Electrochemical Site-selective Alkylation of Tropones via Formal C(sp^3)-C(sp^2) Coupling Reaction

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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 ($CHCl_3$: 7.26 ppm). 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 ($CDCl_3$: 77.0 ppm).

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

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

Melting points (m.p.) measurements were performed on Bibby Stuart Scientific SMP3 apparatus and are uncorrected.

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

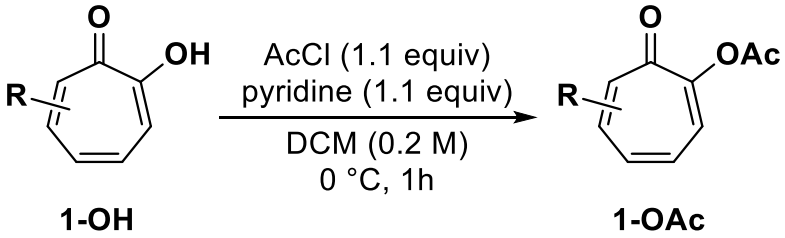
Compounds **2a**,[1] **2b**,[2] **2c**,[1] **2d**,[1] **2e**,[3] **2f**,[1] **2g**,[1] **2h**,[4] **2i**,[5] **2j**,[3] **2k**,[6] **2l**,[7] **2m**,[8] **2n**,[1] **2o**,[9] **2p**,[10] **2q**,[11] **2r**[12] and **2u**[1] are known compounds and were synthesized according to the procedure reported for **2t** (*vide infra*).

Electrochemical characterization of **1a-OAc**, **1a-Cl** and **2a** were 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. 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 ferrocene/ferrocenium 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 ($TEABF_4$) anhydrous DMF solution.

2. Synthesis of starting materials

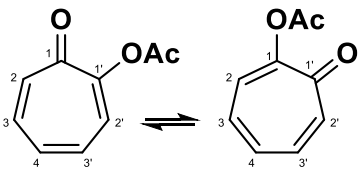
2.1 Synthesis of Tropolone acetates **1-OAc**

Acetate **1a-OAc** was prepared from commercially available tropolone (**1a-OH**) and acetate **1f-OAc** from commercially available Hinokitiol (**1f-OH**), following the procedure reported below. Acetates **1b-OAc** – **1e-OAc** were prepared (following the same procedure) from the corresponding 7-aryltropolones. These are known compounds and were prepared following an unmodified literature procedure.[13] Colchiceine acetate **1g-OAc** is a known compound and was prepared in two steps from naturally occurring and commercially available Colchicine following an unmodified literature procedure.[14] 2-Chlorotropone **1a-Cl** is a known compound and was prepared following an unmodified literature procedure.[13]



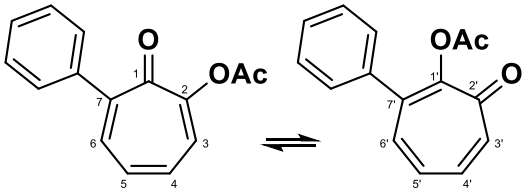
1-OH **1-OAc**

In a heat gun-dried Schlenk tube under N_2 atmosphere, the desired tropolone (1.0 mmol), dry DCM (5 mL) and pyridine (1.1 mmol, 87 mg, 89 µL) were added sequentially. The solution was cooled to 0 °C and acetyl chloride (1.1 mmol, 86 mg, 79 µL) was added dropwise. The resulting yellow-brown suspension was stirred at 0 °C until TLC indicated full consumption of the starting materials (ca. 1 h). The reaction was quenched with H_2O (5 mL) and std. NH_4Cl_{aq} (5 mL) and transferred to a separatory funnel where the aqueous phase was extracted with DCM (2 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography (FC) on silica gel to afford pure compounds **1-OAc**.

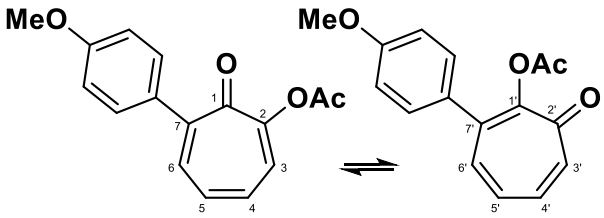


1a-OAc. Pale yellow solid (m.p. = 68-70 °C). FC eluent: *n*-hexane/EtOAc: 3:1. Yield = 85%, (0.85 mmol, 139.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 10.7 Hz, 2H), 7.06 (t, *J* = 10.1 Hz, 2H), 7.02 – 6.96 (m, 1H), 2.27 (s, 3H). Due to the rapid acetyl shift in solution, **1a-OAc** appears as a symmetrical molecule with protons on C2-C2' and C3-C3' giving rise to the same signal, respectively; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.2, 134.1 (b), 133.5, 20.7. Due to the rapid acetyl shift in solution, some signals

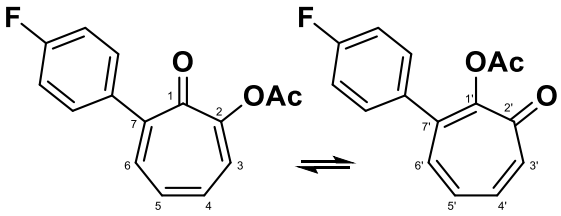
(probably the ones relative to C1-C1' and C2-C2') were not detected in the spectrum; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_9H_9O_3$ 165.0546; found 165.0541.



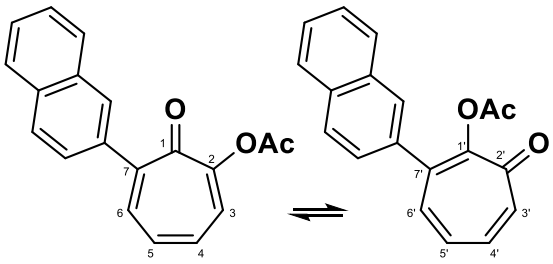
1b-OAc. Yellow solid (m.p. = 122-124 °C). FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 80%, (0.80 mmol, 192 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.43 – 7.40 (m, 4H), 7.40 – 7.35 (m, 2H), 7.26 – 7.23 (m, 1H), 7.12 – 7.04 (m, 2H), 2.27 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.4, 139.9, 137.0, 132.5, 131.9 (b), 128.7, 128.5, 128.2, 20.7. Due to the rapid acetyl shift in solution, some signals (probably the ones relative to C1-C1', C2-C2', C3-C3' and C7-C7') were not detected in the spectrum; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{13}O_3$ 241.0859; found 241.0850.



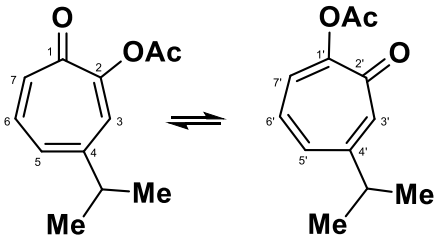
1c-OAc. Pale pink solid (m. p. = 155-158 °C). FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 76%, (0.76 mmol, 216 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.42 – 7.37 (m, 3H), 7.23 (dd, *J* = 9.6, 1.2 Hz, 1H), 7.08 (td, *J* = 9.9, 1.3 Hz, 1H), 7.02 (td, *J* = 10.0, 1.2 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.84 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.5, 159.9, 136.7, 132.5, 132.2, 131.3 (b), 130.3, 113.7, 55.3, 20.7. Due to the rapid acetyl shift in solution, some signals (probably the ones relative to C1-C1', C2-C2', C3-C3' and C7-C7') were not detected in the spectrum; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{15}O_4$ 271.0965; found 271.0977.



1d-OAc. Pale pink solid (m. p. = 110-112 °C). FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 81%, (0.81 mmol, 206 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.44 – 7.40 (m, 2H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.25 (dd, *J* = 9.4, 1.4 Hz, 1H), 7.13 – 7.03 (m, 4H), 2.30 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 168.4, 162.8 (d, *J* = 248.4 Hz), 136.9, 135.8 (d, *J* = 3.6 Hz), 132.5, 131.7 (b), 130.8 (d, *J* = 8.3 Hz), 115.2 (d, *J* = 21.7 Hz), 20.7. Due to the rapid acetyl shift in solution, some signals (probably the ones relative to C1-C1', C2-C2', C3-C3' and C7-C7') were not detected in the spectrum; **^{19}F NMR** (576 MHz, $CDCl_3$) δ = -112.98 – -113.10 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{12}FO_3$ 259.0765; found 259.0766.



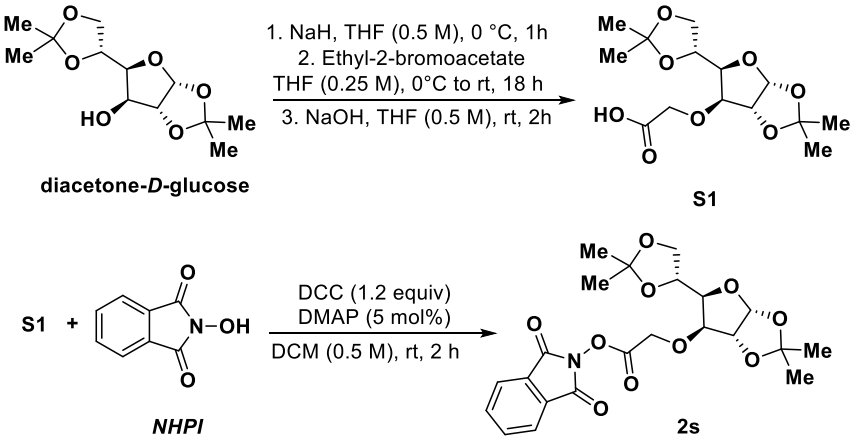
1e-OAc. Orange solid (m. p. = 177-181 °C). FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 91%, (0.91 mmol, 232 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.88 – 7.84 (m, 3H), 7.54 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.28 (dd, *J* = 9.5, 1.4 Hz, 1H), 7.14 (t, *J* = 9.6 Hz, 1H), 7.09 (t, *J* = 10.0 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 167.4, 136.6, 136.3, 132.2, 132.1, 131.5, 130.9, 127.3, 127.0, 126.6, 126.6, 125.6, 125.5, 125.2, 19.7. Due to the rapid acetyl shift in solution, some signals (probably the ones relative to C1-C1', C2-C2', C3-C3' and C7-C7') were not detected in the spectrum; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{19}H_{15}O_3$ 291.1016; found 291.1020.



1f-OAc. Orange oil. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 95%, (0.95 mmol, 204 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.34 – 7.29 (m, 2H minor), 7.22 (dd, *J* = 10.9, 0.8 Hz, 1H minor), 7.15 (d, *J* = 1.6 Hz, 1H major), 7.11 (dd, *J* = 10.7, 1.0 Hz, 1H major), 7.05 (t, *J* = 10.3 Hz, 1H major), 6.95 (dt, *J* = 9.8, 1.4 Hz, 1H major overlapped with m, 1H minor), 2.89 (hept, *J* = 6.9 Hz, 1H minor), 2.79 (hept, *J* = 6.9 Hz, 1H major), 2.34 (s, 3H major), 2.08 (s, 3H minor), 1.26 (d, *J* = 6.9 Hz, 6H minor), 1.23 (d, *J* = 6.9 Hz, 6H major), probably due to a slower -OAc shift in solution, the presence of two distinct structural isomers (ca. 6:1 ratio) is visible. **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 175.0, 171.3, 171.0, 168.3, 160.1, 155.5, 137.3, 133.5 (b), 132.6 (b), 127.8, 123.4, 122.4, 39.0 (minor), 38.4 (major), 23.4 (2C minor), 22.9 (2C major), 20.7 (major), 20.6 (minor). probably due to a slower -OAc shift in solution, the presence of two distinct structural isomers is visible in the aliphatic region; all the peaks of the aromatic region are given without assignment; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{12}H_{15}O_3$ 207.1016; found 207.1008.

2.2 Synthesis of *RAEs* **2s** and **2t**

RAE **2s** was prepared from commercially available diacetone-*D*-glucose as reported below.



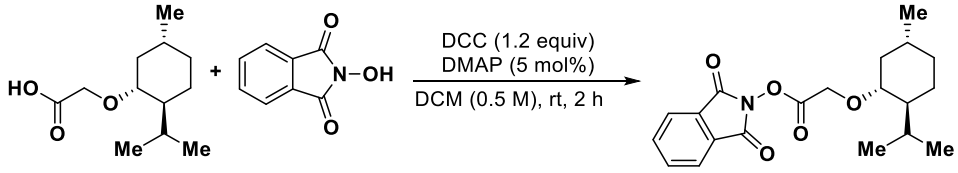
In a flame dried round bottom flask under N_2 atmosphere, NaH (60% in mineral oil, 5.5 mmol, 0.22 g) was washed three times with dry *n*-hexane (3 x 10 mL), subsequently suspended with stirring in dry THF (10 mL) and cooled to 0 °C. A solution of 1,2,5,6-di-*O*-isopropylidene-alpha-*D*-glucofuranose (diacetone-*D*-glucose, 5.0 mmol, 1.30 g) in dry THF (5 mL) was added dropwise and the resulting slurry was stirred at 0 °C for 1 h. Then, a solution of ethyl 2-bromoacetate (5.5 mmol, 0.61 mL) in dry THF (5 mL) was added dropwise at 0 °C. The reaction mixture was then stirred at room temperature for 18 h. The reaction was quenched with H_2O (10 mL) and std. NH_4Cl_{aq} (10 mL) and transferred to a separatory funnel where the aqueous phase was extracted with EtOAc (30 mL). The combined organic phases were washed with std. $NH_4Cl_{(aq)}$ (3 x 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was then dissolved in THF (10 mL), cooled to 0 °C and $NaOH_{(aq)}$ (10 M, 8 mL) was added. The resulting mixture was stirred at room temperature for 2 h, then poured in a separatory funnel and washed with EtOAc (2 x 10 mL). The pH was then carefully adjusted to 3 and the aqueous phase was extracted three times with EtOAc (3 x 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to obtain crude product **S1** that was used in the next step without purification.

In a flame dried Schlenk tube under N_2 atmosphere, crude **S1** (from previous step, ca. 5 mmol), N-hydroxyphthalimide (*NHPI*, 5.5 mmol, 0.81 g) and 4-dimethylaminopyridine (DMAP, 0.5 mmol, 60 mg) were dissolved in dry DCM (10 mL). The reaction mixture was cooled to 0 °C and *N,N'*-dicyclohexylcarbodiimide (DCC, 5.5 mmol, 1.13 g) was added portion-wise. The reaction mixture was stirred at room temperature for 2 h, then quenched with H_2O (10 mL) and std. NH_4Cl_{aq} (10 mL) and transferred to a separatory funnel where the

aqueous phase was extracted with DCM (20 mL). The combined organic phases were washed with std. $NH_4Cl_{(aq)}$ (3 x 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was finally purified by FC (*n*-hexane/EtOAc 2:1) to afford *RAE* **2s** as a white solid (1.53, 3.3 mmol, 60% yield; m. p. > 150 °C with decomposition).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 – 7.88 (m, 2H), 7.83 – 7.78 (m, 2H), 5.90 (d, *J* = 3.6 Hz, 1H), 4.74 (d, *J* = 3.7 Hz, 1H), 4.71 (d, *J* = 17.3 Hz, 1H), 4.66 (d, *J* = 17.3 Hz, 1H), 4.32 (ddd, *J* = 8.1, 6.2, 5.2 Hz, 1H), 4.15 – 4.11 (m, 2H), 4.08 (d, *J* = 2.9 Hz, 1H), 4.01 (dd, *J* = 8.7, 5.2 Hz, 1H), 1.49 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 166.9, 161.6 (2C), 135.0 (2C), 128.8 (2C), 124.1 (2C), 112.1, 109.3, 105.3, 84.3, 83.2, 81.1, 72.5, 67.4, 66.5, 26.9, 26.8, 26.2, 25.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{26}NO_{10}$ 464.1551; found 464.1560.

RAE **2t** was prepared from commercially available menthyloxyacetic acid, as reported below.

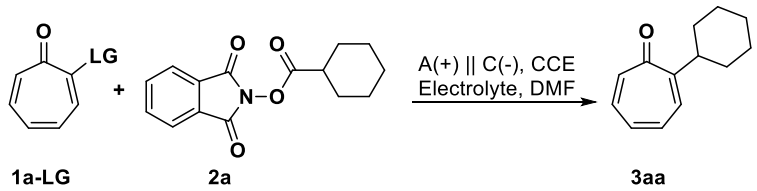


In a flame dried Schlenk tube under N_2 atmosphere, menthyloxyacetic acid (5.0 mmol, 1.05 g), *N*-hydroxyphthalimide (*NHPI*, 5.5 mmol, 0.81 g) and DMAP (0.5 mmol, 60 mg) were dissolved in dry DCM (10 mL). The reaction mixture was cooled to 0 °C and DCC (5.5 mmol, 1.13 g) was added portion-wise. The reaction mixture was stirred at room temperature for 2 h, then quenched with H_2O (10 mL) and std. NH_4Cl_{aq} (10 mL) and transferred to a separatory funnel where the aqueous phase extracted with DCM (20 mL). The combined organic phases were washed with std. $NH_4Cl_{(aq)}$ (3 x 10 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was finally purified by FC (*n*-hexane/EtOAc 3:1) to afford *RAE* **2t** as a white solid (1.58 g, 4.4 mmol, 88% yield; m. p. > 140 °C with decomposition).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 – 7.80 (m, 2H), 7.75 – 7.70 (m, 2H), 4.45 (s, 2H), 3.22 (td, *J* = 10.6, 4.2 Hz, 1H), 2.23 (heptd, *J* = 7.0, 2.5 Hz, 1H), 2.07 (dtd, *J* = 12.1, 3.8, 1.8 Hz, 1H), 1.64 – 1.54 (m, 2H), 1.36 – 1.27 (m, 1H), 1.27 – 1.21 (m, 1H), 0.96 – 0.85 (m, 2H) partially overlapped with 0.88 (d, *J* = 6.6 Hz, 3H), 0.84 – 0.75 (m, 1H), 0.84 (d, *J* = 7.1 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 167.3, 161.7 (2C), 134.8 (2C), 128.9 (2C), 124.0 (2C), 80.9, 63.5, 48.2, 39.8, 34.3, 31.5, 25.4, 23.2, 22.3, 21.0, 16.; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{26}NO_5$ 360.1805; found 360.1798.

3. Additional Optimization Tables

3.1. **Table S1**: Additional reaction optimization results.[a]



1a-LG 2a 3aa

Entry	LG	**1a**:**2a** (F/mol$_{1a}$)	A(+) || C(-)	Electrolyte	I (mA)	**3aa** (%)	**4aa**/**5aa** (%)
1	**OTs**	1:1.5 (2)	Zn || Ag	$TEABF_4$	2	-	-
2	**OTf**	1:1.5 (2)	Zn || Ag	$TEABF_4$	2	-	-
3	**OH*HCl**	1:1.5 (2)	Zn || Ag	$TEABF_4$	2	-	-
4	**OPiv**	1:1.5 (2)	Zn || Ag	$TEABF_4$	2	50	-
5	OAc	1:1.5 (2)	Zn || Ag	**$TBAPF_6$**	2	52	-
6	OAc	1:1.5 (2)	Zn || Ag	**TEAI**	2	38	3/4
7	OAc	1:1.5 (2)	Zn || Ag	**TEABr**	2	36	6/7
8	OAc	1:1.5 (2)	Zn || Ag	**$TBAClO_4$**	2	38	-/3
9	OAc	1:1.5 (2)	**Zn || GC**	$TEABF_4$	2	36	2/-
10	OAc	1:1.5 (2)	**Zn || Al**	$TEABF_4$	2	-	-
11	OAc	1:1.5 (2)	**Zn || Pt**	$TEABF_4$	2	12	-
12	OAc	1:1.5 (2)	**Zn || Ni**	$TEABF_4$	2	31	2/7
13	OAc	1:1.5 (2)	**Zn || Ni_{foam}**	$TEABF_4$	2	-	-
14	OAc	1:1.5 (2)	Zn || Ag	$TEABF_4$	2	53	7/4
15	OAc	2:1 (1)	Zn || Ag	$TEABF_4$	**4**	33	-
16	OAc	2:1 (1)	Zn || Ag	$TEABF_4$	**1.5**	41	-
17	OAc	2:1 (1)	Zn || Ag	$TEABF_4$	**1**	18	-
18	OAc	2:1 (1)	Zn || Ag	$TEABF_4$	3	71	-

[a] All reactions were carried out with ElectraSyn 2.0 apparatus under constant current electrolysis (CCE, A: anode, C: cathode). The reported yields are isolated yields after flash chromatography.

Compare entries 1-13 with entry 14. Leaving groups such as OTs or OTf (entries 1 and 2) led to a suppression of reactivity of the desired starting material **1-LG**, while a pivalate ester (entry 4) proved to be comparable with optimal acetate. Tropolone **1-OH** was also converted into its hydrochloric acid adduct and tested in the electrochemical alkylation (entry 3), however this resulted only in decomposition products.

Entries 5-8 and 9-13 show the behavior of different electrolytes and electrodic couples, respectively, being less efficient of the optimal choice.

A fine tuning of current values is presented in entries 15-18.

4. Electrochemical Alkylation of Tropones 1

4.1 General procedures for the electrochemical alkylation of tropones **1**.

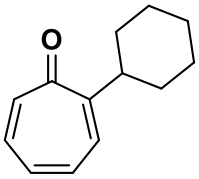
General Procedure A. The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with 2-acetoxytropone **1a** (0.30 mmol, 2.0 equiv, 49.2 mg), *RAE* **2** (0.15 mmol, 1 equiv) and $TEABF_4$ (0.30 mmol, 65.0 mg). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ag), was inserted into 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 the mixture was bubbled with Ar (balloon). The reaction mixture was electrolyzed (under Ar, balloon) at a constant current of 3.0 mA, until a total charge of 0.30 mF (2.0 F/mol_2) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and $NH_4Cl_{(aq)}$ (1 M, 10 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 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was finally purified by FC to afford pure products **3**.

General Procedure B. The ElectraSyn vial (5 mL), equipped with a stir bar, was charged with tropone derivative **1** (0.15 mmol, 1.0 equiv), *RAE* **2a** (0.23 mmol, 1.5 equiv, 63.0 mg) and $TEABF_4$ (0.30 mmol, 65.0 mg). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ag), 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 the mixture was bubbled with Ar (balloon). The reaction mixture was electrolyzed (under Ar, balloon) at a constant current of 2.0 mA, until a total charge of 0.30 mF (2.0 F/mol_1) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and $NH_4Cl_{(aq)}$ (1 M, 10 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 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was finally purified by FC to afford pure products **3**.

Additional notes:

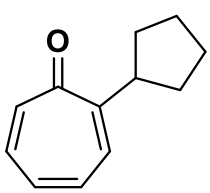
For products **3ag**, **3ai**, **3aj**, **3ak**, and **3at** chromatographic separation from phthalimide coproduct was troublesome. Therefore, after FC a basic wash (aqueous 1M NaOH / Et_2O) was carried out to obtain the pure compounds.

4.2 Characterization data of compounds **3**.

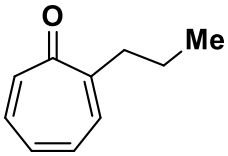


3aa. Obtained following *General Procedure A*. Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 71%, (0.107 mmol, 20.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.15 (d, *J* = 9.0 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.99 (ddd, *J* = 10.2, 9.0, 1.1 Hz, 1H), 6.90 – 6.85 (m, 1H), 3.14 (tt, *J* = 11.9, 2.9 Hz, 1H), 1.86 – 1.73 (m, 5H), 1.52 – 1.42 (m, 2H), 1.29 – 1.17 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.1, 160.2, 140.4, 134.9, 134.0, 132.4, 132.2, 40.2, 33.2 (2C), 26.8 (2C), 26.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{13}H_{17}O$ 189.1274; found 189.1285. Product **3aa** is a known compound, spectroscopic data match with the ones reported in literature.[15]

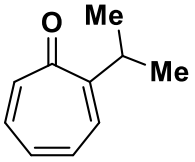
Preparation of **3aa** on 1.0 mmol scale. The ElectraSyn vial (10 mL), equipped with a stir bar, was charged with 2-acetoxytropone **1a** (2.0 mmol, 2.0 equiv, 328 mg), *RAE* **2a** (1.0 mmol, 1 equiv, 272 mg) and $TEABF_4$ (0.90 mmol, 195 mg). The ElectraSyn vial cap, equipped with anode (Zn) and cathode (Ag), was inserted into the mixture and closed with a rubber septum. The vessel was evacuated and backfilled with Ar three times, then dry DMF (9.0 mL) was added and the mixture stirred until complete dissolution of the solids occurred while the mixture was bubbled with Ar (balloon). The reaction mixture was electrolyzed (under Ar, balloon) at a constant current of 2 mA, until a total charge of 2.0 mF (2.0 F/mol$_{\mathbf{2a}}$) was reached. The ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (20 mL) and $NH_4Cl_{(aq)}$ (1 M, 20 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 20 mL). The combined organic layers were washed with $NH_4Cl_{(aq)}$ (0.1 M, 5 x 40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was finally purified by FC (*n*-hexane/EtOAc: 8:1) to afford pure product **3aa** as a yellow sticky oil (122 mg, 0.65 mmol, 65%yield).



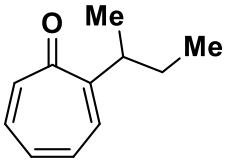
3ab. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 66%, (0.099 mmol, 17.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.7 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.97 (t, *J* = 9.9 Hz, 1H), 6.88 (dd, *J* = 10.8, 7.9 Hz, 1H), 3.44 (p, *J* = 8.7 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.82 – 1.66 (m, 4H), 1.49 – 1.39 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.5, 159.4, 139.9, 134.9, 133.8, 132.2, 131.9, 43.0, 33.0 (2C), 25.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{12}H_{15}O$ 175.1117; found 175.1122. Product **3ab** is a known compound, spectroscopic data match with the ones reported in literature.[15]



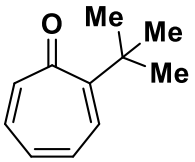
3ac. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 6:1. Yield = 51%, (0.077 mmol, 11.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 1.0 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.99 – 6.87 (m, 2H), 2.63 (t, 2H), 1.65 – 1.55 (m, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.2, 155.9, 140.4, 135.3, 134.8, 133.8, 132.5, 37.5, 22.0, 14.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{10}H_{13}O$ 149.0961; found 149.0967.



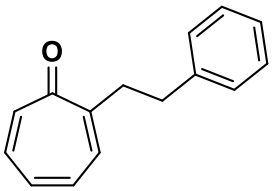
3ad. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 6:1. Yield = 60%, (0.09 mmol, 13.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.9 Hz, 1H), 7.08 – 7.06 (m, 2H), 7.04 – 6.97 (m, 1H), 6.93 – 6.86 (m, 1H), 3.46 (hept, *J* = 6.9 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.1, 161.4, 140.5, 135.0, 134.0, 132.4, 131.9, 30.2, 22.4 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{10}H_{13}O$ 149.0961; found 149.0968.



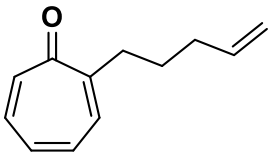
3ae. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 10:1. Yield = 65%, (0.098 mmol, 15.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 8.9 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.01 (t, *J* = 9.9 Hz, 1H), 6.93 – 6.87 (m, 1H), 3.31 – 3.22 (m, 1H), 1.64 – 1.54 (m, 1H), 1.54 – 1.44 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.3, 160.4, 140.4, 135.1, 133.9, 132.7, 132.4, 36.8, 29.6, 20.3, 12.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{15}O$ 163.1117; found 163.1125.



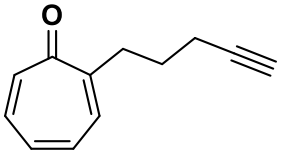
3af. Obtained following <u>*General Procedure B*</u> (from **1a** and *RAE* **2f**) but electrolyzing the mixture at a constant current of 3.0 mA until a total charge of 0.46 mF (2.0 F/mol$_{2e}$) was reached. Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 25:1. Yield = 47%, (0.071 mmol, 11.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.27 (d, 1H, partially overlapped with residual solvent), 7.00 – 6.91 (m, 2H), 6.89 – 6.79 (m, 2H), 1.39 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 188.9, 160.5, 138.3, 132.9, 132.9, 131.8, 130.9, 38.0, 29.9 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{15}O$ 163.1117; found 163.1110.



3ag. Obtained following <u>*General Procedure A*</u> but using 0.45 mmol (3.0 equiv) of **1a**. Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 5:1. Yield = 54%, (0.081 mmol, 17.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.30 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 7.15 – 7.05 (m, 3H), 6.93 – 6.84 (m, 2H), 2.98 – 2.92 (m, 2H), 2.92 – 2.86 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.0, 153.7, 140.5, 139.6, 134.4 (2C overlapped), 132.7, 131.7, 127.6, (2C) 127.3 (2C), 124.9, 37.0, 33.8; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{15}H_{15}O$ 211.1117; found 211.1109.

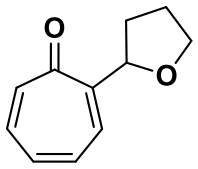


3ah. Obtained following <u>*General Procedure A.*</u> Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 8:1. Yield = 46%, (0.069 mmol, 12.0 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.18 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.03 (ddd, *J* = 12.1, 7.3, 1.5 Hz, 1H), 6.99 (dt, *J* = 12.0, 1.2 Hz, 1H), 6.91 – 6.86 (m, 1H), 6.86 – 6.81 (m, 1H), 5.76 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.96 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.90 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 2.65 – 2.47 (m, 2H), 2.11 – 2.02 (m, 2H), 1.65 – 1.56 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.1, 154.9, 139.4, 137.4, 134.3, 133.9, 132.8, 131.5, 113.8, 34.1, 32.6, 27.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{12}H_{15}O$ 175.1117; found 175.1118.

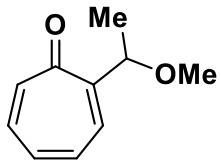


3ai. Obtained following <u>*General Procedure A.*</u> Yellow sticky oil. FC (performed twice) eluent: first *n*-hexane/EtOAc: 8:1, then DCM/Et_2O: from 100:1 to 30:1. Yield = 63%, (0.095 mmol, 16.3 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 8.5 Hz, 1H), 7.04 (ddd, *J* = 12.1, 7.3, 1.6 Hz, 1H), 7.00 (d, *J* = 12.5 Hz, 1H), 6.92 – 6.84 (m, 2H), 2.70 (dd, *J* = 8.4, 6.7 Hz, 2H), 2.17 (td, *J* = 7.0, 2.7 Hz, 2H), 1.92 (t, *J* = 2.6 Hz, 1H), 1.79 – 1.72 (m, 2H); **^{13}C NMR** (150 MHz,

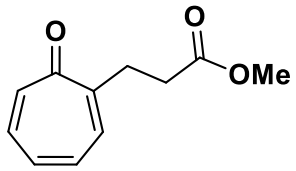
$CDCl_3$) δ = 187.0, 154.9, 140.5, 135.5, 135.4, 133.8, 132.9, 84.1, 68.9, 34.7, 27.3, 18.2; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{12}H_{13}O$ 173.0961; found 173.0955.



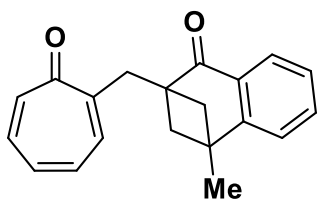
3aj. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 3:1. Yield = 66%, (0.099 mmol, 17.4 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 9.0 Hz, 1H), 7.15 (ddt, *J* = 12.1, 8.0, 1.1 Hz, 1H), 7.09 (t, *J* = 9.9 Hz, 1H), 7.05 (d, *J* = 12.1 Hz, 1H), 6.96 (dd, *J* = 10.8, 8.1 Hz, 1H), 5.04 (t, *J* = 7.2 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.93 (q, *J* = 7.3 Hz, 1H), 2.68 – 2.56 (m, 1H), 2.04 – 1.94 (m, 1H), 1.94 – 1.81 (m, 1H), 1.60 – 1.52 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.5, 156.4, 141.1, 135.7, 134.2, 133.1, 131.3, 78.0, 68.8, 32.7, 25.8; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}O_2$ 177.0910; found 177.0893.



3ak. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 55%, (0.083 mmol, 13.5 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.51 (dt, *J* = 8.9, 0.8 Hz, 1H), 7.19 – 7.04 (m, 3H), 7.02 – 6.94 (m, 1H), 4.66 (q, *J* = 6.3 Hz, 1H), 3.27 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.7, 156.0, 141.3, 135.6, 134.3, 133.5, 132.2, 75.8, 56.8, 22.0; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{10}H_{13}O_2$ 165.0910; found 165.0916.

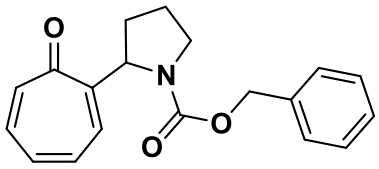


3al. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 63%, (0.095 mmol, 18.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.36 – 7.32 (m, 1H), 7.13 – 7.09 (m, 1H), 7.06 (dt, *J* = 12.1, 1.1 Hz, 1H), 6.98 – 6.91 (m, 2H), 3.65 (s, 3H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.8, 172.5, 152.6, 139.7, 134.9, 134.6, 132.8, 132.2, 50.6, 31.5, 30.5; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{11}H_{13}O_3$ 193.0859; found 193.0851.

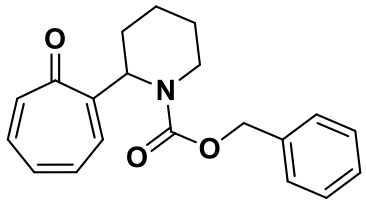


3am. Obtained following *General Procedure A.* Yellow sticky oil. FC (performed twice) eluent: first *n*-hexane/EtOAc: 5:1, then DCM/Et_2O: from 50:1. Yield = 58%, (0.087 mmol, 25.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.35 – 7.30 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.97 (t, *J* = 9.8 Hz, 1H), 6.94 – 6.89 (m, 1H), 3.22 (s, 2H), 2.46 (s, 4H), 1.46 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 200.9, 186.7, 152.7, 151.1, 139.4, 136.6, 134.4, 132.7, 131.9, 131.9, 127.9,

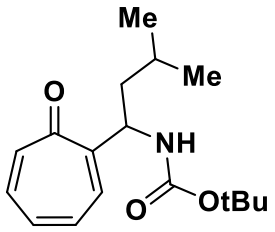
125.8, 125.6, 120.7, 52.0, 50.8, 37.5, 35.3, 28.7; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{19}O_2$ 291.1380; found 291.1386.



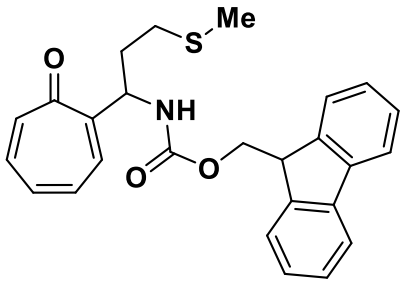
3an. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: DCM/Acetone: from 50:1 to 20:1. Yield = 64%, (0.096 mmol, 29.7 mg). 1.5:1 Mixture of rotamers **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.41 – 7.28 (m, 2H major + minor), 7.22 – 7.09 (m, 3H major + 3H minor), 7.09 – 7.02 (m, 3H major + 3H minor), 7.01 – 6.90 (m, 2H major + 2H minor), 5.22 – 5.06 (m, 2H major + 3H minor), 4.94 (d, *J* = 12.6 Hz, 1H major), 3.71 – 3.57 (m, 2H major + 2H minor), 2.50 – 2.35 (m, 1H major + 1H minor), 1.95 – 1.86 (m, 1H major + 1H minor), 1.82 – 1.71 (m, 2H major + 2H minor); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.3 (minor), 185.3 (major), 154.4 (major), 153.8 (major), 153.6 (minor), 153.4 (minor), 140.3 (minor), 140.1 (major), 135.8 (minor), 135.6 (major), 134.6 (major), 134.5 (minor), 132.6 (2C major + 2C minor), 132.2 (2C major + 2C minor), 130.3 (major), 130.1 (minor), 127.5 (minor), 127.3 (major), 127.0 (minor), 126.9 (major), 126.6 (minor), 126.4 (major), 65.9 (minor), 65.6 (major), 59.0 (minor), 58.1 (major), 46.7 (major), 46.4 (minor), 32.0 (major), 31.0 (minor), 22.6 (minor), 21.9 (major); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{19}H_{20}NO_3$ 310.1438; found 310.1444.



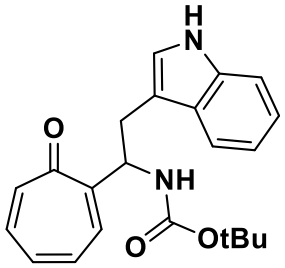
3ao. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 3:1. Yield = 61%, (0.092 mmol, 29.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.29 – 7.22 (m, 3H), 7.22 – 7.15 (m, 2H), 7.12 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 6.99 (d, *J* = 12.0 Hz, 1H), 6.95 – 6.89 (m, 2H), 5.51 (t, *J* = 5.6 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 5.03 (d, *J* = 12.6 Hz, 1H), 4.20 (ddd, *J* = 13.7, 6.1, 2.8 Hz, 1H), 3.22 (ddd, *J* = 13.5, 11.8, 4.5 Hz, 1H), 1.99 – 1.93 (m, 2H), 1.76 – 1.55 (m, 3H), 1.38 – 1.28 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.4, 156.1, 154.5, 140.4, 136.6, 135.1, 133.2, 133.0, 131.8, 128.3 (2C), 127.7, 127.6 (2C), 67.0, 54.1, 41.3, 26.8, 24.2, 19.2; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{22}NO_3$ 324.1594; found 324.1589.



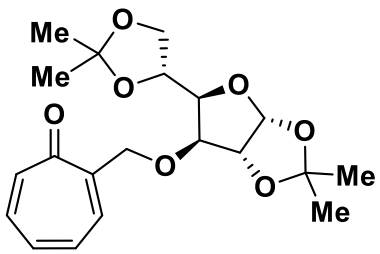
3ap. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: DCM/Acetone: 80:1. Yield = 58%, (0.087 mmol, 25.2 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.25 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.11 (ddd, *J* = 12.1, 7.2, 2.1 Hz, 1H), 7.01 (d, *J* = 12.1 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.12 (t, *J* = 9.7 Hz, 1H), 2.34 – 2.25 (m, 1H), 1.40 (s, 9H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.98 – 0.81 (m, 2H), 0.75 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.4, 155.8, 152.2, 141.7, 136.7, 135.7, 134.1, 133.9, 79.0, 65.5, 30.0, 28.4 (3C), 20.9, 19.6; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{17}H_{26}NO_3$ 292.1907; found 292.1899.



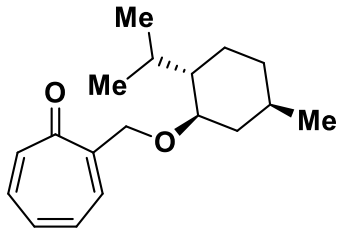
3aq. Obtained following *General Procedure A.* Yellow sticky oil. FC (performed twice) eluent: first *n*-hexane/EtOAc: 3:2, then DCM/Et_2O: from 50:1 to 20:1. Yield = 59%, (0.089 mmol, 38.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.33 – 7.26 (m, 2H), 7.19 – 7.10 (m, 1H), 7.07 (d, *J* = 11.9 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.36 (d, *J* = 9.7 Hz, 1H), 4.80 (q, *J* = 8.2 Hz, 1H), 4.38 (dd, *J* = 10.6, 7.4 Hz, 1H), 4.31 (dd, *J* = 10.6, 7.2 Hz, 1H), 4.19 (t, *J* = 7.1 Hz, 1H), 2.54 – 2.43 (m, 2H), 2.27 – 2.19 (m, 1H), 2.16 – 2.10 (m, 1H), 2.09 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.3, 156.1, 151.4, 144.0, 142.0 (2C), 141.3 (2C), 136.5, 136.0, 134.5, 134.2, 127.6 (2C), 127.0 (2C), 125.1 (2C), 119.9 (2C), 66.8, 58.2, 47.2, 32.3, 31.2, 15.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{26}NO_3S$ 432.1628; found 432.1637.



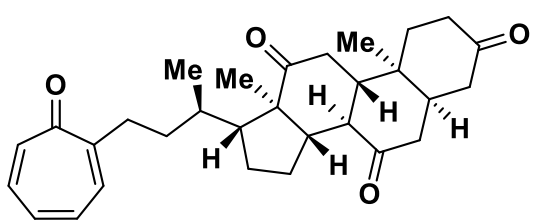
3ar. Obtained following *General Procedure A.* Yellow sticky oil. FC eluent: DCM/Acetone: from 50:1 to 20:1. Yield = 51%, (0.077 mmol, 27.8 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.18 – 7.03 (m, 4H), 6.98 – 6.80 (m, 3H), 6.70 (t, *J* = 10.0 Hz, 1H), 6.05 (s, 1H), 5.09 – 4.91 (m, 1H), 3.41 – 3.31 (m, 1H), 3.28 – 3.16 (m, 1H), 1.38 (s, 9H) all signals are broad due to the slow rotation of the N-C(O) bond of the carbamate unit; **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 187.4, 155.4, 152.3, 141.7, 136.2, 135.9, 135.8, 133.9, 133.8, 127.6, 122.8, 121.9, 119.4, 119.2, 112.3, 111.0, 79.3, 58.2, 29.6, 28.4 (3C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{22}H_{25}N_2O_3$ 365.1860; found 365.1849.



