Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Cerium photocatalyzed dehydrogenative lactonization of 2-arylbenzoic acids

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General Considerations:

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All reactions were conducted in 10 ml crimp glass vials. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization via TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (100-200 mesh) using a proper eluent system. NMR spectra were recorded in chloroform-d at 300, 400 and 500 MHz for ^{1}H NMR spectra and 75, 100 or 125 MHz for ^{13}C NMR spectra. ^{19}F NMR NMR spectra were recorded in chloroform-d at 377 MHz. Chemical shifts are quoted in parts per million referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; dd, doublet of doublets; td, triplet of doublets; m, multiplet. Coupling constants, J, are reported in hertz. For ^{13}C NMR, chemical shifts are reported in parts per million referenced to the center of a triplet at 77.0 ppm of chloroform-d. FTIR spectra were recorded on KBr thin film. High-resolution mass spectra (HRMS) [ESI^{+}] were obtained using either a TOF or a double-focusing spectrometer. All carboxylic acids was synthesized according to the literature.[1]

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

Synthesis and characterization of 2-aryl-carboxylic acids:

2-aryl-carboxylic acids **1c, 1h**, **1q** were prepared according to known literature procedure[1]

2-aryl-carboxylic acids **1d, 1v**, **1w** were prepared according to known literature procedure[2]

2-aryl-carboxylic acids **1e-f**, **1l-m, 1u** were prepared according to known literature procedure[3]

2-aryl-carboxylic acids **1g, 1j** were prepared according to known literature procedure[4]

2-aryl-carboxylic acid **1i** was prepared according to known literature procedure[5]

2-aryl-carboxylic acid **1k** was prepared according to known literature procedure[6]

2-aryl-carboxylic acid **1p** was prepared according to known literature procedure[7]

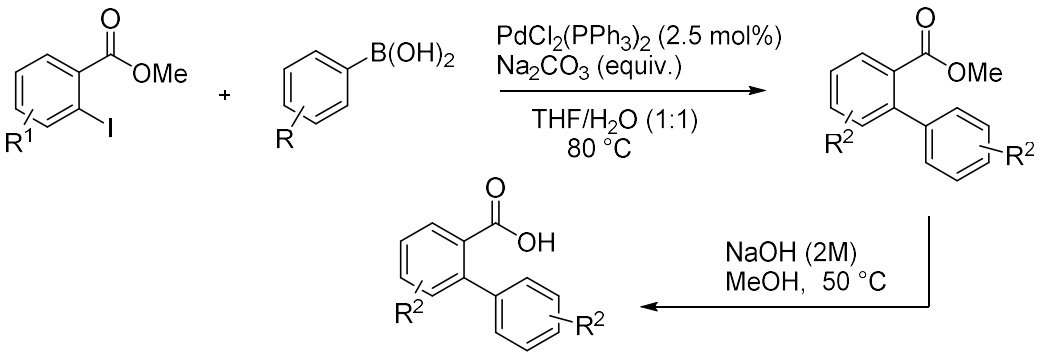
2-aryl-carboxylic acid **1r** was prepared according to known literature procedure[8]

2-aryl-carboxylic acid **1z** was prepared according to known literature procedure[9]

2-aryl-carboxylic acids **1aa-1ac** were prepared according to known literature procedure[10]

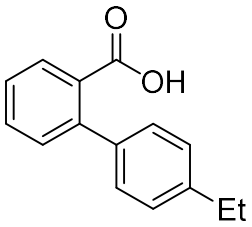
Synthesis of compounds 1b, 1n, 1o, 1s, 1t, 1x, 1y

General procedure for the synthesis of other biaryl 2-carboxylic acids using Suzuki Cross-coupling reaction (Scheme 1).[3]

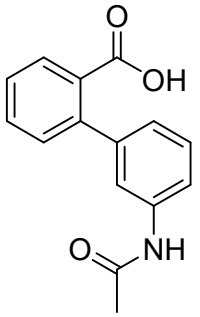


To a 25 ml RBF was charged with arylboronic acid (2.1 mmol, 1.05 equiv.), methyl 2-iodobenzoate (2 mmol), Na_2CO_3 (2 equiv.) $PdCl_2(PPh_3)_2$ (5 mol%) and degassed THF/H_2O (1:1) ration (5 ml). The reaction mixture was heated at 80 ºC for 12 h under N_2 atmosphere. The resultant mixture was extracted with EtOAc (3 × 10 mL). The combined layers were washed with brine (1 × 5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (95:5 Hexane/EtOAc) to provide the corresponding methyl esters as pale yellow oils.

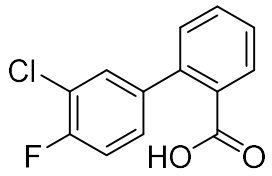
A NaOH aqueous solution (5 mL, 4 M) was added to a stirring mixture of the desired ester (1.8 mmol) in MeOH (5 mL). The reaction mixture was heated to 60 ºC, observing complete hydrolysis by TLC after 12 h. The reaction mixture was concentrated under reduced pressure. The residue was quenched with 5 M HCl until pH < 3 and was extracted with EtOAc (3 × 10 mL). The combined layers were washed with brine (1 × 5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford the desired pure biaryl 2-carboxylic acids.



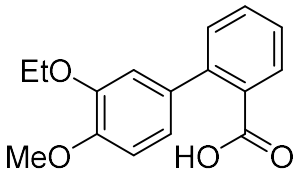
4'-ethyl-[1,1'-biphenyl]-2-carboxylic acid (1b) was prepared from 4-ethylphenylboronic acid following the general procedure described above, obtained **1b** as a white solid (380 mg, 84% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) 7.94 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.42-7.37 (m, 2H), 7.28-7.22 (m, 4H), 2.70 (q, J = 7.5 Hz, 2H), 1.29 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.57, 143.40, 138.25, 132.06, 131.29, 130.70, 129.38, 128.47 (2C), 127.68 (2C), 127.00, 28.58, 15.38.



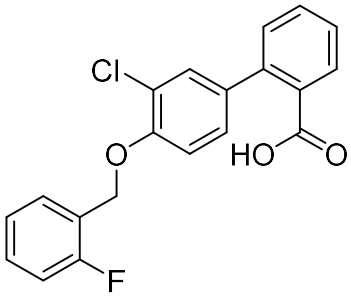
3'-acetamido-[1,1'-biphenyl]-2-carboxylic acid (1o) was prepared from (3-acetamidophenyl)boronic acid following the general procedure described above, obtained **1o** as a white solid (340 mg, 66% over two steps). ^{1}H NMR (400 MHz, CD_3OD) 7.70 (d, J = 7.6 Hz, 1.2 Hz, 1H), 7.48-7.42 (m, 3H), 7.70 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.26 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.20 (t, J = 8 Hz, 1H), 6.97-6.94 (m, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.3, 142.0, 141.9, 138.4, 131.8, 130.8, 130.4, 129.2, 128.07, 126.9, 124.0, 119.8, 118.5, 22.5.



3'-chloro-4'-fluoro-[1,1'-biphenyl]-2-carboxylic acid (**1s)** was prepared from 3-chloro-4-fluoro phenylboronic acid following the general procedure described above, obtained **1r** as a white solid (400 mg, 80% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) 8.6 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 8.51 (td, J = 7.6, 1.2 Hz, 1H), 7.43 (td, J = 7.6, 1.2 Hz, 1H), 7.3 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.18-7.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 157.0 (d, JC-F = 247 Hz), 141.40, 138.3 (d, JC-F = 3 Hz),, 132.5, 131.2, 131.1, 130.5, 128.9, 128.4 (d, JC-F = 7 Hz), 127.93, 120.5 (d, JC-F = 18 Hz), 116.1 (d, JC-F = 21 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -117.7.

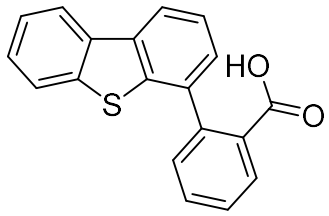


3'-ethoxy-4'-methoxy-[1,1'-biphenyl]-2-carboxylic acid (**1t)** was prepared from 3-ethoxy-4-methoxy-phenylboronic acid following the general procedure described above, obtained **1s** as a white solid (410 mg, 75% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) 7.91 (dd, J = 7.6, 0.8 Hz, 1H), 7.54 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.42-7.37 (m, 2H), 6.89-6.87 (m, 3H), 4.10 (q, J = 6.8 Hz, 2H), 3.91 (s, 3H), 1.24 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.18, 148.92, 147.77, 142.90, 133.58, 131.96, 131.15, 130.52, 129.50, 126.96, 120.81, 113.56, 111.20, 64.34, 55.95, 14.78.



3'-chloro-4'-((2-fluorobenzyl)oxy)-[1,1'-biphenyl]-2-carboxylic acid (**1x)** was prepared from (3-chloro-4-((2-fluorobenzyl)oxy)phenyl)boronic acid following the general procedure described above, obtained **1x** as a white solid (500 mg, 70% over two steps).^{1}H NMR (400

MHz, $CDCl_3$) 7.96 (dd, J = 7.6, 1.6 Hz, 1H), 7.52 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.55 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.42 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.39 (d, J = 2.2 Hz, 1H), 7.34-7.28 (m, 2H), 7.20-7.17 (m, 2H), 7.11-7.01 (m, 2H), 5.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.0 (d, J = 247 Hz), 153.41, 1418, 134.9, 132.3, 131.2, 130.9, 130.4, 129.7 (d, JC-F = 8 Hz), 129.4 (d, JC-F = 3.0 Hz), 129.1, 127.98, 127.46, 124.4 (d, JC-F = 2 Hz), 123.7 (d, JC-F = 14Hz), 122.93, 115.2 (d, JC-F = 21.2 Hz) 113.48, 64.65 (d, JC-F = 4.4 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -118.8.



2-(dibenzo[b,d]thiophen-4-yl)benzoic acid (1y) was prepared from dibenzo[*b,d*]thiophen-4-ylboronic acid following the general procedure described above, obtained **1y** as a white solid (500 mg, 82% over two steps). ^1H NMR (500 MHz, $CDCl_3$) 8.18-8.16 (m, 1H), 8.12-8.10 (dd, J = 7.6, 1.2 Hz, 1H), 8.04 (dd, J = 7.6, 1.2 Hz, 1H), 7.76-7.75 (m, 1H), 7.65-7.62 (m, 1H), 7.52-7.41 (m, 5H), 7.28 (dd, J = 7.6, 1.2 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.94, 141.68, 139.57, 139.31, 136.41, 135.92, 135.55, 132.77, 131.41, 131.08, 129.09, 128.28, 126.70, 126.65, 124.62, 124.40, 122.76, 121.83, 120.54.

Optimization details:

General procedure for screening reactions: A 10 mL glass vial was charged with biphenyl 2-carboxylic acid (0.2 mmol), Ce-photocatalyst (10 mol%), $NaHCO_3$ (2 equiv.) and a PTFE-coated stirring bar. Solvent (1 mL) was added. The glass vial was sealed with a PTFE septum and the reaction was opened to air via a needle. The reactions were placed in a pre-programed temperature (25°C) controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED. After 20 hours, a sample of this solution was analyzed by ^1H NMR using trimethoxy benzene as the internal standard to determine the yield.

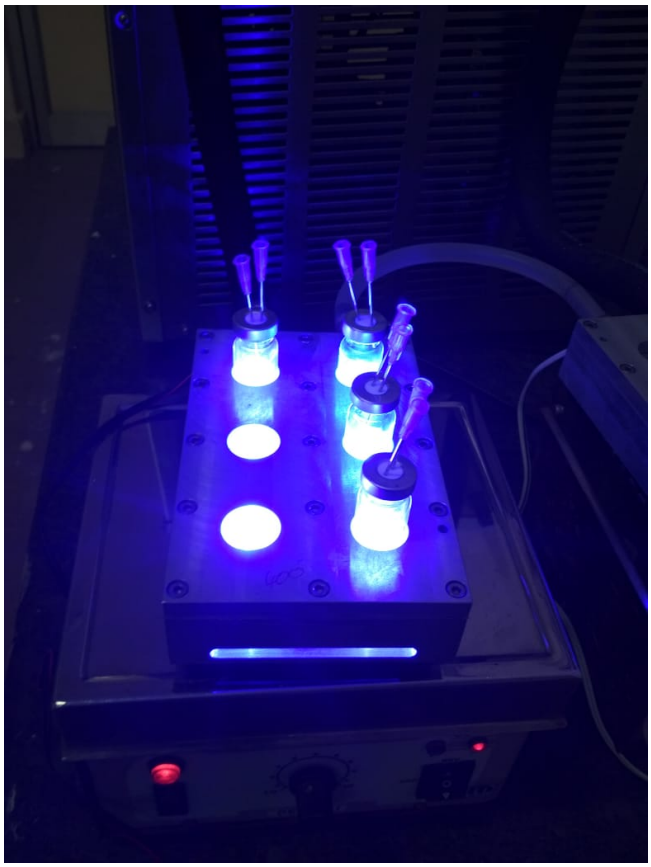
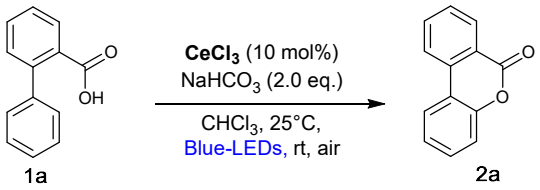


Figure 1: Blue LED reactor with magnetic stirring plate

Table S1: Screening of Solvents

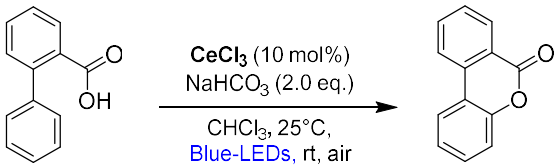


1a 2a

Entry	Deviation from standard conditions	3a (%)[a]
1	***none***	*95(90)*[b]
2	**CH_3CN** instead of **$CHCl_3$**	85
3	**DMSO** instead of **$CHCl_3$**	56
4	**THF** instead of **$CHCl_3$**	62
5	**EtOAc** instead of **$CHCl_3$**	92
6	**DCM** instead of **$CHCl_3$**	60
7	**Toulene** instead of **$CHCl_3$**	75
8	**Acetone** instead of **$CHCl_3$**	90
9	**Dioxane** instead of **$CHCl_3$**	68
10	**DCE** instead of **$CHCl_3$**	63
11	**DMF** instead of **$CHCl_3$**	56
12	**DMA** instead of **$CHCl_3$**	49

[a]Determined by ^{1}H NMR, using trimethoxy benzene as internal standard

Table S2: Screening of other reaction parameters

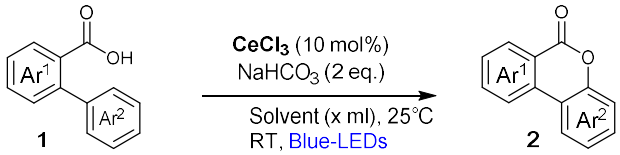


1a 2a

Entry	Deviation from standard conditions	3a (%)[a]
1	**$CeCl_3 \cdot 7H_2O$** instead of **$CeCl_3$**	85
2	$(NH_4)_2Ce(NO_3)_6$ instead of **$CeCl_3$**	60
3	$(^tBu_4)_2CeCl_6$ instead of **$CeCl_3$**	80
4	**K_2CO_3** instead of **$NaHCO_3$**	66
5	**Cs_2CO_3** instead of **$NaHCO_3$**	25
6	**Na_2CO_3** instead of **$NaHCO_3$**	54
7	**KH_2PO_4** instead of **$NaHCO_3$**	0
8	**with 1.0 equiv. of base**	80
9	**without base**	60
10	**Blue Leds (410 nm)**	90
11	with 2.0 eq. of$(NH_4)_2S_2O_8$ instead of air	6
12	with 2.0 eq. of $K_2S_2O_8$ instead of air	4
13	with O2 ballon	78
14	Under nitrogen	6
15	without light	0
16	without **$CeCl_3$**	0

[a]Determined by ^{1}H NMR, using trimethoxy benzene as internal standard

General procedure for Dehydrogenative lactonization of 2-Aryl carboxylic acids

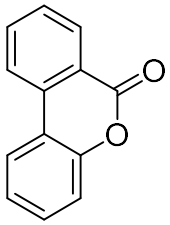


General procedure (GP1): A 10 mL glass vial equipped with a teflon-coated stirring bar was charged with carboxylic acid **1a-1ad** (0.2 mmol), $CeCl_3$ (10 mol%), $NaHCO_3$ (2 equiv.). Solvent (2 mL) was added. The glass vial was sealed with a PTFE septum and the reaction was opened to air via a needle. The reaction was placed in a pre-programed temperature (25°C) controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED. After 24 hours, the reaction mixture was concentrated under reduced pressure. The product **2a-2ad** was purified by flash chromatography on silica using hexane/EtOAc.

Visual representation of the reaction set-up

Figure 1: Visual representation of the reaction set-up.

Synthesis and characterization of products:

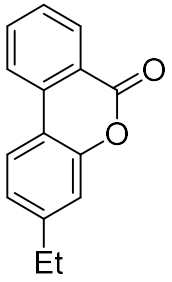


6*H*-benzo[*c*]chromen-6-one (3a): Following the general procedure **GP1**, two reactions of **1a** (0.2 mmol each one) afforded **2a** as an off-white solid in 90% yield (70.5 mg). Mp. = 88-89 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 7.9 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.83 (td, *J* = 7.8, 10 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.50-7.47 (m, 1H), 7.38- 7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 151.4, 134.9, 134.9, 130.7, 130.6, 129.0, 124.7, 122.9, 121.8, 121.4, 118.1, 117.9. The analytical data are consistent with published ones.[3]

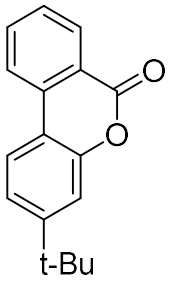
Set up for gram scale reaction

For gram scale reaction the **1a** (5 mmol) and the reaction time was increased to 72 hours yielded **2a** in 70% yield.

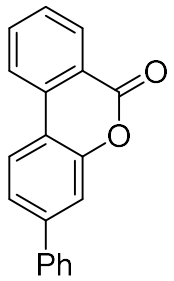
Set up for gram scale reaction



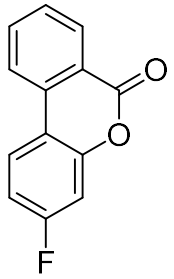
3-ethyl-6*H*-benzo[*c*]chromen-6-one (2b): Following the general procedure **GP1**, two reactions of **1b** (0.2 mmol each one) afforded **2b** as an off-white solid in 67% yield (60.0 mg). Mp:69-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (m, 2H), 8.09 (d, 1H, 7.8 Hz), 7.83-7.79 (m 1H), 7.57-7.54 (m, 1H), 7.21-7.18 (m, 2H), 2.75 (q, 7.6 Hz, 2H), 1.30 (t, 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 151.4, 147.6, 135.1, 134.8, 130.6, 128.4, 124.5, 122.6, 121.5, 121.1, 116.7, 115.7, 28.7, 15.2. IR (KBr):1739, 1620, 1474, 1267, 1107. HRMS (ESI): m/z calcd for $C_{15}H_{13}O_2$ (M+H)+ : 224.0837, found: 225.0900.



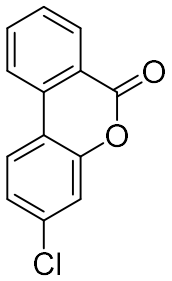
3-(tert-butyl)-6*H*-benzo[*c*]chromen-6-one (2c) Following the general procedure **GP1**, two reactions of **1c** (0.2 mmol each one) afforded **2c** as an off-white solid in 73% yield (73.0 mg). Mp: 150-152 °C. and analytical data are consistent with published ones.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 7.9 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.37-7.35 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 154.7, 151.2, 134.9, 134.8, 130.5, 128.4, 122.4, 122.0, 121.5, 121.0, 115.4, 114.5, 35.1, 31.1. The analytical data are consistent with published ones.[1]



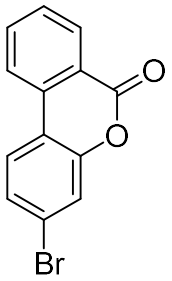
3-phenyl-6*H*-benzo[*c*]chromen-6-one (2d): Following the general procedure **GP1**, two reactions of **1d** (0.2 mmol each one) afforded **2d** as an off-white solid in 81% yield (88.0 mg). Mp. = 113-114 °C. The analytical data are consistent with published ones.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 7.9 Hz, 1H), 8.06 (dd, J = 10.7, 8.5 Hz, 2H), 7.80 (td, J = 7.7, 1.4 Hz, 1H), 7.61-7.40 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.3, 151.6, 143.5, 139.2, 134.9, 134.6, 130.6, 129.1 (2C), 128.8, 128.3, 127.1 (2C), 123.3, 123.2, 121.7, 121.1, 116.9, 115.8.



3-fluoro-6*H*-benzo[*c*]chromen-6-one (2e): Following the general procedure **GP1**, two reactions of **1e** (0.2 mmol each one) afforded **2e** as an off-white solid in 87% yield (74.0 mg). Mp. = 153-154 °C. The analytical data are consistent with published ones.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, J = 8.0, 1.0 Hz, 1H), 8.07-8.05 (m, 2H), 7.86-7.82 (m, 1H), 7.61-7.57 (m, 1H), 7.11-7.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7 (d, JC-F = 252 Hz), 160.8, 152.1 (d, JC-F = 12.1 Hz), 135.1, 134.3, 130.7, 128.8, 124.4 (d, JC-F = 9.1 Hz), 121.5, 120.4, 114.6 (d, JC-F = 3.0 Hz), 112.5 (d, JC-F = 22.2 Hz), 105.3 (d, JC-F = 25.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -108.34.

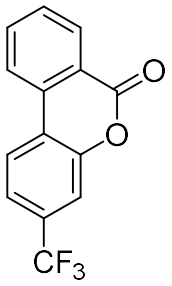


3-chloro-6*H*-benzo[*c*]chromen-6-one (2f): Following the general procedure **GP1**, two reactions of **1f** (0.2 mmol each one) afforded **2f** as an off-white solid in 89% yield (81 mg). Mp.= 145-146 ^{o}C. The analytical data are consistent with published ones.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, J = 7.9 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.85-7.80 (m, 1H), 7.62-7.59 (m, 1H), 7.37-7.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.6, 151.6, 135.9, 135.1, 134.0, 130.7, 129.2, 125.1, 123.8, 121.7, 120.9, 118.1, 116.7.

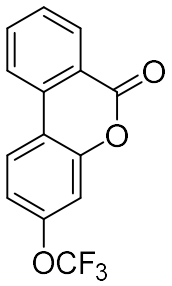


3-bromo-6*H*-benzo[*c*]chromen-6-one (2g): Following the general procedure **GP1**, two reactions of **1g** (0.2 mmol each one) afforded **2g** as an off-white solid in 91% yield (99.0 mg). Mp. = 151-152 ^{o}C. The analytical data are consistent with published ones.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J = 8.0, 1.4 Hz, 1H), 8.09-8.07 (m, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.84 (ddd, J = 8.2, 7.4, 1.5 Hz, 1H), 7.61 (ddd, J = 8.2, 7.3, 1.1 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.46 (dd, J = 8.5, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 151.5, 135.1, 134.0, 130.8, 129.3, 127.9, 124.0, 123.7, 121.7, 121.0, 120.9, 117.1.

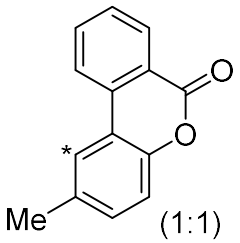
For gram scale **1g** (3.6 mmol) and the reaction time was increased to 72 hours yielded **2g** in 70% yield.



3-(trifluoromethyl)-6*H*-benzo[*c*]chromen-6-one (2h): Following the general procedure **GP1**, two reactions of **1h** (0.2 mmol each one) afforded **2h** as an off-white solid in 85% yield (89.7 mg). Mp. = 123-124 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 7.9 Hz, 1H), 8.11 (t, J = 8.1 Hz, 2H), 7.84-7.81 (m, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 151.0 ,135.2, 133.4, 132.8 (q, *J* = 33.5 Hz), 131.7, 130.9, 124.7, 124.7 (q, *J* = 273.0), 122.2, 121.9, 121.7, 121.2 (q, *J* = 3.4 Hz), 115.3 (q, *J* = 4.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.82. The analytical data are consistent with published ones.[1]

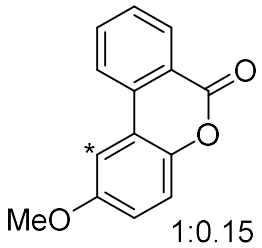


3-(trifluoromethoxy)-6*H*-benzo[*c*]chromen-6-one (2i): Following the general procedure **GP1**, two reactions of **1i** (0.2 mmol each one) afforded **2i** as an off-white solid in 83% yield (92.0 mg), and analytical data are consistent with published ones.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4-8.39 (m, 1H), 8.09-8.07 (m, 2H), 7.86 (m, 1H), 7.64-7.60 (m, 1H), 7.25-7.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 151.8, 150.2, 135.2, 133.8, 130.8, 129.4, 124.2, 121.8, 121.6, 120.9 (q, J = 259 Hz), 117.0, 116.8, 110.2. ^{19}F NMR (377 MHz, $CDCl_3$): δ -57.85.

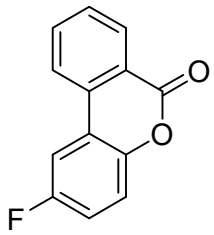


2-methyl-6*H*-benzo[*c*]chromen-6-one (2j): Following the general procedure **GP1**, two reactions of **1j** (0.2 mmol each one) afforded **2j** (1:1) as an off-white solid in 81% yield (68.0 mg), and analytical data are consistent with published ones.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.36 (m, 1H), 8.09-8.05 (m, 1H), 7.87-7.77 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.32-7.18 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.3, 149.3, 134.8, 134.7, 134.1, 131.3, 130.5, 128.7, 122.7, 121.6, 121.2, 117.6, 117.4, 21.1.

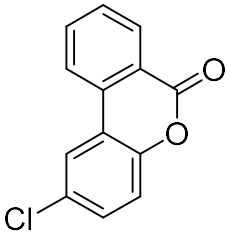
other isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.36 (m, 1H), 8.09-8.05 (m, 1H), 7.87-7.77 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.32-7.18 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.22, 149.62, 135.10, 137.7**,** 131.78, 130.43, 128.65, 127.00, 123.99, 121.86, 121.06, 120.38, 117.59, 16.00.



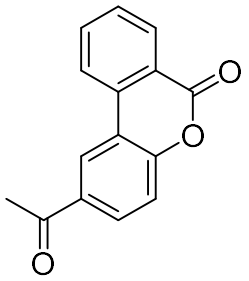
2-methoxy-6*H*-benzo[*c*]chromen-6-one (2k): Following the general procedure **GP1**, two reactions of **1k** (0.2 mmol each one) afforded **2k** (1:0.15) as an off-white solid in 76% yield (68.0 mg), and analytical data are consistent with published ones.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39-8.38 (m, 1H), 8.05-8.03 (m, 1H), 7.82-7.79 (m, 1H), 7.59-7.56 (m, 1H), 7.47-7.45 (m, 1H), 7.29-7.28 (m, 1H), 7.04-7.02 (m, 1H), 3.9 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.37, 156.40, 145.6, 134.7, 134.6, 130.6, 129.0, 121.3, 121.40, 118.6, 118.6, 117.20, 106.4, 55.9.



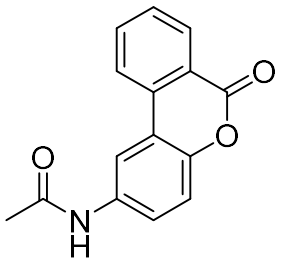
2-fluoro-6*H*-benzo[*c*]chromen-6-one (2l): Following the general procedure **GP1**, two reactions of **1l** (0.2 mmol each one) afforded **2l** as an off-white solid in 56% yield (48.0 mg), and analytical data are consistent with published ones.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.41 (d, J = 7.7 Hz, 1H), 8.04-8.02 (d, J = 8.0 Hz, 1H), 7.88-7.84 (t, J = 7.6 Hz, 1H), 7.73-7.71 (d, J = 8.8 Hz, 1H), 7.65-7.62 (t, J = 7.5 Hz, 1H), 7.37-7.34 (m, 1H), 7.22-7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 159 (d, JC-F = 241.7 Hz), 147.4, 135.0, 133.9, 130.7, 129.6, 121.9, 121.3, 119.3 (d, JC-F = 8.3 Hz), 119.2, 117.8 (d, JC-F = 24.3 Hz), 108.9 (d, JC-F = 24.7 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ -117.2.



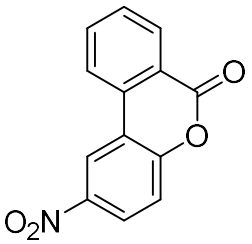
2-chloro-6*H*-benzo[*c*]chromen-6-one (2m): Following the general procedure **GP1**, two reactions of **1m** (0.2 mmol each one) afforded **2m** as an off-white solid in 84% yield (77.3 mg), and analytical data are consistent with published ones.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.0, 0.9 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 2.4 Hz, 1H), 7.83-7.63 (m, 1H), 7.66-7.61 (m, 1H), 7.44 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 149.7, 135.1, 133.6, 130.8, 130.4, 130.1, 129.2, 122.7, 121.8, 121.3, 119.4, 119.2.



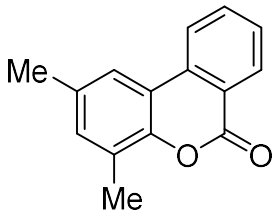
2-acetyl-6*H*-benzo[*c*]chromen-6-one (2n): Following the general procedure **GP1**, two reactions of **1n** (0.2 mmol each one) afforded **2n** as an off-white solid in 63% yield (60.0 mg). Mp:194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.69 (m, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 8.04 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.90-7.85 (m, 1H), 7.66-7.61 (m, 1H), 7.40 (dd, *J* = 8.8 Hz, 1H), 2.7 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 159.4, 153.2, 134.2, 133.0, 132.4, 129.7, 129.5, 128.6, 122.5, 121.0, 120.2, 117.2, 117.0, 25.63. IR (KBr):1737, 1682, 1610, 1362, 1265, 1093. HRMS (ESI): m/z calcd for $C_{15}H_{11}O_3$ (M+H)+ : 239.0630, found: 239.0692.



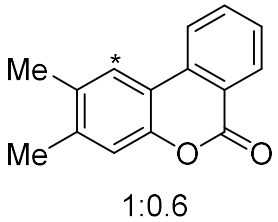
***N*-(6-oxo-6*H*-benzo[*c*]chromen-2-yl)acetamide (2o):** Following the general procedure **GP1**, two reactions of **1o** (0.2 mmol each one) DMSO+$CHCl_3$ (1:1) afforded **2o** as an off-white solid in 60% yield (59.0 mg). Mp:212-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.49 (m, 1H), 8.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.77-7.74 (m, 1H), 7.56-7.52 (m, 1H), 7.3-7.23 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.58, 160.16, 146.73, 133.91, 133.63, 133.48, 129.57, 128.16, 121.12 (2C), 120.26, 117.41, 117.13, 112.97, 23.63. IR (KBr): 1721, 1668, 1561, 1502, 1269. HRMS (ESI): m/z calcd for $C_{15}H_{12}NO_3$ (M+H)+ : 254.0739, found: 254.0799.



2-nitro-6*H*-benzo[*c*]chromen-6-one (2p): Following the general procedure **GP1**, two reactions of **1p** (0.2 mmol each one) in mixture of DMSO+$CHCl_3$ (1:1) afforded **2p** as an off-white solid in 30% yield (29.0 mg), and analytical data are consistent with published ones.[7] ^{1}H NMR (400 MHz, Acetone-d_6) 9.04 (d, J=2.55 Hz, 1H), 8.52 (d, J=7.9 Hz, 1H), 8.32 (d, J=9.05, 2.6 Hz, 1H), 8.27-8.25 (m, 1H), 7.96-7.92 (m, 1H), 7.72-7.68 (m, 1H), 7.52 (d, J=9.05 Hz, 1H), 2.68 (DMSO).



2,4-dimethyl-6*H*-benzo[*c*]chromen-6-one (2q): Following the general procedure **GP1**, two reactions of **1q** (0.2 mmol each one) afforded **2q** as an off-white solid in 80% yield (71.0 mg), and analytical data are consistent with published ones.[1] Mp. = 171-173 ºC.^{1}H NMR (400 MHz, $CDCl_3$) 8.38 (d, J=7.8 Hz, 1H), 8.07 (d, J=8.1Hz, 1H), 7.80-7.76 (m, 1H), 7.65 (s, 1H), 7.56-7.52 (m, 1H), 7.12 (s, 1H), 2.44 (s. 3H), 2.40 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$), 161.45, 147.75, 135.18, 134.63, 133.42, 132.84, 130.48, 128.49, 126.67, 121.80, 121.13, 120.35, 117.33, 21.08, 15.91. The analytical data are consistent with published ones.[1]

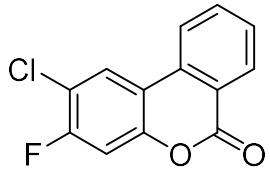


1:0.6

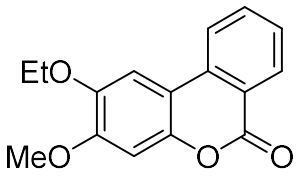
2**,3-dimethyl-6*H*-benzo[*c*]chromen-6-one (2r):** Following the general procedure **GP1**, two reactions of **1r** (0.2 mmol each one) afforded **2r** in 1:0.6 as an off-white solid in 84% yield (74.0 mg) and analytical data are consistent with published ones.[8] ^{1}H NMR (400 MHz, $CDCl_3$).8.35-8.32 (m, 1H), 8.03-7.99 (m, 1H), 7.77-7.69 (m, 2H), 7.52-7.47 (m, 1H), 7.09-

7.06 (m, 1H), 7.03 (1H, s), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 161.60, 149.5, 140.03, 135.03, 134.66, 133.09, 130.51, 128.19, 123.08, 121.36, 119.47, 118.20, 115.39, 20.02, 19.55.

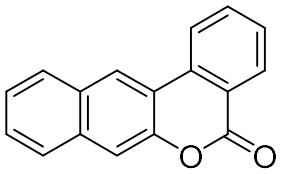
minor isomer: 161.53, 149.46, 139.81, 135.43, 130.36, 125.82, 125.24, 121.59, 120.98, 120.57, 115.52, 20.26, 11.83.



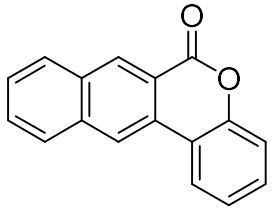
2-chloro-3-fluoro-6*H*-benzo[*c*]chromen-6-one (2s): Following the general procedure **GP1**, two reactions of **1s** (0.2 mmol each one) afforded **2s** as an off-white solid in 66% yield (65.0 mg). Mp:188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.40 (dd, J = 8.6, 2.3 Hz, 1H), 8.07 (d, J=7.9 Hz, 1H), 8.0 (d, J=9.05 Hz, 1H), 7.88-7.84 (m, 1H), 7.64-7.61 (m, 1H), 7.19 (d, J=9.05 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 159.26, 158.7 (d, JC-F = 253 Hz), 149.44 (d, JC-F = 11 Hz), 134.3, 132.2, 129.9, 128.4, 123.5, 120.6, 119.6, 116.8 (d, JC-F = 19 Hz), 114.6 (d, JC-F = 4 Hz, 105.3 (d, JC-F = 25 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -109.5. IR (KBr): 1726, 1609, 1398, 1160. HRMS (ESI): m/z calcd for $C_{13}H_7ClFO_2$ (M+H)+ : 249.0040, found: 249.0103.



