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Electronic Supplementary Information

Free-amine-directed Ru(II)-catalyzed *peri*-selective C–H activation and annulation *via* ring-strain release

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1. General Information:

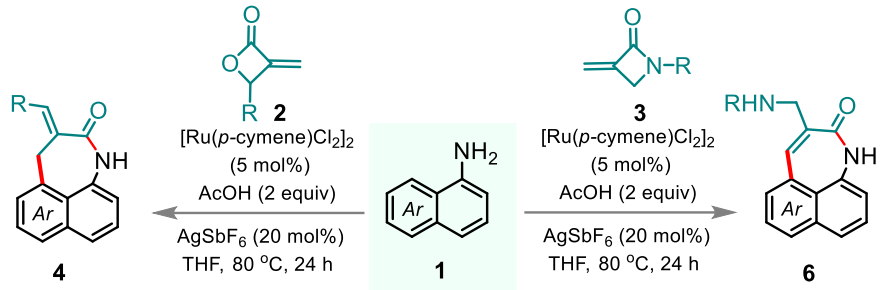
All non-aqueous reactions were carried out under in flame dried glassware and were stirred using a magnetic stir plate. All reactions were performed using commercial-grade solvent unless otherwise noted. Dry DMF and DMSO were purchased from commercial sources and stored under nitrogen. CH_3CN, DCE, toluene and CH_2Cl_2 were dried over calcium hydride. Dry THF and dry dioxane were prepared by distilling over sodium ketyl. All reactions were monitored by thin layer chromatography (TLC) on Merck 60 F 254 precoated silica plates and visualized using a UV lamp (366 or 254 nm) or by use of potassium permanganate, 5 g K_2CO_3/100 mL water. Products were isolated by column chromatography (Merck silica gel 100-200 μm).

^{13}C and ^{1}HNMR spectra were recorded on a Bruker 400 MHz or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak- $CDCl_3$ δ = 7.26 ppm for ^{1}H, δ = 77.16 for ^{13}C; DMSO-d_6 δ = 2.51 ppm for ^{1}H, δ = 39.5 ppm for ^{13}C; or calibrated to tetramethyl silane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad.

Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source. The crystal data were collected and integrated using a Bruker Axs kappa apex 2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

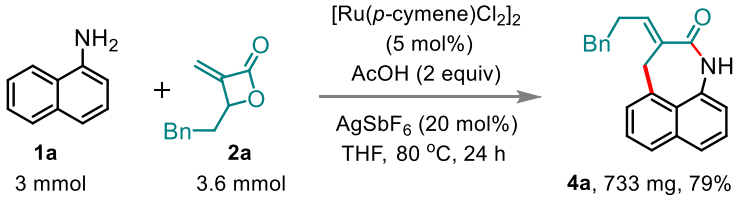
[Ru(*p*-cymene)Cl_2]$_2$ was received from Alfa Aesar company. α-Naphthylamine, aldehydes and inorganic bases were purchased from commercial sources and used without further purification. Alkylidene β-lactones (**2**) and β-lactams (**3**) were prepared following previous literature report (*Angew. Chem. Int. Ed.*, 2021, **60**, 4221; *Org. Lett.*, 2023, **25**, 8688; *Angew. Chem. Int. Ed.*, 2023, **62**, e202303795).

2. Typical Ruthenium(II)-catalyzed *peri*-functionalization of α-naphthylamines (1) with alkylidene β-lactones (2) *or* alkylidene β-lactams (3):



An oven-dried screw cap reaction tube (10 × 1.5 cm) was charged with the appropriate α-naphthylamine **1** (0.2 mmol, 1.0 equiv), corresponding alkylidene *β*-lactone **2** *or* alkylidene *β*-lactam **3** (1.2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol%), and AcOH (2.0 equiv). Silver hexafluoroantimonate (20 mol%) was weighed in a glass vial inside the glovebox and subsequently added to the tube. Dry THF (1.0 mL) was then added, the tube was quickly capped, and the reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The crude product was purified through silica-gel column chromatography (hexane/ethyl acetate as eluent) to get the desired naphtho-fused seven-membered lactam **4–6** in pure form.

3. Scale-up reaction with α-naphthylamine (1a) and alkylidene β-lactone (2a):

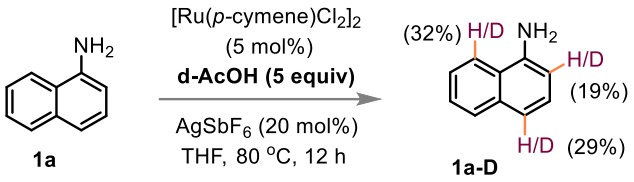


An oven-dried screw cap reaction tube was charged with the α-naphthylamine **1a** (3 mmol, 1.0 equiv), alkylidene *β*-lactone **2a** (1.2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol%), AcOH (2.0 equiv). Silver hexafluoroantimonate (20 mol%) was weighed in a glass vial inside the glovebox and subsequently added to the tube. Dry THF (15 mL) was then added, the tube was capped, and the reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The resulting residue was purified through silica-gel column chromatography (hexane/ethyl acetate as eluent) to get the desired naphtho-fused lactam **4a** (733 mg, 79% yield).

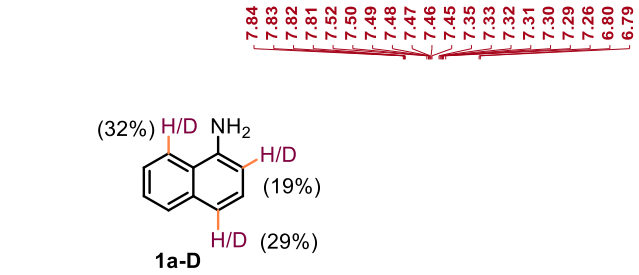
4. Synthesis of compound 7:

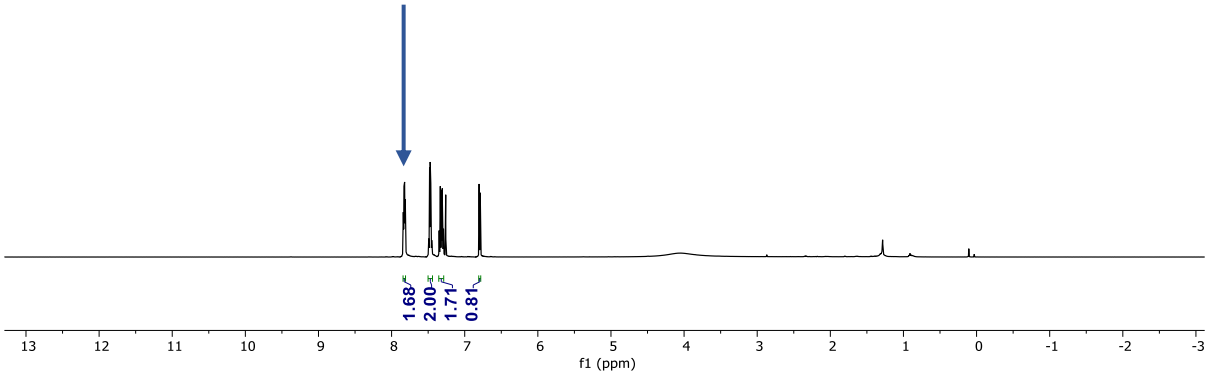
An oven-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with appropriate product **4** (0.20 mmol, 1.0 equiv), followed by the addition of DMSO (3.0 mL). The resulting mixture was stirred at 0 °C for 10 min and then NaH (1.2 equiv) was added, and the mixture was stirred further at rt until complete consumption of the starting material (monitored by TLC). After completion, the mixture was diluted with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford compounds **7** in pure form.

5. Deuterium Exchange Experiment of α naphthyl amine:

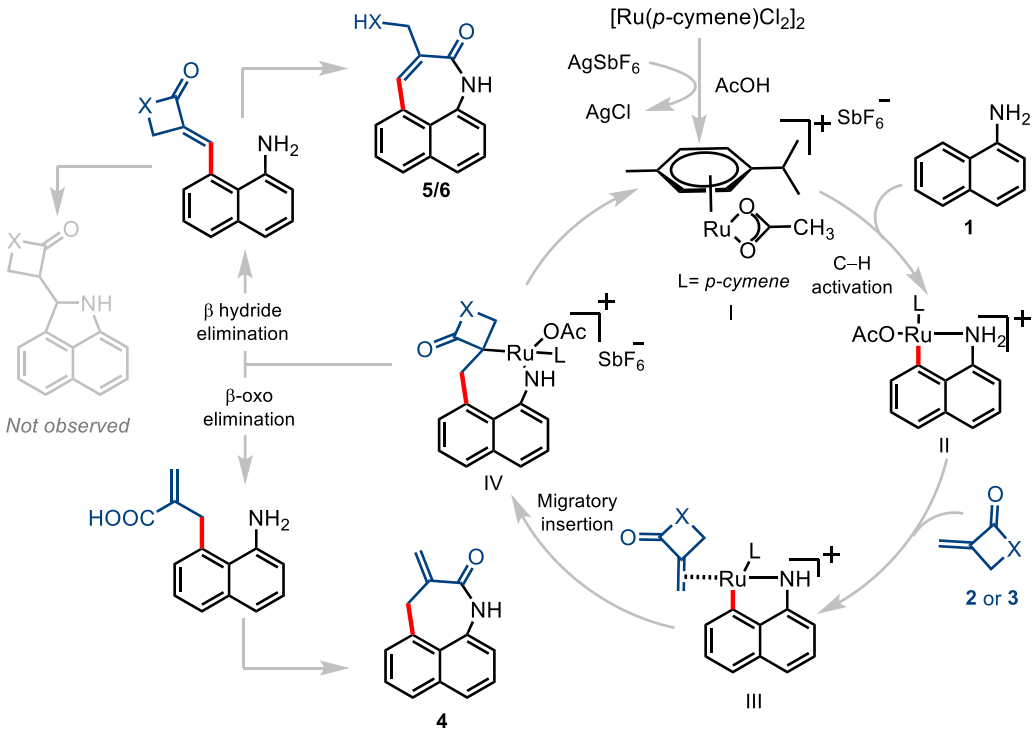


An oven-dried screw cap reaction tube was charged with the α-naphthylamine **1a** (0.2 mmol, 1.0 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol%), d_4-AcOH (5.0 equiv). Silver hexafluoroantimonate (20 mol%) was weighed in a glass vial inside the glovebox and subsequently added to the tube. Dry THF (1 mL) was then added, the tube was capped, and the reaction mixture was stirred at 80 °C for 12 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the volatiles were removed under reduced pressure. Subsequent purification through silica-gel column chromatography (hexane/ethyl acetate as eluent) furnished the **1a-D**. The H/D-scrambling was observed through ^{1}H NMR spectroscopy.





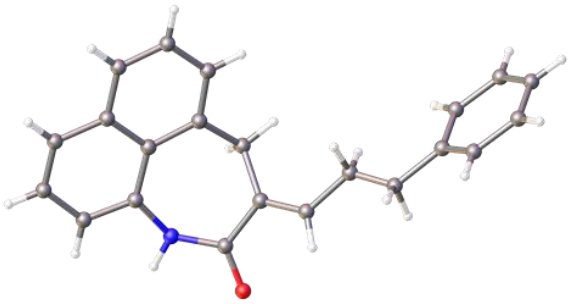
Catalytic Cycle:



6. X-ray crystal data of compounds 4a and 6e

Crystallographic Experimental Section: Crystals of compound **4a** were obtained through a slow evaporation technique at room temperature from hexane/DCM solvent mixture.

X-ray crystal data of compound 4a: (CCDC 2521104, Ellipsoid Probability 50%)

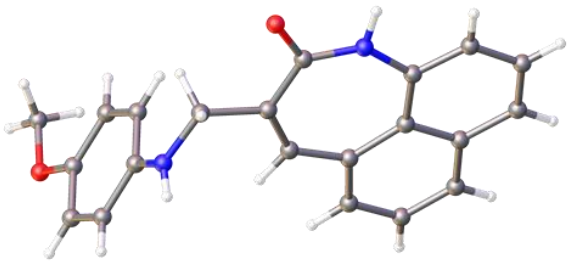


Identification code	**4a**
Chemical formula	$C_{22}HNO$
Formula weight	295.24 g/mol
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal size	0.160 x 0.250 x 0.320 mm
Crystal habit	clear light pink Block
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 8.8979(4) Å α = 97.870(2)° b = 9.6890(5) Å β = 91.598(2)° c = 10.6306(5) Å γ = 111.305(2)°
Volume	842.81(7) $Å^3$
Z	2
Density (calculated)	1.163 g/cm^3
Absorption coefficient	0.073 mm^{-1}
F(000)	296
Theta range for data collection	1.94 to 25.00°
Index ranges	-10<=h<=10, -11<=k<=11, -12<=l<=11
Reflections collected	10106
Independent reflections	2982 [R(int) = 0.0200]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.9880 and 0.9770
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	2982 / 47 / 245
Goodness-of-fit on F2	1.038

Final R indices	2214 data; R1 = 0.0523, wR2 = 0.1380 I>2σ(I)
	all data R1 = 0.0708, wR2 = 0.1538
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0749P)^2+0.2290P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.212 and -0.276 eÅ^{-3}

Crystallographic Experimental Section: Crystals of compound **6e** were obtained through a slow evaporation technique at room temperature from hexane/DCM solvent mixture.

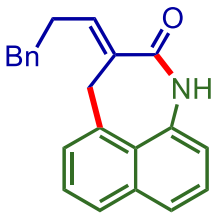
X-ray crystal data of compound 6e: (CCDC 2520804, Ellipsoid Probability 50%)



Identification code	**6e**
Empirical formula	C21 H18 N2 O2
Formula weight	330.37
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 5.4675(13) A alpha = 90 deg.
	b = 13.060(3) A beta = 95.515(4) deg.
	c = 23.252(6) A gamma = 90 deg.
Volume	1652.7(7) A^3
Z, Calculated density	4, 1.328 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	696
Crystal size	0.594 x 0.381 x 0.265 mm
Theta range for data collection	2.351 to 25.254 deg.
Limiting indices	-6<=h<=6, -15<=k<=15, -27<=l<=27
Reflections collected / unique	23859 / 2997 [R(int) = 0.0708]
Completeness to theta = 25.242	99.9 %

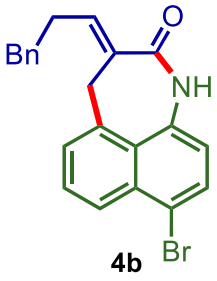
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9108
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2997 / 0 / 222
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1246
R indices (all data)	R1 = 0.1033, wR2 = 0.1515
Extinction coefficient	0.0092(17)
Largest diff. peak and hole	0.282 and -0.244 e.A^-3

7. NMR spectroscopic data of synthesized compounds



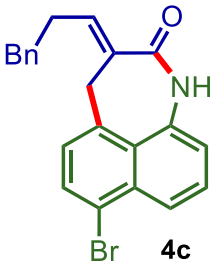
4a

(E)-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4a): White solid; Eluent: 15–20% EtOAc in Hexane; yield = 88% (55 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.31 – 7.28 (m, 3H), 7.23 – 7.19 (m, 3H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 3.95 (s, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 141.1, 138.5, 136.1, 135.9, 134.7, 133.2, 128.6, 128.4, 127.9, 126.3 (2×C), 126.1, 125.6, 124.8, 123.4, 116.6, 35.3, 34.8, 29.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{20}NO^+$ 314.1539 Found 314.1536.



4b

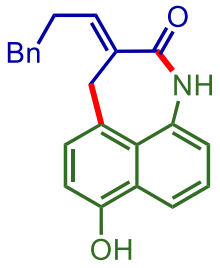
(E)-8-bromo-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4b): Sticky solid; Eluent: 15–20% EtOAc in Hexane; yield = 75% (58 mg); **^{1}HNMR** (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.19 (d, *J* = 9.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.48 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.12 (m, 3H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 2H), 2.71 (t, *J* = 8.1 Hz, 2H), 2.63 – 2.57 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 141.0, 139.2, 136.0, 135.3, 133.9, 132.7, 130.2, 128.6, 128.4, 127.7, 127.3, 126.7, 126.3, 124.7, 117.9, 116.8, 35.2, 34.7, 29.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{19}BrNO^+$ 392.0645 Found 392.0640.



4c

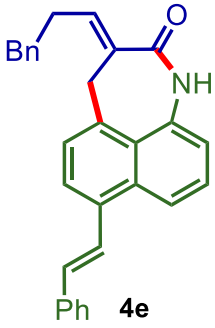
(E)-7-bromo-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4c): Sticky solid ; Eluent: 20–25% EtOAc in Hexane; yield = 87% (68 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 1H), 8.00 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.24 – 7.20 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.12 (d, *J* = 9.7 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.61 (t, *J* = 7.4 Hz, 1H), 3.84 (s, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.61 – 2.57 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 140.9, 139.2, 136.3, 134.9, 134.1, 132.5, 130.6, 128.6, 128.4,

127.4, 126.3, 125.7, 124.5, 124.2, 122.2, 117.6, 35.1, 34.7, 30.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{19}BrNO^+$ 392.0645 Found 392.0638.



4d

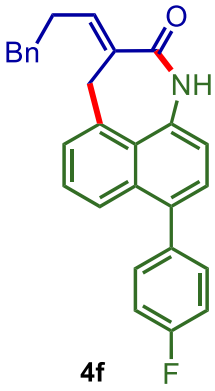
(E)-7-hydroxy-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4d): Brown solid; Eluent: 20–25% EtOAc in Hexane; yield = 80% (53 mg); **^{1}H NMR** (400 MHz, DMSO) δ 10.00 (s, 1H), 9.71 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 4H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.25 (t, *J* = 7.2 Hz, 1H), 3.75 (s, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.54 (d, *J* = 7.1 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO) δ 172.8, 152.0, 141.0, 136.2, 135.6, 134.4, 128.2 (2×C), 127.0, 125.8, 125.4, 124.8, 124.6, 123.7, 117.5, 116.7, 107.8, 34.0 (2×C), 28.5 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{20}NO_2^+$ 330.1489 Found 330.1489.



4e

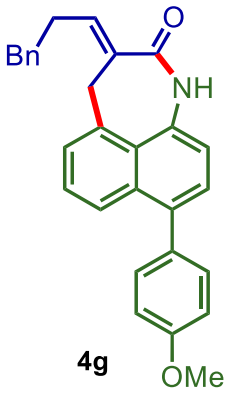
(E)-3-(3-phenylpropylidene)-7-((E)-styryl)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4e): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 79% (66 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 – 8.01 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 15.9 Hz, 1H), 7.62 – 7.59 (m, 3H), 7.44 – 7.39 (m, 3H), 7.33 – 7.30 (m, 1H), 7.24 (dd, *J* = 12.2, 5.4 Hz, 3H), 7.19 – 7.16 (m, 3H), 7.09 – 7.02 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 3.92 (s, 2H), 2.73 (t, *J* = 7.8 Hz, 2H), 2.64 – 2.60 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.0, 141.1, 138.6, 137.6, 136.4, 135.0, 134.6, 134.1, 132.9, 132.2, 128.9, 128.6, 128.5, 128.0, 126.8, 126.5, 126.3, 126.2, 125.6, 124.6, 123.6, 120.6, 116.8, 35.5, 34.8, 29.9 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{30}H_{25}NNaO^+$ 438.1828 Found 438.1843.

(E)-8-(4-fluorophenyl)-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4f): Sticky solid; Eluent: 20–25% EtOAc in Hexane; yield = 78% (63 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 9.9 Hz, 1H), 7.37 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.26 –



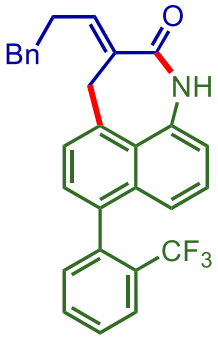
4f

7.24 (m, 3H), 7.20 – 7.14 (m, 5H), 7.01 (d, *J* = 9.9 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 3.94 (s, 2H), 2.73 (dd, *J* = 9.5, 6.7 Hz, 2H), 2.61 (q, *J* = 8.2 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 162.4 (d, *J* = 246.3 Hz), 141.1, 138.8, 136.8 (d, *J* = 3.6 Hz), 135.8, 135.5, 135.0, 134.3, 133.0, 131.9 (d, *J* = 7.9 Hz), 128.6, 128.5, 127.4, 126.5, 126.3, 125.90, 125.85, 123.6, 115.9, 115.4 (d, *J* = 21.4 Hz), 35.5, 34.8, 30.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.23 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{28}H_{23}FNO^+$ 408.1758 Found 408.1759.



4g

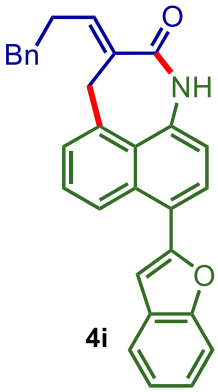
(E)-8-(4-methoxyphenyl)-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4g): Sticky solid; Eluent: 20–25% EtOAc in Hexane; yield = 84% (70 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.80 (d, *J* = 9.9 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 3H), 7.24 (t, *J* = 4.6 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 3.95 (s, 2H), 3.89 (s, 3H), 2.73 (dd, *J* = 9.6, 6.7 Hz, 2H), 2.65 – 2.59 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 159.1, 141.2, 138.5, 136.6, 135.2, 134.8, 134.4, 133.2, 133.1, 131.3, 128.6, 128.4, 127.3, 126.3, 126.2, 126.1, 125.7, 123.6, 116.1, 113.9, 55.5, 35.6, 34.8, 29.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{29}H_{26}NO_2^+$ 420.1958 Found 420.1959.



4h

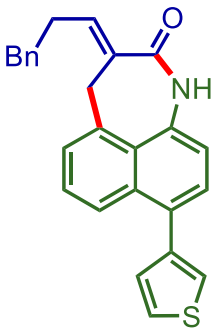
(E)-3-(3-phenylpropylidene)-7-(2-(trifluoromethyl)phenyl)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4h): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 70% (64 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.30 – 7.26 (m, 4H), 7.24 – 7.17 (m, 4H), 7.04 (d, *J* = 9.7 Hz, 1H), 7.00 – 6.98 (m, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.01 – 3.93 (m, 2H), 2.78 – 2.72 (m, 2H), 2.70 – 2.62 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 141.2, 139.6, 138.9, 136.3, 136.0, 135.1, 134.9, 132.9, 132.8, 131.4, 129.8 (q, *J* = 30.0 Hz), 128.6, 128.5, 128.0, 127.7, 126.4, 126.3, 126.0, 124.6, 123.3, 123.2, 121.4 (q, *J* = 274.4 Hz), 116.5, 35.4, 34.8, 30.0 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.54 ppm;

HRMS (ESI) m/z: [M+Na]+ Calcd. For $C_{29}H_{22}F_3NNaO^+$ 480.1546 Found 480.1571.



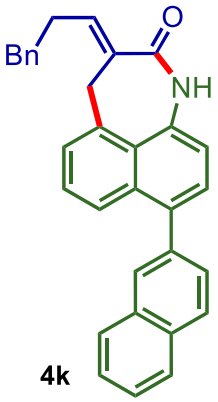
4i

(E)-8-(benzofuran-2-yl)-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4i): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 71% (61 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.35 – 7.32 (m, 1H), 7.30 – 7.27 (m, 3H), 7.24 (d, 1H), 7.19 – 7.16 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 3.94 (s, 2H), 2.73 (t, *J* = 7.8 Hz, 2H), 2.65 – 2.60 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6, 155.4, 155.0, 141.0, 139.2, 136.8, 135.1, 133.6, 132.6, 129.1, 128.6, 128.4, 128.0, 127.3, 126.3, 126.1, 125.4, 125.0, 124.5, 123.6, 123.1, 121.0, 115.9, 111.4, 106.1, 35.4, 34.7, 30.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{30}H_{24}NO_2^+$ 430.1802 Found 430.1802.



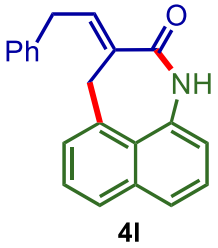
4j

(E)-3-(3-phenylpropylidene)-8-(thiophen-3-yl)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4j): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 83% (65 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.32 – 7.25 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.18 – 7.16 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 3H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.58 (t, *J* = 7.3 Hz, 1H), 3.88 (s, 2H), 2.66 (t, *J* = 7.9 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 141.2, 141.1, 138.6, 135.5, 134.9, 134.4, 133.0, 131.6, 129.8, 128.6, 128.4, 127.4, 126.5, 126.3, 125.9 (2×C), 125.5, 123.7, 123.6, 116.1, 35.5, 34.8, 29.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{26}H_{22}NOS^+$ 396.1417 Found 396.1413.



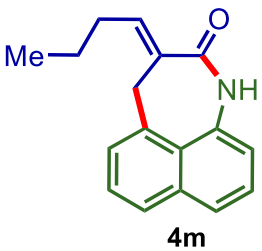
4k

(E)-8-(naphthalen-2-yl)-3-(3-phenylpropylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4k): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 81% (71 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 5.7 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 3.97 (s, 2H), 2.74 (dd, *J* = 9.3, 6.3 Hz, 2H), 2.63 (q, *J* = 7.6 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 141.1, 138.7, 138.4, 136.8, 135.5, 135.0, 134.3, 133.5, 133.1, 132.7, 128.9, 128.6 (2×C), 128.5, 128.2, 127.9 (2×C), 127.6, 126.53, 126.46, 126.31, 126.27, 126.2, 125.9, 123.6, 116.1, 35.6, 34.8, 30.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{32}H_{26}NO^+$ 440.2009 Found 440.2009.



4l

(E)-3-(2-phenylethylidene)-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4l): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 72% (43 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.19 (dd, *J* = 17.6, 7.2 Hz, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 4.07 (s, 2H), 3.63 (d, *J* = 7.6 Hz, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 138.5, 137.8, 136.2, 135.8, 134.7, 133.2, 128.8, 128.7, 128.0, 126.6, 126.4, 126.1, 125.8, 124.9, 123.4, 116.5, 35.4, 34.0 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{21}H_{17}NNaO^+$ 322.1202 Found 322.1215.

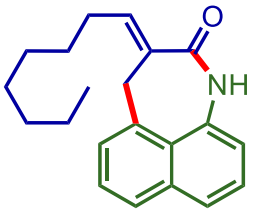


4m

(E)-3-butylidene-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one (4m); Colourless liquid, Eluent: 20–25% EtOAc in Hexane; yield = 75% (37 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.71 (d, *J* = 9.7 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.26 (s, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 3.95 (s, 2H), 2.26 (q, *J* = 7.4 Hz, 2H), 1.44 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.2, 140.0, 136.2, 136.0, 135.0, 132.7, 127.8, 126.3, 126.1, 125.6, 124.7, 123.4, 116.4, 35.3, 29.9,

21.9, 14.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{18}NO^+$ 252.1383 Found 252.1379.

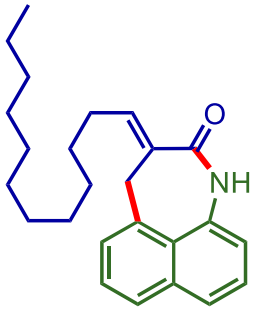
(E)-3-octylidene-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one



4n

(4n): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 88% (54 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 17.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 9.3 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 3.95 (s, 2H), 2.27 (q, *J* = 7.5 Hz, 2H), 1.40 (q, *J* = 7.4 Hz, 2H), 1.27 – 1.19 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 140.2, 136.1, 136.0, 135.0, 132.5, 127.8, 126.3, 126.1, 125.6, 124.7, 123.4, 116.5, 35.3, 31.8, 29.5, 29.2, 28.6, 27.9, 22.7, 14.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{26}NO^+$ 308.2009 Found 308.2005

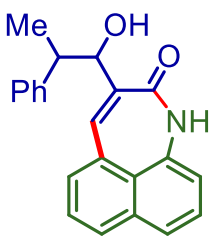
(E)-3-dodecylidene-3,4-dihydronaphtho[1,8-bc]azepin-2(1H)-one



4o

(4o): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 87% (63 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 – 8.52 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.08 – 7.06 (m, 1H), 6.57 (t, *J* = 7.5 Hz, 2H), 3.95 (s, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 1.42 – 1.37 (m, 2H), 1.29 – 1.21 (m, 16H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 140.3, 136.3, 136.2, 135.1, 132.7, 127.9, 126.3, 126.2, 125.7, 124.8, 123.6, 116.6, 35.4, 32.1, 29.8 (2×C), 29.7, 29.6 (2×C), 29.5, 28.0, 22.9, 14.3 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{25}H_{33}NNaO^+$ 386.2454 Found 386.2470.

