Electronic Supplementary Material (ESI) for ChemComm.

Electrochemical Synthesis of 3a-Bromofuranoindolines and 3a-Bromopyrroloindolines Mediated by $MgBr_2$

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Supporting Information

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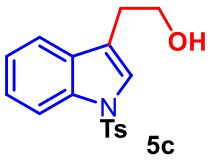
1. General Information

Unless otherwise stated, all reactions were carried out under air atmosphere. Dichloromethane was distilled under argon over CaH_2. Unless otherwise noted, all reagent-grade chemicals and other solvents were obtained from commercial suppliers and were used as received. Reactions were visualized under UV (254 nm) and/or by staining with Phospho Molybdic Acid or $KMnO_4$ solution followed by heating. Flash chromatography were performed on silica gel (Chromagel Si60ACC [70-200 μm]) as stationary phase. 1H NMR spectra were recorded on Bruker AC250 (250 MHz), Bruker DRX300 (300 MHz), Bruker AM360 (360 MHz) and Bruker 400 (400 MHz) instruments; chemical shifts (δ) are given in parts per million with respect to the residual protonated solvent (δ = 7.26 ppm for $CDCl_3$, δ = 2.50 ppm for d_6-DMSO), which served as an internal standard. ^{13}C NMR spectra were recorded on Bruker AC250 (62 MHz), DRX300 (75 MHz), AM360 (90 MHz) and chemical shifts are expressed with respect to the deuterated solvent (δ = 77.16 ppm for $CDCl_3$, δ = 39.52 ppm for d_6-DMSO). Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). High resolution mass spectra (HRMS) were recorded using Electrospray Ionization (ESI) method with a Bruker Daltonics MicrOTOF-Q instrument. Electrochemical experiments were performed with ElectraSyn 2.0 (IKA).

2. Cyclic voltammetry

Cyclic voltammetry were performed with AUTOLAB potentiostat/galvanostat PGSTAT302N. A glassy carbon disc (diameter 3 mm) working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference electrode were used at a scan rate of 100 mV/s. The experiments were conducted in a 20 mL vial without stirring in CH_3CN (10 mL) or CH_3CN/H_2O (8.0 mL/2.0 mL) with **5c** (0.05 mmol) and/or $MgBr_2$ (0.025 mmol) and nBu_4NBF_4 (1 mmol).



5c

***Figure S1**: Cyclic voltammetry of N-Ts tryptophol **5c** and/or $MgBr_2$ in the [0-1.4 V] range vs SCE.*

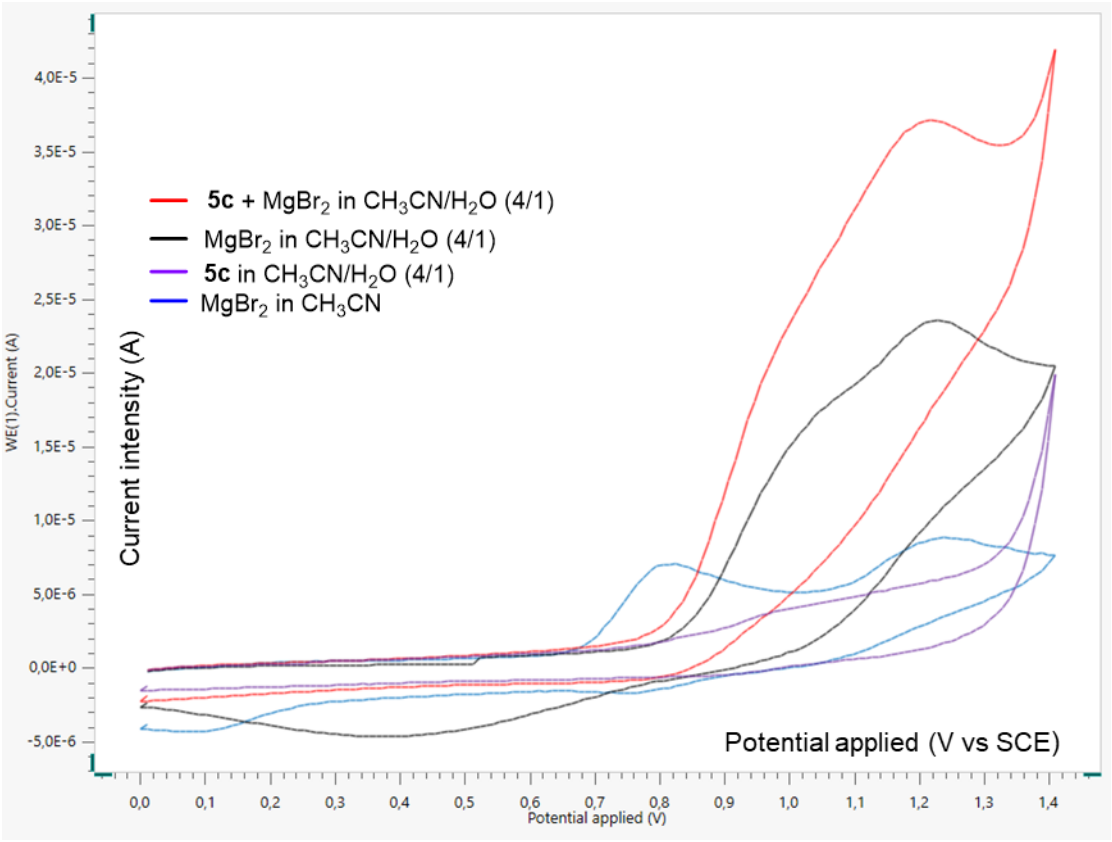
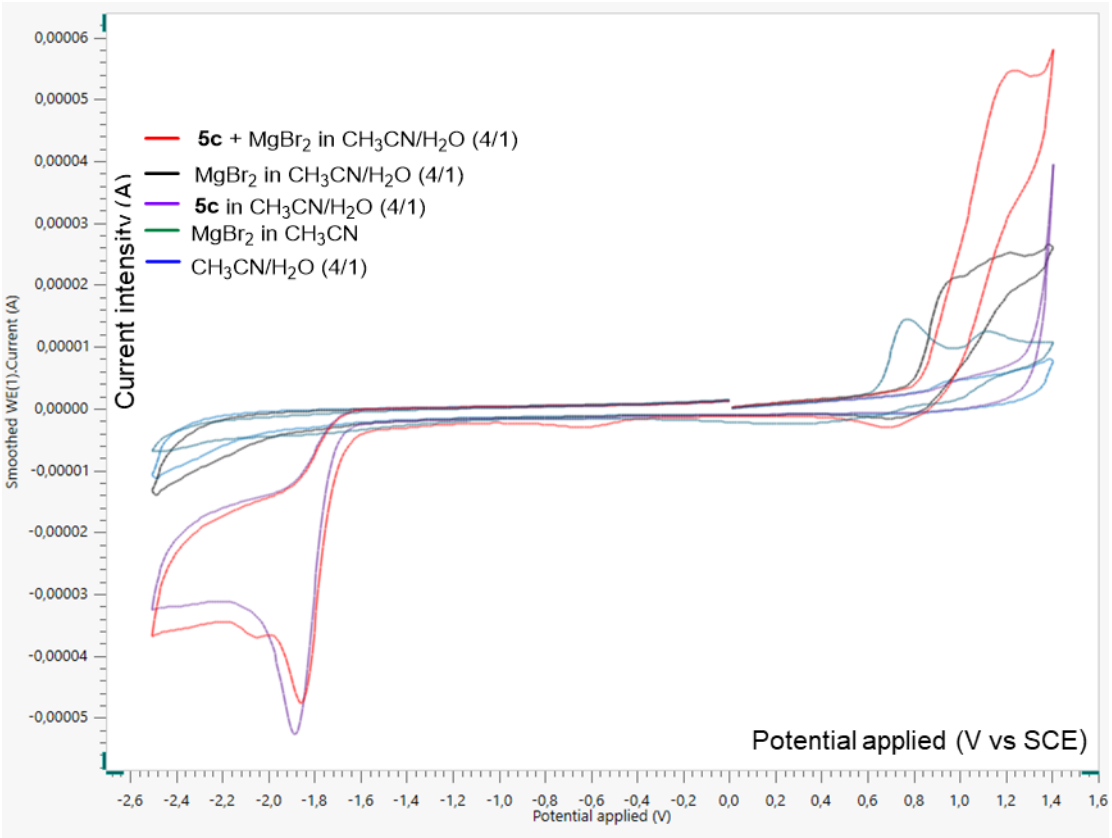


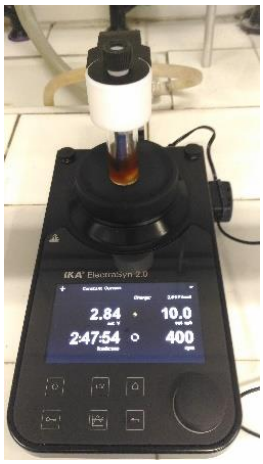
***Figure S2**: Cyclic voltammetry of N-Ts tryptophol **5c** and/or $MgBr_2$ in the [-2.5 to 1.5 V] range vs SCE.*



3. General experimental procedures

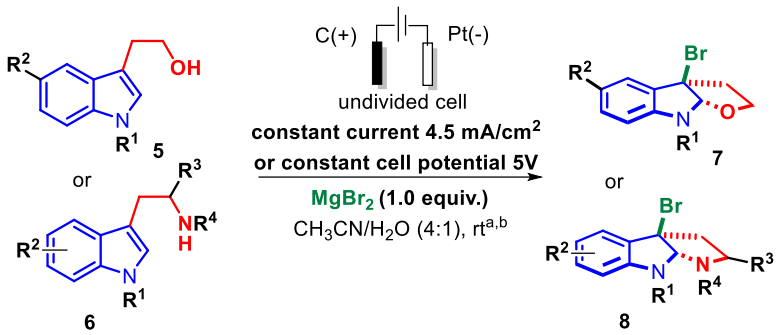
Electrolysis general informations

Electrochemical reactions were performed with ElectraSyn 2.0 package (IKA) using the constant current or constant voltage modes. The reactions were conducted in a 10 mL vial for 5 mL of solvent (20 mL vial for 15 mL of solvent) with a stir bar and a graphite-SK-50 (5.0 x 0.8 x 0.2 cm) working electrode (anode) and a platinum-plated (5.0 x 0.8 x 0.2 cm) counter-electrode (cathode) with a distance of 0.6 cm between the two electrodes.



Starting tryptophol, tryptamine and tryptophan derivatives were prepared according to known procedures.[1]

General Procedure A for the bromocyclization of tryptophol derivatives 1, tryptamine and tryptophan derivatives 3.



To a 10 mL vial with a stir bar were successively added a tryptophol derivative **5**, tryptamine or tryptophan derivative **6** (0.2 mmol), $MgBr_2$ (37 mg, 0.2 mmol, 1.0 equiv), 1.0 mL of distilled H_2O and 4.0 mL of CH_3CN (0.04 M). The vial was covered with the electrode holder. The electrolysis was carried out at RT using a **constant current of 5.0 mA (4.5 mA/cm^2) or a constant cell potential of 5V** between a graphite anode and a platinum plate cathode (1.4 x 0.8 x 0.2 cm submerged in solution) with stirring (1000 rpm). The complete consumption of the starting indole derivative was checked by TLC (15% to 30% AcOEt/petroleum ether). The reaction was then quenched with H_2O and diluted with AcOEt. The organic and aqueous phases were separated. The

[1] (a) Xu, J.; Tong, R. *Green Chem.* **2017**, *19*, 2952-2956.

aqueous phase was then extracted twice with AcOEt. The combined organic phases were then dried over $MgSO_4$, filtered and concentrated under vacuum. The crude was then purified by flash column chromatography or preparative TLC (15% to 25% AcOEt/ petroleum ether or 1% MeOH/ DCM).

4. Optimization Study

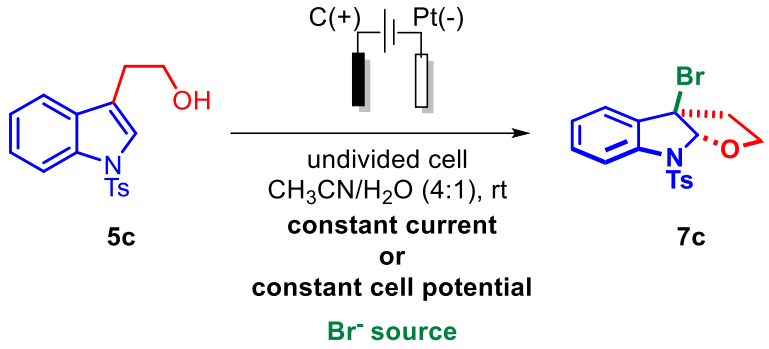
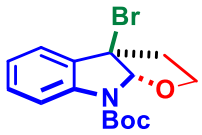


Table S1. *Optimization of the bromocyclyzation of* ***5c*** *into* ***7c*** *according to general procedure* ***A***.

Br source	Equiv.	Constant Current	Constant Cell Potential	Isolated Yield of 7c
NaBr	1.0	4.5 mA/cm^2		15%
KBr	1.0	4.5 mA/cm^2		10%
$FeBr_3$	1.0	4.5 mA/cm^2		13%
$FeBr_2$	1.0	4.5 mA/cm^2		70%
$ZnBr_2$	1.0	4.5 mA/cm^2		76%
$MgBr_2$	1.0	4.5 mA/cm^2		90%
$MgBr_2$	0.5	4.5 mA/cm^2		56%
$MgBr_2$	10.0	4.5 mA/cm^2		89%
$MgBr_2$	1.0	9 mA/cm^2		88%
$MgBr_2$	1.0	2.7 mA/cm^2		82%
$MgBr_2$	1.0		5 V	93%
$MgBr_2$	1.0		6 V	73%
$MgBr_2$	1.0		4 V	83%

5. Experimental details and characterization of compounds

***tert*-butyl 3a-bromo-3,3a-dihydro-2H-furo[2,3-b]indole-8(8aH)-carboxylate (7a)**



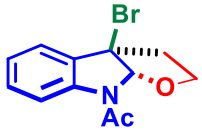
7a *(dr 95:5)*

7a was prepared from *tert*-butyl 3-(2-hydroxyethyl)-1H-indole-1-carboxylate **5a** (52 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 144 minutes at room temperature (2.20 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 95:5) led to **7a** (54 mg, 0.159 mmol, **80%**, 95:5 dr) as white solid.

7a was prepared from *tert*-butyl 3-(2-hydroxyethyl)-1H-indole-1-carboxylate **5a** (52 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 62 min minutes at room temperature (2.23 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 95:5) led to **7a** (51 mg, 0,150 mmol, **75%**, 95:5 dr) as white solid.

Rf: 0.62 (PE/EtOAc 9:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.82 (br, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 8.3 Hz, 1H), 7.06 (td, *J* = 7.6, 0.9 Hz, 1H), 6.19 (s, 1H), 4.02-3.94 (m, 1H), 3.52-3.40 (m, 1H), 2.94-2.82 (m, 1H), 2.82-2.74 (m, 1H), 1.59 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 151.8, 141.8, 131.7, 130.5, 124.9, 123.7, 114.9, 100.8, 82.0, 67.8, 61.8, 45.0, 28.4.
HRMS-ESI: *m/z* 362.0350 ([M+Na]$^+$, $C_{15}H_{18}BrNNaO_3^+$ calcd. 362.0362).

1-(3a-bromo-3,3a-dihydro-2H-furo[2,3-b]indol-8(8aH)-yl)ethanone (7b)



7b *(dr 95:5)*

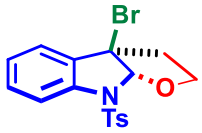
7b was prepared from 1-(3-(2-hydroxyethyl)-1H-indol-1-yl)ethanone **5b** (41 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 144 minutes at room temperature (2.20 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **7b** (45 mg, 0.160 mmol, **80%**, 95:5 dr) as colorless oil.

7b was prepared from 1-(3-(2-hydroxyethyl)-1H-indol-1-yl)ethanone **5b** (41 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 68 minutes at room temperature (2.19 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **7b** (39 mg, 0.138 mmol, **69%**, 95:5 dr) as colorless oil.

Rf: 0.74 (PE/EtOAc 7:3).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 8.15 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 1 Hz,

1H), 7.32-7.27 (m, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 6.13 (s, 1H), 4.00 (ddd, *J* = 9.0, 7.4, 1.8 Hz, 1H), 3.54-3.47 (m, 1H), 2.96-2.86 (m, 1H), 2.84-2.78 (m, 1H), 2.37 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 169.9, 141.9, 131.7, 130.7, 124.9, 124.7, 116.7, 101.7, 68.1, 62.3, 45.4, 23.7.
HRMS-ESI: *m/z* 303.9947 ([M+Na]$^+$, $C_{12}H_{12}BrNNaO_2^+$ calcd. 303.9944).

3a-bromo-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7c):



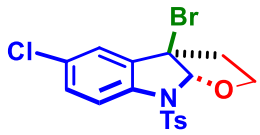
7c *(dr 95:5)*

7c was prepared from tert-butyl 2-(1-tosyl-1H-indol-3-yl)ethanol **5c** (63 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 150 minutes at room temperature (2.37 F/mol), followed by aqueous work-up, preparative TLC purification (DCM/MeOH 100:1) led to **7c** (71 mg, 0.180 mmol, **90%**, 95:5 dr) as colorless solid.

7c was prepared from tert-butyl 2-(1-tosyl-1H-indol-3-yl)ethanol **5c** (63 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 108 minutes at room temperature (3.00 F/mol) followed by aqueous work-up, preparative TLC purification (DCM/MeOH 100:1) led to **7c** (73 mg, 0.186 mmol, **93%**, 95:5 dr) as colorless solid.

Rf: 0.55 (PE/EtOAc 5:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.79 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.28-7.22 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.23 (s, 1H), 3.99 (t, *J* = 8.2 Hz, 1H), 3.46-3.38 (m, 1H), 2.88-2.78 (m, 1H), 2.74-2.69 (m, 1H), 2.36 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 144.5, 140.7, 135.8, 132.6, 130.7, 129.8, 127.5, 125.4, 124.9, 114.3, 103.4, 68.1, 61.5, 44.8, 21.7.
HRMS-ESI: *m/z* 415.9926 ([M+Na]$^+$, $C_{17}H_{16}BrNNaO_3S^+$ calcd. 415.9926).

3a-bromo-5-chloro-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7d):



7d *(dr 95:5)*

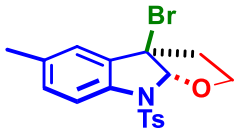
7d was prepared from 2-(5-chloro-1-tosyl-1H-indol-3-yl)ethanol **5d** (69.8 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 128 minutes at room temperature (2.00 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **7d** (60 mg, 0.144 mmol, **72%**, 95:5 dr) as colorless solid.

7d was prepared from 2-(5-chloro-1-tosyl-1H-indol-3-yl)ethanol **5d** (69.8 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 80 minutes at room temperature (2.50 F/mol) followed by aqueous work-up, preparative TLC purification

(PE/EtOAc 8:2) led to **7d** (53 mg, 0.124 mmol, **62%**, 95:5 dr) as colorless solid.

Rf: 0.35 (PE/EtOAc 7:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.77 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.32-7.22 (m, 4H), 6.21 (s, 1H), 4.04-3.99 (m, 1H), 3.47-3.40 (m, 1H), 2.86-2.77 (m, 1H), 2.71-2.66 (m, 1H), 2.38 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 144.8, 139.3, 135.3, 134.3, 130.9, 130.1, 129.9, 127.5, 125.5, 115.5, 103.7, 68.1, 60.4, 44.6, 21.7.
HRMS-ESI: *m/z* 449.9523 ([M+Na]$^+$, $C_{17}H_{15}BrClNNaO_3S^+$ calcd. 449.9537).

3a-bromo-5-methyl-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7e):



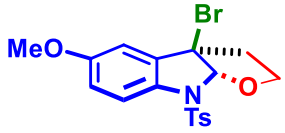
7e *(dr 95:5)*

7e was prepared from 2-(5-methyl-1-tosyl-1H-indol-3-yl)ethanol **5e** (65.8 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 138 minutes at room temperature (2.13 F/mol), followed by aqueous work-up, preparative TLC purification (DCM/MeOH 110:1) led to **7e** (51 mg, 0.126 mmol, **63%**, 95:5 dr) as colorless solid.

7e was prepared from 2-(5-methyl-1-tosyl-1H-indol-3-yl)ethanol **5e** (65.8 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 95 minutes at room temperature (2.96 F/mol) followed by aqueous work-up, preparative TLC purification (DCM/MeOH 110:1) led to **7e** (48 mg, 0.118 mmol, **59%**, 95:5 dr) as colorless solid.

Rf: 0.63 (PE/EtOAc 8:2).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.76 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 7.07 (dd, *J* = 8.3 Hz, *J* = 1.2 Hz, 1H), 6.19 (s, 1H), 4.02-3.97 (m, 1H), 3.47-3.40 (m, 1H), 2.85-2.77 (m, 1H), 2.73-2.68 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 144.4, 138.4, 135.6, 134.9, 132.5, 131.6, 129.8, 127.5, 125.6, 114.4, 103.5, 68.1, 61.8, 44.8, 21.7, 21.0.
HRMS-ESI: *m/z* 408.0248 ([M+H]$^+$, $C_{18}H_{19}BrNO_3S^+$ calcd.408.0264).

3a-bromo-5-methoxy-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7f):



7f *(dr 95:5)*

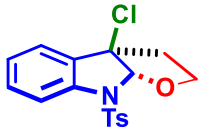
7f was prepared from 2-(5-methoxy-1-tosyl-1H-indol-3-yl)ethanol **7f** (69 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 128 minutes at room temperature (2.00 F/mol), followed by aqueous work-up, preparative TLC

purification (PE/EtOAc 8:2) led to **7f** (62 mg, 0.146 mmol, **73%**, 95:5 dr) as colorless solid.

7f was prepared from 2-(5-methoxy-1-tosyl-1H-indol-3-yl)ethanol **5f** (69 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 70 minutes at room temperature (2.56 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **7f** (70 mg, 0.166 mmol, **83%**, 95:5 dr) as colorless solid.

Rf: 0.68 (PE/EtOAc 7:3).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.72 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.85-6.81 (m, 2H), 6.15 (s, 1H), 4.01-3.96 (m, 1H), 3.76 (s, 3H), 3.49-3.41 (m, 1H), 2.84-2.73 (m, 1H), 2.71-2.66 (m, 1H), 2.35 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 157.6, 144.4, 135.4, 134.1, 133.9, 129.8, 127.5, 116.9, 116.0, 109.8, 103.8, 68.0, 61.6, 55.8, 44.7, 21.6.
HRMS-ESI: *m/z* 446.0022 ([M+Na]$^+$, $C_{18}H_{18}BrNNaO_4S^+$ calcd.446.0032).

3a-chloro-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7g):



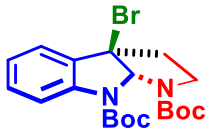
7g *(dr 95:5)*

7g was prepared from tert-butyl 2-(1-tosyl-1H-indol-3-yl)ethanol **5c** (63 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)** and $MgCl_2$ (18.8 mg, 0.2 mmol). After stirring 128 minutes at room temperature(2.00 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **7g** (24 mg, 0.068 mmol, **34%**, 95:5 dr) as colorless solid.

7g was prepared from tert-butyl 2-(1-tosyl-1H-indol-3-yl)ethanol **5c** (63 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V** and $MgCl_2$ (18.8 mg, 0.2 mmol). After stirring 303 minutes at room temperature (6.96 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **7g** (26 mg, 0.074 mmol, **37%**, 95:5 dr) as colorless solid.

Rf: 0.33 (PE/EtOAc 5:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.79 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.35-7.25 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.10 (td, *J* = 7.5 Hz, *J* = 0.9 Hz, 1H), 6.12 (s, 1H), 4.13-4.07 (m, 1H), 3.53-3.44 (m, 1H), 2.80-2.69 (m, 1H), 2.66-2.59 (m, 1H), 2.37 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 144.6, 141.2, 135.7, 131.4, 130.9, 129.8, 127.5, 125.0, 124.9, 114.3, 102.7, 72.9, 68.3, 43.9, 21.7.
HRMS-ESI: *m/z* 372.0428 ([M+Na]$^+$, $C_{17}H_{16}ClNNaO_3S^+$ calcd. 372.0432).

di-tert-butyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (8a):



8a *(dr 95:5)*

8a was prepared from tert-butyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate **6a** (69.2 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 138 minutes at room temperature (2.15 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8a** (53 mg, 0.122 mmol, **61%**, 95:5 dr) as colorless oil.

8a was prepared from tert-butyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate **6a** (69.2 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 60 minutes at room temperature, the solution was charged to 2.36 F/mol followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8a** (40 mg, 0.092 mmol, **46%**, 95:5 dr) as colorless oil.

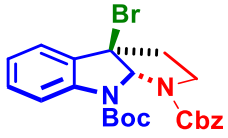
Rf: 0.54 (PE/EtOAc 9:1).

^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.58 (d, *J* = 6.5 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.28 (td, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.08 (td, *J* = 7.4 Hz, *J* = 0.8 Hz, 1H), 6.43 (s, 1H), 3.75-3.69 (m, 1H), 2.84-2.69 (m, 3H), 1.58 (s, 9H), 1.48 (s, 9H).

^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.5, 152.3, 142.2, 132.8, 130.4, 124.2, 123.9, 117.5, 83.9, 82.2, 80.9, 62.3, 46.3, 41.7, 28.5, 28.4.

HRMS-ESI: *m/z* 461.1029 ([M+Na]$^+$, $C_{20}H_{27}BrN_2NaO_4^+$ calcd. 461.1046).

1-benzyl 8-tert-butyl 3a-bromo-3,3a-dihydropyrrolo[2,3-b]indole-1,8(2H,8aH)-dicarboxylate (8b)



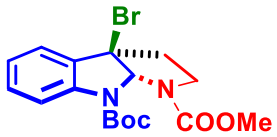
8b *(dr 95:5)*

8b was prepared from *tert*-butyl 3-(2-(((benzyloxy)carbonyl)amino)ethyl)-1H-indole-1-carboxylate **6b** (39 mg, 0.1 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 140 minutes at room temperature (2.20 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8b** (33 mg, 0.069 mmol, **70%**, 95:5 dr) as white solid.

8b was prepared from *tert*-butyl 3-(2-(((benzyloxy)carbonyl)amino)ethyl)-1H-indole-1-carboxylate **6b** (79 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 67 minutes at room temperature, (2.4 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8b** (60 mg, 0.127 mmol, **63%**, 95:5 dr) as white solid.

Rf: 0.41 (PE/EtOAc 9:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.64 (d, *J* = 7.6 Hz, 1H), 7.45-7.27 (m, 7H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.46 (s, 1H), 5.18 (s, 2H), 3.85-3.75 (m, 1H), 2.99-2.67 (m, 3H), 1.55 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 154.1, 152.2, 142.1, 136.6, 132.5, 130.6, 128.5, 128.1, 128.0, 124.3, 123.8, 117.5, 84.1, 82.3, 67.3, 62.1, 46.4, 40.9, 28.3.
HRMS-ESI: *m/z* 495.0870 ([M+Na]$^+$, $C_{23}H_{25}BrN_2NaO_4^+$ calcd. 495.0890).

8-*tert*-butyl 1-methyl 3a-bromo-3,3a-dihydropyrrolo[2,3-b]indole-1,8(2H,8aH)-dicarboxylate (8c)



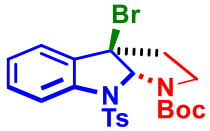
8c *(dr 95:5)*

8c was prepared from *tert*-butyl 3-(2-((methoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate **6c** (64 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 150 minutes at room temperature (2.30 F/mol), followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8c** (70 mg, 0.176 mmol, **89%**, 95:5 dr) as white solid.

8c was prepared from *tert*-butyl 3-(2-((methoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate **6c** (64 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 94 minutes at room temperature (2.61 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8c** (69 mg, 0.174 mmol, **87%**, 95:5 dr) as white solid.

