Supporting Information

Electrochemical Chemo- and Regioselective Hetero-functionalization of Tropones *via* C(sp^2)-H Derivatization

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1. General Methods

^{1}H-NMR spectra were recorded on a Bruker 600 spectrometer (600 MHz). Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= double doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Bruker 600 spectrometer (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard.

When regioisomeric mixtures were isolated, the description of the minor diastereoisomer is given for ratios below 4:1. In this case, in the reported spectra images, all peaks of both isomers are integrated (^{1}H NMR) and reported (^{1}H and ^{13}C NMR). When regioisomeric ratios higher than 4:1 were isolated, only the description of the major isomer is given. In the reported ^{1}H NMR spectra images, along with all the signals of the major isomer, one signal of the minor isomer is integrated to show the regioisomeric ratios; in the ^{13}C NMR spectra images, only the peaks of the major isomer are reported.

HRMS spectra were obtained with a G2XS QTof mass spectrometer using ESI ionization techniques, as specified case by case.

Chromatographic purification was done with 240-400 mesh silica gel.

Anhydrous solvents, including DCM for the catalytic processes, were supplied by Merck in Sureseal® bottles and used without any further purification.

Compounds **1a-1i**, **1k**, **1l**,[1] **1j**[2] and **1m**[3] are known compounds and were synthesized following unmodified literature procedures.

Computational Methods

We used Density Functional Theory (DFT) at the M06 [4]/def2svpp[5] level for all the calculations presented in this manuscript. All geometry optimizations have been optimized using tight convergence criteria in the SCF and an ultrafine grid to guarantee the accuracy of the reported results. Solvent effects were modelled using the polarized continuum model (PCM),[6] as implemented in the Gaussian 16 package.[7] Acetonitrile was used as the solvent, while the calculations were performed considering 1.0 atm and 298 K to simulate the reaction conditions. The nature of all optimized structures was determined using frequency analysis to correctly identify them as minima or transition states. For all stationary points, the stability of the wave function was also examined.[8] Additional energy corrections

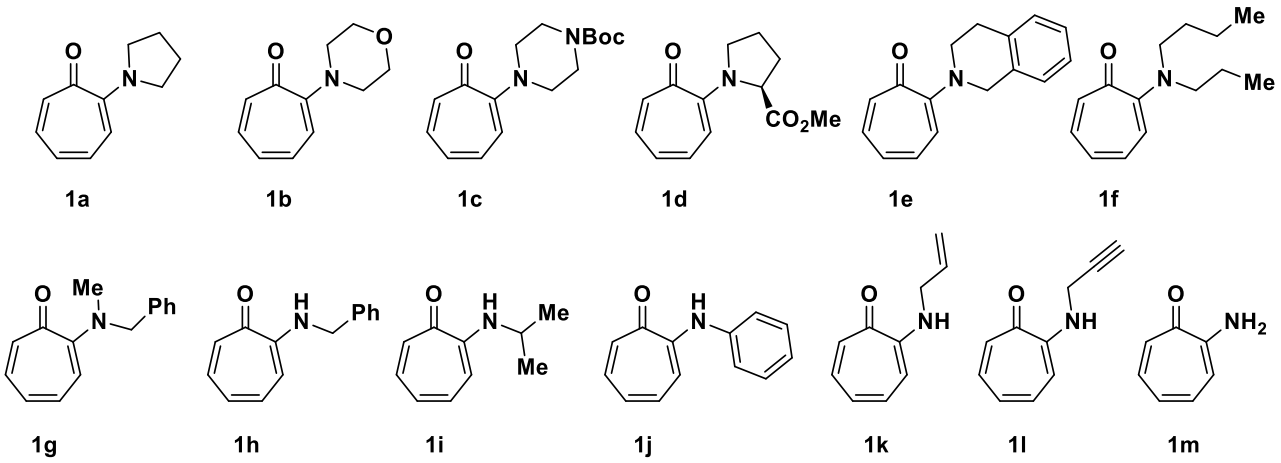
were computed using single point energy calculations at the more robust DLPNO-CCSDT(T) using ORCA 5.0.4.

Electrochemical Methods

Electrochemical characterization of the compounds was performed by cyclic voltammetry (CV). These experiments were carried out with a PGSTAT128N potentiostat driven by a Nova 2.0 software. The voltammetric responses were collected at room temperature in a three-electrode cell under N_2 flux, at 0.05 Vs^{-1} potential scan rate. The working electrode consisted of a 3 mm diameter glassy carbon electrode (Metrohm), the counter electrode was a Pt wire (Metrohm) and an Ag wire was used as the pseudo-reference electrode. The potentials of the working electrode were finally referred to the ferrocenium/ferrocene redox couple ($E_{Fc^+/Fc}$ = +0.40 V vs. SCE) by adding a few crystals of ferrocene in the solution. The working electrode surface was polished with 1 and 0.3 μm alumina and sonicated in deionized water for 5 min before the use. The electrochemical experiments were recorded by dissolving the compound under investigation in a 0.1 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in anhydrous DMF. Where not differently specified, the concentration of the solution was 5 mM.

2. Preparation and characterization of compounds 2-13.

2.1 Substrates **1** employed in the present heterofunctionalization



2.2 General Procedures

General procedure **A** for the mono-bromination of compounds **1**.

The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with the appropriate 2-aminotropone **1**, **6** or **11** (0.15 mmol), $LiClO_4$ (0.30 mmol, 32.0 mg) and NaBr (0.15 mmol, 15.4 mg). The ElectraSyn vial cap, equipped with a graphite anode and a nickel cathode, was inserted into the mixture and sealed with a rubber septum. Then, acetonitrile (3 mL) was added, and the mixture was stirred until the complete dissolution of the solids. The solution was subsequently bubbled with air (balloon) while stirring for 1 minute. The reaction mixture was electrolyzed (under air, balloon) at a constant current of 4 mA, until a total charge of 0.30 mF (2.0 F/mol$_1$) was reached. Then, the ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL), a solution of K_2CO_3 (aqueous, 1.0 M, 10 mL), and water (5 mL), which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with K_2CO_3 (aqueous, 0.1 M, 3 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was finally purified by FC to afford pure products **2**.

General procedure **B** for the other hetero-functionalizations.

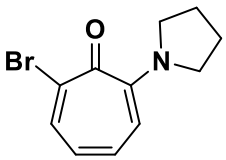
The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with the appropriate 2-aminotropone **1**, **6** or **11** (0.15 mmol), $LiClO_4$ and/or $TEABF_4$ (0.30 mmol – 1.2 mmol, 32 – 128 mg) and the *appropriate salt* (0.15 – 0.60 mmol). The ElectraSyn vial cap, equipped with a graphite anode and a nickel cathode, was inserted into the mixture and sealed with a

rubber septum. Then, acetonitrile (3 mL) was added, and the mixture was stirred until the complete dissolution of the solids. The solution was subsequently bubbled with air (balloon) while stirring for 1 minute. The reaction mixture was electrolyzed (under air, balloon) at a constant current of 4 mA, until *the appropriate charge* was reached. Then, the ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL), a solution of K_2CO_3 (aqueous, 1.0 M, 10 mL), and water (5 mL), which were combined with the crude mixture in a separatory funnel. Then, the organic layer was separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with K_2CO_3 (aqueous, 0.1 M, 3 x 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was finally purified by FC to afford the pure products.

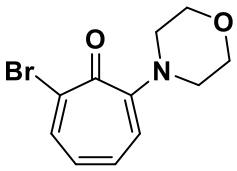
General procedure **C** for the Suzuki-coupling.

In a Schlenk tube, under an Ar atmosphere and magnetic stirring, the appropriate bromo-derivative **2aa**, **3aa** or **7aa** (0.30 mmol), Cs_2CO_3 (1.5 mmol, 244 mg) and the desired boronic acid (0.60 mmol) were suspended in a THF/H_2O mixture (10:1, 1.1 mL). The resulting suspension was de-gassed by bubbling Ar for 1 min, then $PdCl_2(PPh_3)_2$ (0.015 mmol, 10.6 mg, 5 mol%) was added and the resulting mixture was stirred at 70 °C for 3 h. The reaction mixture was cooled to room temperature and a saturated aqueous solution of K_2CO_3 (2 mL), H_2O (5 mL) and EtOAc (5 mL) were added, and the resulting biphasic mixture was transferred to a separatory funnel. The phases were separated, the aqueous layer was extracted again with EtOAc (5 mL), the combined organic phases were washed with a saturated aqueous solution of K_2CO_3 (2 x 5 mL), dried with Na_2SO_4, evaporated *in vacuo* and finally purified by flash chromatography on silica gel to obtain desired products.

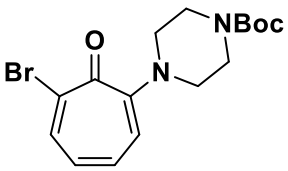
2.3 Characterization data of compounds **2**-**12**.



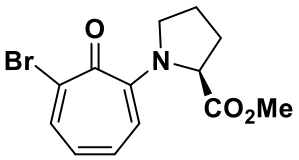
2aa. Orange solid [m.p. = 108 – 110 °C]. Obtained following *General Procedure **A*** [starting material: **1a**]. FC eluent: *n*-hexane/EtOAc: from 20:1 to 10:1. Yield = 93%, (0.140 mmol, 34.7 mg). **2aa**:**3aa** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 9.8 Hz, 1H), 6.97 (t, *J* = 10.8 Hz, 1H), 6.27 (d, *J* = 10.7 Hz, 1H), 6.17 (t, *J* = 9.8 Hz, 1H), 3.62 – 3.52 (m, 4H), 1.97 – 1.84 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.7, 153.9, 139.0, 134.6, 128.7, 117.9, 111.7, 51.5 (2C), 25.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}BrNO$ 254.0175 (^{79}Br) and 256.0155 (^{81}Br); found 254.0180 (^{79}Br) and 256.0149 (^{81}Br).



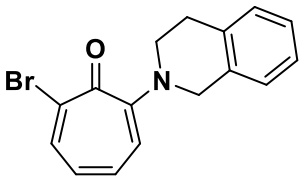
2ba. Orange sticky oil. Obtained following *General Procedure **A*** [starting material: **1b**]. FC eluent: *n*-hexane/EtOAc: from 20:1 to 10:1. Yield = 95%, (0.142 mmol, 38.5 mg). **2ba**:**3ba** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 9.5, 1.1 Hz, 1H), 7.04 (td, *J* = 10.3, 1.1 Hz, 1H), 6.66 (d, *J* = 10.2 Hz, 1H), 6.47 (t, *J* = 9.9 Hz, 1H), 3.85 – 3.77 (m, 4H), 3.35 – 3.27 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 175.8, 156.9, 139.1, 136.4, 133.9, 123.9, 118.7, 66.8 (2C), 49.8 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}BrNO_2$ 270.0125 (^{79}Br) and 272.0104 (^{81}Br); found 270.0129 (^{79}Br) and 272.0111 (^{81}Br).



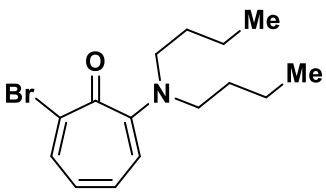
2ca. Orange amorphous solid. Obtained following *General Procedure **A*** [starting material: **1c**]. FC eluent: *n*-hexane/EtOAc: from 10:1 to 8:1. Yield = 60%, (0.090 mmol, 33.1 mg). **2ca**:**3ca** = 6.9:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.08 (dd, *J* = 9.5, 1.1 Hz, 1H), 7.09 (td, *J* = 10.3, 1.1 Hz, 1H), 6.71 (d, *J* = 10.2 Hz, 1H), 6.52 (t, *J* = 9.9 Hz, 1H), 3.61 (t, *J* = 5.1 Hz, 4H), 3.34 – 3.30 (m, 4H), 1.47 (s, 9H), only the peaks relative to **2ca** are reported; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 175.8, 157.0, 154.7, 139.2, 136.4, 133.9, 123.9, 119.0, 80.1, 49.3 (2C), 44.0 and 43.1 (b, 2C, rotamers), 28.4 (3C), only the peaks relative to **2ca** are reported; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{22}BrN_2O_3$ 369.0809 (^{79}Br) and 371.0788 (^{81}Br); found 369.0800 (^{79}Br) and 371.0795 (^{81}Br).



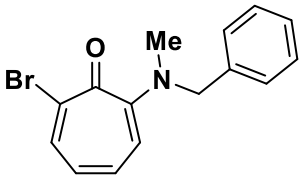
2da. Orange solid. Obtained following *General Procedure **A*** [starting material: **1d**]. FC eluent: *n*-hexane/EtOAc: from 20:1 to 12:1. Yield = 75%, (0.114 mmol, 35.8 mg). **2da**:**3da** = 7.4:1. $[\alpha]_D^{25\ °C}$ = -44 (c = 0.05 in $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 9.6, 1.1 Hz, 1H), 7.01 (td, *J* = 10.3, 1.1 Hz, 1H), 6.41 (d, *J* = 0.8 Hz, 1H), 6.27 (t, *J* = 9.8 Hz, 1H), 5.28 – 5.24 (m, 1H), 3.66 (s, 3H), 3.56 – 3.43 (m, 2H), 2.28 – 2.21 (m, 1H), 2.04 – 1.92 (m, 3H), only the peaks relative to **2da** are reported; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 174.0, 172.5, 152.5, 139.3, 134.6, 130.7, 119.7, 113.0, 63.0, 52.4, 51.8, 31.1, 23.0, only the peaks relative to **2da** are reported; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{13}H_{15}BrNO_3$ 312.0230 (^{79}Br) and 314.0210 (^{81}Br); found 312.0224 (^{79}Br) and 314.0218 (^{81}Br).



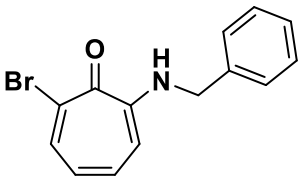
2ea. Orange solid. Obtained following *General Procedure **A*** [starting material: **1e**]. FC eluent: *n*-hexane/EtOAc: from 20:1 to 15:1. Yield = 79%, (0.119 mmol, 37.3 mg). **2da**:**3da** = 10:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.03 (dd, *J* = 9.6, 1.1 Hz, 1H), 7.21 – 7.16 (m, 3H), 7.14 – 7.09 (m, 2H), 6.77 (d, *J* = 10.4 Hz, 1H), 6.44 (t, *J* = 9.8 Hz, 1H), 4.59 (s, 2H), 3.69 (t, *J* = 5.7 Hz, 2H), 3.10 (t, *J* = 5.7 Hz, 2H), only the peaks relative to **2ea** are reported; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 174.5, 155.4, 138.0, 134.1, 133.1, 132.7, 132.2, 127.6, 125.8, 125.3, 125.2, 120.8, 115.1, 51.1, 46.5, 28.2, only the peaks relative to **2ea** are reported; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{15}BrNO$ 316.0332 (^{79}Br) and 318.0312 (^{81}Br); found 316.0327 (^{79}Br) and 318.0314 (^{81}Br).



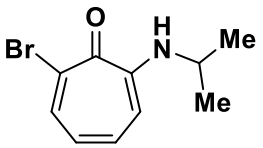
2fa. Orange sticky oil. Obtained following *General Procedure **A*** [starting material: **1f**]. FC eluent: *n*-hexane/EtOAc: 20:1. Yield = 89%, (0.119 mmol, 37.3 mg). **2fa**:**3fa** = 5.4:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.82 (dd, *J* = 9.6, 1.1 Hz, 1H), 7.01 (t, *J* = 10.9 Hz, 1H), 6.45 (d, *J* = 10.7 Hz, 1H), 6.24 (t, *J* = 9.7 Hz, 1H), 3.52 – 3.48 (m, 4H), 1.61 – 1.54 (m, 4H), 1.37 – 1.29 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H), only the peaks relative to **2fa** are reported; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 153.6, 138.0, 133.6, 127.2, 118.2, 111.4, 52.9 (2C), 29.4 (2C), 20.3 (2C), 13.9 (2C), only the peaks relative to **2fa** are reported; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{23}BrNO$ 312.0958 (^{79}Br) and 314.0938 (^{81}Br); found 312.0966 (^{79}Br) and 314.0941 (^{81}Br).



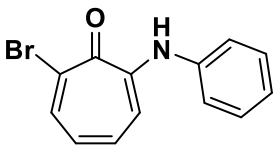
2ga. Orange sticky oil. Obtained following *General Procedure* ***A*** [starting material: **1g**]. FC eluent: *n*-hexane/EtOAc: from 20:1 to 10:1. Yield = 79%, (0.12 mmol, 39.1 mg). **2ga**:**3ga** > 20:1 **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 9.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.16 (m, 3H), 6.97 (t, *J* = 1.1 Hz, 1H), 6.50 (d, *J* = 10.5 Hz, 1H), 6.30 (t, *J* = 9.8 Hz, 1H), 4.67 (s, 2H), 2.98 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 174.9, 155.7, 138.7, 136.9, 134.0, 131.6, 128.6 (2C), 127.7 (2C), 127.4, 120.7, 114.8, 57.1, 40.8; **HRMS (ESI)** m/z: [M + H]$^+$ calcd. for $C_{15}H_{15}BrNO$ 304.0332 (^{79}Br) and 306.0312 (^{81}Br); found 304.0339 (^{79}Br) and 306.0318 (^{81}Br).



2ha. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1h**]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 47%, (0.070 mmol, 22.2 mg). **2ha**:**3ha** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.07 (dd, *J* = 10.1, 1.1 Hz, 1H), 7.88 (s, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.16 (ddd, *J* = 10.7, 10.0, 1.1 Hz, 1H), 6.53 (d, *J* = 10.5 Hz, 1H), 6.44 (t, *J* = 0.7 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.5, 153.0, 140.7, 136.6, 135.9, 129.1 (2C), 129.0, 128.0, 127.2 (2C), 120.4, 109.8, 47.2; **HRMS (ESI)** m/z: [M + H]$^+$ calcd. for $C_{14}H_{13}BrNO$ 290.0176 (^{79}Br) and 292.0155 (^{81}Br); found 290.0169 (^{79}Br) and 292.0148 (^{81}Br).

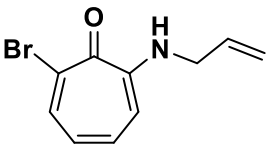


2ia. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1i**]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 70%, (0.105 mmol, 25.3 mg). **2ia**:**3ia** = 4.4:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.09 (dd, *J* = 10.2, 1.1 Hz, 1H), 7.53 (bs, 1H), 7.28 (t, *J* = 10.2 Hz, 0H), 6.62 (dt, *J* = 10.6, 0.8 Hz, 1H), 6.47 (t, *J* = 10.0 Hz, 1H), 3.89 – 3.81 (m, 1H), 1.33 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 169.9, 152.3, 140.5, 136.6, 127.9, 119.5, 109.5, 44.3, 22.0 (2C); **HRMS (ESI)** m/z: [M + H]$^+$ calcd. for $C_{10}H_{13}BrNO$ 242.0175 (^{79}Br) and 244.0155 (^{81}Br); found 242.0170 (^{79}Br) and 244.0154 (^{81}Br).

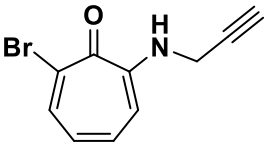


2ja. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1j**]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 86%, (0.129 mmol, 35.5 mg). **2ja**:**3ja** = 2.6:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 9.02 (bs, 1H **2ja**), 8.74 (bs, 1 H **3ja**), 8.19 (dd, *J* = 10.1, 1.0 Hz, 1H **2ja**), 7.54 (dd, *J* = 12.4, 2.3 Hz, 1H **3ja**), 7.48 – 7.43 (m, 2H **2ja** + 2H **3ja**) partially overlapped with 7.41 (dd, *J* = 12.4,

2.3 Hz, 1H **3ja**), 7.31 – 7.26 (m, 3H **2ja** + 3H **3ja**), 7.22 – 7.15 (m, 2H **2ja**), 7.05 (d, *J* = 12.4 Hz, 1H **3ja**), 6.91 (d, *J* = 11.2 Hz, 1H **3ja**), 6.59 (ddd, *J* = 10.4, 8.8, 1.8 Hz, 1H **2ja**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.1 (**3ja**), 170.5 (**2ja**), 153.1 (**3ja**), 151.6 (**2ja**), 140.9 (**2ja**), 140.5 (**3ja**), 138.1 (**3ja**), 137.8 (**2ja**), 137.8 (**3ja**), 136.3 (**2ja**), 130.4 (**3ja**), 129.9 (2C **2ja**), 129.9 (2C **3ja**), 129.6 (**2ja**), 126.7 (**2ja**), 126.5 (**3ja**), 124.7 (2C **2ja**), 124.1 (2C **3ja**), 122.1 (**2ja**), 118.0 (**3ja**), 111.1 (**3ja**), 109.7 (**2ja**); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{13}H_{11}BrNO$ 276.0019 (^{79}Br) and 277.9999 (^{81}Br); found 276.0021 (^{79}Br) and 278.0003 (^{81}Br).

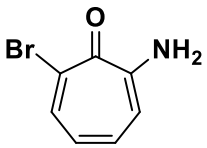


2ka. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1k**]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 26%, (0.040 mmol, 9.5 mg). **2ka**:**3ka** = 3.3:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.07 (dd, *J* = 10.2, 1.1 Hz, 1H **2ka**), 7.66 (bs, 1H **2ka**), 7.45 – 7.42 (m, 2H **3ka**), 7.32 (bs, 1H **3ka**), 7.22 (td, *J* = 10.4, 1.3 Hz, 1H **2ka**), 6.87 (d, *J* = 13.1 Hz, 1H **3ka**), 6.52 (d, *J* = 10.5 Hz, 1H **2ka**), 6.45 (t, *J* = 10.0 Hz, 1H **2ka**), 6.21 (d, *J* = 11.0 Hz, 1H **3ka**), 5.88 – 5.78 (m, 1H **2ka** + 1H **3ka**), 5.24 – 5.17 (m, 2H **2ka** + 2H **3ka**), 3.98 – 3.95 (m, 2H **2ka**), 3.92 – 3.89 (m, 2H **3ka**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.1 (**3ka**), 170.3 (**2ka**), 154.8 (**3ka**), 153.1 (**2ka**), 140.7 (**2ka**), 140.2 (**3ka**), 138.4 (**3ka**), 136.5 (**2ka**), 131.6 (**3ka**), 131.5 (**2ka**), 128.7 (**3ka**), 128.0 (**3ka**), 120.2 (**2ka**), 117.8 (**2ka**), 117.8 (**2ka**), 116.0 (**3ka**), 109.7 (**2ka**), 108.2 (**3ka**), 45.4 (**3ka**), 45.3 (**3ka**); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{10}H_{11}BrNO$ 240.0019 (^{79}Br) and 241.9999 (^{81}Br); found 240.0011 (^{79}Br) and 241.9993 (^{81}Br).

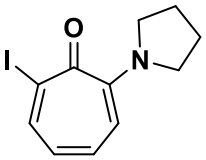


2la. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1l**]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 55%, (0.082 mmol, 19.8 mg). **2la**:**3la** = 2.7:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.17 (dd, *J* = 10.1, 1.1 Hz, 1H **2la**), 7.64 (bs, 1H **2la**), 7.55 (dd, *J* = 11.0, 2.3 Hz, 1H **3la**), 7.51 (dd, *J* = 12.4, 2.3 Hz, 1H **3la**), 7.34 (td, *J* = 10.2, 1.1 Hz, 1H **2la**) partially overlapped with 7.30 (s, 1H **3la**), 6.95 (d, *J* = 12.4 Hz, 1H **3la**), 6.70 (d, *J* = 10.4 Hz, 1H **2la**), 6.58 (t, *J* = 10.1 Hz, 1H **2la**), 6.37 (d, *J* = 11.0 Hz, 1H **3la**), 4.17 (dd, *J* = 6.0, 2.5 Hz, 2H **2la**), 4.11 (dd, *J* = 5.9, 2.5 Hz, 2H **3la**), 2.30 (t, *J* = 2.5 Hz, 1H **2la** + 1H **3la**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 175.4 (**3la**), 169.7 (**2la**), 152.8 (**3la**), 151.0 (**2la**), 139.8 (**2la**), 139.4 (**3la**), 137.1 (**3la**), 135.4 (**2la**), 128.9 (**2la**), 128.1 (**3la**), 120.0 (**2la**), 116.0 (**3la**), 108.8 (**2la**), 107.3 (**3la**), 76.3 (**2la**), 76.3 (**3la**), 71.9 (**3la**), 71.8 (**2la**), 31.7 (**2la**), 31.5 (**3la**); **HRMS (ESI)** m/z: $[M + H]^+$

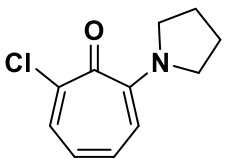
calcd. for $C_{10}H_9BrNO$ 237.9862 (^{79}Br) and 239.9842 (^{81}Br); found 237.9890 (^{79}Br) and 239.9899 (^{81}Br).



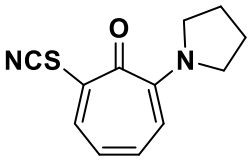
2ma. Yellow solid. Obtained following *General Procedure* ***A*** [starting material: **1m**]. FC eluent: *n*-hexane/EtOAc: 3:1 to 1:1. Yield = 27%, (0.041 mmol, 8.1 mg). **2ma**:**3ma** = 2.4:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.09 (dd, *J* = 10.1, 1.1 Hz, 1H **2ma**), 7.43 (dd, *J* = 12.5, 2.3 Hz, 1H **3ma**), 7.36 (dd, *J* = 10.9, 2.3 Hz, 1H **3ma**), 7.15 (td, *J* = 10.1, 1.1 Hz, 1H **2ma**), 6.91 (d, *J* = 12.5 Hz, 1H **3ma**), 6.85 (dd, *J* = 10.3, 0.8 Hz, 1H **2ma**), 6.55 (d, *J* = 10.9 Hz, 1H **3ma**), 6.51 (td, *J* = 10.1, 0.8 Hz, 1H **2ma**), 6.19 (bs, 2H **2ma**), 5.97 (bs, 2H **3ma**); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.0 (**3ma**), 170.1 (**2ma**), 156.2 (**3ma**), 154.4 (**2ma**), 140.4 (**2ma**), 140.1 (**3ma**), 138.2 (**3ma**), 136.4 (**2ma**), 131.2 (**3ma**), 130.1 (**2ma**), 121.7 (**2ma**), 117.6 (**3ma**), 112.9 (**3ma**), 111.4 (**2ma**); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for C_7H_7BrNO 199.9706 (^{79}Br) and 201.9686 (^{81}Br); found 199.9700 (^{79}Br) and 201.9682 (^{81}Br).



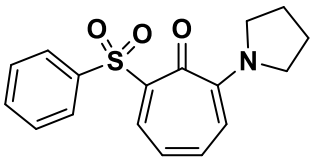
2ab. Orange amorphous solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, TEAI (0.30 mmol, 78.0 mg), $LiClO_4$ (0.60 mmol, 64.0 mg),[9] 4 F/mol$_{1a}$]. FC eluent: *n*-hexane/EtOAc: 10:1 Yield = 83%, (0.125 mmol, 40.7 mg). **2ab**:**3ab** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.14 (dd, *J* = 9.6, 1.1 Hz, 1H), 7.02 (t, *J* = 10.3 Hz, 1H), 6.30 (d, *J* = 10.6 Hz, 1H), 6.09 (t, *J* = 9.7 Hz, 1H), 3.70 – 3.49 (m, 4H), 1.97 – 1.92 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 174.4, 151.5, 145.3, 135.1, 118.9, 111.0, 109.0, 51.4 (2C), 25.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}INO$ 302.0036; found 302.0031.



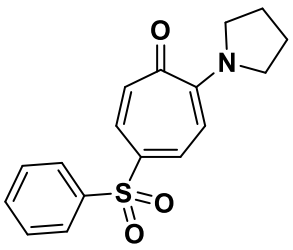
2ac. Orange amorphous solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, TEACl (0.15 mmol, 25.0 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 3 F/mol$_{1a}$]. FC eluent: *n*-hexane/EtOAc: 7:1 Yield = 35%, (0.053 mmol, 13.9 mg). **2ac**:**3ac** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 9.8, 1.1 Hz, 1H), 6.97 (ddd, *J* = 10.9, 9.9, 1.2 Hz, 1H), 6.33 (d, *J* = 10.7 Hz, 1H), 6.28 (t, *J* = 9.8 Hz, 1H), 3.64 – 3.57 (m, 4H), 1.93 – 1.87 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.6, 154.7, 136.4, 135.9, 134.3, 117.6, 112.2, 51.5 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}ClNO$ 210.0680 (^{35}Cl) and 212.0651 (^{37}Cl); found 210.0675 (^{35}Cl) and 212.0659 (^{37}Cl).



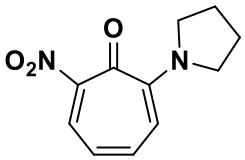
2ad. Orange amorphous solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, KSCN (0.45 mmol, 43.7 mg), $TEABF_4$ (0.45 mmol, 98.0 mg),[10] 2 F/$mol_{\mathbf{1a}}$]. FC eluent: *n*-hexane/EtOAc: 1:1. Yield = 30%, (0.045 mmol, 13.0 mg). **2ad**:**3ad** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.75 (dd, *J* = 9.8, 1.1 Hz, 1H), 7.08 (ddd, *J* = 11.0, 9.8, 1.1 Hz, 1H), 6.58 (t, *J* = 9.8 Hz, 1H), 6.50 (d, *J* = 11.0 Hz, 1H), 3.78 – 3.63 (m, 4H), 1.93 – 1.83 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.5, 151.4, 134.1, 133.7, 130.4, 119.0, 114.0, 113.1, 51.0 (2C), 24.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{12}H_{13}N_2OS$ 233.0743; found 233.0749.



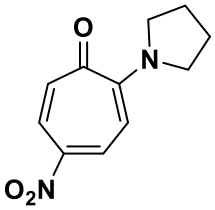
2ae. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, $PhSO_2Na$ (0.15 mmol, 25.0 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 F/$mol_{\mathbf{1a}}$, a 2.75:1 ACN/DMSO solvent mixture (3 mL) was used].[11] Isolated (first eluting fraction) along with **3ae** (**2ae**:**3ae** = 3.0:1). FC eluent: DCM/Acetone: 50:1. Yield = 65%, (0.097 mmol, 30.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.12 (dd, *J* = 9.6, 1.2 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.39 (m, 2H), 7.11 (ddd, *J* = 10.8, 9.7, 1.2 Hz, 1H), 6.39 (t, *J* = 9.6 Hz, 1H), 6.13 (d, *J* = 0.7 Hz, 1H), 3.70 – 3.19 (bm, 4H), 1.96 – 1.77 (bm, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 173.3, 156.9, 142.8, 139.8, 136.9, 135.5, 132.4, 128.4 (2C), 128.3 (2C), 115.5, 109.8, (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{17}H_{18}NO_3S$ 316.1002; found 316.1007.



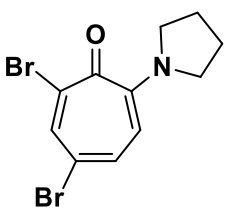
3ae. Orange solid. Isolated (second eluting fraction) along with **2ae** (**2ae**:**3ae** = 3.0:1). FC eluent: DCM/Acetone: 50:1. Yield = 21%, (0.032 mmol, 9.9 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.82 – 7.74 (m, 3H), 7.51 – 7.38 (m, 4H), 6.64 (d, *J* = 12.3 Hz, 1H), 6.13 (d, *J* = 11.3 Hz, 1H), 3.87 – 3.75 (bm, 2H), 3.48 – 3.34 (bm, 2H), 2.01 – 1.86 (bm, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 178.7, 157.9, 142.6, 135.5, 132.7, 132.4, 129.3, 129.2 (2C), 127.4, 127.1 (2C), 107.4, (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{17}H_{18}NO_3S$ 316.1002; found 316.1008.



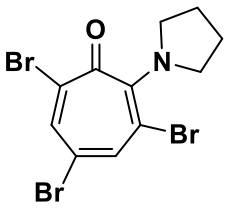
2af. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, $NaNO_2$ (0.15 mmol, 12.7 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 F/mol$_{\mathbf{1a}}$]. Isolated (first eluting fraction) along with **3af** (**2af**:**3af** = 2.5:1). FC eluent: *n*-hexane/EtOAc: 3:1. Yield = 59%, (0.089 mmol, 19.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 9.9, 1.1 Hz, 1H), 7.14 (ddd, *J* = 10.9, 9.7, 1.2 Hz, 1H), 6.27 – 6.22 (m, 2H), 4.06 – 3.31 (bm, 4H), 2.08 – 1.92 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.8, 157.7, 139.5, 130.7, 114.0, 110.7, 29.7 (2C), (one aromatic quaternary carbon and one methylene carbon of the pyrrolidine unit were not detected due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}N_2O_3$ 221.0921; found 221.0917.



3af. Orange solid. Isolated (first eluting fraction) along with **2af** (**2af**:**3af** = 2.5:1). FC eluent: *n*-hexane/EtOAc: 3:1. Yield = 24%, (0.036 mmol, 7.9 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.26 (dd, *J* = 11.9, 2.7 Hz, 1H), 8.11 (dd, *J* = 12.8, 2.7 Hz, 1H), 6.62 (d, *J* = 12.7 Hz, 1H), 6.10 (d, *J* = 11.9 Hz, 1H), 3.95 – 3.88 (m, 2H), 3.54 – 3.44 (m, 2H), 2.04 – 1.90 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 178.7, 158.3, 139.4, 132.2, 129.3, 125.4, 106.0, 29.7 (2C), (one methylene carbon of the pyrrolidine unit was not detected due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}N_2O_3$ 221.0921; found 221.0922.

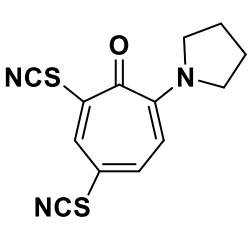


4aa. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, NaBr (0.30 mmol, 30.8 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 4 F/mol$_{\mathbf{1a}}$]. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 86%, (0.129 mmol, 42.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.23 (d, *J* = 11.4 Hz, 1H), 6.04 (d, *J* = 11.5 Hz, 1H), 3.60 – 3.50 (m, 4H), 1.94 – 1.88 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.1, 152.9, 141.1, 136.6, 127.3, 110.9, 110.4, 51.7 (2C), 25.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{12}Br_2NO$ 331.9281 ($^{79}Br^{79}Br$), 333.9260 ($^{79}Br^{81}Br$) and 335.9240 ($^{81}Br^{81}Br$); found 331.9285 ($^{79}Br^{79}Br$), 333.9257 ($^{79}Br^{81}Br$) and 335.9247 ($^{81}Br^{81}Br$).

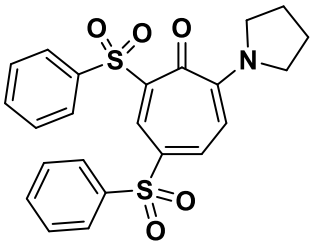


5aa. Cherry-red solid. Obtained following *General Procedure* ***B*** [starting material: **1a**, NaBr (0.60 mmol, 61.6 mg), $LiClO_4$ (1.2 mmol, 128 mg), $TEABF_4$ (1.2 mmol, 260.5 mg),[12] 8 F/mol$_{\mathbf{1a}}$]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 25%, (0.038 mmol, 16.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.63 (s, 1H), 3.64 – 3.57 (m, 4H), 1.94 – 1.91 (m, 4H); **^{13}C**

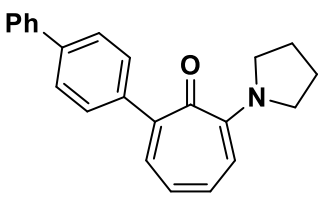
NMR (150 MHz, $CDCl_3$) δ = 164.7, 152,2 140.9, 138.5, 119.2, 105.8, 96.7, 55.0 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{11}Br_3NO$ 409.8386 ($^{79}Br^{79}Br^{79}Br$), 411.8365 ($^{79}Br^{79}Br^{81}Br$), 413.8345 ($^{79}Br^{81}Br^{81}Br$) and 415.8324 ($^{81}Br^{81}Br^{81}Br$); found 409.8391 ($^{79}Br^{79}Br^{79}Br$), 411.8370 ($^{79}Br^{79}Br^{81}Br$), 413.8347 ($^{79}Br^{81}Br^{81}Br$) and 415.8330 ($^{81}Br^{81}Br^{81}Br$).



4ad. Orange solid [m.p. = 150 – 152 °C]. Obtained following *General Procedure **B*** [starting material: **1a**, KSCN (0.45 mmol, 43.7 mg), $LiClO_4$ (1.05 mmol, 112 mg),[9] 7 $F/mol_{\mathbf{1a}}$]. FC eluent: *n*-hexane/EtOAc: 1:1. Yield = 54%, (0.081 mmol, 23.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 2.0 Hz, 1H), 7.41 (dd, *J* = 11.6, 2.0 Hz, 1H), 6.38 (d, *J* = 11.6 Hz, 1H), 4.35 – 3.22 (bm, 4H), 2.07 – 1.88 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.1, 153.0, 140.3, 134.7, 132.4, 113.2, 112.7, 112.0, 111.2, 52.8 (b, 2C), 25.4 (b, 2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{13}H_{12}N_3OS_2$ 290.0416; found 290.0421.

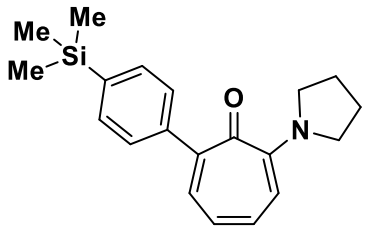


4ae. Orange solid [m.p. > 200 °C with decomposition]. Obtained following *General Procedure **B*** [starting material: **1a**, $PhSO_2Na$ (0.30 mmol, 50.0 mg), $LiClO_4$ (0.60 mmol, 64.0 mg),[9] 4 $F/mol_{\mathbf{1a}}$, a 2.75:1 ACN/DMSO solvent mixture (3 mL) was used.[11] FC eluent: *n*-hexane/EtOAc: 2:1. Yield = 26%, (0.039 mmol, 17.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 1.8 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.88 – 7.83 (m, 3H), 7.51 – 7.39 (m, 6H), 6.09 (d, *J* = 11.4 Hz, 1H), 3.58 (t, *J* = 7.0 Hz, 2H), 3.46 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.91 – 1.84 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.9, 157.7, 142.4, 142.1, 138.8, 135.4, 133.1, 132.9, 132.9, 129.4 (2C), 128.7 (2C), 128.5 (2C), 127.3 (2C), 125.7, 107.2, 53.1, 51.0, 25.6, 24.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO_5S_2$ 456.0934; found 456.0940.

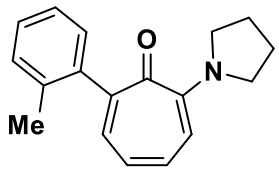


6a. Orange solid. Obtained following *General Procedure **C*** [starting materials: **2aa** and 4-biphenylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 67%, (0.202 mmol, 65.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 – 7.50 (m, 6H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 6.92 (t, *J* = 10.1 Hz, 1H), 6.40 (t, *J* = 9.5 Hz, 1H), 6.22 (d, *J* = 10.2 Hz, 1H), 3.51 – 3.45 (m, 4H), 1.95 – 1.86 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.8, 155.4, 141.7, 141.1, 140.2, 139.8, 135.7, 133.2, 130.1 (2C), 128.7 (2C), 127.2, 127.1 (2C), 127.0

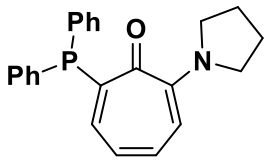
(2C), 119.0, 110.0, 50.7 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO$ 328.1696; found 328.1702.



6b. Orange oil. Obtained following *General Procedure* ***C*** [starting materials: **2aa** and 4-(trimethylsilyl)phenylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 76%, (0.228 mmol, 73.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.48 – 7.45 (m, 2H), 7.44 – 7.41 (m, 2H), 7.23 (dd, *J* = 9.0, 1.1 Hz, 1H), 6.91 (td, *J* = 10.1, 1.1 Hz, 1H), 6.39 (t, *J* = 9.5 Hz, 1H), 6.21 (d, *J* = 10.2 Hz, 1H), 3.48 – 3.45 (m, 4H), 1.94 – 1.86 (m, 4H), 0.20 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 180.9, 156.4, 144.2, 141.9, 139.8, 136.8, 134.4 (2C), 134.2, 130.0 (2C), 120.0, 110.9, 51.7 (2C), 26.5 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{26}NOSi$ 324.1779; found 324.1785.

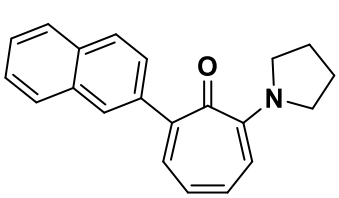


6c. Orange solid. Obtained following *General Procedure* ***C*** [starting materials: **2aa** and 2-tolylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 70%, (0.210 mmol, 55.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.17 – 7.05 (m, 5H), 6.95 (td, *J* = 10.2, 1.3 Hz, 1H), 6.39 (t, *J* = 9.5 Hz, 1H), 6.28 (d, *J* = 10.4 Hz, 1H), 3.54 – 3.49 (m, 4H), 2.15 (s, 3H), 1.90 – 1.85 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 178.7, 156.1, 143.1, 142.4, 136.8, 135.7, 133.6, 129.9, 129.8, 127.2, 125.7, 119.4, 110.9, 50.8 (2C), 25.5 (2C), 20.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{20}NO$ 266.1539; found 266.1541.

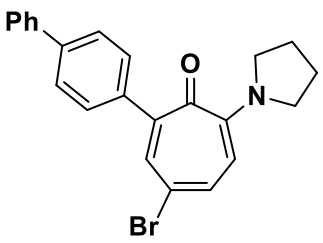


6d. In an oven dried Schlenk tube under Ar, **2aa** (0.25 mmol, 77.5 mg) was dissolved in 1 mL of toluene. Subsequently, $Pd(OAc)_2$ (2.8 mg, 5 mol%), dppf (8.3 mg, 0.015 mmol, 6 mol%) and NaOtBu (29 mg, 0.3 mmol) were added, followed by diphenylphosphine (0.3 mmol, 52 μL) and the resulting mixture was heated to 120° C for 18 h. The reaction was cooled to room temperature, 5 mL of water and 5 mL of EtOAc were added, the aqueous phase was extracted with EtOAc (3x5 mL), the organic phases were collected, dried over Na_2SO_4 and the solvent was evaporated. The crude mixture was finally purified by FC (*n*-hexane/EtOAc: 8:1) to obtain the desired product (52.1 mg, 0.145 mmol, 58% yield) as a yellow powder.[13] **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38 – 7.33 (m, 4H), 7.33 – 7.29 (m, 6H), 6.99 (t, *J* = 10.2 Hz, 1H), 6.80 (dd, *J* = 9.4, 5.3 Hz, 1H), 6.31 (t, *J* = 9.5 Hz, 1H), 6.28 (d, *J* = 10.5 Hz, 1H), 3.55 – 3.43 (m, 4H), 1.92 – 1.87 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.9 (d, *J* = 17.6

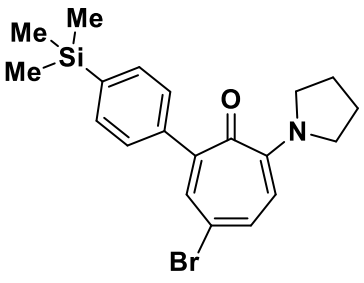
Hz), 153.0 (d, *J* = 2.8 Hz), 138.9 (d, *J* = 5.6 Hz), 138.7 (d, *J* = 11.5 Hz), 137.3 (d, *J* = 13.6 Hz, 2C), 133.6, 132.9 (d, *J* = 20.6 Hz, 4C), 127.5 (2C), 127.3 (d, *J* = 6.9 Hz, 4C), 118.0 (d, *J* = 1.5 Hz), 109.5, 49.6 (2C), 24.3 (2C); **^{31}P NMR** (243 MHz, $CDCl_3$) δ = -3.9 ppm; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{23}NOP$ 360.1512; found 360.1507.



6e. Orange solid. Obtained following *General Procedure* ***C*** [starting materials: **2aa** and 2-naphthaleneboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 80%, (0.240 mmol, 72.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 1.8 Hz, 1H), 7.90 – 7.80 (m, 3H), 7.61 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.03 (td, *J* = 10.1, 1.1 Hz, 1H), 6.51 (t, *J* = 9.5 Hz, 1H), 6.32 (d, *J* = 10.2 Hz, 1H), 3.60 – 3.55 (m, 4H), 2.02 – 1.93 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.8, 155.5, 140.7, 140.4, 136.1, 133.6, 133.3, 132.5, 128.3, 128.2, 128.1, 127.5, 127.4, 125.9, 125.8, 119.1, 110.0, 50.7 (2C), 25.5.(2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{20}NO$ 302.1539; found 302.1544.

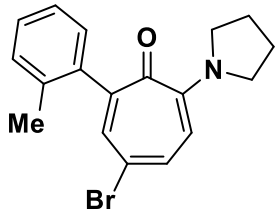


7aa. Orange solid [m.p. = 122 – 124 °C]. Obtained following *General Procedure* ***A*** [starting material: **6a**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 77%, (0.116 mmol, 46.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.65 – 7.58 (m, 8H), 7.48 – 7.43 (m, 2H), 7.39 – 7.34 (m, 1H), 7.28 (dd, *J* = 11.0, 2.1 Hz, 1H), 6.03 (d, *J* = 11.0 Hz, 1H), 3.58 – 3.45 (m, 4H), 2.01 – 1.96 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.4, 154.2, 140.8, 140.3, 140.3, 139.3, 138.2, 135.0, 130.1 (2C), 128.8 (2C), 127.4, 127.1 (2C), 127.1 (2C), 112.1, 108.8, 50.8 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}BrNO$ 406.0802 (^{79}Br) and 408.0781 (^{81}Br); found 406.0797 (^{79}Br) and 408.0783 (^{81}Br).

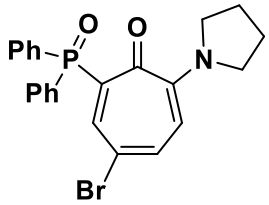


7ba. Orange sticky oil. Obtained following *General Procedure* ***A*** [starting material: **6b**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 67%, (0.101 mmol, 40.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.57 – 7.52 (m, 3H), 7.49 – 7.46 (m, 2H), 7.26 (dd, *J* = 11.0, 2.1 Hz, 1H), 6.02 (d, *J* = 11.0 Hz, 1H), 3.50 (t, *J* = 5.9 Hz, 4H), 2.00 – 1.93 (m, 4H), 0.28 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 180.5, 155.3, 142.8, 140.9, 140.6, 139.3, 136.0, 134.5 (2C), 129.9 (2C), 113.2, 109.8, 51.9

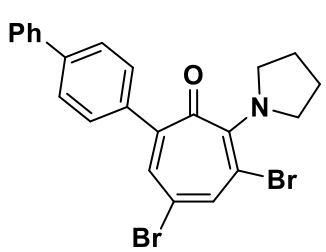
(2C), 26.5 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{25}BrNOSi$ 402.0884 (^{79}Br) and 404.0863 (^{81}Br); found 402.0879 (^{79}Br) and 404.0857 (^{81}Br).



7ca. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **6c**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 70%, (0.105 mmol, 36.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 11.2, 2.2 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.16 (dt, *J* = 6.7, 1.4 Hz, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 3.61 – 3.51 (m, 4H), 2.22 (s, 3H), 1.99 – 1.93 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 178.0, 155.0, 141.8, 141.5, 139.4, 135.5, 135.5, 130.0, 129.9, 127.7, 125.8, 112.5, 109.8, 51.0, 25.5 (2C), 20.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{19}BrNO$ 344.0645 (^{79}Br) and 346.0625 (^{81}Br); found 344.0650 (^{79}Br) and 346.0631 (^{81}Br).

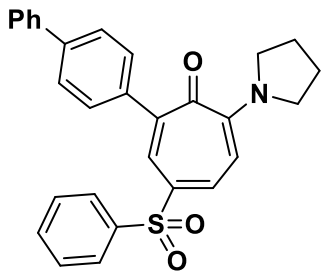


7da. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **6d**]. FC eluent: DCM/Acetone: 50:1. Yield = 58%, (0.087 mmol, 39.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.32 (dd, *J* = 18.4, 2.2 Hz, 1H), 7.86 – 7.81 (m, 4H), 7.51 – 7.48 (m, 2H), 7.44 (dd, *J* = 11.5, 2.2 Hz, 1H) partially overlapped with 7.43 – 7.39 (m, 4H), 5.98 (d, *J* = 11.4 Hz, 1H), 3.56 – 2.66 (bm, 4H), 2.00 – 1.54 (bm, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.5 (d, *J* = 9.2 Hz), 155.3 (d, *J* = 8.7 Hz), 144.1 (d, *J* = 8.1 Hz), 140.3 (d, *J* = 1.4 Hz), 133.3, 132.9 (d, *J* = 108.6 Hz, 2C) partially overlapped with 132.6 (d, *J* = 10.4 Hz, 4C), 131.6 (d, *J* = 2.8 Hz, 2C), 129.7 (d, *J* = 95.9 Hz), 128.0 (d, *J* = 12.9 Hz, 4C), 111.5 (d, *J* = 20.2 Hz), 109.3 (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **^{31}P NMR** (243 MHz, $CDCl_3$) δ = 32.9 ppm; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}BrNO_2P$ 454.0567 (^{79}Br) and 456.0546 (^{81}Br); found 454.0561 (^{79}Br) and 456.0550 (^{81}Br).

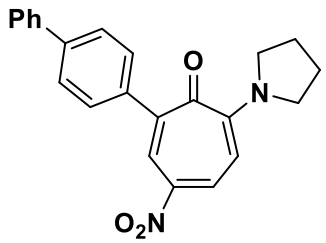


8aa. Cherry-red solid [m.p. = 155 -157 °C]. Obtained following *General Procedure* ***B*** [starting material: **6a**, NaBr (0.30 mmol, 30.8 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 4 F/mol_{6a}]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 45%, (0.068 mmol, 32.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.71 – 7.68 (m, 2H), 7.64 – 7.60 (m, 5H), 7.48 – 7.43 (m, 2H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.35 (m, 1H), 3.59 – 3.54 (m, 4H), 1.92 – 1.88 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.4, 149.6, 140.7, 140.4, 138.7, 136.9,

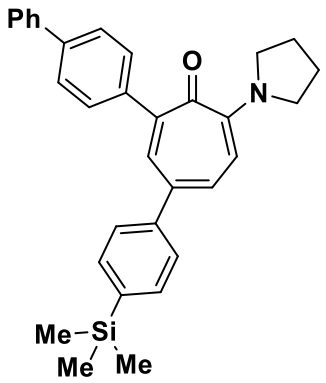
134.3, 133.8, 129.5 (2C), 128.9 (2C), 127.5, 127.2 (2C), 127.1 (2C), 108.9, 95.3, 53.9 (2C), 25.7 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{20}Br_2NO$ 483.9907 ($^{79}Br^{79}Br$), 485.9886 ($^{79}Br^{81}Br$) and 487.9866 ($^{81}Br^{81}Br$); found 483.9911 ($^{79}Br^{79}Br$), 485.9891 ($^{79}Br^{81}Br$) and 487.9873 ($^{81}Br^{81}Br$).



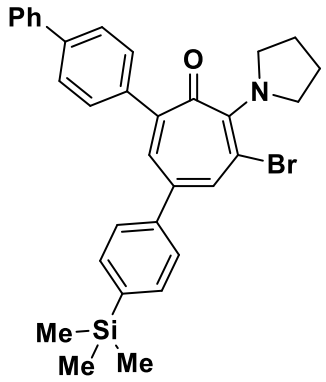
7ae. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **6a**, $PhSO_2Na$ (0.15 mmol, 25.0 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 F/mol_{6a}, a 2.75:1 ACN/DMSO solvent mixture (3 mL) was used].[11] FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 50%, (0.075 mmol, 35.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.91 – 7.88 (m, 3H), 7.87 (dd, *J* = 10.8, 1.9 Hz, 1H), 7.64 – 7.59 (m, 4H), 7.58 – 7.55 (m, 2H), 7.55 – 7.52 (m, 1H), 7.51 – 7.47 (m, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.33 (m, 1H), 6.19 (d, *J* = 10.8 Hz, 1H), 3.75 – 3.43 (bm, 4H), 2.12 – 1.92 (bm, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.8, 156.3, 142.8, 140.6, 140.5, 139.5, 137.1, 134.2, 132.6, 131.5, 129.9 (2C), 129.3 (2C), 128.8 (2C), 127.9, 127.4, 127.2 (2C), 127.1 (2C), 127.1 (2C), 106.0, (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{29}H_{26}NO_3S$ 468.1628; found 468.1620.



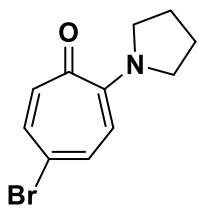
7af. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **6a**, $NaNO_2$ (0.15 mmol, 12.7 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 F/mol_{6a}]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 82%, (0.123 mmol, 45.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.51 (d, *J* = 2.5 Hz, 1H), 8.37 (dd, *J* = 11.4, 2.5 Hz, 1H), 7.68 – 7.60 (m, 6H), 7.48 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 6.15 (d, *J* = 11.4 Hz, 1H), 3.77 (t, *J* = 7.0 Hz, 2H), 3.60 (t, *J* = 6.9 Hz, 2H), 2.15 – 2.08 (m, 2H), 2.07 – 1.99 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.9, 156.9, 140.7, 140.6, 139.1, 138.2, 135.0, 131.0, 129.8 (2C), 128.8 (2C), 128.6, 127.5, 127.2 (2C), 127.1 (2C), 104.5, 52.6, 50.8, 25.9, 24.5; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}N_2O_3$ 373.1547; found 373.1542.



9. Orange solid. Obtained following *General Procedure* ***C*** [starting materials: **7aa** and 4-(trimethylsilyl)phenylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 76%, (0.228 mmol, 108 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 1.9 Hz, 1H), 7.69 – 7.61 (m, 6H), 7.60 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.43 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (dd, *J* = 10.7, 1.9 Hz, 1H), 6.43 (d, *J* = 10.7 Hz, 1H), 3.68 – 3.54 (m, 4H), 2.05 – 1.93 (m, 4H), 0.32 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 180.2, 155.5, 145.3, 143.1, 142.1, 141.4, 140.9, 139.5, 137.6, 134.8 (2C), 133.5, 133.4, 131.3 (2C), 129.8 (2C), 128.2, 128.2 (2C), 128.0 (2C), 127.6 (2C), 111.5, 51.8 (2C), 26.5 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{32}H_{34}NOSi$ 476.2405; found 476.2413.

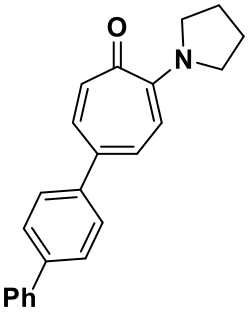


10. Cherry-red solid [m.p. = 177 -179 °C]. Obtained following *General Procedure* ***A*** [starting material: **9**]. FC eluent: *n*-hexane/EtOAc: 2:1. Yield = 40%, (0.060 mmol, 33.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.76 – 7.73 (m, 2H), 7.64 – 7.60 (m, 4H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.42 (m, 5H), 7.37 – 7.33 (m, 1H), 3.69 – 3.62 (m, 4H), 1.95 – 1.90 (m, 4H), 0.29 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 177.1, 151.4, 144.6, 141.7, 141.2, 140.0, 139.8, 138.1, 136.0, 134.8, 134.0 (2C), 131.0, 130.9 (2C), 129.9 (2C), 128.4, 128.2 (2C), 128.1 (2C), 127.8 (2C), 99.6, 55.0 (2C), 26.8 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{32}H_{33}BrNOSi$ 554.1510 (^{79}Br) and 556.1489 (^{81}Br); found 554.1510 (^{79}Br) and 556.1492 (^{81}Br).

