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Synthesis of enantiomerically pure Tröger's base derivatives via chiral disulfoxides

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General

Flash chromatography was performed with Fluka silica gel (pore size 60 Å, 230-400 mesh particle size). NMR spectra were measured on Bruker Avance III HD Nanobay-300 and III HD Nanobay-400 spectrometers. The chemical shifts are given in ppm and are referenced to tetramethylsilane (^{1}H and ^{13}C). The ^{2}H lock frequency of $CDCl_3$ was used as the internal secondary reference in all cases. High-resolution mass spectra were measured by the MS-Service of the "Laboratorium für Organische Chemie der ETH" on a Bruker Daltonics maXis ESI-QTOF. Optical rotation was measured on a MCP 200 Polarimeter from Anton Paar. X-ray structures of (*S*$_S$,*S*$_S$,5*S*,11*S*)-**3**, (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** and (5*R*,11*R*)-**1** were measured on a Bruker APEX2 platform with a CCD area detector applying Mo-K_α radiation. Single crystal was coated at room temperature with perfluoroalkylether oil and mounted on a polymer pin. The structures were solved by direct methods in SHELXTL and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). CCDC 987100 ((*S*$_S$,*S*$_S$,5*S*,11*S*)-**3**), CCDC 987101 ((*S*$_S$,*S*$_S$,5*R*,11*R*)-**3**) and CCDC 987102 ((5*R*,11*R*)-**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and isolation of the disulfoxides

4,10-Dibromo-Tröger's base (*rac*-**1**) (3.2 g, 7.84 mmol) was placed into a Schlenk flask (250 mL) under argon and THF (140 mL) was added. The clear solution was cooled to -78 °C and *n*-BuLi (1.6 M in hexanes, 10.3 mL, 16.5 mmol, 2.1 equiv) was added dropwise to form a pale-yellow suspension. After 5 min, it was transferred via cannula to a solution of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate **2** (5.8 g, 19.6 mmol, 2.5 equiv) in THF (100 mL) at -78 °C. The resulting mixture was stirred overnight at ambient temperature. The color changed to orange-yellow. It was quenched with NH_4Cl (aq., 100 mL) and extracted with EtOAc (3 x 100 mL). Combined org. layers were dried over $MgSO_4$ and concentrated. The crude mixture was treated with THF (30 mL) and filtered to afford a white solid (disulfoxide (*S*$_S$,*S*$_S$,5*S*,11*S*)-**3**). The filtrate was concentrated and purified by column chromatography (SiO_2 (200 g)). A mixture of DCM:acetone = 9:1 was used at first to elute additional amount of the disulfoxide (*S*$_S$,*S*$_S$,5*S*,11*S*)-**3** (R_f = 0.79, DCM:acetone = 5:1). Subsequently, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** was eluted with DCM:acetone = 5:1 (R_f = 0.28, DCM:acetone = 5:1). Since the reaction mixture contains numerous by-products with similar R_f-values as the sulfoxides, several fractions were contaminated. However, all the fractions containing separated diastereomers (in case of (*S*$_S$,*S*$_S$,5*S*,11*S*)-**3** also the fraction obtained by washing with THF) were combined, evaporated and recrystallized by dissolving in hot DCM followed by the addition of cyclohexane. Disulfoxide (*S*$_S$,*S*$_S$,5*S*,11*S*)-**3** was isolated as a white solid (1.5 g, 37%). Disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** was obtained as a white solid (1.4 g, 33%).

(*S*$_S$,*S*$_S$,5*S*,11*S*)-2,8-Dimethyl-4,10-bis(*p*-tolylsulfinyl)-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine ((*S*$_S$,*S*$_S$,5*S*,11*S*)-3):

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.28 (s, 6H, C*H*$_3$), 2.35 (s, 6H, C*H*$_3$), 3.97 (s, 2H, NC*H*$_2$N), 4.48 (d, ^{2}J = 17.2 Hz, 2H, ArC*H*^{endo}N), 4.54 (d, ^{2}J = 17.2 Hz, 2H, ArC*H*^{exo}N), 6.82 (s, 2H, Ar*H*), 7.20 (d, ^{2}J = 8.0 Hz, 4H, Ar*H*), 7.58 (s, 2H, Ar*H*), 7.64 (d, ^{2}J = 8.0 Hz, 4H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 21.2 (*C*H$_3$), 21.5 (*C*H$_3$), 56.5 (*C*H$_2$N), 66.1 (NCH$_2$N), 123.1, 125.0, 128.6, 129.7, 130.2, 136.0, 140.1, 141.2, 141.9, 142.9; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{31}H_{31}N_2O_2S_2$: 527.1821, found: 527.1821; $[\alpha]_D^{20}$ -445.4 (*c* 0.41, $CHCl_3$); m.p. 316 – 317 °C; HPLC (IA, Hex:*i*PrOH = 30:70, 1 ml/min): 17.3 min.

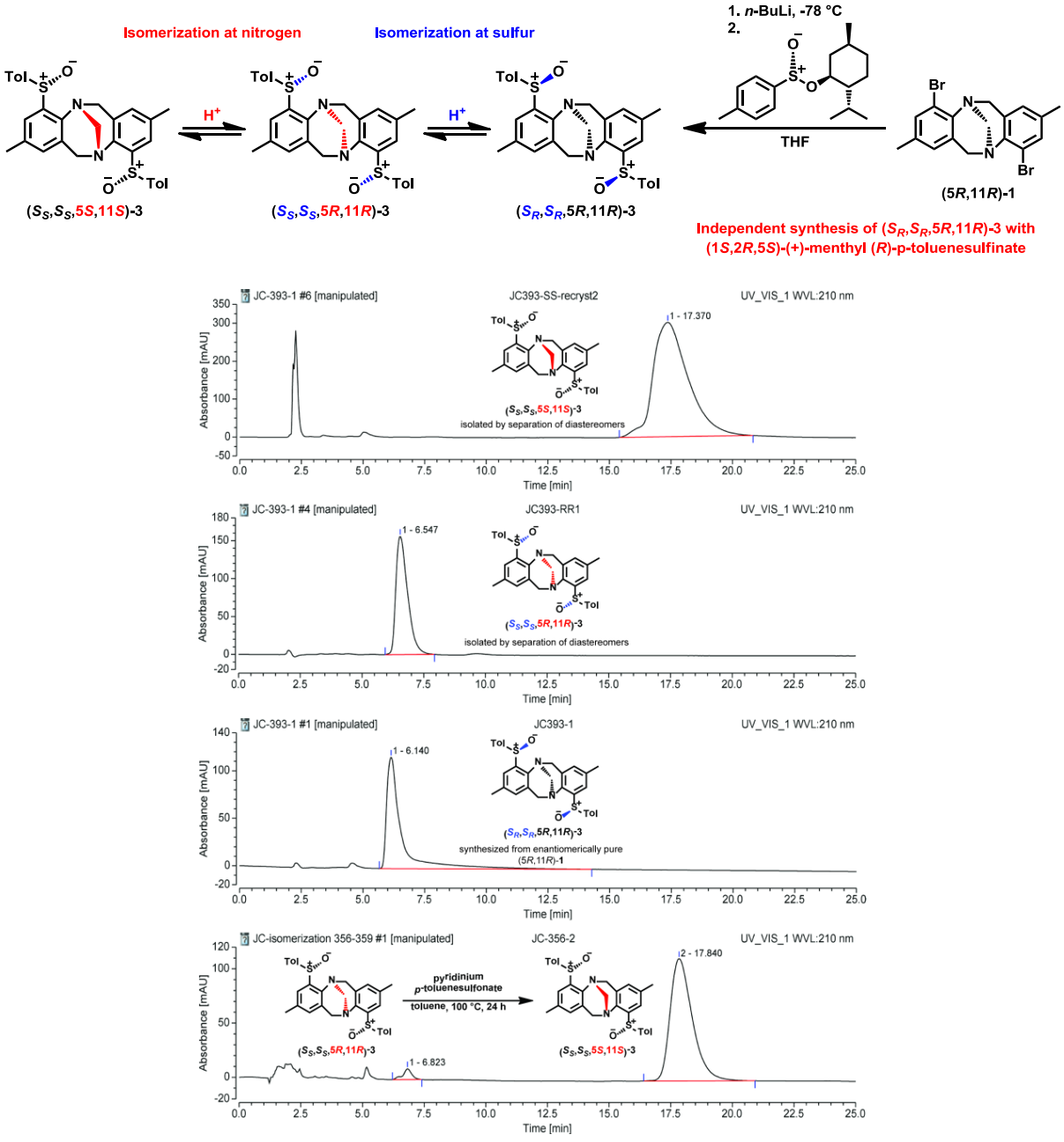
(*S*$_S$,*S*$_S$,5*R*,11*R*)-2,8-Dimethyl-4,10-bis(*p*-tolylsulfinyl)-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine ((*S*$_S$,*S*$_S$,5*R*,11*R*)-3):

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.23 (s, 6H, C*H*$_3$), 2.43 (s, 6H, C*H*$_3$), 3.62 (d, ^{2}J = 17.4 Hz, 2H, ArC*H*^{endo}N), 4.21 (s, 2H, NC*H*$_2$N), 4.44 (d, ^{2}J = 17.4 Hz, 2H, ArC*H*^{exo}N), 6.60 (s, 2H, Ar*H*), 7.30 (d, ^{2}J = 7.5 Hz, 4H, Ar*H*), 7.36 (s, 2H, Ar*H*), 7.56 (d, ^{2}J = 7.6 Hz, 4H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 21.1 (*C*H$_3$), 21.6 (*C*H$_3$), 57.9 (*C*H$_2$N), 66.8 (NCH$_2$N), 126.6, 126.8, 128.8, 130.0, 130.7, 135.8, 139.7, 141.1, 141.7, 144.6; HRMS (ESI): m/z [M

+ H]$^+$ calcd for $C_{31}H_{31}N_2O_2S_2$: 527.1821, found: 527.1826; $[\alpha]_D^{20}$ +144.3 (*c* 1.01, $CHCl_3$); m.p. 192 – 194 °C; HPLC (IA, Hex:*i*PrOH = 30:70, 1 ml/min): 6.5 min.

Isomerization studies

The exposure of diastereomerically pure sulfoxides (S_S,S_S,5*S*,11*S*)-**3** and (S_S,S_S,5*R*,11*R*)-**3** to acidic conditions can result at in isomerization of both sulfur[1] and nitrogen[2] stereogenic centers. A summary of the isomerization experiments is given in Table 1. In order to unambiguously distinguish between the enantiomeric structures (S_S,S_S,5*S*,11*S*)-**3** and (S_R,S_R,5*R*,11*R*)-**3**, we have synthesized (S_R,S_R,5*R*,11*R*)-**3** independently starting from the enantiomerically pure dibromide (5*R*,11*R*)-**1** (^{1}H and ^{13}C NMR spectra were in agreement with those of (S_S,S_S,5*S*,11*S*)-**3**. The comparison of HPLC traces confirms that isomerization occurred exclusively at the nitrogen centers (Scheme 1).



Scheme 1: Acid-catalyzed isomerization of diastereomerically pure disulfoxides.

[1] M. Mikołajczyk, J. Drabowicz, in *Topics in Stereochemistry*, John Wiley & Sons, Inc., **2007**, pp. 333-468.
[2] A. Greenberg, N. Molinaro, M. Lang, *J. Org. Chem.* **1984**, *49*, 1127-1130.

Table 1: Acid-catalyzed isomerization of diastereomerically pure disulfoxides.[a]

Entry	Starting material	Acid [equiv]	Solvent	t / °C	Ratio (S_S,S_S,5*S*,11*S*)-**3** / (S_S,S_S,5*R*,11*R*)-**3**
1	(S_S,S_S,5*S*,11*S*)-**3**	PPTS [2]	DCM	25	99:1
2	(S_S,S_S,5*S*,11*S*)-**3**	PTSA [0.35]	DCM	25	100:0
3	(S_S,S_S,5*S*,11*S*)-**3**	AcOH [0.35]	DCM	25	98:2
4	(S_S,S_S,5*S*,11*S*)-**3**	PPTS [0.35]	DCE	100	97:3
5	(S_S,S_S,5*S*,11*S*)-**3**	PPTS [0.35]	toluene	100	97:3
6	(S_S,S_S,5*R*,11*R*)-**3**	PPTS [0.35]	DCM	25	0:100
7	(S_S,S_S,5*R*,11*R*)-**3**	PPTS [0.35]	DCE	100	97:3
8	(S_S,S_S,5*R*,11*R*)-**3**	PPTS [0.35]	toluene	100	94:6

[a] Disulfoxide was dissolved in the corresponding solvent and the acid was added. The resulting mixture was stirred at a given temperature for 24 h. [b]Determined by HPLC with a chiral stationary phase (Chiralpak® IA, hexane/*i*PrOH 30:70, 1.0 ml/min).

Replacement of the sulfinyl moieties

(5*R*,11*R*)-4,10-Dibromo-2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-1): Iodobenzene (465 mg, 2.28 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and anhydrous diethylether (20 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 2.9 mL, 4.56 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (S_S,S_S,5*R*,11*R*)-**3** (200 mg, 0.38 mmol) was placed into a separate Schlenk flask (20 mL) under argon and ahydrous THF (6 mL) was added. It was cooled down to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes, 1,2-dibromo-1,1,2,2-tetrafluoroethane (0.46 mL, 3.8 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The crude mixture was purified by column chromatography (SiO_2 (60 g), Hex: EtOAc = 9:1, 15 ml fractions) to afford the title compound as a white solid (114 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.21 (s, 6H, C*H*$_3$), 4.28 (d, ^3J = 17.3 Hz, 2H, C*H*^{endo}), 4.35 (s, 2H, NC*H*$_2$N), 4.54 (d, ^3J = 17.3 Hz, 2H, C*H*^{exo}), 6.73 (s, 2H, Ar*H*), 7.26 (s, 2H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 20.6, 55.6, 68.0, 119.7, 126.9, 130.4, 132.0, 135.5, 142.2; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{17}Br_2N_2$: 406.9753; found: 406.9763; $[\alpha]_D^{20}$ +169.0 (*c* 0.41, $CHCl_3$); m.p. 174-175 °C (racemic: 188-189 °C); HPLC (AM, Hex:*i*PrOH = 90:10, 0.5 ml/min): 8.6 min ((5*R*,11*R*)-**1**), 10.1 min ((5*S*,11*S*)-**1**, not observed).

(5*S*,11*S*)-4,10-Dibromo-2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*S*,11*S*)-1): Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and anhydrous diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (S_S,S_S,5*S*,11*S*)-**3** (100 mg, 0.19 mmol) was placed into a separate Schlenk flask (50 mL) under argon and ahydrous THF (30 mL) was added to form a white suspension which was placed into an ultrasound bath for 30 minutes. Then it was cooled down to -78 °C and added via cannula to the phenyl lithium solution prepared above. After 10 minutes, 1,2-dibromo-1,1,2,2-tetrafluoroethane (226 µL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The crude mixture was purified by column chromatography (SiO_2 (30 g), Hex: EtOAc = 9:1, 15 ml fractions) to afford the title compound as a white solid (41 mg, 53%).

^{1}H and ^{13}C NMR data were identical with those of (5*R*,11*R*)-1; $[\alpha]_D^{20}$ -164.1 (*c* 0.91, $CHCl_3$); m.p. 175 – 176 °C, HPLC (AM, Hex:*i*PrOH = 90:10, 0.5 ml/min): 8.6 min ((5*R*,11*R*)-**1**, not observed), 10.1 min ((5*S*,11*S*)-**1**).

(5*R*,11*R*)-4,10-Diiodo-2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-4a):

Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes a solution of iodine (482 mg, 1.9 mmol, 10 equiv) in THF (5 mL) was added in one portion and the stirring was continued overnight at ambient temperature. It was quenched with aqueous solution of $Na_2S_2O_3$ (10 mL) and extracted with EtOAc (2 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (20 g), Hex: EtOAc = 15:1) to give a brownish amorphous solid. This was washed with hexane to afford the title compound as a yellowish solid (37 mg, 39%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.20 (s, 6H, C*H*$_3$), 4.19 (d, ^2J = 17.3 Hz, 2H, ArC*H*^{endo}N), 4.35 (s, 2H, NC*H*$_2$N), 4.50 (d, ^2J = 17.2 Hz, 2H, ArC*H*^{exo}N), 6.77 (s, 2H, Ar*H*), 7.55 (s, 2H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 20.5 (*C*H$_3$), 56.7 (*C*H$_2$N), 68.1 (NC*H*$_2$N), 97.4, 127.8, 130.3, 136.3, 138.4, 144.9; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{17}H_{17}N_2I_2$: 502.9476; found: 502.9474; $[\alpha]_D^{20}$ +225.3 (*c* 0.49, $CHCl_3$); m.p. 214-216 °C (racemic 220-221 °C); HPLC (AM, Hex:*i*PrOH = 90:10, 0.5 ml/min): 8.1 min ((5*R*,11*R*)-**4a**), 8.7 min ((5*S*,11*S*)-**4a**, not observed).

(5*R*,11*R*)-2,8-Dimethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine ((5*R*,11*R*)-4b):
Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes water (34 µL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (30 g), Hex: EtOAc = 15:1) to afford the title compound as a white solid (42 mg, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.21 (s, 6H, C*H*$_3$), 4.11 (d, ^2J = 16.7 Hz, 2H, ArC*H*^{endo}N), 4.30 (s, 2H, NC*H*$_2$N), 4.65 (d, ^2J = 16.6 Hz, 2H, ArC*H*^{exo}N), 6.71 (s, 2H, Ar*H*), 6.96 (dd, 2H, ^3J = 8.2 Hz, ^4J = 1.2 Hz, Ar*H*), 7.02 (d, 2H, ^3J = 8.2 Hz, Ar*H*); ^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 21.0 (*C*H$_3$), 58.8 (*C*H$_2$N), 67.2 (NC*H*$_2$N), 124.9, 127.4, 127.7, 128.3, 133.6, 145.6; $[\alpha]_D^{20}$ -255.1 (*c* 0.22, hexane); m.p. 129 – 130 °C (racemic 133 – 134 °C); HPLC (OD-H, Hex:*i*PrOH = 90:10, 0.5 ml/min): 13.4 min ((5*S*,11*S*)-**4b**, not observed), 15.3 min ((5*R*,11*R*)-**4b**).

