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Supporting Information

Palladium-Catalyzed Diastereoselective Cross-Coupling of Two Aryl Halides via C–H Activation: Synthesis of Chiral Eight-Membered Nitrogen Heterocycles

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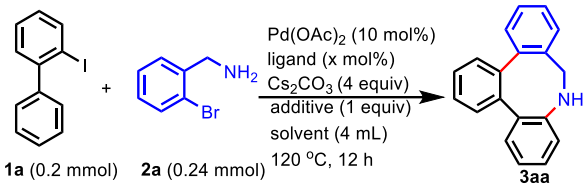
1. General Information:

$Pd(OAc)_2$ was purchased from Strem Chemicals. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400 instrument (400 MHz) or Bruker DRX-600 instrument (600 MHz). High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. Optical rotations were taken on AUTOPOL VI. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase using a Shimadzu instrument. NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2-Iodobiphenyls (**1**) were synthesized by following the reported procedures.[1] 2-Bromobenzylamine derivatives (**2a**, **2p** - **2r**, **4a**) are commercially available. Other 2-bromobenzylamines derivative (**2b** - **2o**) were synthesized by following the reported procedure.[2]

2. Optimization of Reaction Conditions:



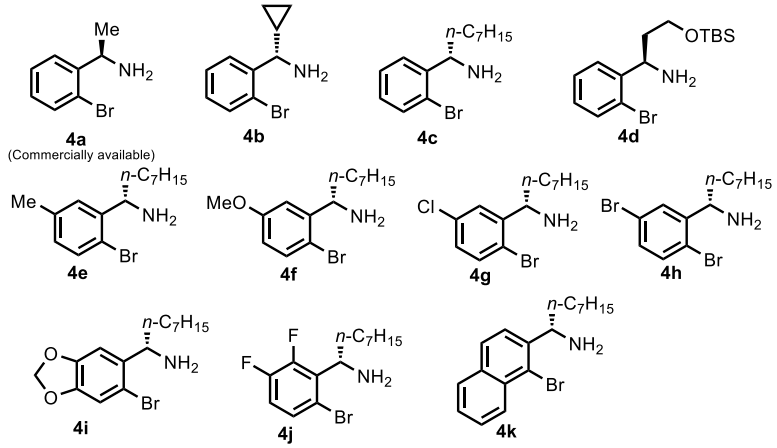
1a (0.2 mmol) **2a** (0.24 mmol) **3aa**

entry	ligand (x mol%)	additive	solvent	yield (%) [a]
1	-		DMF	-
2	PPh_3 (20)		DMF	45
3	PCy_3 (20)		DMF	27
4	$P(4\text{-}MeC_6H4)_3$ (20)		DMF	31
5	$P(o\text{-}tol)_3$ (20)		DMF	trace
6	BINAP (12)		DMF	49
7	Dppe (12)		DMF	-
8	Dppp (12)		DMF	-
9	Dppb (12)		DMF	trace
10	Dppf (12)		DMF	28
11	DPEphos (12)		DMF	58
12	Xantphos (12)		DMF	60
13	Xantphos (12)	TBACl	DMF	48
14	Xantphos (12)	TBAB	DMF	60
15	Xantphos (12)	TBAI	DMF	77
16	Xantphos (12)	TBAI	DMA	85
17	Xantphos (12)	TBAI	DMSO	50
18	Xantphos (12)	TBAI	toluene	46
19	Xantphos (12)	TBAI	MeCN	45
20	Xantphos (12)	TBAI	1.4-dioxane	20

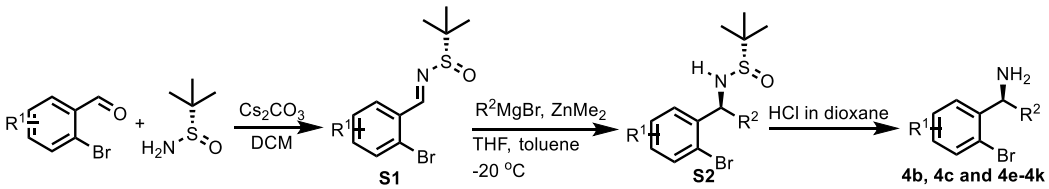
21	Xantphos (12)	TBAI	DMA	93%[b] (91%[c], 62%[d])
22	Xantphos (12)	TBAI	DMA	78[b],[e]
23	Xantphos (12)	TBAI	DMA	Trace[b],[f]
24	Xantphos (12)	TBAI	DMA	Trace[b],[g]

[a] The yields were determined by ^{1}H NMR analysis of the crude reaction mixture using $CHCl_2CHCl_2$ as the internal standard. [b] 130 °C. [c] Isolated yield. [d] (2-Chlorophenyl)methanamine was used. [e] K_2CO_3 instead of Cs_2CO_3. [f] Na_2CO_3 instead of Cs_2CO_3. [g] CsOAc instead of Cs_2CO_3.

3. General Procedures for the Synthesis of Substrates 4.



3.1 General procedure for the synthesis of substrates 4b, 4c and 4e - 4k [3].



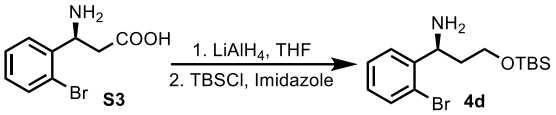
Step 1: To dry DCM (20 mL) was added aldehyde (5 mmol, 1.0 equiv), (S)-2-methylpropane-2-sulfinamide (1.2 equiv) and anhydrous Cs_2CO_3 (2.0 equiv). The reaction vessel was fitted with a dry reflux condenser, and the reaction was heated to reflux. Once being complete as monitored by TLC, the mixture was cooled to room temperature, and then the contents were filtered over Celite® which was subsequently washed with DCM. The collected filtrate was concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel with petroleum ether/ethyl acetate to afford sulfinyl imines **S1**.

Step 2: To a solution of R^2MgBr (1.0 M in THF, 6.0 mmol, 1.5 equiv) at room temperature was added a solution of $ZnMe_2$ (1.0 M in toluene, 6.0 mmol, 1.5 equiv) under nitrogen and the mixture was stirred for 30 min before cooling to -20 °C. This mixture was then added to a solution of sulfinyl imines **S1** (4.0 mmol, 1.0 equiv) in anhydrous THF (20 mL) at -20 °C and the resulting mixture was stirred for 3 h before slowly warming to 0 °C. Once being complete as monitored by TLC, the mixtrue quenched carefully with saturated aqueous NH_4Cl solution, then the insoluble salts were filtered. The resulting clear aqueous layer was extracted with CH_2Cl_2 for three times. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel using the indicated mobile phase to afford **S2**.

Step 3: A flame-dried flask was cooled under a stream of N_2 and charged with a 0.2 M solution of compound **S2** (1.0 mmol, 1.0 equiv) in methanol. A 4 M solution of HCl in dioxane (4.0 equiv) was then added and the resulting solution was stirred at room temperature. Once being complete as monitored by TLC, the reaction mixture was basified to pH > 11 with 10 M NaOH

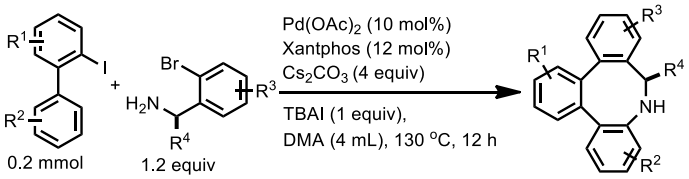
and extracted with CH_2Cl_2 for three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel using the indicated mobile phase to afford **4**.

3.2 Procedure for the synthesis of substrate 4d [4].



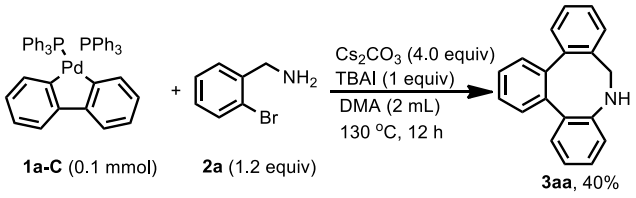
To a solution of lithium aluminium hydride (4.0 mmol, 1.0 equiv) suspended in anhydrous THF (6 mL) at 0 °C was added **S3** (4.0 mmol, 1.0 equiv) in portions. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with aqueous NaOH solution (1.0 M). The solids were filtered off, rinsed with EtOAc and the combined organic phases were concentrated in vacuo to provide the amino alcohol, which was used directly in the next step without further purification. To a solution of the newly prepared amino alcohol (4.0 mmol, 1.0 equiv) and imidazole (12.0 mmol, 3.0 equiv) in CH_2Cl_2 (12 mL) was added TBSCl (8.0 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature for 2 h, and then washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to afford amine **4d** (0.69 g, 50% yield) as a colorless oil.

4. General Procedures for the Synthesis of Eight-Membered Nitrogen Heterocycles.



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (10 mol %), Xantphos (12 mol %), Cs_2CO_3 (0.8 mmol, 4.0 equiv), TBAI (0.2 mmol, 1 equiv), 2-iodobiphenyls (0.2 mmol, 1.0 equiv), 2-bromobenzylamines (0.24 mmol, 1.2 equiv) and DMA (4 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). The mixture was stirred at 130 °C (oil bath heating) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate to give eight-membered nitrogen heterocycles.

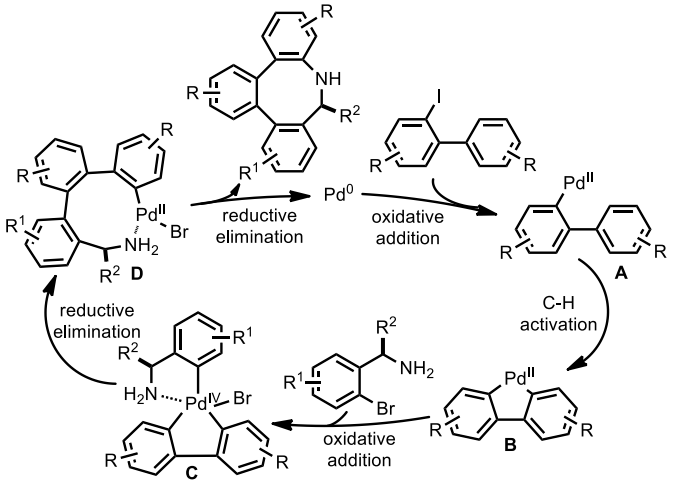
5. Preliminary Mechanistic Studies and Bromination of 5aa.



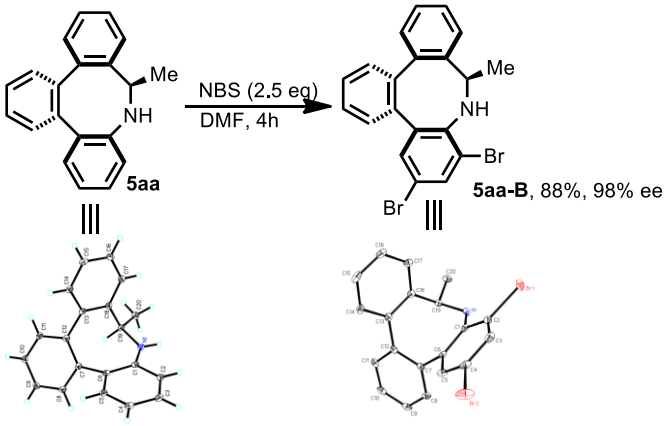
Procedure for preliminary mechanistic studies: A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with biphenylpalladacycle **1a-C** (0.1 mmol, 78.2 mg, 1.0 equiv), Cs_2CO_3 (0.4 mmol, 130.3 mg, 4.0 equiv), TBAI (0.1 mmol, 36.9 mg. 1 equiv), 2-bromobenzylamines **2a** (0.12 mmol, 1.2 equiv) and DMA (2 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). The mixture was stirred at 130 °C (oil bath heating) for 12 hours. After cooling to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The

residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20/1) to give **3aa** (10.3 mg, 40% yield) as a colorless oil.

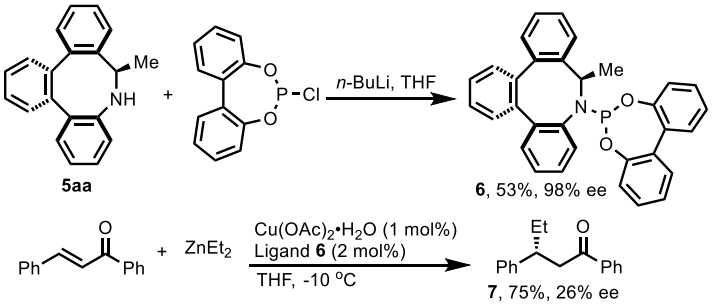
Based on the above experimental results, a tentative mechanism was proposed as shown below for the eight-membered ring-forming reaction. The catalytic cycle starts with the oxidative addition of compound **1** to Pd(0) to yield Pd(II) species **A**. The subsequent intramolecular C–H activation delivers *C,C*-palladacycle **B** as the key intermediate. A second oxidative addition of 2-bromobenzylamine derivatives to **B** affords chelated Pd(IV) species **C**. Nine-membered pallada(II)cycle **D** was then formed by C–C coupling after the reductive elimination of intermediate **C**. Finally, C–N coupling by reductive elimination affords eight -membered cyclic products.



Bromination of 5aa: To a solution of **5aa** (0.2 mmol) in DMF (2 mL) was added NBS (0.5 mmol, 2.5 equiv), and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20/1) to give **5aa-B** (75.1 mg mg, 88% yield) as a white solid.



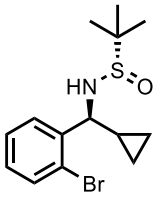
6. Procedure for the Synthesis of a Chiral Phosphoramidite Ligand and Application in Asymmetric Reactions.



The ligands were prepared according to a modified procedure[5]: A solution of (R)-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine **5aa** (0.5 mmol, 135.6 mg, 1.0 equiv) in anhydrous THF (5 mL) was cooled to −78°C under nitrogen, and then a solution of *n*-butyllithium in hexanes (1.6 M, 0.6 mmol) was added carefully. The resulting mixture was stirred for 30 min, after which a solution of 6-chlorodibenzo[d,f][1,3,2]dioxaphosphepine (0.55 mmol, 1.1 equiv) in THF (2 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography over silica gel with petroleum ether/ethyl acetate (15/1) to give phosphoramidite **6** (128.5 mg, 53% yield) as a white solid.

Copper-catalyzed asymmetric conjugate addition to chalcone[6]: A solution of $Cu(OAc)_2 \cdot H_2O$ (0.006 mmol, 1.2 mg) and ligand (0.012 mmol, 5.8 mg) in anhydrous toluene (4 mL) was stirred under nitrogen at room temperature for 30 min. The solution was cooled to -10 °C, and chalcone (0.20 mmol, 41.6 mg) and $ZnEt_2$ solution in hexane (0.3 mmol, 0.3 mL) were added dropwise under nitrogen. After 8 h at -10 °C, the reaction was quenched by aqueous NH_4Cl and the mixture was extracted with EtOAc for three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford **7** (35.6 mg, 75% yield) as a white solid.

7. Characterization of the Substrates



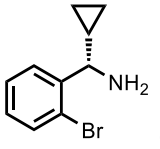
S2-b

(S)-N-((S)-(2-bromophenyl)(cyclopropyl)methyl)-2-methylpropane-2-sulfinamide S2-b. The crude product was formed as 8:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.52 g, 45% yield) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +74.4 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 – 7.12 (m, 1H), 4.23 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.60 (d, *J* = 3.2 Hz, 1H), 1.31 – 1.26 (m, 1H), 1.19 (s, 9H), 0.71 – 0.67 (m, 1H), 0.57 – 0.45 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 133.0, 129.4, 128.9, 127.5, 123.8, 62.3, 55.7, 22.5, 18.5, 5.1, 3.5.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{21}BrNOS$ 330.0522; found 330.0513.



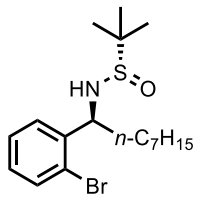
4b

(S)-(2-bromophenyl)(cyclopropyl)methanamine 4b: Colorless oil, actual mass 0.18 mg, 82% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -6.5 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.32 (td, *J* = 7.5, 1.3 Hz, 1H), 7.09 (td, *J* = 7.6, 1.7 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 1.23 – 1.14 (m, 1H), 0.65 – 0.60 (m, 1H), 0.46 – 0.33 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 132.7, 128.3, 128.1, 127.7, 123.5, 58.3, 18.0, 4.1, 2.2.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{13}BrN$ 226.0226; found 226.0199.



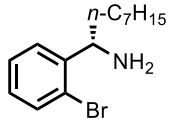
S2-c

(S)-N-((S)-1-(2-bromophenyl)octyl)-2-methylpropane-2-sulfinamide S2-c. The crude product was formed as 20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.86 g, 58% yield) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +16.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.7 Hz, 1H), 4.79 – 4.76 (m, 1H), 3.62 (d, *J* = 6.2 Hz, 1H), 1.90 – 1.77 (m, 2H), 1.36 – 1.21 (m, 10H), 1.20 (s, 9H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.7, 133.1, 128.8, 128.3, 127.6, 123.4, 58.3, 56.0, 36.3, 31.7, 29.2, 29.0, 25.5, 22.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{31}BrNOS$ 388.1304; found 388.1300.



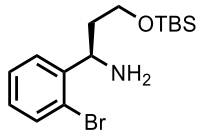
4c

(S)-1-(2-bromophenyl)octan-1-amine 4c: Colorless oil, actual mass 0.23g, 83% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -25.7 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 (td, *J* = 7.6, 1.7 Hz, 1H), 4.35 – 4.31 (m, 1H), 1.77 – 1.68 (m, 1H), 1.44 – 1.39 (m, 1H), 1.30 – 1.25 (m, 10H), 0.87 (t, *J* = 7.0, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 132.8, 128.1, 127.7, 127.2, 123.5, 54.4, 38.1, 31.8, 29.5, 29.2, 26.5, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{23}BrN$ 284.1008; found 284.1005.



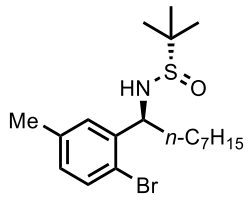
4d

(R)-1-(2-bromophenyl)-3-((tert-butyldimethylsilyl)oxy)propan-1-amine 4d: Colorless oil, actual mass 0.69g, 50% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = +25.1 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.32 – 7.30 (m, 1H), 7.10 – 7.07 (m, 1H), 4.52 – 4.50 (m, 1H), 3.77 – 3.74 (m, 2H), 1.99 – 1.93 (m, 1H), 1.82 – 1.77 (m, 1H), 0.90 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 132.9, 128.2, 127.7, 127.4, 123.2, 61.1, 52.5, 40.0, 25.9, 18.2, -5.4, -5.4.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{27}BrNOSi$ 344.1040; found 344.1009.



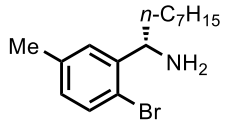
S2-e

(S)-N-((S)-1-(2-bromo-5-methylphenyl)octyl)-2-methylpropane-2-sulfinamide S2-e: The crude product was formed as 20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.84 g, 56% yield) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +14.9 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 8.1, 2.1 Hz, 1H), 4.73 – 4.70 (m, 1H), 3.60 (br, 1H), 2.30 (s, 3H), 1.90 – 1.84 (m, 1H), 1.81 – 1.75 (m, 1H), 1.37 – 1.21 (m, 10H), 1.20 (s, 9H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 137.5, 132.8, 129.8, 129.0, 120.0, 58.5, 56.0, 36.4, 31.7, 29.2, 29.0, 25.6, 22.5, 22.5, 21.0, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{33}BrNOS$ 402.1461; found 402.1463.



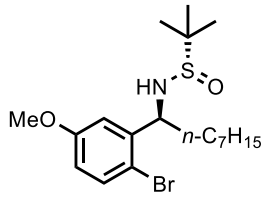
4e

(S)-1-(2-bromo-5-methylphenyl)octan-1-amine 4e: Colorless oil, actual mass 0.24 g, 80% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -24.5 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.31 – 4.28 (m, 1H), 2.31 (s, 3H), 1.74 – 1.68 (m, 1H), 1.44 – 1.40 (m, 1H), 1.30 – 1.25 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 137.5, 132.5, 129.0, 127.9, 120.1, 54.3, 38.1, 31.8, 29.5, 29.2, 26.5, 22.6, 21.0, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{25}BrN$ 298.1165; found 298.1150.



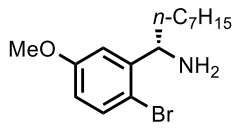
S2-f

(S)-N-((S)-1-(2-bromo-5-methoxyphenyl)octyl)-2-methylpropane-2-sulfinamide S2-f. The crude product was formed as 11:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 8/1 → 3/1 to afford the title compound (0.84 g, 55%) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +23.3 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 3.0 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.1 Hz, 1H), 4.73 – 4.68 (m, 1H), 3.78 (s, 3H), 3.59 (d, *J* = 5.8 Hz, 1H), 1.88 – 1.76 (m, 2H), 1.36 – 1.22 (m, 10H), 1.20 (s, 9H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 142.8, 133.6, 114.5, 114.2, 113.7, 58.3, 56.0, 55.4, 36.2, 31.7, 29.3, 29.1, 25.5, 22.6, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{33}BrNO_2S$ 418.1410; found 418.1409.



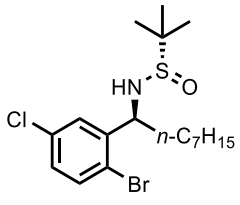
4f

(S)-1-(2-bromo-5-methoxyphenyl)octan-1-amine 4f: Colorless oil, actual mass 0.27g, 85% yield, (eluent: petroleum ether/ethyl acetate = 1:1). $[\alpha]_D^{25}$ = -12.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.66 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.29 – 4.27 (m, 1H), 3.80 (s, 3H), 1.74 – 1.68 (m, 1H), 1.42 – 1.38 (m, 1H), 1.31 – 1.23 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 146.4, 133.3, 113.9, 113.8, 112.8, 55.5, 54.5, 38.0, 31.8, 29.5, 29.2, 26.4, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{25}BrNO$ 314.1114; found 314.1108.



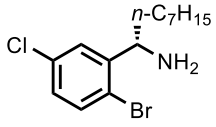
S2-g

(S)-N-((S)-1-(2-bromo-5-chlorophenyl)octyl)-2-methylpropane-2-sulfinamide S2-g. The crude product was formed as 11:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.69 g, 45% yield) as a white solid with >20:1 dr. $[\alpha]_D^{25}$ = +95.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.10 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.74 – 4.71 (m, 1H), 3.61 (br, 1H), 1.90 – 1.84 (m, 1H), 1.80 – 1.74 (m, 1H), 1.35 – 1.22 (m, 10H), 1.21 (s, 9H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.7, 134.2, 133.8, 129.0, 128.5, 121.2, 58.1, 56.1, 36.2, 31.7, 29.2, 29.0, 25.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{30}BrClNOS$ 422.0915; found 422.0918.



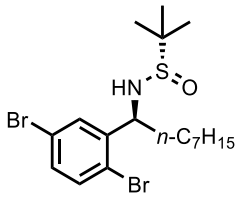
4g

(S)-1-(2-bromo-5-chlorophenyl)octan-1-amine 4g: Colorless oil, actual mass 0.26 g, 82% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -15.6 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.6 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.29 – 4.27 (m, 1H), 1.71 – 1.65 (m, 1H), 1.41 – 1.37 (m, 1H), 1.32 – 1.25 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 133.8, 133.8, 128.2, 127.6, 121.0, 54.3, 38.0, 31.8, 29.4, 29.2, 26.4, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}BrClN$ 318.0619; found 318.0610.



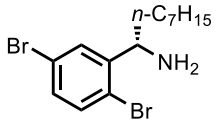
S2-h

(S)-N-((S)-1-(2,5-dibromophenyl)octyl)-2-methylpropane-2-sulfinamide S2-h. The crude product was formed as 10:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.73 g, 43% yield) as a white solid with >20:1 dr. $[\alpha]_D^{25}$ = +155.5 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.4 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.26 – 7.24 (m, 1H), 4.74 – 4.71 (m, 1H), 3.59 (br, 1H), 1.90 – 1.85 (m, 1H), 1.80 – 1.75 (m, 1H), 1.35 – 1.22 (m, 10H), 1.21 (s, 9H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 134.5, 132.0, 131.4, 122.0, 121.7, 58.2, 56.2, 36.2, 31.7, 29.2, 29.1, 25.5, 22.6, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{30}Br_2NOS$ 466.0409; found 466.0403.



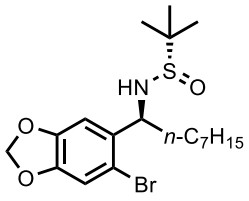
4h

(S)-1-(2,5-dibromophenyl)octan-1-amine 4h: Colorless oil, actual mass 0.31g, 80% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -11.9 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.36 – 4.33 (m, 1H), 1.75 – 1.70 (m, 1H), 1.65 – 1.60 (m, 1H), 1.31 – 1.21 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 134.2, 131.5, 130.6, 122.0, 121.9, 54.3, 37.4, 31.8, 29.3, 29.1, 26.2, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}Br_2N$ 362.0114; found 362.0111.



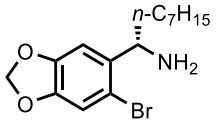
S2-i

(S)-N-((S)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)octyl)-2-methylpropane-2-sulfinamide S2-i: The crude product was formed as 14:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 8/1 → 3/1 to afford the title compound (0.80 g, 50% yield) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +41.4 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.82 (s, 1H), 5.94 (d, *J* = 4.4 Hz, 2H), 4.73 – 4.69 (m, 1H), 3.48 (br, 1H), 1.88 – 1.84 (m, 1H), 1.71 – 1.65 (m, 1H), 1.29 – 1.20 (m, 10H), 1.18 (s, 9H), 0.83 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 147.5, 134.9, 113.8, 112.6, 107.7, 101.7, 57.9, 55.9, 36.3, 31.7, 29.3, 29.0, 25.4, 22.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{31}BrNO_3S$ 432.1203; found 432.1199.



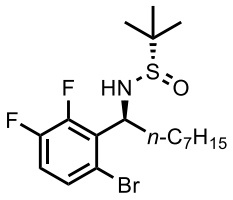
4i

(S)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)octan-1-amine 4i: Colorless oil, actual mass 0.27 g, 83% yield, (eluent: petroleum ether/ethyl acetate = 1:1). $[\alpha]_D^{25}$ = -11.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (d, *J* = 3.3 Hz, 2H), 5.95 (s, 2H), 4.27 (t, *J* = 6.8 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.39 – 1.35 (m, 1H), 1.30 – 1.24 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 146.9, 138.8, 113.4, 112.5, 107.0, 101.6, 54.2, 38.2, 31.8, 29.5, 29.2, 26.4, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{23}BrNO_2$ 328.0907; found 328.0893.



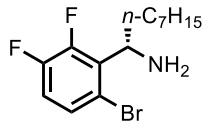
S2-j

(S)-N-((S)-1-(6-bromo-2,3-difluorophenyl)octyl)-2-methylpropane-2-sulfinamide S2-j: The crude product was formed as 7:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.56 g, 38% yield) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +58.2 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 1H), 6.99 – 6.94 (m, 1H), 4.83 – 4.79 (m, 1H), 3.94 (br, 1H), 1.92 – 1.80 (m, 2H), 1.46 – 1.24 (m, 10H), 1.22 (s, 9H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2 (d, *J* = 250.0, 13.4 Hz), 150.1 (d, *J* = 250.4, 13.8 Hz), 132.9 – 132.8 (m), 128.5 – 128.4 (m), 117.2, 117.1, 60.0, 56.3, 35.7, 31.8, 29.1, 29.0, 26.2, 22.6, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{29}BrF_2NOS$ 424.1116; found 424.1115.



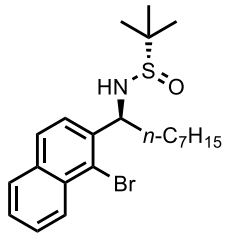
4j

(S)-1-(1-bromonaphthalen-2-yl)octan-1-amine 4j: Colorless oil, actual mass 0.25 g, 78% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -10.1 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 6.96 – 6.92 (m, 1H), 4.37 (t, *J* = 7.5 Hz, 1H), 1.86 – 1.82 (m, 1H), 1.46 – 1.40 (m, 1H), 1.31 – 1.18 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4 (dd, *J* = 249.5, 13.7 Hz), 149.3 (dd, *J* = 249.3, 12.8 Hz), 135.4(d, *J* = 10.8 Hz), 128.4 – 128.3 (m), 117.1 (m), 116.2 (d, *J* = 18.0 Hz), 55.0, 36.6, 31.8, 29.4, 29.1, 26.7, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{21}BrF_2N$ 320.0820; found 320.0808.



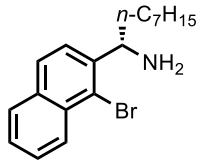
S2-k

(S)-N-((S)-1-(1-bromonaphthalen-2-yl)octyl)-2-methylpropane-2-sulfinamide S2-k: The crude product was formed as 8:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by silica gel column chromatography with petroleum ether/ethyl acetate 10/1 → 5/1 to afford the title compound (0.79 g, 51%) as a colorless oil with >20:1 dr. $[\alpha]_D^{25}$ = +119.7 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.6 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.53 – 7.47 (m, 2H), 5.23 – 5.18 (m, 1H), 3.67 (d, *J* = 5.3 Hz, 1H), 2.05 – 1.97 (m, 1H), 1.89 – 1.81 (m, 1H), 1.41 – 1.22 (m, 19H), 0.84 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.6, 133.9, 132.2, 128.1, 128.0, 127.8, 127.5, 126.6, 124.8, 123.5, 58.7, 56.0, 36.4, 31.7, 29.3, 29.0, 25.6, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{33}BrNOS$ 438.1461; found 438.1457.



4k

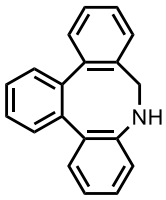
(S)-(2-bromophenyl)(cyclopropyl)methanamine 4k: Colorless oil, actual mass 0.28 g, 83% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -20.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 4.73 (t, *J* = 6.9 Hz, 1H), 1.81 – 1.75 (m, 1H), 1.46 – 1.40 (m, 1H), 1.33 – 1.22 (m, 10H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 133.8, 132.3, 128.1, 128.0, 127.7, 127.3, 126.2, 124.4, 122.9, 55.2, 38.1, 31.8, 29.5, 29.2, 26.4, 22.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{25}BrN$ 334.1165; found 334.1160.

8. Characterization of the Products.



3aa

9,10-dihydrotribenzo[b,d,f]azocine 3aa: Colorless oil, actual mass 46.8 mg, 91% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

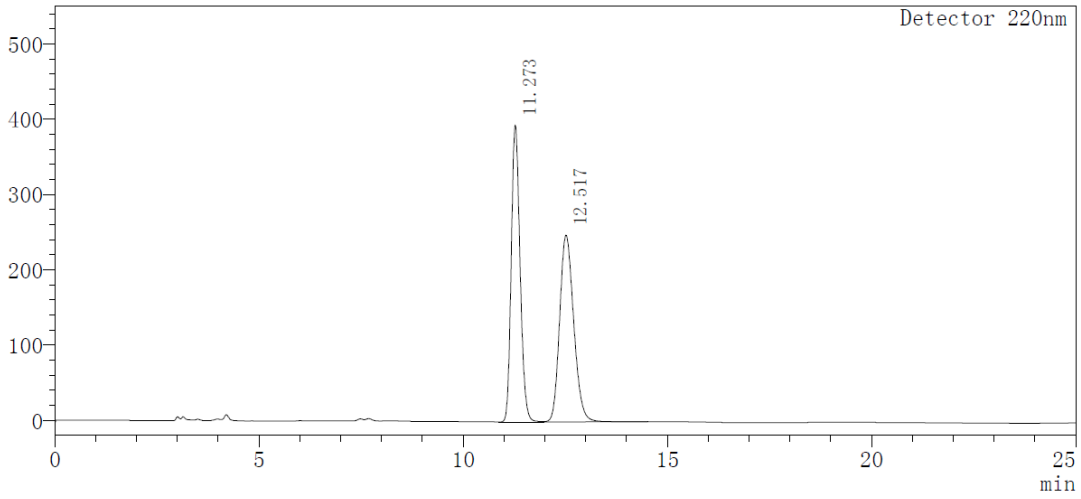
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 2H), 7.31 – 7.20 (m, 6H), 6.99 – 6.94 (m, 1H), 6.78 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.66 (td, *J* = 7.4, 1.2 Hz, 1H), 6.48 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H), 4.17 (br, 1H), 3.89 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 143.4, 142.6, 141.2, 136.7, 133.8, 131.4, 129.0, 128.7, 128.2, 128.1, 128.0, 127.8, 127.8, 127.2, 118.6, 118.2, 49.2.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}N$ 258.1277; found 258.1265.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm: t_{R1} = 11.27 min, t_{R2} = 12.52 min.

<chromatogram>
mV



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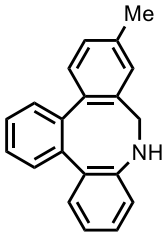


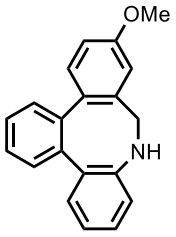
3ab

12-methyl-9,10-dihydrotribenzo[b,d,f]azocine 3ab: Colorless oil, actual mass 51.5 mg, 95% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.32 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.00 (td, *J* = 8.4, 1.6 Hz, 1H), 6.81 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.69 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.31 (d, *J* = 14.4 Hz, 1H), 4.18 (br, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 142.6, 141.2, 140.6, 137.8, 136.5, 133.9, 131.4, 129.1, 128.9, 128.8, 128.6, 128.0, 127.7, 127.1, 118.6, 118.2, 49.3, 21.2.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}N$ 272.1434; found 272.1415.



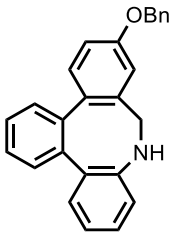
3ac

12-methoxy-9,10-dihydrotribenzo[b,d,f]azocine 3ac: Colorless oil, actual mass 50.5 mg, 88% yield, (eluent: petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.85 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.81 (dd, *J* = 8.3, 2.2 Hz, 2H), 6.69 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.31 (d, *J* = 14.4 Hz, 1H), 4.20 (br, 1H), 3.86 (d, *J* = 14.5 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 145.5, 142.6, 140.9, 138.0, 136.0, 133.8, 131.4, 129.1, 128.9, 128.9, 128.0, 127.9, 127.1, 118.7, 118.2, 113.6, 113.0, 55.2, 49.5.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO$ 288.1383; found 288.1363.



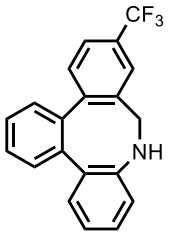
3ad

12-(benzyloxy)-9,10-dihydrotribenzo[b,d,f]azocine 3ad: White solid, actual mass 67.5 mg, 93% yield, (eluent: petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 6H), 7.33 – 7.28 (m, 2H), 7.23 – 7.17 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.88 – 6.85 (m, 2H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.00 (s, 2H), 4.26 (d, *J* = 14.4 Hz, 1H), 4.22 (br, 1H), 3.79 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 145.4, 142.6, 140.9, 138.0, 136.8, 136.2, 133.8, 131.4, 129.1, 128.9, 128.8, 128.5, 128.0, 128.0, 127.9, 127.5, 127.1, 118.7, 118.2, 114.5, 113.9, 67.0, 49.4.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}NO$ 364.1696; found 364.1702.



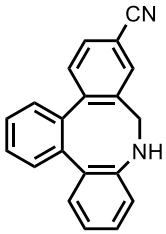
3ae

12-(trifluoromethyl)-9,10-dihydrotribenzo[b,d,f]azocine 3ae: Colorless oil, actual mass 48.7 mg, 70% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.45 – 7.42 (m, 2H), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.20 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.80 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.71 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.36 (d, *J* = 14.5 Hz, 1H), 4.21 (br, 1H), 3.96 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 147.1, 144.9, 142.4, 139.9, 137.5, 133.9, 131.7, 130.3 (q, *J* = 32.4 Hz), 128.9, 128.3, 128.1, 127.4, 125.2 (q, *J* = 3.7 Hz), 124.7 (d, *J* = 3.7 Hz), 124.1 (d, *J* = 272.2 Hz), 119.0, 118.3, 48.9.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}F_3N$ 326.1151; found 326.1148.



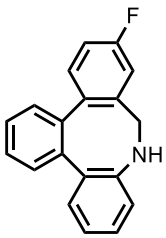
3af

9,10-dihydrotribenzo[b,d,f]azocine-12-carbonitrile 3af: Colorless oil, actual mass 16.9 mg, 30% yield, (eluent: petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.56 (m, 2H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.01 (td, *J* = 7.7, 1.7 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 4.31 (d, *J* = 14.6 Hz, 1H), 4.20 (br, 1H), 3.94 (d, *J* = 14.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 144.7, 142.3, 139.4, 138.2, 133.9, 132.1, 131.8, 131.5, 129.2, 128.7, 128.5, 128.0, 127.5, 119.1, 118.7, 118.4, 111.9, 48.6.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}N_2$ 283.1230; found 283.1227.



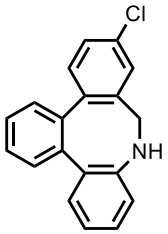
3ag

12-fluoro-9,10-dihydrotribenzo[b,d,f]azocine 3ag: Colorless oil, actual mass 41.3 mg, 75% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.20 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.03 – 6.97 (m, 3H), 6.80 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.70 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.30 (dd, *J* = 14.5, 1.4 Hz, 1H), 4.17 (br, 1H), 3.87 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.6 Hz), 145.14, 142.58, 140.23, 139.4 (d, *J* = 3.1 Hz), 138.8 (d, *J* = 6.6 Hz), 133.81, 131.47, 129.4 (d, *J* = 8.2 Hz), 129.06, 128.59, 128.35, 128.17, 127.28, 118.87, 118.22, 114.8 (d, *J* = 21.4 Hz), 114.7 (d, *J* = 21.0 Hz), 49.11.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}FN$ 276.1183; found 276.1176.



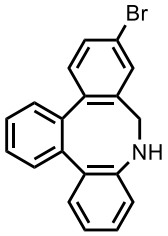
3ah

12-chloro-9,10-dihydrotribenzo[b,d,f]azocine 3ah: Colorless oil, actual mass 46.6 mg, 80% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.30 (s, 3H), 7.22 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.83 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.74 (td, *J* = 7.4, 1.2 Hz, 1H), 6.56 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.32 (d, *J* = 14.5 Hz, 1H), 4.21 (br, 1H), 3.90 (d, *J* = 14.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 142.5, 141.9, 140.1, 138.5, 133.9, 133.5, 131.6, 129.2, 128.9, 128.5, 128.4, 128.2, 128.2, 128.0, 127.3, 118.9, 118.3, 48.9.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}ClN$ 292.0888; found 292.0886.



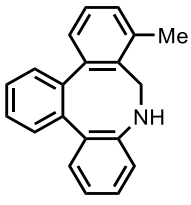
3ai

12-bromo-9,10-dihydrotribenzo[b,d,f]azocine 3ai: Colorless oil, actual mass 30.1 mg, 45% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 – 7.39 (m, 3H), 7.31 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.02 – 6.99 (m, 1H), 6.78 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.69 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 – 6.51 (m, 1H), 4.26 (d, *J* = 14.5 Hz, 1H), 4.16 (br, 1H), 3.86 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.0, 142.4, 142.4, 140.1, 138.9, 133.9, 131.6, 131.1, 130.9, 129.5, 128.9, 128.6, 128.4, 128.3, 127.3, 121.7, 118.9, 118.3, 48.9.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}BrN$ 336.0382; found 336.0382.



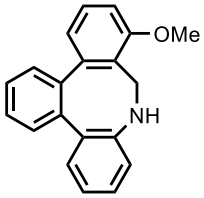
3aj

11-methyl-9,10-dihydrotribenzo[b,d,f]azocine 3aj: Yellow solid, actual mass 51.0 mg, 94% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.28 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.17 – 7.09 (m, 3H), 6.96 – 6.93 (m, 1H), 6.76 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.66 – 6.63 (m, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 4.26 (d, *J* = 14.9 Hz, 1H), 4.12 (br, 1H), 4.07 (d, *J* = 14.8 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 144.0, 142.8, 142.0, 135.1, 134.7, 133.7, 131.3, 129.7, 128.8, 128.8, 128.1, 128.0, 127.5, 127.2, 125.6, 118.7, 117.7, 45.6, 19.2.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}N$ 272.1434; found 272.1418.



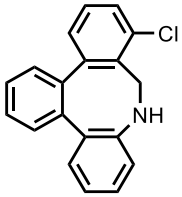
3ak

11-methoxy-9,10-dihydrotribenzo[b,d,f]azocine 3ak: Yellow solid, actual mass 54.0 mg, 94% yield, (eluent: petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.29 – 7.27 (m, 1H), 7.23 – 7.20 (m, 2H), 6.96 – 6.91 (m, 2H), 6.79 – 6.75 (m, 2H), 6.64 – 6.61 (m, 1H), 6.49 – 6.47 (m, 1H), 4.32 (dd, *J* = 14.3, 2.3 Hz, 1H), 4.22 (br, 1H), 4.02 (dd, *J* = 14.3, 2.1 Hz, 1H), 3.81 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 146.4, 144.9, 143.1, 141.1, 134.1, 131.6, 128.7, 128.4, 128.1, 127.9, 127.1, 125.2, 119.8, 118.2, 117.9, 109.4, 55.5, 42.4.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO$ 288.1383; found 288.1368.



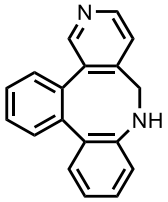
3al

11-chloro-9,10-dihydrotribenzo[b,d,f]azocine 3al: Yellow solid, actual mass 39.6 mg, 68% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.24 – 7.18 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.33 – 4.30 (m, 2H), 4.23 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 145.5, 142.9, 140.8, 134.5, 134.0, 133.2, 131.7, 128.7, 128.7, 128.6, 128.6, 128.2, 128.0, 127.3, 126.3, 118.7, 118.1, 46.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}ClN$ 292.0888; found 292.0892.



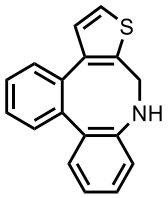
3am

9,10-dihydrodibenzo[b,d]pyrido[3,4-f]azocine 3am: Colorless oil, actual mass 16.5 mg, 32% yield, (eluent: petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 – 8.52 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 5.0 Hz, 1H), 7.04 – 7.01 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 1H), 4.34 (d, *J* = 14.5 Hz, 1H), 4.10 (br, 1H), 3.95 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 148.9, 145.2, 144.8, 142.6, 138.8, 137.4, 133.6, 131.6, 129.2, 129.1, 128.5, 127.6, 122.8, 119.9, 119.0, 49.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{15}N_2$ 259.1230; found 259.1217.



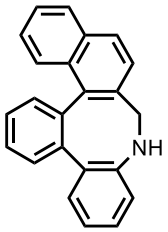
3an

8,9-dihydrodibenzo[b,d]thieno[3,2-f]azocine 3an: Colorless oil, actual mass 15.8 mg, 30% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.38 – 7.34 (m, 2H), 7.22 – 7.18 (m, 1H), 7.10 – 7.06 (m, 2H), 7.00 – 6.93 (m, 2H), 6.86 (d, *J* = 5.1 Hz, 1H), 4.54 (d, *J* = 16.4 Hz, 1H), 4.37 (d, *J* = 16.4 Hz, 1H), 3.81 (br, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 139.9, 139.6, 136.8, 136.8, 134.5, 131.1, 130.5, 129.7, 128.7, 128.1, 127.5, 122.7, 122.2, 122.0, 48.2.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NS$ 264.0841; found 264.0833.



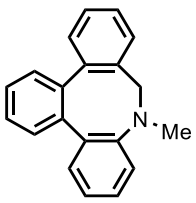
3ao

7,8-dihydrodibenzo[b,d]naphtho[1,2-f]azocine 3ao: Colorless oil, actual mass 46.7 mg, 76% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 3H), 7.55 – 7.32 (m, 7H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 4.42 (d, *J* = 14.0 Hz, 1H), 4.21 (br, 1H), 4.04 (d, *J* = 14.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 143.7, 139.6, 138.5, 133.4, 133.2, 133.1, 131.8, 131.2, 130.5, 128.8, 128.4, 128.3, 128.0, 127.9, 126.6, 126.3, 126.2, 126.1, 125.5, 118.5, 118.0, 49.8.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}N$ 308.1434; found 308.1436.



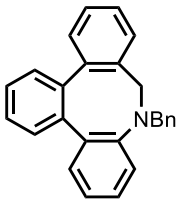
3ap

9-methyl-9,10-dihydrotribenzo[b,d,f]azocine 3ap: Colorless oil, actual mass 49.9 mg, 92% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.29 – 7.20 (m, 6H), 7.10 – 7.07 (m, 1H), 6.77 – 6.70 (m, 3H), 4.52 (d, *J* = 13.5 Hz, 1H), 3.87 (d, *J* = 13.5 Hz, 1H), 3.04 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 143.6, 143.2, 141.0, 135.7, 133.5, 132.9, 130.6, 129.1, 128.2, 127.9, 127.8, 127.7, 127.6, 127.1, 119.6, 118.6, 58.8, 44.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}N$ 272.1434; found 272.1415.



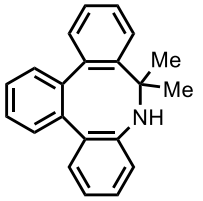
3aq

9-benzyl-9,10-dihydrotribenzo[b,d,f]azocine 3aq: Yellow solid, actual mass 41.6 mg, 60% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.29 – 7.16 (m, 11H), 7.11 – 7.08 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.81 – 6.80 (m, 2H), 4.48 – 4.41 (m, 2H), 4.26 (d, *J* = 12.6 Hz, 1H), 3.84 (d, *J* = 12.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 143.1, 142.6, 141.1, 139.5, 136.2, 136.1, 131.9, 130.4, 129.5, 128.3, 128.2, 128.2, 128.1, 127.8, 127.6, 127.5, 127.5, 127.1, 126.9, 122.4, 121.3, 61.3, 56.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}N$ 348.1747; found 348.1745.



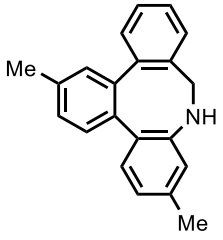
3ar

10,10-dimethyl-9,10-dihydrotribenzo[b,d,f]azocine 3ar: Colorless oil, actual mass 43.9 mg, 77% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 2H), 7.39 – 7.38 (m, 1H), 7.31 – 7.29 (m, 1H), 7.25 – 7.24 (m, 1H), 7.21 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.18 – 7.13 (m, 3H), 7.07 (td, *J* = 7.4, 1.1 Hz, 1H), 7.00 (td, *J* = 7.4, 1.3 Hz, 1H), 6.84 (dd, *J* = 7.5, 1.4 Hz, 1H), 3.42 (br, 1H), 1.91 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 145.4, 144.4, 140.3, 138.6, 138.5, 133.1, 130.4, 128.7, 128.2, 127.9, 127.5, 127.5, 126.0, 125.9, 125.2, 124.2, 60.1, 32.2, 30.4.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}N$ 286.1590; found 286.1570.



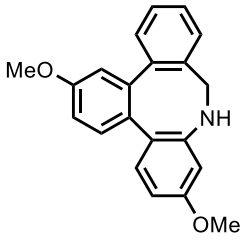
3ba

2,7-dimethyl-9,10-dihydrotribenzo[b,d,f]azocine 3ba: Colorless oil, actual mass 24.5 mg, 43% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 6H), 7.02 (s, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 6.47 (d, *J* = 7.7 Hz, 1H), 6.28 (s, 1H), 4.32 (d, *J* = 14.4 Hz, 1H), 4.11 (br, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 2.41 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.3, 143.6, 141.1, 139.7, 137.6, 136.9, 136.7, 133.9, 131.4, 129.9, 128.8, 128.1, 128.0, 127.8, 127.8, 125.8, 119.7, 118.6, 49.1, 21.0, 20.8.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}N$ 286.1590; found 286.1570.



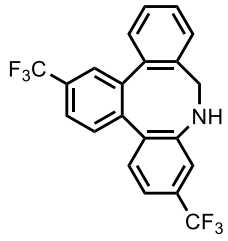
3ca

2,7-dimethoxy-9,10-dihydrotribenzo[b,d,f]azocine 3ca: Yellow solid, actual mass 35.5 mg, 56% yield, (eluent: petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.97 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.01 (d, *J* = 2.5 Hz, 1H), 4.34 (d, *J* = 14.4 Hz, 1H), 4.17 (br, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 158.7, 146.6, 143.5, 142.5, 136.8, 135.0, 134.8, 132.6, 128.2, 128.2, 127.8, 127.7, 121.3, 114.6, 113.4, 104.6, 102.9, 55.3, 54.9, 49.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_2$ 318.1489; found 318.1492.



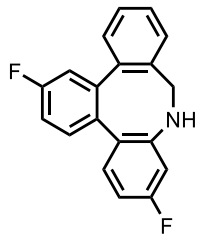
3da

2,7-bis(trifluoromethyl)-9,10-dihydrotribenzo[b,d,f]azocine 3da: Yellow solid, actual mass 31.4 mg, 40% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.40 – 7.30 (m, 5H), 6.89 – 6.83 (m, 2H), 6.72 (s, 1H), 4.41 (br, 1H), 4.27 (dd, *J* = 14.6, 7.5 Hz, 1H), 3.95 (dd, *J* = 14.6, 7.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 145.1, 141.9, 141.7, 135.8, 134.4, 131.9, 130.9 (q, *J* = 32.3 Hz), 130.0 (q, *J* = 32.6 Hz), 130.0, 129.2, 128.6, 128.5, 127.7, 126.0 (q, *J* = 3.6 Hz), 125.2 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.2 Hz), 123.9 (q, *J* = 272.4 Hz) 114.9 (q, *J* = 3.7 Hz), 48.68.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}F_6N$ 394.1025; found 394.1026.



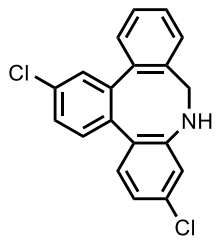
3ea

2,7-difluoro-9,10-dihydrotribenzo[b,d,f]azocine 3ea: Yellow solid, actual mass 44.0 mg, 75% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.23 – 7.21 (m, 1H), 7.14 (td, *J* = 8.4, 2.7 Hz, 1H), 6.95 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.68 (dd, *J* = 8.5, 6.7 Hz, 1H), 6.35 (td, *J* = 8.2, 2.5 Hz, 1H), 6.18 (dd, *J* = 10.8, 2.5 Hz, 1H), 4.30 (d, *J* = 14.5 Hz, 1H), 4.25 (br, 1H), 3.90 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 244.9 Hz), 162.2 (d, $J_{C\text{-}F}$ = 247.4 Hz), 147.2 (d, $J_{C\text{-}F}$ = 10.2 Hz), 143.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 142.3 (d, $J_{C\text{-}F}$ = 1.5 Hz), 137.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 136.2, 135.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 133.1 (d, $J_{C\text{-}F}$ = 8.2 Hz), 128.7, 128.4, 128.1, 127.6, 123.5 (d, $J_{C\text{-}F}$ = 2.7 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 114.9 (d, $J_{C\text{-}F}$ = 20.8 Hz), 105.7 (d, $J_{C\text{-}F}$ = 21.2 Hz), 104.2 (d, $J_{C\text{-}F}$ = 24.0 Hz), 48.8.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}F_2N$ 294.1089; found 294.1090.



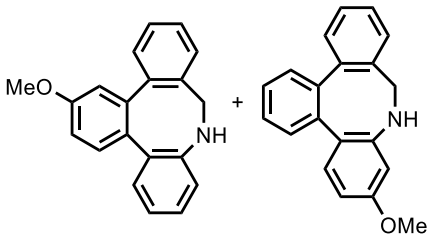
3fa

2,7-dichloro-9,10-dihydrotribenzo[b,d,f]azocine 3fa: Yellow solid, actual mass 28.6 mg, 44% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.22 – 7.18 (m, 2H), 6.65 – 6.60 (m, 2H), 6.46 (d, *J* = 2.0 Hz, 1H), 4.28 (d, *J* = 14.8 Hz, 1H), 4.23 (br, 1H), 3.89 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 142.9, 141.9, 140.1, 136.1, 134.9, 1338, 133.5, 132.6, 129.1, 128.9, 128.4, 128.3, 128.2, 127.6, 125.7, 118.7, 117.6, 48.7.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}Cl_2N$ 326.0498; found 326.0509.



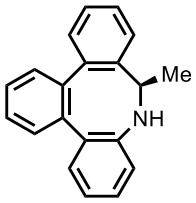
3ga-1 and **3ga-2**

2-methoxy-9,10-dihydrotribenzo[b,d,f]azocine and **7-methoxy-9,10-dihydrotribenzo[b,d,f]azocine 3ga-1** and **3ga-2:** Yellow solid, actual mass 37.9 mg, 66% yield, (eluent: petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 6.5H), 7.00 – 6.93 (m, 1H), 6.77 – 6.76 (m, 1H), 6.70 – 6.63 (m, 1H), 6.46 (d, *J* = 8.0 Hz, 0.5H), 6.25 (dd, *J* = 8.5, 2.4 Hz, 0.5H), 6.01 (d, *J* = 2.4 Hz, 0.5H), 4.35 – 4.29 (m, 1H), 3.90 – 3.87 (m, 1H), 3.84 (s, 1.5H), 3.67 (s, 1.5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 158.8, 146.6, 145.6, 143.5, 143.4, 142.4, 142.4, 141.4, 136.7, 135.0, 135.0, 134.0, 132.4, 131.6, 129.0, 128.3, 128.2, 128.2, 128.1, 128.1, 127.8, 127.8, 127.8, 127.7, 126.9, 121.7, 118.6, 118.1, 114.6, 113.5, 104.7, 102.9, 55.3, 54.9, 49.3, 48.9.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO$ 288.1383; found 288.1372.



5aa

(R)-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5aa: White solid, actual mass 40.1 mg, 74% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -195.8 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.35 – 7.21 (m, 6H), 6.95 – 6.92 (m, 1H), 6.77 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.65 – 6.62 (m, 1H), 6.42 – 6.41 (m, 1H), 4.69 (q, *J* = 6.7 Hz, 1H), 3.58 (br, 1H), 1.48 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.0, 143.1, 143.1, 141.3, 140.3, 133.8, 131.1, 128.9, 128.4, 128.2, 128.2, 128.0, 127.8, 127.3, 127.2, 123.1, 118.5, 118.0, 50.5, 20.3.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}N$ 272.1434; found 272.1421.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm)

: t_R = 8.23 min (major enantiomer), t_R = 6.72 min (minor enantiomer).

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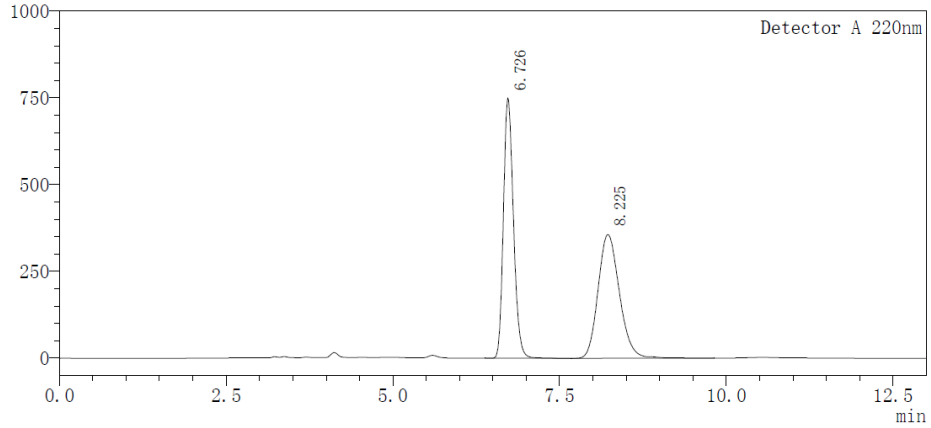
mV



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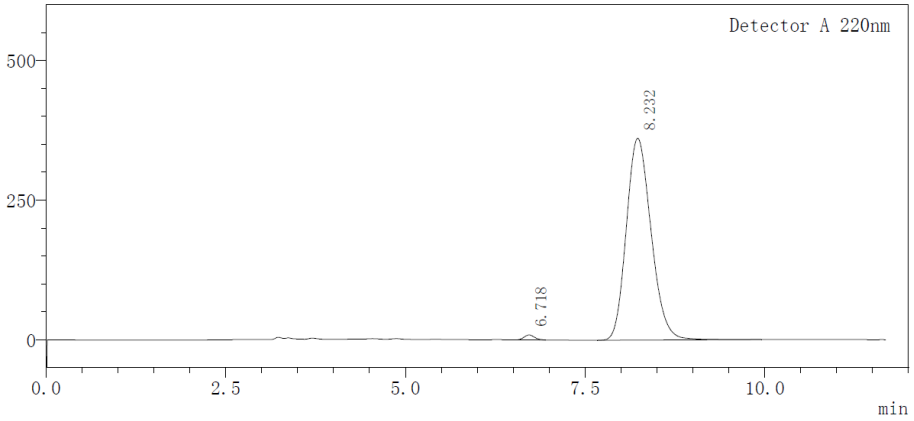

<Peak table>

Peak#	Ret. Time	Height	Area	Area%
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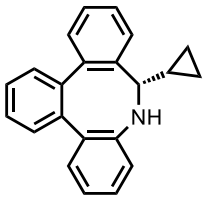
Total		370259	8749633	100.000



5ab

(S)-10-cyclopropyl-9,10-dihydrotribenzo[b,d,f]azocine 5ab: Colorless oil, actual mass 39.2 mg, 66% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +169.1 (c = 0.2, $CHCl_3$).

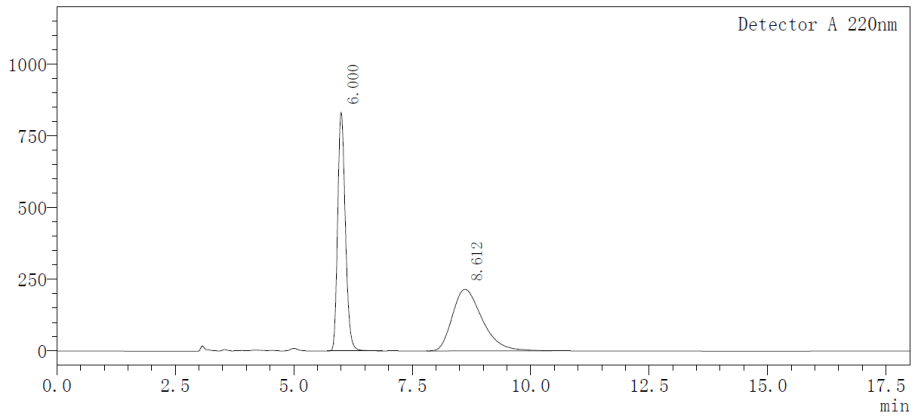
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.24 (m, 6H), 7.19 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.75 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.65 – 6.61 (m, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.91 (br, 1H), 3.59 (d, *J* = 9.4 Hz, 1H), 1.37 – 1.29 (m, 1H), 0.73 – 0.66 (m, 1H), 0.50 – 0.35 (m, 2H), -0.07 – -013 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 143.1, 142.9, 141.3, 140.2, 133.6, 131.1, 128.8, 128.6, 128.1, 128.1, 128.0, 127.6, 127.3, 127.2, 124.5, 118.6, 118.1, 61.6, 15.5, 5.4, 3.4.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N$ 298.1590; found 298.1577.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 8.73 min (major enantiomer), t_R = 6.16 min (minor enantiomer).