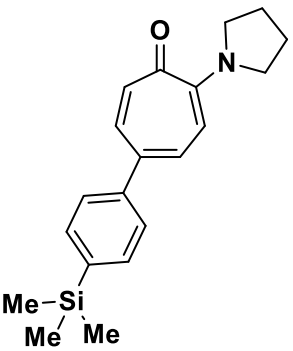


3aa. In a 3-necked round bottom flask equipped with a dropping funnel and a magnetic stirring bar, compound **1a** (2.0 mmol, 350 mg), $LiClO_4$ (4.0 mmol, 427 mg) and AcOH (2.0 mmol, 120 μL) were dissolved in dry ACN (15 mL) at 0 °C under Ar. Then, a solution of Br_2 (2.0 mmol, 103 μL) in dry ACN (15 mL) was added dropwise over a period of 30 min. The reaction was then stirred at 0 °C for 1 h and then quenched with a saturated aqueous solution of K_2CO_3 (10 mL). Subsequently, H_2O (5 mL) and EtOAc (10 mL) were added, and the resulting biphasic mixture was transferred to a separatory funnel. The phases were separated, the aqueous layer was extracted again with EtOAc (5 mL), the combined organic phases were washed with a saturated aqueous solution of K_2CO_3 (2 x 10 mL), dried with Na_2SO_4, evaporated *in*

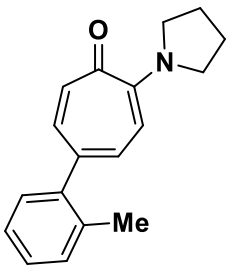
vacuo and finally purified by FC on silica gel (*n*-hexane/EtOAc: 10:1) to obtain the desired product (467 mg, 1.84 mmol, 92% yield) as an orange solid [m. p. = 90 – 92 °C]. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.26 (dd, *J* = 11.3, 2.3 Hz, 1H), 7.23 (dd, *J* = 12.4, 2.4 Hz, 1H), 6.63 (d, *J* = 12.4 Hz, 1H), 6.03 (d, *J* = 11.3 Hz, 1H), 3.65 – 3.50 (m, 4H), 1.98 – 1.89 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 178.8, 155.5, 138.3, 136.4, 129.7, 113.8, 110.6, 51.1, 25.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}BrNO$ 254.0175 (^{79}Br) and 256.0155 (^{81}Br); found 254.0181 (^{79}Br) and 256.0147 (^{81}Br).



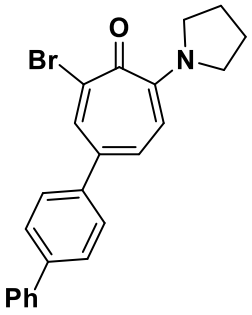
11a. Orange solid. Obtained following *General Procedure* ***C*** [starting materials: **3aa** and 4-biphenylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 80%, (0.240 mmol, 78.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.65 – 7.61 (m, 4H), 7.56 – 7.52 (m, 2H), 7.48 – 7.45 (m, 2H), 7.42 (dd, *J* = 12.1, 2.2 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.32 (dd, *J* = 11.0, 2.1 Hz, 1H), 7.00 (d, *J* = 12.1 Hz, 1H), 6.44 (d, *J* = 11.1 Hz, 1H), 3.77 – 3.62 (m, 4H), 2.04 – 1.93 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.1, 155.4, 142.1, 140.6, 139.6, 135.9, 133.5, 133.4, 131.0, 128.8 (2C), 127.4 (2C), 127.3, 127.3 (2C), 127.0 (2C), 112.0, 51.0 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{22}NO$ 328.1696; found 328.1701.



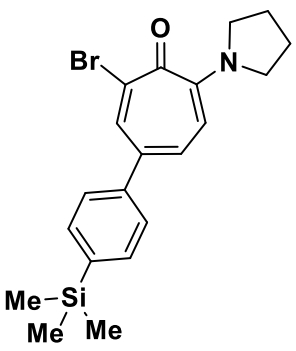
11b. Orange oil. Obtained following *General Procedure* ***C*** [starting materials: **3aa** and 4-(trimethylsilyl)phenylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 83%, (0.249 mmol, 80.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 – 7.53 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 (dd, *J* = 12.1, 2.2 Hz, 1H), 7.27 (dd, *J* = 12.1, 2.2 Hz, 1H, partially overlapped with the residual solvent peak), 6.98 (d, *J* = 12.1 Hz, 1H), 6.43 (d, *J* = 11.1 Hz, 1H), 3.79 – 3.56 (m, 4H), 2.05 – 1.92 (m, 4H), 0.29 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 180.1, 156.5, 144.6, 139.7, 137.1, 135.0, 134.9 (2C), 134.7, 132.0, 127.3 (2C), 113.0, 52.0 (2C), 26.6 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{26}NOSi$ 324.1779; found 324.1785.



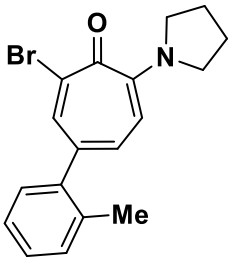
11c. Orange solid. Obtained following *General Procedure* ***C*** [starting materials: **3aa** and 2-tolylboronic acid]. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 95%, (0.285 mmol, 75.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.25 – 7.17 (m, 4H), 7.09 (dd, *J* = 12.0, 2.0 Hz, 1H), 6.99 (dd, *J* = 10.9, 2.0 Hz, 1H), 6.92 (d, *J* = 12.0 Hz, 1H), 6.37 (d, *J* = 10.9 Hz, 1H), 3.71 – 3.61 (m, 4H), 2.26 (s, 3H), 2.04 – 1.91 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 179.3, 155.6, 143.4, 137.7, 135.4, 135.1, 134.5, 130.4, 130.1, 129.5, 127.2, 125.9, 111.5, 50.9 (2C), 25.5 (2C), 20.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{20}NO$ 266.1539; found 266.1540.



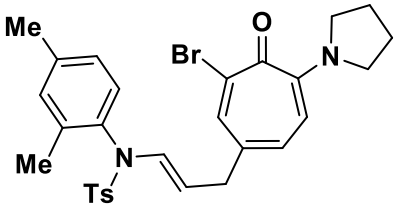
12aa. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **11a**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 73%, (0.110 mmol, 44.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 1.9 Hz, 1H), 7.65 – 7.59 (m, 4H), 7.52 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32 (dd, *J* = 11.1, 2.0 Hz, 1H), 6.45 (d, *J* = 11.1 Hz, 1H), 3.80 – 3.59 (m, 4H), 2.00 – 1.94 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.1, 153.0, 141.2, 140.4, 139.9, 139.2, 133.8, 131.1, 129.4, 128.9 (2C), 127.5 (2C), 127.5, 127.4 (2C), 127.0 (2C), 112.2, 51.6 (2C), 25.5 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}BrNO$ 406.0802 (^{79}Br) and 408.0781 (^{81}Br); found 406.0806 (^{79}Br) and 408.0787 (^{81}Br).



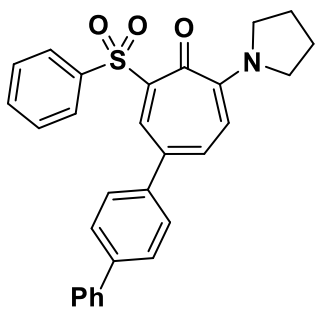
12ba. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **11b**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 92%, (0.138 mmol, 55.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 2.0 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.46 – 7.40 (m, 2H), 7.29 (dd, *J* = 11.1, 2.0 Hz, 1H), 6.46 (d, *J* = 11.2 Hz, 1H), 3.77 – 3.61 (m, 4H), 2.01 – 1.94 (m, 4H), 0.29 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 173.1, 154.1, 143.7, 140.5, 140.2, 135.0 (2C + C overlapped), 132.7, 130.4, 127.4 (2C), 113.3, 52.7 (2C), 26.6 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{25}BrNOSi$ 402.0884 (^{79}Br) and 404.0863 (^{81}Br); found 402.0884 (^{79}Br) and 404.0866 (^{81}Br).



12ca. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **11c**]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 75%, (0.113 mmol, 38.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.18 – 7.15 (m, 1H), 7.02 (dd, *J* = 11.0, 1.8 Hz, 1H), 6.40 (d, *J* = 11.0 Hz, 1H), 3.81 – 3.55 (m, 4H), 2.26 (s, 3H), 2.02 – 1.94 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.3, 153.1, 142.5, 140.8, 135.4, 135.4, 131.9, 130.5, 129.5, 128.5, 127.5, 126.0, 111.6, 51.5 (2C), 25.5 (2C), 20.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{19}BrNO$ 344.0645 (^{79}Br) and 346.0625 (^{81}Br); found 344.0651 (^{79}Br) and 346.0629 (^{81}Br).

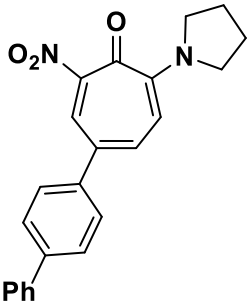


12da. Orange solid. Obtained following *General Procedure* ***A*** [starting material: **11d**].[14] FC eluent: DCM/Acetone: 20:1. Yield = 25%, (0.038 mmol, 21.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 1.9 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.35 – 7.29 (m, 2H), 7.10 – 7.06 (m, 1H), 7.03 (dt, *J* = 13.8, 1.3 Hz, 1H), 6.86 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.81 (dd, *J* = 10.9, 1.9 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.26 (d, *J* = 10.9 Hz, 1H), 4.24 (dt, *J* = 14.1, 7.2 Hz, 1H), 3.65 – 3.56 (m, 4H), 3.15 – 3.06 (m, 2H), 2.45 (s, 3H), 2.29 (s, 3H), 2.13 (s, 3H), 1.96 – 1.92 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.3, 152.9, 143.9, 140.3, 139.2, 138.7, 136.5, 134.3, 132.5, 132.3, 130.3, 129.8, 129.8 (2C), 129.5, 129.1, 127.4, 127.4 (2C), 112.1, 109.5, 51.3 (2C), 38.6, 25.5 (2C), 21.6, 21.1, 17.8; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{32}BrN_2O_3S$ 567.1312 (^{79}Br) and 569.1292 (^{81}Br); found 567.1311 (^{79}Br) and 569.1288 (^{81}Br).

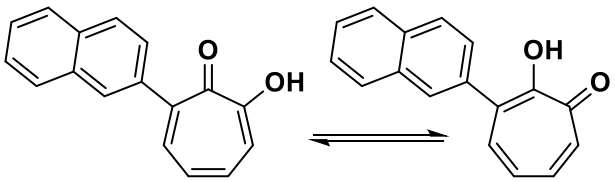


12ae. Orange solid. Obtained following *General Procedure* ***B*** [starting material: **11a**, $PhSO_2Na$ (0.15 mmol, 25.0 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 $F/mol_{\mathbf{11a}}$, a 2.75:1 ACN/DMSO solvent mixture (3 mL) was used].[11] FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 46%, (0.069 mmol, 32.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 2.0 Hz, 1H), 8.14 – 8.08 (m, 2H), 7.68 – 7.65 (m, 2H), 7.65 – 7.63 (m, 2H), 7.58 – 7.52 (m, 3H), 7.52 – 7.47 (m, 3H), 7.47 – 7.45 (m, 2H), 7.39 – 7.34 (m, 1H), 6.34 (d, *J* = 11.1 Hz, 1H), 3.82 – 3.32 (bm, 4H), 2.36 – 1.78 (bm, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 172.7, 155.8, 142.7, 141.4, 140.5, 139.9, 138.7, 136.8, 136.2, 132.5, 129.0, 128.9 (2C), 128.5, (2C + 2C overlapped), 127.6 (2C), 127.5, 127.4 (2C), 127.0

(2C), 110.5, (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{29}H_{26}NO_3S$ 468.1628; found 468.1633.



12af. Orange solid. Obtained following *General Procedure **B*** [starting material: **11a**, $NaNO_2$ (0.15 mmol, 12.7 mg), $LiClO_4$ (0.30 mmol, 32.0 mg), 2 F/mol$_{\mathbf{11a}}$]. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 40%, (0.060 mmol, 22.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 2.0 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.64 – 7.60 (m, 2H), 7.53 – 7.50 (m, 3H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 1H), 6.47 (d, *J* = 11.3 Hz, 1H), 4.25 – 3.38 (bm, 4H), 2.11 – 2.01 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.0, 156.7, 148.9, 140.7, 140.3, 140.2, 138.1, 130.6, 128.9 (2C), 128.0, 127.7 (2C), 127.5, 127.3 (2C), 127.0 (2C), 111.6 (the two methylene carbons of the pyrrolidine unit were not detected, due to excessive broadening); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{21}N_2O_3$ 373.1547; found 373.1544.



13. In a screw-capped vial equipped with a magnetic stirring bar, compound **6e** (0.10 mmol, 30.1 mg) was suspended in a 1:1 EtOH/H_2O mixture (0.5 mL) and NaOH was added (6 N, 0.7 mL). The resulting bright yellow solution was then heated to 100 °C for 6 h, until the yellow color faded completely, and then cooled to room temperature. EtOAc (5 mL) was added and the biphasic mixture was transferred to a separatory funnel where the phases were separated and the aqueous phase was washed again with EtOAc (2x3 mL). The aqueous phase was then neutralized, and the pH was subsequently adjusted to 3 with a 2 N HCl aqueous solution while cooling in an ice bath. The mixture was then back-transferred to a separatory funnel and EtOAc (5 mL) was added, the phases were separated and the aqueous phase was extracted again with EtOAc (2 x 3 mL). The combined organic phases were then dried with Na_2SO_4 and evaporated *in vacuo* to obtain pure **13** as a pale brown waxy solid (23.3 mg, 0.094 mmol, 94% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.01 – 7.81 (m, 4H), 7.73 – 7.61 (m, 2H), 7.55 – 7.34 (m, 4H), 7.14 – 7.05 (m, 1H) all signals appear as broad multiplets due to the equilibrium between the two tautomers; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 171.6, 170.9, 140.8, 138.9, 137.7, 136.8, 133.3, 133.0, 132.2, 132.1, 128.4, 128.3, 127.7, 127.6, 127.2, 126.5, 126.3, 122.1 all peaks are given without assignment;

HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{13}O_2$ 249.0910; found 249.0906. Data in agreement with the literature.[15]

3. Voltammetry Analysis

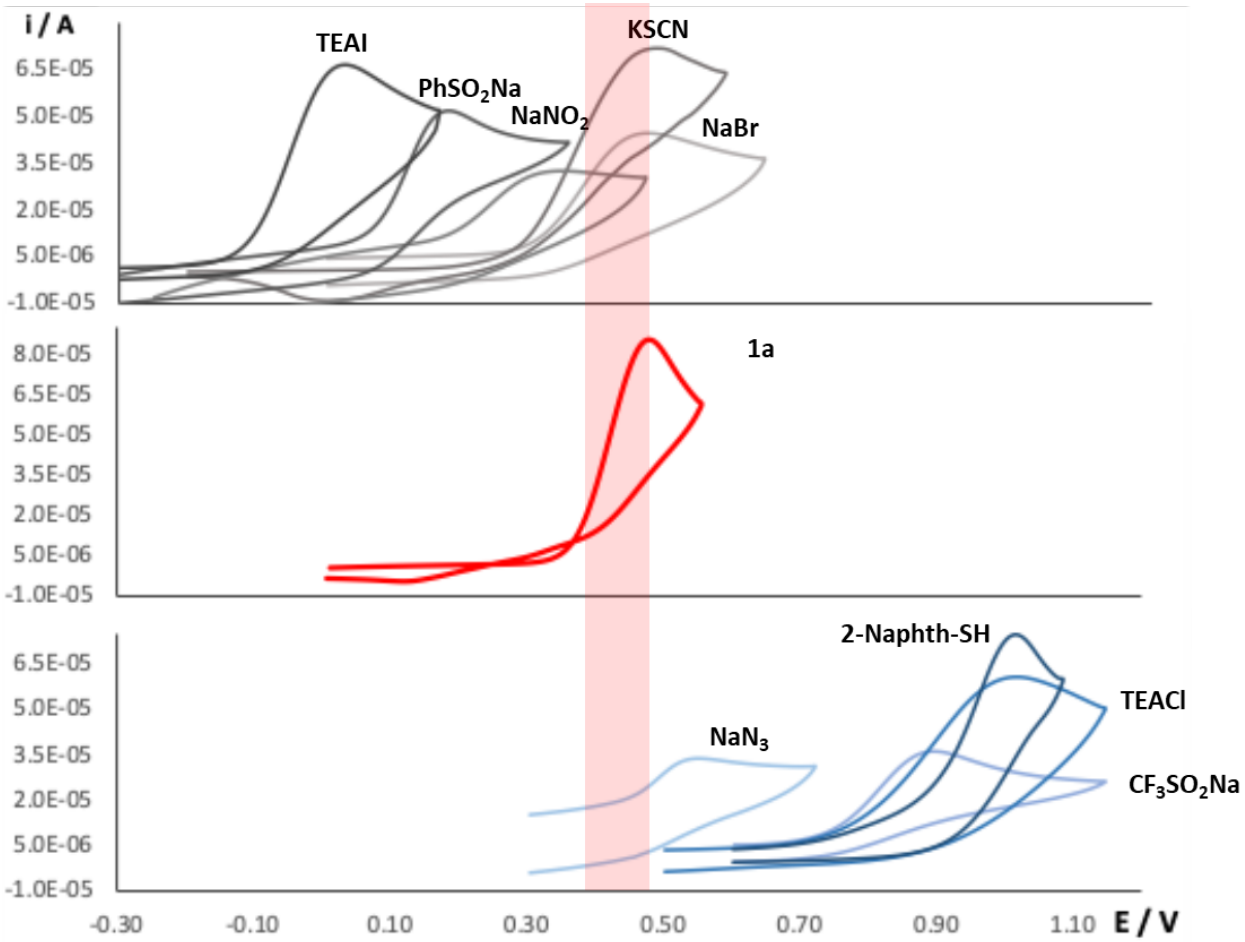
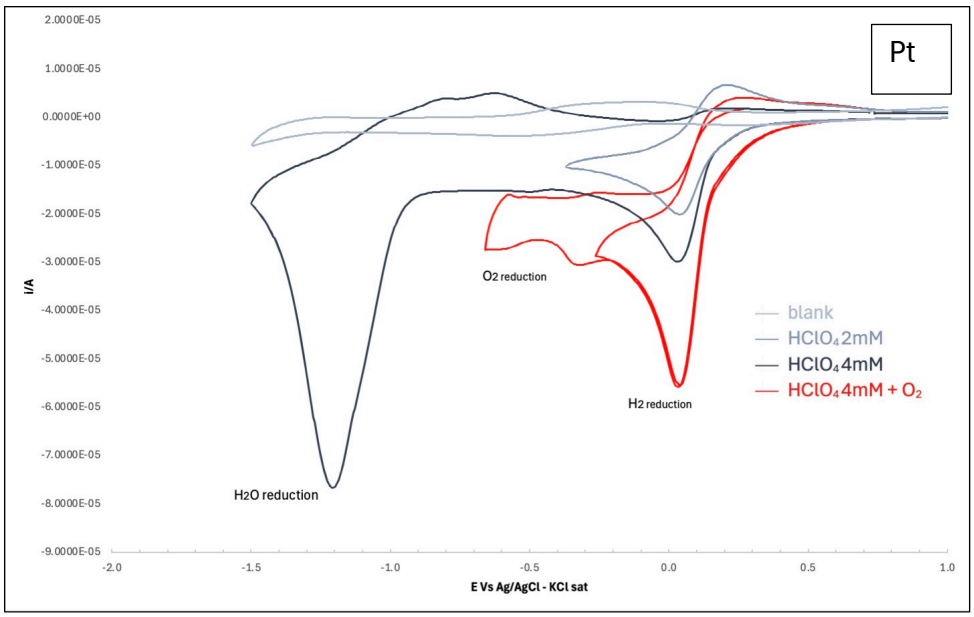


Figure S1. Upper: CV responses collected in a 5 mM solution of (respectively) TEAI (Tetraethylammonium iodide), $PhSO_2Na$, $NaNO_2$, KSCN, NaBr, 0.1 M $LiClO_4$ electrolyte, in anhydrous ACN, 0.050 V^{-1} potential scan rate. Middle: CV response collected in a 5mM solution of **1a**, 0.1 M $LiClO_4$ electrolyte, in anhydrous ACN, 0.050 V^{-1} potential scan rate. Lower: CV responses collected in a 5mM solution of (respectively) NaN_3, Naphthalene-thiol (2-Naphth-SH), TEACl (Tetraethylammonium chloride), and CF_3SO_2Na, 0.1 M $LiClO_4$ electrolyte, in anhydrous ACN, 0.050 V^{-1} potential scan rate. All potentials (values in the main text) are reported versus the Fc/Fc^+ redox couple.


Pt
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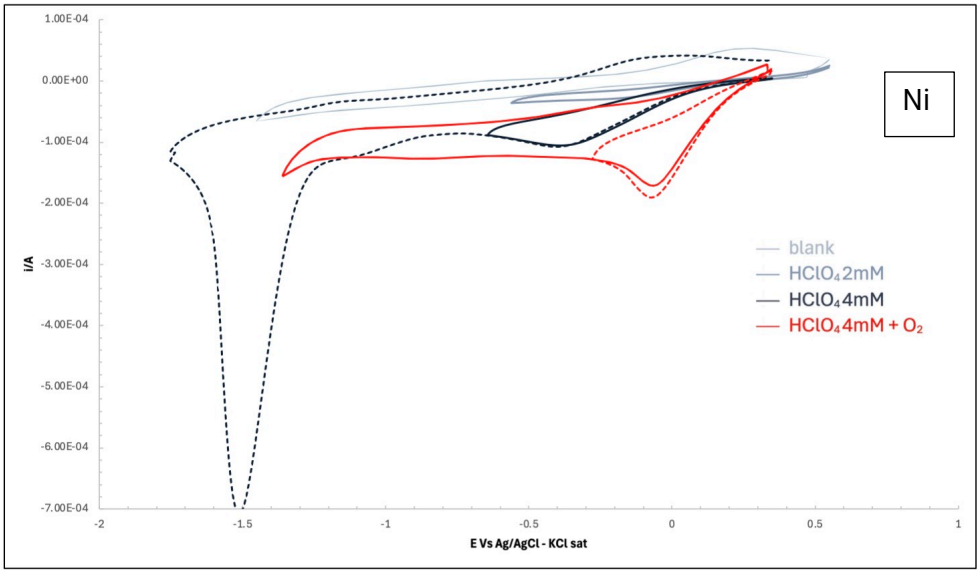
0.0000E+00
-1.0000E-05
-2.0000E-05
-3.0000E-05
-4.0000E-05
-5.0000E-05
-6.0000E-05
-7.0000E-05
-8.0000E-05
-9.0000E-05
i/A
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
E Vs Ag/AgCl - KCl sat
O2 reduction
H2 reduction
H2O reduction
blank
HClO4 2mM
HClO4 4mM
HClO4 4mM + O2


Ni
1.00E-04
0.00E+00
-1.00E-04
-2.00E-04
-3.00E-04
-4.00E-04
-5.00E-04
-6.00E-04
-7.00E-04
i/A
-2
-1.5
-1
-0.5
0
0.5
1
E Vs Ag/AgCl - KCl sat
blank
HClO4 2mM
HClO4 4mM
HClO4 4mM + O2

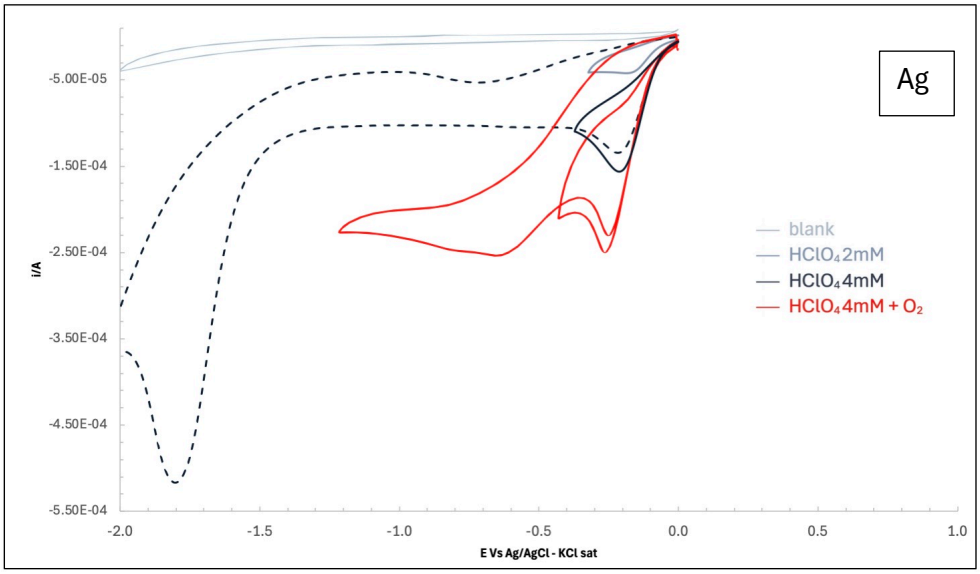

Ag
-5.00E-05
-1.50E-04
-2.50E-04
-3.50E-04
-4.50E-04
-5.50E-04
i/A
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
E Vs Ag/AgCl - KCl sat
blank
HClO4 2mM
HClO4 4mM
HClO4 4mM + O2

Figure S2. CV response of H_2, O_2 and H_2O reduction using Pt (upper), Ni (middle), and Ag (lower) as cathodes, with 0.1 M $LiClO_4$ electrolyte in anhydrous ACN, 0.050 V^{-1} potential scan rate. All potentials are reported versus the Ag/AgCl – KCl_{sat} redox couple.

Figure S2 shows that the reduction of H_2 occurs at less negative potentials (0.02 V) compared to O_2 (-0.28 V). However, under voltammetric analysis performed in air, the presence of O_2 appears to facilitate H_2 reduction. This observation reinforces our experimental findings, where the reported reaction proceeds better under air than under Ar. This indicates that air plays a dual role: initially counterbalancing the reaction (when the concentration of H^+ liberated from the reacted starting material is very low) and subsequently enhancing the hydrogen evolution process.

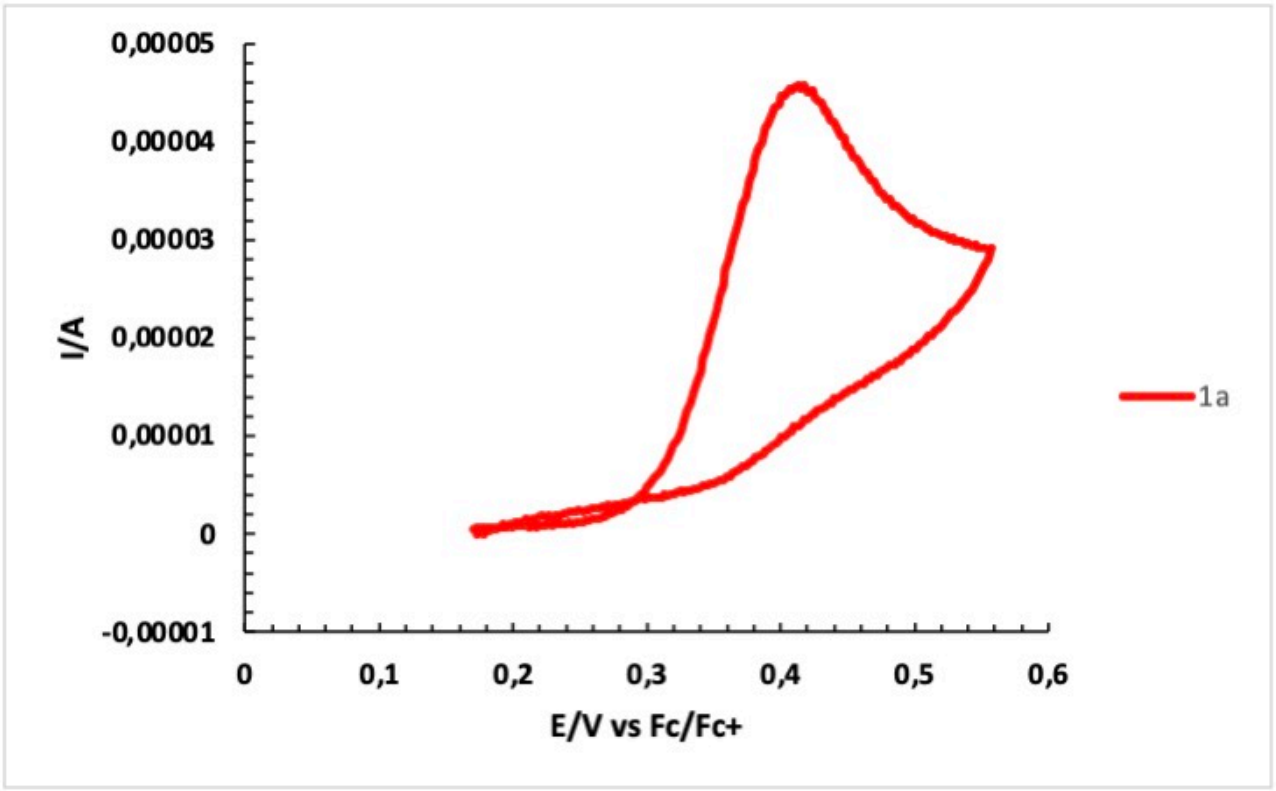
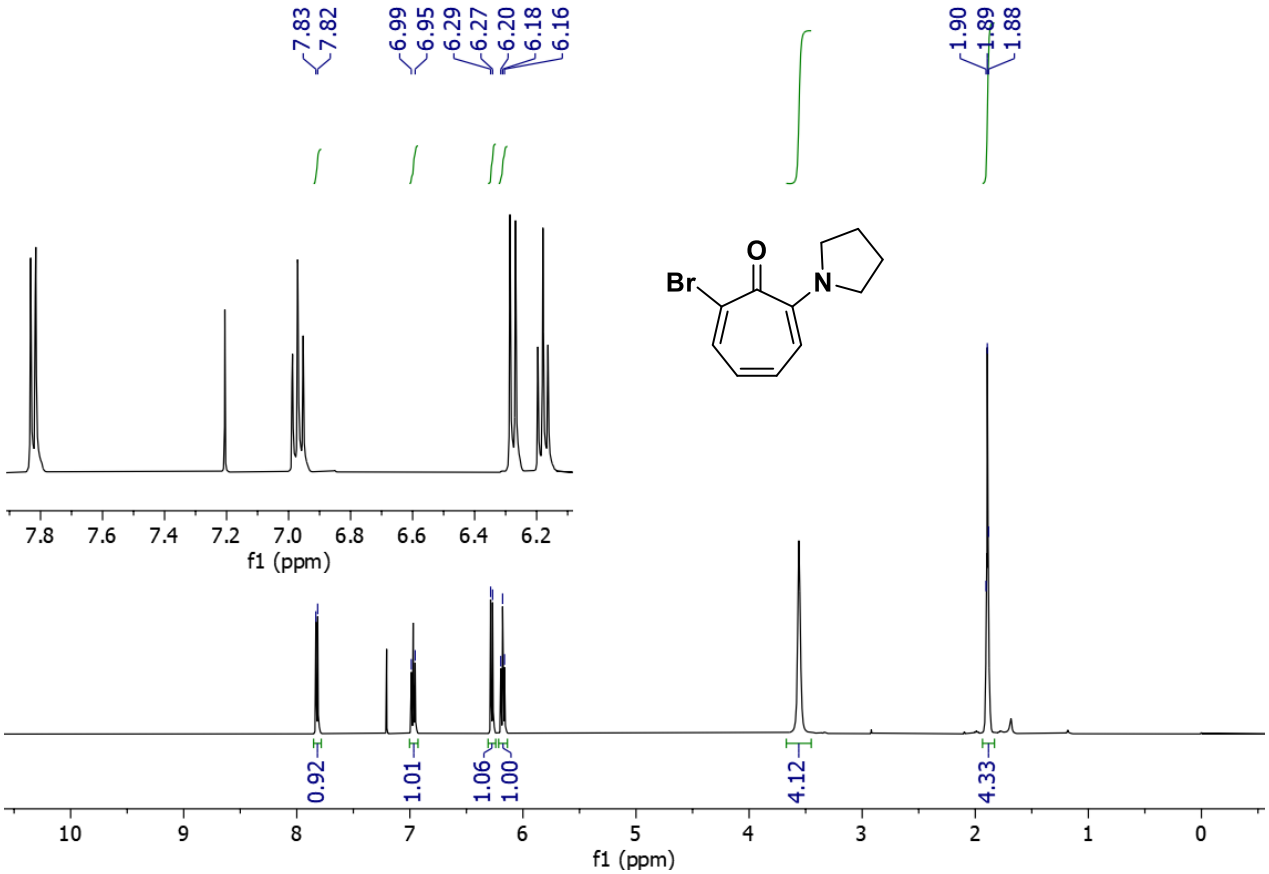


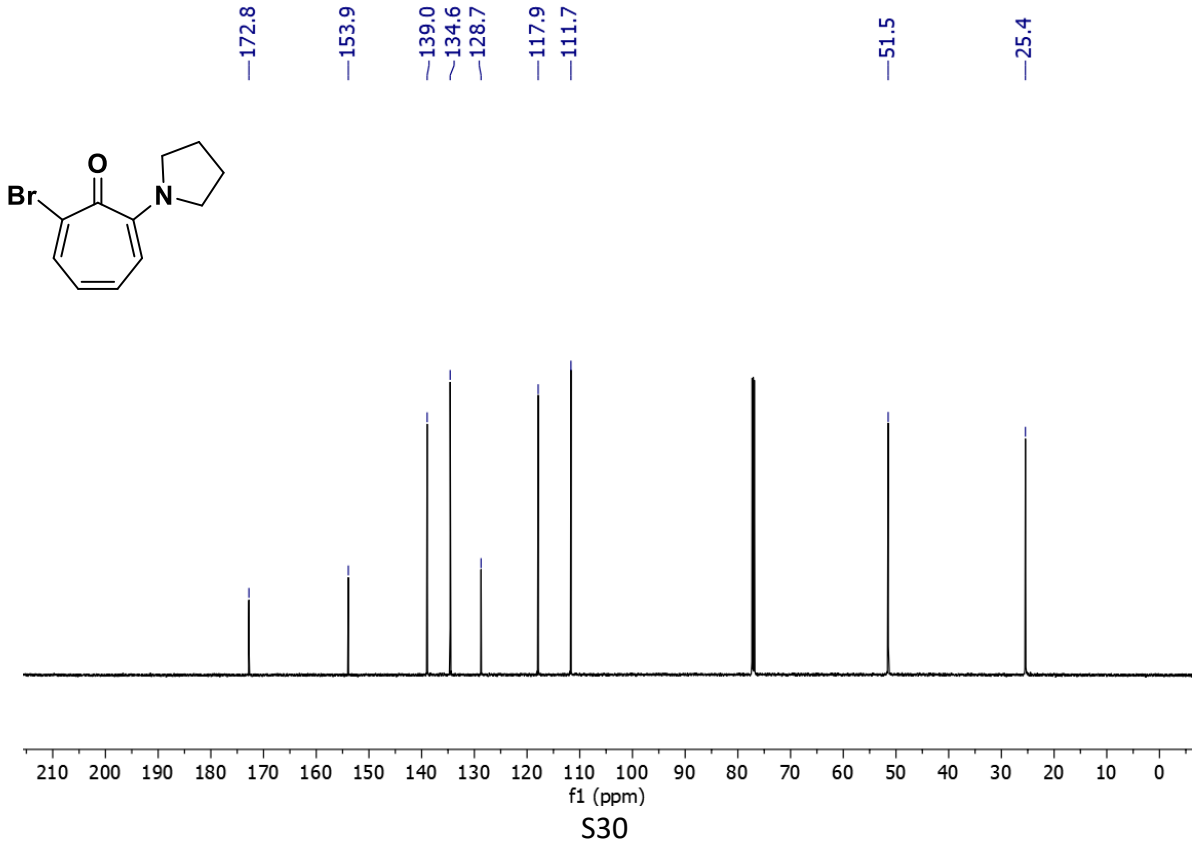
Figure S3. CV response collected in a 5mM solution of **1a**, 0.1 M $TBAClO_4$ (tetrabutylammonium perchlorate) electrolyte, in anhydrous ACN, 0.050 V^{-1} potential scan rate. The potential (0.41 V) is reported versus the Fc/Fc^+ redox couple.

4. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of new compounds

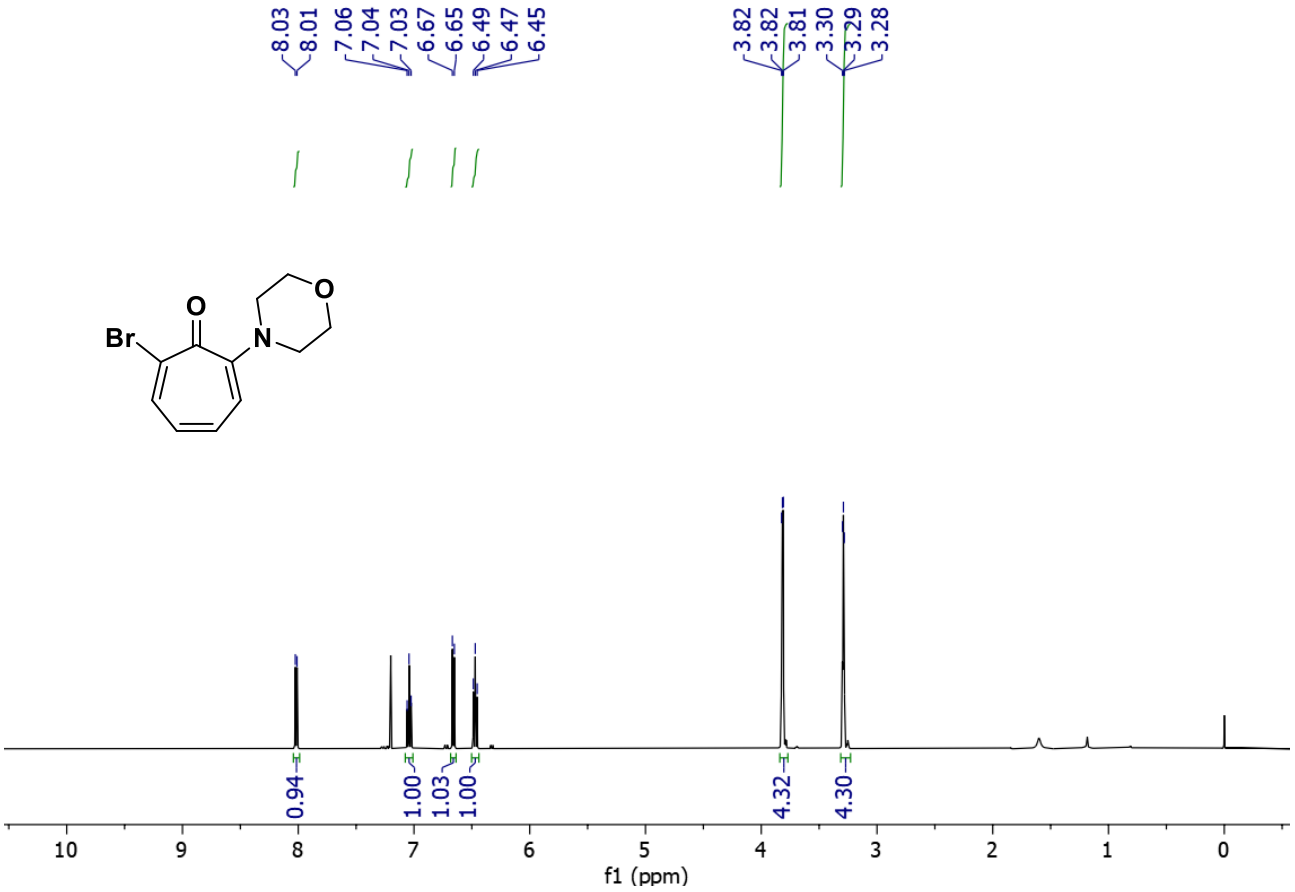
2aa ^{1}H NMR (600 MHz, $CDCl_3$)



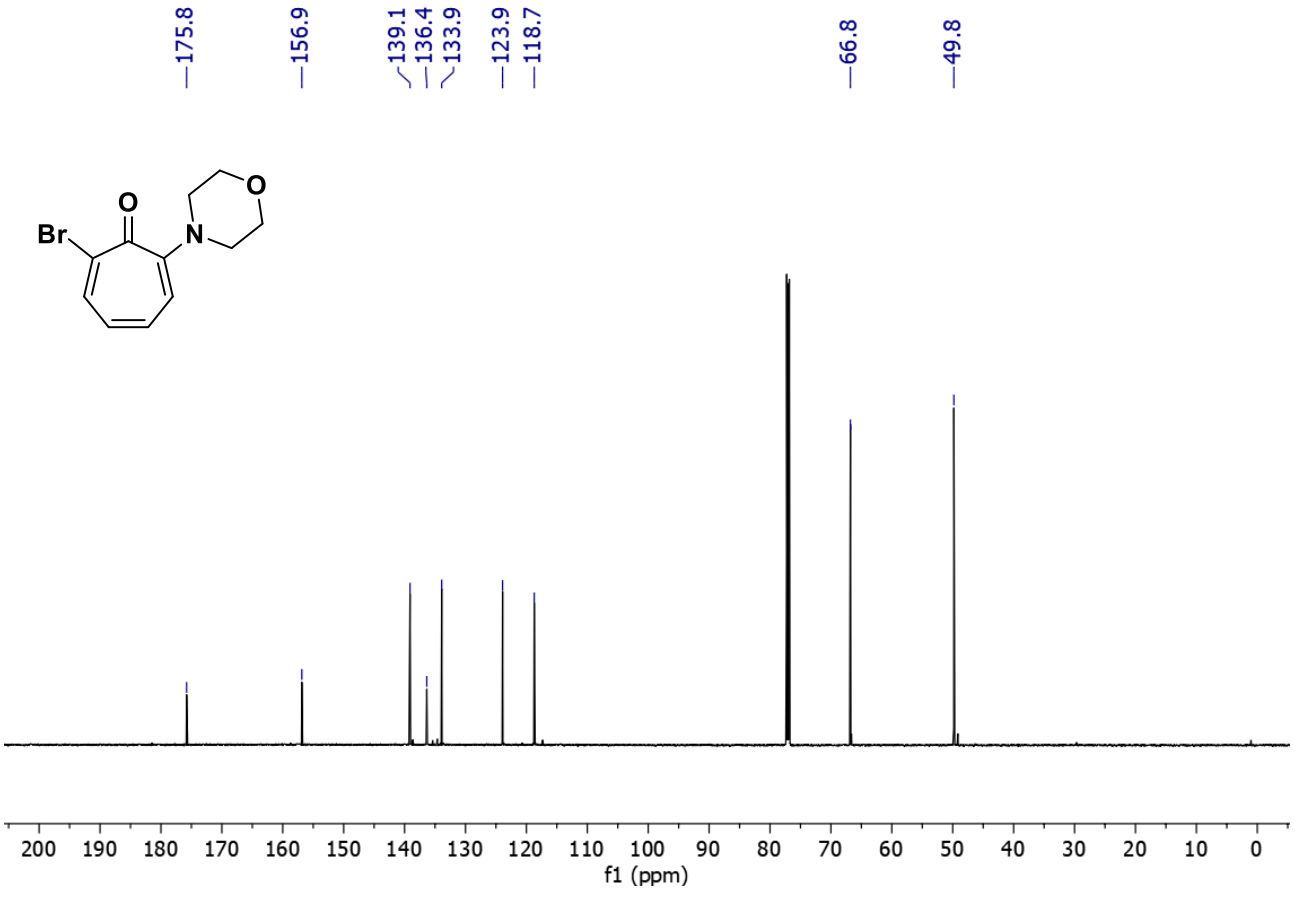
2aa ^{13}C NMR (150 MHz, $CDCl_3$)



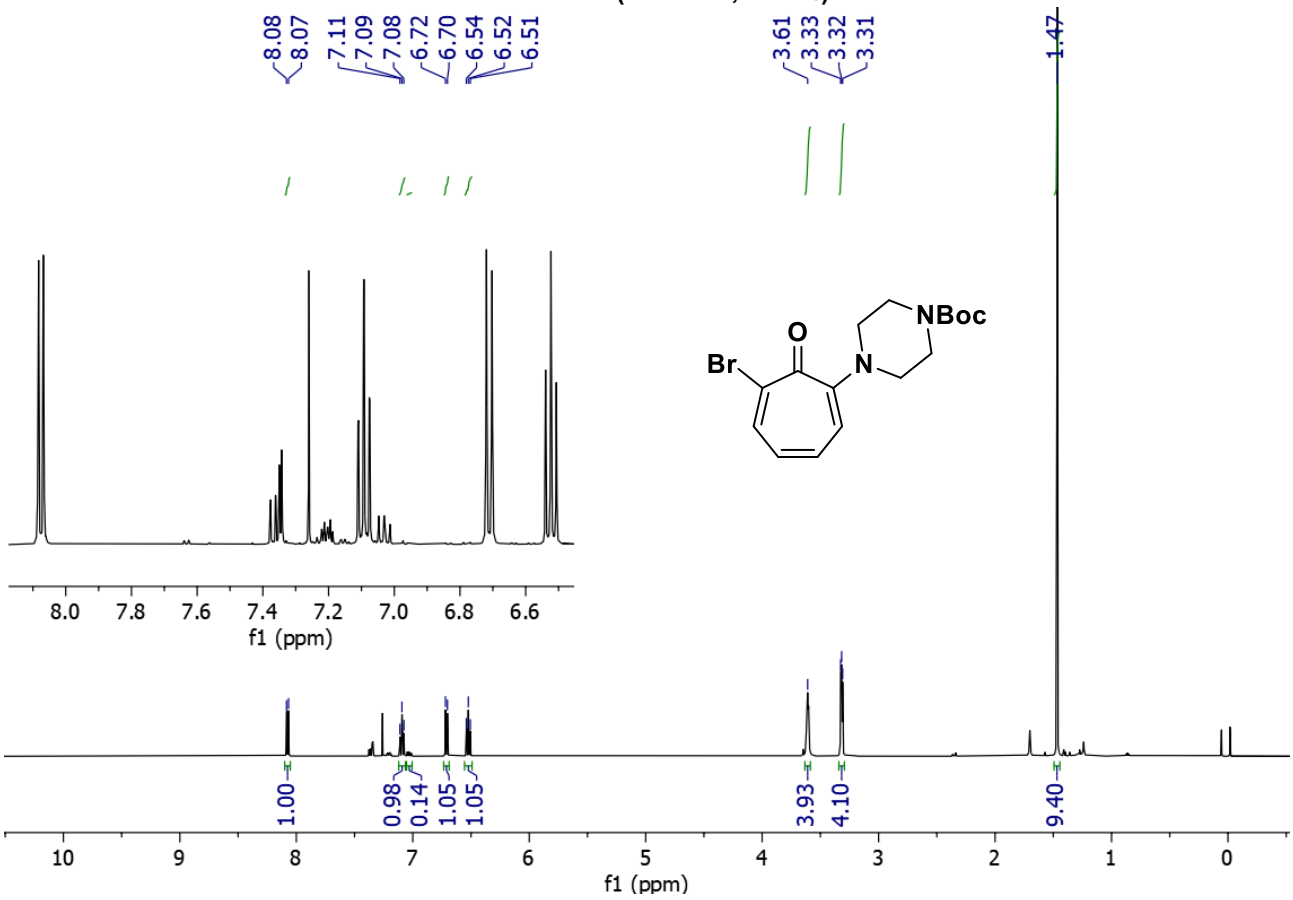
2ba ^{1}H NMR (600 MHz, $CDCl_3$)



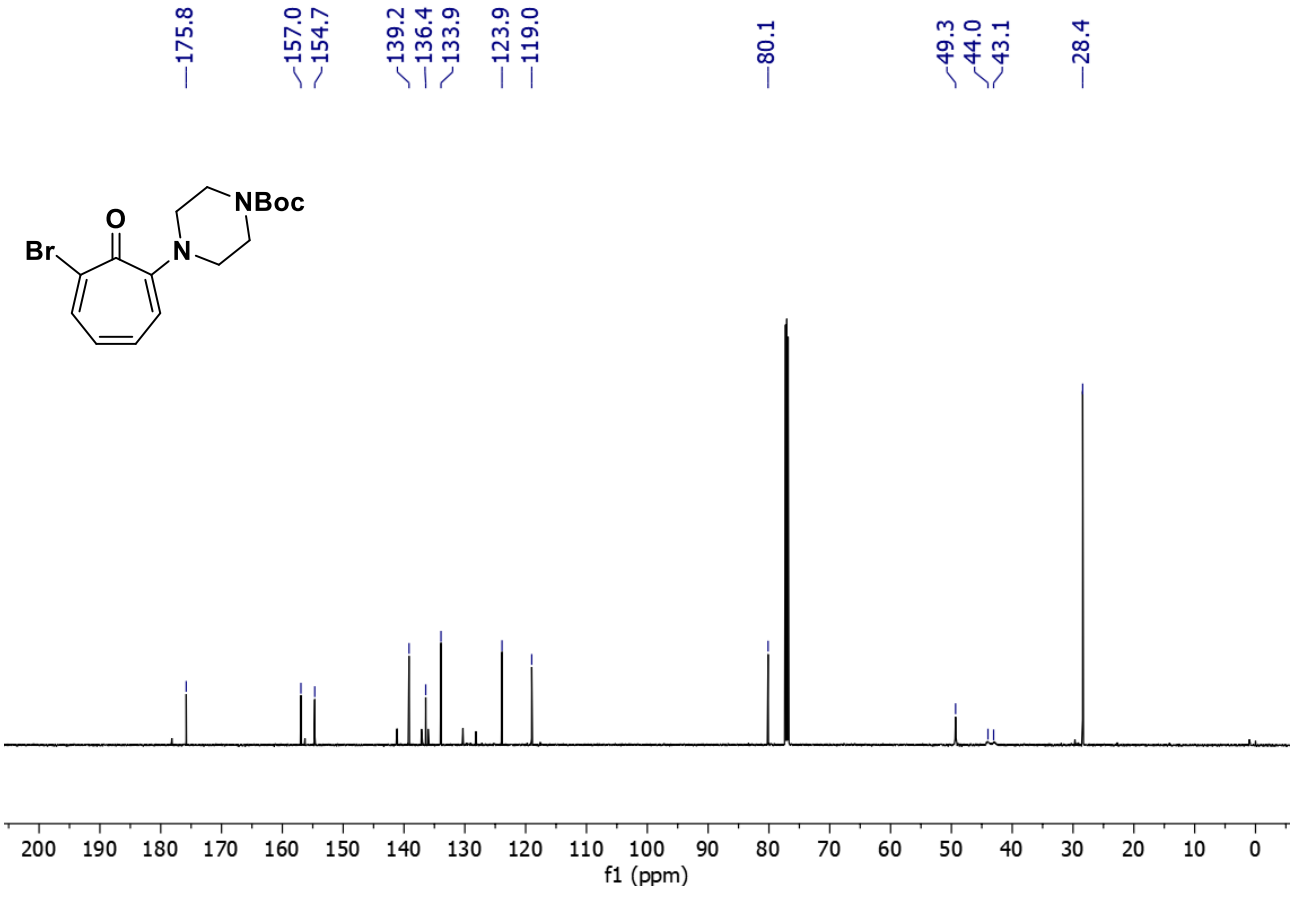
2ba ^{13}C NMR (150 MHz, $CDCl_3$)



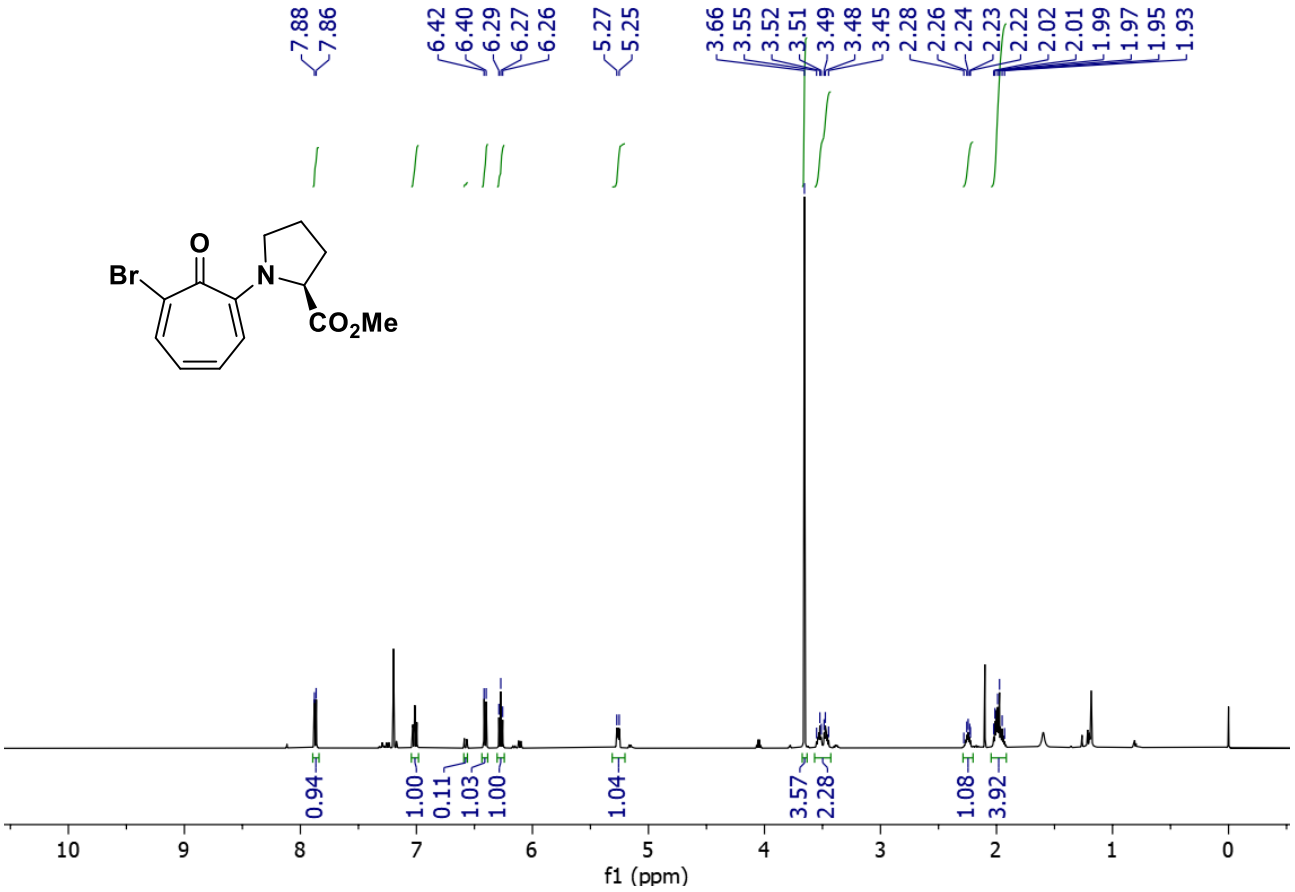
2ca ^{1}H NMR (600 MHz, $CDCl_3$)



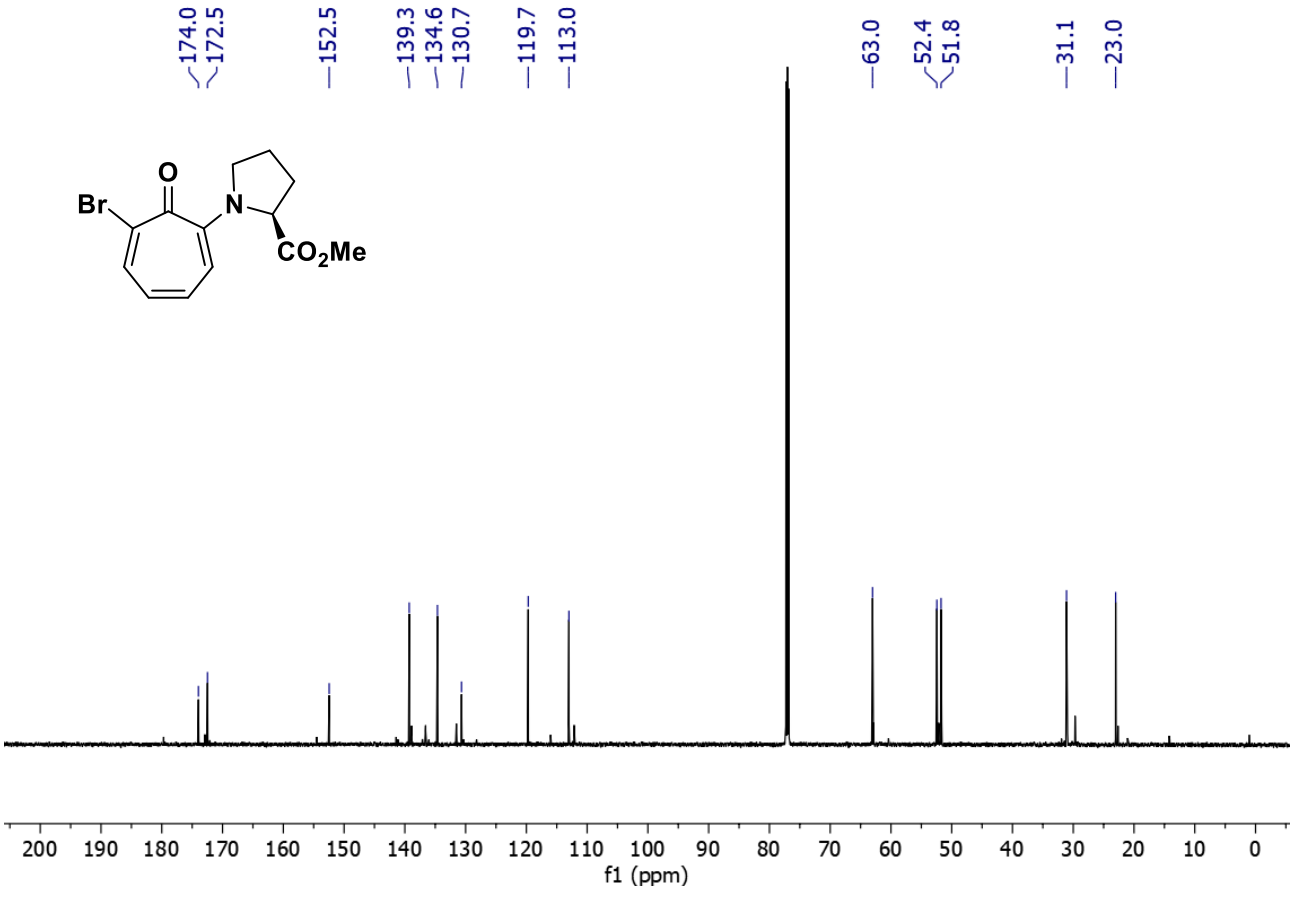
2ca ^{13}C NMR (150 MHz, $CDCl_3$)