(5*R*,11*R*)-2,8-Dimethyl-4,10-bis(trimethylsilyl)-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine ((5*R*,11*R*)-4c):
Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes chlorotrimethylsilane (241 µL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (30 g), Hex: EtOAc = 100:1) to afford the title compound as a white solid (46 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.42 (s, 18H, Si(*C*H$_3$)$_3$), 2.27 (s, 6H, C*H*$_3$), 3.99 (d, ^2J = 16.7 Hz, 2H, ArC*H*^{endo}N), 4.29 (s, 2H, NC*H*$_2$N), 4.59 (d, ^2J = 16.7 Hz, 2H, ArC*H*^{exo}N), 6.74 (s, 2H, Ar-*H*), 7.18 (s, 2H, Ar-*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 0.7 (Si(*C*H$_3$)$_3$), 21.1 (*C*H$_3$), 59.4 (*C*H$_2$N), 66.6 (NC*H*$_2$N), 128.2, 128.7, 133.2,

134.8, 136.2, 152.1; HRMS (ESI): m/z $[M]^+$ calcd for $C_{23}H_{35}N_2Si_2$: 395.2333, found: 395.2338; $[\alpha]_D^{20}$ +156.7 (*c* 0.52, $CHCl_3$); m.p. not determined, the compound turns amorphous and glassy in the range of 40-50 °C (racemic 151 – 152 °C); HPLC: no suitable conditions for the baseline-separation of the two enantiomers were identified, the compound is too nonpolar.

(5*R*,11*R*)-2,8-Dimethyl-4,10-bis(phenylthio)-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-4d):

Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes diphenyl disulfide (0.42 g, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (30 g), Hex:EtOAc = 15:1) to afford the title compound as a white solid (53 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.09 (s, 6H, C*H*$_3$), 4.38 (d, ^2J = 16.9 Hz, 2H, ArC*H*$_{endo}$N), 4.39 (s, 2H, NC*H*$_2$N), 4.58 (d, ^2J = 17.4 Hz, 2H, ArC*H*$_{exo}$N), 6.56 (s, 2H, Ar*H*), 6.61 (s, 2H, Ar*H*), 7.32–7.41 (m, 6H, Ar*H*), 7.47–7.49 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1 (*C*H$_3$), 55.2 (*C*H$_2$N), 67.9 (NCH$_2$N), 125.4, 127.7, 128.0, 128.8, 129.6, 132.9, 133.5, 133.7, 134.6, 142.2; HRMS (ESI): m/z $[M]^+$ calcd for $C_{29}H_{27}N_2S_2$: 467.1610, found: 467.1619; $[\alpha]_D^{20}$ +175.9 (*c* 0.81, $CHCl_3$); m.p. 176-178 °C (racemic 174-176 °C); HPLC (AM, Hex:*i*PrOH = 90:10, 0.5 ml/min): 9.5 min ((5*S*,11*S*)-**4d**, not observed), 11.6 min ((5*R*,11*R*)-**4d**).

(5*R*,11*R*)-2,8-Dimethyl-4,10-bis(phenylselanyl)-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-4e):

Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes phenylselenyl chloride (0.36 g, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (40 g), Hex:EtOAc = 9:1) to afford the title compound as a brownish solid (74 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.07 (s, 6H, C*H*$_3$), 4.37 (d, ^2J = 17.7 Hz, 2H, ArC*H*^{endo}N), 4.39 (s, 2H, NC*H*$_2$N), 4.56 (d, ^2J = 17.1 Hz, 2H, ArC*H*^{exo}N), 6.56 (s, 2H, Ar*H*), 6.61 (s, 2H, Ar*H*), 7.35-7.43 (m, 6H, Ar*H*), 7.62-7.67 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1 (*C*H$_3$), 55.3 (*C*H$_2$N), 67.8 (NCH$_2$N), 125.4, 128.4, 128.6, 128.8, 129.7, 130.7, 135.1, 136.3, 142.5; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{27}N_2Se_2$: 563.0504, found: 563.0498; $[\alpha]_D^{20}$ +127.3 (*c* 0.23, $CHCl_3$); m.p. 226.5 °C (racemic 228–230 °C); HPLC (AD-H, Hex:*i*PrOH = 90:10, 0.5 ml/min): 9.1 min ((5*S*,11*S*)-**4e**, not observed), 10.3 min ((5*R*,11*R*)-**4e**).

2,2'-(2,8-Dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-4,10-diyl)bis(propan-2-ol) ((5*R*,11*R*)-4f):

Iodobenzene (254 µL, 2.28 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (20 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 2.8 mL, 4.55 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (200 mg, 0.38 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (6 mL) was added. It was cooled to 0 °C and added to the phenyl lithium

solution prepared above. After 10 minutes acetone (0.29 mL, 3.8 mmol, 10 equiv) was added in one portion and the stirring was continued at -78 °C for 30 min. The cooling bath was then removed and the stirring was continued at ambient temperature overnight. Water (10 mL) was added, organic solvents were removed on rotavap and the residue was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (50 g), Hex:EtOAc = 5:1) to afford a colorless solid. It was recrystallized by dissolving in minimal amount of hot EtOH followed by addition of large excess of water providing the title compound as a white solid (41 mg, 29%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.61 (s, 6H, CH_3), 1.69 (s, 6H, CH_3), 2.24 (s, 6H, ArCH_3), 4.19 (d, ^2J = 17.3 Hz, 2H, ArCH_{endo}N), 4.35 (s, 2H, NCH_2N), 4.66 (d, ^2J = 17.2 Hz, 2H, ArCH_{exo}N), 6.64 (s, 2H, Ar*H*), 6.95 (s, 2H, Ar*H*), 8.53 (brs, 2H, O*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 21.2 (Ar*C*H_3), 33.5 (*C*H_3COH), 33.9 (*C*H_3COH), 57.7, 65.3, 74.9, 126.0, 127.1, 128.1, 135.2, 141.9, 142.1; HRMS (ESI): m/z [M+H]$^+$ calcd for $C_{23}H_{31}N_2O_2$: 367.2380, found: 367.2376; $[\alpha]_D^{20}$ +116.2 (*c* 0.23, $CHCl_3$); m.p. 187-188 °C (racemic: 223-224 °C); HPLC (AM, Hex:*i*PrOH = 99.5:0.5, 0.5 ml/min): 14.0 min ((5*S*,11*S*)-**4f**, not observed), 16.4 min ((5*R*,11*R*)-**4f**).

(5*R*,11*R*)-2,8-Dimethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine-4,10 dicarbaldehyde ((5*R*,11*R*)-4g):

Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes DMF (147 µL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued at -78 °C for 30 min and then at RT for 2 h. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (40 g), toluene:MTBE = 4:1, the mixture was preabsorbed to silica before loading) to afford the title compound as a colorless solid (31 mg, 53%).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.27 (s, 6H, CH_3), 4.09 (d, ^2J = 16.8 Hz, 2H, ArCH^{endo}N), 4.41 (s, 2H, NCH_2N), 4.85 (d, ^2J = 16.8 Hz, 2H, ArCH^{exo}N), 6.95 (s, 2H, Ar*H*), 7.53 (s, 2H, Ar*H*), 10.51 (s, 2H, C*H*O); ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 20.8 (*C*H_3), 59.5 (Ar*C*H_2N), 66.8 (N*C*H_2N), 128.4, 129.2, 129.6, 133.6, 134.1, 148.1, 191.2 (*C*HO); HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{19}H_{19}N_2O_2$: 307.1441; found: 307.1441; $[\alpha]_D^{20}$ +874.6 (*c* 0.39, $CHCl_3$); m.p. 219-221 °C (racemic 228-230 °C); HPLC (OD-H, Hex:*i*PrOH = 80:20, 0.5 ml/min): 20.1 min ((5*R*,11*R*)-**4g**), 22.9 min ((5*S*,11*S*)-**4g**, not observed).

(5*R*,11*R*)-Dimethyl 2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine-4,10-dicarboxylate ((5*R*,11*R*)-4h):

Iodobenzene (127 µL, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (*S*$_S$,*S*$_S$,5*R*,11*R*)-**3** (100 mg, 0.19 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes methyl chloroformate (0.15 mL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued at -78 °C for 30 min. The cooling bath was then removed and the stirring was continued at ambient temperature for 2 h. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The product was isolated by column chromatography (SiO_2 (30 g), Hex:EtOAc = 1:1) to afford the title compound as a yellow solid (22 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.24 (s, 6H, CH_3), 3.93 (s, 6H, CH_3), 4.34 (s, 2H, NCH_2N), 4.41 (d, ^2J = 17.6 Hz, 2H, CH^{endo}), 4.71 (d, ^2J = 17.5 Hz, 2H, CH^{exo}), 6.91 (s, 2H, Ar*H*), 7.55 (s, 2H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ

[ppm] = 20.8 (*C*H_3), 52.2 (*C*H_2N), 57.9 (O*C*H_3), 67.5 (N*C*H_2N), 125.6, 129.6, 130.5, 131.9, 133.3, 145.9, 166.8 (*C*O); HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_4$: 367.1652, found: 367.1660; $[\alpha]_D^{20}$ +65.5 (*c* 0.3, $CHCl_3$); m.p. decomposition, the sample turned black at 120 °C (racemic: 150-151 °C); HPLC (AM, Hex:*i*PrOH = 90:10, 0.5 ml/min): 18.1 min ((5*S*,11*S*)-**4h**, not observed), 21.3 min ((5*R*,11*R*)-**4h**).

(5*R*,11*R*)-2,4,8,10-Tetramethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-4i):
Iodobenzene (232 mg, 1.14 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and anhydrous diethylether (10 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.4 mL, 2.28 mmol, 12 equiv) was added slowly. It was stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (S_S,S_S,5*R*,11*R*)-**3** (100 mg, 0.19 mmol) was placed into a separate Schlenk flask (10 mL) under argon and THF (3 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 minutes, methyl iodide (0.12 mL, 1.9 mmol, 10 equiv) was added in one portion and the stirring was continued overnight at ambient temperature. Water (10 mL) was added and the aqueous layer was extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The crude mixture was purified by column chromatography (SiO_2 (30 g), Hex: EtOAc = 9:1, 15 ml fractions) to afford the title compound as a white solid (13 mg, 24%).

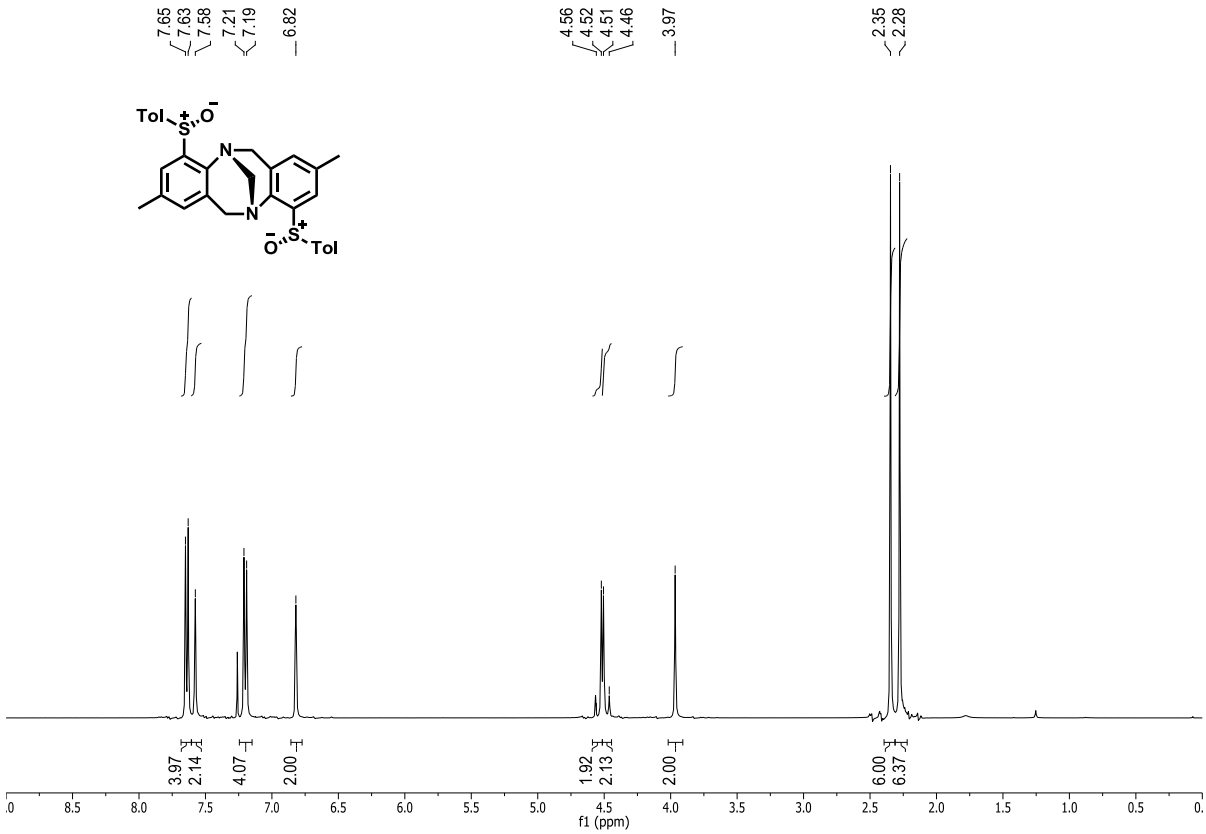
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.26 (s, 6H, C*H*$_3$), 2.45 (s, 6H, C*H*$_3$), 4.01 (d, ^3J = 16.8 Hz, 2H, C*H*^{endo}), 4.38 (s, 2H, NC*H*$_2$N), 4.61 (d, ^3J = 16.8 Hz, 2H, C*H*^{exo}), 6.64 (s, 2H, Ar*H*), 6.93 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 17.1 (*C*H_3), 20.9 (*C*H_3), 55.2 (*C*H_2N), 67.8 (N*C*H_2N), 124.9, 127.8, 129.8, 132.6, 133.1, 143.4; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{23}N_2$: 279.1856; found: 279.1862; $[\alpha]_D^{20}$ -31.3 (*c* 0.38, $CHCl_3$); m.p. 109-111 °C (racemic 112-113 °C); HPLC (AM, Hex:*i*PrOH = 99.5:0.5, 0.5 ml/min): 8.3 min ((5*S*,11*S*)-**4i**, not observed), 9.2 min ((5*R*,11*R*)-**4i**).

(5*R*,11*R*)-4,10-Diallyl-2,8-dimethyl-6,12-dihydro-5,11-methanodibenzo[*b*,*f*][1,5]diazocine ((5*R*,11*R*)-4j):
Iodobenzene (142 µL, 1.27 mmol, 6 equiv) was placed into a Schlenk flask (50 mL) under argon and diethylether (11 mL) was added. It was cooled to 0 °C and *n*-BuLi (1.6 M in hexanes, 1.6 mL, 2.55 mmol, 12 equiv) was added slowly. It was then stirred at the same temperature for 30 min. Then it was cooled to -78 °C. In the meantime, disulfoxide (S_S,S_S,5*R*,11*R*)-**3** (112 mg, 0.21 mmol, 1 equiv) was placed into a separate Schlenk flask (20 mL) under argon and THF (4 mL) was added. It was cooled to 0 °C and added to the phenyl lithium solution prepared above. After 10 min, the mixture was warmed to -30 °C and a solution of CuCN•2LiCl (1M in THF, 1.3 mL, 1.27 mmol, 6 equiv) was added. It was then stirred at 0 °C for 20 min, cooled to -30 °C and allyl bromide (0.18 mL, 2.1 mmol, 10 equiv) was added. The resulting mixture was stirred at ambient temperature overnight. It was quenched with an aqueous solution of ammonium hydroxide (10 mL), stirred for 20 minutes and extracted with EtOAc (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (SiO_2, Hex:EtOAc = 9:1) to afford the title compound as a yellowish oil (47 mg, 67%).

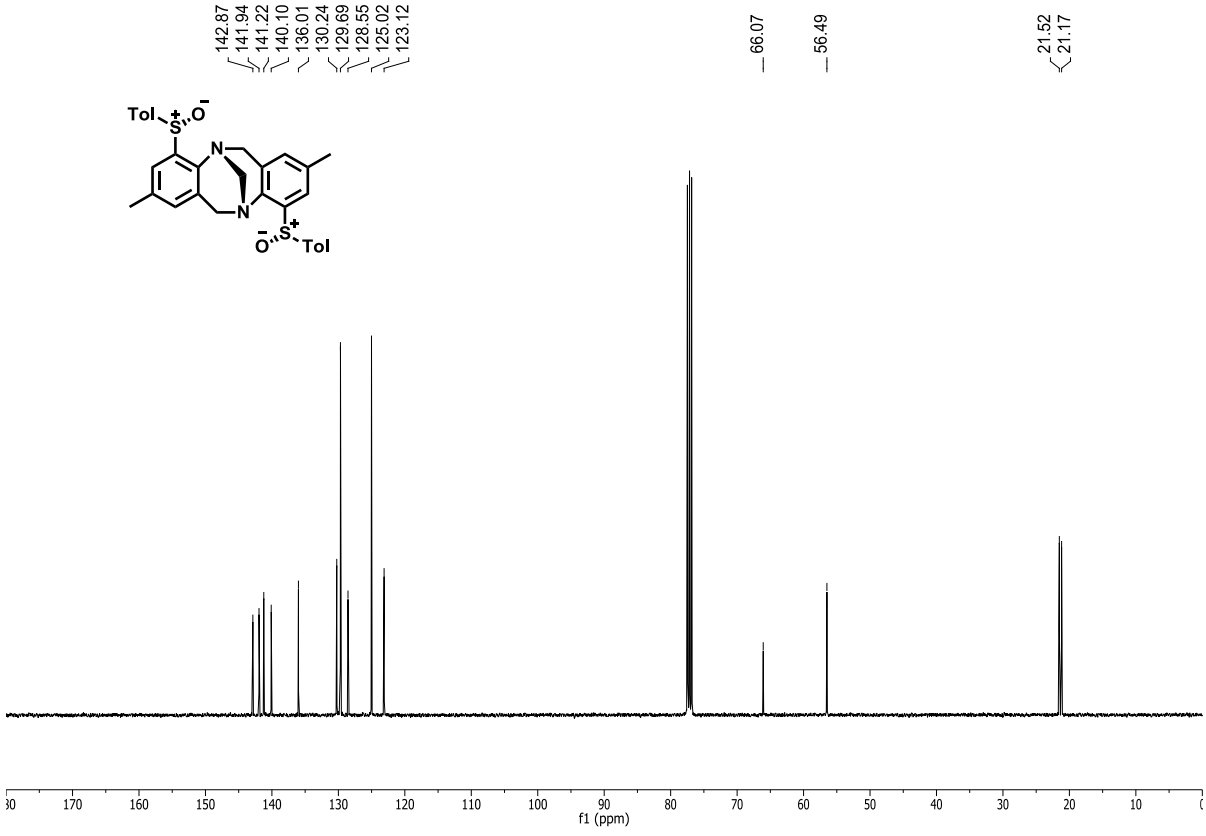
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.24 (s, 6H, C*H*$_3$), 3.48 (dd, ^2J = 15.7 Hz, ^3J = 7.4 Hz, 2H, C*H*^{A}), 3.70 (dd, ^2J = 15.7 Hz, ^3J = 5.4 Hz, 2H, C*H*^{B}), 3.99 (d, ^2J = 16.8 Hz, 2H, ArC*H*^{endo}N), 4.32 (s, 2H, NC*H*$_2$N), 4.58 (d, ^2J = 16.8 Hz, 2H, ArC*H*^{exo}N), 5.17 (m, 4H, C*H*$_2$=C), 6.08 (m, 2H, C=C*H*), 6.61 (s, 2H, Ar*H*), 6.91 (s, 2H, Ar*H*); ^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 21.0 (*C*H_3), 34.0 (*C*H_2), 56.2 (*C*H_2N), 67.8 (N*C*H_2N), 116.1 (*C*H_2=C), 125.4, 128.0, 129.0, 133.3, 134.5, 137.8 (C=*C*H), 143.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{27}N_2$: 331.2169, found: 331.2168; $[\alpha]_D^{20}$ +67.2 (*c* 0.99, $CHCl_3$); HPLC (AM, Hex:*i*PrOH = 99.5:0.5, 0.5 ml/min): 7.2 min ((5*S*,11*S*)-**4j**, not observed), 7.6 min ((5*R*,11*R*)-**4j**).

