Supporting Information

Electrochemical Nickel Catalyzed C(sp^2)-H Functionalization of Tropones with Aldehydes.

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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.

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**, **1c**-**e**, **1h**-**l**, **1o**, **1p** and **1s**[1] are known compounds and were synthesized according to a modification of the reported literature procedures (*vide infra*). Compounds **1b**, **1f**, **1g**, **1m, 1n**, **1q** and **1r** were synthesized following the same protocol and the characterization data are reported in the dedicated sections.

Liquid aldehydes were distilled under vacuum immediately prior to use. The solid ones were used without purification.

Computational Methods

We used Density Functional Theory (DFT) at the M06 [2]/def2svpp[3] 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 universal solvation model based on solute's electron density (SMD)[4] with the default parameters for the main mechanism and using the non-equilibrium solvent cage for the SET calculations, as implemented in the Gaussian 09 package.[5] The *N*,*N*-dimethylformamide, abbreviated as DMF, 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.[6]

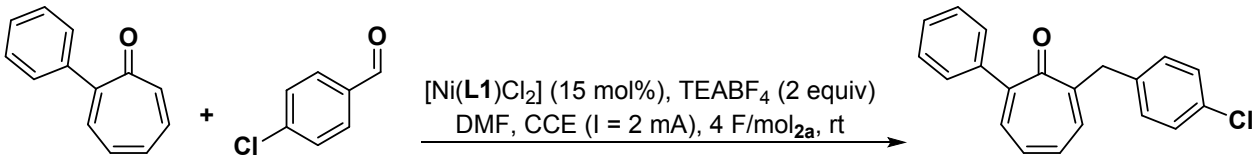
Electrochemical and Spectroelectrochemical Methods

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.

The spectroelectrochemical experiments were carried out coupling the potentiostat with an HP diode array 8453 UV/Vis spectrophotometer, working in the wavelength range 190 ± 1100 nm. The electrochemical cell consisted in this case in quartz cuvette with an optical path of 100 μm filled with a Pt grid as the working electrode. The 3-electrode cell was completed by a Pt wire and Ag wire as the counter and the pseudo-reference electrodes. The composition of the solutions was similar to that previously reported for CV experiments, but with a concentration of the electroactive species of 2.5 mM, in order to avoid complete saturation of the signal. UV-Vis adsorption spectra were collected while polarizing the working electrode at different potentials in a CV experiment performed at 0.005 Vs^{-1} and the spectra reported are the variation with respect to the reference one recorded at open circuit potential (Figure S2a). Also in this case, the potentials finally reported are referred to the ferrocenium/ferrocene redox couple, by adding a few crystals of this species in the solution. It is possible to estimate that in such a system all the electroactive molecules present in the optical path are reduced on the time scale of the electrochemical tests.

2. Additional Optimization Data

2.1. **Table S1**: Additional reaction optimization results.



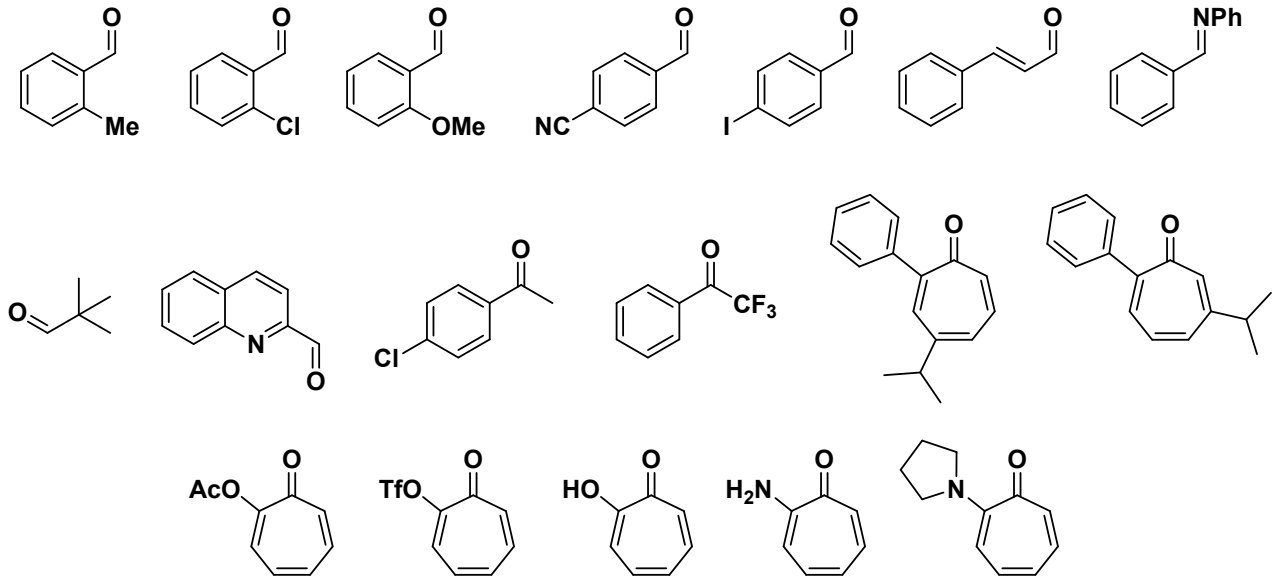
1a (2 equiv) **2a** **3a**, 83% yield

Entry	Deviation from Optimal	Yield (%)[a]
1	[Ni(**L1**)$_2$Cl$_2$] instead of [Ni(**L1**)Cl$_2$]	56
2	[Ni(**L1**)$_3$Cl$_2$] instead of [Ni(**L1**)Cl$_2$]	NR
3	[Ni(**PtBu$_3$**)$_2$Cl$_2$] instead of [Ni(**L1**)Cl$_2$]	NR
4	ACN as the solvent	NR
5	DMSO as the solvent	NR
6	TEABF$_4$ 10 mol%	52
7	Au cathode instead of Ni	72
8	Ag cathode instead of Ni	NR
9	CVE (V = 0.65 V) instead of CCE	22
10	**1a** (1 equiv), 2 F/mol$_{2a}$	29
11	**1a** (1.5 equiv), 3 F/mol$_{2a}$	55
12	**1a** (2 equiv), 2 F/mol$_{2a}$	61

[a] Isolated yield after chromatography. NR: no reaction. **L1** = 4,4'-dimethoxy-2,2'-bipyridine.

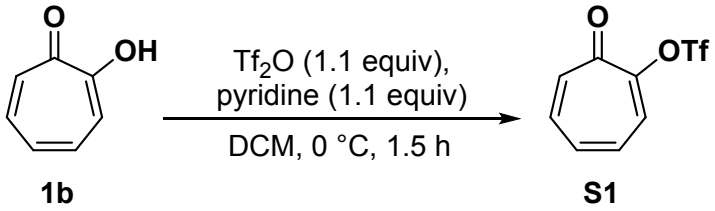
2.2. Failed Substrates

The following substrates failed to render the desired products in satisfactory amounts.



3. Preparation and characterization data of starting materials

3.1 Preparation of Tropolone triflate **S1**.



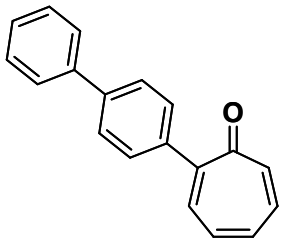
1b **S1**

Tropolone triflate **S1** was prepared by a slight modification of the procedure reported by Jørgensen *et al.* [1] In a Schlenk tube, under an Ar atmosphere and magnetic stirring, tropolone **1b** (8.0 mmol, 976 mg) was dissolved in dry DCM (25 mL) and the resulting solution was cooled to 0 °C. Then, pyridine (8.8 mmol, 708 μL, 1.1 equiv) and triflic anhydride (8.8 mmol, 1.48 mL, 1.1 equiv) were added dropwise in this order and the resulting suspension was stirred at 0 °C for 1.5 h. Then, while keeping the reaction mixture at 0 °C, a saturated solution of NH_4Cl (10 mL) was added dropwise and the resulting biphasic mixture was transferred to a separatory funnel. The phases were separated, and the aqueous layer was extracted again with DCM (2 x 10 mL). The combined organic phases were then dried with Na_2SO_4, evaporated *in vacuo* and finally purified by FC on silica gel (*n*-hexane/EtOAc 2:1) to obtain desired product **S1** as a light-yellow oil that solidifies in off-white crystals upon standing at -20 °C overnight (7.6 mmol, 1.93 g, 95% yield). Spectroscopic data match with the one reported in literature.[1]

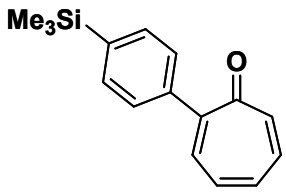
3.2 Preparation and characterization of 2-aryl tropones **1**.

In a Schlenk tube, under an Ar atmosphere and magnetic stirring, tropolone triflate **S1** (2.0 mmol, 528 mg), Cs_2CO_3 (5.0 mmol, 1.63 g, 2.5 equiv) and the desired boronic acid (4.0 mmol, 2.0 equiv) were suspended in a THF/H_2O mixture (10:1, 5.5 mL). The resulting suspension was de-gassed by bubbling Ar for 1 min, then $PdCl_2(PPh_3)_2$ (0.10 mmol, 70.0 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 (5 mL), H_2O (10 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 (10 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*

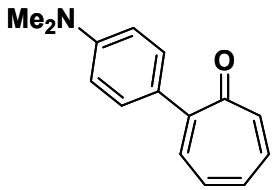
and finally purified by FC on silica gel (*c*-hexane/EtOAc mixtures) to obtain desired products **1**.



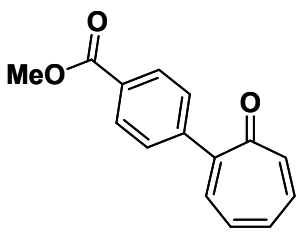
1b. Pale yellow solid. FC eluent: *c*-hexane/EtOAc: 3:1. Yield = 78% (1.56 mmol, 402 mg). **MP** = 115-117 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.65 – 7.61 (m, 4H), 7.61 – 7.58 (m, 2H), 7.48 – 7.44 (m, 2H), 7.43 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.21 (dt, *J* = 12.0, 1.0 Hz, 1H), 7.15 (ddd, *J* = 12.1, 7.8, 1.3 Hz, 1H), 7.06 (ddt, *J* = 10.9, 8.8, 1.1 Hz, 1H), 6.98 (ddt, *J* = 10.9, 7.7, 1.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.6, 152.2, 142.3, 141.3, 140.7, 138.9, 136.3, 135.2, 133.7, 133.3, 129.6 (2C), 128.8(2C), 127.5, 127.2 (2C), 126.9 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{19}H_{15}O$ 259.1117; found 259.1121.



1f. Pale yellow solid. FC eluent: *c*-hexane/EtOAc: 4:1. Yield = 83% (1.66 mmol, 422 mg). **MP** = 80-81 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 – 7.54 (m, 2H), 7.49 – 7.45 (m, 2H), 7.36 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.18 (dt, *J* = 12.1, 1.1 Hz, 1H), 7.13 (ddd, *J* = 12.1, 7.7, 1.3 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.96 (ddt, *J* = 10.8, 7.7, 1.1 Hz, 1H), 0.28 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.7, 153.8, 143.5, 142.0, 141.5, 137.5, 136.3, 134.9, 134.4, 134.3 (2C), 129.4 (2C), 0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{19}OSi$ 255.1200; found 255.1208.

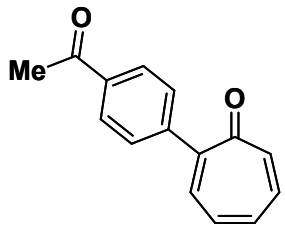


1g. Yellow-brown solid. FC eluent: *c*-hexane/EtOAc: 1.5:1. Yield = 61% (1.22 mmol, 275 mg). **MP** = 130-133 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.54 – 7.47 (m, 2H), 7.37 (dd, *J* = 9.1, 0.9 Hz, 1H), 7.14 (dt, *J* = 12.1, 1.0 Hz, 1H), 7.08 (ddd, *J* = 12.1, 7.8, 1.3 Hz, 1H), 7.01 (dddd, *J* = 10.4, 9.1, 1.3, 0.8 Hz, 1H), 6.88 (ddt, *J* = 10.8, 7.8, 1.0 Hz, 1H), 6.78 – 6.69 (m, 2H), 3.00 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.9, 152.2, 150.8, 141.3, 134.9, 134.7, 133.8, 131.7, 130.4 (2C), 127.4, 111.7 (2C), 40.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{16}NO$ 226.1226; found 226.1230.

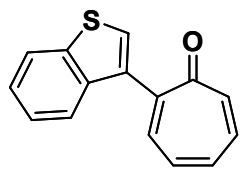


1m. Pale yellow solid. FC eluent: *c*-hexane/EtOAc: 2:1. Yield = 57% (1.14 mmol, 274 mg). **MP** = 120-123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.09 – 8.04 (m, 2H), 7.58 – 7.53 (m, 2H), 7.36 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.19 (ddd, *J* = 12.1, 1.6, 0.8 Hz, 1H), 7.15 (ddd, *J* = 12.1,

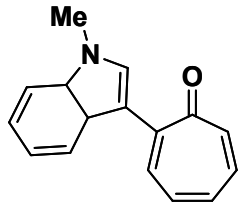
7.3, 1.4 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.03 – 6.98 (m, 1H), 3.93 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.1, 166.8, 151.6, 144.6, 142.6, 136.8, 135.4, 133.9, 133.6, 129.9, 129.4 (2C), 129.2 (2C), 52.2; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{13}O_3$ 241.0859; found 241.0866.



1n. Pale yellow solid. FC eluent: *c*-hexane/EtOAc: 2:1. Yield = 48% (0.96 mmol, 215 mg). **MP** = 118-120 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.02 – 7.96 (m, 2H), 7.60 – 7.54 (m, 2H), 7.36 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.20 (ddd, *J* = 12.1, 1.6, 0.8 Hz, 1H), 7.16 (ddd, *J* = 12.2, 7.2, 1.4 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.04 – 6.99 (m, 1H), 2.63 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.7, 186.1, 151.5, 144.7, 142.7, 136.8, 136.7, 135.5, 134.0, 133.6, 129.4 (2C), 128.2 (2C), 26.7; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{13}O_2$ 225.0910; found 225.0908.



1q. Red solid. FC eluent: *c*-hexane/EtOAc: 2:1. Yield = 66% (1.23 mmol, 293 mg). **MP** = 117-120 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.90 – 7.86 (m, 1H), 7.80 (s, 1H), 7.66 – 7.61 (m, 1H), 7.59 – 7.55 (m, 1H), 7.37 – 7.32 (m, 2H), 7.24 – 7.18 (m, 2H), 7.10 – 7.03 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.8, 146.3, 141.7, 139.8, 137.6, 136.8, 135.2, 134.8, 133.8, 133.3, 128.0, 124.4, 124.3, 122.8, 122.8; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{11}OS$ 239.0525; found 239.0531.



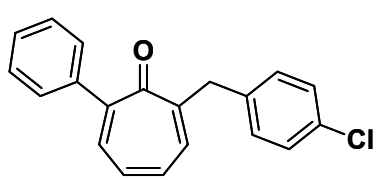
1r. Red solid. FC eluent: *c*-hexane/EtOAc: 2:1. Yield = 44% (0.88 mmol, 209 mg). **MP** = 129-132 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.79 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.45 (dd, *J* = 9.0, 0.9 Hz, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.32 (dt, *J* = 8.5, 0.8 Hz, 1H), 7.19 (dt, *J* = 12.1, 1.0 Hz, 1H), 7.11 (ddd, *J* = 12.1, 7.9, 1.3 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.92 (ddt, *J* = 10.8, 7.9, 1.0 Hz, 1H), 6.50 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.1, 153.8, 141.9, 136.7, 136.2, 135.0, 133.7, 132.2, 131.3, 129.3, 128.4, 123.0, 122.0, 108.7, 101.7, 32.9; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{14}NO$ 236.1070; found 236.1077.

4. Preparation and characterization of compounds 3

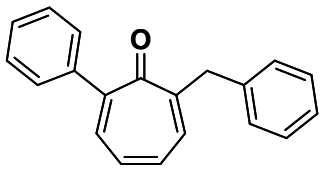
4.1 General procedure.

The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with the appropriate tropone derivative **1** (0.30 mmol, 2.0 equiv.), Ni**L$_1$**Cl$_2$ (0.023 mmol, 15 mol%, 7.8 mg), TEABF$_4$ (0.30 mmol, 65 mg) and the appropriate aldehyde **2** (0.15 mmol, 1 equiv). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ni), was inserted into the mixture and closed with a rubber septum. The vessel was evacuated and backfilled with Ar three times, then dry DMF (3.0 mL) was added, and the mixture stirred until complete dissolution of the solids occurred, while bubbling with Ar (balloon,1 min). The reaction mixture was electrolyzed (under Ar, balloon) at a constant current of 2.0 mA, until a total charge of 0.60 mF (4.0 F/mol$_{\mathbf{2}}$) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and $NH_4Cl_{(aq)}$ (saturated, 5 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 $NH_4Cl_{(aq)}$ (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 **3**.

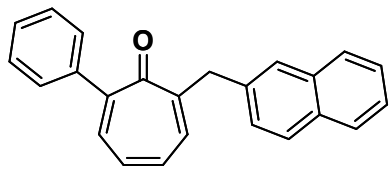
4.2 Characterization data of compounds **3**.



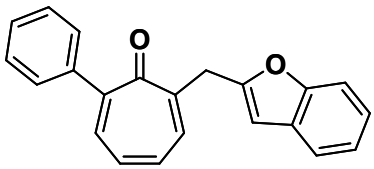
3aa. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 83% (0.125 mmol, 38.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 4.5 Hz, 4H), 7.36 – 7.32 (m, 2H), 7.28 – 7.25 (m, 2H), 7.24 – 7.22 (m, 2H), 7.15 (dq, *J* = 8.5, 1.0 Hz, 1H), 6.98 (ddd, *J* = 10.8, 8.6, 1.2 Hz, 1H), 6.91 (ddd, *J* = 10.8, 8.5, 1.1 Hz, 1H), 4.01 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.8, 152.7, 149.7, 139.9, 137.1, 134.7, 133.7, 131.2, 131.2, 131.1, 129.8 (2C), 128.1 (2C), 127.6 (2C), 127.1, 127.1 (2C), 40.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{16}ClO$ 307.0884; found 307.0891.



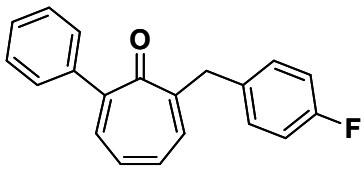
3ab. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 74% (0.111 mmol, 30.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38 – 7.24 (m, 10H), 7.23 – 7.17 (m, 1H); 7.09 (d, *J* = 8.5 Hz, 1H), 6.91 (t, *J* = 9.6 Hz, 1H), 6.85 (dd, *J* = 10.9, 8.4 Hz, 1H), 4.03 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.0, 153.3, 149.4, 140.0, 138.6, 134.5, 133.5, 131.2, 130.8, 128.5 (2C), 128.1 (2C), 127.5 2C), 127.0 (2C), 127.0, 125.4, 40.4. **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{17}O$ 273.1274; found 273.1277.



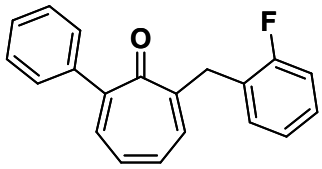
3ac. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 44% (0.066 mmol, 21.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.85 – 7.78 (m, 3H), 7.76 (s, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.39 (m, 3H), 7.39 – 7.31 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 1H), 6.96 (dd, *J* = 10.9, 8.4 Hz, 1H), 6.88 (dd, *J* = 10.9, 8.5 Hz, 1H), 4.23 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.0, 153.2, 149.4, 140.0, 136.1, 134.6, 133.7, 132.6, 131.2 (2C overlapped), 130.9, 128.1 (2C), 127.1, 127.0 (2C overlapped), 127.0 (2C), 127.0, 126.6, 126.6, 125.0, 124.5, 40.4. **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{24}H_{19}O$ 323.1430; found 323.1439.



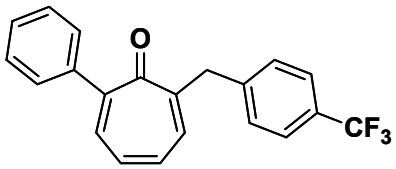
3ad. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 15:1. Yield = 41% (0.062 mmol, 19.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.52 – 7.49 (m, 1H), 7.47 – 7.44 (m, 2H), 7.43 – 7.41 (m, 1H), 7.41 – 7.34 (m, 4H), 7.28 (dq, *J* = 8.6, 1.0 Hz, 1H), 7.23 (td, *J* = 7.7, 1.6 Hz, 1H), 7.19 (td, *J* = 7.4, 1.2 Hz, 1H), 7.01 (ddd, *J* = 9.8, 8.6, 1.1 Hz, 1H), 6.94 (ddd, *J* = 10.8, 8.6, 1.1 Hz, 1H), 6.60 (d, *J* = 1.0 Hz, 1H), 4.22 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.4, 155.9, 155.0, 150.8, 150.3, 140.8, 136.0, 134.8, 132.6, 132.3, 129.2 (2C), 128.9, 128.2, 128.1 (2C), 123.5, 122.6, 120.6, 110.9, 104.8, 34.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{17}O_2$ 313.1223; found 313.1217.



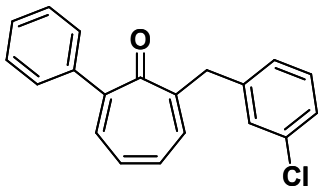
3ae. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 69% (0.104 mmol, 30.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.39 – 7.36 (m, 4H), 7.36 – 7.32 (m, 2H), 7.27 – 7.23 (m, 2H partially overlapped with the residual solvent signal), 7.14 (dq, *J* = 8.4, 1.1 Hz, 1H), 7.01 – 6.95 (m, 3H), 6.91 (ddd, *J* = 10.8, 8.5, 1.2 Hz, 1H), 4.02 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.9, 160.6 (d, *J* = 244.3 Hz), 153.1, 149.6, 139.9, 134.7, 134.2 (d, *J* = 3.2 Hz), 133.6, 131.2, 131.0, 129.9 (d, *J* = 8.0 Hz, 2C), 128.1 (2C), 127.1 (2C), 127.0, 114.3 (d, *J* = 21.2 Hz, 2C), 39.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -116.75 – -116.85 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{16}FO$ 291.1180; found 291.1188.



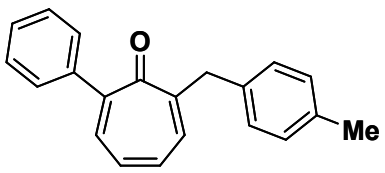
3af. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 46% (0.069 mmol, 20.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.43 – 7.30 (m, 7H), 7.23 (q, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 9.3 Hz, 1H), 6.97 (t, *J* = 9.8 Hz, 1H), 6.90 (t, *J* = 9.7 Hz, 1H), 4.08 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.8, 160.4 (d, *J* = 245.9 Hz), 151.7, 149.5, 140.0, 134.7, 133.4, 131.3, 131.1 (d, *J* = 5.2 Hz) partially overlapped with 131.0, 128.1 (2C), 127.3 (d, *J* = 8.1 Hz), 127.1 (2C), 127.0, 125.4 (d, *J* = 15.6 Hz), 123.1 (d, *J* = 3.7 Hz), 114.3 (d, *J* = 21.9 Hz), 33.6 (d, *J* = 2.7 Hz); **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -117.05 – -117.13 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{16}FO$ 291.1180; found 291.1187.



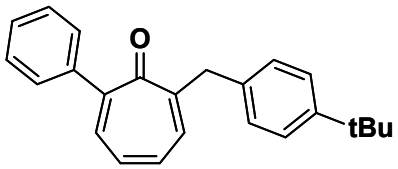
3ag. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 43% (0.065 mmol, 21.9 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 – 7.53 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 6H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.00 (dd, *J* = 10.9, 8.5 Hz, 1H), 6.93 (dd, *J* = 10.9, 8.5 Hz, 1H), 4.09 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.7, 152.1, 149.8, 142.8, 139.8, 134.8, 134.0, 131.4, 131.1, 128.6 (2C), 128.0 (2C), 127.7 (q, *J* = 32.4 Hz), 127.1, 127.1 (2C), 124.4 (q, *J* = 3.8 Hz, 2C), 123.3 (q, *J* = 271.9 Hz), 40.6; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -62.44 (s, 3F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{16}F_3O$ 341.1148; found 341.1155.



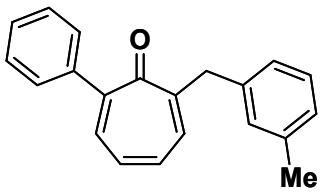
3ah. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 77% (0.116 mmol, 35.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.40 – 7.37 (m, 4H), 7.36 – 7.32 (m, 2H), 7.28 – 7.27 (m, 1H), 7.24 – 7.17 (m, 3H), 7.16 (dq, *J* = 8.5, 1.0 Hz, 1H), 6.99 (ddd, *J* = 10.8, 8.6, 1.2 Hz, 1H), 6.92 (ddd, *J* = 10.9, 8.5, 1.1 Hz, 1H), 4.01 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.8, 153.4, 150.7, 141.7, 140.9, 135.8, 134.9, 134.3, 132.2, 132.2, 129.7, 129.4, 129.1 (2C), 128.1, 128.1 (2C), 127.7, 126.6, 41.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{16}ClO$ 307.0884; found 307.0878.



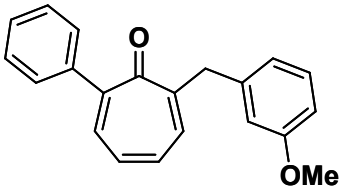
3ai. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 52% (0.078 mmol, 22.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.42 – 7.30 (m, 6H), 7.20 – 7.16 (m, 2H), 7.15 – 7.10 (m, 3H), 6.95 (dd, *J* = 10.7, 8.2 Hz, 1H), 6.89 (ddd, *J* = 10.7, 8.7, 1.3 Hz, 1H), 4.02 (s, 2H), 2.34 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.1, 153.6, 149.3, 140.1, 135.4, 134.9, 134.5, 133.4, 131.2, 130.7, 128.5 (2C), 128.2 (2C), 128.1 (2C), 127.0 (2C), 126.9, 39.9, 20.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}O$ 287.1430; found 287.1436.



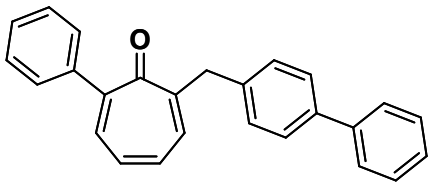
3aj. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 25:1. Yield = 48% (0.072 mmol, 23.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.40 – 7.31 (m, 8H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.95 (dd, *J* = 10.9, 8.2 Hz, 1H), 6.90 (dd, *J* = 11.2, 8.1 Hz, 1H), 4.04 (s, 2H), 1.32 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.2, 154.4, 150.3, 149.2, 141.1, 136.4, 135.4, 134.4, 132.2, 131.7, 129.2 (2C), 129.1 (2C), 128.0 (2C), 128.0, 125.4 (2C), 40.9, 34.4, 31.4 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{24}H_{25}O$ 329.1900; found 329.1907.



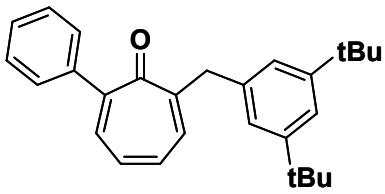
3ak. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 68% (0.102 mmol, 29.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.28 – 7.19 (m, 7H), 7.15 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.12 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.94 (m, 2H), 4.03 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.5, 154.0, 152.1, 141.5, 139.2, 138.1, 135.9, 134.7, 132.7, 131.8, 130.4, 129.9, 129.2, 127.8 (2C), 127.1 (2C), 126.6, 125.8, 41.3, 19.6; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}O$ 287.1430; found 287.1434.



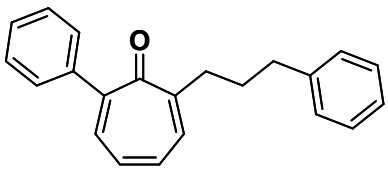
3al. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 15:1. Yield = 81% (0.077 mmol, 36.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.44 – 7.31 (m, 6H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.95 (t, *J* = 9.6 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.83 (s, 1H), 6.79 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.04 (s, 2H), 3.78 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.0, 158.8, 153.1, 149.3, 140.2, 140.0, 134.5, 133.5, 131.2, 130.8, 128.5, 128.1 (2C), 127.0 (2C), 127.0, 120.9, 114.2, 110.8, 54.2, 40.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{19}O_2$ 303.1380; found 303.1375.



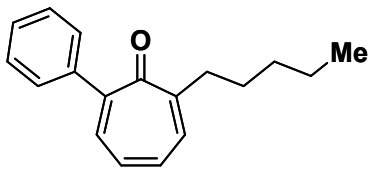
3am. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 51% (0.122 mmol, 26.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.60 – 7.58 (m, 2H), 7.56 – 7.53 (m, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.32 (m, 9H), 7.20 (dq, *J* = 8.4, 1.1 Hz, 1H), 6.98 (ddd, *J* = 10.8, 8.4, 1.3 Hz, 1H), 6.92 (ddd, *J* = 10.8, 8.4, 1.3 Hz, 1H), 4.10 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.1, 154.2, 150.5, 141.0, 141.0, 139.4, 138.7, 135.6, 134.6, 132.3, 131.9, 130.0 (2C), 129.2 (2C), 128.8 (2C), 128.1 (2C), 128.0, 127.3 (2C), 127.1, 127.0 (2C), 41.2; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{26}H_{21}O$ 349.1587; found 349.1591.



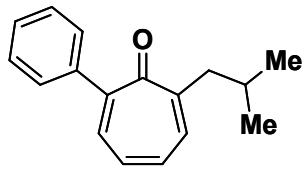
3an. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 42% (0.063 mmol, 24.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 7H), 7.10 (d, *J* = 1.8 Hz, 2H), 7.07 (dq, *J* = 8.3, 1.2 Hz, 1H), 6.93 (ddd, *J* = 9.7, 8.4, 1.3 Hz, 1H), 6.88 (ddd, *J* = 10.8, 8.4, 1.2 Hz, 1H), 4.07 (s, 2H), 1.31 (s, 18H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.6, 154.6, 150.9 (2C), 149.8, 141.1, 138.5, 135.1, 134.0, 132.2, 131.4, 129.1 (2C), 128.0 (2C), 128.0, 123.8 (2C), 120.4, 41.6, 34.8 (2C), 31.5 (6C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{28}H_{33}O$ 385.2526; found 385.2530.



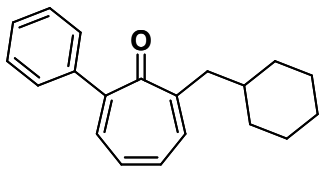
3ao. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 43% (0.065 mmol, 19.4 mg). **3an**:**3''an** = 12:1, only the characterization of **3an** is given. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.47 – 7.44 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.25 (m, 2H, overlapped with the residual solvent signal), 7.23 (ddt, *J* = 8.0, 1.6, 0.8 Hz, 1H), 7.20 – 7.16 (m, 3H), 6.96 (ddd, *J* = 10.9, 8.2, 1.5 Hz, 1H), 6.92 (ddd, *J* = 10.8, 8.1, 1.5 Hz, 1H), 2.80 – 2.75 (m, 2H), 2.72 – 2.67 (m, 2H), 1.98 – 1.91 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.3, 155.3, 150.1, 142.1, 141.1, 135.5, 133.9, 132.4, 131.6, 129.2 (2C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 128.0, 125.8, 36.4, 35.9, 31.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{21}O$ 301.1587; found 301.1582.



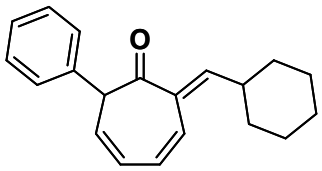
3ap. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 48% (0.072 mmol, 18.1 mg). **3ao**:**3''ao** = 9:1, only the characterization of **3ao** is given. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.48 – 7.44 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 7.33 – 7.30 (m, 1H), 7.26 – 7.23 (m, 1H), 6.97 – 6.90 (m, 2H), 2.77 – 2.64 (m, 2H), 1.64 – 1.57 (m, 2H), 1.39 – 1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.4, 154.9, 148.9, 140.1, 134.3, 132.6, 131.4, 130.4, 128.2, 127.0 (2C), 126.9 (2C), 35.6, 30.9, 28.2, 21.5, 13.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{21}O$ 253.1587; found 253.1596.



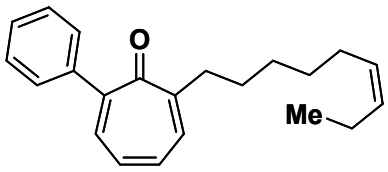
3aq. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 52% (0.078 mmol, 18.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 1H), 7.32 – 7.29 (m, 1H), 7.19 (ddt, *J* = 8.3, 1.6, 0.8 Hz, 1H), 6.97 – 6.87 (m, 2H), 2.61 (dd, *J* = 7.1, 0.7 Hz, 2H), 1.99 (dh, *J* = 13.5, 6.8 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.6, 153.3, 148.8, 140.1, 134.2, 133.5, 131.2, 130.4, 128.1, 127.0 (2C), 126.9 (2C), 44.9, 26.9, 21.6 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{17}H_{19}O$ 239.1430; found 239.1433.



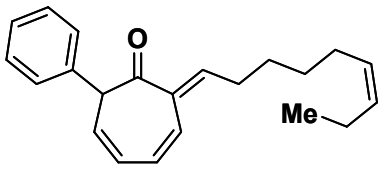
3ar. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 35% (0.053 mmol, 14.6 mg). Isolated (second eluting fraction) along with **3''aq** (**3aq**:**3''aq** = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.46 – 7.43 (m, 2H), 7.40 – 7.37 (m, 2H), 7.35 – 7.32 (m, 1H), 7.31 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 6.97 – 6.88 (m, 2H), 3.19 – 3.13 (m, 1H), 2.61 (d, *J* = 6.8 Hz, 2H), 1.77 – 1.58 (m, 5H), 1.48 – 1.39 (m, 1H), 1.21 – 1.11 (m, 3H), 0.99 – 0.92 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.5, 154.1, 149.9, 141.2, 135.3, 134.7, 132.2, 131.4, 129.2 (2C), 128.1 (2C), 127.9, 44.7, 37.3, 33.5 (2C), 26.5, 26.3 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}O$ 279.1743; found 279.1738.



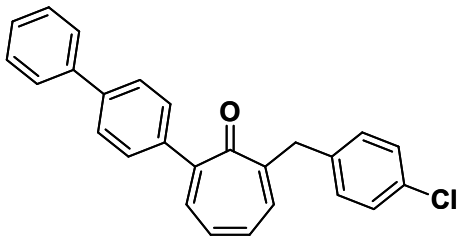
3''ar. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 11% (0.017 mmol, 4.6 mg). Isolated (first eluting fraction) along with **3aq** (**3aq**:**3''aq** = 3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.55 (d, *J* = 11.2 Hz, 1H), 6.28 (ddd, *J* = 9.7, 5.3, 2.0 Hz, 1H), 6.24 (dd, *J* = 11.2, 5.3 Hz, 1H), 5.87 (dd, *J* = 9.9, 5.4 Hz, 1H), 4.46 (d, *J* = 4.9 Hz, 1H), 2.56 – 2.46 (m, 1H), 1.83 – 1.59 (m, 5H), 1.38 – 1.13 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 192.9, 151.2, 137.8, 134.9, 129.4 (2C), 129.3, 128.3 (2C), 127.8, 127.4, 127.1, 124.2, 58.8, 37.8, 32.0, 31.9, 25.7, 25.5, 25.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}O$ 279.1743; found 279.1749.



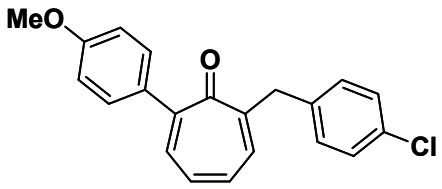
3as. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 39% (0.059 mmol, 17.9 mg). Isolated (second eluting fraction) along with **3''ar** (**3ar**:**3''ar** = 2.3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.47 – 7.44 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 7.33 – 7.31 (m, 1H), 7.25 – 7.22 (m, 1H), 6.97 – 6.89 (m, 2H), 5.38 – 5.26 (m, 2H), 2.74 – 2.70 (m, 2H), 2.06 – 1.97 (m, 4H), 1.64 – 1.57 (m, 2H), 1.42 – 1.35 (m, 4H), 0.94 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.3, 154.8, 148.9, 140.1, 134.4, 132.7, 131.4, 130.6, 130.4, 128.2 (2C), 128.1, 127.0 (2C), 126.9, 35.6, 28.6, 28.4, 28.4, 26.0, 19.5, 13.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{27}O$ 307.2056; found 307.2060.



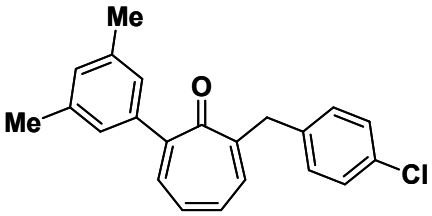
3''as. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 11% (0.011 mmol, 5.0 mg). Isolated (first eluting fraction) along with **3ar** (**3ar**:**3''ar** = 2.3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 3H), 6.78 (tt, *J* = 7.9, 1.4 Hz, 1H), 6.54 (dd, *J* = 11.1, 1.2 Hz, 1H), 6.30 (ddd, *J* = 9.6, 5.0, 2.1 Hz, 1H), 6.26 (dd, *J* = 11.6, 5.3 Hz, 1H), 5.89 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.40 – 5.35 (m, 1H), 5.33 – 5.27 (m, 1H), 4.47 (dd, *J* = 5.6, 2.1 Hz, 1H), 2.42 – 2.28 (m, 2H), 2.07 – 2.00 (m, 4H), 1.56 – 1.48 (m, 2H), 1.43 – 1.37 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 192.6, 146.6, 137.7, 136.8, 132.0, 129.4 (2C), 129.3, 128.6, 128.3 (2C), 127.8, 127.5, 127.1, 124.1, 58.8, 29.5, 28.7, 28.1, 26.8, 20.5, 14.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}O$ 307.2056; found 307.2061.



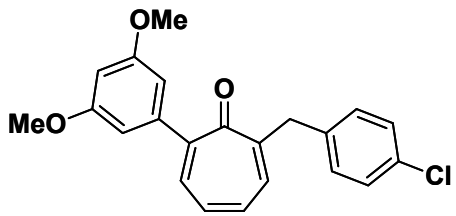
3ba. Pale brown solid. FC eluent: *n*-hexane/EtOAc: 15:1. **MP** = 155-157 °C. Yield = 83% (0.125 mmol, 42.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.62 – 7.55 (m, 4H), 7.48 – 7.40 (m, 4H), 7.37 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.28 – 7.20 (m, 4H, partially overlapped with the residual solvent signal), 7.14 (dq, *J* = 8.5, 1.0 Hz, 1H), 6.96 (ddd, *J* = 10.8, 8.6, 1.1 Hz, 1H), 6.89 (ddd, *J* = 10.8, 8.5, 1.1 Hz, 1H), 4.00 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.9, 153.7, 150.3, 141.0, 140.8, 139.9, 138.1, 135.6, 134.8, 132.3 (2C), 132.2, 130.8 (2C), 129.6 (2C), 128.8 (2C), 128.7 (2C), 127.5, 127.2 (2C), 126.9 (2C), 41.1 **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{26}H_{20}ClO$ 383.1197; found 383.1197.



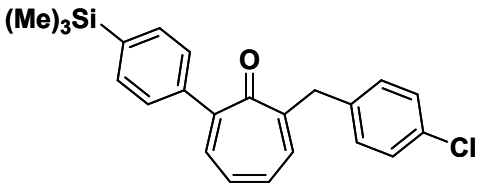
3ca. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 60% (0.090 mmol, 30.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38 – 7.35 (m, 2H), 7.33 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.27 – 7.24 (m, 2H, partially overlapped with the residual solvent signal), 7.23 – 7.21 (m, 2H), 7.15 – 7.10 (m, 1H), 6.95 (ddd, *J* = 10.8, 8.7, 1.1 Hz, 1H), 6.92 – 6.85 (m, 3H), 4.00 (s, 2H), 3.82 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.9, 158.6, 152.2, 149.0, 137.2, 134.1, 133.6, 132.1, 131.1, 131.1, 130.6, 129.8 (2C), 129.5 (2C), 127.6 (2C), 112.5 (2C), 54.3, 40.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{18}ClO_2$ 337.0990; found 337.0984.



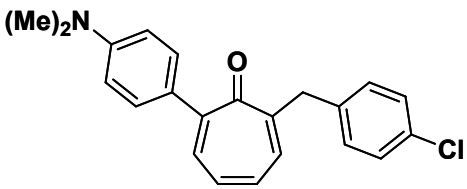
3da. Pale brown sticky oil. FC eluent: 100% DCM. Yield = 55% (0.083 mmol, 27.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 3H, partially overlapped with the residual solvent signal), 7.23 (d, *J* = 8.5 Hz, 2H), 7.14 – 7.10 (m, 1H), 6.98 – 6.86 (m, 5H), 4.01 (s, 2H), 2.31 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) = 186.4, 153.3, 150.9, 140.9, 138.2, 137.6 (2C), 135.2, 134.3, 132.2, 132.1, 131.9, 130.9 (2C), 129.8, 128.6 (2C), 126.7 (2C), 41.0, 21.3 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{20}ClO$ 335.1197; found 335.1204.



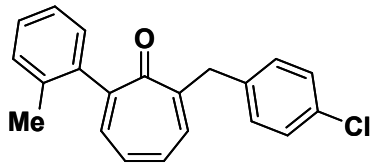
3ea. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 9:1. Yield = 70% (0.105 mmol, 38.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.31 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.27 – 7.22 (m, 4H, partially overlapped with residual solvent signal), 7.16 – 7.13 (m, 1H), 6.98 – 6.93 (m, 1H), 6.90 (ddd, *J* = 10.9, 8.3, 1.3 Hz, 1H), 6.46 – 6.44 (m, 3H), 4.01 (s, 2H), 3.76 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) = 186.0, 160.5 (2C), 153.5, 150.4, 142.9, 138.0, 135.3, 134.4, 132.3, 132.0, 130.9 (2C), 128.6 (2C), 107.1 (2C), 100.5 (2C), 55.4 (2C), 41.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{20}ClO_3$ 367.1095; found 367.1091.



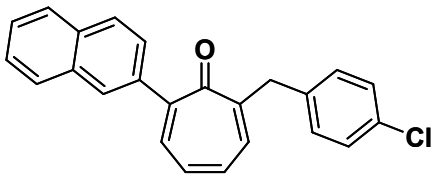
3fa. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 61% (0.092 mmol, 34.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.56 – 7.51 (m, 2H), 7.38 – 7.31 (m, 3H), 7.29 – 7.21 (m, 4H, partially overlapped with residual solvent signal), 7.18 – 7.12 (m, 1H), 7.01 – 6.94 (m, 1H), 6.91 (ddd, *J* = 10.9, 8.5, 1.1 Hz, 1H), 4.00 (s, 2H), 0.28 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.0, 154.9, 151.9, 142.4, 141.6, 139.3, 136.8, 135.8, 134.3 (2C), 133.4, 133.3 (2C), 132.0 (2C), 129.8 (2C), 129.4 (2C), 42.2, -0.0 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{24}ClOSi$ 379.1279; found 379.1285.



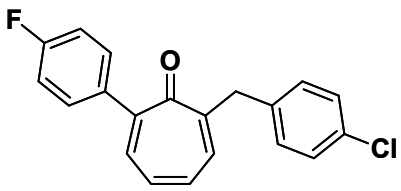
3ga. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 49% (0.074 mmol, 25.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.40 – 7.37 (m, 2H), 7.34 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.27 – 7.21 (m, 4H, partially overlapped with residual solvent signal), 7.11 – 7.06 (m, 1H), 6.98 – 6.91 (m, 1H), 6.81 (ddd, *J* = 10.8, 8.6, 1.0 Hz, 1H), 6.74 – 6.68 (m, 2H), 4.01 (s, 2H), 2.99 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.3, 152.3, 150.6, 150.3, 138.5, 134.4, 133.9, 132.2, 132.1, 130.8 (2C), 130.7, 130.4 (2C), 128.5 (2C), 128.3, 111.8 (2C), 41.1, 40.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{210}ClNO$ 350.1306; found 350.1298.



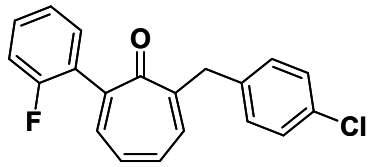
3ha. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 48% (0.073 mmol, 23.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.29 – 7.15 (m, 10H, partially overlapped with the residual solvent signal), 7.10 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.01 – 6.92 (m, 2H), 3.98 (s, 2H), 1.96 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.2, 153.3, 152.4, 141.3, 137.8, 136.1, 135.2, 134.8, 132.6, 132.2, 132.2, 130.9 (2C), 129.9, 129.2, 128.5 (2C), 127.9, 125.8, 41.1, 19.6; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{18}ClO$ 321.1041; found 321.1048.



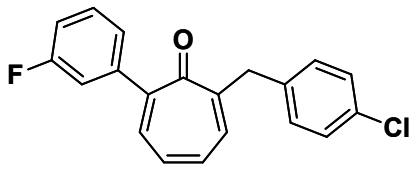
3ia. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 49% (0.074 mmol, 28.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.87 – 7.80 (m, 4H), 7.53 – 7.45 (m, 4H), 7.32 – 7.22 (m, 4H, partially overlapped with residual solvent signal), 7.18 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.94 (ddd, *J* = 10.8, 8.5, 1.1 Hz, 1H), 4.04 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.1, 153.8, 150.7, 138.7, 138.1, 136.0, 134.8, 133.3, 133.1, 132.3, 132.3, 132.2, 130.9 (2C), 128.7 (2C), 128.3, 128.3, 127.6, 127.4, 127.0, 126.4, 126.1, 41.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{24}H_{18}ClO$ 357.1041; found 357.1036.



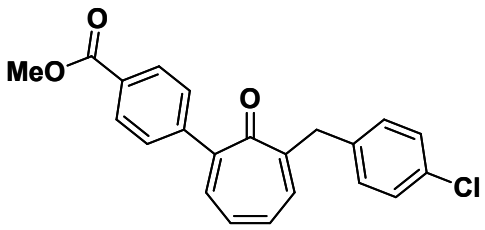
3ja. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 15:1. Yield = 63% (0.095 mmol, 30.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.26 – 7.24 (m, 2H, partially overlapped with the residual solvent signal), 7.22 – 7.19 (m, 2H), 7.17 – 7.14 (m, 1H), 7.10 – 7.01 (m, 2H), 6.99 – 6.94 (m, 1H), 6.91 (ddd, *J* = 10.8, 8.4, 1.3 Hz, 1H), 3.99 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.6, 162.7 (d, *J* = 247.8 Hz),153.8, 149.6, 138.0, 136.8 (d, *J* = 3.6 Hz), 135.8, 134.9, 132.4, 132.3, 132.1, 131.0 (d, *J* = 8.2 Hz, 2C), 130.8 (2C), 128.6 (2C), 115.0 (d, *J* = 21.7 Hz, 2C), 41.1; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -113.61 – -113.77 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{15}ClFO$ 325.0790; found 325.0792.



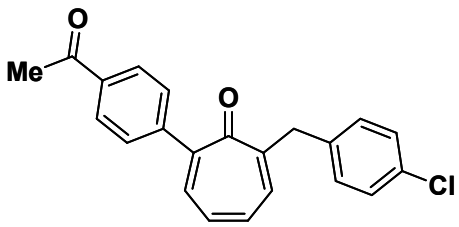
3ka. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 12:1. Yield = 65% (0.098 mmol, 31.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.36 – 7.32 (m, 2H), 7.30 – 7.25 (m, 3H, partially overlapped with the residual solvent signal), 7.23 – 7.21 (m, 2H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.09 (ddd, *J* = 9.6, 8.2, 1.2 Hz, 1H), 6.99 – 6.93 (m, 2H), 4.01 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.0, 159.5 (d, *J* = 247.9 Hz), 153.4, 146.4, 137.9, 136.7, 134.8, 133.1, 132.3, 131.8, 131.1 (d, *J* = 3.7 Hz),130.8 (2C), 129.9 (d, *J* = 8.3 Hz), 129.1 (d, *J* = 15.3 Hz), 128.6 (2C), 124.1 (d, *J* = 3.3 Hz), 115.6 (d, *J* = 22.2 Hz) 40.7; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -112.82 – -112.93 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{15}ClFO$ 325.0790; found 325.0797.



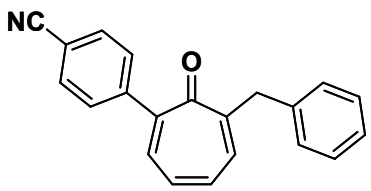
3la. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 12:1. Yield = 77% (0.116 mmol, 37.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.37 – 7.30 (m, 2H), 7.29 – 7.25 (m, 2H, partially overlapped with the residual solvent signal), 7.25 – 7.19 (m, 2H), 7.16 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.14 – 7.09 (m, 2H), 7.04 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 7.01 – 6.91 (m, 2H), 4.00 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.4, 162.4 (d, *J* = 245.6 Hz), 154.0, 149.3 (d, *J* = 2.1 Hz), 142.9 (d, *J* = 7.7 Hz), 137.9, 135.9, 134.8, 132.7, 132.3, 132.0, 130.8 (2C), 129.6 (d, *J* = 8.5 Hz), 128.7 (2C), 124.8 (d, *J* = 2.9 Hz), 116.3 (d, *J* = 22.4 Hz), 115.0 (d, *J* = 21.2 Hz), 41.0; **^{19}F NMR** (565 MHz, $CDCl_3$) δ = -113.49 – -113.56 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{15}ClFO$ 325.0790; found 325.0796.



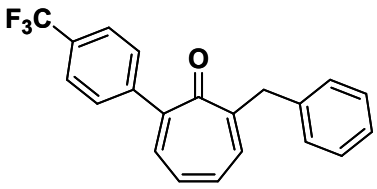
3ma. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 9:1. Yield = 56% (0.84 mmol, 30.6 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.07 – 8.00 (m, 2H), 7.46 – 7.41 (m, 2H), 7.33 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.29 – 7.25 (m, 2H, partially overlapped with the residual solvent signal), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 1H), 7.03 – 6.92 (m, 2H), 4.00 (s, 2H), 3.93 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.4, 166.8, 154.1, 149.7, 145.5, 137.8, 136.0, 134.9, 132.9, 132.3, 132.0, 130.8 (2C), 129.6, 129.4 (2C), 129.1 (2C), 128.6 (2C), 52.1, 41.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{18}ClO_3$ 365.0939; found 365.0935.



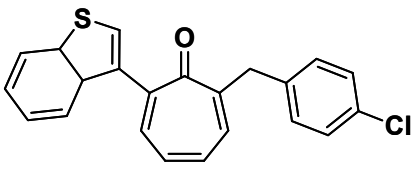
3na. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 15:1. Yield = 47% (0.071 mmol, 24.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H), 7.28 – 7.25 (m, 2H, partially overlapped with the residual solvent signal), 7.24 – 7.21 (m, 2H), 7.20 – 7.17 (m, 1H), 7.03 – 6.93 (m, 2H), 4.00 (s, 2H), 2.61 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 197.7, 185.4, 154.2, 149.6, 145.7, 137.8, 136.5, 136.0, 134.9, 133.0, 132.4, 132.1, 130.8 (2C), 129.4 (2C), 128.7 (2C), 128.2 (2C), 41.0, 26.7; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{18}ClO_2$ 349.0990; found 349.0995.



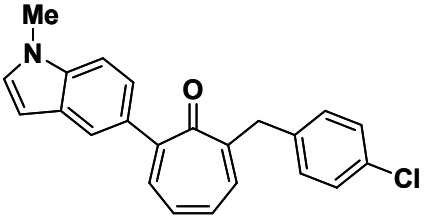
3ob. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 43% (0.065 mmol, 21.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.68 – 7.62 (m, 2H), 7.49 – 7.42 (m, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.22 (m, 3H, partially overlapped with the residual solvent signal), 7.21 – 7.17 (m, 1H), 7.02 – 6.94 (m, 2H), 4.04 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 184.3, 154.1, 147.5, 144.7, 138.1, 135.1, 133.9, 132.5, 130.8 (2C), 130.6, 128.9 (2C), 128.5 (2C), 127.6 (2C), 125.6, 117.8, 110.6, 40.5; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{16}NO$ 298.1226; found 298.1230.



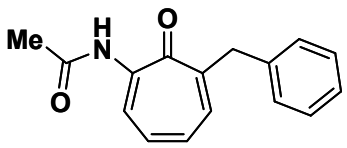
3pb. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 18:1. Yield = 52% (0.078 mmol, 26.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H), 7.50 – 7.45 (m, 2H), 7.34 – 7.30 (m, 3H), 7.29 – 7.27 (m, 2H), 7.25 (d, *J* = 11.1 Hz, 1H, partially overlapped with the residual solvent signal), 7.20 – 7.17 (m, 1H), 7.02 – 6.92 (m, 2H), 4.05 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.6, 154.9, 149.1, 144.6 (q, *J* = 1.7 Hz), 139.3, 136.0, 134.8, 133.1, 131.7, 130.0 (q, *J* = 32.5 Hz), 129.6 (2C), 129.5 (2C), 128.6 (2C), 126.5, 125.0 (q, *J* = 3.8 Hz, 2C), 124.1 (q, *J* = 272 Hz), 41.50; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.65 (s, 3F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{16}F_3O$ 341.1148; found 341.1141.



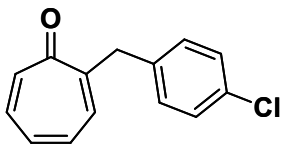
3qa. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 48% (0.072 mmol, 26.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.87 – 7.82 (m, 1H), 7.65 (s, 1H), 7.55 – 7.52 (m, 1H), 7.32 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.30 – 7.24 (m, 5H, partially overlapped with the residual solvent signal), 7.21 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.11 – 7.09 (m, 1H), 7.06 – 6.97 (m, 2H), 4.04 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.0, 153.3, 144.9, 139.8, 137.8, 137.3, 136.4, 136.4, 134.8, 132.8, 132.3, 131.9, 131.0 (2C), 128.6 (2C), 127.1, 124.4, 124.2, 122.8, 122.8, 41.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{16}ClOS$ 363.0605; found 363.0611.



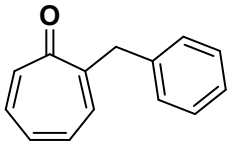
3ra. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 41% (0.062 mmol, 22.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.68 – 7.66 (m, 1H), 7.43 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.28 – 7.23 (m, 5H, partially overlapped with the residual solvent signal), 7.13 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.01 – 6.95 (m, 1H), 6.87 (ddd, *J* = 10.8, 8.5, 1.0 Hz, 1H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.03 (s, 2H), 3.80 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.6, 153.0, 151.7, 138.4, 136.6, 135.3, 134.4, 132.2, 132.1, 131.2, 130.9 (2C), 129.3, 128.6 (2C), 128.4, 123.1, 121.9, 108.7, 101.6, 41.1, 32.9; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{19}ClNO$ 360.1150; found 360.1146.



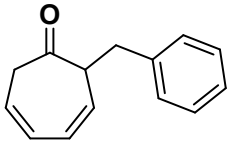
3sb. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 56% (0.084 mmol, 21.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58 (s, 1H), 9.06 – 9.01 (m, 1H), 7.47 – 7.43 (m, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 3H, partially overlapped with the residual solvent signal), 7.02 – 6.96 (m, 1H), 4.12 (s, 2H), 2.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 176.6, 169.1, 147.8, 144.6, 138.3, 137.2, 133.5, 128.9, 128.1 (2C), 127.6 (2C), 125.5, 120.3, 40.9, 24.7; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{16}NO_2$ 254.1176; found 254.1171.



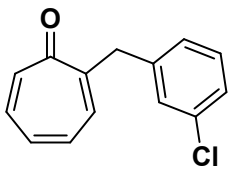
3ta. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 63% (0.095 mmol, 21.7 mg). **3ta**:**3'ta** = 18:1, only the characterization of **3ta** is given. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.27 – 7.24 (m, 2H, partially overlapped with the residual solvent peak), 7.20 – 7.15 (m, 2H), 7.14 – 7.06 (m, 3H), 6.95 – 6.89 (m, 2H), 3.92 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = ^{13}C NMR (151 MHz, $CDCl_3$) δ 185.6, 153.2, 139.8, 136.6, 134.6, 134.6, 132.6, 132.1, 131.3, 129.8, 127.7, 39.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{14}H_{12}ClO$ 231.0571; found 231.0572.



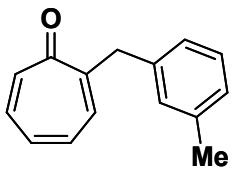
3tb. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 63% (0.095 mmol, 18.5 mg). Isolated (second eluting fraction) along with **3'tb** (**3tb**:**3'tb** = 2.3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.33 – 7.29 (m, 2H), 7.26 – 7.21 (m, 3H), 7.12 – 7.10 (m, 2H), 7.10 – 7.07 (m, 1H), 6.93 – 6.88 (m, 2H), 3.98 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.8, 154.8, 140.7, 139.1, 135.6, 135.5, 133.7, 132.8, 129.6 (2C), 128.6 (2C), 126.5, 40.6; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{14}H_{13}O$ 197.0961; found 197.0955.



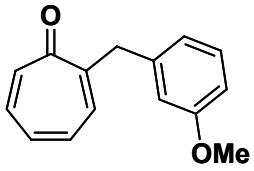
3'tb. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 27% (0.041 mmol, 8.0 mg). Isolated (first eluting fraction) along with **3tb** (**3tb**:**3'tb** = 2.3:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 3H), 6.27 (ddd, *J* = 10.6, 4.6, 2.3 Hz, 1H), 6.20 (dddd, *J* = 10.3, 4.7, 2.1, 1.0 Hz, 1H), 5.82 (ddd, *J* = 10.8, 7.5, 3.7 Hz, 1H), 5.56 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.36 – 3.31 (m, 2H), 3.22 (dd, *J* = 18.8, 7.5 Hz, 1H), 3.01 (ddtd, *J* = 18.9, 3.7, 2.6, 1.0 Hz, 1H), 2.95 – 2.88 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 208.2, 139.8, 129.4, 129.2, 129.1 (2C), 128.6, 128.4 (2C), 126.2, 125.6, 55.1, 44.9, 34.6; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{14}H_{15}O$ 199.1117; found 199.1122.



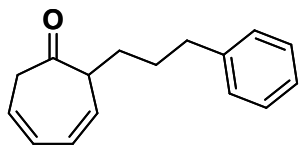
3th. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 57% (0.086 mmol, 19.7 mg). **3th**:**3'th** = 18:1, only the characterization of **3th** is given. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.25 – 7.19 (m, 3H), 7.17 – 7.07 (m, 4H), 6.97 – 6.91 (m, 2H), 3.94 (d, *J* = 0.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.5, 153.8, 141.2, 140.9, 135.8, 135.6, 134.3, 133.6, 133.2, 129.8, 129.4, 127.7, 126.7, 40.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{14}H_{12}ClO$ 231.0571; found 231.0577.



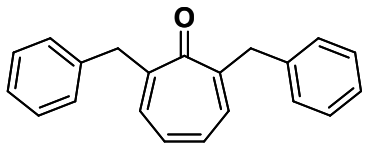
3tk. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 55% (0.083 mmol, 17.3 mg). **3tk**:**3'tk** > 20:1. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.10 – 7.07 (m, 1H), 7.07 – 7.02 (m, 3H), 6.94 – 6.88 (m, 2H), 3.94 (s, 2H), 2.46 – 2.17 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.8, 154.9, 140.7, 139.0, 138.2, 135.6, 135.5, 133.7, 132.7, 130.3, 128.5, 127.2, 126.6, 40.4, 21.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{15}O$ 211.1117; found 211.1112.



3tl. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 5:1. Yield = 64% (0.096 mmol, 21.7 mg). **3tl**:**3'tl** = 9:1, only the characterization of **3tl** is given. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.22 (t, *J* = 8.1 Hz, 1H), 7.13 – 7.10 (m, 2H), 7.10 – 7.07 (m, 1H), 6.93 – 6.89 (m, 2H), 6.83 (ddd, *J* = 7.5, 1.6, 0.9 Hz, 1H), 6.80 – 6.76 (m, 2H), 3.95 (s, 2H), 3.79 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.8, 159.8, 154.6, 140.7, 140.7, 135.6, 135.6, 133.8, 132.8, 129.5, 122.0, 115.3, 111.9, 55.2, 40.5; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{15}O_2$ 227.1067; found 227.1074.



3'ts. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 44% (0.066 mmol, 14.9 mg). Isolated as the only product in the reaction between **1t** and **2s** (**3'ts**:**3ts** > 20:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.29 – 7.25 (m, 2H, overlapped with the residual solvent signal), 7.20 – 7.15 (m, 3H), 6.28 (ddd, *J* = 10.4, 4.7, 2.0 Hz, 1H), 6.22 (dddd, *J* = 10.3, 4.8, 2.3, 0.9 Hz, 1H), 5.81 (ddd, *J* = 10.8, 7.5, 3.7 Hz, 1H), 5.51 (dd, *J* = 10.3, 4.7 Hz, 1H), 3.24 – 3.13 (m, 1H), 3.01 – 2.92 (m, 2H), 2.70 – 2.57 (m, 2H), 2.03 – 1.92 (m, 1H), 1.74 – 1.62 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 208.8, 142.3, 129.9, 129.3, 128.4 (2C), 128.4, 128.3 (2C), 125.7, 125.5, 53.9, 44.9, 35.9, 29.1, 28.5; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{19}O$ 227.1430; found 227.1435.



4tb. Pale brown sticky oil. FC eluent: *n*-hexane/EtOAc: 7:1. Yield = 35% (0.053 mmol, 15.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.31 – 7.27 (m, 4H), 7.24 – 7.20 (m, 6H), 7.13 – 7.08 (m, 2H), 6.87 – 6.83 (m, 2H), 4.03 (s, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.5, 152.6 (2C), 139.6 (2C), 135.1 (2C), 131.9 (2C), 129.5 (4C), 128.5 (2C),

126.3 (2C), 41.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{21}H_{21}O$ 289.1587; found 289.1590.