3as. Obtained following <u>*General Procedure A.*</u> Yellow sticky oil. FC eluent: *n*-hexane/Acetone: from 3.5:1. Yield = 53%, (0.080 mmol, 30.1 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ =7.59 (d, *J* = 8.8 Hz, 1H), 7.19 (dd, *J* = 12.2, 8.0 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.00 (t, *J* = 9.5 Hz, 1H), 5.91 (d, *J* = 3.7 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H), 4.66 (d, *J* = 3.7 Hz, 1H), 4.60 (d, *J* = 17.1 Hz, 1H), 4.40 (dt, *J* = 8.4, 5.8 Hz, 1H), 4.16 – 4.11 (m, 2H), 4.08 (d, *J* = 2.7 Hz, 1H), 4.02 (dd, *J* = 8.6, 5.5 Hz, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.2, 149.5, 139.7, 135.1, 133.0, 132.5, 131.8, 110.9, 108.2, 104.2, 81.3, 81.2, 80.2, 71.3, 68.1, 66.6, 25.9, 25.8, 25.1, 24.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{27}O_7$ 379.1751; found 379.1759.

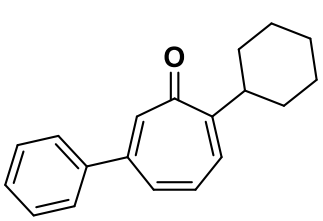


3at. Obtained following <u>*General Procedure A.*</u> Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 4:1. Yield = 55%, (0.083 mmol, 22.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.9 Hz, 1H), 7.18 (dd, *J* = 11.9, 8.4 Hz, 1H), 7.13 (t, *J* = 9.9 Hz, 1H), 7.07 (d, *J* = 12.0 Hz, 1H), 6.98 (dd, *J* = 10.7, 8.2 Hz, 1H), 4.65 (d, *J* = 17.7 Hz, 1H), 4.37 (d, *J* = 17.7 Hz, 1H), 3.28 (td, *J* = 10.6, 4.0 Hz, 1H), 2.31 – 2.17 (m, 2H), 1.70 – 1.62 (m, 2H), 1.43 – 1.32 (m, 2H), 1.06 – 0.97 (m, 1H), 0.92 (d, *J* = 6.1 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.4, 152.6, 140.5, 135.9, 134.3, 132.9, 132.5, 80.0, 67.5, 48.3, 40.5, 34.5, 31.5, 25.9, 23.4, 22.3, 21.0, 16.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{18}H_{27}O_2$ 275.2006; found 275.1998.

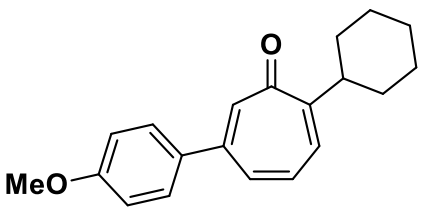


3au. Obtained following <u>*General Procedure A.*</u> Yellow sticky solid. FC (performed twice) eluent: first *n*-hexane/Acetone: from 3:1 to 2:1, then DCM:Et_2O 10:1. Yield = 44%, (0.060 mmol, 27.7 mg). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 8.7 Hz, 1H), 7.09 (ddd, *J* = 12.1, 7.5, 1.4 Hz, 1H), 7.04 (dt, *J* = 12.1, 1.1 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.92 – 6.87 (m, 1H), 2.96 – 2.80 (m, 3H), 2.69 (ddd, *J* = 12.9, 11.3, 4.7 Hz, 1H), 2.58 (ddd, *J* = 12.9, 10.6, 5.0 Hz, 1H), 2.38 – 2.25 (m, 4H), 2.25 – 2.18 (m, 2H), 2.18 – 2.05 (m, 2H), 2.05 – 1.99 (m, 2H), 1.96 (ddd, *J* = 14.5, 5.4, 3.0 Hz, 1H), 1.84 (td, *J* = 11.5, 7.1 Hz, 1H), 1.68 (tdd, *J* = 11.8, 4.7, 1.9 Hz, 2H), 1.61 (td, *J* = 14.5, 4.5 Hz, 1H), 1.39 (s, 3H) partially overlapped with 1.37 – 1.19 (m, 4H), 1.07 (s, 3H), 0.95 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR**

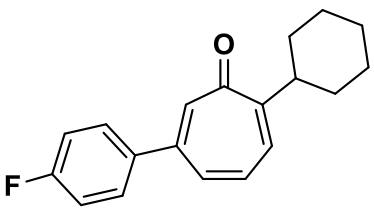
(150 MHz, $CDCl_3$) δ = 212.0, 209.1, 208.8, 187.0, 156.7, 140.3, 135.3, 134.7, 133.9, 132.4, 56.9, 51.7, 49.0, 46.8, 45.7, 45.5, 45.0, 42.8, 38.6, 36.5, 36.4, 36.0, 35.3, 34.8, 33.0, 27.6, 25.1, 21.9, 19.0, 11.9; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{30}H_{38}O_4$ 462.2770; found 462.2777.



3ab. Obtained following *General Procedure B.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 20:1. Yield = 47%, (0.071 mmol, 18.7 mg). The regiochemistry of **3ab** was assigned in analogy with products **3ac**, **3ad** and **3ae** given that the characteristic signal, not showing a ^3J coupling, is overlapped with the residual $CHCl_3$ peak. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.53 – 7.50 (m, 2H), 7.45 – 7.39 (m, 3H), 7.26 (s, 1H, partially overlapped with the residual solvent peak), 7.18 – 7.10 (m, 2H), 7.03 (dd, *J* = 11.4, 8.9 Hz, 1H), 3.17 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.91 – 1.74 (m, 3H), 1.48 (qt, *J* = 13.1, 3.1 Hz, 2H), 1.33 – 1.21 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.3, 160.5, 148.1, 142.2, 139.0, 134.3, 133.0, 131.8, 128.8 (2C), 128.7, 127.7 (2C), 40.2, 33.1 (2C), 26.8 (2C), 26.3; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{19}H_{21}O$ 265.1587; found 265.1596.

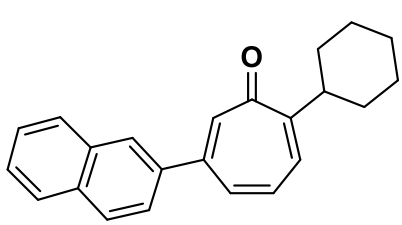


3ac. Obtained following *General Procedure B.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 20:1 then DCM/Acetone: 100:1. Yield = 44%, (0.066 mmol, 19.4 mg). The regiochemistry of **3ac** was assigned on the basis of the multiplicity of the aromatic peaks in the ^{1}H NMR spectrum. The signal at 7.25 ppm, lacking a ^3J coupling, is indicative of thee 2,6-disubstituted isomer. was assigned **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.49 – 7.42 (m, 2H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.01 (dd, *J* = 11.2, 9.0 Hz, 1H), 6.97 – 6.94 (m, 2H), 3.85 (s, 3H), 3.17 (tt, *J* = 11.9, 3.0 Hz, 1H), 1.89 – 1.74 (m, 5H), 1.48 (qt, *J* = 13.2, 4.1 Hz, 2H), 1.30 – 1.19 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.2, 160.4, 160.2, 147.6, 138.2, 134.5, 134.3, 132.8, 131.6, 129.1 (2C), 114.2 (2C), 55.4, 40.2, 33.1 (2C), 26.8 (2C), 26.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{20}H_{23}O_2$ 295.1693; found 295.1697.

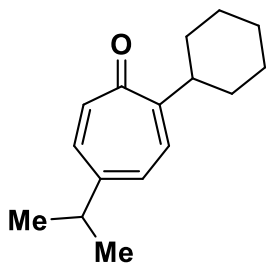


3ad. Obtained following *General Procedure B.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 30:1 then DCM/Acetone: 100:1. Yield = 32%, (0.048 mmol, 13.5 mg). The regiochemistry of **3ad** was assigned based on the multiplicity of the aromatic peaks

in the ^{1}H NMR spectrum. The signal at 7.22 ppm, lacking a ^{3}J coupling, is indicative of thee 2,6-disubstituted isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.52 – 7.46 (m, 2H), 7.22 (s, 1H), 7.17 – 7.07 (m, 4H), 7.03 (dd, *J* = 11.1, 8.8 Hz, 1H), 3.16 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.89 – 1.74 (m, 5H), 1.48 (qt, *J* = 13.2, 3.8 Hz, 2H), 1.31 – 1.19 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.2, 164.0, 162.3 - 160.7 (d, *J* = 251.6 Hz, 1C), 147.0, 138.8 - 138.2 (d, *J* = 3.3 Hz, 1C), 138.3, 134.1, 133.2, 131.8, 129.6 - 129.5 (d, *J* = 8.4 Hz, 2C), 115.9 - 115.7 (d, *J* = 21.5 Hz, 2C), 40.2, 40.2, 33.1, 26.8, 26.3; **^{19}F NMR** (576 MHz, $CDCl_3$) δ = -111.17 – -111.28 (m, 1F); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{19}H_{20}FO$ 283.1493; found 283.1505.

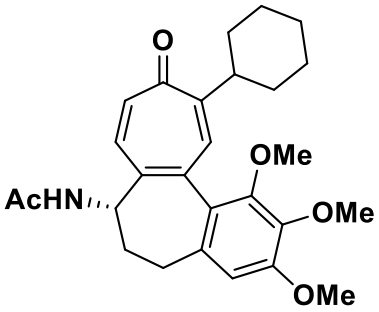


3ae. Obtained following *General Procedure B.* Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 30:1 then DCM/Acetone: 100:1. Yield = 31%, (0.047 mmol, 15.9 mg). The regiochemistry of **3ae** was assigned based on the multiplicity of the aromatic peaks in the ^{1}H NMR spectrum. The signal at 7.40 ppm, lacking a ^{3}J coupling, is indicative of thee 2,6-disubstituted isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 1.9 Hz, 1H), 7.93 – 7.86 (m, 3H), 7.63 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.40 (d, *J* = 1.9 Hz, 1H), 7.30 – 7.25 (m, 1H, partially overlapped with residual solvent), 7.19 (d, *J* = 8.9 Hz, 1H), 7.08 (dd, *J* = 11.2, 9.0 Hz, 1H), 3.20 (tt, *J* = 11.9, 3.1 Hz, 1H), 1.92 – 1.76 (m, 5H), 1.50 (qt, *J* = 13.1, 3.4 Hz, 2H), 1.33 – 1.21 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.3, 160.6, 148.1, 139.5, 139.2 (2C), 134.5, 133.2, 133.1, 131.8, 128.6, 128.4, 127.7, 127.3, 126.8, 126.7, 125.4, 40.3, 33.2, 26.8, 26.4; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{23}H_{23}O$ 315.1743; found 315.1733.



3af. Obtained following *General Procedure B* but electrolyzing the reaction mixture at a constant current of 3.0 mA. Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 12:1. Yield = 51%, (0.077 mmol, 17.7 mg). The regiochemistry of **3af** was assigned based on the multiplicity of the aromatic peaks in the ^{1}H NMR spectrum. The presence of four signals showing a single ^{3}J coupling is indicative of the 2,5-disubstituted isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 9.4 Hz, 1H), 7.06 (dd, *J* = 12.5, 0.7 Hz, 1H), 7.01 (dd, *J* = 12.5, 2.0 Hz, 1H), 6.85 (dd, *J* = 9.4, 1.9 Hz, 1H), 3.12 (tt, *J* = 12.1, 2.8 Hz, 1H), 2.76 (hept, *J* = 6.9 Hz, 1H), 1.84 – 1.71 (m, 5H), 1.51 – 1.40 (m, 2H), 1.28 – 1.15 (m, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 186.6, 157.8, 153.0, 140.1, 136.3, 133.1, 129.7, 39.7,

37.3, 33.2 (2C), 26.8 (2C), 26.4, 23.0 (2C); **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{16}H_{23}O$ 231.1743; found 231.1751.



3ag. Obtained following *General Procedure B*. Yellow sticky oil. FC eluent: *n*-hexane/EtOAc: 12:1. Yield = 49%, (0.074 mmol, 33.1 mg). The regiochemistry of **3ag** was assigned based on the multiplicity of the aromatic peaks in the ^{1}H NMR spectrum. The presence of two doublets (7.18 and 7.06 ppm) and one singlet (7.36 ppm) relative to the tropone scaffold is indicative of the 2,4,5-trisubstituted isomer. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.36 (s, 1H), 7.18 (d, *J* = 12.8 Hz, 1H), 7.06 (d, *J* = 12.7 Hz, 1H), 6.55 (s, 1H), 6.00 – 5.94 (bm, 1H), 4.50 (dt, *J* = 12.9, 6.6 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.66 (s, 3H), 3.15 (tt, *J* = 11.7, 2.9 Hz, 1H), 2.50 (dd, *J* = 13.4, 6.5 Hz, 1H), 2.40 (td, *J* = 13.1, 7.4 Hz, 1H), 2.34 – 2.24 (m, 1H), 2.01 (s, 3H), 1.96 – 1.88 (m, 1H), 1.86 – 1.76 (m, 2H), 1.76 – 1.67 (m, 2H), 1.46 – 1.38 (m, 2H), 1.33 – 1.26 (m, 2H), 1.21 – 1.13 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 185.9, 169.6, 156.4, 153.8, 151.3, 142.4, 141.6, 140.0, 139.0, 137.9, 134.9, 131.3, 126.5, 107.5, 61.6, 61.5, 56.1, 51.8, 40.1, 38.6, 33.0, 32.8, 30.0, 26.8 (2C overlapped), 26.2, 23.1; **HRMS (ESI)** m/z: $[M + H]^+$ calcd. for $C_{27}H_{34}NO_5$ 452.2431; found 452.2443.

5. Crystallographic data for compound 1b-OAc.

The X-ray intensity data were measured on a Bruker Apex III CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in four sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.5° ω steps. All data were processed using the Bruker suite of programs,[16] and an empirical absorption correction was applied using SADABS.[17] The structures were solved by direct methods (SIR 2014)[18] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[19] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic and methyl hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters *U(H)* = 1.2 *Ueq*(C) and allowed to ride on their carrier carbons.

Crystal data and details of the data collection for compounds **1b-OAc** are reported in **Table S2.** Molecular drawings were generated using Mercury.[20]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 2320922. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

Figure S1. ORTEP molecular drawing of **1b-OAc**, thermal ellipsoids are draw at 30% of the probability level.

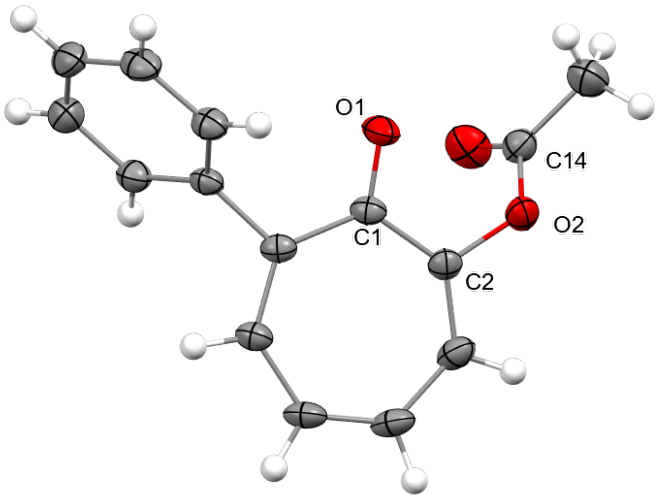


Table S2. Crystal data and structure refinement for compound **1b-OAc.**

Compound	**1b-OAc**
Formula	$C_{15}H_{12}O_3$
Fw	240.25
T, K	296 (2)
λ, Å	0.71073
Crystal symmetry	Orthorhombic
Space group	*Fdd2*
a, Å	13.3291(8)
b, Å	63.548(4)
c, Å	5.8474(4)
α	90
β	90
γ	90
Cell volume, Å^3	4953.0(5)
Z	16
D_C, Mg m^{-3}	1.289
μ(Mo-K$_\alpha$), mm^{-1}	0.090
F(000)	2016
Crystal size/ mm	0.37 x 0.12 x 0.11
θ limits, °	3.819 to 25.500
Reflections collected	14929
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	2262 [R(int) = 0.0327]
Goodness-of-fit-on F^2	0.899
R_1 (F)[a], wR_2 (F^2)[b] [$I > 2\sigma(I)$]	R1 = 0.0366, wR2 = 0.1111
Largest diff. peak and hole, e. Å^{-3}	0.165 d -0.143

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.[b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

SC-XRD analysis shows unambiguously C2 as the *O*-acetylated moiety in solid state. The conformation adopted is similar to previously reported O-acetylated tropolones (CCDC 613581 and CCDC 1151526) with the acetyl moiety titled toward the tropolone carbonylic oxygen (C1-C2-O2-C14 60.63°, O1…C14 2.669 Å).

6. Additional CV Experiments

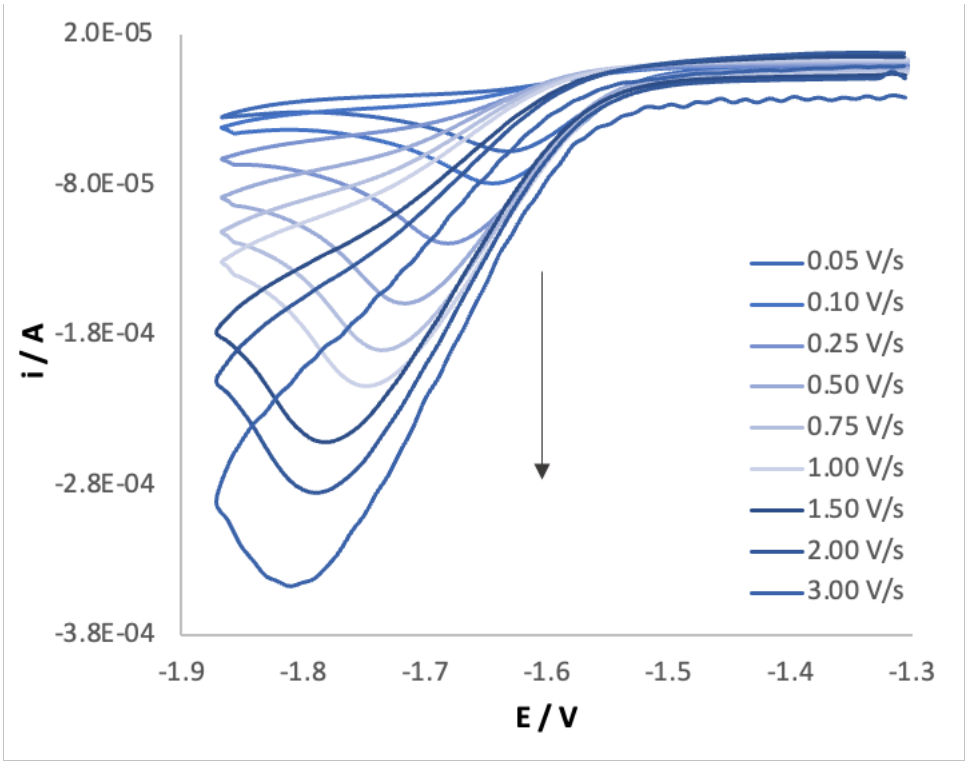


Figure S2. CV responses, collected at different scan rates, of 5 mM **2a** in 0.1 M $TEABF_4$, anhydrous DMF solution. Potentials are reported versus the Fc/Fc^+ redox couple.

A well-defined reduction peak, ascribable to a kinetically fast charge transfer process is evident in the forward scan starting from 0.0 V and directed toward negative potential values. The absence of any anodic current in the backward scan for scan rates up to 3 Vs^{-1} indicates that the species generated by electrochemical reduction undergoes a fast chemical reaction after being formed in the forward scan of the potential.

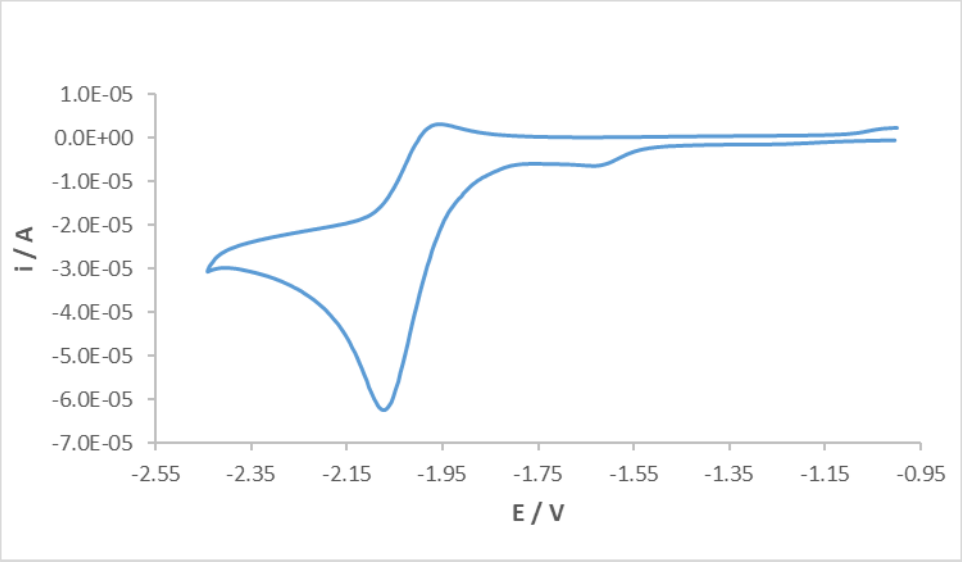
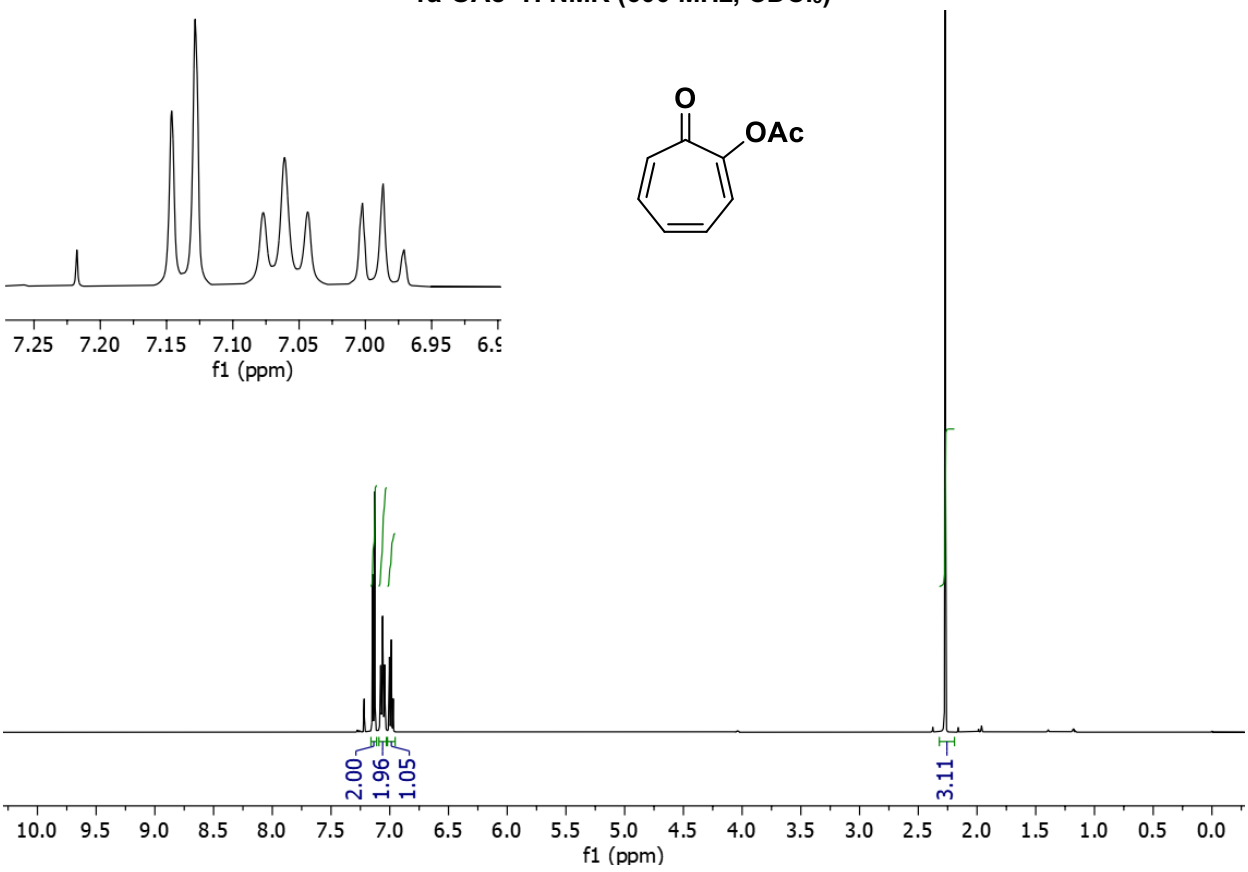


Figure S3. CV response of 5 mM **3aa** in 0.1 M $TEABF_4$, anhydrous DMF solution. Potentials are reported versus the Fc/Fc^+ redox couple.

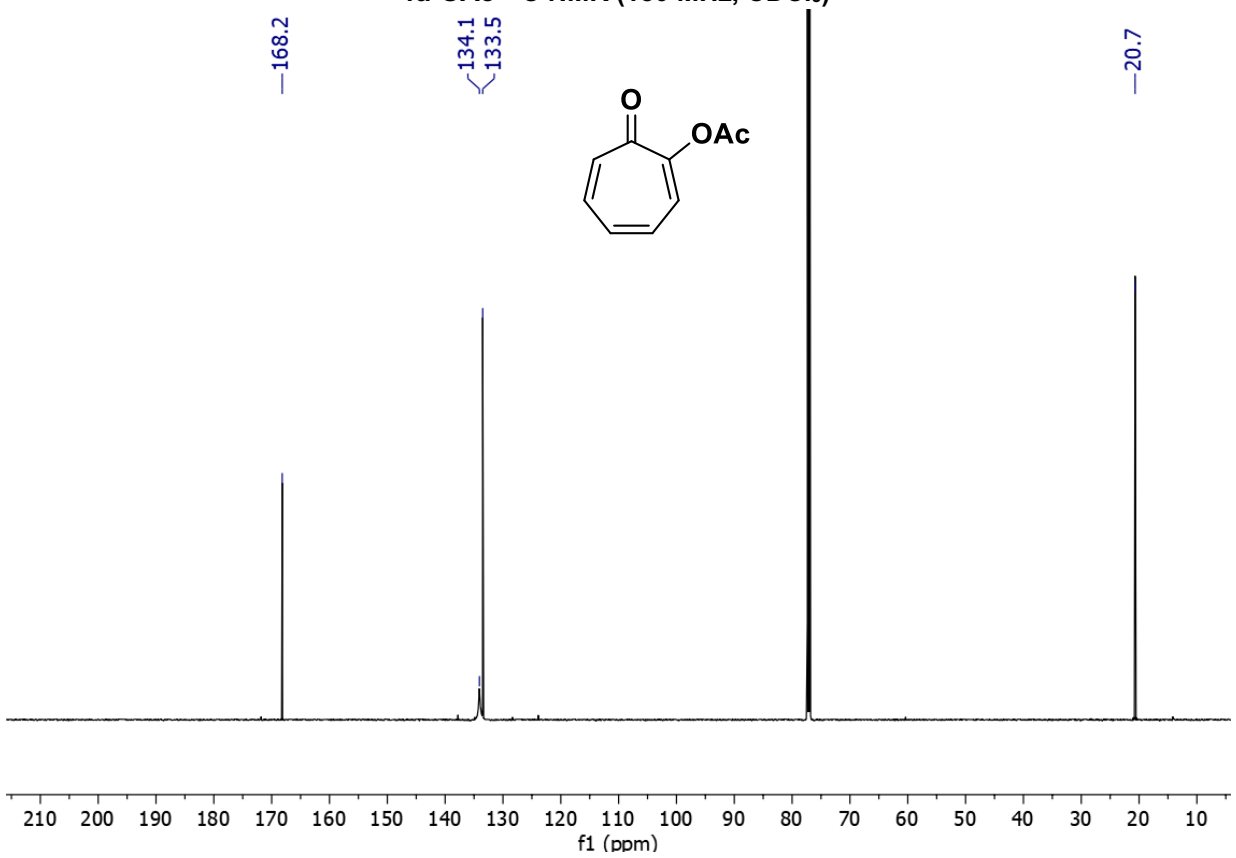
A well-defined reversible cathodic event is registered at -2.07 V *vs* the Fc/Fc^+ redox couple, showing that product **3aa** is reduced at more negative potentials compared to **2a** (-1.63 V), **1a-Cl** (-1.73 V) and **1a-OAc** (-1. 87 V).

7. ^{1}H-, ^{19}F-, ^{13}C-NMR Spectra of New Compounds

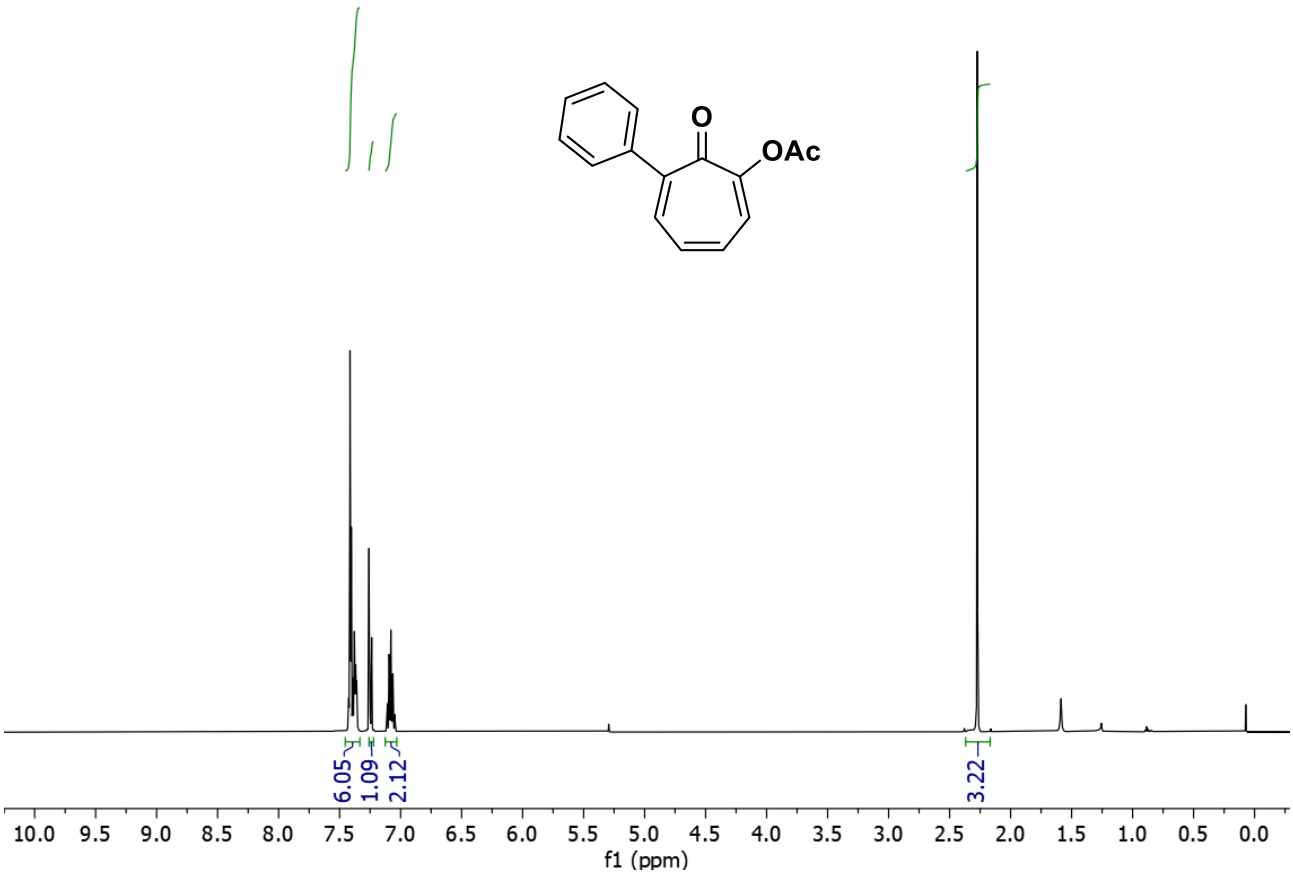
1a-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



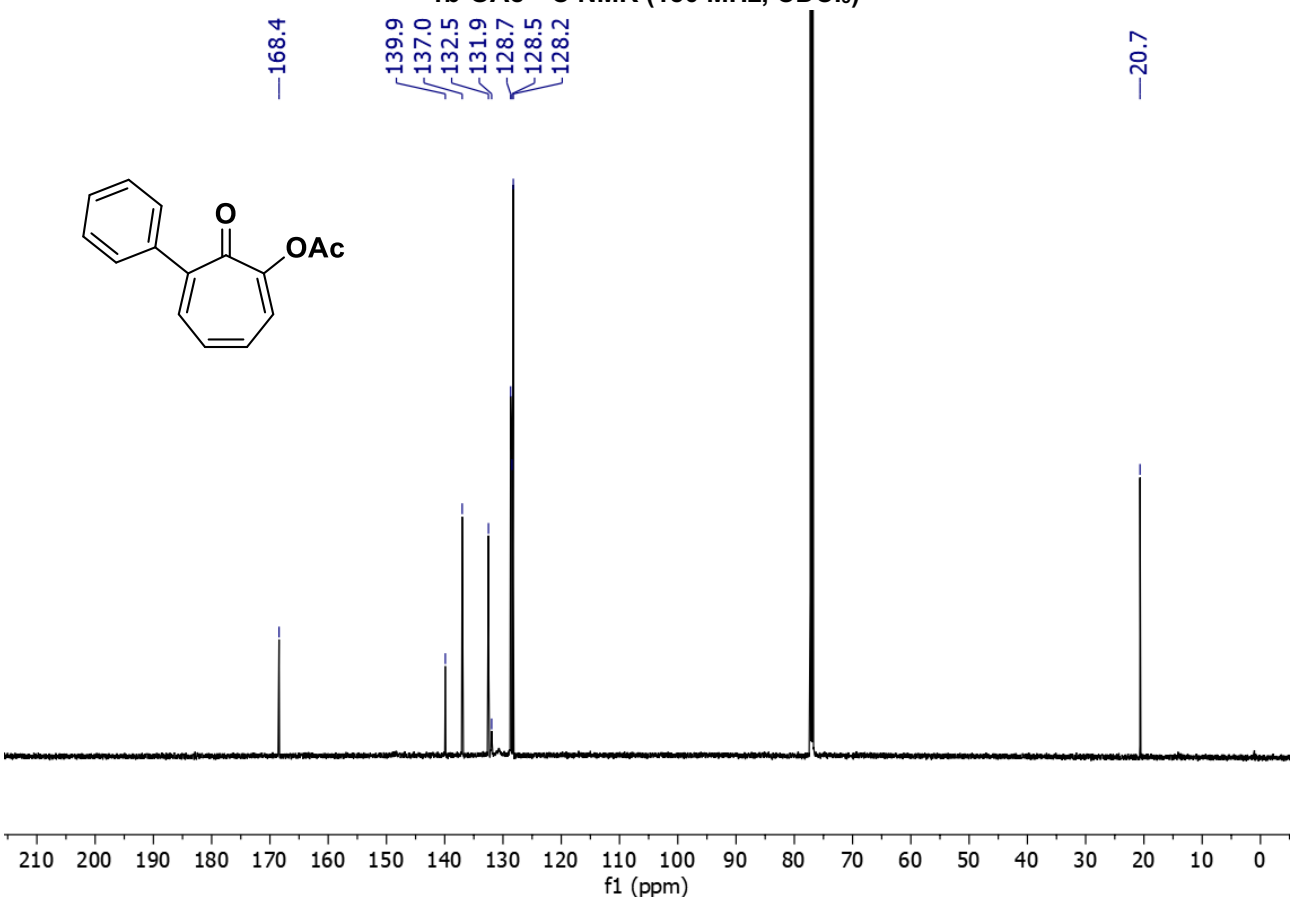
1a-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



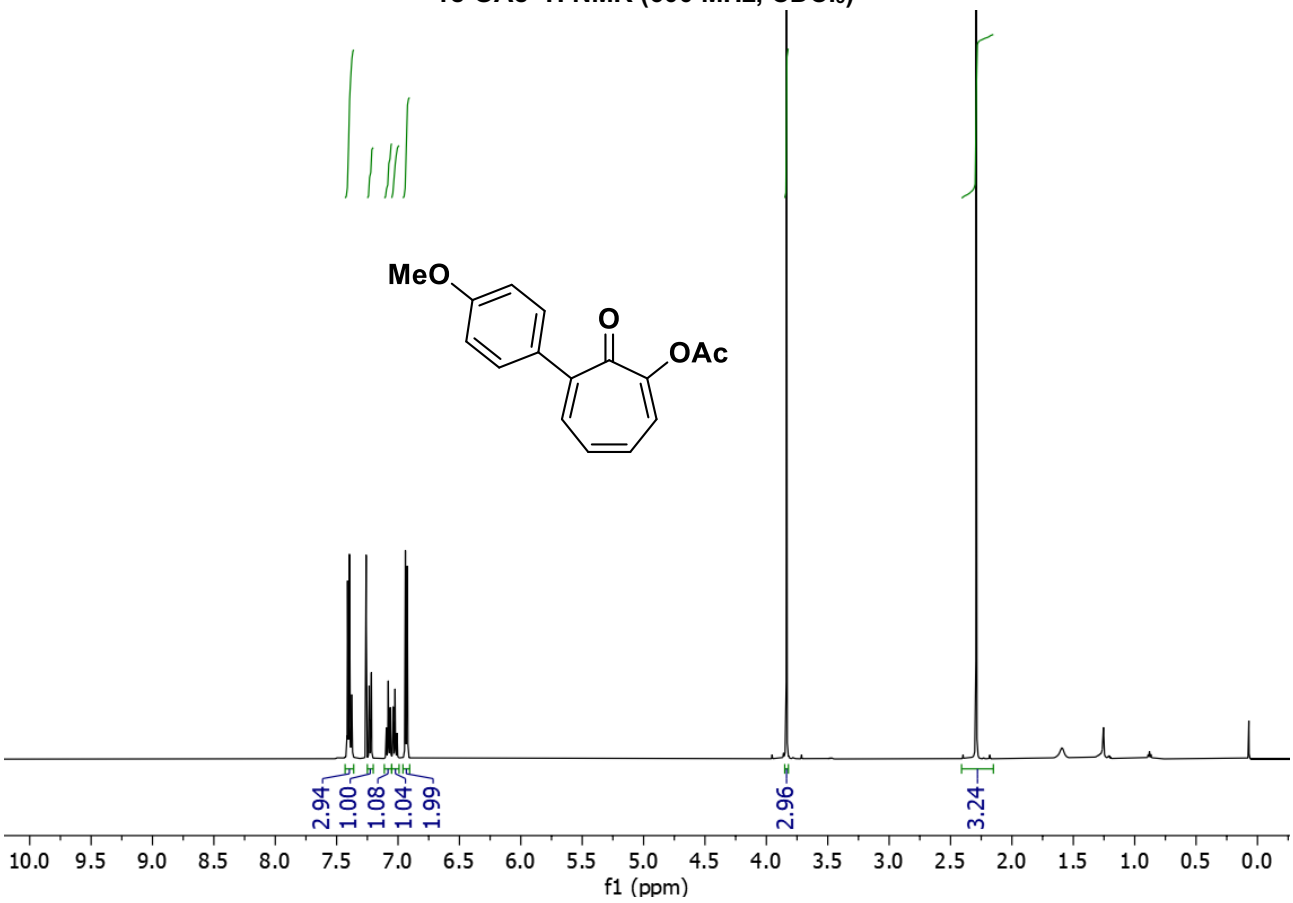
1b-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