^{1}H and ^{13}C NMR Spectra of synthesized compounds

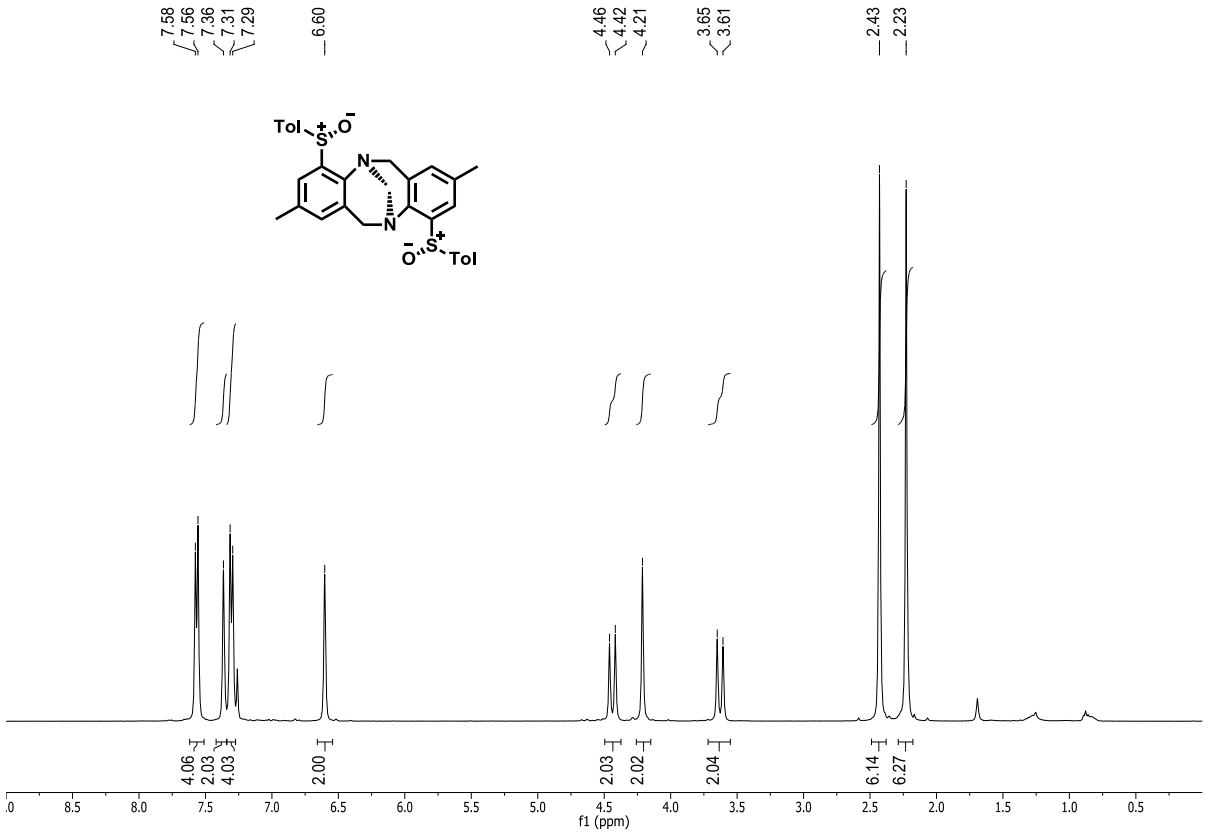
^{1}H NMR of (S_S,S_S,5*S*,11*S*)-**3**



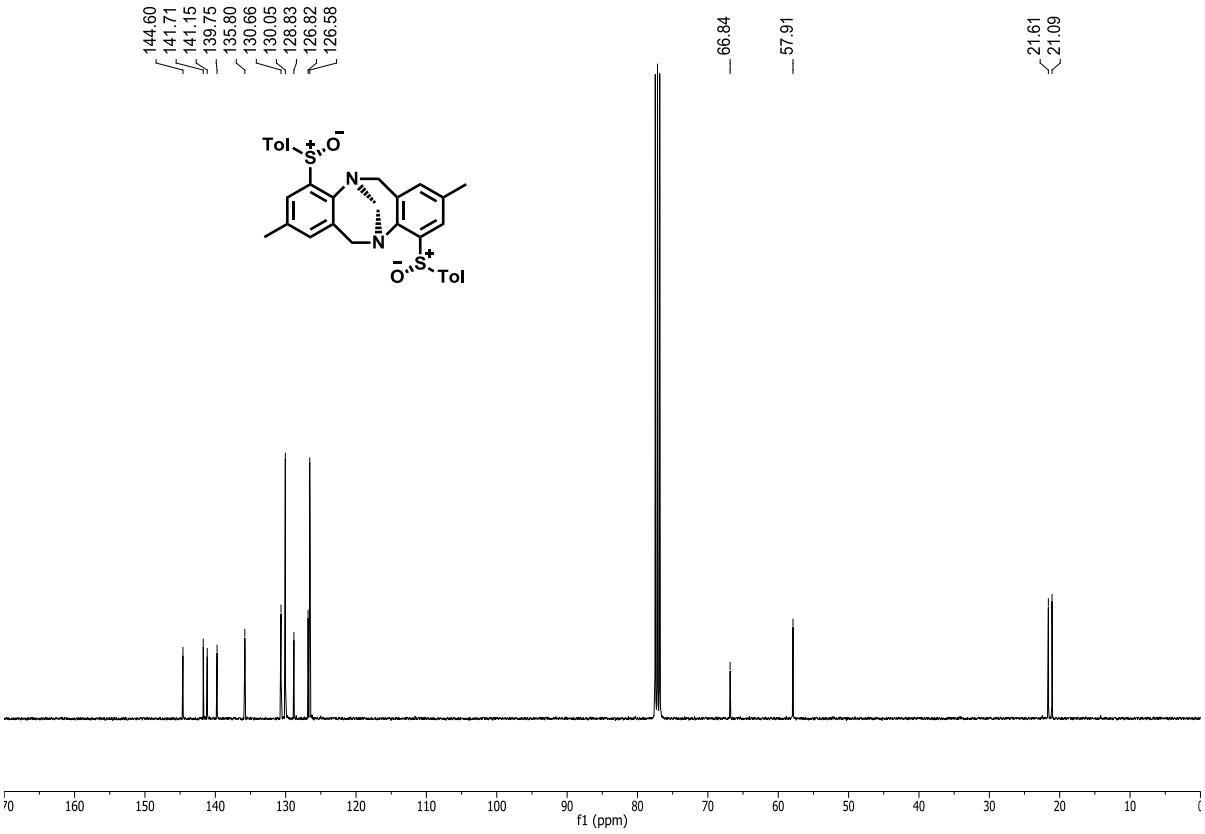
^{13}C NMR of (S_S,S_S,5*S*,11*S*)-**3**



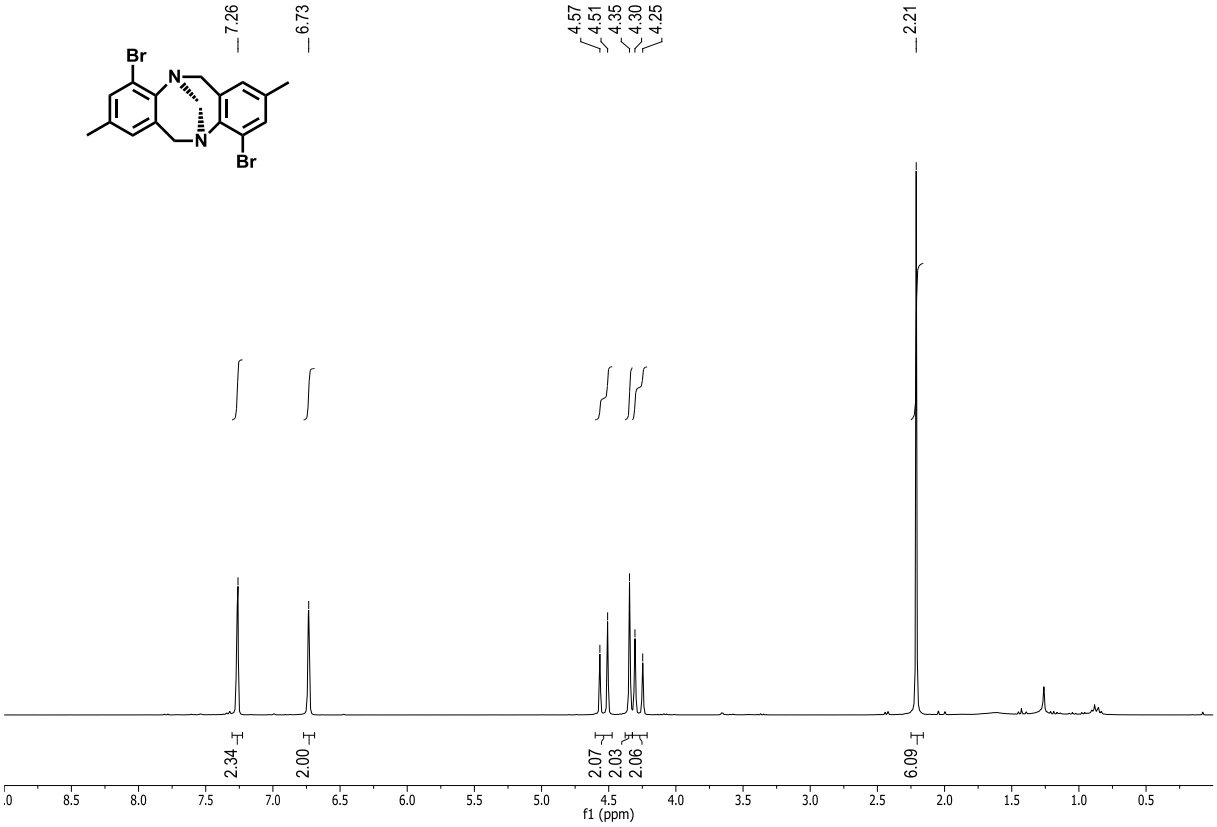
^{1}H NMR of (S_S,S_S,5*R*,11*R*)-**3**



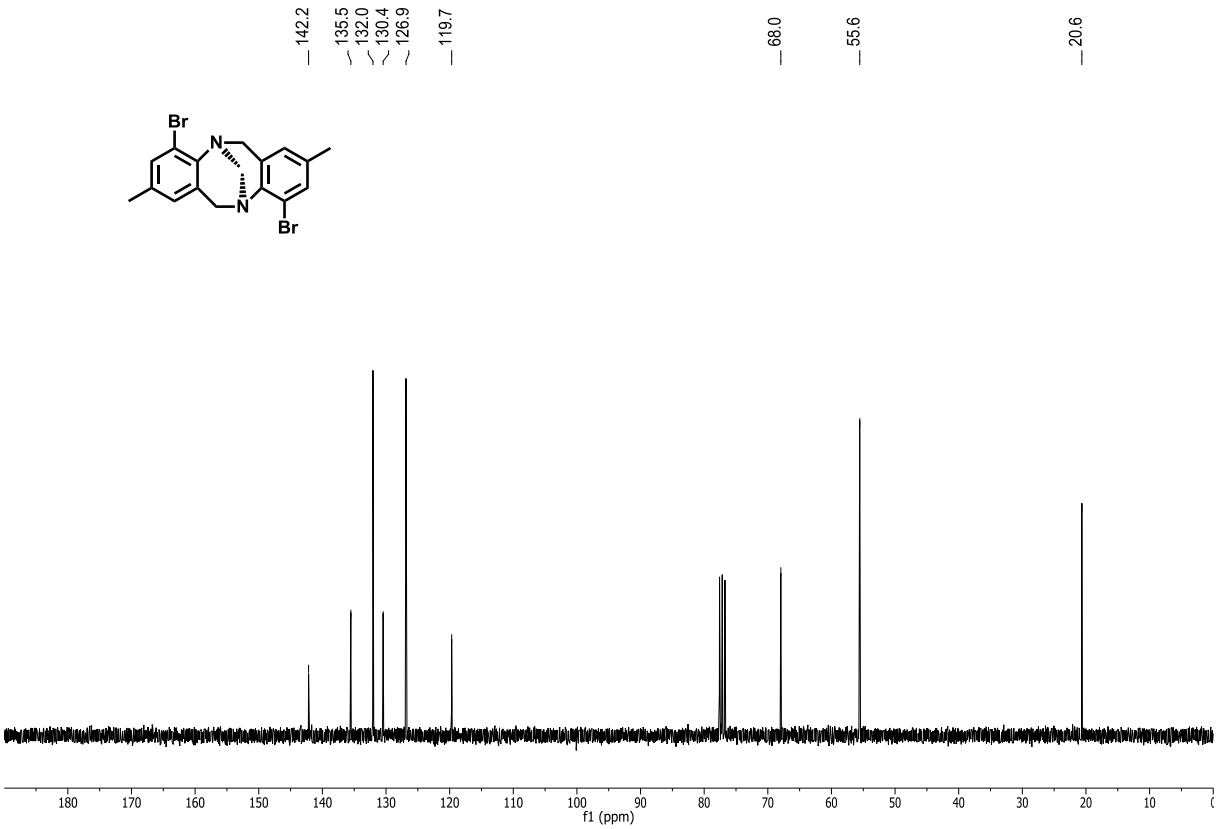
^{13}C NMR of (S_S,S_S,5*R*,11*R*)-**3**