5. Mechanistic investigation

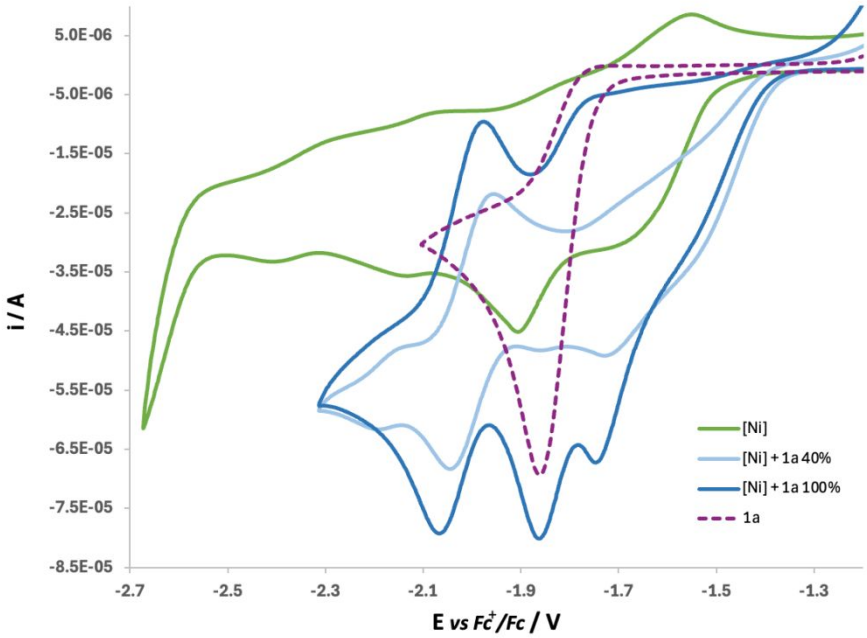


Figure S1. CV responses collected in a 5 mM solution of **[Ni]**, 0.1 M $TEABF_4$ and anhydrous DMF, in absence and in presence of different amount of **1a**. The response of 5 mM **1a** in the same solvent medium is also reported for comparison. 0.050 Vs^{-1} potential scan rate.

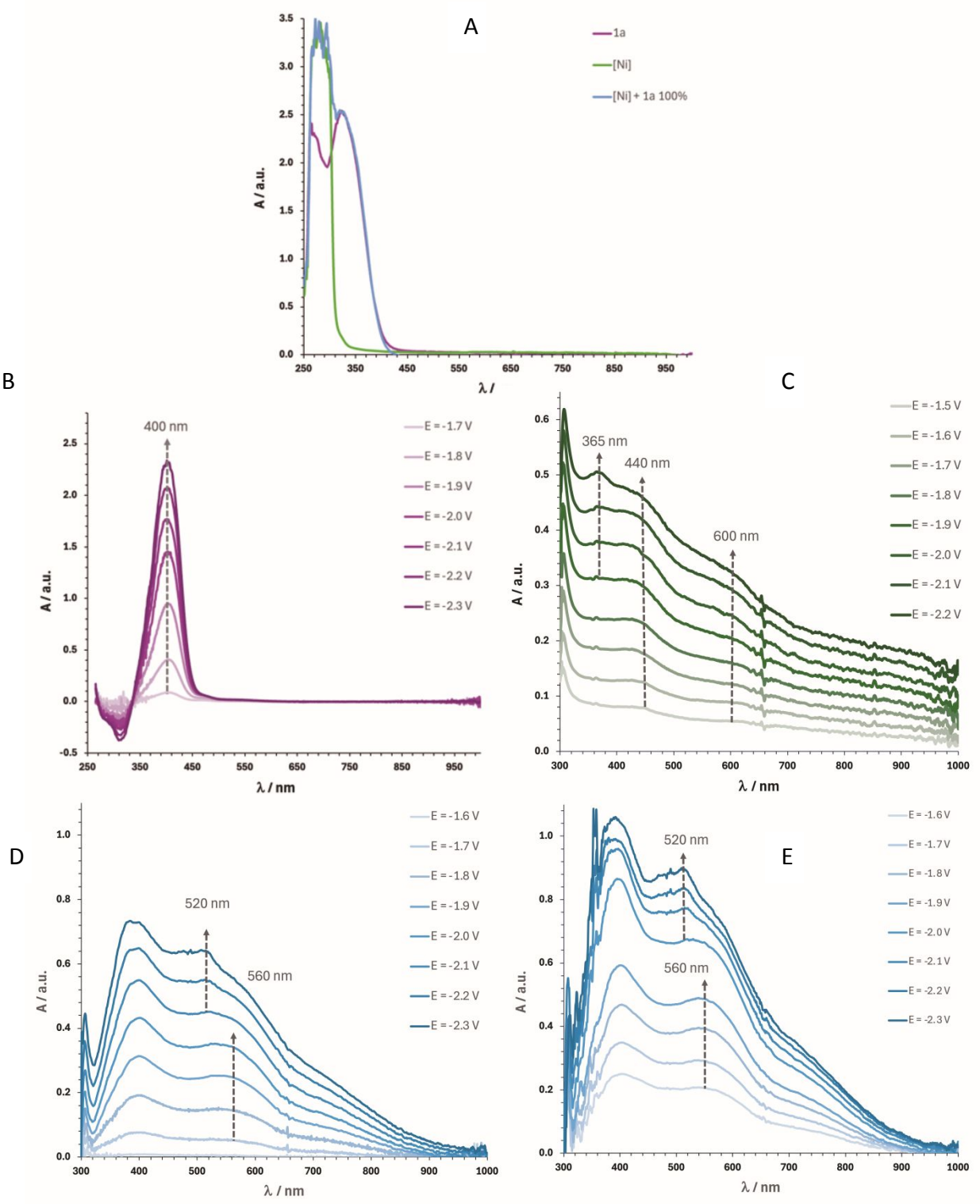


Figure S2. a) UV-Vis spectra recorded at open circuit potential; these spectra were used as the reference of the following ones recorded at various potentials. The following figures report spectra recorded at different applied potentials in solutions of b) 2.5 mM **1a**, c) 2.5 mM **[Ni]**, d) 2.5 mM **[Ni]** + 1.25 mM **1a**, e) 2.5 mM [Ni] + 2.5 mM **1a**. In all cases 0.1 M $TEABF_4$ and anhydrous DMF was the solvent medium. Arrows indicate the evolution of the main adsorption peak at the various applied potentials.

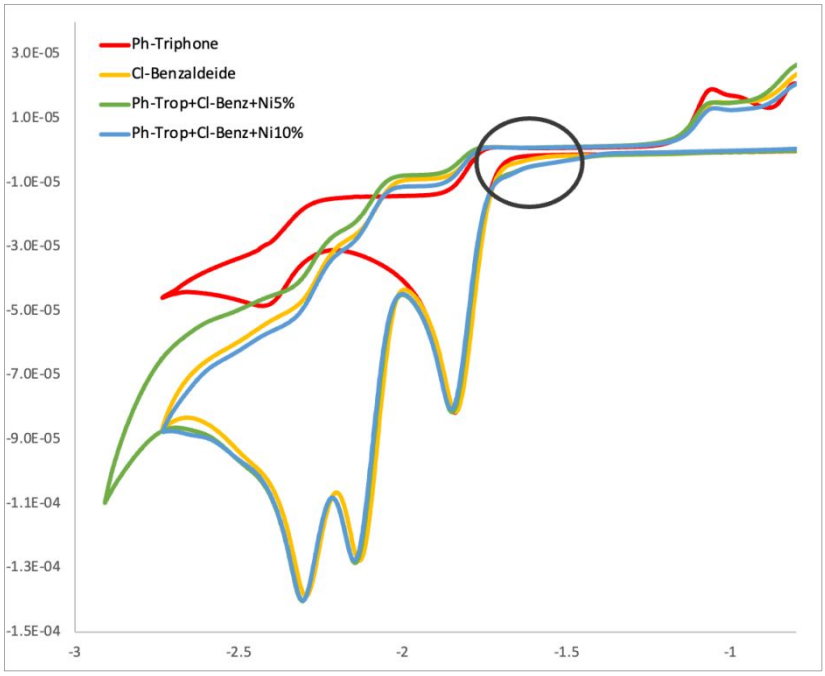


Figure S3. CV responses collected for **1a**: red trace, **2a**: yellow trace, **1a**+**2a**+[Ni] 5 mol%: green trace, **1a**+**2a**+[Ni] 10 mol%: blue trace. Highlighted in black the only slight difference observed in the last two cases compared with the traces of the pristine species, however not attributable to the formation of **3aa**. In all cases 0.1 M $TEABF_4$ and anhydrous DMF was the solvent medium.

Having verified that product **3aa** is observable by CV analysis, as it is an electro-active species, we considered the possibility to check its formation by adding aldehyde **2a** to the [Ni]-**1a** mixtures analyzed in the previous traces. Unfortunately, the $E_{1/2}$ shown (-1.88 V *vs* Fc/Fc^+) is almost superimposed with the one of **1a**. Therefore, when the aldehyde was added to these mixtures we were not able to say if was formed or not, since the signal arising from this compound was hidden by the one relative to pristine **1a**.

5.2 Computational mechanistic investigation

Absorption Spectra of Ni^{I}(L1)Cl and the Ni-1a species

The identity of the reacting Ni species was confirmed through UV-Vis spectra calculation for the **Ni^{I}(L1)Cl** catalyst and comparison with the experimental spectra. The computational peaks at 376 and 442 nm are in excellent agreement with the reported experimental peaks at 365 and 440nm when the voltage is between -1.75 (reduction from N^{II} to N^{I}) and -1.9 V (reduction from N^{I} to N^{0}). Next, we sought to elucidate the nature of the organonickel species formed after mixing [Ni] with **1a** and applying a voltage of -1.90V. The resulting structure, suggested by our calculations showed a Ni coordination on the tropone scaffold, through interactions with the double bond of the phenyl and the lone pair of the carboxylic oxygen. The computational DFT spectra show peaks at 430, 572, 604 and 607 nm, which are in very good agreement with the experimental spectra shown in Figure S4 of the main text.

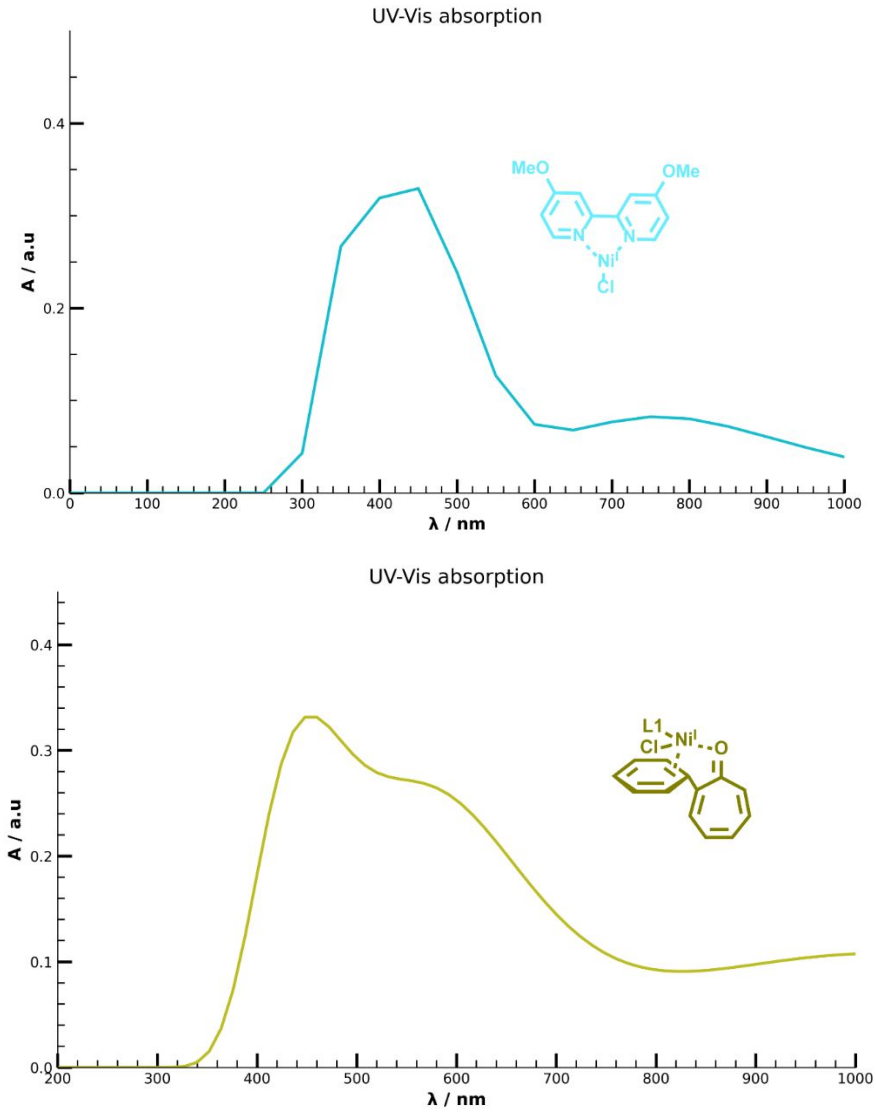


Figure S4. (top) DFT computed UV-Vis spectra of the **NiI(L1)Cl** catalyst. The peaks are at 376 and 442 nm, in very good agreement with the experimental values (365 and 440 nm), thus confirming that the reacting catalyst is a Ni(I) species. (bottom) DFT computed UV-Vis spectra of the **int-1** organonickel compound. The peaks are at 430, 572, 604 and 607 nm, in very good agreement with the experimental values (400 and 560 nm).

Ni-tropone coordination mechanism

Due to Ni(I) association with single electron mechanisms, we decided to calculate the relative radical process using Marcus Theory[7] for the estimation of the activation energy, ΔG^{++}. We first performed a geometry optimization and frequency calculation of the neutral tropone **1a** and the neutral catalyst, **Ni(L1)Cl**, while saving the solvent environment using the non-equilibrium solvent cage implemented in Gausian09. The sum of the corresponding free energies is represented as point **1** (reactants) in the Potential Energy curve of Figure

S5. Next, we performed the same type of calculations for the cationic catalyst and the anionic tropone, after the transfer of one electron, corresponding to point **2** (products) in the energy diagram. Point **3** corresponds to single point calculations of the products in the reactants' geometry and solvent cage, while point **4** corresponds to single point calculations of the reactants in the products' geometry and solvent cage. The ΔG^{++} is then calculated by the formula presented in Figure S5. Due to the high activation energy of 30.9 kcal/mol, this path is not competitive, and the SET mechanism was ruled out.

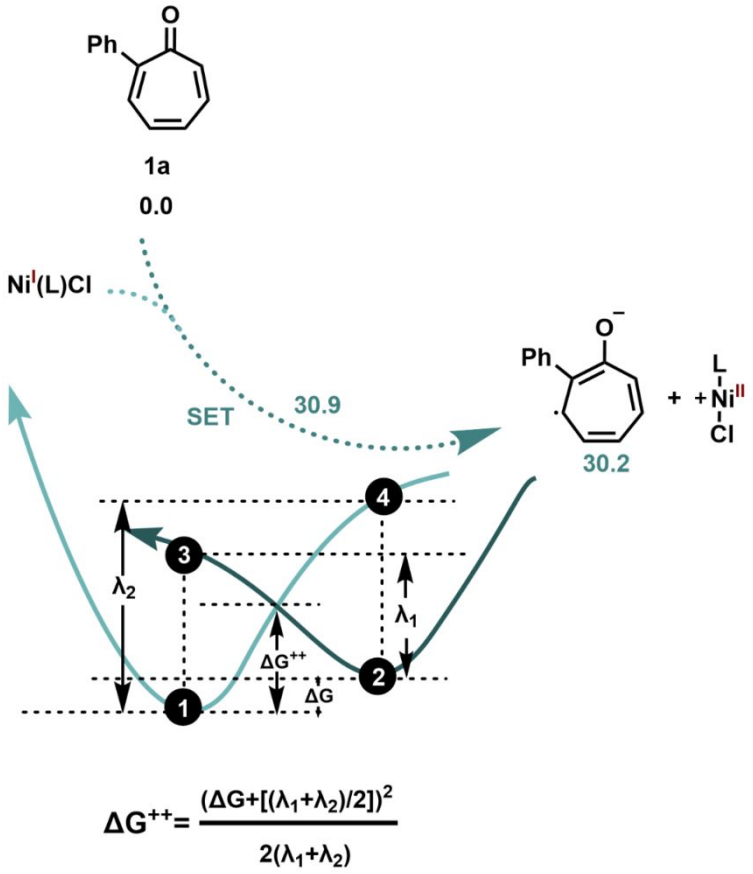


Figure S5. (top) Relative Gibbs Free Energies differences (kcal/mol) of Ni coordination on the tropone ring. The η^2 coordination between the carbons ε and ζ is the most stable by 3.5 kcal/mol relative to the one between carbons α and β. (bottom) Alternative SET mechanism for the coordination of Ni.

As a means to further confirm the two electron process, we selected four points along the scan coordinate and we conducted wavefunction stability calculations to rule out any involvement of a singlet state, that would imply a d^6-Ni(II) species. As expected, the wavefunctions were stable along the scan coordinate, confirming once again the proposed path.

Cross-electrophile coupling step

In order to shed light on the cross-coupling, C-C bond formation step, we calculated the Electrostatic Potential Surface (ESP) map, using the wavefunction generated by Gaussian 09 and the ESP analysis[8] algorithm as implemented in the MultiWfn code[9] and the relevant NBO charges of the aldehyde and tropone scaffolds (Figure S6).[10]

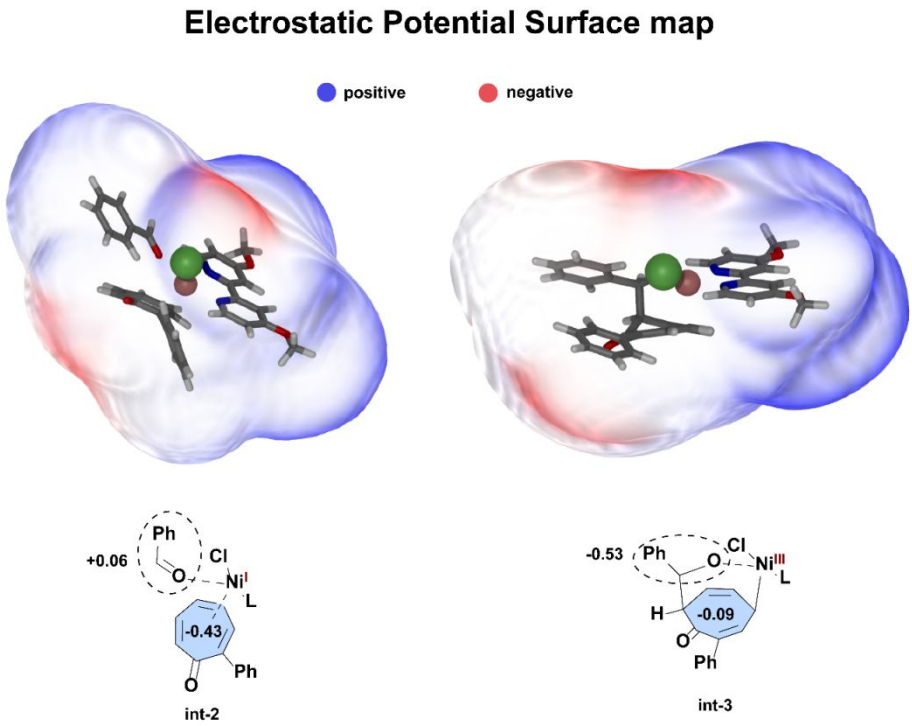
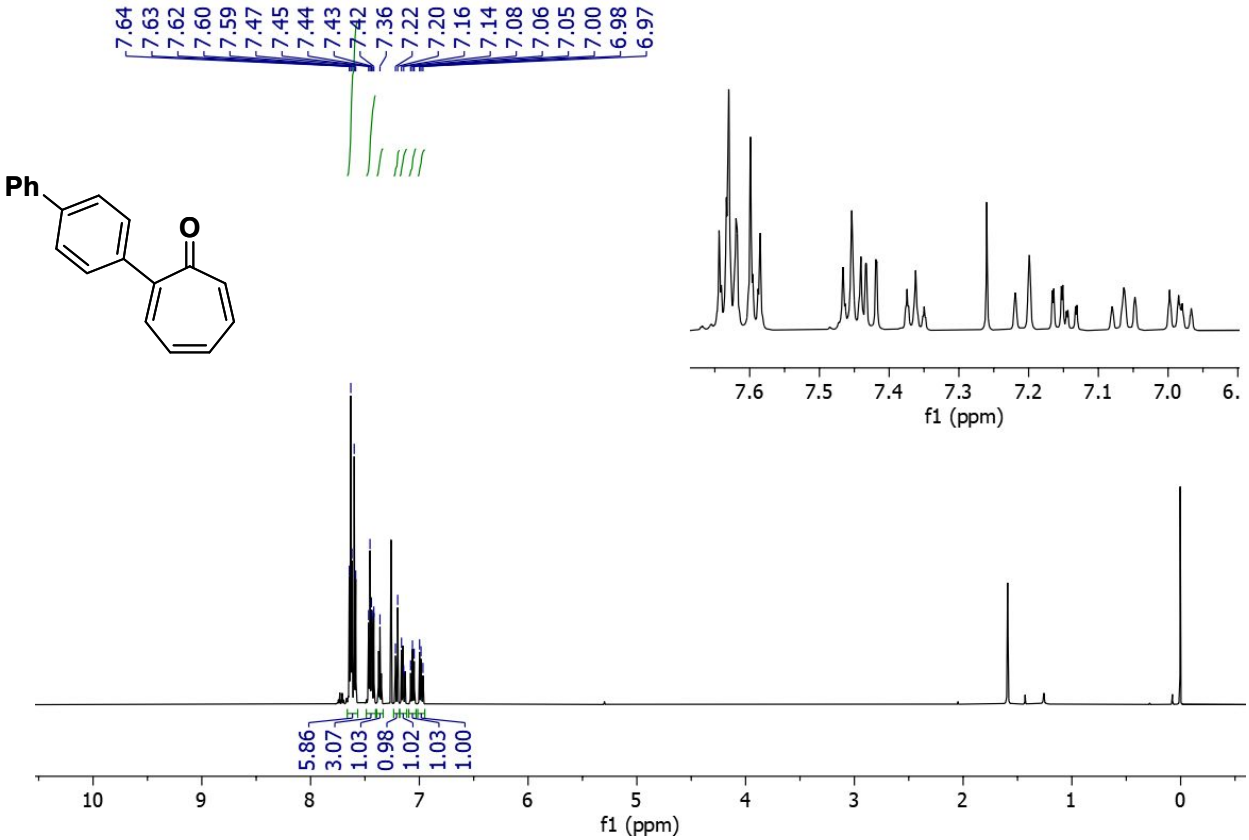


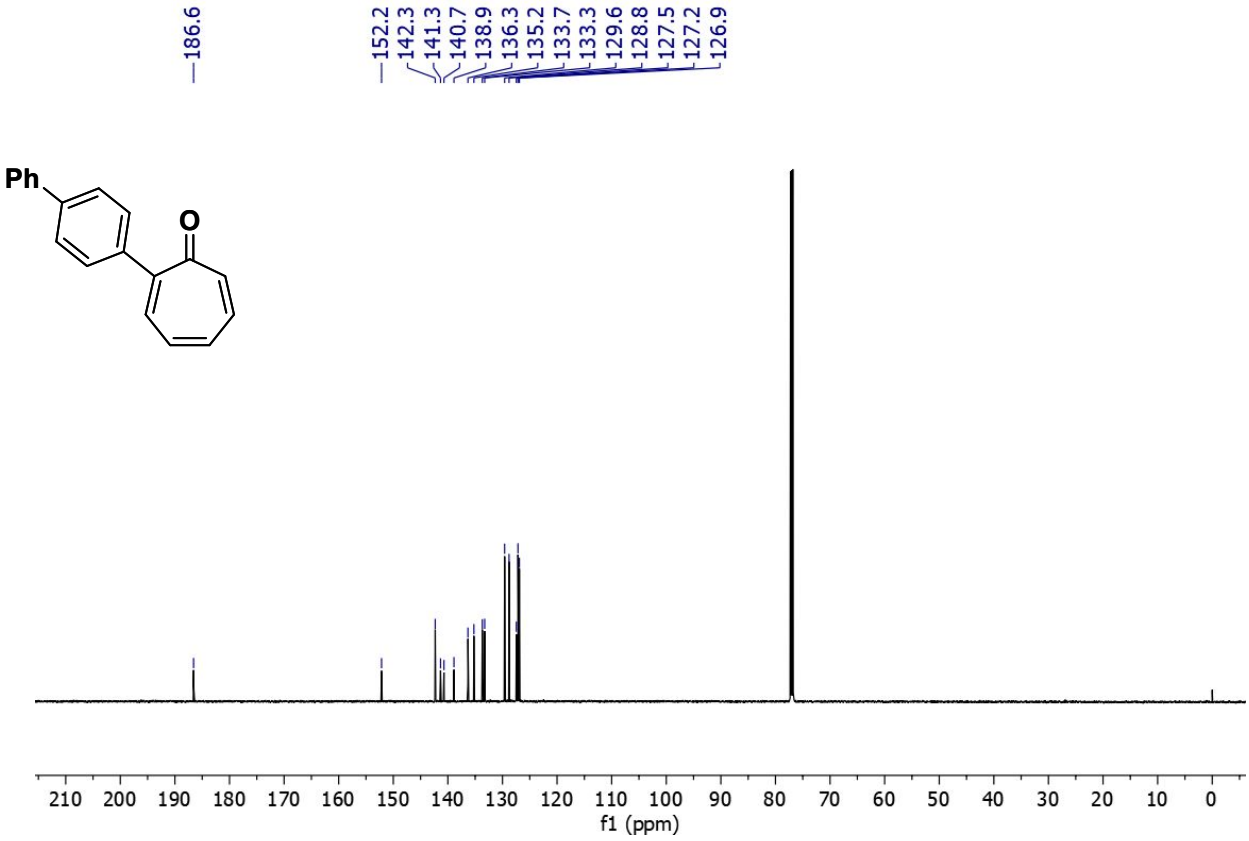
Figure S6. Electrostatic potential surface map (top) and NBO charges for the aldehyde and the tropone moieties (bottom).

6. ^{1}H-, and ^{13}C-NMR spectra of new compounds

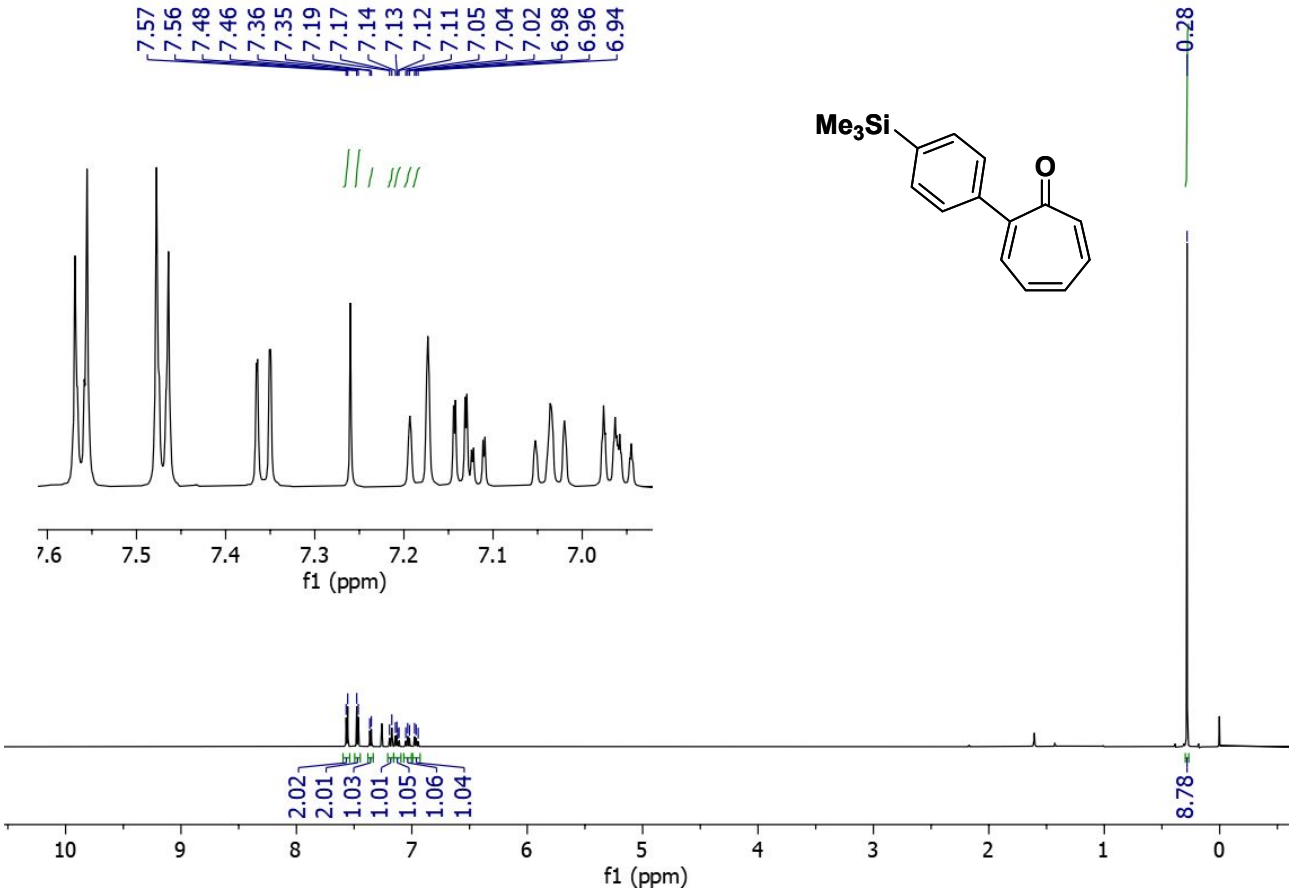
1b ^{1}H NMR (600 MHz, $CDCl_3$)



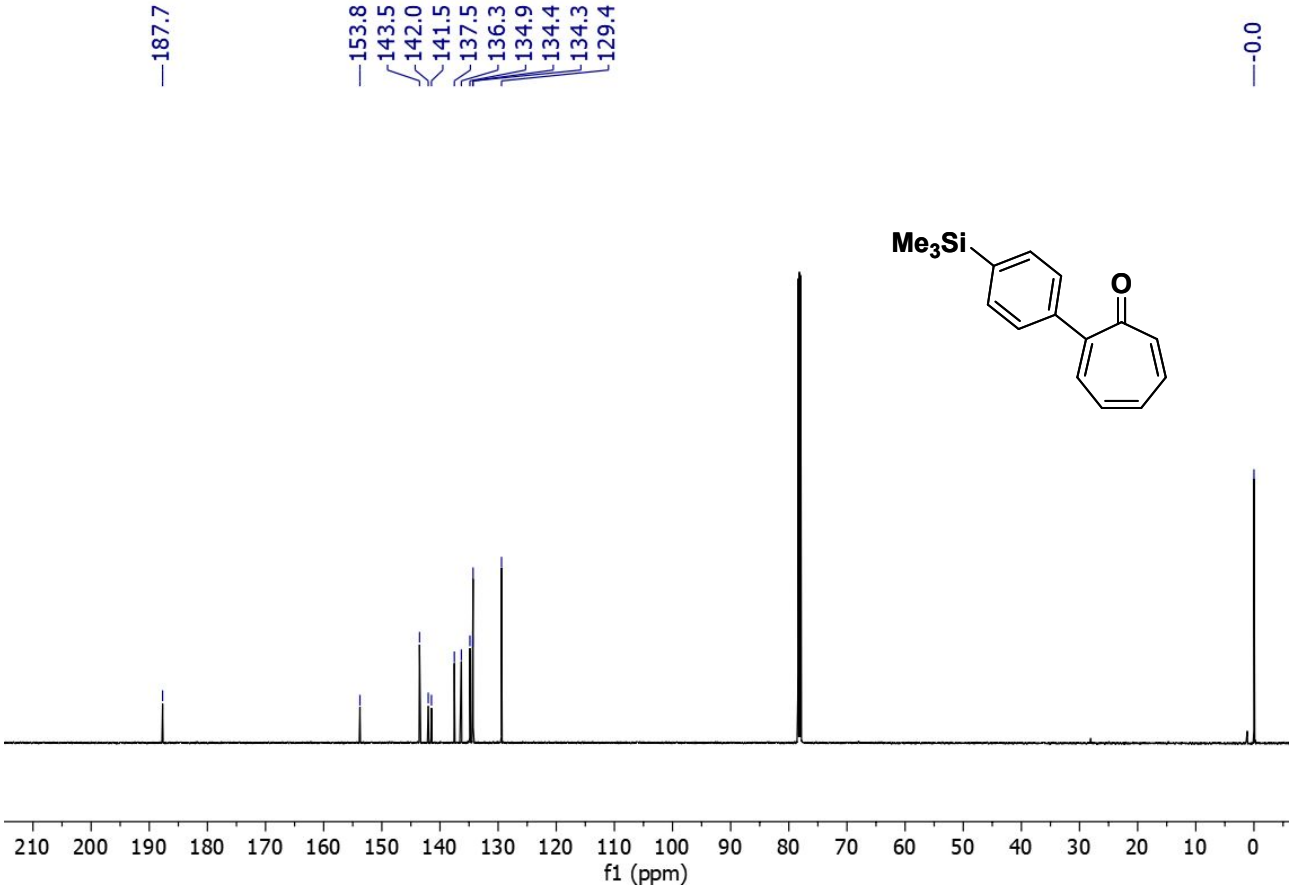
1b ^{13}C NMR (150 MHz, $CDCl_3$)



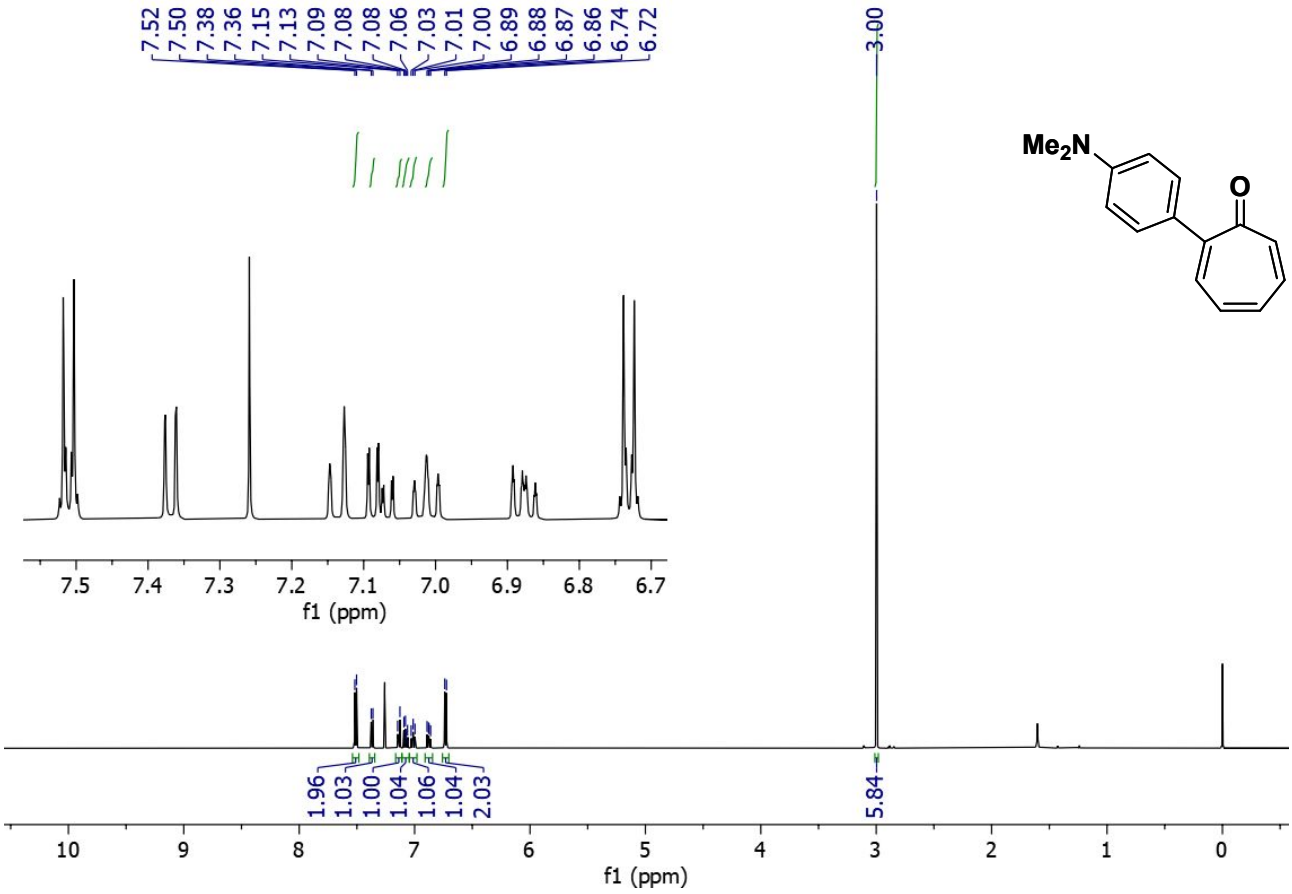
1f ^{1}H NMR (600 MHz, $CDCl_3$)



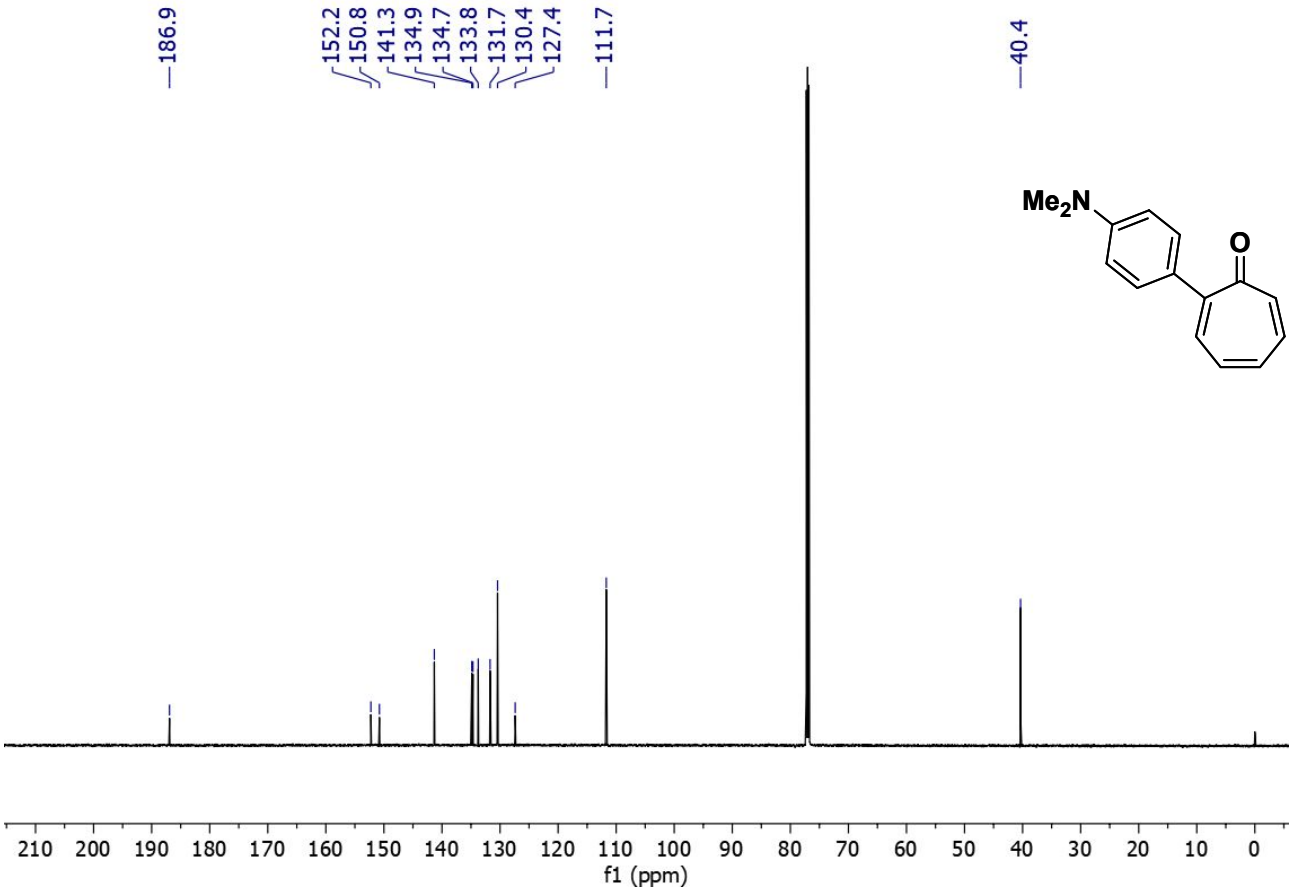
1f ^{13}C NMR (150 MHz, $CDCl_3$)



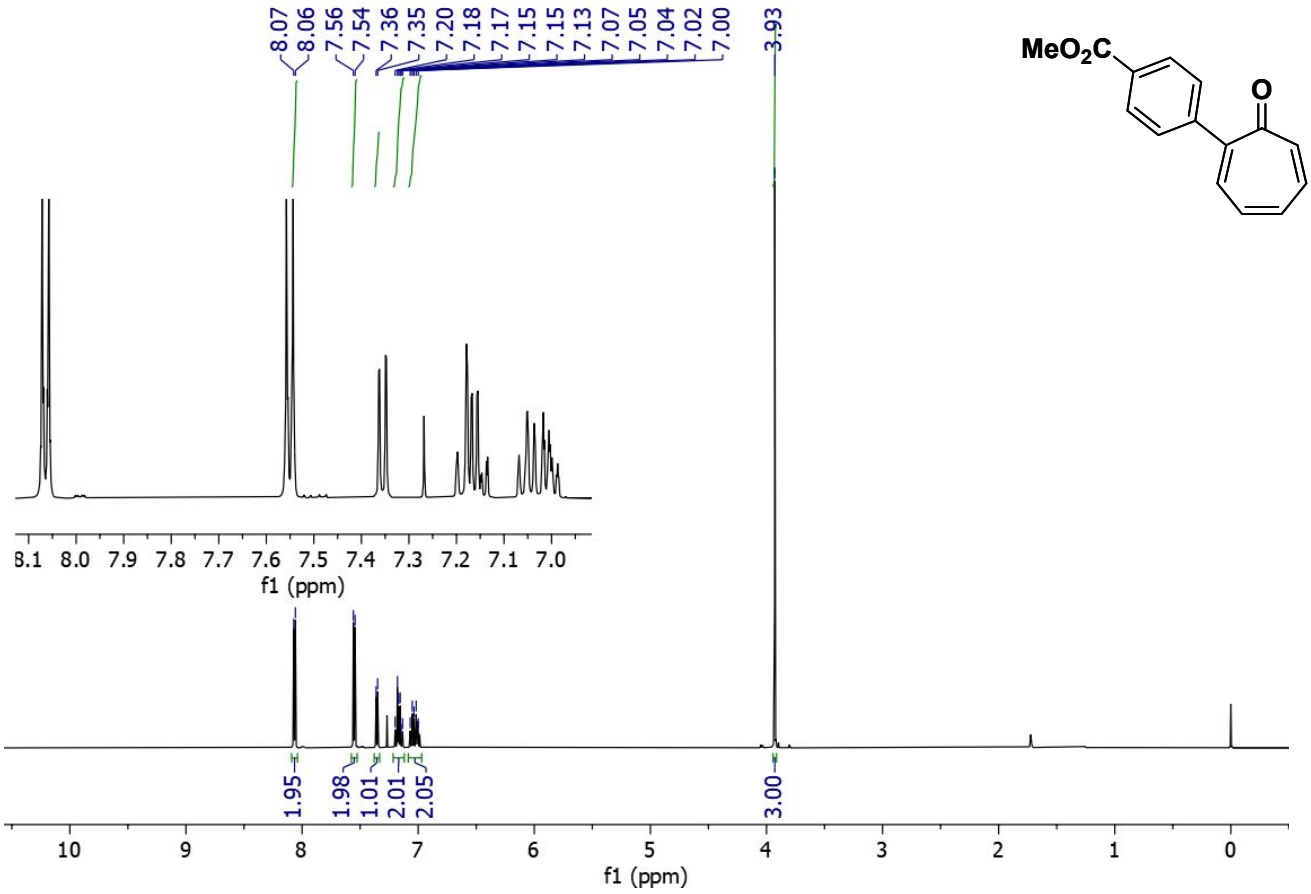
1g ^{1}H NMR (600 MHz, $CDCl_3$)



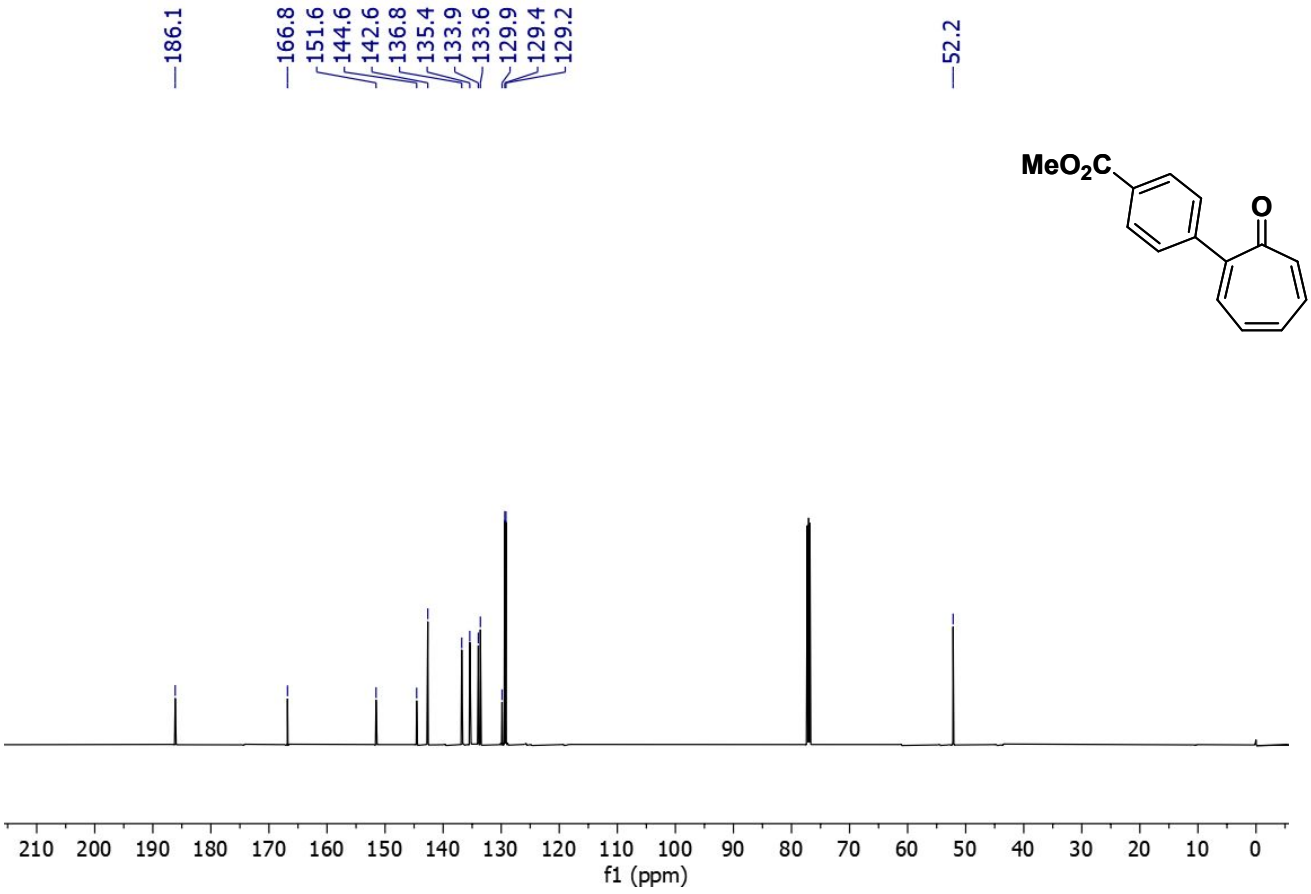
1g ^{13}C NMR (150 MHz, $CDCl_3$)



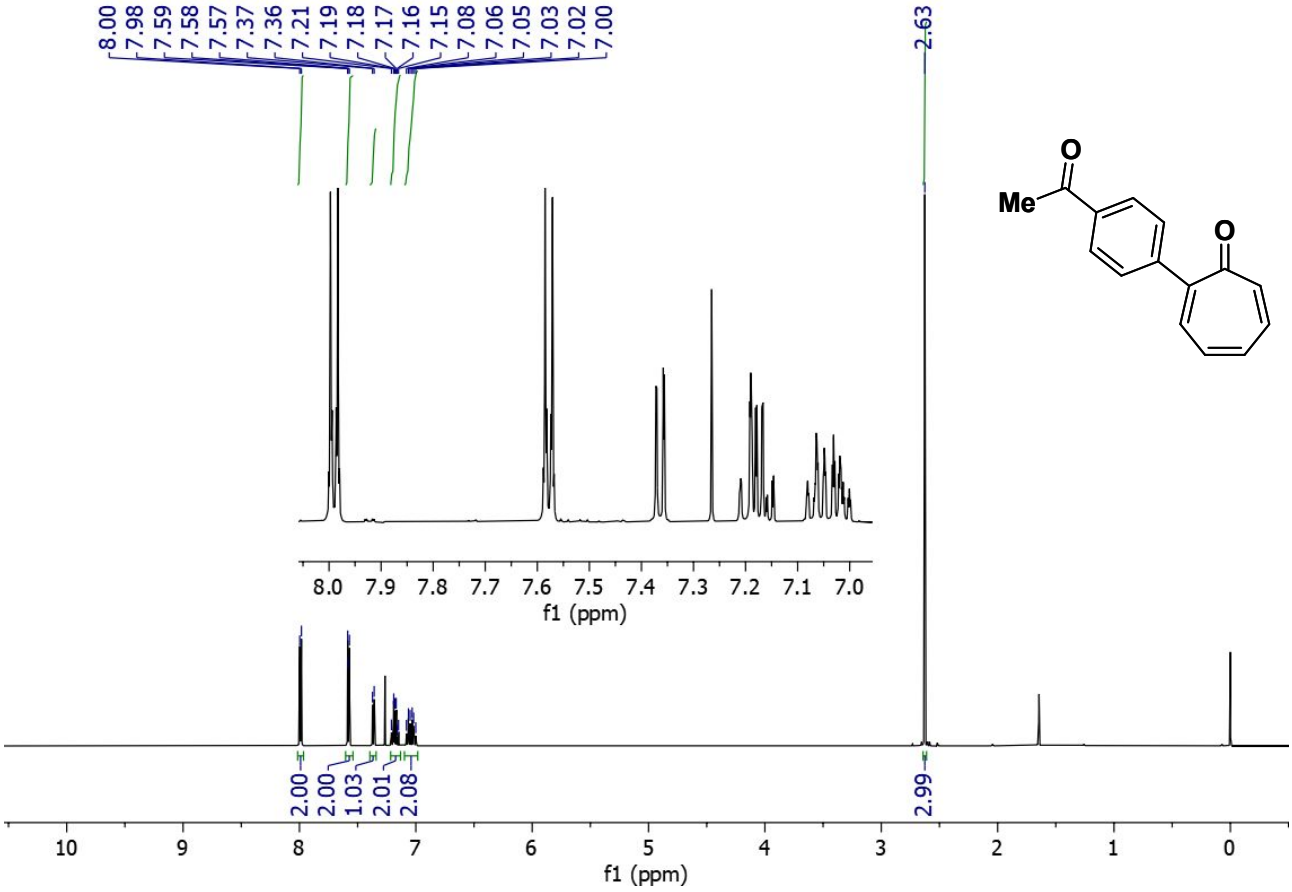
1m ^{1}H NMR (600 MHz, $CDCl_3$)



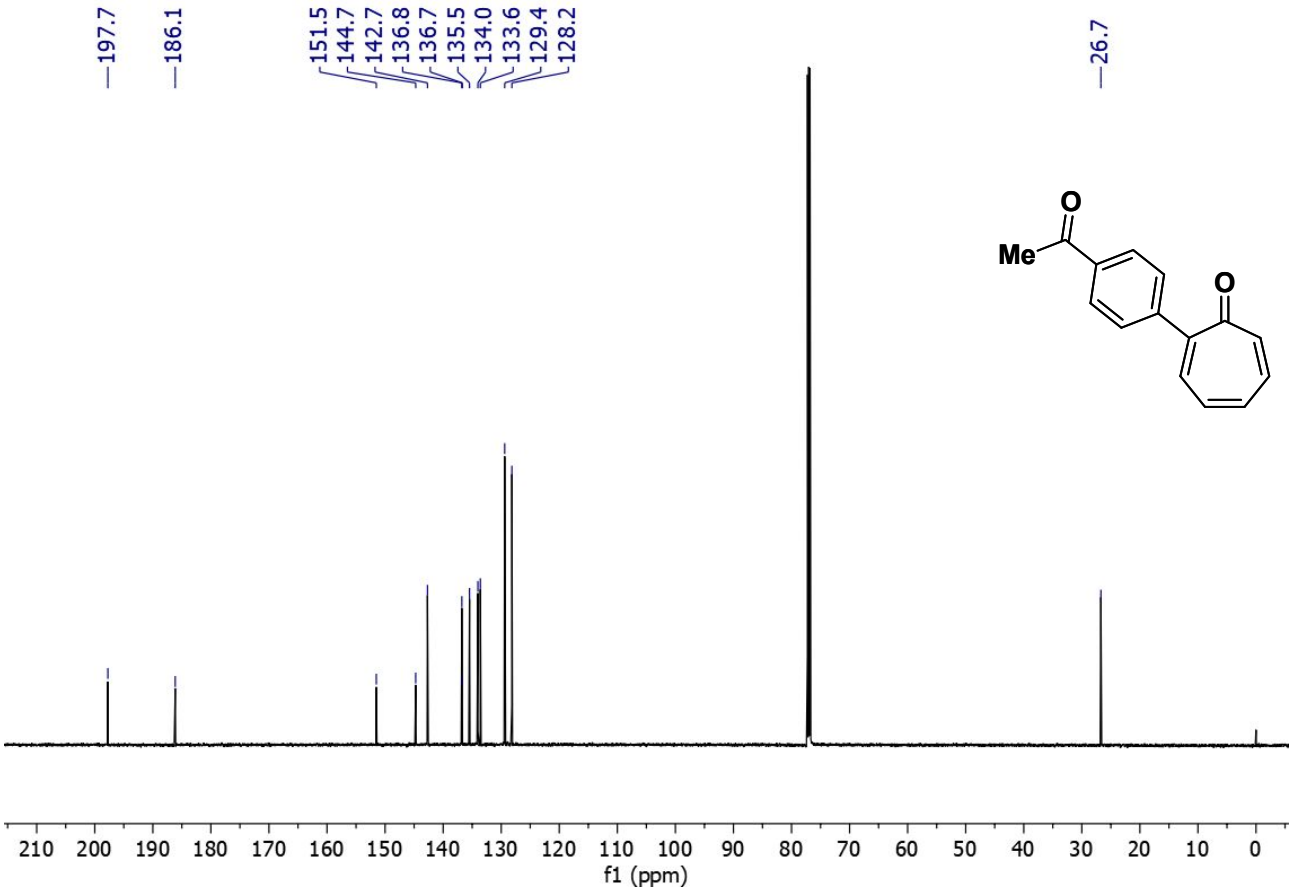
1m ^{13}C NMR (150 MHz, $CDCl_3$)



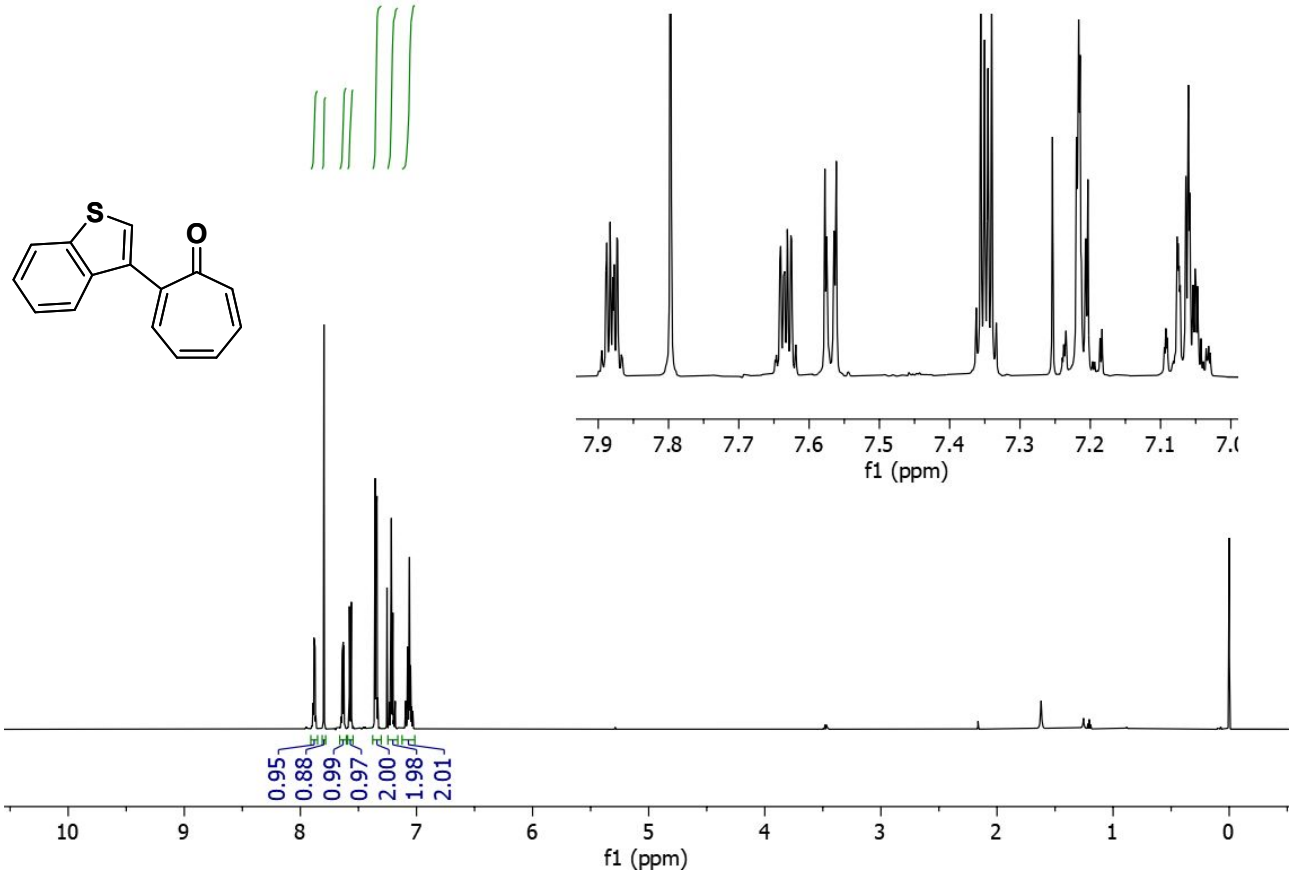
1n ^{1}H NMR (600 MHz, $CDCl_3$)



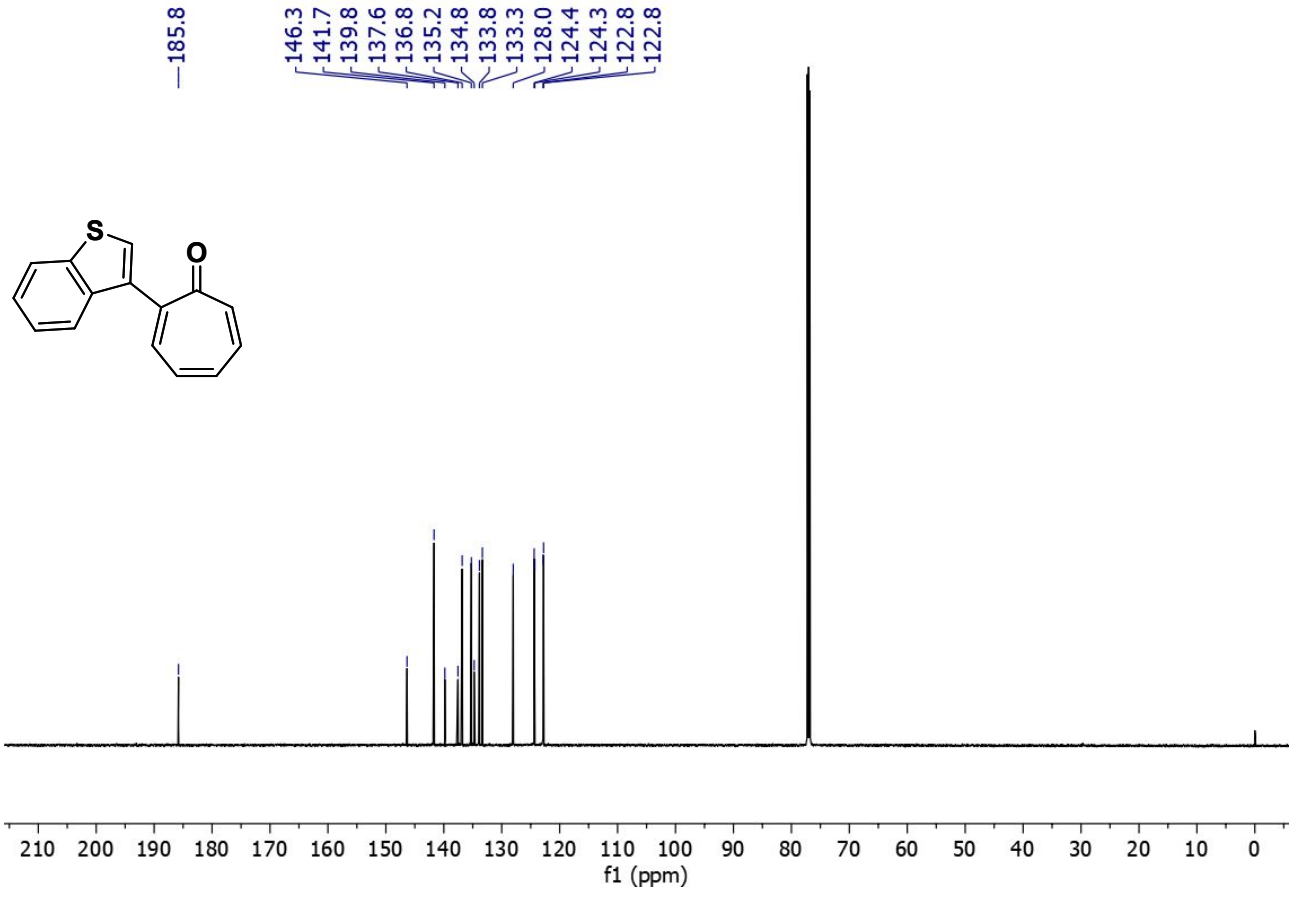
1n ^{13}C NMR (150 MHz, $CDCl_3$)



