Supporting Information

Synthesis of Annulated Bis-indoles through Au(I)/Brønsted Acid-Catalyzed Reactions of (1*H*-indol-3-yl)(aryl)methanols with 2-(arylethynyl)-1*H*-indoles

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1. Experimental Section

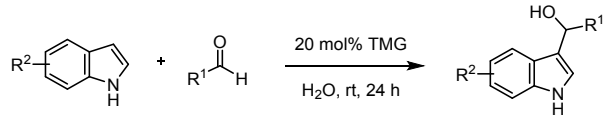
1.1 General Information:

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ or anisaldehyde and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in petroleum ether and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump. Melting points are uncorrected and recorded using digital Melting Point Apparatus. The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on 200/400/500 MHz spectrometers in appropriate solvents using TMS as an internal standard or the solvent signals as secondary standards and the chemical shifts are shown in δ scales. Multiplicities of ^{1}H NMR signals are designated as s (singlet), brs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet) etc. HRMS (ESI) data were recorded using quadrupole analyser. The gold catalysts Ph_3PAuCl was prepared according to literature known procedures.[1] The chiral Brønsted acid catalyst **BH*** was prepared by following literature known procedures.[2]

1.2. Synthesis of (1*H*-indol-3-yl)(aryl)methanols 1:

Preparation method for **1a**, **1b**, **1d**, **1g**, **1j** and **1k** (1*H*-indol-3-yl)(aryl)methanols were known in the literature.[3] Other substrates such as **1c**, **1e**, **1f**, **1h**, **1i**, **1l** and **1m** were prepared according to following representative procedure.

Representative procedure: A 50 mL round-bottomed flask was charged with indole **8a** (1g, 8.54 mmol), benzaldehyde **9a** (300 mg, 2.85 mmol) and tetramethylguanidine (65 mg, 0.57 mmol). Then the water (3 mL) was added and the resultant mixture was stirred for 24 h. Water (20 mL) was introduced in the flask and the reaction mixture was extracted with EtOAc (20 mL x 3). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography using EtOAc:petroleum ether (3:7) as eluent to give (1*H*-indol-3-yl)(phenyl)methanol **1a**.



8a R^2= H
8b R^2= 5-NO_2
8c R^2= 4-CN
8d R^2= 6-CO_2Me
8e R^2= 7-OBn

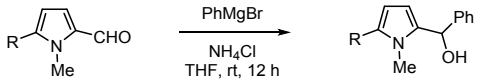
9a R^1 = Ph
9b R^1 = 1-naphthyl
9c R^1 = 9-anthracenyl
9d R^1 = 3-FC_6H_4
9e R^1 = 2-Br, 4-FC_6H_3
9f R^1 = 2-Br, 4-MeC_6H_3
9g R^1 = 3-$MeOC_6H_4$
9h R^1 = 2-furyl
9i R^1 = 2-thiophen

1a R^1 = Ph, R^2= H, 72%
1b R^1 = 1-naphthyl, R^2= H, 70%
1c R^1 = 9-anthracenyl, R^2= H, 76%
1d R^1 = 3-FC_6H_4, R^2= H, 64%
1e R^1 = 2-Br, 4-FC_6H_3, R^2= H, 73%
1f R^1 = 2-Br, 4-MeC_6H_3, R^2= H, 66%
1g R^1 = 3-$MeOC_6H_4$, R^2= H, 69%
1h R^1 = 2-furyl, R^2= H, 76%
1i R^1 = 2-thiophen, R^2= H, 71%
1j R^1 = Ph, R^2= 5-NO_2, 59%
1k R^1 = Ph, R^2= 4-CN, 68%
1l R^1 = Ph, R^2= 6-CO_2Me, 62%
1m R^1 = Ph, R^2= 7-OBn, 80%

1.3. Synthesis of aryl(1*H*-pyrrol-2-yl)methanol 4:

Representative procedure: To a 50 mL round-bottom flask, *N*-methyl-1*H*-pyrrole-2-carbaldehyde **10a** (220 mg, 2 mmol) and 10 mL dry THF was charged under N_2. The phenyl magnesium bromide (3 mmol) (3 mL, 1 M solution in THF) was added and the mixture was continued to stir at room temperature for 1 h. After completion of reaction, the mixture was quenched by adding sat. NH_4Cl solution. The product was extracted with EtOAc (20 mL x 3)

and the combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude phenyl(1*H*-pyrrol-2-yl)methanol **4a** obtained was used without further purification.



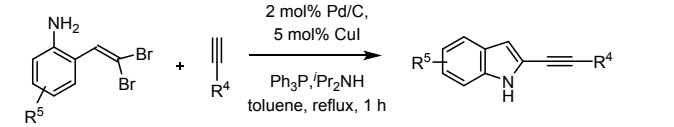
10a R= H
10b R= 2-$NO_2C_6H_4$

4a R= H, 75%
4b R= 2-$NO_2C_6H_4$, 70%

1.4. Synthesis of 2-(arylethynyl)-1*H*-indoles 2:

Preparation methods for **2a-k** alkynyl indoles were known in the literature,[4] while, **2l** and **2m** were prepared according to following procedure in two steps from *ortho-gem*-dibromovinylaniline **11a**.

Representative procedure: To a 50 mL round-bottom flask, *ortho-gem*-dibromovinylaniline **11a** (275 mg, 1 mmol), phenylacetylene **12a** (153 mg, 1.5 mmol), PPh_3 (30 mg, 0.11 mmol), $^{i}Pr_2NH$ (350 µL, 2.5 mmol) and 10 mL dry toluene was charged under N_2. Finally, 10% Pd/C (52 mg, 0.02 mmol) and CuI (9.6 mg, 0.05 mmol) were added. The resulting mixture was heated at 100 °C for 1 h. The mixture was diluted with EtOAc (30 mL), washed with H_2O (20 mL), brine (15 mL) and dried over Na_2SO_4. The crude material after removal of solvent was purified by chromatography using EtOAc:petroleum ether (1:9) to give 2-(phenylethynyl)-1*H*-indole **2a**.



11a R^5 = H
11b R^5 = 4-F
11c R^5 = 5-Me
11d R^5 = 4-OMe

12a R^4 = Ph
12b R^4 = 4-ClC_6H_4
12c R^4 = 4-CNC_6H_4
12d R^4 = 4-MeC_6H_4
12e R^4 = 4-$MeOC_6H_4$
12f R^4 = 2-Py

2a R^4 = Ph, R^5 = H, 80%
2b R^4 = 4-ClC_6H_4, R^5 = H, 59%
2c R^4 = 4-CNC_6H_4, R^5 = H, 64%
2d R^4 = 4-MeC_6H_4, R^5 = H, 60%
2e R^4 = 4-$MeOC_6H_4$, R^5 = H, 70%
2f R^4 = 2-Py, R^5 = H, 65%
2g R^4 = Ph, R^5 = 5-F, 65%
2h R^4 = Ph, R^5 = 6-Me, 64%
2i R^4 = Ph, R^5 = 5-MeO, 71%

Representative procedure for the synthesis of 2k: To a 50 mL round-bottom flask, **2a** (217 mg, 1 mmol) and dry DMF 10 mL were added under N_2. The mixture was cooled to 0 °C and NaH (58 mg, 1.5 mmol) followed by benzyl bromide (255 mg, 1.5 mmol), were added. The mixture was heated to room temperature and stirred for 2 h, the mixture was quenched by adding sat. NH_4Cl solution. The crude product was extracted with EtOAc (20 mL x 3). The combined extracts were dried over Na_2SO_4, concentrated in vacuum and purified by column chromatography using EtOAc:petroleum ether (1:9) to give 1-benzyl-2-(phenylethynyl)-indole **2k**.

1.5. Synthesis of annulated bis-indoles 3:

Representative procedure: To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1*H*-indol-3-yl)(phenyl)methanol **1a** (25 mg, 0.115 mmol), 2-(phenylethynyl)-1*H*-indole **2a** (26 mg, 0.115 mmol), Ph_3PAuCl (2.9 mg, 0.0058 mmol), AgOTf (1.5 mg, 0.0058 mmol), **BH** (4 mg, 0.0115 mmol) in one portion, was dissolved in DCE (2 mL) under nitrogen. The solution was heated to 80 °C for 8 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product **3a**.

Synthesis of enantioenriched 3a: To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1*H*-indol-3-yl)(phenyl)methanol **1a** (25 mg, 0.115 mmol), 2-(phenylethynyl)-1*H*-indole **2a** (26 mg, 0.115 mmol), Ph_3PAuMe (2.74 mg, 0.0058 mmol), **BH*** (8 mg, 0.0115 mmol) in one portion, was dissolved in DCE (2 mL) under nitrogen. The solution was stirred at 0 °C for 12 h then heated to 80 °C for 4 h, the solvent was removed to

obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford enantio-pure **3a**.

Synthesis of 3a from phenyl (1H-pyrrol-2-yl)methanol 1a with 2-(phenylbuta-1,3-diyn-1-yl)aniline 7:

To a oven-dried screw-capped vial equipped with magnetic stir bar, were added 2-(phenylbuta-1,3-diyn-1-yl)aniline **7** (25 mg, 0.115 mmol), (1*H*-indol-3-yl)(phenyl)methanols **1a** (26 mg, 0.115 mmol), $PdCl_2$(1.1 mg, 0.0058 mmol), **BH** (4 mg, 0.0115 mmol) followed by DCE (2 mL) under nitrogen atmosphere. The solution was heated to 80 ˚C for 12 h. The reaction mixture was bought to room temperature. The flask was charged with Ph_3PAuCl (2.9 mg, 0.0058 mmol) and AgOTf (1.5 mg, 0.0058 mmol) and the reaction mixture was again heated to 80 ˚C for 8 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product **3a**.

1.6. Synthesis of annulated pyrrole 5:

Representative procedure: To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1-methyl-1*H*-pyrrol-2-yl)(phenyl)methanol **4a** (21 mg, 0.115 mmol), 2-(phenylethynyl)-1*H*-indoles **2a** (26 mg, 0.115 mmol), Ph_3PAuCl (2.9 mg, 0.0058 mmol), AgOTf (1.5 mg, 0.0058 mmol) and **BH** (4 mg, 0.0115 mmol) followed by DCE (2 mL) under nitrogen atmosphere. The solution was heated to 80 ˚C. After 8 h, the solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (2:8) as an eluent to afford product **5a**.

1.7. Synthesis of 3-((1*H*-indol-3-yl)(phenyl)methyl)-2-(phenylethynyl)-1*H*-indole 6:

To a oven-dried screw-capped vial equipped with magnetic stir bar, were added (1*H*-indol-3-yl)(phenyl)methanol **1a** (25 mg, 0.115 mmol), 2-(phenylethynyl)-1*H*-indole **2a** (26 mg,

0.115 mmol), **BH** (4 mg, 0.0115 mmol) and DCE (2 mL) under nitrogen. The reaction mixture was stirred at room temperature for 12 h. The solvent was removed to obtain the residue which was purified by silica gel column chromatography using EtOAc:petroleum ether (1:9) as an eluent to afford product **6**.

2. Analytical data

Anthracen-9-yl(*1H-indol-3-yl*)*methanol* (**1c**): white solid, 1.44 g, 62% yield; mp = 214 °C; R_f = 0.25 (petroleum ether/EtOAc = 75/25); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.63 - 8.56 (m, 2 H), 8.49 (s, 1 H), 8.02 - 7.99 (m, 2 H), 7.99 - 7.91 (m, 1 H), 7.88 - 7.79 (m, 1 H), 7.74 - 7.70 (m, 1 H), 7.46 - 7.30 (m, 6 H), 7.25 - 7.10 (m, 2 H), 6.56 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 136.6, 133.9, 131.7, 129.7, 129.1, 128.7, 128.4, 128.2, 126.5, 125.4, 125.3, 124.8, 123.5, 123.4, 122.2, 119.9, 118.5, 111.1, 66.8; HRMS (ESI) calcd for $C_{23}H_{17}NO$ (M^++ H) 324.1382, found 324.1383.

(*2-Bromo-5-fluorophenyl*)(*1H-indol-3-yl*)*methanol* (**1e**): yellow solid, 1.6 g, 59% yield; mp = 168 °C; R_f = 0.32 (petroleum ether/EtOAc = 75/25); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.33 (s, 1 H), 7.66 - 7.61 (m, 1 H), 7.54 (dd, *J* = 2, 8 Hz, 1 H), 7.36 (dd, *J* = 6, 8 Hz, 1 H), 7.26 - 7.23 (m, 1 H), 7.04 - 6.90 (m, 2 H), 6.95 - 6.79 (m, 1 H), 6.76 - 6.72 (m, 1 H), 6.19 (s, 1 H), 5.45 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 163.9-159.0(d, *J* = 245.5 Hz), 146.3-146.2 (d, *J* = 6.6 Hz), 136.2, 133.0-132.9 (d, *J* = 7.68 Hz), 125.6, 123.0, 120.9, 118.6, 118.4, 116.7, 115.6, 115.3, 115.1, 114.8, 114.6, 111.0, 67.7; HRMS (ESI) calcd for $C_{15}H_{11}BrFNO$ (M^++ H) 320.0008, found 320.0010.

(*2-Bromo-4-methylphenyl*)(*1H-indol-3-yl*)*methanol* (**1f**): white solid, 1.40 g, 52% yield; mp = 159 °C; R_f = 0.23 (petroleum ether/EtOAc = 75/25); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.01 (s, 1 H), 7.63 - 7.58 (m, 1 H), 7.51 (d, *J* = 8 Hz, 1 H), 7.31 - 7.23 (m, 2 H), 7.18 - 7.01 (m, 3 H),

6.82 - 6.77 (m, 2 H), 6.38 (s, 1 H), 2.25 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 139.2, 139.0, 136.4, 133.1, 128.3, 128.0, 125.8, 123.1, 122.4, 122.2, 119.7, 119.5, 117.9, 111.2, 69.2, 20.6; HRMS (ESI) calcd for $C_{16}H_{14}BrNO$ (M^++ H) 316.0256, found 316.0259.

(*1H-indol-3-yl*)(*thiophen-2-yl*)*methanol* (**1i**): white solid, 1.08 g, 55% yield; mp = 187 °C; R_f = 0.2 (petroleum ether/EtOAc = 75/25); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 10.07 (s, 1 H), 7.83 - 7.80 (m, 3 H), 7.72 - 7.69 (m, 1 H), 7.49 - 7.42 (m, 2 H), 7.38 - 7.33 (m, 1 H), 7.28 - 7.25 (m, 2 H), 6.52 - 6.44 (s, 1 H).; ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.4, 140.4, 137.2, 136.3, 133.5, 131.9, 131.7, 128.9, 128.3, 127.5, 127.1, 126.4, 123.38, 123.2, 123.2 122.7, 120.0, 119.9, 118.7, 118.3, 117.5, 110.6, 110.6, 32.4; HRMS (ESI) calcd for $C_{13}H_{11}NOS$ (M^++ H) 230.0639, found 230.0634.

Methyl 3-(*hydroxy*(*phenyl*)*methyl*)*-1H-indole-6-carboxylate* (**1l**): white solid, 1.44 g, 60% yield; mp = 158 °C; R_f = 0.27 (petroleum ether/EtOAc = 80/20); ^{1}H NMR (500 MHz, DMSO **d_6**) δ = 11.32 (s, 1 H), 8.03 (s, 1 H), 7.58 (m, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.41 - 7.38 (m, 1 H), 7.31 (m, 3 H), 7.21(m, 1 H), 6.0 (s, 1 H), 5.71 (s, 3H); ^{13}C NMR (125 MHz, DMSO d_6) δ = 167.2, 145.5, 135.8, 129.1, 127.9, 126.7, 126.6, 126.2, 122.0, 120.3, 119.3, 119.0, 113.4, 68.6, 51.7; HRMS (ESI) calcd for $C_{17}H_{15}NO_3$ (M^++ H) 281.1047, found 281.1046.

(*7-*(*Benzyloxy*)*-1H-indol-3-yl*)(*phenyl*)*methanol* (**1m**): gray solid, 1.46 g, 54% yield; mp = 118 °C; R_f = 0.34 (petroleum ether/EtOAc = 70/30); ^{1}H NMR (200 MHz, DMSO d_6) δ = 11.00 (s, 1 H), 7.56 - 7.51 (m, 2 H), 7.44 - 7.38 (m, 3 H), 7.36 - 7.19 (m, 5 H), 7.11 - 6.98 (m, 2 H), 6.80 - 6.75 (m, 1 H), 6.71 (s, 1 H), 5.94 - 5.87 (m, 1 H), 5.59 (d, *J* = 4 Hz, 1 H), 5.24 (s, 2 H).; ^{13}C NMR (50 MHz, DMSO d_6) δ = 145.8, 144.9, 137.4, 128.3, 127.7, 127.6, 127.4, 127.3, 126.7, 126.3, 126.3, 122.3, 120.2, 118.8, 112.6, 102.8, 69.0, 68.8; HRMS (ESI) calcd for $C_{22}H_{19}NO_2$ (M^++ H) 330.1415, found 330.1419.

1-benzyl-2-(*phenylethynyl*)*-1H-indole* (**2l**): white solid, 257 mg, 84% yield; mp = 153 °C; R_f = 0.70 (petroleum ether/EtOAc = 95/05); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7 Hz, 1 H), 7.48 - 7.45 (m, 2 H), 7.36 - 7.32 (m, 4 H), 7.24 - 7.18 (m, 6 H), 7.21 - 7.11 (m, 1 H), 6.93 (s, 1 H), 5.52 (s, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 137.6, 136.8, 132.5, 131.4, 128.6, 128.5, 128.4, 127.8, 127.5, 127.4, 126.8, 123.2, 122.6, 121.9, 121.0, 120.2, 110.0, 108.0, 95.4, 81.1, 48.0; HRMS (ESI) calcd for $C_{23}H_{17}N$ (M^++ H) 308.1361, found 308.1360.

1-allyl-2-(*phenylethynyl*)*-1H-indole* (**2m**): brown liquid, 175 mg, 68% yield; R_f = 0.72 (petroleum ether/EtOAc = 95/05); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 - 7.40 (m, 4 H), 7.45 - 7.27 (m, 2 H), 7.28 - 7.19 (m, 2 H), 7.16 - 6.04 (s, 1 H), 6.79 (s, 1 H), 6.06 - 5.80 (m, 1 H), 5.12 - 4.98 (m, 2 H), 4.86 (d, *J* = 6 Hz, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 136.7, 133.2, 132.4, 131.4, 129.2, 128.5, 128.4, 127.4, 123.0, 122.7, 121.0, 120.1, 116.8, 109.8, 107.8, 95.1, 80.9, 46.7; HRMS (ESI) calcd for $C_{19}H_{15}N$ (M^++ H) 258.1204, found 258.1210.

6,13-Diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3a**): yellow solid, 44.6 mg, 92% yield; mp = 207 °C; R_f = 0.5 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.54 (s, 1 H), 9.61 (s, 1 H), 7.80 (d, *J* = 8 Hz, 2 H), 7.65 - 7.48 (m, 3 H), 7.52 (d, *J* = 7.9 Hz, 3 H), 7.31 (d, *J* = 6 Hz, 5 H), 7.07 - 6.99 (m, 5 H), 6.87 (s, 1 H), 6.18 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 145.9, 140.6, 136.9, 136.5, 132.7, 131.5, 131.5, 128.3, 128.1, 127.5, 127.4, 127.1, 126.8, 126.4, 125.2, 122.2, 121.9, 119.2, 118.7, 117.5, 117.3, 116.7, 116.3, 111.0, 110.4, 36.8; HRMS (ESI) calcd for $C_{31}H_{22}N_2$ (M^++ H) 423.1785, found 423.1786; HPLC conditions: Chiralpak IA, 70:30 *n*-hexane/IPA, flow rate 1 mL/min; λ = 254 nm; t_{major} = 12.34 min, t_{minor} = 25.63 min.