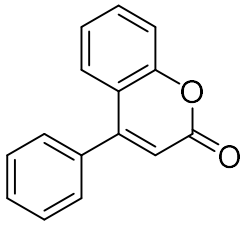
2-ethoxy-3-methoxy-6*H*-benzo[*c*]chromen-6-one (2t): Following the general procedure **GP1**, two reactions of **1t** (0.2 mmol each one) afforded **2t** as an off-white solid in 57% yield (61.0 mg). Mp:120-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.35 (d, J = 8.6 Hz, 1H), 7.93 (d, J=7.9 Hz, 1H), 7.79-7.75 (m, 1H), 7.51-7.47 (m, 1H), 7.41 (s, 1H), 6.86 (s, 1H), 4.19 (q, 3J = 7.6 Hz, 2H), 3.93 (s, 3H), 1.52 (t, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) 161.66, 151.92, 146.45, 145.77, 135.20, 134.75, 130.67, 127.70, 121.04, 120.24, 110.02, 105.81, 100.94, 65.26, 56.27, 14.86. IR (KBr): 1724, 1617, 1480, 1274, 1205, 1044. HRMS (ESI): m/z calcd for $C_{16}H_{15}O_4$ (M+H)+ : 271.0892, found: 271.0953.



5*H*-dibenzo[*c,g*]chromen-5-one (2u): Following the general procedure **GP1**, two reactions of **1u** (0.2 mmol each one) afforded **2u** as an off-white solid in 80% yield (78.0 mg). Mp: 190-192 °C. The analytical data are consistent with published ones.[3] ^{1}H NMR (400 MHz, $CDCl_3$) 8.57 (d, *J* = 7.6 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.87-7.83 (m, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.65-7.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 147.3, 135.4, 134.9, 134.3, 130.7, 128.6, 127.9, 127.6, 127.1, 124.5, 123.9, 122.3, 122.06, 121.2, 119.2, 113.05.

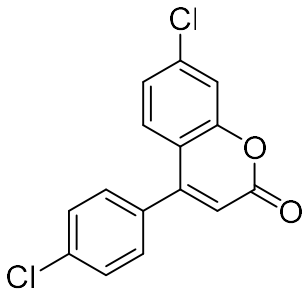


6*H*-naphtho[2,3-*c*]chromen-6-one (2v): Following the general procedure **GP1**, two reactions of **1v** (0.2 mmol each one) afforded **2v** as an off-white solid in 78% yield (77 mg) and analytical data are consistent with published ones.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.54 (s, 1H), 8.21 (dd, J = 7.9, 1.5 Hz, 1H), 8.02 (dd, J = 10.8, 8.3 Hz, 2H), 7.69 (ddd, J = 8.1, 6.6, 1.2 Hz, 1H), 7.60 (ddd, J = 8.0, 6.7, 1.2 Hz, 1H), 7.47 (td, J = 7.7, 1.5 Hz, 1H), 7.38-7.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 150.9, 136.3, 132.9, 132.5, 130.2, 129.7, 129.6 (2C), 128.2, 127.3, 124.7, 123.0, 120.8, 119.3, 118.4, 118.0

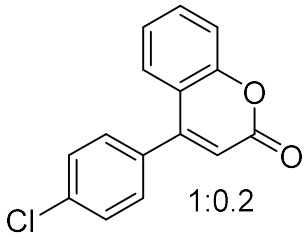


4-phenyl-2*H*-chromen-2-one (2w): Following the general procedure **GP1**, two reactions of **1w** (0.2 mmol each one) afforded **2w** as an off-white solid in 61% yield (54.0 mg), and analytical data are consistent with published ones.[2] ^{1}H NMR (400 MHz, $CDCl_3$) 7.57-7.40

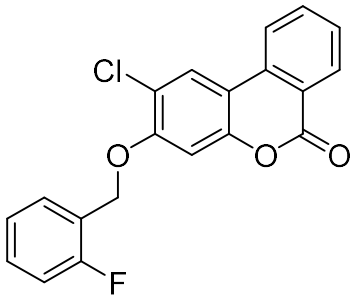
(m, 8H), 7.23-7.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.81, 155.72, 154.22, 135.24, 131.97, 129.73, 128.92 (2C), 128.48(2C), 127.05, 124.22, 119.03, 117.37, 115.22.



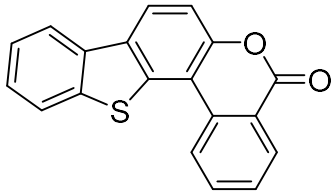
4-phenyl-2*H*-chromen-2-one (2x): Following the general procedure **GP1**, two reactions of **1x** (0.2 mmol each one) afforded **2x** as an off-white solid in 73% yield (86.0 mg), and analytical data are consistent with published ones.[2] ^{1}H NMR (400 MHz, $CDCl_3$) 7.53 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 2.1 Hz, 1H), 7.39-7.36 (m, 3H), 7.22 (dd, J = 8.6, 2.1 Hz, 1H), 6.35 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.6, 153.9, 138.3, 136.4, 133.3, 129.8 (2C), 128.52(2C), 127.7, 127.01, 117.8, 117.5, 115.3.



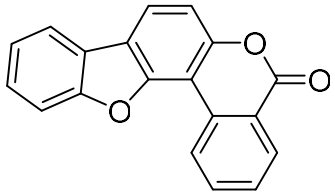
4-phenyl-2*H*-chromen-2-one (2y): Following the general procedure **GP1**, two reactions of **1y** (0.2 mmol each one) afforded **2y** as an off-white solid in 64% yield (6.0 mg), and analytical data are consistent with published ones.[2] ^{1}H NMR (400 MHz, $CDCl_3$) 7.59-7.51 (m, 3H), 7.45-7.39 (m, 4H), 7.24=7.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.5, 154.2, 136.02, 133.6, 132.2, 129.8, 129.3, 126.7, 124.3, 118.7, 117.9, 115.4.



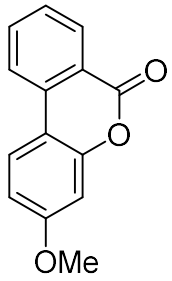
2-chloro-3-((2-fluorobenzyl)oxy)-6*H*-benzo[*c*]chromen-6-one (2z): Following the general procedure **GP1**, two reactions of **1z** (0.2 mmol each one) afforded **2z** as an off-white solid in 59% yield (83.0 mg). Mp:198-200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.34 (dd, J = 7.8, 2.4 Hz), 8.02 (s, 3H), 7.94 (d, J = 7.6 Hz), 7.82-7.79 (m, 1H), 7.59-7.53 (m, 2H), 7.37-7.32 (m, 1H), 7.21-7.18 (m, 1H), 7.14-7.10 (m, 1H), 6.97 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.93, 160.0 (d, JC-F = 245 Hz), 155.3, 150.8, 135.1, 134.0, 130.7, 130.2 (d, JC-F = 7.5 Hz), 129.3 (d, JC-F = 2.5 Hz), 128.5, 124.52, 124.50, 122.7 (d, JC-F = 13 Hz), 121.2, 120.2, 119.9, 115.6 (d, JC-F = 20 Hz),, 112.1, 102.6, 64.9 (d, JC-F = 3.75 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -118.23. IR (KBr): 1742, 1614, 1459, 1280, 1040. HRMS (ESI): m/z calcd for $C_{20}H_{13}ClFO_3$ (M+H)+ : 355.0459, found: 355.0521.



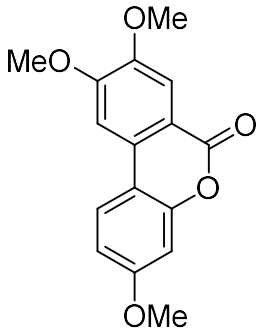
5*H*-benzo[*c*]benzo[4,5]thieno[2,3-*f*]chromen-5-one (2aa): Following the general procedure **GP1**, two reactions of **1aa** (0.2 mmol each one) afforded **2aa** as an off-white solid in 66% yield (79.0 mg). Mp:222-224 °C.^{1}H NMR (400 MHz, $CDCl_3$) 8.6 (d, J = 8.0 Hz, 1H), 8.51 (dd, J = 8.0, 2.4 Hz),), 8.2 (d, J = 8.2 Hz), 8.15-8.13 (m, 1H), 7.89-7.98 (m, 2H), 7.67-7.63 (m, 1H), 7.53-7.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 151.03, 138.5, 134.9, 134.3, 134.0, 133.2, 130.9, 128.6, 126.8, 125.2, 125.0, 122.9, 122.3, 121.5, 121.2, 115.5, 113.6. IR (KBr): 1730, 1605, 1381, 1232. HRMS (ESI): m/z calcd for $C_{20}H_{11}O_2S$ (M+H)+ : 303.0402, found: 303.0462.



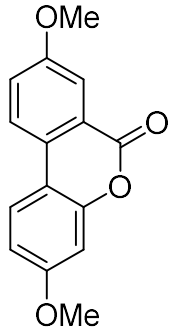
5*H*-benzo[*c*]benzofuro[2,3-*f*]chromen-5-one (2ab): Following the general procedure **GP1**, two reactions of **1ab** (0.2 mmol each one) afforded **2ab** as an off-white solid in 60% yield (68 mg). Mp. = 189-191ºC. The analytical data are consistent with published ones.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, J = 8.1 Hz, 1H), 8.36 (d, J = 7.9 Hz, 1H), 7.87-.80 (m, 3H), 7.60-7.55 (m, 2H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 1H), 7.24 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 160.91, 156.36, 152.09, 150.56, 135.00, 132.73, 130.20, 128.79, 126.90, 126.43, 123.52, 123.05, 121.17, 120.83, 120.81, 120.24, 112.78, 111.70, 105.42.



3-methoxy-6*H*-benzo[*c*]chromen-6-one (2ac): Following the general procedure **GP1**, two reactions of **1ac** (0.2 mmol each one) afforded **2ac** as an off-white solid in 60% yield (54.0 mg), and analytical data are consistent with published ones.[10] Mp. = 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 8.02-7.94 (m, 2H), 7.81-7.79 (m, 1H), 7.53-7.51 (m, 1H), 6.94-6.88 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (2C), 152.7, 135.32, 134.9, 130.7, 127.9, 123.9, 121.2, 120.1, 112.6, 111.30, 101.8, 55.8.



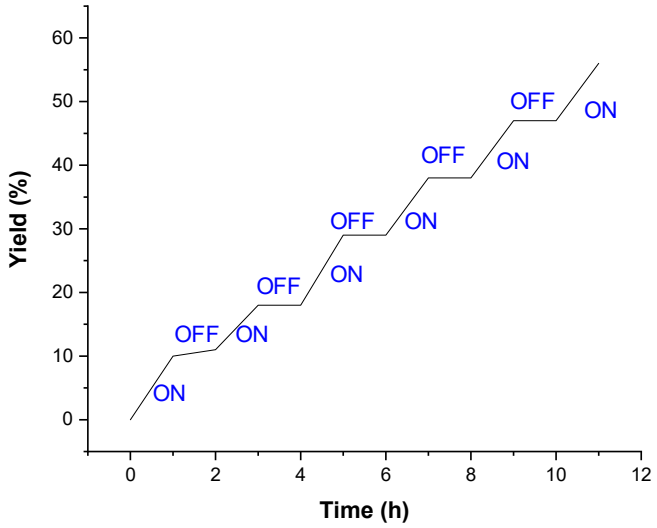
3,8,9-trimethoxy-6*H*-benzo[*c*]chromen-6-one (2ad): Following the general procedure **GP1**, two reactions of **1ad** (0.2 mmol each one) in acetone afforded **2ad** as an off-white solid in 54% yield (61 mg). mp 176-177 °C. The analytical data are consistent with published ones.[10]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.85 (d, J = 8.8 Hz, 1H), 7.72 (s, 1H), 7.33 (s, 1H), 6.91-6.86 (m, 2H), 6.84 (d, J = 2.6 Hz, 1H), 4.08 (s, 3H), 3.99 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 160.9, 155.2, 152.3, 149.3, 130.5, 123.1, 113.0, 112.3, 111.2, 110.4, 102.1, 101.5, 56.3, 56.2, 55.7.



3,8-dimethoxy-6*H*-benzo[*c*]chromen-6-one (2ae): Following the general procedure **GP1**, two reactions of **1ae** (0.2 mmol each one) in acetone afforded **2ae** as an off-white solid in 65% yield (66 mg). Mp: 147-148 °C. The analytical data are consistent with published ones.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.9 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 2.8 Hz, 1H), 7.37 (dd, J = 8.8, 2.8 Hz, 1H), 6.91 (dd, J = 8.7, 2.6 Hz, 1H), 6.87 (d, J = 2.5 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 160.7, 159.2, 151.7, 128.7, 124.5, 123.2, 122.8, 121.0, 112.4, 111.3, 111.0, 101.6, 55.8, 55.7

Mechanistic studies

ON/OFF experiment: A 10 mL glass vial was charged with carboxylic acid (0.2 mmol), $CeCl_3$ (10 mol%), $NaHCO_3$ (2 equiv.), trimethoxybenzene (0.2 mmol, internal standard), stirring bar and $CHCl_3$ (2 ml). The glass vial was sealed with a PTFE septum and the reaction was opened to air via a needle. The reactions were placed in a pre-programmed temperature controlled blue LED reactor (as shown in **Figure 1**) and the reaction mixture was irradiated with a 455 nm blue LED. After the selected time has expired, a small aliquot was removed and concentrated under reduced pressure, analyzed by ^1H NMR to determine the yield.



The above reaction profile upon the alternating irradiation shows that the reaction can only proceed in presence of light, whereas the catalytic activity is inhibited under darkness, thus confirming the previous results from the conditions screening.

UV-Vis experiments:

In order to verify whether the interaction with the substrate carboxylic acids **1a-z** and cerium (IV) could lead to the overall LMCT process, which reduced the Ce(IV) species to Ce(III), a similar approach to the one reported by Zuo *et al.* was used.[1] $(^{n}Bu_4)_2Ce^{IV}Cl_6$ was chosen as a Ce(IV) source to ensure sufficient solubility in organic solvents and facilitate the detection of the species.

Synthesis of $(^{n}Bu_4)_2Ce^{IV}Cl_6$

In a round-bottom flask equipped with a teflon-coated stirring bar, tetrabutylammonium chloride (3.24 g, 11.7 mmol, 2.0 equiv.) and $Ce(SO_4)_2\cdot(H_2O)_n$ (2.36 g, 5.8 mmol, 1.0 equiv.) were charged, then HCl 37% (15 ml) was added at room temperature. After the formation of a yellow-orange precipitate, additional tetrabutylammonium chloride (324 mg, 1.2 mmol, 0.1 equiv.) was added and the reaction additionally stirred for 20 minutes. The suspension was cooled-down to 5°C using an ice-water bath, then the solid was collected by suction-filtration over a sintered funnel, then the yellow-orange solid was washed three times with the minimal amount of acetone (approx. 10 ml each time) and dried under high vacuum, to afford an intensely yellow powder (1g, 1.44 mmol, 24% yield).

Preparation of* $(^{n}Bu_4)_2Ce^{IV}Cl_6$ *in* $CHCl_3$*(solution A).

In a glass vial equipped with a teflon-coated stirring bar and a septum, $(^{n}Bu_4)_2Ce^{IV}Cl_6$ (0.4 mg, 0.5 μmol) were dissolved in $CHCl_3$ (4 ml) under vigorous stirring.

Preparation of a basic solution of* $(^{n}Bu_4)_2Ce^{IV}Cl_6$ and biphenyl 2-carboxylic acid 1a *in* $CHCl_3$ *(solution B).

In a glass vial equipped with a teflon-coated stirring bar and a septum, $(^{n}Bu_4)_2Ce^{IV}Cl_6$ (0.4 mg, 0.5 μmol), $NaHCO_3$ (8.0 mg, 0.1 mmol) and **1a** (10 mg, 0.05 mmol) were dissolved in $CHCl_3$ (3 ml) under vigorous stirring.

[1] A. Hu, J.-J. Guo, H. Pan, H. Tang, Z. Gao, Z. Zuo, *J. Am. Chem. Soc*. **2018,** 140, 1612−1616

Experimental procedure and sampling

The UV-Vis measurement where performed using an Agilent Cary 100 spectrometer using a temperature-controlled (20.0 °C) fluorescence cuvette (1 cm optical pathway, both faces can transmit light) A single blue LED OSRAM Oslon® SSL 80 royal-blue LEDs (λ_{max}= 455 nm (± 15 nm), 3.5 V, 700 mA), equipped with a metallic passive cooling element, was placed approx. 2 mm away from one transmitting side of the cuvette, at 90° from the measuring beam. The spectra were recorded in the 200-550 nm range.

In order to record the spectra, the corresponding previously prepared solution was withdrawn using a syringe, filtered-off a Macherey-Nagel CHROMAFIL® O-20/15 MS PTFE filter and the cuvette sealed with a PTFE stopper. The acquisition routine was started (one scan every 30 seconds) and after a certain amount of time the illumination was started.

Spectra acquisition of **$(^n Bu_4)_2Ce^{IV}Cl_6$**

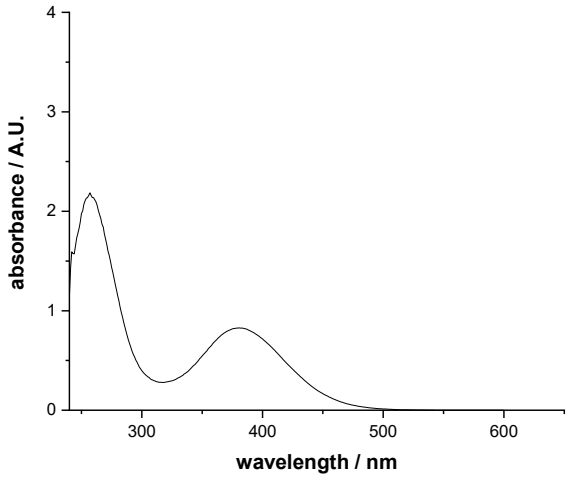


Figure 4: UV-Vis spectra of of $(^n Bu_4)_2Ce^{IV}Cl_6$

As visible in **Figure 4**, the typical Ce(IV) LMCT transition could be detected at around 380 nm.

Spectra acquisition in the presence of biphenyl 2-carboxylic acid (*1a*)

Solution B was used, each spectrum was acquired after 30 seconds from the previous. The ***first 3 acquisitions*** (**Figure 5**) have been recorded in the absence of light irradiation, while the latter **4 acquisitions** (**Figure 5**) were recorded under blue light irradiation.

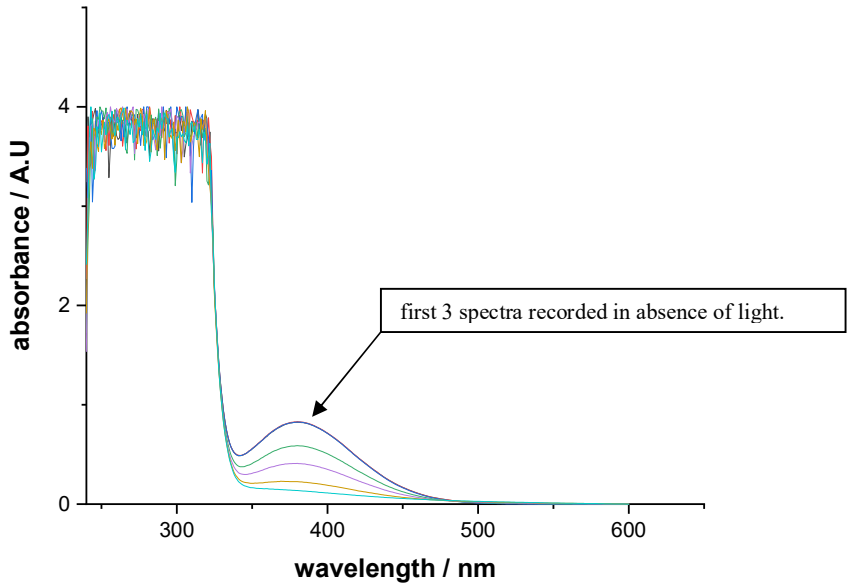
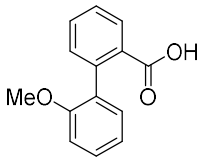
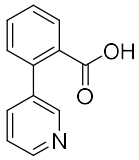


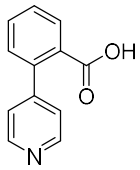
Figure 5: Overlay of the spectra in the presence of biphenyl 2-carboxylic acid (**1a**). **first 3 acquisitions**: before the illumination with 455 nm light; later **4 acquisitions**: after the illumination with 455 nm light.

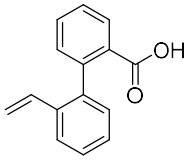
In the presence of 2-aryl carboxylic acid **1a**, the concentration of Ce(IV) species remained almost constant without blue light irradiation (**Figure 5**, **First 3 acquisitions**). Upon irradiation with 455 nm light, an extremely fast reduction of the Ce(IV) species ($\lambda_{max} \approx$ 380 nm) to Ce(III) species (broad and partially overlapped peak at lower wavelengths) (**Figure 5**) was observed.

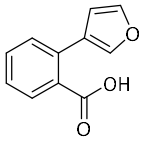
Substrates did not work in our reaction conditions

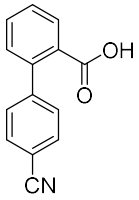


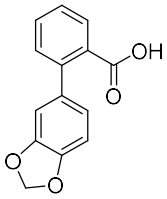


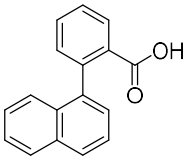


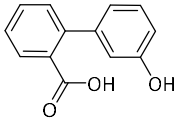


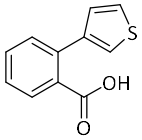


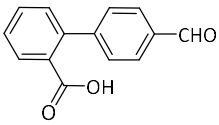


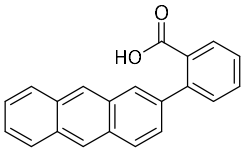


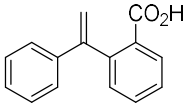


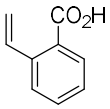




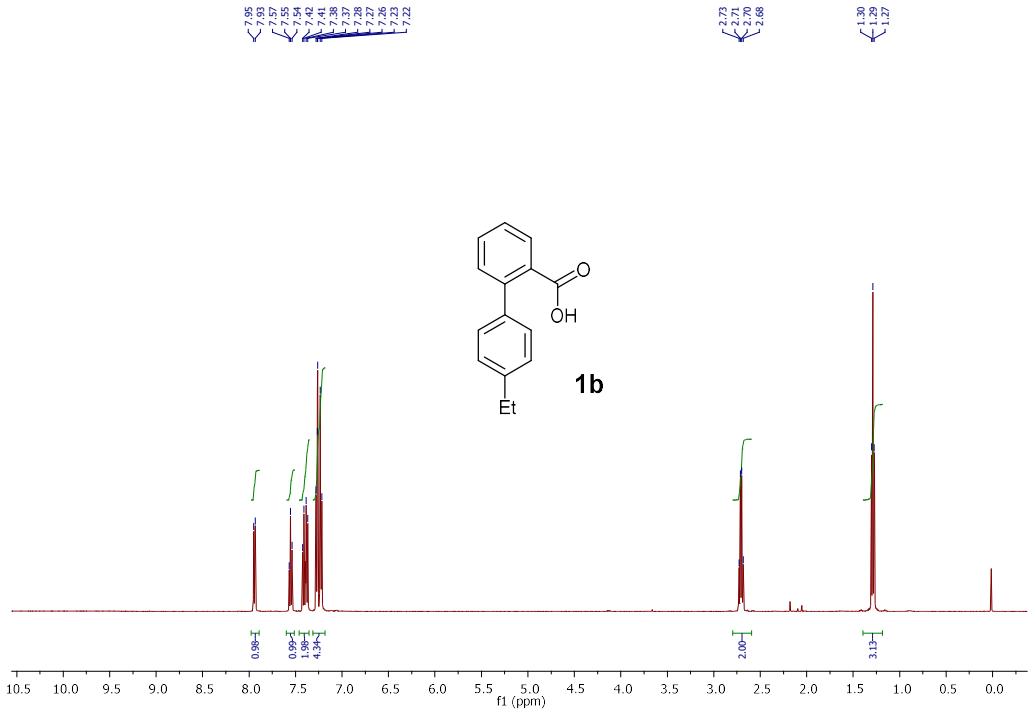








NMR spectra


7.95
7.93
7.57
7.55
7.54
7.42
7.41
7.38
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7.28
7.27
7.26
7.23
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2.71
2.70
2.68
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1.27
O
OH
Et
1b
0.98
0.99
1.98
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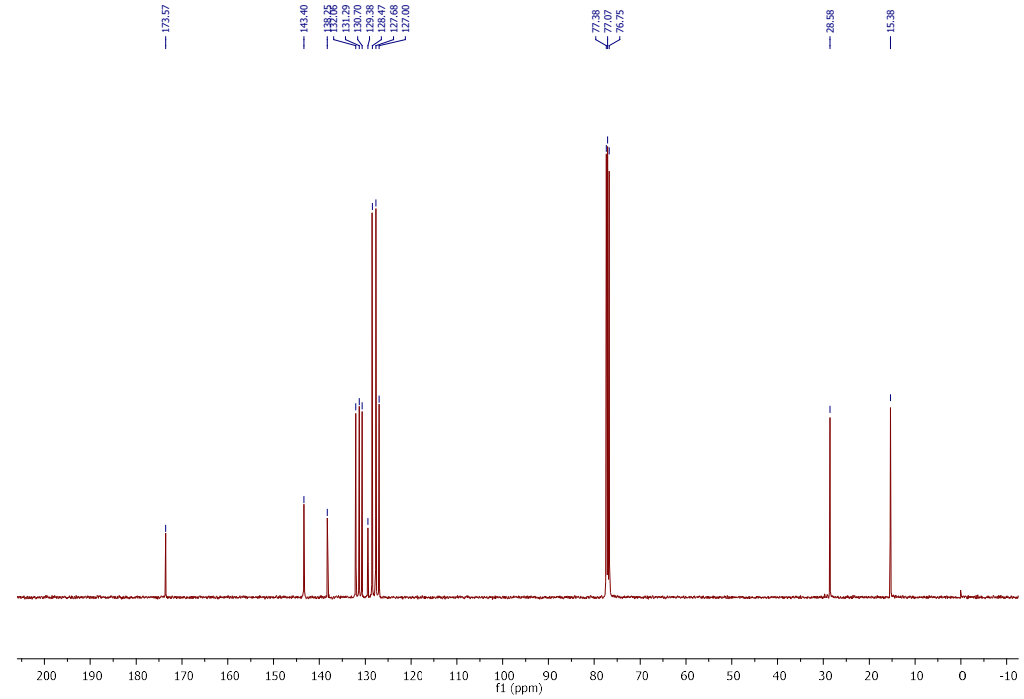
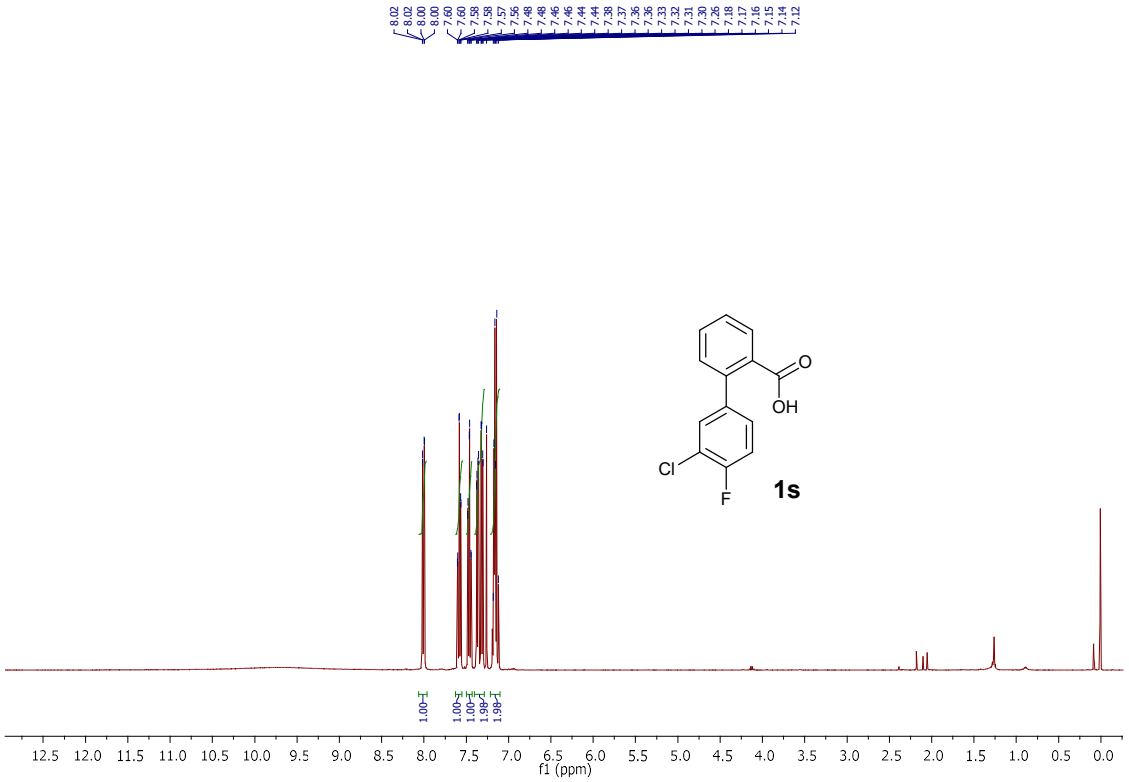
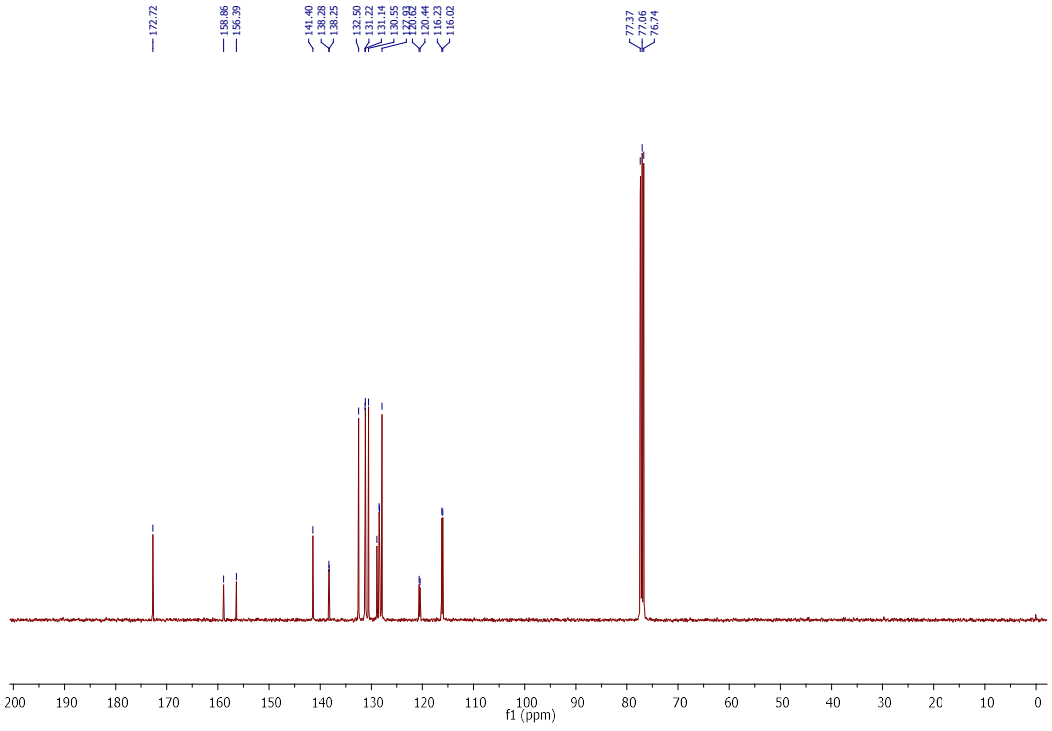
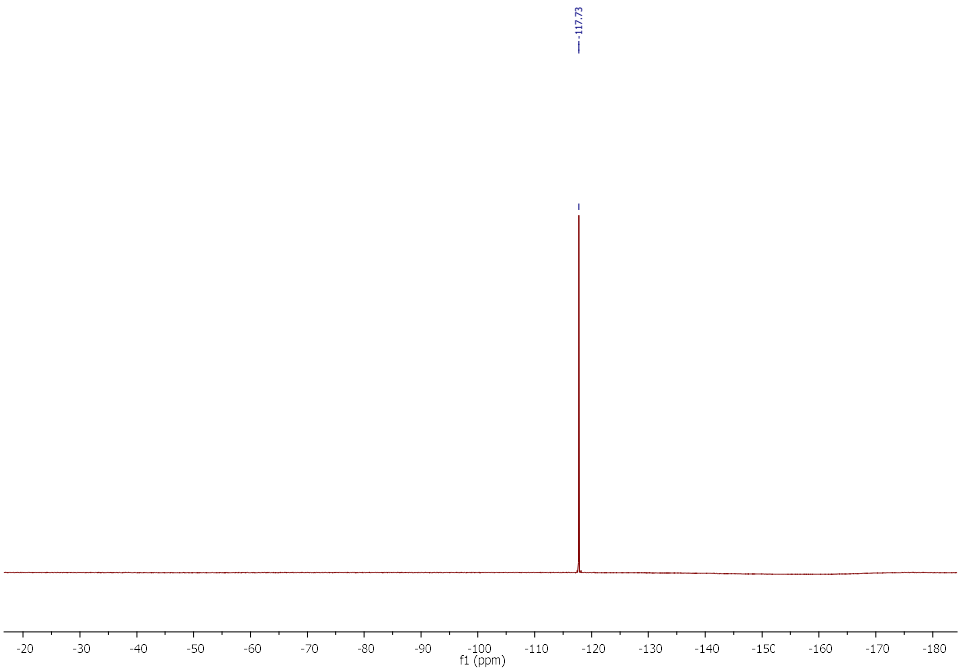
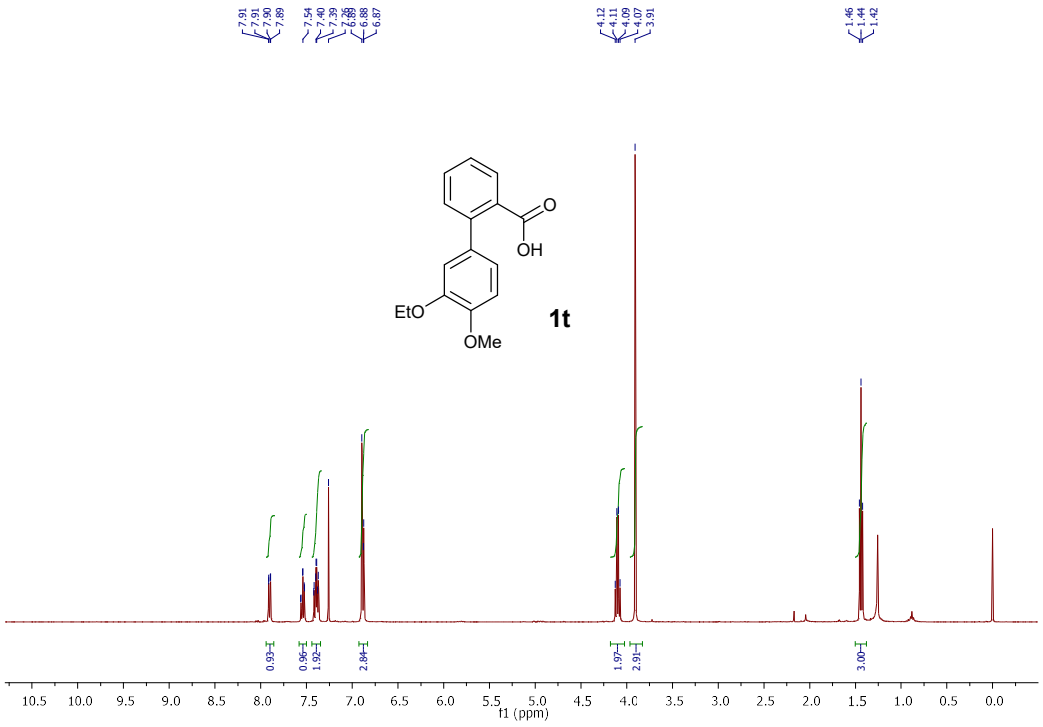
2.00
3.13
f1 (ppm)