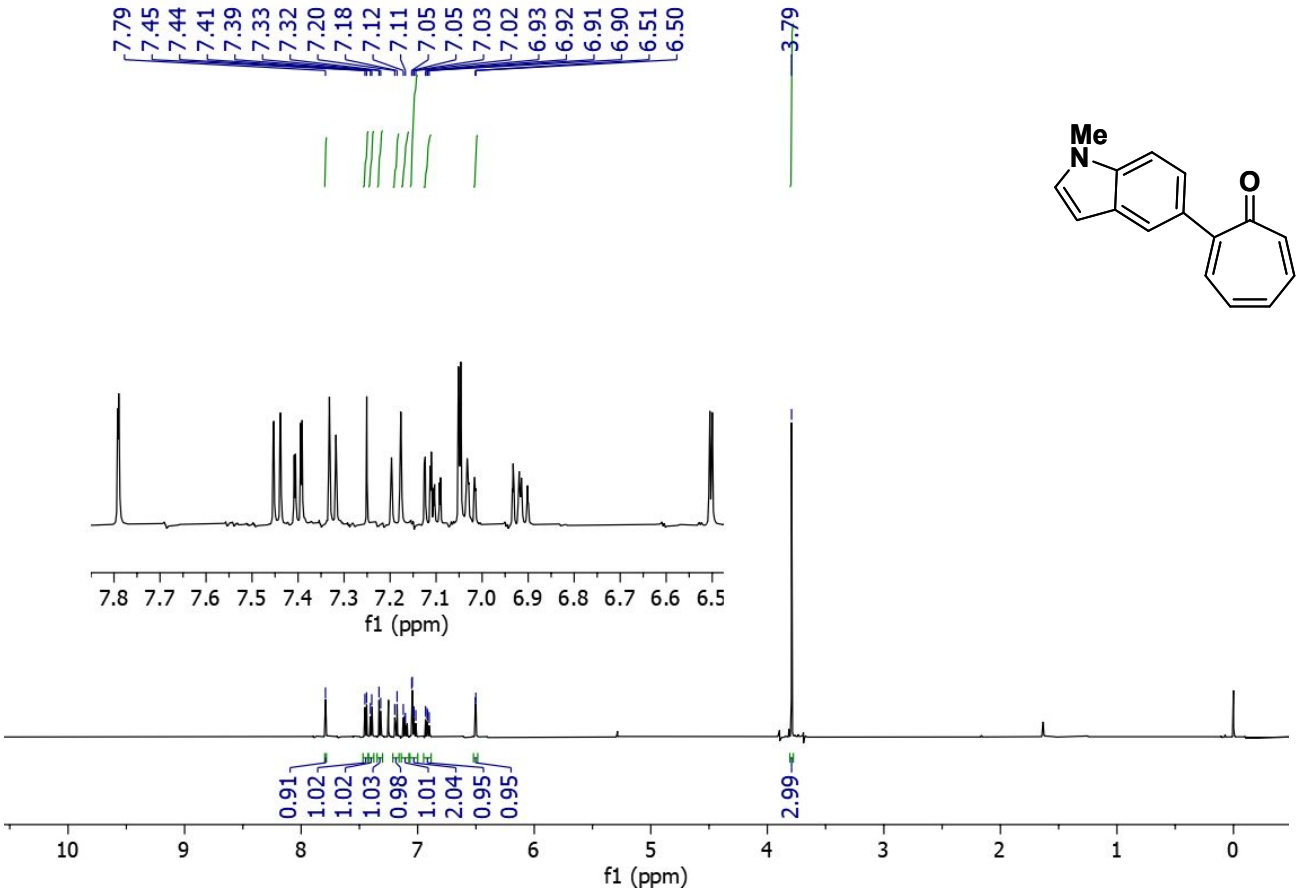
1q ^{1}H NMR (600 MHz, $CDCl_3$)



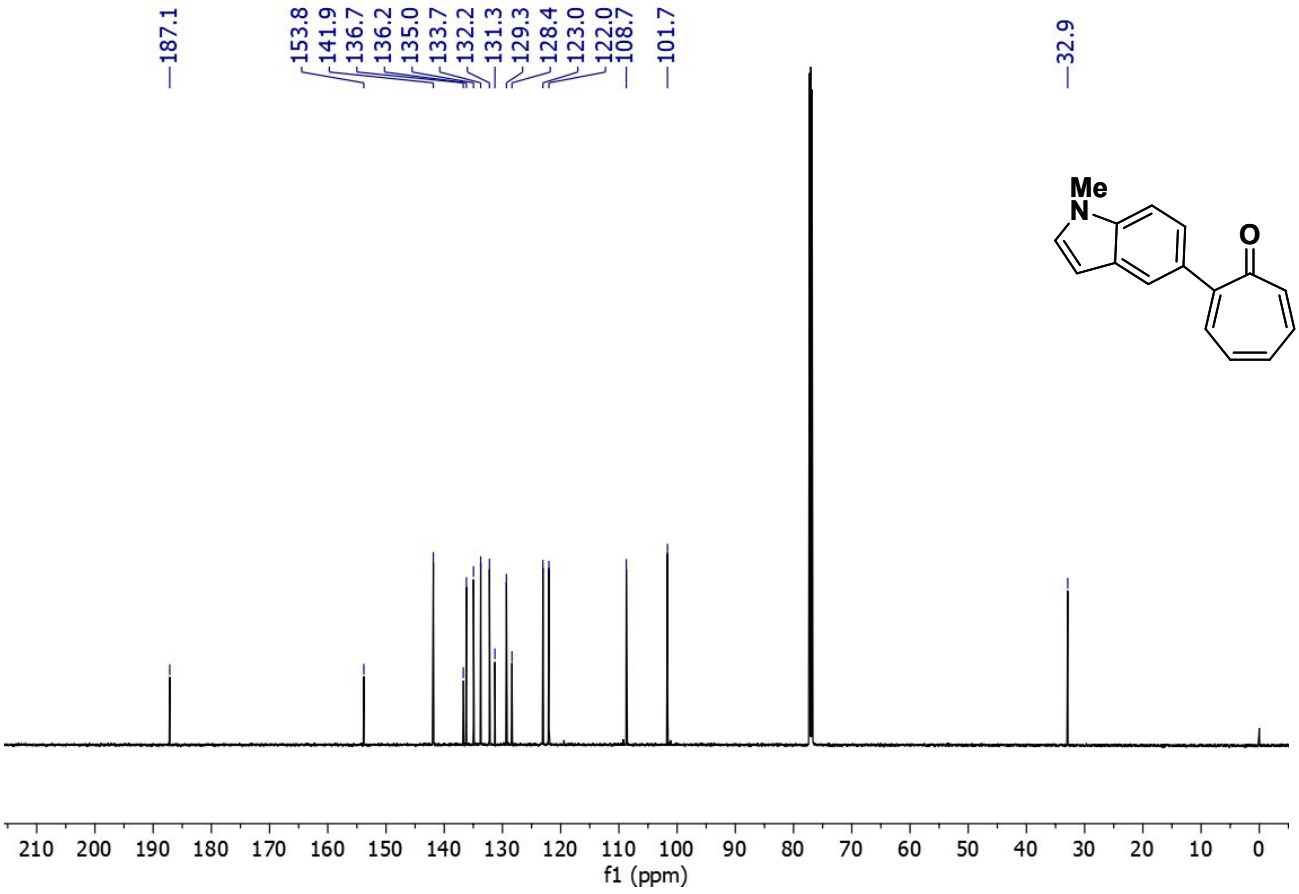
1q ^{13}C NMR (150 MHz, $CDCl_3$)



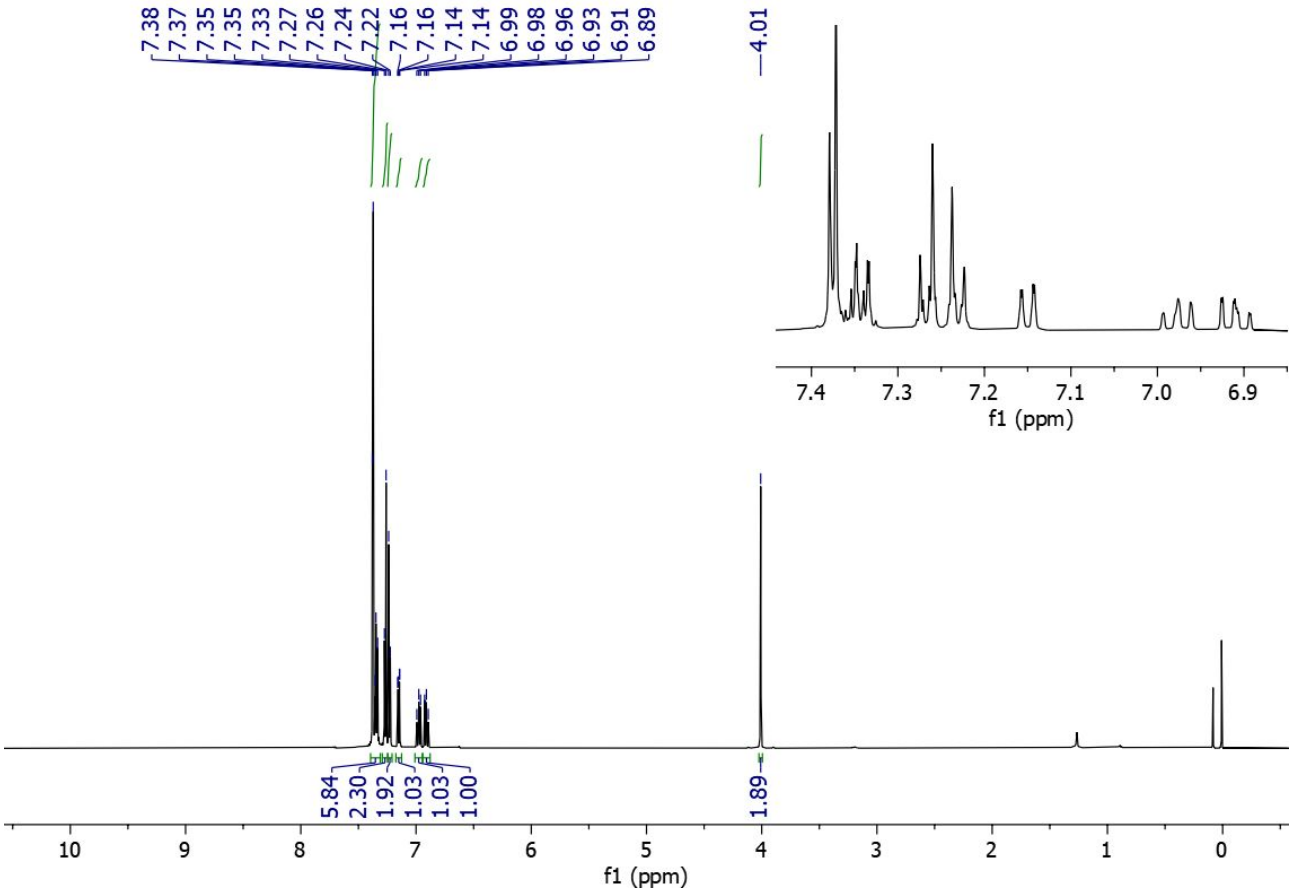
1r ^{1}H NMR (600 MHz, $CDCl_3$)



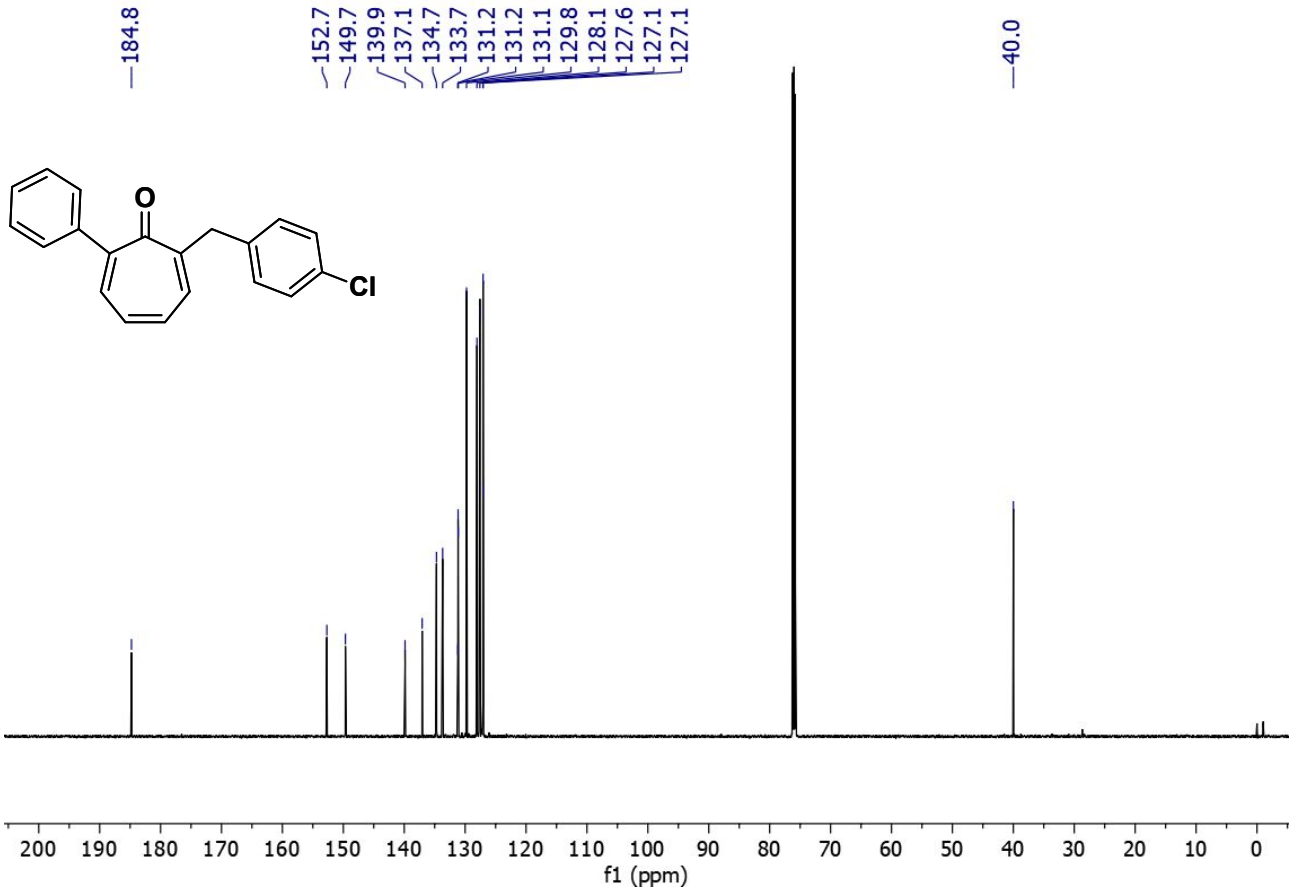
1r ^{13}C NMR (150 MHz, $CDCl_3$)



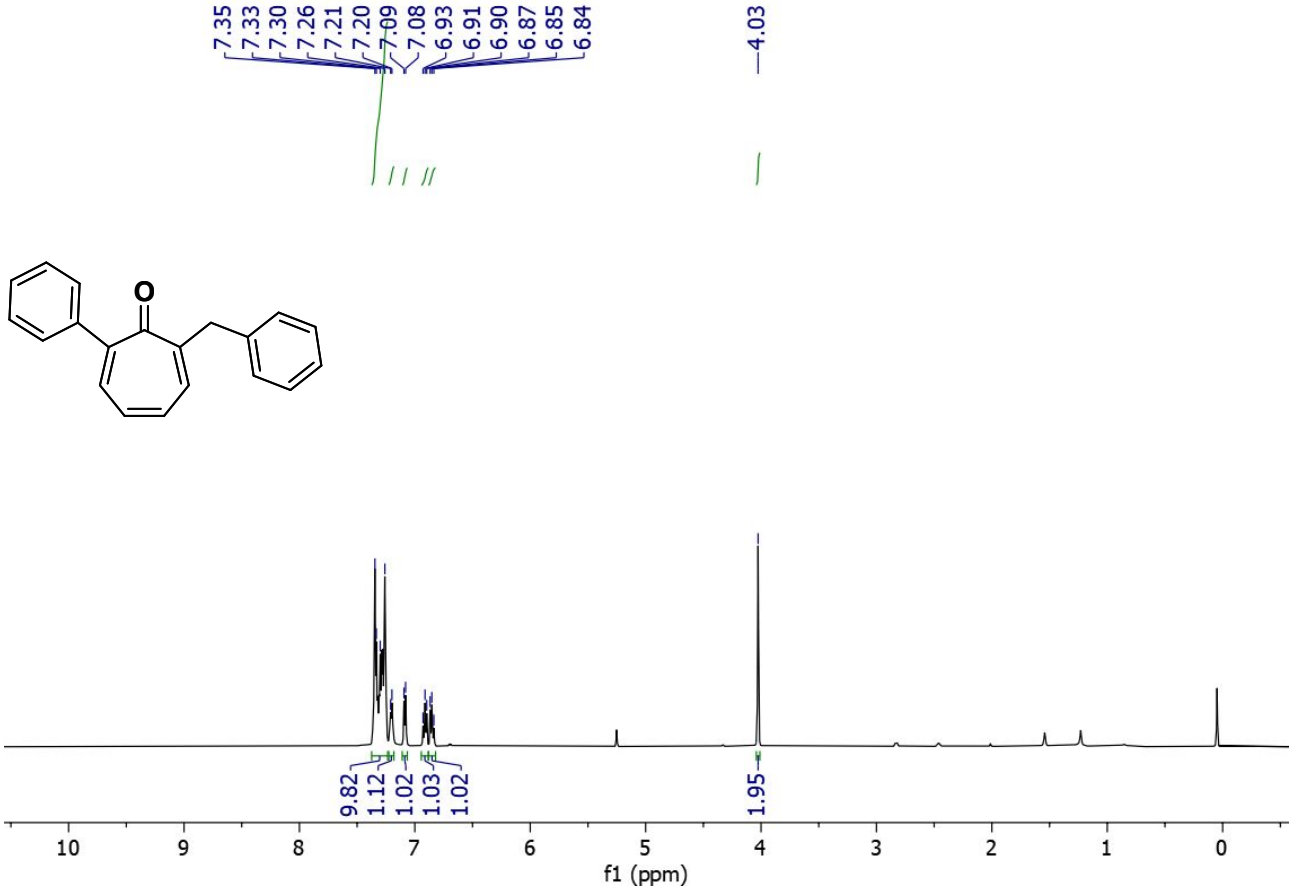
3aa ^{1}H NMR (600 MHz, $CDCl_3$)



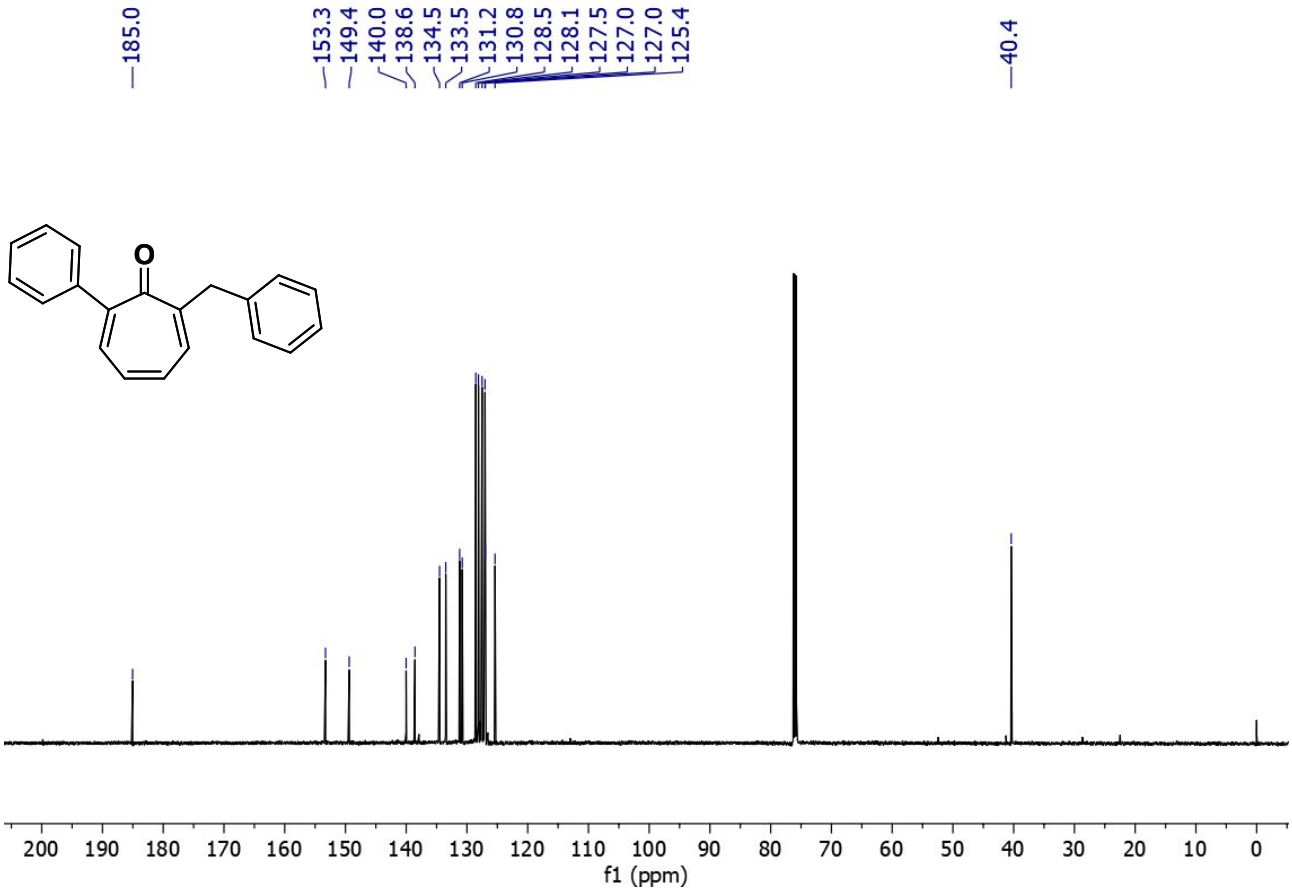
3aa ^{13}C NMR (150 MHz, $CDCl_3$)



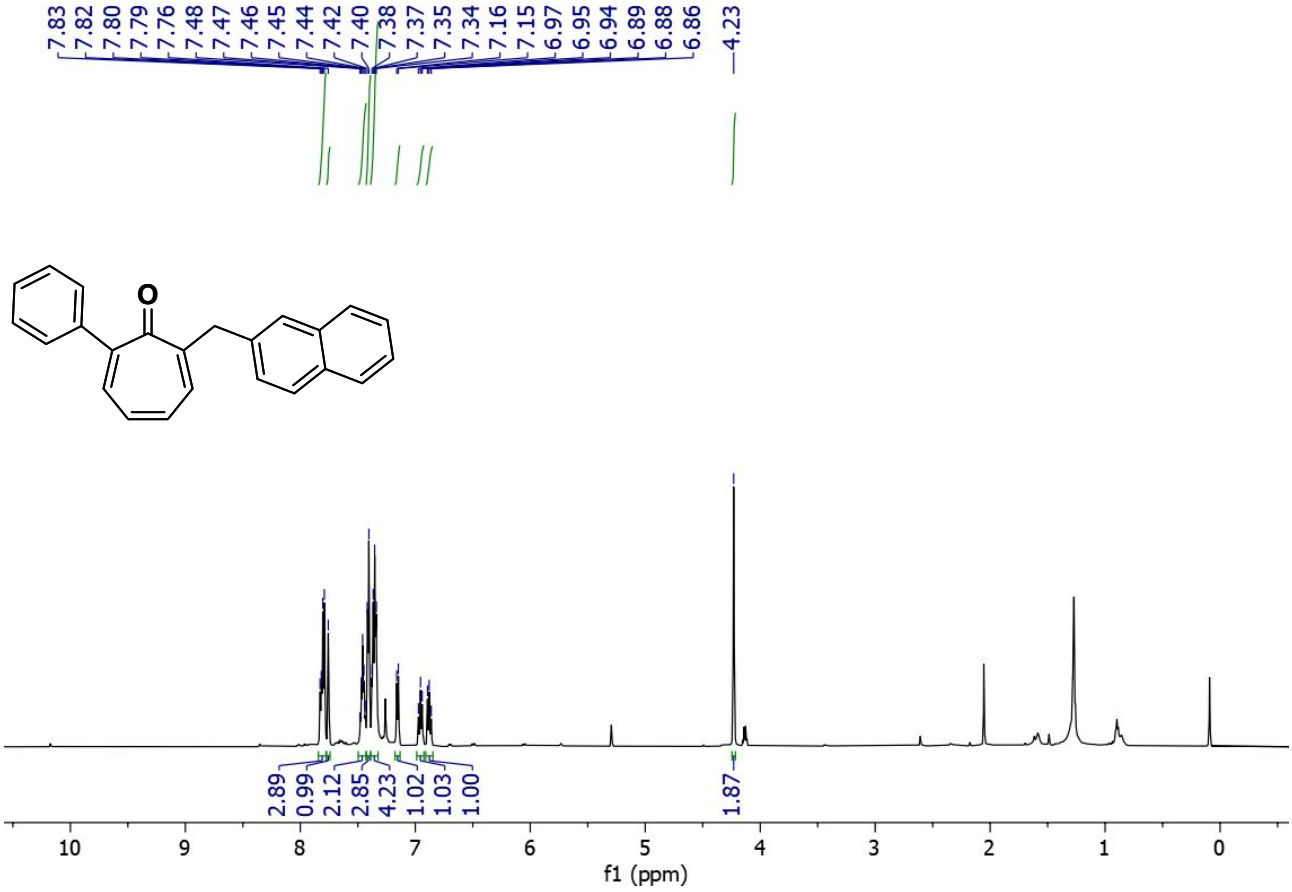
3ab ^{1}H NMR (600 MHz, $CDCl_3$)



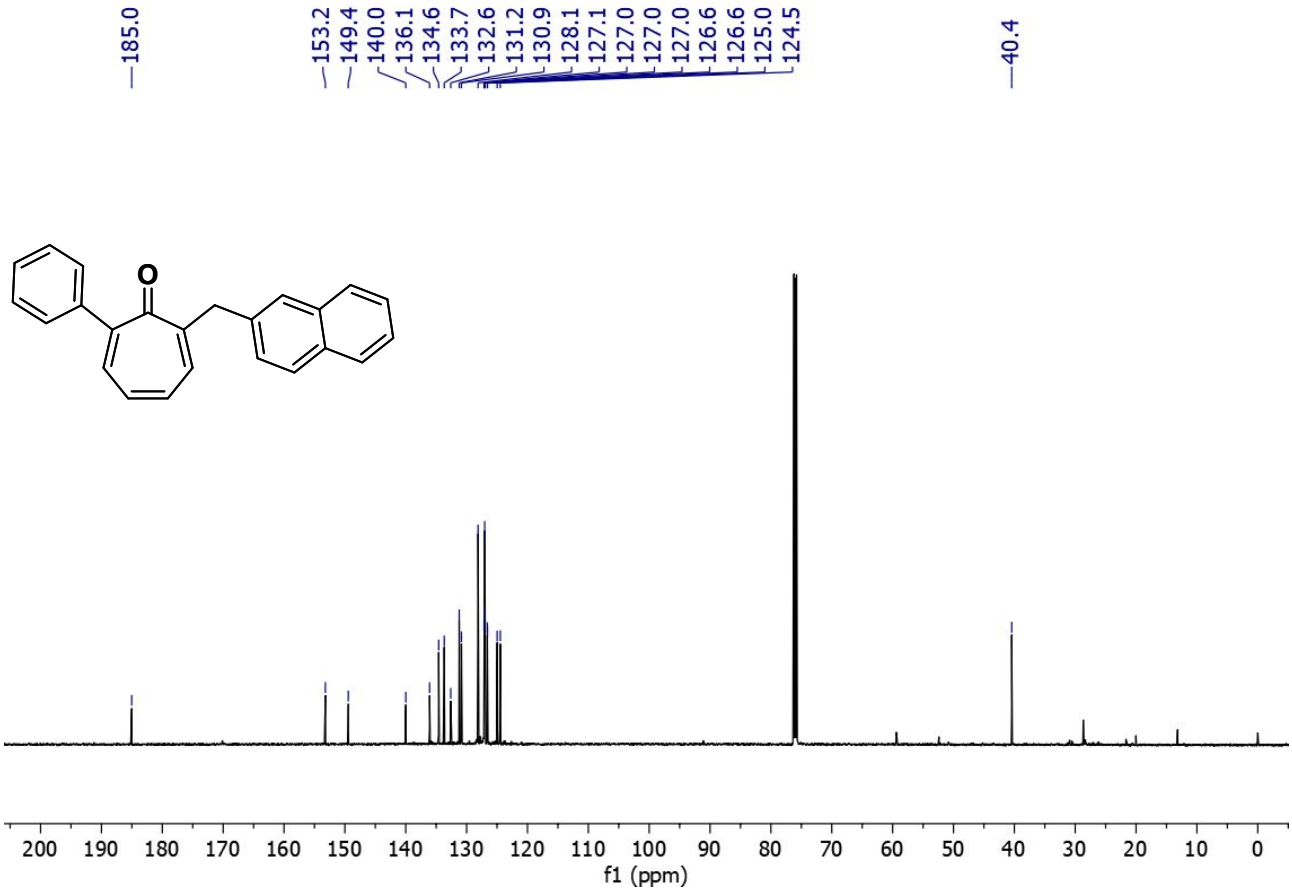
3ab ^{13}C NMR (150 MHz, $CDCl_3$)



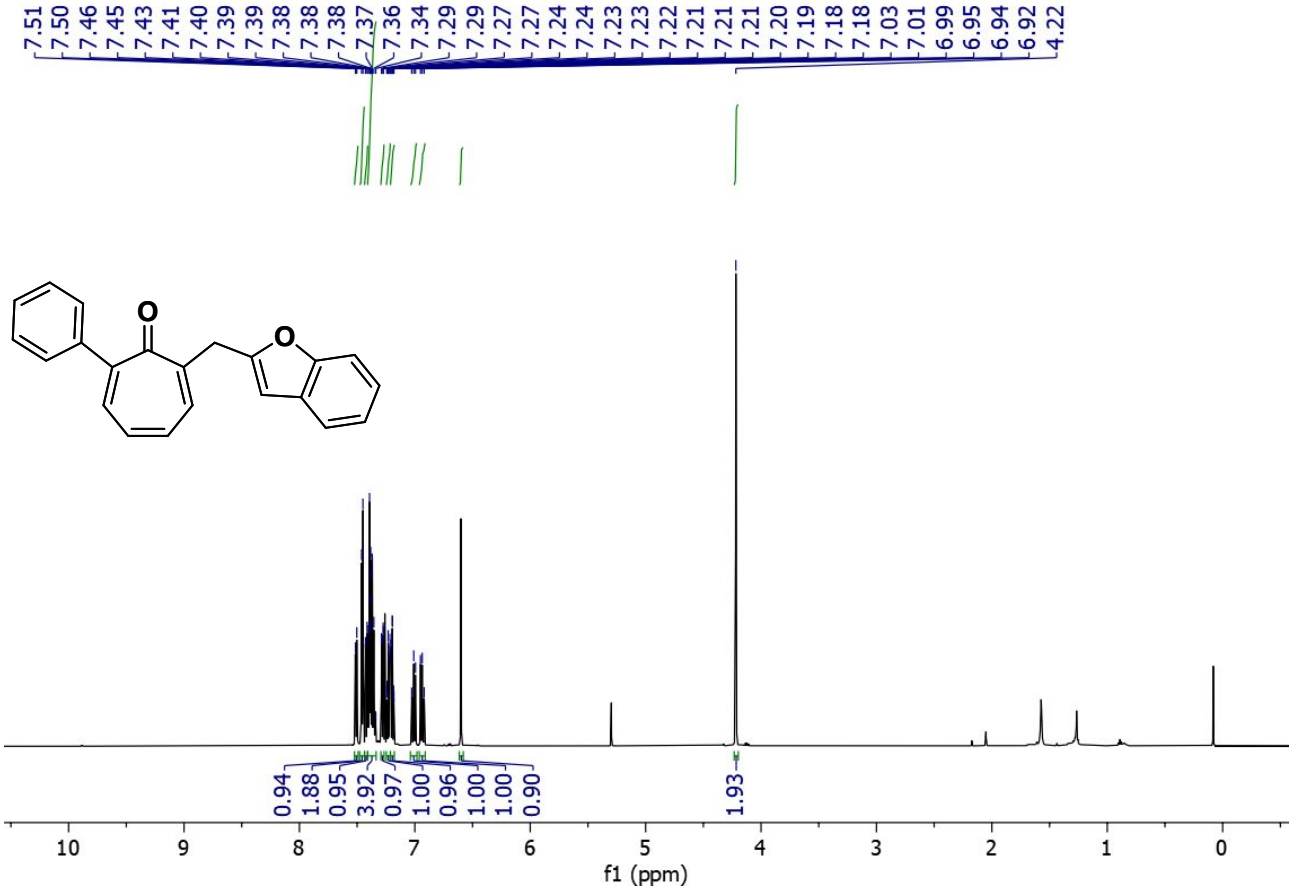
3ac ^{1}H NMR (600 MHz, $CDCl_3$)



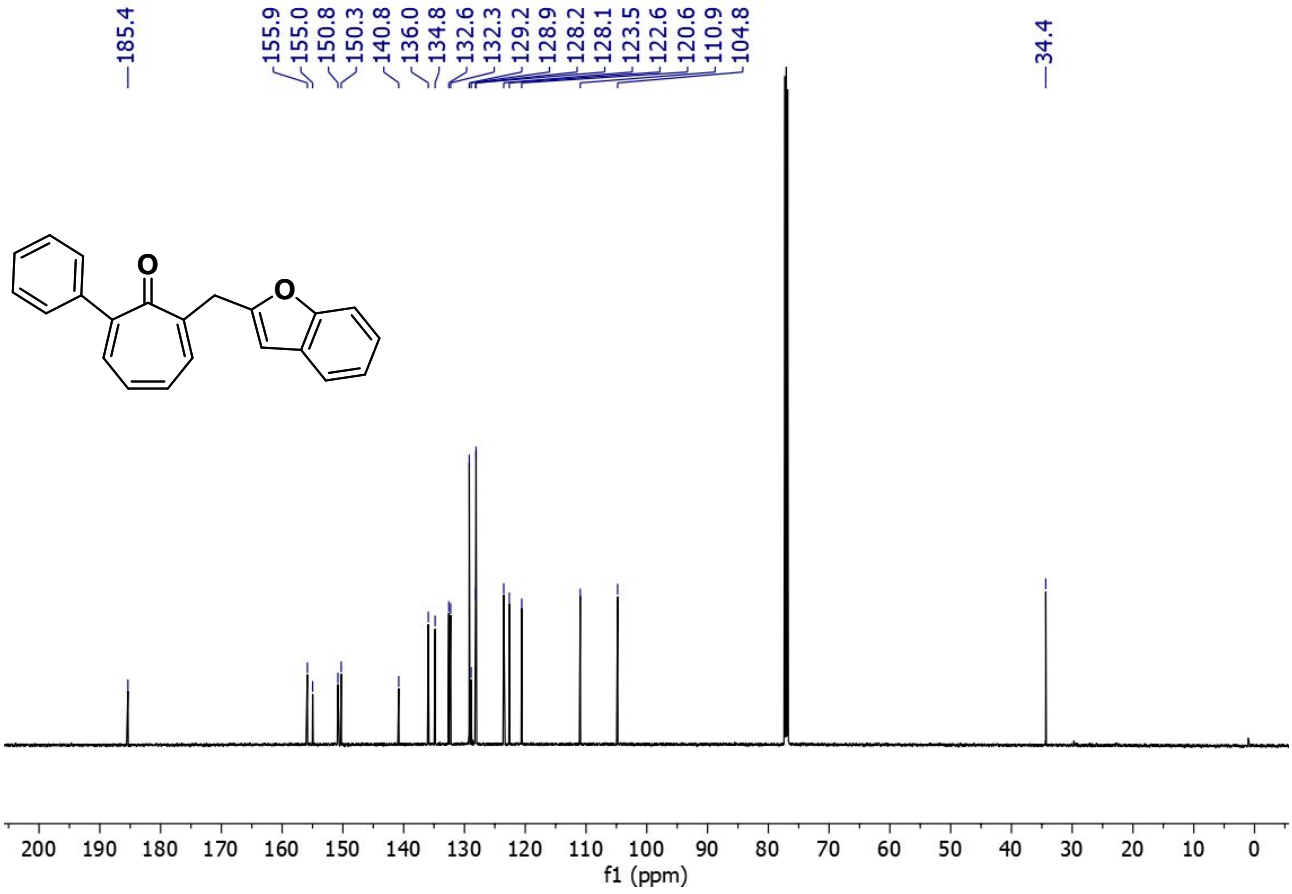
3ac ^{13}C NMR (150 MHz, $CDCl_3$)



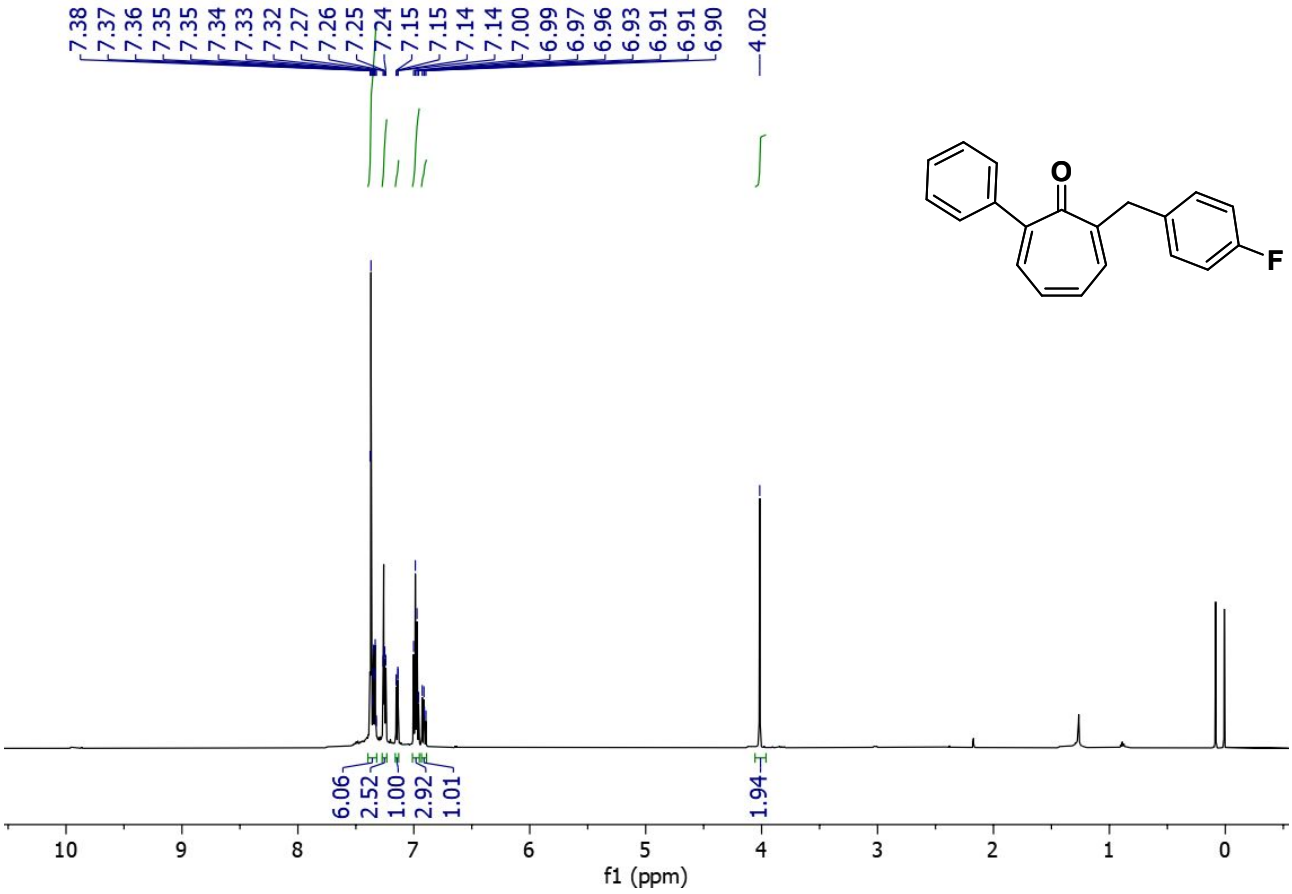
3ad ^{1}H NMR (600 MHz, $CDCl_3$)



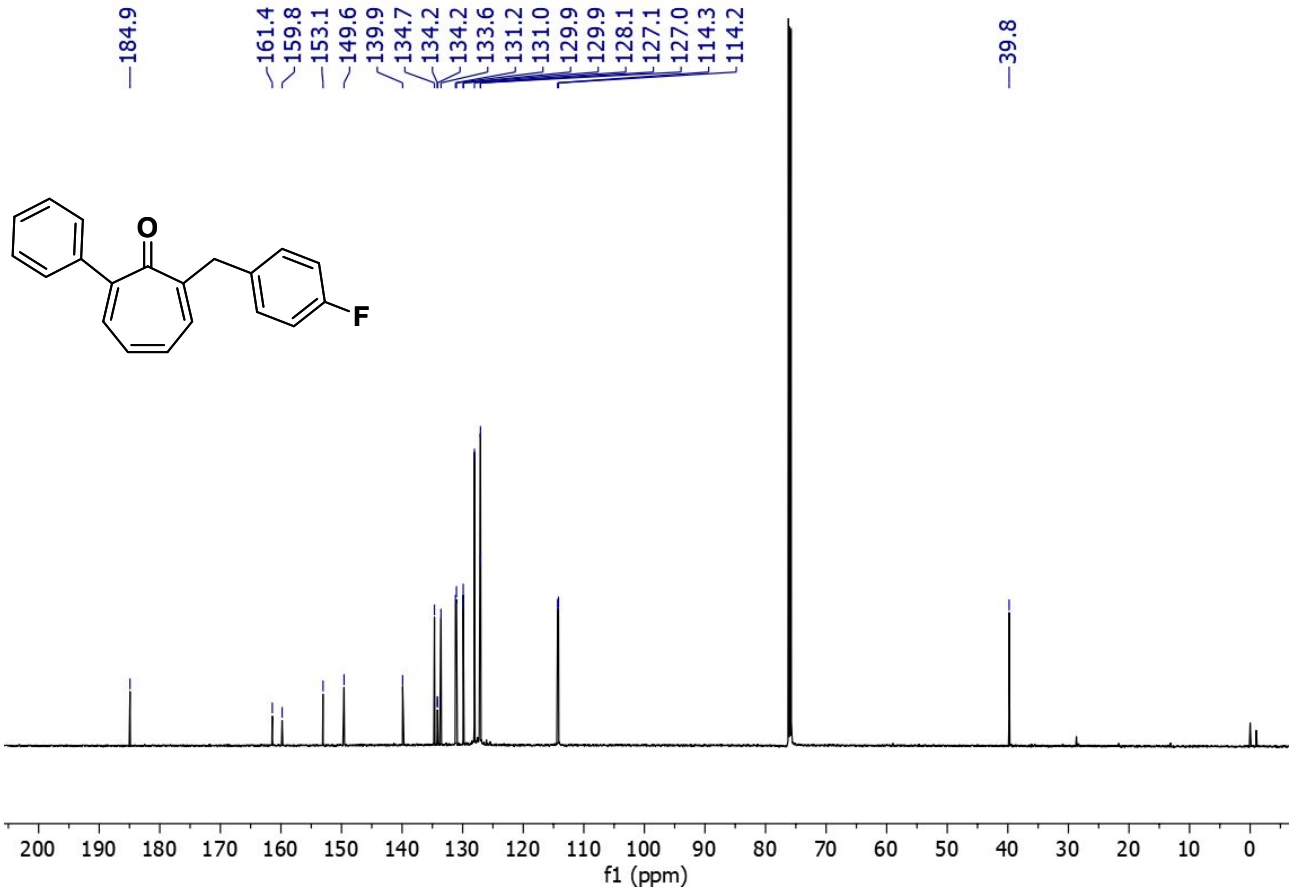
3ad ^{13}C NMR (150 MHz, $CDCl_3$)



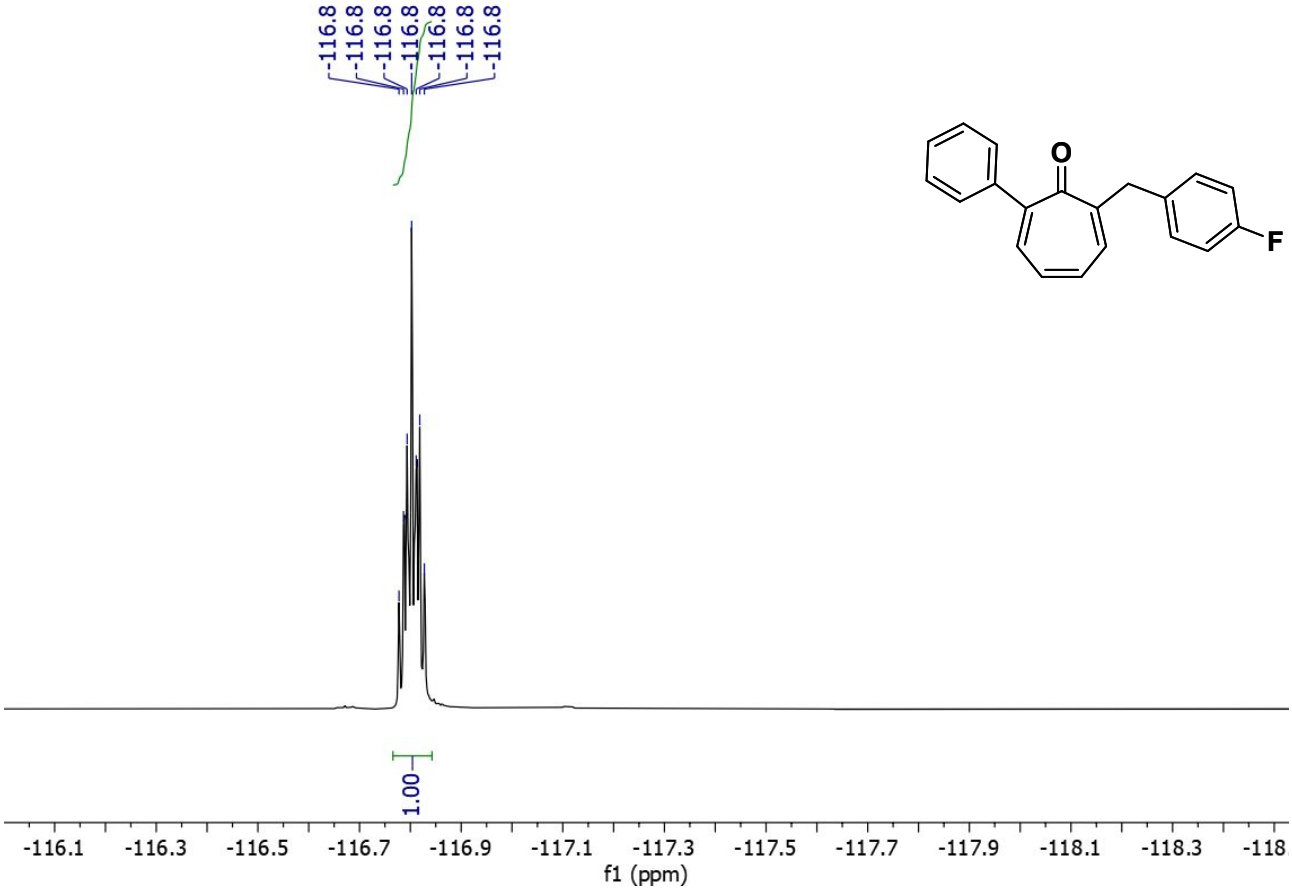
3ae ^{1}H NMR (600 MHz, $CDCl_3$)



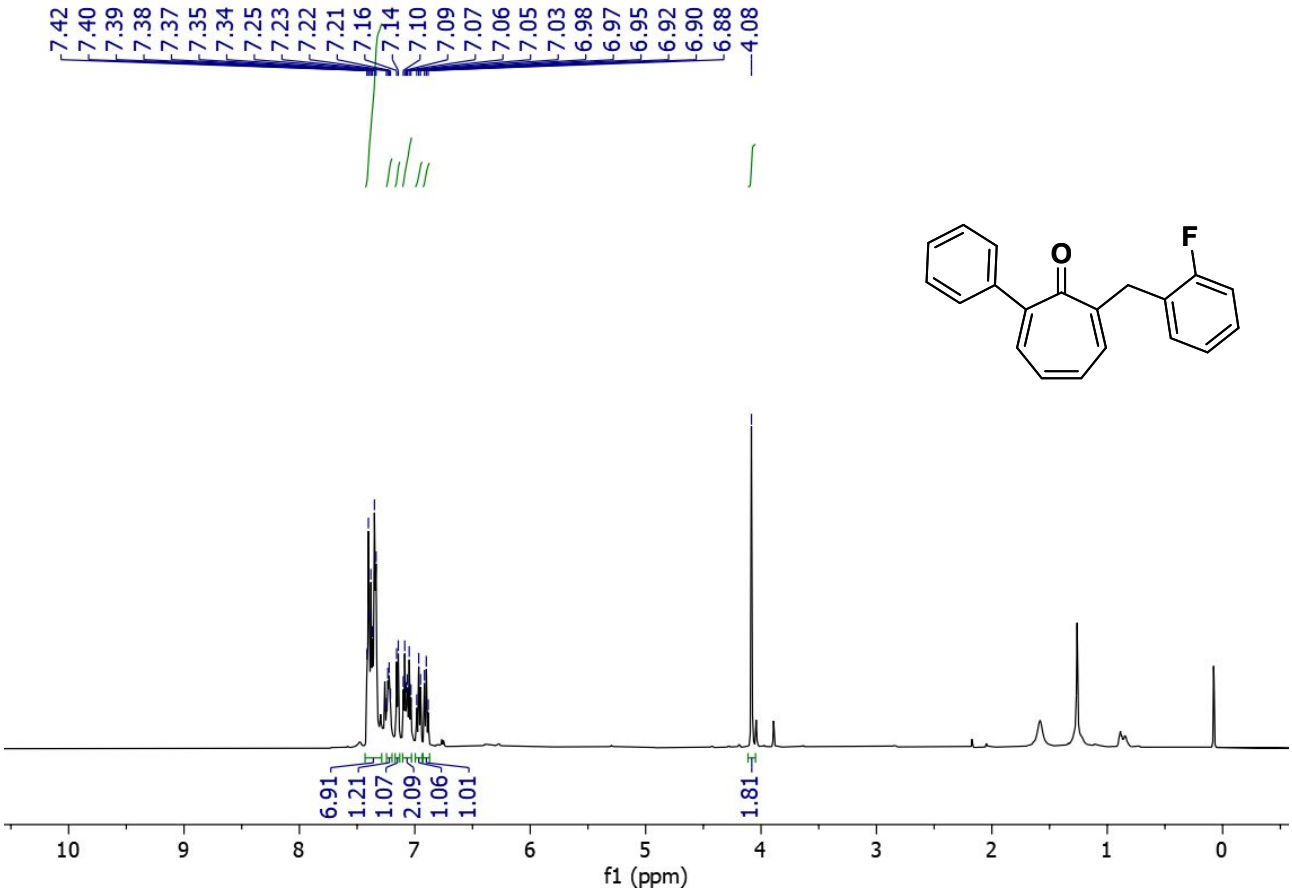
3ae ^{13}C NMR (150 MHz, $CDCl_3$)



3ae ^{19}F NMR (565 MHz, $CDCl_3$)



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



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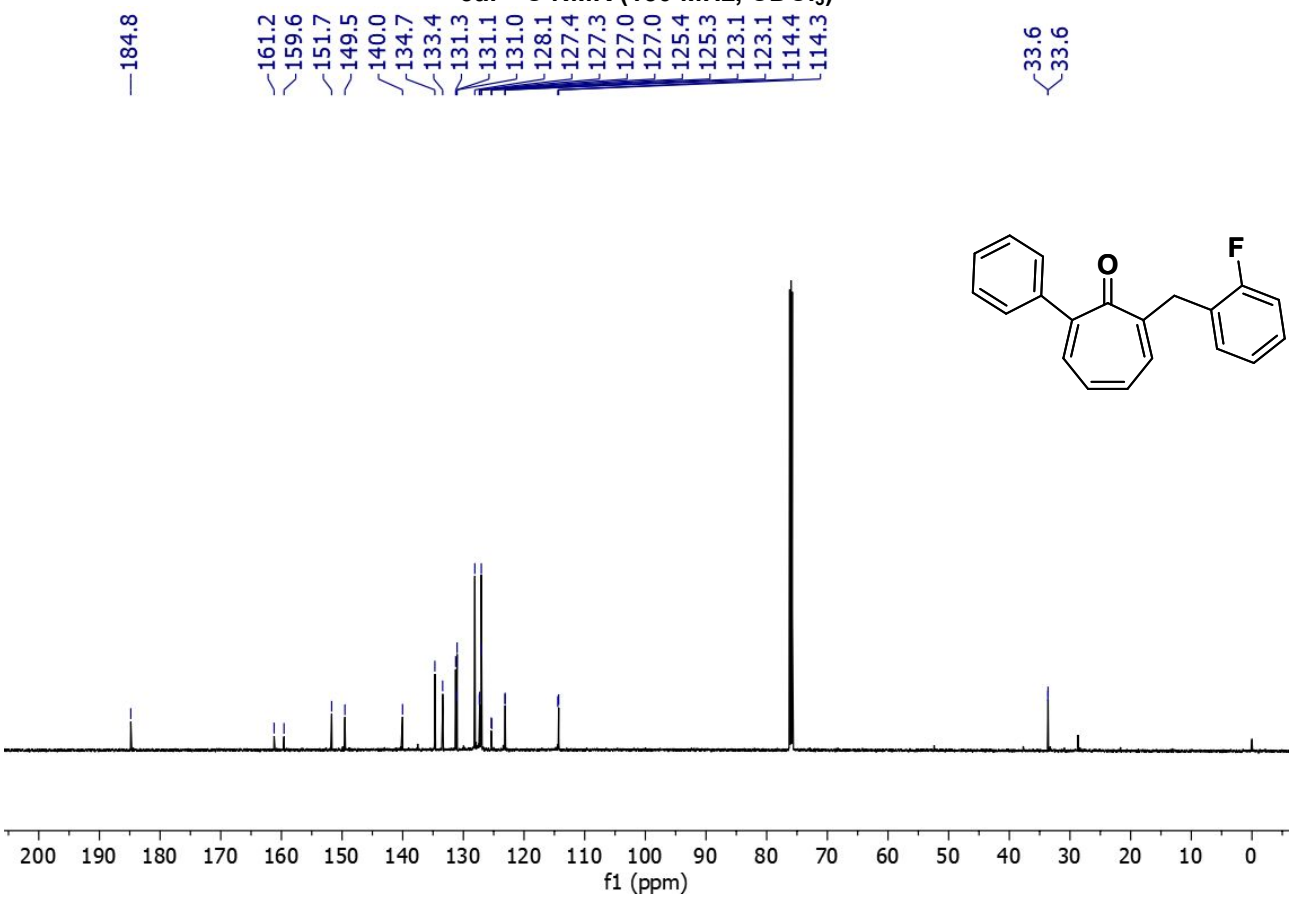
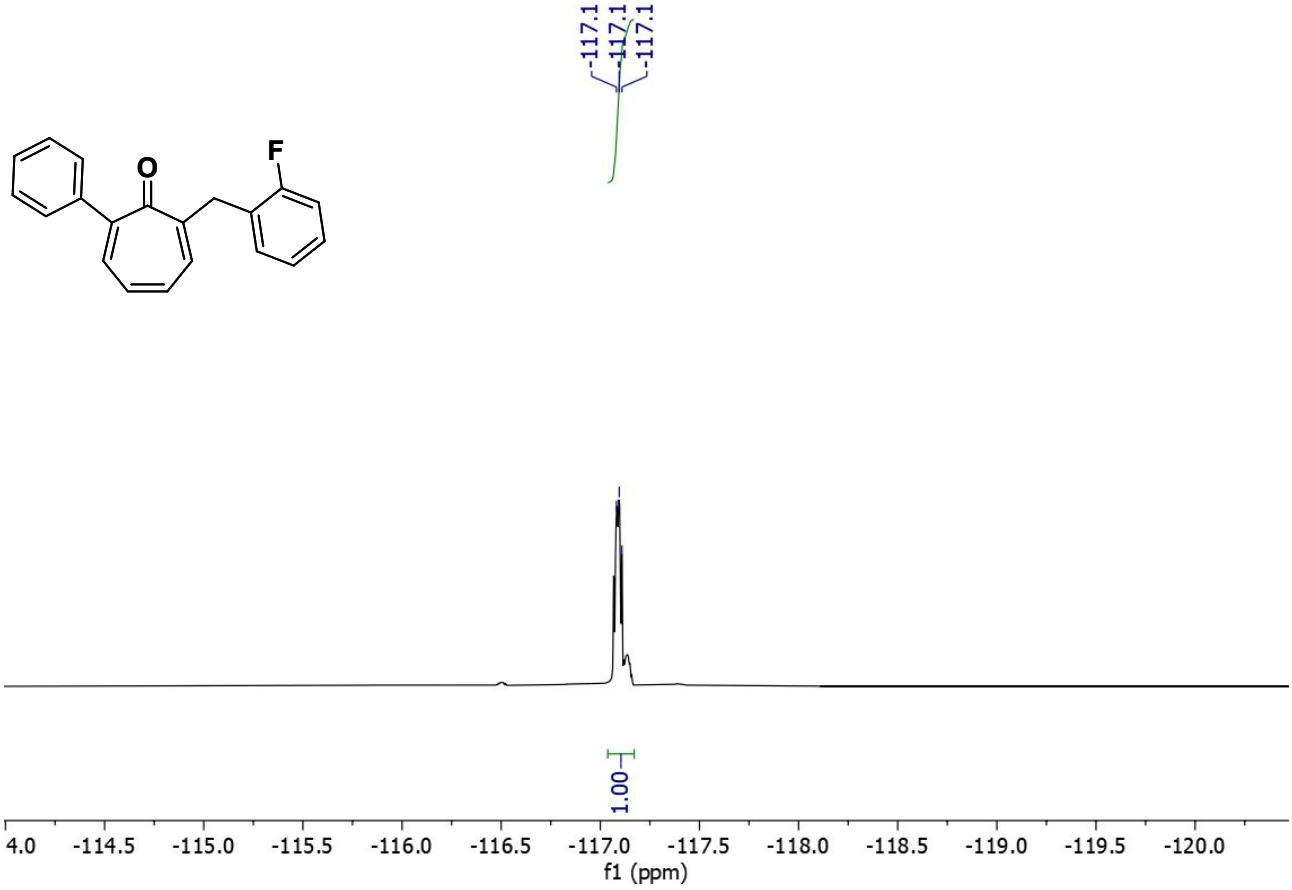
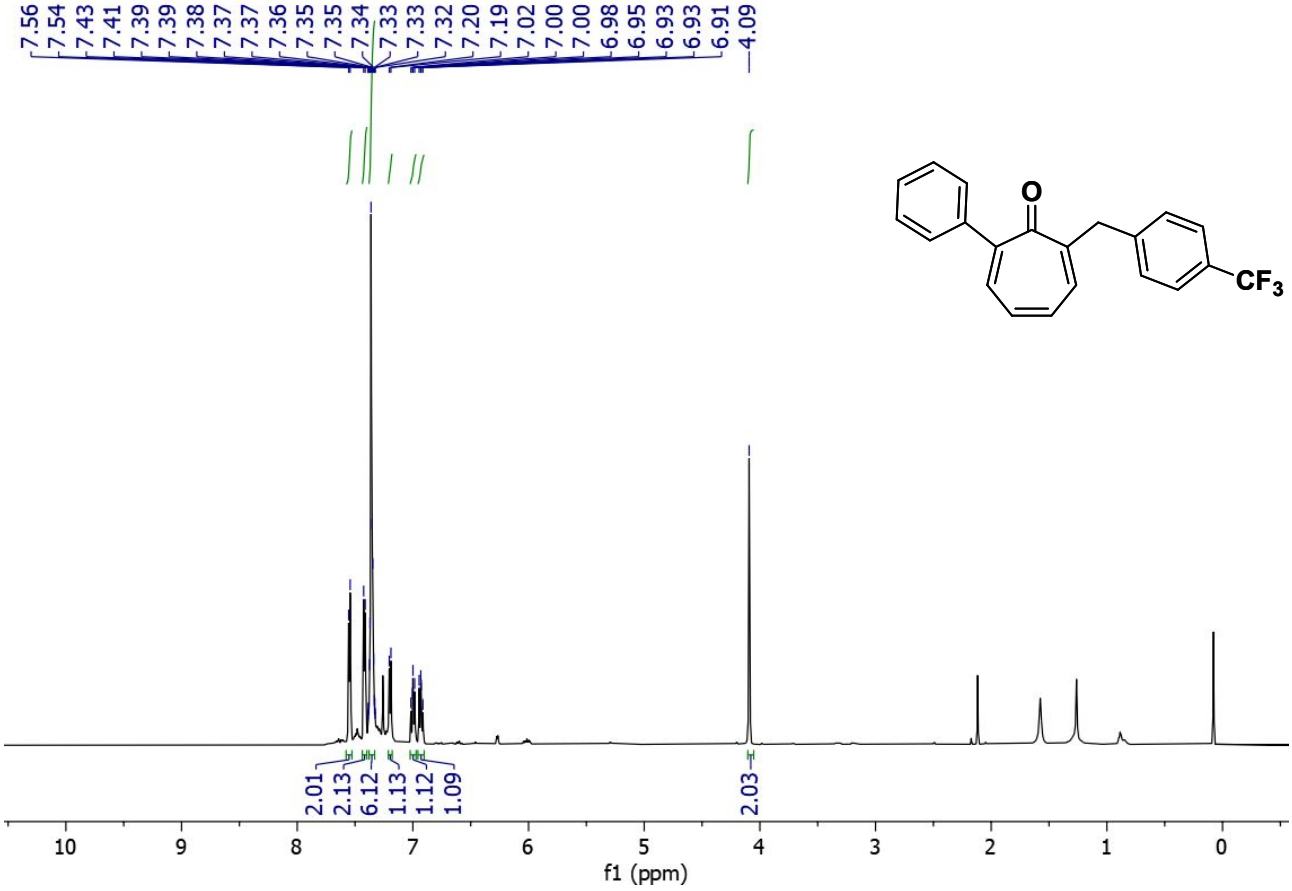