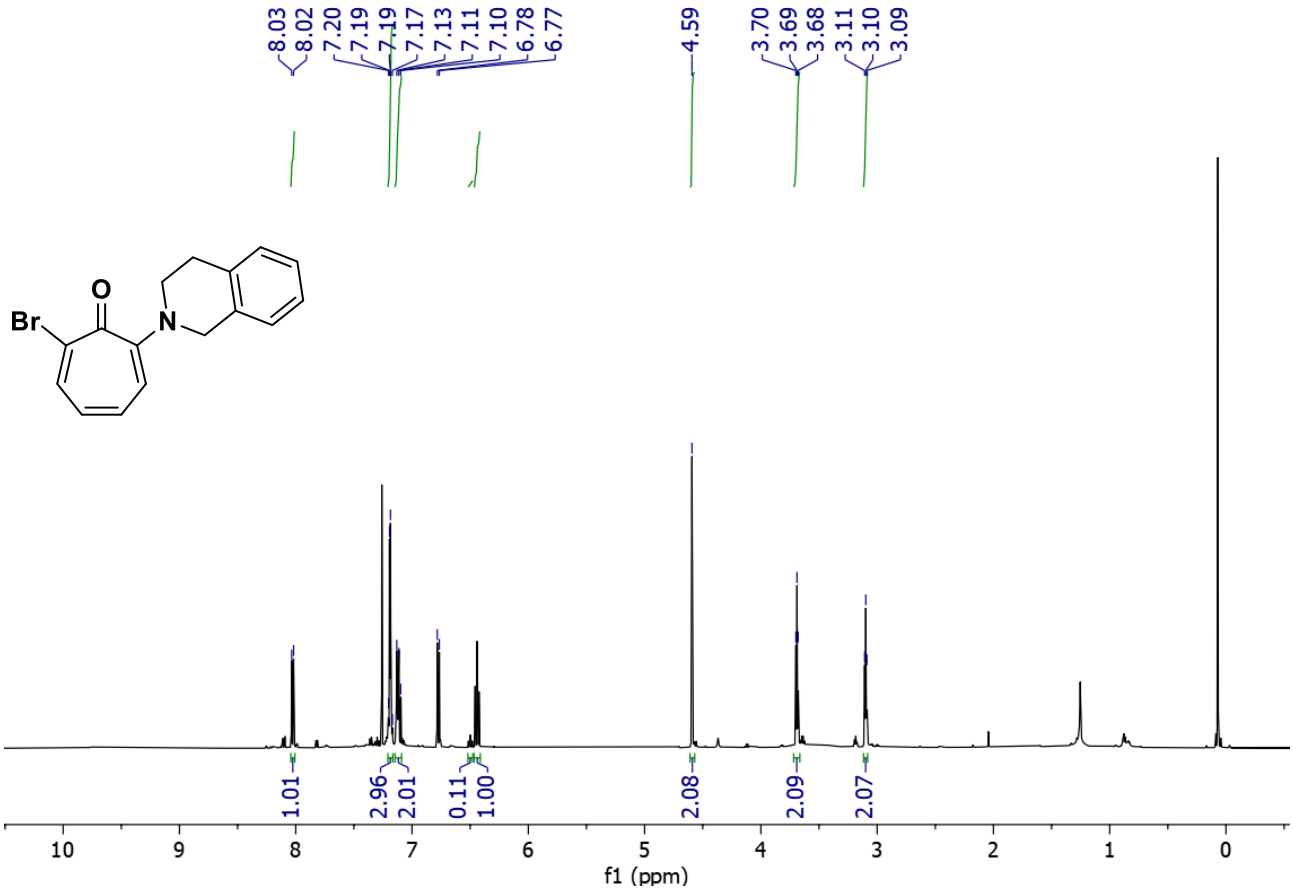
2da ^{1}H NMR (600 MHz, $CDCl_3$)



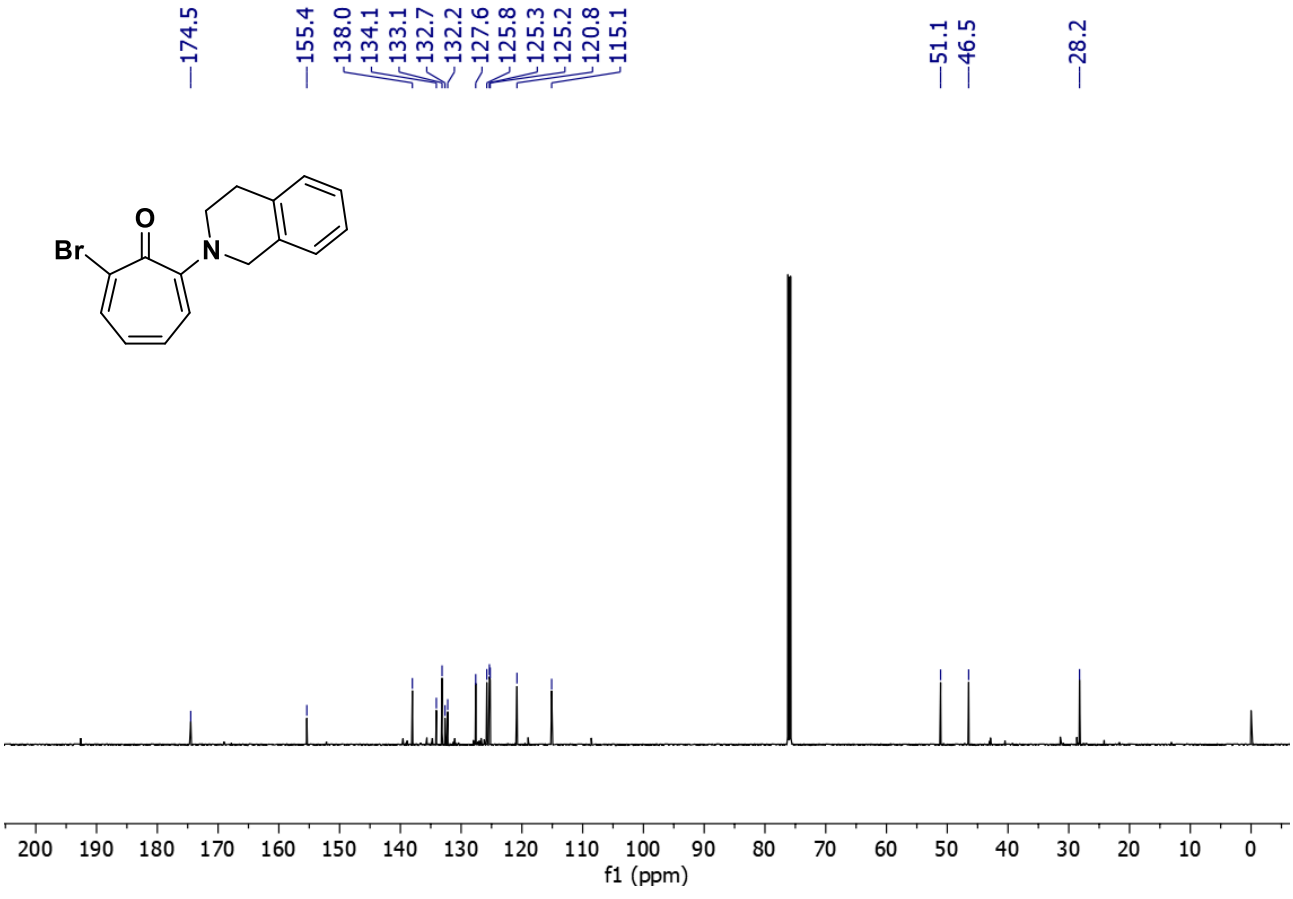
2da ^{13}C NMR (150 MHz, $CDCl_3$)



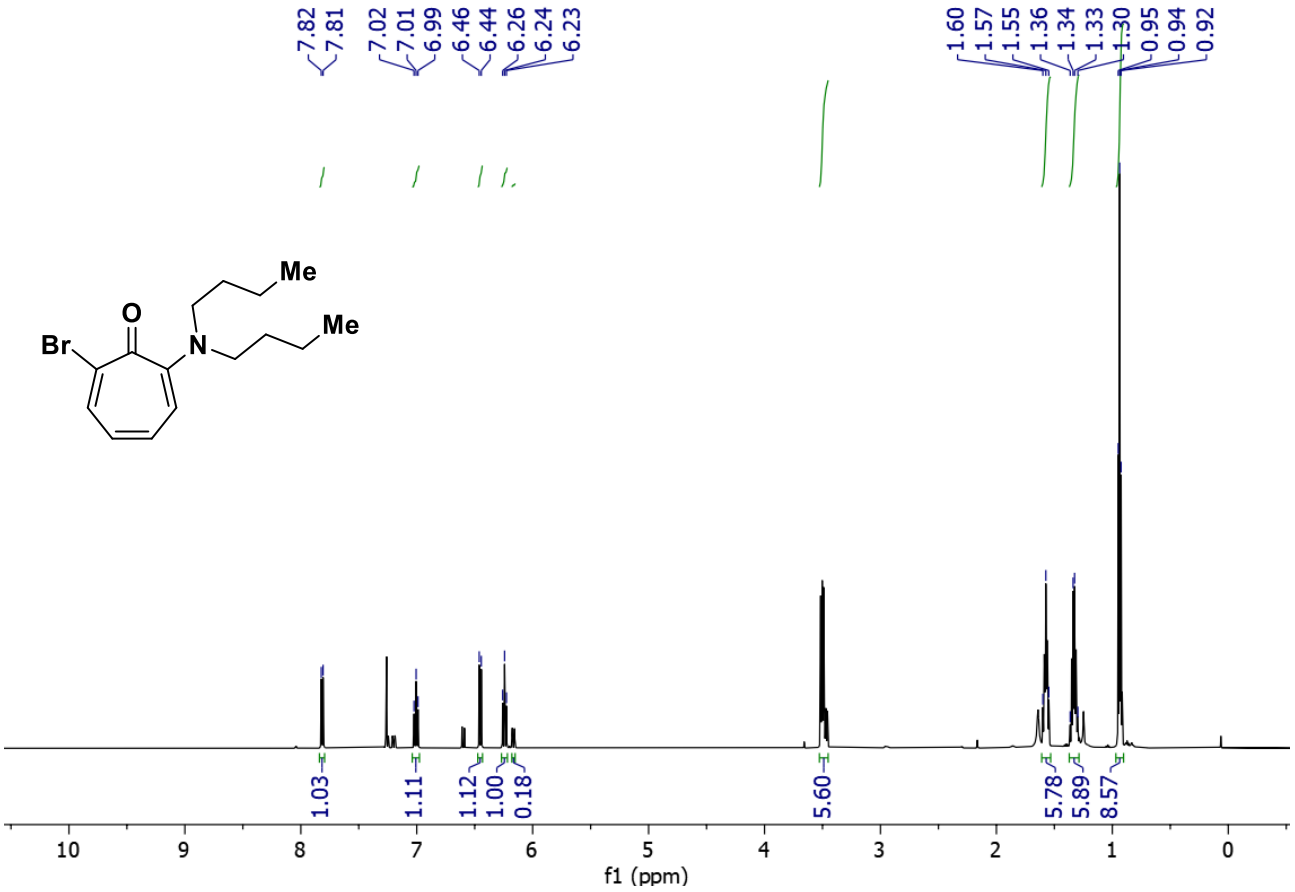
2ea ^{1}H NMR (600 MHz, $CDCl_3$)



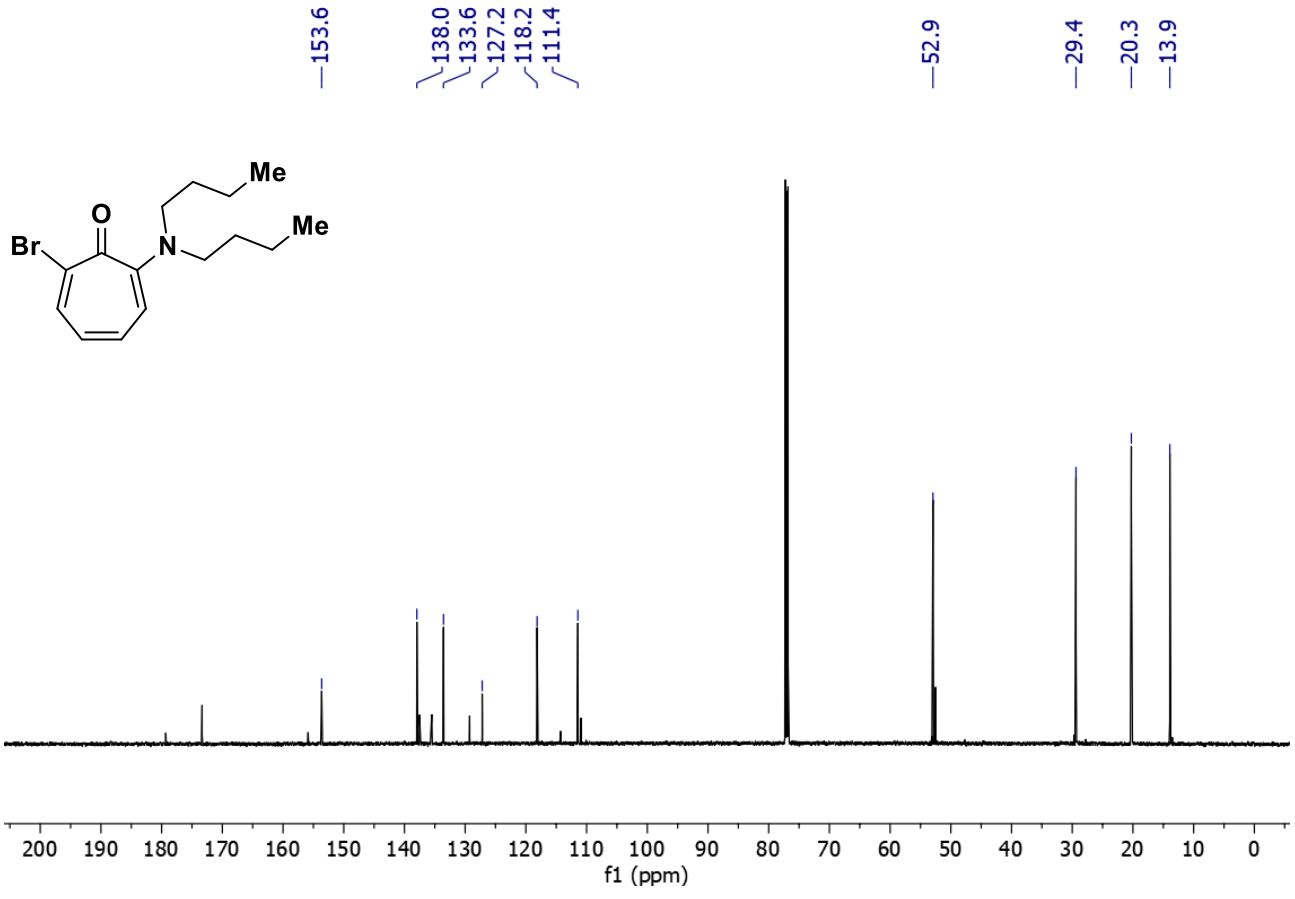
2ea ^{13}C NMR (150 MHz, $CDCl_3$)



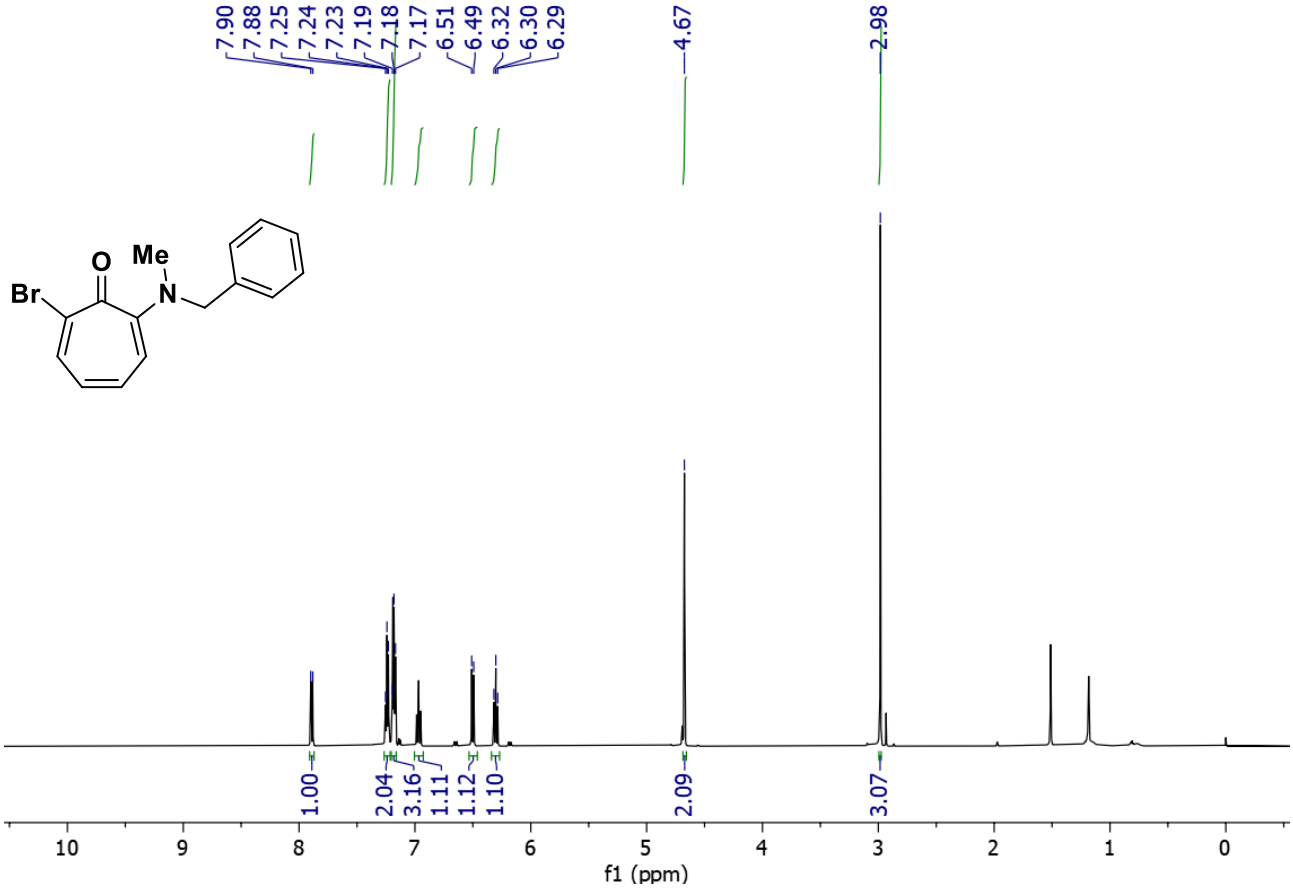
2fa ^{1}H NMR (600 MHz, $CDCl_3$)



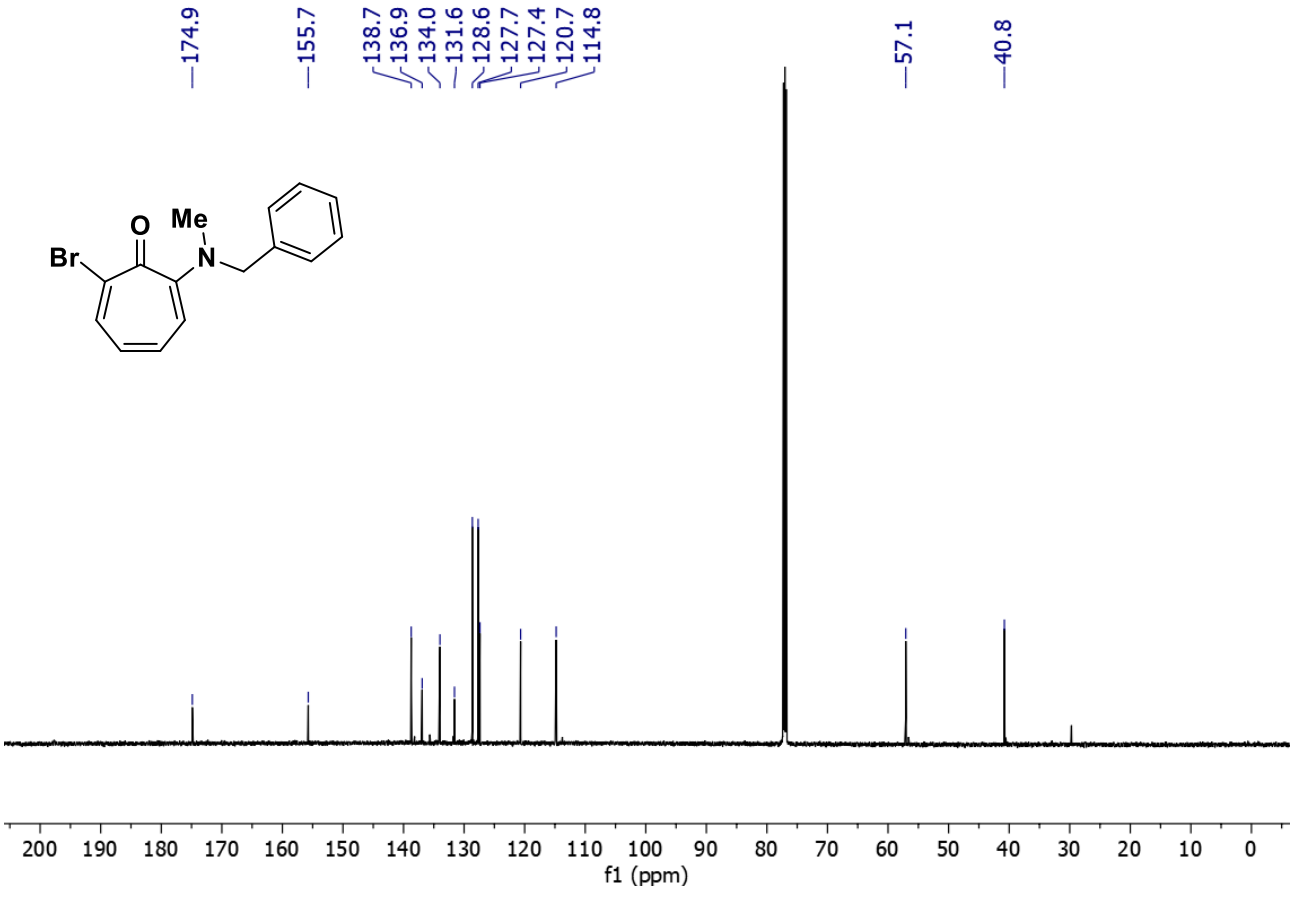
2fa ^{13}C NMR (150 MHz, $CDCl_3$)



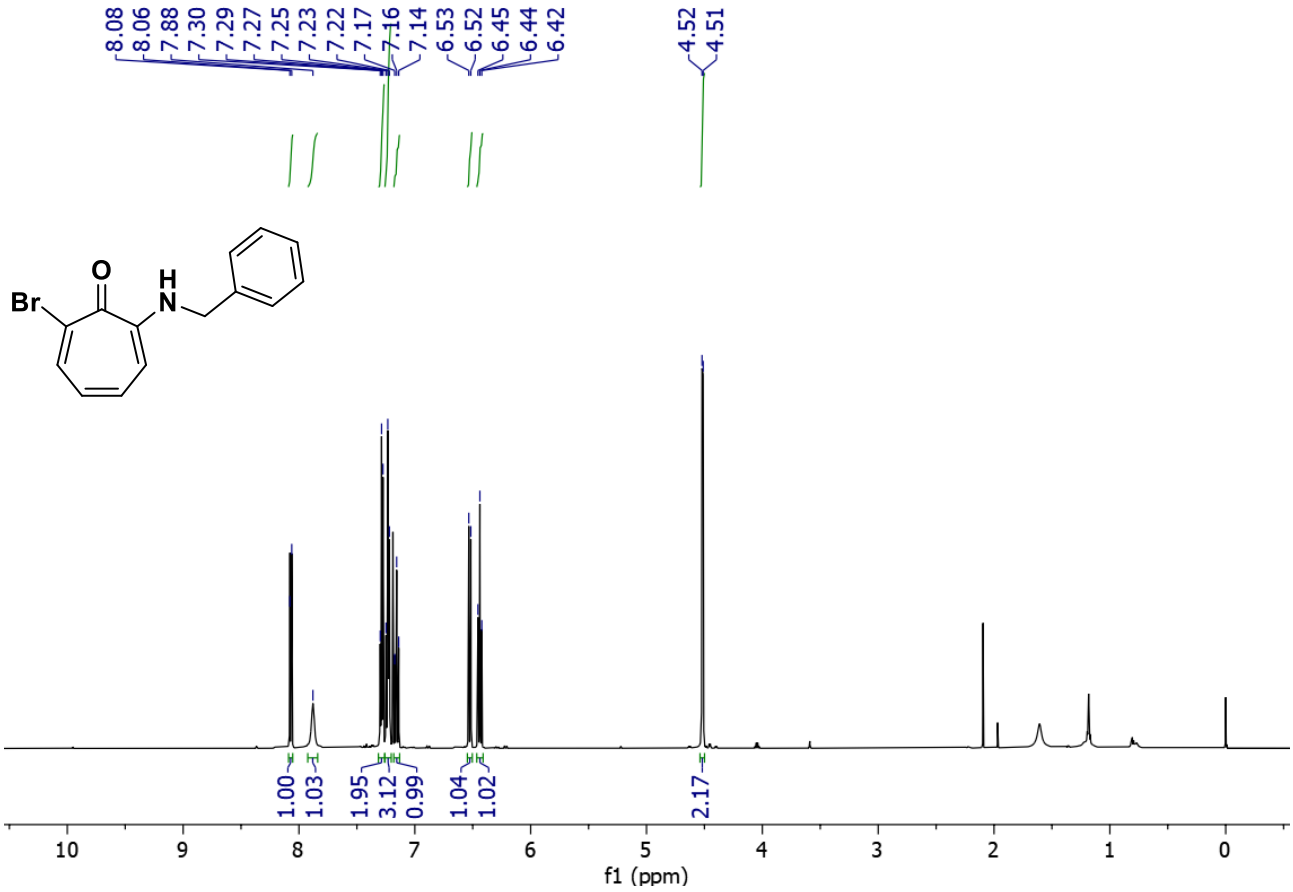
2ga ^{1}H NMR (600 MHz, $CDCl_3$)



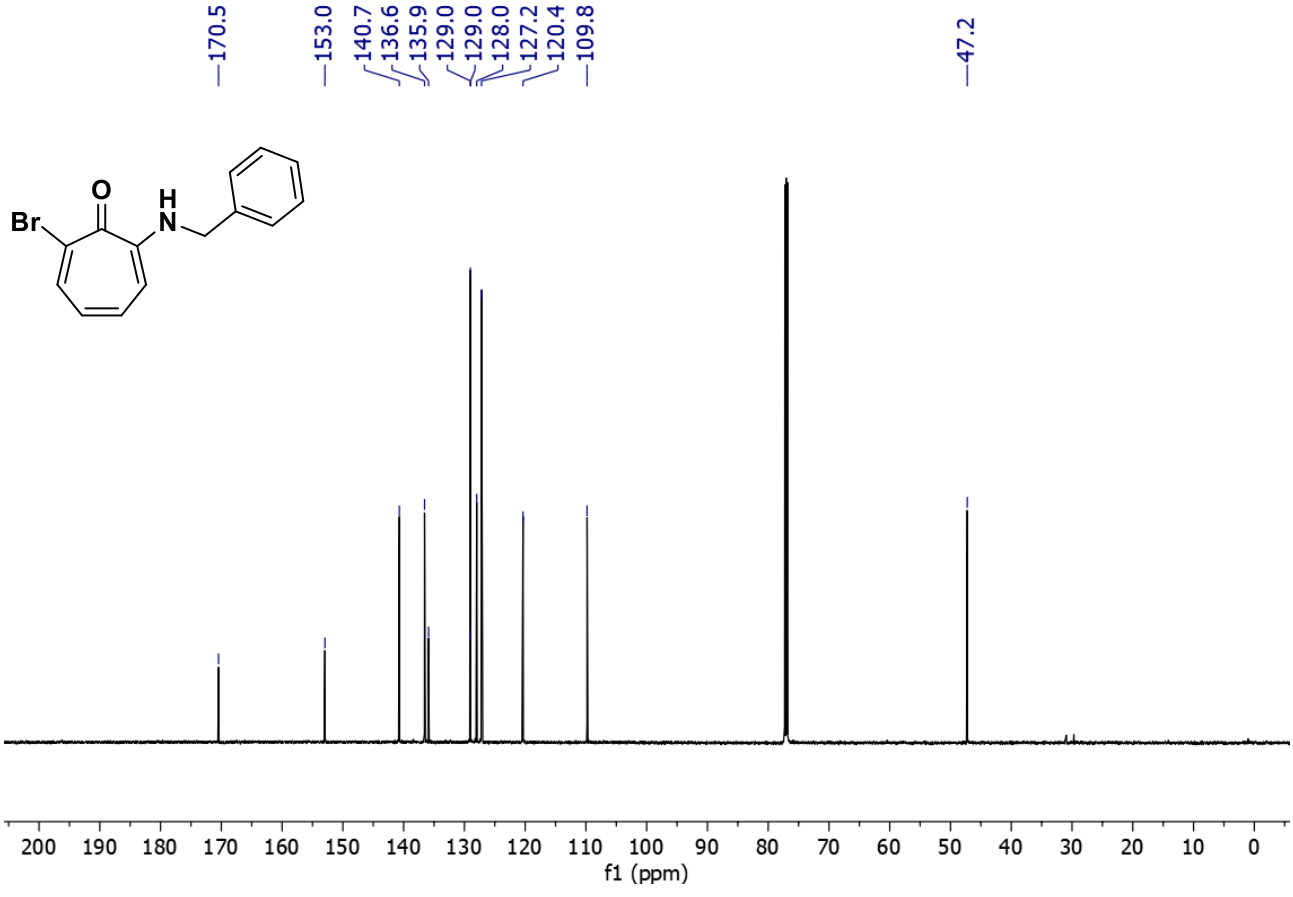
2ga ^{13}C NMR (150 MHz, $CDCl_3$)



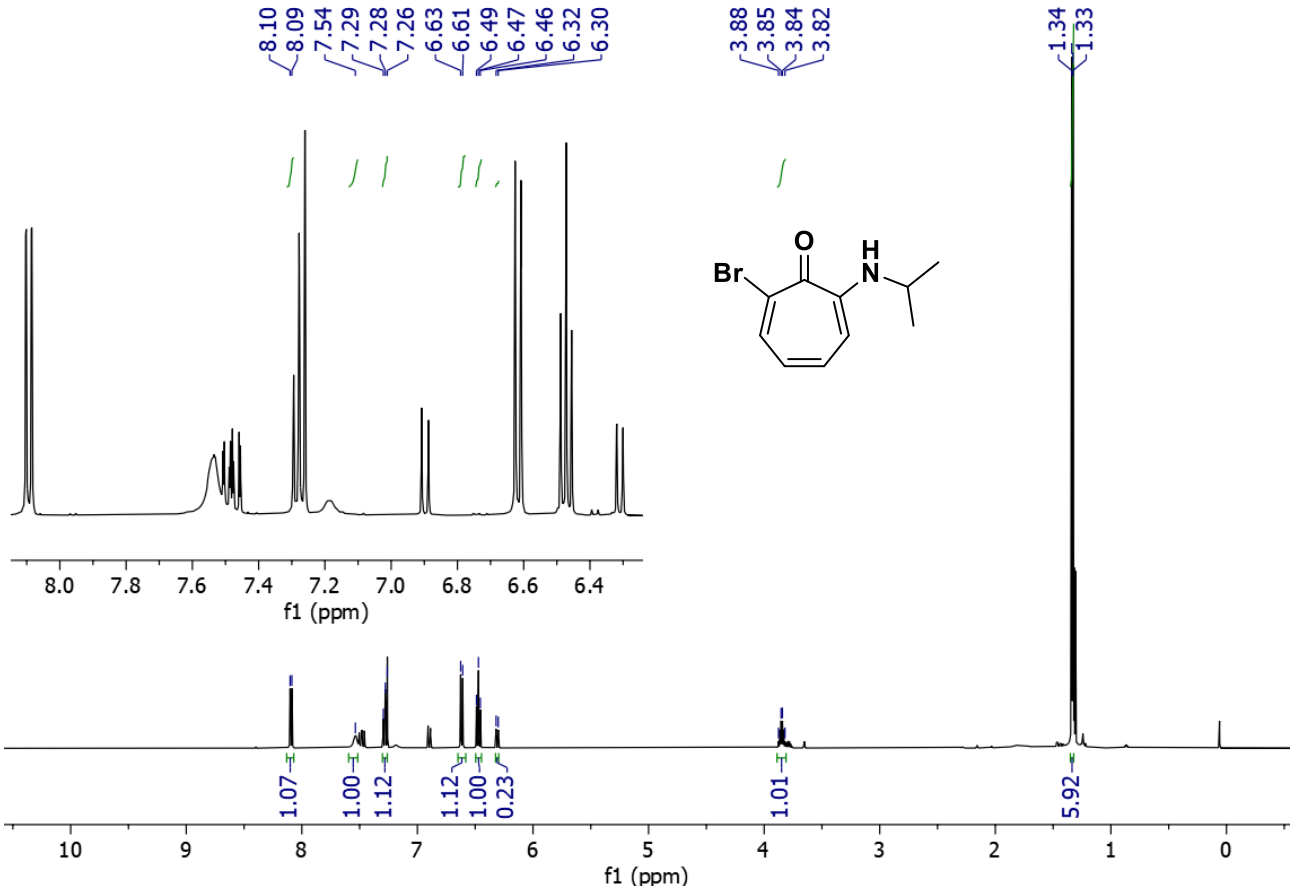
2ha ^{1}H NMR (600 MHz, $CDCl_3$)



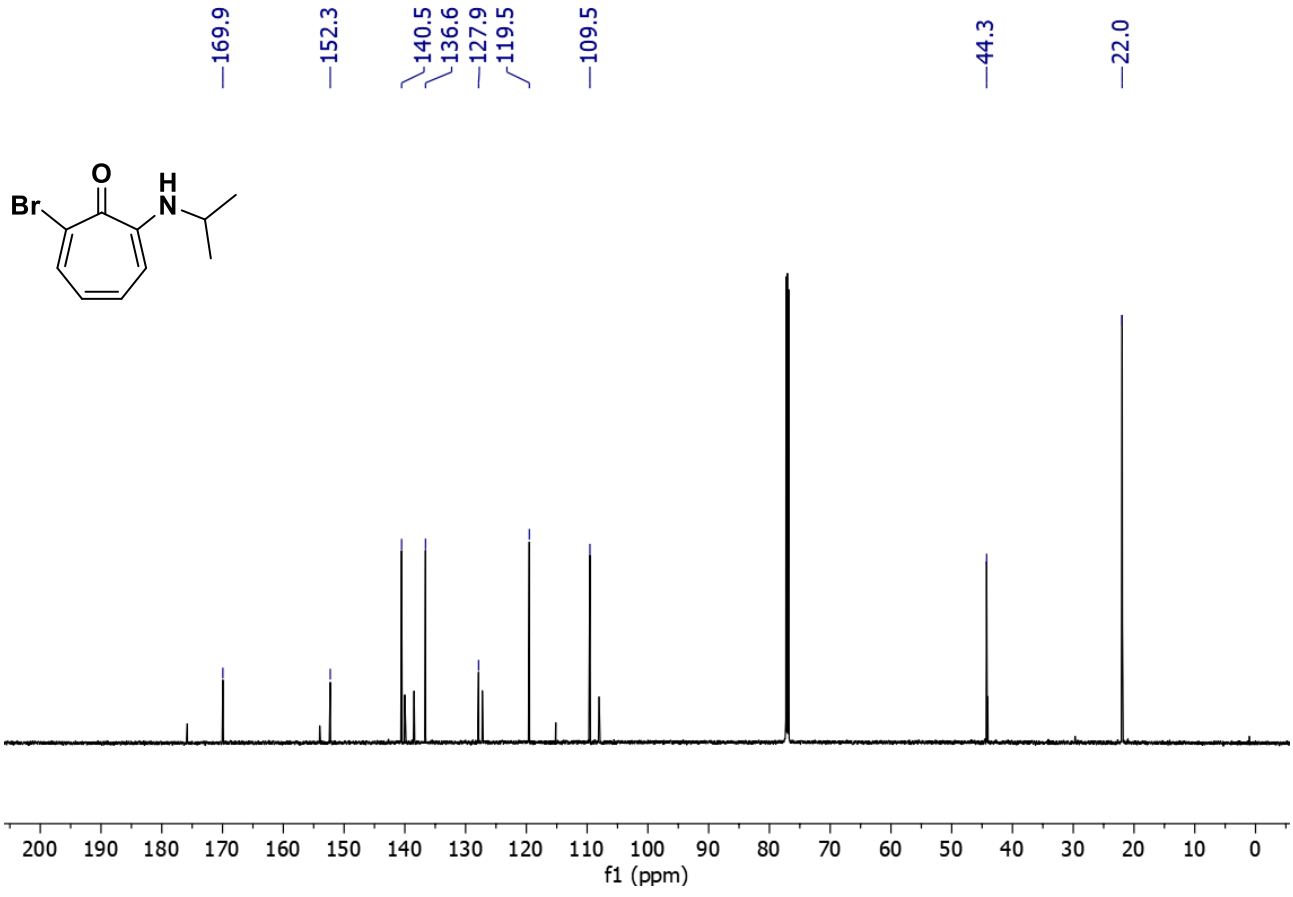
2ha ^{13}C NMR (150 MHz, $CDCl_3$)



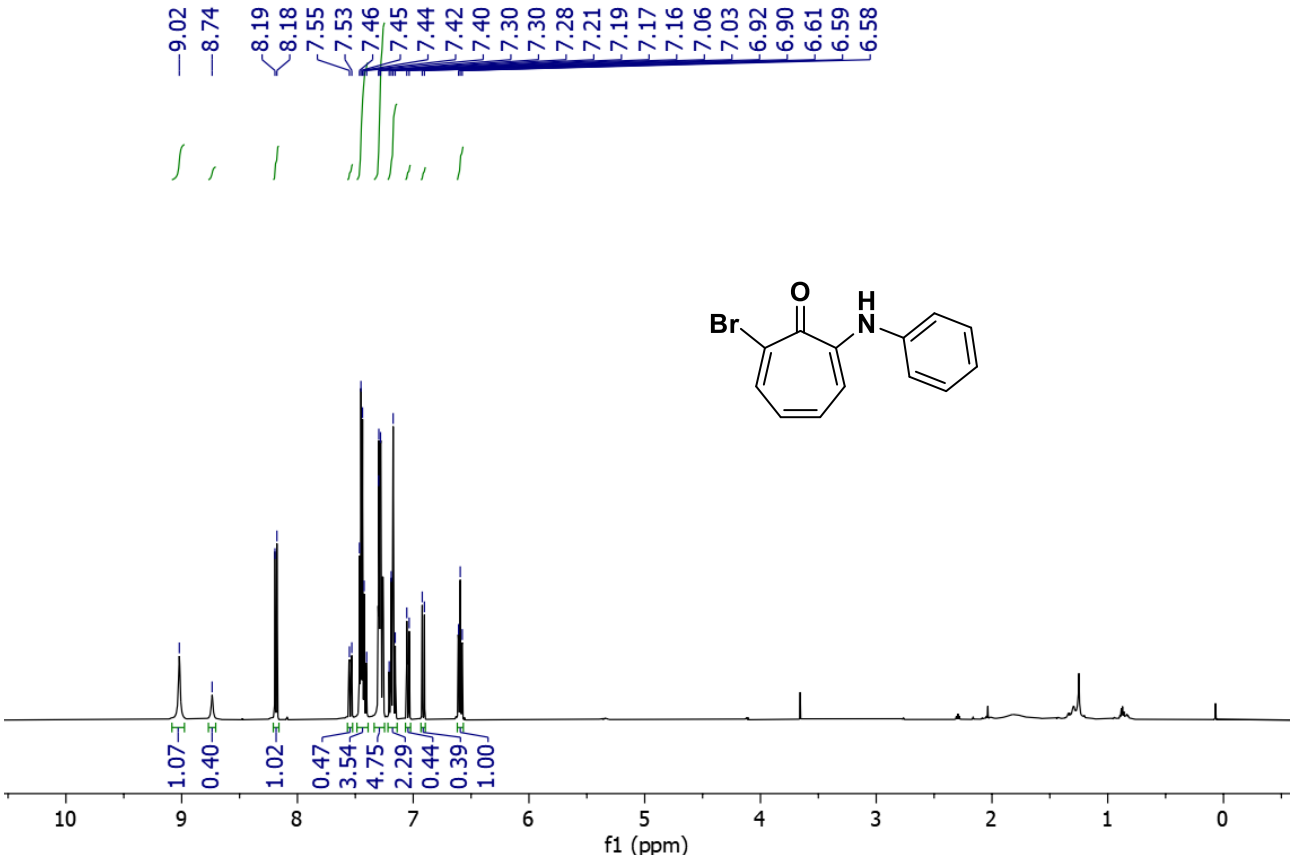
2ia ^{1}H NMR (600 MHz, $CDCl_3$)



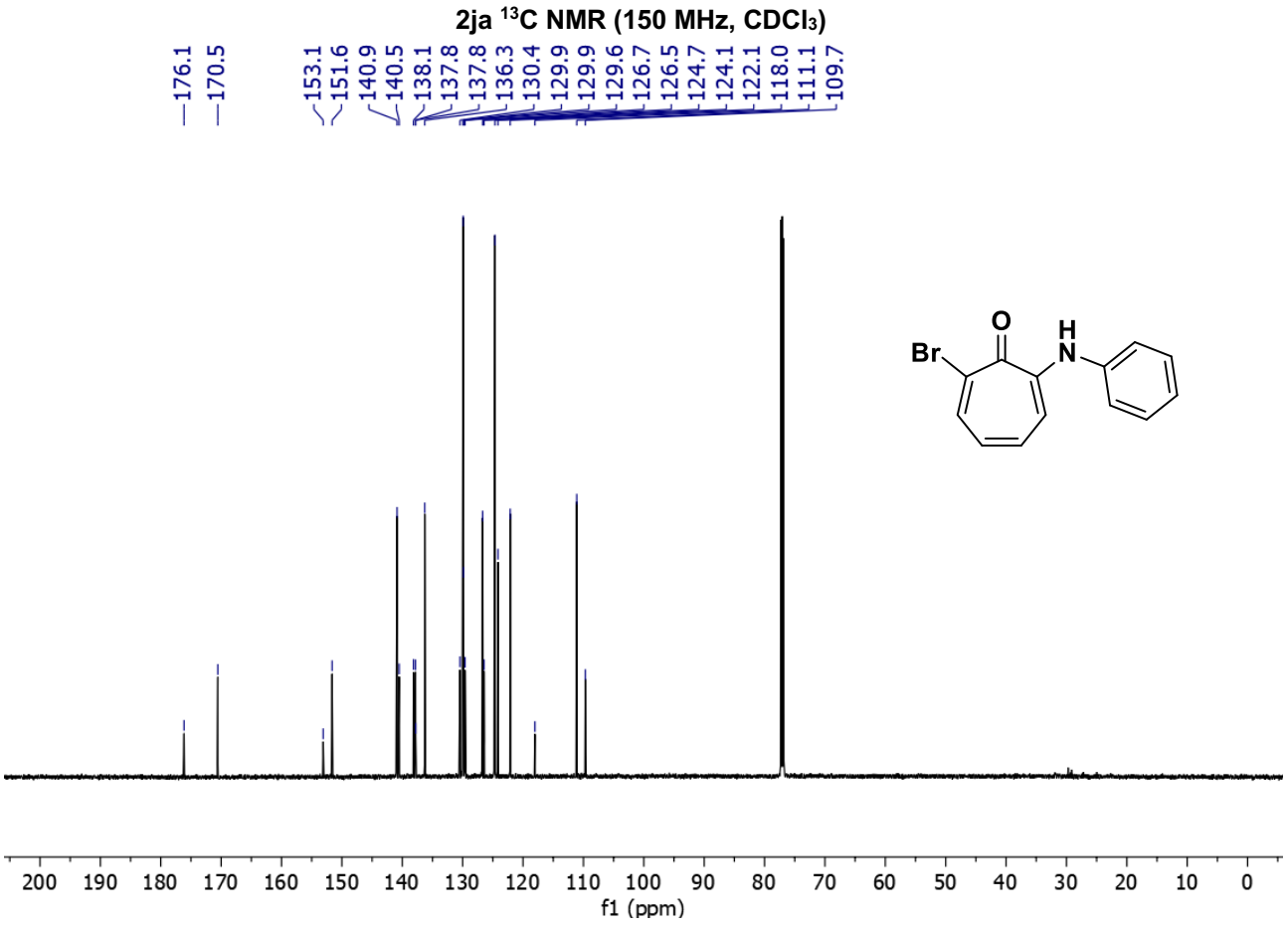
2ia ^{13}C NMR (150 MHz, $CDCl_3$)



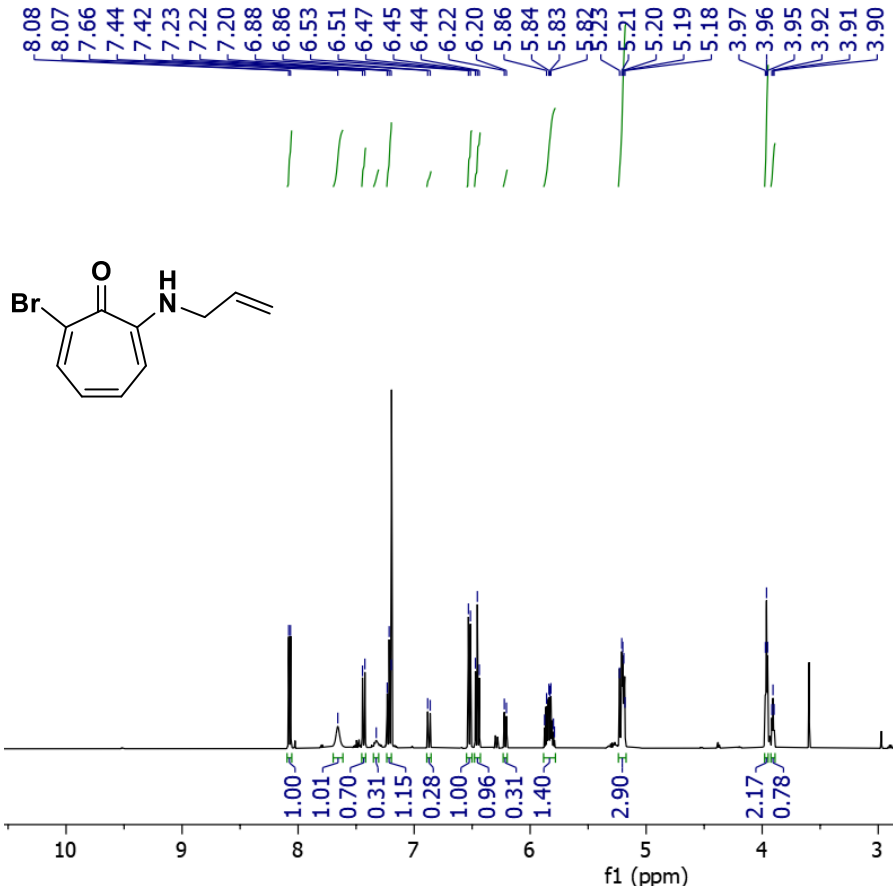
2ja ^{1}H NMR (600 MHz, $CDCl_3$)



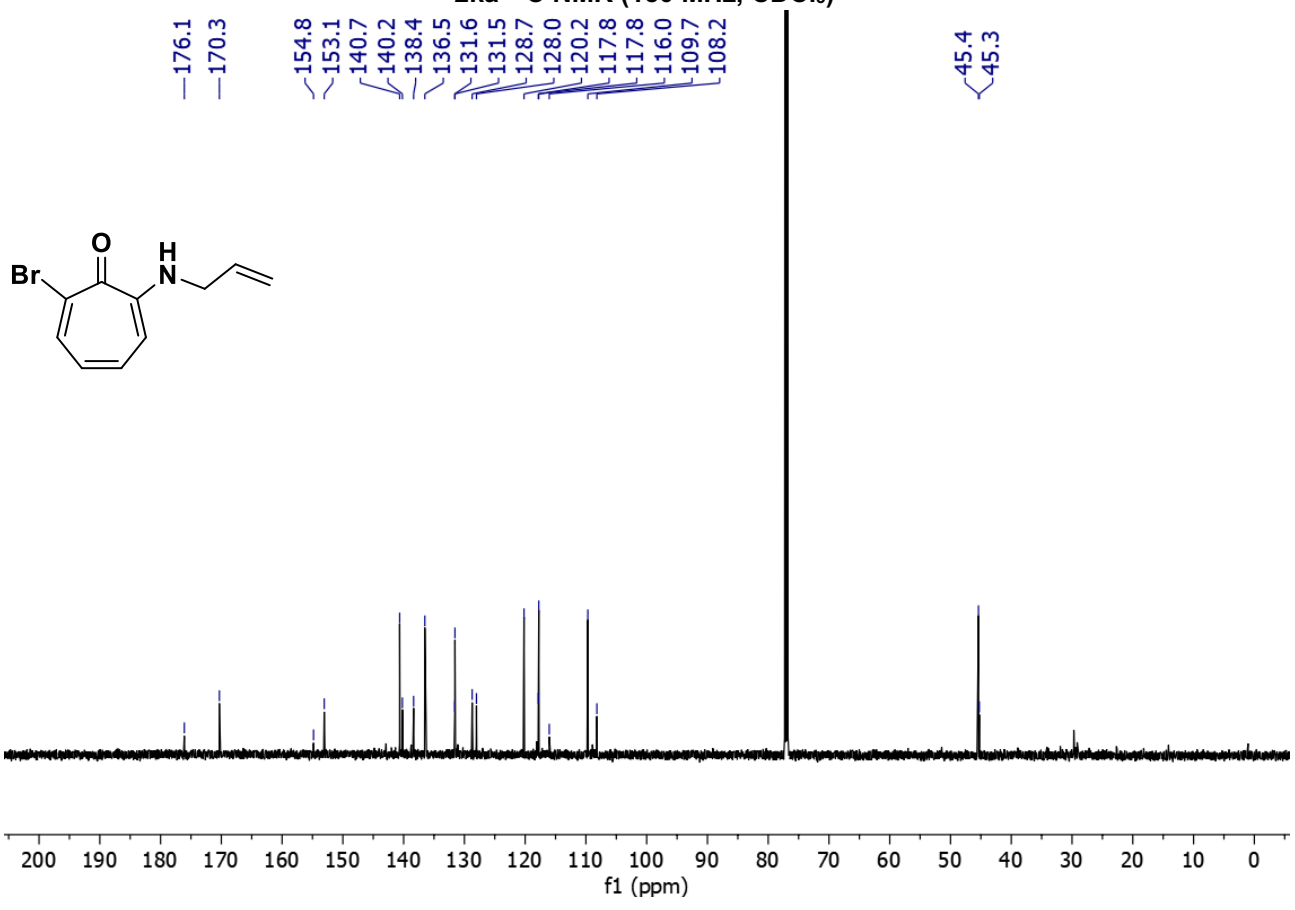
2ja ^{13}C NMR (150 MHz, $CDCl_3$)



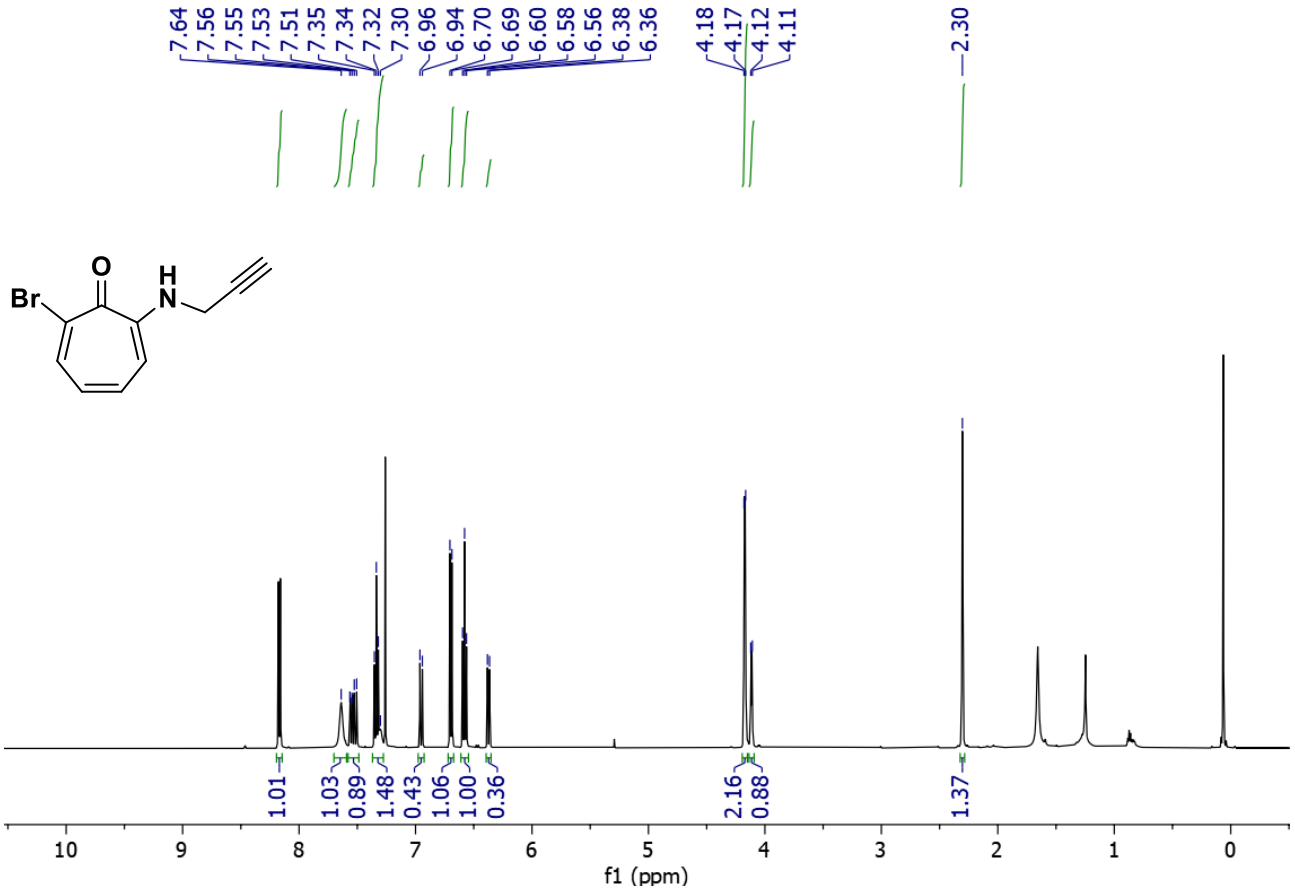
2ka ^{1}H NMR (600 MHz, $CDCl_3$)