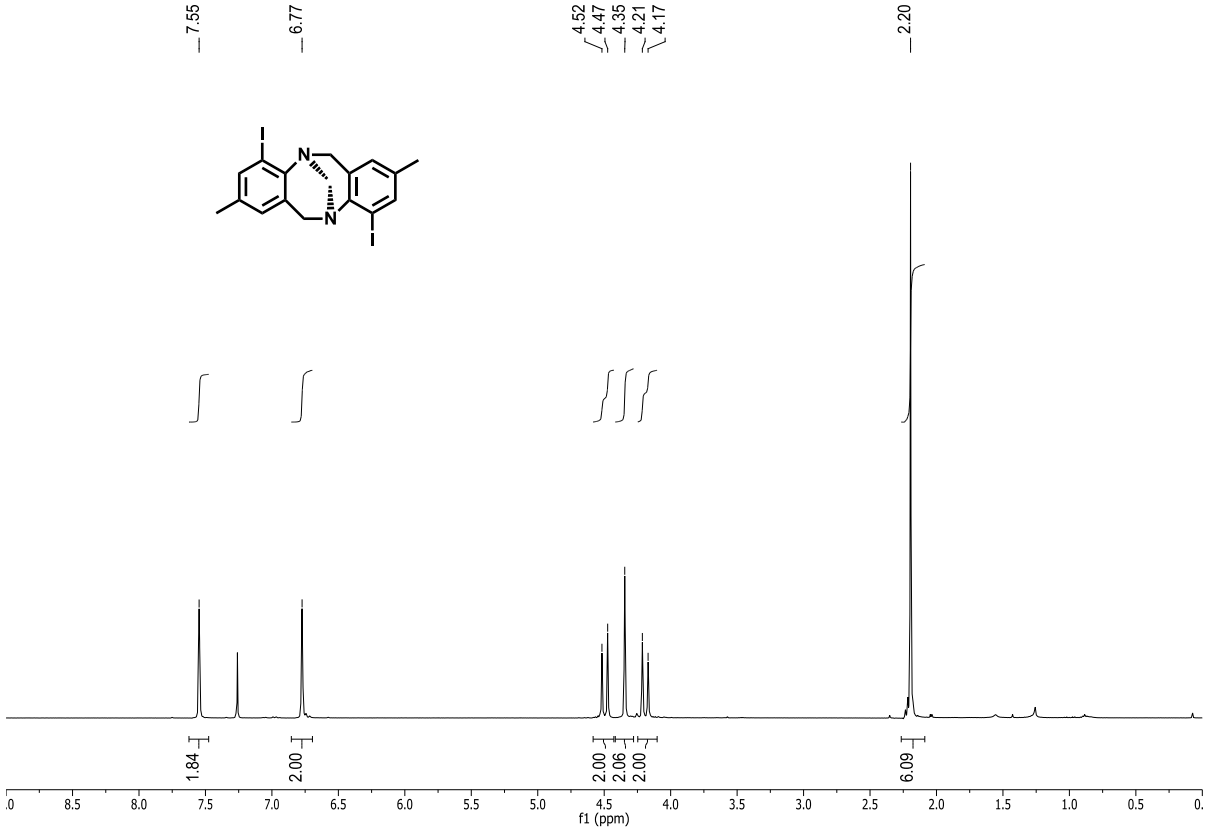
^{1}H NMR of ((5*R*,11*R*)-**1**



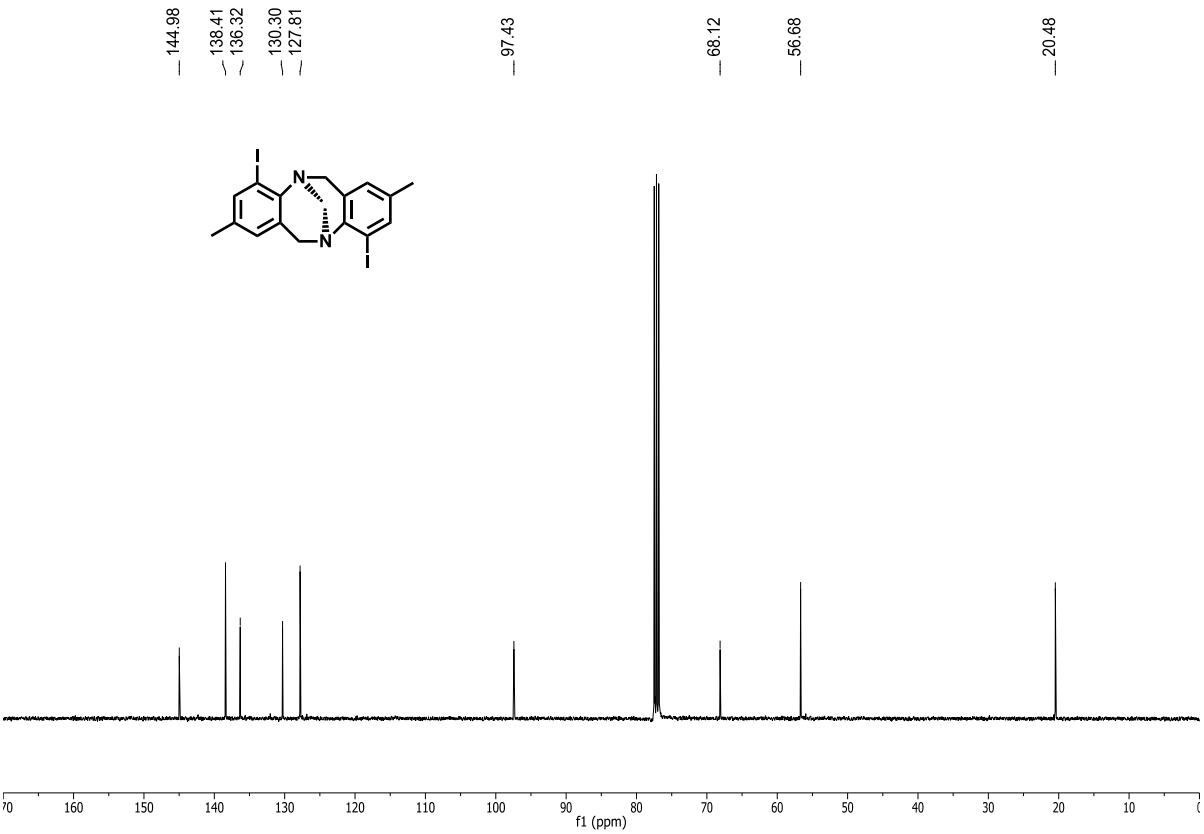
^{13}C NMR of (5*R*,11*R*)-**1**



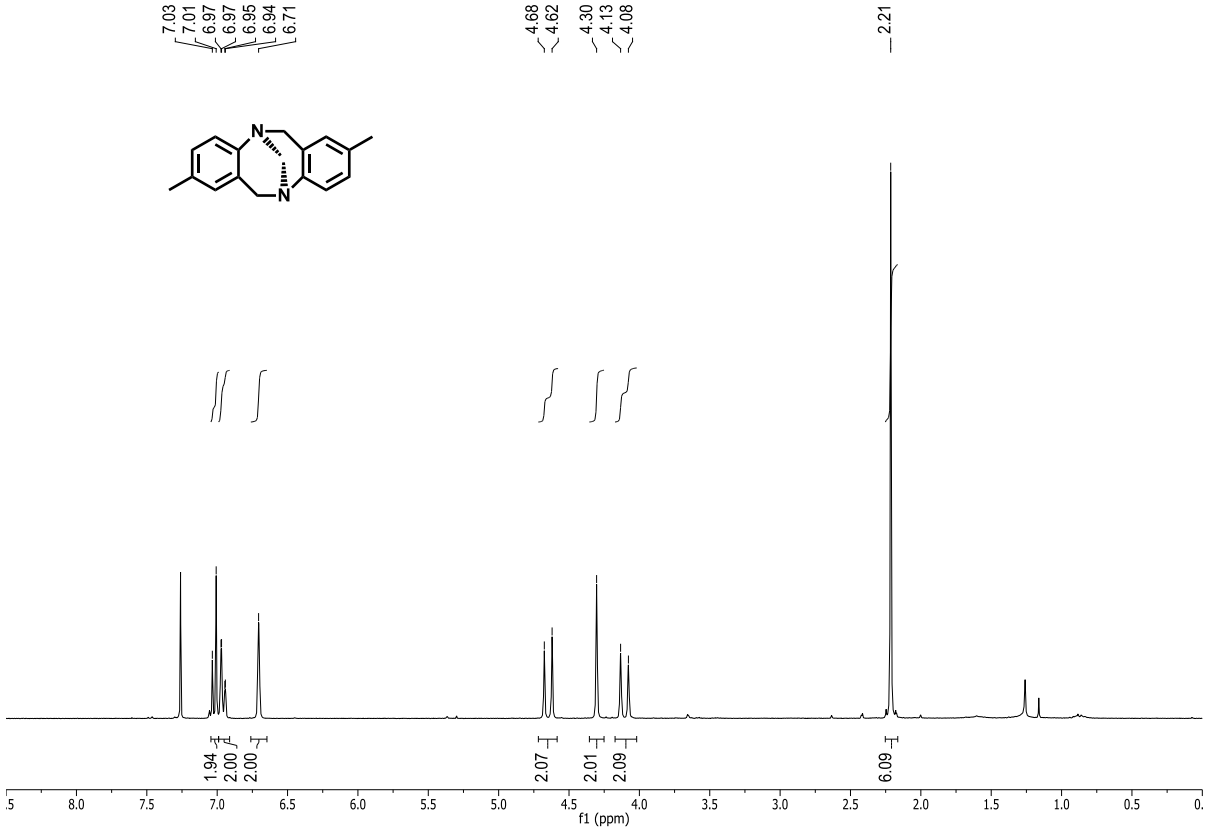
^{1}H NMR of (5*R*,11*R*)-**4a**



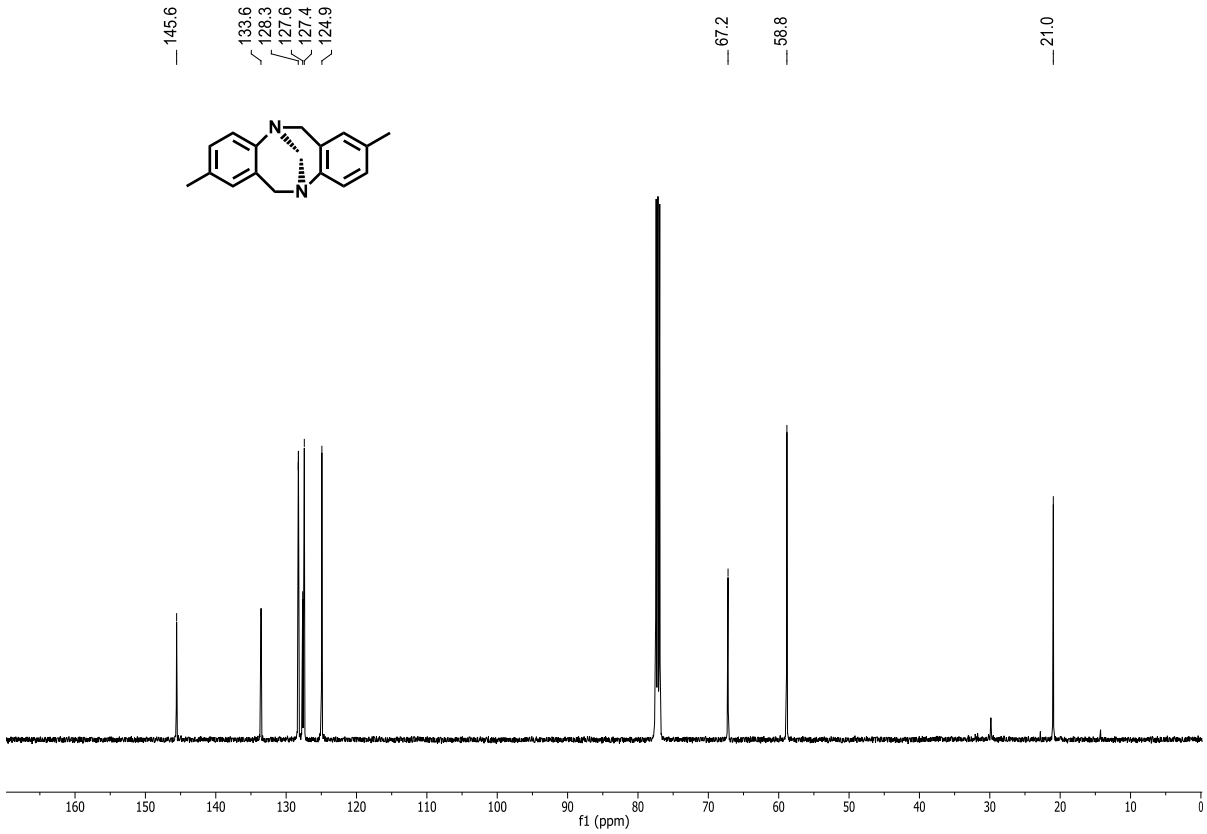
^{13}C NMR of (5*R*,11*R*)-**4a**



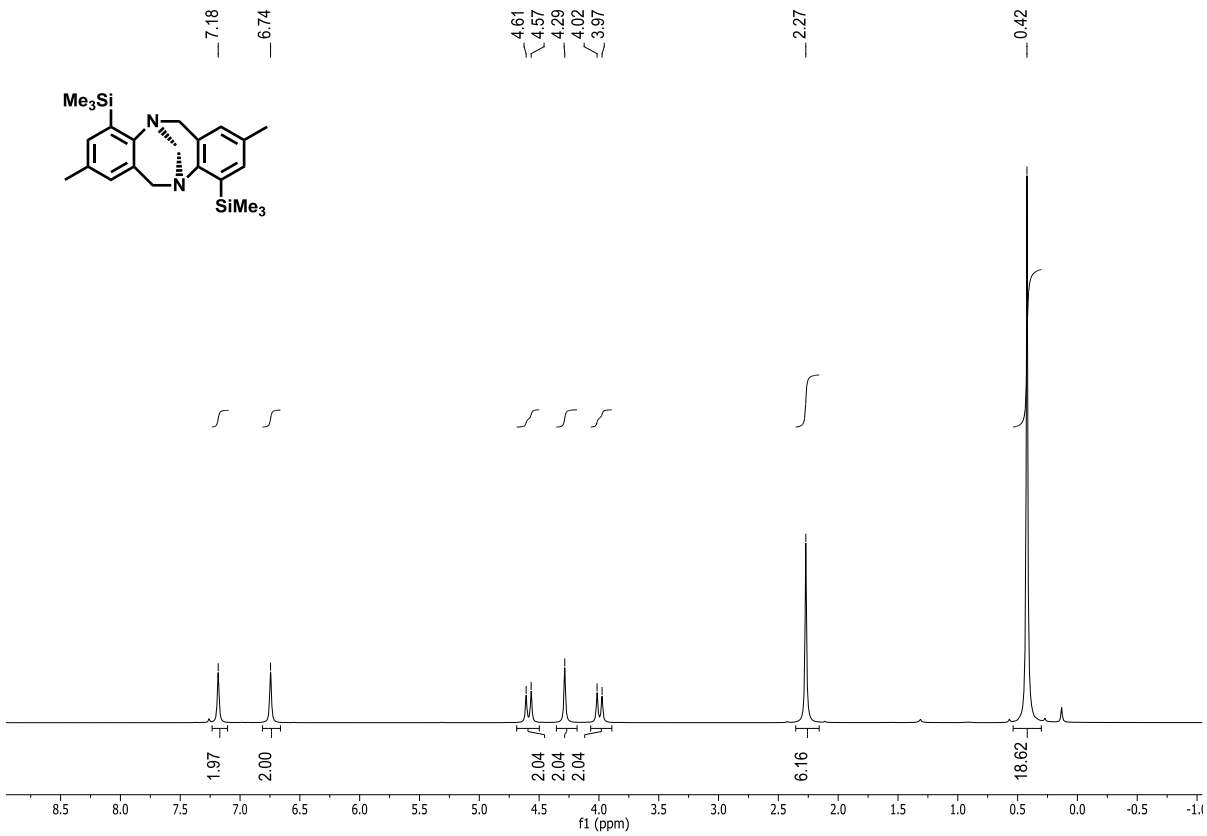
^{1}H NMR of (5*R*,11*R*)-**4b**



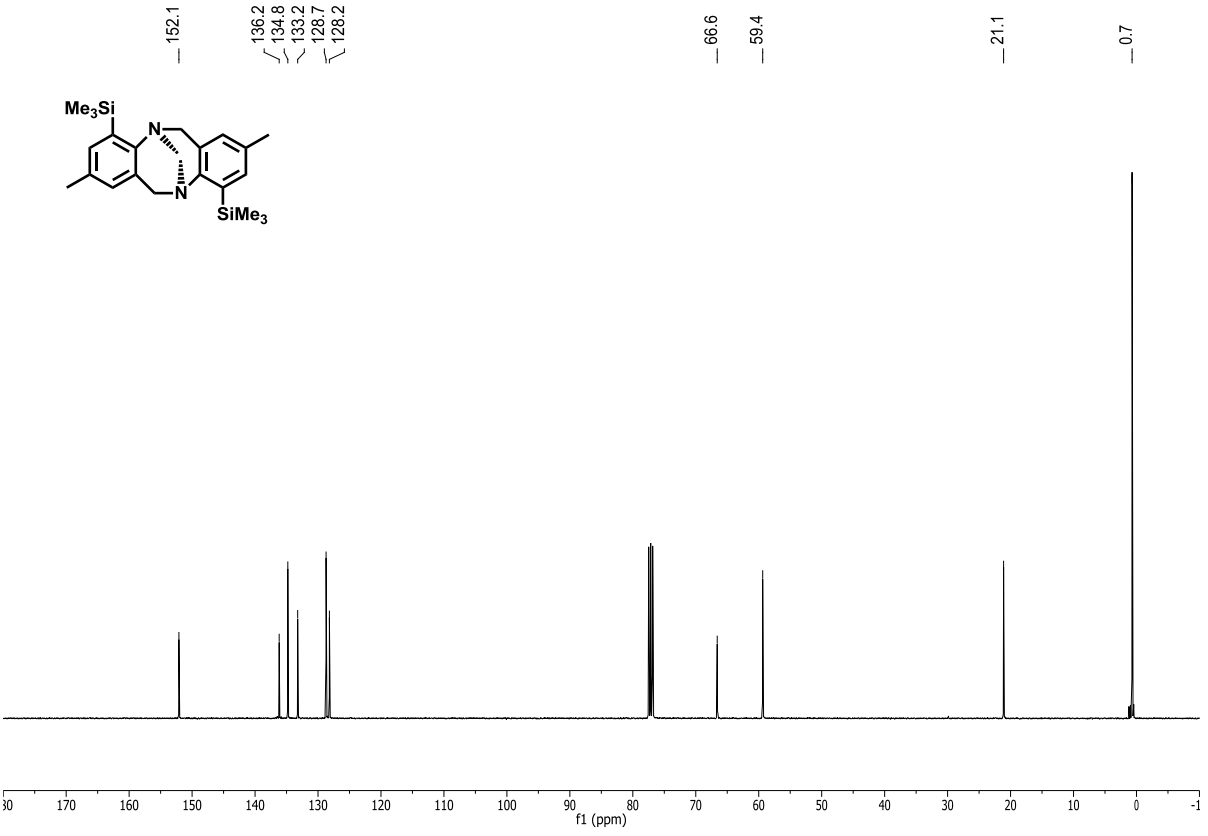
^{13}C NMR of (5*R*,11*R*)-**4b**