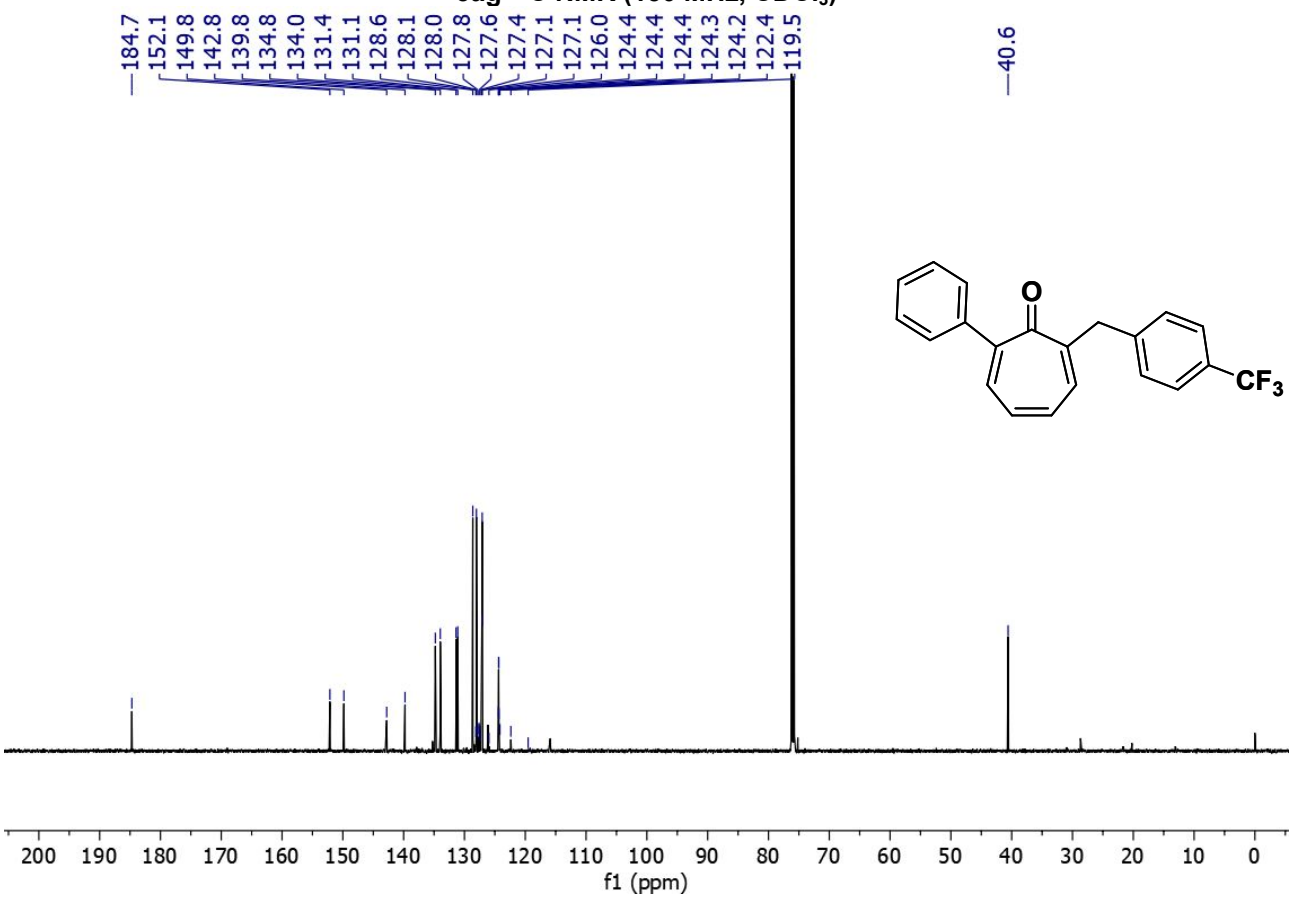
3af ^{19}F NMR (565 MHz, $CDCl_3$)



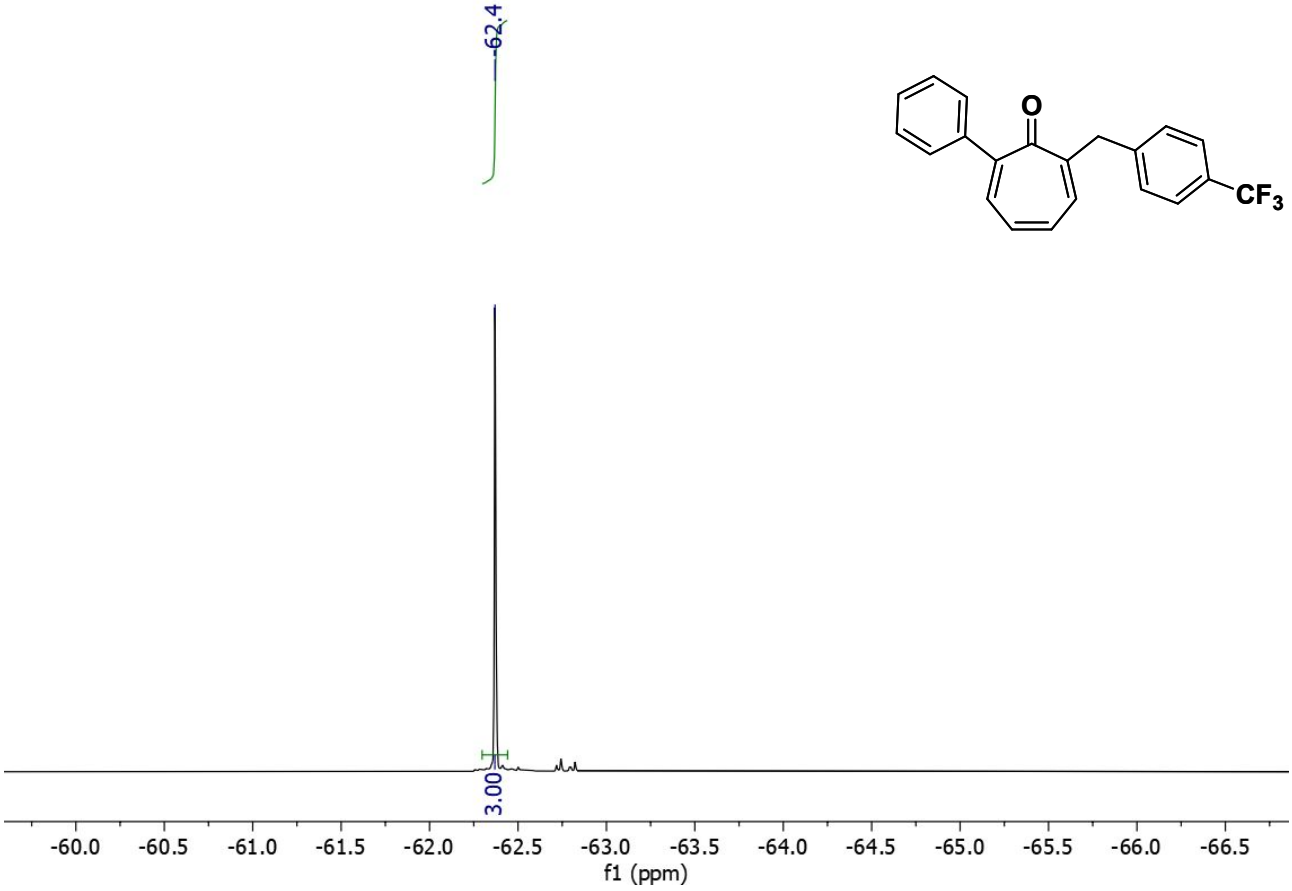
3ag ^{1}H NMR (600 MHz, $CDCl_3$)



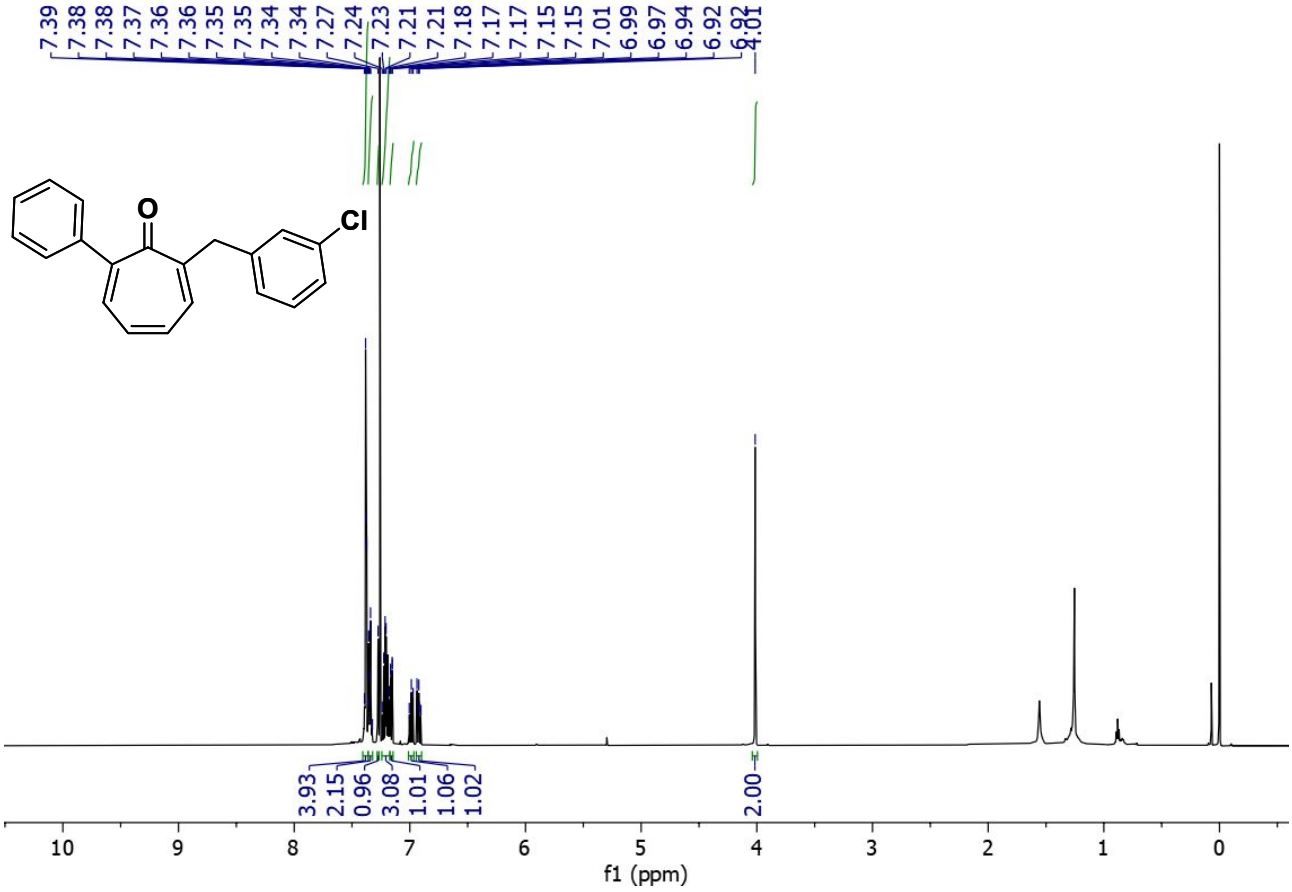
3ag ^{13}C NMR (150 MHz, $CDCl_3$)



3ag ^{19}F NMR (565 MHz, $CDCl_3$)



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



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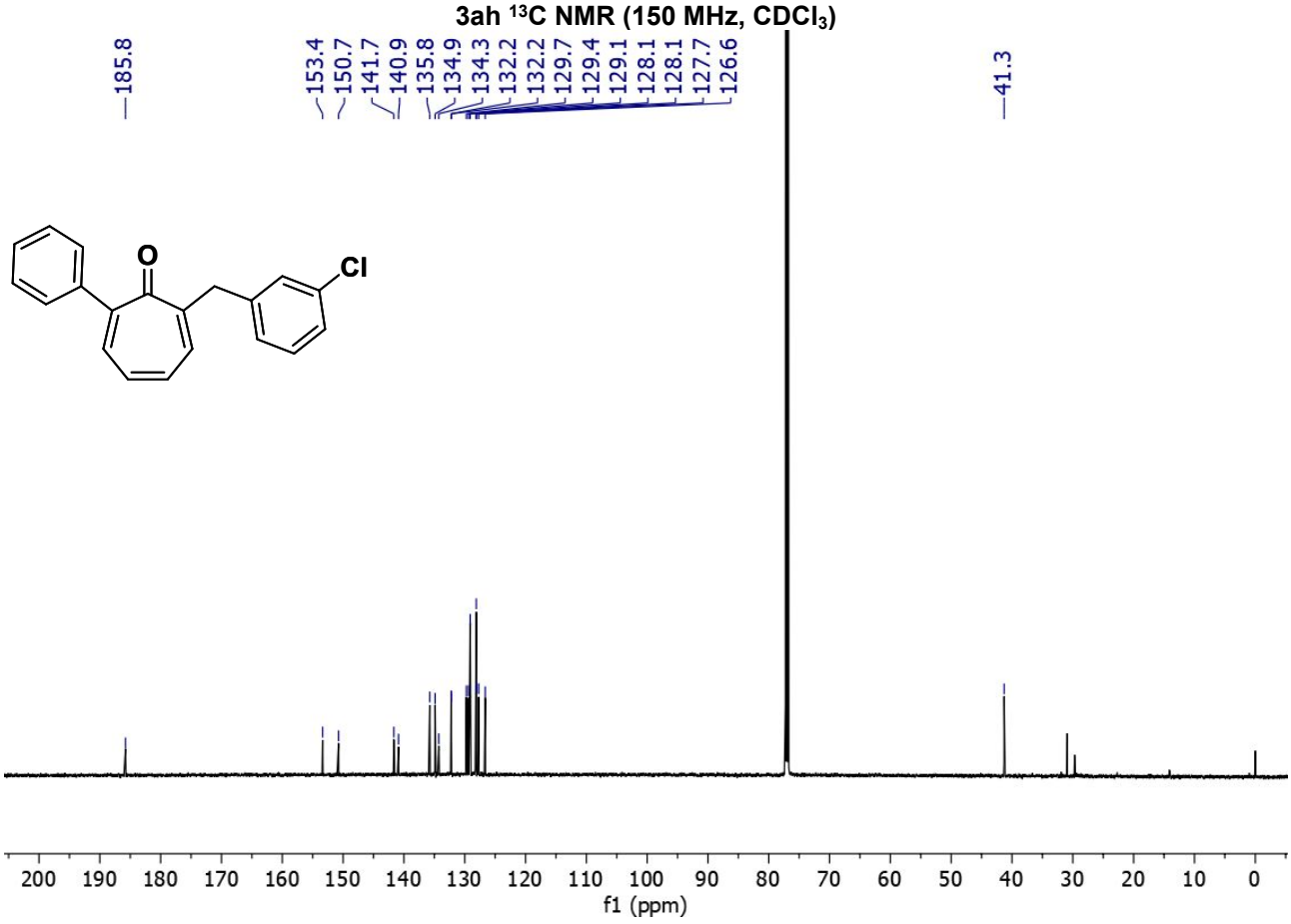
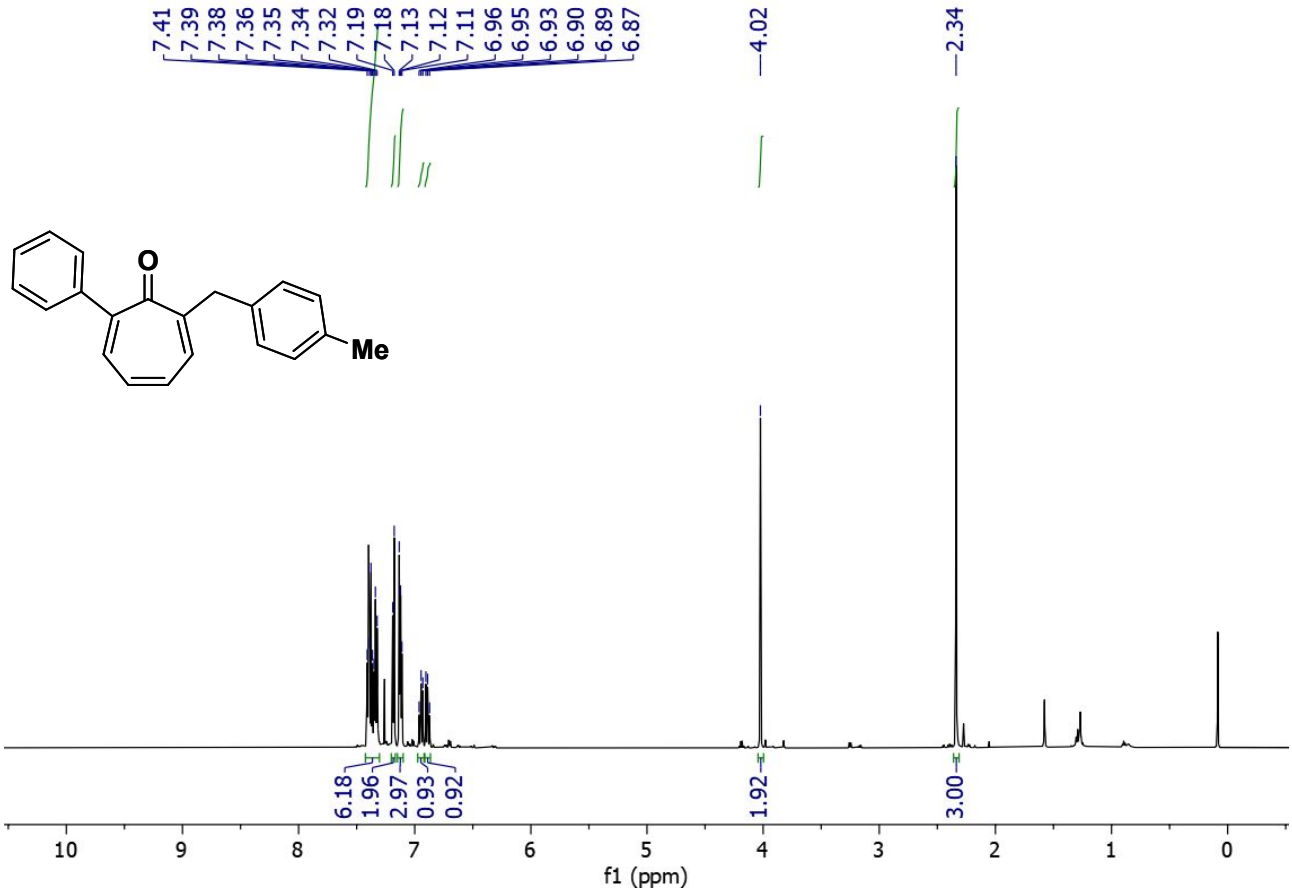
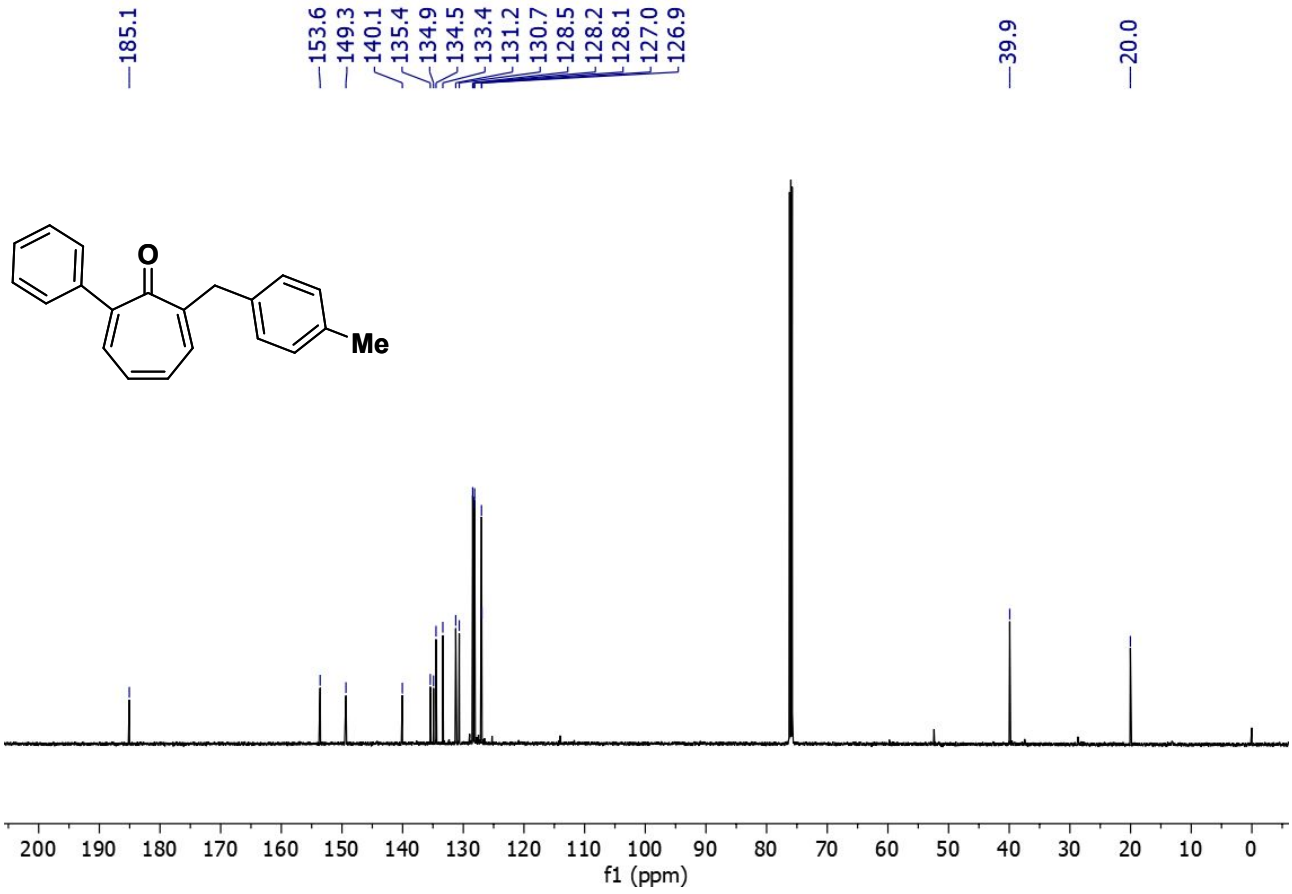


3ai ^{1}H NMR (600 MHz, $CDCl_3$)



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



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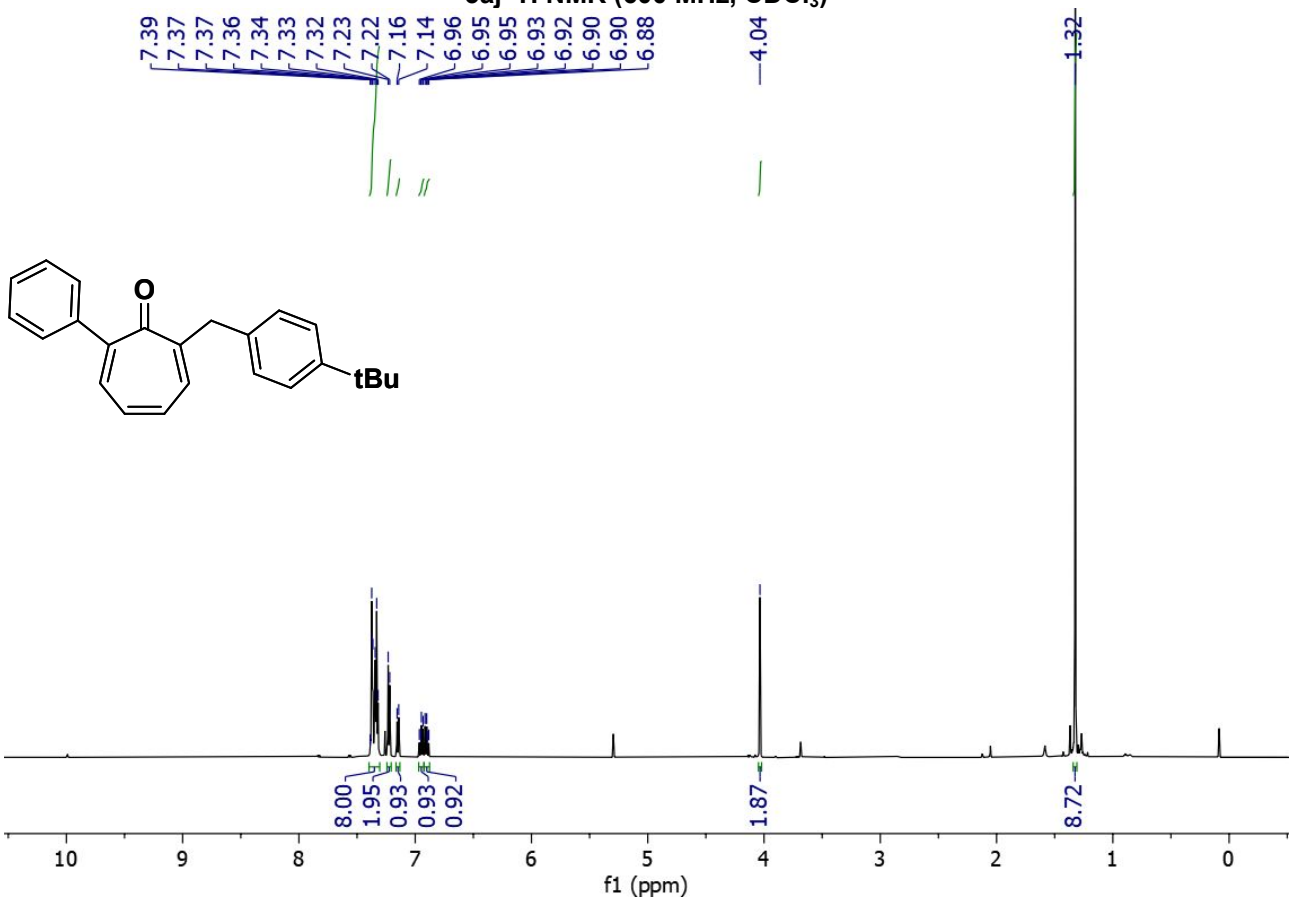
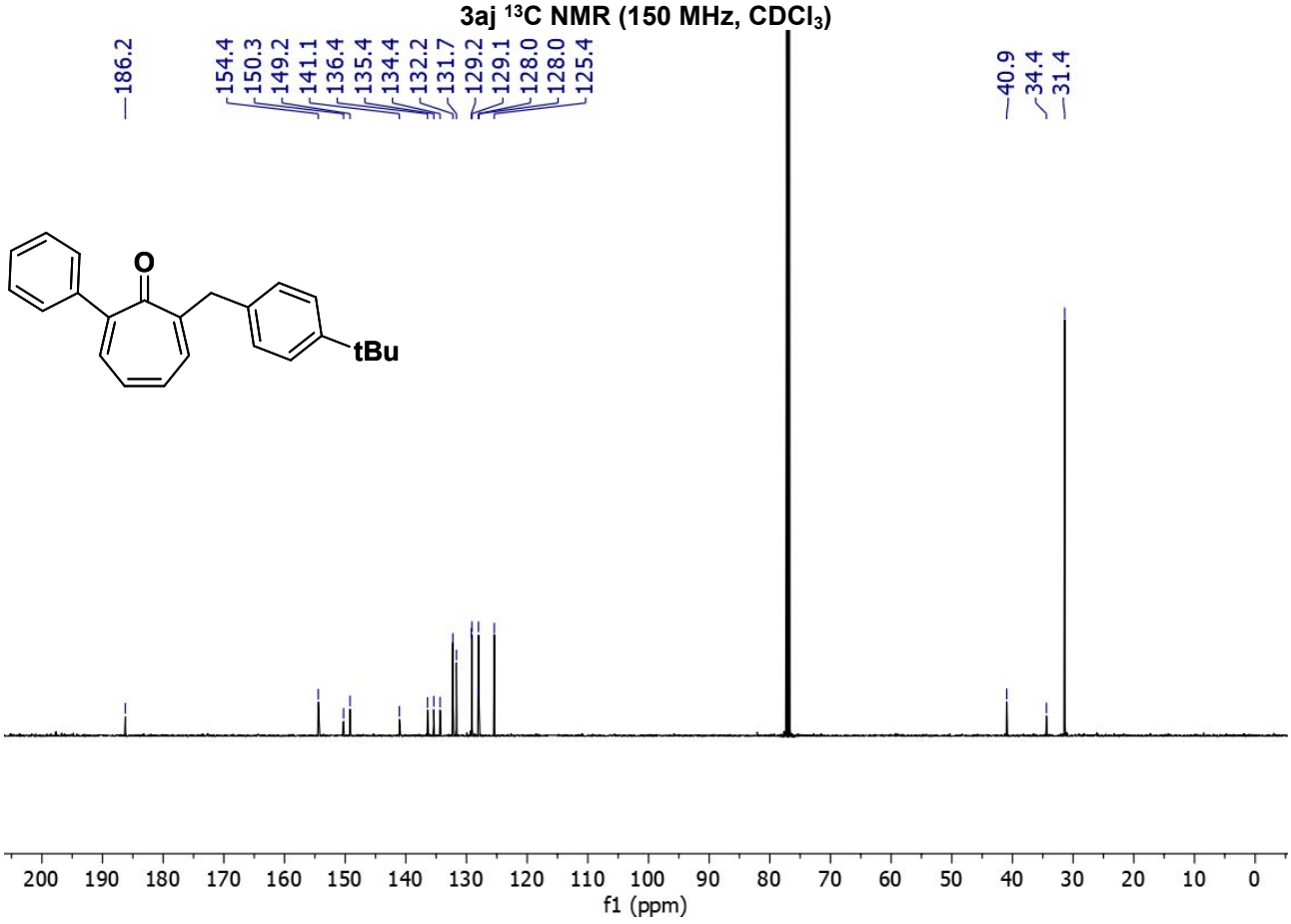
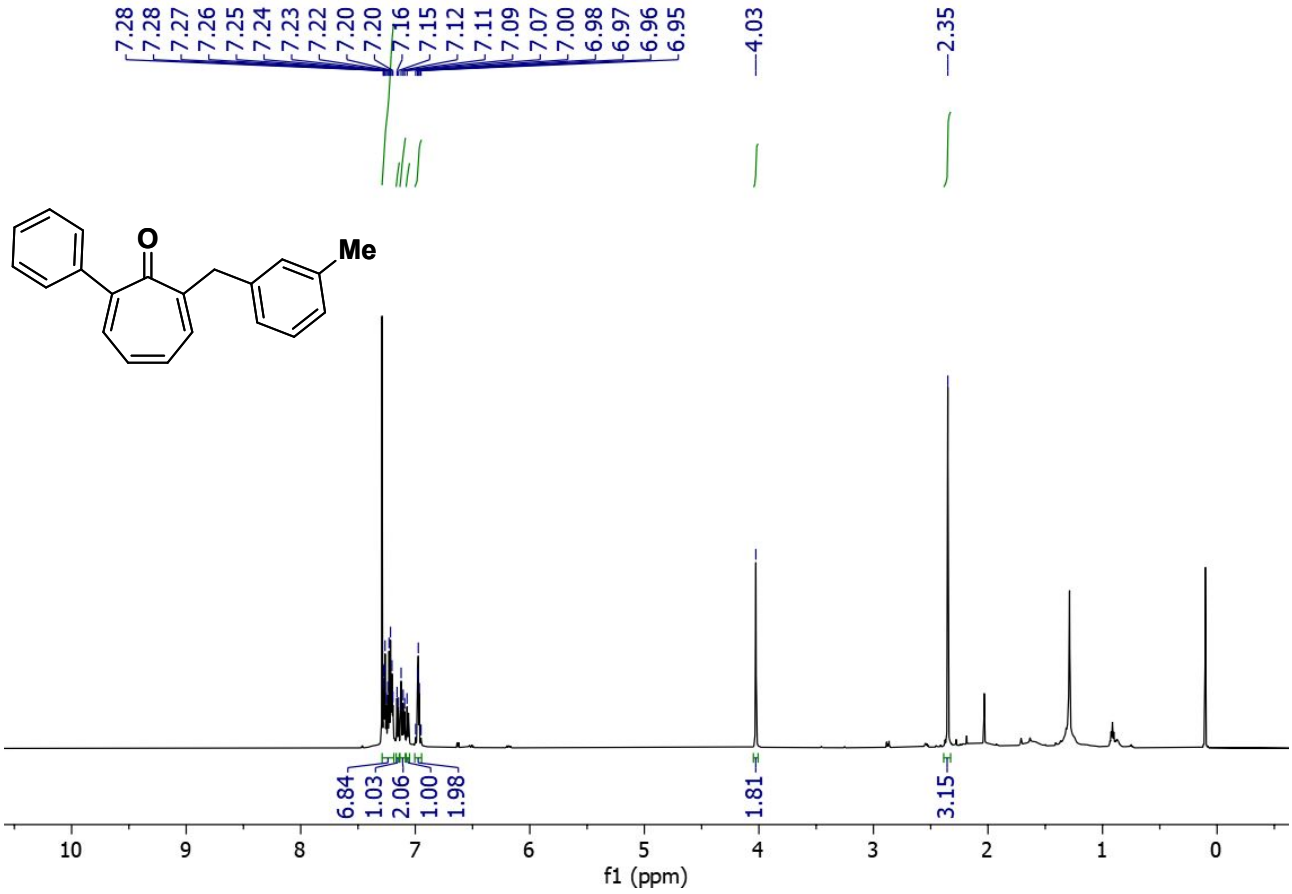


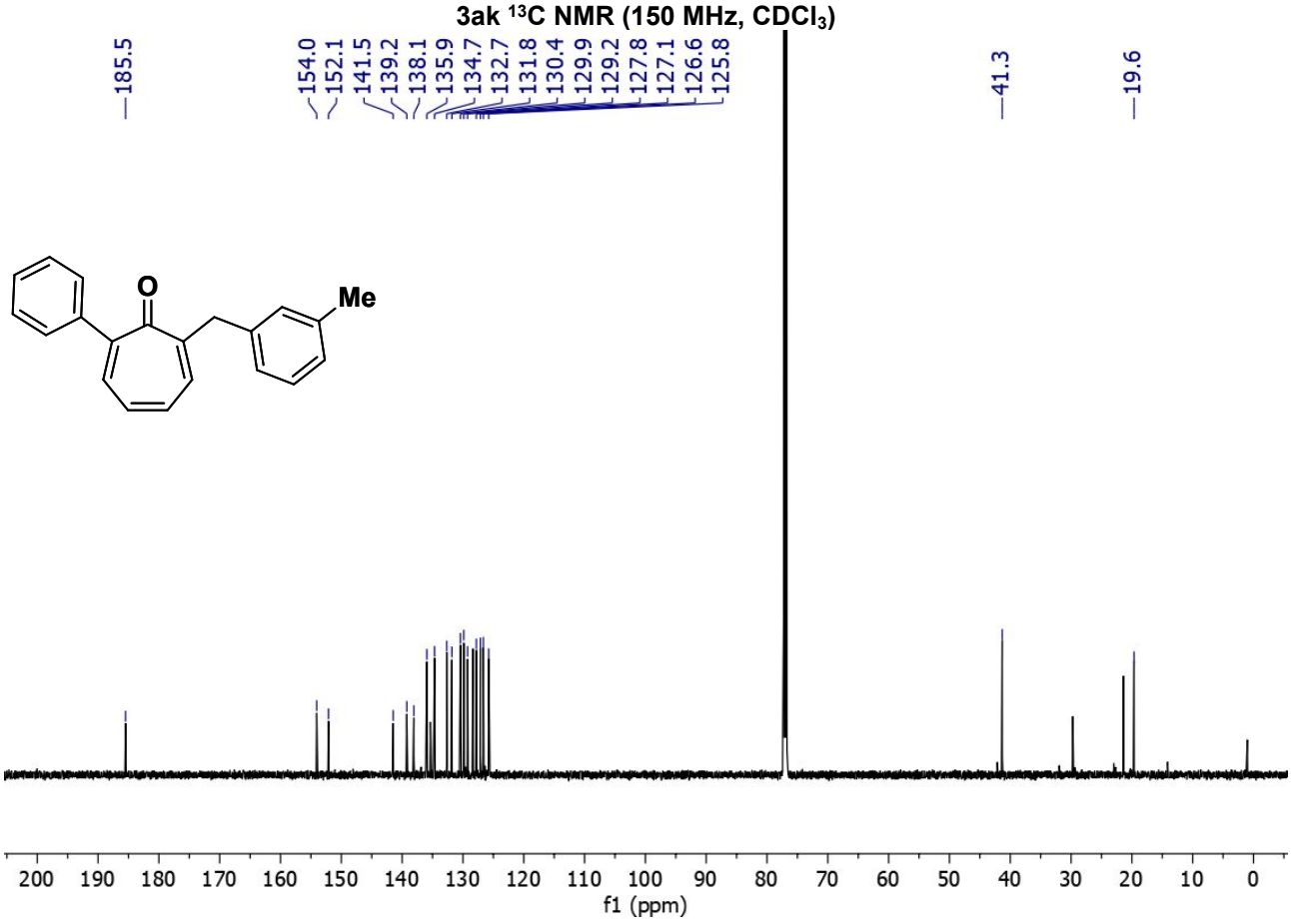
3aj ^{13}C NMR (150 MHz, $CDCl_3$)



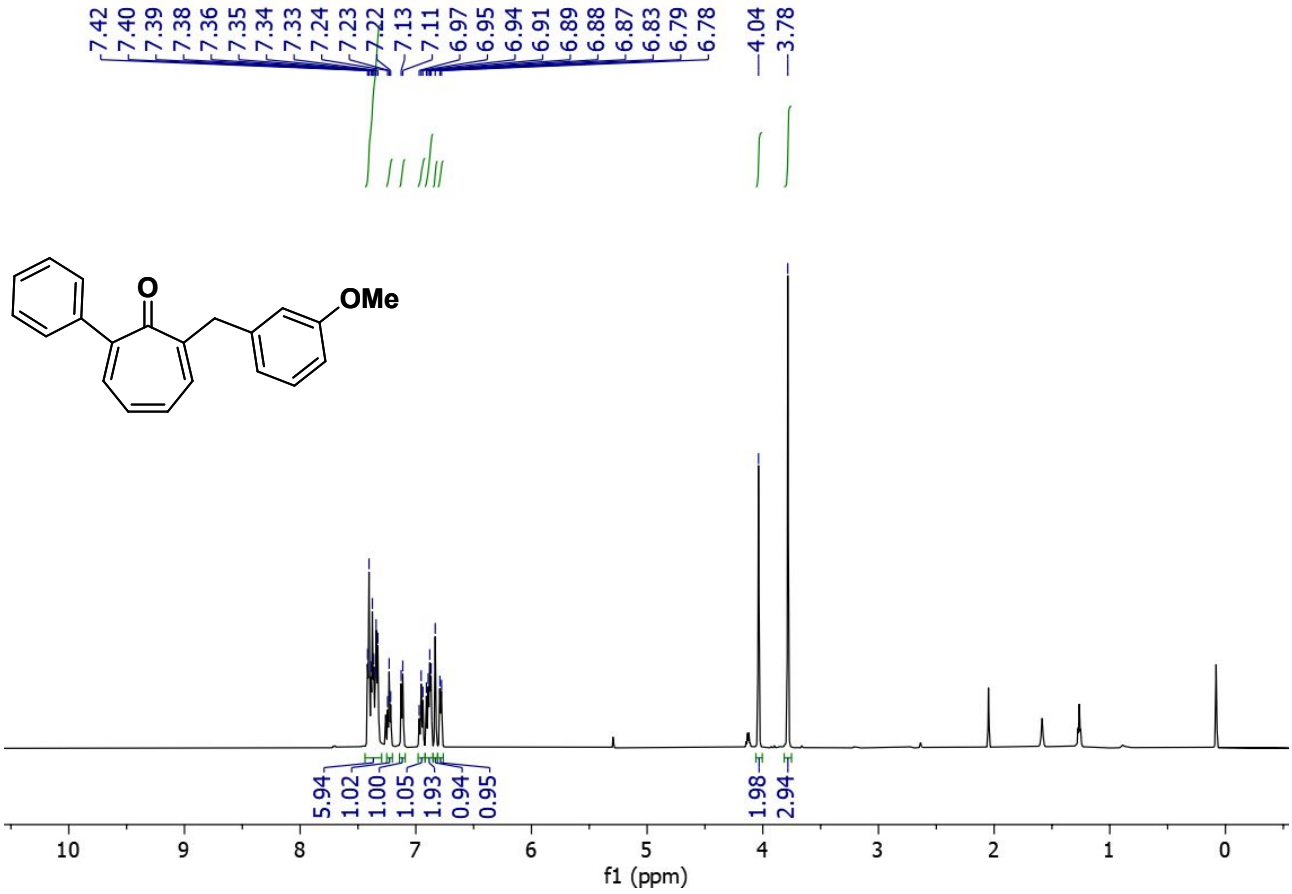
3ak ^{1}H NMR (600 MHz, $CDCl_3$)



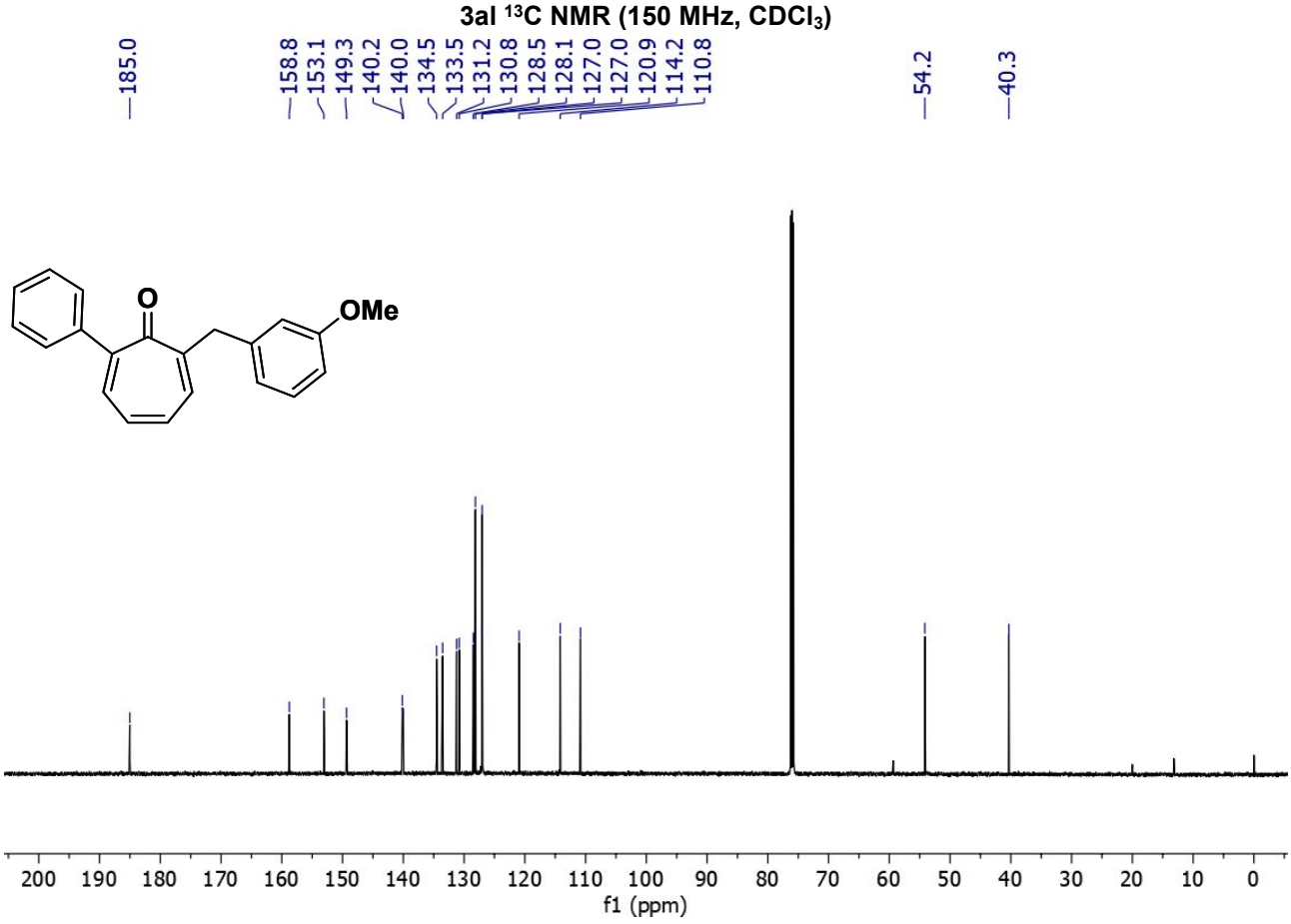
3ak ^{13}C NMR (150 MHz, $CDCl_3$)



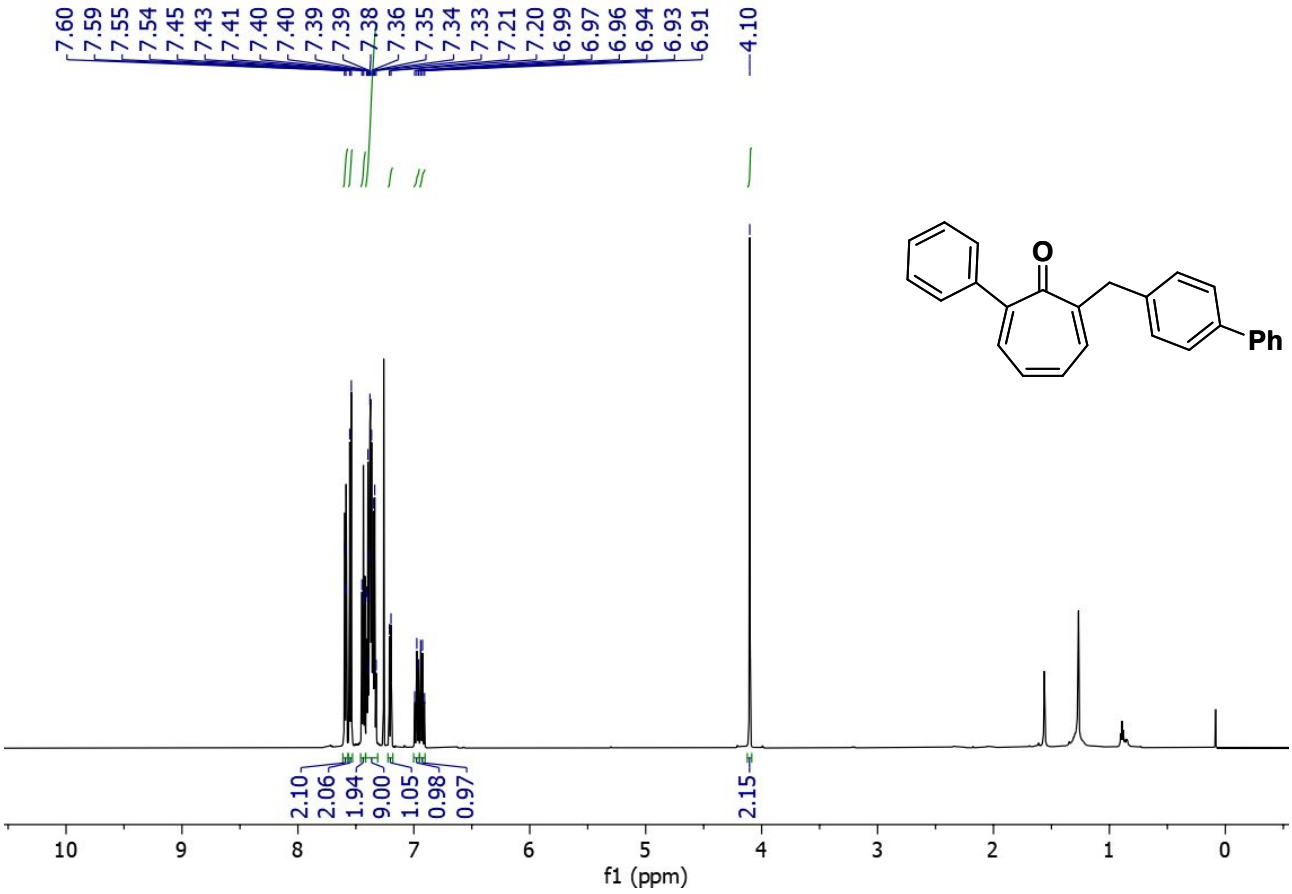
3al ^{1}H NMR (600 MHz, $CDCl_3$)



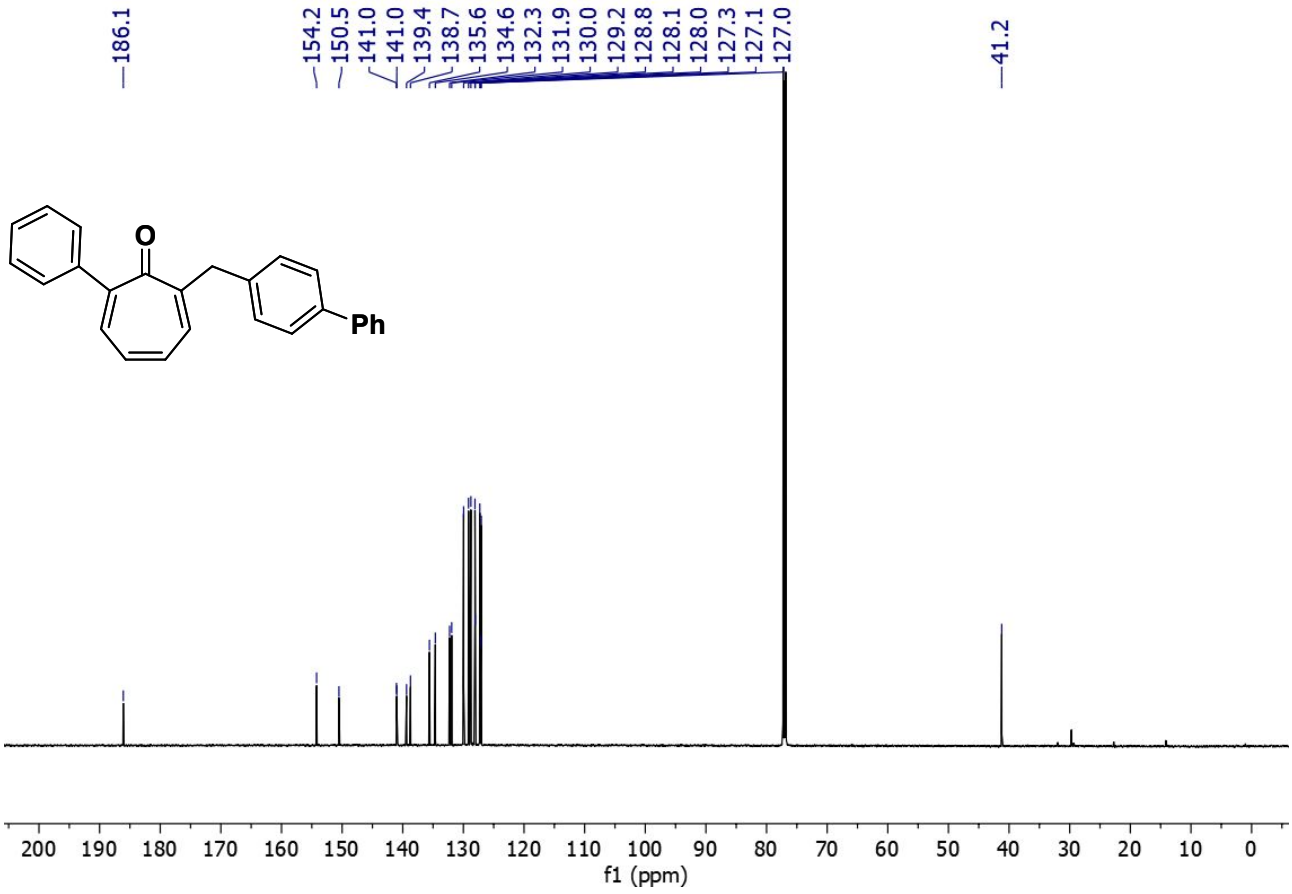
3al ^{13}C NMR (150 MHz, $CDCl_3$)



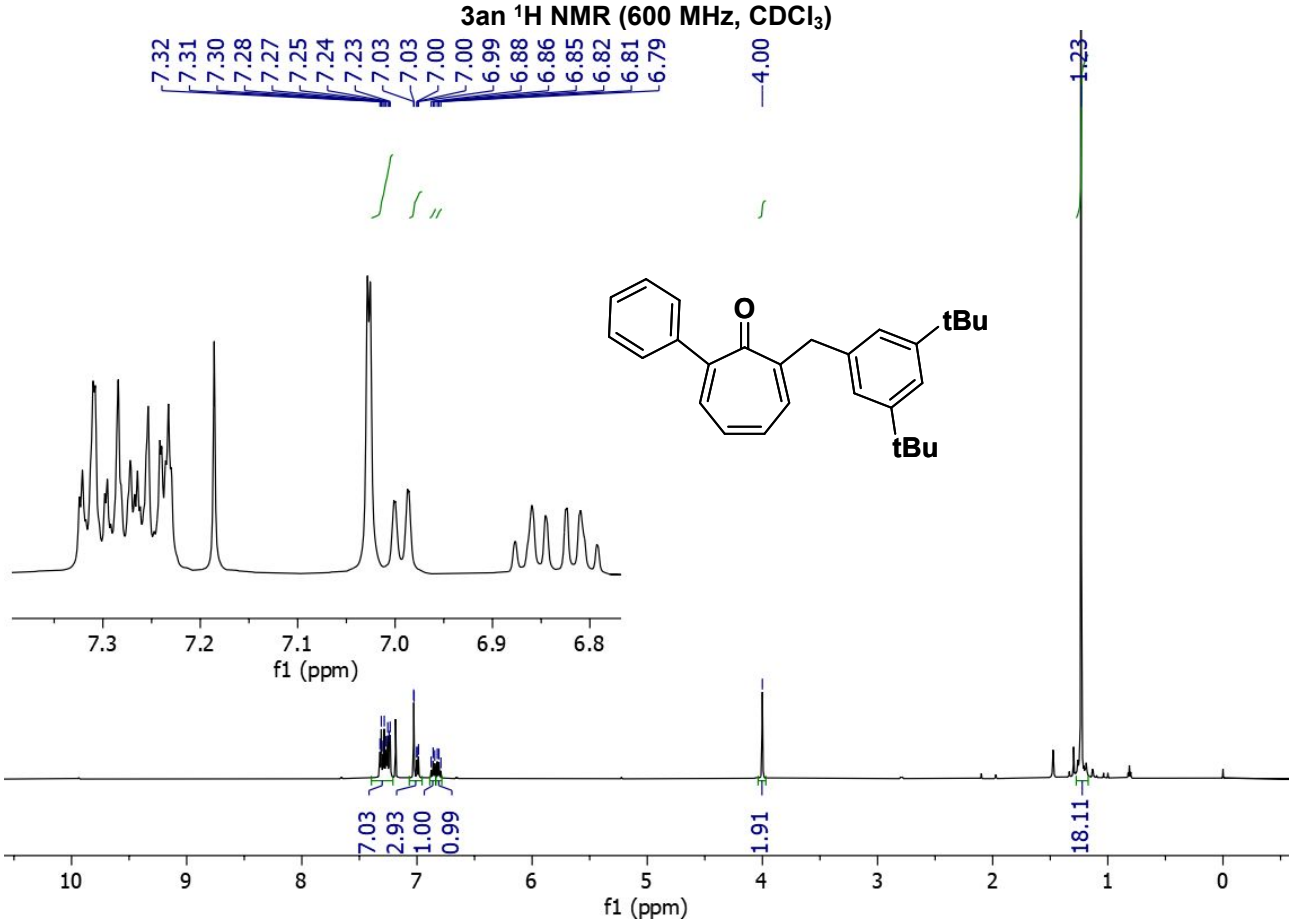
3am ^{1}H NMR (600 MHz, $CDCl_3$)



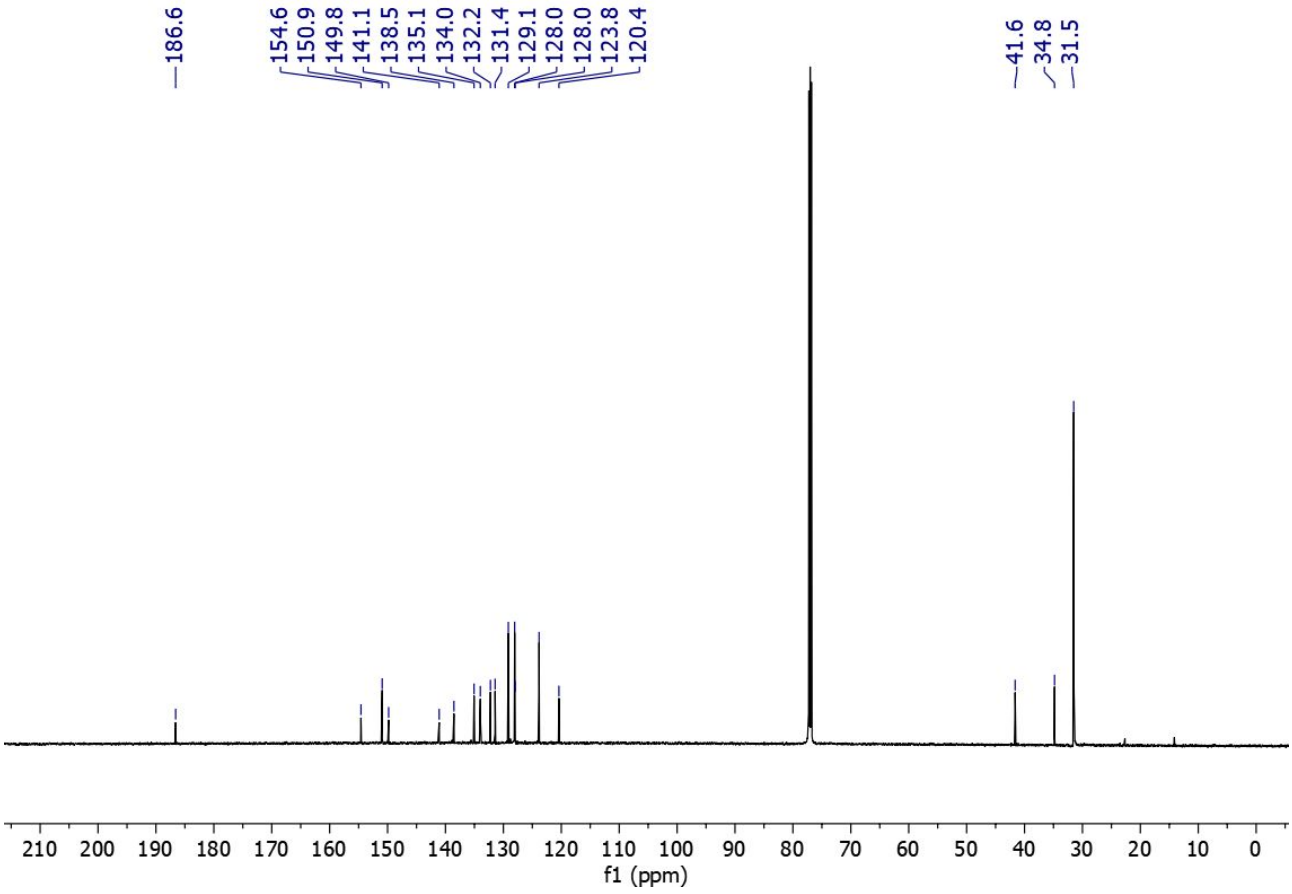
3am ^{13}C NMR (150 MHz, $CDCl_3$)