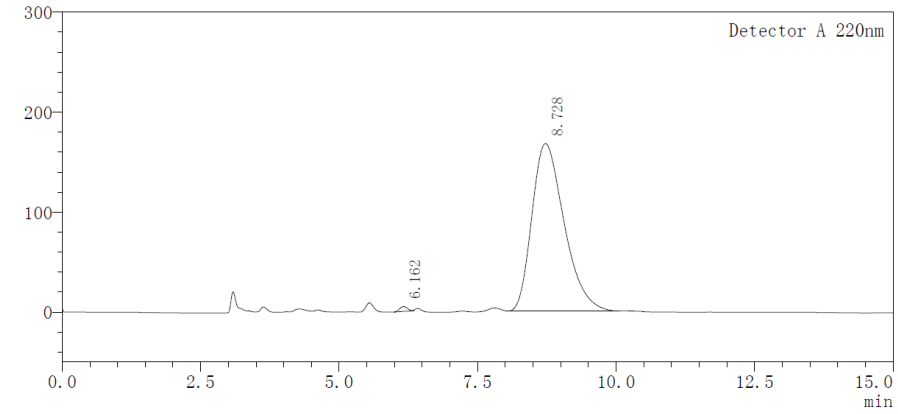
<chromatogram>
mV



<Peak table>

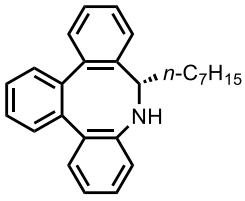
Peak#	Ret. Time	Height	Area	Area%
1	6.000	832133	9352587	49.824
2	8.612	214721	9418674	50.176
Total		1046854	18771262	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	6.162	4881	48836	0.718
2	8.728	167413	6748352	99.282
Total		172294	6797188	100.000



5ac

(S)-10-heptyl-9,10-dihydrotribenzo[b,d,f]azocine 5ac: Yellow oil, actual mass 53.3 mg, 75% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +188.6 (c = 0.2, $CHCl_3$).

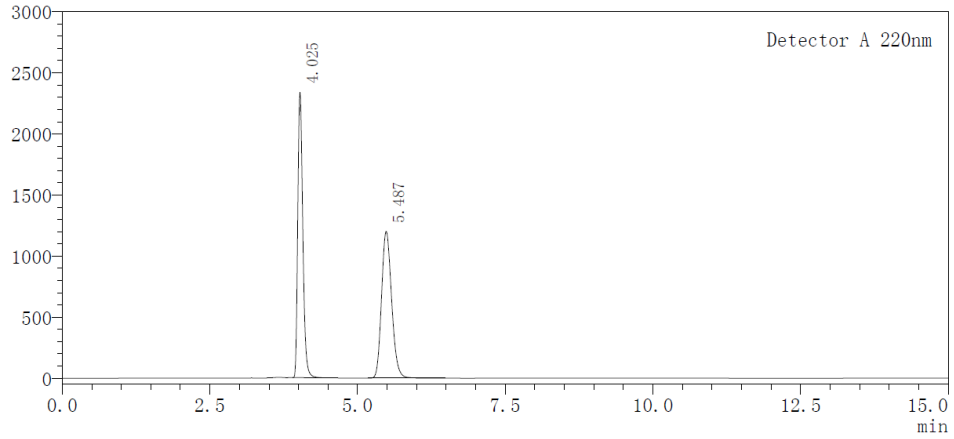
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.21 (m, 6H), 6.94 – 6.91 (m, 1H), 6.76 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.63 – 6.61 (m, 1H), 6.41 – 6.40 (m, 1H), 4.50 (t, *J* = 7.3 Hz, 1H), 3.55 (br, 1H), 1.90 – 1.81 (m, 2H), 1.25 – 1.16 (m, 10H), 0.83 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1, 143.6, 143.3, 141.3, 139.5, 133.9, 131.1, 128.7, 128.2, 128.2, 128.1, 128.0, 127.7, 127.2, 127.1, 123.4, 118.3, 117.9, 55.2, 34.3, 31.7, 29.3, 29.0, 26.6, 22.5, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{30}N$ 356.2373; found 356.2365.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 5.73 min (major enantiomer), t_R = 4.15 min (minor enantiomer).

<chromatogram>
mV



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Peak#	Ret. Time	Height	Area	Area%
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2	5.487	1201677	14316338	50.750
Total		3540943	28209809	100.000

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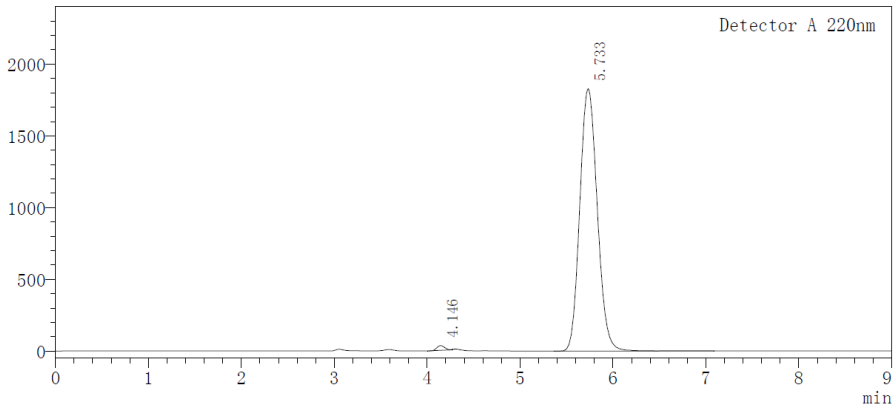
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
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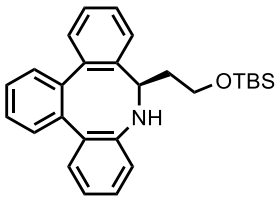
Total		1860999	24156121	100.000



5ad

(R)-10-(2-((tert-butyldimethylsilyl)oxy)ethyl)-9,10-dihydrotribenzo[b,d,f]azocine 5ad: Yellow oil, actual mass 52.7 mg, 65% yield, (eluent: petroleum ether/ethyl acetate = 10:1). $[\alpha]_D^{25}$ = -178.7 (c = 0.2, $CHCl_3$).

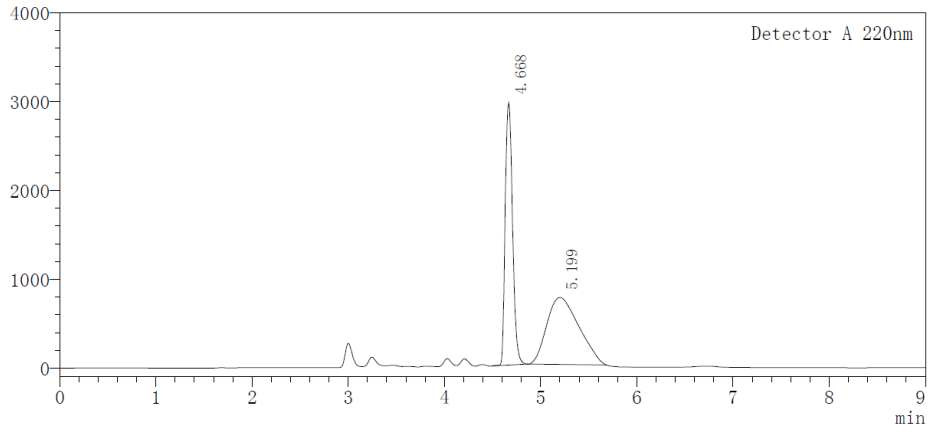
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.34 – 7.21 (m, 6H), 6.96 – 6.93 (m, 1H), 6.77 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.65 – 6.62 (m, 1H), 6.43 – 6.41 (m, 1H), 4.75 –4.73 (m, 1H), 3.71 – 3.60 (m, 3H), 2.14 – 2.01 (m, 2H), 0.76 (s, 9H), -0.09 and –0.11 (2s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1, 143.5, 143.1, 141.1, 139.5, 134.1, 131.2, 128.9, 128.2, 128.2, 128.1, 127.9, 127.8, 127.3, 127.2, 123.6, 118.3, 117.9, 60.1, 51.8, 37.9, 25.8, 18.1, -5.5, -5.6.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{34}NOSi$ 416.2404; found 416.2390.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 4.67 min (major enantiomer), t_R = 5.23 min (minor enantiomer).

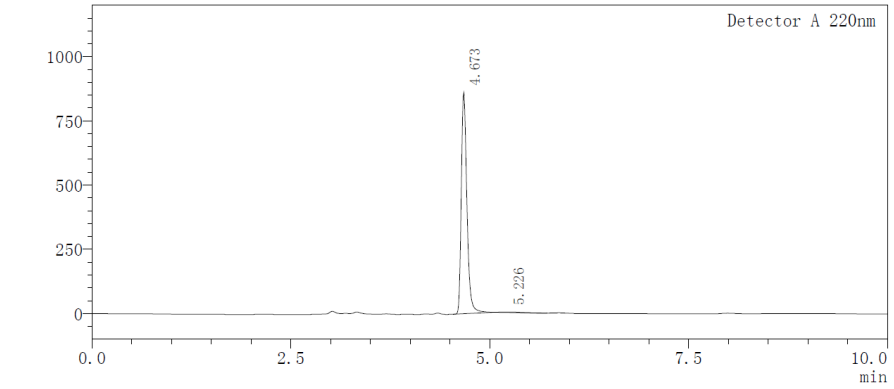
<chromatogram>
mV



<Peak table>

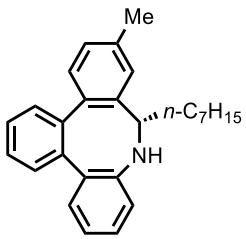
Peak#	Ret. Time	Height	Area	Area%
1	4.668	2956853	15692007	47.211
2	5.199	754805	17546114	52.789
Total		3711658	33238121	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.673	859706	4234824	99.076
2	5.226	2285	39483	0.924
Total		861991	4274307	100.000



5ae

(S)-10-heptyl-12-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5ae: Yellow oil, actual mass 56.1 mg, 76% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +172.1 (c = 0.2, $CHCl_3$).

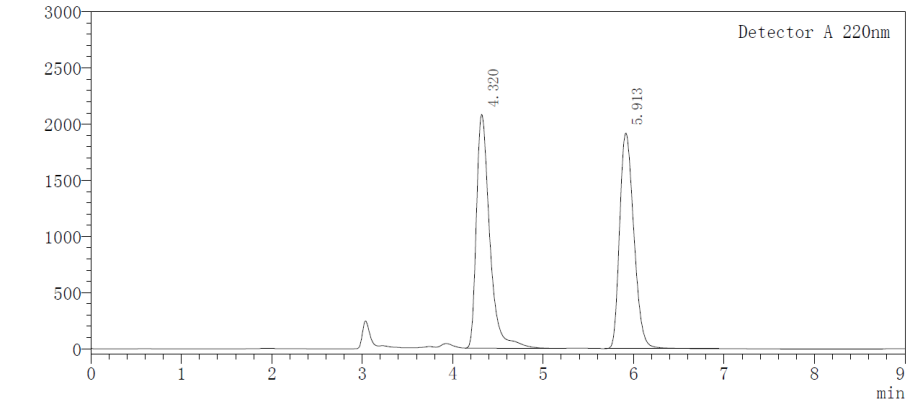
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.31 – 7.29 (m, 1H), 7.22 – 7.18 (m, 2H), 7.08 – 7.06 (m, 2H), 6.97 – 6.94 (m, 1H), 6.78 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 1H), 4.50 (t, *J* = 7.2 Hz, 1H), 3.55 (br, 1H), 2.36 (s, 3H), 1.90 – 1.81 (m, 2H), 1.27 – 1.19 (m, 10H), 0.86 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 143.3, 141.3, 140.8, 139.3, 137.7, 134.0, 131.1, 128.8, 128.2, 128.0, 127.9, 127.9, 127.5, 127.2, 124.0, 118.2, 117.8, 55.1, 34.3, 31.7, 29.3, 28.9, 26.6, 22.5, 21.6, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{32}N$ 370.2529; found 370.2521.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 5.70 min (major enantiomer), t_R = 4.52 min (minor enantiomer).

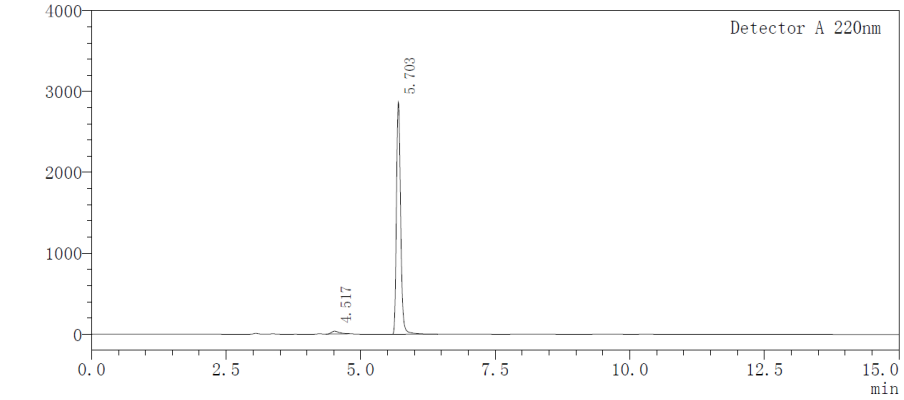
<chromatogram>



<Peak table>

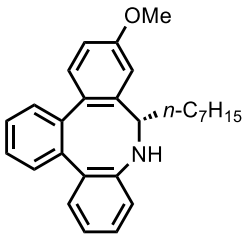
Peak#	Ret. Time	Height	Area	Area%
1	4.320	2079900	21364979	50.539
2	5.913	1918589	20909201	49.461
Total		3998489	42274179	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.517	34597	349845	2.182
2	5.703	2868659	15679921	97.818
Total		2903256	16029766	100.000



5af

(S)-10-heptyl-12-methoxy-9,10-dihydrotribenzo[b,d,f]azocine 5af: Yellow oil, actual mass 69.4 mg, 85% yield, (eluent: petroleum ether/ethyl acetate = 10:1). $[\alpha]_D^{25}$ = +144.6 (c = 0.2, $CHCl_3$).

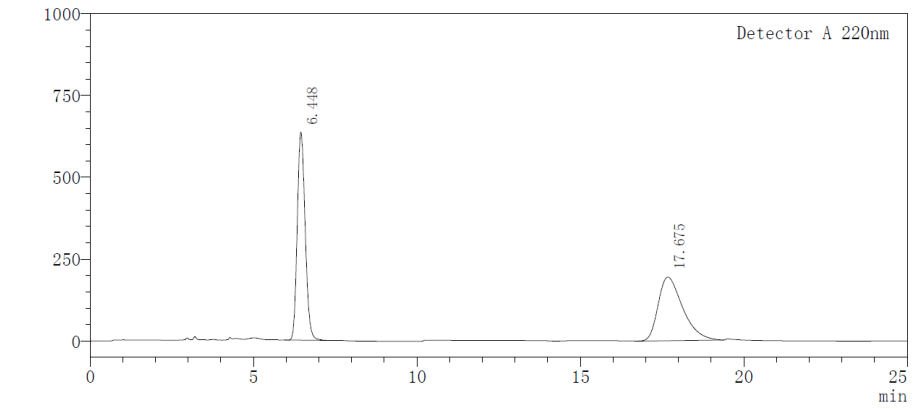
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.97 – 6.94 (m, 1H), 6.82 – 6.76 (m, 3H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 4.49 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.56 (br, 1H), 1.89 – 1.77 (m, 2H), 1.27 – 1.17 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 146.0, 143.5, 141.0, 141.0, 136.3, 134.0, 131.1, 128.9, 128.7, 128.2, 127.9, 127.9, 127.2, 118.3, 117.9, 111.9, 109.5, 55.3, 55.2, 34.3, 31.7, 29.3, 28.9, 26.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{32}NO$ 386.2478; found 386.2473.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 17.58 min (major enantiomer), t_R = 6.62 min (minor enantiomer).

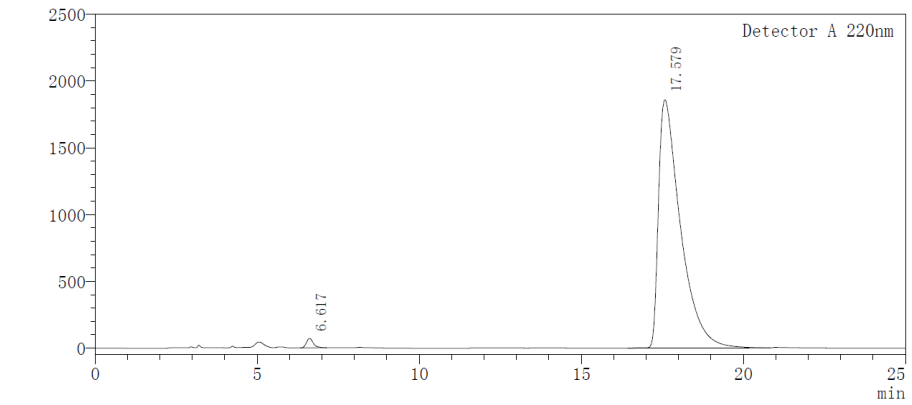
<chromatogram>



<Peak table>

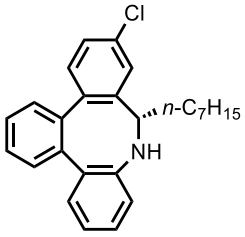
Peak#	Ret. Time	Height	Area	Area%
1	6.448	635358	10748162	51.462
2	17.675	194308	10137327	48.538
Total		829666	20885489	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	6.617	70788	1046159	1.179
2	17.579	1859089	87663712	98.821
Total		1929877	88709872	100.000



5ag

(S)-12-chloro-10-heptyl-9,10-dihydrotribenzo[b,d,f]azocine 5ag: Yellow oil, actual mass 59.1 mg, 76% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +89.3 (c = 0.2, $CHCl_3$).

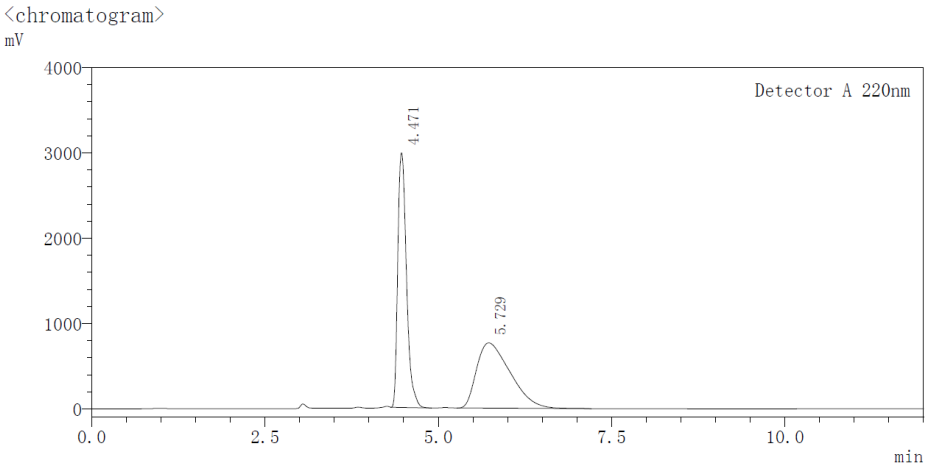
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.24 – 7.16 (m, 4H), 6.98 – 6.95 (m, 1H), 6.76 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.66 – 6.64 (m, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 4.47 (t, *J* = 7.1 Hz, 1H), 3.54 (br, 1H), 1.89 – 1.75 (m, 2H), 1.26 – 1.16 (m, 10H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.7, 143.2, 142.0, 141.6, 140.1, 134.0, 133.8, 131.3, 129.1, 128.7, 128.5, 128.1, 127.8, 127.4, 127.3, 123.9, 118.5, 118.0, 55.1, 34.1, 31.7, 29.2, 28.9, 26.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{29}ClN$ 390.1983; found 390.1991.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 5.41 min (major enantiomer), t_R = 4.37 min (minor enantiomer).

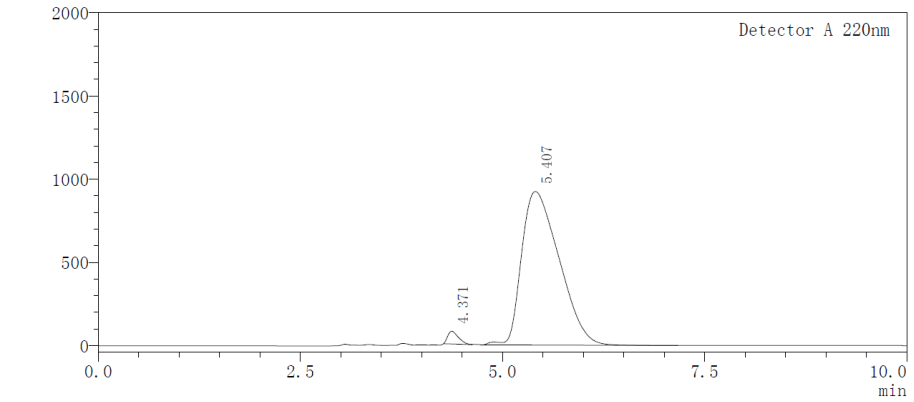
<chromatogram>



<Peak table>

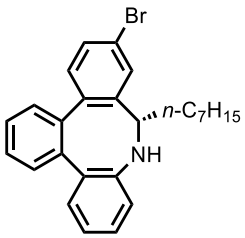
Peak#	Ret. Time	Height	Area	Area%
1	4.471	2983871	26087827	50.365
2	5.729	764734	25709381	49.635
Total		3748604	51797209	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.371	76415	700079	2.289
2	5.407	922673	29887755	97.711
Total		999089	30587834	100.000



5ah

(S)-12-bromo-10-heptyl-9,10-dihydrotribenzo[b,d,f]azocine 5ah: Yellow oil, actual mass 53.7 mg, 62% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +66.3 (c = 0.2, $CHCl_3$).

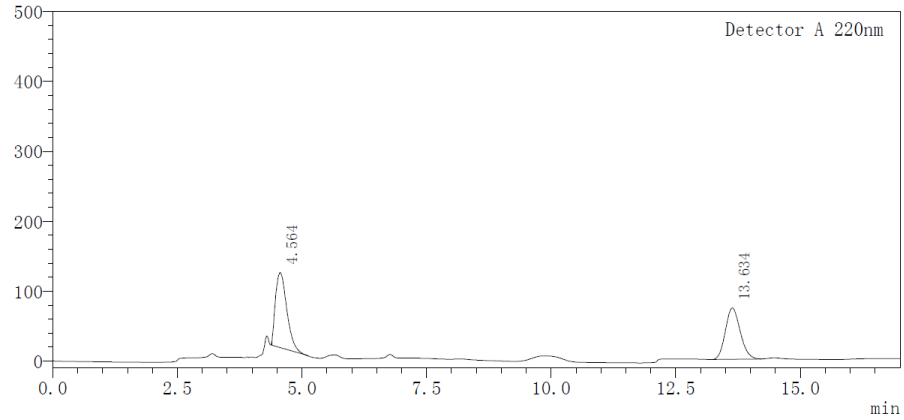
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 1H), 7.42 – 7.36 (m, 3H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.18 – 7.16 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.96 (m, 1H), 6.78 – 6.76 (m, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.48 (t, *J* = 6.9 Hz, 1H), 3.55 (br, 1H), 1.88 – 1.76 (m, 2H), 1.27 – 1.18 (m, 10H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 143.1, 142.4, 141.9, 140.1, 134.0, 131.3, 130.3, 129.5, 128.6, 128.5, 128.1, 127.8, 127.3, 126.8, 122.1, 118.5, 118.0, 55.0, 34.1, 31.7, 29.2, 28.9, 26.4, 22.5, 14.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{29}BrN$ 434.1478; found 434.1480.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 13.37 min (major enantiomer), t_R = 4.76 min (minor enantiomer).

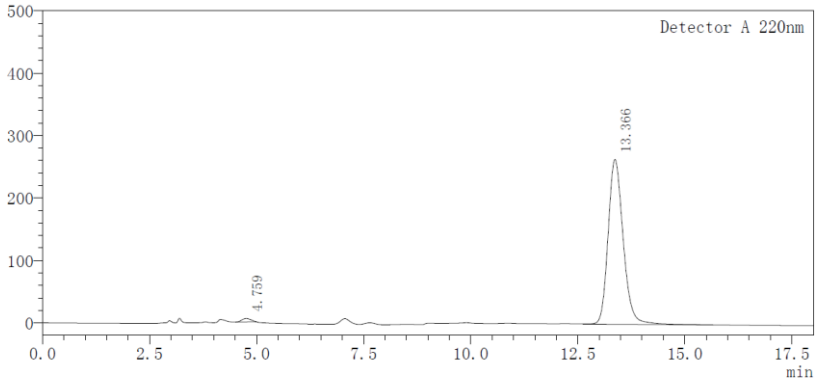
<chromatogram>
mV



<Peak table>

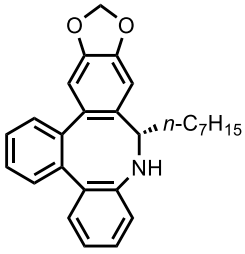
Peak#	Ret. Time	Height	Area	Area%
1	4.564	107270	1692843	52.751
2	13.634	73392	1516283	47.249
Total		180662	3209126	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.759	5349	81369	1.242
2	13.366	263997	6468532	98.758
Total		269347	6549901	100.000



5ai

(S)-10-heptyl-9,10-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-f]benzo[b]benzo[d]azocine 5ai: Yellow oil, actual mass 64.7 mg, 81% yield, (eluent: petroleum ether/ethyl acetate = 10:1). $[\alpha]_D^{25}$ = +159.3 (c = 0.2, $CHCl_3$).

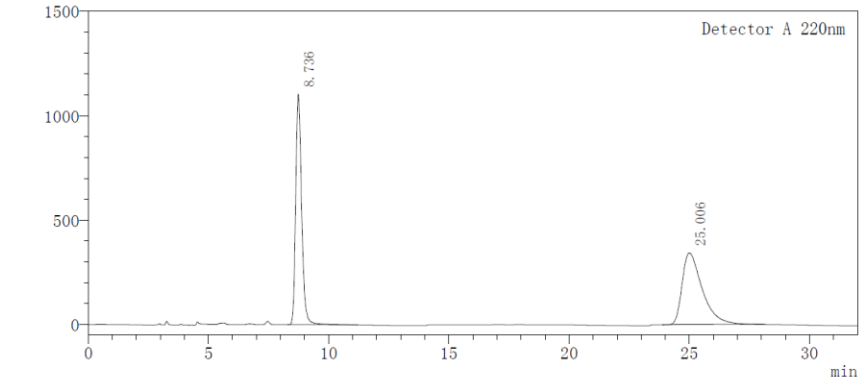
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.27 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.19 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.99 – 6.96 (m, 1H), 6.78 – 6.74 (m, 3H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.95 – 5.88 (m, 2H), 4.43 (t, *J* = 7.3 Hz, 1H), 3.54 (br, 1H), 1.85 – 1.70 (m, 2H), 1.24 – 1.16 (m, 10H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.6, 146.3, 146.1, 143.3, 141.2, 137.2, 133.8, 133.1, 131.2, 128.7, 128.3, 128.0, 128.0, 127.2, 118.3, 117.8, 108.0, 103.7, 100.9, 55.1, 34.4, 31.7, 29.2, 29.0, 26.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{30}NO_2$ 400.2271; found 400.2265.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 24.62 min (major enantiomer), t_R = 8.71 min (minor enantiomer).

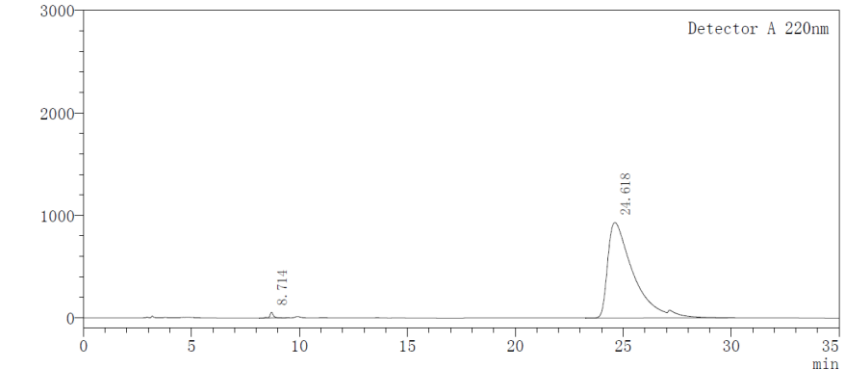
<chromatogram>
mV



<Peak table>

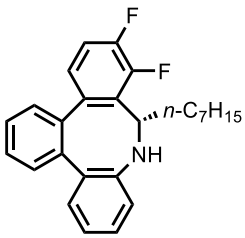
Peak#	Ret. Time	Height	Area	Area%
1	8.736	1102157	19009650	48.920
2	25.006	343249	19848958	51.080
Total		1445406	38858607	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	8.714	56838	686233	0.881
2	24.618	932581	77217632	99.119
Total		989419	77903865	100.000



5aj

(S)-11,12-difluoro-10-heptyl-9,10-dihydrotribenzo[b,d,f]azocine 5aj: Yellow oil, actual mass 62.6 mg, 80% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +125.3 (c = 0.2, $CHCl_3$).

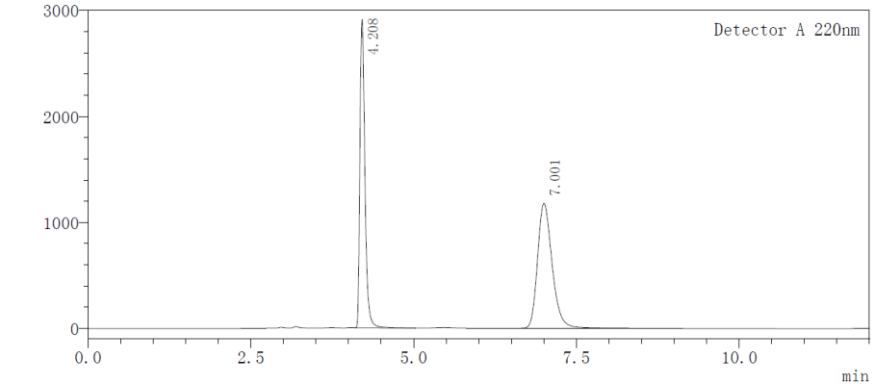
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.07 – 6.99 (m, 3H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 3.84 (d, *J* = 7.4 Hz, 1H), 2.12 – 1.97 (m, 2H), 1.22 – 1.15 (m, 10H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1 (dd, $J_{C\text{-}F}$ = 223.4, 13.8 Hz), 148.5 (dd, $J_{C\text{-}F}$ = 225.4, 13.1 Hz), 146.0, 143.4, 140.7 – 140.6 (m), 139.9, 134.1, 131.5, 128.7, 128.7 (d, *J* = 9.6 Hz), 128.5, 128.2, 127.7, 127.4, 123.3 (dd, *J* = 6.0, 3.4 Hz), 118.75, 117.92, 115.9 (d, *J* = 17.3 Hz), 56.12, 33.6 (d, *J* = 8.0 Hz), 31.69, 29.08, 28.91, 26.91, 22.51, 14.04.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{28}F_2N$ 392.2184; found 392.2188.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 7.52 min (major enantiomer), t_R = 4.80 min (minor enantiomer).

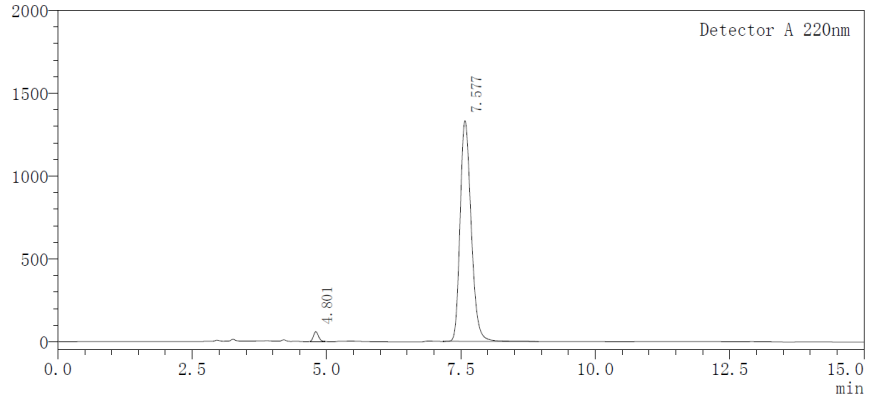
<chromatogram>
mV



<Peak table>

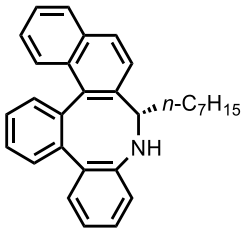
Peak#	Ret. Time	Height	Area	Area%
1	4.208	2910938	15681472	45.980
2	7.001	1179531	18423780	54.020
Total		4090469	34105253	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.801	58793	380038	1.945
2	7.577	1332879	19162925	98.055
Total		1391672	19542963	100.000



5ak

(S)-7-heptyl-7,8-dihydrodibenzo[b,d]naphtho[1,2-f]azocine 5ak: Yellow oil, actual mass 69.7 mg, 86% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = +105.5 (c = 0.2, $CHCl_3$).

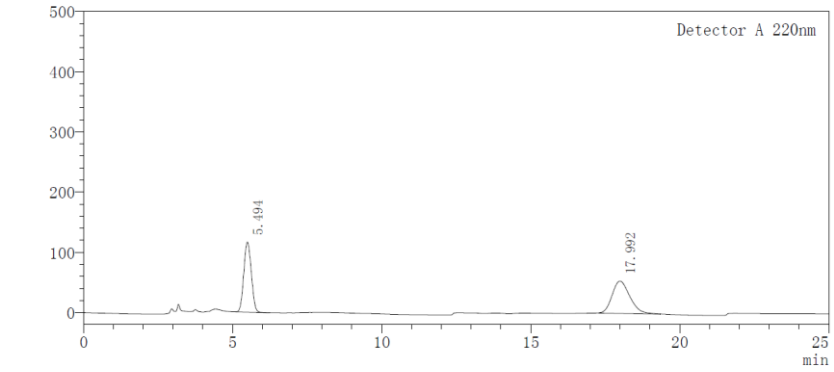
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 3H), 7.54 – 7.30 (m, 7H), 6.89 – 6.81 (m, 2H), 6.55 (t, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.63 (t, *J* = 7.3 Hz, 1H), 3.59 (br, 1H), 1.97 – 1.93 (m, 2H), 1.27 – 1.17 (m, 10H), 0.84 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.9, 144.2, 139.6, 138.4, 135.8, 133.1, 132.9, 131.6, 131.2, 130.4, 128.6, 128.4, 128.3, 127.9, 127.9, 126.7, 126.4, 126.0, 125.4, 121.3, 118.3, 117.8, 55.9, 33.9, 31.7, 29.2, 29.0, 26.5, 22.5, 14.0.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{32}N$ 406.2529; found 406.2529.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 17.27 min (major enantiomer), t_R = 5.52 min (minor enantiomer).

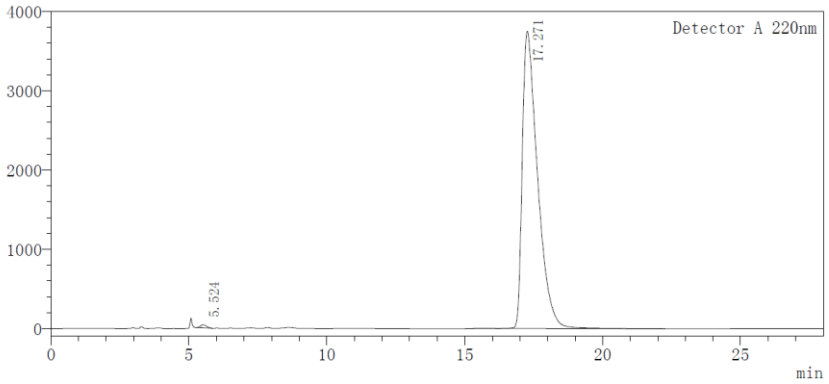
<chromatogram>
mV



<Peak table>

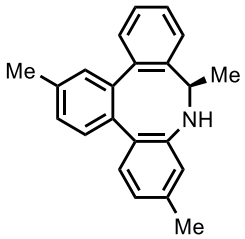
Peak#	Ret. Time	Height	Area	Area%
1	5.494	116552	2057237	48.060
2	17.992	53802	2223311	51.940
Total		170354	4280548	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	5.524	39059	612140	0.421
2	17.271	3752566	144665792	99.579
Total		3791626	145277932	100.000



5ba

(R)-2,7,10-trimethyl-9,10-dihydrotribenzo[b,d,f]azocine 5ba: Yellow oil, actual mass 34.7 mg, 58% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -188.5 (c = 0.2, $CHCl_3$).

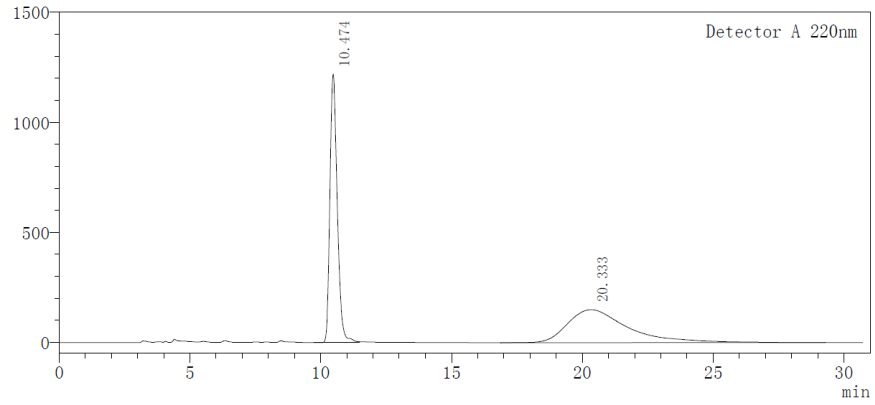
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 5H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.38 – 6.36 (m, 1H), 6.15 (s, 1H), 4.64 (q, *J* = 6.7 Hz, 1H), 3.44 (br, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 143.3, 141.1, 140.5, 140.2, 137.5, 136.7, 133.9, 131.1, 129.8, 128.8, 128.0, 127.8, 127.2, 125.4, 123.1, 119.5, 118.4, 50.3, 21.0, 20.8, 20.3.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}N$ 300.1747; found 300.1727.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 19.84 min (major enantiomer), t_R = 10.35 min (minor enantiomer).

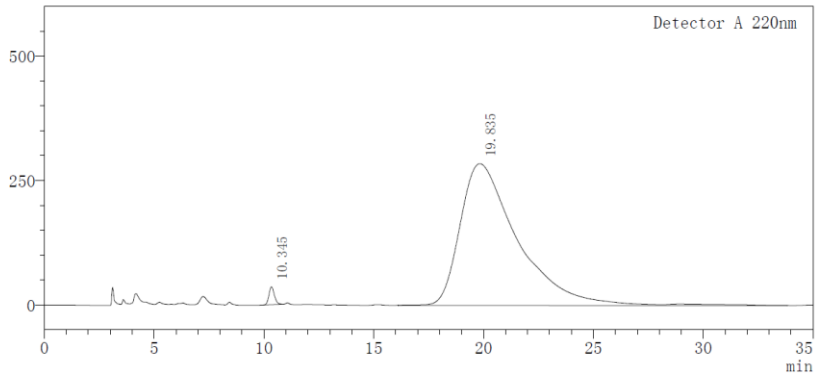
<chromatogram>
mV



<Peak table>

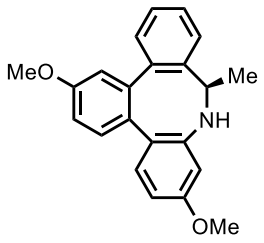
Peak#	Ret. Time	Height	Area	Area%
1	10.474	1215956	23586504	49.422
2	20.333	149628	24138363	50.578
Total		1365584	47724866	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	10.345	35861	625796	1.192
2	19.835	284826	51882992	98.808
Total		320686	52508788	100.000



5ca

(R)-2,7-dimethoxy-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5ca: Yellow oil, actual mass 44.4 mg, 67% yield, (eluent: petroleum ether/ethyl acetate = 10:1). $[\alpha]_D^{25}$ = -238.4 (c = 0.2, $CHCl_3$).

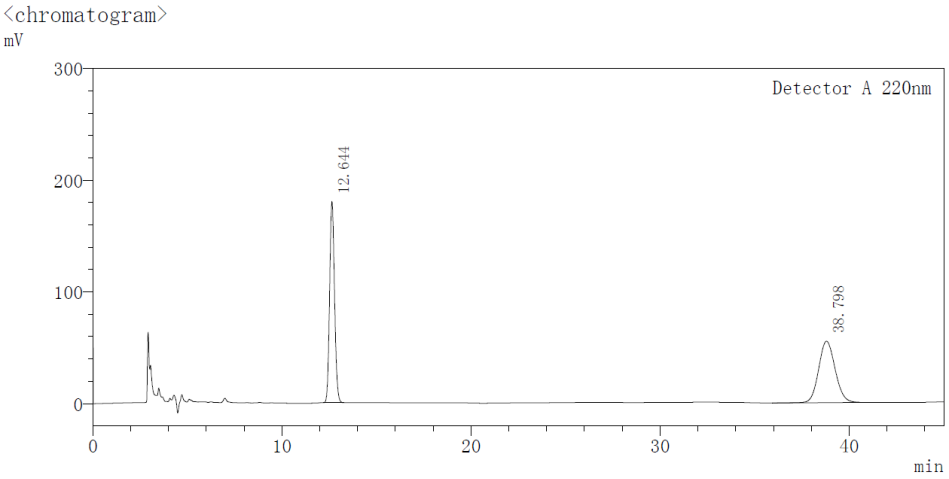
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.97 (d, *J* = 2.5 Hz, 1H), 4.77 (q, *J* = 6.7 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.61 (br, 1H), 1.50 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 158.7, 147.1, 143.0, 142.5, 140.4, 135.3, 135.0, 132.2, 128.2, 127.6, 127.3, 123.2, 121.0, 114.6, 113.3, 104.5, 102.6, 55.3, 54.9, 50.2, 20.3.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO_2$ 332.1645; found 332.1640.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 75 : 25, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 12.89 min (major enantiomer), t_R = 40.25 min (minor enantiomer).

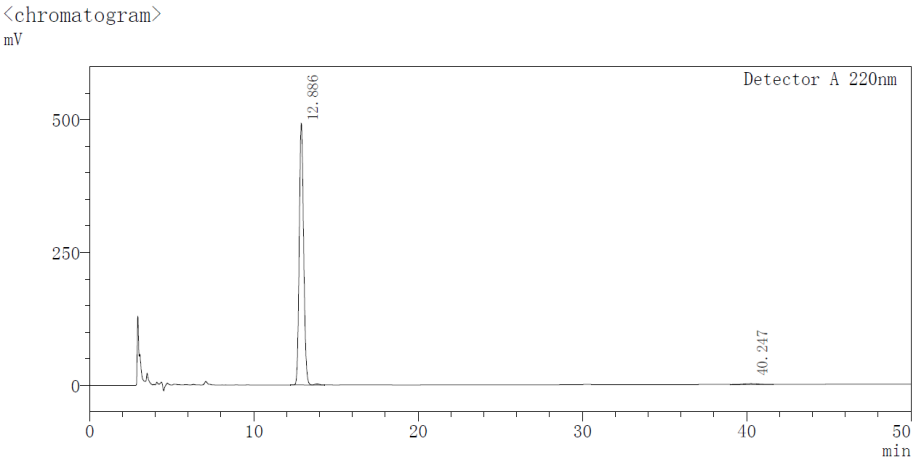
<chromatogram>



<Peak table>

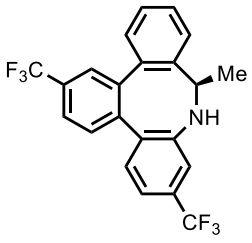
Peak#	Ret. Time	Height	Area	Area%
1	12.644	179864	3259002	49.423
2	38.798	55068	3335045	50.577
Total		234932	6594047	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	12.886	492900	9224737	98.859
2	40.247	1720	106424	1.141
Total		494620	9331161	100.000



5da

(R)-10-methyl-2,7-bis(trifluoromethyl)-9,10-dihydrotribenzo[b,d,f]azocine 5da: Yellow oil, actual mass 40.7 mg, 50% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -162.3 (c = 0.2, $CHCl_3$).

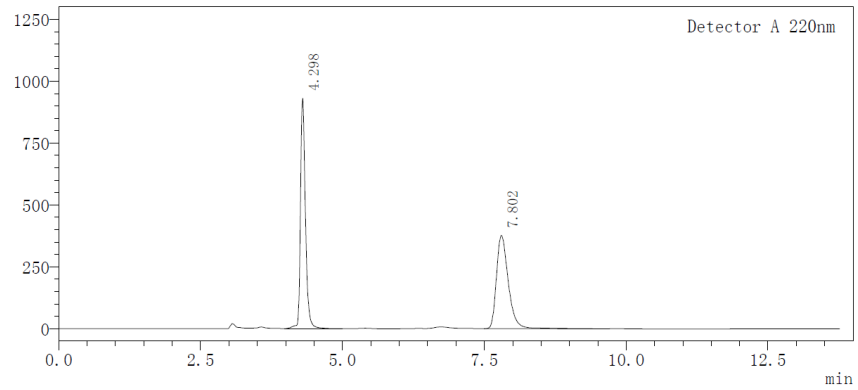
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 1H), 7.51 (s, 1H), 7.43 – 7.31 (m, 5H), 6.88 – 6.82 (m, 2H), 6.69 (s, 1H), 4.70 – 6.63 (m, 1H), 3.82 (d, *J* = 8.5 Hz, 1H), 1.53 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 145.6, 142.0, 141.3, 139.4, 134.2, 131.5, 130.7 (q, *J* = 32.3 Hz), 130.2 (q, *J* = 32.6 Hz), 129.8, 129.2, 127.92, 127.74, 125.9 (q, *J* = 3.7 Hz), 125.2 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 272.4 Hz), 123.9 (q, *J* = 273.8 Hz), 123.54, 114.8 – 114.7 (m), 50.4, 20.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{16}F_6N$ 408.1181; found 408.1186.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 4.17 min (major enantiomer), t_R = 6.47 min (minor enantiomer).

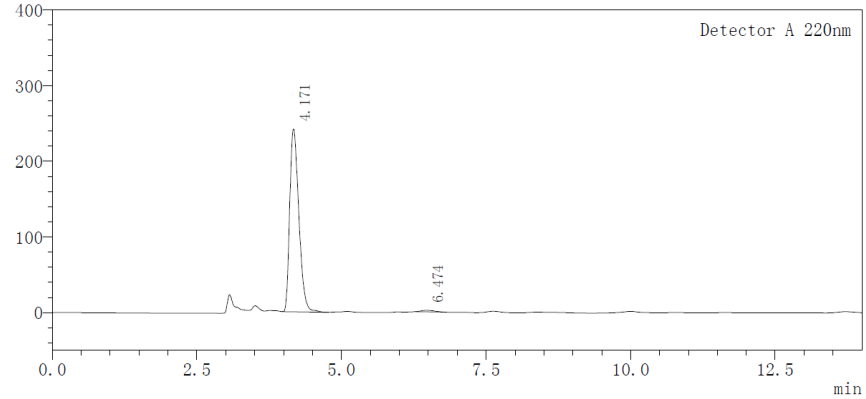
<chromatogram>
mV



<Peak table>

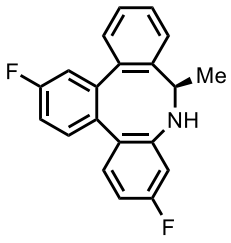
Peak#	Ret. Time	Height	Area	Area%
1	4.298	931003	5663955	50.798
2	7.802	376587	5486031	49.202
Total		1307590	11149985	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	4.171	241495	2655882	98.791
2	6.474	2089	32503	1.209
Total		243584	2688385	100.000



5ea

(R)-2,7-difluoro-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5ea: Yellow oil, actual mass 54.0 mg, 88% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -227.5 (c = 0.2, $CHCl_3$).

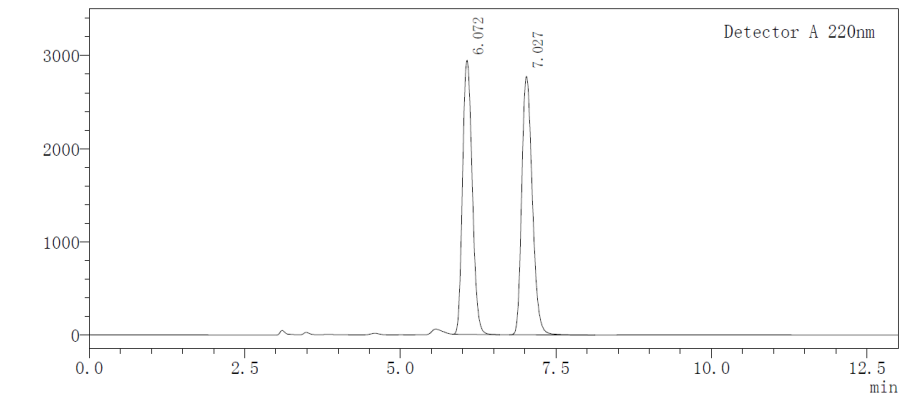
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.20 (m, 1H), 7.16 – 7.13 (m, 1H), 6.96 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.69 – 6.67 (m, 1H), 6.34 (td, *J* = 8.4, 2.5 Hz, 1H), 6.13 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.70 (br, 1H), 3.65 (br, 1H), 1.50 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, *J* = 244.8 Hz), 162.3 (d, *J* = 247.1 Hz), 147.7(d, *J* = 10.2 Hz), 143.3 (d, *J* = 7.7 Hz), 141.9, 139.8, 138.2 (d, *J* = 3.1 Hz), 135.3 (d, *J* = 9.6 Hz), 132.6 (d, *J* = 8.2 Hz), 128.8, 127.6, 127.5, 123.3, 123.3, 116.0 (d, *J* = 21.6 Hz), 114.8 (d, *J* = 20.8 Hz), 105.5 (d, *J* = 21.2 Hz), 104.0 (d, *J* = 24.1 Hz), 50.3, 20.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}F_2N$ 308.1245; found 308.1253.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 6.40 min (major enantiomer), t_R = 7.34 min (minor enantiomer).

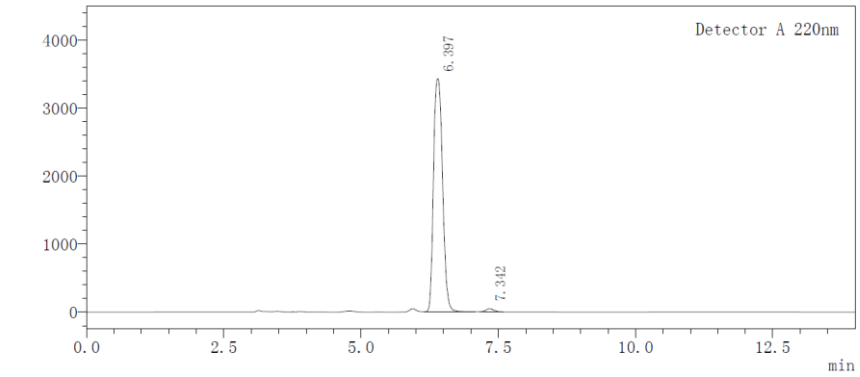
<chromatogram>



<Peak table>

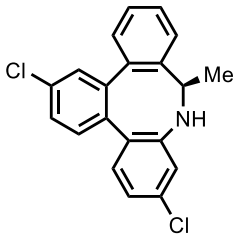
Peak#	Ret. Time	Height	Area	Area%
1	6.072	2942329	31916370	49.296
2	7.027	2775592	32828465	50.704
Total		5717921	64744835	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	6.397	3431562	39223999	98.897
2	7.342	45750	437434	1.103
Total		3477312	39661434	100.000



5fa

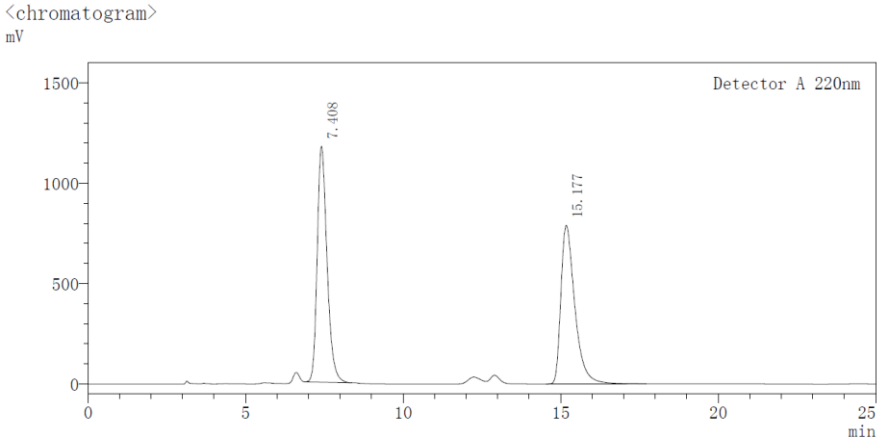
(R)-2,7-dichloro-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5fa: Yellow oil, actual mass 44.1 mg, 65% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -155.5 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.57 – 6.50 (m, 2H), 6.34 (d, *J* = 2.0 Hz, 1H), 4.60 (br, 1H), 3.55 (br, 1H), 1.41 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 143.0, 141.5, 140.6, 139.7, 134.8, 133.7, 133.5, 132.3, 129.0, 128.9, 128.3, 127.7, 127.6, 125.5, 123.4, 118.6, 117.4, 50.3, 20.1.

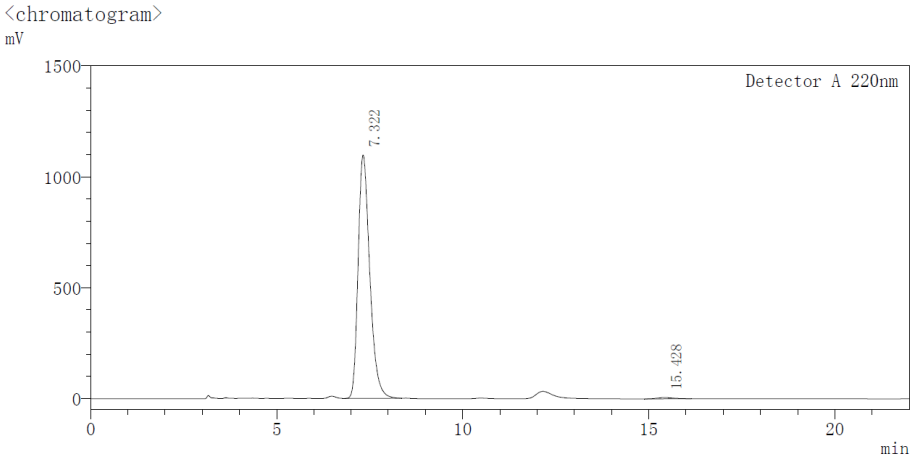
HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}Cl_2N$ 340.0654; found 340.0648.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98.5 : 1.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 7.32 min (major enantiomer), t_R = 15.43 min (minor enantiomer).



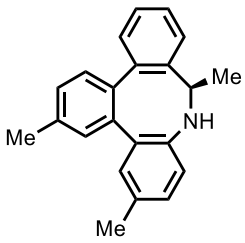
〈Peak table〉

Peak#	Ret. Time	Height	Area	Area%
1	7.408	1174716	25517785	51.203
2	15.177	789614	24318254	48.797
Total		1964329	49836039	100.000



〈Peak table〉

Peak#	Ret. Time	Height	Area	Area%
1	7.322	1096880	23928613	99.356
2	15.428	5196	155125	0.644
Total		1102076	24083739	100.000



5ga

(R)-3,6,10-trimethyl-9,10-dihydrotribenzo[b,d,f]azocine 5ga: Yellow oil, actual mass 32.9 mg, 55% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -224.0 (c = 0.2, $CHCl_3$).

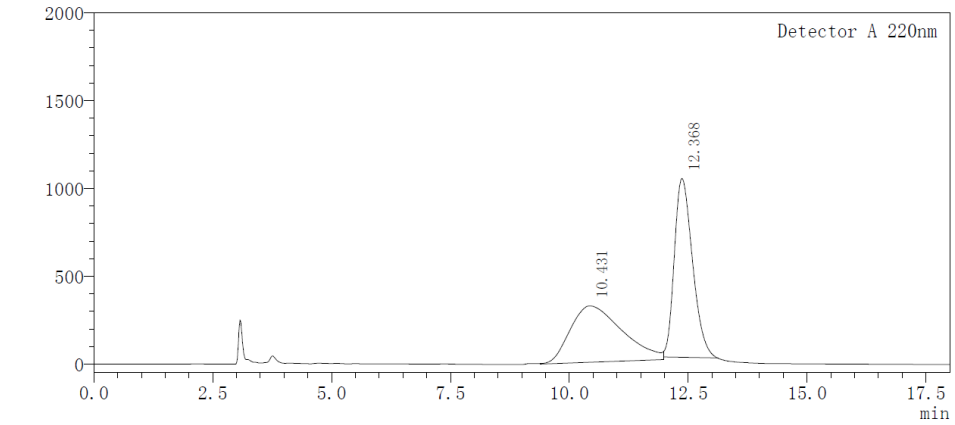
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 5H), 7.13 – 7.10 (m, 2H), 6.73 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.58 (d, *J* = 1.7 Hz, 1H), 6.32 (d, *J* = 8.1 Hz, 1H), 4.66 (q, *J* = 6.7 Hz, 1H), 3.46 (br, 1H), 2.43 (s, 3H), 2.11 (s, 3H), 1.46 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 143.1, 143.0, 140.6, 138.4, 137.7, 134.1, 131.8, 128.8, 128.6, 128.4, 128.0, 127.8, 127.4, 127.2, 123.1, 118.0, 50.6, 21.1, 20.3, 20.1.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{22}N$ 300.1747; found 300.1723.

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 99 : 1, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 9.83 min (major enantiomer), t_R = 11.70 min (minor enantiomer).

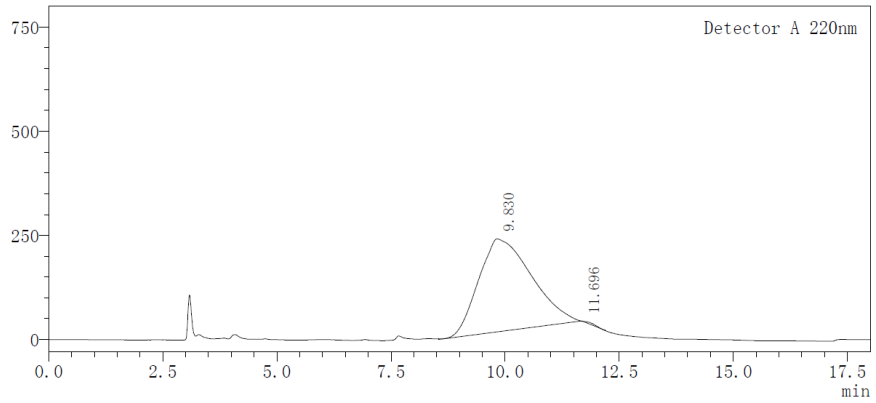
<chromatogram>
mV



<Peak table>

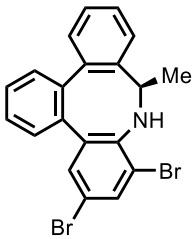
Peak#	Ret. Time	Height	Area	Area%
1	10.431	321821	24427004	47.355
2	12.368	1018275	27155966	52.645
Total		1340096	51582970	100.000

<chromatogram>
mV



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	9.830	223317	17923877	99.720
2	11.696	-107	50310	0.280
Total		223210	17974186	100.000



5aa-B

(R)-6,8-dibromo-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 5aa-B: White solid, actual mass 75.1 mg, 88% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -220.6 (c = 0.2, $CHCl_3$).