Rf: 0.66 (PE/EtOAc 7:3).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.62 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5, 1H), 6.37 (s, 1H), 3.78-3.73 (m, 1H), 3.72 (s, 3H), 2.92-2.65 (m, 3H), 1.58 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 154.7, 152.1, 142.0, 132.4, 130,6, 124.3, 123.8, 117.4, 84.0, 82.2, 62.1, 52.8, 46.3, 41.1, 28.3.
HRMS-ESI: *m/z* 419.0558 ([M+Na]$^+$, $C_{17}H_{21}BrN_2NaO_4^+$ calcd. 419.0577).

tert-butyl 3a-bromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (8d)



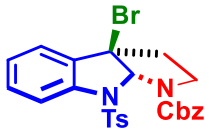
8d *(dr 95:5)*

8d was prepared from *tert*-butyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6d** (83 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 140 minutes at room temperature (2.25 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8d** (90 mg, 0.182 mmol, **91%**, 95:5 dr) as white solid.

8d was prepared from *tert*-butyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6d** (83 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 58 minutes at room temperature, (1.93 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8d** (80 mg, 0.162 mmol, **81%**, 95:5 dr) as white solid.

Rf: 0.56 (PE/EtOAc 8:2).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.68 (d, *J* = 6.9 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.31-7.26 (m, 2H), 7.16-7.11 (m, 3H), 6.29 (s, 1H), 3.78-3.73 (m, 1H), 2.76-2.62 (m, 3H), 2.31 (s, 3H), 1.54 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.2, 144.2, 141.3, 135.7, 133.8, 130.6, 129.5, 127.9, 125.9, 124.3, 117.8, 86.8, 81.9, 62.2, 45.9, 42.5, 28.4, 21.6.
HRMS-ESI: *m/z* 515.0585 ([M+Na]$^+$, $C_{22}H_{25}BrN_2NaO_4S^+$ calcd. 515.0611).

benzyl 3a-bromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (8e)



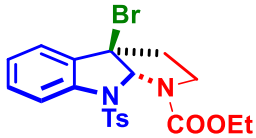
8e *(dr 95:5)*

8e was prepared from benzyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6e** (90 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 140 minutes at room temperature (2.20 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **4e** (73 mg, 0.138 mmol, **69%**, 95:5 dr) as white solid.

8e was prepared from benzyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6e** (90 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 73 minutes at room temperature, (2.32 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8e** (44 mg, 0.083 mmol, **42%**, 95:5 dr) as white solid.

Rf: 0.55 (PE/EtOAc 8:2).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.64 (br, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.56-7.43 (m, 2H), 7.43-7.25 (m, 5H), 7.20-7.09 (m, 3H), 6.30 (s, 1H), 5.41-5.11 (m, 2H), 3.86-3.80 (m, 1H), 2.86-2.79 (m, 1H), 2.75-2.61 (m, 2H), 2.32 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.9, 144.4, 141.3, 136.3, 135.5, 133.6, 130.8, 129.6, 128.8, 128.6, 128.3, 128.0, 126.1, 124.4, 118.0, 86.9, 67.9, 61.8, 46.1, 42.4, 21.7.
HRMS-ESI: *m/z* 549.0441 ([M+Na]$^+$, $C_{25}H_{23}BrN_2NaO_4S^+$ calcd. 549.0454).

Ethyl-3a-bromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (8f):



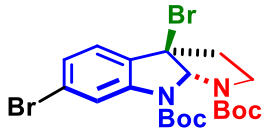
8f *(dr 95:5)*

8f was prepared from ethyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6f** (77.2 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 130 minutes at room temperature (2.13 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **4f** (72 mg, 0.156 mmol, **78%**, 95:5 dr) as colorless oil.

8f was prepared from ethyl (2-(1-tosyl-1H-indol-3-yl)ethyl)carbamate **6f** (77.2 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 83 minutes at room temperature (2.55 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **8f** (76 mg, 0.164 mmol, **82%**, 95:5 dr) as colorless oil.

Rf: 0.69 (PE/EtOAc 7:3).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.67 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.33-7.26 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 3H), 6.27 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.81-3.76 (m, 1H), 2.83-2.62 (m, 3H), 2.32 (s, 3H), 1.36 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 154.2, 144.4, 141.3, 135.6, 133.7, 130.8, 129.5, 128.0, 126.1, 124.3, 118.1, 86.8, 62.3, 61.9, 45.9, 42.2, 21.6, 14.6.
HRMS-ESI: *m/z* 487.0289 ([M+Na]$^+$, $C_{20}H_{21}BrN_2NaO_4S^+$ calcd. 487.0298).

di-tert-butyl
(3aR,8aR)-3a,6-dibromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (8g):

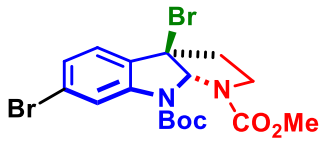


8g *(dr 95:5)*

8g was prepared from tert-butyl 6-bromo-3-(2-((tert-butoxycarbonyl)amino)ethyl)-1H-indole-1-carboxylate **6g** (87.6 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 140 minutes at room temperature (2.18 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8g** (91 mg, 0.176 mmol, **88%**, 95:5 dr) as white solid.

Rf: 0.61 (PE/EtOAc 9:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.82 (br, 1H), 7.20 (s, 2H), 6.40 (s, 1H), 3.76-3.71 (m, 1H), 2.83-2.75 (m, 1H), 2.74-2.63 (m, 2H), 1.57 (s, 9H), 1.46 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.3, 151.8, 143.2, 131.7, 127.1, 125.1, 124.3, 120.5, 84.4, 82.8, 80.9, 61.5, 46.3, 42.0, 28.4, 28.3.
HRMS-ESI: *m/z* 517.0311 ([M+H]$^+$, $C_{20}H_{27}Br_2N_2O_4^+$ calcd. 517.0332).

8-tert-butyl 1-methyl
3a,6-dibromo-3,3a-dihydropyrrolo[2,3-b]indole-1,8(2H,8aH)-dicarboxylate (8h)



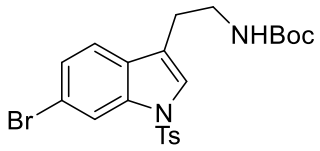
8h *(dr 95:5)*

8h was prepared from *tert*-butyl 6-bromo-3-(2-(((methylperoxy)methylene)amino)ethyl)-1H-indole-1-carboxylate **6h** (79 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 140 minutes at room temperature (2.21 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8h** (77 mg, 0.162 mmol, **81%**, 95:5 dr) as colorless oil.

8h was prepared from *tert*-butyl 6-bromo-3-(2-(((methylperoxy)methylene)amino)ethyl)-1H-indole-1-carboxylate **6h** (79 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 78 minutes at room temperature, (2.15 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8h** (78 mg, 0.164 mmol, **82%**, 95:5 dr) as colorless oil.

Rf: 0.60 (PE/EtOAc 8:2).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.86 (s, 1H), 7.24-7.19 (m, 2H), 6.35 (s, 1H), 3.79 (dd, *J* = 10.4, 7.3 Hz, 1H), 3.72 (s, 3H), 2.91-2.82 (m, 1H), 2.80-2.66 (m, 2H), 1.58 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 154.6, 151.8, 143.1, 131.4, 127.3, 125.0, 124.5, 120.6, 84.5, 82.8, 61.4, 52.9, 46.4, 41.3, 28.3.
HRMS-ESI: *m/z* 496.9663 ([M+Na]$^+$, $C_{17}H_{20}Br_2N_2NaO_4^+$ calcd. 496.9682).

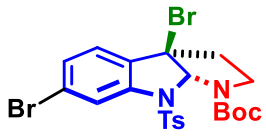
***tert*-butyl (2-(6-bromo-1-tosyl-1H-indol-3-yl)ethyl)carbamate (6i)**



6i (white solid, 718 mg, **76%**) was prepared from 2-(6-bromo-1H-indol-3-yl)ethanamine (458 mg, 1.91 mmol), according to the procedure reported by Tong.[1]

Rf: 0.26 (PE/EtOAc 8:2).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 8.15 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.37-7.30 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.61 (brs, 1H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.82 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 1.44 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 155.9, 145.3, 136.0, 135.1, 130.1, 129.7, 126.9, 126.6, 123.9, 120.7, 119.9, 118.6, 116.9, 79.6, 40.2, 28.5, 25.7, 21.7.
HRMS-ESI: *m/z* 515.0592 ([M+Na]$^+$, $C_{22}H_{25}BrN_2NaO_4S^+$ calcd. 515,0611).

tert-butyl 3a,6-dibromo-8-tosyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (8i)



8i *(dr 95:5)*

8i was prepared from *tert*-butyl (2-(6-bromo-1-tosyl-1H-indol-3-yl)ethyl)carbamate **6i** (99 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 135 minutes at room temperature (2.1 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **4i** (100 mg, 0.175 mmol, **88%**, 95:5 dr) as colorless oil.

8i was prepared from *tert*-butyl (2-(6-bromo-1-tosyl-1H-indol-3-yl)ethyl)carbamate **6i** (99 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V.** After stirring 80 minutes at room temperature, (2.31 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8i** (95 mg, 0.166 mmol, **83%**, 95:5 dr) as colorless oil.

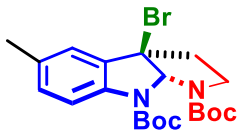
Rf: 0.65 (PE/EtOAc 8:2).

^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.75-7.68 (m, 3H), 7.26 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 3.78 (m, 1H), 2.73 (m, 1H), 2.66-2.58 (m, 2H), 2.35 (s, 3H), 1.53 (s, 9H).

^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.1, 144.6, 142.5, 135.5, 132.8, 129.7, 129.0, 127.9, 125.6, 124.5, 120.7, 87.3, 82.0, 61.5, 46.0, 42.6, 28.4, 21.7.

HRMS-ESI: *m/z* 592.9703 ([M+Na]$^+$, $C_{22}H_{24}Br_2N_2NaO_4S^+$calcd. 592.9716).

di-tert-butyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (8j):



8j *(dr 95:5)*

8j was prepared from tert-butyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-5-methyl-1H-indole-1-carboxylate **6j** (74.8 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 128 minutes at room temperature (2.00 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 9:1) led to **8j** (69 mg, 0.154 mmol, **77%**, 95:5 dr) as white solid.

Rf: 0.52 (PE/EtOAc 9:1).

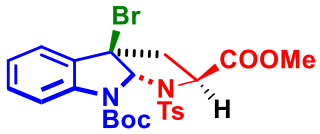
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.43 (br, 1H), 7.14 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.41 (s, 1H), 3.73-3.69 (m, 1H), 2.83-2.68 (m, 3H), 2.32 (s, 3H), 1.57 (s, 9H), 1.48 (s, 9H).

^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 153.5, 152.3, 139.9, 133.9, 132.7, 131.2, 124.1, 117.4, 84.0, 82.0, 80.8, 77.5, 77.2, 76.8, 62.6, 46.2, 41.6, 28.5, 28.4, 21.1.

HRMS-ESI: *m/z* 475.1182 ([M+Na]$^+$, $C_{21}H_{29}BrN_2NaO_4^+$ calcd. 475.1203).

(2S,3aR,8aS)-8-tert-butyl-2-methyl-3a-bromo-1-tosyl-1,3,3a,8a-tetrahydropyrrolo[2,3-b]indo

le-2,8(2H)-dicarboxylate (8k):



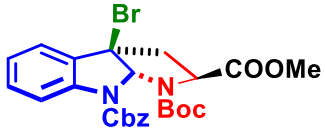
8k *(dr 90:10)*

8k was prepared from (S)-tert-butyl 3-(3-methoxy-2-(4-methylphenylsulfonamido)-3-oxopropyl)-1H-indole-1-carboxylate **6k** (47.2 mg, 0.1 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)** and 18.4 mg of $MgBr_2$ (0.1 mmol). After stirring 65 minutes at room temperature (2.00 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8k** (50 mg, 0.091 mmol, **91%**, 90:10 dr in favor of the *exo* isomer) as colorless oil.

8k was prepared from (S)-tert-butyl 3-(3-methoxy-2-(4-methylphenylsulfonamido)-3-oxopropyl)-1H-indole-1-carboxylate **6k** (47.2 mg, 0.1 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 61 minutes at room temperature (2.78 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8k** (48 mg, 0.087 mmol, **87%**, 90:10 dr in favor of the *exo* isomer) as colorless oil.

Data for the mixture of diastereoisomers (dr 90:10).
Rf: 0.65 (PE/EtOAc 7:3). $[\alpha]_D^{25}$ = +99.5 (c = 0.5, $CHCl_3$).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.93 (d, *J* = 7.8 Hz, 0.2H), 7.52 (br, 1.8H), 7.29-7.00 (m, 6H), 6.48 (s, 0.1H), 6.37 (s, 0.9H), 4.03-3.90 (m, 1H), 3.79 (s, 2.7H), 3.22 (dd, *J* = 12.9 Hz, *J* = 6.3 Hz, 1H), 3.14 (s, 0.3H), 2.96 (t, *J* = 10.6 Hz, 1H), 2.40 (s, 0.3H), 2.35 (s, 2.7H), 1.63 (s, 8H), 1.44 (s, 1H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 171.2, 151.8, 143.6, 140.4 (minor), 136.9, 131.2 (minor), 130.4, 129.5 (minor), 129.4 (two C), 127.3 (two C), 124.8, 124.2 (minor), 122.9, 117.9, 117.4 (minor), 85.5, 83.2, 61.9, 61.6 (minor), 59.9, 53.1, 52.4 (minor), 44.9 (minor), 42.1, 28.3, 28.1 (minor), 21.6.
HRMS-ESI: *m/z* 573.0658 ($[M+Na]^+$, $C_{24}H_{27}BrN_2NaO_6S^+$ calcd. 573.0665).

(2S,3aR,8aR)-8-benzyl-1-tert-butyl-2-methyl-3a-bromo-3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2H,8aH)-tricarboxylate (8l):



8l *(dr 90:10)*

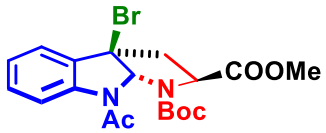
8l was prepared from ethyl benzyl (S)-3-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-1H-indole-1-carboxylate **7l** (90.4 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**.

After stirring 128 minutes at room temperature (2.00 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **8l** (73 mg, 0.138 mmol, **69%**, 90:10 dr in favor of the *exo* isomer) as colorless oil.

8l was prepared from ethyl benzyl (S)-3-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-1H-indole-1-carboxylate **7l** (90.4 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 145 minutes at room temperature (3.42 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 7:3) led to **8l** (76 mg, 0.144 mmol, **72%**, 90:10 dr in favor of the *exo* isomer) as colorless oil.

Data for the mixture of diastereoisomers (dr 90:10).
Rf: 0.34 (PE/EtOAc 7:3). $[\alpha]_D^{25}$ = -91.2 (c = 0.5, $CHCl_3$).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.63 (br, 1H), 7.46 (d, *J* = 6.0 Hz, 2H), 7.41-7.28 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.50 (s, 0.1H), 6.46 (s, 0.9H), 5.46 (d, *J* = 12.4 Hz, 1H), 5.25 (br, 1H), 3.93 (dd, *J* = 10.5 Hz, *J* = 6.5 Hz, 1H), 3.75 (s, 3H), 3.24 (dd, *J* = 12.1 Hz, *J* = 6.5 Hz, 1H), 2.82 (dd, *J* = 12.3 Hz, *J* = 10.4 Hz, 1H), 1.43 (s, 1H), 1.38 (s, 8H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 171.5, 153.4, 153.3, 142.0 (minor), 140.9, 135.9, 132.8, 132.5 (minor), 131.0, 128.7, 128.3, 128.0, 124.9, 124.4 (minor), 124.0 (minor), 123.5, 118.4, 84.6, 83.8, 81.9, 68.2, 59.6, 52.6, 52.2 (minor), 41.7, 28.4 (minor), 28.3.
HRMS-ESI: *m/z* 553.0921 ($[M+Na]^+$, $C_{25}H_{27}BrN_2NaO_6^+$ calcd.553.0945).

(2S,3aR,8aS)-1-tert-butyl-2-methyl-8-acetyl-3a-bromo-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1,2(2H)-dicarboxylate (8m):



8m *(dr 90:10)*

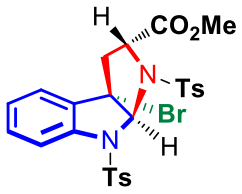
8m was prepared from methyl 1-acetyl-N^a-(tert-butoxycarbonyl)-L-tryptophanate **6m** (72 mg, 0.2 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)**. After stirring 120 minutes at room temperature (2.00 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8m** (82 mg, 0.188 mmol, **94%**, 90:10 dr in favor of the *exo* isomer) as white solid.

8m was prepared from methyl 1-acetyl-N^a-(tert-butoxycarbonyl)-L-tryptophanate **6m** (72 mg, 0.2 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 68 minutes at room temperature (2.50 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 8:2) led to **8m** (84 mg, 0.192 mmol, **96%**, 90:10 dr in favor of the *exo* isomer) as white solid.

Data for the mixture of diastereoisomers (dr 90:10).
Rf: 0.46 (PE/EtOAc 8:2), $[\alpha]_D^{25}$ = -200.8 (c = 0.5, $CHCl_3$).

^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.98 (br, 1H), 7.39-7.33 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.14 (s, 1H), 3.89 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.25 (dd, *J* = 12.6 Hz, *J* = 6.5 Hz, 1H), 2.81 (t, *J* = 11.2 Hz, 1H), 2.64 (s, 3H), 1.32 (s, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 171.7, 170.9, 151.7, 141.5, 132.4, 130.9, 125.3, 123.1, 119.9, 85.4, 81.9, 59.9, 59.7, 52.6, 42.1, 28.1, 23.7.
HRMS-ESI: *m/z* 439.0846 ($[M+H]^+$, $C_{19}H_{24}BrN_2O_5^+$ calcd. 439.0863).

(2R,3aS,8aS)-methyl-3a-bromo-1,8-ditosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylatecarboxylate (8n):



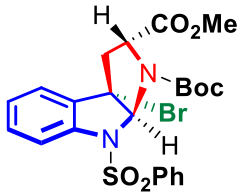
4n *(dr 95:5)*

8n was prepared from (S)-methyl 2-(4-methylphenylsulfonamido)-3-(1-tosyl-1H-indol-3-yl)propanoate **6n** (52.6 mg, 0.1 mmol), following general procedure A **using a constant current of 5.0 mA (4.5 mA/cm^2)** and 18.4 mg of $MgBr_2$ (0.1 mmol). After stirring 65 minutes at room temperature (2.02 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 6:4) led to **8n** (31 mg, 0.051 mmol, **51%**, 95:5 dr in favor of the *exo* isomer) as colorless solid.

8n was prepared from (S)-methyl 2-(4-methylphenylsulfonamido)-3-(1-tosyl-1H-indol-3-yl)propanoate **6n** (52.6 mg, 0.1 mmol), following general procedure A **using a constant cell potential of 5 V**. After stirring 111 minutes at room temperature, the solution was charged to 3.69 F/mol followed by aqueous work-up, preparative TLC purification (PE/EtOAc 6:4) led to **8n** (33 mg, 0.055 mmol, **55%**, 95:5 dr in favor of the *exo* isomer) as colorless solid.

Rf: 0.53 (PE/EtOAc 6:4). $[\alpha]_D^{25}$ = +215.7 (c = 0.5, $CHCl_3$).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.75 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.15-7.03 (m, 6H), 6.24 (s, 1H), 3.84 (dd, *J* = 8.9 Hz, *J* = 6.3Hz, 1H), 3.80 (s, 3H), 3.05 (dd, *J* = 12.6 Hz, *J* = 6.2 Hz, 1H), 2.88 (dd, *J* = 13.0 Hz, *J* = 9.4 Hz, 1H), 2.39 (s, 3H), 2.26 (s, 3H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 170.8, 144.8, 143.6, 139.5, 136.8, 135.4, 134.2, 130.6, 129.5, 129.3, 128.2, 128.1, 126.9, 123.5, 118.9, 87.9, 61.6, 59.1, 53.1, 43.2, 21.6 (two C).
HRMS-ESI: *m/z* 627.0212 ($[M+Na]^+$, $C_{26}H_{25}BrN_2NaO_6S_2^+$ calcd. 627.0230).

1-(tert-butyl)-2-methyl-(2R,3aS,8aS)-1-tert-butyl-2-methyl-3a-bromo-8-(phenylsulfonyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1,2(2H)-dicarboxylate (8o):



8o *(dr 95:5)*

To a 20 mL vial with a stir bar were successively added **6o** (0.6 mmol), $MgBr_2$ (0.6 mmol, 1.0 equiv), 3.0 mL of distilled H_2O and 12.0 mL of CH_3CN (0.04 M). The vial was covered with the electrode holder. The electrolysis was carried out at room temperature **using a constant current of 5.0 mA (1.8 mA/cm^2)** between a graphite anode and a platinum plate cathode (0.8 cm x 3.4 cm x 0.2 cm submerged in solution) with stirring (1000 rpm). The complete consumption of the starting indole derivative was checked by TLC (15% AcOEt/petroleum ether). After stirring 385 minutes at room temperature (2.00 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 75:25) led to **8o** (260 mg, 0.486 mmol, **81%**, dr 95:5 in favor of the *exo* isomer) as white foam.

To a 20 mL vial with a stir bar were successively added **6o** (0.6 mmol), $MgBr_2$ (0.6 mmol, 1.0 equiv), 3.0 mL of distilled H_2O and 12.0 mL of CH_3CN (0.04 M), The vial was covered with a screw-cap. The electrolysis was carried out at room temperature **using a constant cell potential of 5 V** between a graphite anode and a platinum plate cathode (0.8 cm x 3.4 cm x 0.2 cm submerged in solution) with stirring (1000 rpm). The complete consumption of the starting indole derivative was checked by TLC (15% AcOEt/petroleum ether). After stirring 120 minutes at room temperature (2.95 F/mol) followed by aqueous work-up, preparative TLC purification (PE/EtOAc 75:25) led to **8o** (270 mg, 0.504 mmol, **84%**, dr 95:5 in favor of the *exo* isomer) as white foam.

Rf: 0.33 (PE/EtOAc 3:1). $[\alpha]_D^{25}$ = +232.8 (c = 0.15, $CHCl_3$).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.89-7.70 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36-7.24 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 3.81 (dd, *J* = 10.4 Hz, *J* = 5.8 Hz, 1H), 3.72 (s, 3H), 3.06 (dd, *J* = 12.6 Hz, *J* = 6.0 Hz, 1H), 2.75 (t, *J* = 11.6 Hz, 1H), 1.53 (br, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 171.0, 153.3, 140.5, 138.5, 134.2, 133.6, 131.1, 128.8, 128.5, 126.5, 124.0, 118.9, 86.8, 83.0, 59.6, 59.5, 52.6, 43.2, 28.4.
HRMS-ESI: *m/z* 537.0672 ($[M+H]^+$, $C_{23}H_{26}BrN_2O_6S^+$ calcd. 537.0689).

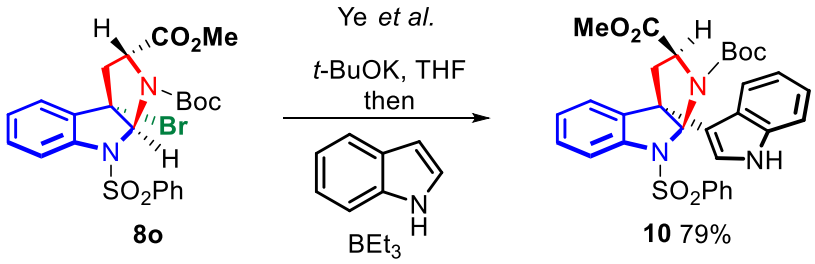
3a-allyl-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (9)

Bromopyrroloindoline **7c** (78.6 mg, 0.2 mmol) was dried under reduced pressure and placed under an argon atmosphere. Anhydrous CH_2Cl_2 (200 µL) and allyltrimethylsilane (95 µL, 0.6 mmol) were added. The solution was cooled to 0 °C and poured into a stirred suspension of AgOTf (77.1 mg, 0.3 mmol) in CH_2Cl_2 (100 µL) via cannula at 0 °C. After stirring at the same temperature for

30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ and the resulting mixture was extracted with CH_2Cl_2 five times. The combined organic extracts were dried over $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 4/1) to afford allylpyrroloindoline **9** (40 mg, 0.112 mmol, **56%**, 95:5 dr) as colorless solid.

Rf: 0.49 (PE/EtOAc 4:1).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.83 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.25-7.17 (m, 3H), 7.10 (dd, *J* = 7.6 Hz, *J* = 1.4 Hz, 1H), 7.01 (td, *J* = 7.4 Hz, *J* = 1.0 Hz, 1H), 5.82 (s, 1H), 5.39-5.28 (m, 1H), 4.93 (d, *J* = 16.7 Hz, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.43-3.36 (m, 1H), 2.46-2.39 (m, 1H), 2.37 (s, 3H), 2.34-2.28 (m, 1H), 2.19-2.10 (m, 1H), 2.06-2.01 (m, 1H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm)144.1, 141.8, 136.5, 134.2, 132.8, 129.6, 128.7, 127.5, 124.1, 123.8, 119.1, 113.2, 99.3, 67.6, 56.7, 42.4, 39.5, 21.6.
HRMS-ESI: *m/z* 378.1118 ([M+Na]$^+$, $C_{20}H_{21}NNaO_3S^+$ calcd. 378.1134).

1-(tert-butyl)-2-methyl-(2S,3aS,8aS)-1-tert-butyl-2-methyl-3a-(1H-indol-3-yl)-8-(phenylsulfonyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1,2(2H)-dicarboxylate (10):

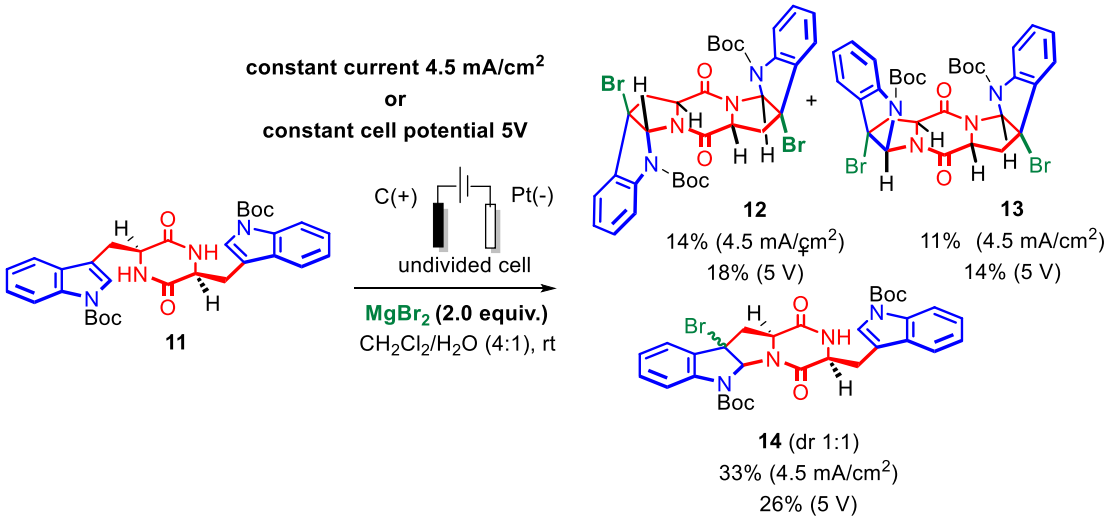


As described by Ye:[2] To a solution of indole (23.4mg, 0.2 mmol) and bromopyrroloindoline **8o** (192 mg, 1.8 equiv) in THF (0.05 M based on indole) at 0 °C was added triethylborane (1.5 equiv), which was followed by dropwise addition of a solution of potassium tert-butoxide in THF (3.5 equiv, 1 M solution). The reaction mixture was stirred at 0 °C. After complete consumption of starting material was observed by TLC analysis, the reaction was quenched by addition of saturated aqueous solution of NH4Cl and diluted with ethyl acetate. Layers were separated. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Preparative TLC purification (PE/EtOAc 65:35) led to **10** (90 mg, 0.158 mmol, **79%**, dr 95:5 in favor of the *endo* isomer) as white solid.