13-(*Naphthalen-1-yl*)*-6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3b**): yellow solid, 47 mg, 88% yield; mp = 192 °C; R_f = 0.52 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$ +DMSO d_6) δ = 10.61 (s, 1 H), 9.87 (s, 1 H), 8.33 (d, *J* = 7 Hz, 1 H),

7.67 (d, *J* = 7.0 Hz, 1 H), 7.67 (d, *J* = 8 Hz, 1 H), 7.48 - 7.41 (m, 3 H), 7.35 (d, *J* = 8 Hz, 3 H), 7.26 (m, 8 H), 7.05 (t, *J* = 7 Hz, 2 H), 6.82 - 6.75 (m, 3 H), 6.68 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$ +DMSO d_6) δ = 145.4, 140.0, 136.3, 130.9, 127.7, 127.0, 126.8, 125.9, 124.7, 118.6, 118.1, 118.1, 116.7, 110.4, 109.9, 36.2.; HRMS (ESI) calcd for $C_{35}H_{24}N_2$ (M^++ H) 473.1939, found 473.1940.

13-(*Anthracen-9-yl*)*-6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3c**): yellowish solid, 49.8 mg, 83% yield; mp = 183 °C; R_f = 0.6 (petroleum ether/EtOAc = 85/15); ^{1}H NMR (500 MHz, $CDCl_3$ +DMSO d_6) δ = 10.56 (s, 1 H), 9.63 (s, 1 H), 7.83 (d, *J* = 6.5 Hz, 2 H), 7.67 - 7.62 (m, 5 H), 7.53 - 7.51 (m, 2 H), 7.45 - 7.43 (m, 2 H), 7.39 (d, *J* = 6.5 Hz, 1 H), 7.29 (m, 5 H), 7.05 - 7.04 (m, 4 H), 6.95 - 6.91 (m, 1 H), 6.87 (s, 1 H), 6.19 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO d_6) δ = 145.9, 131.7, 128.2, 128.1, 127.5, 127.3, 126.5, 125.2, 121.9, 119.1, 118.6, 117.5, 111.1, 110.4, 36.8.; HRMS (ESI) calcd for $C_{39}H_{26}N_2$ (M^++ H) 523.2096, found 523.2098.

13-(*3-Fluorophenyl*)*-6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3d**): yellow solid, 47.5 mg, 94% yield; mp = 160 °C; R_f = 0.57 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, DMSO d_6) δ = 11.22 (s, 1 H), 10.53 (s, 1 H), 8.07 (dd, *J* = 2, 7.4 Hz, 2 H), 7.56 (d, *J* = 2 Hz, 4 H), 7.50 - 7.45 (m, 1 H), 7.41 - 7.35 (m, 2 H), 7.24 (d, *J* = 7.4 Hz, 1 H), 7.19 - 7.07 (m, 6 H), 6.95 (s, 1 H), 6.87 - 6.80 (m, 1 H), 6.38 (s, 1 H); ^{13}C NMR (125 MHz, DMSO d_6) δ = 163.5-161.5(d, *J* = 243.17 Hz), 150.1-150.0 (d, *J* = 5.72 Hz), 141.2, 137.5-137.4 (d, *J* = 12.4 Hz), 133.6, 132.6, 132.3, 130.4-130.4 (d, *J* = 7.6 Hz), 129.3, 128.8, 128.4, 127.6, 127.4, 123.4, 123.0 (d, *J* = 7.6 Hz), 119.9, 119.5, 119.5, 118.9, 118.7, 117.1, 116.7, 113.9, 113.7, 113.0, 112.8, 112.1, 111.4, 36.8; HRMS (ESI) calcd for $C_{31}H_{21}FN_2$ (M^++ H) 441.1689, found 441.1690.

13-(*2-Bromo-5-fluorophenyl*)-*6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3e**): brown solid, 57 mg, 96% yield; mp = 159 °C; R_f = 0.59 (petroleum ether/EtOAc = 80/20); ^{1}H NMR (500 MHz, DMSO d_6) δ = 11.37 (s, 1 H), 10.60 (s, 1 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8 Hz, 1 H), 7.63 - 7.59 (m, 4 H), 7.57 - 7.51 (m, 3 H), 7.38 (t, *J* = 8 Hz, 2 H), 7.21 - 7.13 (m, 2 H), 7.13 - 7.08 (m, 2 H), 7.07 (s, 1 H), 6.89 (m, 1 H), 6.65 (s, 1 H); ^{13}C NMR (125 MHz, DMSO d_6) δ = 162.7-160.8 (d, *J* = 244.4 Hz), 149.8-149.8 (d, *J* = 6.68 Hz), 140.5, 136.9-136.7 (d, *J* = 18.12 Hz), 133.9-133.8 (d, *J* = 7.63 Hz), 133.4, 131.9, 131.5, 129.0, 128.3, 128.1, 126.9, 126.7, 122.8- 122.8 (d, *J* = 3.82 Hz), 119.7, 119.2, 118.7, 118.5, 117.2, 117.0, 116.8, 116.3, 116.1, 115.9, 113.8, 111.8, 111.0, 37.8.; HRMS (ESI) calcd for $C_{31}H_{20}FBrN_2$ (M^++ H) 519.0704, found 519.0710.

13-(*2-bromo-4-methylphenyl*)-*6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b*']*bisindole* (**3f**): gray solid, 53.2 mg, 90% yield; mp = 173 °C; R_f = 0.54 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.60 (s, 1 H), 9.69 (s, 1 H), 7.87 - 7.77 (m, 2 H), 7.44 (d, *J* = 8.0 Hz, 3 H), 7.32 (d, *J* = 2 Hz, 2 H), 7.29 - 7.23 (m, 5 H), 7.10 - 7.05 (m, 3 H), 7.05 - 6.96 (m, 4 H), 6.86 (s, 1 H), 6.18 (s, 1 H), 2.40 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 146.0, 137.6, 136.9, 136.8, 136.4, 132.6, 131.8, 128.8, 128.0, 127.5, 126.4, 125.2, 118.6, 117.4, 111.0, 36.7, 20.7.; HRMS (ESI) calcd for $C_{32}H_{23}BrN_2$ (M^++ H) 515.1045, found 515.1046.

13-(*3-Methoxyphenyl*)-*6-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3g**): yellow solid, 45.7 mg, 88% yield; mp = 124 °C; R_f = 0.56 (petroleum ether/EtOAc = 85/15); ^{1}H NMR (500 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.58 (s, 1 H), 9.41 (s, 1 H), 8.28 - 8.21 (m, 2 H), 7.93 (d, *J* = 6 Hz, 2 H), 7.83 (t, *J* = 8 Hz, 3 H), 7.77 (d, *J* = 7 Hz, 1 H), 7.67 (d, *J* = 8 Hz, 2 H), 7.64 (d, *J* = 7 Hz, 1 H), 7.47 (d, *J* = 7.0 Hz, 3 H), 7.51 (d, *J* = 4 Hz, 2 H), 7.35 - 7.33 (m, 1 H), 6.89 (s, 1 H), 6.59 (s, 1 H), 3.94 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio)

δ = 158.8, 147.4, 140.4, 137.0, 136.3, 132.6, 131.7, 131.4, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 126.9, 123.4, 122.3, 122.0, 120.7, 119.1, 118.9, 118.9, 118.7, 118.0, 117.6, 117.5, 116.7, 116.2, 112.6, 110.8, 110.7, 110.4, 110.2, 54.3, 36.9.; HRMS (ESI) calcd for $C_{32}H_{24}N_2O$ (M^++ H) 453.1966, found 453.1961.

6-Phenyl-13-(*furyl-2-yl*)*-8,13-dihydro-5I-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3h**): brown solid, 45 mg, 95% yield; mp = 139 °C; R_f = 0.55 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, DMSO d_6) δ = 11.11 (s, 1 H), 10.46 (s, 1 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 7.57 - 7.49 (m, 4 H), 7.49 - 7.38 (m, 2 H), 7.36 - 7.30 (m, 3 H), 7.16 - 7.11 (m, 1 H), 7.10 - 7.07 (m, 2 H), 6.86 (s, 1 H), 6.78 (d, *J* = 2 Hz, 1 H), 6.69 (dd, *J* = 2, 8 Hz, 1 H), 6.52 (s, 1 H); ^{13}C NMR (125 MHz, DMSO d_6) δ = 150.7, 140.4, 136.6, 136.5, 132.9, 131.6, 131.5, 130.6, 128.4, 128.5, 128.0, 127.6, 126.4, 126.1, 125.8, 124.8, 123.2, 123.1, 122.1, 118.9, 118.7, 118.6, 118.0, 117.7, 116.6, 116.5, 111.3, 110.5, 31.4.; HRMS (ESI) calcd for $C_{29}H_{20}N_2O$ (M^++ H) 413.1576, found 413.1578.

6-Phenyl-13-(*thiophen-2-yl*)*-8,13-dihydro-5I-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3i**): dark brown solid, 47.2 mg, 96% yield; mp = 148 °C; R_f = 0.43 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, DMSO d_6) δ = 11.19 (s, 1 H), 10.55 (s, 1 H), 8.08 (t, *J* = 8 Hz, 2 H), 7.57 (d, *J* = 2 Hz, 3 H), 7.52 - 7.41 (m, 3 H), 7.41 - 7.23 (m, 2 H), 7.13 - 7.05 (m, 4 H), 6.93 (s, 1 H), 6.82 (d, *J* = 2 Hz, 1 H), 6.73 (dd, *J* = 2, 8 Hz, 1 H), 6.60 (s, 1 H); ^{13}C NMR (50 MHz, DMSO d_6) δ = 151.1, 140.8, 136.9, 136.8, 133.2, 131.9, 128.8, 128.3, 126.4, 126.1, 123.6, 122.5, 118.9, 116.9, 111.6, 31.8.; HRMS (ESI) calcd for $C_{29}H_{20}N_2S$ (M^++ H) 429.1347, found 429.1348.

2-Nitro-6,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3j**): yellow solid, 43 mg, 80% yield; mp = 149 °C; $\boldsymbol{R_f}$ = 0.46 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, DMSO d_6) δ = 11.27 (s, 1 H), 11.24 (s, 1 H), 9.14 (d, *J* = 2 Hz, 1 H), 8.23 (d, *J* = 7.6 Hz,

1 H), 8.02 (dd, *J* = 2, 8 Hz, 1 H), 7.57 - 7.50 (m, 5 H), 7.43 - 7.33 (m, 5 H), 7.13 (t, *J* = 7.6 Hz, 4 H), 7.05 (s, 1 H), 6.55 (s, 1 H).; ^{13}C NMR (50 MHz, DMSO d_6) δ = 163.1, 161.1, 140.9, 137.2, 133.7, 132.2, 131.9, 129.3, 128.6, 128.5, 123.1, 120.1, 119.5, 119.0, 118.8, 112.1, 111.4; HRMS (ESI) calcd for $C_{31}H_{21}N_3O_2$ (M^++ H) 468.1634, found 468.1635.

6,13-Diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole-1-carbonitrile* (**3k**): yellowish solid, 42 mg, 82% yield; mp = 138 °C; R_f = 0.67 (petroleum ether/EtOAc = 80/20); ^{1}H NMR (400 MHz, DMSO d_6) δ = = 11.31 (s, 1 H), 11.27 (s, 1 H), 7.83 (d, *J* = 7.3 Hz, 1 H), 7.71 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 7.3 Hz, 2 H), 7.54 (br. s., 4 H), 7.50 - 7.46 (m, 1 H), 7.42 (d, *J* = 7.8 Hz, 1 H), 7.26 - 7.23 (m, 3 H), 7.16 - 7.12 (m, 3 H), 7.10 (s, 1 H), 7.04 (d, *J* = 6.8 Hz, 1 H), 6.96 (s, 1 H); ^{13}C NMR (100 MHz, DMSO d_6) δ = 145.1, 140.2, 137.3, 137.0, 135.8, 133.7, 132.5, 131.8, 129.6, 129.5, 129.0, 128.7, 128.2, 128.1, 126.9, 126.6, 126.6, 125.9, 124.9, 122.7, 121.9, 121.5, 119.8, 119.5, 117.6, 117.1, 115.9, 111.4, 99.3, 34.5; HRMS (ESI) calcd for $C_{32}H_{21}N_3$ (M^++ H) 448.1735, found 448.1736.

Methyl 6,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole-3-carboxylate* (**3l**): gray solid, 53 mg, 96% yield; mp = 153 °C; R_f = 0.51 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.64 (s, 1 H), 10.24 (s, 1 H), 8.02 (d, *J* = 7.8 Hz, 2 H), 7.50 (d, *J* = 8 Hz, 2 H), 7.40 (s, 6 H), 7.07 (d, *J* = 2.4 Hz, 3 H), 7.06 - 6.99 (m, 3 H), 6.94 (d, *J* = 8 Hz, 1 H), 6.88 (s, 1 H), 6.18 (s, 1 H), 2.81 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 166.7, 145.1, 135.2, 131.1, 127.8, 127.7, 127.2, 127.0, 125.9, 124.9, 120.2, 119.0, 118.3, 116.4, 113.0, 110.1, 50.7, 38.4; HRMS (ESI) calcd for $C_{33}H_{24}N_2O_2$ (M^++ H) 481.1838, found 481.1840.

4-(*Benzyloxy*)*-6,13-diphenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3m**): yellow solid, 55.9 mg, 92% yield; mp = 131 °C; $\boldsymbol{R_f}$ = 0.46 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (400 MHz, DMSO d_6) δ = 11.17 (s, 1 H), 10.18 (s, 1 H), 8.03 (d, *J* = 7.9 Hz, 1 H), 7.56 (d, *J* =

7.9 Hz, 1 H), 7.54 (t, *J* = 6.4 Hz, 3 H), 7.46 (d, *J* = 7.3 Hz, 3 H), 7.32 (d, *J* = 5.5 Hz, 5 H), 7.27 (d, *J* = 7.3 Hz, 2 H), 7.16 (d, *J* = 7.3 Hz, 1 H), 7.10 (d, *J* = 7.9 Hz, 3 H), 7.04 - 6.97 (m, 2 H), 6.95 (s, 1 H), 6.76 (d, *J* = 7.9 Hz, 1 H), 6.26 (s, 1 H), 5.24 (d, *J* = 4.9 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO d_6) δ = 146.2, 144.8, 141.1, 137.3, 137.0, 133.3, 132.0, 132.0, 128.9, 128.6, 128.3, 128.2, 128.0, 127.6, 127.6, 127.6, 127.4, 127.2, 126.7, 125.6, 122.3, 119.5, 118.9, 118.8, 118.4, 117.3, 111.1, 110.9, 104.8, 69.1, 36.5.; HRMS (ESI) calcd for $C_{38}H_{28}N_2O$ (M^++ H) 529.2202, found 529.2203.

5-Methyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3n**): gray solid, 44.6 mg, 89% yield; mp = 155 °C; $\boldsymbol{R_f}$ = 0.58 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 - 7.96 (m, 2 H), 7.85 (s, 1 H), 7.62 (d, *J* = 7.0 Hz, 2 H), 7.54 - 7.50 (m, 2 H), 7.49 - 7.45 (m, 1 H), 7.34 - 7.28 (m, 4 H), 7.25 - 7.20 (m, 4 H), 7.15 (t, *J* = 7 Hz, 2 H), 7.05 (t, *J* = 7 Hz, 1 H), 6.96 (s, 1 H), 6.40 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.2, 140.9, 138.7, 136.7, 133.5, 132.9, 131.7, 128.9, 128.3, 128.0, 127.6, 126.9, 126.8, 125.7, 123.3, 122.8, 119.8, 119.5, 118.5, 118.4, 118.3, 117.7, 117.2, 110.6, 108.9, 36.4, 29.9.; HRMS (ESI) calcd for $C_{32}H_{24}N_2$ (M^++ H) 437.1939, found 437.1941.

5-Benzyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3o**): gray solid, 50 mg, 85% yield; mp = 143 °C; R_f = 0.62 (petroleum ether/EtOAc = 85/15); ^{1}H NMR (500 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.43 (s, 1 H), 8.07 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 1 H), 7.43 (d, *J* = 7 Hz, 2 H), 7.41 - 7.37 (m, 3 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 7.39 (d, *J* = 7 Hz, 2 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 7.25 - 7.18 (m, 2 H), 7.17 - 7.12 (m, 2 H), 7.10 - 7.07 (m, 5 H), 6.99 (d, *J* = 7 Hz, 1 H), 6.92 (s, 1 H), 6.32 (s, 1 H), 5.63 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 145.7, 140.8, 138.3, 137.9, 137.0, 133.8, 132.3, 131.3, 128.4, 128.4, 128.3, 127.7, 126.9, 126.5, 126.6, 126.3, 126.1, 125.5, 122.6, 122.3,

119.3, 118.7, 118.2, 117.8, 117.8, 117.6, 117.0, 111.4, 109.4, 45.8, 35.9.; HRMS (ESI) calcd for $C_{38}H_{28}N_2$ (M^++ H) 513.2308, found 513.2325.

5-Allyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3p**): yellow solid, 46.75 mg, 88% yield; mp = 152 °C (decomposition); R_f = 0.54 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.48 (s, 1 H), 8.04 (d, *J* = 7.6 Hz, 1 H), 7.99 (d, *J* = 8 Hz, 1 H), 7.57 - 7.54 (m, 2 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.45 - 7.41 (m, 1 H), 7.39 (d, *J* = 8 Hz, 1 H), 7.34 (d, *J* = 8 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 3 H), 7.19 (t, *J* = 7.4 Hz, 1 H), 7.12 - 7.07 (m, 6 H), 6.98 (t, *J* = 7.2 Hz, 1 H), 6.91 (s, 1 H), 6.30 (s, 1 H), 6.00 (dt, *J* = 6, 11.1 Hz, 1 H), 5.11 (d, *J* = 10.3 Hz, 1 H), 5.05 - 4.95 (m, 2 H), 4.87 (d, *J* = 17.2 Hz, 1 H).; ^{13}C NMR (125 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 144.0, 139.1, 135.7, 135.3, 132.3, 132.1, 130.4, 129.7, 126.8, 126.7, 126.0, 124.8, 124.8, 124.5, 123.7, 120.7, 120.6, 117.4, 117.0, 116.4, 116.0, 115.9, 115.9, 115.1, 114.0, 109.7, 107.5, 43.0, 34.1.; HRMS (ESI) calcd for $C_{34}H_{26}N_2$ (M^++ H) 463.2159, found 463.2166.

6-(*4-Chlorophenyl*)*-13-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3q**): gray solid, 48.72 mg, 93% yield; mp = 144 °C; R_f = 0.55 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (400 MHz, DMSO d_6) δ = 11.71 (s, 1 H), 10.89 (s, 1 H), 8.61 (d, *J* = 4 Hz, 1 H), 7.80 (t, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 7.9 Hz, 1 H), 7.42 - 7.32 (m, 5 H), 7.32 - 7.25 (m, 3 H), 7.20 - 7.17 (m, 2 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 7.3 Hz, 1 H), 6.93 - 6.84 (m, 2 H), 6.84 (br. s., 1 H), 6.12 (s, 1 H); ^{13}C NMR (100 MHz, DMSO d_6) δ = 162.2, 160.3, 149.3, 149.3, 140.0, 136.4, 136.3, 133.4, 133.4, 132.8, 131.5, 131.1, 128.5, 127.8, 127.7, 126.4, 126.2, 122.3, 122.3, 119.2, 118.7, 118.2, 118.0, 116.7, 116.5, 116.3, 115.8, 115.6, 115.4, 113.3, 111.3, 110.5, 37.2.; HRMS (ESI) calcd for $C_{31}H_{21}ClN_2$ (M^++ H) 457.1442, found 457.1450.

