv.) and *p*-cresol (259.2 mg, 2.40 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1s** was obtained as a pale-yellow solid (264 mg, 1.03 mmol, 52% over two steps): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 153 - 154 ºC; **IR** v 2986, 2920, 1688, 1666, 1614, 1496, 1403, 1239, 1203, 1082, 834, 790, 696 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.06 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.00 - 6.97 (m, 3H), 6.62 (br s, 1H), 2.38 (s, 3H), 2.29 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 166.7 (C), 157.7 (C), 152.4 (C), 146.4 (C), 135.2 (C), 133.4 (CH), 130.8 (2 x CH), 124.5 (CH), 120.2 (2 x CH), 118.0 (CH), 116.8 (C), 21.8 (CH_3), 20.9 (CH_3) ppm; **GC** R_T 12.911 min; **LRMS (EI)** *m/z* (%) = 242 (M+, 36), 136 (9), 135 (100), 107 (7), 77 (9).

2-(4-Fluorophenoxy)-4-methylbenzoic acid (**1t**) [CAS 1274871-01-0]:

Compound **1t** was prepared from methyl 2-bromo-4-methylbenzoate (348 mg, 1.53 mmol, 1 equiv.) and *p*-fluorophenol (132.2 mg, 1.84 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

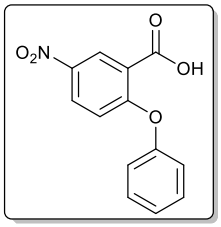


Compound **1t** was obtained as a pale-yellow solid (184 mg, 0.70 mmol, 46%): **TLC** R_f 0.13 (0.13 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 185 ºC; **IR** v 2986, 2900, 1686, 1667, 1615, 1495, 1438, 1309, 1252, 1196, 1087, 959, 841, 776, 693 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.03 (d, J = 8.0 Hz, 1H), 7.12 - 6.99 (m, 5H), 6.63 (br s, 1H), 2.31 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.0 (C), 159.7 (d, J = 242.3 Hz, C), 157.6 (C), 151.4 (d, J = 3.0 Hz, C), 146.5 (CH), 133.4 (CH), 124.7 (CH), 121.4 (d, J = 8.3 Hz, 2 × CH), 118.8 (CH), 117.4 (C), 116.8 (d, J = 23.3 Hz, 2 × CH), 21.8 (CH_3)

ppm; **GC** R_T 12.191 min; **LRMS (EI)** *m/z* (%) = 246 (M^+, 34), 207 (12), 136 (9), 135 (100), 134 (9), 77 (13).

5-Nitro-2-phenoxybenzoic acid (**1u**):[7]

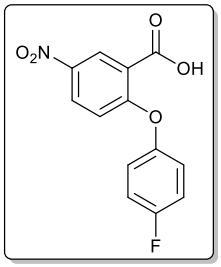
Compound **1u** was prepared from methyl 5-nitrobenzoate (**5a**) (410 mg, 1.34 mmol, 1 equiv.) and phenol (127 mg, 1.60 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1u** was obtained as a pale-yellow solid (139 mg, 0.54 mmol, 40% over two steps): **TLC** R_f 0.08 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 159 - 160 ºC/lit.[7] 160 - 162 ºC; **IR** *v* 2848, 1686, 1614, 1452, 1346, 1257, 1147, 1073, 919, 849, 743, 688 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 8.59 (d, *J* = 2.9 Hz, 1H), 8.34 (dd, *J* = 9.2, 3.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 9.2 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, DMSO)** δ 164.9 (C), 161.1 (C), 154.9 (C), 141.9 (C), 130.5 (2 x CH), 128.6 (CH), 127.0 (CH), 125.2 (CH), 123.4 (C), 119.9 (2 x CH), 118.9 (CH) ppm; **LRMS (DIP)** *m/z* (%) = 259 (M^+, 49), 167 (10), 166 (100), 139 (15), 120 (15), 94 (37), 77 (22), 51 (11).

2-(4-Fluorophenoxy)-5-nitrobenzoic acid (**1v**):[12]

Compound **1v** was prepared from methyl 5-nitrobenzoate (**5a**) (424 mg, 1.38 mmol, 1 equiv.) and *p*-fluorophenol (188 mg, 1.66 mmol, 1.20 equiv.) following the general *method B* described above for **1c**.

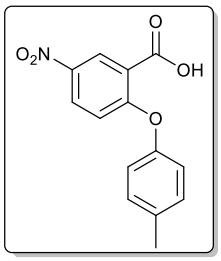


Compound **1v** was obtained after purification by column chromatography (85:15 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]) as a white solid (167 mg, 0.59 mmol, 43% over two steps): **TLC** R_f 0.08 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 174 - 176 ºC/lit.[12] 170 - 171ºC; **IR** *v* 2922, 1699, 1615, 1500, 1475, 1453, 1344, 1226, 1180, 1090, 1077, 919, 834, 745 cm^{-1}; **^{1}H-NMR (300 MHz, $(CD_3)_2CO$)** δ 8.73 (d, *J* = 2.8 Hz, 1H), 8.36 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.30 – 7.21 (m,4H), 7.09 (d, *J* = 9.2 Hz 1H) ppm; **^{13}C-NMR (101 MHz, $(CD_3)_2CO$)** δ 164.9 (C), 162.7 (C), 160.6 (d, *J* = 243.4 Hz, C), 152.1 (d, *J* = 2.0 Hz, C), 143.2 (C), 129.3 (CH), 128.3 (CH), 122.8 (d, *J* = 9.1 Hz, 2 x CH), 119.1 (CH), 117.7 (d, *J* = 23.2 Hz, 2 x CH) ppm; **LRMS (DIP)** *m/z* (%) = 277 (M^+, 46), 166 (100), 157 (16), 120 (19), 112 (27), 95 (10), 75 (12), 43 (15).

[12] Z. Wang, L.-J. Zhou, Y.-L. Wang, Y.-B. Weng, J. He and K. Nie, *J. Chem. Res.* 2011, 373.

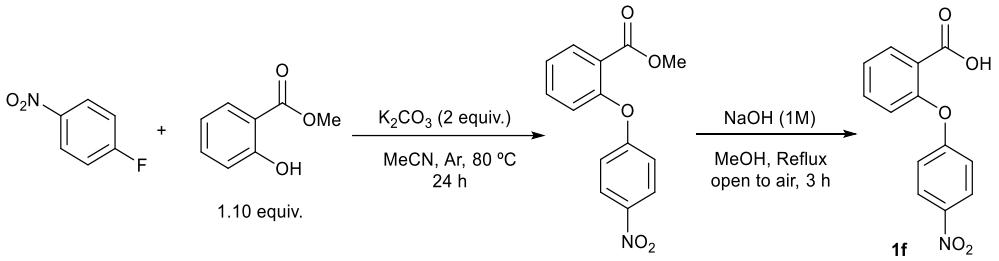
5-Nitro-2-(*p*-tolyloxy)benzoic acid (**1w**):[12]

Compound **1w** was prepared from methyl 5-nitrobenzoate (**4a**) (424 mg, 1.38 mmol, 1 equiv.) and *p*-cresol (179 mg, 1.66 mmol 1.20 equiv.) following the general *method B* described above for **1c**.



Compound **1w** was obtained after purification by column chromatography (85:15 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]) as a white solid (174 mg, 0.60 mmol, 44% over two steps): **TLC** R_f 0.10 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 178 - 180 ºC/lit.[12] 181 - 182 ºC; **IR** *v* 2924, 1704, 1677, 1611, 1452, 1339, 1251, 1164, 919, 838, 745 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 8.97 (d, *J* = 2.8 Hz, 1H), 8.26 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 1H), 2.37 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 167.2 (C), 163.2 (C), 151.6 (C), 142.2 (C), 136.4 (C), 131.2 (2 × CH), 129.6 (CH), 129.3 (CH), 120.7 (2 × CH), 119.9 (C), 117.2 (CH), 21.0 (CH_3) ppm; **LRMS (DIP)** *m/z* (%) = 274 (M^+ + 1, 10), 273 (62), 166 (40), 120 (10), 108 (100), 107 (22), 91 (17), 77 (10), 65 (14), 43 (14).

Synthesis of acid **1f**.[13]



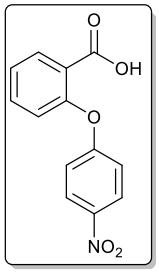
Into a flame dried Pyrex tube, a solution of 1-fluoro-4-nitrobenzene (214 µL, 2 mmol, 1 equiv.) in dry MeCN (4 mL) was added, followed by anhydrous K_2CO_3 (552.8 mg, 4 mmol, 2 equiv.) and methyl salicylate (334 mg, 2.20 mmol, 1.10 equiv.). The reaction mixture was stirred at 80 ºC under Ar atmosphere for 24 h (monitored by TLC). The mixture was cooled down to room temperature, before adding H_2O (10 mL) and stirred for 5 min. Then, EtOAc (10 mL) was added, and the resulting two-layer mixture was stirred another 5 min. Then, layers were separated and the aqueous one was extracted with EtOAc (3 x 10 mL). Organic extracts were recombined and washed with H_2O (2 x 10 mL) followed by brine (1 x 5 mL). Organics were dried over anhydrous $MgSO_4$,

[13] N. Teno, K. Gohda, K. Wanaka, Y. Tsuda, T. Sueda, Y. Yamashita and T. Otsubu, *Bioorg. Med. Chem.*, 2014, **22**, 2339.

filtered, and concentrated under reduced pressure to afford a yellow residue, which was purified by column chromatography (95:5 to 80:20 Hexane/EtOAc).

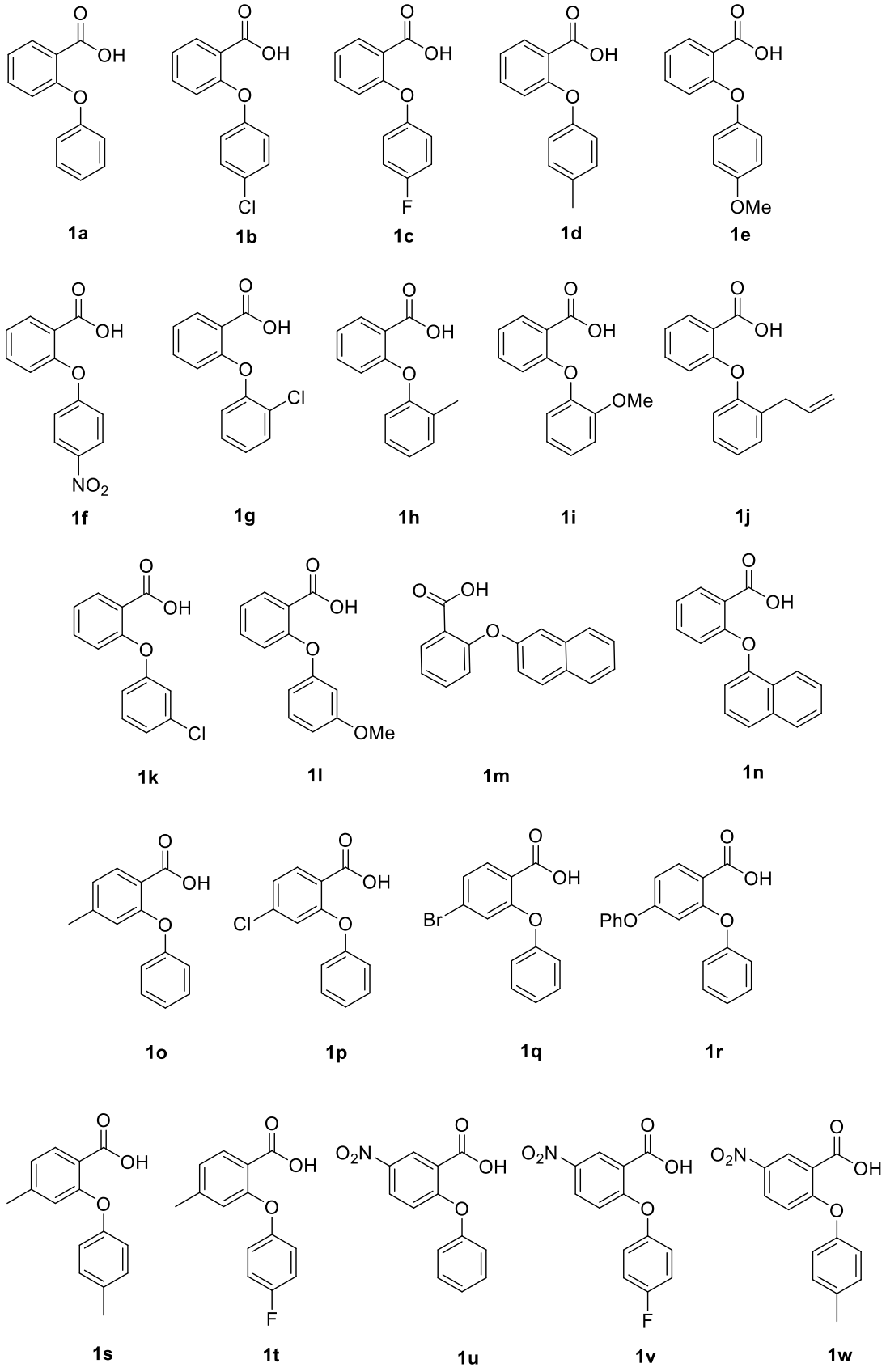
The title methyl ester was hydrolyzed according to *method B* described for the synthesis of 2-aryloxybenzoic acids.

2-(4-Nitrophenoxy)benzoic acid (**1f**) [CAS 6082-87-7]:



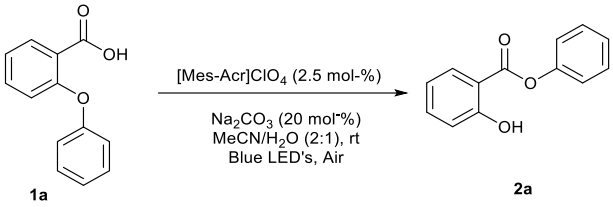
Compound **1f** was obtained as a (409 mg, 1.5 mmol, 75 % over two steps): **TLC** R_f 0.13 (9:1 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]); **mp** ($CHCl_3$) 157-158 ºC; **IR** *v* 2861, 1686, 1602, 1591, 1572, 1485, 1343, 1298, 1234, 878, 849, 750, 654 cm^{-1}; **^{1}H-NMR (300MHz, $CDCl_3$)** δ 8.22 (d, *J* = 9.0 Hz, 1H), 8.22 (dd, *J* = 5.8 Hz, 4.7 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.66 (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H), 7.38 (td, *J* = 7.7, 1.1 Hz, 1H), 7.14 (dd, *J* = 8.2, 1.0, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.93 (dd, *J* = 5.8, 4.7 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 169.7 (C), 163.3 (C), 154.7 (C), 142.9 (C), 135.6 (CH), 133.4 (CH), 126.1 (2 x CH), 126.0 (2 x CH), 123.0 (CH), 122.6 (C), 116.9 (CH), ppm; **LRMS (DIP)** *m/z* (%) =259 (M^+, 47), 139 (15), 121 (100), 120 (19), 65 (12).

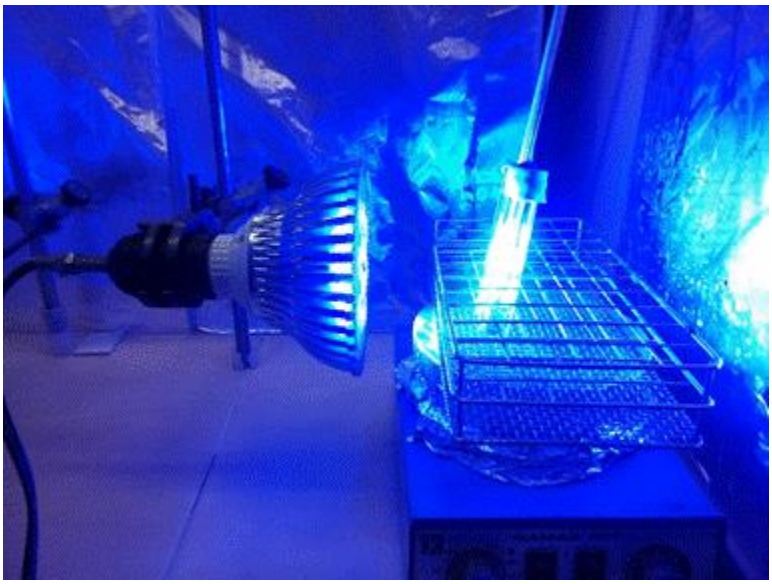
Figure S2: *Syntheses of 2-Aryloxybenzoic acids*



5. Synthesis of Phenyl salicylates

Typical procedure A for the visible-light-promoted Smiles rearrangement of 2-aryloxibenzoic acids.



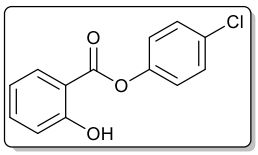


Into a microwave tube (Pyrex, 10 mL), equipped with a stirring bar, the 2-phenoxybenzoic acid (**1a**, 42.8 mg, 0.20 mmol), Na_2CO_3 (4.24 mg, 0.04 mmol, 20 mol-%) and [Mes-Acr]ClO_4 (2.08 mg, 2.5 mol-%) were introduced, followed by a 2:1 MeCN/H_2O (2:1) mixture (2 mL). The yellow solution was irradiated using blue LED's (1 bulb) and stirred at room temperature,[14] without any inert atmosphere, for 16 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography.

It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a white solid (32 mg, 0.15 mmol, 75%): **TLC** R_f 0.33 (98:2 Hexane/ EtOAc); **mp** 34 – 36 ºC; **IR** *v* 3176, 1682, 1616, 1584, 1482, 1405, 1299, 1180, 1065, 865, 745, 692 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.51 (s, 1H), 8.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.50 - 7.42 (m, 2H), 7.35 - 7.28 (m, 1H), 7.24 - 7.19 (m, 2H), 7.04 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.98 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 169.1 (C), 162.4 (C), 150.3 (C), 136.6 (CH), 130.5 (CH), 129.8 (2 × CH), 126.5 (CH), 121.8 (2 × CH), 119.6 (CH), 118.0 (CH), 112.0 (C); **GC** R_T 10.908 min; **LRMS (EI)** *m/z* (%) = 214 (M+, 11), 121 (100), 65 (12).

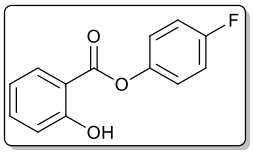
[14] The bulb was placed at 8 cm from the reaction tube. At this distance, the light intensity of the led source was 101 mW·cm^{-2}, which corresponds to 3.79 10^{-7} Einstein cm^{-2} s^{-1}.

4-Chlorophenyl 2-hydroxybenzoate (**2b**):[7]



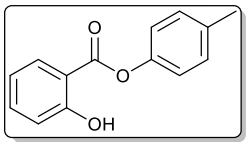
Compound **2b** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a white solid (37.2 mg, 0.15 mmol, 75%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 75 - 80 ºC; **IR** ν 3252, 1682, 1615, 1579, 1479, 1303, 1186, 1057, 754 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.40 (s, 1H), 8.05 (dd, J = 8.0, 1.7 Hz, 1H), 7.55 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.42 (dd, J = 5.4, 4.6 Hz, 1H), 7.42 (d, J = 8.9 Hz, 1H), 7.16 (dd, J = 5.4, 4.6 Hz, 1H), 7.16 (dd, J = 8.9 Hz, 1H), 7.04 (dd, J = 8.4, 0.9 Hz, 1H), 6.97 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.8 (C), 162.4 (C), 148.7 (C), 136.8 (CH), 132.0 (C), 130.4 (CH), 129.8 (2 × CH), 123.2 (2 × CH), 119.7 (CH), 118.0 (CH), 111.7 (C) ppm; **GC** R_T 12.065 min; **LRMS (EI)** *m/z* (%) = 248 (M^{+} ^{35}Cl, 6), 124 (^{35}Cl 15), 121 (100), 93 (9), 65 (14).

4-Fluorophenyl 2-hydroxybenzoate (**2c**):[7]



Compound **2c** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (33 mg, 0.14 mmol, 70%): **TLC** R_f 0.36 (98:2 Hexane/EtOAc); **IR** ν 3247, 1686, 1615, 1581, 1501, 1481, 1300, 1178, 1156, 1062, 879, 810, 753, 695 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.42 (s, 1H), 8.06 (dd, J = 8.0, 1.7 Hz, 1H), 7.55 (ddd, J = 8.7, 7.5, 1.8 Hz, 1H), 7.21 - 7.10 (m, 3H), 7.04 (dd, J = 8.4, 0.8 Hz, 1H), 6.97 (ddd, J = 8.0, 7.3, 1.1 Hz, 1H) (m, 1H) ppm; **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 169.0 (C), 162.4 (C), 160.7 (d, J = 245.7 Hz, C), 146.1 (d, J = 2.5 Hz, C), 136.8 (CH), 130.5 (CH), 123.3 (d, J = 7.6 Hz, 2 x CH), 119.7 (CH), 118.1 (CH), 116.5 (d, J = 23.9 Hz, 2 × CH), 111.8 (C); **GC** R_T 10.861 min; **LRMS (EI)** *m/z* (%) = 232 (M^{+}, 12), 122 (10), 121 (100), 93 (12).

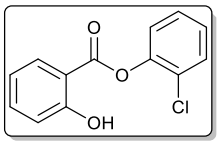
p-Tolyl 2-hydroxybenzoate (**2d**):[7]



Compound **2d** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (39 mg, 0.17 mmol, 85%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **IR** ν 3215, 1686, 1615, 1585, 1507, 1298, 1248, 1187, 1165, 1154, 1066, 754, 696 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.47 (s, 1H), 8.00 (dd, J = 8.0, 1.7 Hz, 1H), 7.46 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.21 - 7.12 (m, 2H), 6.96 (dd, J = 8.4, 1.1 Hz, 1H), 6.93 - 6.86 (m, 1H), 2.31 (s, 2H) ppm; **^{13}C-**

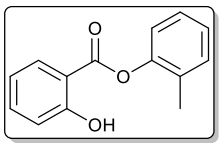
NMR (101 MHz, $CDCl_3$) δ 169.3 (C), 162.3 (C), 148.0 (C), 136.5 (CH), 136.3 (C), 130.3 (2 × CH), 121.4 (2 × CH), 119.6 (CH), 117.9 (CH), 112.1 (C), 21.1 (CH_3) ppm; **GC** R_T 11.654 min; **LRMS (EI)** *m/z* (%) = 228 (M^+, 8), 136 (9), 135 (100), 128 (10), 77 (11).

2-Chlorophenyl 2-hydroxybenzoate (**2g**):[15]



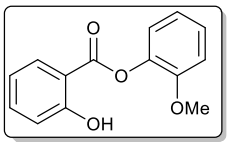
Compound **2g** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow solid (36 mg, 0.15 mmol, 75%): **TLC** R_f 0.36 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 85 - 87 ºC; **IR** *v* 3205, 1682, 1581, 1476, 1300, 1205, 1154, 1067, 751, 696 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.32 (s, 1H), 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.56 (ddd, *J* = 8.9, 7.4, 1.8 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.37 - 7.32 (m, 1H), 7.31 - 7.23 (m, 2H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.99 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.1 (C), 162.4 (C), 146.5 (C), 136.9 (CH), 130.7 (CH), 130.6 (CH), 128.0 (CH), 127.7 (CH), 127.1 (C), 123.9 (CH), 119.8 (CH), 118.0 (CH), 111.5 (C) ppm; **GC** R_T 12.118 min; **LRMS (EI)** *m/z* (%) = 248 (M^+, 6), 122 (8), 121 (100), 93 (8), 65 (11).

o-Tolyl 2-hydroxybenzoate (**2h**):[7]



Compound **2h** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (34 mg, 0.15 mmol, 75%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **IR** *v* 3215, 1685, 1615, 1582, 1482, 1298, 1169, 1154, 1109, 746, 668 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.55 (s, 1H), 8.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.55 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.32 - 7.19 (m, 4H), 7.15 - 7.12 (m, 1H), 7.05 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.98 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 2.24 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.8 (C), 162.3 (C), 148.8 (C), 136.6 (CH), 131.5 (CH), 130.4 (CH), 127.2 (CH), 126.7 (CH), 122.0 (CH), 119.6 (CH), 118.0 (CH), 111.8 (C), 16.3 (CH_3) ppm; **GC** R_T 11.243 min; **LRMS (EI)** *m/z* (%) = 228 (M^+, 8), 121 (100), 93 (8), 65 (14).

2-Methoxyphenyl 2-hydroxybenzoate (**2i**):[7]

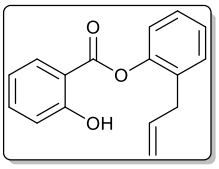


Compound **2i** was prepared following the *typical procedure A*, as described above for **2a**, after 37 h. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid

[15] M. Black, J. I. G. Cadogan and H. McNab, *Org. Biomol. Chem.*, 2010, **8**, 2961.

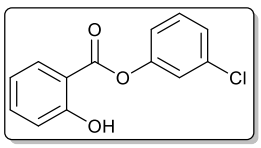
(28.3 mg, 0.116 mmol, 58%): **TLC** R_f 0.27 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 91 - 93 ºC; **IR** *v* 3000, 1691, 1615, 1500, 1300, 1256, 1172, 1156, 1111, 1066, 908, 745 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 8.11 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.53 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.28 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.05 - 6.99 (m, 3H), 6.97 (ddd, *J* = 8.2, 7.4, 1.0 Hz, 1H), 3.79 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.6 (C), 162.1 (C), 151.3 (C), 139.3 (C), 136.4 (CH), 130.8 (CH), 127.6 (CH), 123.0 (CH), 121.0 (CH), 119.6 (CH), 117.9 (CH), 112.8 (CH), 112.0 (C), 56.1 (CH_3) ppm; **GC** R_T 12.006 min; **LRMS (EI)** *m/z* (%) = 244 (M^+, 19), 124 (19), 122 (8), 121 (100), 109 (14), 65 (11).

2-allylphenyl 2-hydroxybenzoate (**2j**):



Compound **2j** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100 Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (38.1 mg, 0.15 mmol, 75%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **IR** *v* 3215, 1686, 1617, 1584, 1484, 1202, 1155, 1064, 750, 697, 669 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.55 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.37 - 7.22 (m, 3H), 7.05 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.02 - 6.94 (m, 1H), 5.90 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.29 - 4.81 (m, 3H), 3.36 (d, *J* = 6.5 Hz, 2H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.9 (C), 162.4 (C), 148.5 (C), 136.6 (CH), 135.7 (CH), 132.3 (C), 130.8 (CH), 130.4 (CH), 127.7 (CH), 126.9 (CH), 122.5 (CH), 119.7 (CH), 118.0 (CH), 116.7 (CH_2), 111.9 (C), 34.8 (CH_2) ppm; **GC** R_T 12.014 min; **LRMS (EI)** *m/z* (%) = 254 (M^+, 17), 122 (9), 121 (100), 65 (8).

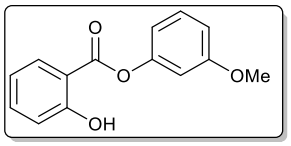
3-Chlorophenyl 2-hydroxybenzoate (**2k**):[7]



Compound **2k** was prepared following the *typical procedure A*, as described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a yellow solid (28 mg, 0.12 mmol, 60%): **TLC** R_f 0.36 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 88 - 89 ºC; **IR** *v* 3244, 1673, 1580, 1479, 1463, 1303, 1189, 1157, 881, 753, 667 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.38 (s, 1H), 8.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.41 - 7.36 (m, 1H), 7.30 (ddd, *J* = 8.0, 1.9, 1.2 Hz, 1H), 7.27 - 7.25 (m, 1H), 7.13 (ddd, *J* = 8.0, 2.2, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.98 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.6 (C), 162.4 (C), 150.7 (C), 136.9 (CH), 135.1 (C), 130.5 (CH), 130.4 (CH), 126.8 (CH), 122.5 (CH), 120.2 (CH),

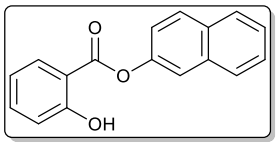
119.7 (CH), 118.1 (CH), 111.6 (C) ppm; **GC** R_T 12.387 min; **LRMS (EI)** *m/z* (%) = 248 (M^+, 7), 122 (8), 121 (100), 93 (9), 65 (11).

3-Methoxyphenyl 2-hydroxybenzoate (**2l**):[7]



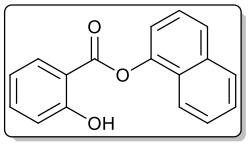
Compound **2l** was prepared following the *typical procedure*, described above for **2a**, but another portion of [Mes-Acr]ClO_4 (2.08 mg, 2.5 mol-%) was added after 39 h and the reaction was continued for a total of 61 h. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (17 mg, 0.07 mmol, 35%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 88 - 89 ºC; **IR** *v* 3196, 1686, 1608, 1581, 1484, 1298, 1247, 1156, 1066, 864, 755 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.07 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.04 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.97 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 6.86 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 6.81 (ddd, *J* = 8.0, 2.2, 0.8 Hz, 1H), 6.76 (t, *J* = 2.3 Hz, 1H), 3.83 (s, 3H) ppm; **^{13}C-NMR (126 MHz, $CDCl_3$)** δ 169.0 (C), 162.4 (C), 160.9 (C), 151.2 (C), 136.6 (CH), 130.5 (CH), 130.2 (CH), 119.6 (CH), 118.0 (CH), 114.0 (CH), 112.4 (CH), 112.0 (C), 107.9 (CH), 55.7 (CH_3); **GC** R_T 12.867 min; **LRMS (EI)** *m/z* (%) = 244 (M^+, 20), 124 (19), 122 (8), 121 (100), 93 (8), 65 (10).

Naphthalen-2-yl 2-hydroxybenzoate (**2m**):[7]



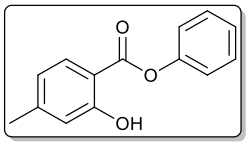
Compound **2m** was prepared following the *typical procedure A*, described above for **2a**, but using DCE/H_2O (2:1) as the solvent mixture to improve the solubility of acid **1m**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-brown solid (42 mg, 0.16 mmol, 80%): **TLC** R_f 0.38 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 105 - 106 ºC; **IR** *v* 3214, 1682, 1614, 1583, 1483, 1300, 1205, 1155, 1064, 905, 806, 759, 743, 676 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.53 (s, 1H), 8.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.90 - 7.83 (m, 2H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.59 - 7.47 (m, 3H), 7.34 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.00 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 169.3 (C), 162.4 (C), 147.8 (C), 136.7 (CH), 133.9 (C), 131.8 (C), 130.5 (CH), 129.8 (CH), 128.0 (CH), 127.9 (CH), 127.0 (CH), 126.2 (CH), 121.1 (CH), 119.7 (CH), 118.9 (CH), 118.0 (CH), 112.0 (C) ppm; **LRMS (DIP)** *m/z* (%) = 264 (M^+, 30), 144 (77), 121 (100), 115 (23), 65 (12).

Naphthalen-1-yl 2-hydroxybenzoate (**2n**):[7]



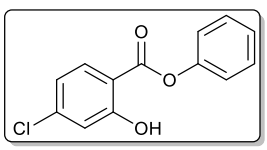
Compound **2n** was prepared following the *typical procedure A*, described above for **2a**, but using DCE/H_2O (2:1) as the solvent mixture to improve the solubility of the substrate **1n**. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow solid (40 mg, 0.15 mmol, 75%): **TLC** R_f 0.39 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 96 - 97 ºC; **IR** *v* 3196, 1686, 1612, 1481, 1389, 1294, 1245, 1202, 1150, 1127, 1087, 787, 752, 694, 672 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.50 (s, 1H), 8.28 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.94 - 7.87 (m, 2H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.58 (ddd, *J* = 8.9, 7.2, 1.7 Hz, 1H), 7.55 - 7.48 (m, 3H), 7.36 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.08 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.04 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 169.2 (C), 162.5 (C), 146.1 (C), 136.8 (CH), 134.9 (C), 130.5 (CH), 128.3 (CH), 126.94 (CH), 126.87 (CH), 126.8 (CH), 126.7 (CH), 125.5 (CH), 121.1 (CH), 119.8 (CH), 118.4 (CH), 118.1 (CH), 111.8 (C) ppm; **LRMS (DIP)** *m/z* (%) = 264 (M+, 19), 144 (29), 121 (100), 115 (16).

Phenyl 2-hydroxy-4-methylbenzoate (**2o**):[15]



Compound **2o** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (34 mg, 0.15 mmol, 75%): **TLC** R_f 0.46 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 89 - 90 ºC; **IR** *v* 3189, 1686, 1641, 1485, 1293, 1189, 1067, 948, 745, 689 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.46 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.49 - 7.40 (m, 2H), 7.33 - 7.27 (m, 1H), 7.23 - 7.17 (m, 2H), 6.85 (br s, 1H), 6.79 (ddd, *J* = 8.2, 1.6, 0.5 Hz, 1H), 2.39 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 169.1 (C), 162.3 (C), 150.3 (C), 148.2 (C), 130.3 (CH), 129.7 (2 × CH), 126.4 (CH), 121.8 (2 × CH), 120.9 (CH), 118.1 (CH), 109.4 (C), 22.1 (CH_3) ppm; **GC** R_T 11.947 min; **LRMS (EI)** *m/z* (%) = 228 (M^+, 9), 136 (10), 135 (100), 77 (11).

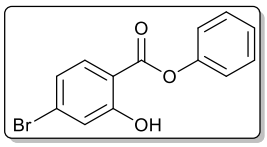
Phenyl 4-chloro-2-hydroxybenzoate (**2p**):[7]



Compound **2p** was prepared following the *typical procedure A*, described above for **2a**, but using DCE/H_2O (2:1) as the solvent mixture to improve the solubility of the substrate **1p**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow solid (34 mg, 0.13 mmol, 65%): **TLC** R_f 0.49 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 93 - 94 ºC; **IR** *v* 3146, 1672, 1574, 1481, 1331, 1279, 1184, 1072, 908, 744, 686 cm^{-1}; **^{1}H-**

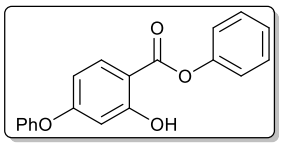
NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.46 - 7.4, (m, 2H), 7.36 - 7.28 (m, 1H), 7.2 - 7.18 (m, 2H), 7.06 (d, J = 2.0 Hz, 1H), 6.96 (ddd, J = 8.6, 2.0 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.5 (C), 162.8 (C), 150.0 (C), 142.5 (C), 131.5 (2 × CH), 129.8 (CH), 121.7 (2 × CH) 120.4 (CH), 118.2 (CH), 110.6 (C) ppm; **GC** R_T 11.922 min; **LRMS (EI)** *m/z* (%) = 250 (M+ 37Cl, 5), 248 (M+, 12), 207 (10), 157 (28), 156 (10), 155 (100), 94 (22).

Phenyl 4-bromo-2-hydroxybenzoate (**2q**):



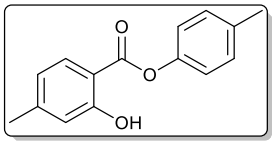
Compound **2q** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (36 mg, 0.12 mmol, 59%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **IR** v 3050, 1672, 1607, 1588, 1572, 1476, 1279, 1186, 1071, 891, 856, 746 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 10.57 (s, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.48 - 7.43 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 (d, J = 1.9 Hz, 1H), 7.21 - 7.18 (m, 2H), 7.11 (dd, J = 8.5, 1.9 Hz, 1H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 168.7 (C), 162.7 (C), 150.1 (C), 131.4 (CH), 131.0 (C), 129.8 (2 × CH), 126.7 (CH), 123.2 (CH), 121.7 (2 × CH), 121.3 (CH), 111.0 (C) ppm; **GC** R_T 12.501 min; **LRMS (EI)** *m/z* (%) = 294 (M^+ ^{81}Br, 9), 292 (M^+ ^{79}Br, 10), 217 (12), 202 (^{81}Br, 8), 201 (^{81}Br, 100), 200 (^{79}Br, 10), 199 (^{79}Br, 96), 171 (8), 149 (11), 107 (13), 94 (34), 65 (11), 63 (14); **HRMS (EI)** *Calcd.* for $C_{13}H_9BrO_3$ 291.9735, found 291.9731.

Phenyl 2-hydroxy-4-phenoxybenzoate (**2r**):

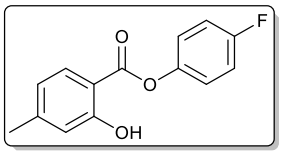


Compound **2r** was prepared following the *typical procedure A*, described above for **2a**. In this case, the reaction was performed at 0.14 mmol of scale. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow solid (27.5 mg, 0.09 mmol, 64%): **TLC** R_f 0.38 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 95 - 96 ºC; **IR** v 3176, 3069, 1678, 1620, 1586, 1483, 1343, 1251, 1184, 1126, 1062, 979, 859, 747, 686 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.66 (s, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.48 - 7.38 (m, 4H), 7.33 - 7.27 (m, 1H), 7.24 - 7.17 (m, 3H), 7.13 - 7.08 (m, 2H), 6.60 (dd, J = 8.9, 2.4 Hz, 1H), 6.50 (d, J = 2.4 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.7 (C), 165.1 (C), 164.4 (C), 154.9 (C), 150.3 (C), 132.2 (CH), 130.2 (2 x CH), 129.8 (2 x CH), 126.4 (CH), 125.2 (CH), 121.8 (2 x CH), 120.9 (2 x CH), 109.8 (CH), 106.6 (C), 105.1 (CH) ppm; **LRMS (DIP)** *m/z* (%) = 306 (M^+, 4), 214 (14), 213 (100); **HRMS (DIP)** *Calcd.* for $C_{19}H_{14}O_4$ 306.0892, found 306.088.

p-Tolyl 2-hydroxy-4-methylbenzoate (**2s**):

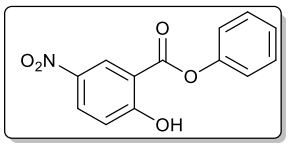


Compound **2s** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (34 mg, 0.14 mmol, 70%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 93 - 94 ºC; **IR** *v* 3184, 1675, 1513, 1341, 1193, 1071, 799, 770, 691 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 9.1, 4.6 Hz, 1H), 6.88 (br s, 1H), 6.81 (ddd, *J* = 8.2, 1.6, 0.5 Hz, 1H), 2.38 (s, 6H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 169.2 (C), 162.3 (C), 148.1 (C), 148.0 (C), 136.1 (C), 130.24 (CH), 130.22 (2 x CH), 121.5 (2 x CH), 120.9 (CH), 118.0 (CH), 109.5 (C), 22.1 (CH_3), 21.0 (CH_3) ppm; **GC** R_T 12.316 min; **LRMS (EI)** *m/z* (%) = 242 (M^+, 11), 136 (11), 135 (100), 108 (9), 107 (13), 77 (12); **HRMS (EI)** *Calcd.* for $C_{15}H_{14}O_3$ 242.0943, found 242.0942.



4-Fluorophenyl 2-hydroxy-4-methylbenzoate (**2t**):Compound **2t** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (30 mg, 0.12 mmol, 60%): **TLC** R_f 0.44 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 112 - 113 ºC; **IR** *v* 3205, 1674, 1498, 1179, 1065, 816, 773, 694 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.37 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.20 - 7.09 (m, 4H), 6.85 (br s, 1H), 6.78 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.39 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 169.0 (C), 162.4 (C), 160.6 (d, *J* = 243.8 Hz, C), 148.3 (C), 146.1 (d, *J* = 3.0 Hz, C), 130.2 (CH), 123.3 (d, *J* = 8.3 Hz, 2 × CH), 121.0 (CH), 118.1 (CH), 116.4 (d, *J* = 24.0 Hz, 2 × CH), 109.2 (C), 22.1 (CH_3) ppm; **GC** R_T 11.545 min; **LRMS (EI)** *m/z* (%) = 246 (M^+, 6), 136 (10), 135 (100), 77 (11); **HRMS (EI):** *Calcd.* for $C_{14}H_{11}FO_3$ 246.0692, found 246.0684.

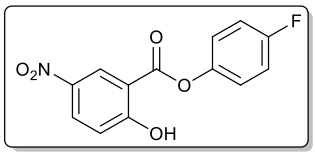
Phenyl 2-hydroxy-5-nitrobenzoate (**2u**):[7]



Compound **2u** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (28 mg, 0.11 mmol, 54%): **TLC** R_f 0.25 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 157 - 158 ºC; **IR** *v* 3108, 1692, 1512, 1331, 1189, 1117, 932, 747, 688 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 11.18 (s, 1H), 9.04 (d, *J* = 2.8 Hz, 1H), 8.42 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.53 - 7.46 (m, 2H), 7.39 - 7.33 (m, 1H), 7.26 - 7.23 (m, 2H), 7.16 (d, *J* = 9.2 Hz, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.9 (C), 166.8 (C), 149.7 (C), 140.4 (C), 131.3 (CH), 130.0 (2 ×

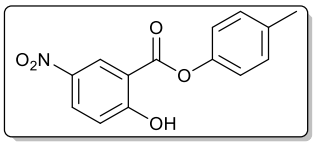
CH), 127.2 (CH), 127.1 (CH), 121.5 (2 × CH), 119.1 (CH), 111.9 (C) ppm; **LRMS (DIP)** *m/z* (%) = 259 (M^+, 21), 167 (8), 166 (100), 120 (29), 94 (31), 92 (11).

4-Flurophenyl-2-hydroxy-5-nitrobenzoate (**2v**):



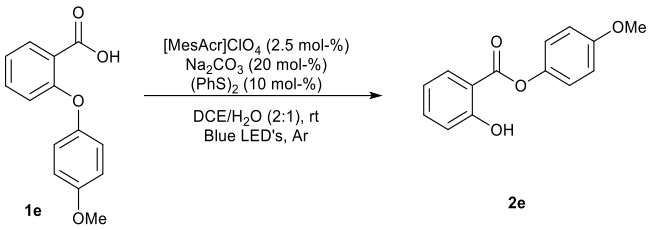
Compound **2v** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (37 mg, 0.134 mmol, 67%): **TLC** R_f 0.13 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 168 - 169 ºC; **IR** *v* 2973, 2885, 1690, 1624, 1526, 1340, 1259, 1173, 1089, 1046, 811, 691 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 11.09 (s, 1H), 9.01 (d, *J* = 2.8 Hz, 1H), 8.42 (dd, *J* = 9.2. 2.8 Hz, 1H), 7.28 - 7.12 (m, 1H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.8 (C), 166.8 (C), 161.1 (d, *J* = 246.4 Hz, C), 145.5 (d, *J* = 2.0 Hz, C), 140.4 (C), 131.4 (CH), 127.2 (CH), 123.0 (d, *J* = 8.1 Hz, 2 × CH), 119.2 (CH), 116.7 (d, *J* = 23.2 Hz, 2 × CH), 111.6 (C) ppm; **LRMS (DIP)** *m/z* (%) = 277 (M+, 13), 166 (100), 120 (30), 112 (20), 92 (10), 43 (12); **HRMS (DIP)** *Calcd.* for $C_{13}H_8FNO_5$ 277.0387, found 277.0380.

p-Tolyl 2-hydroxy-5-nitrobenzoate (**2w**):



Compound **2w** was prepared following the *typical procedure A*, described above for **2a**. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow solid (31 mg, 0.112 mmol, 56%): **TLC** R_f 0.13 (98:2 Hexane/EtOAc); **mp** ($CHCl_3$) 168 - 169 ºC; **IR** *v* 3084, 2926, 1677, 1582, 1524, 1471, 1337, 1278, 1253, 1184, 1063, 1022, 926, 843, 801, 746, 693 cm^{-1}; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 11.21 (s, 1H), 9.02 (d, *J* = 2.8 Hz, 1H), 8.41 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 9.3 Hz, 1H), 7.13 - 7.09 (m, 2H), 2.40 (s, 3H) ppm; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.1 (C), 166.8 (C), 147.5 (C), 140.4 (C), 136.9 (C), 131.2 (CH), 130.5 (2 x CH), 127.2 (CH), 121.1 (2 x CH), 119.1 (CH), 112.0 (C), 21.1 (CH_3) ppm; **LRMS (DIP)** *m/z* (%) = 273 (M^+, 19), 166 (26), 120 (17), 109 (7), 108 (100), 107 (17), 92 (8); **HRMS (DIP)** *Calcd.* for $C_{14}H_{11}NO_5$ 273.0637, found 273.0644.

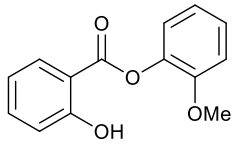
Typical procedure B for the synthesis of methoxyphenylsalycilates derivatives by using diphenyldisulfide as co-catalyst.



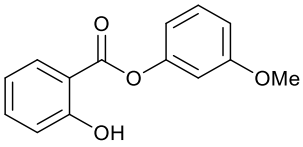
A microwave tube, equipped with a stirring bar, was charged with **1e** (48.8 mg, 0.20 mmol), Na_2CO_3 (4.24 mg, 0.04 mmol, 20 mol-%), $(PhS)_2$ (4.40 mg, 10 mol %), [Mes-Acr]ClO_4 (2.08 mg, 2.5 mol-%), DCE (1.32 mL) and H_2O (0.68 mL). The reaction mixture was deoxygenated by cycles of freeze-vacuum-argon and then, it was put under Ar atmosphere. The mixture was irradiated with blue LED's and stirred at room temperature, observing full conversion (monitored by TLC) after 10 h and a color change from yellow to darkness. The mixture was concentrated under reduced pressure and the residue was purified by column chromatograph (100% Hexane to 95:5 Hexane/EtOAc) and **2e**[7] was obtained as a colorless oil (39 mg, 0.16 mmol, 80%).