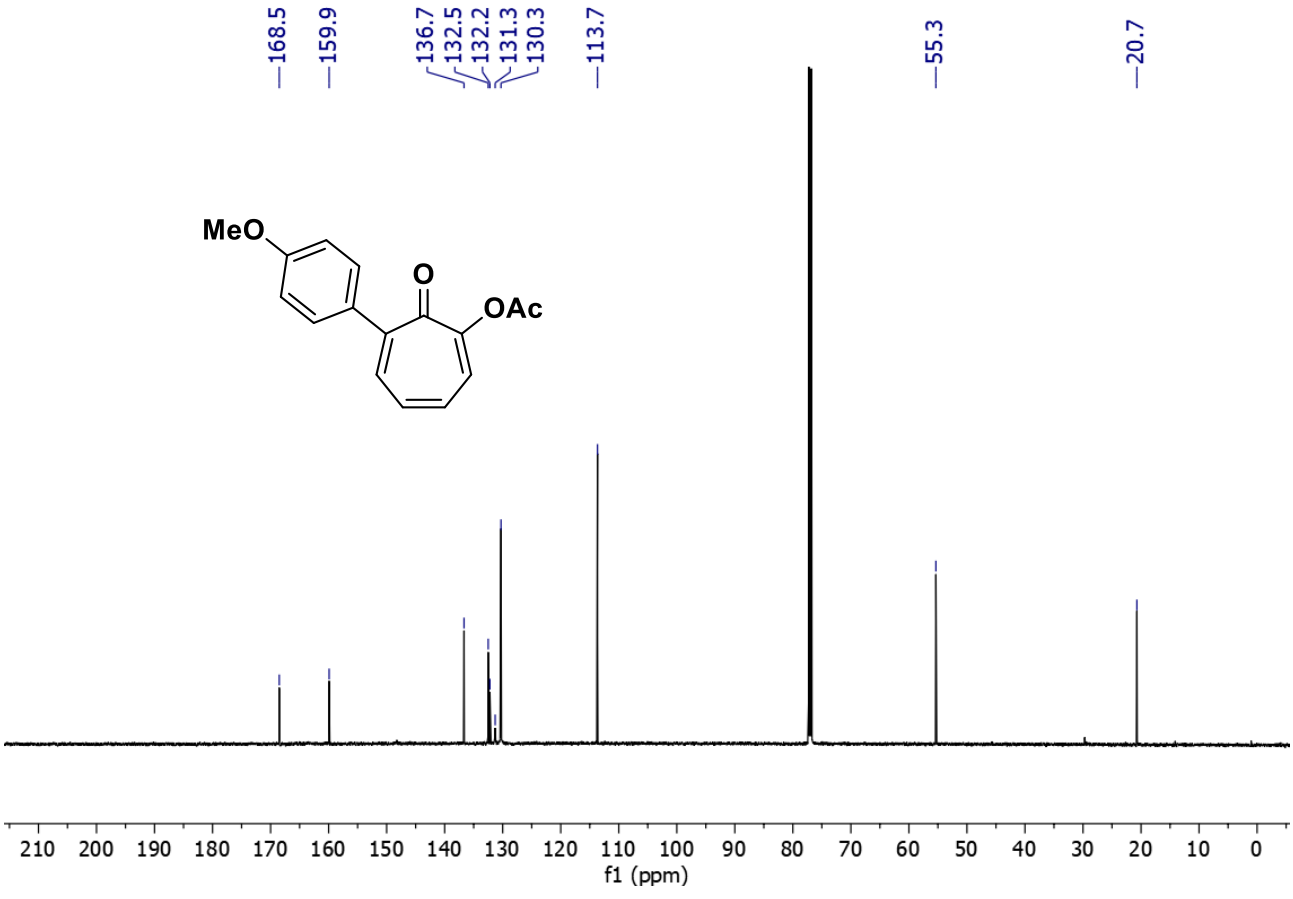
1b-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



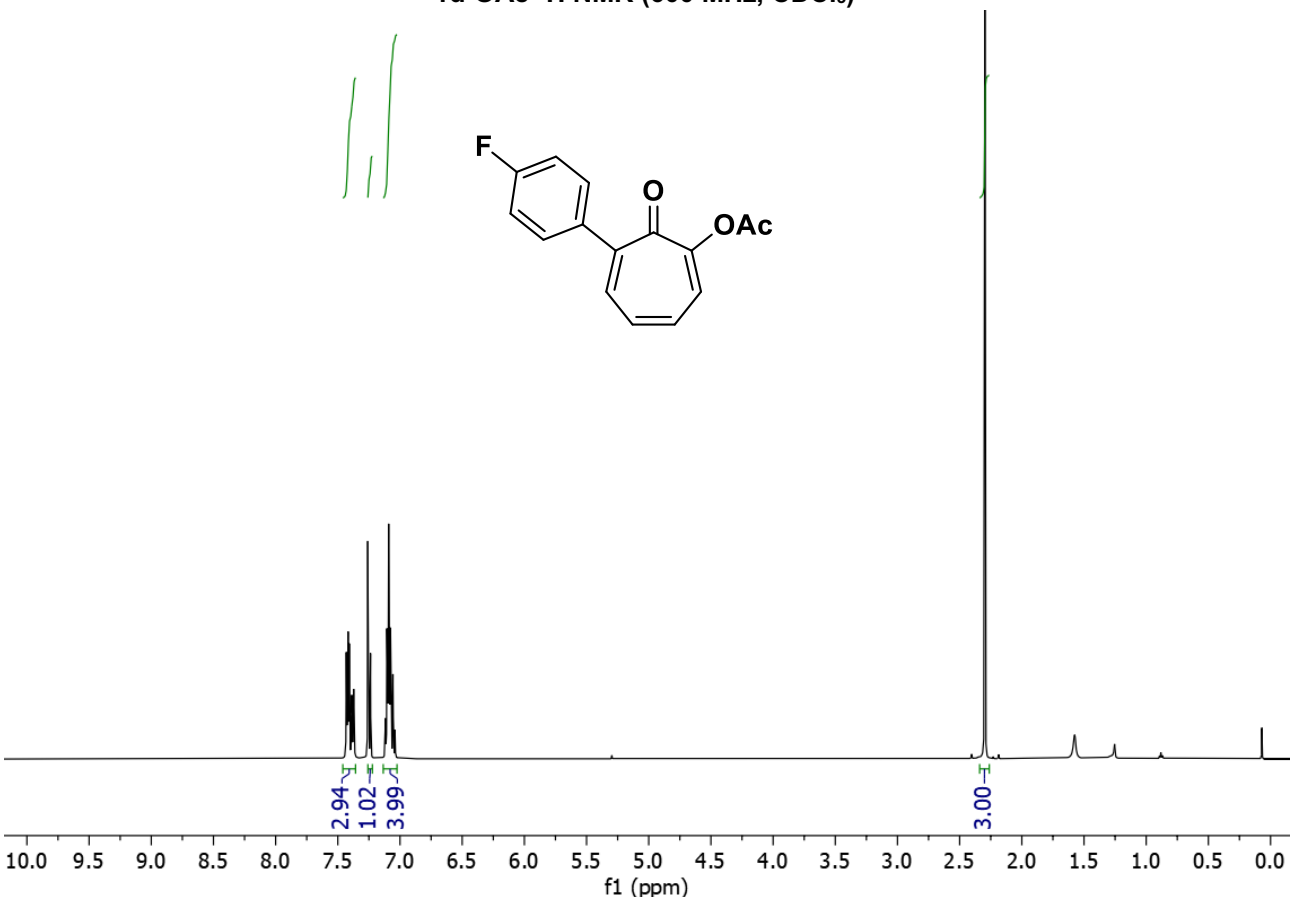
1c-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



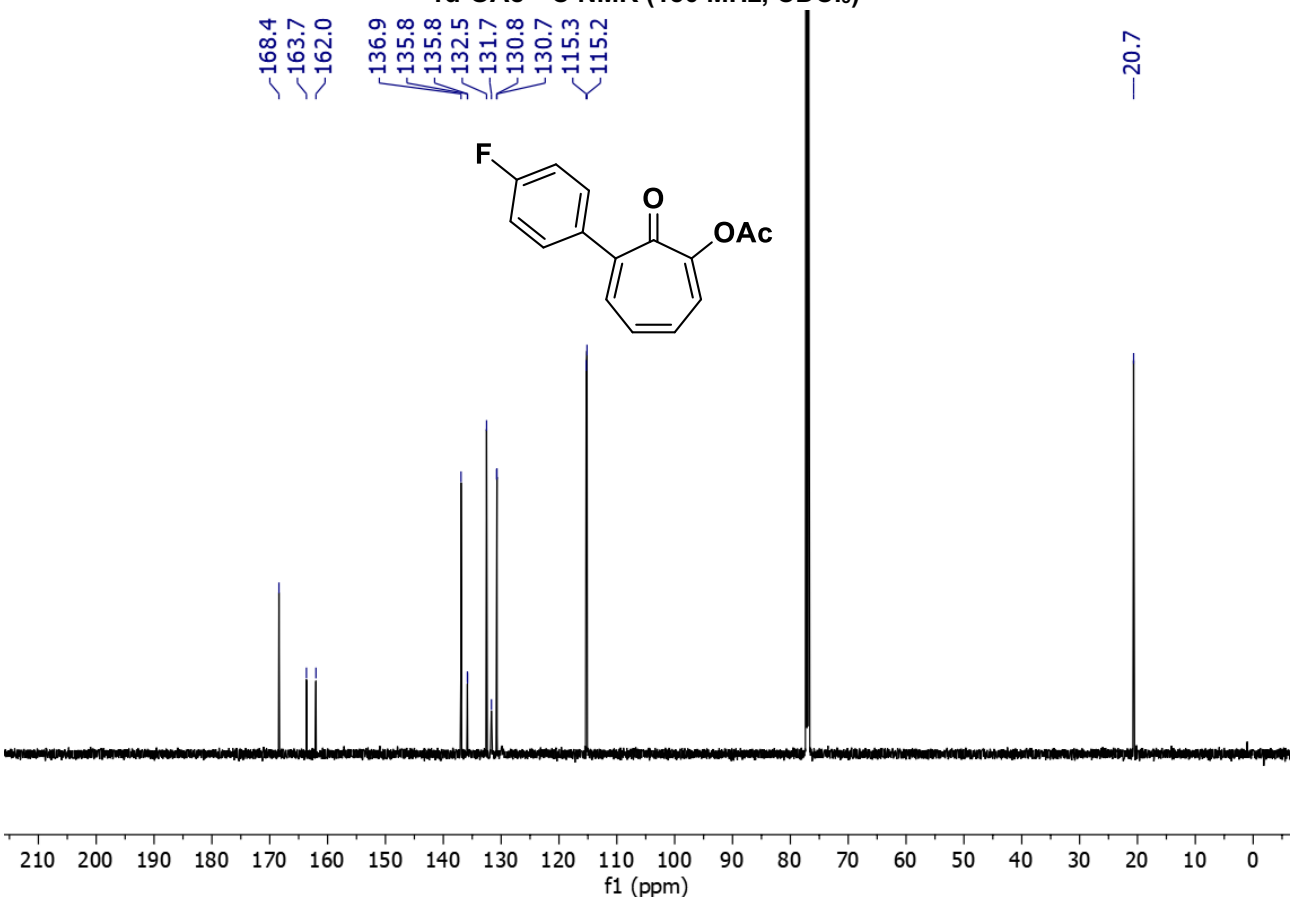
1c-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



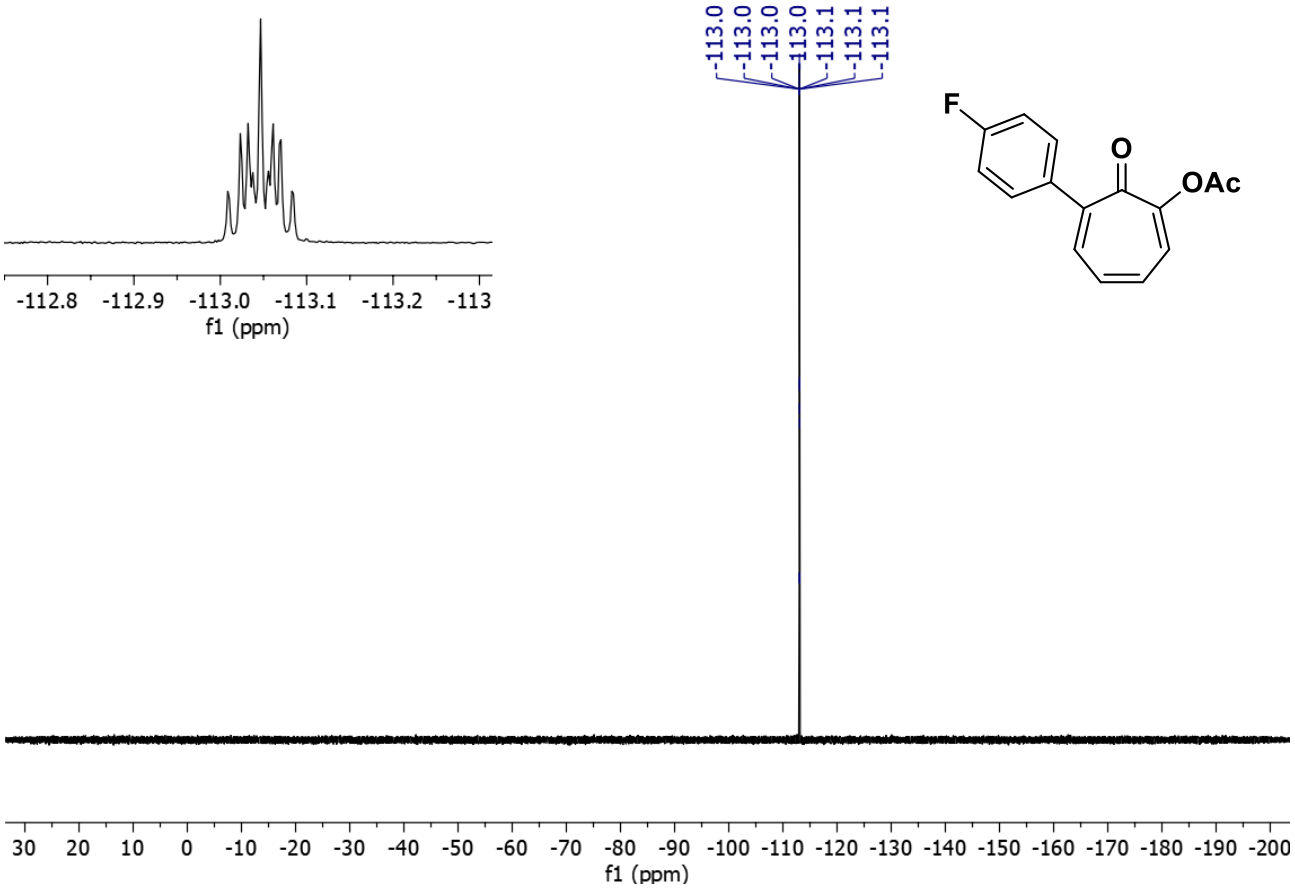
1d-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



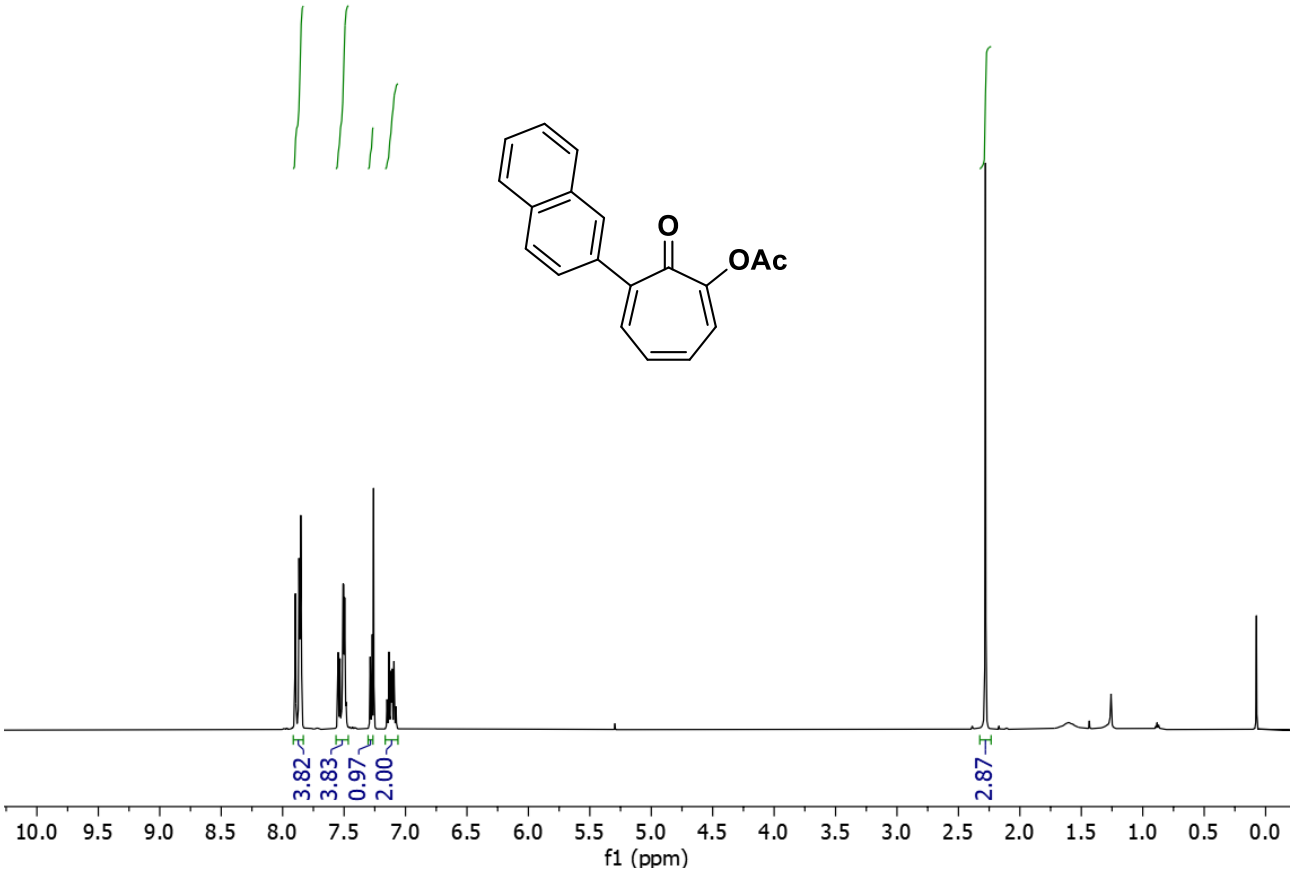
1d-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



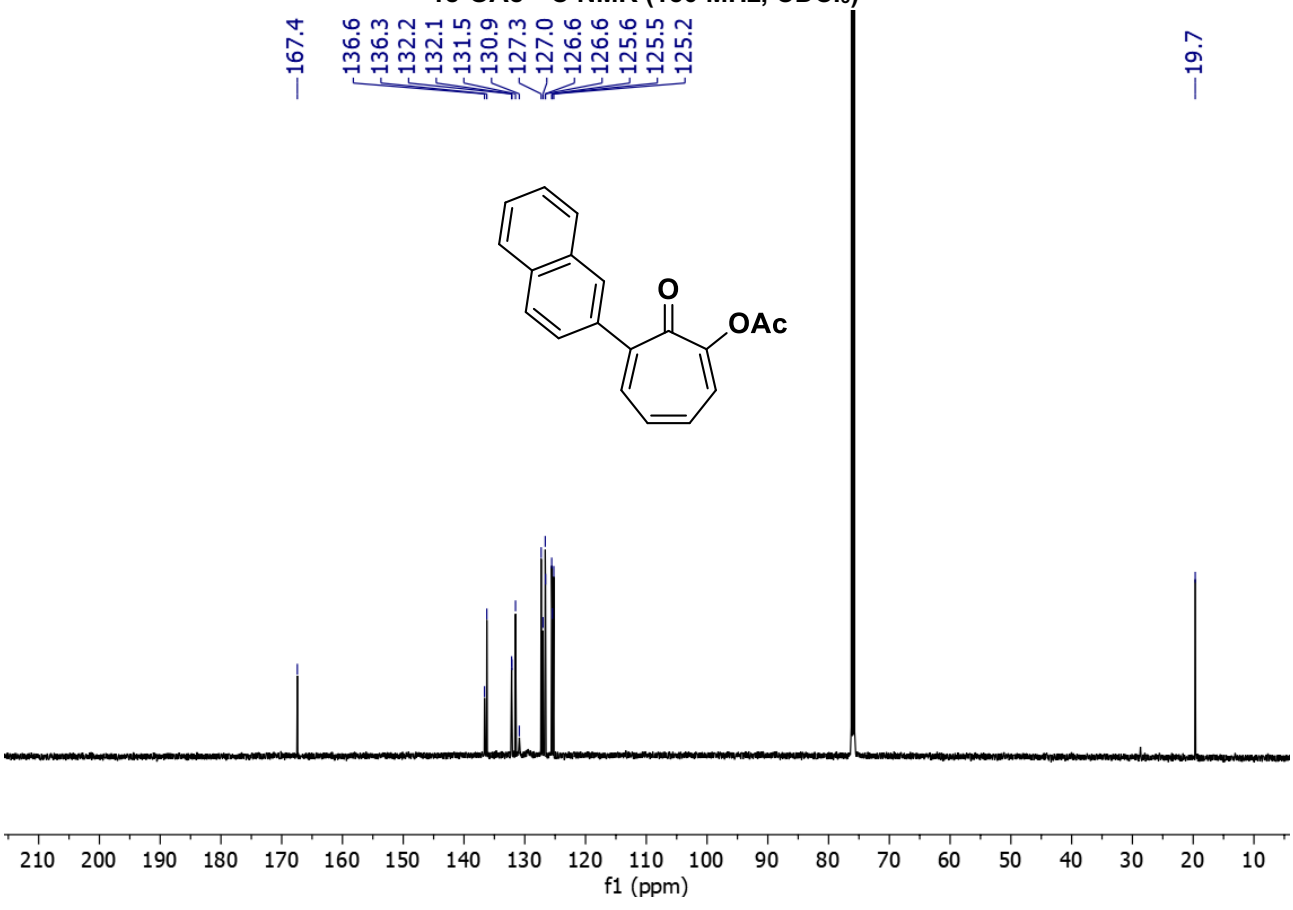
1d-OAc ^{19}F NMR (576 MHz, $CDCl_3$)



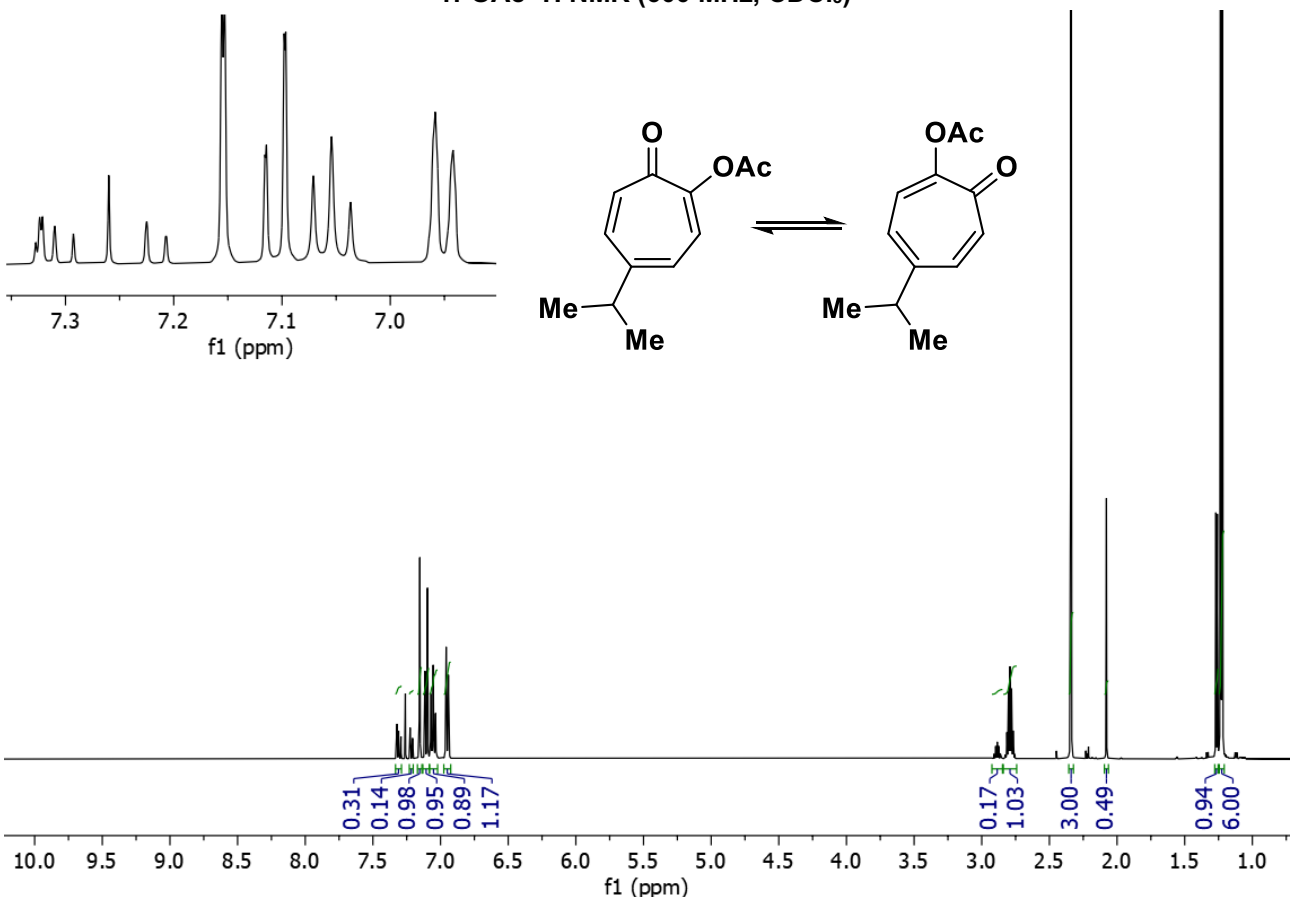
1e-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



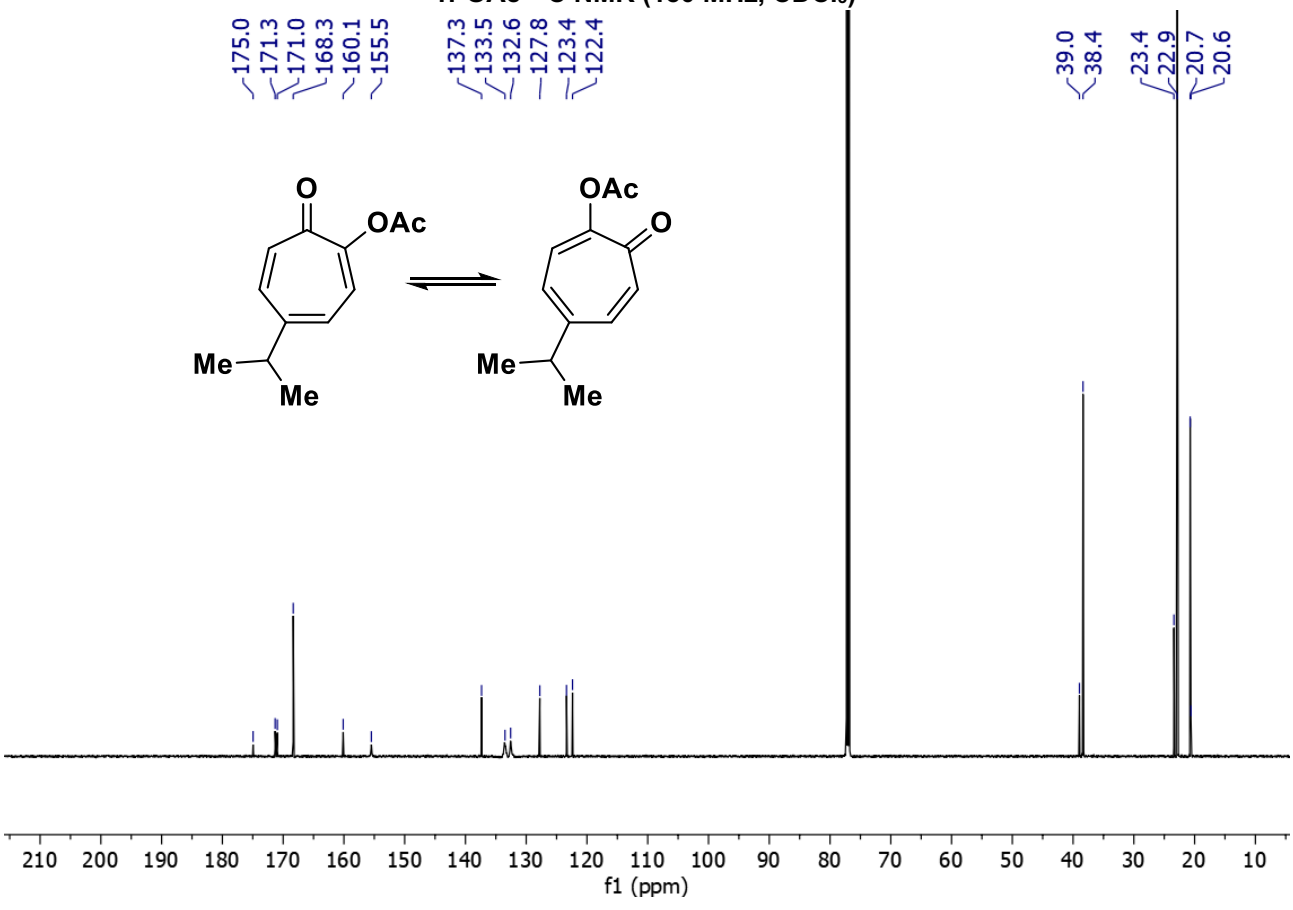
1e-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



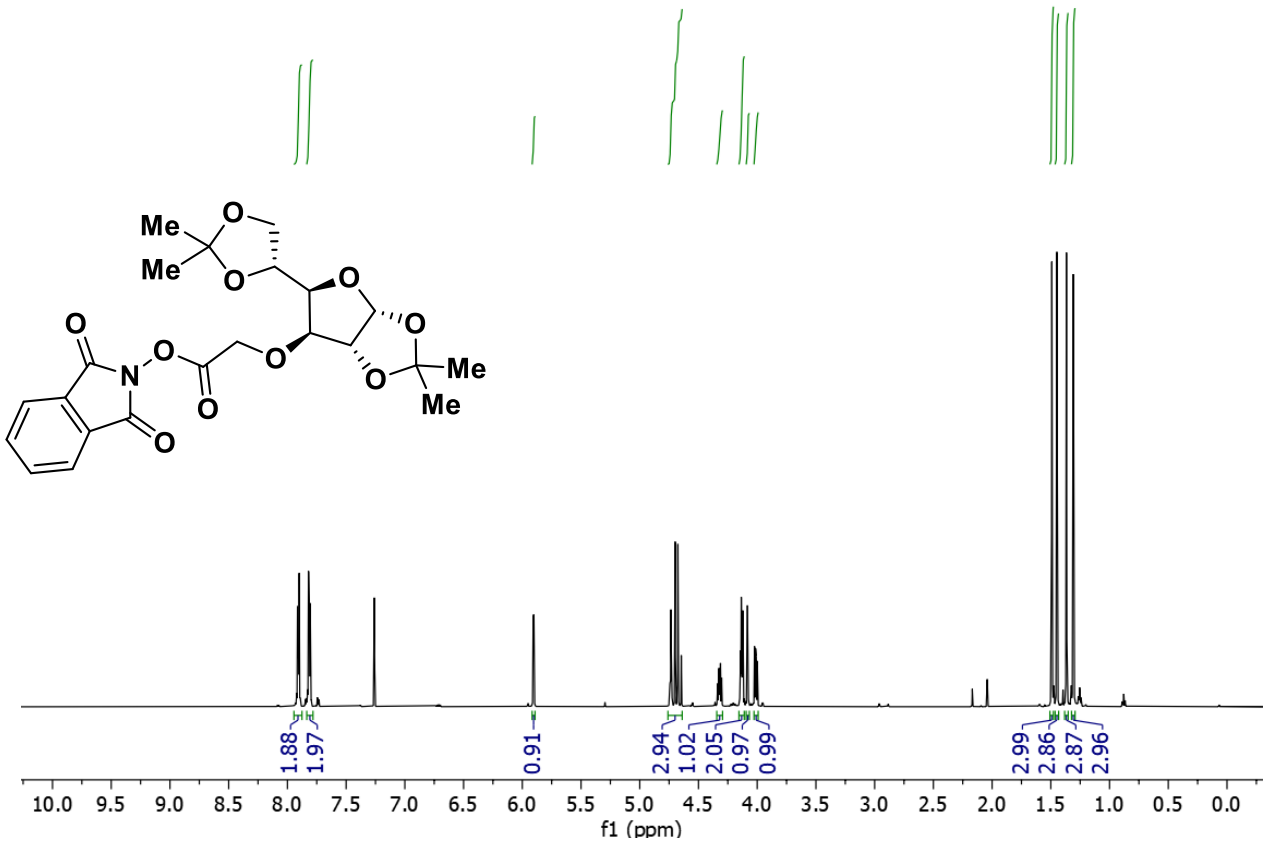
1f-OAc ^{1}H NMR (600 MHz, $CDCl_3$)



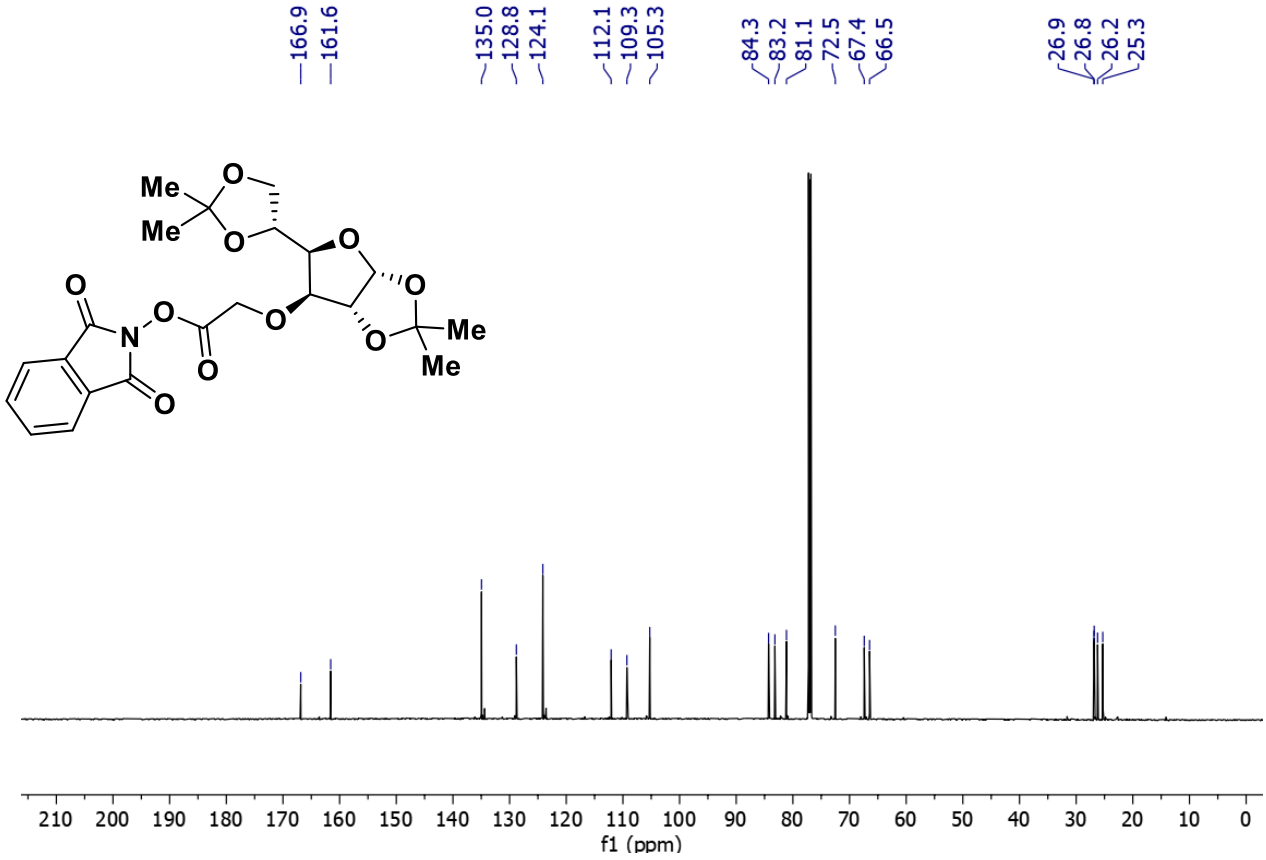
1f-OAc ^{13}C NMR (150 MHz, $CDCl_3$)



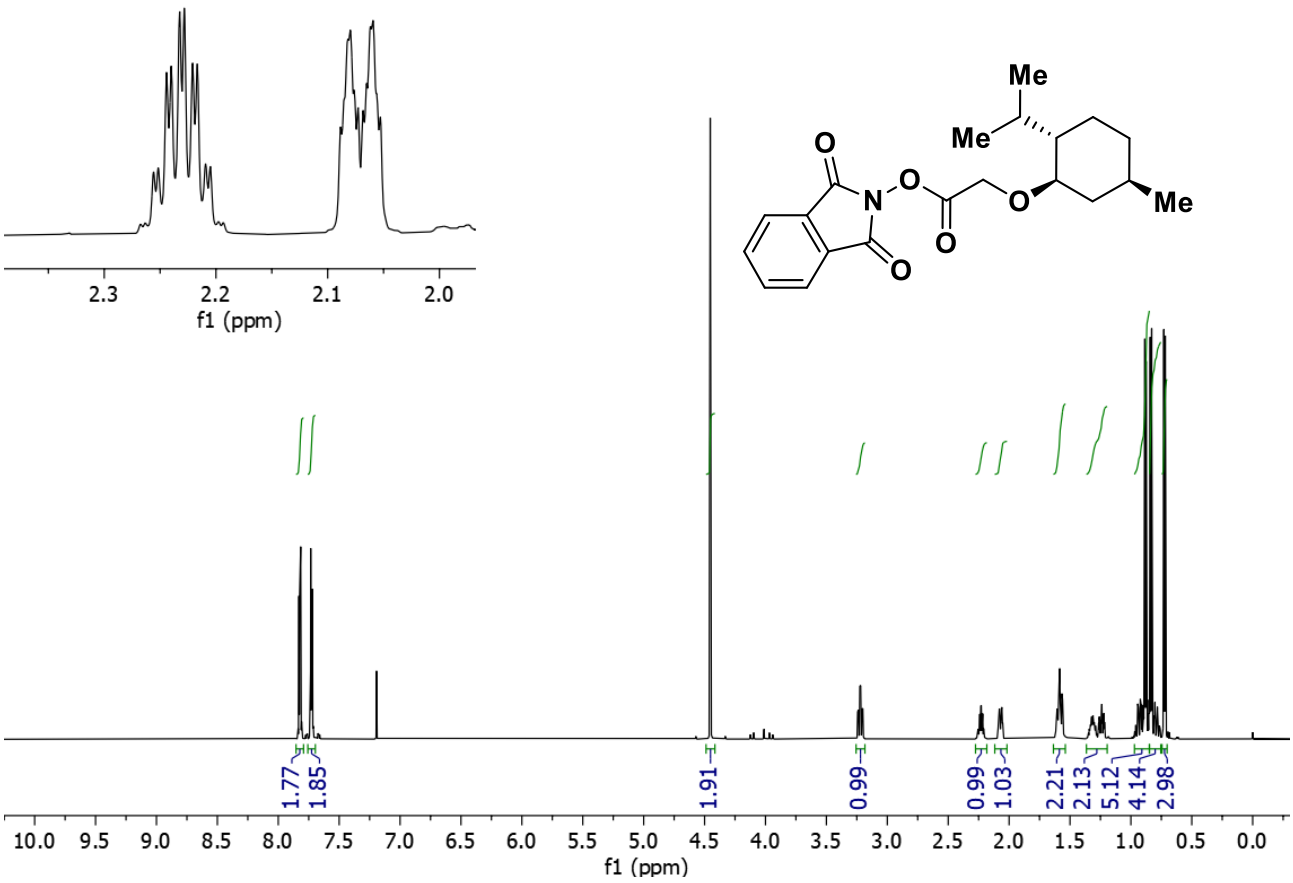
2s ^{1}H NMR (600 MHz, $CDCl_3$)