Rf: 0.27 (PE/EtOAc 65:35). $[\alpha]_D^{25}$ = -70.1 (c = 0.1, $CHCl_3$).
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.84 (br, 1H), 7.58 (br, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.35-7.26 (m, 5H), 7.24-7.19 (m, 2H), 7.17-7.09 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 6.00 (s, 1H), 5.02-4.67 (m, 1H), 3.25-3.06 (m, 4H), 2.78 (d, *J* = 13.2 Hz, 1H), 1.52 (br, 9H).
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 171,8, 154.2, 142.3, 139.5, 137.2, 135.3, 132.3, 129.4, 128.2, 126.8, 125.1, 124.9, 124.4, 123.3, 122.7, 120.3, 119.0, 118.4, 116.0, 111.9, 84.7, 82.6, 60.2, 57.1, 52.1, 40.3, 28.5.
HRMS-ESI: *m/z* 596.1807 ([M+Na]$^+$, $C_{31}H_{31}N_3NaO_6S^+$ calcd. 596.1826).

[2] H. Lei, L. Wang, Z. Xu, T. Ye, *Org. Lett.* **2017**, *19*, 5134–5137.

The spectral data matched the reported data by Ye.[2]

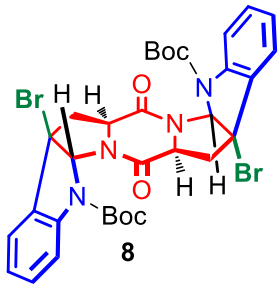


To a 10 mL vial with a stir bar were successively added bistryptophan diketopiperazine **11** (57.2 mg, 0.1 mmol, prepared according to Tokuyama[3]), $MgBr_2$ (0.2mmol, 2.0 equiv), 1.0 mL of distilled H_2O and 4.0 mL of CH_2Cl_2 (0.02 M), The vial was covered with a screw-cap. The electrolysis was carried out at room temperature **using a constant cell potential of 5 V** between a graphite anode and a platinum plate cathode (1.4 x 0.8 x 0.2 cm submerged in solution) with stirring (400 rpm). The complete consumption of the starting indole derivative was checked by TLC (30% to 50% toluene/AcOEt). The reaction was then quenched with H_2O and diluted with CH_2Cl_2. The organic and aqueous phases were separated. The aqueous phase was then extracted twice with CH_2Cl_2. The combined organic phases were then dried over $MgSO_4$, filtered and concentrated under vacuum. The crude was then purified by preparative TLC (8:2 to 7:3 toluene/AcOEt) and led to **12** (13 mg, 0.018 mmol, **18%**) as white solid, to **13** (10 mg, 0.014 mmol, **14%**) as white solid and to **14** (17 mg, 0.026 mmol, **26%,** dr 50:50) as white foam.

To a 10 mL vial with a stir bar were successively added bistryptophan diketopiperazine **11** (57.2 mg, 0.1 mmol), $MgBr_2$ (0.2 mmol, 2.0 equiv), 1.0 mL of distilled H_2O and 4.0 mL of CH_2Cl_2 (0.02 M), The vial was covered with the electrode holder. The electrolysis was carried out at room temperature **using a constant current of 5.0 mA (4.5 mA/cm^2)** between a graphite anode and a platinum plate cathode (1.4 x 0.8 x 0.2 cm submerged in solution) with stirring (1000 rpm). The complete consumption of the starting indole derivative was checked by TLC (30% to 50% toluene/AcOEt). The reaction was then quenched with H_2O and diluted with CH_2Cl_2. The organic and aqueous phases were separated. The aqueous phase was then extracted twice with CH_2Cl_2. The combined organic phases were then dried over $MgSO_4$, filtered and concentrated under vacuum. The crude was then purified by preparative TLC (8:2 to 7:3 toluene/AcOEt) and led to **12** (11 mg, 0.014 mmol, **14%**) as white solid, to **13** (8 mg, 0.011 mmol, **11%**) as white solid and to **14** (21 mg, 0.033 mmol, **33%,** dr 50:50) as white foam.

Bis-bromopyrroloindoline 8:

[3] Hakamata, H.; Sato, S.; Ueda, H.; Tokuyama, H. *Org. Lett.* **2017**, *19*, 5308–5311.



8

Rf: 0.45 (toluene/EtOAc 85:15). $[\alpha]_D^{25}$ = -70.2 (c = 0.2, $CHCl_3$).

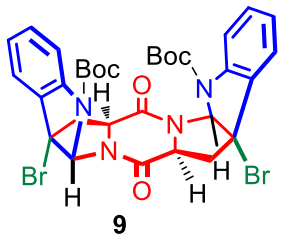
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.66 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.36-7.30 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.24 (s, 1H), 6.15 (s, 1H), 4.26 (dd, *J* = 9.7 Hz, *J* = 4.1 Hz, 1H), 3.82 (dd, *J* = 10.3 Hz, *J* = 5.9 Hz, 1H), 3.75 (dd, *J* = 14.3 Hz, *J* = 4.2 Hz, 1H), 3.25 (dd, *J* = 13.5 Hz, *J* = 6.2 Hz, 1H), 3.05 (dd, *J* = 14.3 Hz, *J* = 10.1 Hz, 1H), 2.86 (dd, *J* = 13.2 Hz, *J* = 10.4 Hz, 1H), 1.63 (s, 9H), 1.56 (s, 9H).

^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 164.7, 163.5, 151.8, 151.6, 141.7, 139.9, 133.0, 131.8, 131.1, 130.9, 124.9, 124.7, 124.5, 123.6, 117.7, 117.1, 85.0, 83.1, 82.9, 82.8, 60.4, 60.2, 58.9, 58.8, 42.3, 38.2, 28.4, 28.2.

HRMS-ESI: *m/z* 753.0703 ($[M+Na]^+$, $C_{32}H_{34}Br_2N_4NaO_6^+$ calcd. 753.0717).

The spectral data matched the reported data by Tokuyama.[3]

Bis-bromopyrroloindoline 9:



9

Rf: 0.28 (toluene/EtOAc 2:1). $[\alpha]_D^{25}$ = +166.8 (c = 0.2, $CHCl_3$).

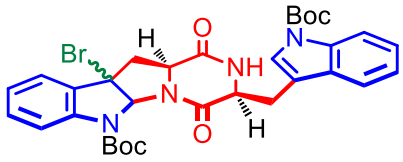
^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, *J* = 7.6 Hz, 2H), 7.04-6.98 (m, 4H), 6.07 (s, 2H), 4.21 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 2H), 3.82 (dd, *J* = 13.7 Hz, *J* = 1.6 Hz, 2H), 2.96 (dd, *J* = 13.8 Hz, *J* = 10.3 Hz, 2H), 1.56 (s, 18H).

^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 164.2, 151.4, 139.2, 131.4, 130.8, 124.6, 123.7, 117.4, 83.9, 82.4, 60.7, 60.1, 36.4, 28.3.

HRMS-ESI: *m/z* 753.0693 ($[M+Na]^+$, $C_{32}H_{34}Br_2N_4NaO_6^+$ calcd. 753.0717).

The spectral data matched the reported data by Tokuyama.[3]

Mono-bromopyrroloindoline product (10):



10

Data for the mixture of diastereoisomers (dr 50:50).

Rf: 0.31 (toluene/EtOAc 2:1).

^{1}H NMR: (300 MHz, $CDCl_3$, 300 K) δ (ppm) 8.14 (t, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 0.5H), 7.62 (d, *J* = 8.2 Hz, 0.5H), 7.49-7.27 (m, 5H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 0.5H), 7.08 (t, *J* = 7.4 Hz, 0.5H), 6.62 (s, 0.5H), 6.34 (s, 0.5H), 5.85 (s, 0.5H), 5.50 (s, 0.5H), 4.36-4.31 (m, 1H), 4.21 (dd, *J* = 10.9 Hz, *J* = 3.5 Hz, 0.5H), 3.84 (dd, *J* = 11.4 Hz, *J* = 5.4 Hz, 0.5H), 3.68 (dd, *J* = 14.3 Hz, *J* = 3.8 Hz, 0.5H), 3.64 (dd, *J* = 10.2 Hz, *J* = 2.7 Hz, 0.5H), 3.58 (dd, *J* = 15.1 Hz, *J* = 2.5 Hz, 0.5H), 3.24 (dd, *J* = 12.8 Hz, *J* = 5.6 Hz, 0.5H), 3.11 (dd, *J* = 14.6 Hz, *J* = 10.1 Hz, 0.5H), 2.99 (dd, *J* = 14.7 Hz, *J* = 10.3 Hz, 0.5H), 2.78-2.68 (m, 1H), 1.68 (s, 9H), 1.65 (s, 9H).

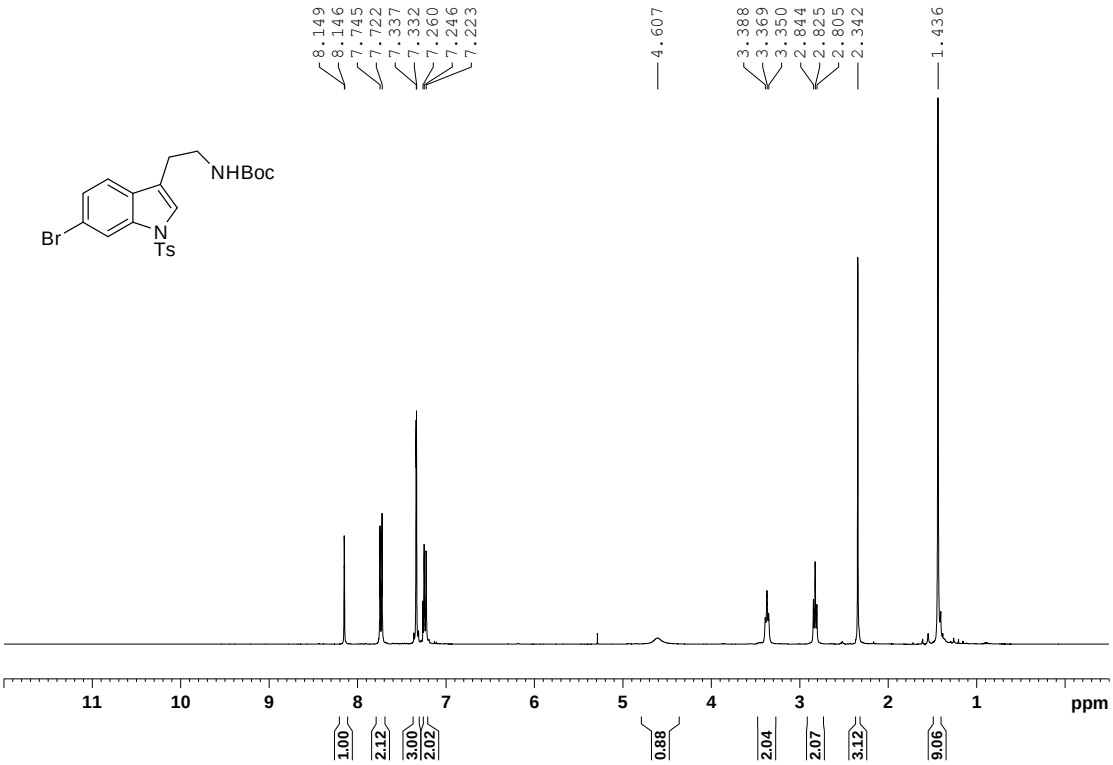
^{13}C NMR: (75 MHz, $CDCl_3$, 300 K) δ (ppm) 167.9, 166.8, 165.8, 164.1, 151.9, 151.8, 149.4, 142.1, 140.0, 135.9, 132.9, 131.5, 131.1, 130.8, 129.4, 125.2, 124.9, 124.7, 124.6, 124.5, 124.0, 122.9, 118.9, 118.7, 117.3, 117.2, 115.8, 114.5, 114.3, 85.0, 84.3, 84.2, 83.8, 83.0, 82.9, 60.2, 58.9, 58.5, 57.9, 54.26, 54.21, 45.1, 38.1, 28.5, 28.32, 28.30, 27.3, 25.8.

HRMS-ESI: *m/z* 673.1599 ($[M+Na]^+$, $C_{32}H_{35}BrN_4NaO_6^+$ calcd. 673.1632).

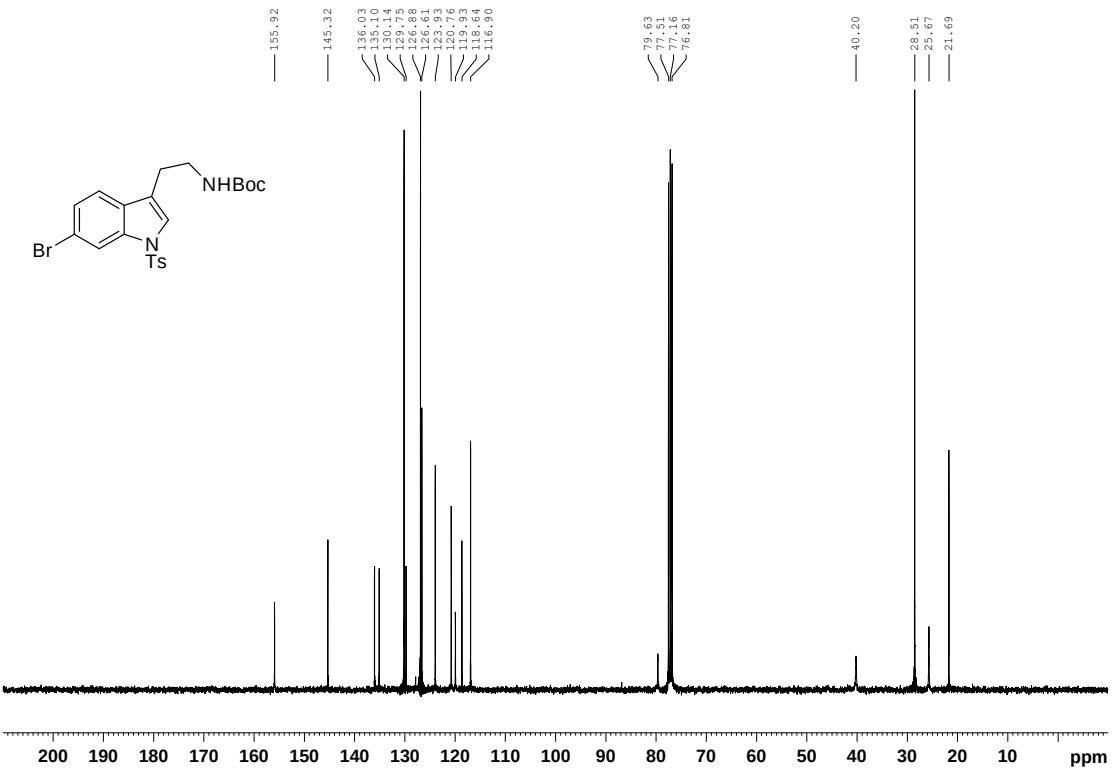
The spectral data matched the reported data by Tokuyama.[3]

