Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

The extended Corey-Chaykovsky reactions: transformation of 2-hydroxychalcones to benzannulated 2,8-dioxabicyclo[3.2.1]octanes and 2,3-dihydrobenzofurans

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Supporting Information

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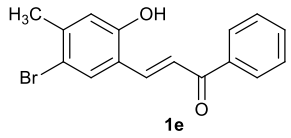
1. GENERAL INFORMATION

^{1}H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C {^{1}H } NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; [D_6] DMSO, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), dtd (doublet of triplets of doublets), and br (broadened). High-resolution mass measurements were carried out using a BrukermicroTOF-QTM ESI-TOF (Electro Spray Ionization/Time of Flight) mass spectrometer. GC/MS analysis was performed on an «Agilent 7890B» interfaced to an «Agilent 5977A» mass selective detector. Melting points were determined with a «Stuart SMP 30. Data sets for X-Ray diffraction were collected with a «New Xcalibur, Ruby» diffractometer. Column chromatography was performed on silica gel Macherey Nagel (40-63 μm), unless otherwise noted. Pre-coated TLC sheets ALUGRAM SIL G/UV_{254} were used for thin-layer analytical chromatography. All the reactions were carried out using freshly distilled and dry solvents from solvent stills. All reagent-grade chemicals and solvents commercially available were used without further purification.

2. SYNTHESIS OF STARTING MATERIALS

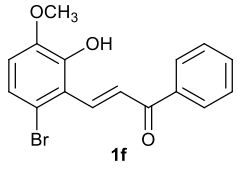
General procedure for the synthesis of starting α,β-unsaturated ketones 1

To a solution of aryl methyl ketone (10 mmol) and corresponding salicylaldehyde (10 mmol) in EtOH (10 mL) was added 20% aqueous solution of NaOH (5 mL), and the mixture was stirred at room temperature (or at an elevated temperature, when the addition of NaOH led to the appearance of precipitate) for 12–48 h until the full conversion of starting material (monitored by TLC). The reaction was quenched by pouring into cold water (250 mL), and the mixture was neutralized with 2 M HCl to slightly acidic pH. The resulting precipitate was filtered, washed with water and air dried to afford the desired product. Crude products were purified by recrystallization from EtOH. All data for **1a-d**,**i-l**,**n**,**o** are consistent with those described earlier.[1-6]



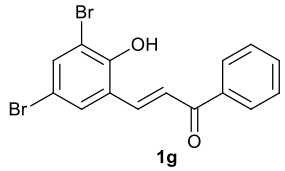
1e

(2*E*)-3-(5-Bromo-2-hydroxy-4-methylphenyl)-1-phenylprop-2-en-1-one (**1e**). Yield: 1965 mg, 62%; yellow solid, mp = 177 – 178 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (br s, 1H), 8.15–8.09 (m, 3H), 7.95 (d, *J* = 15.8 Hz, 1H), 7.88 (d, *J* = 15.8 Hz, 1H), 7.68–7.63 (m, 1H), 7.59–7.53 (m, 2H), 6.91 (s, 1H), 2.30 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 189.2, 156.3, 140.8, 137.7, 137.6, 132.8, 131.1, 128.6 (2C), 128.3 (2C), 121.4, 121.2, 118.4, 113.6, 22.6. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{14}{}^{79}BrO_2^+$ 317.0172, found 317.0178.



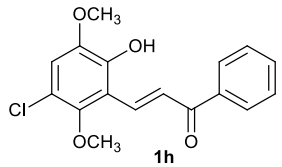
1f

(2*E*)-3-(6-Bromo-2-hydroxy-3-methoxyphenyl)-1-phenylprop-2-en-1-one (**1f**). Yield: 2198 mg, 66%; yellow solid, mp = 140 – 141 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (br s, 1H), 8.10 (d, *J* = 15.7 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.92 (d, *J* = 15.7 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.61 – 7.55 (m, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 190.1, 148.1, 147.5, 139.6, 137.7, 132.9, 128.8 (2C), 128.0 (2C), 126.8, 123.0, 120.3, 116.5, 114.1, 56.3. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{14}{}^{79}BrO_3^+$ 333.0121, found 333.0133.



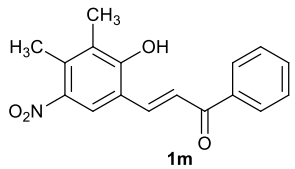
1g

(2*E*)-3-(3,5-Dibromo-2-hydroxyphenyl)-1-phenylprop-2-en-1-one (**1g**). Yield: 2445 mg, 64%; yellow solid, mp = 149 – 150 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (br s, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 8.18 – 8.15 (m, 2H), 8.02 (d, *J* = 15.7 Hz, 1H), 7.95 (d, *J* = 15.7 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.60 – 7.55 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 189.0, 152.5, 137.4, 137.0, 136.0, 133.1, 129.5, 128.6 (2C), 128.5 (2C), 126.7, 123.8, 113.7, 112.0. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{11}{}^{79}Br_2O_2^+$ 380.9120, found 380.9108.



1h

(2*E*)-3-(3-Chloro-6-hydroxy-2,5-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**1h**). Yield: 2099 mg, 66%; yellow solid, mp = 127 – 128 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.11 (d, *J* = 16.0 Hz, 1H), 7.99 – 7.95 (m, 2H), 7.92 (d, *J* = 16.0 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.61 – 7.56 (m, 2H), 7.16 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 190.3, 148.9, 146.7, 144.7, 137.8, 134.9, 132.8, 128.8 (2C), 128.0 (2C), 125.5, 116.5, 115.9, 114.2, 60.8, 56.6. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{16}{}^{35}ClO_4^+$ 319.0732, found 319.0730.



1m

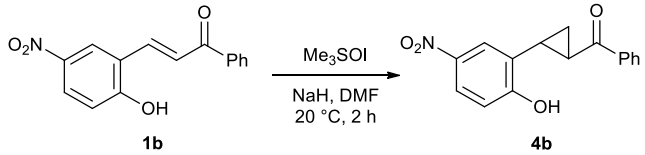
(2*E*)-3-(2-Hydroxy-3,4-dimethyl-5-nitrophenyl)-1-phenylprop-2-en-1-one (**1m**). Yield: 2405 mg, 81%; yellow solid, mp = 182 – 183 °C (EtOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (br s, 1H), 8.34 (s, 1H), 8.16 – 8.14 (m, 2H), 8.10 (d, *J* = 15.5 Hz, 1H), 7.92 (d, *J* = 15.5 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.57 – 7.54 (m, 2H), 2.33 (s, 3H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 190.0, 157.4, 143.9 137.7, 137.6, 134.0, 132.6, 128.6 (2C), 128.4 (2C), 126.9, 122.8, 121.2, 120.6, 15.8, 12.8. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{16}NO_4^+$ 298.1074, found 298.1071.

3. SYNTHESIS OF SIDE PRODUCTS

Synthesis of [2-(2-hydroxyaryl)cyclopropyl](aryl)methanones 4.

[2-(2-Hydroxyphenyl)cyclopropyl](phenyl)methanone (4a) was synthesized according to the described procedure.[2]

[2-(2-Hydroxy-5-nitrophenyl)cyclopropyl](phenyl)methanone (4b)



1b **4b**

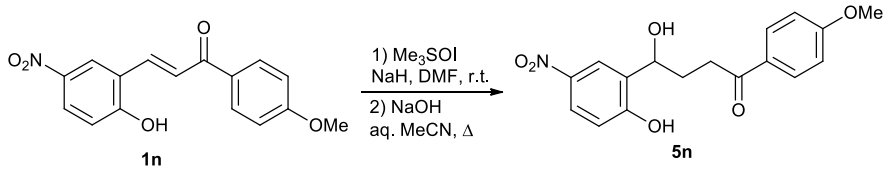
To a stirred solution of α,β-unsaturated ketone **1b** (135 mg, 0.5 mmol) and trimethylsulfoxonium iodide (110 mg, 0.5 mmol) in DMF (5 mL), sodium hydride (80 mg, 60% dispersion in mineral oil) was added at rt in one portion. The reaction mixture was stirred at the same temperature for 2 h. After consumption of the starting ketone **1b**, acetic acid (0.25 mL) was added, the reaction mixture was stirred for 5 min and carefully poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded pale yellow solid, which was washed with petroleum ether and recrystallized from ethyl acetate. Yield: 99 mg, 70%; pale yellow solid. All data for **4b** are consistent with those described earlier.[2]

Synthesis of 4-hydroxy-4-(2-hydroxyaryl)-1-arylbutan-1-ones 5.

4-Hydroxy-4-(2-hydroxyphenyl)-1-phenylbutan-1-one (5a)

All our attempts to isolate **5a** in a pure form led predominantly to its cyclization to ketal **2a**. According to NMR spectra, the obtained product was the mixture of **5a** and **2a**. However, alcohol **5n** was found to be more stable. Its synthesis and spectral data are given below.

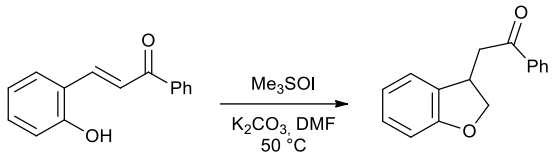
4-Hydroxy-4-(2-hydroxy-5-nitrophenyl)-1-(4-methoxyphenyl)butan-1-one (5n).



1n **5n**

To a stirred solution of α,β-unsaturated ketone **1n** (149.5 mg, 0.5 mmol) and trimethylsulfoxonium iodide (110 mg, 0.5 mmol) in DMF (5 mL), sodium hydride (80 mg, 60% dispersion in mineral oil) was added at rt in one portion. The reaction mixture was stirred at the same temperature for 2 h. After consumption of the starting ketone **1n**, acetic acid (0.25 mL) was added, the reaction mixture was stirred for 5 min and carefully poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL) and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded yellow oil, which was dissolved in MeCN (0.5 mL), then a solution of NaOH (22 mg, 1.1 eq.) in water (4.5 mL) was added, and the reaction mixture was stirred at reflux for 8 h. Then a second portion of NaOH (22 mg, 1.1 eq.) was added, and the reflux was continued for 21 h. After cooling to rt and dilution with water (10 mL), acetic acid (50 µL) was added. The aqueous phase was extracted with ethyl acetate (3 × 5 mL) and combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, 4:1). Yield: 78 mg, 47%; pale yellow transparent oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (br s, 1H), 8.26 (d, J = 2.8 Hz, 1H), 8.00 (dd, J = 8.9, 2.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.05 – 6.99 (m, 2H), 6.94 (d, J = 8.9 Hz, 1H), 5.41 (br s, 1H), 4.99 – 4.89 (m, 1H), 3.83 (s, 3H), 3.01 (t, J = 7.4 Hz, 2H), 2.08 – 2.00 (m, 1H), 1.92 – 1.81 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 198.1, 162.9, 160.0, 139.7, 133.4, 130.0 (2C), 129.6, 123.9, 122.5, 115.1, 113.8 (2C), 65.5, 55.4, 33.8, 31.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{18}NO_6^+$ 332.1129, found 332.1129.

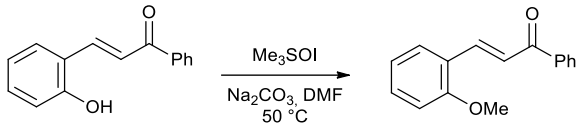
Synthesis of 2-(2,3-dihydrobenzofuran-3-yl)-1-phenylethanone (6a).



1a **6a**

To a stirred solution of α,β-unsaturated ketone **1a** (224 mg, 1 mmol) and trimethylsulfoxonium iodide (75 mg, 0.34 mmol) in DMF (10 mL), potassium carbonate (690 mg) was added at rt in one portion. After 1 h of stirring at 50 ºC, the second portion of trimethylsulfoxonium iodide (73 mg, 0.34 mmol) was added, followed by the third portion (73 mg, 0.34 mmol) in the next hour. The reaction mixture was stirred at 50 ºC for 5 h, after which the reaction was quenched by addition of acetic acid (2 mL), and the undissolved inorganic material was filtered off and washed with ethyl acetate (5 mL). Then, obtained solution was diluted with water (100 mL), extracted with ethyl acetate (3 × 15 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent afforded yellow oil, which was subjected to flash column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, gradient from 20:1 to 5:1) to afford crude **6a** and recovered starting α,β-unsaturated ketone **1a** (61 mg, 27%). The obtained crude **6a** was dissolved in MeOH (4.2 mL), methanesulfonic acid (2.7 μL, 10 mol. %) was added, and the resulting solution was refluxed for 1 h, during which all chromatographically inseparable impurities were destructed. After cooling to rt, K_2CO_3 (15 mg) was added, and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, 40:1). Yield BRSM: 76 mg, 43%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.43 (m, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.12 (m, 1H), 6.92 – 6.84 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.88 (t, *J* = 9.1 Hz, 1H), 4.22 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.12 – 4.05 (m, 1H), 3.53 (dd, *J* = 18.0, 4.6 Hz, 1H), 3.27 (dd, *J* = 18.0, 9.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.4, 160.2, 136.8, 133.5, 129.9, 128.9 (2C), 128.7, 128.2 (2C), 124.5, 120.7, 109.9, 77.5, 44.7, 37.7. 198.1, 162.9, 160.0, 139.7, 133.4, 130.0 (2C), 129.6, 123.9, 122.5, 115.1, 113.8 (2C), 65.5, 55.4, 33.8, 31.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}NO_6^+$ 332.1129, found 332.1129.

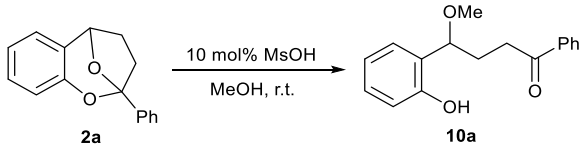
Synthesis of (2*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one (7a).[7]



1a **7a**

To a stirred solution of α,β-unsaturated ketone **1a** (56 mg, 0.25 mmol) and trimethylsulfoxonium iodide (55 mg, 0.25 mmol) in DMF (2.5 mL), sodium carbonate (106 mg) was added at rt in one portion. The reaction mixture was stirred at 50 ºC for 48 h. Than acetic acid (0.4 mL) was added, the reaction mixture was stirred for 5 min and carefully poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded pale yellow oil, which was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, gradient from 20:1 to 5:1). Yield BRSM: 76 mg, 85%; yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.9 Hz, 1H), 8.04 – 8.00 (m, 2H), 7.65 – 7.55 (m, 3H), 7.52 – 7.47 (m, 2H), 7.40 – 7.35 (m, 1H), 7.02 – 6.97 (m, 1H), 6.96 – 6.92 (m, 1H), 3.91 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2, 158.9, 140.5, 138.7, 132.6, 131.9, 129.3, 128.6 (4C), 124.1, 123.0, 120.9, 111.4, 55.7.

Synthesis of 4-(2-hydroxyphenyl)-4-methoxy-1-phenylbutan-1-one (10a).

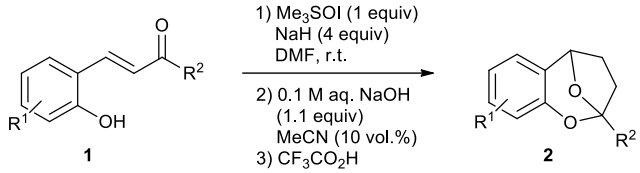


2a **10a**

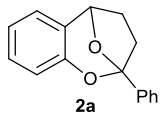
To a stirred solution of **2a** (60 mg, 0.25 mmol) in MeOH (2 mL) was added methanesulfonic acid solution in MeOH (4.8 mg/mL, 0.5 mL, 10% mol.) and water (5 μL). The reaction mixture was stirred at rt for 30 minutes, poured into water (20 mL), extracted with ethyl acetate (3 × 5 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent afforded pale yellow oil, which was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, 20:1). Yield 58 mg, 86%; yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.85 (br s, 1H), 7.58 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.21 – 7.17 (m, 1H), 7.01 – 6.99 (m, 1H), 6.90 – 6.82 (m, 2H), 4.45 (dd, *J* = 8.3, 5.5 Hz, 1H), 3.39 (s, 3H), 3.16 – 3.01 (m, 2H), 2.36 – 2.27 (m, 1H), 2.24 – 2.15 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.9, 155.6, 137.1, 133.2, 129.3, 128.7 (2C), 128.3, 128.2 (2C), 124.8, 120.0, 117.2, 84.4, 57.5, 34.5, 30.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{19}O_3^+$ 271.1329, found 271.1331.

4. SYNTHESIS OF PRODUCTS

General procedure for synthesis of ketals 2

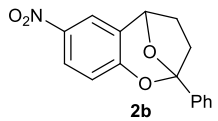


To a stirred solution of α,β-unsaturated ketone **1** (0.5 mmol) and trimethylsulfoxonium iodide (110 mg, 0.5 mmol) in DMF (5 mL), sodium hydride (80 mg, 60% dispersion in mineral oil) was added at rt in one portion. The red-colored reaction mixture was stirred at the same temperature for 2 h (the color of reaction mixture usually changes to pale brown or yellow). After consumption of the starting ketone **1**, acetic acid (0.25 mL) was added, the reaction mixture was stirred for 5 min and carefully poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded yellow oil, which was dissolved in MeCN (0.5 mL), then a solution of NaOH (22 mg) in water (4.5 mL) was added, and the reaction mixture was stirred at 50 ºC (for compounds **1a,c,e,f,h-l**) or at reflux (compounds**1b,d,g**), until full conversion of cyclopropane **4** (TLC control, typically no longer than 8 h). After cooling to rt and dilution with water (10 mL), acetic acid (50 µL) was added. The aqueous phase was extracted with ethyl acetate (3 × 5 mL) and combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, eluent: petroleum ether/CH_2Cl_2, 4:1). After collection of a fraction, containing ketal **2** ($R_f \approx 0.6$, petroleum ether/ethyl acetate, 3:1), the eluent was changed to petroleum ether/ethyl acetate, 1:1 and a fraction of the corresponding alcohol **5** was collected separately and evaporated *in vacuo*. Then the remaining oil was dissolved in toluene (2 mL), trifluoroacetic acid (10 µL) was added, and the solution was immediately evaporated *in vacuo* at 60 ºC. Then remaining oil dissolved in mixture of petroleum ether/CH_2Cl_2, 7:3 and passed through a thin pad of silica gel. The combined fractions of ketal **2** were evaporated *in vacuo* at 50 ºC.



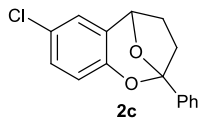
2a

9-Phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2a**).[8] Yield: 86 mg, 72%; colorless solid, mp = 106 – 107 °C (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.82 – 7.64 (m, 2H), 7.49 – 7.34 (m, 3H), 7.23 – 7.15 (m, 1H), 7.07 – 6.99 (m, 1H), 6.93 – 6.76 (m, 2H), 5.33 (d, *J* = 5.7 Hz, 1H), 2.83 – 2.72 (m, 1H), 2.49 – 2.29 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 151.4, 140.0, 128.9, 128.7, 128.4 (2C), 126.9, 125.4 (2C), 124.4, 120.2, 116.4, 107.8, 78.8, 39.8, 37.0.



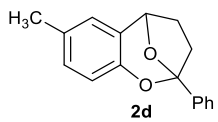
2b

4-Nitro-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2b**). Yield: 114 mg, 80%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.10 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.99 (d, *J* = 2.6 Hz, 1H), 7.77 – 7.62 (m, 2H), 7.51 – 7.37 (m, 3H), 6.91 (d, *J* = 9.0 Hz, 1H), 5.43 (d, *J* = 6.1 Hz, 1H), 2.86 – 2.73 (m, 1H), 2.57 – 2.41 (m, 2H), 2.36 – 2.29 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): 157.2, 141.1, 138.4, 129.2, 128.6 (2C), 127.2, 125.3 (2C), 125.2, 120.7, 116.9, 109.4, 78.5, 40.3, 36.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}NO_4^+$ 284.0917, found 284.0916.



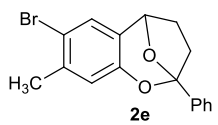
2c

4-Chloro-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2c**). Yield: 92 mg, 68%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.73 – 7.67 (m, 2H), 7.46 – 7.36 (m, 3H), 7.13 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 5.28 (d, *J* = 5.9 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.48 – 2.28 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 150.0, 139.5, 128.9, 128.8, 128.5 (2C), 128.2, 125.4 (2C), 125.1, 124.3, 117.9, 108.2, 78.4, 39.8, 36.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}{}^{35}ClO_2^+$ 273.0677, found 273.0678.



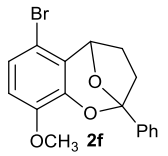
2d

4-Methyl-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2d**). Yield: 83 mg, 66%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.77 – 7.64 (m, 2H), 7.47 – 7.33 (m, 3H), 6.98 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.83 (d, *J* = 2.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.27 (d, *J* = 5.8 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.45 – 2.26 (m, 3H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 149.1, 140.1, 129.5, 129.4, 128.7, 128.4 (2C), 126.6, 125.4 (2C), 124.9, 116.2, 107.7, 78.8, 39.7, 37.1, 20.7. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_2^+$ 253.1223, found 253.1227.



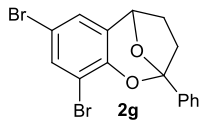
2e

4-Bromo-5-methyl-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2e**). Yield: 112 mg, 60%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.75 – 7.60 (m, 2H), 7.47 – 7.33 (m, 3H), 7.18 (s, 1H), 6.76 (s, 1H), 5.26 (d, *J* = 5.7 Hz, 1H), 2.77 – 2.64 (m, 1H), 2.47 – 2.23 (m, 3H), 2.33 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 150.6, 139.6, 138.4, 128.8, 128.4 (2C), 127.8, 126.3, 125.4 (2C), 118.7, 114.7, 108.0, 78.1, 39.7, 36.9, 23.0. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}{}^{79}BrO_2^+$ 331.0328, found 331.0328.



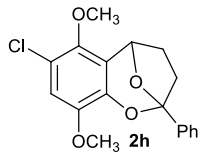
2f

3-Bromo-6-methoxy-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2f**). Yield: 118 mg, 68%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.70 (m, 2H), 7.46 – 7.35 (m, 3H), 7.01 (d, J = 8.7 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 5.55 (d, J = 5.6 Hz, 1H), 3.82 (s, 3H), 2.79 – 2.69 (m, 1H), 2.48 – 2.30 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.9, 142.3, 139.3, 128.9, 128.5 (2C), 126.8, 125.6 (2C), 123.3, 113.1, 110.3, 108.6, 78.8, 56.5, 39.9, 35.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}{}^{79}BrO_3^+$ 347.0277, found 347.0270.



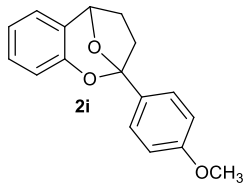
2g

4,6-Dibromo-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2g**). Yield: 99 mg, 50%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.71 (m, 2H), 7.56 (d, J = 2.2 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.11 (d, J = 2.2 Hz, 1H), 5.28 (d, J = 6.2 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.52 – 2.35 (m, 2H), 2.31 – 2.26 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.8, 138.8, 134.5, 129.7, 129.0, 128.5 (2C), 126.4, 125.4 (2C), 112.2, 111.2, 109.1, 78.3, 40.6, 36.6. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{13}{}^{79}Br_2O_2^+$ 394.9277, found 394.9268.



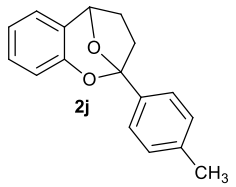
2h

4-Chloro-3,6-dimethoxy-9-phenyl-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2h**). Yield: 105 mg, 63%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.66 (m, 2H), 7.46 – 7.33 (m, 3H), 6.79 (s, 1H), 5.59 (d, J = 5.9 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.80 – 2.70 (m, 1H), 2.50 – 2.29 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.2, 144.9, 139.4, 128.9, 128.5 (2C), 125.5 (2C), 122.2, 117.4, 113.3, 108.1, 100.2, 74.9, 61.4, 56.8, 40.0, 36.6. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}{}^{35}ClO_4^+$ 333.0888, found 333.0886.



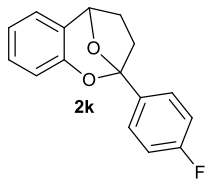
2i

9-(4-Methoxyphenyl)-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2i**). Yield: 59 mg, 44%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.57 (m, 2H), 7.20 – 7.14 (m, 1H), 7.03 – 6.99 (m, 1H), 6.97 – 6.93 (m, 2H), 6.88 – 6.82 (m, 2H), 5.29 (d, J = 5.6 Hz, 1H), 3.84 (s, 3H), 2.79 – 2.67 (m, 1H), 2.46 – 2.26 (m, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.0, 151.5, 132.3, 128.9, 126.9 (2C), 124.4, 120.2, 116.4, 113.8 (2C), 107.9, 100.2, 78.8, 55.5, 39.6, 37.0. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_3^+$ 269.1172, found 269.1172.



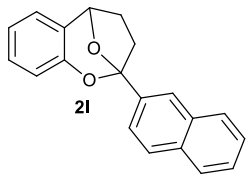
2j

9-(4-Methylphenyl)-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2j**). Yield: 76 mg, 60%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.60 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.09 – 7.03 (m, 1H), 6.95 – 6.86 (m, 2H), 5.34 (d, J = 5.7 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.49 – 2.32 (m, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.5, 138.4, 137.1, 129.0 (2C), 128.8, 126.9, 125.4 (2C), 124.3, 120.1, 116.4, 107.9, 78.8, 39.7, 37.0, 21.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_2^+$ 253.1223, found 253.1226.



2k

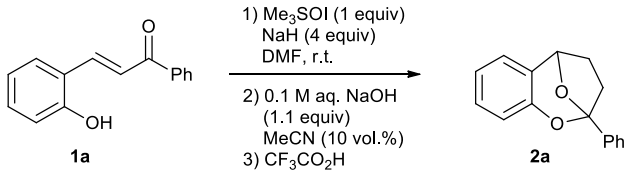
9-(4-Fluorophenyl)-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2k**). Yield: 81 mg, 63%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.64 (m, 2H), 7.21 – 7.15 (m, 1H), 7.15 – 7.07 (m, 2H), 7.05 – 7.00 (m, 1H), 6.92 – 6.82 (m, 2H), 5.31 (d, J = 6.0 Hz, 1H), 2.79 – 2.70 (m, 1H), 2.50 – 2.40 (m, 1H), 2.38 – 2.28 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $J_{C\text{-}F}$ = 247 Hz), 151.3, 136.0 (d, $J_{C\text{-}F}$ = 3 Hz), 129.0, 127.4 (d, $J_{C\text{-}F}$ = 8 Hz, 2C), 126.8, 124.4, 120.4, 116.4, 115.2 (d, $J_{C\text{-}F}$ = 22 Hz, 2C), 107.5, 78.9, 39.8, 37.0. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}FO_2^+$ 257.0972, found 257.0976.



2l

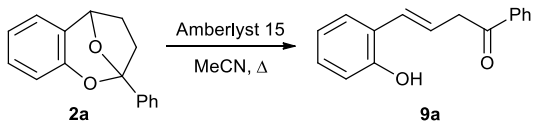
9-(Naphthalen-2-yl)-8,12-dioxatricyclo[7.2.1.$0^{2,7}$]dodeca-2,4,6-triene (**2l**). Yield: 86 mg, 51%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.96 – 7.91 (m, 2H), 7.90 – 7.87 (m, 1H), 7.85 – 7.81 (m, 1H), 7.56 – 7.50 (m, 2H), 7.25 – 7.20 (m, 1H), 7.08 – 7.03 (m, 1H), 6.96 – 6.89 (m, 2H), 5.39 (d, J = 5.4 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.56 – 2.45 (m, 2H), 2.39 – 2.33 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.4, 137.2, 133.5, 133.1, 128.9, 128.7, 128.3, 127.8, 126.9, 126.5, 126.4, 124.5, 124.4, 123.4, 120.3, 116.5, 108.0, 79.0, 39.9, 37.1. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}O_2^+$ 289.1223, found 289.1224.

Gram-scale synthesis of ketal 2a



To a stirred solution of α,β-unsaturated ketone **1a** (1.12 g, 5 mmol) and trimethylsulfoxonium iodide (1.1 g, 5 mmol) in DMF (50 mL), sodium hydride (800 mg, 60% dispersion in mineral oil) was added at rt portionwise. The red-colored reaction mixture was stirred at the same temperature for 4 h. After consumption of the starting ketone **1a**, acetic acid (2.5 mL) was added, the reaction mixture was stirred for 15 min and carefully poured into ice-cooled water (250 mL). The aqueous phase was extracted with ethyl acetate (3 × 50 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded yellow oil, which was dissolved in MeCN (5 mL), then a solution of NaOH (220 mg) in water (45 mL) was added, and the reaction mixture was stirred at 50 ºC until full conversion of cyclopropane **4a**. After cooling to rt and dilution with water (50 mL), acetic acid (0.5 mL) was added. The aqueous phase was extracted with ethyl acetate (3 × 50 mL) and combined extracts were dried with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the residue was subjected to column chromatography (silica gel, eluent: petroleum ether/CH_2Cl_2, 4:1). After collection of a fraction, containing ketal **2a** (R_f ≈ 0.6, petroleum ether/ethyl acetate, 3:1), the eluent was changed to petroleum ether/ethyl acetate, 1:1 and a fraction of the corresponding alcohol **5a** was collected separately and evaporated *in vacuo*. Then the remaining oil was dissolved in toluene (20 mL), trifluoroacetic acid (100 μL) was added, and the solution was immediately evaporated *in vacuo* at 60 ºC. Then remaining oil dissolved in mixture of petroleum ether/CH_2Cl_2, 7:3 and passed through a thin pad of silica gel. The combined fractions of ketal **2a** were evaporated *in vacuo* at 50 ºC.

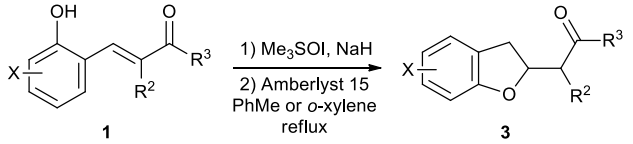
Synthesis of (3*E*)-4-(2-hydroxyphenyl)-1-phenylbut-3-en-1-one (9a)



2a **9a**

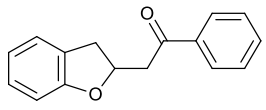
To a solution of ketal **2a** (119 mg, 0.5 mmol) in MeCN (10 mL) Amberlyst® 15 (wet, 600 mg) was added, and the reaction mixture was stirred at 80 ºC for 1.5 h (TLC control). Then the Amberlyst® 15 was filtered off, washed with MeCN (5 mL), the solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, 10:1). Yield: 24 mg, 20%; colorless transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.05 – 7.98 (m, 2H), 7.60 – 7.55 (m, 1H), 7.51 – 7.46 (m, 2H), 7.37 – 7.33 (m, 1H), 7.14 – 7.08 (m, 1H), 6.91 – 6.86 (m, 1H), 6.83 – 6.79 (m, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 6.44 (dt, *J* = 16.1, 6.9 Hz, 1H), 5.36 (br s, 1H), 3.94 (d, *J* = 6.9 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 198.4, 153.1, 136.9, 133.4, 128.9 (2C), 128.8, 128.6, 128.5 (2C), 127.9, 125.0, 124.5, 121.0, 116.1, 43.2. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}O_2^+$ 239.1067, found 239.1071.