4-(*13-Phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindol-6-yl*)*benzonitrile* (**3r**): gray solid, 48.83 mg, 95% yield; mp = 143 °C; R_f = 0.55 (petroleum ether/EtOAc = 90/10); ^{1}H

NMR (200 MHz, DMSO d_6) δ = 11.31 (s, 1 H), 11.27 (s, 1 H), 7.83 (dd, *J* = 3, 8.1 Hz, 1 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.60 - 7.55 (m, 4 H), 7.54 (s, 3 H), 7.44 - 7.40 (m, 1 H), 7.32 - 7.25 (m, 3 H), 7.24 - 7.15 (m, 3 H), 7.14 - 7.09 (m, 1 H), 7.1 - 7.02 (s, 1 H), 6.96 (s, 1 H); ^{13}C NMR (50 MHz, DMSO d_6) δ = 144.3, 139.3, 136.4, 136.1, 135.0, 131.6, 130.9, 128.1, 127.3, 126.0, 125.7, 125.0, 118.6, 116.8, 33.6; HRMS (ESI) calcd for $C_{32}H_{21}N_3$ (M^++ H) 448.1735, found 448.1737.

13-Phenyl-6-(*p-tolyl*)*-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3s**): yellow solid, 40.1 mg, 80% yield; mp = 162 °C; R_f = 0.53 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (s, 1 H), 7.87 (s, 1 H), 7.5 (d, *J* = 7.2 Hz, 2 H), 7.37 (d, *J* = 7.2 Hz, 2 H), 7.33 (d, *J* = 7.6 Hz, 3 H), 7.24 (m, 6 H), 7.15 (t, *J* = 7.2 Hz, 2 H), 7.06 (t, *J* = 7.2 Hz, 2 H), 6.77 (s, 1 H), 6.37 (s, 1 H), 2.49 (s, 3 H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.6, 138.2, 137.6, 137.3, 136.4, 133.4, 131.9, 131.9, 129.5, 128.7, 128.2, 128.1, 127.7, 127.0, 125.8, 123.2, 123.0, 121.9, 119.8, 119.7, 118.5, 118.4, 118.37, 117.7, 117.5, 110.6, 110.5, 36.97, 21.24; HRMS (ESI) calcd for $C_{32}H_{24}N_2$ (M^++ H) 437.1995, found 437.1998.

6-(*4-Methoxyphenyl*)*-13-phenyl-8,13-dihydro-5H-cyclohepta*[*1,2-b:5,4-b'*]*bisindole* (**3t**): yellow solid, 39.72 mg, 82% yield; mp = 147 °C; R_f = 0.57 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.02 - 7.97 (m, 2 H), 7.86 (s, 1 H), 7.63 (d, *J* = 7.0 Hz, 2 H), 7.54 - 7.51 (dd, *J* = 2, 7.5 Hz, 2 H), 7.51 - 7.47 (m, 1 H), 7.32 - 7.29 (m, 4 H), 7.25 - 7.21 (m, 4 H), 7.15 (t, *J* = 7.5 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.96 (s, 1 H), 6.40 (s, 1 H), 3.86 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 145.2, 140.9, 138.7, 136.7, 133.5, 132.9, 131.7, 128.9, 128.3, 128.0, 127.6, 126.9, 126.8, 125.7, 123.3, 122.8, 119.8, 119.5, 118.5, 118.4, 118.3, 117.7, 117.1, 110.6, 108.9, 36.3, 29.7; HRMS (ESI) calcd for $C_{32}H_{24}ON_2$ (M^++ H) 453.1939, found 453.1950.

13-Phenyl-6-(pyridin-2-yl)-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (**3u**): dark brown solid, 38.9 mg, 80% yield; mp = 190 °C (decomposition); R_f = 0.38 (petroleum ether/EtOAc = 85/15); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 11.72 (s, 1 H), 10.89 (s, 1 H), 8.61 (d, *J* = 4 Hz, 1 H), 7.90 - 7.76 (m, 2 H), 7.50 (d, *J* = 7.8 Hz, 1 H), 7.43 - 7.33 (m, 5 H), 7.31 - 7.23 (m, 3 H), 7.21 (d, *J* = 8 Hz, 2 H), 7.17 - 7.08 (m, 1 H), 7.03 (t, *J* = 7.8 Hz, 1 H), 6.94 - 6.87 (m, 1 H), 6.84 (s, 1 H), 6.12 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 145.4, 140.0, 136.3, 136.0, 132.2, 131.3, 130.9, 127.7, 127.6, 127.0, 126.8, 126.5, 126.2, 125.9, 124.7, 121.6, 121.4, 118.6, 118.2, 117.0, 116.8, 116.1, 115.7, 110.4, 109.9, 36.2.; HRMS (ESI) calcd for $C_{30}H_{21}N_3$ (M^++ H) 424.1735, found 424.1736.

2-Fluoro-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole (**3v**): yellow solid, 41 mg, 81% yield; mp = 167 °C; R_f = 0.54 (petroleum ether/EtOAc = 85/15); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.03 (s, 1 H), 7.94 (dd, *J* = 7.6, 7.2 Hz, 2 H), 7.86 (s, 1 H), 7.59 (d, *J* = 6.9 Hz, 2 H), 7.55 - 7.45 (m, 3 H), 7.36 (d, *J* = 7.2 Hz, 1 H), 7.30 - 7.21 (m, 5 H), 7.17 - 7.06 (m, 2 H), 7.01 (d, *J* = 8.2 Hz, 1 H), 6.81 (s, 1 H), 6.75 (t, *J* = 7.6 Hz, 1 H), 6.36 (s, 1 H).; ^{13}C NMR (50 MHz, $CDCl_3$) δ = 163.8-161.8 (d, *J* = 247 Hz), 148.2-148.1 (d, *J* = 5.72 Hz), 140.3, 137.4, 136.4, 133.5, 131.8-131.8 (d, *J* = 4.77 Hz), 129.4-129.4 (d, *J* = 7.63 Hz), 129.0, 128.8, 128.4, 127.9, 127.5, 123.4, 123.3, 122.5-122.6 (d, *J* = 1.91 Hz), 120.1, 120.0, 118.7, 118.3, 117.3, 116.9, 114.0, 113.9, 112.8, 112.7, 110.7, 110.6, 36.6.; HRMS (ESI) calcd for $C_{31}H_{21}FN_2$ (M^++ H) 441.1689, found 441.1690.

3-*Methyl-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[1,2-b:5,4-b']bisindole* (**3w**): gray solid, 41.62 mg, 83% yield; mp = 154 °C; R_f = 0.6 (petroleum ether/EtOAc = 80/20); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.73 (s, 1 H), 9.87 (s, 1 H), 7.83 (d, *J* = 7 Hz, 2 H), 7.46 (d, *J* = 8 Hz, 2 H), 7.30 (m, 6 H), 7.08 (d, *J* = 2 Hz, 3 H), 7.06 - 6.99 (m, 3 H), 6.96 (d, *J* = 7 Hz, 1 H), 6.88 (s, 1 H), 6.19 (s, 1 H), 2.41 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1

ratio) δ = 145.2, 140.8, 138.7, 136.7, 133.5, 133.0, 131.7, 128.9, 128.3, 128.0, 127.6, 127.19, 126.8, 125.8, 123.3, 122.8, 119.8, 119.5, 118.5, 118.4, 118.3, 117.7, 117.2, 110.2, 39.8, 19.8; HRMS (ESI) calcd for $C_{32}H_{24}N_2$ (M^++ H) 437.1939, found 437.1940.

2-Methoxy-7,13-diphenyl-8,13-dihydro-5H-cyclohepta[*1,2-b:5,4-b'*]*bisindole* (**3x**): yellow solid, 40.5 mg, 78% yield; mp = 168 °C; R_f = 0.53 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$) δ = = 8.03 (s, 1 H), 7.95 - 7.90 (m, 2 H), 7.83 (s, 1 H), 7.55 - 7.43 (m, 6 H), 7.25 - 7.16 (m, 5 H), 7.19 - 6.96 (m, 3 H), 6.94 (s, 1 H), 6.76 (s, 1 H), 6.66 - 6.55 (m, 1 H), 6.32 (s, 1 H), 3.63 (s, 3 H).; ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.4, 147.3, 140.4, 137.3, 131.7, 129.0, 128.9, 128.8, 128.2, 123.2, 123.0, 119.8, 119.5, 118.4, 113.2, 110.8, 110.5, 54.9, 37.1; HRMS (ESI) calcd for $C_{32}H_{24}ON_2$ (M^++ H) 453.1889, found 453.1890.

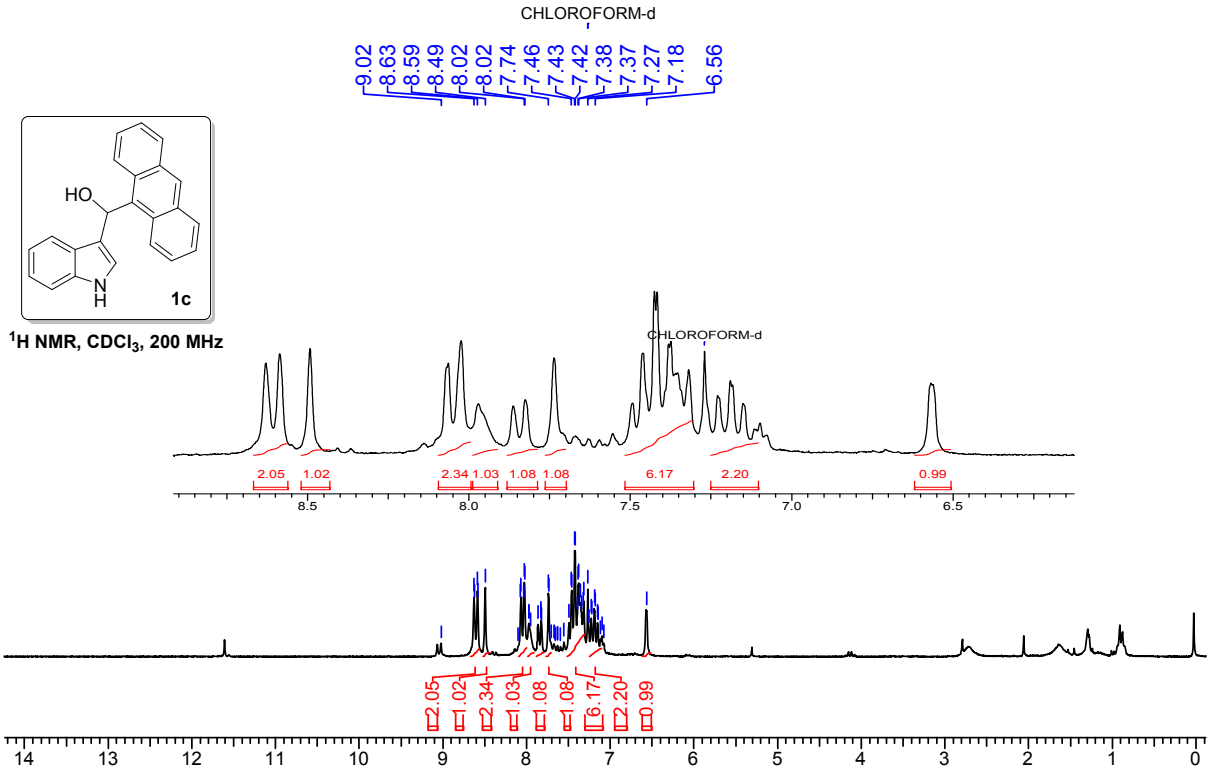
1-Methyl-4,11-diphenyl-6,11-dihydro-1H-pyrrolo[*2',3':4,5*]*cyclohepta*[*1,2-b*]*indole* (**5a**): brown solid, 27.5 mg, 62% yield; mp = 152 °C; R_f = 0.64 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.45 (s, 1 H), 7.74 - 7.72 (m, 1 H), 7.56 - 7.48 (m, 2 H), 7.34 (dd, *J* = 2, 7 Hz, 2 H), 7.26 - 7.22 (dd, *J* = 2, 7.1 Hz, 2 H), 7.18 (m, 2 H), 7.11 (m, 2 H), 7.00 (m, 3 H), 6.53 (d, *J* = 4 Hz, 1 H), 6.51 (s, 1 H), 5.85 (s, 1 H), 5.80 (d, *J* = 4 Hz, 1 H), 3.71 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 143.9, 142.4, 136.6, 135.7, 127.3, 127.1, 126.8, 126.4, 125.9, 125.6, 124.9, 117.8, 116.1, 112.6, 111.9, 109.6, 33.1, 28.3; HRMS (ESI) calcd for $C_{28}H_{22}N_2$ (M^++ H) 387.1858, found 387.1856.

1-Methyl-2-(*2-nitrophenyl*)*-4,11-diphenyl-6,11-dihydro-1H-pyrrolo*[*2',3':4,5*]*cyclohepta[1,2-b]indole* (**5b**): yellow solid, 39.5 mg, 68% yield; mp = 138 °C (decomposition); R_f = 0.54 (petroleum ether/EtOAc = 90/10); ^{1}H NMR (200 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 10.86 (s, 1 H), 7.91 - 7.87 (t, *J* = 6.0 Hz, 2 H), 7.64 (t, *J* = 6.0 Hz,1 H), 7.57 - 7.54 (m, 1 H), 7.53 - 7.47 (m, 3 H), 7.40 - 7.34 (m, 2 H), 7.32 - 7.27 (m, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.17 - 7.11 (d, *J* = 8.0 Hz, 2 H), 7.10 - 6.99 (m, 3 H), 6.60 (s, 1 H), 6.04 (s, 1 H), 5.85 (s, 1 H), 3.53 (s, 3

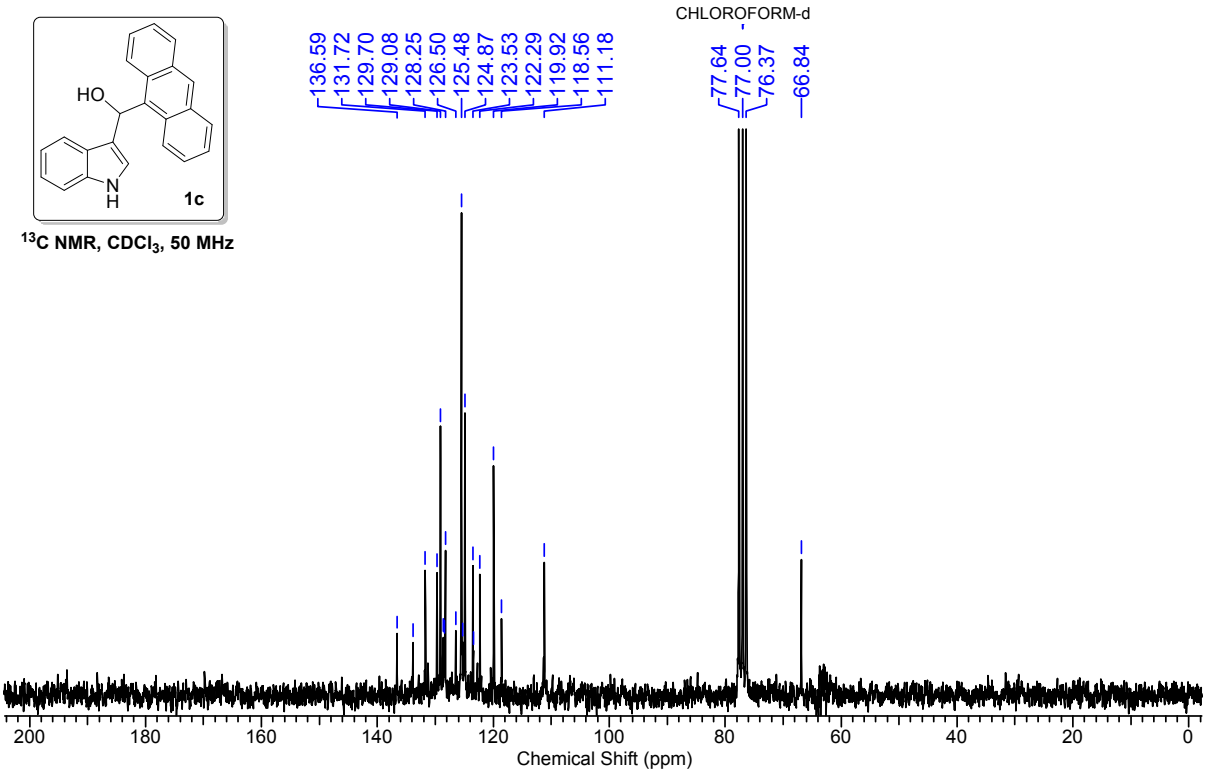
H); ^{13}C NMR (50 MHz, $CDCl_3$:DMSO d_6, 4:1 ratio) δ = 147.8, 142.9, 141.5, 135.3, 135.1, 131.7, 131.6, 131.4, 131.0, 127.6, 126.7, 126.6, 126.4, 125.9, 125.8, 125.5, 125.3, 125.1, 124.4, 122.2, 120.1, 118.0, 117.3, 115.9, 112.7, 111.5, 109.1, 108.4, 36.6, 30.1.; HRMS (ESI) calcd for $C_{34}H_{25}N_3O_2$ (M^++ H) 508.1947, found 508.1946.

3-((*1H-indol-3-yl*)(*phenyl)methyl*)-*2*-(*phenylethynyl*)-*1H-indole* (**6**): yellowish solid, 41 mg, 84% yield; mp = 175 °C (decomposition); R_f = 0.63 (petroleum ether/EtOAc = 85/15); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.1 - 8.05 (s, 1 H), 7.88 s, 1 H), 7.45 - 7.36 (m, 4 H), 7.35 (td, *J* = 2, 2.8 Hz, 2 H), 7.30 - 7.28 (m, 4 H), 7.24 (dd, *J* = 2, 2.8 Hz, 2 H), 7.23 - 7.16 (m, 2 H), 7.16 - 7.08 (m, 2 H), 7.03 - 6.91 (m, 2 H), 6.93 (d, *J* = 2 Hz, 1 H), 6.16 - 6.11 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 143.3, 136.2, 131.3, 128.8, 128.3, 128.0, 126.0, 123.8, 121.8, 120.7, 119.8, 119.2, 117.0, 110.9, 110.8, 95.6, 81.3, 40.2; HRMS (ESI) calcd for $C_{31}H_{22}N_2$ (M^++ H) 423.1870, found 423.1875.