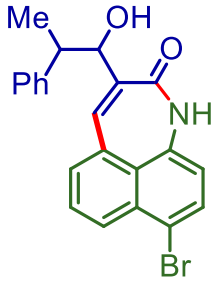
3-(1-hydroxy-2-phenylpropyl)naphtho[1,8-bc]azepin-2(1H)-one



5a

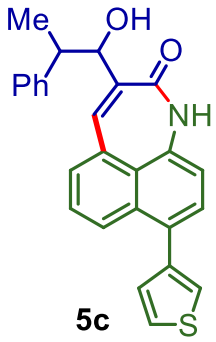
(5a): Orange solid; Eluent: 20–25% EtOAc in Hexane; yield = 72% (47 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.25 – 7.18 (m, 3H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 4.46 (t, *J* = 7.5 Hz, 1H), 3.44 (d, *J* = 8.1 Hz, 1H), 3.39 – 3.34 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 144.6,

143.4, 136.6, 136.5, 132.4, 131.5, 131.1, 130.9, 128.5, 127.9, 127.1, 126.5, 126.4, 125.3, 123.7, 114.8, 80.7, 45.2, 15.9 ppm. **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{22}H_{19}NNaO_2^+$ 352.1308 Found 352.1301.



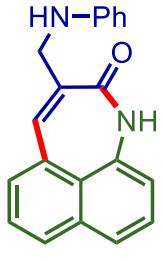
5b

8-bromo-3-(1-hydroxy-2-phenylpropyl)naphtho[1,8-bc]azepin-2(1H)-one (5b): Orange solid; Eluent: 20–25% EtOAc in Hexane; yield = 75% (61 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.88 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.24 (m, 4H), 7.16 – 7.12 (m, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 6.66 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.48 (t, *J* = 7.4 Hz, 1H), 3.37 – 3.32 (m, 2H), 1.42 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.0, 144.4, 142.9, 136.5, 134.0, 133.3, 131.8, 131.5, 131.2, 130.3, 128.6, 127.9, 127.8, 126.7, 126.6, 116.7, 115.1, 80.3, 45.2, 15.8 ppm.; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{19}BrNO_2^+$ 408.0594 Found 408.0600.



5c

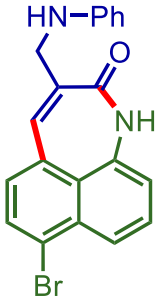
3-(1-hydroxy-2-phenylpropyl)-8-(thiophen-3-yl)naphtho[1,8 bc] azepin-2(1H)-one (5c): Orange solid; Eluent: 20–25% EtOAc in Hexane; yield = 71% (58 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.60 (s, 1H), 7.43 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.29 – 7.27 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.18 (m, 1H), 7.16 – 7.14 (m, 2H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 4.44 (t, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 8.3 Hz, 1H), 3.36 (q, *J* = 7.1 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.3, 144.5, 143.7, 140.7, 136.1, 134.7, 132.7, 131.6, 130.8, 130.6, 129.3, 129.0, 128.6, 128.4, 128.0, 126.6 (2×C), 125.8, 125.7, 123.6, 114.4, 80.9, 45.3, 16.1 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{26}H_{21}NNaO_2S^+$ 434.1185 Found 434.1197.



6a

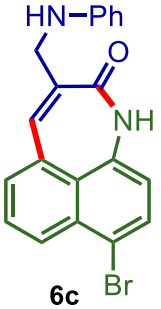
3-((phenylamino)methyl)naphtho[1,8-bc]azepin-2(1H)-one (6a): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 82% (49 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.8 Hz,

2H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.01 (s, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 13.2, 7.8 Hz, 3H), 4.18 (s, 2H) ppm (one amine NH is missing); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 147.9, 142.0, 136.9, 136.6, 132.3, 131.9, 131.2, 129.4, 128.5, 127.2, 126.5, 125.2, 123.7, 117.9, 114.7, 113.4, 47.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{20}H_{17}N_2O^+$ 301.1335 Found 301.1340.



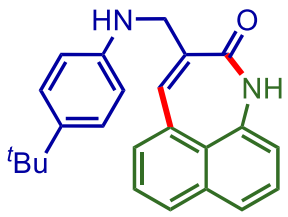
6b

7-bromo-3-((phenylamino)methyl)naphtho[1,8-bc]azepin-2(1H)-one (6b): Brown solid; Eluent: 20–25% EtOAc in Hexane; yield = 76% (57 mg); **^{1}H NMR** (500 MHz, DMSO) δ 10.14 (s, 1H), 7.73 – 7.69 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.04 (m, 3H), 7.00 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.54 (t, *J* = 7.3 Hz, 1H), 5.97 (t, *J* = 6.2 Hz, 1H), 4.01 (d, *J* = 5.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO) δ 165.3, 148.7, 139.2, 138.4, 133.8, 132.1, 131.6, 131.3, 130.5, 129.3 (2×C), 125.9, 124.4, 121.5, 116.6, 116.5, 112.7, 45.6 ppm. **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{20}H_{16}BrN_2O^+$ 379.0441 Found 379.0444.



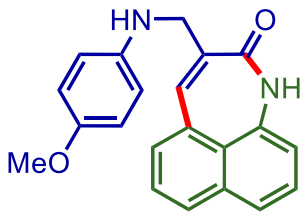
6c

8-bromo-3-((phenylamino)methyl)naphtho[1,8-bc]azepin-2(1H)-one (6c): Brown solid; Eluent: 20–25% EtOAc in Hexane; yield = 70% (53 mg); **^{1}H NMR** (500 MHz, DMSO) δ 10.14 (s, 1H), 7.99 (d, *J* = 9.9 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.04 (m, 4H), 6.62 – 6.60 (m, 2H), 6.55 – 6.52 (m, 1H), 5.97 (t, *J* = 6.1 Hz, 1H), 4.03 (d, *J* = 6.5 Hz, 2H) ppm; **^{13}C NMR** (126 MHz, DMSO) δ 165.2, 148.7, 139.5, 138.2, 133.5, 132.7, 132.5, 132.0, 130.5, 129.4, 129.2, 128.6, 126.5, 116.4, 115.8, 114.8, 112.7, 45.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{20}H_{16}BrN_2O^+$ 379.0441 Found 379.0441.



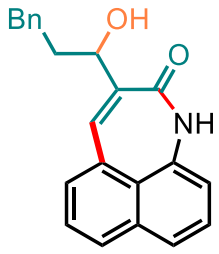
6d

3-(((4-(tert-butyl)phenyl)amino)methyl)naphtho[1,8-bc]azepin-2(1H)-one (6d): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 77% (55 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.58 (d, *J* = 9.6 Hz, 1H), 7.32 (d, *J* = 9.5 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.20 (d, *J* = 10.3 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 1H), 7.03 (s, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 4.16 (s, 2H), 1.27 (s, 9H) ppm (amine NH is missing); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 145.6, 142.0, 140.6, 137.0, 136.6, 132.2, 132.0, 131.1, 128.9, 127.2, 126.4, 126.2, 125.2, 123.6, 114.7, 113.1, 47.9, 34.0, 31.7 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{24}H_{25}N_2O^+$ 357.1961 Found 357.1952.



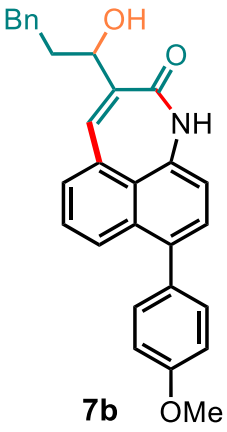
6e

3-(((4-methoxyphenyl)amino)methyl)naphtho[1,8-bc]azepin-2(1H)-one (6e): White solid; Eluent: 20–25% EtOAc in Hexane; yield = 81% (53 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.58 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.00 (s, 1H), 6.79 – 6.76 (m, 2H), 6.63 (d, *J* = 7.0 Hz, 3H), 4.12 (s, 2H), 3.73 (d, *J* = 1.8 Hz, 3H) ppm. (amine NH is missing); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 152.6, 142.2 (2×C), 137.0, 136.7, 132.2, 132.0, 131.1, 128.9, 127.2, 126.5, 125.2, 123.6, 115.2, 115.0, 114.7, 56.0, 48.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{19}N_2O_2^+$ 331.1441 Found 331.1431.



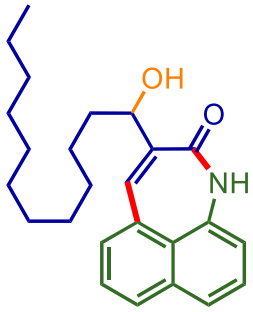
7a

3-(1-hydroxy-3-phenylpropyl)naphtho[1,8-bc]azepin-2(1H)-one (7a): Orange solid ; Eluent: 20–25% EtOAc in Hexane; yield = 70% (46 mg); **^{1}H NMR** (500 MHz, DMSO) δ 9.83 (s, 1H), 7.70 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.39 (d, *J* = 9.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 7.27 – 7.24 (m, 2H), 7.22 – 7.19 (m, 3H), 7.16 – 7.13 (m, 1H), 7.05 (d, *J* = 9.1 Hz, 1H), 5.19 (d, *J* = 4.9 Hz, 1H), 4.69 (dd, *J* = 8.0, 4.1 Hz, 1H), 2.83 – 2.77 (m, 1H), 2.69 – 2.63 (m, 1H), 2.00 – 1.93 (m, 1H), 1.71 – 1.63 (m, 1H) ppm; **^{13}C NMR** (126 MHz, DMSO) δ 164.9, 142.2, 138.5, 137.5, 136.3, 136.0, 131.7, 131.4, 130.5, 128.24, 128.21, 127.3, 126.4, 125.5, 124.7, 122.5, 114.6, 68.3, 39.2, 31.7 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{22}H_{20}NO_2^+$ 330.1489 Found 330.1487.



7b

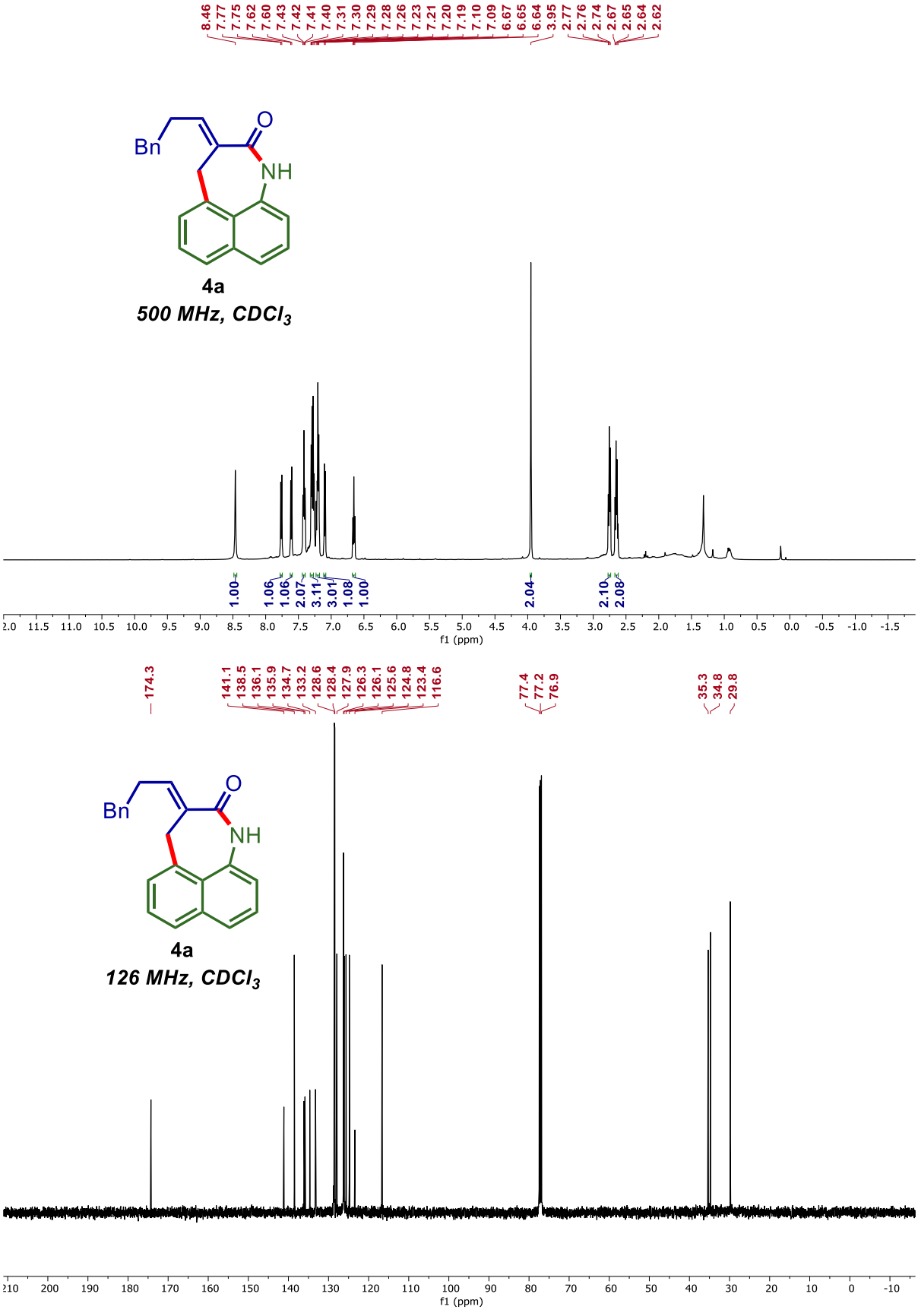
3-(1-hydroxy-3-phenylpropyl)-8-(4-methoxyphenyl)naphtho[1,8-bc]azepin-2(1H)-one (7b): Orange solid ; Eluent: 20–25% EtOAc in Hexane; yield = 64% (56 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 (d, *J* = 9.8 Hz, 1H), 7.29 – 7.21 (m, 7H), 7.19 – 7.16 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.93 (s, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.69 (d, *J* = 8.0 Hz, 1H), 2.93 – 2.74 (m, 2H), 2.23 – 2.10 (m, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 159.2, 142.6 (2×C), 141.9, 135.75, 135.66, 134.8, 132.8, 132.7, 132.5, 131.7, 131.0, 129.6, 128.7, 128.5, 128.4, 126.4, 125.9, 114.7, 114.1, 75.3, 55.5, 38.6, 32.6 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{29}H_{25}NNaO_3$+ 458.1727 Found 458.1723.

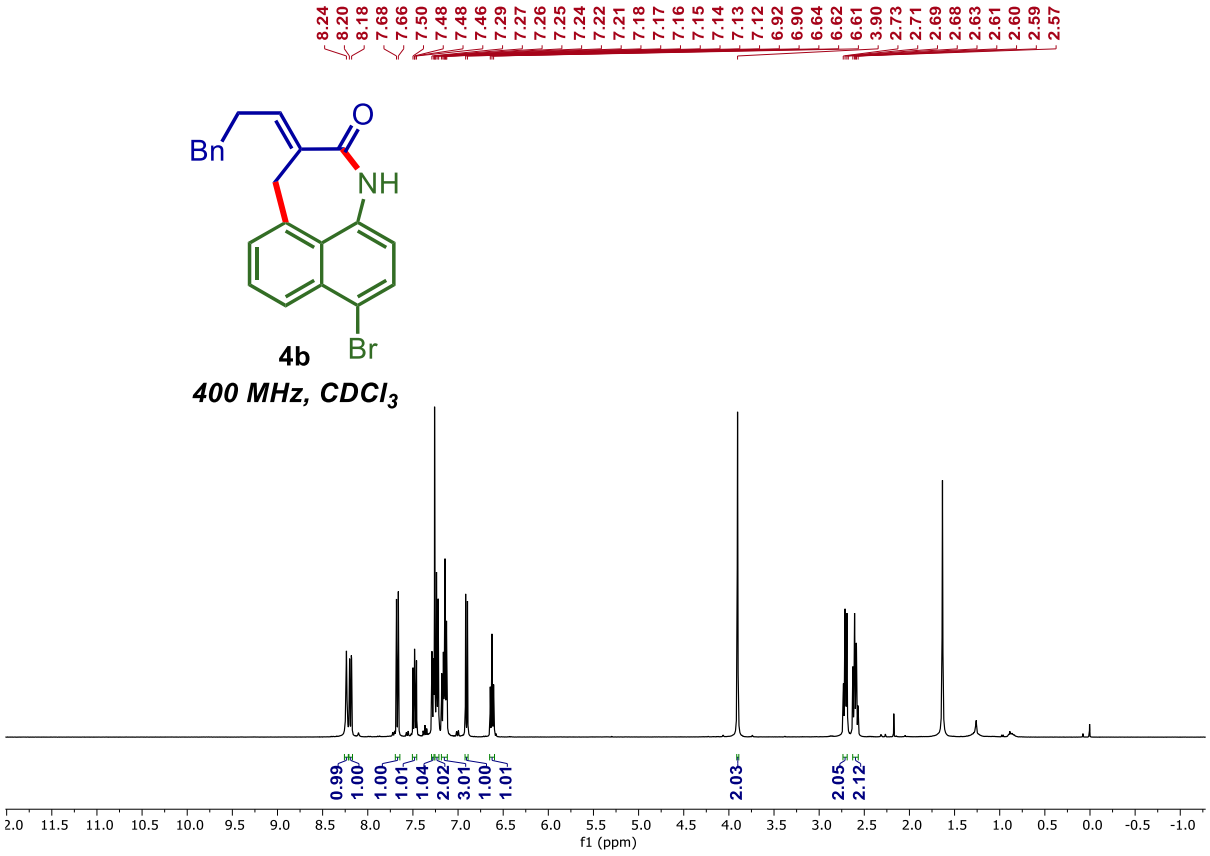


7c

3-(1-hydroxydodecyl)naphtho[1,8-bc]azepin-2(1H)-one (7c): Orange solid ; Eluent: 20–25% EtOAc in Hexane; yield = 73% (55 mg); **^{1}H NMR** (400 MHz, CDCl3) δ 7.76 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (d, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.94 (s, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 1H), 1.82 – 1.76 (m, 2H), 1.30 – 1.24 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 142.0, 136.62, 136.55, 133.1, 132.5, 131.8, 131.3, 127.2, 126.5, 125.4, 123.8, 114.9, 75.8, 37.3, 32.0, 29.8, 29.7 (3×C), 29.6, 29.4, 26.5, 22.8, 14.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{25}H_{34}NO_2^+$ 380.2584 Found 380.2588.

8. NMR spectra of synthesized compounds

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7.50
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7.48
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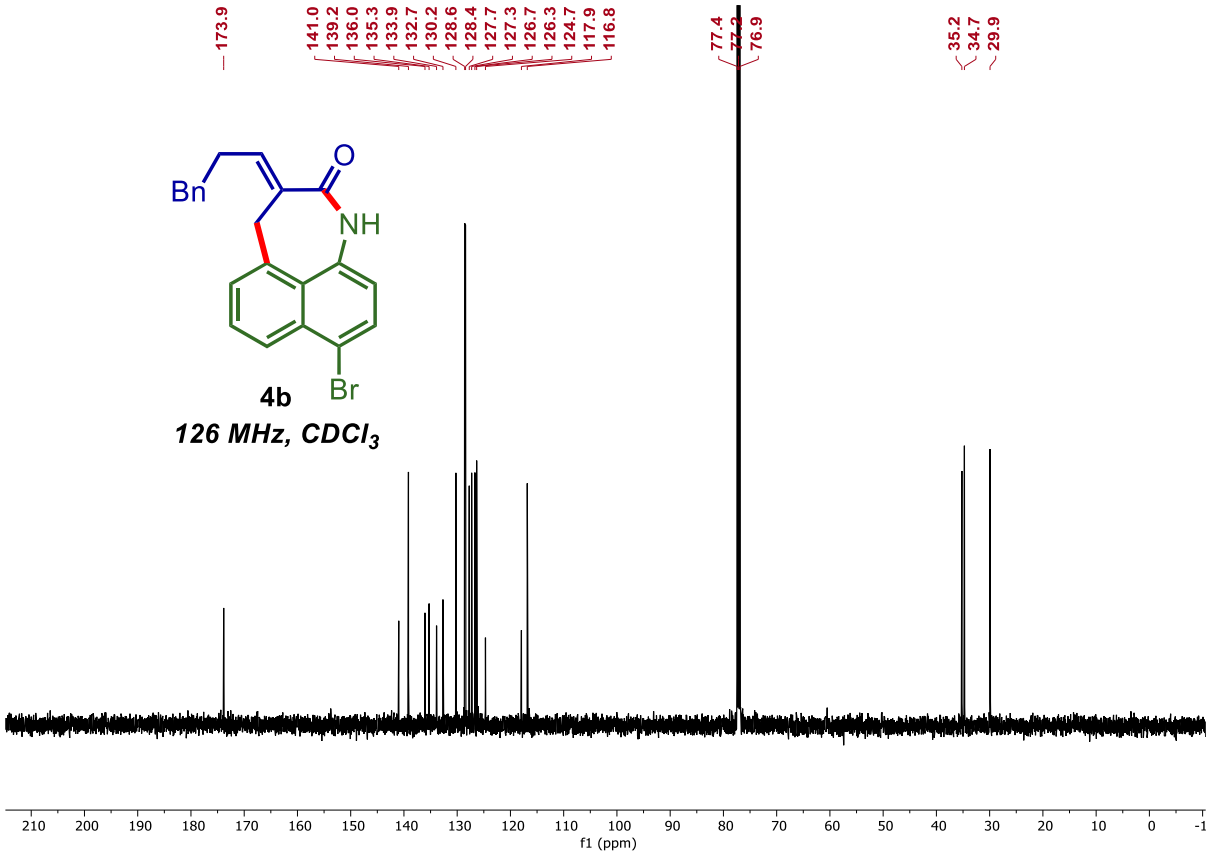
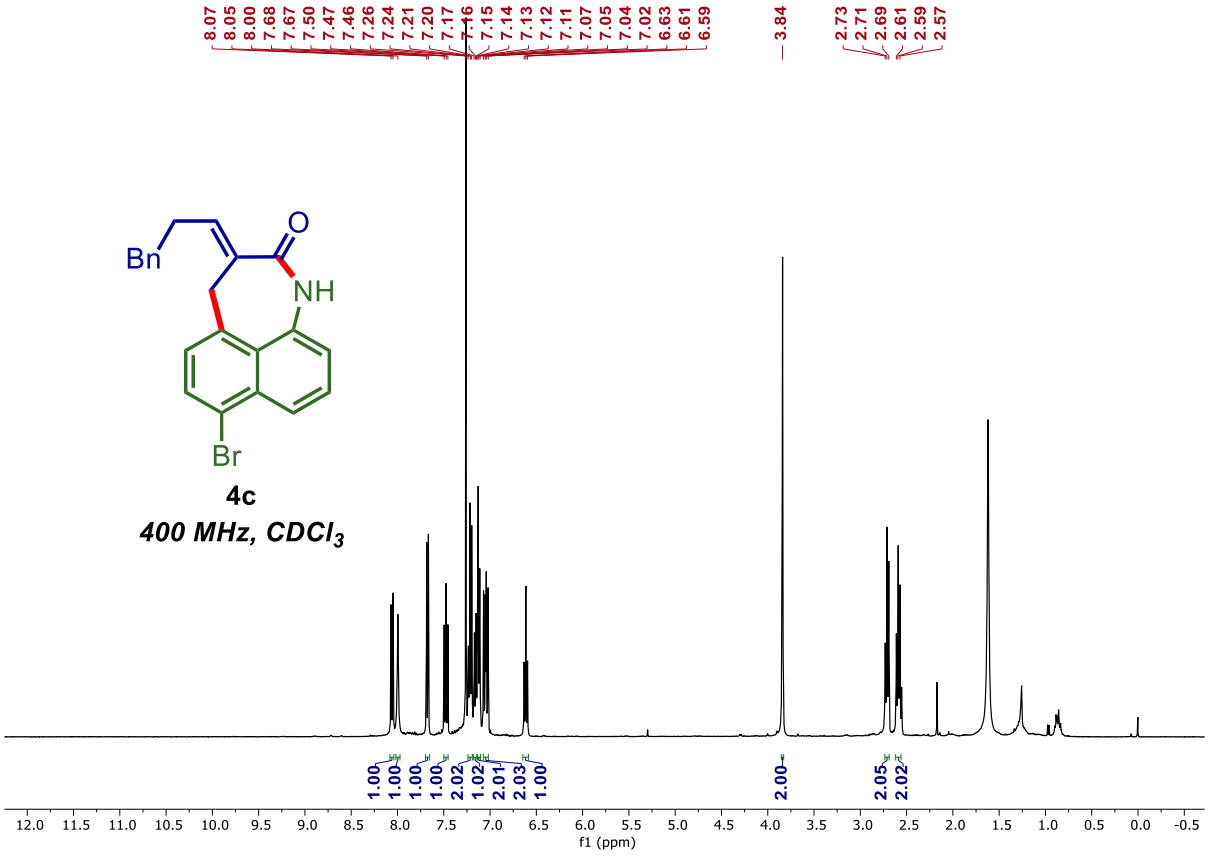
7.27
7.26
7.25
7.24
7.22
7.21
7.18
7.17
7.16
7.15
7.14
7.13
7.12
6.92
6.90
6.64
6.62
6.61
3.90
2.73
2.71
2.69
2.68
2.63
2.61
2.60
2.59
2.57
Bn
O
NH
Br
4b
400 MHz, CDCl3
0.99
1.00
1.00
1.01
1.04
2.02
3.01
1.00
1.01
2.03
2.05
2.12
f1 (ppm)