General procedure for synthesis of dihydrobenzofurans 3



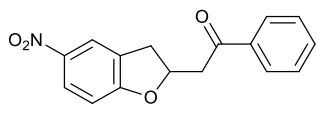
1 **3**

To a stirred solution of α,β-unsaturated ketone **1** (0.5 mmol) and trimethylsulfoxonium iodide (110 mg, 0.5 mmol) in DMF (5 mL) sodium hydride (80 mg, 60% dispersion in mineral oil) was added at rt in one portion. The red-colored reaction mixture was stirred at the same temperature for 2 h. After consumption of the starting ketone **1**, acetic acid (0.25 mL) was added, the reaction mixture was stirred for 5 min and was carefully poured into water (50 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL), and combined extracts were dried with anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* at 70 ºC afforded yellow oil, which was dissolved in toluene (for compounds **1b,c,e,l,n,m**) or *o*-xylene (for compounds **1a,f,h,j,k,l,o**), and Amberlyst® 15 (wet, 600 mg) was added. The reaction mixture was refluxed for 1–3 h (TLC control). Then the Amberlyst® 15 was filtered off, washed with ethyl acetate (5 mL), the solvent was evaporated *in vacuo*, and the residue was subjected to column chromatography (silica gel, eluent: petroleum ether/ethyl acetate, 40:1).



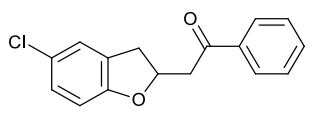
3a

2-(2,3-Dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3a**).[9] Yield: 36 mg, 30%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.98 – 7.96 (m, 2H), 7.60 – 7.57 (m, 1H), 7.49 – 7.46 (m, 2H), 7.19 – 1.17 (m, 1H), 7.13 – 7.10 (m, 1H), 6.87 – 6.84 (m, 1H), 6.79 – 6.77 (m, 1H), 5.38 (dtd, *J* = 9.0, 7.1, 5.8 Hz, 1H), 3.66 (dd, *J* = 17.0, 5.8 Hz, 1H), 3.54 (dd, *J* = 15.8, 9 Hz, 1H), 3.28 (dd, *J* = 17.0, 7.1 Hz, 1H), 2.95 (dd, *J* = 15.8, 7.1 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.6, 159.3, 137.0, 133.6, 128.8 (2C), 128.3 (2C), 128.2, 126.6, 125.2, 120.7, 109.7, 79.2, 44.9, 36.1.



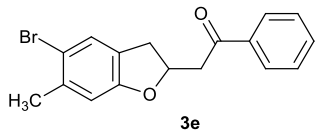
3b

2-(5-Nitro-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3b**). Yield: 106 mg, 75%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.10 – 8.08 (m, 2H), 7.98 – 7.96 (m, 2H), 7.63 – 7.59 (m, 1H), 7.49 – 7.47 (m, 2H), 6.81 – 6.79 (m, 1H), 5.60 – 5.53 (m, 1H), 3.71 (dd, *J* = 17.4, 5.9 Hz, 1H), 3.63 (dd, *J* = 16.4, 9.2 Hz, 1H), 3.36 (dd, *J* = 17.4, 7.2 Hz, 1H), 3.03 (dd, *J* = 16.4, 7.2 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 196.8, 164.7, 142.1, 136.5, 133.9, 128.9 (2C), 128.2 (3C), 126.0, 121.5, 109.5, 81.6, 44.5, 35.1. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}NO_4^+$ 284.0917, found 284.0921.



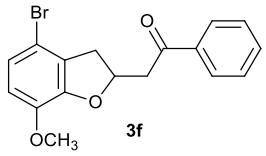
3c

2-(5-Chloro-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3c**). Yield: 78 mg, 57%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 – 7.95 (m, 2H), 7.60 – 7.57 (m, 1H), 7.49 – 7.46 (m, 2H), 7.13 (br s, 1H), 7.06 (dd, *J* = 8.5, 2 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.39 (dtd, *J* = 9.0, 7.1, 5.8 Hz, 1H), 3.64 (dd, *J* = 17.0, 5.8 Hz, 1H), 3.52 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.28 (dd, *J* = 17.0, 7.1 Hz, 1H), 2.94 (dd, *J* = 16.1, 7.1 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.3, 158.0, 136.9, 133.6, 128.9 (2C), 128.6, 128.3 (2C), 128.1, 125.4, 125.3, 110.56, 79.9, 44.7, 36.0. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}{}^{35}ClO_2^+$ 273.0677, found 273.0679.



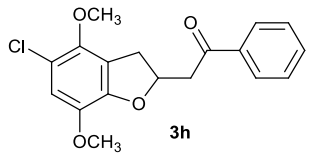
3e

2-(5-Bromo-6-methyl-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3e**). Yield: 61 mg, 37%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 – 7.95 (m, 2H), 7.60 – 7.57 (m, 1H), 7.49 – 7.45 (m, 2H), 7.30 (s, 1H), 6.66 (s, 1H), 5.37 (dtd, *J* = 8.9, 7.0, 5.8 Hz, 1H), 3.63 (dd, *J* = 17.0, 5.8 Hz, 1H), 3.50 (dd, *J* = 15.8, 8.9 Hz, 1H), 3.26 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.91 (dd, 15.8, 7.0 Hz, 1H), 2.33 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.4, 158.9, 137.6, 137.0, 133.6, 128.7 (2C), 128.6, 128.3 (2C), 126.3, 114.9, 111.9, 80.0, 44.7, 35.7, 23.3. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{16}{}^{81}BrO_2^+$ 333.0308, found 333.0305.



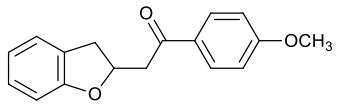
3f

2-(4-Bromo-7-methoxy-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3f**). Yield: 95 mg, 55%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 – 7.95 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.48 – 5.40 (m, 1H), 3.84 (s, 3H), 3.75 (dd, *J* = 17.3, 4.7 Hz, 1H), 3.59 (dd, *J* = 16.3, 9.1 Hz, 1H), 3.39 (dd, *J* = 17.3, 8.8 Hz, 1H), 2.96 (dd, *J* = 16.3, 7.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.1, 148.1, 144.1, 136.8, 133.6, 128.9 (2C), 128.2 (2C), 123.7, 113.5, 110.1, 80.0, 56.5, 44.9, 38.2. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{16}{}^{79}BrO_3^+$ 347.0277, found 347.0272.



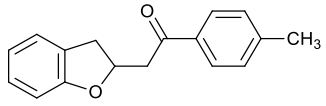
3h

2-(5-Chloro-4,7-dimethoxy-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3h**). Yield: 98 mg, 59%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.96 – 7.94 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H) 6.75 (s, 1H), 5.48 – 5.36 (m, 1H), 3.82 (s, 6H), 3.74 (dd, *J* = 17.2, 4.5 Hz, 1H), 3.65 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.38 (dd, *J* = 17.2, 8.7 Hz, 1H), 3.02 (dd, *J* = 16.0, 7.5 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.2, 147.5, 146.6, 140.9, 136.8, 133.7, 128.9 (2C), 128.2 (2C), 120.6, 117.6, 113.7, 81.1, 60.4, 56.7, 44.7, 35.0. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{18}H_{18}{}^{35}ClO_4^+$ 333.0888, found 333.0880.



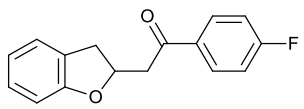
3i

2-(2,3-Dihydro-1-benzofuran-2-yl)-1-(4-methoxyphenyl)ethanone (**3i**).[10] Yield: 30 mg, 22%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.96 – 7.94 (m, 2H), 7.18 – 7.16 (m, 1H), 7.13 – 7.09 (m, 1H), 6.95 – 6.93 (m, 2H), 6.86 – 6.83 (m, 1H), 6.78 – 6.76 (m, 1H), 5.36 (dtd, *J* = 9.0, 7.2, 5.8 Hz, 1H), 3.87 (s, 3H), 3.61 (dd, *J* = 16.7, 5.8 Hz, 1H), 3.53 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.22 (dd, *J* = 16.7, 7.2 Hz, 1H), 2.95 (dd, *J* = 15.8, 7.2 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 196.1, 163.9, 159.3, 130.6 (2C), 130.2, 128.2, 126.7, 125.2, 120.6, 114.0 (2C), 109.7, 79.4, 55.6, 44.5, 36.1.



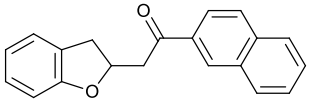
3j

2-(2,3-Dihydro-1-benzofuran-2-yl)-1-(4-methylphenyl)ethanone (**3j**).[10] Yield: 43 mg, 34%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.88 – 7.86 (m, 2H), 7.28 – 7.26 (m, 2H), 7.18 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 6.87 – 6.83 (m, 1H), 6.78 – 6.76 (m, 1H), 5.40 – 5.33 (m, 1H), 3.63 (dd, *J* = 16.9, 5.8 Hz, 1H), 3.53 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.25 (dd, *J* = 16.9, 7.3 Hz, 1H), 2.94 (dd, *J* = 15.8, 7.0 Hz, 1H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.3, 159.3, 144.4, 134.6, 129.5 (2C), 128.4 (2C), 128.2, 126.6, 125.2, 120.6, 109.7, 79.3, 44.8, 36.1, 21.8.



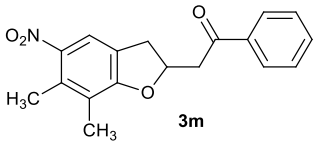
3k

2-(2,3-Dihydro-1-benzofuran-2-yl)-1-(4-fluorophenyl)ethanone (**3k**). Yield: 28 mg, 22%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.02 – 7.98 (m, 2H), 7.19 – 7.09 (m, 4H), 6.87 – 6.86 (m, 1H), 6.78 – 6.76 (m, 1H), 5.36 (br dq, *J* = 9.0, 6.8 Hz, 1H), 3.62 (dd, *J* = 16.9, 6.0 Hz, 1H), 3.54 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.23 (dd, *J* = 16.9, 7.0 Hz, 1H), 2.95 (dd, *J* = 15.8, 6.9 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 196.0, 166.1 (d, $J_{C\text{-}F}$ = 255 Hz), 159.2, 133.5 (d, $J_{C\text{-}F}$ = 3 Hz), 131.0 (d, $J_{C\text{-}F}$ = 9 Hz, 2C), 128.4, 126.5, 125.2, 120.7, 115.9 (d, $J_{C\text{-}F}$ = 22 Hz, 2C), 109.7, 79.1, 44.8, 36.0. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{14}FO_2^+$ 257.0972, found 257.0971.



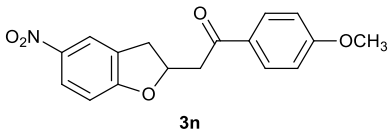
3l

2-(2,3-Dihydro-1-benzofuran-2-yl)-1-(naphthalen-2-yl)ethanone (**3l**).[10] Yield: 48 mg, 33%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.48 (s, 1H), 8.06 – 8.04 (m, 1H), 7.96 – 7.94 (m, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.54 (m, 2H), 7.21 – 7.19 (m, 1H), 7.15 – 7.11 (m, 1H), 6.89 – 6.87 (m, 1H), 6.80 – 6.79 (m, 1H), 5.47 – 5.40 (m, 1H), 3.80 (dd, *J* = 16.8, 5.9 Hz, 1H), 3.57 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.40 (dd, *J* = 16.8, 7.2 Hz, 1H), 3.01 (dd, *J* = 15.8, 6.9 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.5, 159.3, 135.9, 134.4, 132.7, 130.2, 129.8, 128.8, 128.7, 128.2, 127.9, 127.0, 126.6, 125.2, 123.8, 120.7, 109.7, 79.3, 45.0, 36.1.



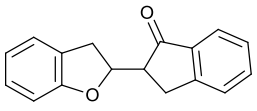
3m

2-(6,7-Dimethyl-5-nitro-2,3-dihydro-1-benzofuran-2-yl)-1-phenylethanone (**3m**). Yield: 93 mg, 60%; pale yellow transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.97 – 7.65 (m, 2H), 7.64 (s, 1H), 7.62 – 7.58 (m, 1H), 7.50 – 7.46 (m, 2H), 5.46 (dtd, *J* = 9.1, 7.2, 5.6 Hz, 1H), 3.68 (dd, *J* = 17.0, 5.6 Hz, 1H), 3.58 (dd, *J* = 16.1, 9.1 Hz, 1H), 3.30 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.99 (dd, *J* = 16.1, 7.2 Hz, 1H), 2.41 (s, 3H), 2.15 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.1, 161.4, 144.5, 136.8, 133.9, 133.7, 128.9 (2C), 128.3 (2C), 124.0, 120.1, 119.7, 80.5, 44.7, 35.7, 16.1, 12.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}NO_4^+$ 312.1230, found 312.1228.



3n

1-(4-Methoxyphenyl)-2-(5-nitro-2,3-dihydro-1-benzofuran-2-yl)ethanone (**3n**). Yield: 109 mg, 70%; pale yellow solid, mp = 163 – 165 °C (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.07 (s, 1H), 7.95 – 7.93 (m, 2H), 6.96 – 6.94 (m, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 5.53 (dtd, *J* = 9.2, 7.3, 5.7 Hz, 1H), 3.88 (s, 3H), 3.65 (dd, *J* = 17.0, 5.7 Hz, 1H), 3.62 (dd, 16.3, 9.2 Hz, 1H), 3.29 (dd, *J* = 17.0, 7.3 Hz, 1H), 3.03 (dd, *J* = 16.3, 7.2 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 195.2, 164.8, 164.2, 142.3, 130.6 (2C), 129.7, 128.3, 125.9, 121.5, 114.1 (2C), 109.4, 81.9, 55.7, 44.2, 35.2. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}NO_5^+$ 314.1023, found 314.1027.



3o

2-(2,3-Dihydro-1-benzofuran-2-yl)-2,3-dihydro-1*H*-inden-1-one (**3o**), mixture of isomers. Combined yield: 50 mg, 40% (*dr* 2:1); pale yellow transparent oil. Major isomer - ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.78 – 7.76 (m, 1H), 7.61-7.58 (m, 1H), 7.46 – 7.45 (m, 1H), 7.40 – 7.37 (m, 1H), 7.15 – 7.07 (m, 2H), 6.83 – 6.76 (m, 2H), 5.42 – 5.37 (m, 1H), 3.46 – 3.42 (m, 1H), 3.29 (dd, *J* = 17.8, 8.0 Hz, 1H), 3.18 (dd, *J* = 15.9, 9.5 Hz, 1H), 3.07 (dd, *J* = 17.8, 3.9 Hz, 1H), 2.82 (dd, *J* = 15.9, 8.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 205.3, 159.8, 154.3, 137.6, 135.2, 128.2, 127.7, 126.8, 126.8, 125.0, 124.1, 120.6, 109.4, 82.4, 51.1, 31.2, 28.2. Minor isomer - ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.82 – 7.80 (m, 1H), 7.62 – 7.58 (m, 1H), 7.47 – 7.45 (m, 1H), 7.41 – 7.37 (m, 1H), 7.21 – 7.19 (m, 1H), 7.10 – 7.06 (m, 1H), 6.87 – 6.83 (m, 1H), 6.70 – 6.68 (m, 1H), 5.29 – 5.24 (m, 1H), 3.49 – 3.43 (m, 1H), 3.34 – 3.26 (m, 2H), 3.22 – 3.17 (m, 1H), 3.03 – 2.99 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 205.4, 159.6, 154.0, 137.1, 135.1, 128.2, 127.6, 126.8, 126.6, 125.1, 124.2, 120.7, 109.5, 81.9, 52.2, 34.2, 28.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}O_2^+$ 251.1067, found 251.1071.

5. REFERENCES

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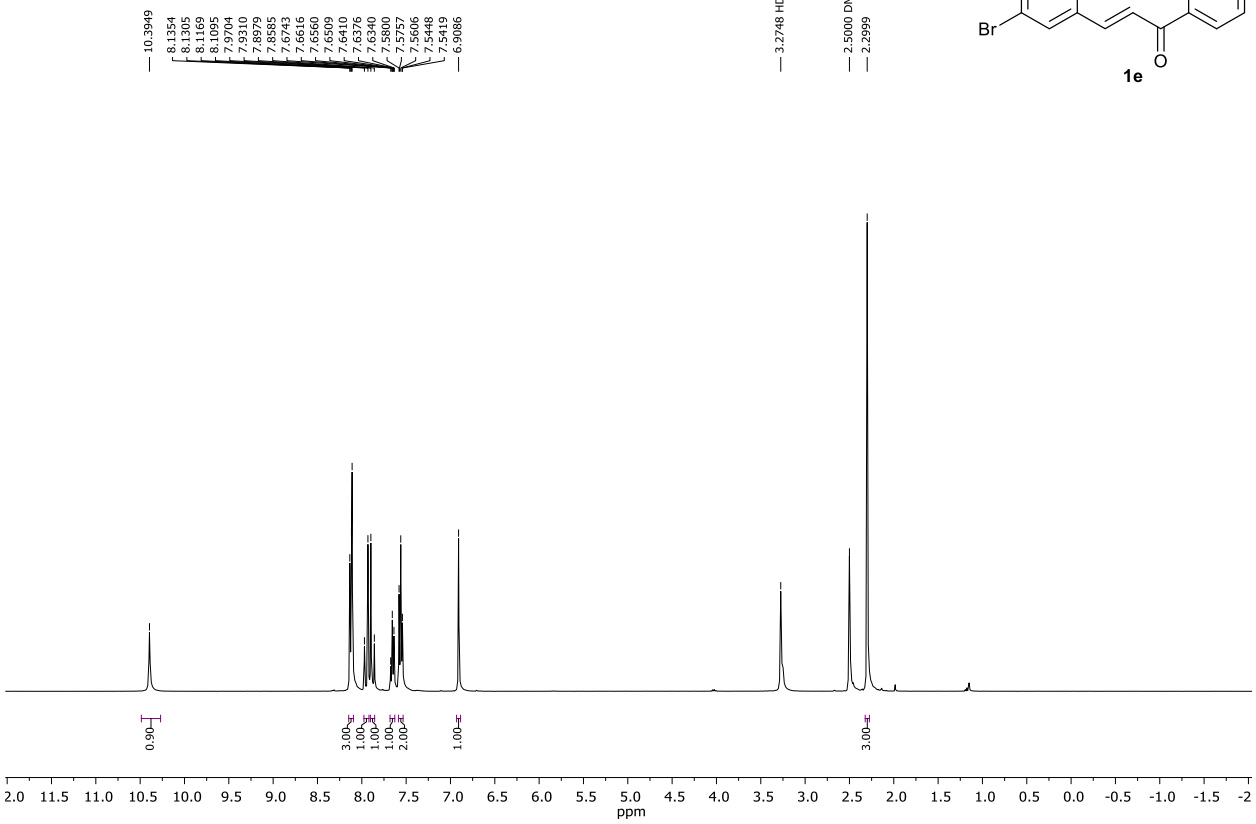
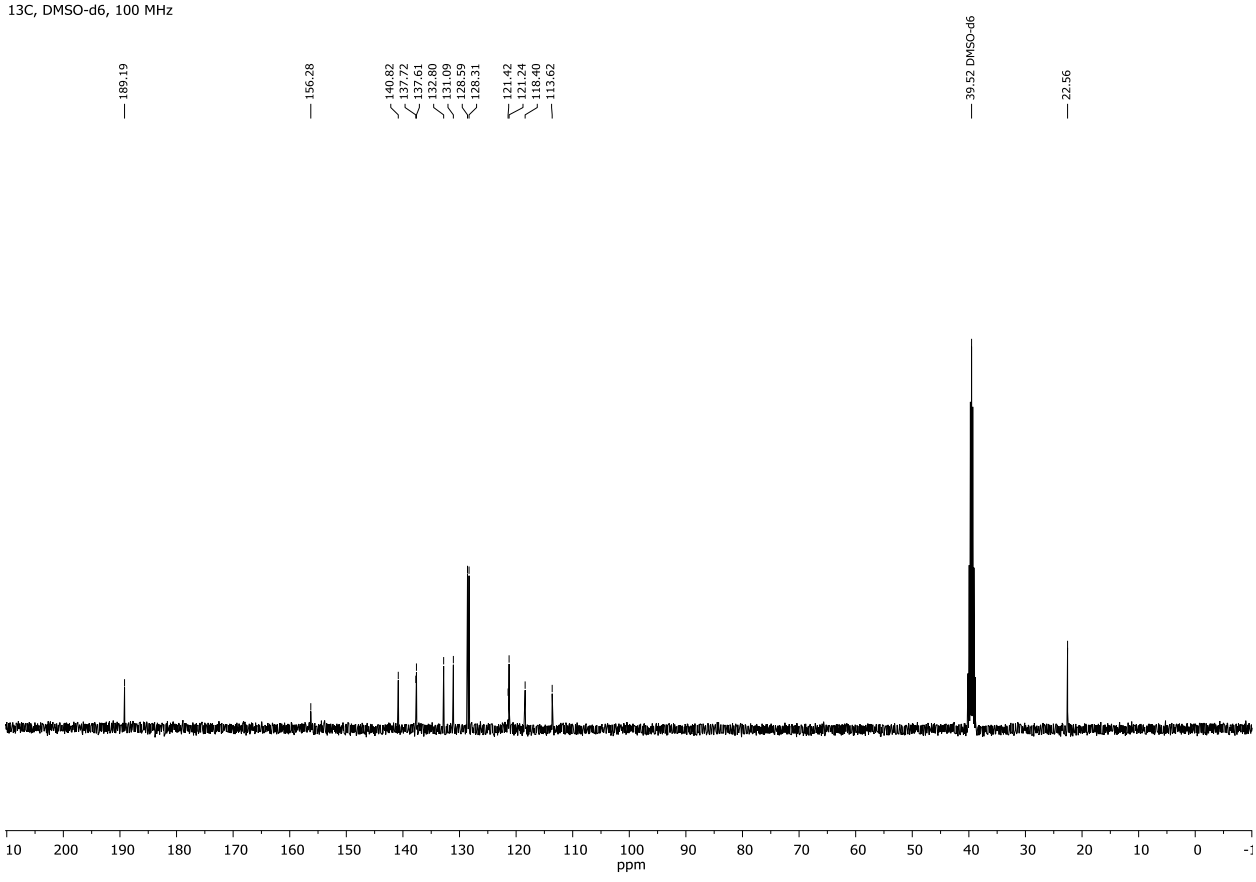
6. COPIES OF NMR SPECTRA

1H, DMSO-d6, 400 MHz



1e

13C, DMSO-d6, 100 MHz



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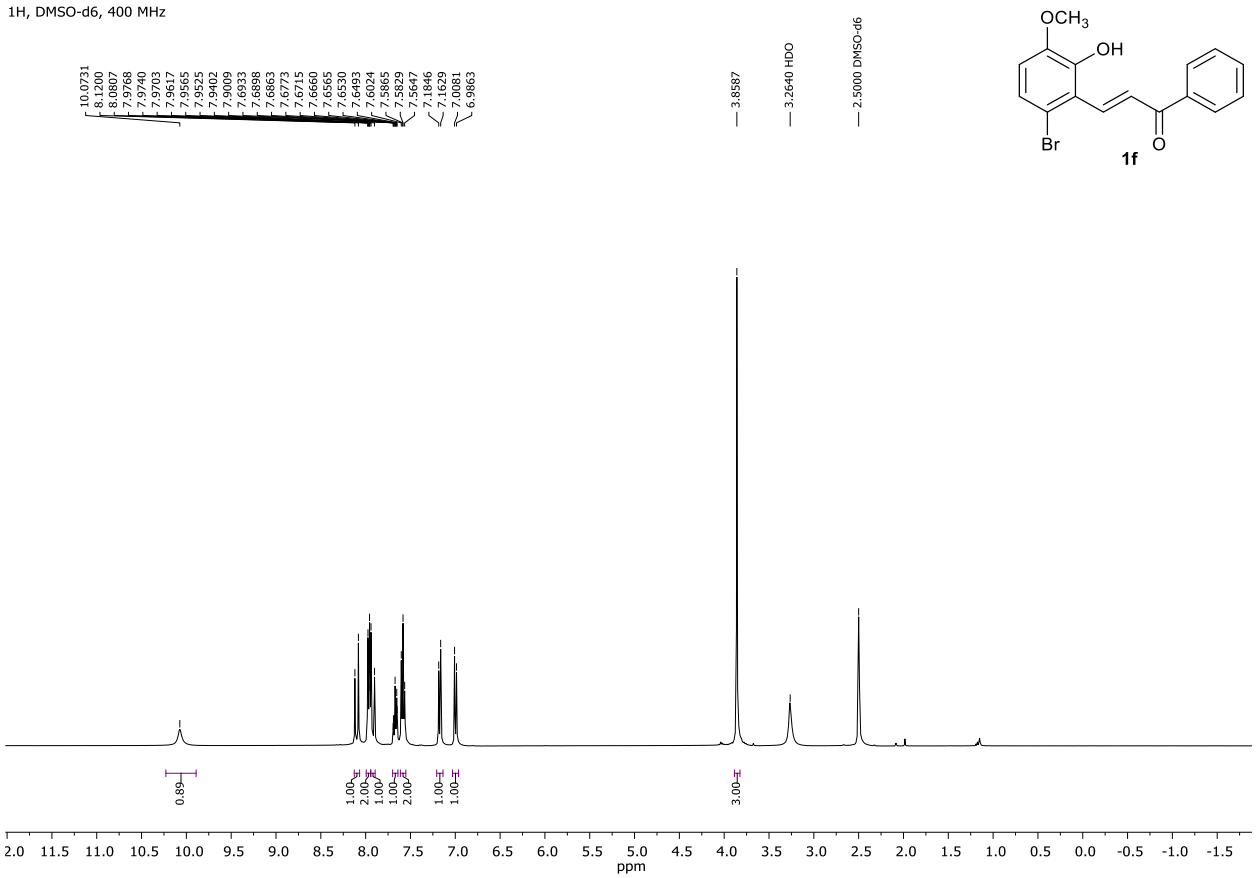

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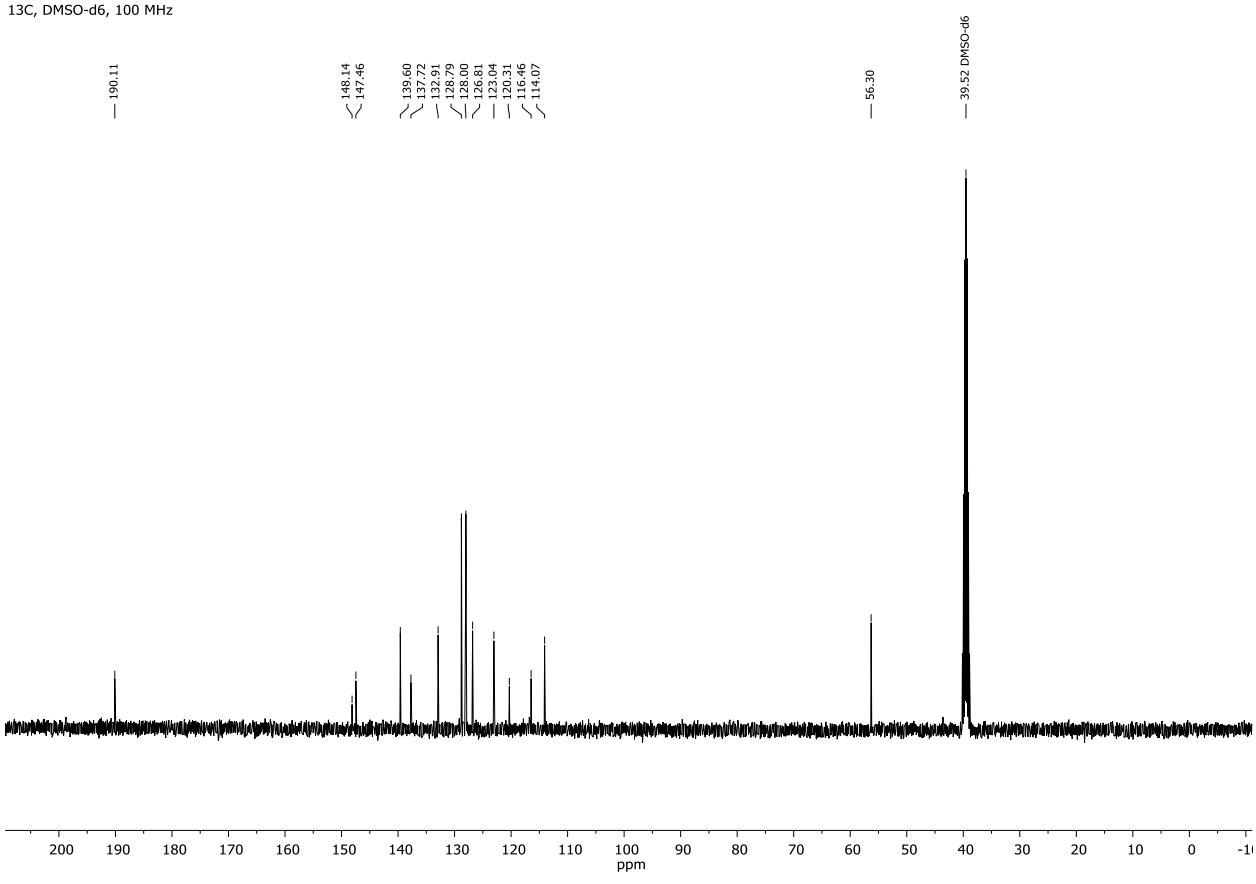