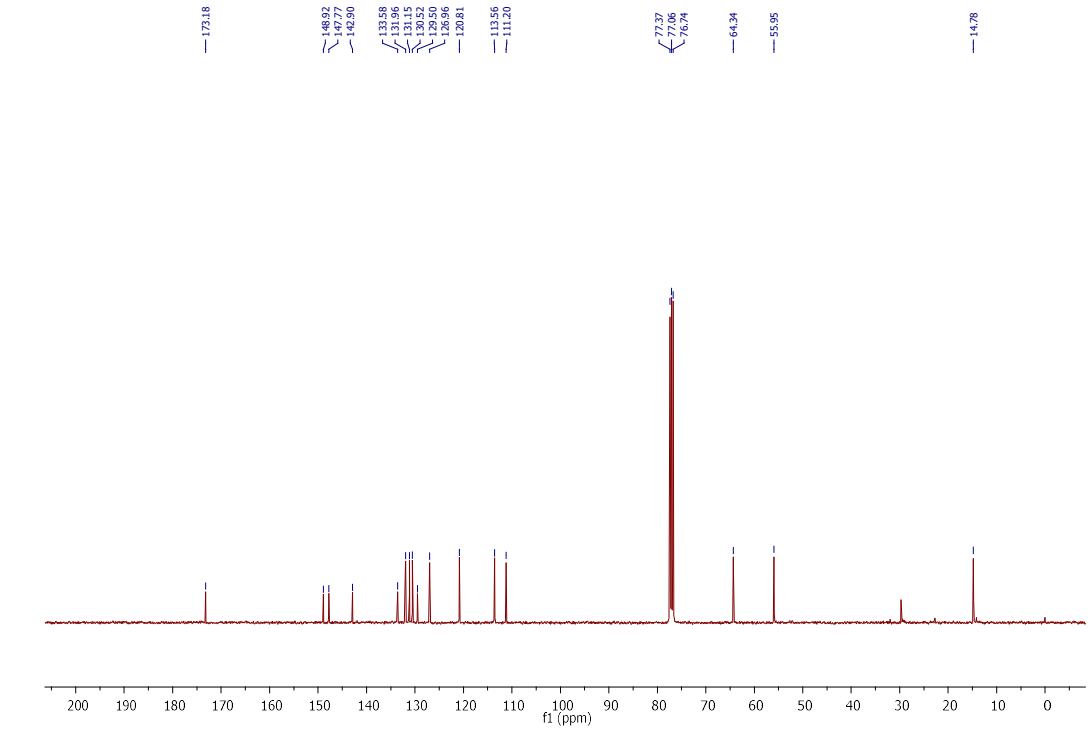

173.57
143.40
138.25
132.06
131.39
130.70
129.38
128.47
127.68
127.00
77.38
77.07
76.75
28.58
15.38
f1 (ppm)

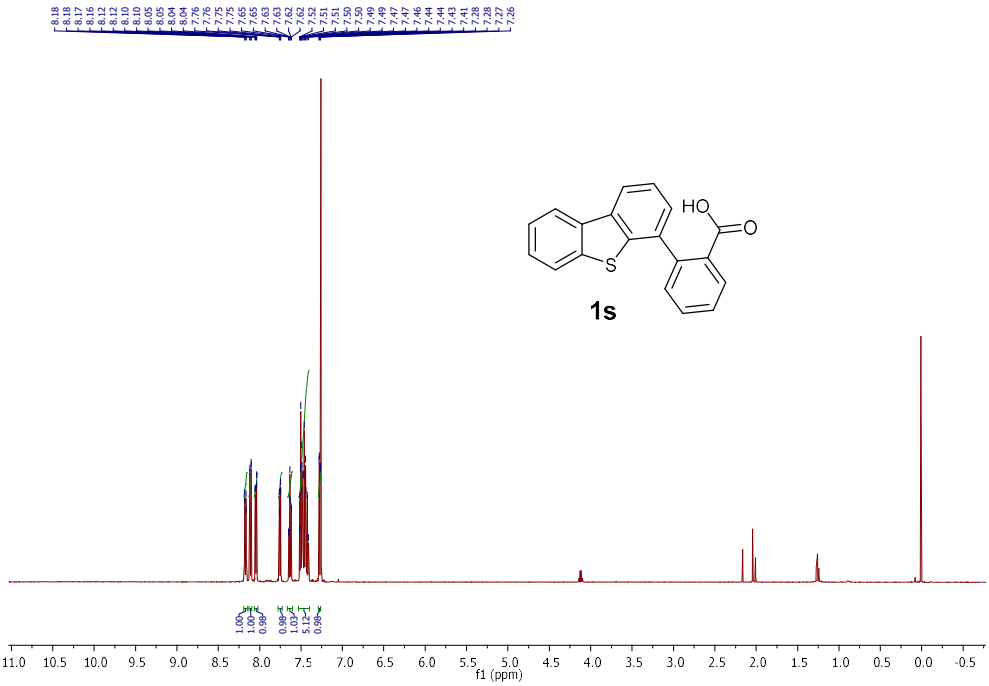

8.02
8.02
8.00
8.00
7.60
7.60
7.58
7.58
7.57
7.56
7.48
7.48
7.46
7.46
7.44
7.44
7.38
7.37
7.36
7.36
7.33
7.32
7.31
7.30
7.26
7.18
7.17
7.16
7.15
7.14
7.12
O
OH
Cl
F
1s
1.00
1.00
1.00
1.98
1.98
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

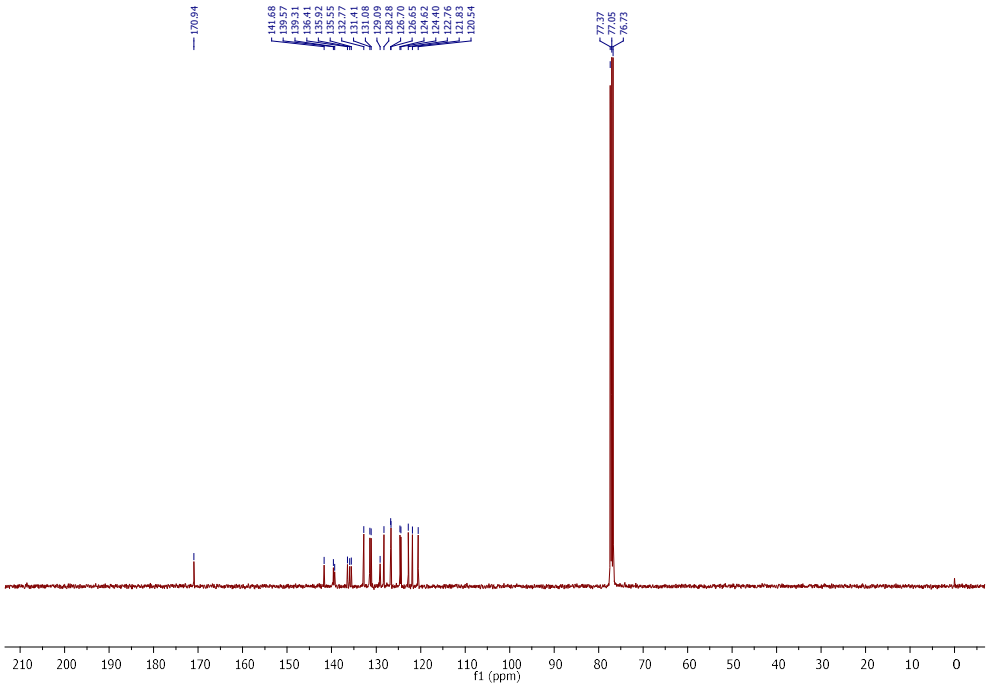

172.72
158.86
156.39
141.40
138.28
138.25
132.50
131.22
131.14
130.55
122.93
122.82
120.44
120.23
116.23
116.02
77.37
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

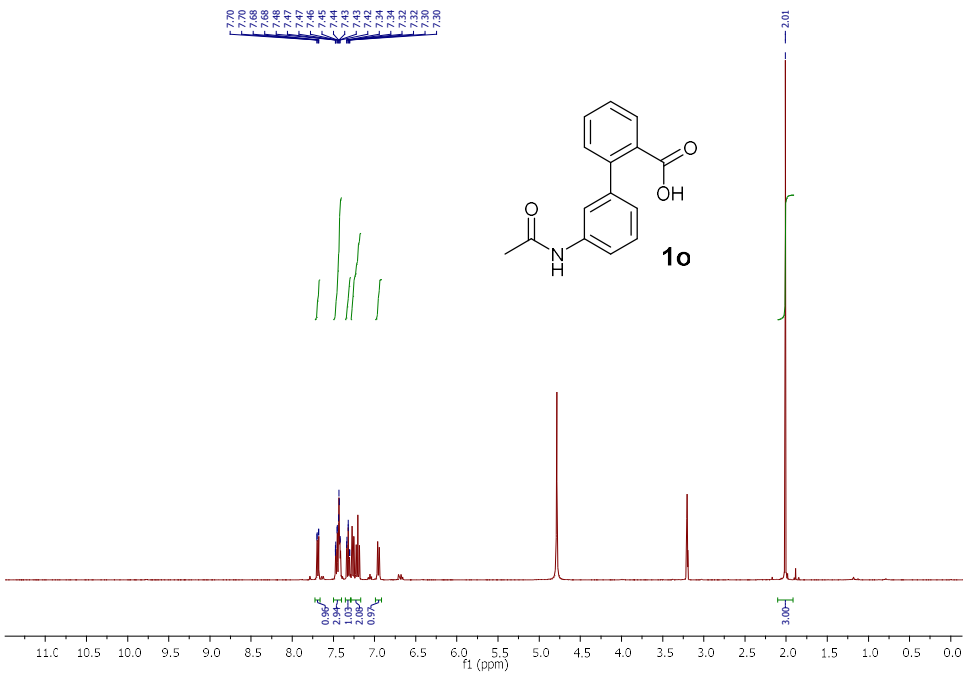

-117.73
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

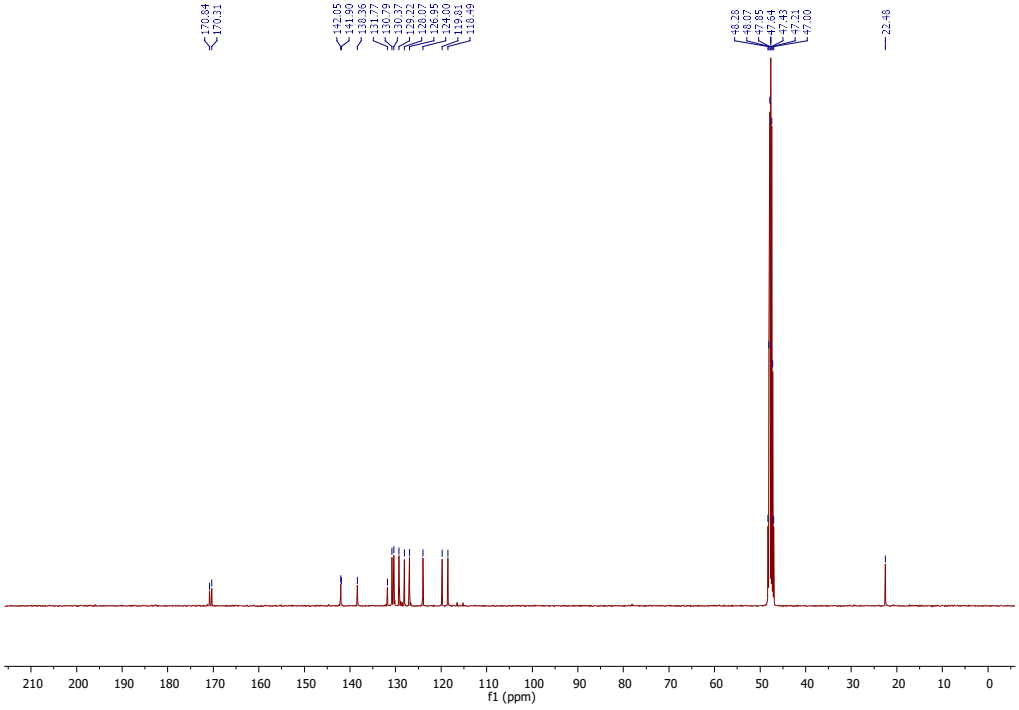

7.91
7.91
7.90
7.89
7.54
7.40
7.39
7.26
6.88
6.87
4.12
4.11
4.09
4.07
3.91
1.46
1.44
1.42
O
OH
EtO
OMe
1t
0.93
0.96
1.92
2.84
1.97
2.91
3.00
f1 (ppm)

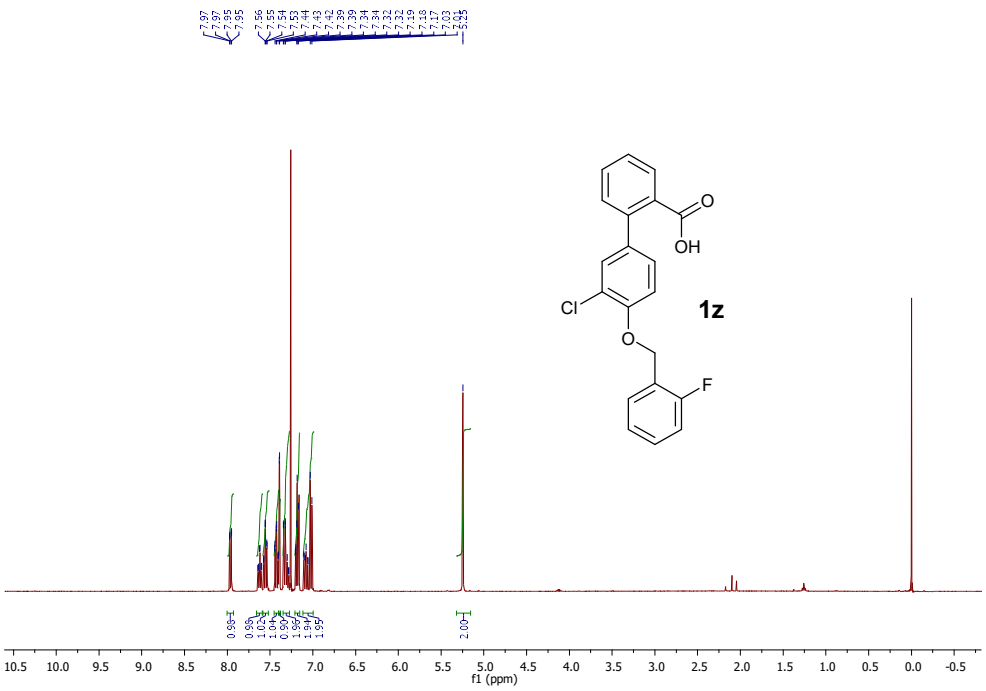

173.18
148.92
147.77
142.90
133.58
131.96
131.15
130.52
129.50
126.96
120.81
113.56
111.20
77.37
77.06
76.74
64.34
55.95
14.78
f1 (ppm)

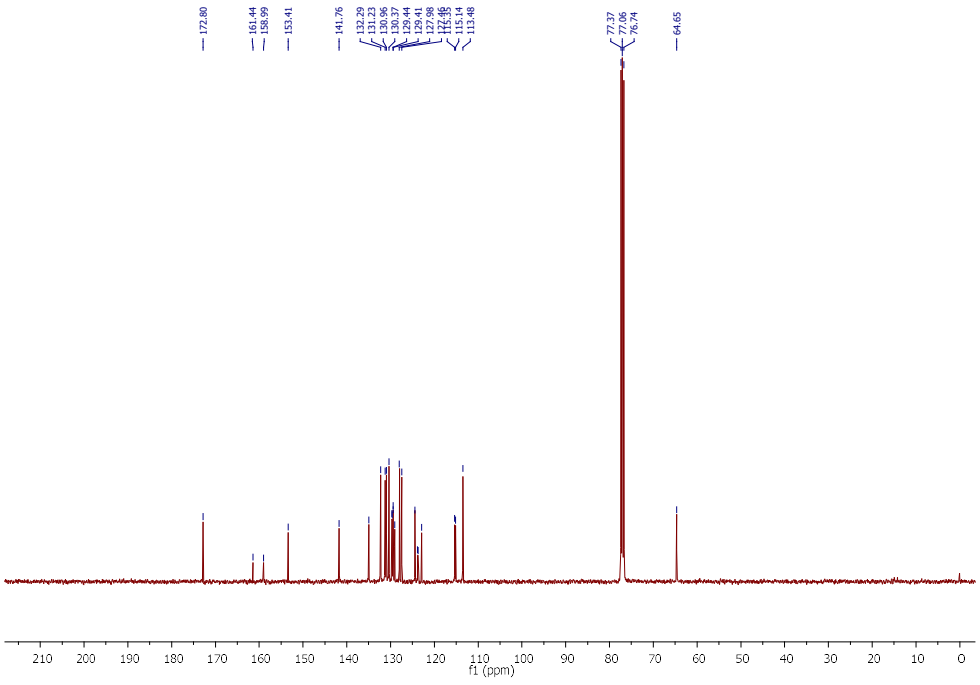

8.18
8.18
8.17
8.16
8.12
8.12
8.10
8.10
8.05
8.05
8.04
8.04
7.76
7.76
7.75
7.75
7.65
7.65
7.63
7.63
7.62
7.62
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.47
7.47
7.46
7.44
7.44
7.43
7.41
7.28
7.28
7.27
7.26
HO
O
S
1s
1.00
1.00
0.98
0.98
1.02
5.12
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

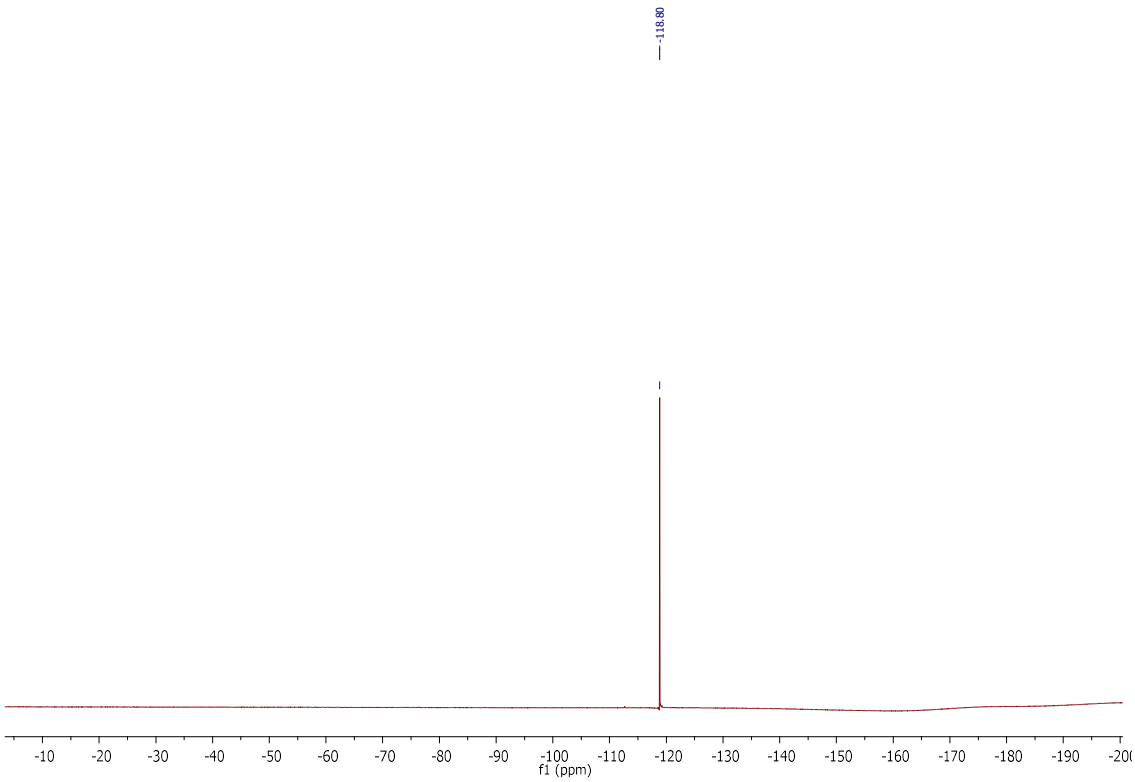

170.94
141.68
139.57
139.31
136.41
135.92
135.55
132.77
131.41
131.08
129.09
128.28
126.70
126.65
124.62
124.40
123.76
121.83
120.54
77.37
77.05
76.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.70
7.70
7.68
7.68
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.43
7.42
7.34
7.34
7.32
7.30
7.30
2.01
O
OH
O
N
H
1o
0.94
3.47
1.03
2.08
0.95
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.84
170.31
142.05
141.90
138.36
131.77
130.79
130.37
129.22
128.77
126.95
124.00
119.81
118.49
48.28
48.07
47.85
47.64
47.43
47.21
47.00
22.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.97
7.97
7.95
7.95
7.56
7.55
7.54
7.53
7.44
7.43
7.42
7.39
7.39
7.34
7.34
7.32
7.32
7.19
7.18
7.17
7.03
7.01
5.25
O
OH
Cl
1z
O
F
0.98
0.93
1.04
1.04
0.96
1.96
1.97
1.99
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


172.80
161.44
158.99
153.41
141.76
132.29
131.23
130.96
130.37
129.44
129.41
127.98
115.14
113.48
77.37
77.06
76.74
64.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-118.80
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


8.41
8.40
8.14
8.12
8.07
8.06
7.85
7.83
7.81
7.60
7.59
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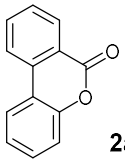
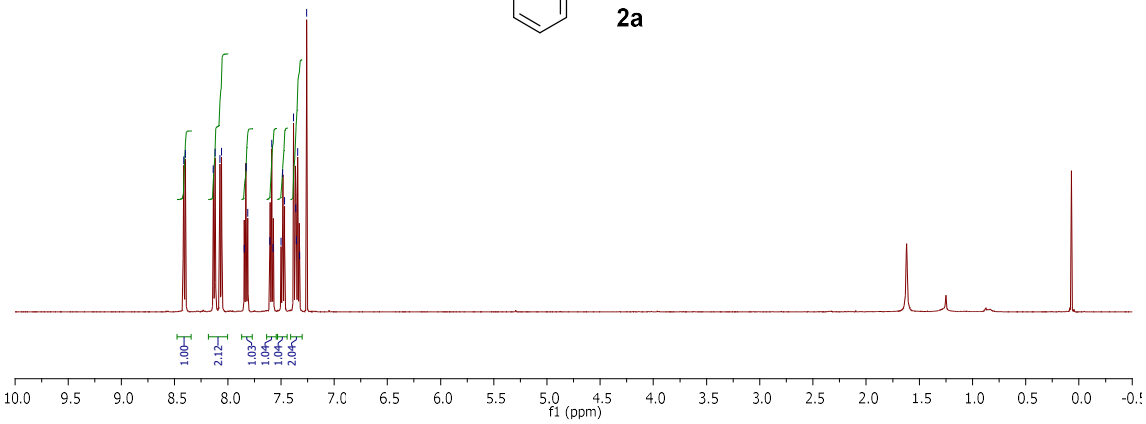
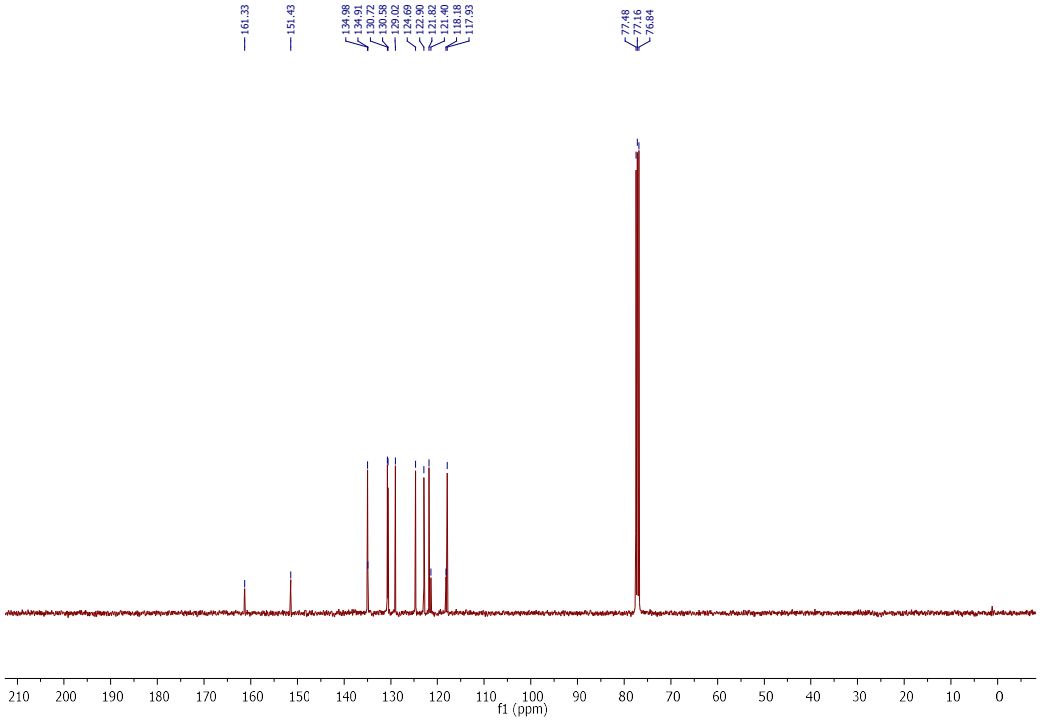
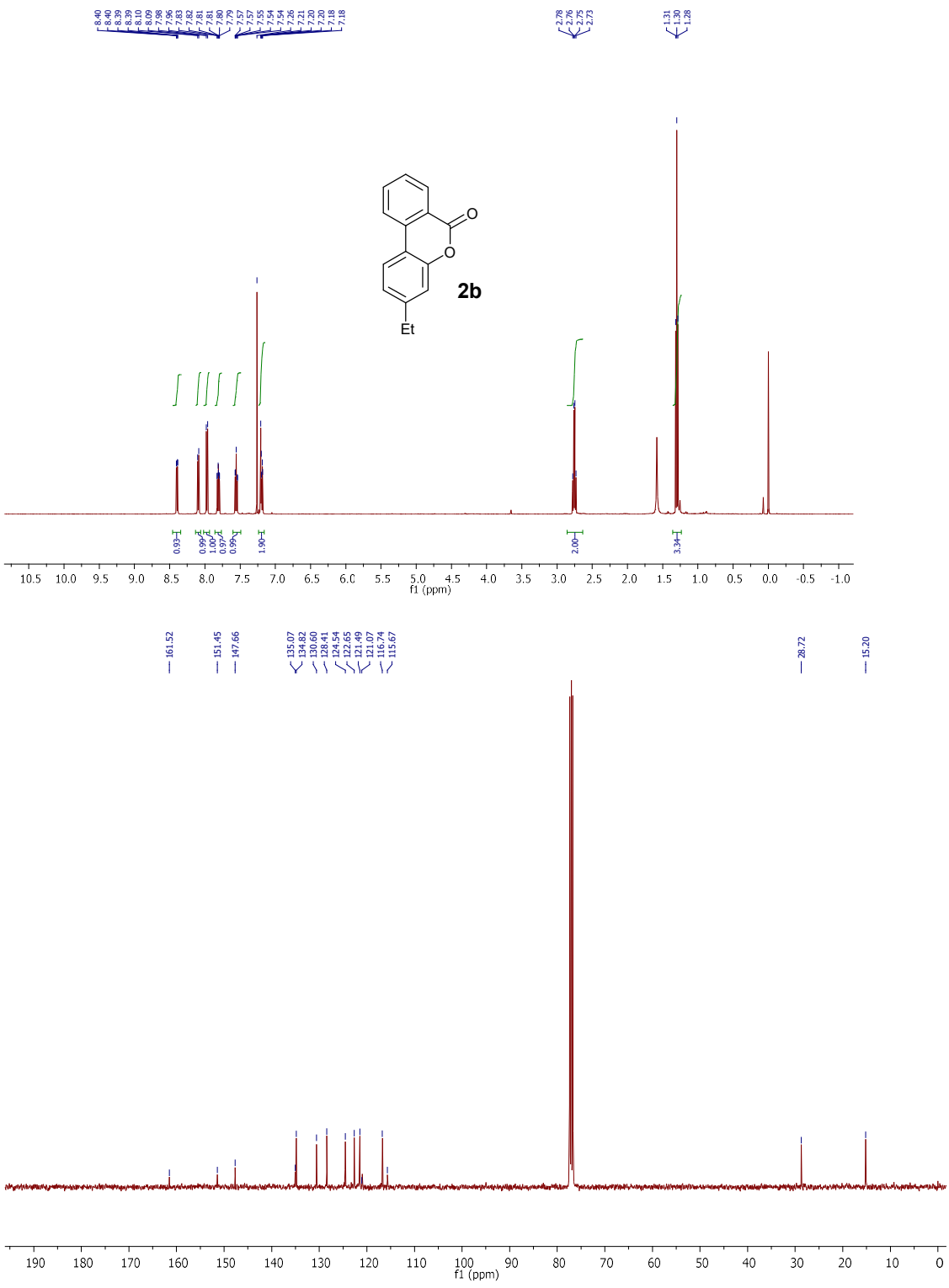
7.38
7.36
7.36
7.34
7.33
7.26