TLC R_f, 0.30 (98:2 Hexane/EtOAc); **IR** *v* 3220, 1685, 1615, 1505, 1296, 1245, 1186, 1177, 1154, 1066, 1032, 755, 696 cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$)** δ 10.53 (s, 1H), 8.06 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.53 (ddd, *J* = 8.7, 7.3, 1.7 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 1H), 7.12 (dd, *J* = 6.0, 4.5 Hz, 1H), 7.03 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.89 - 6.96 (m, 3H), 3.82 (s, 3H) ppm; **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 169.4 (C), 162.3 (C), 157.8 (C), 143.6 (C), 136.5 (CH), 130.5 (CH), 122.5 (2 × CH), 119.6 (CH), 117.9 (CH), 114.8 (2 × CH), 112.0 (C), 55.8 (CH_3) ppm; **GC** R_T 12.475 min; **LRMS (EI)** *m/z* (%) = 244 (M^+, 28), 124 (75), 121 (100), 110 (23), 93 (10), 65 (14),

Methoxyphenylsalycilates **2i** and **2l** was also synthesized employing this procedure, observing a faster reaction and a better yield of the corresponding isolated pure products.



2i (37 mg, 0.15 mmol, 75%)



2l (34 mg, 0.14 mmol, 70%)

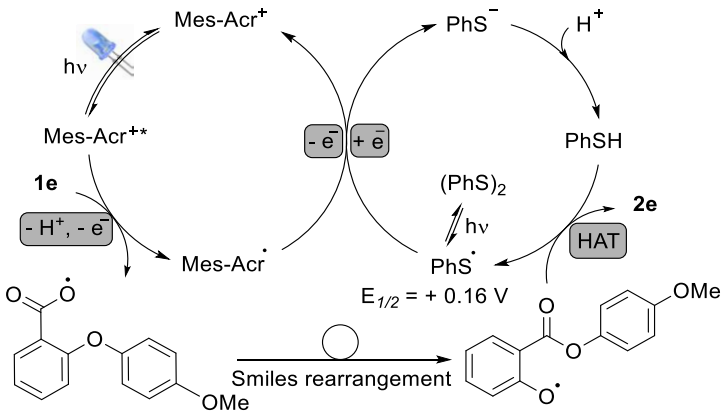


Figure S3: Plausible mechanism for the formation of methoxyphenylsalycilates derivatives by using diphenyldisulfide as co-catalyst.

6. Flow Experiments

Calculation of the pathlength for 90% absorption of light by [Mes-Acr$^+$] solution:

Using the Lambert-Beer Law: $A = \varepsilon_{422}\, d\, c$

Where: ε_{422} is 5600 $M^{-1}cm^{-1}$; d is the pathlength and c is [Mes-Acr$^+$]/M

$$[Acr^+\text{-Mes}] = 0.025 \times 0.10\ M = 0.0025\ M$$

$$A = \log (I_0/I_t) = 1 = \varepsilon_{422} \times [\text{Mes-Acr}^+] \times d$$

$$d = 1/5600 \times 0.0025 = 0.07\ cm = 0.7\ mm.$$

For a reaction 0.100 M in substrate, 90% of the light is absorbed after only 0.7 mm.

Kinetic studies to optimize the residence time:

The reactor was built out of a 1.5 m PFA tube with an internal diameter (ID) of 0.508 mm. The effective length was 1.15 m and the volume of the reactor was 0.23 mL.

Procedure for the photoredox-neutral Smiles rearrangement in Flow:

Into a microwave tube, equipped with a stirring bar, were introduced 2-phenoxybenzoic acid (**1a**, 32.1 mg, 0.15 mmol), Na_2CO_3 (3.18 mg, 0.03 mmol, 20 mol-%) and [Mes-Acr]ClO_4 (1.56 mg, 2.5 mol-%), followed by a 2:1 mixture of MeCN/H_2O (1.5 mL). The mixture was wrapped in aluminum foil and stirred at room temperature for 5 min to give the stock solution for flow experiments. Once the microreactor was homogenized with 2:1 MeCN/H_2O, the syringe was charged with the reaction mixture (1.5 mL), which was pushed with a syringe pump through the microreactor, while irradiating with two bulbs of blue LEDs. Different flow rates were examined, giving a reaction yield for each corresponding residence time (Figure S4). To work under the same steady-state conditions, we washed out the volume eluted during the first 2 min and then started to collect until a small volume of the reaction mixture remained in the syringe (c.a. 1 mL pumped). The exact time of elution (t/min) and exact volume (V/mL) were determined to calculate the flow rate ($\phi = V/t$) and the residence time ($R_T = 0.23/\phi$). The collected mixture was filtered through a short pad of silica gel, eluting with EtOAc (15 mL). The organic residue was dried over anhydrous $MgSO_4$ and the amount of **2a** (n/mmol) formed was estimated by GC using durene as internal standard (the calibration was shown before) in order to determine the yield (%yield = n/0.1V x 100).

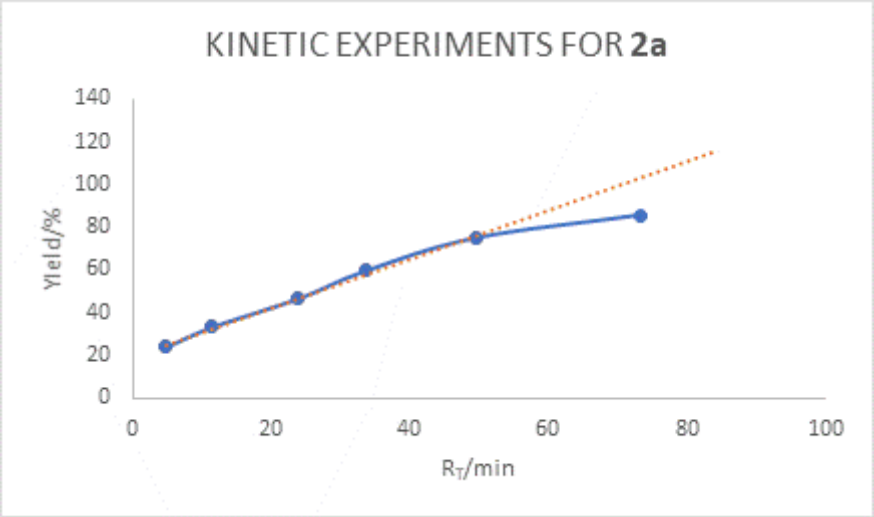
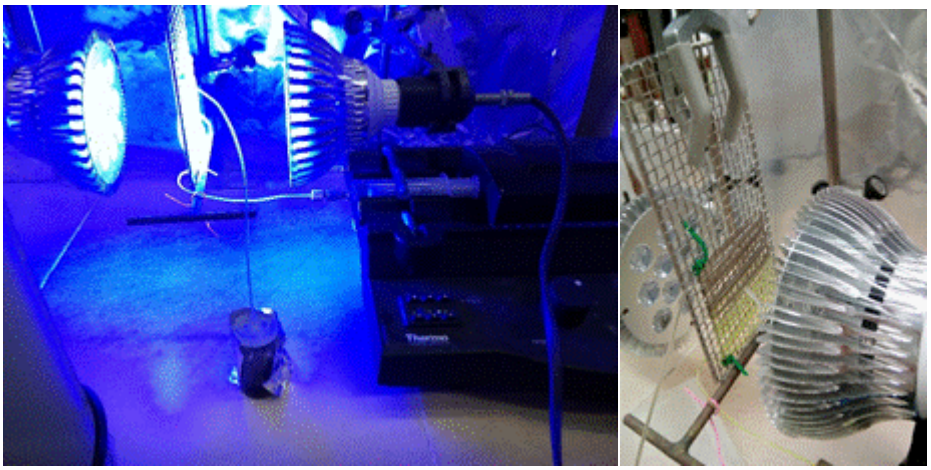


Figure S4. Yield *vs* Residence time (R_T).

Scale up for **2a**, **2b** and **2o** using flow chemistry:

Set up: A larger reactor was used, built out of a 3 m PFA tube with 0.762 mm of internal diameter. The effective length was 1.15 m and the volume of the reactor was 1.14 mL.



Stock solutions: A pear-shaped flask was charged with the desired carboxylic acid (1 mmol of **1a**, **1b** or **1o**), Na_2CO_3 (21.2 mg, 0.20 mmol) and [Mes-Acr]ClO_4 (10.4 mg, 2.5 mol-%), followed by a 2:1 mixture of MeCN/H_2O (8 mL, 0.125 M). The mixture was wrapped in aluminum foil and stirred at room temperature for 5 min.

Procedure: Once the microreactor was homogenized with 2:1 MeCN/H_2O, the 10 mL-syringe was charged with the reaction mixture (8 mL), which was pumped through the microreactor, while irradiating with two bulbs of blue LEDs. at a flow rate to achieve the specific residence times indicated in the table below. To work under the same steady-state conditions, we washed out the volume eluted during the first 15 min. The

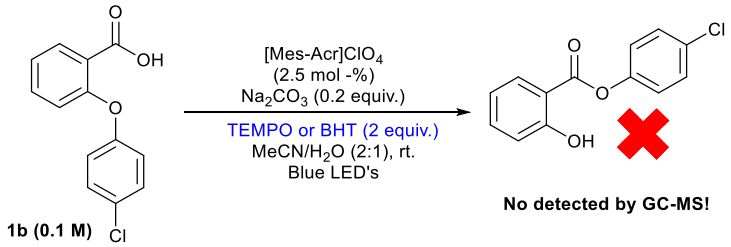
reaction mixture was collected in a vial (V_R/mL) until almost all initial mixture was pumped. The obtained solution was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford a brown residue. Purification by column chromatography (100% Hexane to 95:5 Hexane/EtOAc) afforded the pure desired compound.

Table S2.

Compound	R_t	V_R	m (2)	n (2)	Yield[a]
2a	42 min	5.7 mL	128 mg	0.60 mmol	84%
2b	60 min	5.7 mL	118 mg	0.47 mmol	69%
2o	60 min	5 mL	100 mg	0.44 mmol	70%

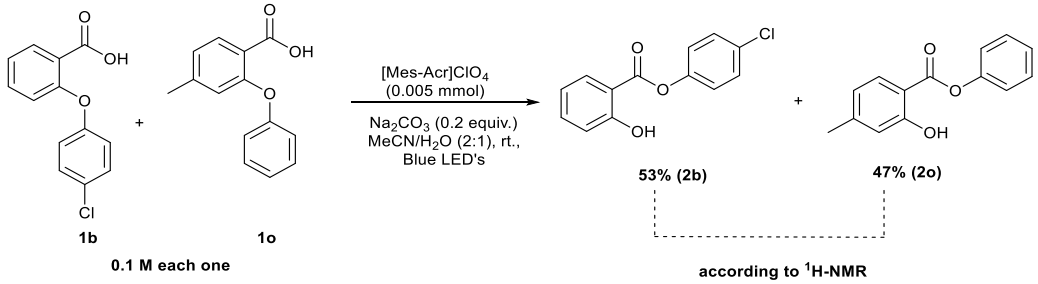
[a] Yield = [n (**2**)/V_R x 0.125] x 100

7. Inhibition Experiments with TEMPO and BHT



Into a Pyrex tube, **1b** (24.8 mg, 0.1 mmol), TEMPO or BHT (2 equiv.), Na_2CO_3 (2.12 mg, 0.02 mmol, 0.02 equiv.) and [Mes-Acr]ClO_4 (1.04 mg, 2.5 mol-%) were added, followed by the mixture of MeCN/H_2O (2:1, 1mL). The mixture was sealed with a septum, stirred at room temperature without any inert atmosphere and irradiated with blue light for 14 h. The reaction mixture was filtered through a short pad of silica gel and eluted with EtOAc (15 mL). The organic residue was dried over anhydrous $MgSO_4$ and diluted with more EtOAc (5 mL). An aliquot (1 µL) was injected into the GC-MS apparatus, observing no Smiles rearrangement. TLC (7:3 [Hexane/(3:1:0.08) EtOAc/EtOH/AcOH][8]) was also indicative of no reaction.

8. Cross-Over Experiment



Into a Pyrex tube were sequentially added, **1b** (22.8 mg, 0.10 mmol), **1o** (24.9 mg, 0.10 mmol), Na_2CO_3 (4.24 mg, 0.04 mmol, 0.02 equiv.) and $[Mes\text{-}Acr]ClO_4$ (2.08 mg, 0.005 mmol), followed by a mixture of $MeCN/H_2O$ (2:1, 2 mL). The mixture was sealed with a septum, stirred at room temperature without (inert atmosphere) and irradiated with blue light for 14 h, observing full conversion by TLC. The reaction mixture was concentrated under vacuum, affording a brown residue, which was purified by column chromatography (100 % Hexane to 95:5 Hexane/EtOAc). An inseparable mixture of phenyl salicylates **2b** and **2o** was isolated as colorless oil (35 mg). ^{1}H-NMR spectra in Figure S5, showed a quasi-equimolar mixture of phenyl salicylates with a 53:47 (**2b**:**2o**) molar ratio.

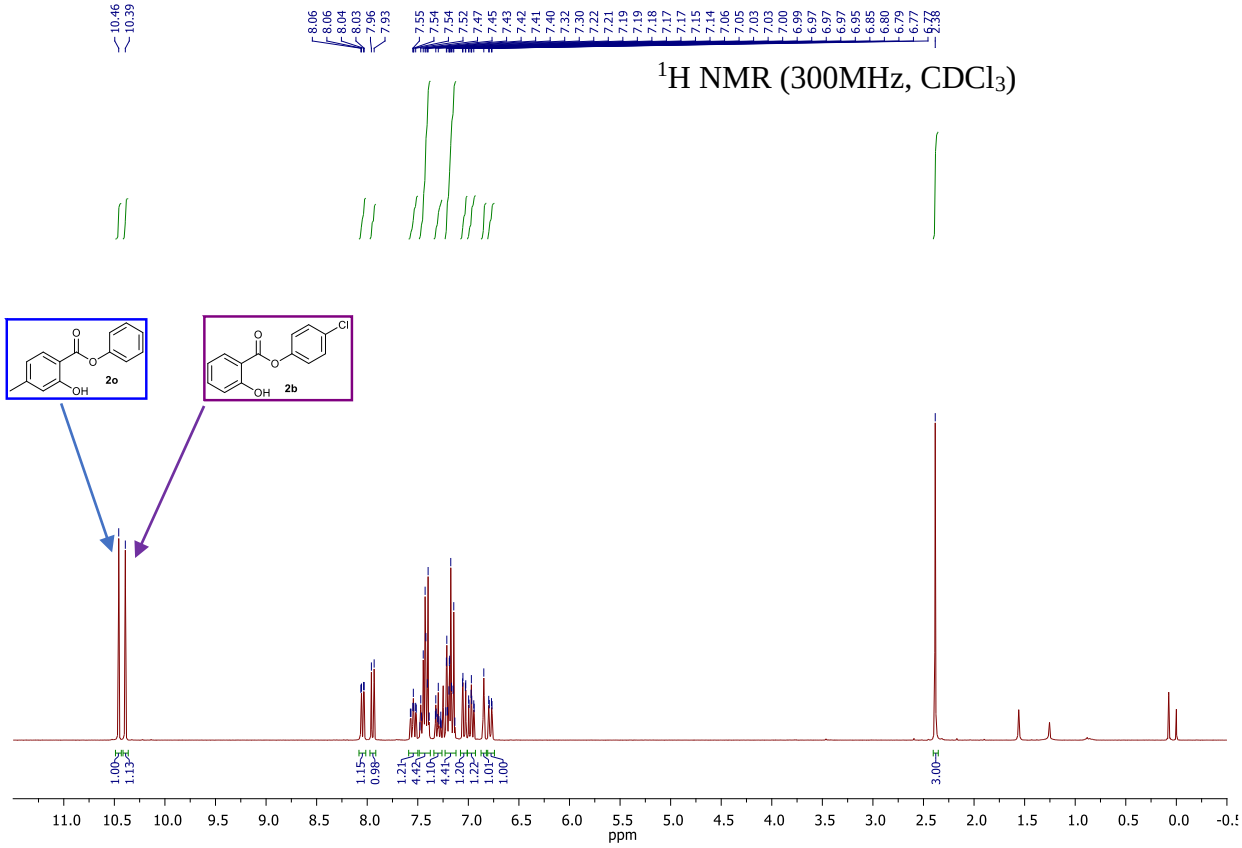


Figure S5. ^{1}H-NMR (300 MHz, $CDCl_3$) obtained for the mixture of **2b** and **2o**.

Importantly, to further demonstrate that no crossover products were obtained during the photochemical reaction, we analyzed the previously obtained mixture by GC-MS. As shown in Figure S6, the GC trace shows only two main products that correspond to the expected intramolecular Smiles rearrangement.

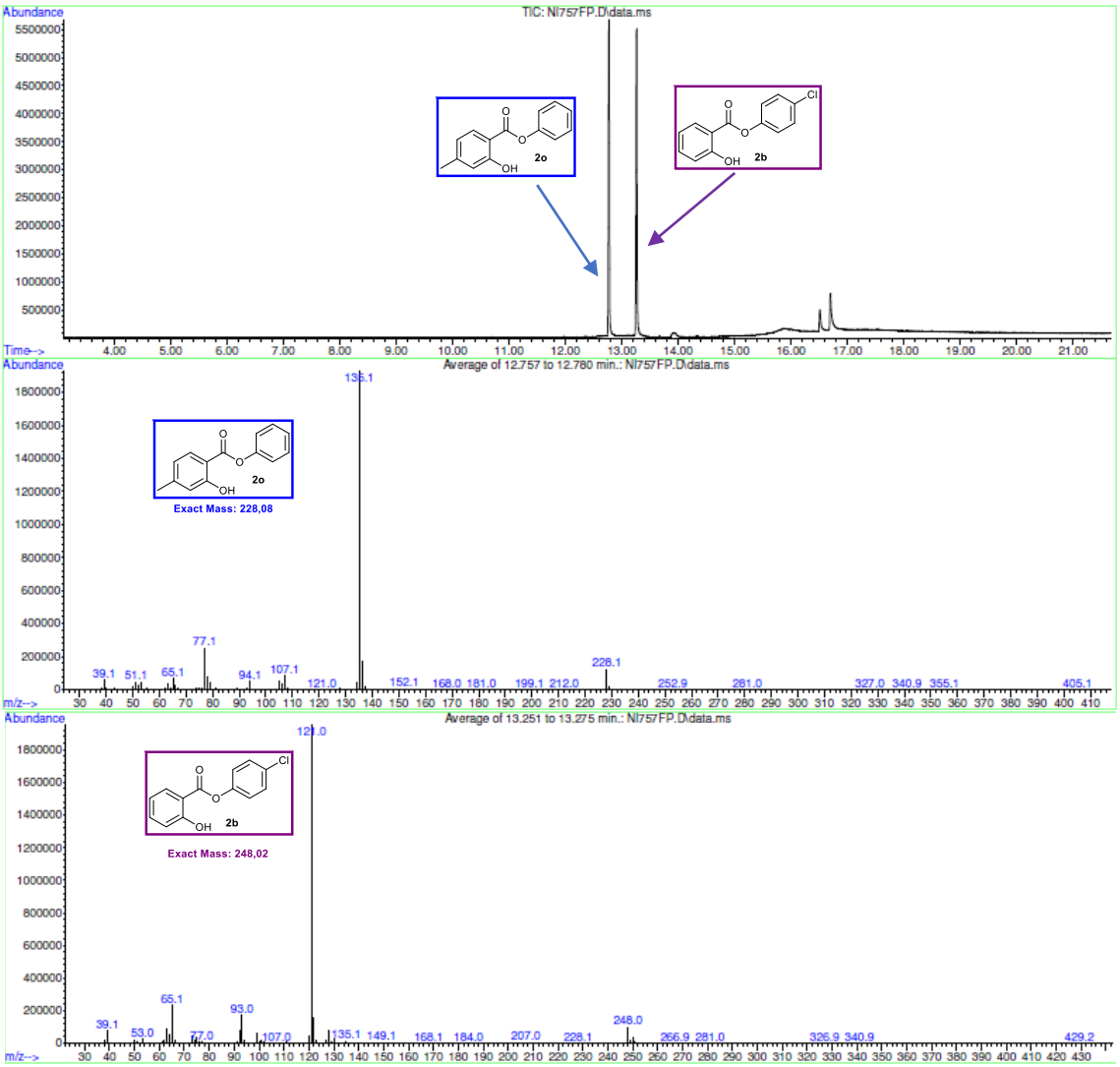


Figure S6. GC-MS for the crossover experiment with **1b** and **1o**.

9. Emission spectra of light sources

The irradiance was measured with a Black-Comet UV-Vis spectrometer from StellarNet Inc.

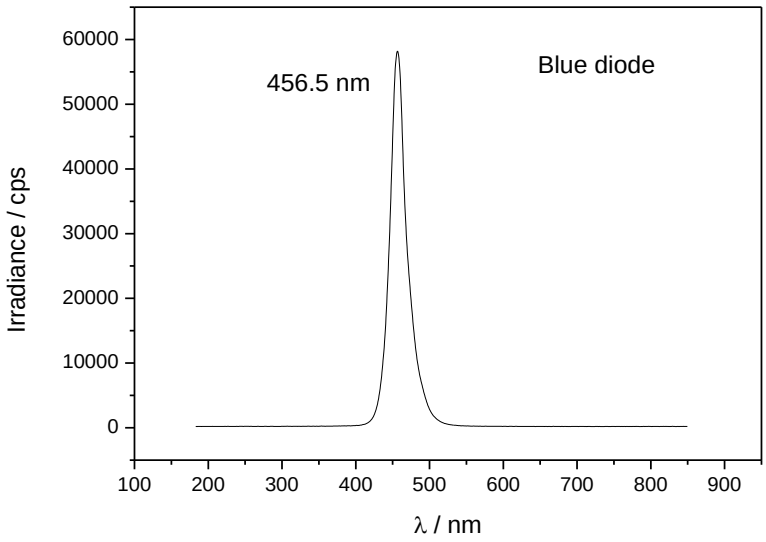


Figure S7. Emission spectrum of the blue light emitting diodes (LEDs) used in the reactions.

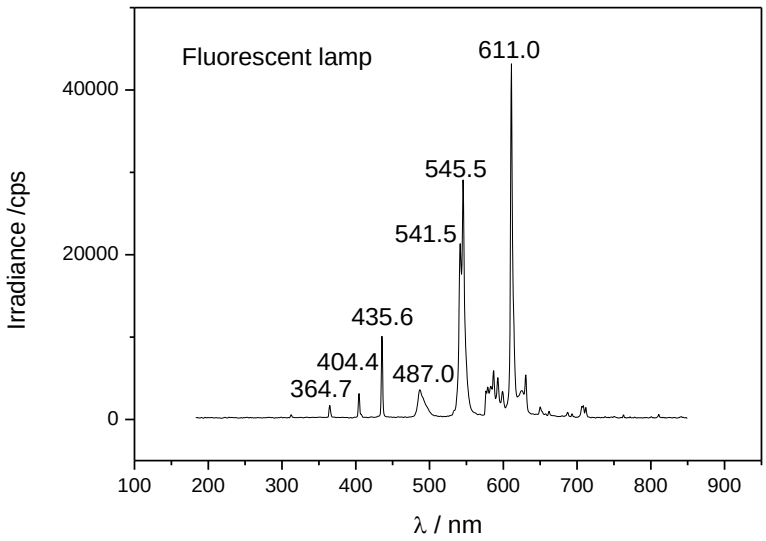


Figure S8. Emission spectrum of the compact fluorescence lamp (CFL).

10. Absorption spectra of [Mes-Acr]$^+$, 1a and 2a

Individual absorption measurements of Fukuzumi's Catalyst, **1a** and **2a** were performed and the results were plot in the same graphic. The experiments were carried out using a *quartz* cuvette (l = 10 mm) and 4 mL of the corresponding solution (Figure S9).

The absorbance spectrum of the photocatalyst (blue series) is in accordance with the previously reported data for Mes-Acr$^+$.[16] For **2a** (grey series), the obtained spectra are also similar to previously reported data.[17] For clarity, we have only represented the region of 250 - 500 nm, omitting the intense absorption band of photocatalyst below 307 nm. From the obtained spectra it is clear that neither **1a**, nor **2a** absorb at $\lambda > 350$ nm, then the photocatalyst is necessary to promote the reaction at 450 nm.

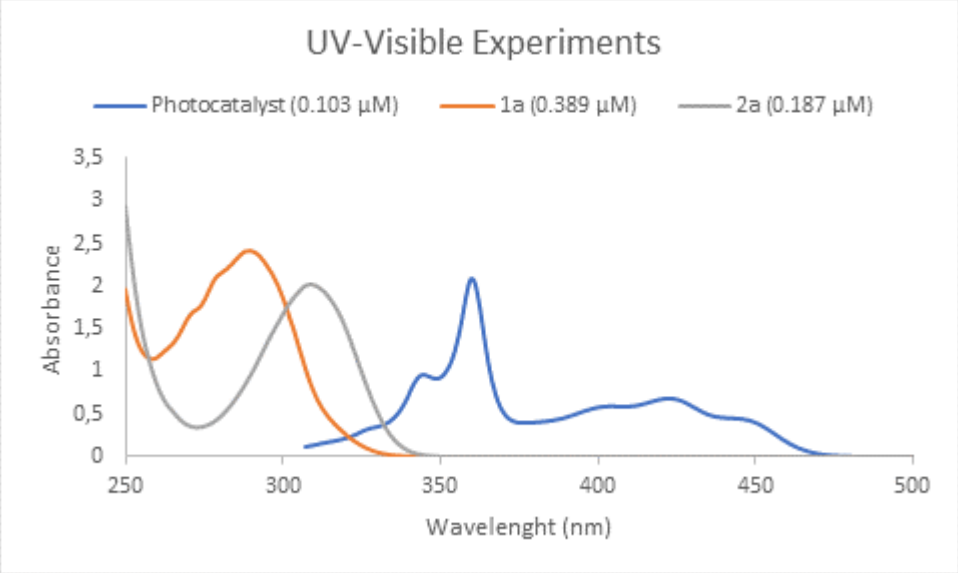


Figure S9. UV-vis spectra for [Mes-Acr$^+$], **1a** and **2a**.

[16] T. Tsudaka, H. Kotani, K. Ohkubo, N. Nakagawa, N. V. Tkachenko, H. Lemmetyinen and S. Fukuzumi, *Chem. Eur. J.*, 2017, **23,** 1306.
[17] A. Gupta, R. Liang, J. Moacanin, R. Goldbeck and D. Kliger, *Macromolecules*, 1980, **13**, 262.

11. Luminescence quenching experiments.

The samples for the quenching experiments were prepared using a solution of 9-mesityl-10-methylacridinium perchlorate [Mes-Acr$^+$] = 9.0 x 10^{-5} M in 2:1 CH_3CN/H_2O and variable amounts of quencher (1:1 **1a**/Na_2CO_3). Samples were added to a fused silica cuvette, irradiated at 430 nm and emission was measured at 550 nm. As expected, the light emission diminishes as the concentration of quencher increases (Figure S10).

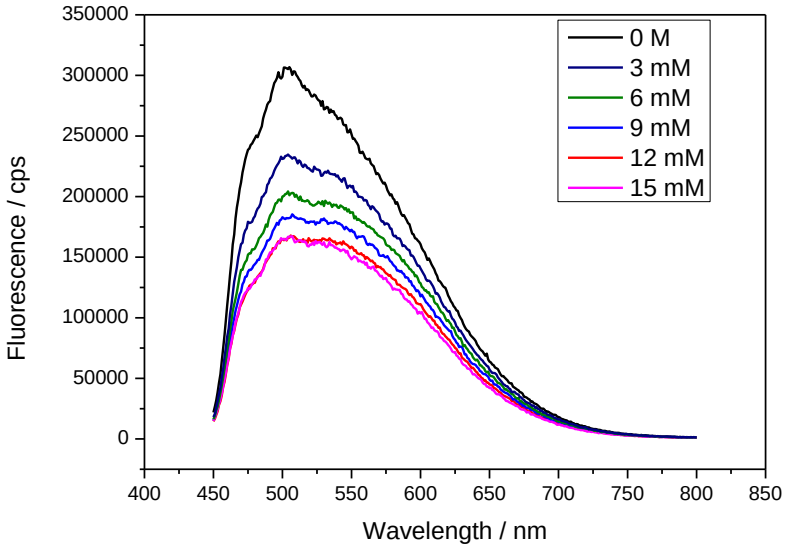


Figure S10. Fluorescence quenching of [Mes-Acr$^+$]* with 1:1 **1a**/Na_2CO_3.

To determine the quenching rate, we have performed lifetime measurements as these measurements are more robust because they do not depend on the intensity of excitation nor on the concentration of fluorophores. The data obtained from the fluorescence decay measured using time-correlated single photon counting (TCSPC) of Mes-Acr$^+$ in CH_3CN/H_2O (2:1) in the presence of increasing amounts of quencher is given in the next table. The luminescence decays (illumination with a 450 nm pulsed nanoled) have been adjusted to a biexponential function (Figure S11). On one hand, the first time constant (τ_1) is not affected in great extension by the presence of the quencher. This short lifetime constant might be ascribed to intramolecular charge transfer in Mes-Acr. On the other hand, the longlived transient species (τ_2) decay faster in the presence of the quencher, most likely due to intermolecular charge transfer processes.

[Quencher]	τ_1 / ns	τ_2 / ns
0	2.51	21.1
3 mM	2.40	15.2
6 mM	2.23	11.2
9 mM	2.22	11.5
12 mM	2.07	9.53
15 mM	1.91	7.61

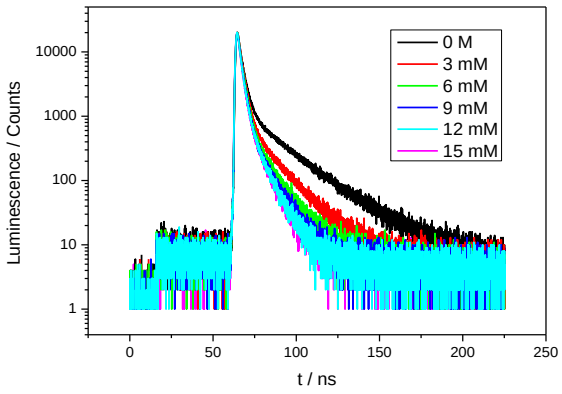


Figure S11. Lifetime measurements of [Mes-Acr$^+$]* (by TCSPC) at different quencher concentrations.

The Stern-Volmer plot is shown in Figure S12, being τ_0 and τ the lifetime of the photocatalyst (Mes-Acr) in the absence and in the presence of variable amounts of quencher, respectively.

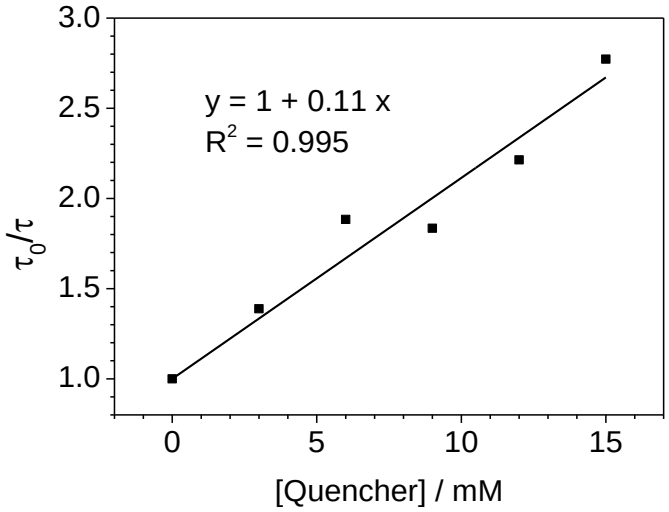


Figure S12. Stern-Volmer plot for the of [Mes-Acr$^+$]* quenching with **1a**-sodium salt.

Considering the following Stern-Volmer equation and the plot, we can calculate the bimolecular quenching constant (k_q):[18]

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Quencher] = 1 + k_q \tau_0 [Quencher] \qquad \textbf{Eq. S2}$$

$$k_q = \frac{k_{SV}}{\tau_0} = \frac{111 M^{-1}}{21.1 \cdot 10^{-9} s} = 5.26 \cdot 10^9 M^{-1} \cdot s^{-1}$$

[18] The obtained value is of the same order that the one reported for the Mes-Acr$^+$ fluorescence quenching by alkenes and HAT catalysis. See: N. A. Romero and D. A. Nicewicz, *J. Am. Chem. Soc.*, 2014, **136**, 17024.

12. **Determination of quantum yield**

1a (0.10 M) **2a**

The quantum yield was determined for the reaction above using two sources of light to consider the possible effect of the light intensity. The measurements were carried out using: (a) The 450 nm led source used in the standard procedure (ABI Blue Led PAR38, 12 x 1 W); and (b) A 150 W Xe arc lamp (Lot Oriel) equipped with a quartz lens and a 440 nm interference filter (Newport 10LF10-440). In both cases, the photon flux was determined by the standard ferrioxalate actinometry procedure.[19]

A 0.15 M solution of $K_2Fe(C_2O_4)_3$ was prepared by mixing 1 ml of solution A (0.811 g $FeCl_3 \cdot 6H_2O$ in 1 mL H_2SO_4 and diluted up to 10 mL) and 1 mL of solution B (1,49 g of oxalic acid and 1,86 g KOH in 10 mL of water).[20] The obtained solution (2 mL) was transferred into a fused silica cuvette and irradiated for: (a) 60 s in the case of the led source and (b) 600 s for the Xe arc lamp.

After the illumination, 100 μL were transferred to a 10 mL volumetric flask, and 4 mL of a phenanthroline solution (20 mg of 1,10-phenanthroline in 10 mL of H_2O) and 500 μL of a buffer solution (0.83 g of NaOAc and 1 mL of H_2SO_4 in H_2O up to 10 mL) were added prior to adding water up to 10 mL.

The amount of ferrous ion production was measured by determining the absorbance of the phenanthroline complex at 510 nm. To assure that the absorbance remains below 1 (in order to assure linearity between the absorbance and the concentration), a dilution 1:2 was also performed. A blank sample was prepared following the same procedure, but keeping the sample in the dark.

The amount of ferrous ion generation was calculated as:

$$mmol\ Fe^{2+} = \frac{\Delta Abs}{\varepsilon \cdot d} \cdot \frac{10mL}{5mL} \cdot \frac{10mL}{0.1mL} \cdot 2mL \qquad \textbf{Eq. S3}$$

Where ΔAbs represents the absorbance of the sample with respect to the blank sample, ε the extinction coefficient of the complex at 510 nm ($\varepsilon = 1.11 \cdot 10^4\ L \cdot mol^{-1} \cdot cm^{-1}$),[19] d is the light path length of the cuvette (d = 1 cm). The different volumes appearing in the equation take into account the different dilutions.

[19] J. N. Demas, W. D. Bowman, E. F. Zalewski and R. A. Velapoldi, *J. Phys. Chem.*, 1981, **85**, 2766.
[20] R. C. Johnson, *J. Chem. Educ.*, 1970, **47**, 702.

The photon flux was estimated considering the illumination time (t), the quantum yield of the photolysis of $K_2Fe(C_2O_4)_3$ ($\Phi_{450nm} = 1$)[21] and total light absorption (f = 1), according to:

$$photon\ flux = \frac{mmol\ Fe^{2+}}{t \cdot \Phi_{450nm} \cdot f} \cdot \frac{10^{-3}\ mol}{mmol} \qquad \textbf{Eq. S4}$$

The results are summarized in the next table:

Table S3.

Light source	ΔAbs	mmol Fe^{2+}	t/ s	Photon flux/ Einstein·s^{-1}
Led source	0.380	0.02353	60	$3.922 \cdot 10^{-7}$
Xe arc lamp+filter	0.648	0.01369	600	$2.282 \cdot 10^{-}$

To determine the quantum yields, the same fused silica cuvettes were employed to perform the reaction, under standard conditions, and from 0.10 mmol of **1a**. They were located in front the illumination sources at the same location as the actinometer. However, to measure more precisely the amount of product generated larger illumination times were employed. Therefore, the samples were illuminated for 3 h in the case of the led source, and for 7 h in the case of the arc lamp.

Finally, the quantum yield was calculated as:

$$\Phi = \frac{mol\ product}{t' \cdot photon\ flux} \cdot 100 \qquad \textbf{Eq. S5}$$

Where *mol product* represents the amount of product generated and *t'* is the reaction time. The results are summarized in the next table:

Table S4.

Light source	Photon flux/ Einstein s^{-1}	2a / mol	t'/ s	Φ/ %
Led source	$4.6 \cdot 10^{-7}$	$5.0\ 10^{-5}$	10800	1.2
Xe arc lamp+filter	$2.7 \cdot 10^{-8}$	$5.3\ 10^{-6}$	25200	0.92

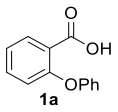
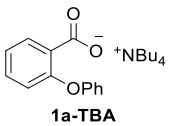
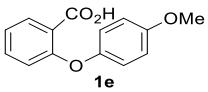
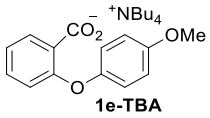
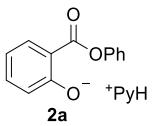
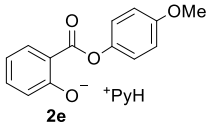
These results clearly indicate that the quantum yield is not highly dependent on the light intensity. The small difference observed could be related to the fact that the wavelength slightly differs for both experiments, being 440 nm in the case of the Xe arc lamp and 450 nm for the led source.

[21] Depending on the reference this value varies from 0.85 to 1. However, we do not pretend to calculate the precise quantum yield of our model reaction. These calculations are only approximate.

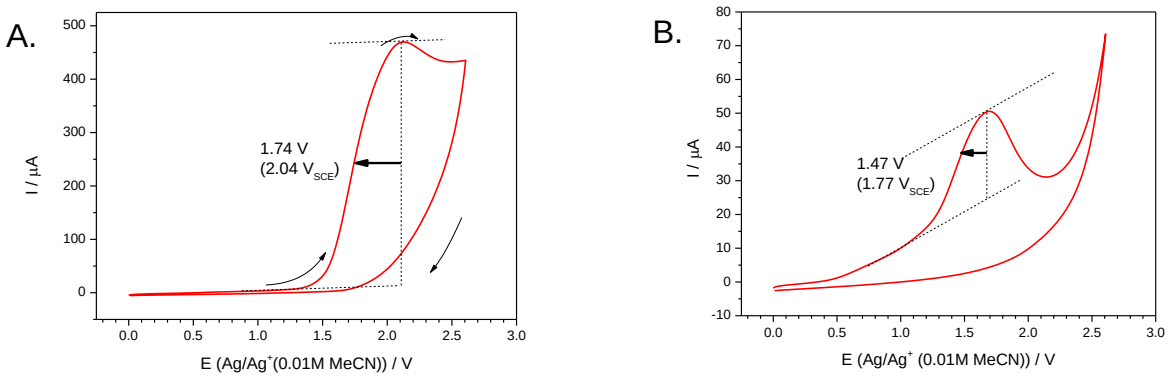
13. Cyclic voltammetry measurements

Cyclic voltammetry (CV) were carried out in a standard three-electrode electrochemical cell using a glassy carbon disk as a working electrode (7 mm^2 geometric area) and a non-aqueous reference electrode (Ag/0.01 M $AgNO_3$ in acetonitrile) as a reference electrode, to which all the potentials are referred unless otherwise stated. To maintain internal consistency, the potential of the reference electrode was verified using ferrocene as an internal reference after each experiment. A platinum wire was used as a counter electrode. The working electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate in dry, degassed acetonitrile solution. A scanning potentiostat/galvanostat AUTOLAB PGSTAT30 was used to record the cyclic voltammograms at a scan rate of 100 $mV \cdot s^{-1}$. The cyclic voltammograms shown correspond to the first scan. To measure the half-peak potential ($E_{p/2}$)[22] of the different compounds, a substrate concentration of 0.01 M was employed. The electrochemical oxidation of **1a** and **1e** and their corresponding tetrabutylammonium salts were studied on the basis of a previous work[23]. On the other hand, the cyclic voltammograms of **2a** and **2b** were recorded after the addition of increasing amounts of pyridine (0.5 M solution in acetonitrile), so as to deprotonate the phenol moiety, according to previous work.[24] All the potentials were corrected against SCE ($E_{SCE} = E_{Ag/AgNO3} + 0.30$ V).

Table S5: Half-wave potential for the oxidation ($E_{1/2}^{ox}$) of some substrates

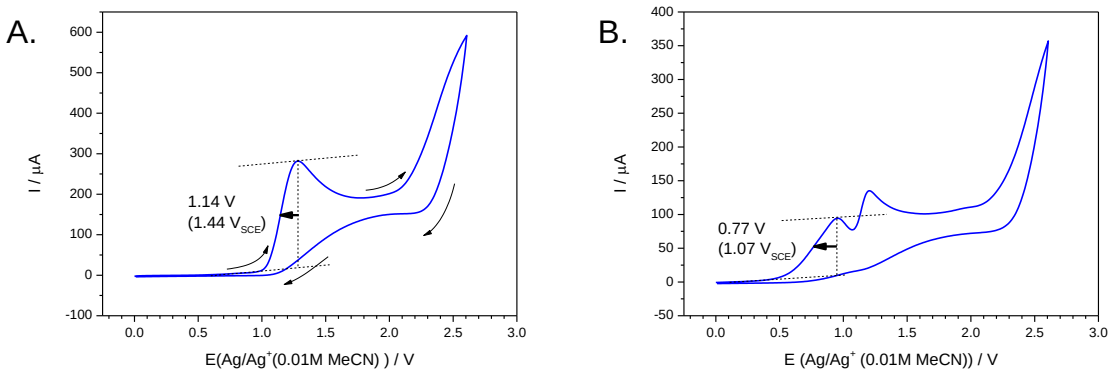
Substrate	$E_{1/2}^{ox}$ *vs* SCE	Substrate	$E_{1/2}^{ox}$ *vs* SCE
 **1a**	+ 2.04 V	 **1a-TBA**	+ 1.77 V
 **1e**	+ 1.44 V	 **1e-TBA**	+ 1.07 V
 **2a**	+ 1.21 V	 **2e**	+ 1.70 V

[22] Half-peak potentials ($E_{p/2}$) are taken as a good approximation to estimate the redox potentials ($E^o_{1/2}$), according to: H. G. Roth, N. A. Romero, and D. A. Nicewicz, *Synlett*, 2016, **27** (05), 714.
[23] M. Galicia and F. J. Gonzalez, *J. Electrochem. Soc*., 2002, **149** (3), D46-D50.
[24] L. Biczok, N. Gupta, and H. Linschitz, *J. Am. Chem. Soc.*, 1997, **119**, 12601.



1a **1a-TBA**

Figure S13. CV for **1a** (A) and **1a-TBA** (B). The small arrows indicate the scan direction.



1e **1e-TBA**

Figure S14. CV for **1e** (A) and **1e-TBA** (B) The small arrows indicate the scan direction.