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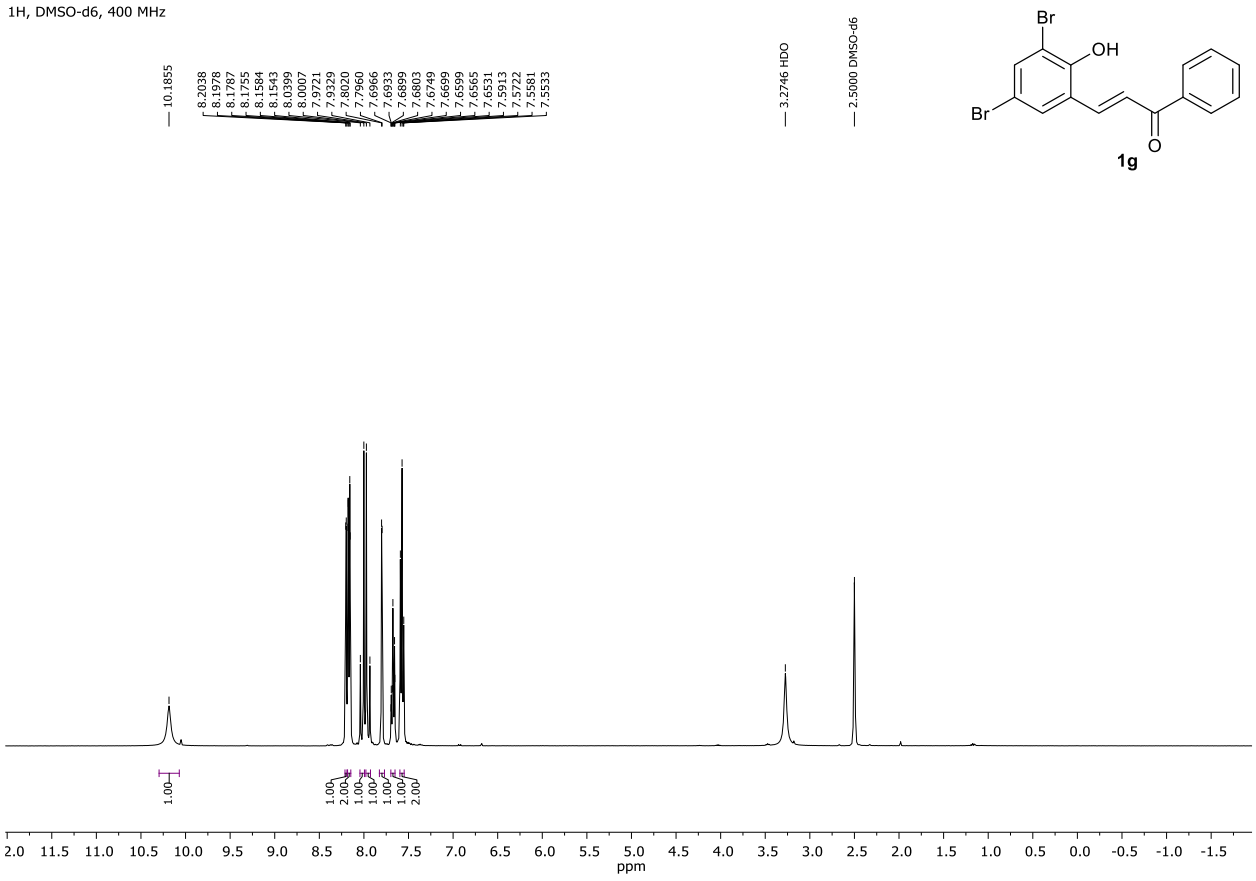

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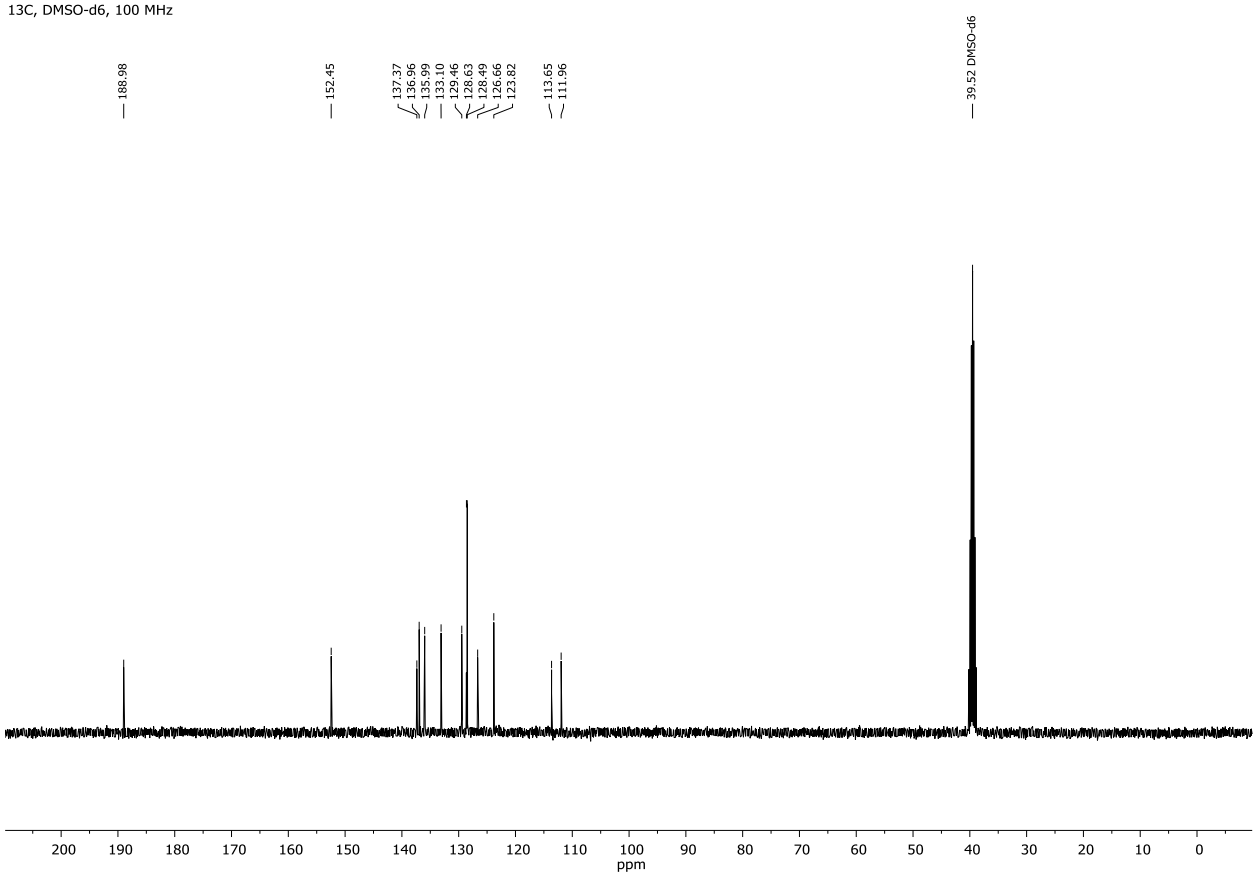

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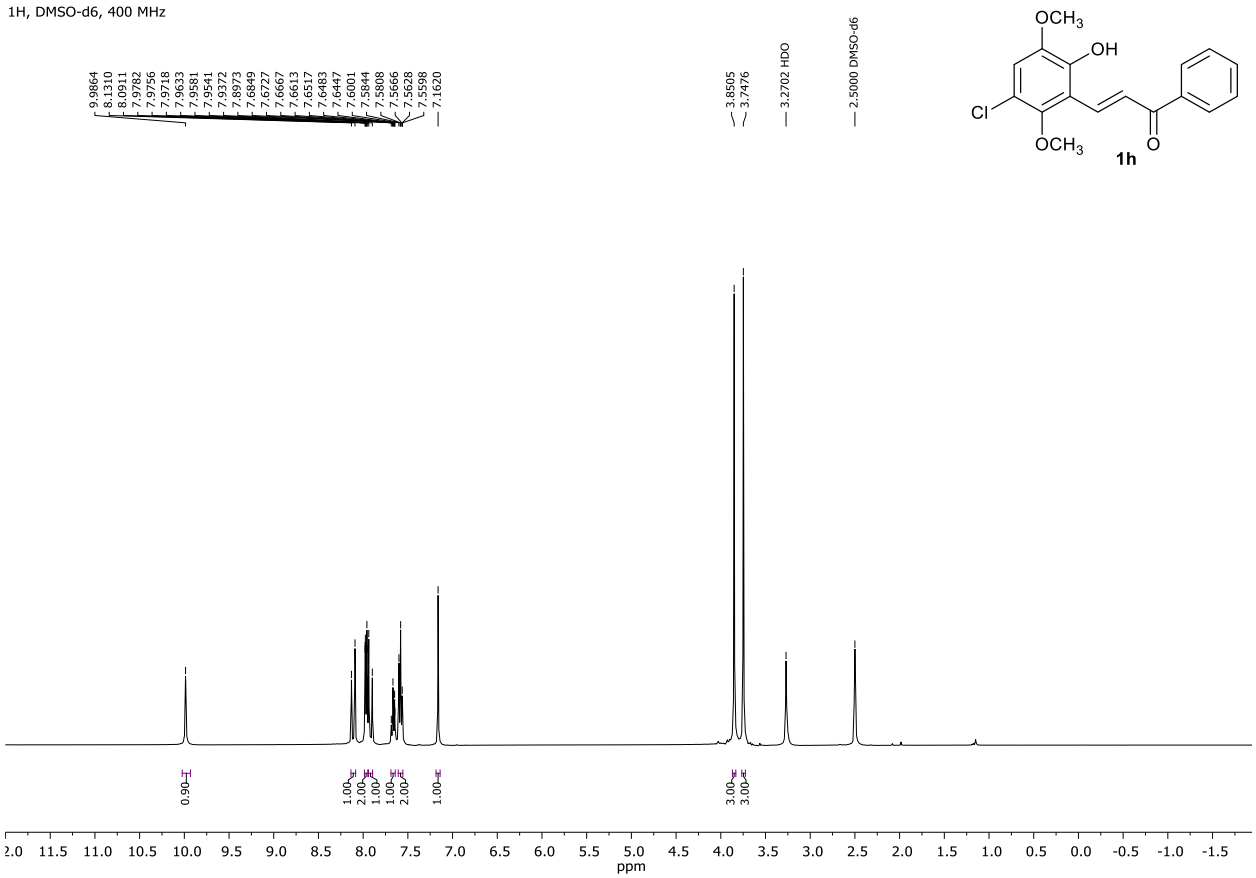
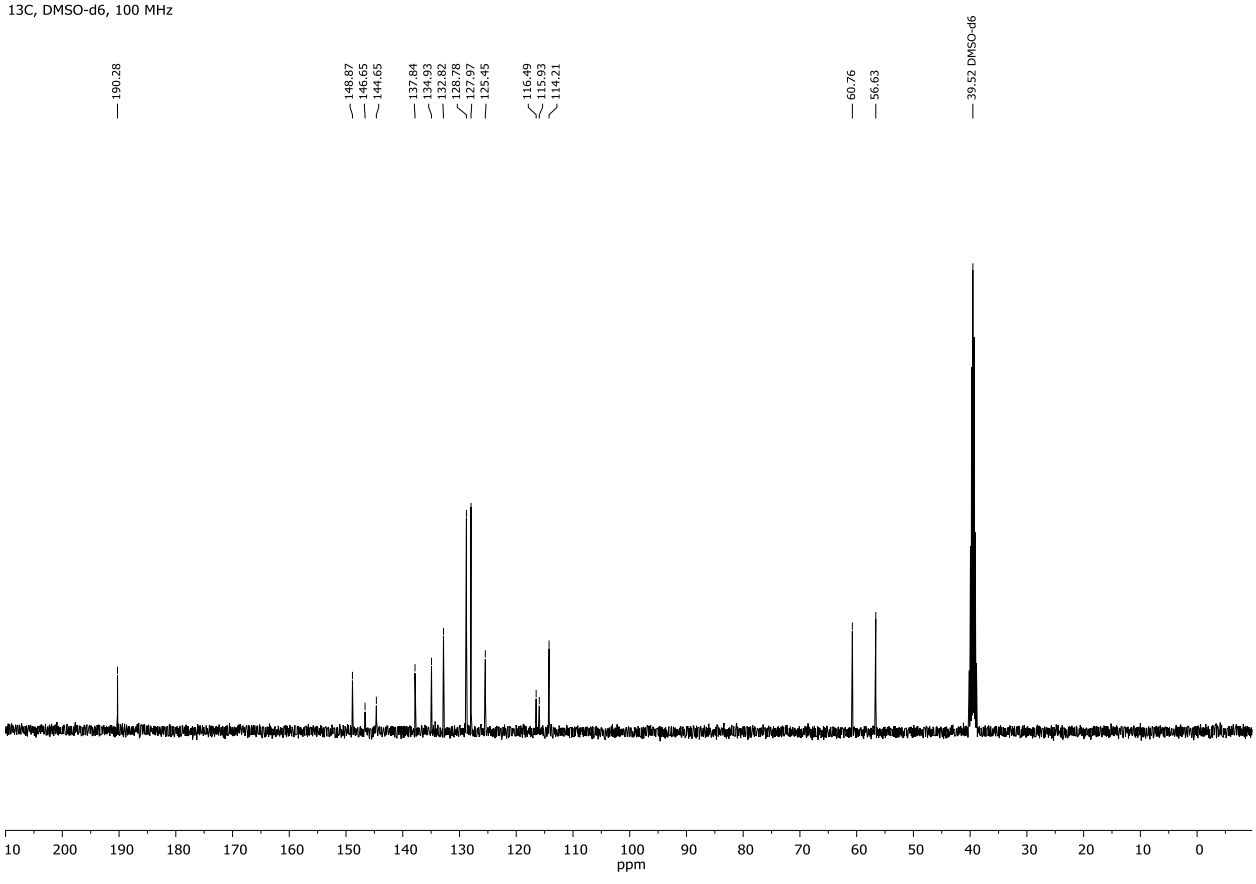
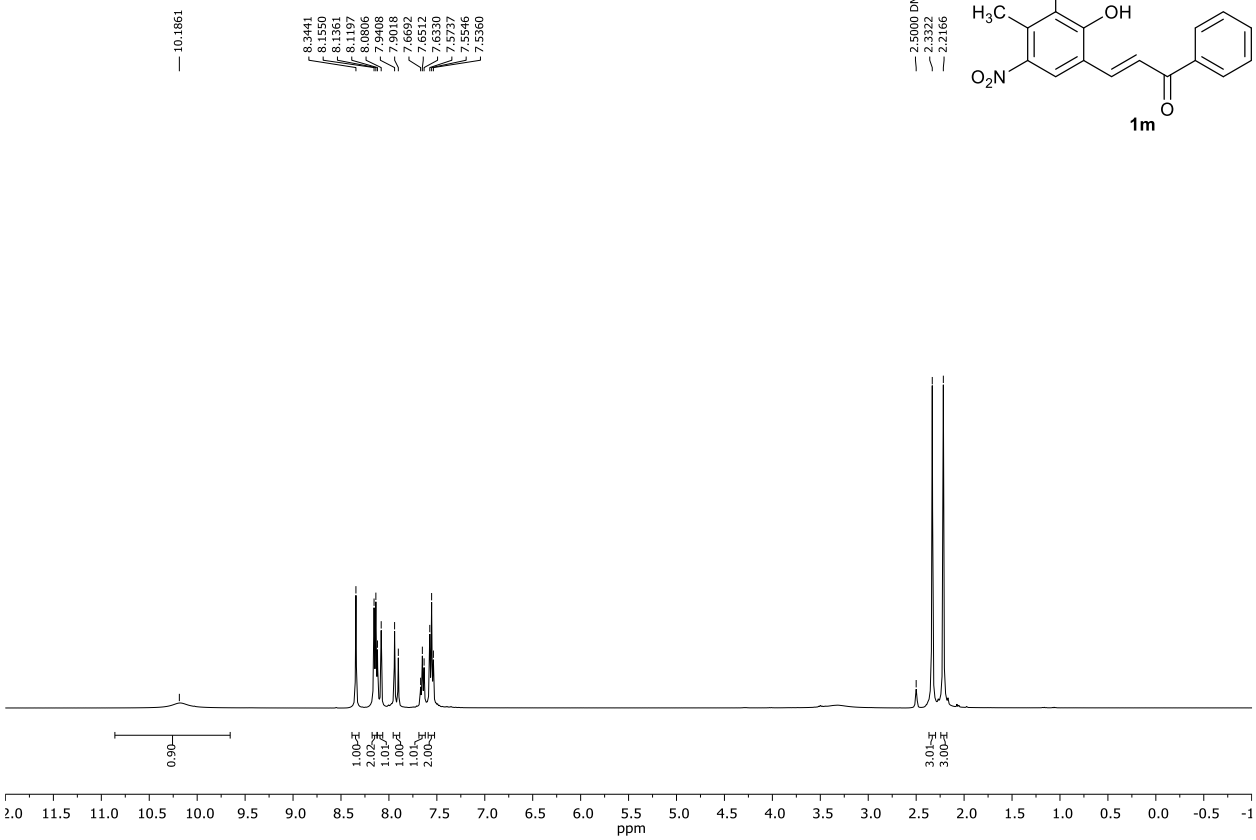