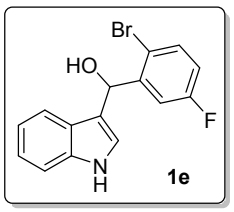
3. Spectral data



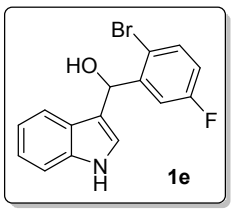
^{1}H NMR, $CDCl_3$, 200 MHz



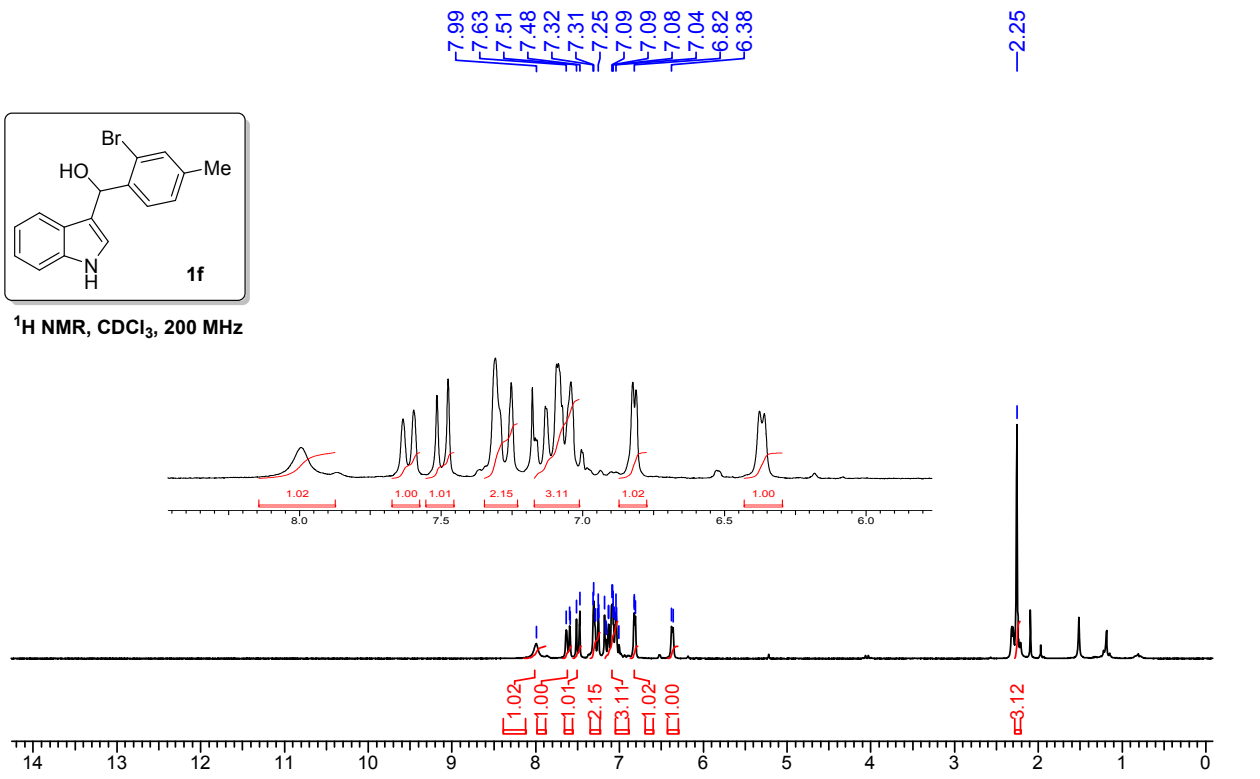
^{13}C NMR, $CDCl_3$, 50 MHz



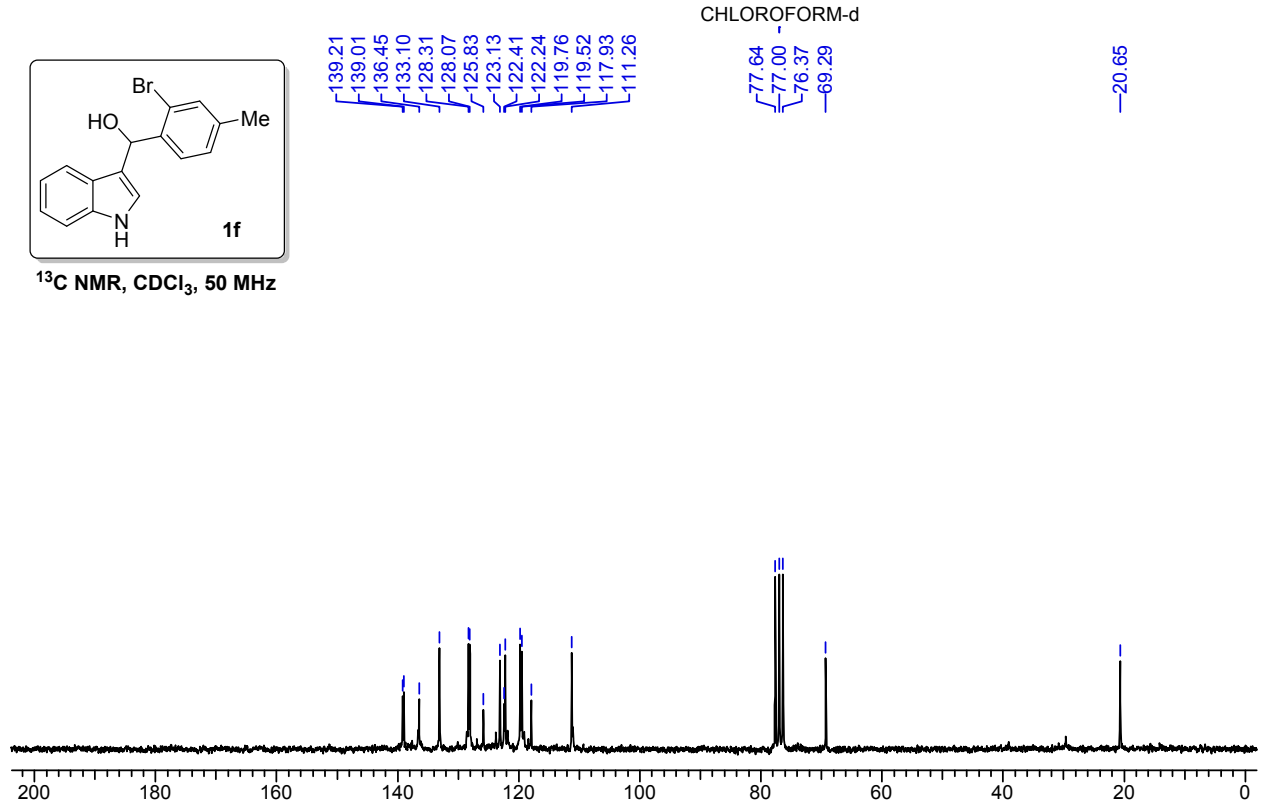
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



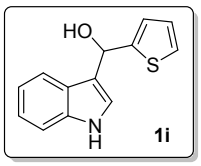
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



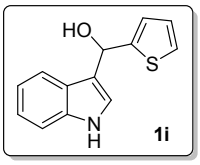
^{1}H NMR, $CDCl_3$, 200 MHz



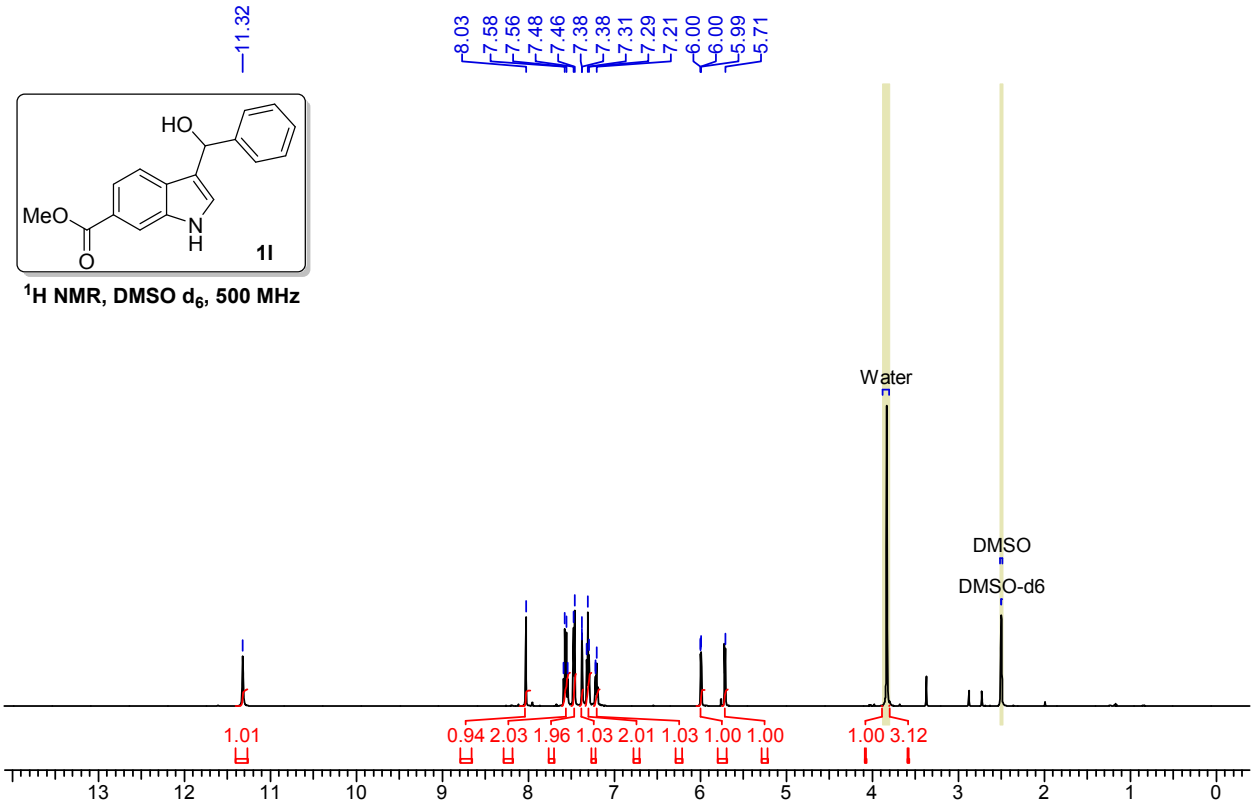
^{13}C NMR, $CDCl_3$, 50 MHz



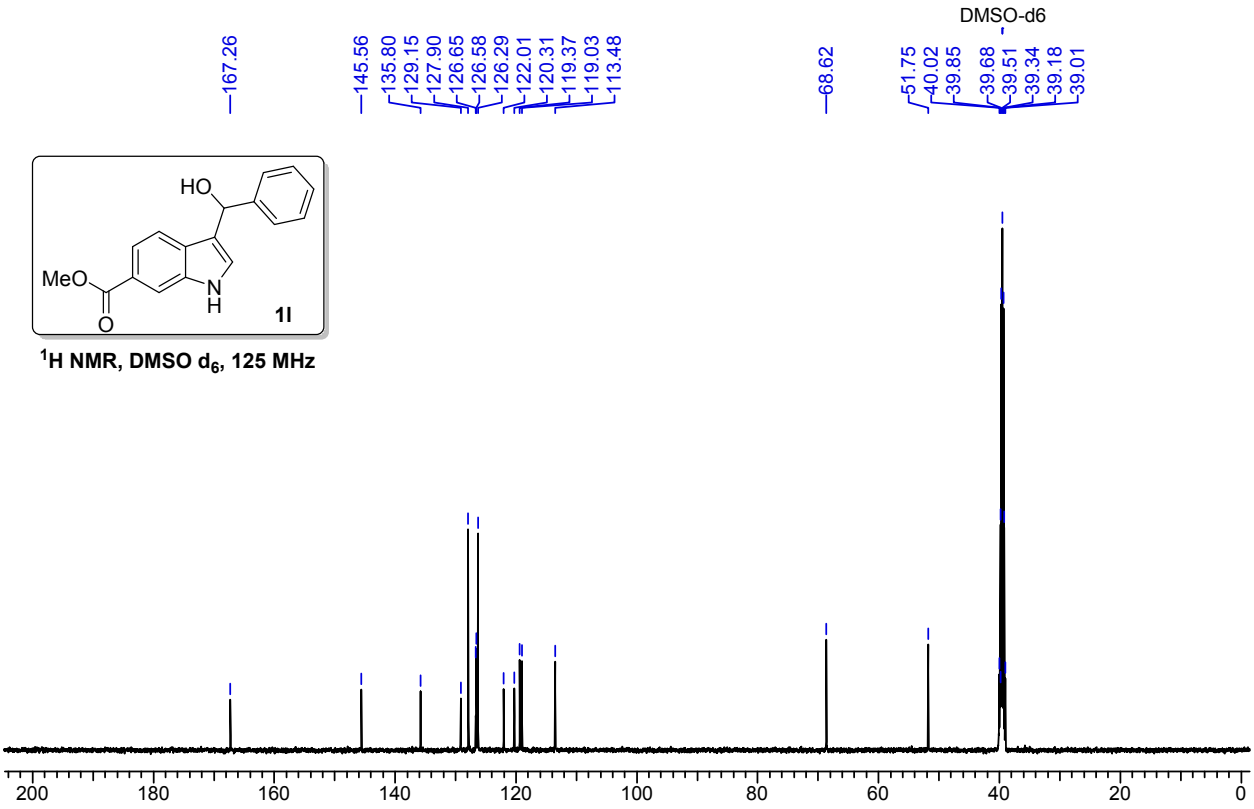
^{1}H NMR, $CDCl_3$, 200 MHz



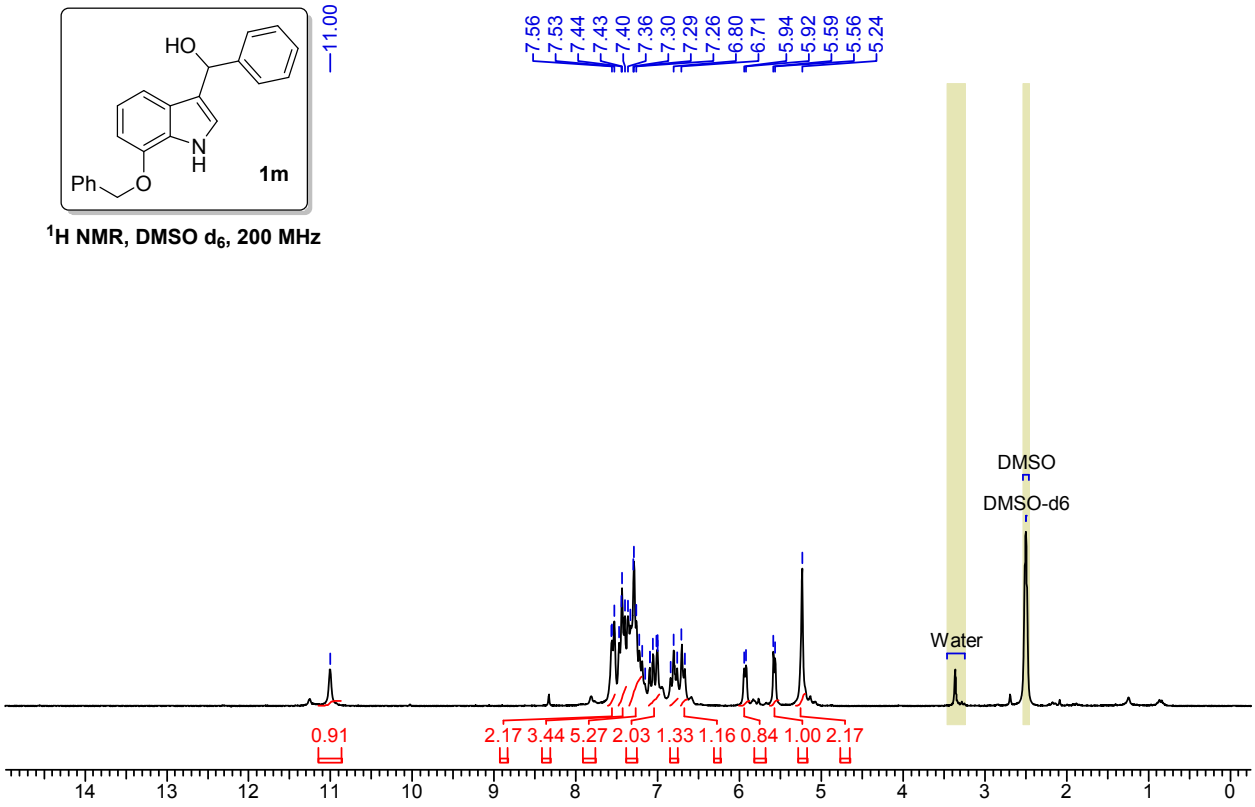
^{13}C NMR, $CDCl_3$, 50 MHz



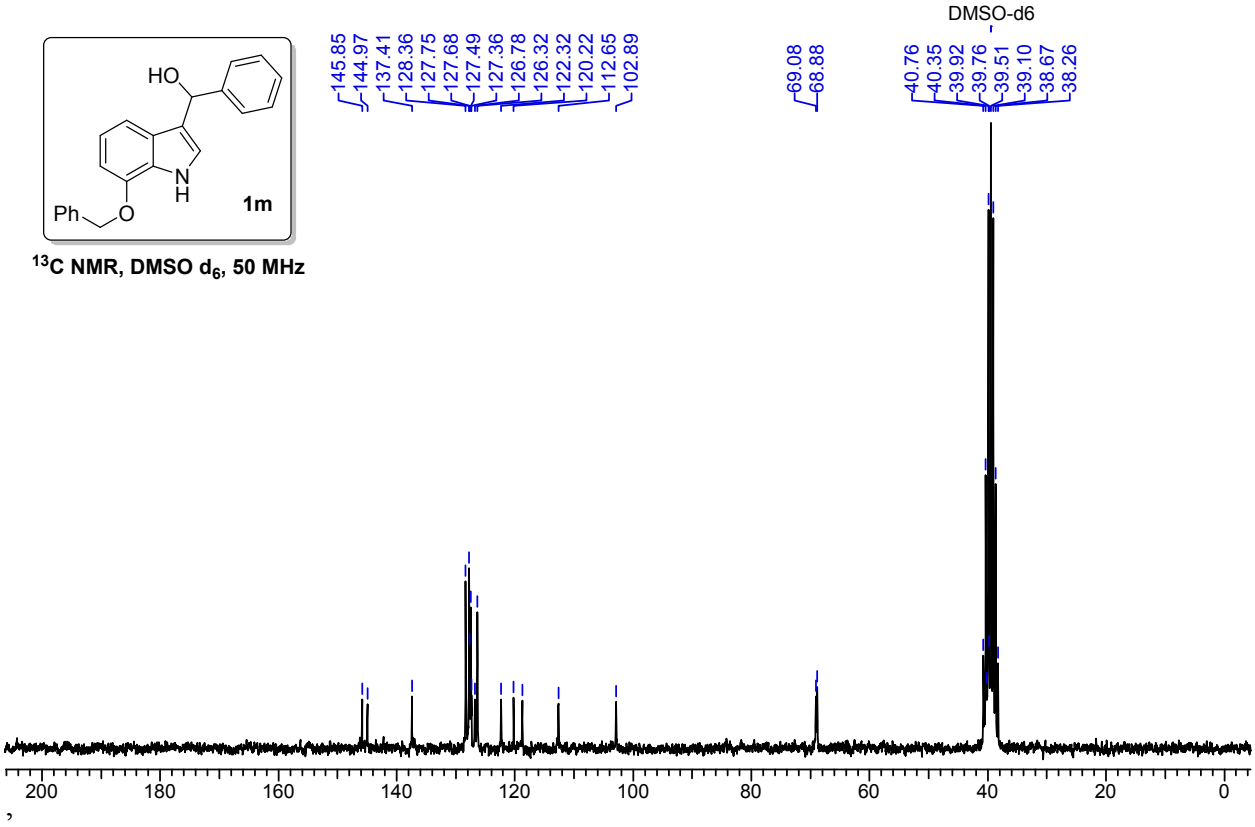
^{1}H NMR, DMSO d_6, 500 MHz



^{1}H NMR, DMSO d_6, 125 MHz



^{1}H NMR, DMSO d_6, 200 MHz



^{13}C NMR, DMSO d_6, 50 MHz

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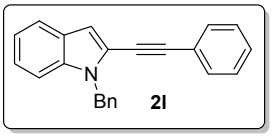
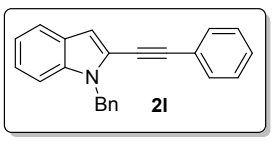
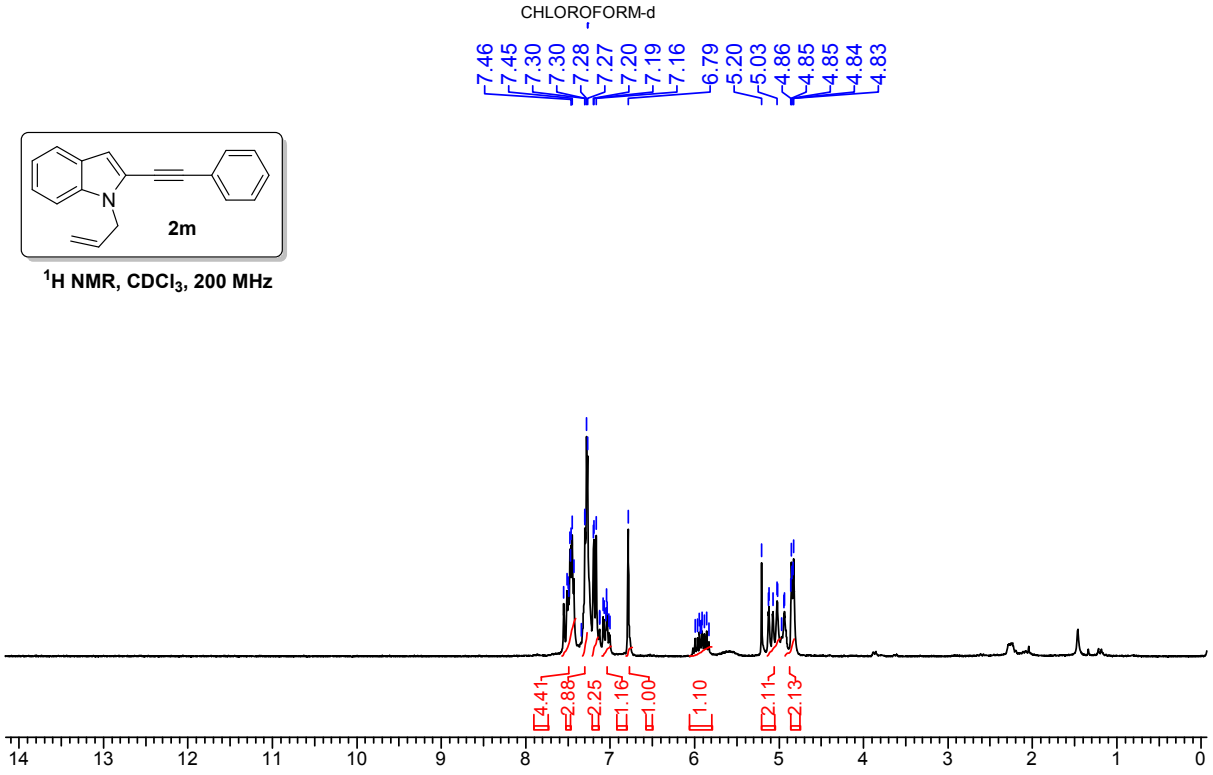