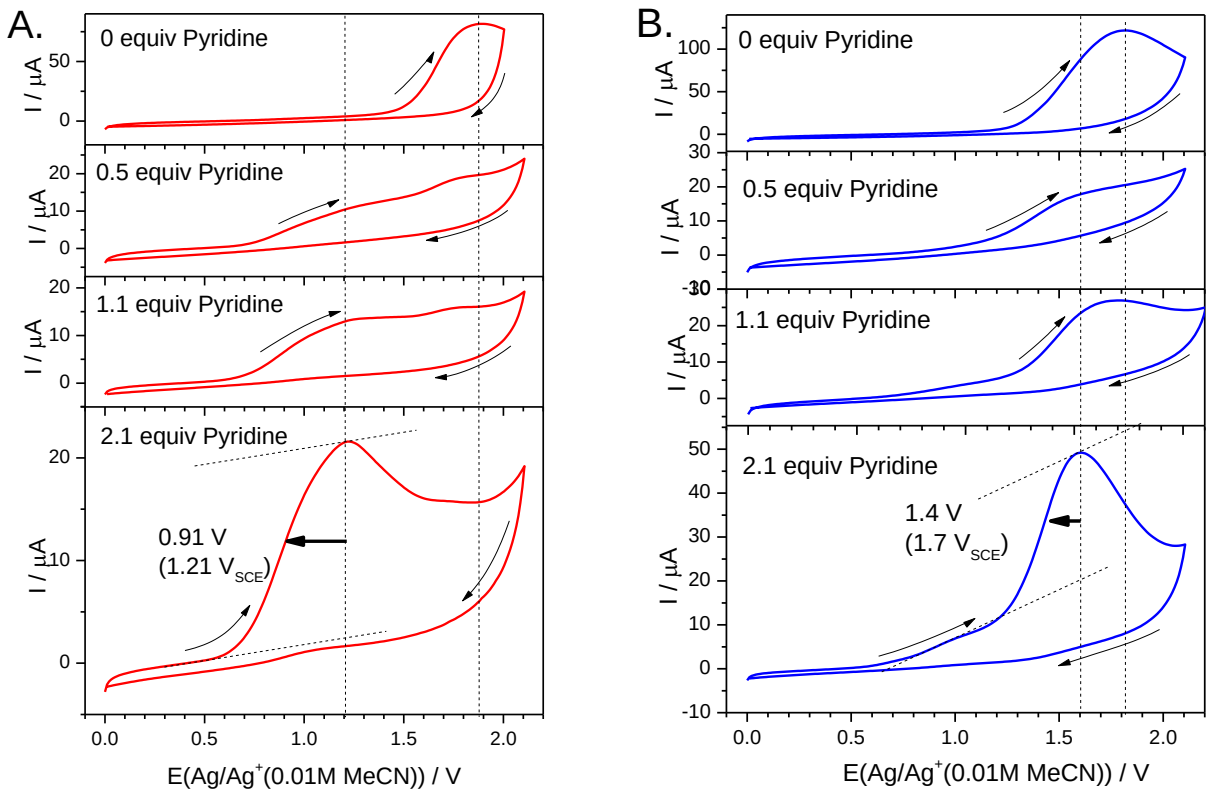
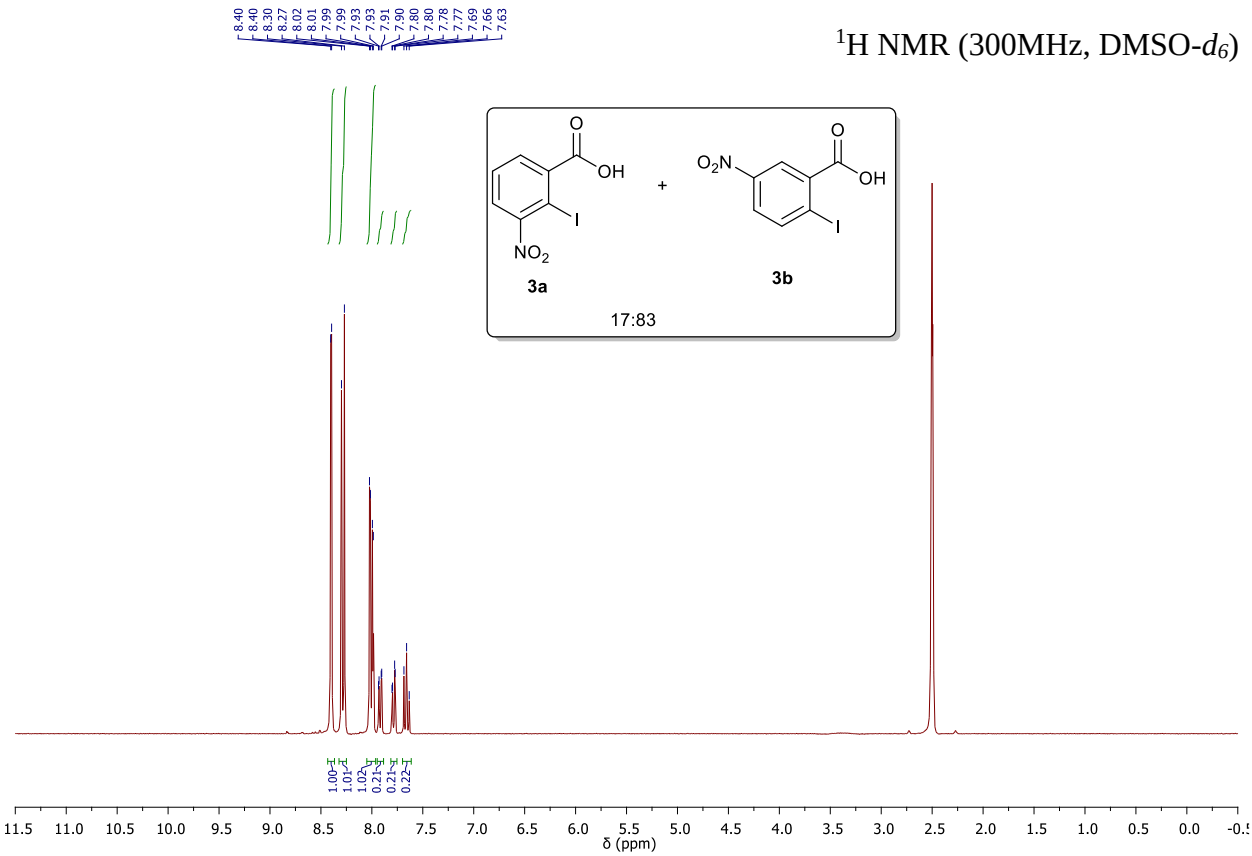
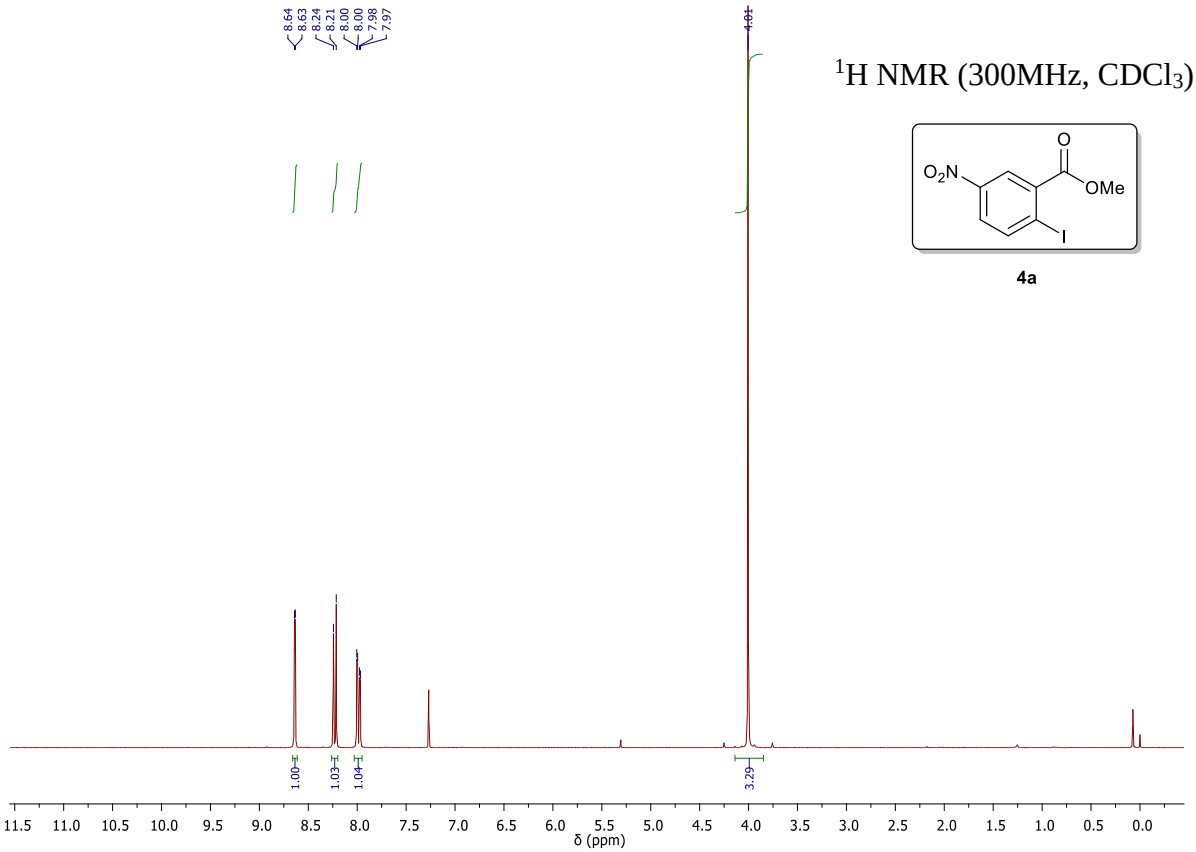


Figure S15. CV for **2a** (A) and **2e** (B) with increasing amounts of pyridine in acetonitrile. The small arrows indicate the scan direction.

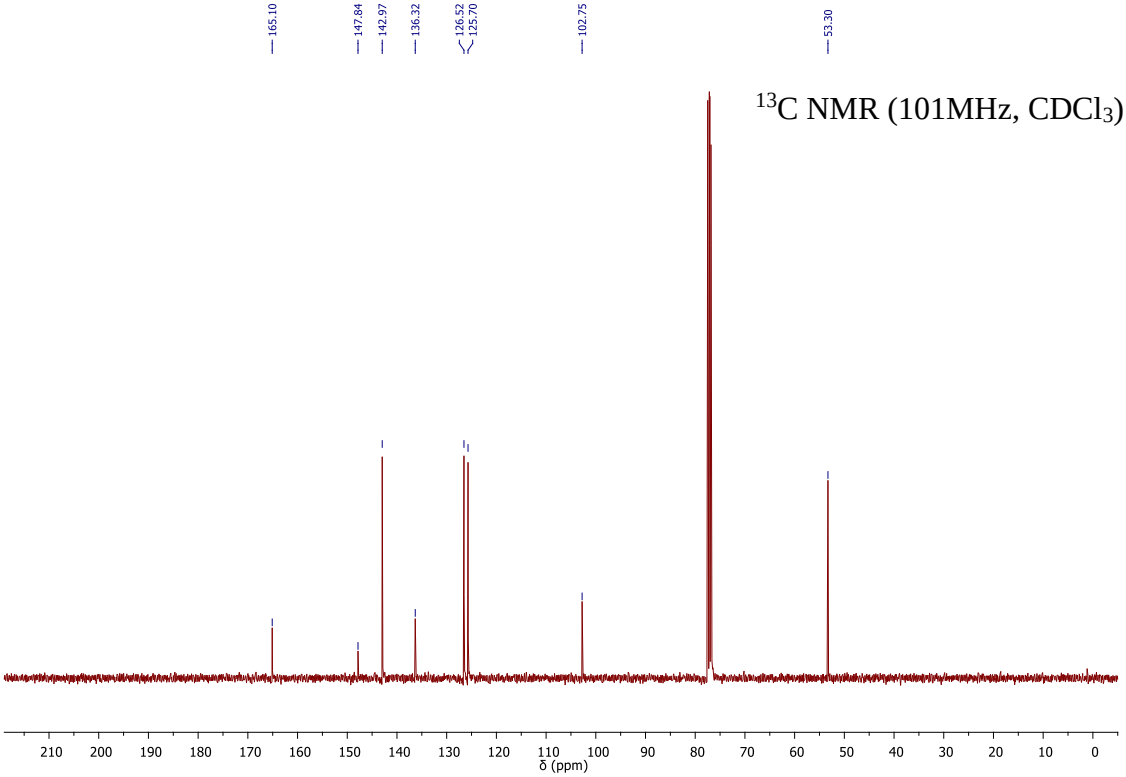
^{1}H NMR (300MHz, DMSO-d_6)





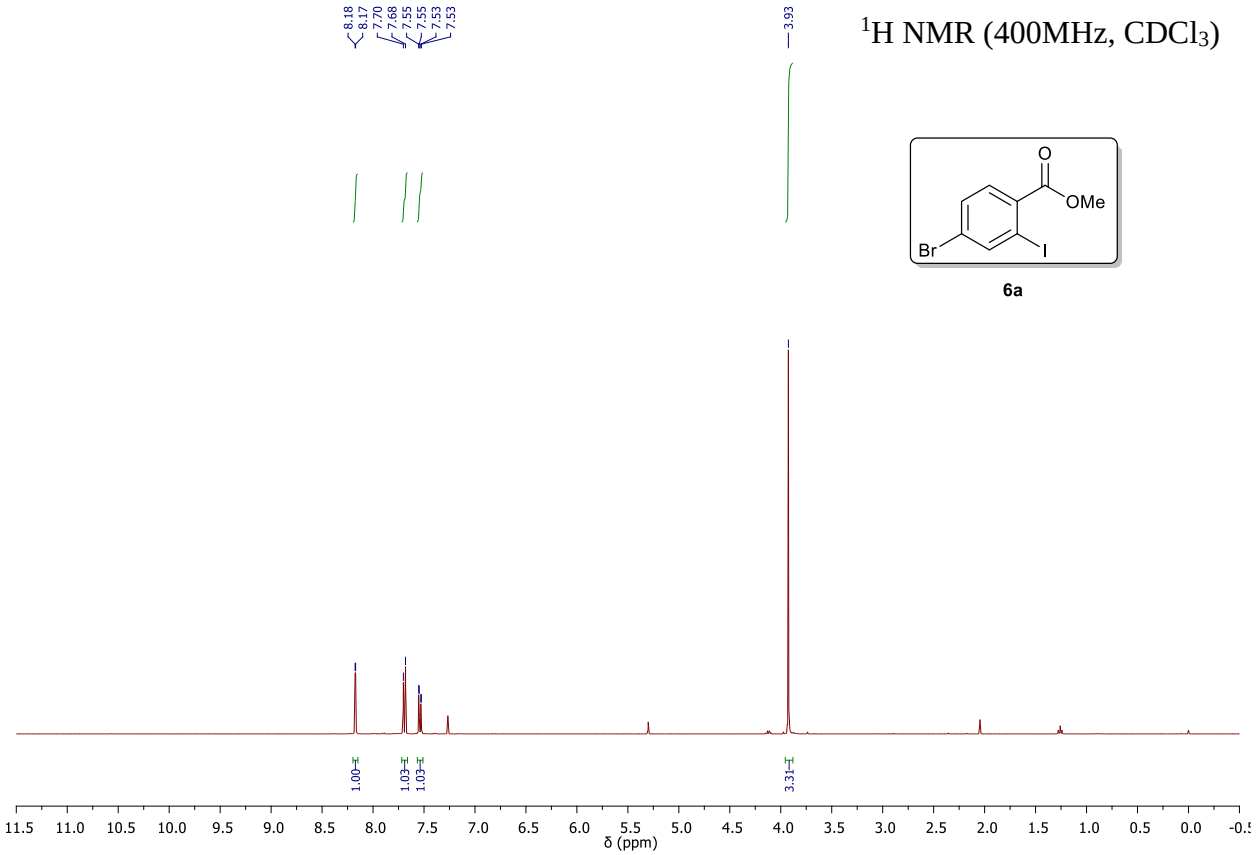
^{1}H NMR (300MHz, $CDCl_3$)

4a



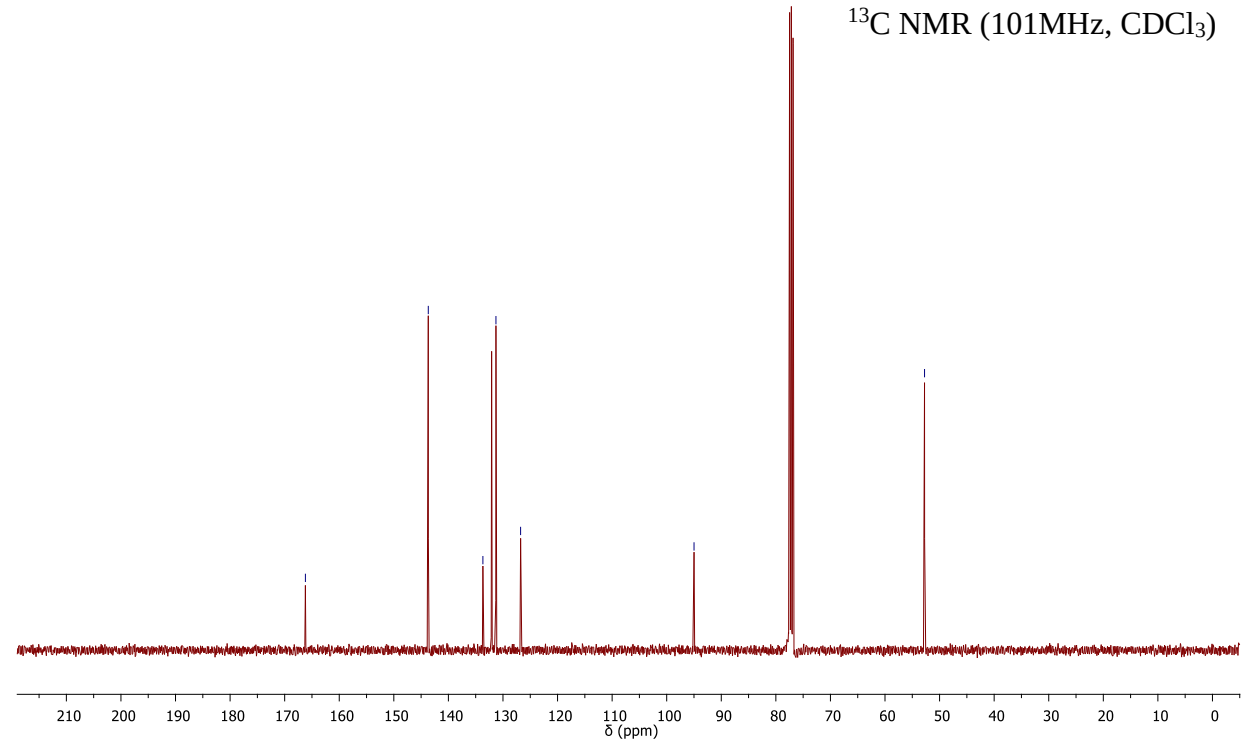
^{13}C NMR (101MHz, $CDCl_3$)

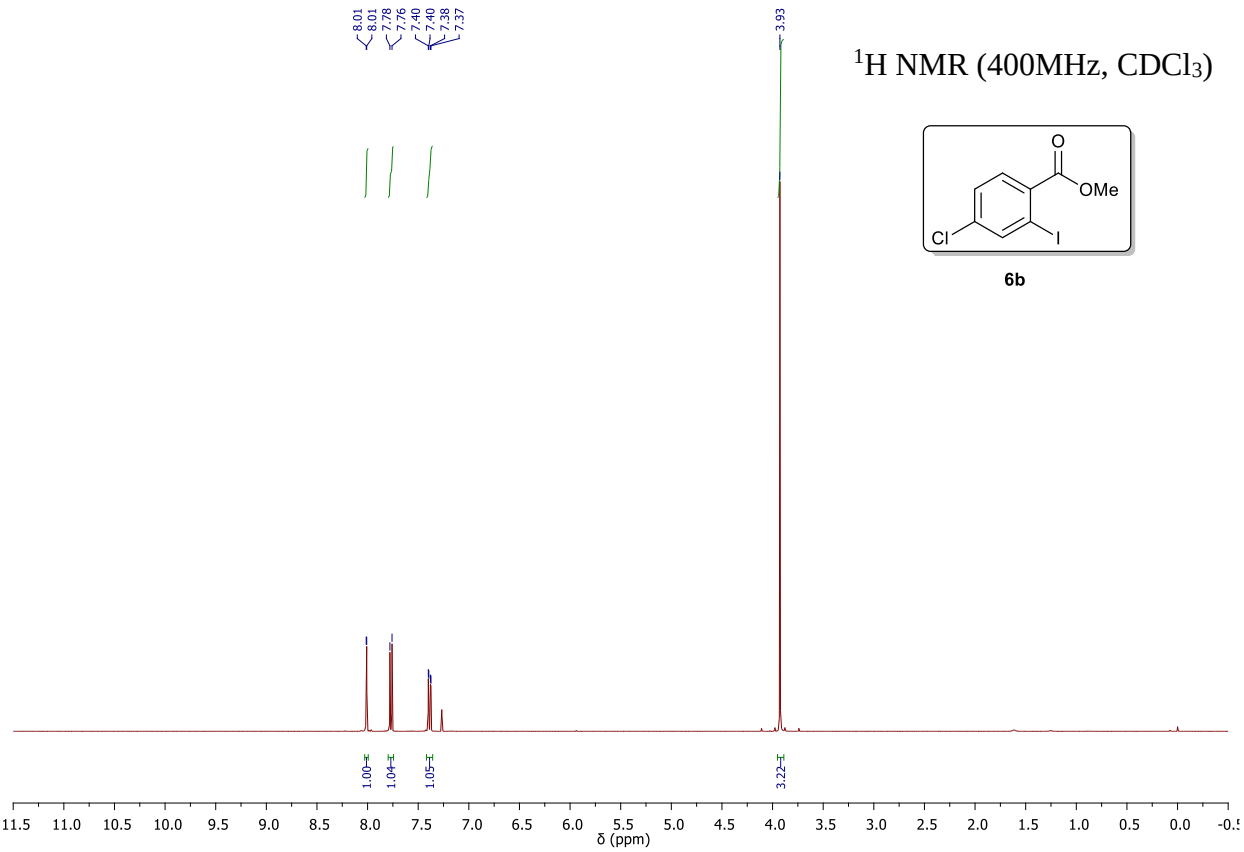
^{1}H NMR (400MHz, $CDCl_3$)



6a

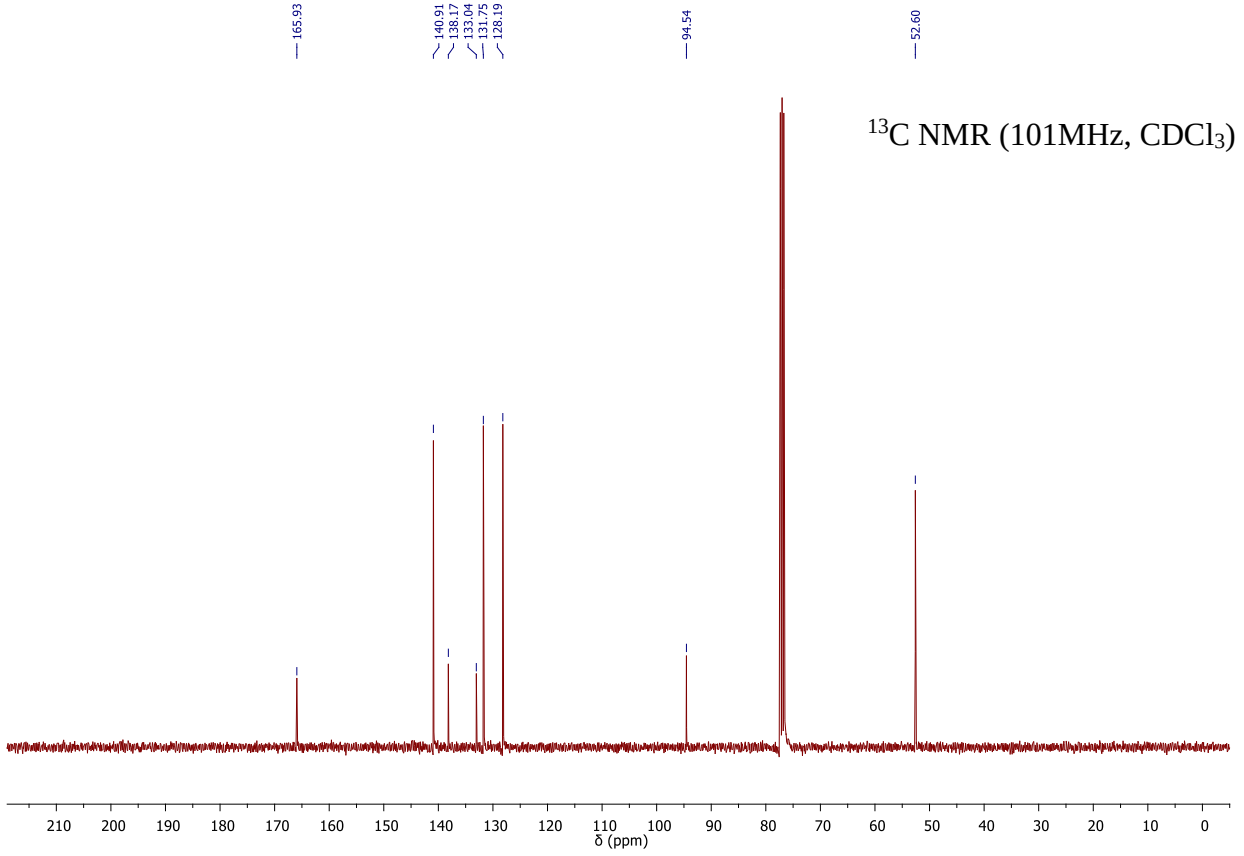
^{13}C NMR (101MHz, $CDCl_3$)





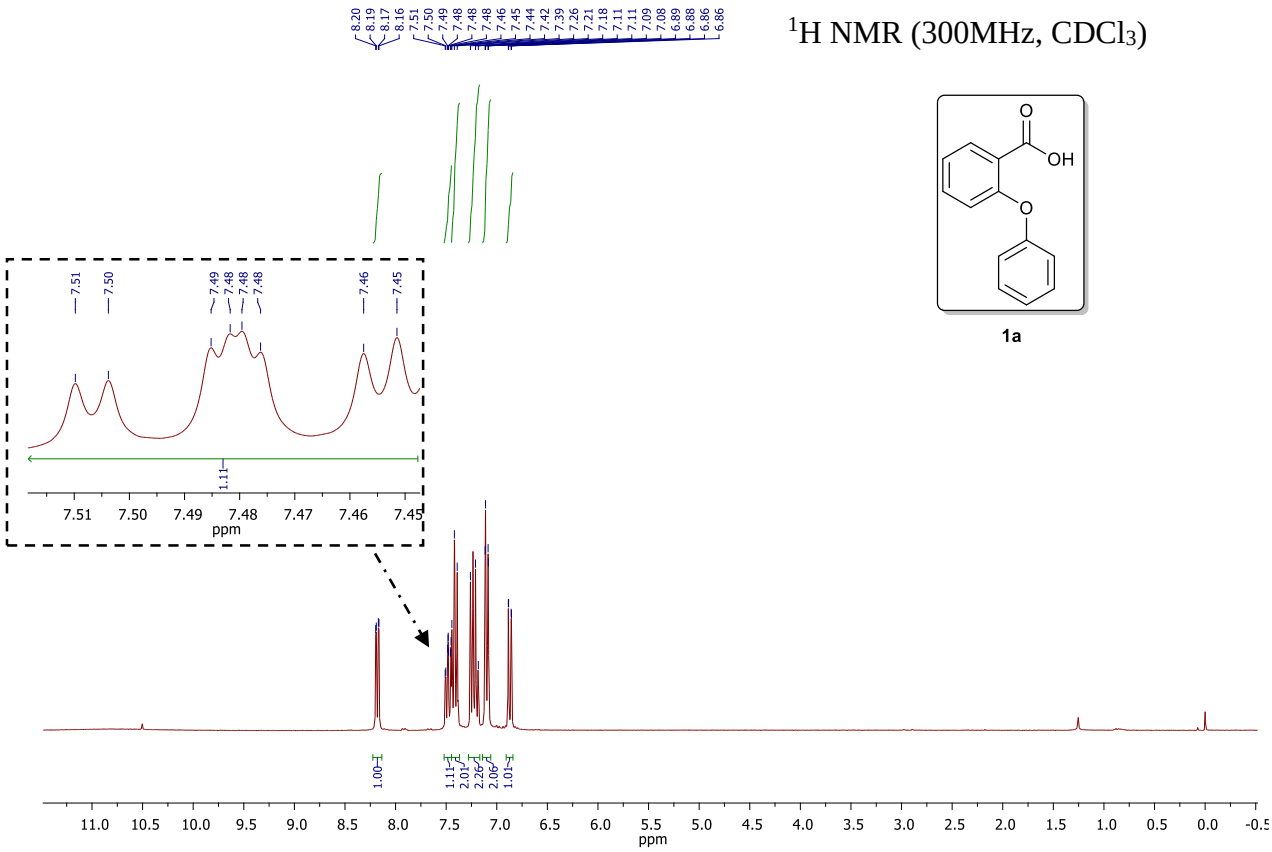
^{1}H NMR (400MHz, $CDCl_3$)

6b



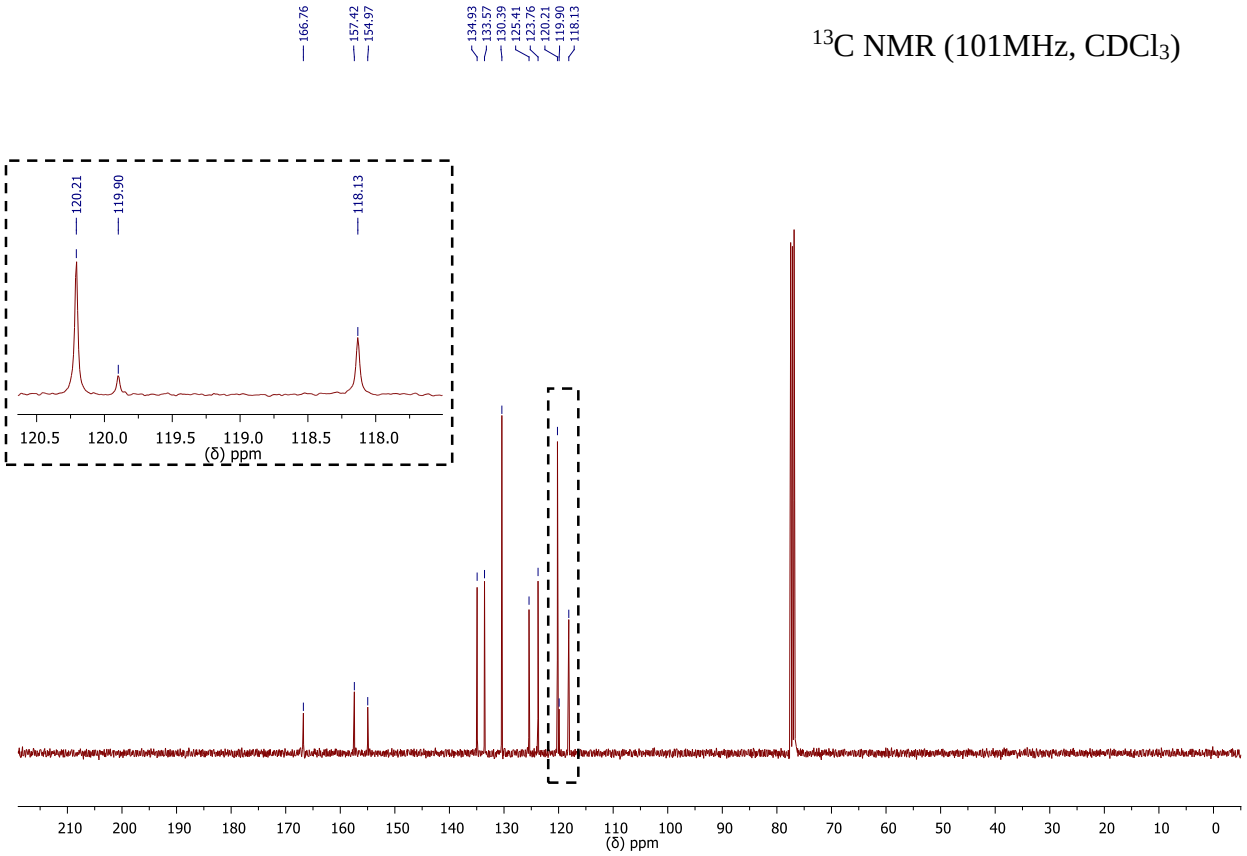
^{13}C NMR (101MHz, $CDCl_3$)

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

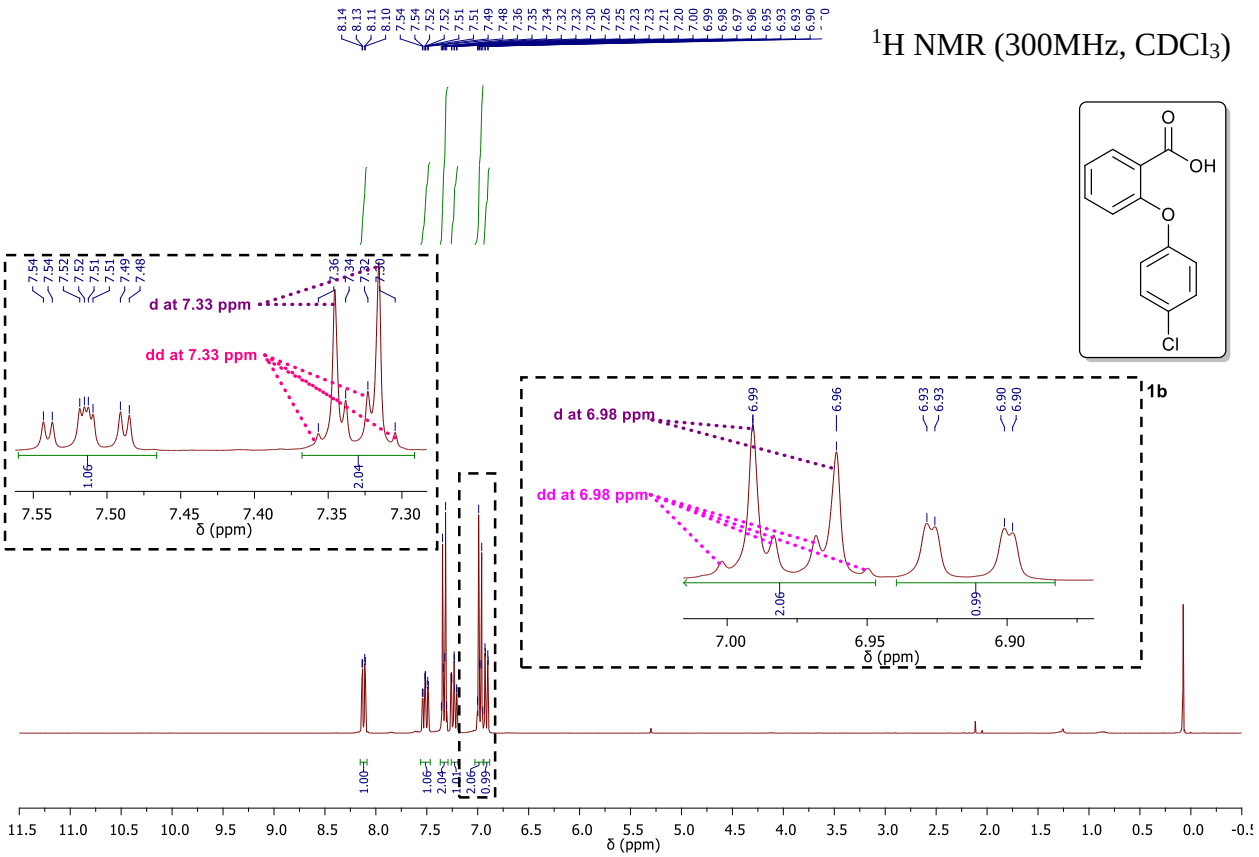


1a

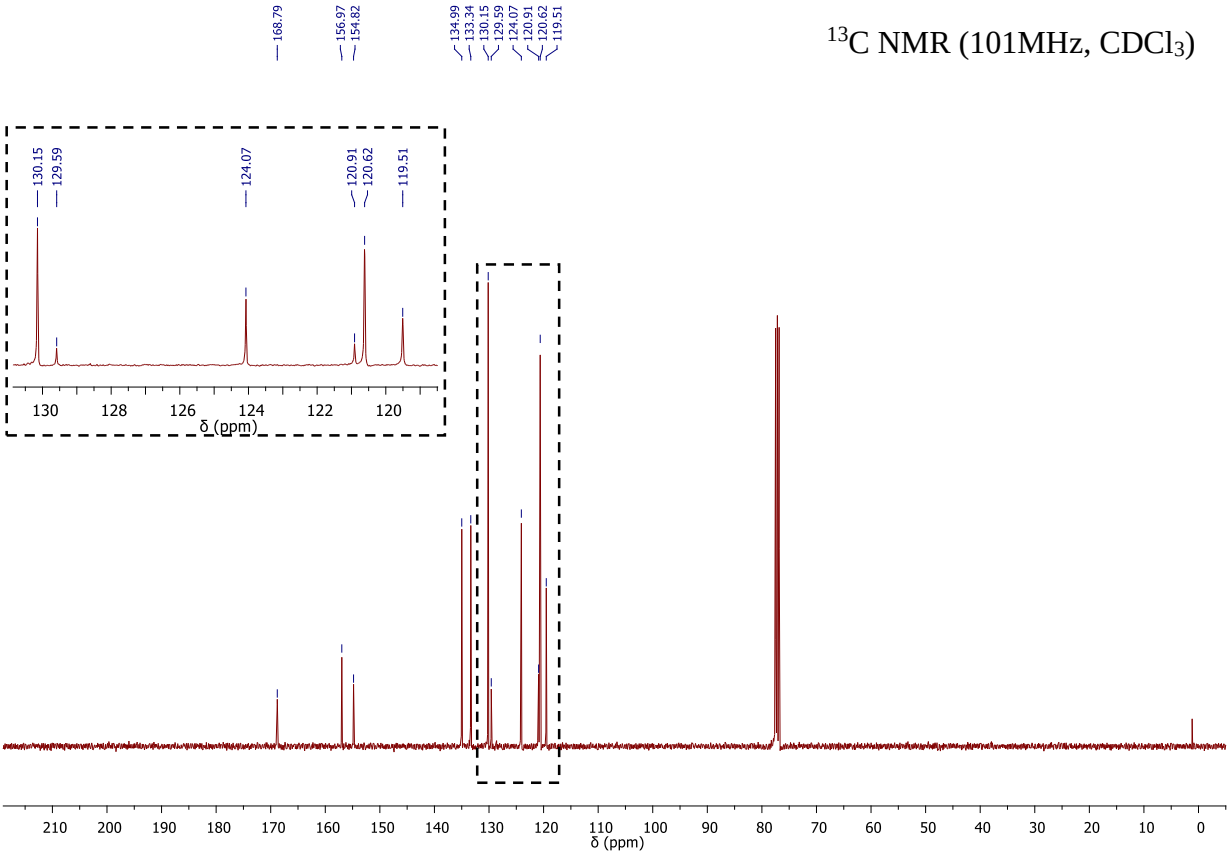
^{13}C NMR (101MHz, $CDCl_3$)



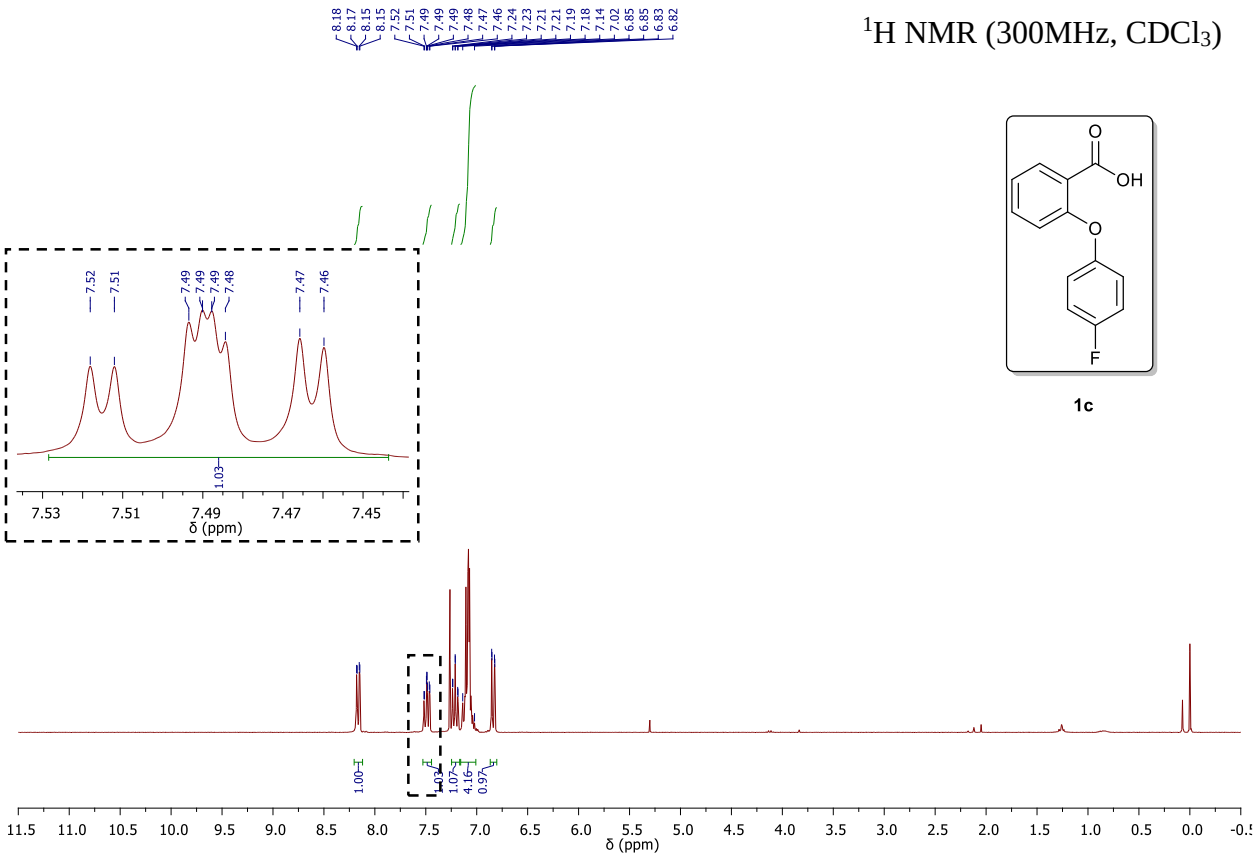
^{1}H NMR (300MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

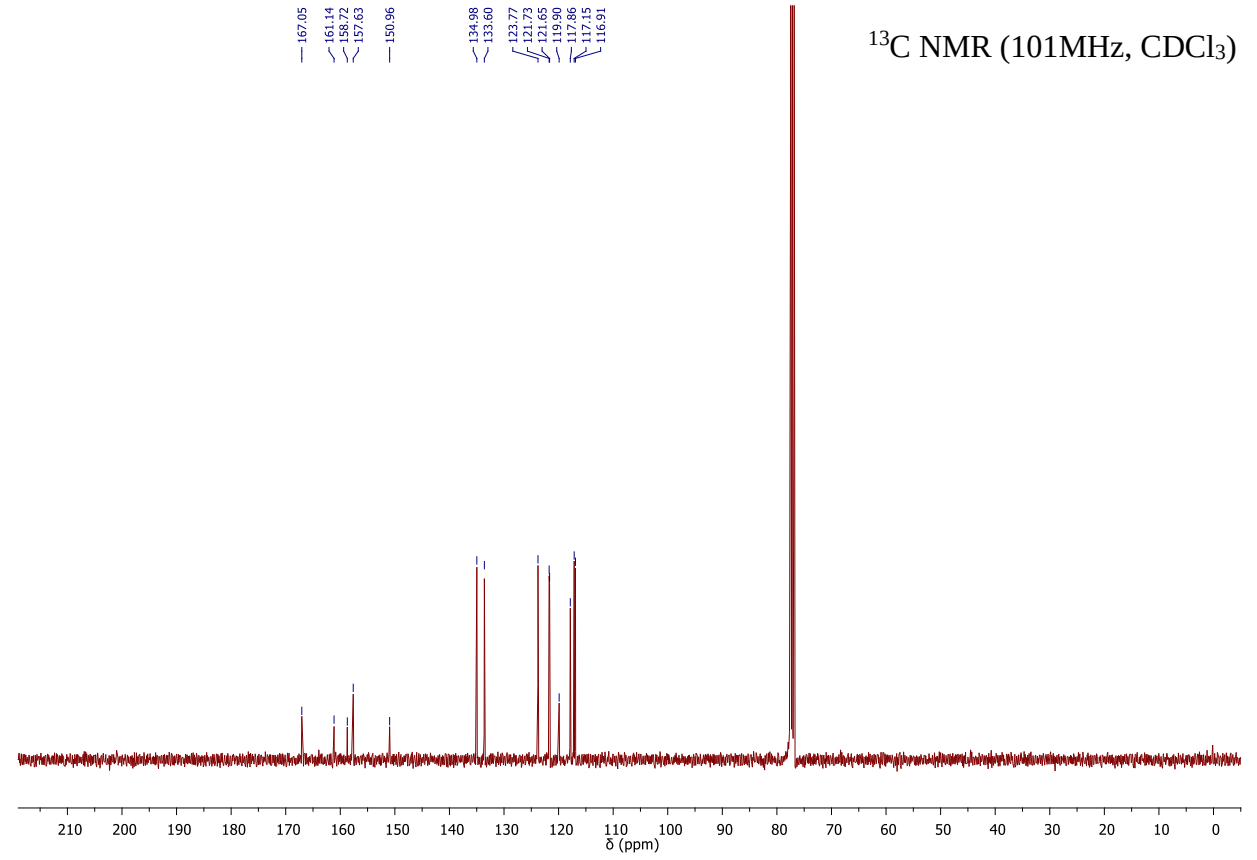


^{1}H NMR (300MHz, $CDCl_3$)