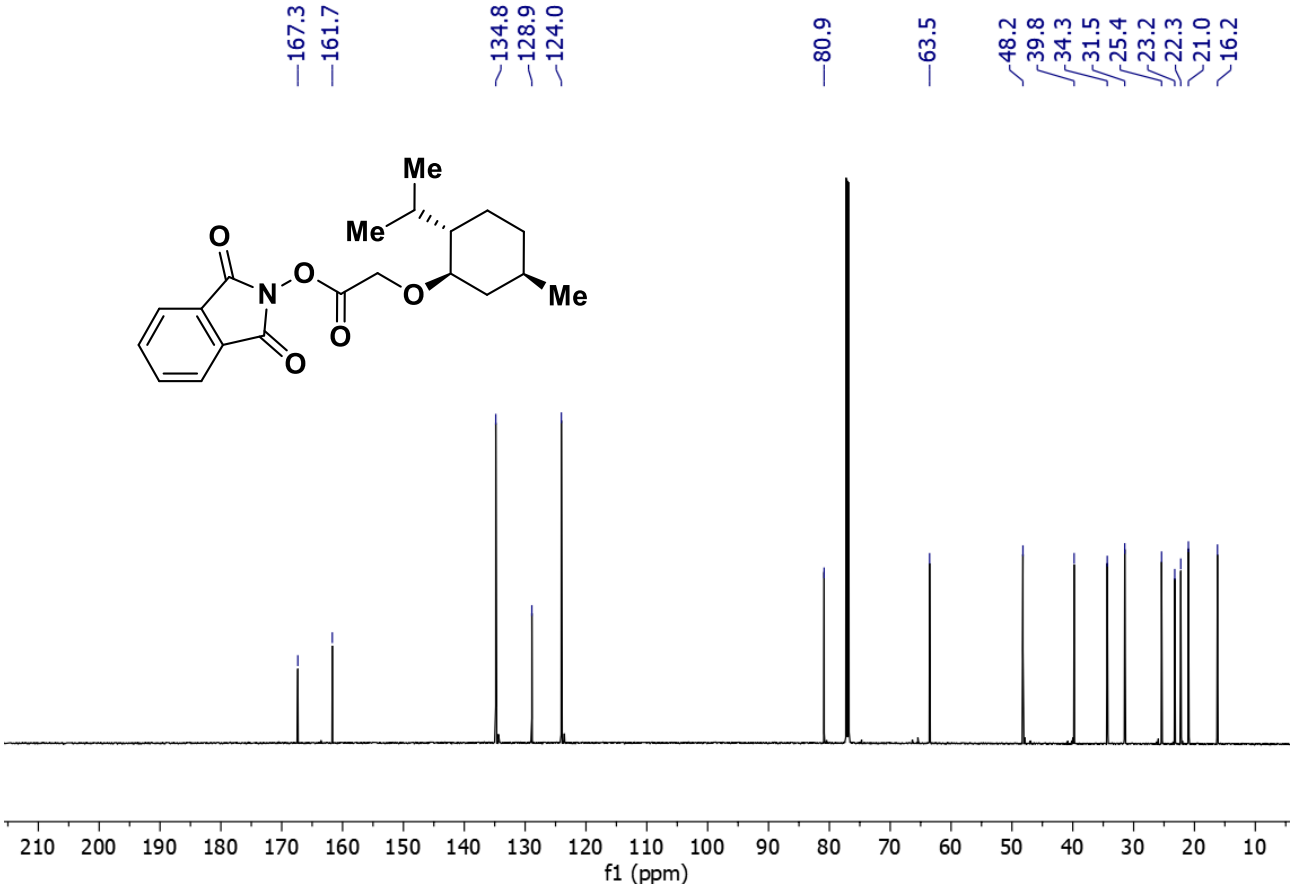
2s ^{13}C NMR (150 MHz, $CDCl_3$)



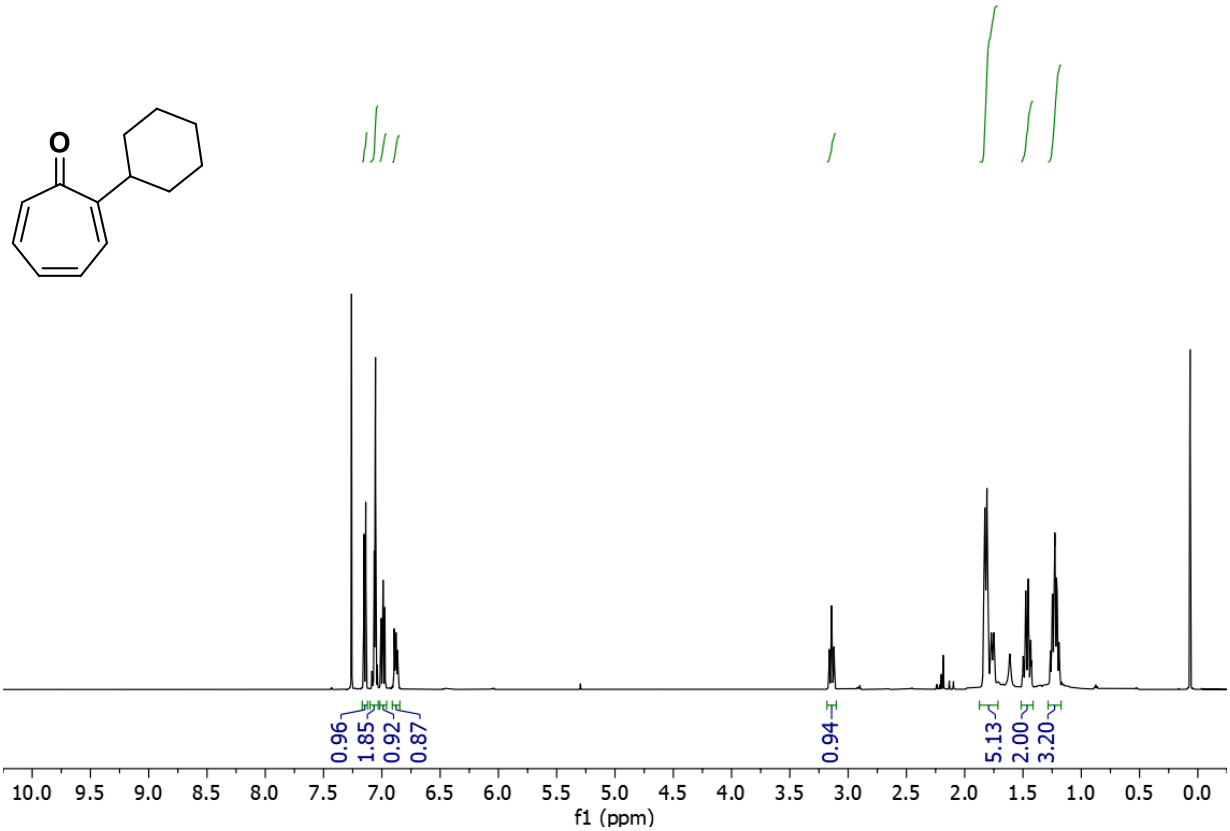
2t ^{1}H NMR (600 MHz, $CDCl_3$)



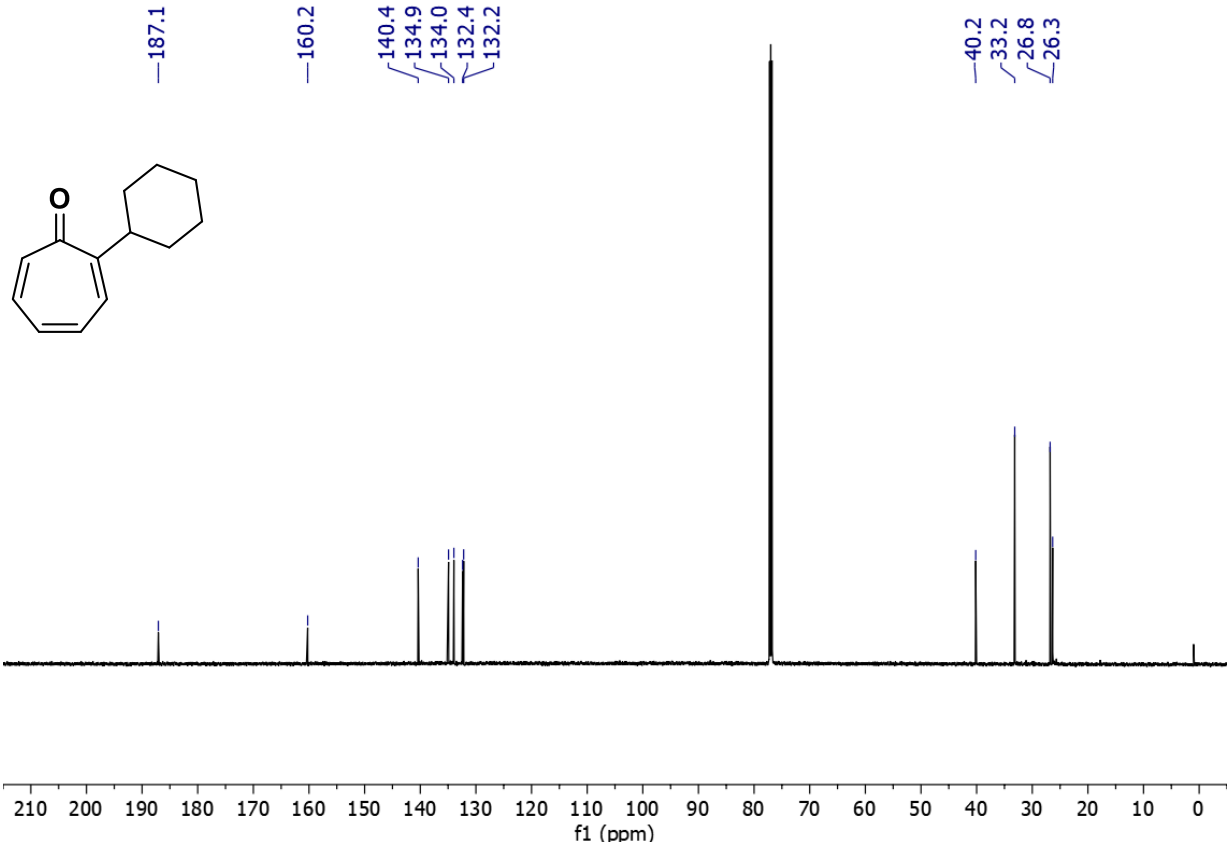
2t ^{13}C NMR (150 MHz, $CDCl_3$)



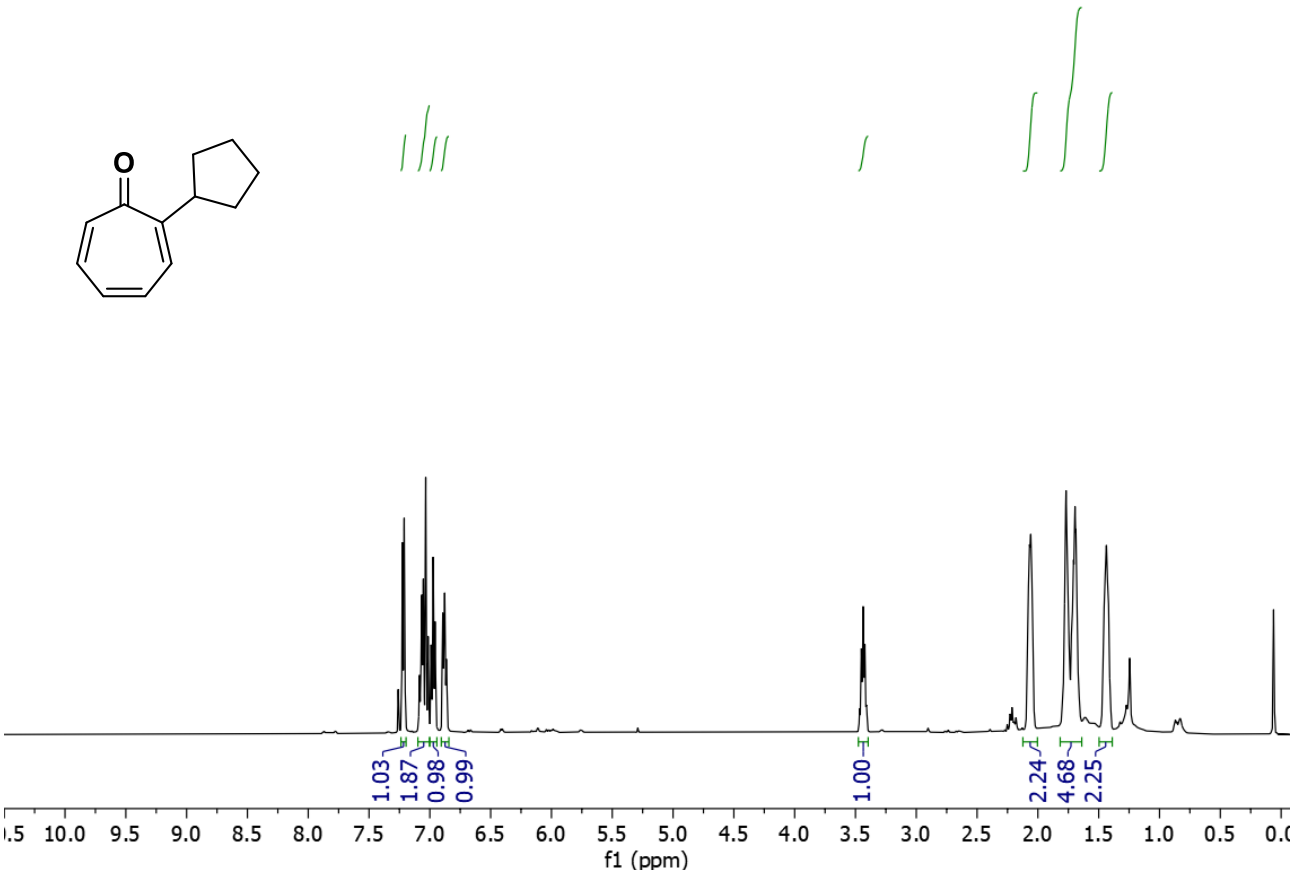
3aa ^{1}H NMR (600 MHz, $CDCl_3$)



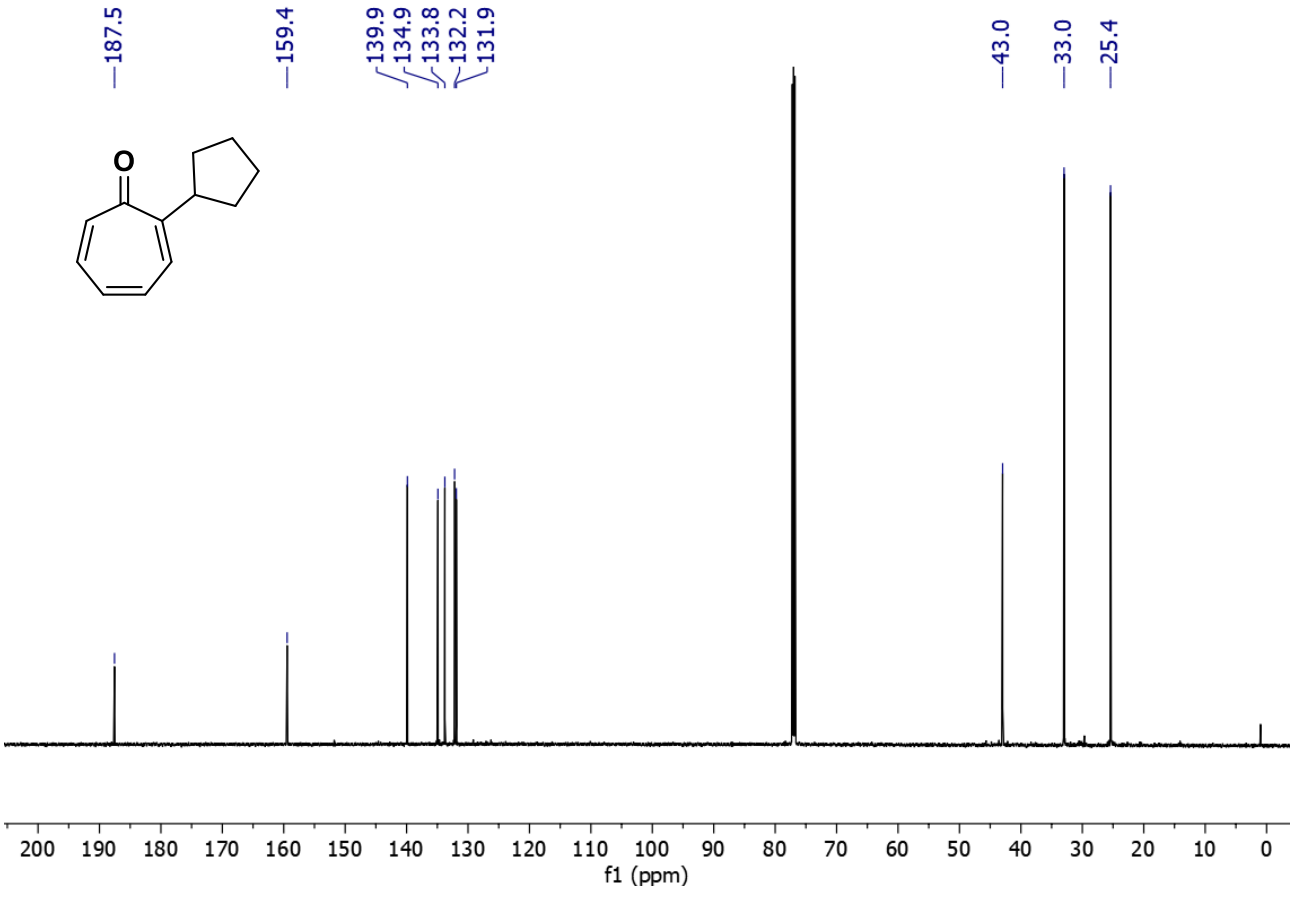
3aa ^{13}C NMR (150 MHz, $CDCl_3$)



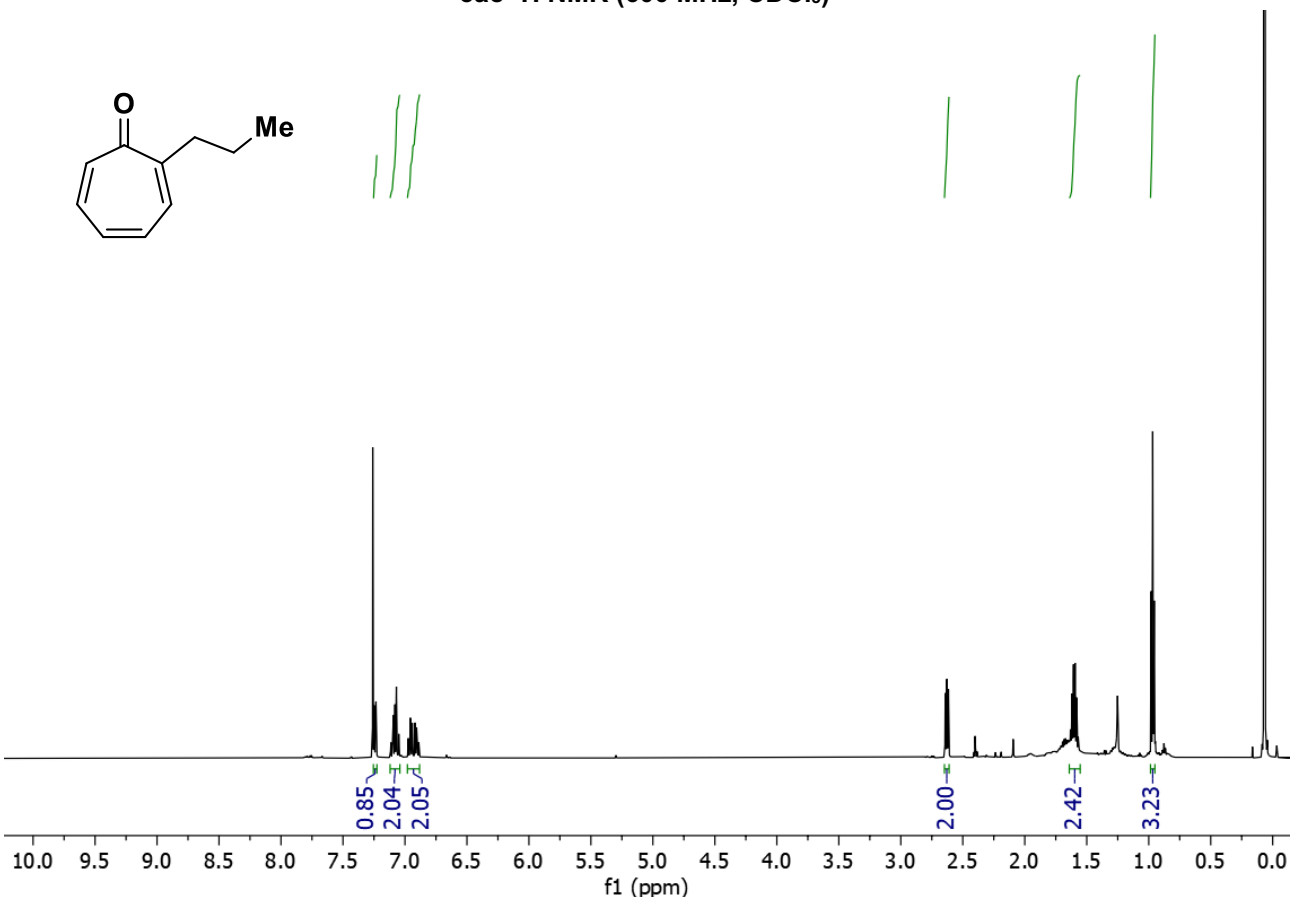
3ab ^{1}H NMR (600 MHz, $CDCl_3$)



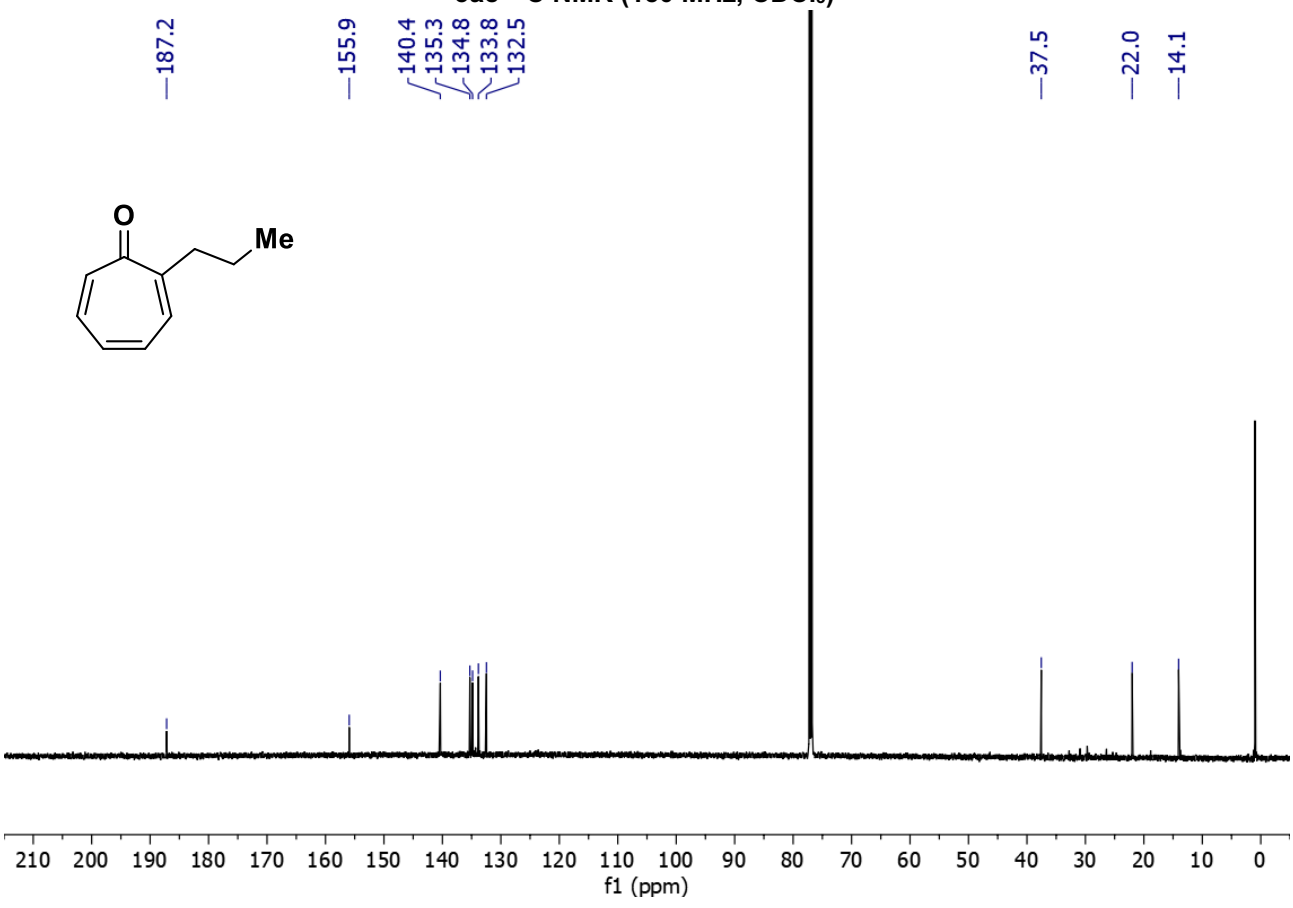
3ab ^{13}C NMR (150 MHz, $CDCl_3$)



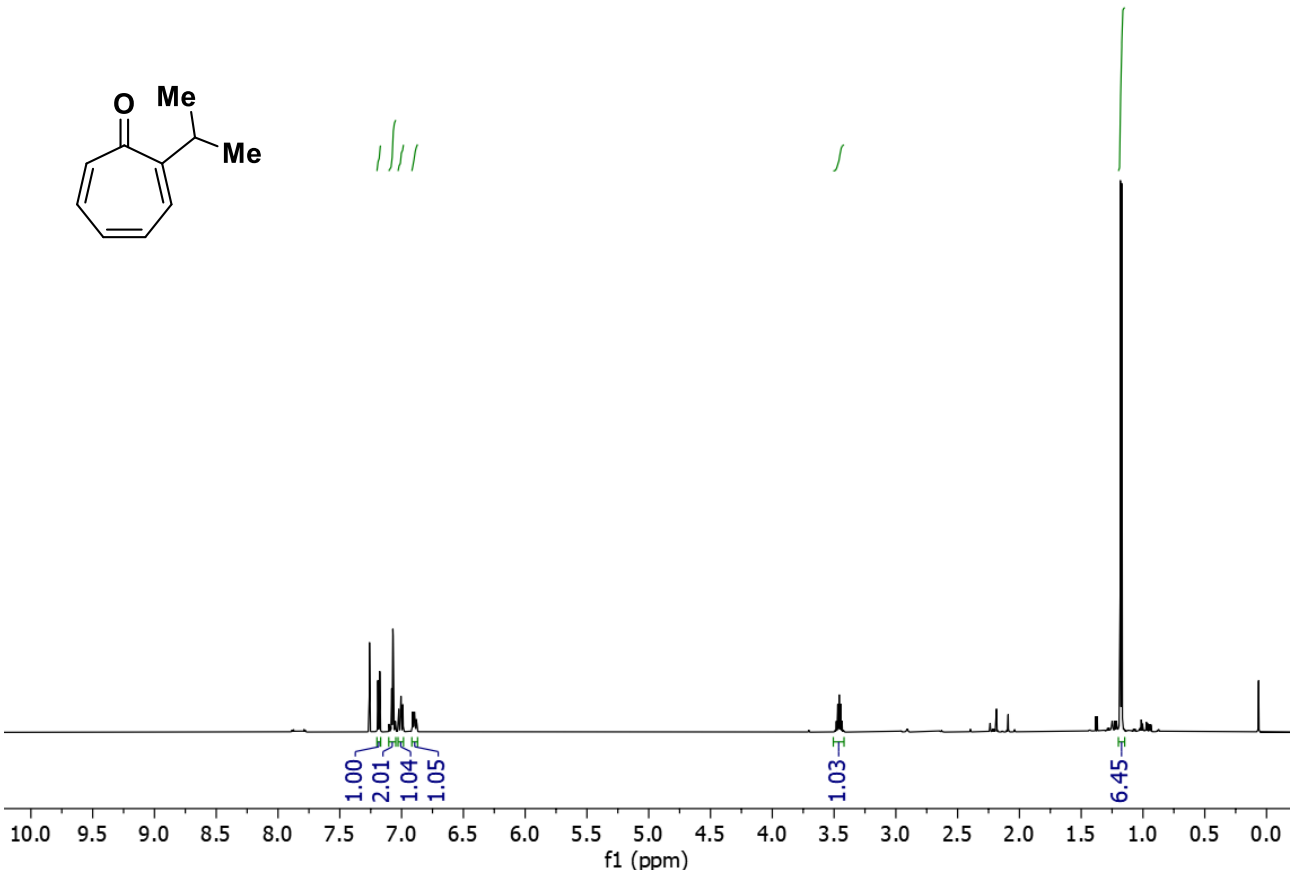
3ac ^{1}H NMR (600 MHz, $CDCl_3$)



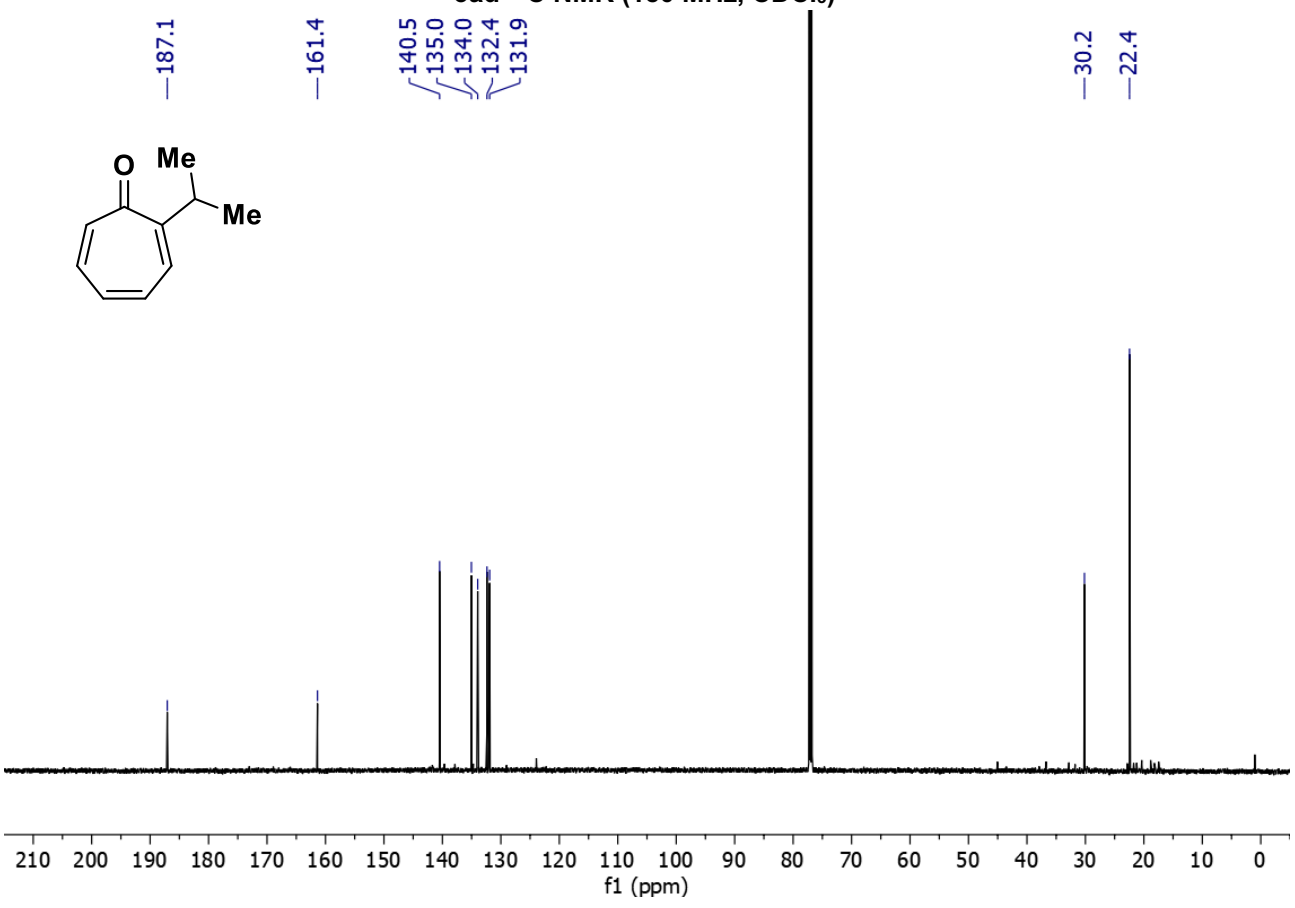
3ac ^{13}C NMR (150 MHz, $CDCl_3$)



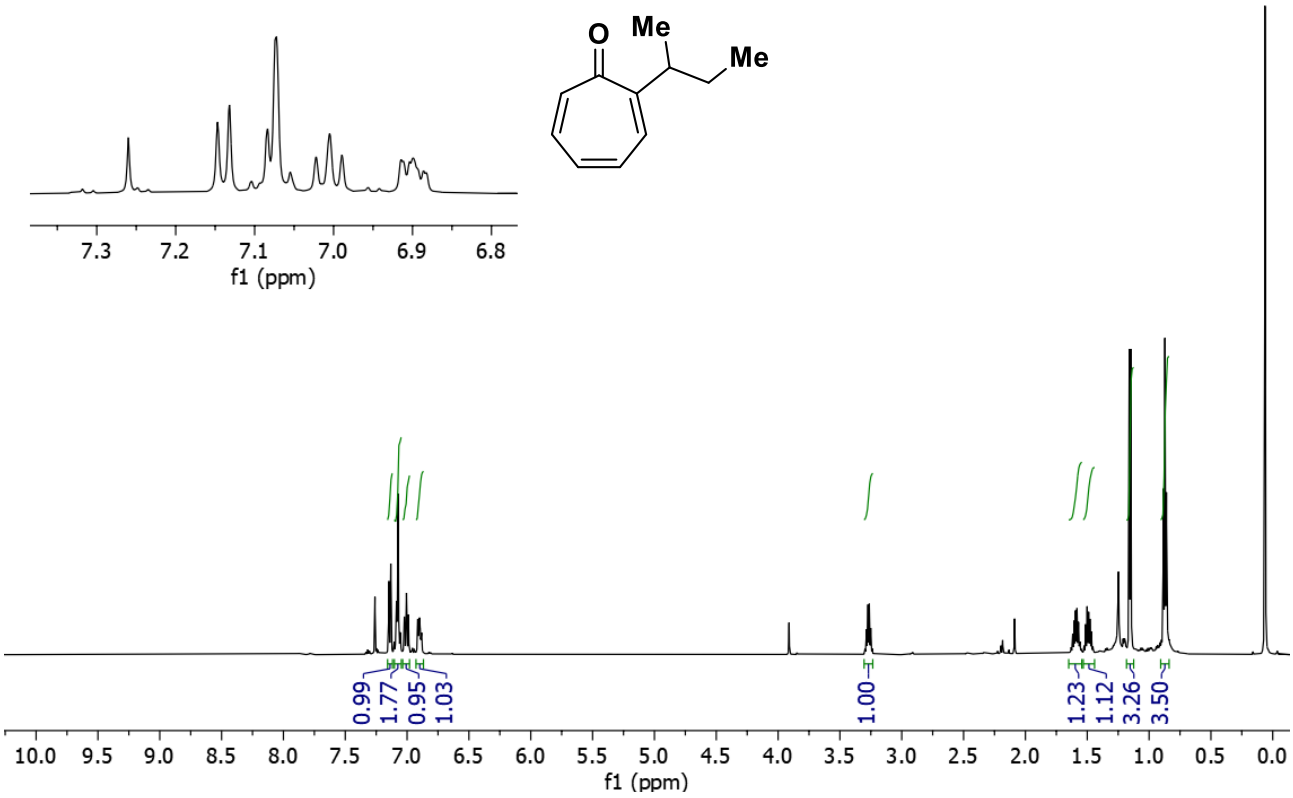
3ad ^{1}H NMR (600 MHz, $CDCl_3$)



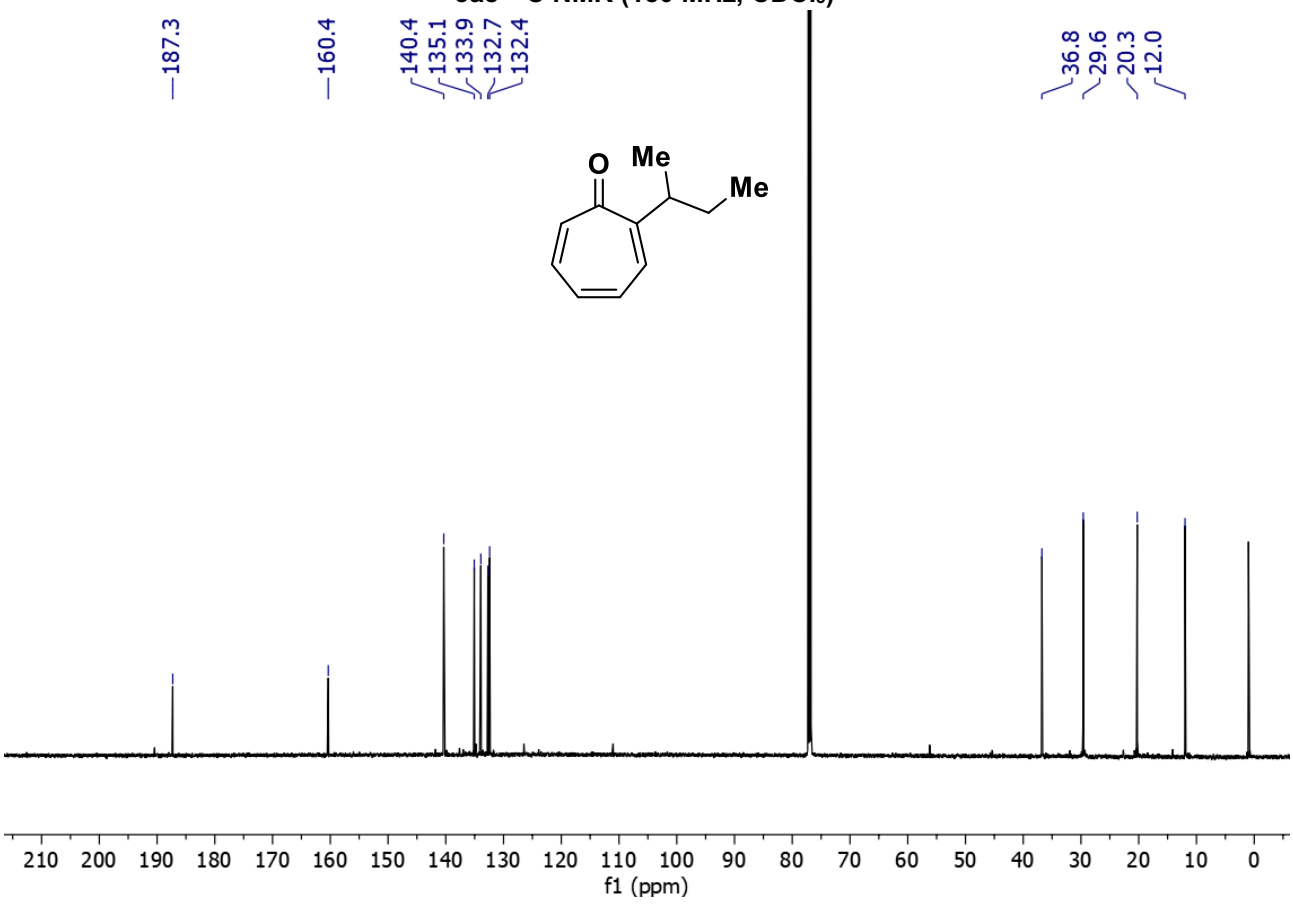
3ad ^{13}C NMR (150 MHz, $CDCl_3$)



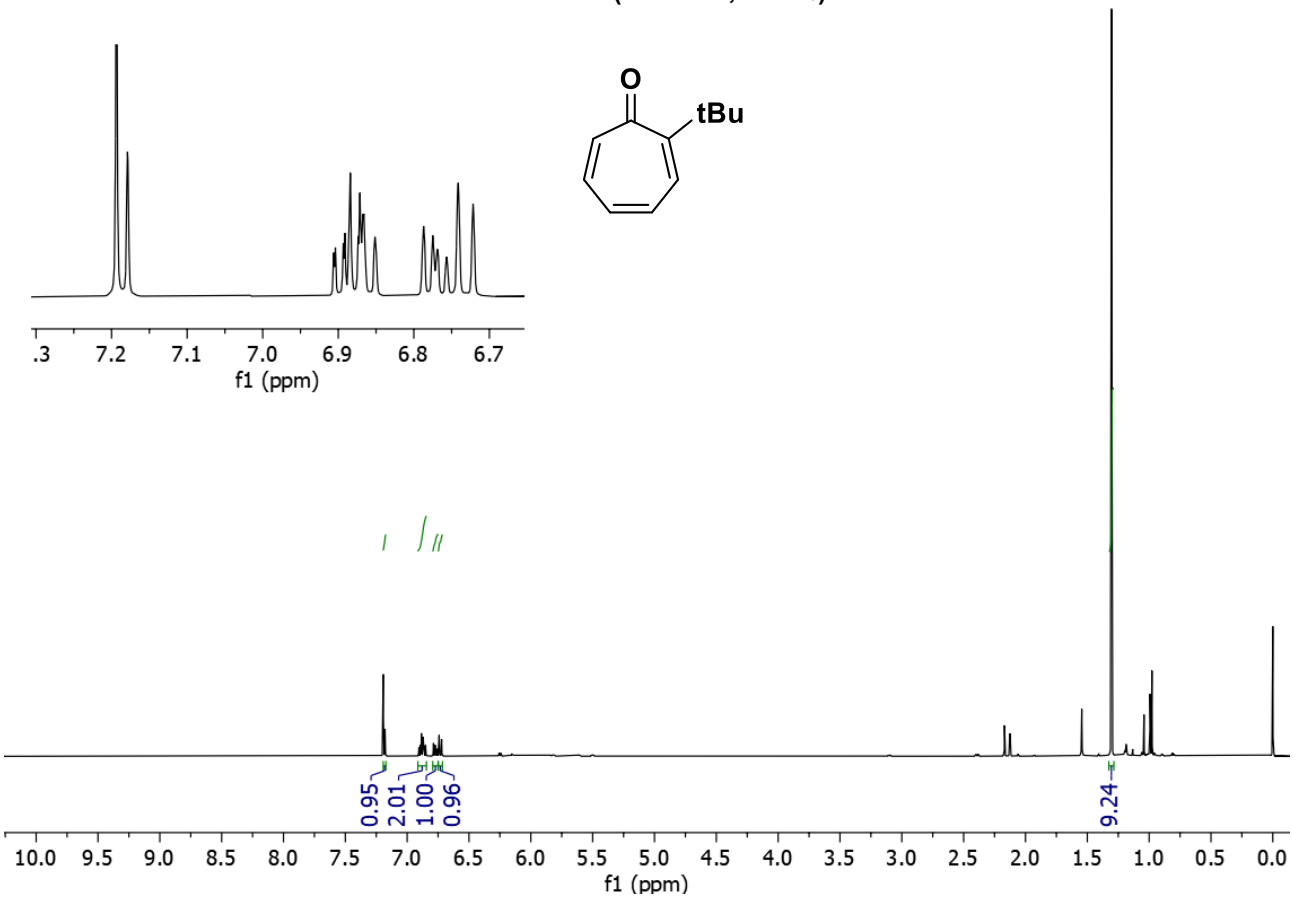
3ae ^{1}H NMR (600 MHz, $CDCl_3$)