173.9
141.0
139.2
136.0
135.3
133.9
132.7
130.2
128.6
128.4
127.7
127.3
126.7
126.3
124.7
117.9
116.8
77.4
77.2
76.9
35.2
34.7
29.9
Bn
O
NH
Br
4b
126 MHz, CDCl3
f1 (ppm)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8.00
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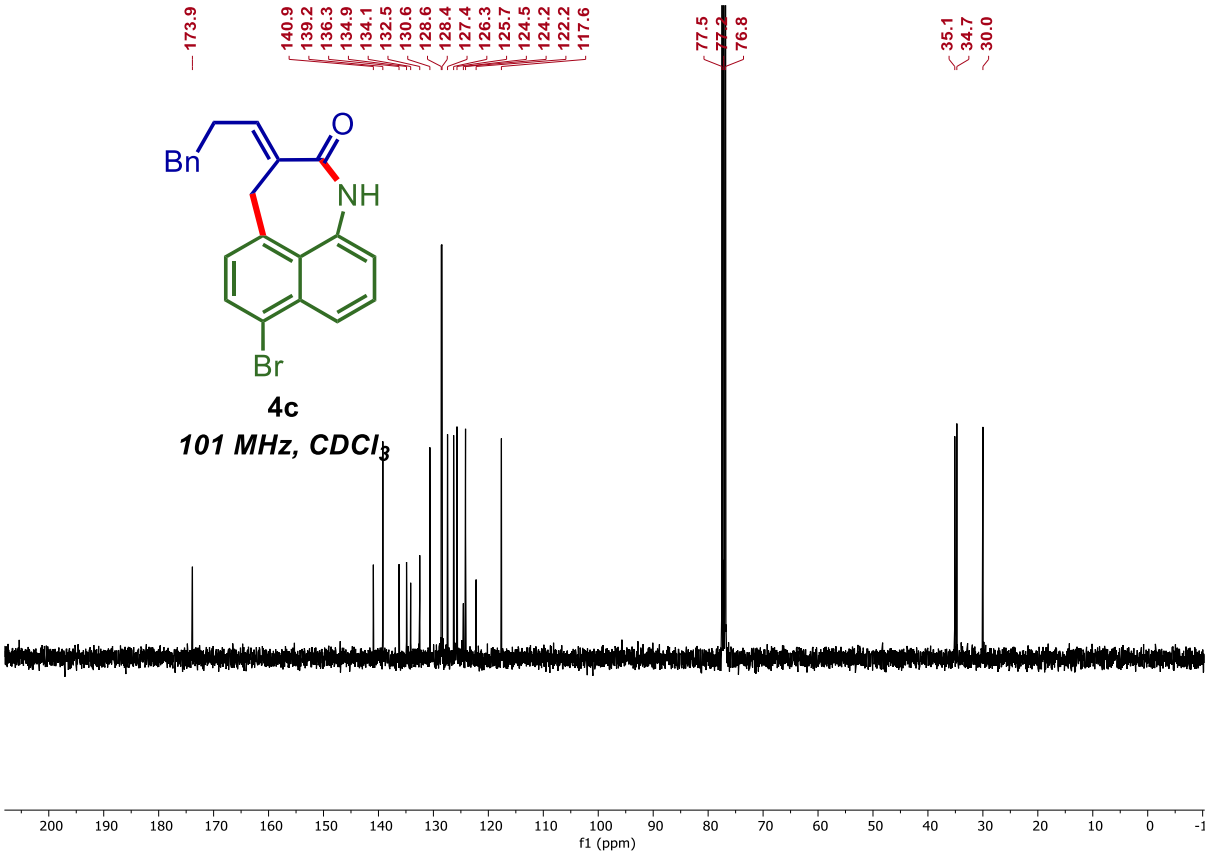
7.67
7.50
7.47
7.46
7.26
7.24
7.21
7.20
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.07
7.05
7.04
7.02
6.63
6.61
6.59
3.84
2.73
2.71
2.69
2.61
2.59
2.57
O
Bn
NH
Br
4c
400 MHz, CDCl3
1.00
1.00
1.00
1.00
2.02
1.02
2.01
2.03
1.00
2.00
2.05
2.02
f1 (ppm)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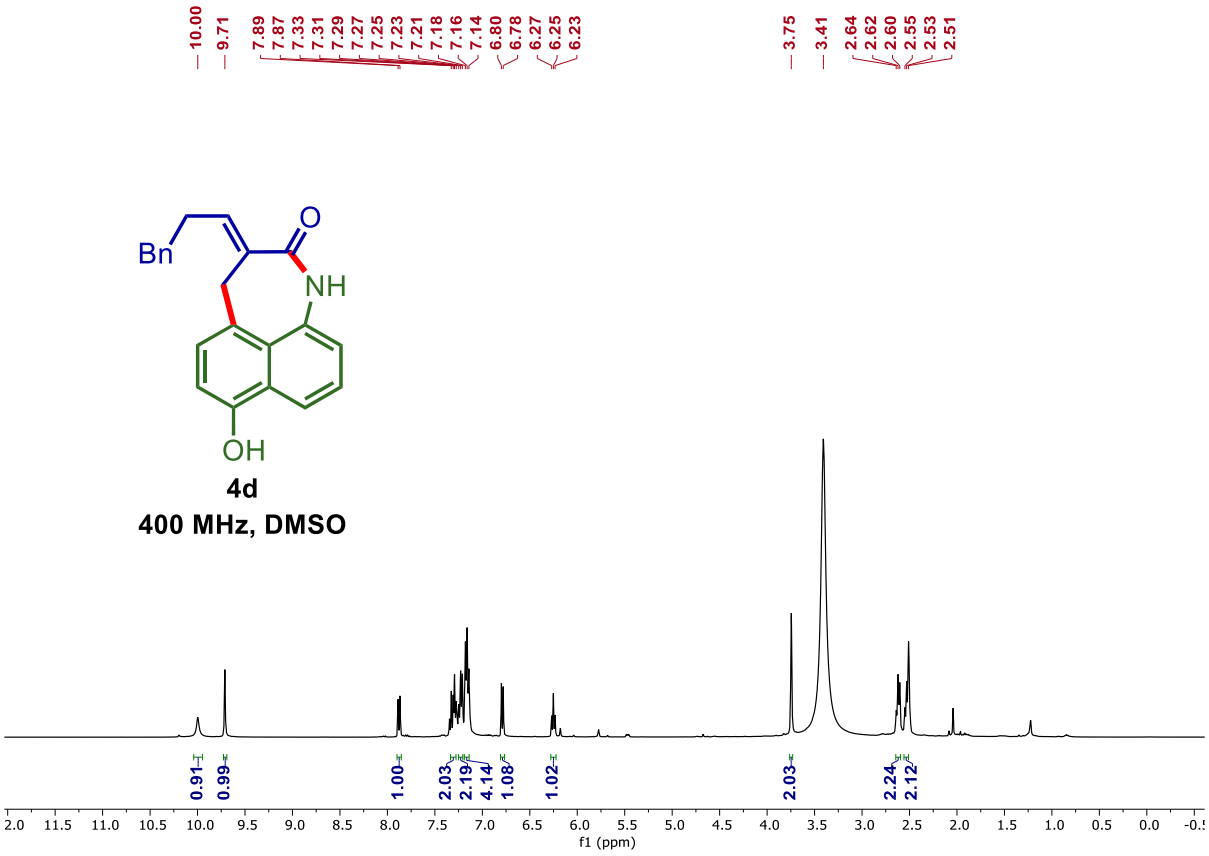
140.9
139.2
136.3
134.9
134.1
132.5
130.6
128.6
128.4
127.4
126.3
125.7
124.5
124.2
122.2
117.6
77.5
77.2
76.8
35.1
34.7
30.0
O
Bn
NH
Br
4c
101 MHz, CDCl3
f1 (ppm)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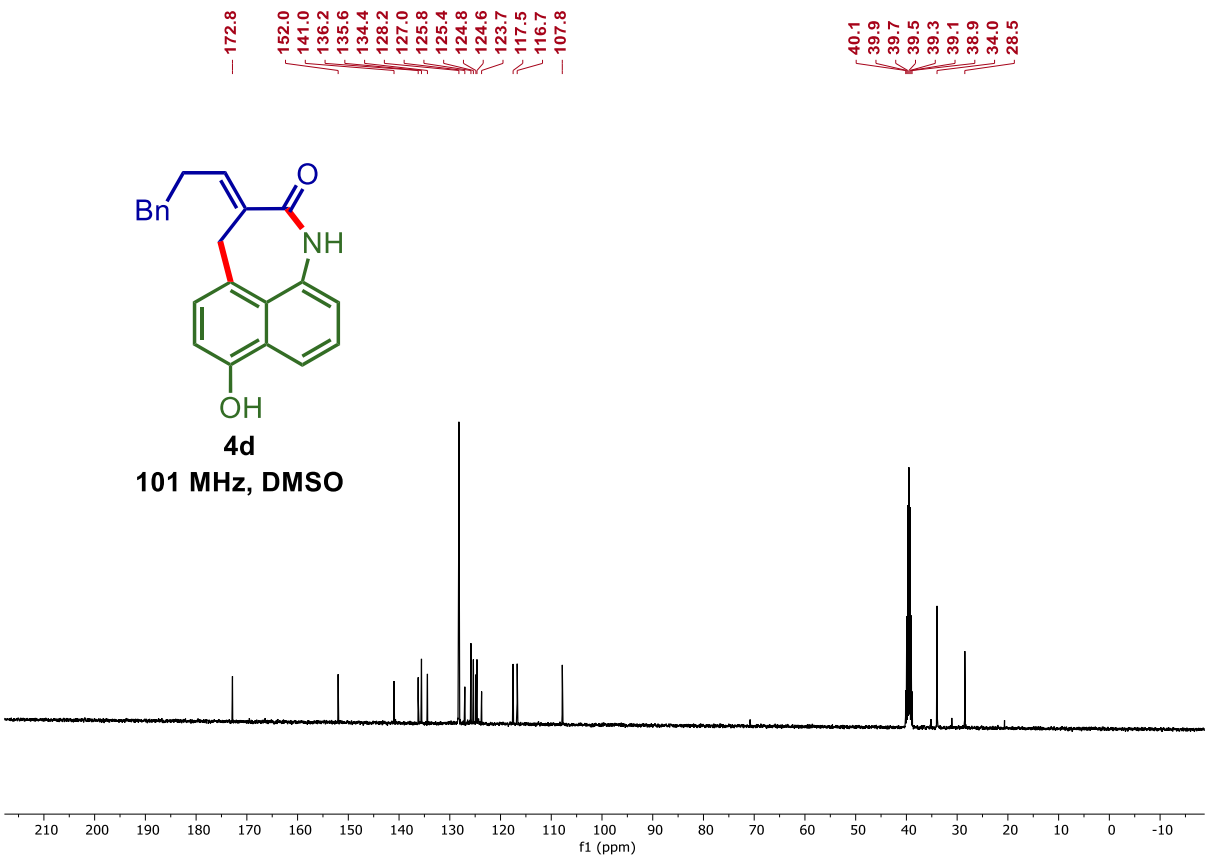
7.89
7.87
7.33
7.31
7.29
7.27
7.25
7.23
7.21
7.18
7.16
7.14
6.80
6.78
6.27
6.25
6.23
3.75
3.41
2.64
2.62
2.60
2.55
2.53
2.51
Bn
O
NH
OH
4d
400 MHz, DMSO
0.91
0.99
1.00
2.03
2.19
4.14
1.08
1.02
2.03
2.24
2.12
f1 (ppm)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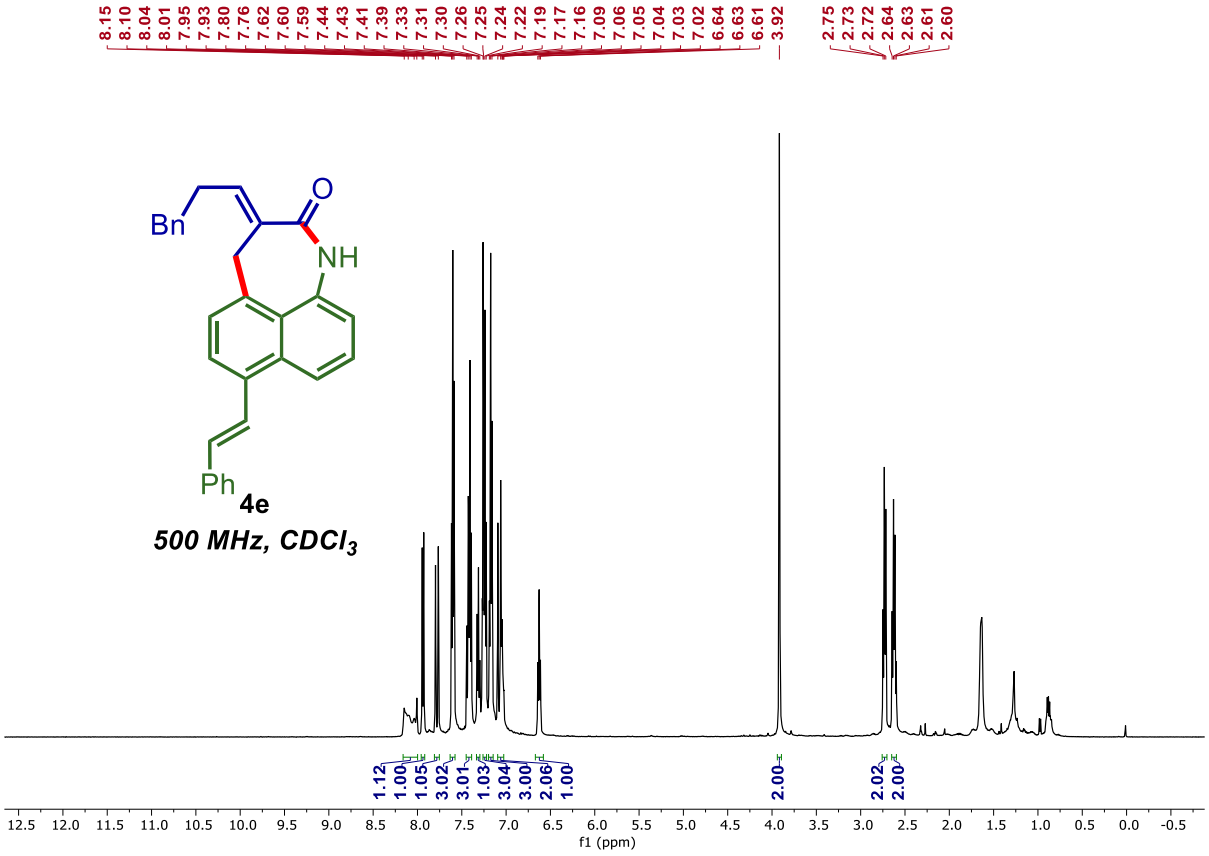
141.0
136.2
135.6
134.4
128.2
127.0
125.8
125.4
124.8
124.6
123.7
117.5
116.7
107.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
34.0
28.5
Bn
O
NH
OH
4d
101 MHz, DMSO
f1 (ppm)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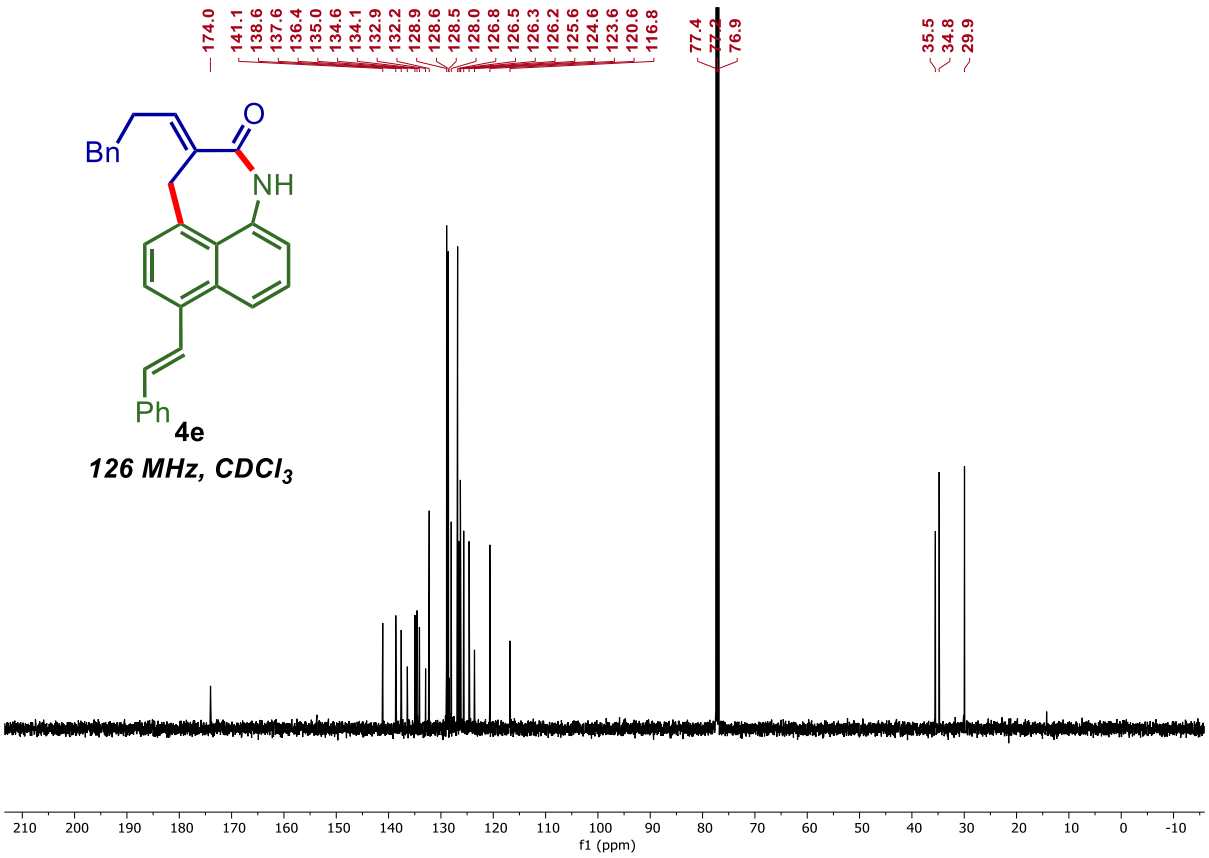
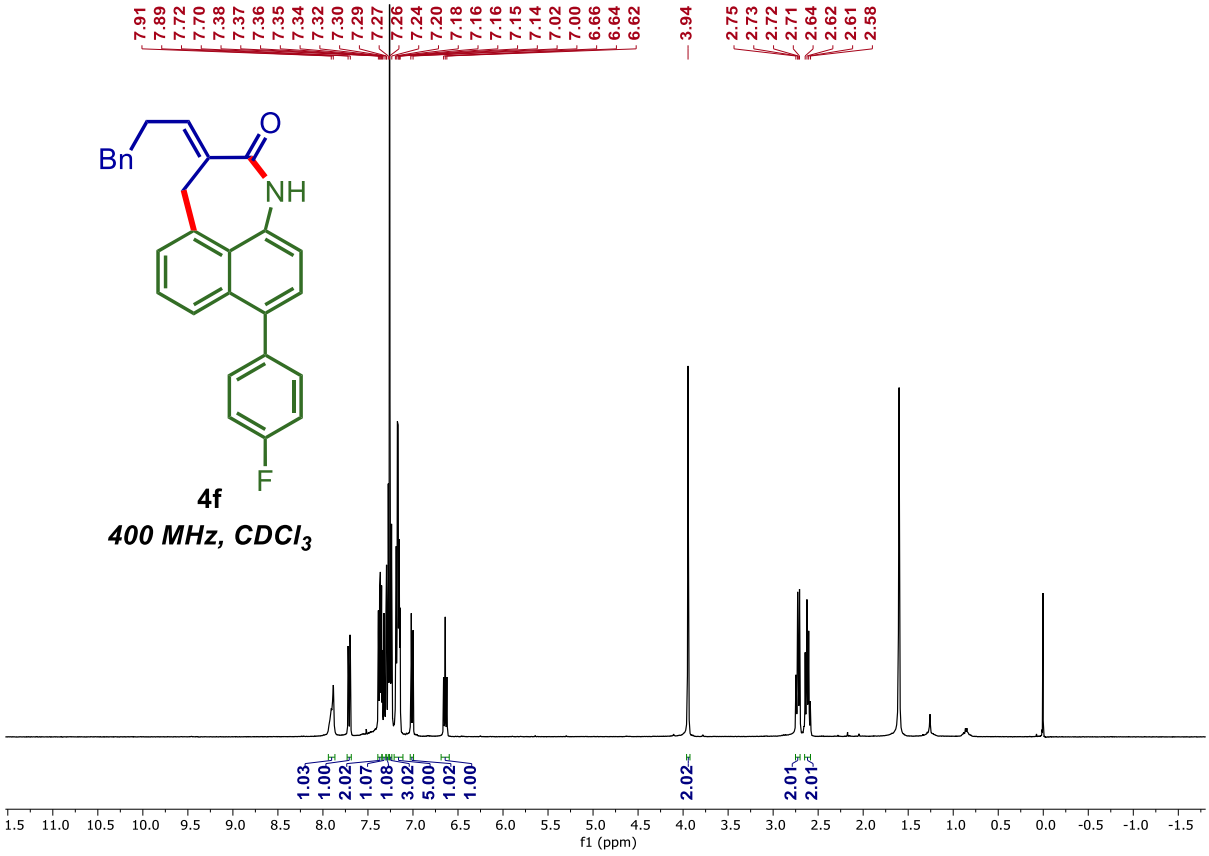
8.10
8.04
8.01
7.95
7.93
7.80
7.76
7.62
7.60
7.59
7.44
7.43
7.41
7.39
7.33
7.31
7.30
7.26
7.25
7.24
7.22
7.19
7.17
7.16
7.09
7.06
7.05
7.04
7.03
7.02
6.64
6.63
6.61
3.92
2.75
2.73
2.72
2.64
2.63
2.61
2.60
Bn
O
NH
Ph
4e
500 MHz, CDCl3
1.12
1.00
1.05
3.02
3.01
1.03
3.04
3.00
2.06
1.00
2.00
2.02
2.00
f1 (ppm)


174.0
141.1
138.6
137.6
136.4
135.0
134.6
134.1
132.9
132.2
128.9
128.6
128.5
128.0
126.8
126.5
126.3
126.2
125.6
124.6
123.6
120.6
116.8
77.4
77.2
76.9
35.5
34.8
29.9
Bn
O
NH
Ph
4e
126 MHz, CDCl3
f1 (ppm)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7.89
7.72
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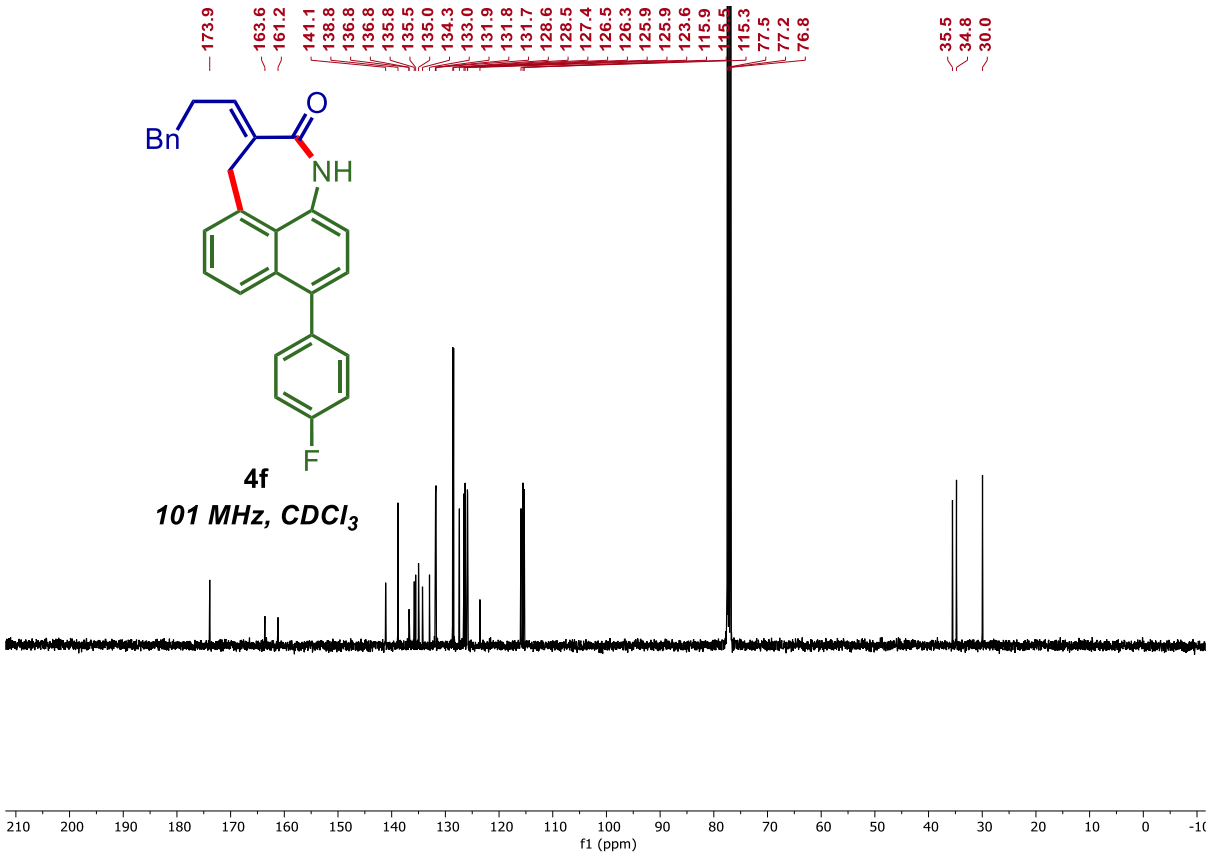
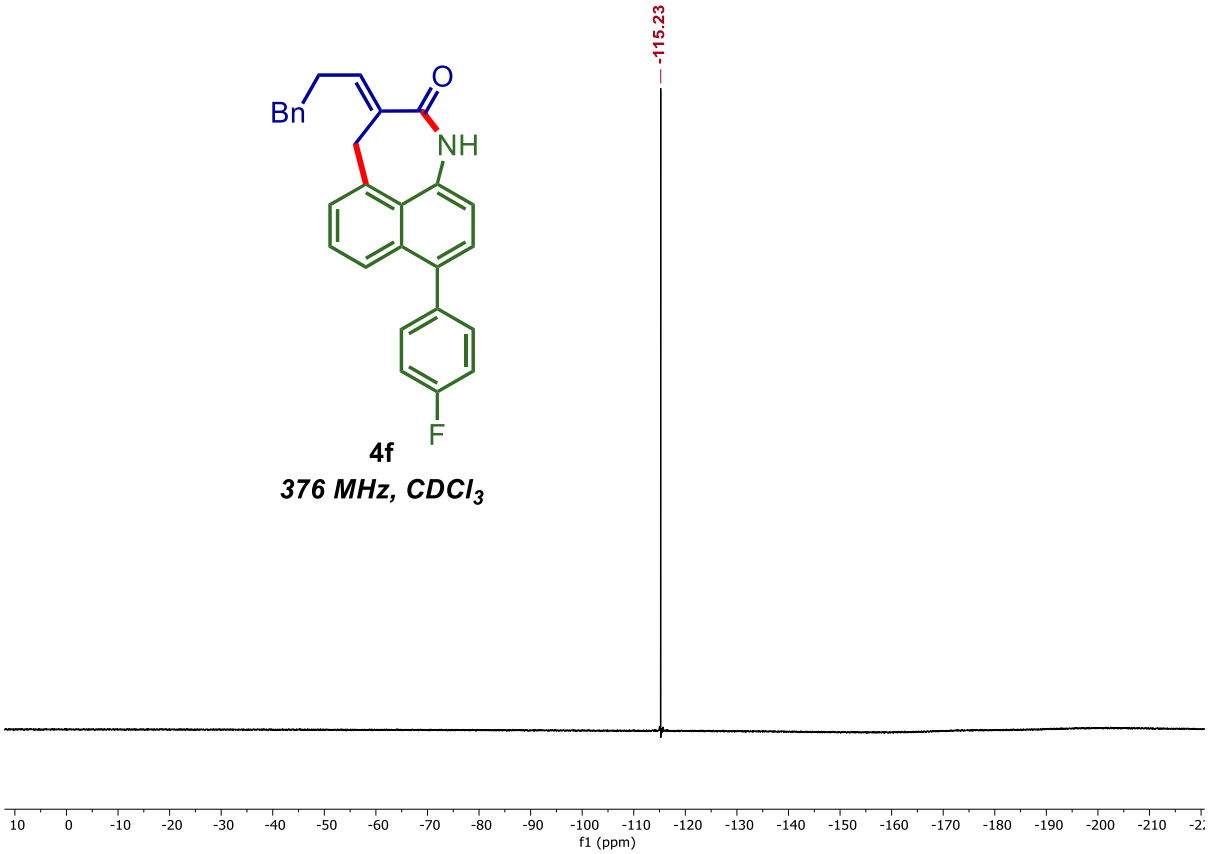
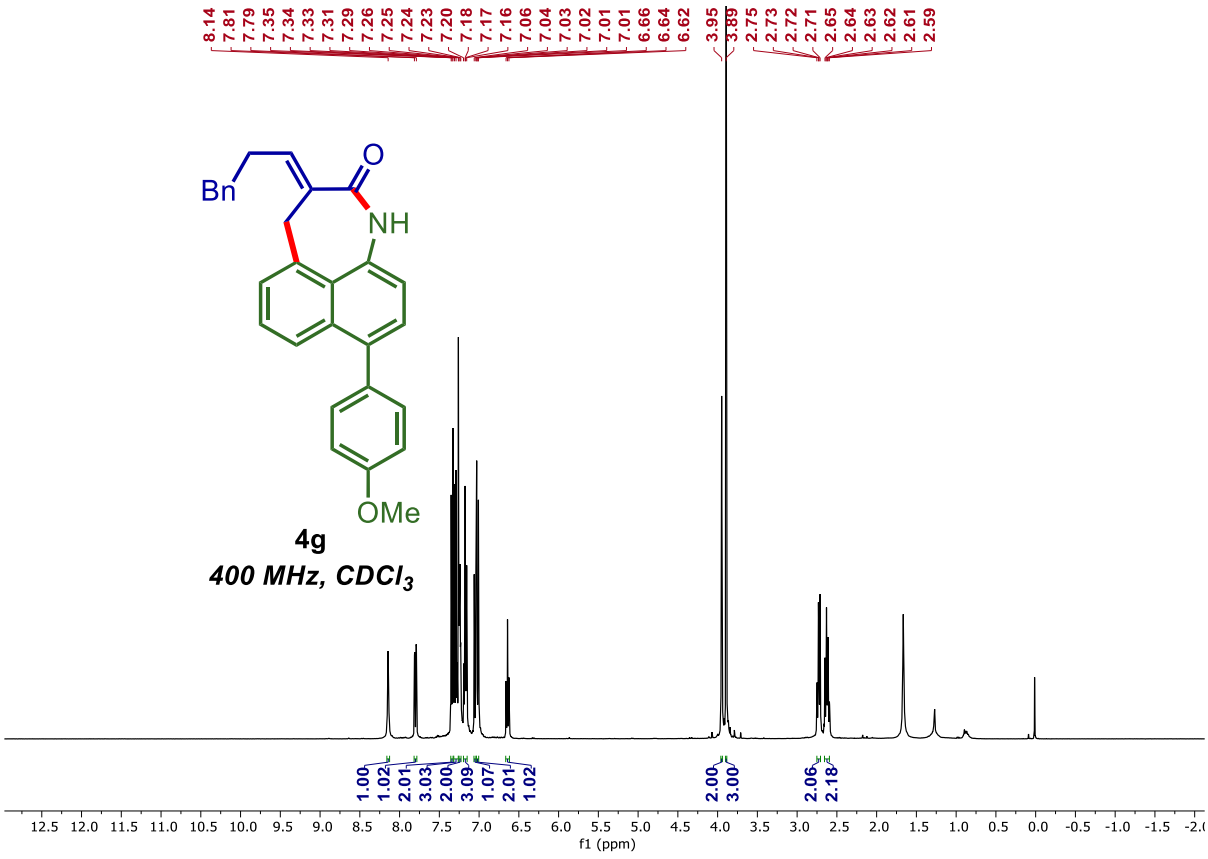
7.38
7.37
7.36
7.35
7.34
7.32
7.30
7.29
7.27
7.26
7.24
7.20
7.18
7.16
7.16
7.15
7.14
7.02
7.00
6.66
6.64
6.62
3.94
2.75
2.73
2.72
2.71
2.64
2.62
2.61
2.58
Bn
O
NH
F
4f
400 MHz, CDCl3
1.03
1.00
2.02
1.07
1.08
3.02
5.00
1.02
1.00
2.02
2.01
2.01
f1 (ppm)