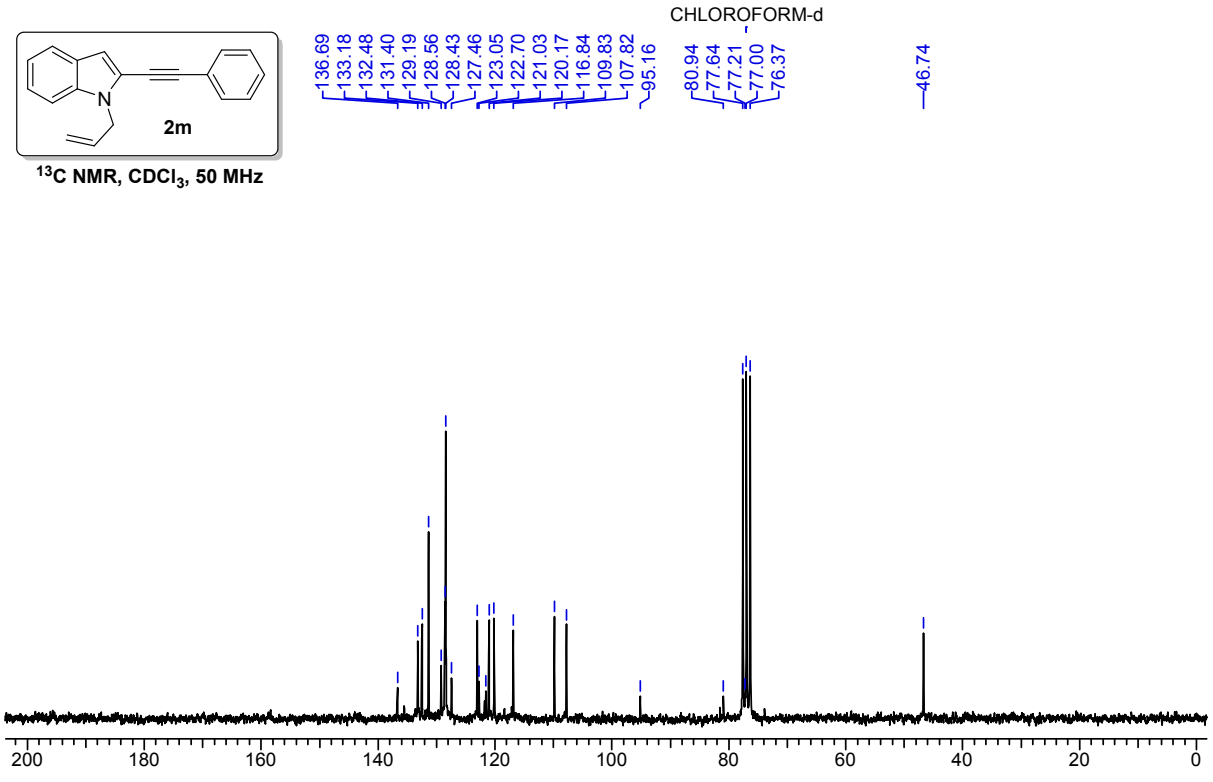
^{1}H NMR, $CDCl_3$, 200 MHz



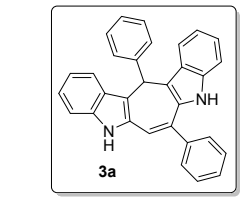
^{13}C NMR, $CDCl_3$, 50 MHz



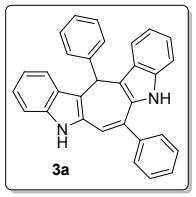
^{1}H NMR, $CDCl_3$, 200 MHz



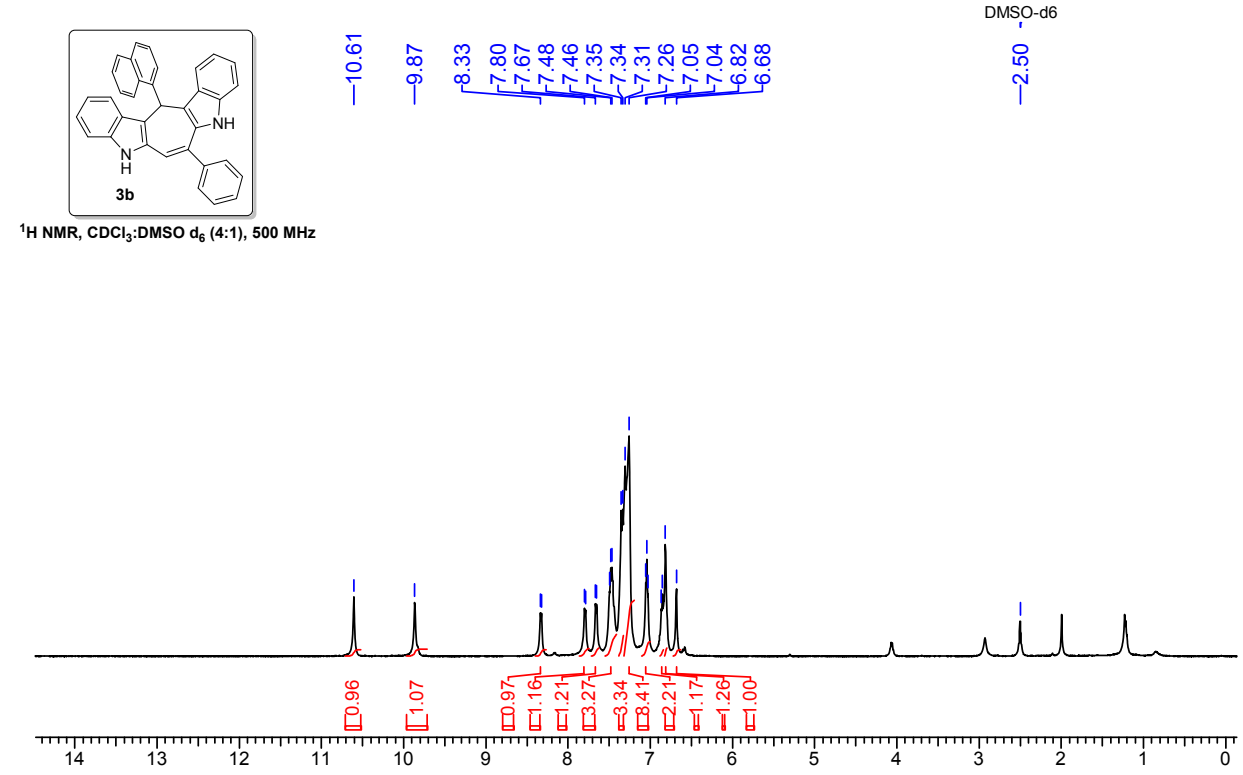
^{13}C NMR, $CDCl_3$, 50 MHz



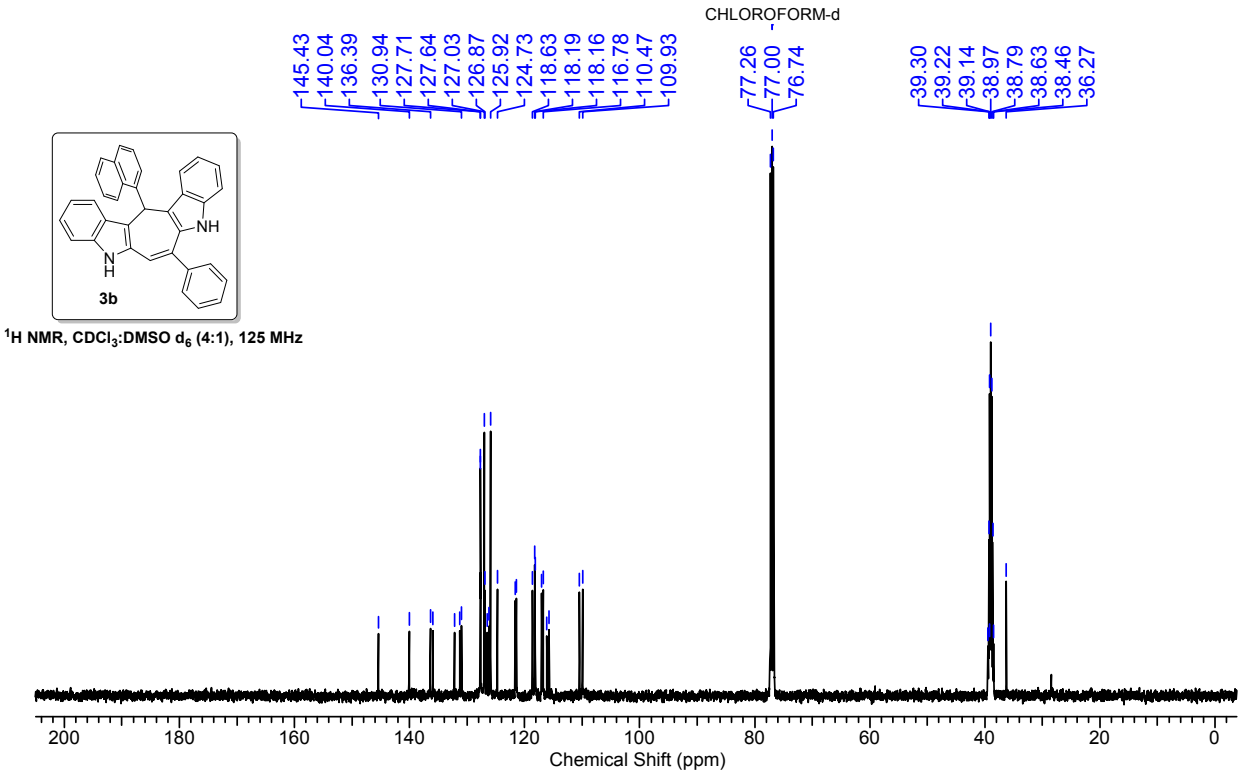
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



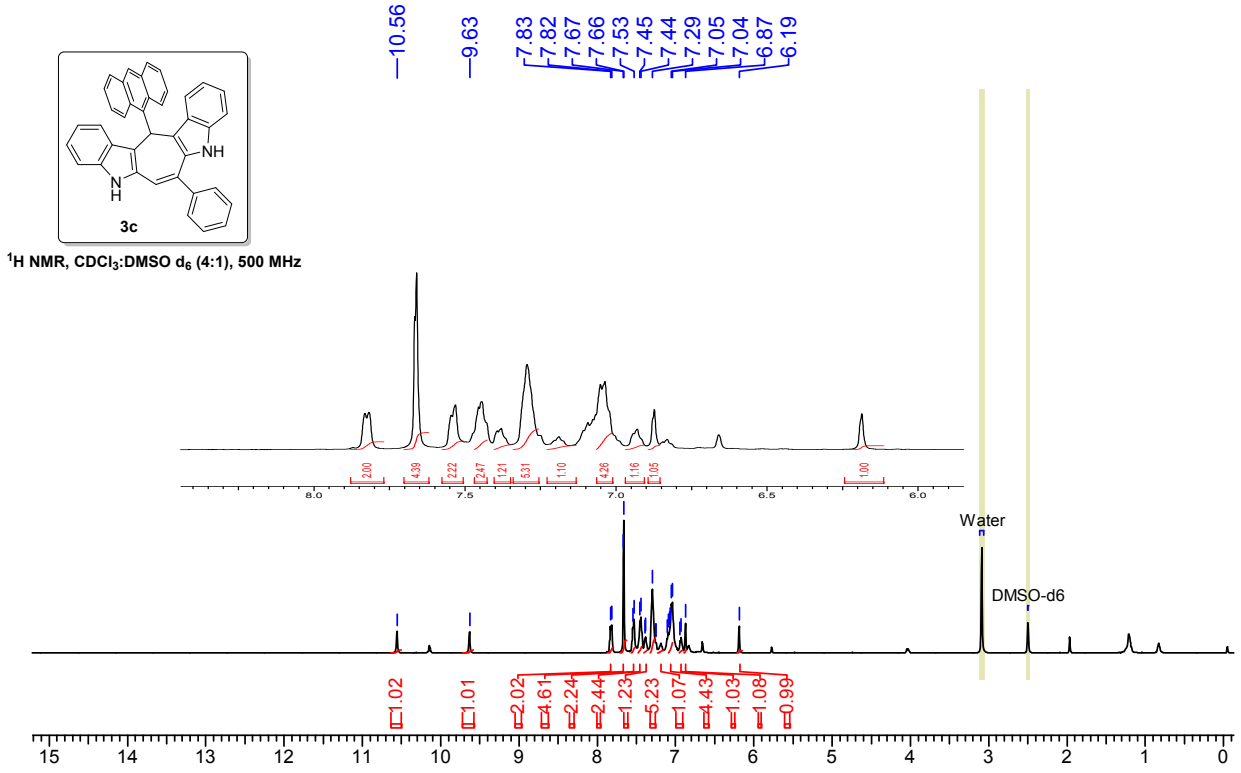
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



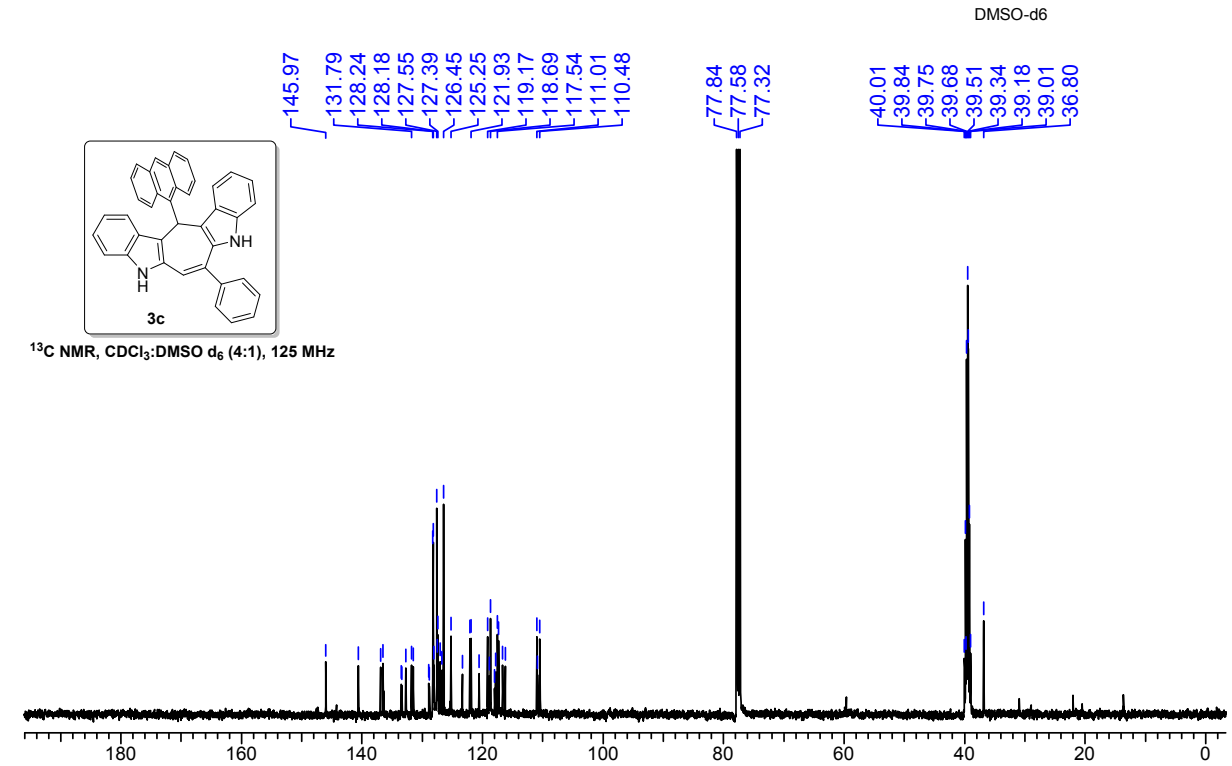
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 500 MHz



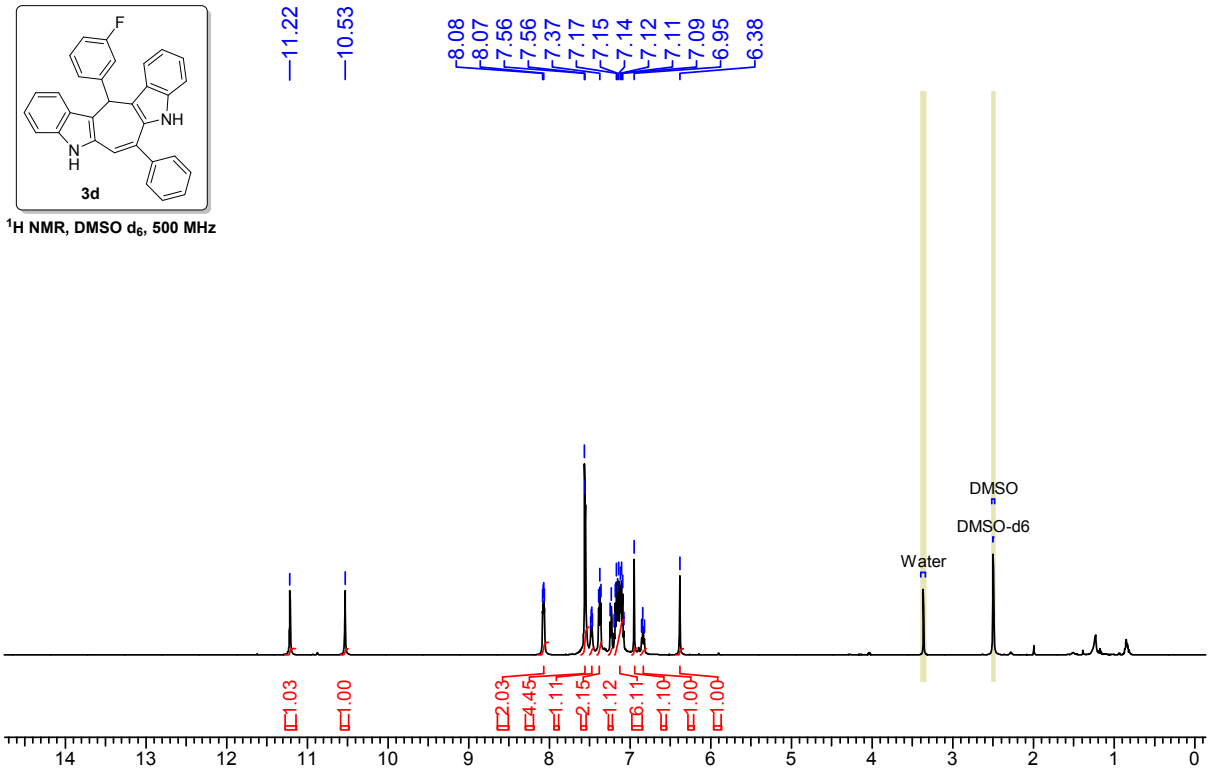
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 125 MHz