1h

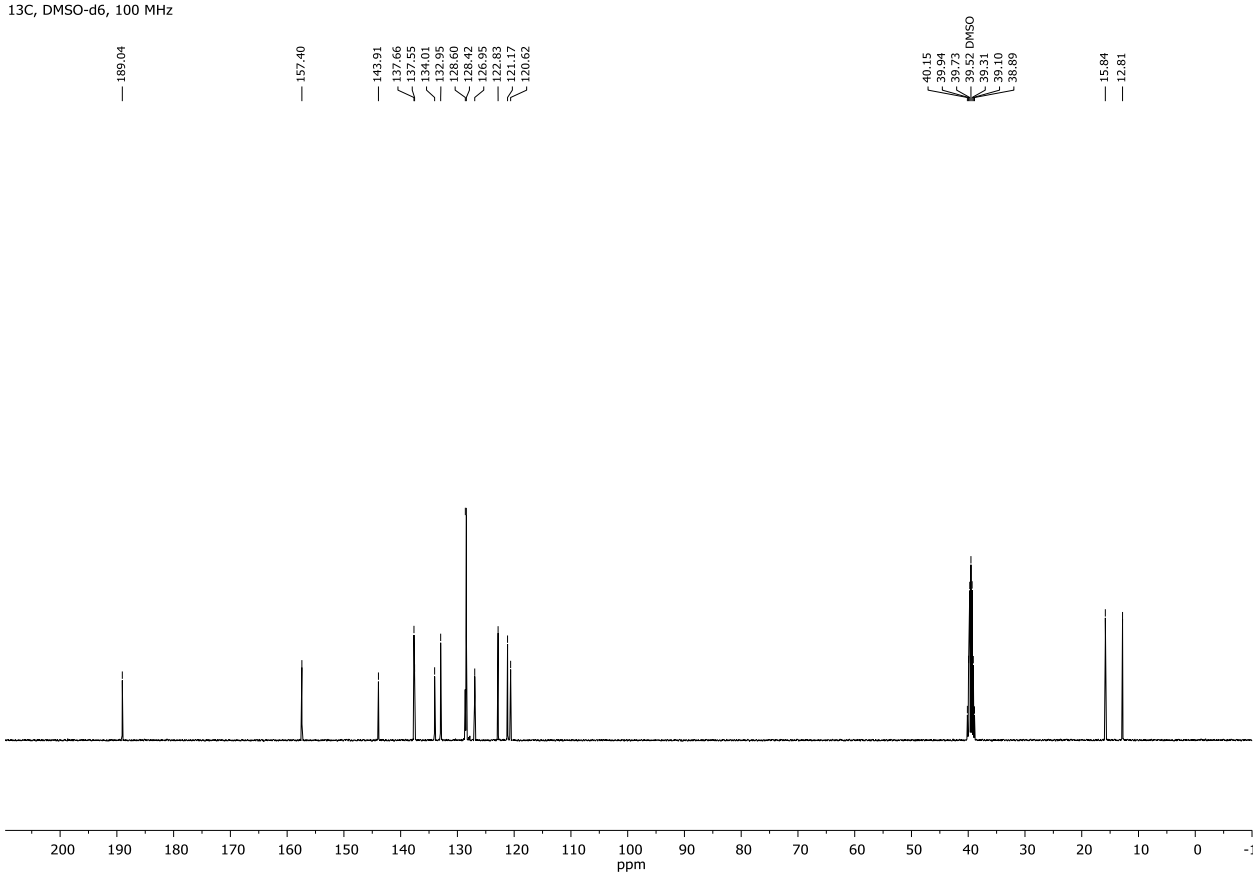
13C, DMSO-d6, 100 MHz



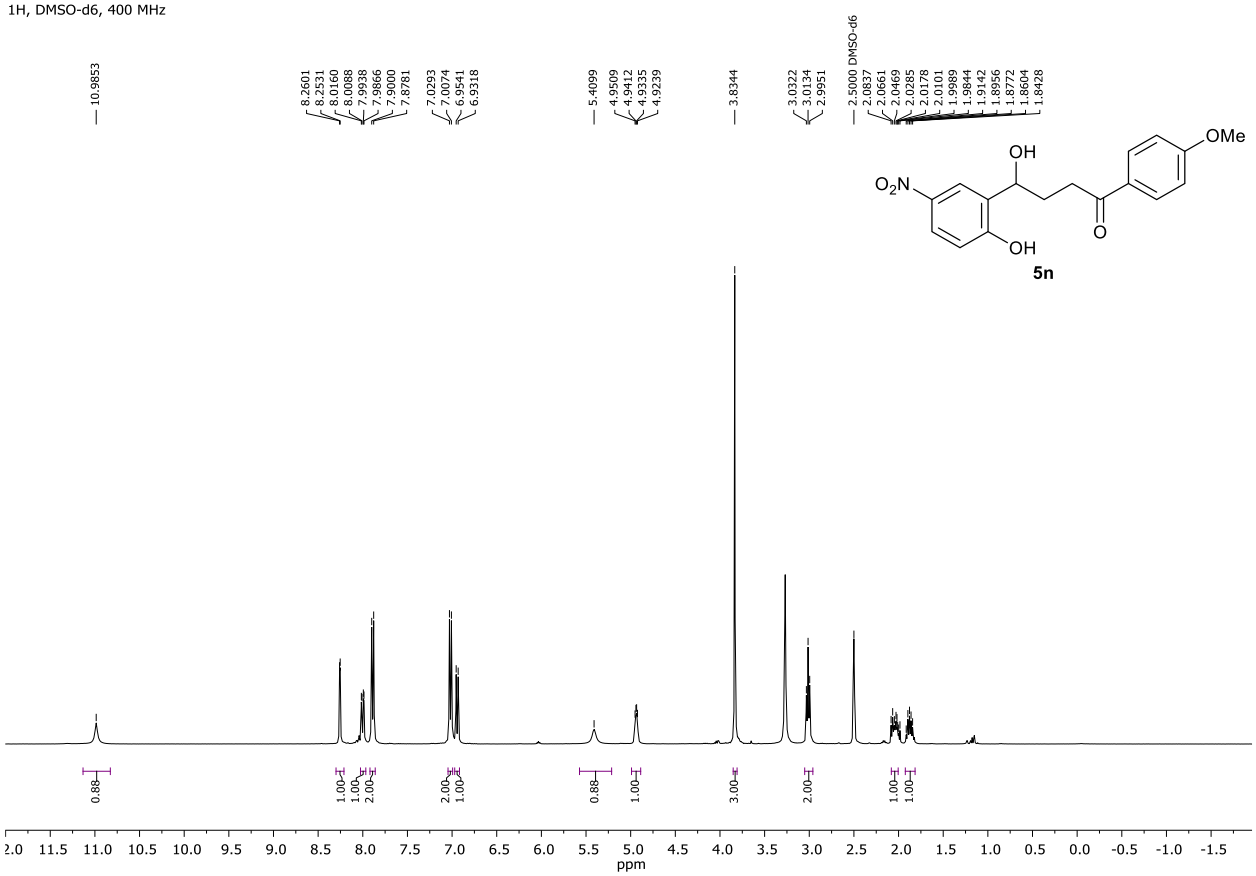
1H, DMSO-d6, 400 MHz



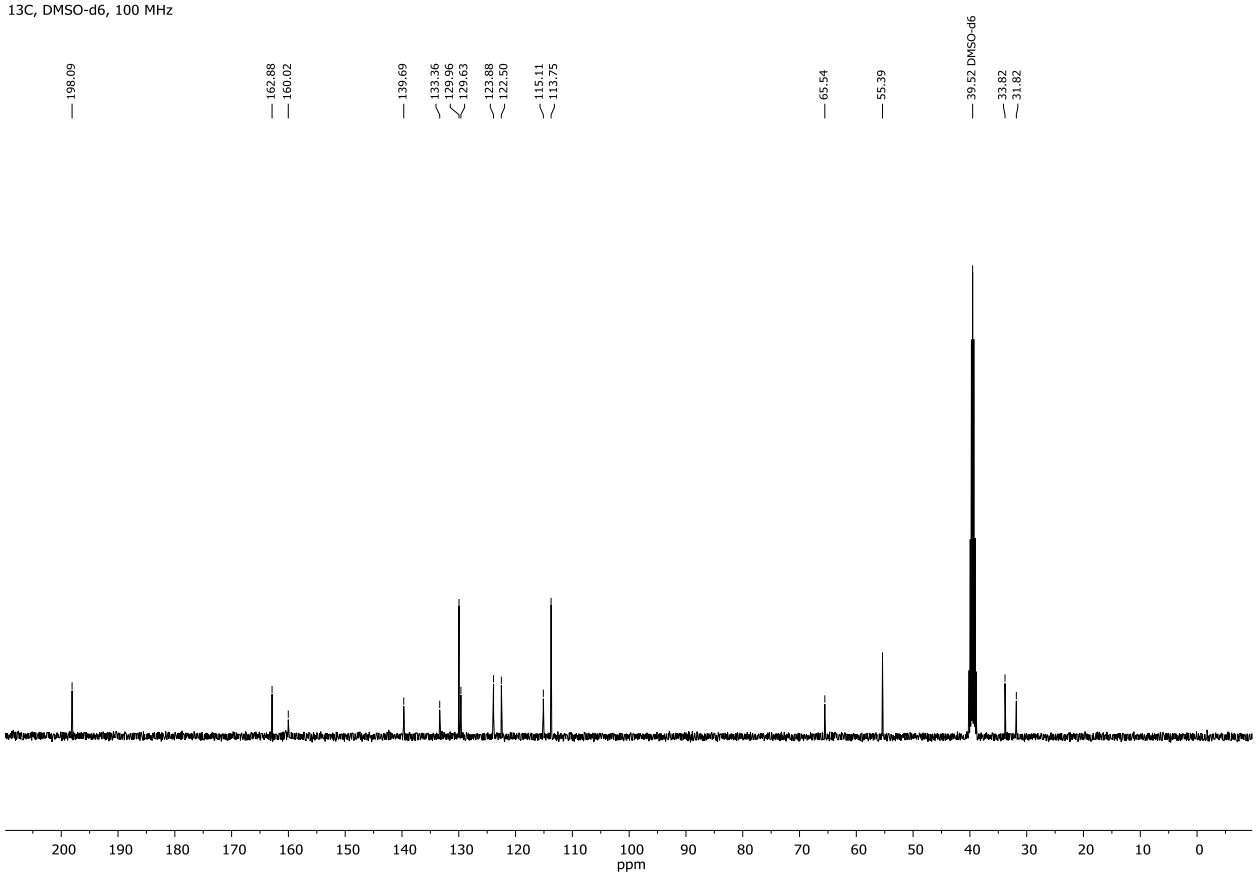
13C, DMSO-d6, 100 MHz



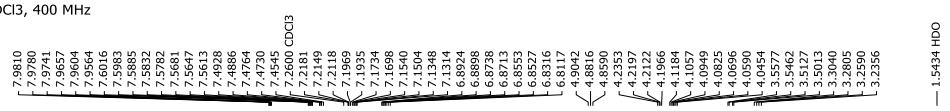
1H, DMSO-d6, 400 MHz

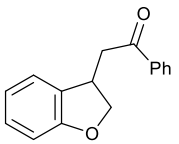


13C, DMSO-d6, 100 MHz

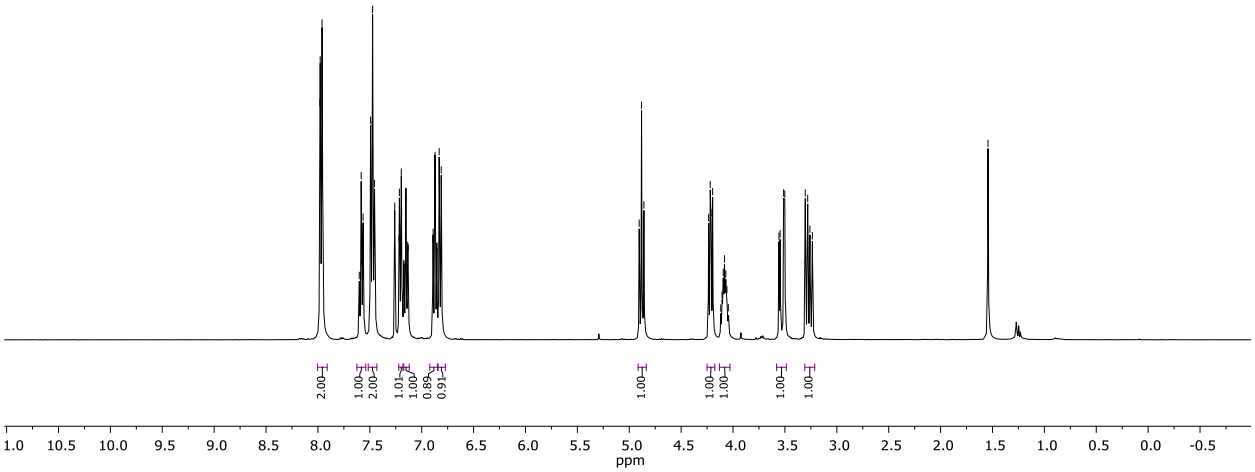


1H, CDCl3, 400 MHz

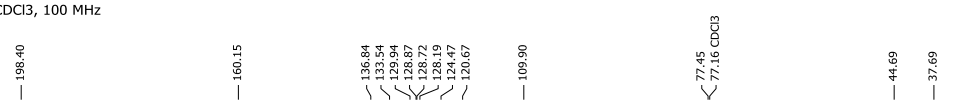


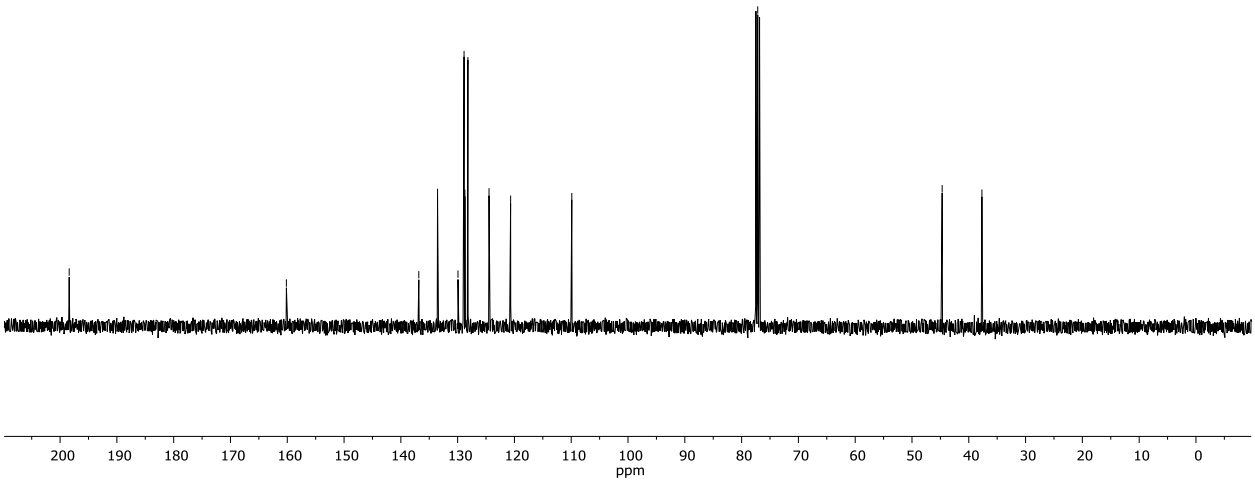


6a

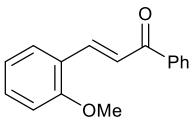


13C, CDCl3, 100 MHz

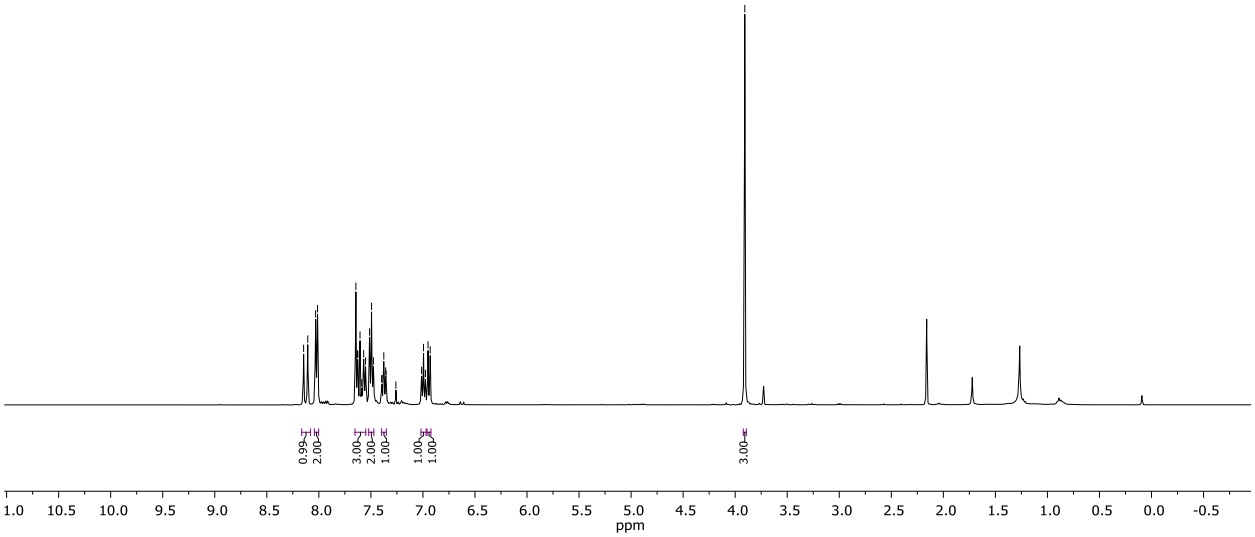




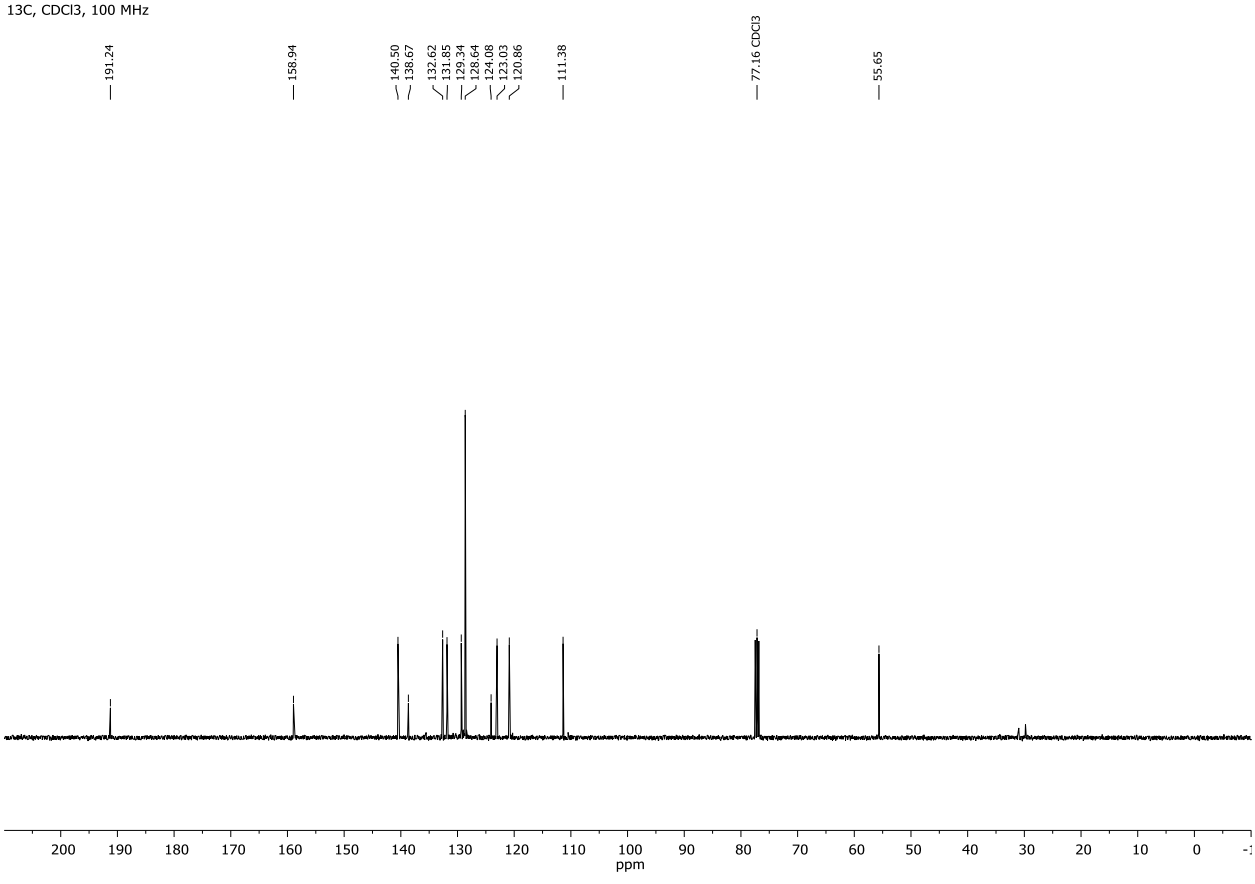
1H, CDCl3, 400 MHz



7a



13C, CDCl3, 100 MHz



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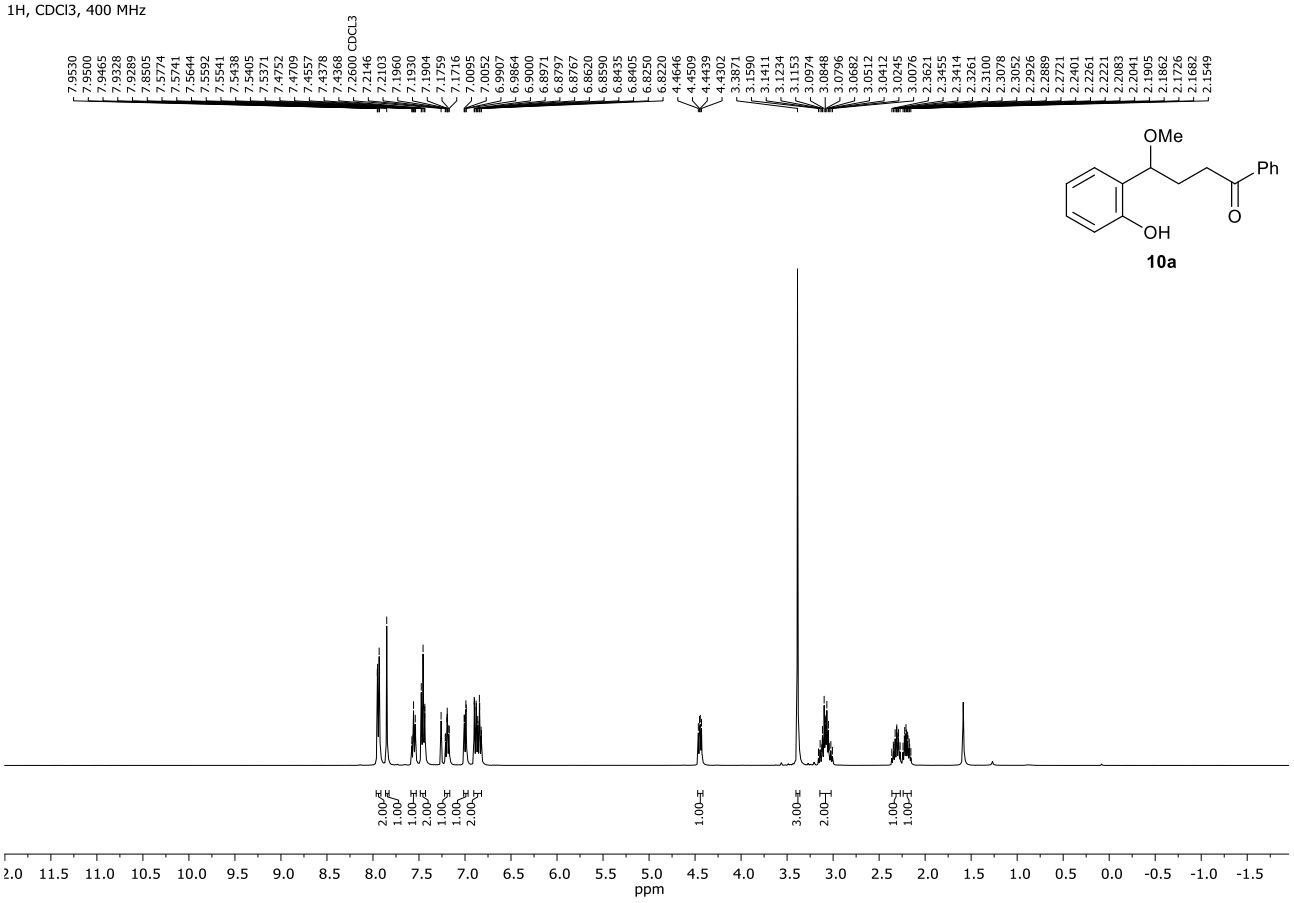
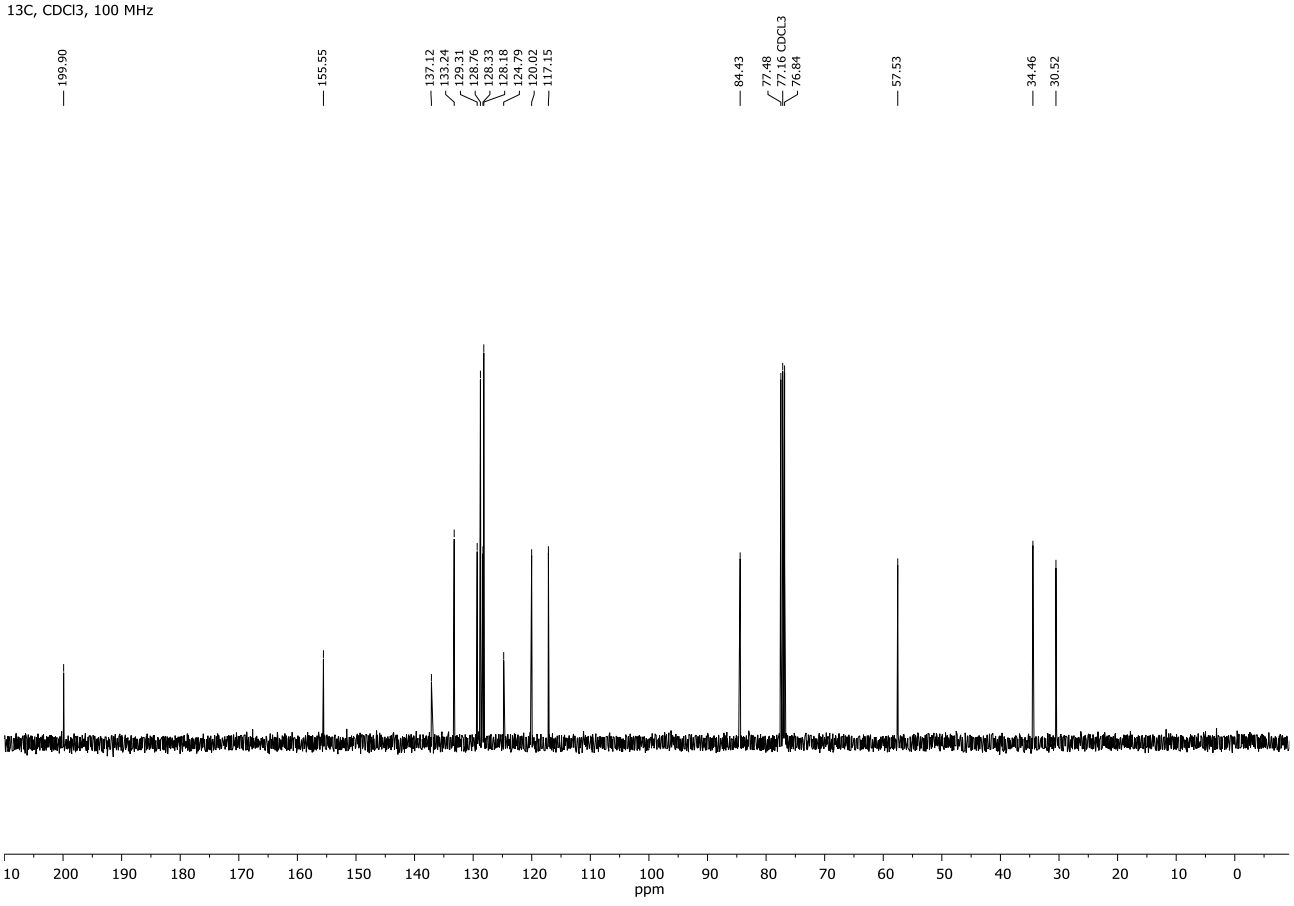


13C, CDCl3, 100 MHz



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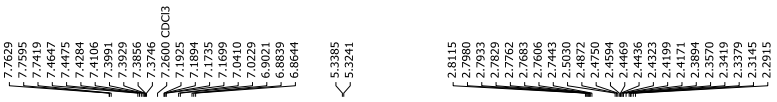

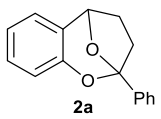

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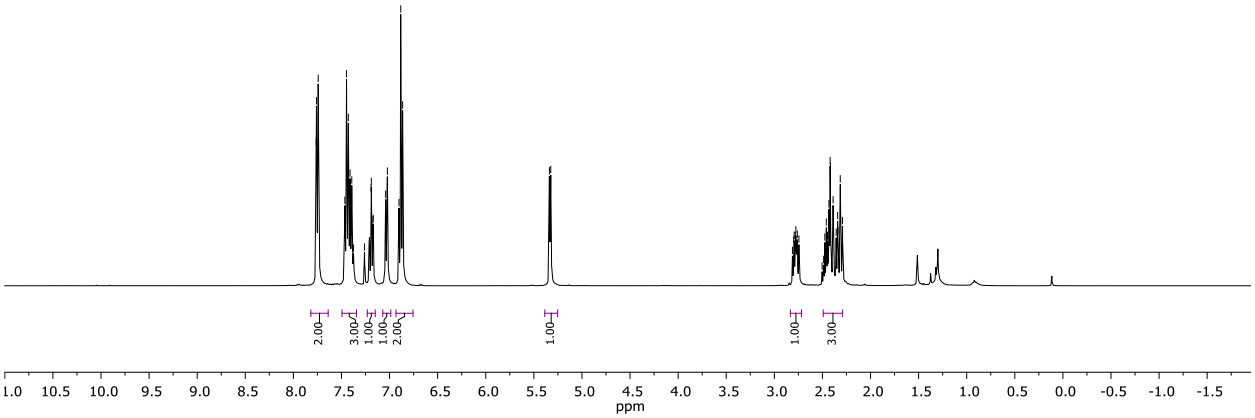
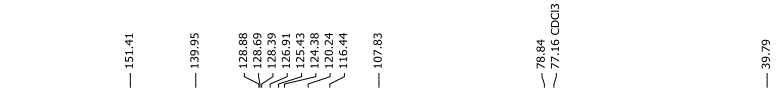
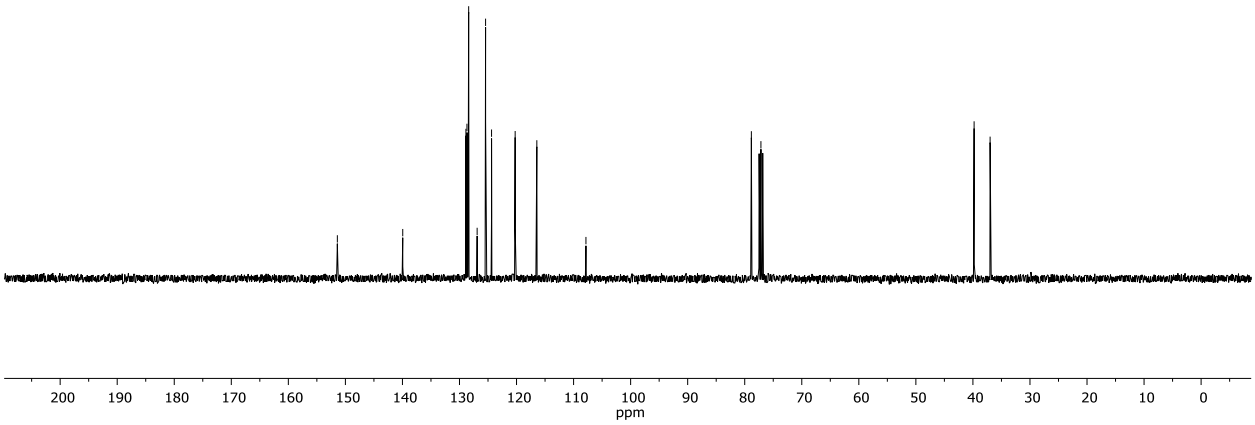
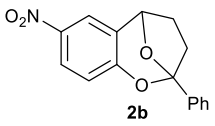


13C, CDCl3, 100 MHz





1H, CDCl3, 400 MHz



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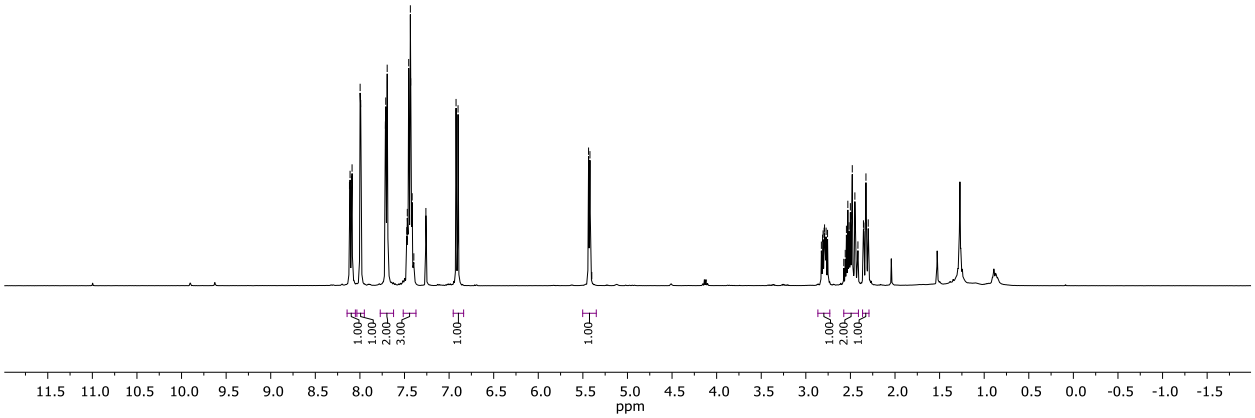
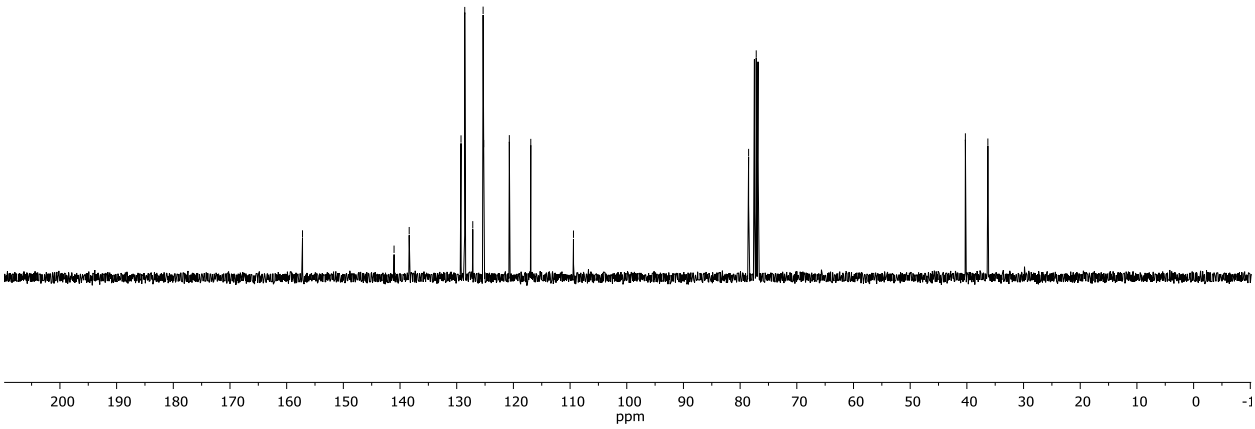


13C, CDCl3, 100 MHz



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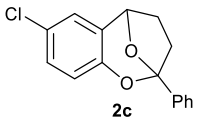

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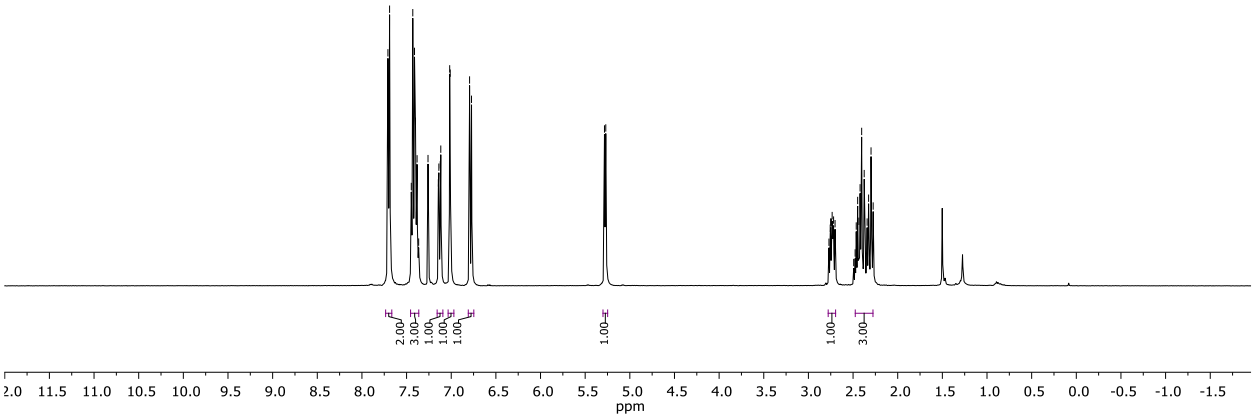
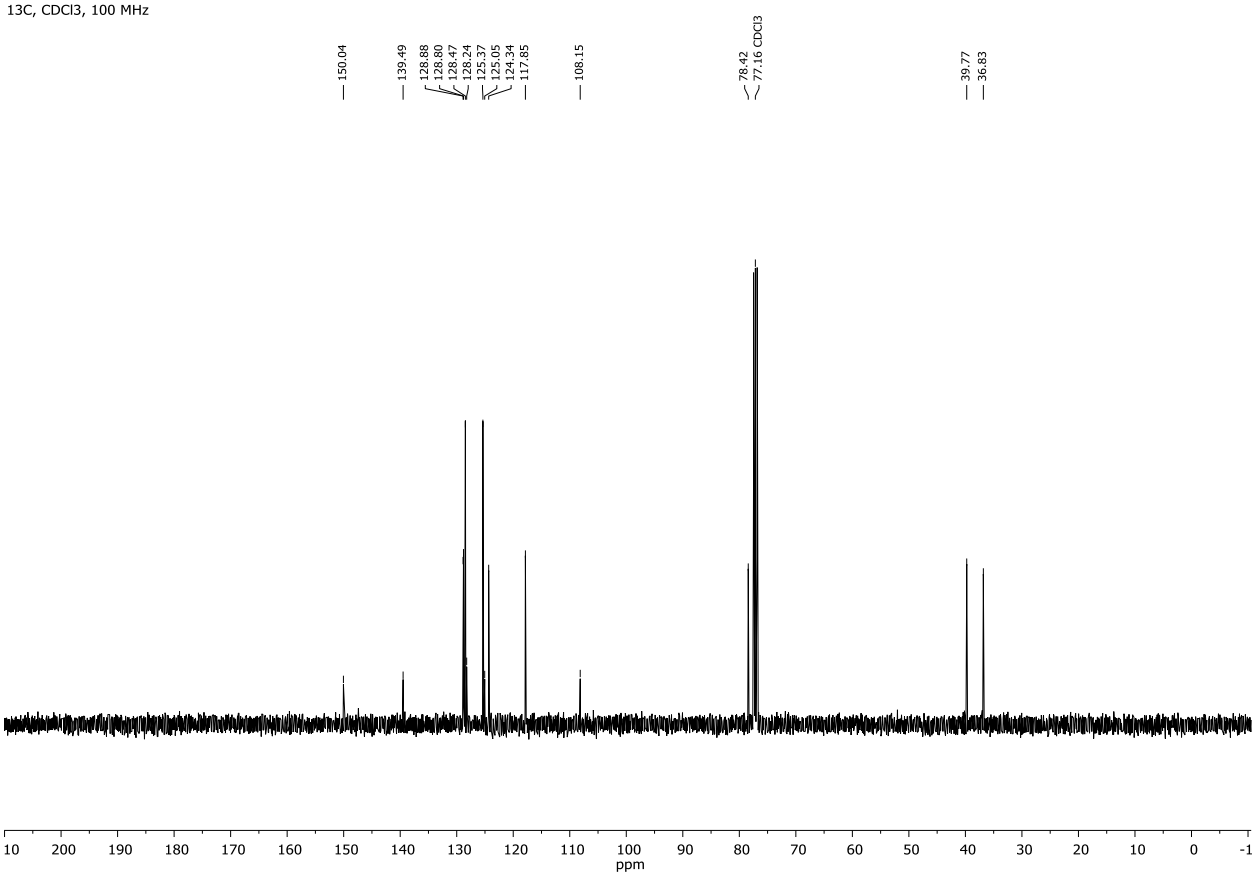


13C, CDCl3, 100 MHz



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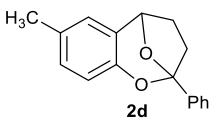
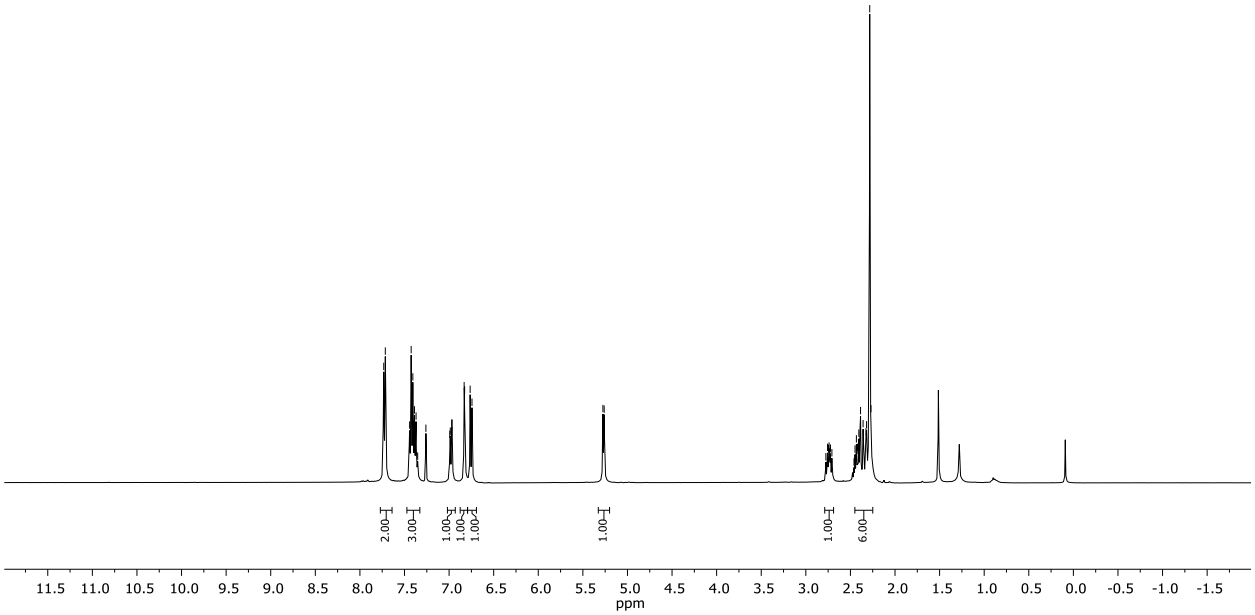
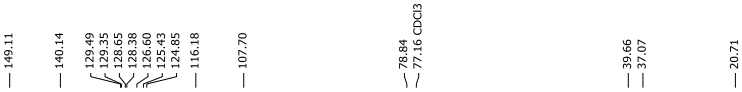
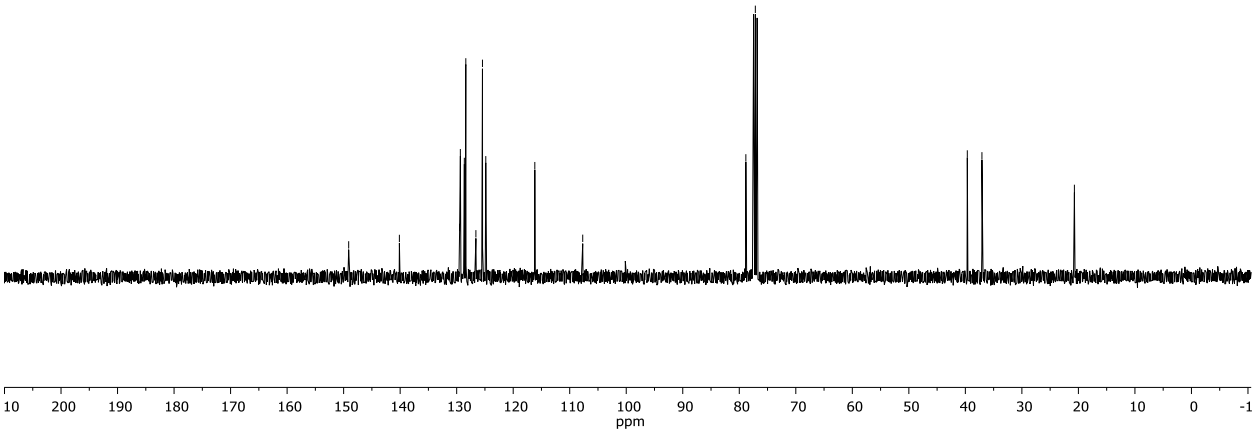