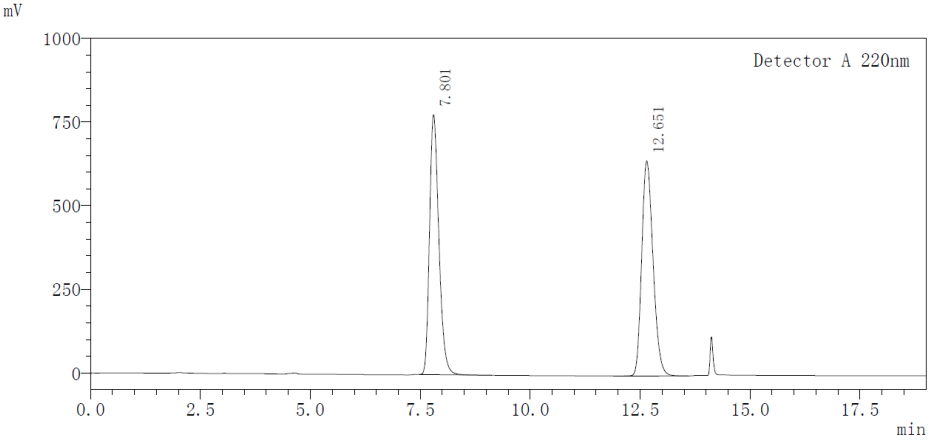
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.31 – 7.30 (m, 2H), 7.26 – 7.24 (m, 2H), 6.83 (d, *J* = 2.3 Hz, 1H), 4.69 – 4.64 (m, 1H), 4.49 (d, *J* = 8.1 Hz, 1H), 1.56 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 142.5, 141.2, 140.9, 139.5, 135.3, 133.5, 131.1, 131,0, 128.9, 128.6, 128.4, 128.1, 127.7, 127.5, 123.4, 112.6, 109.2, 50.7, 20.1.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}Br_2N$ 427.9644; found 427.9595.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99.5 : 0.5, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 7.42 min (major enantiomer), t_R = 12.24 min (minor enantiomer).

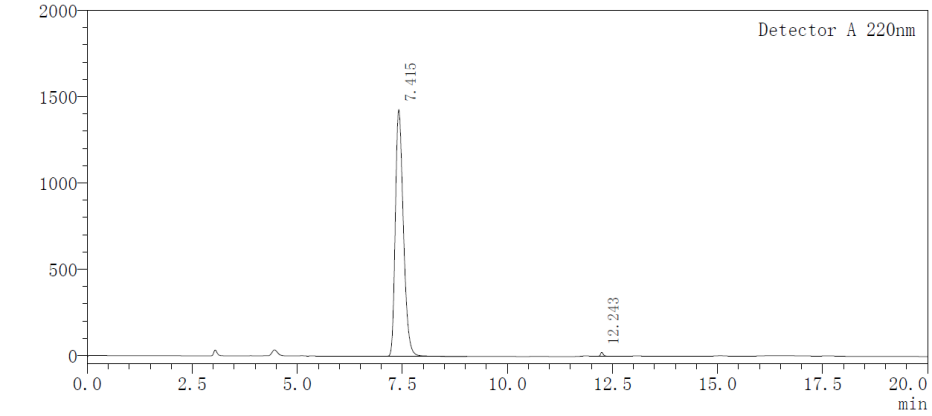
<chromatogram>



<Peak table>

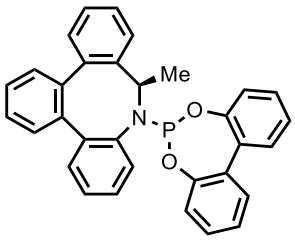
Peak#	Ret. Time	Height	Area	Area%
1	7.801	777292	11485796	49.826
2	12.651	643160	11566088	50.174
Total		1420452	23051884	100.000

<chromatogram>



<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	7.415	1429690	19131951	99.507
2	12.243	22166	94739	0.493
Total		1451856	19226689	100.000



6

(R)-9-(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)-10-methyl-9,10-dihydrotribenzo[b,d,f]azocine 6: White solid, actual mass 128.5 mg, 53% yield, (eluent: petroleum ether/ethyl acetate = 20:1). $[\alpha]_D^{25}$ = -41.0 (c = 0.2, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.45 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.20 – 7.09 (m, 6H), 7.07 – 7.02 (m, 2H), 7.00 – 6.91 (m, 4H), 5.12 – 5.08 (m, 1H), 1.76 (d, *J* = 6.7 Hz, 3H).

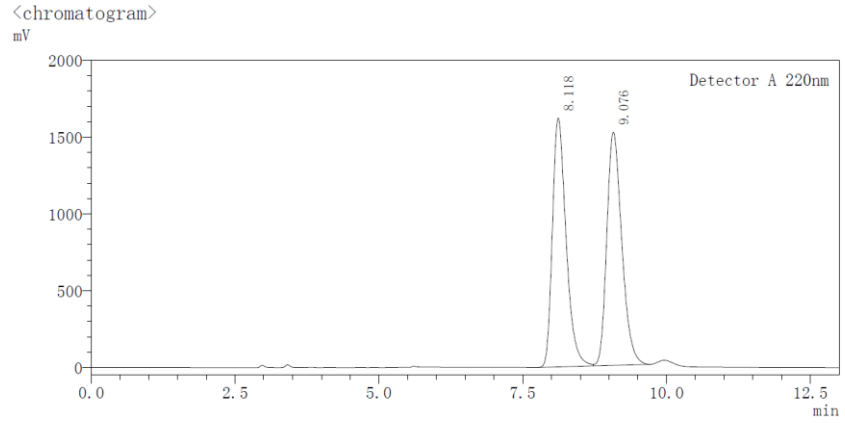
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3 (d, J_{C-P} = 6.6), 150.8 (d, J_{C-P} = 3.9), 144.3 (d, J_{C-P} = 4.3), 142.7, 142.1, 140.6, 139.6 (d, J_{C-P} = 10.1), 138.3 (d, J_{C-P} = 5.6), 131.3 (d, J_{C-P} = 3.7), 131.1 (d, J_{C-P} = 3.5), 131.1, 130.5 (d, J_{C-P} = 2.9), 129.7 (d, J_{C-P} = 6.4),

128.9 (d, $J_{C\text{-}P}$ = 4.9), 128.8, 128.3, 128.0, 127.7, 127.6, 127.3 (d, $J_{C\text{-}P}$ = 2.1), 127.2, 126.7, 126.3, 124.4, 124.1, 122.2 (d, $J_{C\text{-}P}$ = 12.2), 54.5 (d, $J_{C\text{-}P}$ = 18.5), 23.3(d, $J_{C\text{-}P}$ = 2.5).

^{31}P NMR (162 MHz, $CDCl_3$) δ 146.25.

HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{24}NNaO_2P$ 508.1437; found 508.1435.

HPLC (Daicel CHIRALPAK OD-H, *n*-hexane : isopropanol = 99.2 : 0.8, Flow rate = 1.0 mL/min, λ = 220 nm): t_R = 8.17 min (major enantiomer), t_R = 8.93 min (minor enantiomer).



<Peak table>

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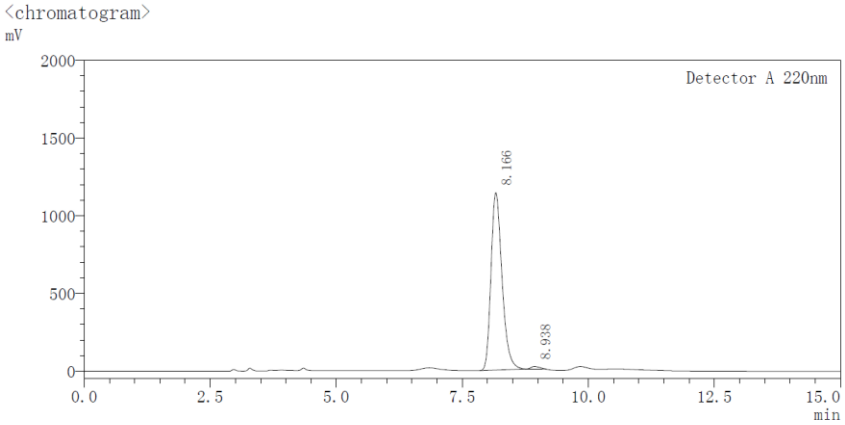
2	9.076	1519754	27563015	50.658
Total		3141238	54409514	100.000



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Peak#	Ret. Time	Height	Area	Area%
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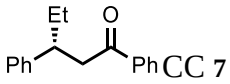
2	8.938	16623	195144	1.108
Total		1159570	17611651	100.000



CC **7**

(S)-(2-bromophenyl)(cyclopropyl)methanamine 7: White solid, actual mass 35.6 mg, 75% yield, (eluent: petroleum ether/ethyl acetate = 3:1). $[\alpha]_D^{25}$ = -6.3 (c = 0.2, $CHCl_3$). The specific rotation is opposite to the value of reported.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.55 – 7.42 (m, 3H), 7.30 – 7.18 (m, 5H), 3.30 – 3.24 (m, 3H), 1.82 – 1.77 (m, 1H), 1.68 – 1.63 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 3H).

HPLC (Daicel CHIRALPAK AD-H, *n*-hexane : isopropanol = 98 : 2, Flow rate = 1.0 mL/min, λ = 254 nm): t_R = 6.41 min (major enantiomer), t_R = 5.72 min (minor enantiomer).

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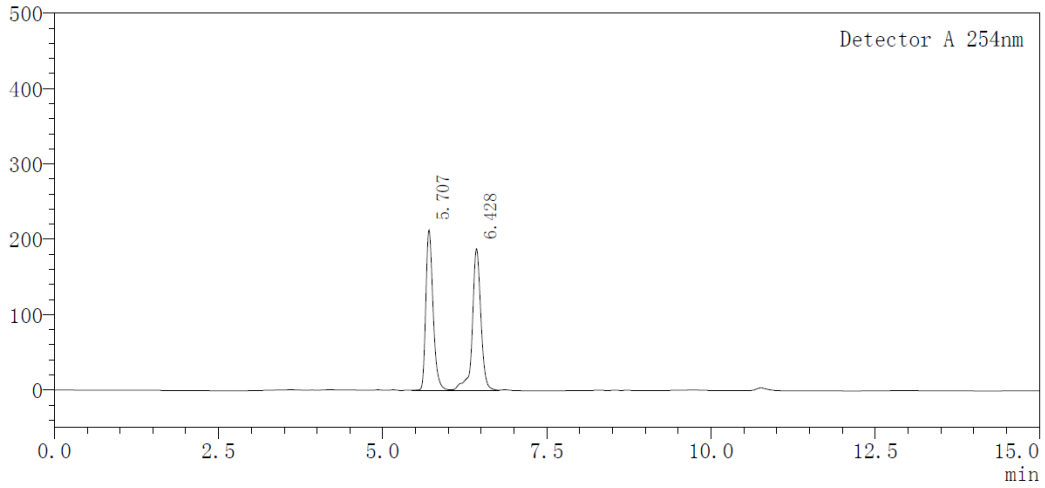

<Peak table>

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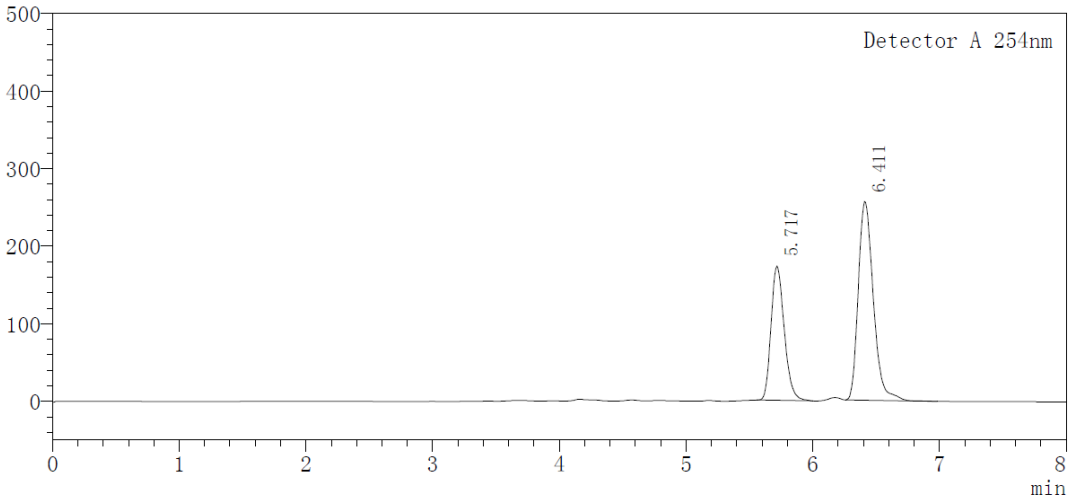

<Peak table>

Peak#	Ret. Time	Height	Area	Area%
1	5.717	173022	1256104	37.299
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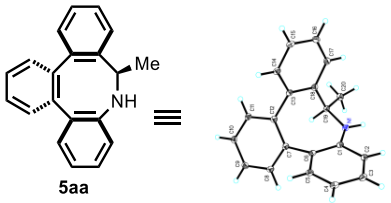
Total		429115	3367628	100.000

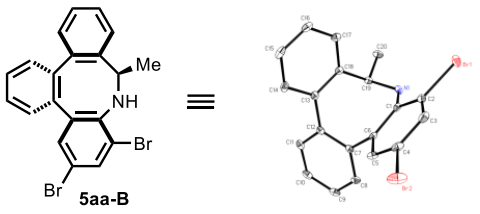
9. Crystal Structure and Corresponding Date of 5aa and 5aa-B



CDDC 2044586

Table 1. Crystal data and structure refinement for **5aa**.

Identification code	**5aa**	
Empirical formula	$C_{20}H_{17}N$	
Formula weight	271.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 16.9144(8) Å	= 90°.
	b = 7.7719(4) Å	= 107.6600(10)°.
	c = 22.6944(10) Å	= 90°.
Volume	2842.7(2) $Å^3$	
Z	8	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	0.558 mm^{-1}	
F(000)	1152	
Crystal size	0.300 x 0.150 x 0.120 mm^3	
Theta range for data collection	4.088 to 74.496°.	
Index ranges	-20<=h<=20, -9<=k<=9, -28<=l<=28	
Reflections collected	21990	
Independent reflections	5677 [R(int) = 0.0337]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5677 / 1 / 381	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1007	
R indices (all data)	R1 = 0.0385, wR2 = 0.1009	
Absolute structure parameter	0.4(4)	
Largest diff. peak and hole	0.469 and -0.358 e.$Å^{-3}$	



CDDC 2044587

Table 2. Crystal data and structure refinement for **5aa-B**

Identification code	**5aa-B**
Empirical formula	$C_{20}H_{15}Br_2N$
Formula weight	429.15
Temperature	101.0 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.4284(6) Å = 90°.
	b = 11.4357(9) Å = 90°.
	c = 17.5925(13) Å = 90°.
Volume	1695.6(2) $Å^3$
Z	4
Density (calculated)	1.681 Mg/m^3
Absorption coefficient	4.779 mm^{-1}
F(000)	848
Crystal size	0.29 x 0.1 x 0.05 mm^3
Theta range for data collection	2.680 to 27.481°.
Index ranges	-10<=h<=10, -14<=k<=14, -22<=l<=22
Reflections collected	20492
Independent reflections	3890 [R(int) = 0.0413]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5139
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3890 / 0 / 209
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	R1 = 0.0225, wR2 = 0.0480
R indices (all data)	R1 = 0.0255, wR2 = 0.0490
Absolute structure parameter	-0.013(5)
Largest diff. peak and hole	0.300 and -0.363 $e.Å^{-3}$

10. References

[1] H. Jiang, Y. Zhang, D. Chen, B. Zhou and Y. Zhang, *Org. Lett*. 2016, **18**, 2032-2035.

[2] M. A. Ayedi, Y. L. Bigot, H. Ammar, S. Abid, R. E. Gharbi, M. Delmas, *Synth. Commun*. 2013, **43**, 2127-2133.

[3] D. M. Schultz and J. P. Wolfe. *Org. Lett*. 2011, **13**, 2962-2965.

[4] K.-J. Xiao, L. Chu, G. Chen and J.-Q. Yu. *J. Am. Chem. Soc*. 2016, **138**, 7796–7800.

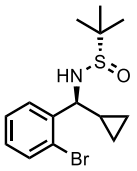
[5] C. R. Smith and T. V. RajanBabu, *Org. Lett.* 2008, **10**, 1657–1659.

[6] (a) A. Alexakis, C. Benhaim, S. Rosset and M. Humam, *J. Am. Chem. Soc*. 2002, **124**, 5262–5263; (b) H. Zhou, W.-H. Wang, Y. Fu, J.-H. Xie, W.-J. Shi, L.-X Wang and Q.-L. Zhou, *J. Org. Chem*. 2003, **68**, 1582-1584; (c) H. Yu, F. Xie, Z. Ma, Y. Liu and W. Zhang, *Org. Biomol. Chem.*, 2012, **10**, 5137-5142.

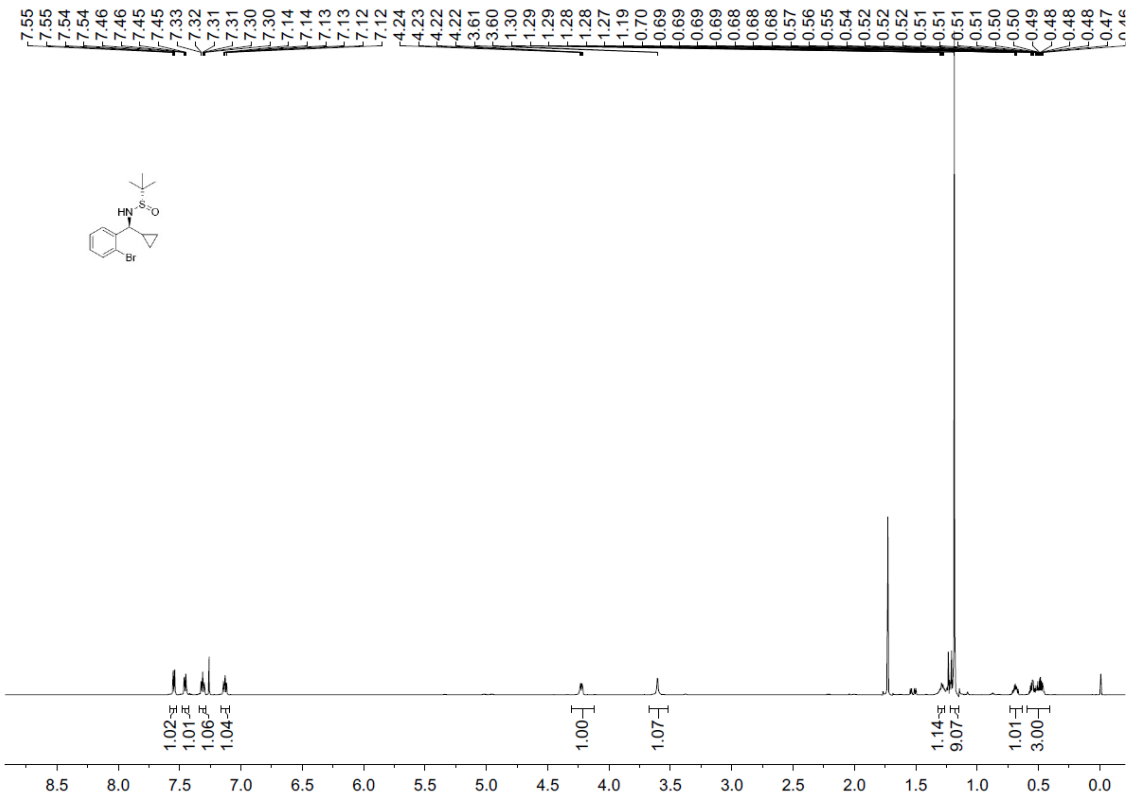
[7] T. Zhang, J. Jiang, L. Yao, H. Geng and X. Zhang. *Chem. Comm*. 2017, **53**, 9258-9261.

11. NMR Spectra

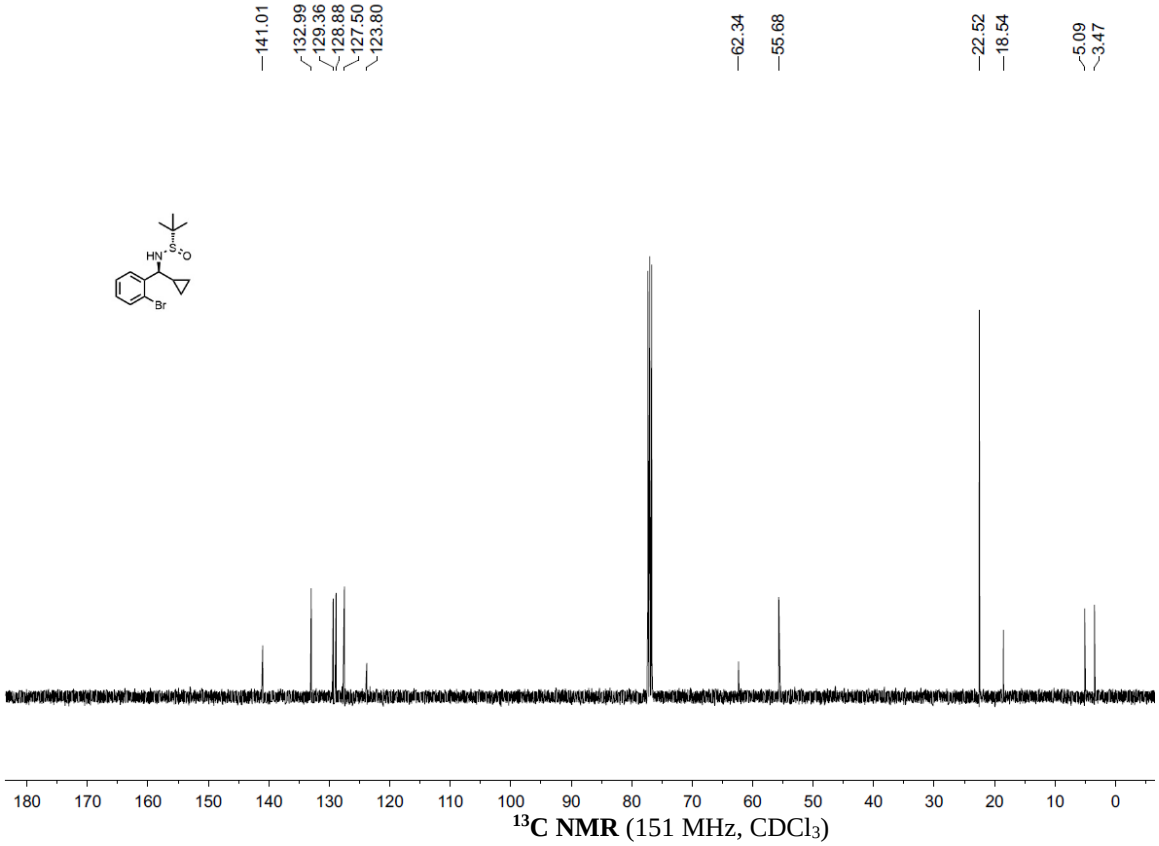
11.1 NMR Spectra of the Substrates



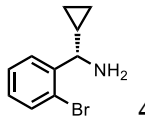
S2-b



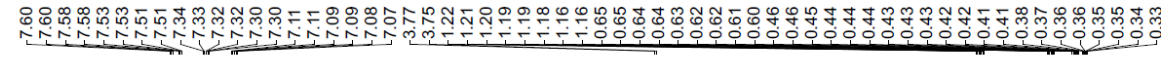
^{1}H NMR (600 MHz, $CDCl_3$)

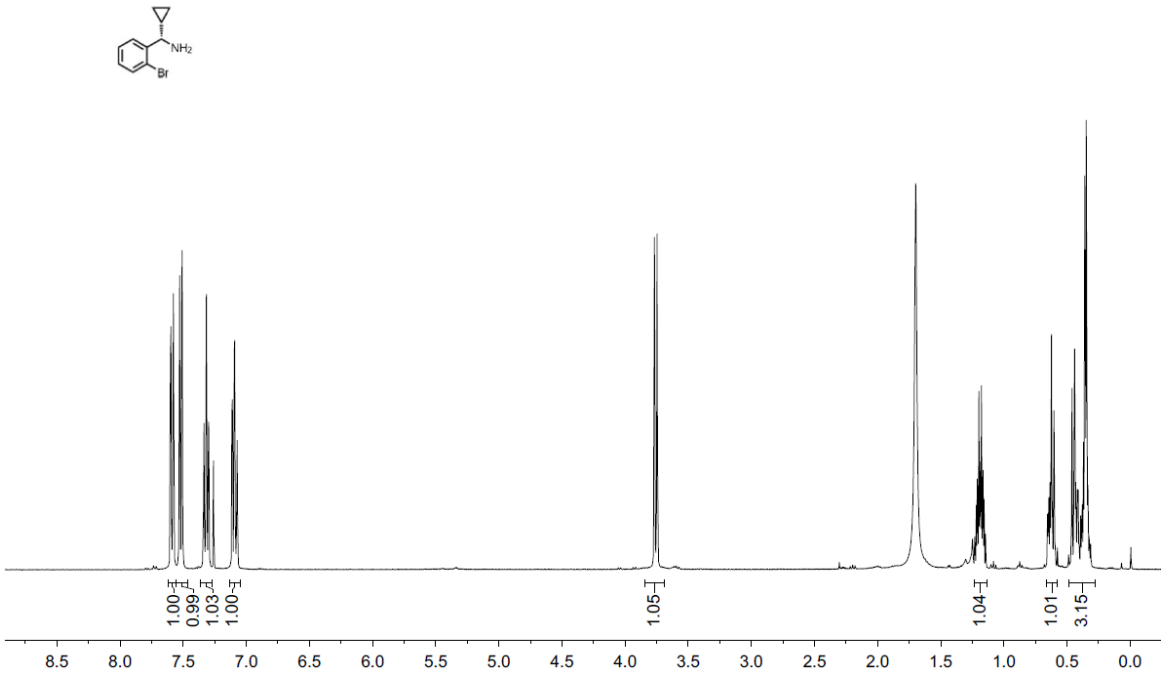


^{13}C NMR (151 MHz, $CDCl_3$)

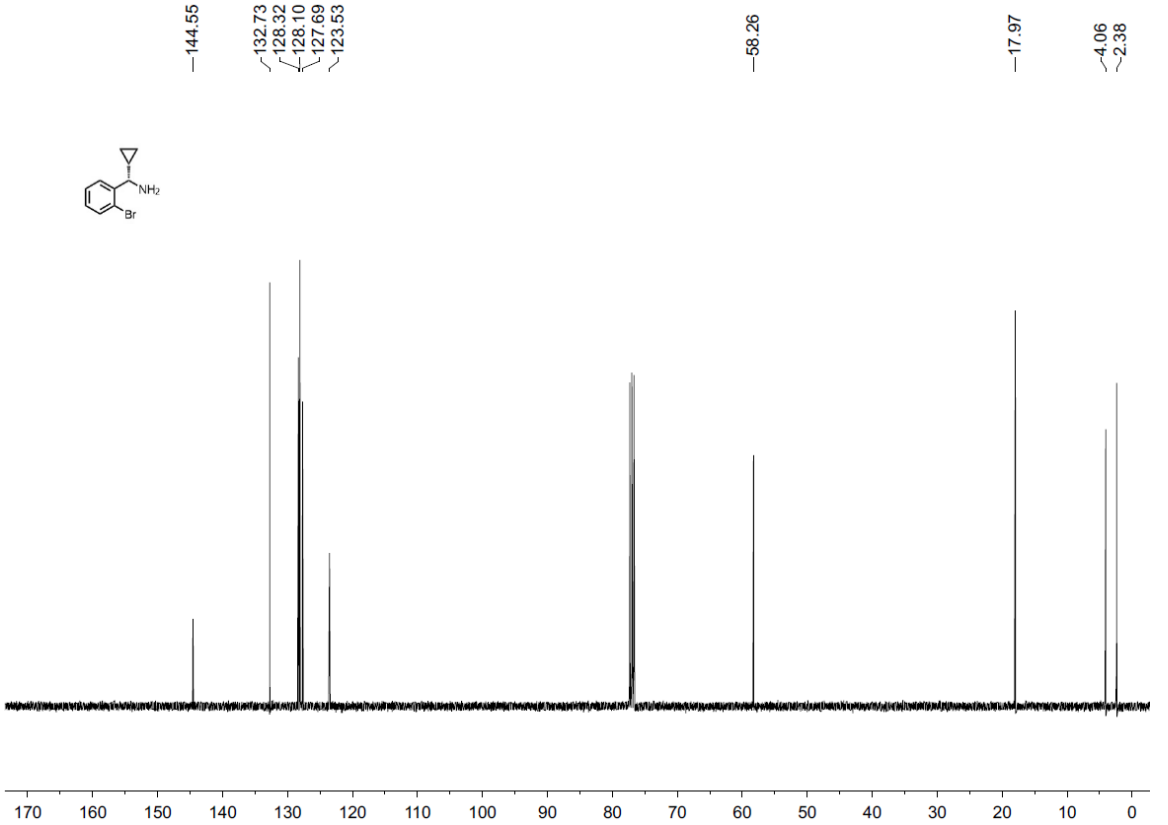


4b

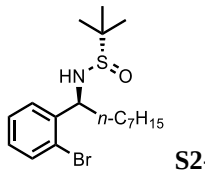




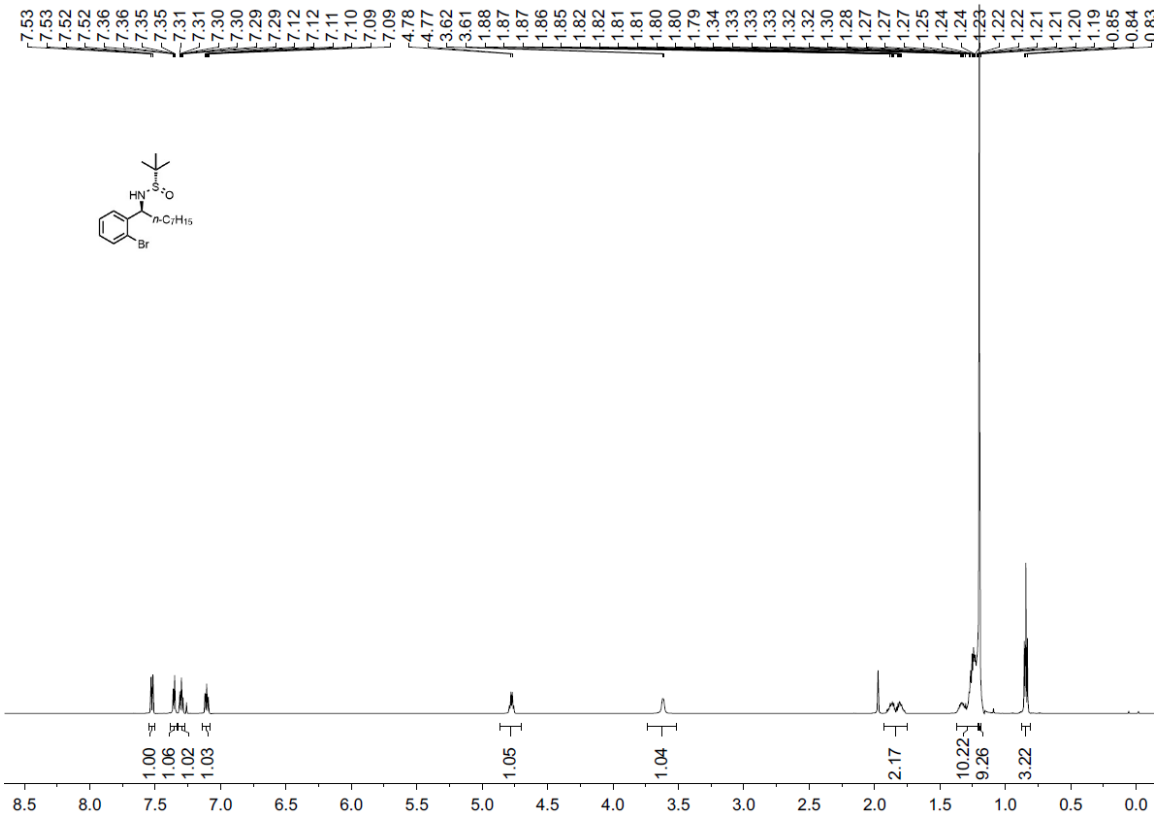
^{1}H NMR (600 MHz, $CDCl_3$)



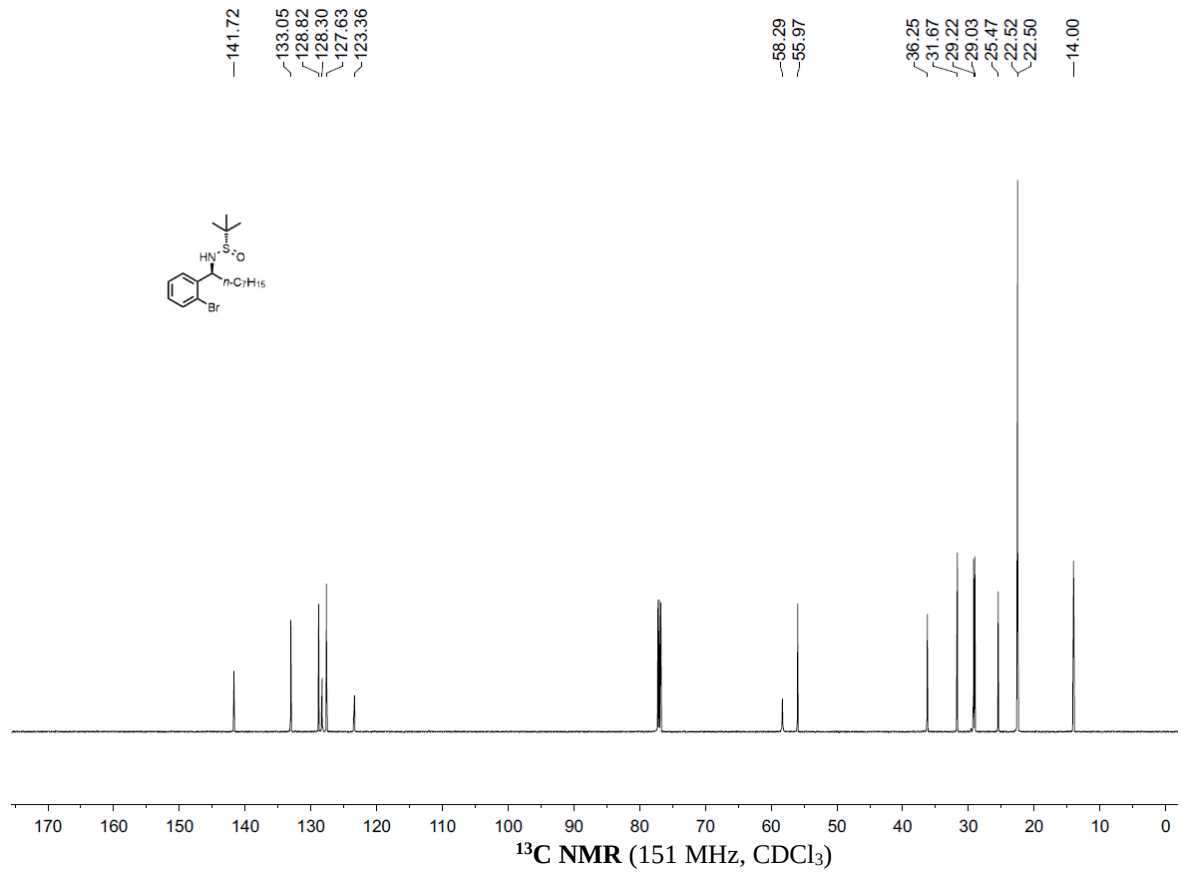
^{13}C NMR (151 MHz, $CDCl_3$)



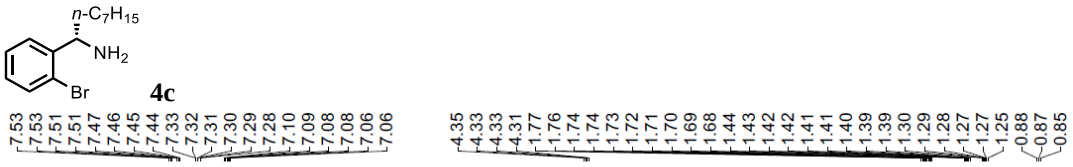
S2-c

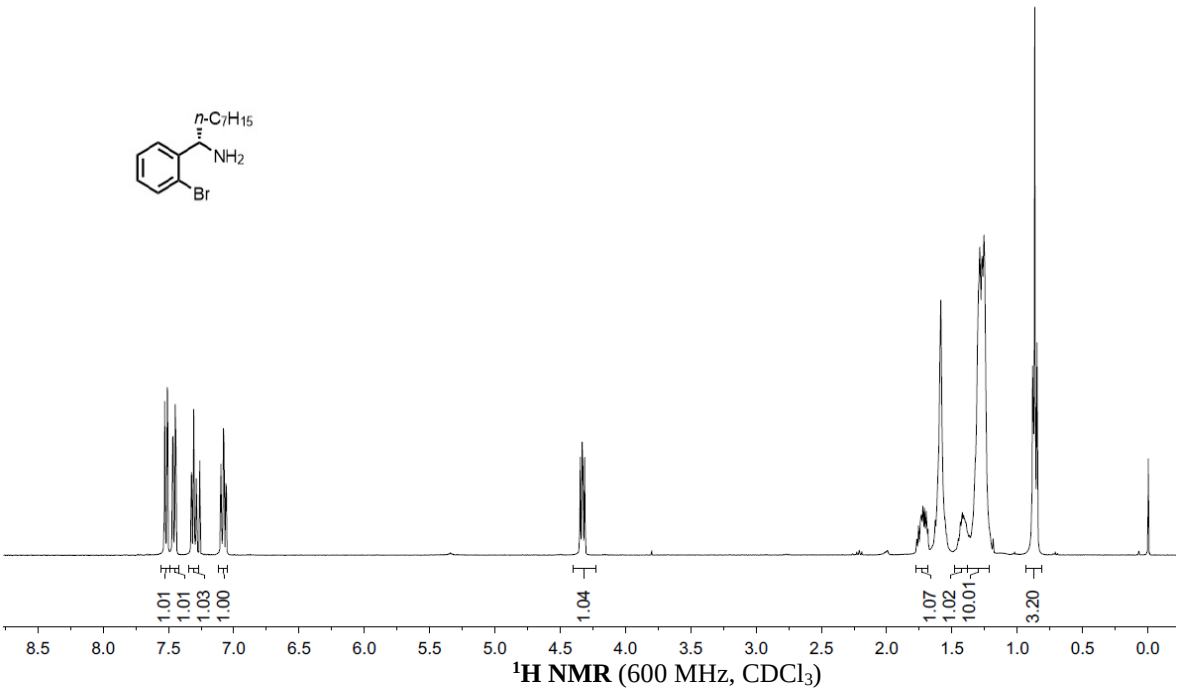


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)





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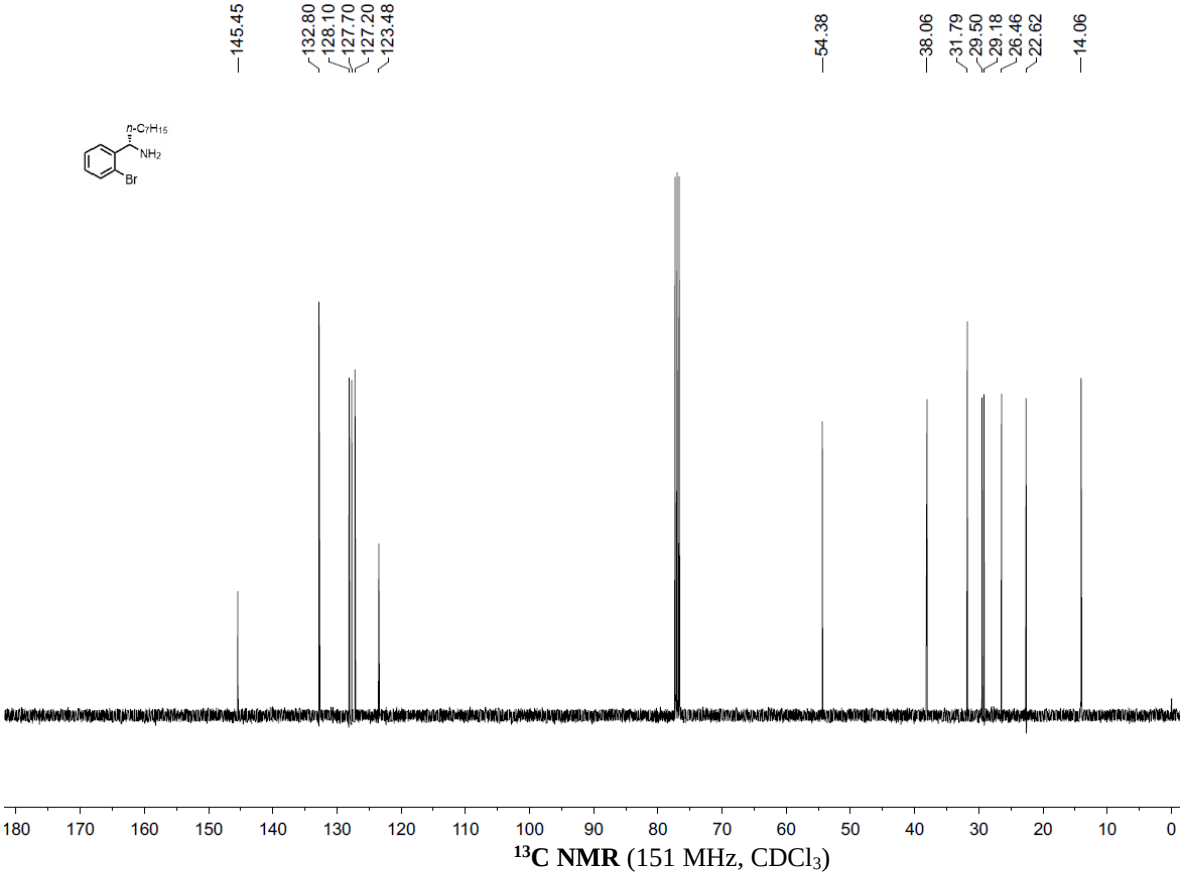

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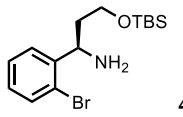
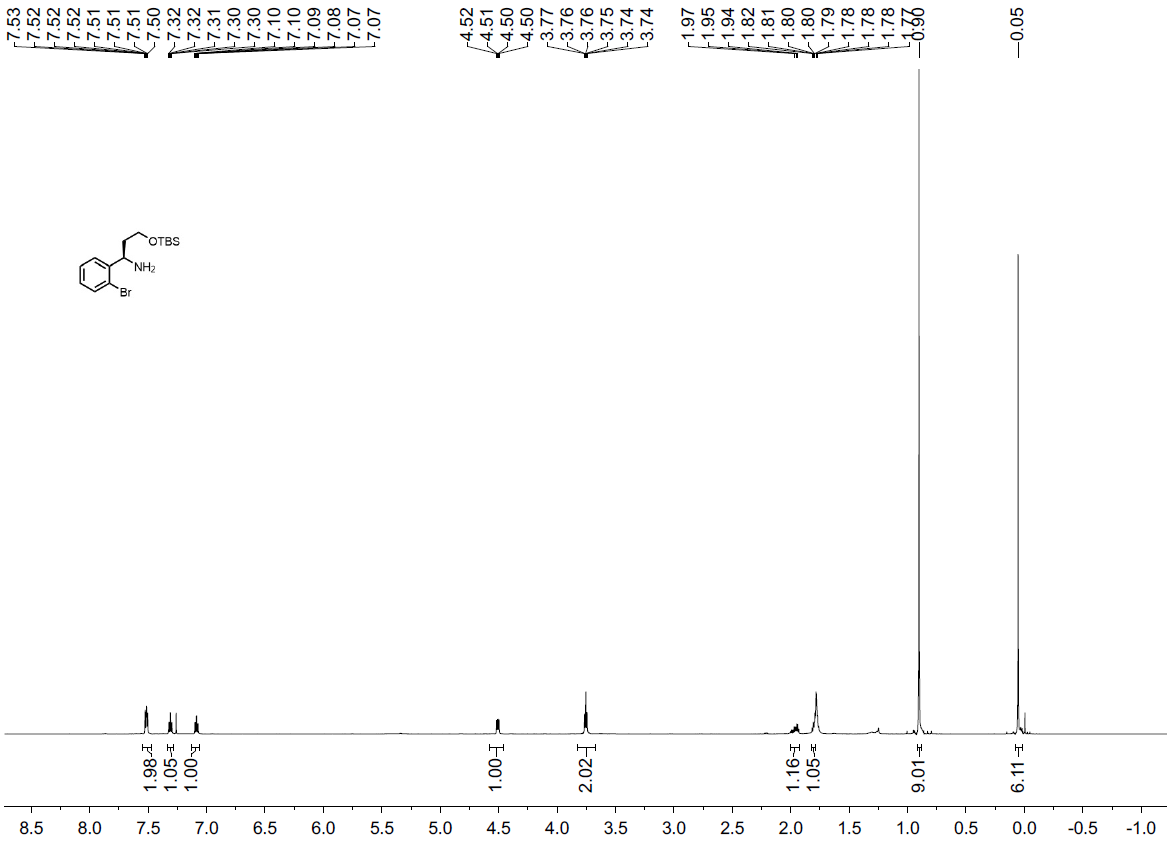


4d



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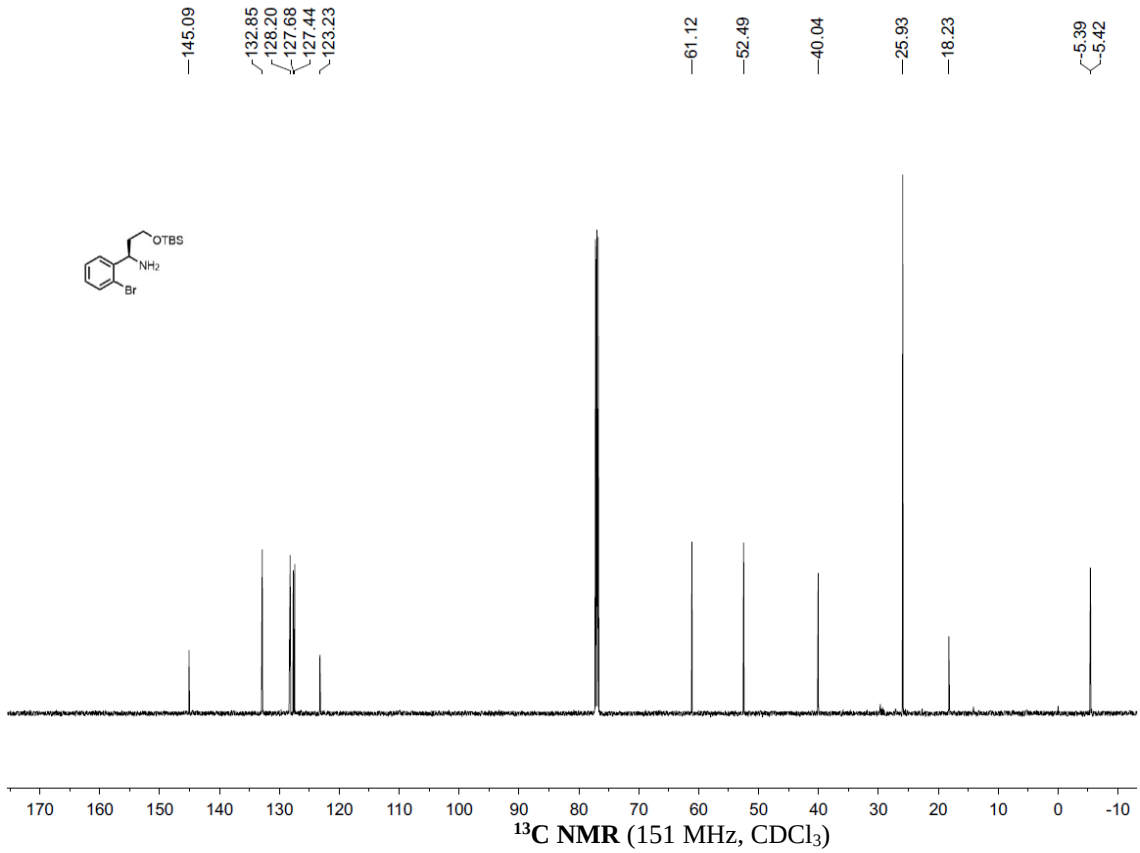

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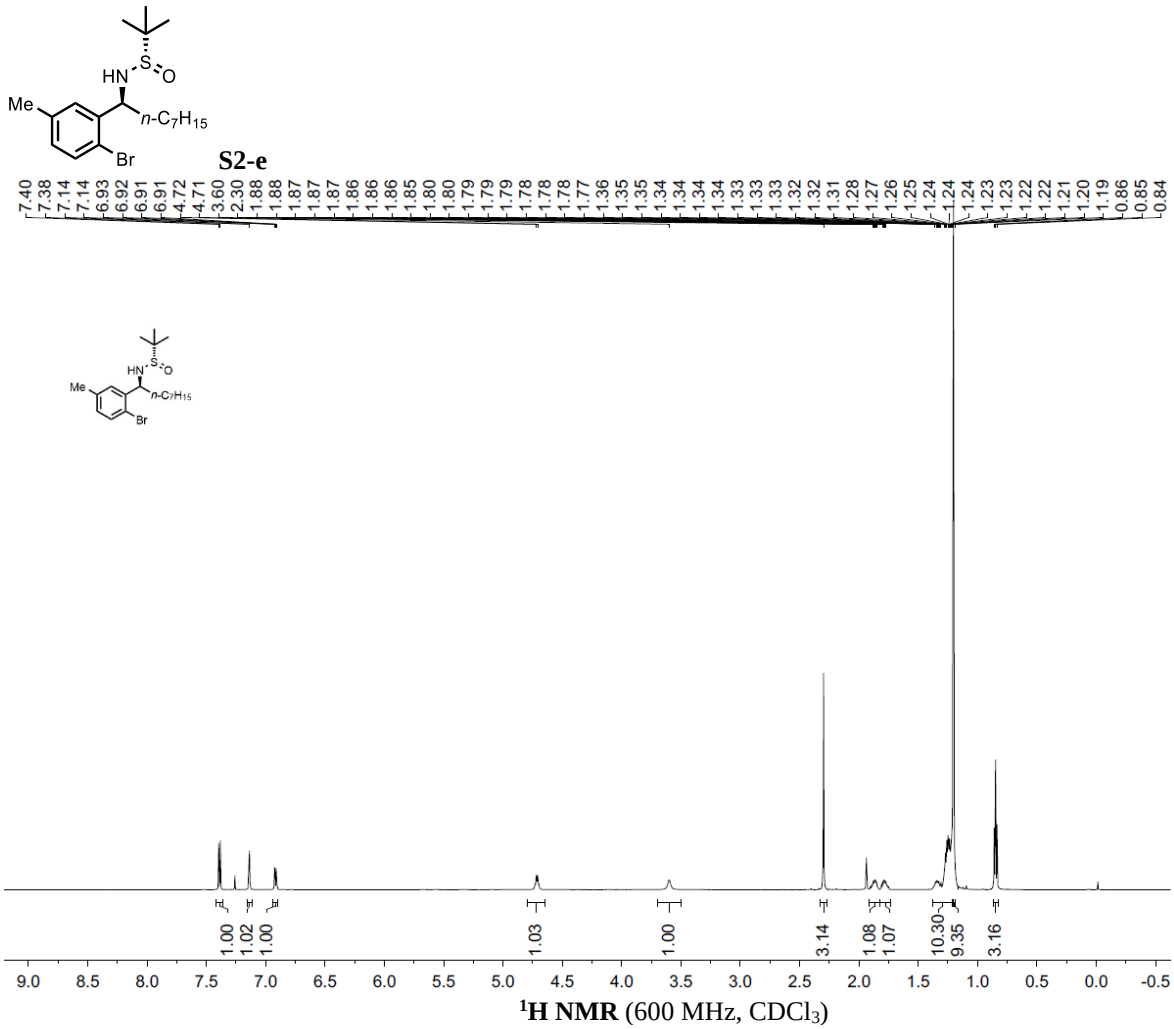

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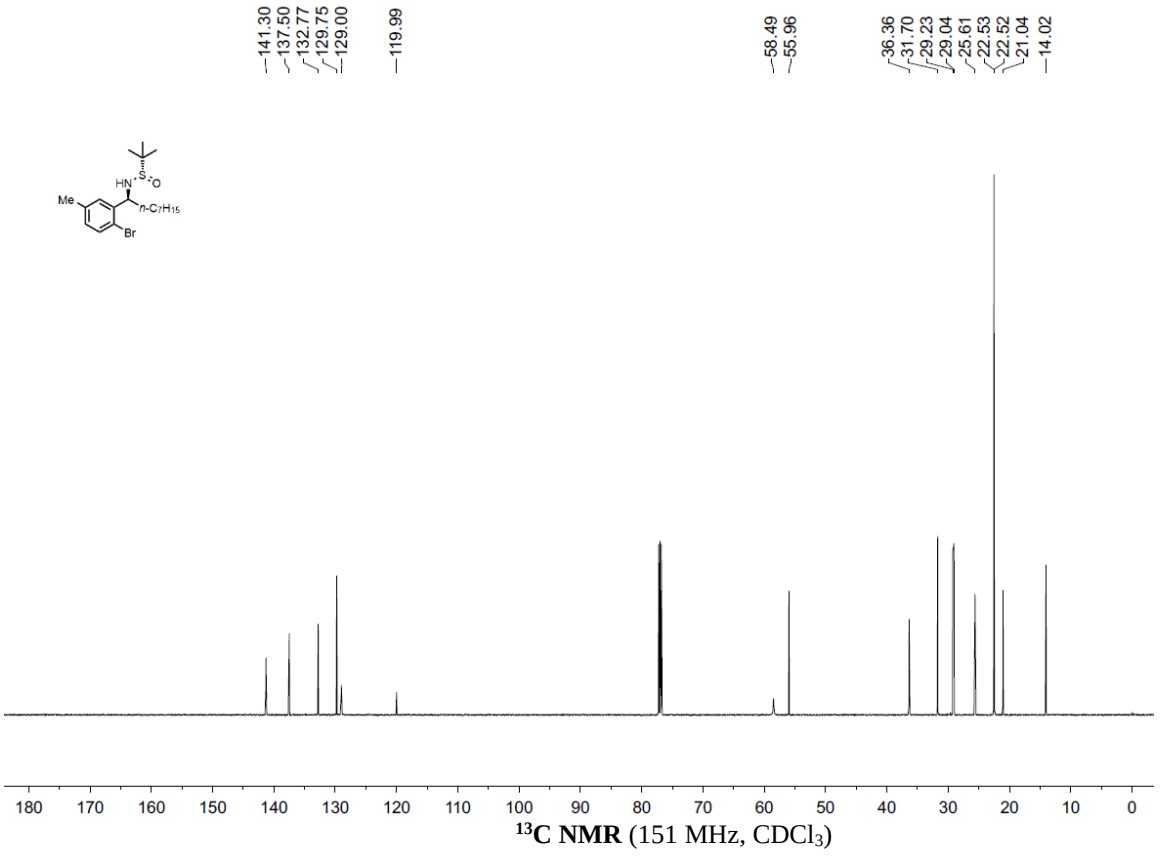
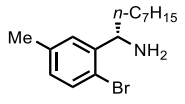
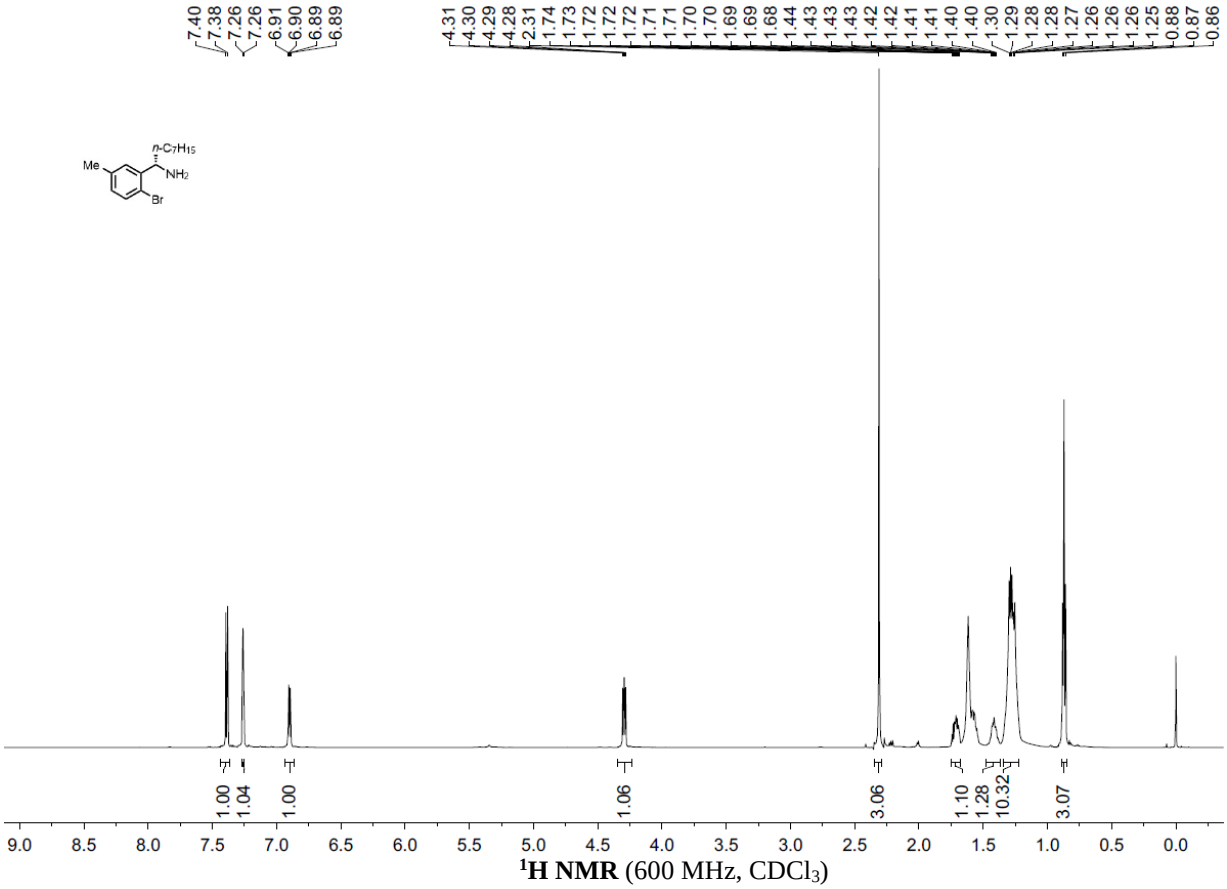


^{13}C NMR (151 MHz, $CDCl_3$)



4e



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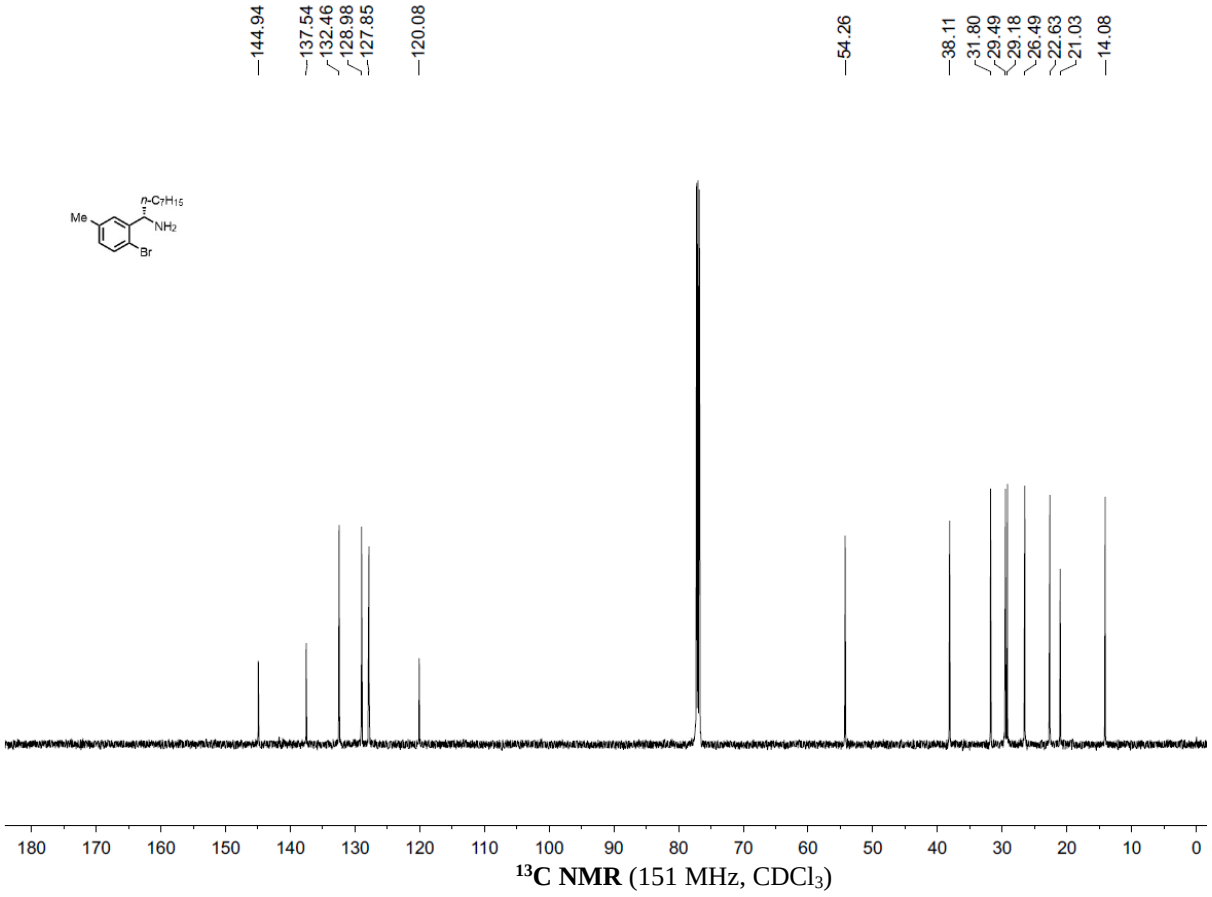