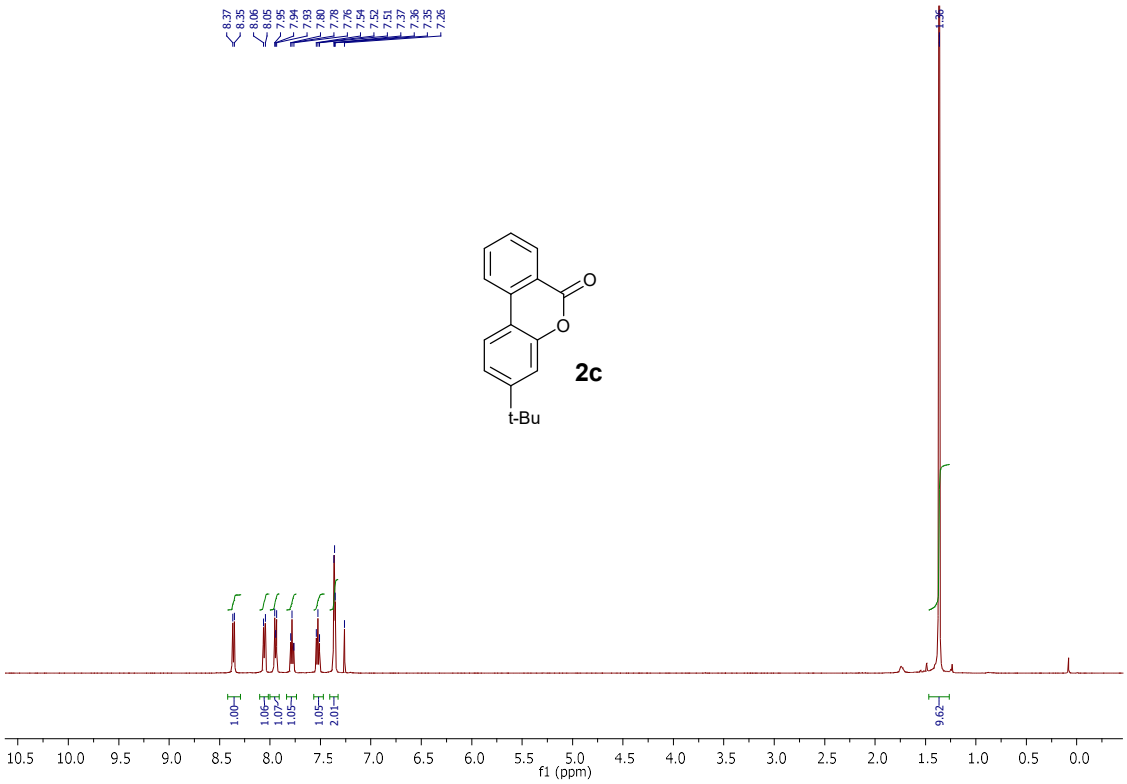

O
O

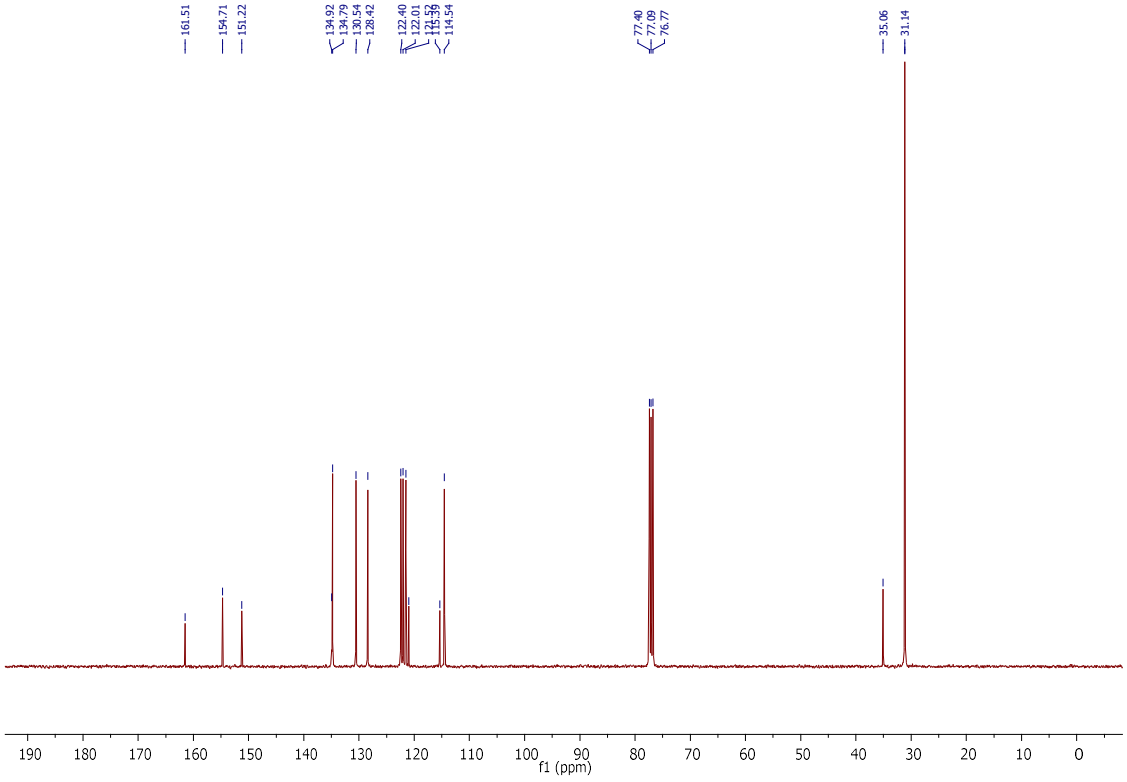
2a

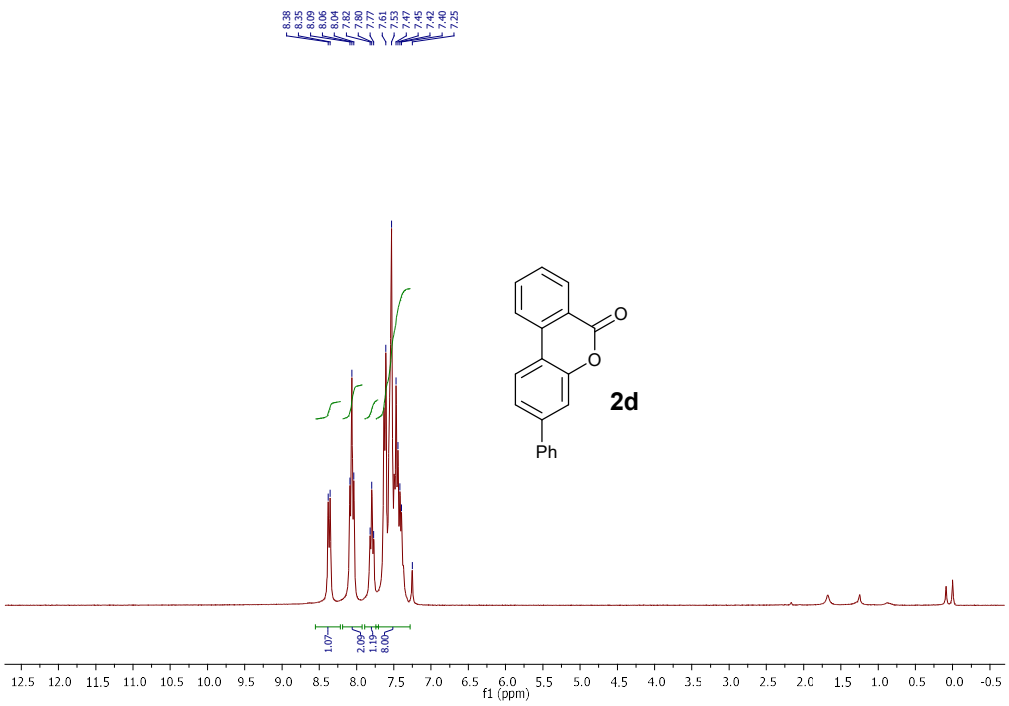

1.00
2.12
1.03
1.04
1.04
2.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

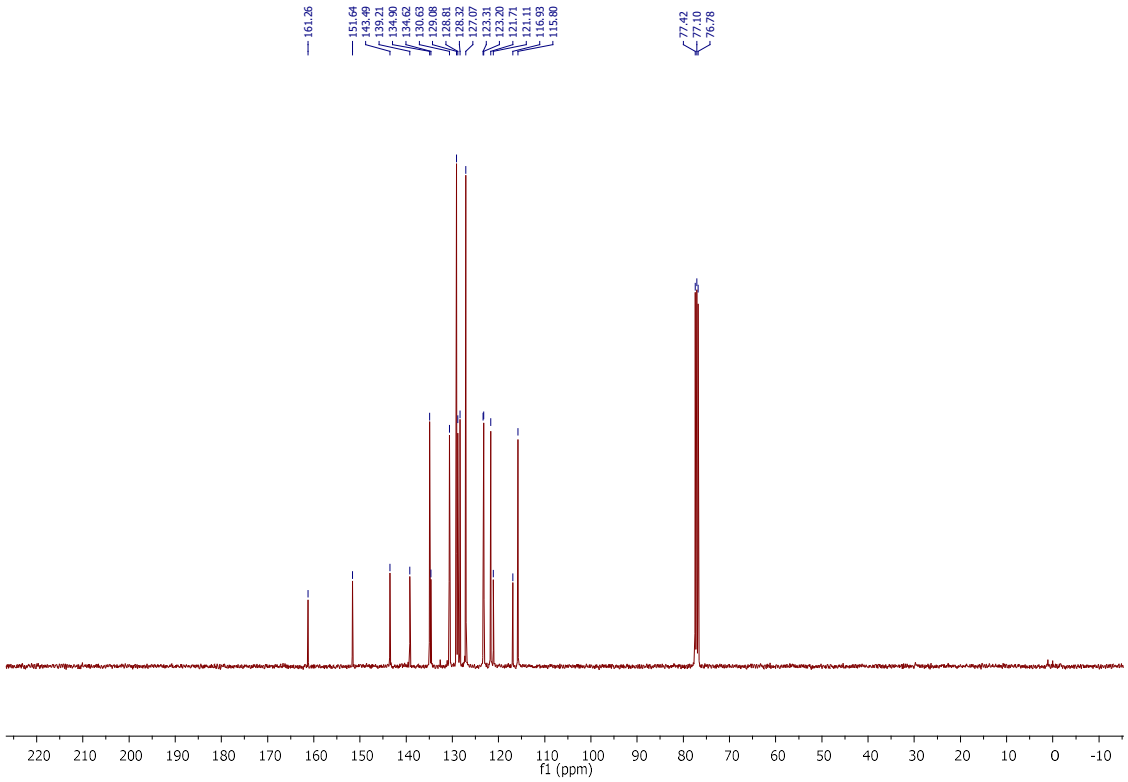

161.33
151.43
134.98
134.91
130.72
130.58
129.02
124.69
123.90
121.82
121.40
118.18
117.93
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

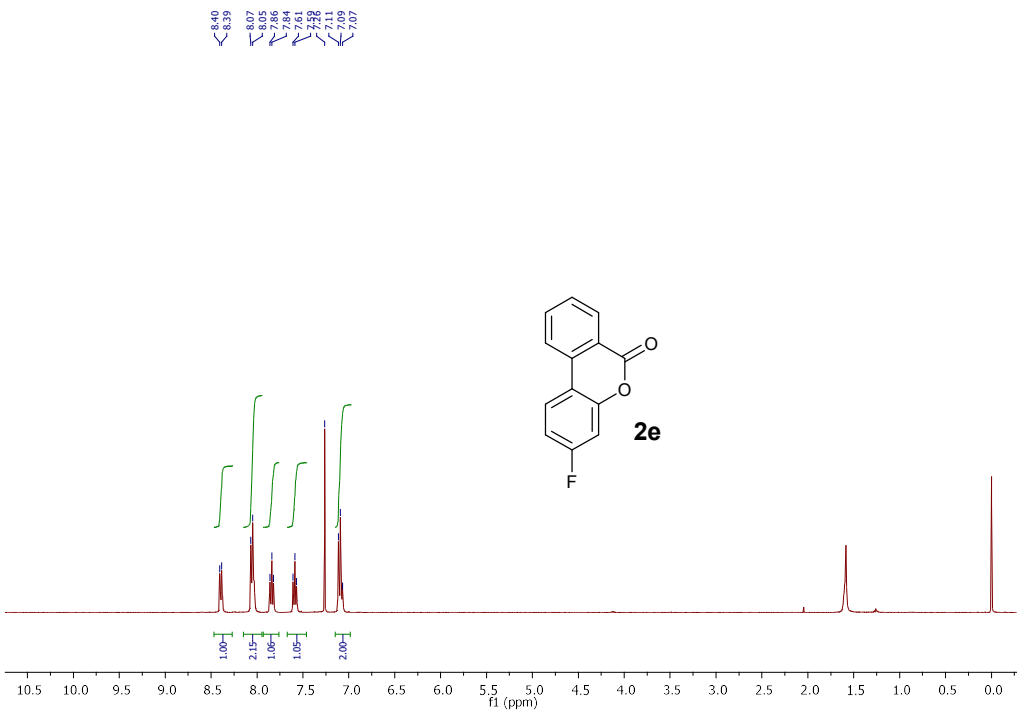

8.40
8.40
8.39
8.39
8.10
8.09
7.98
7.96
7.83
7.82
7.81
7.81
7.80
7.79
7.57
7.57
7.55
7.55
7.54
7.54
7.26
7.21
7.20
7.20
7.18
7.18
2.78
2.76
2.75
2.73
1.31
1.30
1.28
O
O
2b
Et
0.93
0.99
1.00
0.97
0.99
1.90
2.00
3.34
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
161.52
151.45
147.66
135.07
134.82
130.60
128.41
124.54
122.65
121.49
121.07
116.74
115.67
28.72
15.20
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

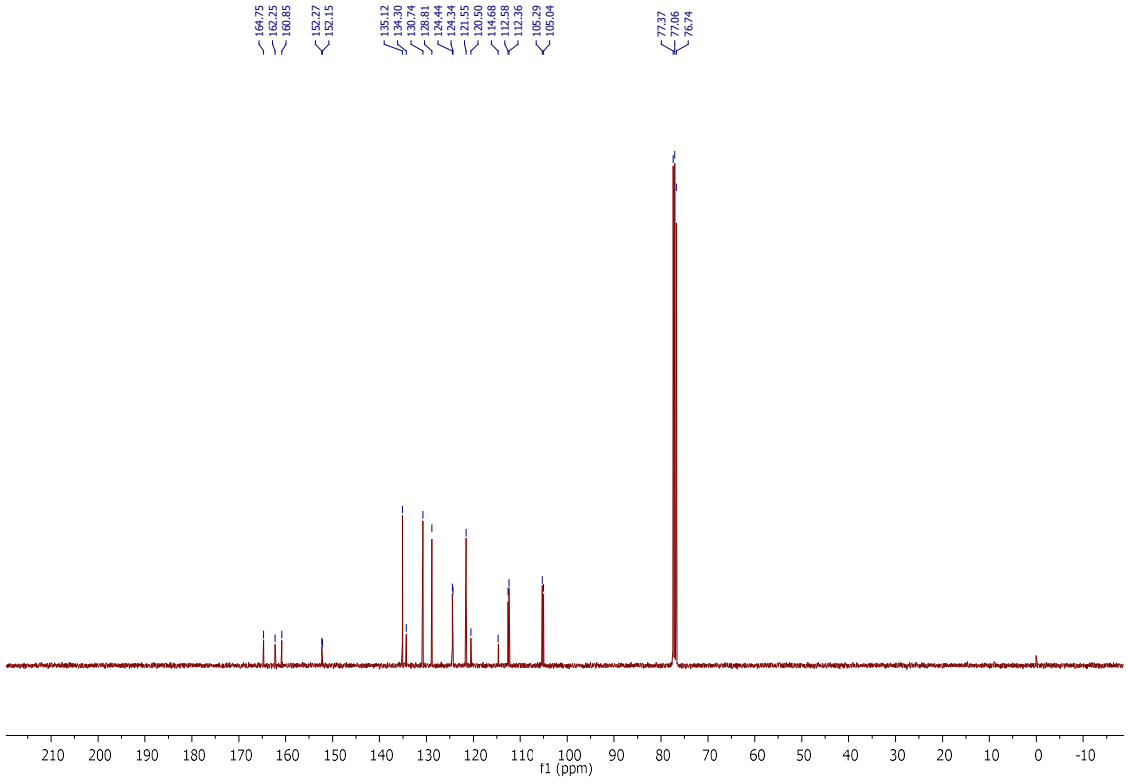

8.37
8.35
8.06
8.05
7.95
7.94
7.83
7.80
7.78
7.76
7.54
7.52
7.51
7.37
7.36
7.35
7.26
1.36
O
O
2c
t-Bu
1.00
1.06
1.07
1.05
1.05
2.01
9.62
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

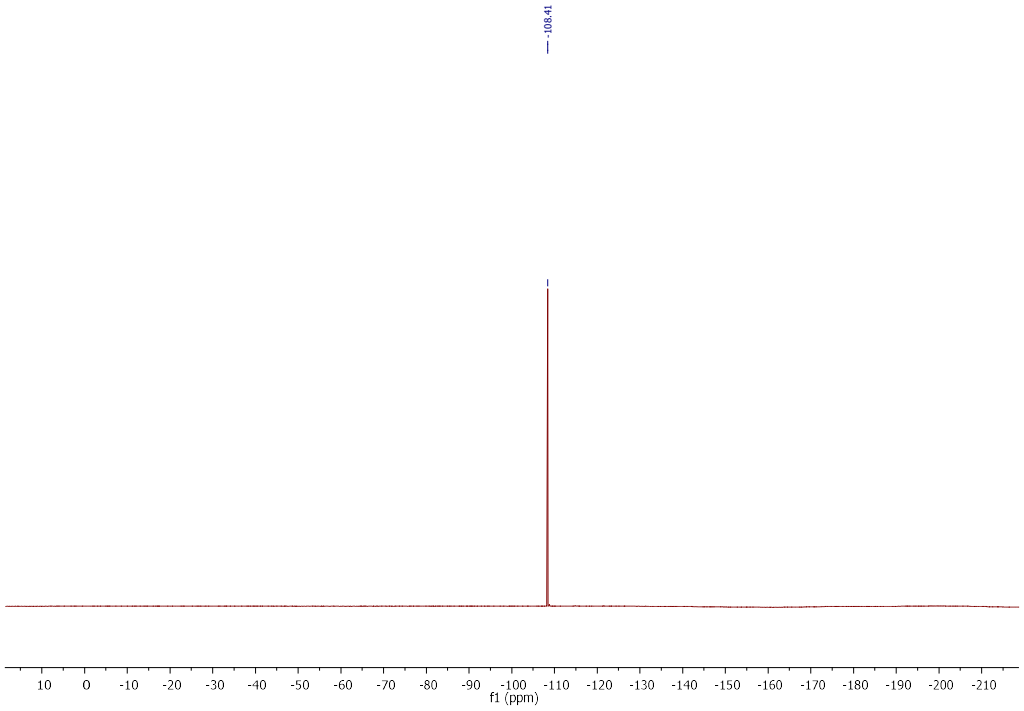

161.51
154.71
151.22
134.92
134.79
130.54
128.42
122.40
122.01
121.52
121.39
114.54
77.40
77.09
76.77
35.06
31.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.38
8.35
8.09
8.06
8.04
7.82
7.80
7.77
7.61
7.53
7.47
7.45
7.42
7.40
7.25
O
O
Ph
2d
1.07
2.09
1.19
8.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

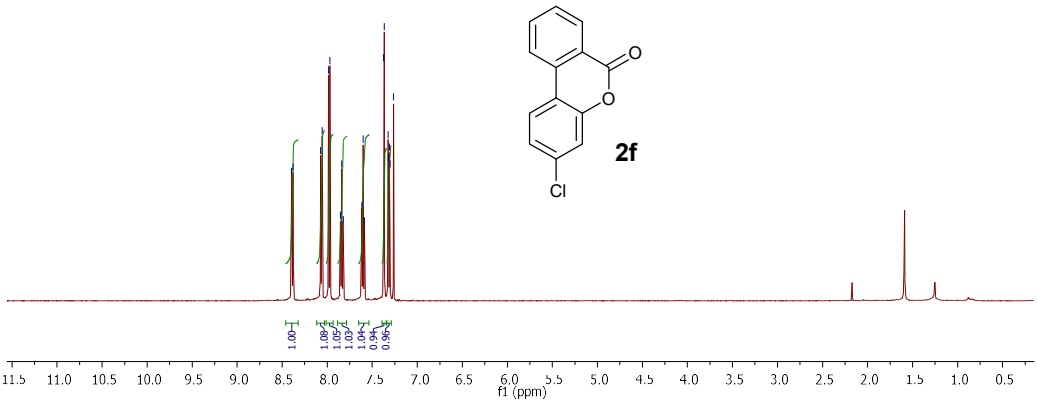

161.26
151.64
143.49
133.21
134.80
134.62
130.63
129.08
128.81
128.32
127.07
123.31
123.20
121.71
121.11
116.93
115.80
77.42
77.10
76.78
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

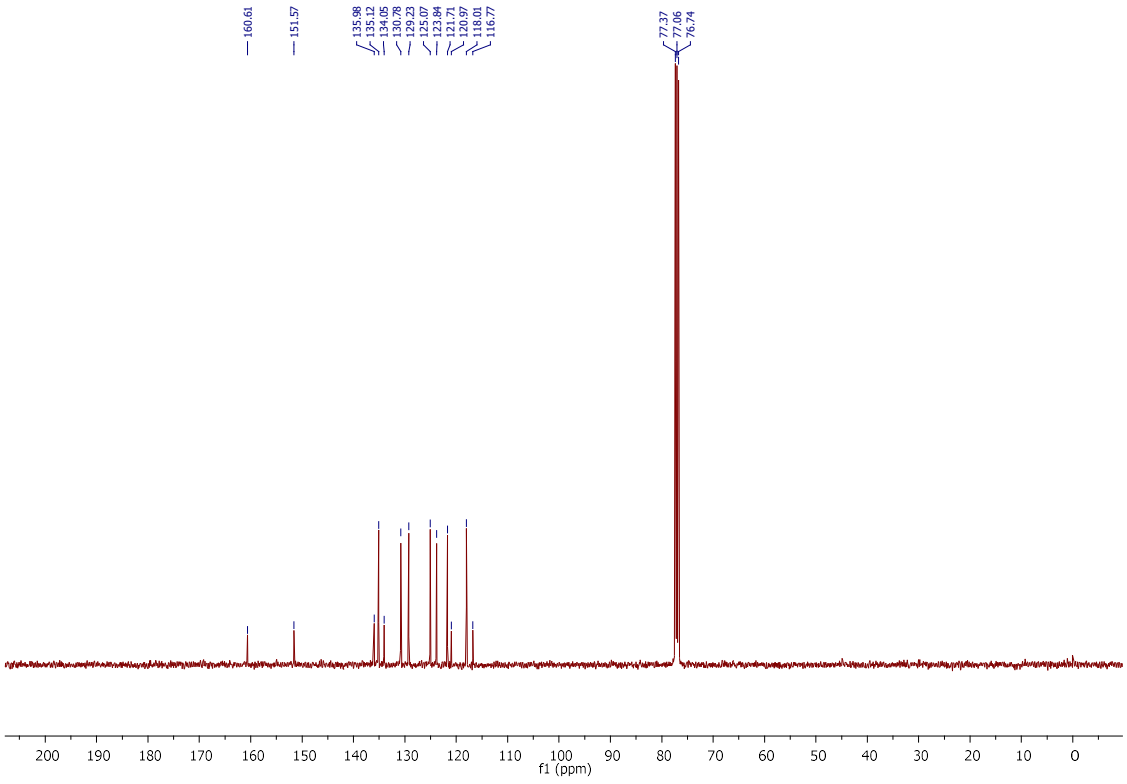

8.40
8.39
8.07
8.05
7.86
7.84
7.61
7.28
7.11
7.09
7.07
O
O
F
2e
1.00
2.15
1.06
1.05
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.75
162.25
160.85
152.27
152.15
135.12
134.30
130.74
128.81
124.44
124.34
121.55
120.50
114.68
112.58
112.36
105.29
105.04
77.37
77.06
76.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

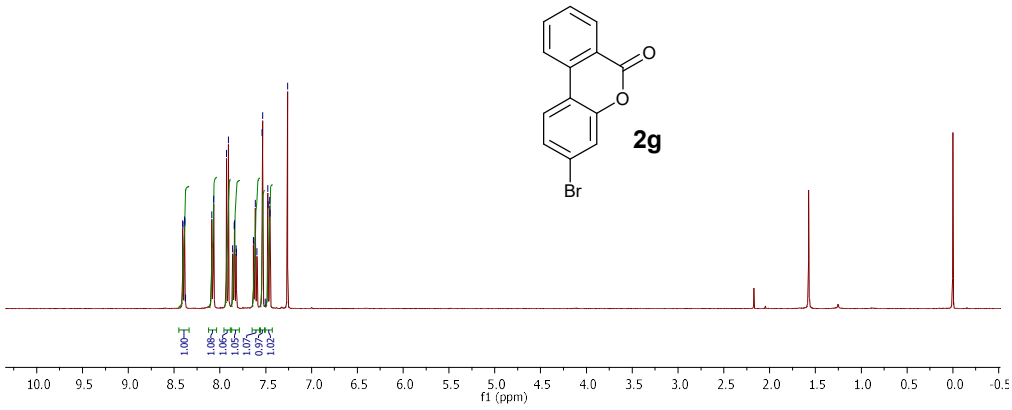

-108.41
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

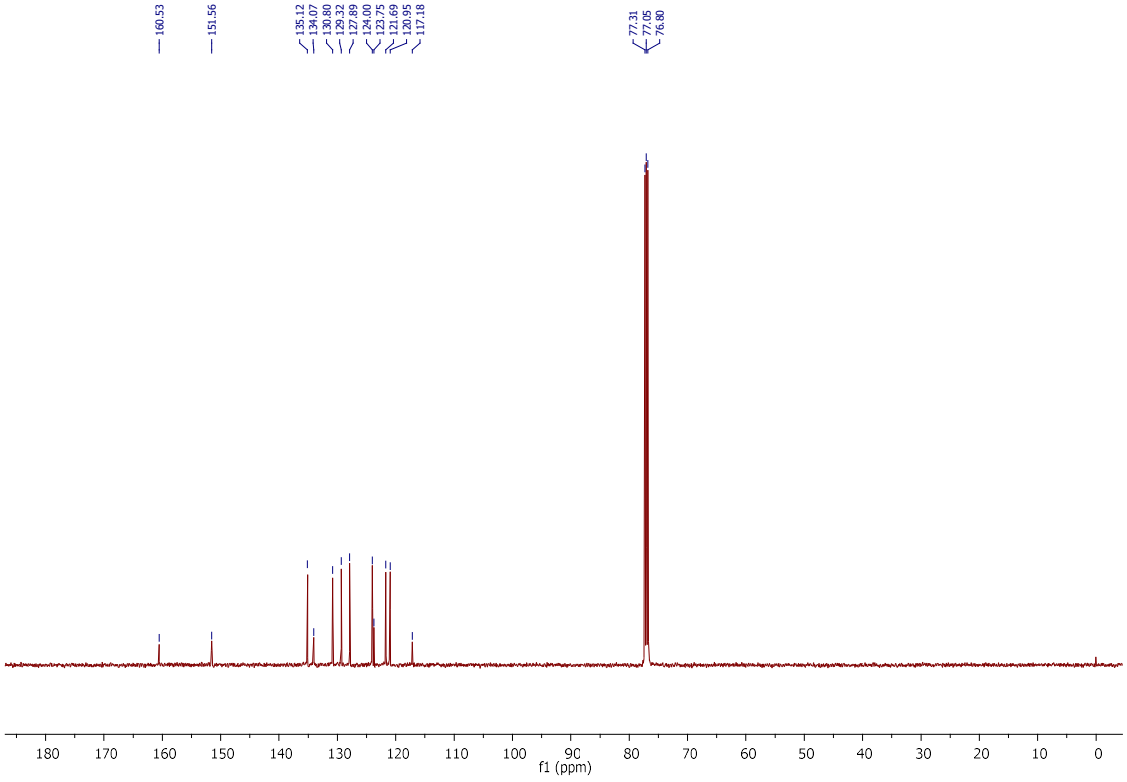

8.40
8.38
8.07
8.06
7.99
7.97
7.85
7.84
7.82
7.62
7.60
7.59
7.37
7.37
7.33
7.32
7.31
7.30
7.26


O
O
Cl
2f
1.00
1.08
1.05
1.03
1.04
0.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


160.61
151.57
135.98
135.12
134.05
130.78
129.23
125.07
123.84
121.71
120.97
118.01
116.77
77.37
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.41
8.40
8.39
8.38
8.38
8.09
8.07
7.93
7.91
7.86
7.84
7.84
7.82
7.82
7.63
7.63
7.61
7.60
7.54
7.54
7.50
7.48
7.47
7.46
7.45
7.26


O
O
2g
Br
1.00
1.08
1.05
1.05
0.97
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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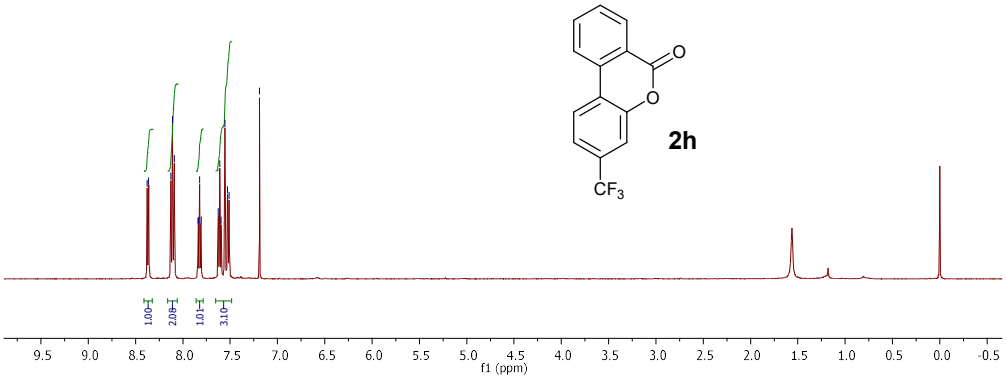
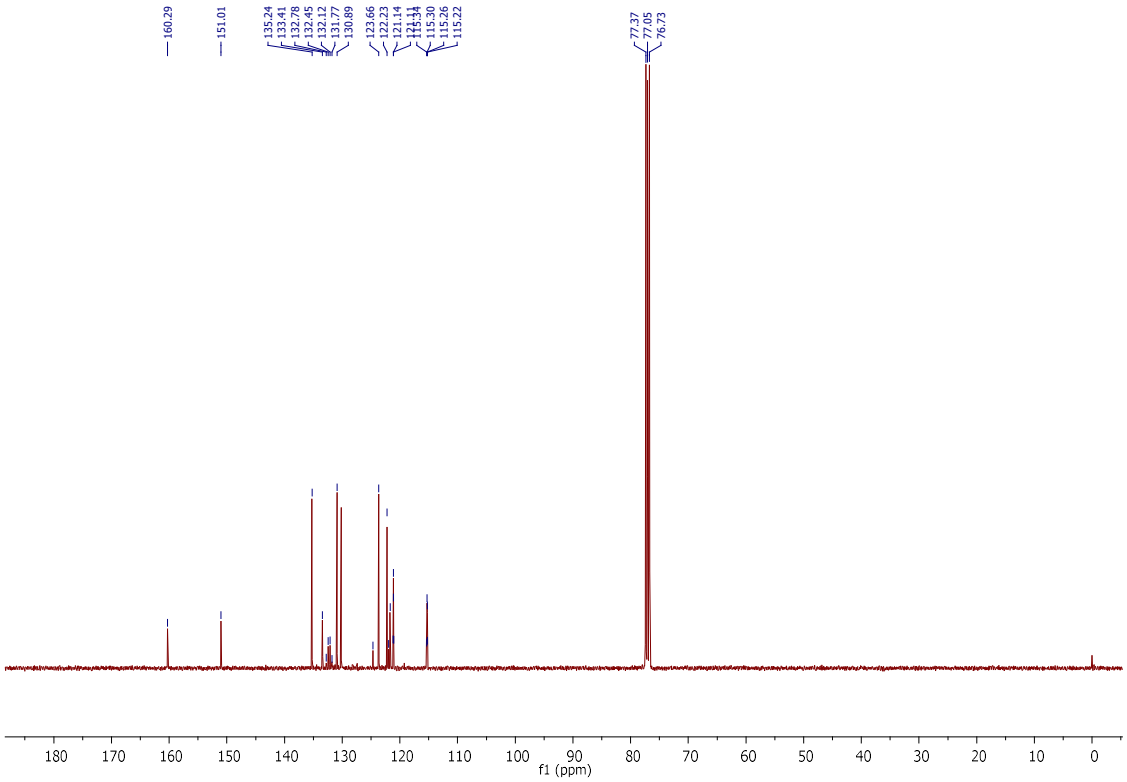
151.56
135.12
134.07
130.80
129.32
127.89
124.00
123.75
121.69
120.95
117.18
77.31
77.05
76.80
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.38
8.36
8.13
8.11
8.09
7.84
7.84
7.82
7.81
7.63
7.61
7.60
7.56
7.53
7.51
7.19