173.9
163.6
161.2
141.1
138.8
136.8
136.8
135.8
135.5
135.0
134.3
133.0
131.9
131.8
131.7
128.6
128.5
127.4
126.5
126.3
125.9
125.9
123.6
115.9
115.5
115.3
77.5
77.2
76.8
35.5
34.8
30.0
Bn
O
NH
F
4f
101 MHz, CDCl3
f1 (ppm)



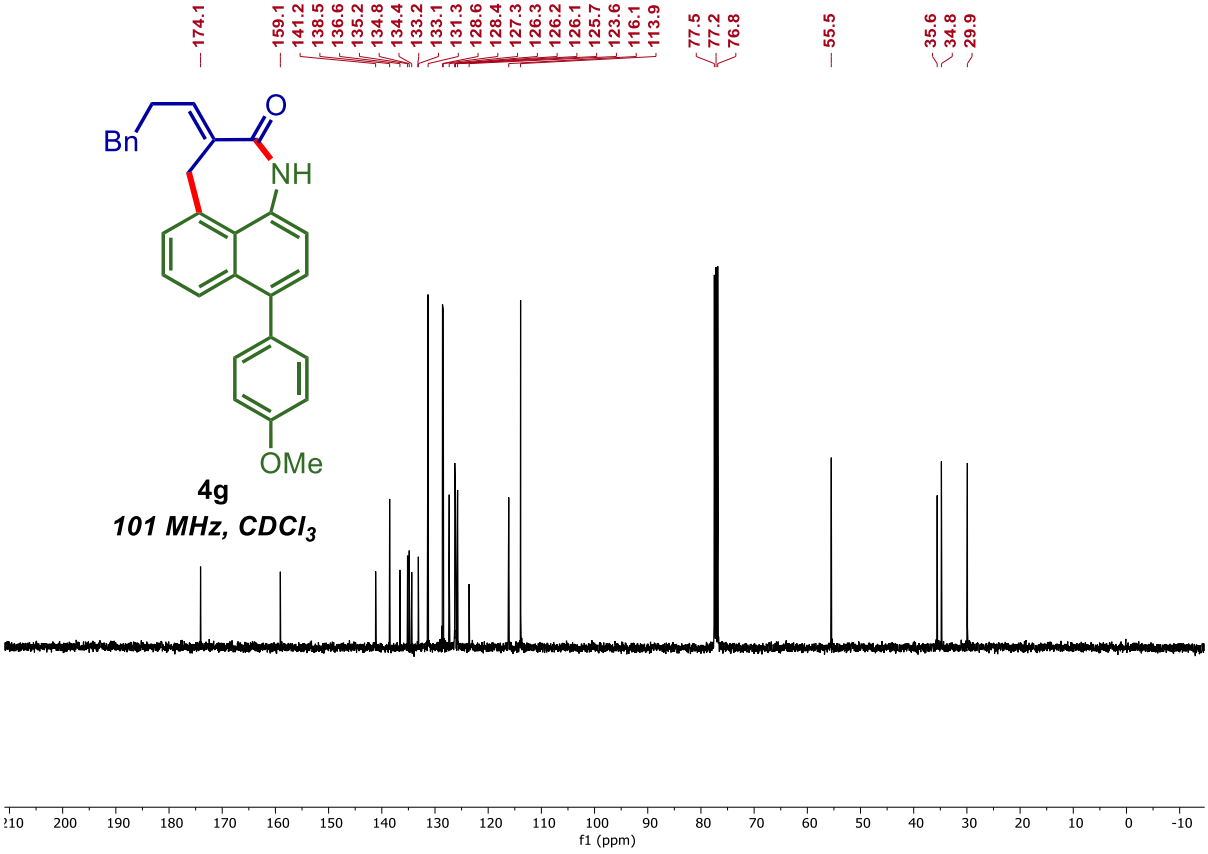
4f

376 MHz, $CDCl_3$



4g

400 MHz, $CDCl_3$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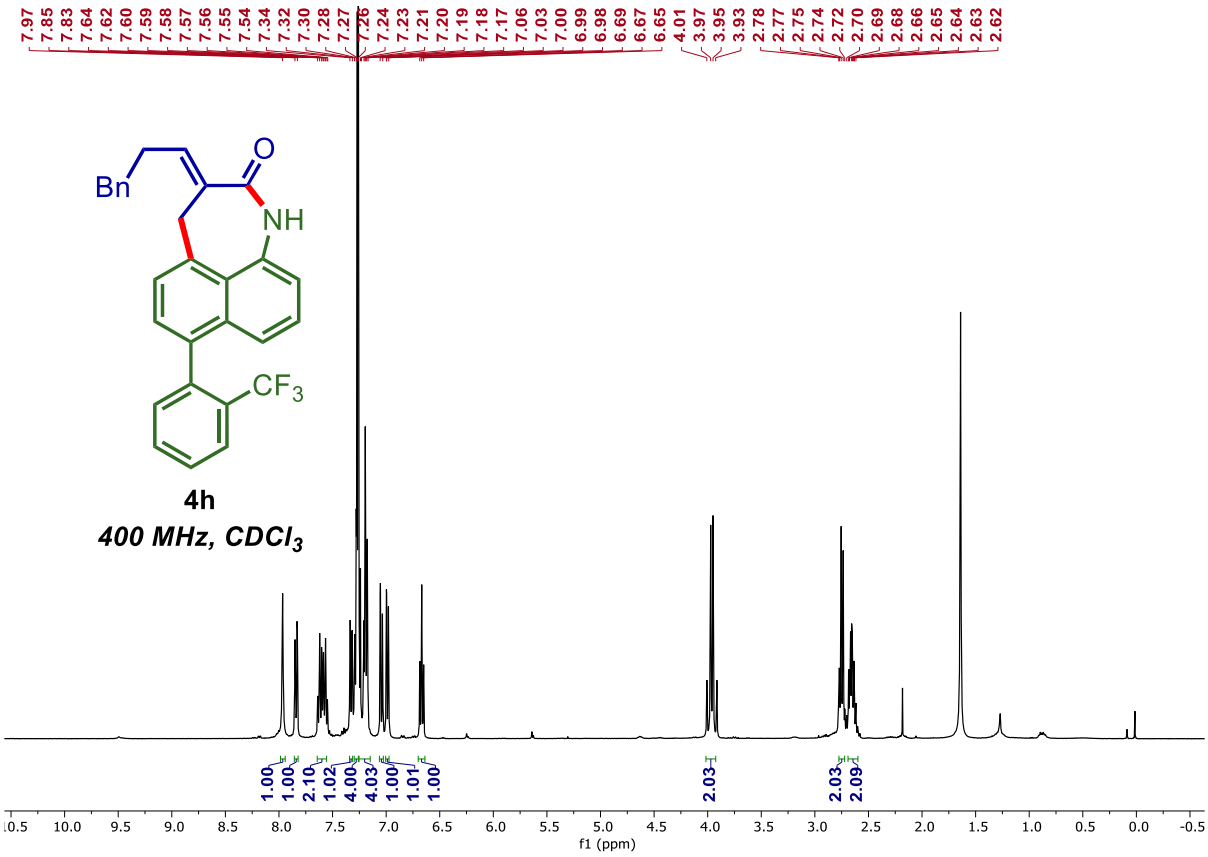
159.1
141.2
138.5
136.6
135.2
134.8
134.4
133.2
133.1
131.3
128.6
128.4
127.3
126.3
126.2
126.1
125.7
123.6
116.1
113.9
77.5
77.2
76.8
55.5
35.6
34.8
29.9
Bn
O
NH
OMe
4g
101 MHz, CDCl3
f1 (ppm)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7.64
7.62
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.34
7.32
7.30
7.28
7.27
7.26
7.24
7.23
7.21
7.20
7.19
7.18
7.17
7.06
7.03
7.00
6.99
6.98
6.69
6.67
6.65
4.01
3.97
3.95
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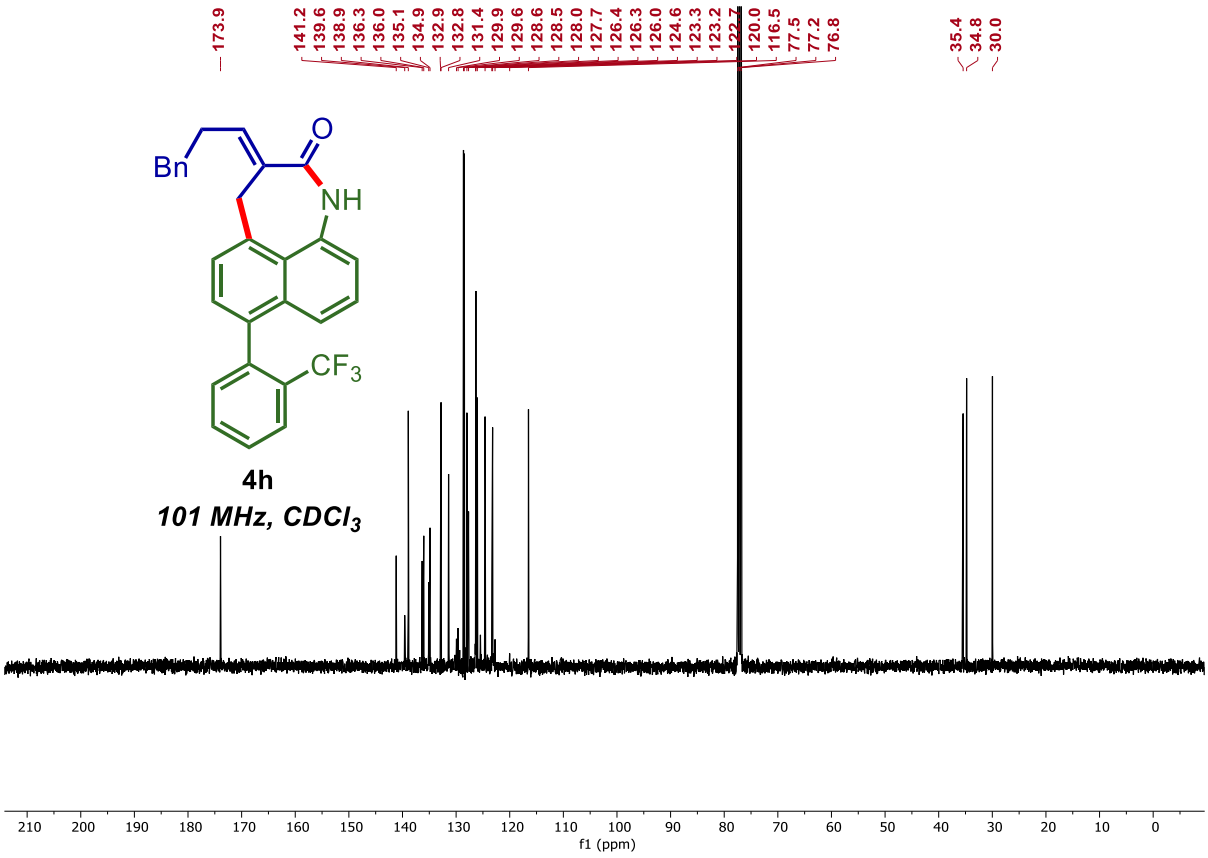
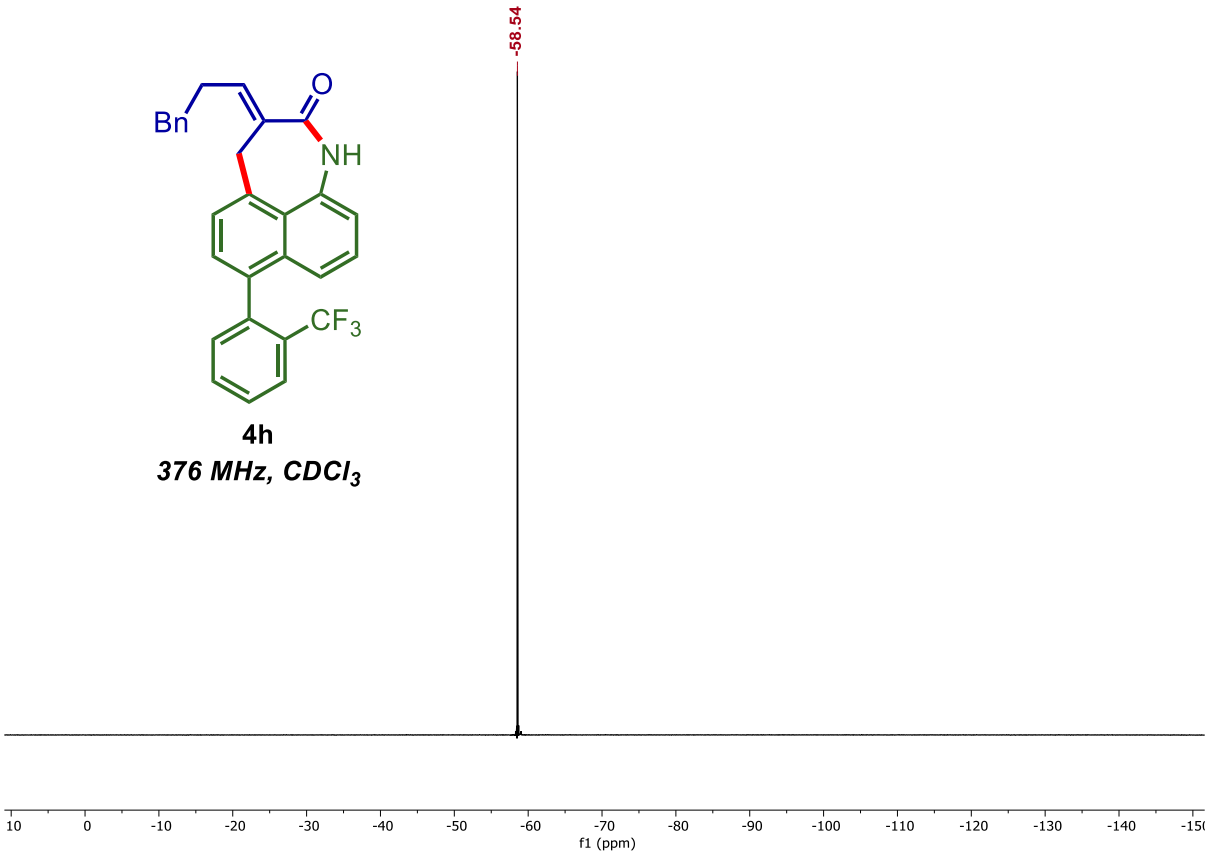
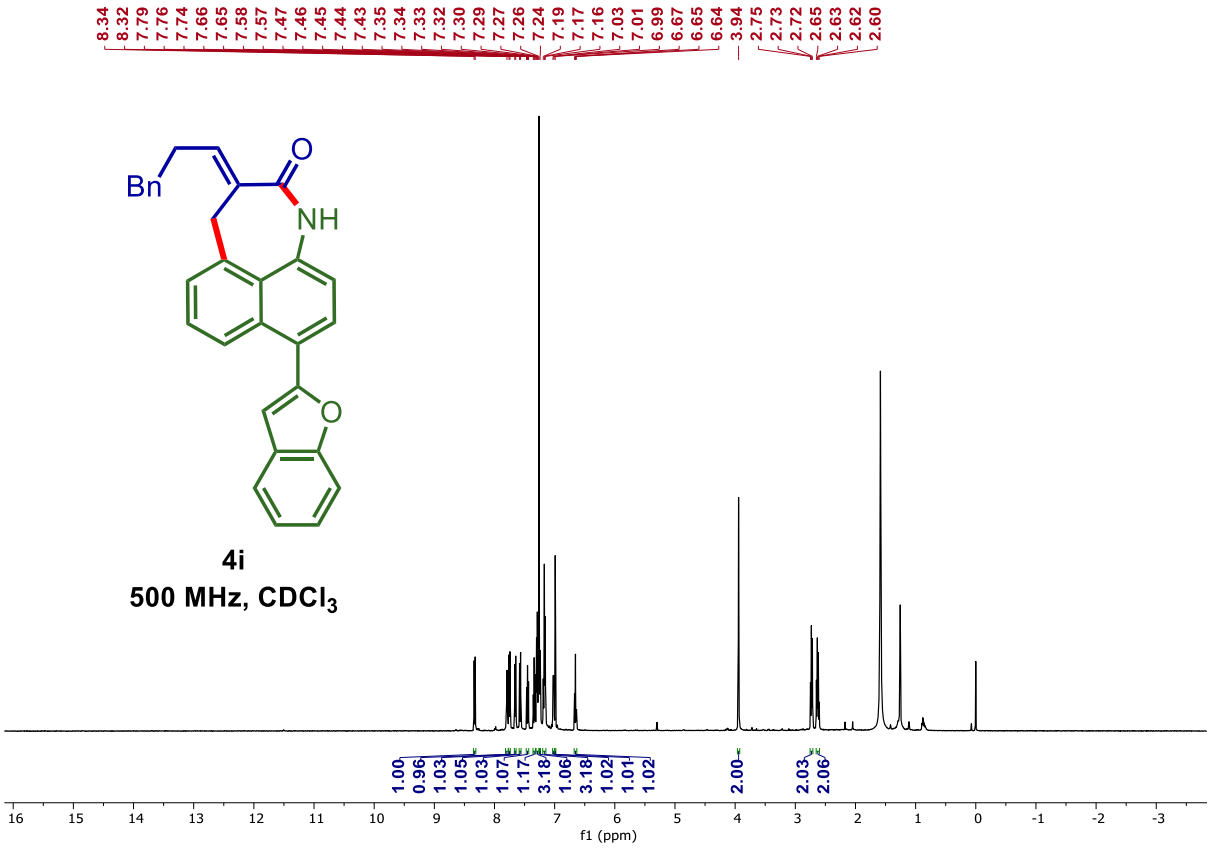
2.77
2.75
2.74
2.72
2.70
2.69
2.68
2.66
2.65
2.64
2.63
2.62
Bn
O
NH
CF3
4h
400 MHz, CDCl3
1.00
1.00
2.10
1.02
4.00
4.03
1.00
1.01
1.00
2.03
2.03
2.09
f1 (ppm)