6. NMR spectra

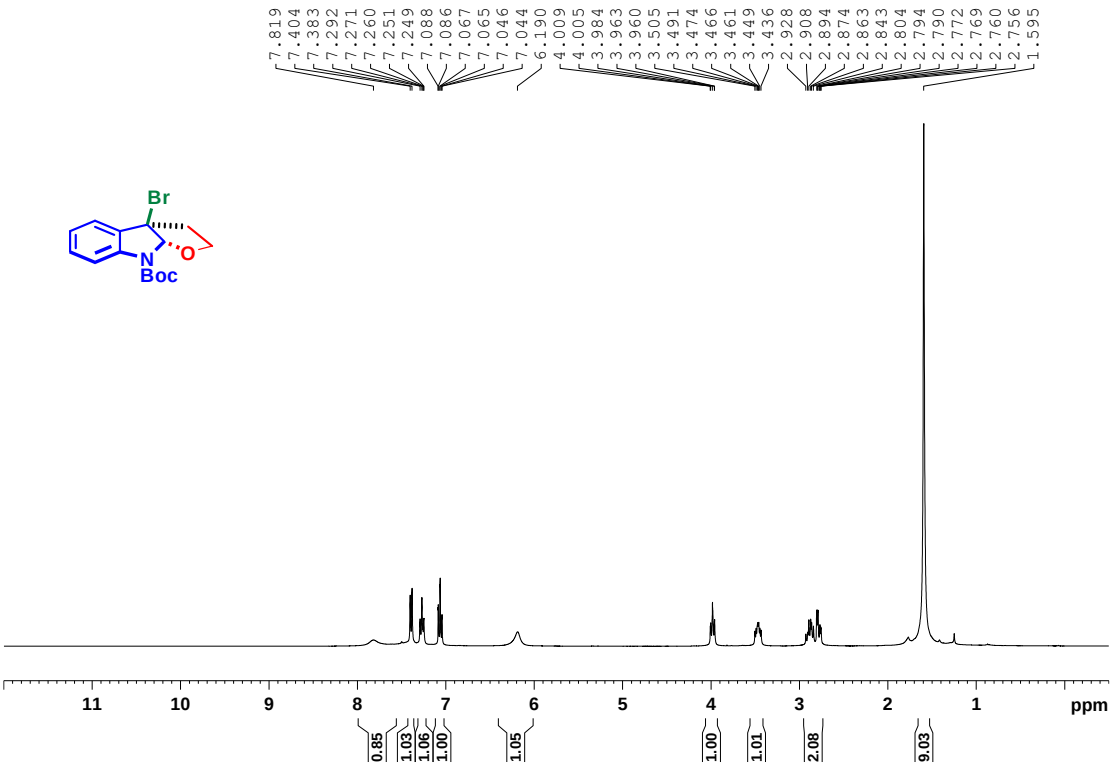
^{1}H NMR (CDCl$_3$, 300K), **6i**



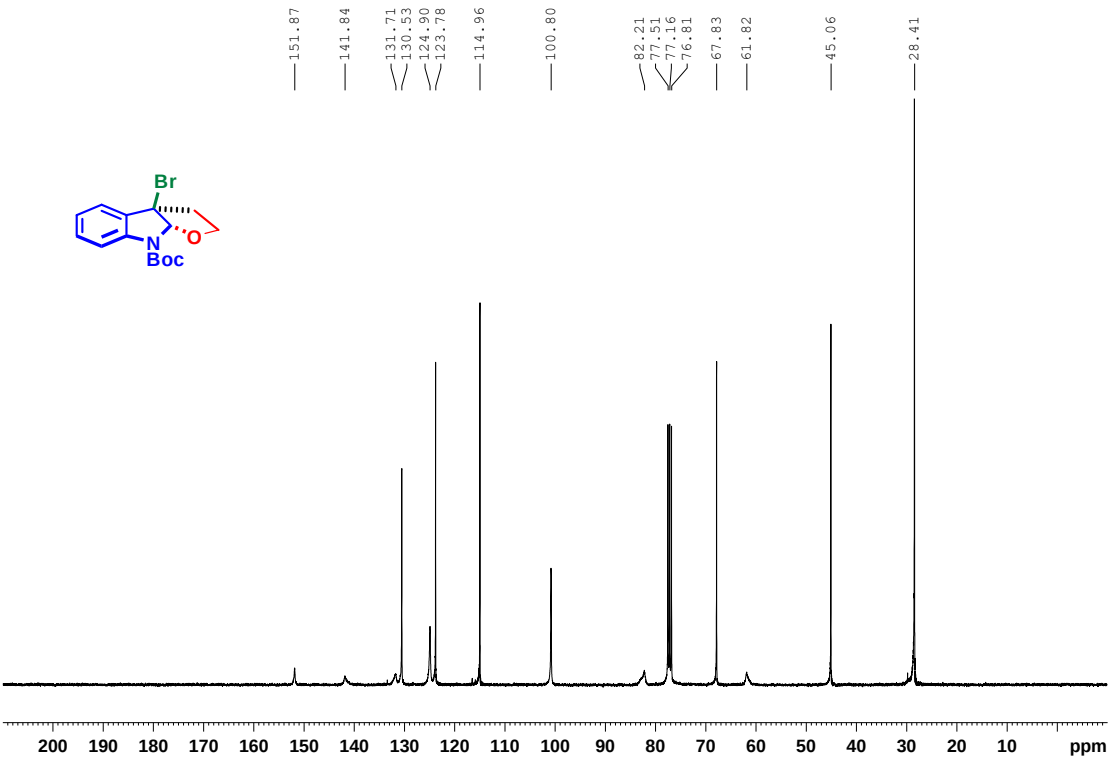
^{13}C NMR (CDCl$_3$, 300K), **6i**



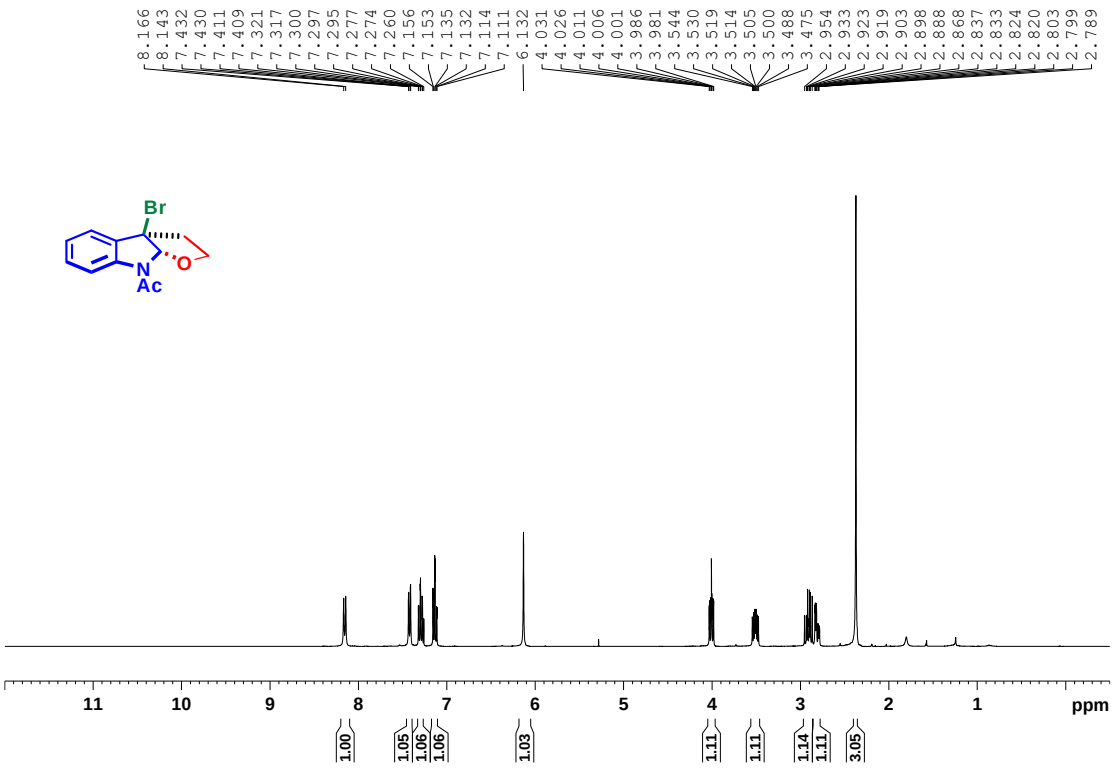
^{1}H NMR (CDCl$_3$, 300K), **7a**



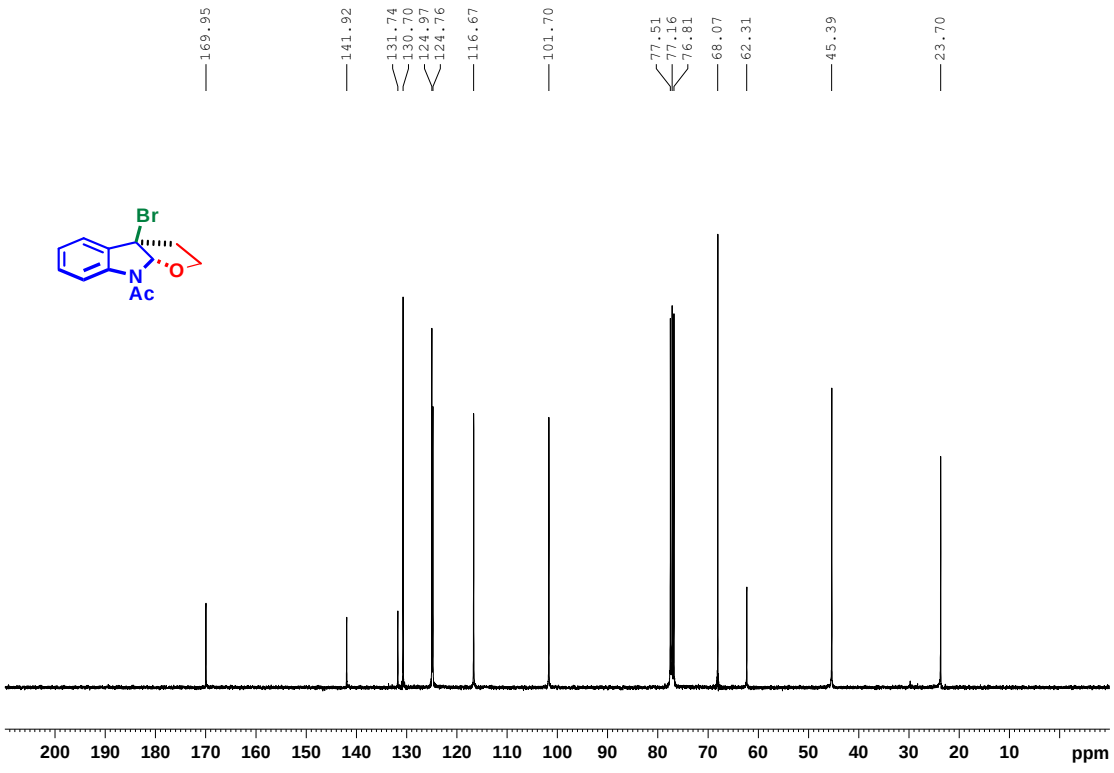
^{13}C NMR (CDCl$_3$, 300K), **7a**



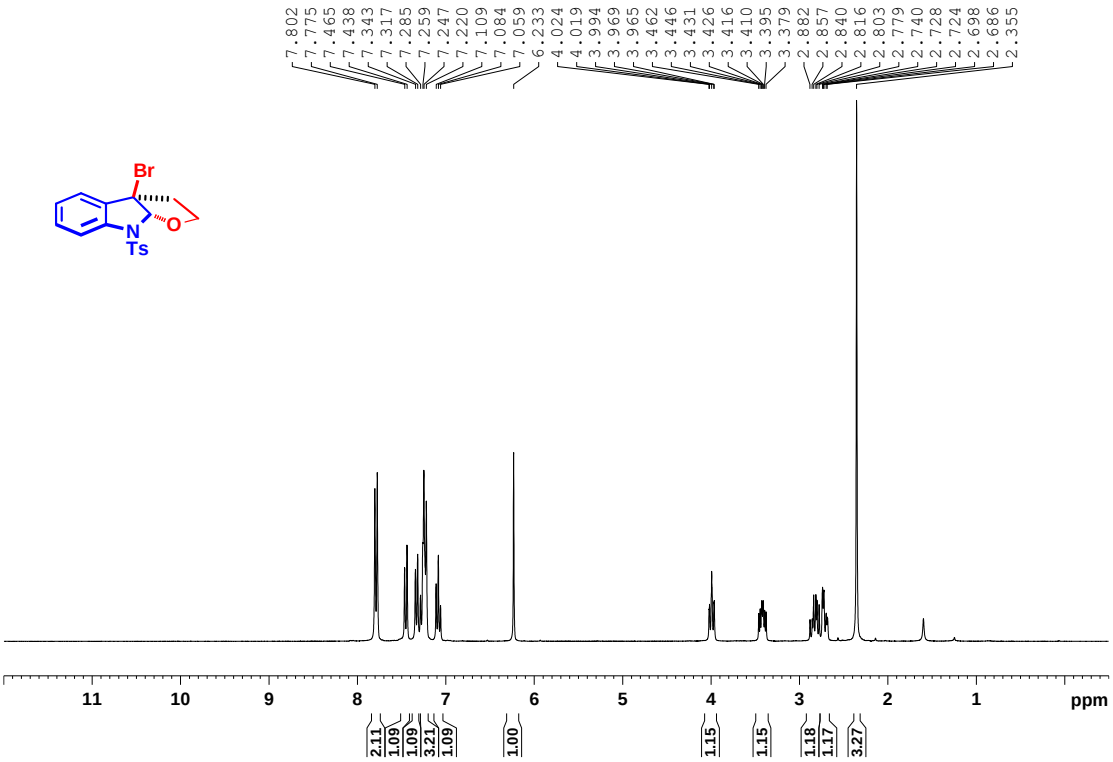
^{1}H NMR (CDCl$_3$, 300K), **7b**



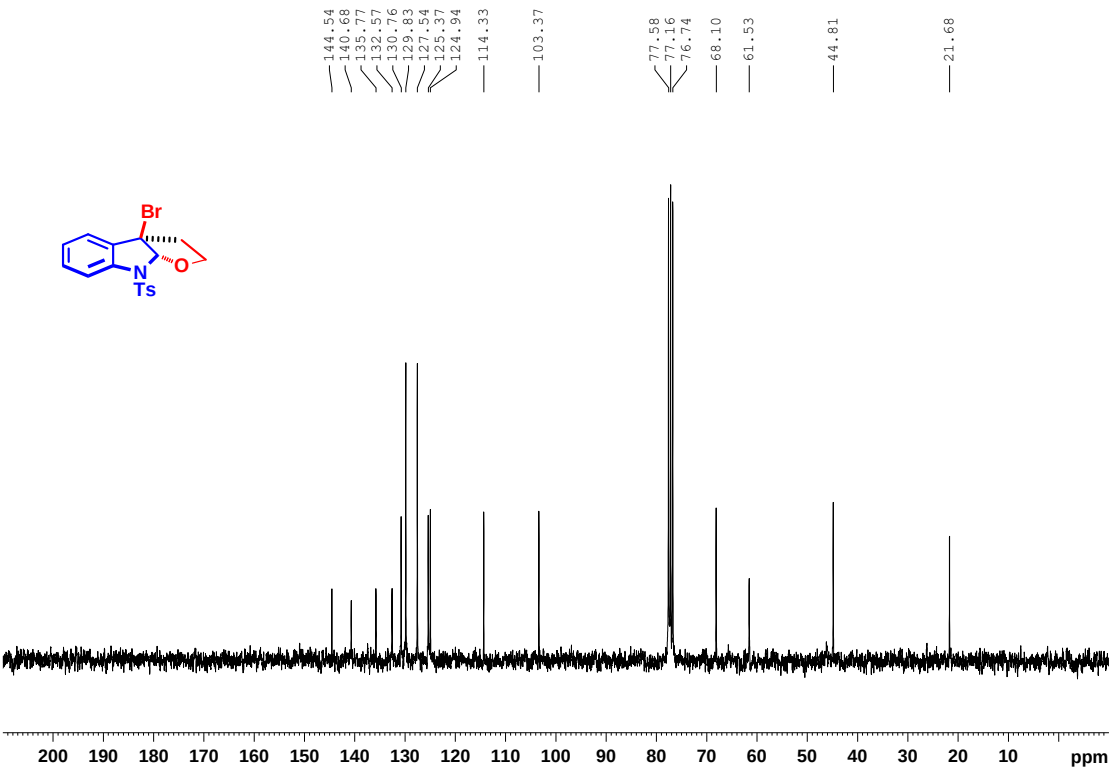
^{13}C NMR (CDCl$_3$, 300K), **7b**



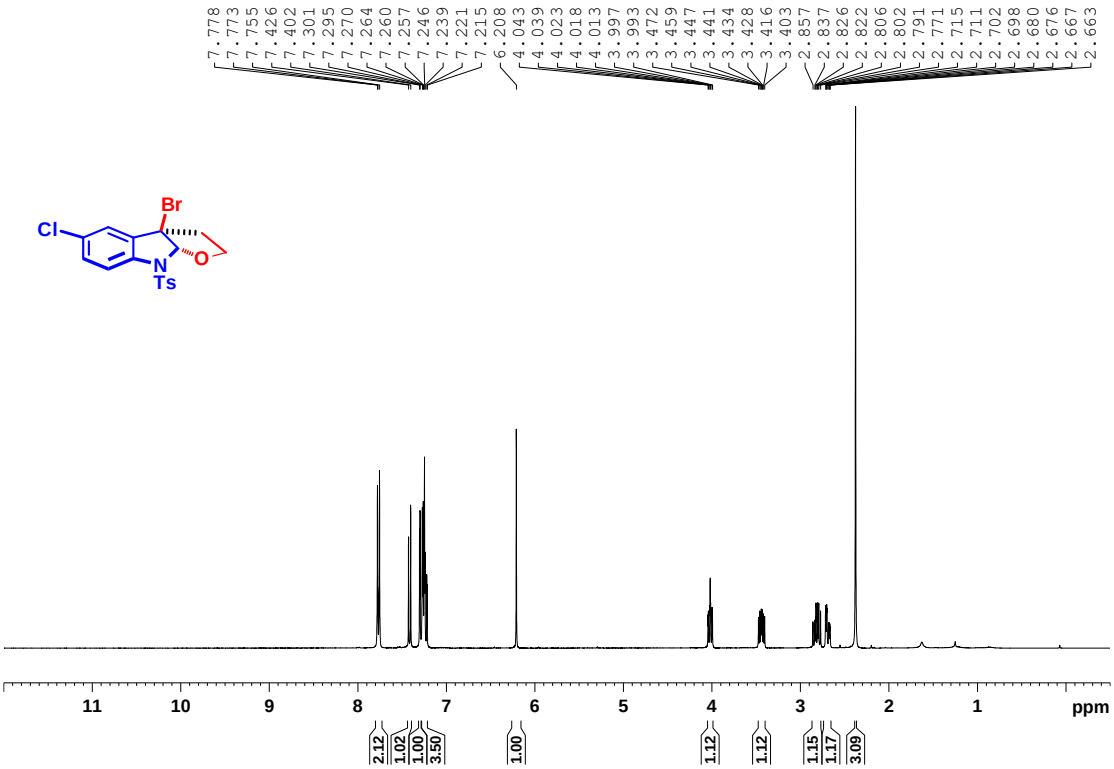
^{1}H NMR (CDCl$_3$, 300K), **7c**



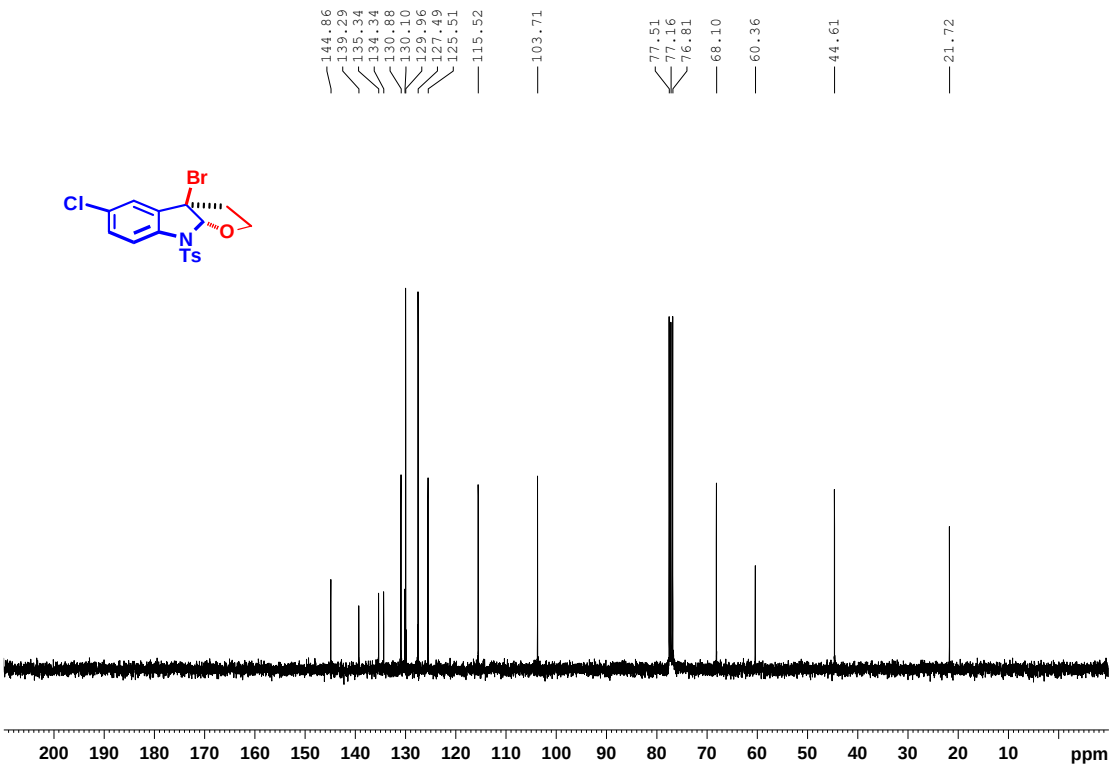
^{13}C NMR (CDCl$_3$, 300K), **7c**



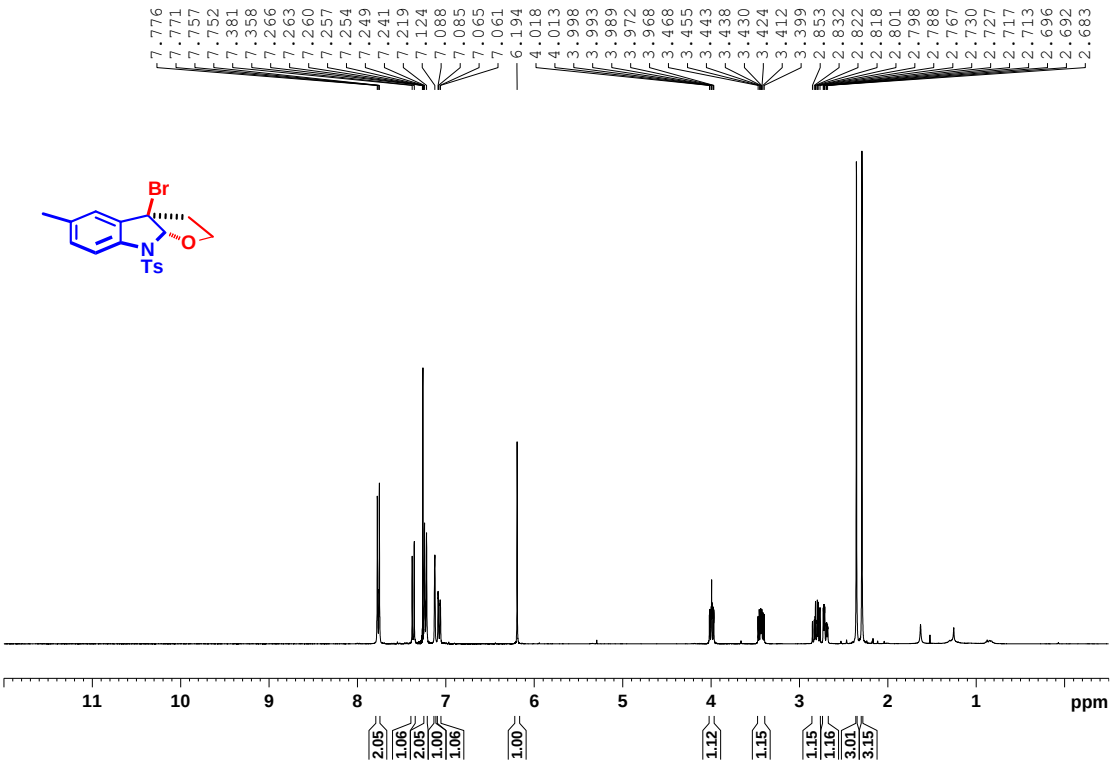
^{1}H NMR (CDCl$_3$, 300K), **7d**



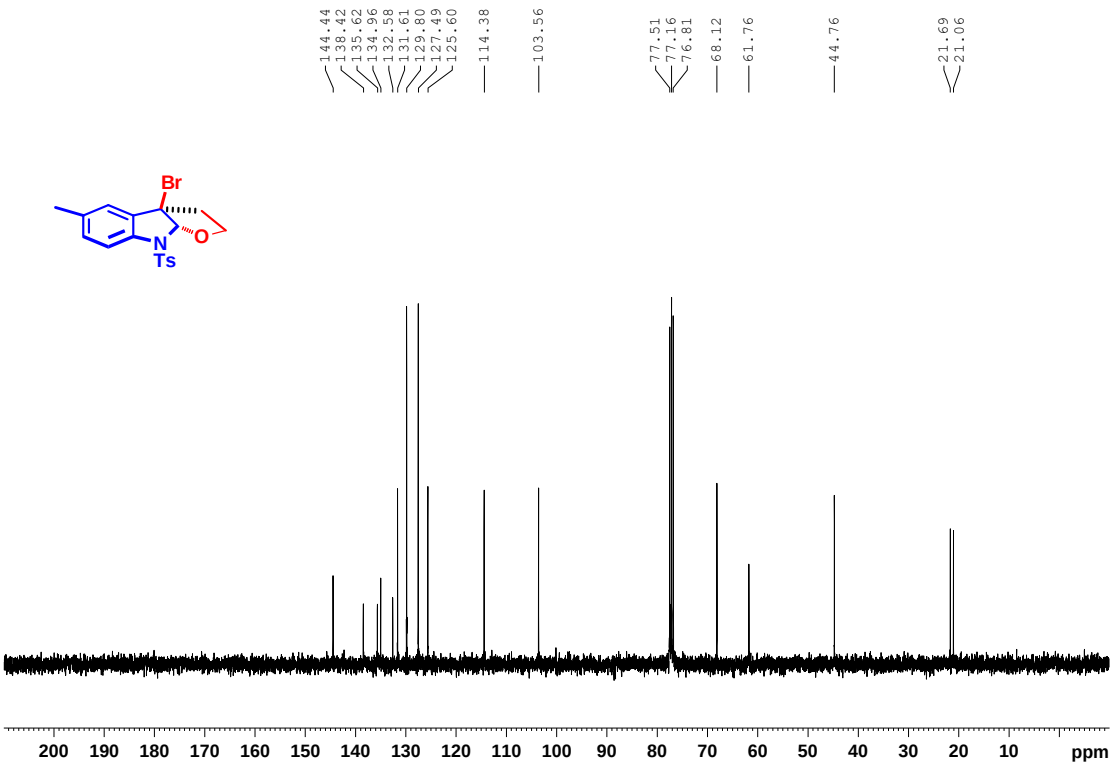
^{13}C NMR (CDCl$_3$, 300K), **7d**



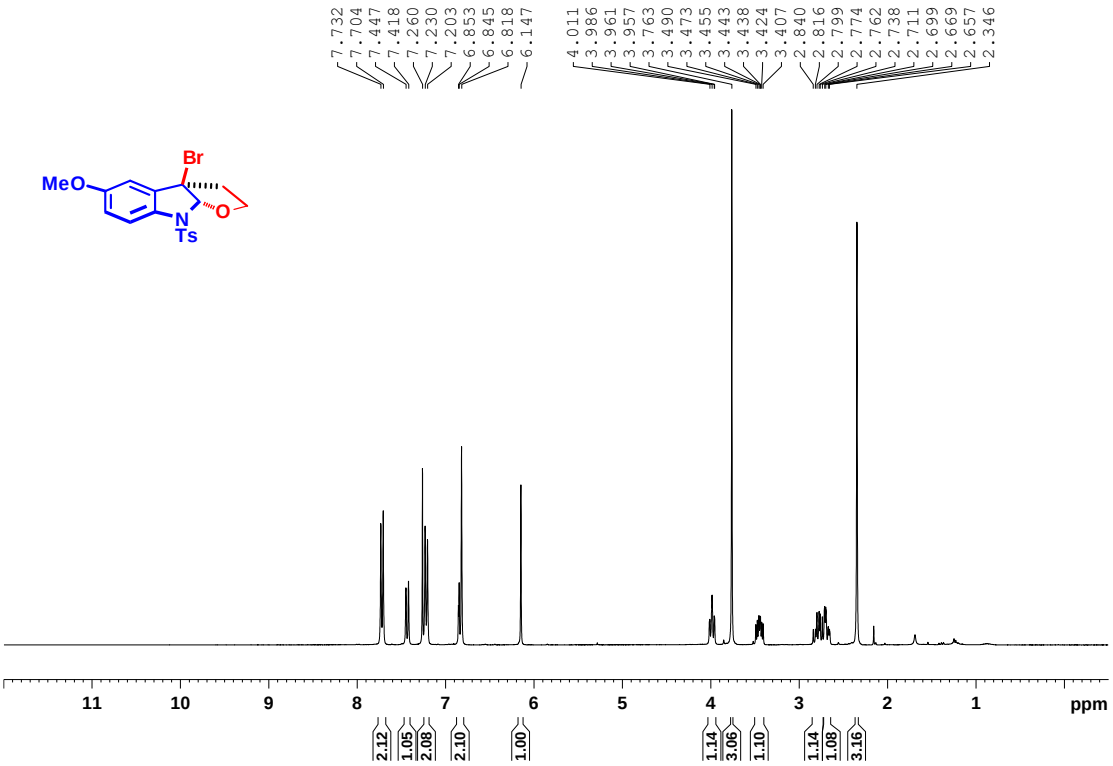
^{1}H NMR (CDCl$_3$, 300K), **7e**