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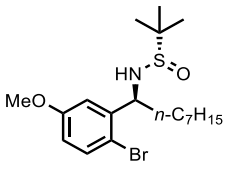
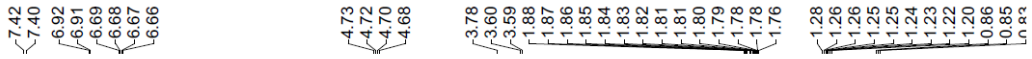
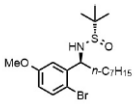
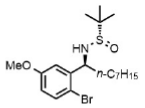


S2-f

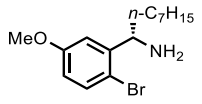




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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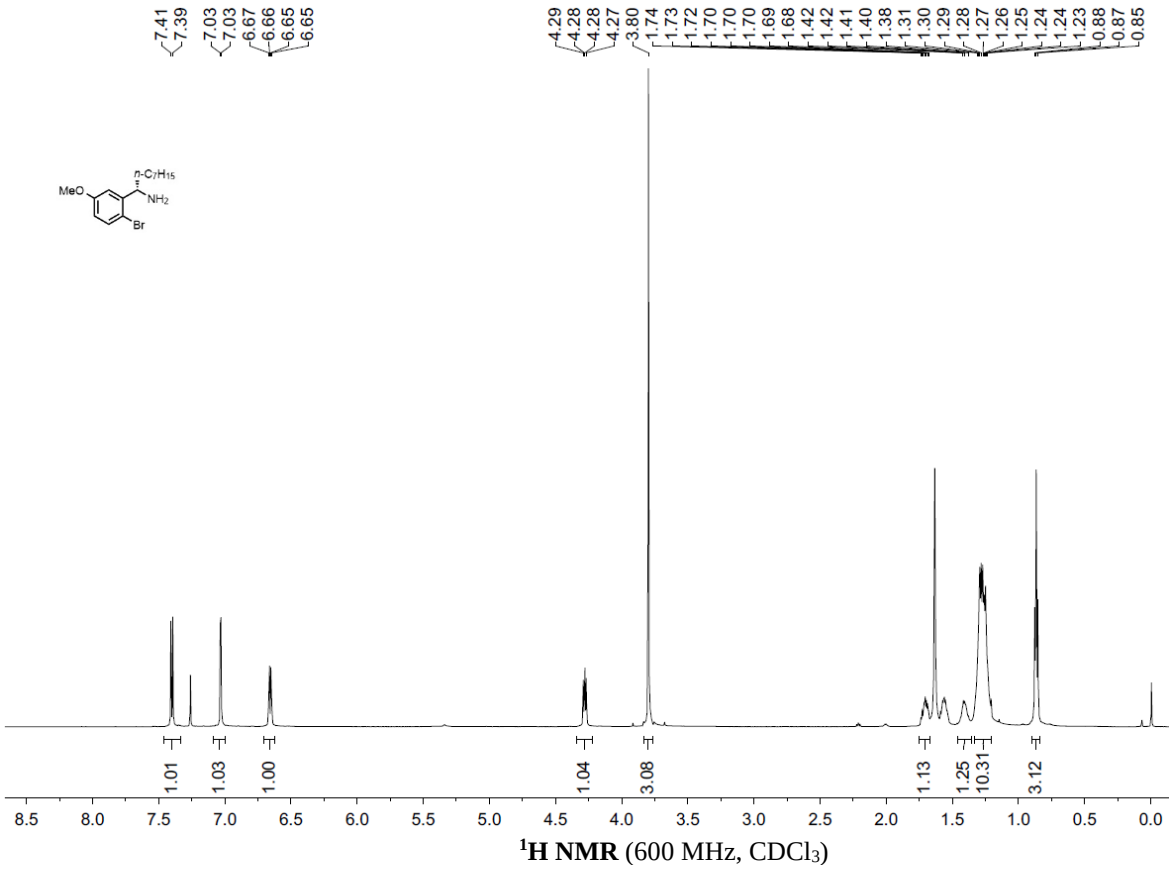
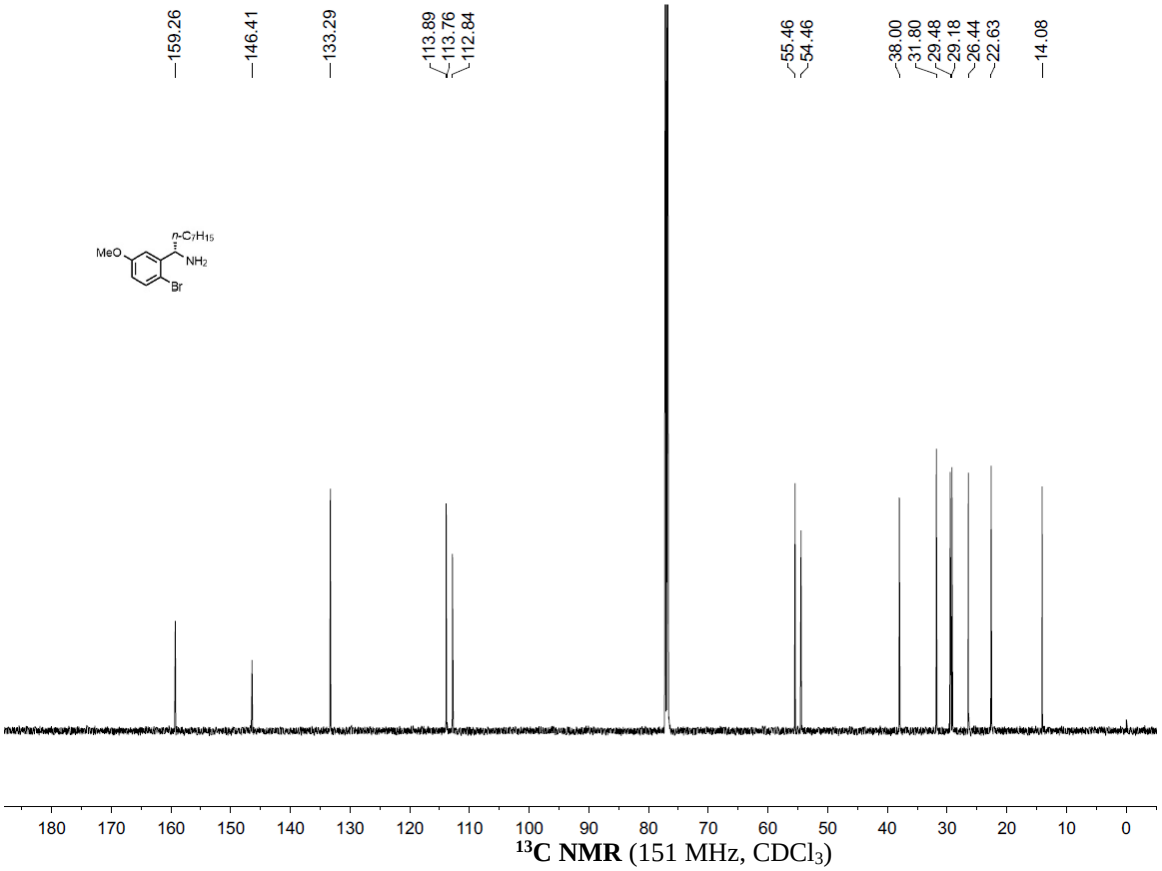


^{1}H NMR (600 MHz, $CDCl_3$)



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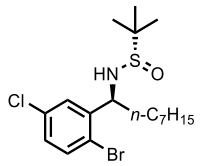
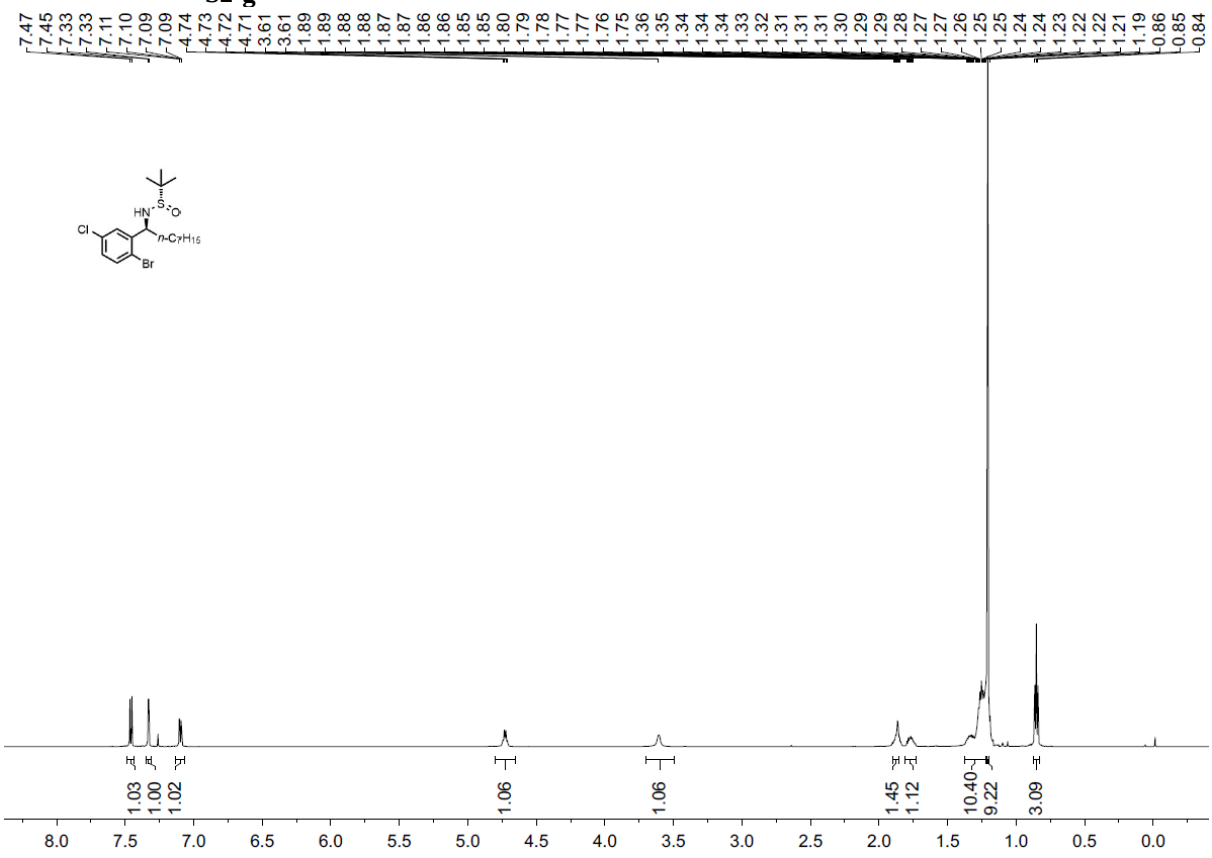
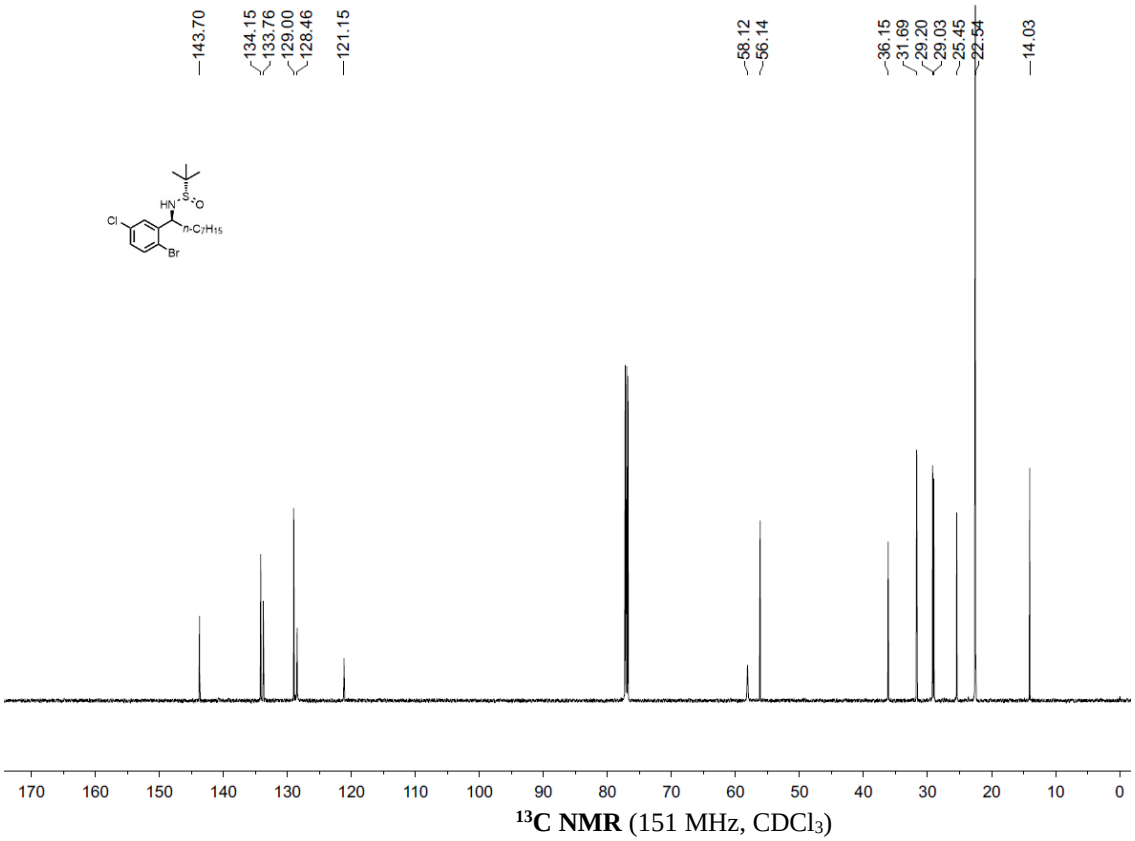


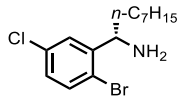
S2-g



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



^{13}C NMR (151 MHz, $CDCl_3$)



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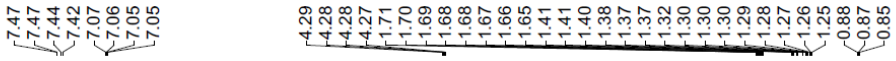
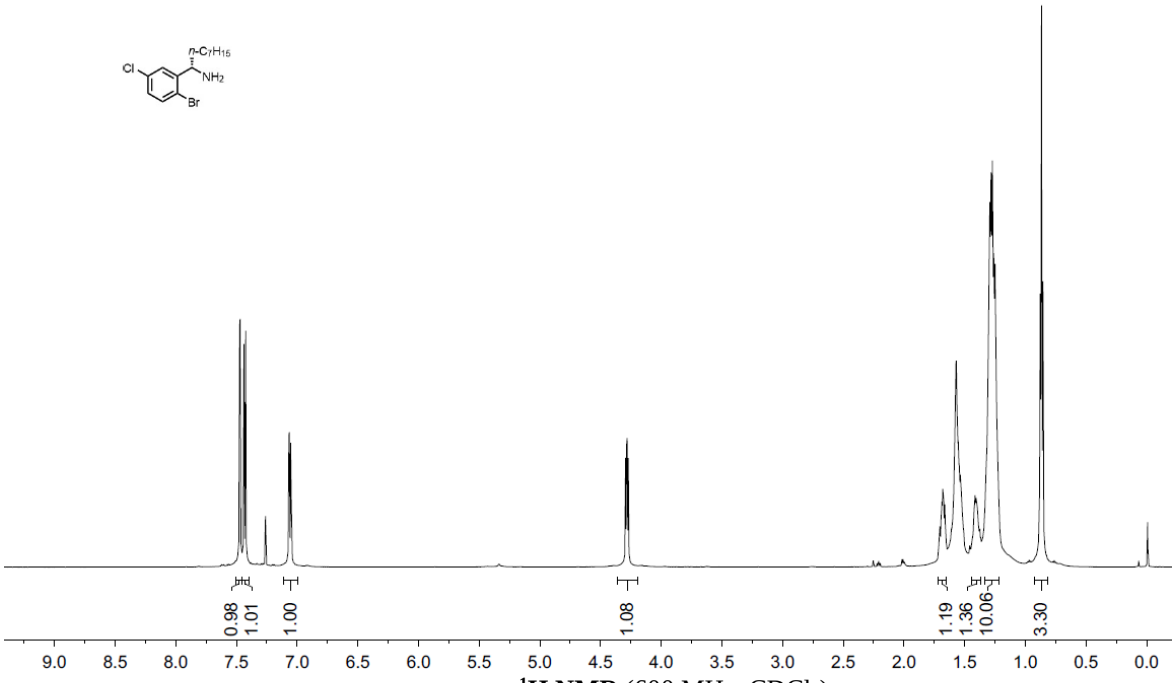
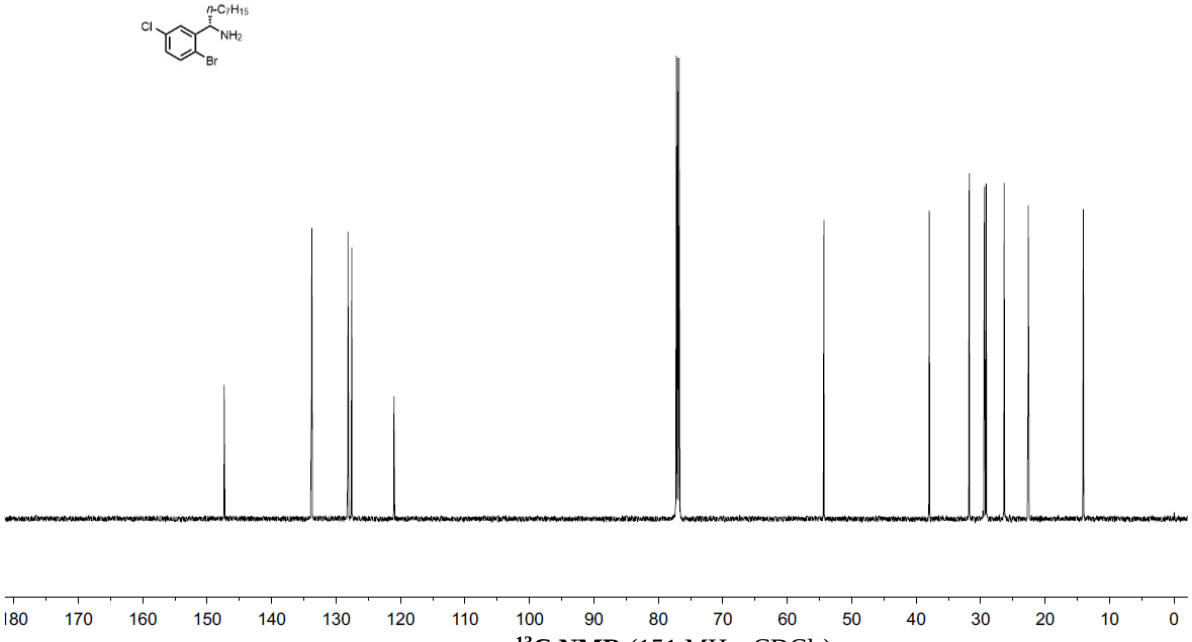
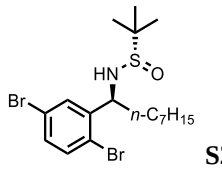




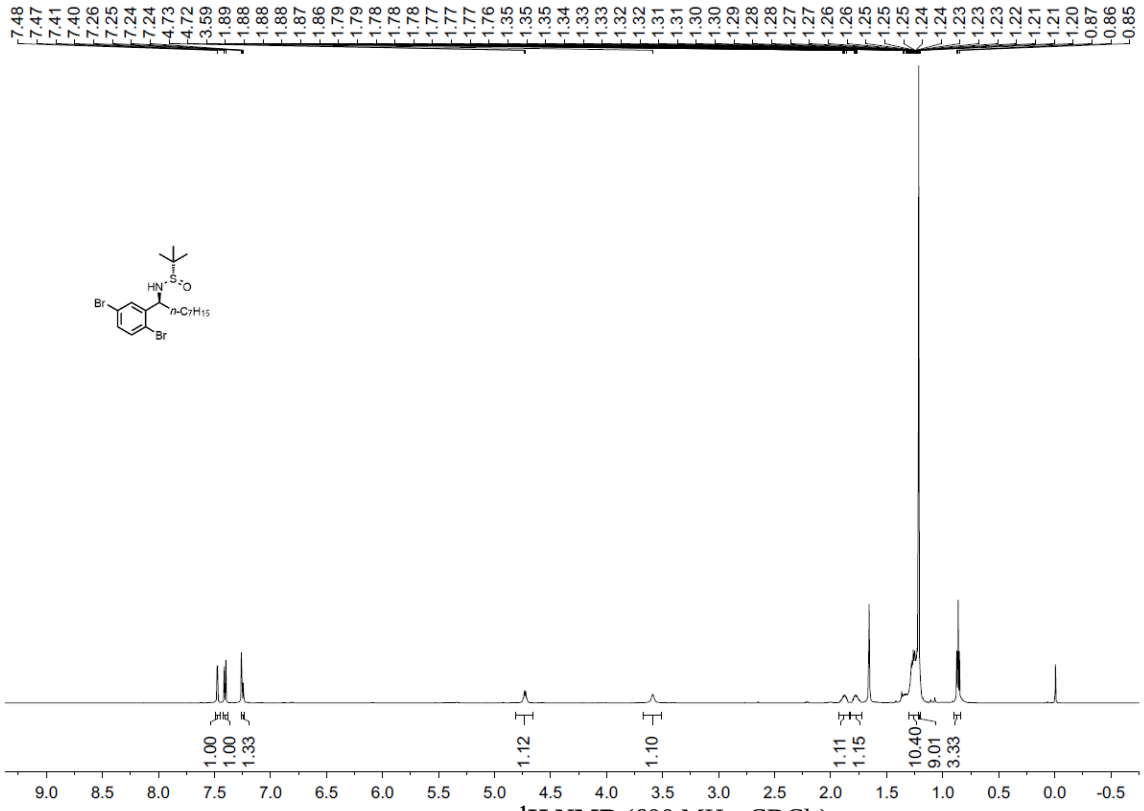
^{1}H NMR (600 MHz, $CDCl_3$)



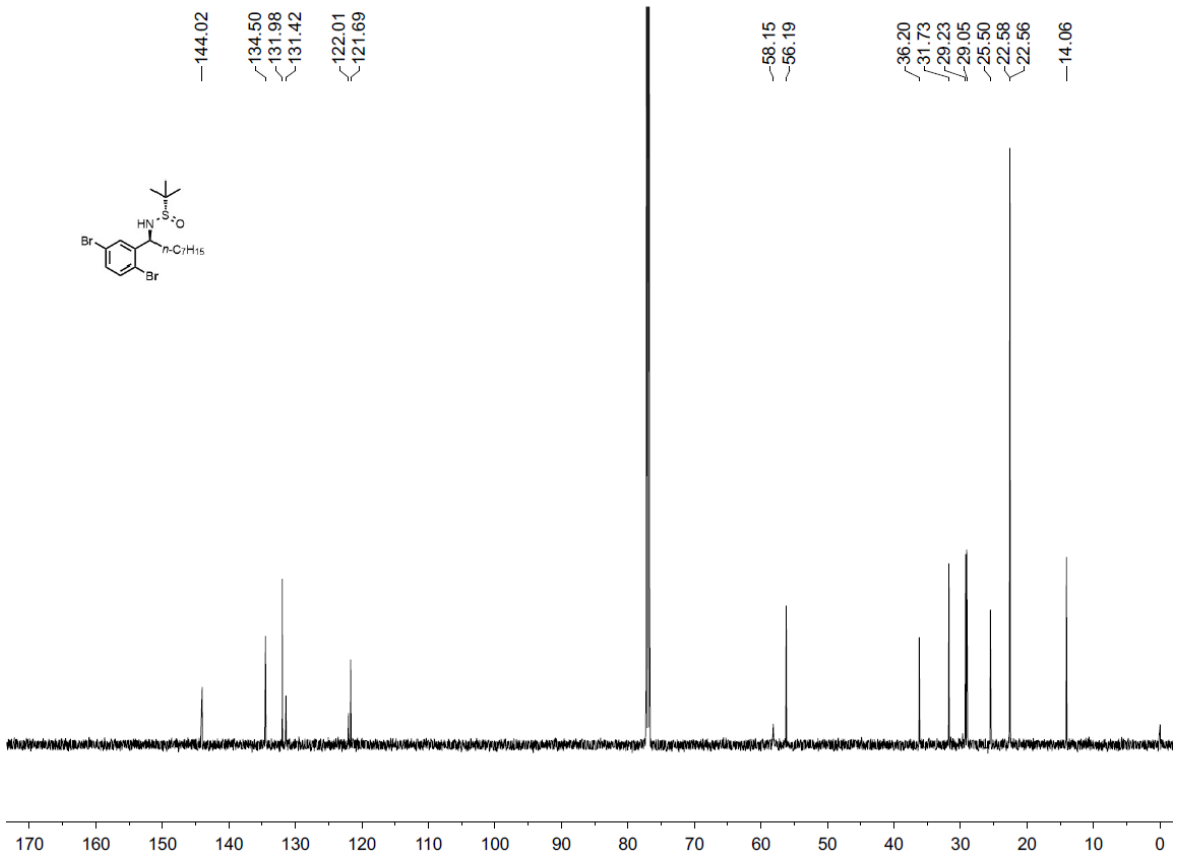
^{13}C NMR (151 MHz, $CDCl_3$)



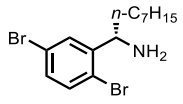
S2-h



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



^{13}C NMR (151 MHz, $CDCl_3$)



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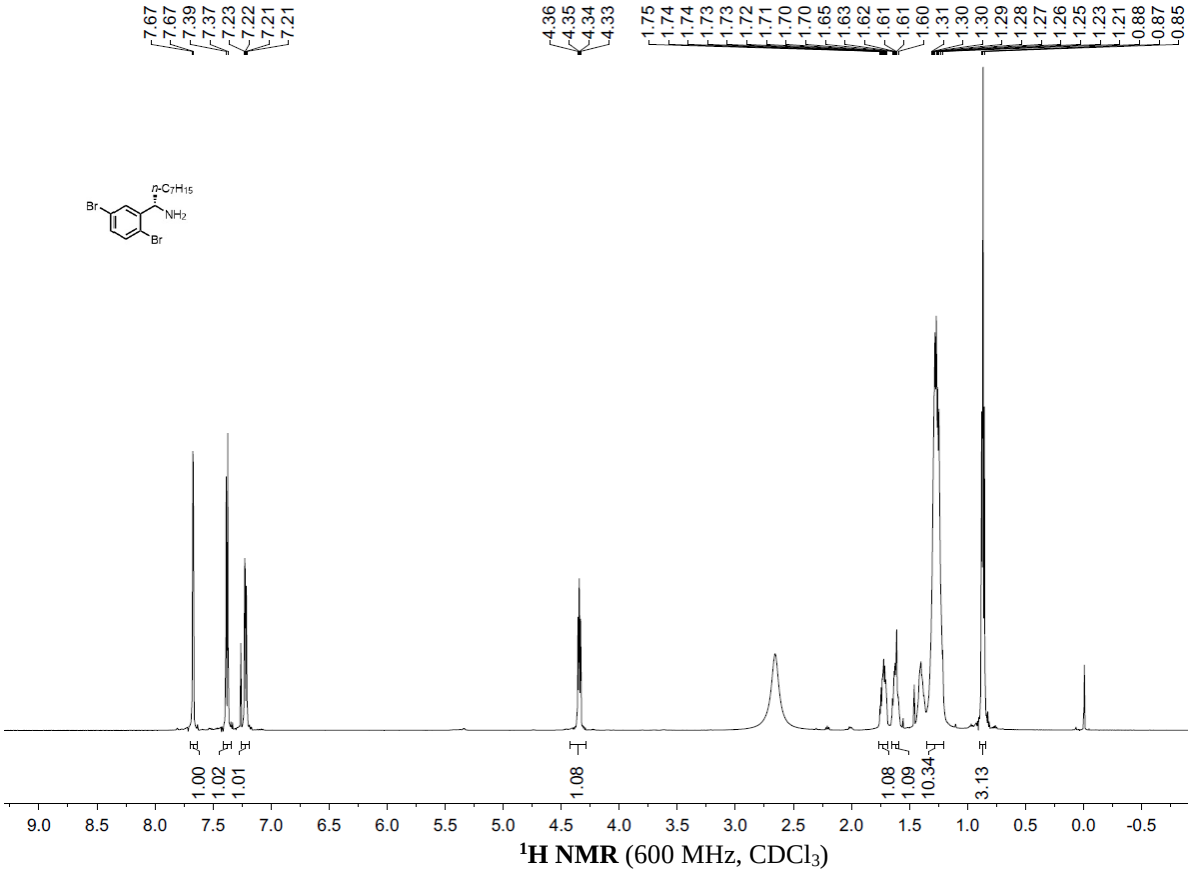
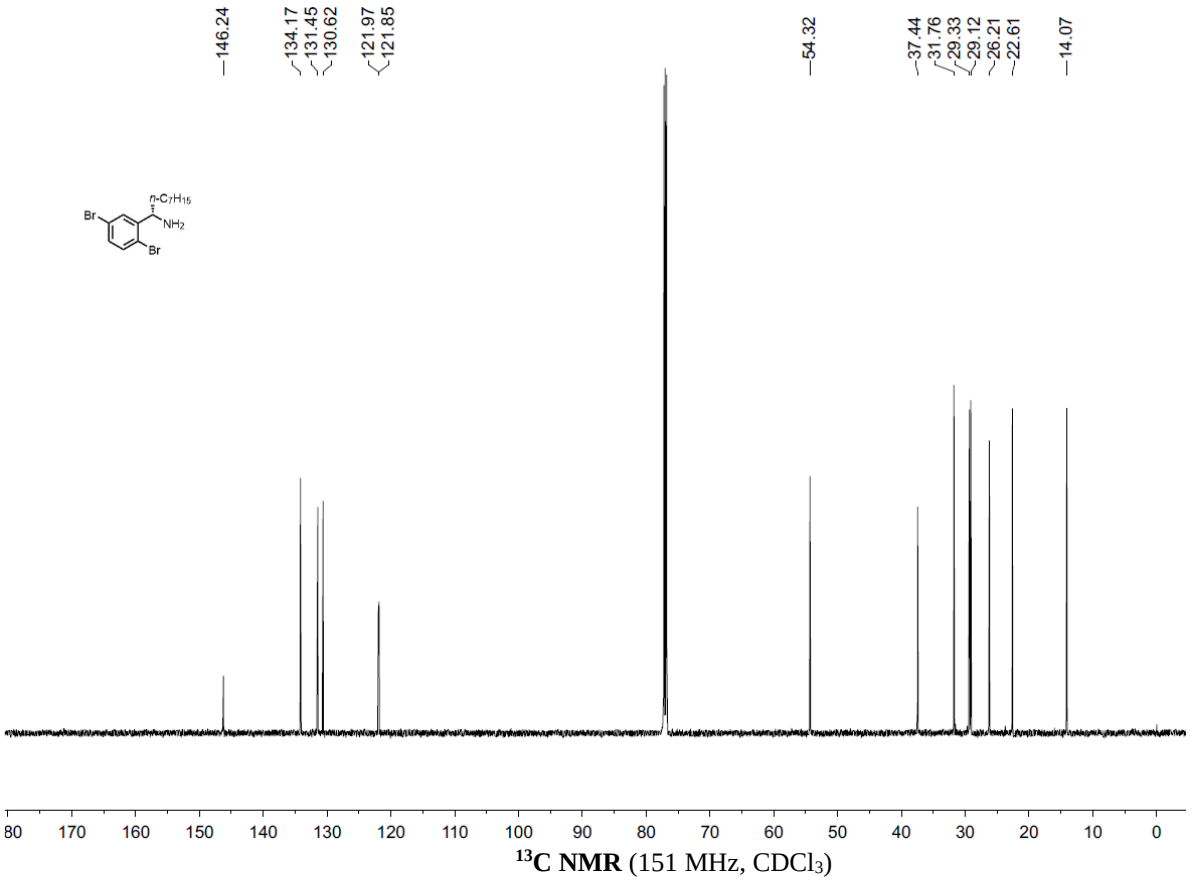
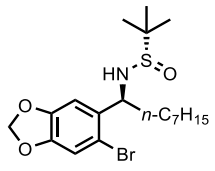


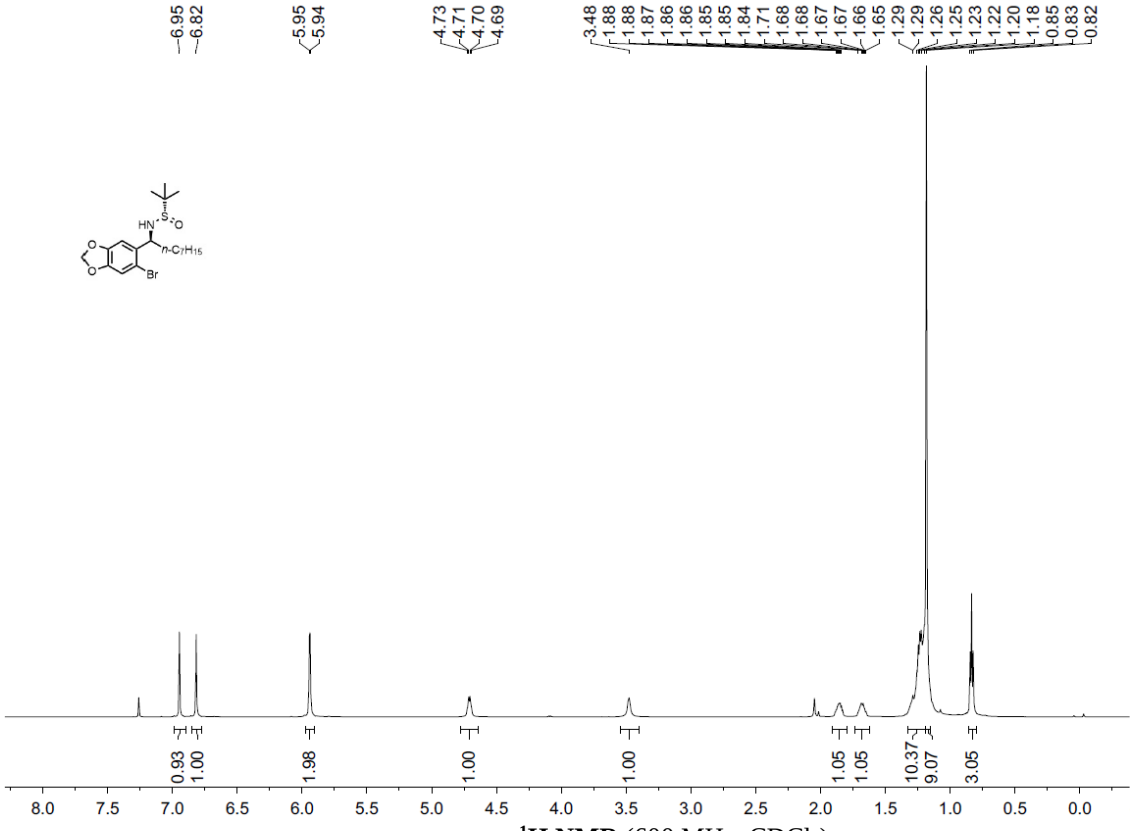
^{1}H NMR (600 MHz, $CDCl_3$)



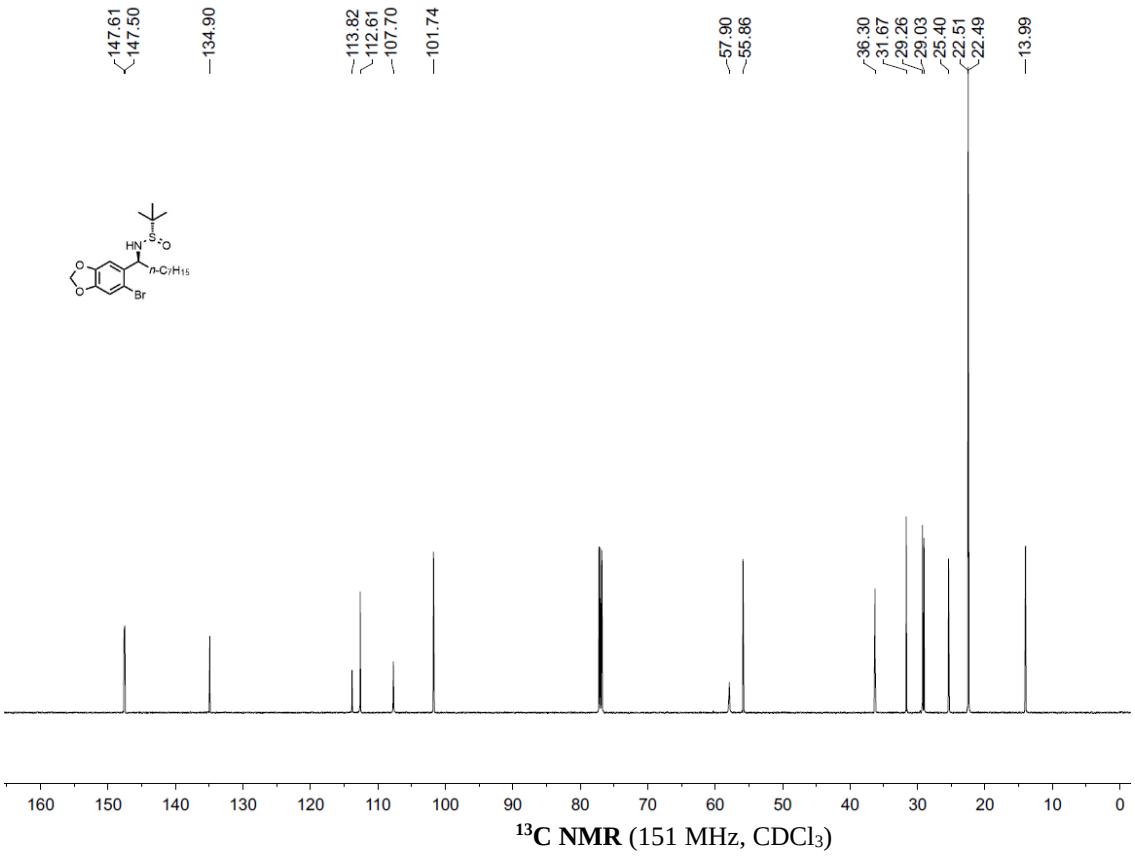
^{13}C NMR (151 MHz, $CDCl_3$)



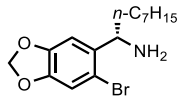
S2-i



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



^{13}C NMR (151 MHz, $CDCl_3$)



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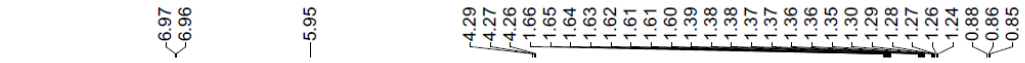
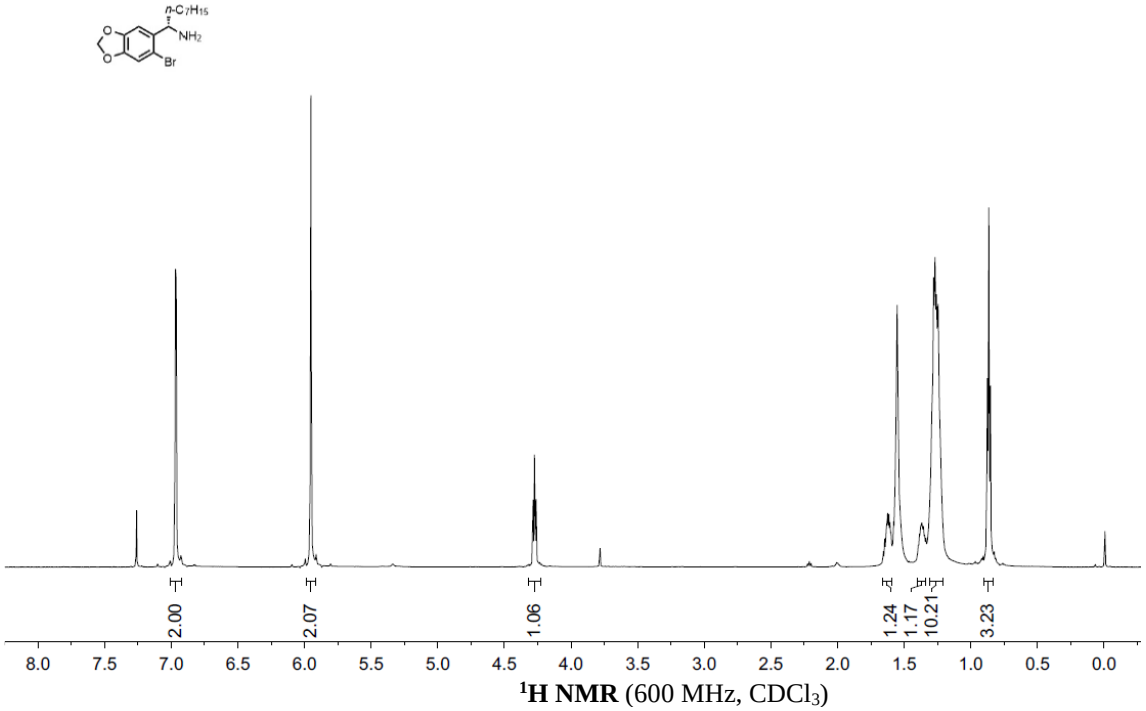
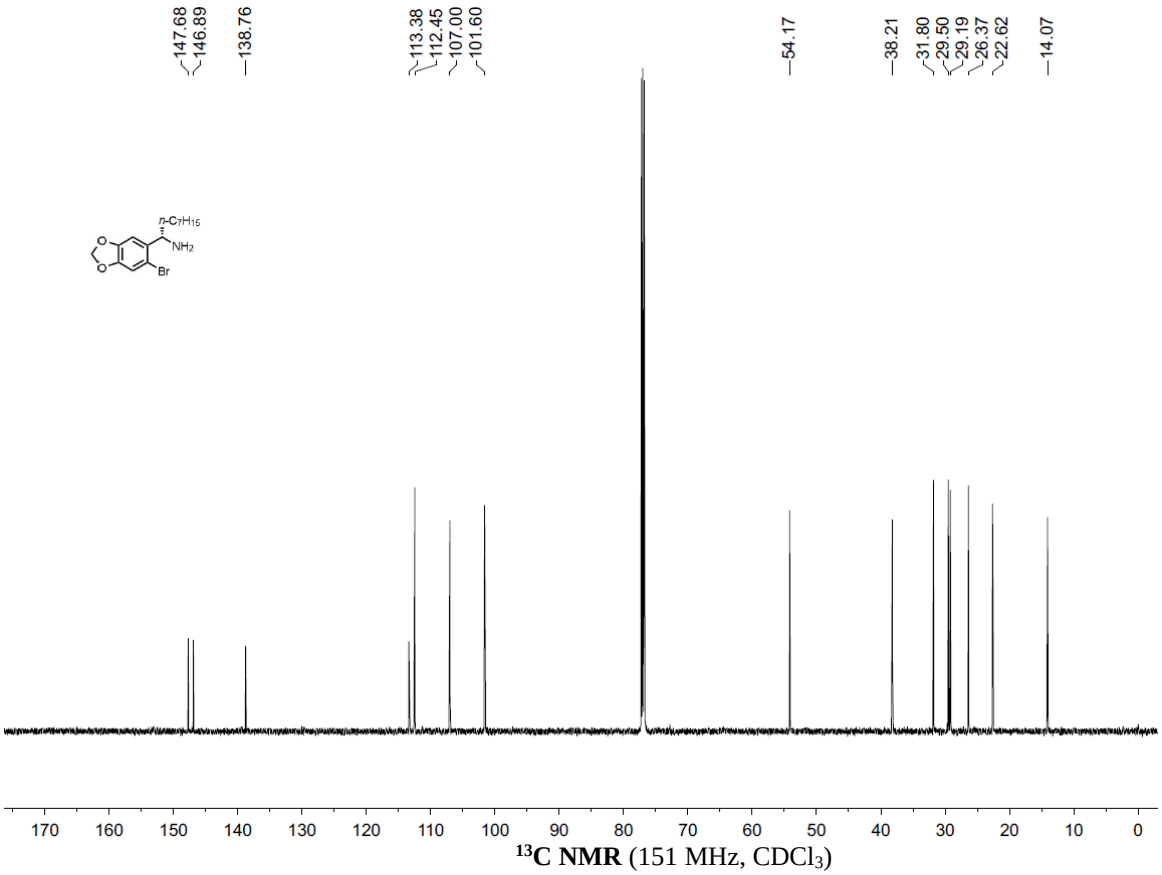
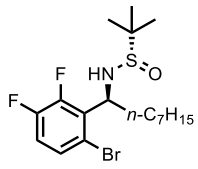




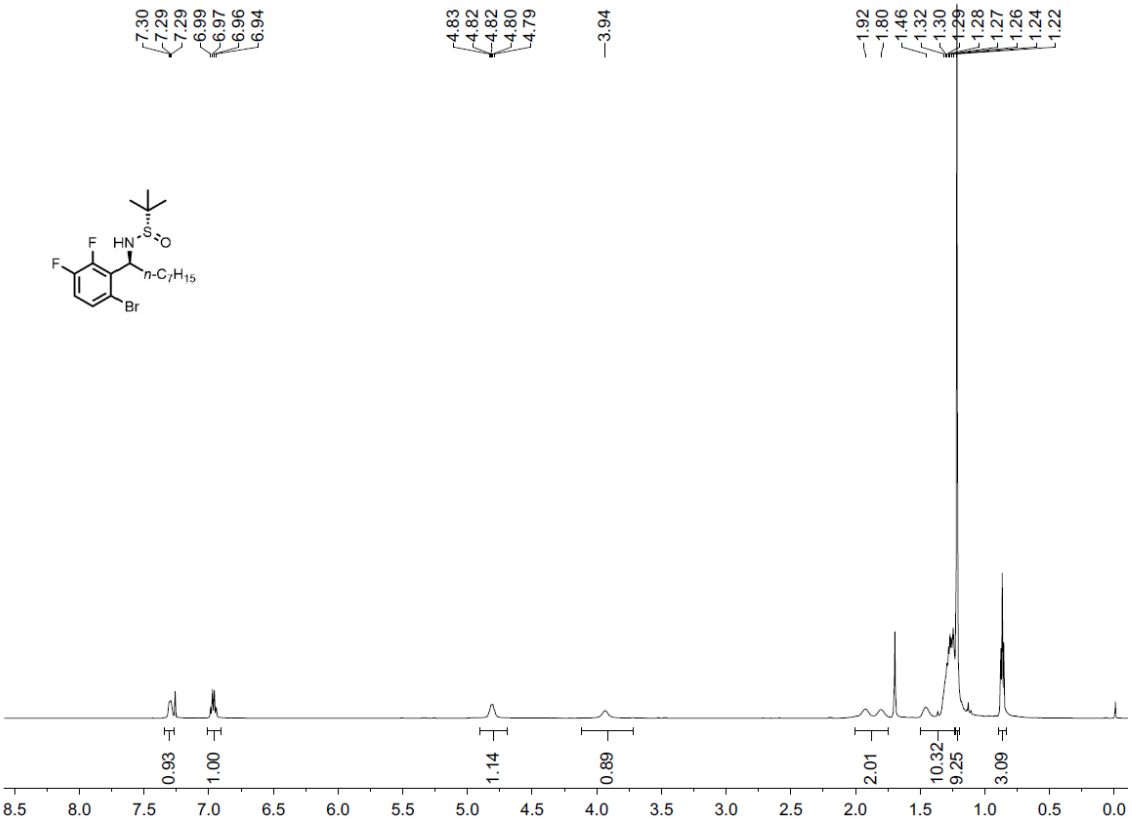
^{1}H NMR (600 MHz, $CDCl_3$)



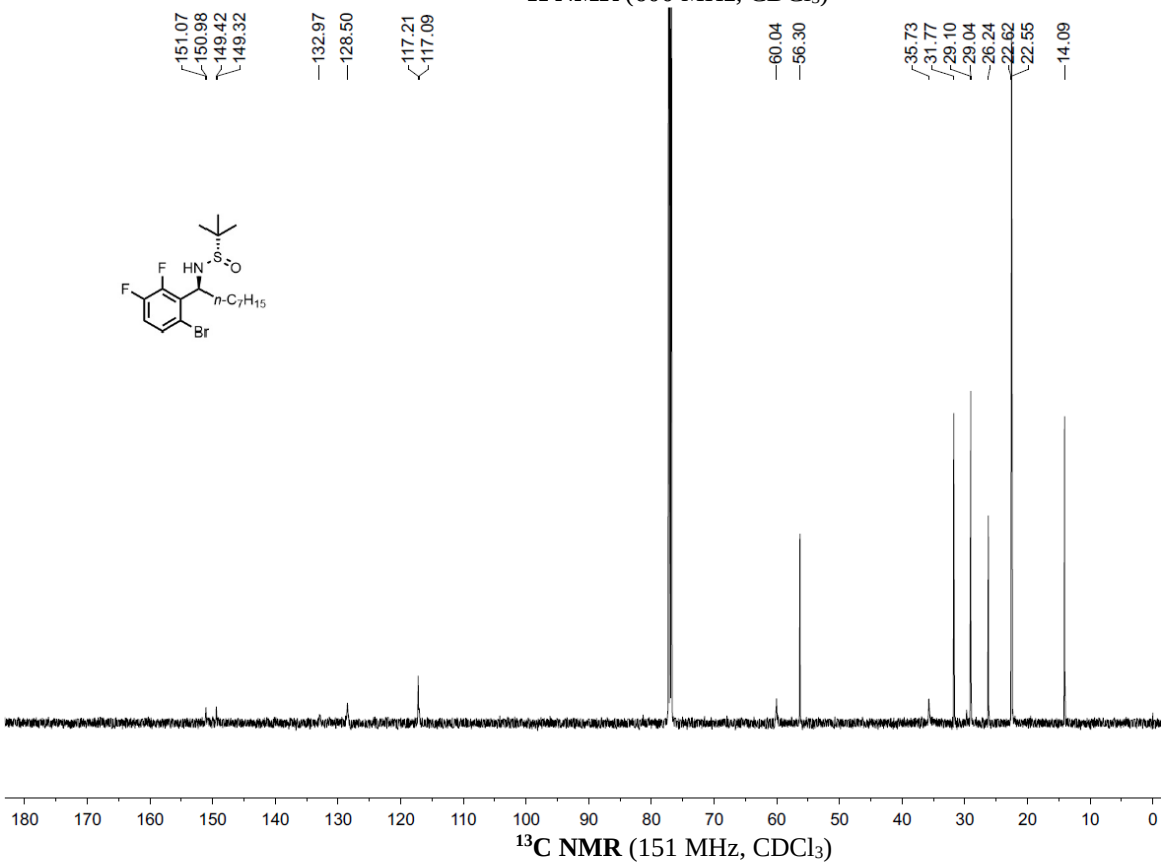
^{13}C NMR (151 MHz, $CDCl_3$)



S2-j



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



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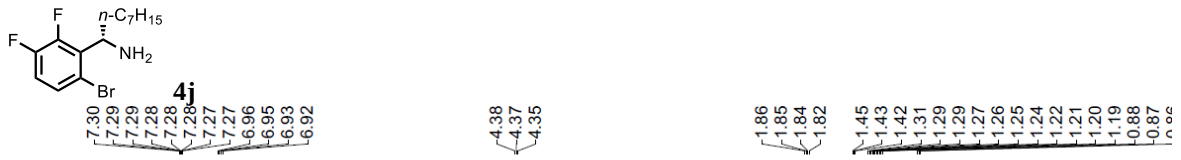
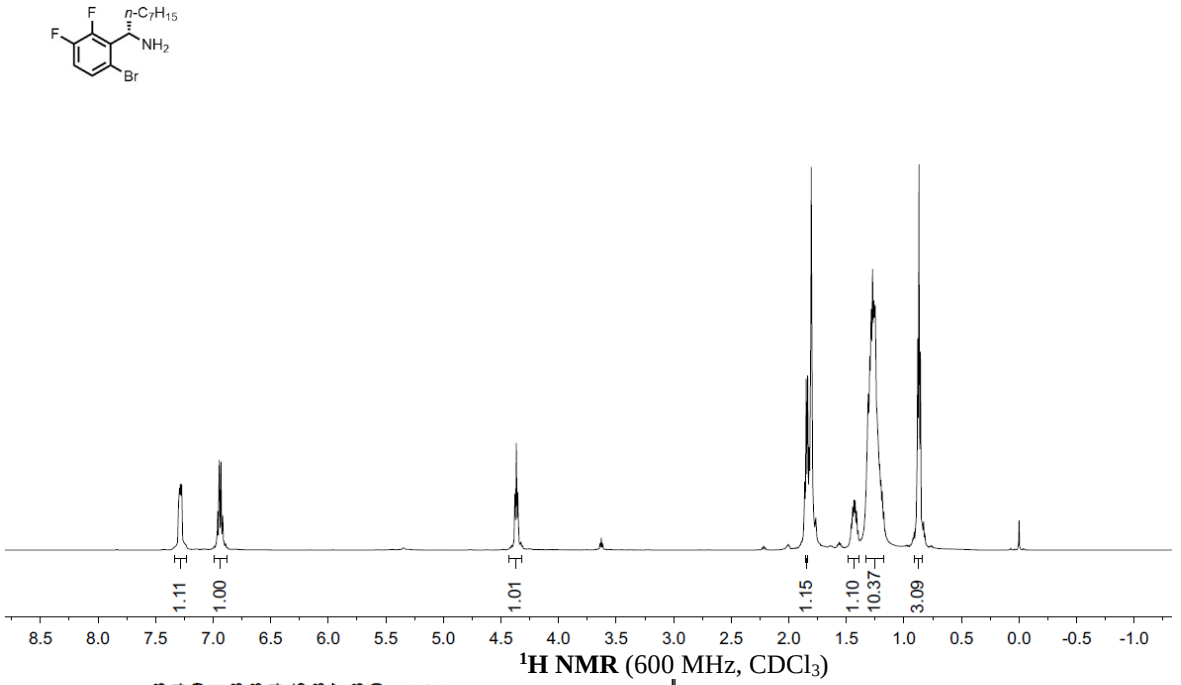
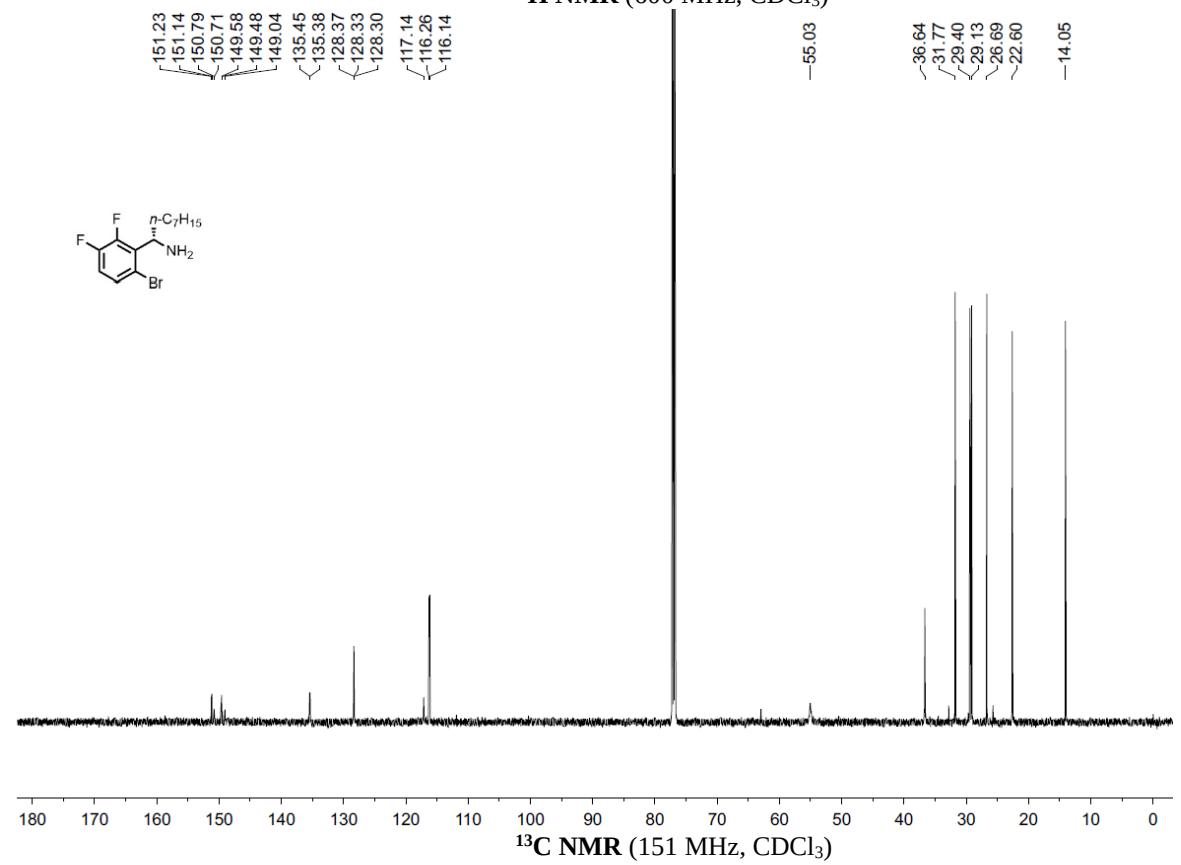
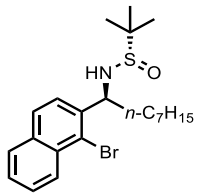