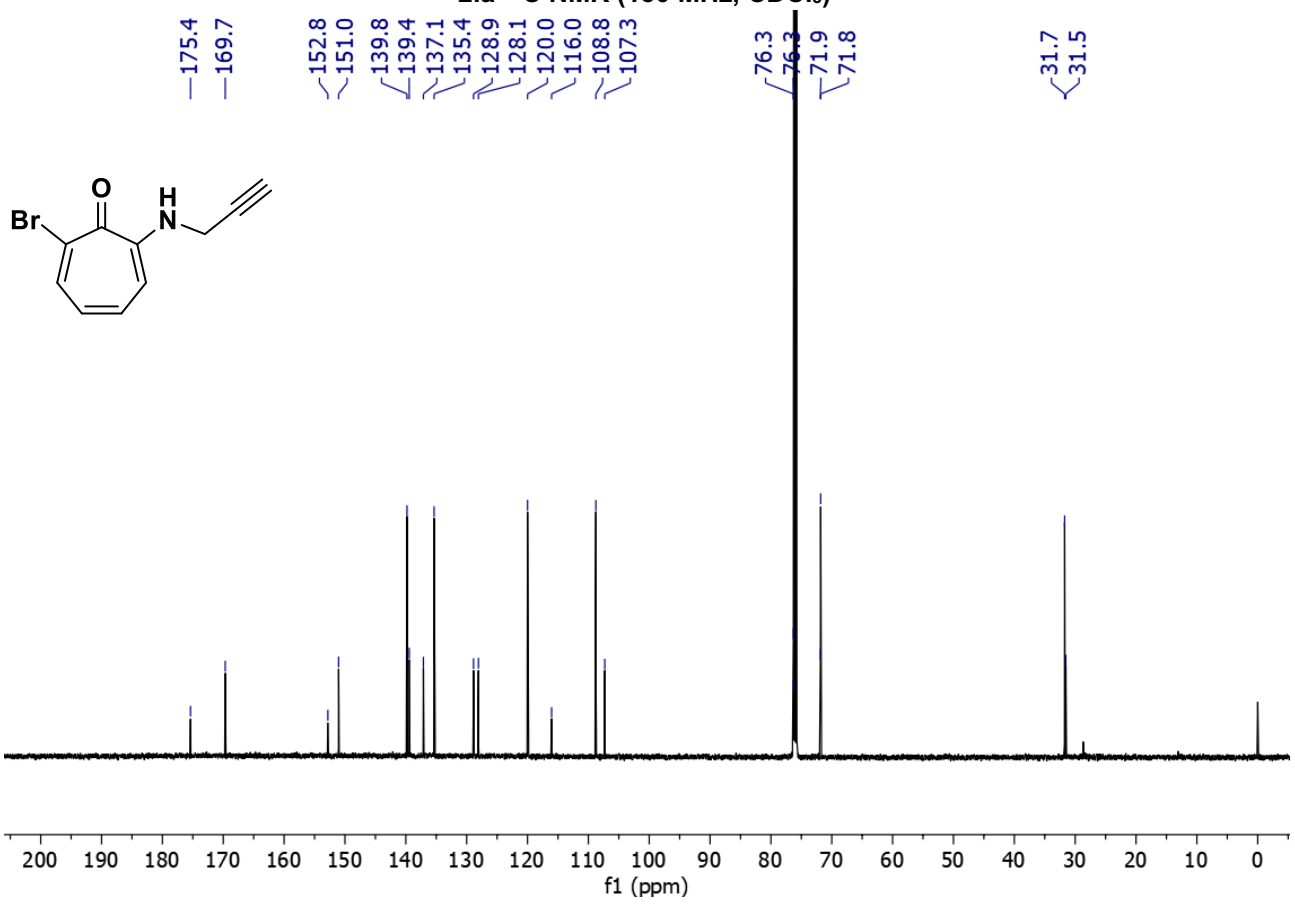
2ka ^{13}C NMR (150 MHz, $CDCl_3$)



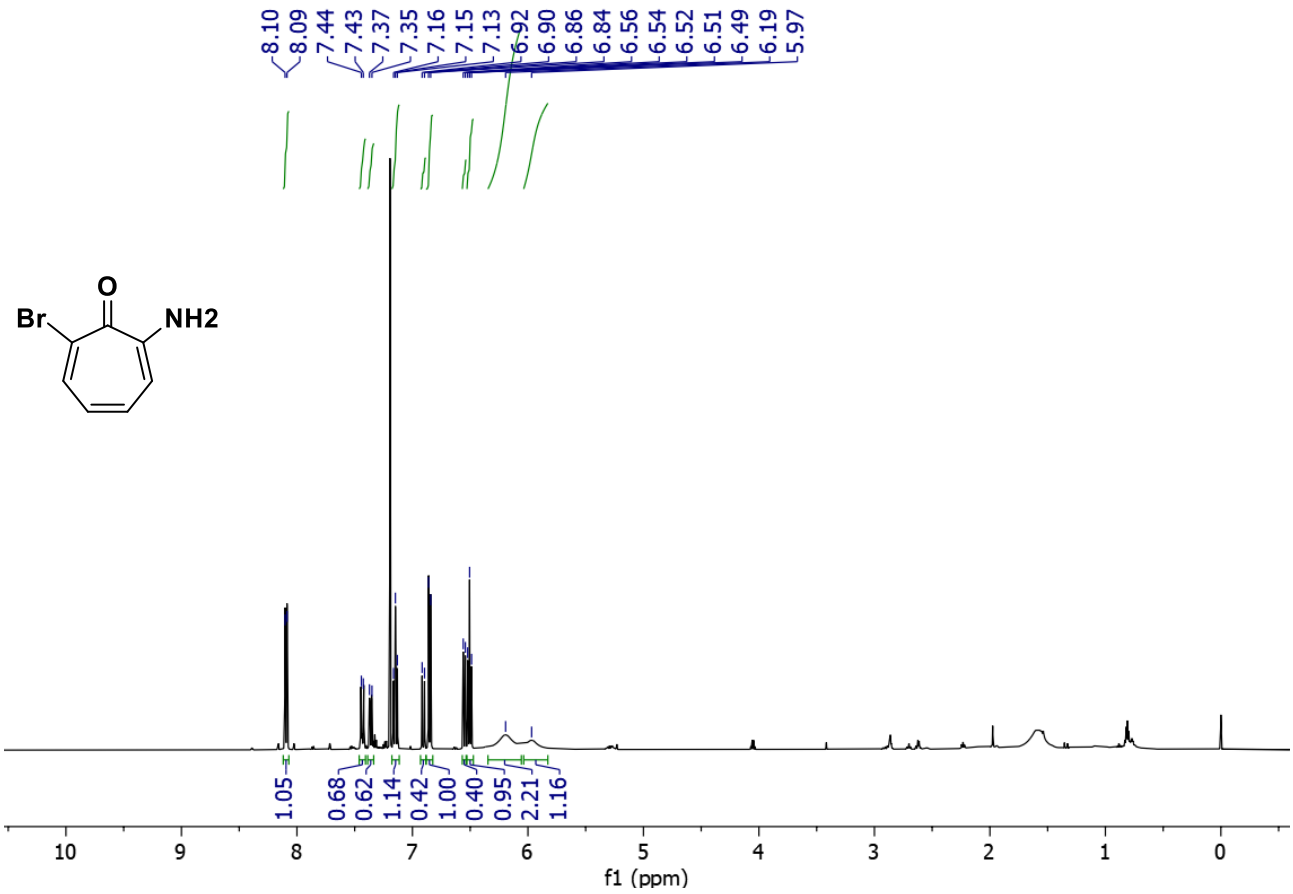
2la ^{1}H NMR (600 MHz, $CDCl_3$)



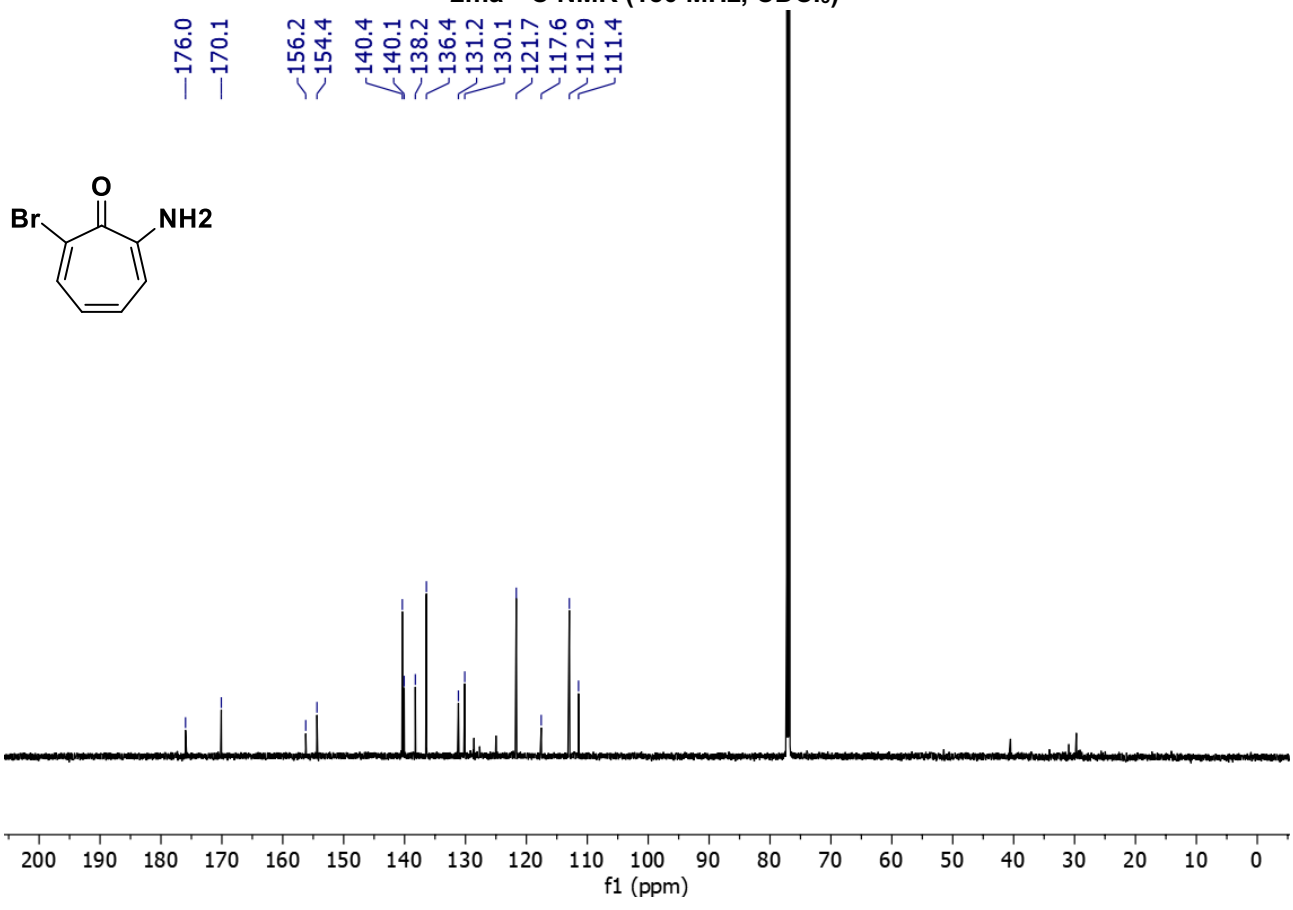
2la ^{13}C NMR (150 MHz, $CDCl_3$)



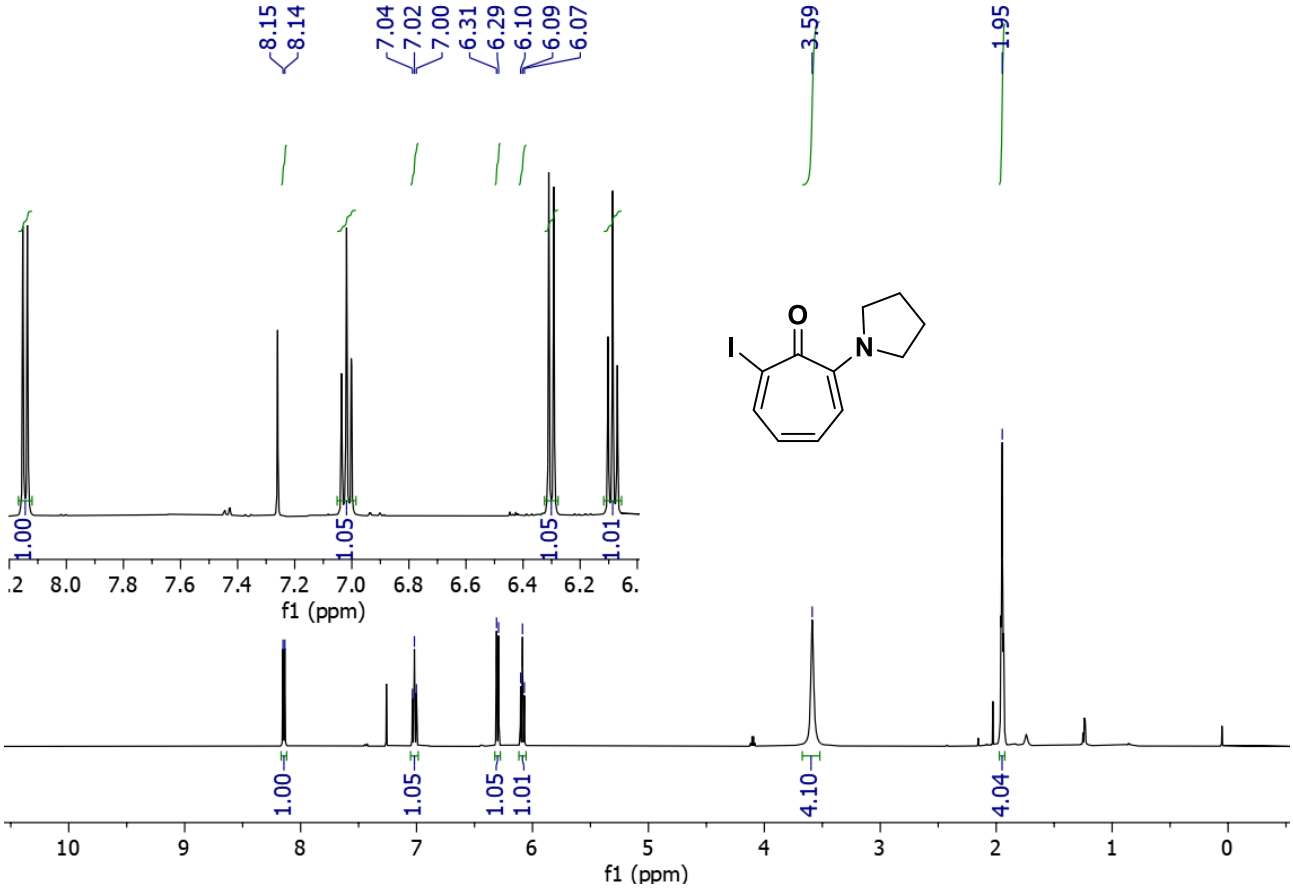
2ma ^{1}H NMR (600 MHz, $CDCl_3$)



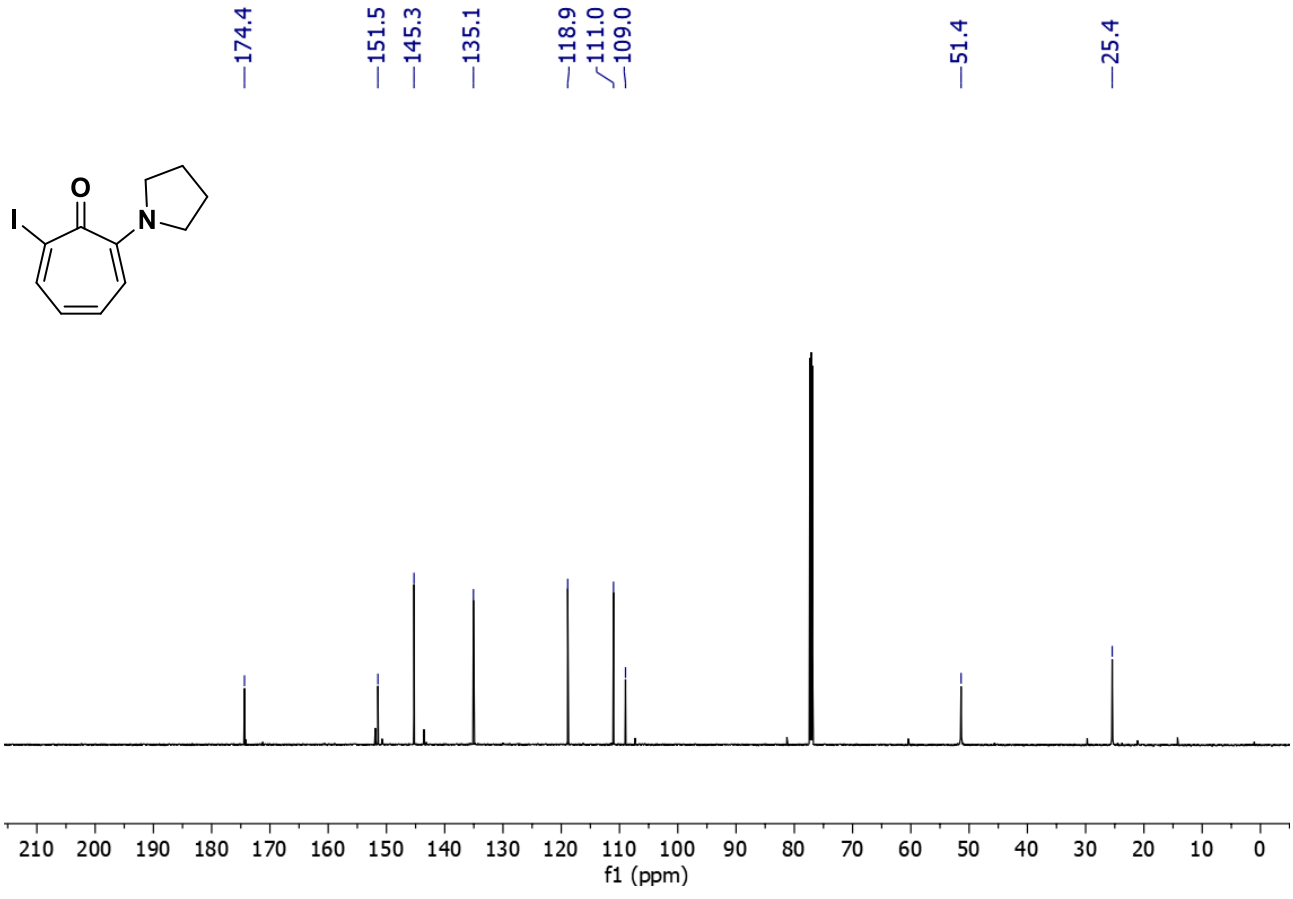
2ma ^{13}C NMR (150 MHz, $CDCl_3$)



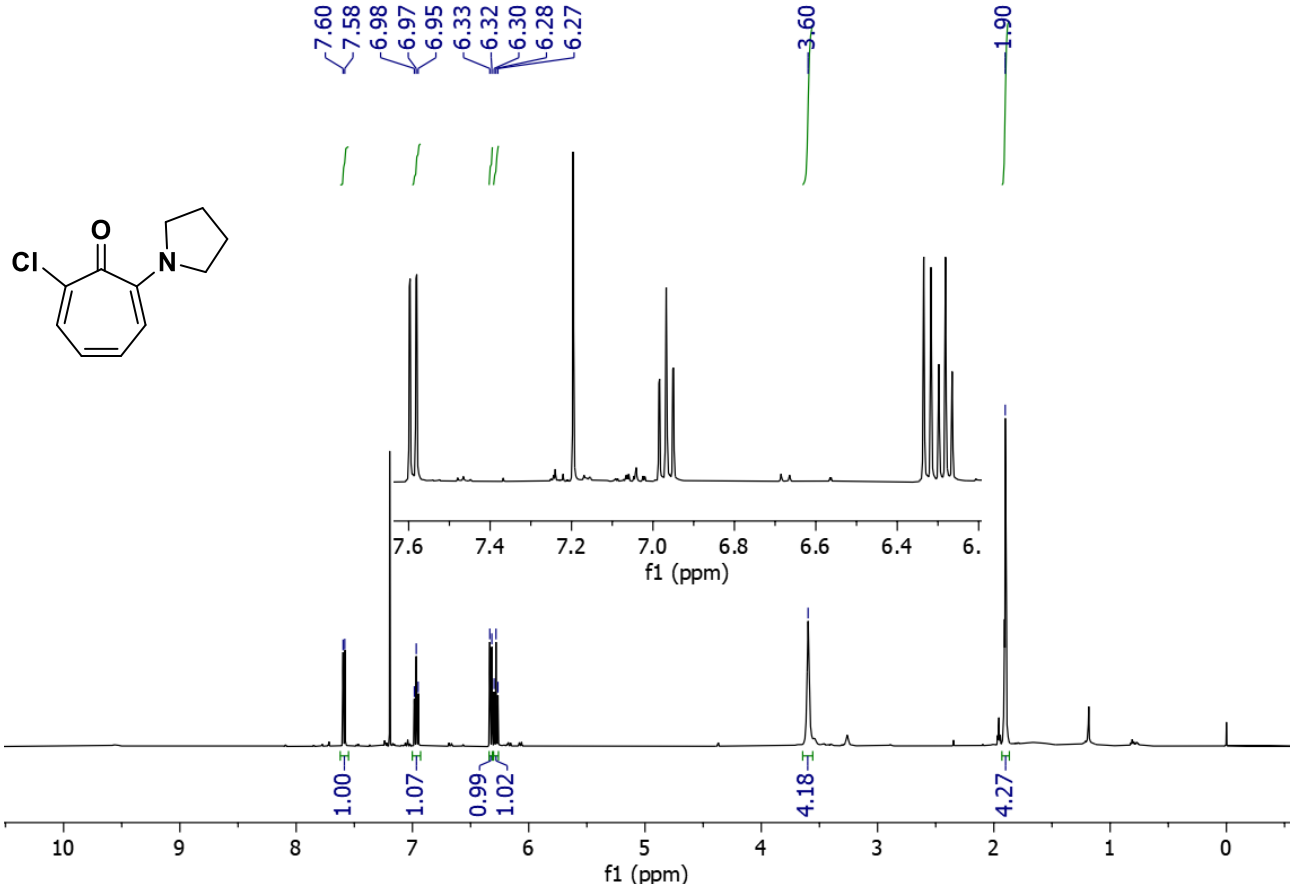
2ab ^{1}H NMR (600 MHz, $CDCl_3$)



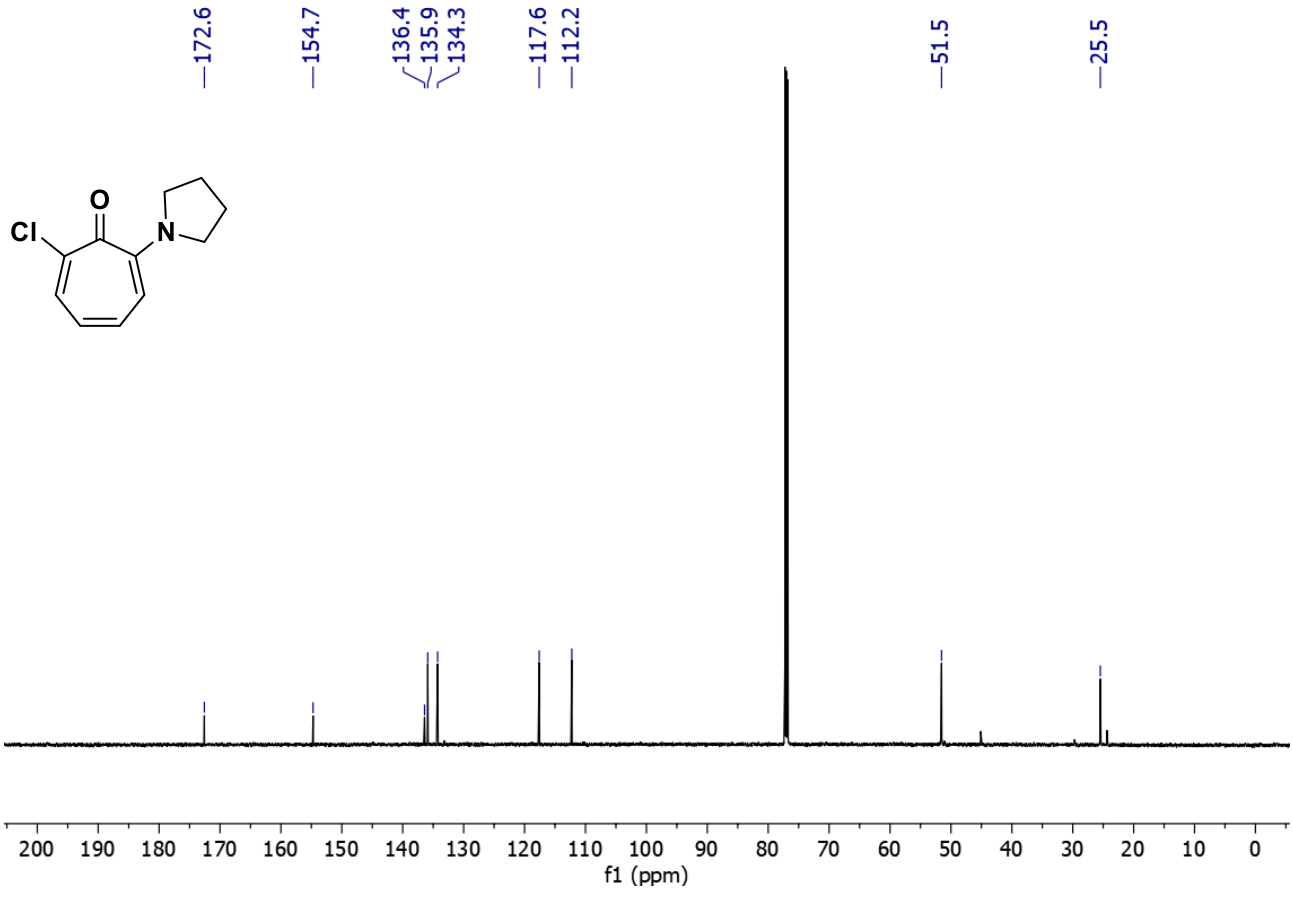
2ab ^{13}C NMR (150 MHz, $CDCl_3$)



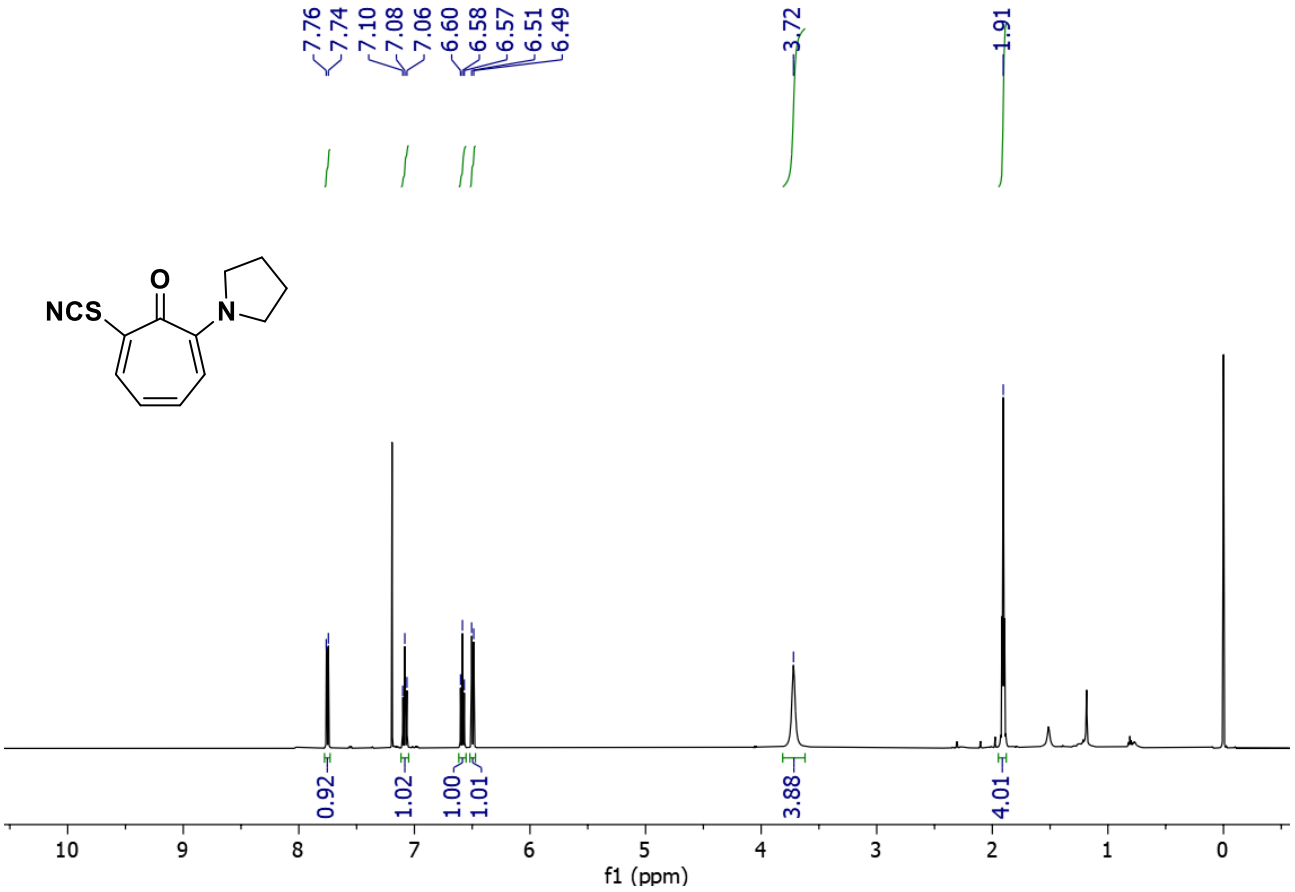
2ac ^{1}H NMR (600 MHz, $CDCl_3$)



2ac ^{13}C NMR (150 MHz, $CDCl_3$)



2ad ^{1}H NMR (600 MHz, $CDCl_3$)



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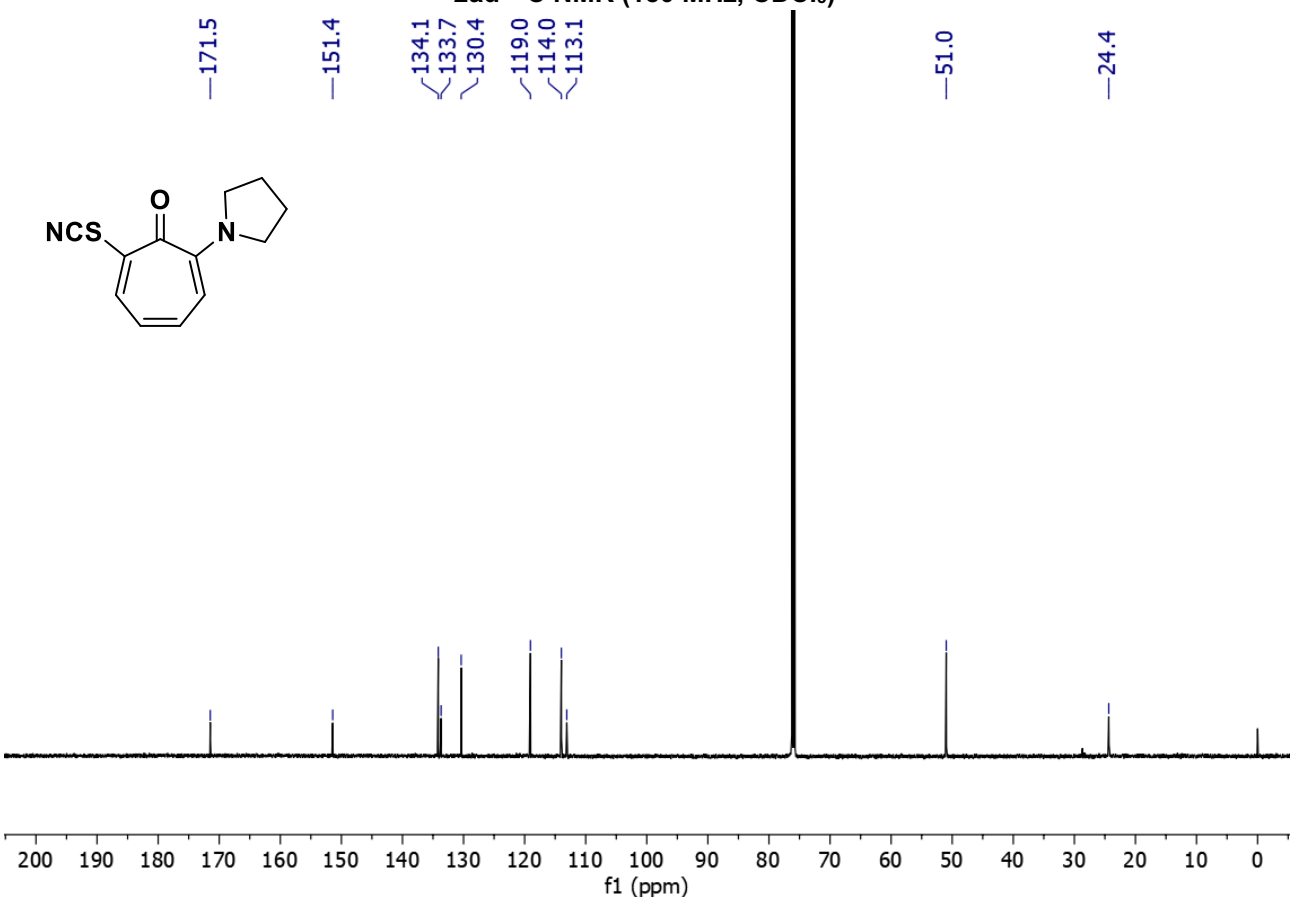
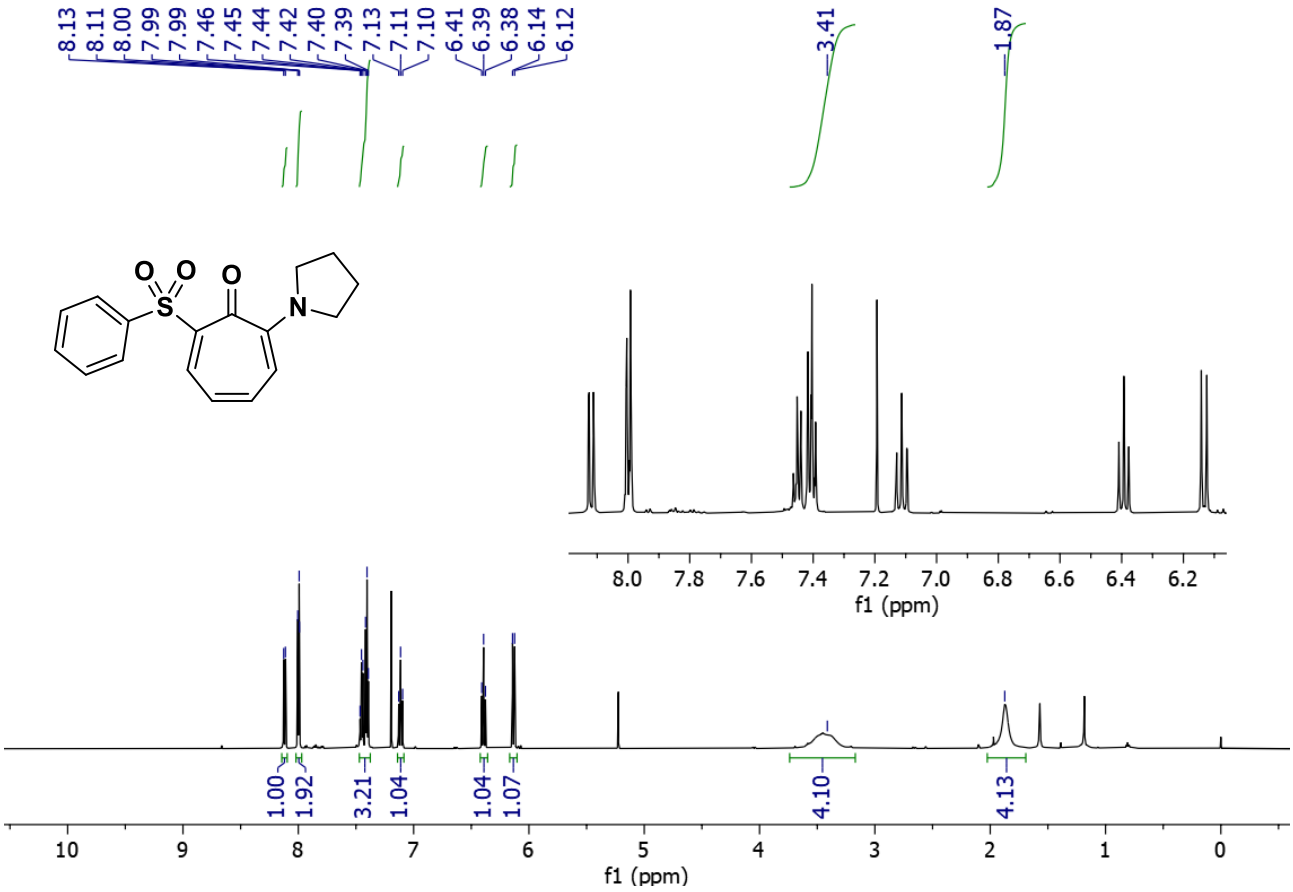
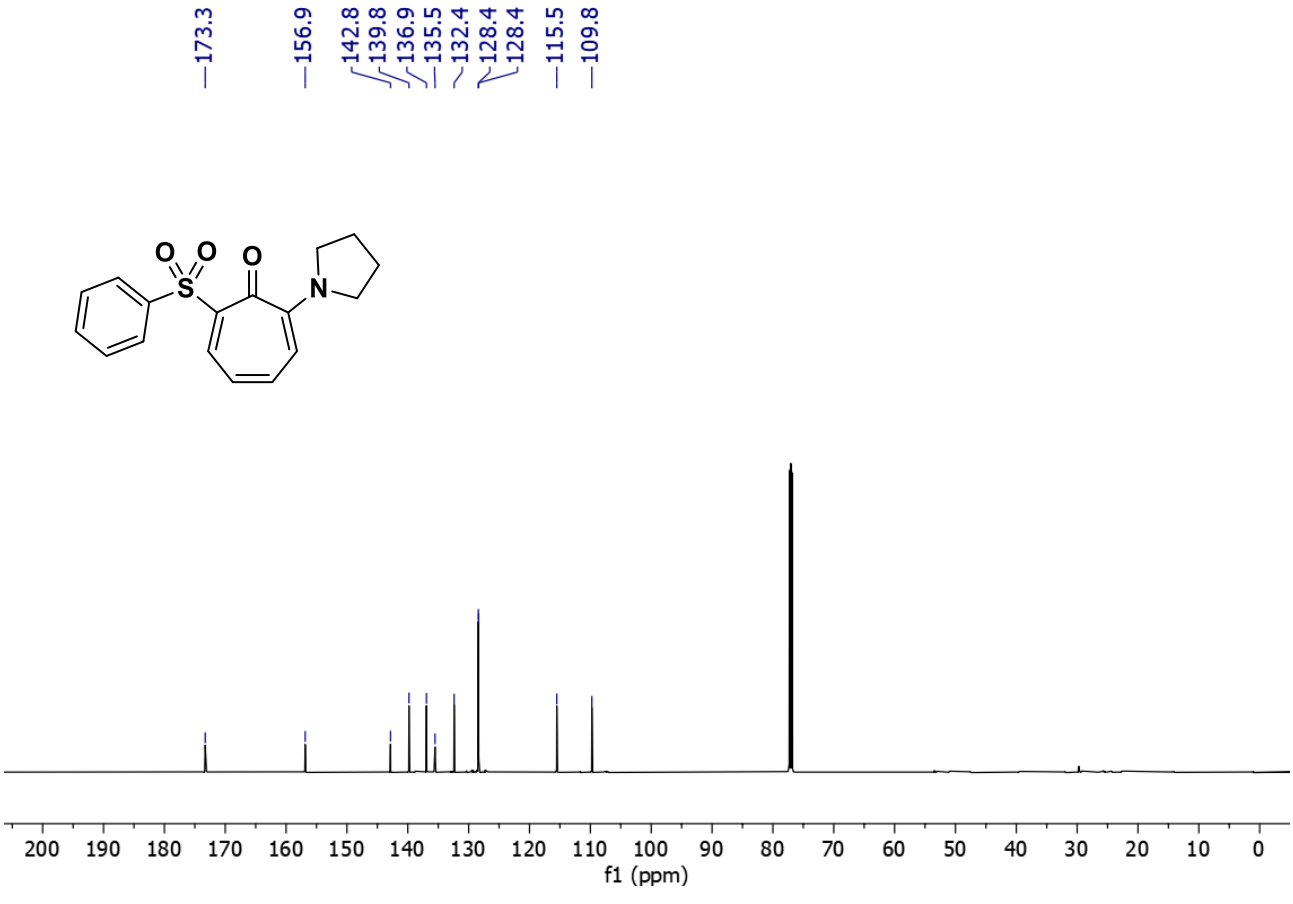


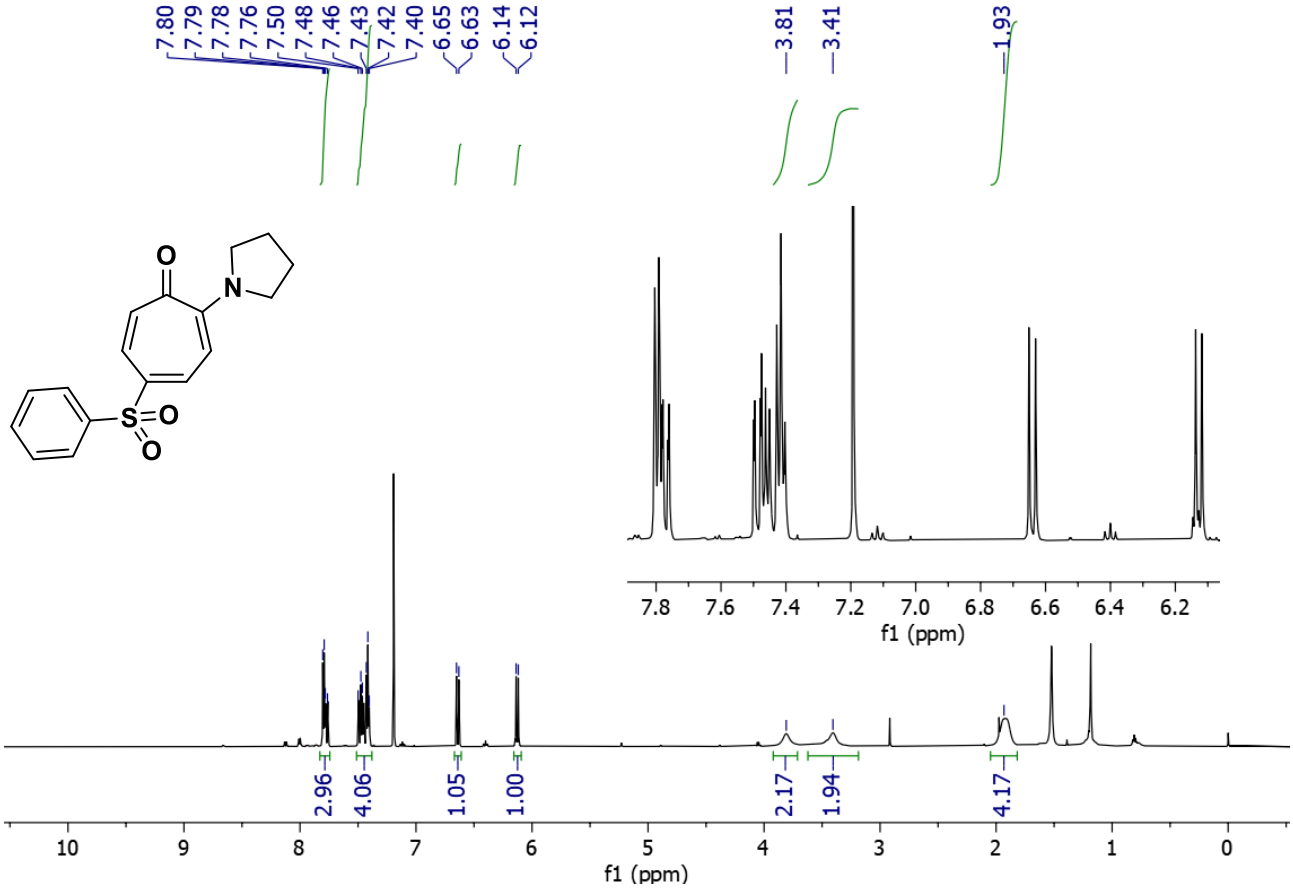
2ae ^{1}H NMR (600 MHz, $CDCl_3$)



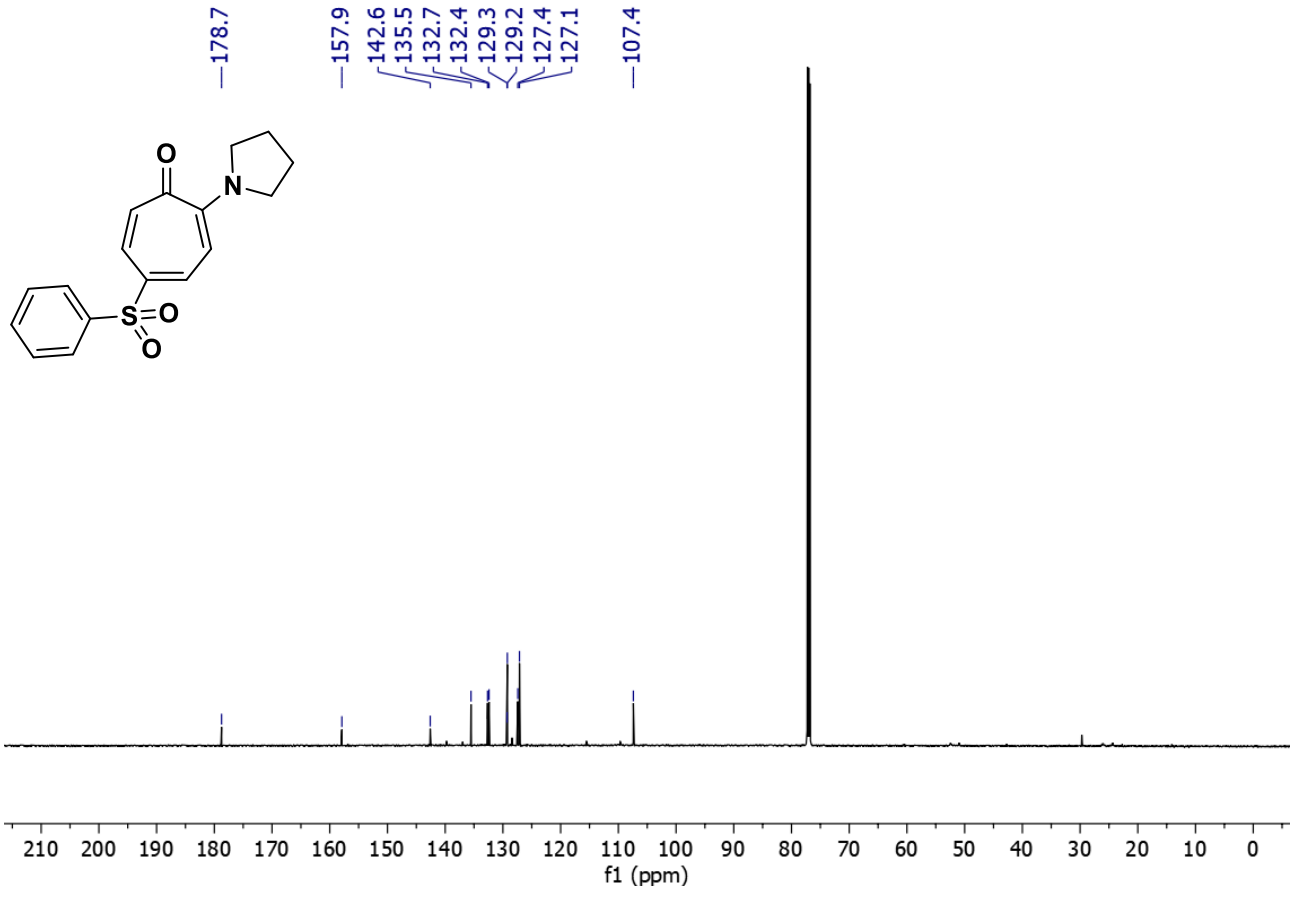
2ae ^{13}C NMR (150 MHz, $CDCl_3$)



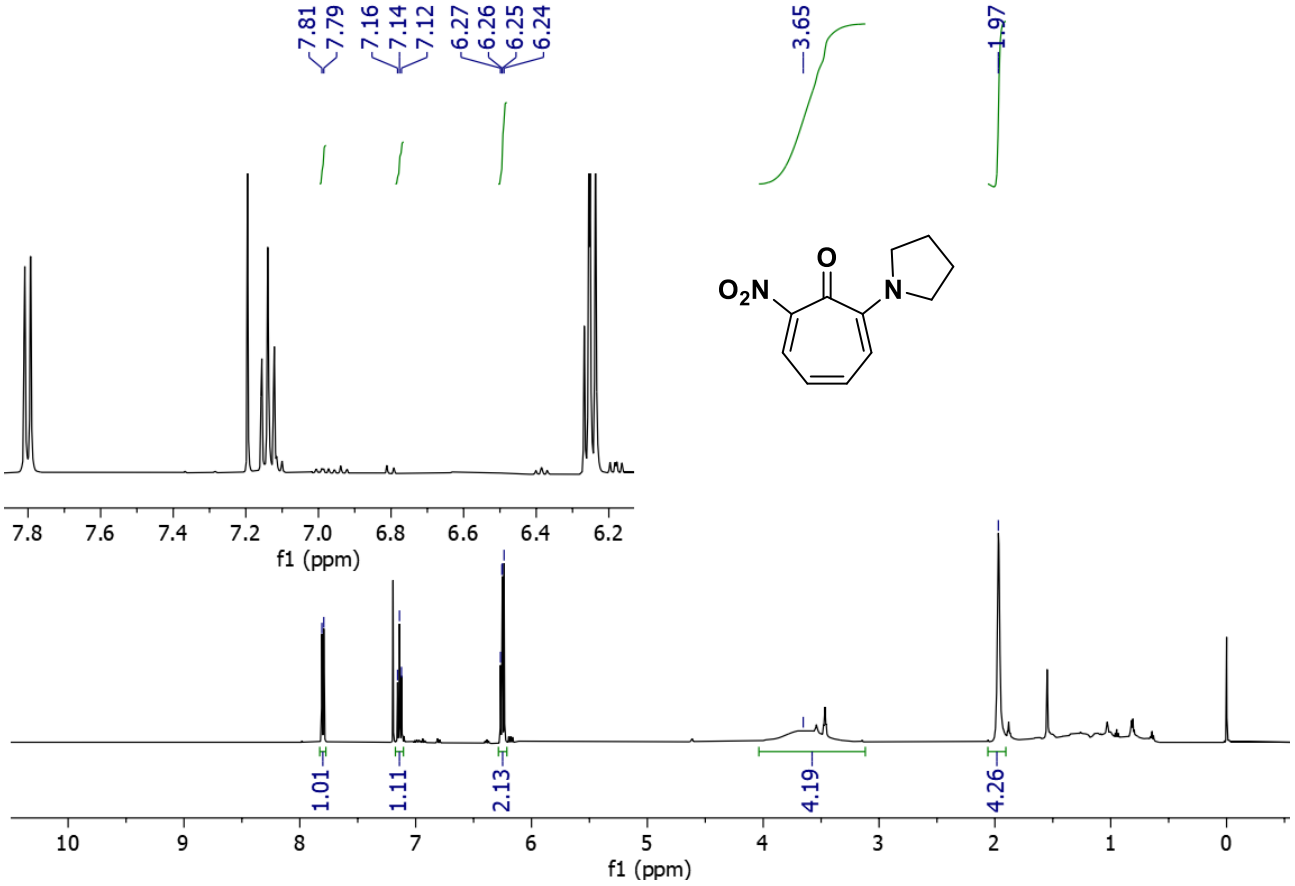
3ae ^{1}H NMR (600 MHz, $CDCl_3$)



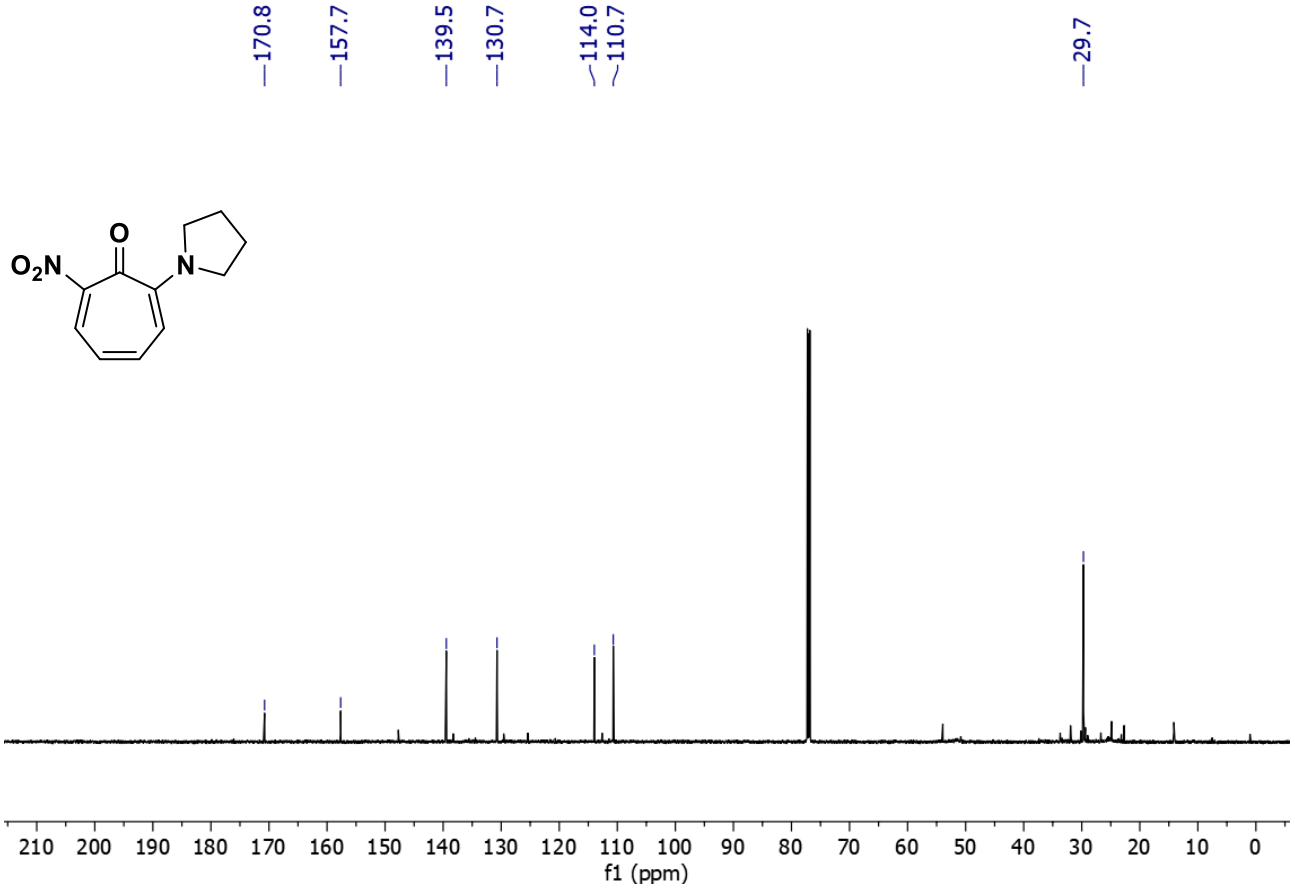
3ae ^{13}C NMR (150 MHz, $CDCl_3$)



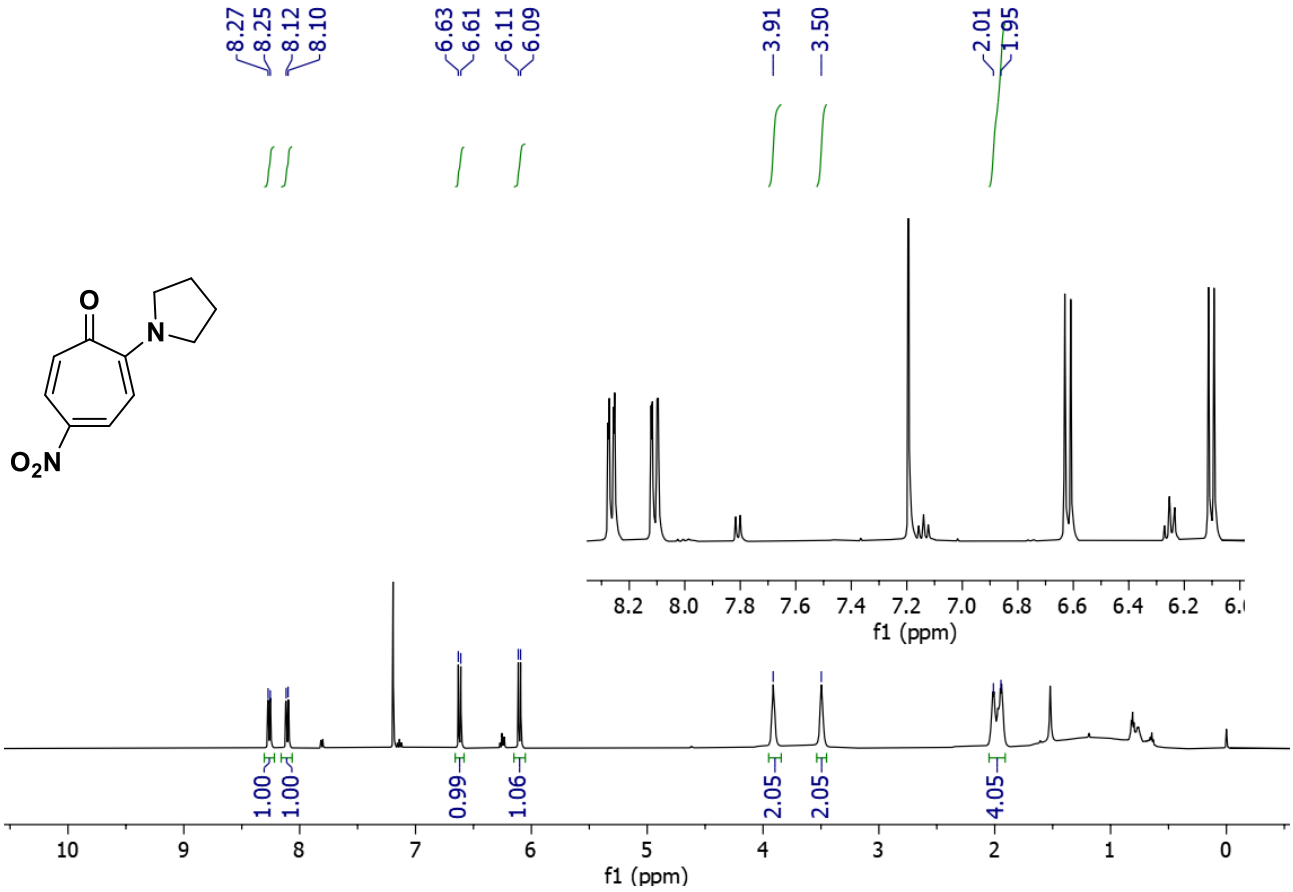
2af ^{1}H NMR (600 MHz, $CDCl_3$)