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



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



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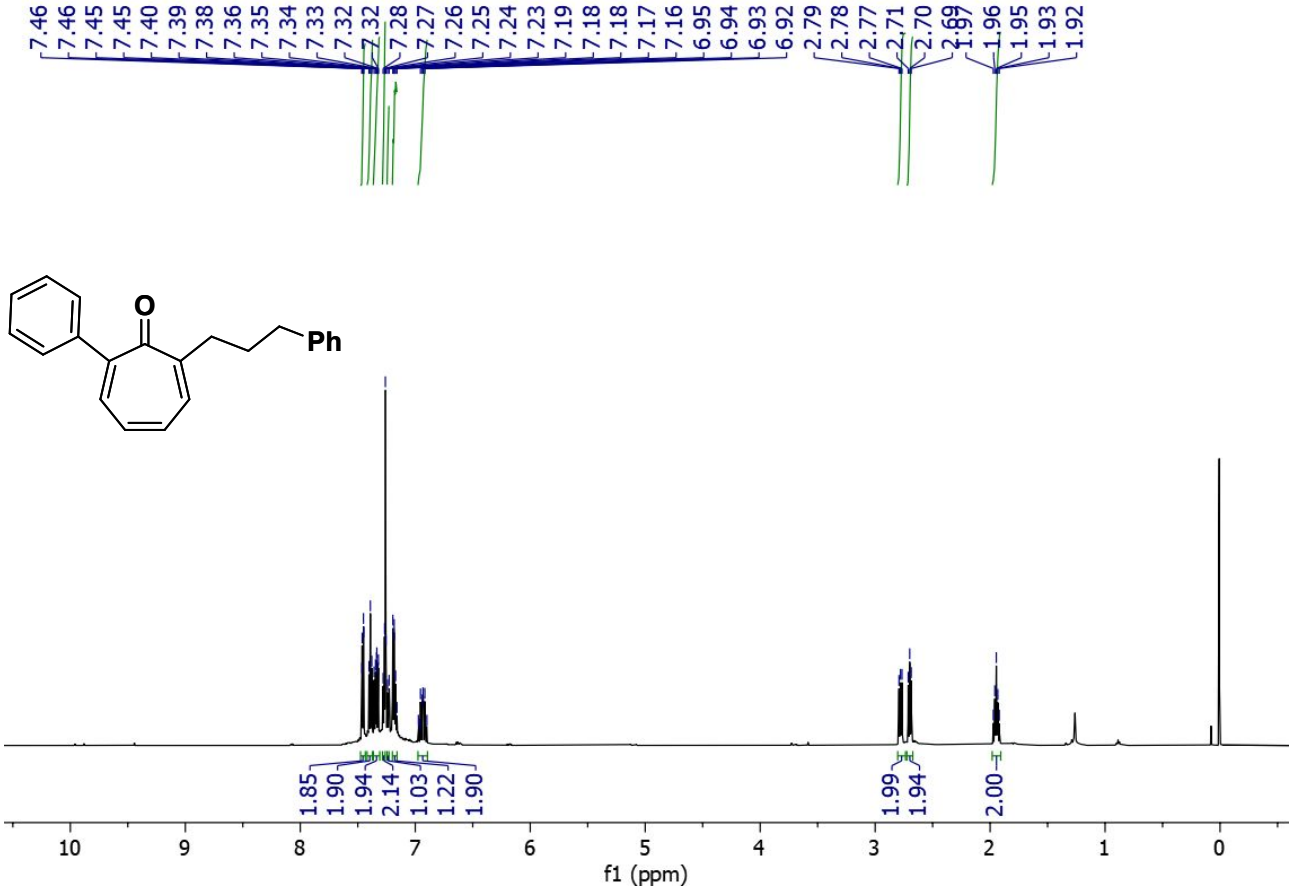
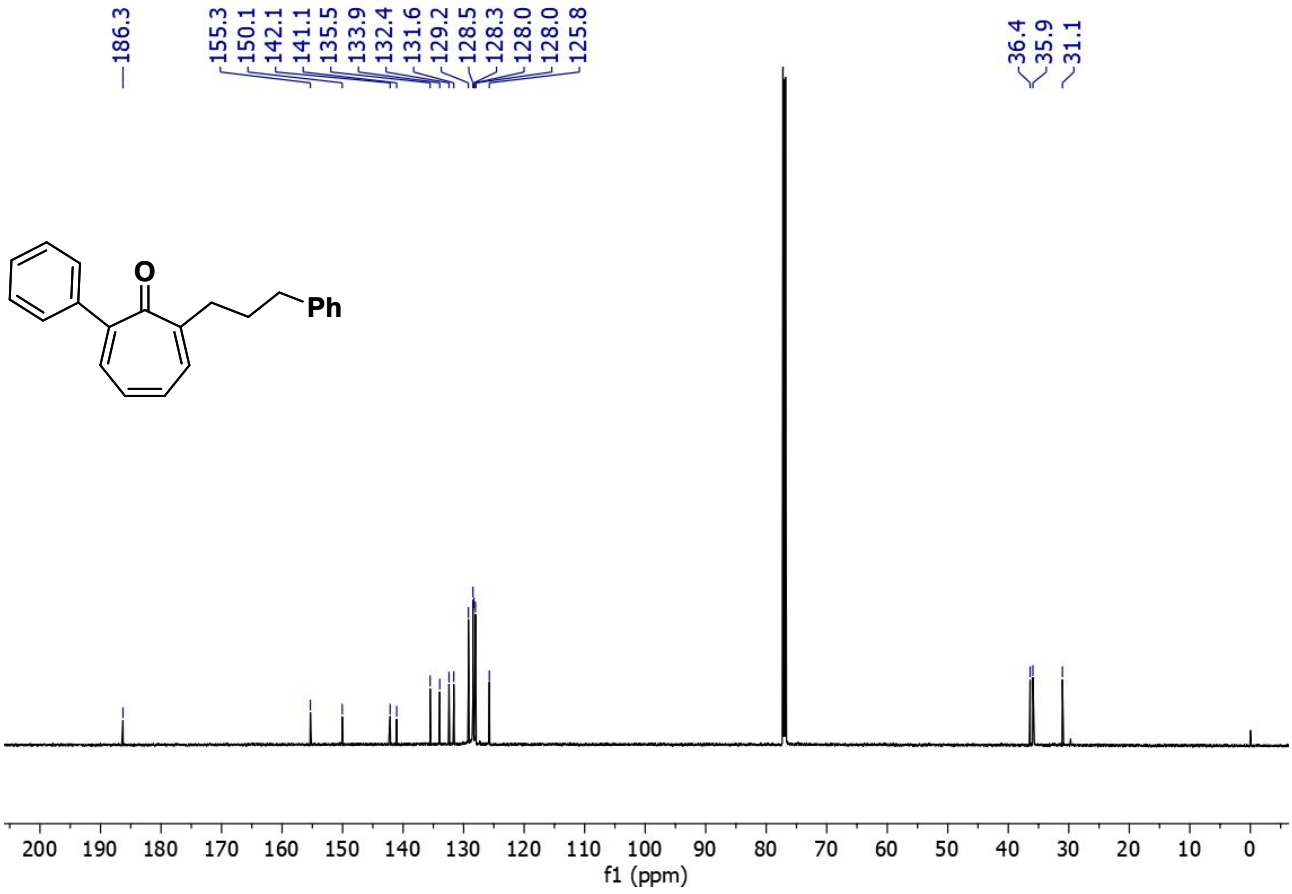
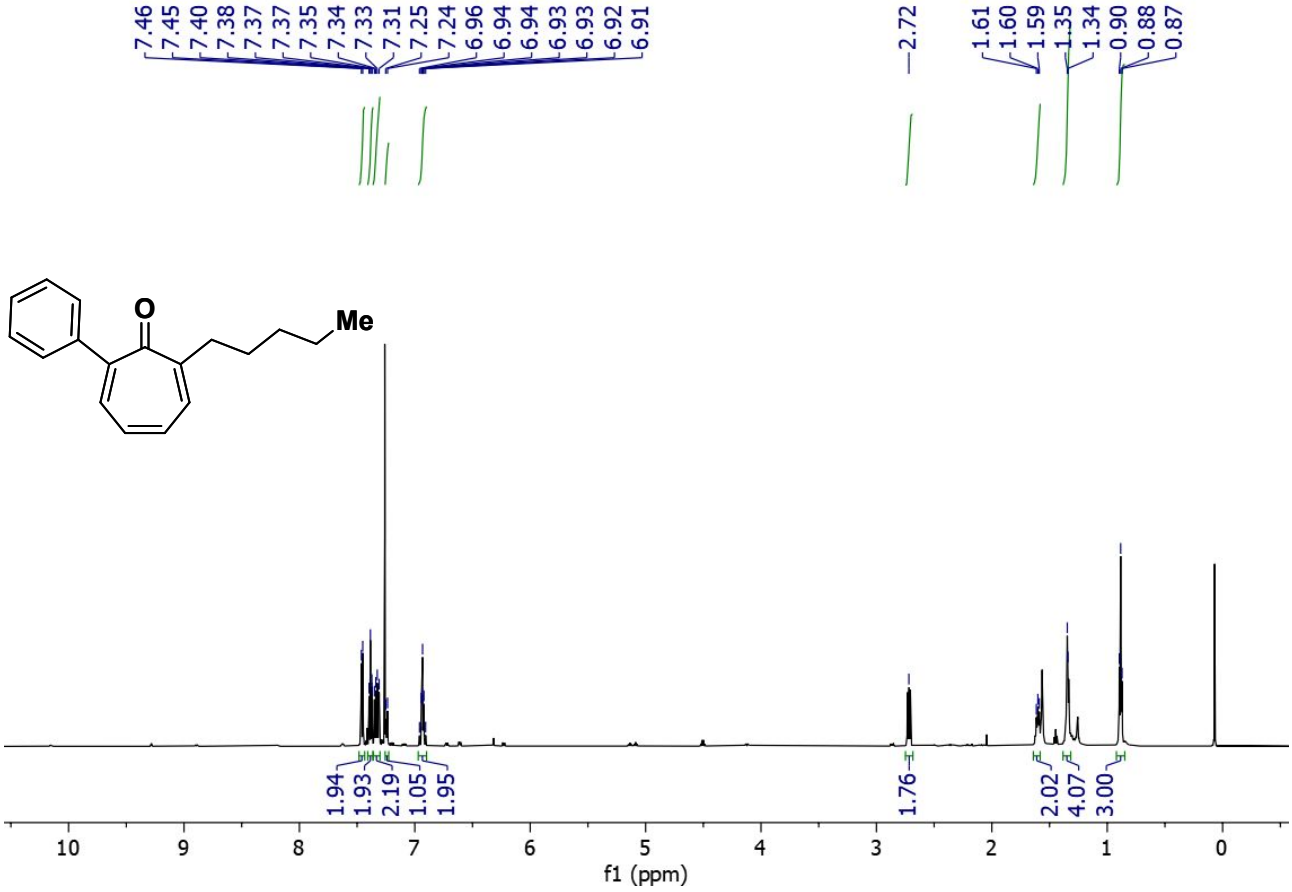


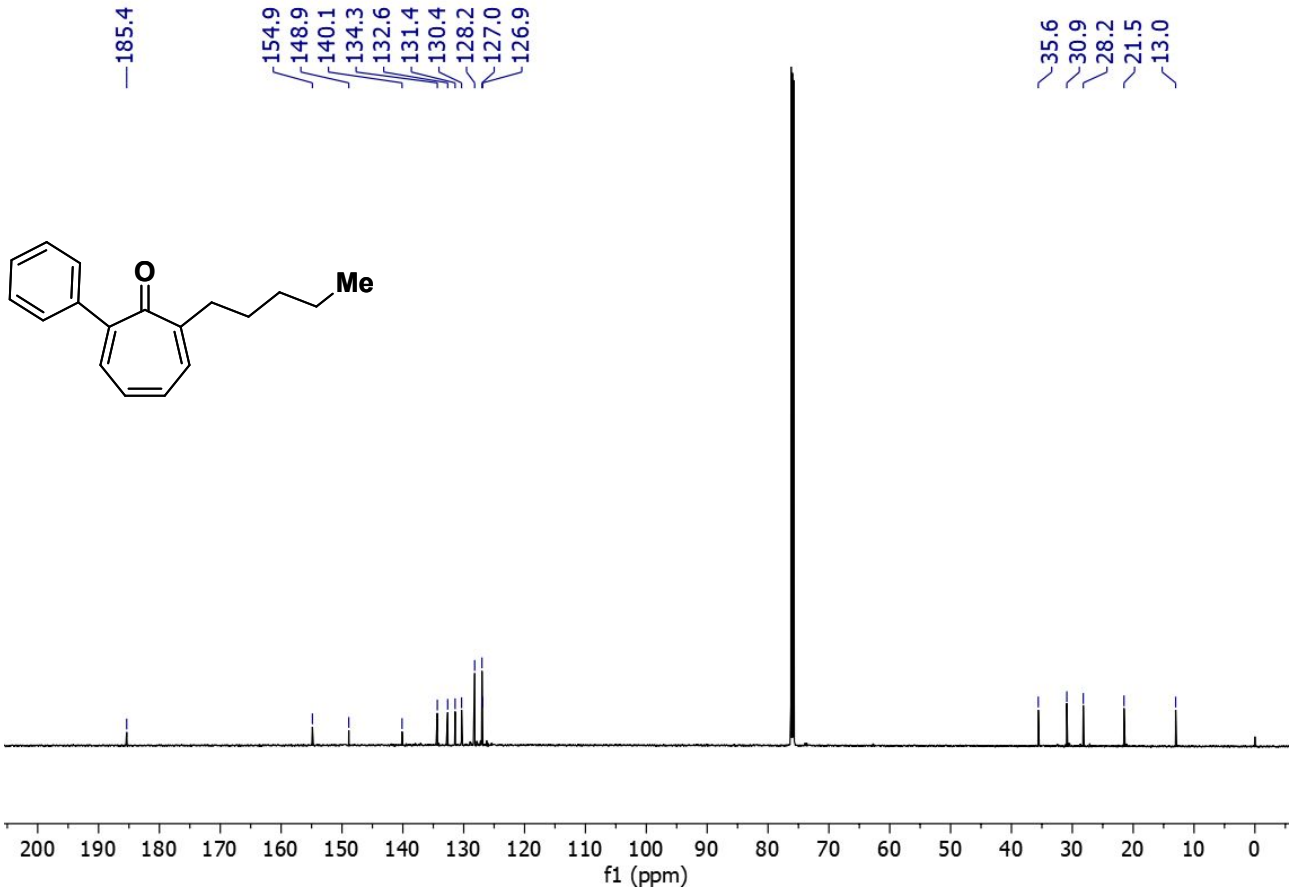
3ao ^{13}C NMR (150 MHz, $CDCl_3$)



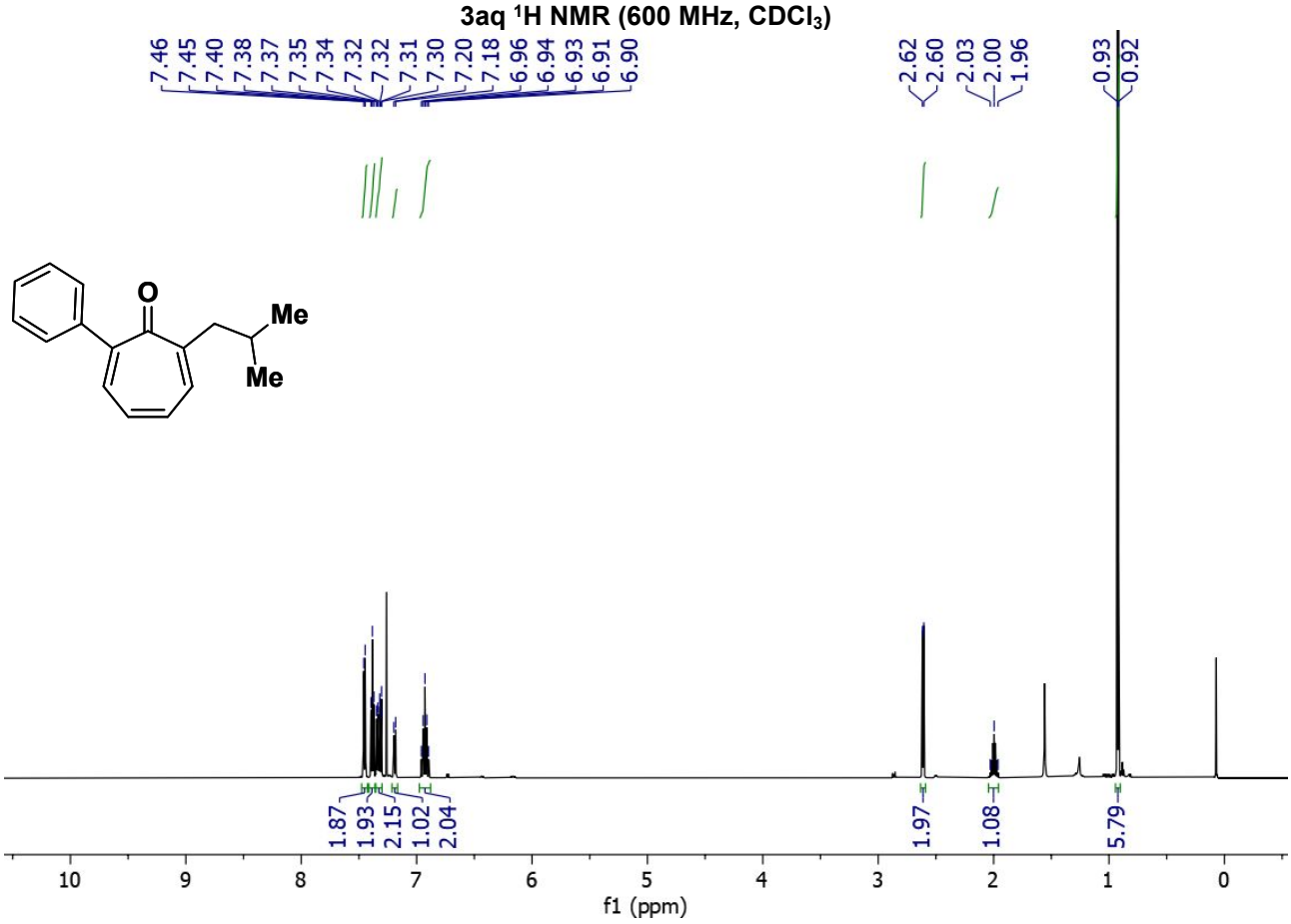
3ap ^{1}H NMR (600 MHz, $CDCl_3$)



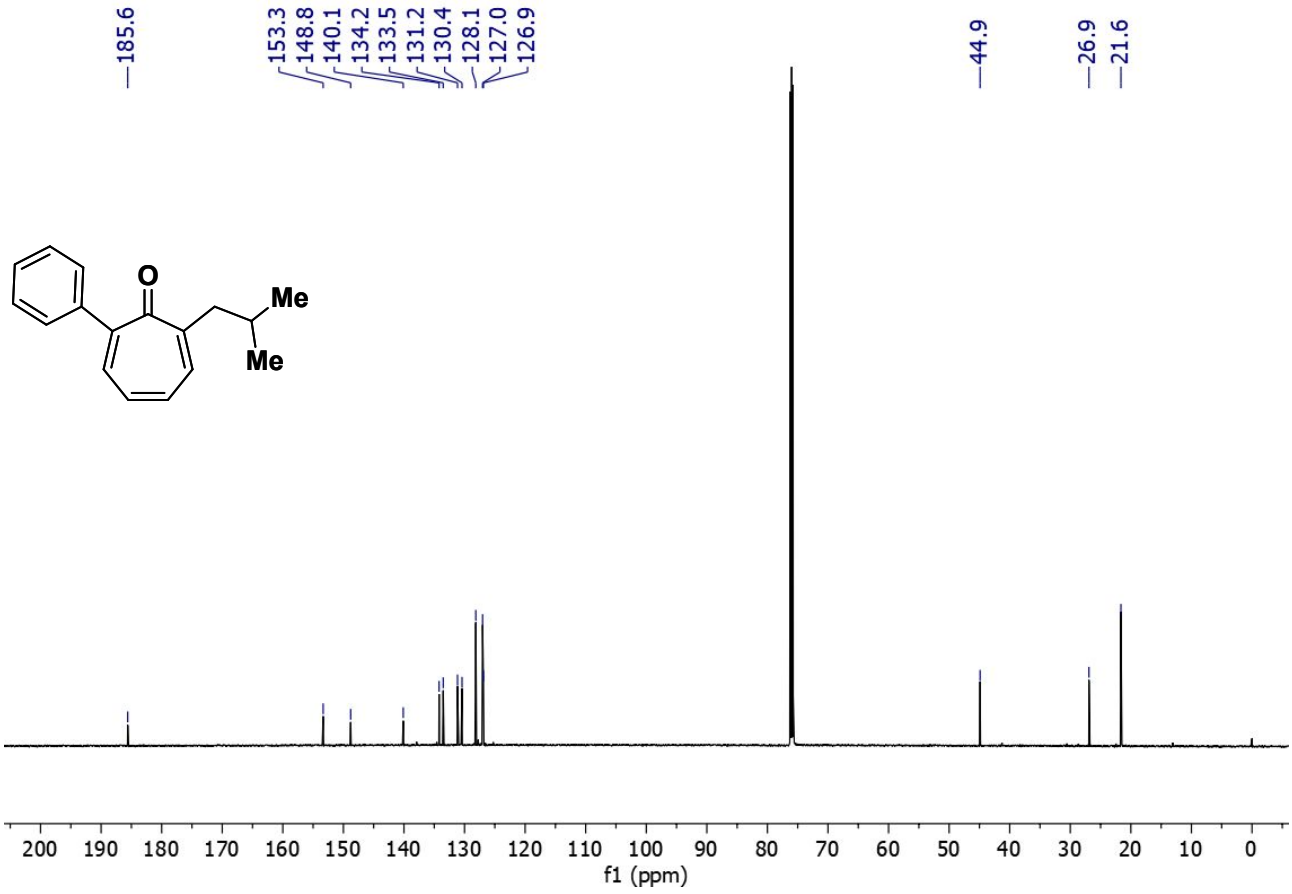
3ap ^{13}C NMR (150 MHz, $CDCl_3$)



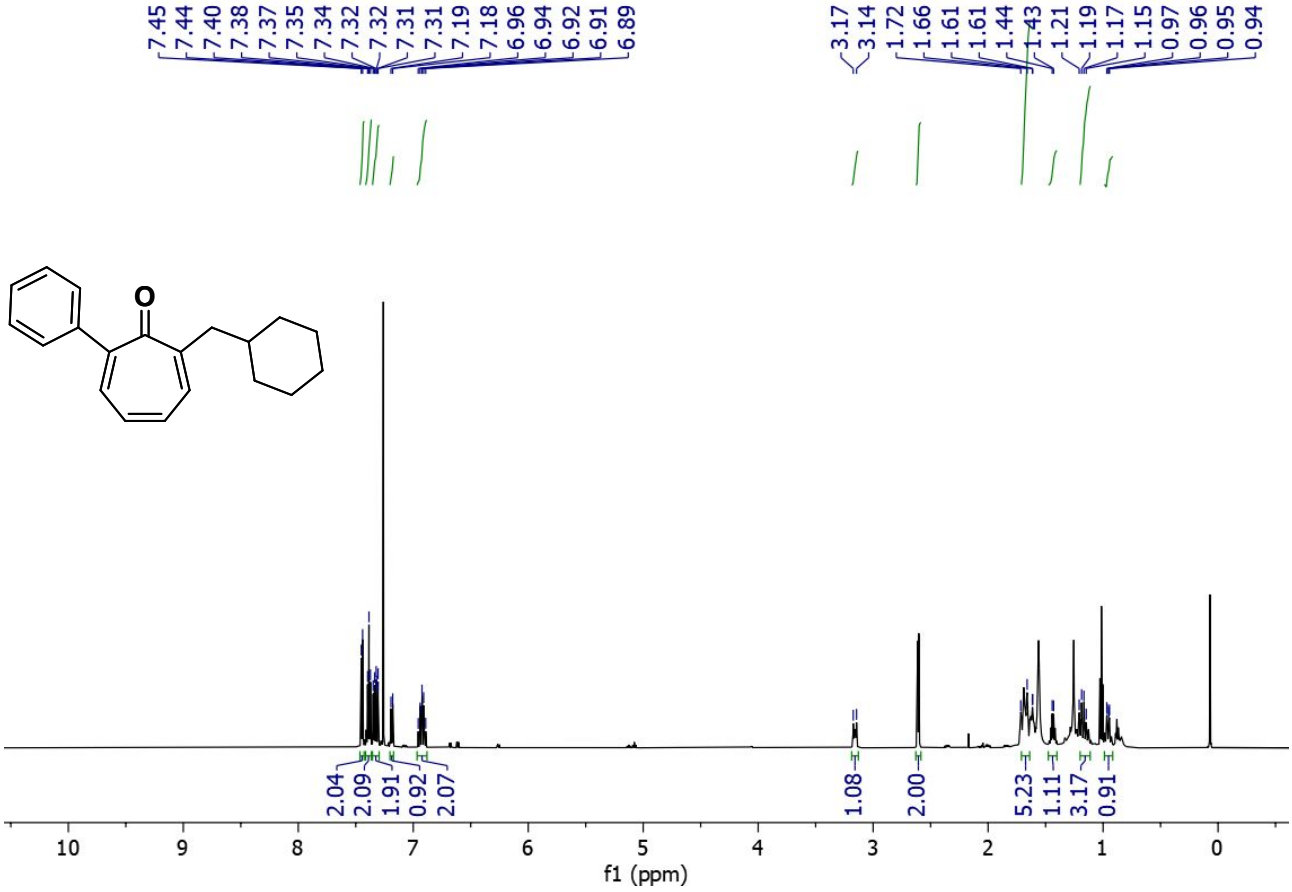
3aq ^{1}H NMR (600 MHz, $CDCl_3$)



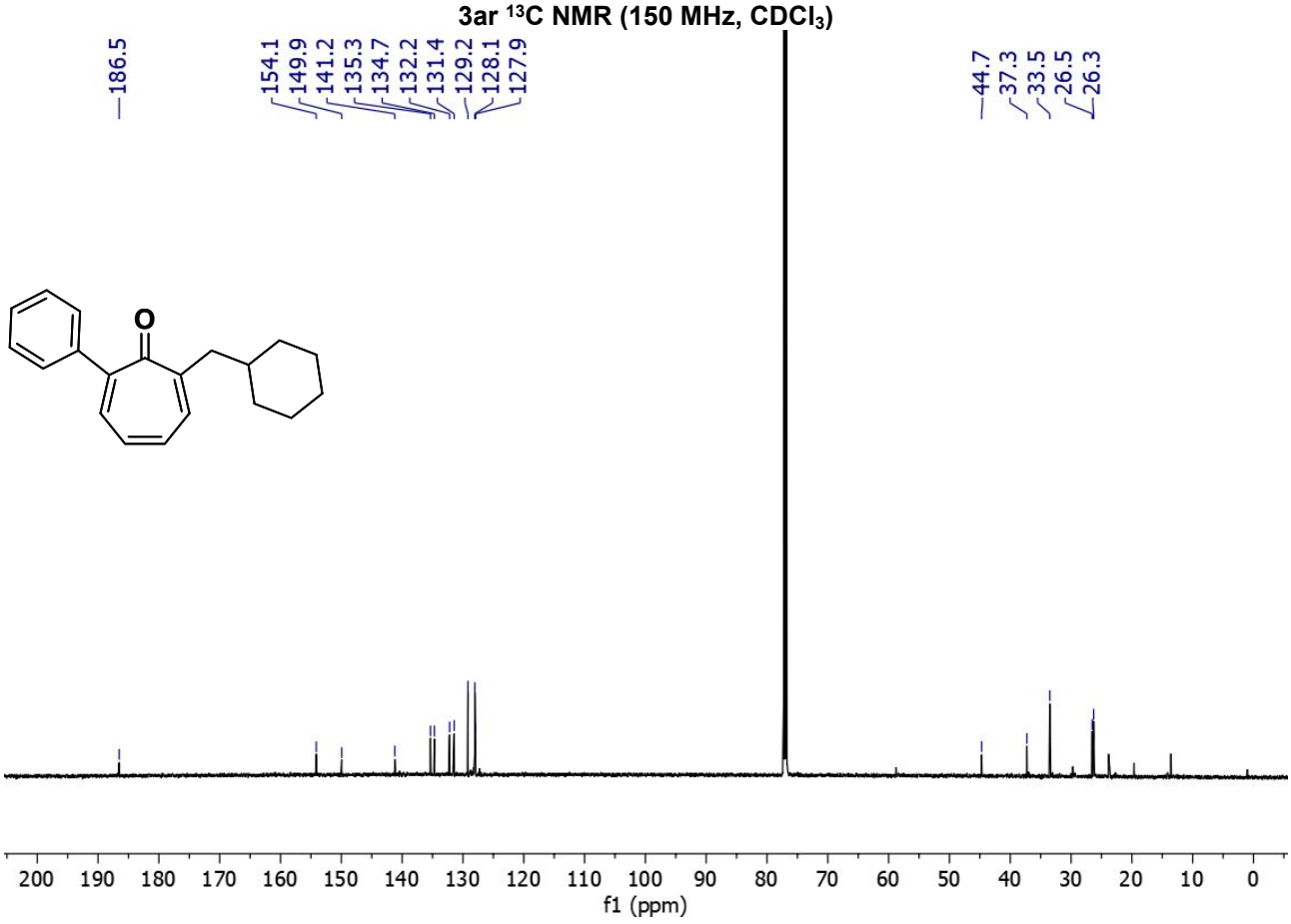
3aq ^{13}C NMR (150 MHz, $CDCl_3$)



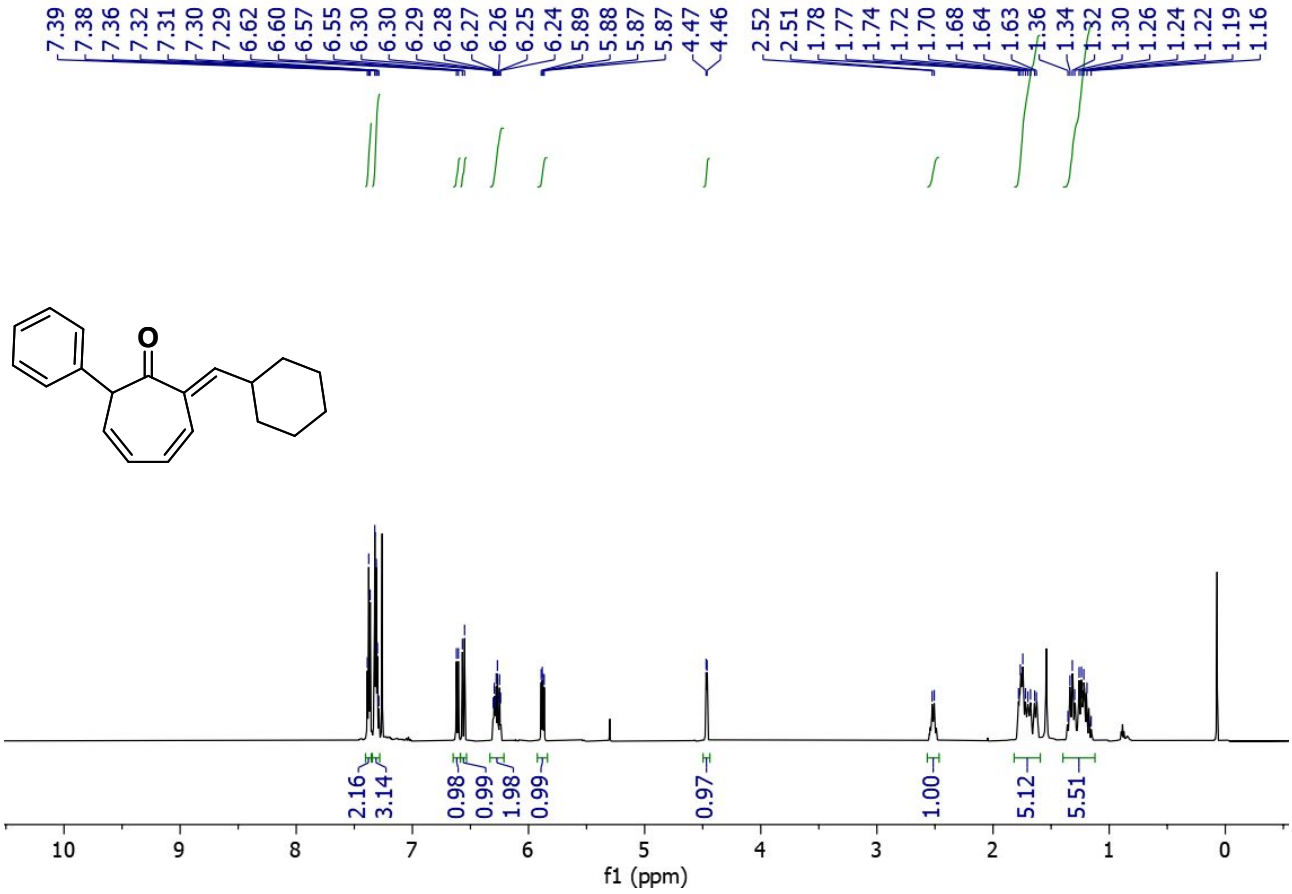
3ar ^{1}H NMR (600 MHz, $CDCl_3$)



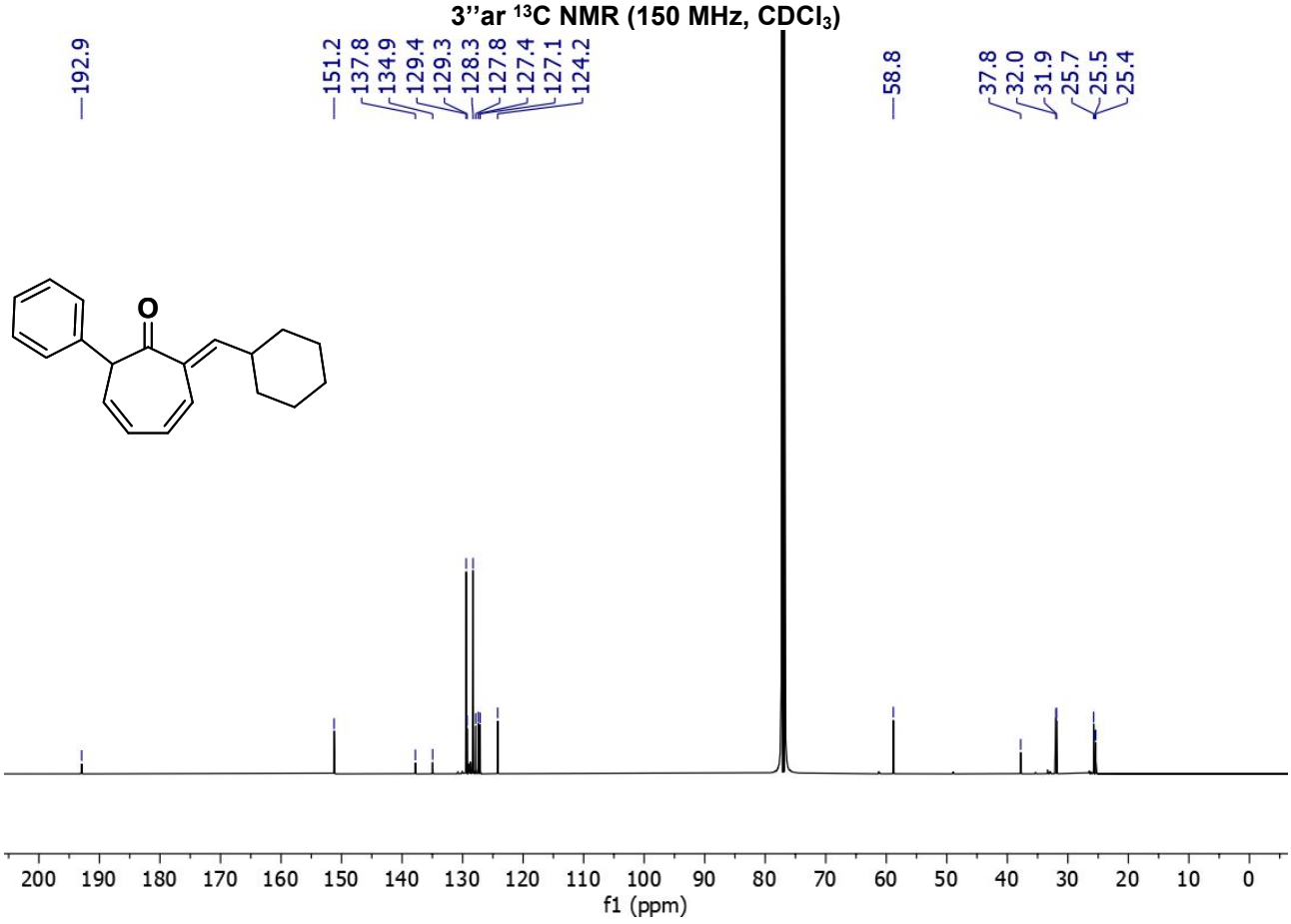
3ar ^{13}C NMR (150 MHz, $CDCl_3$)



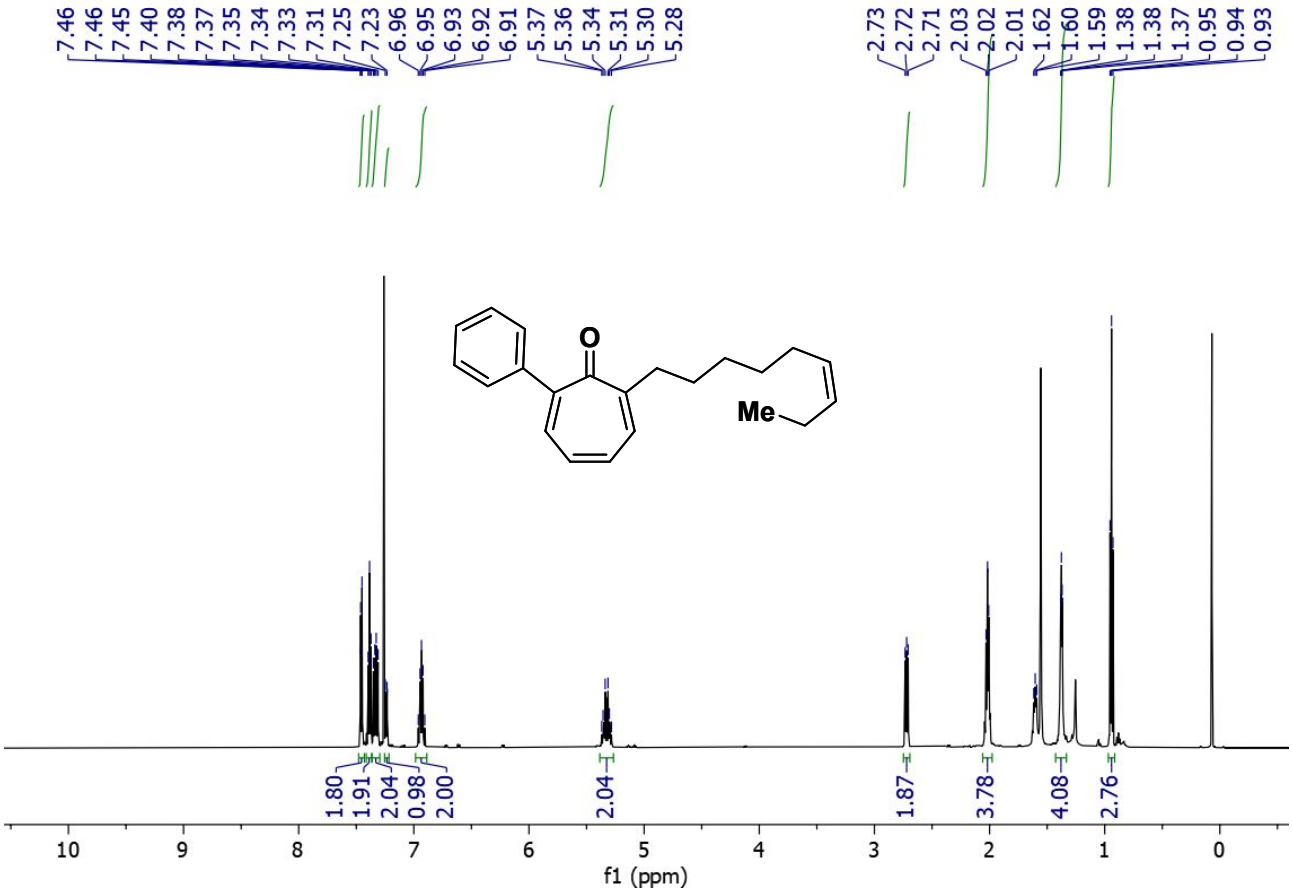
3''ar ^{1}H NMR (600 MHz, $CDCl_3$)



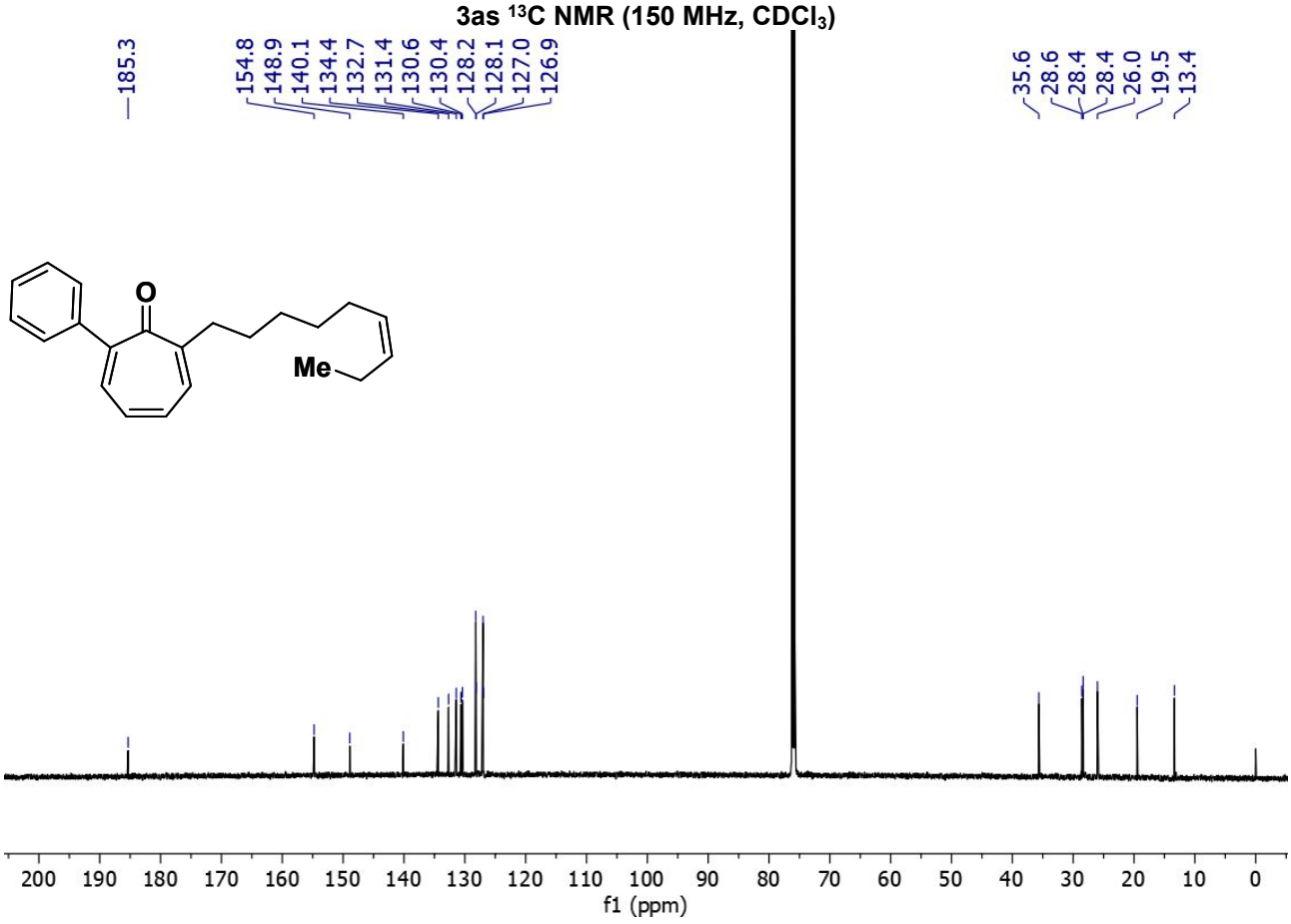
3''ar ^{13}C NMR (150 MHz, $CDCl_3$)



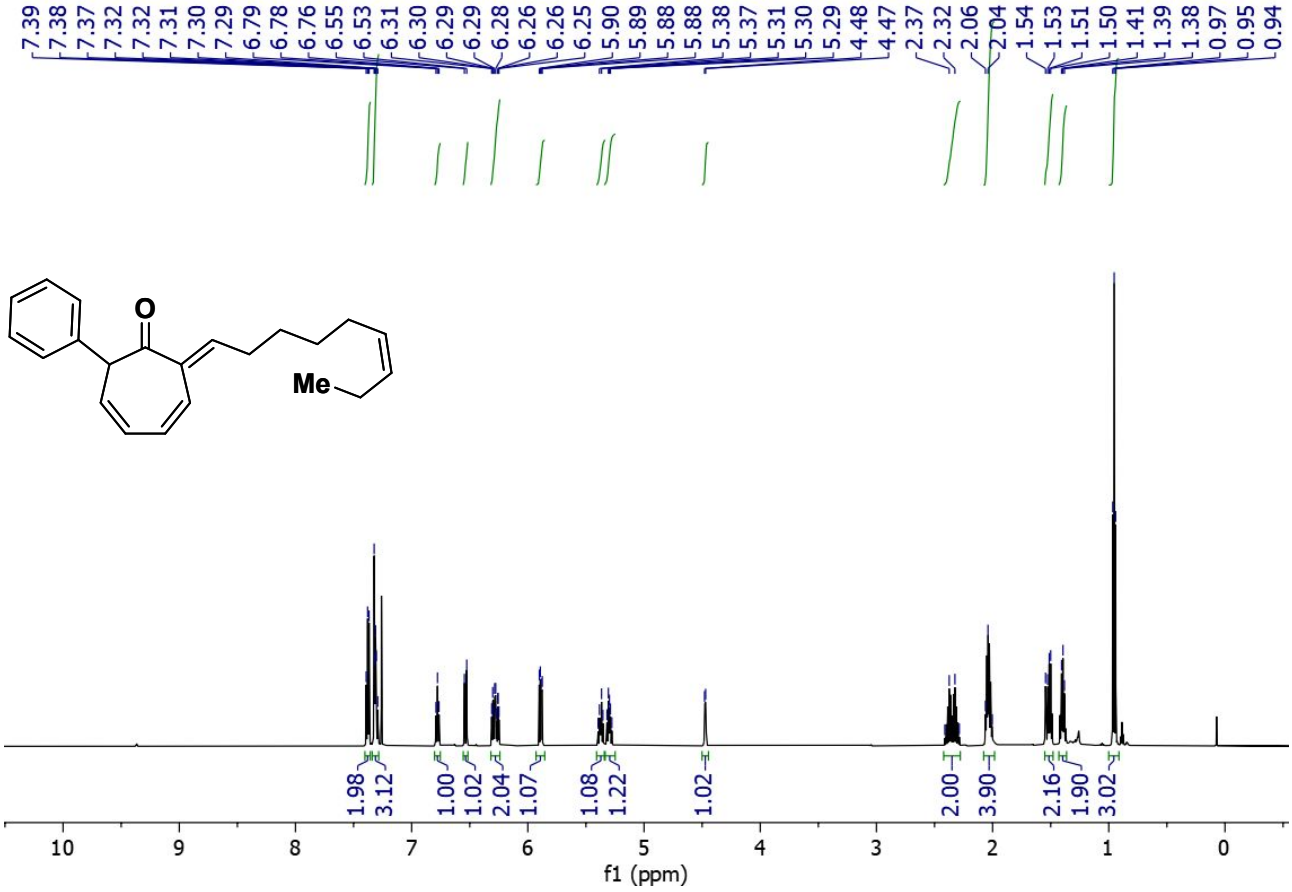
3as ^{1}H NMR (600 MHz, $CDCl_3$)



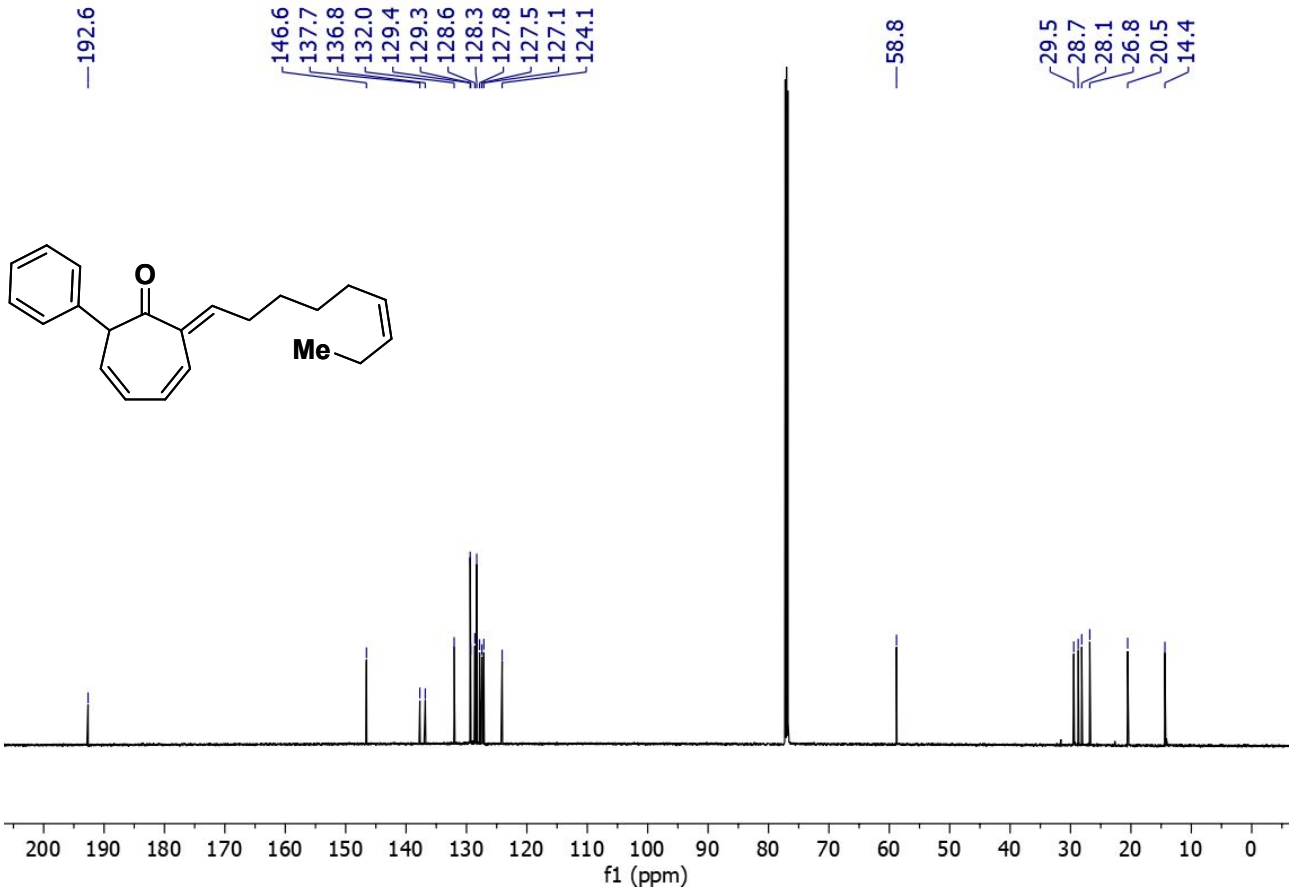
3as ^{13}C NMR (150 MHz, $CDCl_3$)



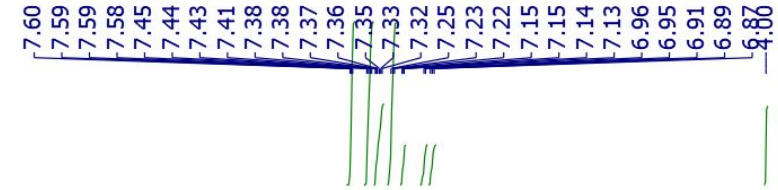
3''as ^{1}H NMR (600 MHz, $CDCl_3$)

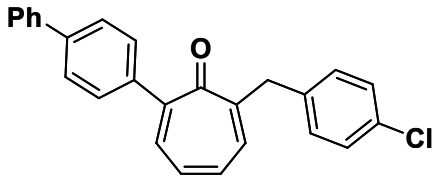


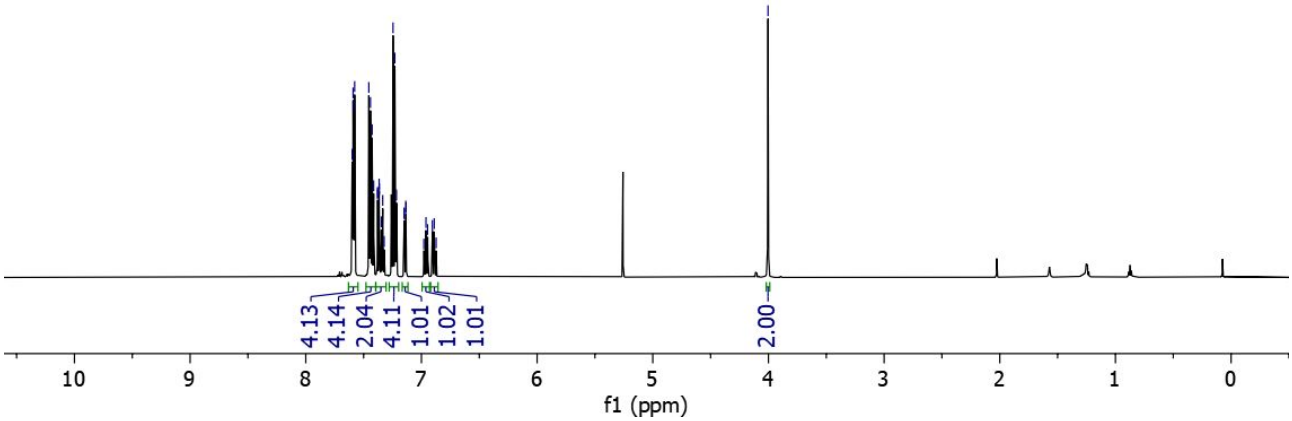
3''as ^{13}C NMR (150 MHz, $CDCl_3$)



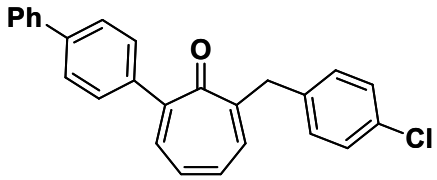
3ba ^{1}H NMR (600 MHz, $CDCl_3$)

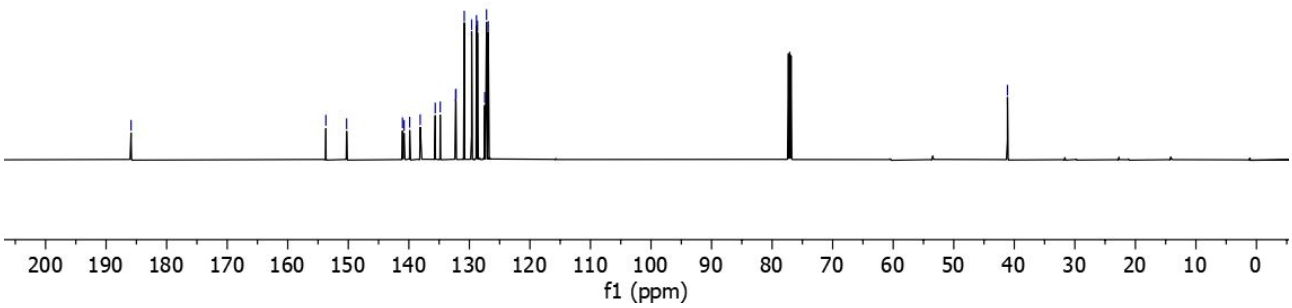




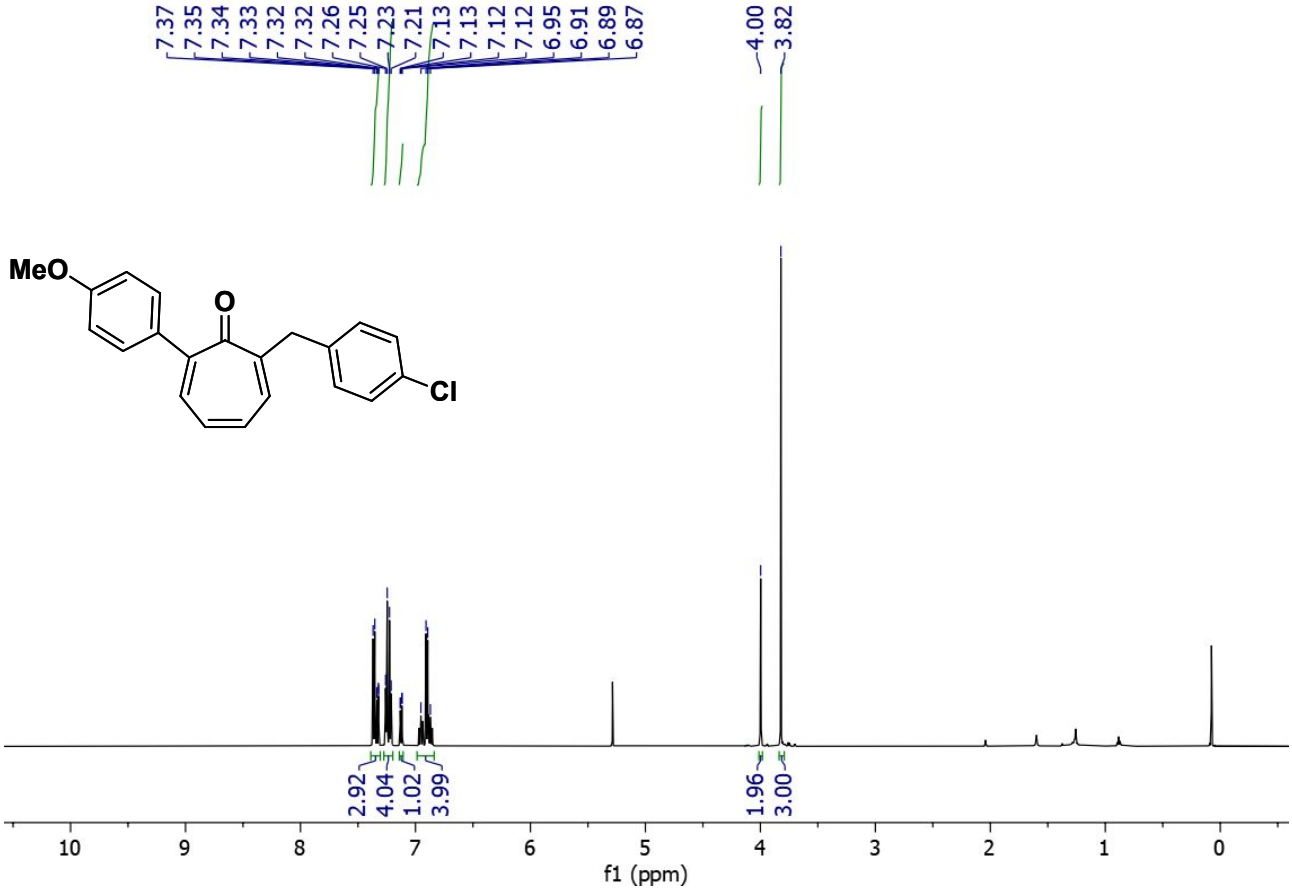


3ba ^{13}C NMR (150 MHz, $CDCl_3$)

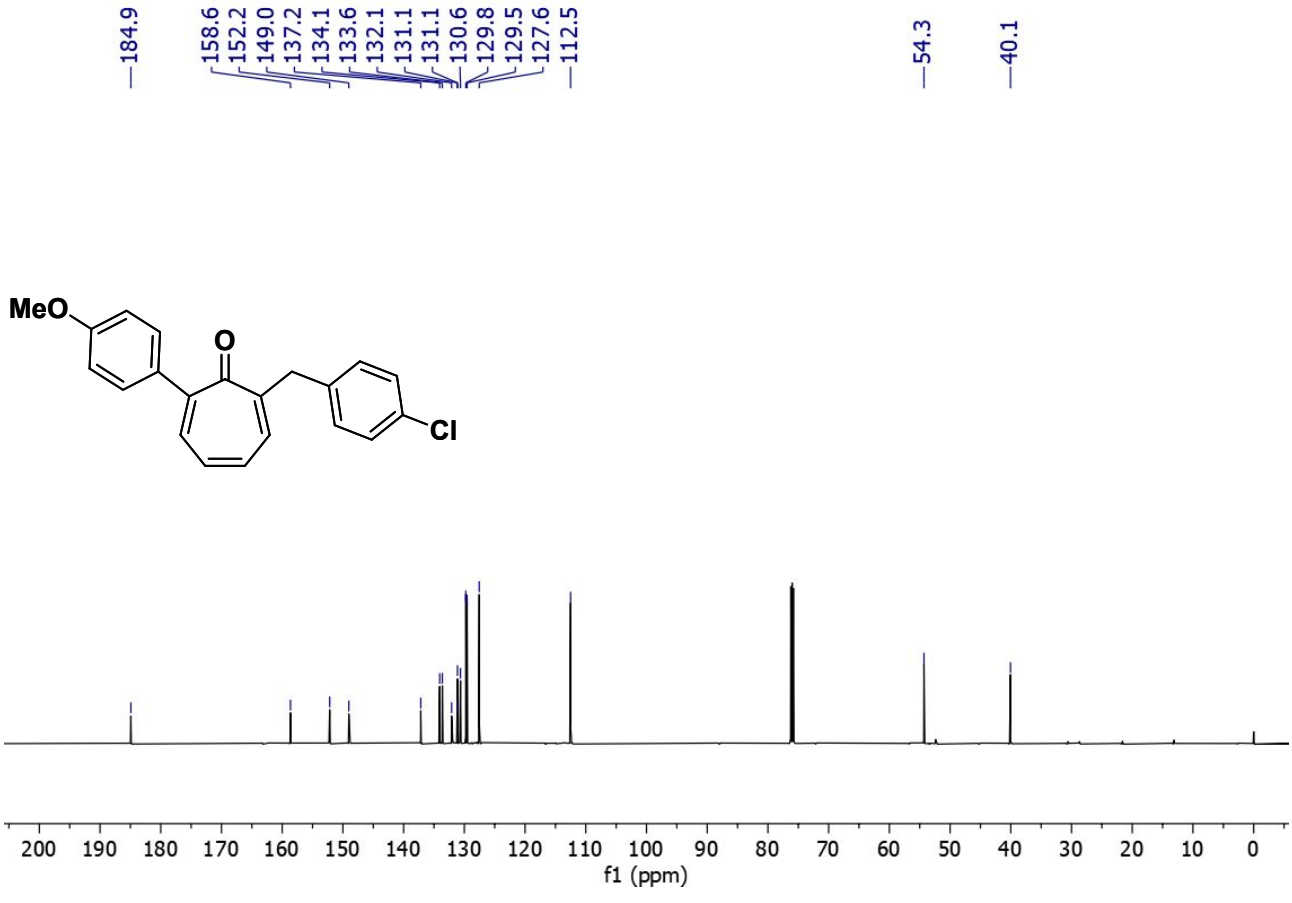




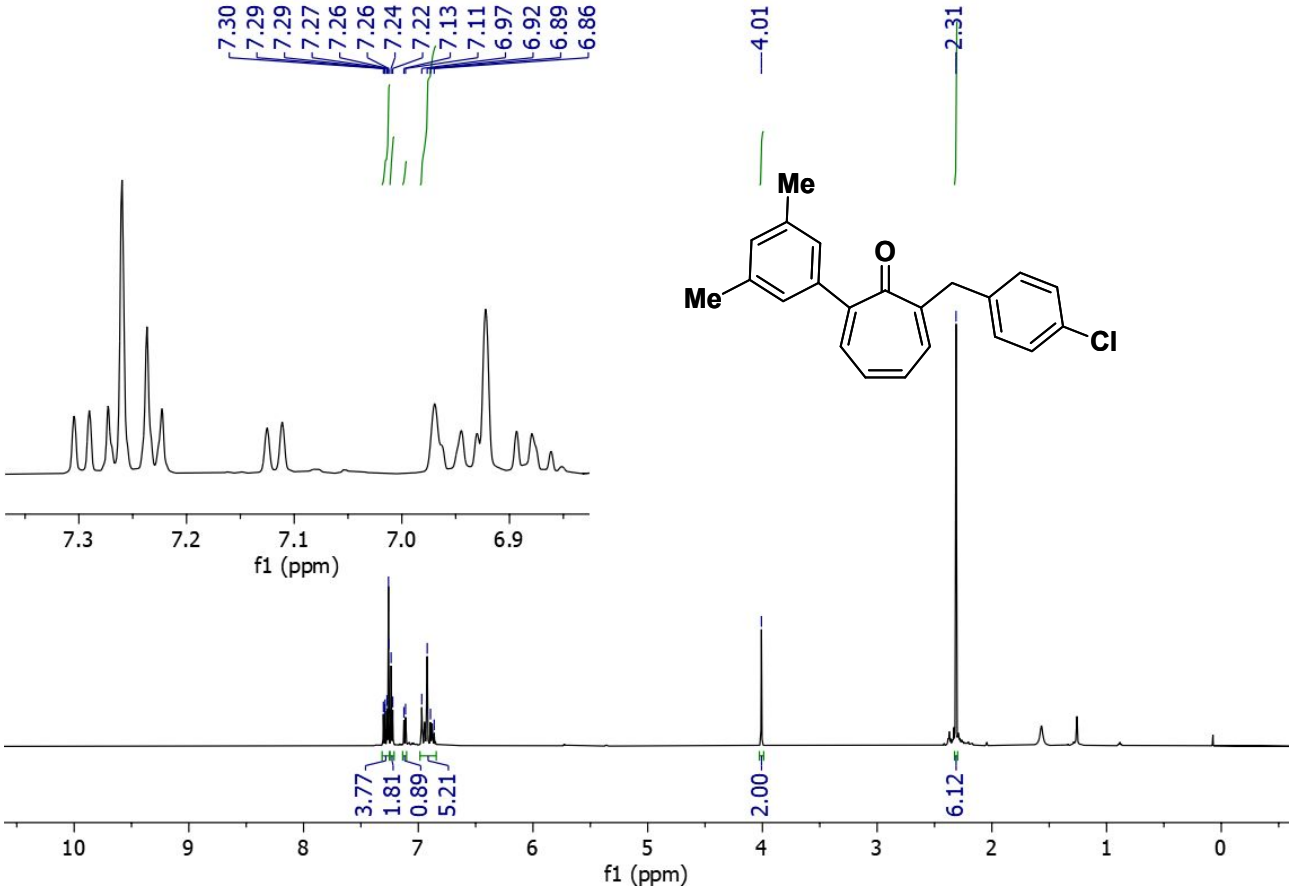
3ca ^{1}H NMR (600 MHz, $CDCl_3$)