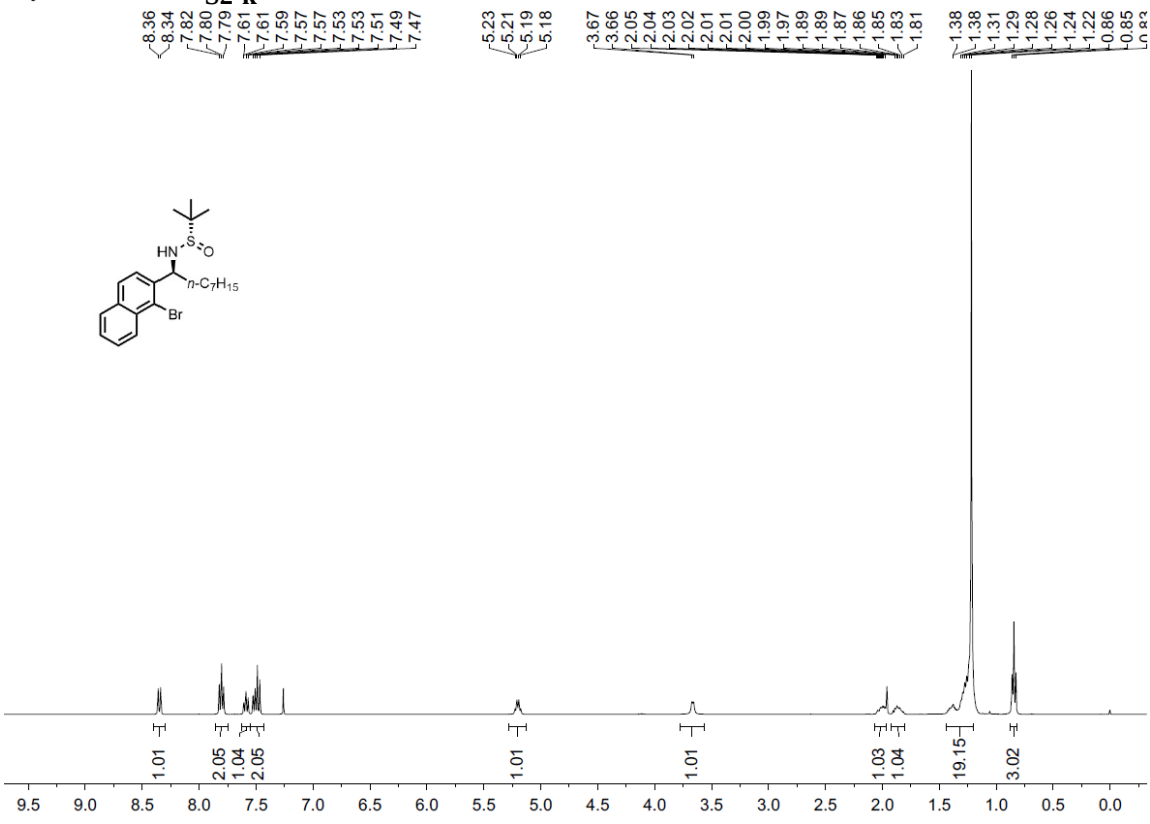
^{1}H NMR (600 MHz, $CDCl_3$)



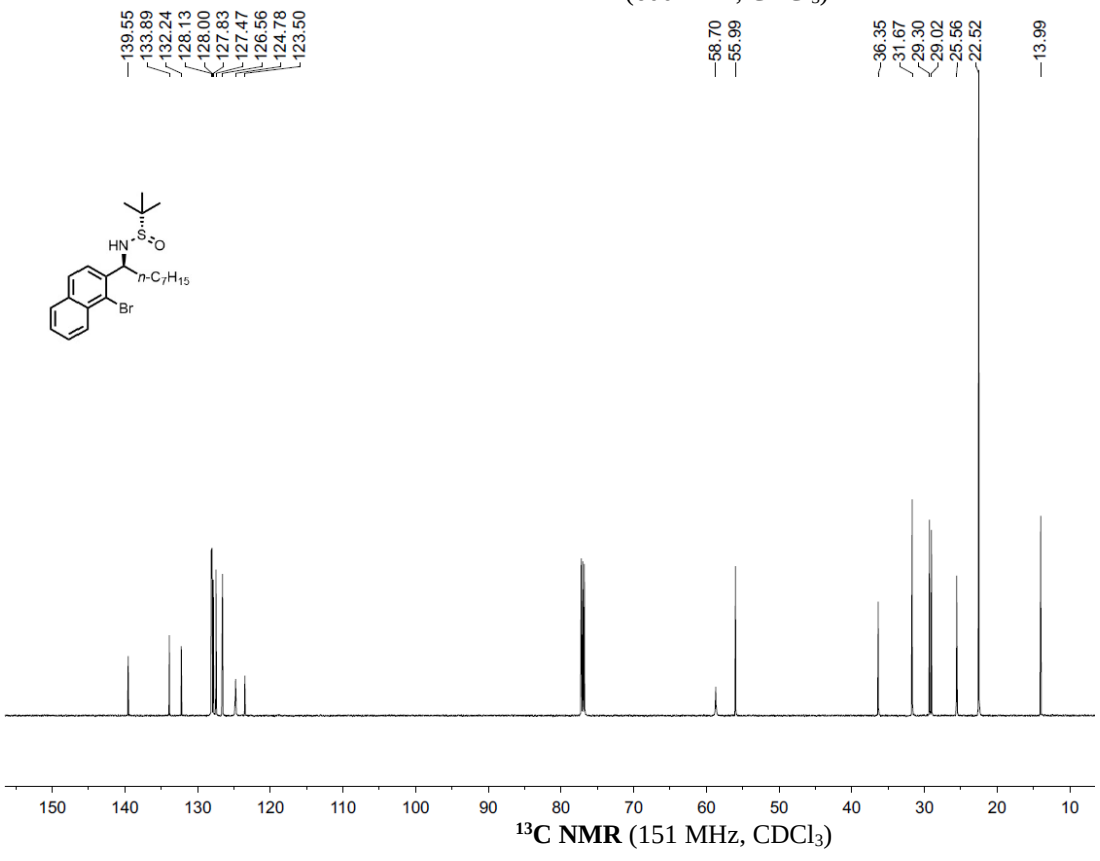
^{13}C NMR (151 MHz, $CDCl_3$)



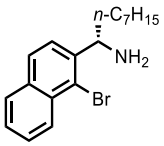
S2-k



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



^{13}C NMR (151 MHz, $CDCl_3$)



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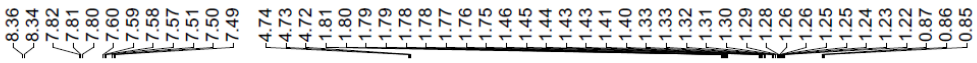
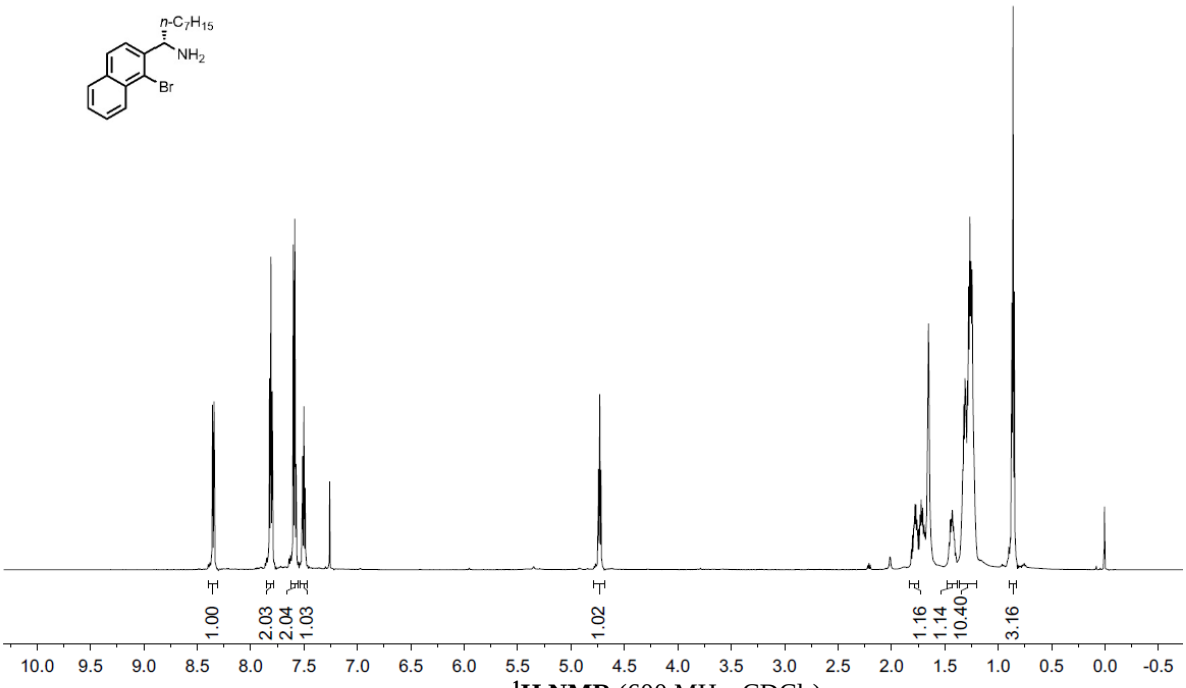
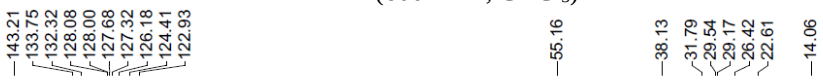
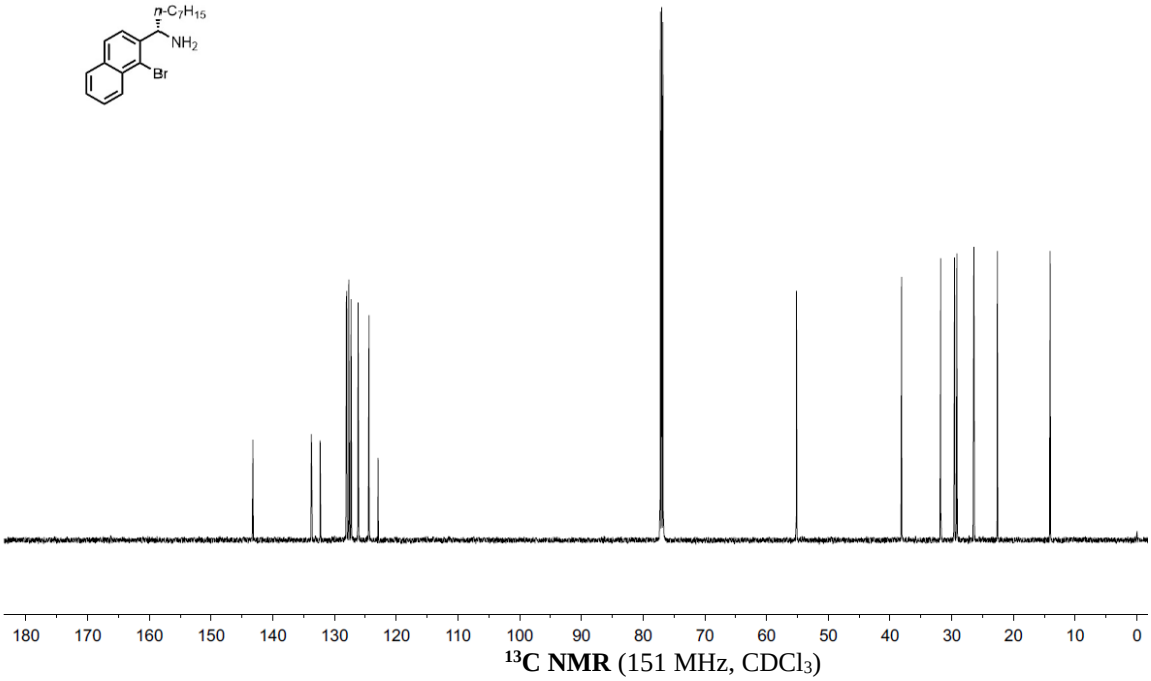




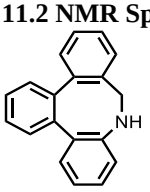
^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)

11.2 NMR Spectra of the Products



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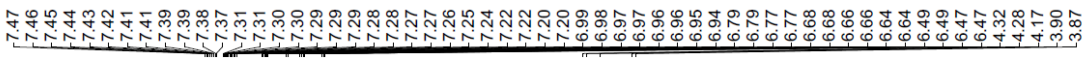
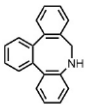
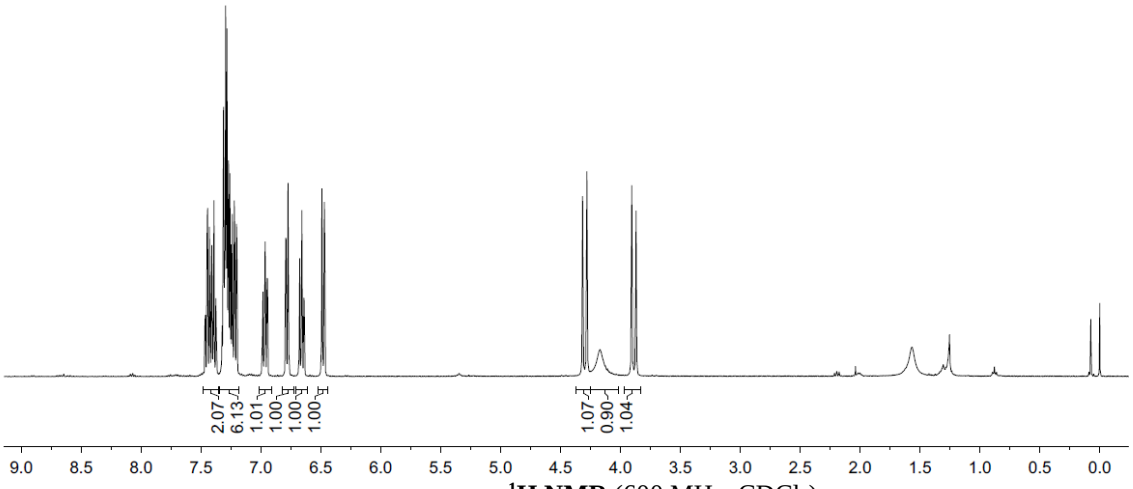
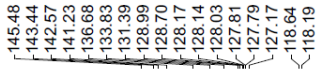
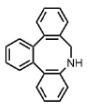




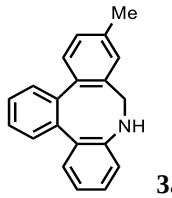


^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)



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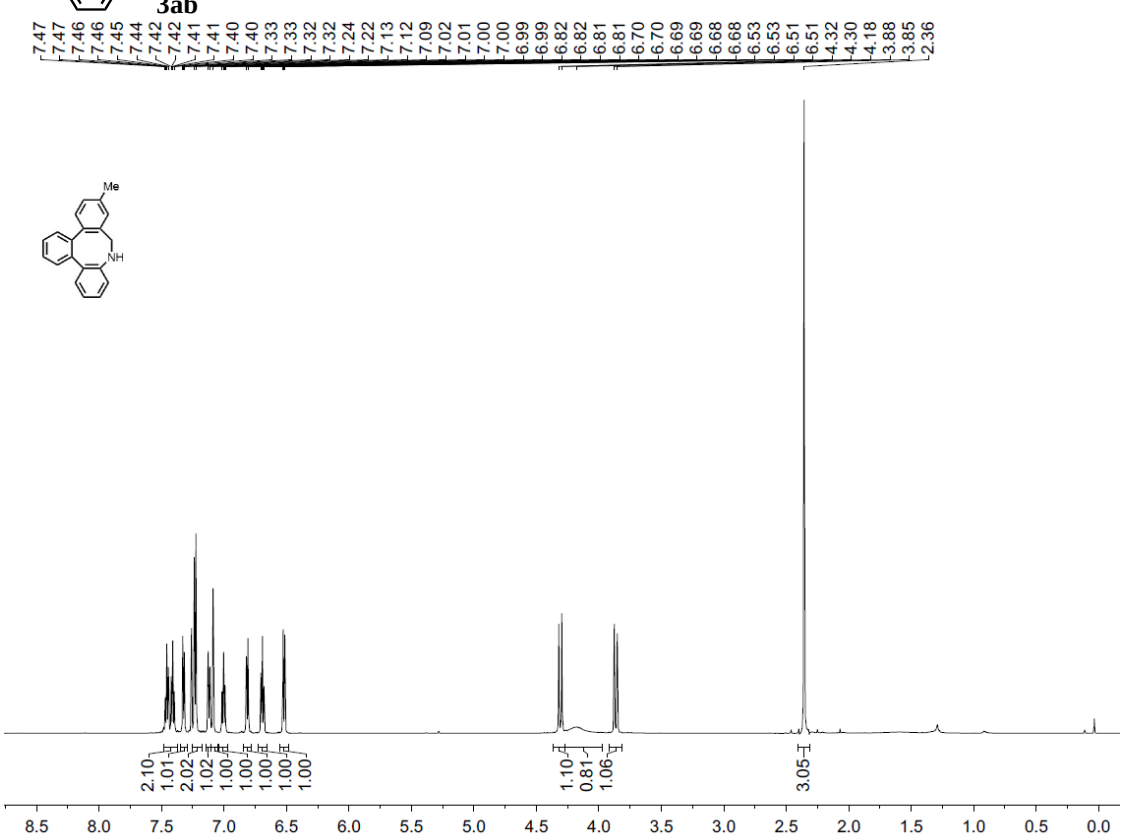
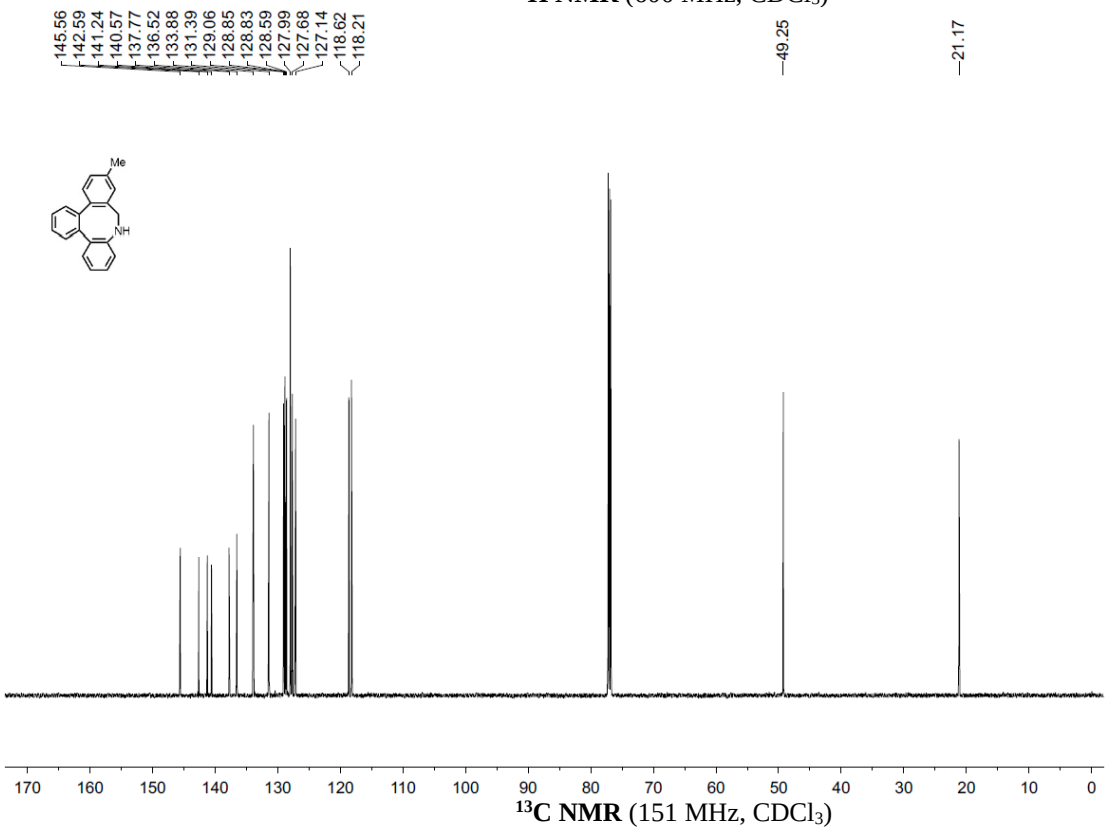
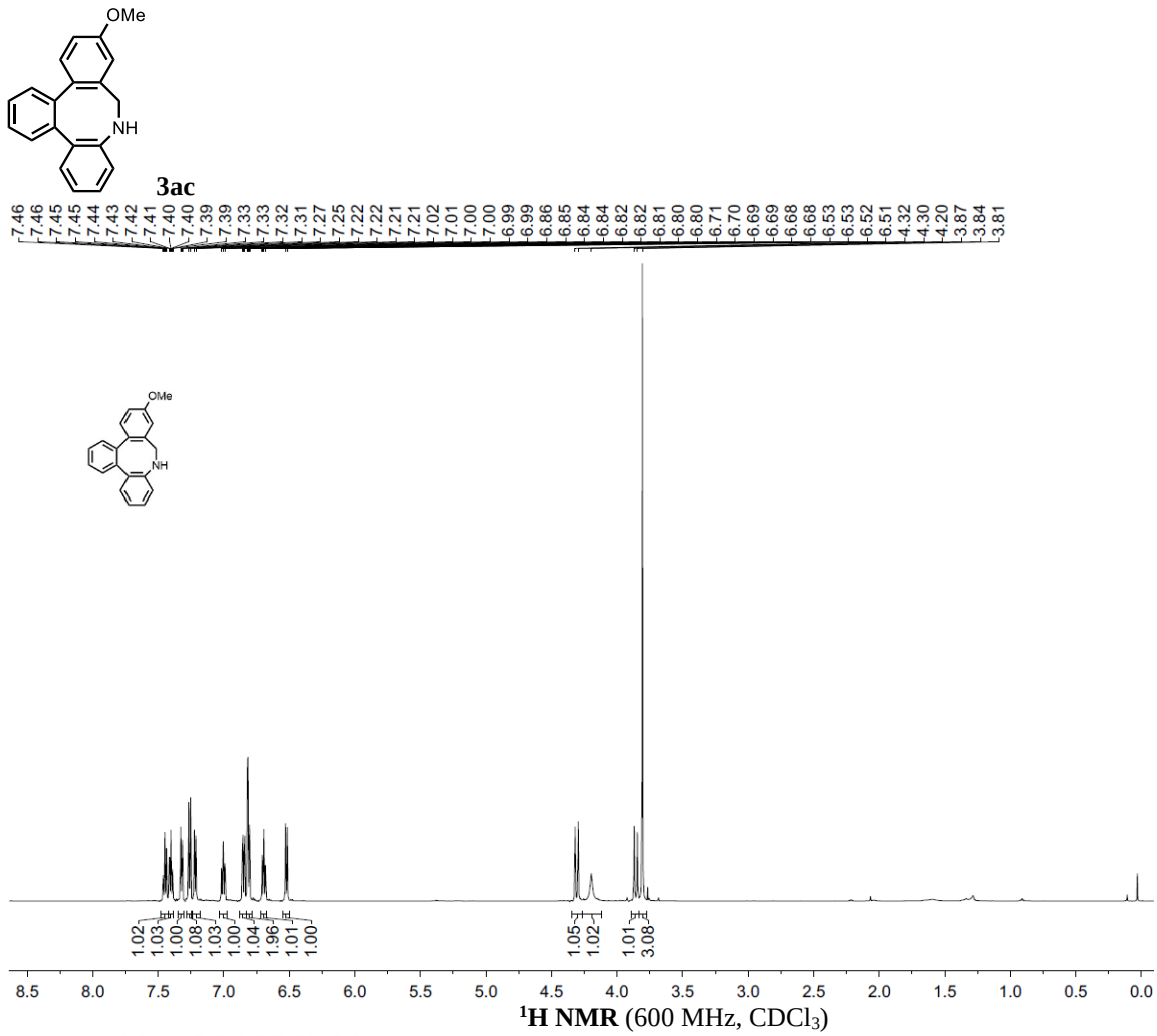


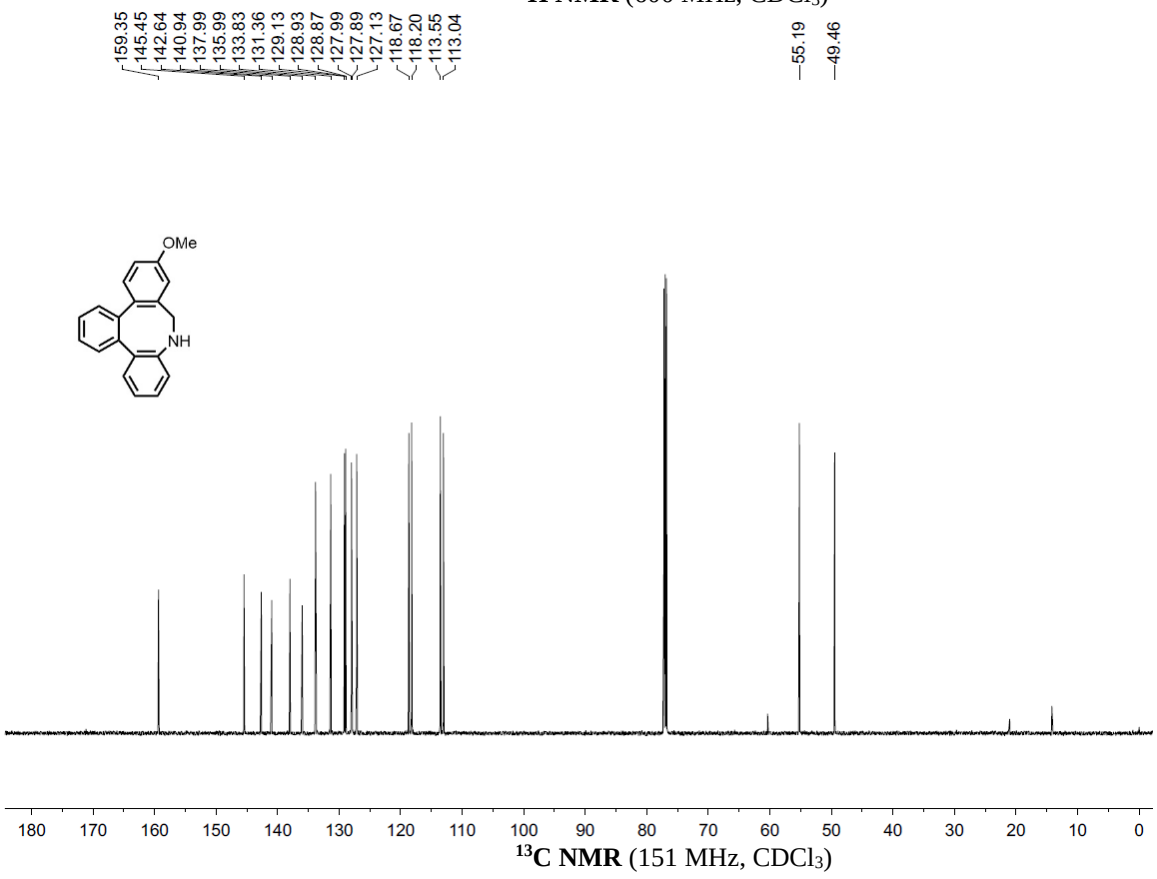
^{1}H NMR (600 MHz, $CDCl_3$)



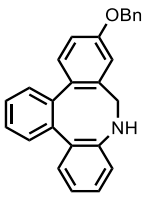
^{13}C NMR (151 MHz, $CDCl_3$)



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



^{13}C NMR (151 MHz, $CDCl_3$)



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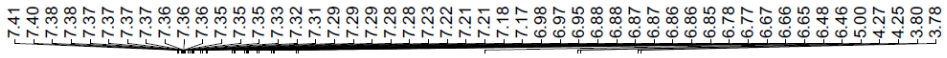
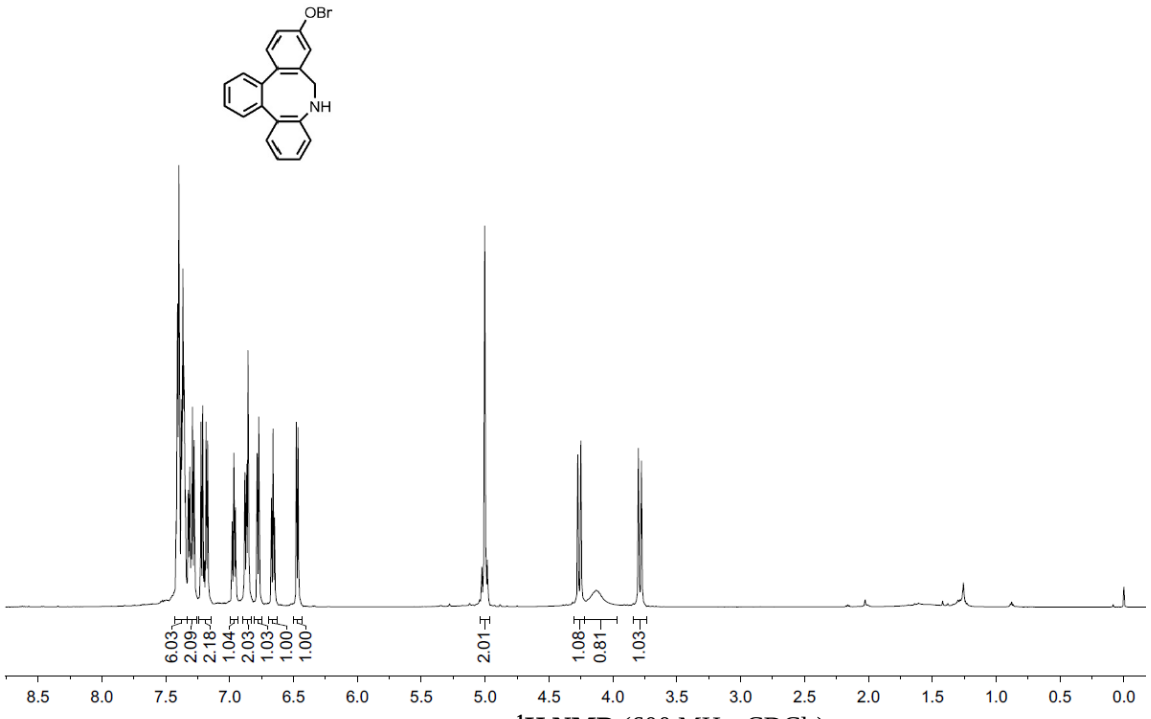
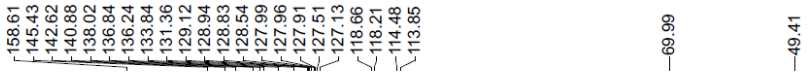
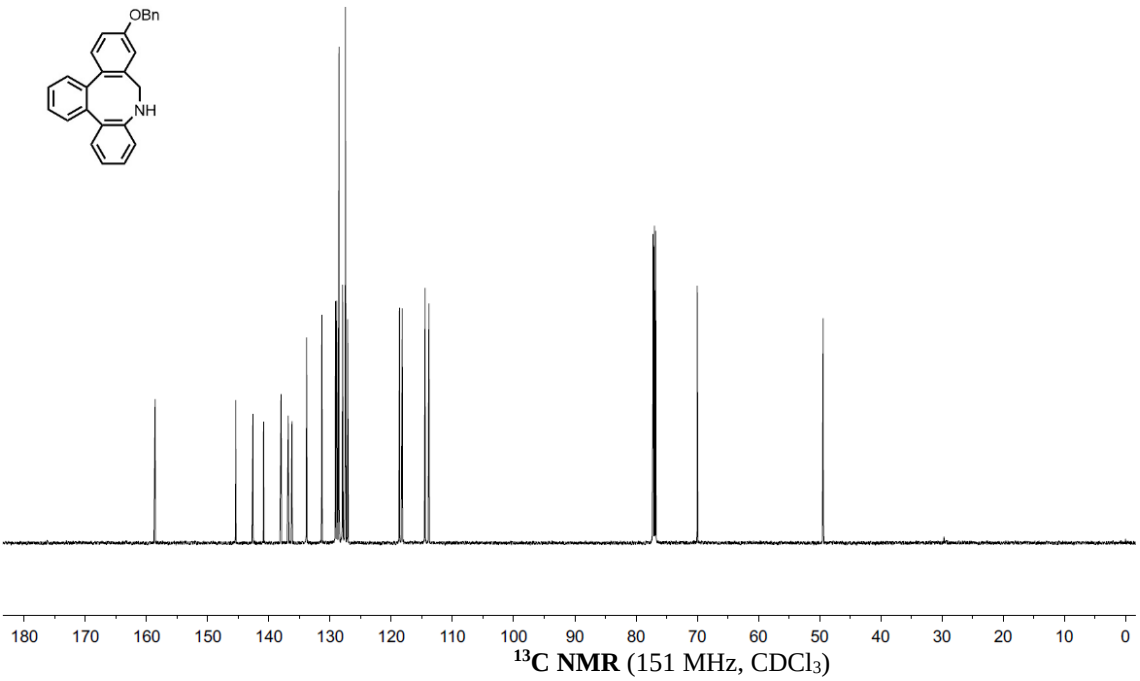


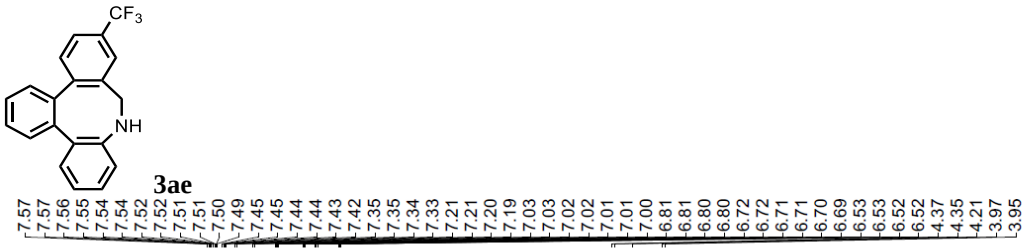


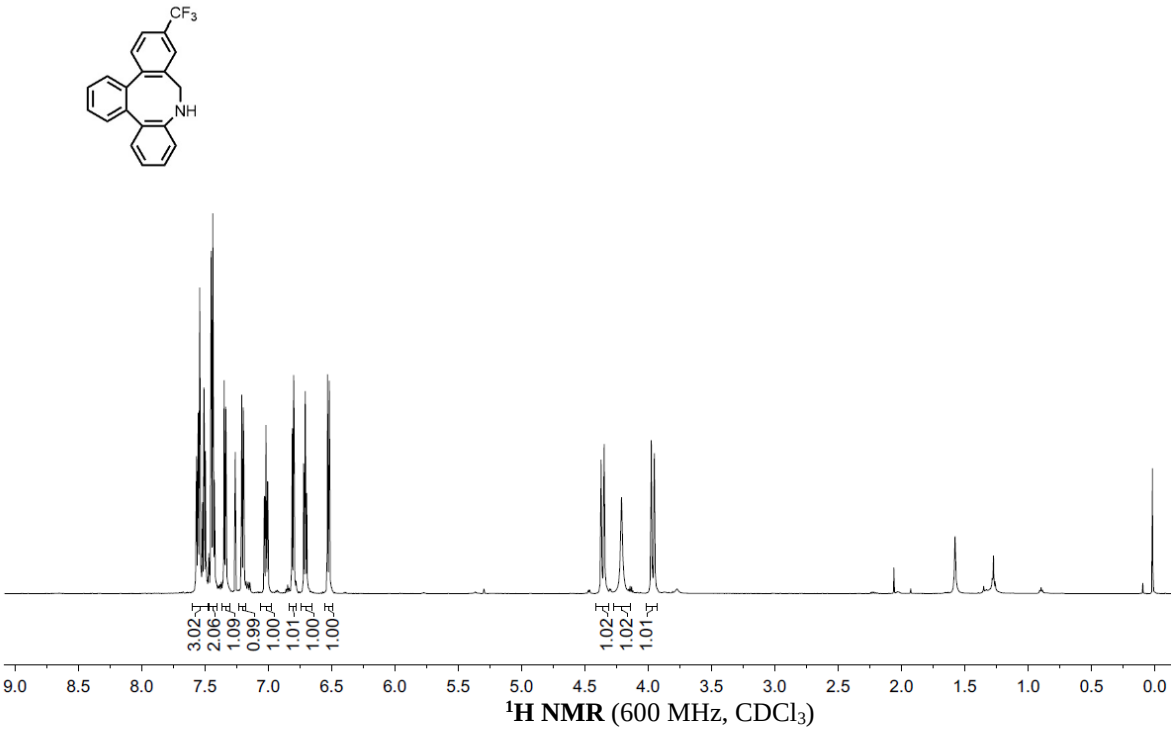
^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)





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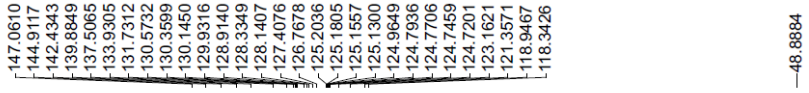
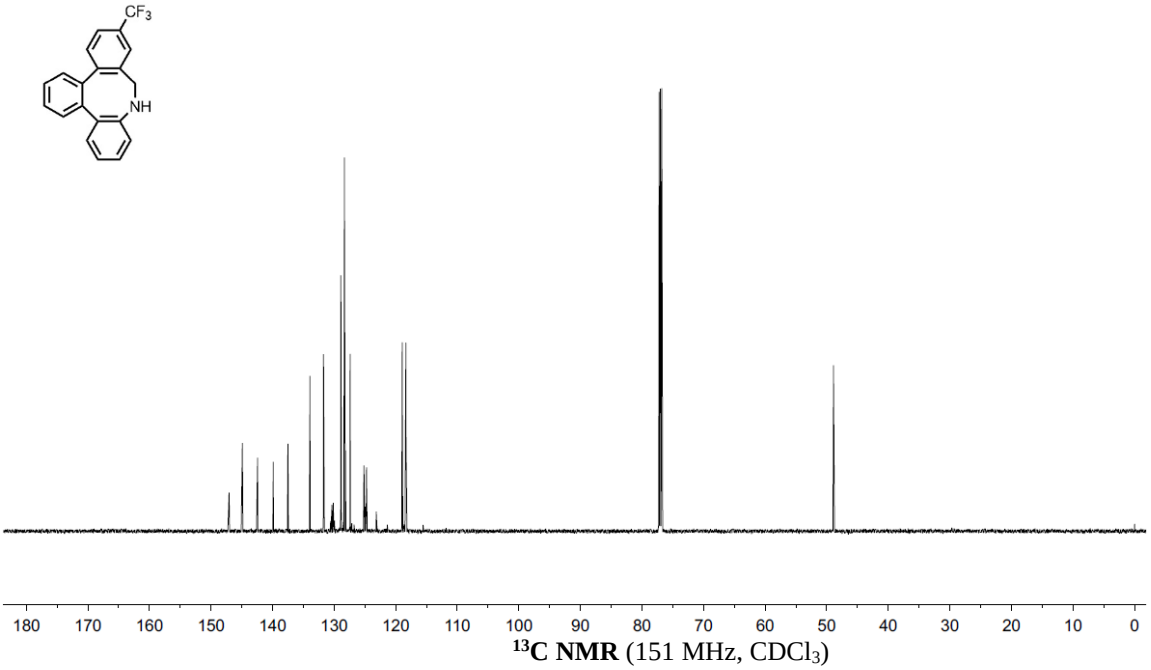
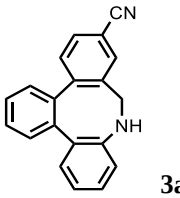




^{13}C NMR (151 MHz, $CDCl_3$)



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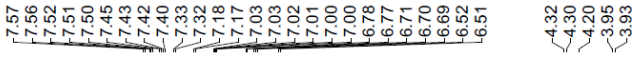
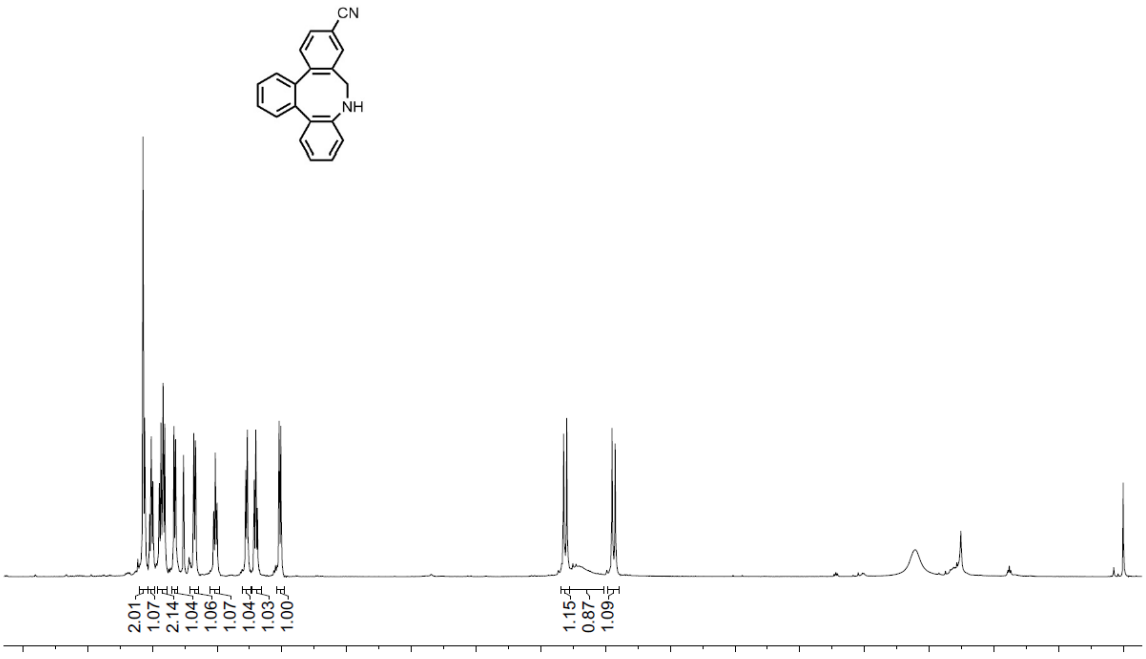
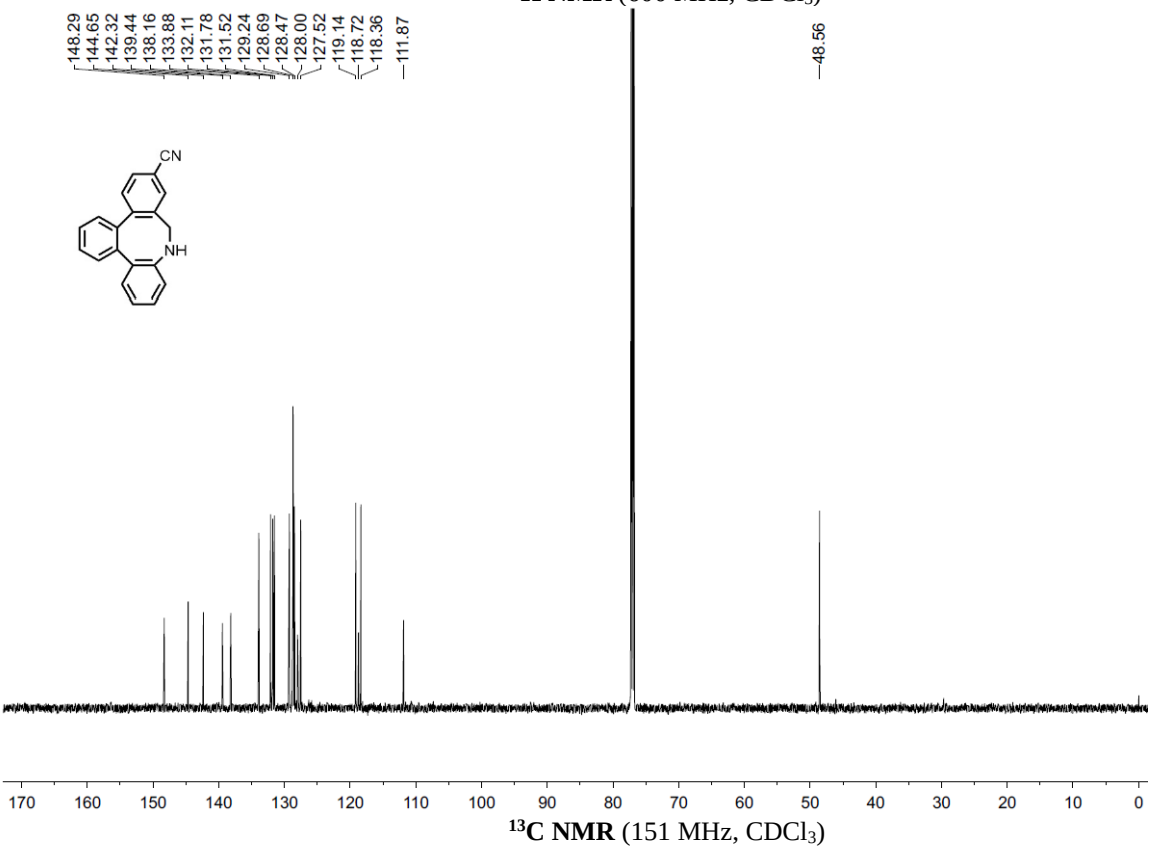
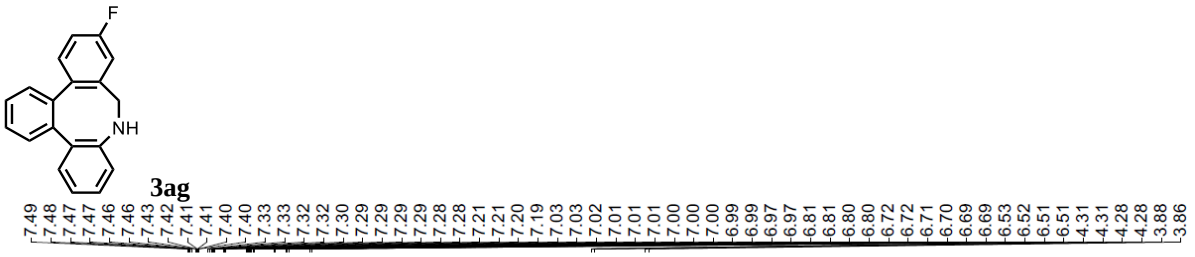


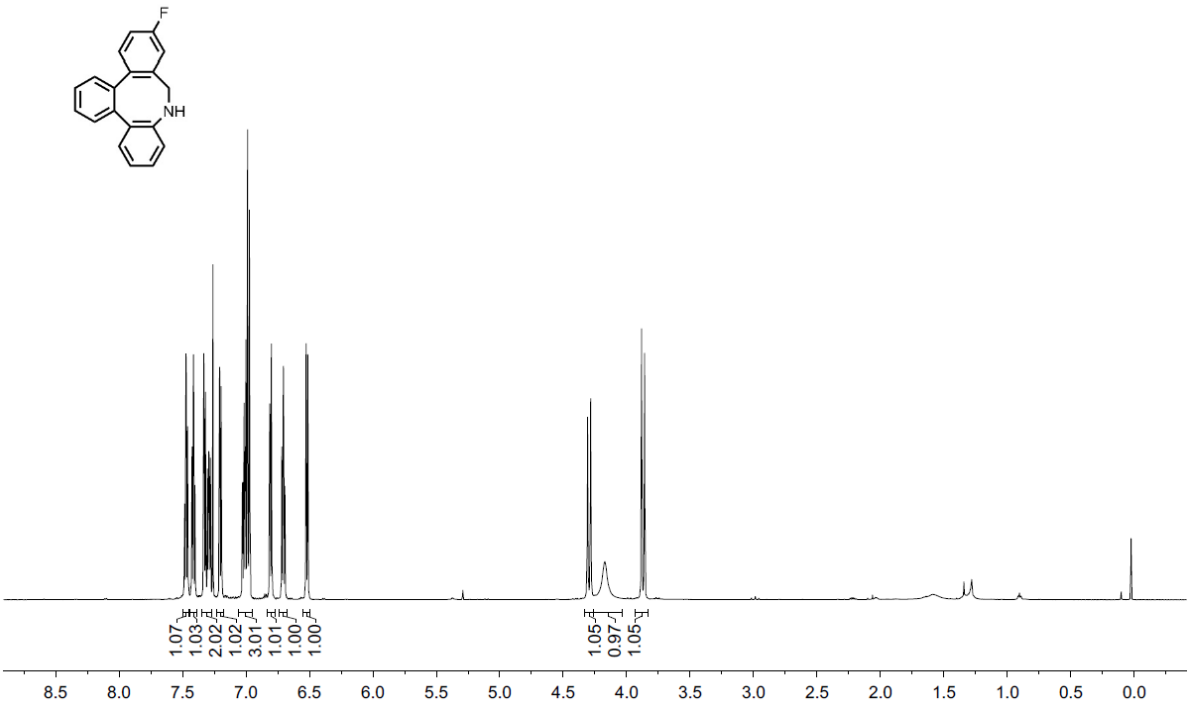


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)





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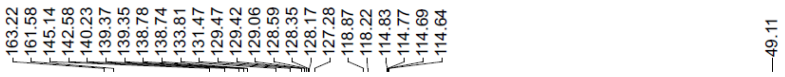

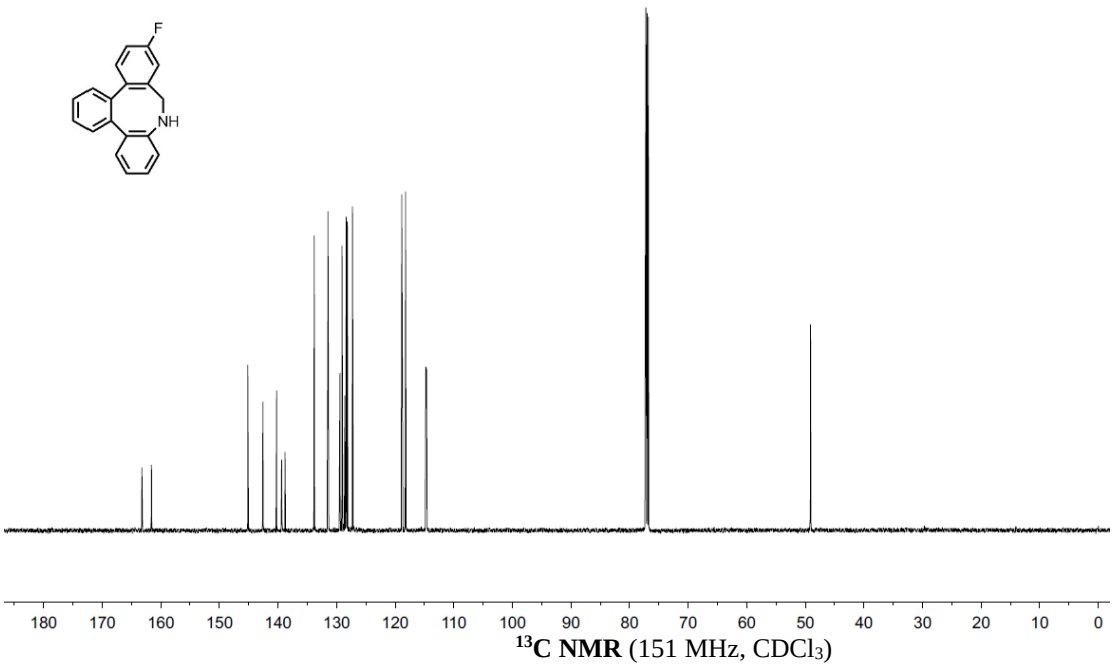

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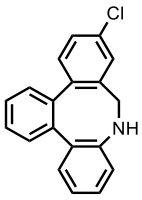

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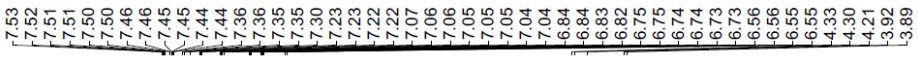
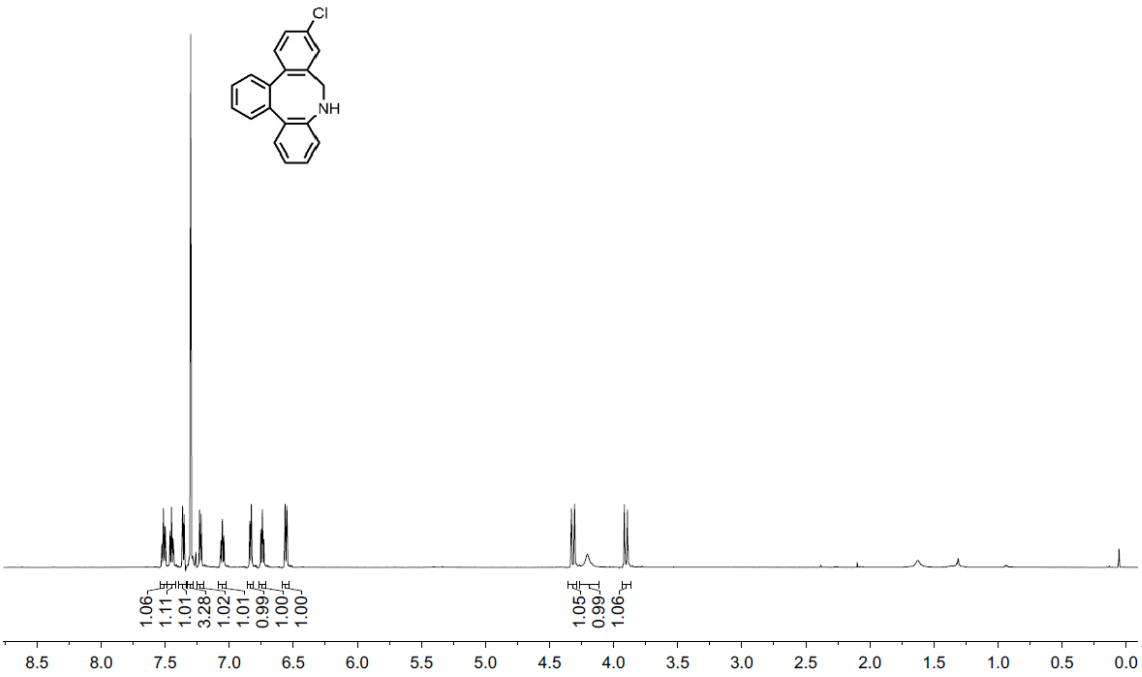
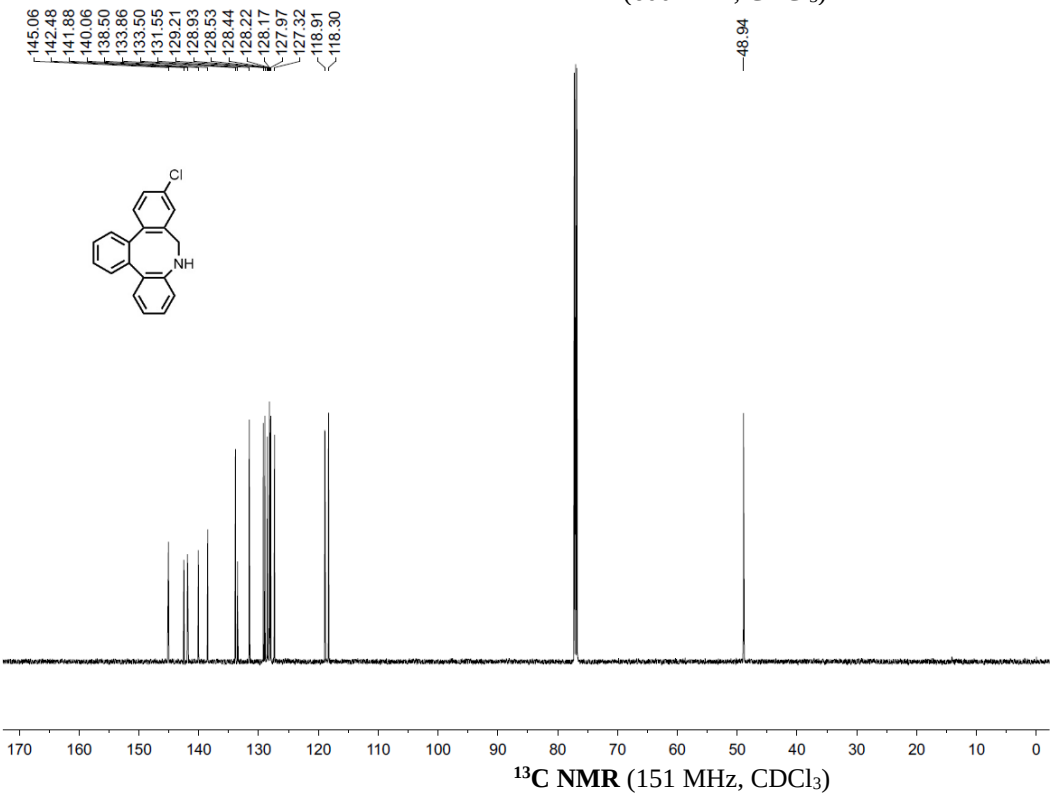




^{1}H NMR (600 MHz, $CDCl_3$)



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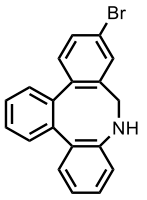

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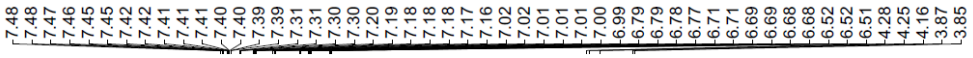

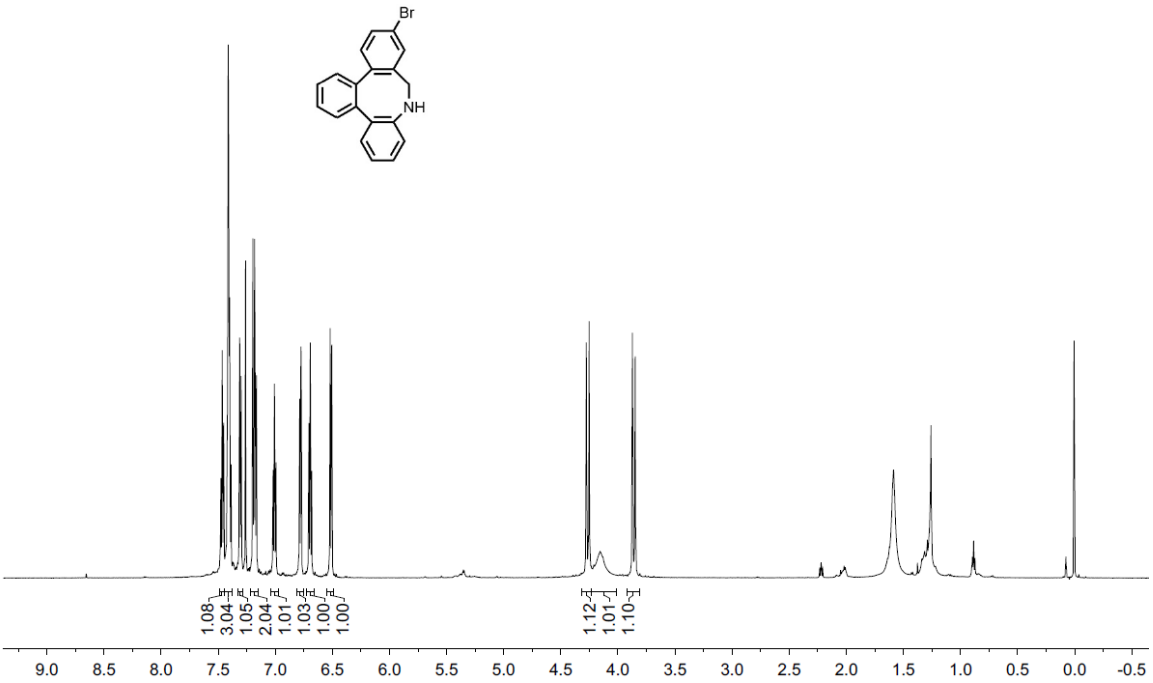

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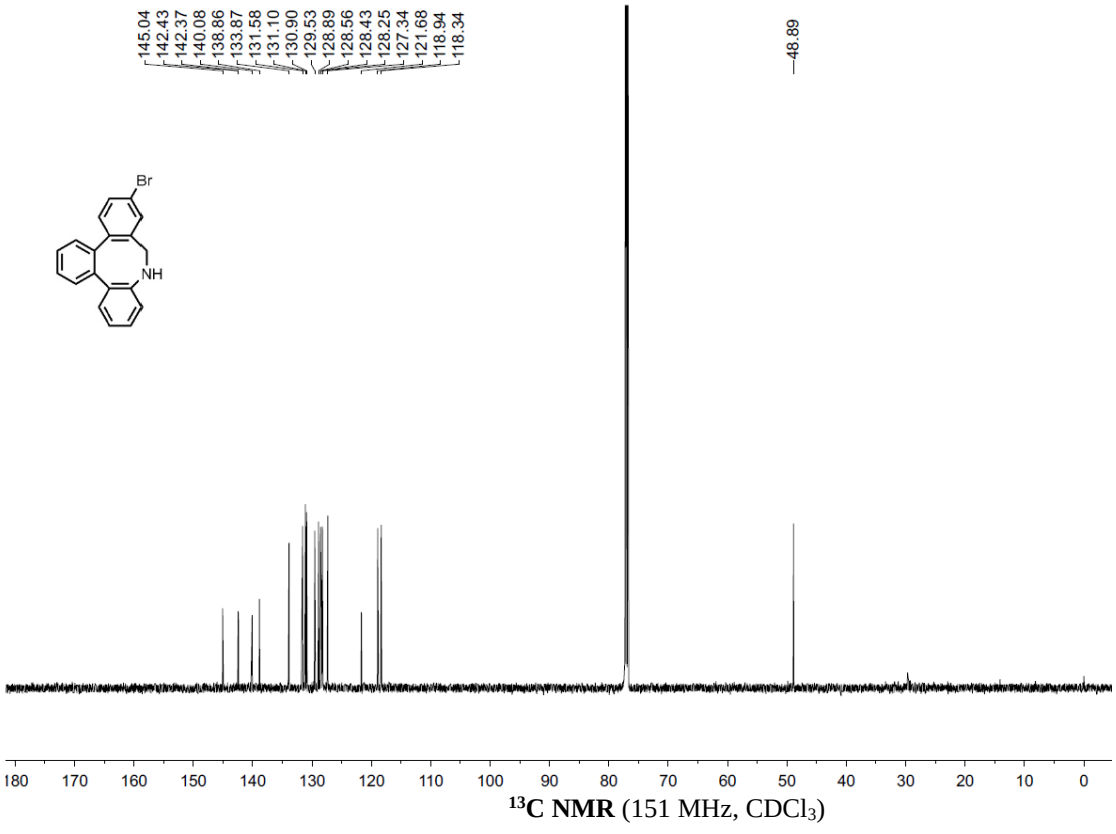