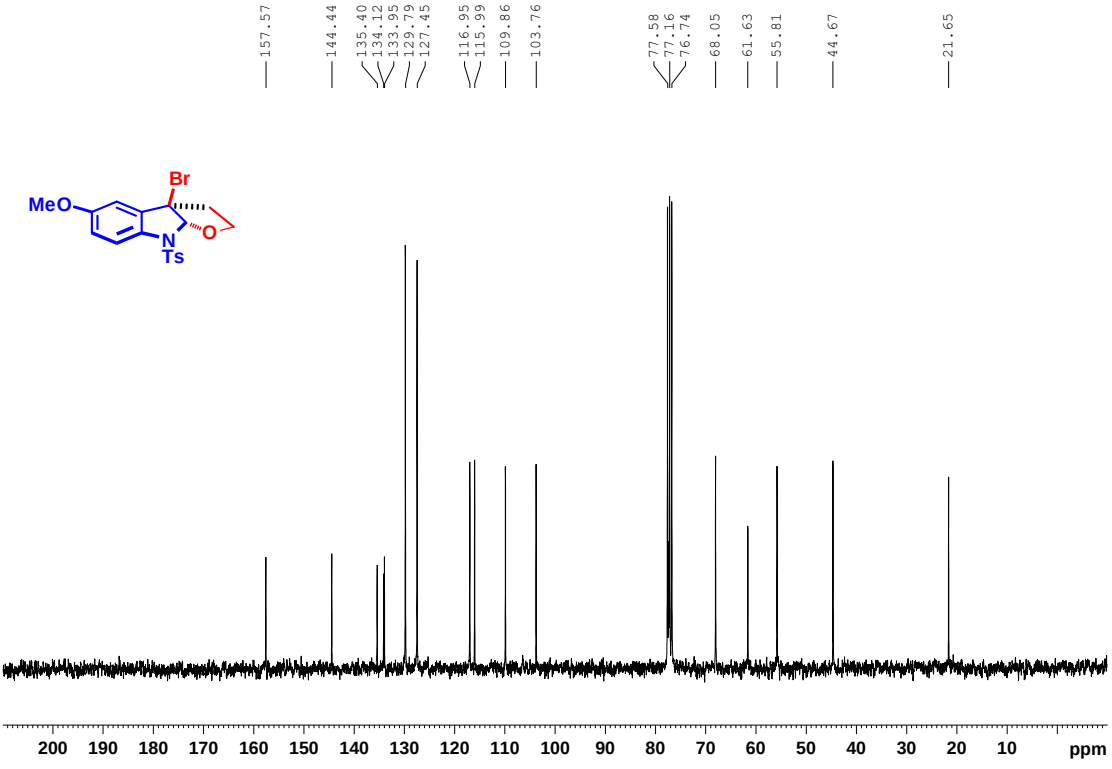
^{13}C NMR (CDCl$_3$, 300K), **7e**



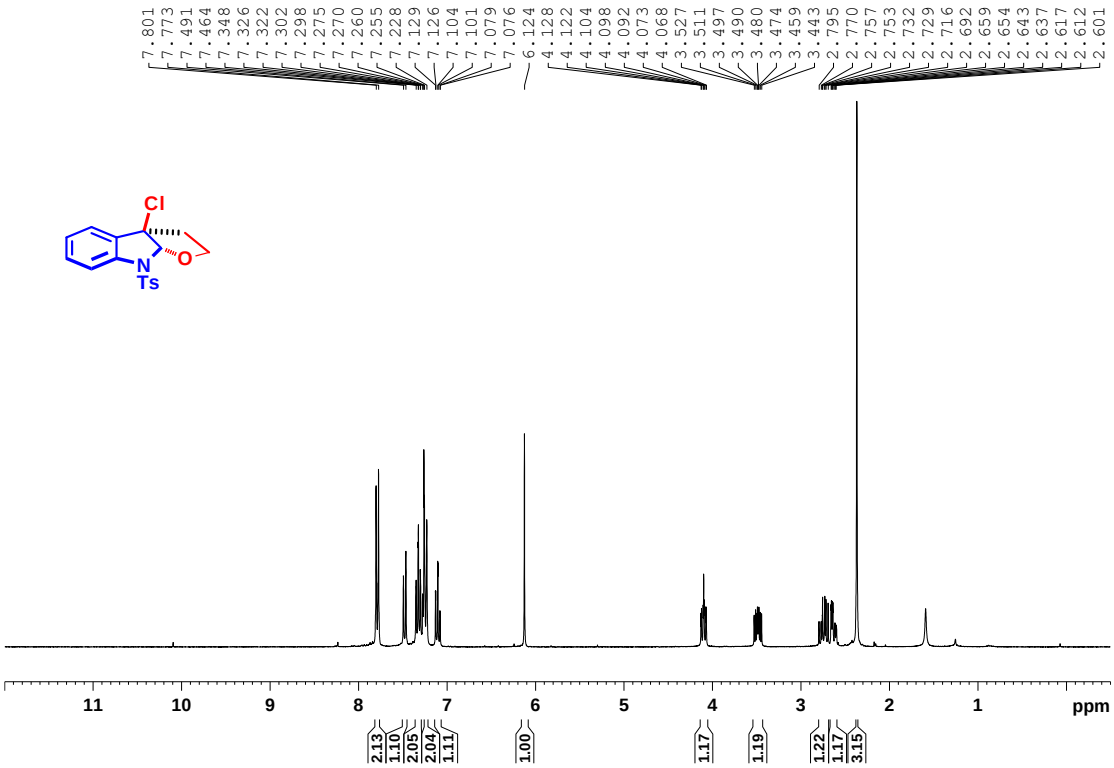
^{1}H NMR (CDCl$_3$, 300K), **7f**



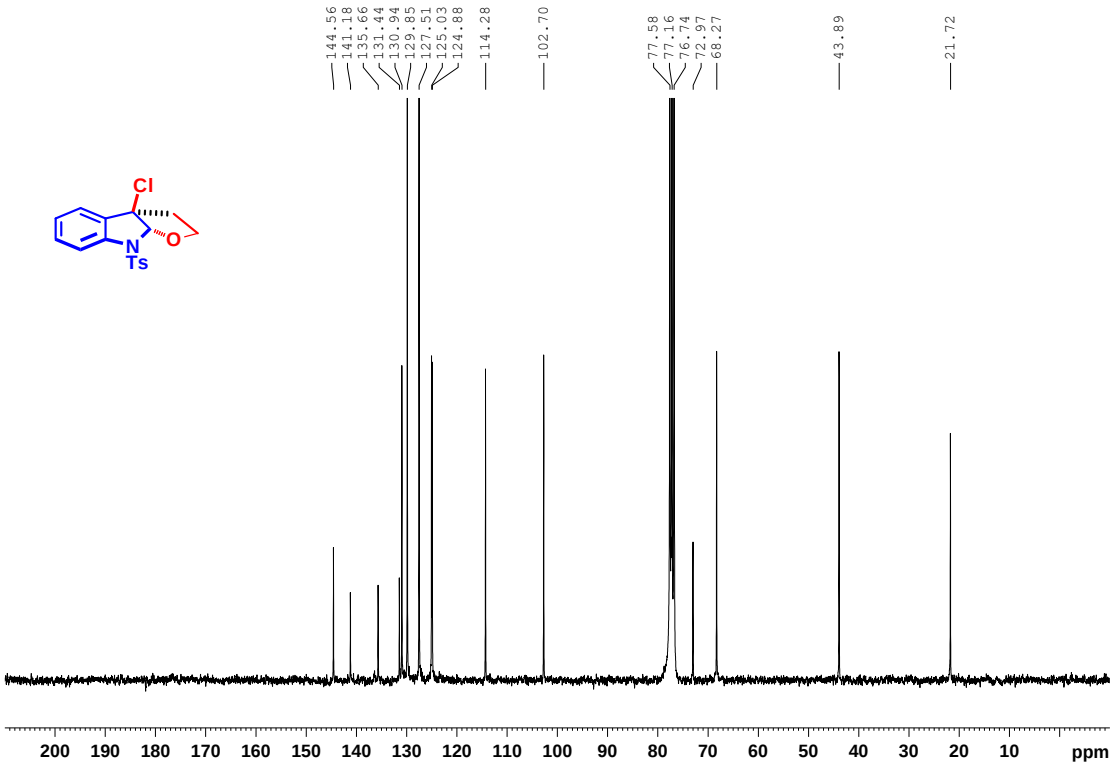
^{13}C NMR (CDCl$_3$, 300K), **7f**



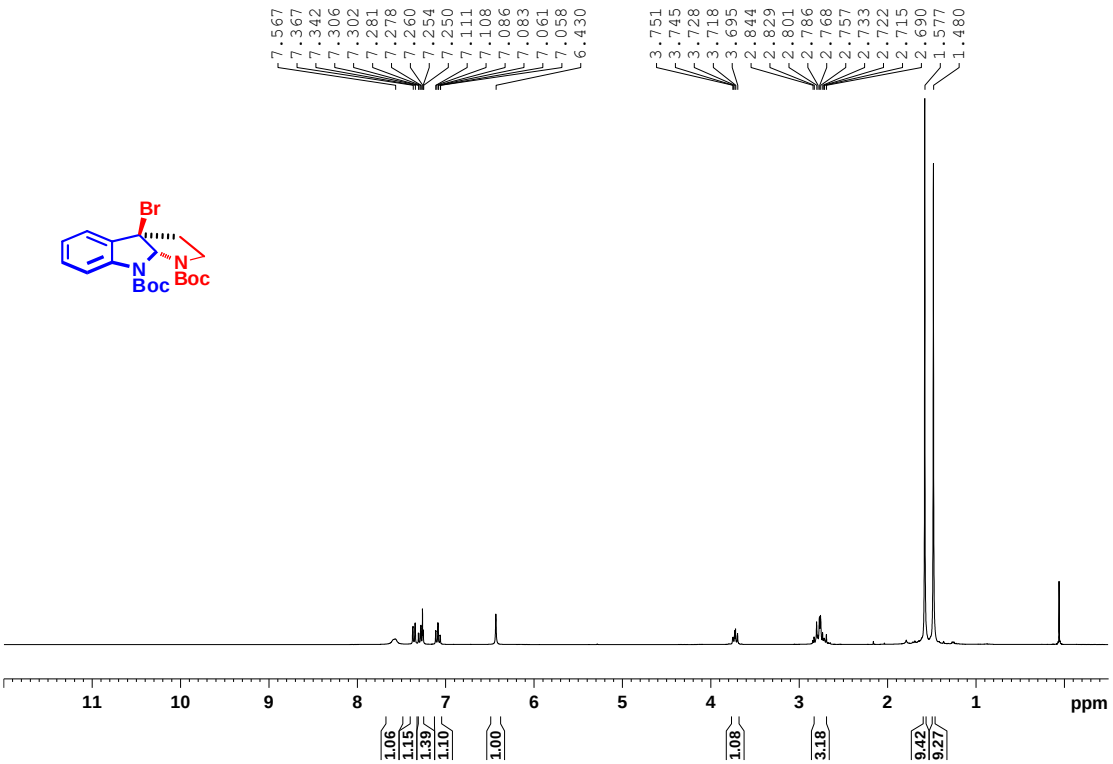
^{1}H NMR (CDCl$_3$, 300K), **7g**



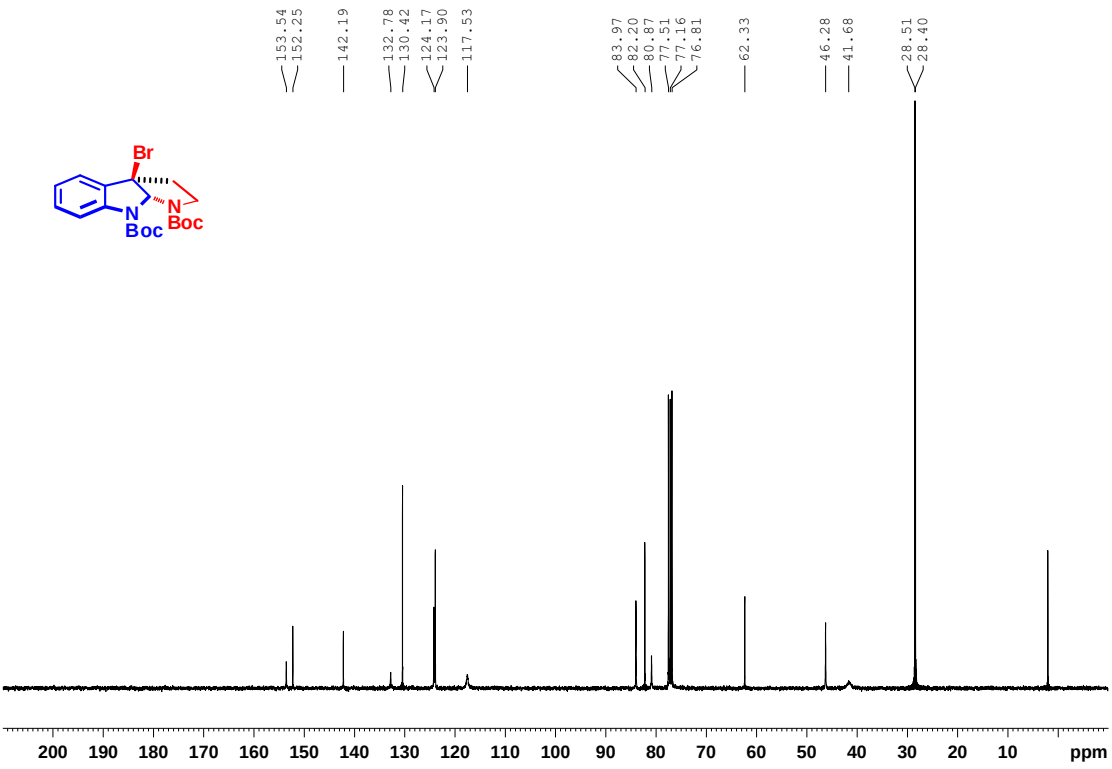
^{13}C NMR (CDCl$_3$, 300K), **7g**



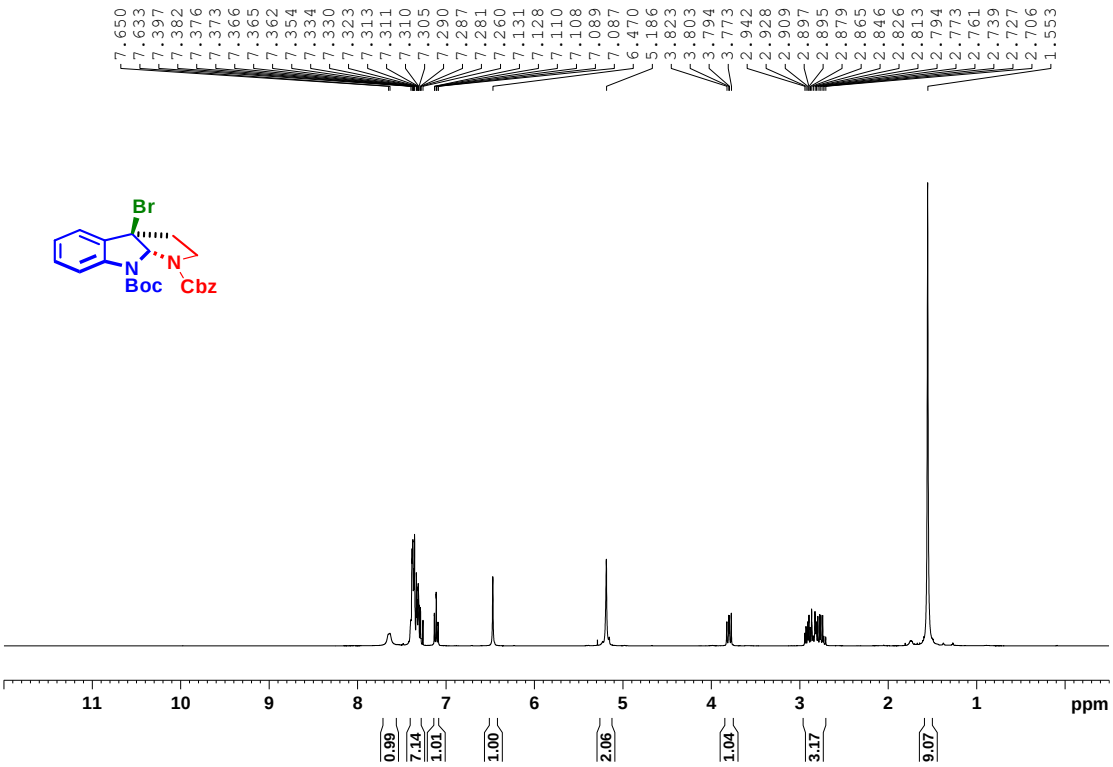
^{1}H NMR (CDCl$_3$, 300K), **8a**



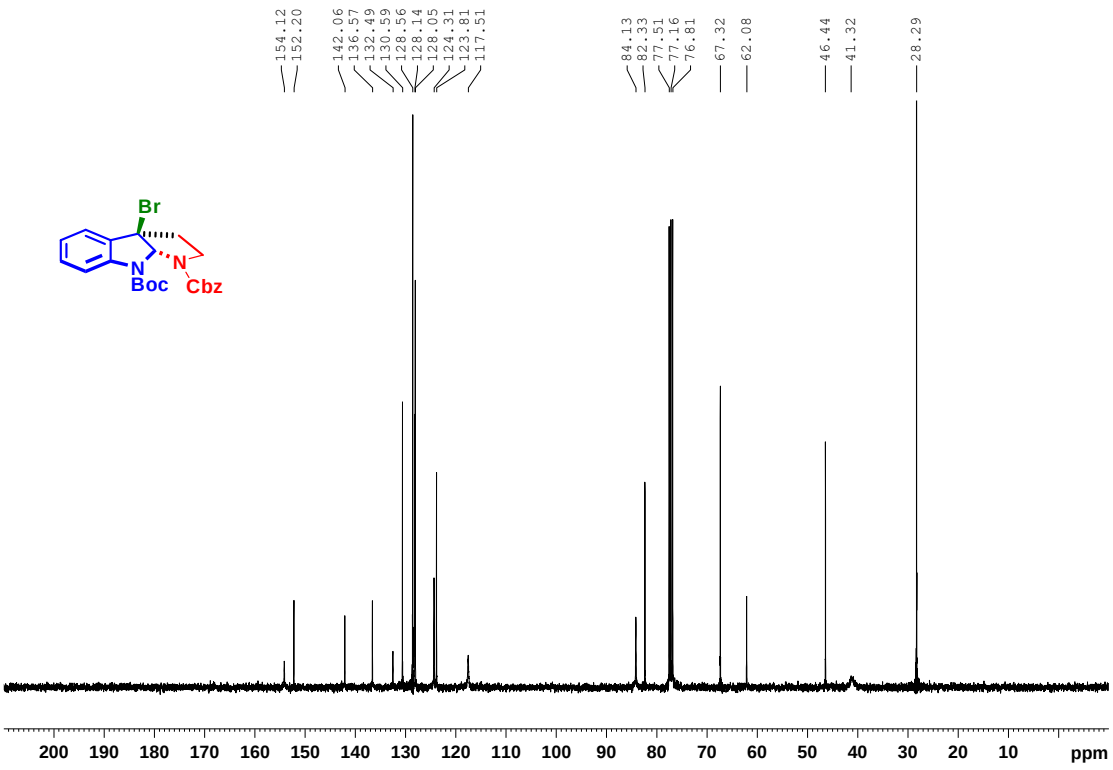
^{13}C NMR (CDCl$_3$, 300K), **8a**



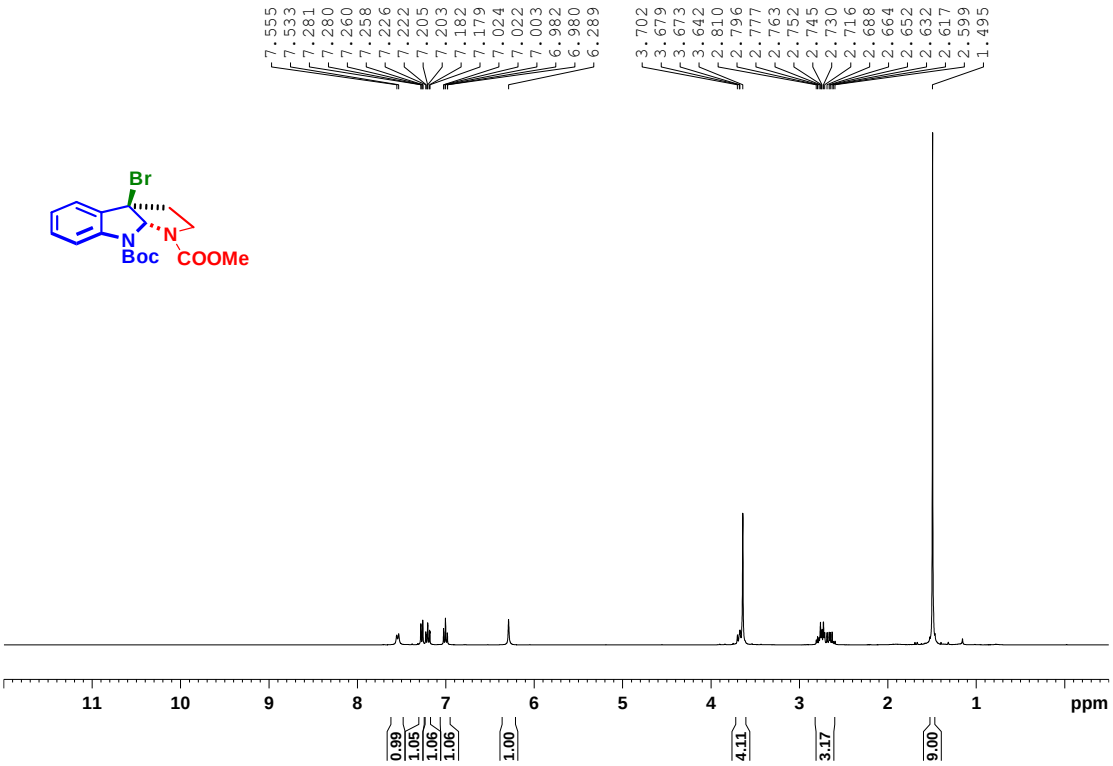
^{1}H NMR (CDCl$_3$, 300K), **8b**



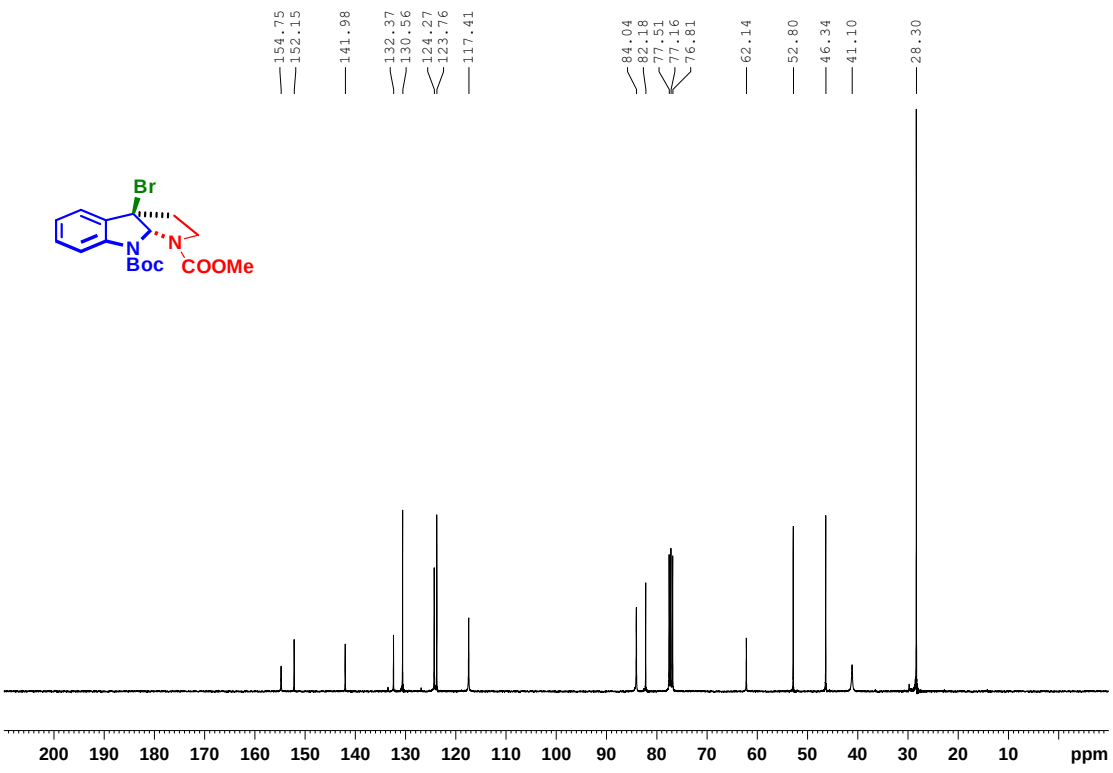
^{13}C NMR (CDCl$_3$, 300K), **8b**



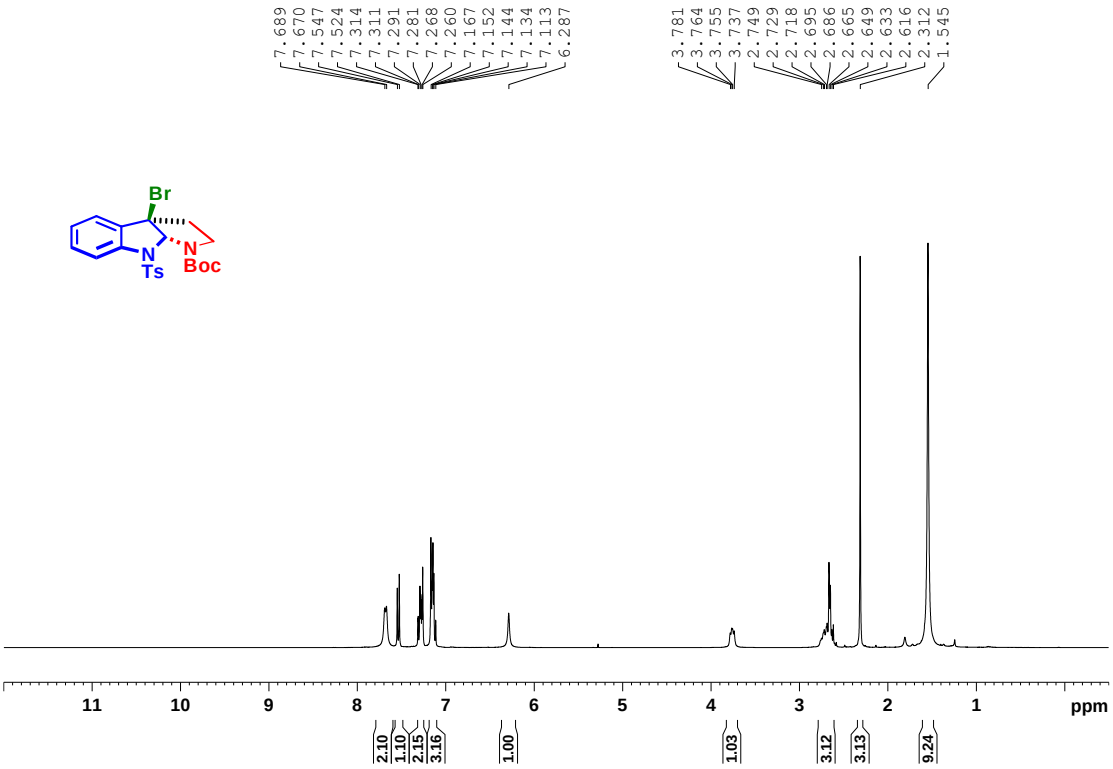
^{1}H NMR (CDCl$_3$, 300K), **8c**



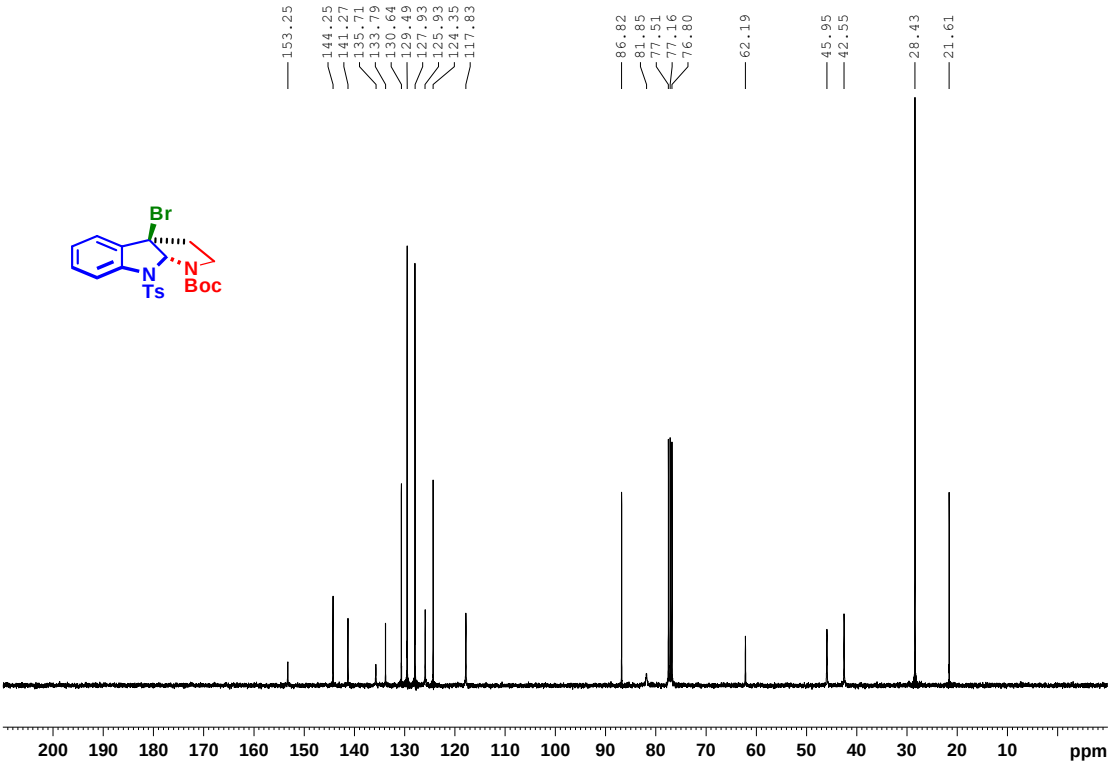
^{13}C NMR (CDCl$_3$, 300K), **8c**



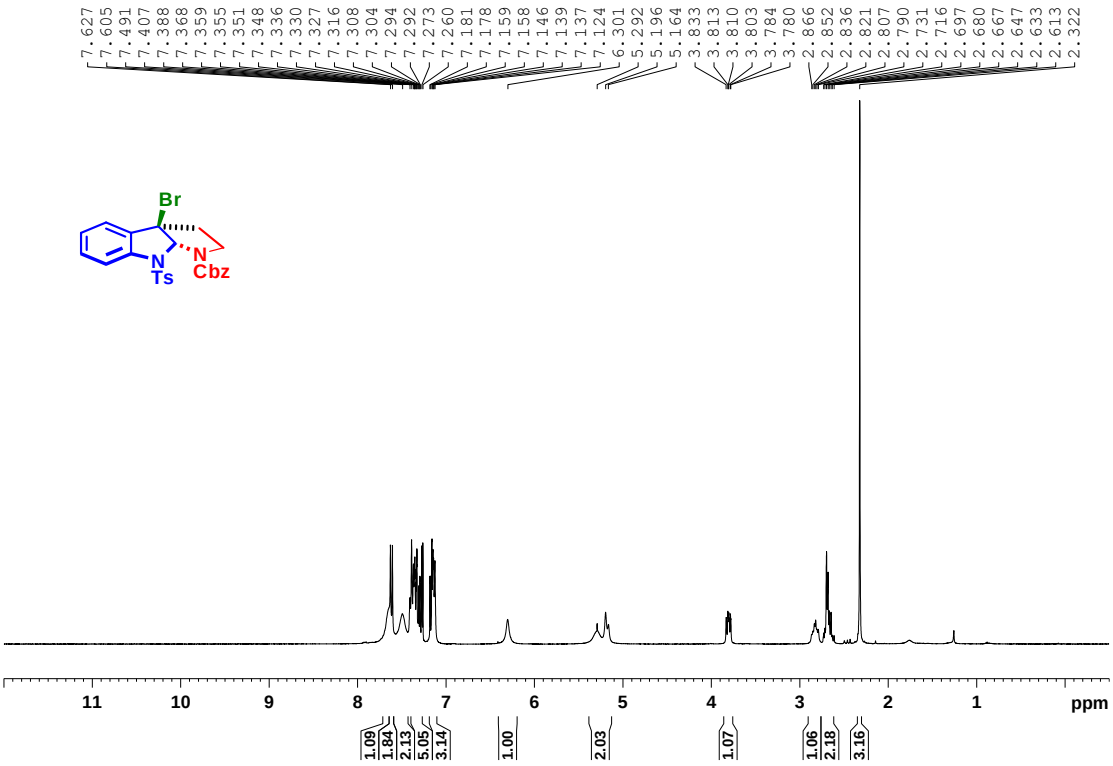