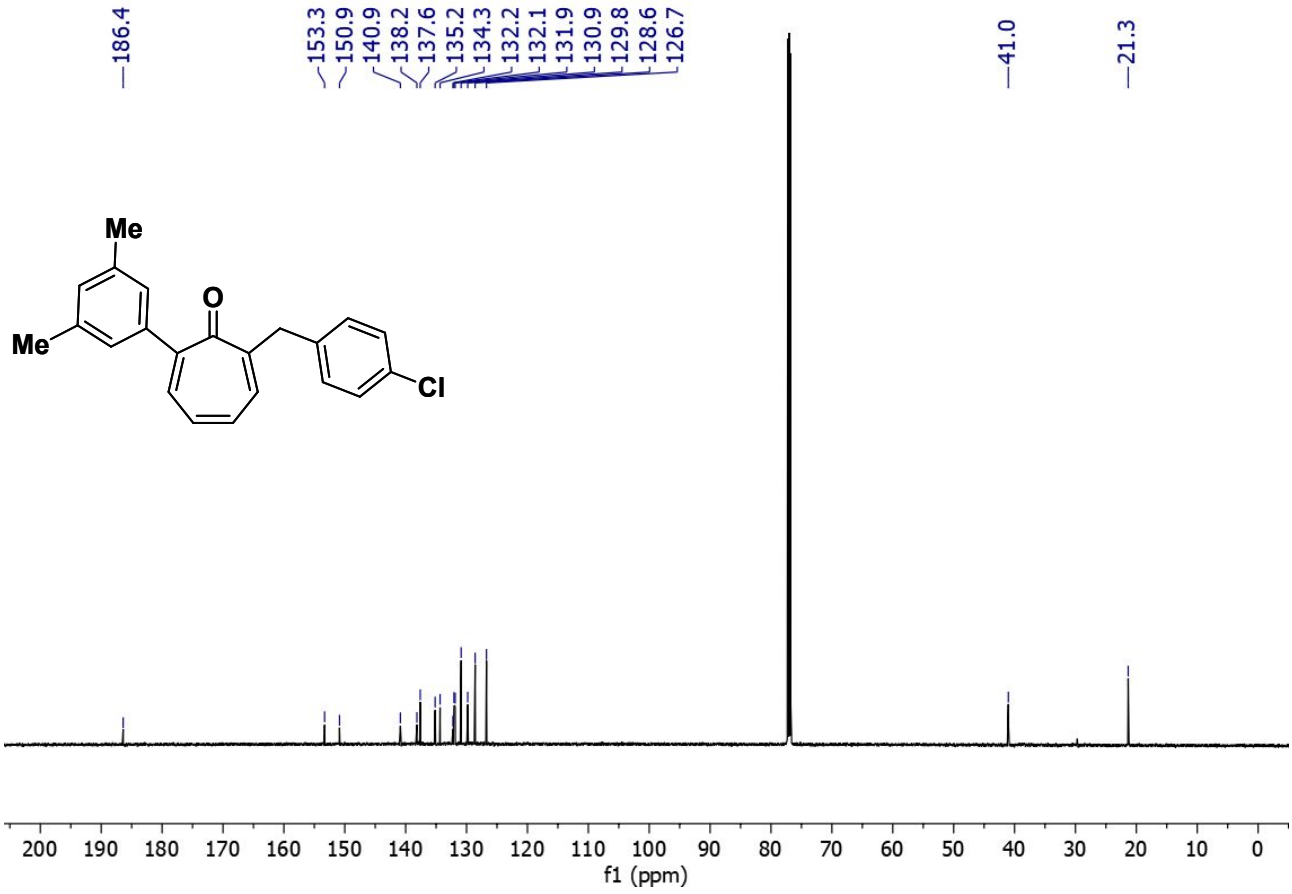
3ca ^{13}C NMR (150 MHz, $CDCl_3$)



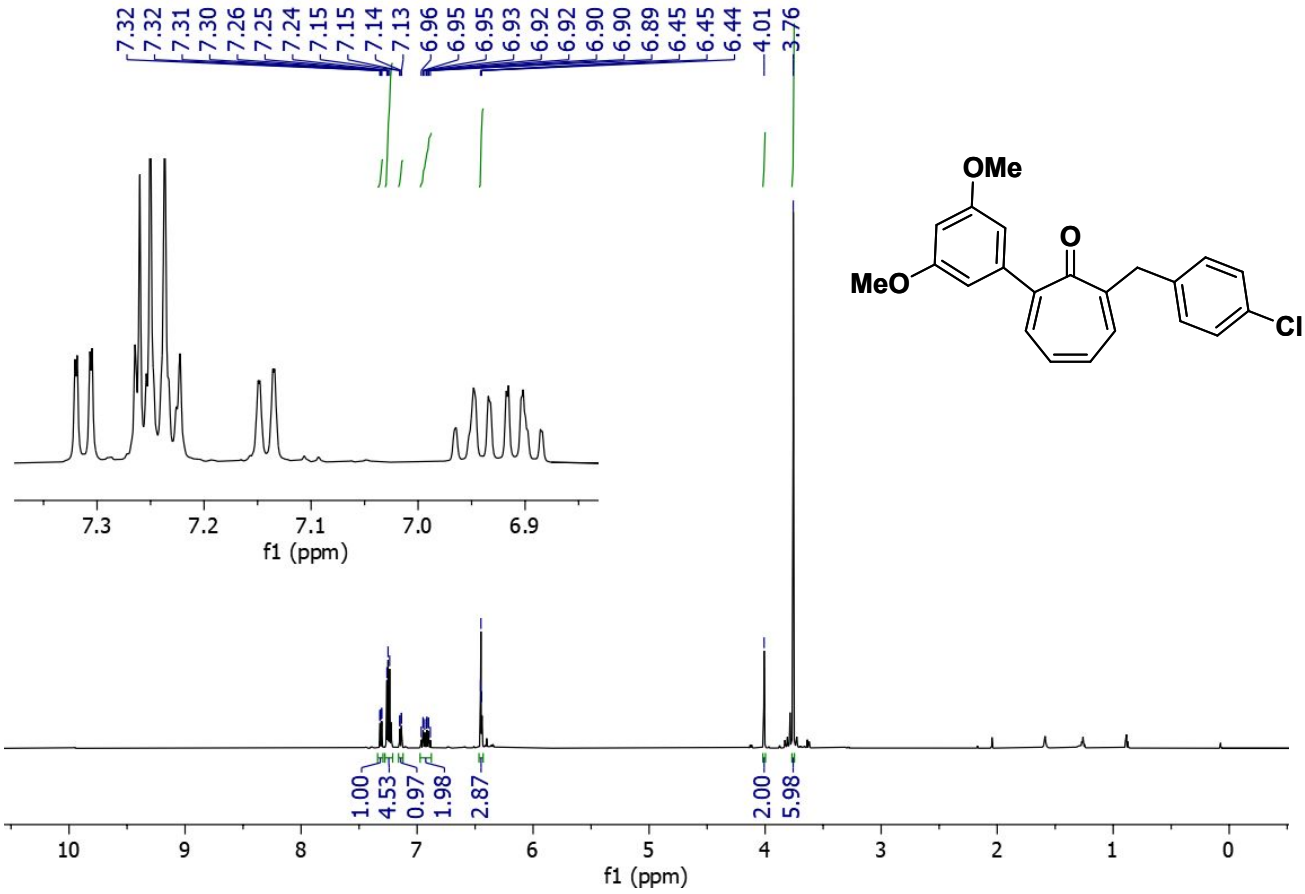
3da ^{1}H NMR (600 MHz, $CDCl_3$)



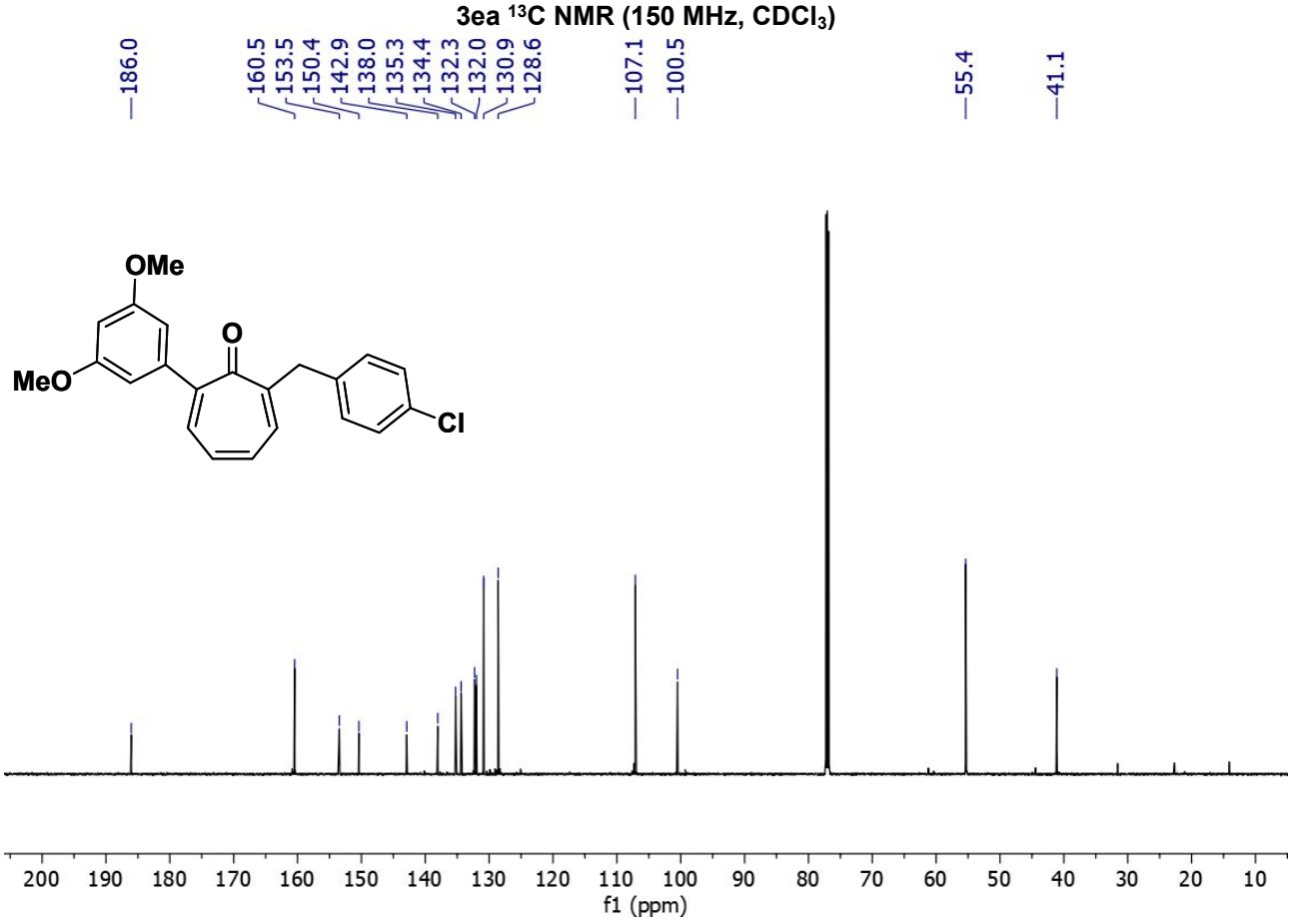
3da ^{13}C NMR (150 MHz, $CDCl_3$)



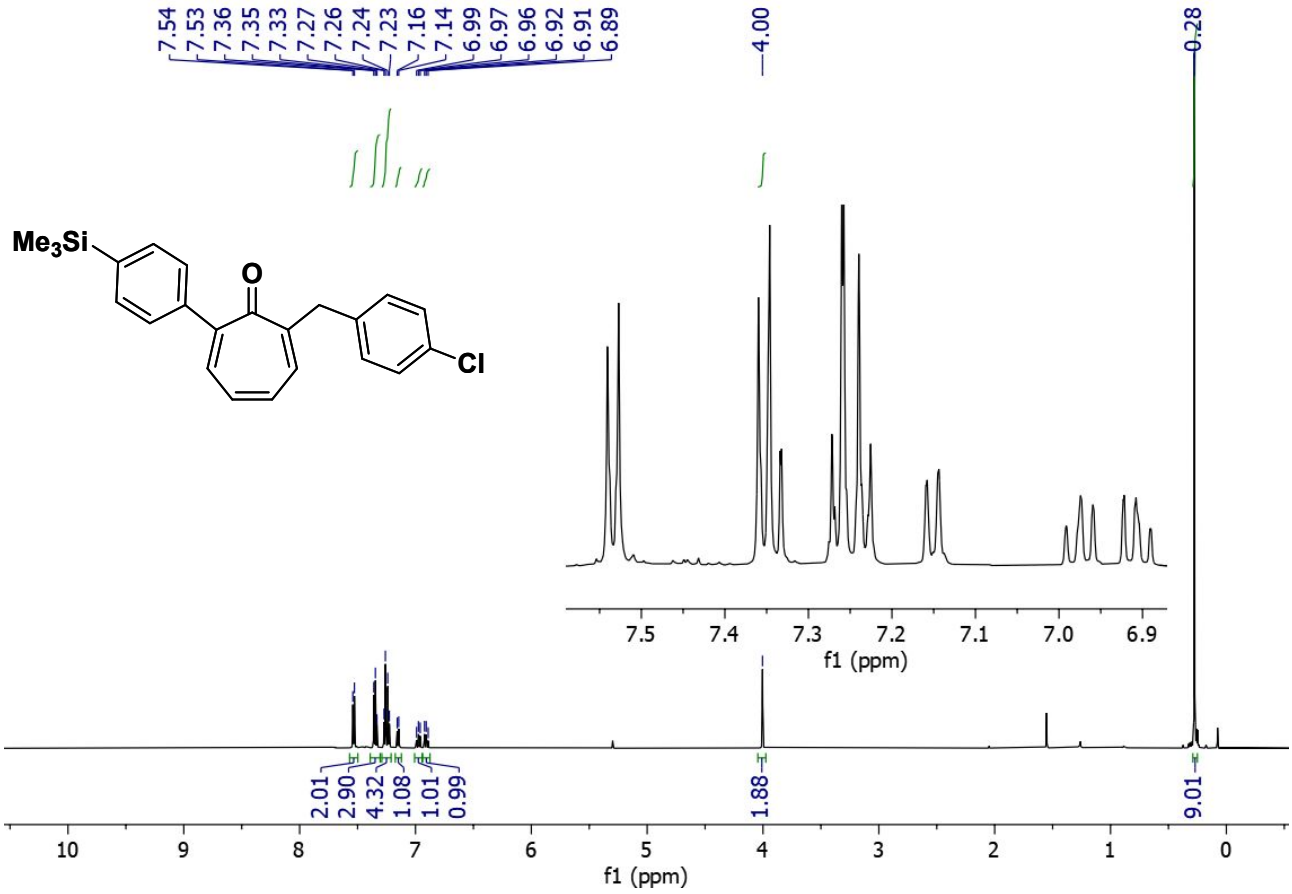
3ea ^{1}H NMR (600 MHz, $CDCl_3$)



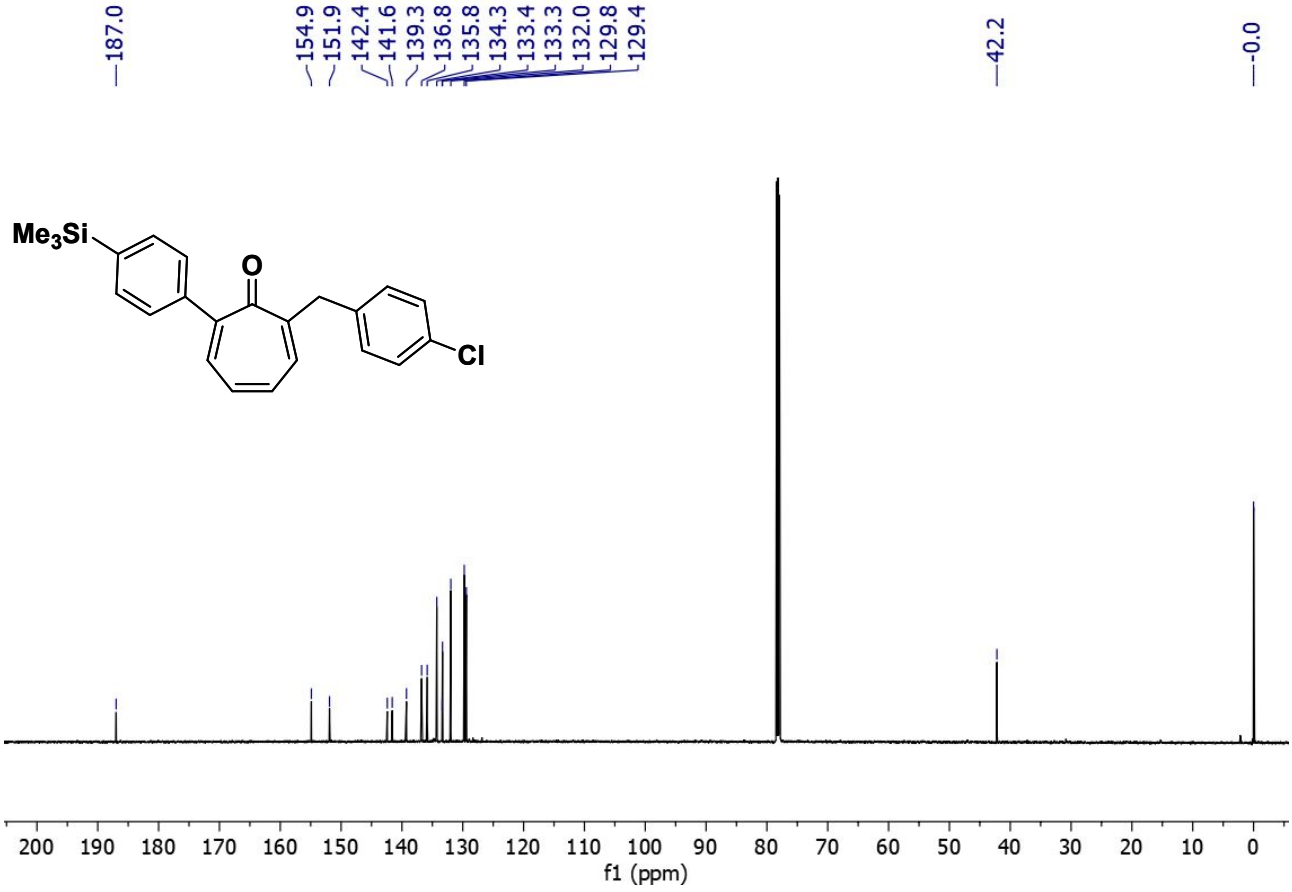
3ea ^{13}C NMR (150 MHz, $CDCl_3$)



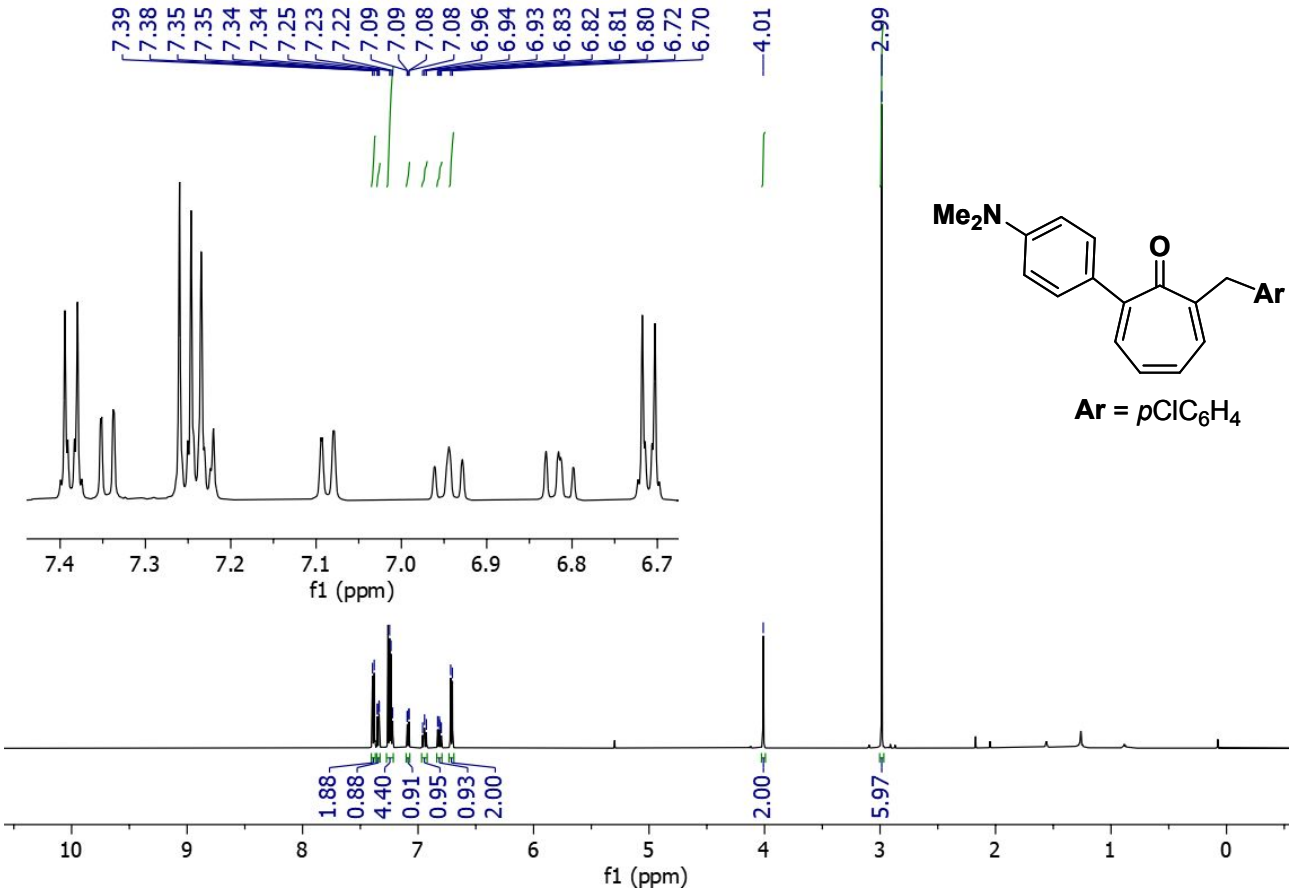
3fa ^{1}H NMR (600 MHz, $CDCl_3$)



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

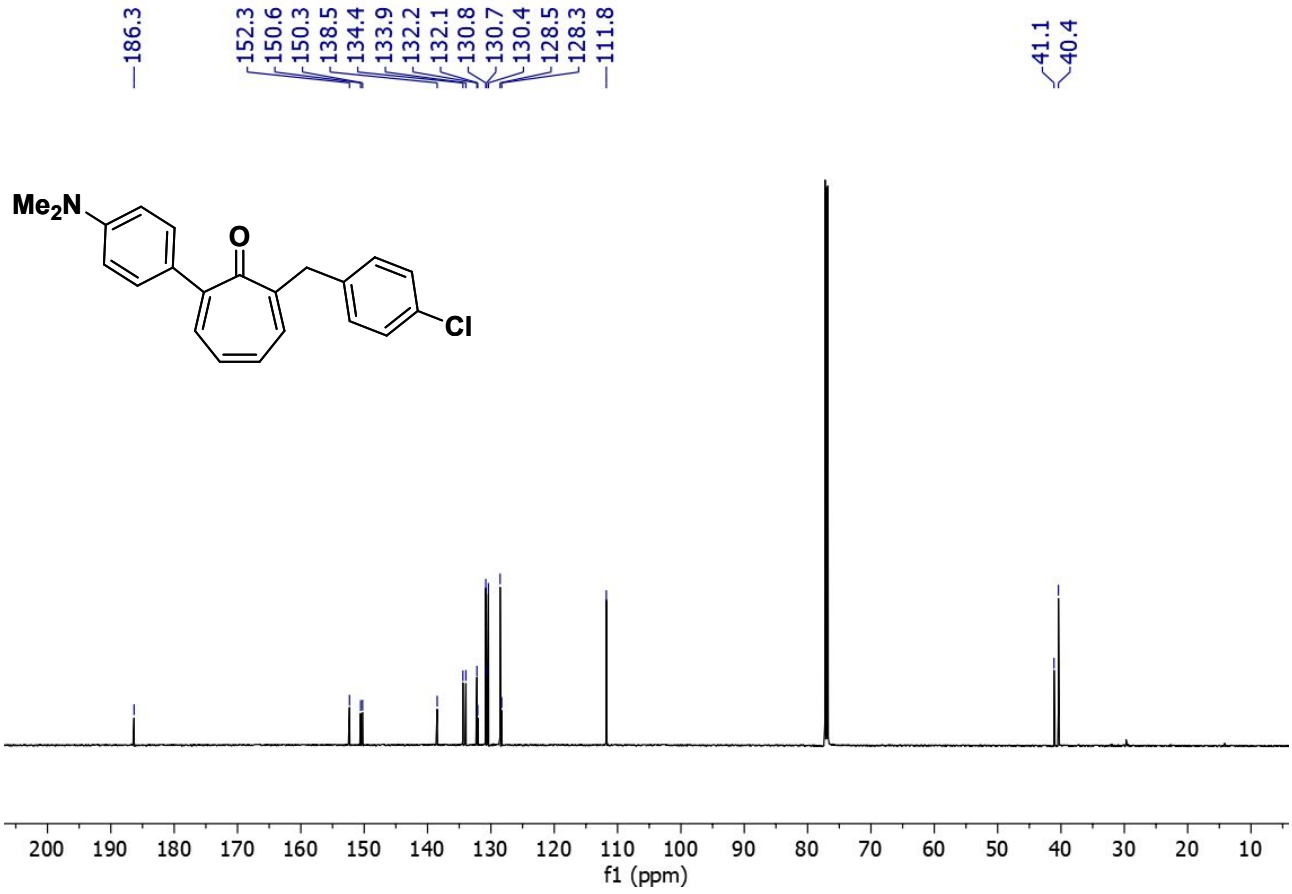


3ga ^{1}H NMR (600 MHz, $CDCl_3$)

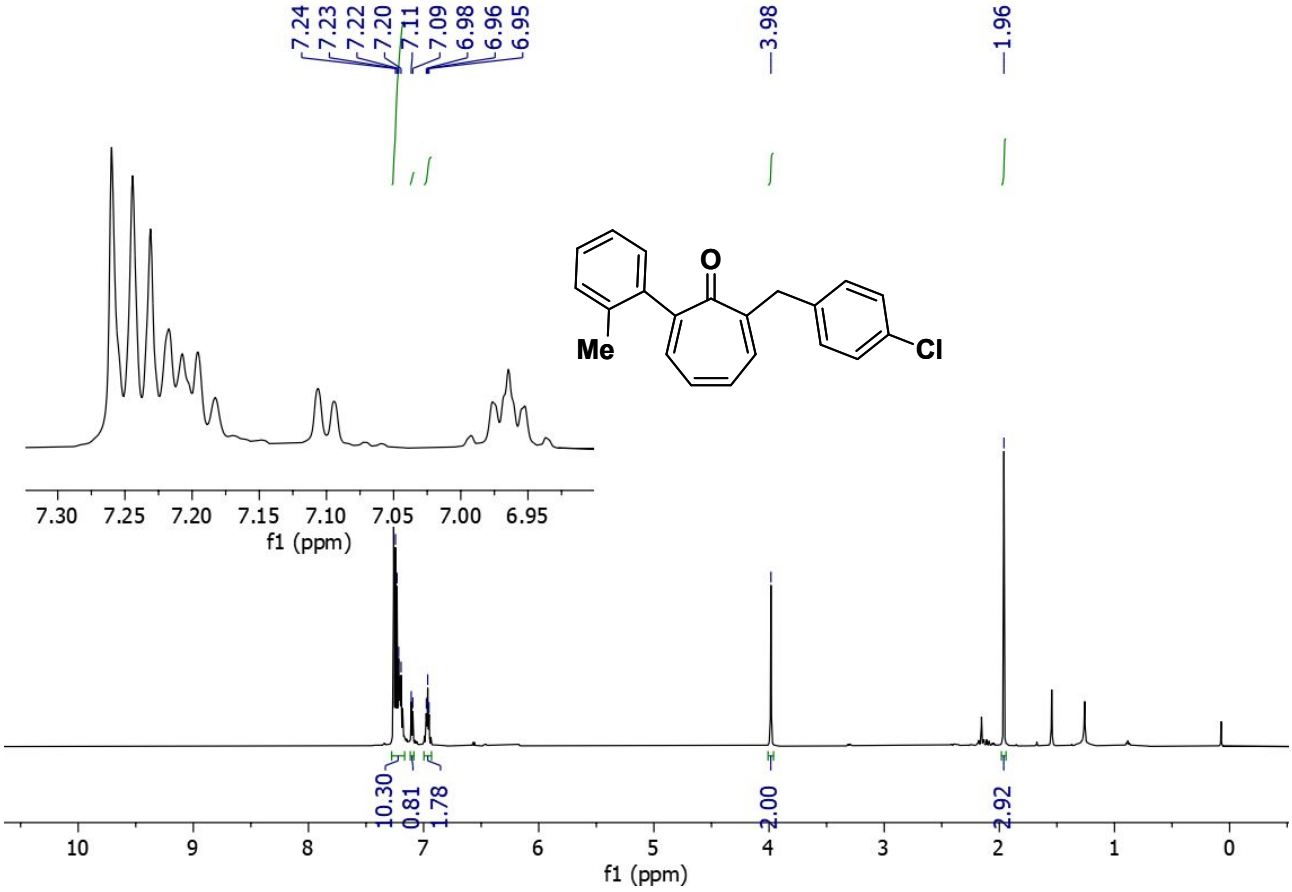


Ar = *p*ClC_6H_4

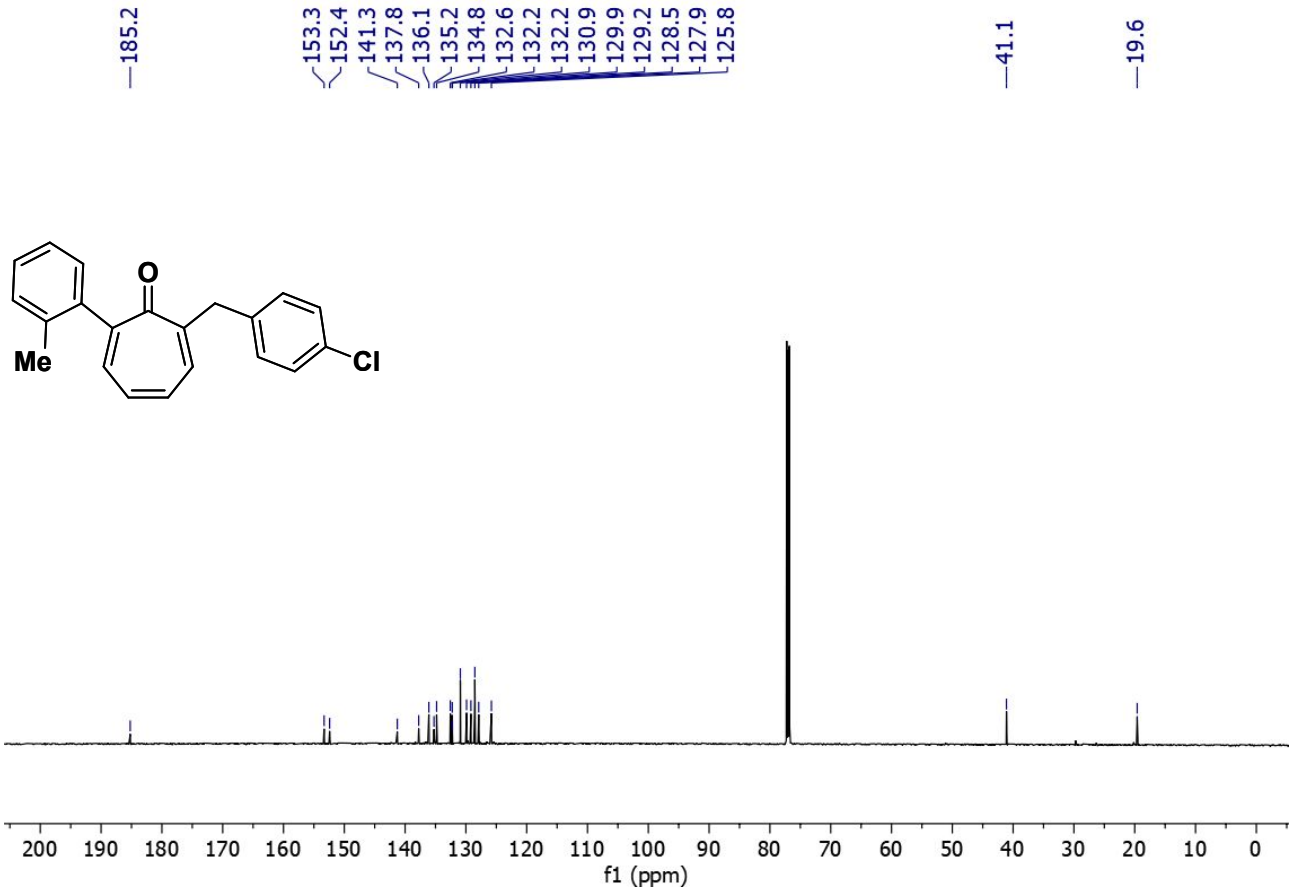
3ga ^{13}C NMR (150 MHz, $CDCl_3$)



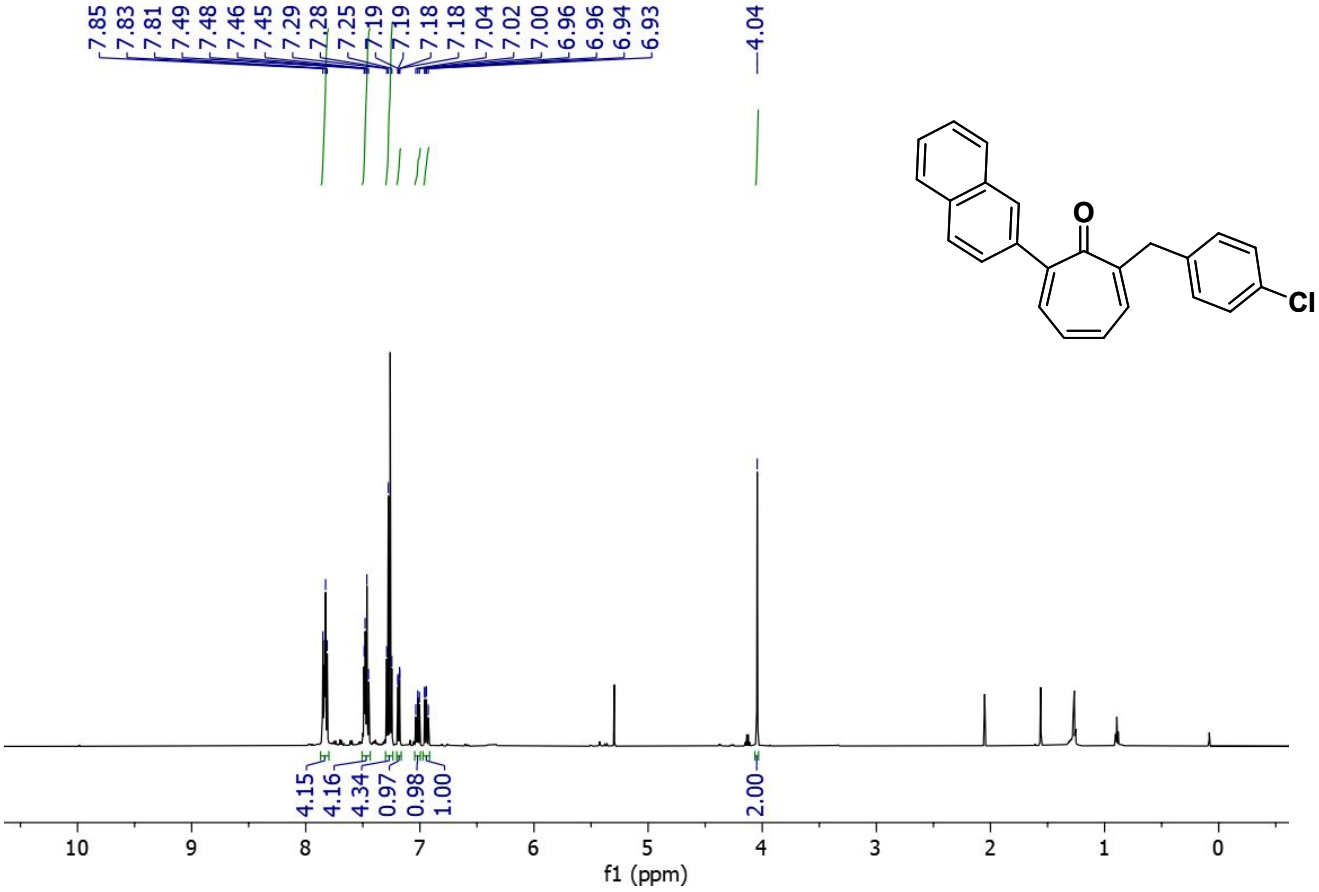
3ha ^{1}H NMR (600 MHz, $CDCl_3$)



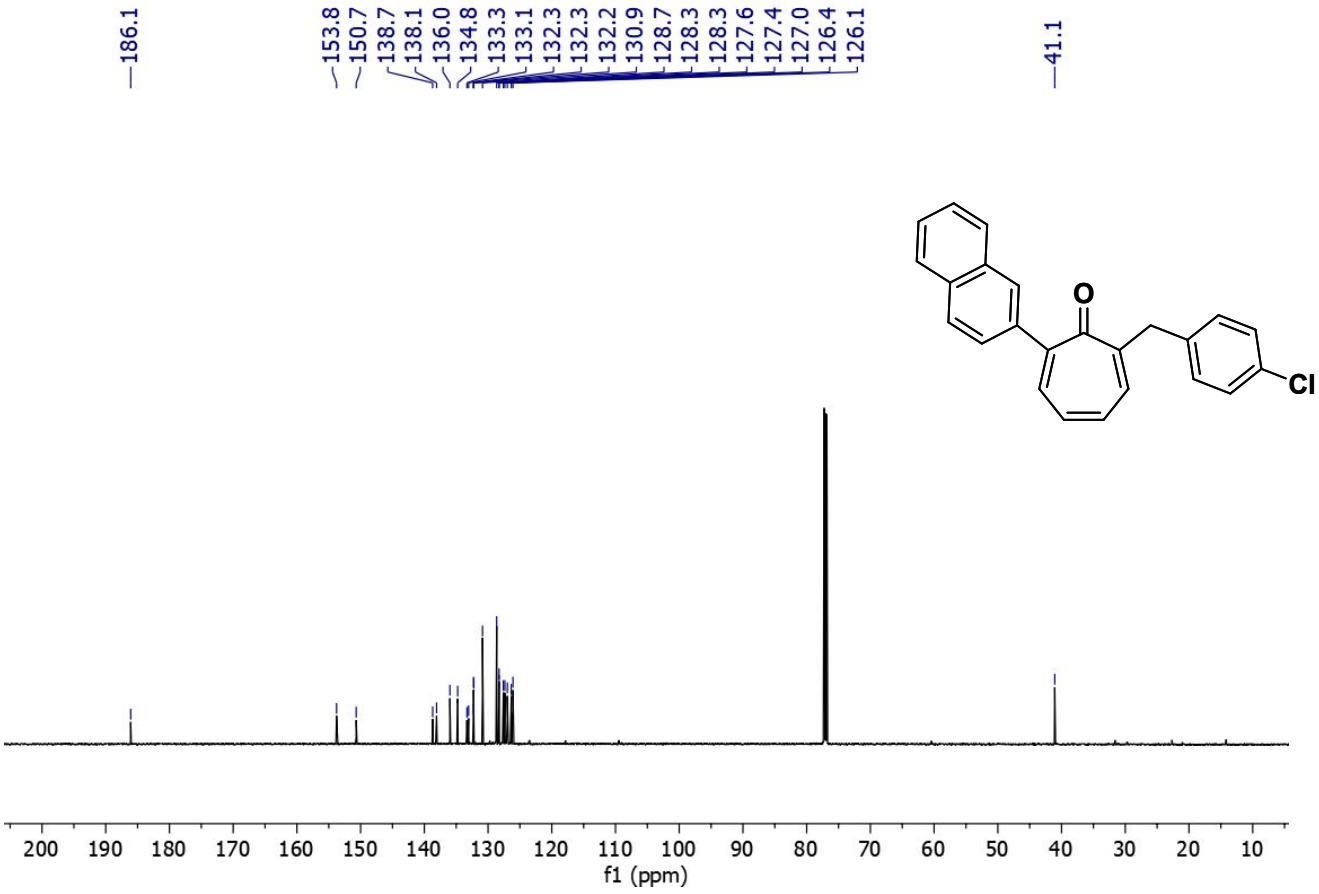
3ha ^{13}C NMR (150 MHz, $CDCl_3$)



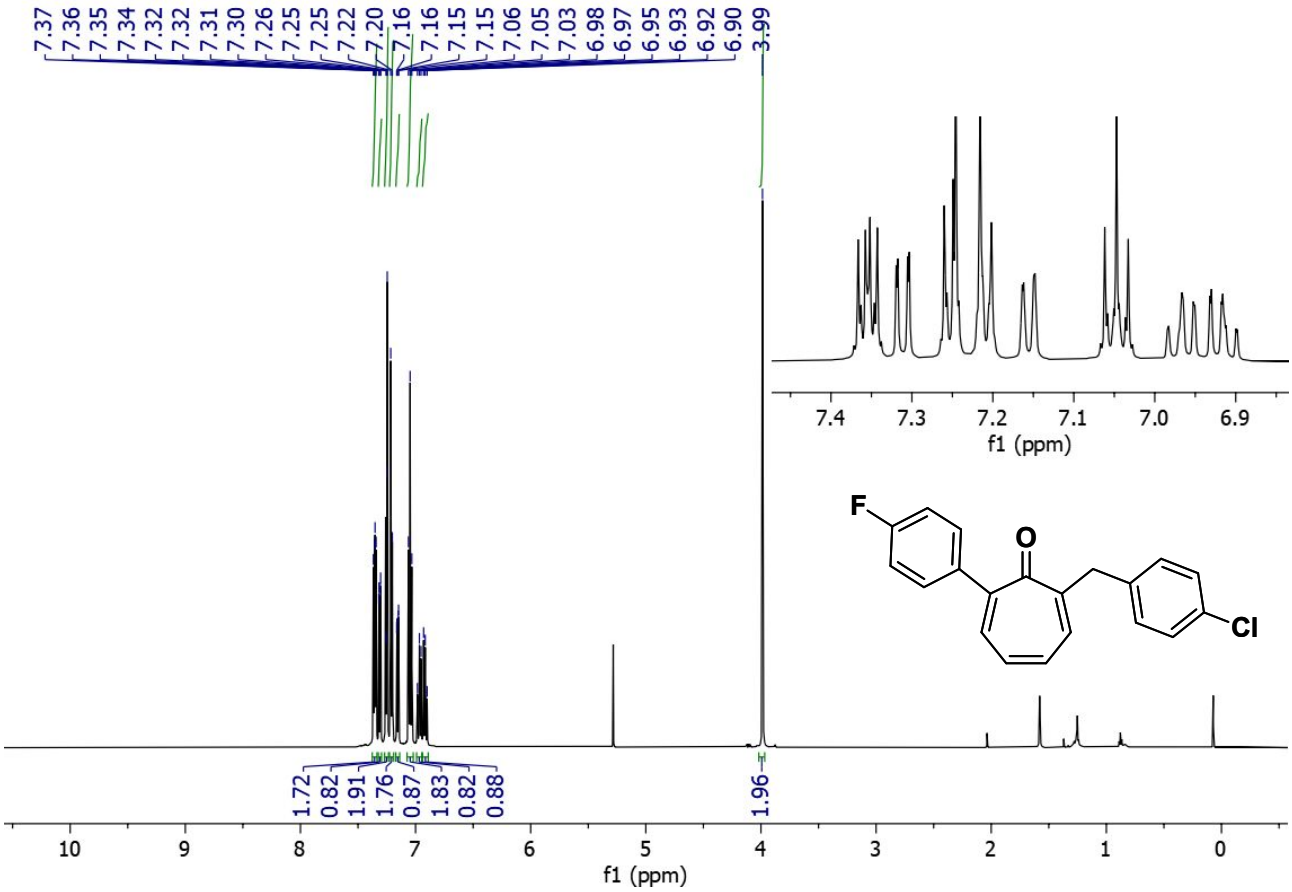
3ia ^{1}H NMR (600 MHz, $CDCl_3$)



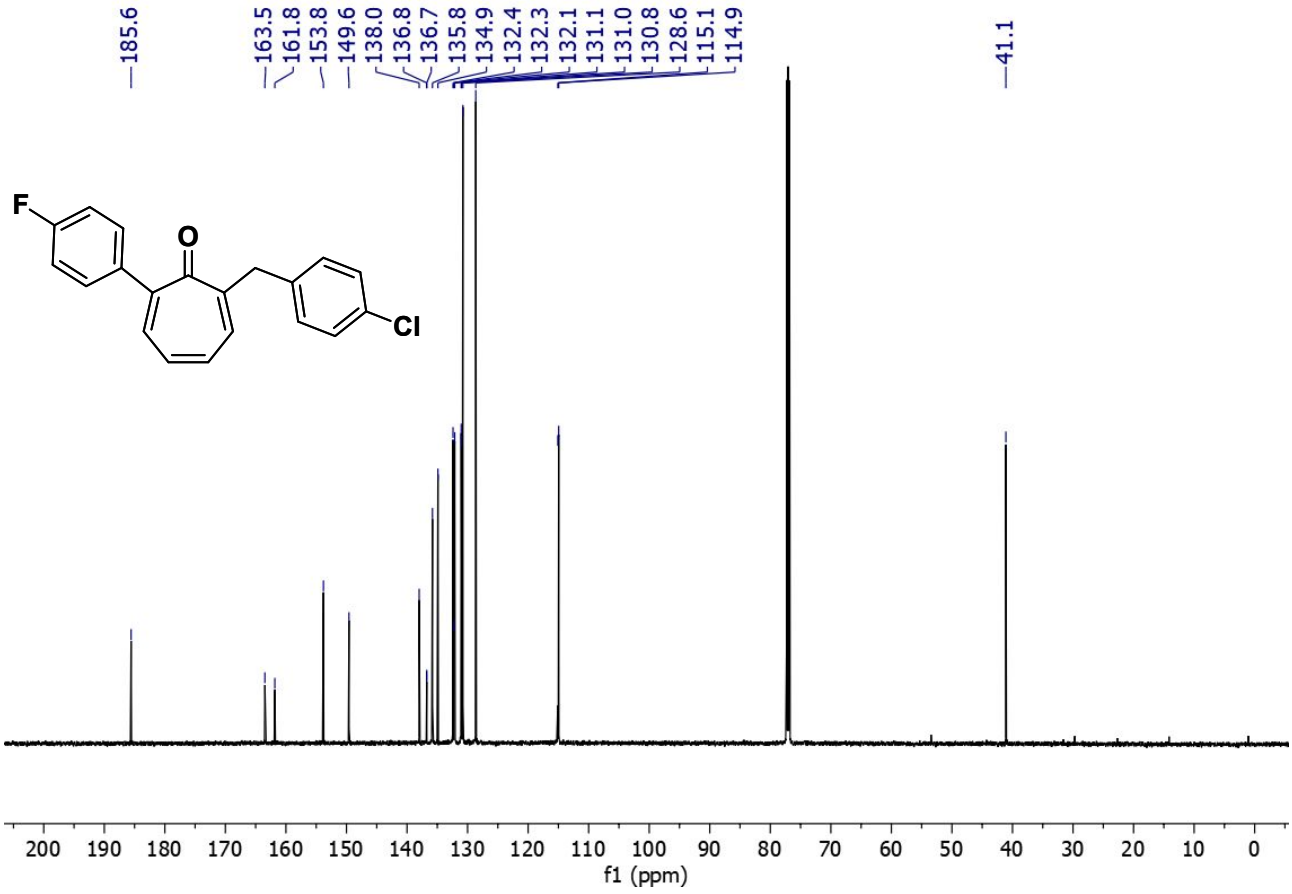
3ia ^{13}C NMR (150 MHz, $CDCl_3$)



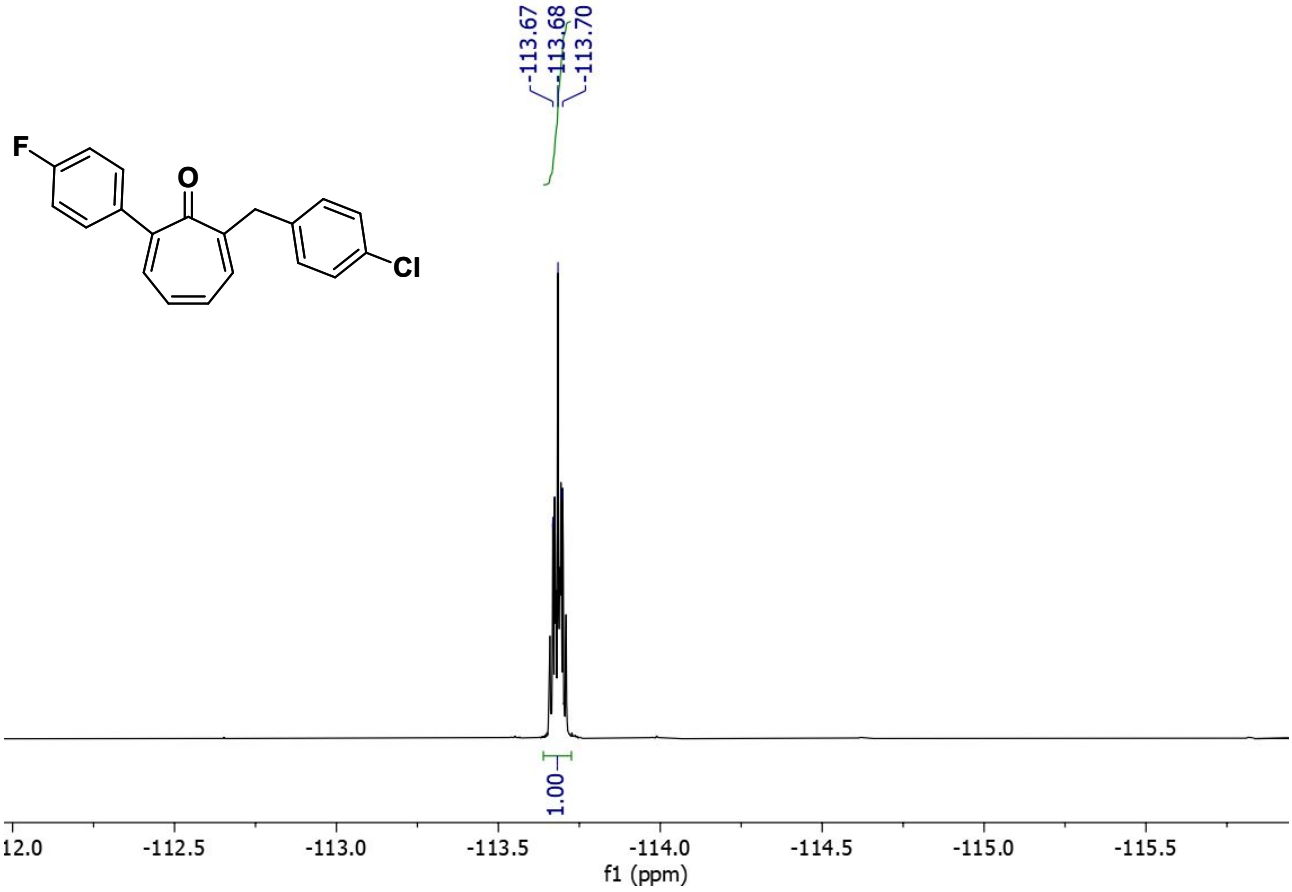
3ja ^{1}H NMR (600 MHz, $CDCl_3$)



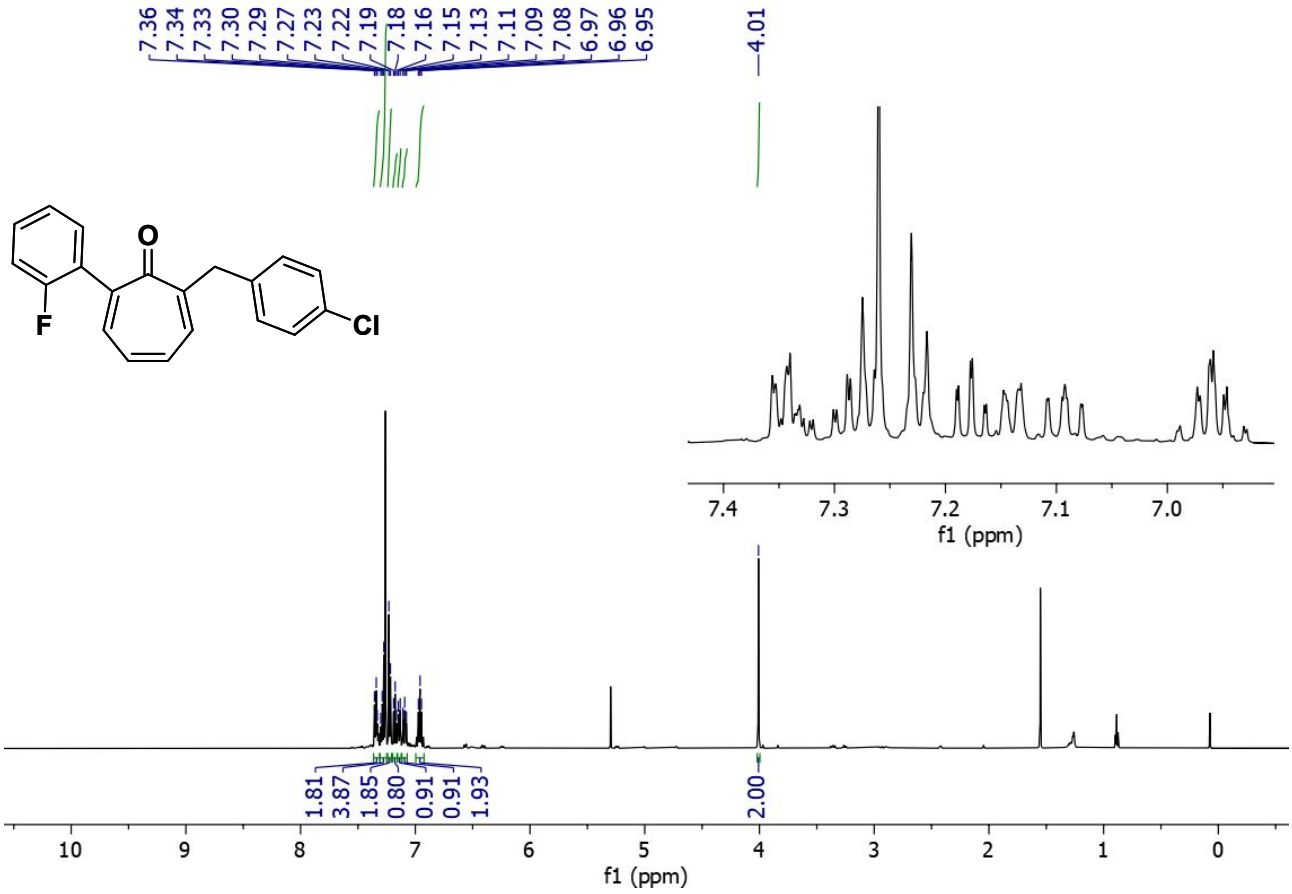
3ja ^{13}C NMR (150 MHz, $CDCl_3$)



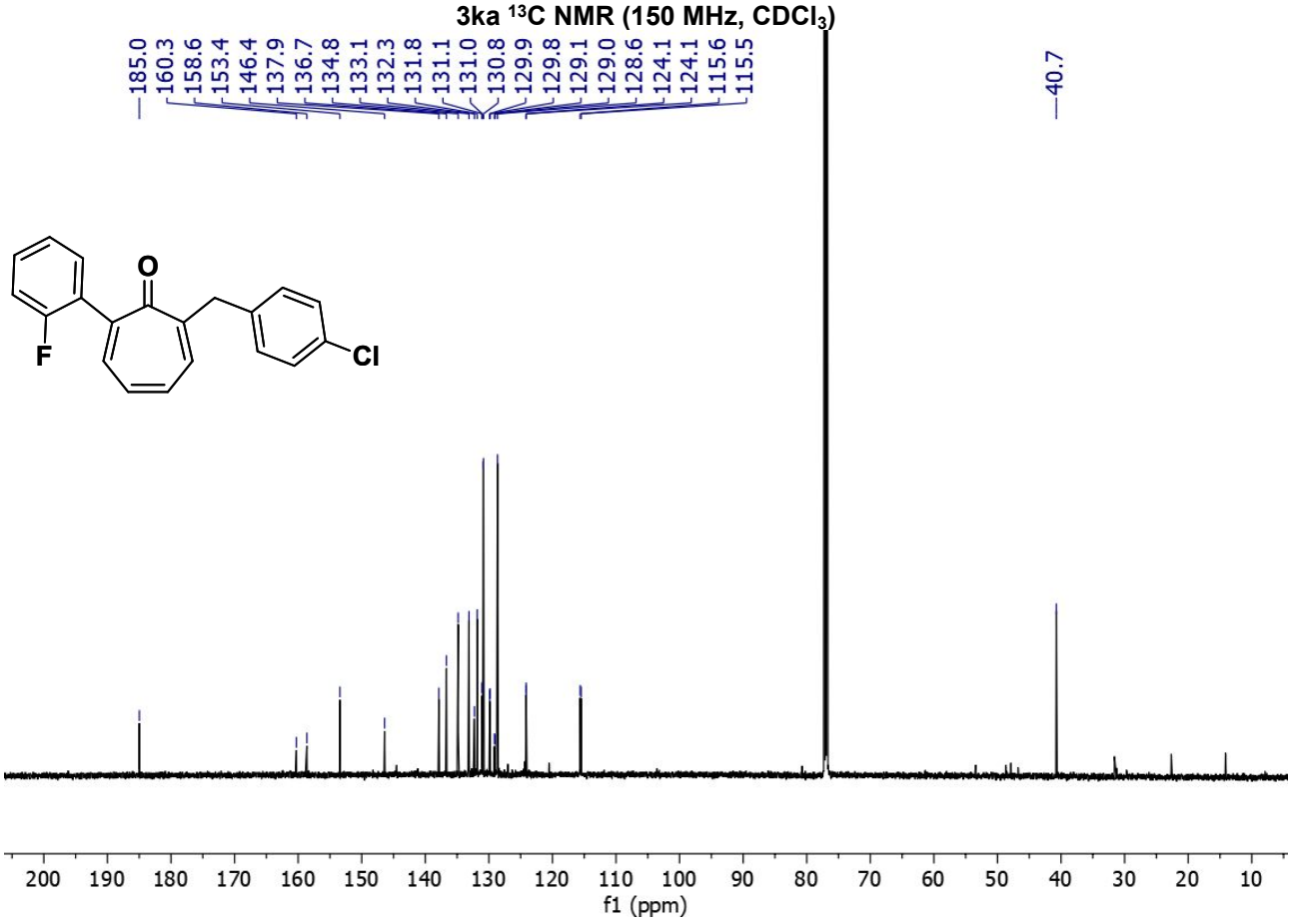
3ja ^{19}F NMR (565 MHz, $CDCl_3$)



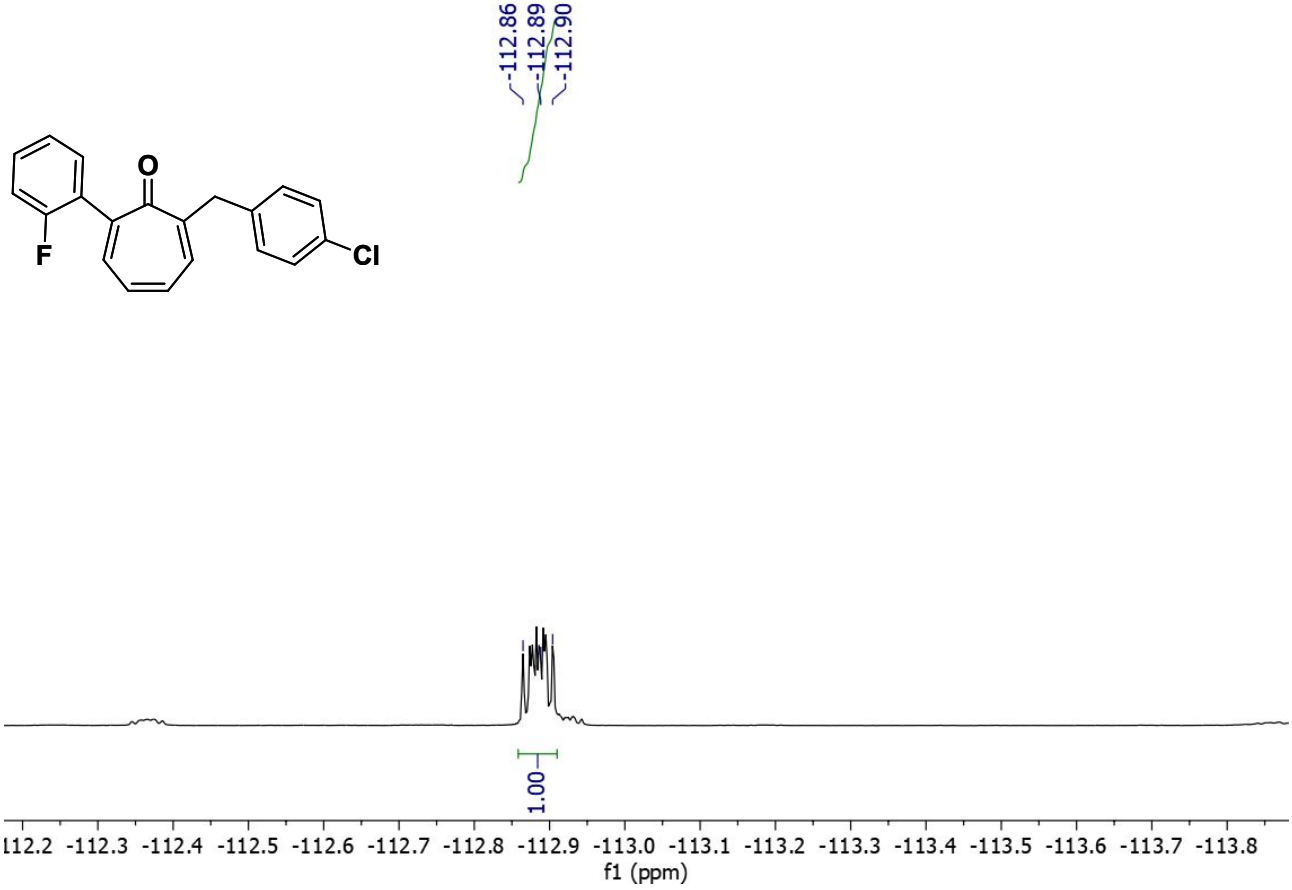
3ka ^{1}H NMR (600 MHz, $CDCl_3$)