O
O
2h
CF3
1.00
2.08
1.01
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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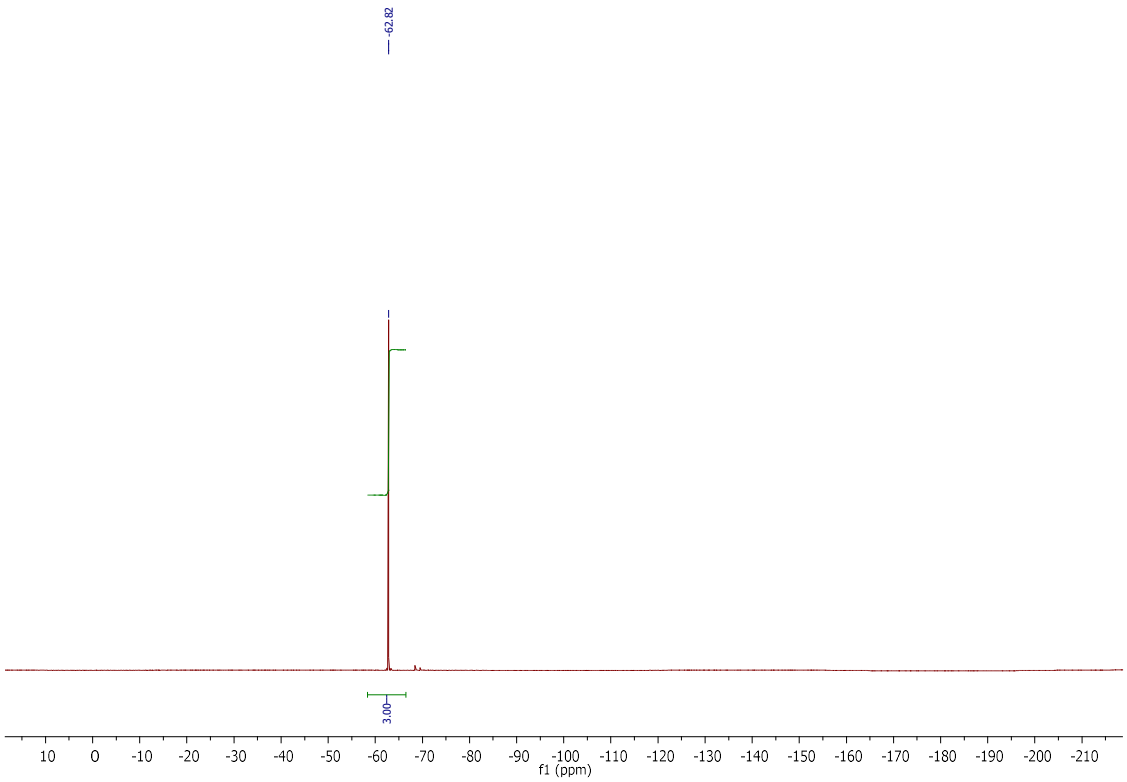
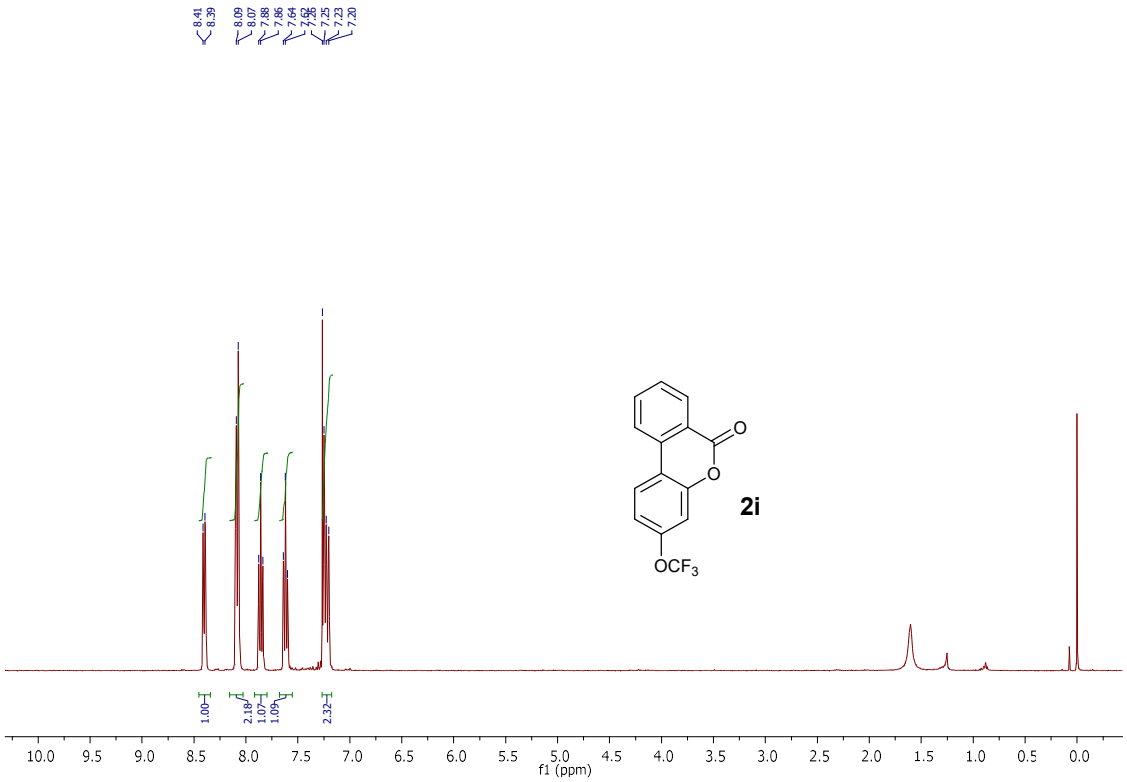
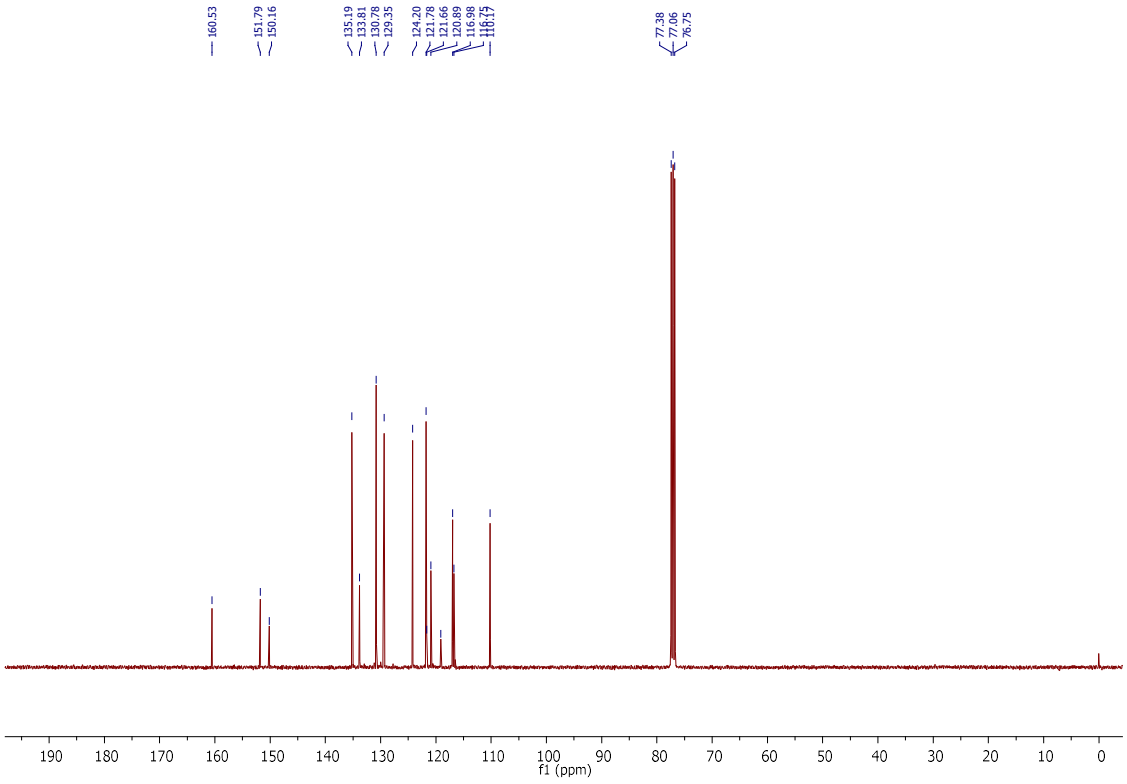
135.24
133.41
132.78
132.45
131.22
131.17
130.89
123.66
122.23
121.14
115.30
115.26
115.22
77.37
77.05
76.73
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.82
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.41
8.39
8.09
8.07
7.88
7.86
7.64
7.62
7.26
7.25
7.23
7.20
O
O
OCF3
2i
1.00
2.18
1.07
1.09
2.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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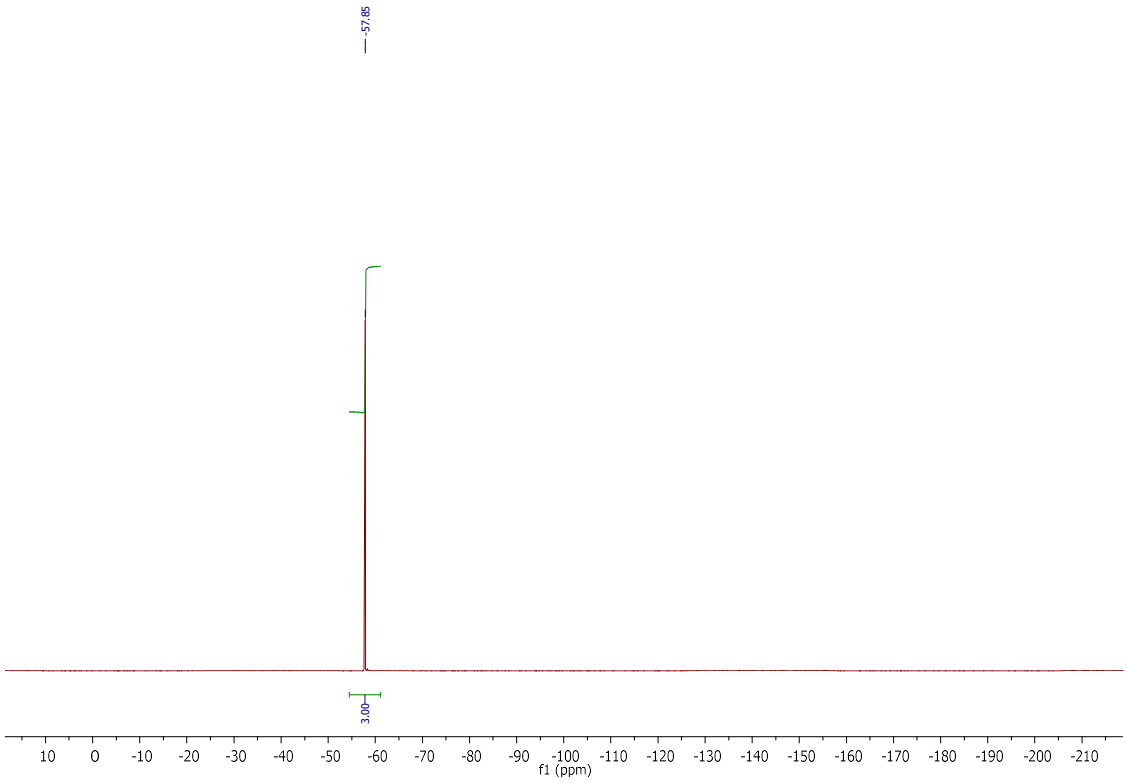
151.79
150.16
135.19
133.81
130.78
129.35
124.20
121.78
121.66
120.89
116.98
77.38
77.06
76.75
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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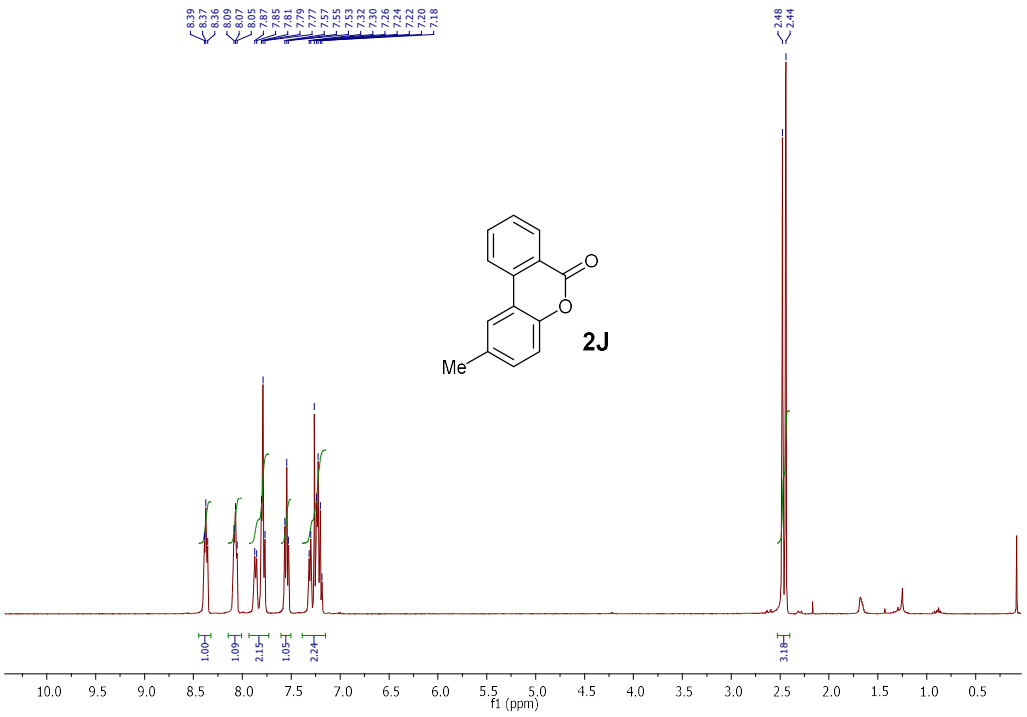
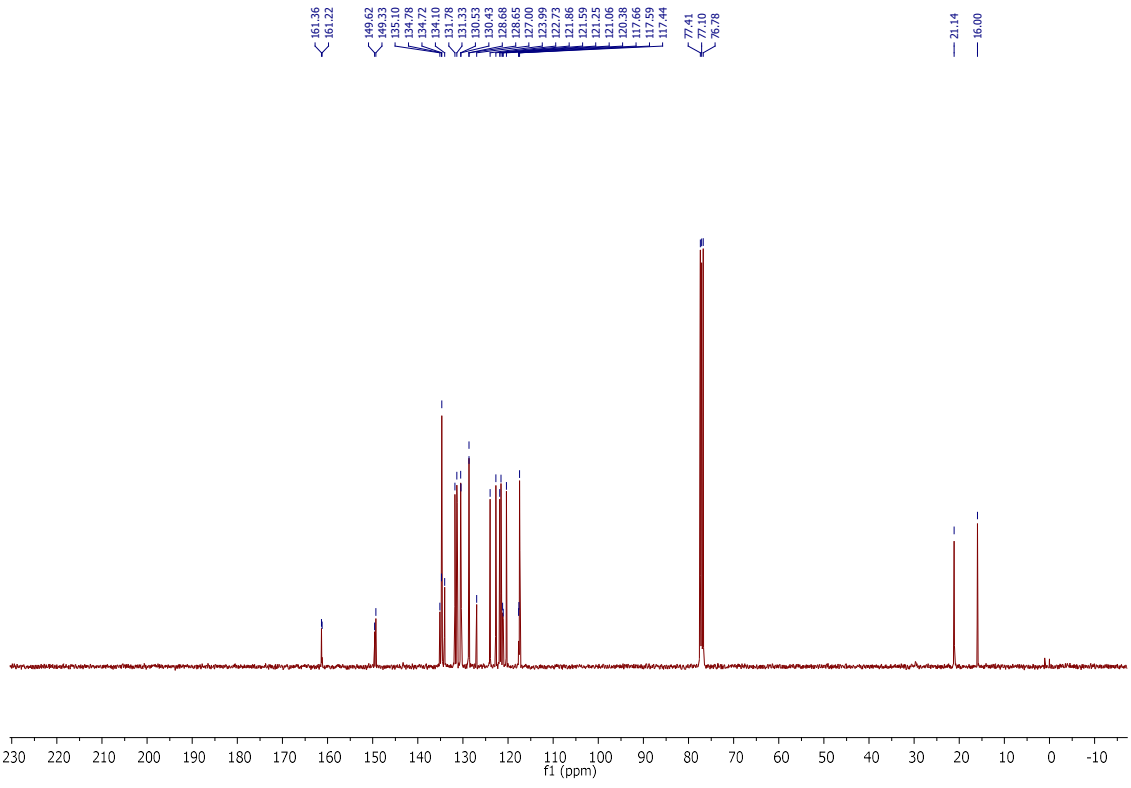
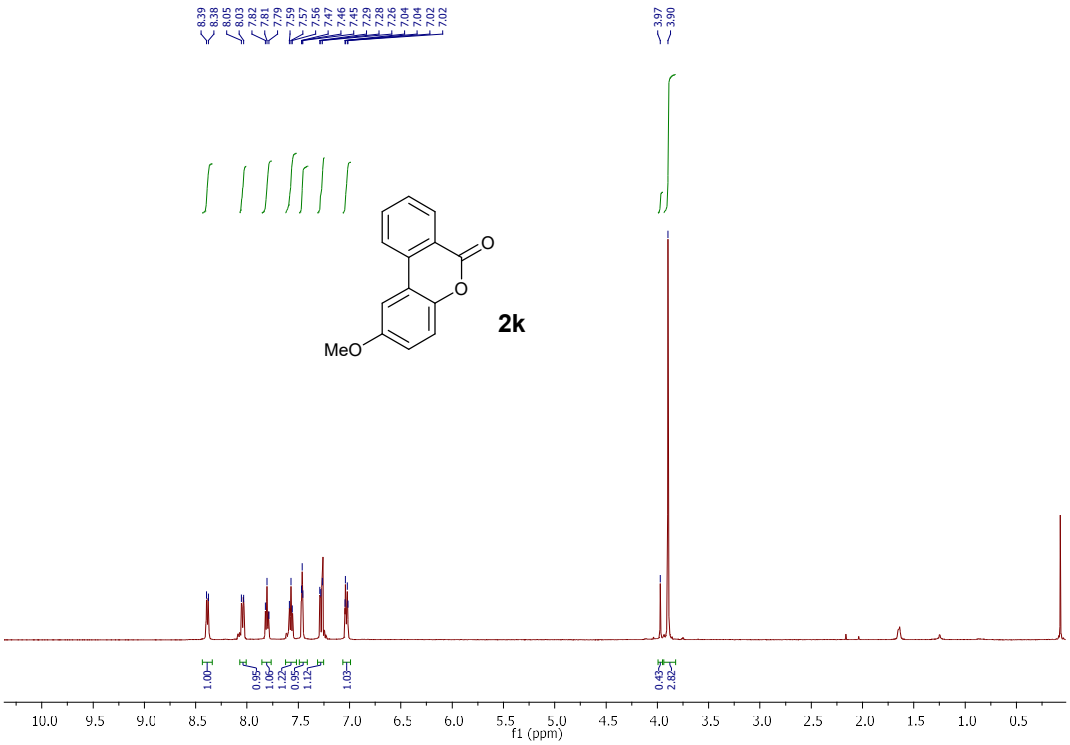
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.39
8.37
8.36
8.09
8.07
8.05
7.87
7.85
7.81
7.79
7.77
7.57
7.55
7.53
7.32
7.30
7.26
7.24
7.22
7.20
7.18
2.48
2.44
O
O
Me
2J
1.00
1.09
2.15
1.05
2.24
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


161.36
161.22
149.62
149.33
135.10
134.78
134.72
134.10
131.78
131.33
130.53
130.43
128.68
128.65
127.00
123.99
122.73
121.86
121.59
121.25
121.06
120.38
117.66
117.59
117.44
77.41
77.10
76.78
21.14
16.00
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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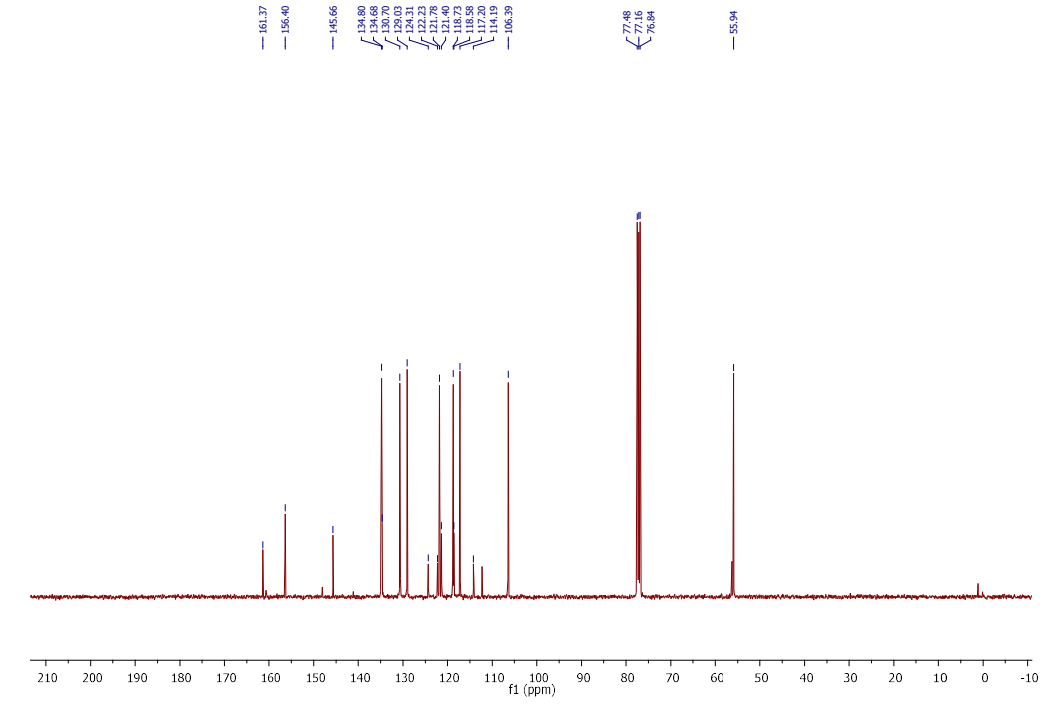
8.38
8.05
8.03
7.82
7.81
7.79
7.59
7.57
7.56
7.47
7.46
7.45
7.29
7.28
7.26
7.04
7.04
7.02
7.02
3.97
3.90
O
O
MeO
2k
1.00
0.95
1.06
1.22
0.95
1.12
1.03
0.43
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


161.37
156.40
145.66
134.80
134.68
130.70
129.03
124.31
122.23
121.78
121.40
118.73
118.58
117.20
114.19
106.39
77.48
77.16
76.84
55.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.43
8.43
8.41
8.41
8.04
8.02
7.88
7.87
7.86
7.86
7.85
7.85
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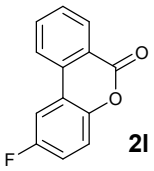
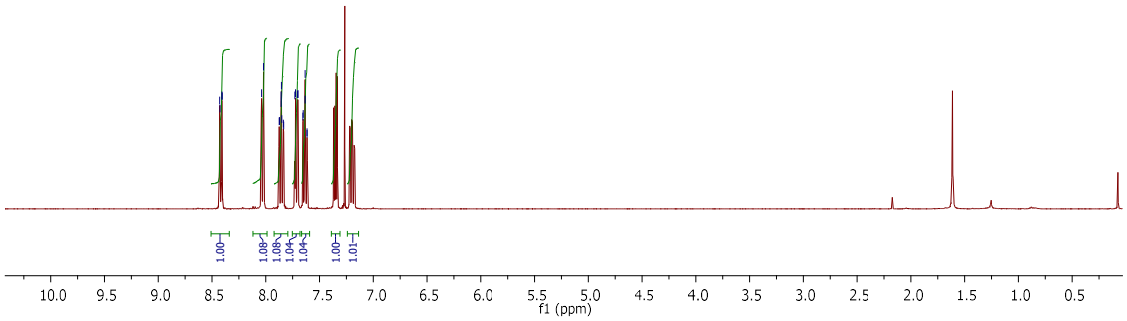
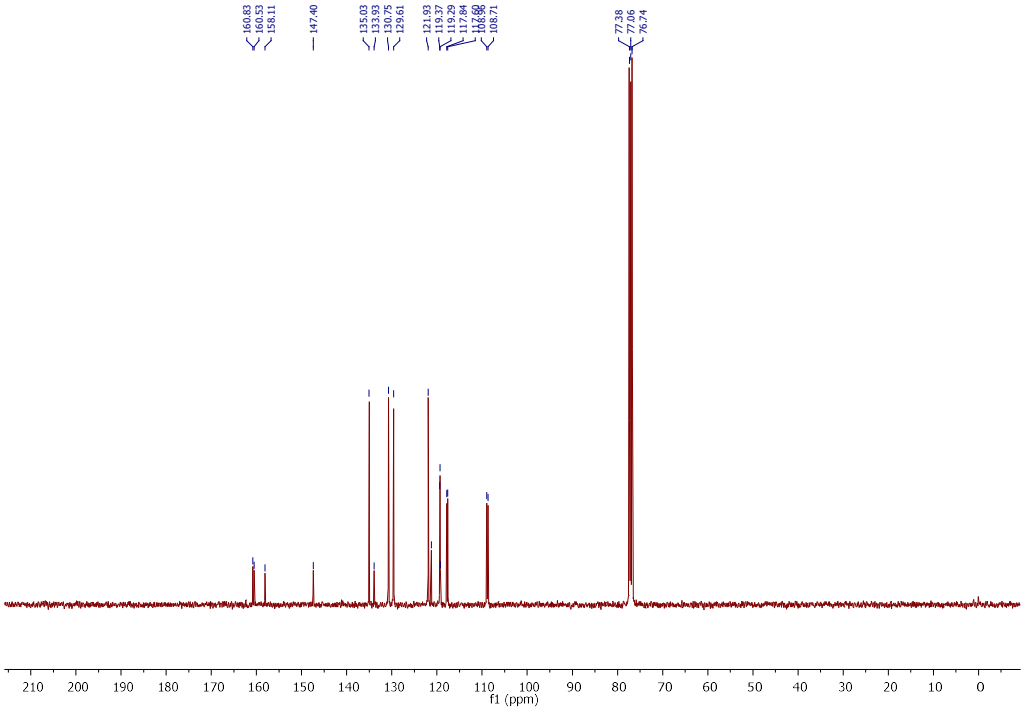
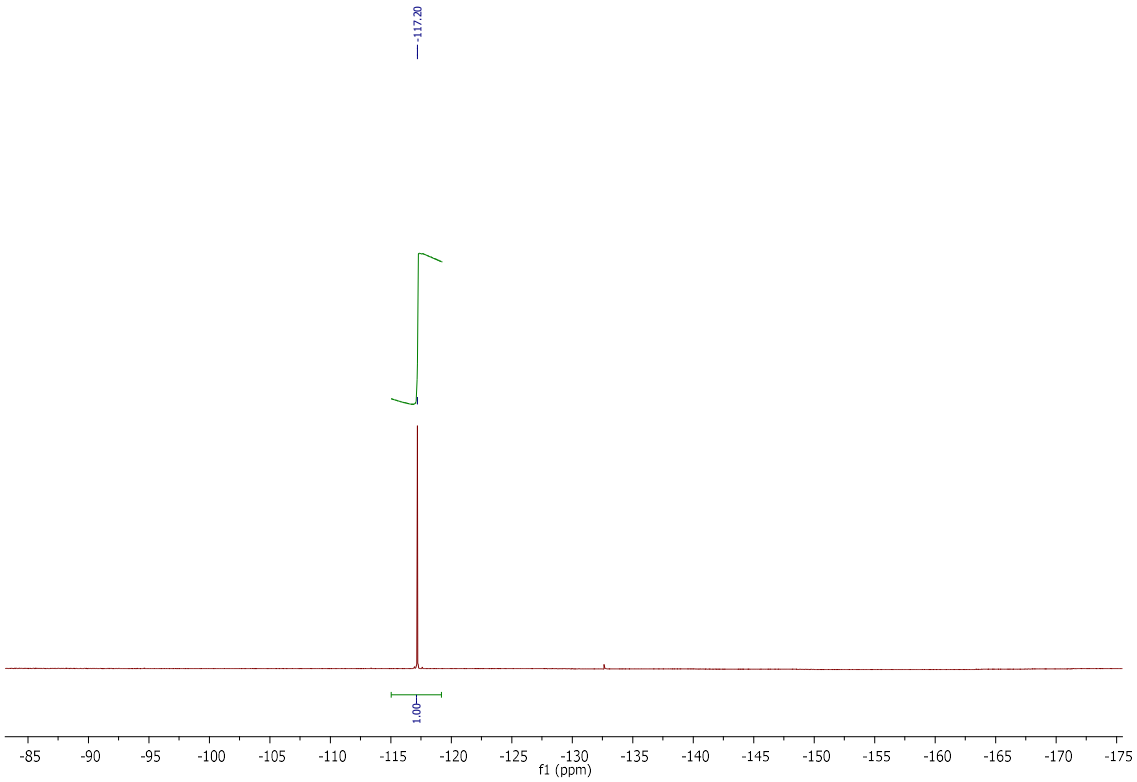
7.66
7.65
7.64
7.63
7.62
7.62


O
O
F

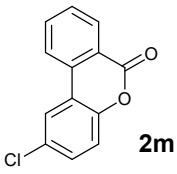
2l


1.00
1.08
1.08
1.04
1.04
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


160.83
160.53
158.11
147.40
135.03
133.93
130.75
129.61
121.93
119.77
119.39
117.84
117.60
117.56
108.71
77.38
77.06
76.74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

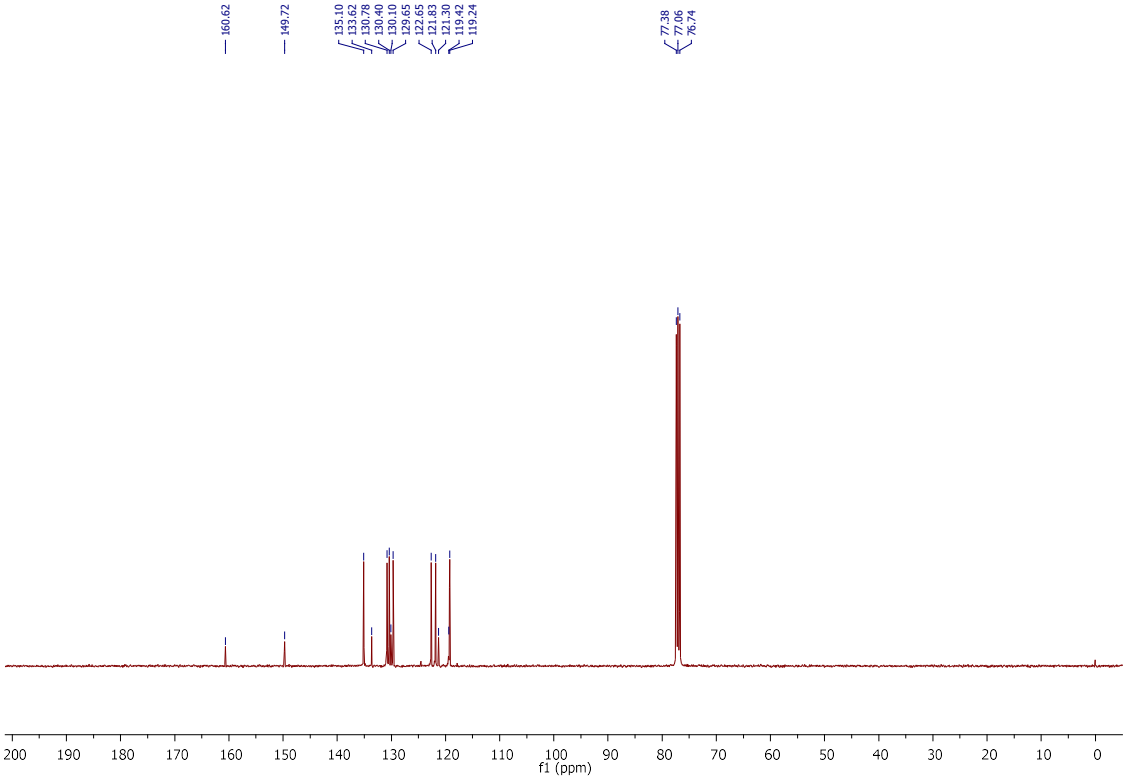

-117.20
1.00
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)

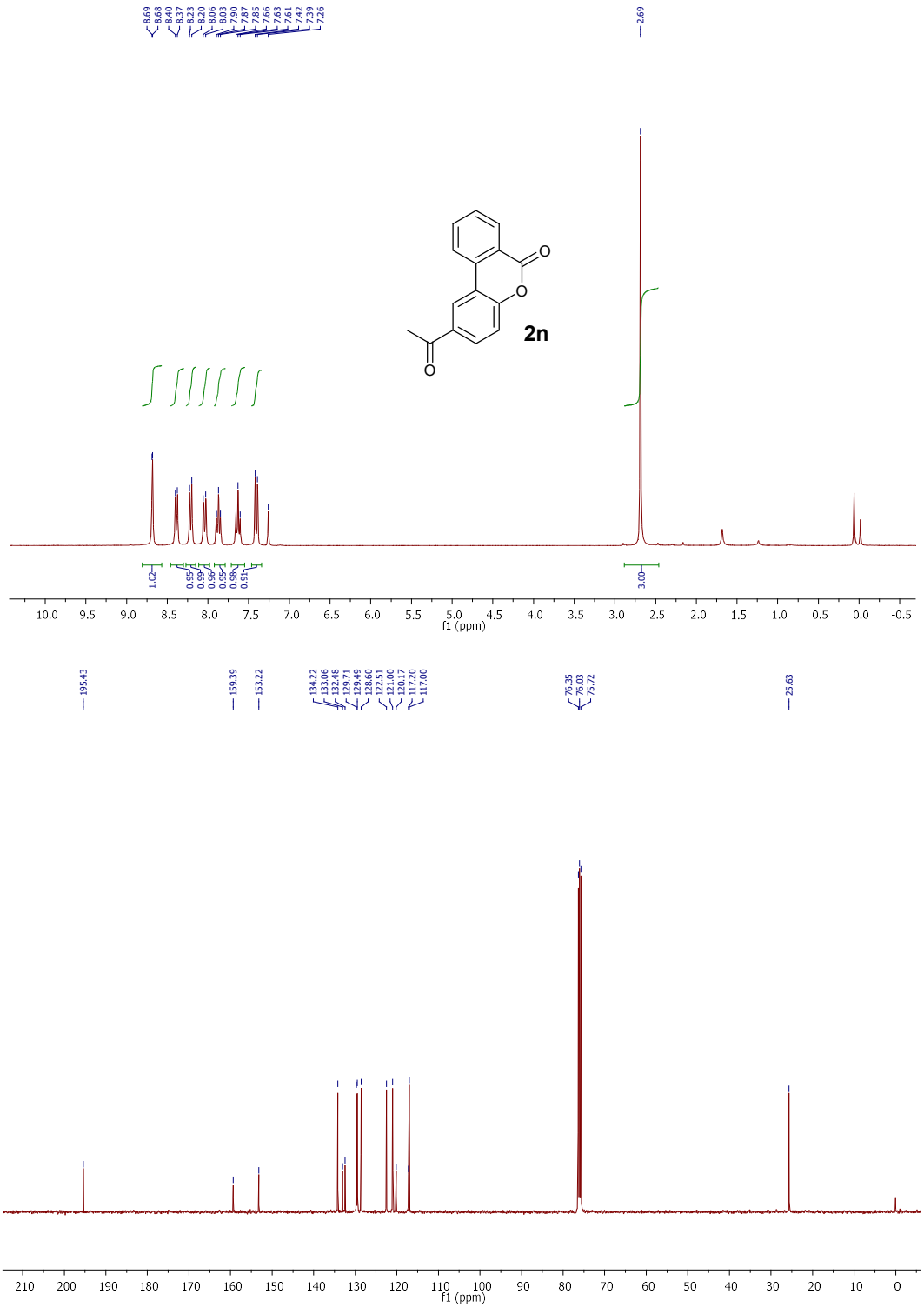

8.42
8.42
8.40
8.40
8.07
8.05
8.02
8.01
7.88
7.87
7.86
7.85
7.84
7.83
7.66
7.65
7.63
7.62
7.61
7.45
7.44
7.43
7.42
7.33
7.30
7.26

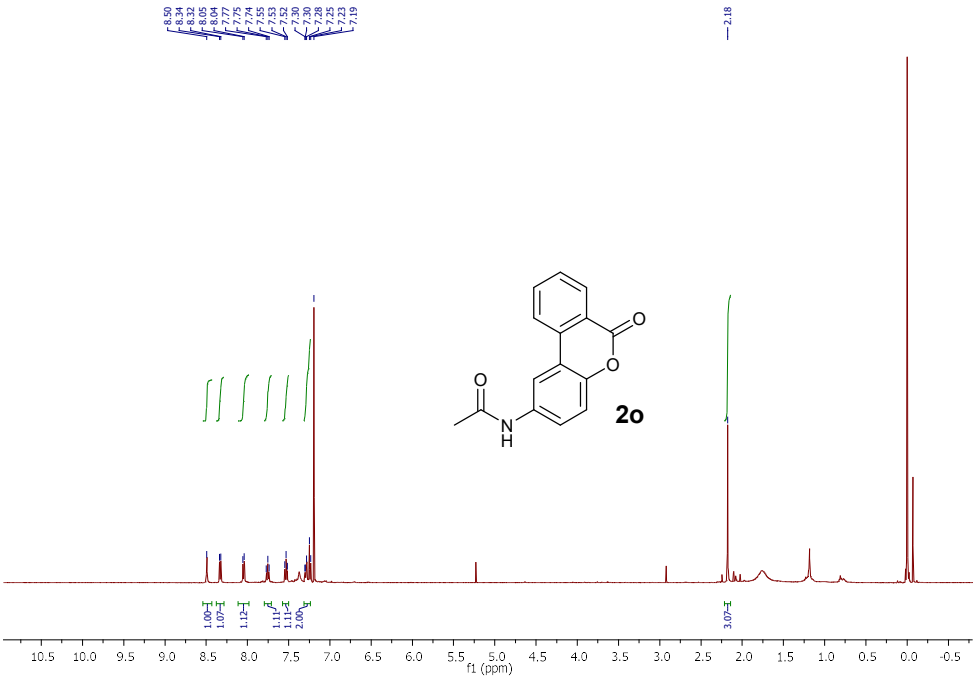

O
O
Cl

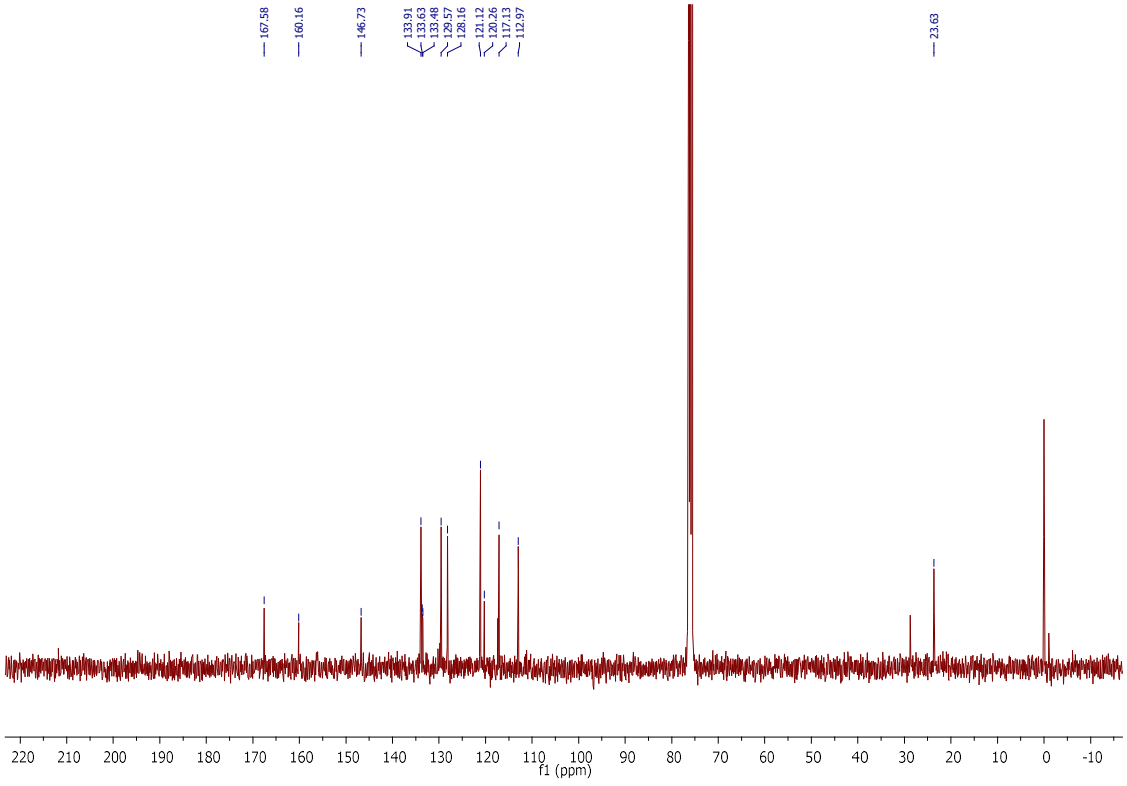
2m

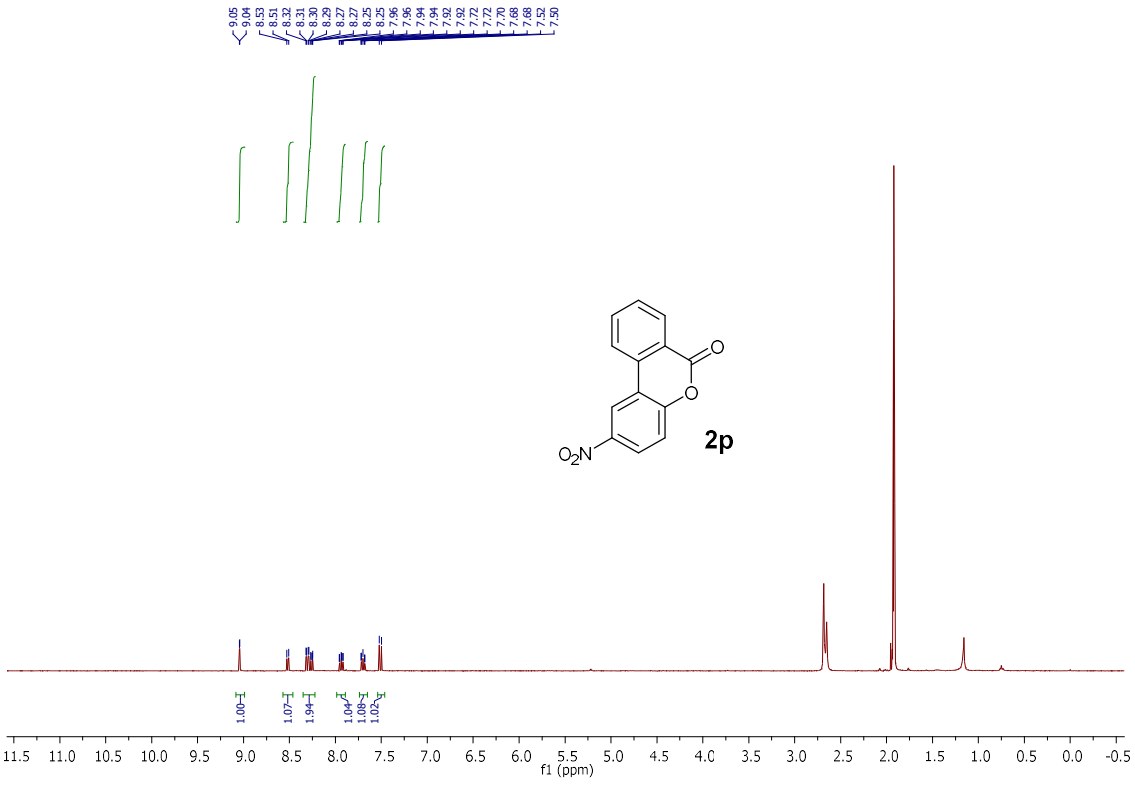
1.00
2.04
1.07
1.05
0.99
0.96
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