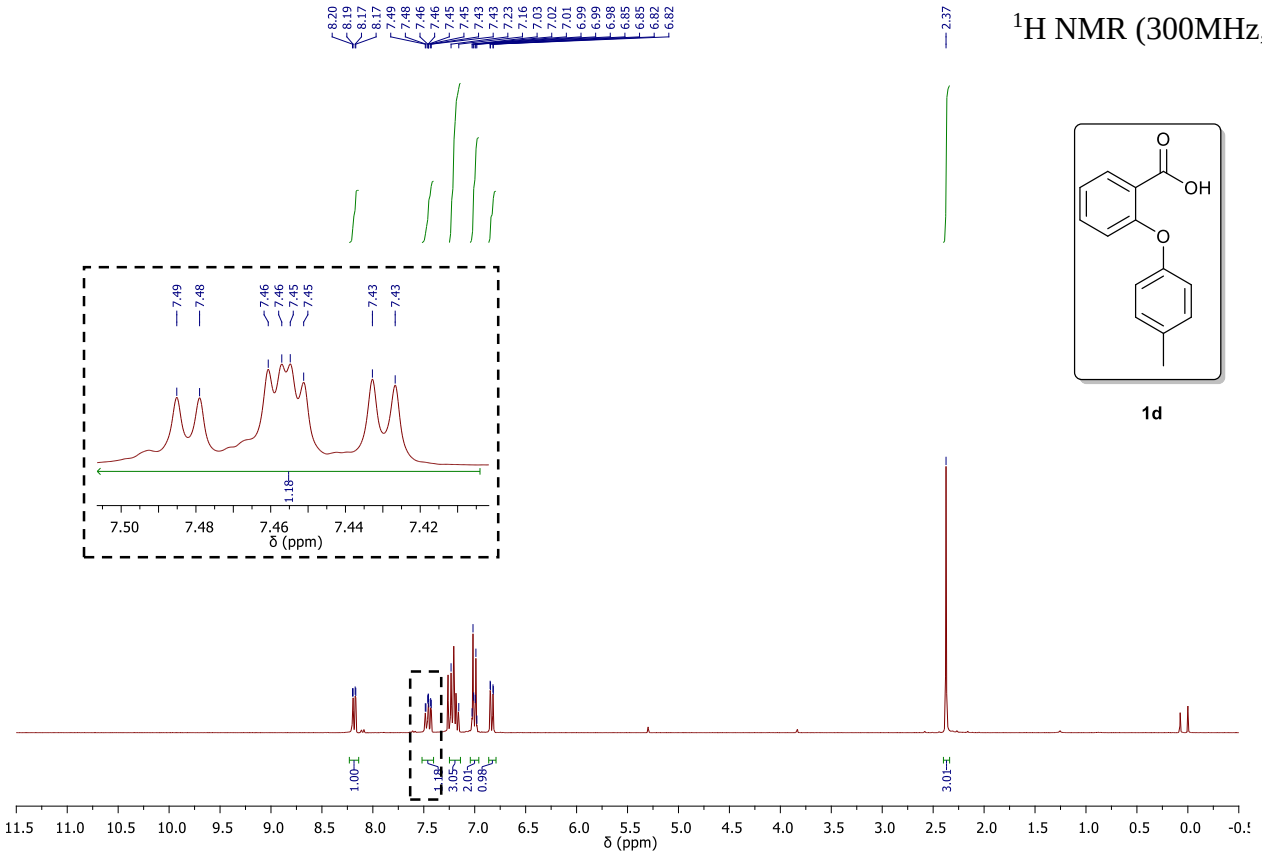


1c

^{13}C NMR (101MHz, $CDCl_3$)

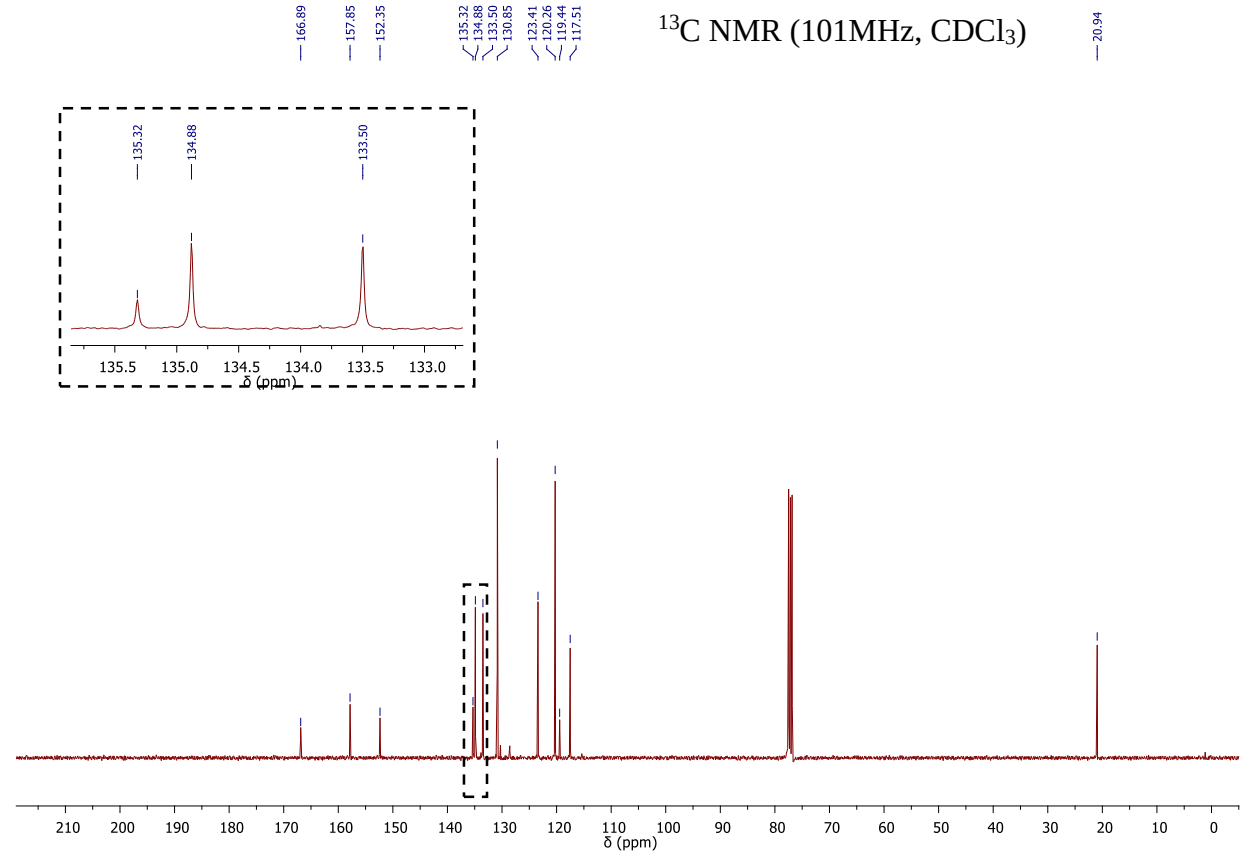


^{1}H NMR (300MHz, $CDCl_3$)

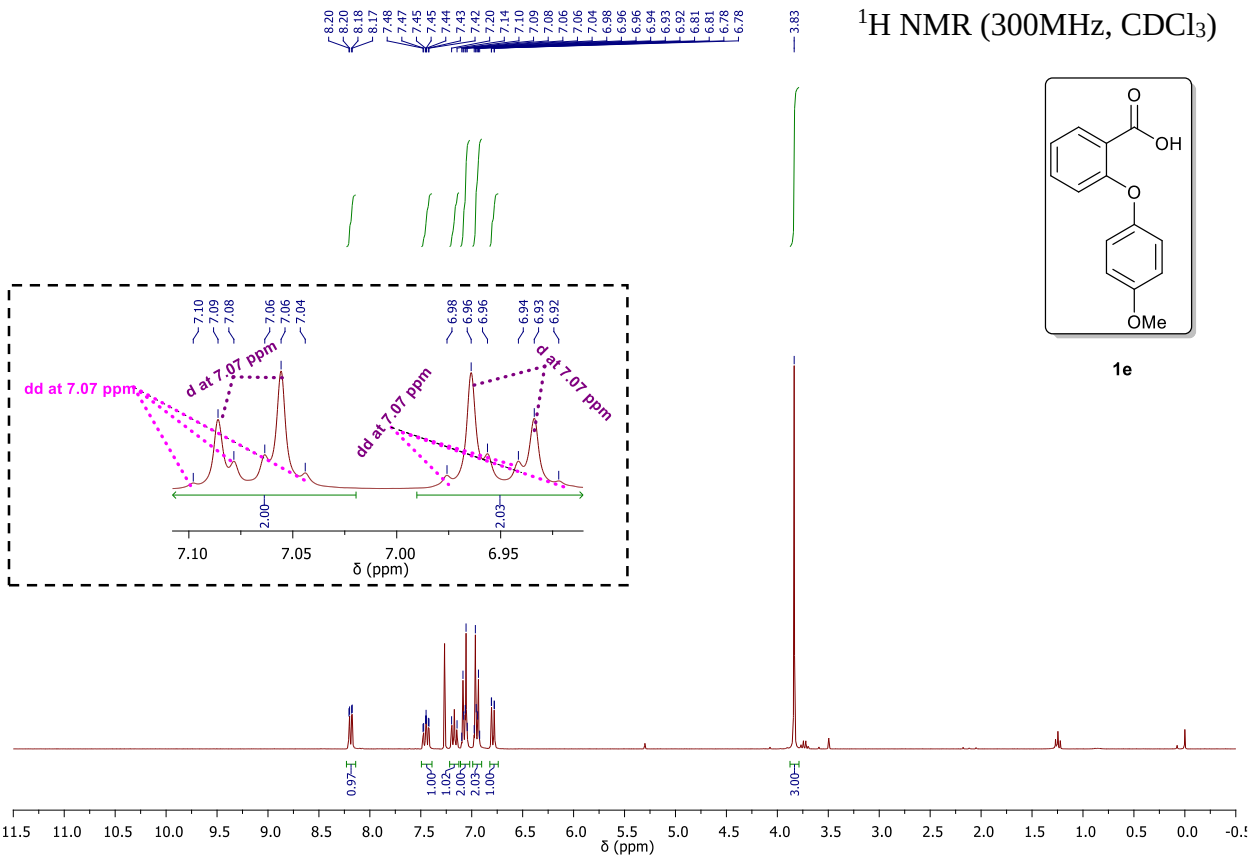


1d

^{13}C NMR (101MHz, $CDCl_3$)

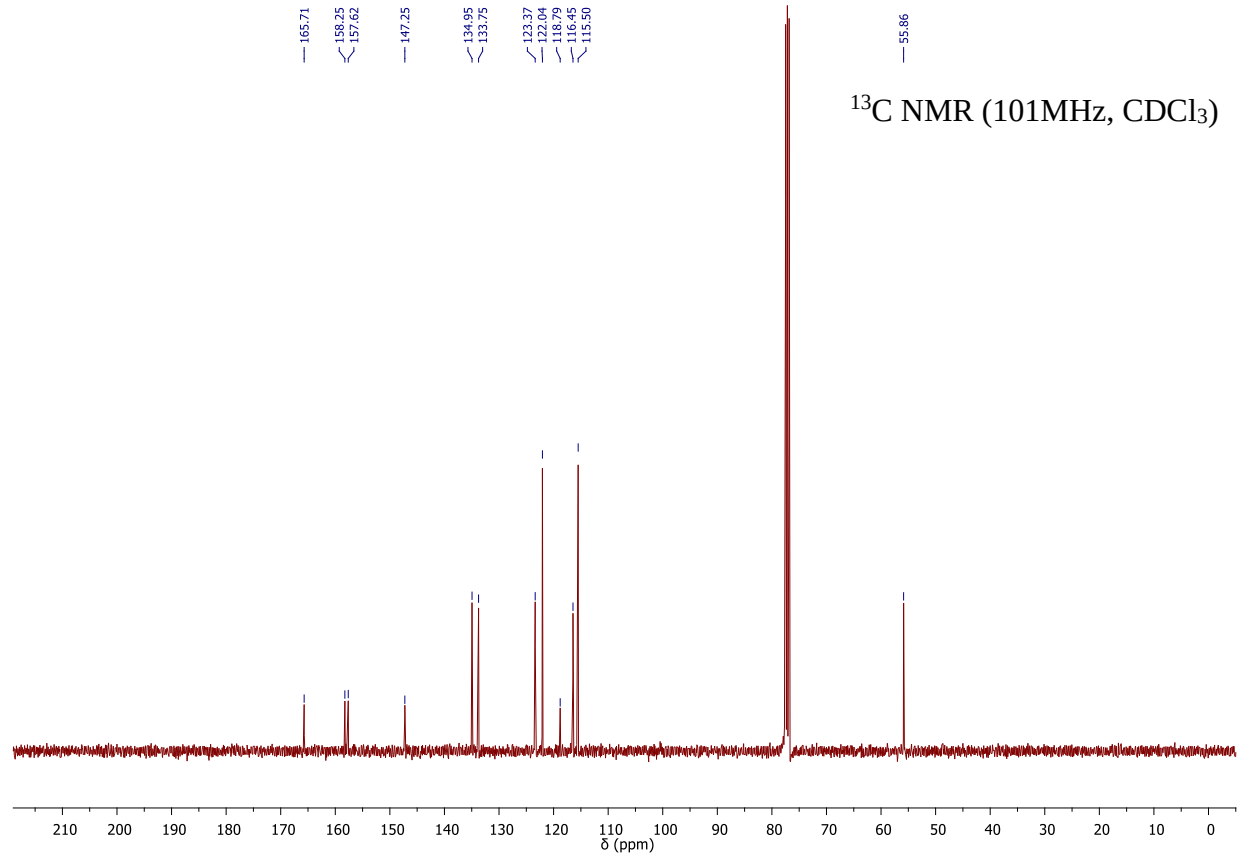


^{1}H NMR (300MHz, $CDCl_3$)

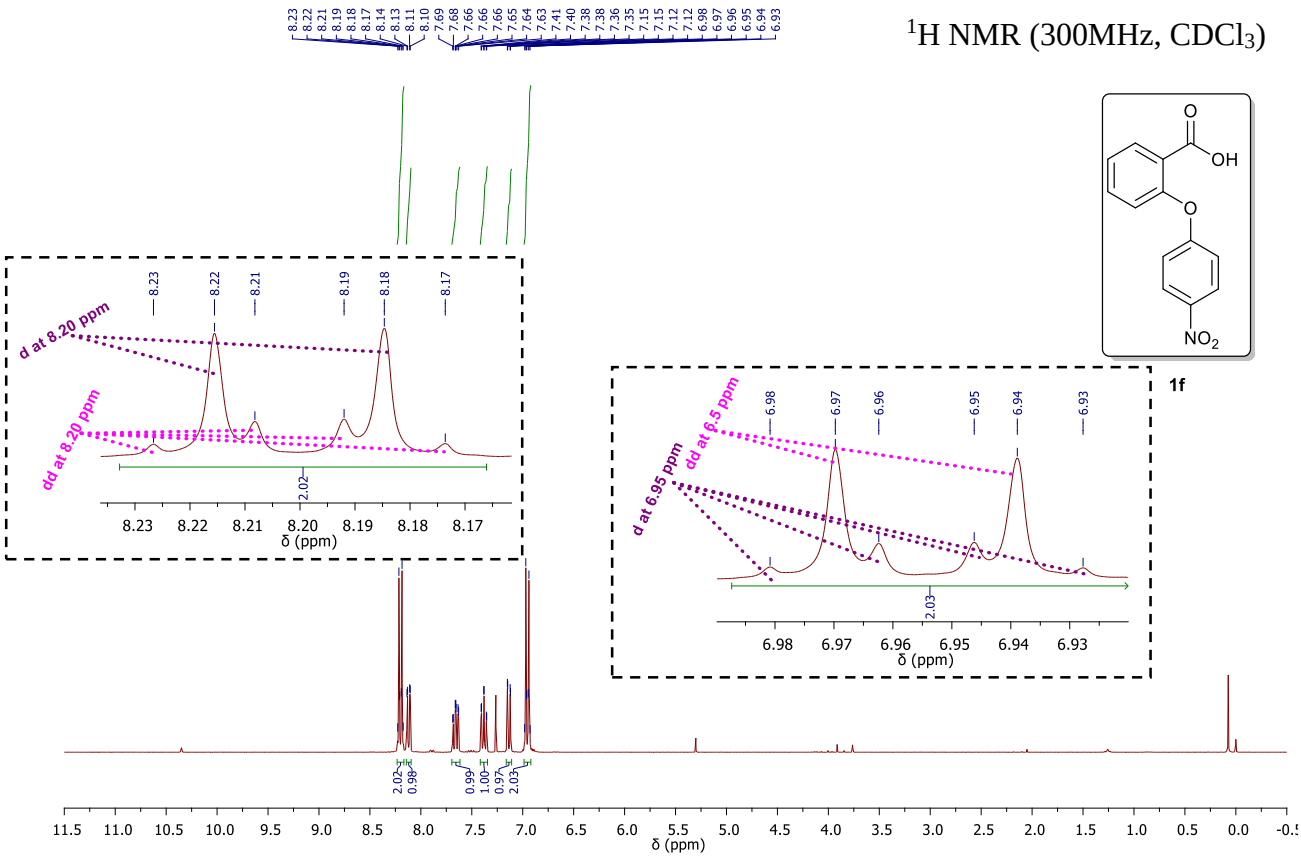


1e

^{13}C NMR (101MHz, $CDCl_3$)

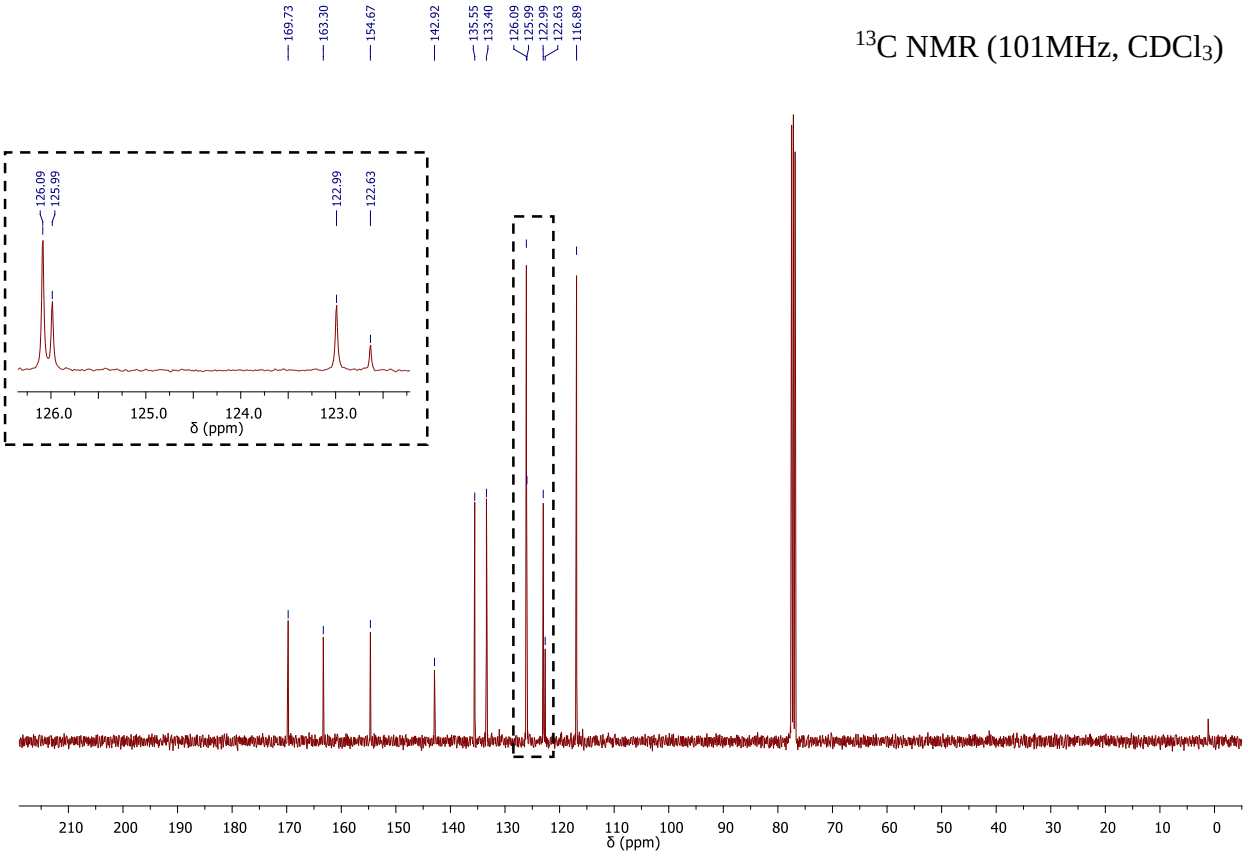


^{1}H NMR (300MHz, $CDCl_3$)

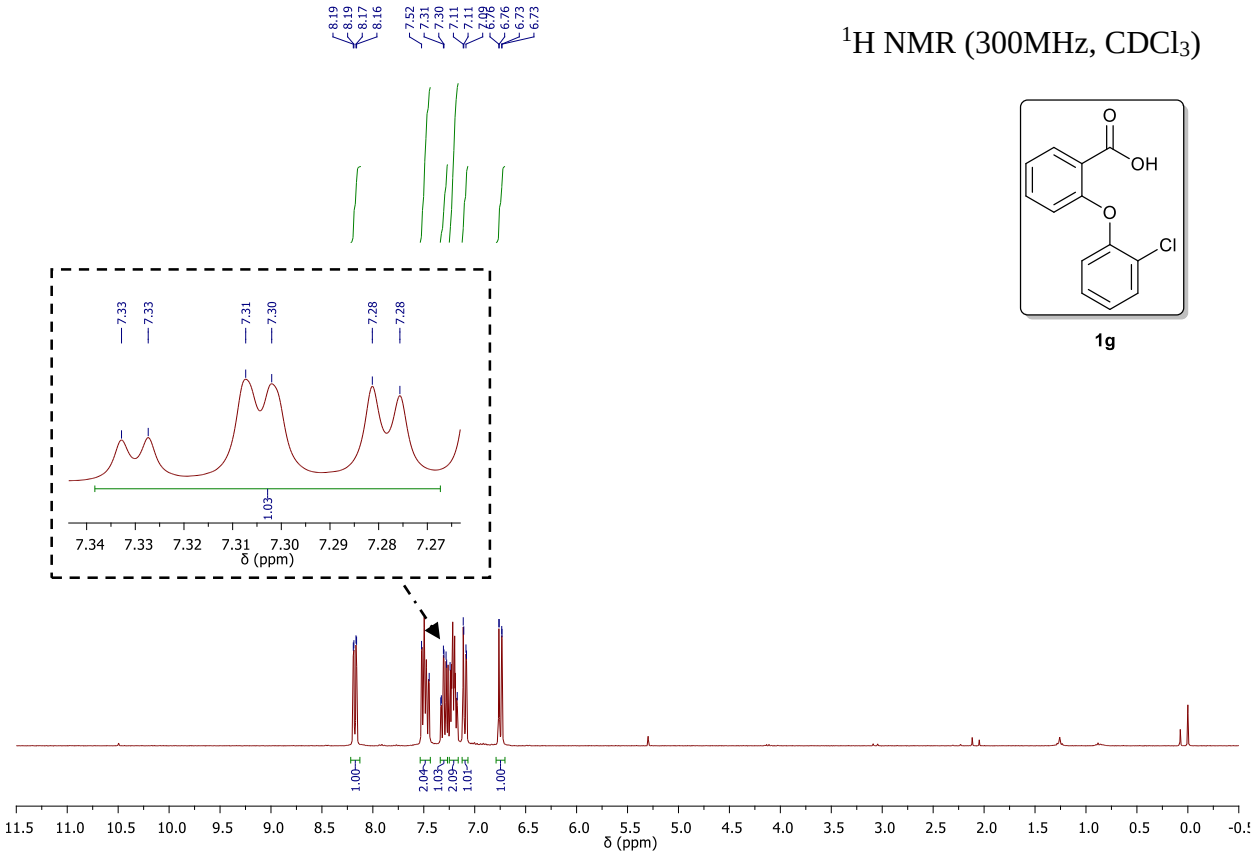


1f

^{13}C NMR (101MHz, $CDCl_3$)

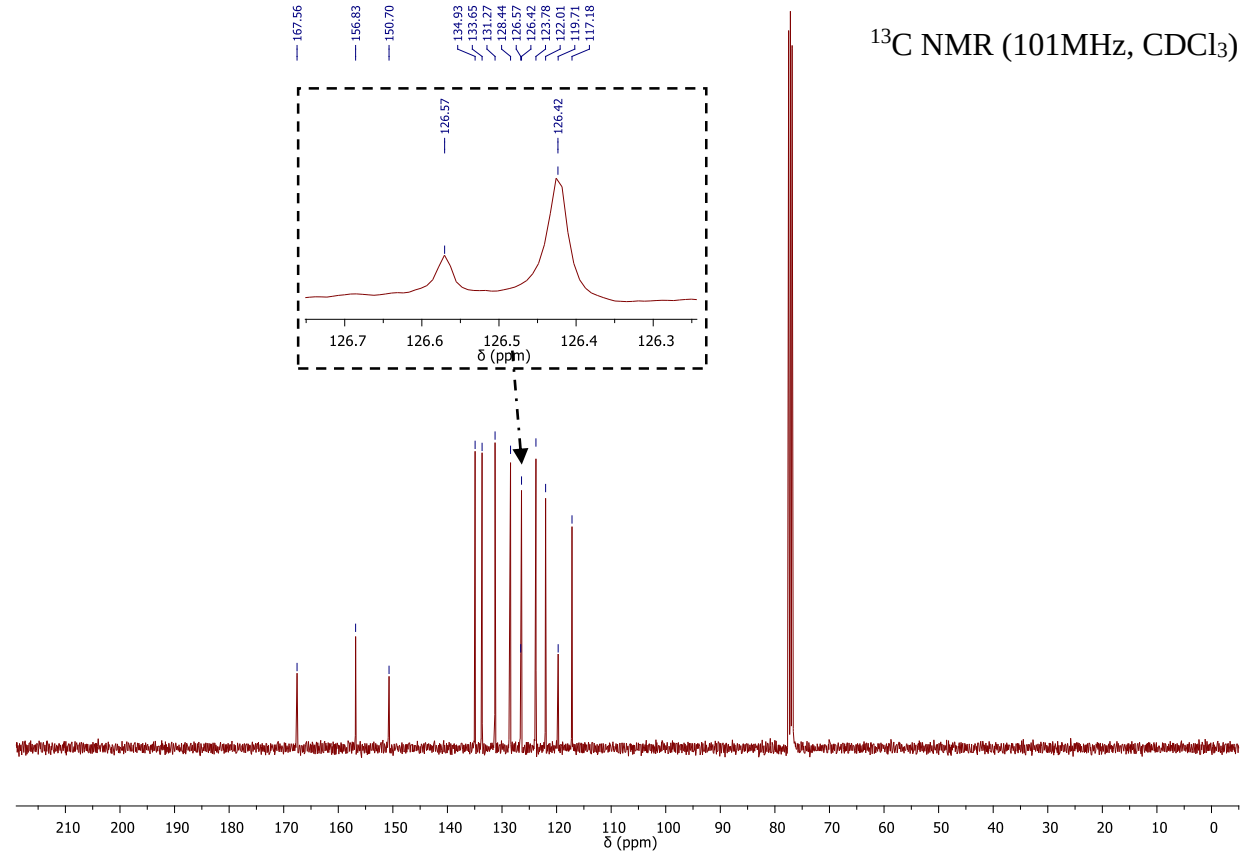


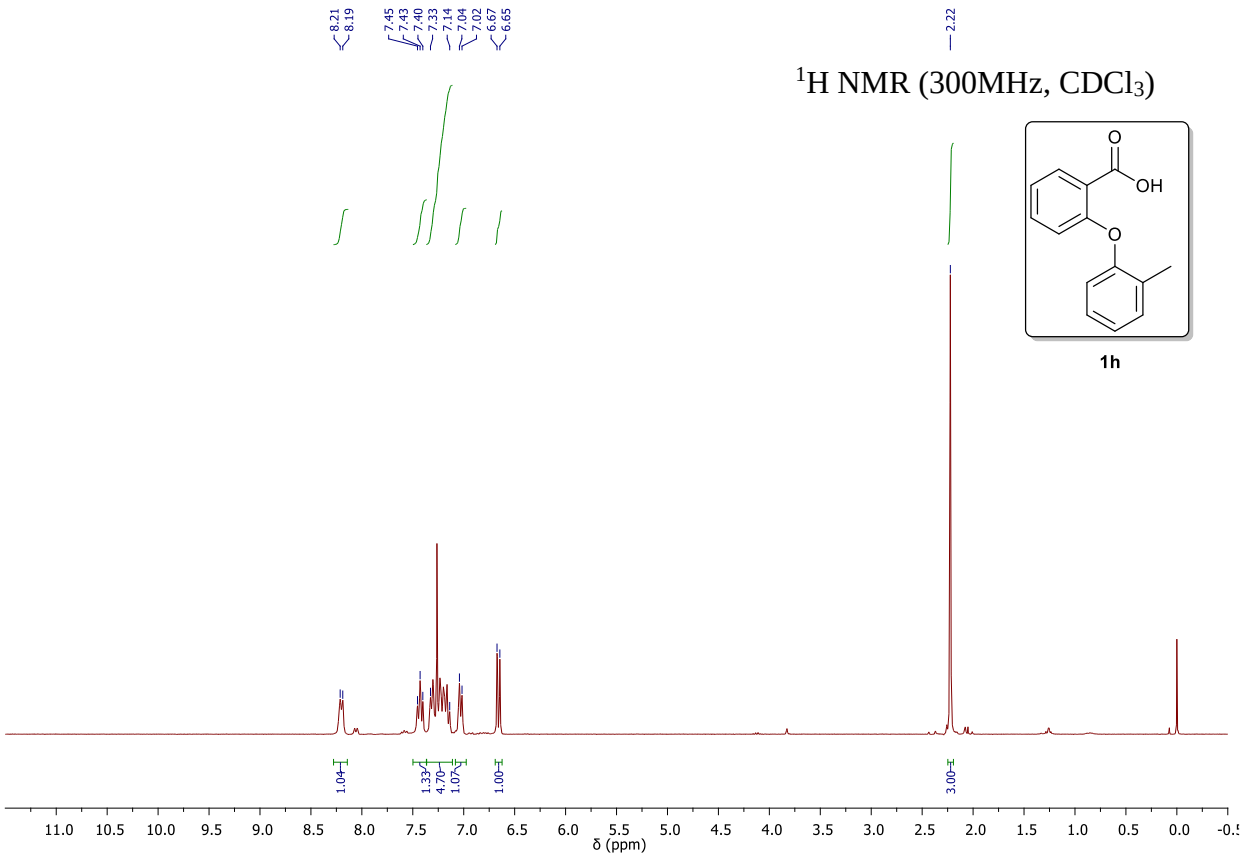
^{1}H NMR (300MHz, $CDCl_3$)



1g

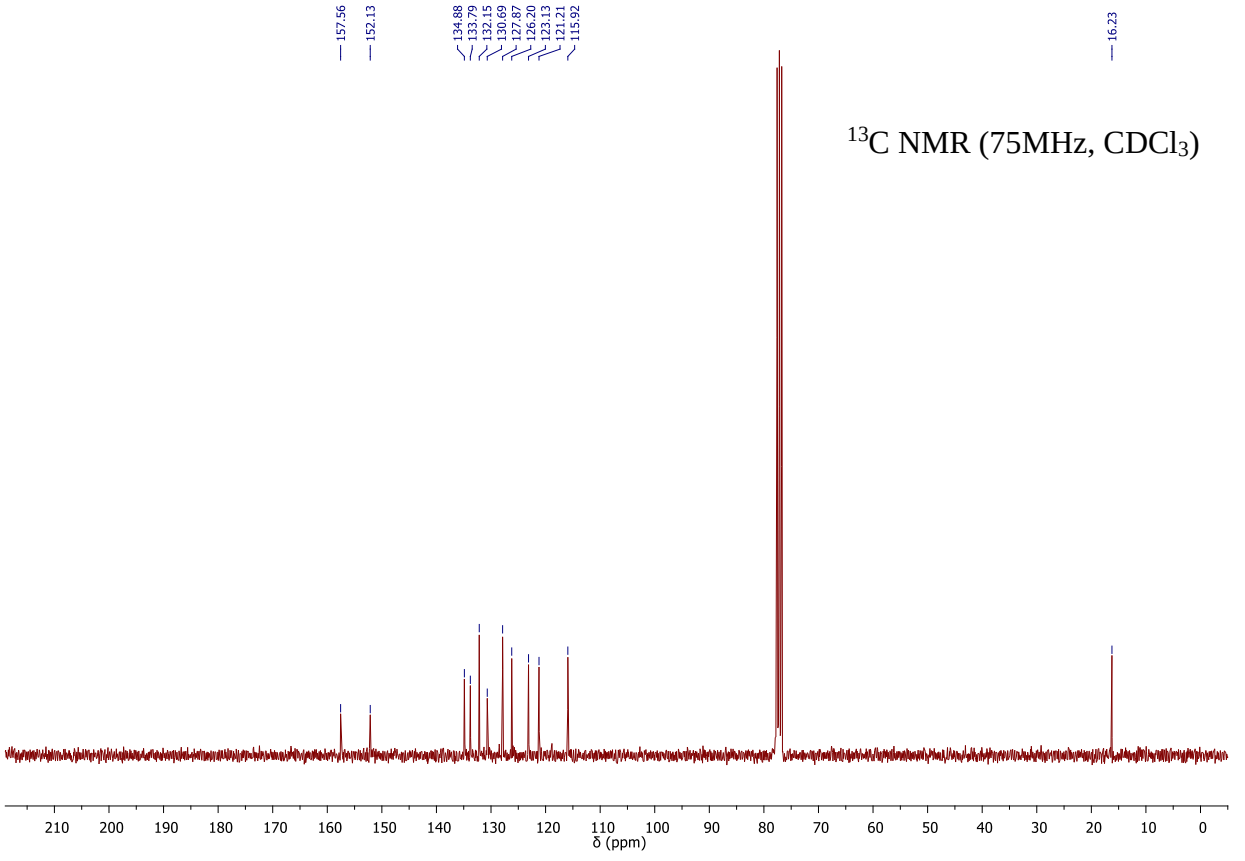
^{13}C NMR (101MHz, $CDCl_3$)





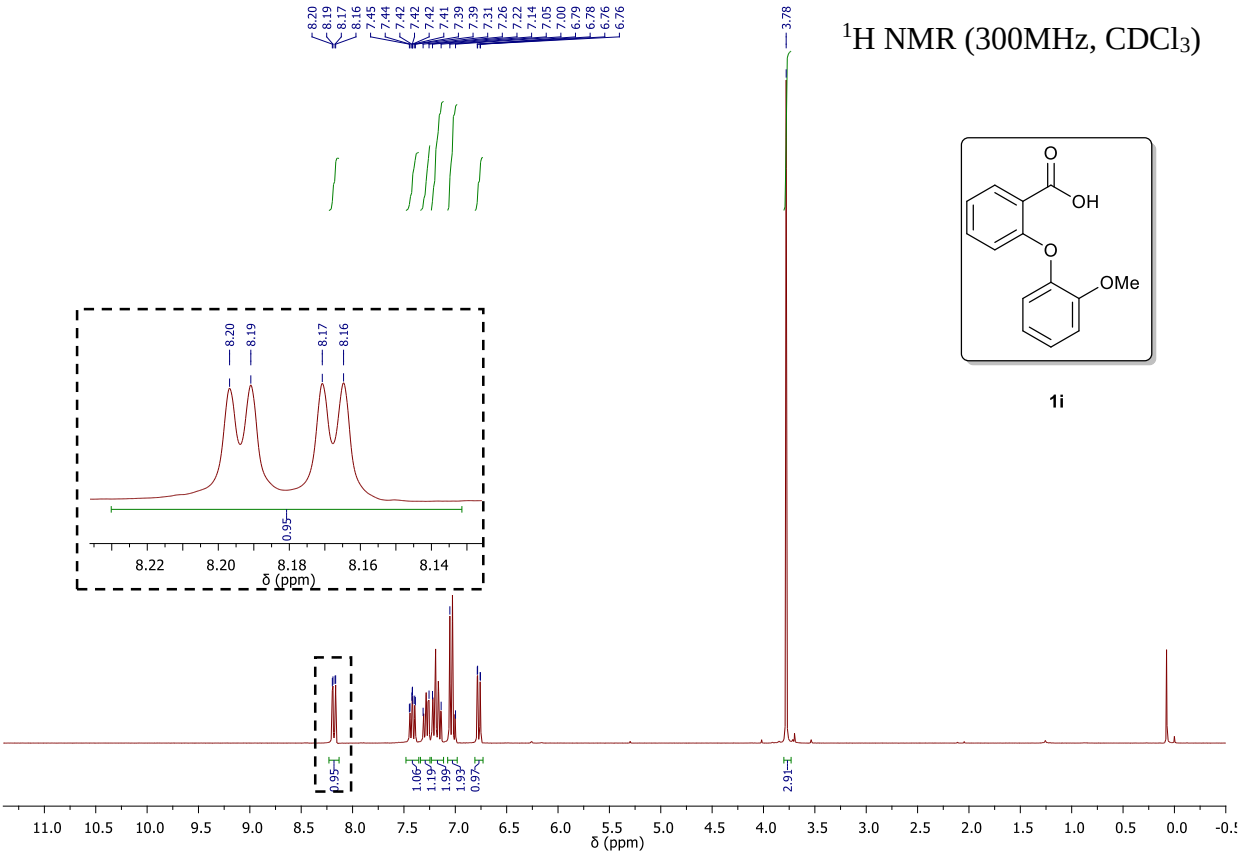
^{1}H NMR (300MHz, $CDCl_3$)

1h

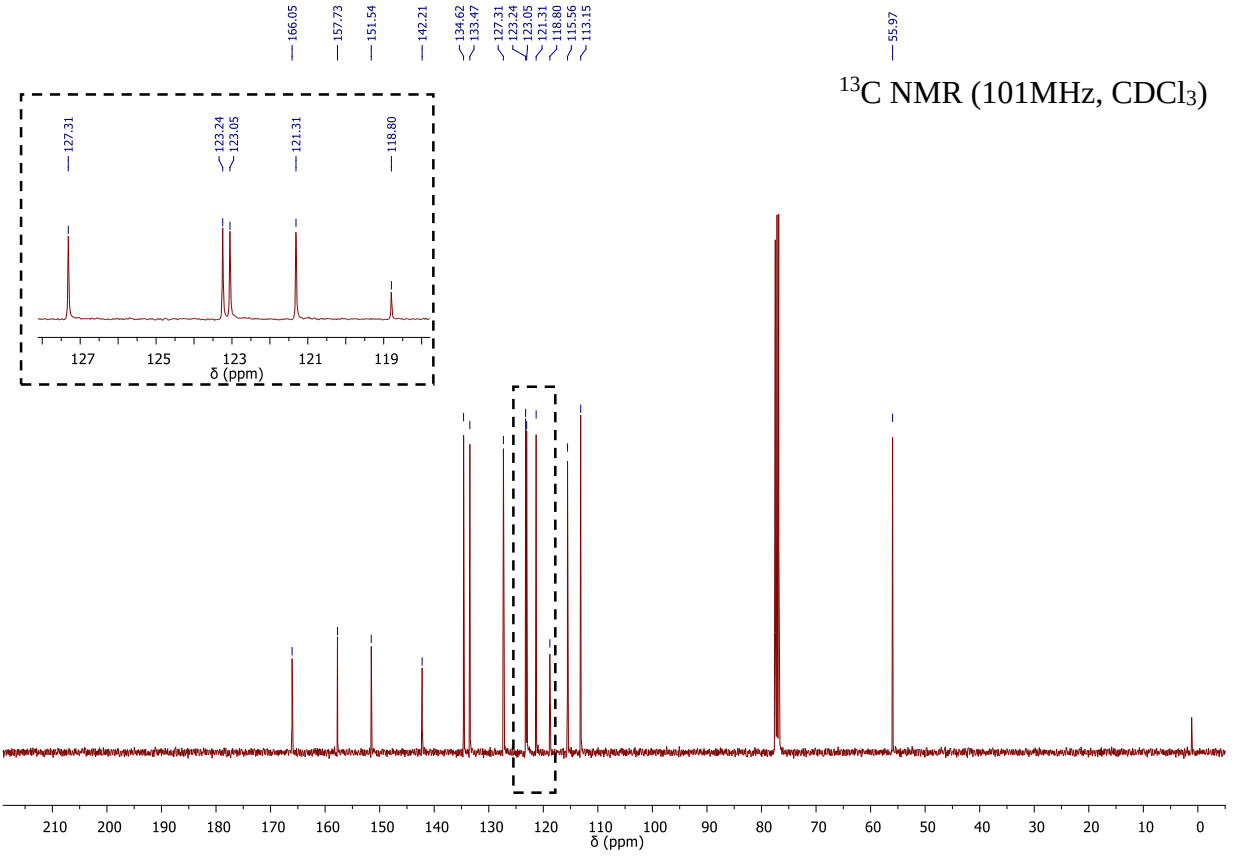


^{13}C NMR (75MHz, $CDCl_3$)

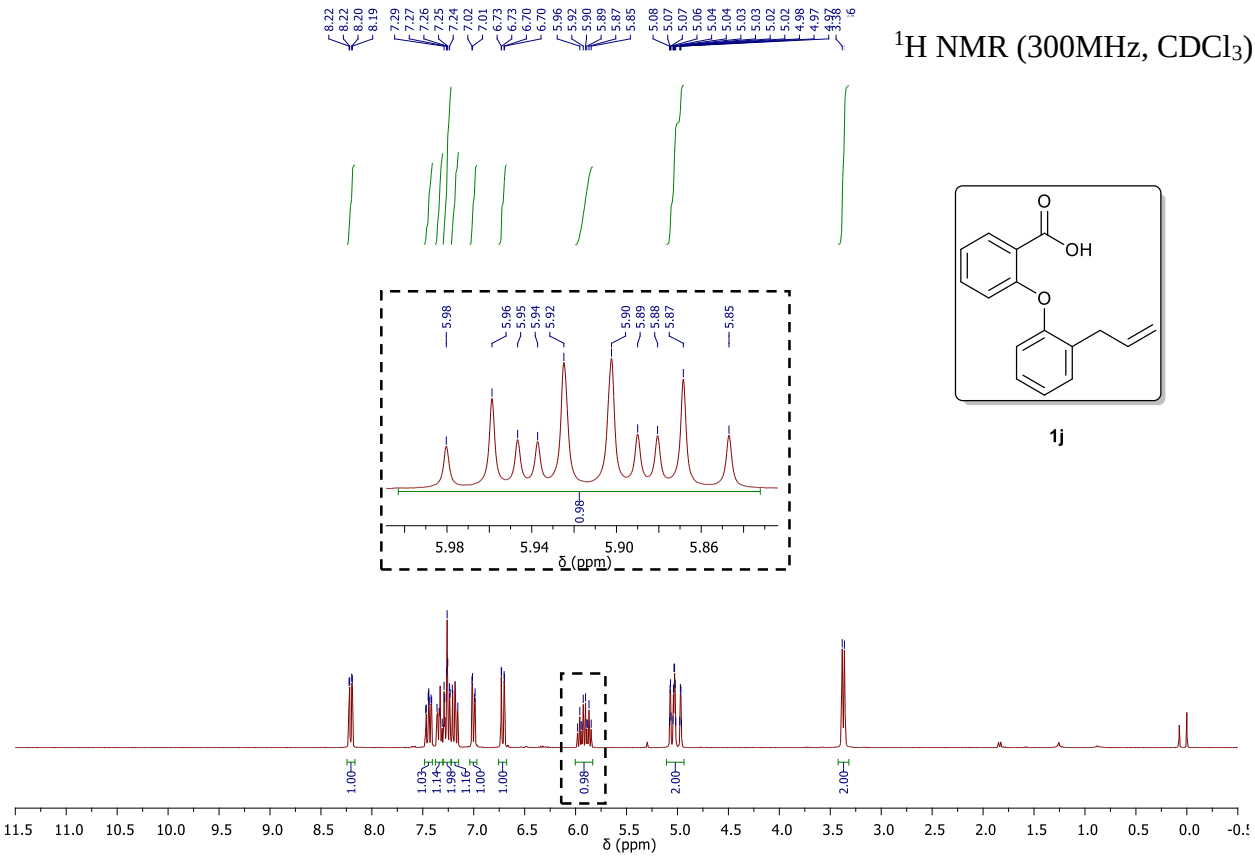
^{1}H NMR (300MHz, $CDCl_3$)



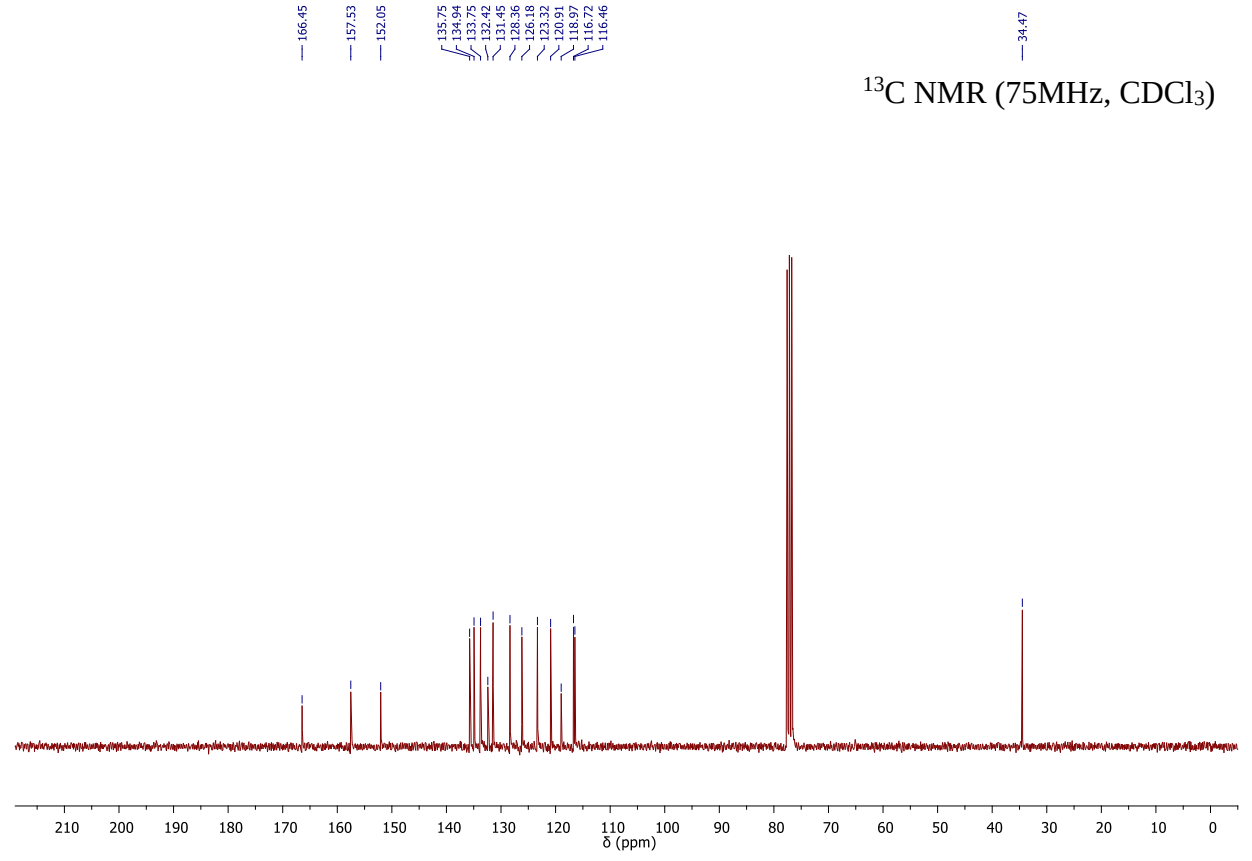
^{13}C NMR (101MHz, $CDCl_3$)