^{1}H NMR (CDCl$_3$, 300K), **8d**



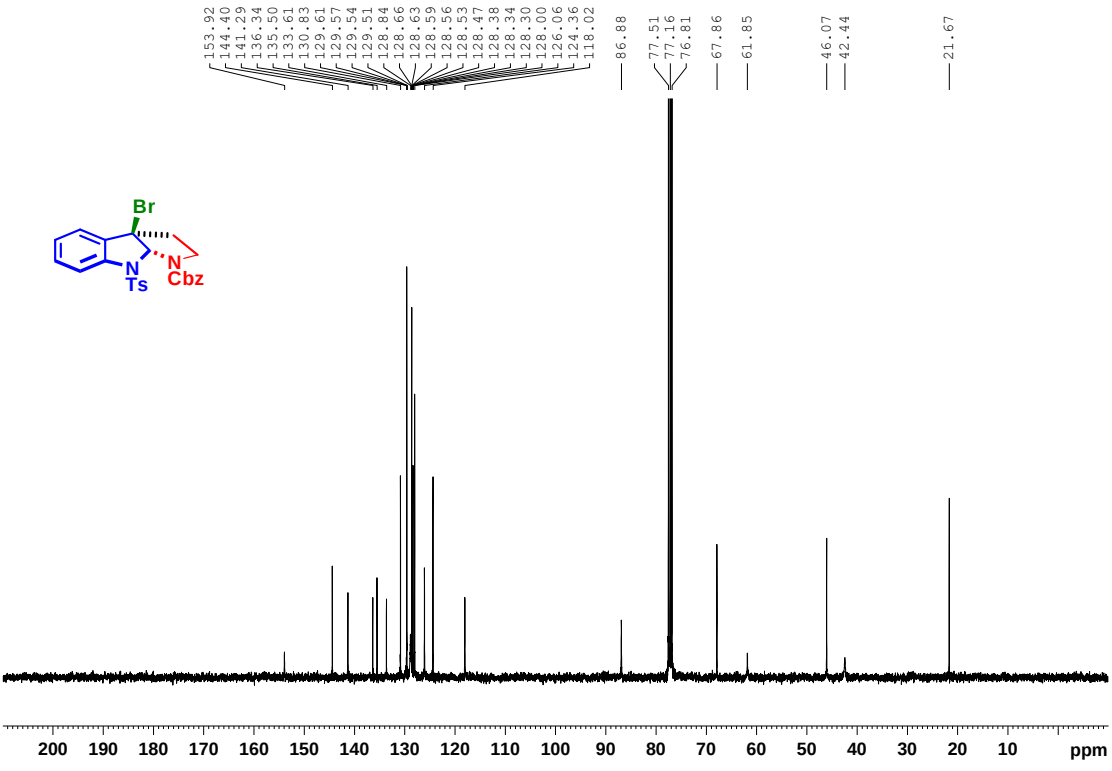
^{13}C NMR (CDCl$_3$, 300K), **8d**



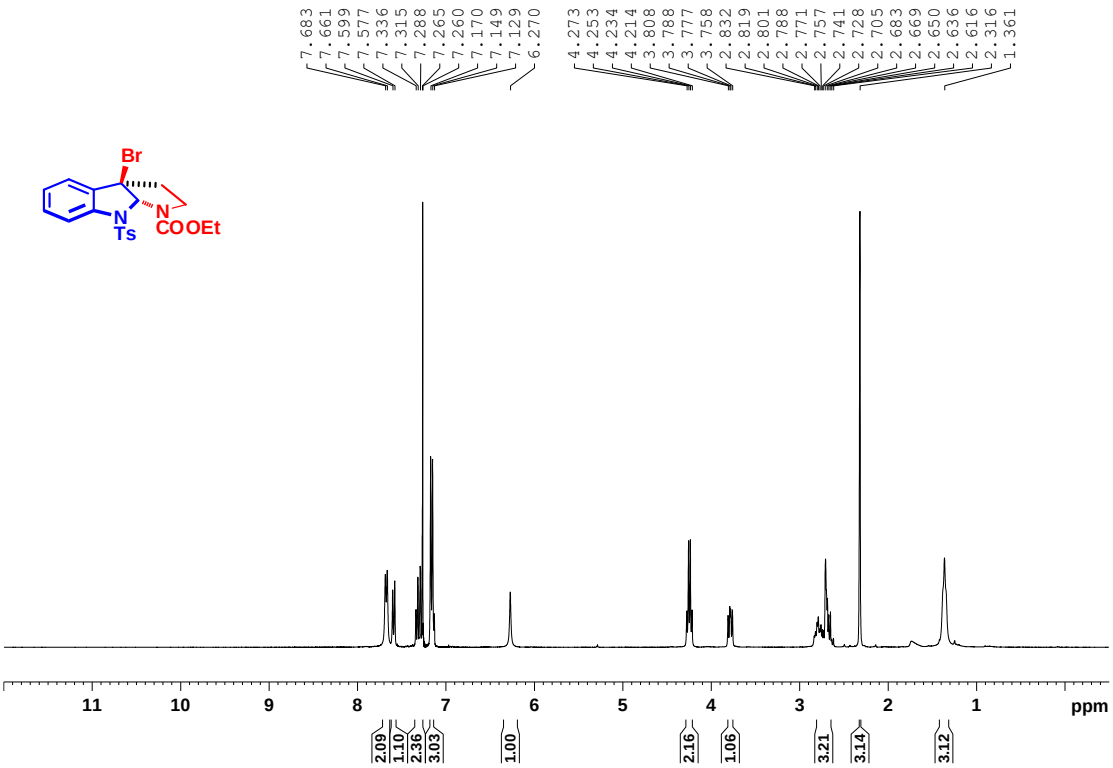
^{1}H NMR (CDCl$_3$, 300K), **8e**



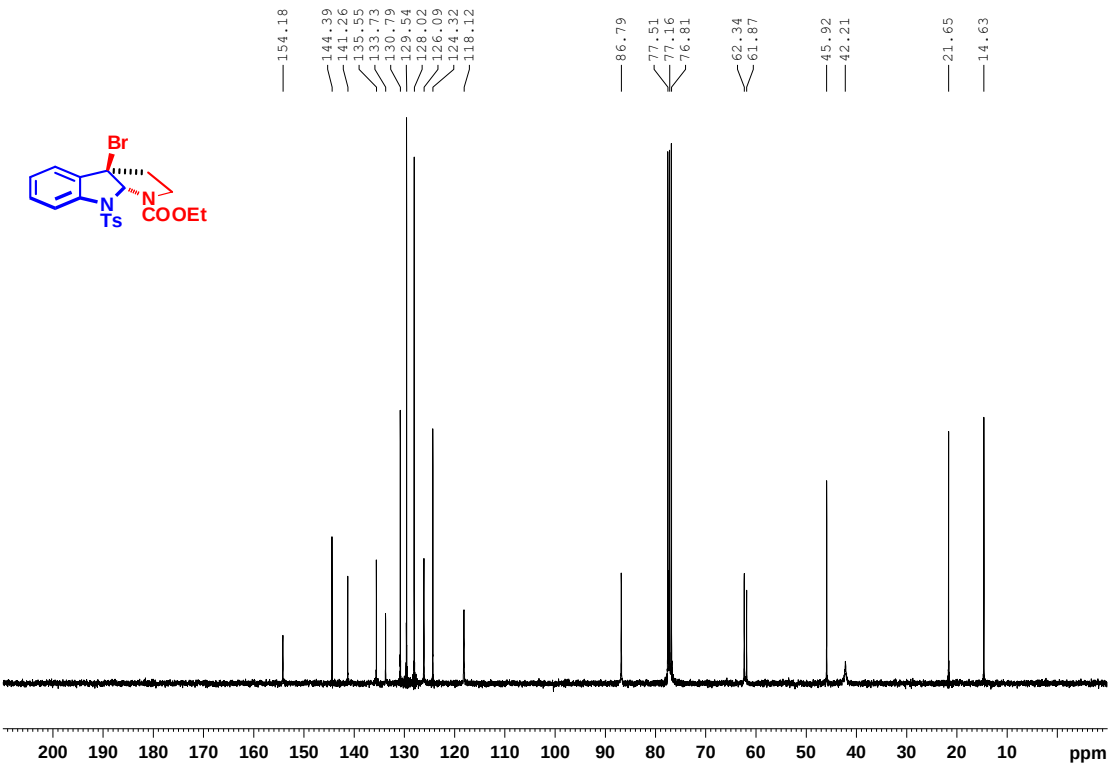
^{13}C NMR (CDCl$_3$, 300K), **8e**



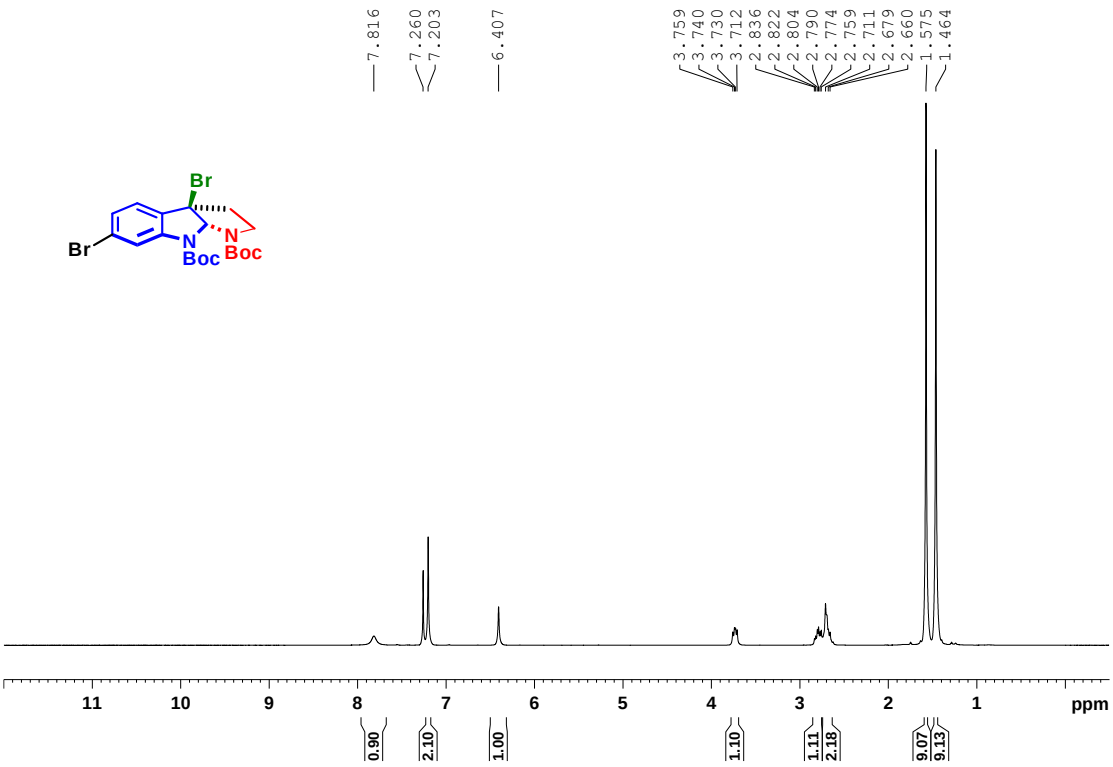
^{1}H NMR (CDCl$_3$, 300K), **8f**



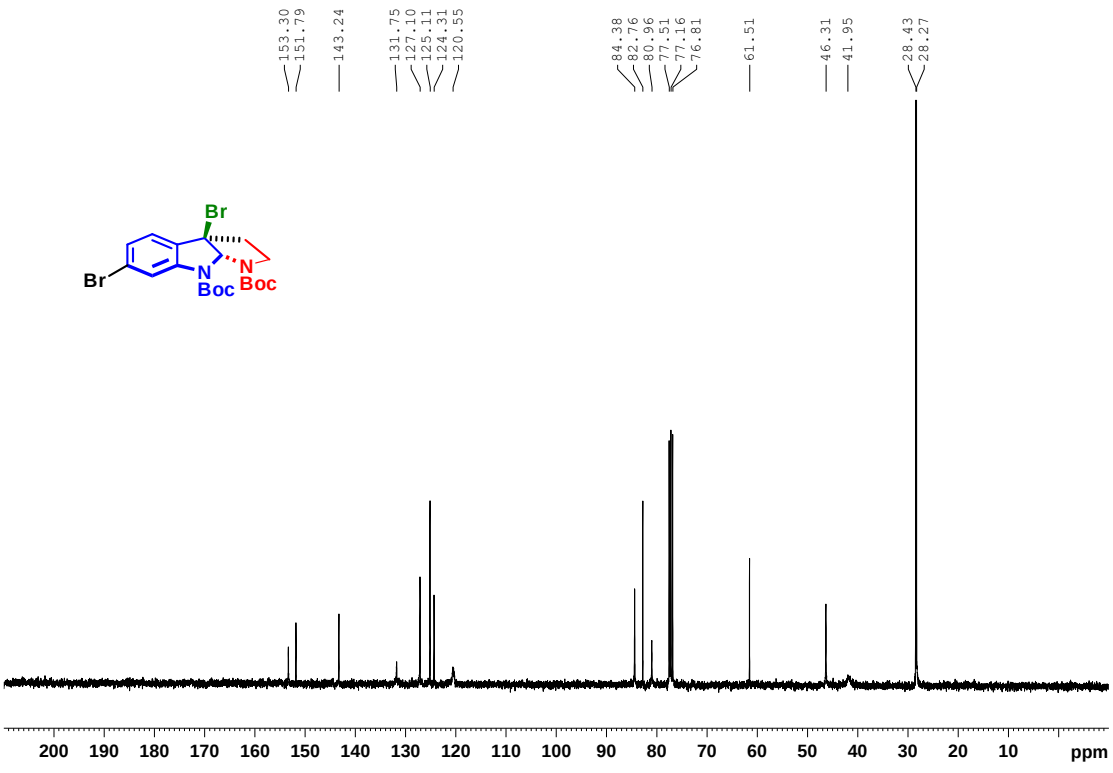
^{13}C NMR (CDCl$_3$, 300K), **8f**



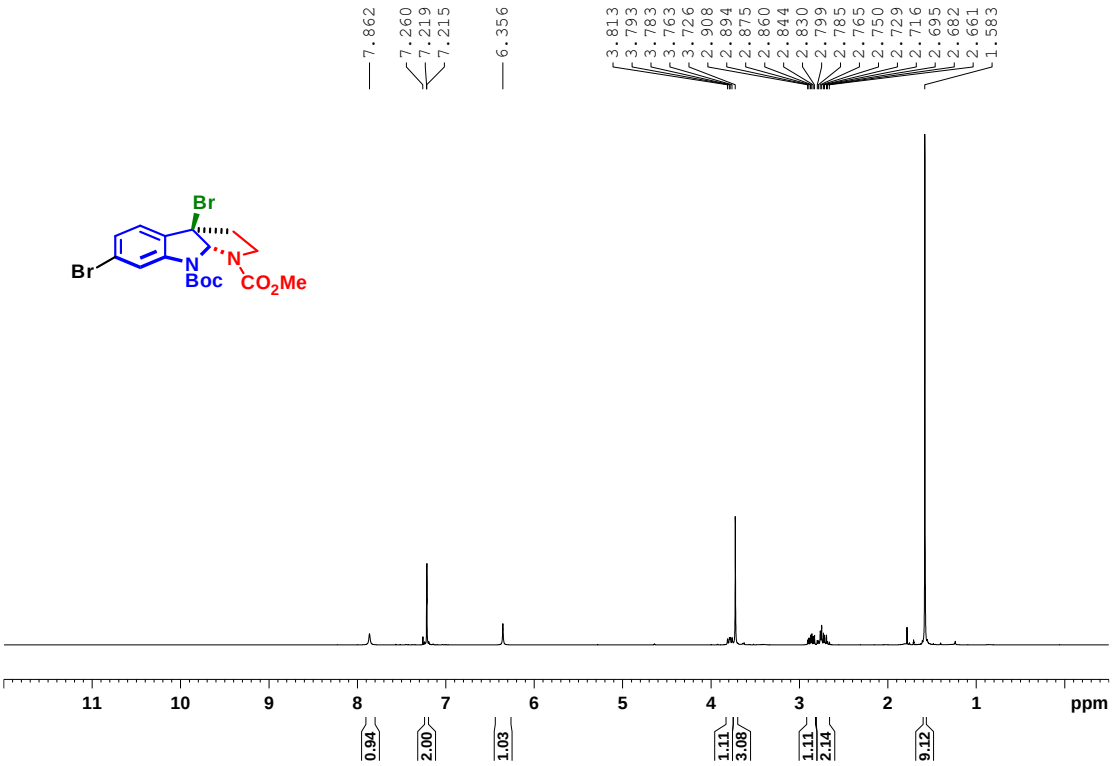
^{1}H NMR (CDCl$_3$, 300K), **8g**



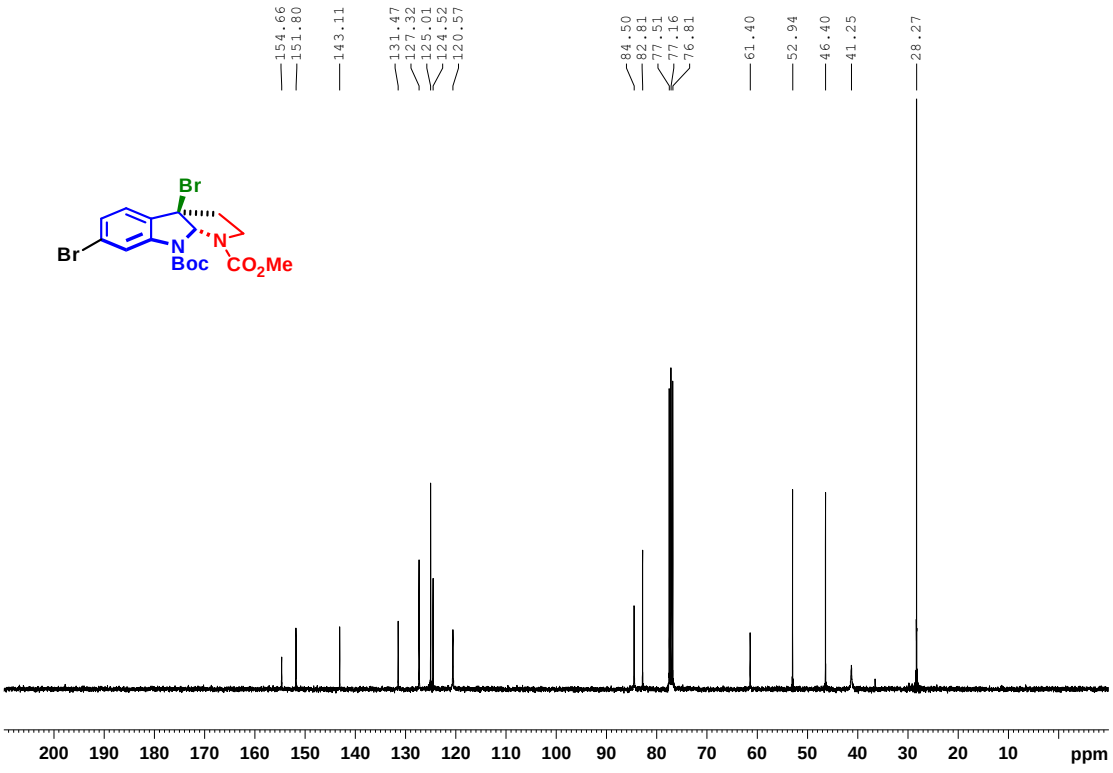
^{13}C NMR (CDCl$_3$, 300K), **8g**



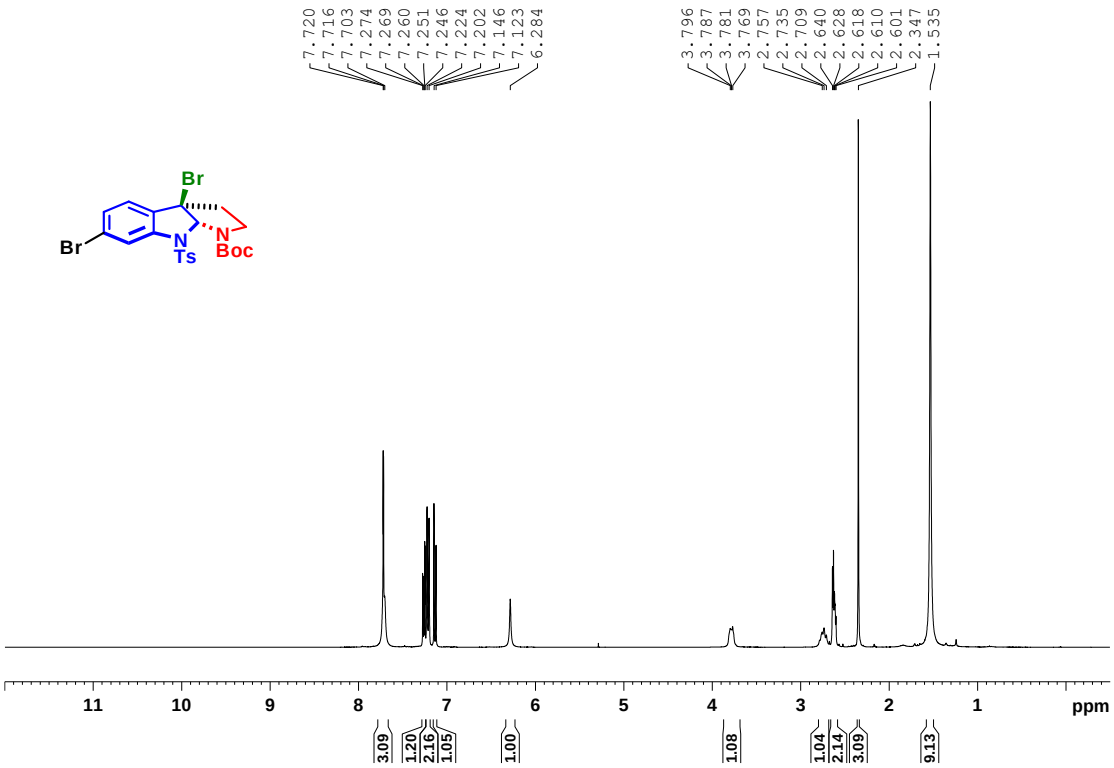
^{1}H NMR (CDCl$_3$, 300K), **8h**



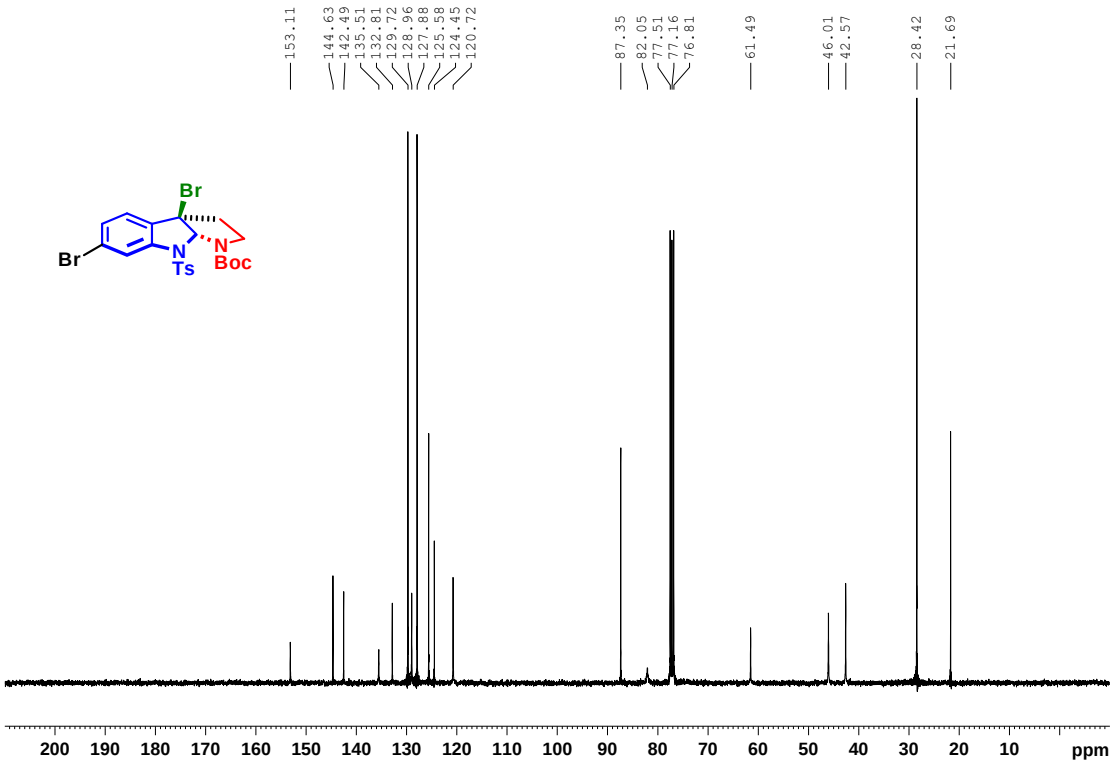
^{13}C NMR (CDCl$_3$, 300K), **8h**



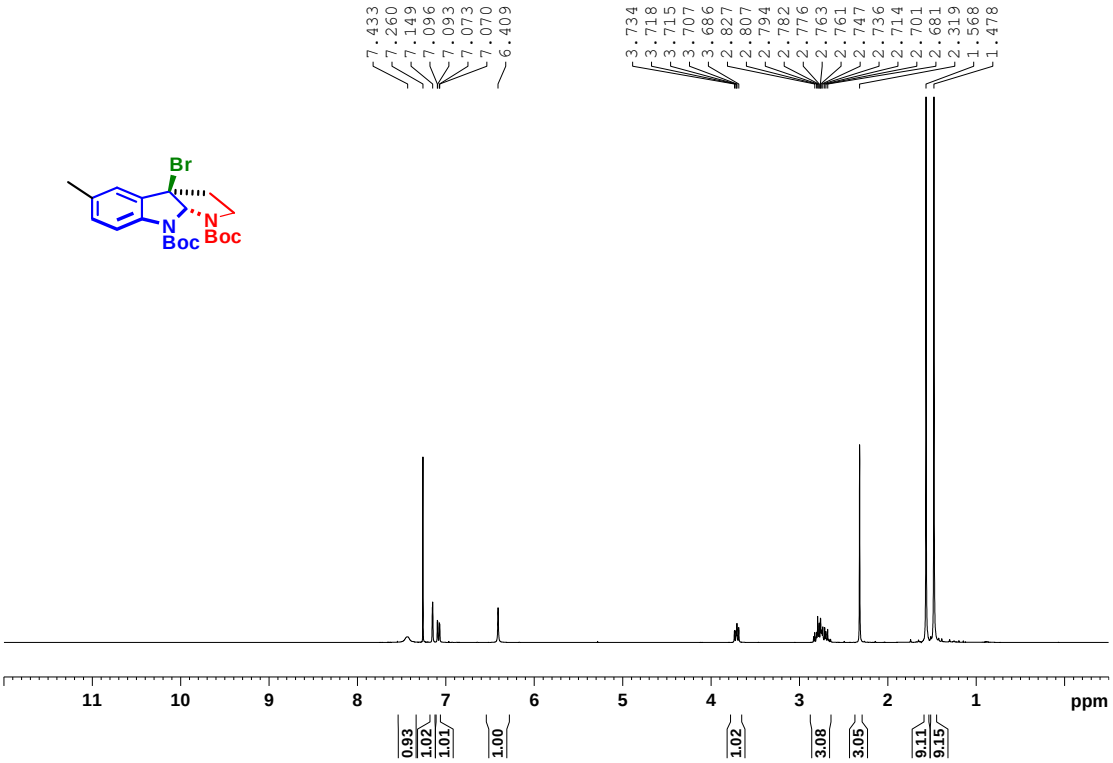
^{1}H NMR (CDCl$_3$, 300K), **8i**



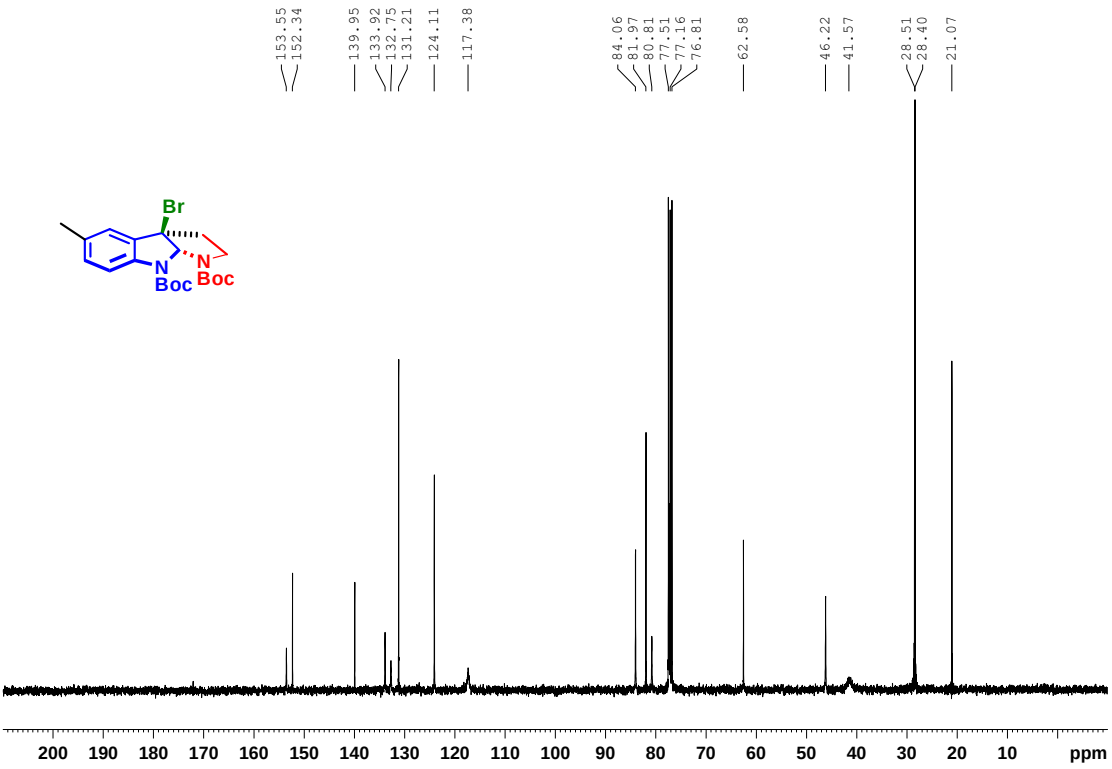
^{13}C NMR (CDCl$_3$, 300K), **8i**