173.9
141.2
139.6
138.9
136.3
136.0
135.1
134.9
132.9
132.8
131.4
129.9
129.6
128.6
128.5
128.0
127.7
126.4
126.3
126.0
124.6
123.3
123.2
122.7
120.0
116.5
77.5
77.2
76.8
35.4
34.8
30.0
Bn
O
NH
CF3
4h
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-58.54
Bn
O
NH
CF3
4h
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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7.47
7.46
7.45
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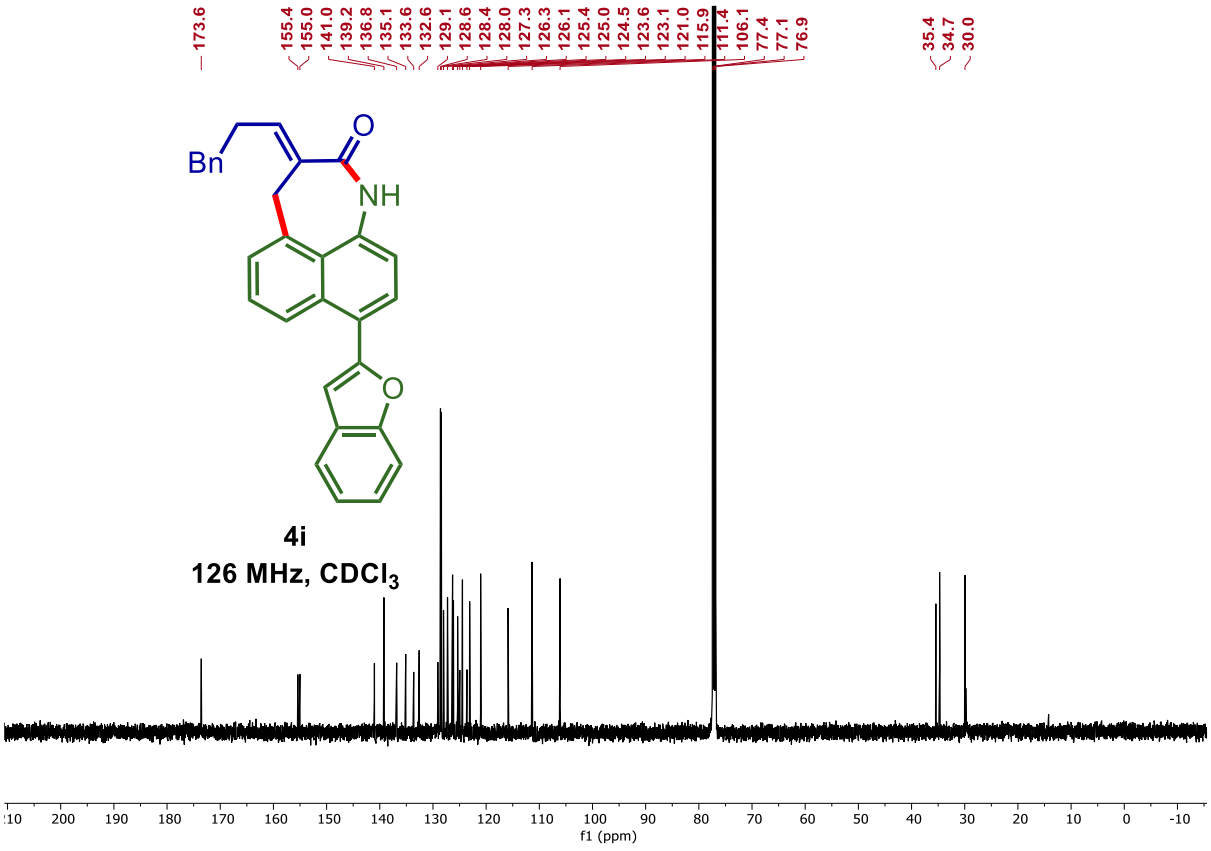
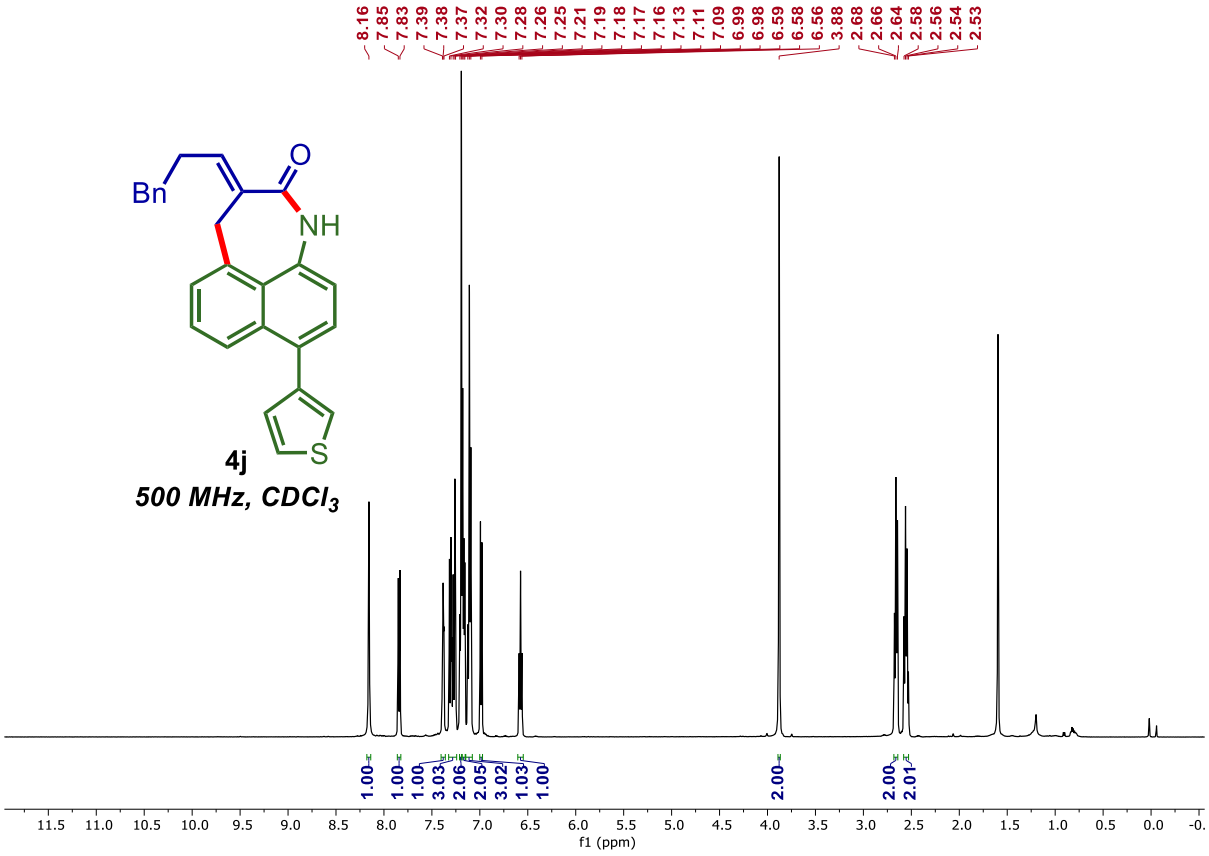
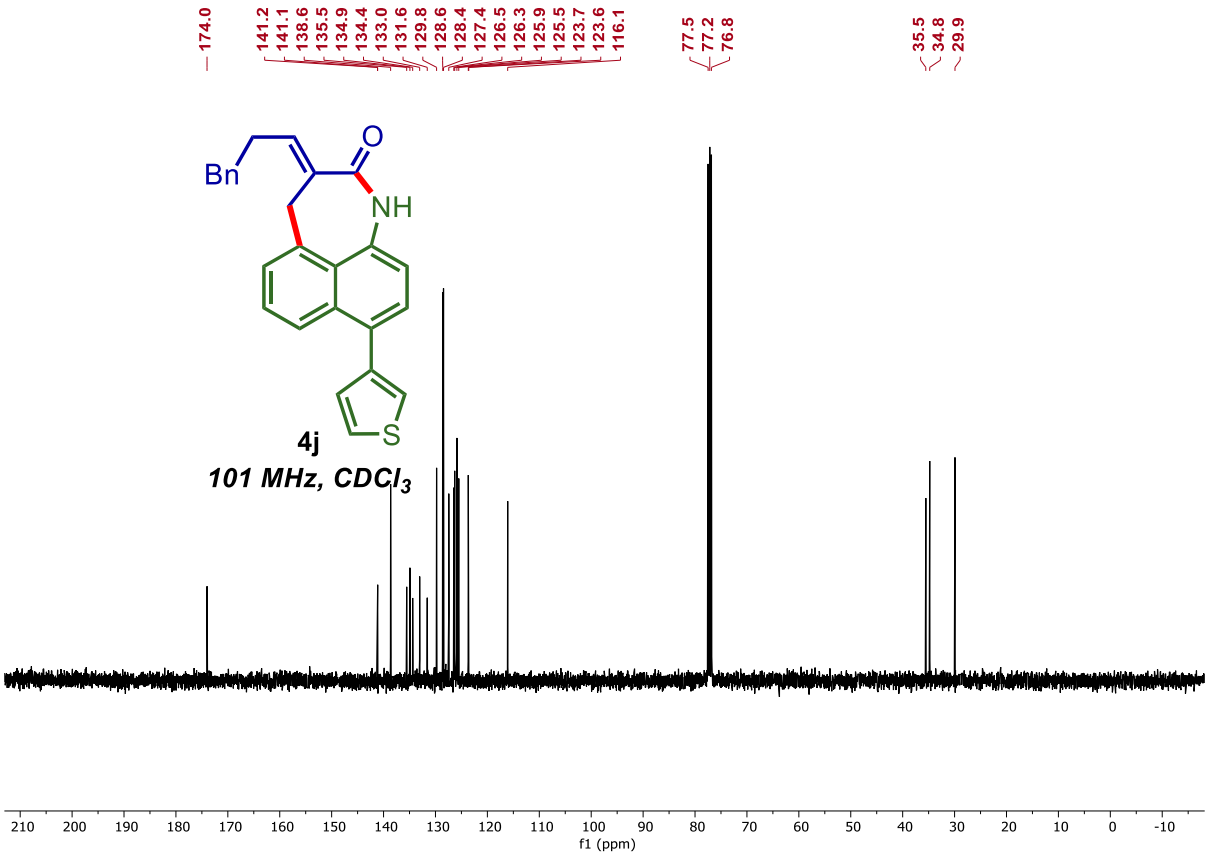
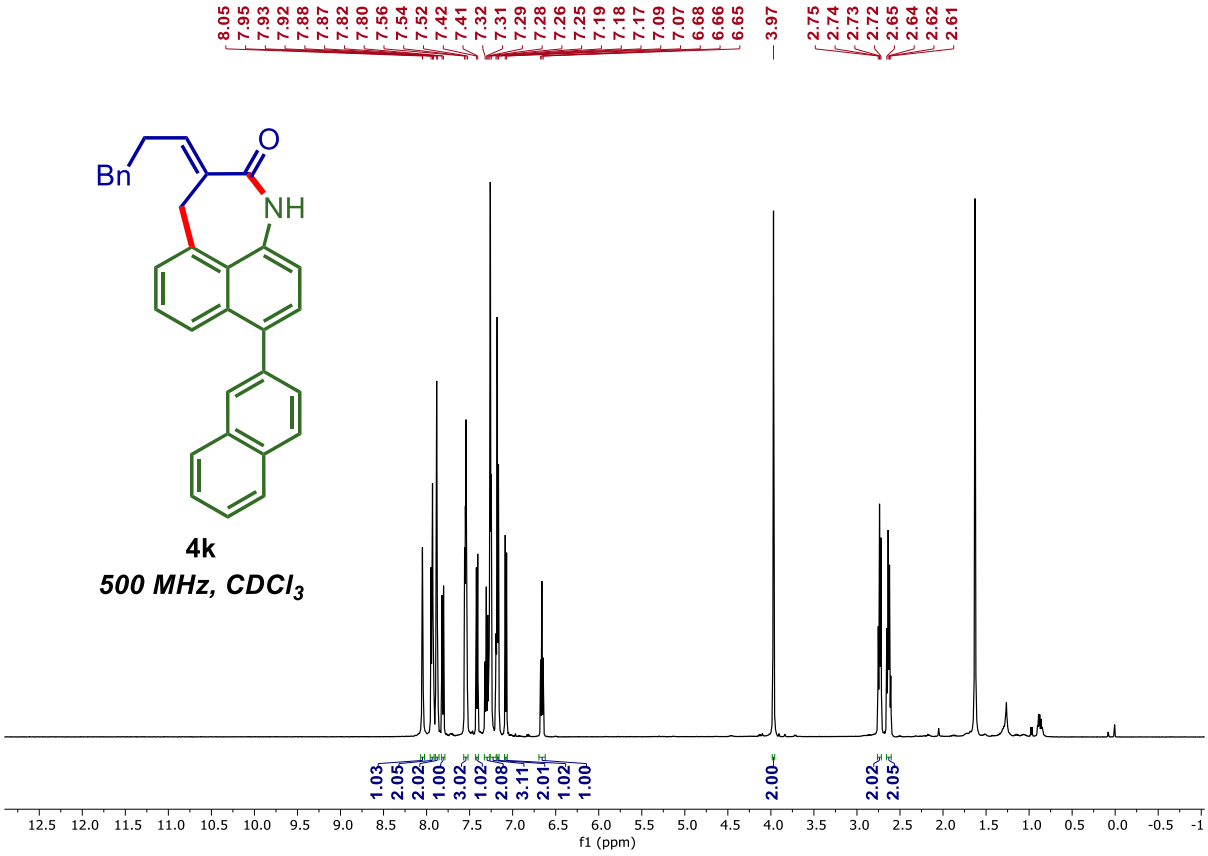
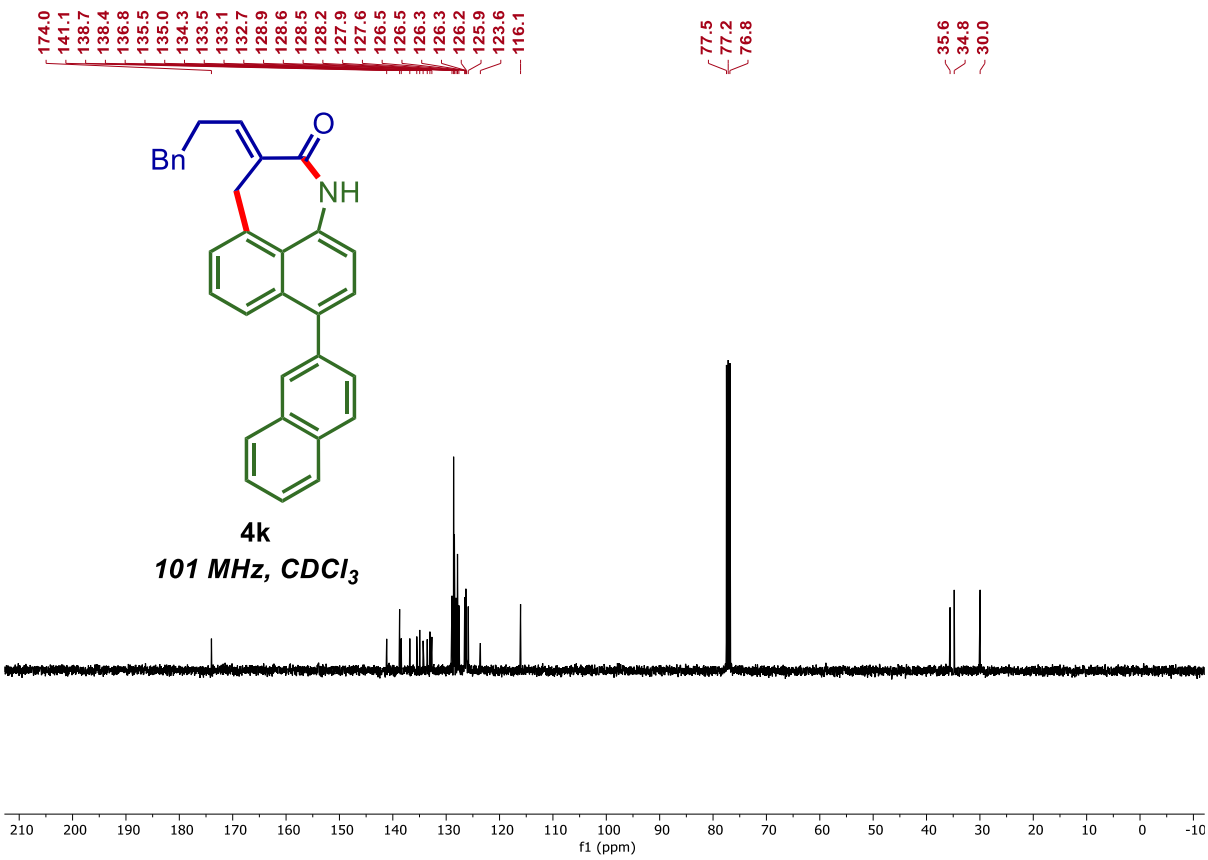
7.43
7.35
7.34
7.33
7.32
7.30
7.29
7.27
7.26
7.24
7.19
7.17
7.16
7.03
7.01
6.99
6.67
6.65
6.64
3.94
2.75
2.73
2.72
2.65
2.63
2.62
2.60
Bn
NH
O
O
4i
500 MHz, CDCl3
1.00
0.96
1.03
1.05
1.03
1.07
1.17
3.18
1.06
3.18
1.02
1.01
1.02
2.00
2.03
2.06
f1 (ppm)

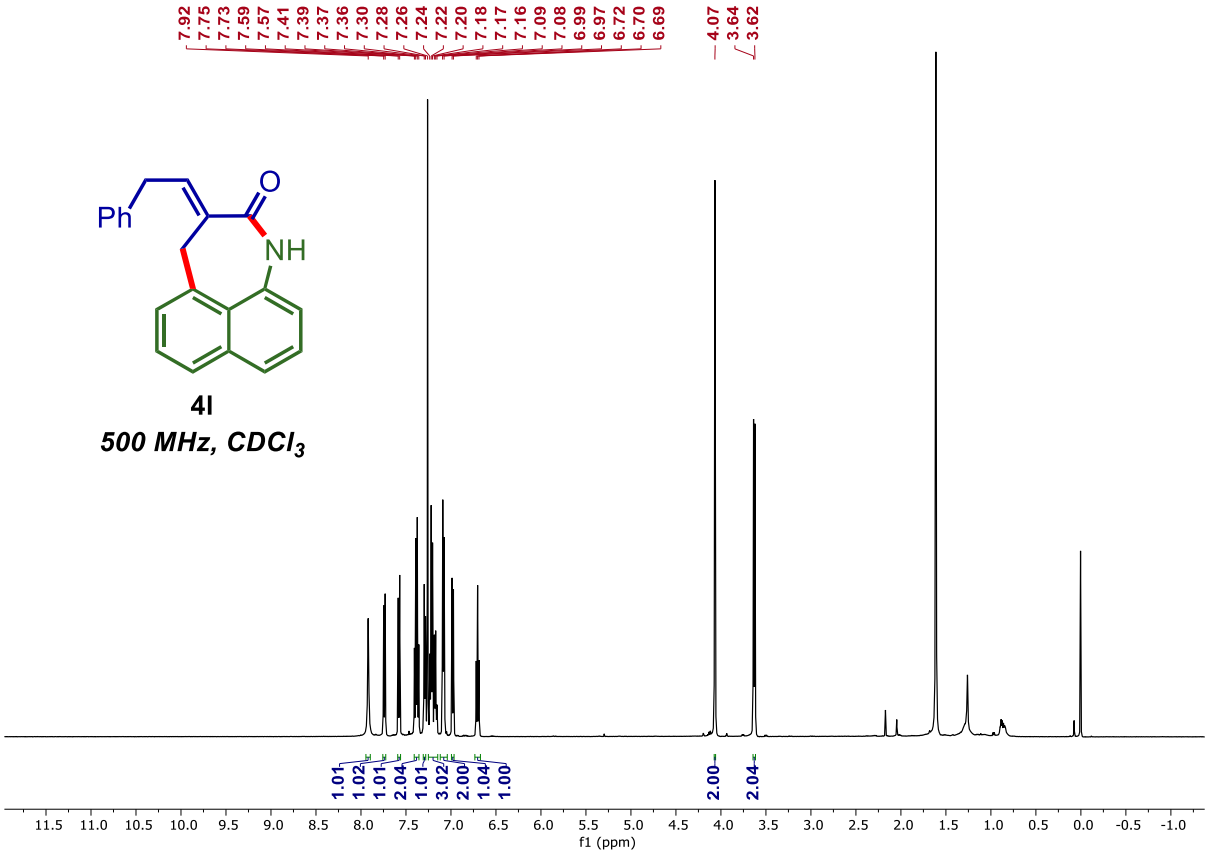

173.6
155.4
155.0
141.0
139.2
136.8
135.1
133.6
132.6
129.1
128.6
128.4
128.0
127.3
126.3
126.1
125.4
125.0
124.5
123.6
123.1
121.0
115.9
111.4
106.1
77.4
77.1
76.9
35.4
34.7
30.0
Bn
NH
O
O
4i
126 MHz, CDCl3
f1 (ppm)


8.16
7.85
7.83
7.39
7.38
7.37
7.32
7.30
7.28
7.26
7.25
7.21
7.19
7.18
7.17
7.16
7.13
7.11
7.09
6.99
6.98
6.59
6.58
6.56
3.88
2.68
2.66
2.64
2.58
2.56
2.54
2.53
Bn
O
NH
S
4j
500 MHz, CDCl3
1.00
1.00
1.00
3.03
2.06
2.05
3.02
1.03
1.00
2.00
2.00
2.01
f1 (ppm)


174.0
141.2
141.1
138.6
135.5
134.9
134.4
133.0
131.6
129.8
128.6
128.4
127.4
126.5
126.3
125.9
125.5
123.7
123.6
116.1
77.5
77.2
76.8
35.5
34.8
29.9
Bn
O
NH
S
4j
101 MHz, CDCl3
f1 (ppm)

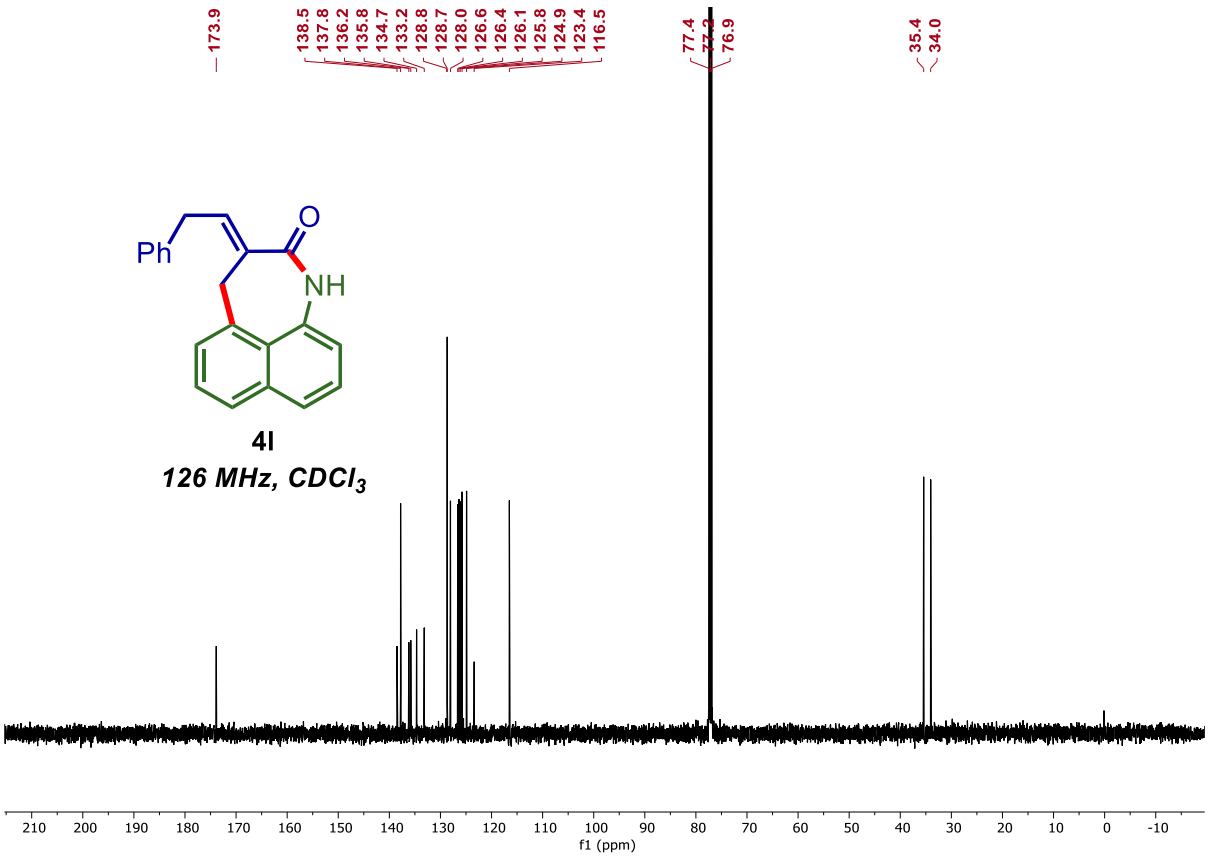

8.05 7.95 7.93 7.92 7.88 7.87 7.82 7.80 7.56 7.54 7.52 7.42 7.41 7.32 7.31 7.29 7.28 7.26 7.25 7.19 7.18 7.17 7.09 7.07 6.68 6.66 6.65
3.97
2.75 2.74 2.73 2.72 2.65 2.64 2.62 2.61
Bn
O
NH
4k
500 MHz, CDCl3
1.03 2.05 2.02 1.00 3.02 1.02 2.08 3.11 2.01 1.02 1.00
2.00
2.02 2.05
f1 (ppm)


174.0 141.1 138.7 138.4 136.8 135.5 135.0 134.3 133.5 133.1 132.7 128.9 128.6 128.5 128.2 127.9 127.6 126.5 126.5 126.3 126.3 126.2 125.9 123.6 116.1
77.5 77.2 76.8
35.6 34.8 30.0
Bn
O
NH
4k
101 MHz, CDCl3
f1 (ppm)