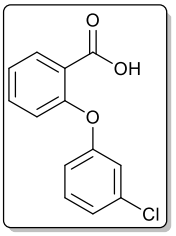
^{1}H NMR (300MHz, $CDCl_3$)



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

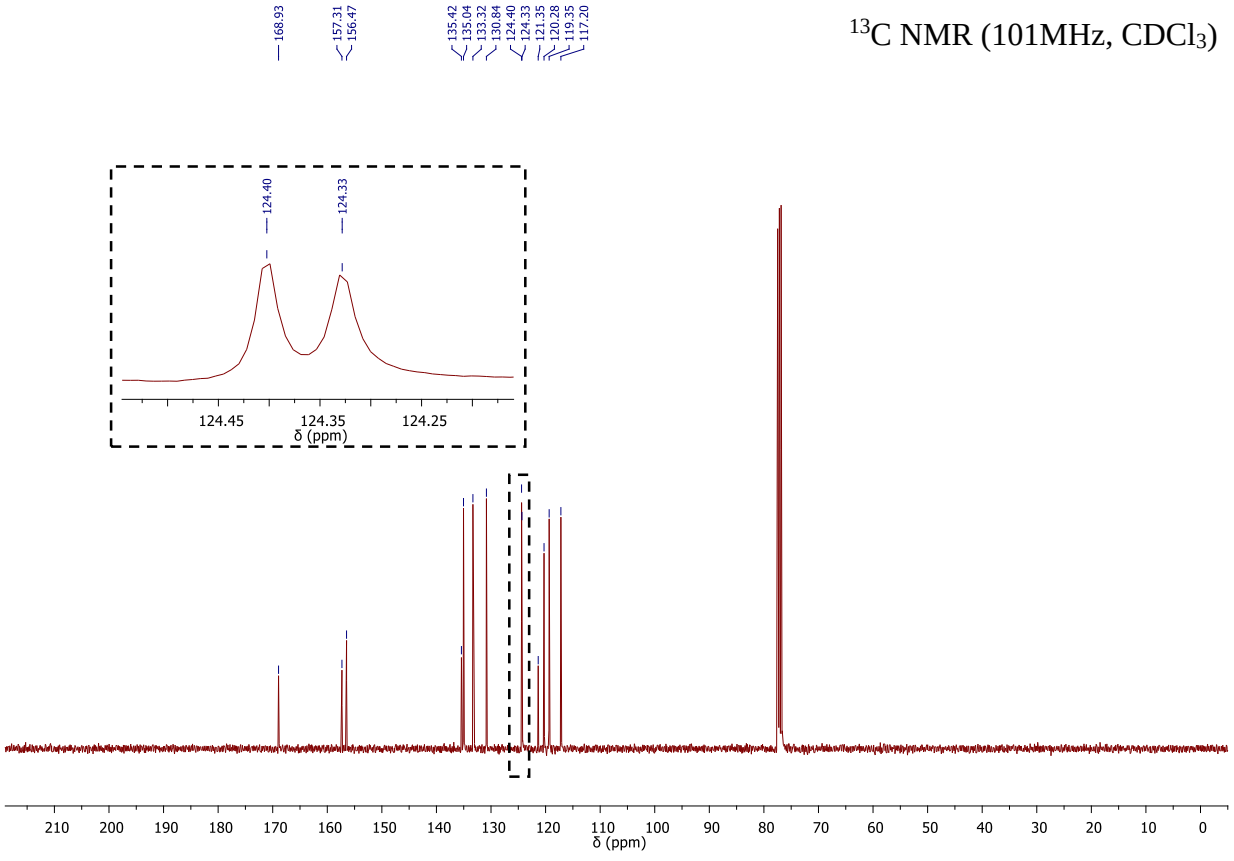


^{1}H NMR (400MHz, $CDCl_3$)

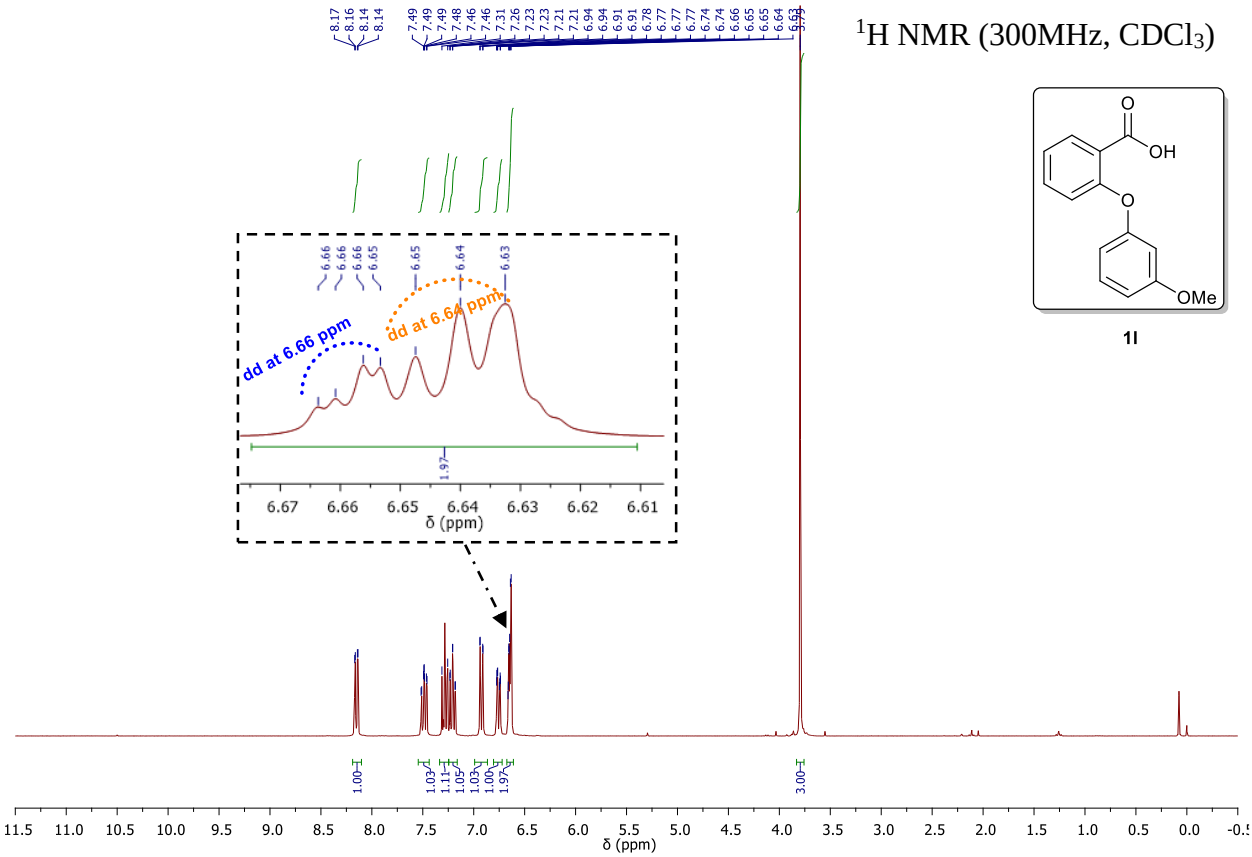


1k

^{13}C NMR (101MHz, $CDCl_3$)

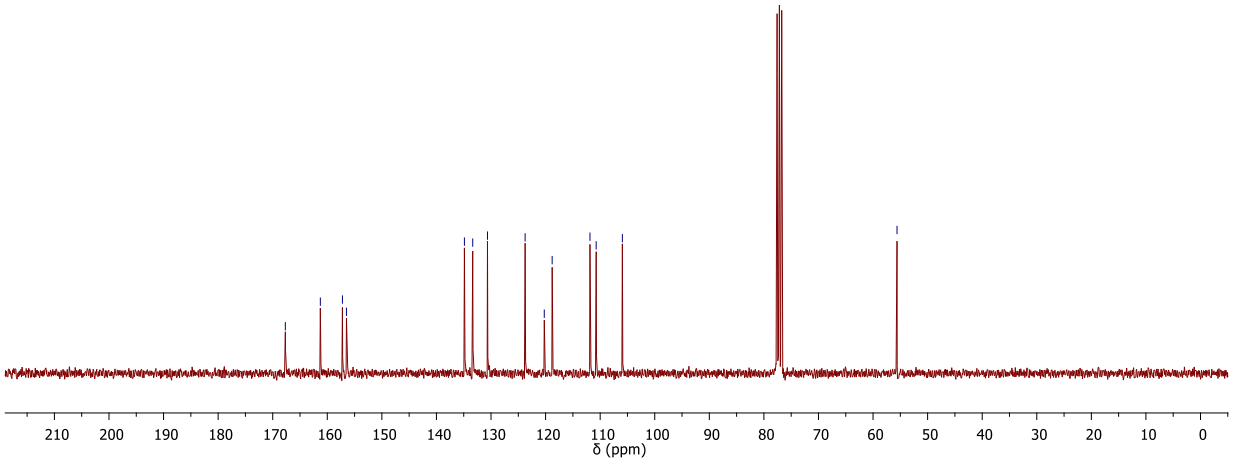


^{1}H NMR (300MHz, $CDCl_3$)

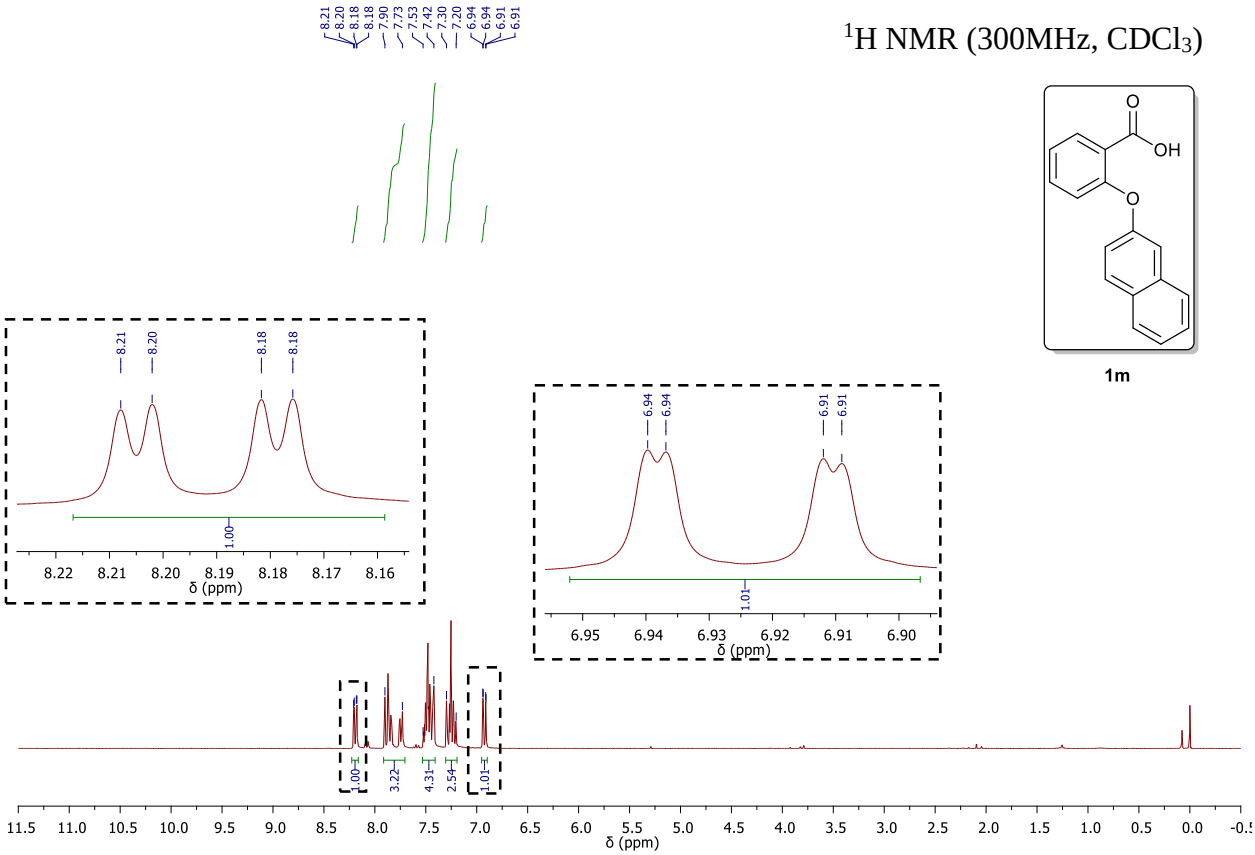


1l

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

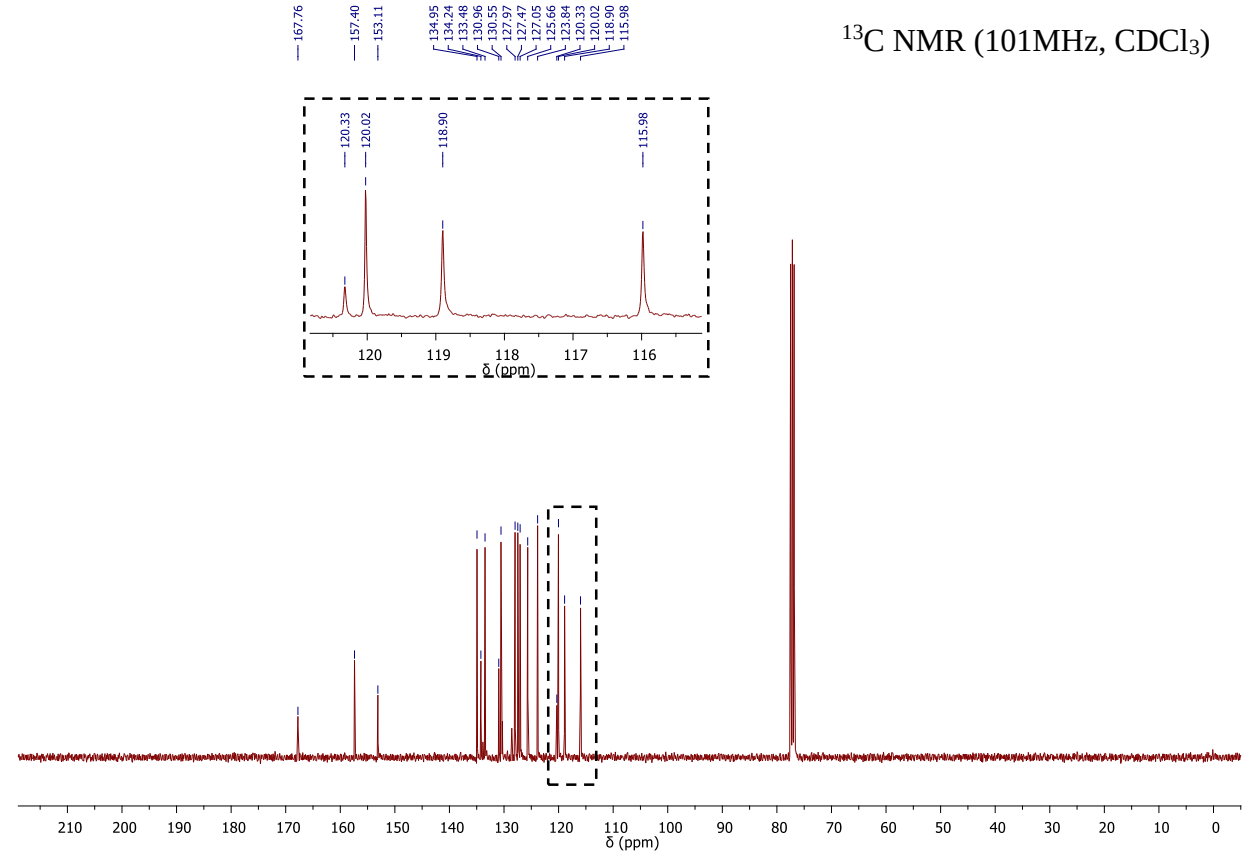


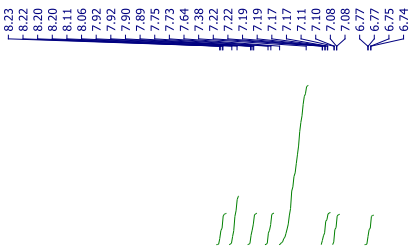
^{1}H NMR (300MHz, $CDCl_3$)



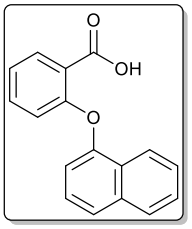
1m

^{13}C NMR (101MHz, $CDCl_3$)

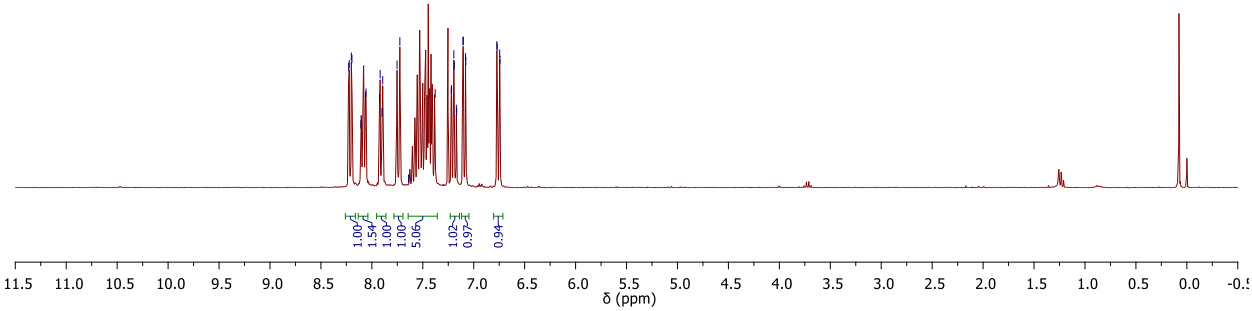


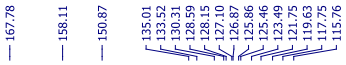


^{1}H NMR (300MHz, $CDCl_3$)

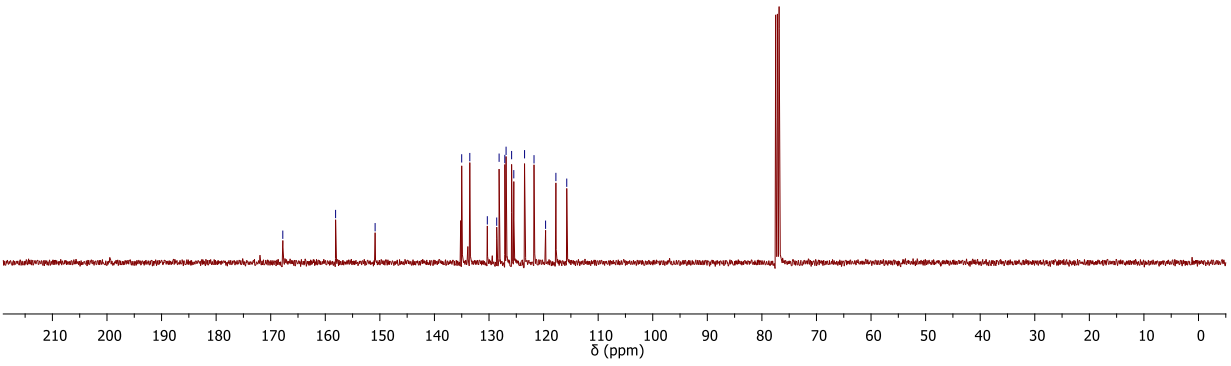


1n

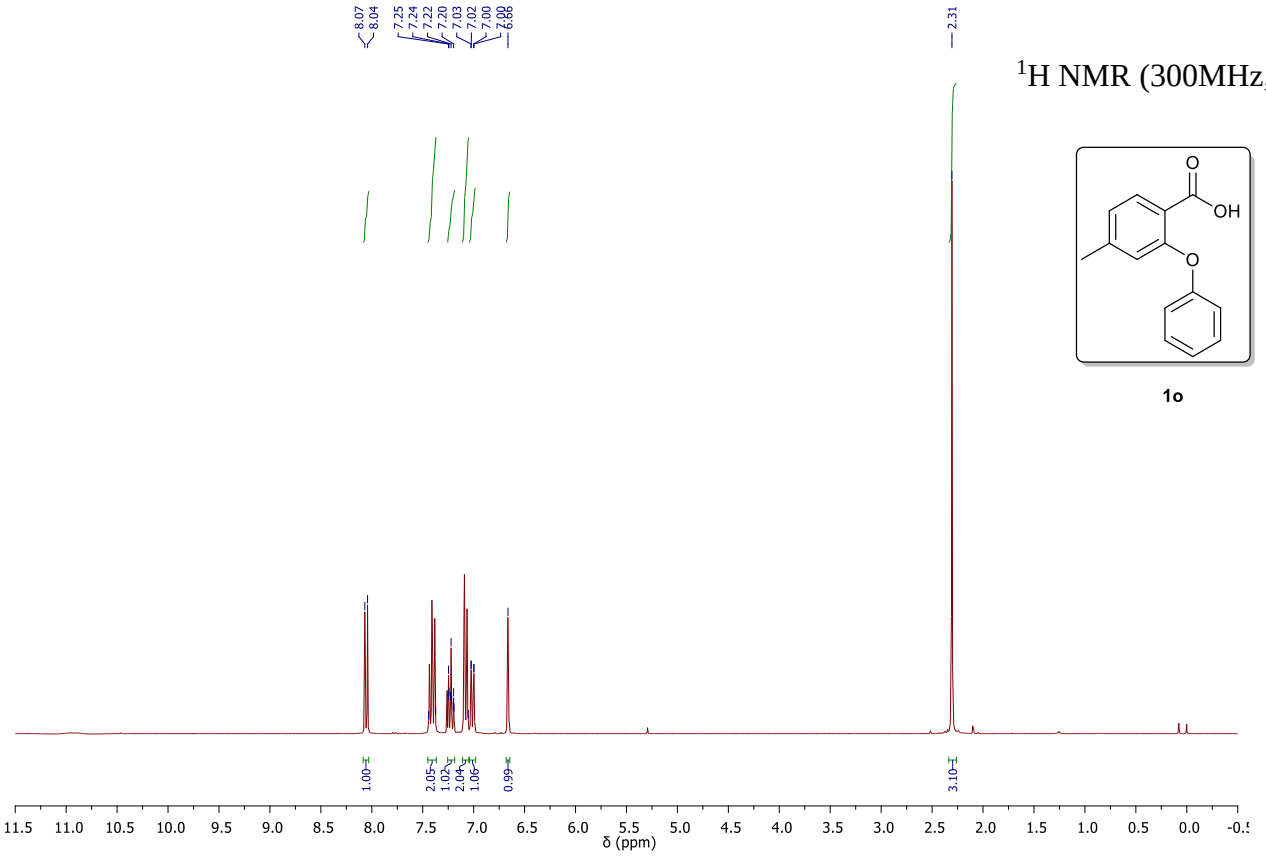




^{13}C NMR (101MHz, $CDCl_3$)

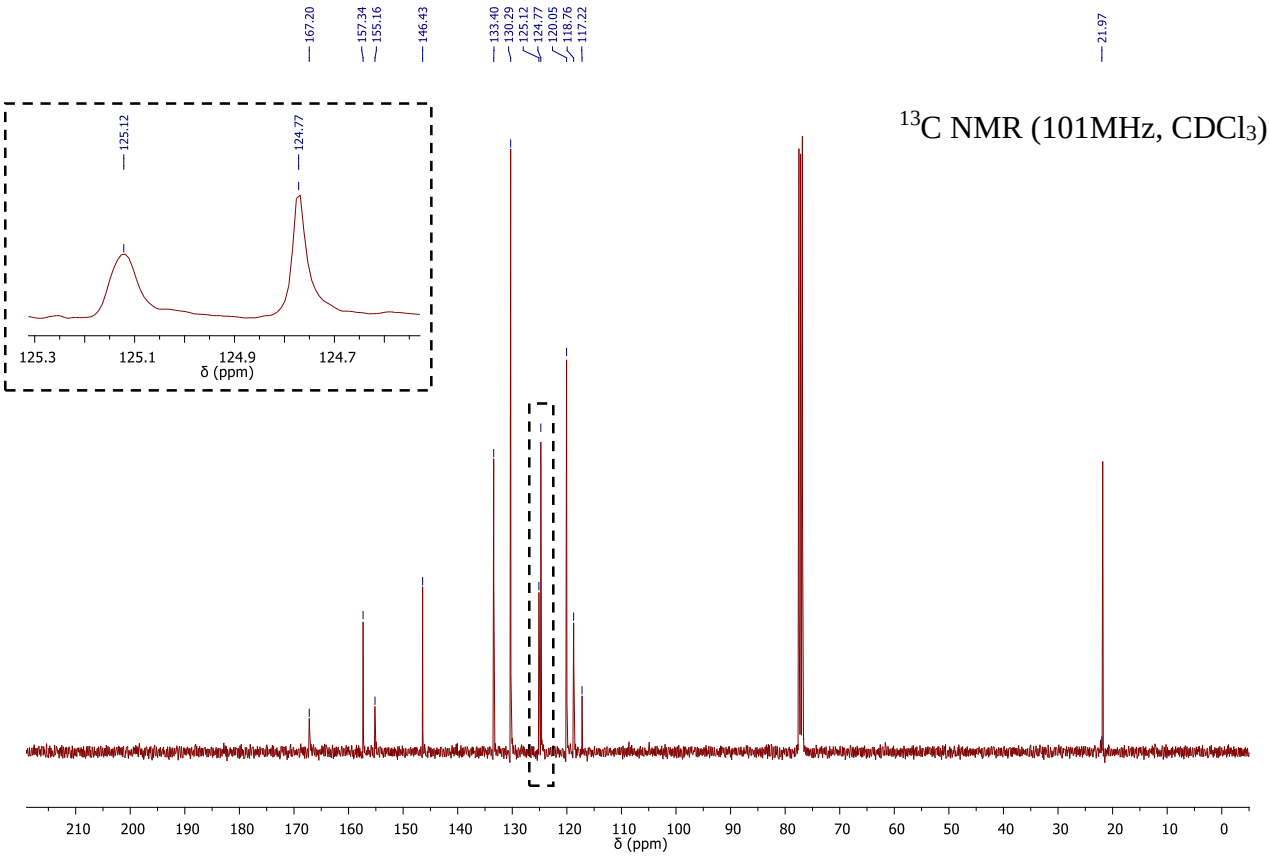


^{1}H NMR (300MHz, $CDCl_3$)

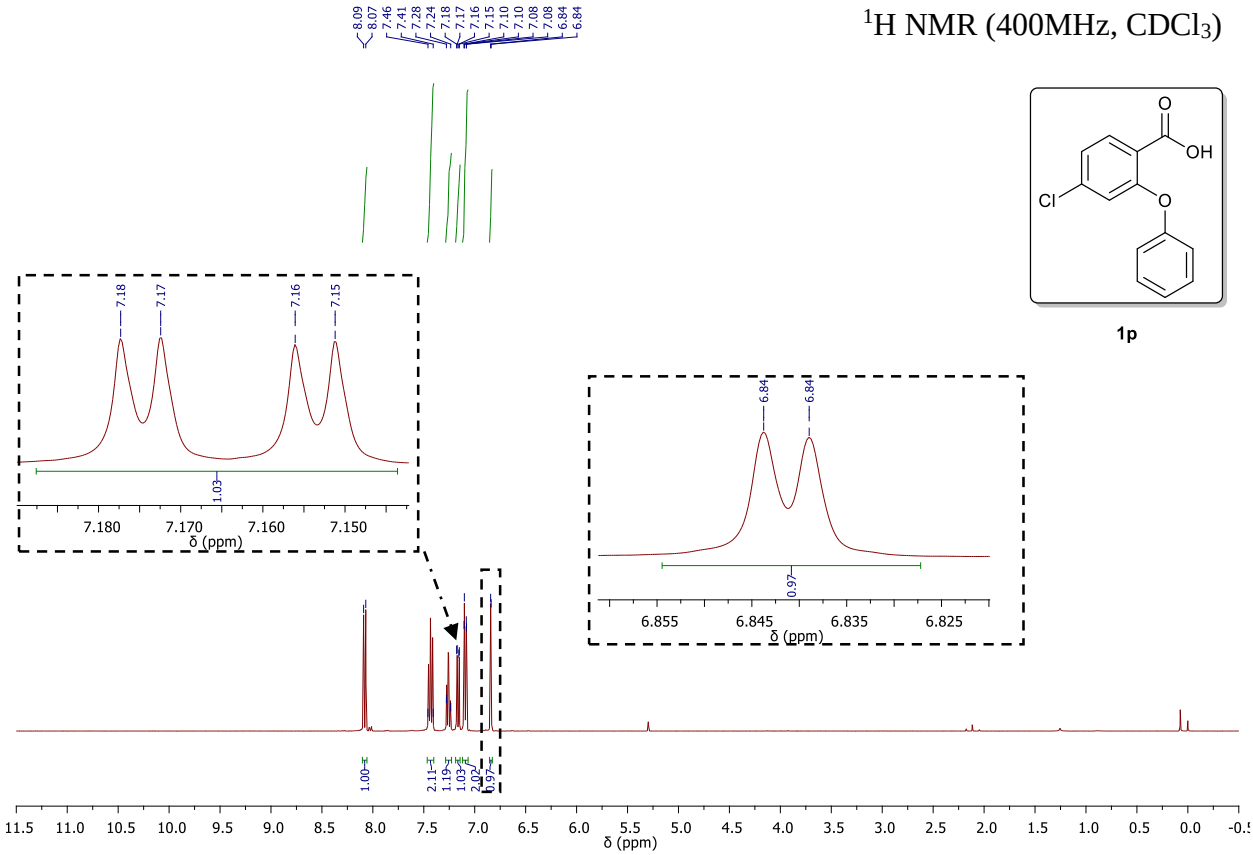


1o

^{13}C NMR (101MHz, $CDCl_3$)

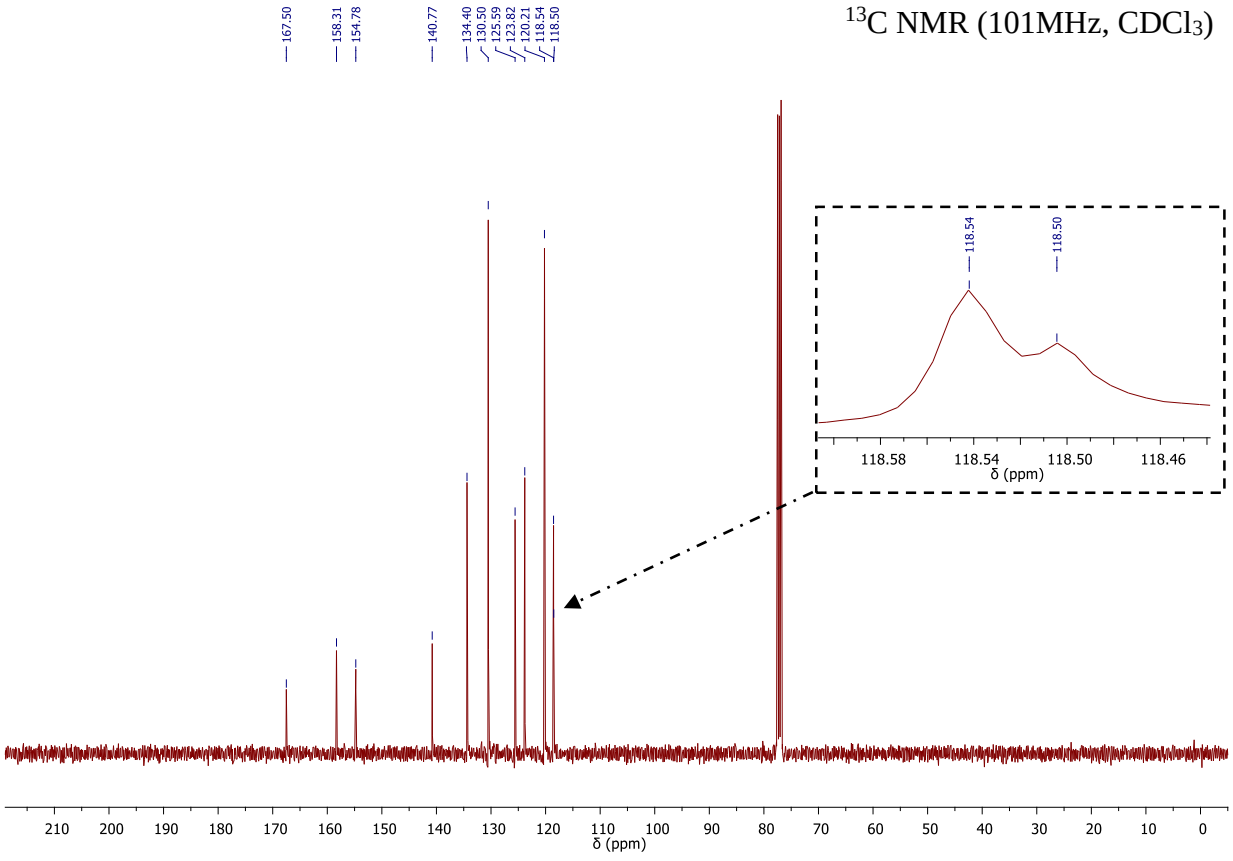


^{1}H NMR (400MHz, $CDCl_3$)

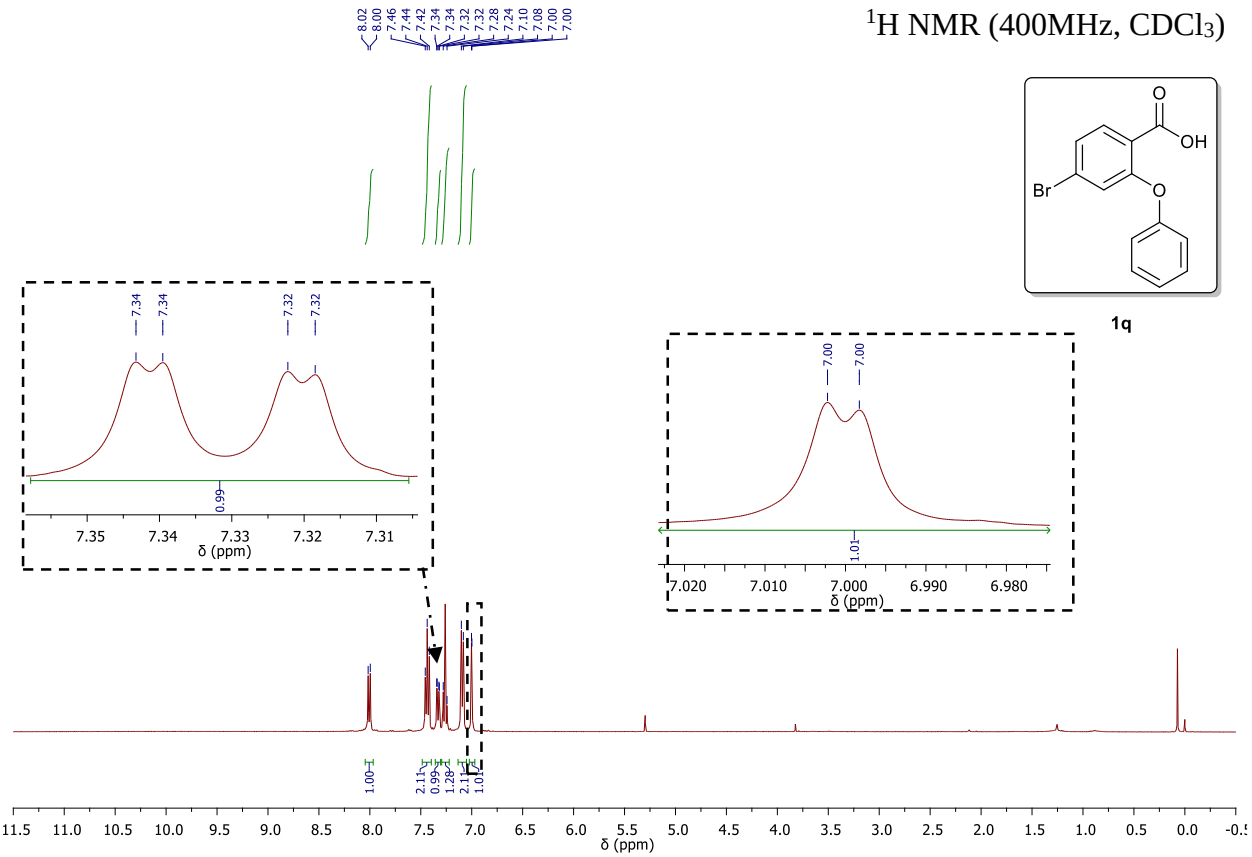


1p

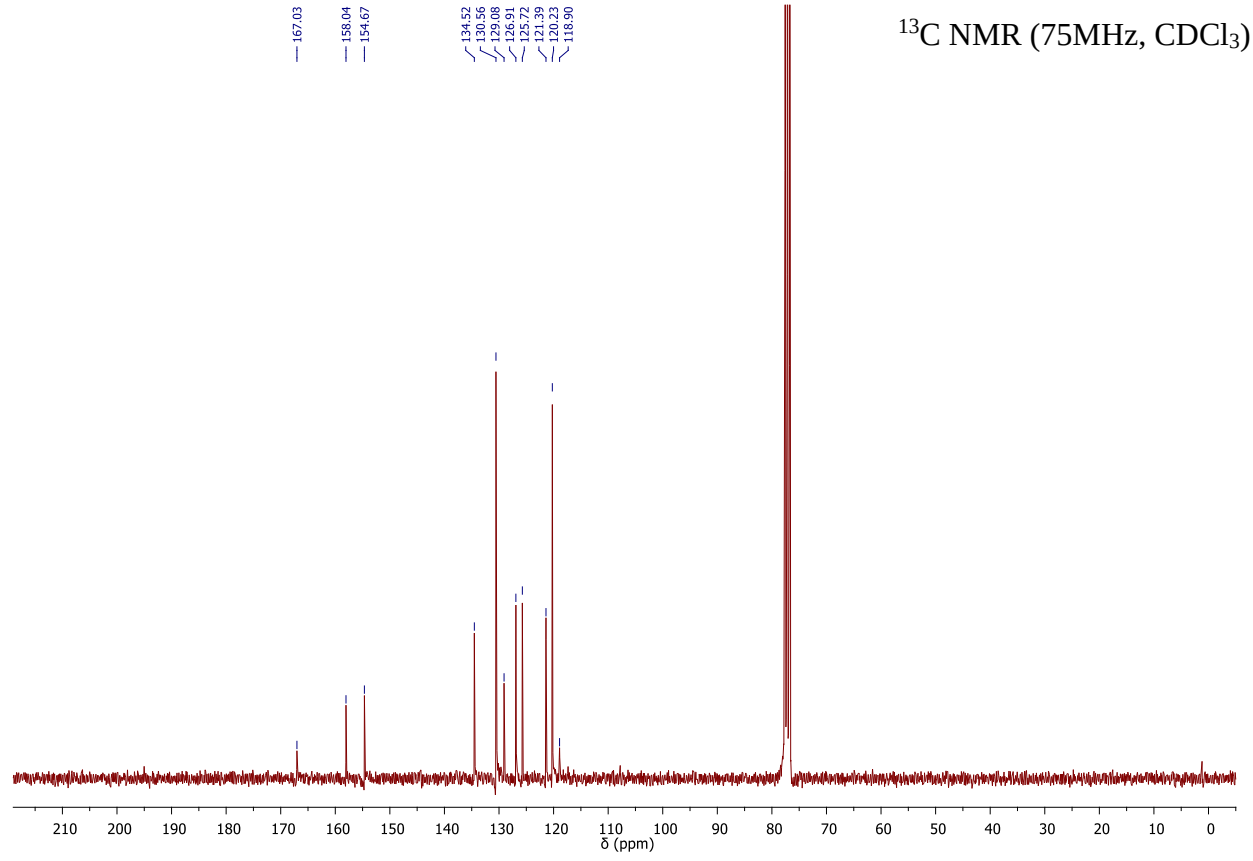
^{13}C NMR (101MHz, $CDCl_3$)



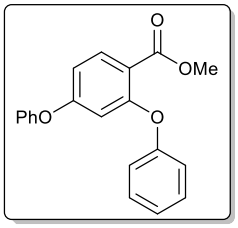
^{1}H NMR (400MHz, $CDCl_3$)



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

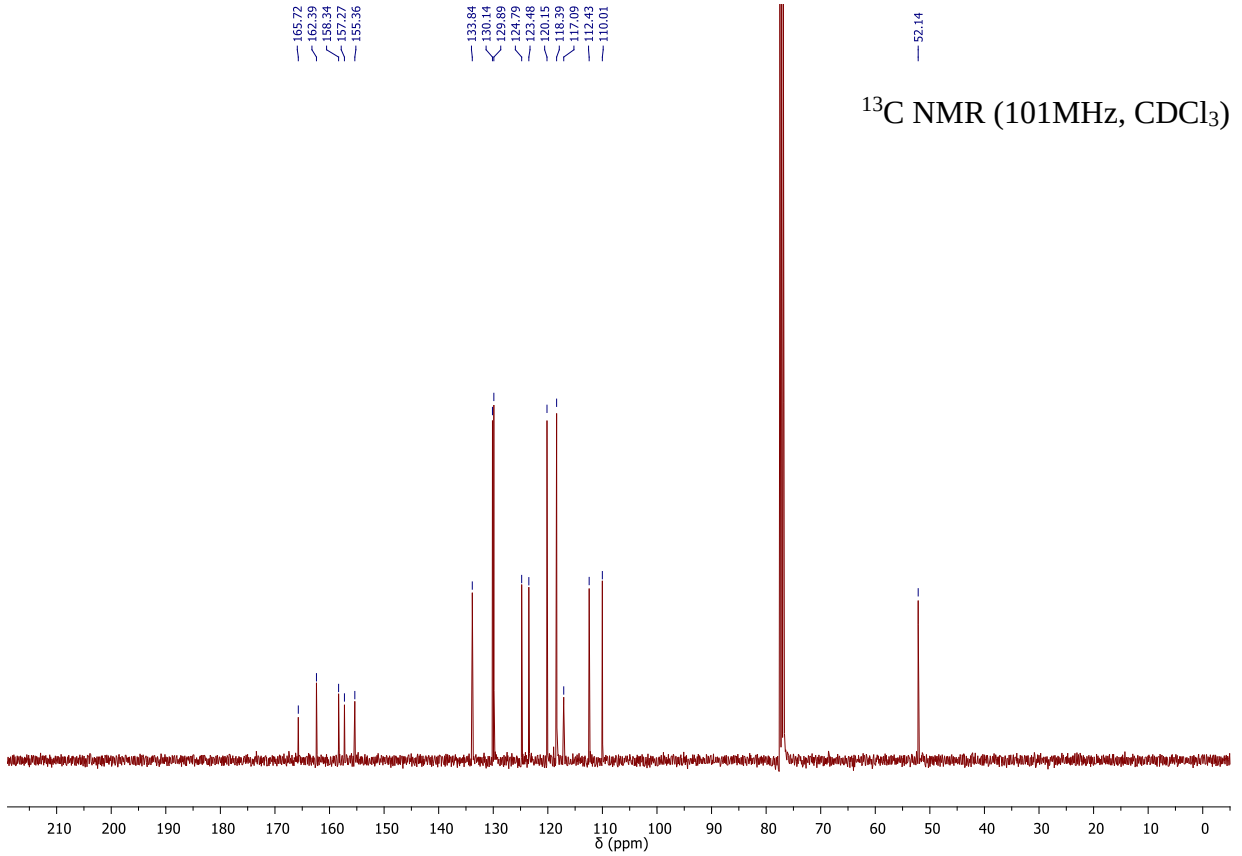


^{1}H NMR (300MHz, $CDCl_3$)