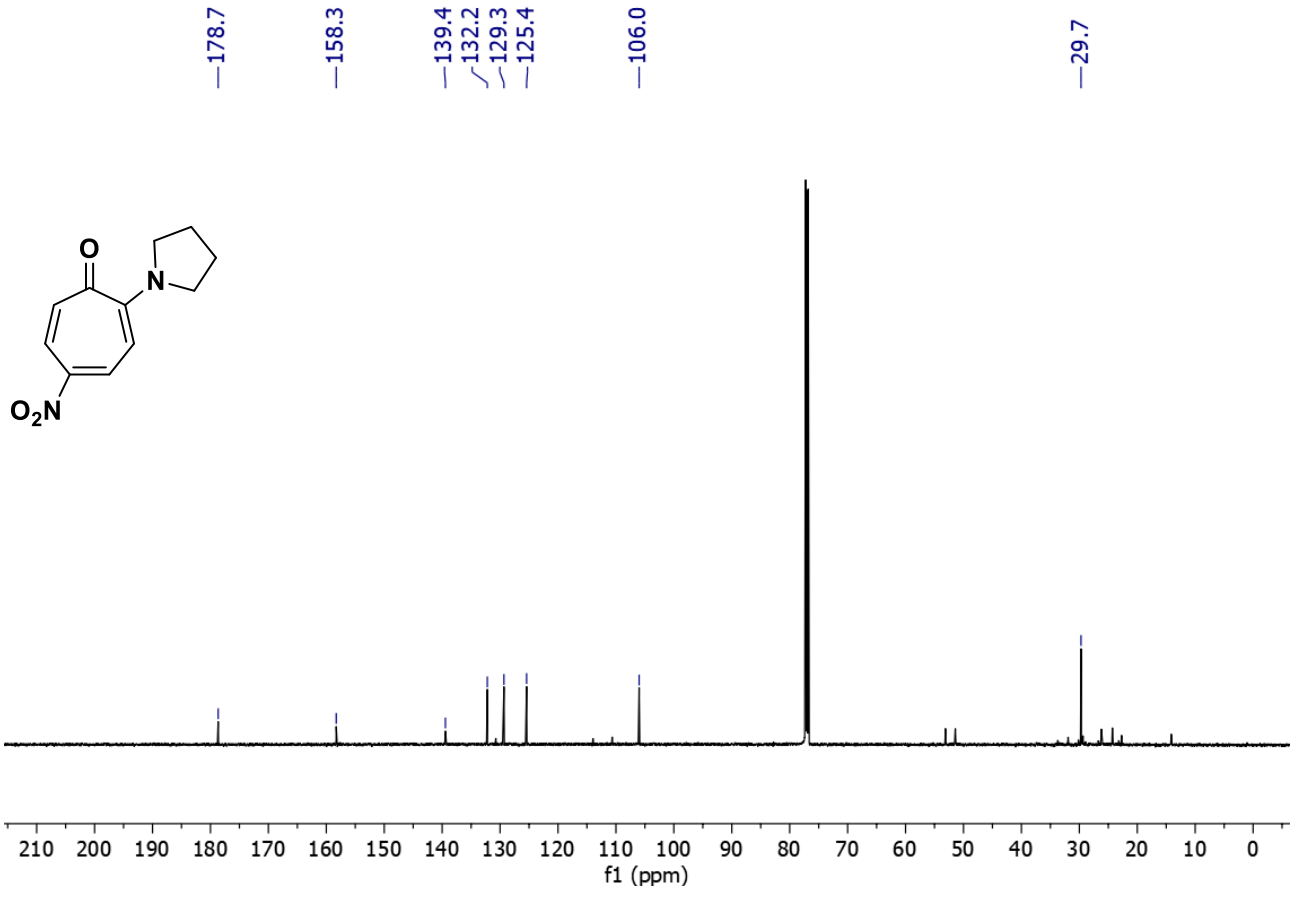
2af ^{13}C NMR (150 MHz, $CDCl_3$)



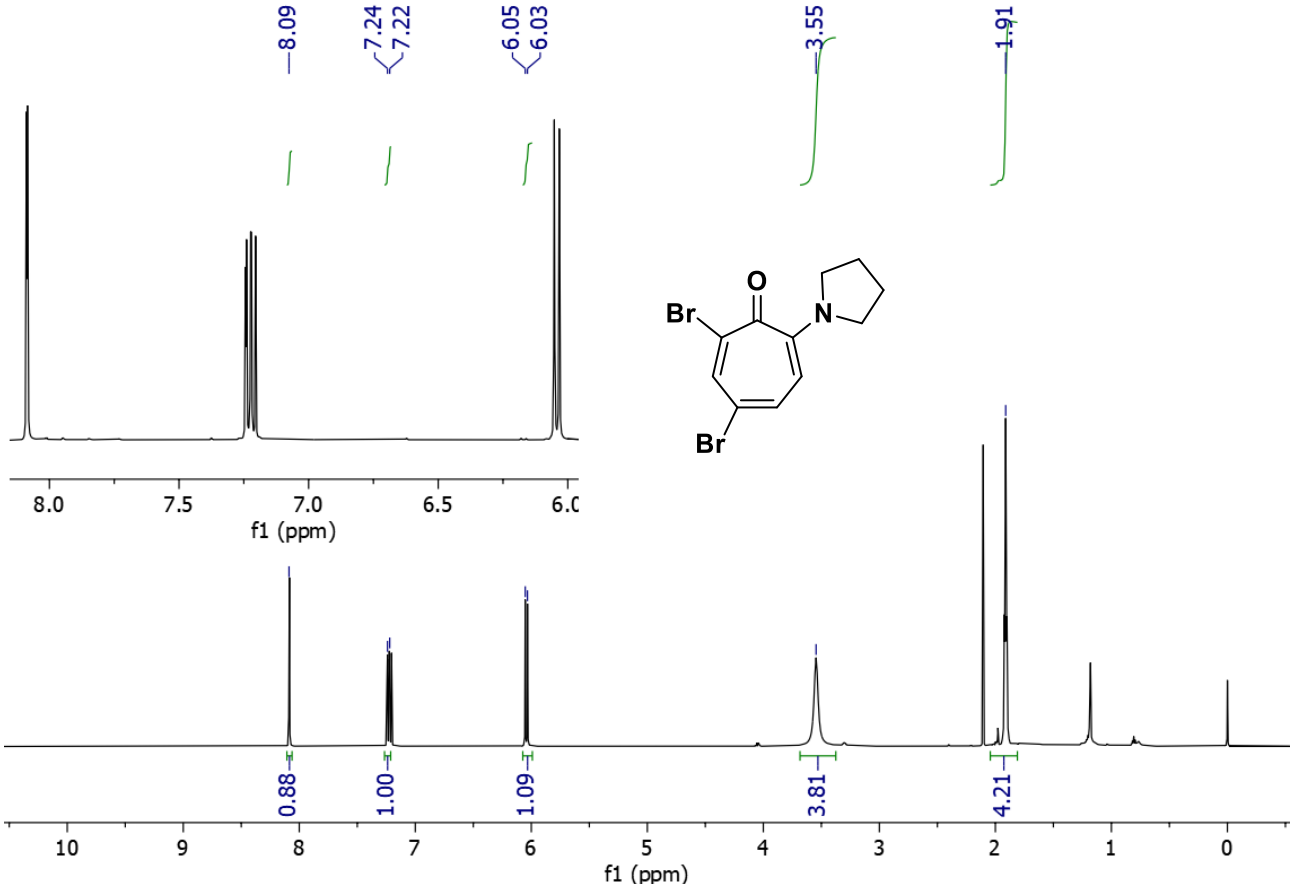
3af ^{1}H NMR (600 MHz, $CDCl_3$)



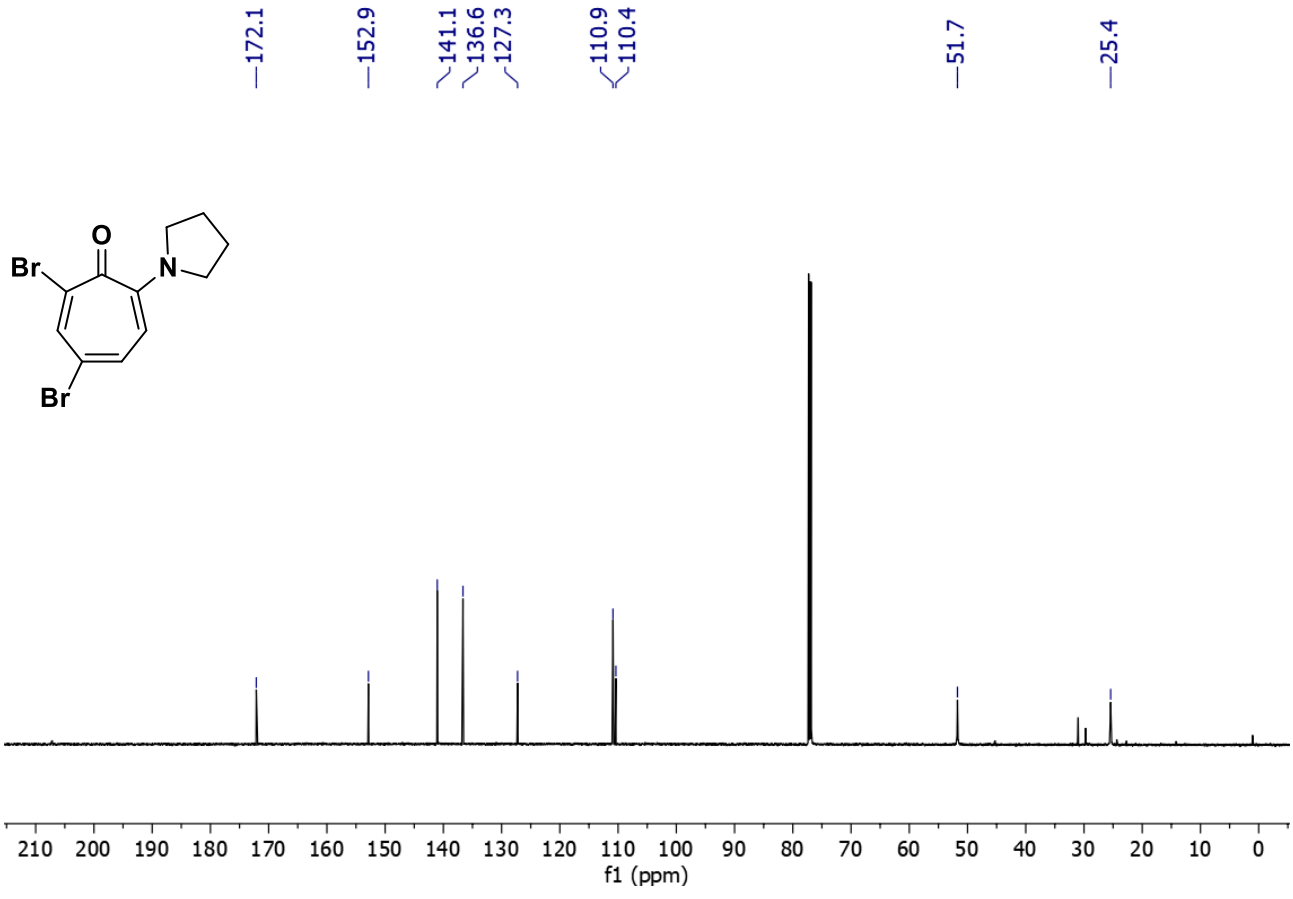
3af ^{13}C NMR (150 MHz, $CDCl_3$)



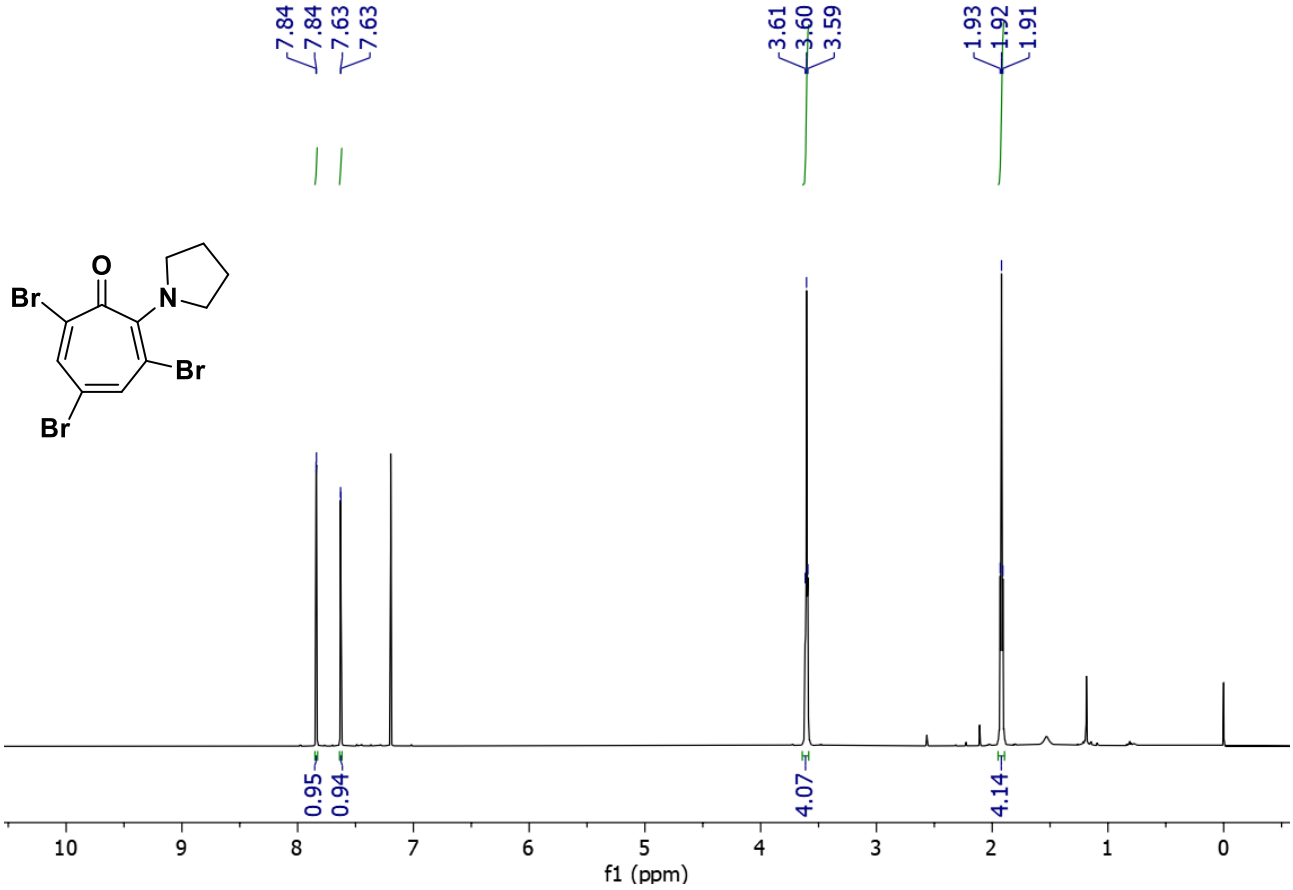
4aa ^{1}H NMR (600 MHz, $CDCl_3$)



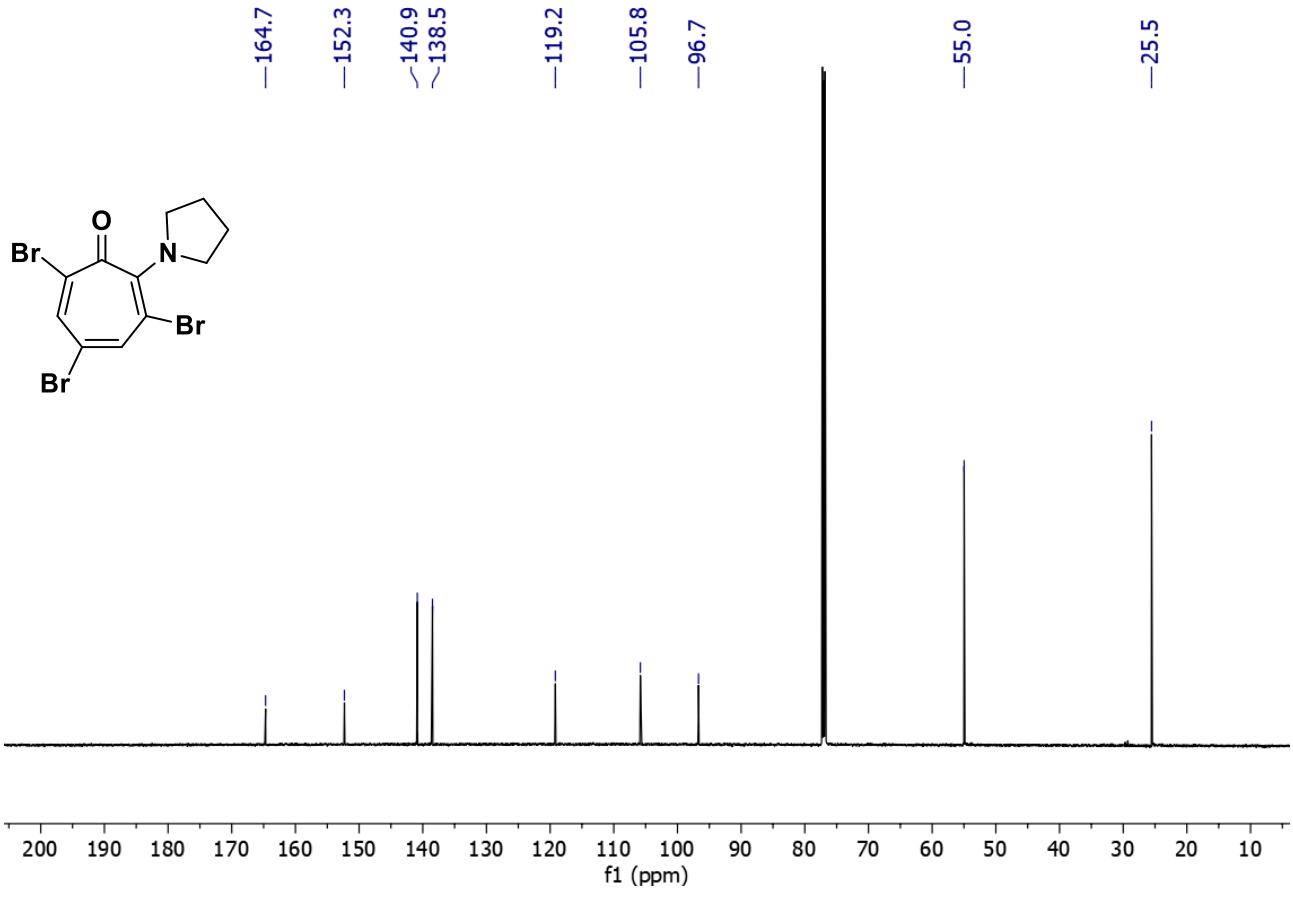
4aa ^{13}C NMR (150 MHz, $CDCl_3$)



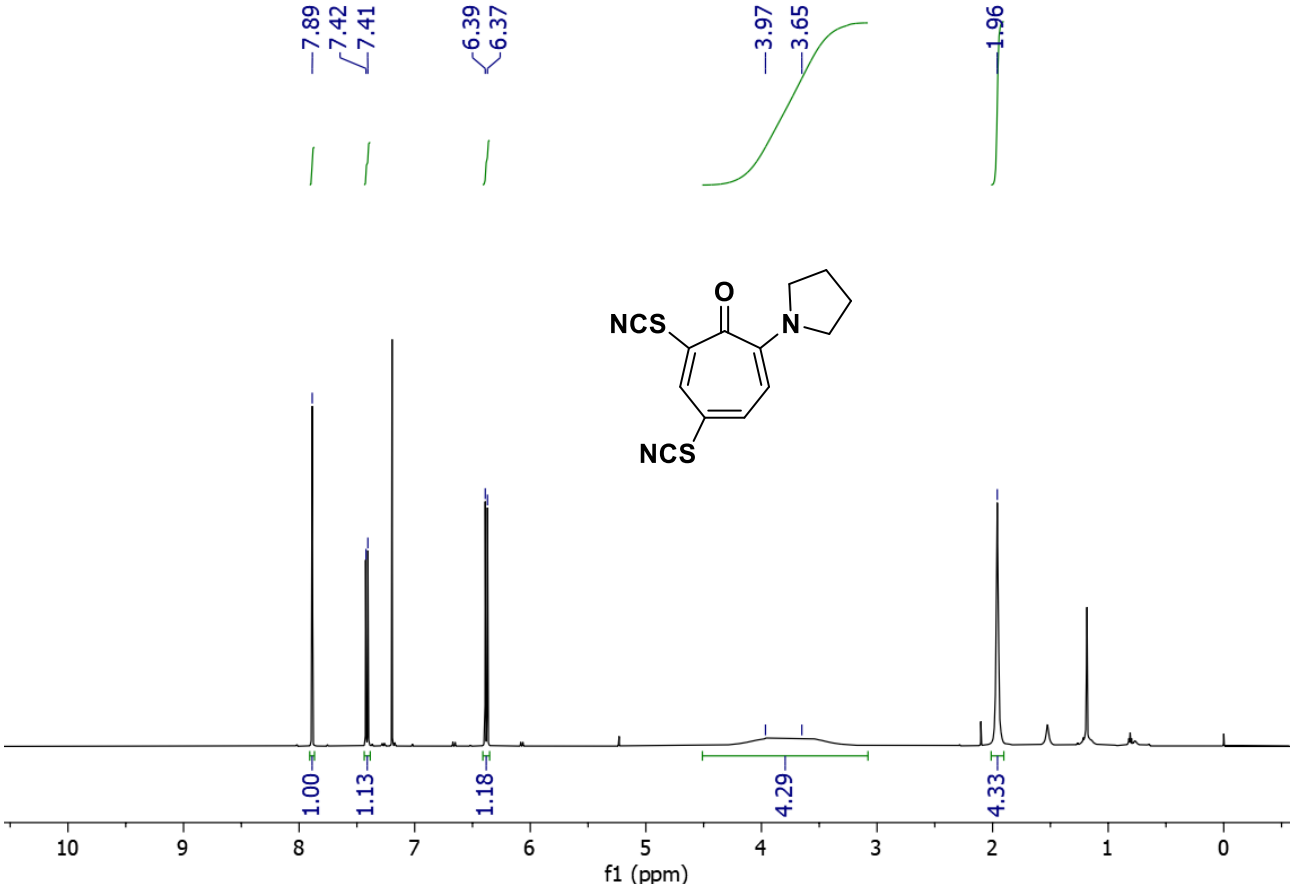
5aa ^{1}H NMR (600 MHz, $CDCl_3$)



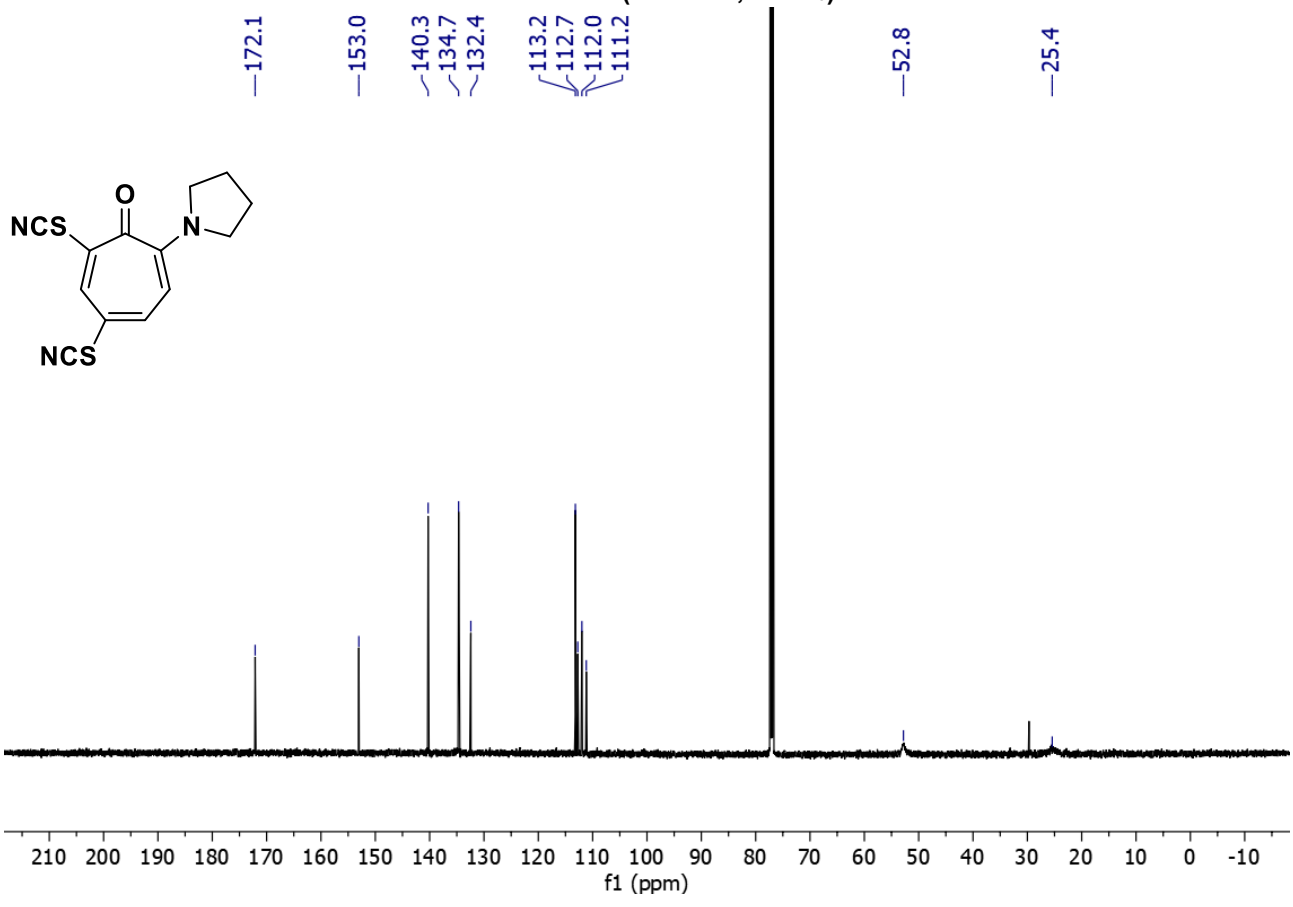
5aa ^{13}C NMR (150 MHz, $CDCl_3$)



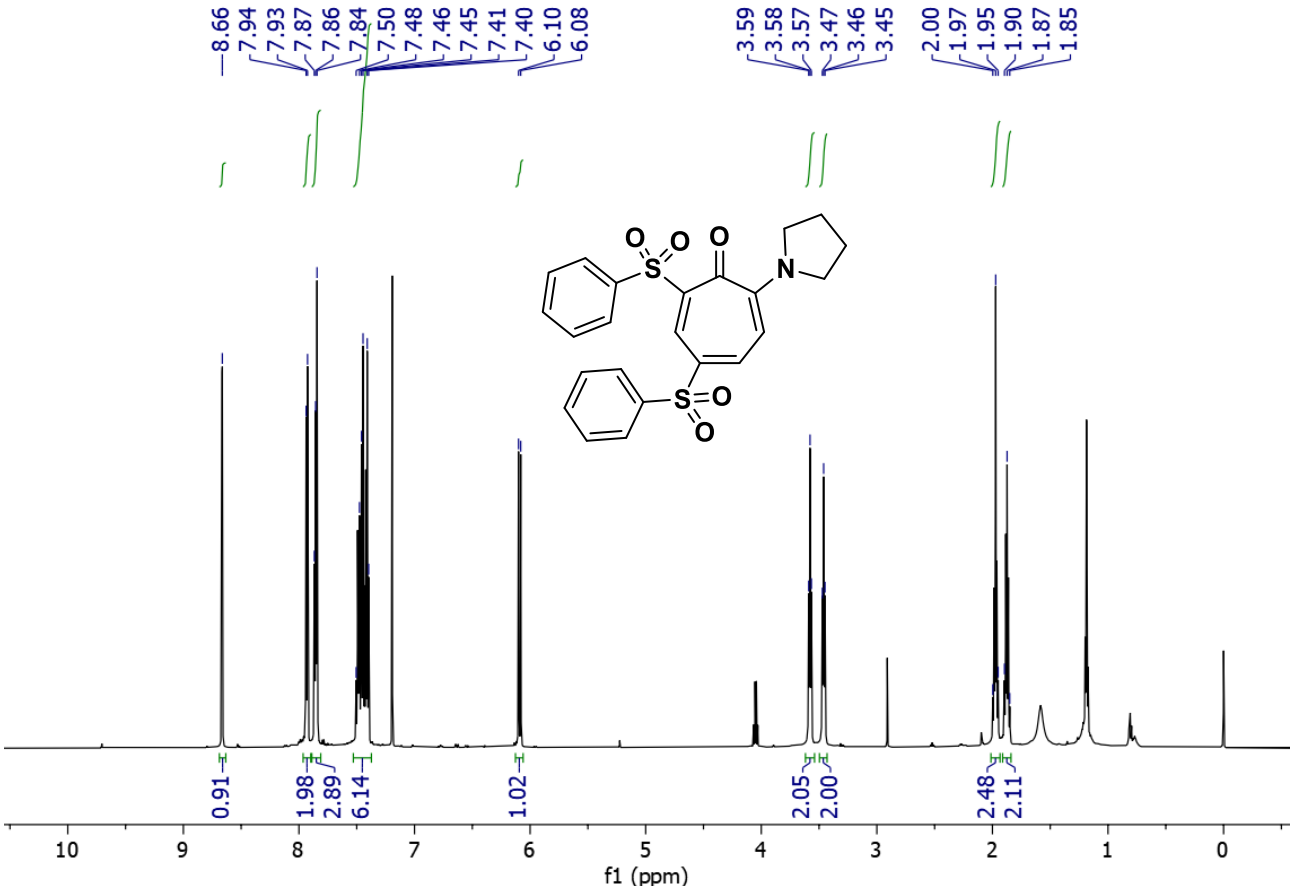
4ad ^{1}H NMR (600 MHz, $CDCl_3$)



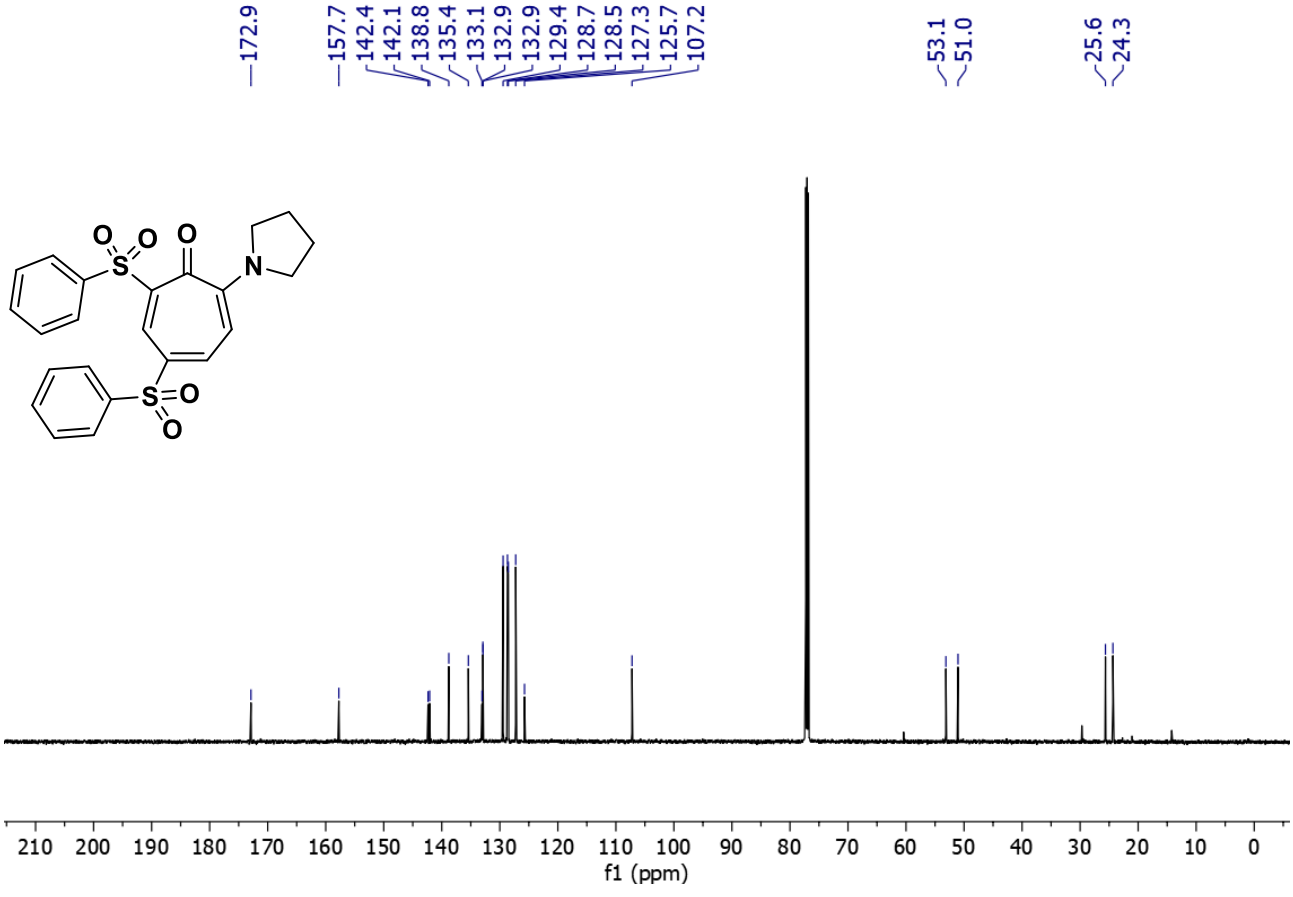
4ad ^{13}C NMR (150 MHz, $CDCl_3$)



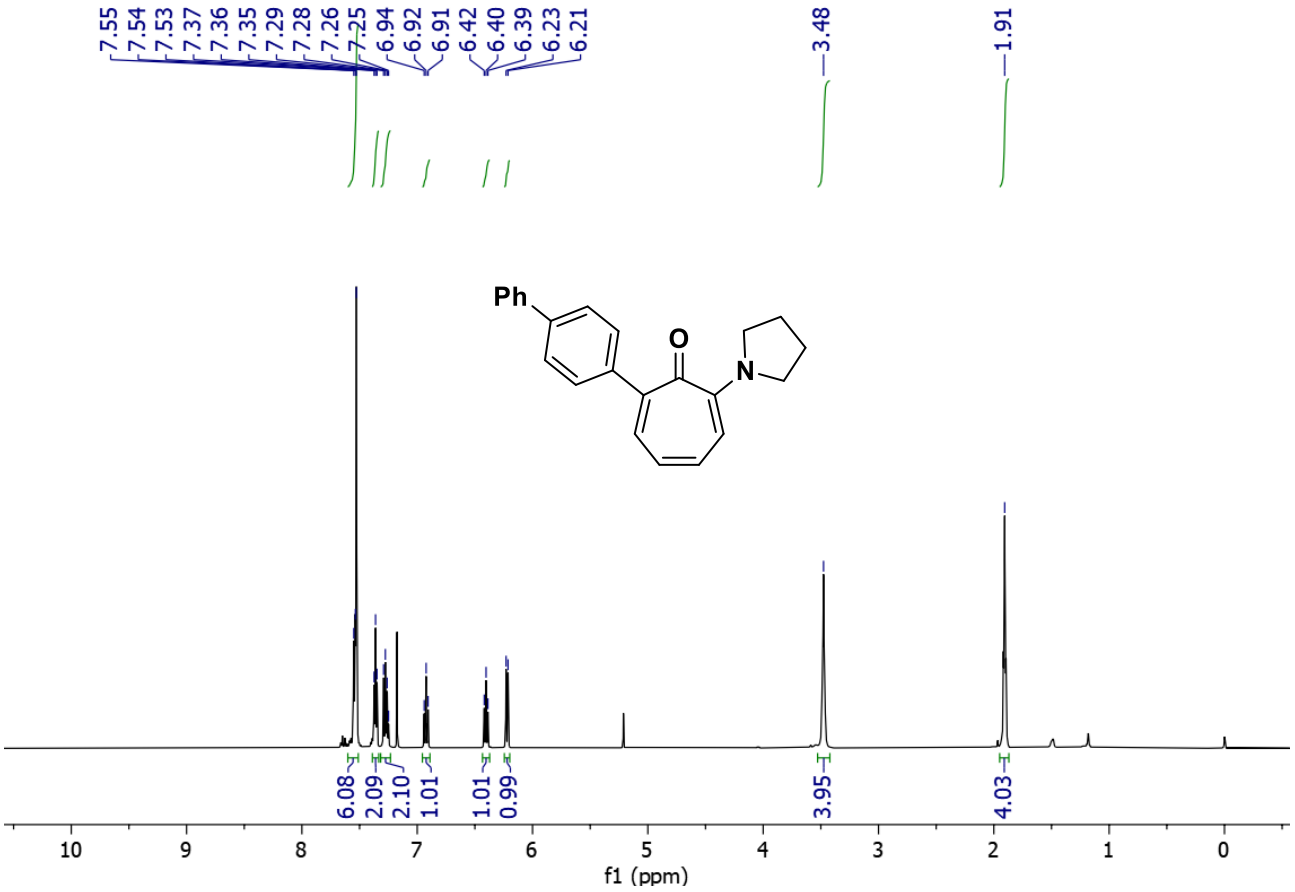
4ae ^{1}H NMR (600 MHz, $CDCl_3$)



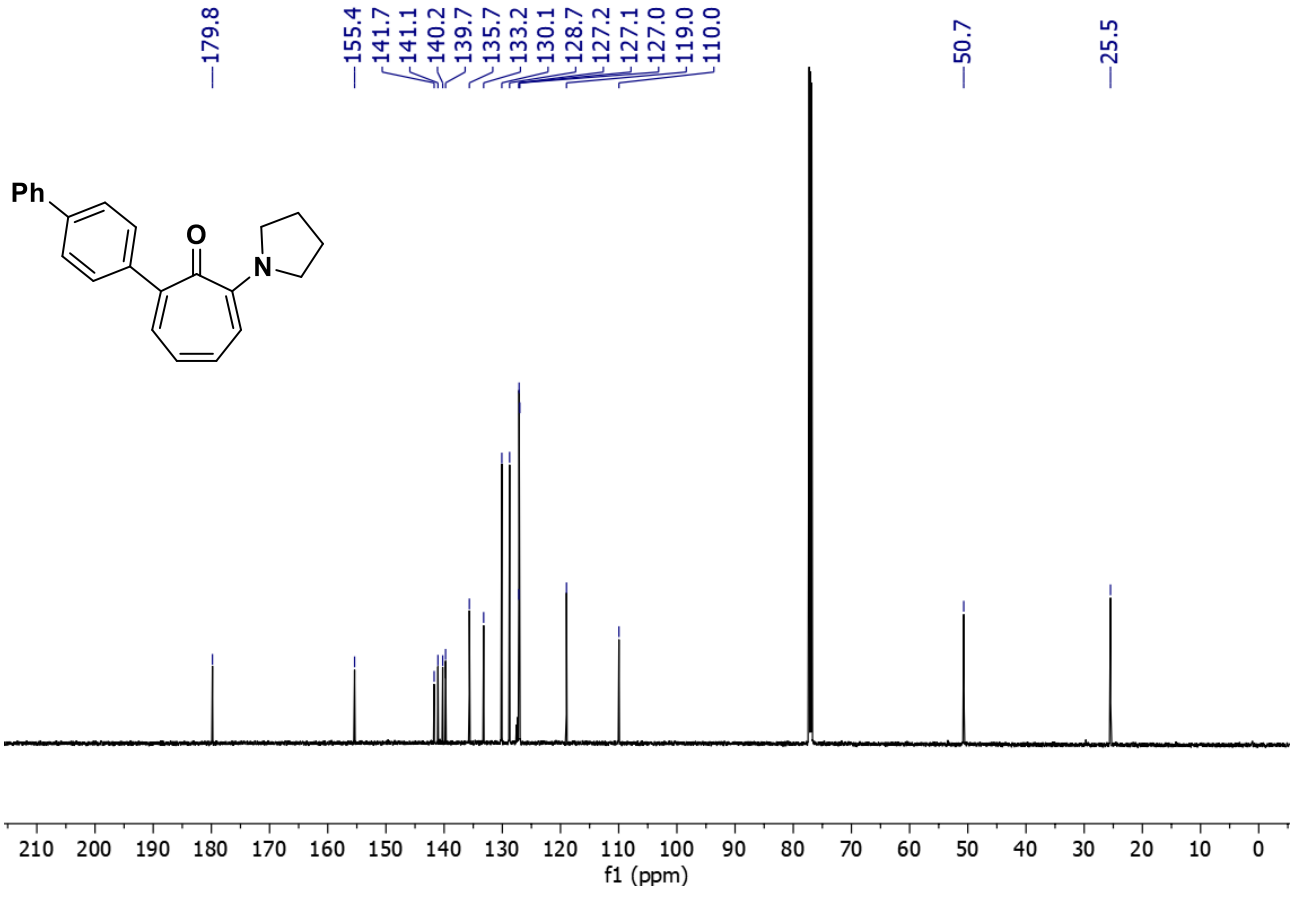
4ae ^{13}C NMR (150 MHz, $CDCl_3$)



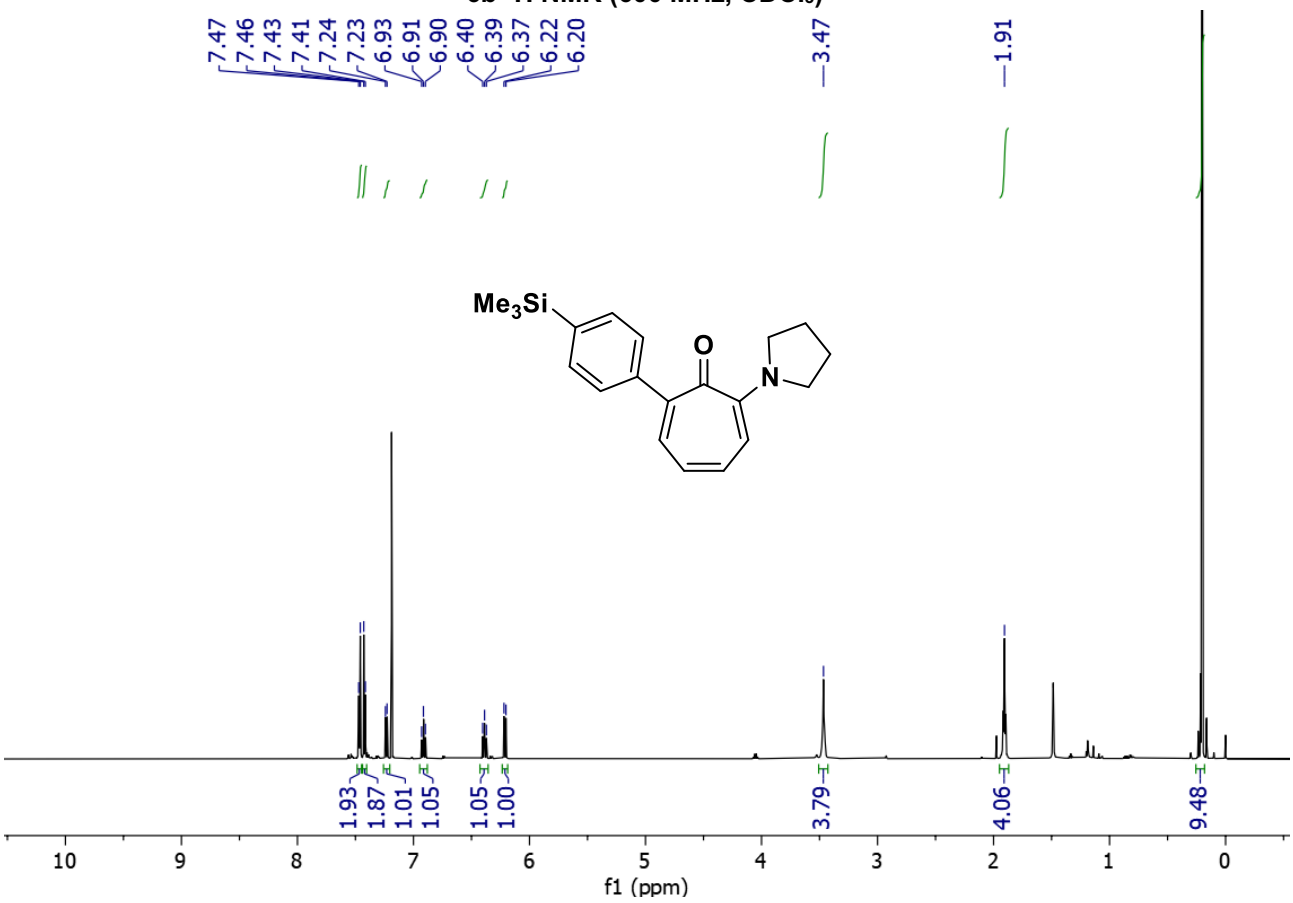
6a ^{1}H NMR (600 MHz, $CDCl_3$)



6a ^{13}C NMR (150 MHz, $CDCl_3$)



6b ^{1}H NMR (600 MHz, $CDCl_3$)



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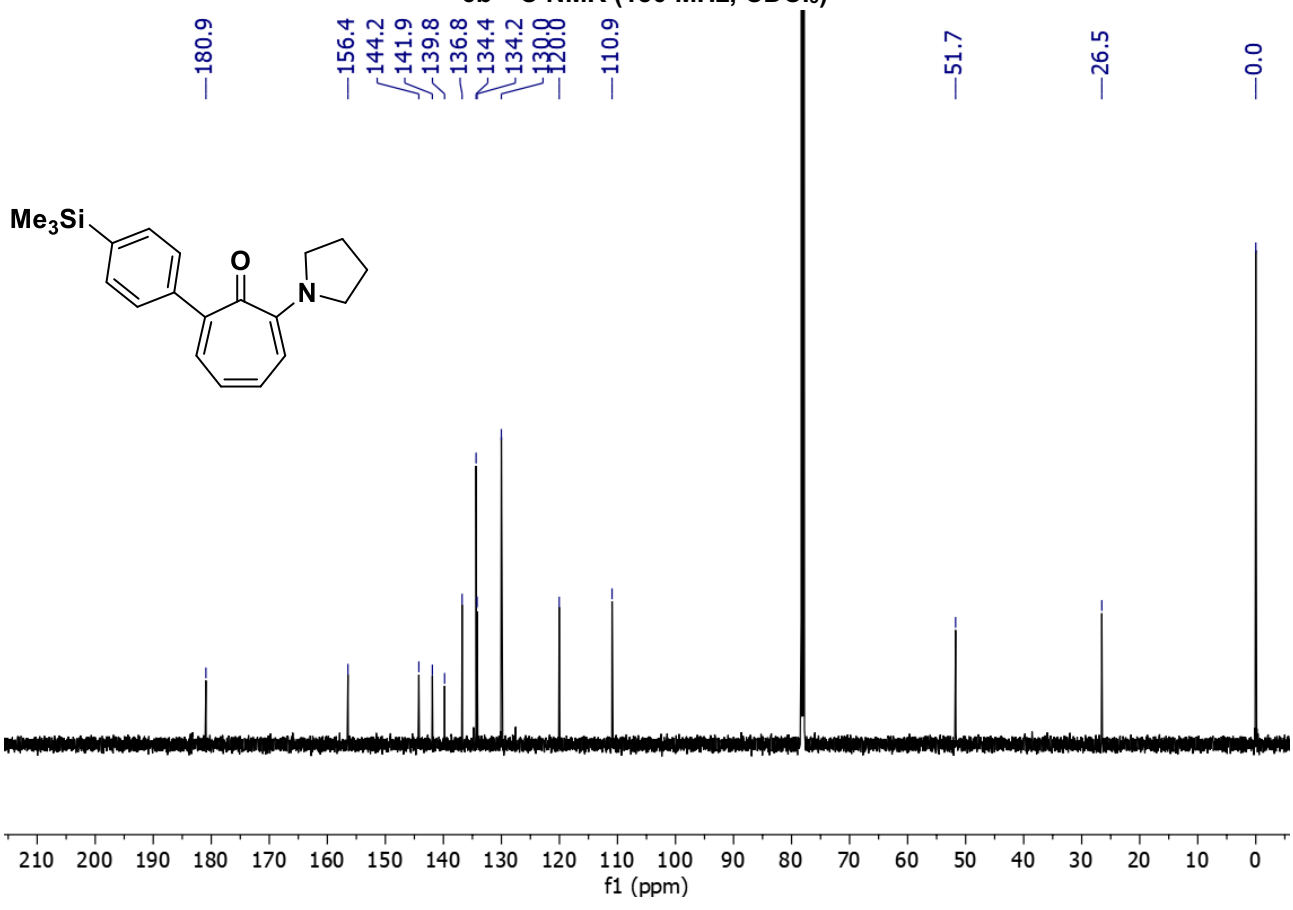

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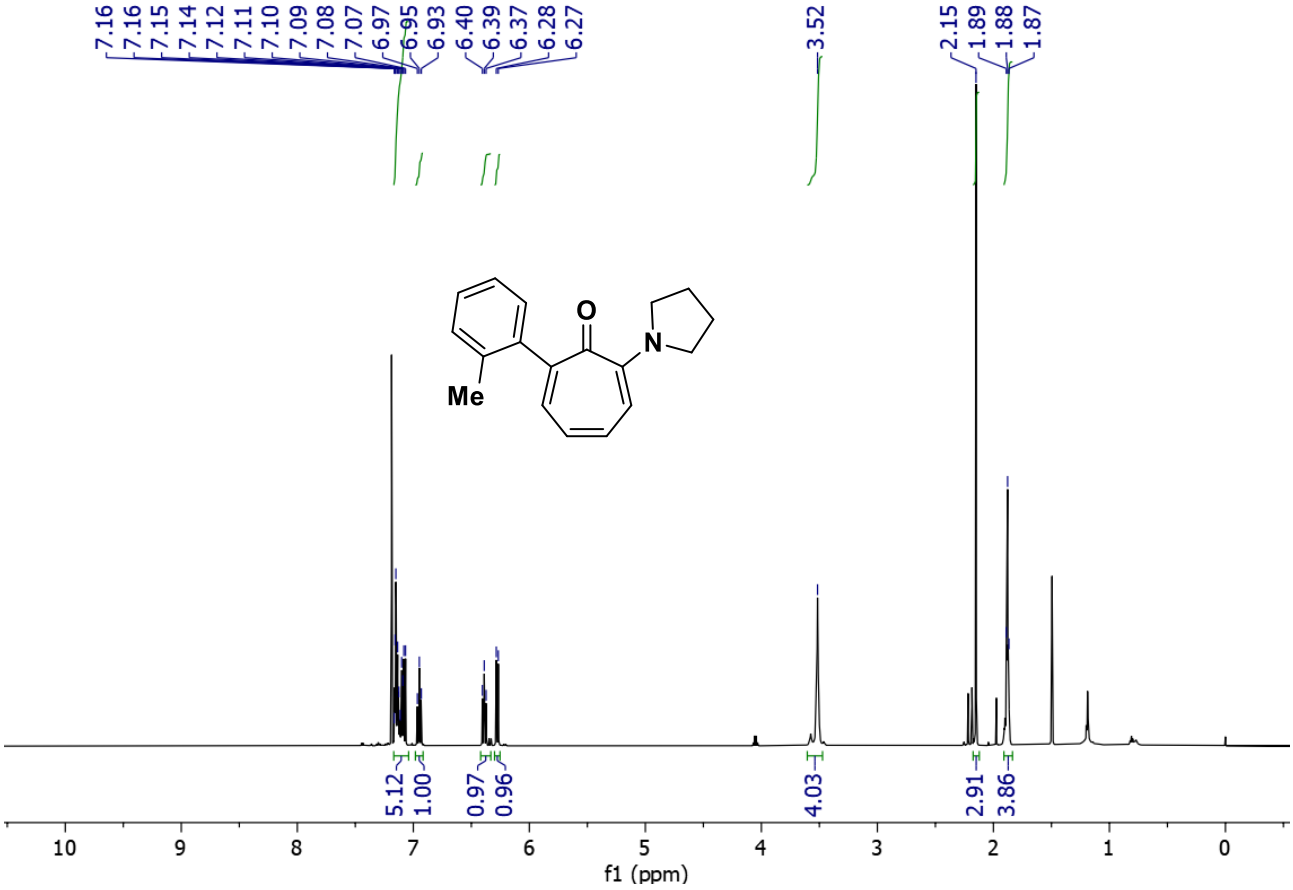

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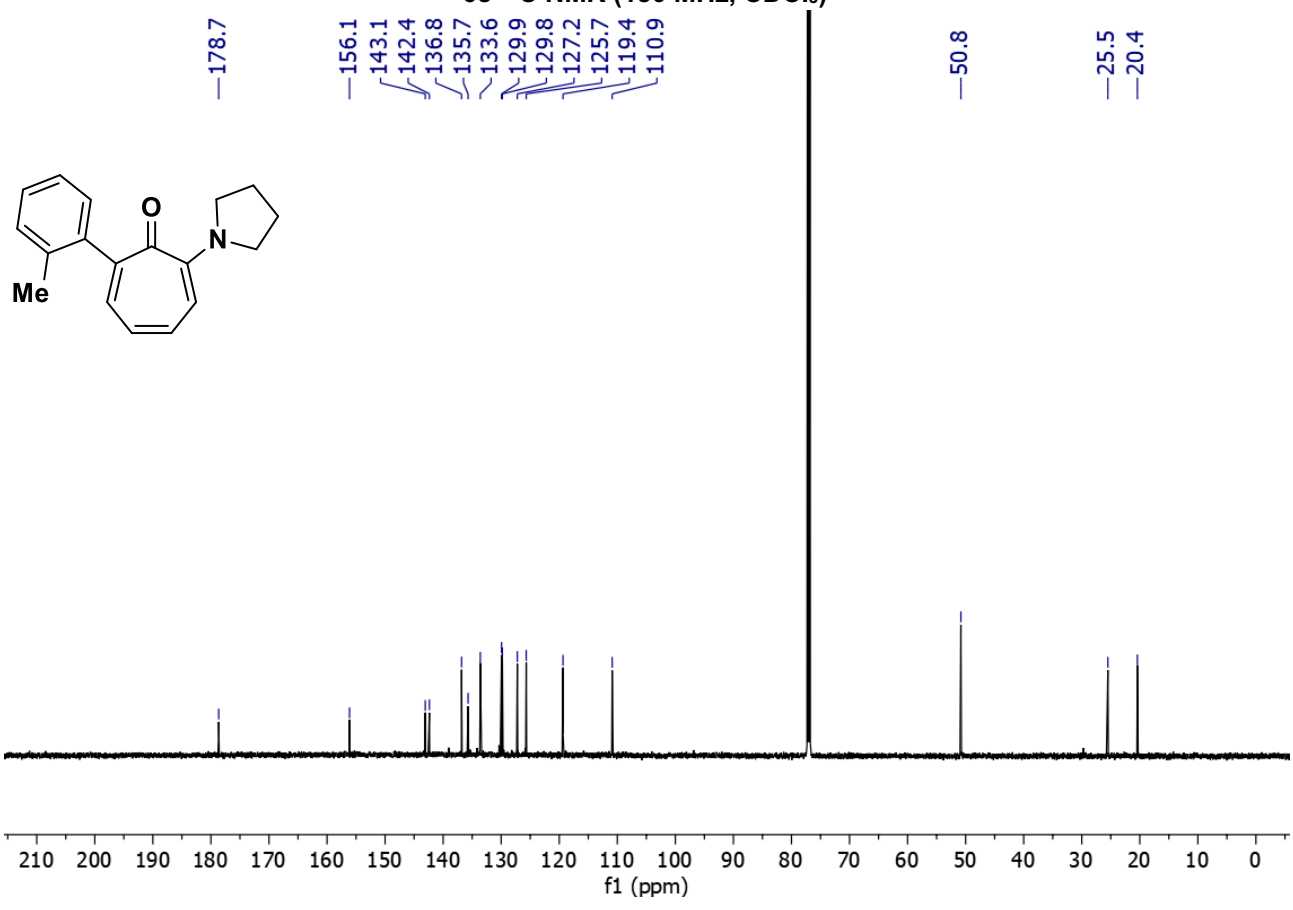