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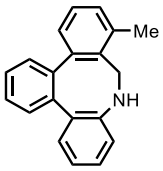

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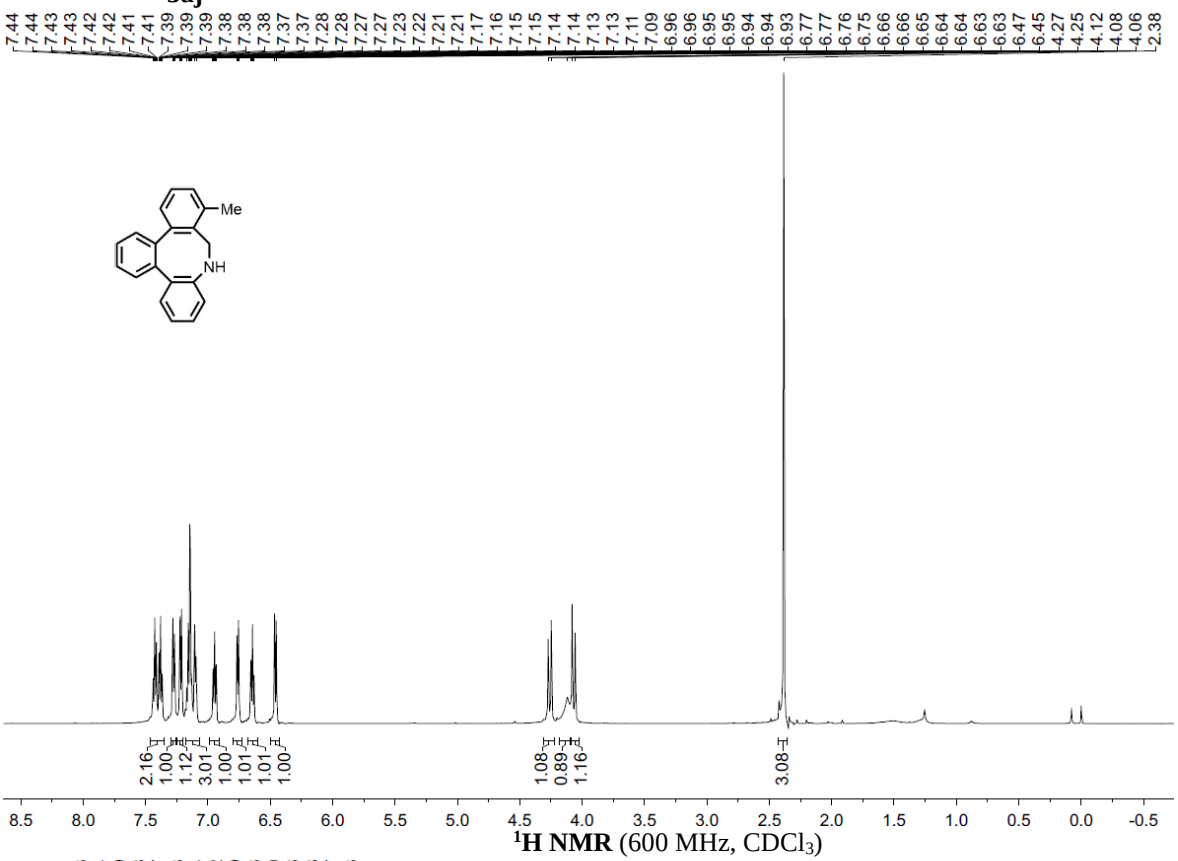

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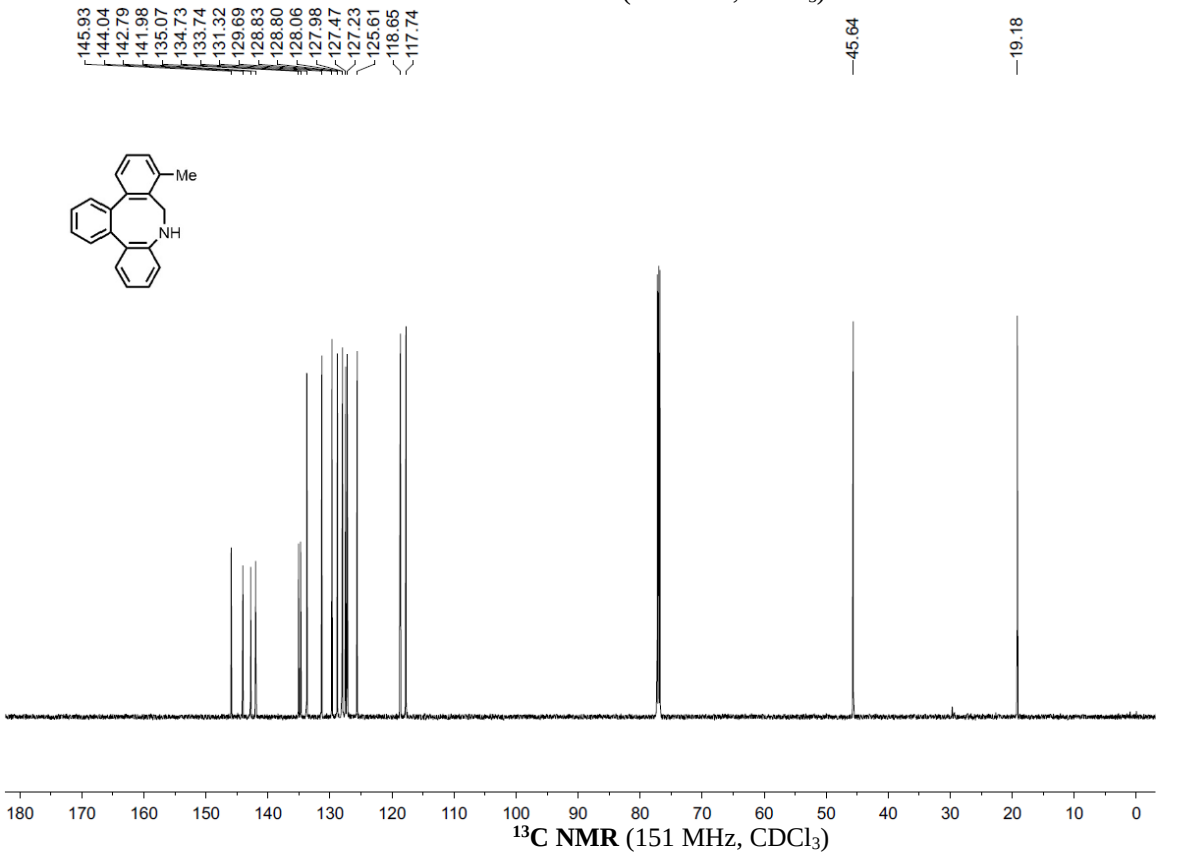

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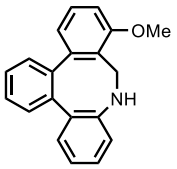

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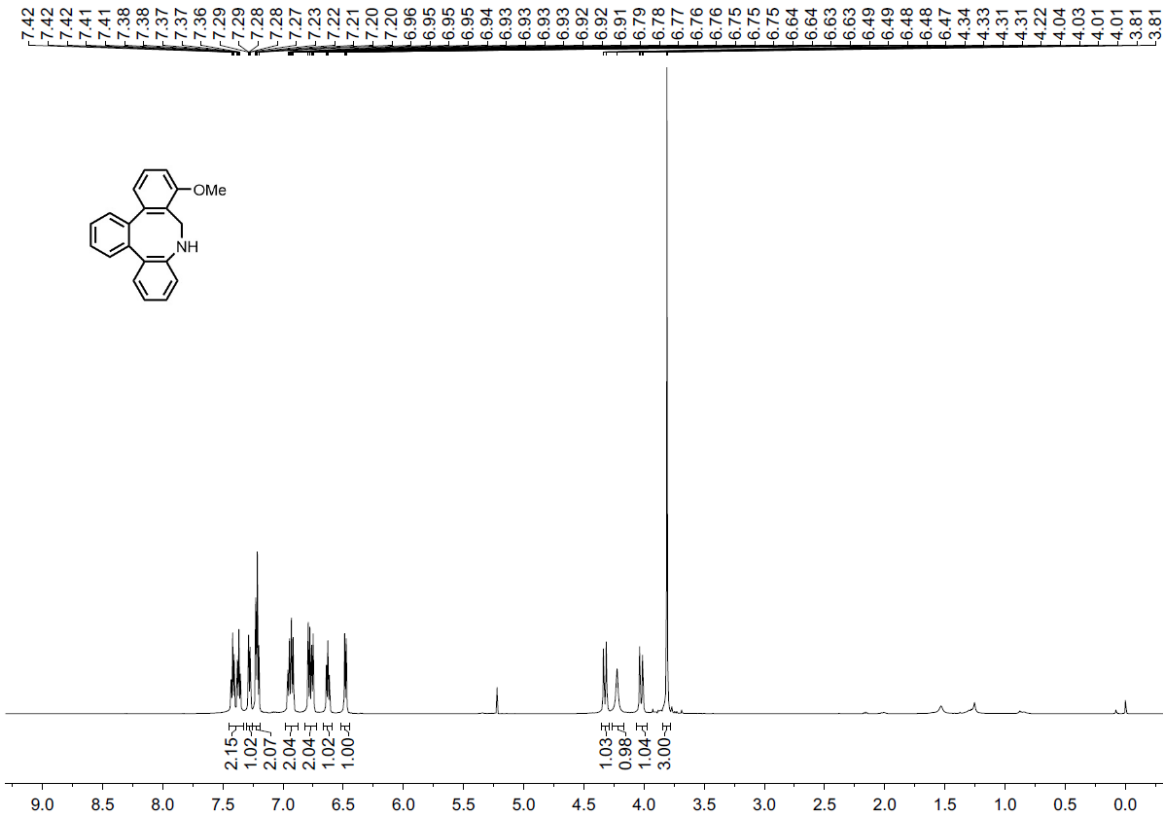
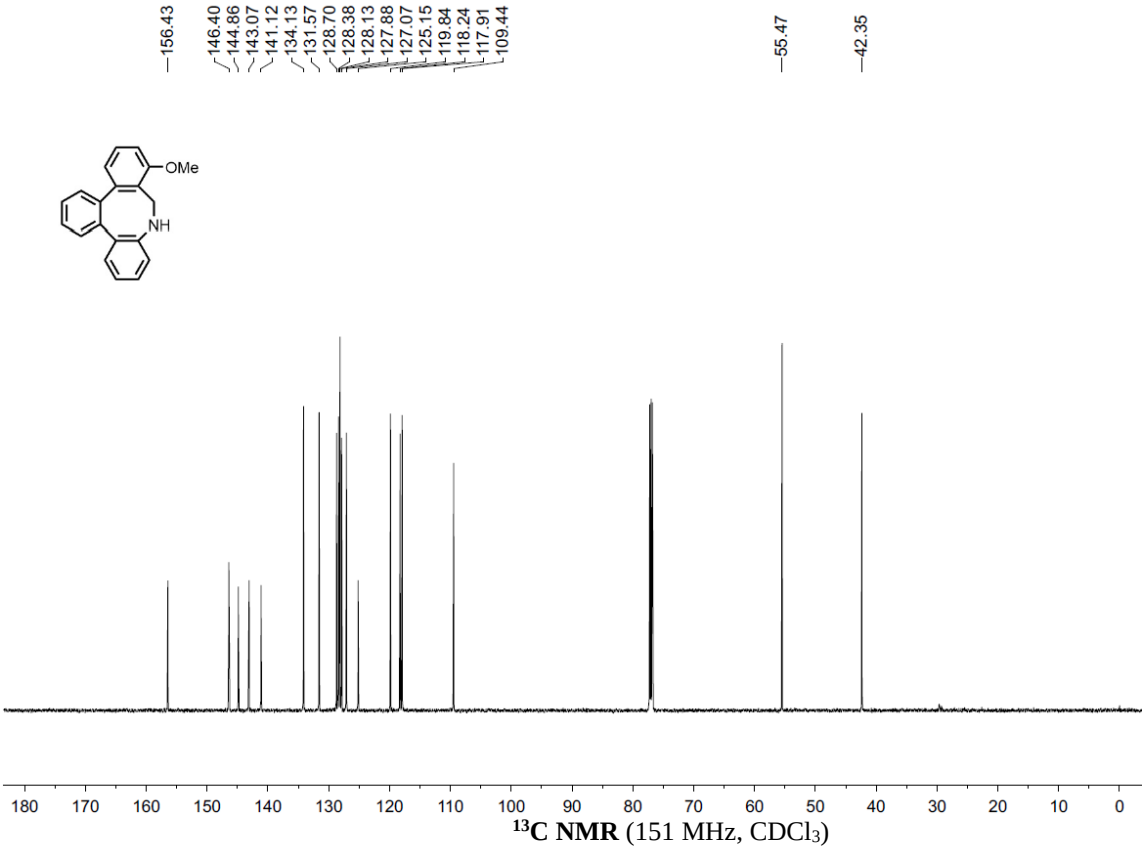


^{1}H NMR (600 MHz, $CDCl_3$)



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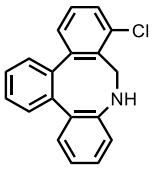

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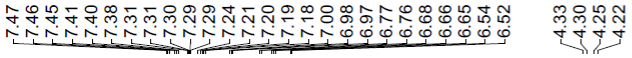

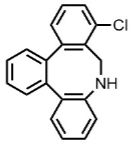

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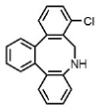

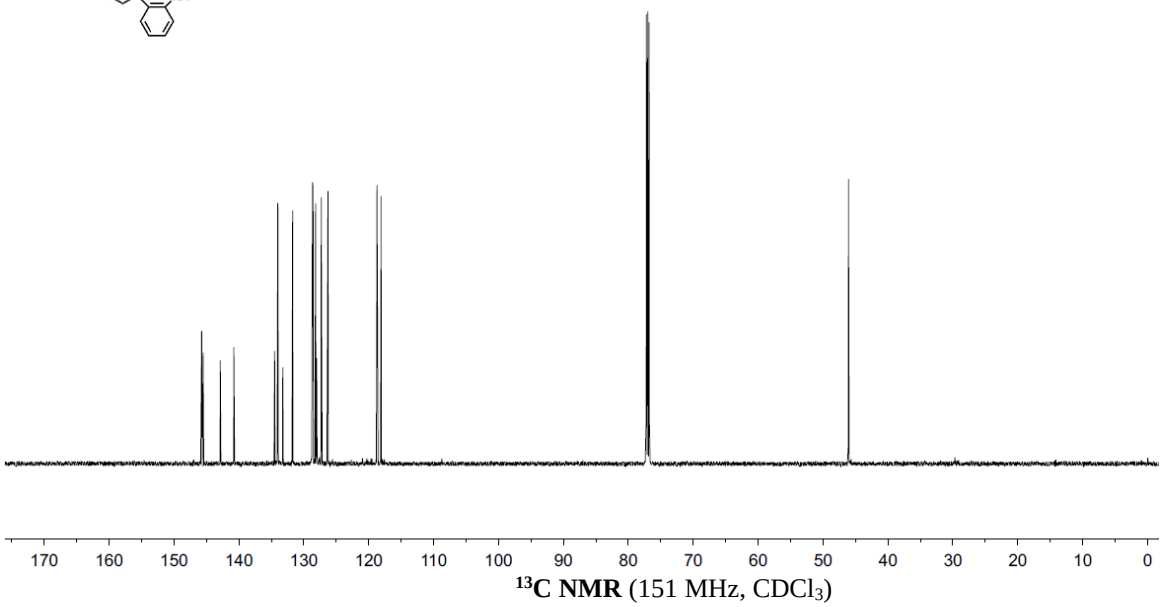

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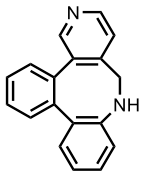

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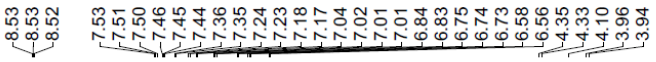

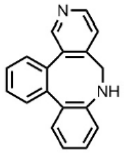

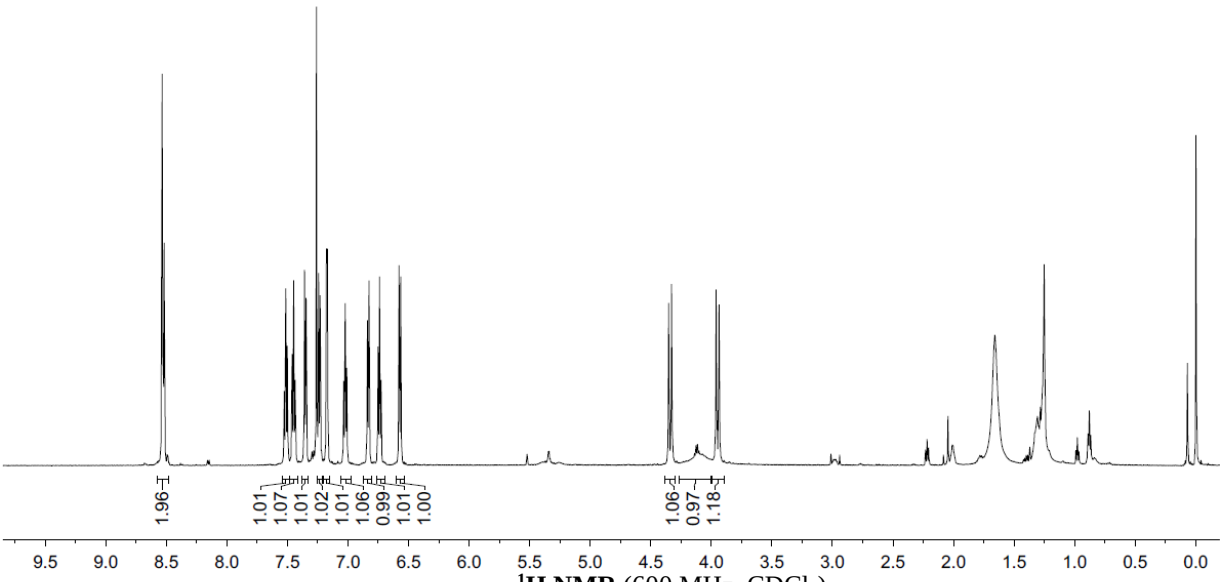

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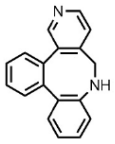

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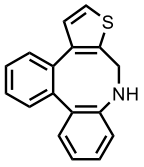

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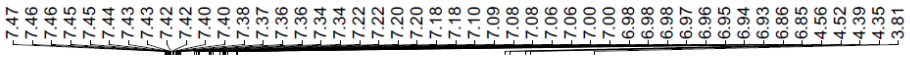

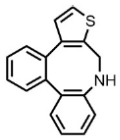

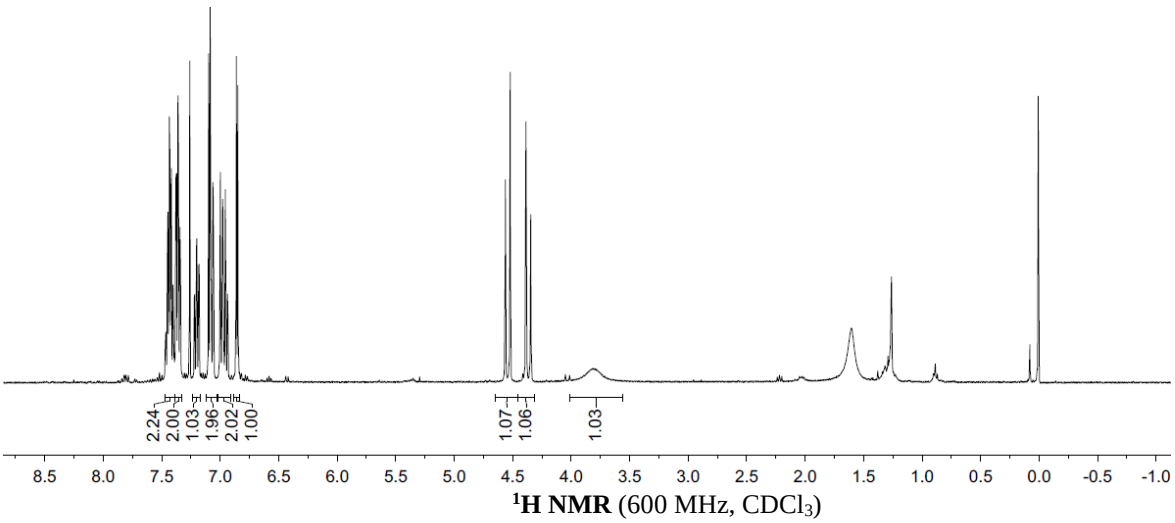

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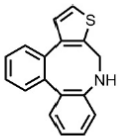

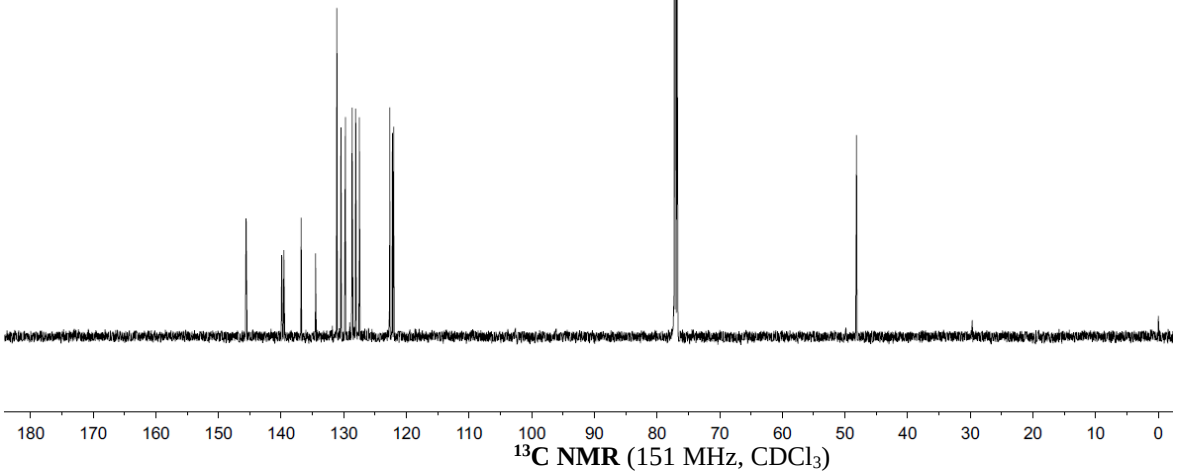

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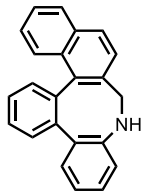

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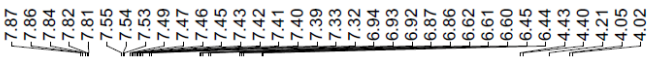

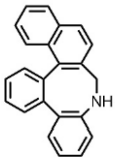

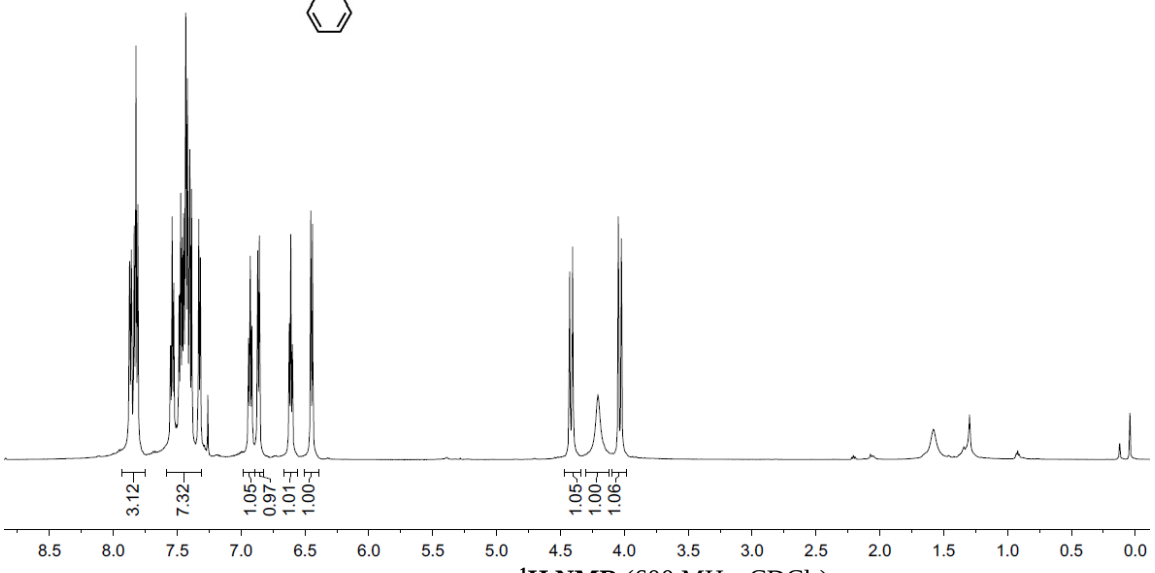

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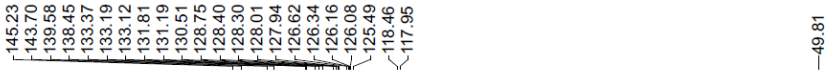

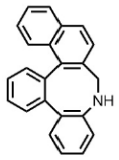

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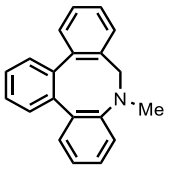

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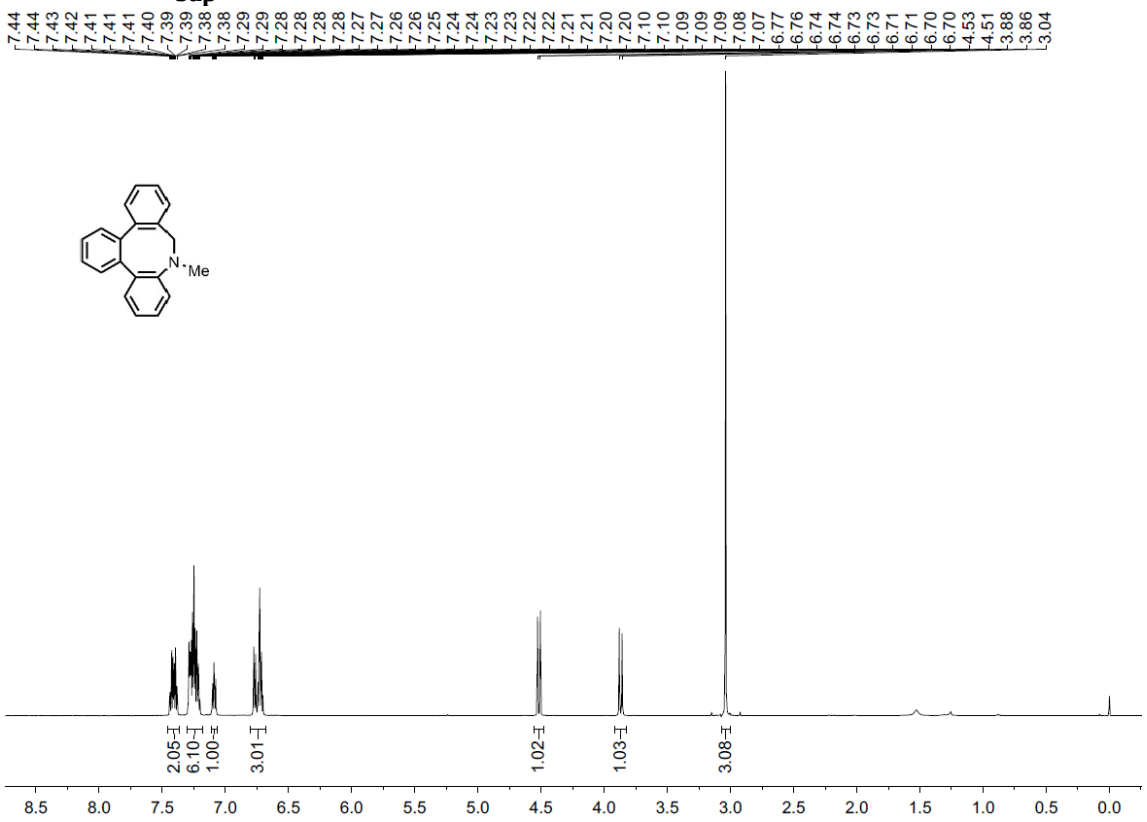
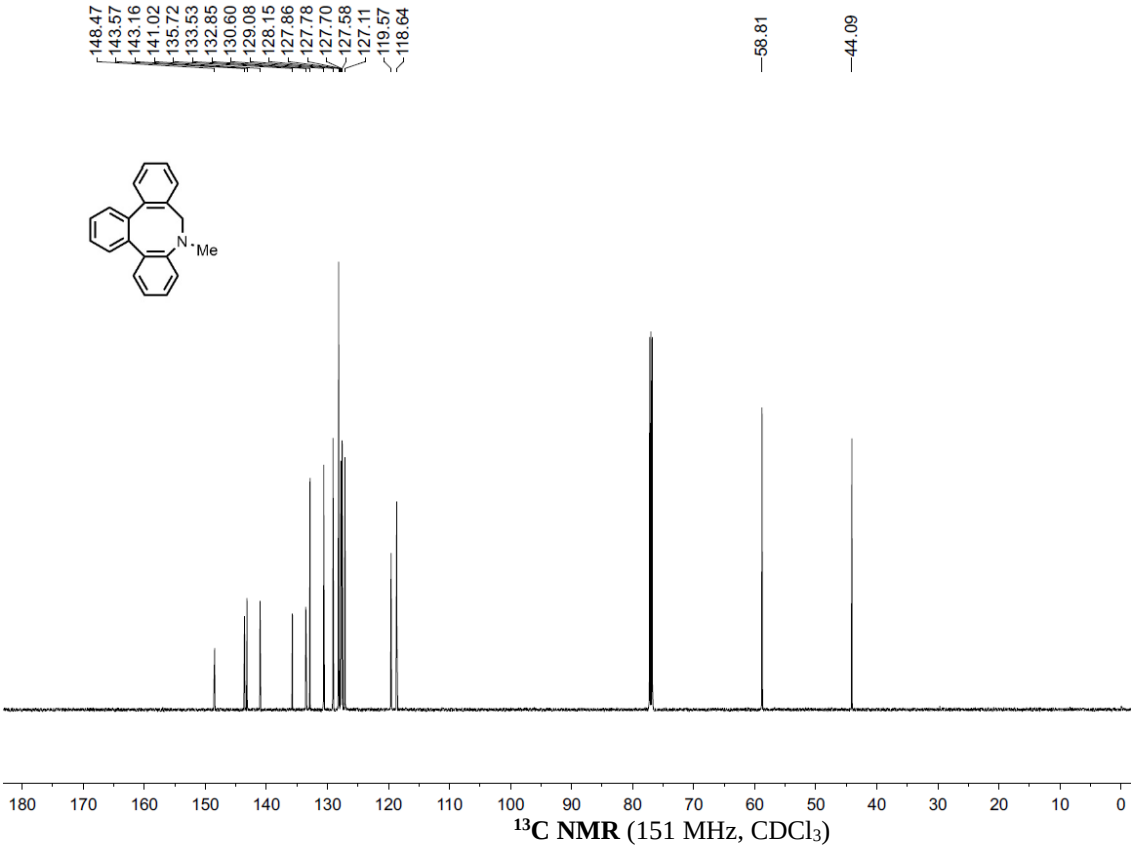


^{1}H NMR (600 MHz, $CDCl_3$)



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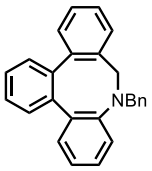

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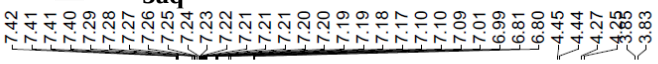
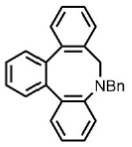
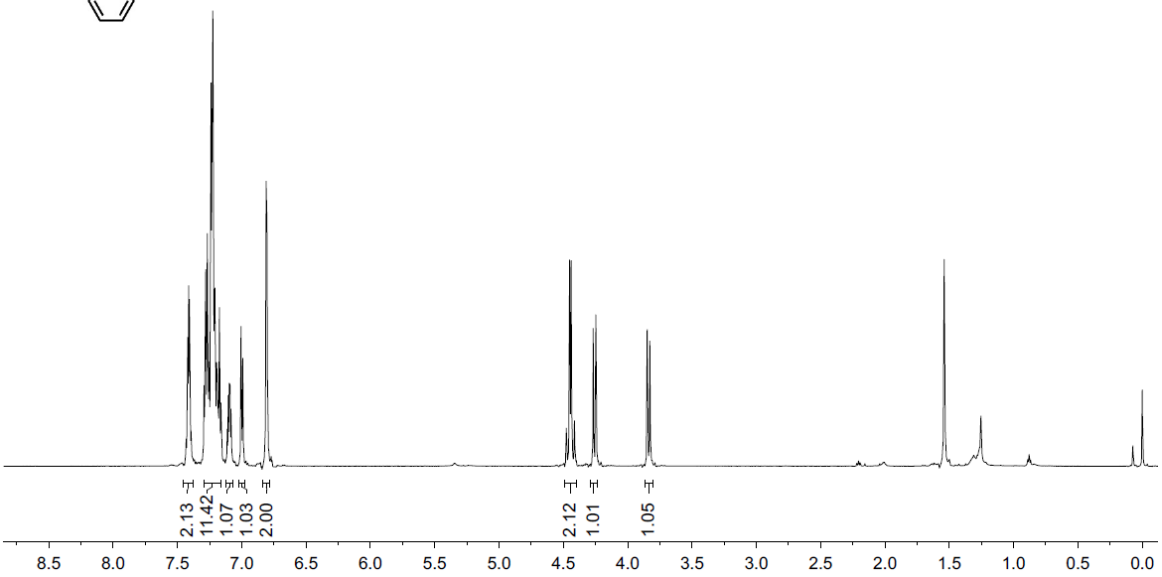
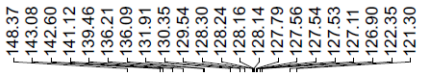
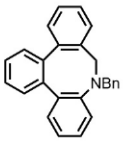






^{1}H NMR (600 MHz, $CDCl_3$)





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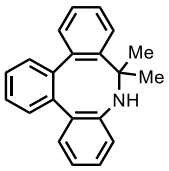

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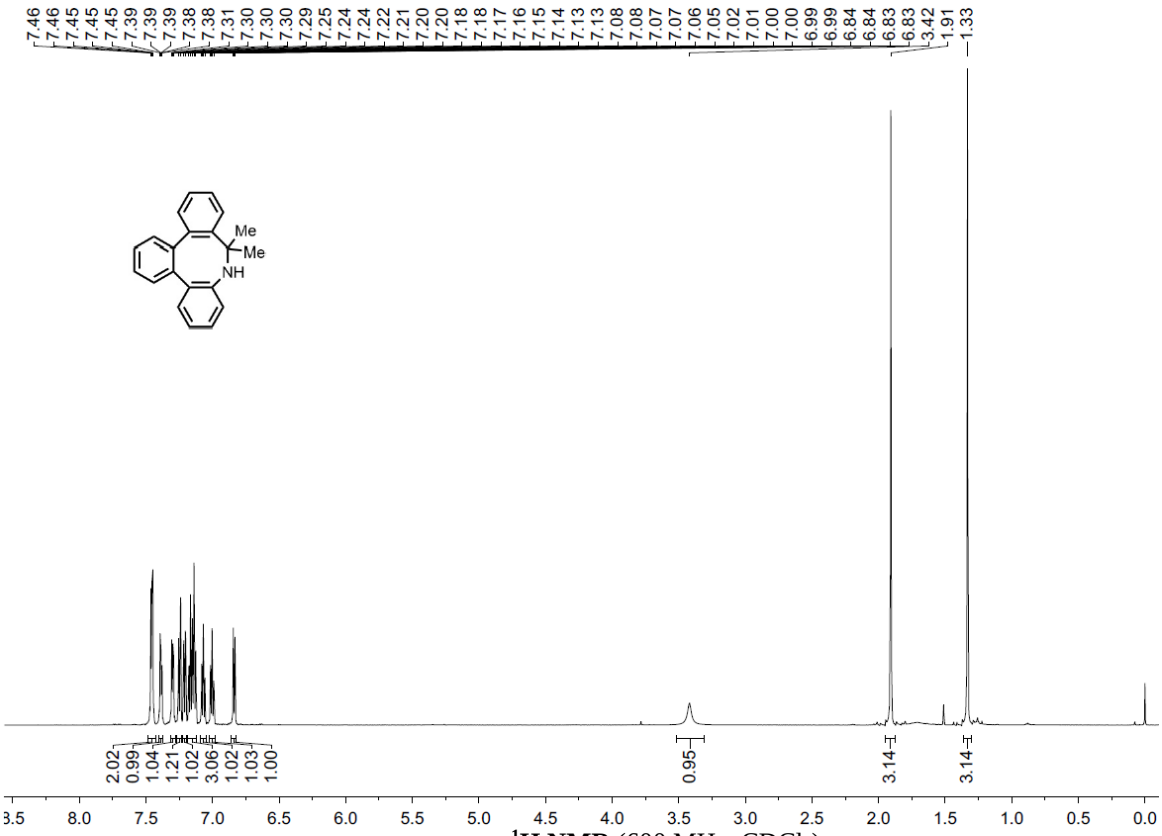

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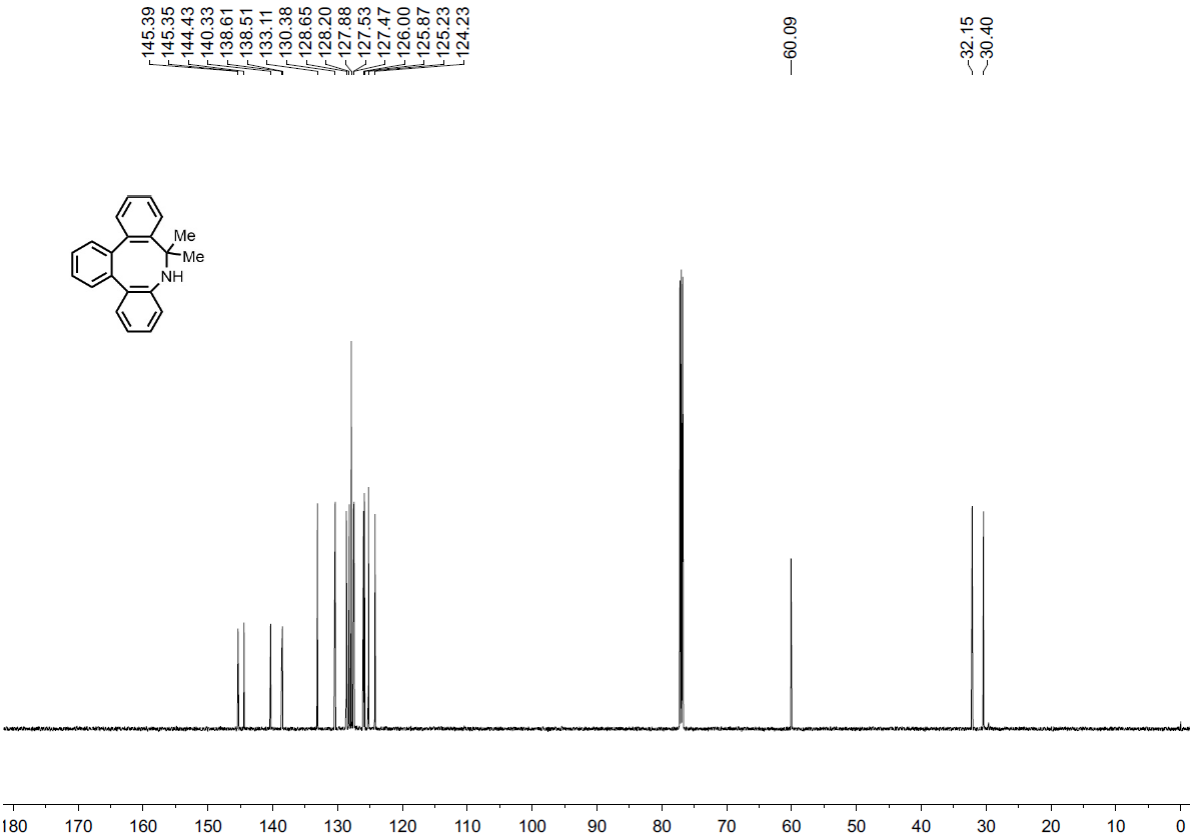

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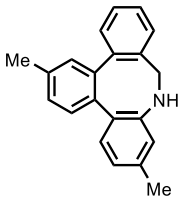

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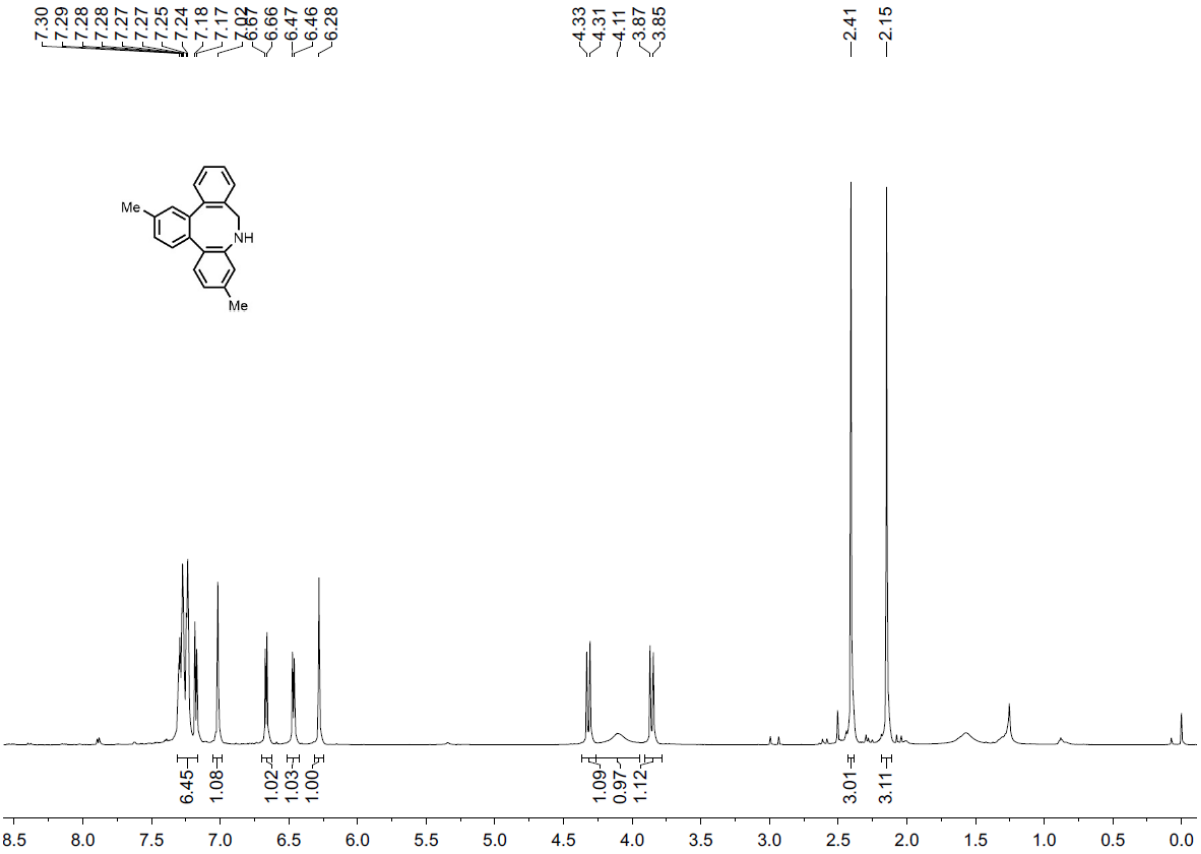

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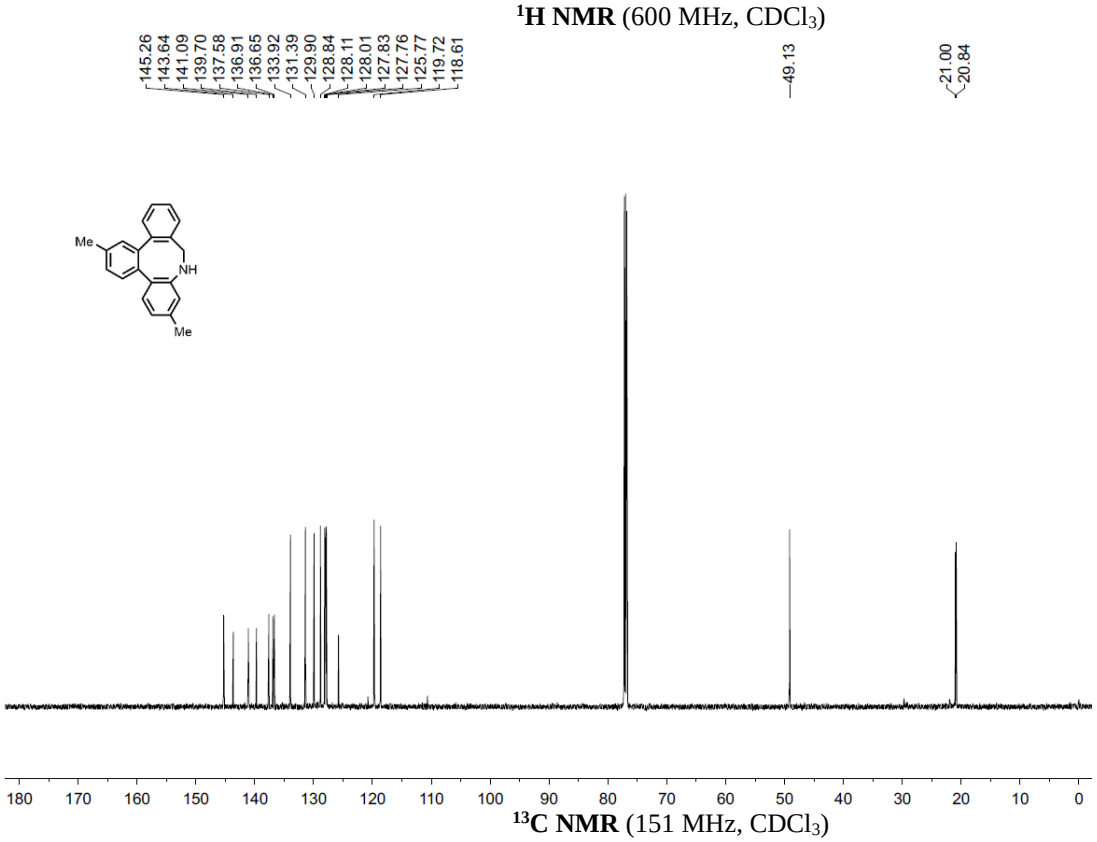
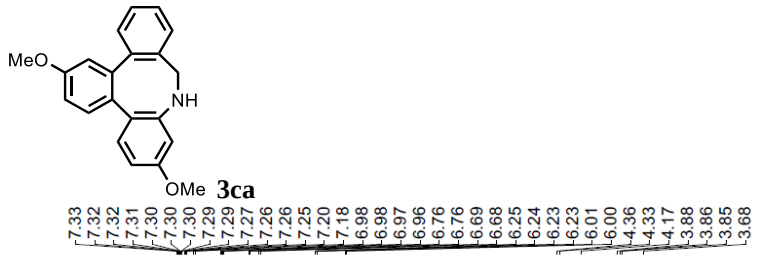
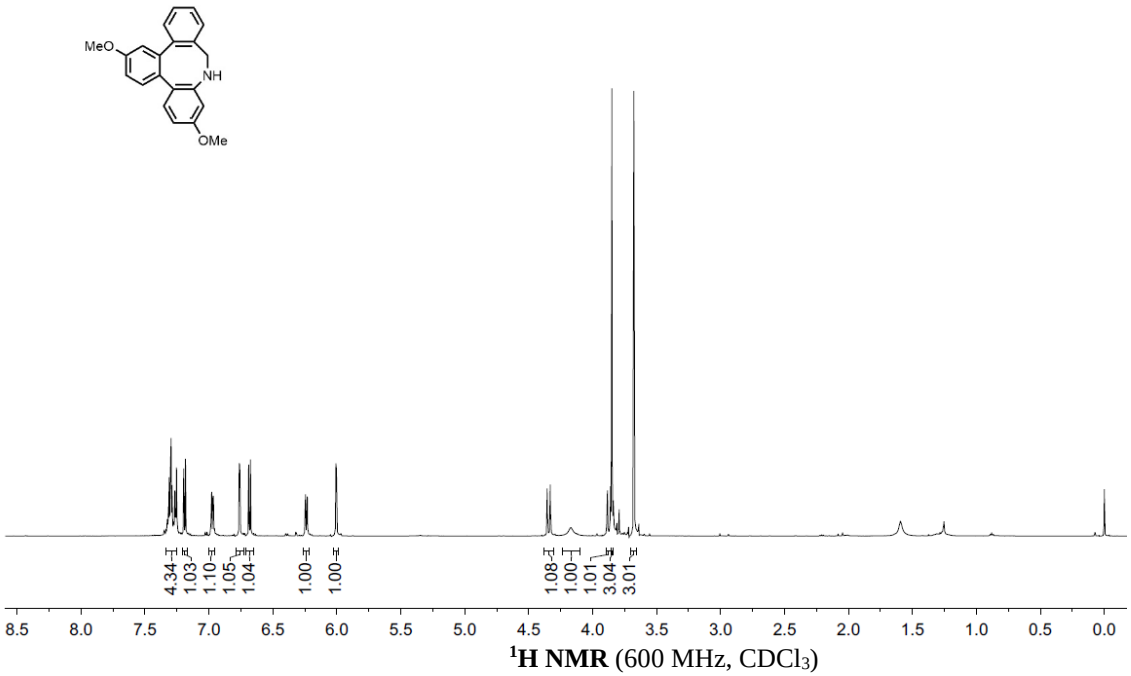
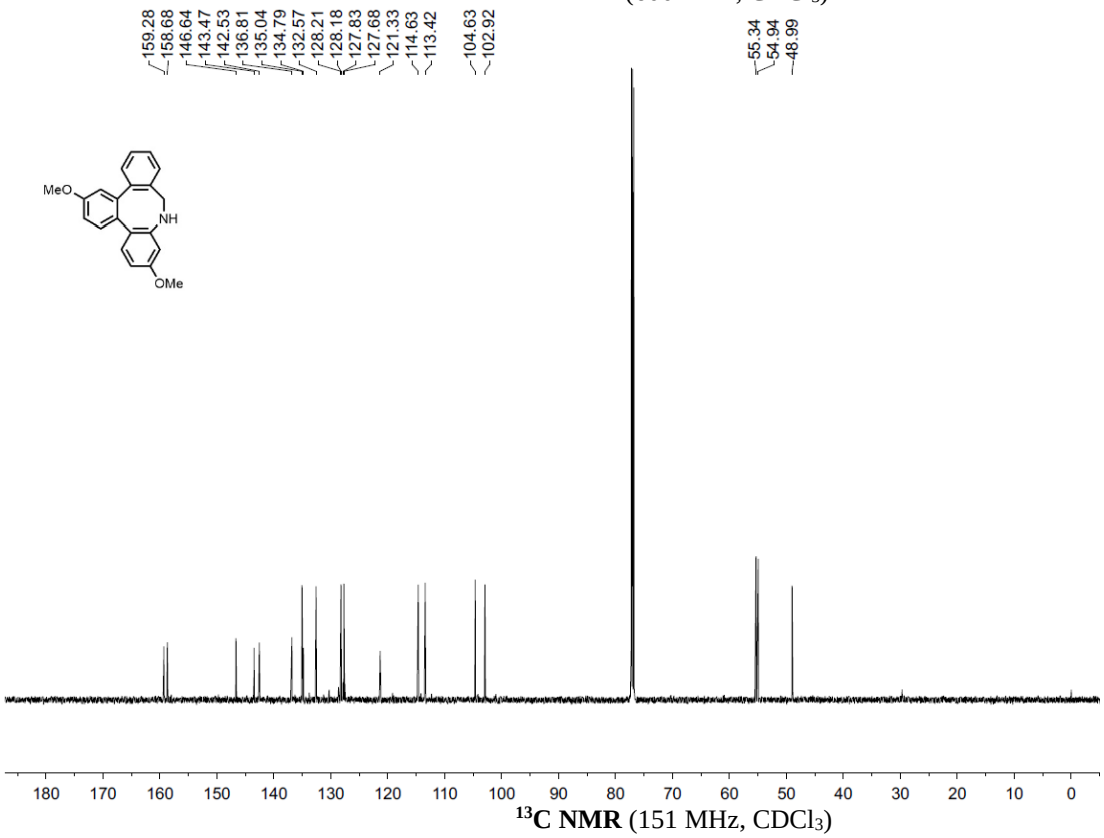


^{13}C NMR (151 MHz, $CDCl_3$)

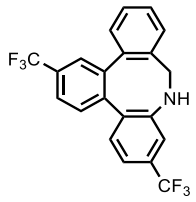




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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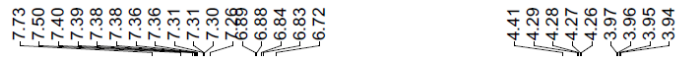
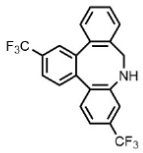
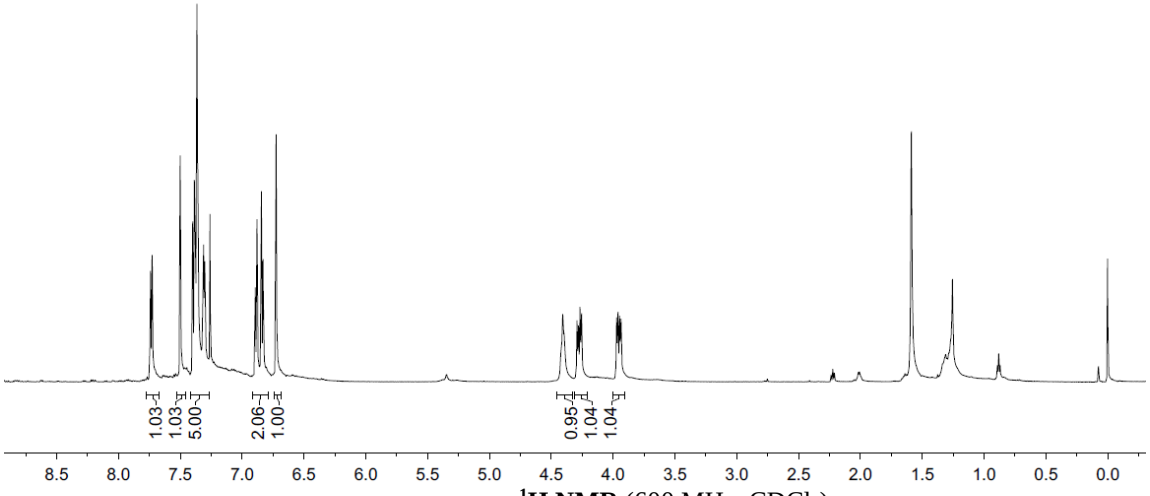
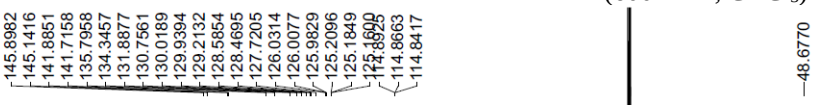
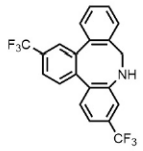




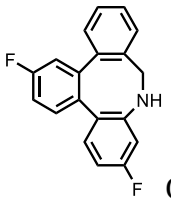


^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)



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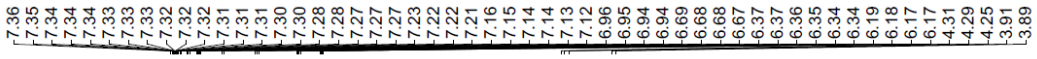
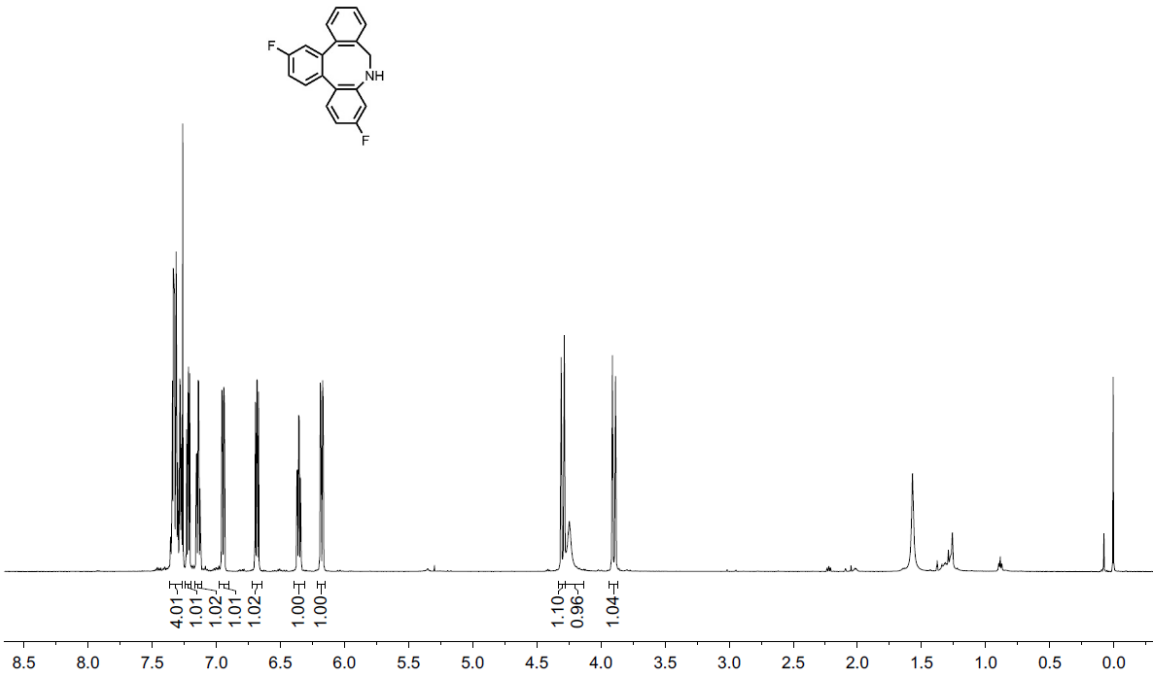
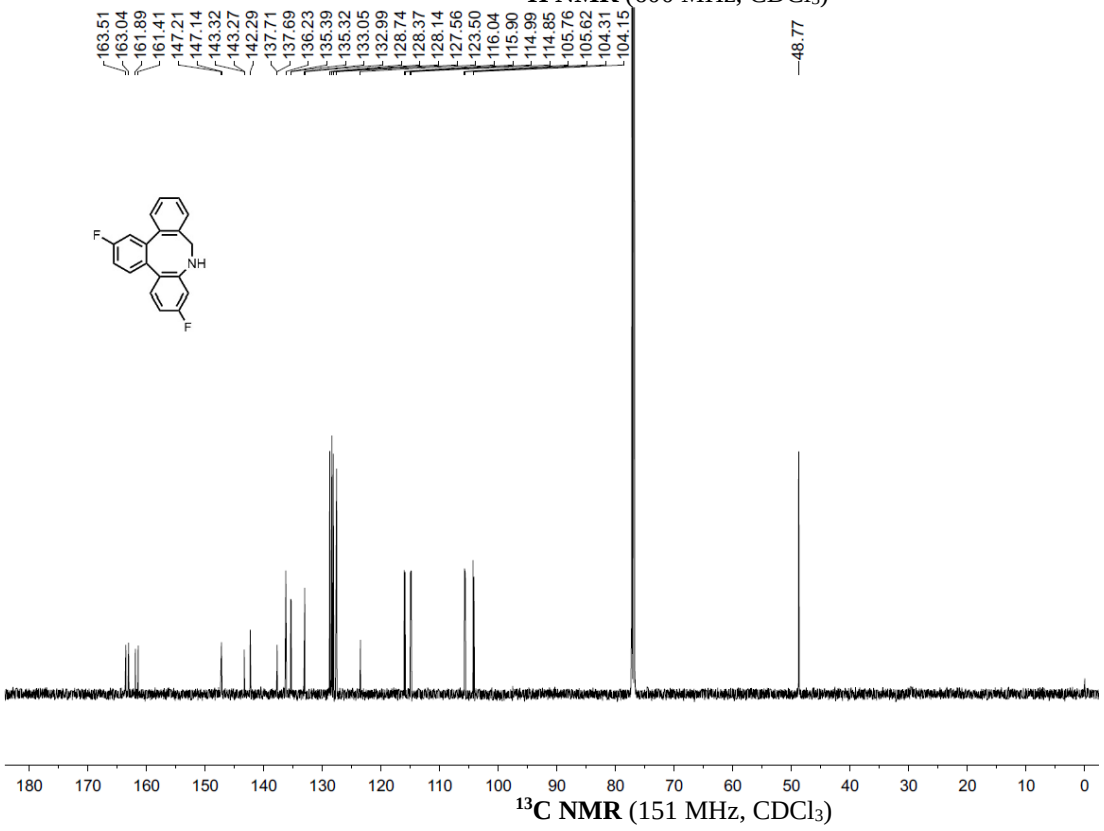
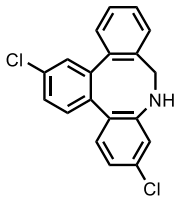