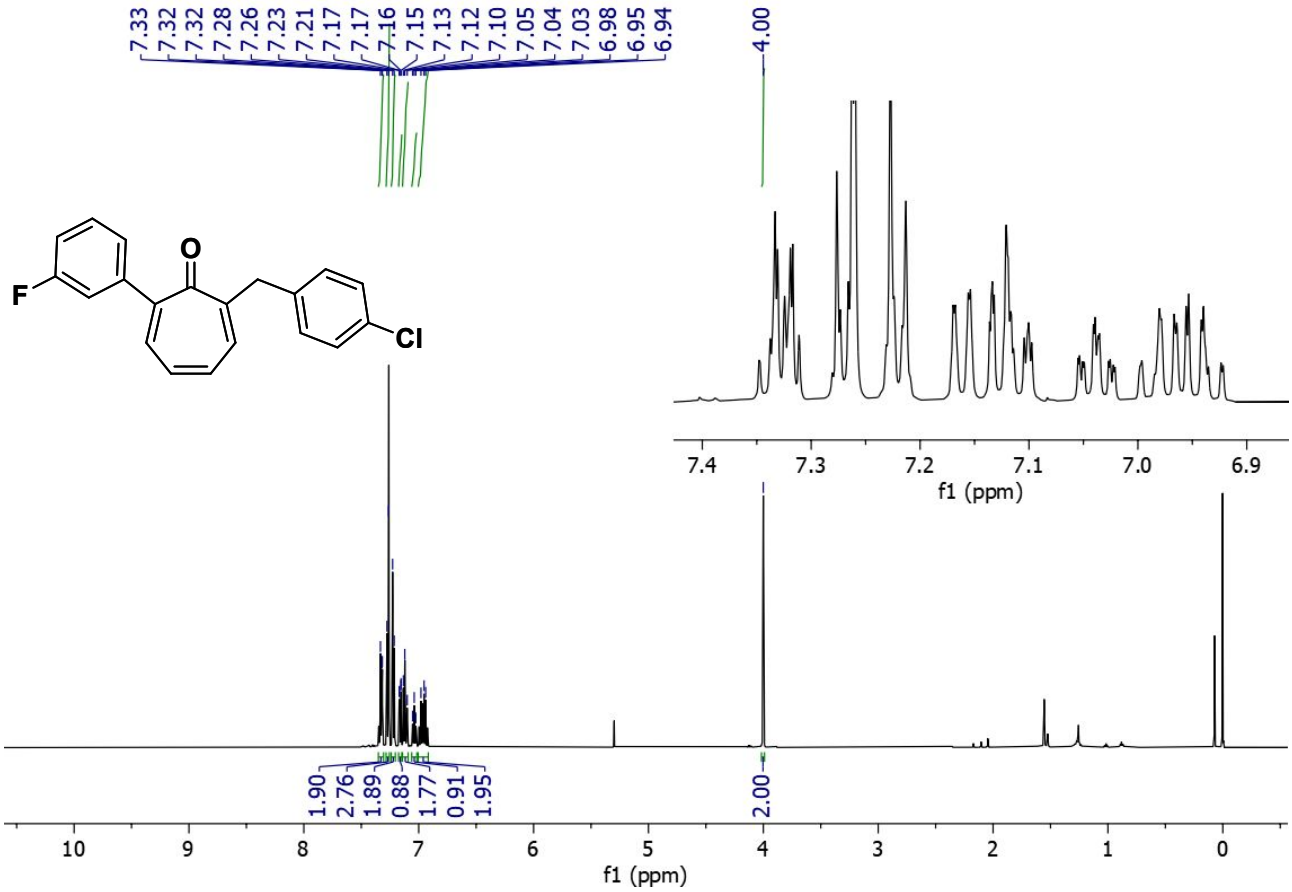
3ka ^{13}C NMR (150 MHz, $CDCl_3$)



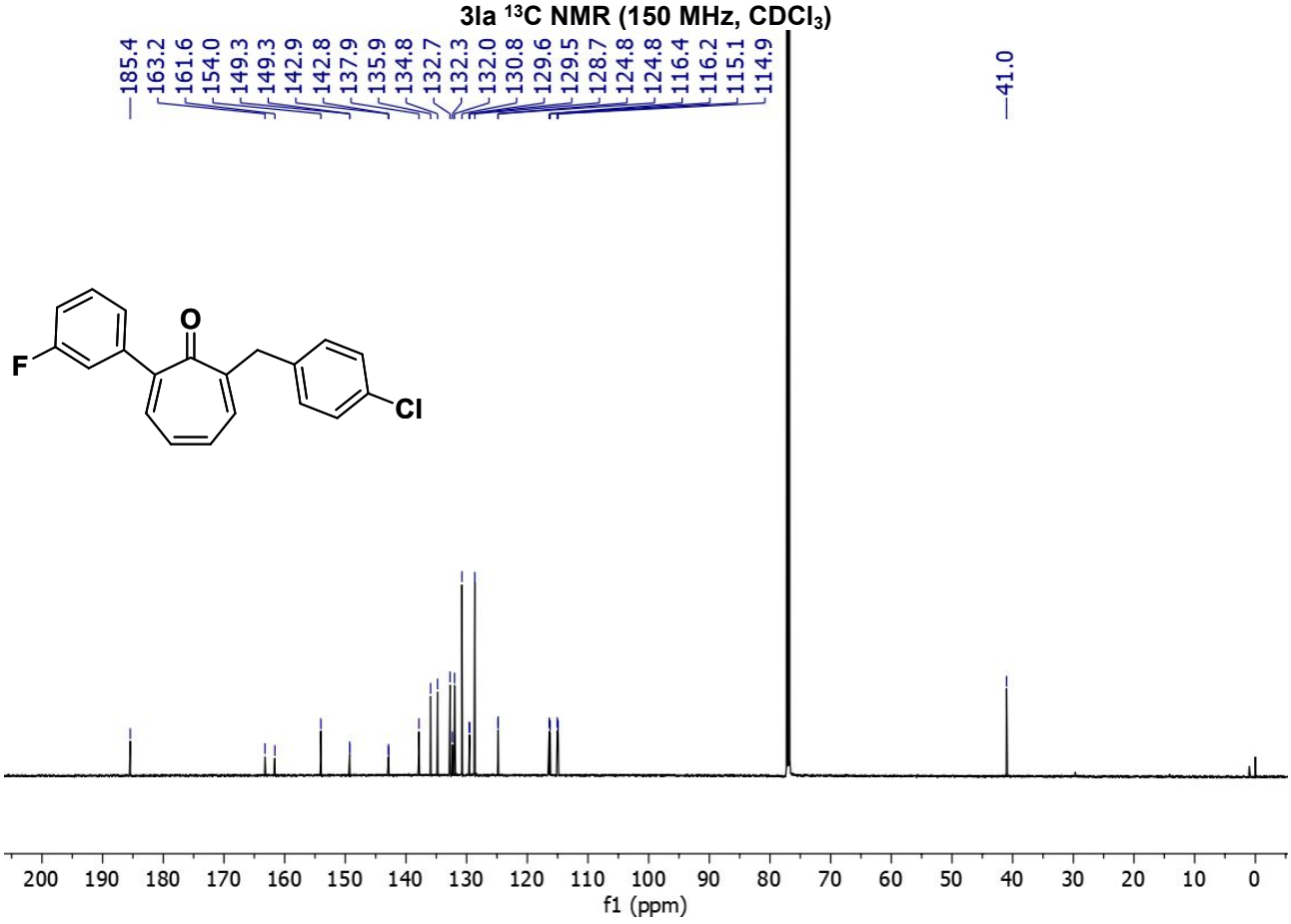
3ka ^{19}F NMR (565 MHz, $CDCl_3$)



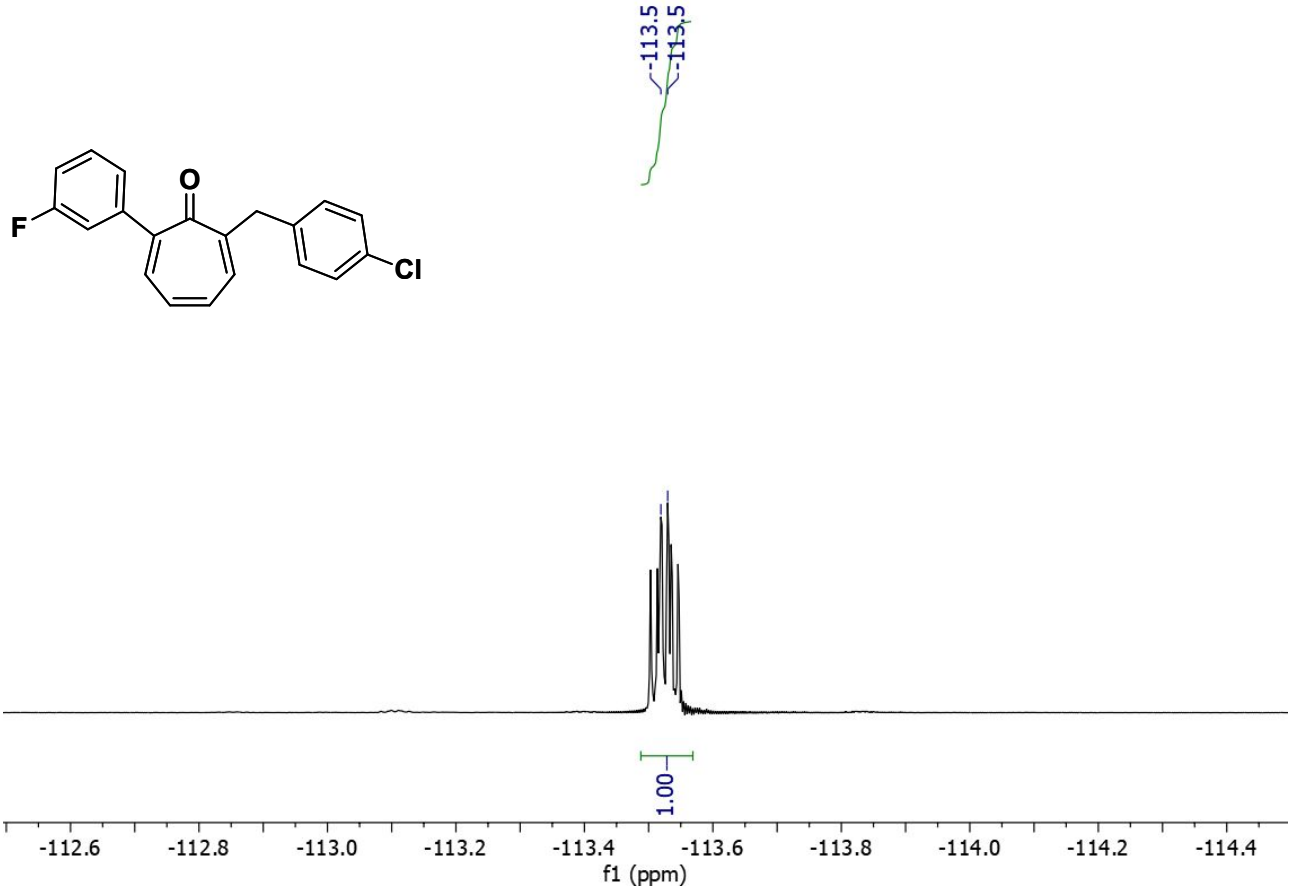
3la ^{1}H NMR (600 MHz, $CDCl_3$)



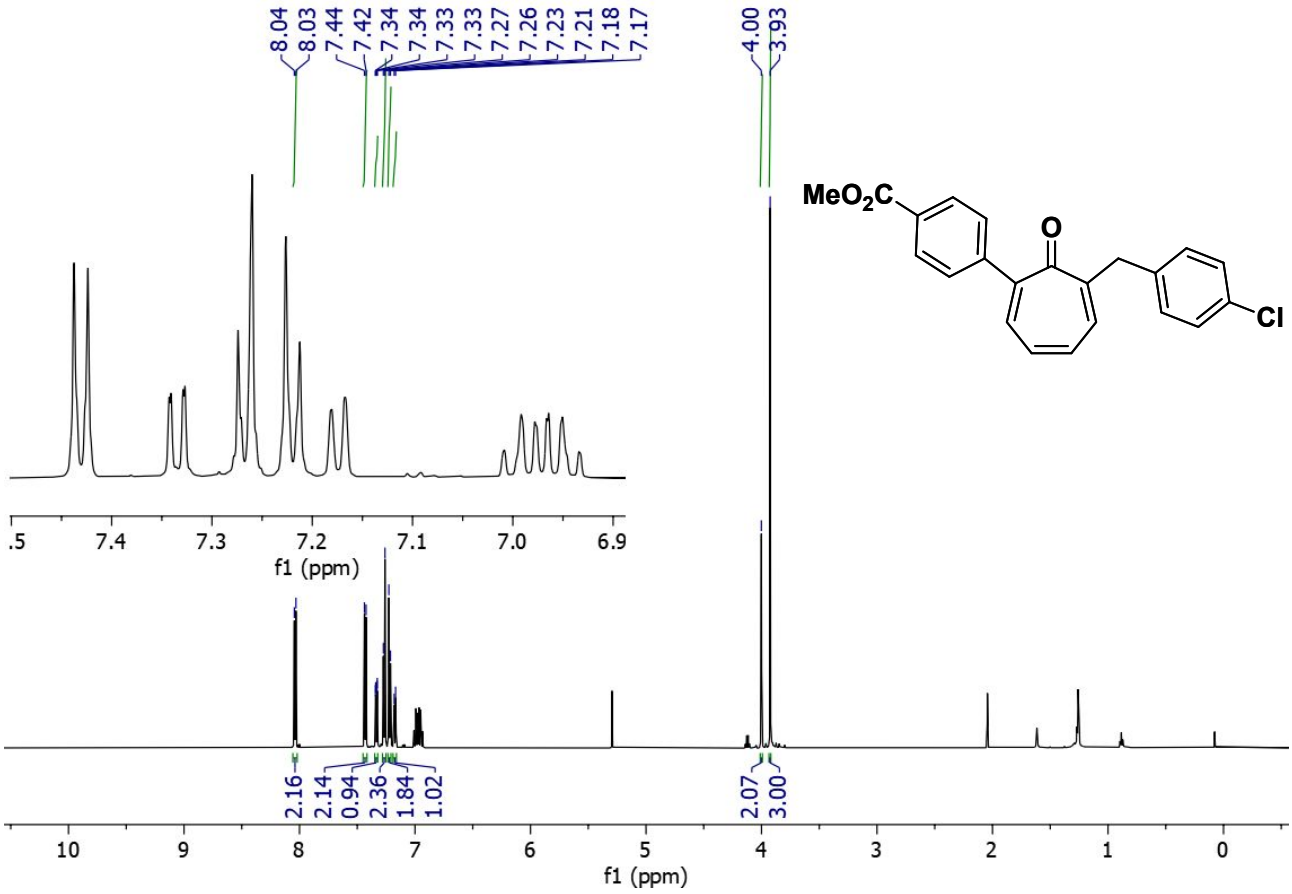
3la ^{13}C NMR (150 MHz, $CDCl_3$)



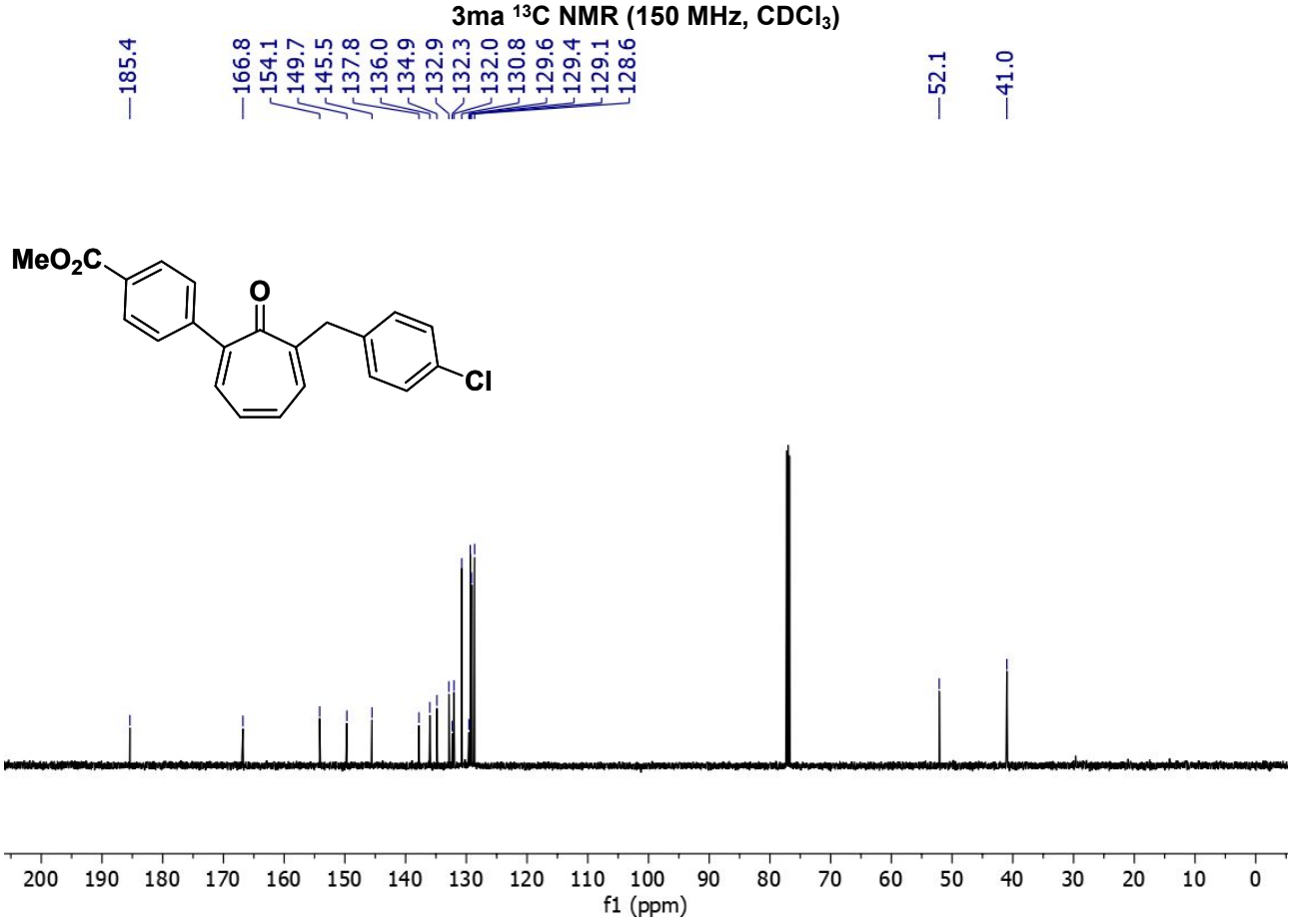
3la ^{19}F NMR (565 MHz, $CDCl_3$)



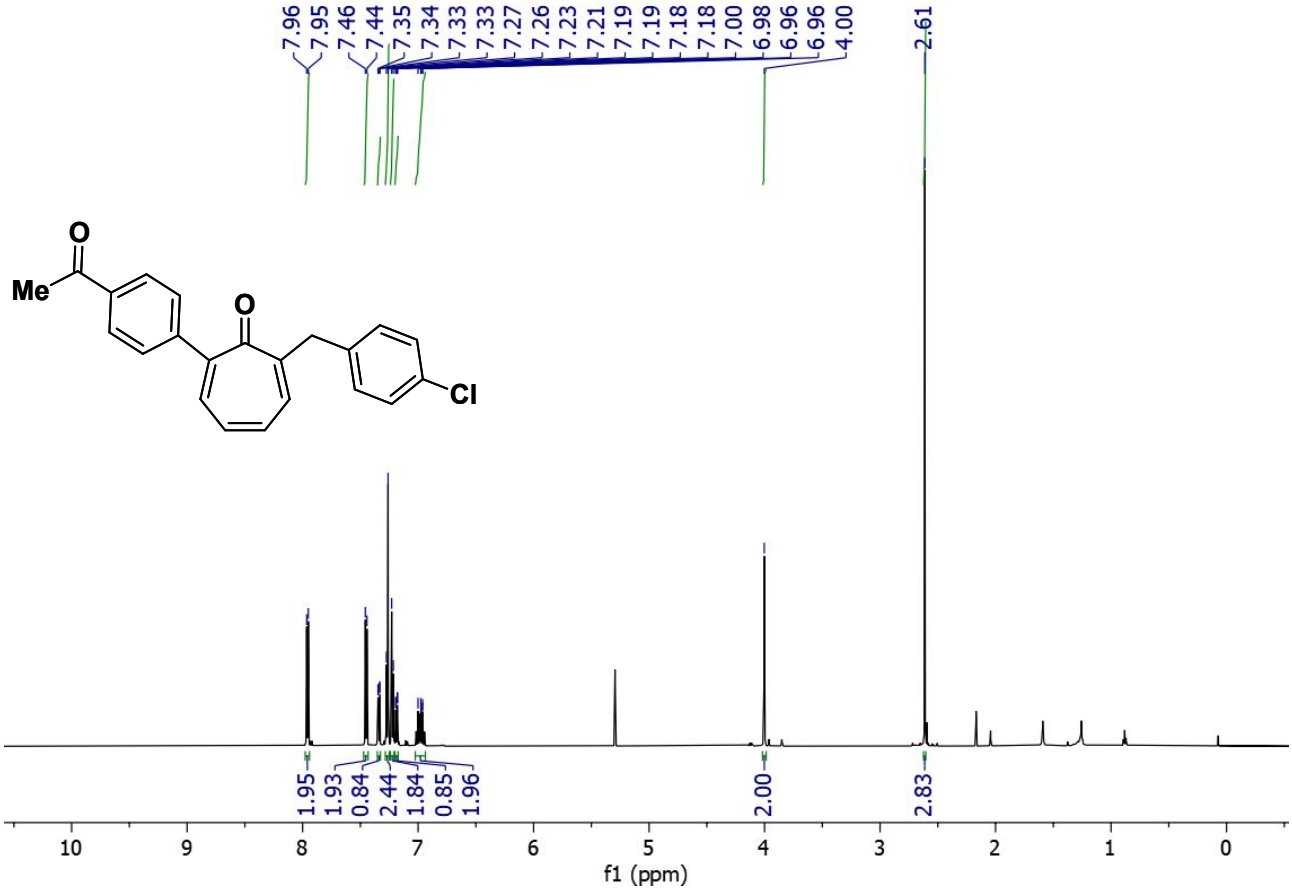
3ma ^{1}H NMR (600 MHz, $CDCl_3$)



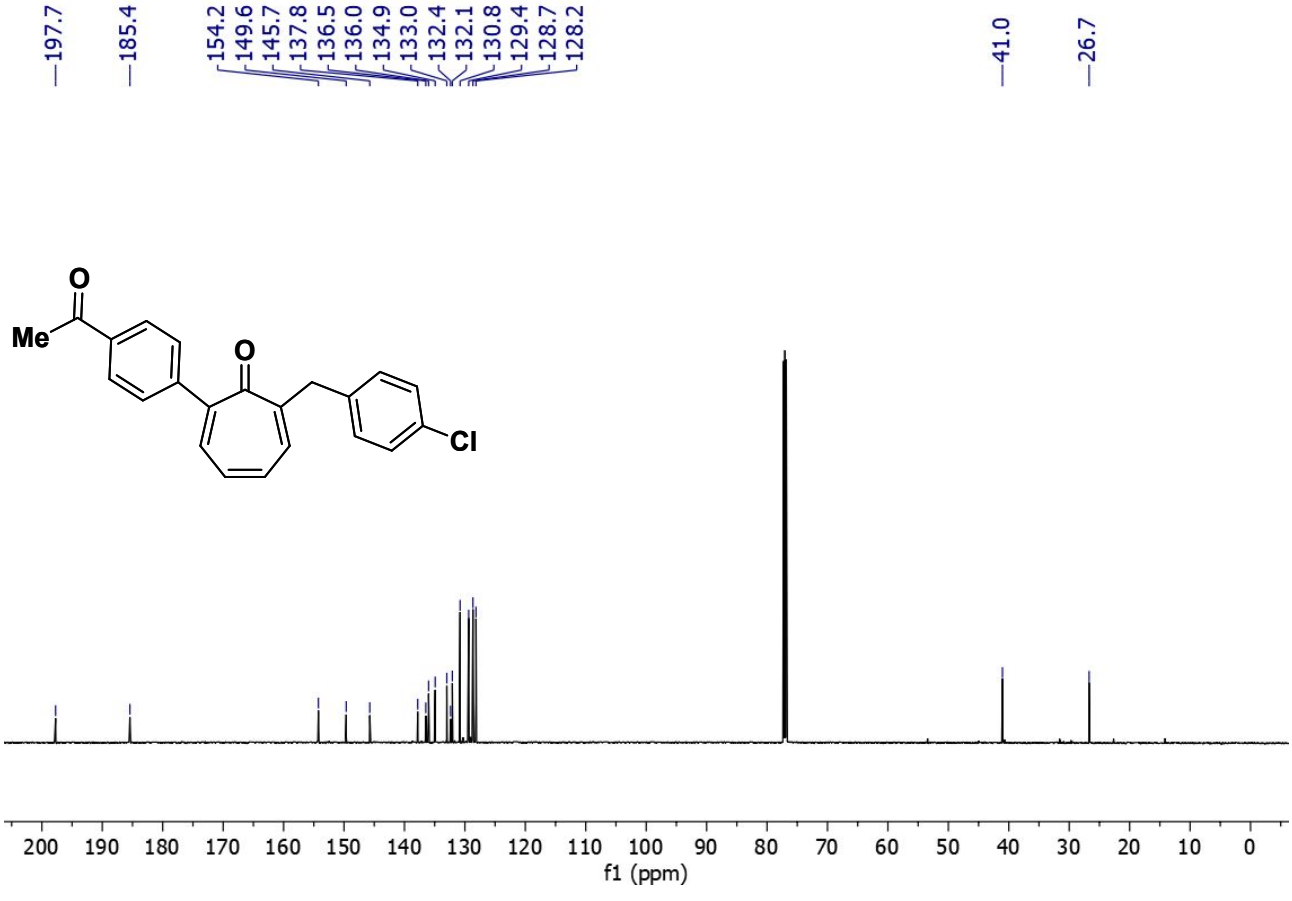
3ma ^{13}C NMR (150 MHz, $CDCl_3$)



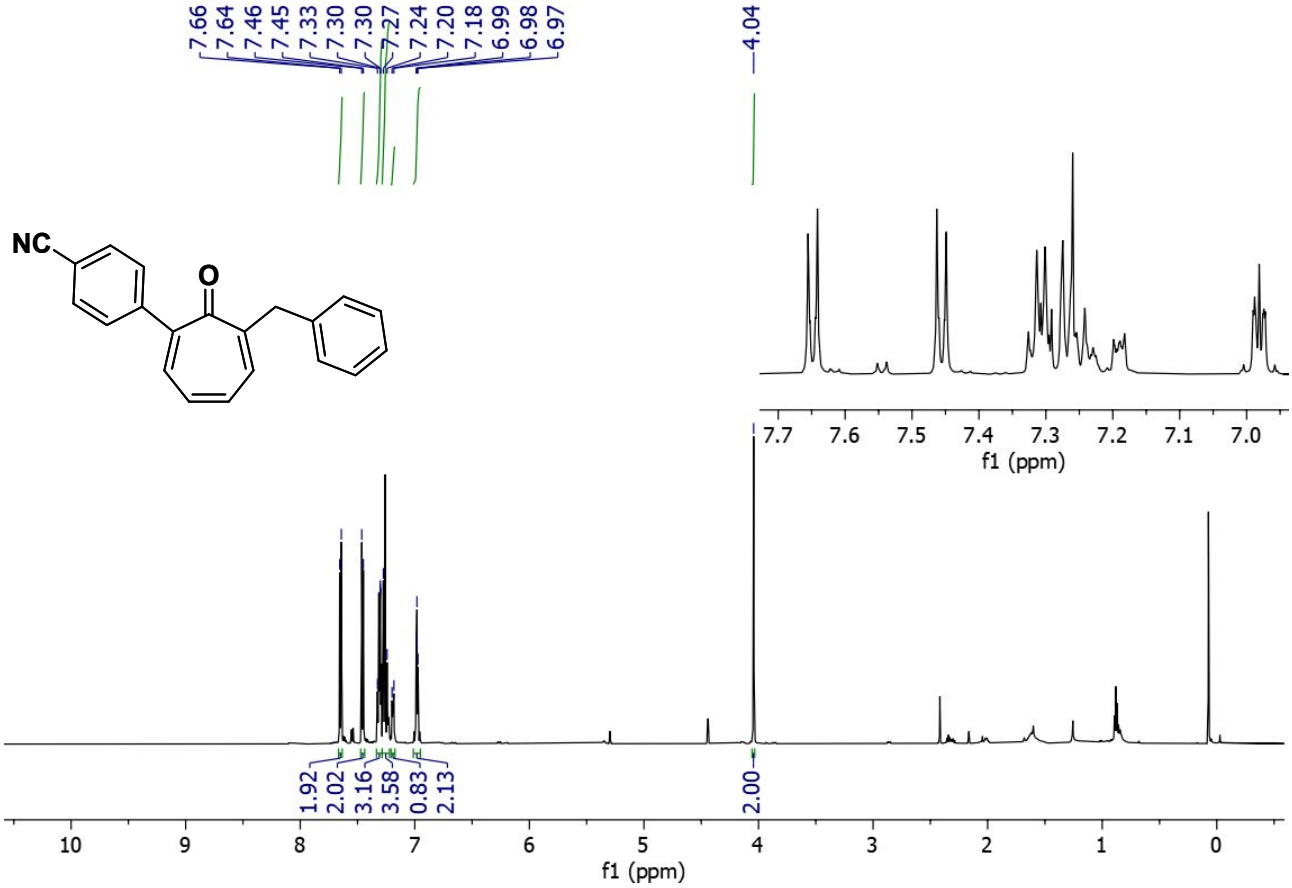
3na ^{1}H NMR (600 MHz, $CDCl_3$)



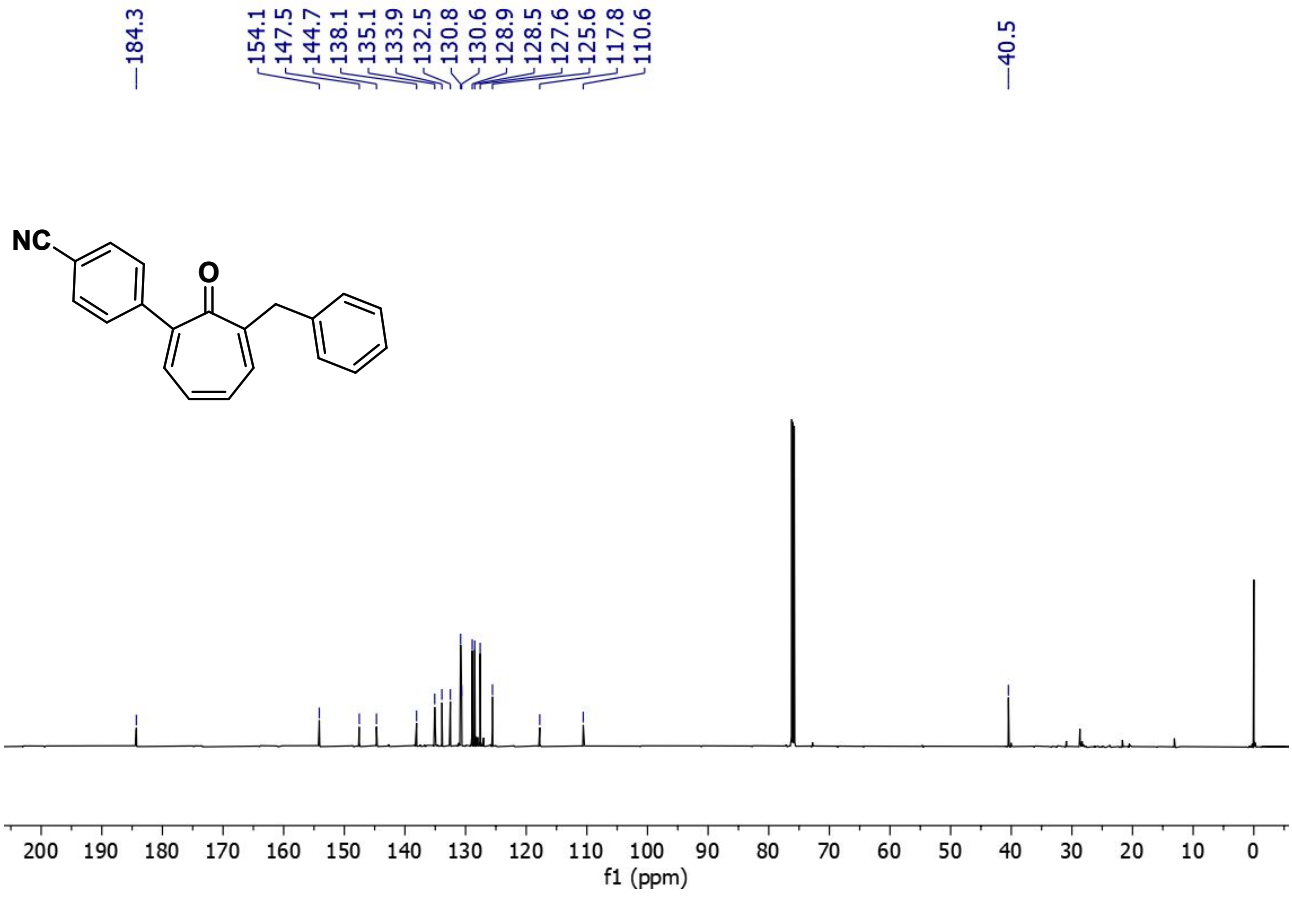
3na ^{13}C NMR (150 MHz, $CDCl_3$)



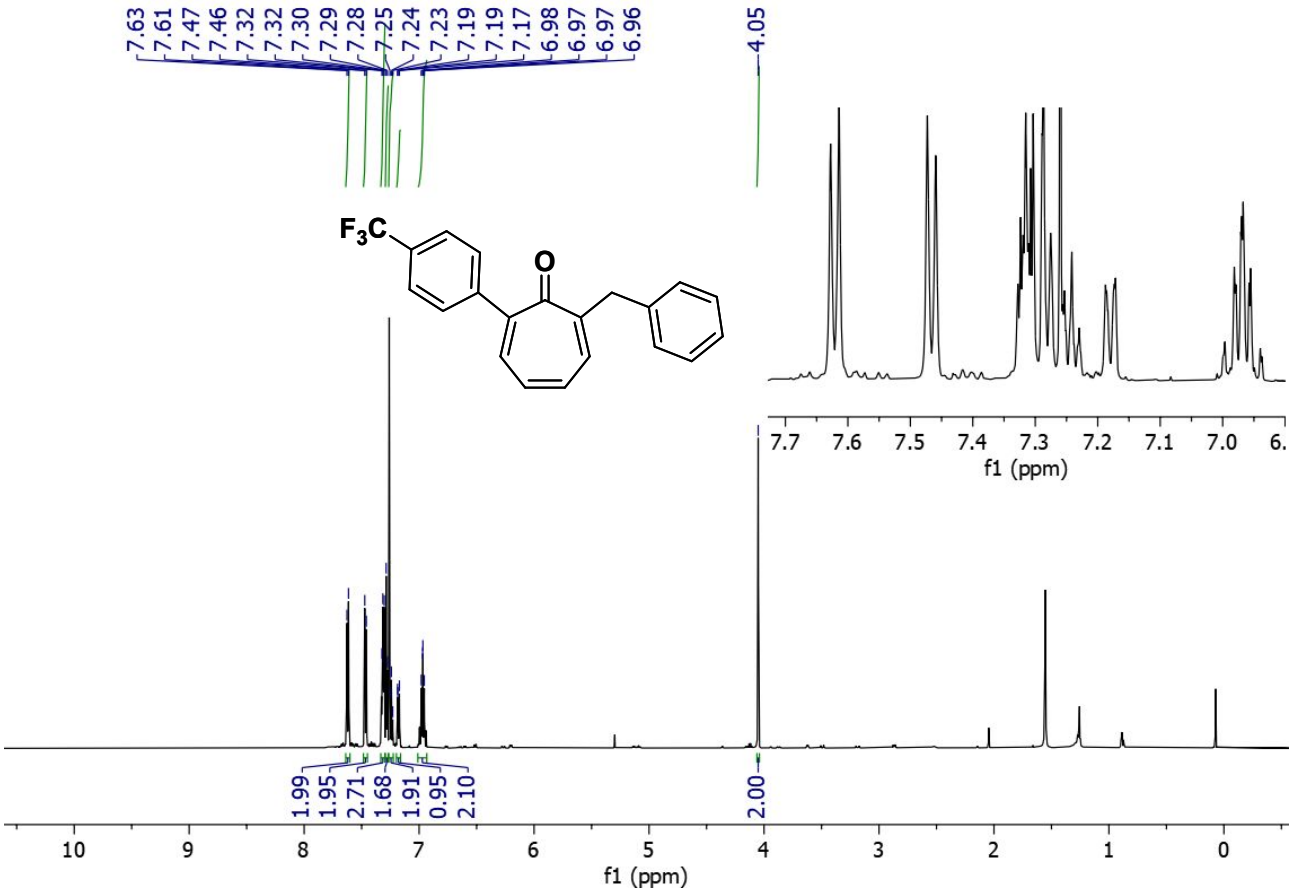
3ob ^{1}H NMR (600 MHz, $CDCl_3$)



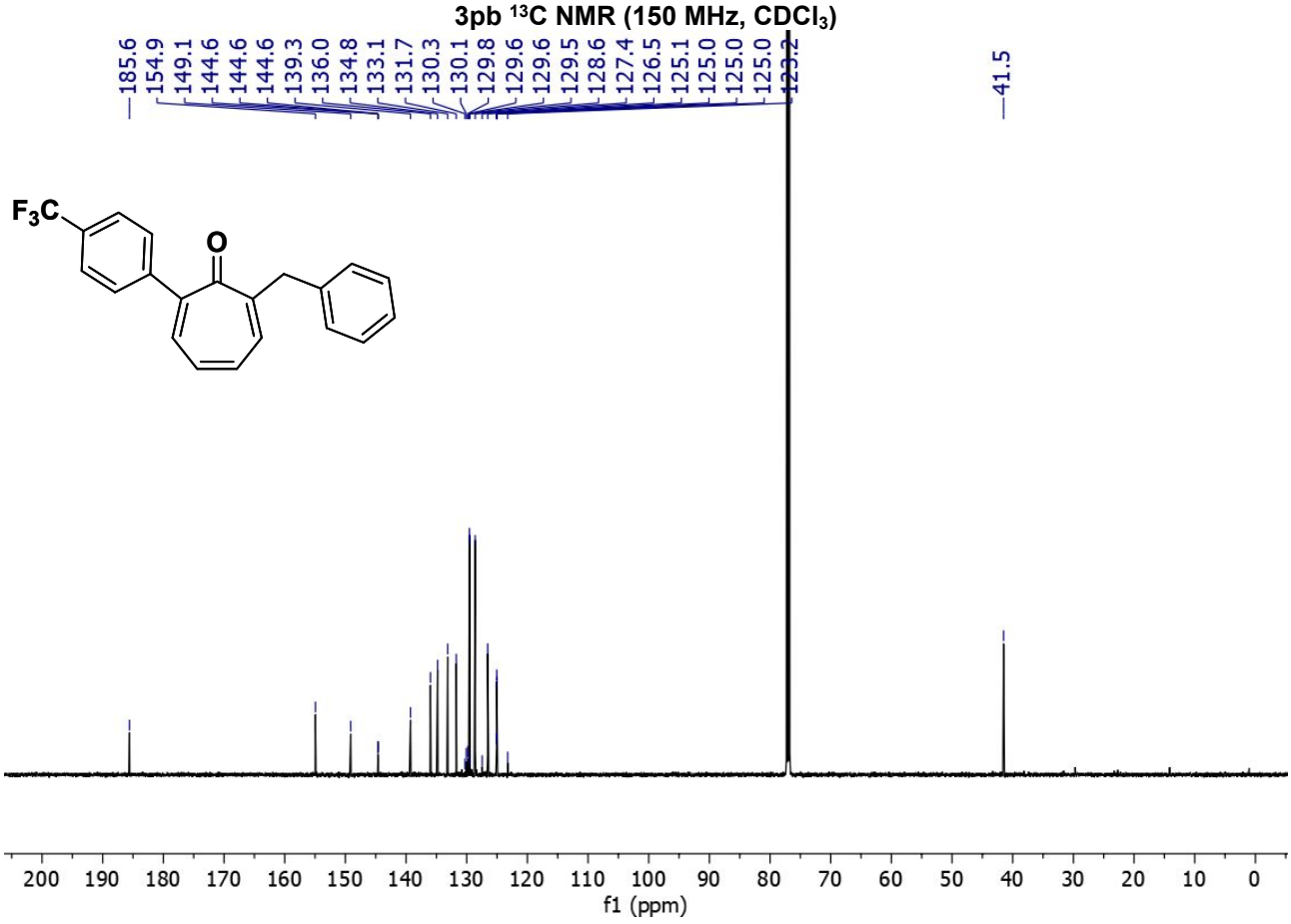
3ob ^{13}C NMR (150 MHz, $CDCl_3$)



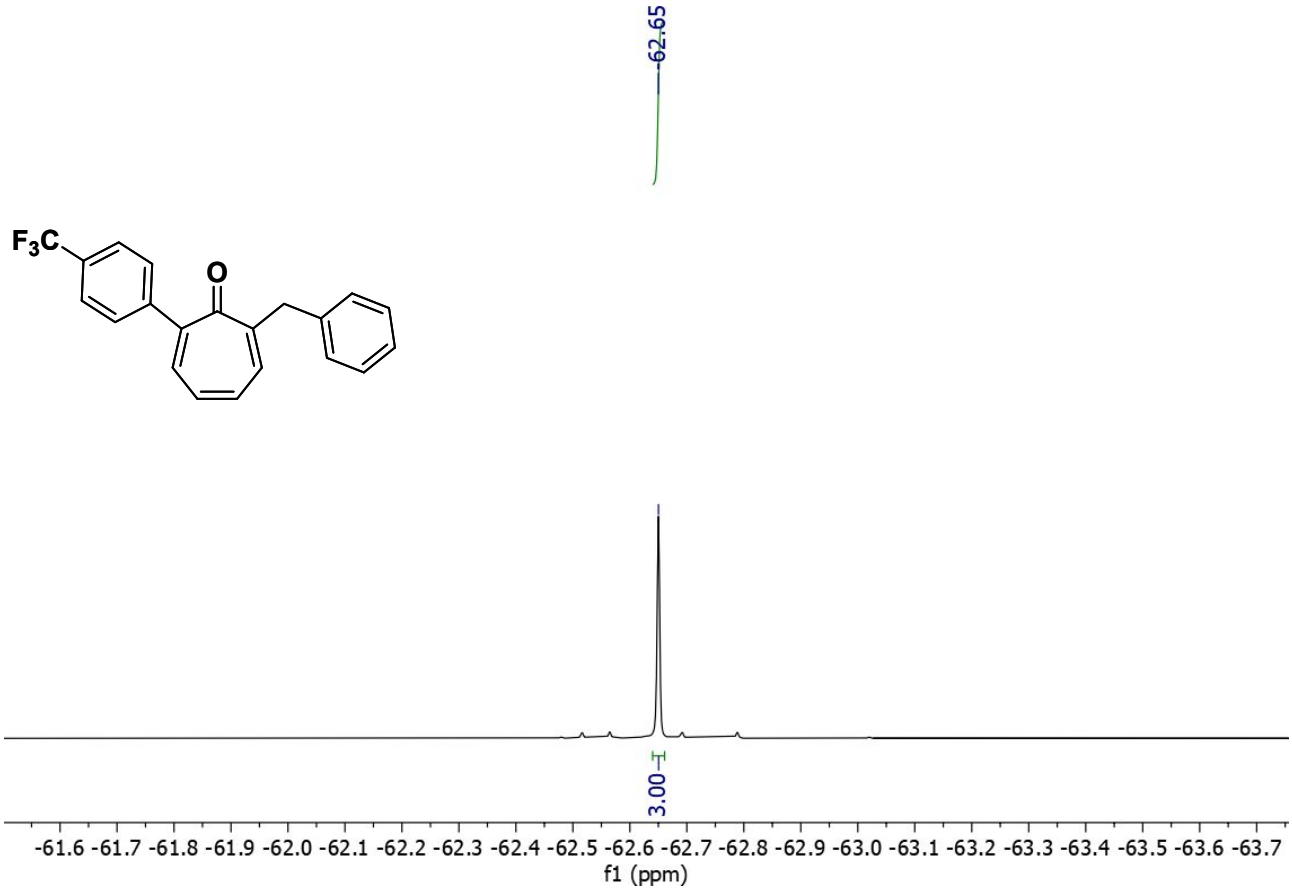
3pb ^{1}H NMR (600 MHz, $CDCl_3$)



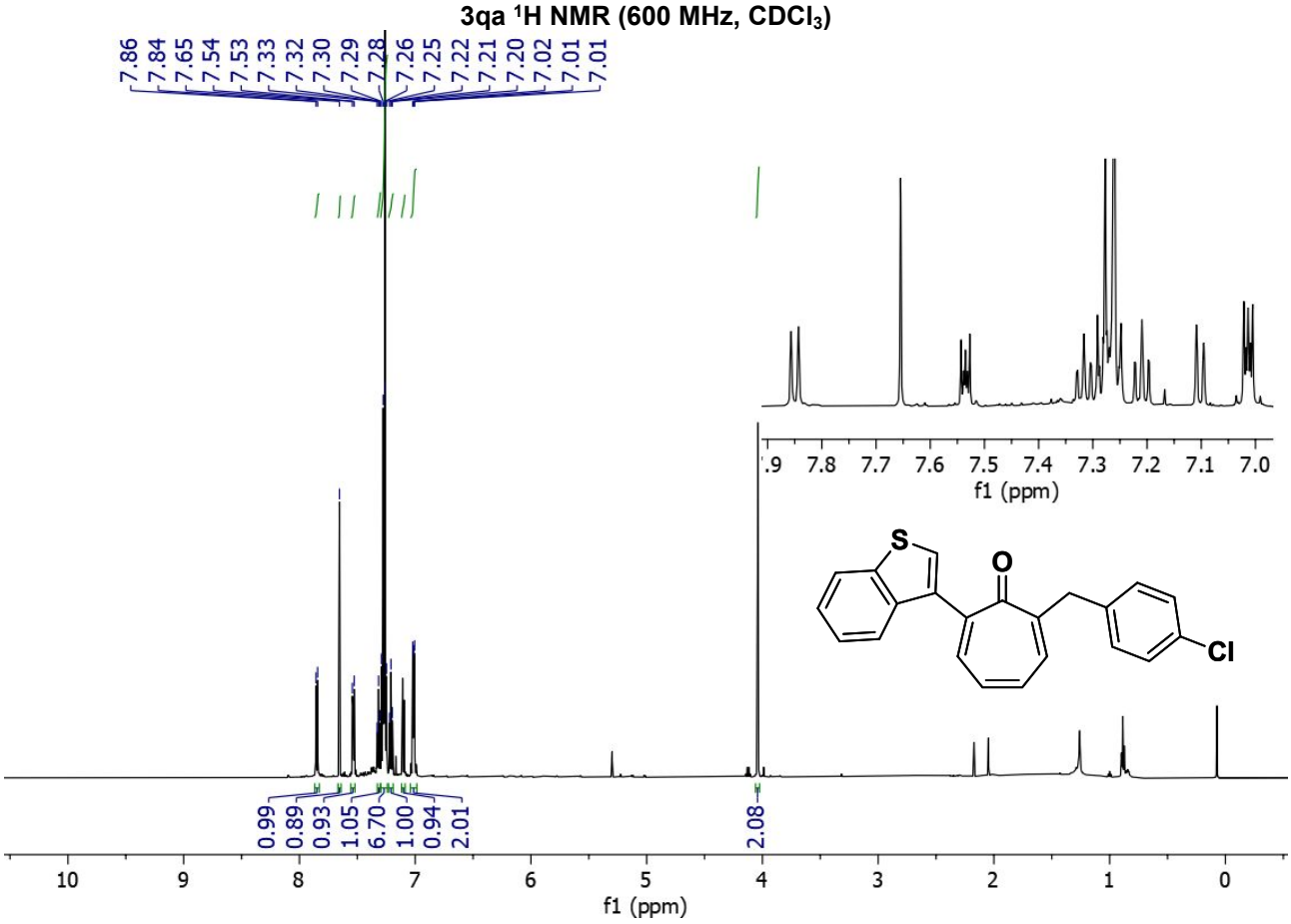
3pb ^{13}C NMR (150 MHz, $CDCl_3$)



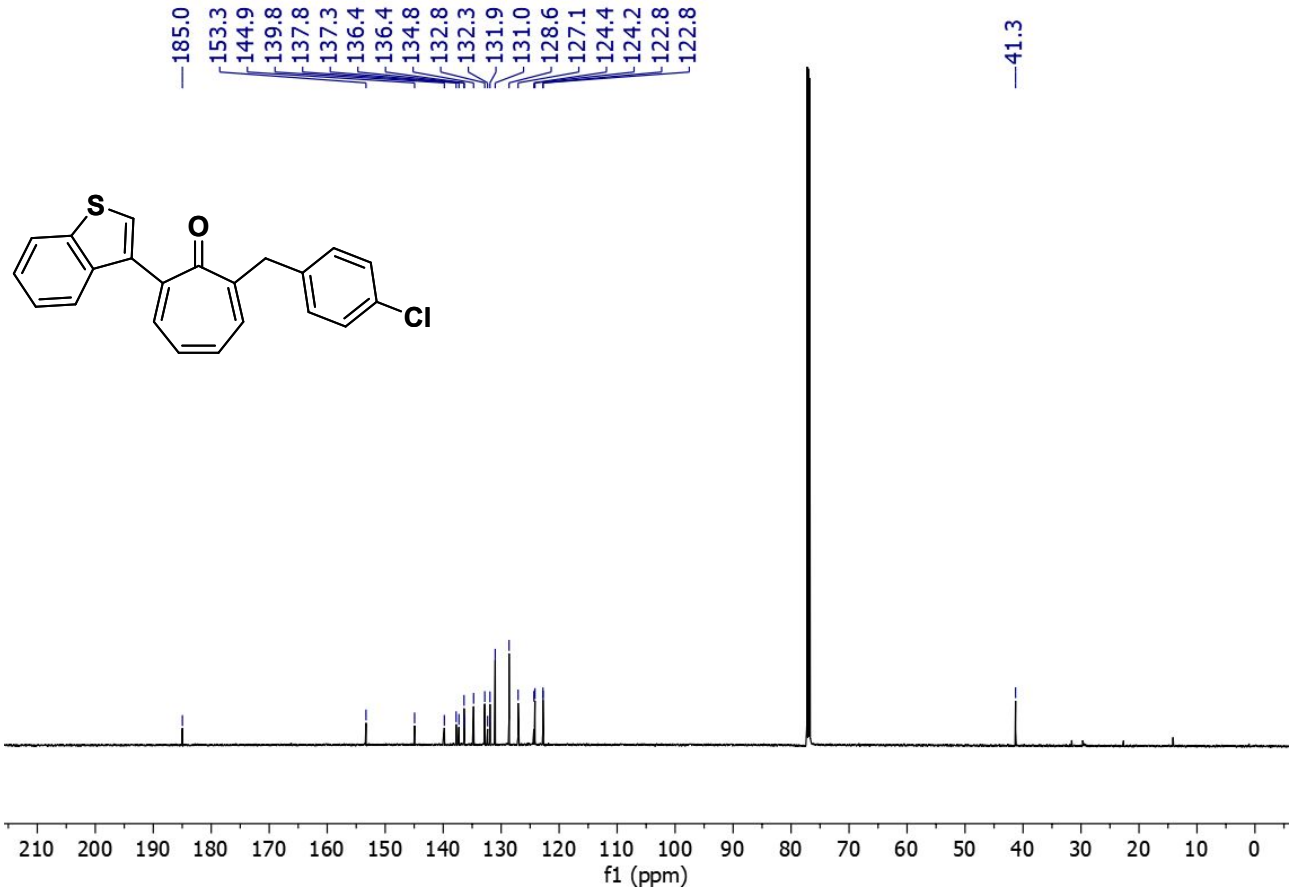
3pb ^{19}F NMR (565 MHz, $CDCl_3$)



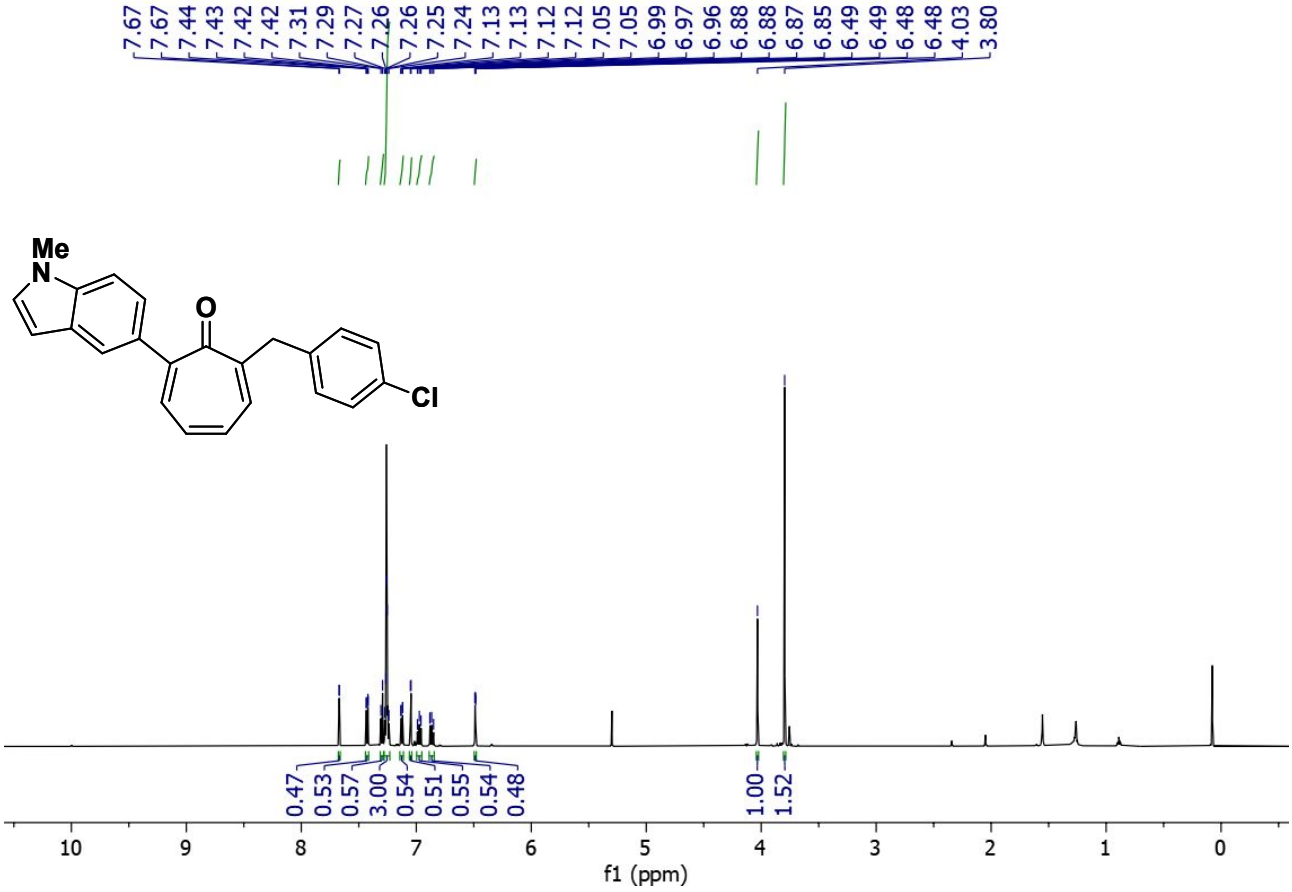
3qa ^{1}H NMR (600 MHz, $CDCl_3$)



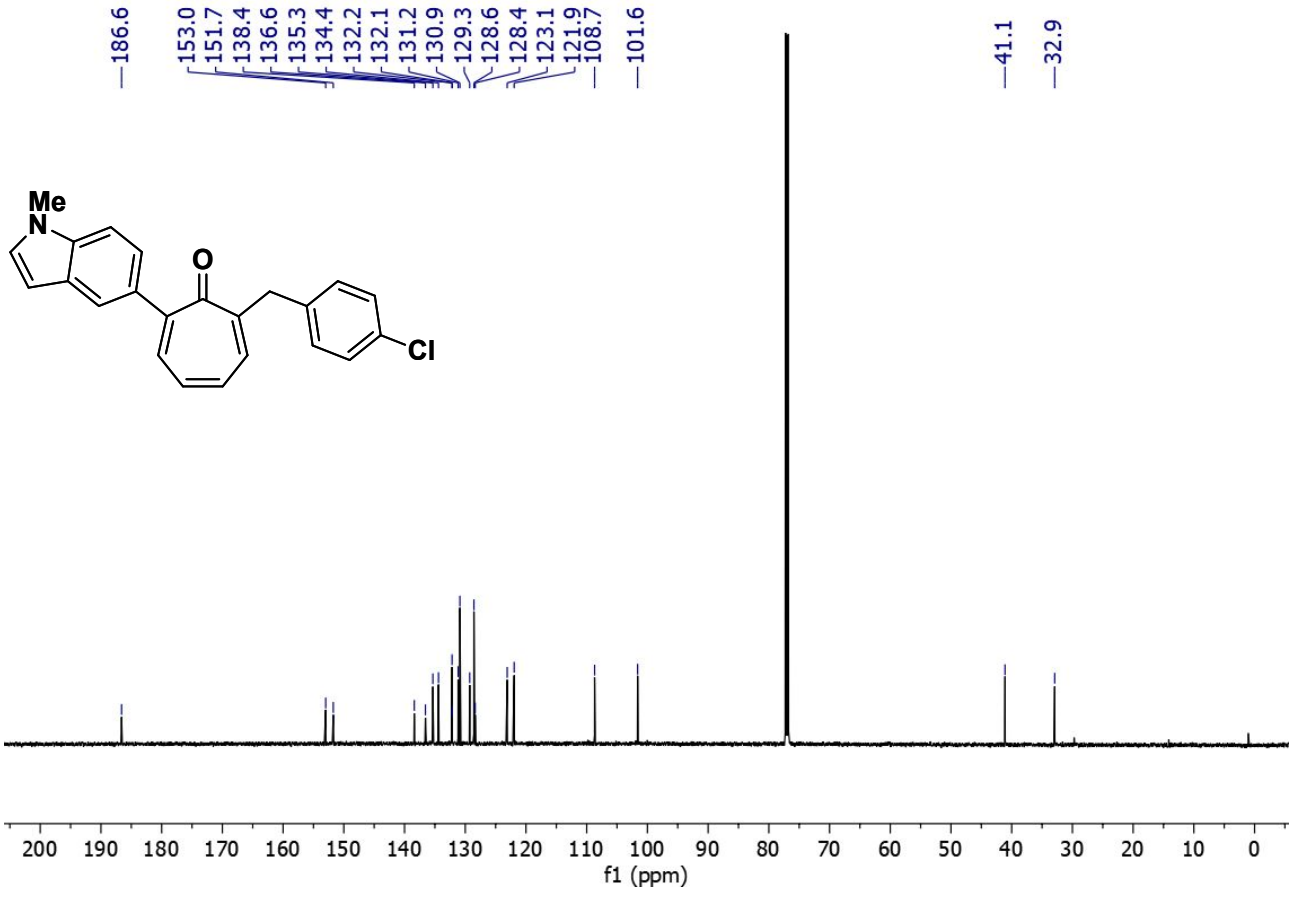
3qa ^{13}C NMR (150 MHz, $CDCl_3$)



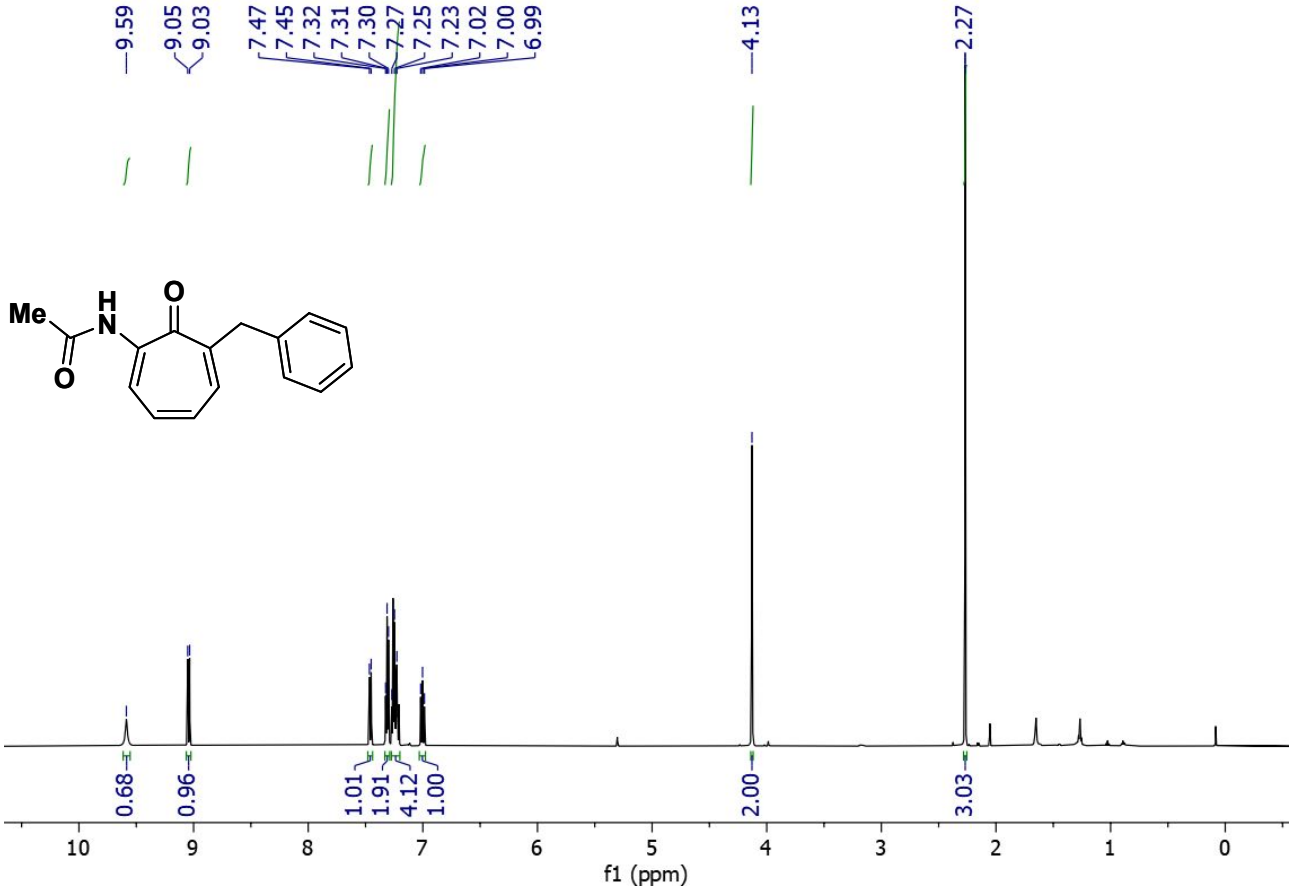
3ra ^{1}H NMR (600 MHz, $CDCl_3$)