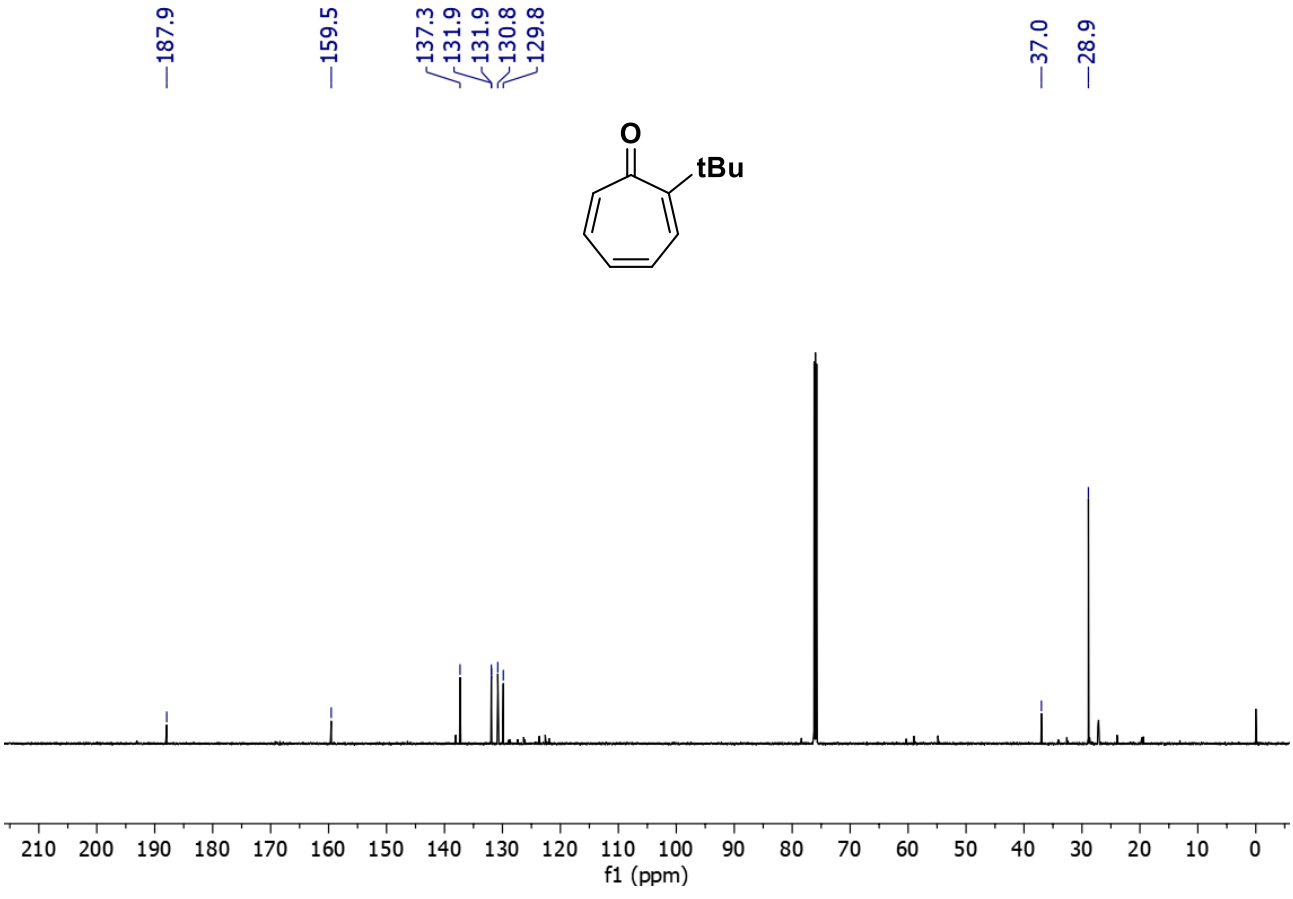
3ae ^{13}C NMR (150 MHz, $CDCl_3$)



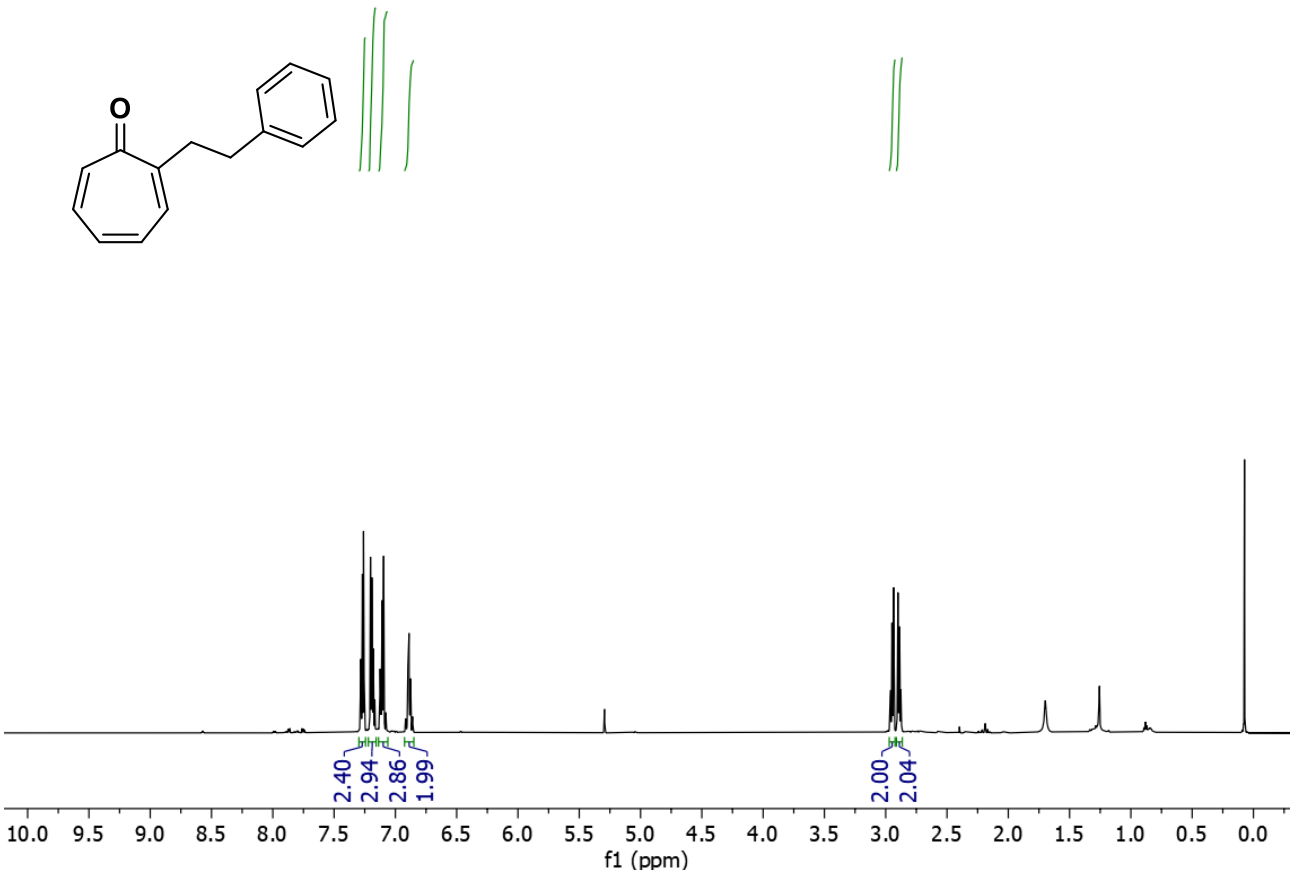
3af ^{1}H NMR (600 MHz, $CDCl_3$)



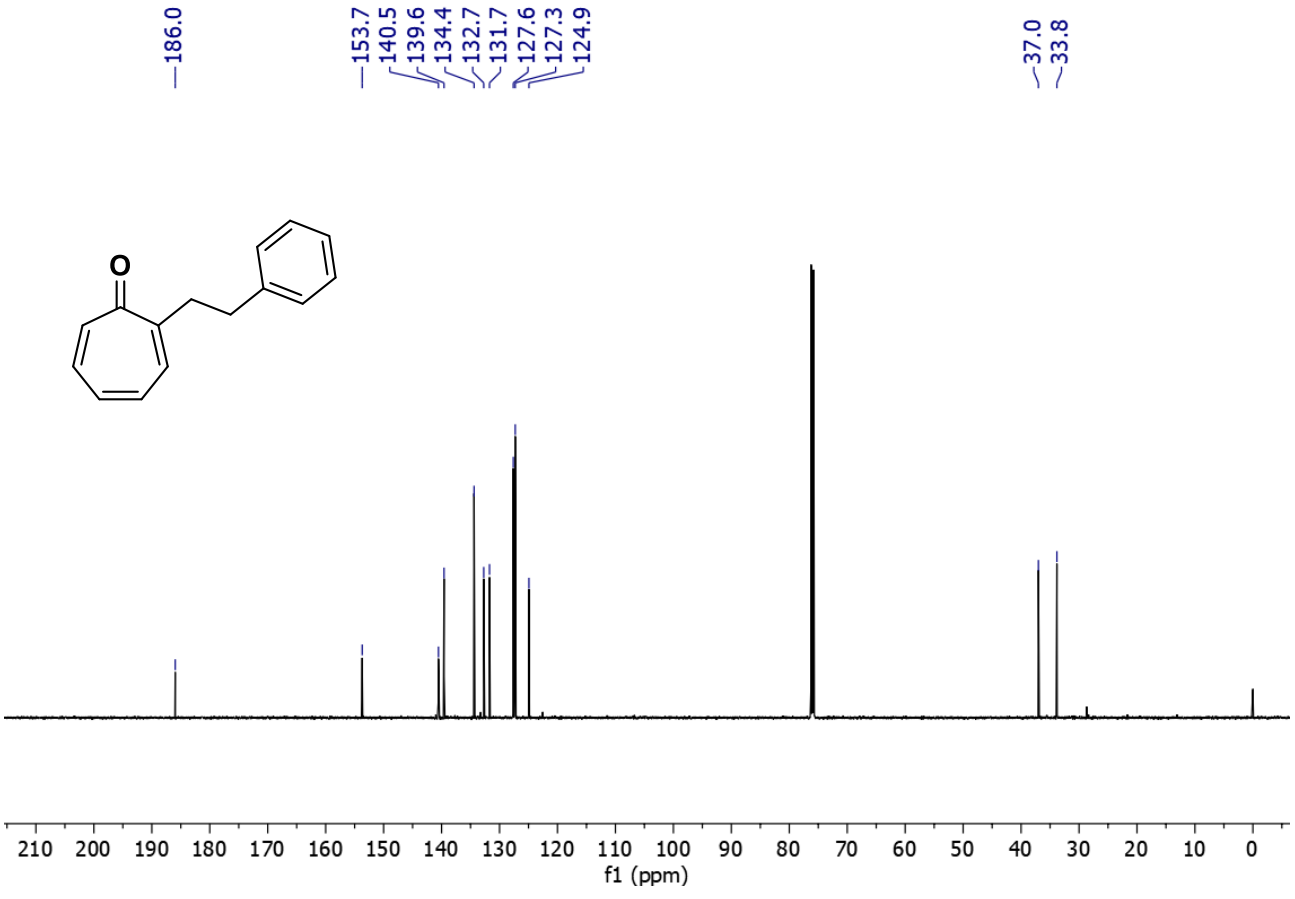
3af ^{13}C NMR (150 MHz, $CDCl_3$)



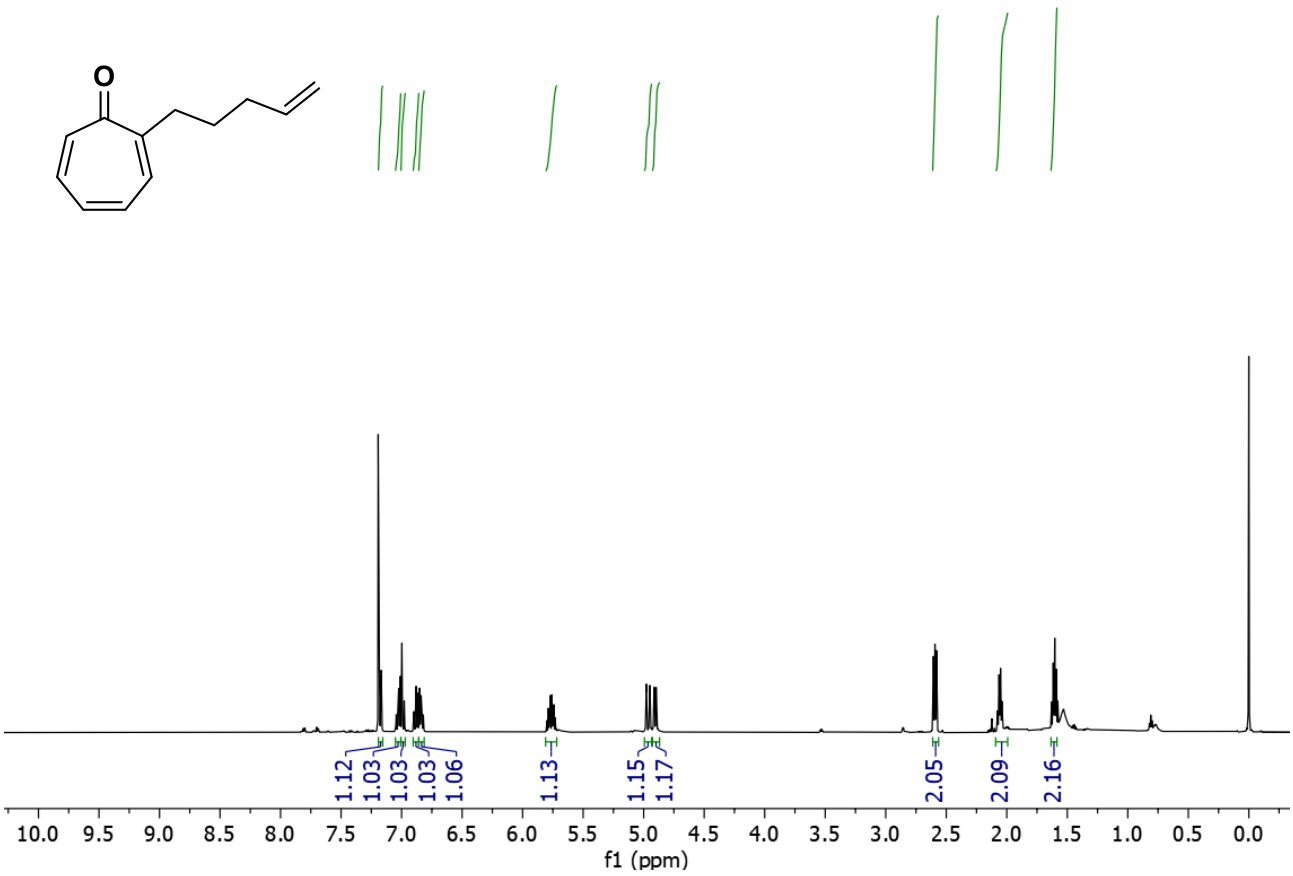
3ag ^{1}H NMR (600 MHz, $CDCl_3$)



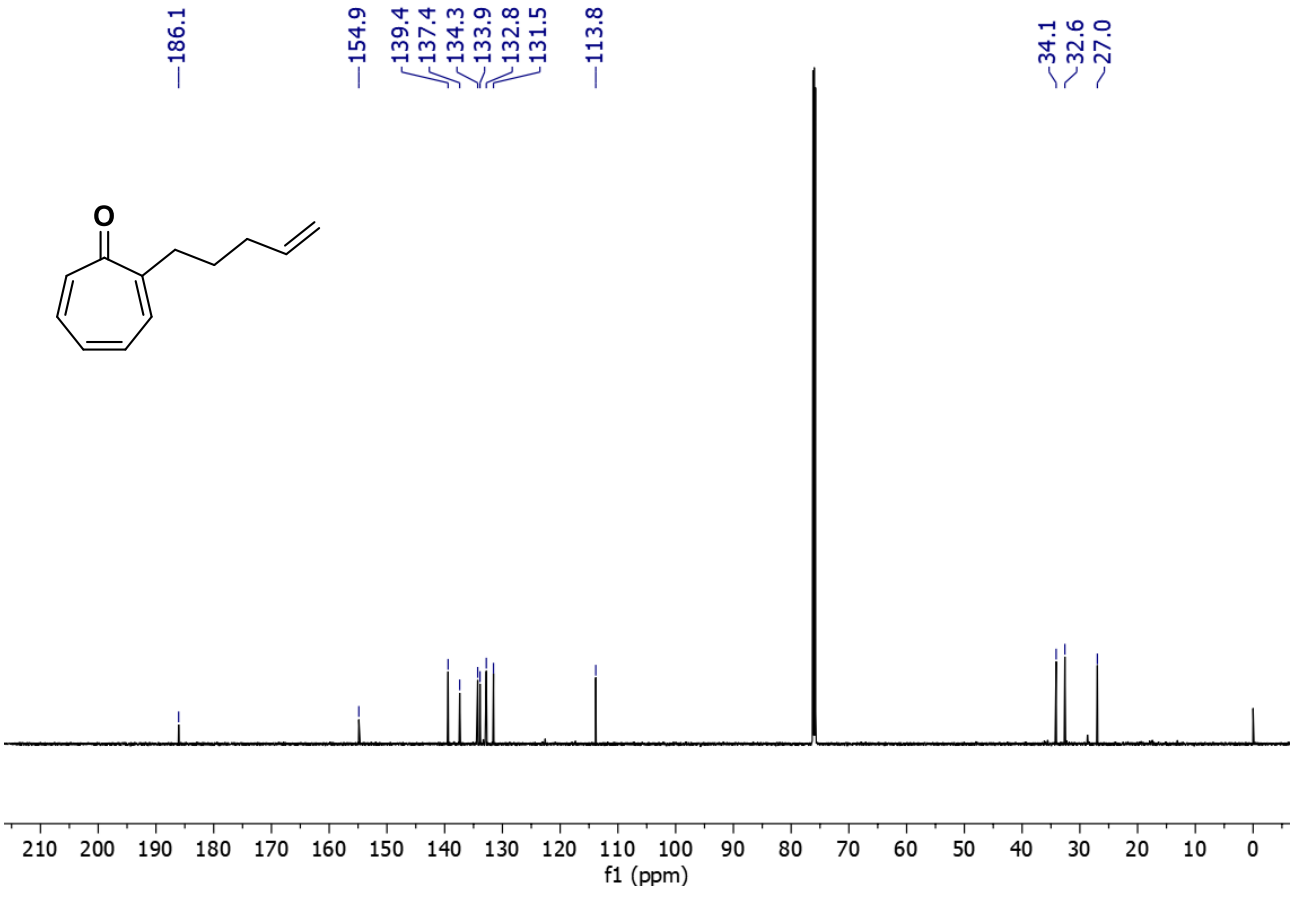
3ag ^{13}C NMR (150 MHz, $CDCl_3$)



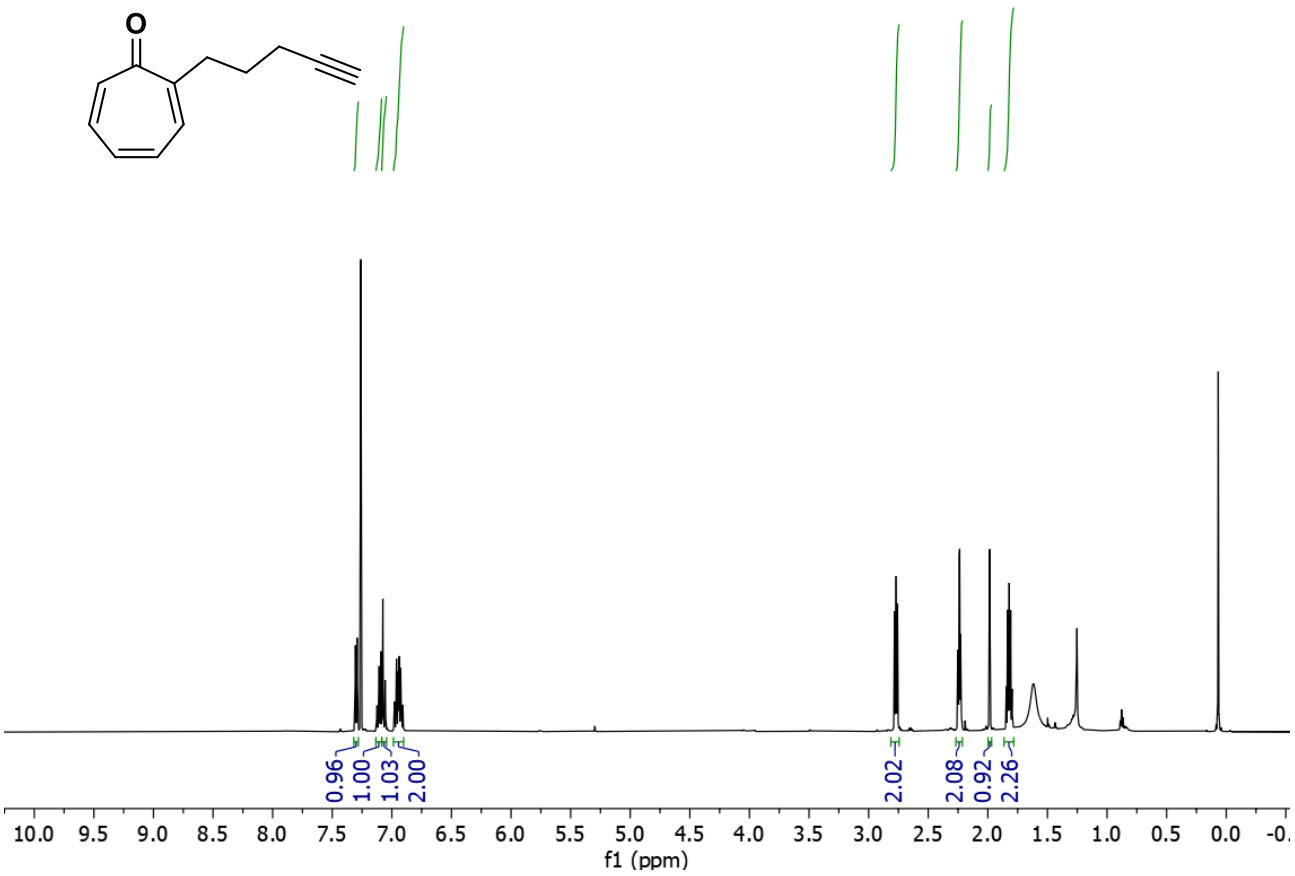
3ah ^{1}H NMR (600 MHz, $CDCl_3$)



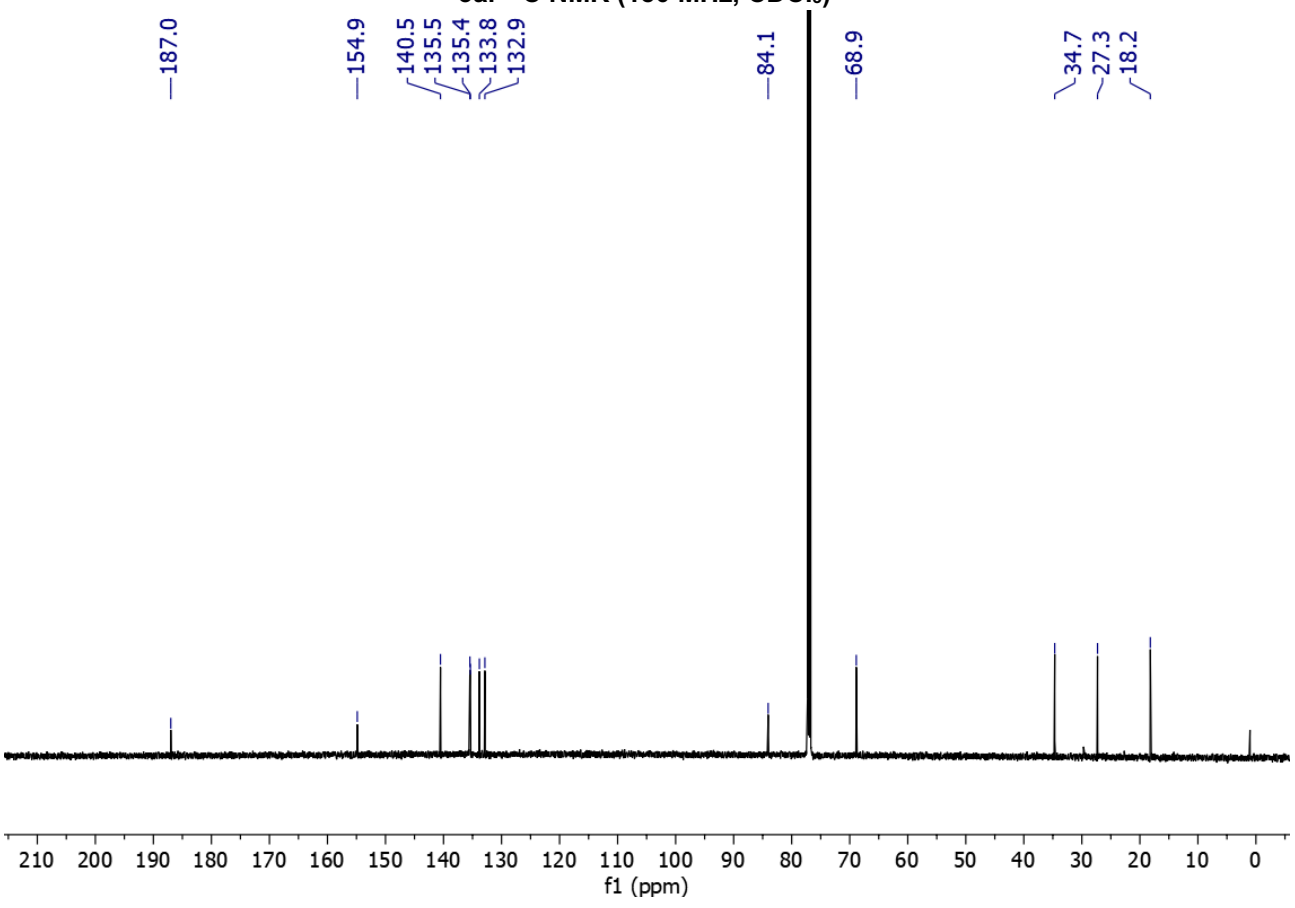
3ah ^{13}C NMR (150 MHz, $CDCl_3$)



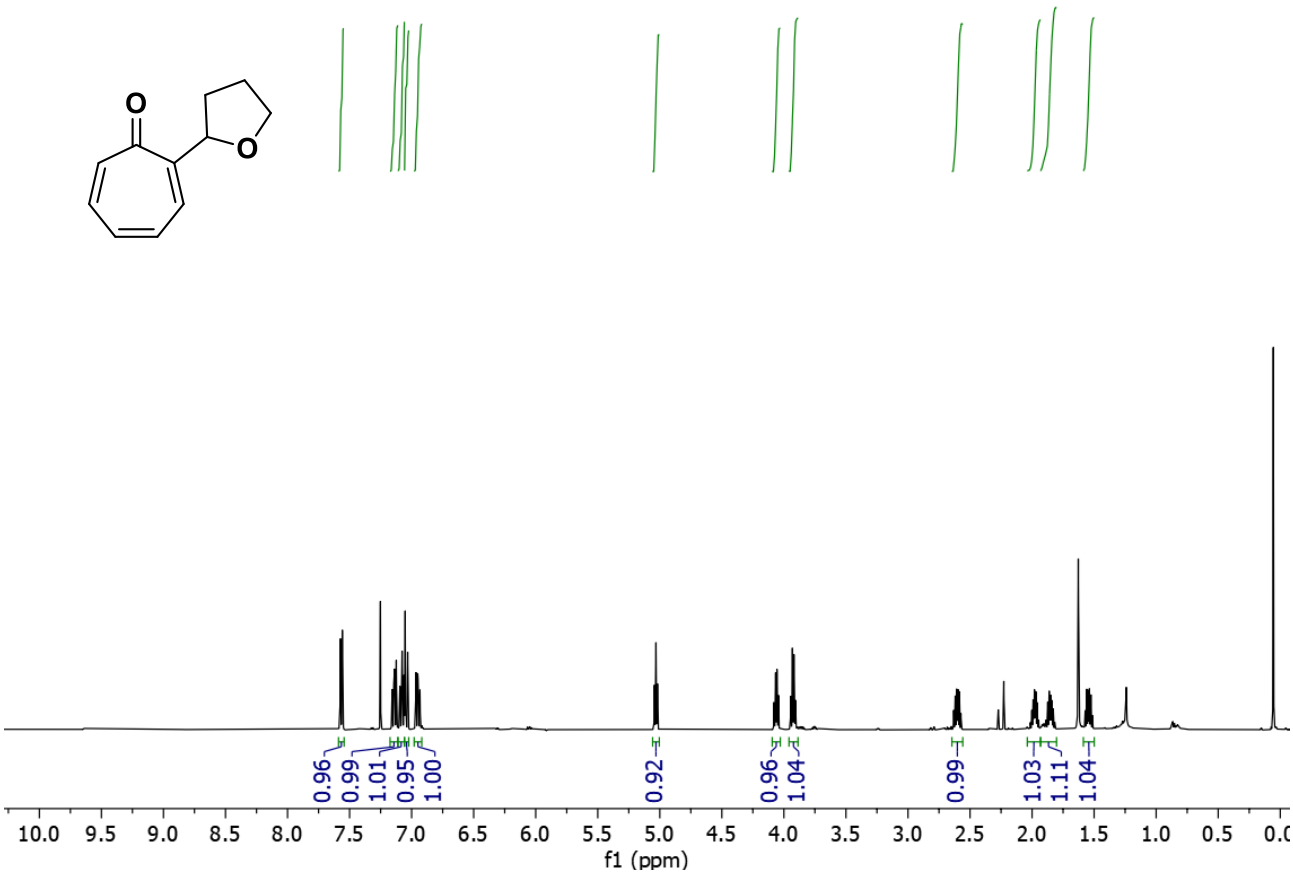
3ai ^{1}H NMR (600 MHz, $CDCl_3$)



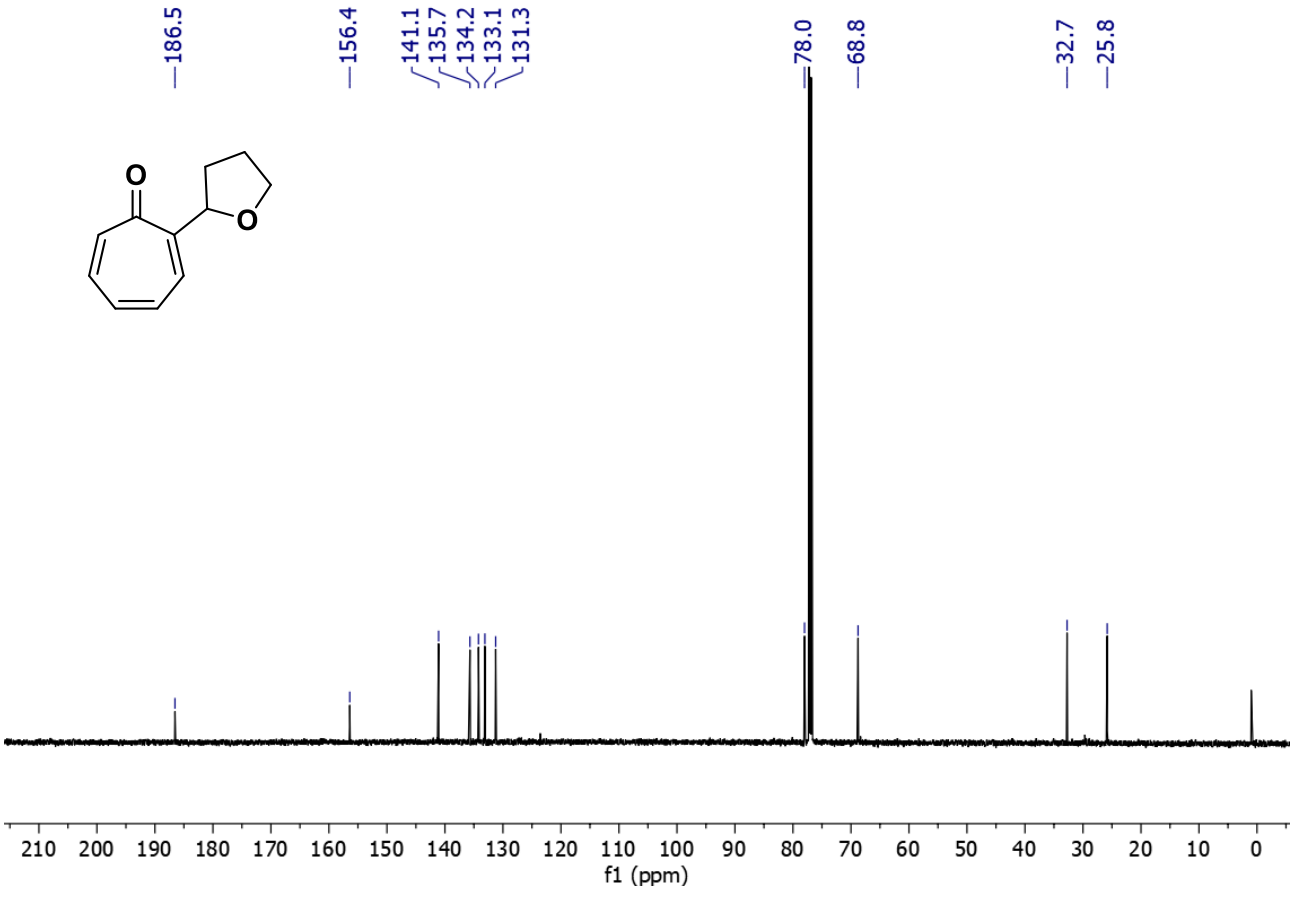
3ai ^{13}C NMR (150 MHz, $CDCl_3$)



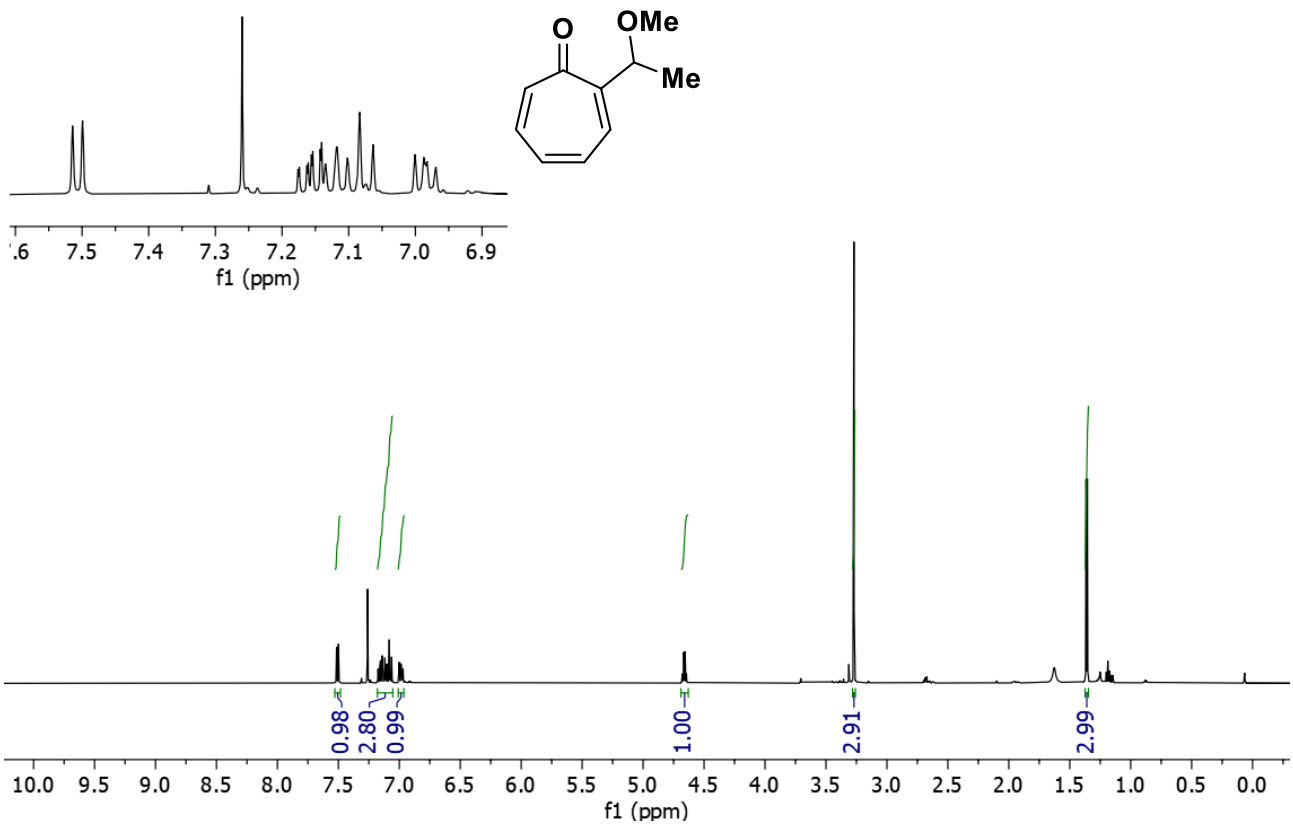
3aj ^{1}H NMR (600 MHz, $CDCl_3$)



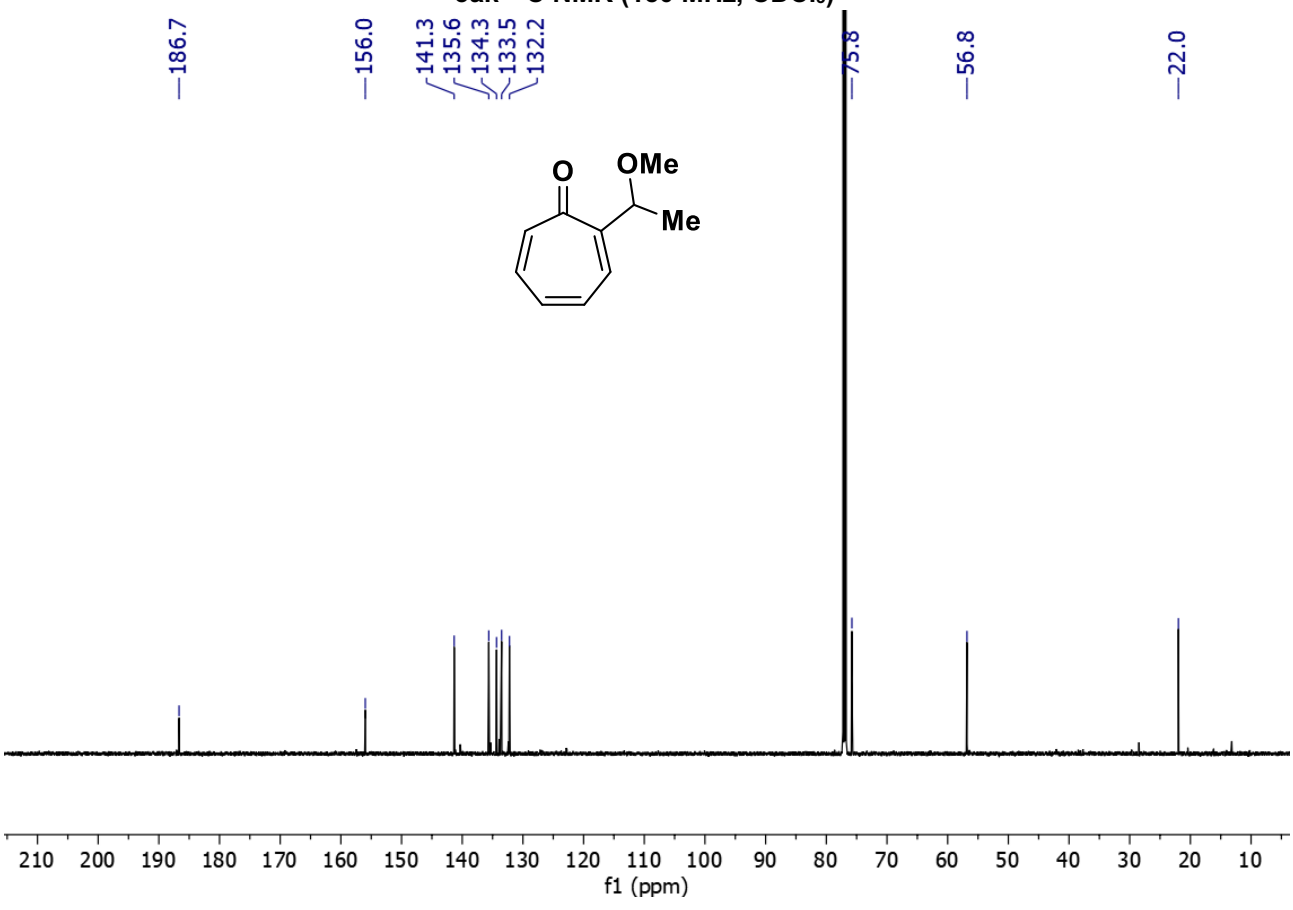
3aj ^{13}C NMR (150 MHz, $CDCl_3$)