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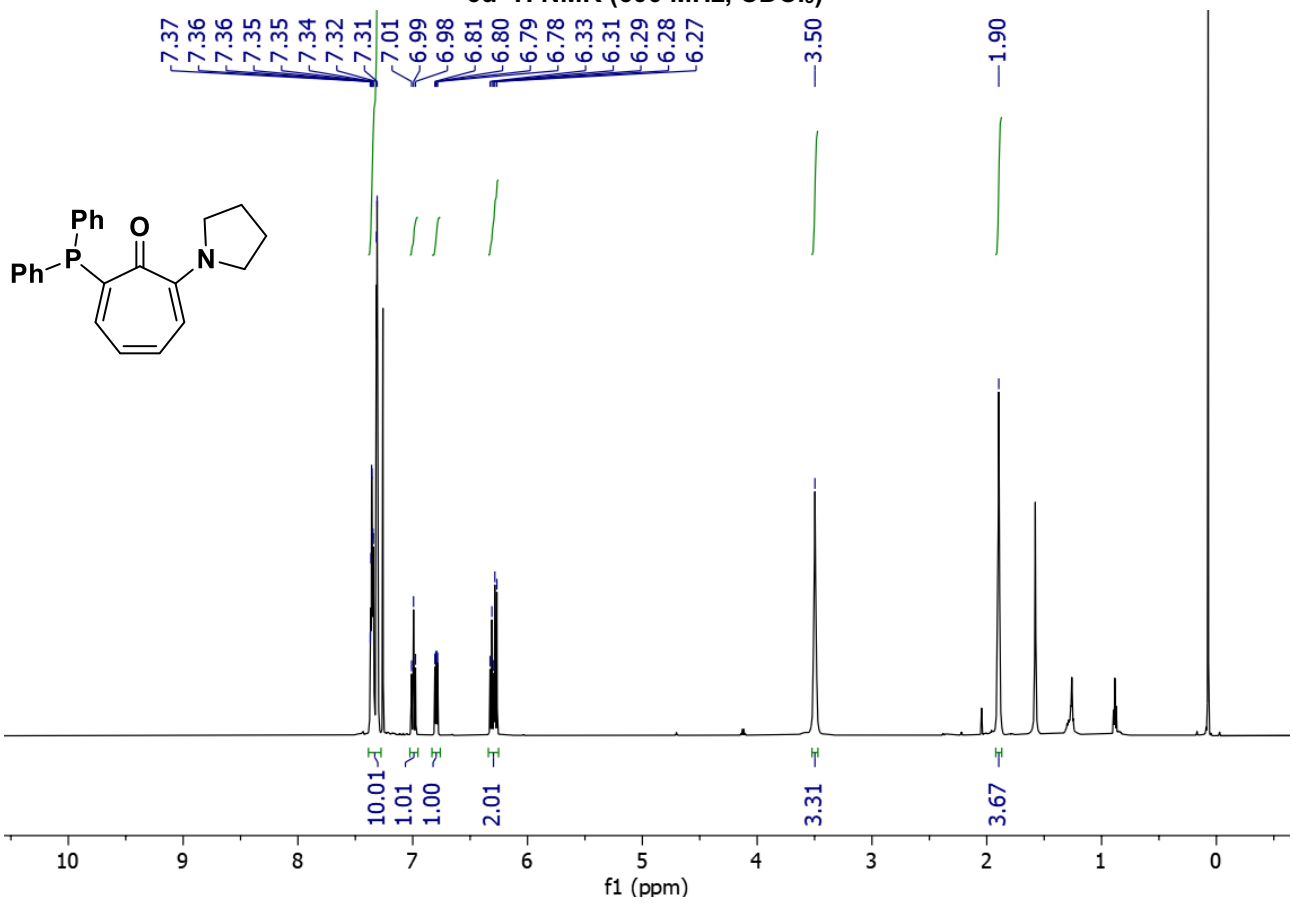

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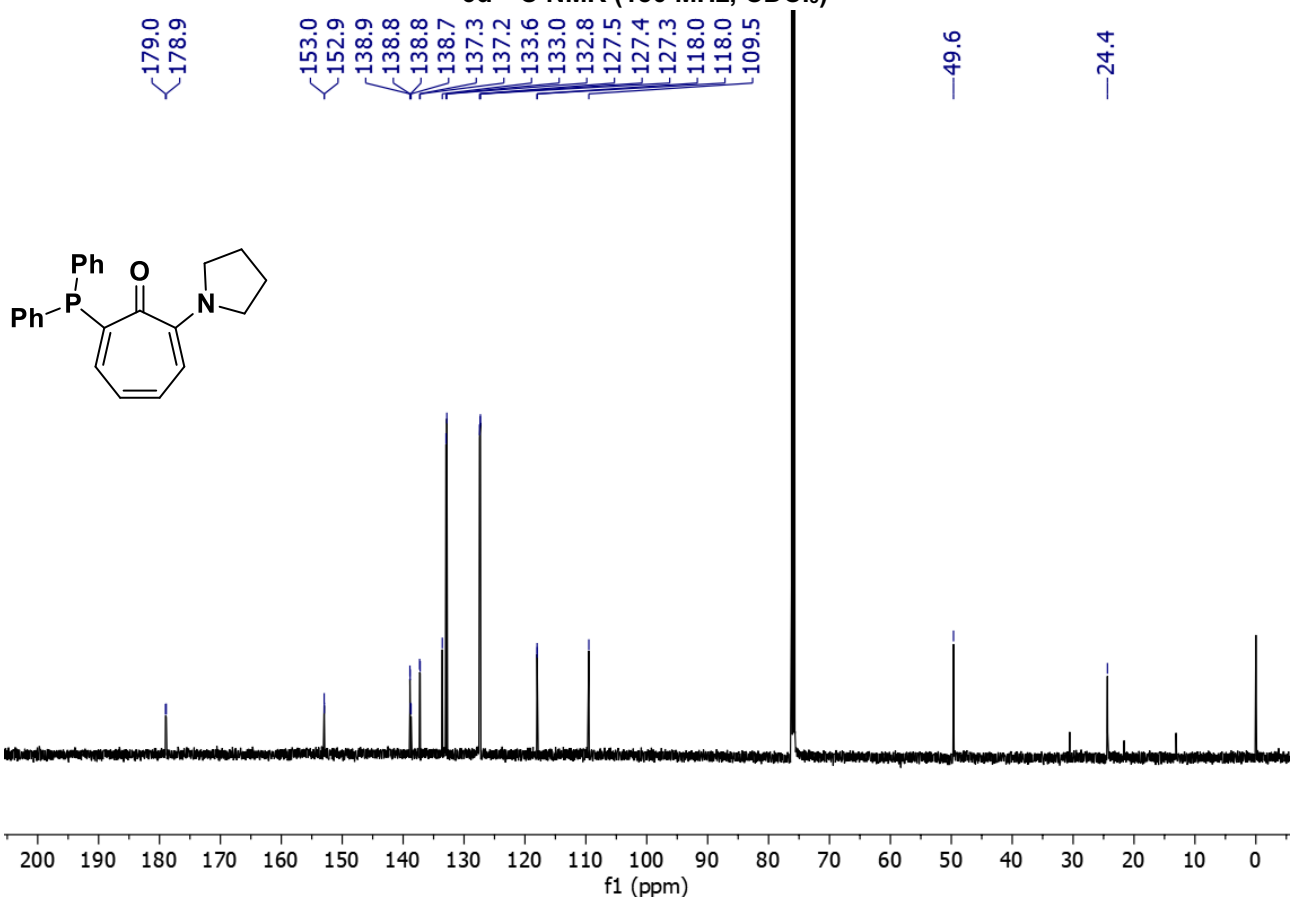

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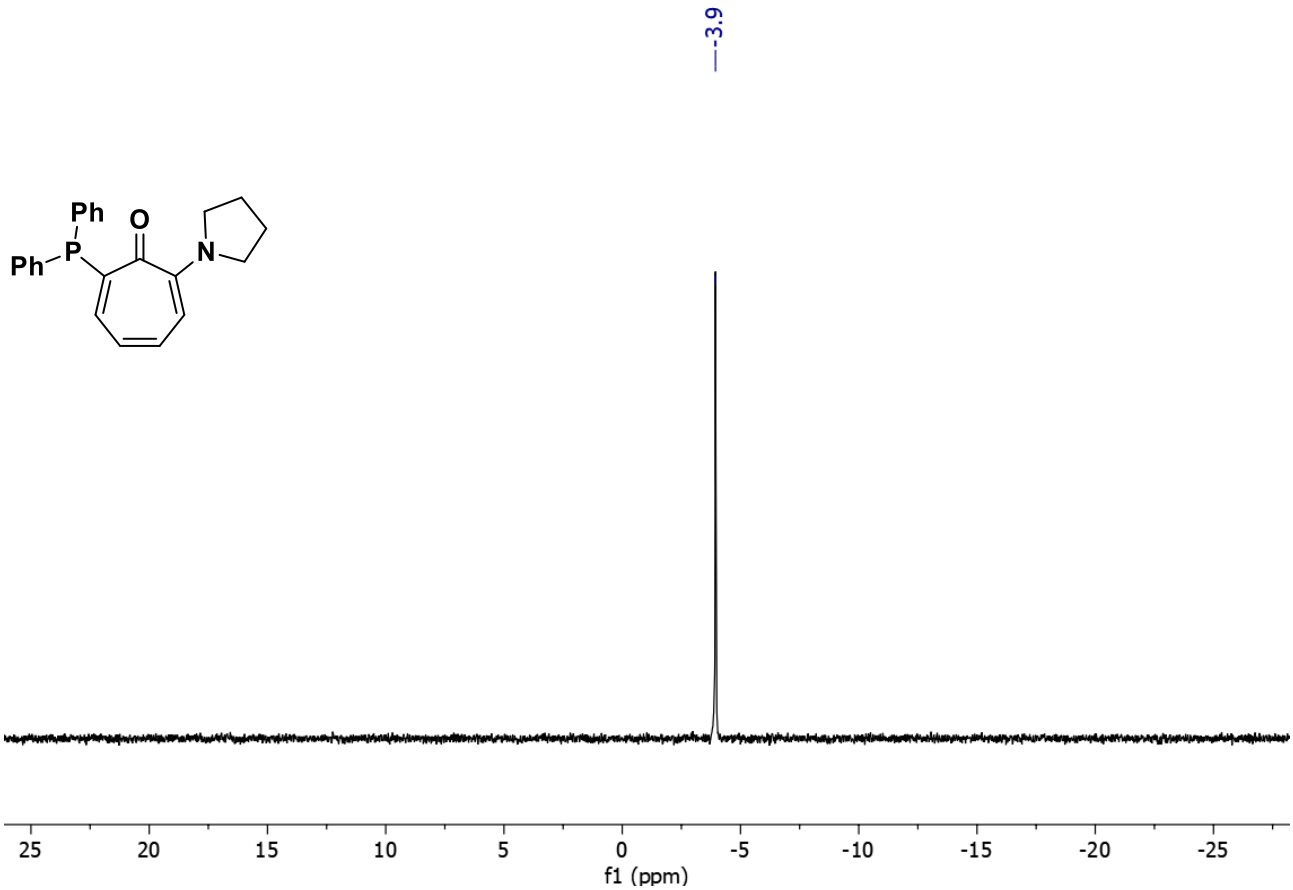

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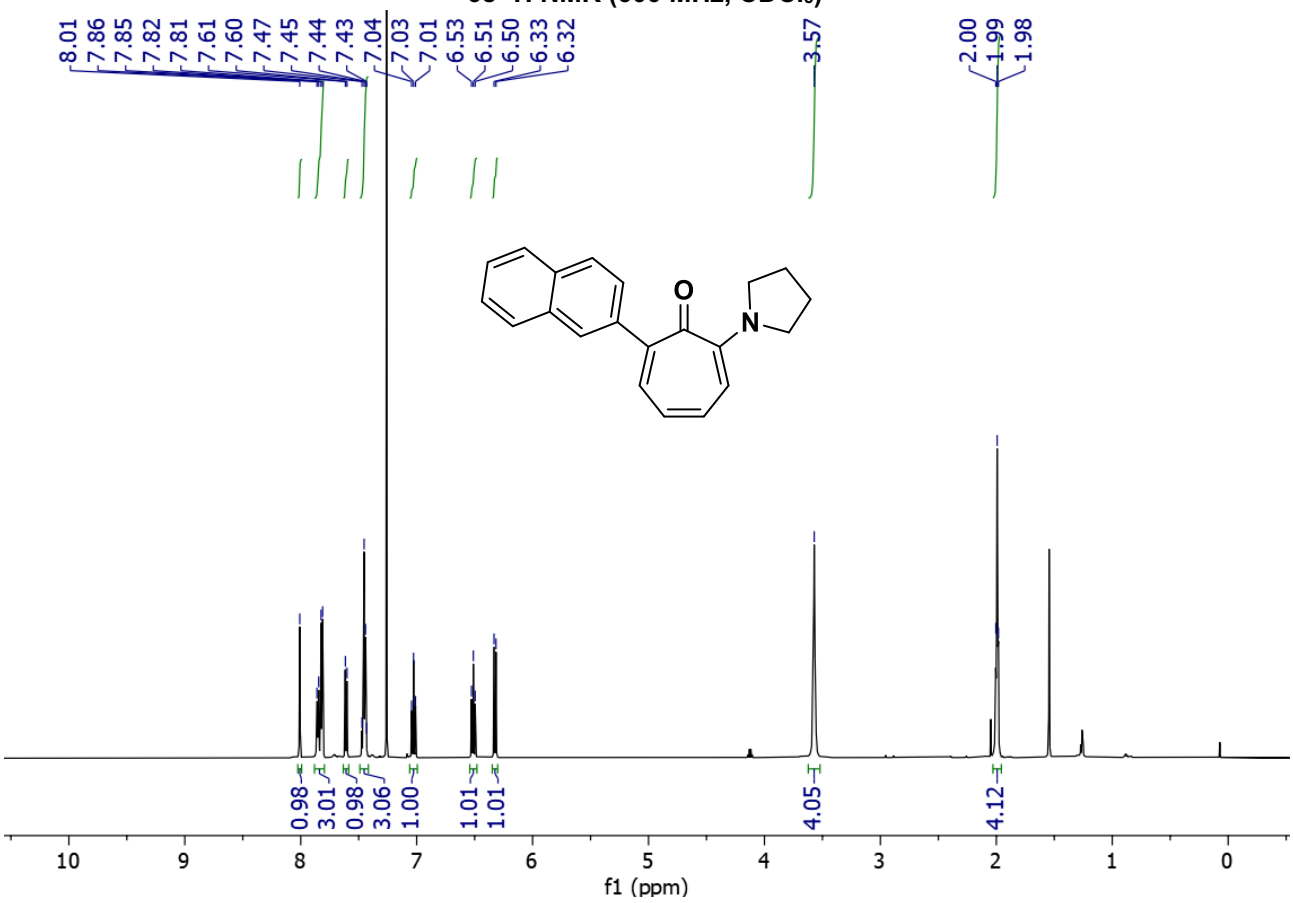

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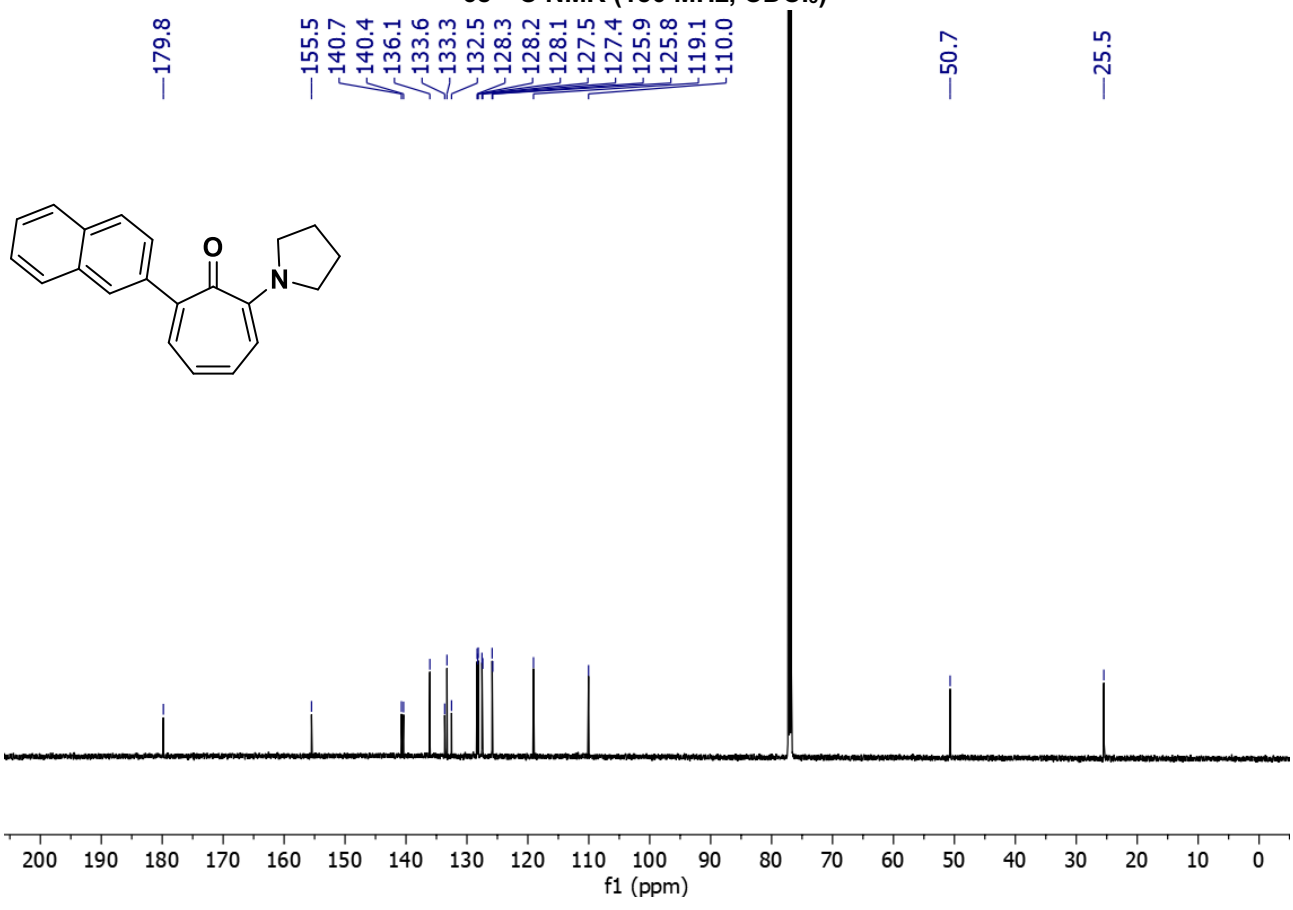
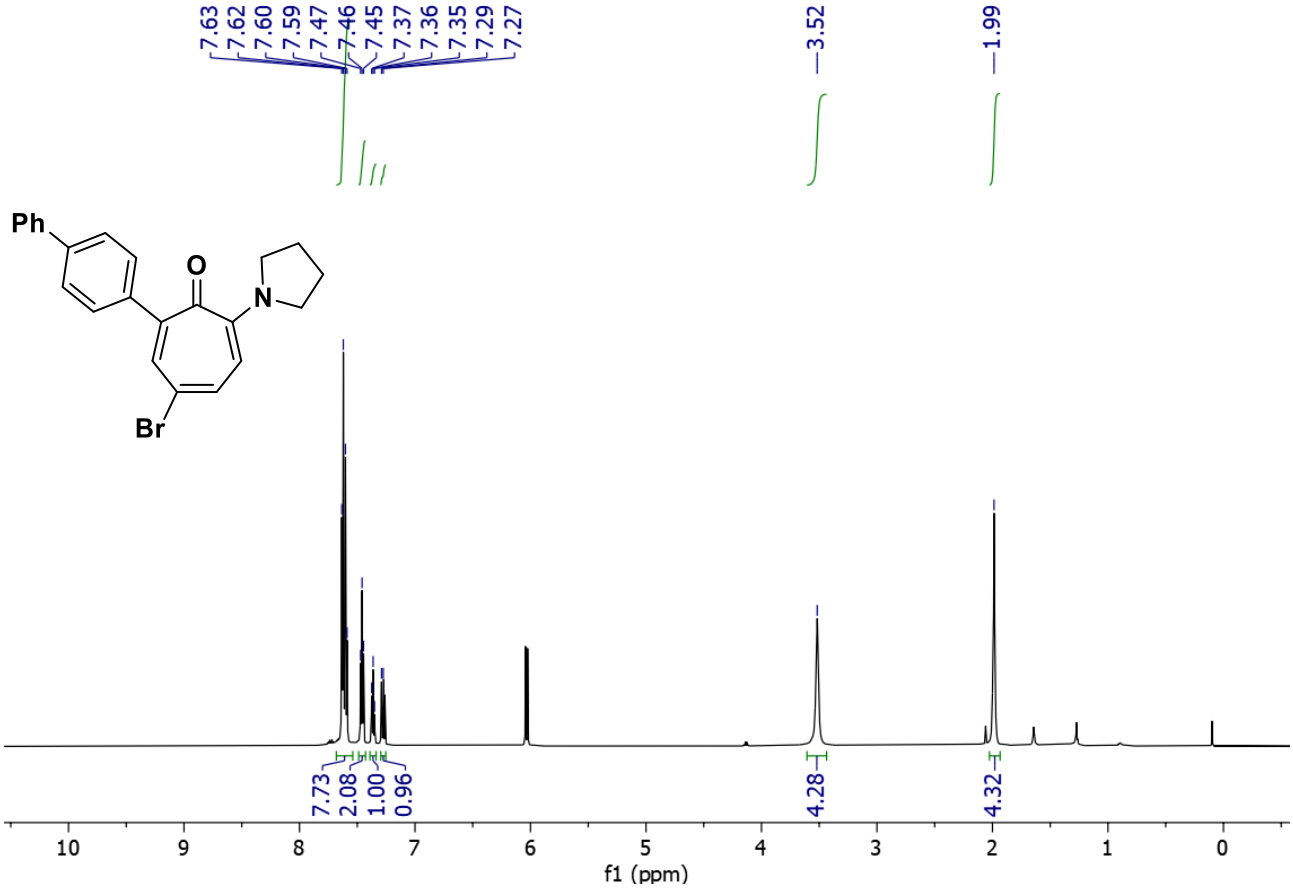


7aa ^{1}H NMR (600 MHz, $CDCl_3$)



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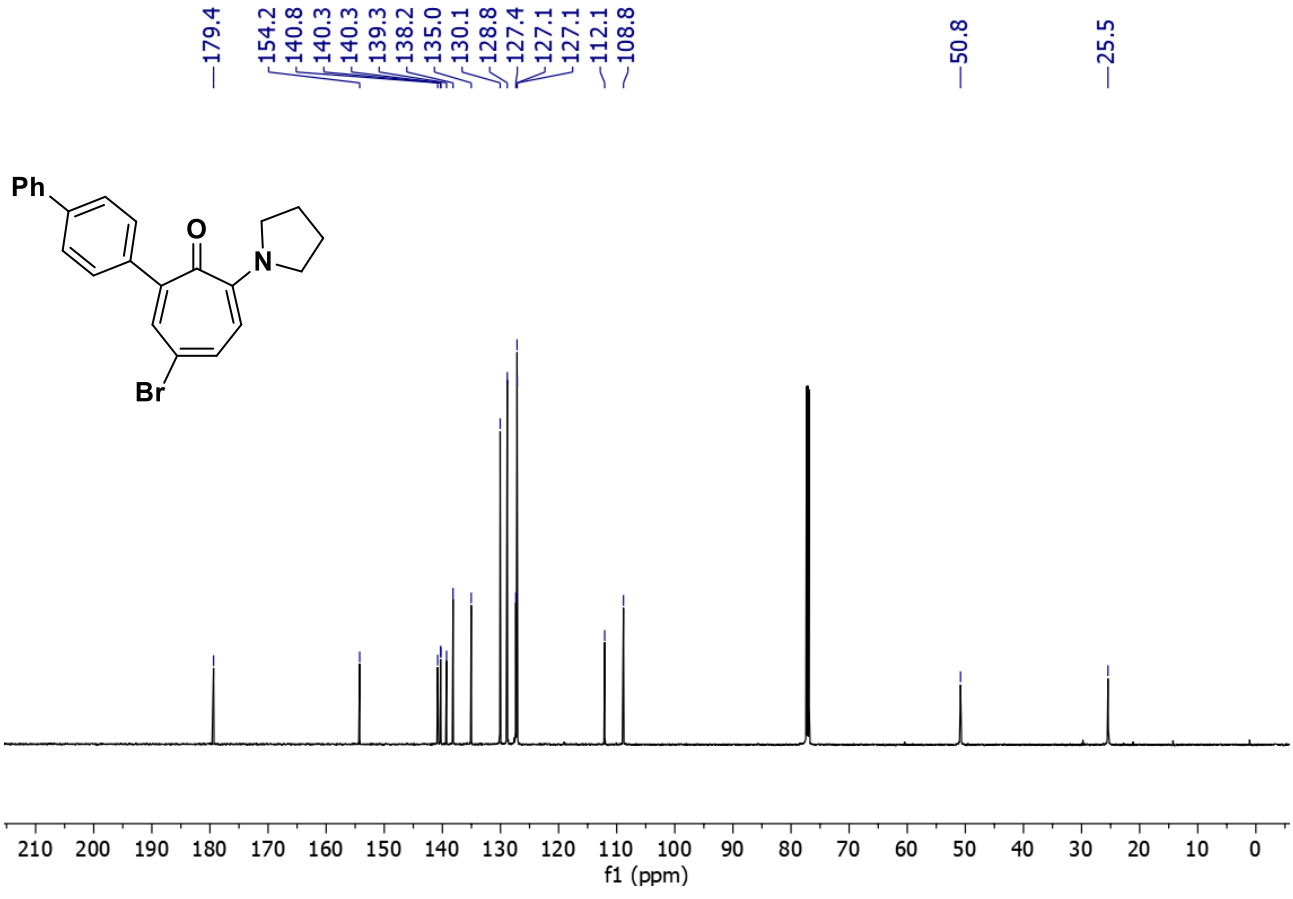

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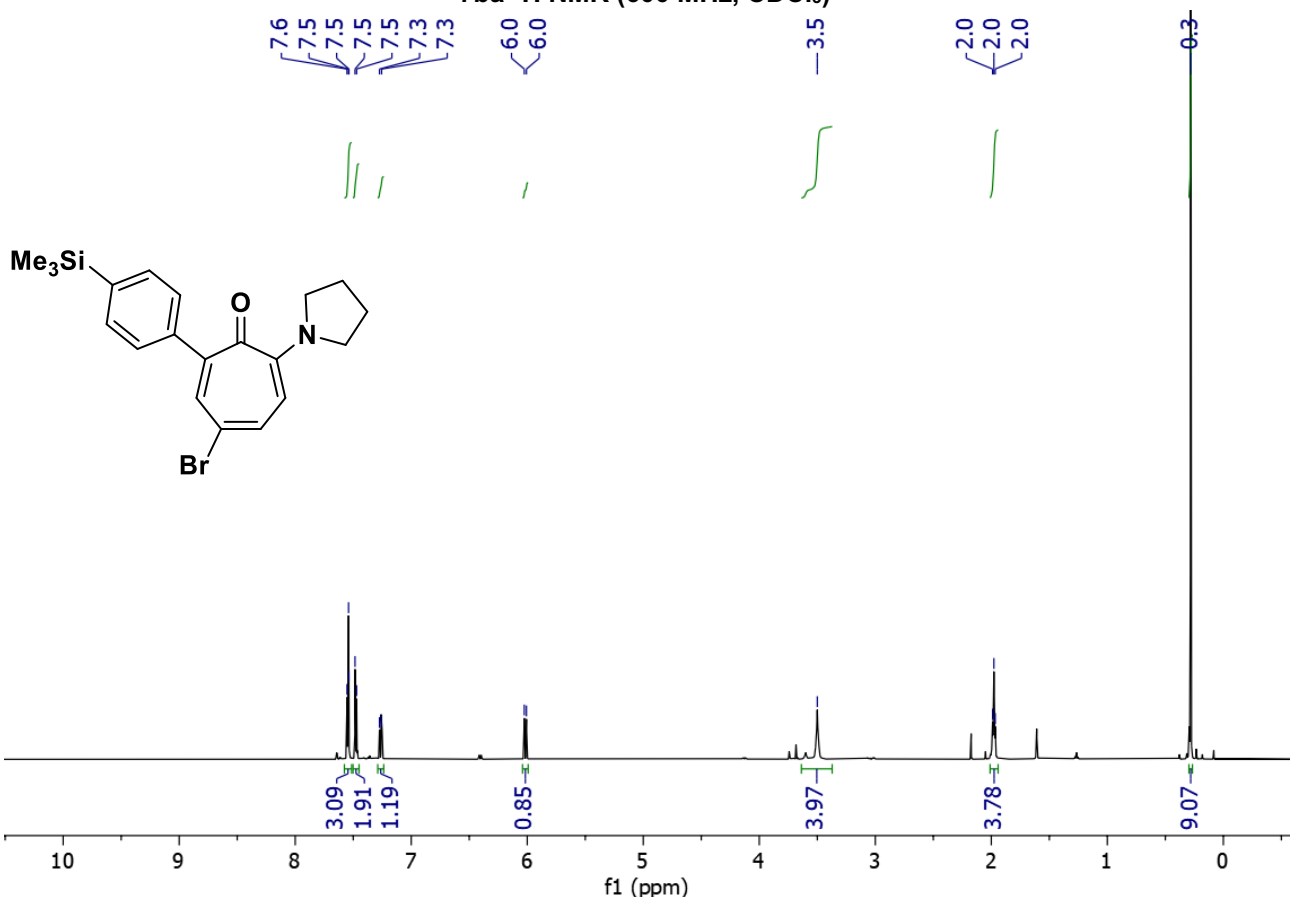

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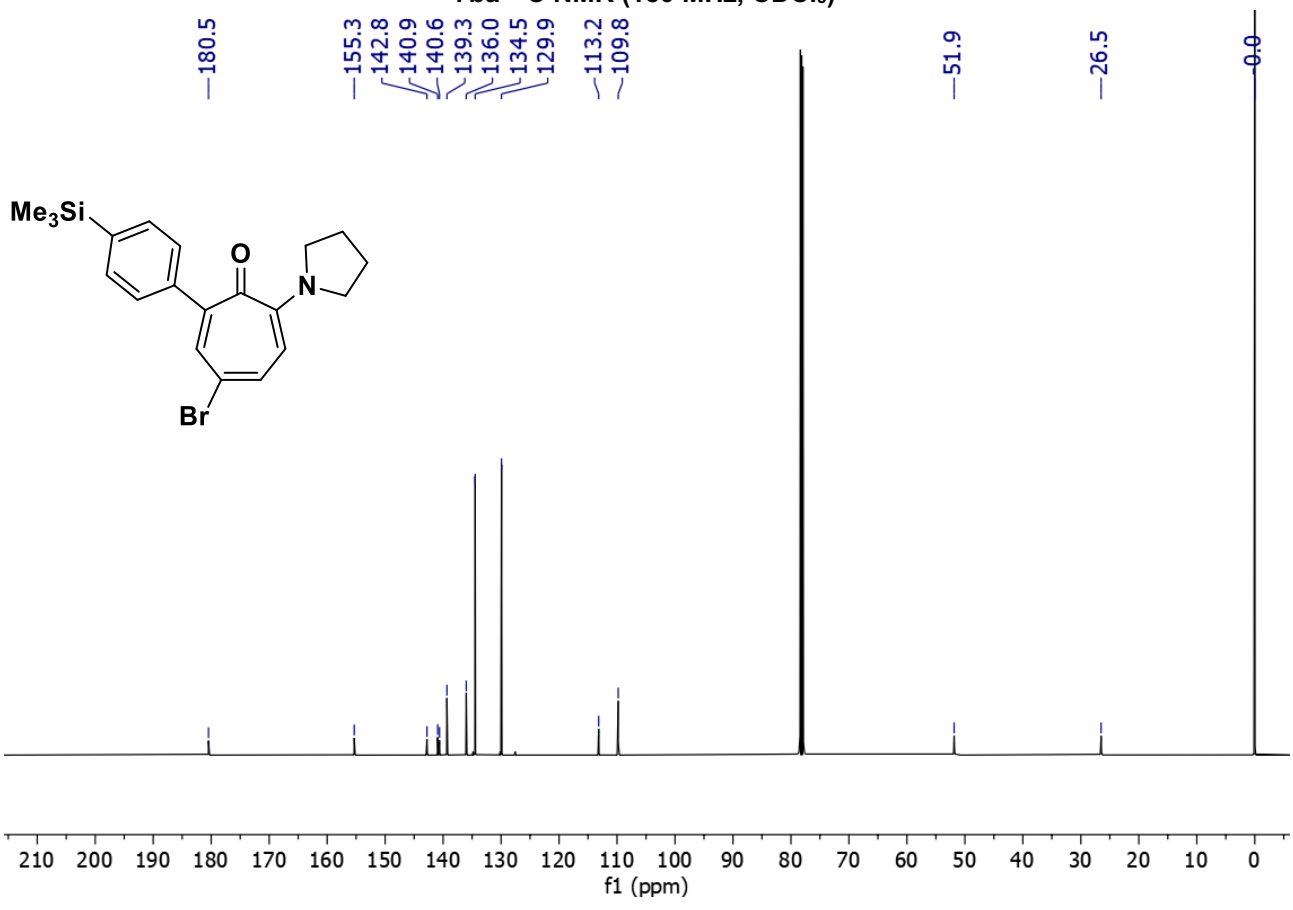

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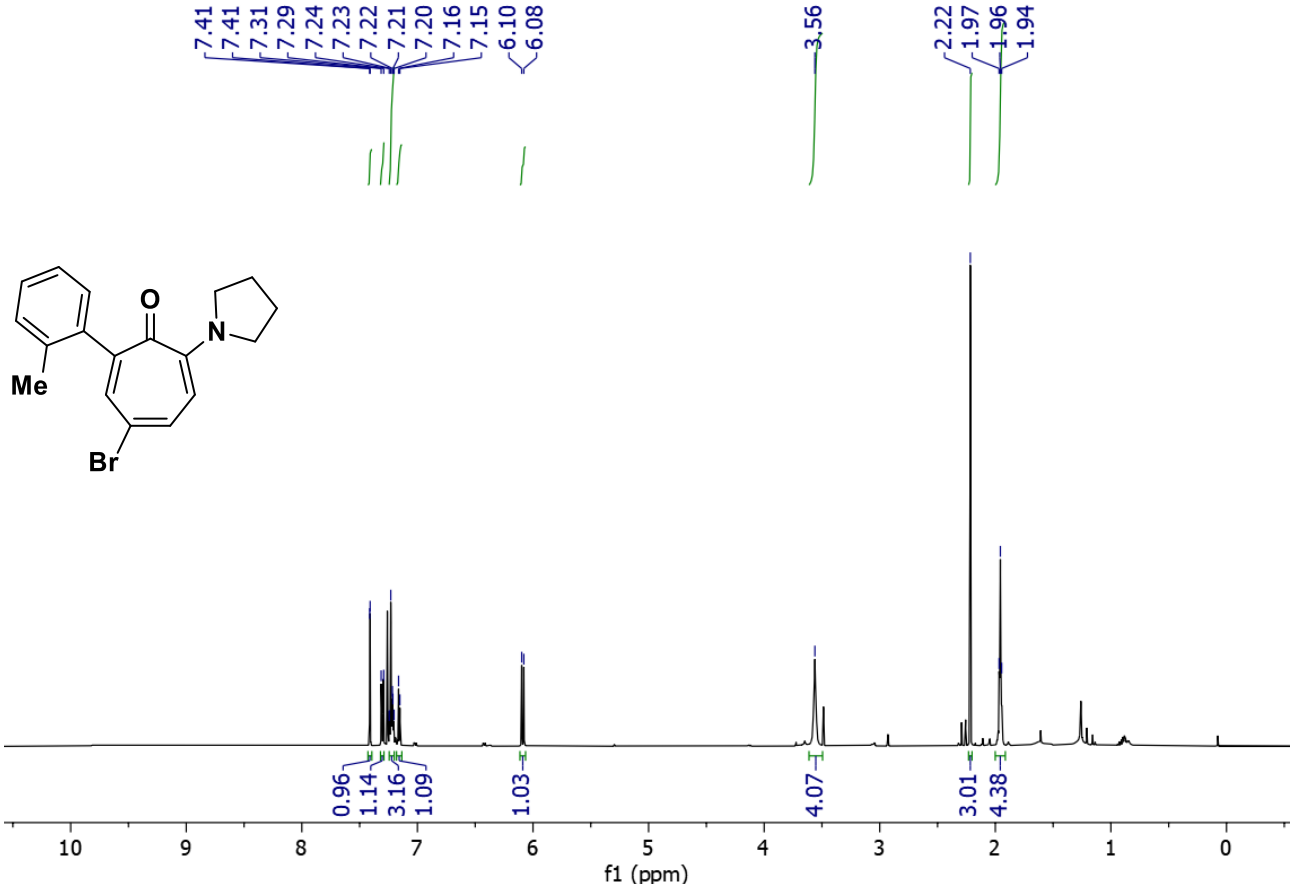

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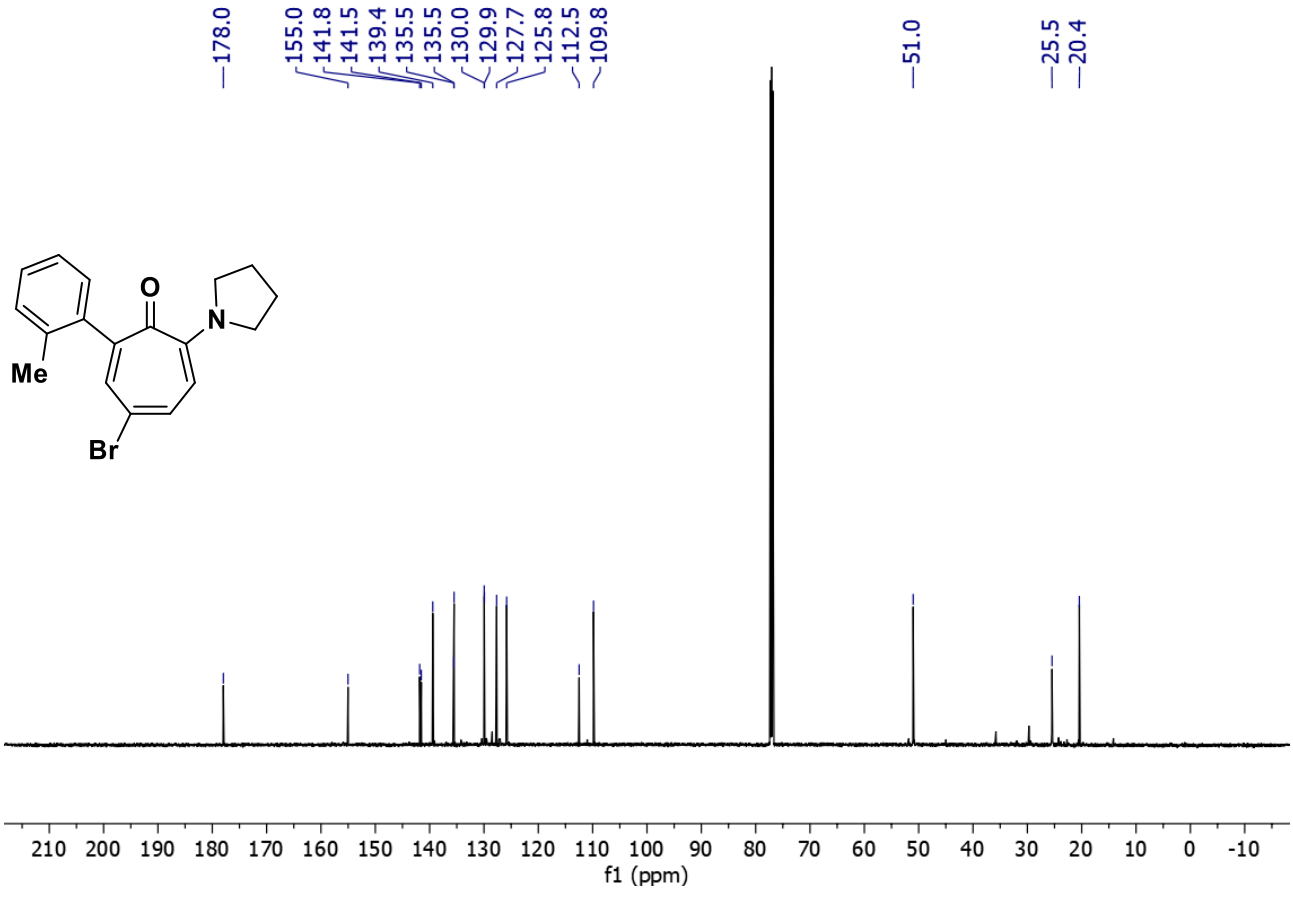

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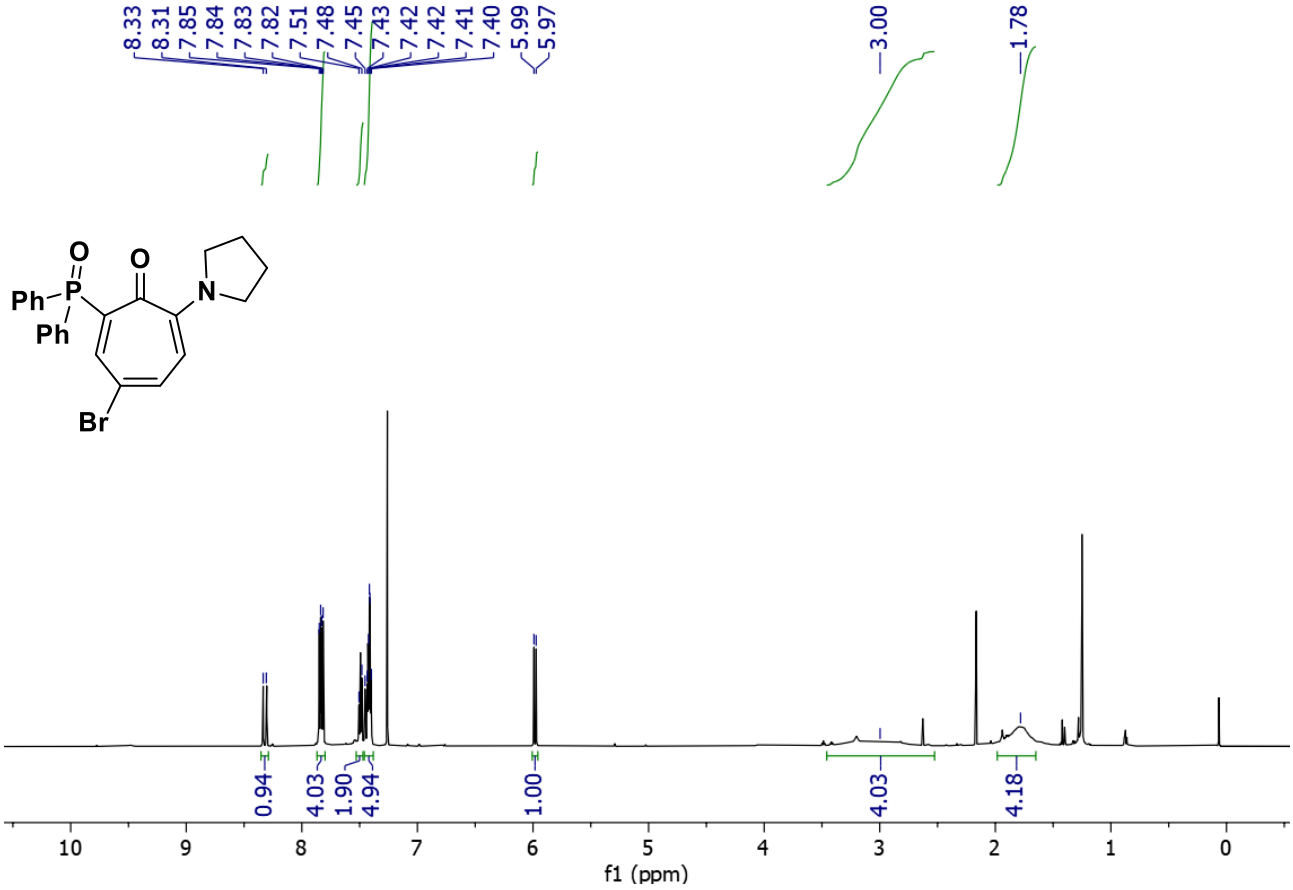

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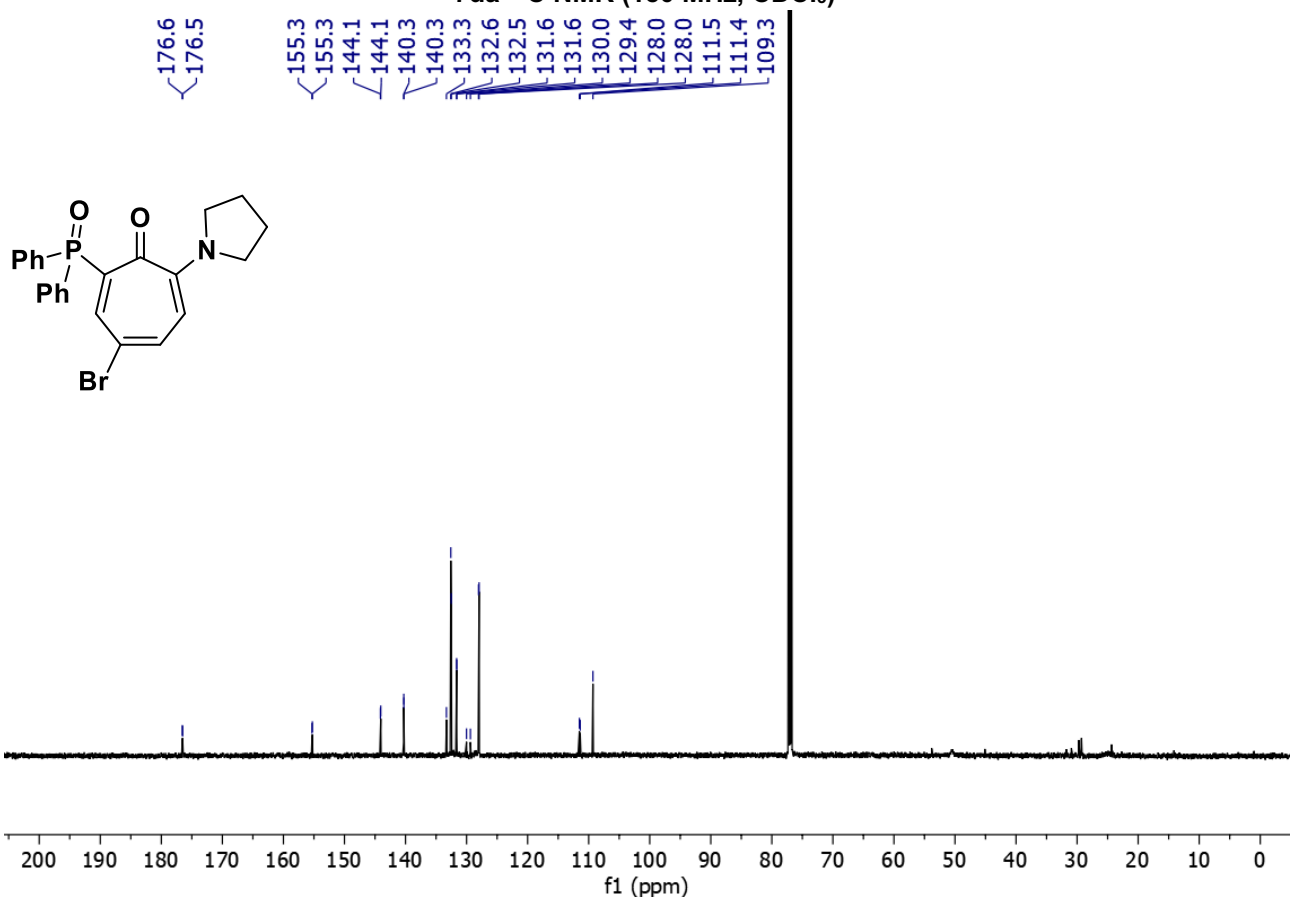
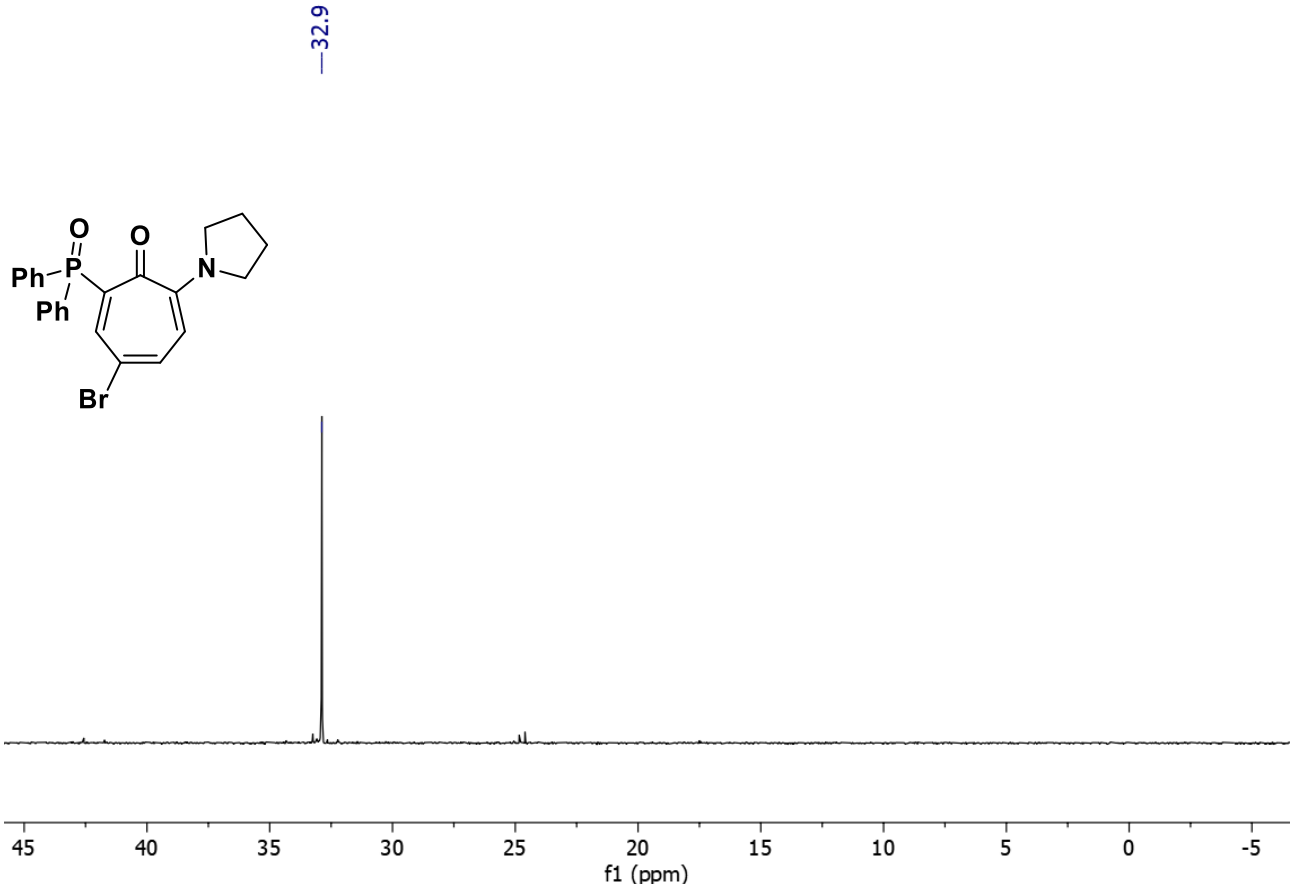


7da ^{31}P NMR (243 MHz, $CDCl_3$)



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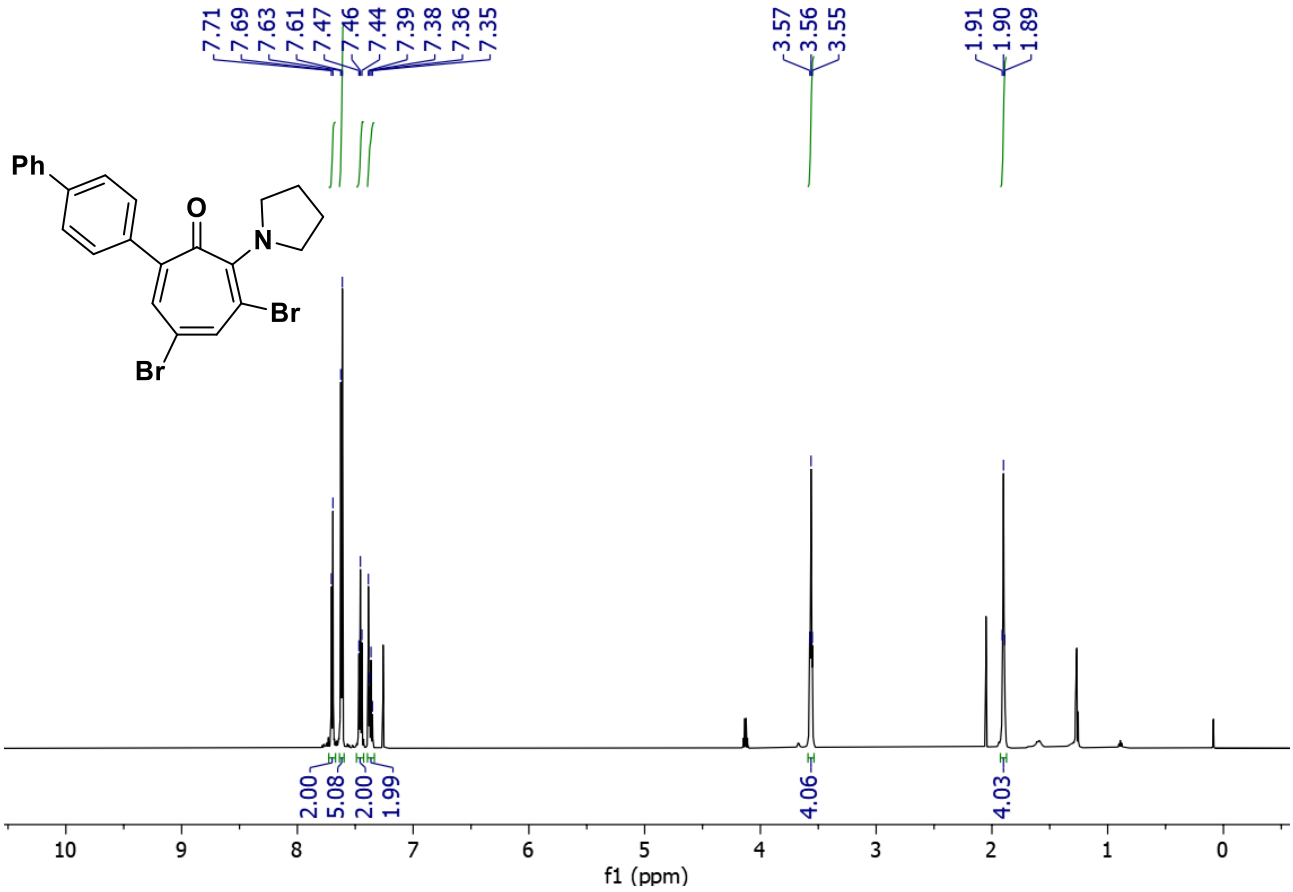