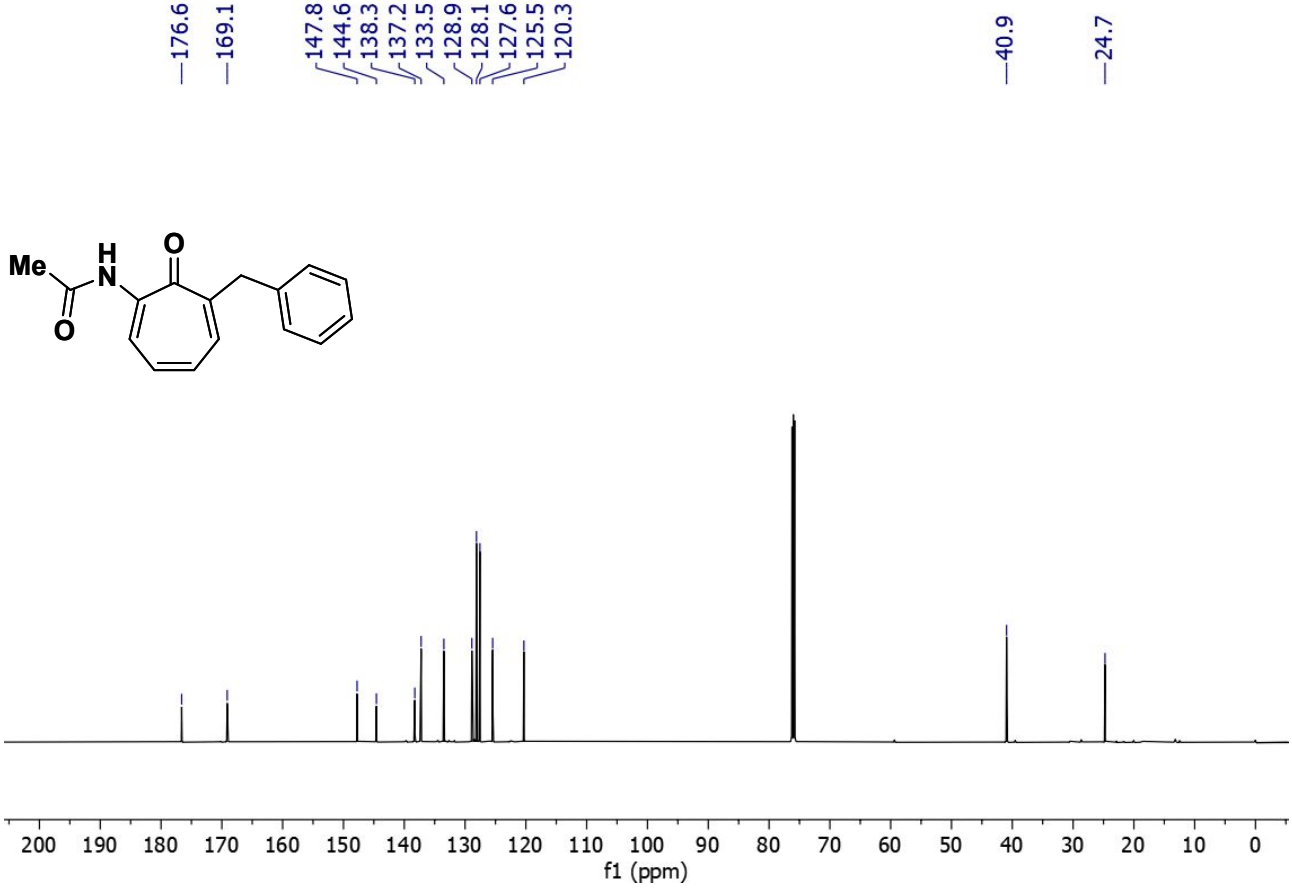
3ra ^{13}C NMR (150 MHz, $CDCl_3$)



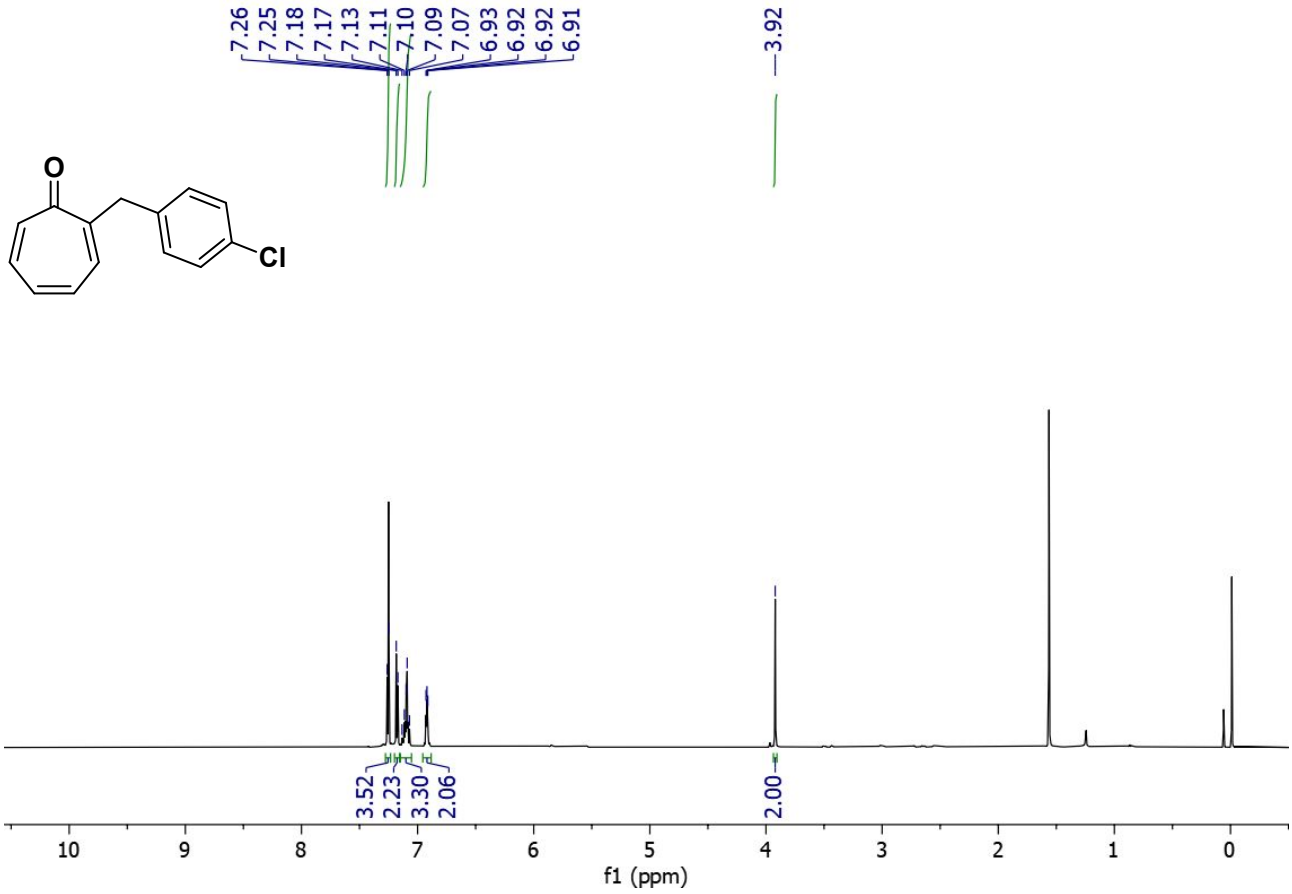
3sb ^{1}H NMR (600 MHz, $CDCl_3$)



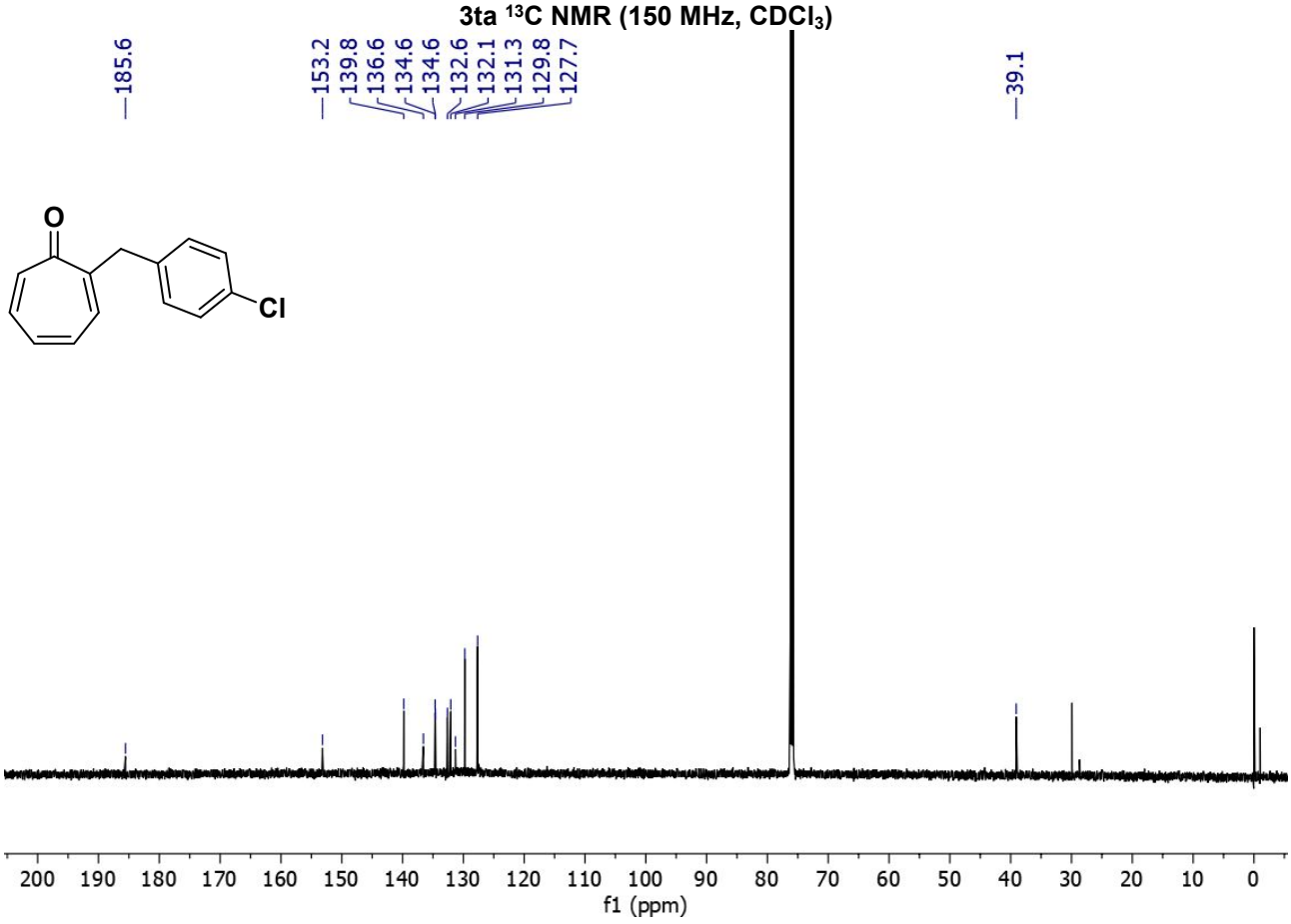
3sb ^{13}C NMR (150 MHz, $CDCl_3$)



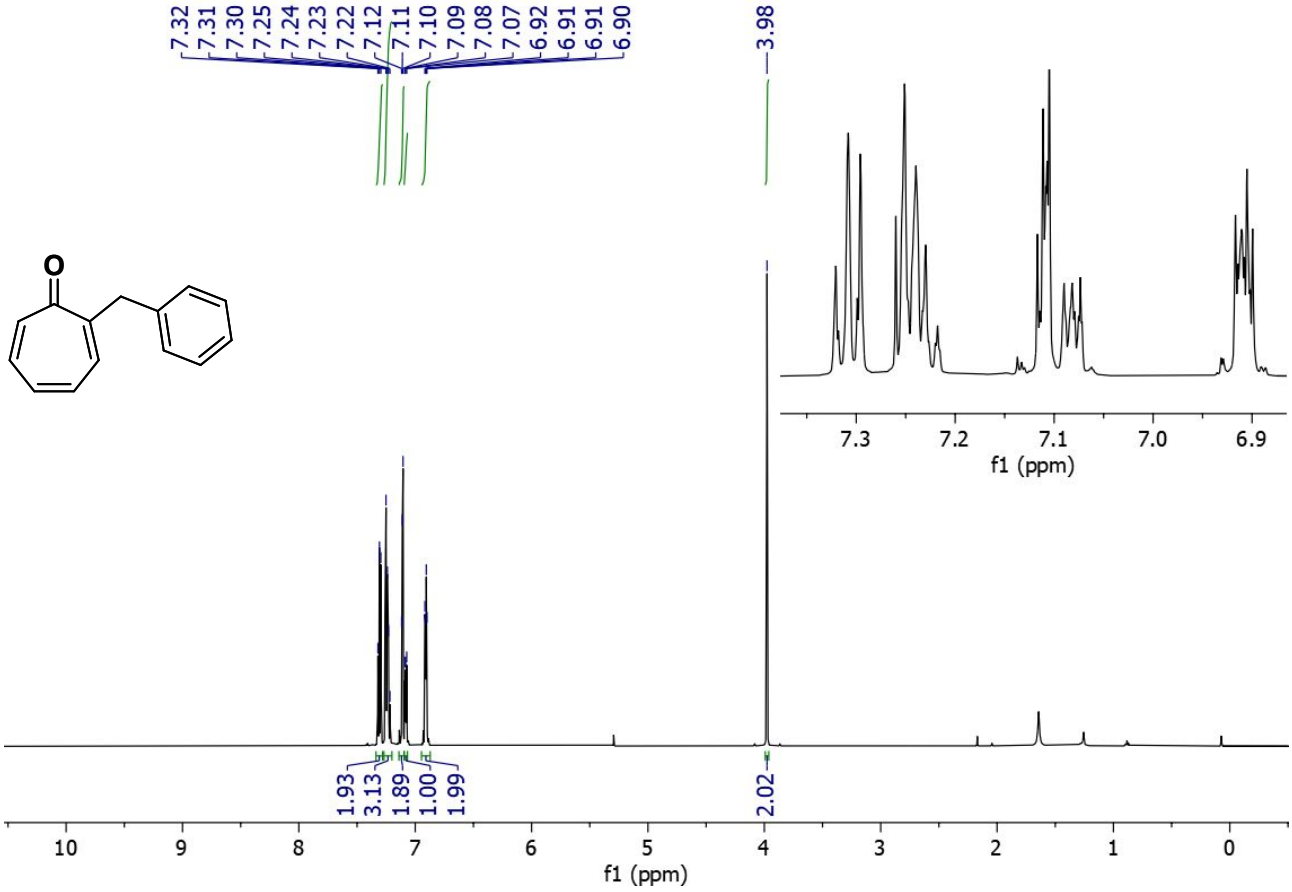
3ta ^{1}H NMR (600 MHz, $CDCl_3$)



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



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



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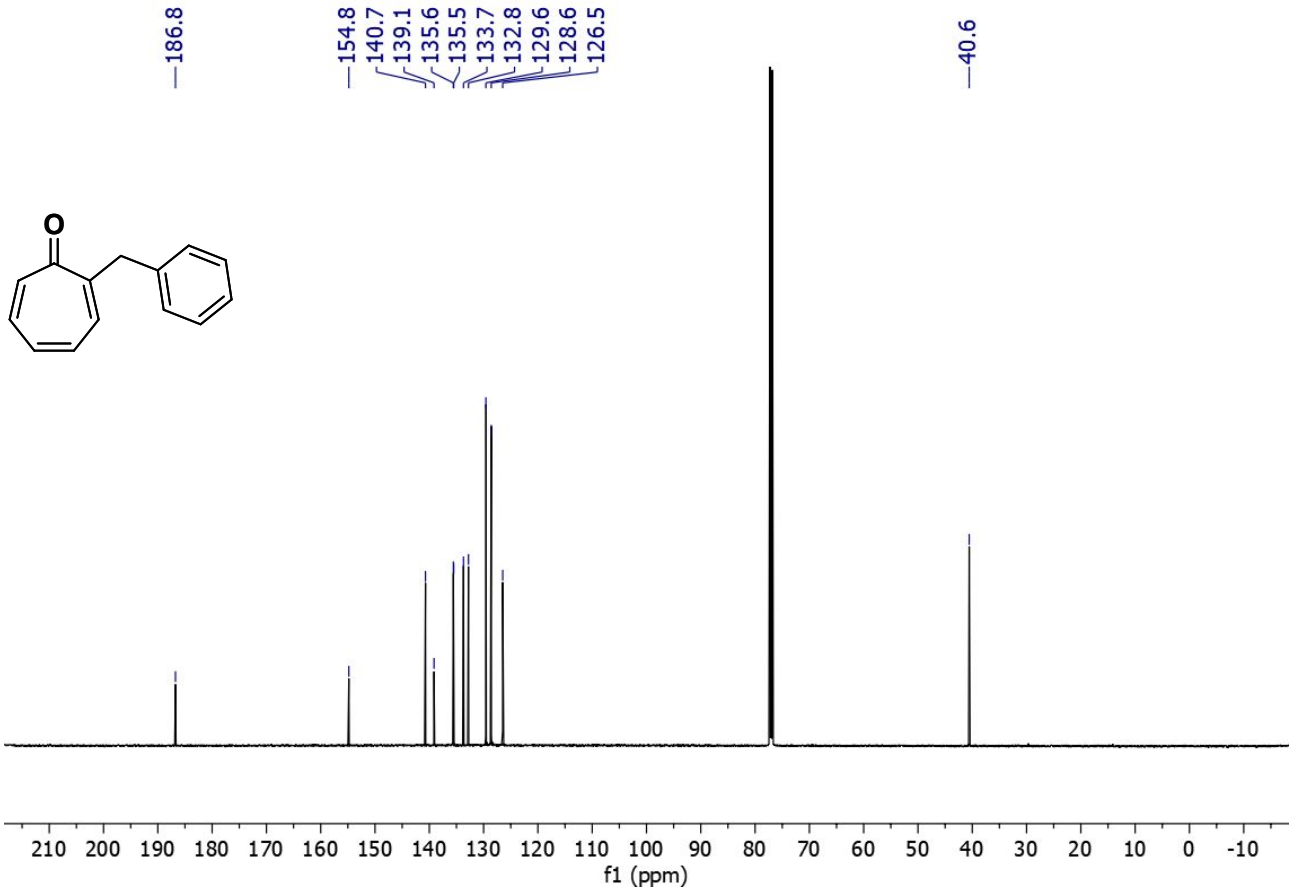

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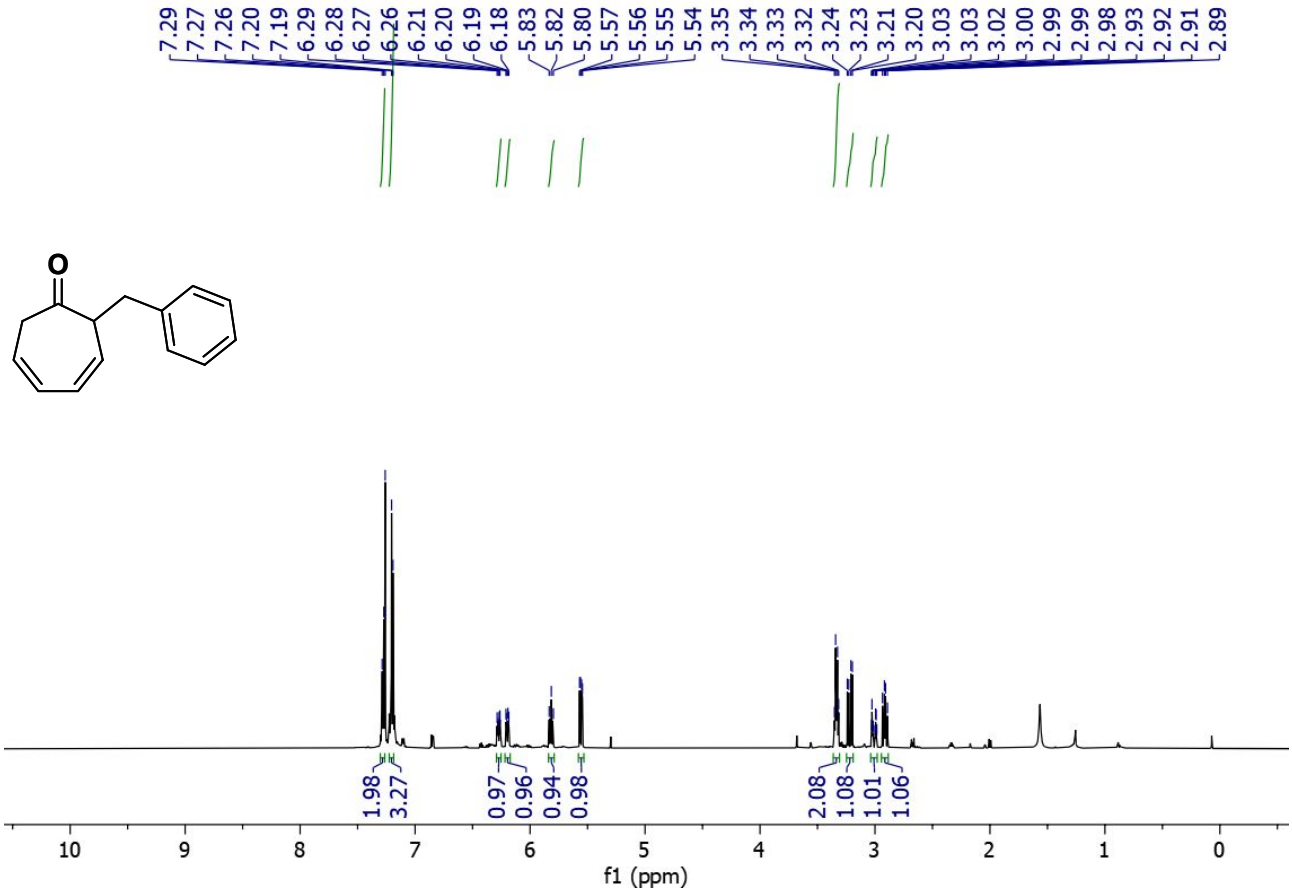

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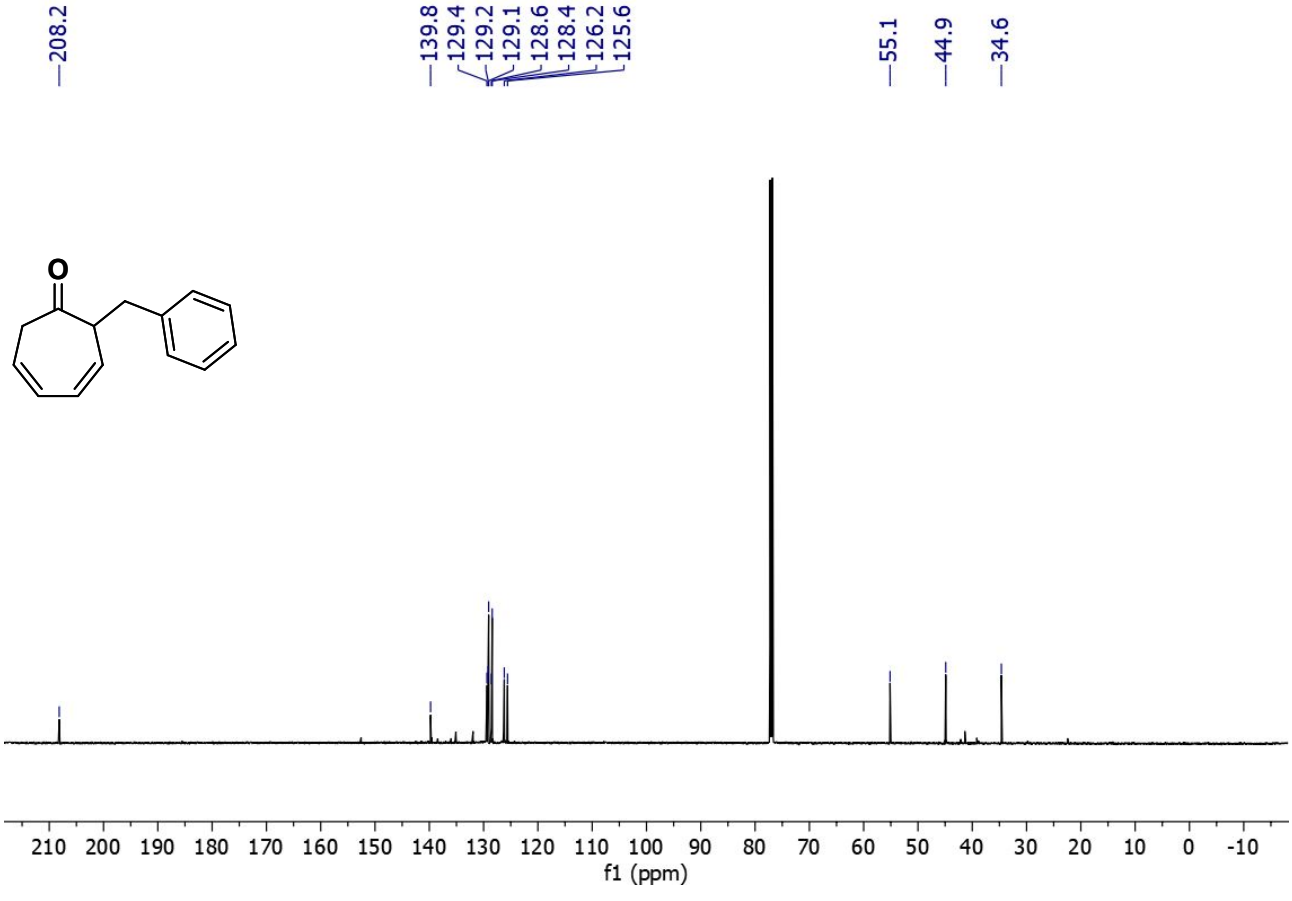

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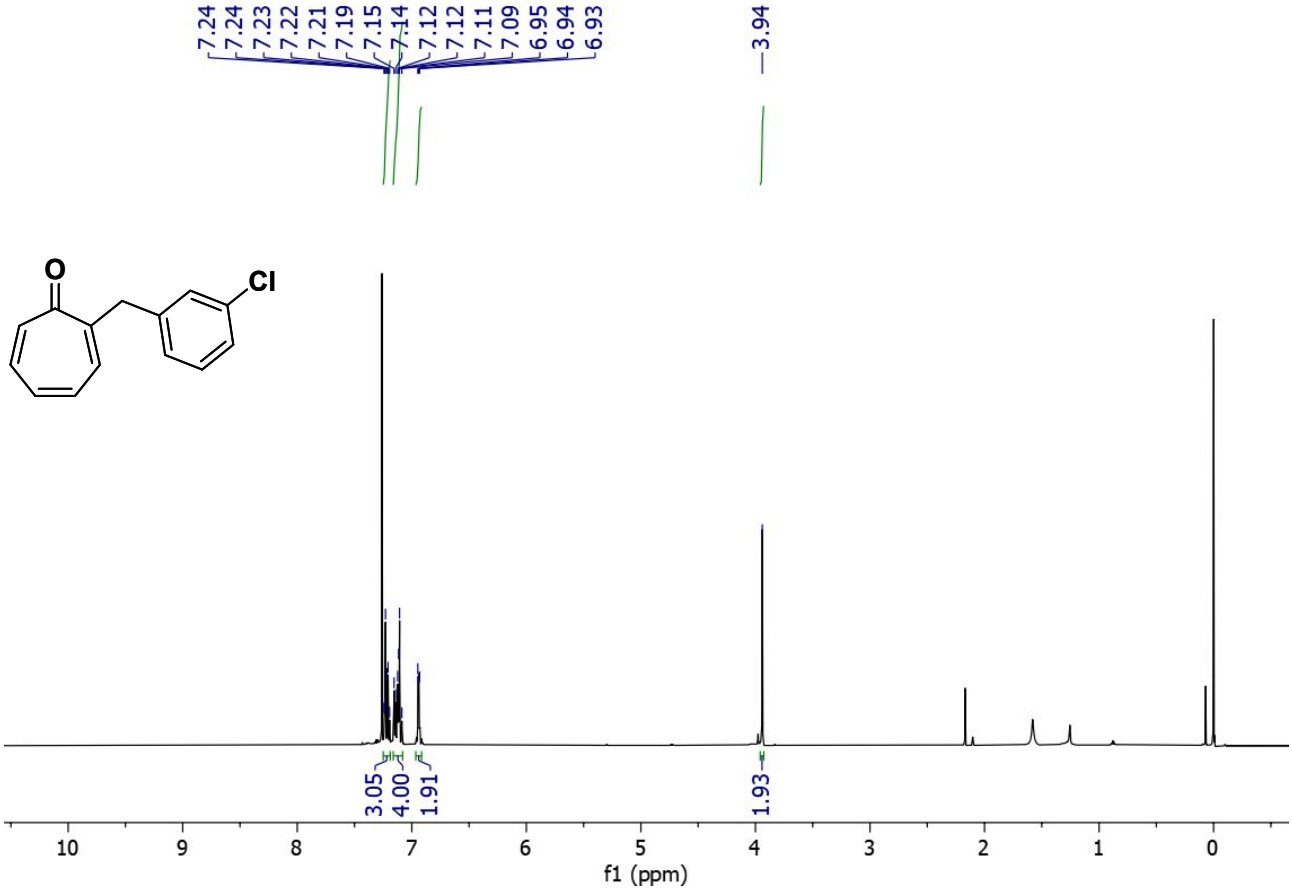

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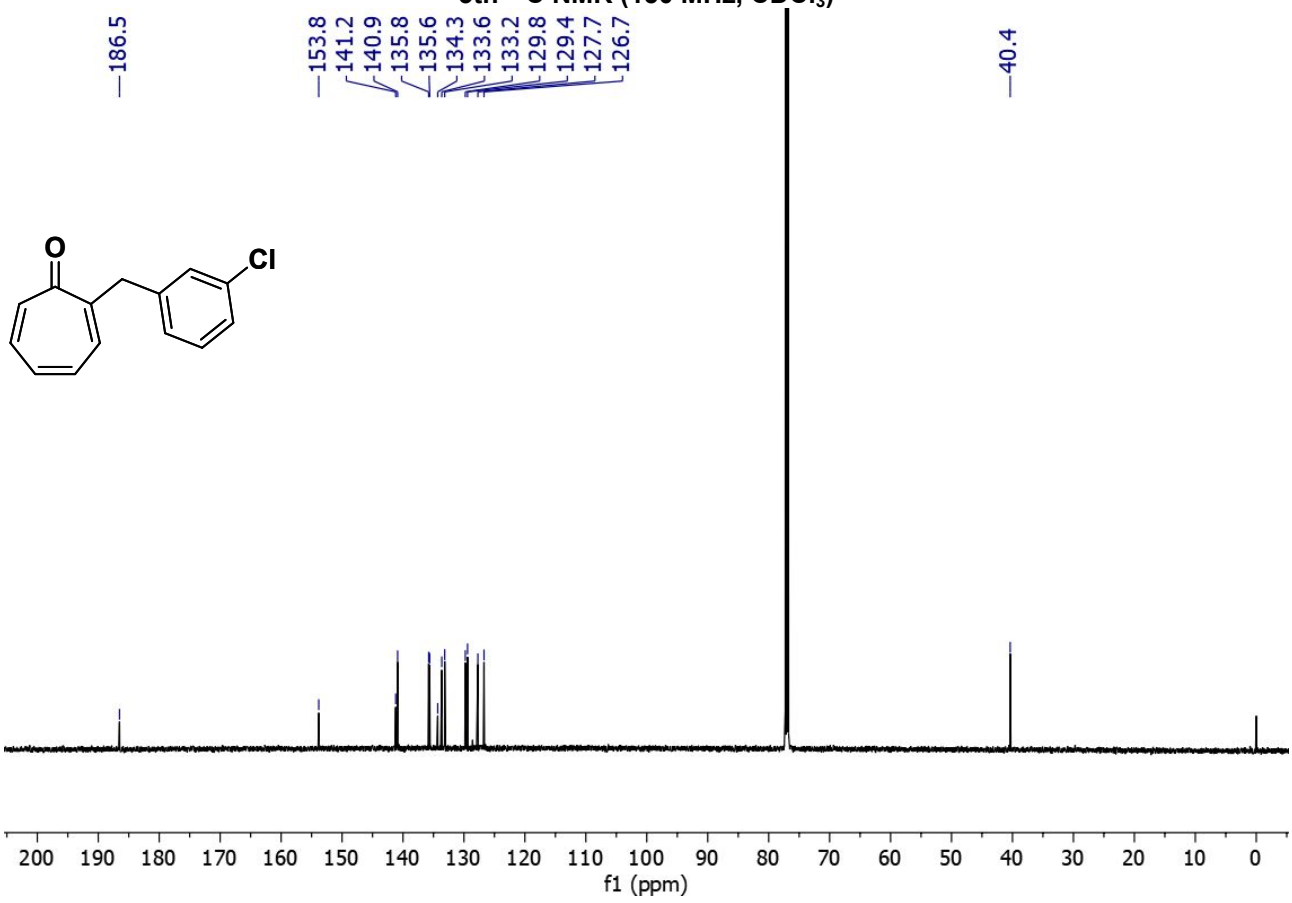

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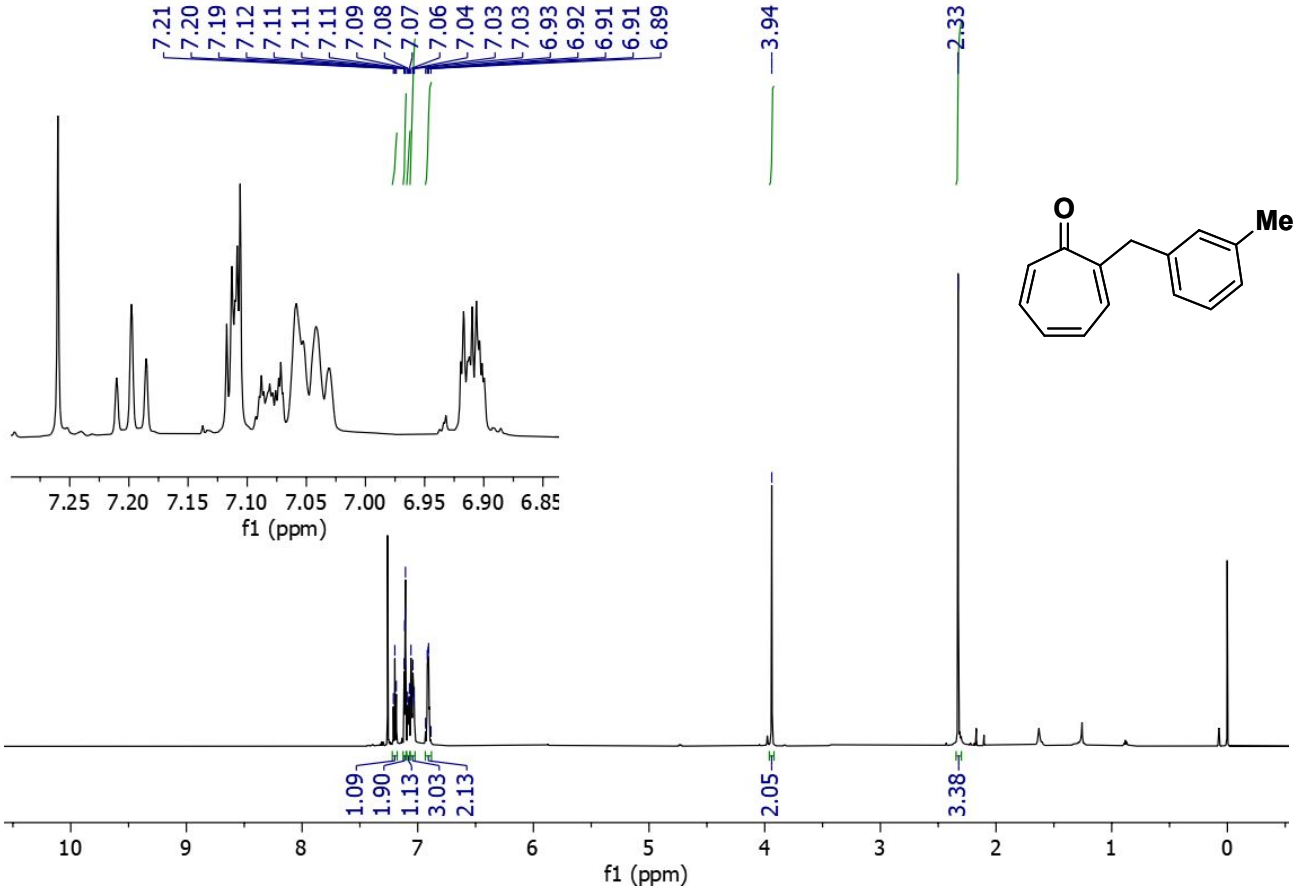

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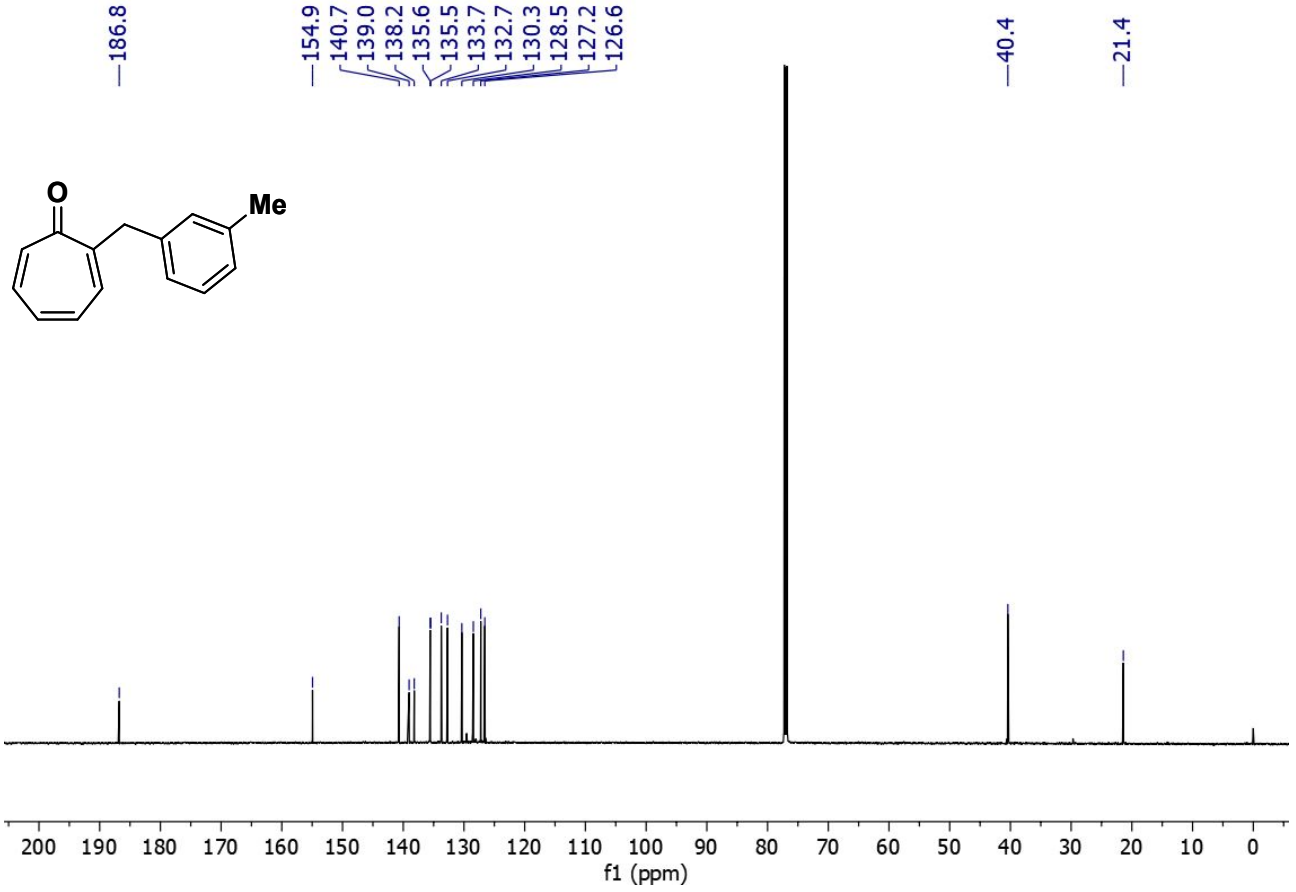

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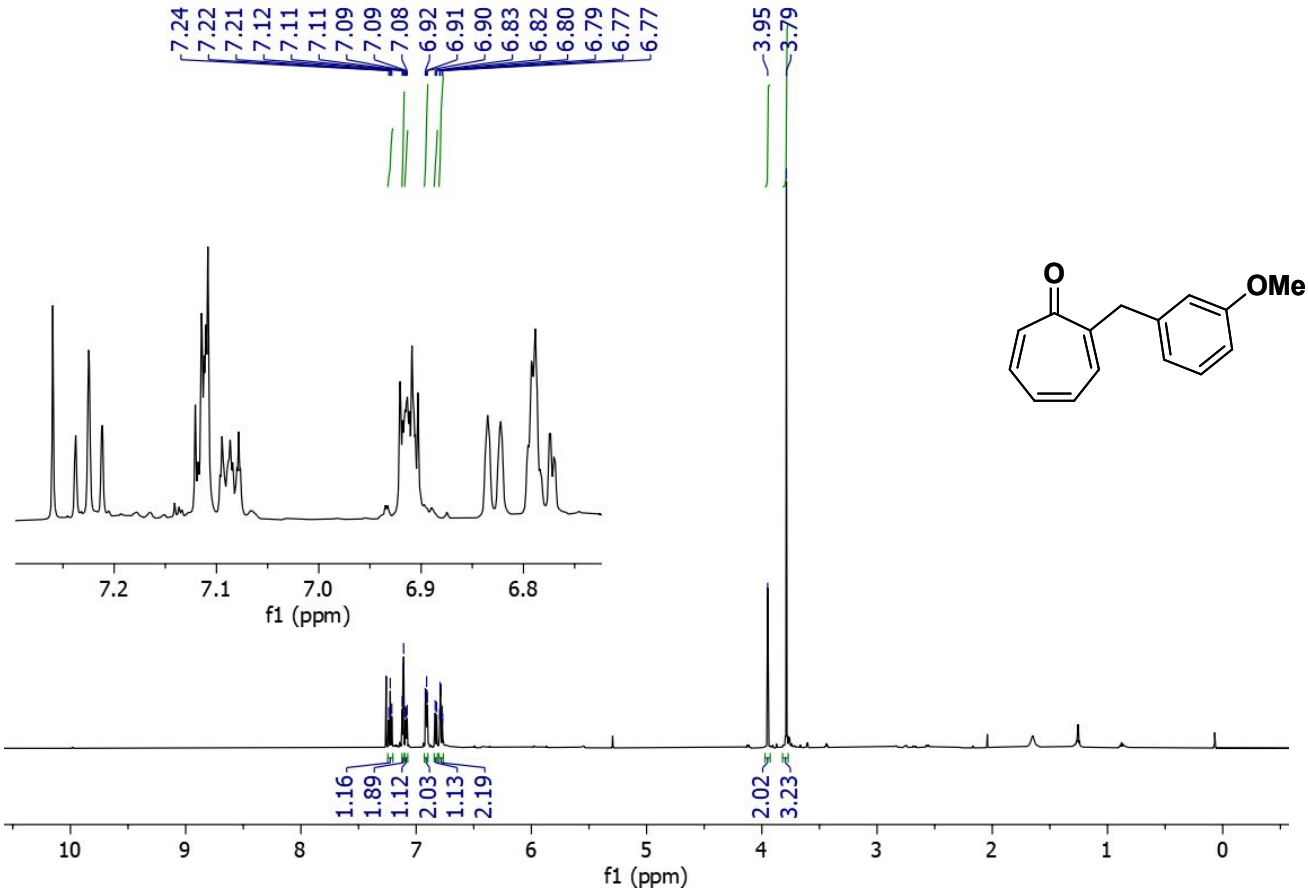

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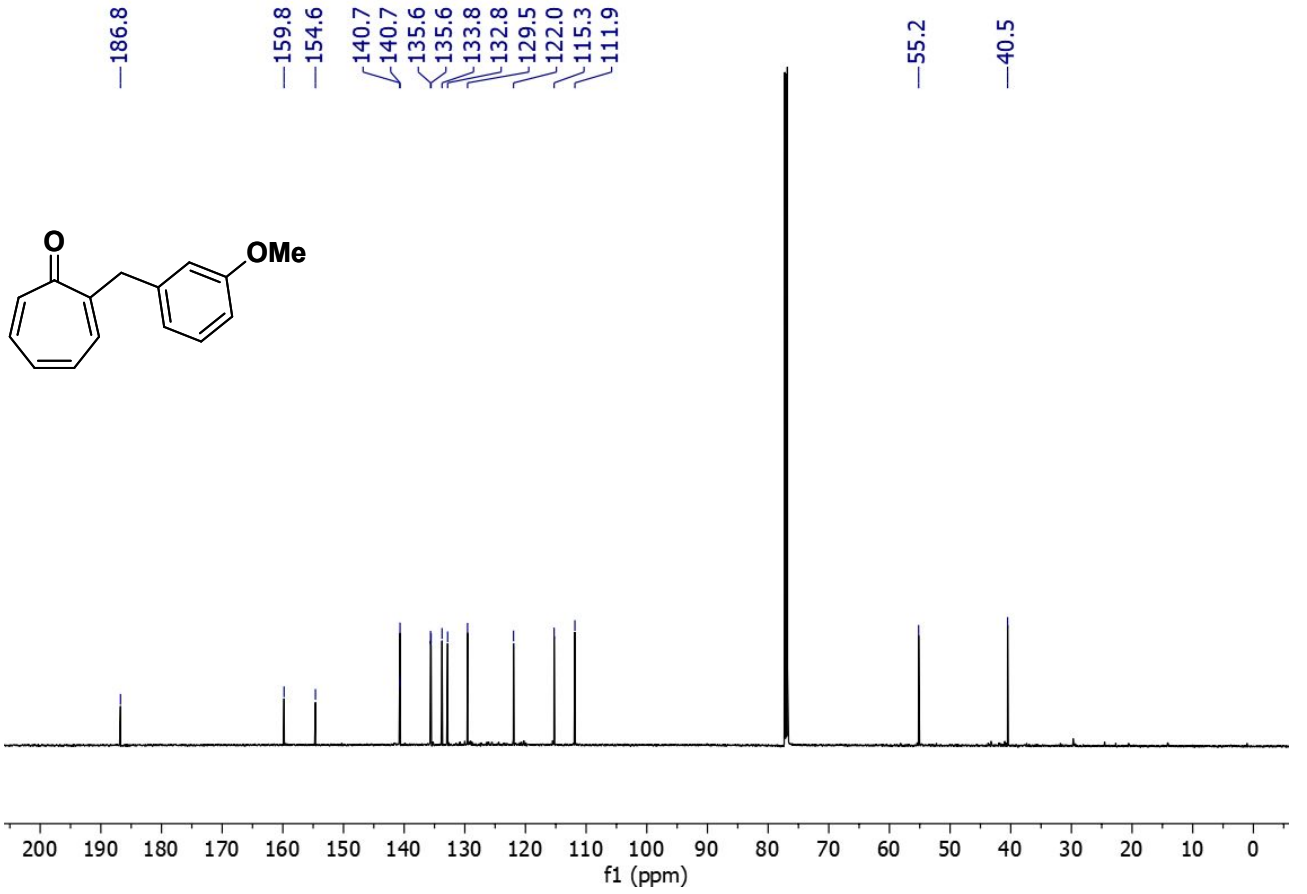

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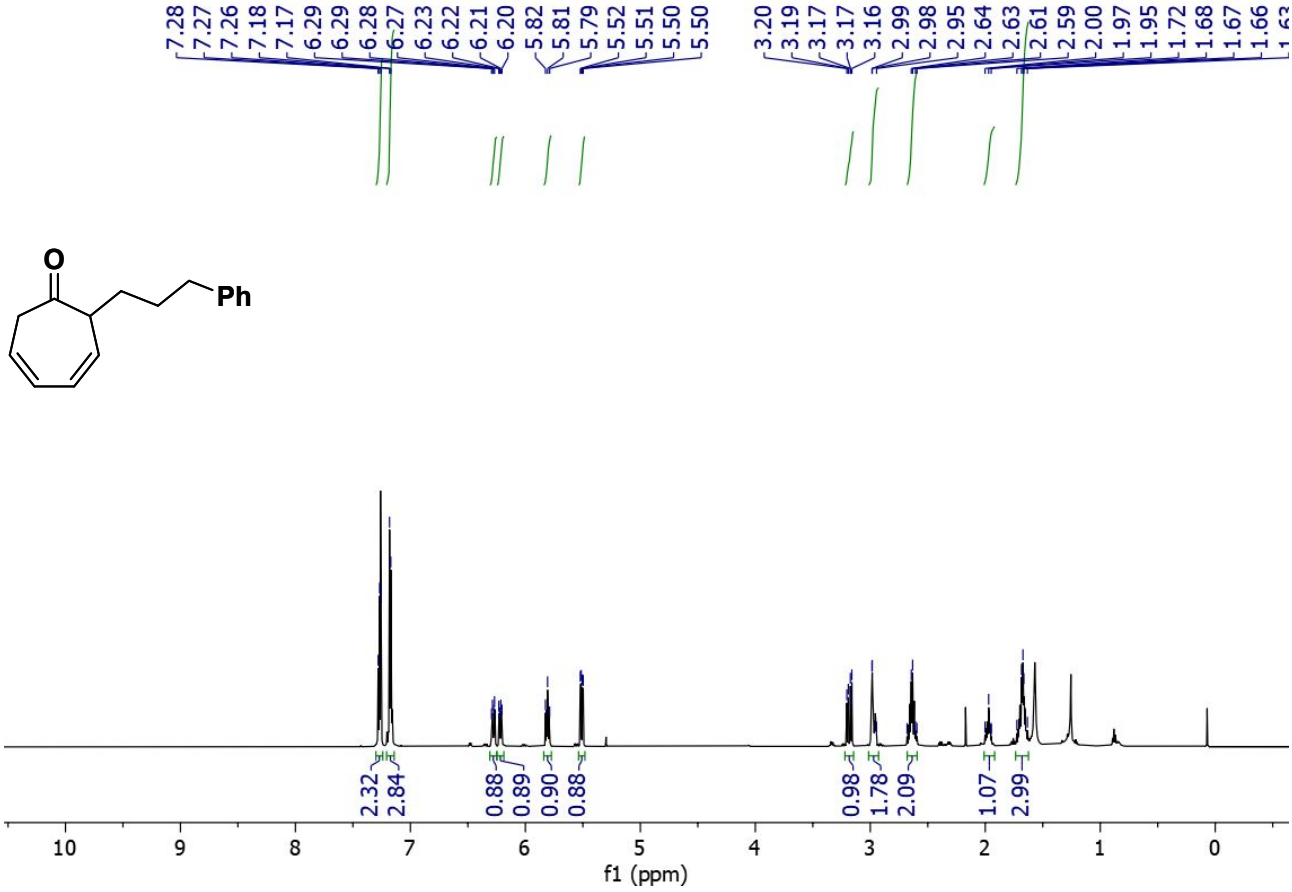

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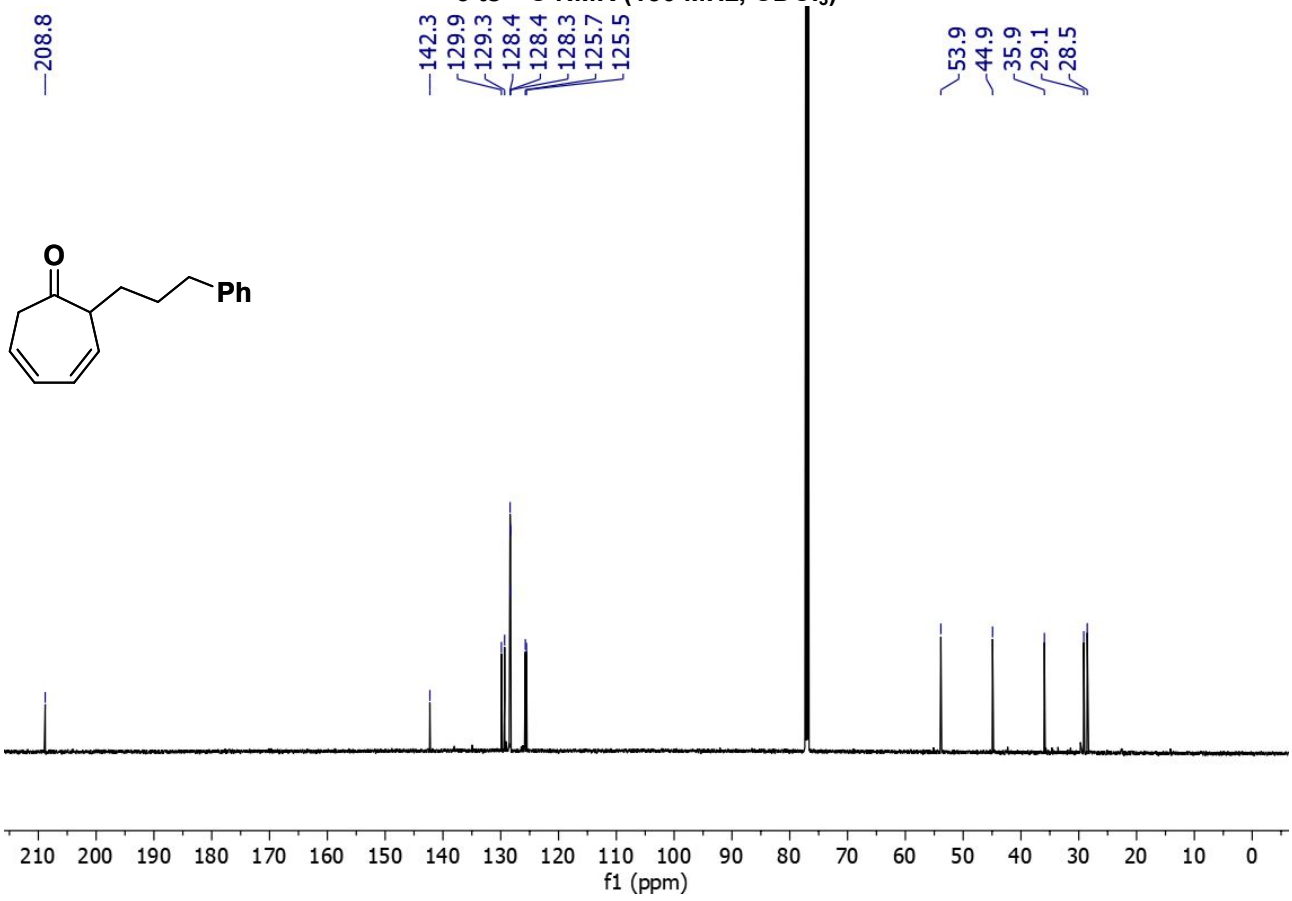

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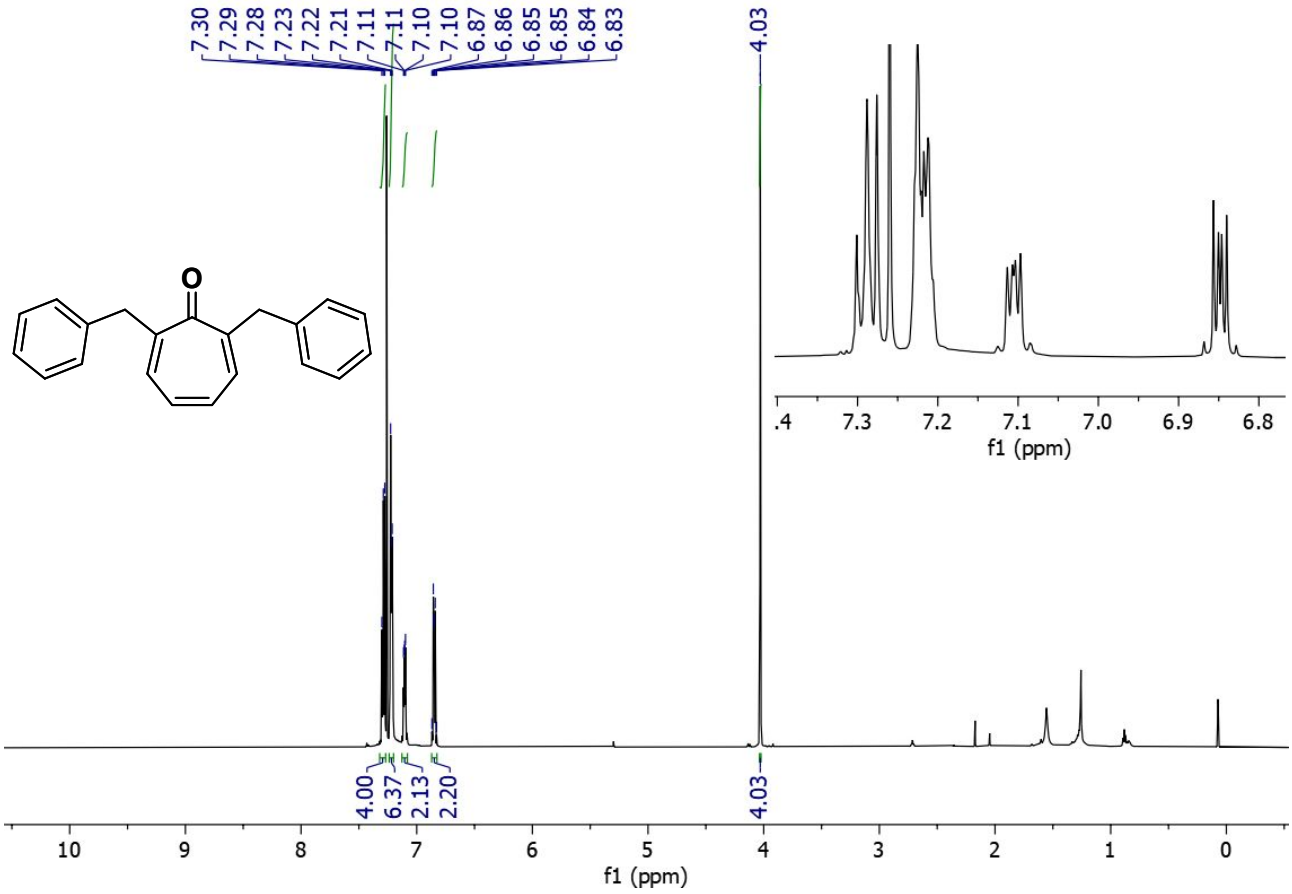
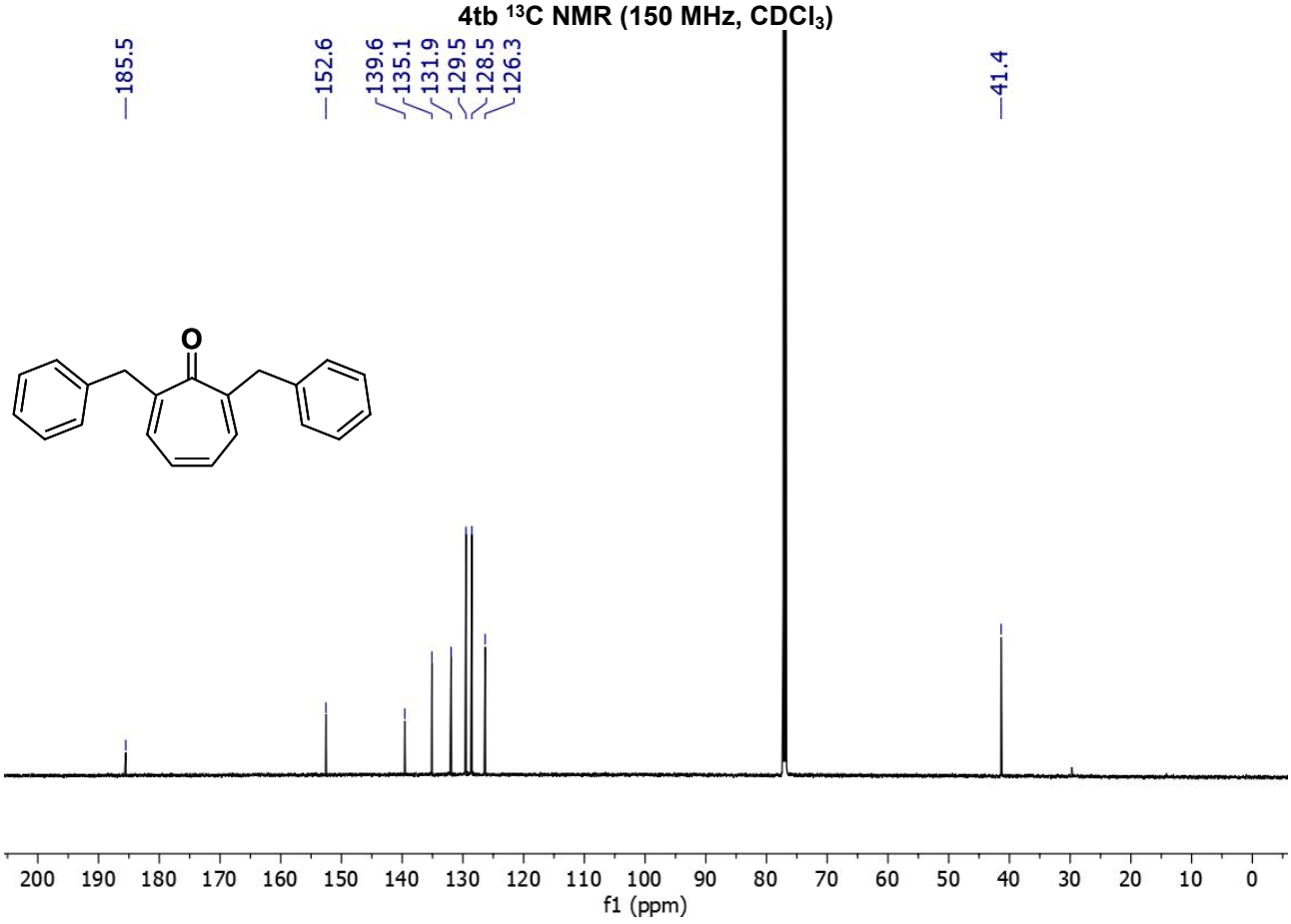


4tb ^{13}C NMR (150 MHz, $CDCl_3$)



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