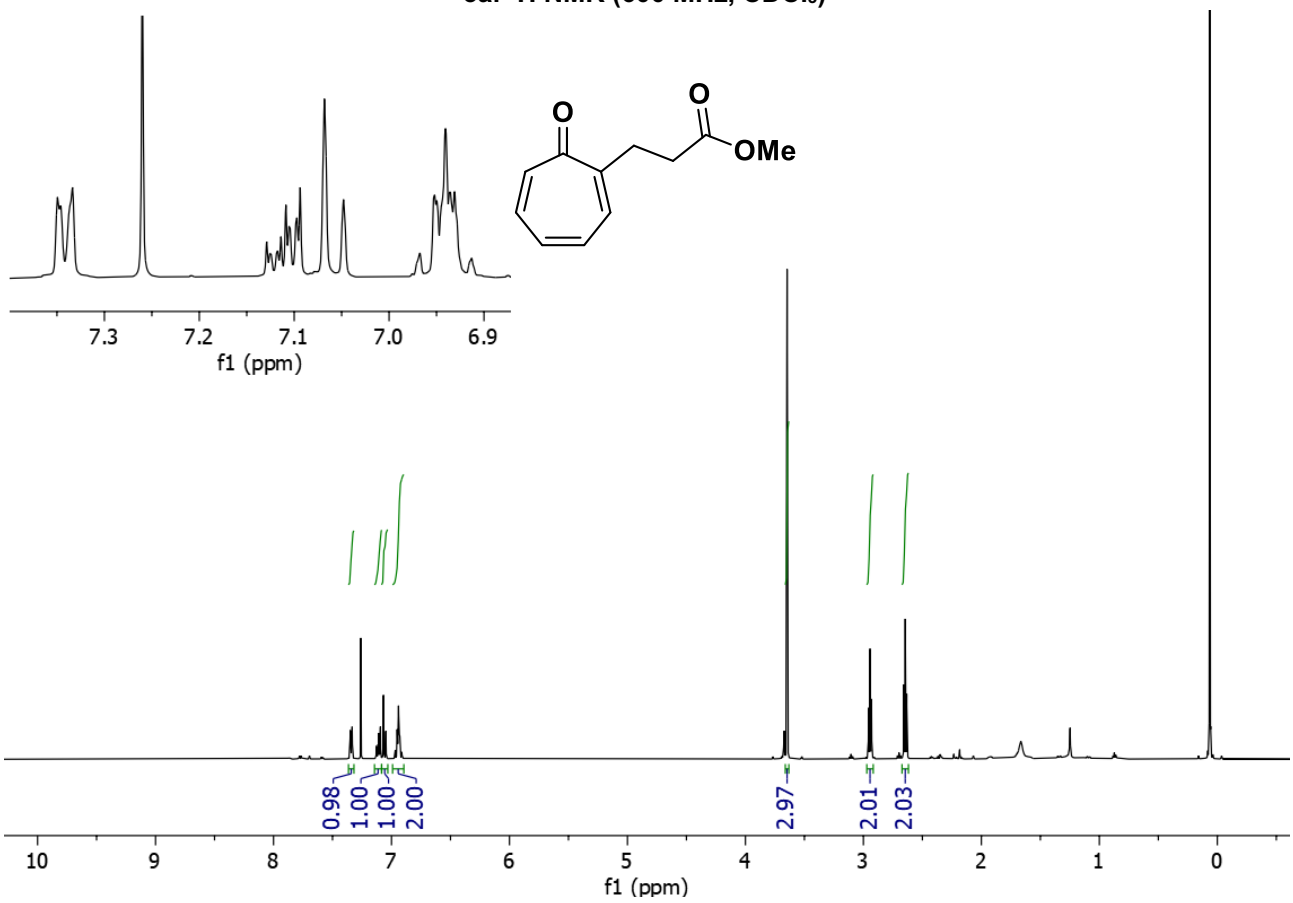
3ak ^{1}H NMR (600 MHz, $CDCl_3$)



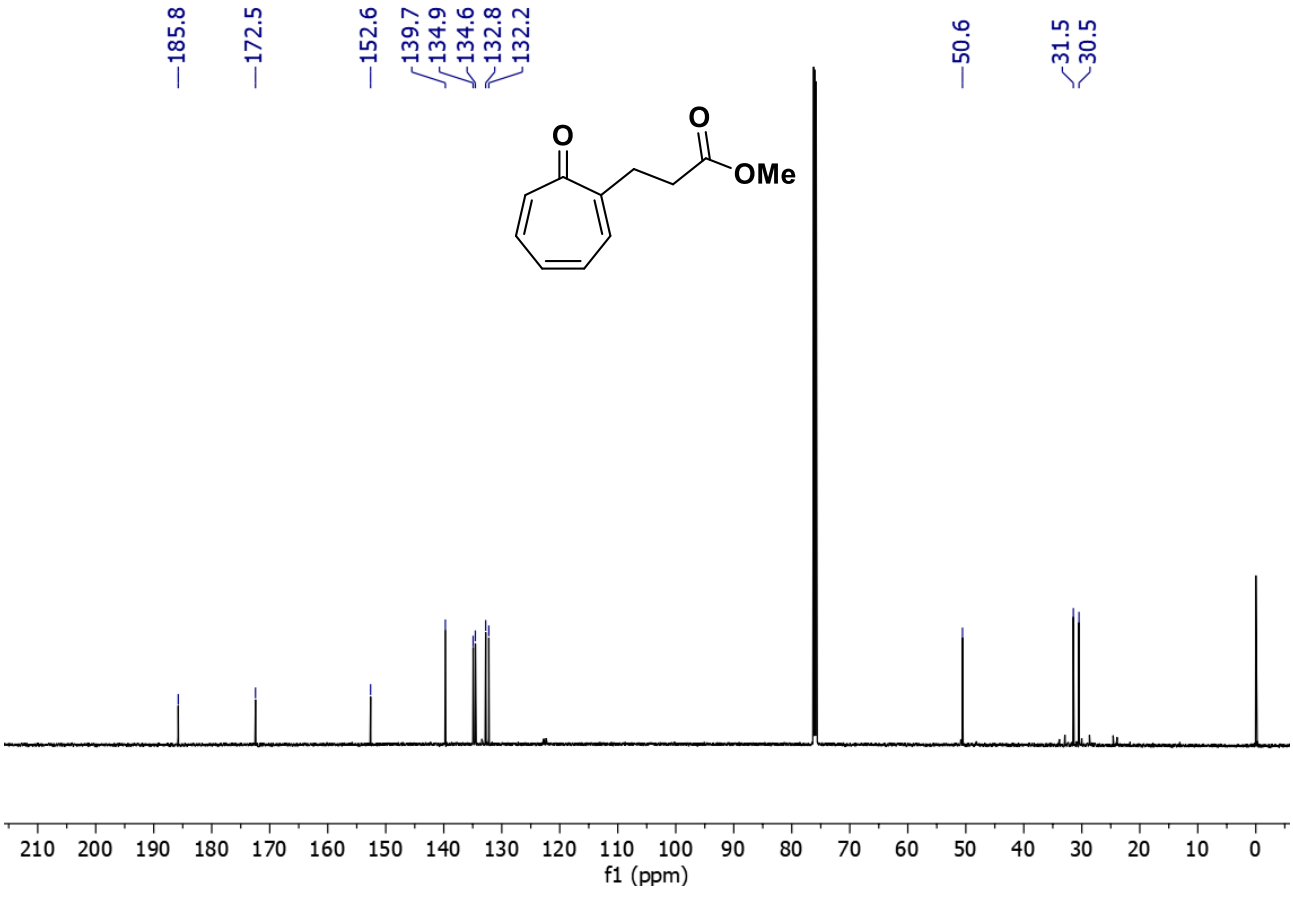
3ak ^{13}C NMR (150 MHz, $CDCl_3$)



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



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



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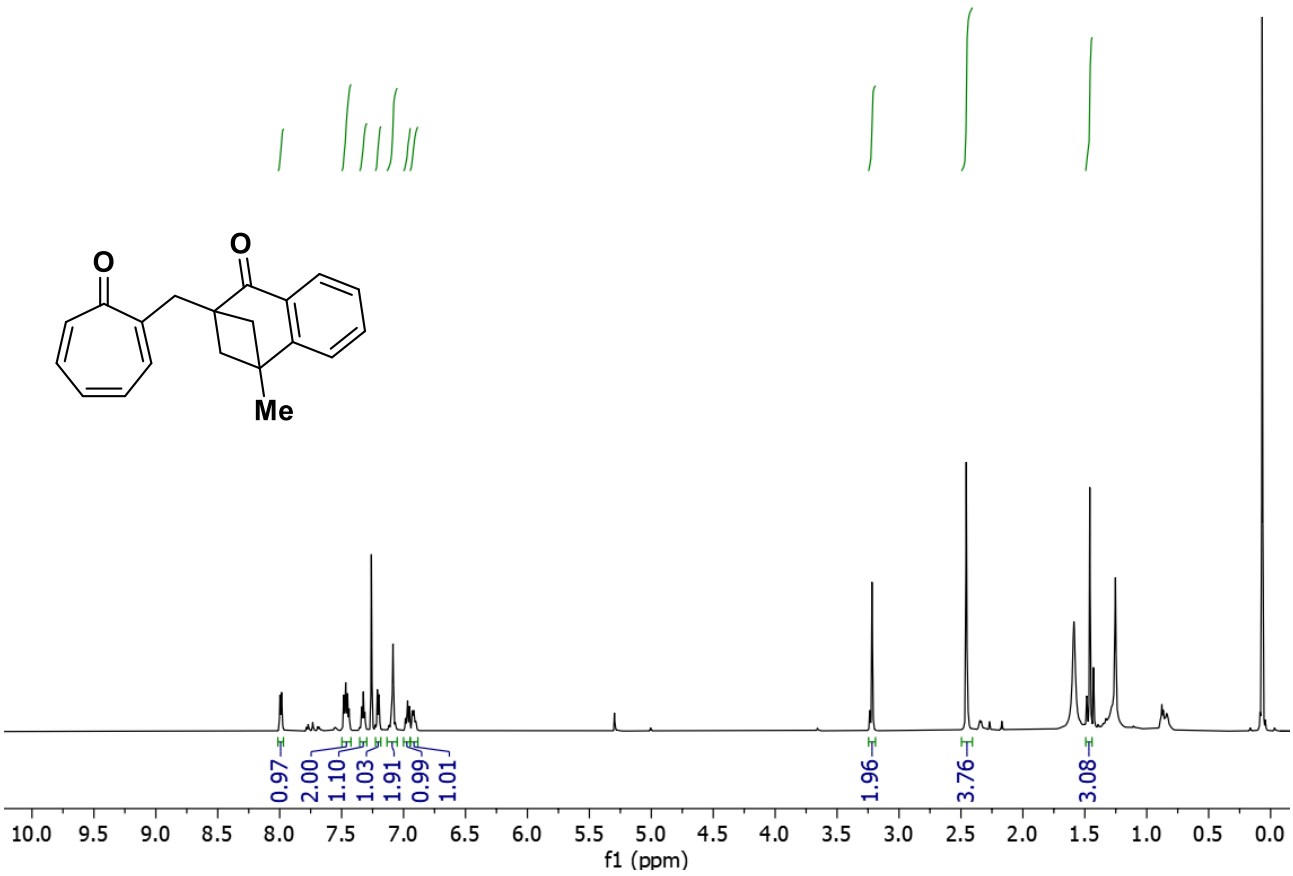

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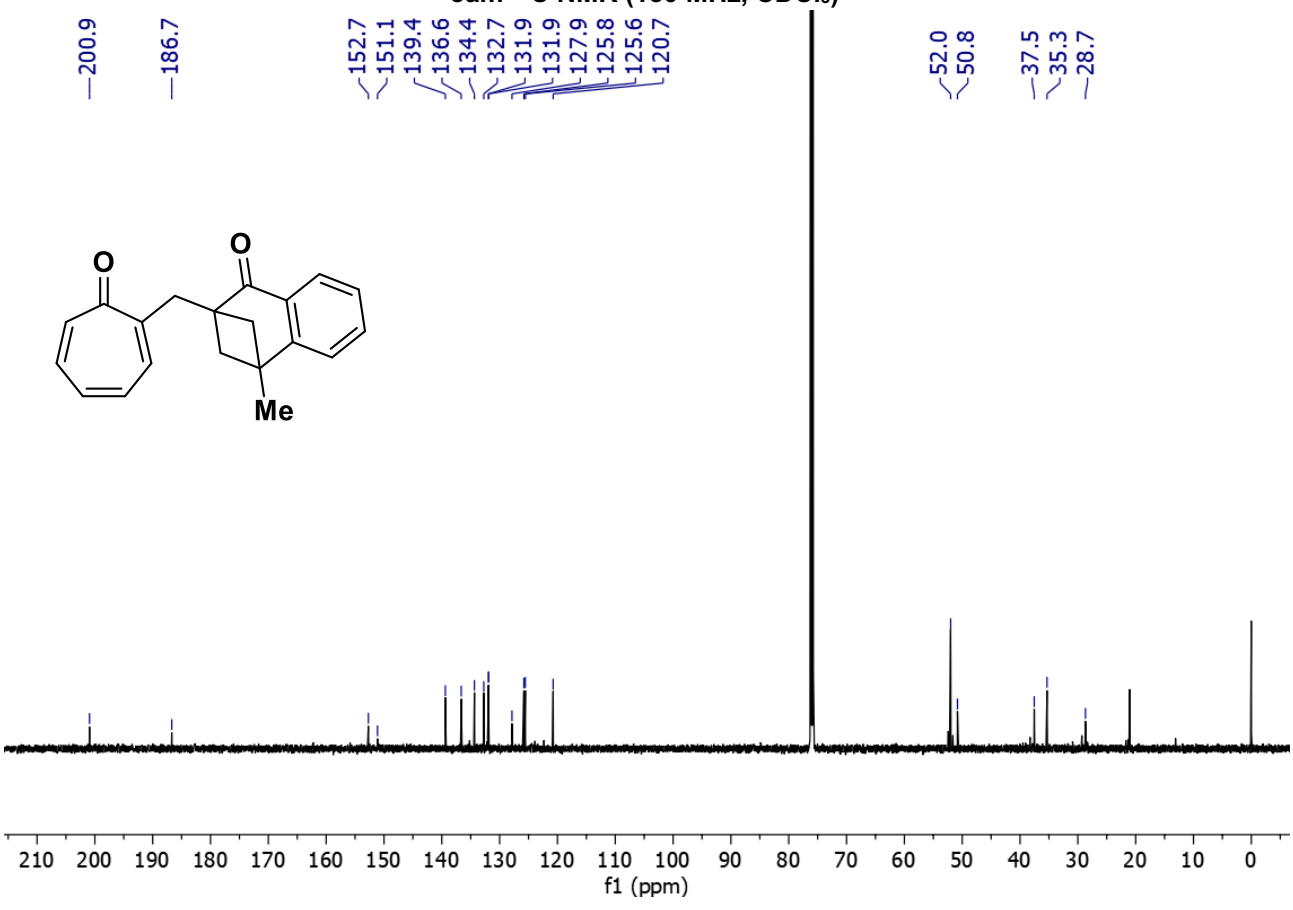

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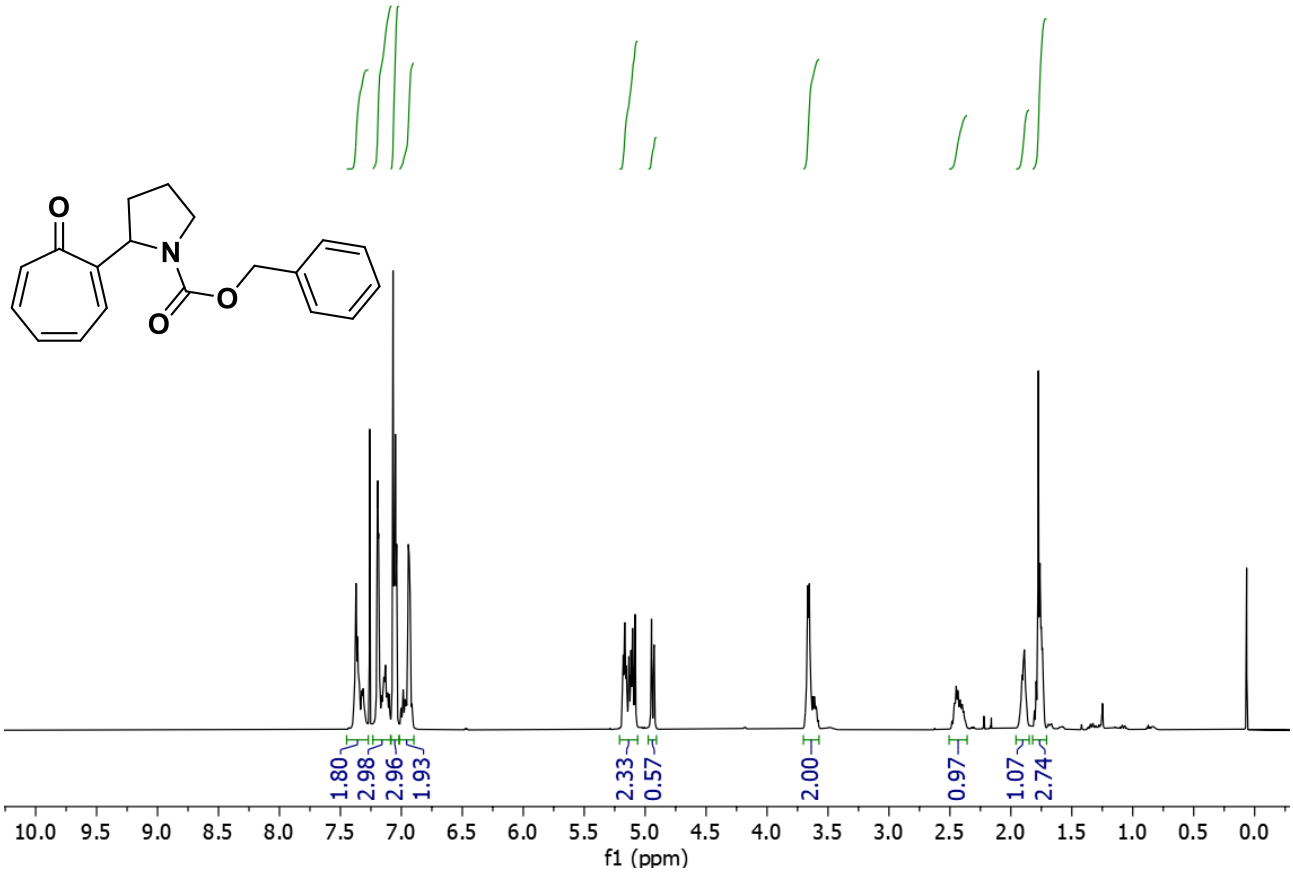
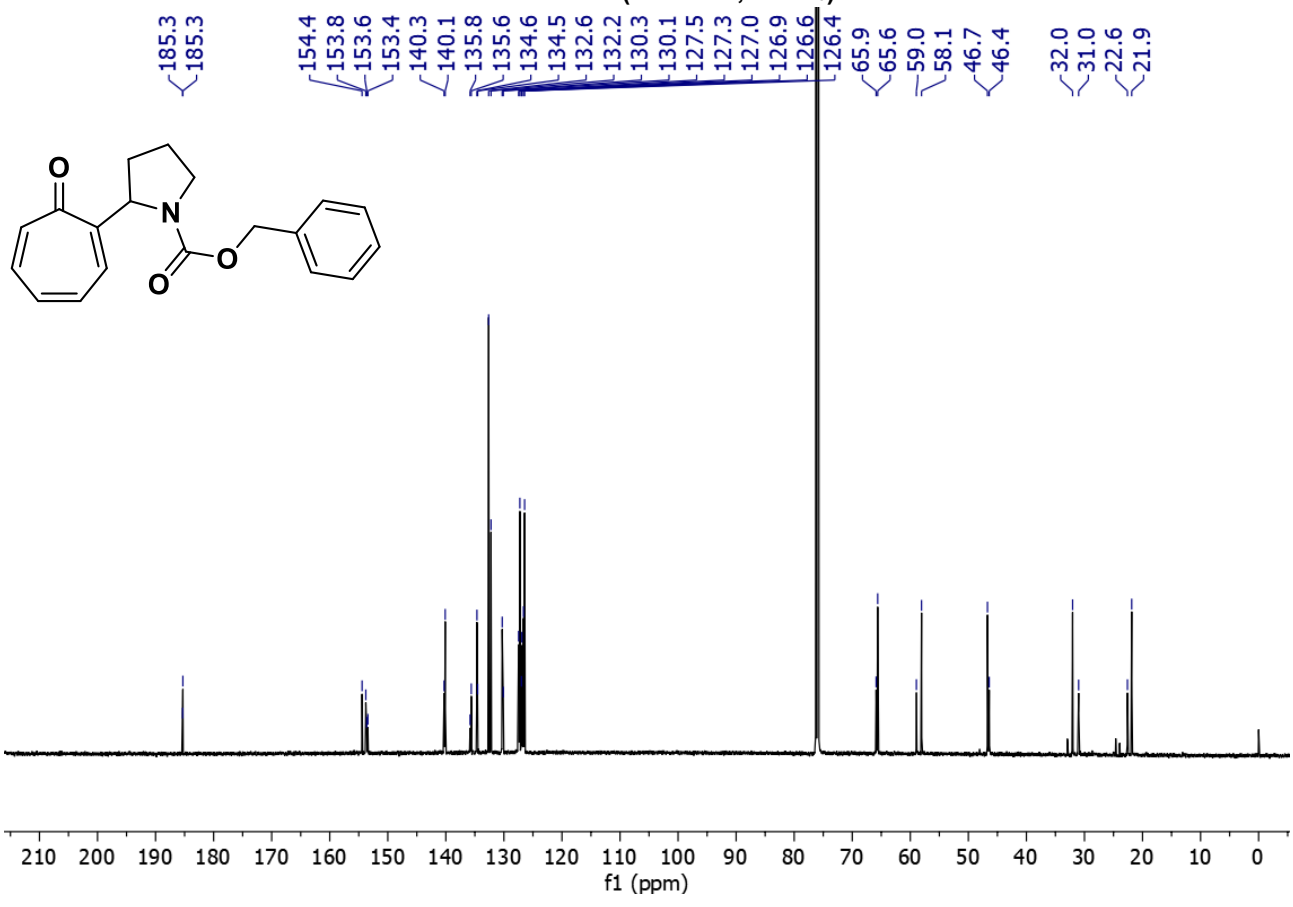


3an ^{13}C NMR (150 MHz, $CDCl_3$)



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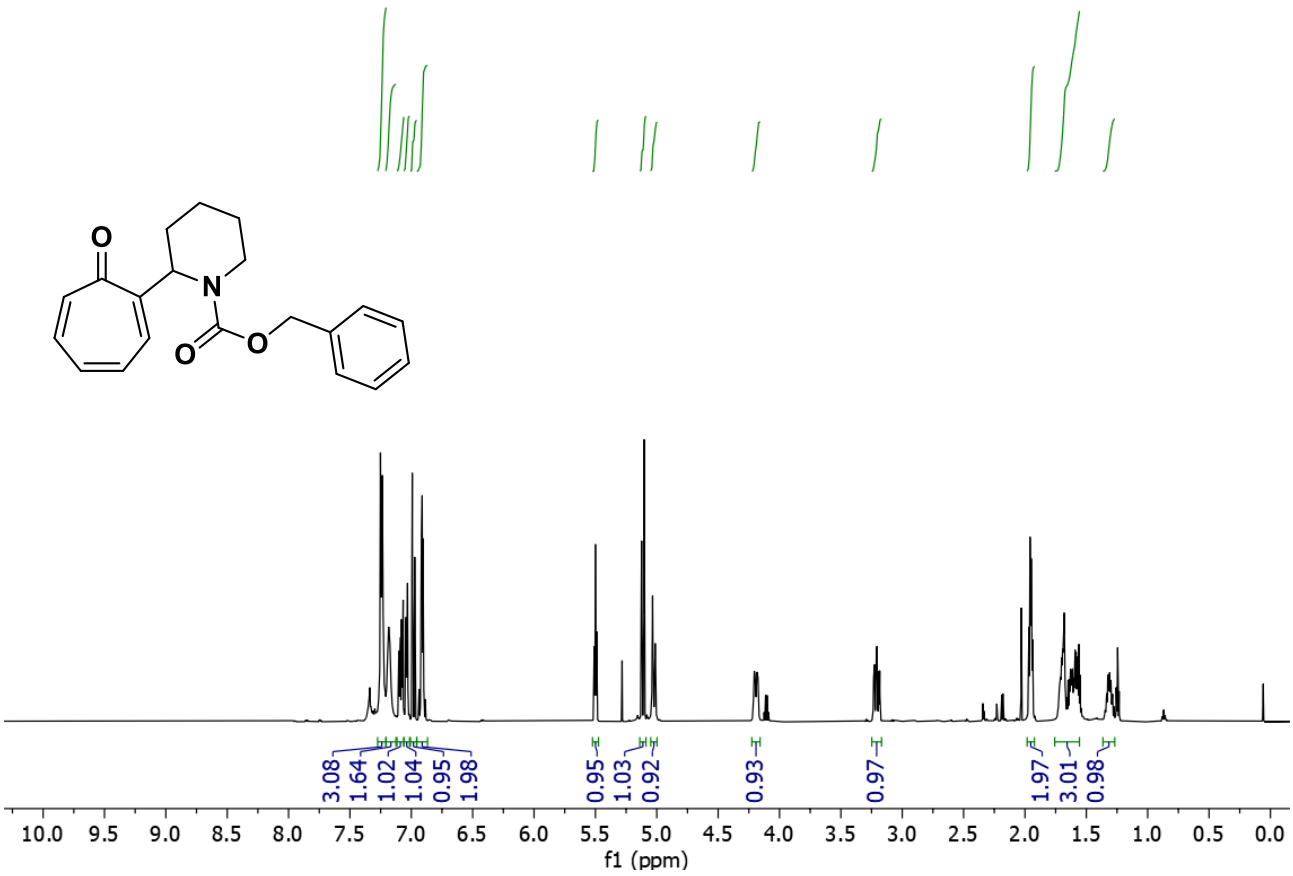

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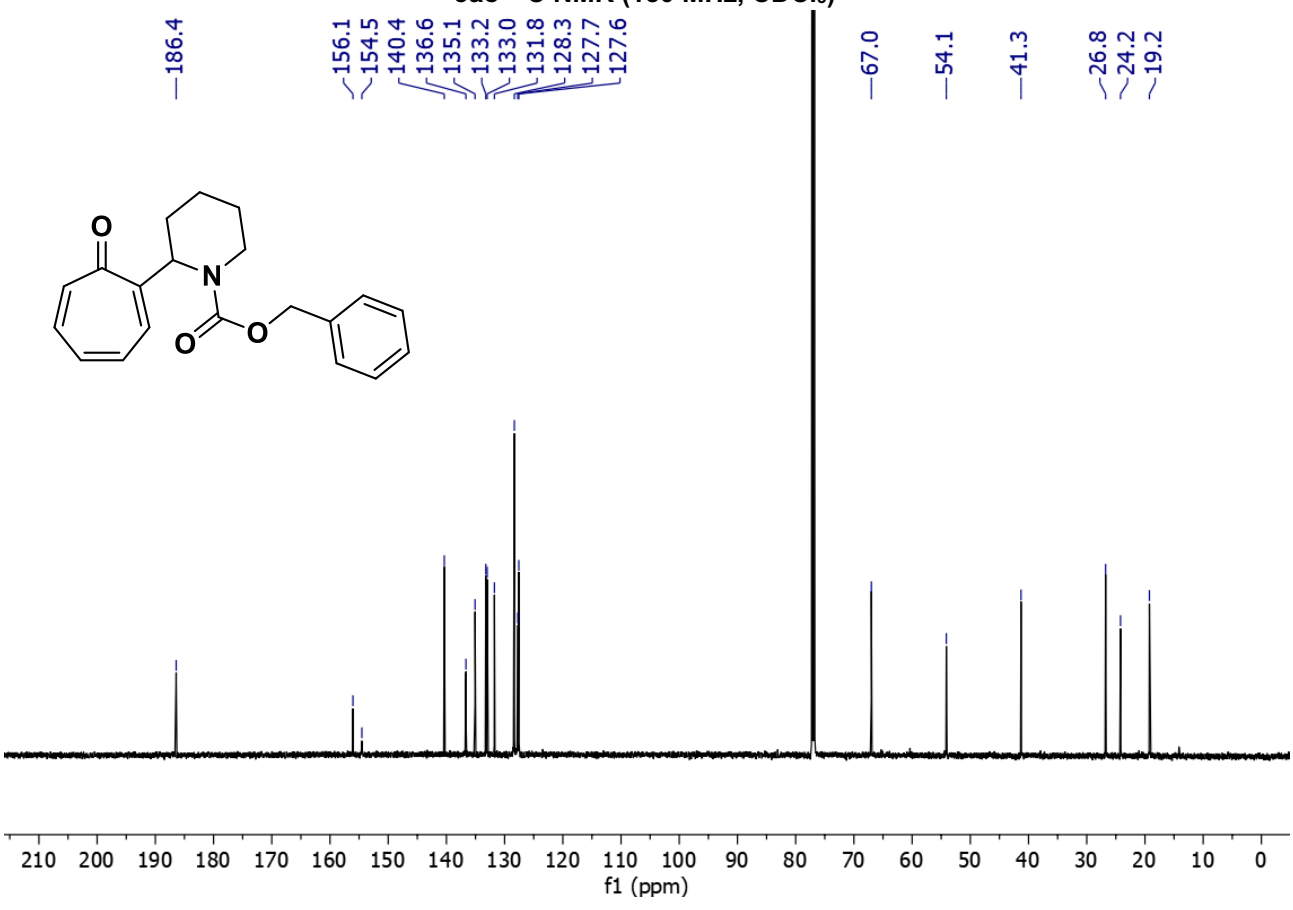

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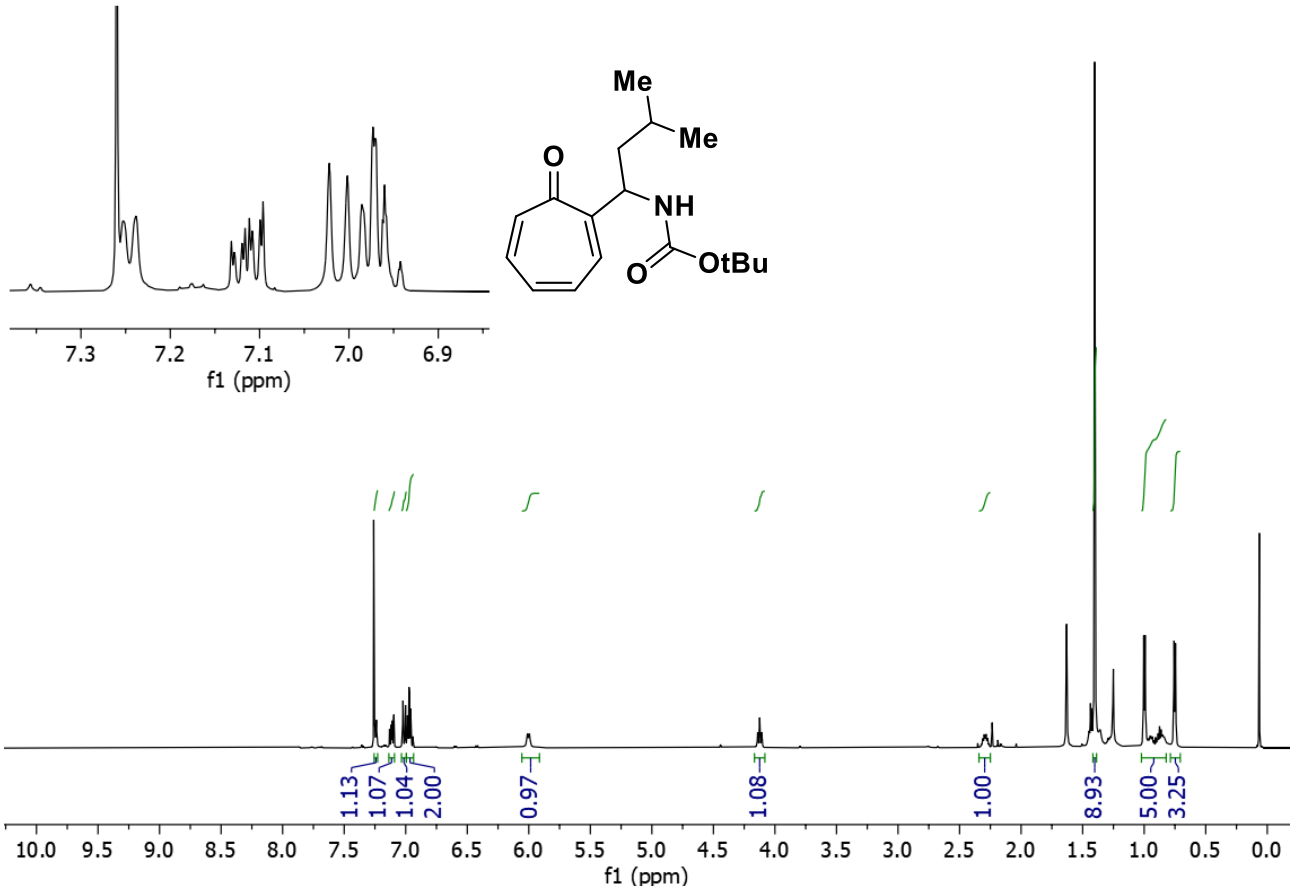
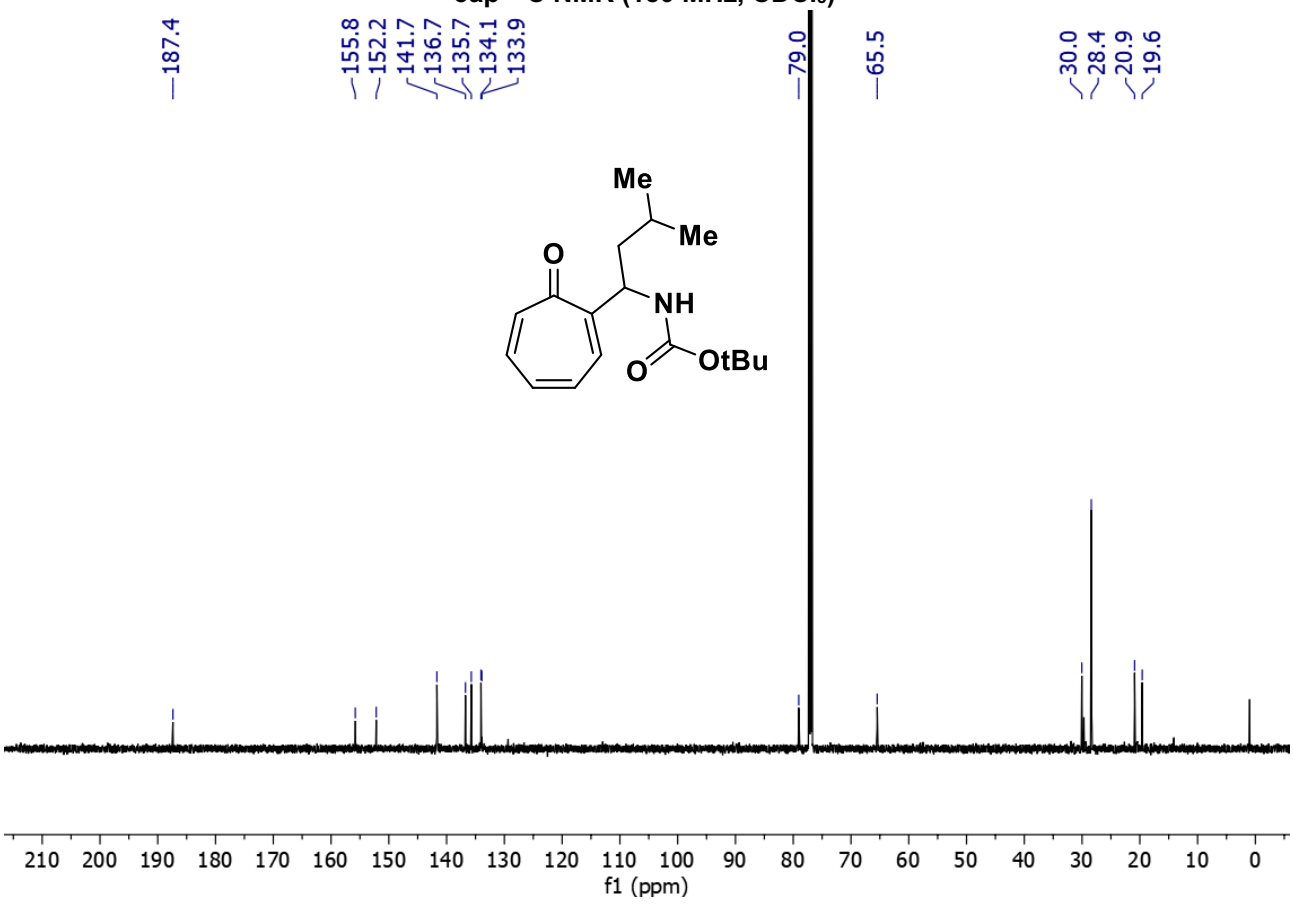


3ap ^{13}C NMR (150 MHz, $CDCl_3$)



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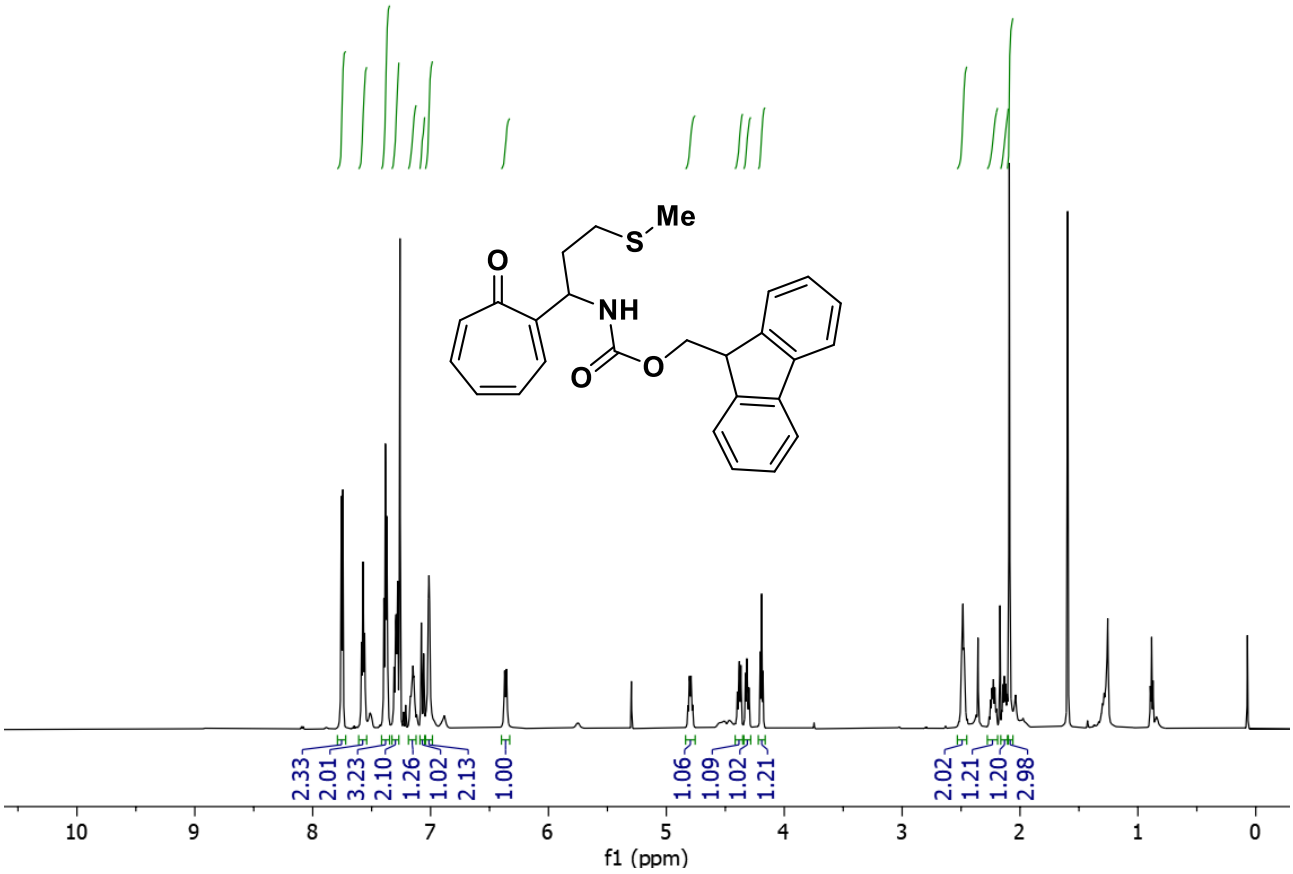