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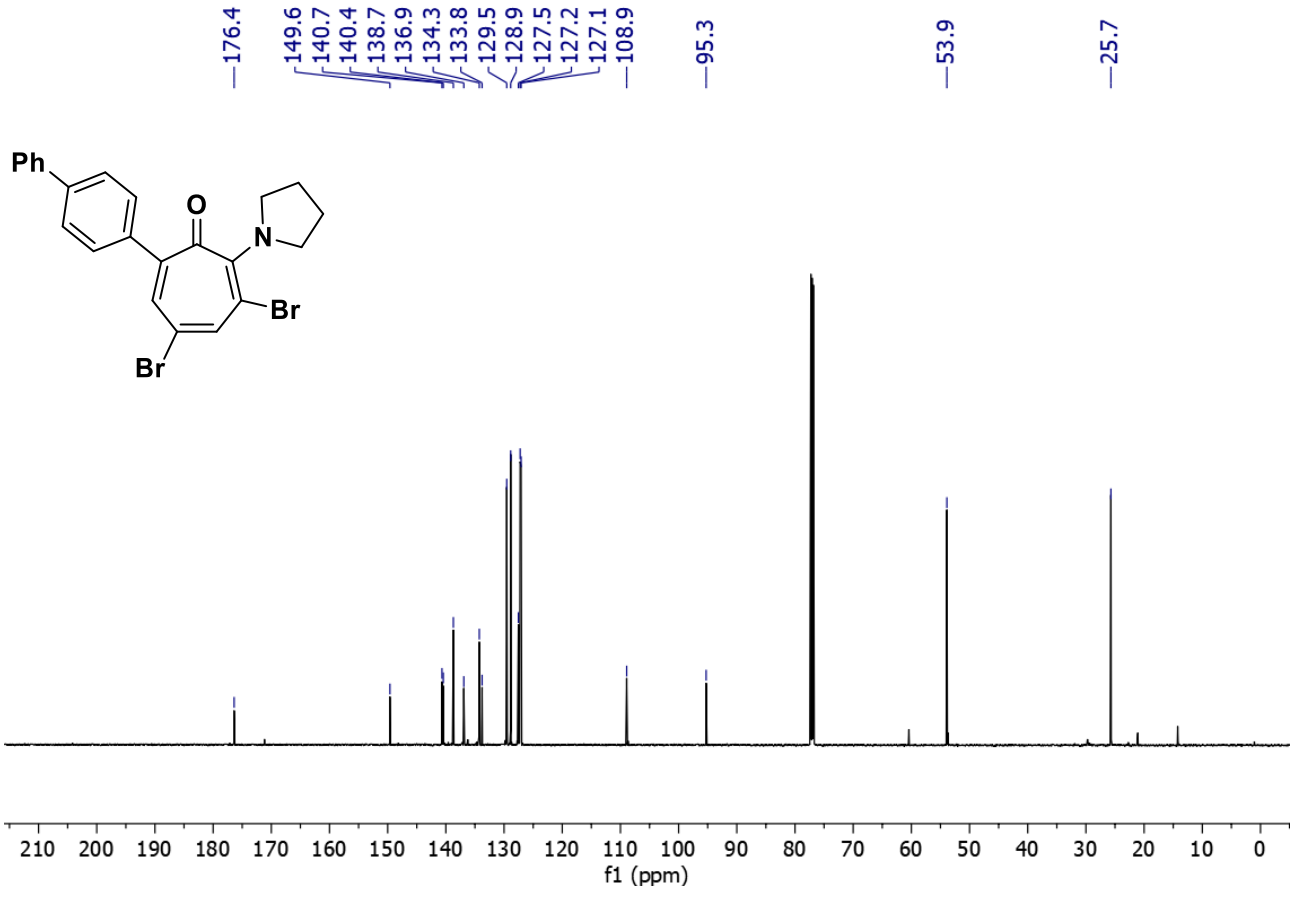

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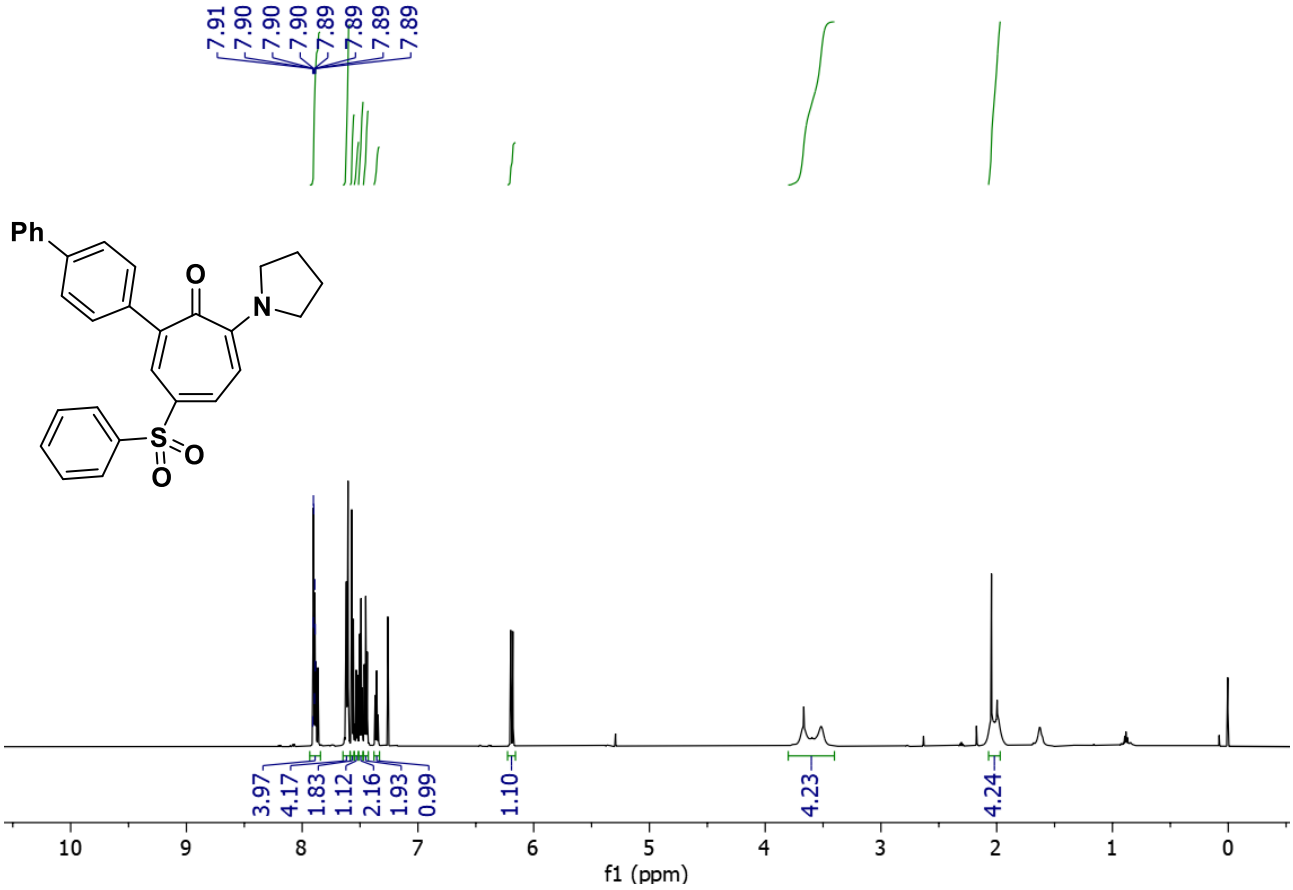

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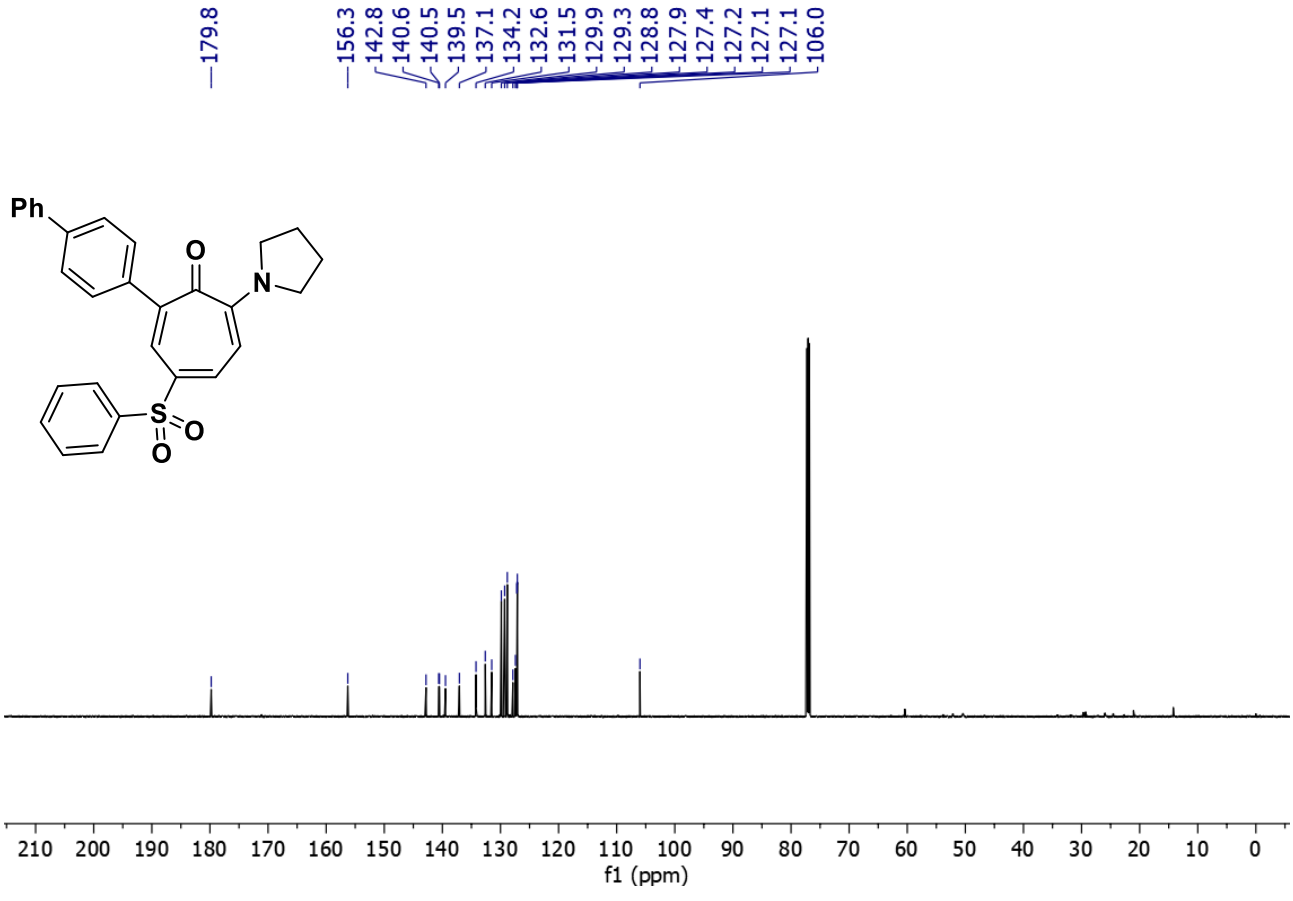

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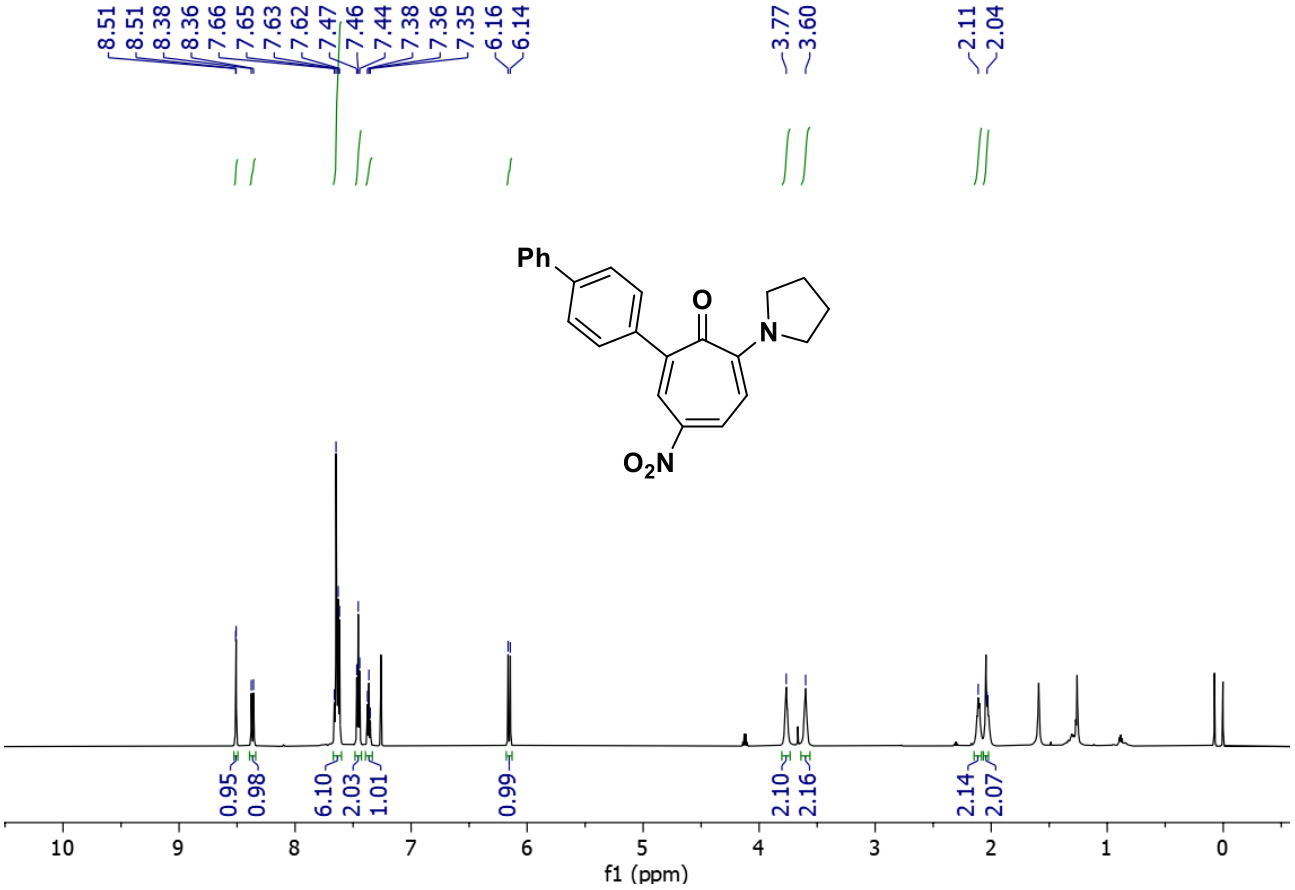

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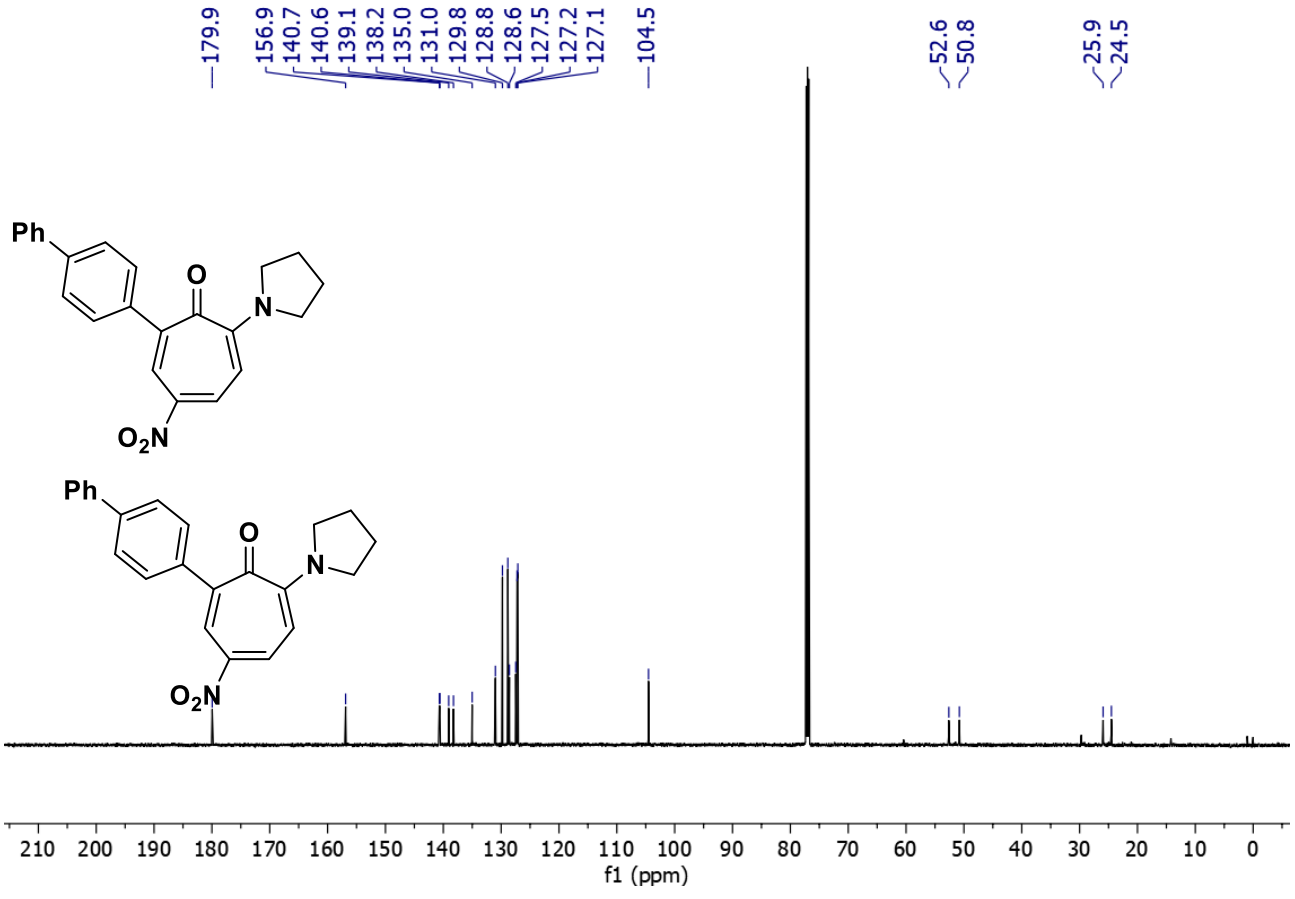

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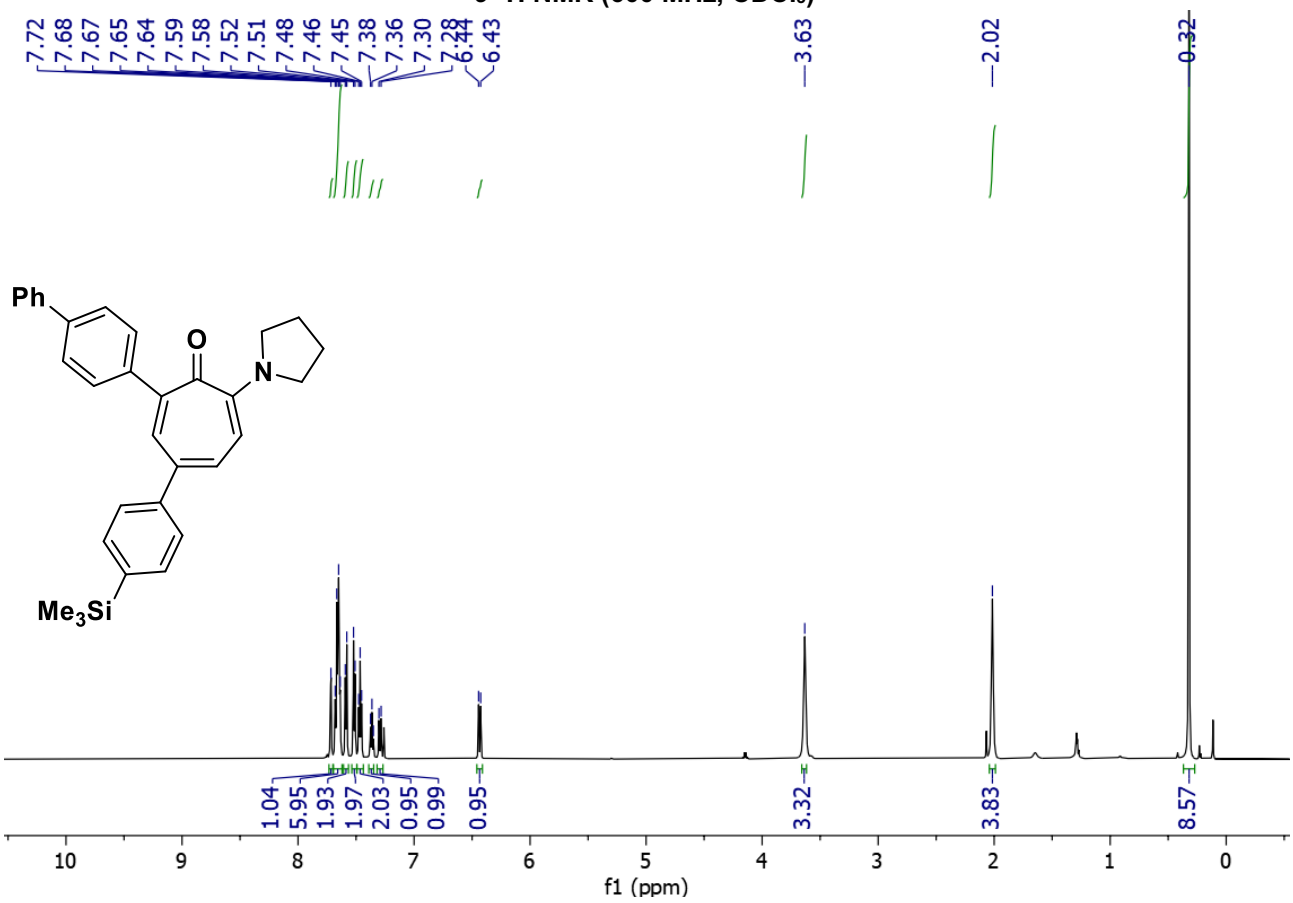
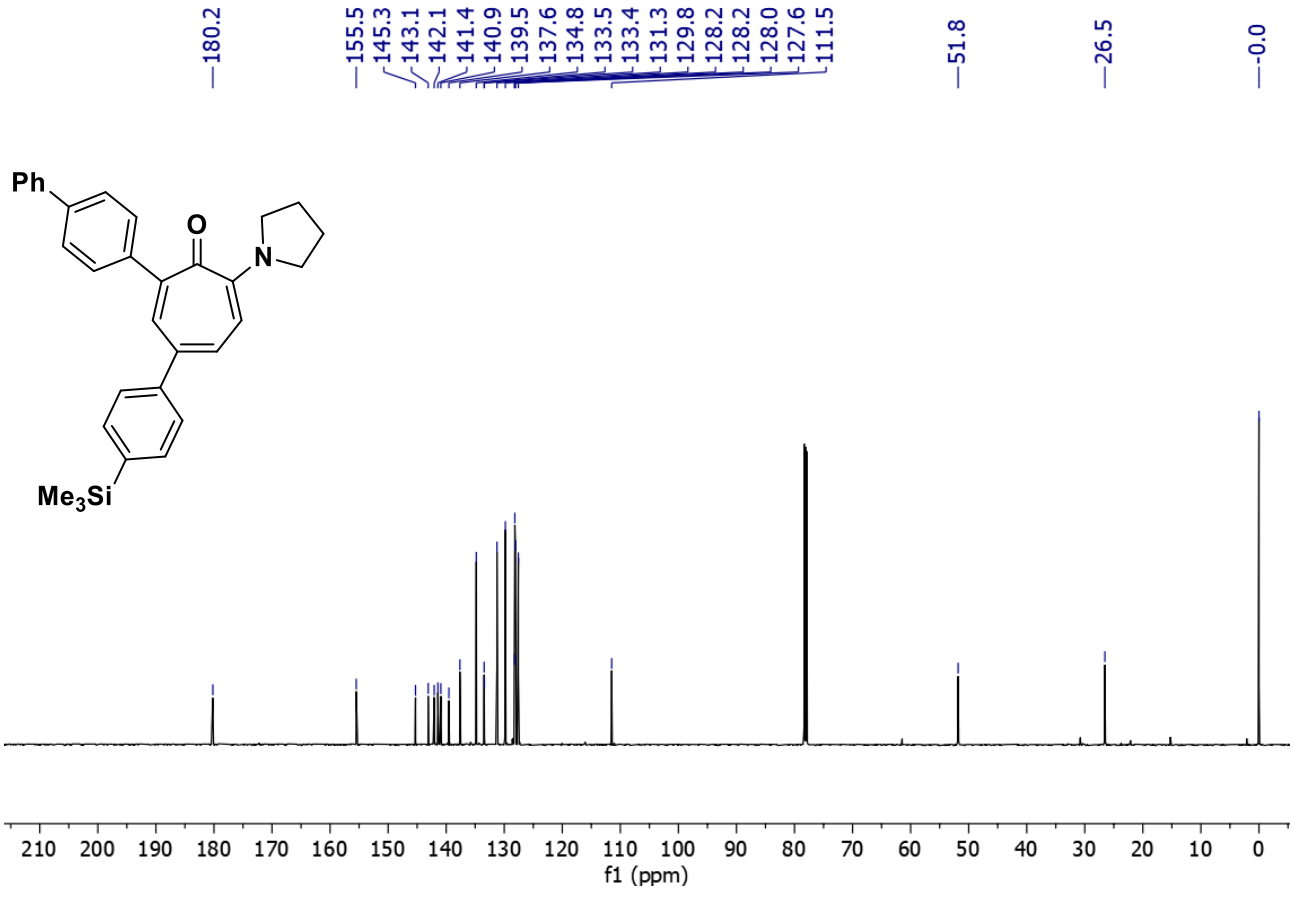


9 ^{13}C NMR (150 MHz, $CDCl_3$)



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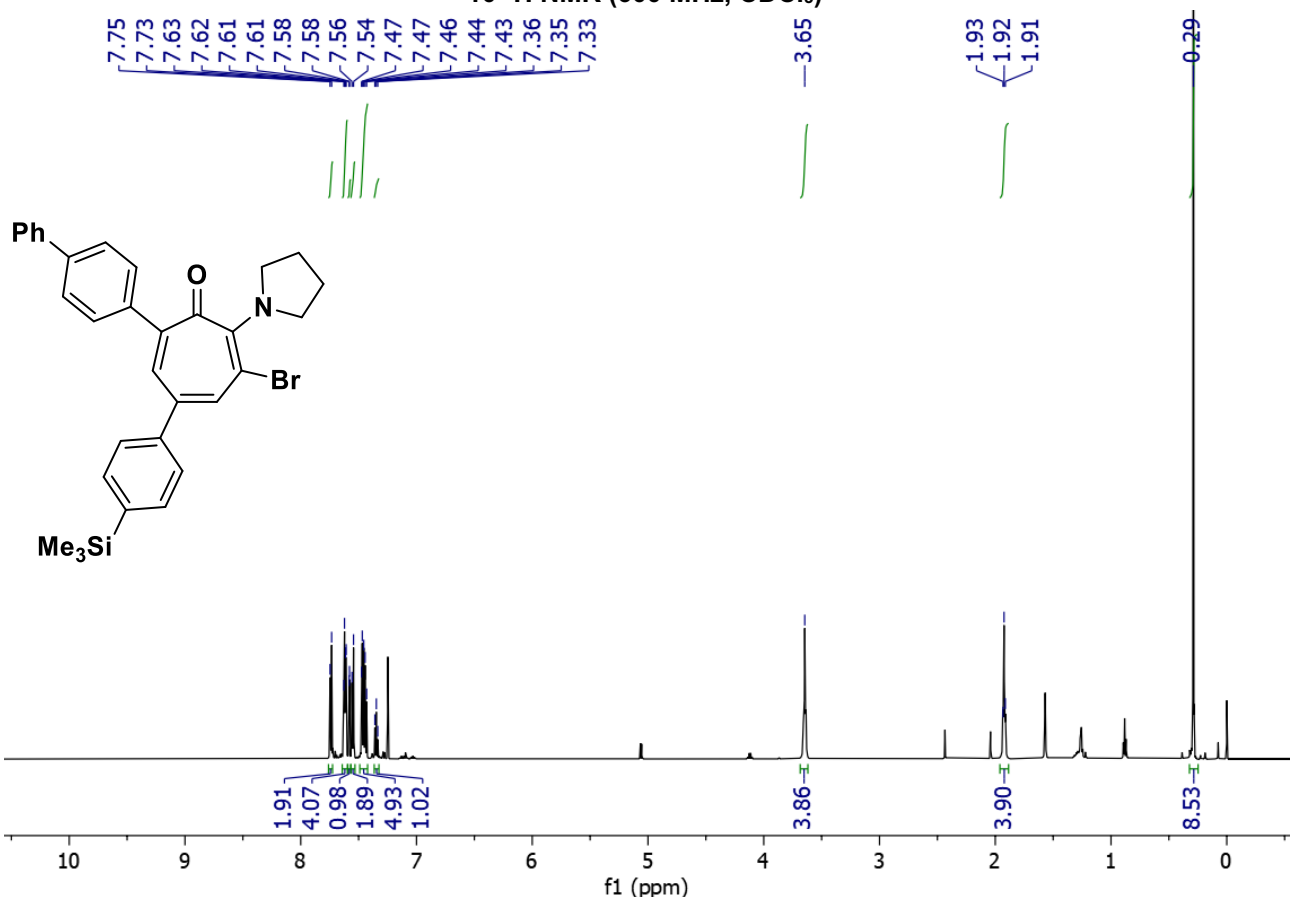

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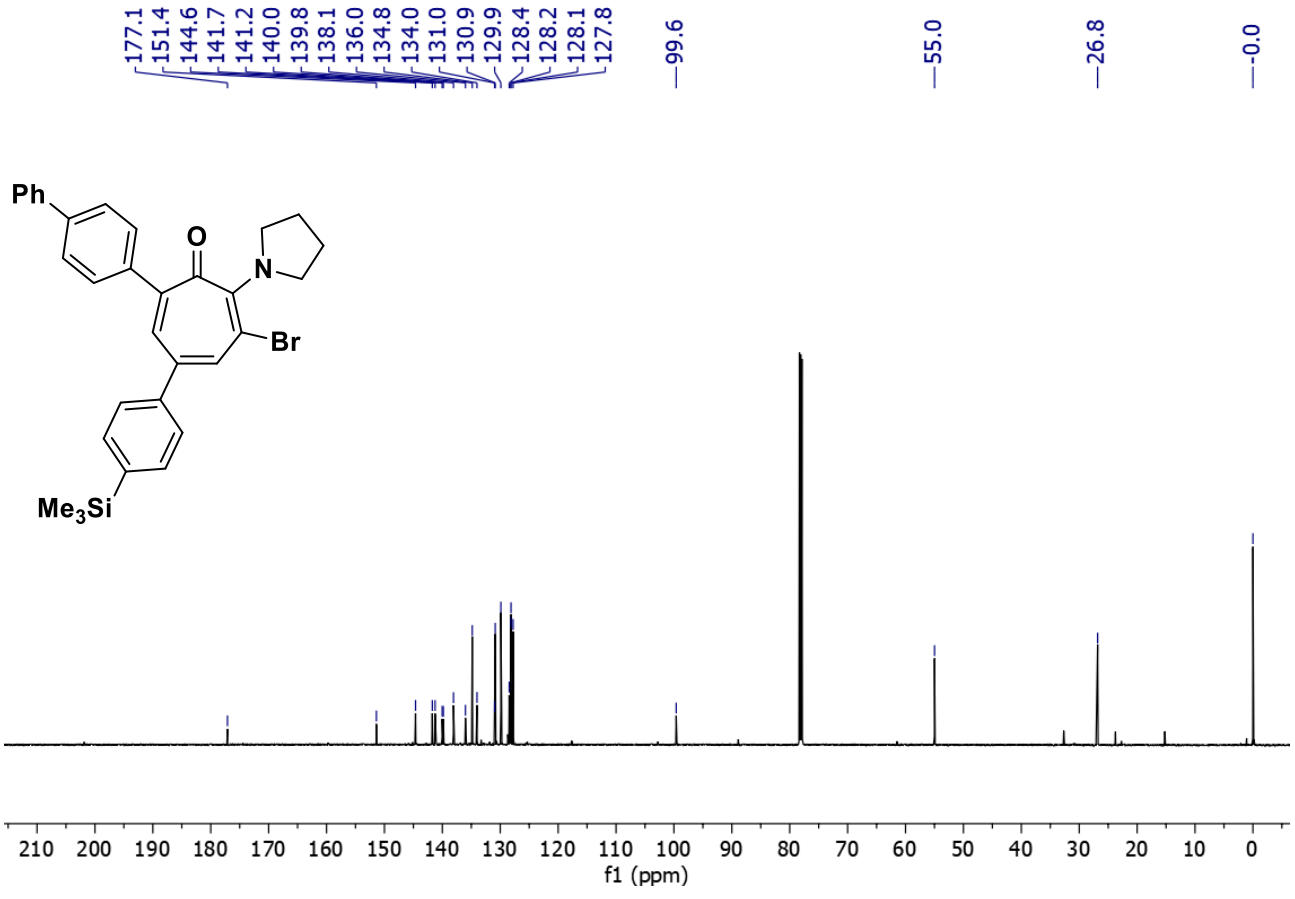

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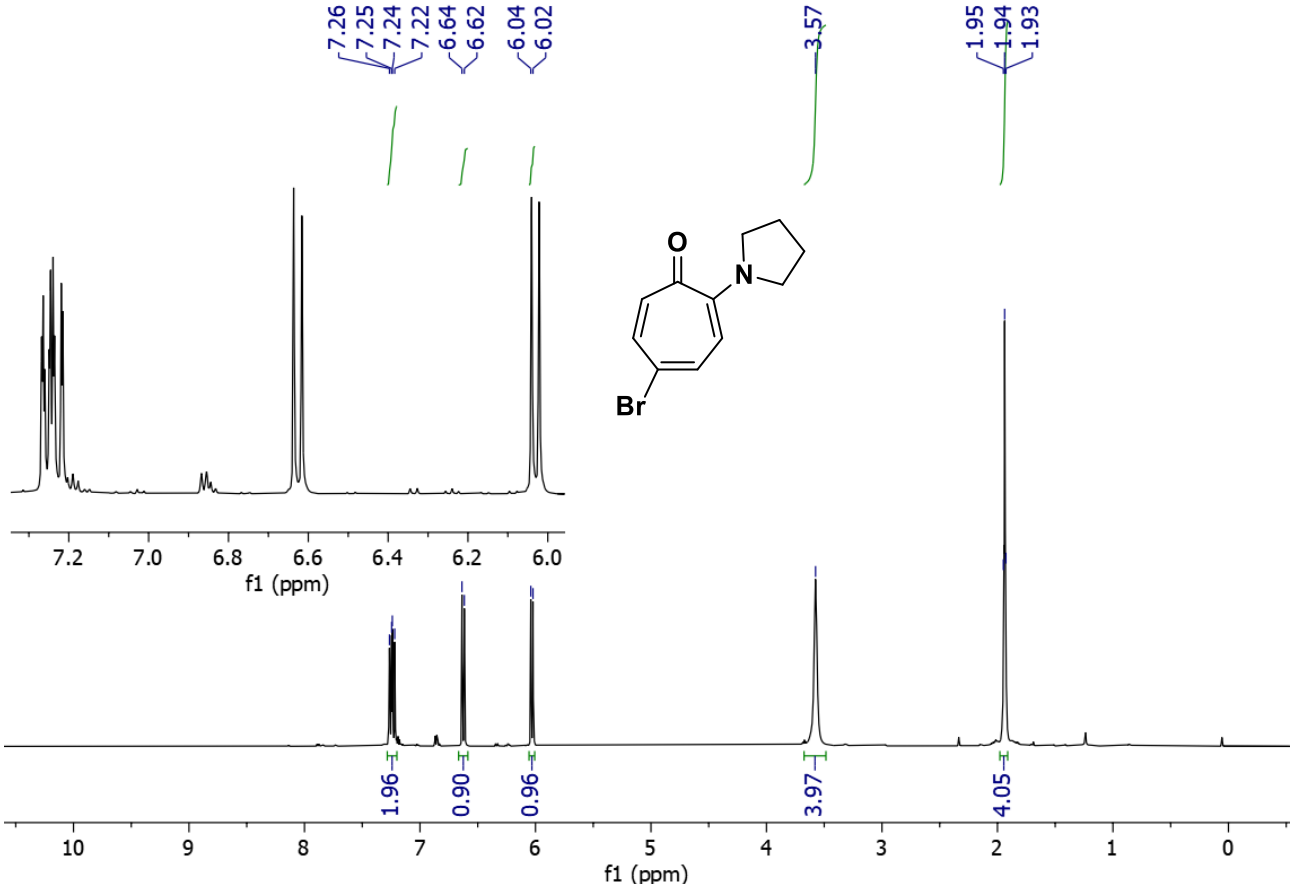
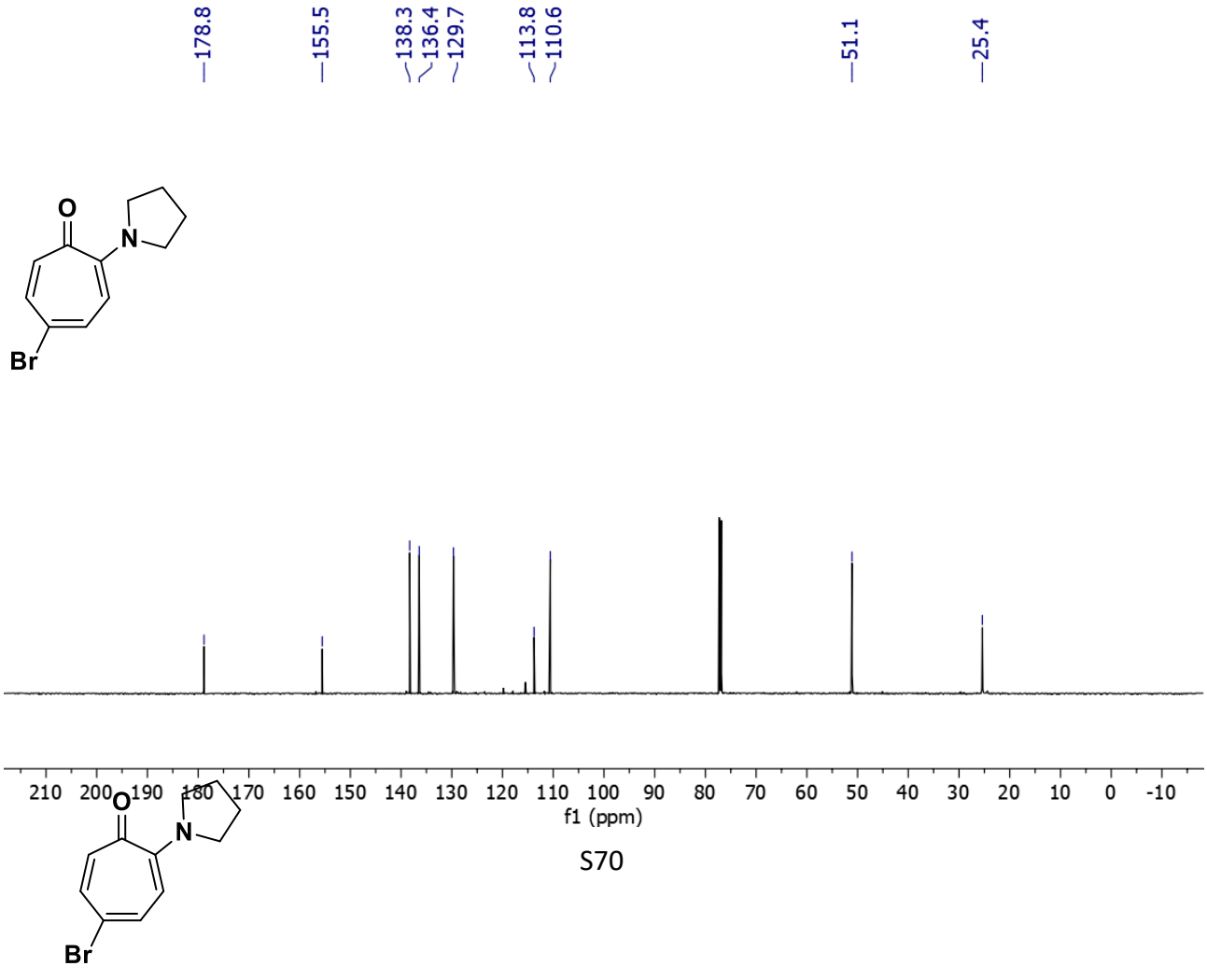
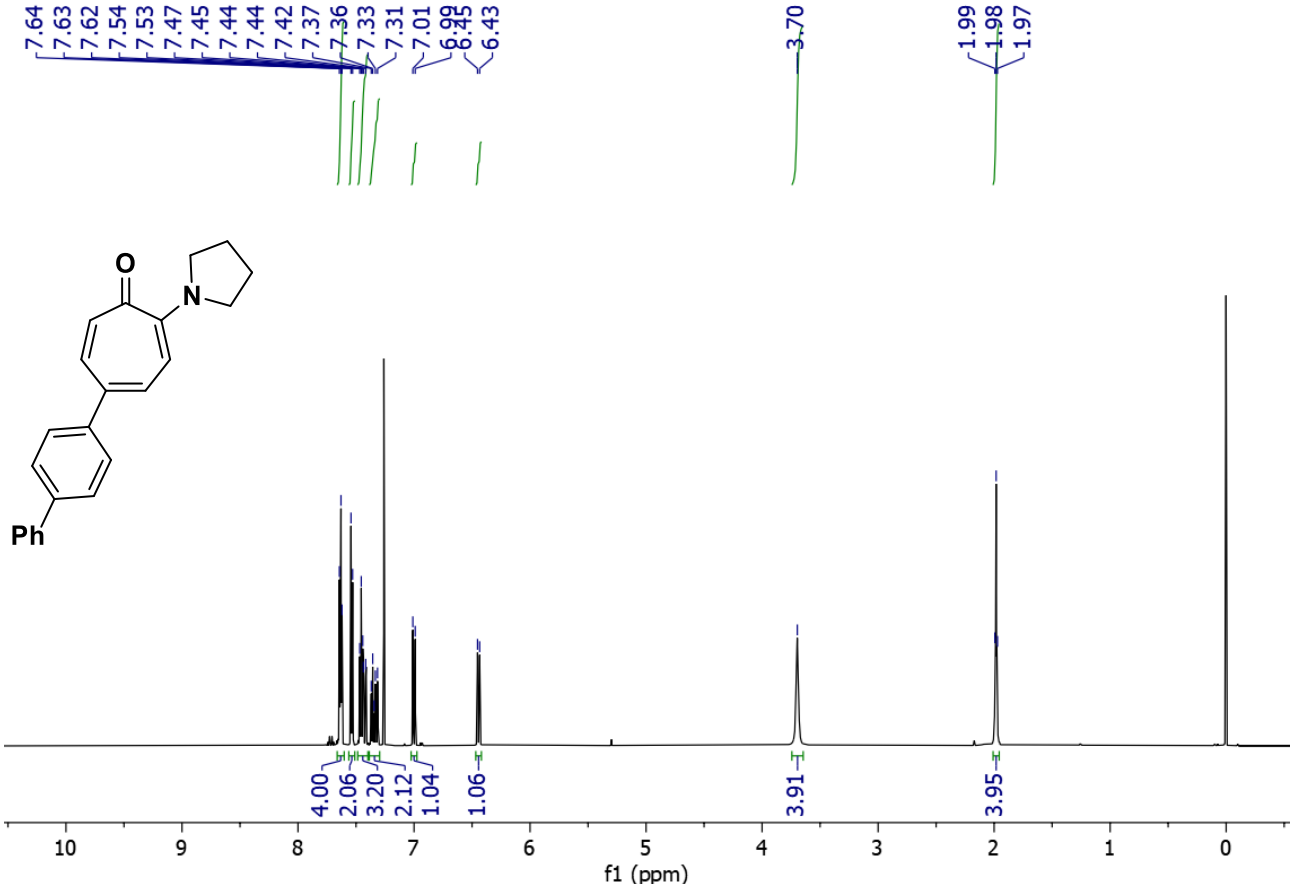


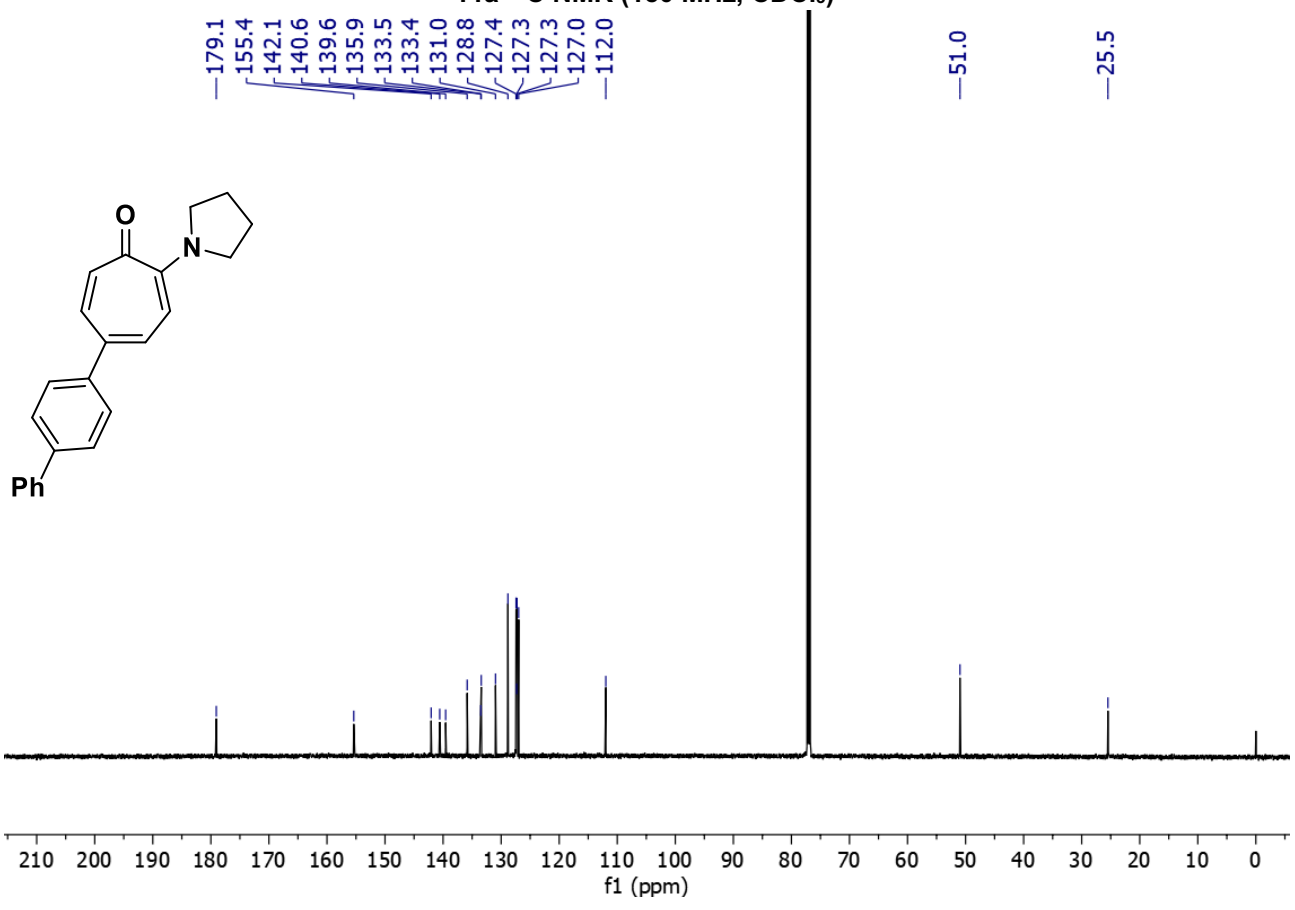
3aa ^{13}C NMR (150 MHz, $CDCl_3$)



11a ^{1}H NMR (600 MHz, $CDCl_3$)



11a ^{13}C NMR (150 MHz, $CDCl_3$)



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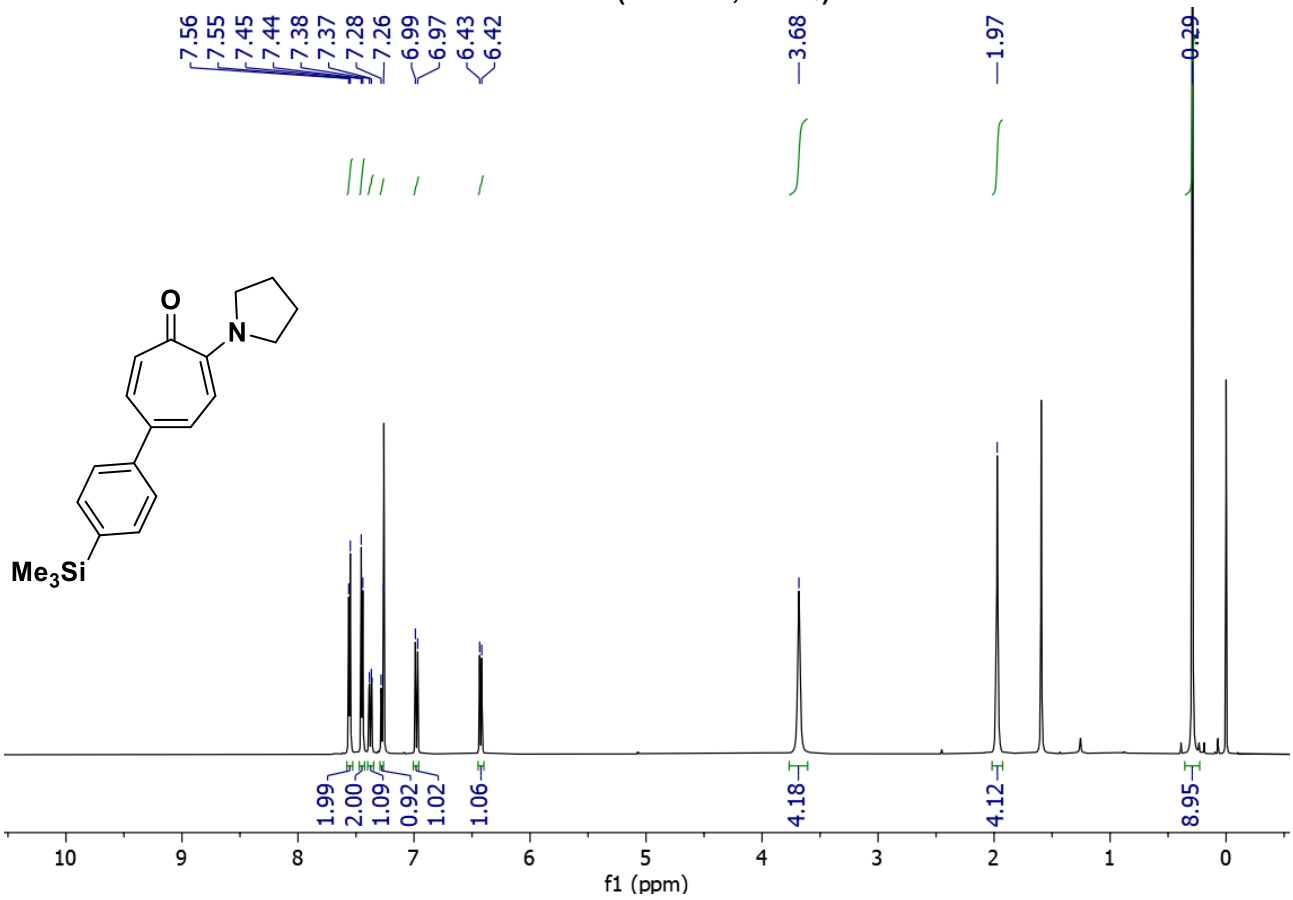

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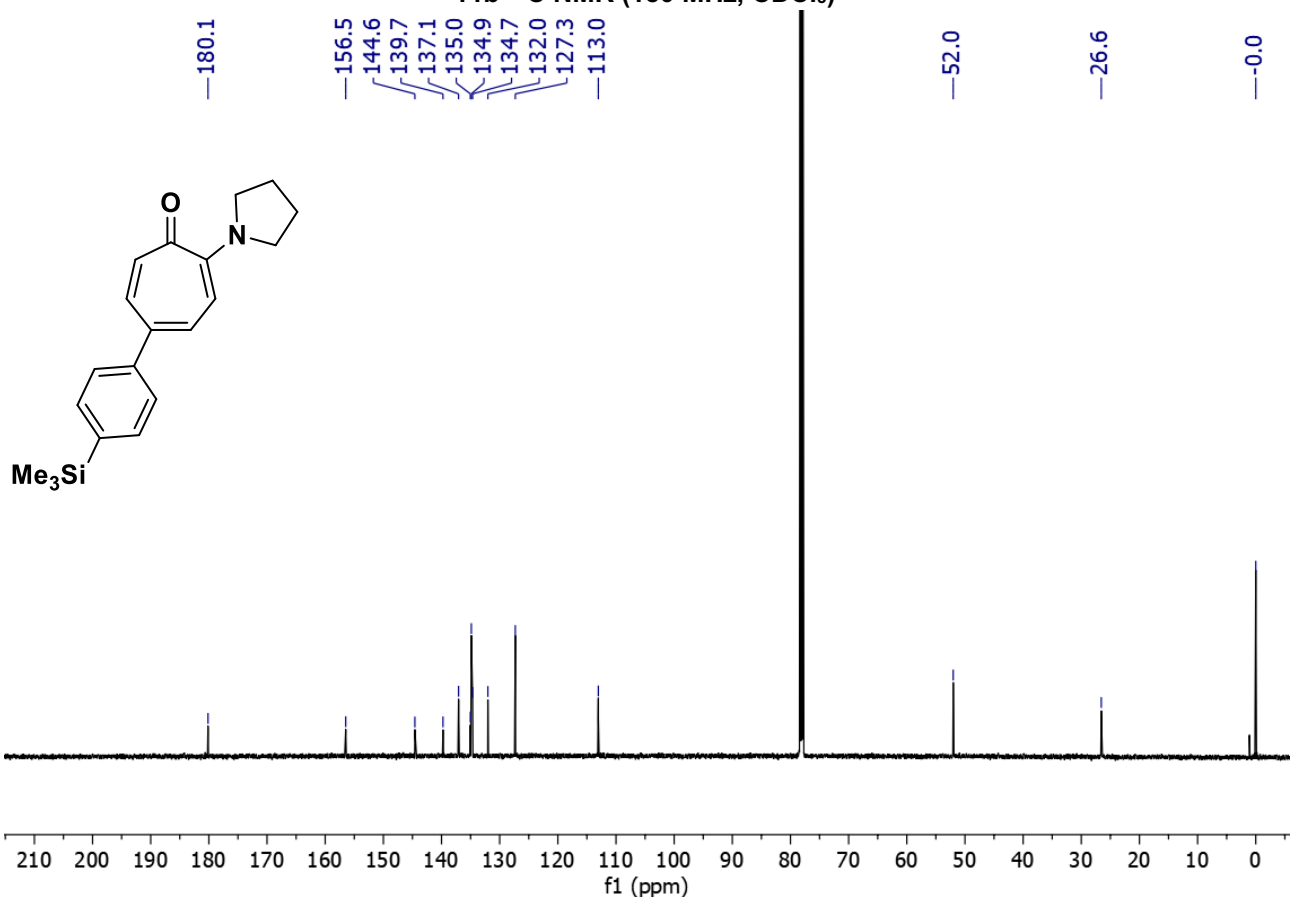

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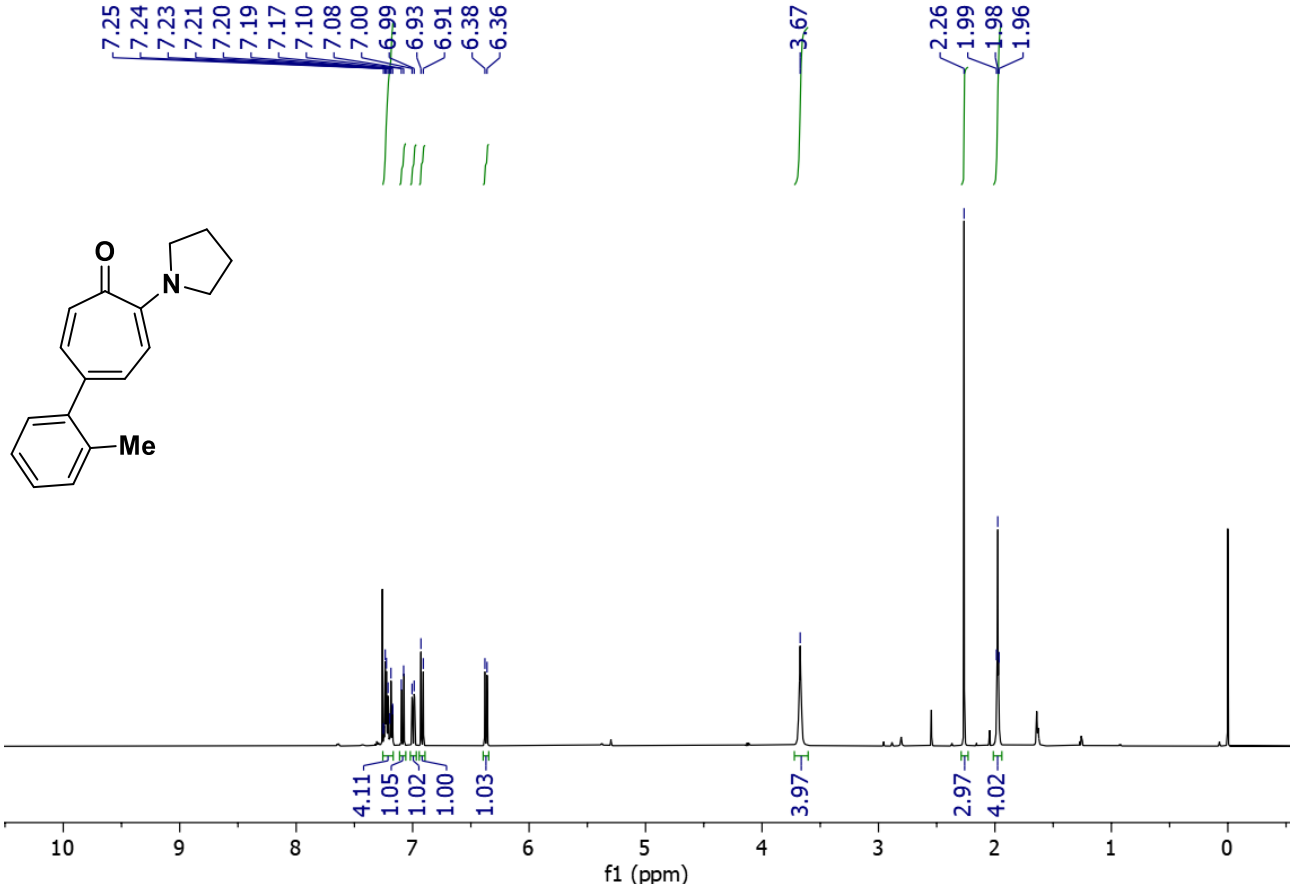