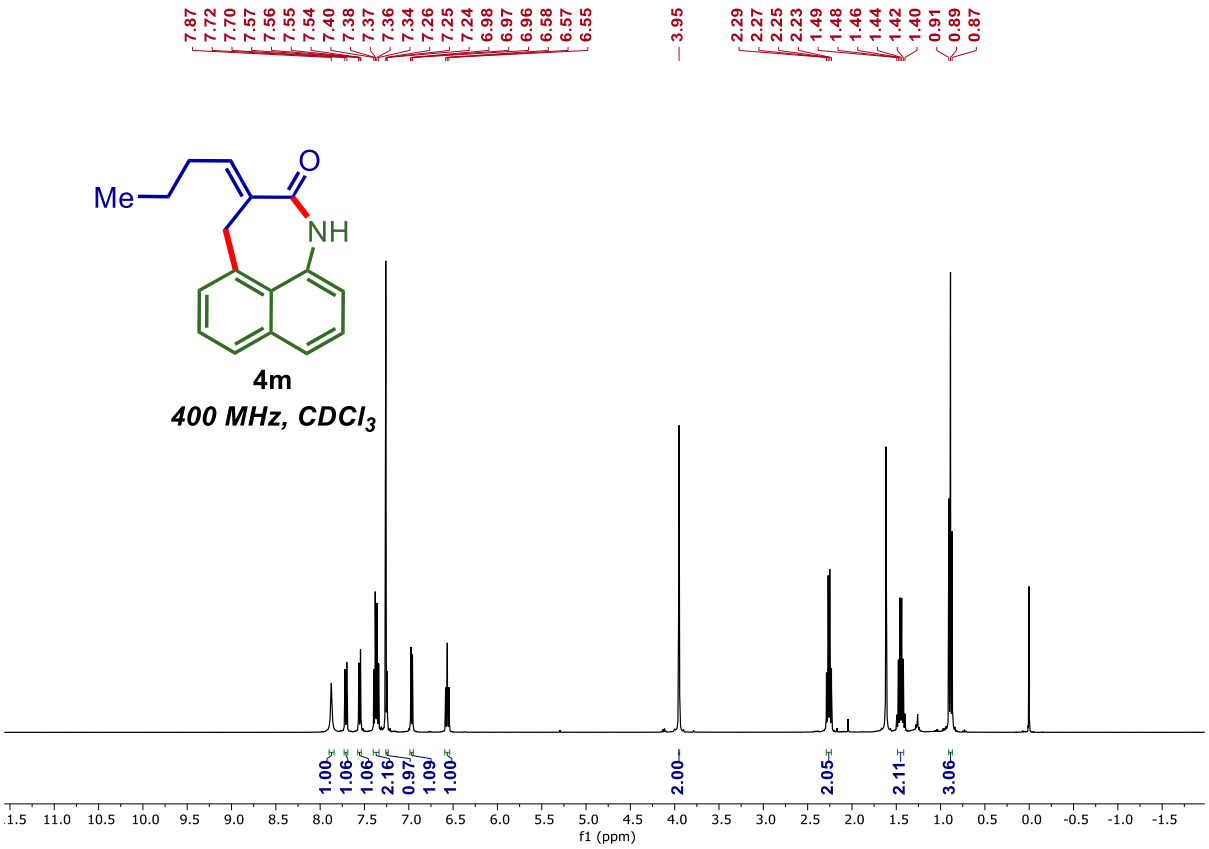
4l

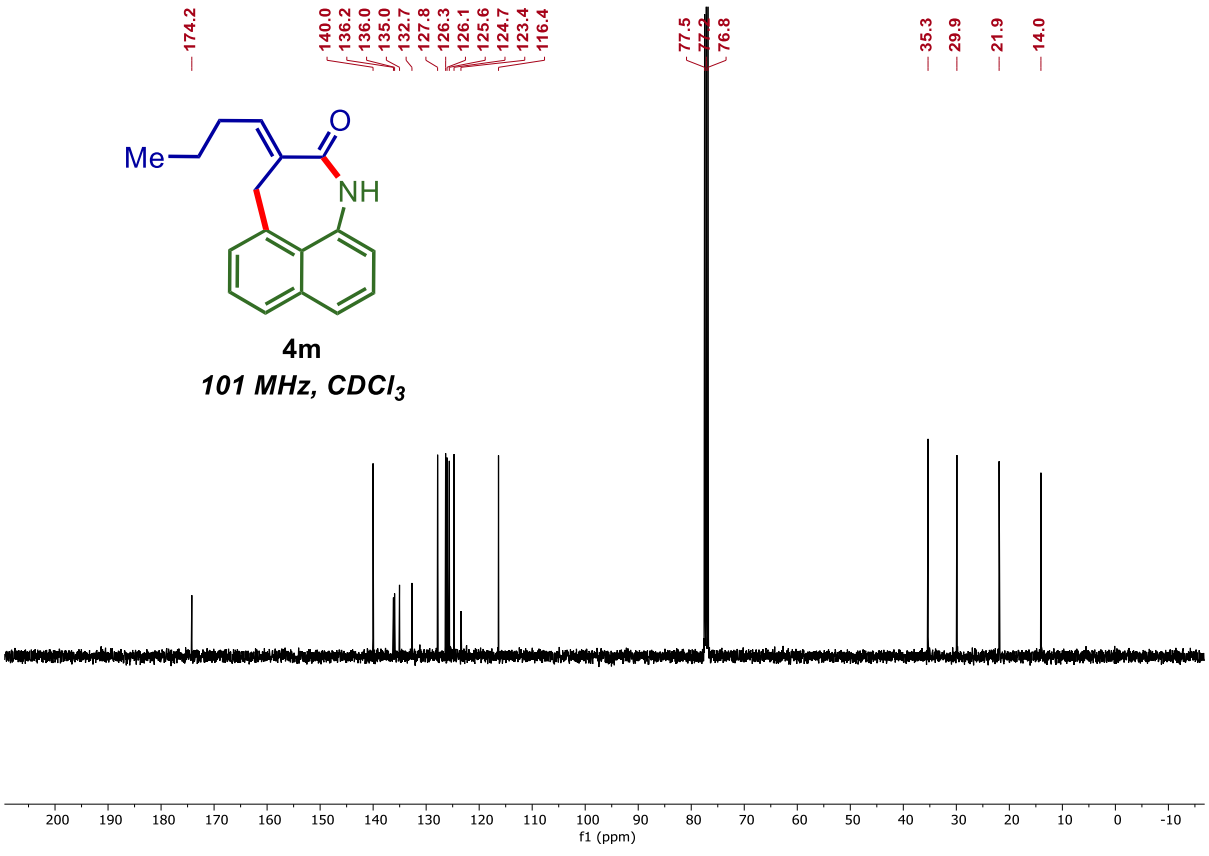
500 MHz, $CDCl_3$

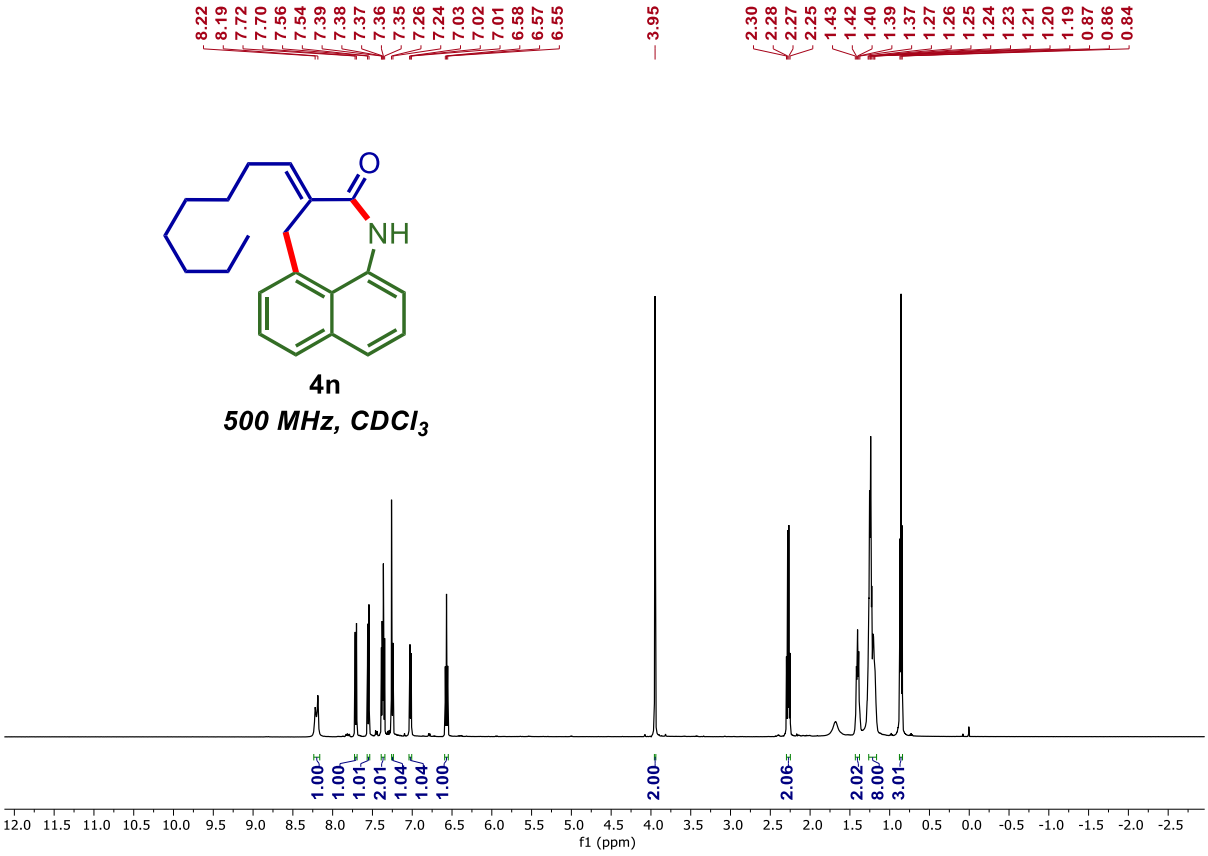


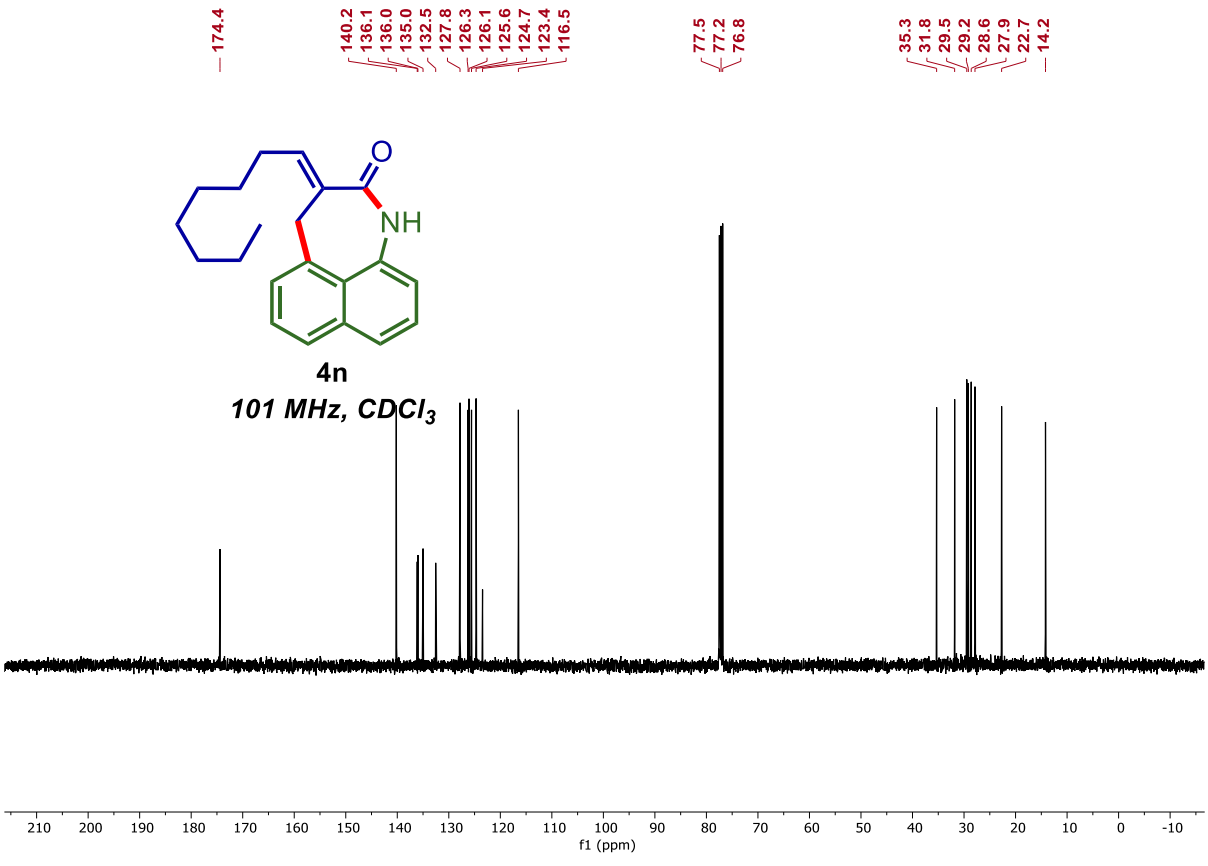
4l

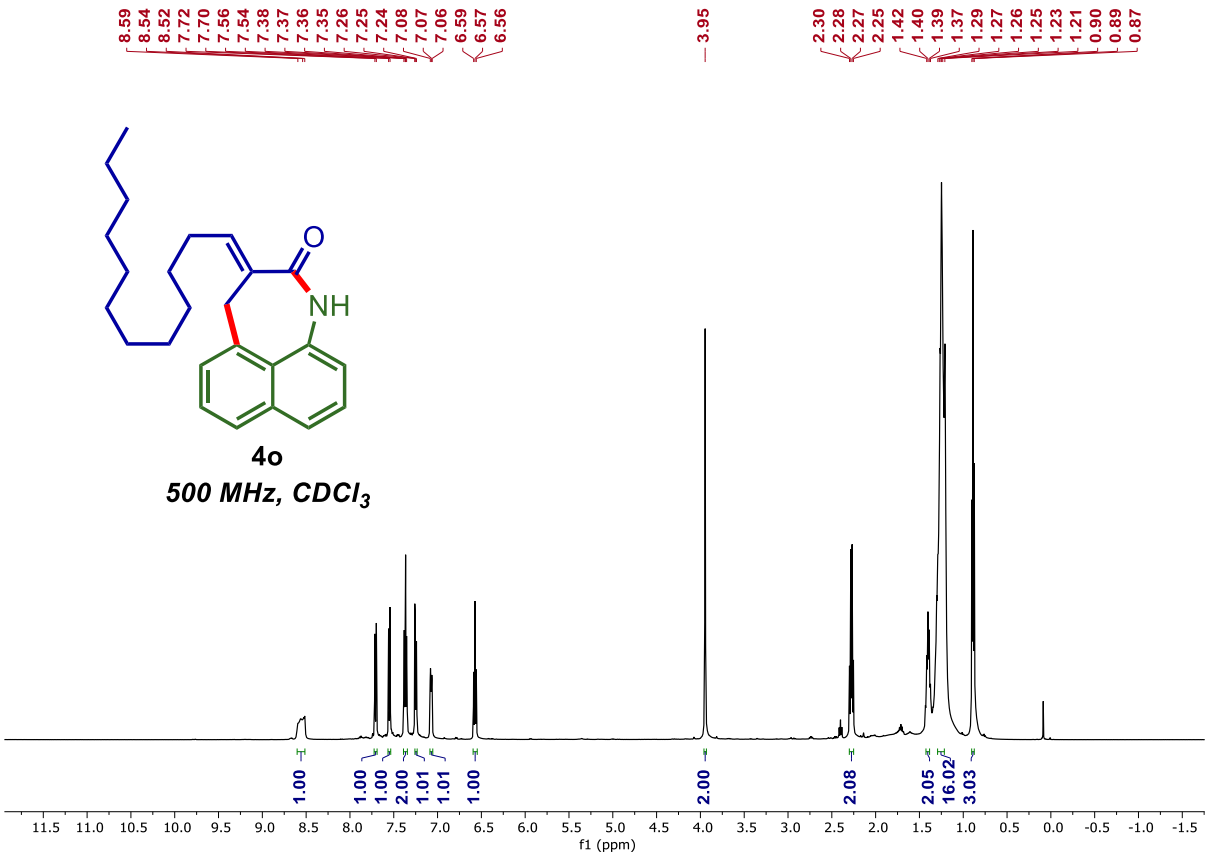
126 MHz, $CDCl_3$

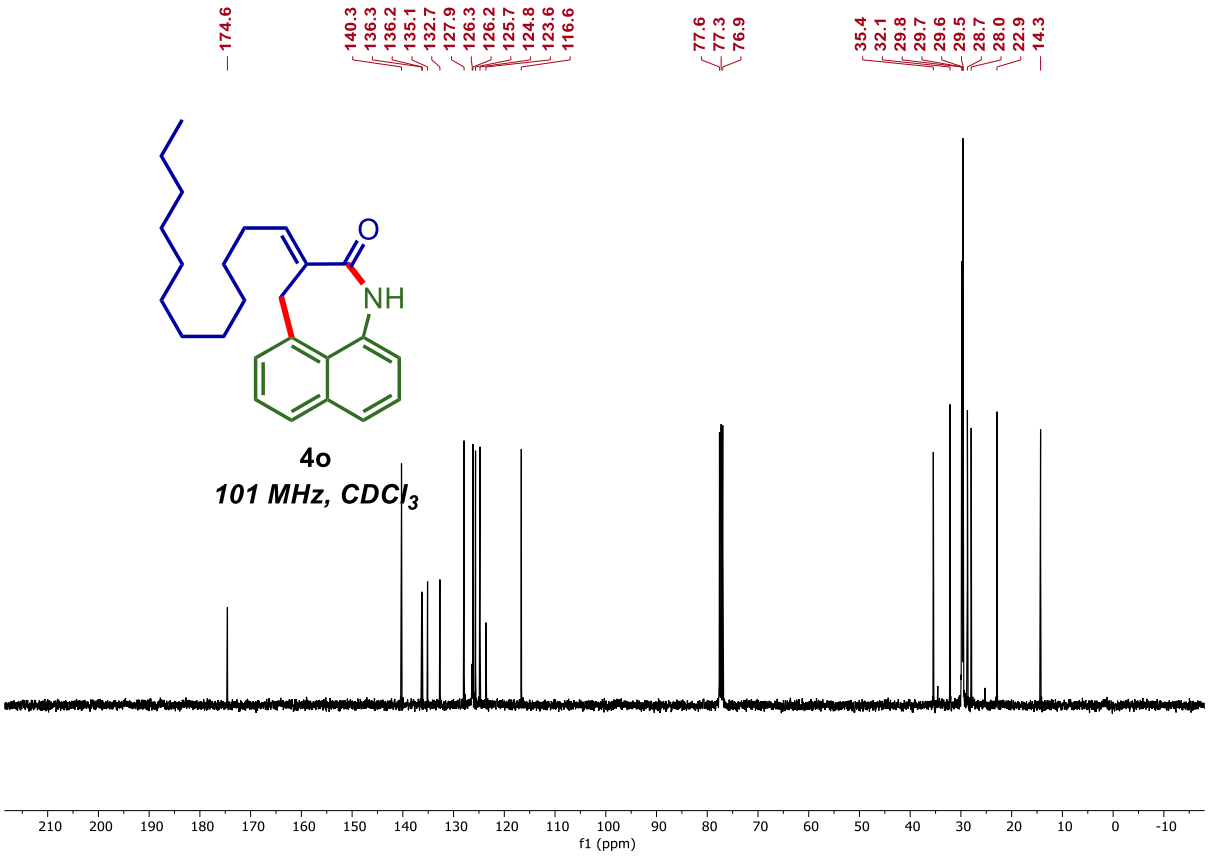

7.87
7.72
7.70
7.57
7.56
7.55
7.54
7.40
7.38
7.37
7.36
7.34
7.26
7.25
7.24
6.98
6.97
6.96
6.58
6.57
6.55
3.95
2.29
2.27
2.25
2.23
1.49
1.48
1.46
1.44
1.42
1.40
0.91
0.89
0.87
Me
O
NH
4m
400 MHz, CDCl3
1.00
1.06
1.06
2.16
0.97
1.09
1.00
2.00
2.05
2.11
3.06
f1 (ppm)

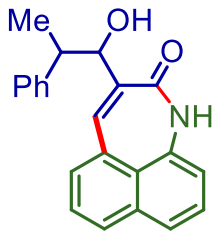

174.2
140.0
136.2
136.0
135.0
132.7
127.8
126.3
126.1
125.6
124.7
123.4
116.4
77.5
77.2
76.8
35.3
29.9
21.9
14.0
Me
O
NH
4m
101 MHz, CDCl3
f1 (ppm)


8.22
8.19
7.72
7.70
7.56
7.54
7.39
7.38
7.37
7.36
7.35
7.26
7.24
7.03
7.02
7.01
6.58
6.57
6.55
3.95
2.30
2.28
2.27
2.25
1.43
1.42
1.40
1.39
1.37
1.27
1.26
1.25
1.24
1.23
1.21
1.20
1.19
0.87
0.86
0.84
O
NH
4n
500 MHz, CDCl3
1.00
1.00
1.01
2.01
1.04
1.04
1.00
2.00
2.06
2.02
8.00
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)


174.4
140.2
136.1
136.0
135.0
132.5
127.8
126.3
126.1
125.6
124.7
123.4
116.5
77.5
77.2
76.8
35.3
31.8
29.5
29.2
28.6
27.9
22.7
14.2
O
NH
4n
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

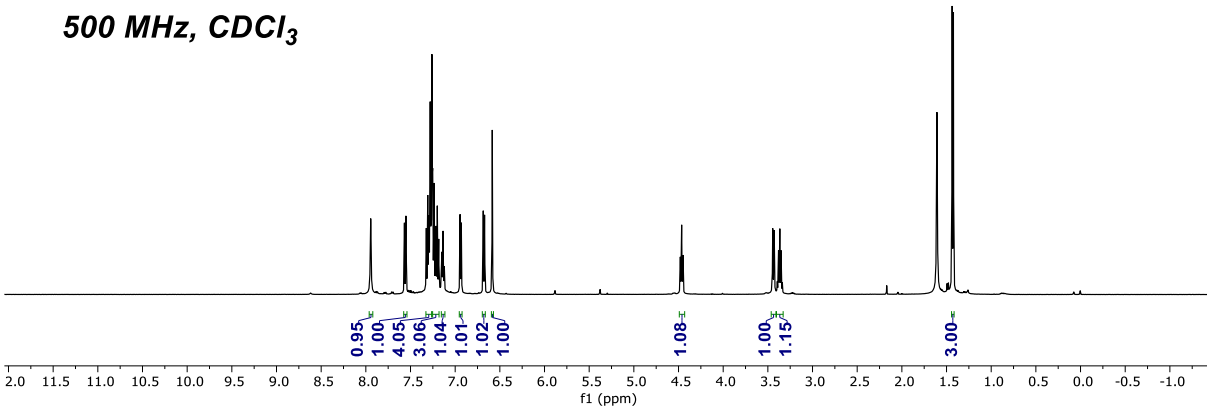

8.59
8.54
8.52
7.72
7.70
7.56
7.54
7.38
7.37
7.36
7.35
7.26
7.25
7.24
7.08
7.07
7.06
6.59
6.57
6.56
3.95
2.30
2.28
2.27
2.25
1.42
1.40
1.39
1.37
1.29
1.27
1.26
1.25
1.23
1.21
0.90
0.89
0.87
O
NH
4o
500 MHz, CDCl3
1.00
1.00
1.00
2.00
1.01
1.01
1.00
2.00
2.08
2.05
16.02
3.03
f1 (ppm)

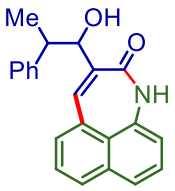

174.6
140.3
136.3
136.2
135.1
132.7
127.9
126.3
126.2
125.7
124.8
123.6
116.6
77.6
77.3
76.9
35.4
32.1
29.8
29.7
29.6
29.5
28.7
28.0
22.9
14.3
O
NH
4o
101 MHz, CDCl3
f1 (ppm)