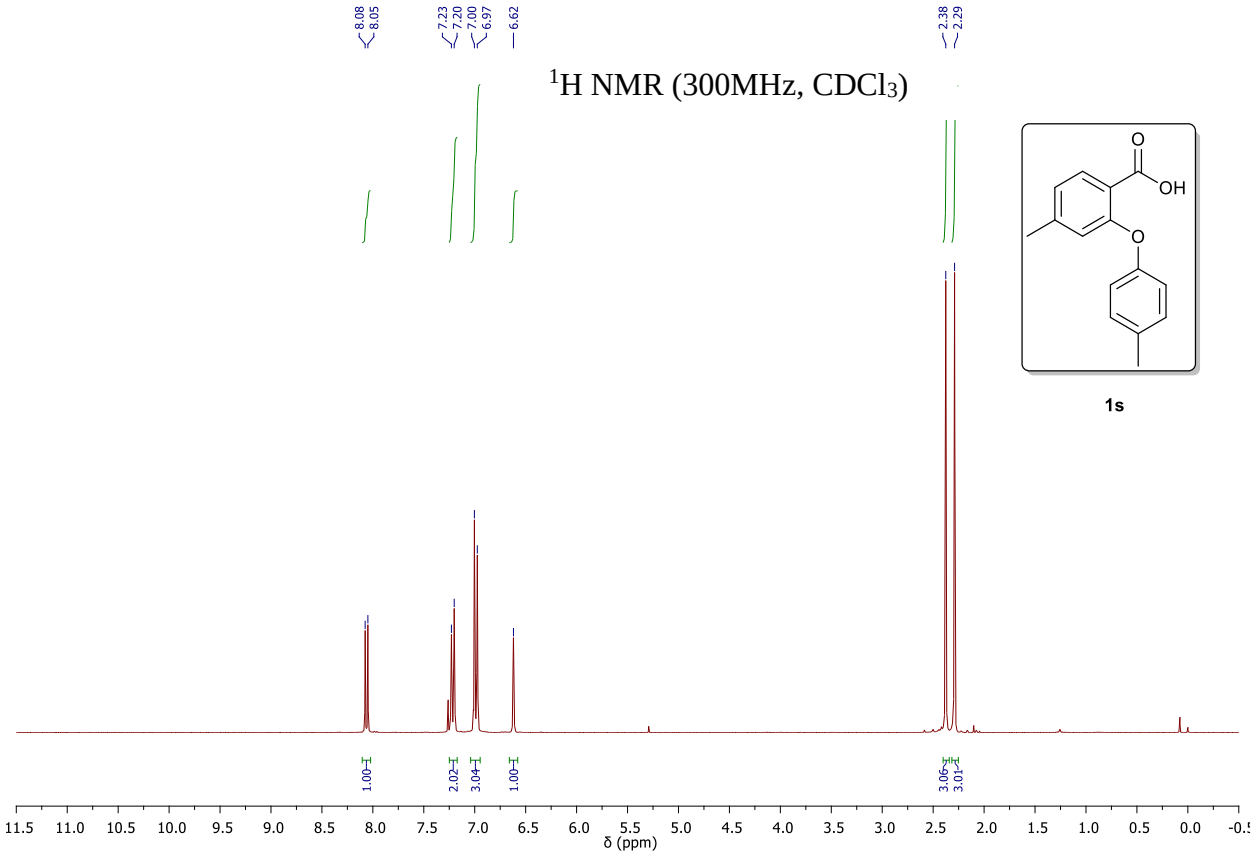


1r

^{13}C NMR (101MHz, $CDCl_3$)

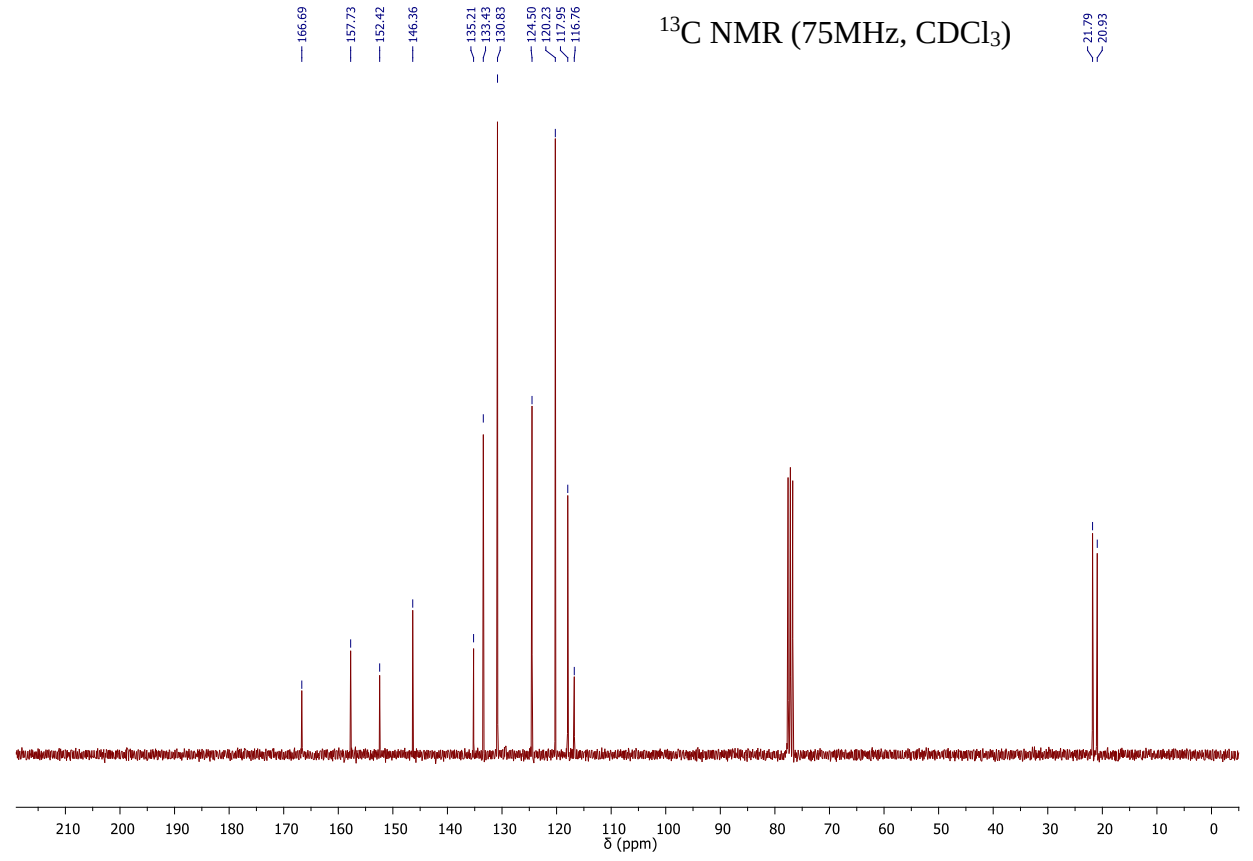


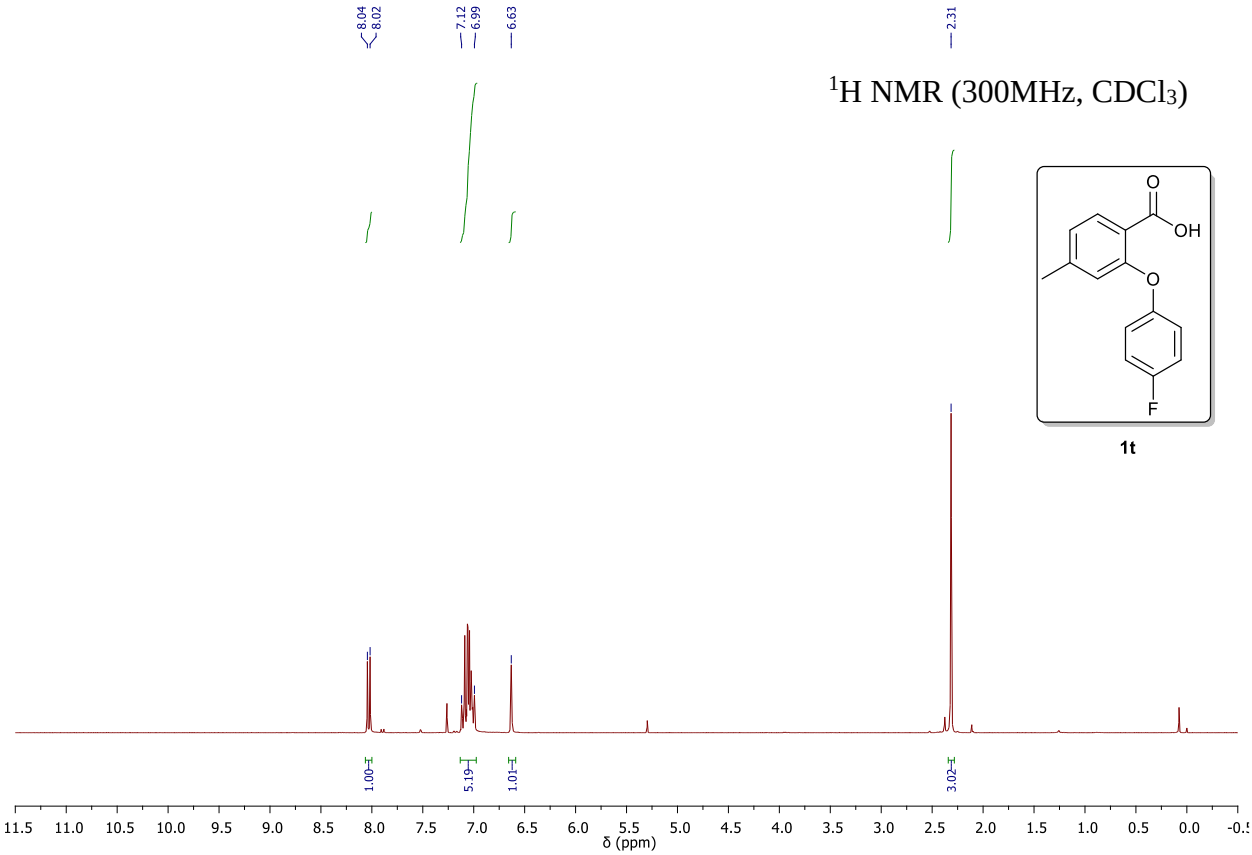
^{1}H NMR (300MHz, $CDCl_3$)



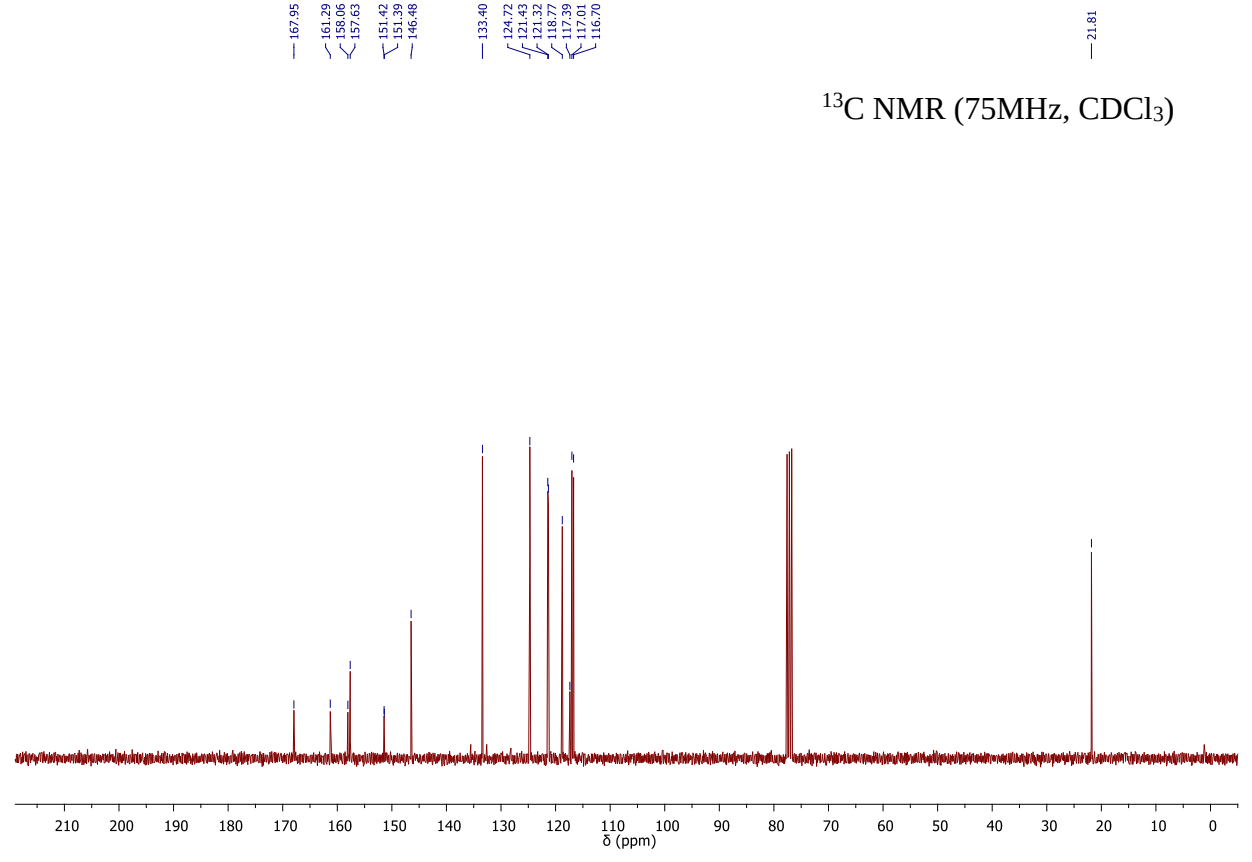
1s

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



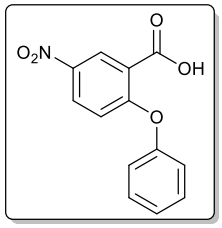


^{1}H NMR (300MHz, $CDCl_3$)

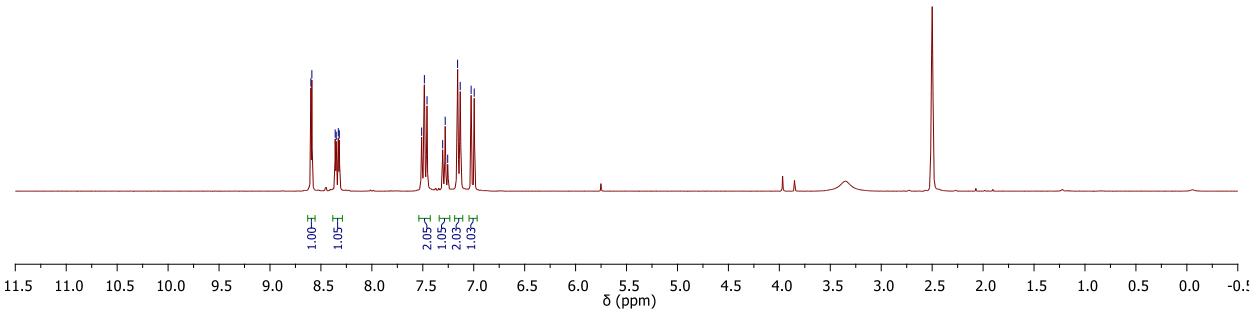


^{13}C NMR (75MHz, $CDCl_3$)

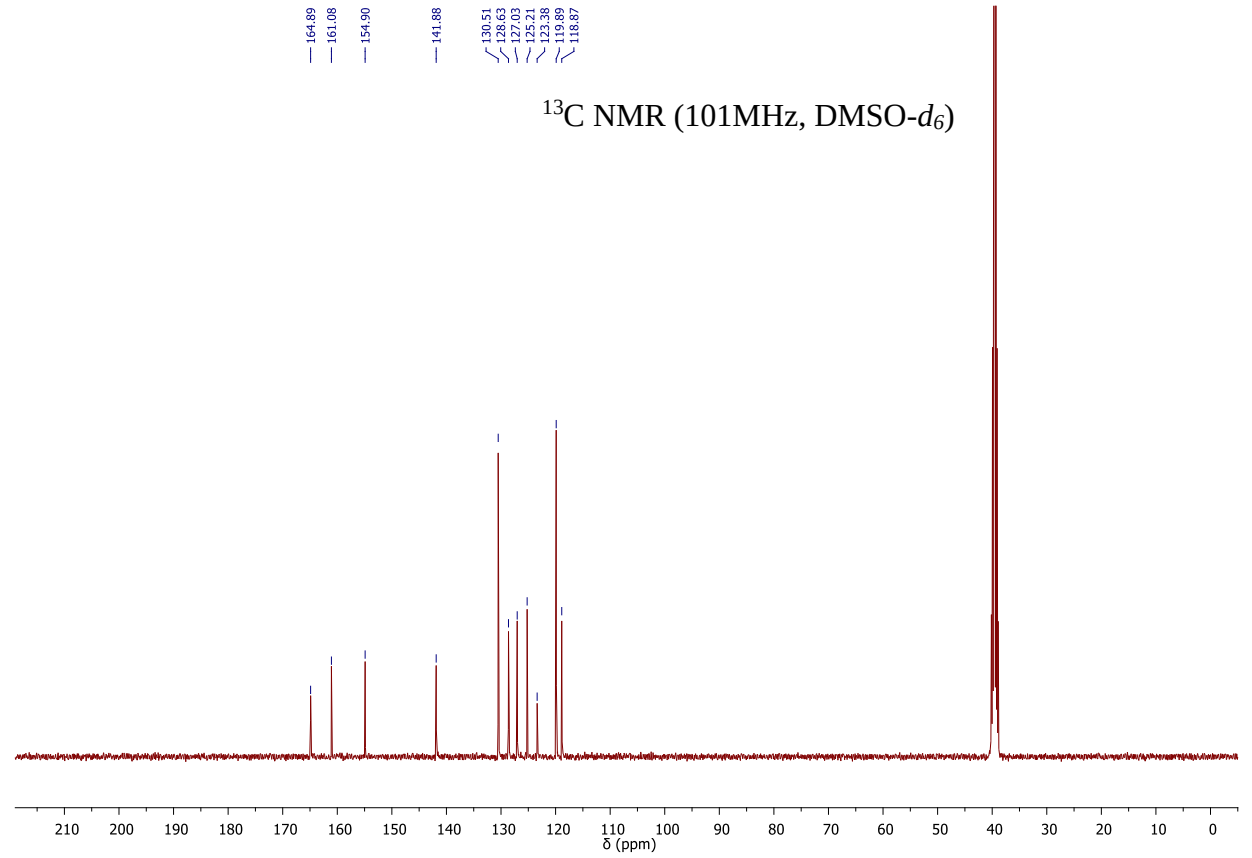
^{1}H NMR (300MHz, DMSO-d_6)



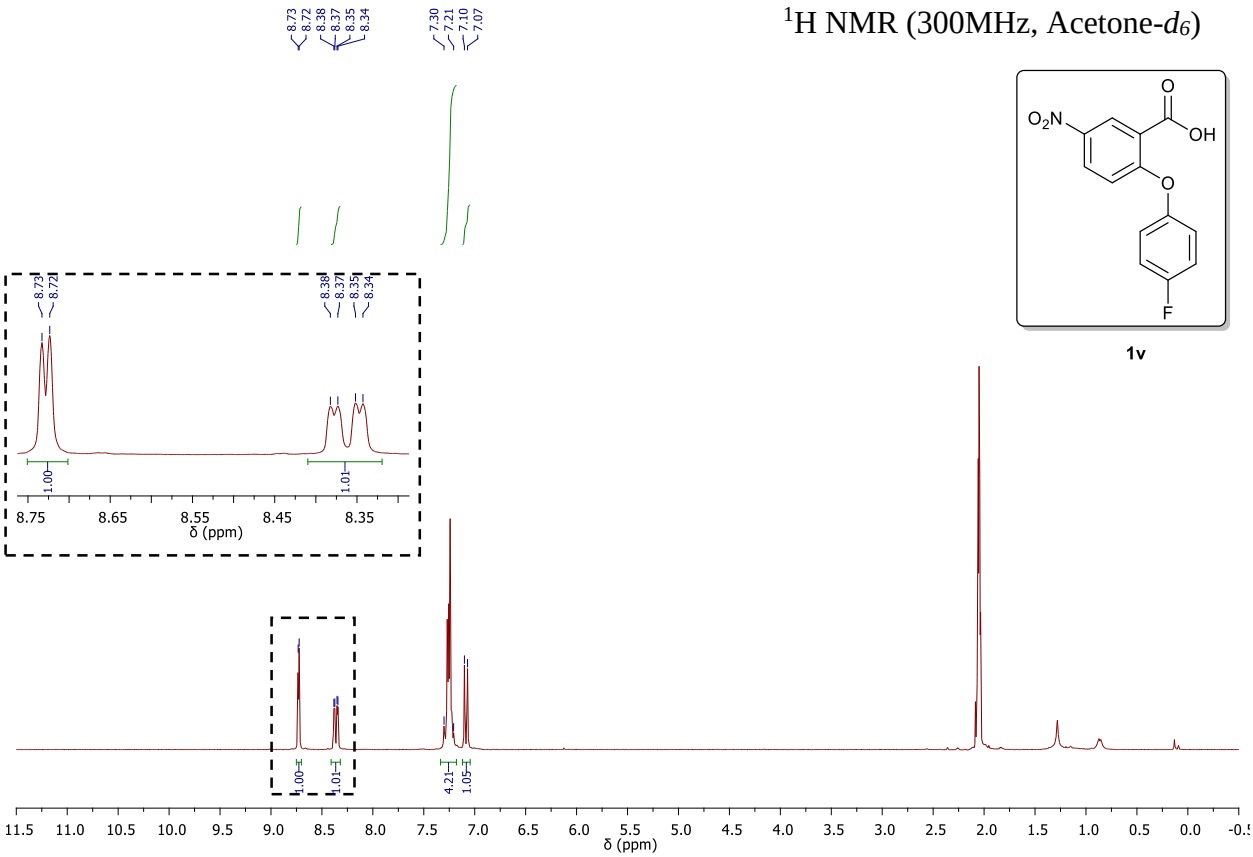
1u



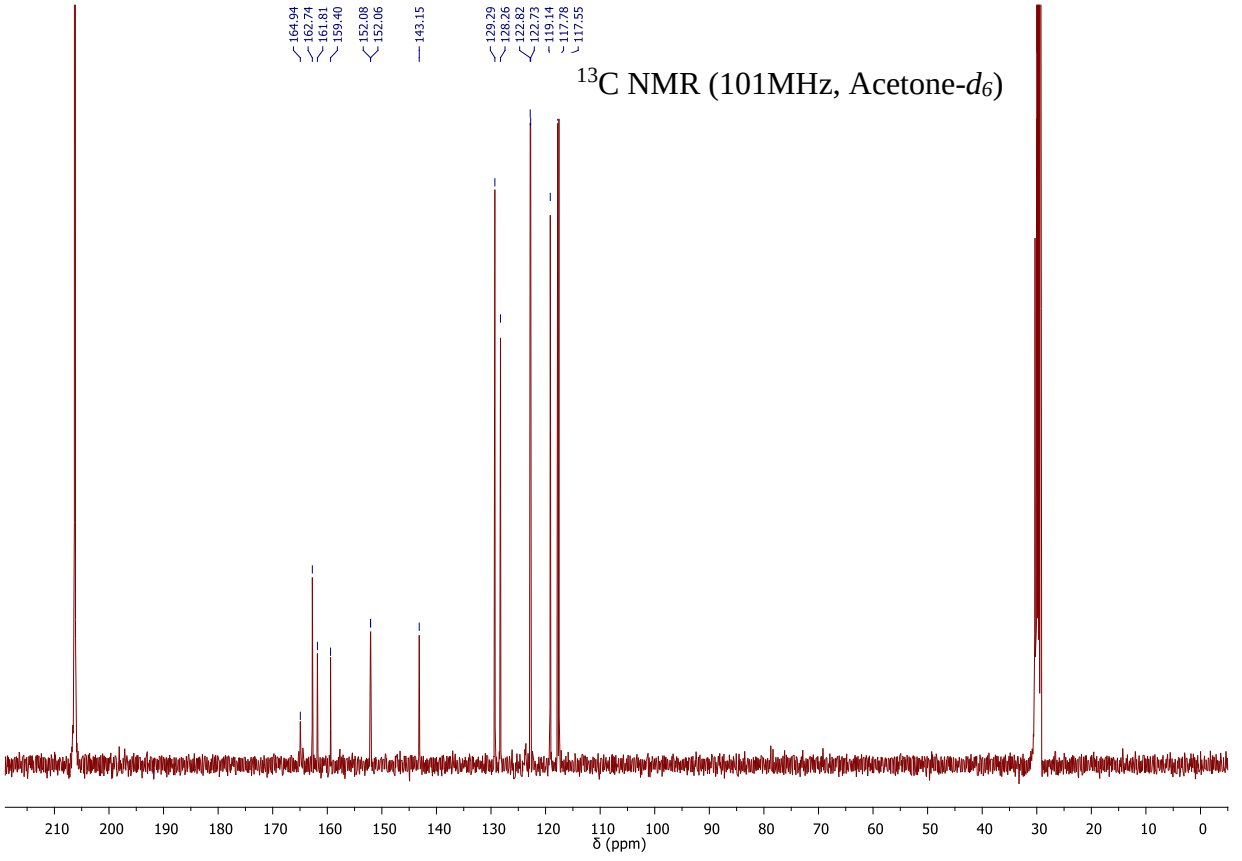
^{13}C NMR (101MHz, DMSO-d_6)

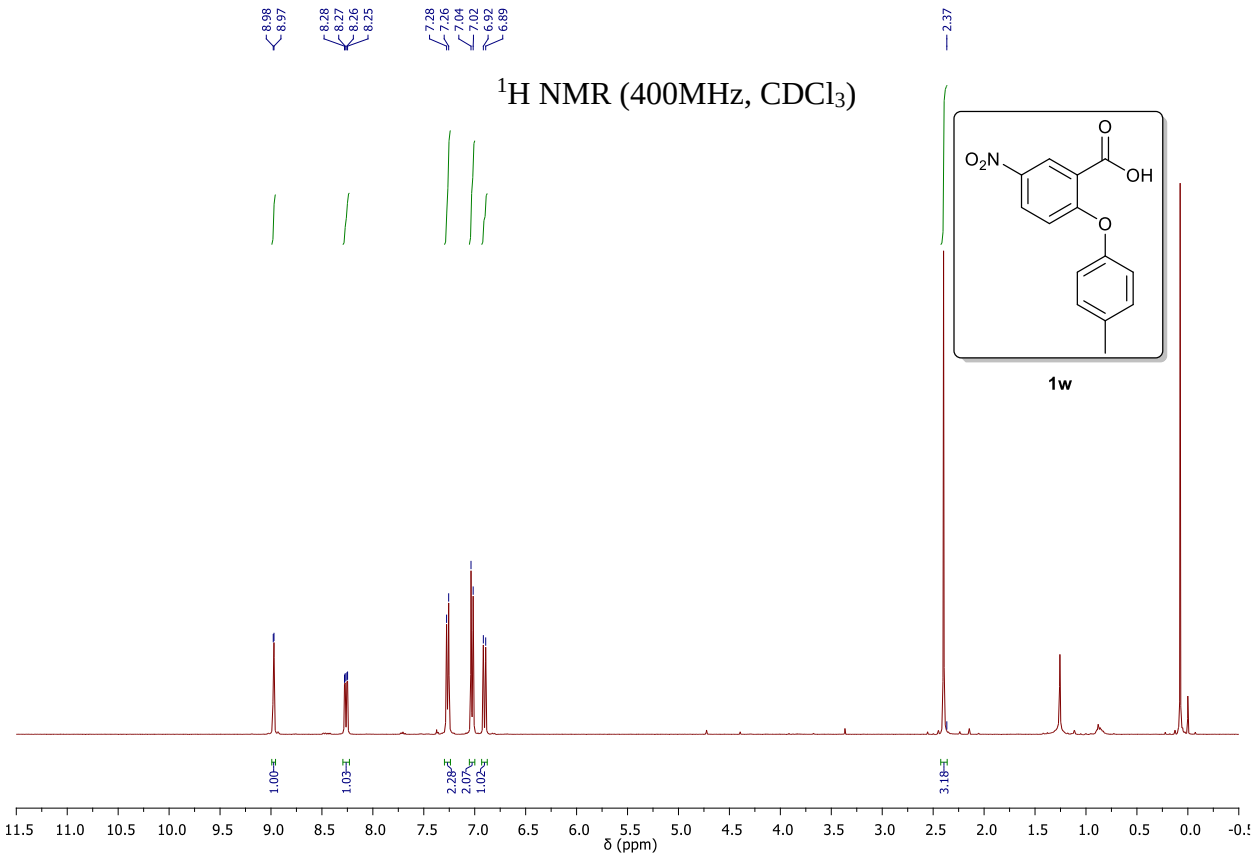


^{1}H NMR (300MHz, Acetone-d_6)



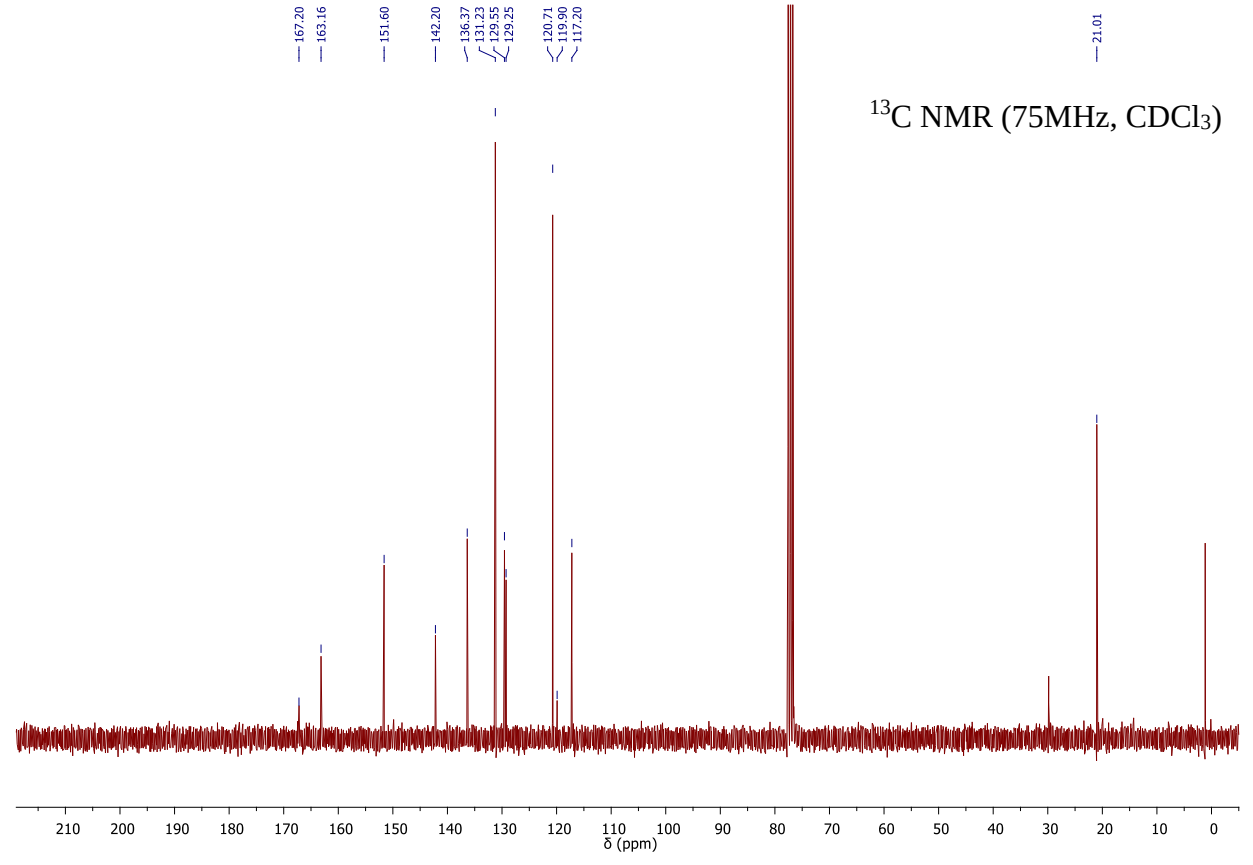
^{13}C NMR (101MHz, Acetone-d_6)





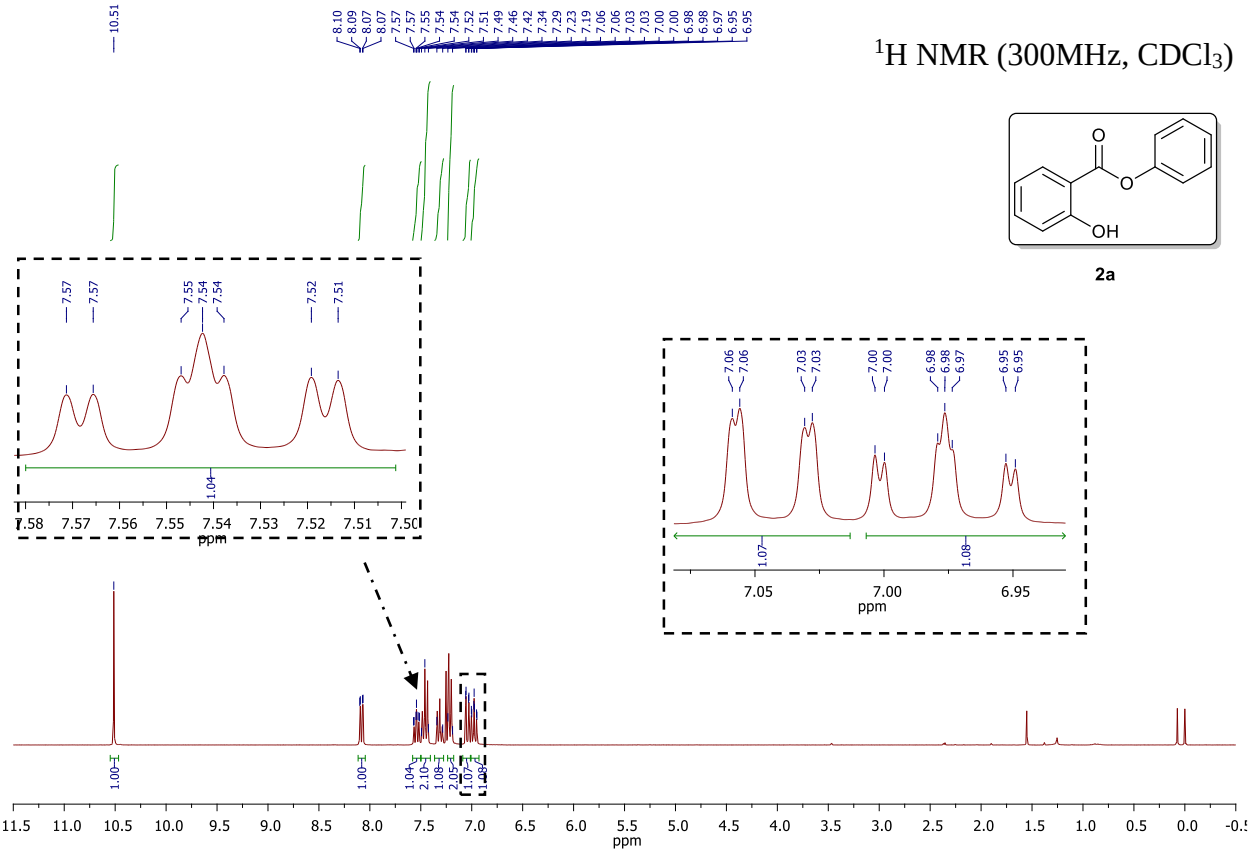
^{1}H NMR (400MHz, $CDCl_3$)

1w



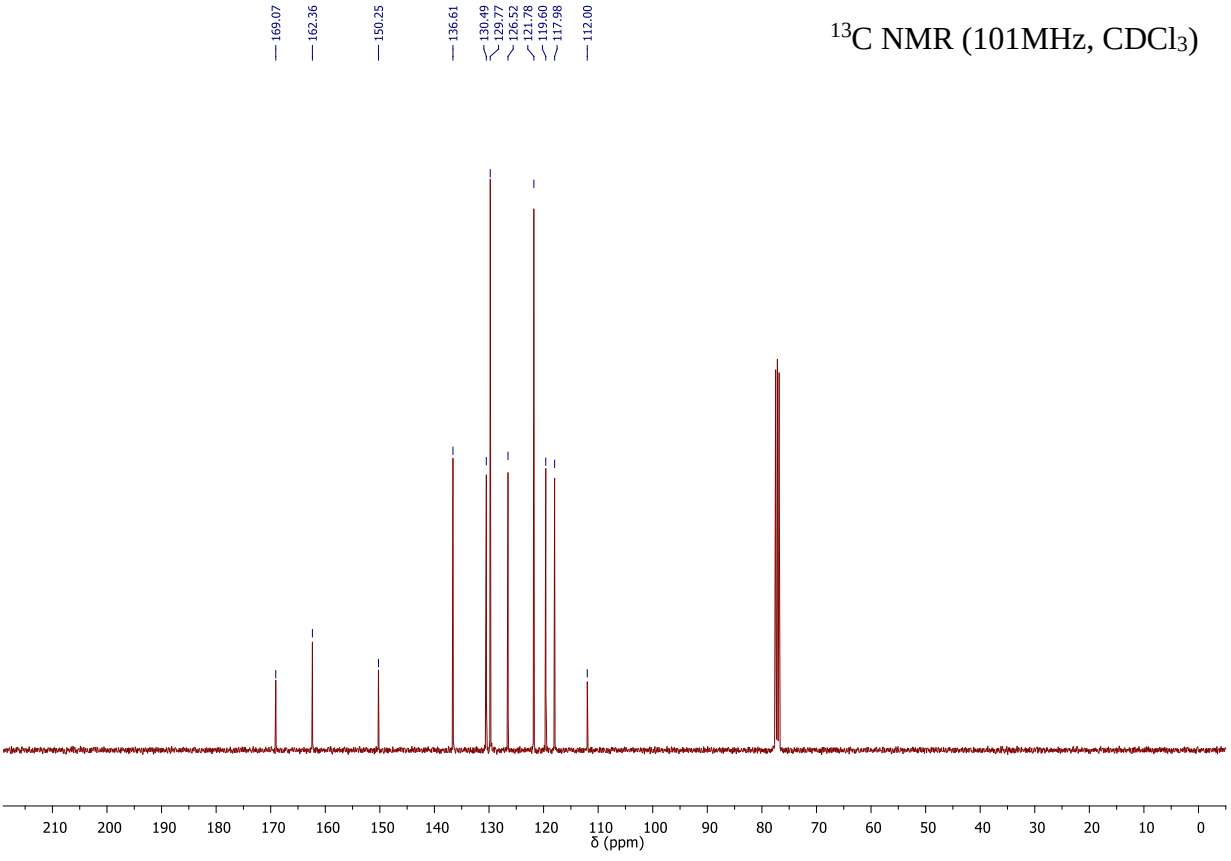
^{13}C NMR (75MHz, $CDCl_3$)

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

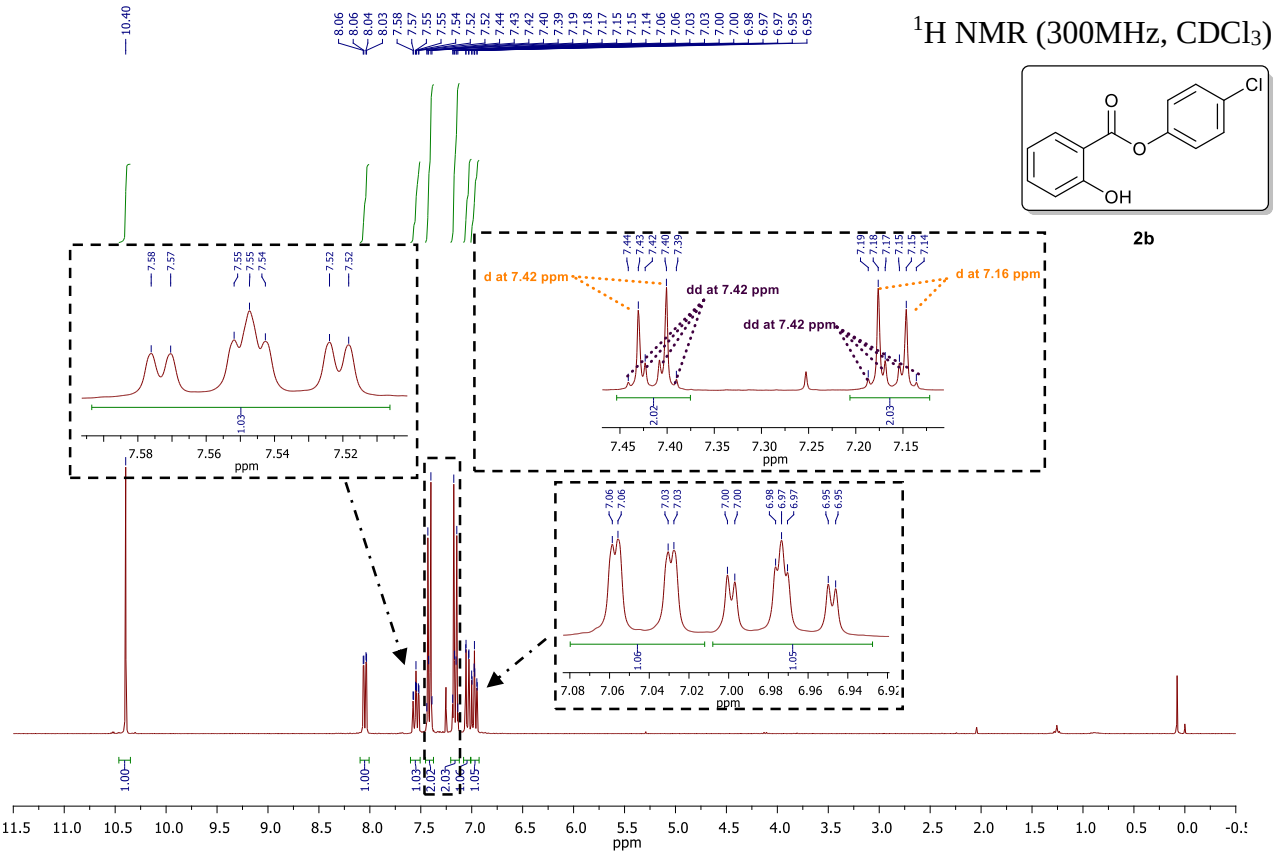


2a

^{13}C NMR (101MHz, $CDCl_3$)

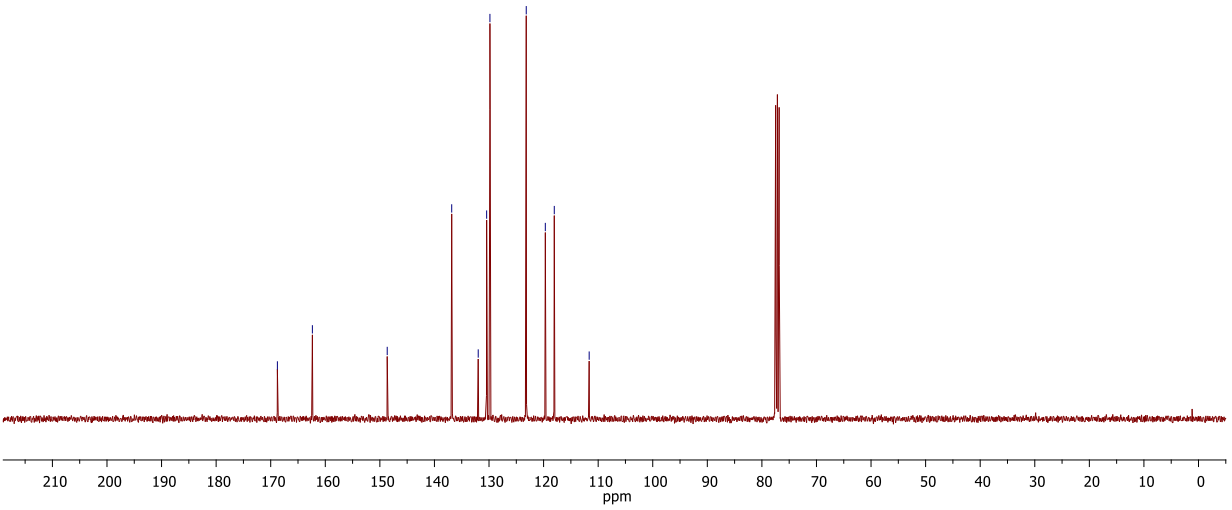


^{1}H NMR (300MHz, $CDCl_3$)

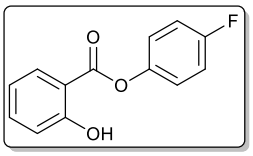


2b

^{13}C NMR (101MHz, $CDCl_3$)