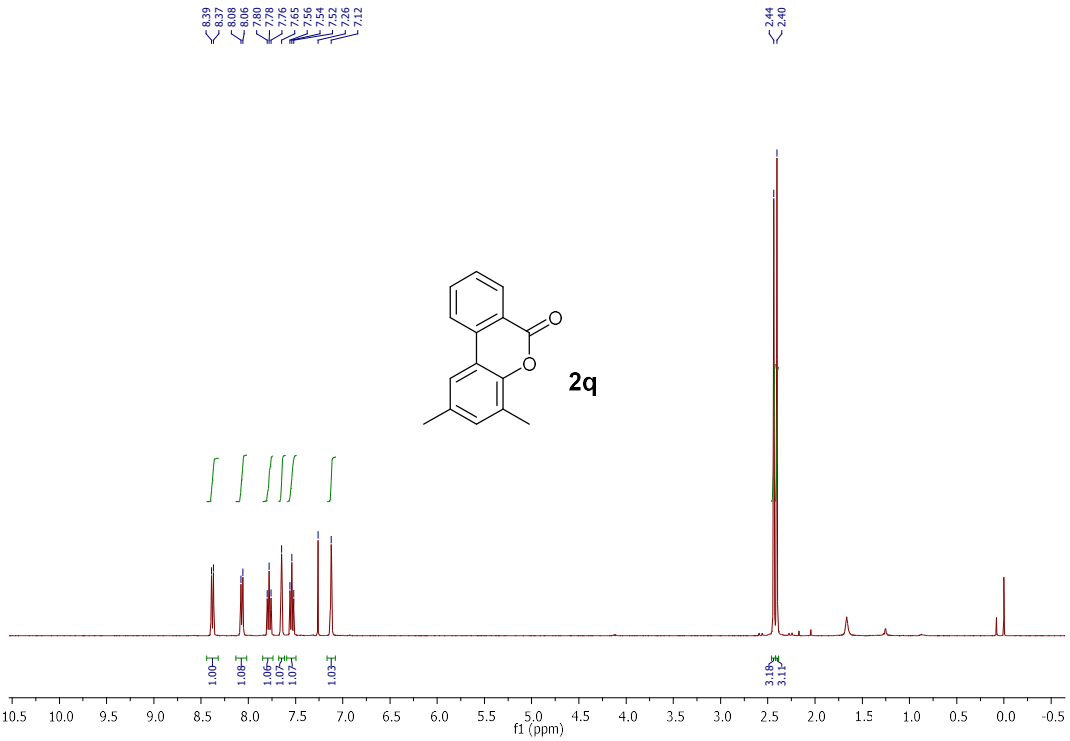

160.62
149.72
135.10
133.62
130.78
130.40
130.10
129.65
122.65
121.83
121.30
119.42
119.24
77.38
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

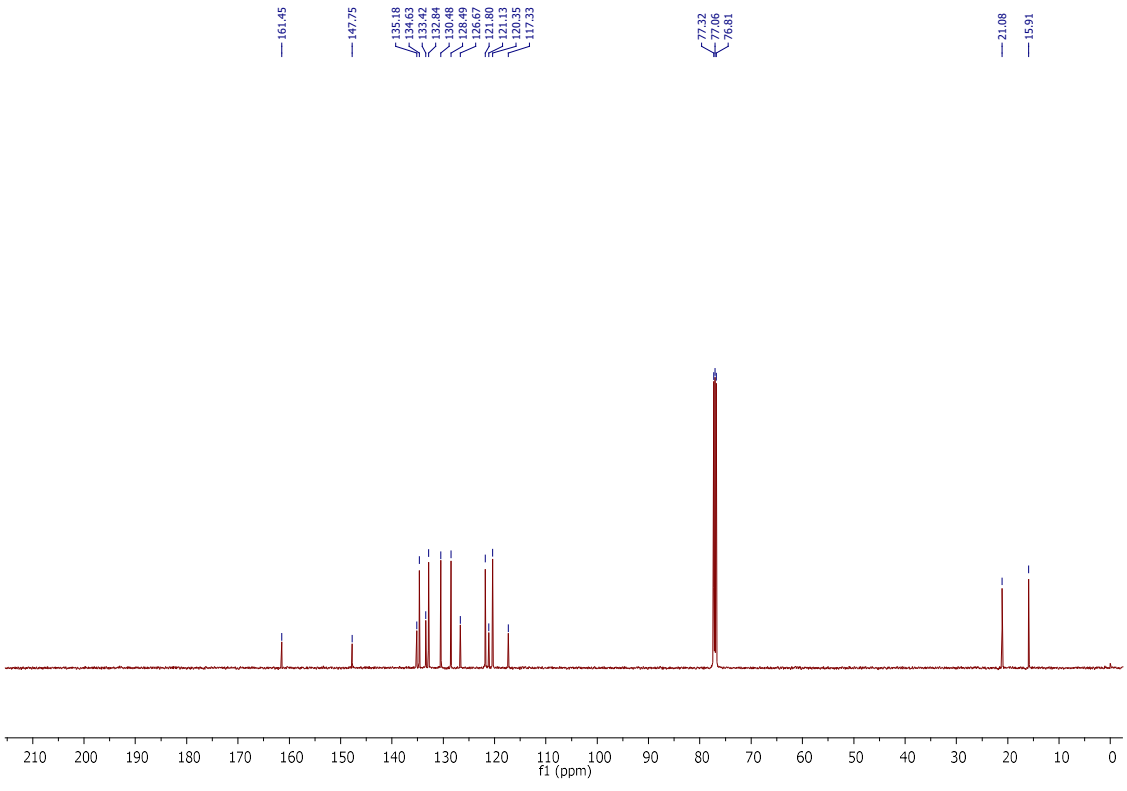

8.69
8.68
8.40
8.37
8.23
8.20
8.06
8.03
7.90
7.87
7.85
7.66
7.63
7.61
7.42
7.39
7.26
2.69
O
O
O
2n
1.02
0.98
0.99
0.96
0.95
0.98
0.91
3.00
f1 (ppm)
195.43
159.39
153.22
134.22
133.66
132.48
129.71
129.49
128.60
122.51
121.00
120.17
117.20
117.00
76.35
76.03
75.72
25.63
f1 (ppm)

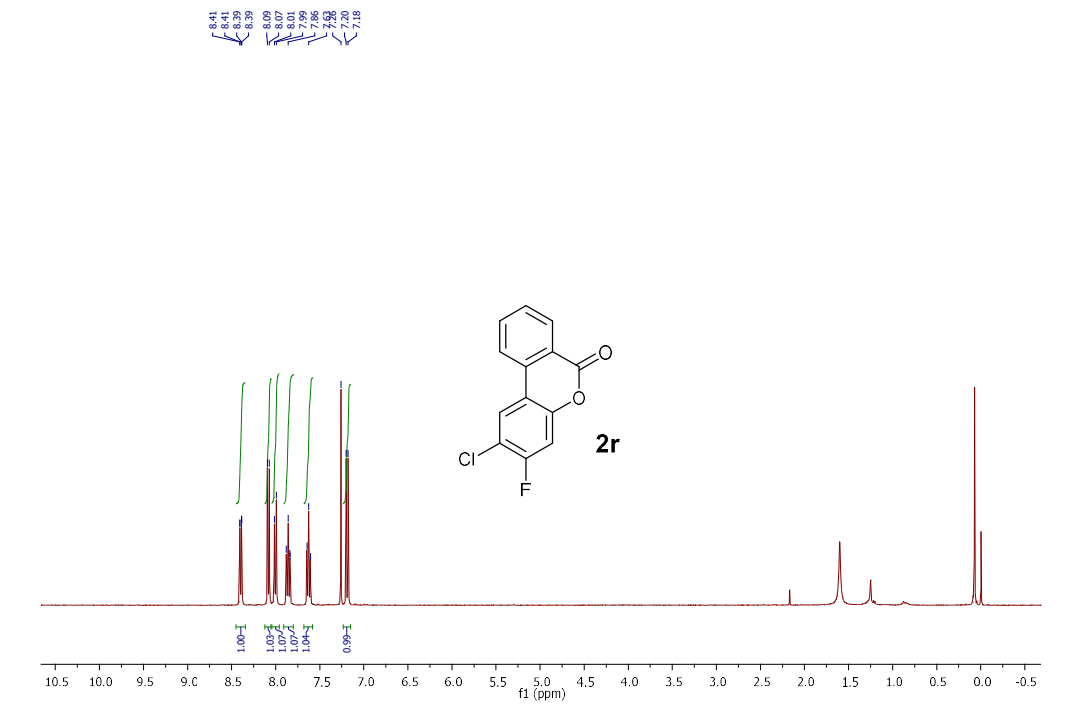

8.50
8.34
8.32
8.05
8.04
7.77
7.75
7.74
7.55
7.53
7.52
7.30
7.28
7.25
7.23
7.19
2.18
O
O
O
N
H
2o
1.00
1.07
1.12
1.11
1.14
2.00
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

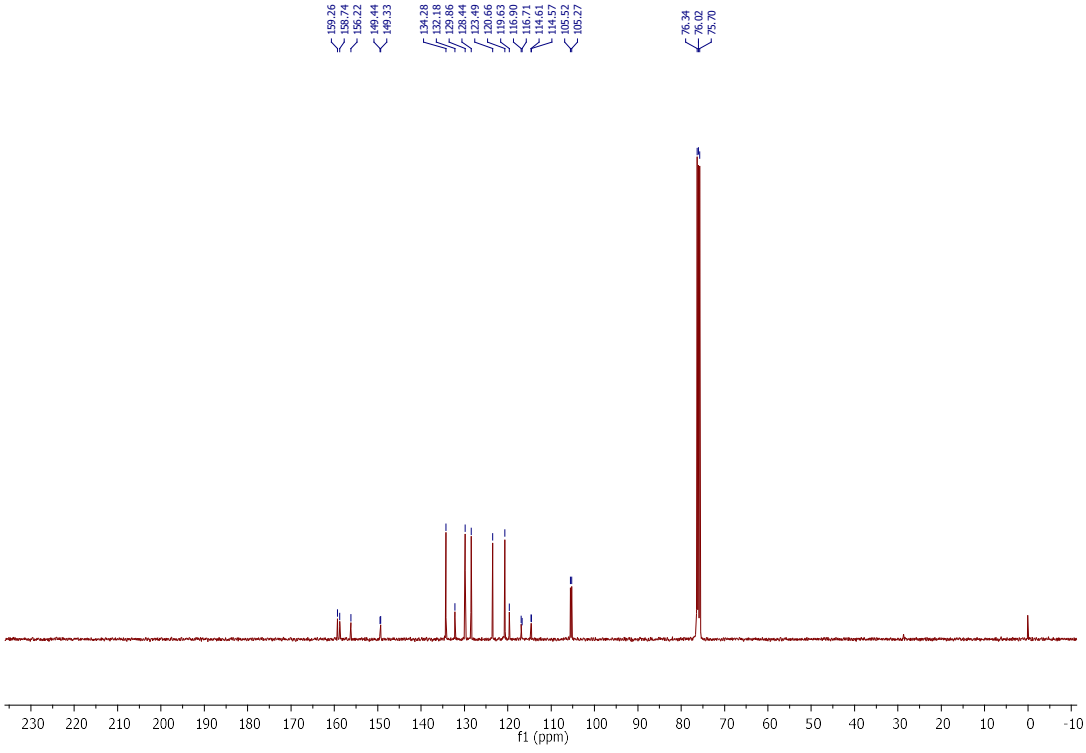

167.58
160.16
146.73
133.91
133.63
133.48
129.57
128.16
121.12
120.26
117.13
112.97
23.63
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

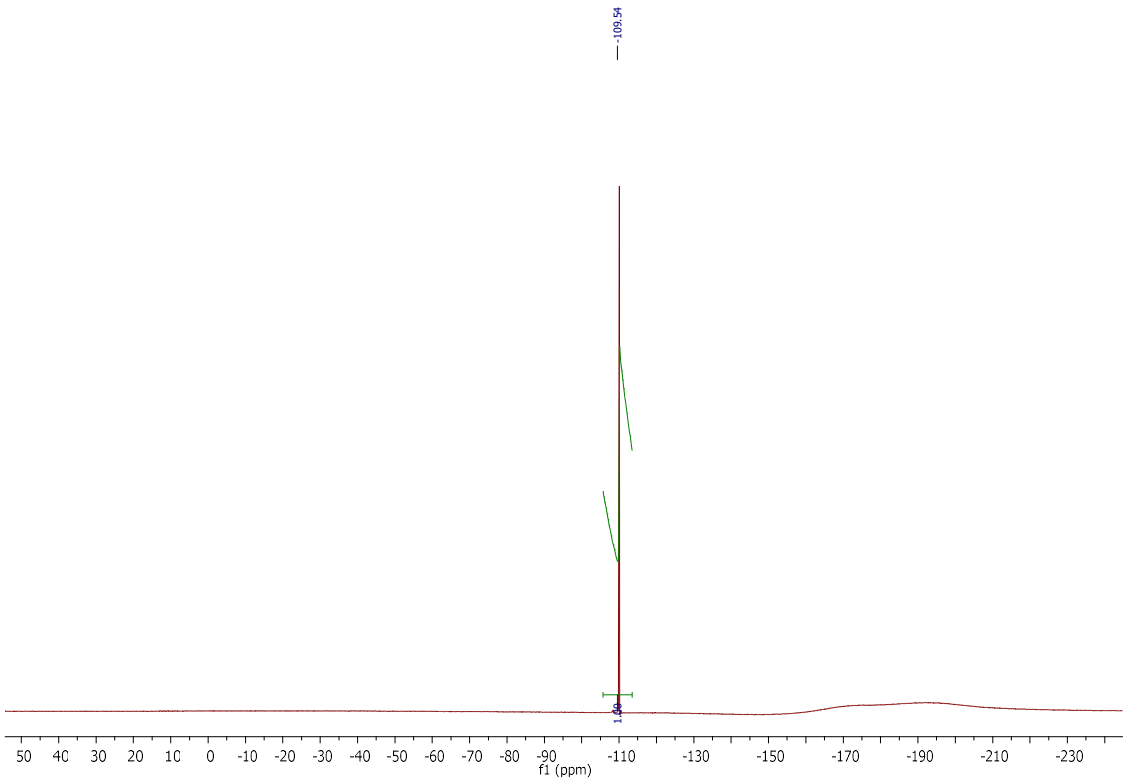

9.05
9.04
8.53
8.51
8.32
8.31
8.30
8.29
8.27
8.27
8.25
8.25
7.96
7.96
7.94
7.94
7.92
7.92
7.72
7.72
7.70
7.68
7.68
7.52
7.50
O
O
O2N
2p
1.00
1.07
1.94
1.04
1.06
1.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

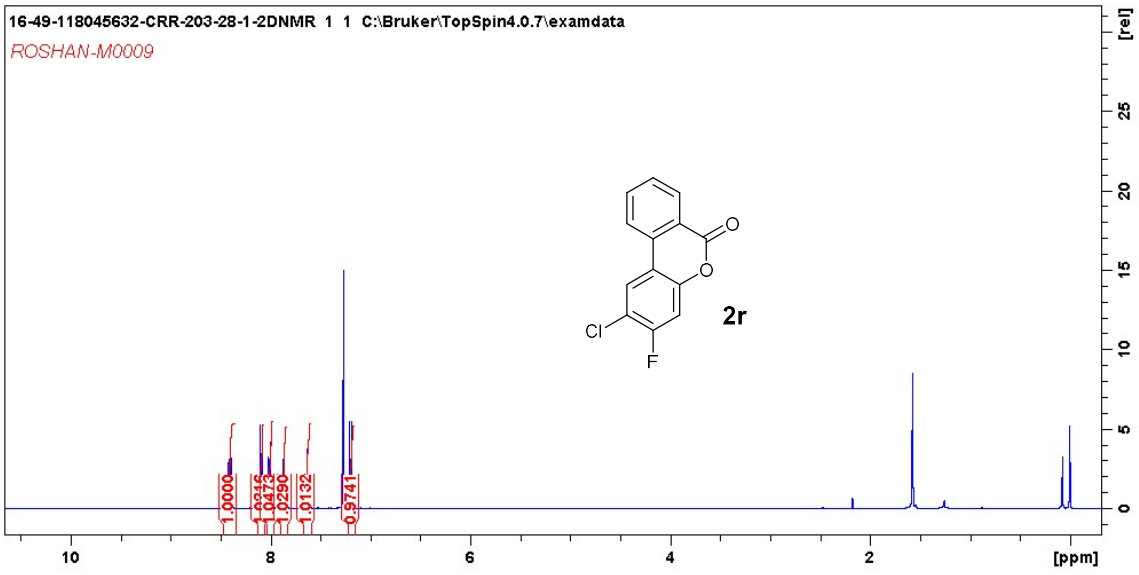

8.39
8.37
8.08
8.06
7.80
7.78
7.76
7.65
7.55
7.54
7.52
7.26
7.12
2.44
2.40
O
O
2q
1.00
1.08
1.06
1.15
1.07
1.03
3.18
3.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.45
147.75
135.18
134.63
133.42
132.84
130.48
128.49
126.67
121.80
121.13
120.35
117.33
77.32
77.06
76.81
21.08
15.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

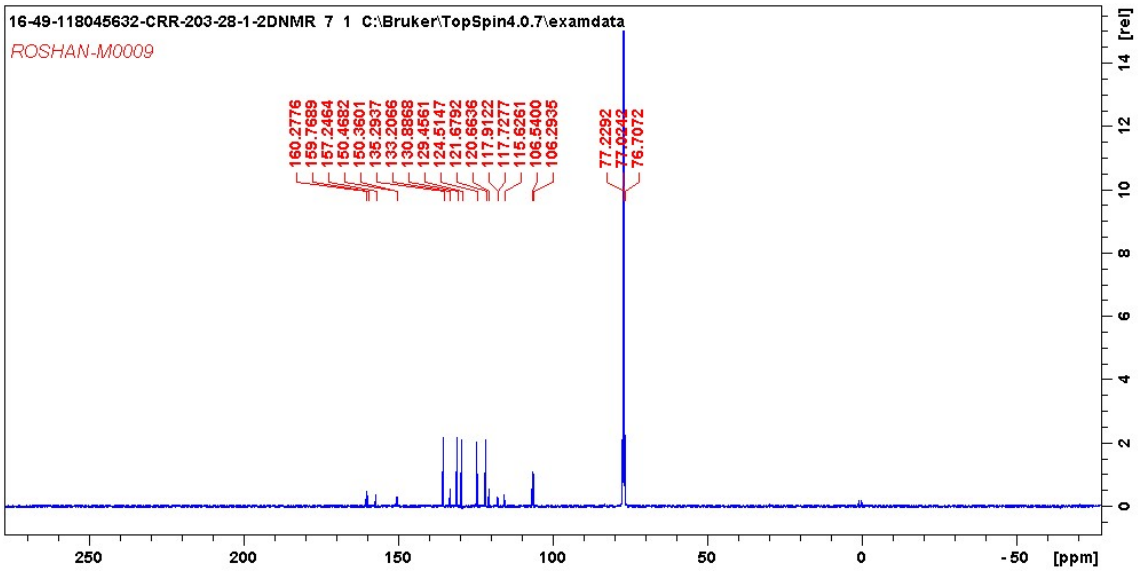

8.41
8.41
8.39
8.39
8.09
8.07
8.01
7.99
7.86
7.84
7.22
7.20
7.18
O
O
Cl
F
2r
1.00
1.03
1.07
1.07
1.04
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.26
158.74
156.22
149.44
149.33
134.28
132.18
129.86
128.44
123.49
120.66
119.63
116.90
116.71
114.57
114.61
105.52
105.27
76.34
76.02
75.70
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

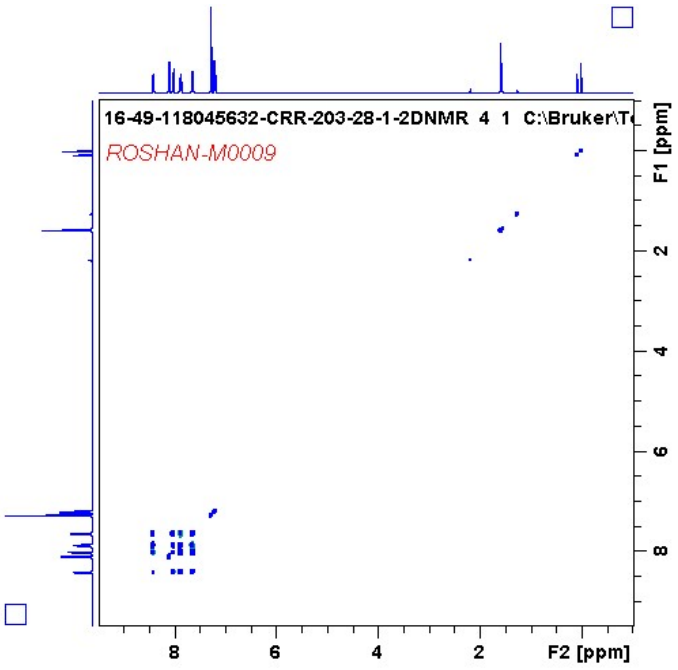

-109.54
1.00
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



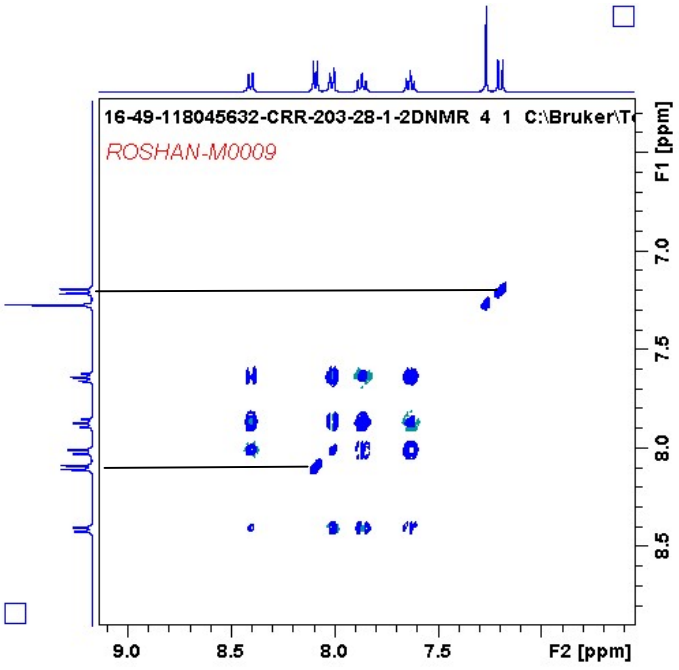
^{1}H (400 Mz) NMR spectrum of **2r** ($CDCl_3$, 298 K).



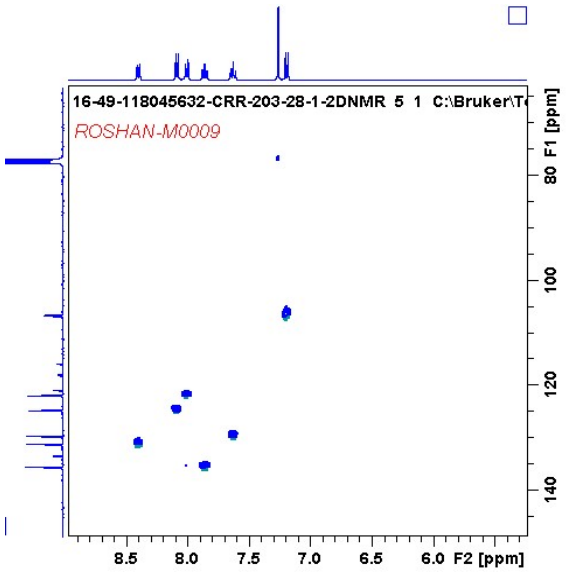
^{13}C (100MHz) NMR spectrum of **2r** ($CDCl_3$, 298 K).



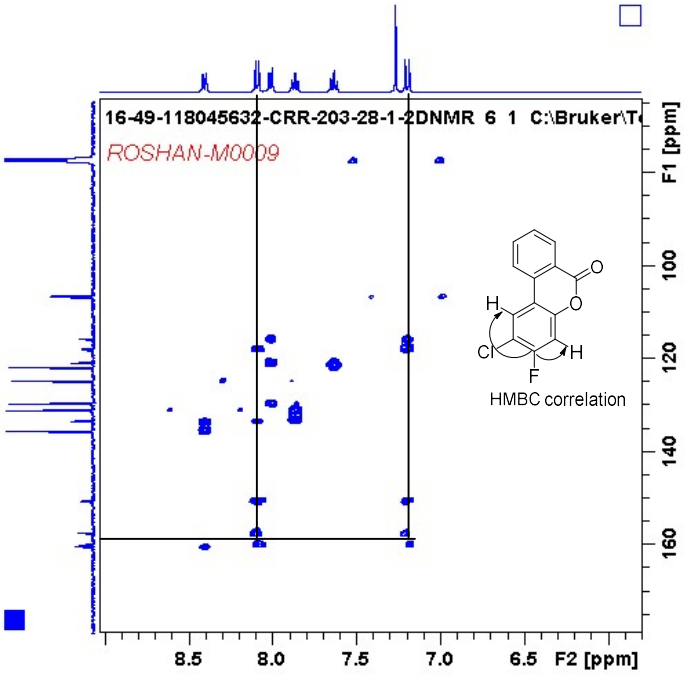
^{1}H, ^{1}H(400MHz) COSY NMR spectrum of **2r** ($CDCl_3$, 298 K).



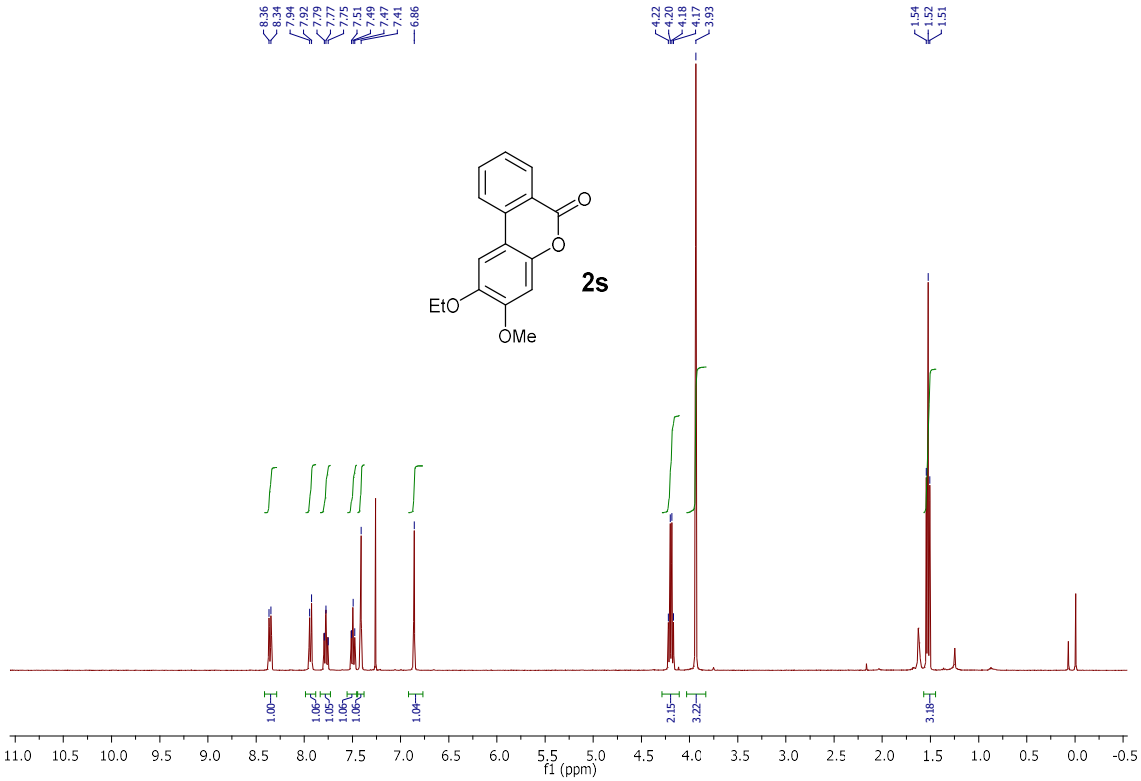
Part of ^{1}H, ^{1}H(400MHz) COSY NMR spectrum of **2r** ($CDCl_3$, 298 K).

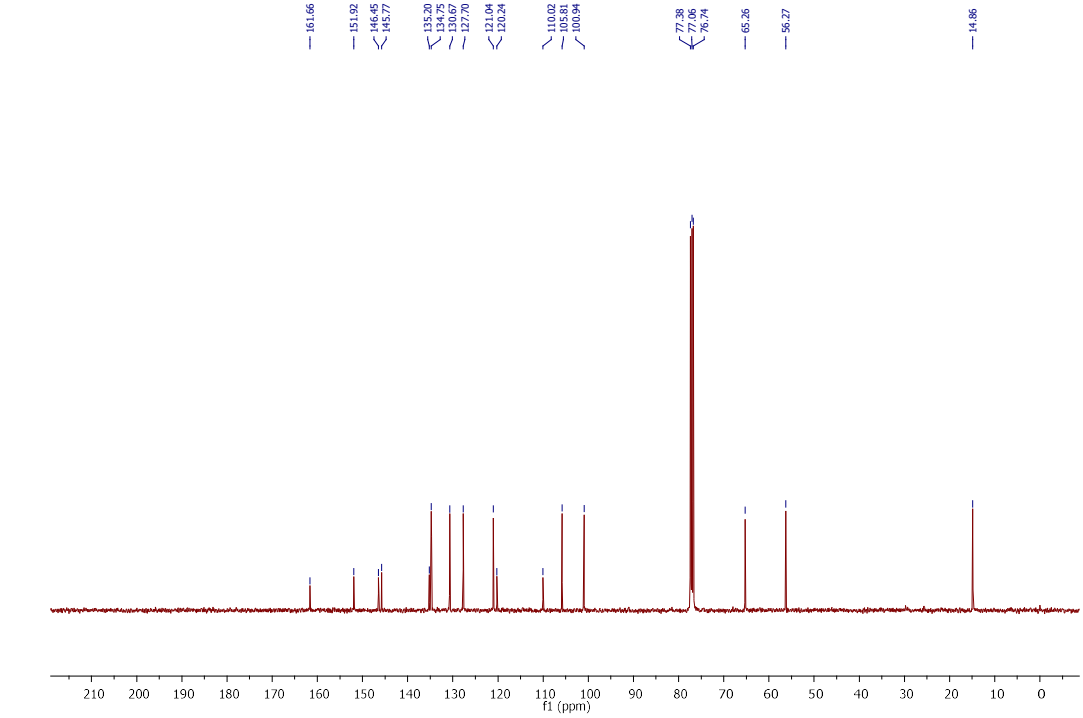


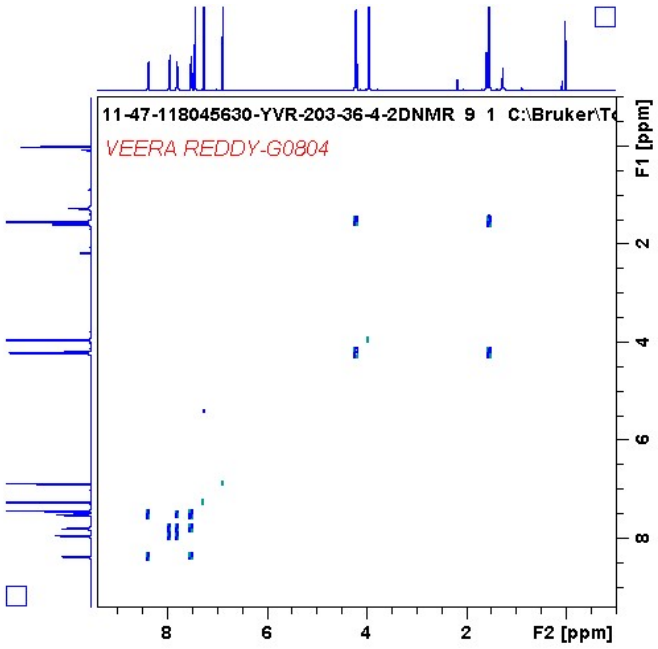
^{1}H(400 MHz),^{13}C(100 MHz) HSQC NMR spectrum of **2r** ($CDCl_3$, 298 K).