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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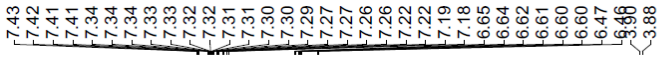
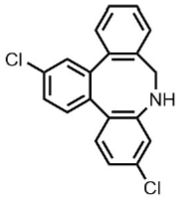
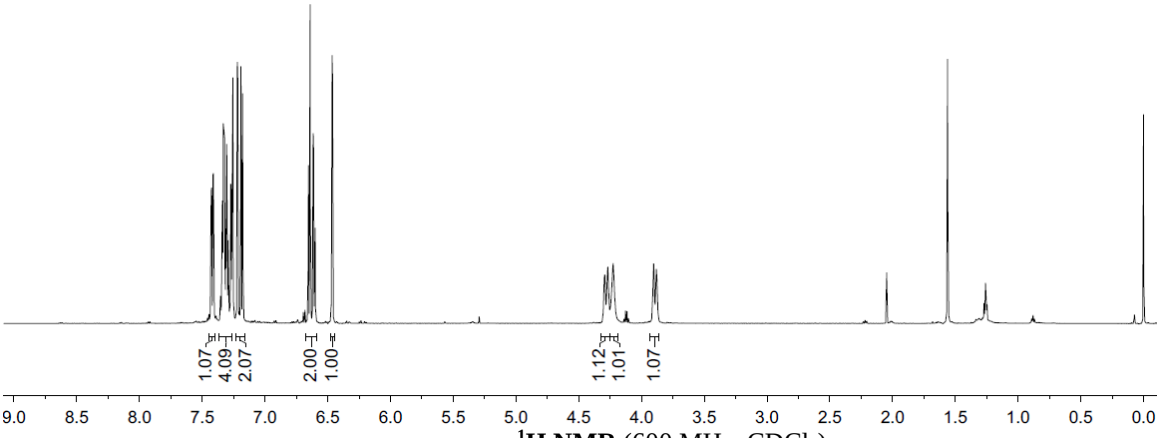
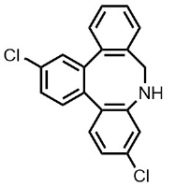
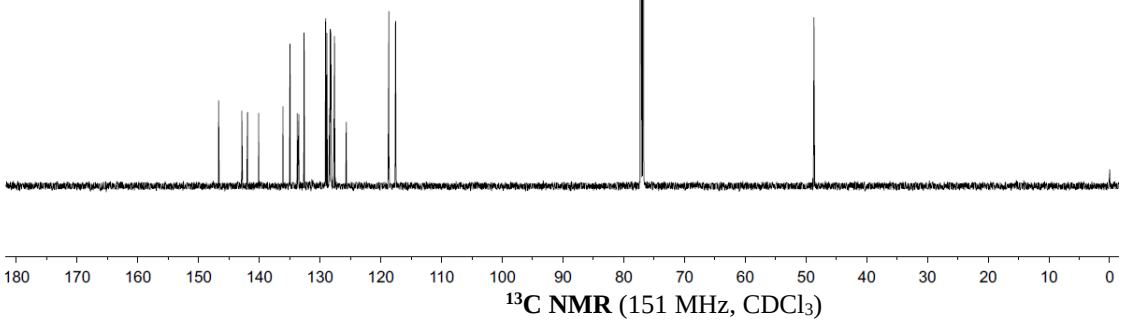




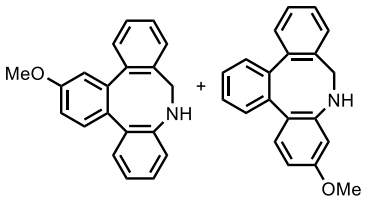


^{1}H NMR (600 MHz, $CDCl_3$)

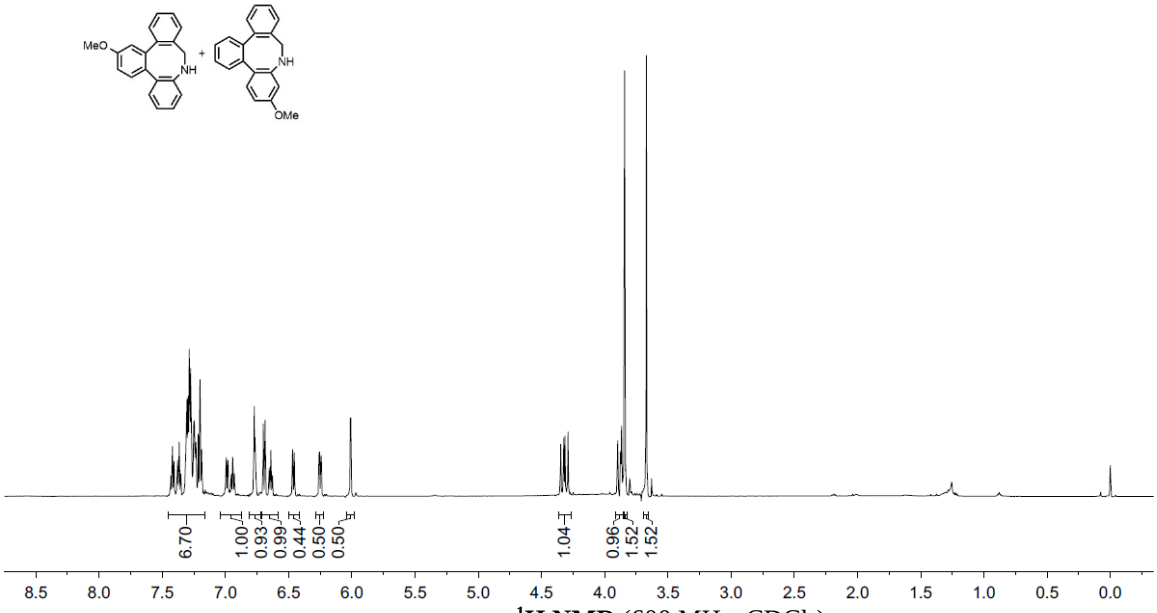




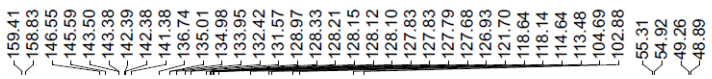
^{13}C NMR (151 MHz, $CDCl_3$)

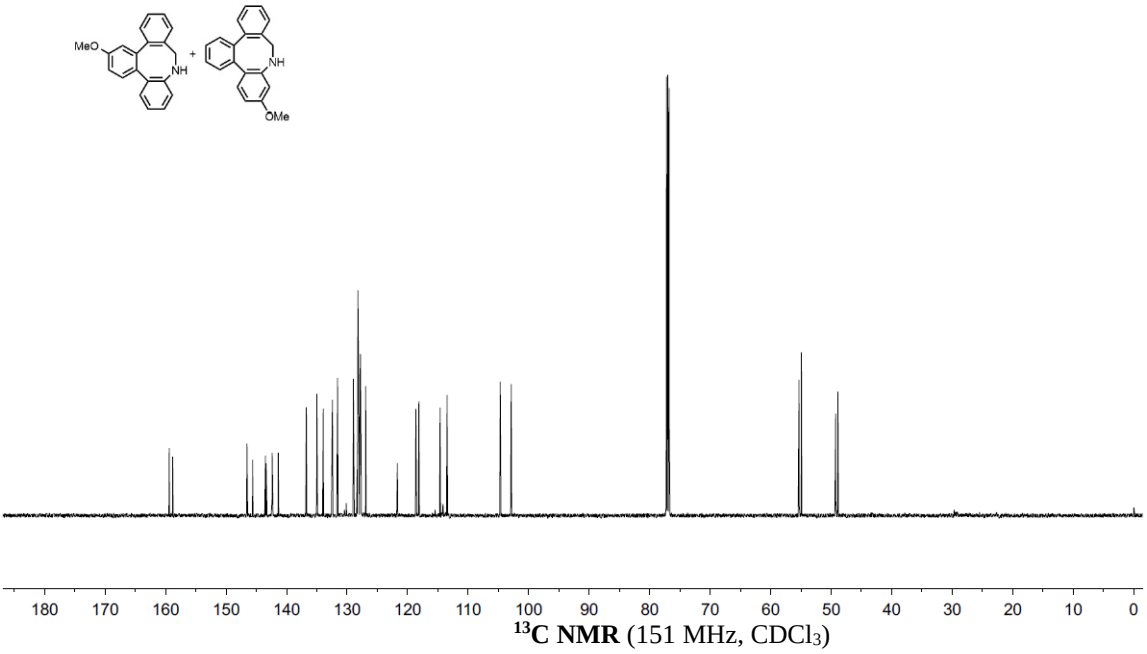


3ga-1 and 3ga-2

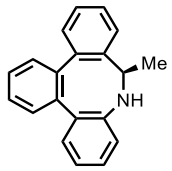


^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)



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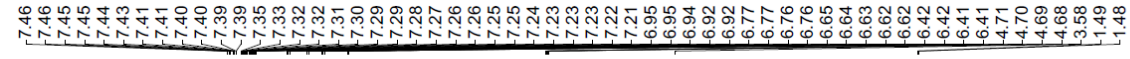
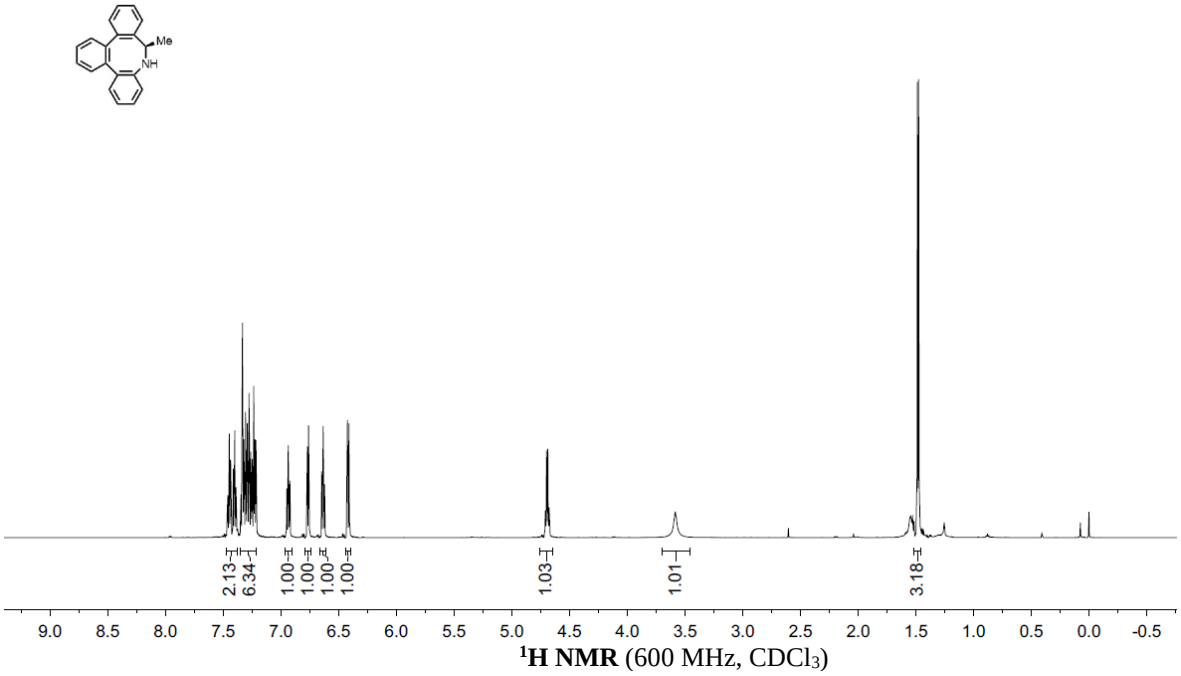
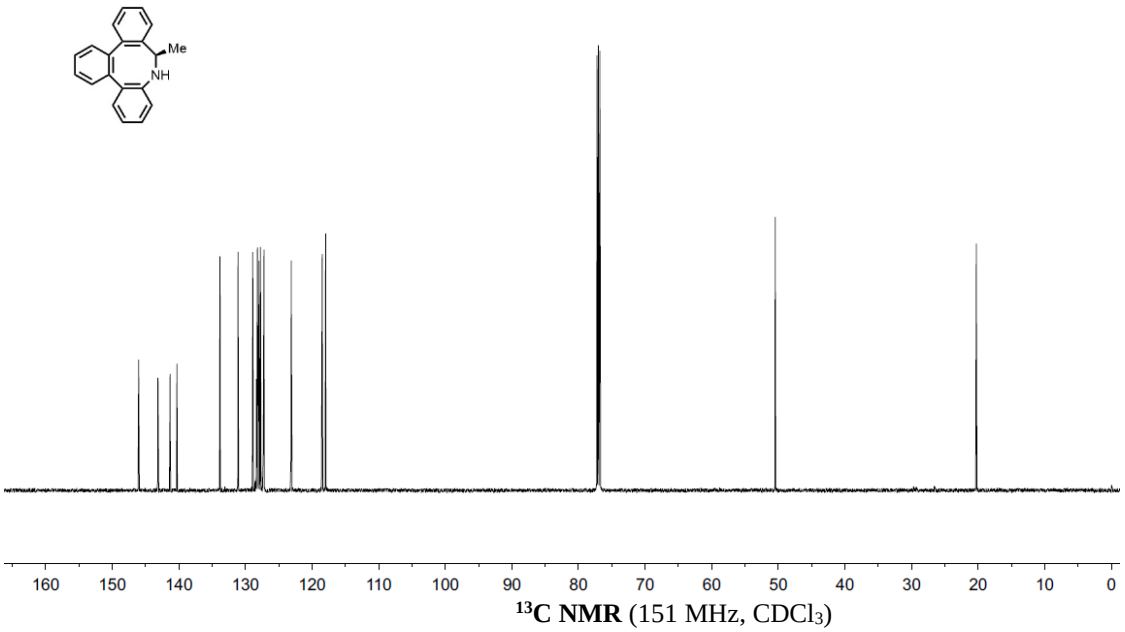
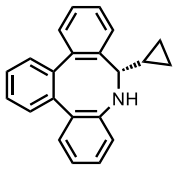




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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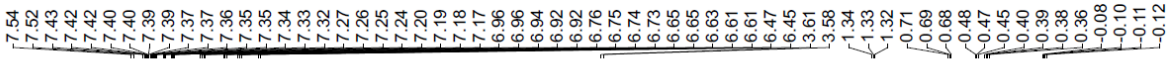
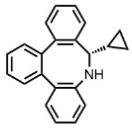
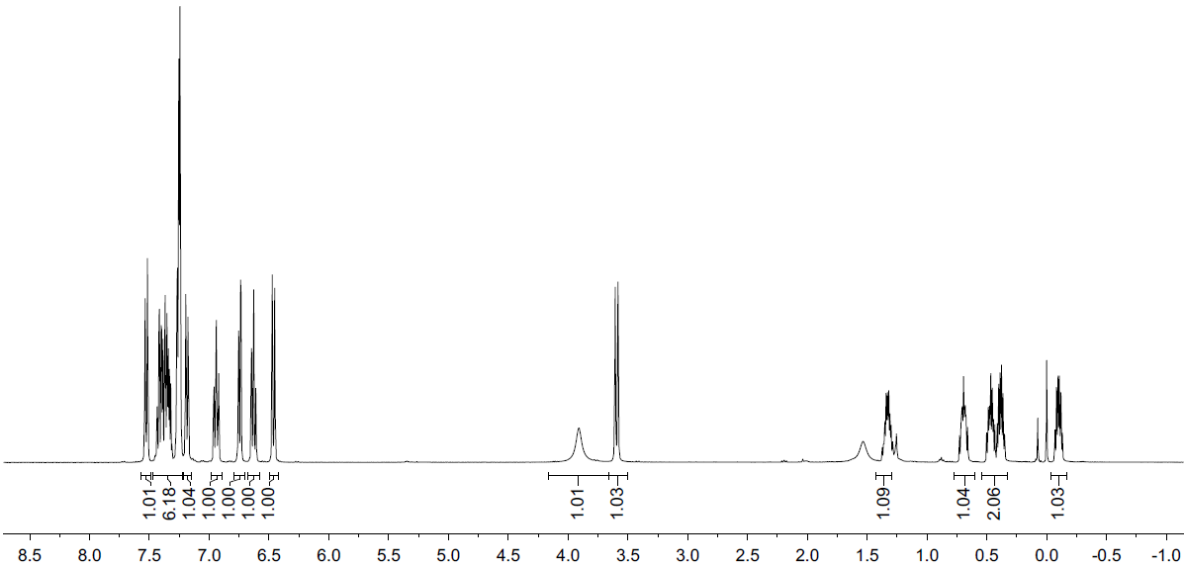
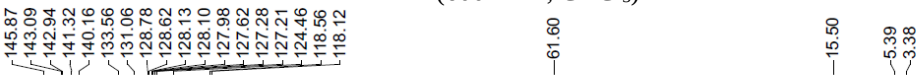
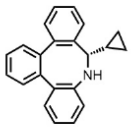


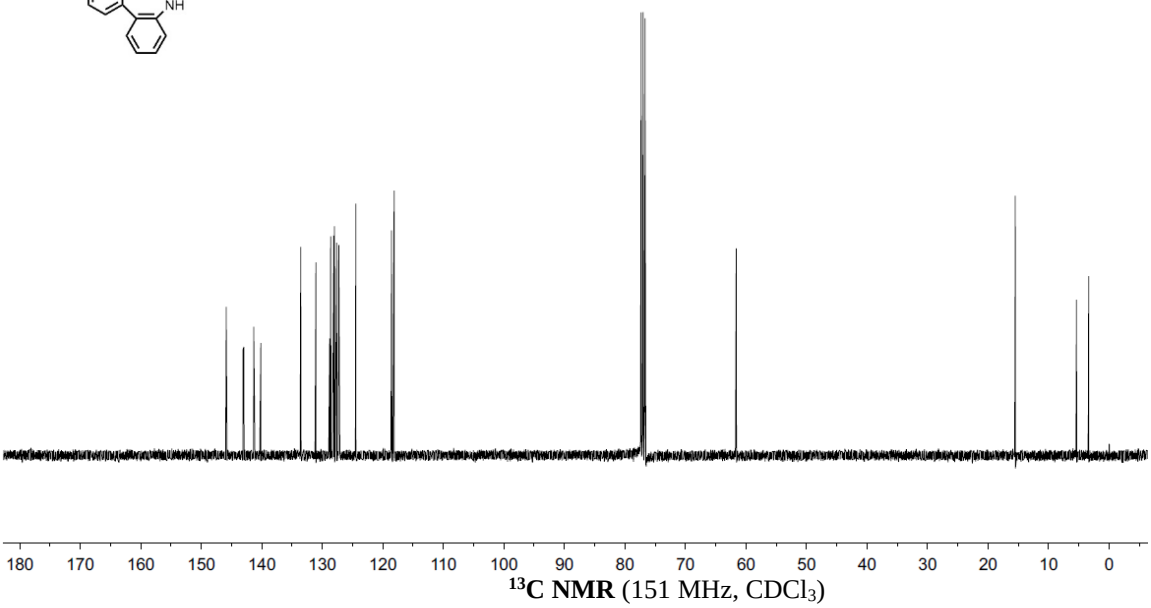




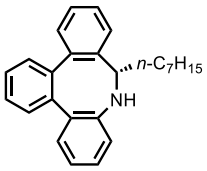
^{1}H NMR (600 MHz, $CDCl_3$)







^{13}C NMR (151 MHz, $CDCl_3$)



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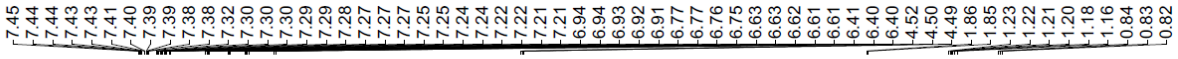
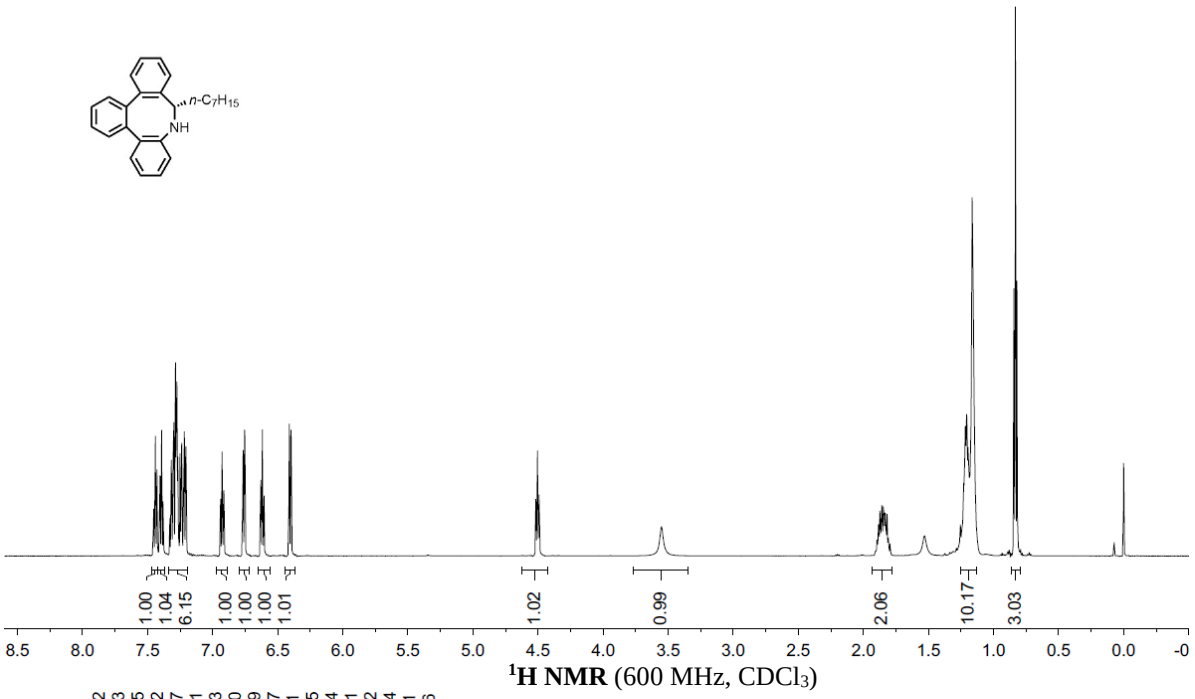
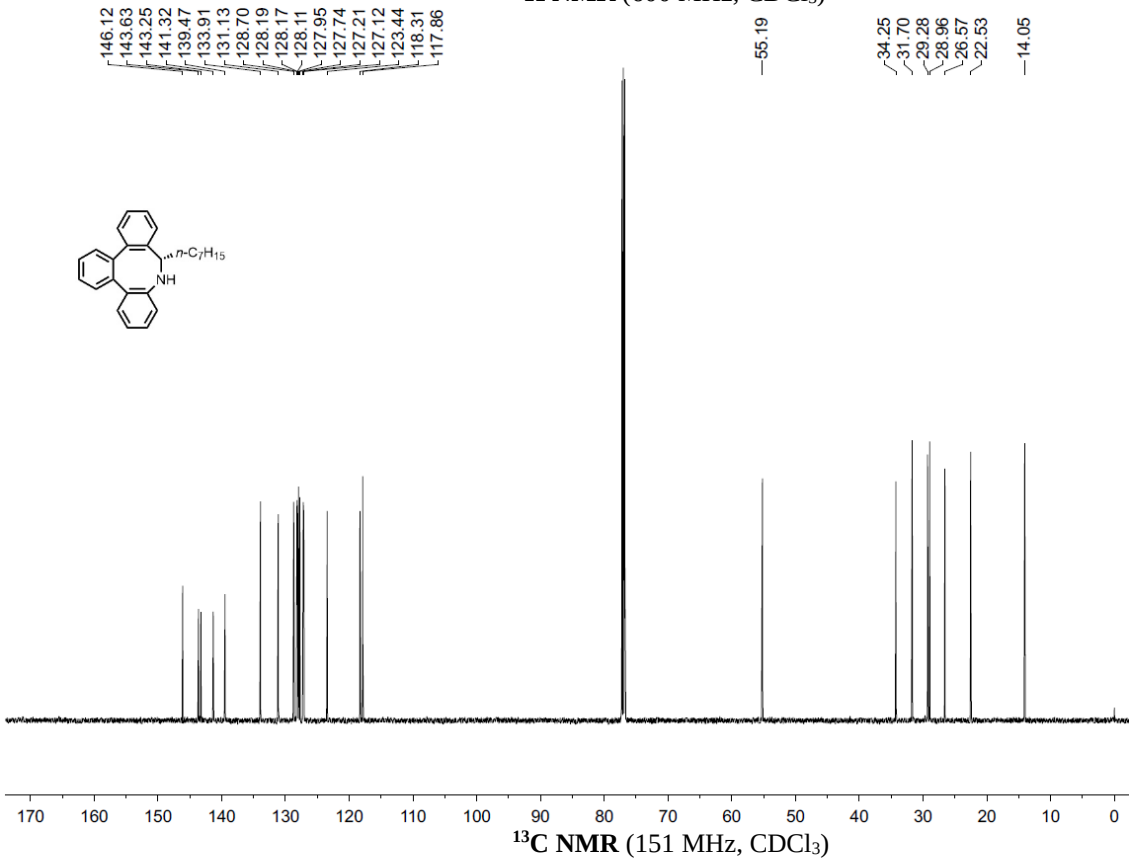
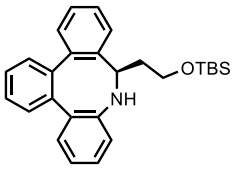




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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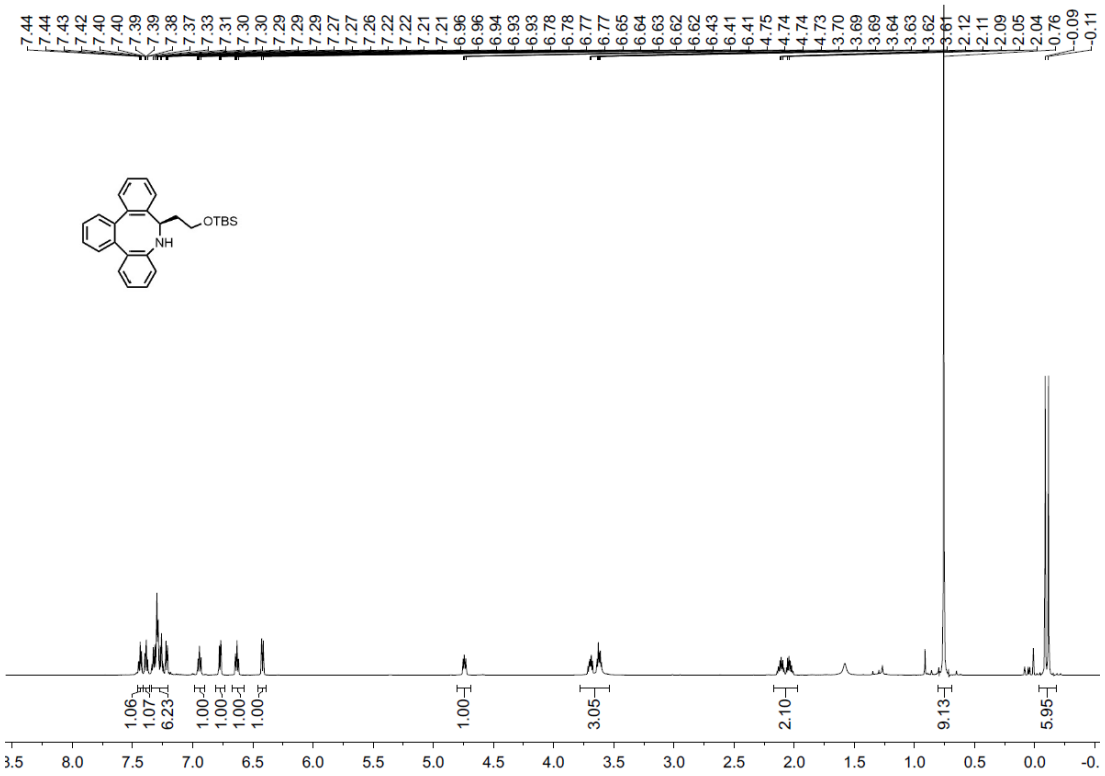
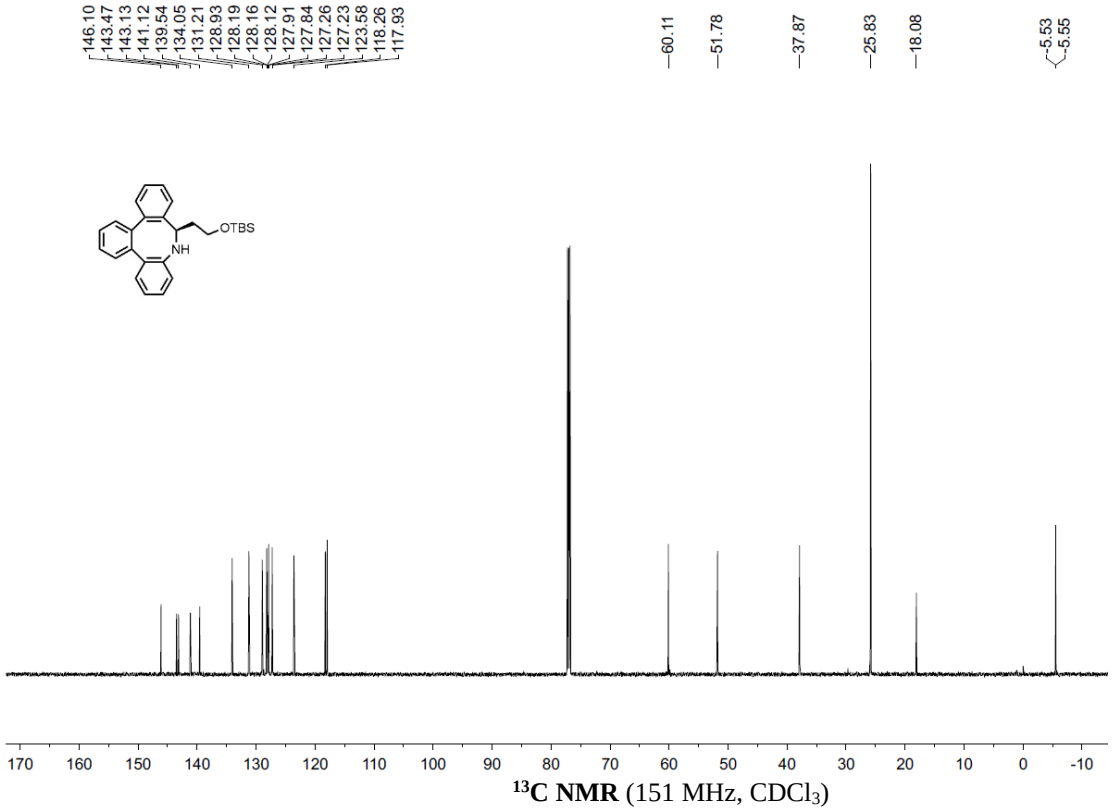
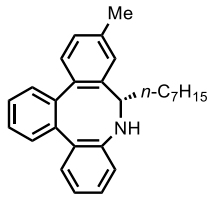


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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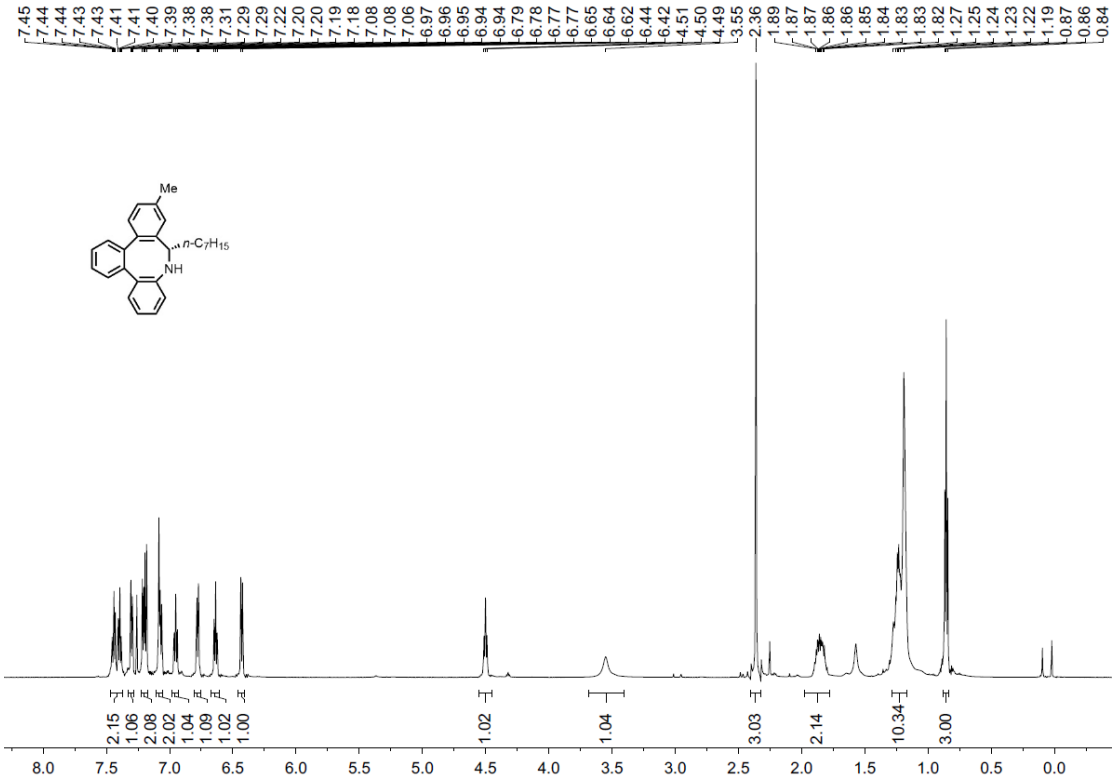
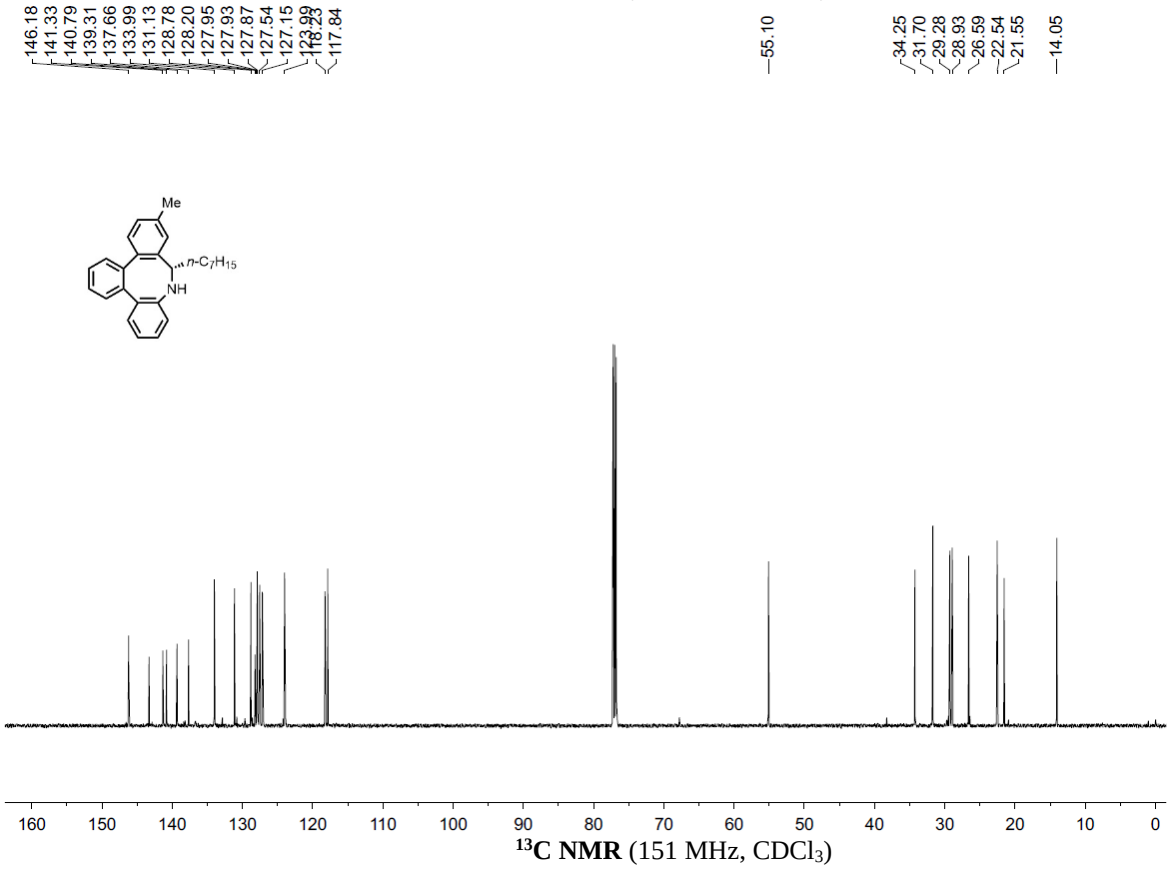
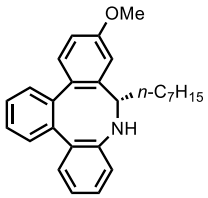


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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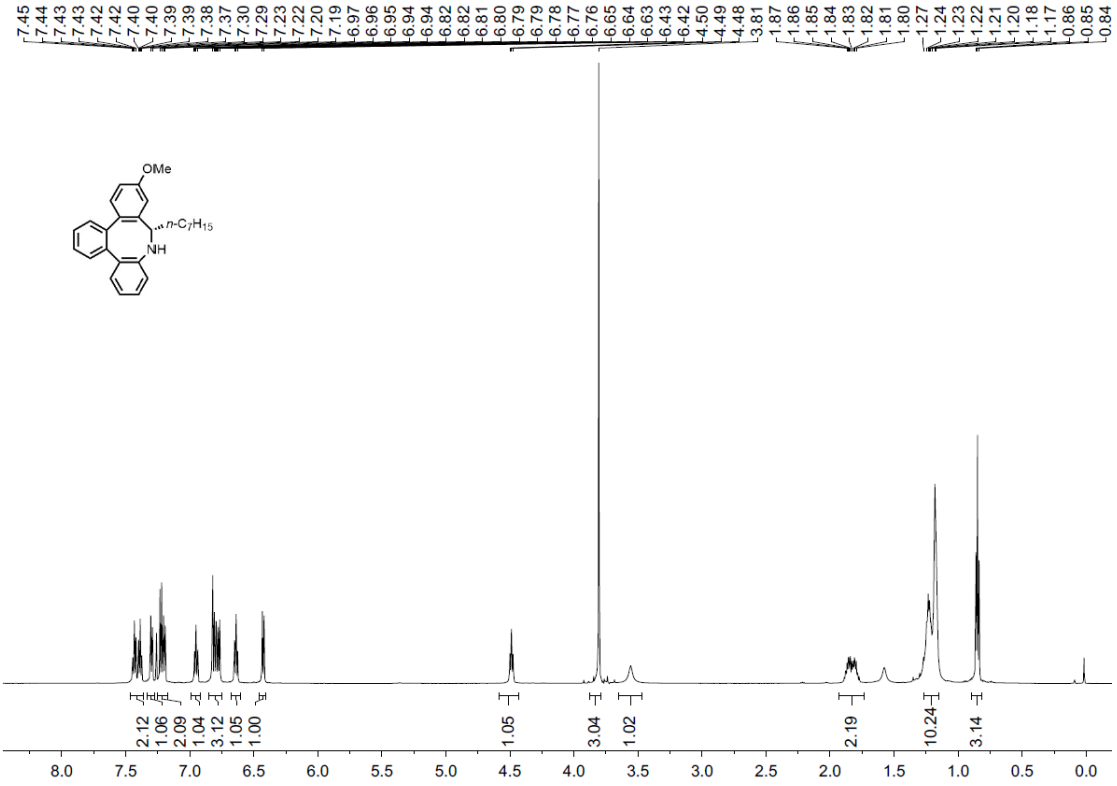
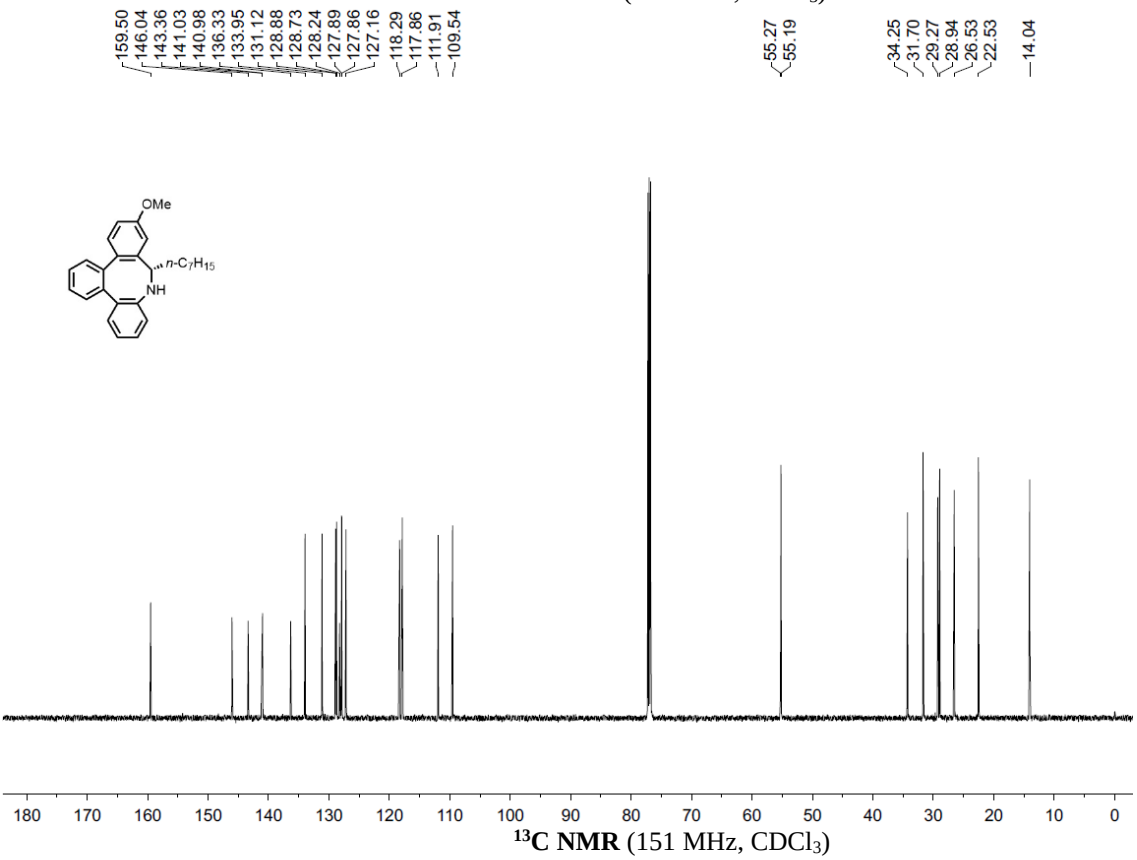
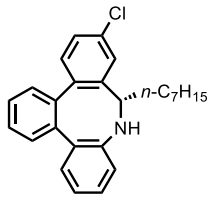


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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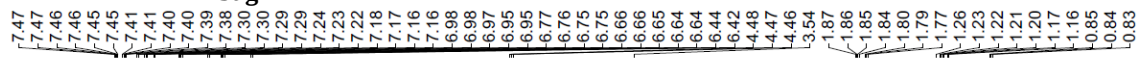
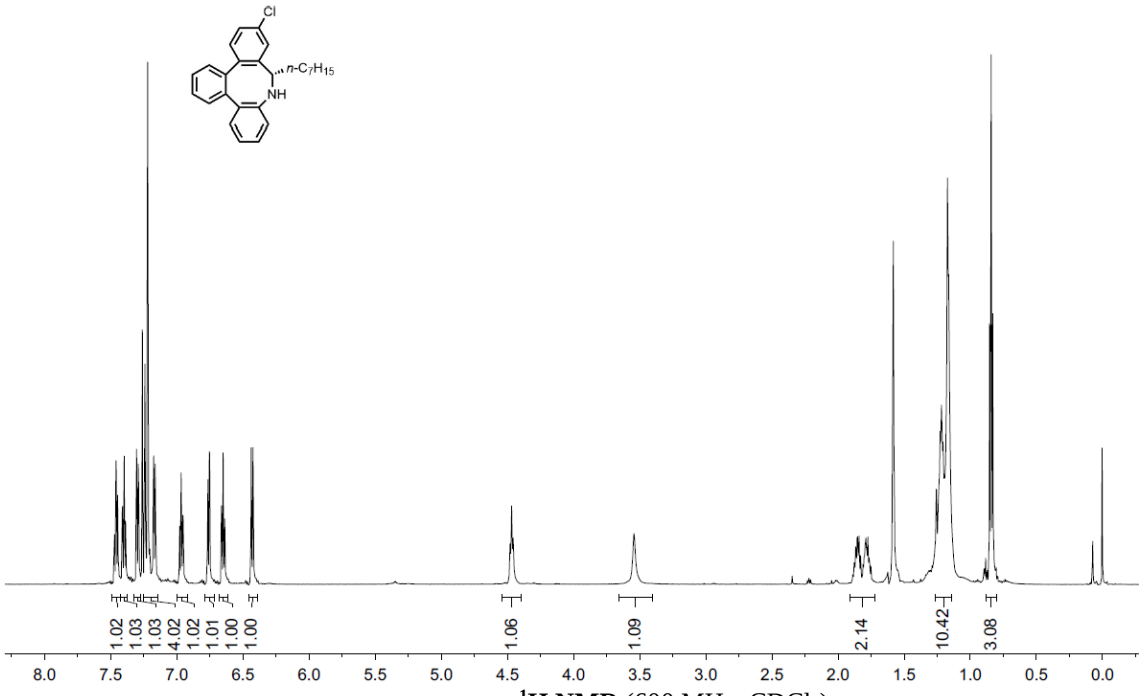
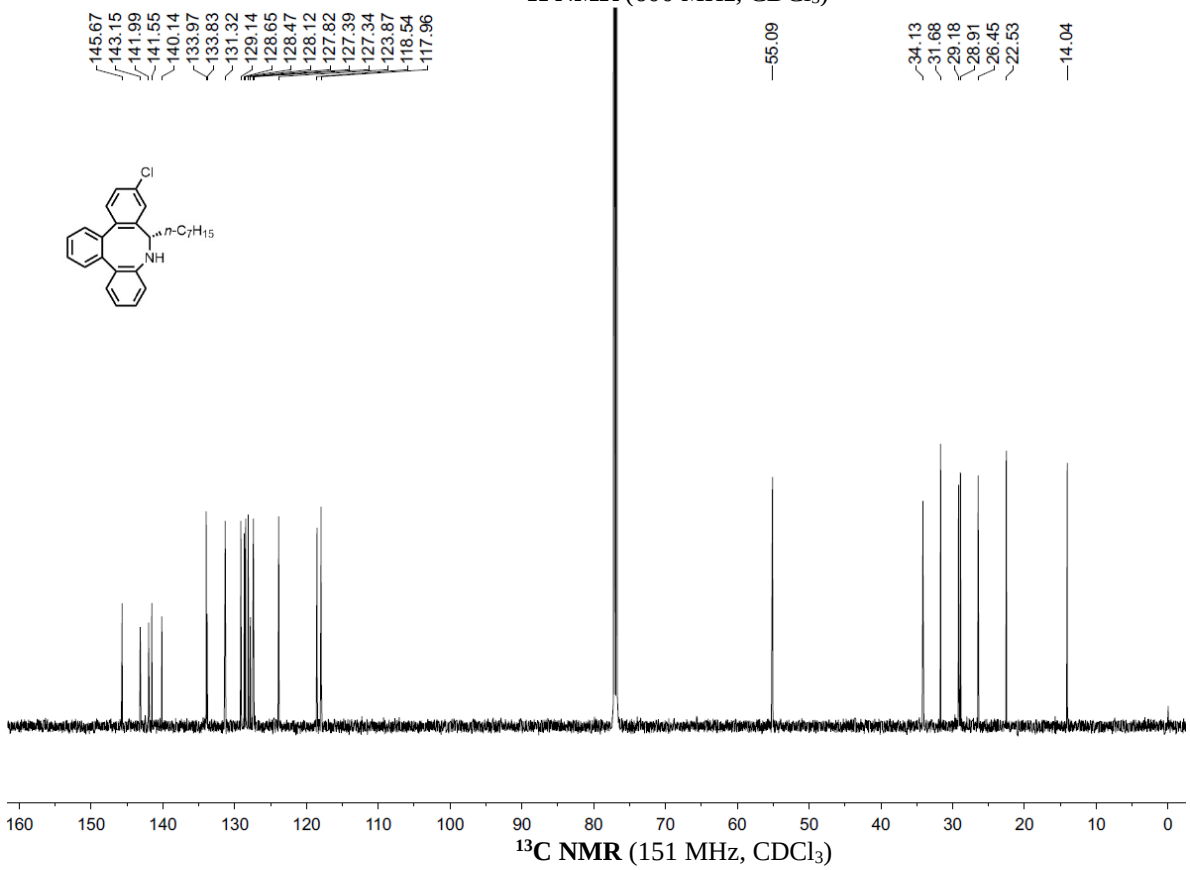
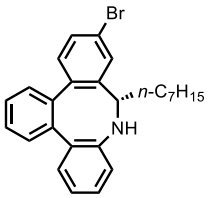




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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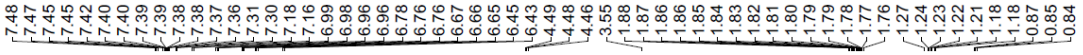
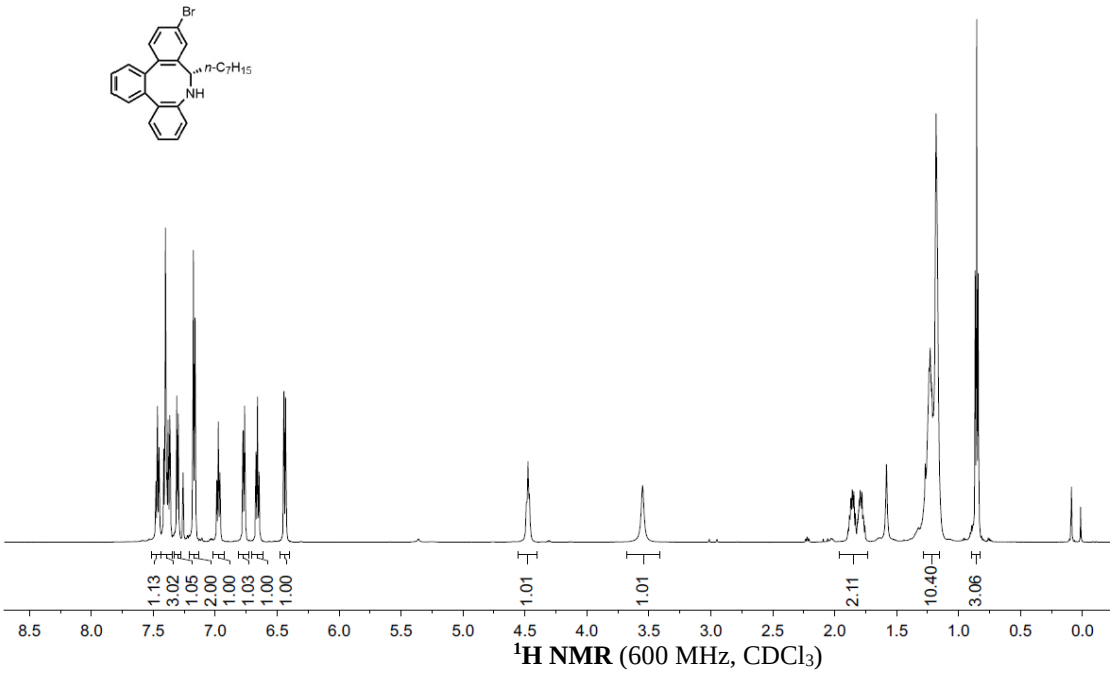
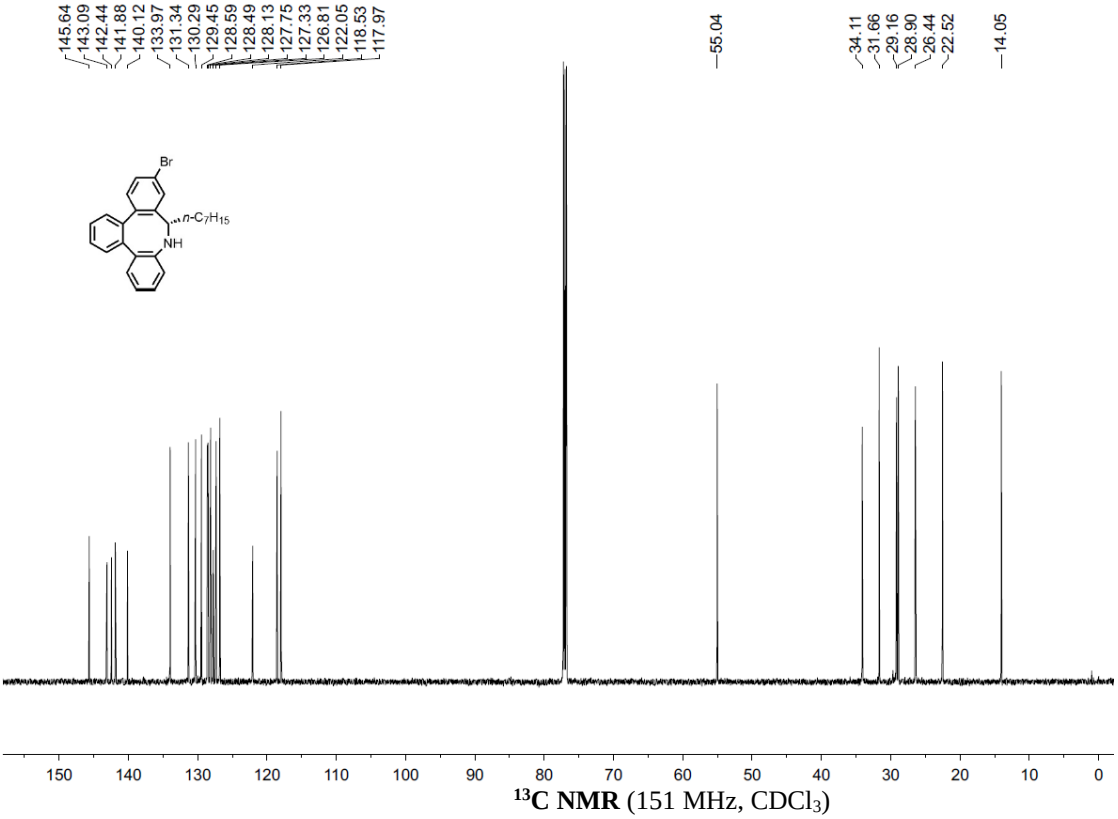




^{1}H NMR (600 MHz, $CDCl_3$)



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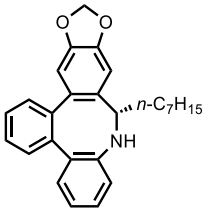