13C, CDCl3, 100 MHz





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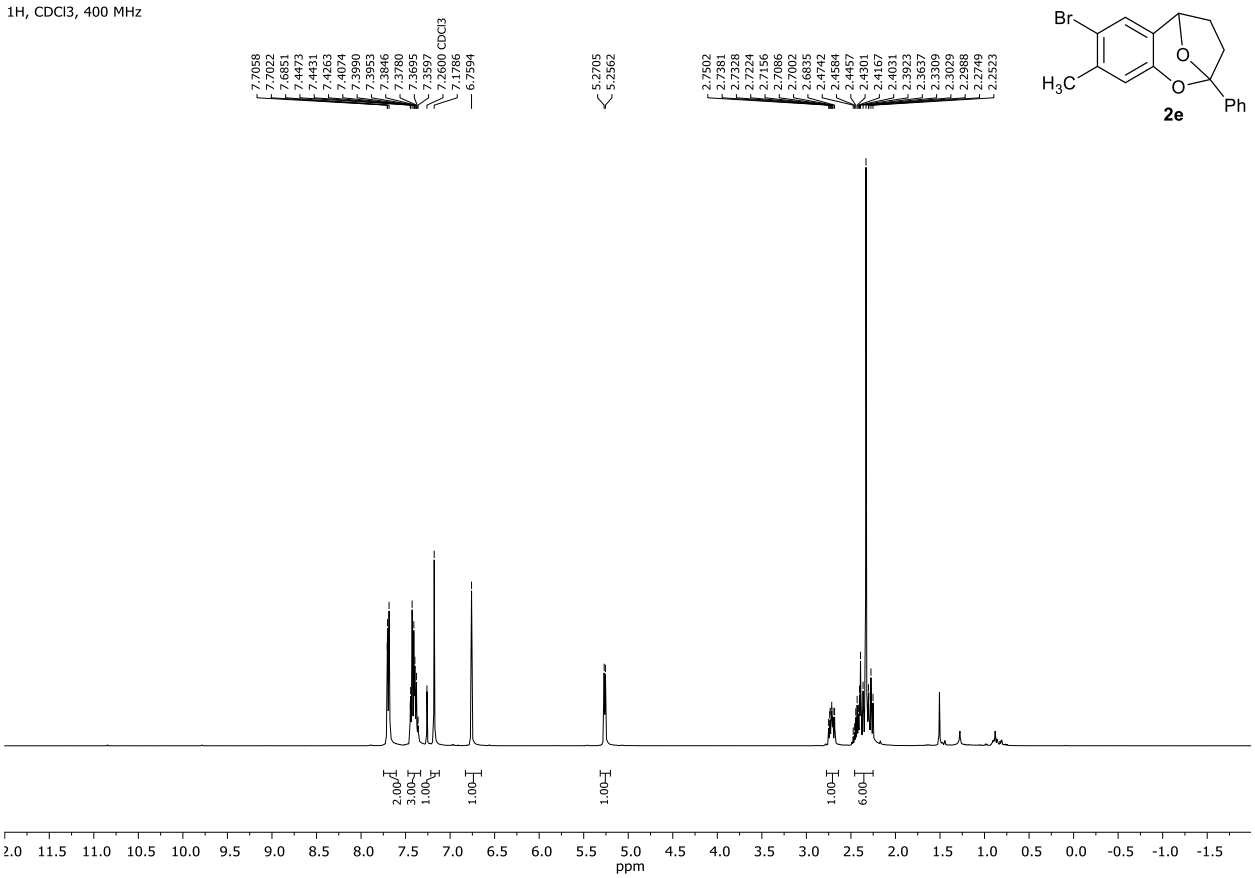
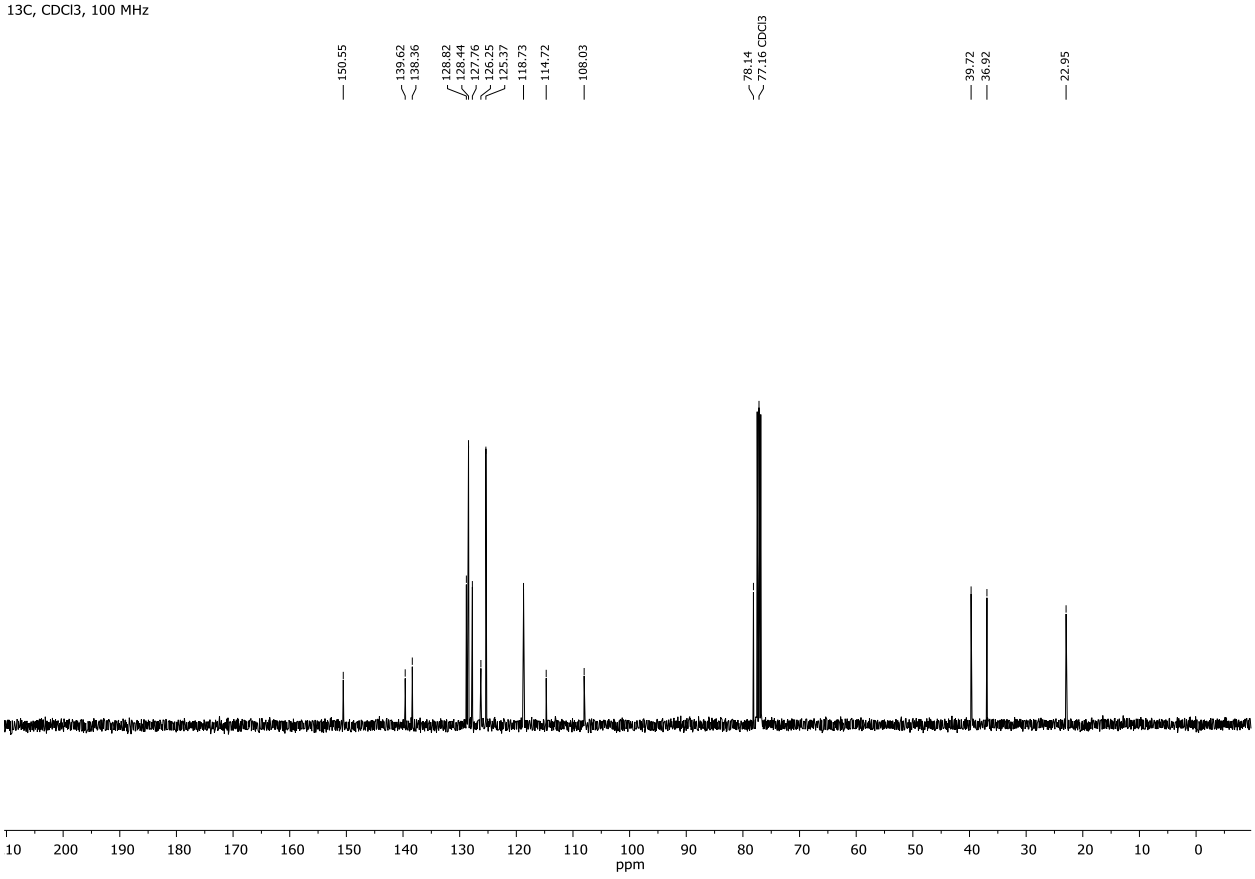


13C, CDCl3, 100 MHz



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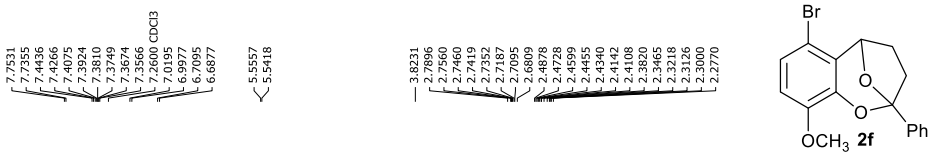

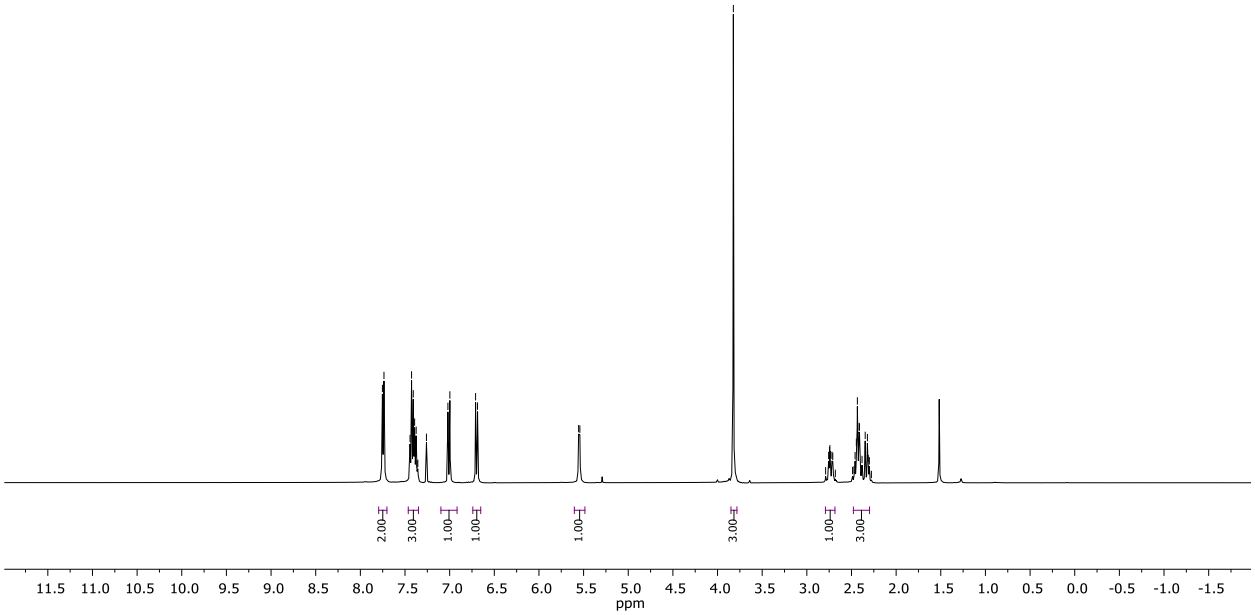

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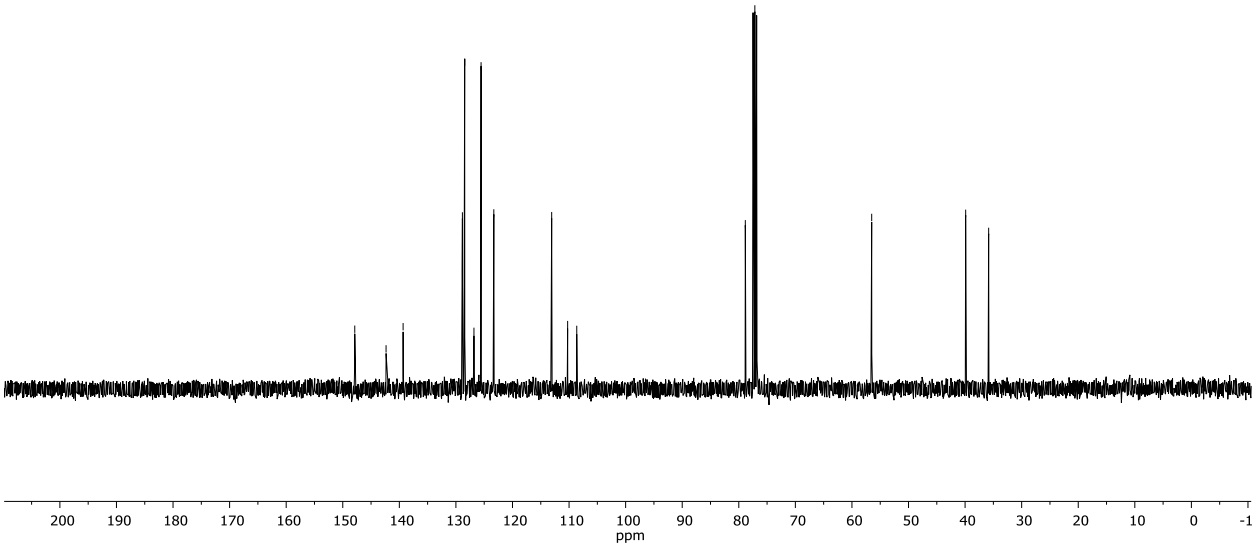

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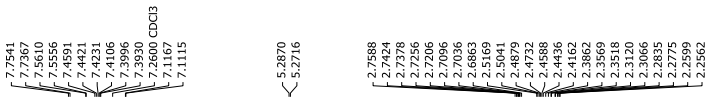
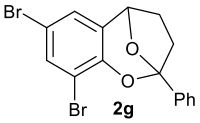
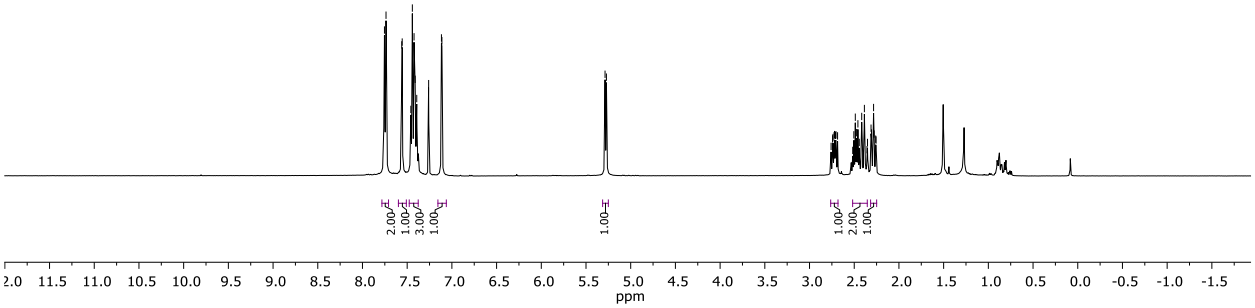
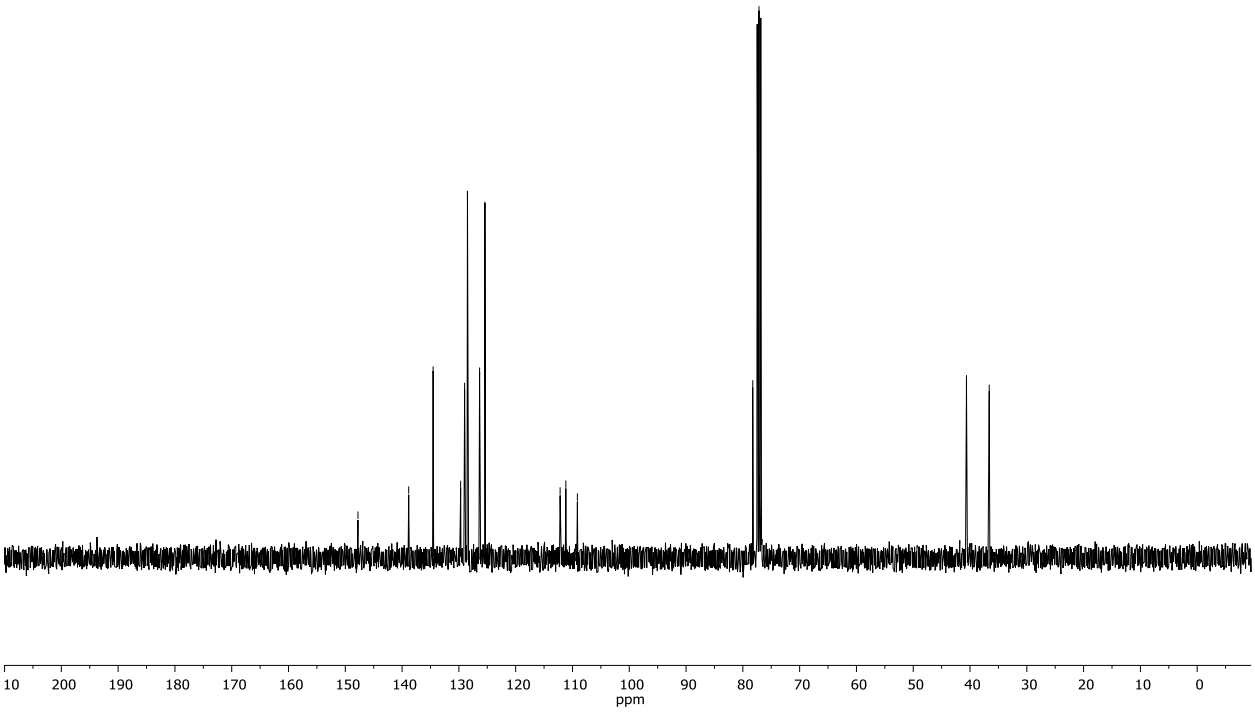


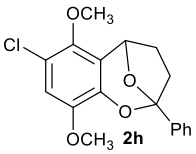




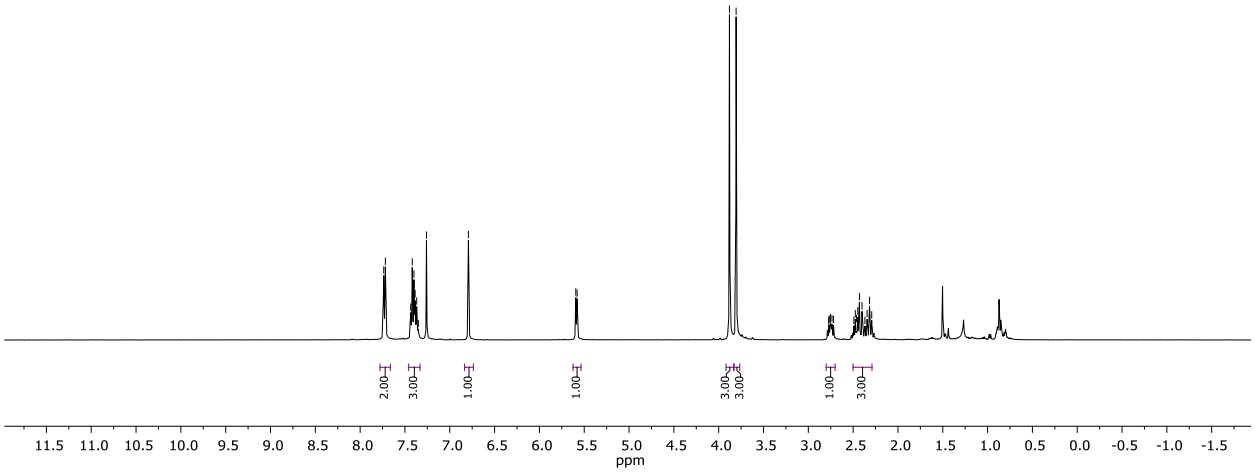
13C, CDCl3, 100 MHz



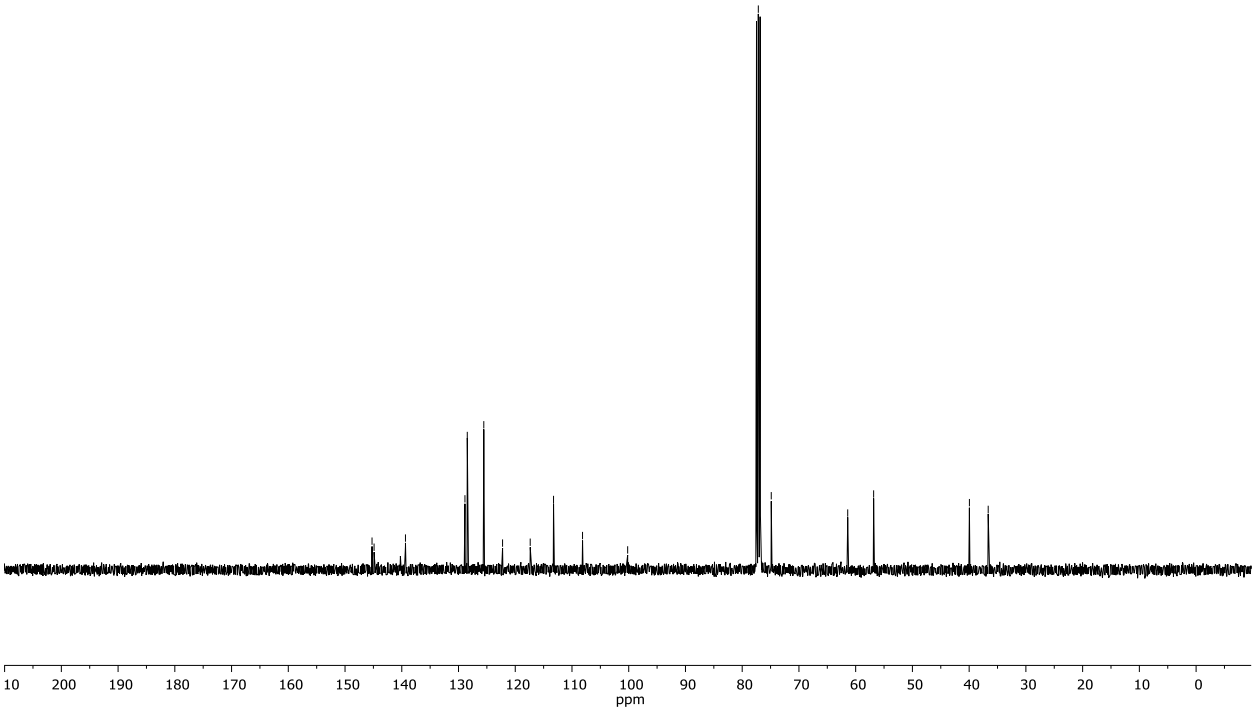
1H, CDCl3, 400 MHz



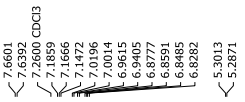
2h

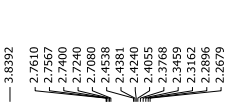


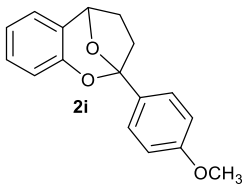
13C, CDCl3, 100 MHz

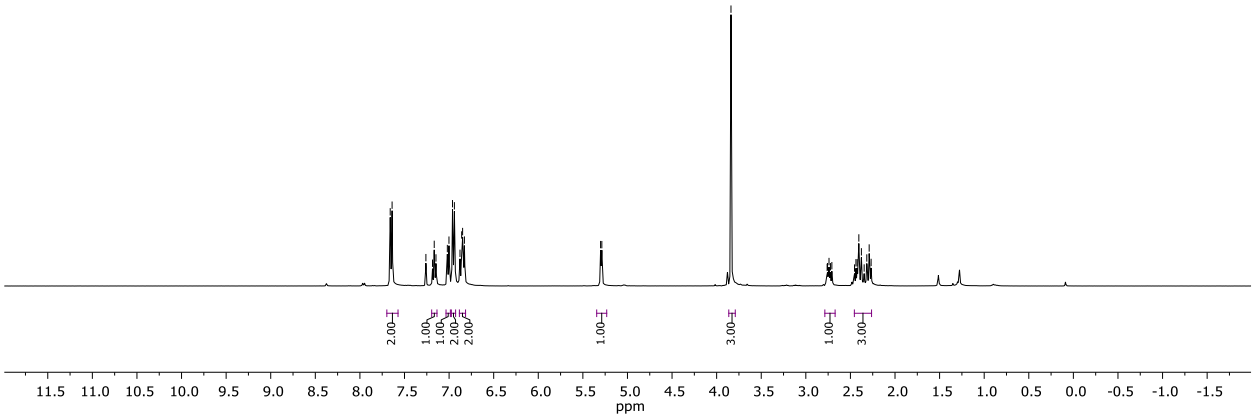


1H, CDCl3, 400 MHz

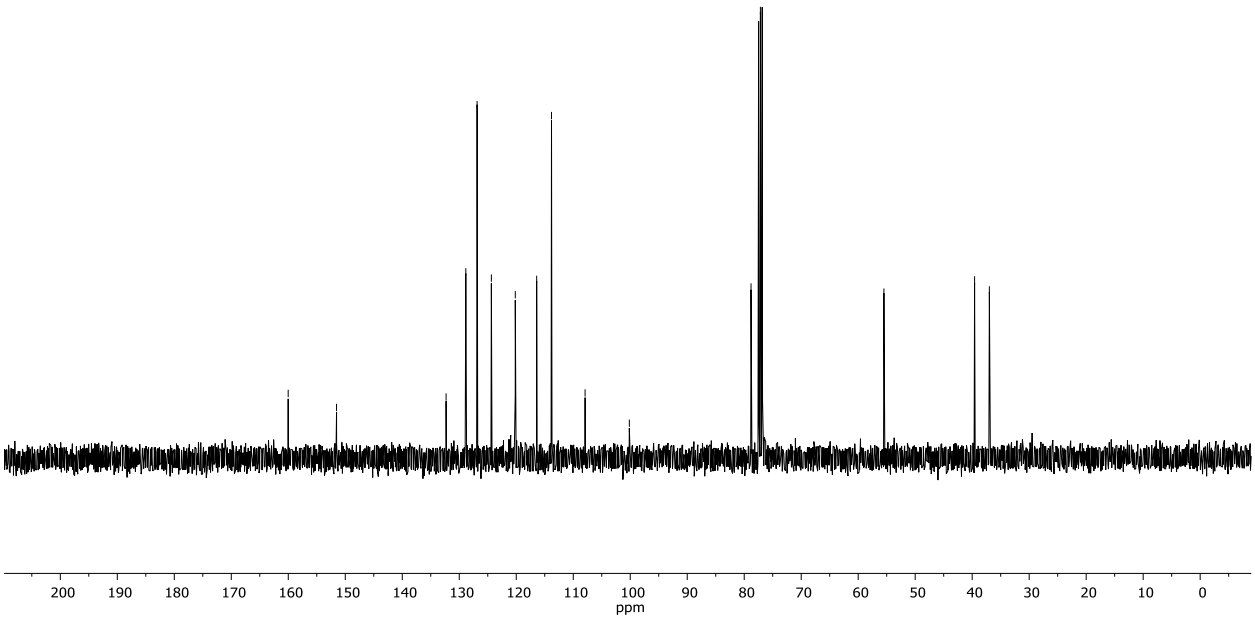








13C, CDCl3, 100 MHz



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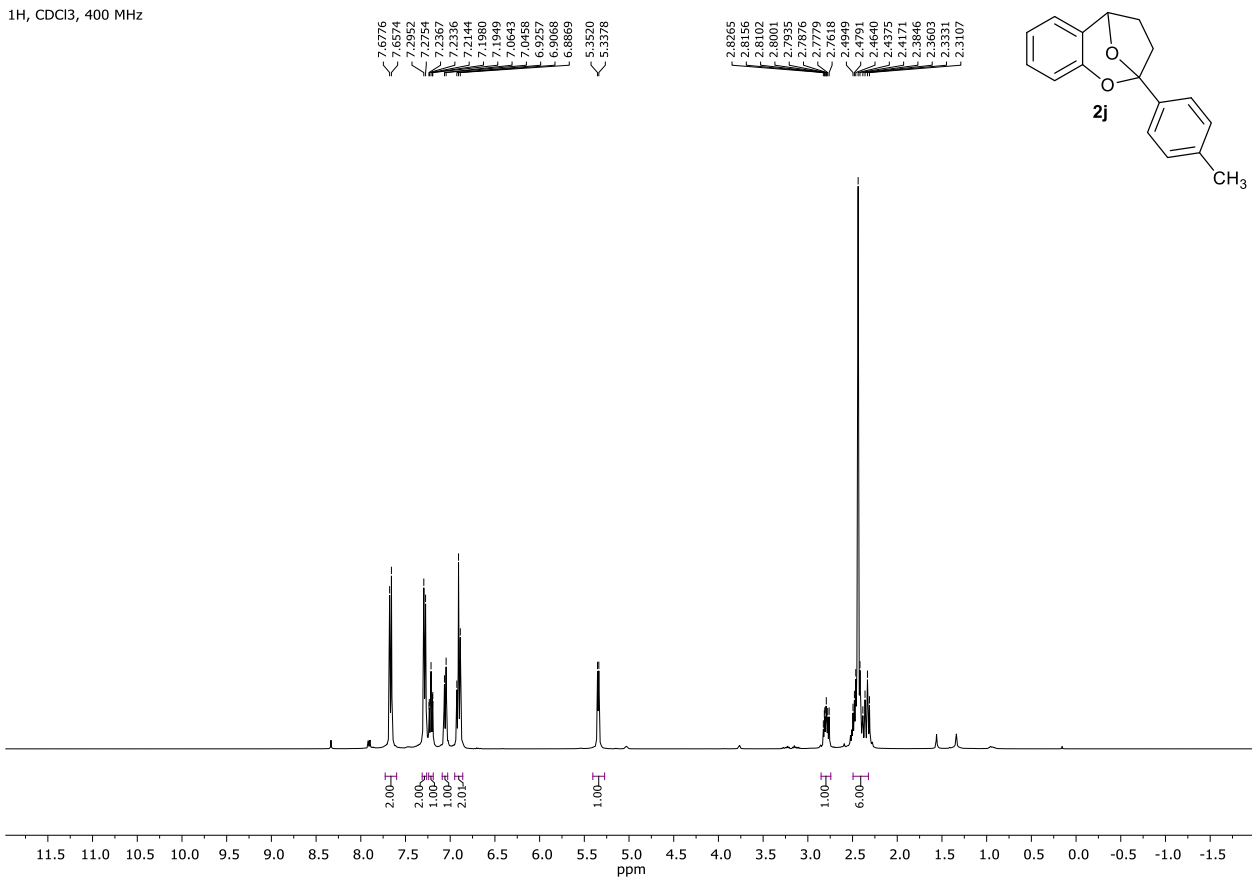
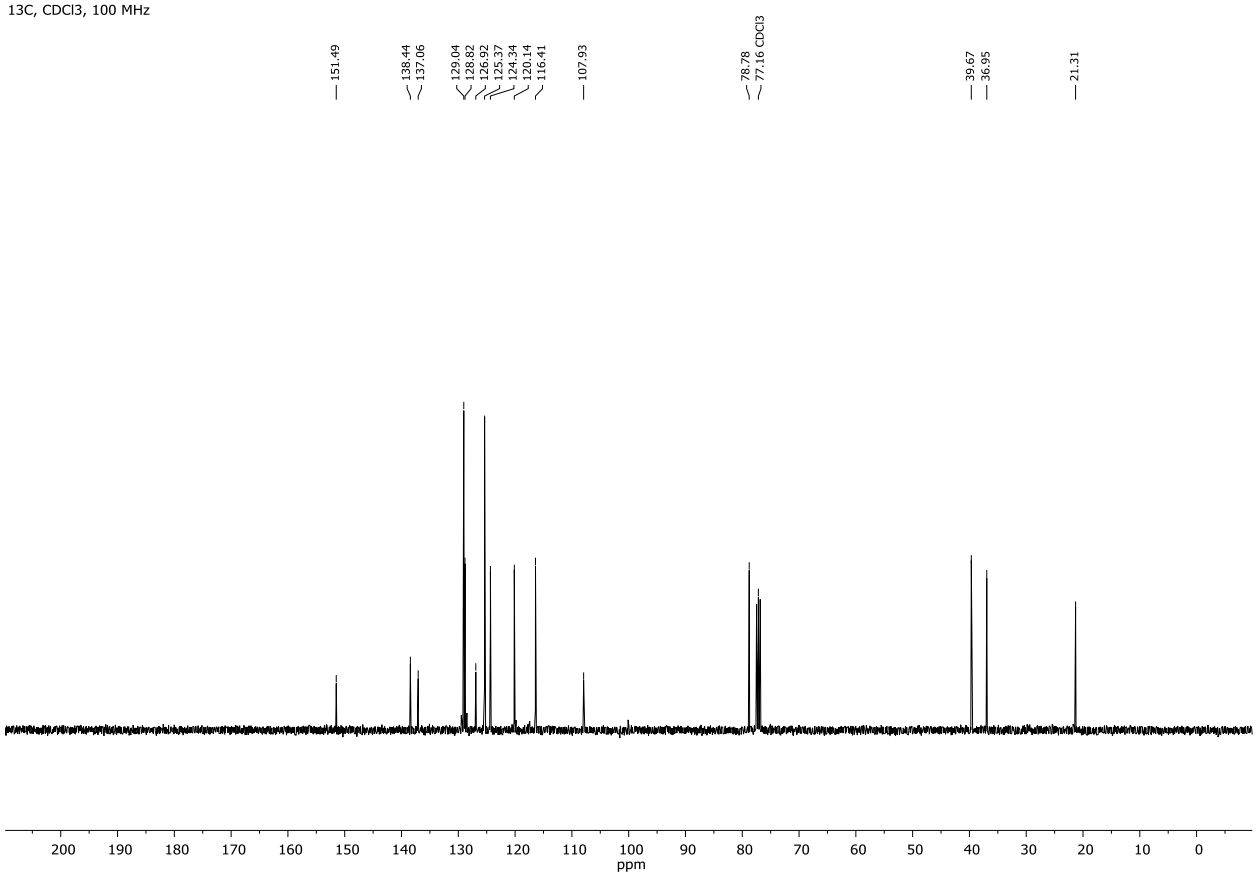