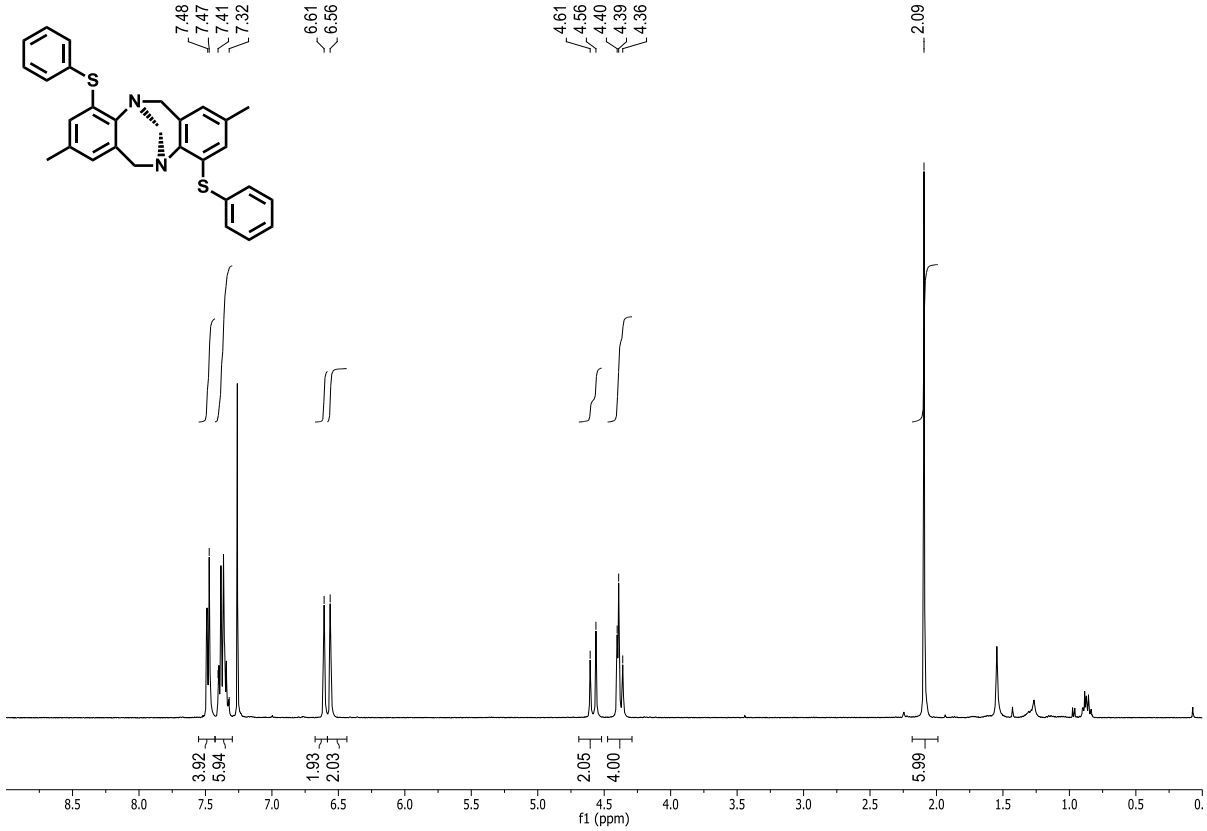
^{1}H NMR of (5*R*,11*R*)-**4c**



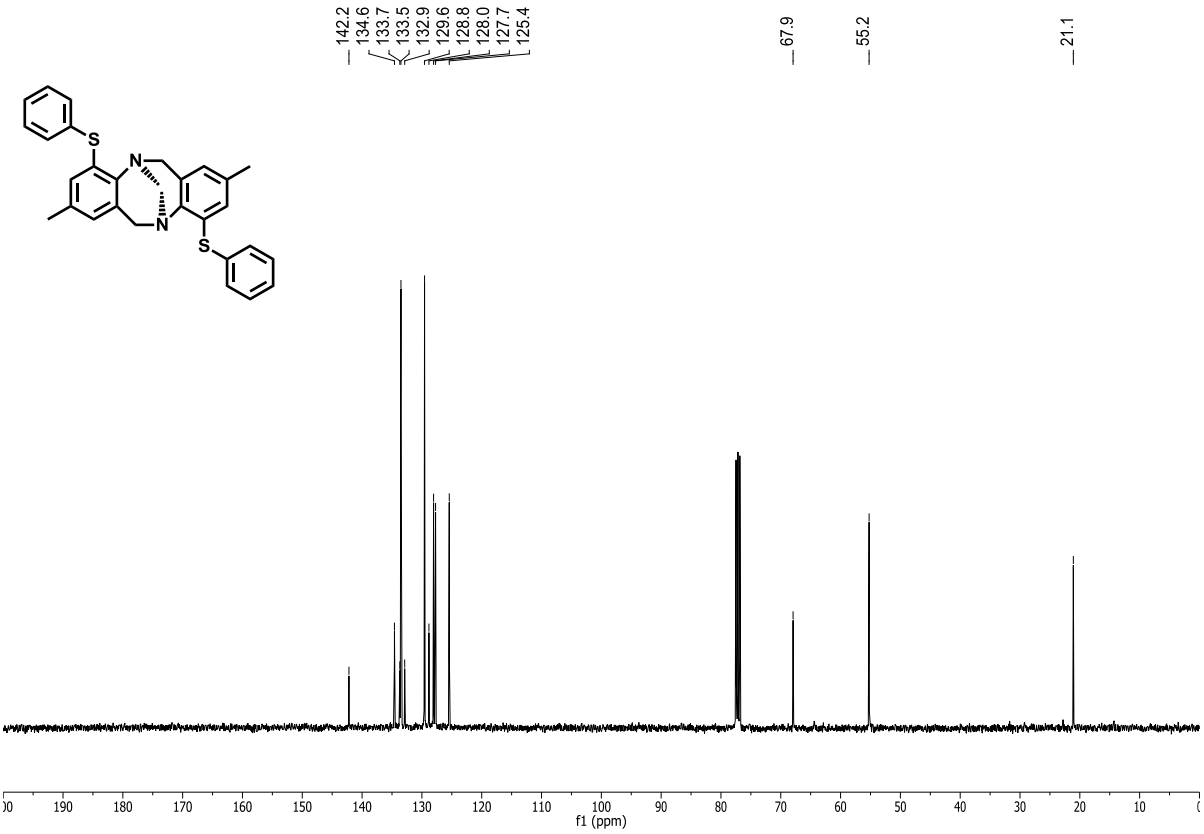
^{13}C NMR of (5*R*,11*R*)-**4c**



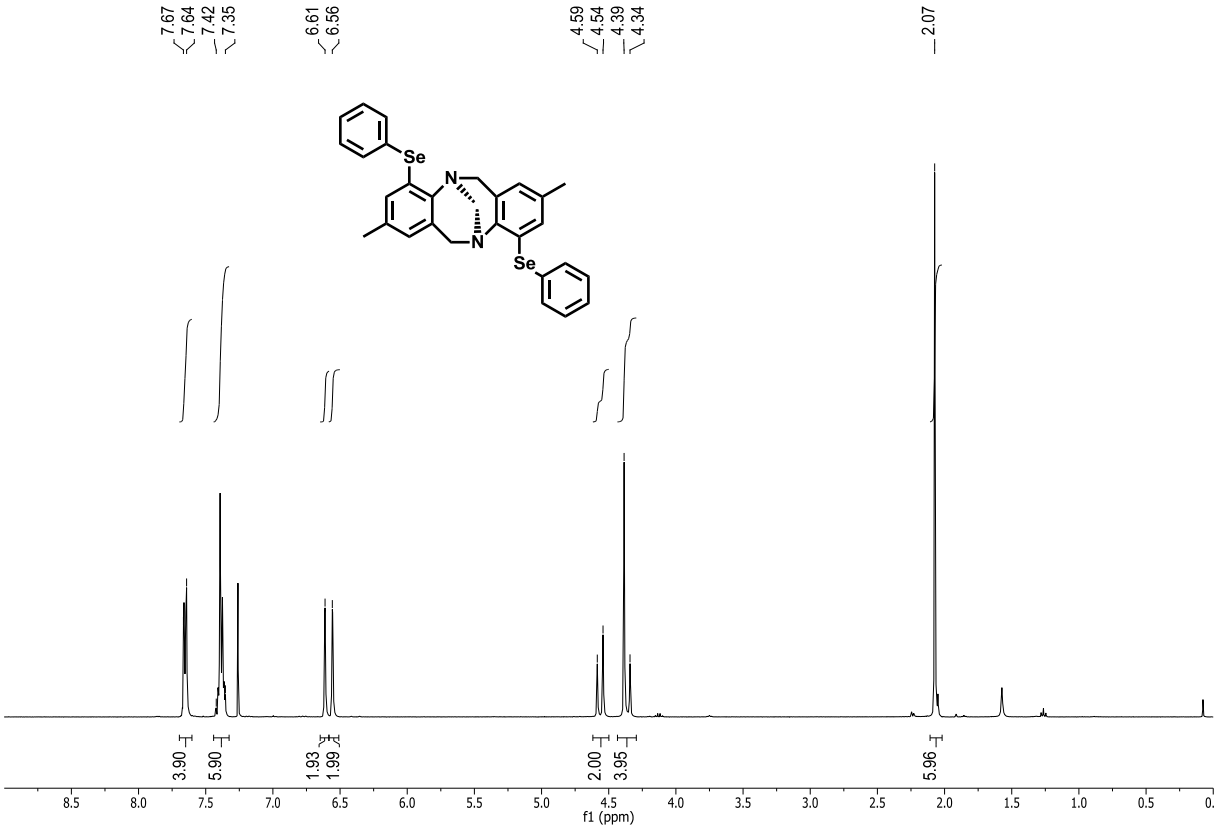
^{1}H NMR of (5*R*,11*R*)-**4d**



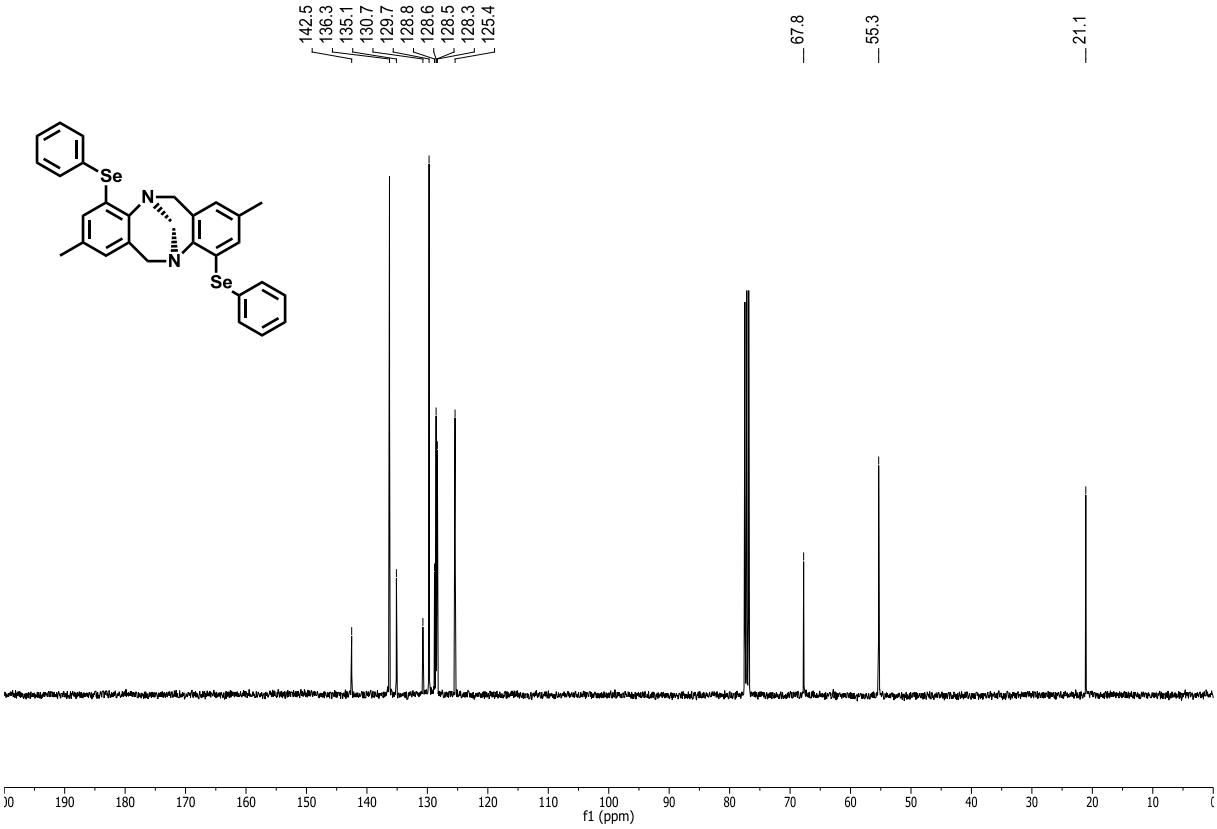
^{13}C NMR of (5*R*,11*R*)-**4d**



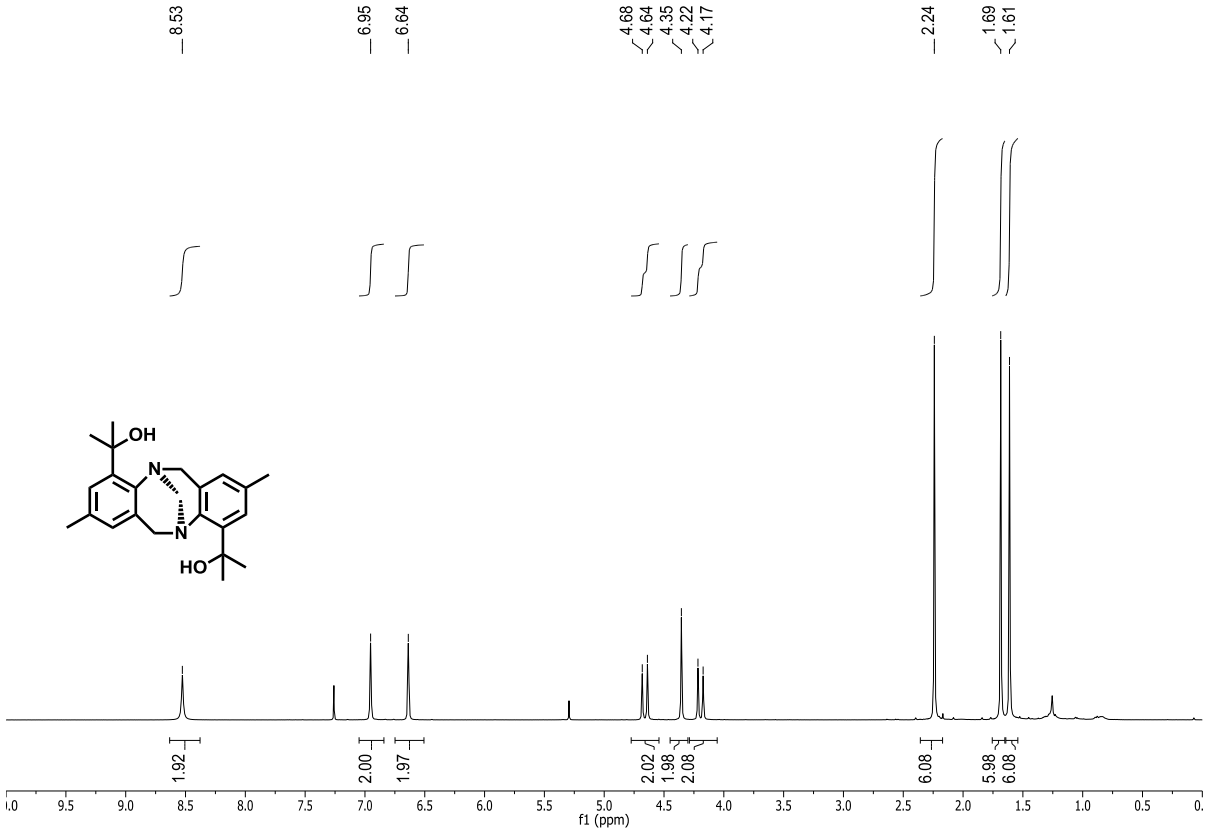
^{1}H NMR of (5*R*,11*R*)-**4e**



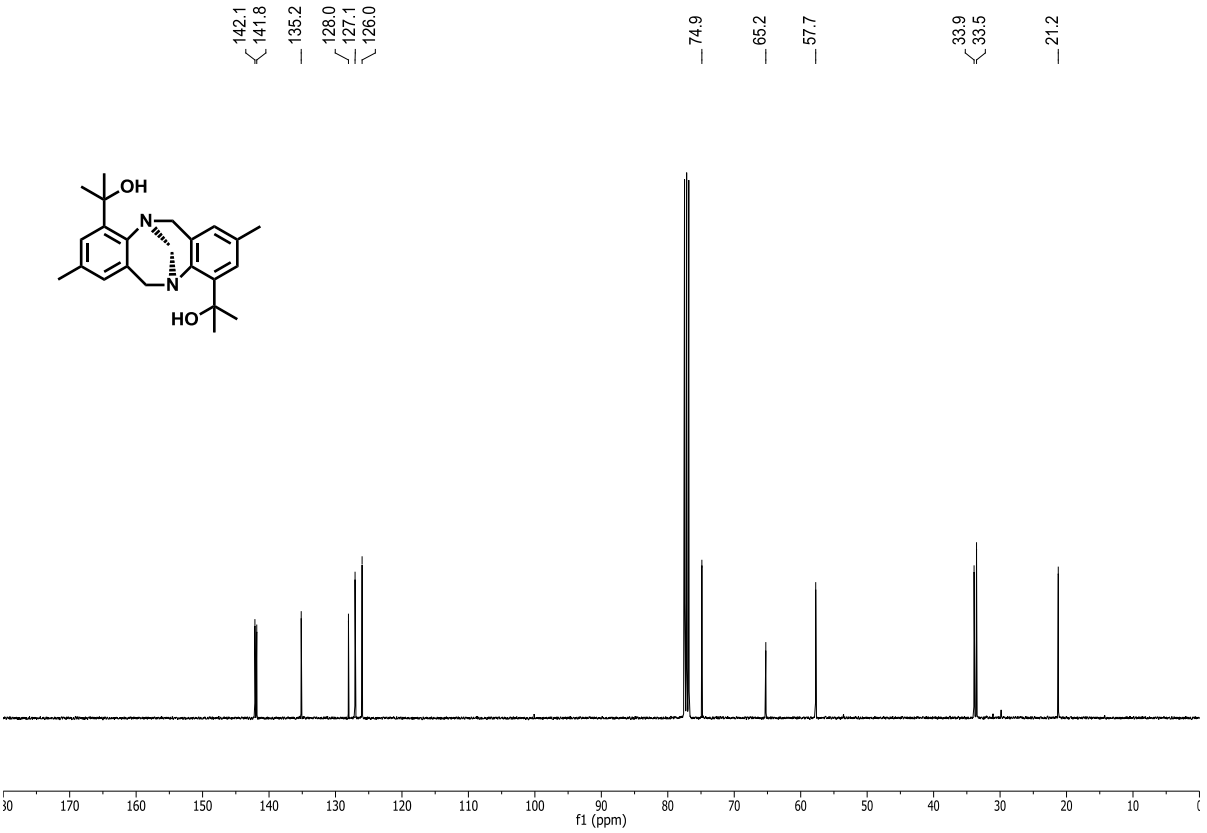
^{13}C NMR of (5*R*,11*R*)-**4e**