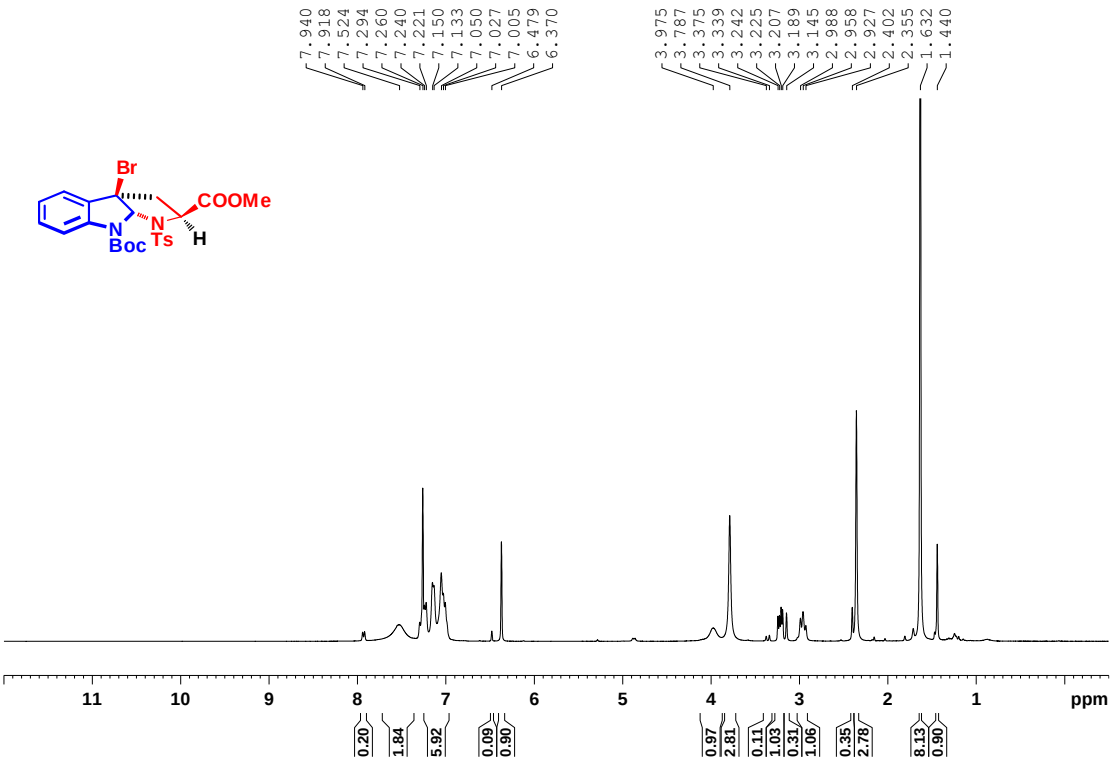
^{1}H NMR (CDCl$_3$, 300K), **8j**



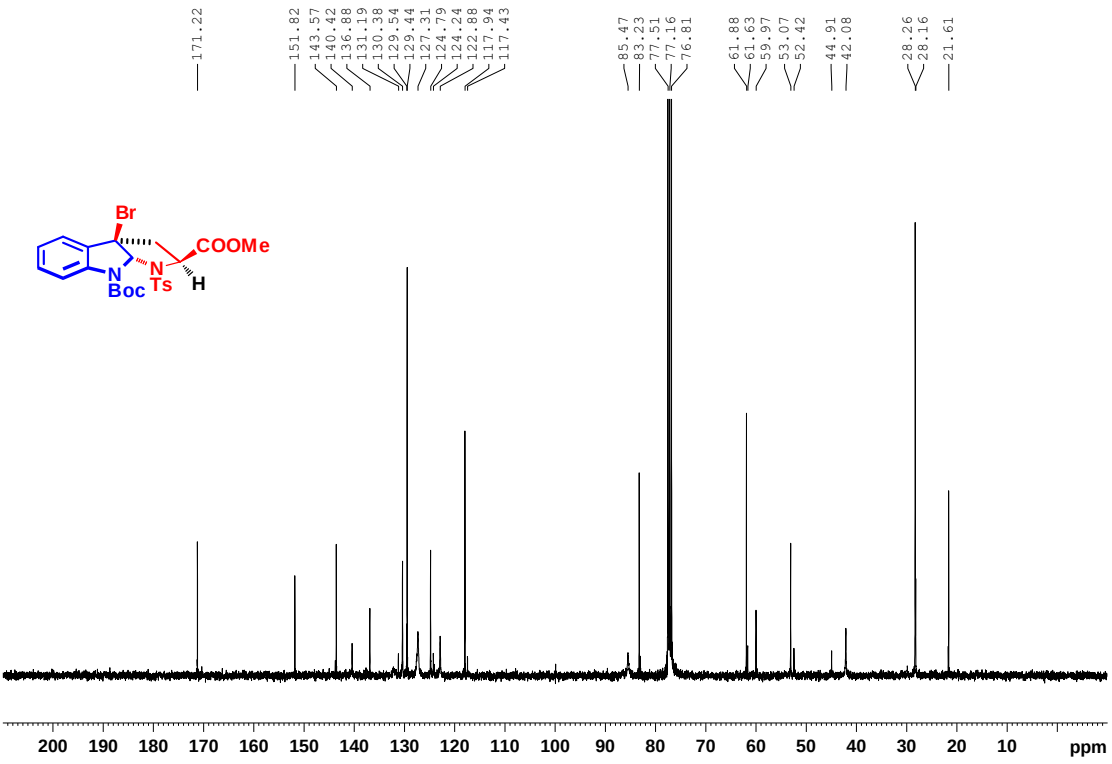
^{13}C NMR (CDCl$_3$, 300K), **8j**



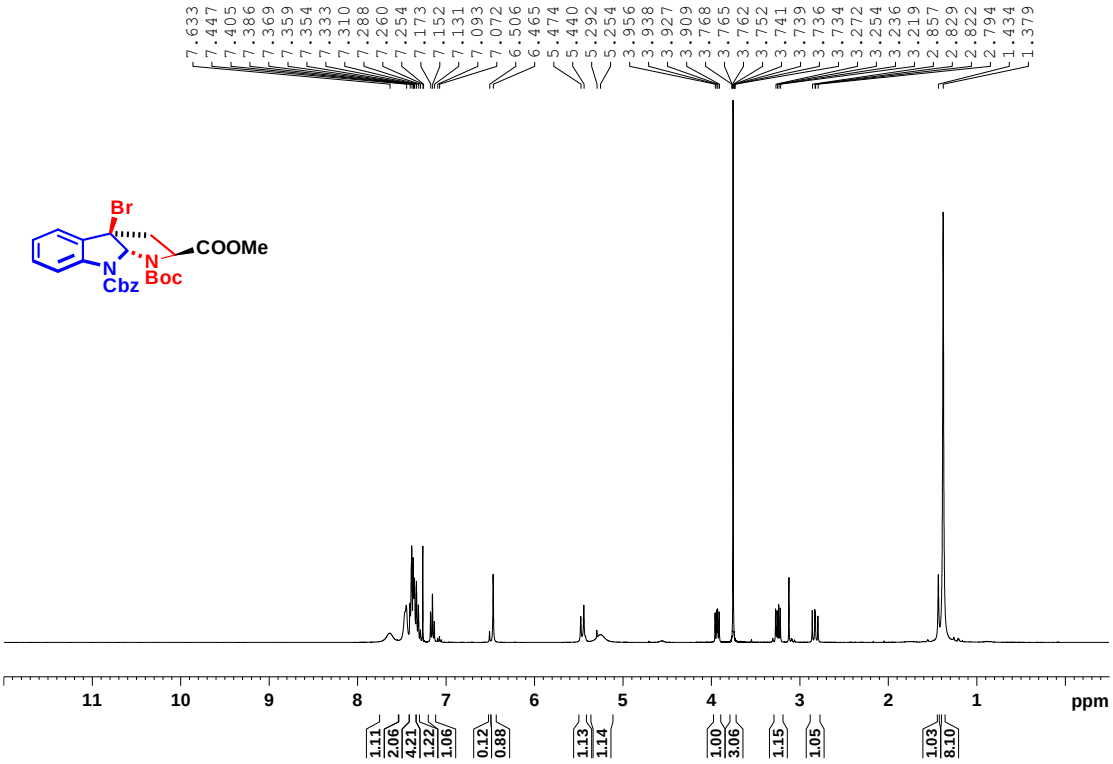
^{1}H NMR (CDCl$_3$, 300K), **8k** (*exo/endo* 90:10 mixture of diastereoisomers)



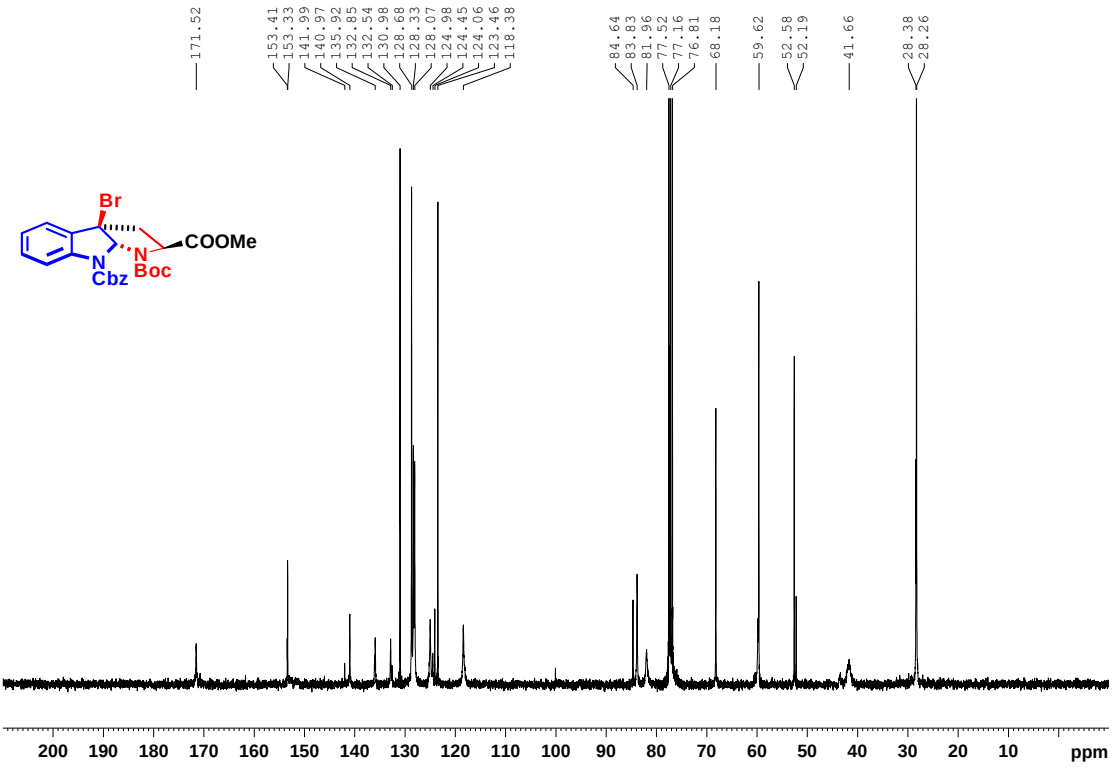
^{13}C NMR (CDCl$_3$, 300K), **8k** (*exo/endo* 90:10 mixture of diastereoisomers)



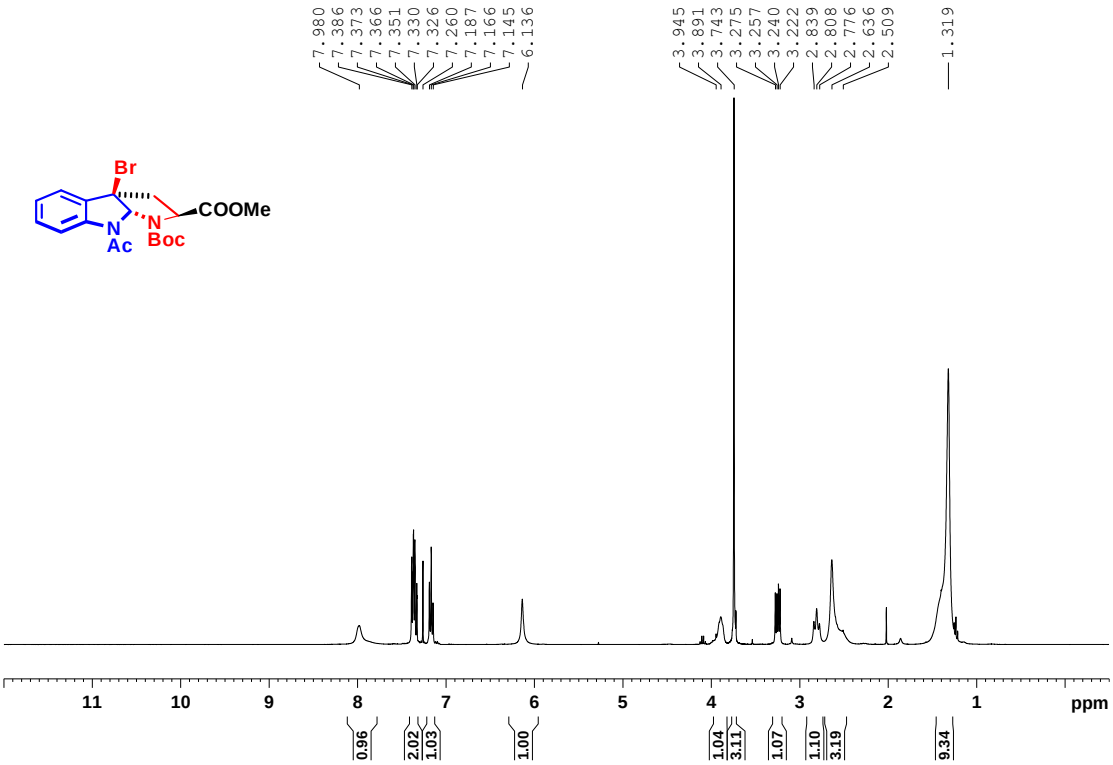
^{1}H NMR (CDCl$_3$, 300K), **8l** (*exo/endo* 90:10 mixture of diastereoisomers)



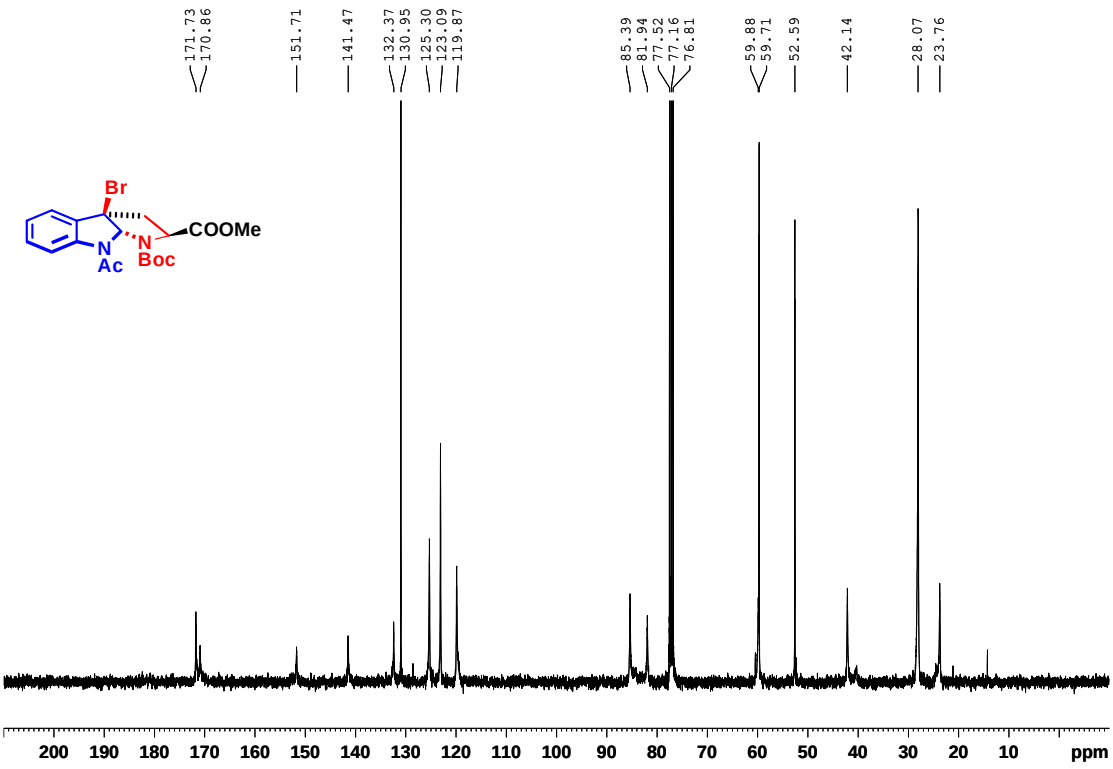
^{13}C NMR (CDCl$_3$, 300K), **8l** (*exo/endo* 90:10 mixture of diastereoisomers)



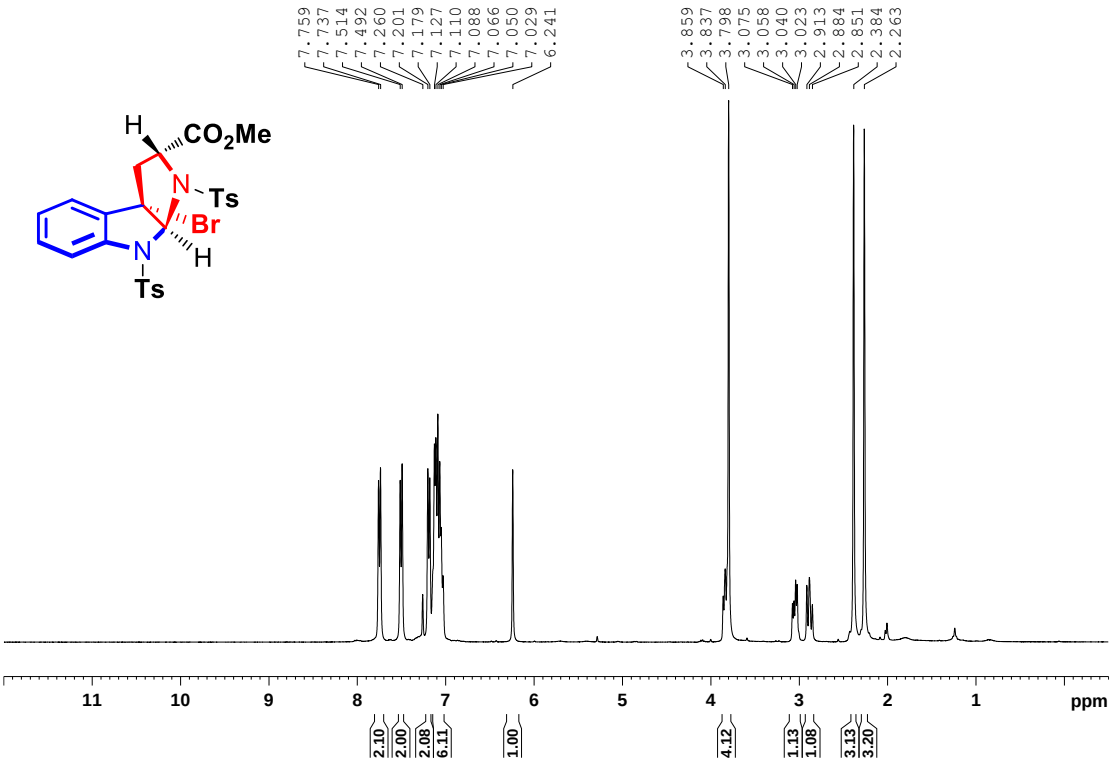
^{1}H NMR (CDCl$_3$, 300K), **8m** (*exo/endo* 90:10 mixture of diastereoisomers)



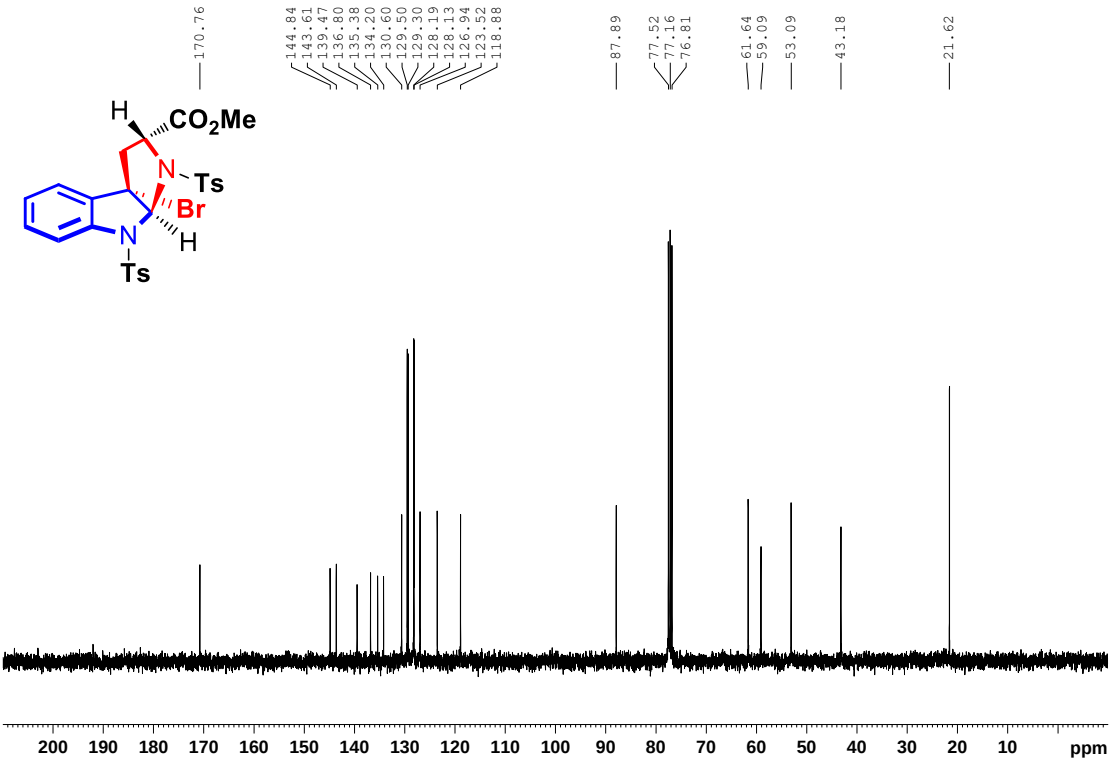
^{13}C NMR (CDCl$_3$, 300K), **8m** (*exo/endo* 90:10 mixture of diastereoisomers)