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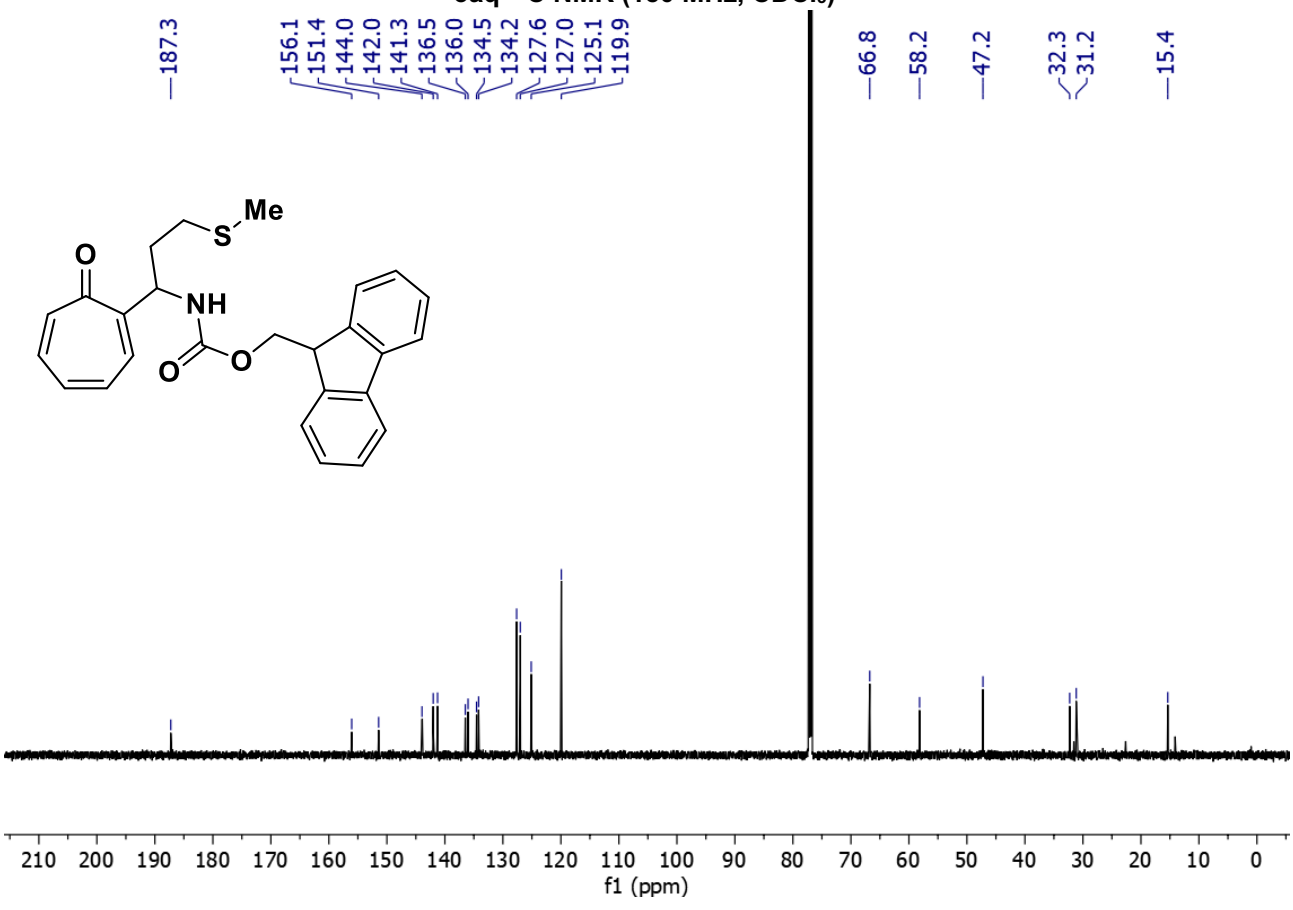

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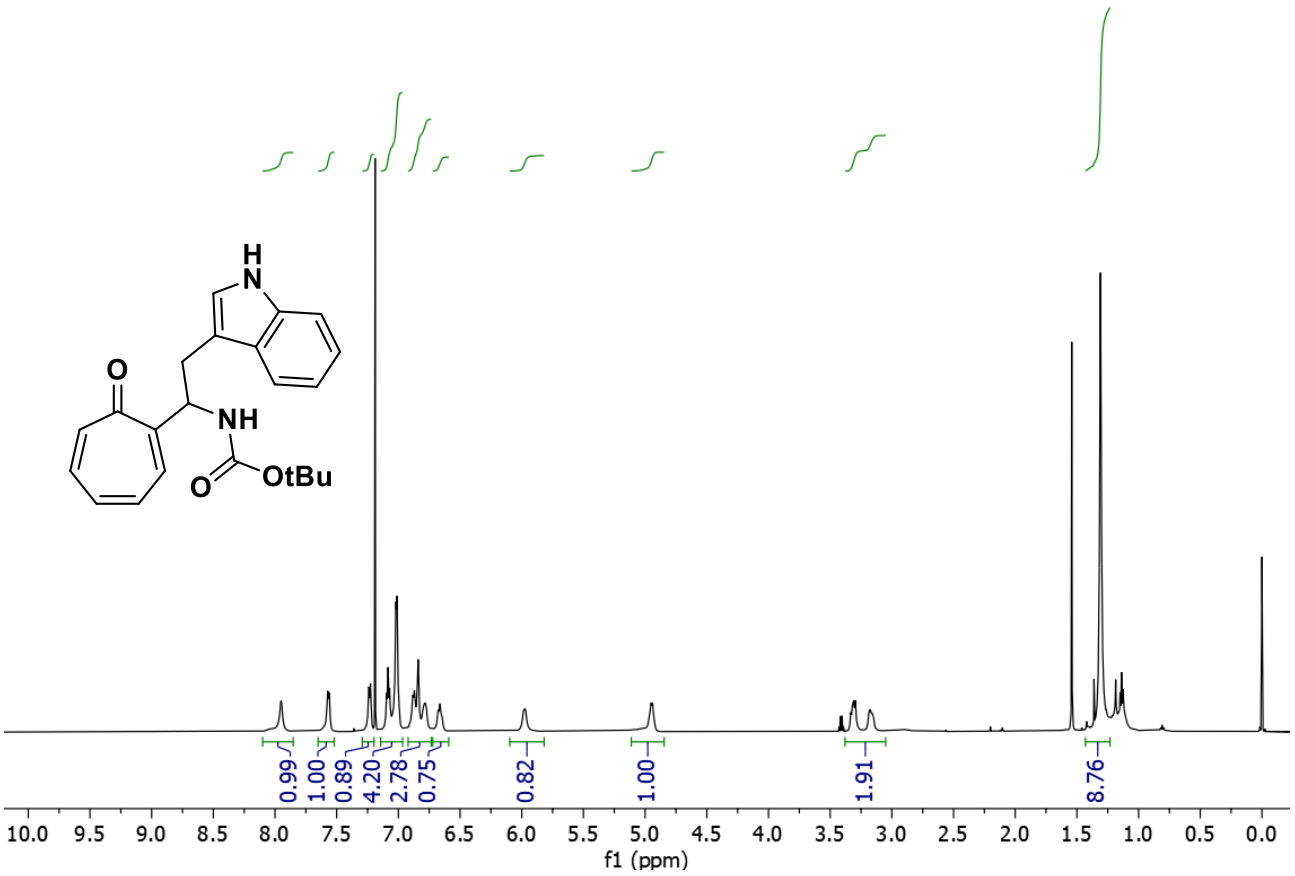

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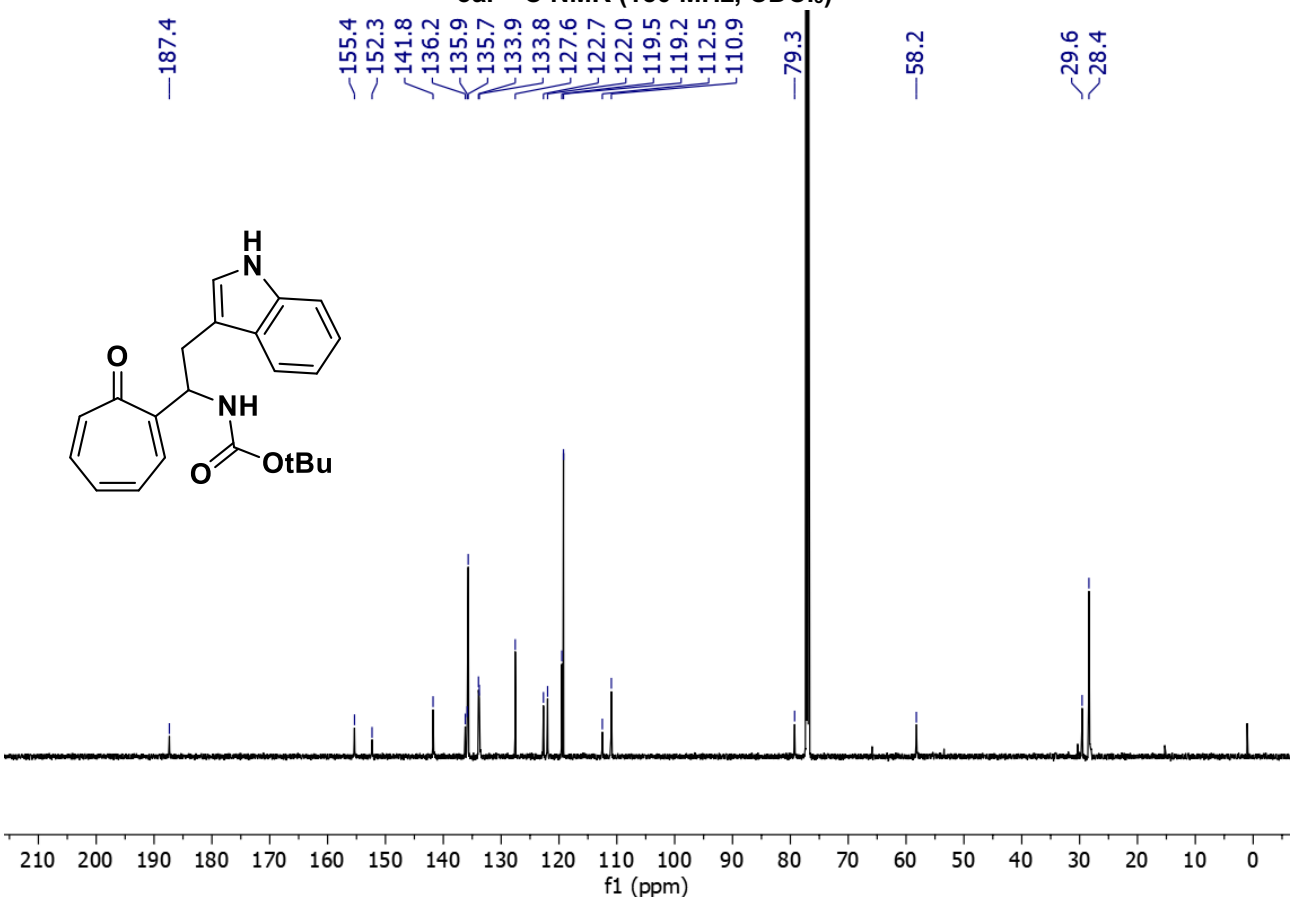

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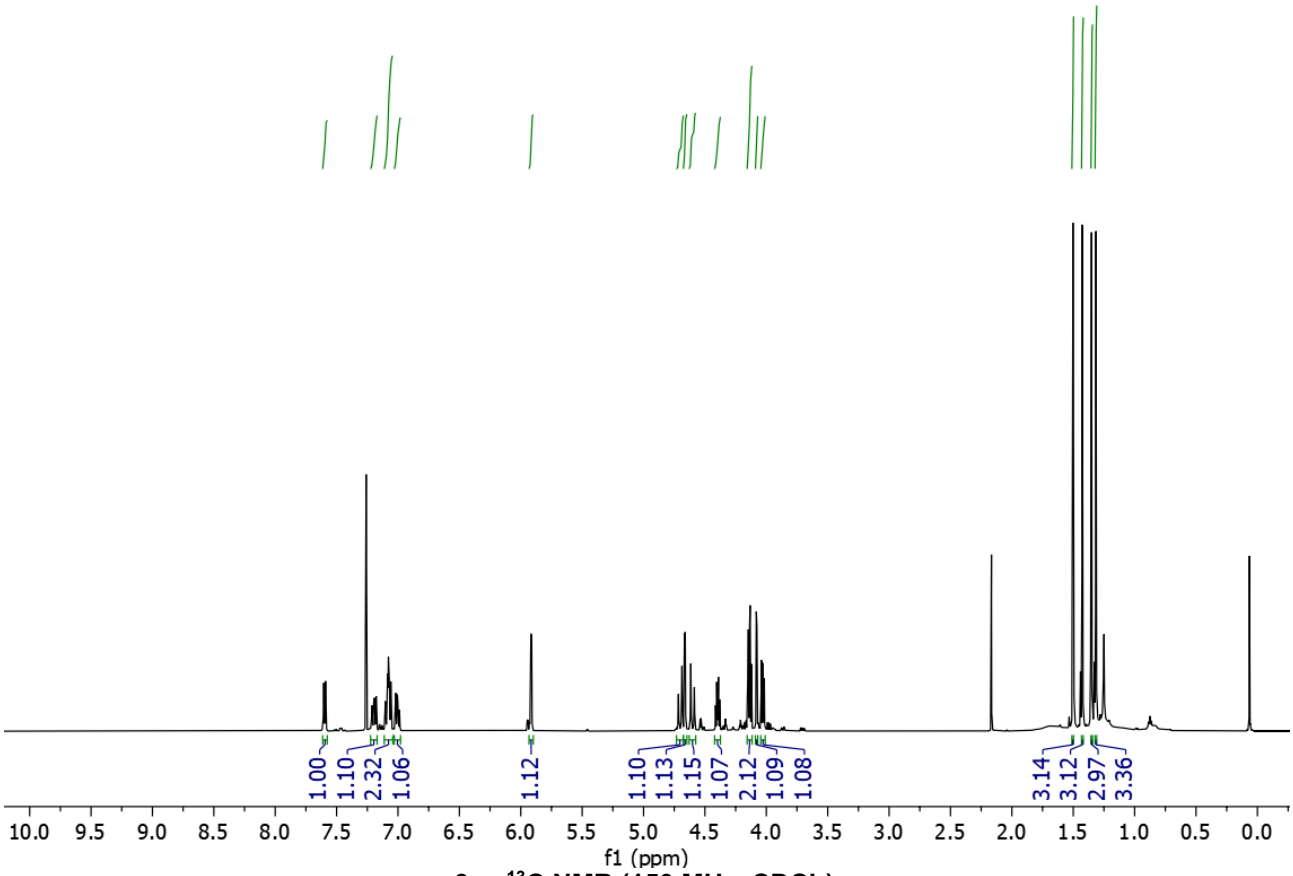

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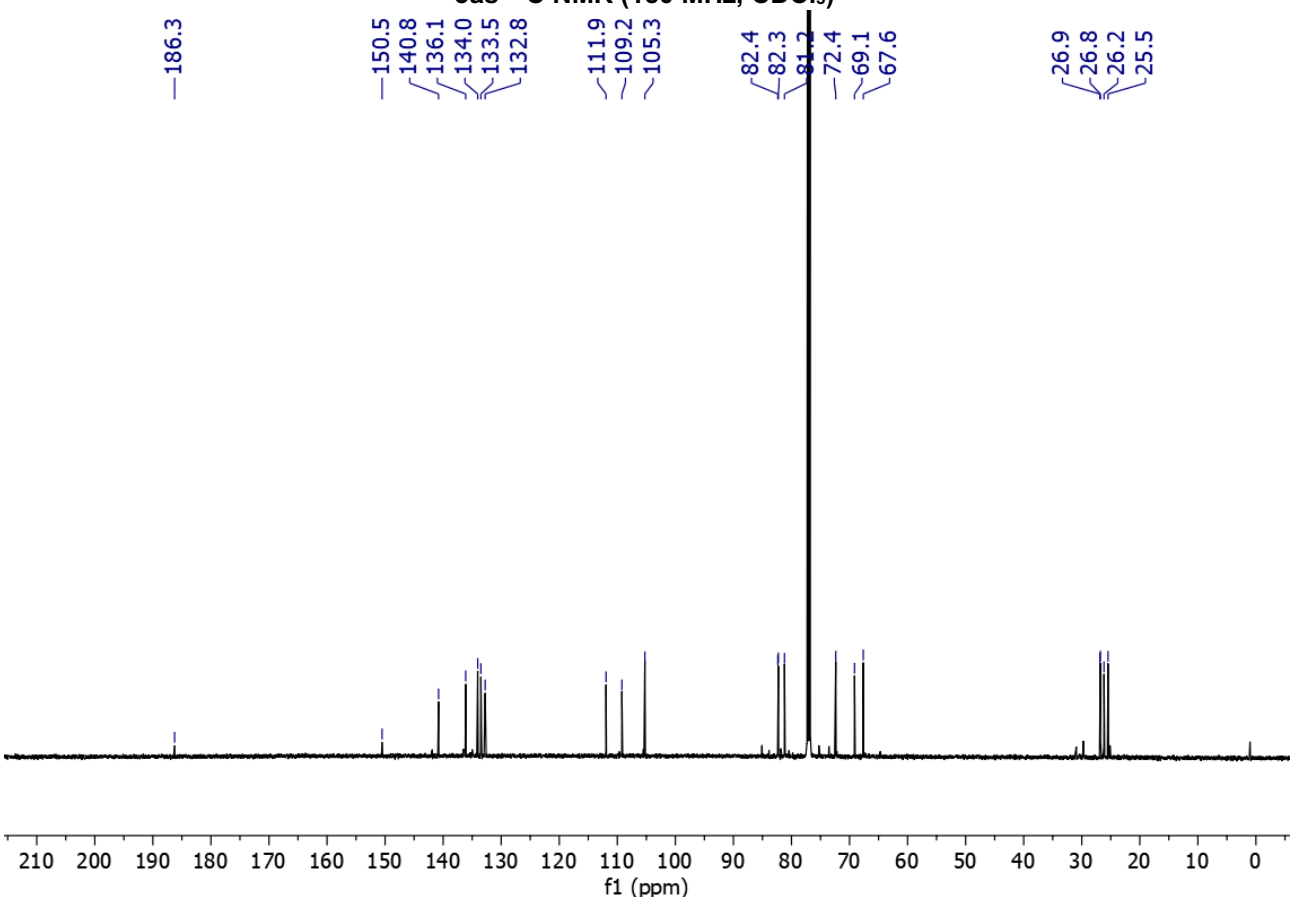

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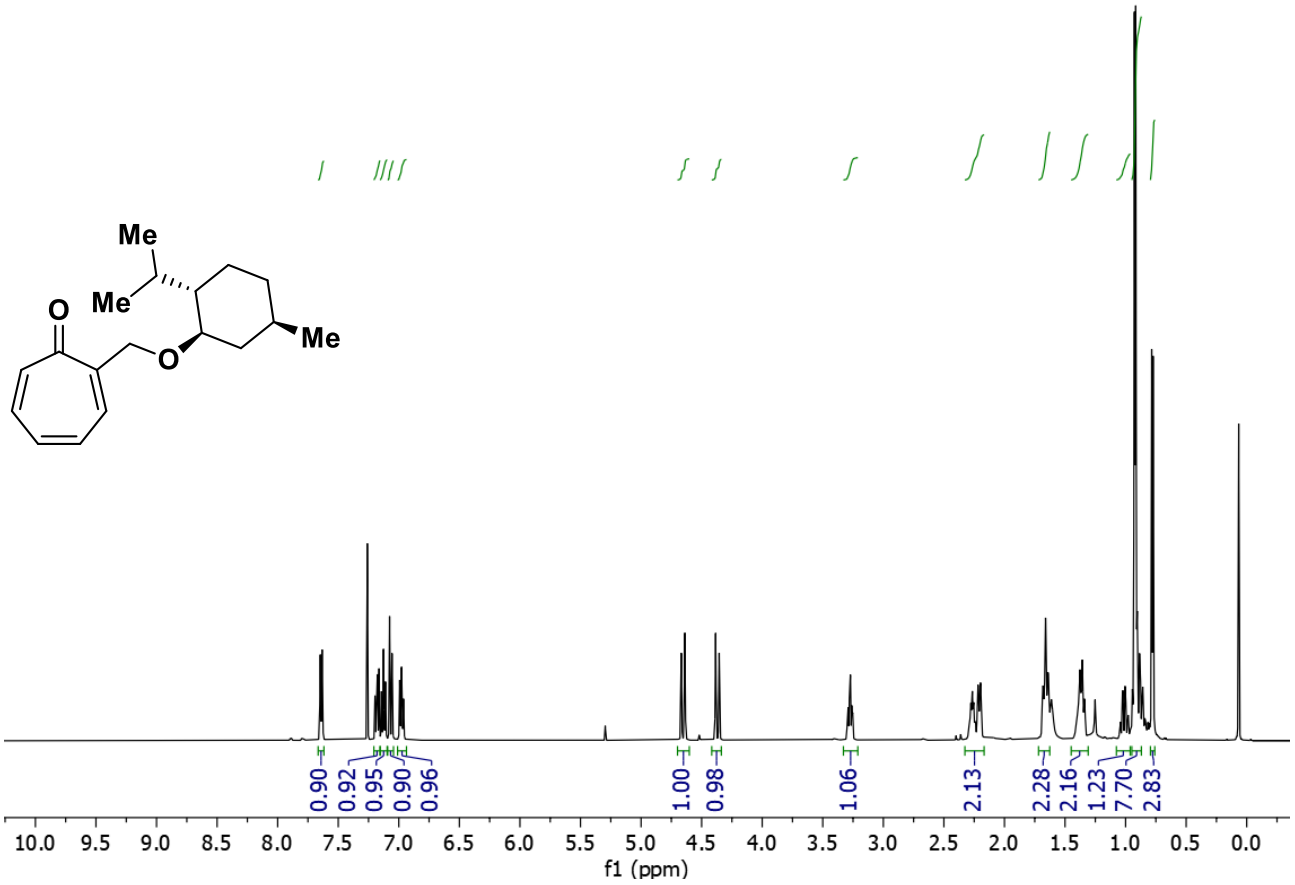
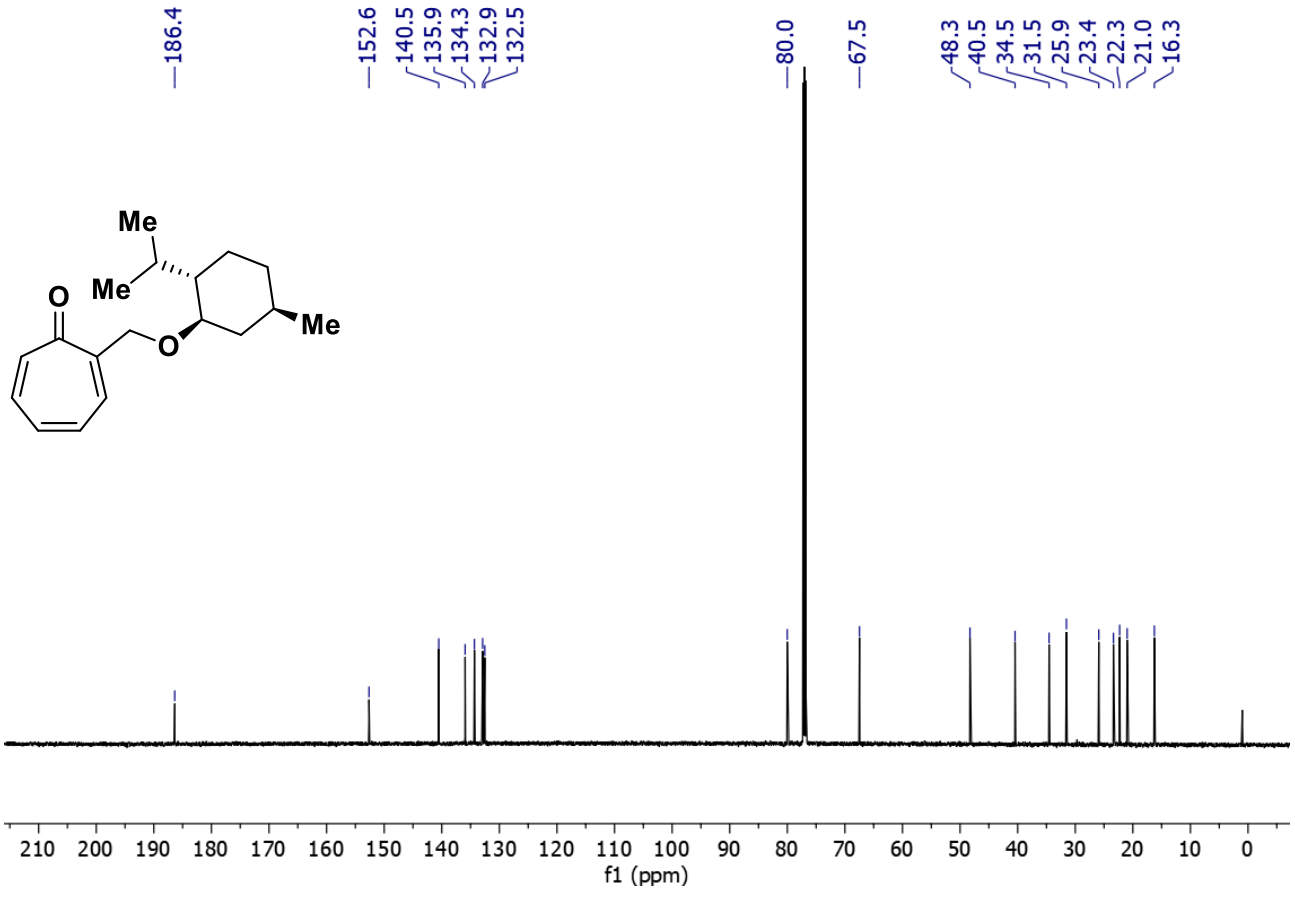


3at ^{13}C NMR (150 MHz, $CDCl_3$)



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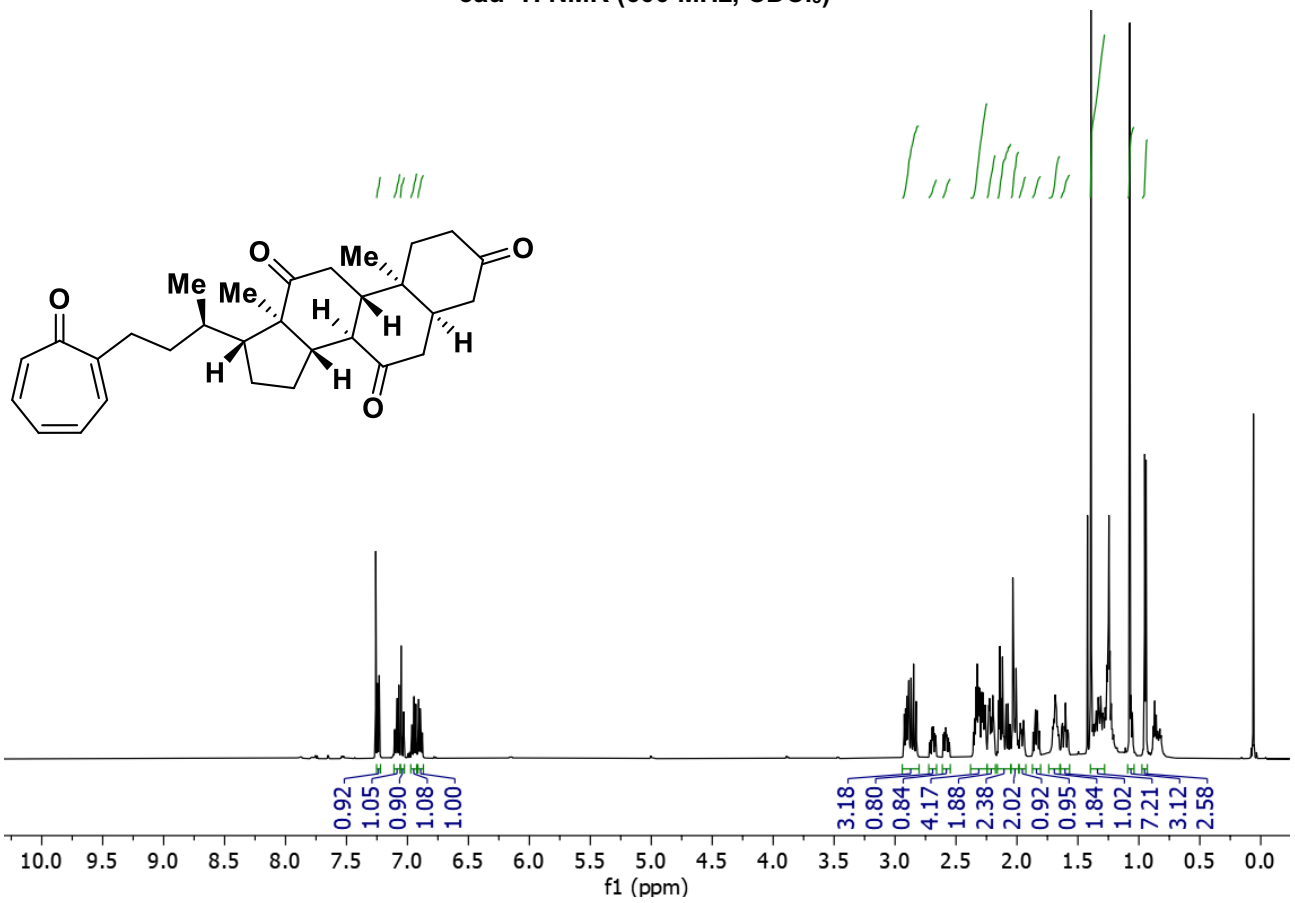

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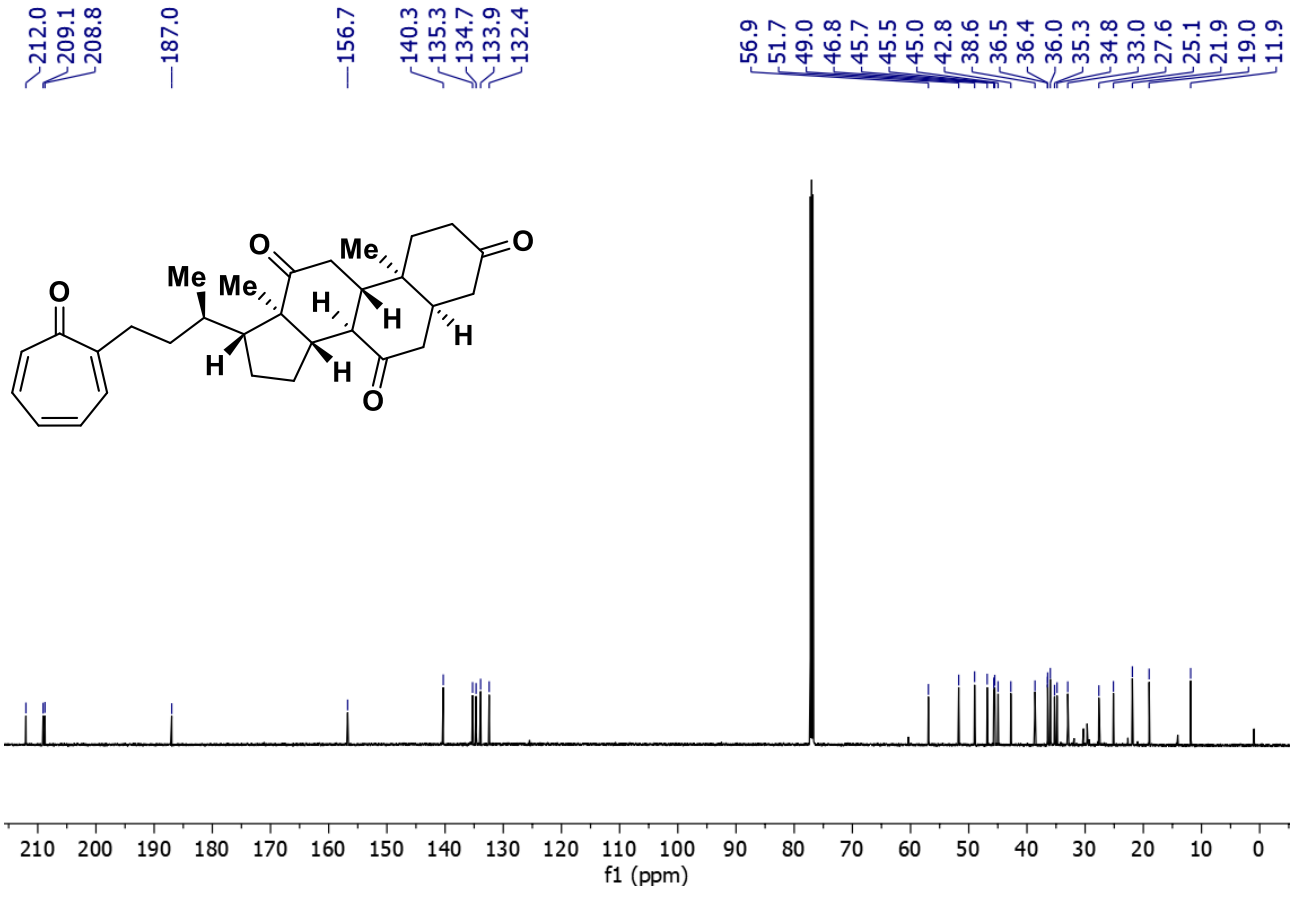
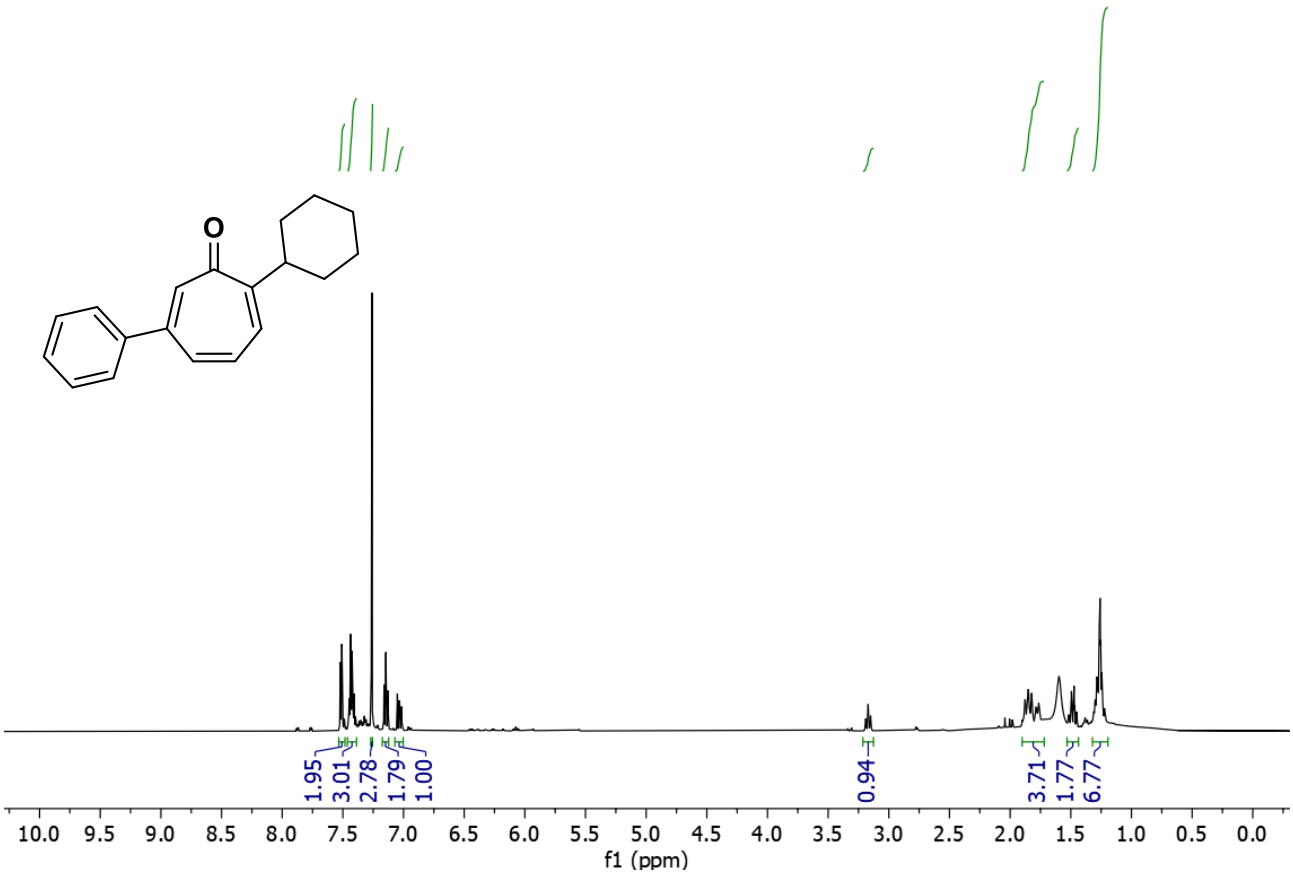
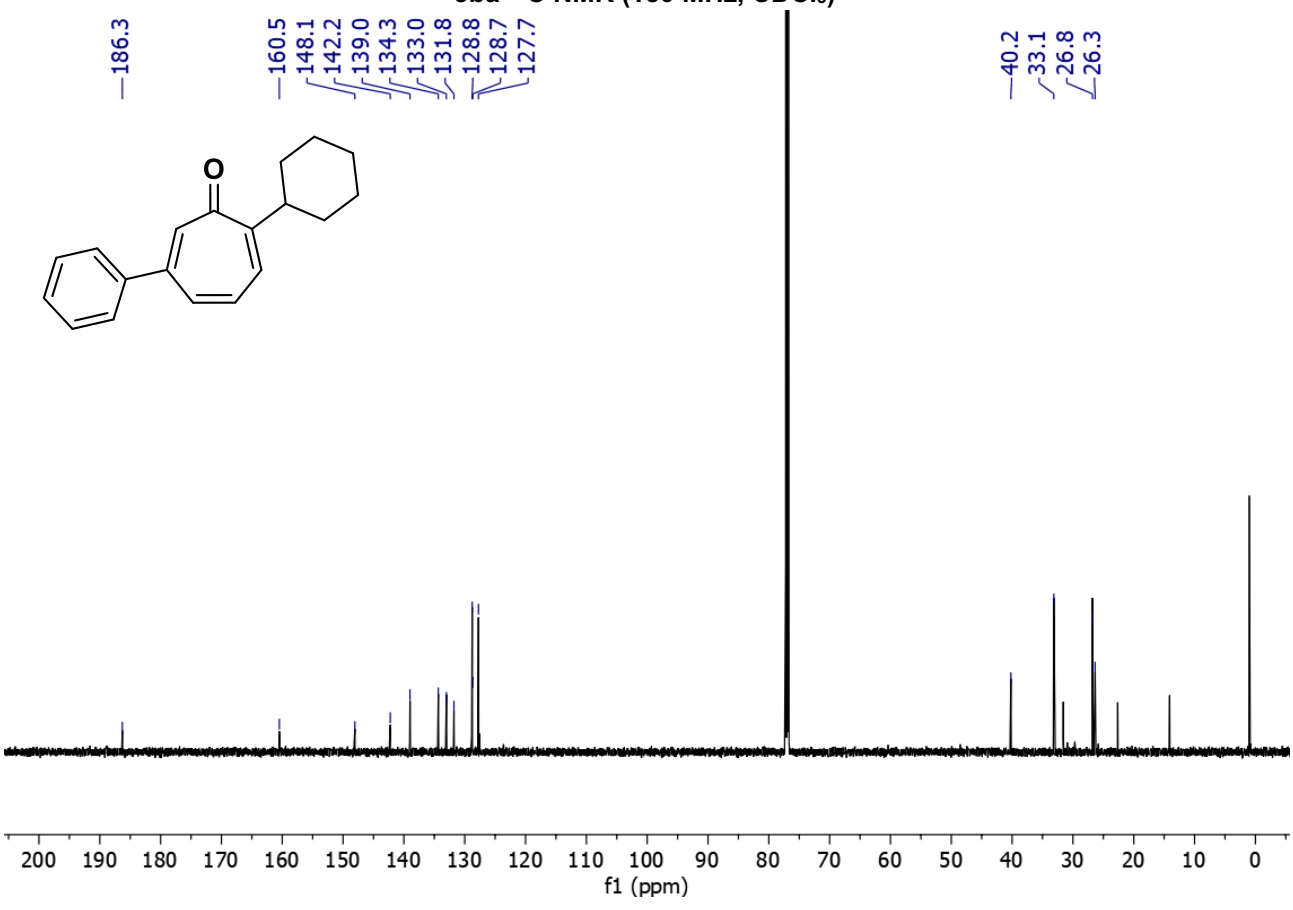