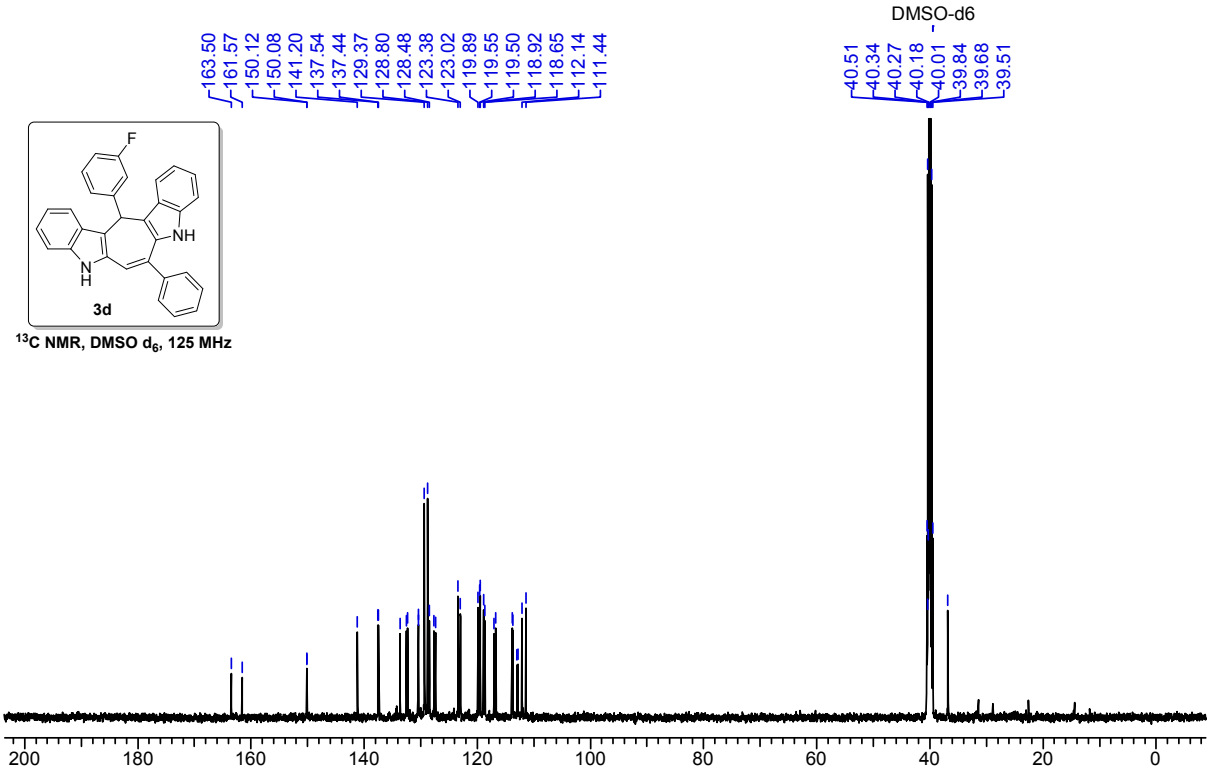
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 500 MHz



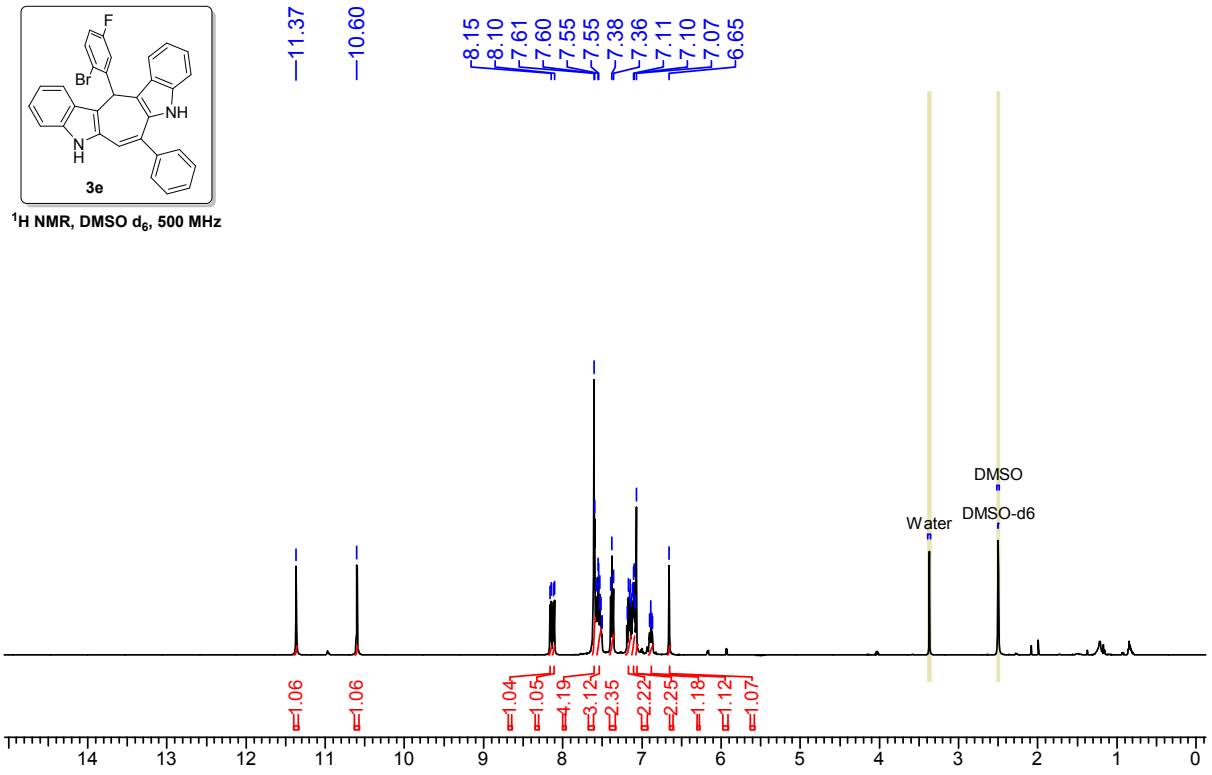
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 125 MHz



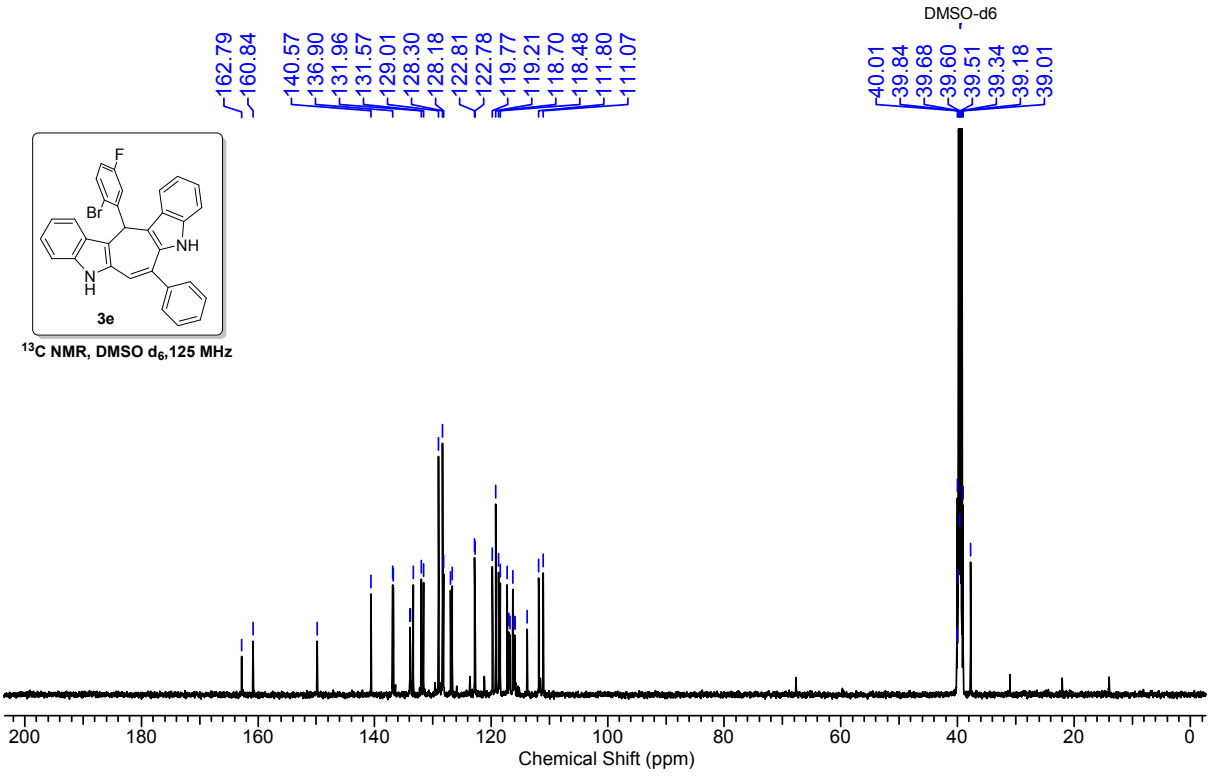
^{1}H NMR, DMSO d_6, 500 MHz



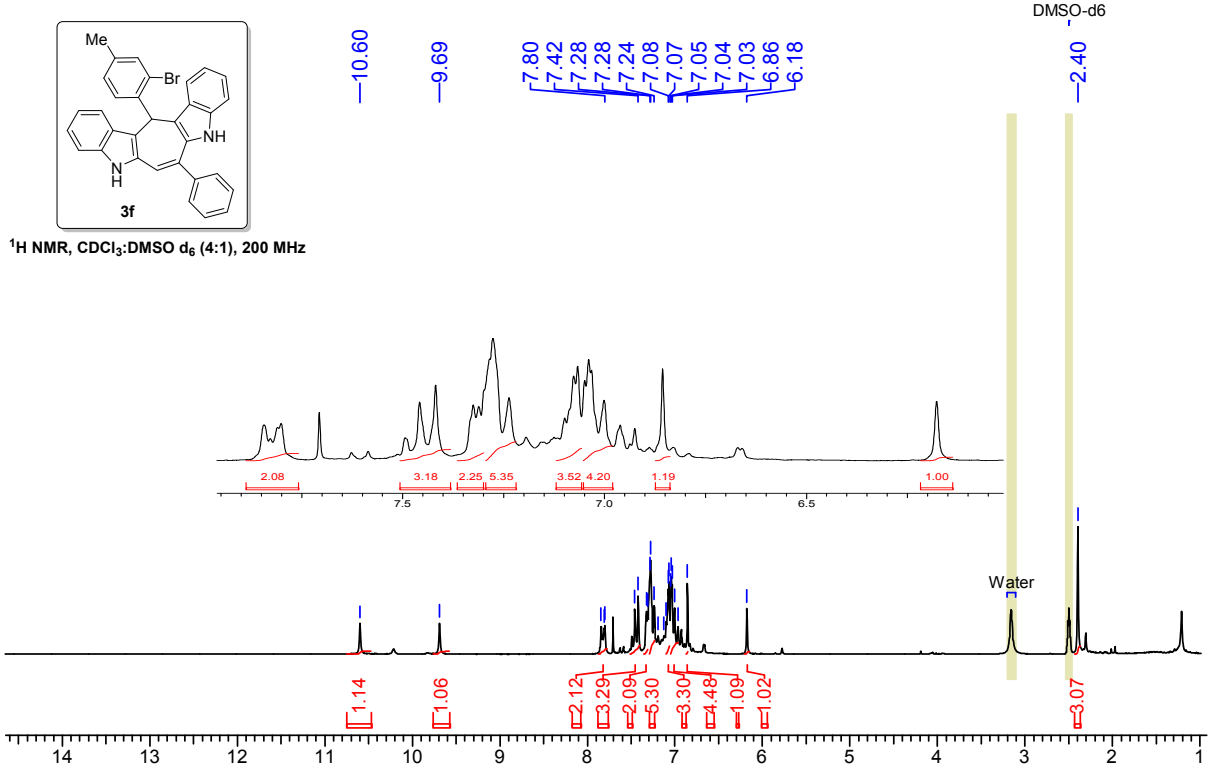
^{13}C NMR, DMSO d_6, 125 MHz



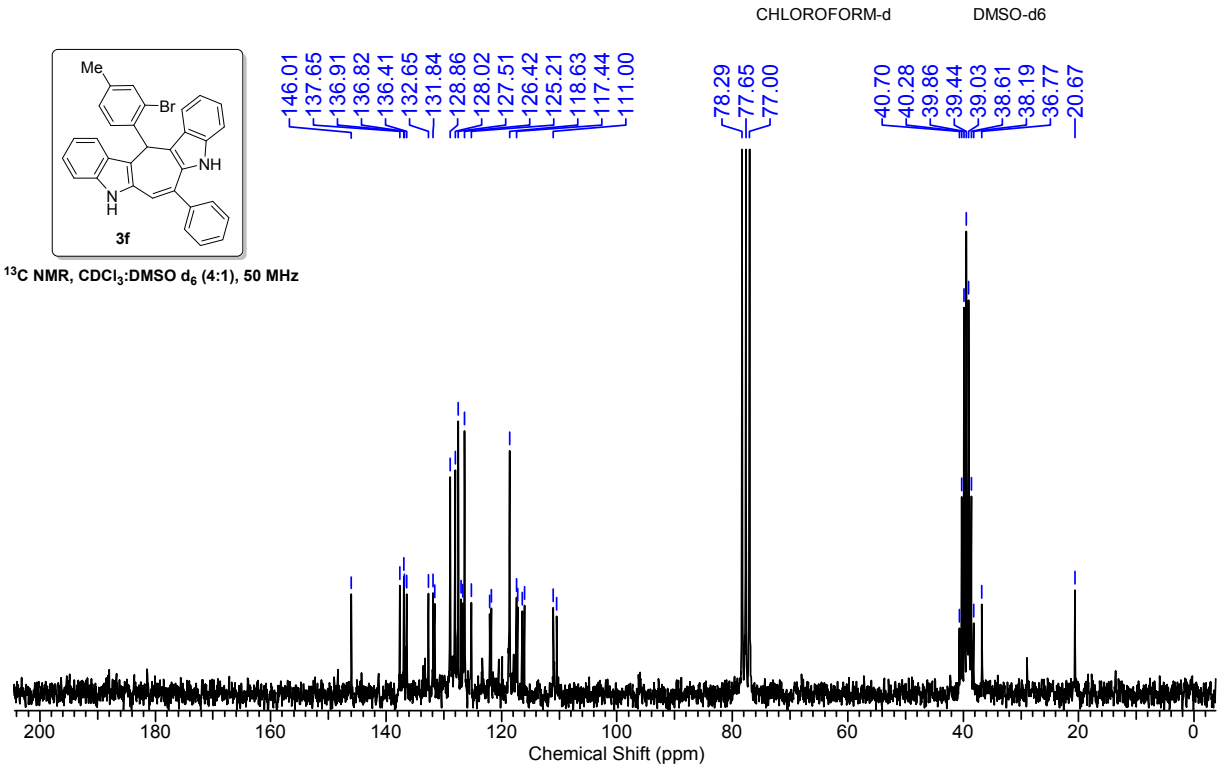
^{1}H NMR, DMSO d_6, 500 MHz



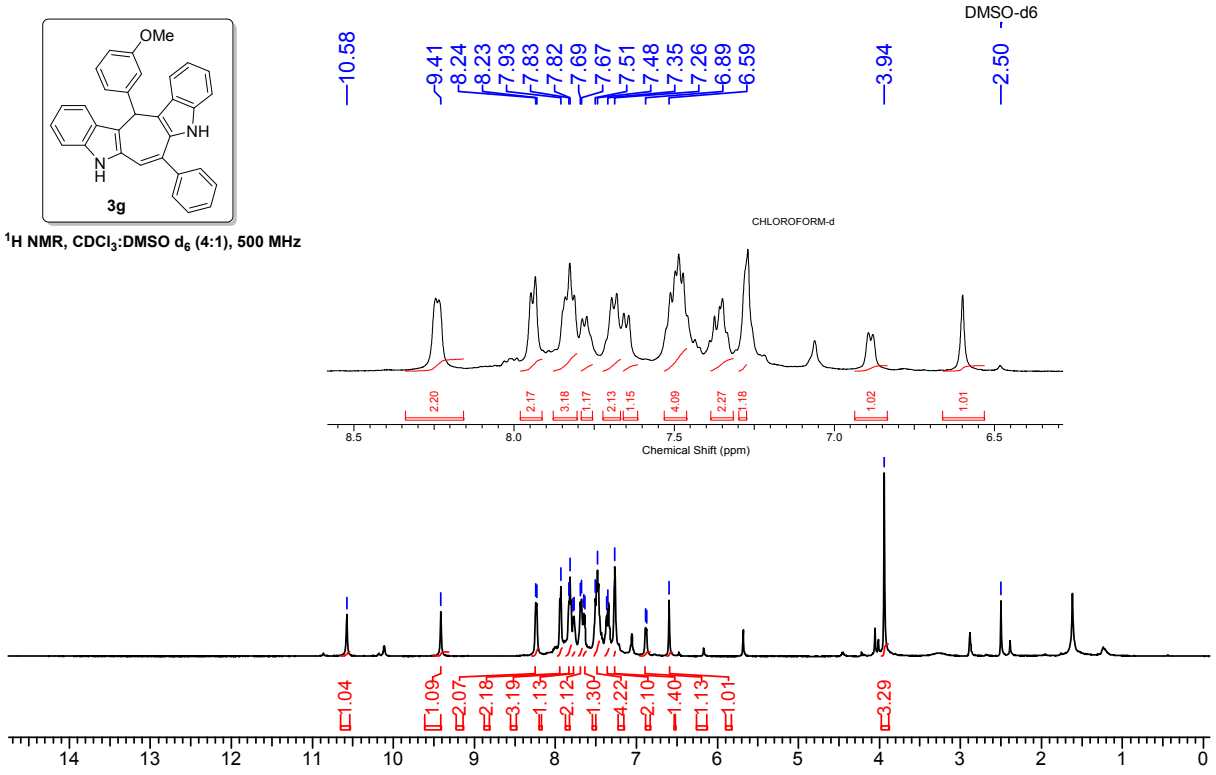
^{13}C NMR, DMSO d_6,125 MHz



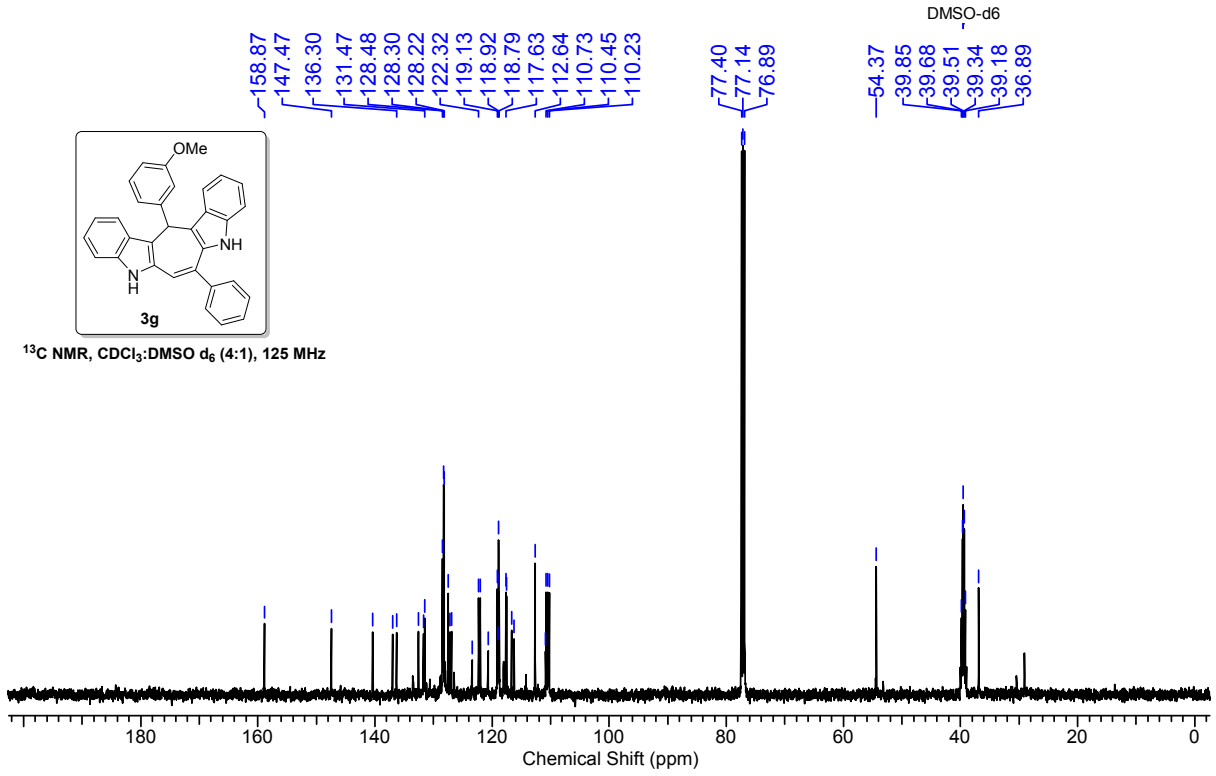
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