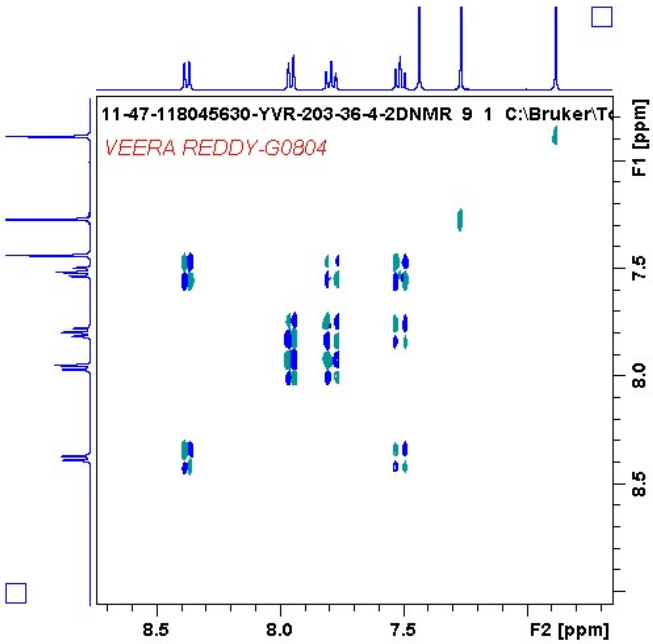
^{1}H(400 MHz),^{13}C(100 MHz) HMBC NMR spectrum of **2r** ($CDCl_3$, 298 K).


8.36
8.34
7.94
7.92
7.79
7.77
7.75
7.51
7.49
7.47
7.41
6.86
4.22
4.20
4.18
4.17
3.93
1.54
1.52
1.51
O
O
EtO
OMe
2s
1.00
1.06
1.05
1.06
1.06
1.04
2.15
3.22
3.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

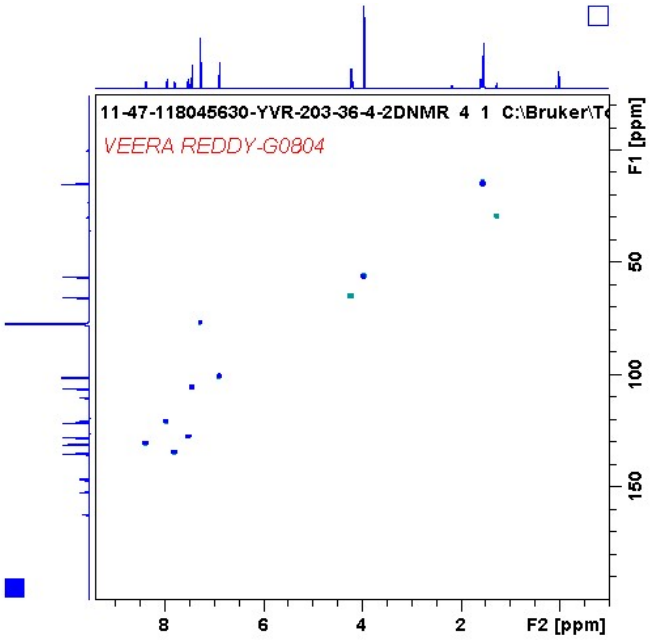

161.66
151.92
146.45
145.77
135.20
134.75
130.67
127.70
121.04
120.24
110.02
105.81
100.94
77.38
77.06
76.74
65.26
56.27
14.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



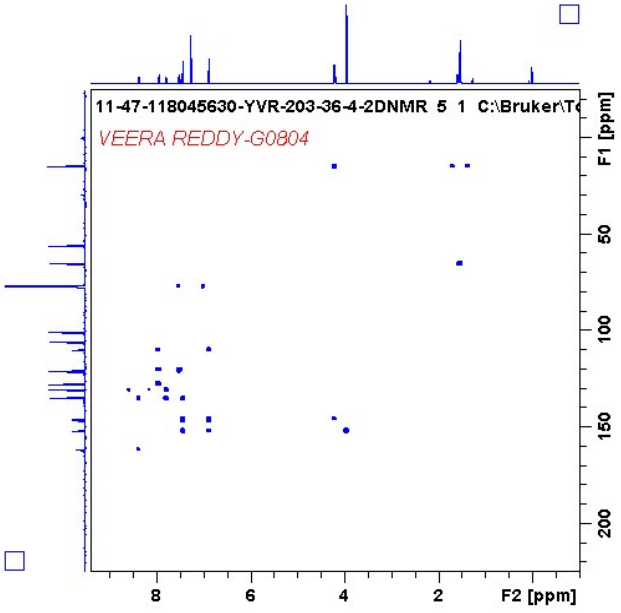
^{1}H, ^{1}H(400MHz) COSY NMR spectrum of **2s** ($CDCl_3$, 298 K).



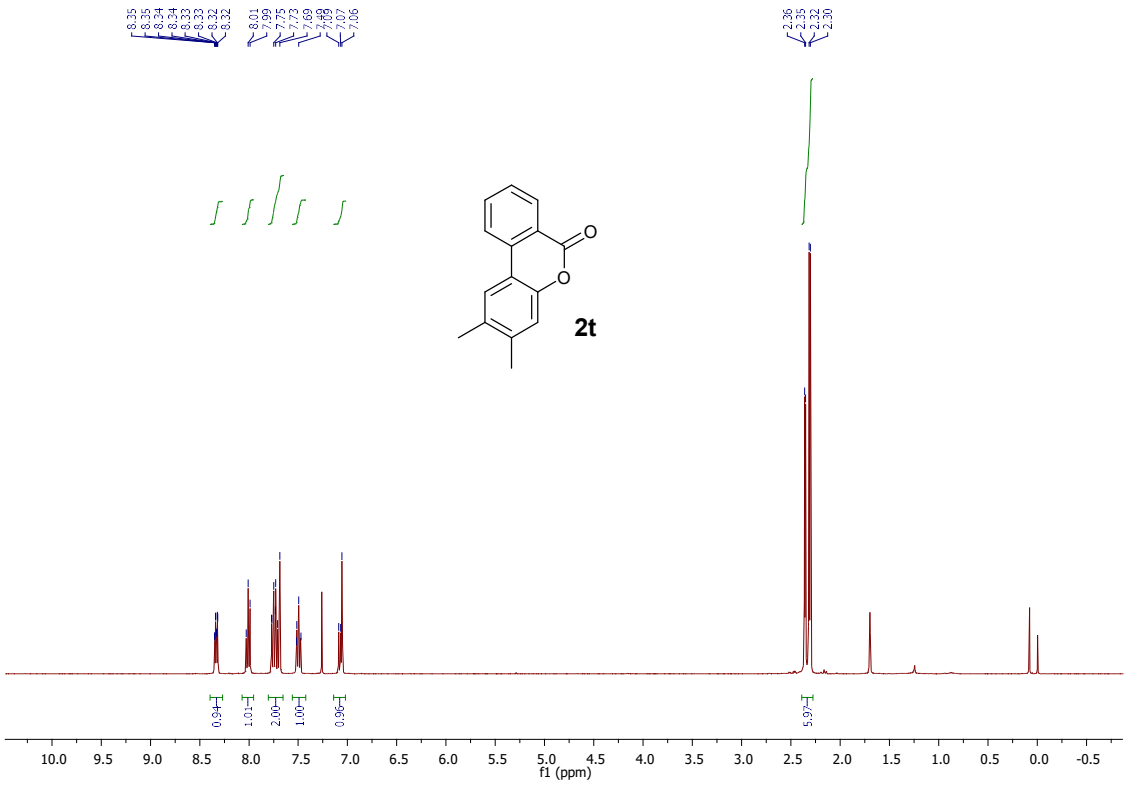
Part of ^{1}H, ^{1}H(400MHz) COSY NMR spectrum of **2s** ($CDCl_3$, 298 K).

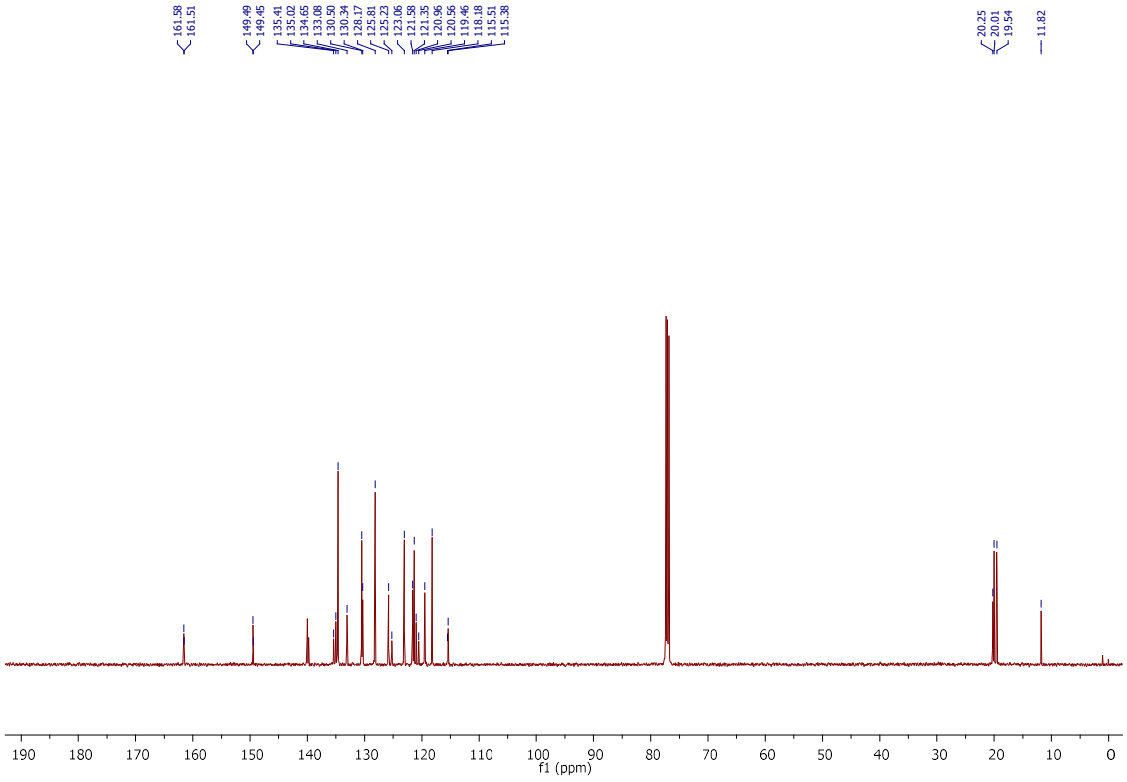


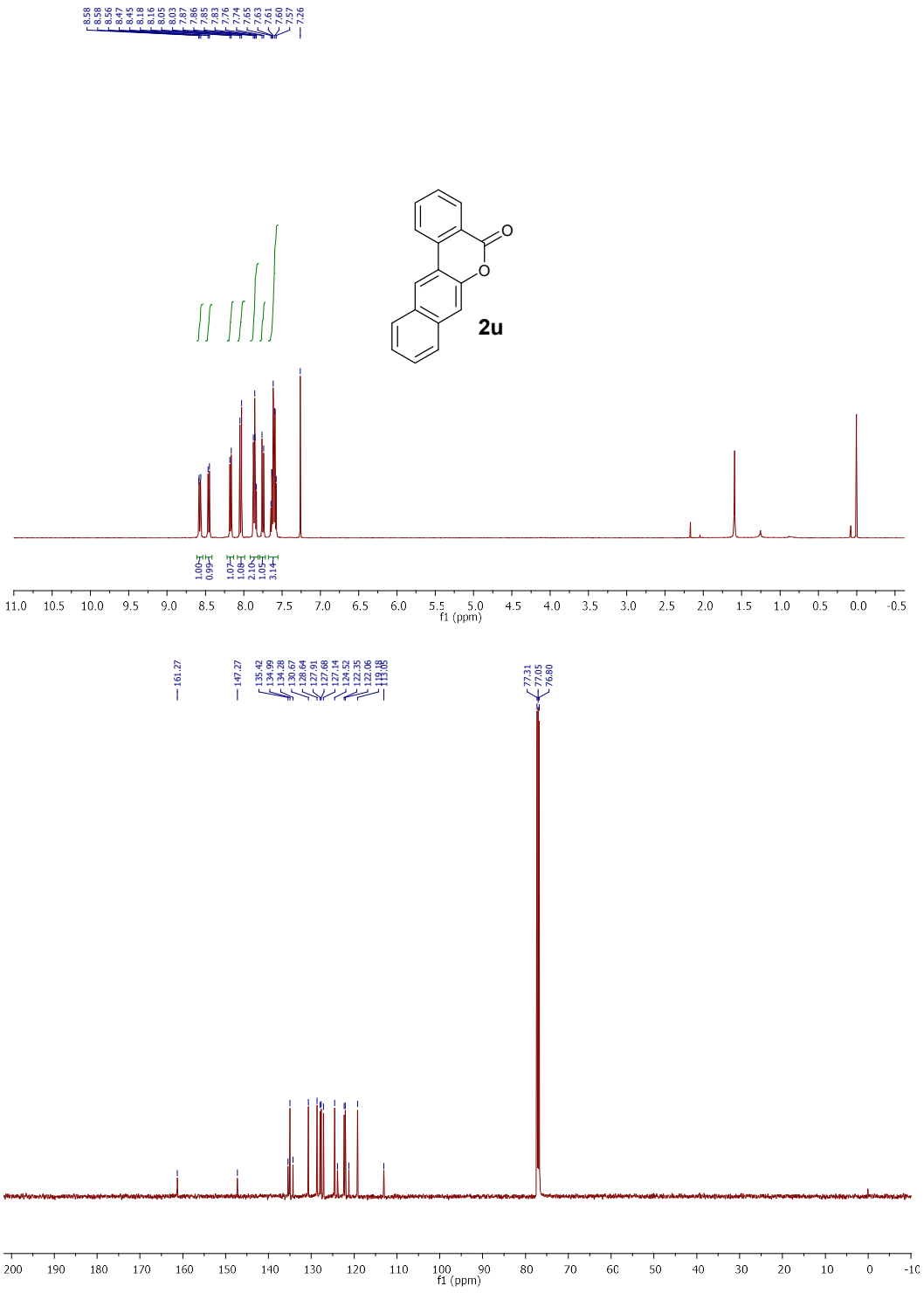
^{1}H(400 MHz),^{13}C(100 MHz) HSQC NMR spectrum of **2s** ($CDCl_3$, 298 K).

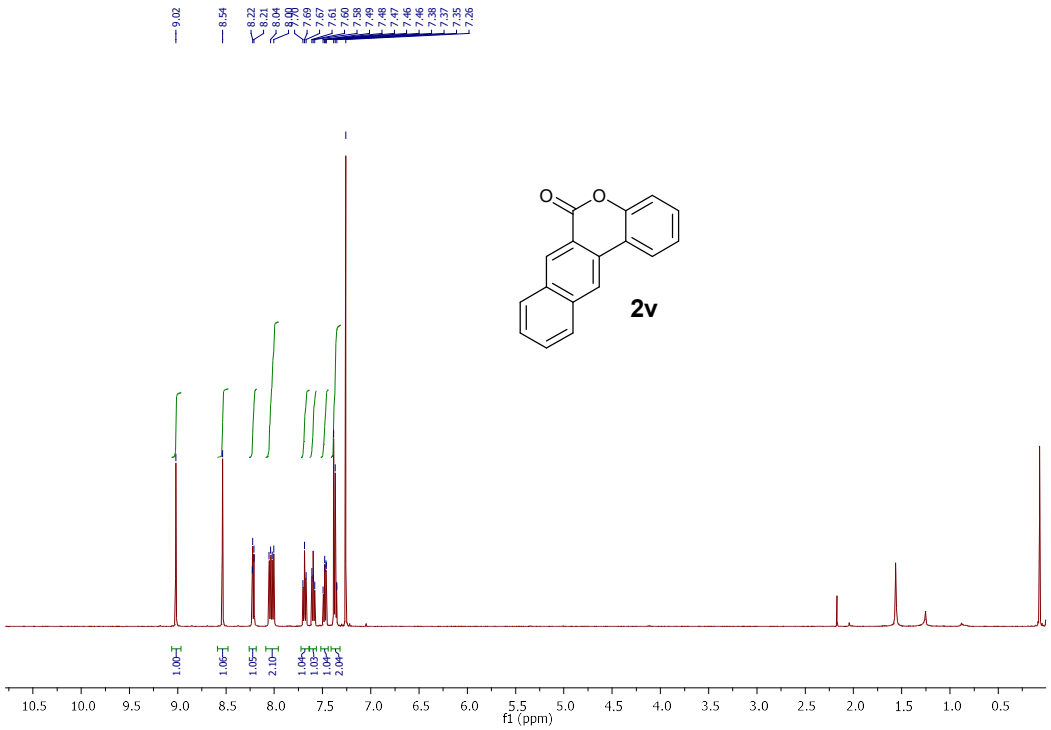


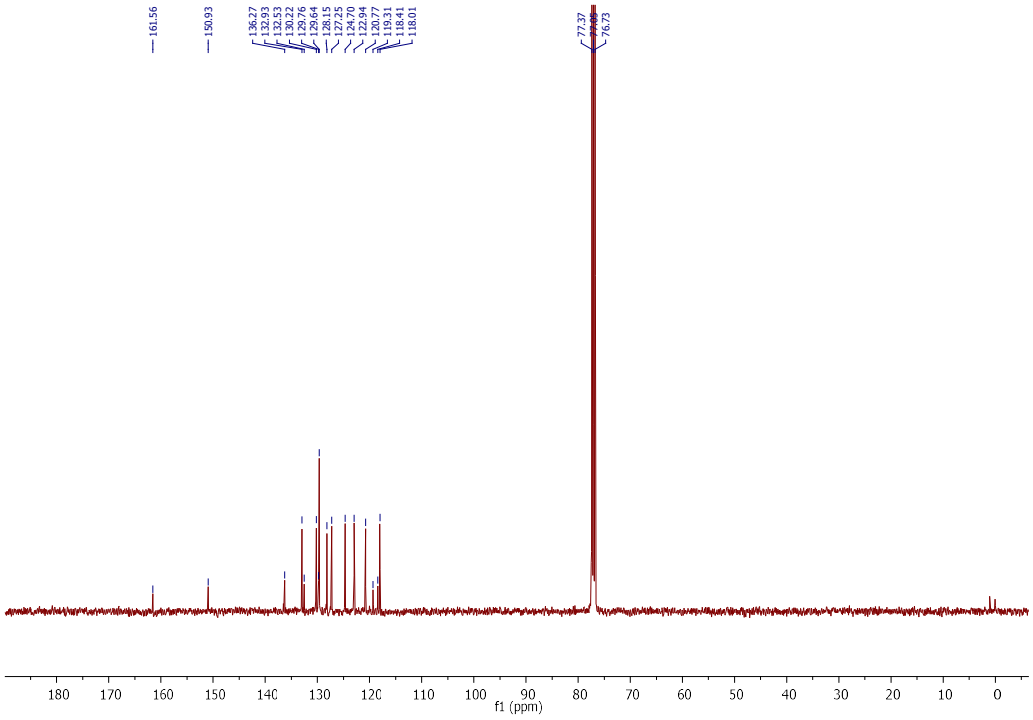
^{1}H(400 MHz),^{13}C(100 MHz) HMBC NMR spectrum of **2s** ($CDCl_3$, 298 K).


8.35
8.35
8.34
8.34
8.33
8.33
8.32
8.32
8.01
7.99
7.75
7.73
7.49
7.49
7.09
7.07
7.06
2.36
2.35
2.32
2.30
O
O
2t
0.94
1.01
2.00
1.00
0.96
5.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

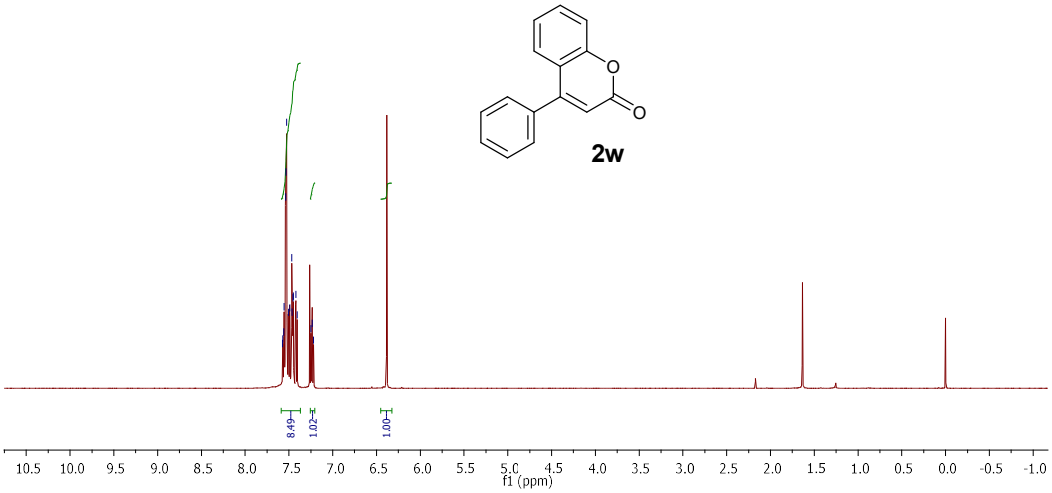

161.58
161.51
149.49
149.45
135.41
135.02
134.65
133.08
130.50
130.34
128.17
125.81
125.23
123.06
121.58
121.35
120.96
120.56
119.46
118.18
115.51
115.38
20.25
20.01
19.54
11.82
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

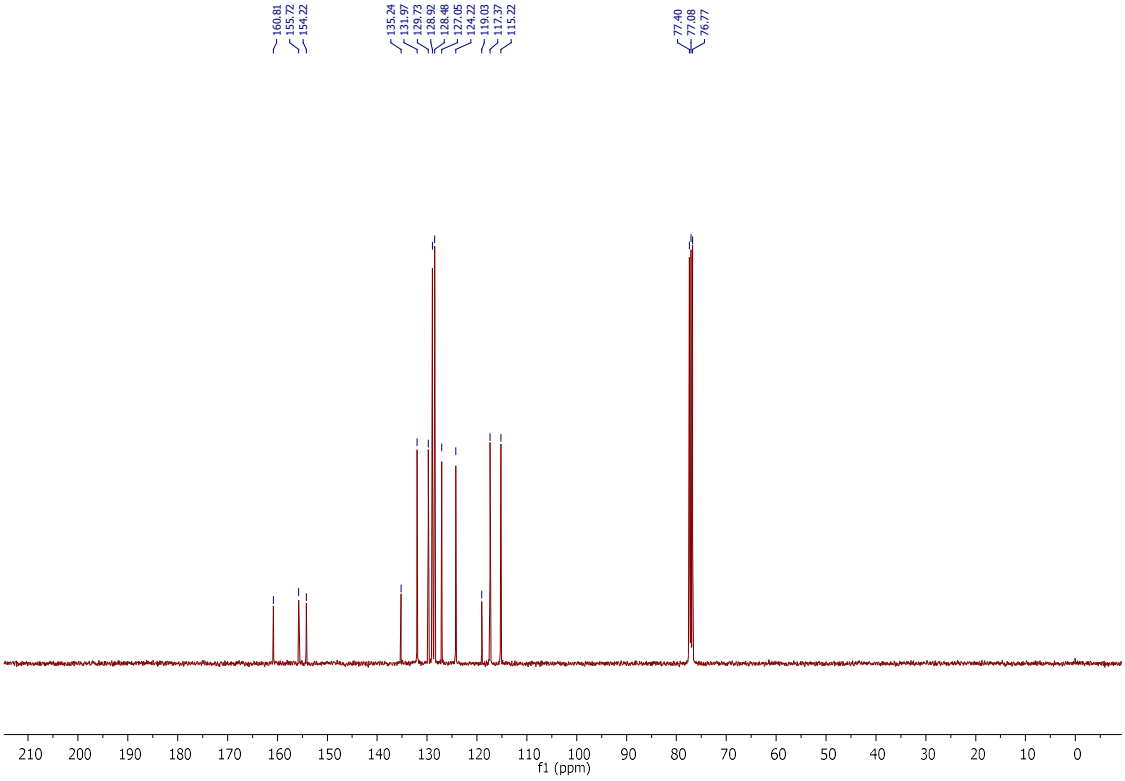

8.58
8.58
8.56
8.47
8.45
8.18
8.16
8.05
8.03
7.87
7.86
7.85
7.83
7.76
7.74
7.65
7.63
7.61
7.60
7.57
7.26
O
O
2u
1.00
0.99
1.07
1.08
2.10
1.05
3.14
f1 (ppm)
161.27
147.27
135.42
134.99
134.28
130.67
128.64
127.91
127.68
127.14
124.52
122.35
122.16
119.18
113.08
77.31
77.05
76.80
f1 (ppm)

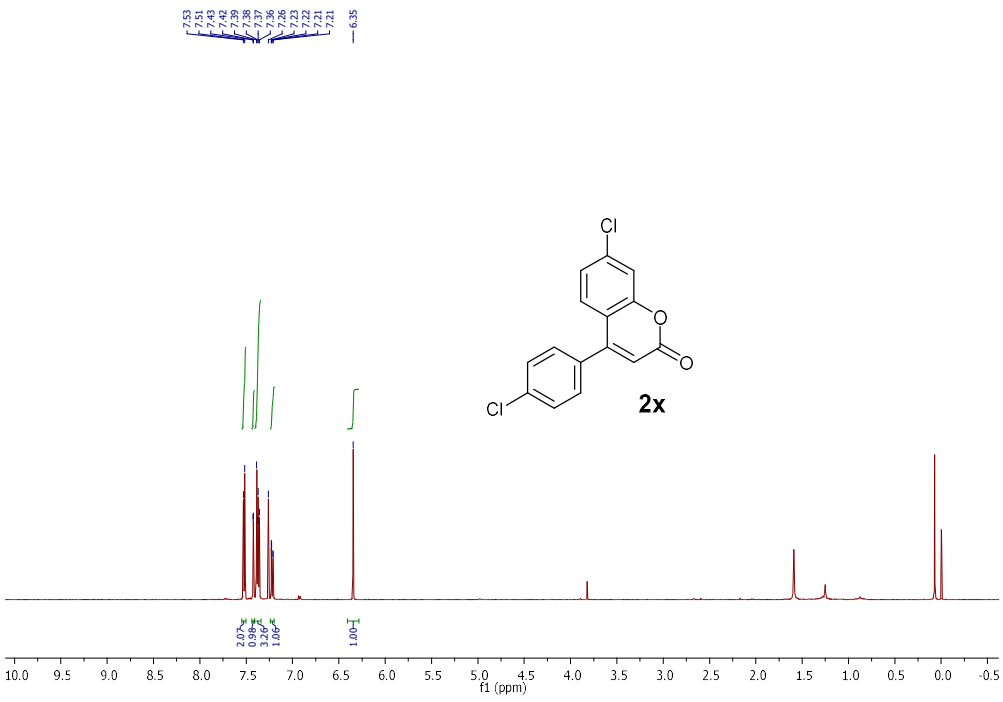

9.02
8.54
8.22
8.21
8.04
7.69
7.67
7.61
7.60
7.58
7.49
7.48
7.47
7.46
7.38
7.37
7.35
7.26
O
O
2v
1.00
1.06
1.05
2.10
1.04
1.03
1.04
2.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

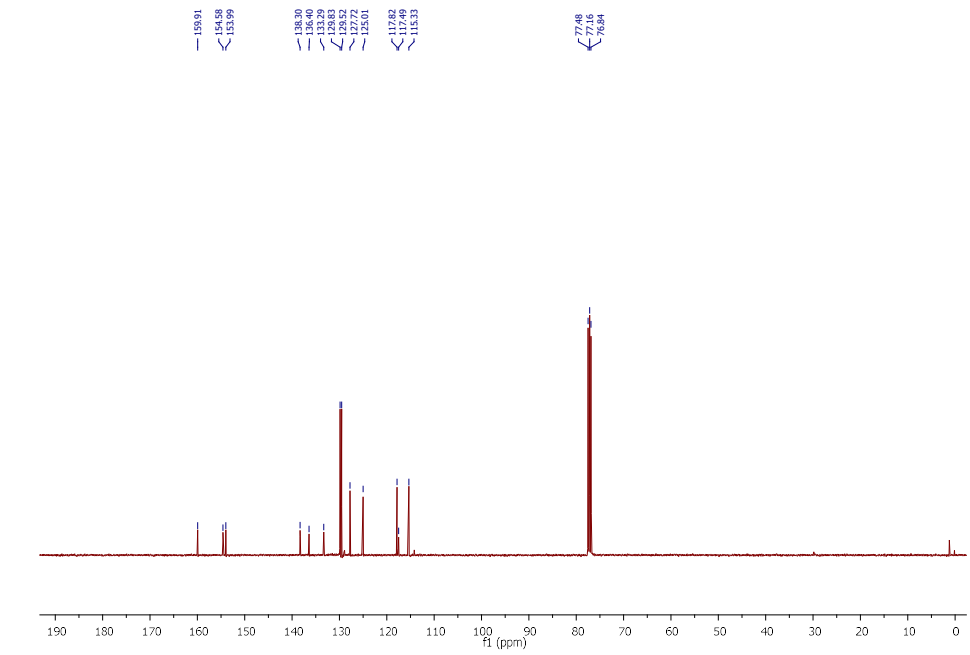

161.56
150.93
136.27
132.83
132.53
130.22
129.76
129.64
128.15
127.25
124.70
122.94
120.77
119.31
118.41
118.01
77.37
77.05
76.73
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

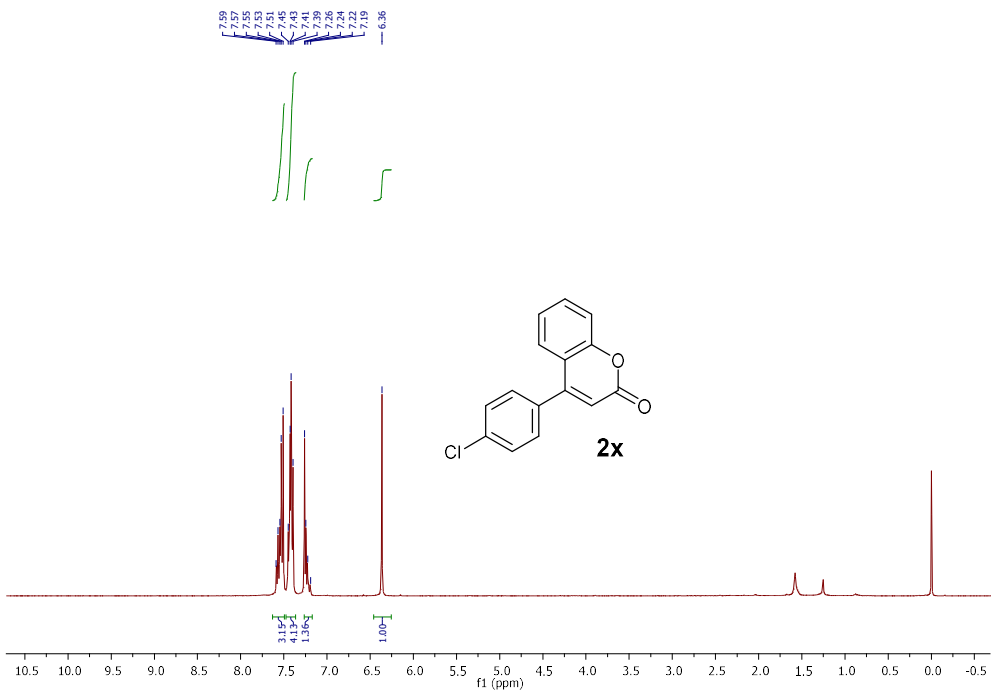

7.57
7.57
7.56
7.56
7.54
7.53
7.53
7.50
7.49
7.47
7.46
7.45
7.45
7.42
7.40
7.25
7.23
7.22

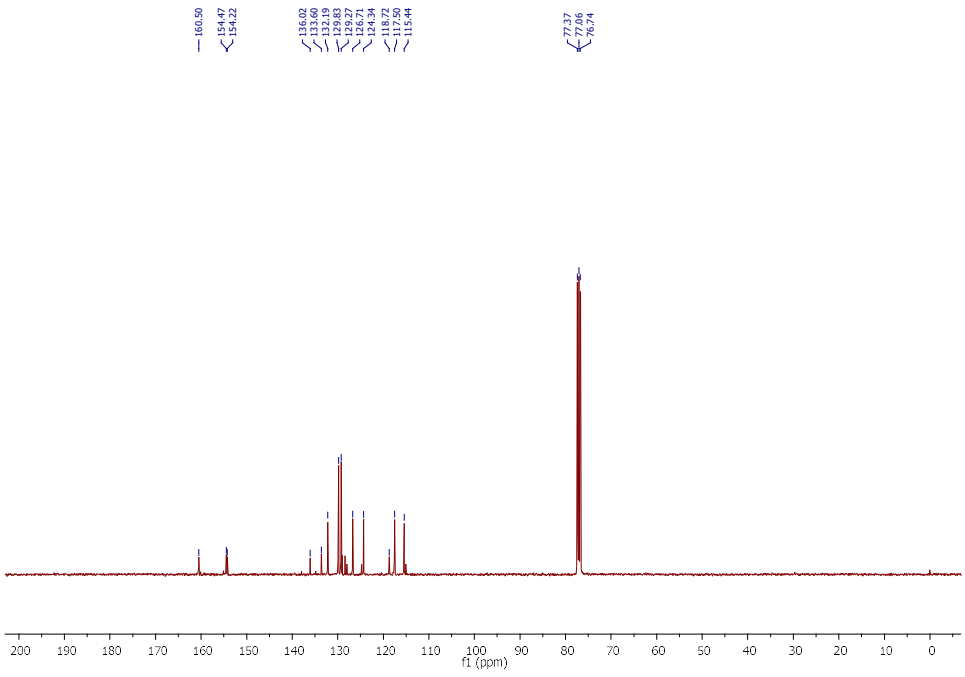

O
O
2w
8.49
1.02
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


160.81
155.72
154.22
135.24
131.97
129.73
128.92
128.48
127.05
124.22
119.03
117.37
115.22
77.40
77.08
76.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

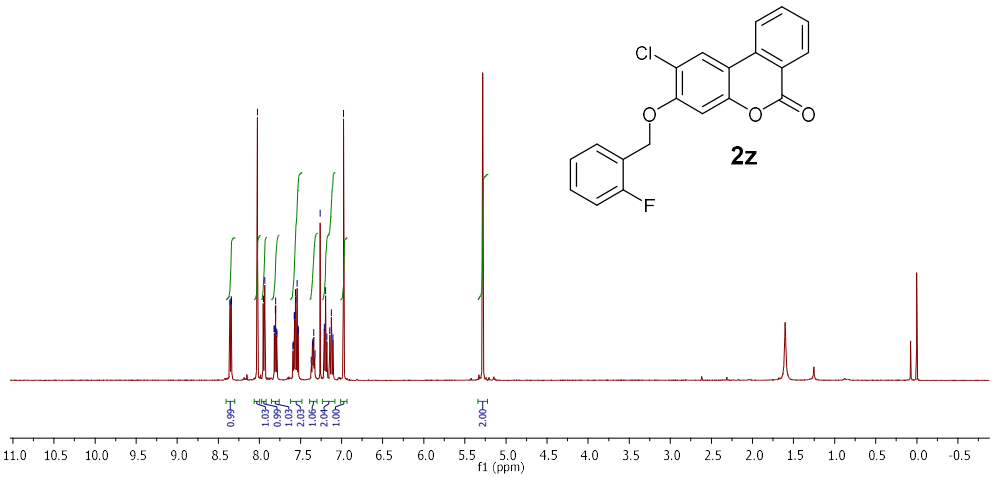

7.53
7.51
7.43
7.42
7.39
7.38
7.37
7.36
7.26
7.23
7.22
7.21
7.21
6.35
Cl
O
O
Cl
2x
2.07
0.98
3.26
1.06
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