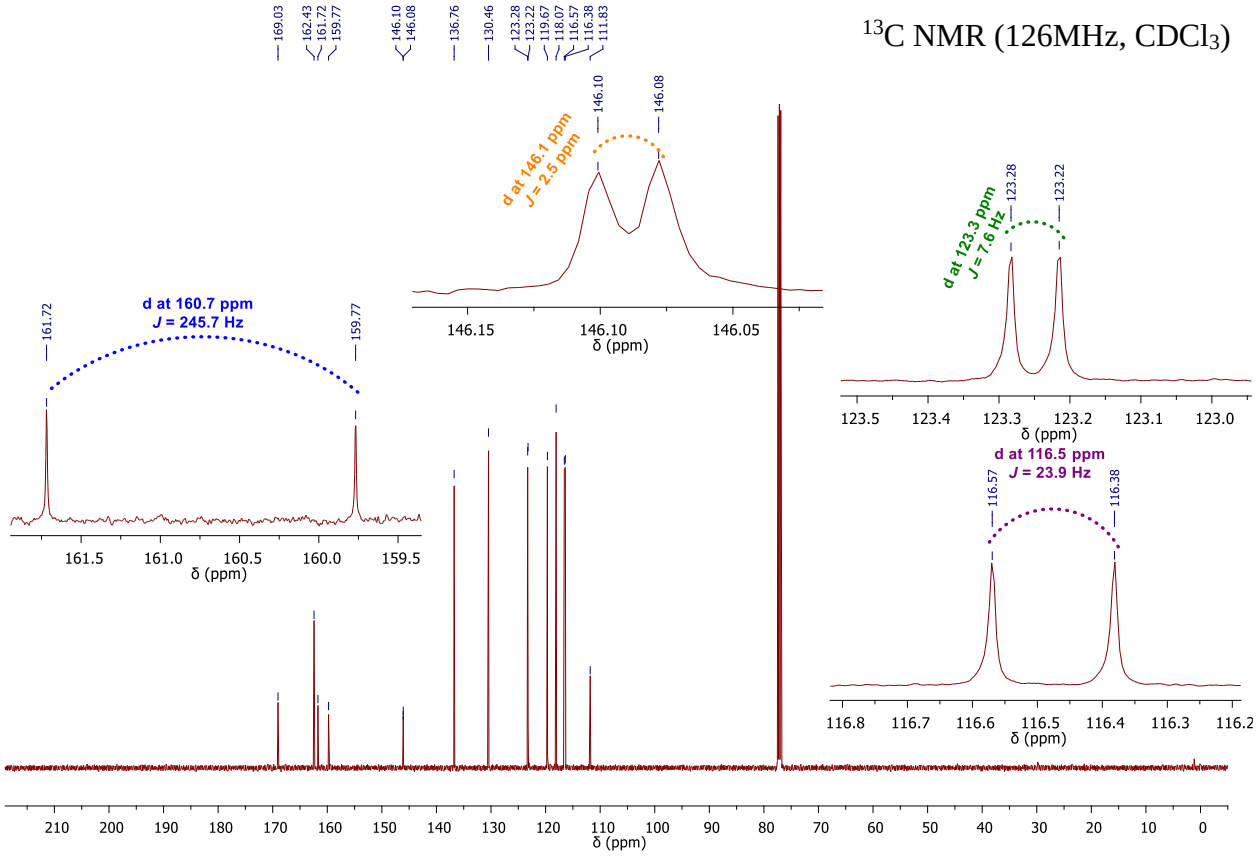


^{1}H NMR (300MHz, $CDCl_3$)

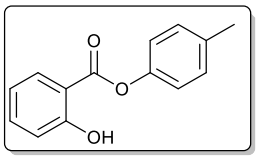


2c

^{13}C NMR (126MHz, $CDCl_3$)

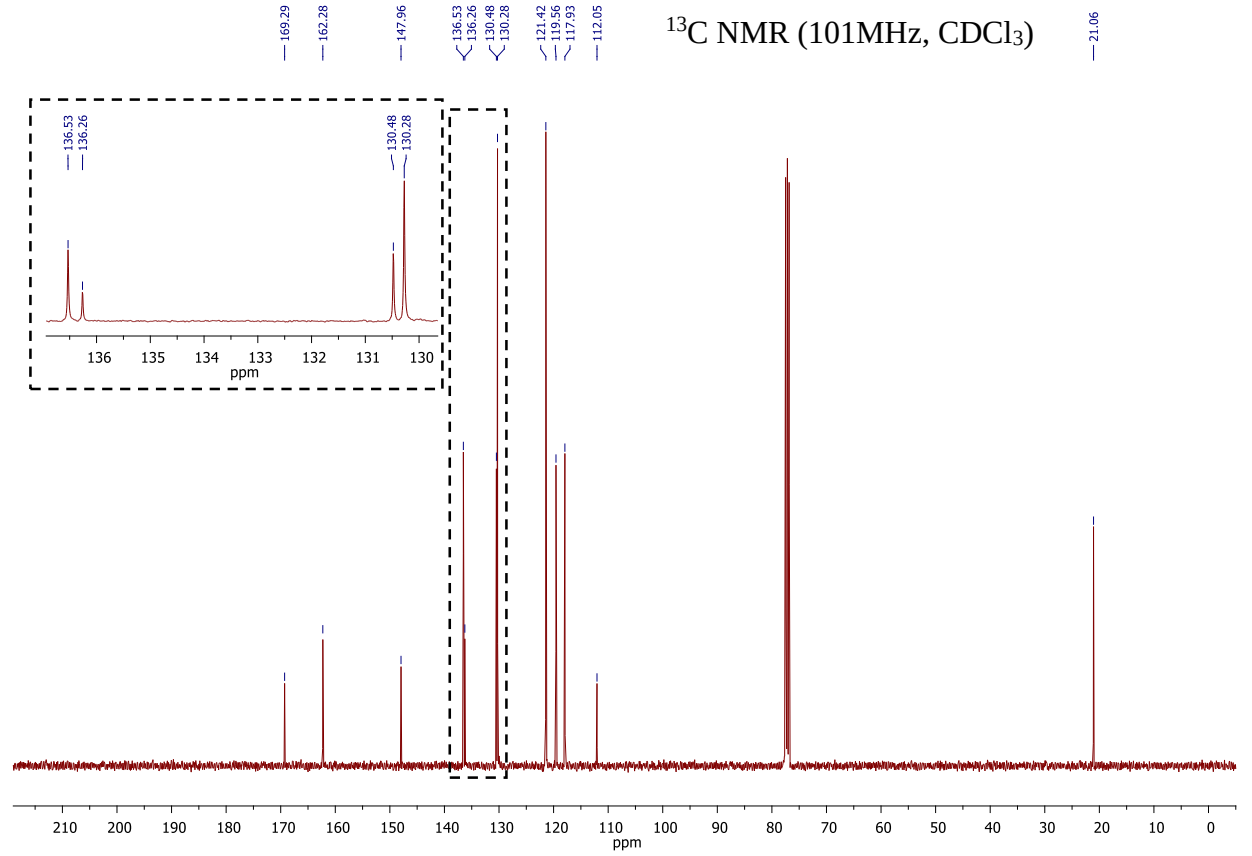


^{1}H NMR (300MHz, $CDCl_3$)

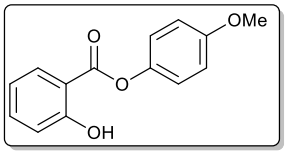


2d

^{13}C NMR (101MHz, $CDCl_3$)

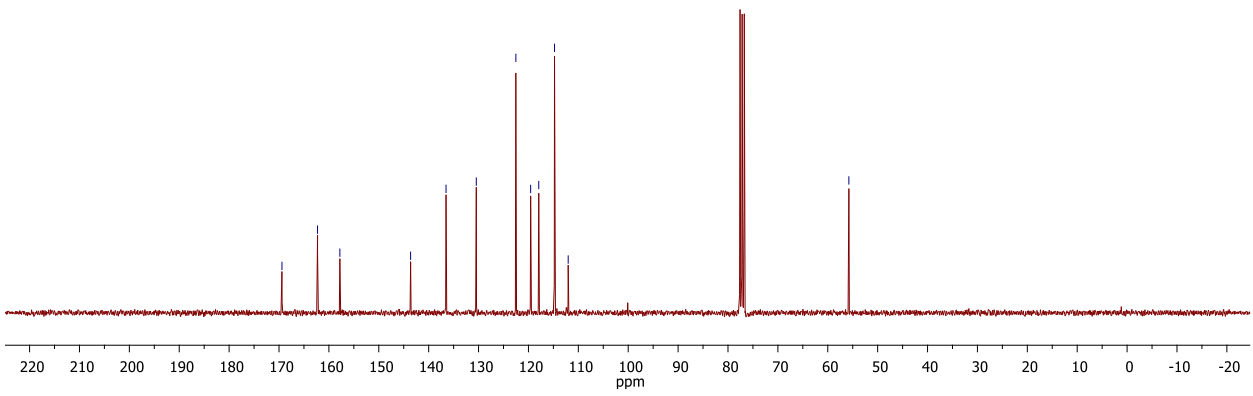


^{1}H NMR (400MHz, $CDCl_3$)

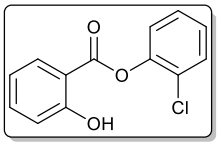


2e

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

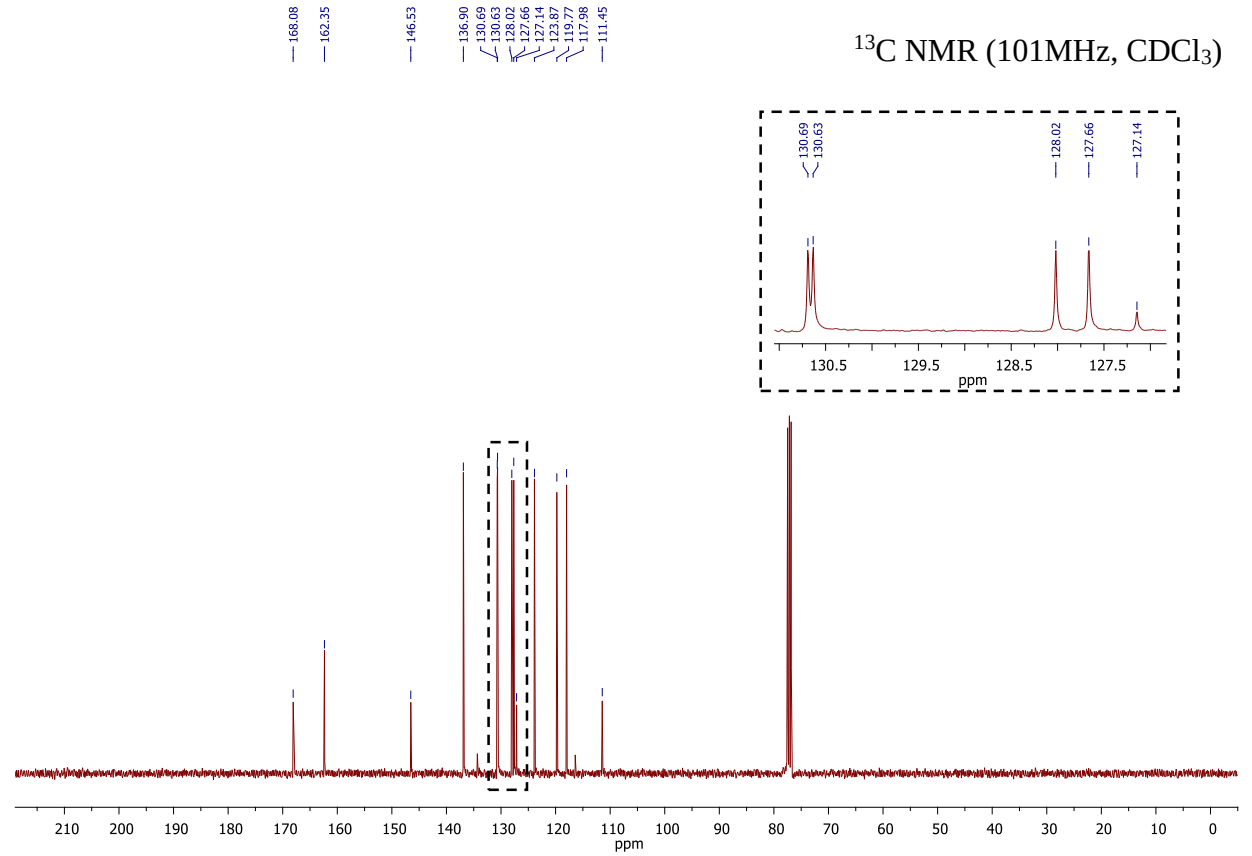


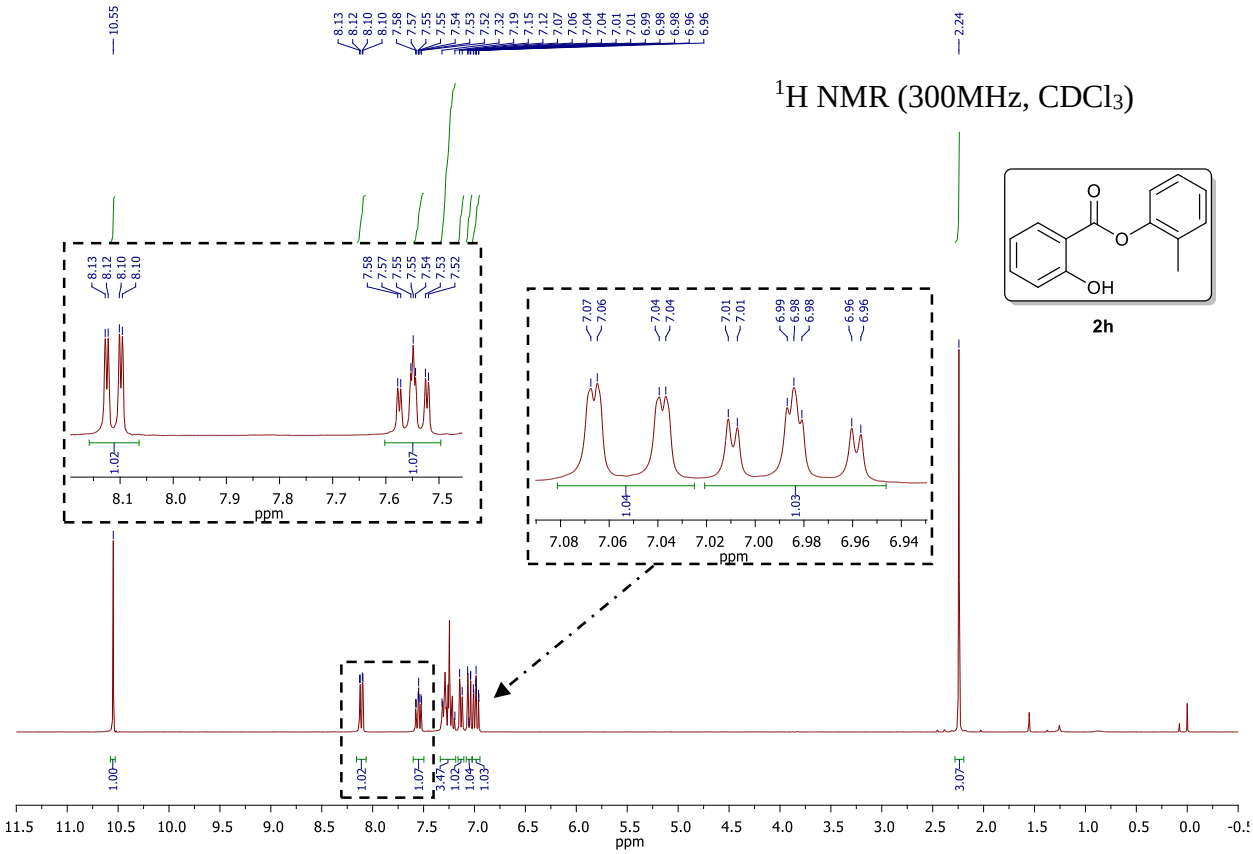
^{1}H NMR (300MHz, $CDCl_3$)

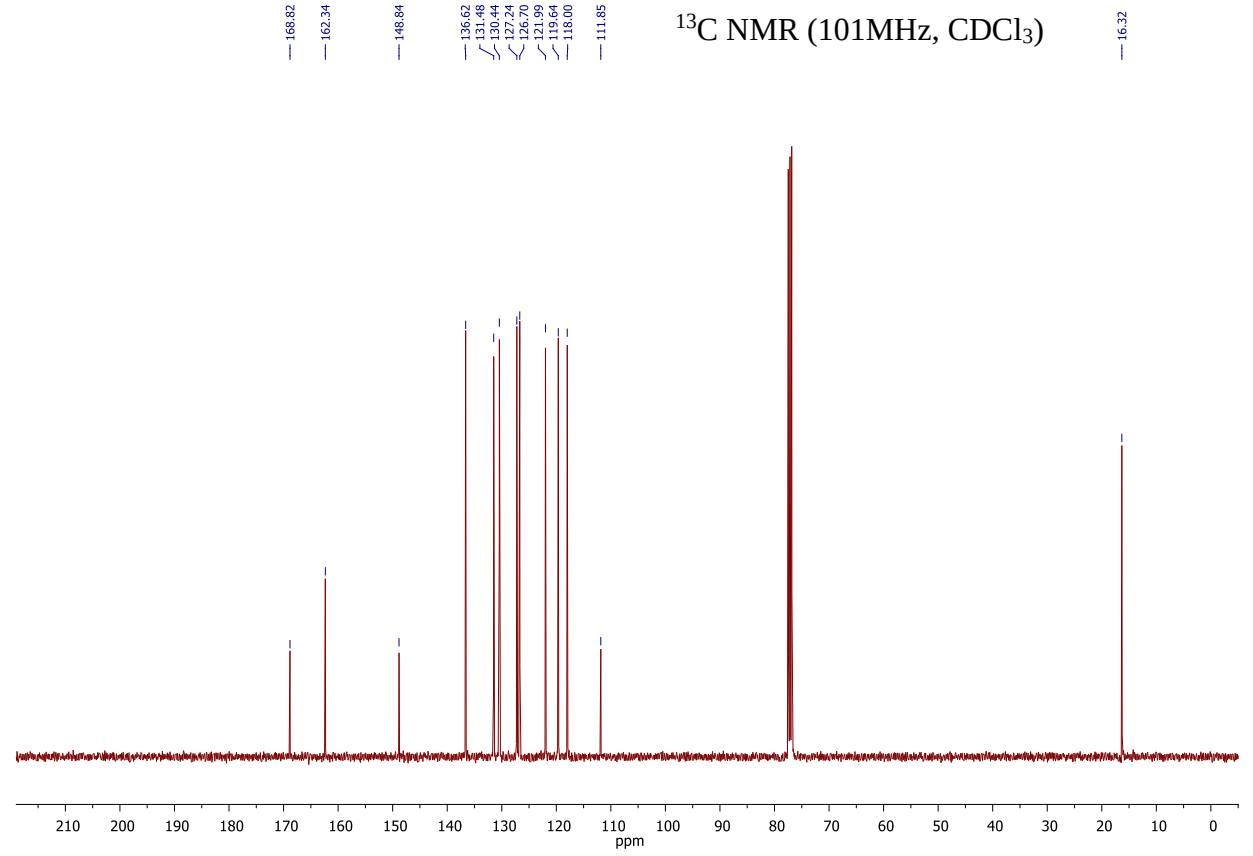


2g

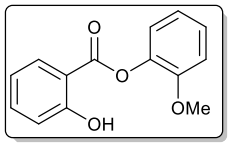
^{13}C NMR (101MHz, $CDCl_3$)




^{1}H NMR (300MHz, CDCl$_3$)
2h
ppm

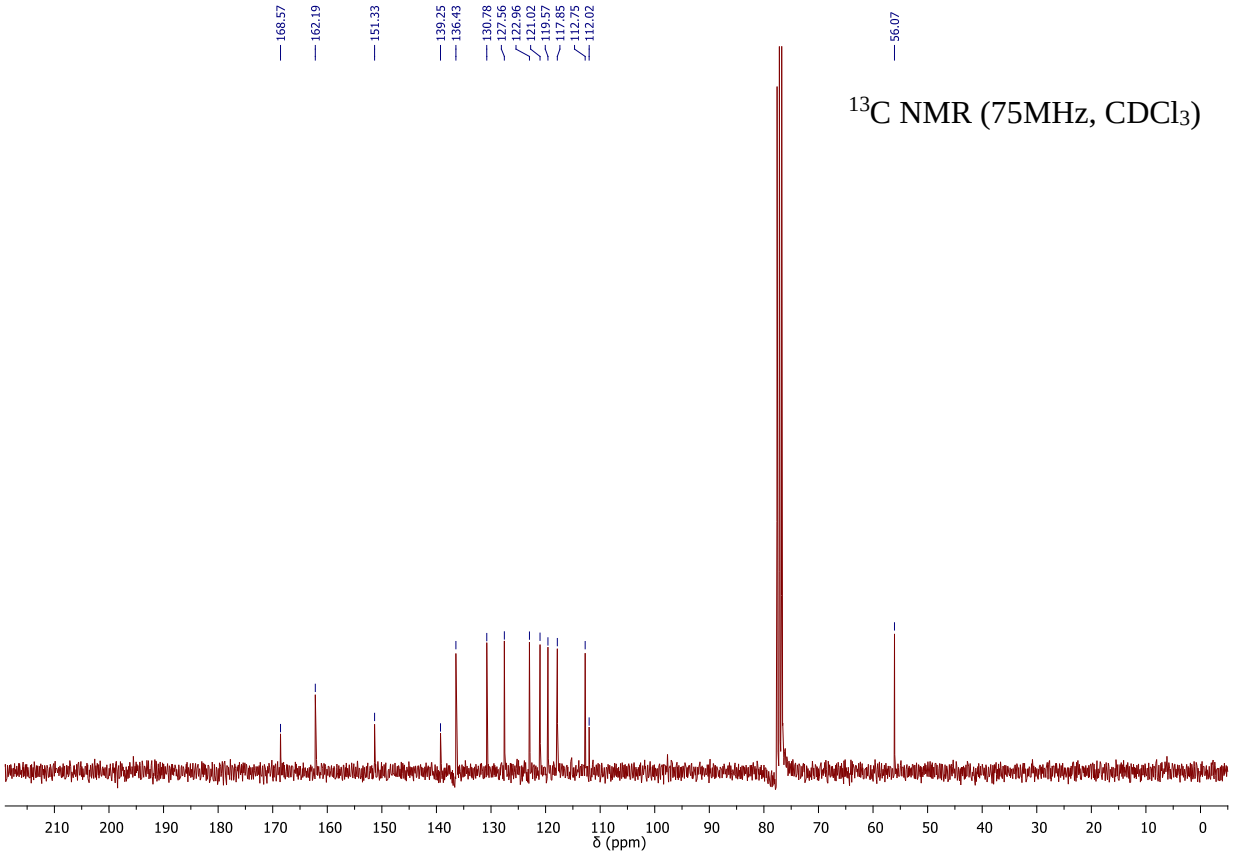

^{13}C NMR (101MHz, CDCl$_3$)
ppm

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

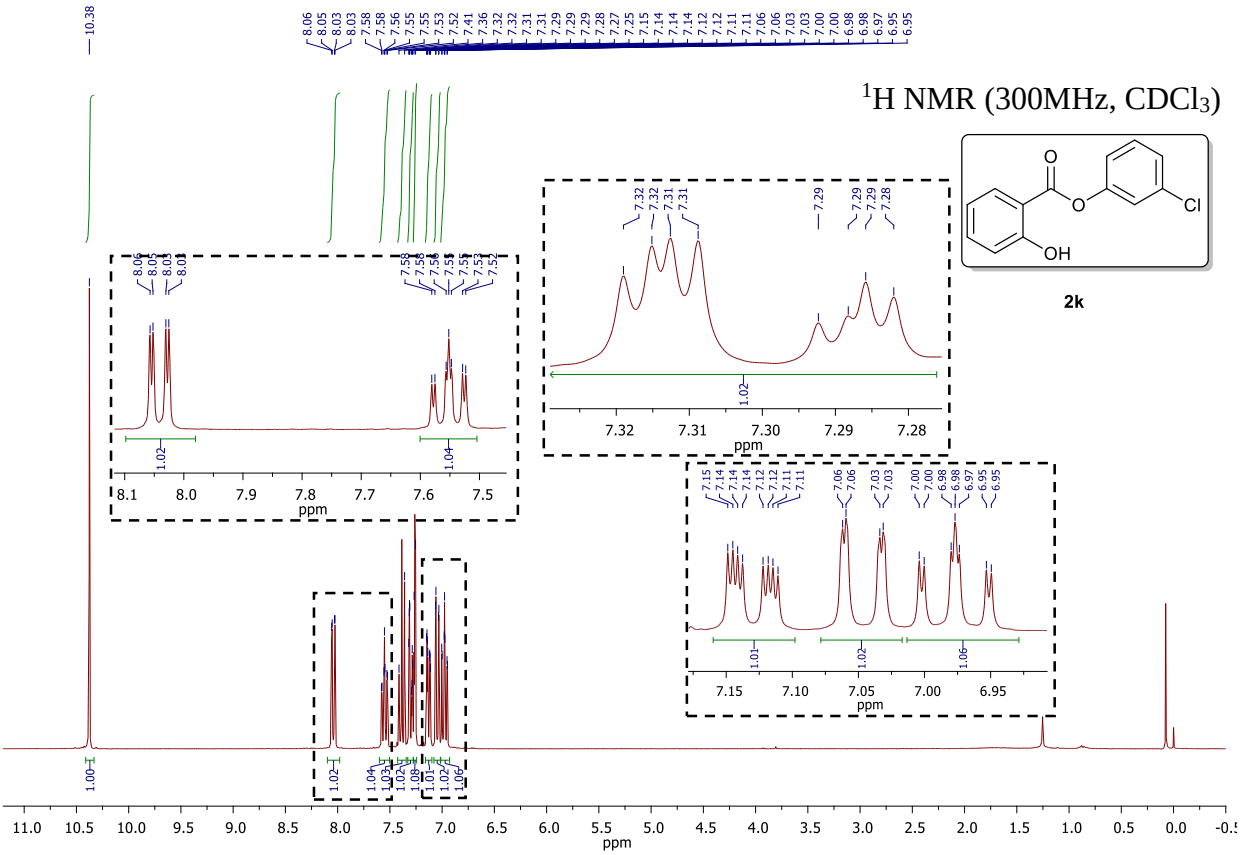


2i

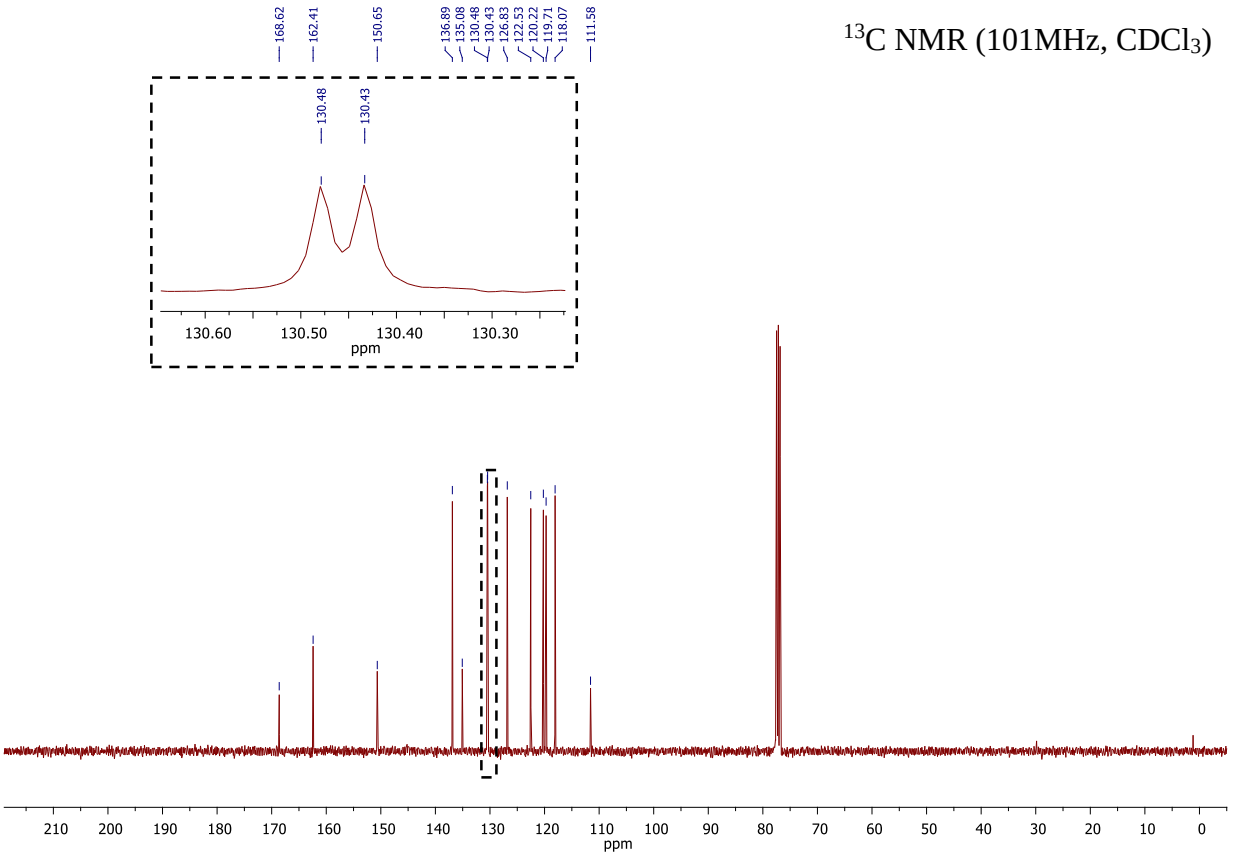
^{13}C NMR (75MHz, $CDCl_3$)



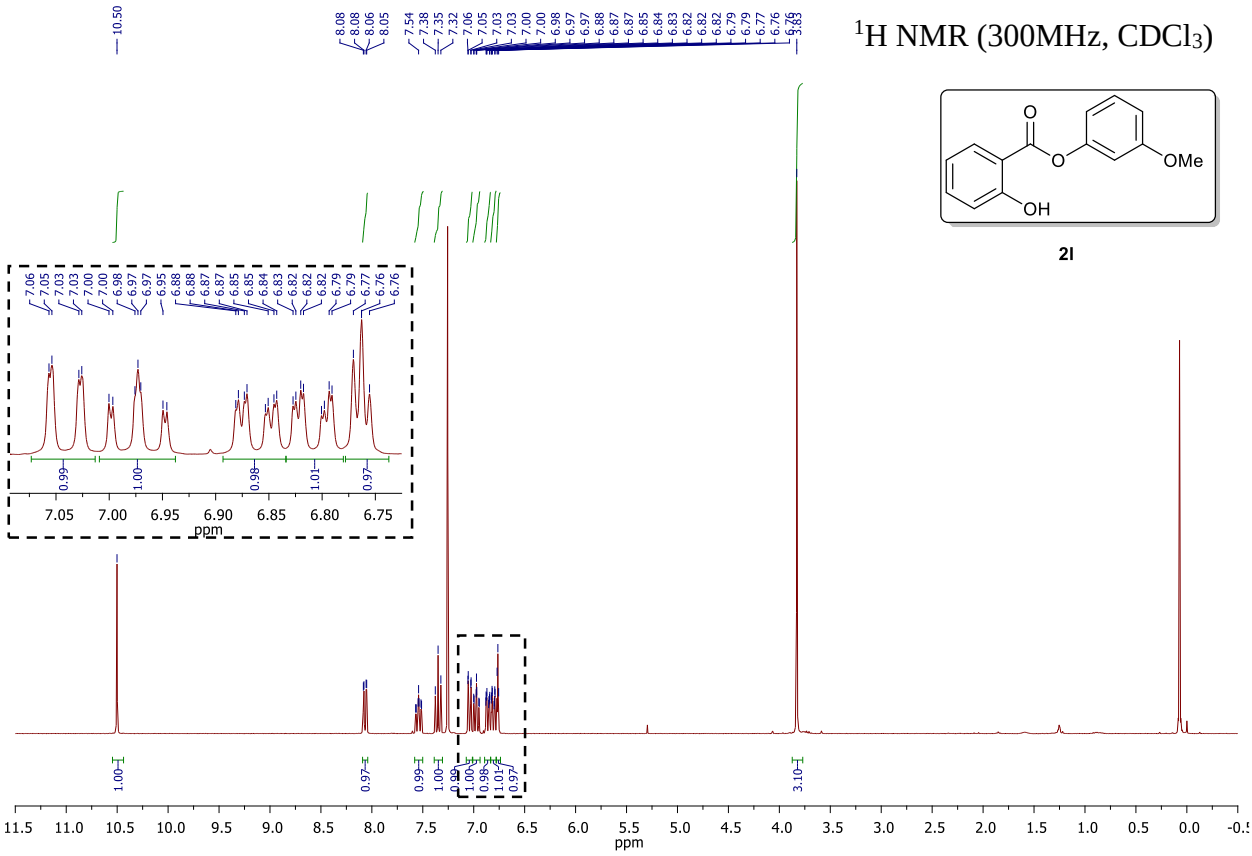
^{1}H NMR (300MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

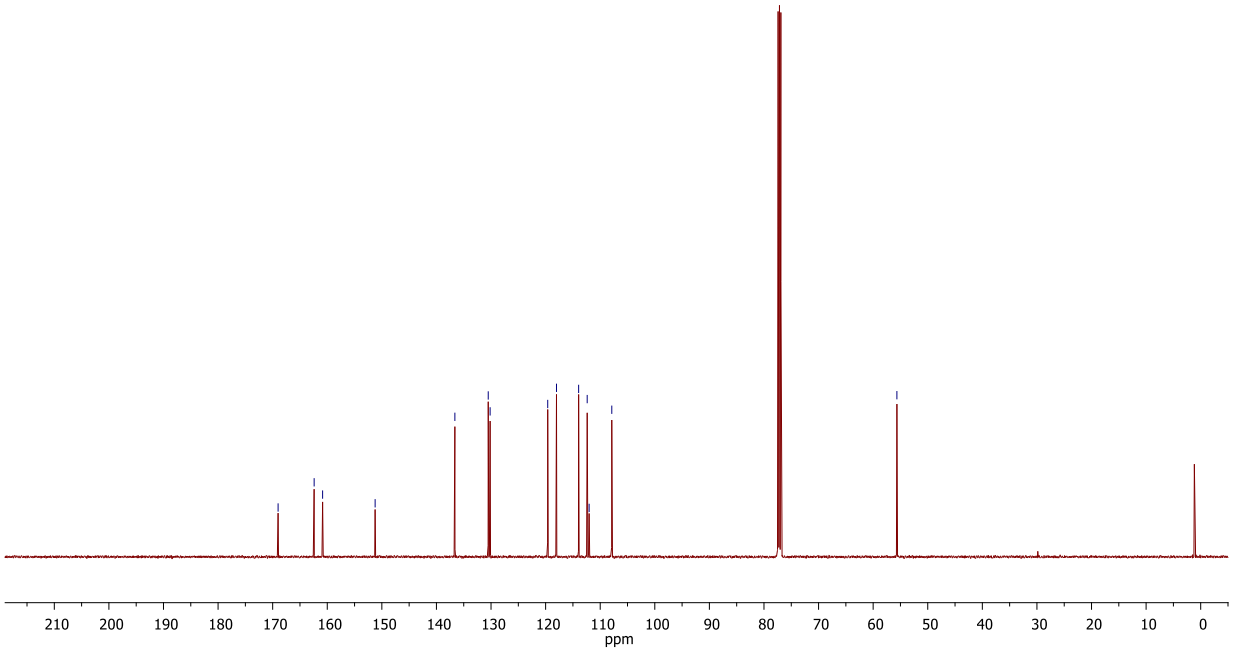


^{1}H NMR (300MHz, $CDCl_3$)

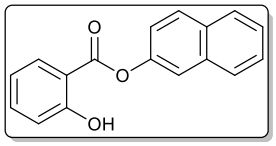


2l

^{13}C NMR (126MHz, $CDCl_3$)

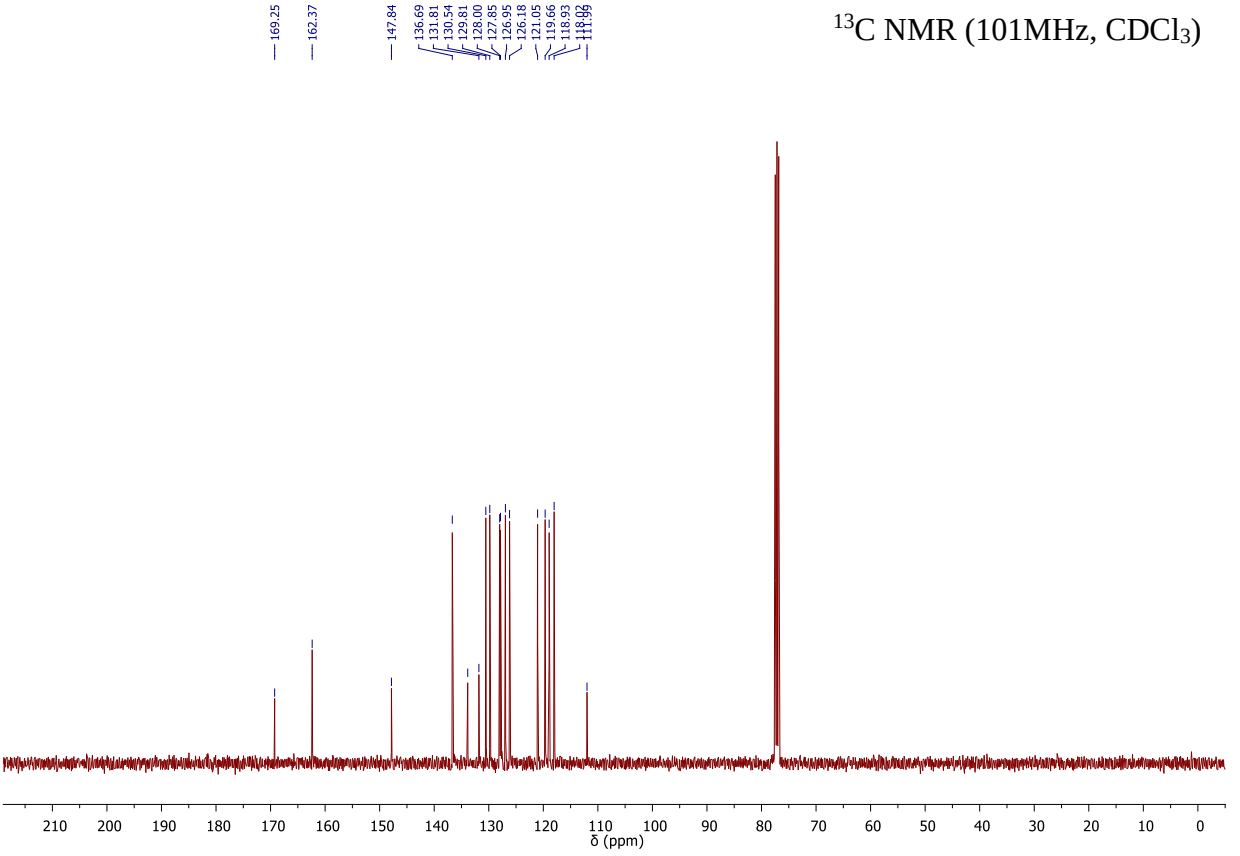


^{1}H NMR (300MHz, $CDCl_3$)

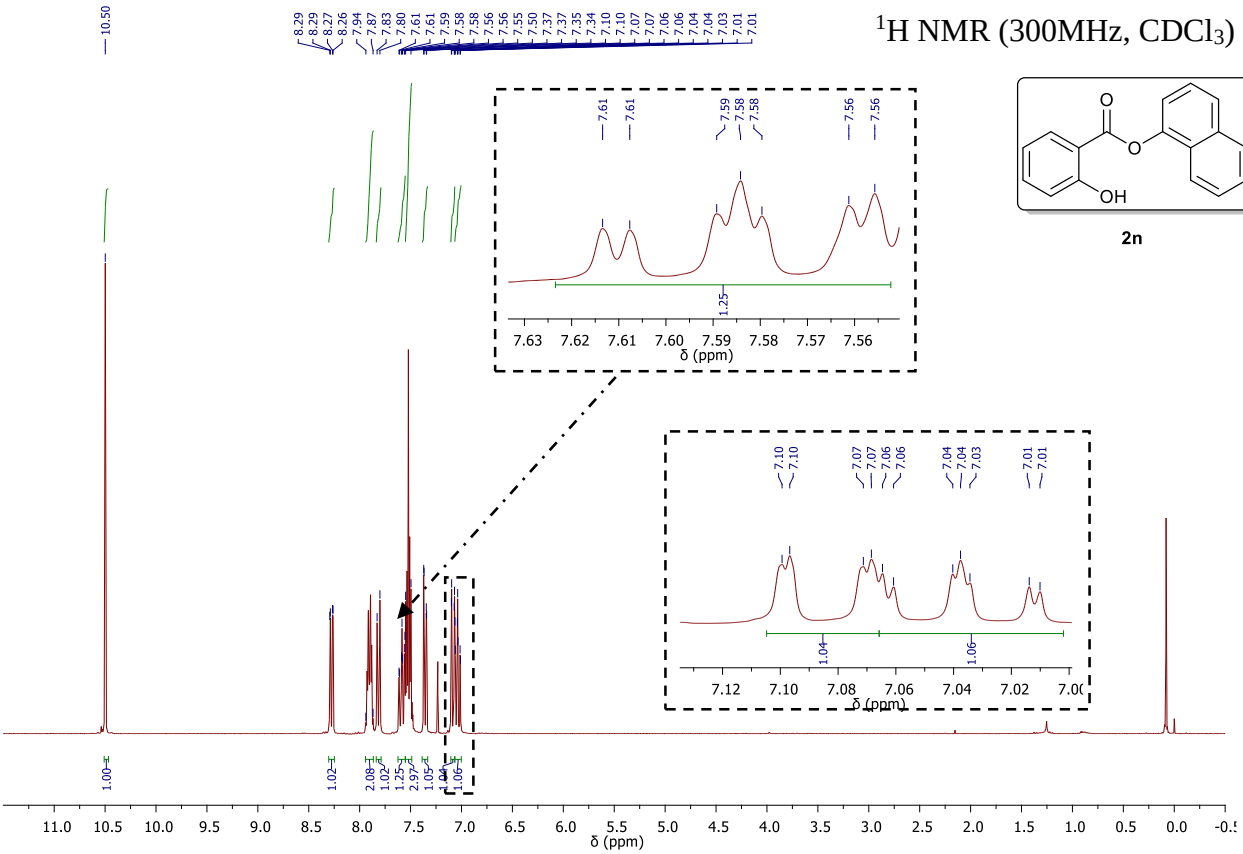


2m

^{13}C NMR (101MHz, $CDCl_3$)

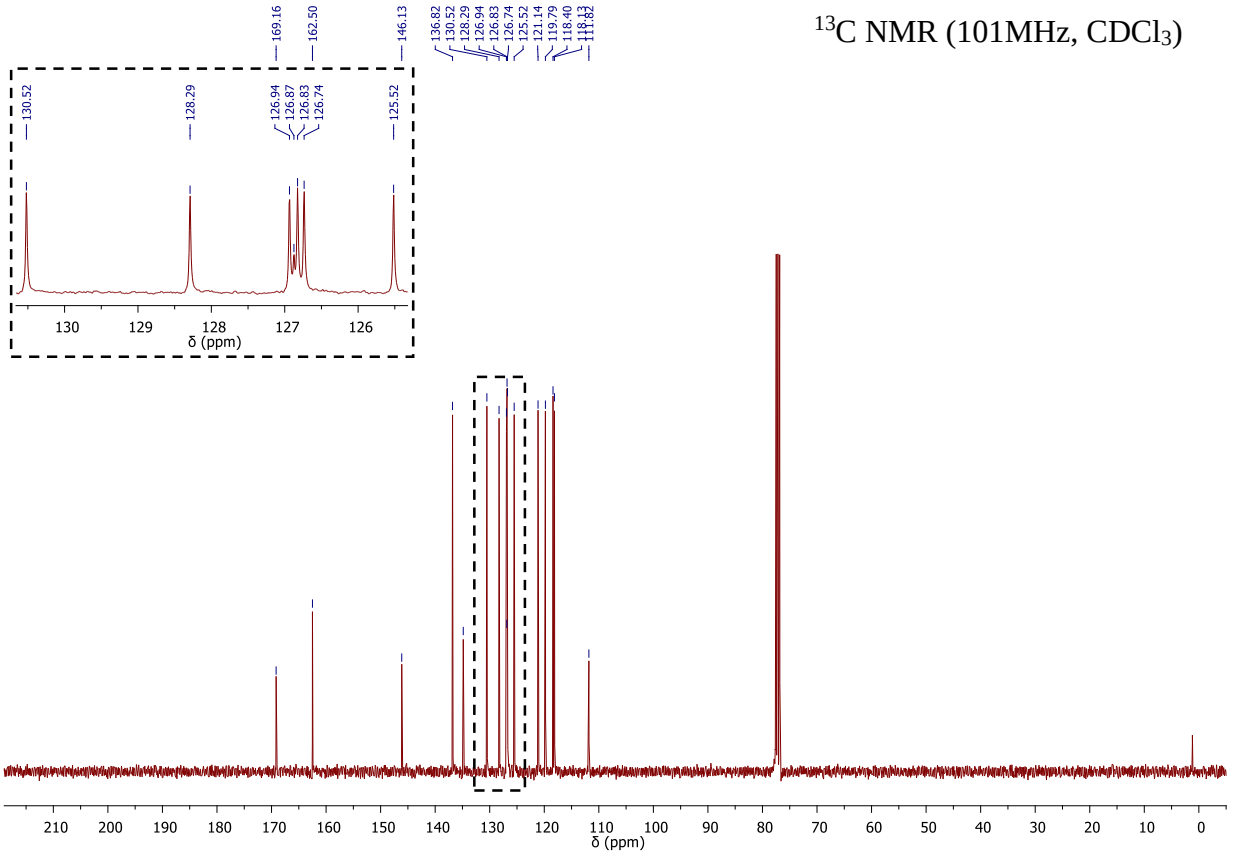


^{1}H NMR (300MHz, $CDCl_3$)