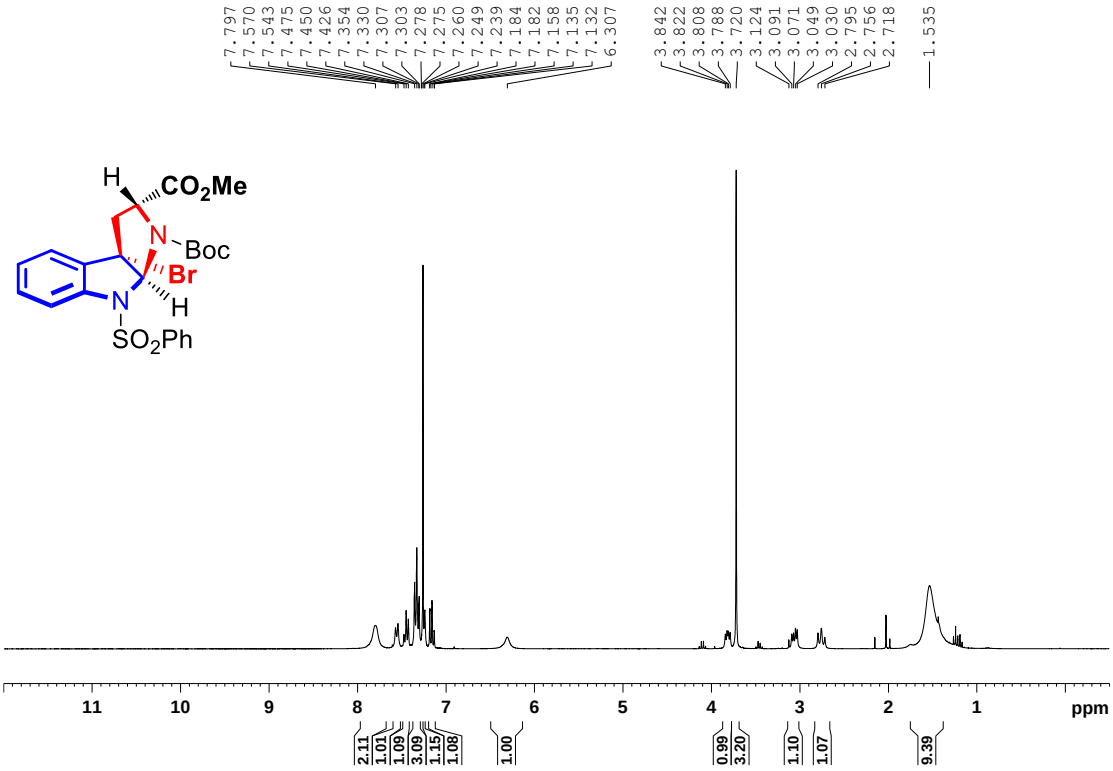
^{1}H NMR (CDCl$_3$, 300K), **8n**



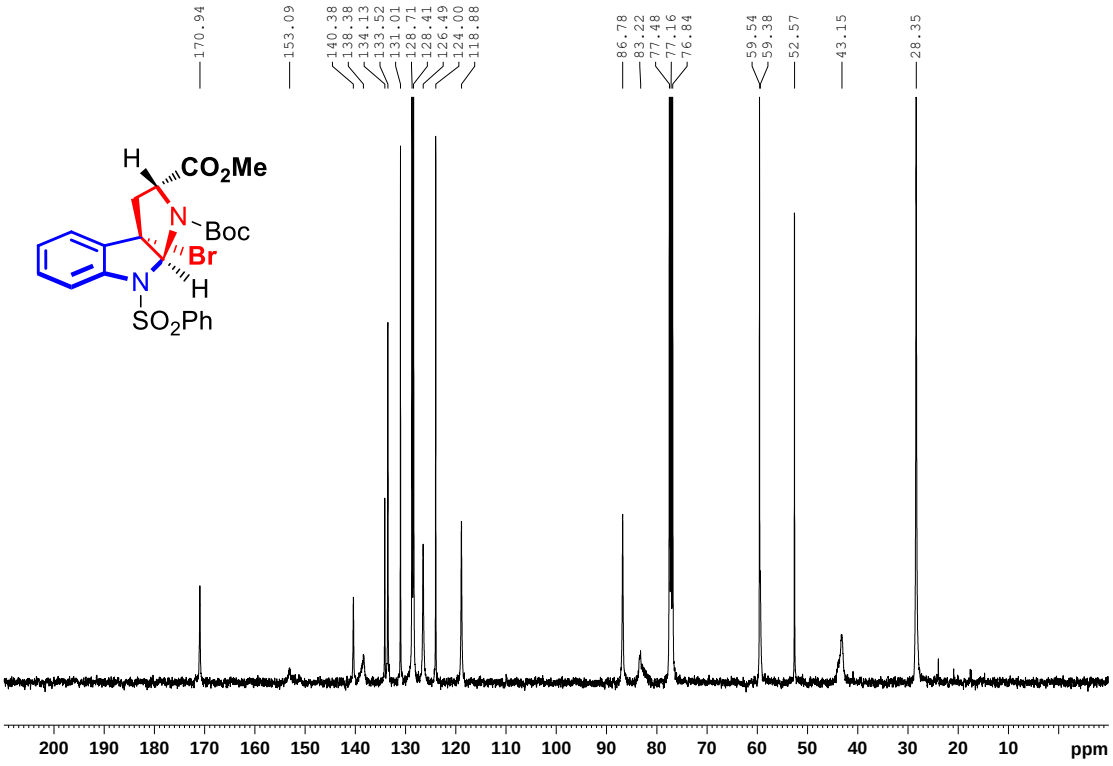
^{13}C NMR (CDCl$_3$, 300K), **8n**



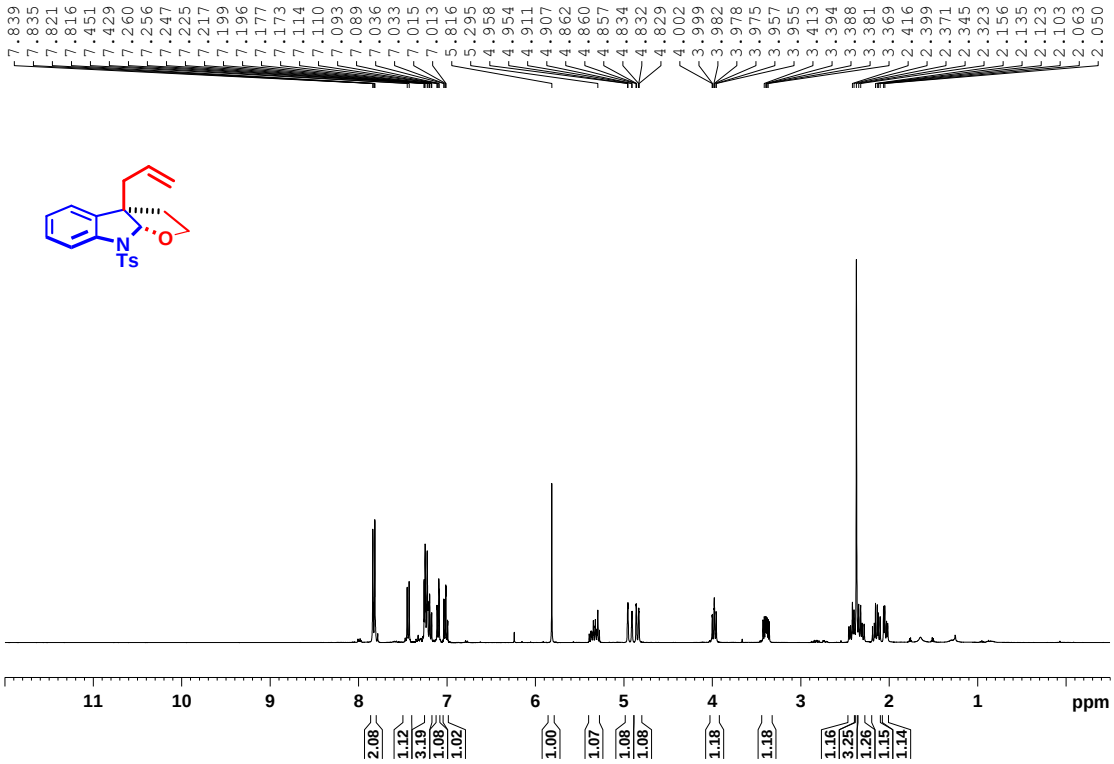
^{1}H NMR (CDCl$_3$, 300K), **8o**



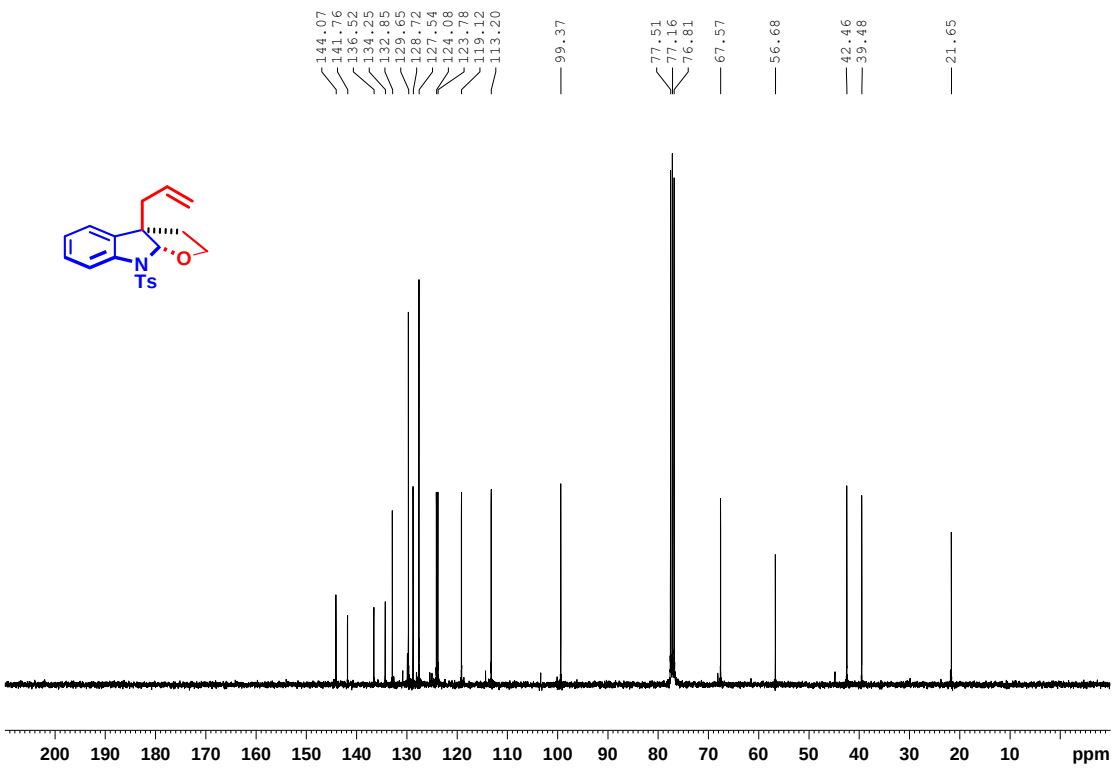
^{13}C NMR (CDCl$_3$, 300K), **8o**



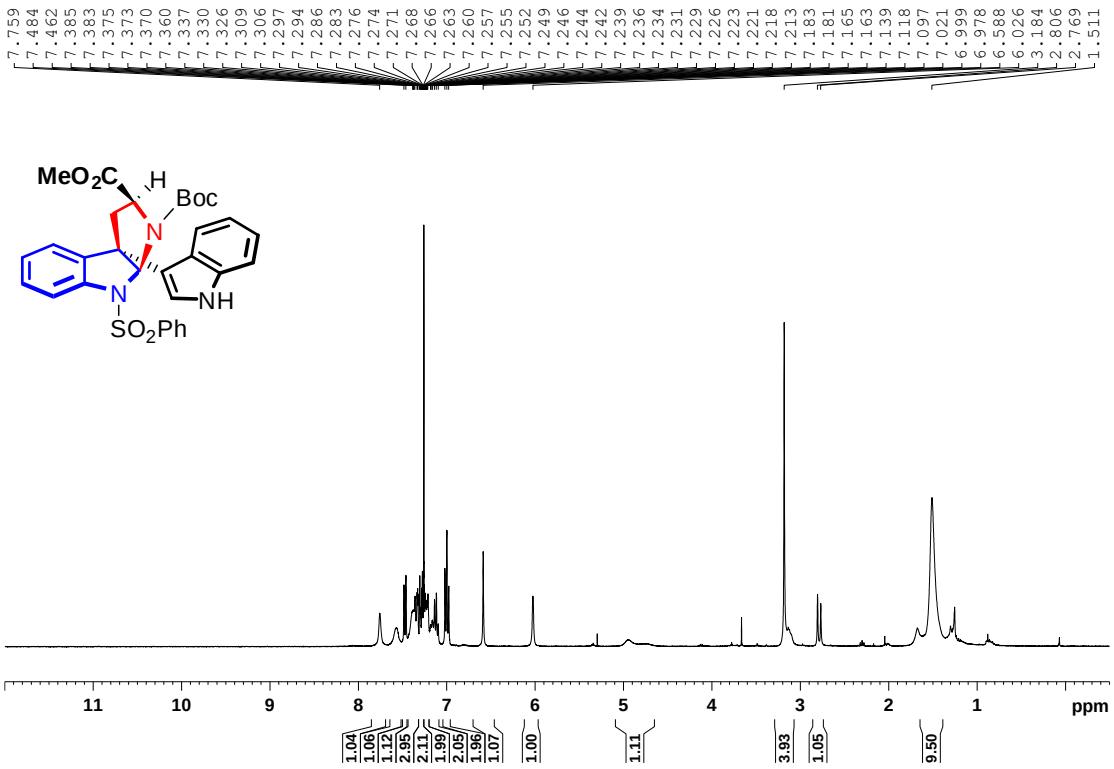
^{1}H NMR (CDCl$_3$, 300K), **9**



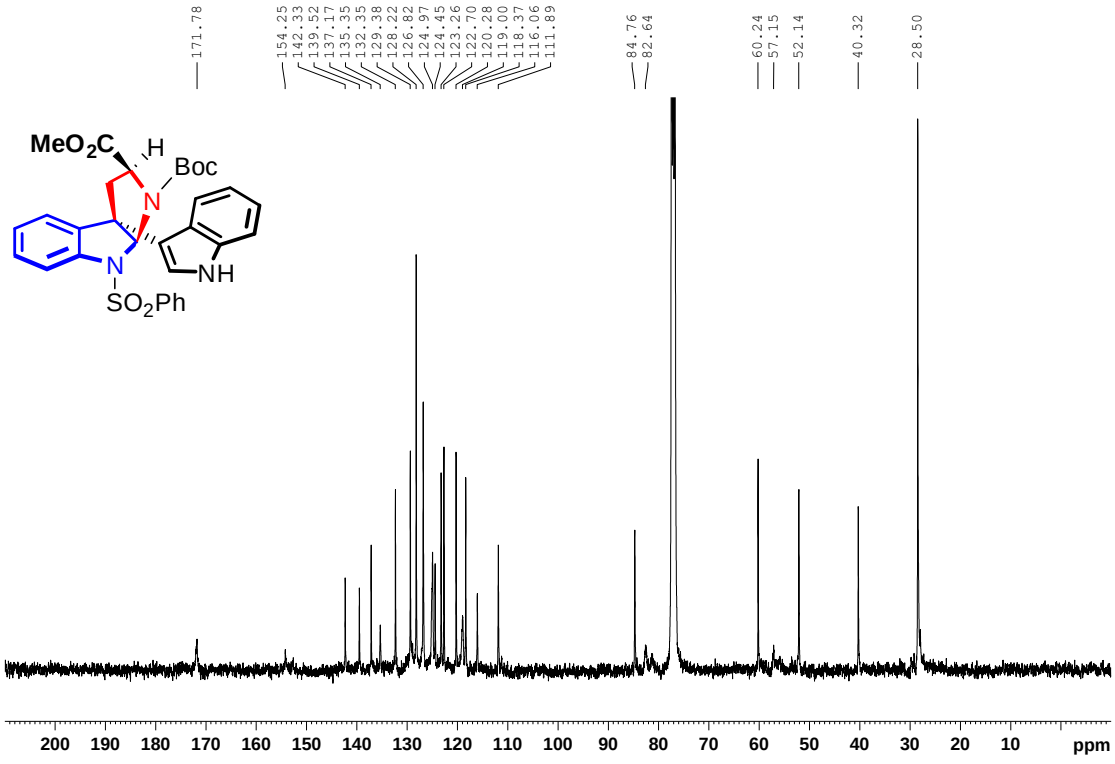
^{13}C NMR (CDCl$_3$, 300K), **9**



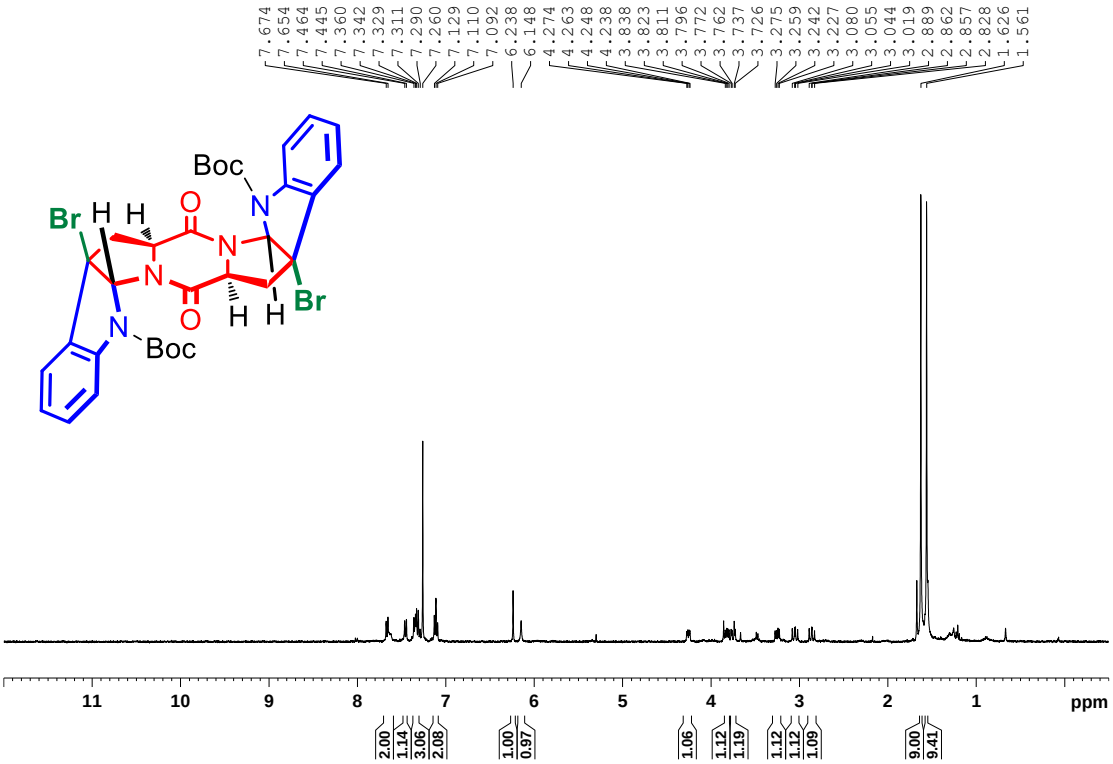
^{1}H NMR (CDCl$_3$, 300K), **10**



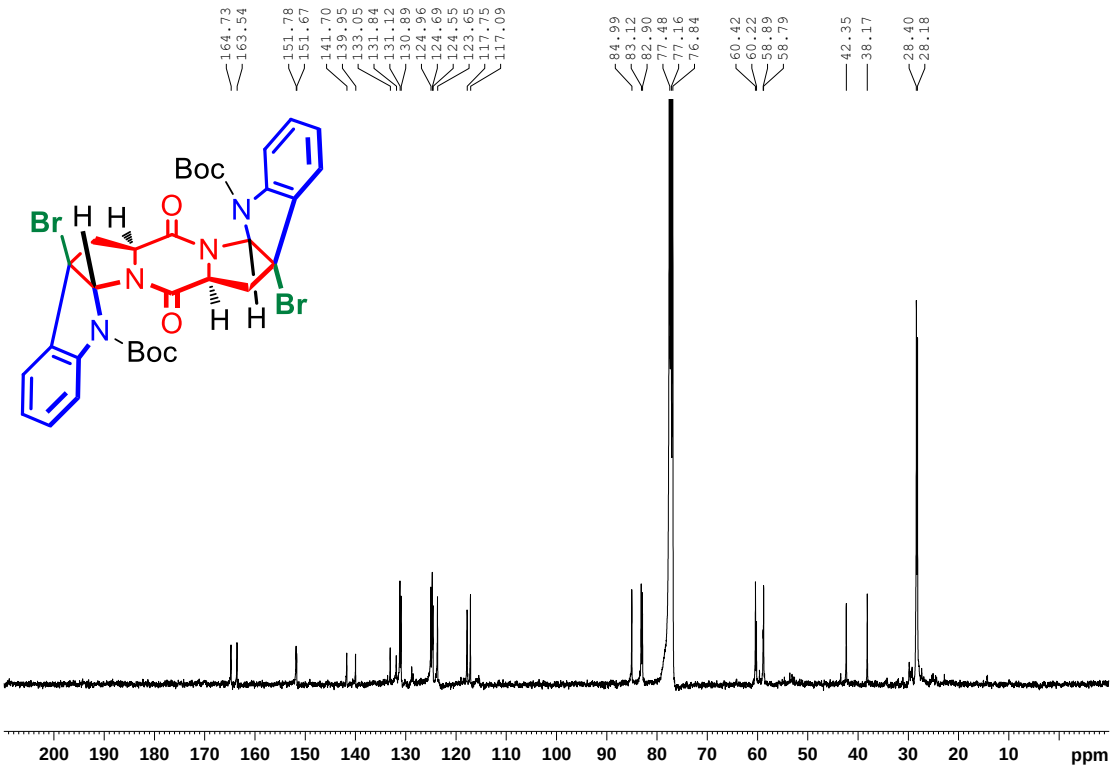
^{13}C NMR (CDCl$_3$, 300K), **10**



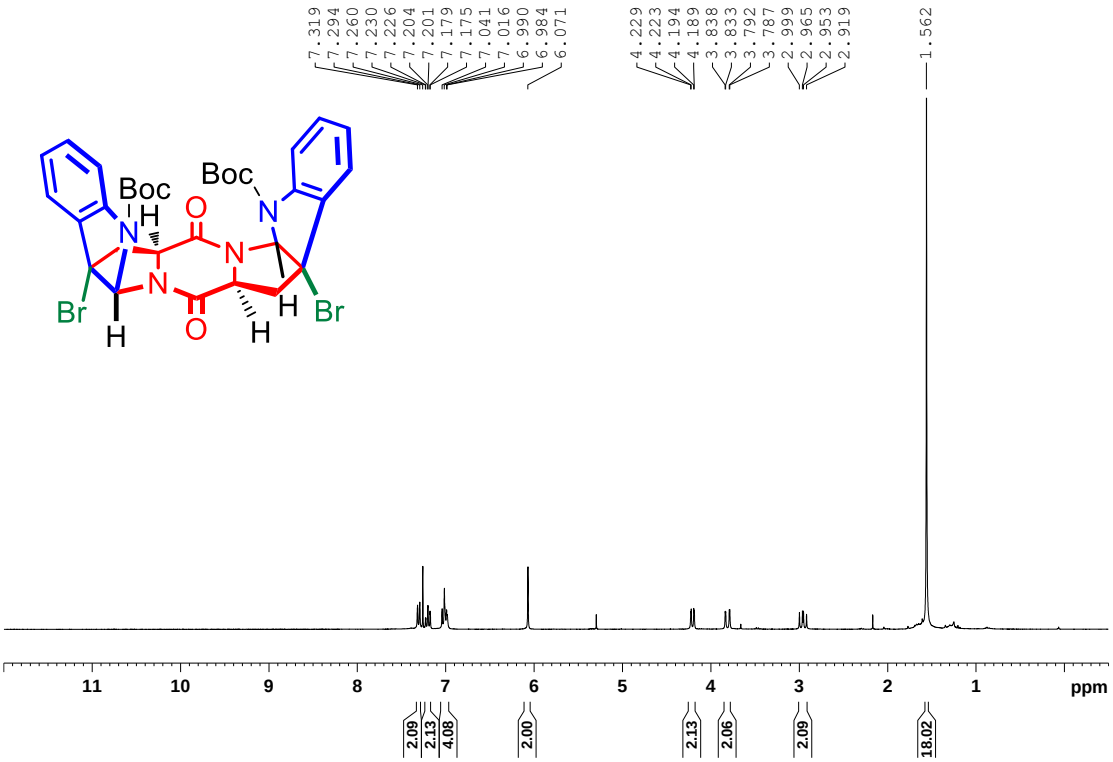
^{1}H NMR (CDCl$_3$, 300K), **12**



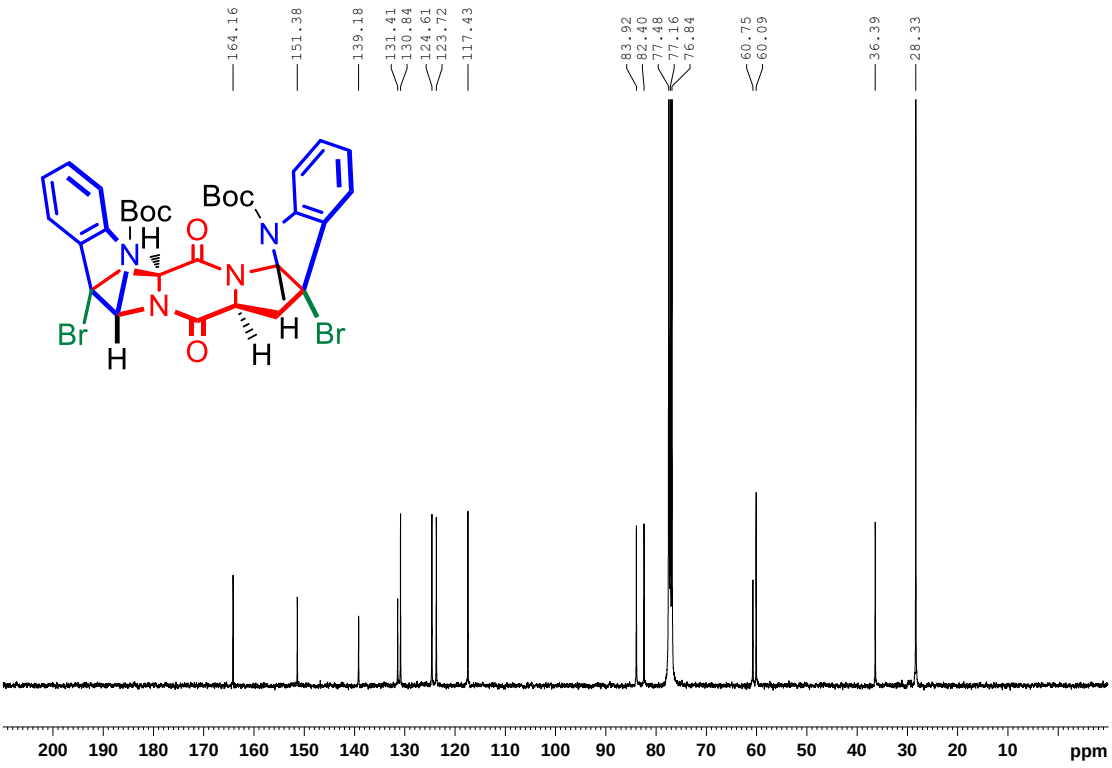
^{13}C NMR (CDCl$_3$, 300K), **12**



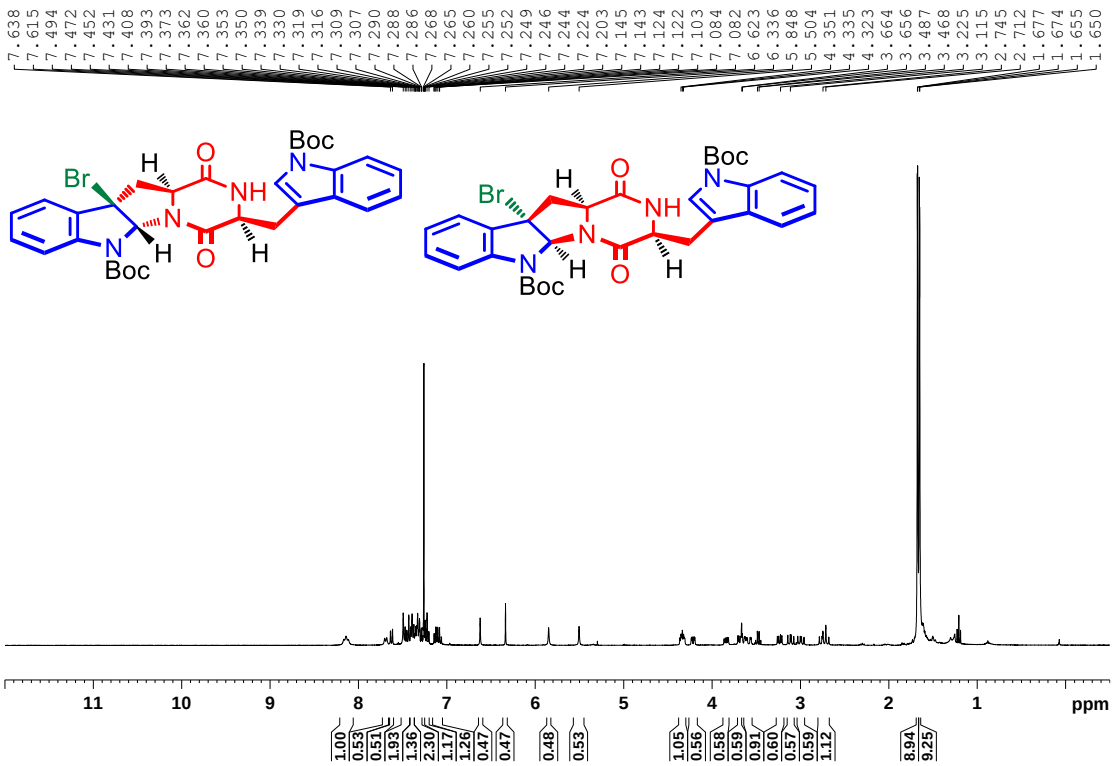
^{1}H NMR (CDCl$_3$, 300K), **13**



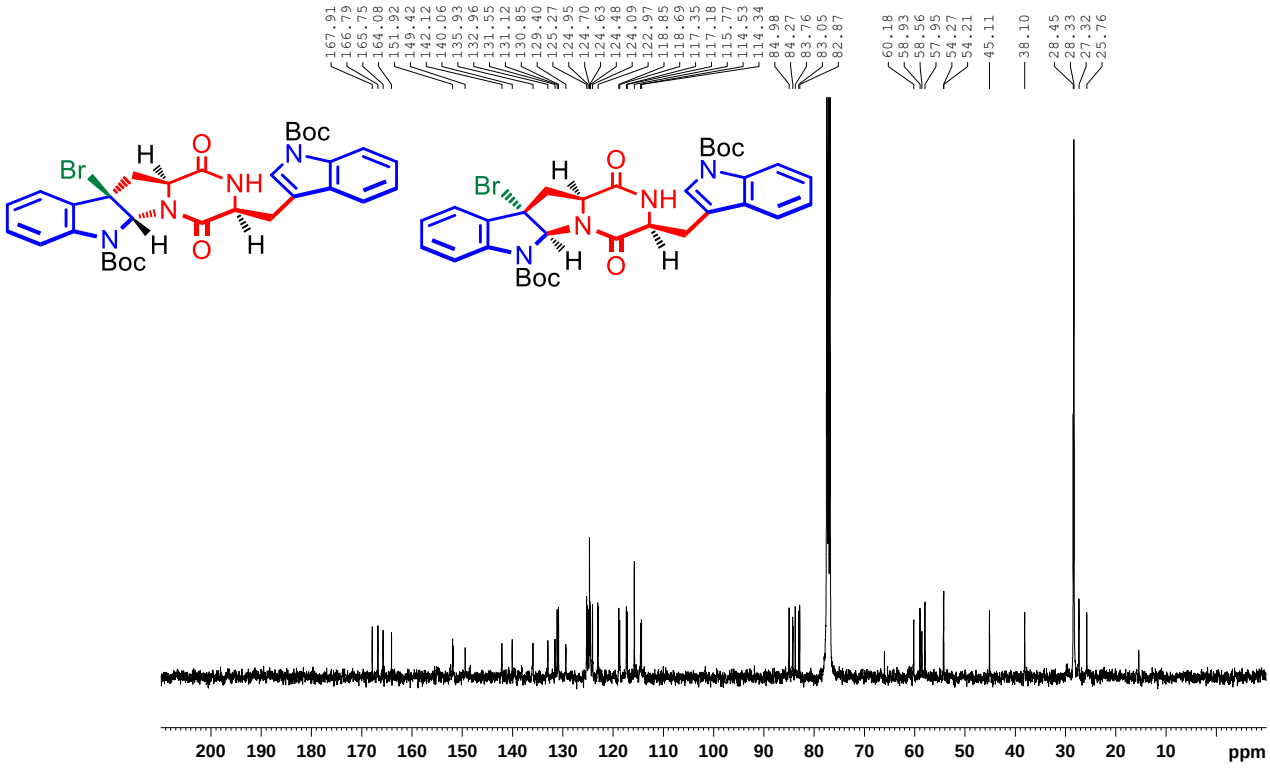
^{13}C NMR (CDCl$_3$, 300K), **13**



^{1}H NMR (CDCl$_3$, 300K), **14** (1:1 mixture of diastereoisomers)



^{13}C NMR (CDCl$_3$, 300K), **14** (1:1 mixture of diastereoisomers)



7. X-ray structure analysis

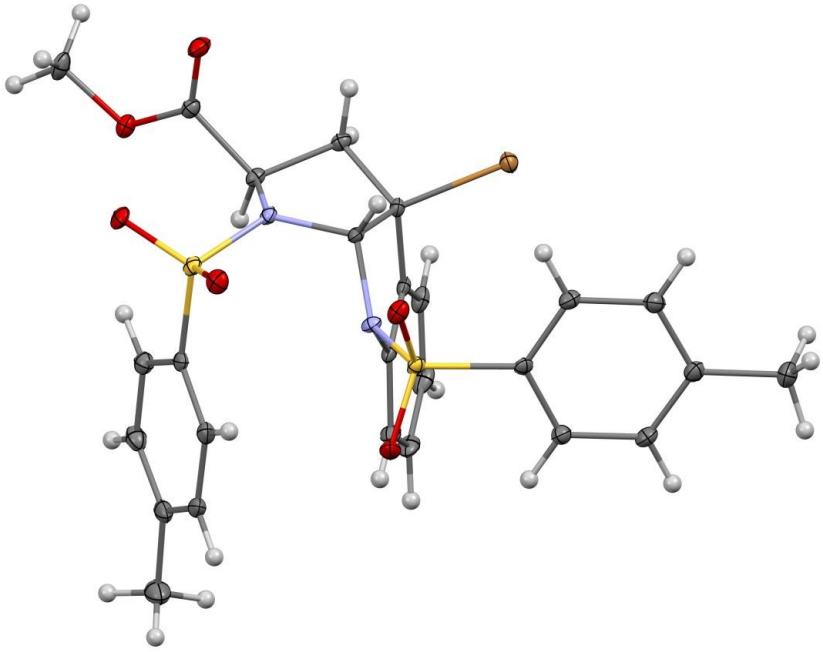


Figure S3. *ORTEP drawing of compound* ***8o****. Thermal ellipsoids are shown at the 30% level.*

X-ray diffraction data for compound **8o** were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Cu Kα radiation. Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value by means of N-Helix cooling device to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structure was solved by direct methods using SHELXS-97 [4] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[5]with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[6]

The crystal data collection and refinement parameters are given in Table S2.

The crystallographic analysis revealed the absolute structure of **8o** with a Flack parameter[7] of in 0.027(6) the monoclinic $P\ 2_1$ space group.

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[4] Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

[5] Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **2008**, 64, 112-122.

[6] Farrugia, L. J. *J. Appl. Cryst*. **1999**, *32*, 837.

[7] G. Bernardinelli and H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **1985**, *41*, 500-511.

CCDC 1910836 (**8o**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S2. *Crystallographic data and structure refinement details for compound* ***8o***.

Empirical Formula	C_{26} H_{25} Br N_2 O_6 S_2
M_r	605.51
Crystal size, mm^3	0.13 x 0.09 x 0.025
Crystal system	monoclinic
Space group	$P\ 2_1$
a, Å	8.6142(9)
b, Å	15.2562(15)
c, Å	10.0113(10)
α, °	90
β, °	93.761(4)
γ, °	90
Cell volume, $Å^3$	1312.9(2)
Z ; Z’	2 ; 1
T, K	100 (1)
Radiation type ; wavelength Å	CuKα; 1.54178
F_{000}	620
μ, mm^{-1}	4.001
θ range, °	4.426 - 66.959
Reflection collected	14 066
Reflections unique	4 552
R_{int}	0.0358
GOF	
Refl. obs. (I>2σ(I))	4 467
Parameters	1.036
wR_2 (all data)	0.0562
R value (I>2σ(I))	0.0227
Flack parameter	0.027(6)
Largest diff. peak and hole (e-.$Å^{-3}$)	0.398 ; -0.235