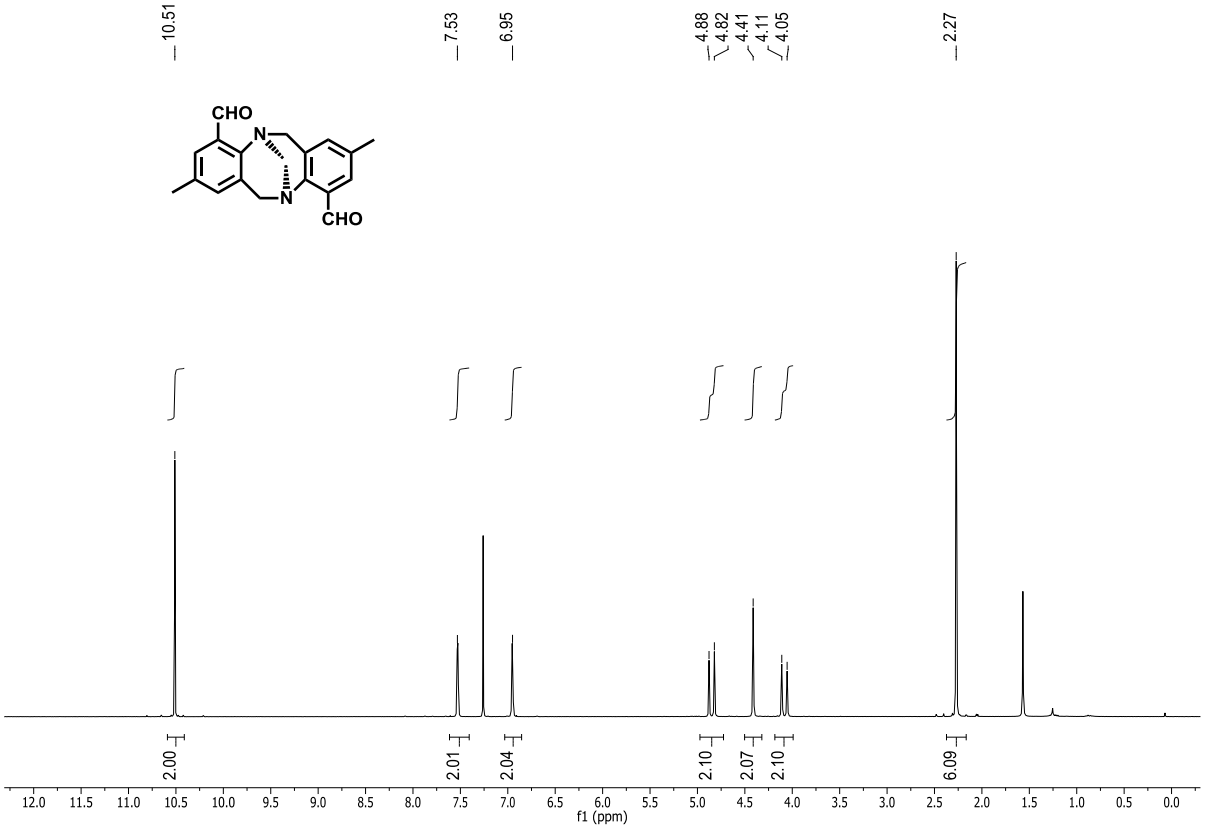
^{1}H NMR of (5*R*,11*R*)-**4f**



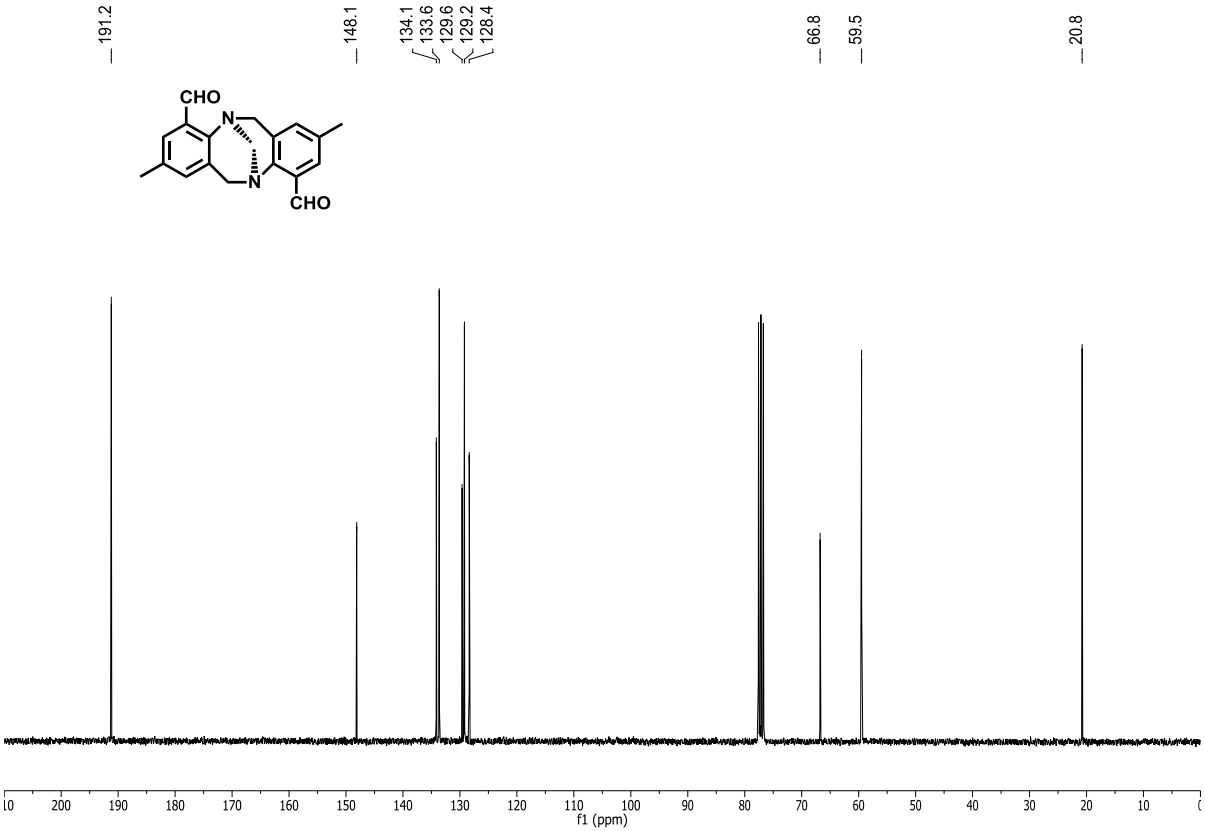
^{13}C NMR of (5*R*,11*R*)-**4f**



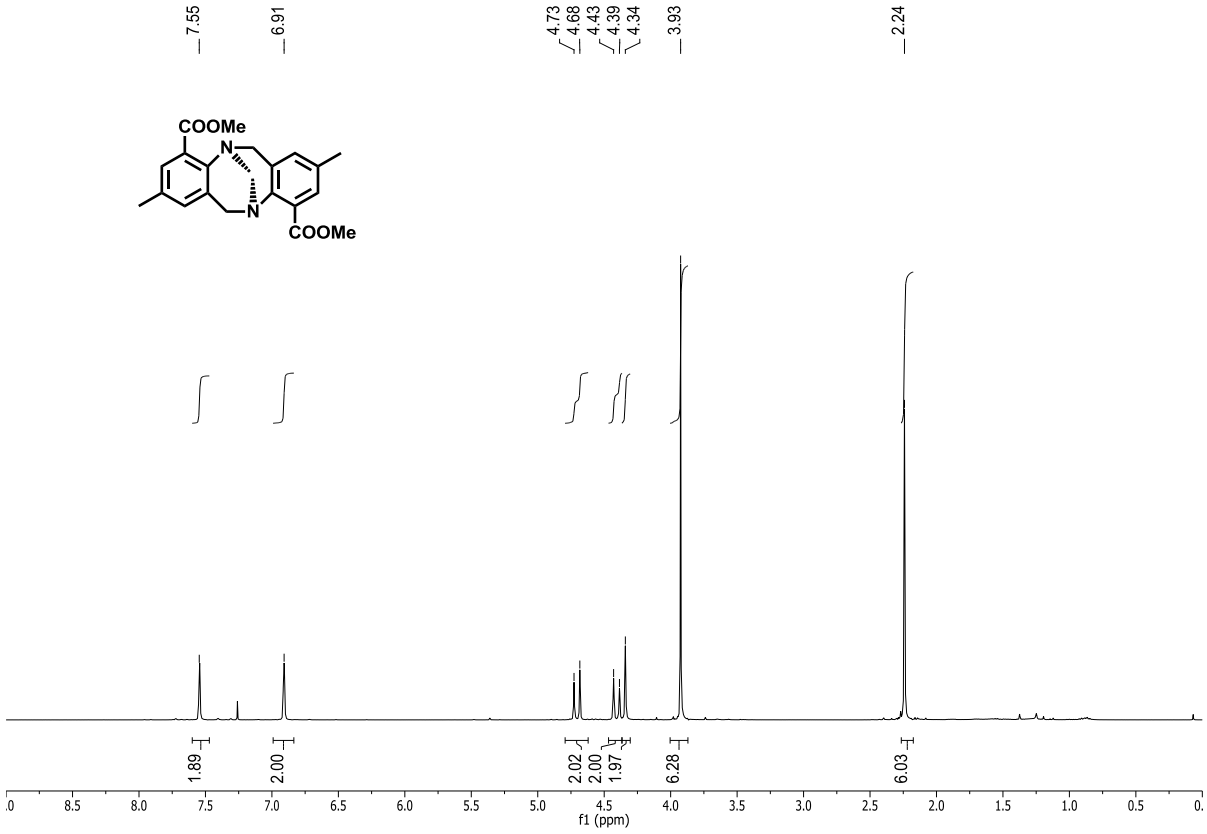
^{1}H NMR of (5*R*,11*R*)-**4g**



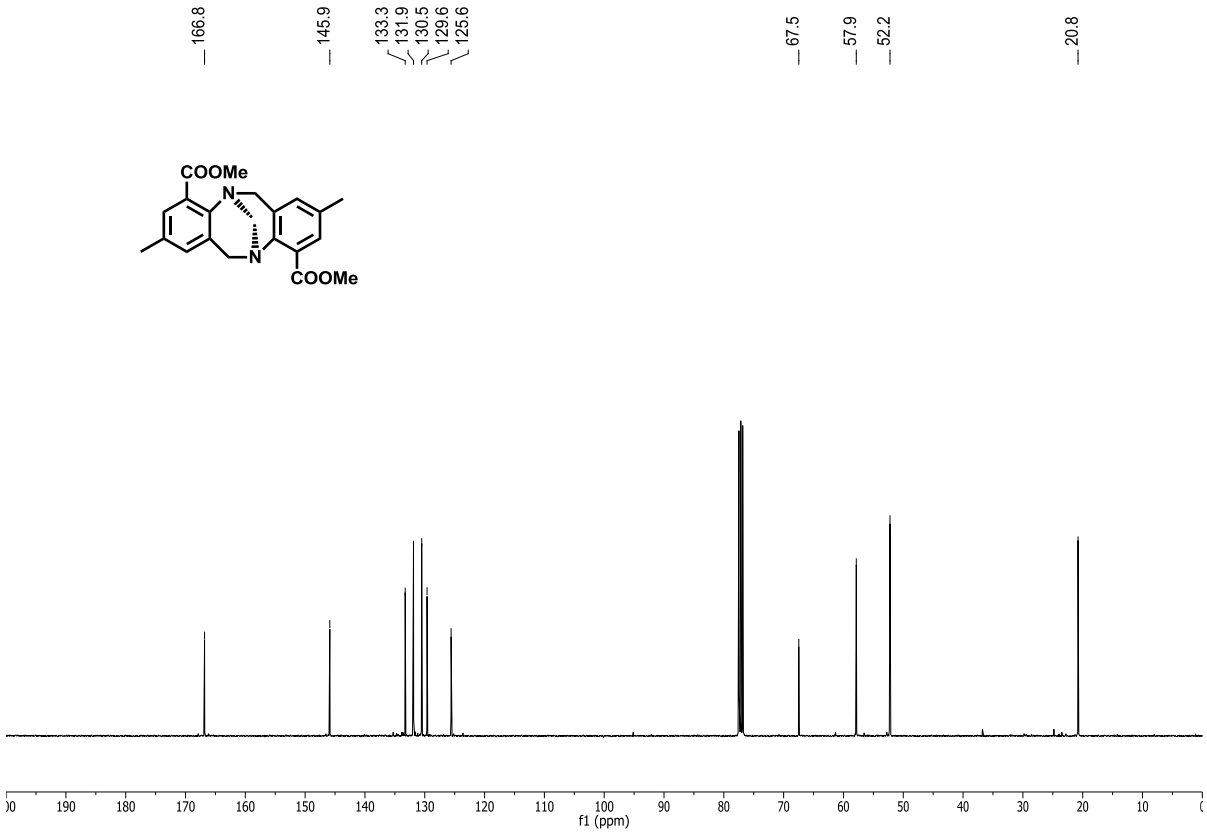
^{13}C NMR of (5*R*,11*R*)-**4g**



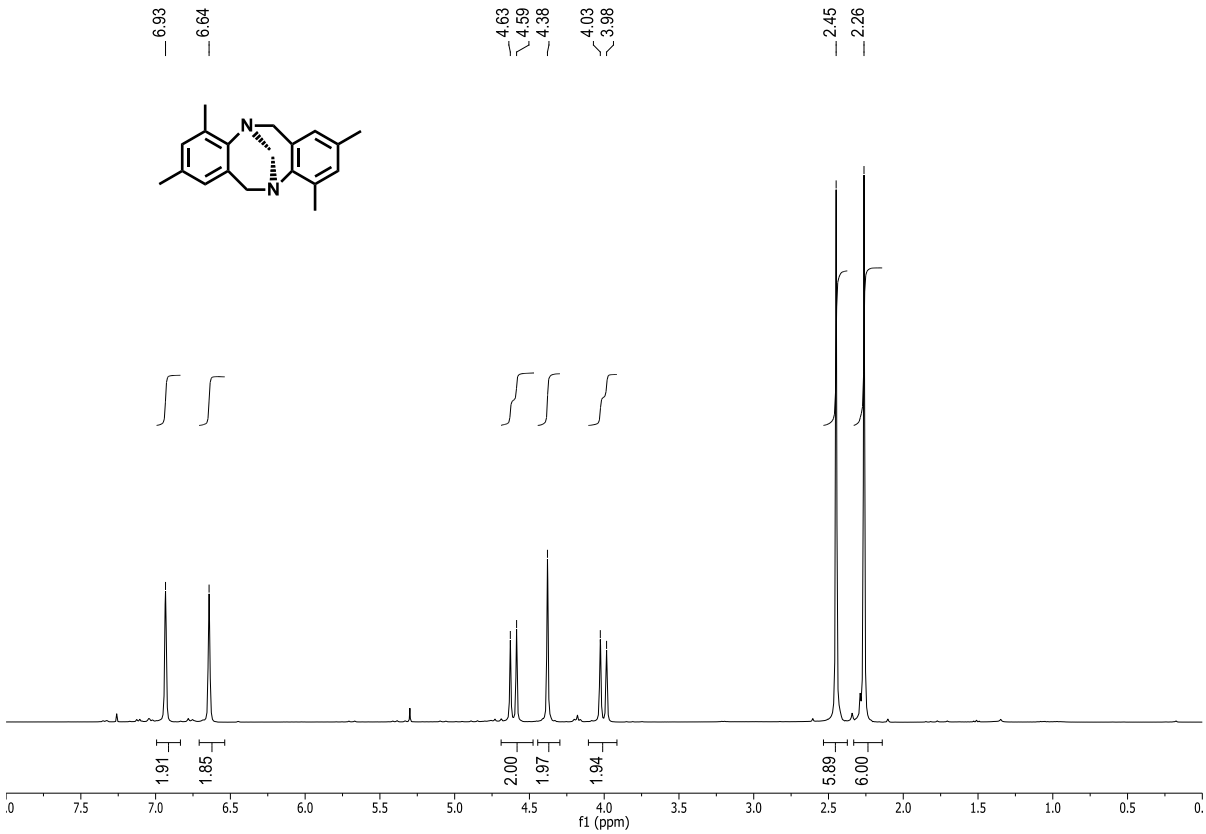
^{1}H NMR of (5*R*,11*R*)-**4h**)



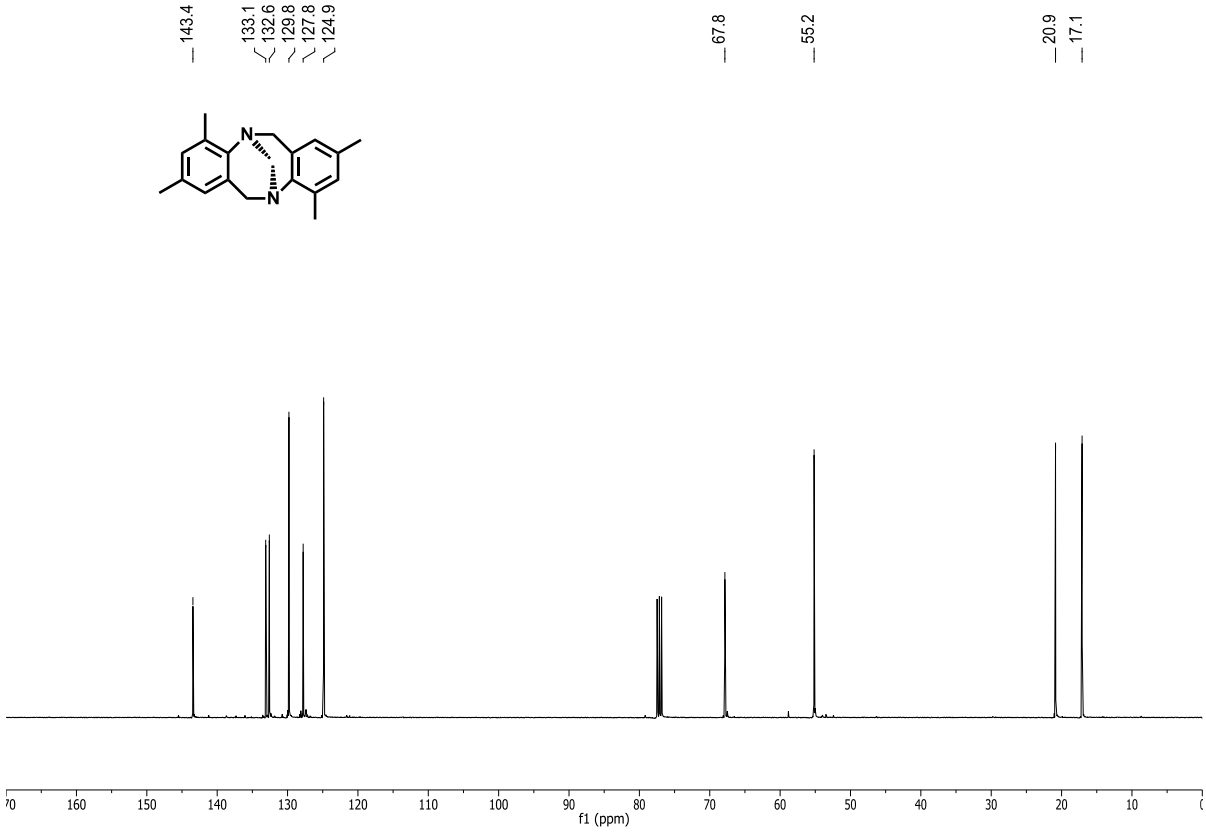
^{13}C NMR of (5*R*,11*R*)-**4h**)