13C, CDCl3, 100 MHz



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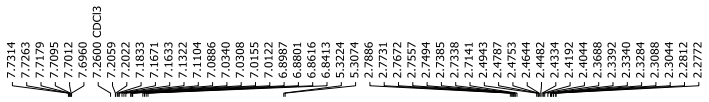

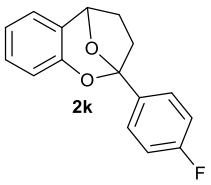

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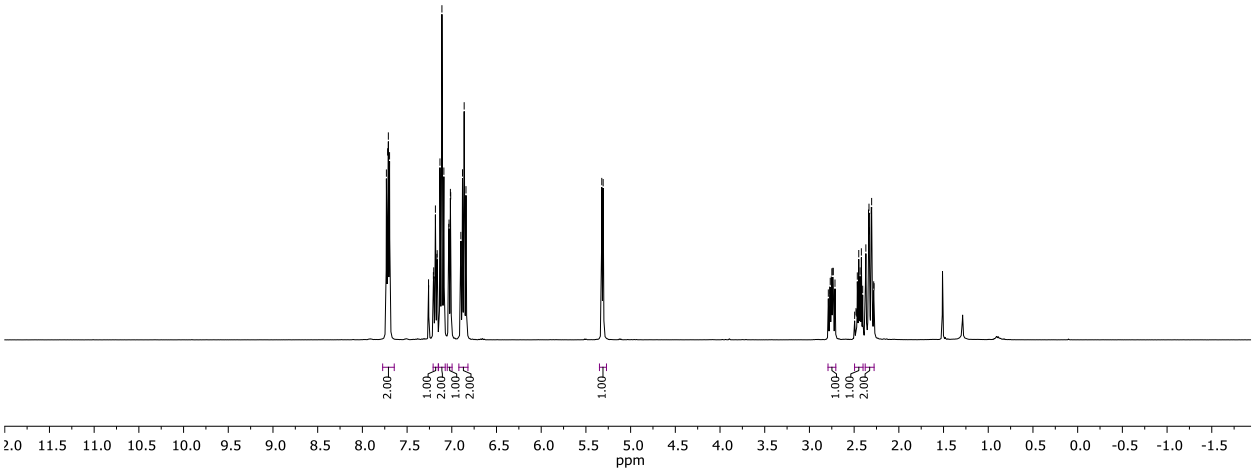
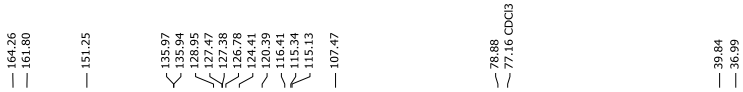
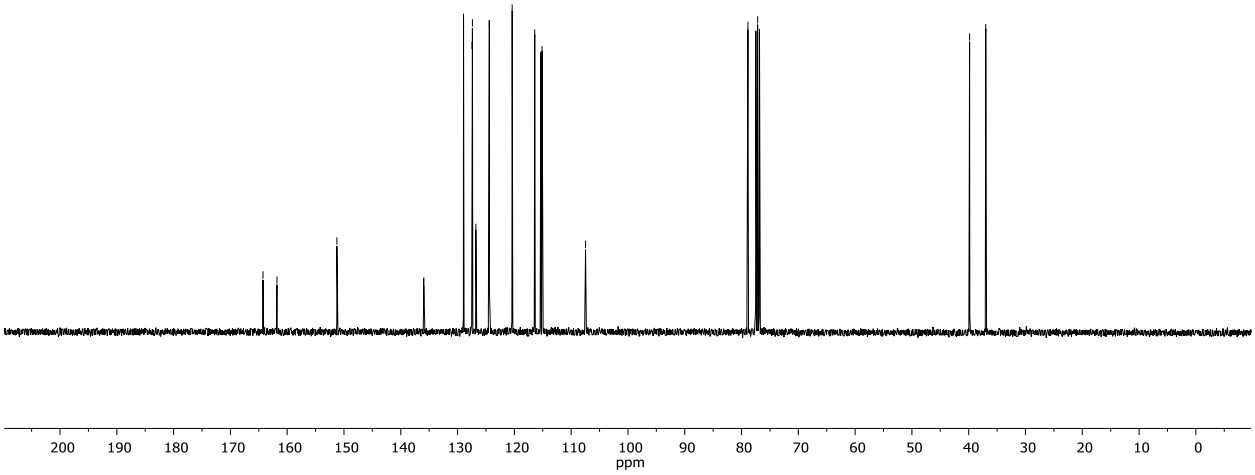


13C, CDCl3, 100 MHz





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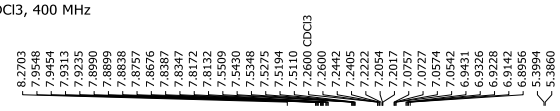
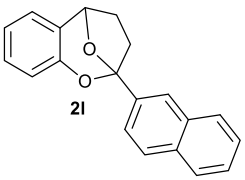
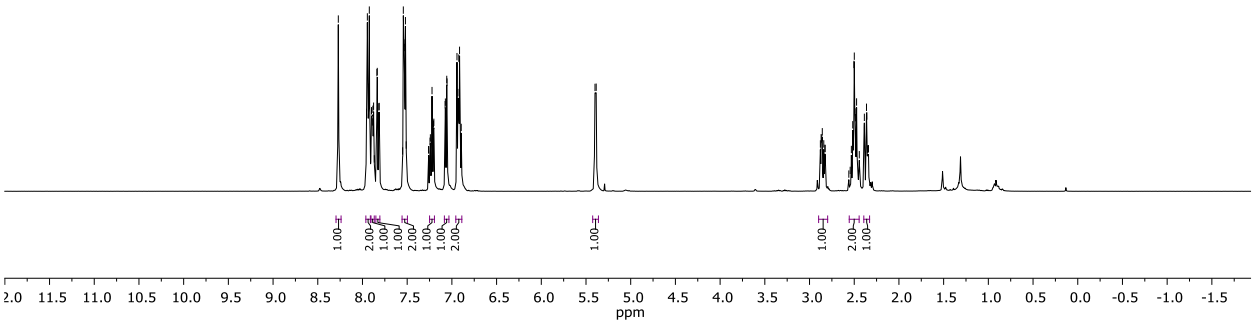
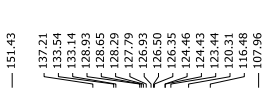
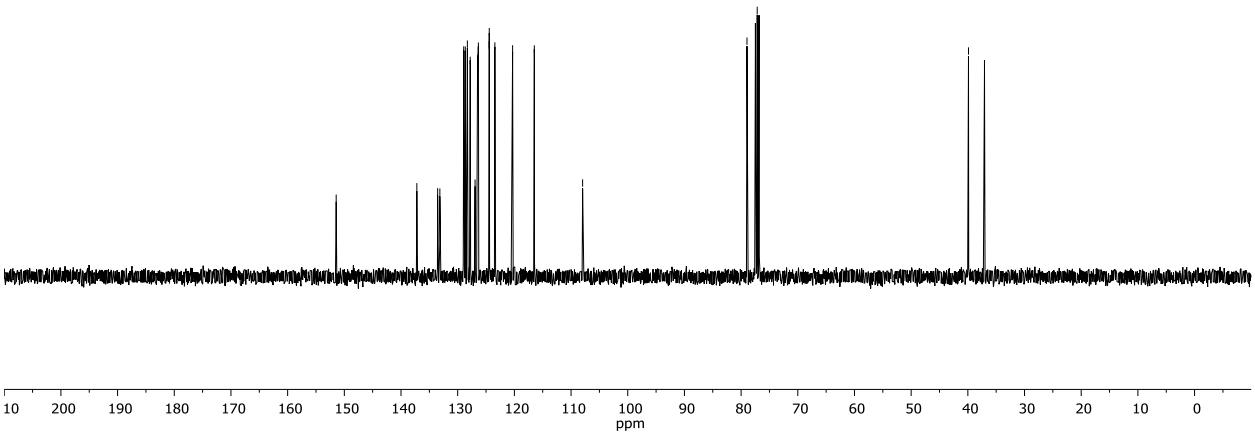




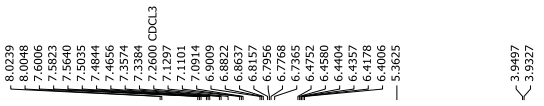


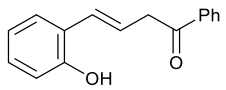
13C, CDCl3, 100 MHz



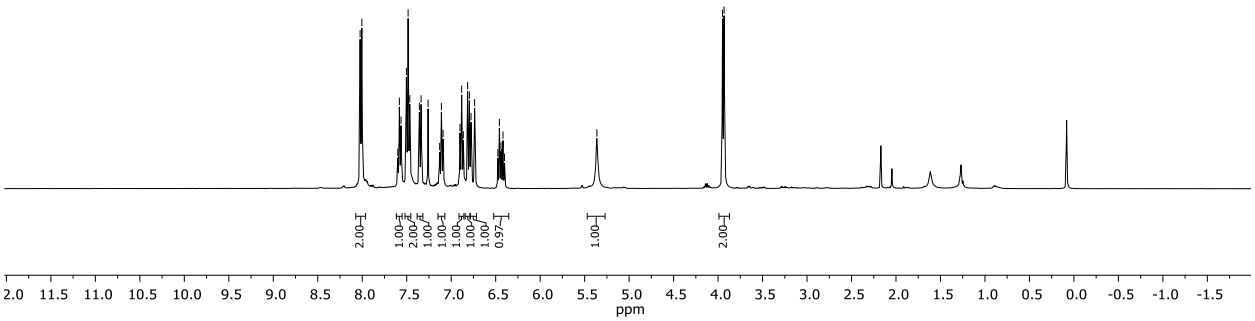


1H, CDCl3, 400 MHz

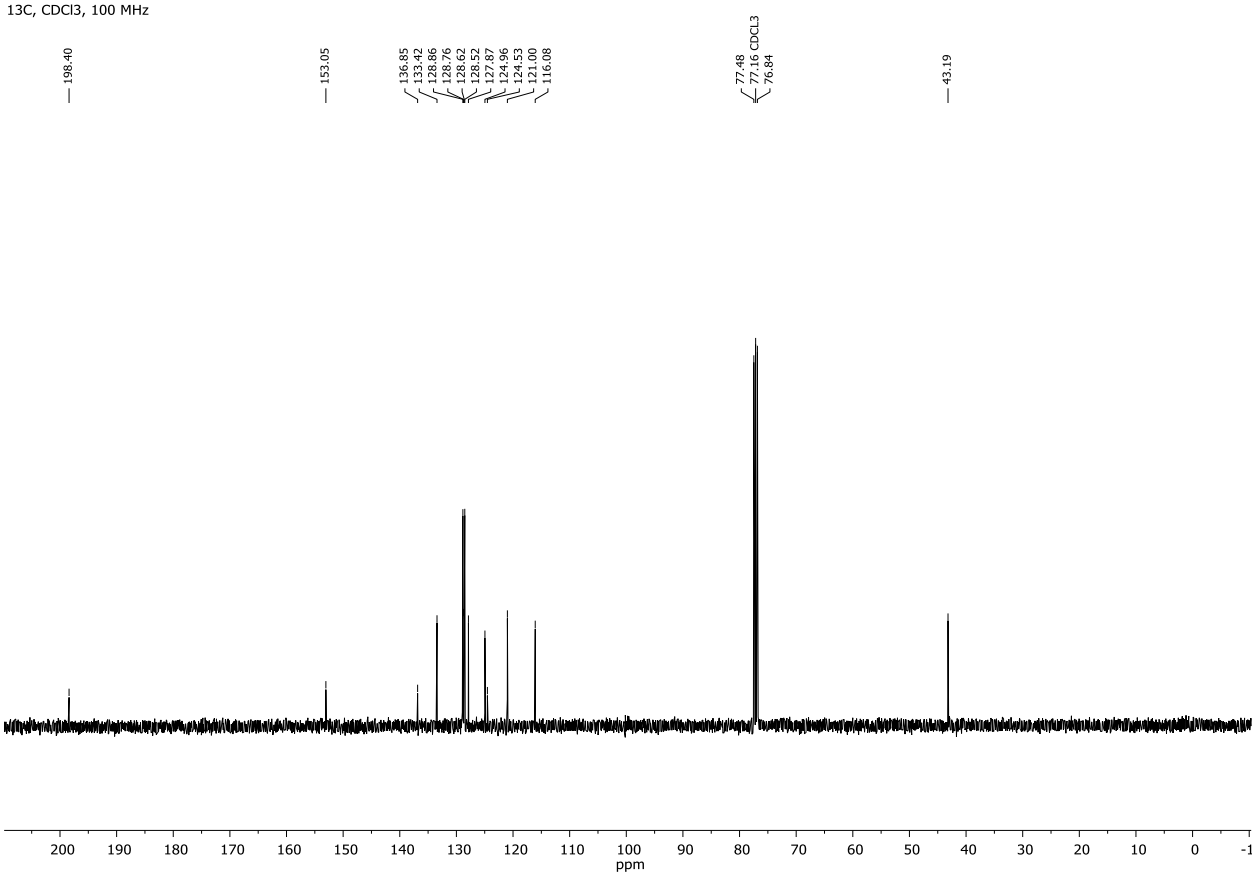




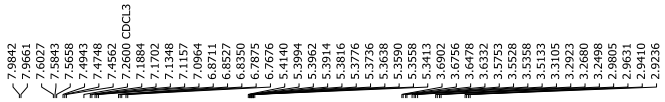
9a

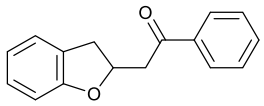


13C, CDCl3, 100 MHz

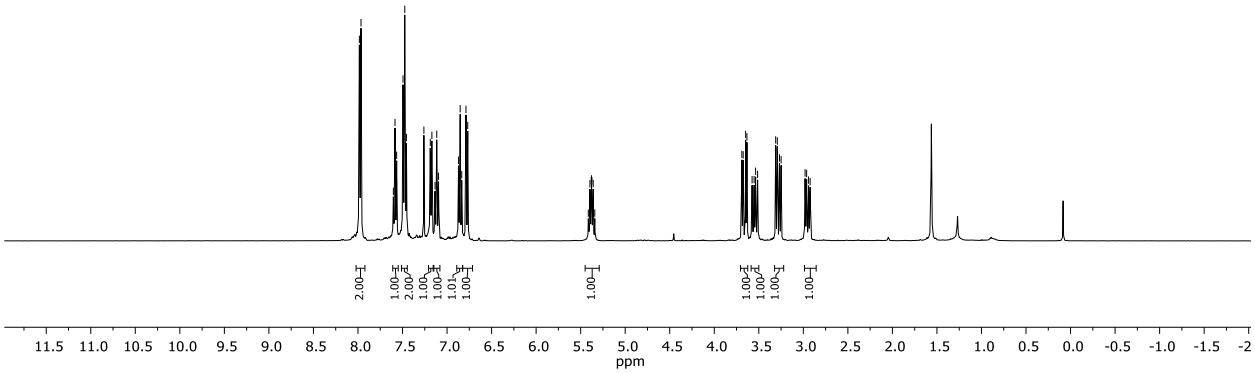


1H, CDCl3, 400 MHz

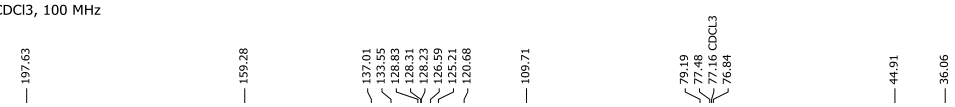


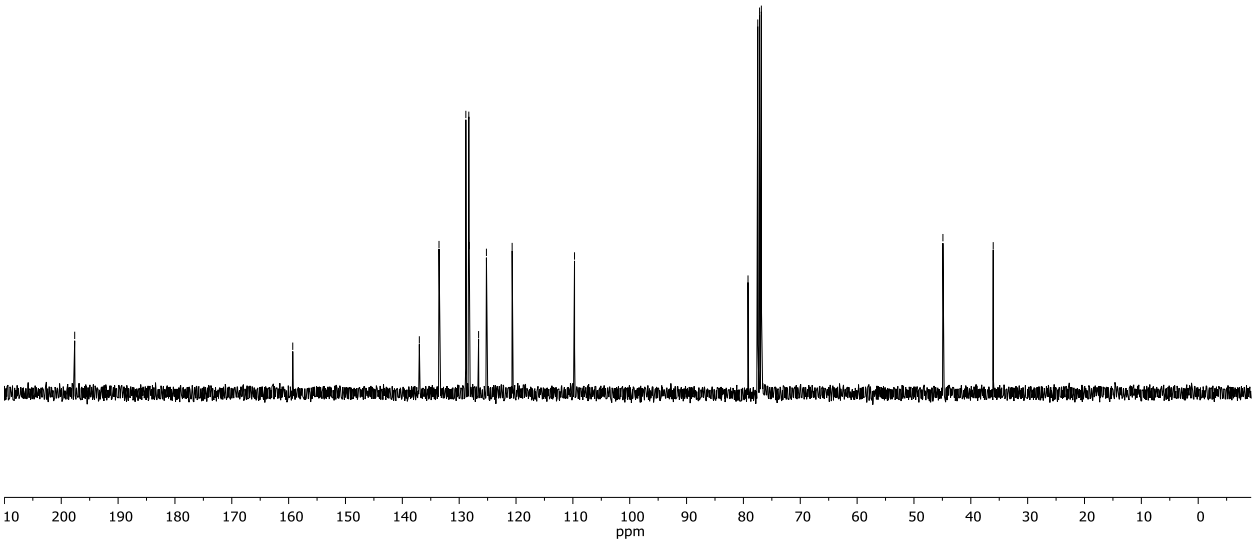


3a



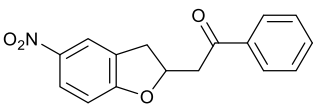
13C, CDCl3, 100 MHz



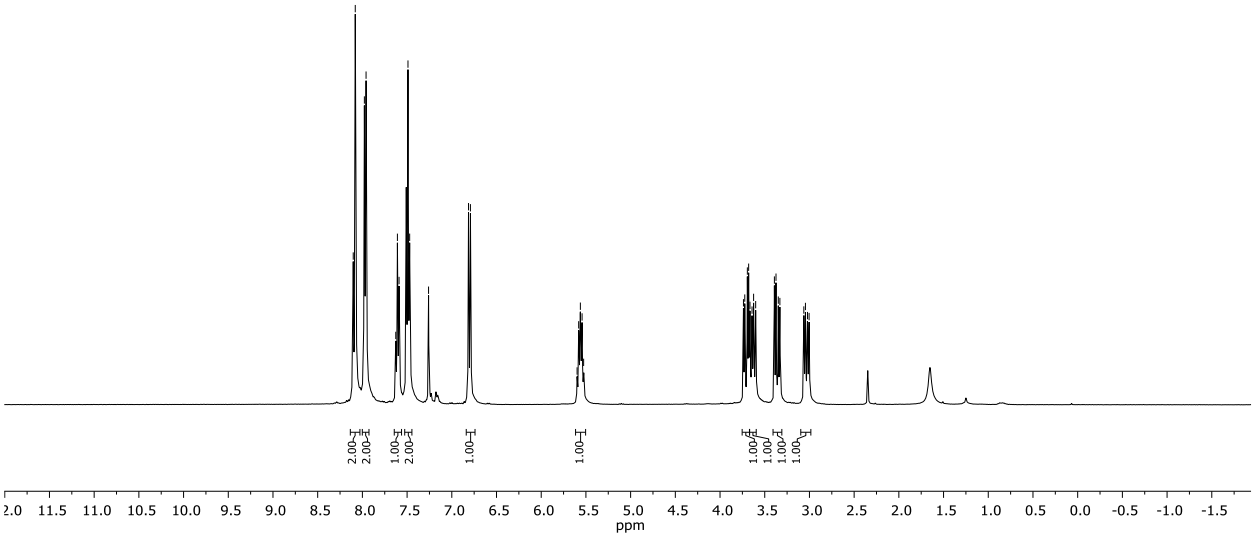


1H, CDCl3, 400 MHz

8.1024
8.0798
7.9777
7.9590
7.6266
7.6083
7.5899
7.4901
7.4712
7.2600 CDCl3
6.8130
6.7917
5.5988
5.5811
5.5620
5.5430
5.5255
3.7380
3.7234
3.6945
3.6799
3.6653
3.6423
3.6244
3.6014
3.3919
3.3740
3.3484
3.3305
3.0627
3.0447
3.0220
3.0039

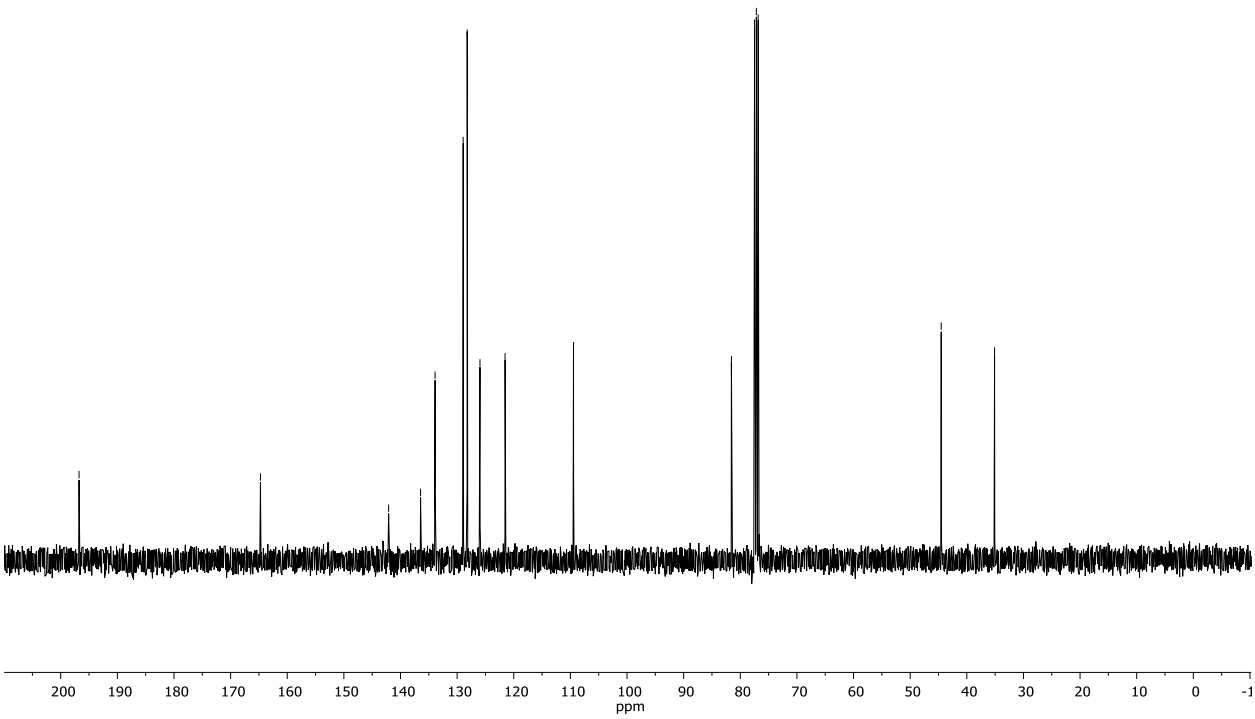


3b

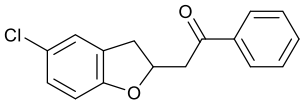


13C, CDCl3, 100 MHz

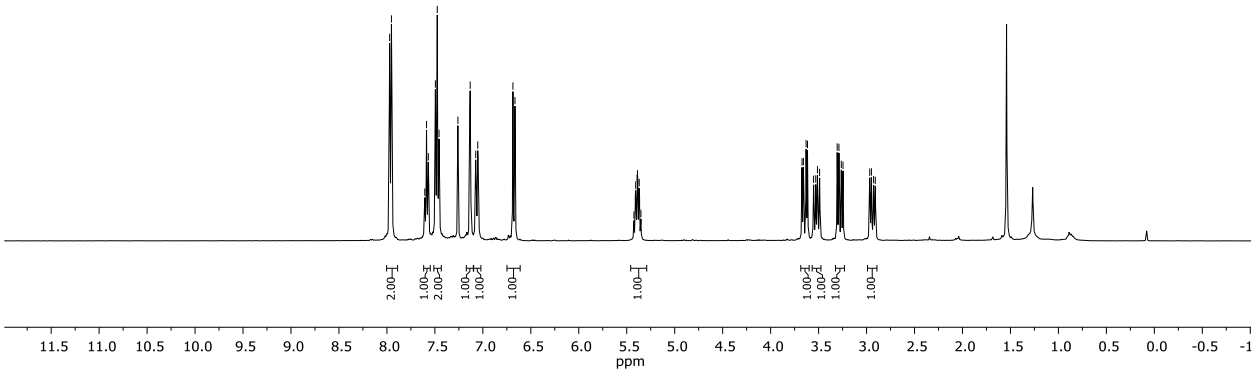
196.77
164.73
142.10
136.46
133.89
128.93
128.22
125.97
121.53
109.45
81.57
77.48
77.16 DMSO
76.84
44.52
35.10