3ba ^{1}H NMR (600 MHz, $CDCl_3$)



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



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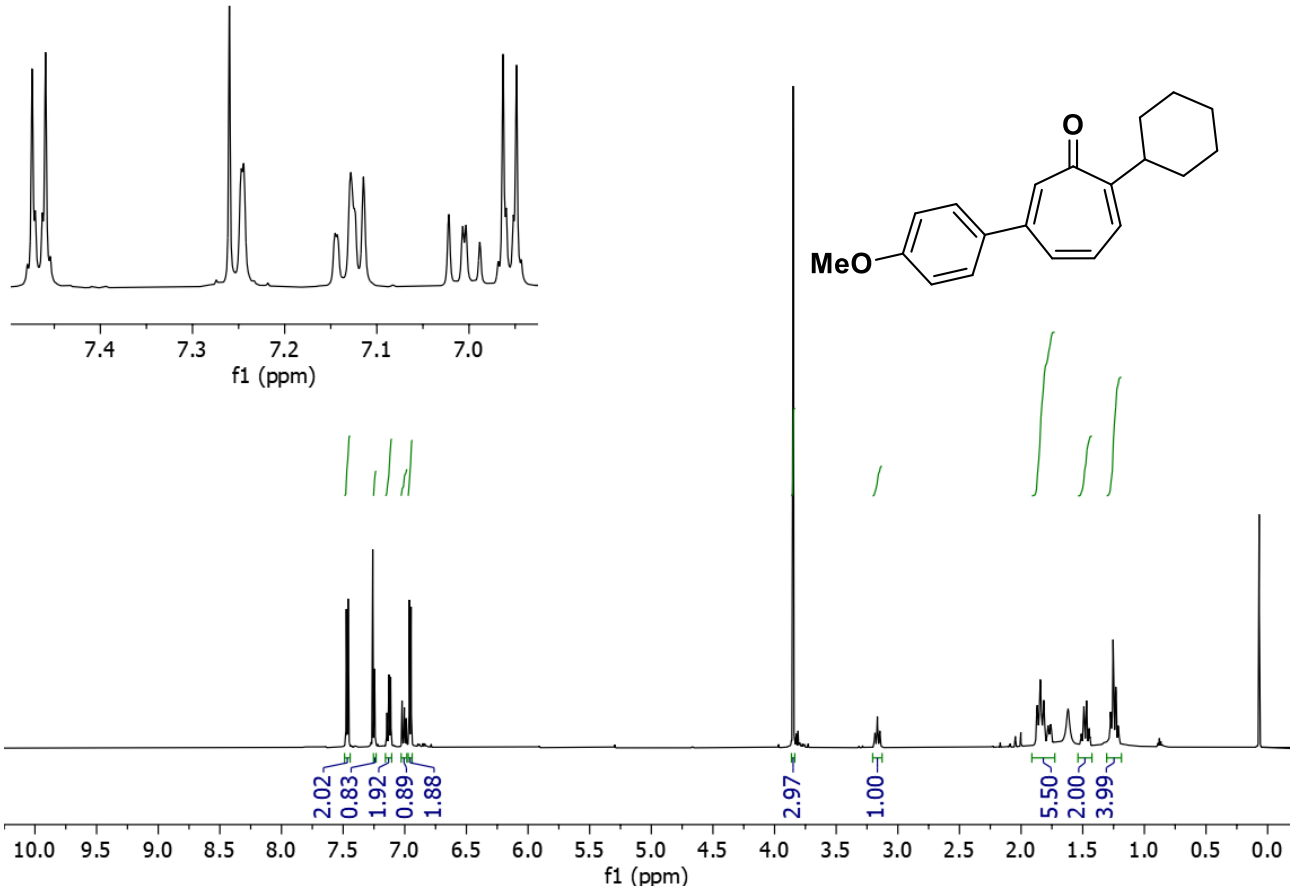
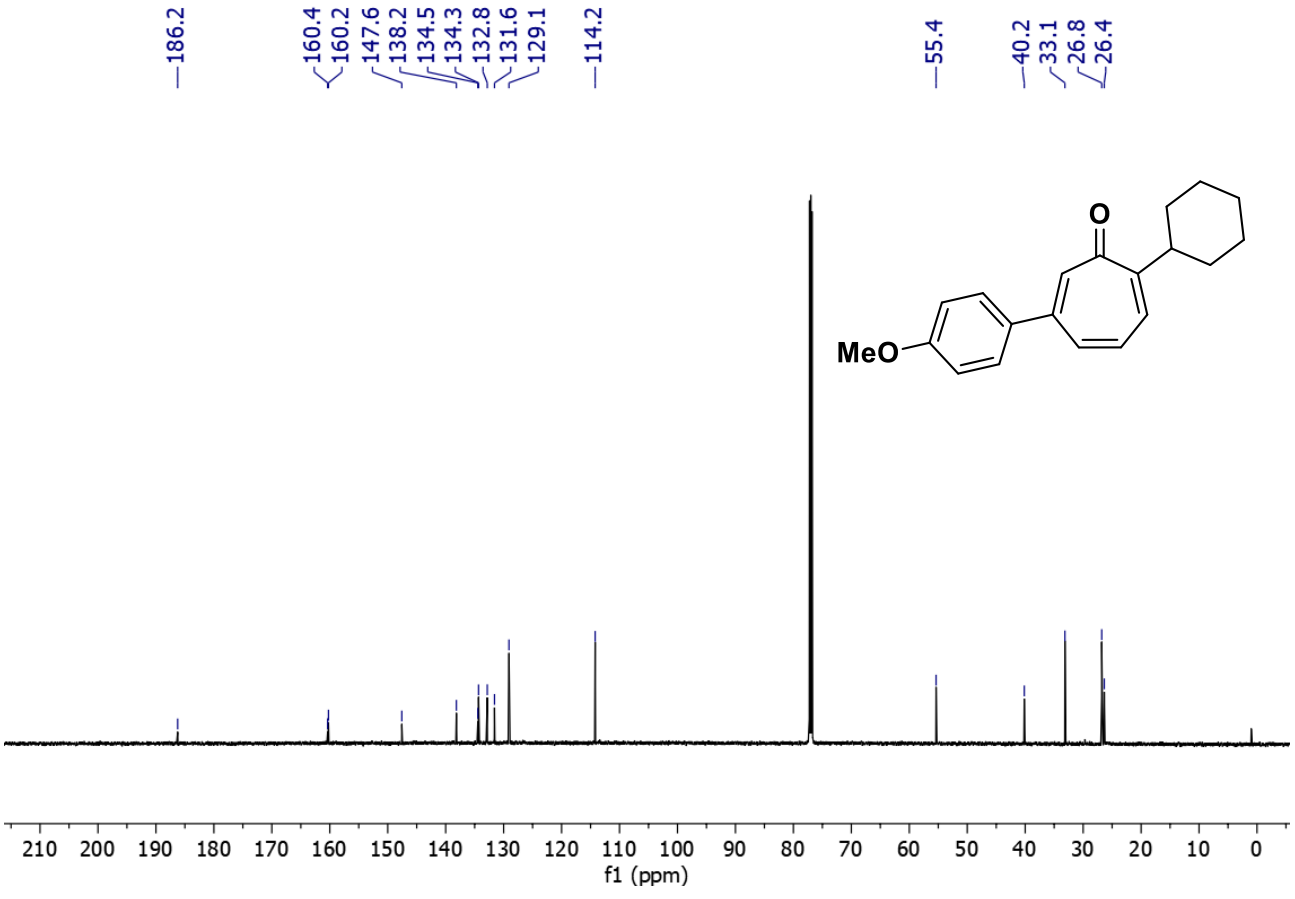
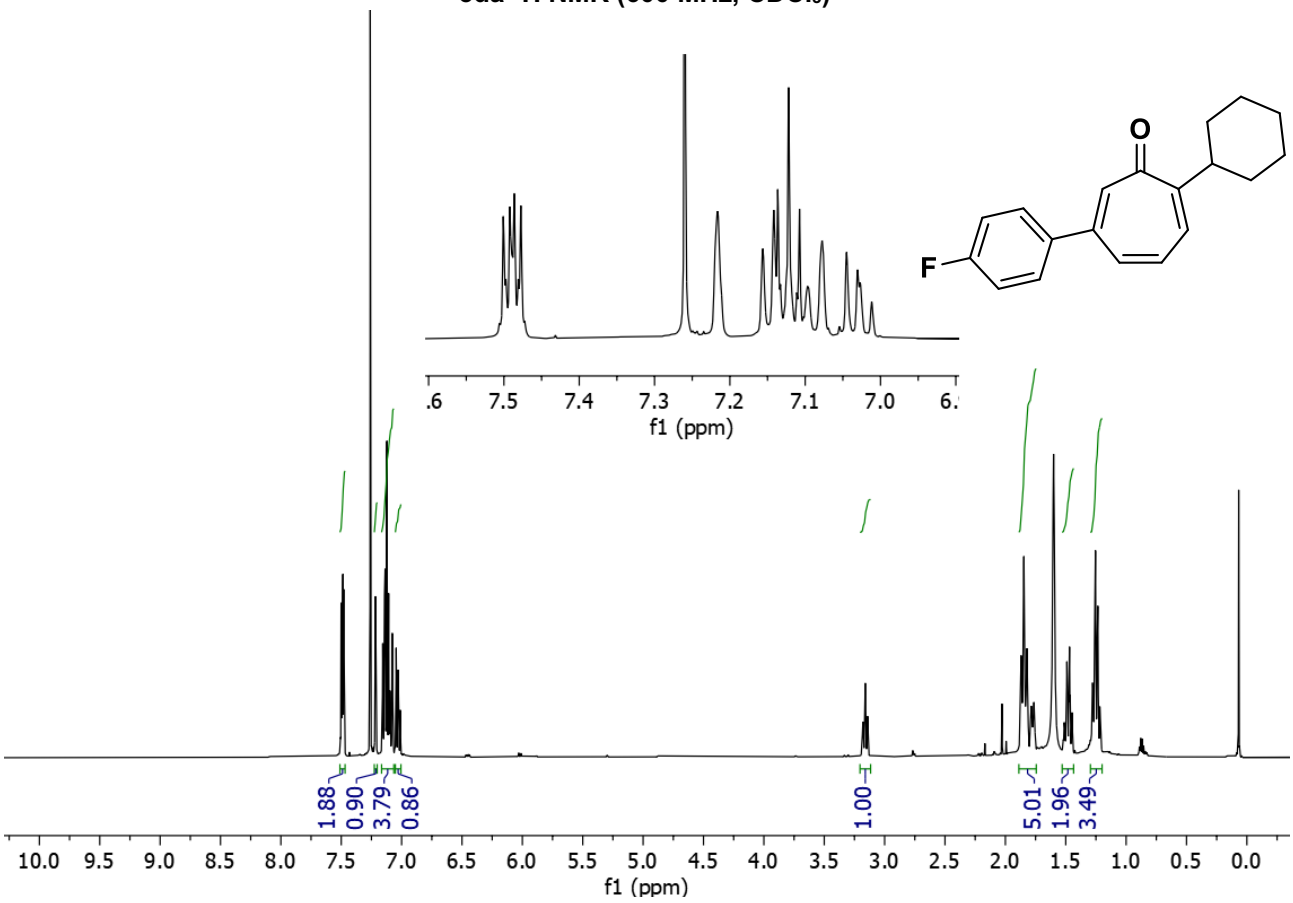


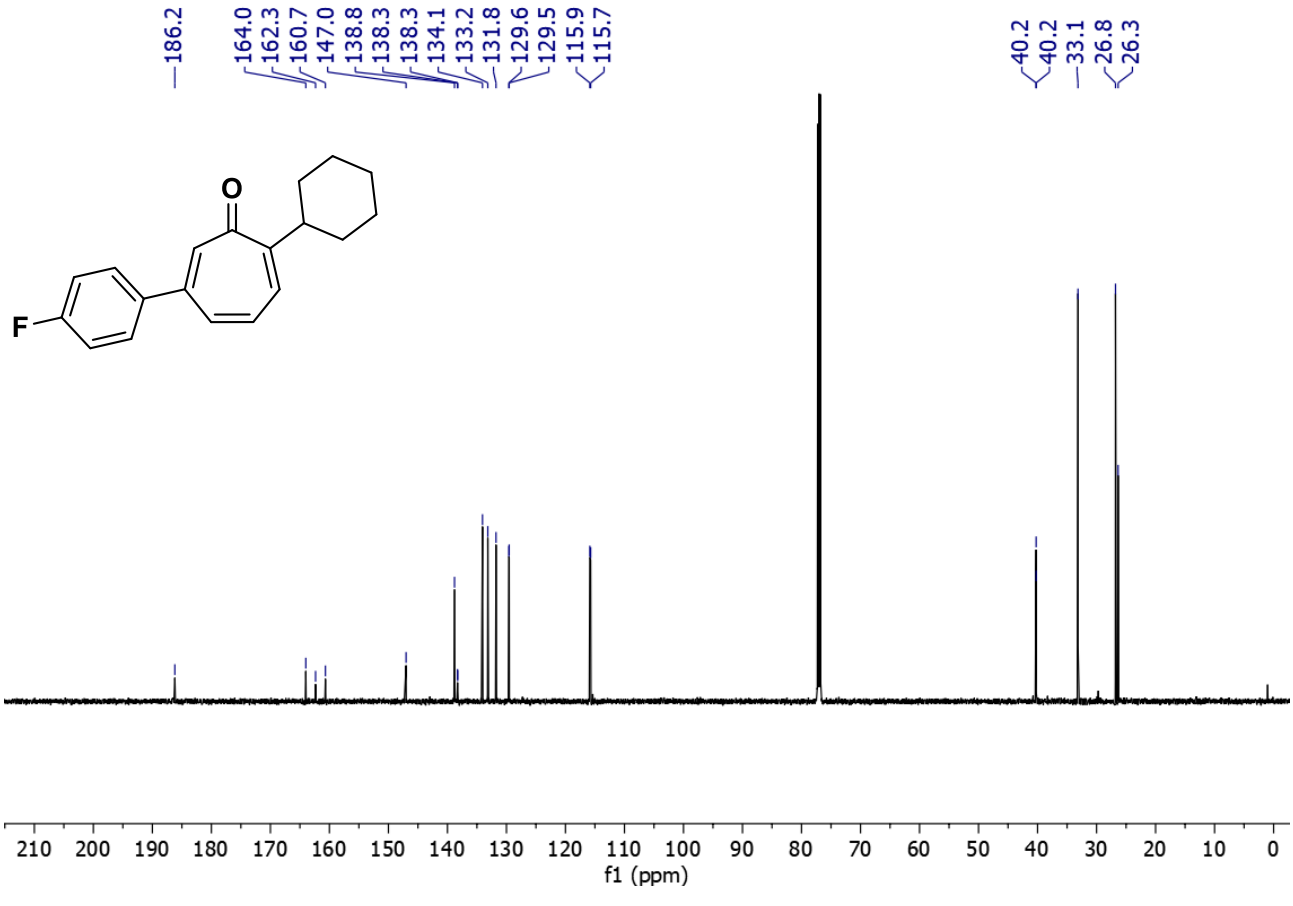
3ca ^{13}C NMR (150 MHz, $CDCl_3$)



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



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



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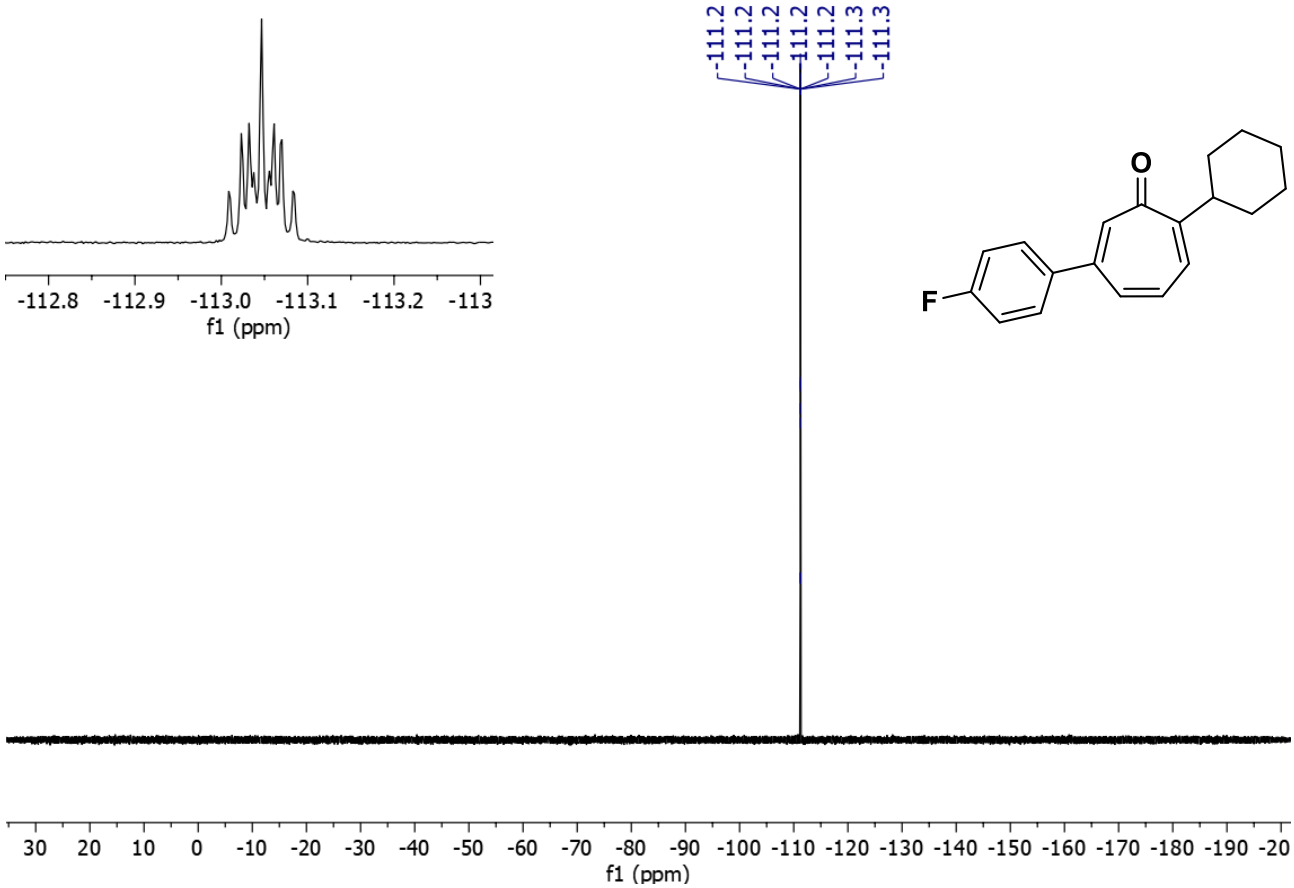
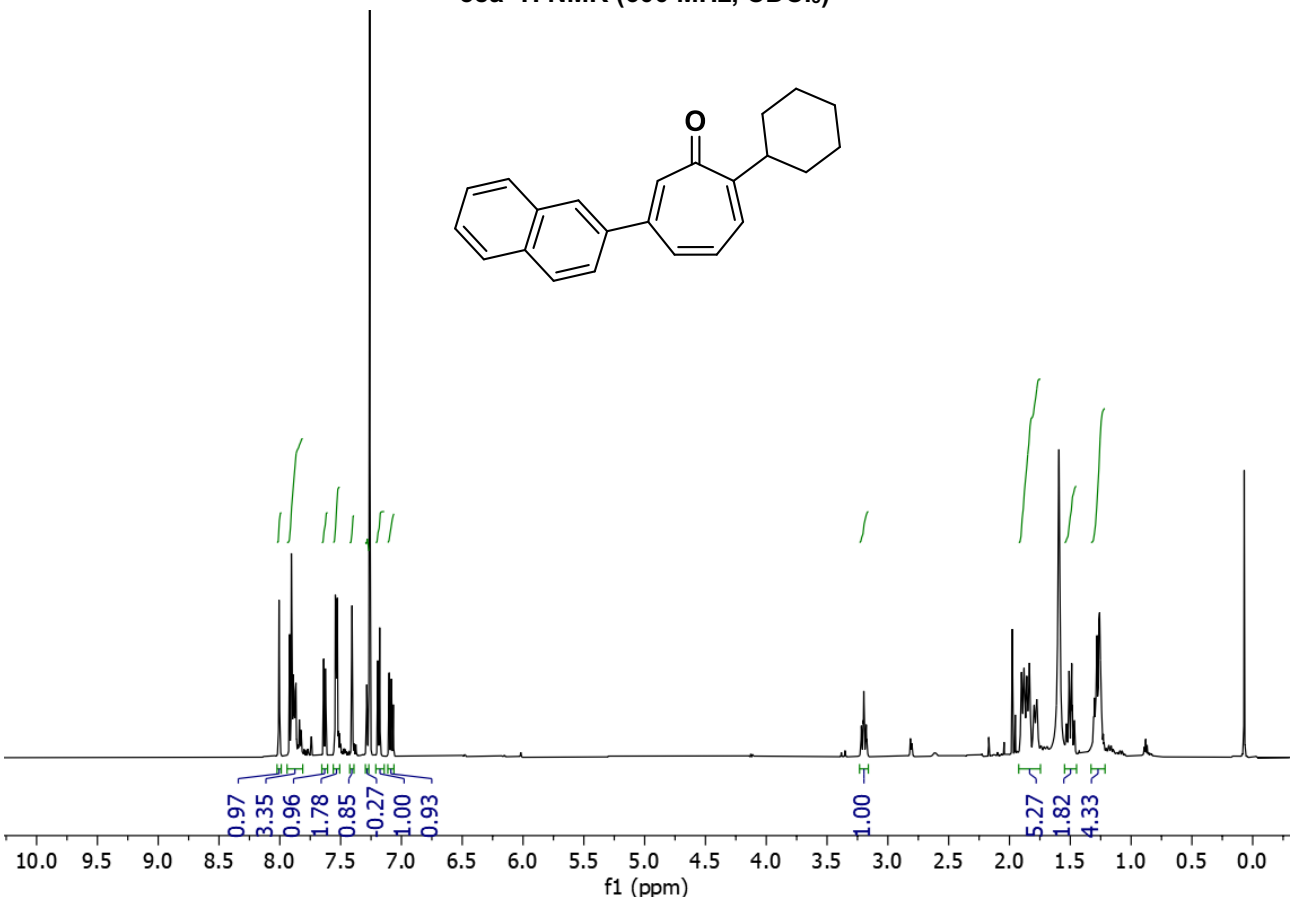
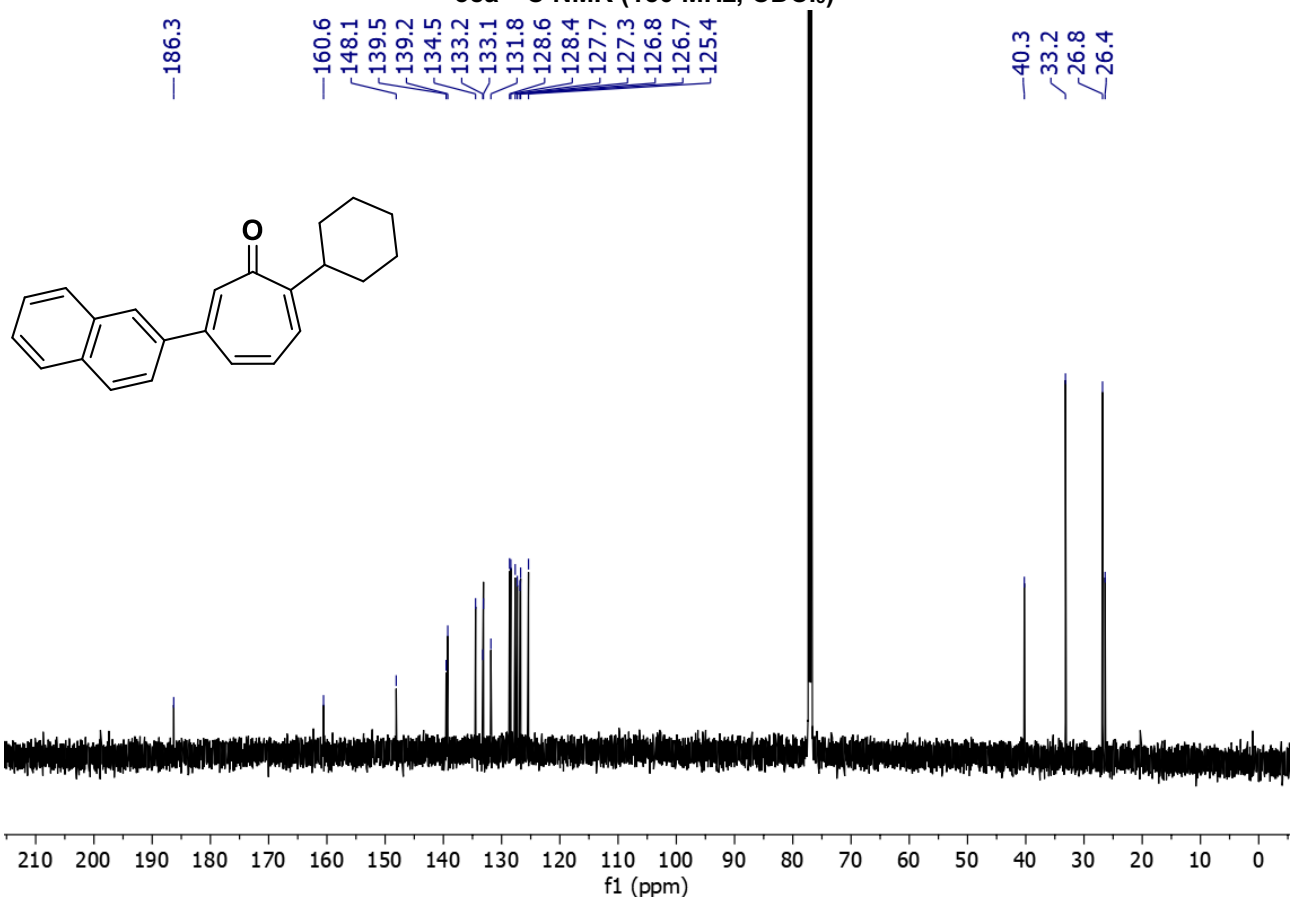


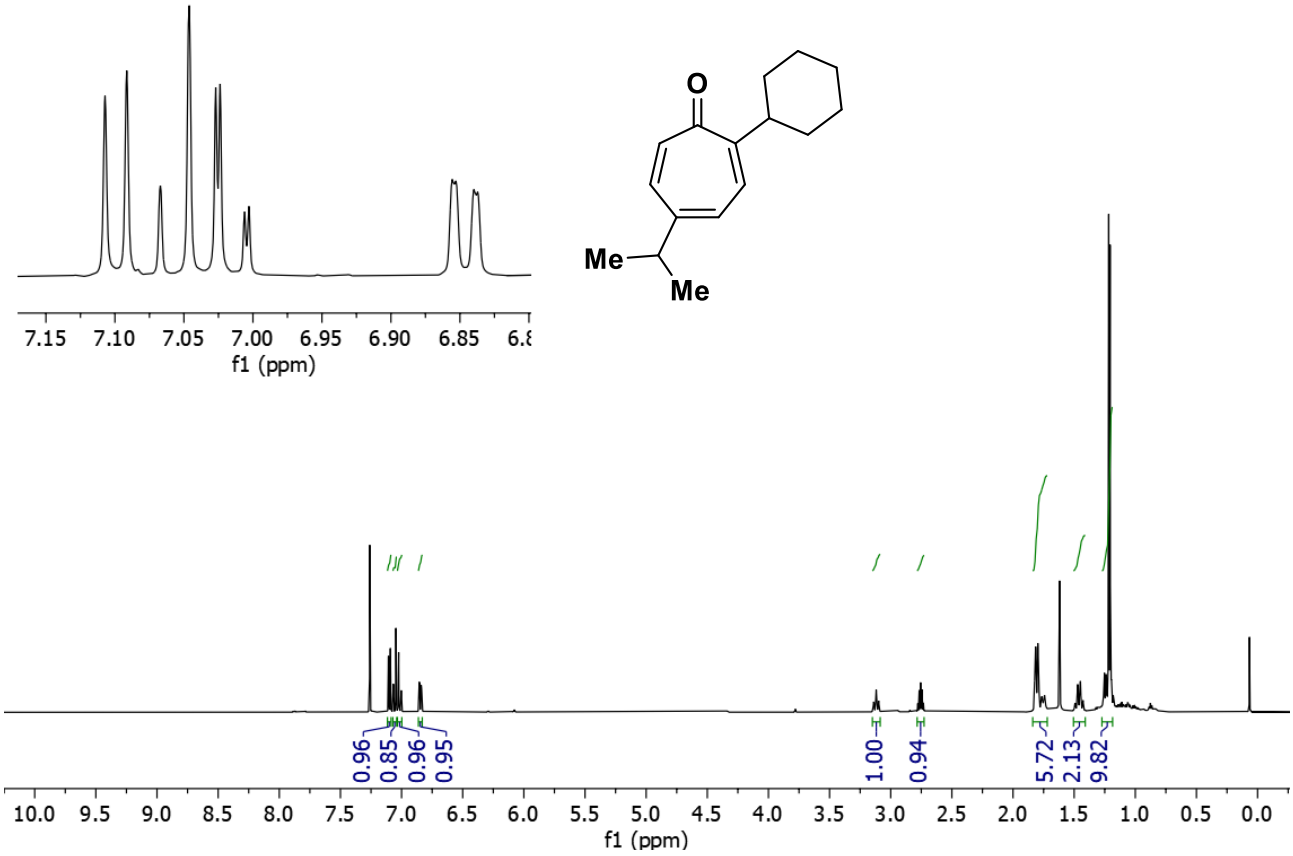
3ea ^{1}H NMR (600 MHz, $CDCl_3$)



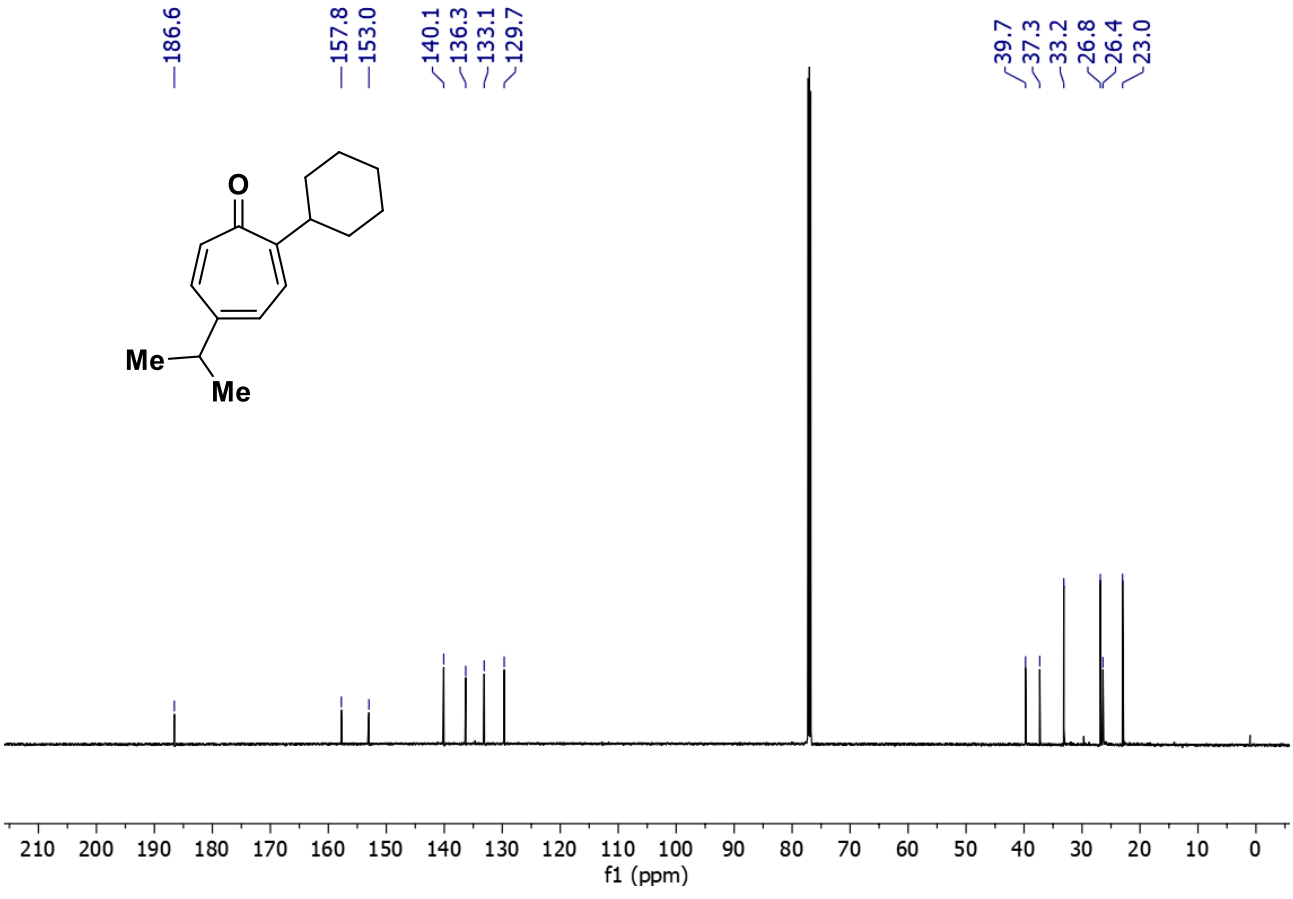
3ea ^{13}C NMR (150 MHz, $CDCl_3$)



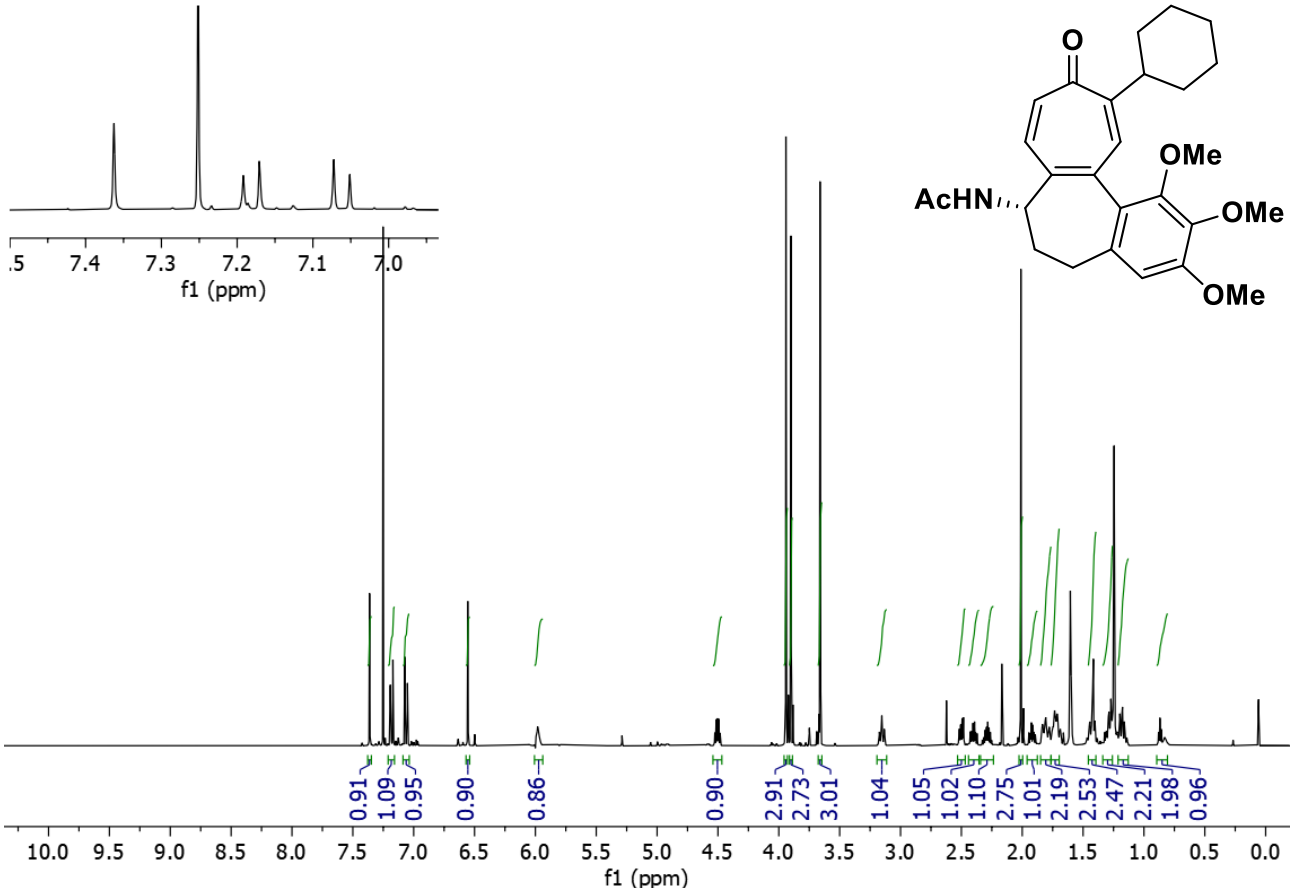
3fa ^{1}H NMR (600 MHz, $CDCl_3$)



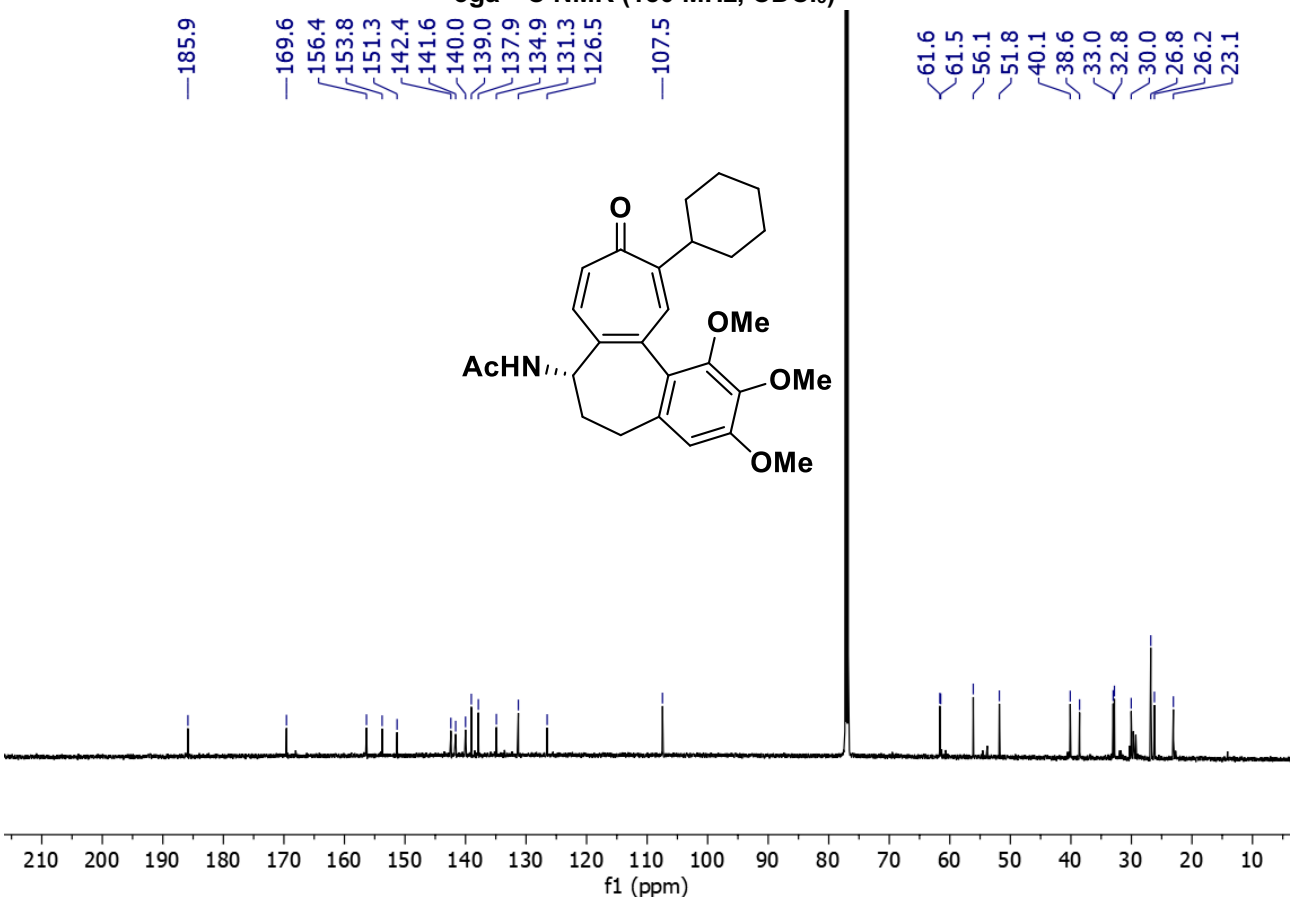
3fa ^{13}C NMR (150 MHz, $CDCl_3$)



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



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



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