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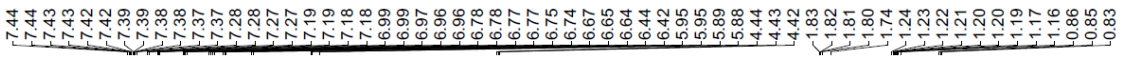
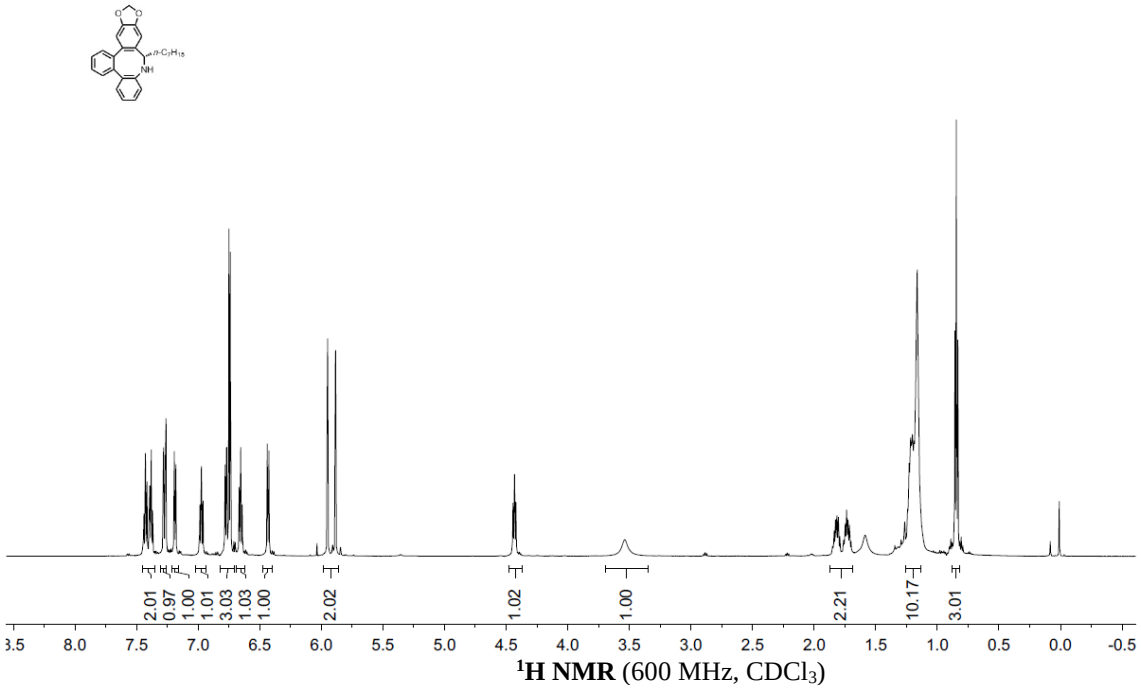
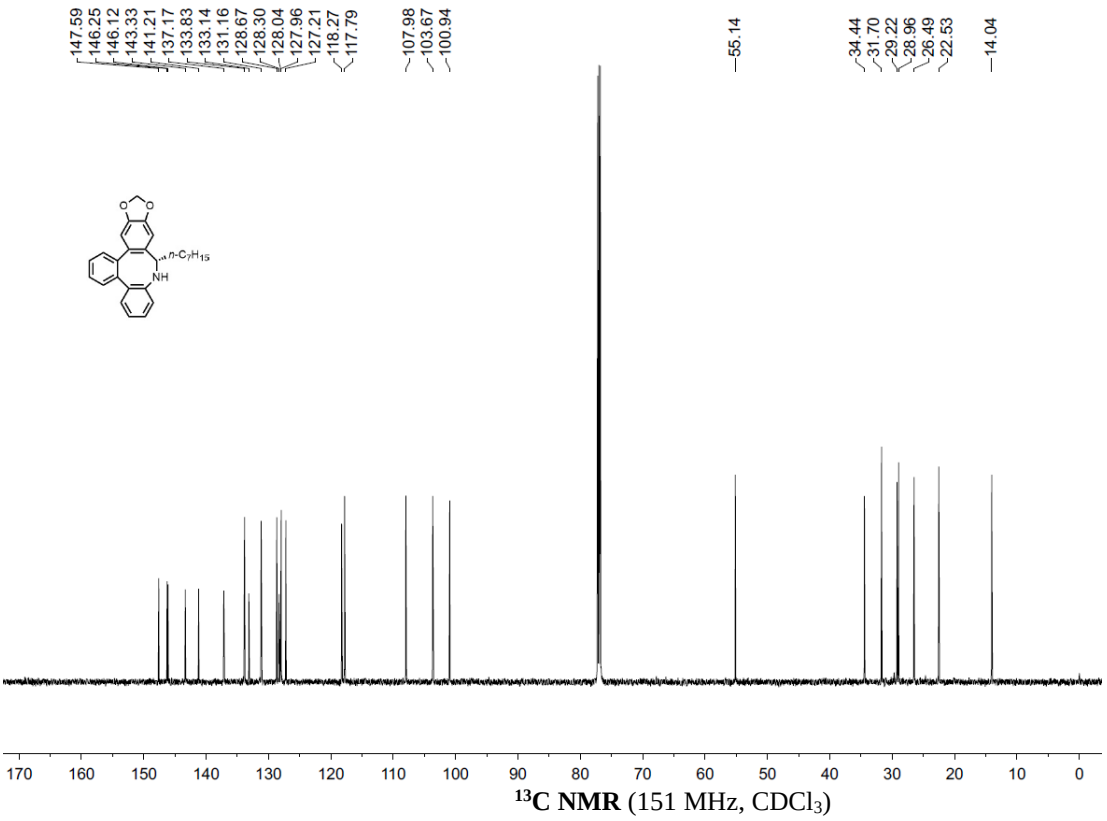
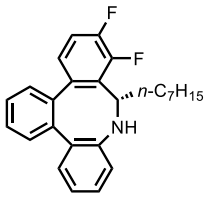




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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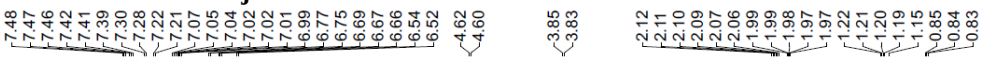
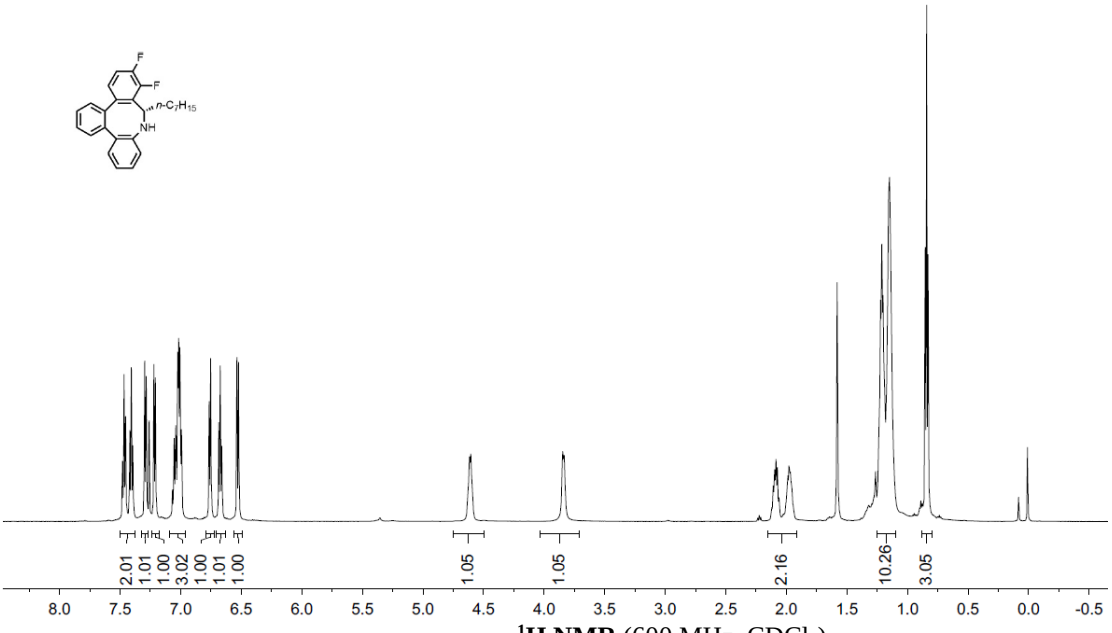
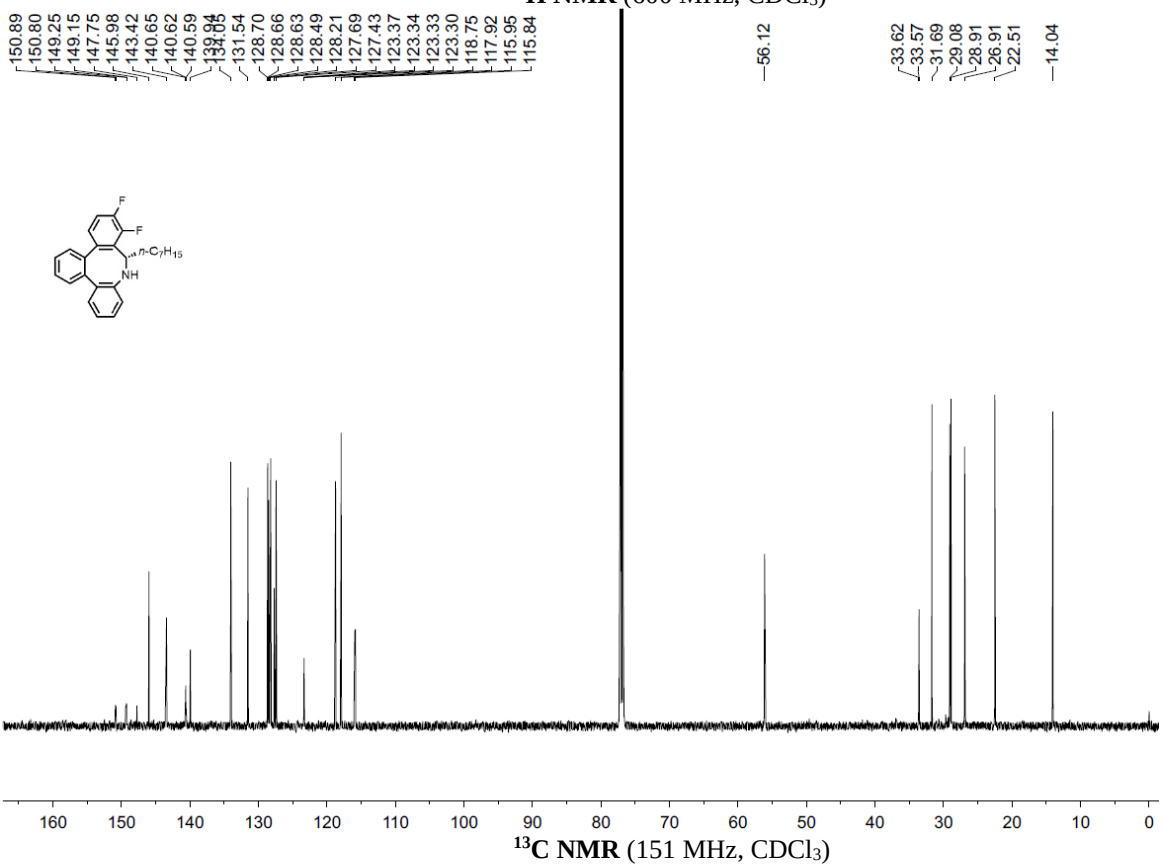
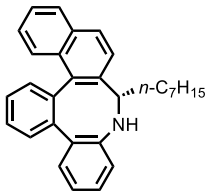




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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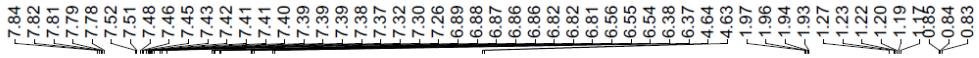
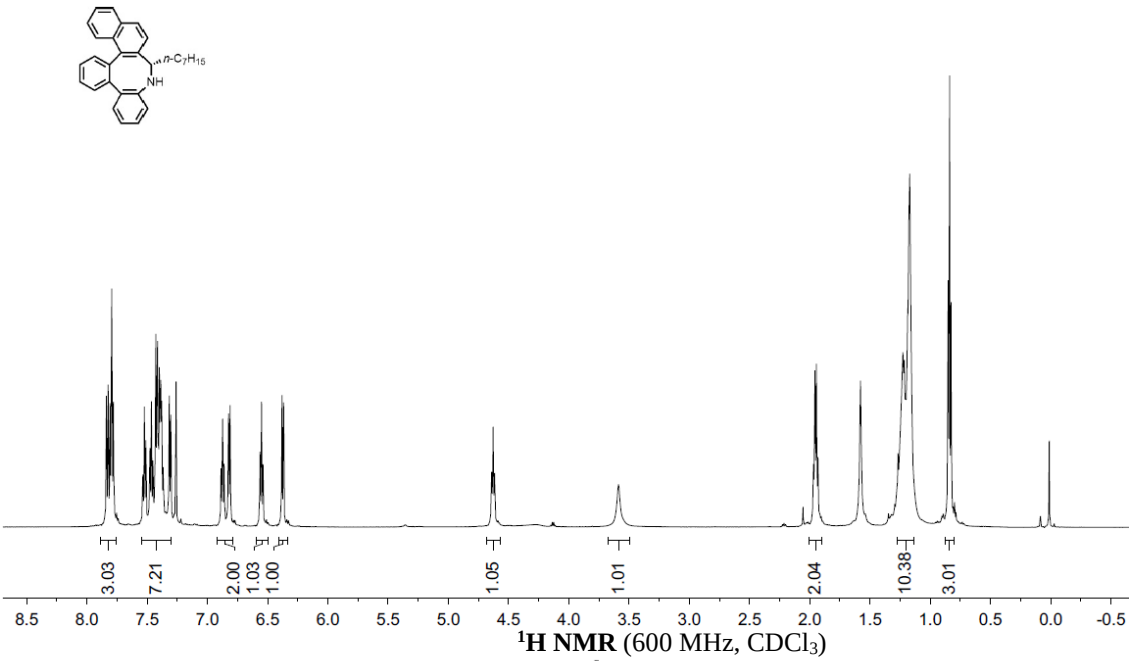
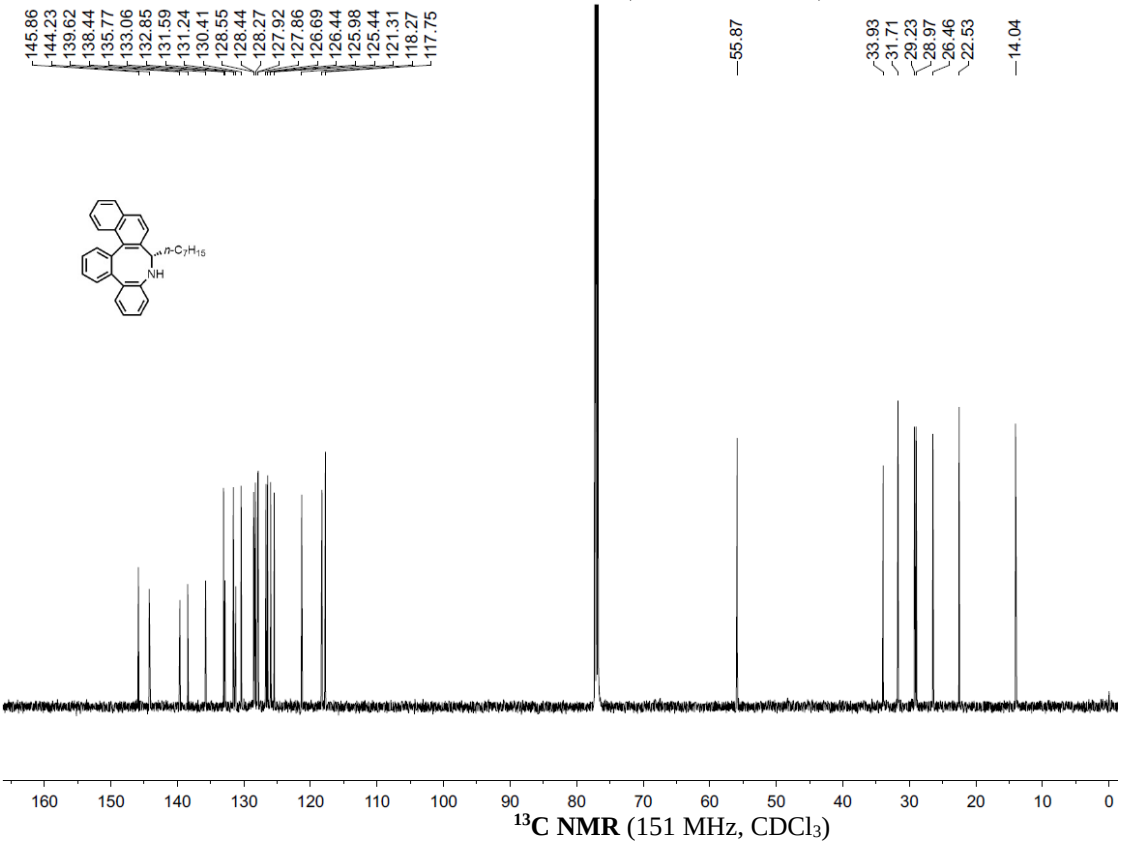
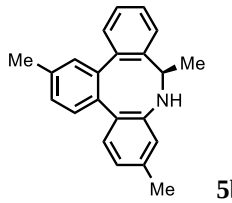




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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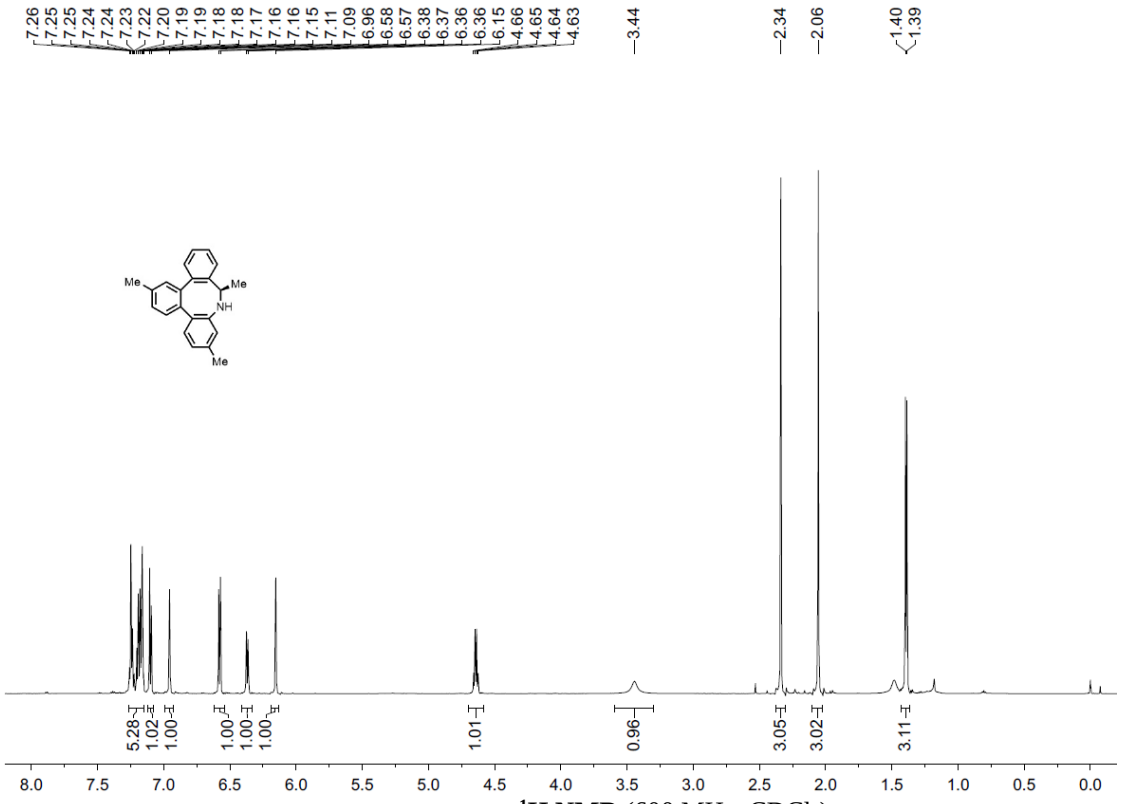
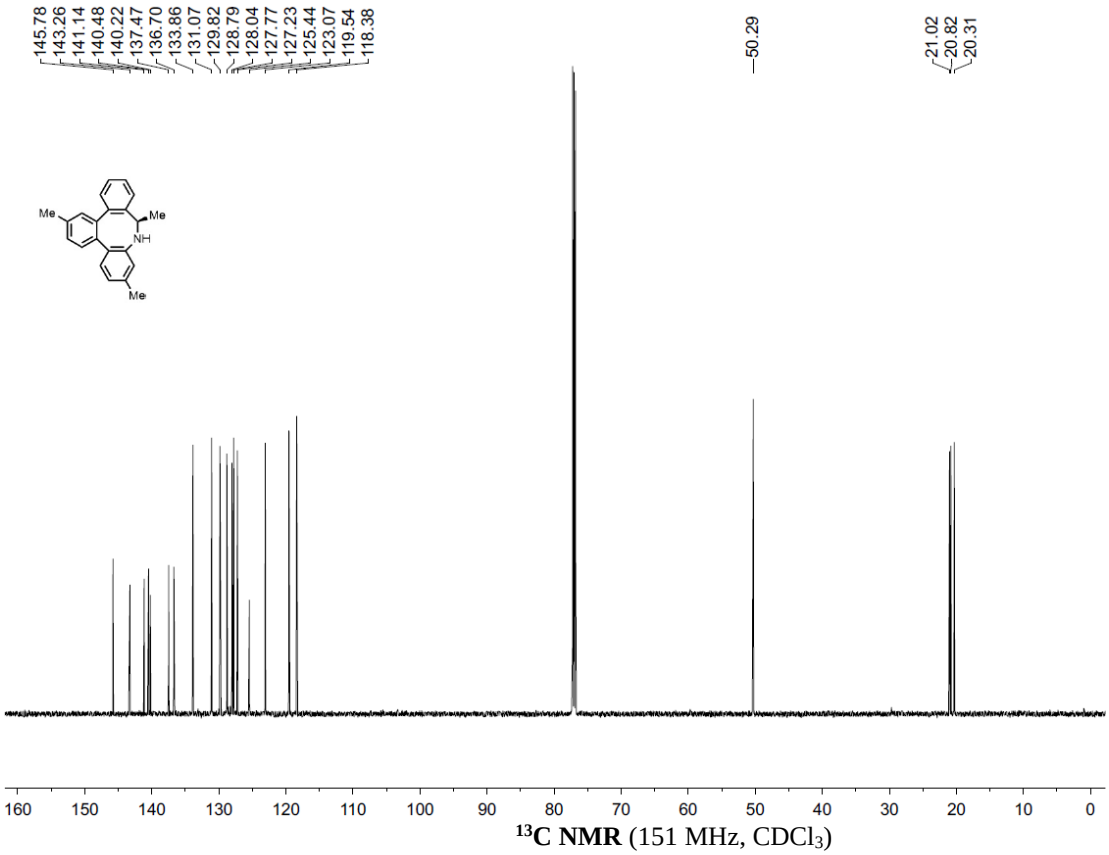
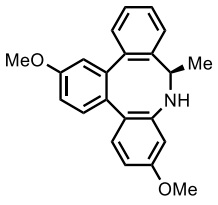


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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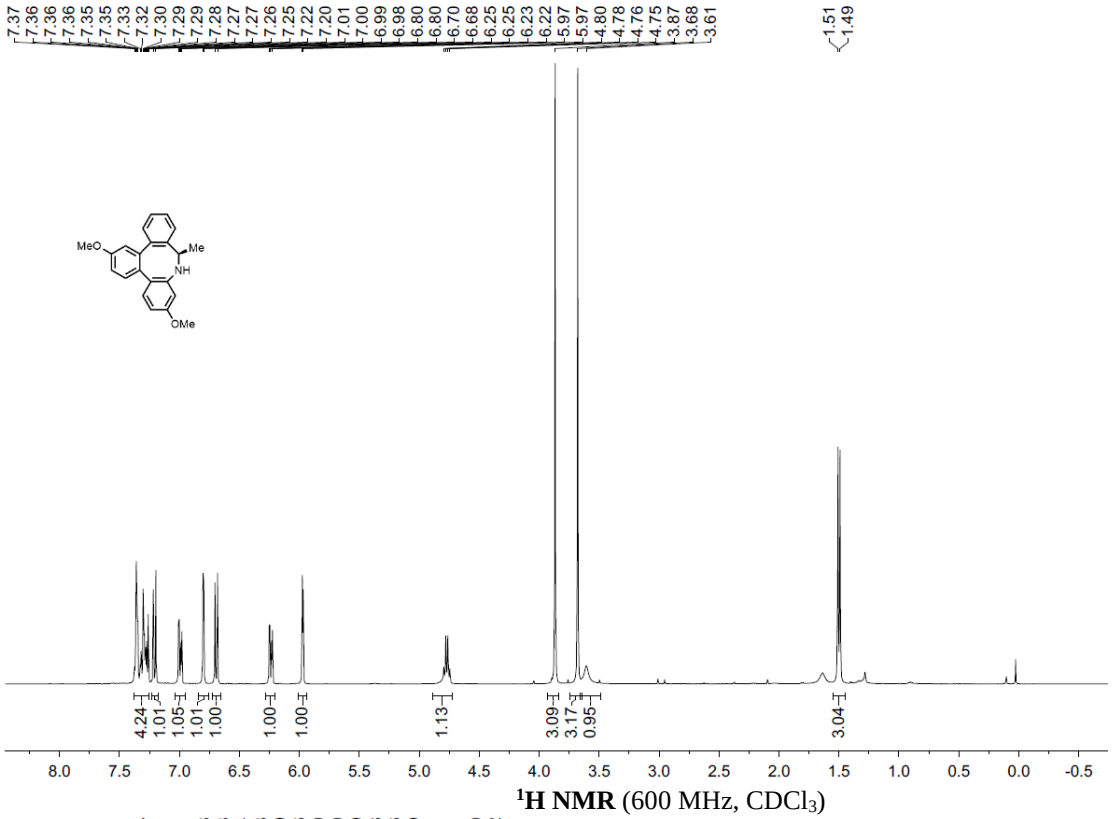
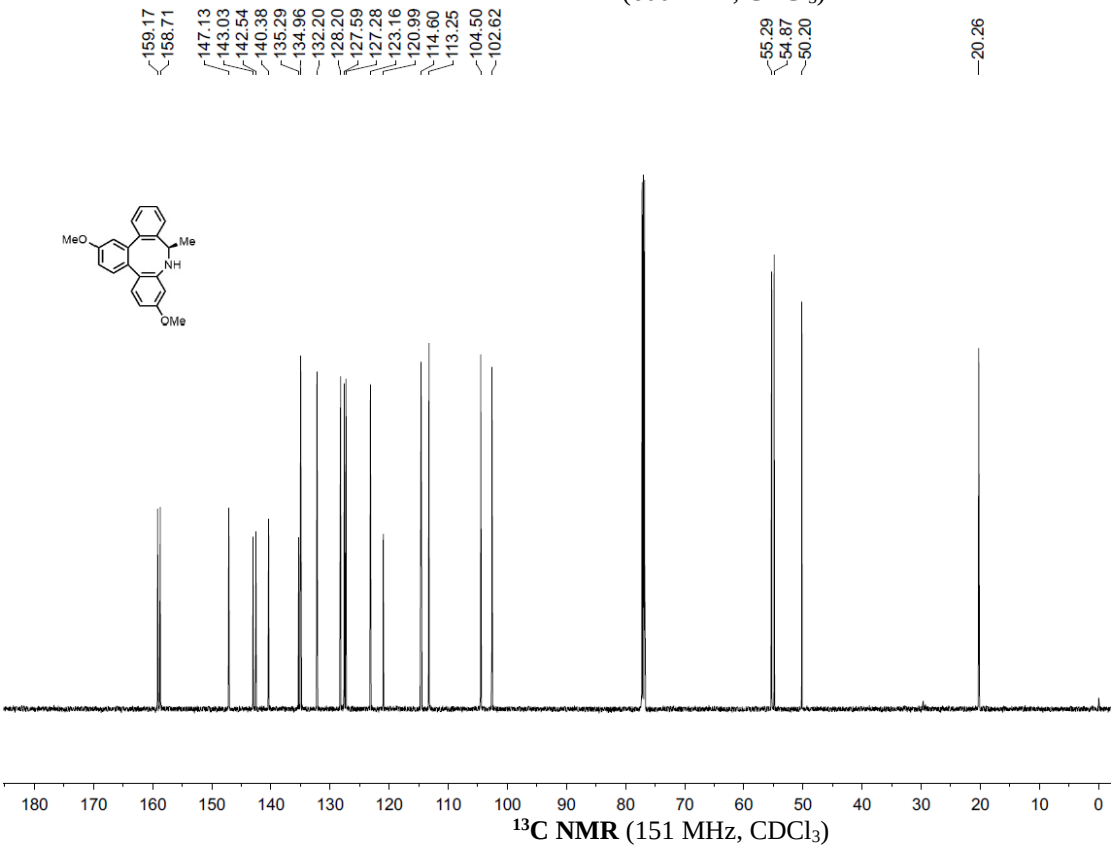
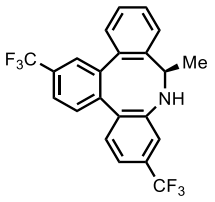


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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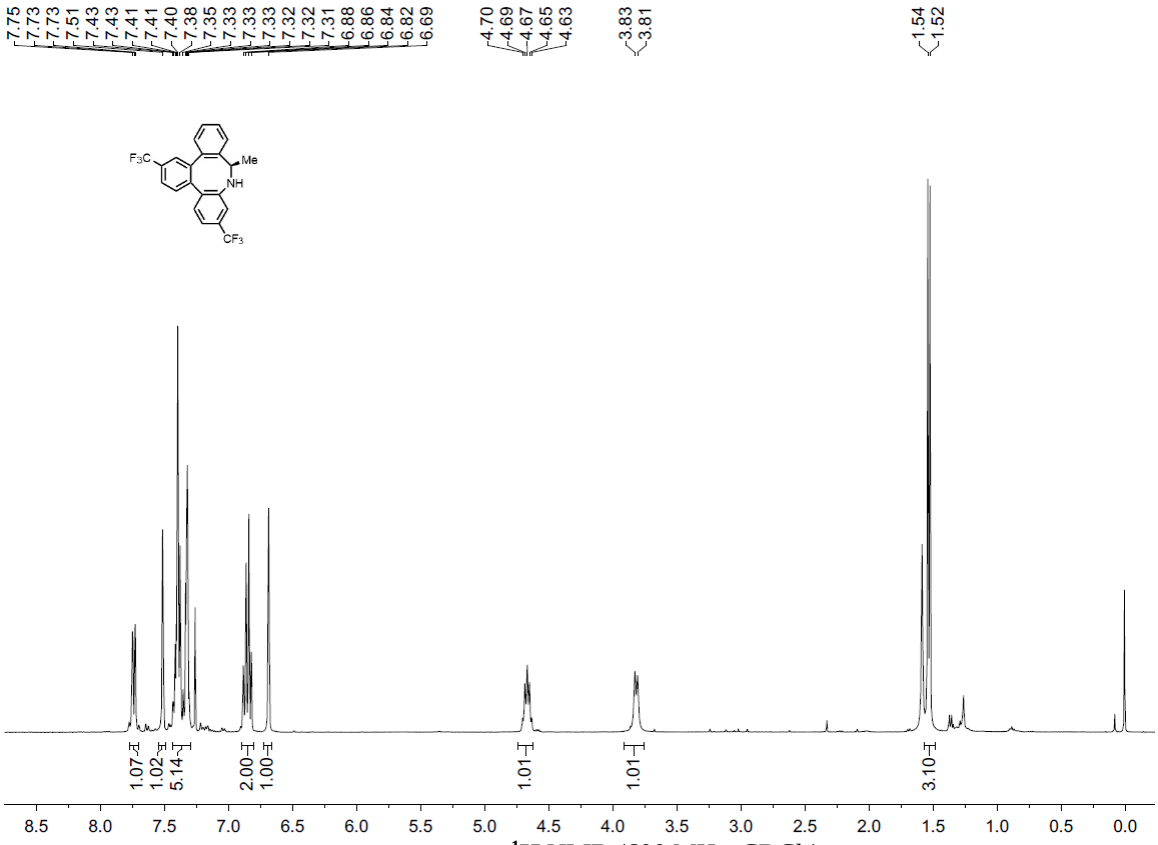
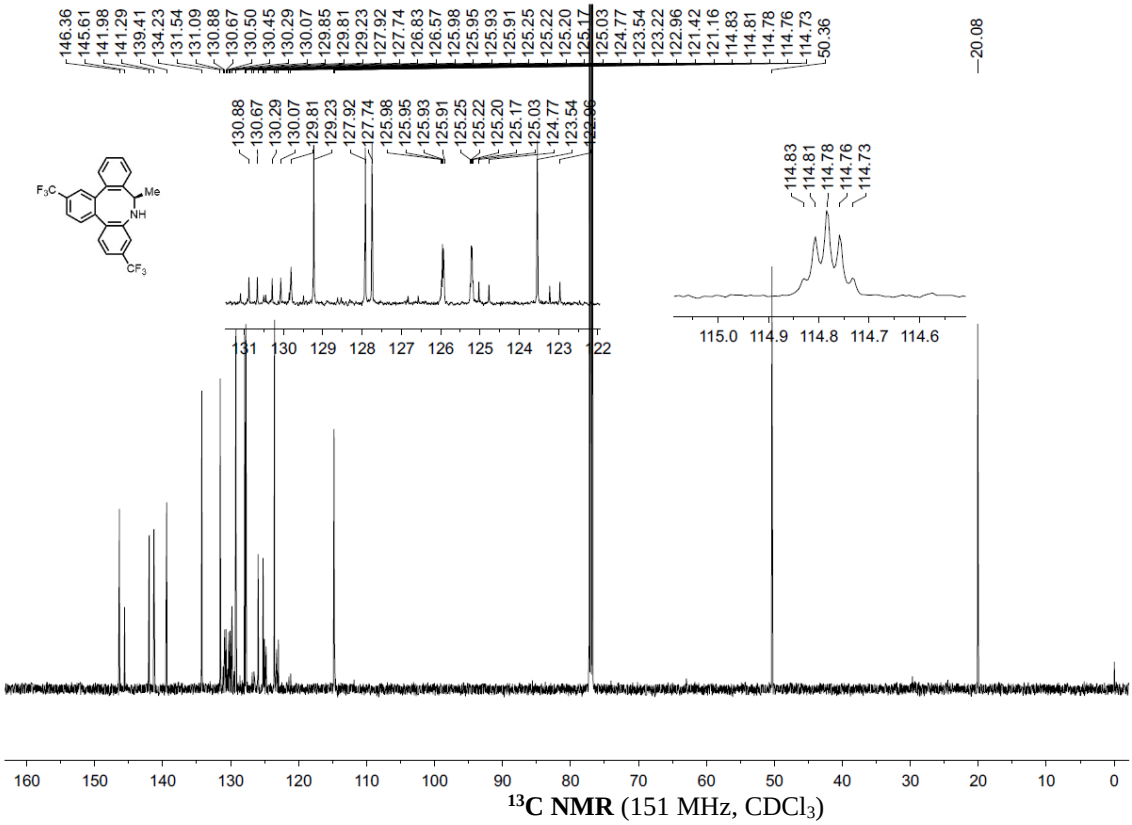
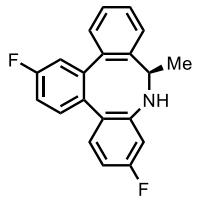


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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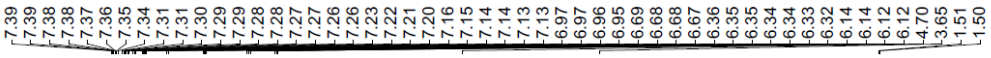
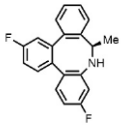
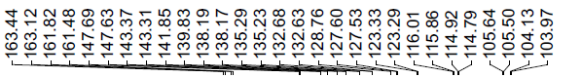
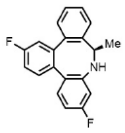


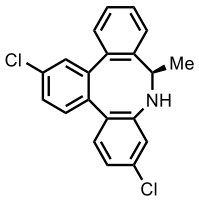


^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)



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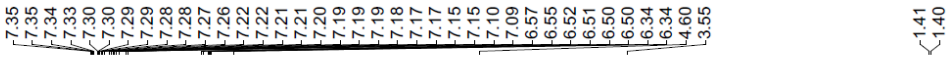
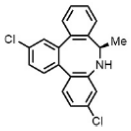
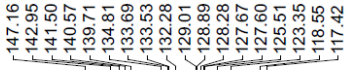
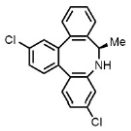
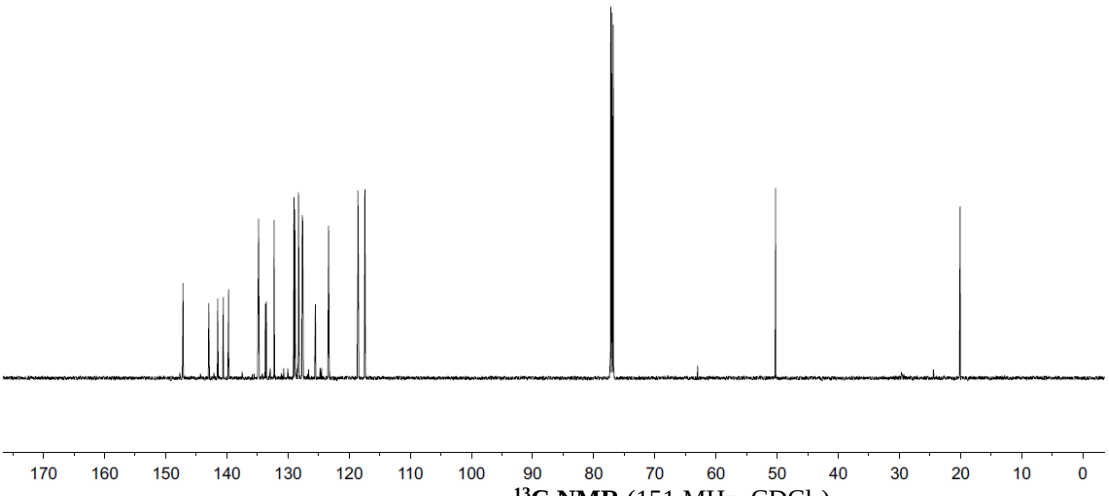




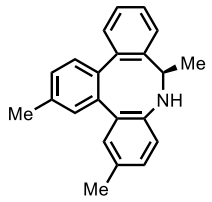
^{1}H NMR (600 MHz, $CDCl_3$)







^{13}C NMR (151 MHz, $CDCl_3$)



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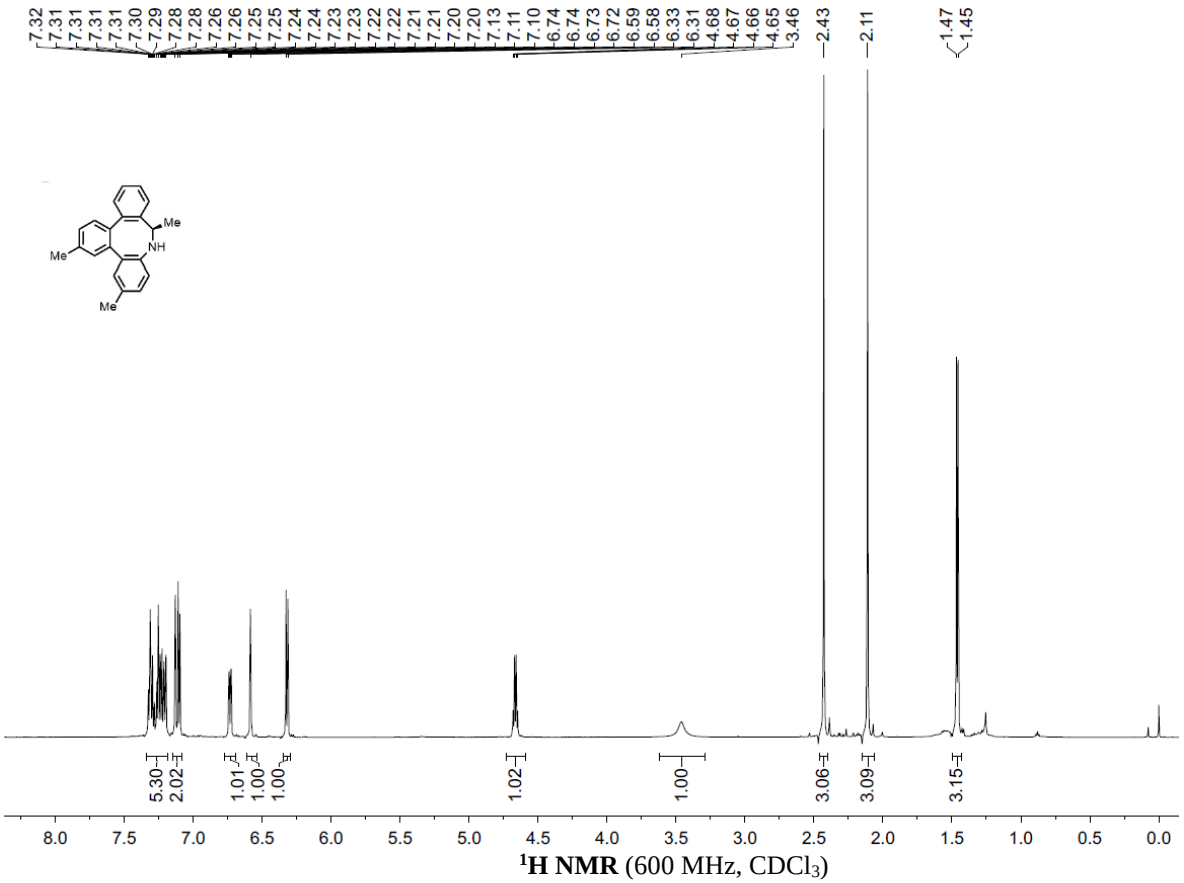
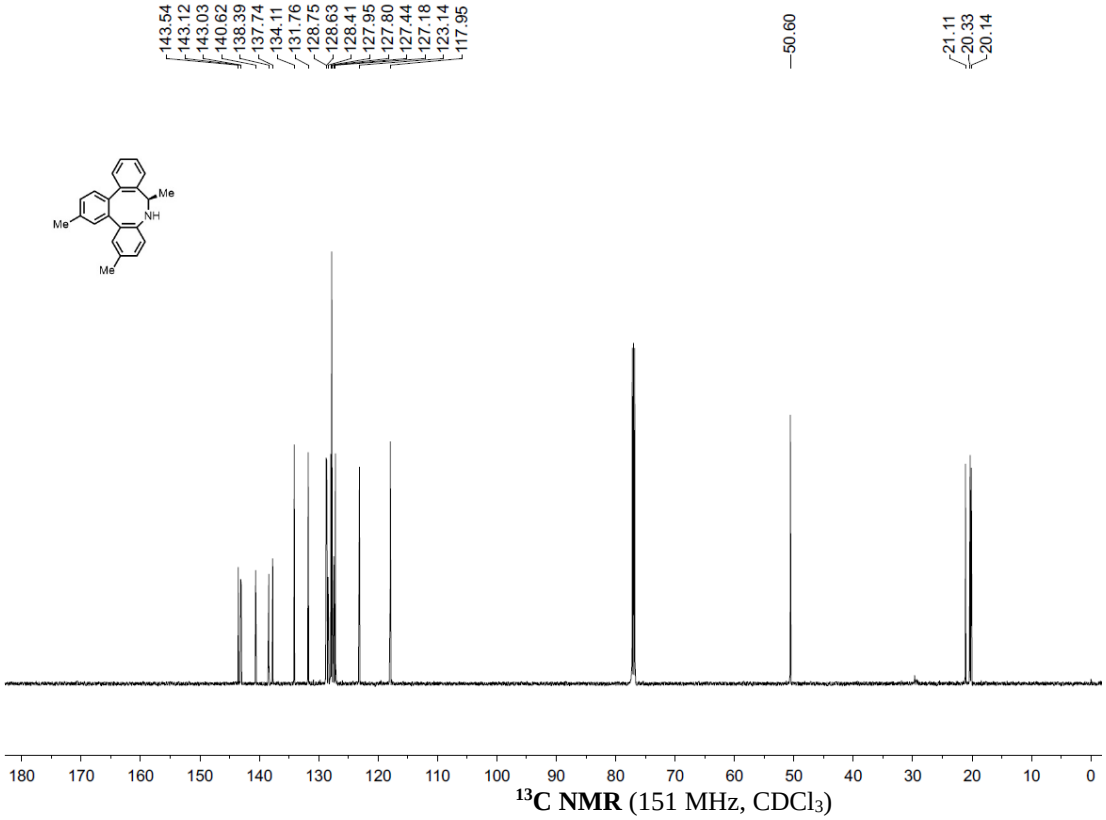
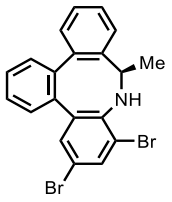


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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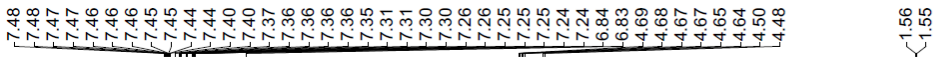
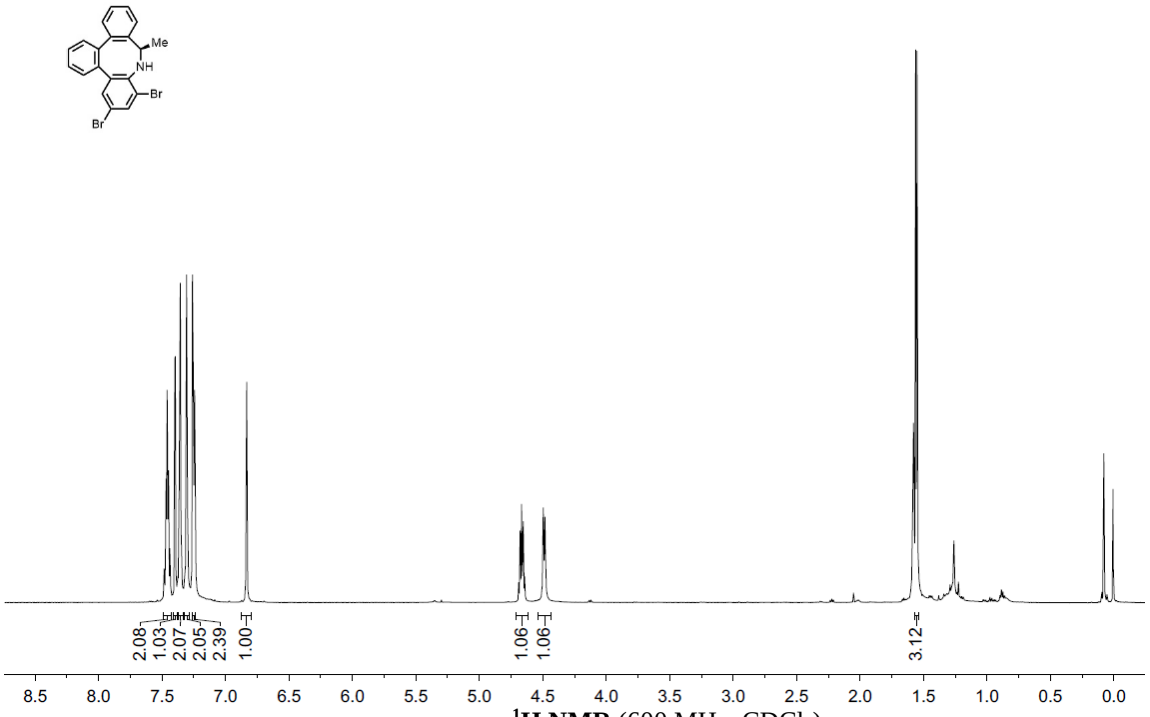
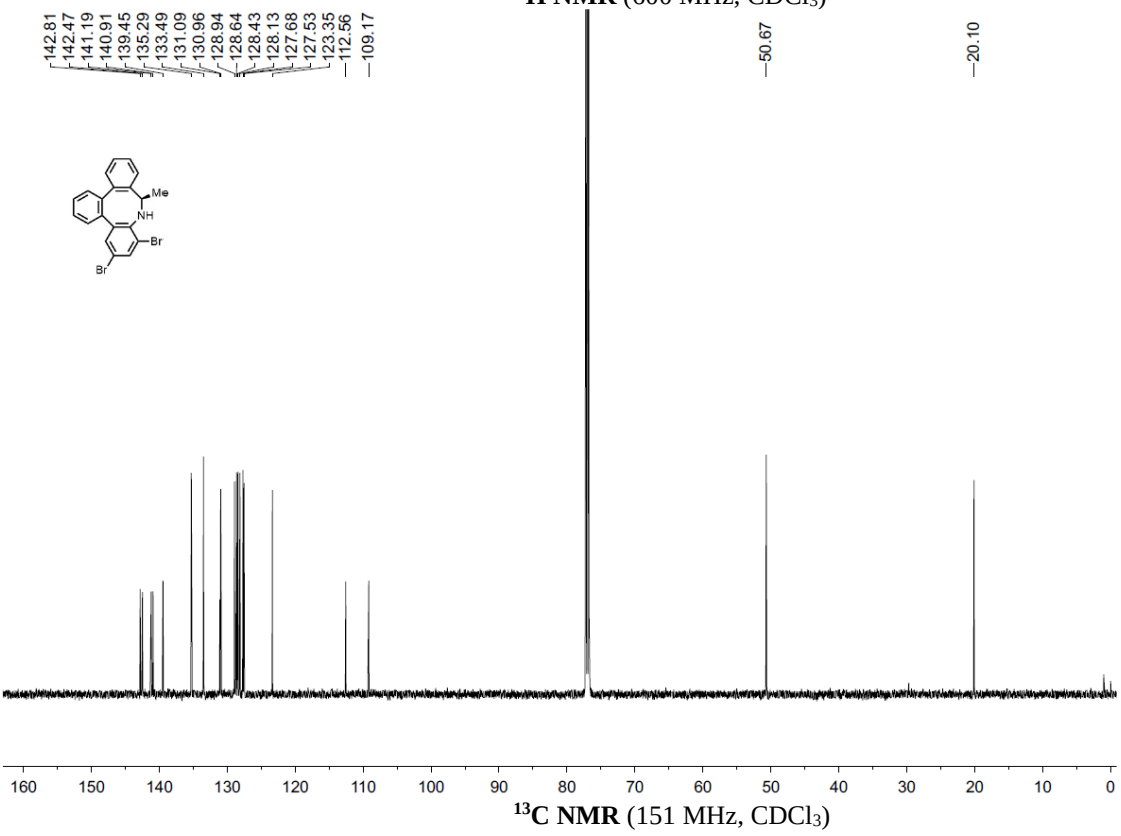
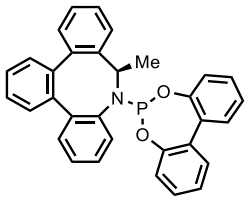




^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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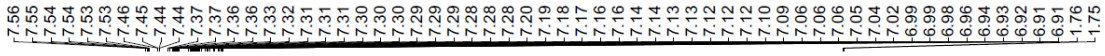
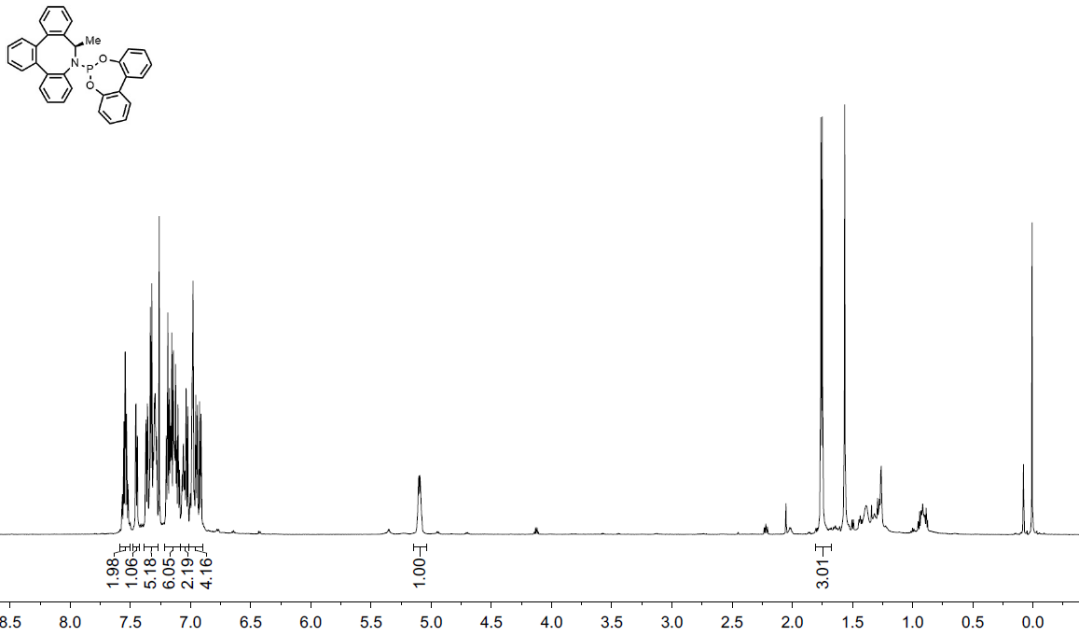
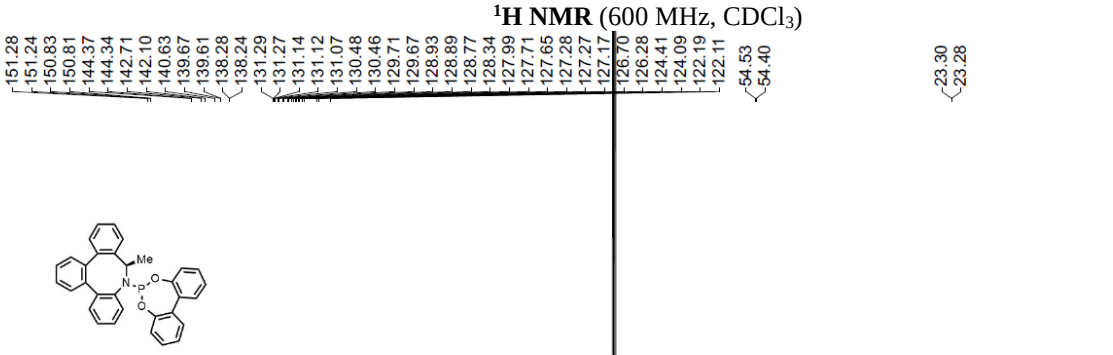
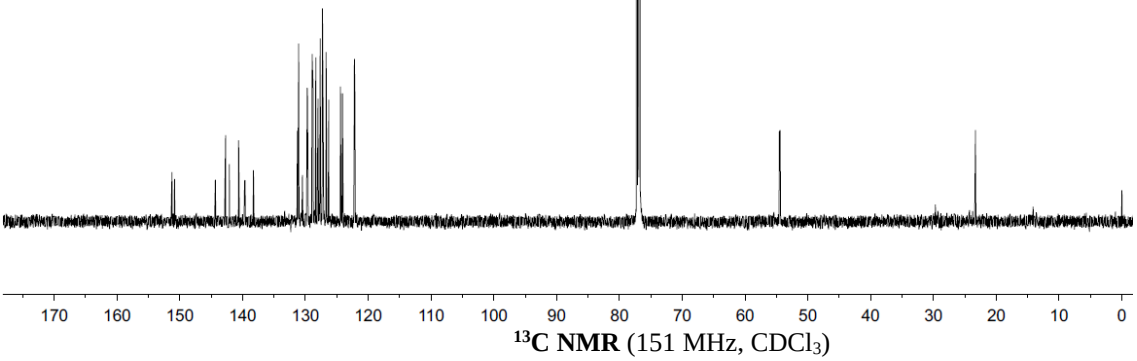


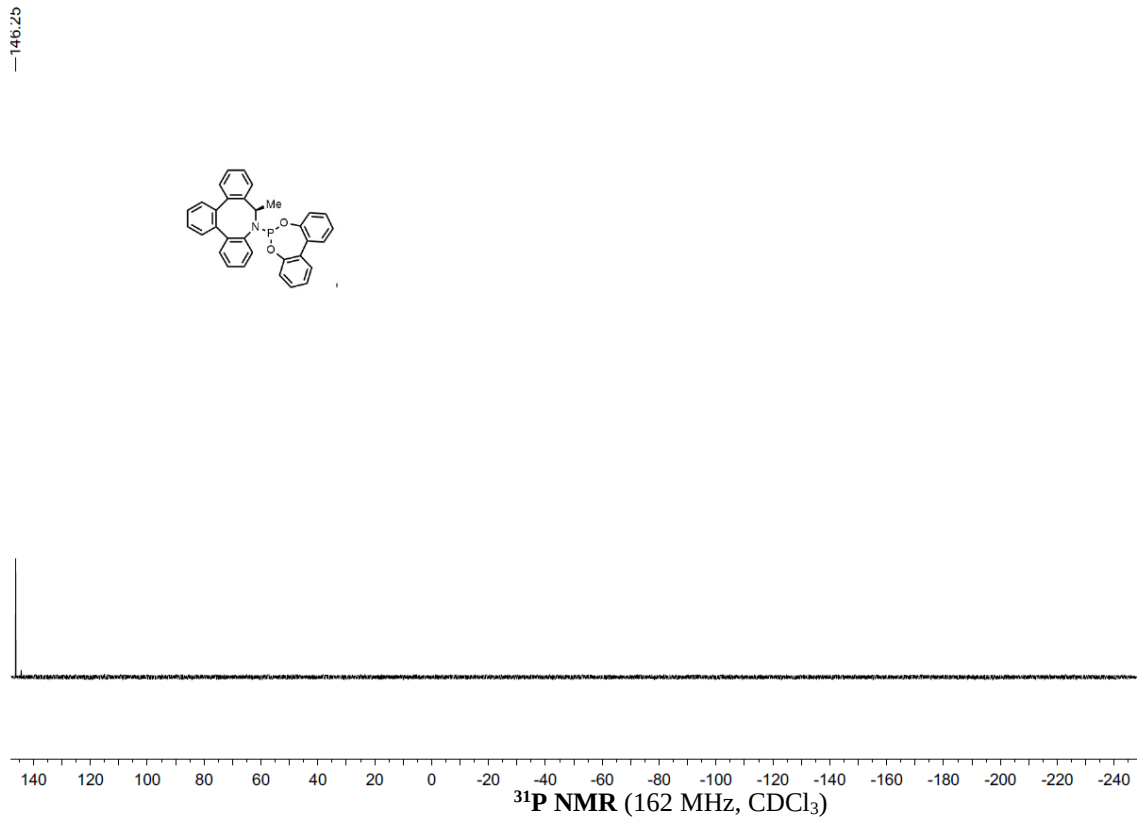


^{1}H NMR (600 MHz, $CDCl_3$)

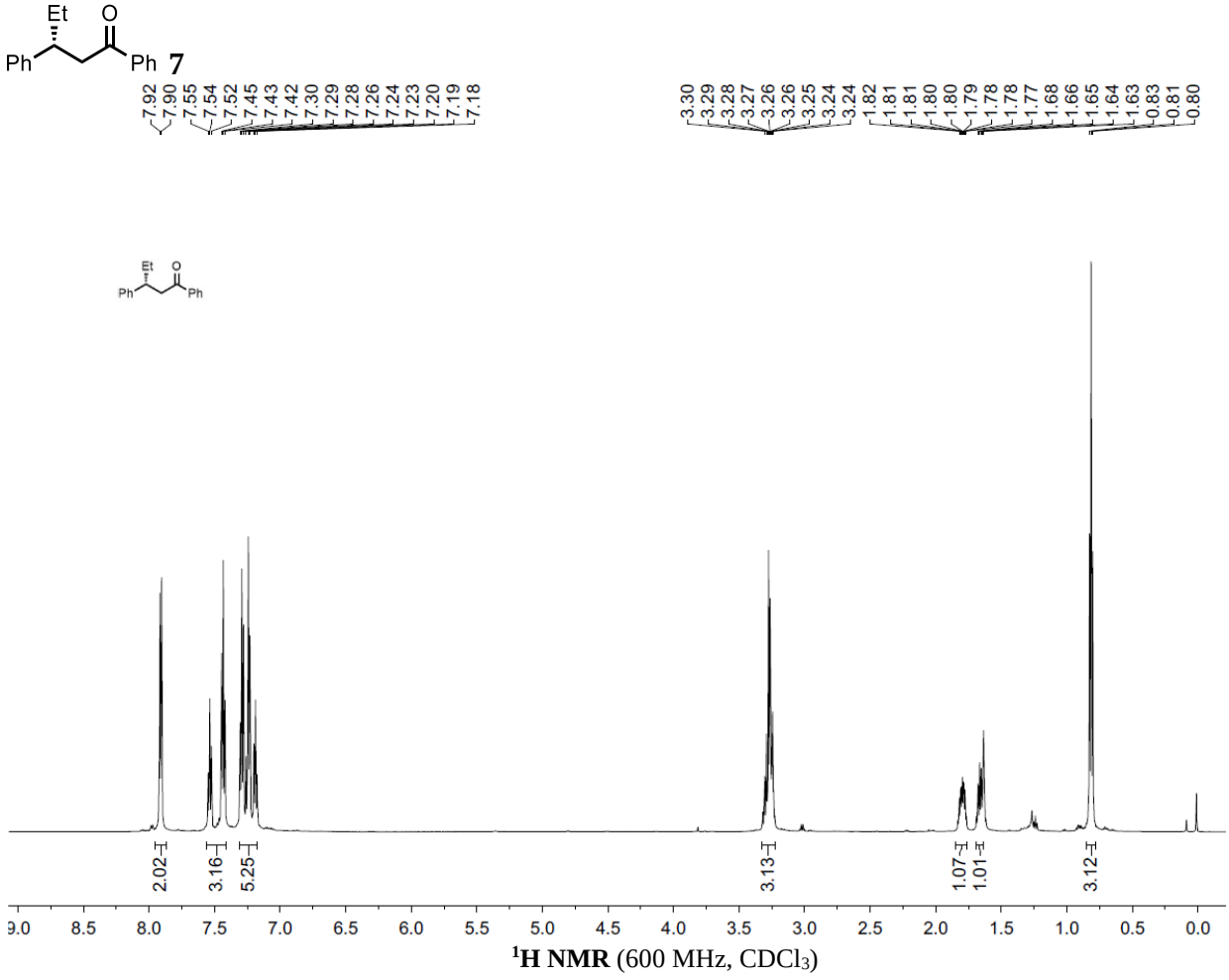




^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



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