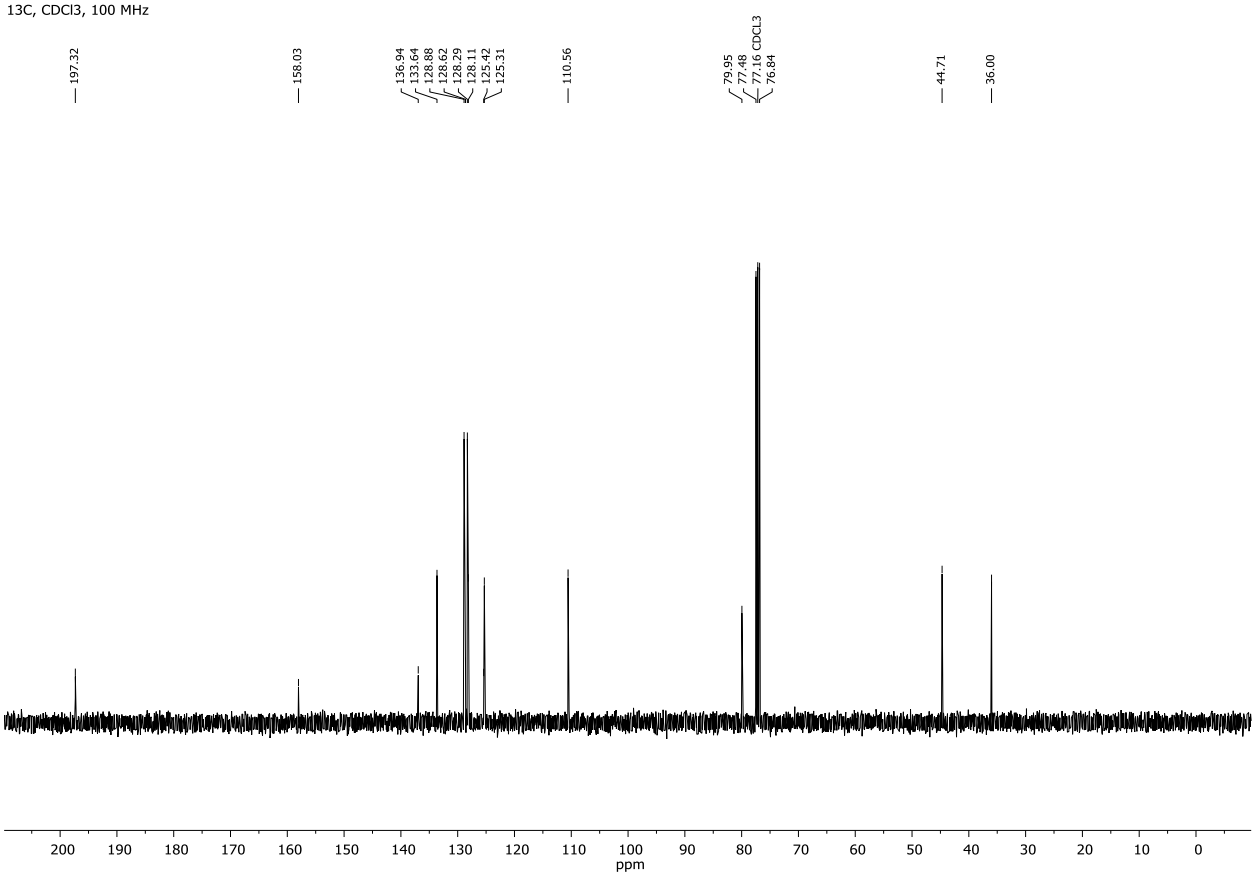
1H, CDCl3, 400 MHz



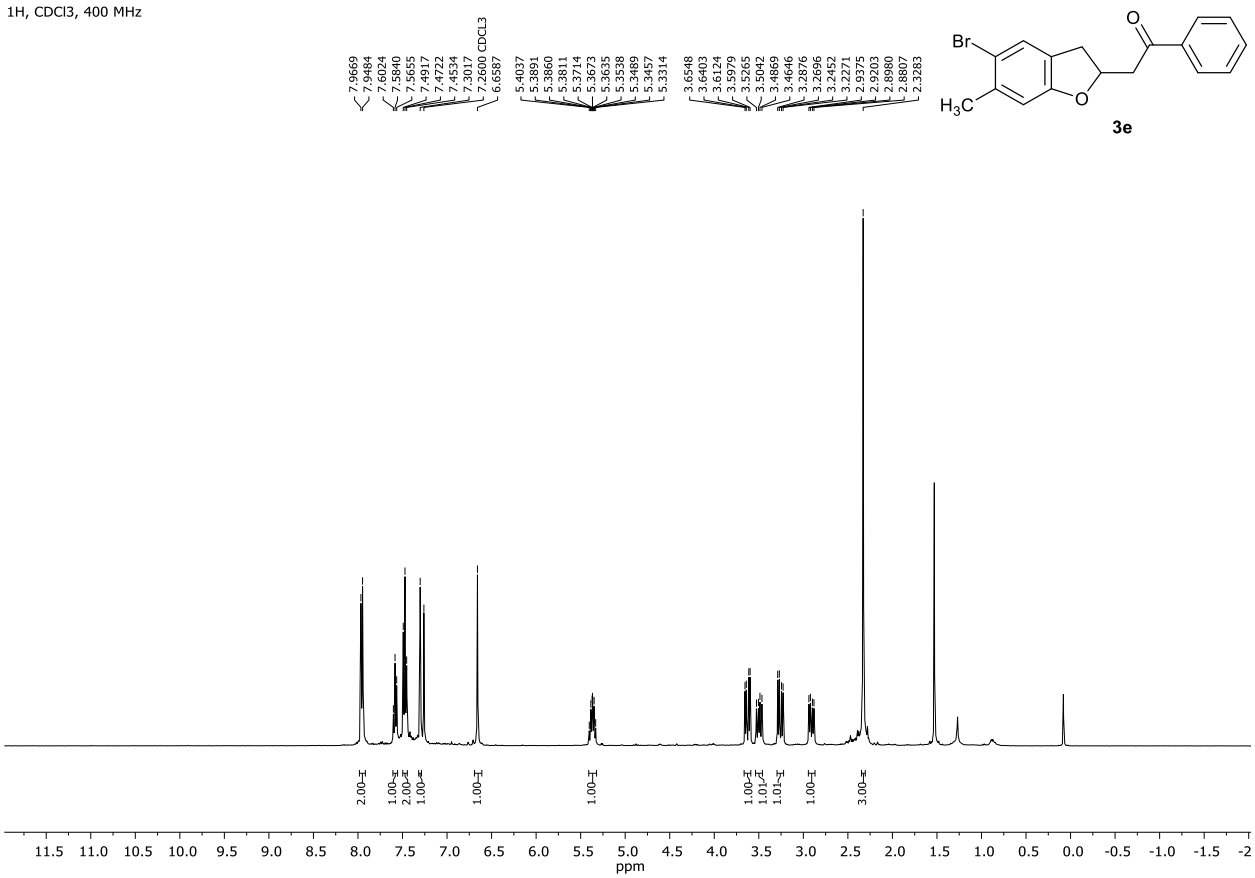
3c



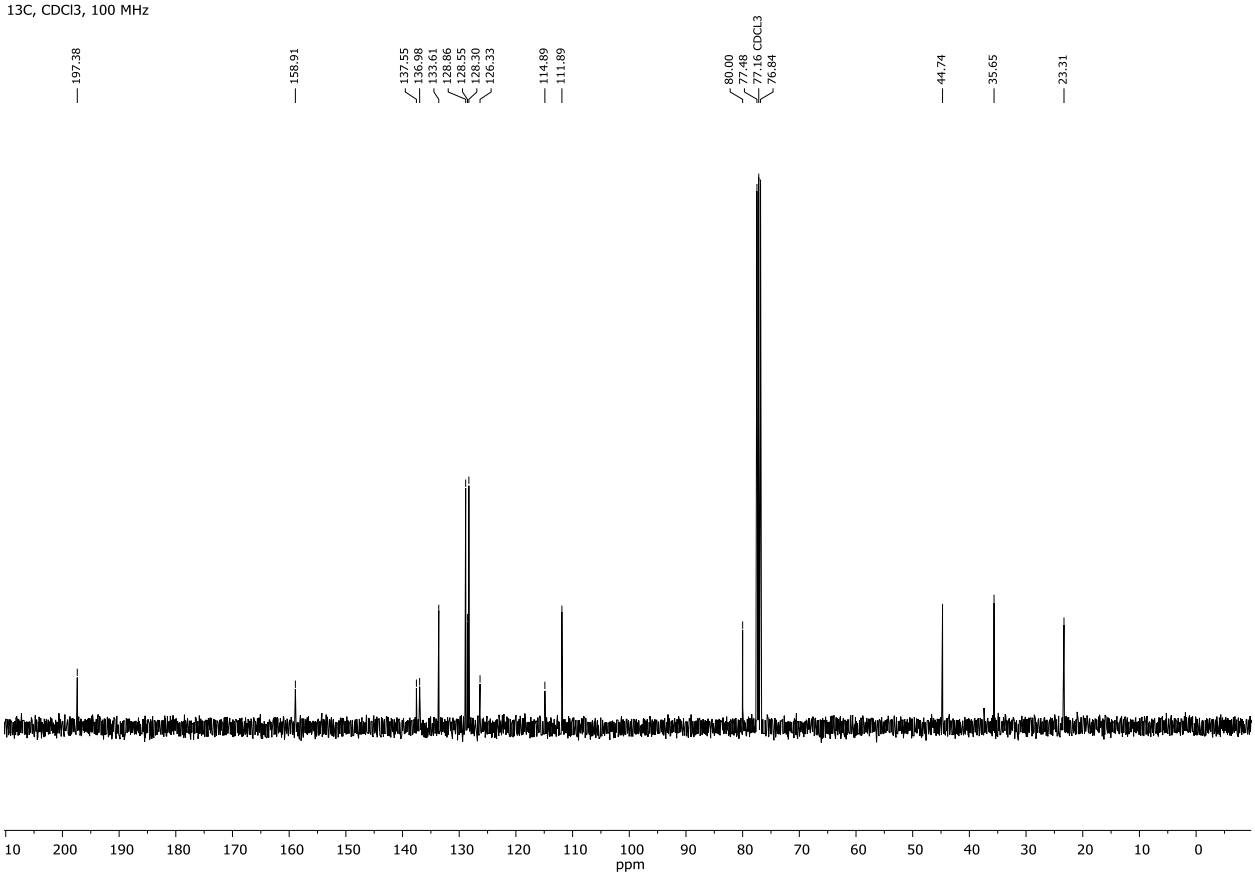
13C, CDCl3, 100 MHz



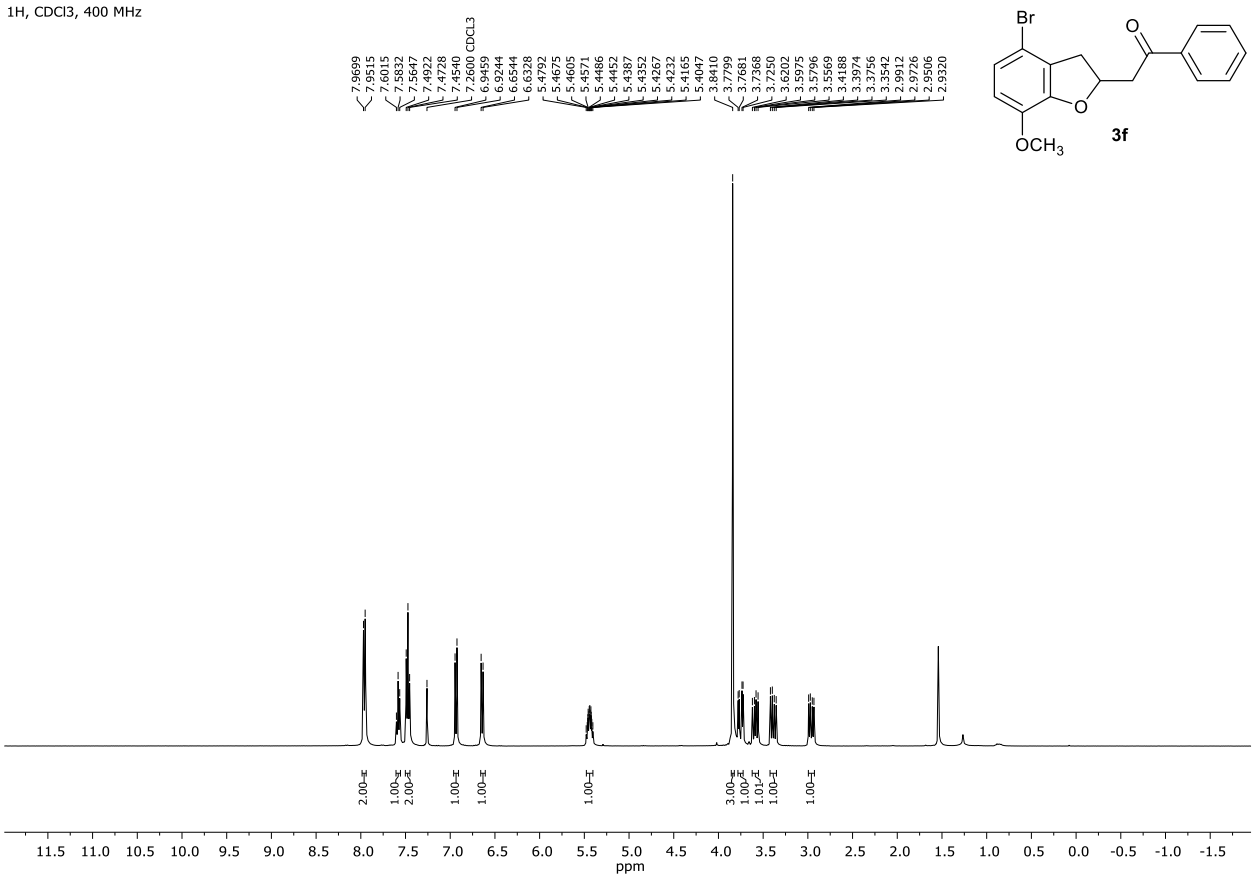
1H, CDCl3, 400 MHz



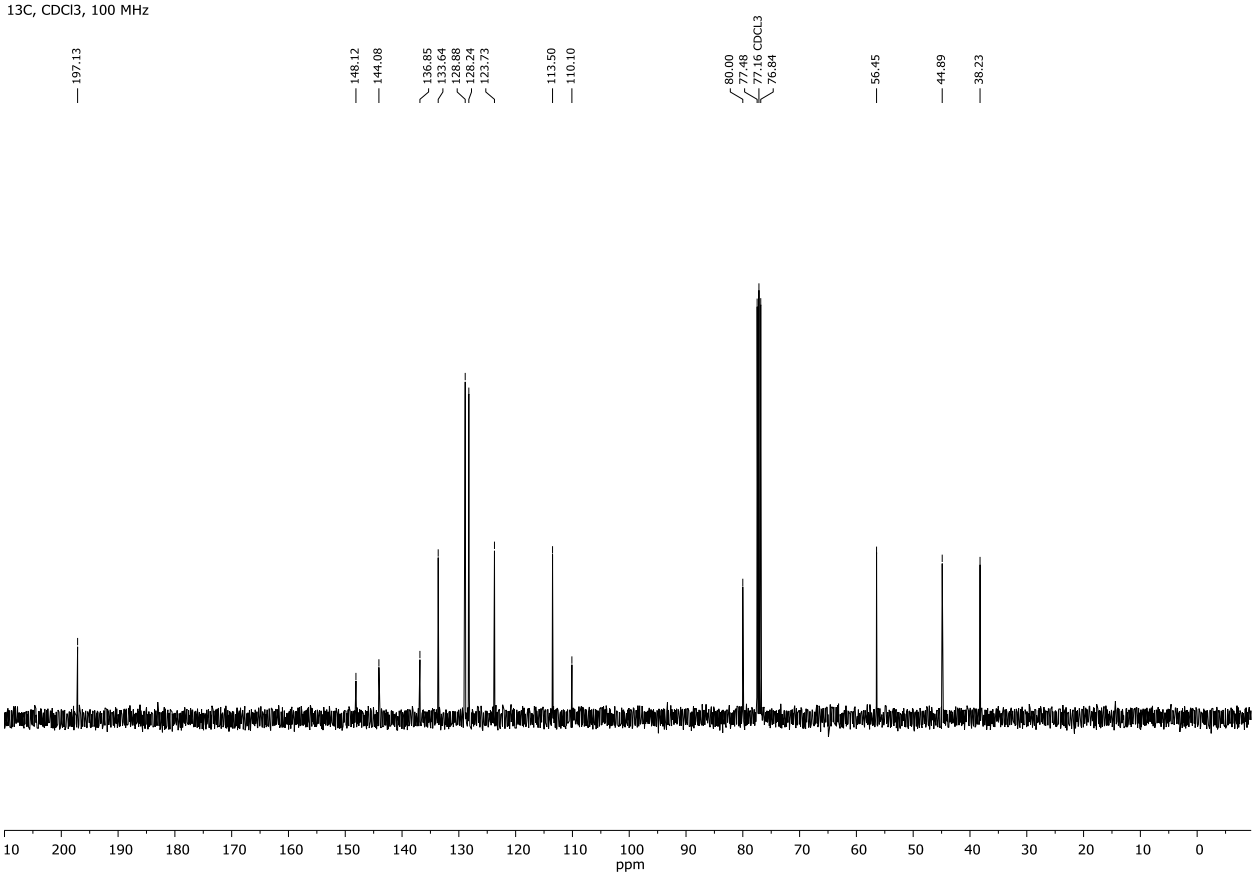
13C, CDCl3, 100 MHz



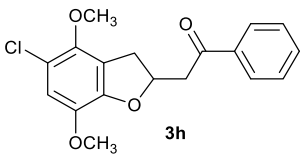
1H, CDCl3, 400 MHz



13C, CDCl3, 100 MHz

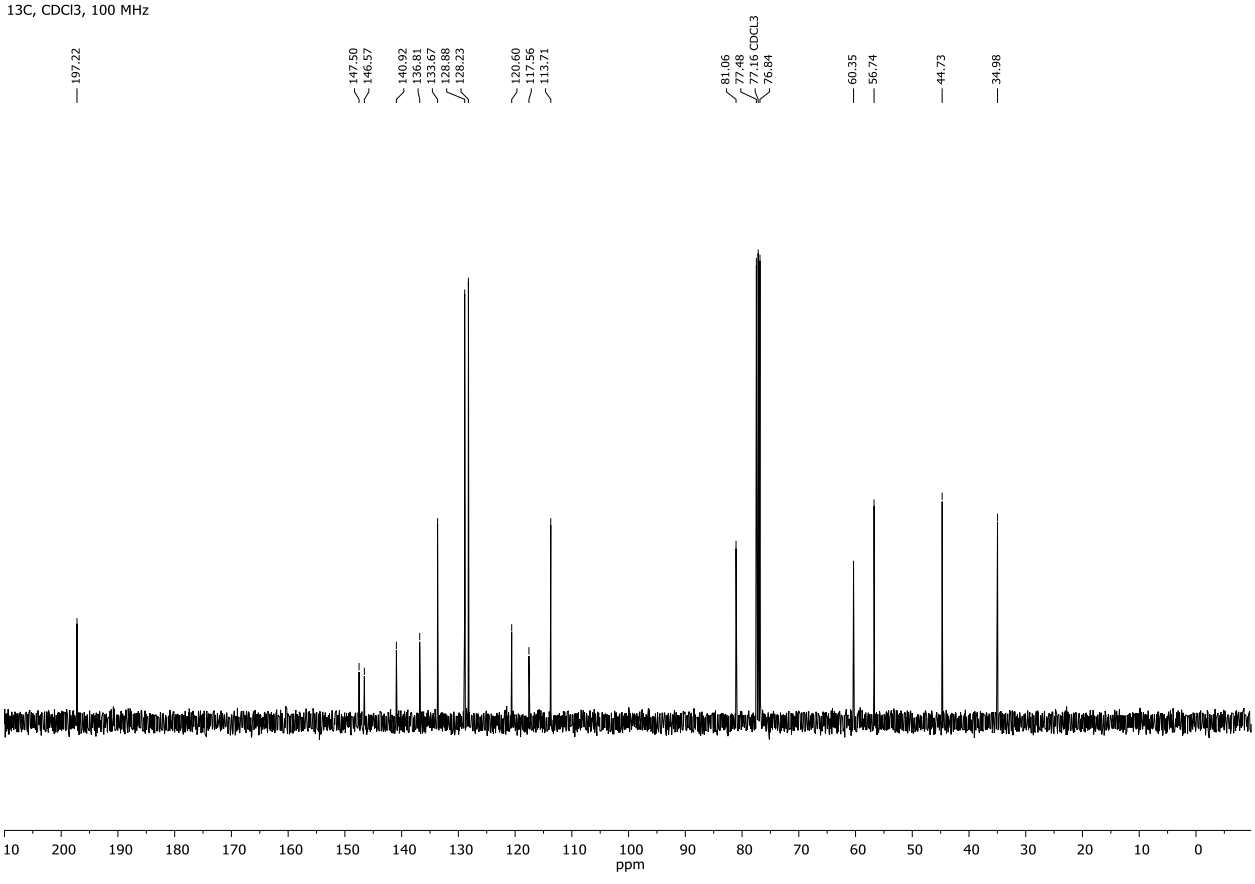


1H, CDCl3, 400 MHz

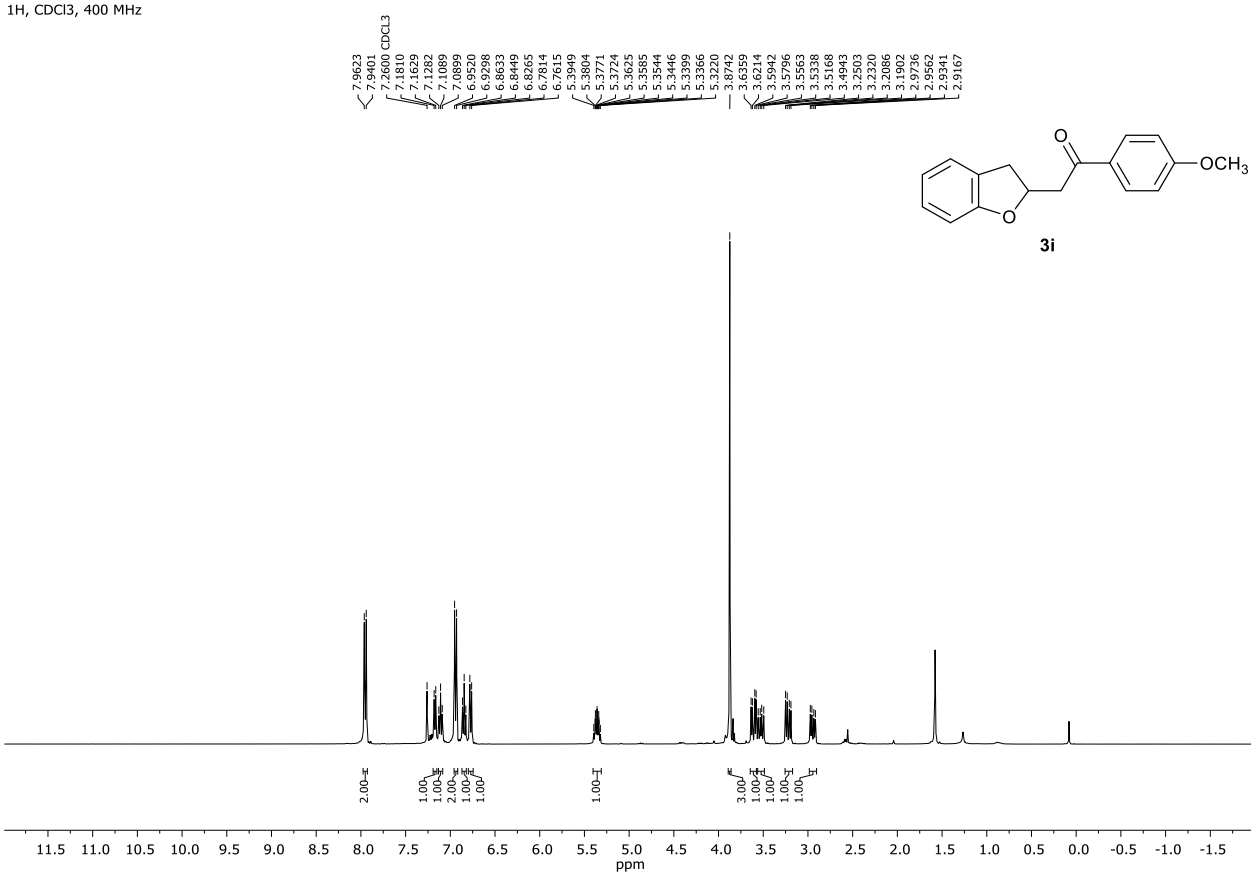


3h

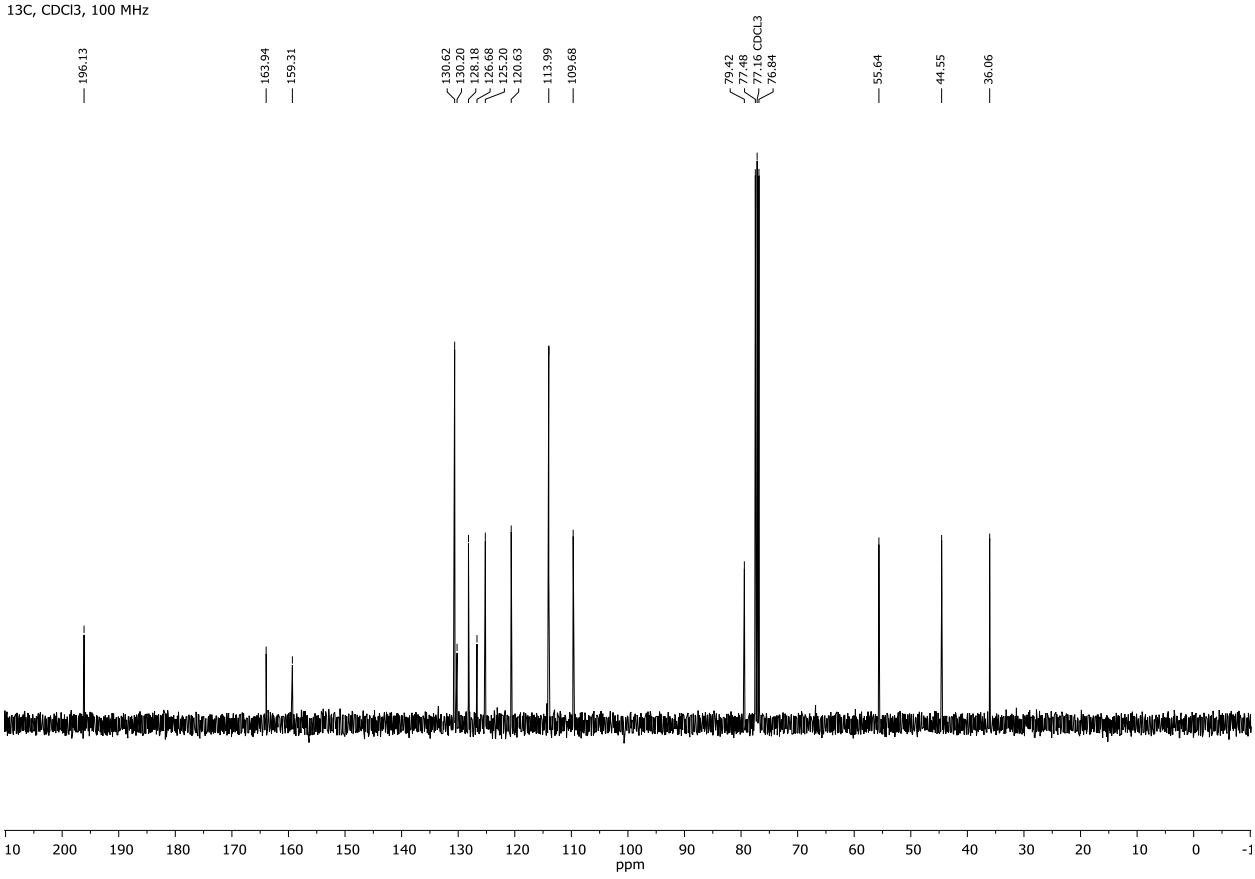
13C, CDCl3, 100 MHz



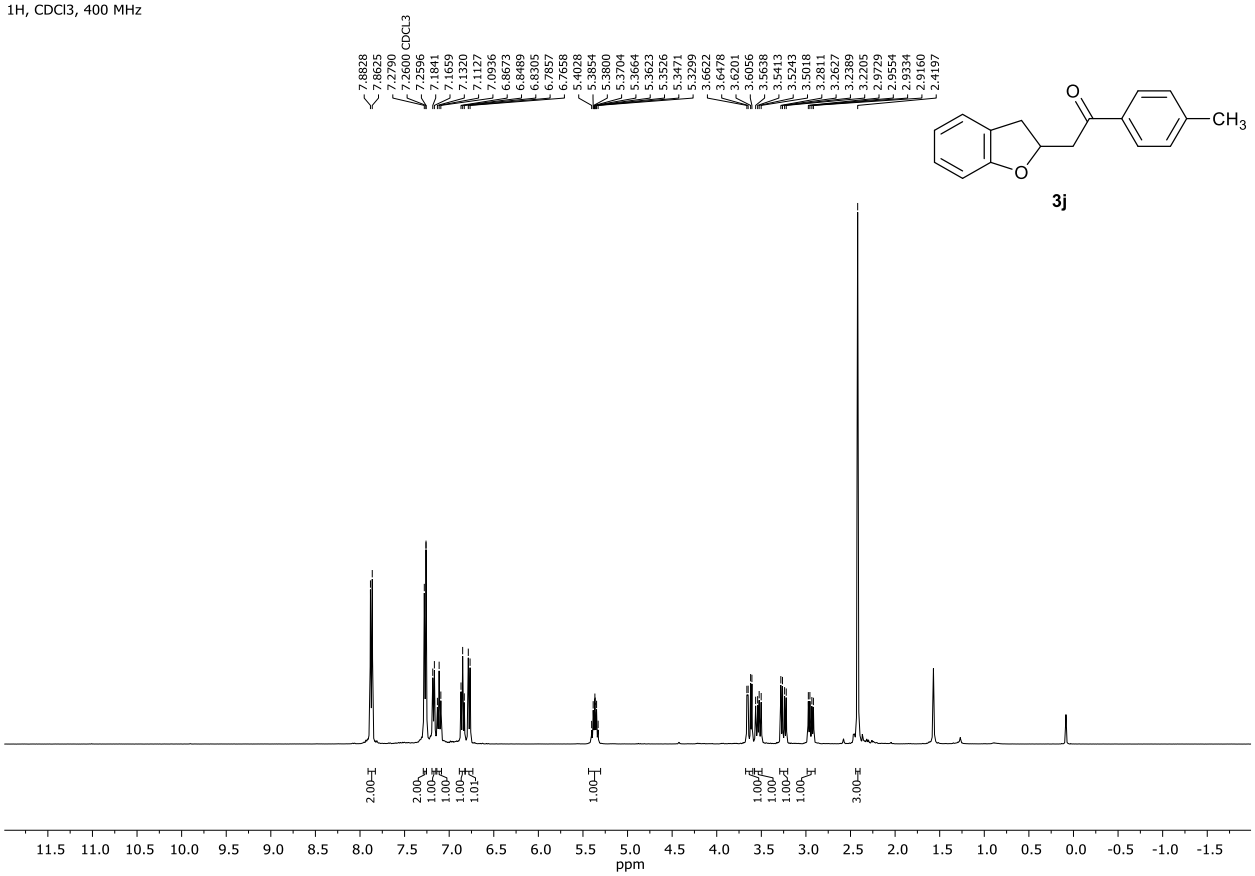
1H, CDCl3, 400 MHz



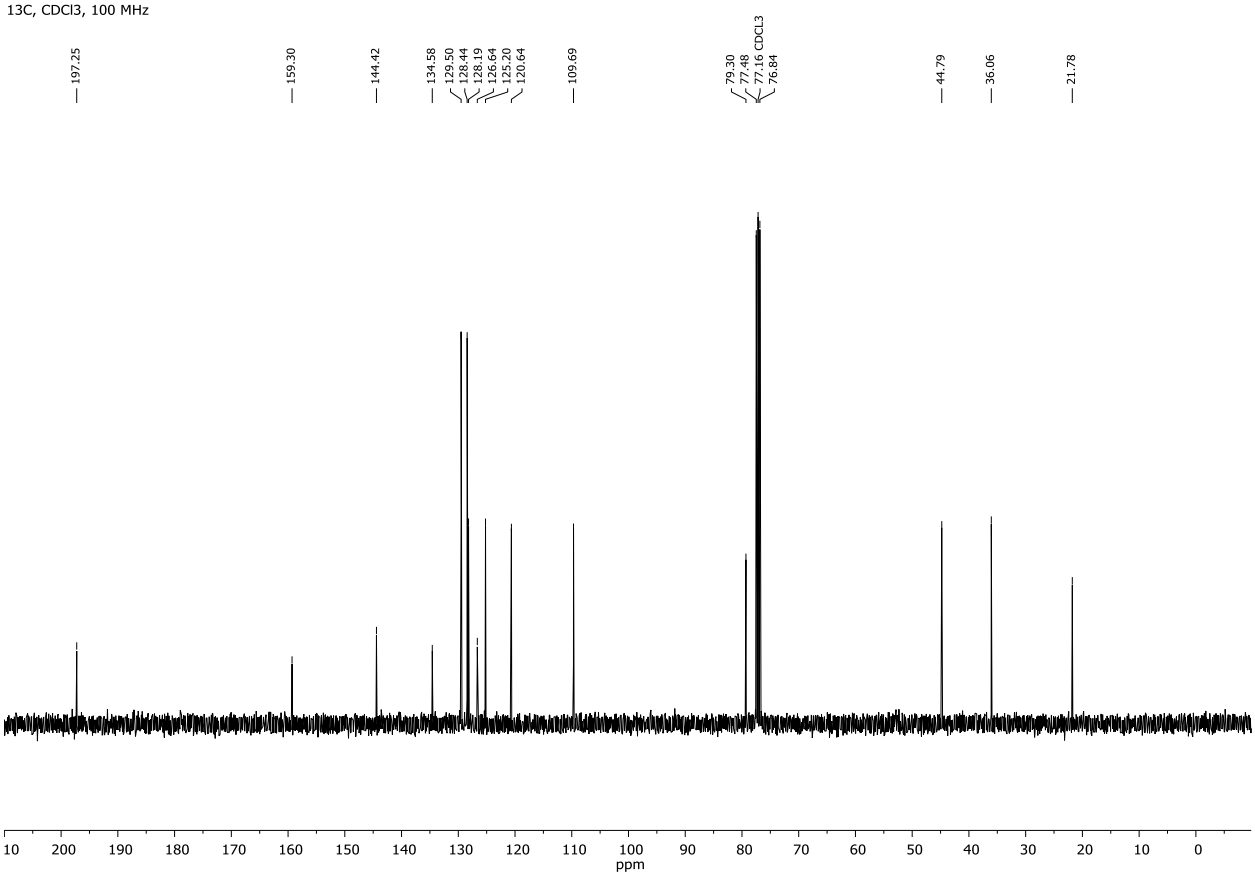
13C, CDCl3, 100 MHz



1H, CDCl3, 400 MHz

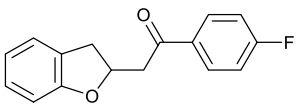


13C, CDCl3, 100 MHz

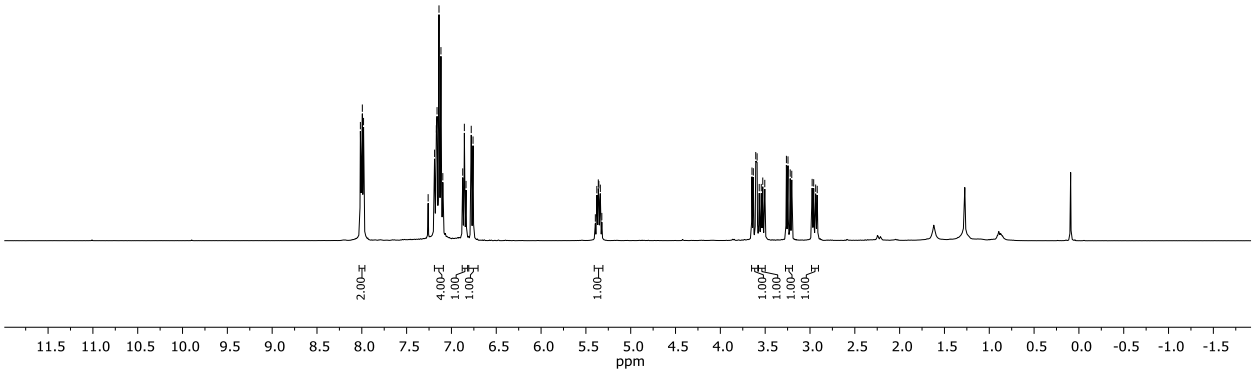


1H, CDCl3, 400 MHz

8.0159
8.0109
7.9940
7.9805
7.2600 CDCl3
7.1881
7.1687
7.1605
7.1388
7.1172
7.0963
6.8742
6.8558
6.8374
6.7791
6.7592
5.3947
5.3778
5.3719
5.3615
5.3554
5.3449
5.3391
5.3224
3.6473
3.6322
3.6052
3.5901
3.5664
3.5437
3.5268
3.5043
3.2630
3.2455
3.2208
3.2033
2.9760
2.9587
2.9365
2.9193