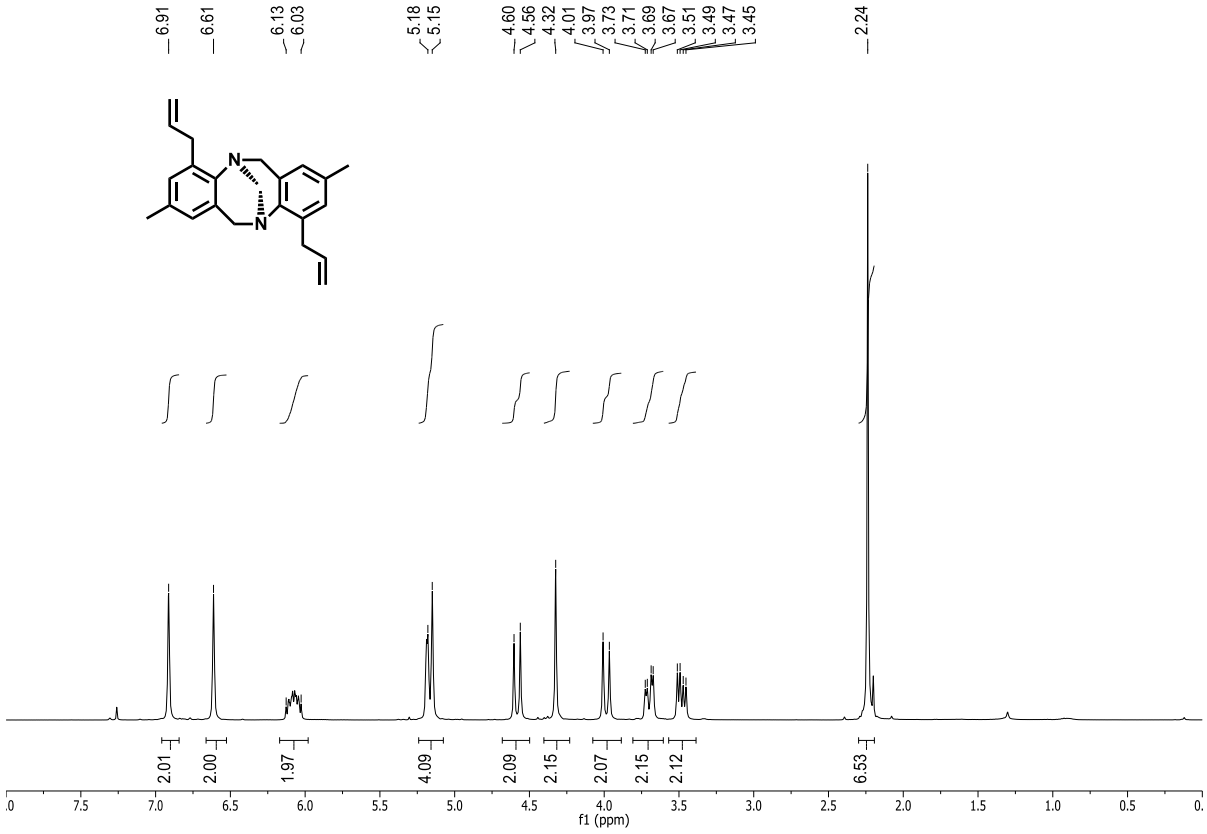
^{1}H NMR of (5*R*,11*R*)-**4i**



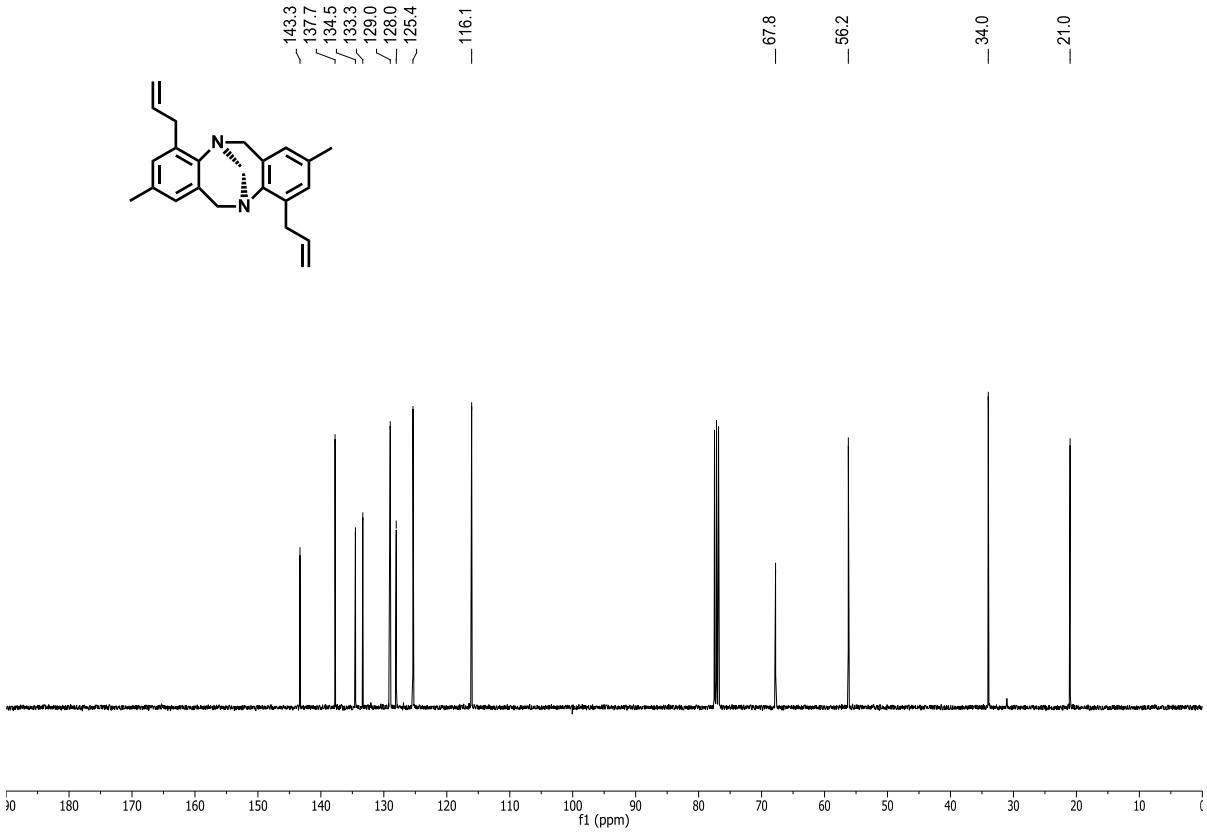
^{13}C NMR of (5*R*,11*R*)-**4i**



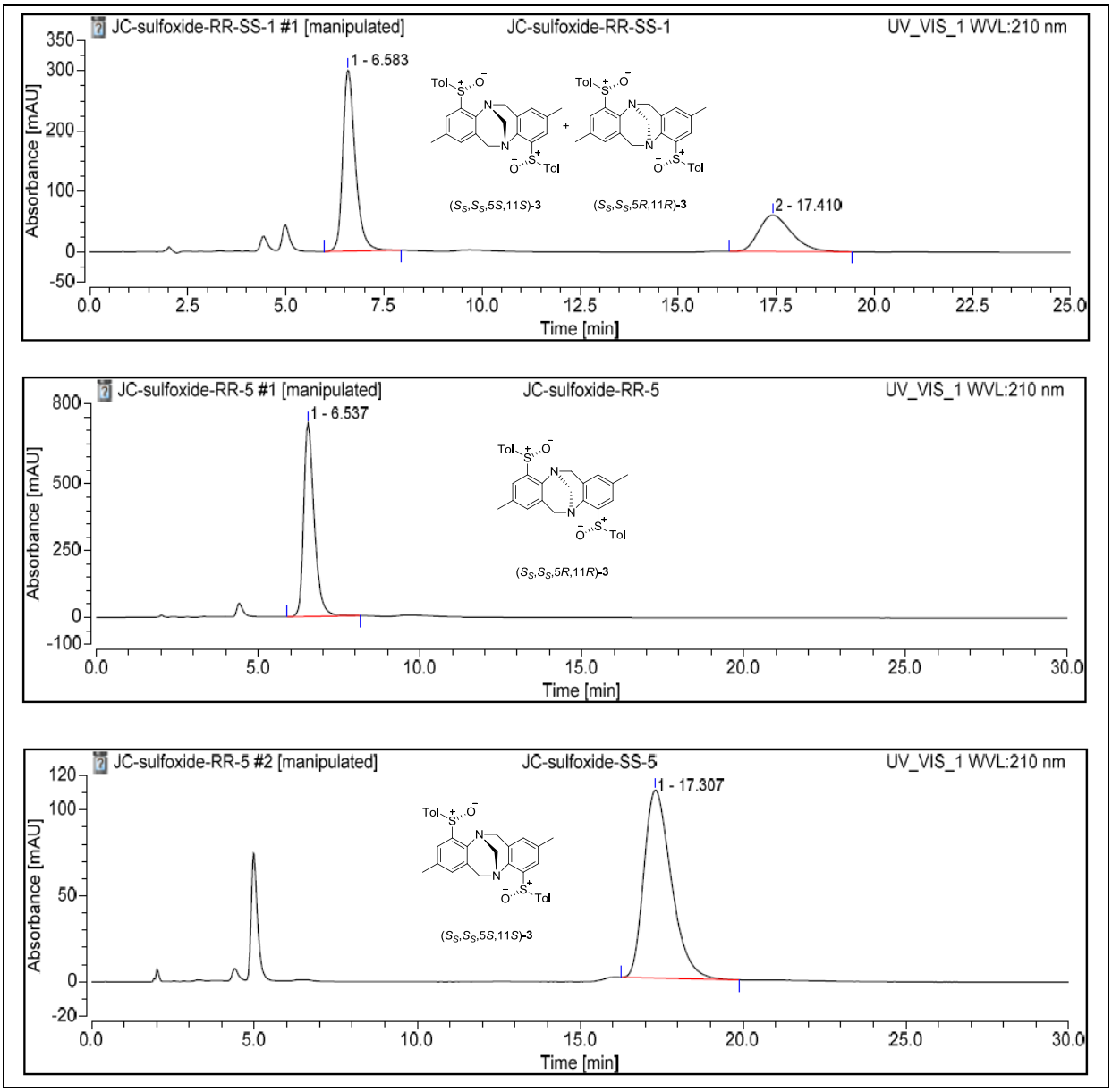
^{1}H NMR of ((5*R*,11*R*)-**4j**

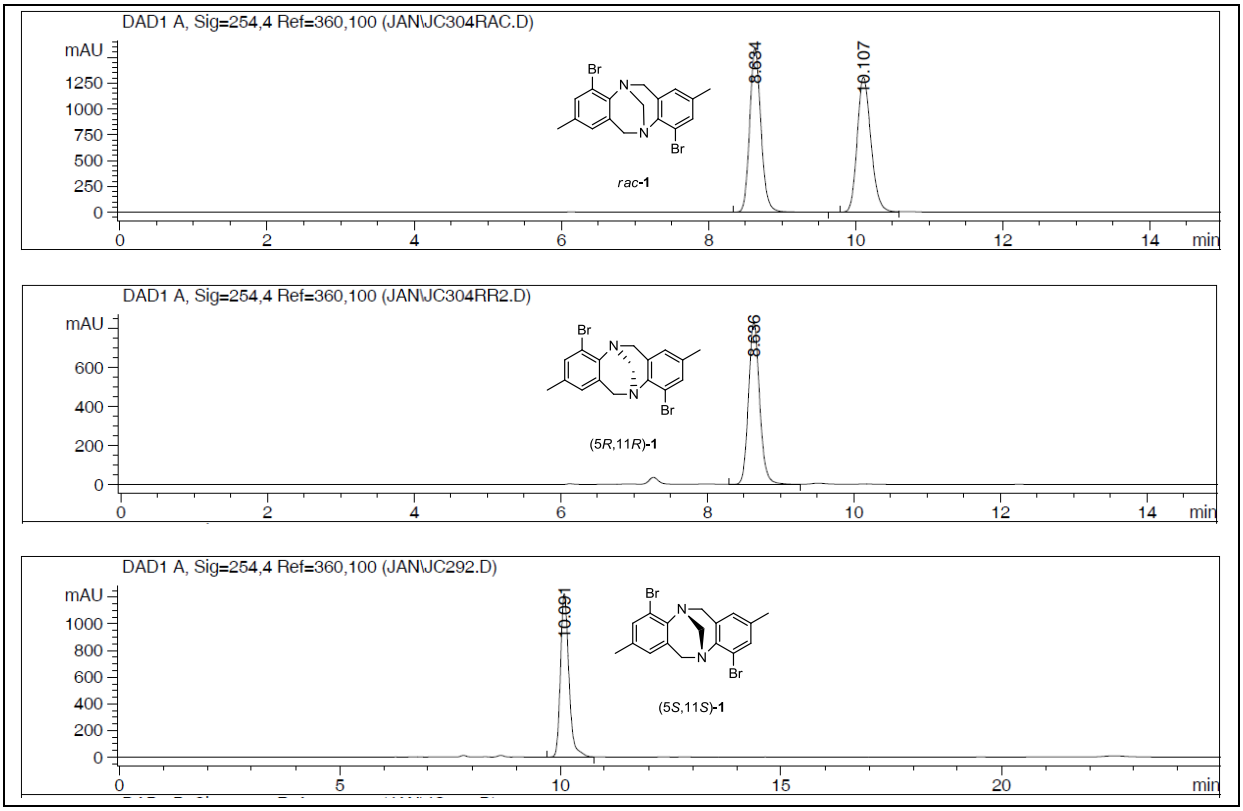


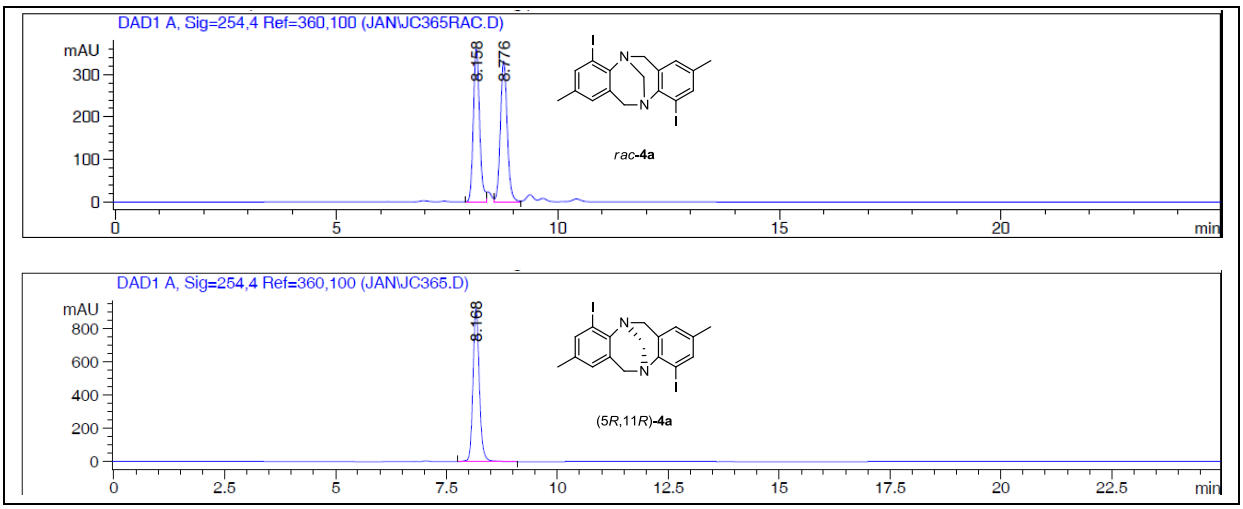
^{13}C NMR of ((5*R*,11*R*)-**4j**

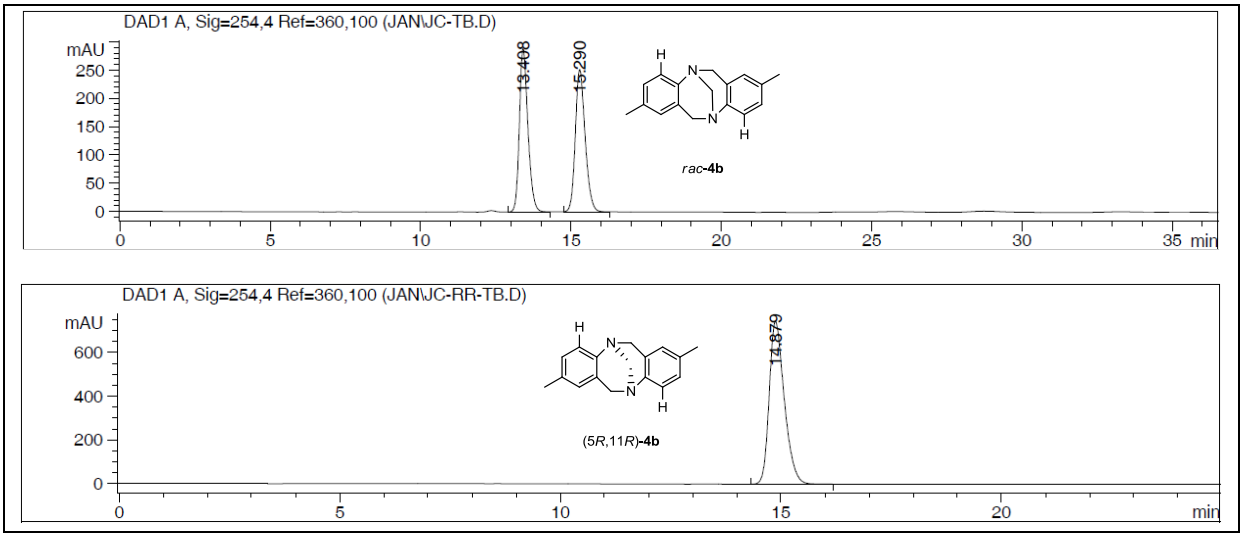


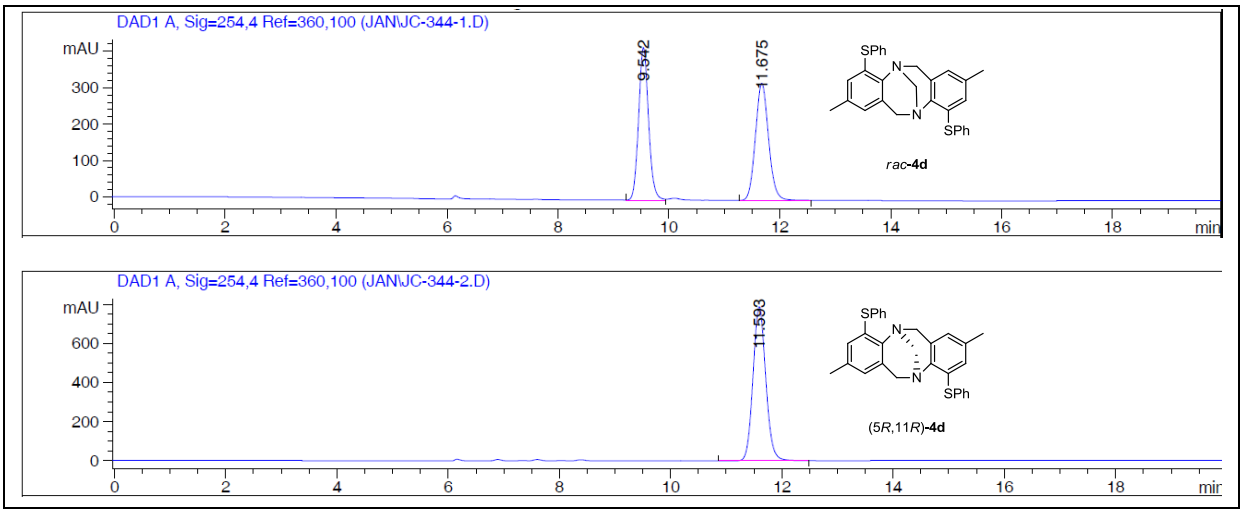
HPLC traces

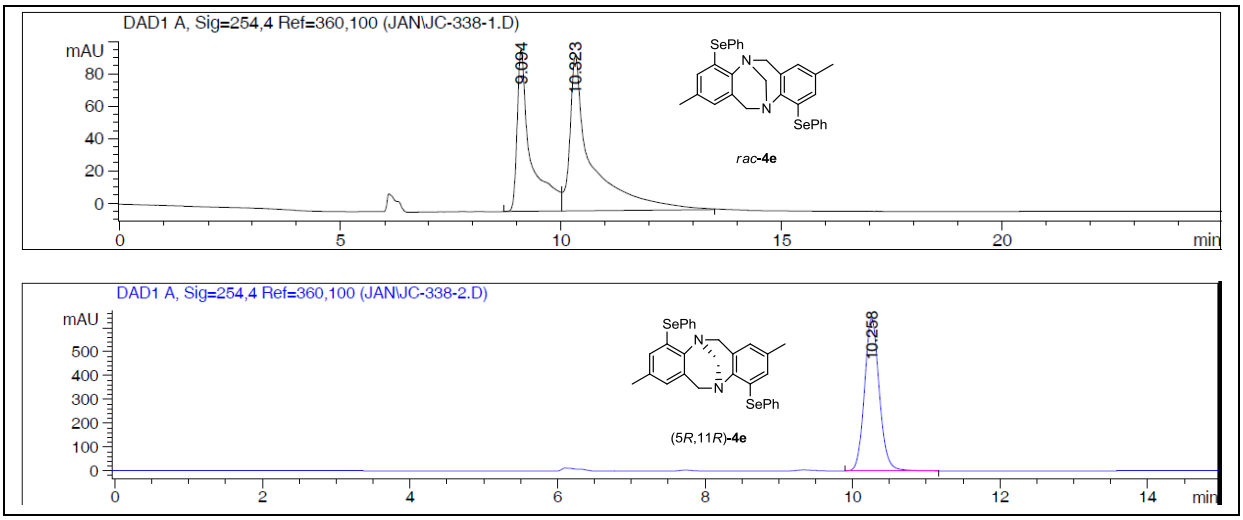

JC-sulfoxide-RR-SS-1 #1 [manipulated]
JC-sulfoxide-RR-SS-1
UV_VIS_1 WVL:210 nm
1 - 6.583
2 - 17.410
(SS,SS,5S,11S)-3
(SS,SS,5R,11R)-3
Absorbance [mAU]
Time [min]
JC-sulfoxide-RR-5 #1 [manipulated]
JC-sulfoxide-RR-5
UV_VIS_1 WVL:210 nm
1 - 6.537
(SS,SS,5R,11R)-3
Absorbance [mAU]
Time [min]
JC-sulfoxide-RR-5 #2 [manipulated]
JC-sulfoxide-SS-5
UV_VIS_1 WVL:210 nm
1 - 17.307
(SS,SS,5S,11S)-3
Absorbance [mAU]
Time [min]

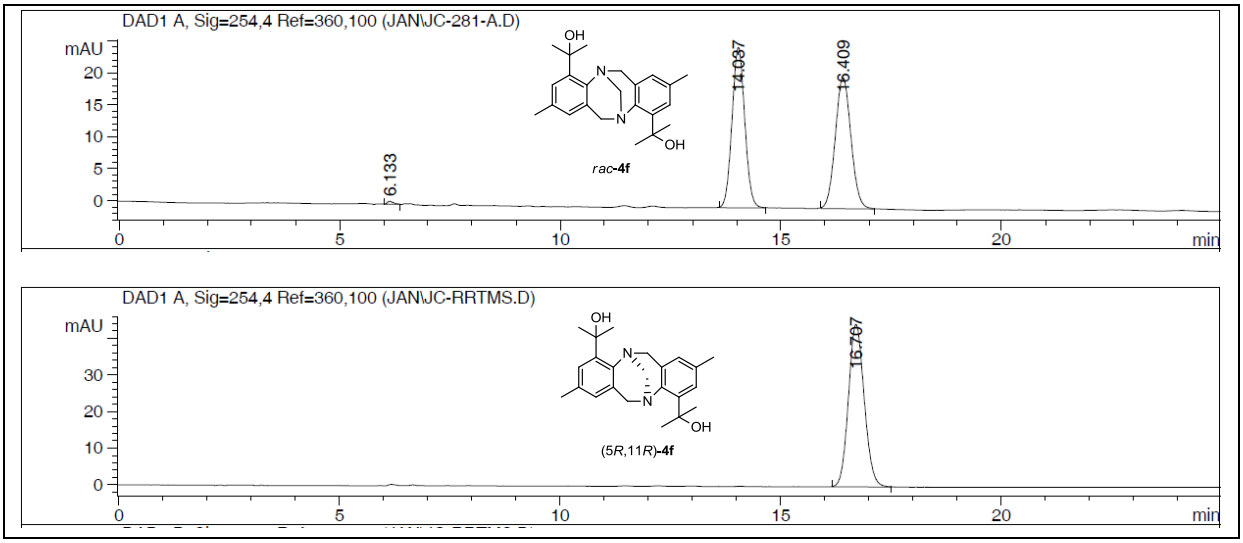

DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC304RAC.D)
mAU
8.694
10.107
rac-1
min
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC304RR2.D)
mAU
8.696
(5R,11R)-1
min
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC292.D)
mAU
10.091
(5S,11S)-1
min

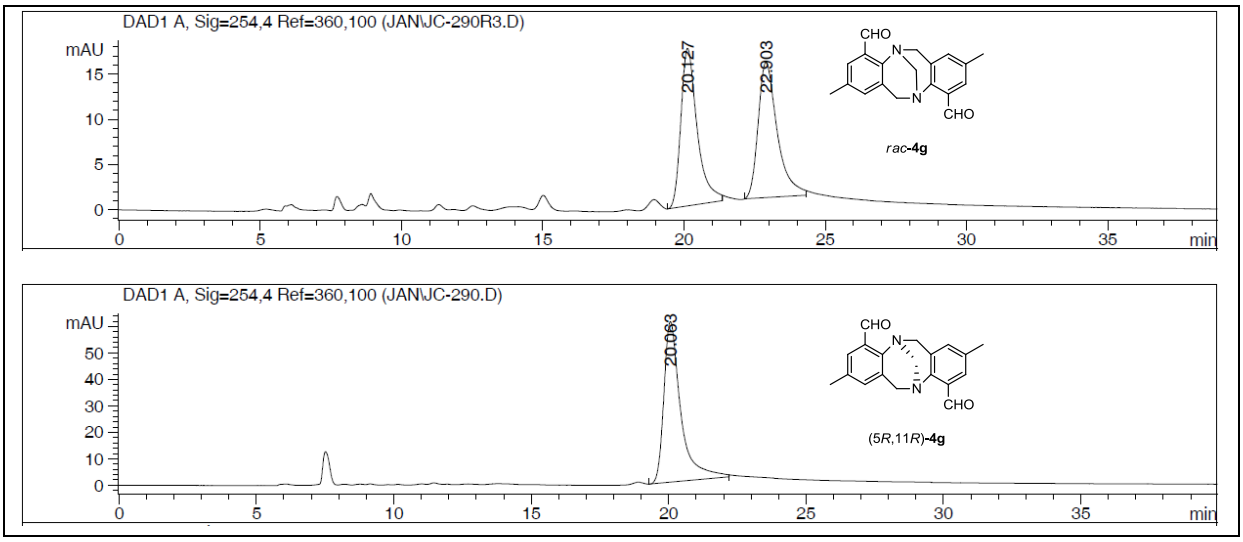

DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC365RAC.D)
mAU
8.158
8.776
rac-4a
min
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC365.D)
mAU
8.168
(5R,11R)-4a
min

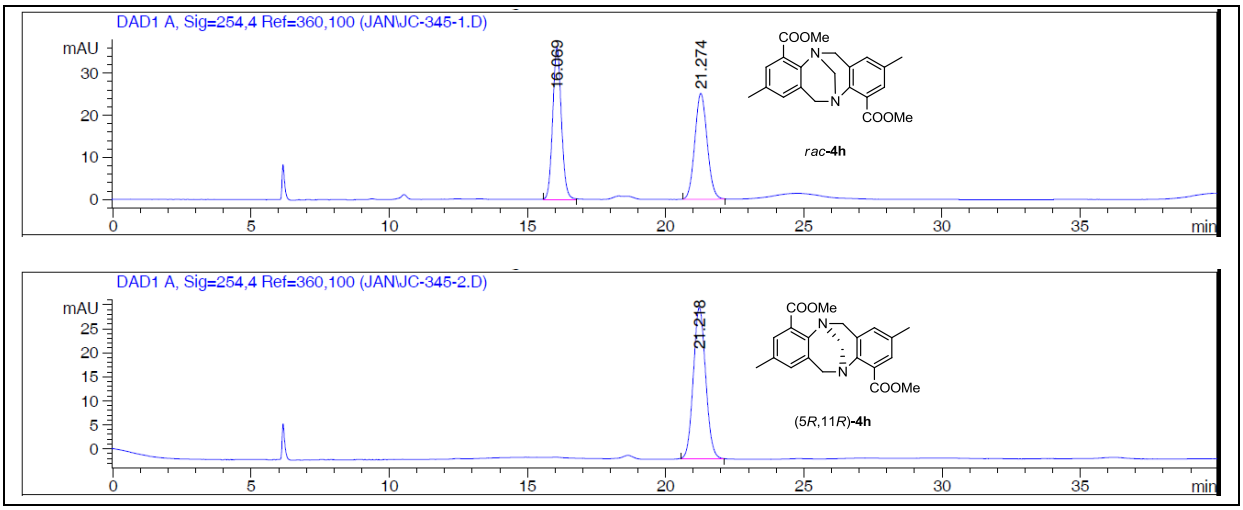

DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-TB.D)
mAU
13.408
15.290
rac-4b
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-RR-TB.D)
mAU
14.879
(5R,11R)-4b
min

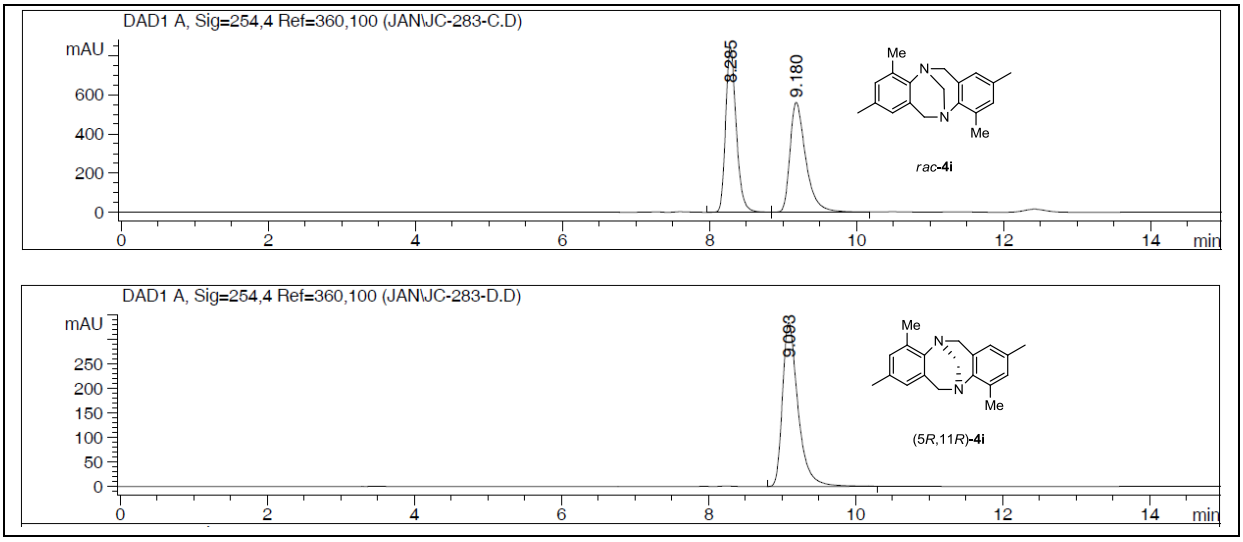

DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-344-1.D)
mAU
9.542
11.675
SPh
rac-4d
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-344-2.D)
mAU
11.593
(5R,11R)-4d
min

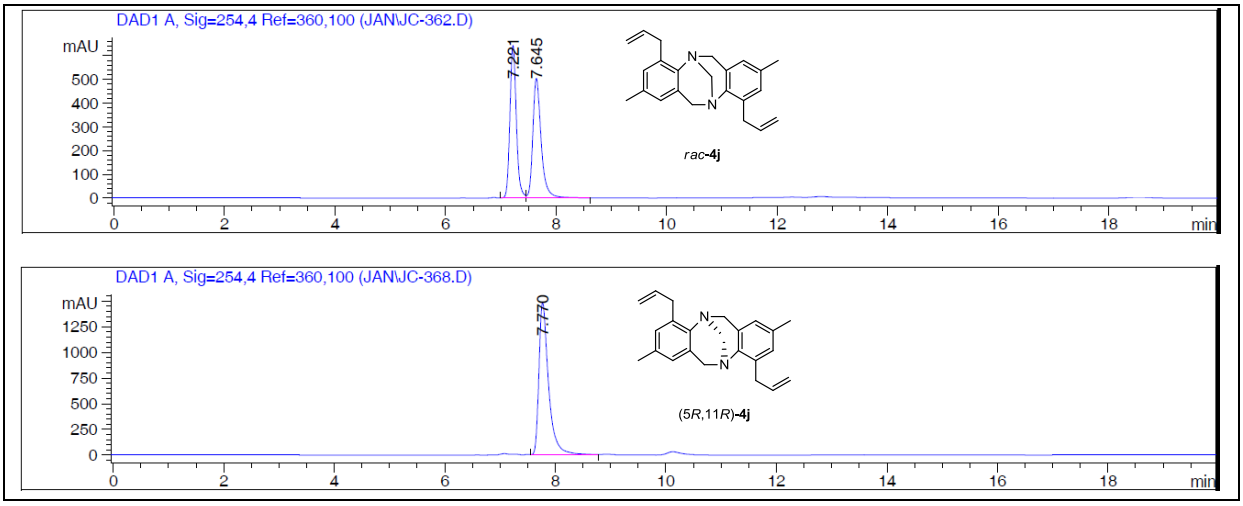

DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-338-1.D)
mAU
9.004
10.323
SePh
rac-4e
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-338-2.D)
mAU
10.258
(5R,11R)-4e
min


DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-281-A.D)
mAU
6.133
14.087
16.409
rac-4f
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-RRTMS.D)
mAU
16.797
(5R,11R)-4f
min


DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-290R3.D)
mAU
20.127
22.903
rac-4g
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-290.D)
mAU
20.063
(5R,11R)-4g
min


DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-345-1.D)
mAU
16.069
21.274
rac-4h
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-345-2.D)
mAU
21.218
(5R,11R)-4h
min


DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-283-C.D)
mAU
8.285
9.180
Me
N
N
Me
rac-4i
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-283-D.D)
mAU
9.093
Me
N
N
Me
(5R,11R)-4i
min


DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-362.D)
mAU
7.221
7.645
N
N
rac-4j
DAD1 A, Sig=254,4 Ref=360,100 (JAN\JC-368.D)
mAU
7.770
N
N
(5R,11R)-4j
min