5a

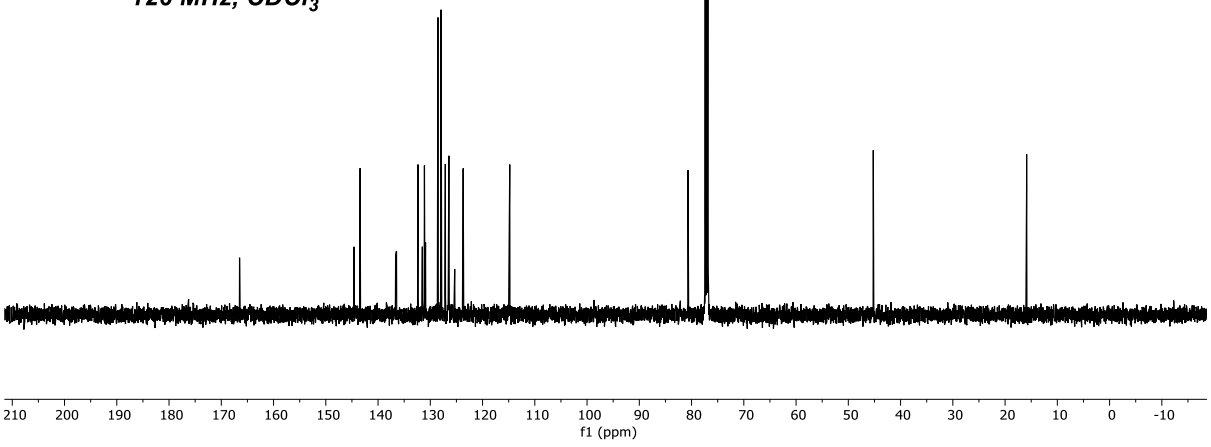
500 MHz, $CDCl_3$

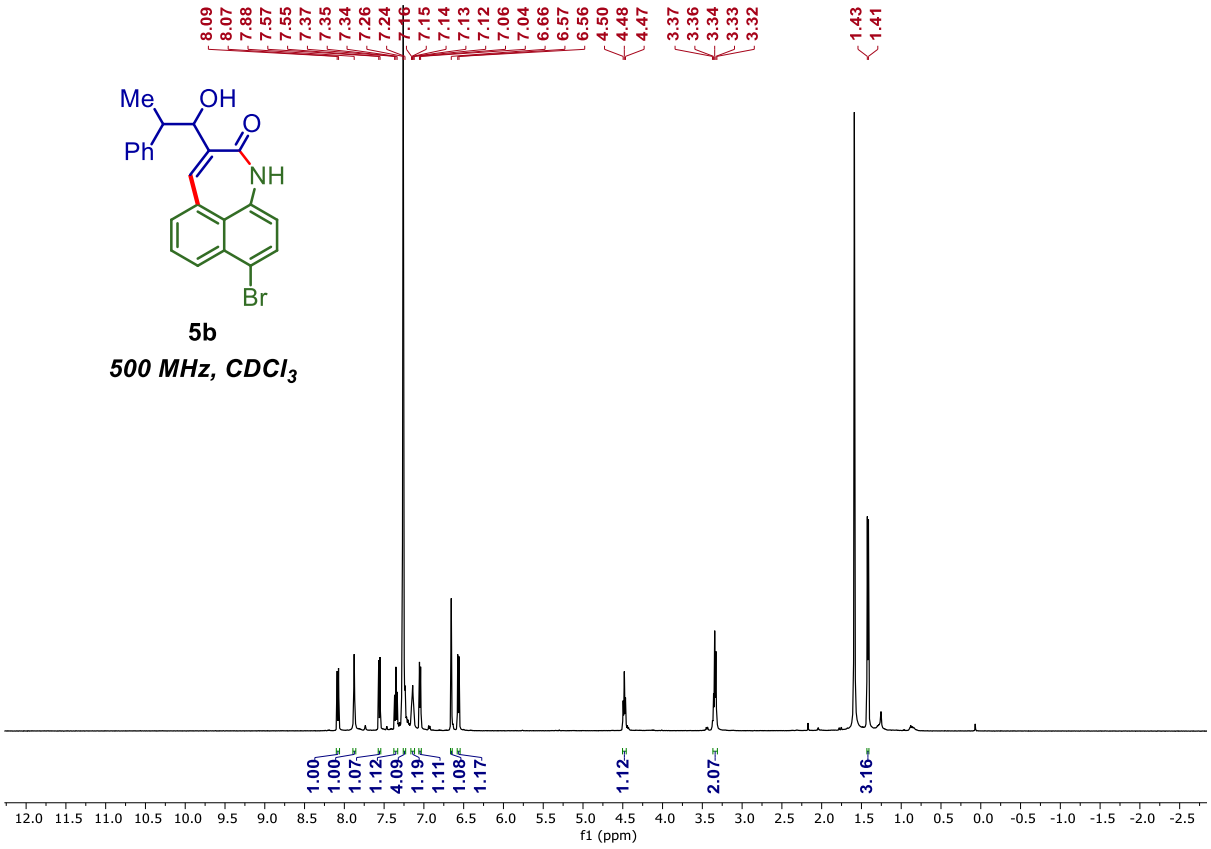




5a

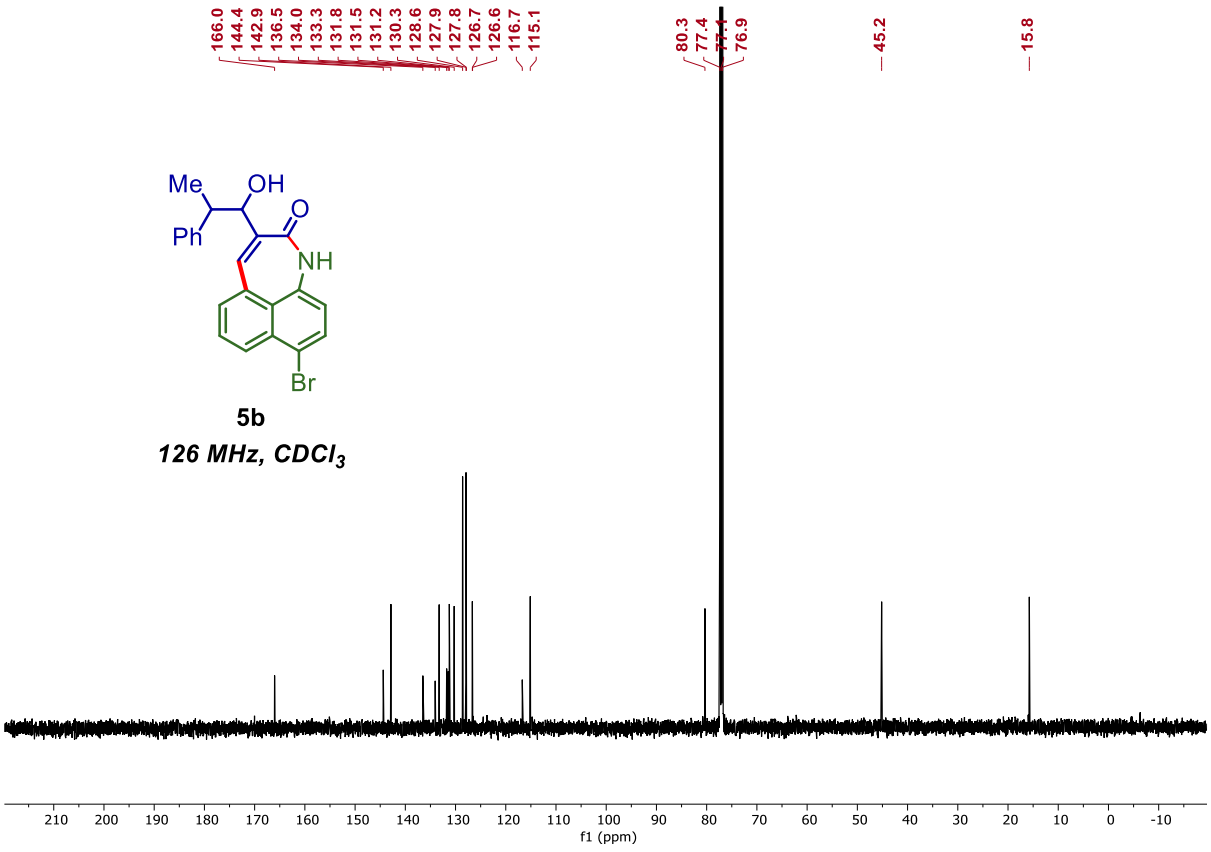
126 MHz, $CDCl_3$





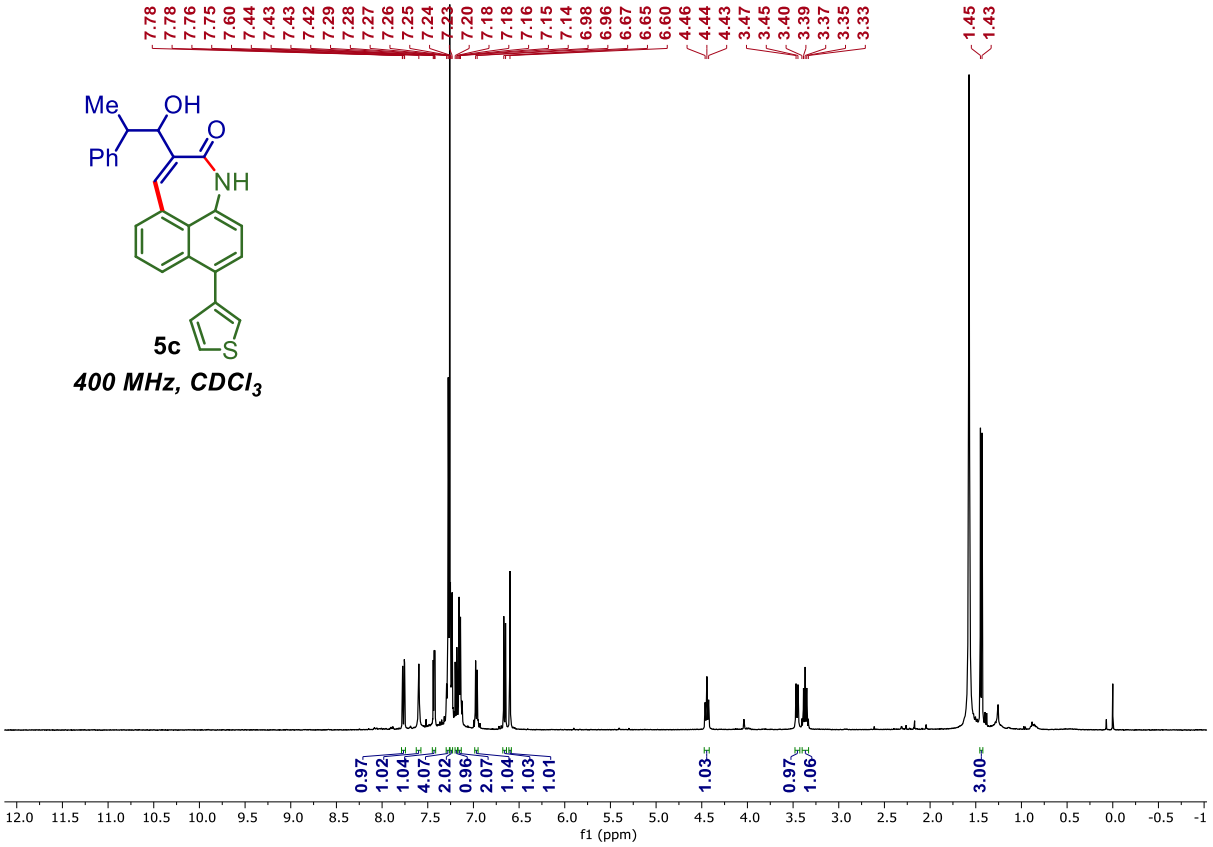
5b

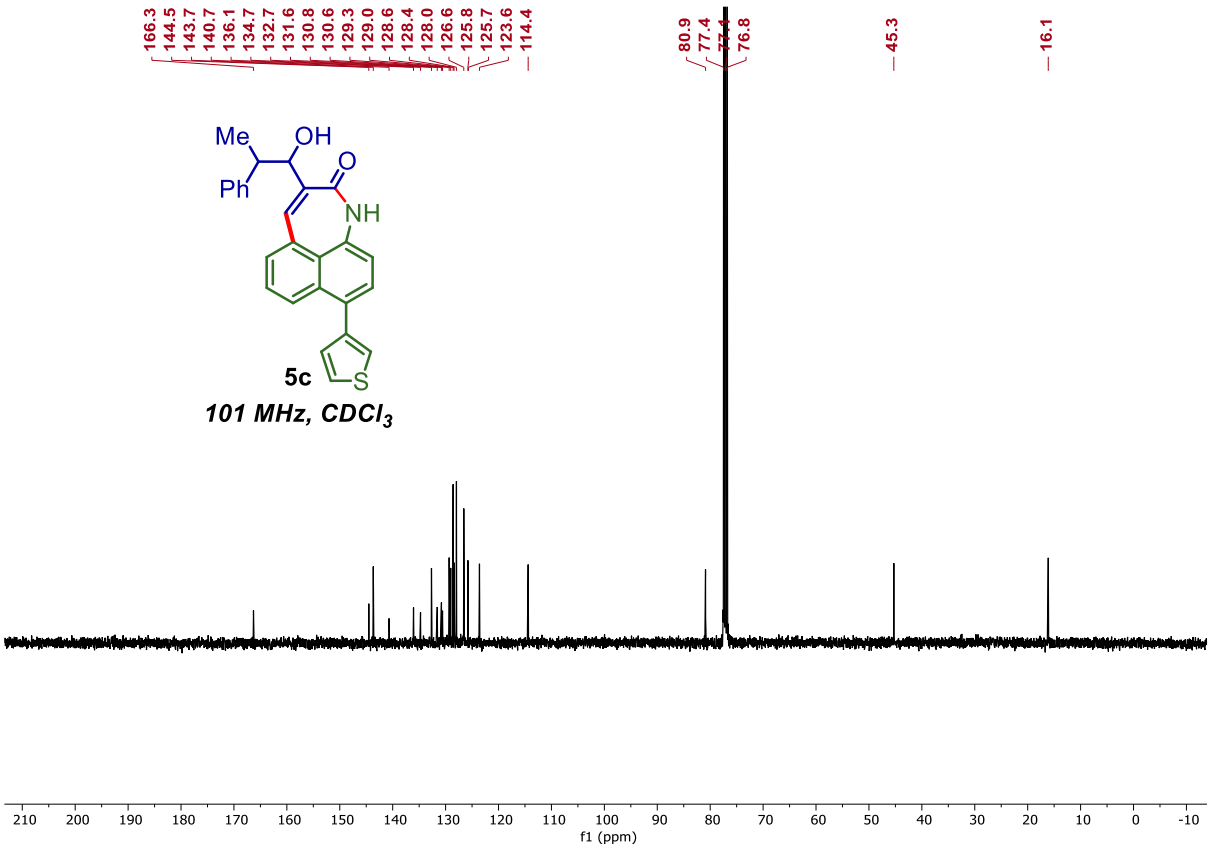
500 MHz, $CDCl_3$

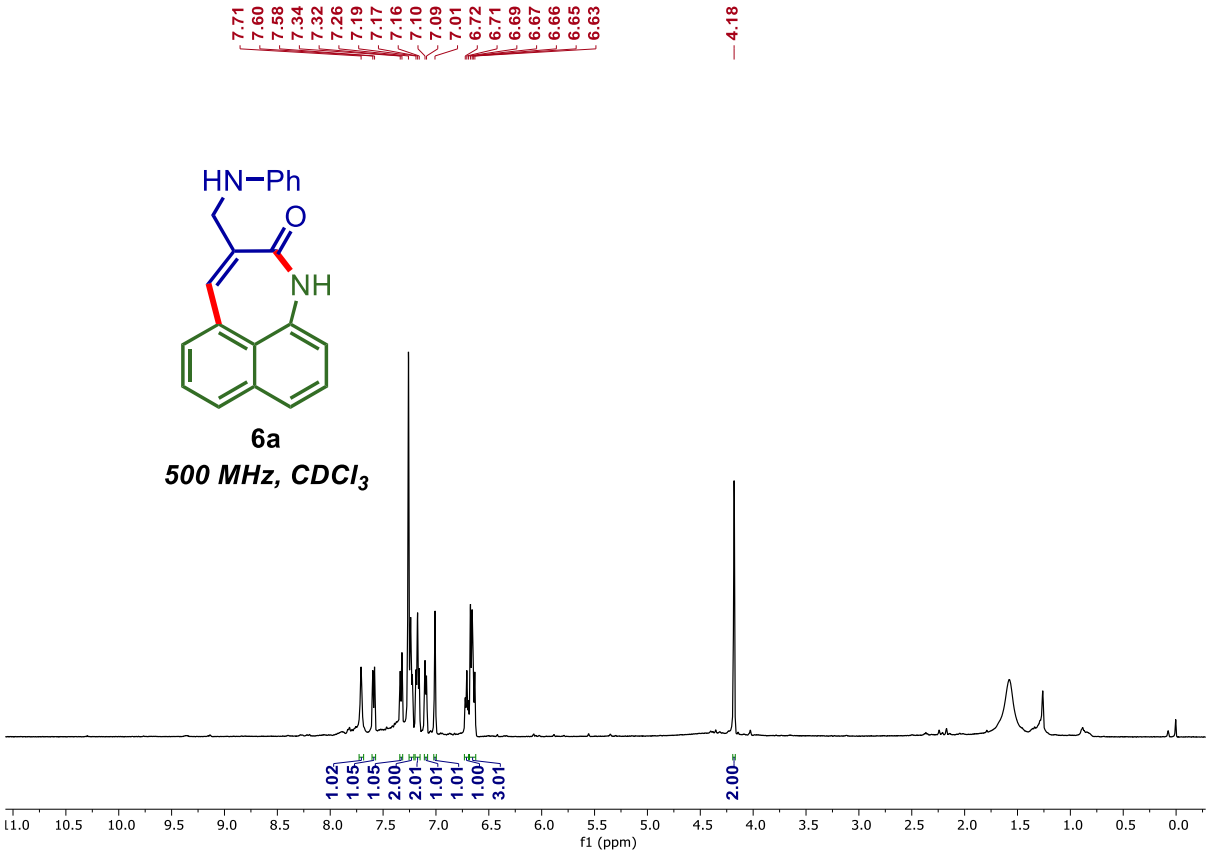


5b

126 MHz, $CDCl_3$

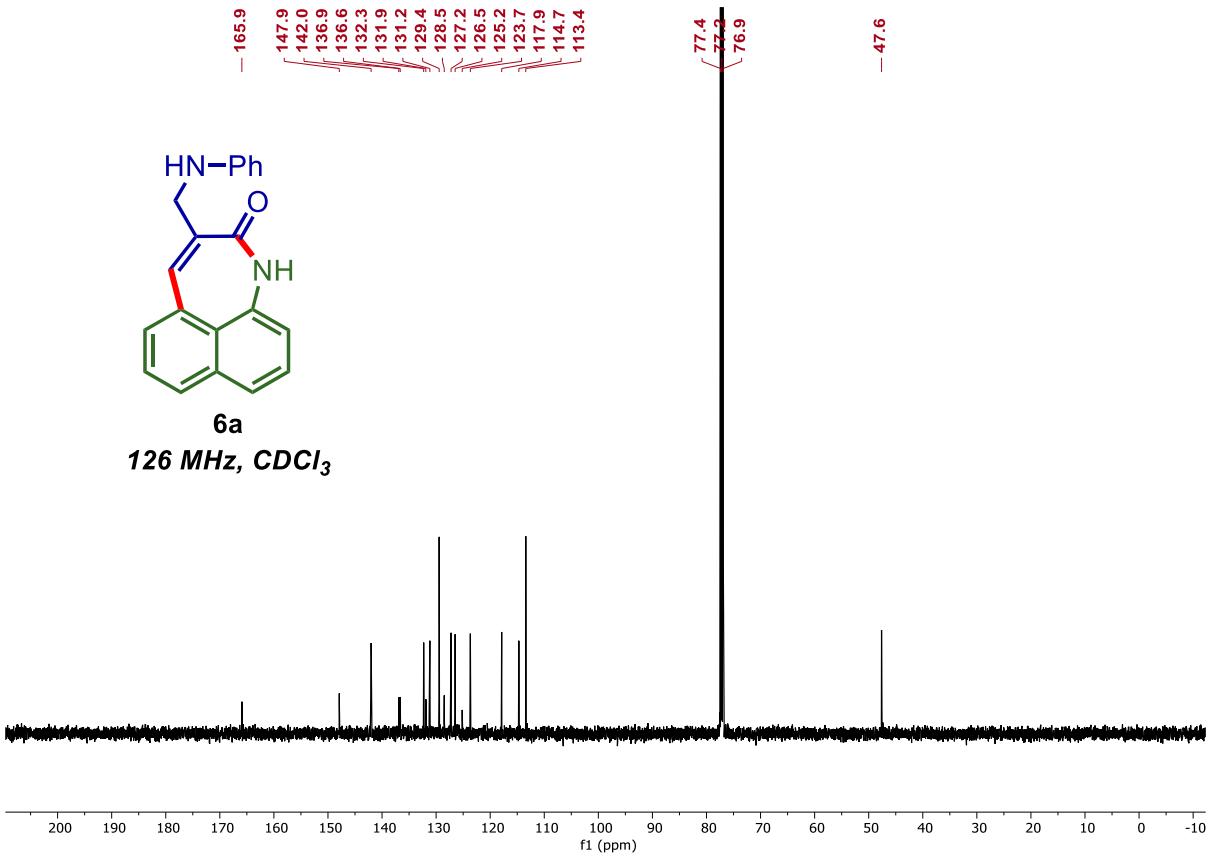

7.78
7.78
7.76
7.75
7.60
7.44
7.43
7.43
7.42
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.20
7.18
7.18
7.16
7.15
7.14
6.98
6.96
6.67
6.65
6.60
4.46
4.44
4.43
3.47
3.45
3.40
3.39
3.37
3.35
3.33
1.45
1.43
Me
OH
Ph
O
NH
S
5c
400 MHz, CDCl3
0.97
1.02
1.04
4.07
2.02
0.96
2.07
1.04
1.03
1.01
1.03
0.97
1.06
3.00
f1 (ppm)


166.3
144.5
143.7
140.7
136.1
134.7
132.7
131.6
130.8
130.6
129.3
129.0
128.6
128.4
128.0
126.6
125.8
125.7
123.6
114.4
80.9
77.4
77.1
76.8
45.3
16.1
Me
OH
Ph
O
NH
S
5c
101 MHz, CDCl3
f1 (ppm)