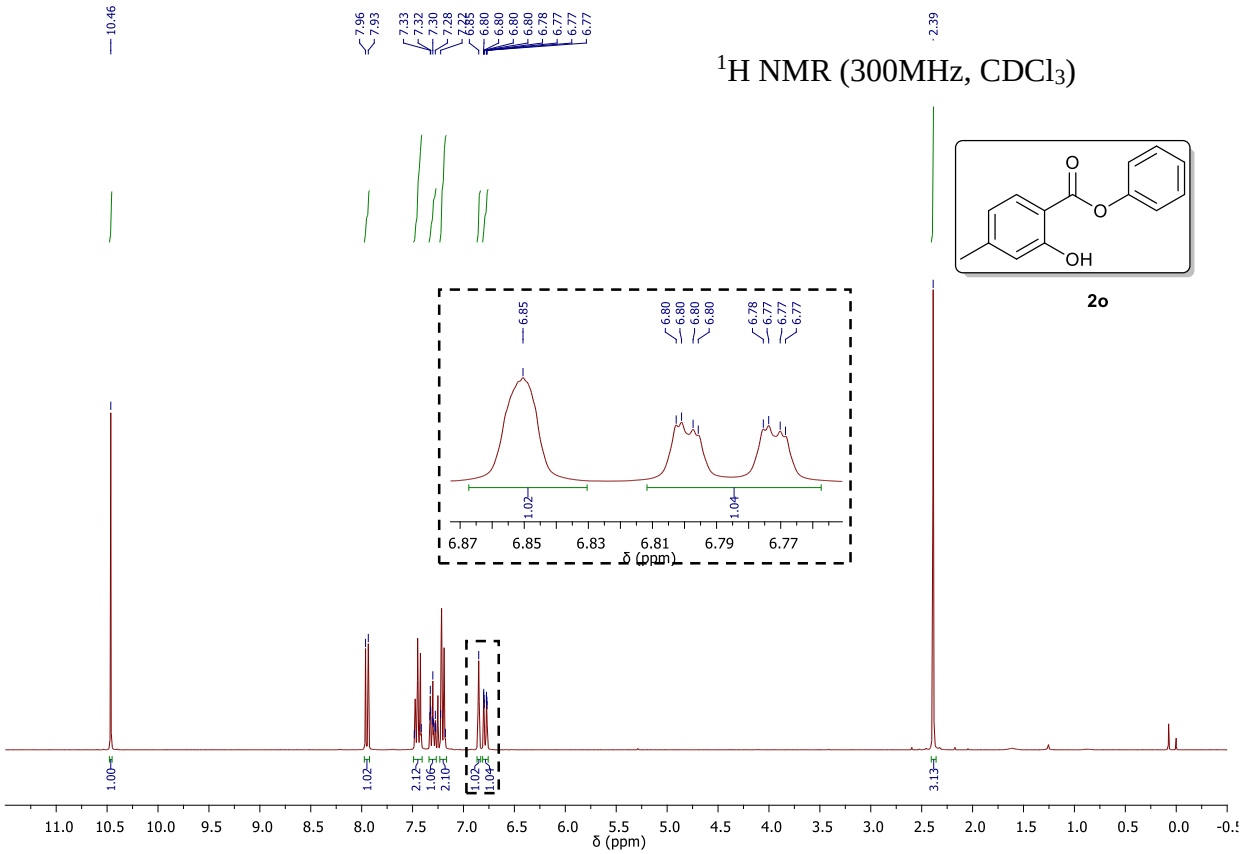


2n

^{13}C NMR (101MHz, $CDCl_3$)

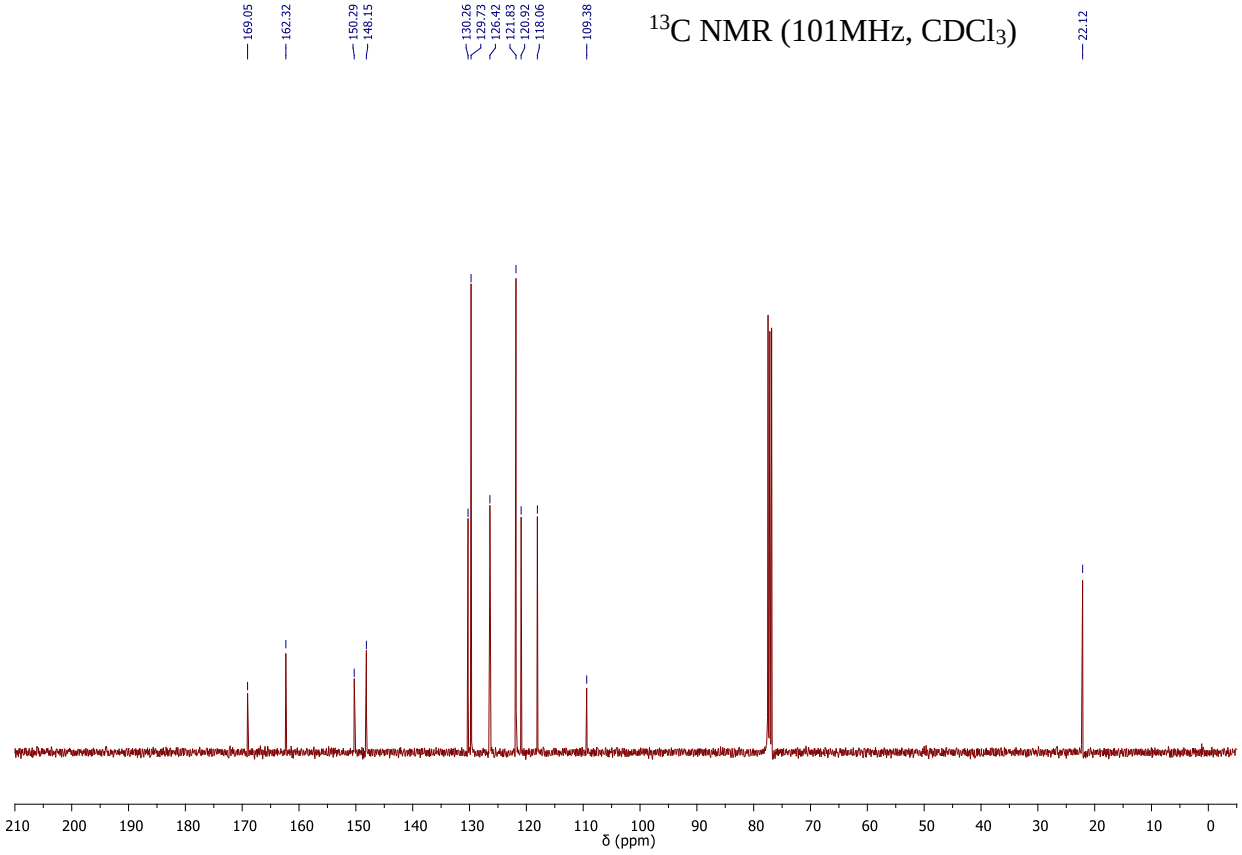


^{1}H NMR (300MHz, $CDCl_3$)

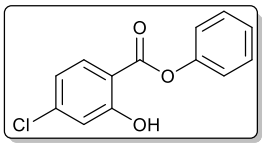


2o

^{13}C NMR (101MHz, $CDCl_3$)

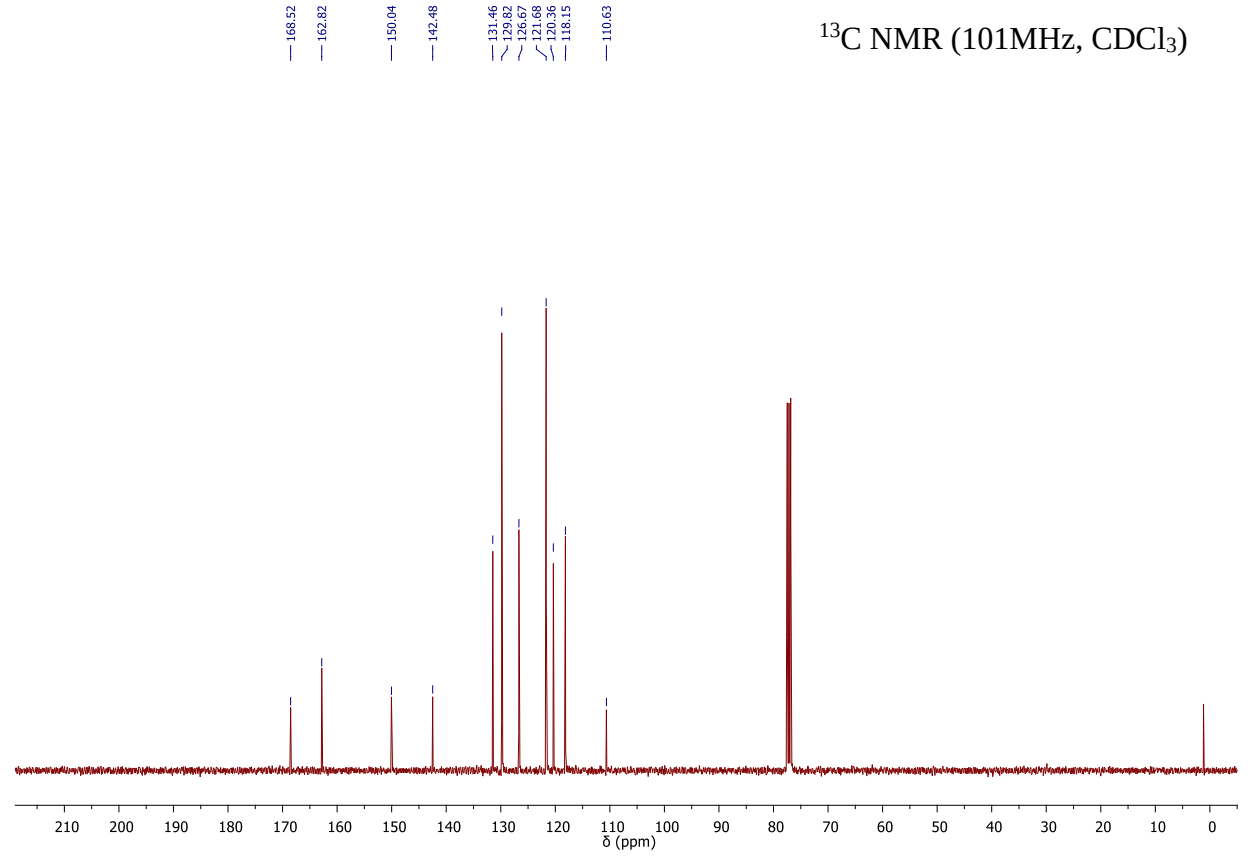


^{1}H NMR (400MHz, $CDCl_3$)

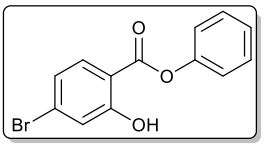


2p

^{13}C NMR (101MHz, $CDCl_3$)

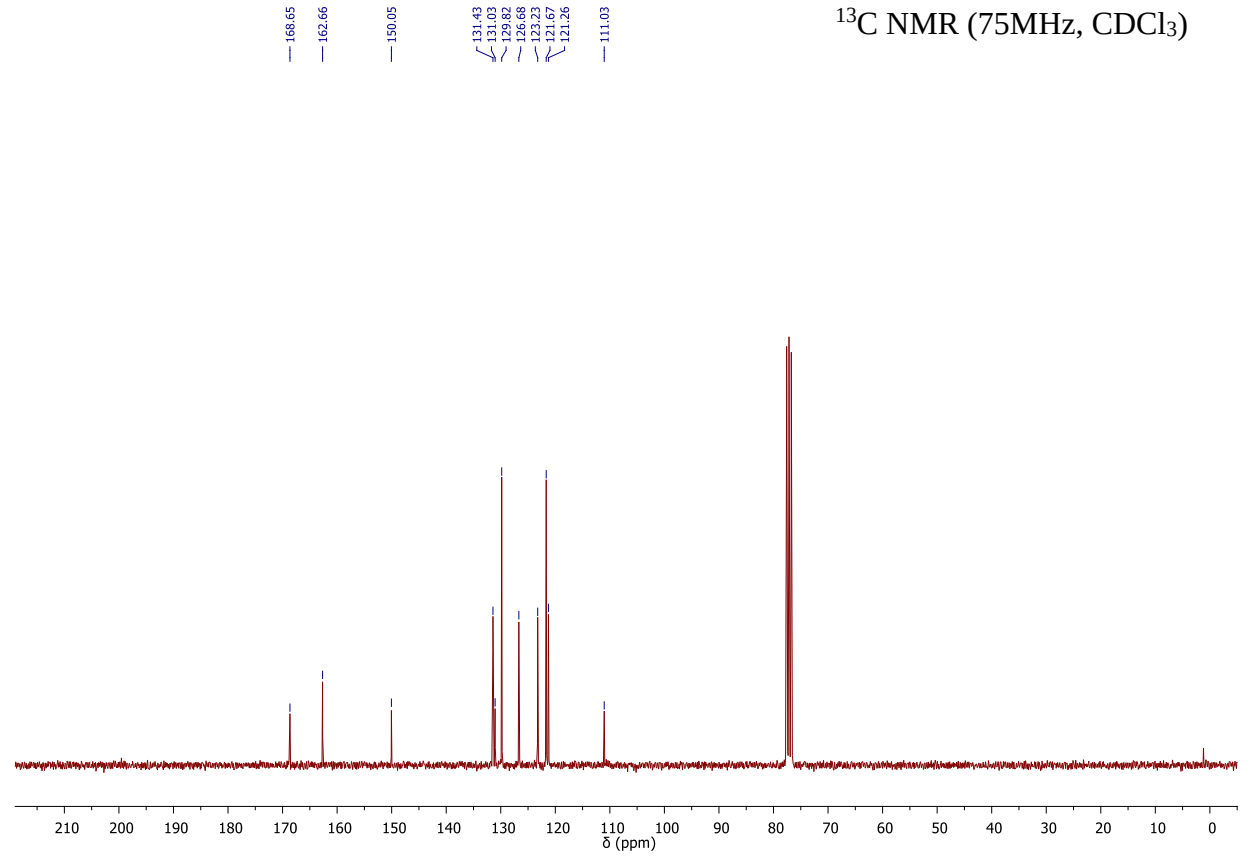


^{1}H NMR (400MHz, $CDCl_3$)

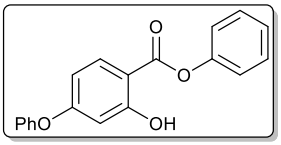


2q

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

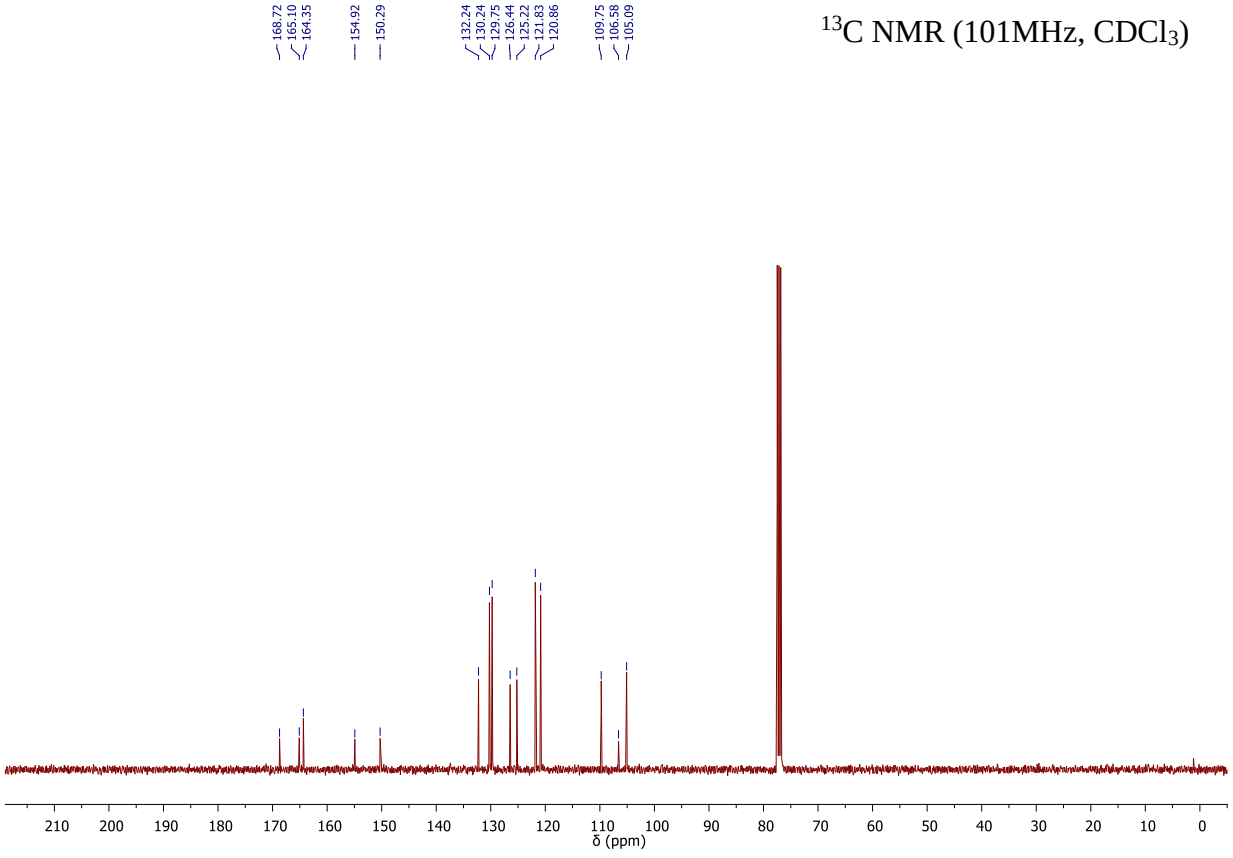


^{1}H NMR (300MHz, $CDCl_3$)

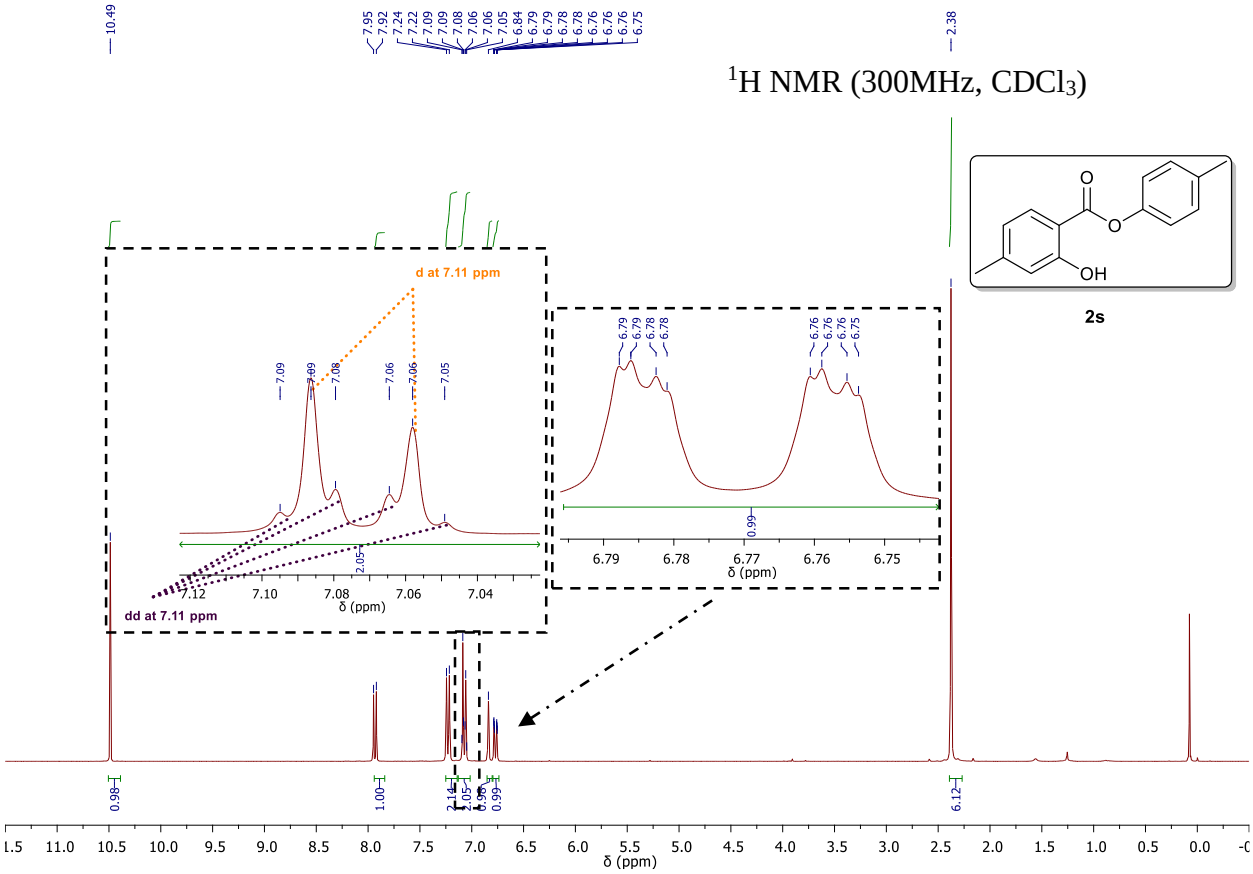


2r

^{13}C NMR (101MHz, $CDCl_3$)

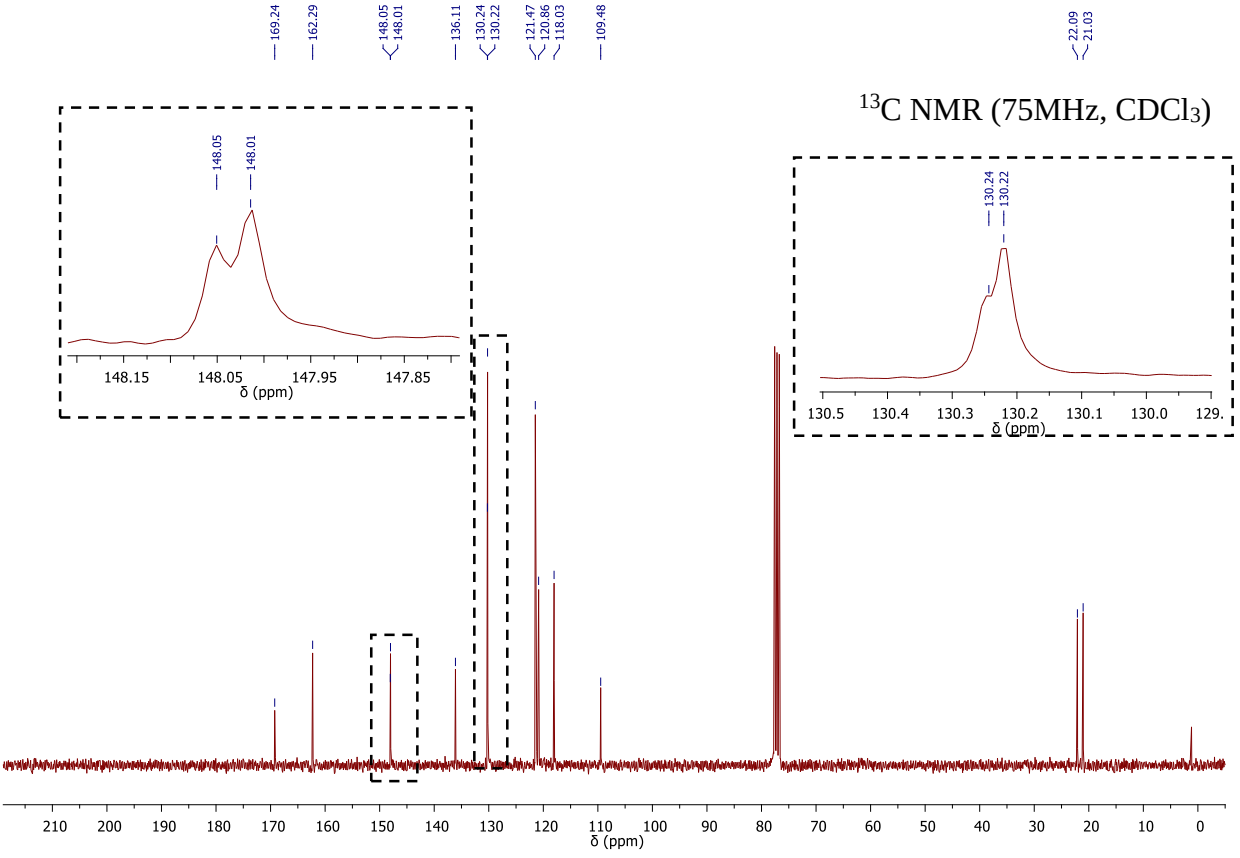


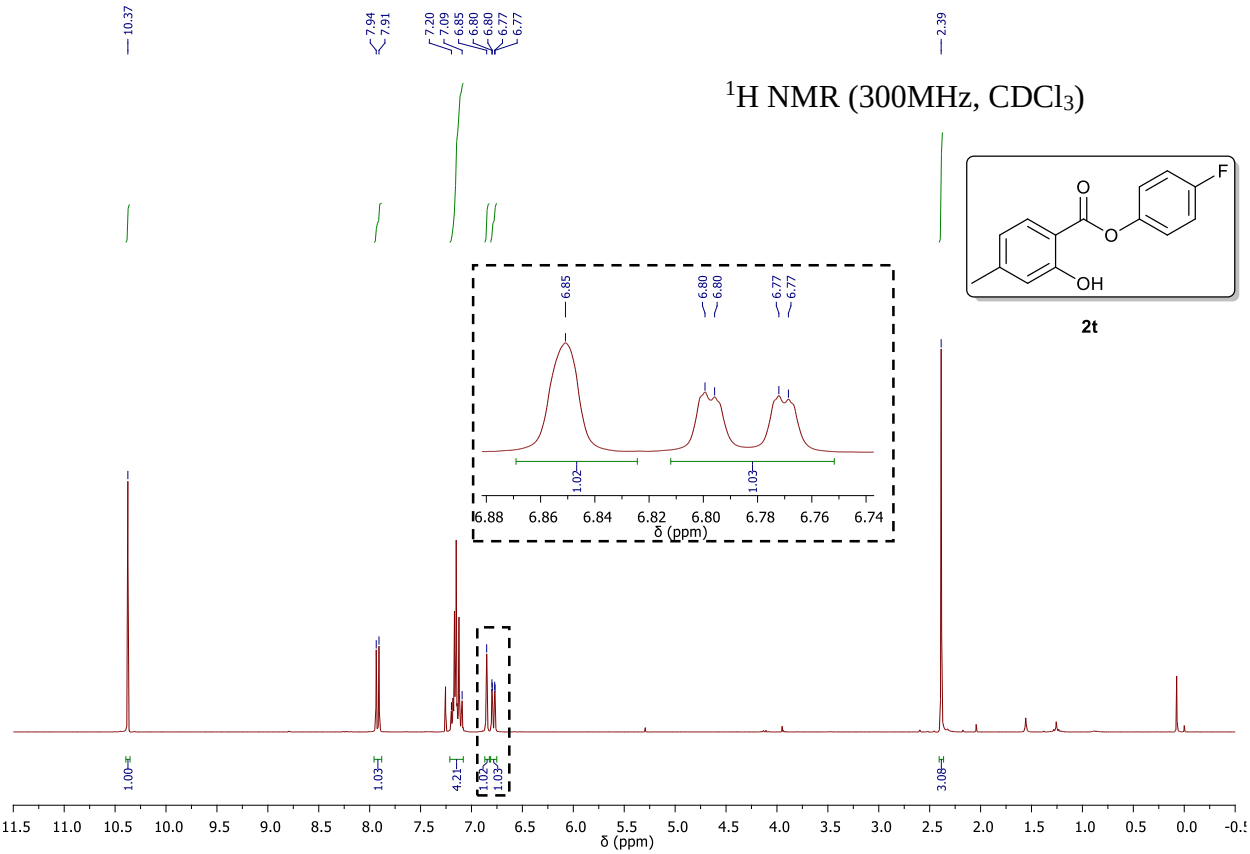
^{1}H NMR (300MHz, $CDCl_3$)

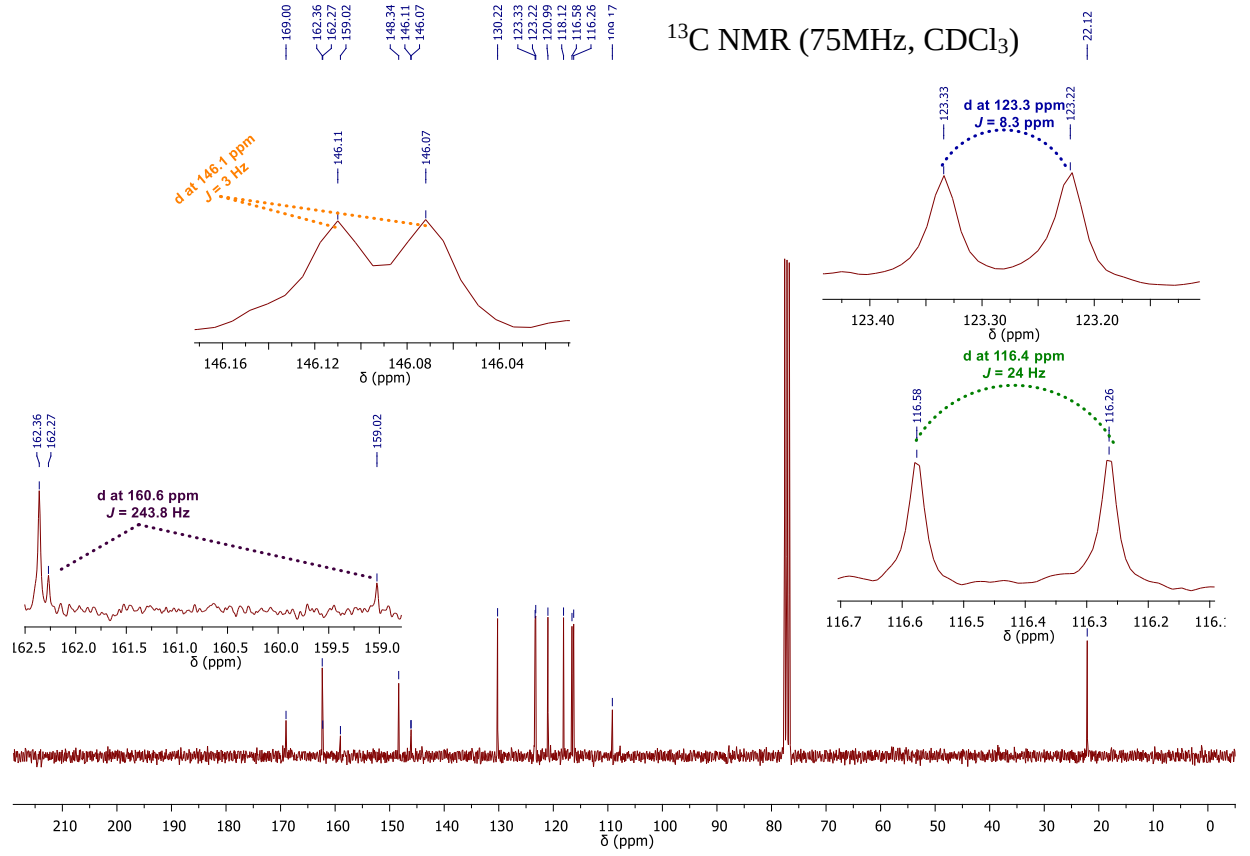


2s

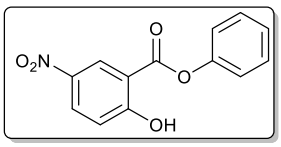
^{13}C NMR (75MHz, $CDCl_3$)




^{1}H NMR (300MHz, $CDCl_3$)
2t
δ (ppm)

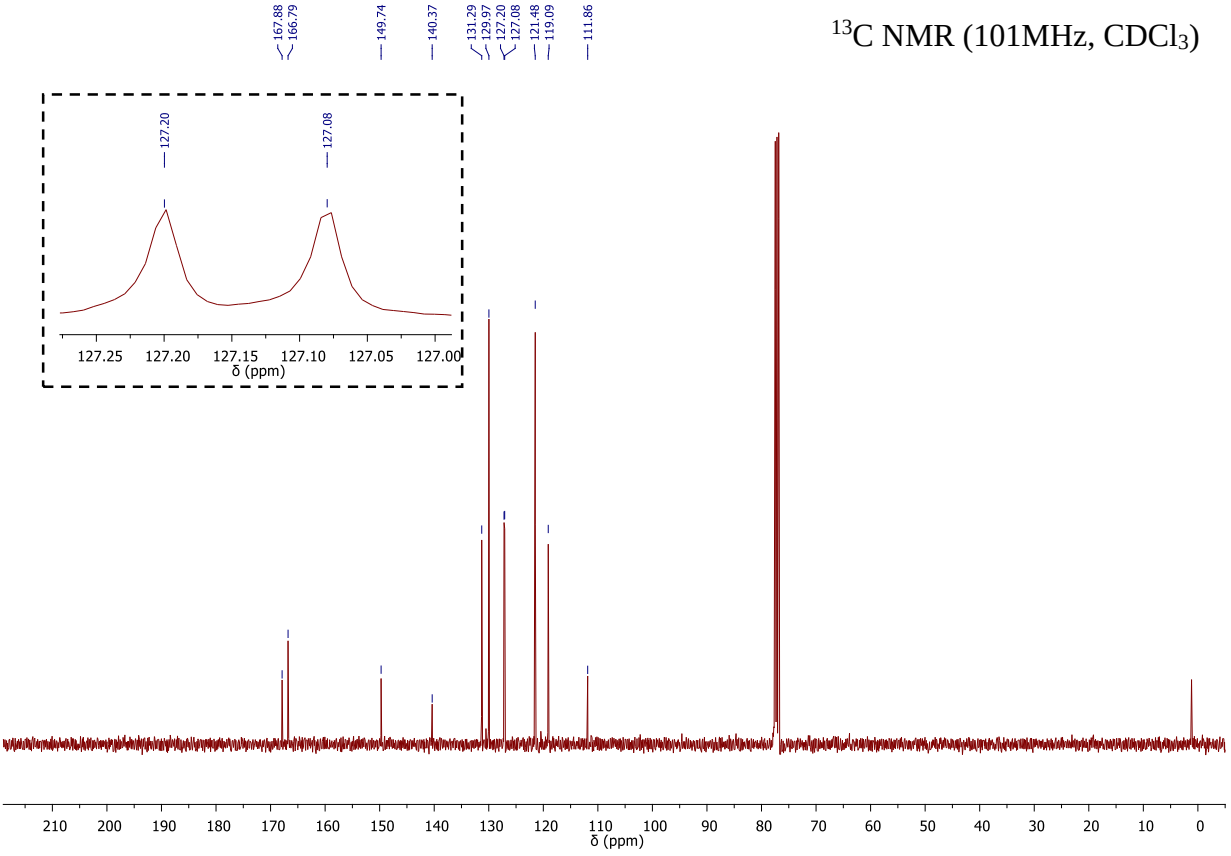

^{13}C NMR (75MHz, $CDCl_3$)
d at 146.1 ppm
J = 3 Hz
d at 123.3 ppm
J = 8.3 ppm
d at 160.6 ppm
J = 243.8 Hz
d at 116.4 ppm
J = 24 Hz
δ (ppm)

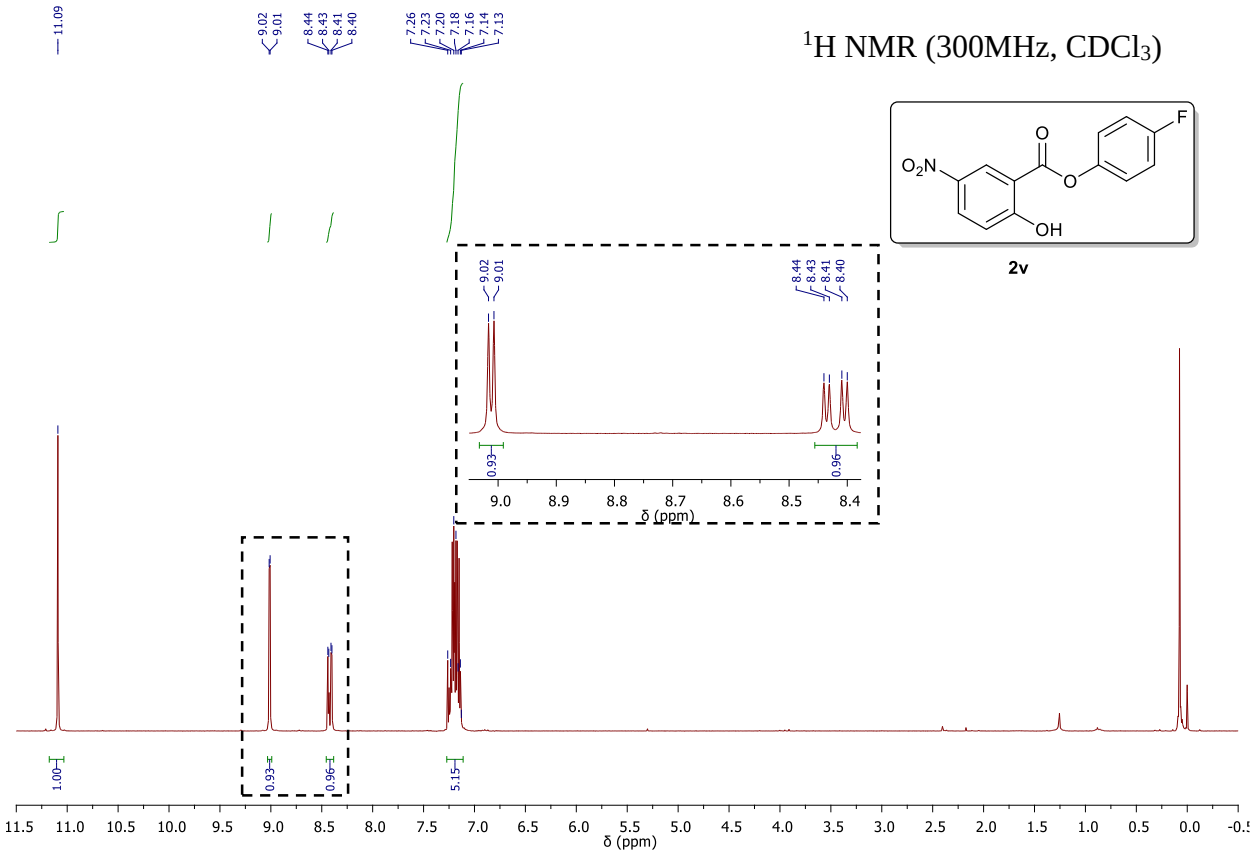
^{1}H NMR (300MHz, $CDCl_3$)

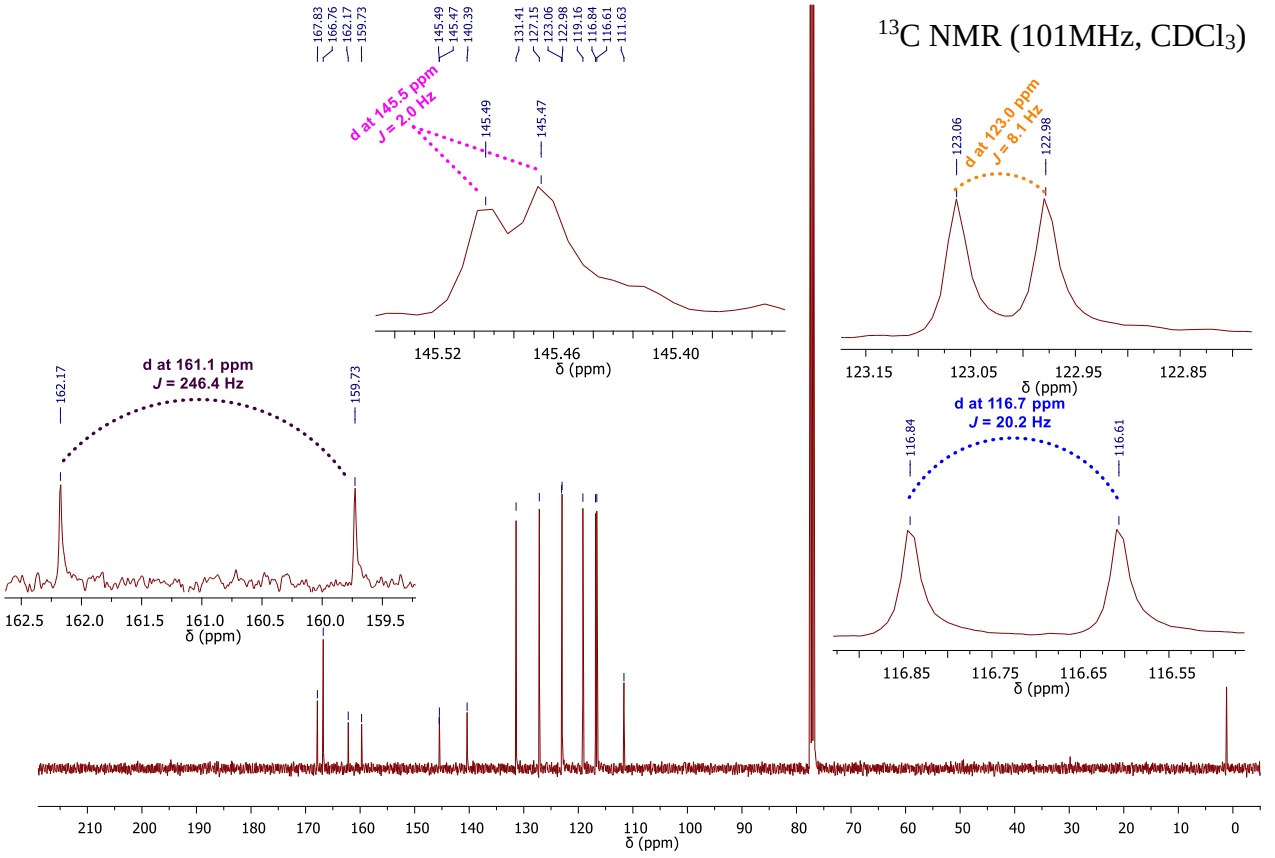


2u

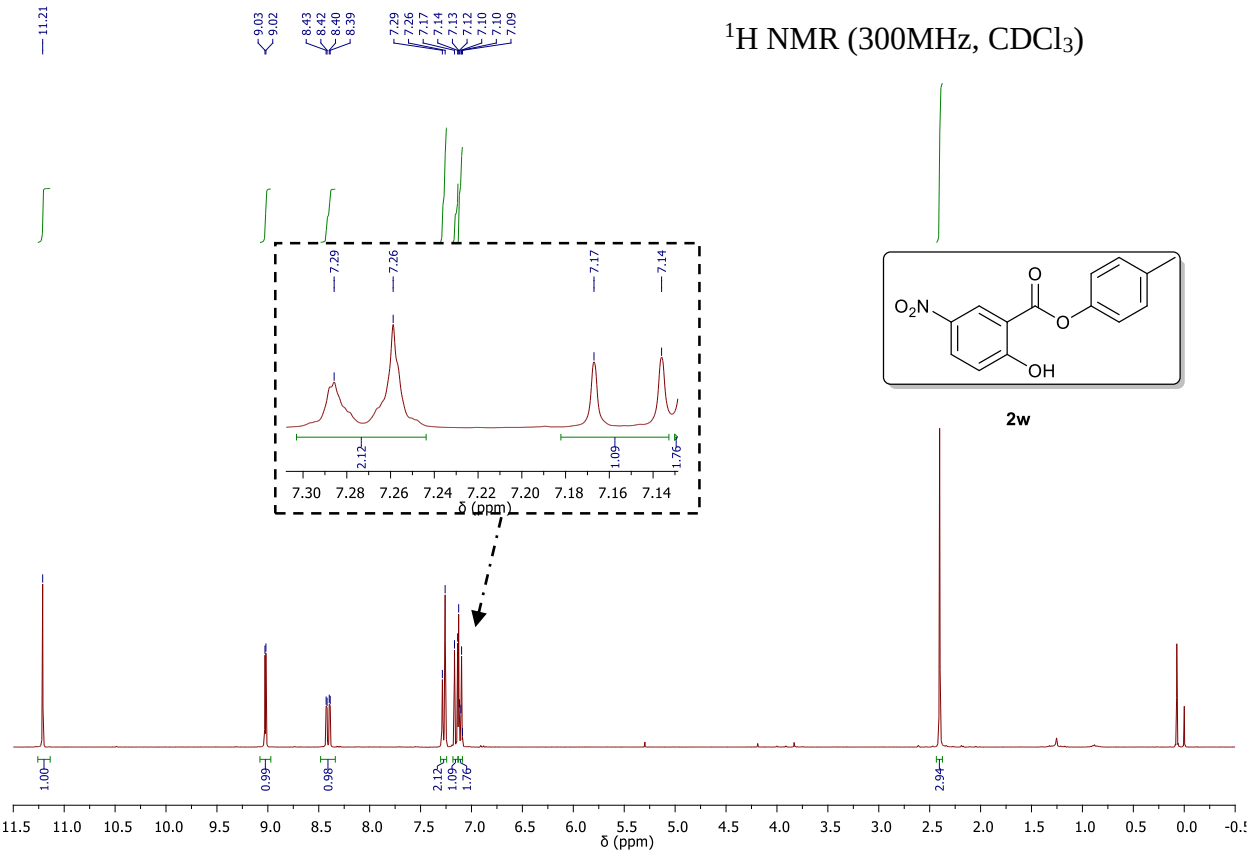
^{13}C NMR (101MHz, $CDCl_3$)




^{1}H NMR (300MHz, CDCl$_3$)
2v
δ (ppm)


^{13}C NMR (101MHz, CDCl$_3$)
d at 145.5 ppm
J = 2.0 Hz
d at 123.0 ppm
J = 8.1 Hz
d at 161.1 ppm
J = 246.4 Hz
d at 116.7 ppm
J = 20.2 Hz
δ (ppm)

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



^{13}C NMR (101MHz, $CDCl_3$)