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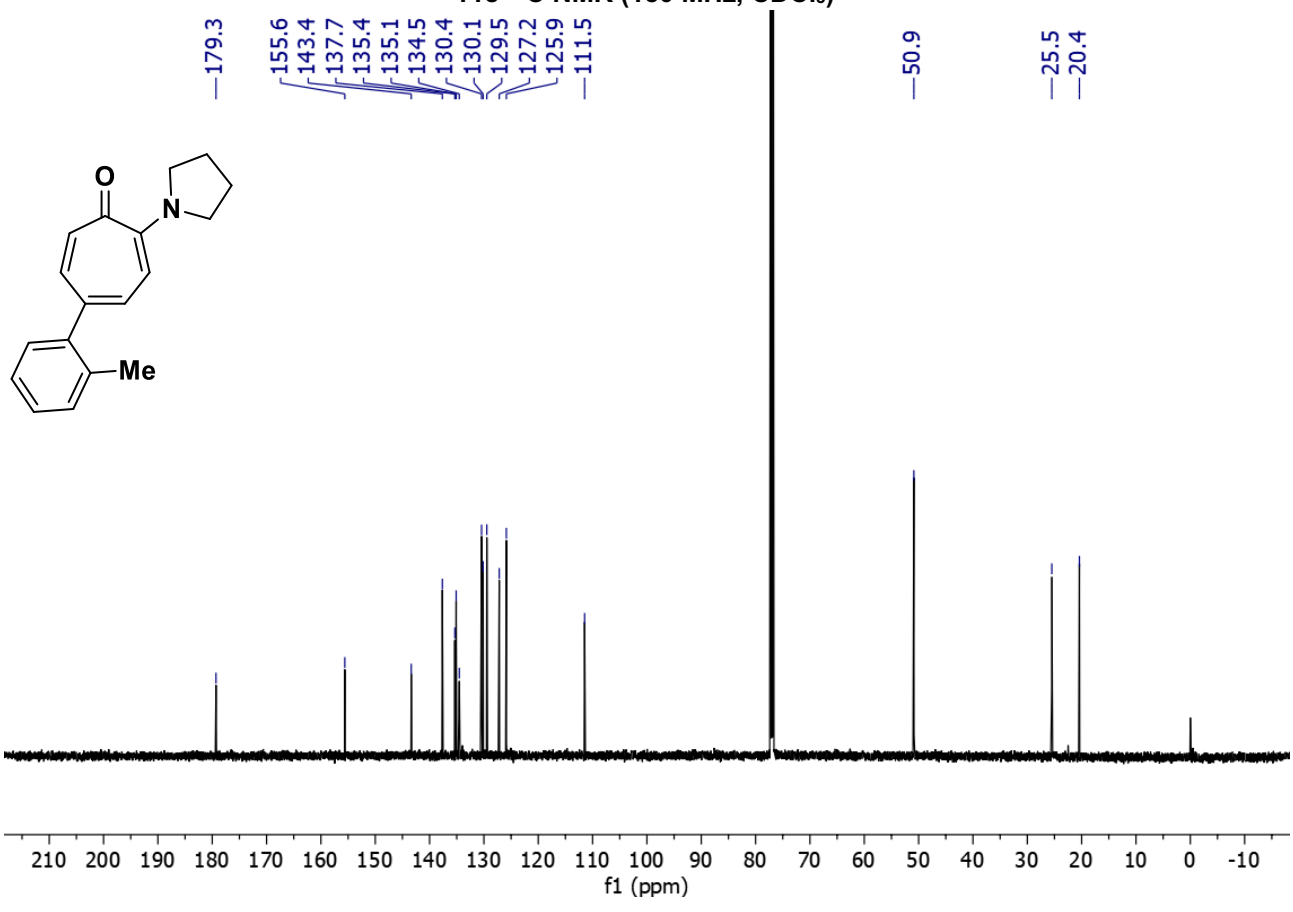

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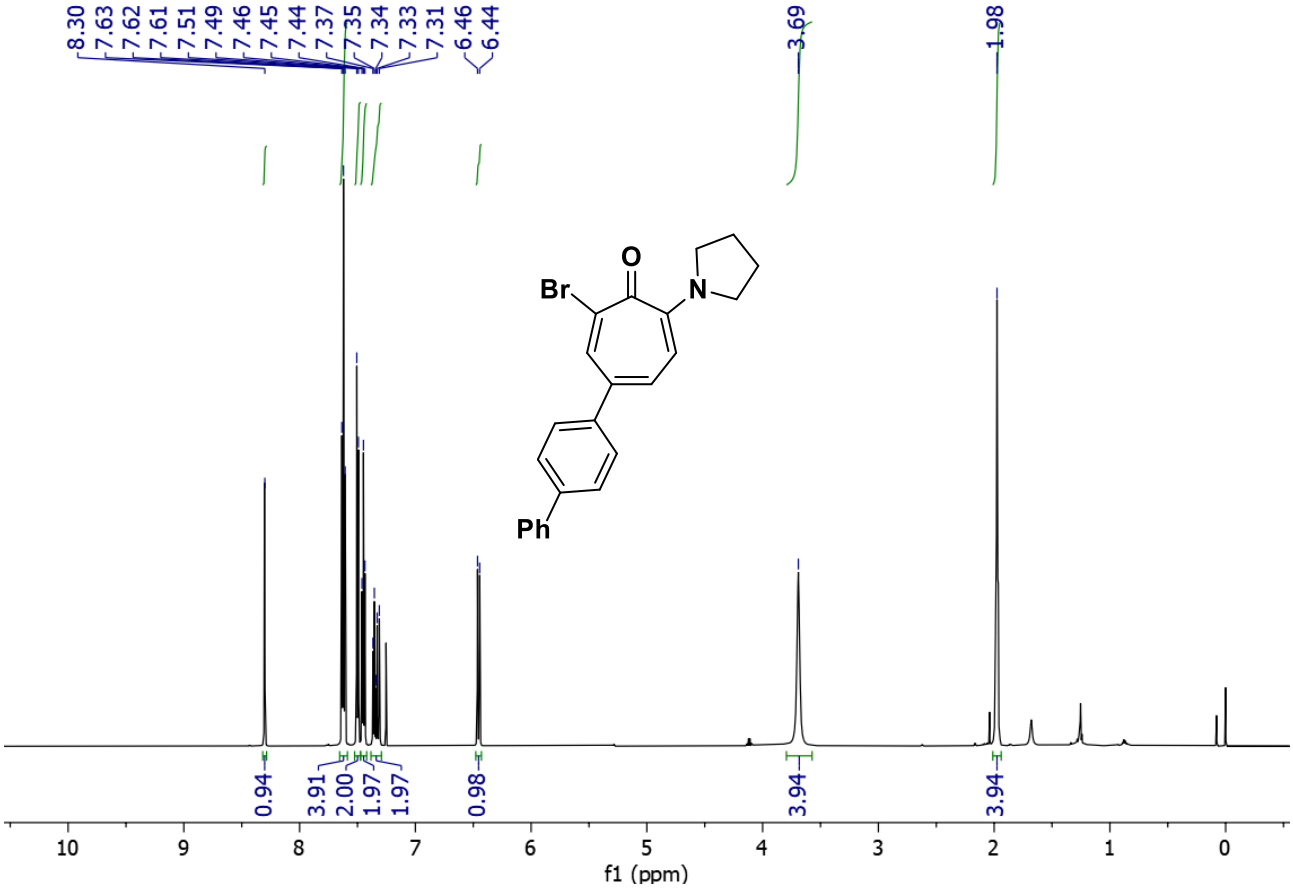

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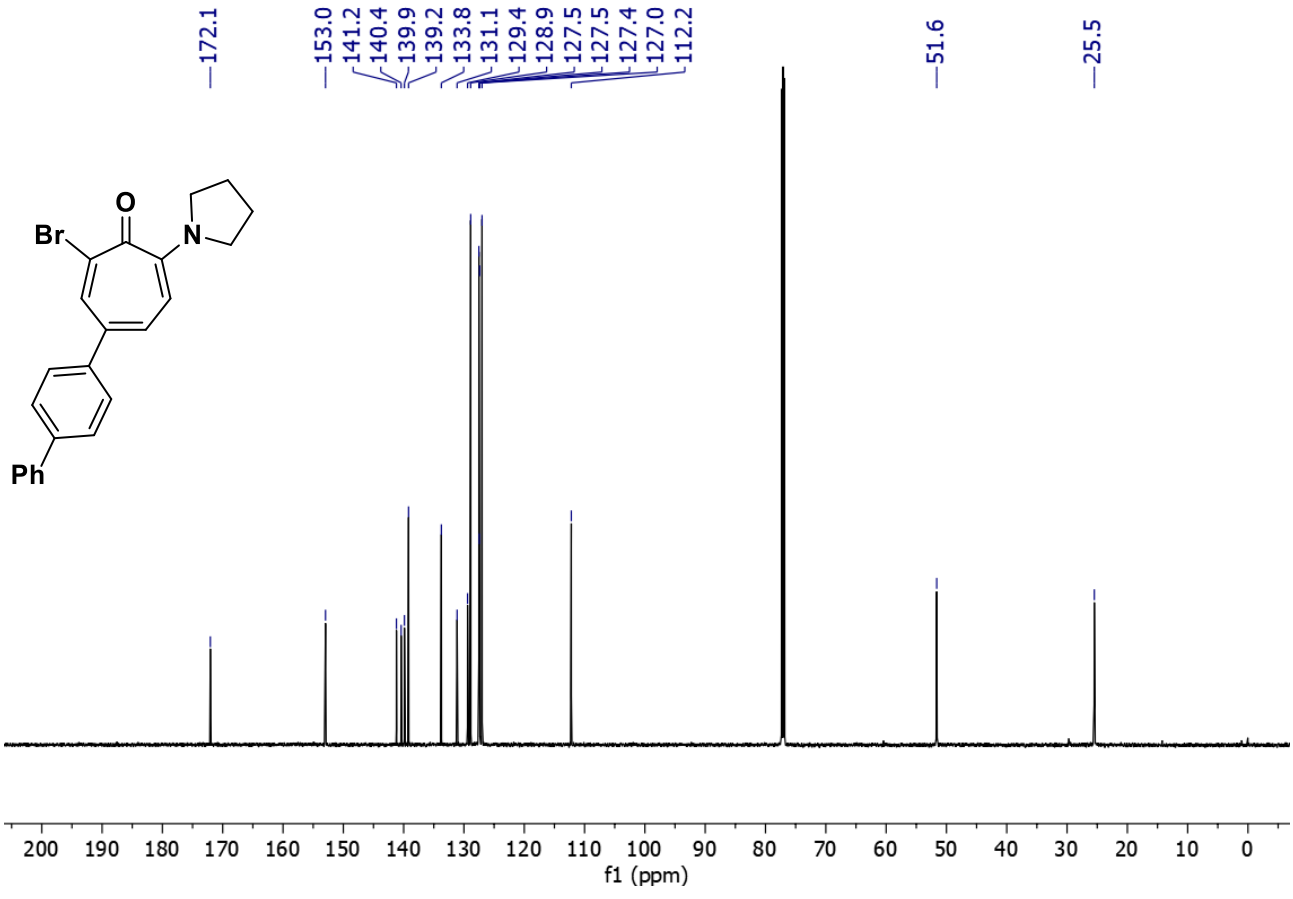

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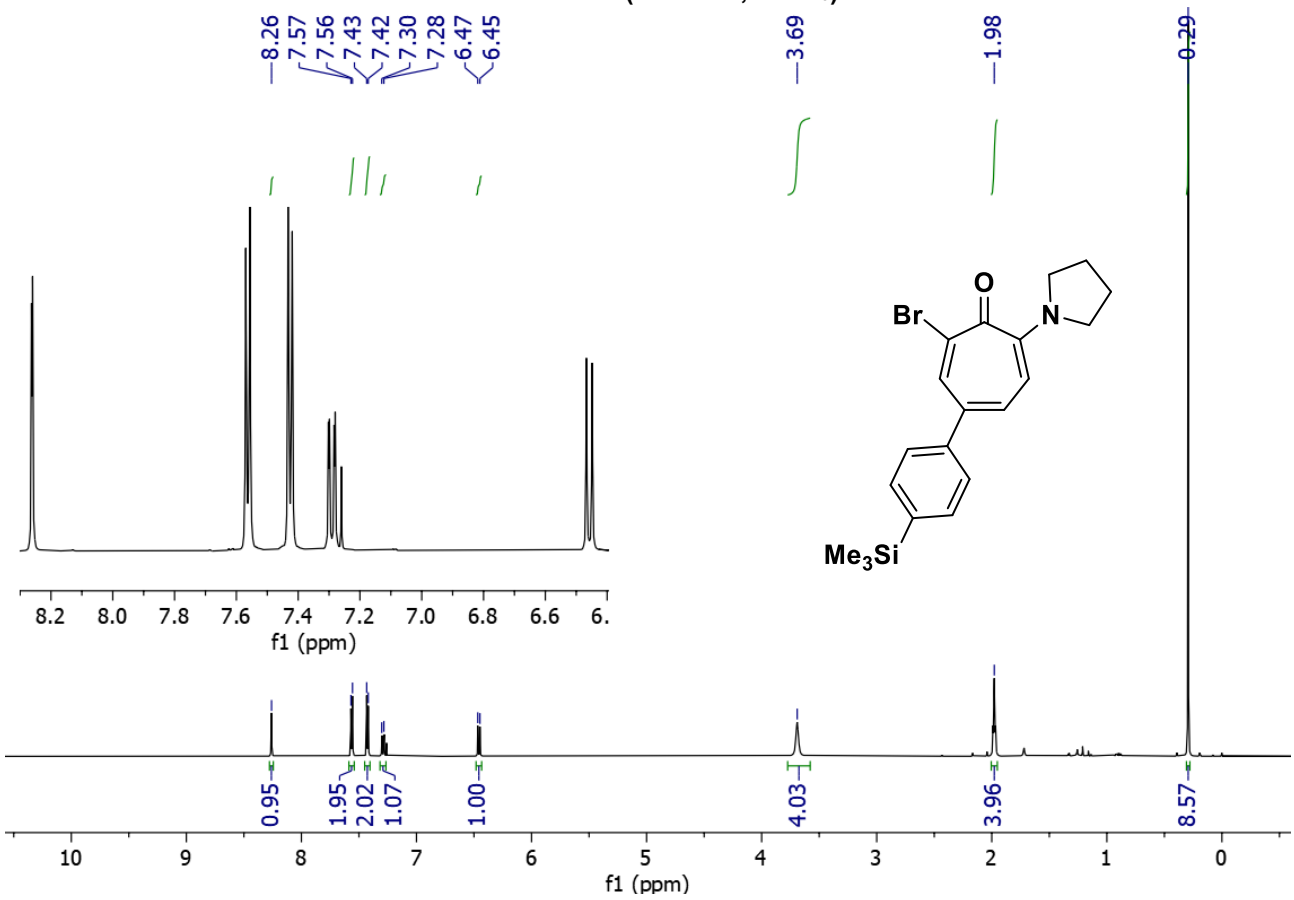

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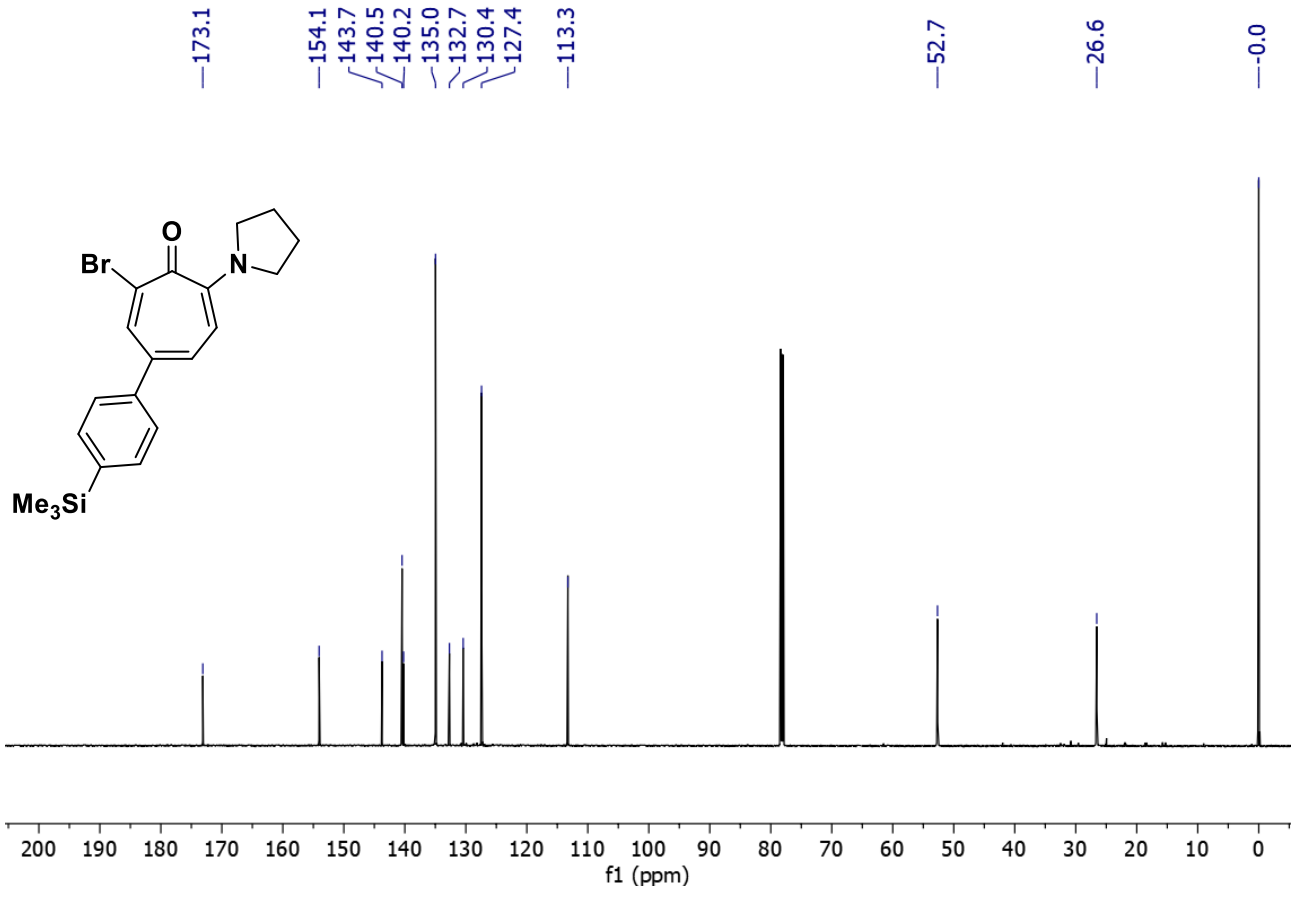

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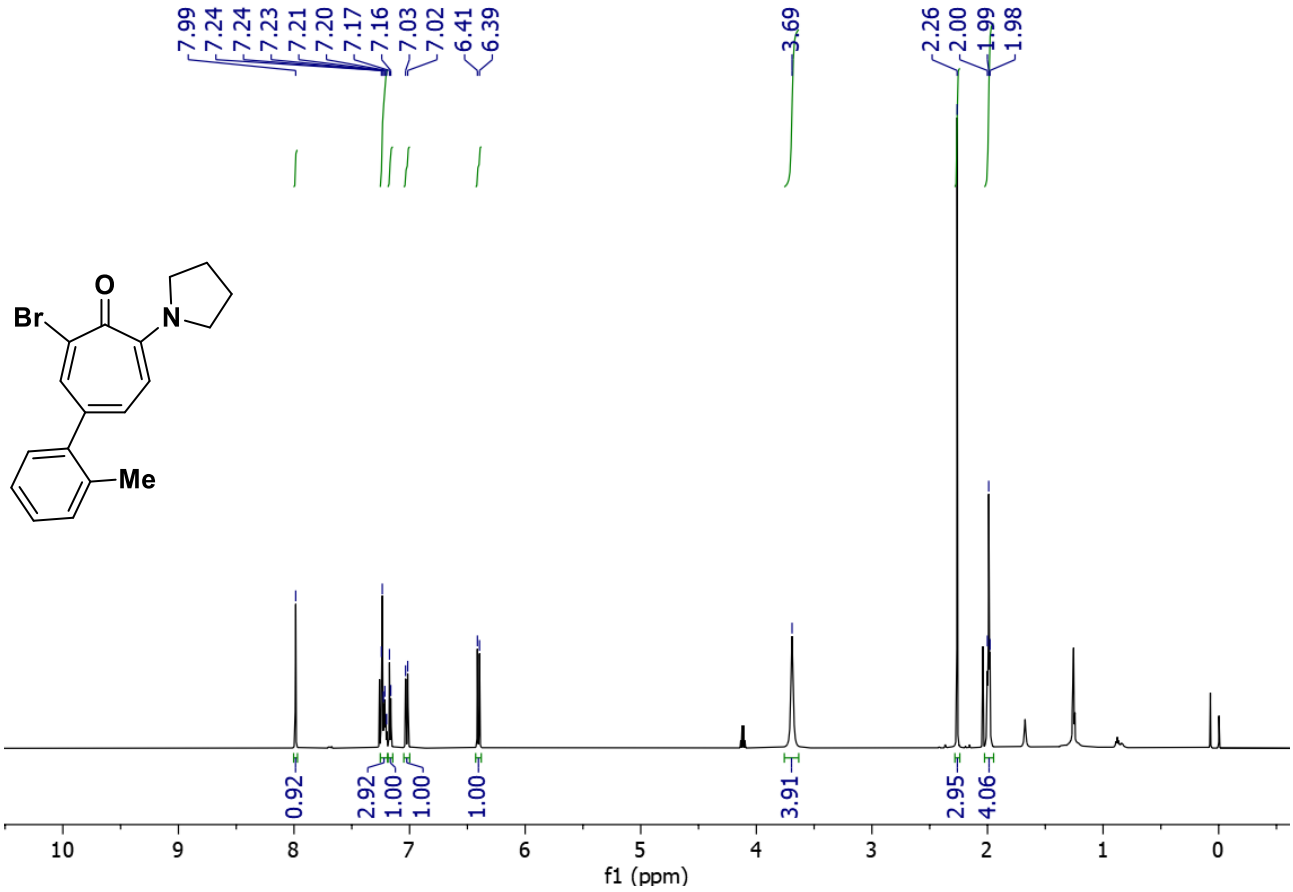

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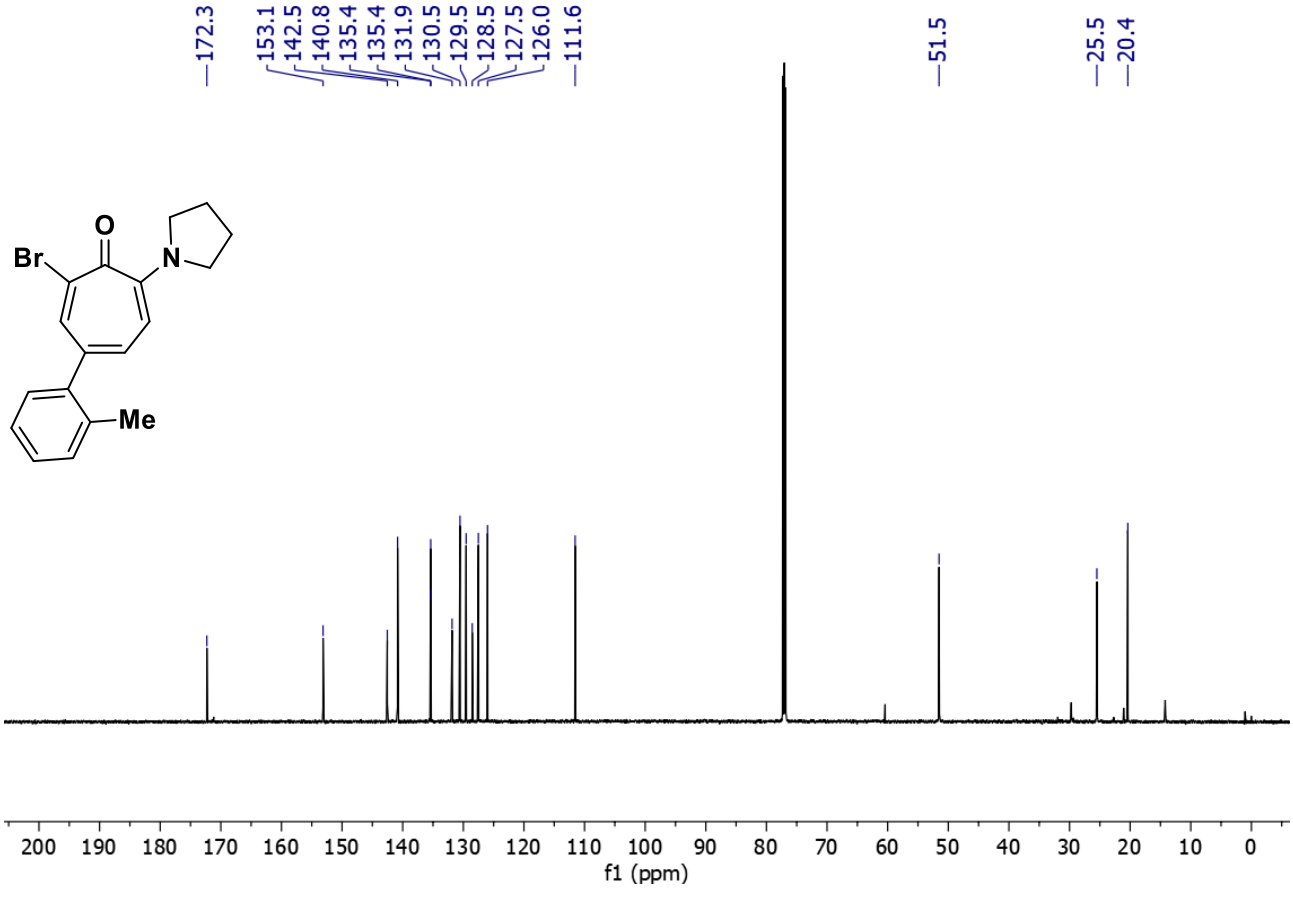

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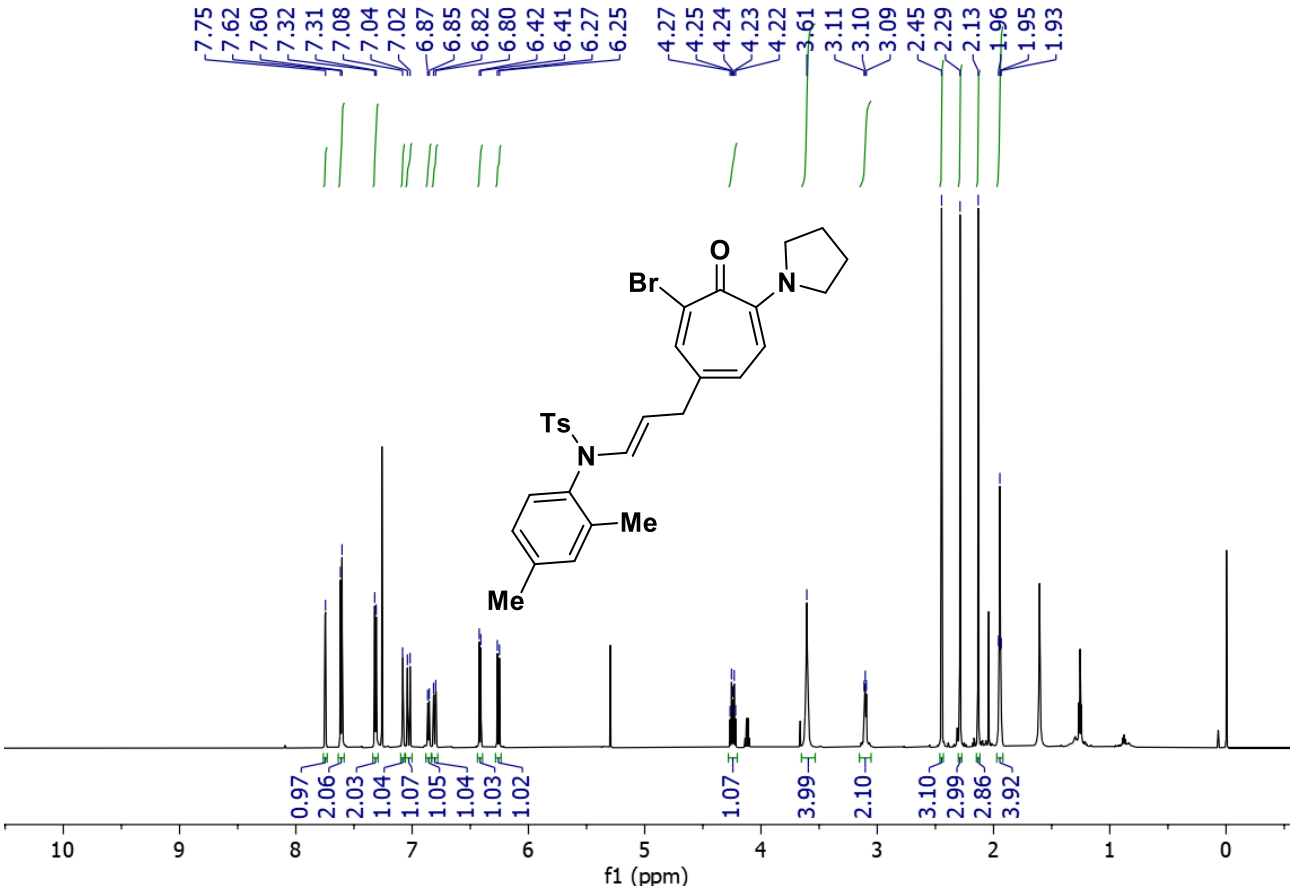

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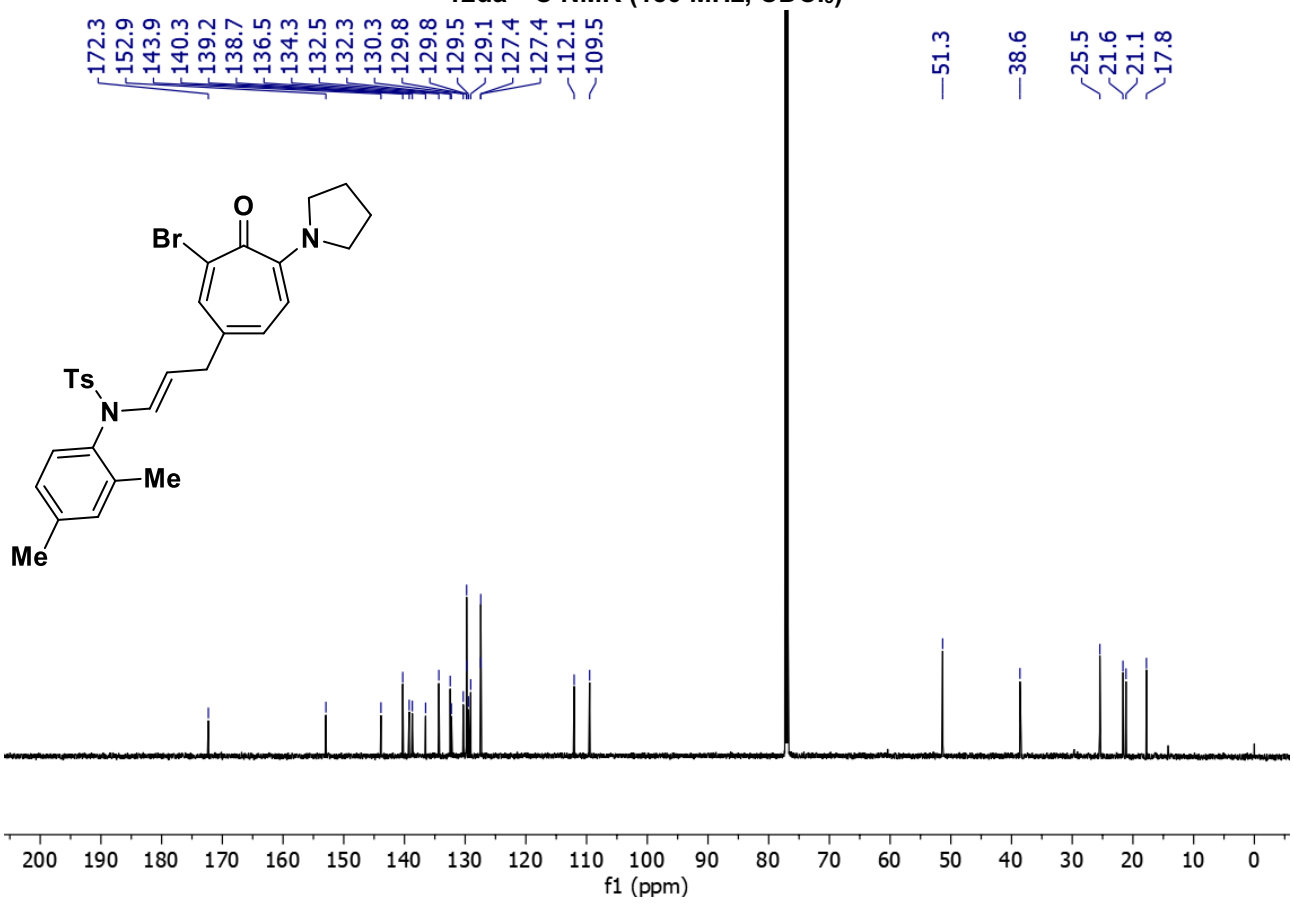

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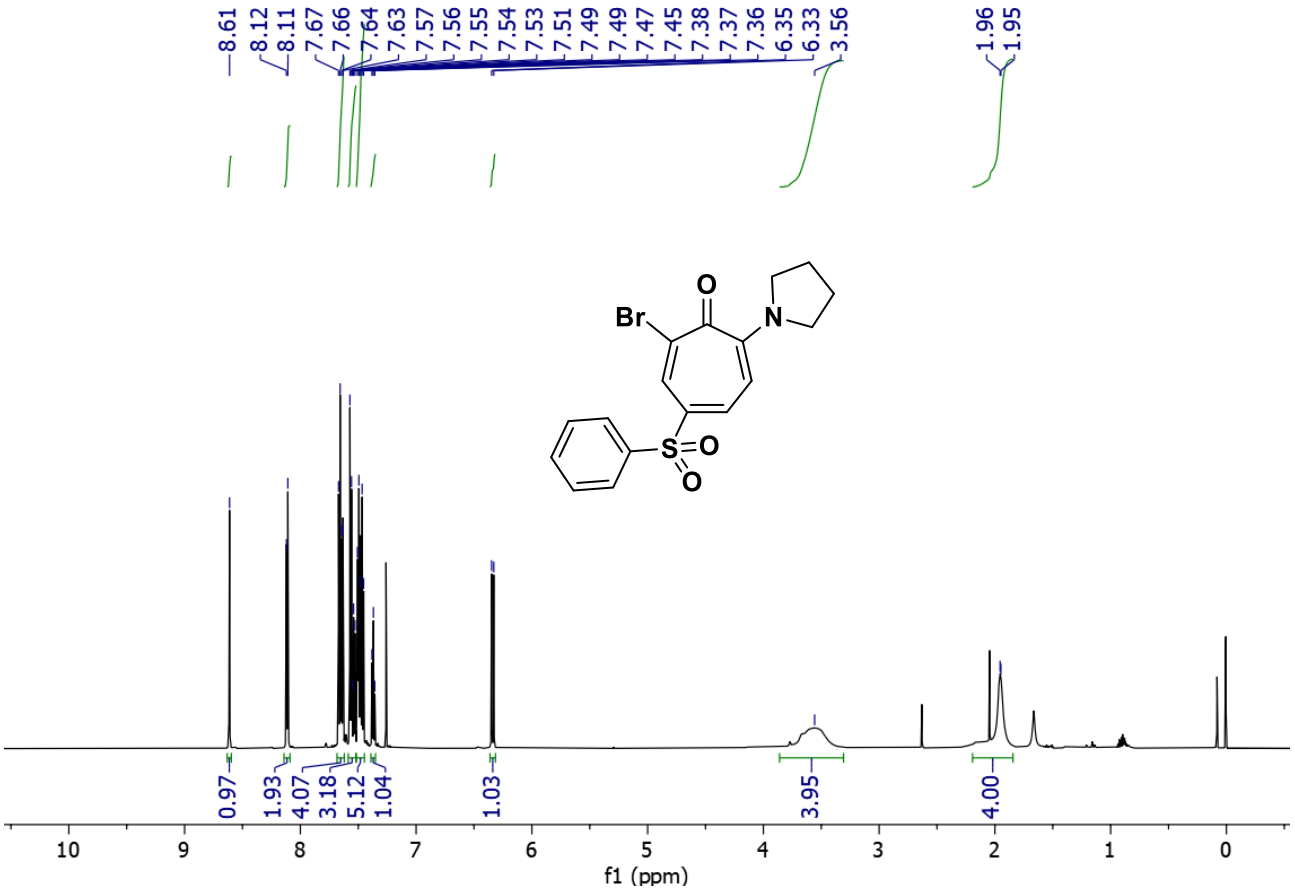

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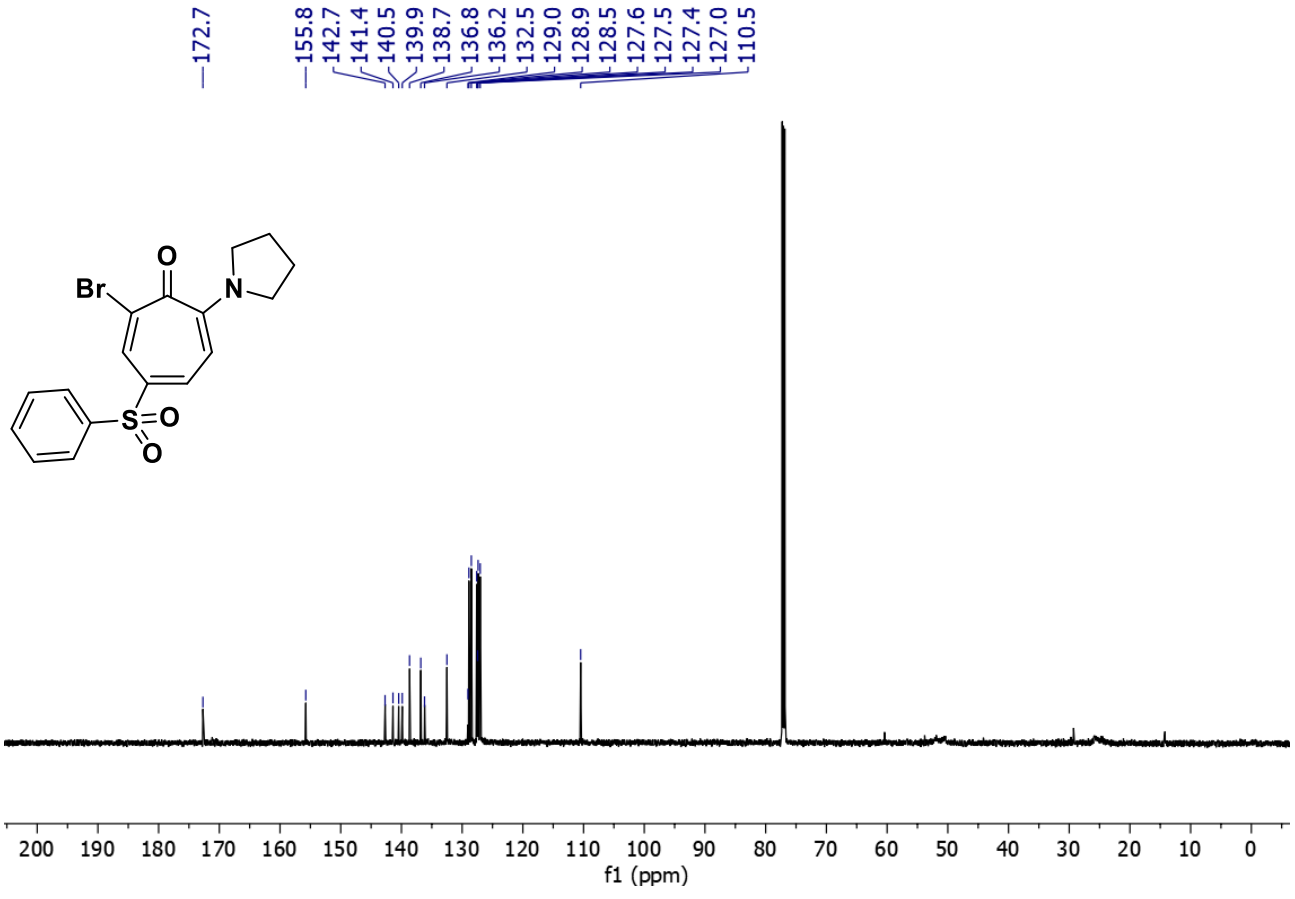

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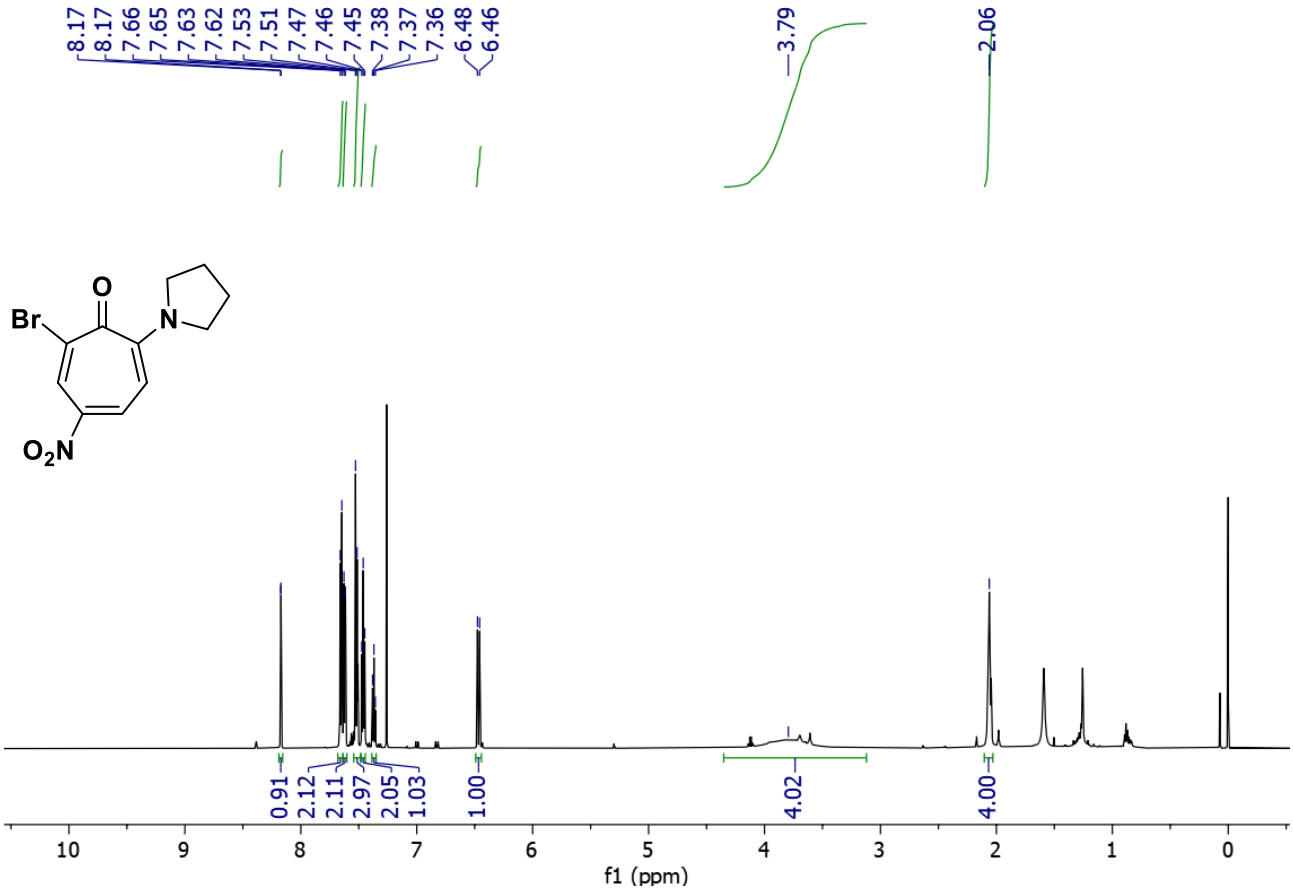

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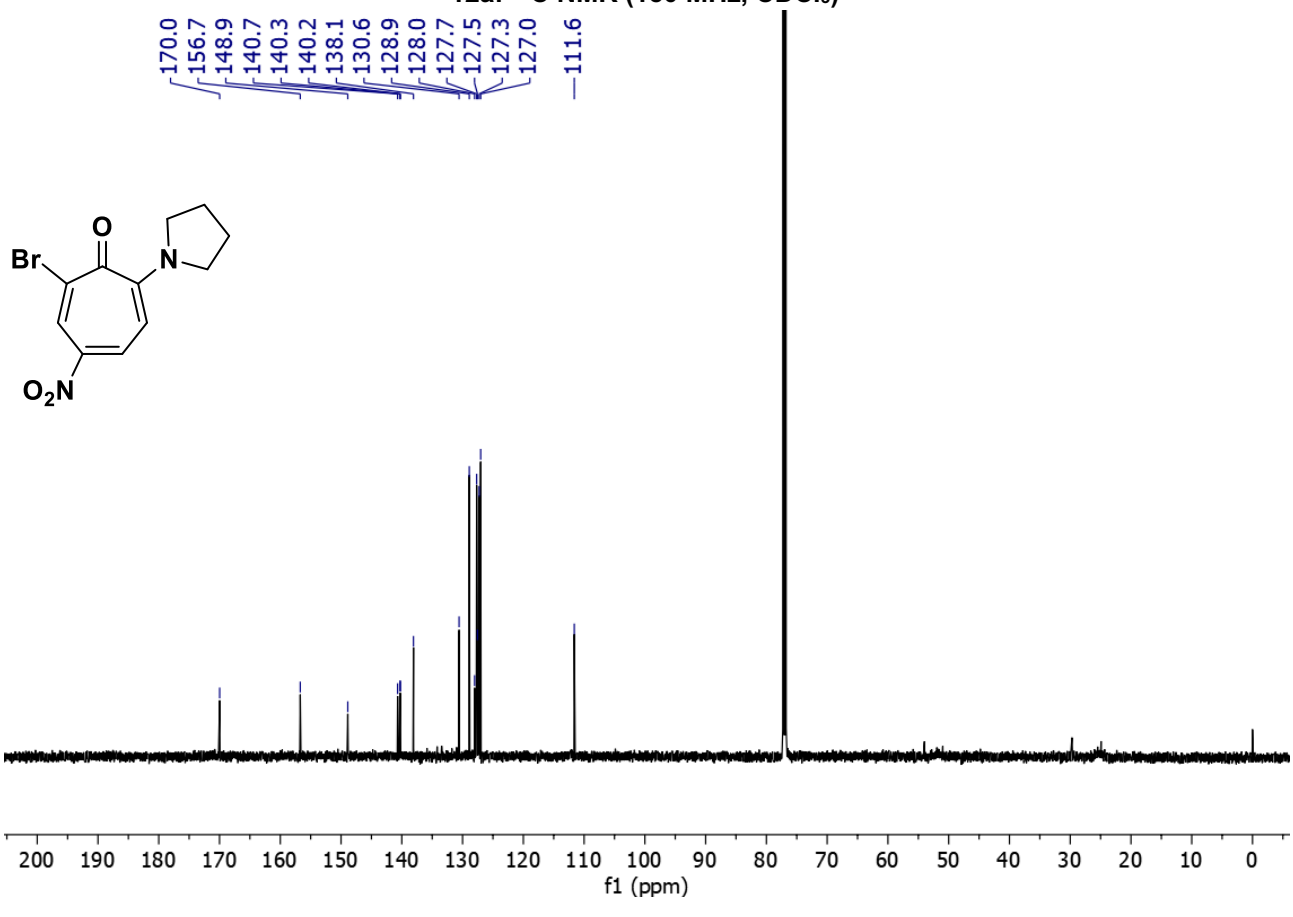

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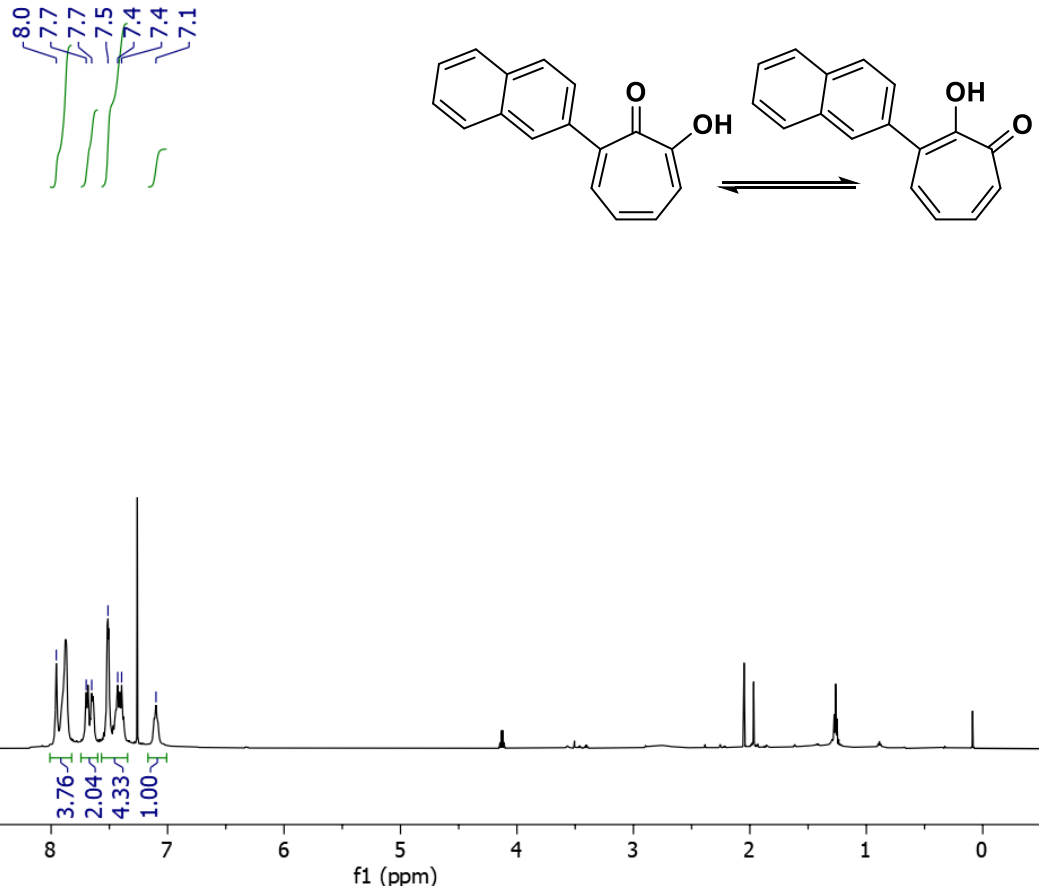

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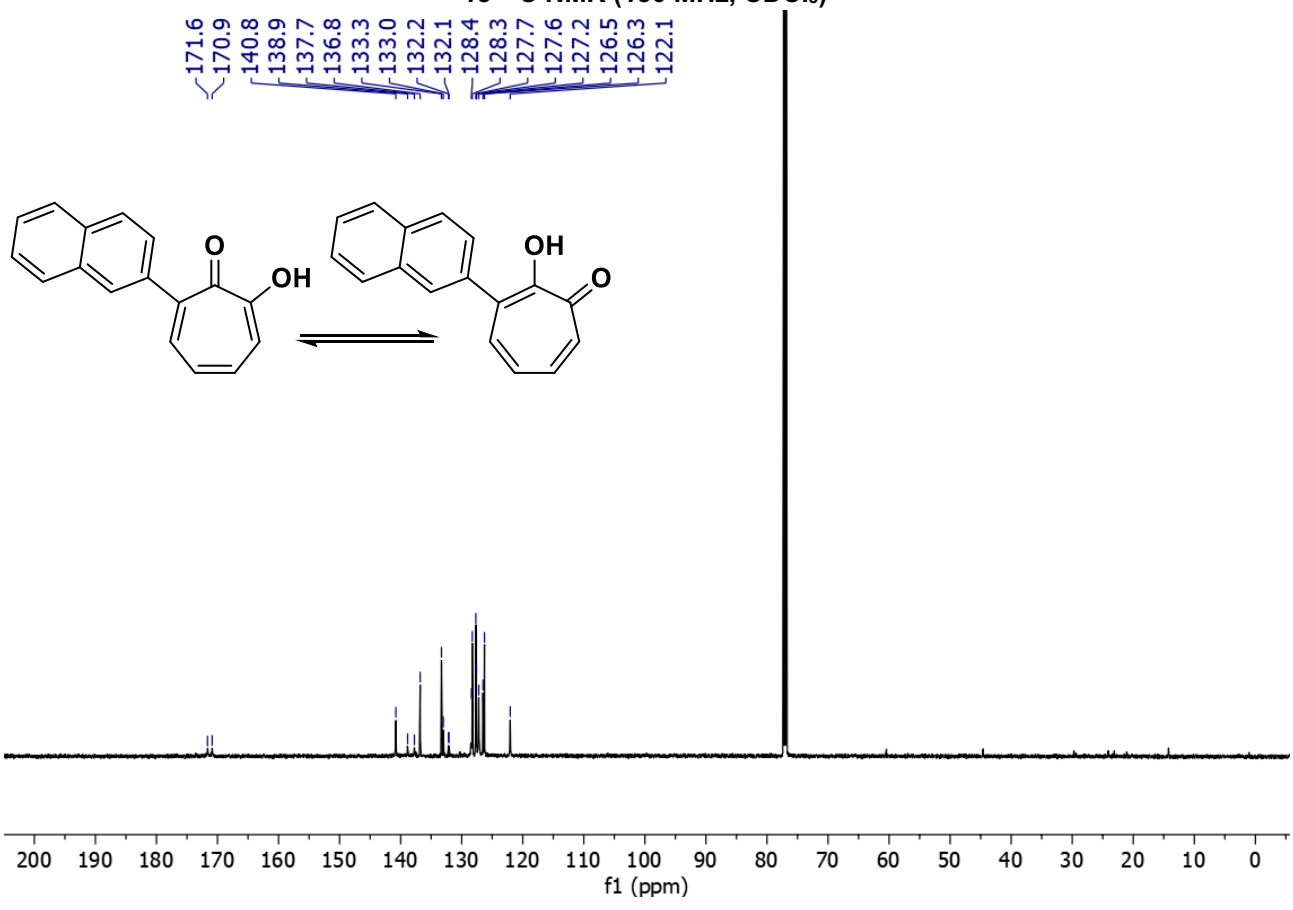

5. References

[1] C. L. Barløse, J. Faghtmann, M. Kaasik, R. Mastroddi, K. A. Jørgensen, *Org. Lett.* **2024**, *26*, 1539-1543.
[2] S. Kernbichl, M. Reiter, D. H. Bucalon, P. J. Altmann, A. Kronast, B. Rieger, *Inorg. Chem.* **2018**, *57*, 9931-9940.
[3] K. Ohtsu, R. Hayami, T. Sagawa, S. Tsukada, K. Yamamoto, T. Gunji. *Tetrahedron* **2019**, *75*, 130658.
[4] (a) Y. Zhao, D. G. Truhlar, The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241. (b) Y. Zhao, D. G. Truhlar, Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157-167.
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[9] In this case, an amount of $LiClO_4$ electrolyte larger than usual was found necessary in order to lower the cell voltage and avoid decomposition of both product and starting material.
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[11] DMSO was employed given the very low solubility of $PhSO_2Na$ in ACN.
[12] In this case, an amount of $LiClO_4$ electrolyte larger than usual and the addition of another, more stable electrolyte such as $TEABF_4$, was found necessary in order to lower the cell voltage and avoid decomposition of both product and starting material.
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