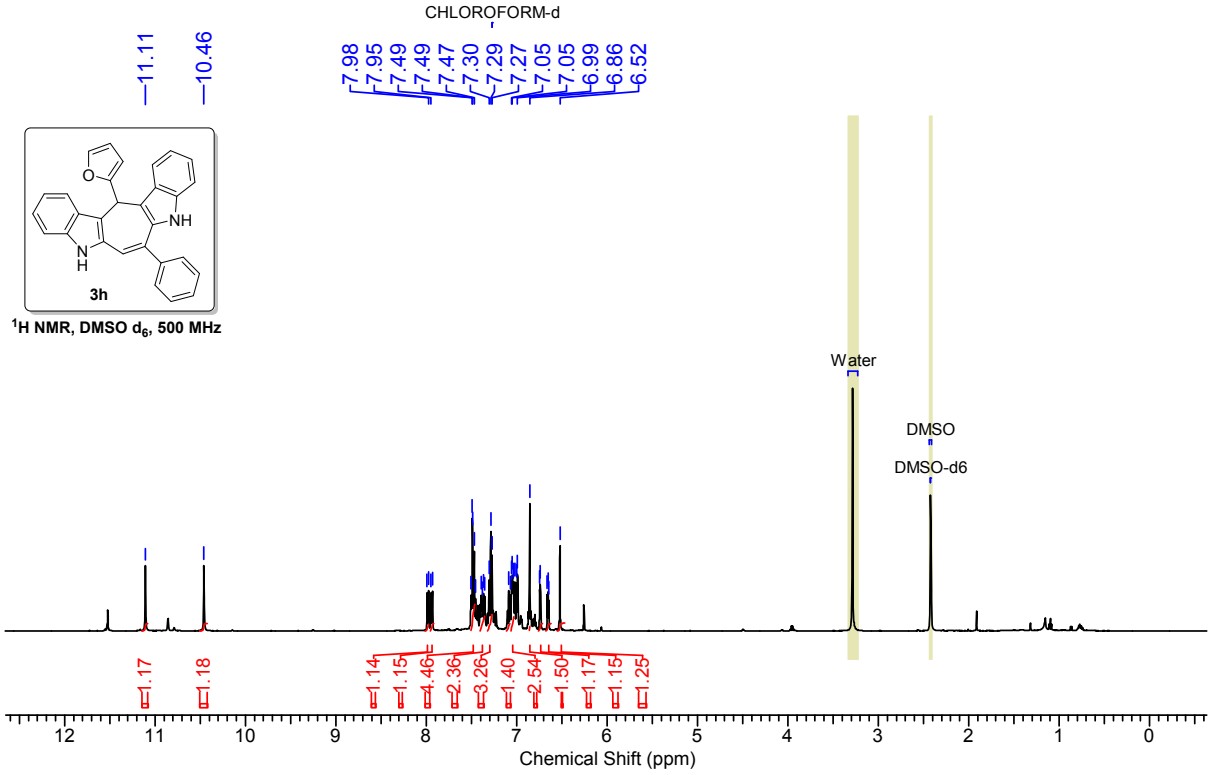
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



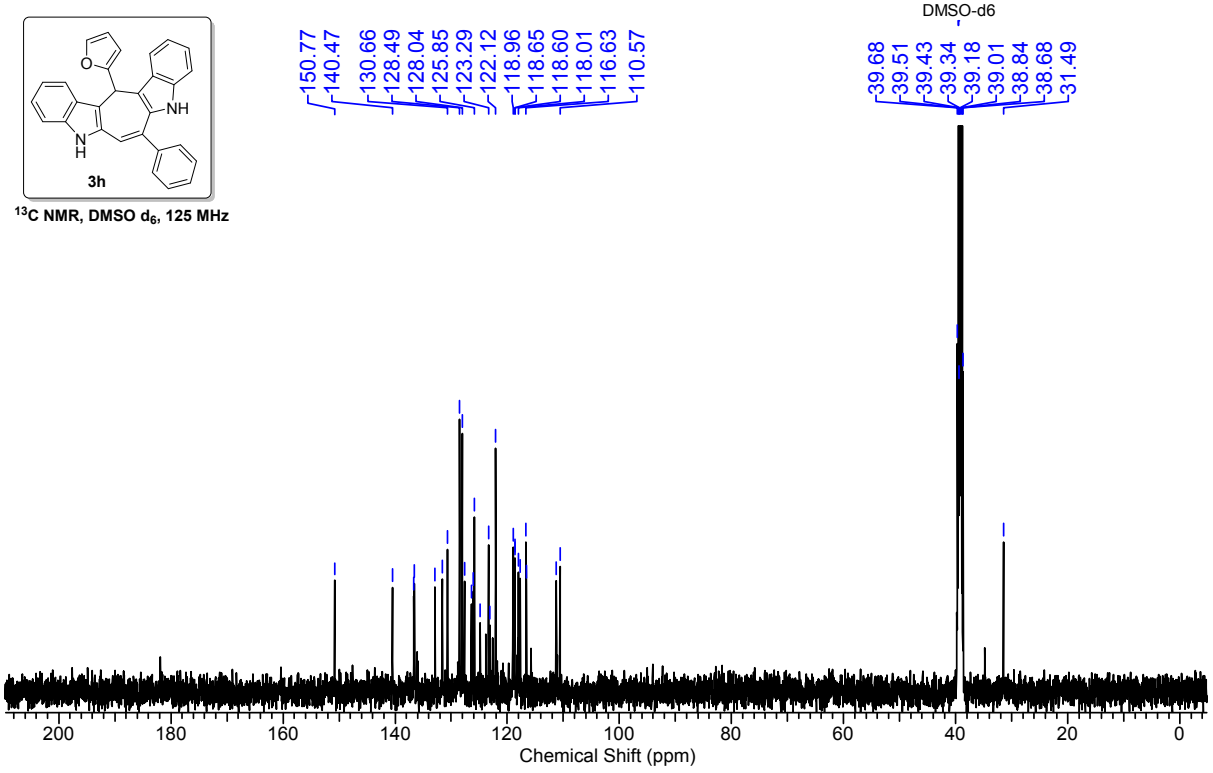
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 500 MHz



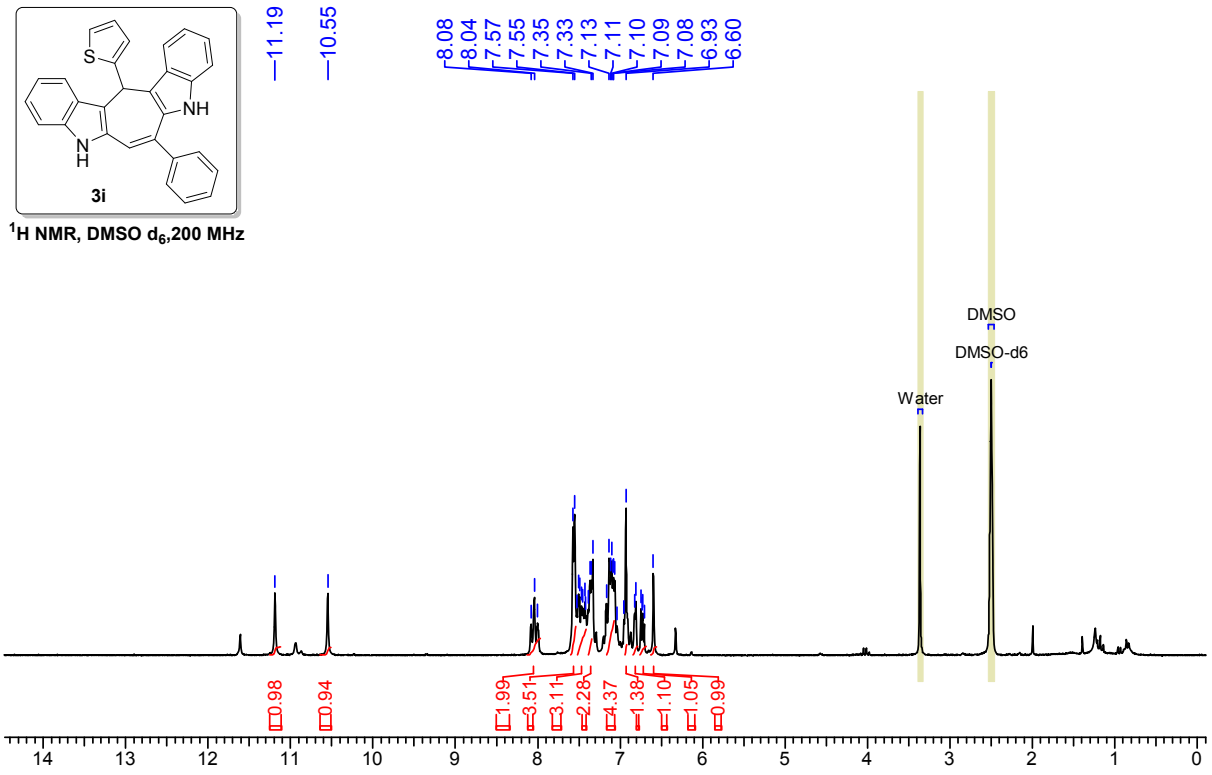
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 125 MHz