159.91
154.58
153.99
138.30
136.40
133.29
129.83
129.52
127.72
125.01
117.82
117.49
115.53
77.48
77.16
76.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

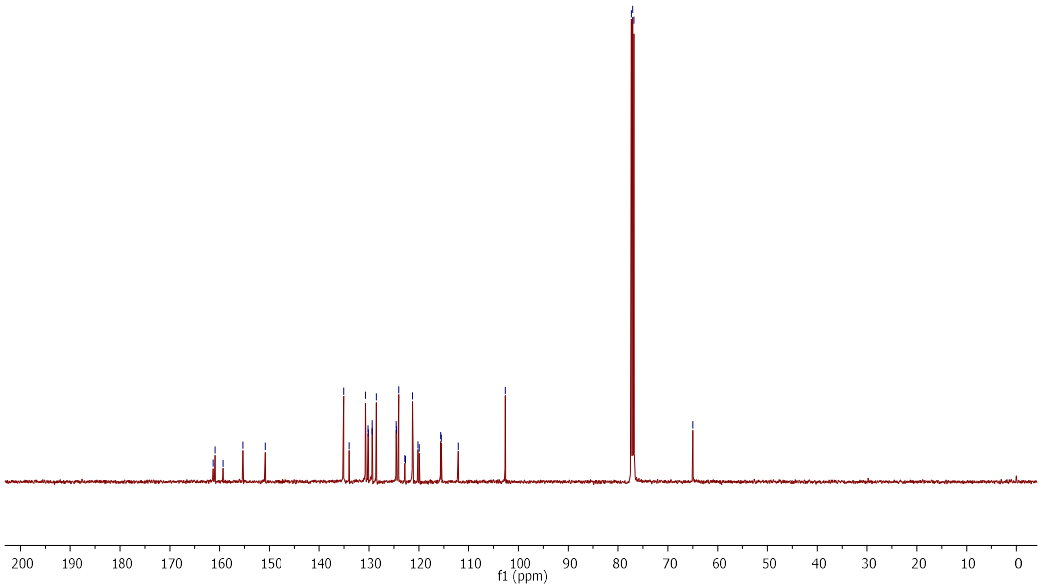

7.59
7.57
7.55
7.53
7.51
7.45
7.43
7.41
7.39
7.26
7.24
7.22
7.19
6.36
O
O
Cl
2x
3.15
4.13
1.36
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

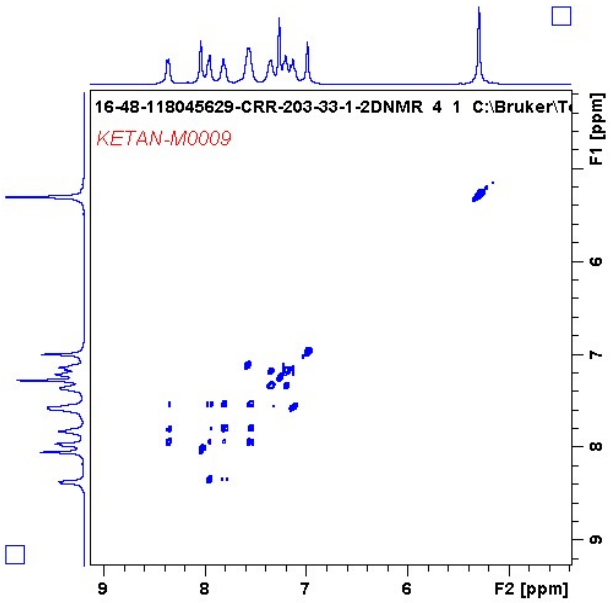

160.50
154.47
154.22
136.02
133.60
132.19
129.83
129.27
126.71
124.34
118.72
117.50
115.44
77.37
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.36
8.35
8.34
8.34
8.02
7.95
7.94
7.82
7.82
7.81
7.80
7.79
7.79
7.59
7.59
7.58
7.57
7.56
7.56
7.54
7.53
7.53
7.37
7.35
7.34
7.32
7.26
7.21
7.19
7.18
7.14
7.12
7.10
6.97

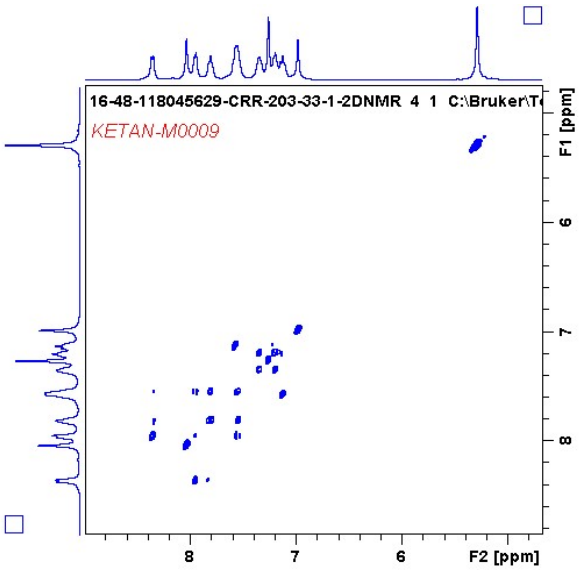

Cl
O
O
O
F
2z
0.99
1.03
0.99
1.03
2.02
1.04
2.04
1.00
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.30
160.93
159.34
155.20
150.02
135.11
134.02
130.71
130.21
130.15
129.37
129.35
128.50
124.52
124.50
124.05
122.80
121.26
120.18
119.69
115.63
115.47
102.10
102.08
77.31
77.05
76.80
64.99

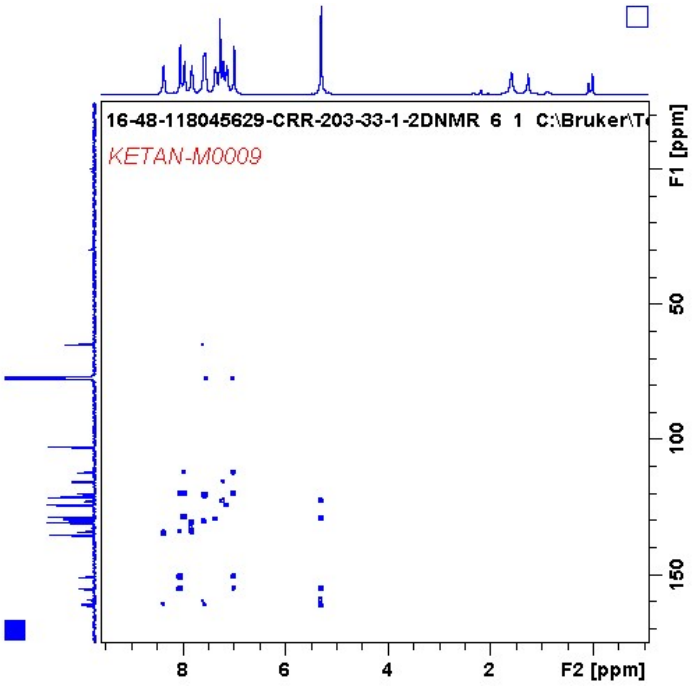

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



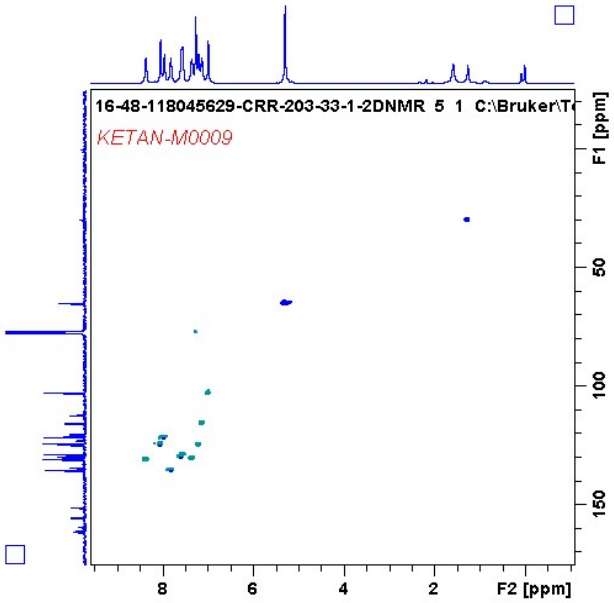
^{1}H, ^{1}H(400MHz) COSY NMR spectrum of **2z** ($CDCl_3$, 298 K).



Part of ^{1}H, ^{1}H(400 MHz) COSY NMR spectrum of **2z** ($CDCl_3$, 298 K).

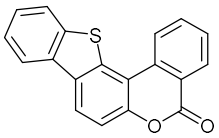


^{1}H(400 MHz),^{13}C(100 MHz) HMBC NMR spectrum of **2z** ($CDCl_3$, 298 K).

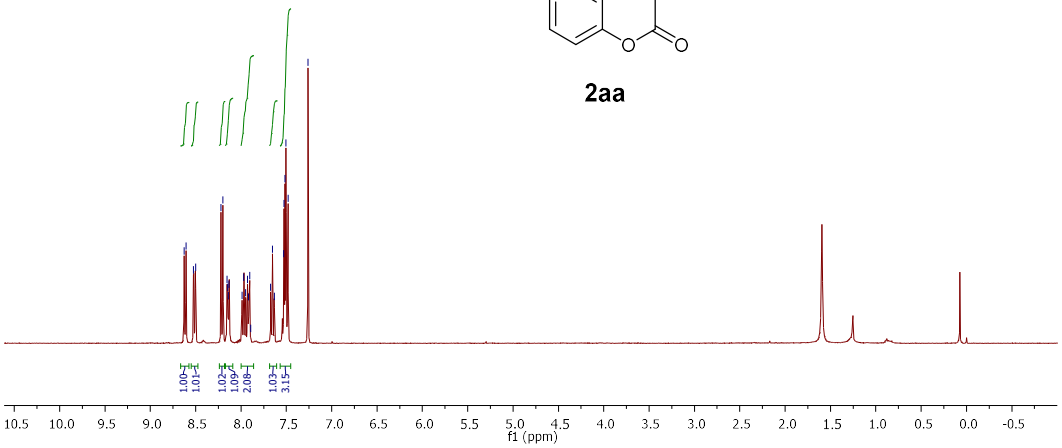


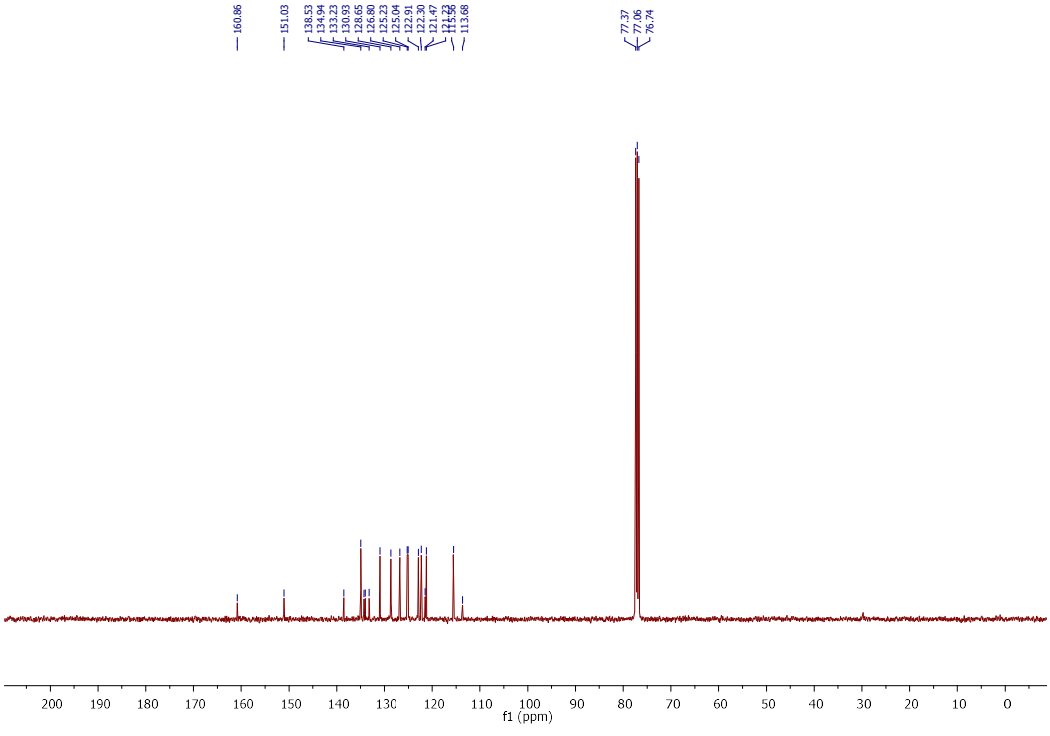
^{1}H(400 MHz),^{13}C(100 MHz) HSQC NMR spectrum of **2z** ($CDCl_3$, 298 K).

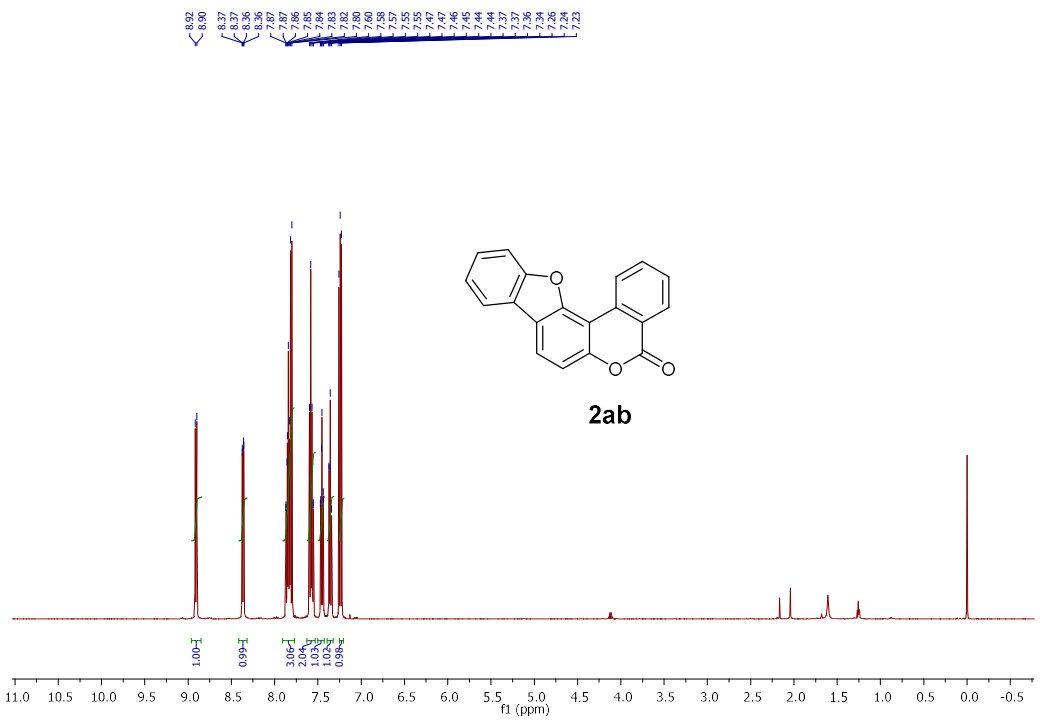

8.63
8.61
8.52
8.50
8.22
8.20
8.15
8.15
8.14
8.13
7.99
7.97
7.95
7.93
7.92
7.90
7.89
7.67
7.65
7.63
7.53
7.52
7.52
7.50
7.48
7.26

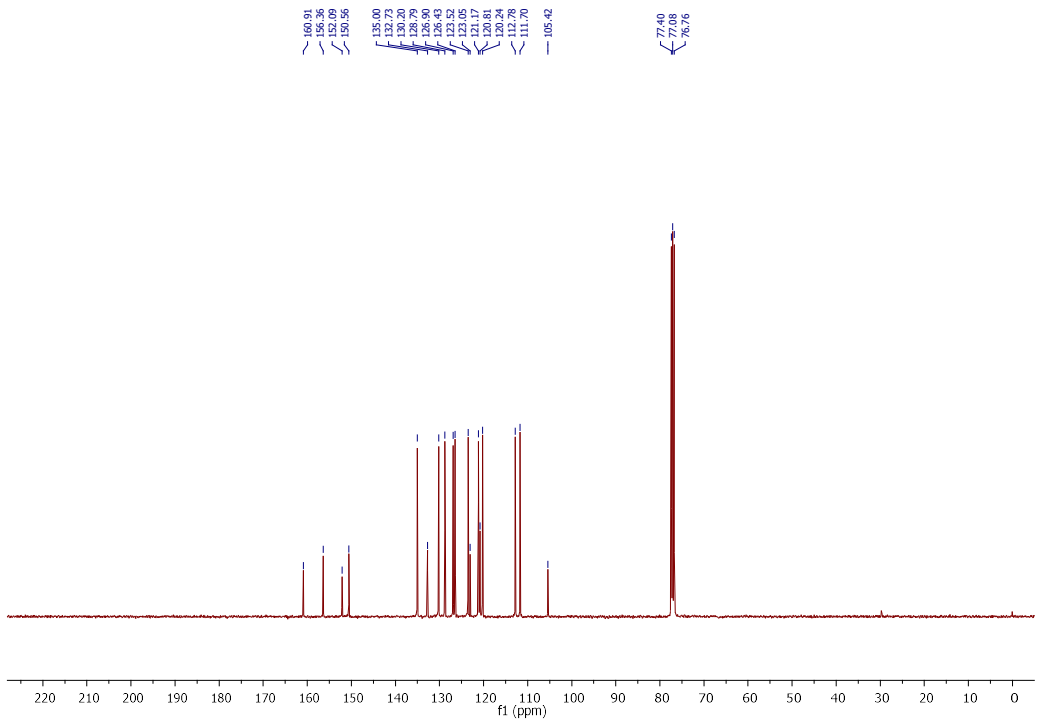

S
O
O

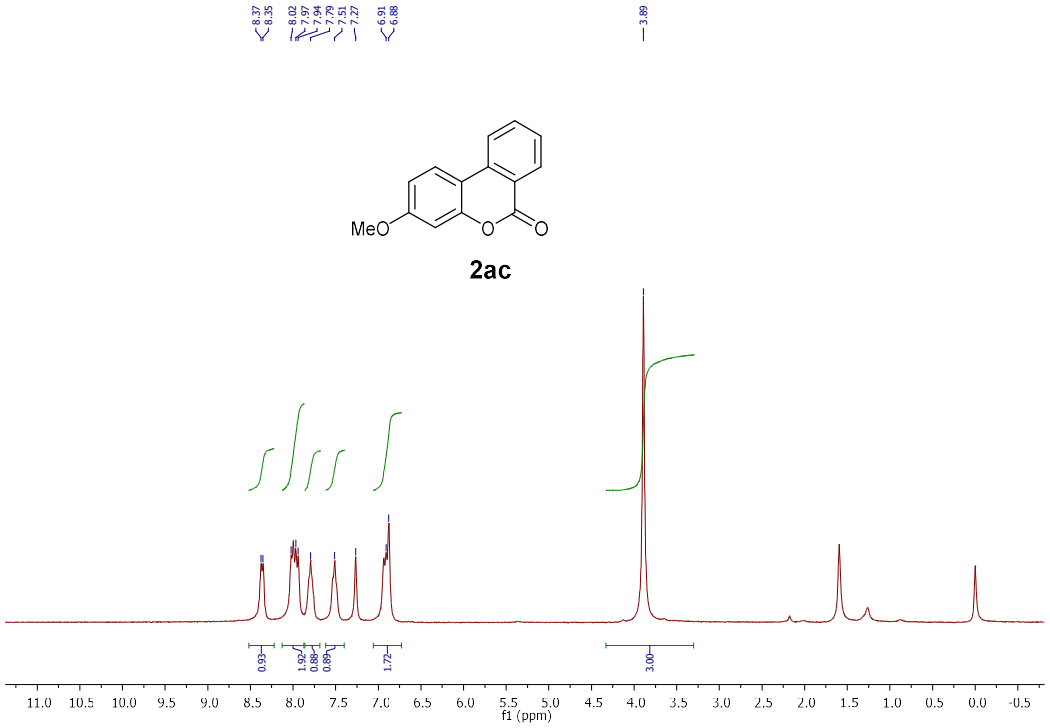
2aa


1.00
1.01
1.02
1.09
2.08
1.03
3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

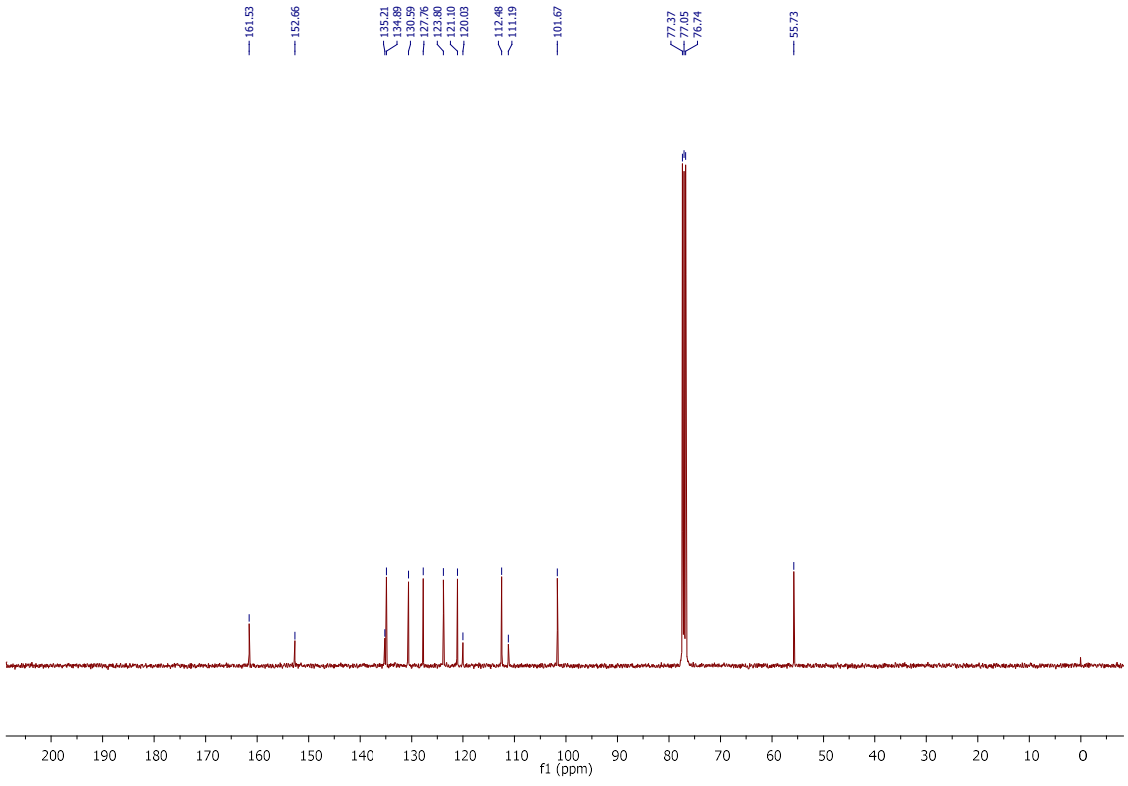

160.86
151.03
138.53
134.94
133.23
130.93
128.65
126.80
125.23
125.04
122.91
122.30
121.47
121.23
115.56
113.68
77.37
77.06
76.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

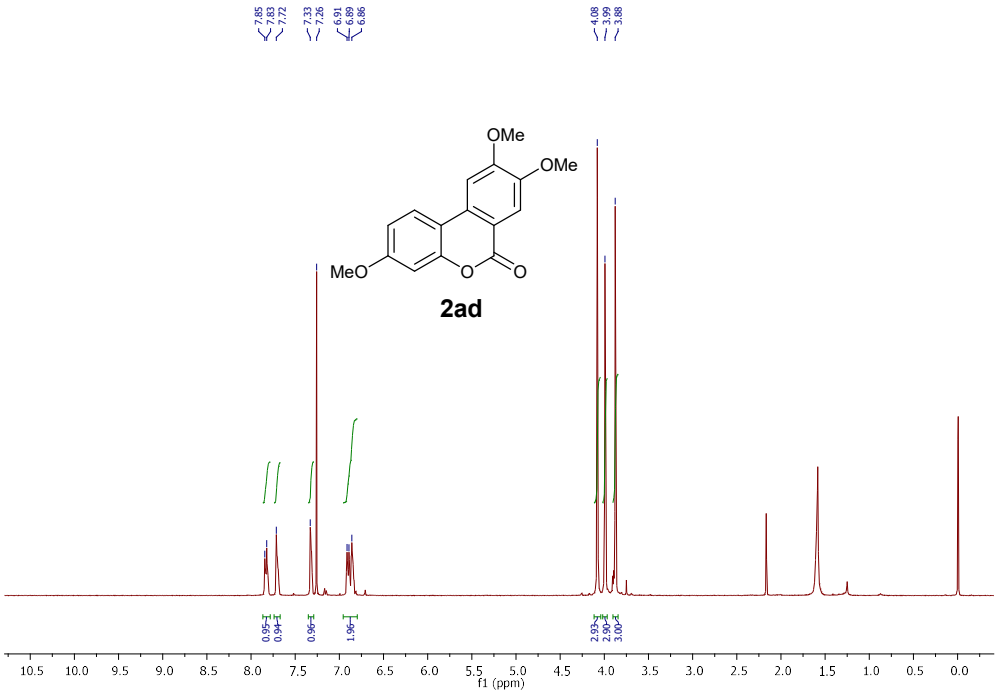

8.92
8.90
8.37
8.37
8.36
8.36
7.87
7.87
7.86
7.85
7.84
7.83
7.82
7.80
7.60
7.58
7.57
7.55
7.55
7.47
7.46
7.45
7.44
7.44
7.37
7.37
7.36
7.34
7.26
7.24
7.23
2ab
1.00
0.99
3.06
2.04
1.03
1.02
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

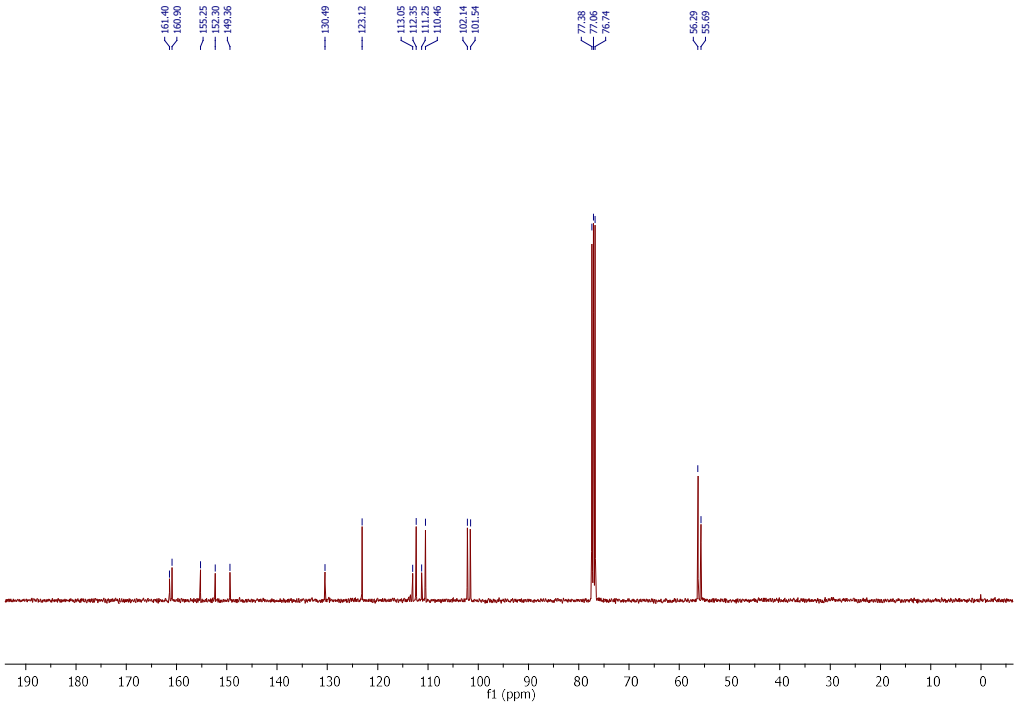

160.91
159.36
152.09
150.56
135.00
132.73
130.20
128.79
126.90
126.43
123.52
123.05
121.17
120.81
120.24
112.78
111.70
105.42
77.40
77.08
76.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

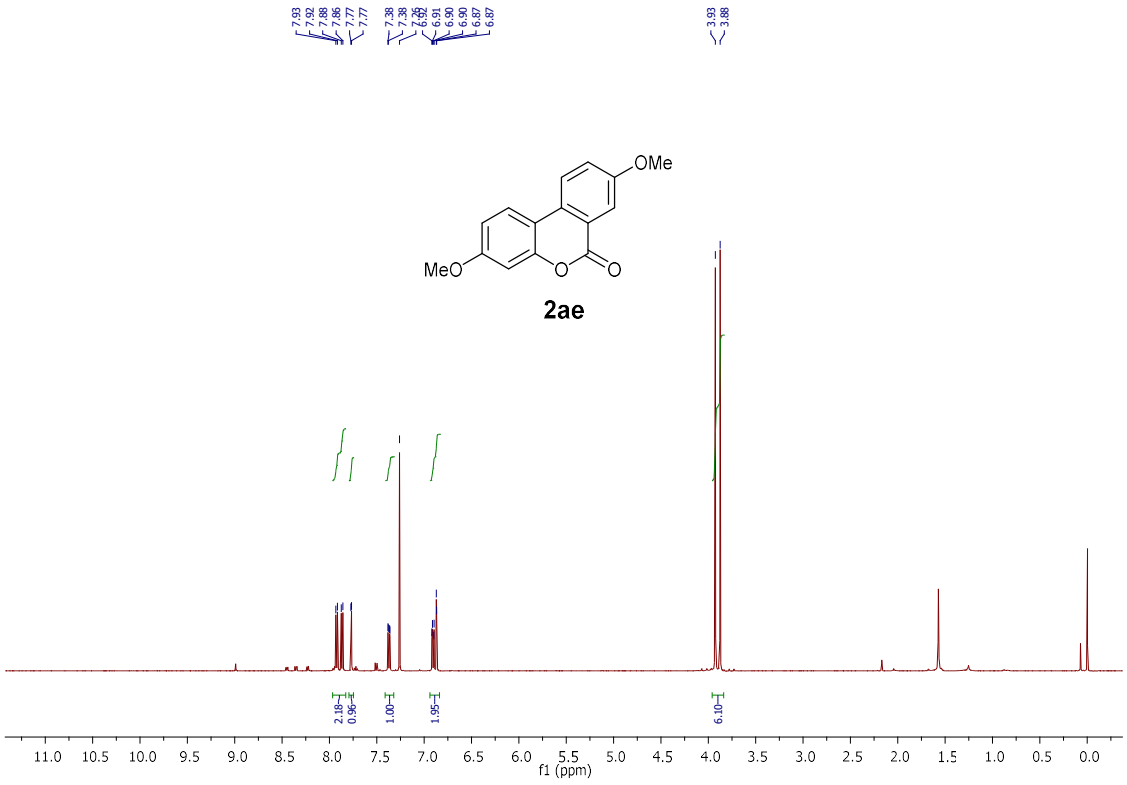

8.37
8.35
8.02
7.97
7.94
7.79
7.51
7.27
6.91
6.88
3.89
MeO
O
O
0.93
1.92
0.88
0.85
1.72
3.00
f1 (ppm)

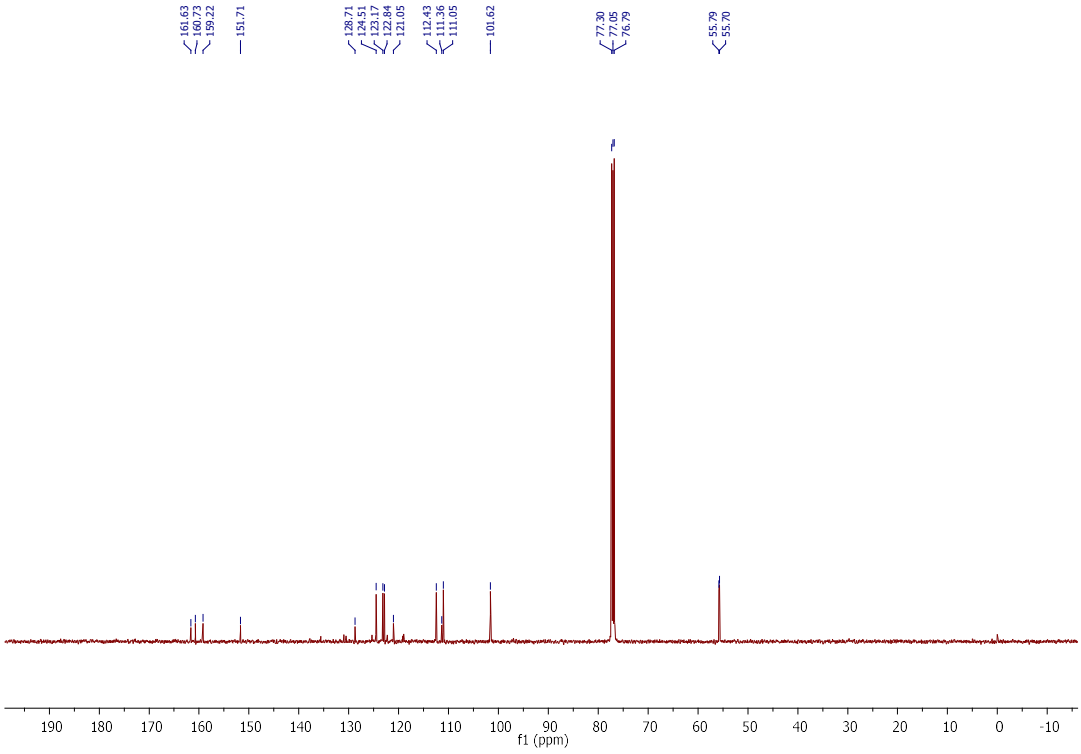
2ac


161.53
152.66
135.21
134.89
130.59
127.76
123.80
121.10
120.03
112.48
111.19
101.67
77.37
77.05
76.74
55.73
f1 (ppm)


7.85
7.83
7.72
7.33
7.26
6.91
6.89
6.86
4.08
3.99
3.88
OMe
OMe
MeO
O
O
2ad
0.95
0.94
0.96
1.96
2.93
2.99
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.40
160.90
155.25
152.30
149.36
130.49
123.12
113.05
112.35
111.25
110.46
102.14
101.54
77.38
77.06
76.74
56.29
55.69
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.93
7.92
7.88
7.86
7.77
7.77
7.38
7.38
7.25
6.92
6.91
6.90
6.90
6.87
6.87
3.93
3.88
OMe
MeO
O
O
2ae
2.18
0.96
1.00
1.95
6.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.63
160.73
159.22
151.71
128.71
124.51
123.17
122.84
121.05
112.43
111.36
111.05
101.62
77.30
77.05
76.79
55.79
55.70
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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