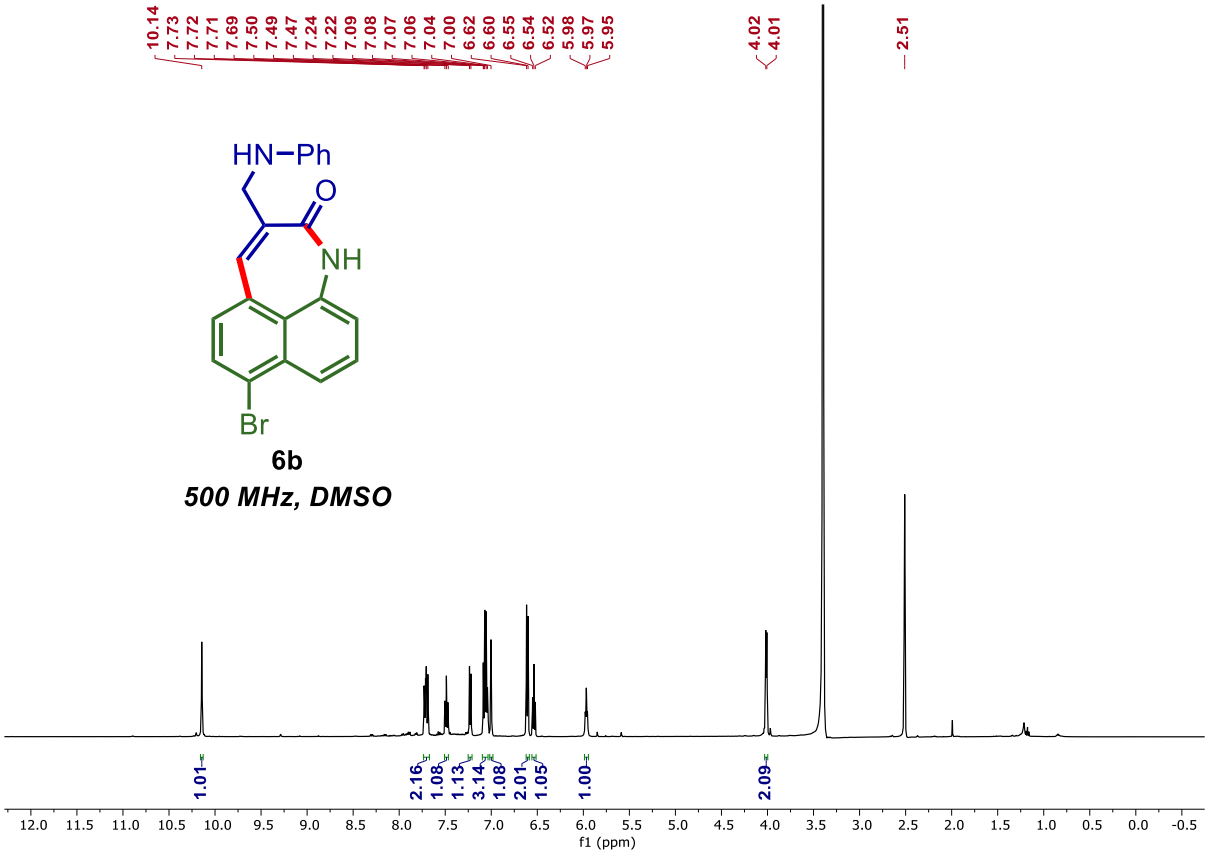
6a

500 MHz, $CDCl_3$



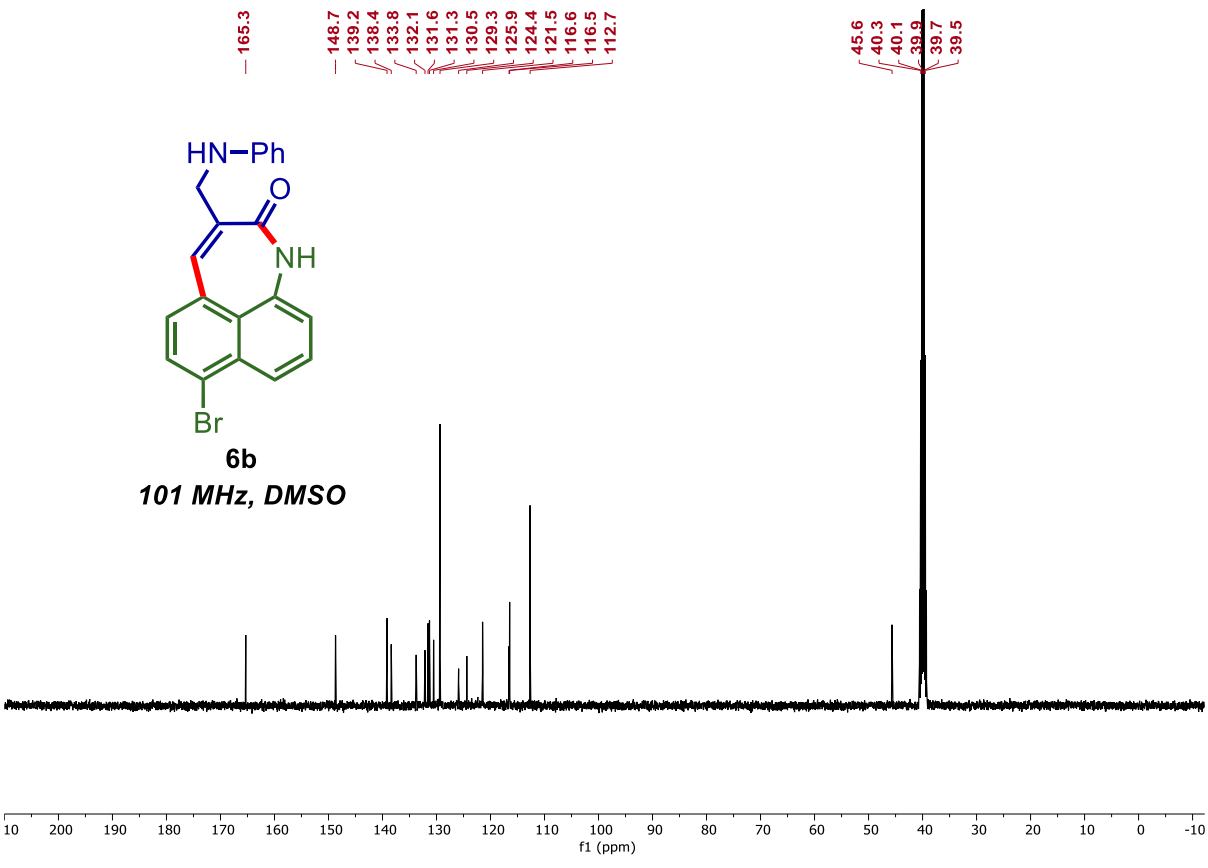
6a

126 MHz, $CDCl_3$



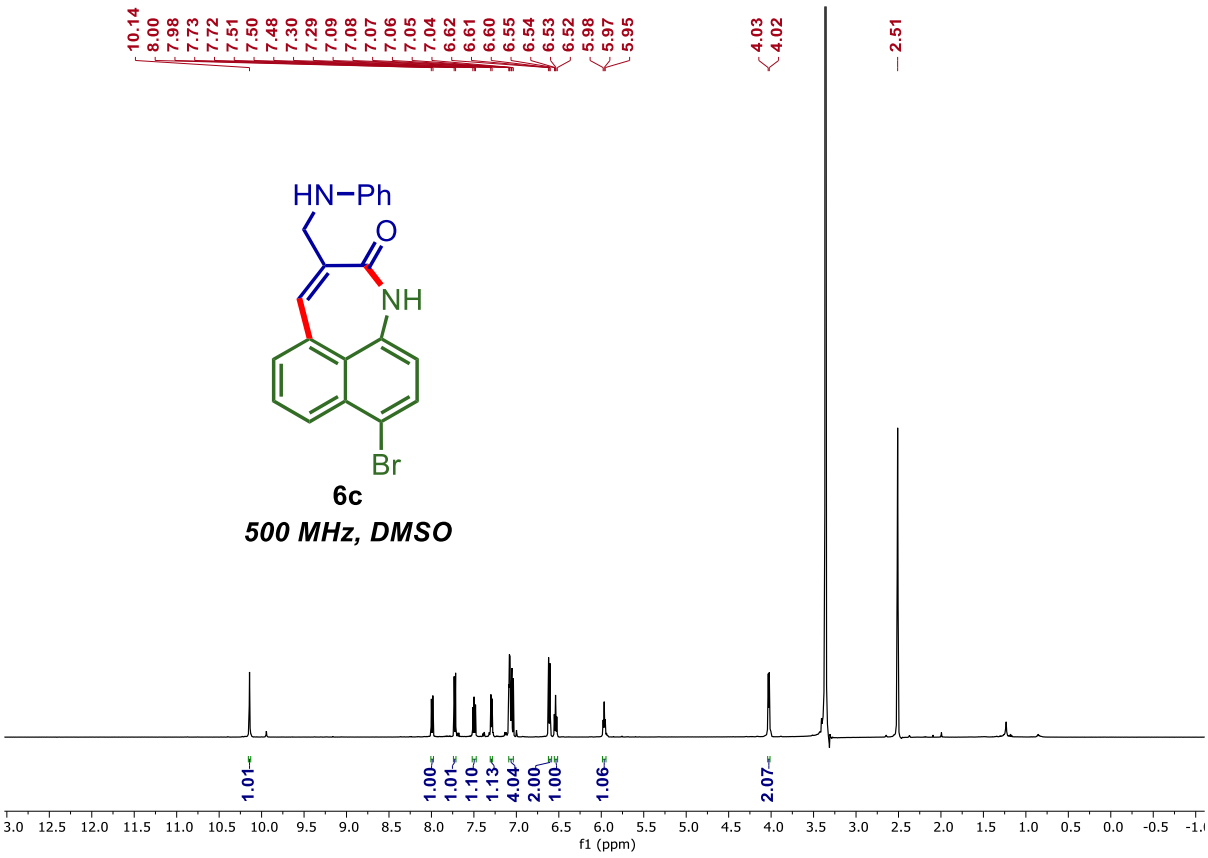
6b

500 MHz, DMSO



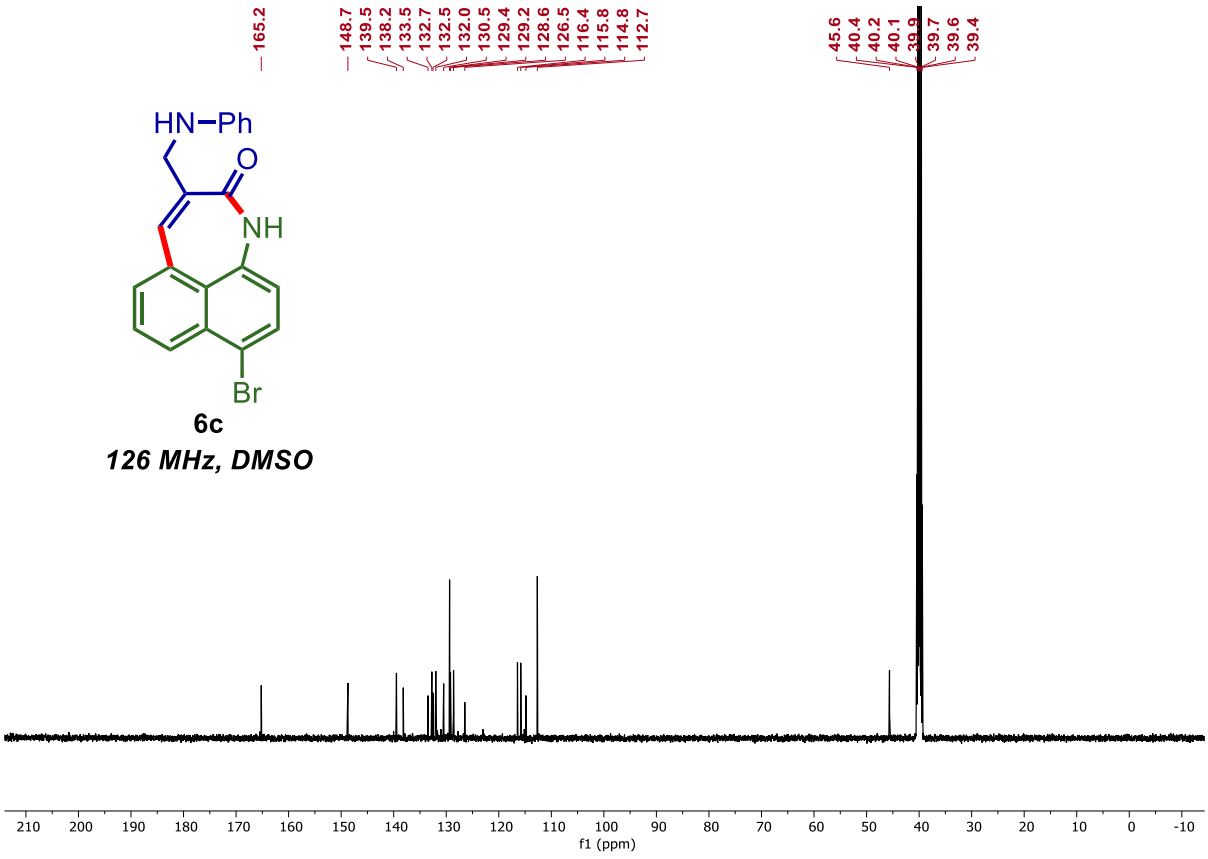
6b

101 MHz, DMSO



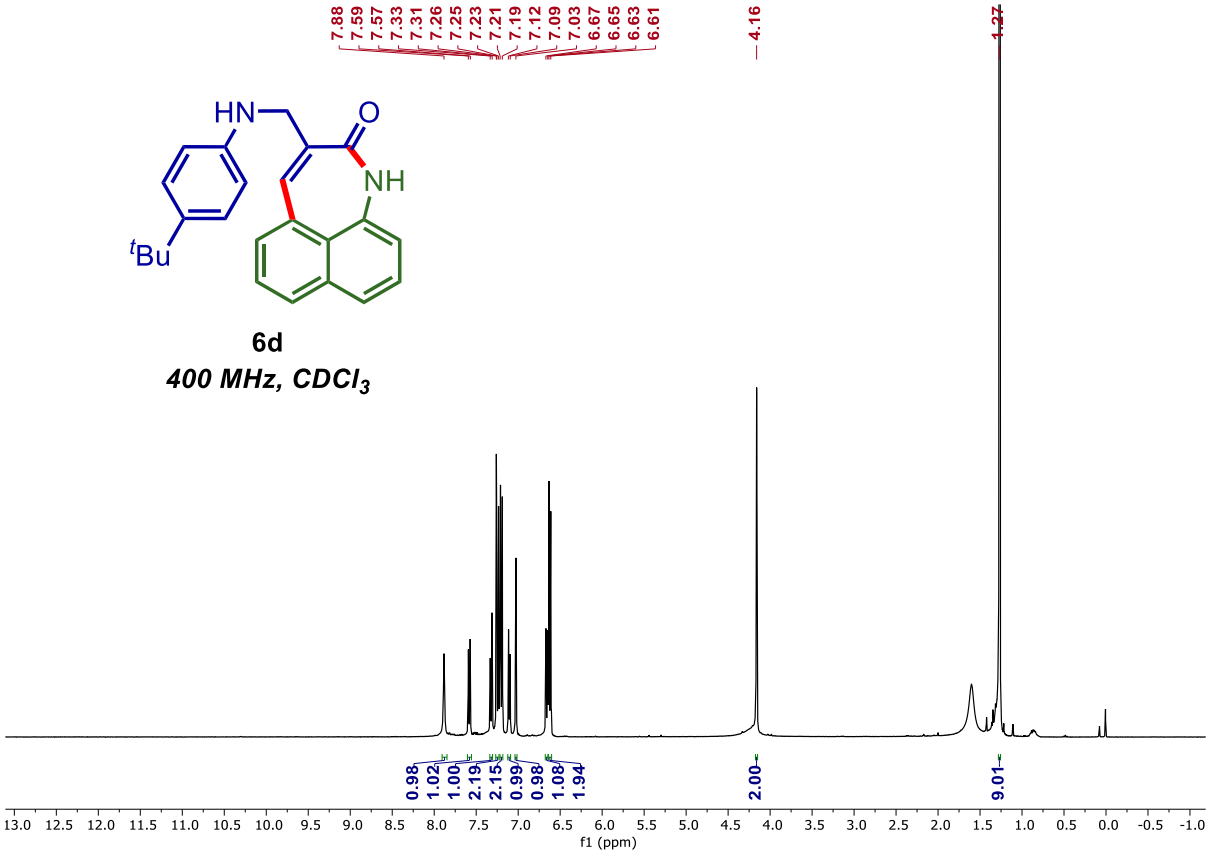
6c

500 MHz, DMSO



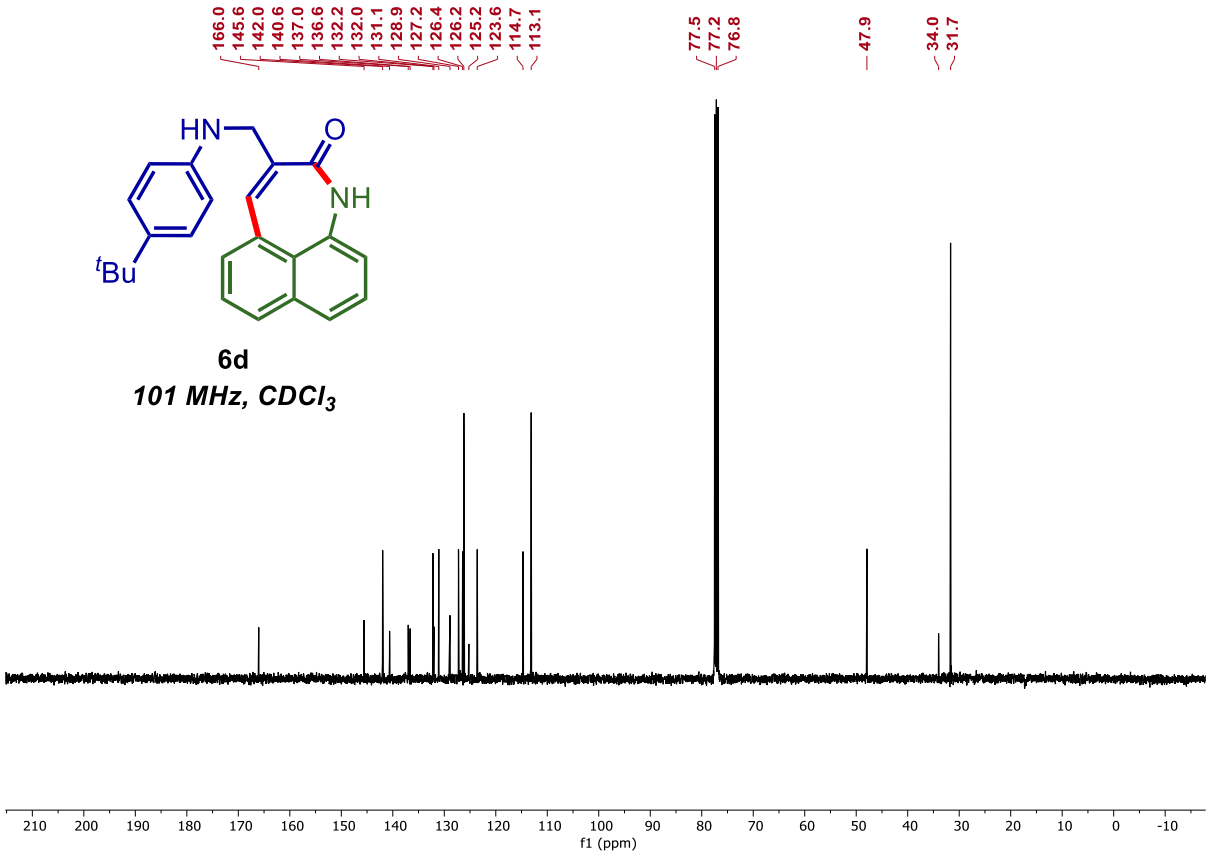
6c

126 MHz, DMSO



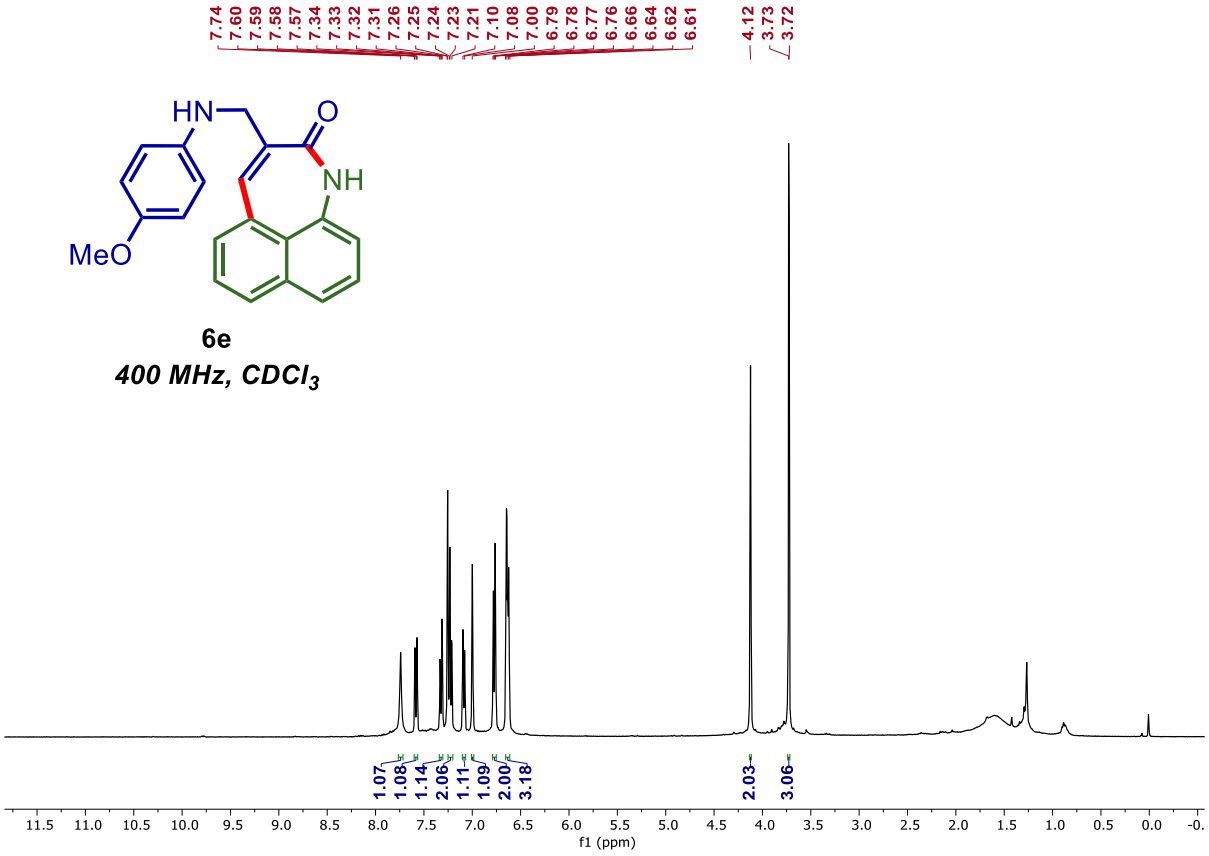
6d

400 MHz, $CDCl_3$



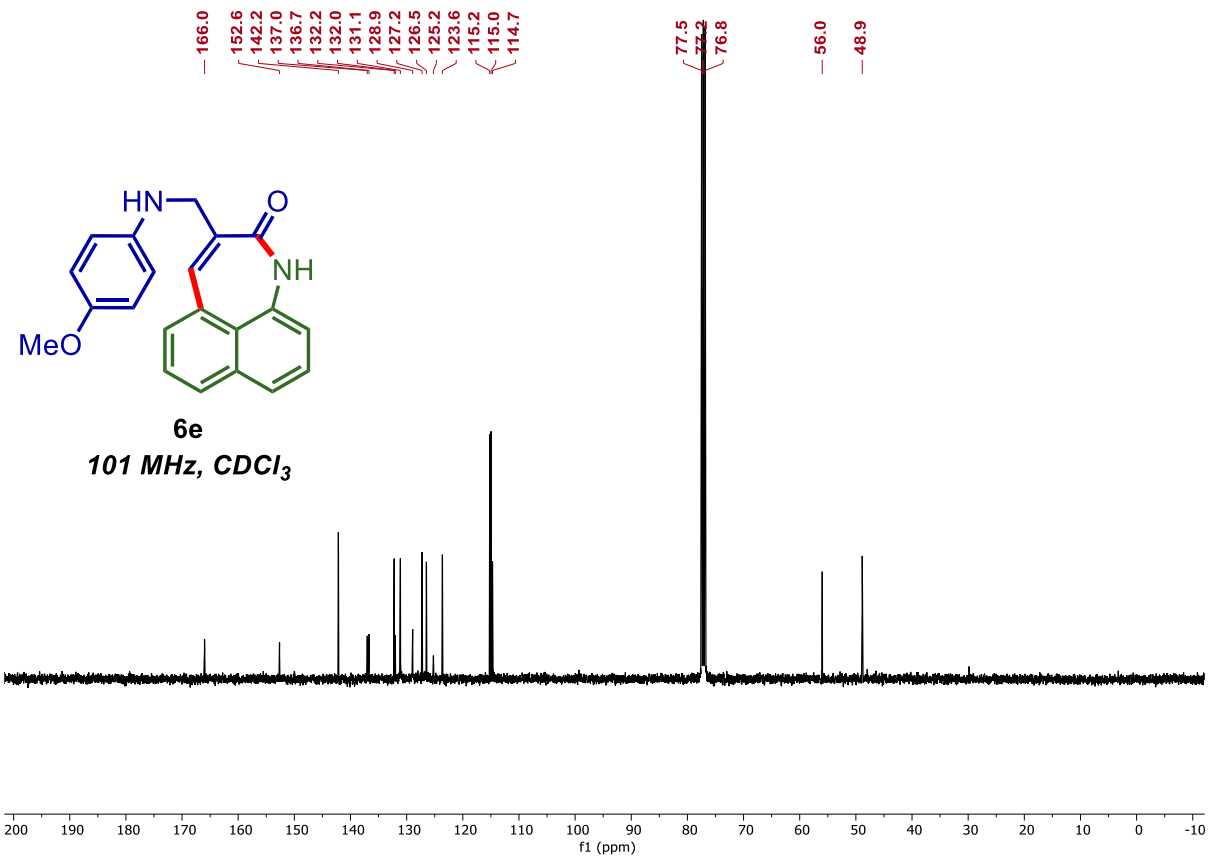
6d

101 MHz, $CDCl_3$



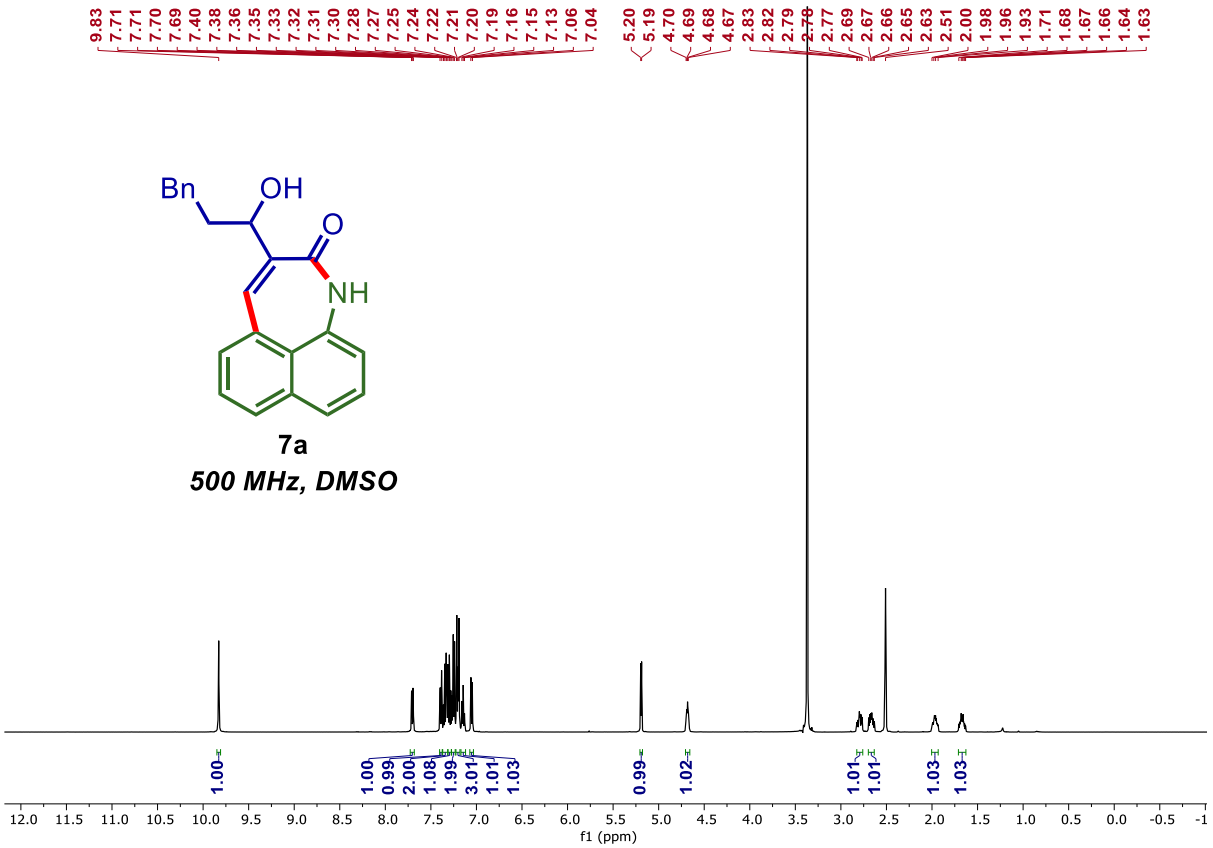
6e

400 MHz, $CDCl_3$



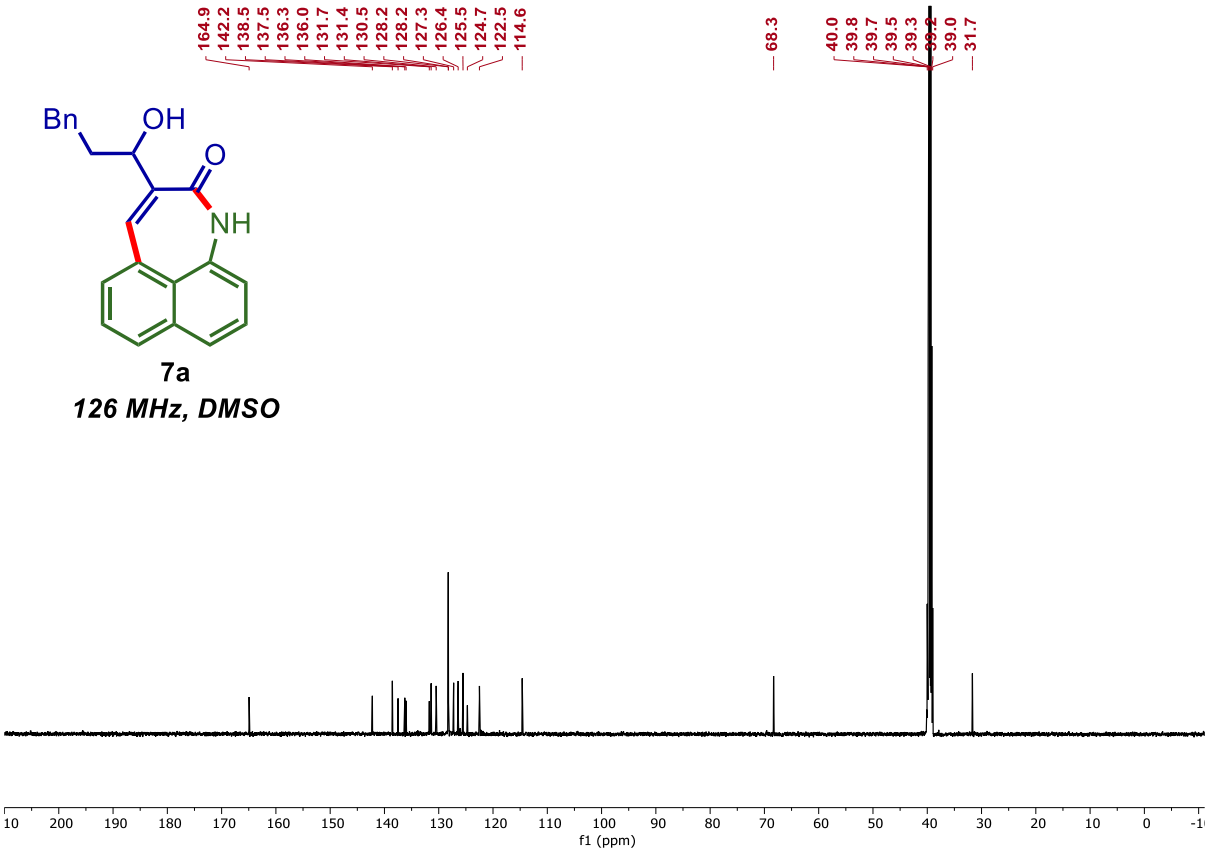
6e

101 MHz, $CDCl_3$



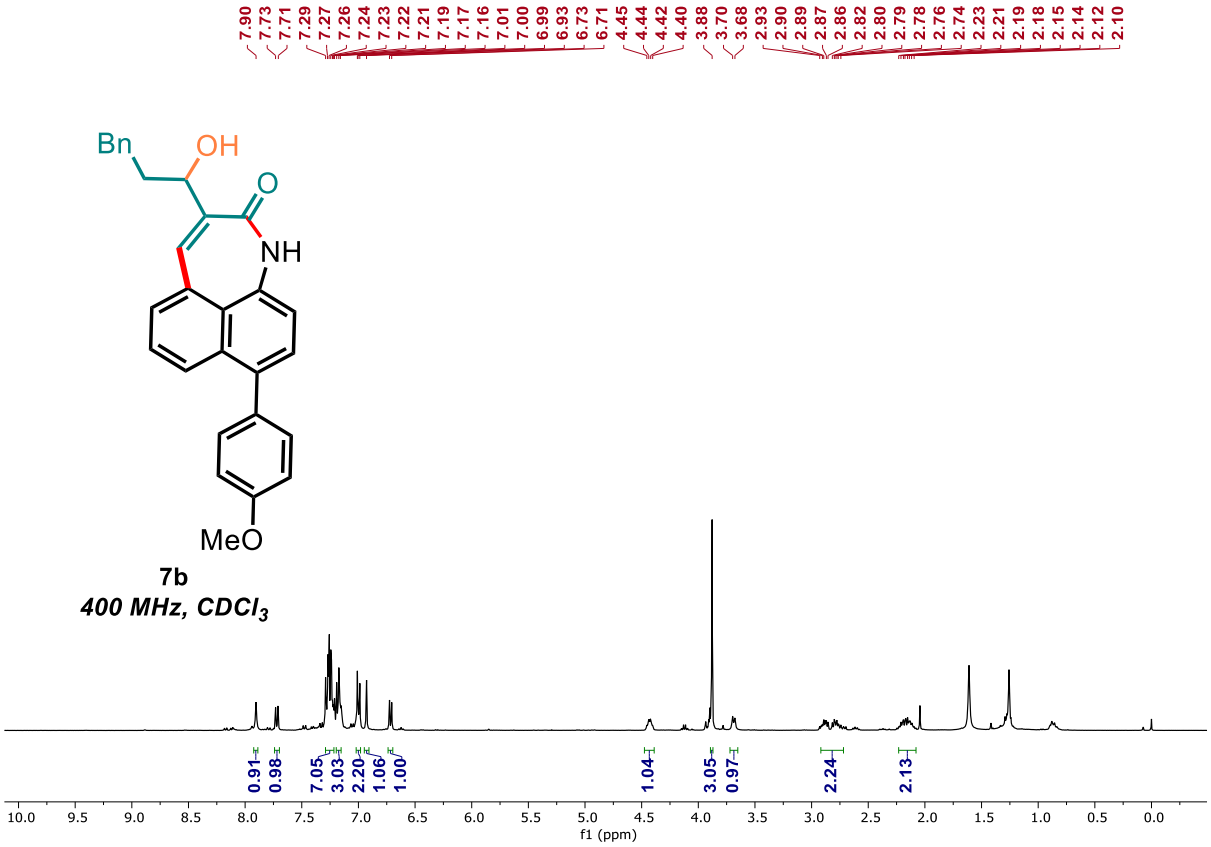
7a

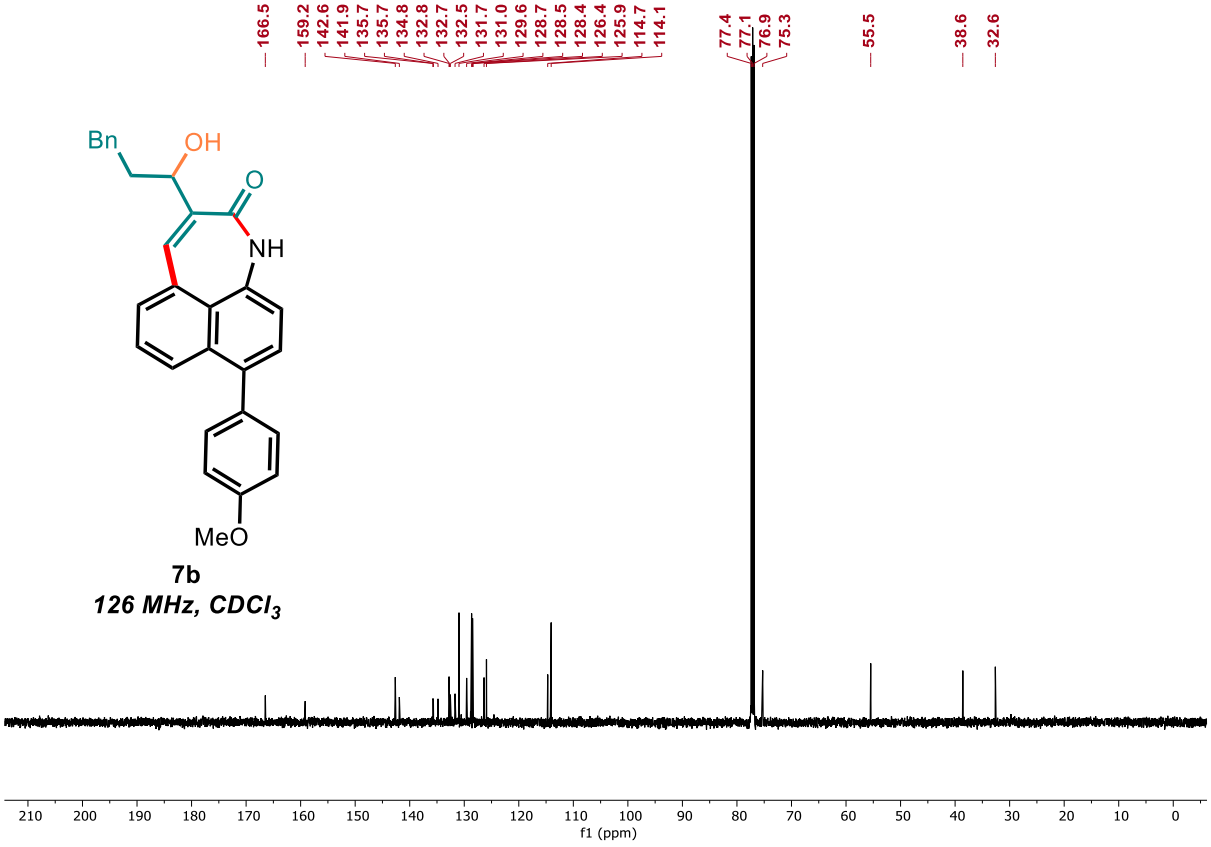
500 MHz, DMSO

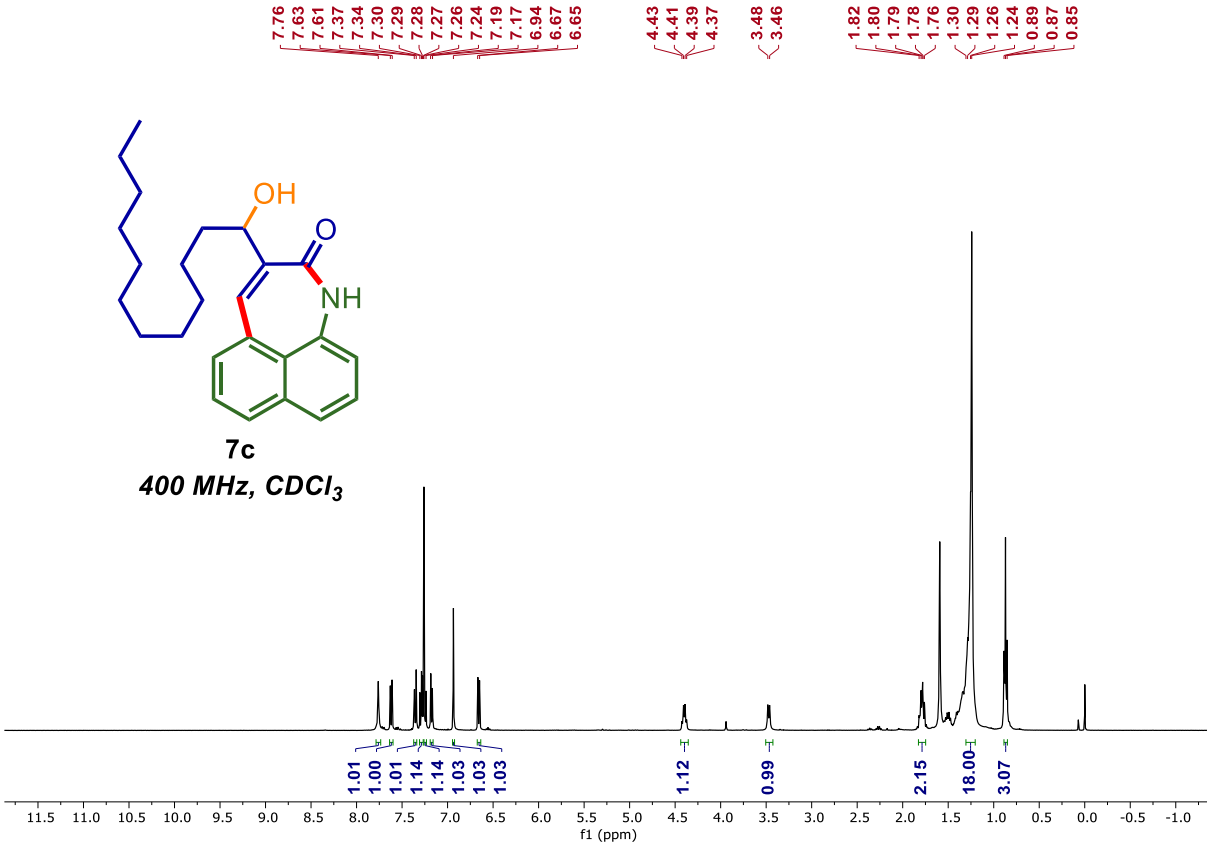


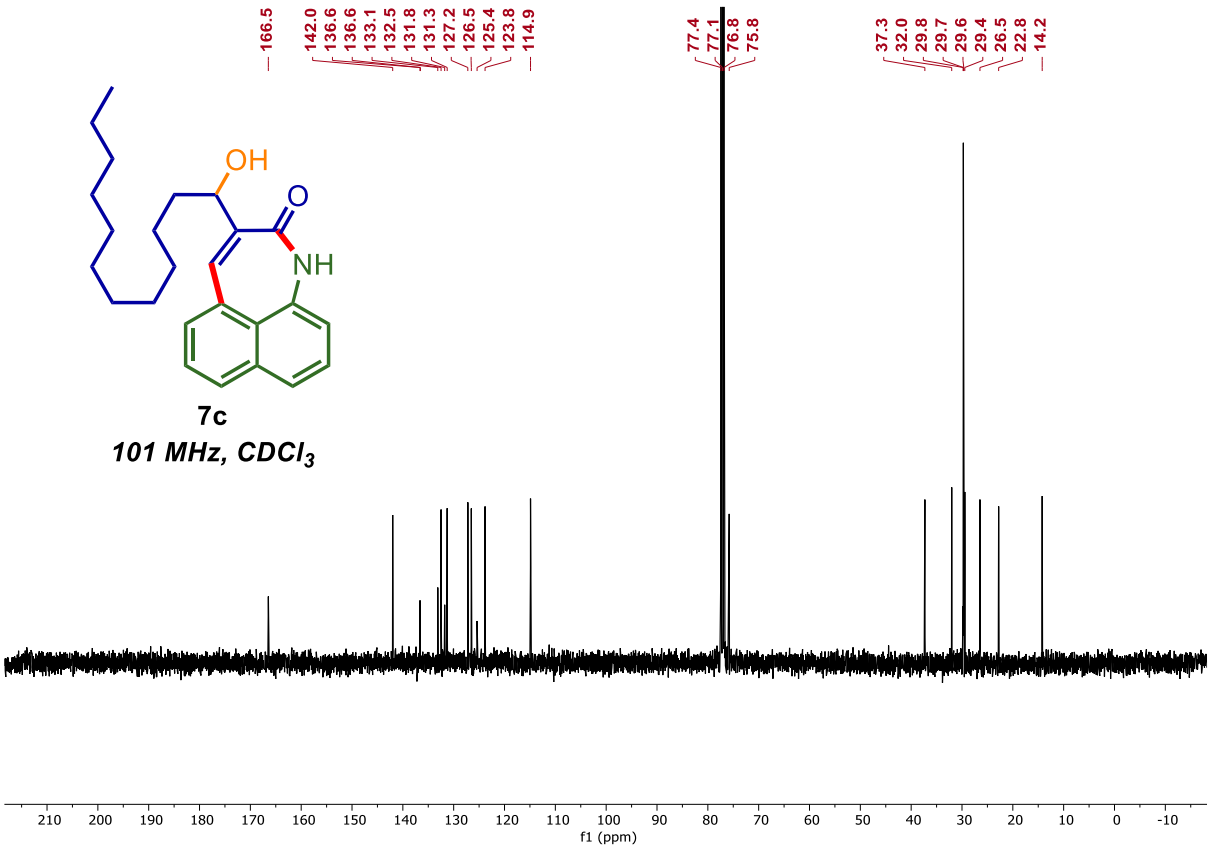
7a

126 MHz, DMSO


7.90
7.73
7.71
7.29
7.27
7.26
7.24
7.23
7.22
7.21
7.19
7.17
7.16
7.01
7.00
6.99
6.93
6.73
6.71
4.45
4.44
4.42
4.40
3.88
3.70
3.68
2.93
2.90
2.89
2.87
2.86
2.82
2.80
2.79
2.78
2.76
2.74
2.23
2.21
2.19
2.18
2.15
2.14
2.12
2.10
Bn
OH
O
NH
MeO
7b
400 MHz, CDCl3
0.91
0.98
7.05
3.03
2.20
1.06
1.00
1.04
3.05
0.97
2.24
2.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.5
159.2
142.6
141.9
135.7
135.7
134.8
132.8
132.7
132.5
131.7
131.0
129.6
128.7
128.5
128.4
126.4
125.9
114.7
114.1
77.4
77.1
76.9
75.3
55.5
38.6
32.6
Bn
OH
O
NH
MeO
7b
126 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.76
7.63
7.61
7.37
7.34
7.30
7.29
7.28
7.27
7.26
7.24
7.19
7.17
6.94
6.67
6.65
4.43
4.41
4.39
4.37
3.48
3.46
1.82
1.80
1.79
1.78
1.76
1.30
1.29
1.26
1.24
0.89
0.87
0.85
OH
O
NH
7c
400 MHz, CDCl3
1.01
1.00
1.01
1.14
1.14
1.03
1.03
1.03
1.12
0.99
2.15
18.00
3.07
f1 (ppm)


166.5
142.0
136.6
136.6
133.1
132.5
131.8
131.3
127.2
126.5
125.4
123.8
114.9
77.4
77.1
76.8
75.8
37.3
32.0
29.8
29.7
29.6
29.4
26.5
22.8
14.2
OH
O
NH
7c
101 MHz, CDCl3
f1 (ppm)