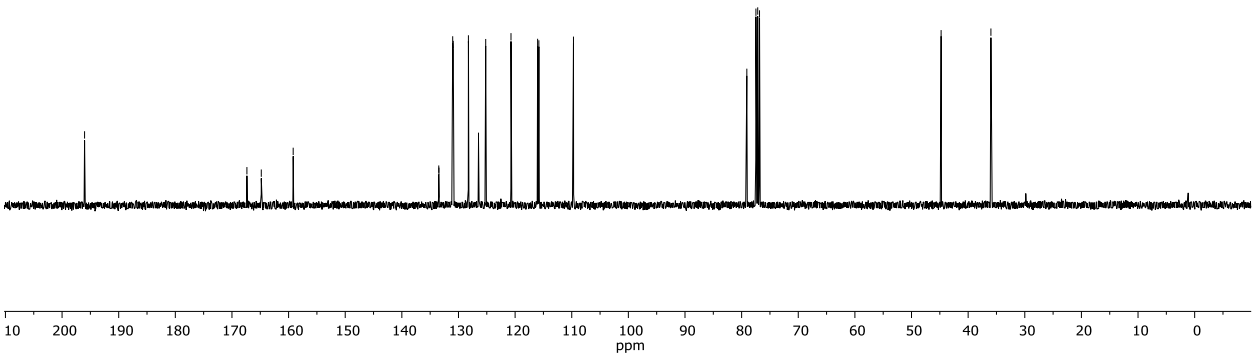


3k



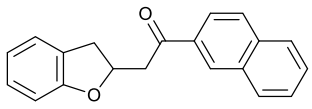
13C, CDCl3, 100 MHz

196.03
167.36
164.82
159.19
133.48
133.45
131.02
130.93
128.24
126.46
125.19
120.73
116.02
115.81
109.69
79.08
77.48
77.16 CDCl3
76.84
44.77
35.98

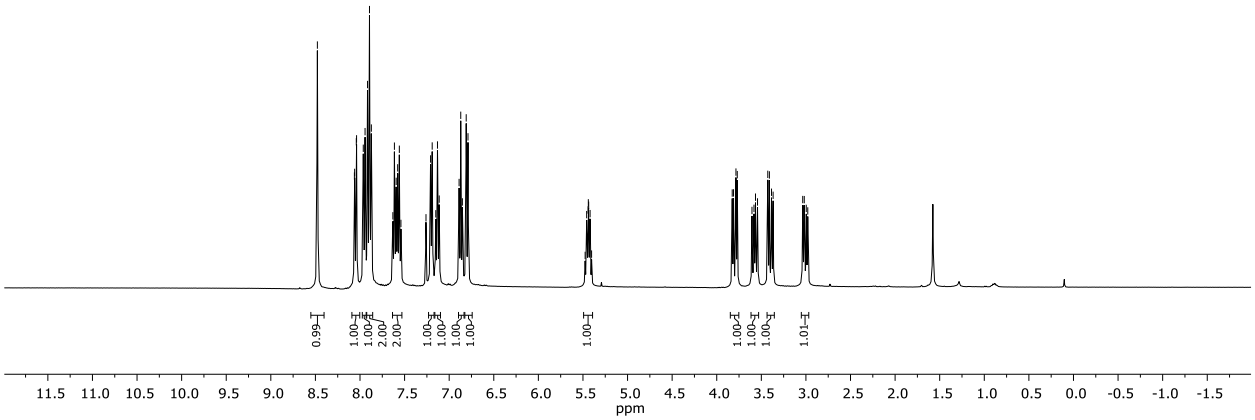


1H, CDCl3, 400 MHz

8.4778
8.0629
8.0600
8.0415
8.0385
7.9633
7.9432
7.9156
7.8937
7.8728
7.6315
7.6142
7.5945
7.5775
7.5590
7.5410
7.2600 CDCl3
7.2087
7.1906
7.1504
7.1313
7.1120
6.8889
6.8704
6.8520
6.8091
6.7891
5.4756
5.4586
5.4529
5.4434
5.4399
5.4358
5.4260
5.4200
5.4032
3.8265
3.8117
3.7846
3.7698
3.6049
3.5823
3.5654
3.5428
3.4277
3.4096
3.3858
3.3678
3.0358
3.0186
2.9963
2.9791

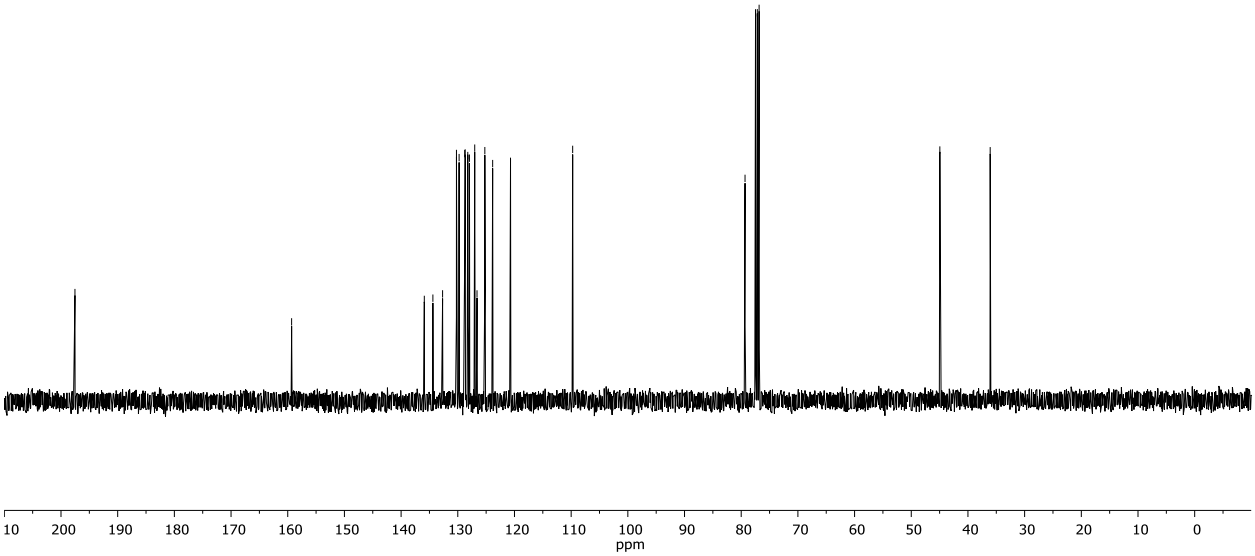


3l

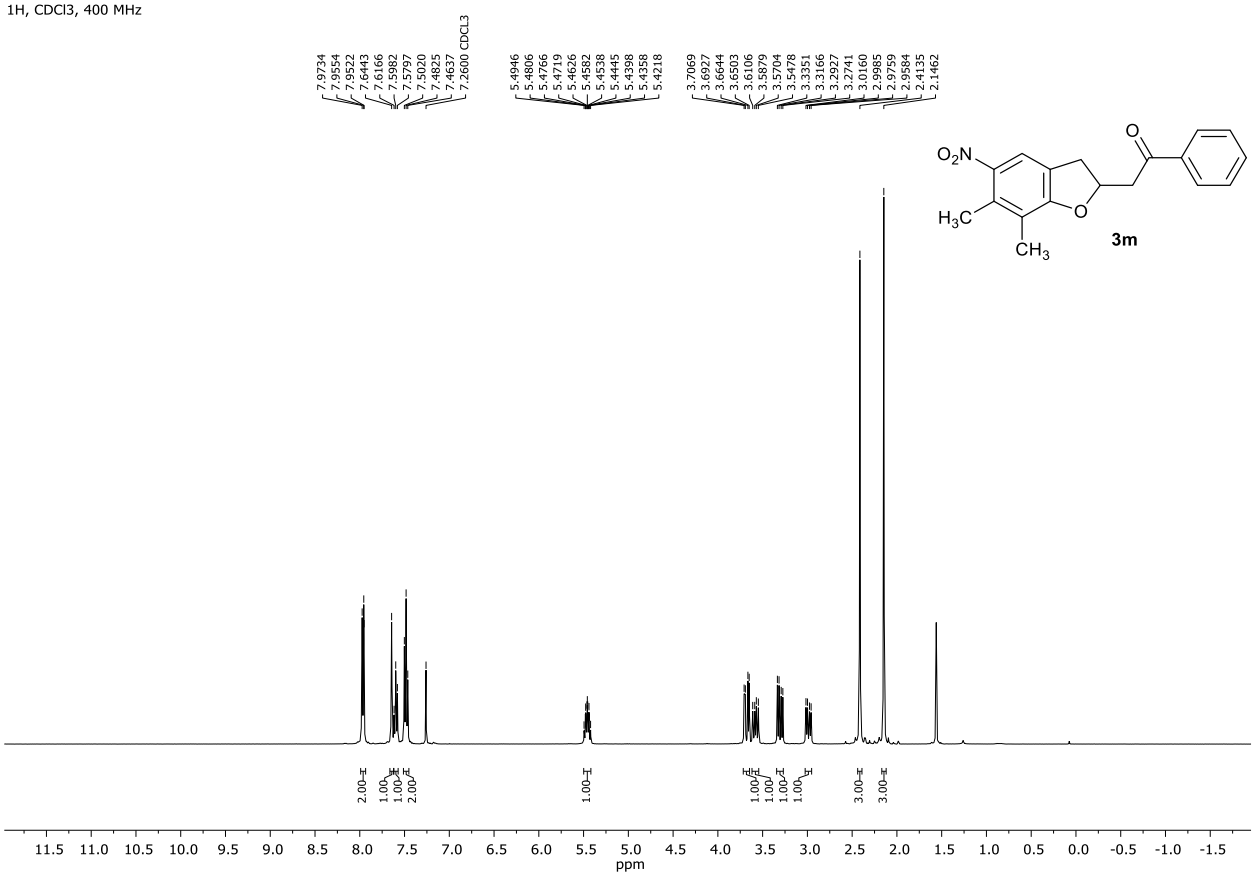


13C, CDCl3, 100 MHz

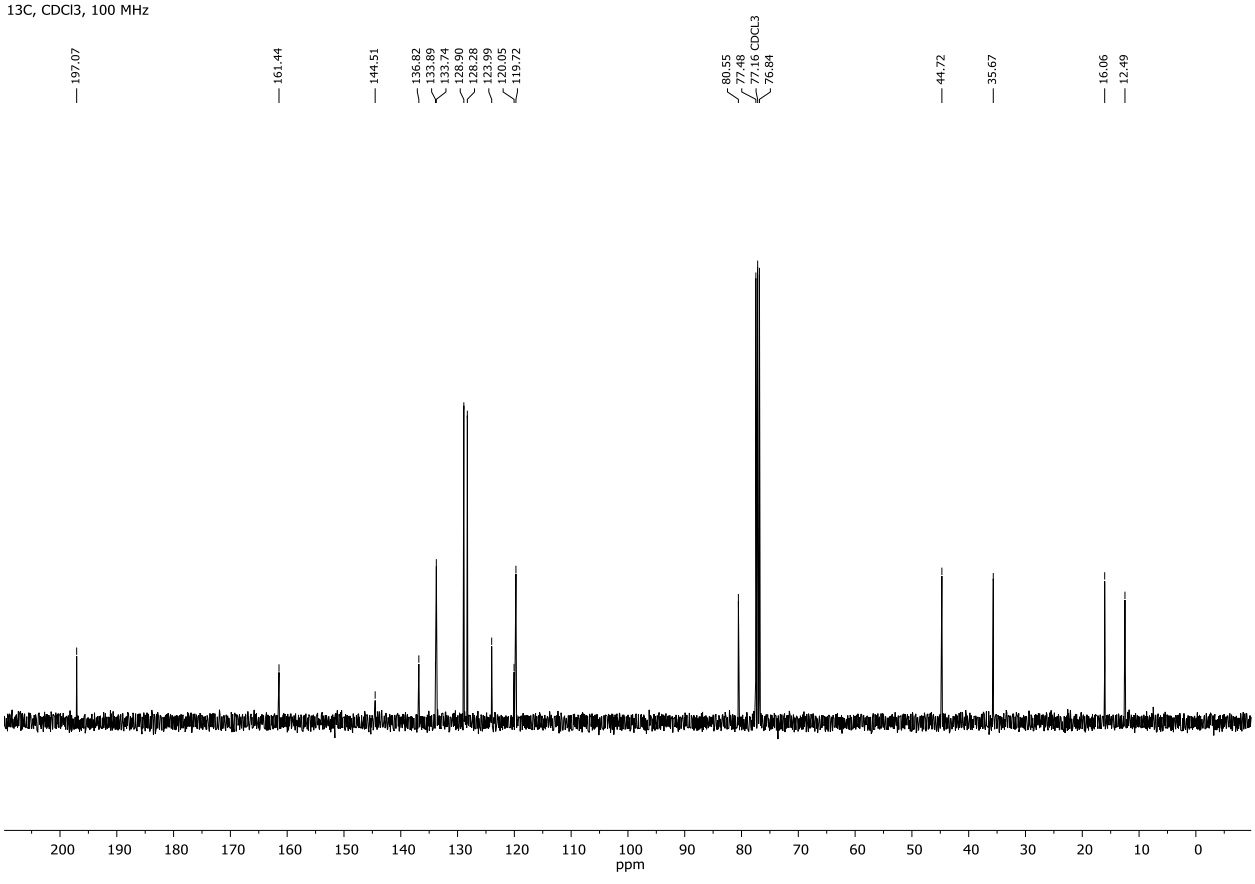
197.54
159.31
135.91
134.39
132.68
130.23
129.77
128.78
128.70
128.24
127.94
127.01
126.61
125.23
123.85
120.70
109.73
79.32
77.48
77.16 CDCl3
76.84
44.96
36.08



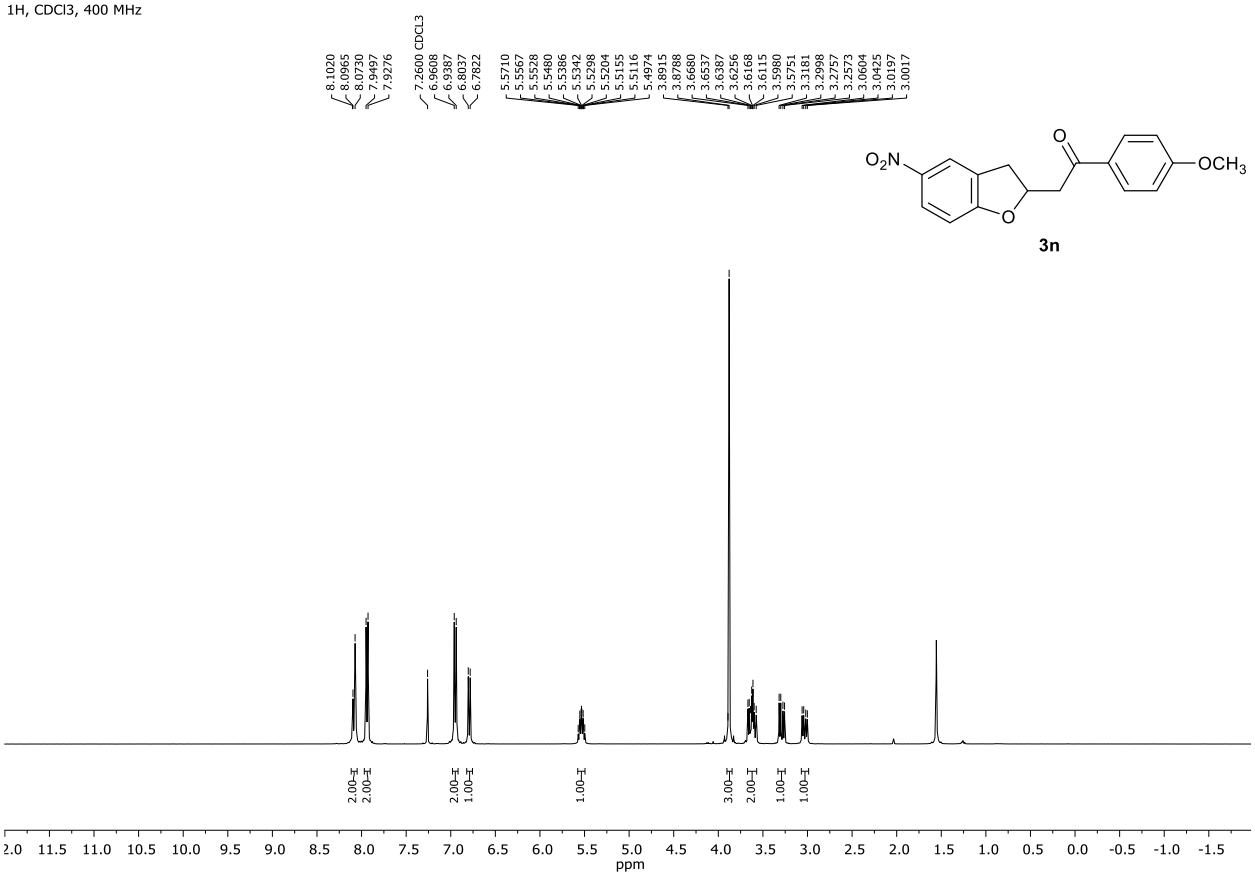
1H, CDCl3, 400 MHz



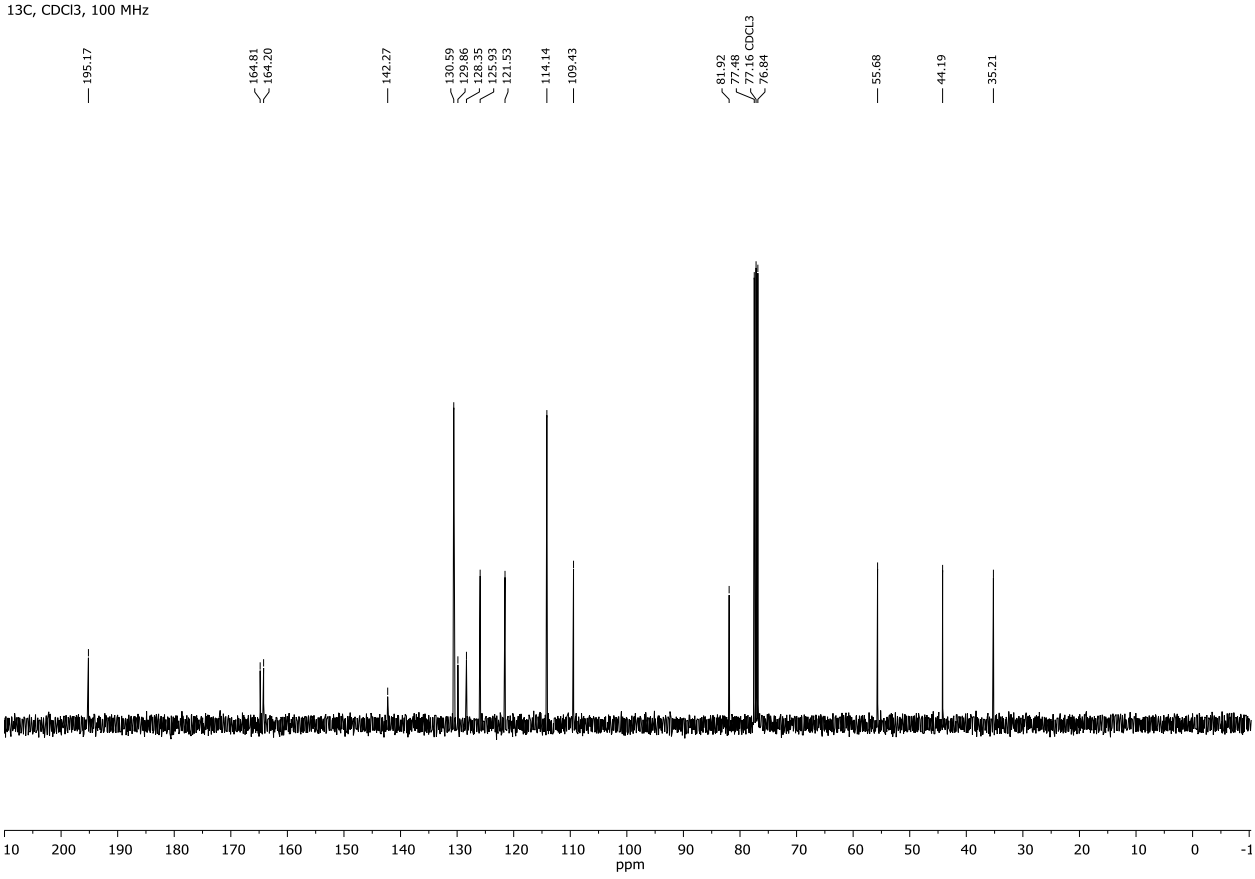
13C, CDCl3, 100 MHz



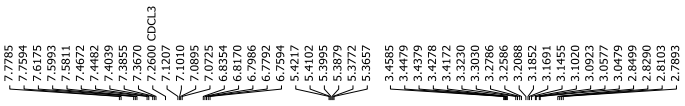
1H, CDCl3, 400 MHz

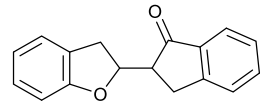


13C, CDCl3, 100 MHz

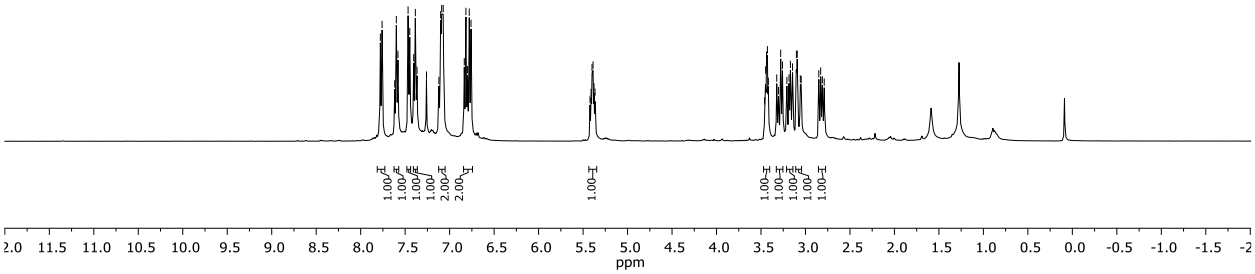


1H, CDCl3, 400 MHz

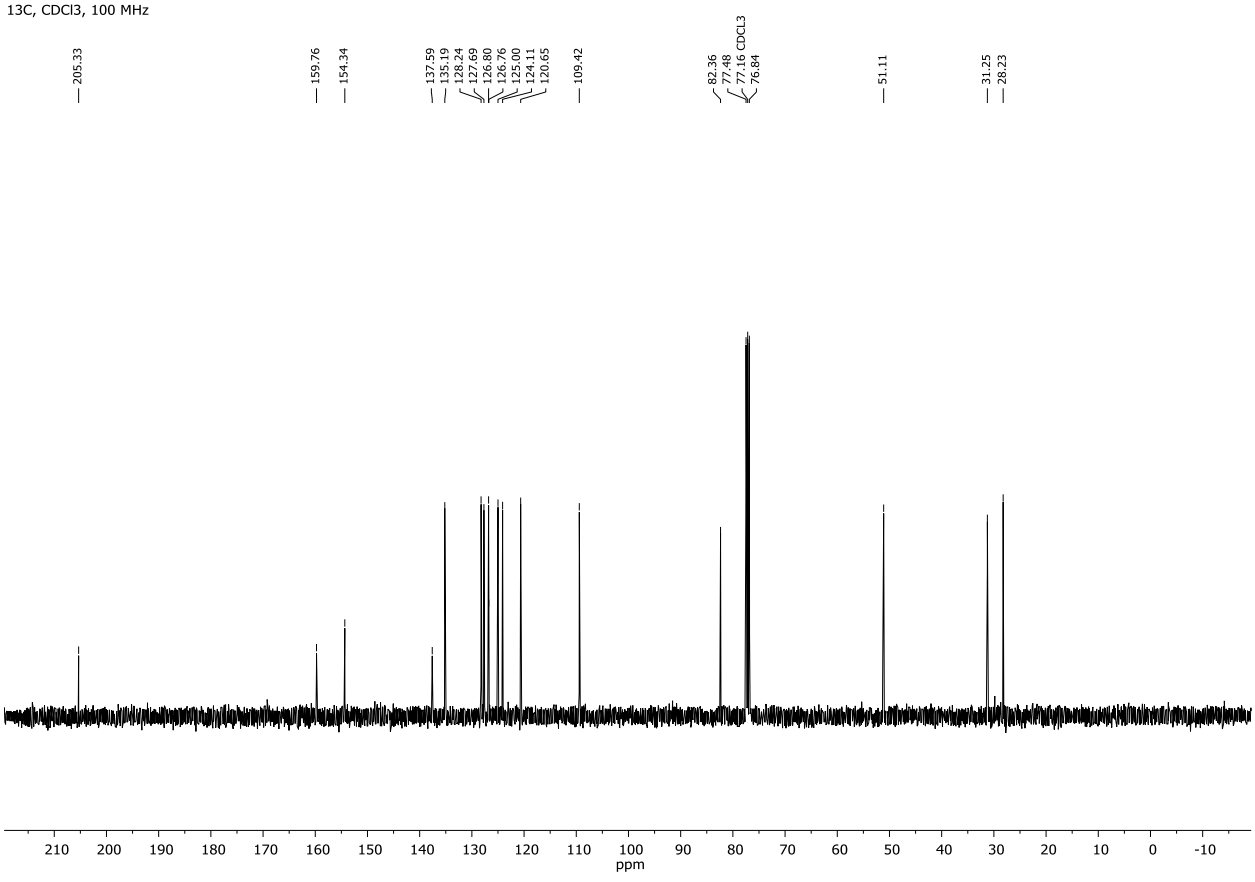




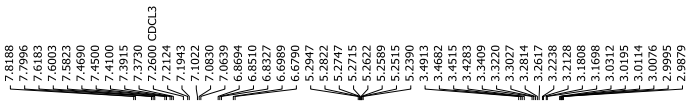
3o
major diastereomer

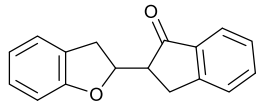


13C, CDCl3, 100 MHz

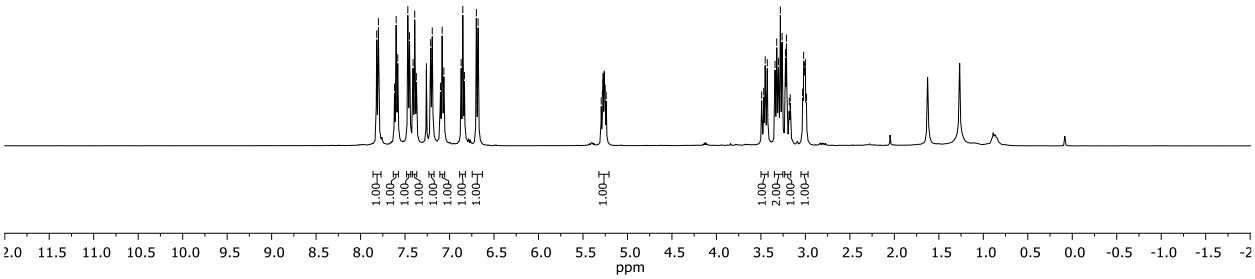


1H, CDCl3, 400 MHz





3o
minor diastereomer



13C, CDCl3, 100 MHz