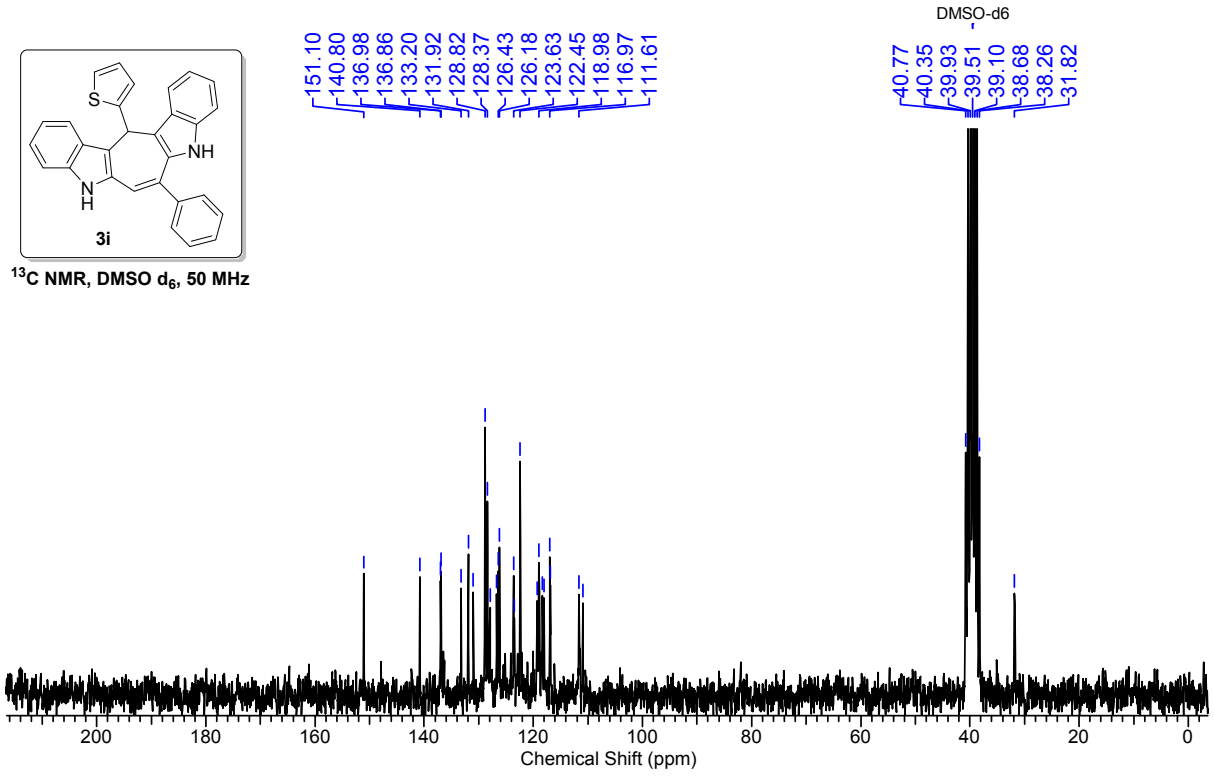


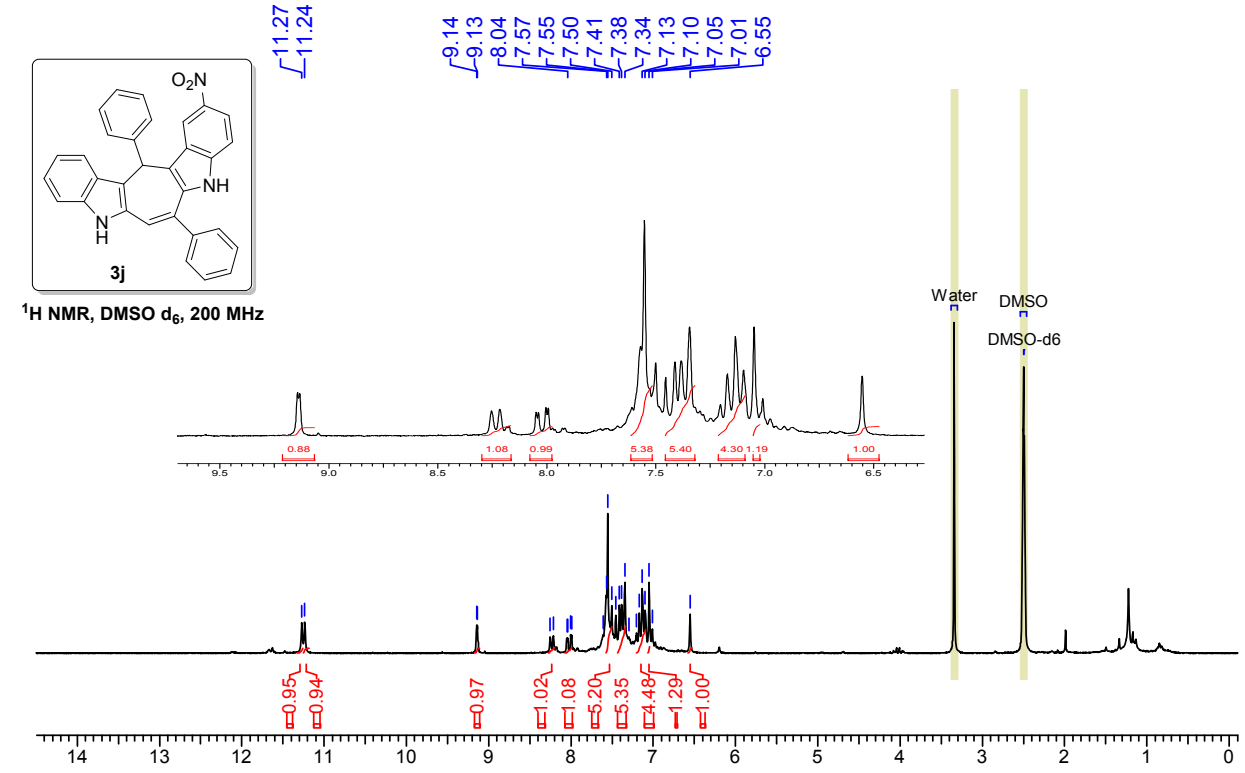
^{1}H NMR, DMSO d_6, 500 MHz

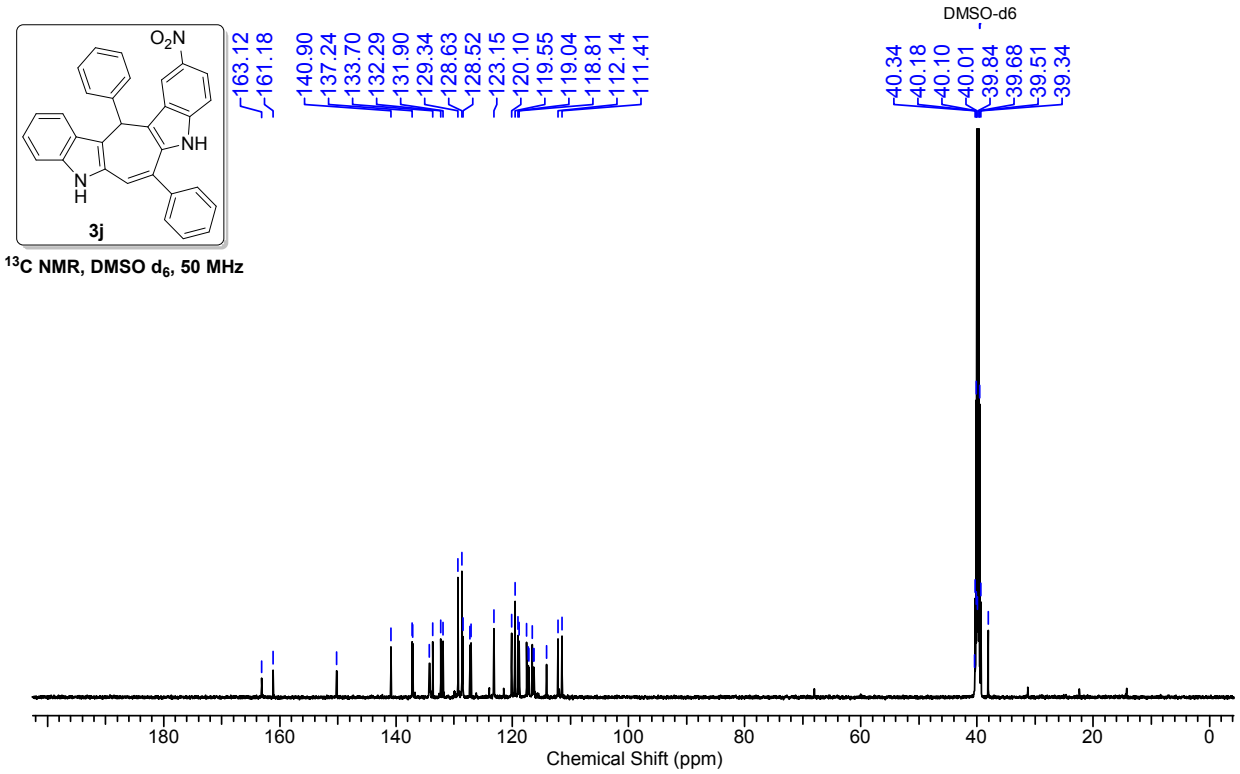


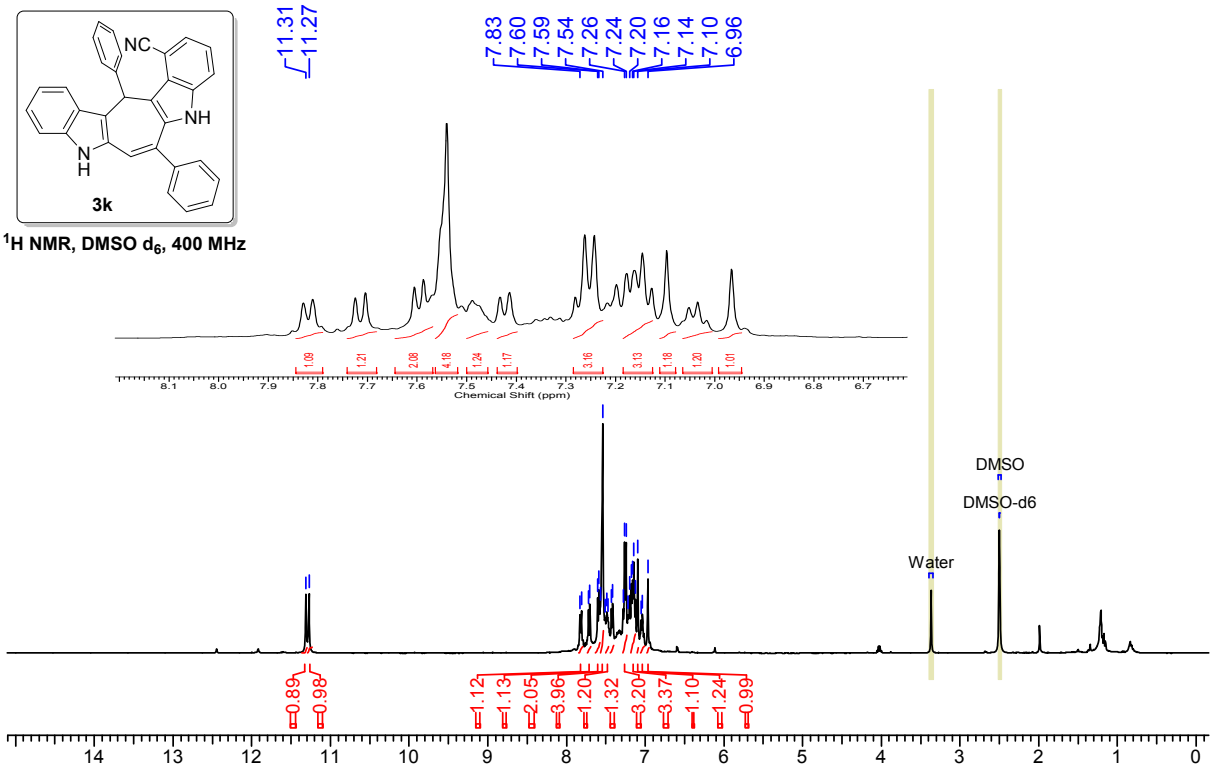
^{13}C NMR, DMSO d_6, 125 MHz


3i
^{1}H NMR, DMSO d$_6$,200 MHz
11.19
10.55
8.08
8.04
7.57
7.55
7.35
7.33
7.13
7.11
7.10
7.09
7.08
6.93
6.60
DMSO
DMSO-d6
Water
0.98
0.94
1.99
3.51
3.11
2.28
4.37
1.38
1.10
1.05
0.99

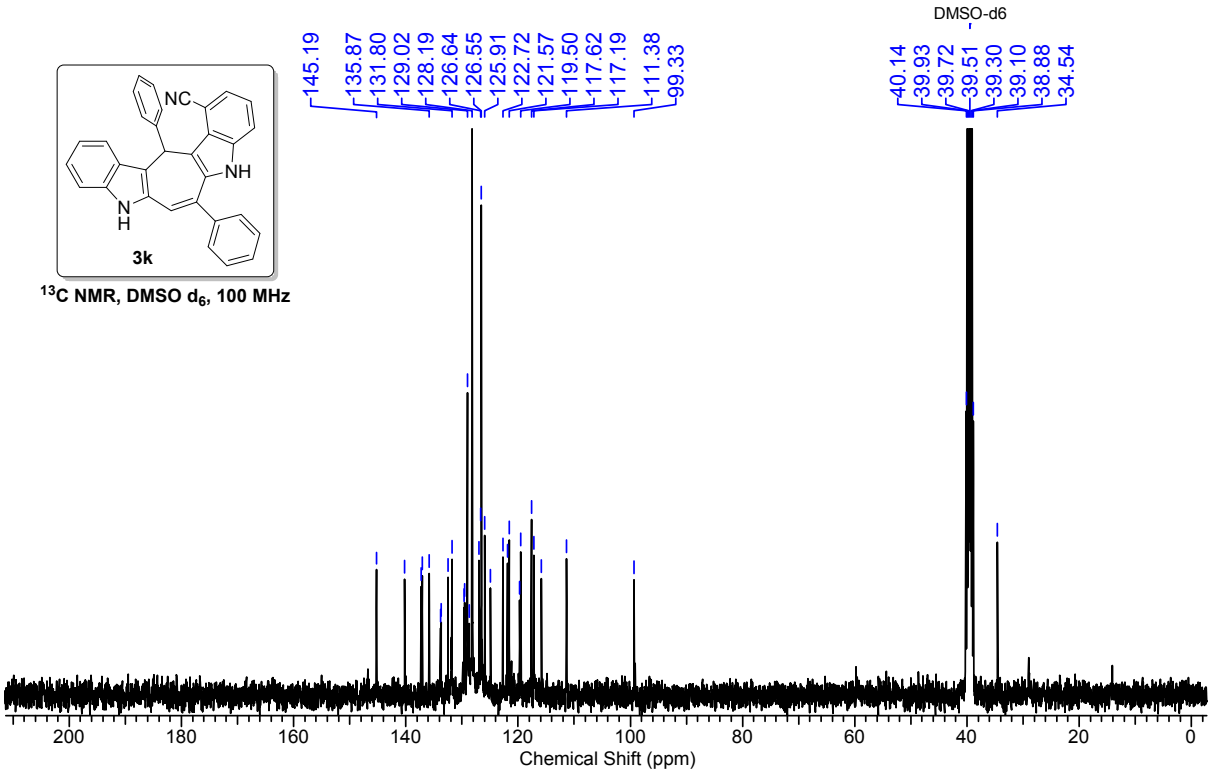

3i
^{13}C NMR, DMSO d$_6$, 50 MHz
151.10
140.80
136.98
136.86
133.20
131.92
128.82
128.37
126.43
126.18
123.63
122.45
118.98
116.97
111.61
DMSO-d6
40.77
40.35
39.93
39.51
39.10
38.68
38.26
31.82
Chemical Shift (ppm)


11.27
11.24
9.14
9.13
8.04
7.57
7.55
7.50
7.41
7.38
7.34
7.13
7.10
7.05
7.01
6.55
O2N
NH
N
H
3j
1H NMR, DMSO d6, 200 MHz
Water
DMSO
DMSO-d6
0.88
1.08
0.99
5.38
5.40
4.30
1.19
1.00
0.95
0.94
0.97
1.02
1.08
5.20
5.35
4.48
1.29
1.00

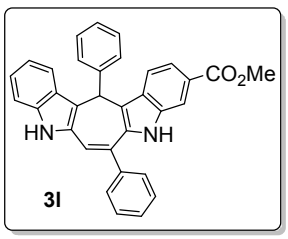

O2N
NH
N
H
3j
13C NMR, DMSO d6, 50 MHz
163.12
161.18
140.90
137.24
133.70
132.29
131.90
129.34
128.63
128.52
123.15
120.10
119.55
119.04
118.81
112.14
111.41
DMSO-d6
40.34
40.18
40.10
40.01
39.84
39.68
39.51
39.34
Chemical Shift (ppm)



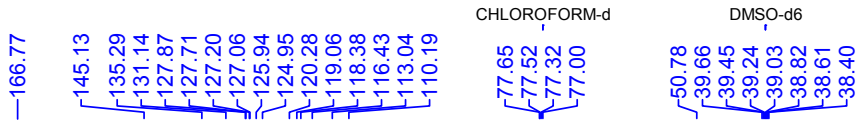
^{1}H NMR, DMSO d_6, 400 MHz

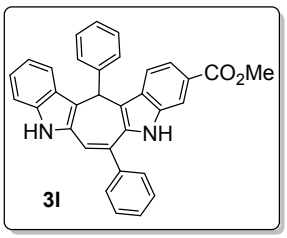


^{13}C NMR, DMSO d_6, 100 MHz

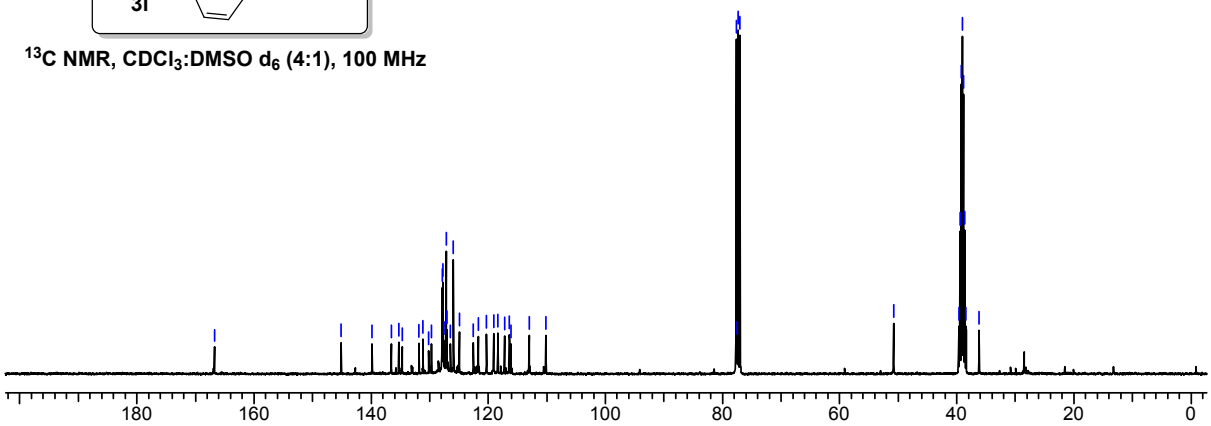


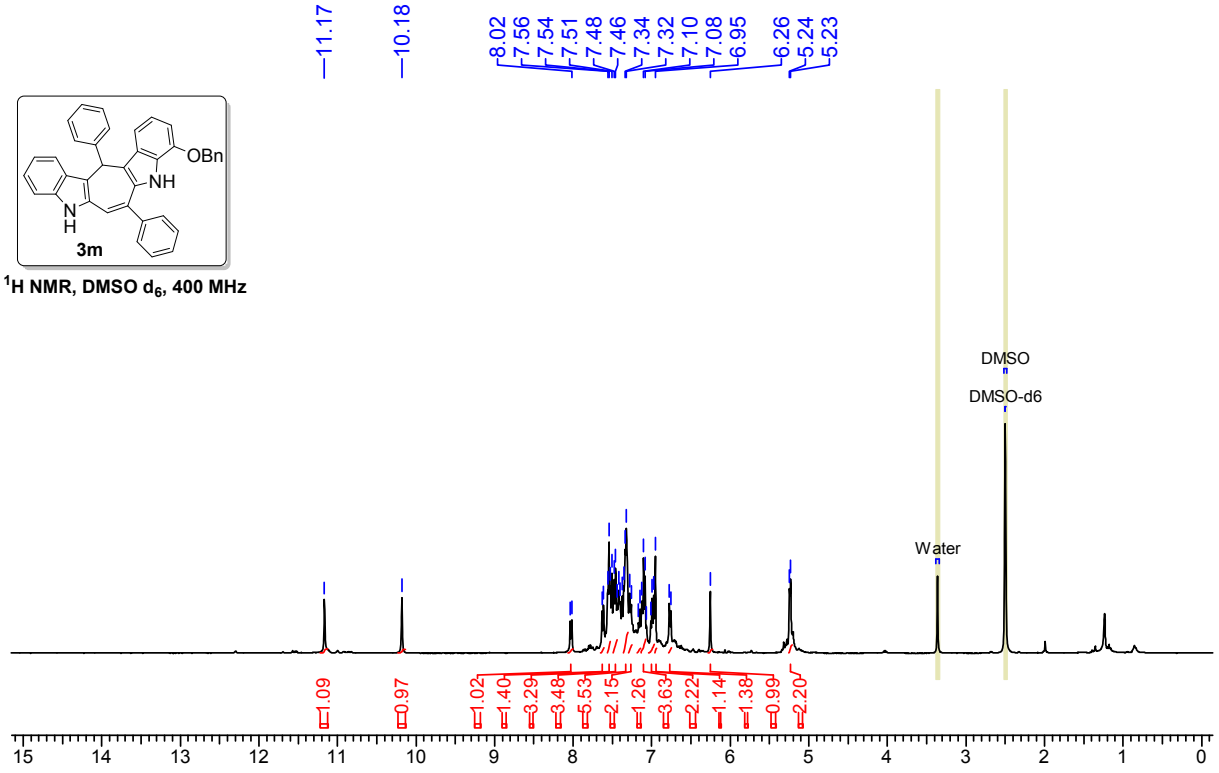
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 400 MHz



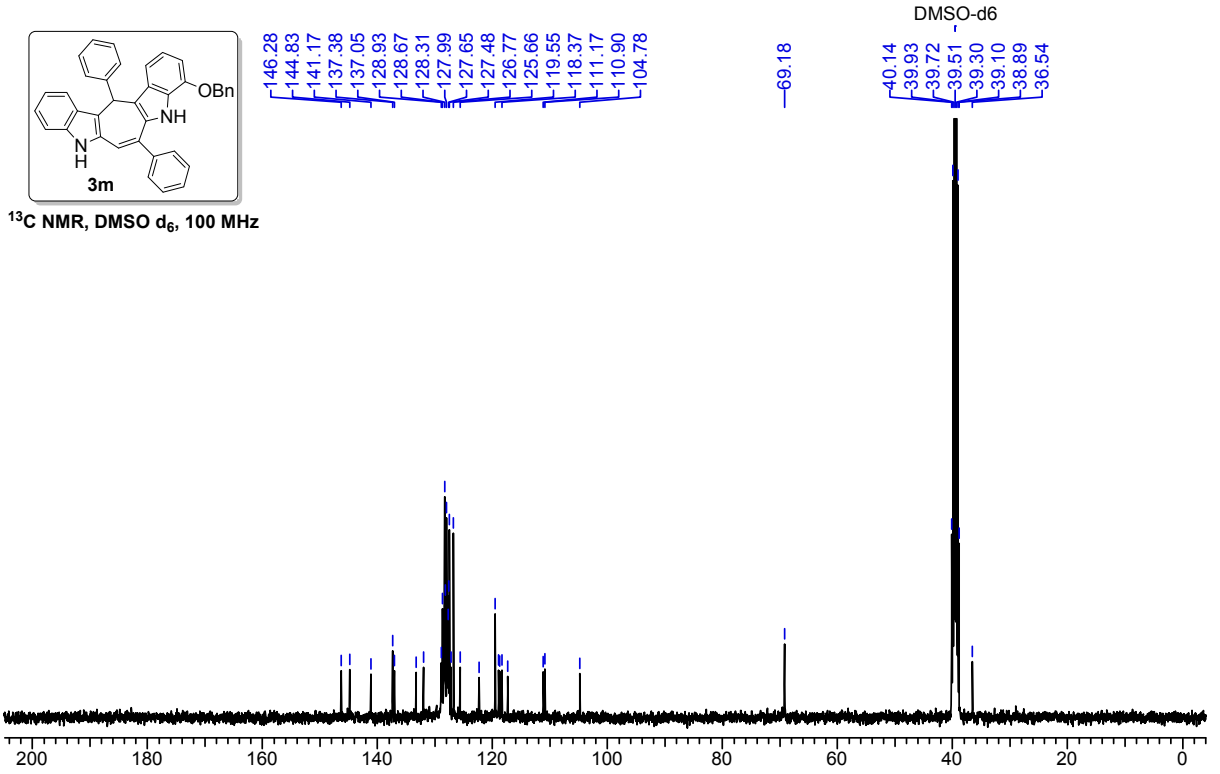


^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 100 MHz

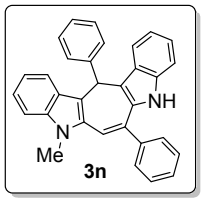




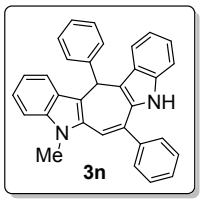
^{1}H NMR, DMSO d_6, 400 MHz



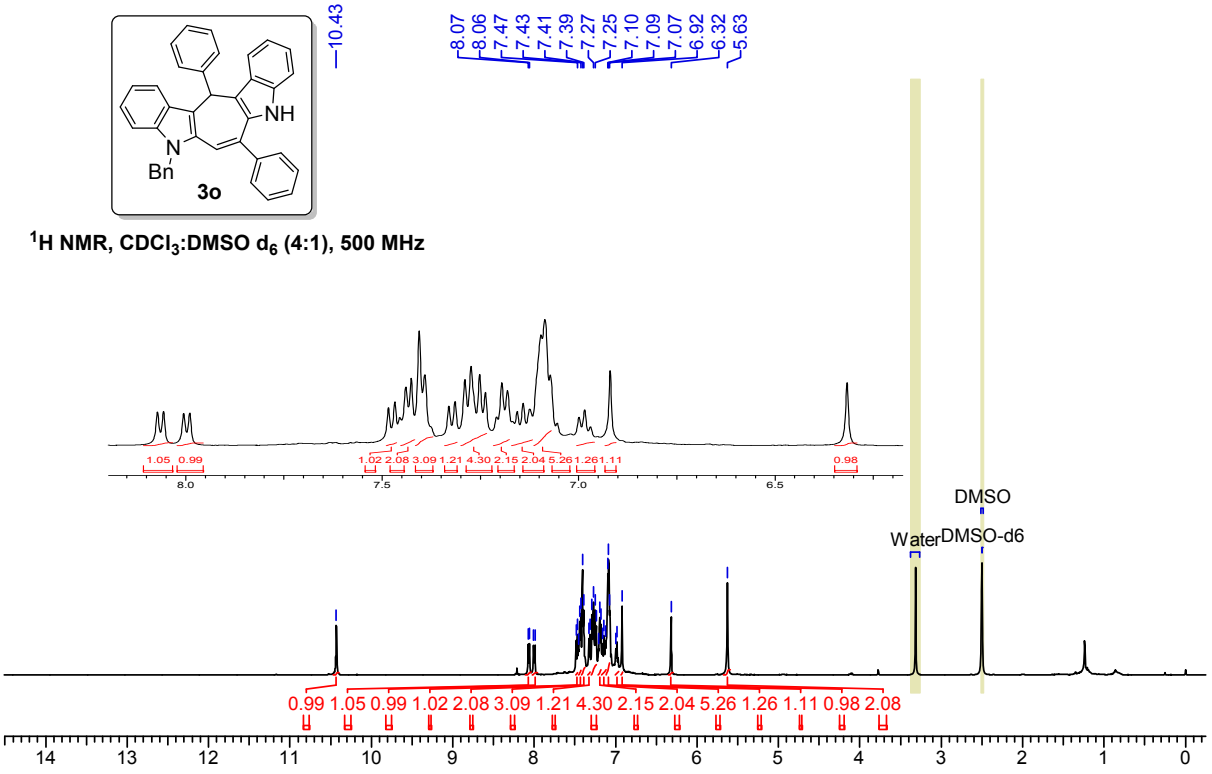
^{13}C NMR, DMSO d_6, 100 MHz



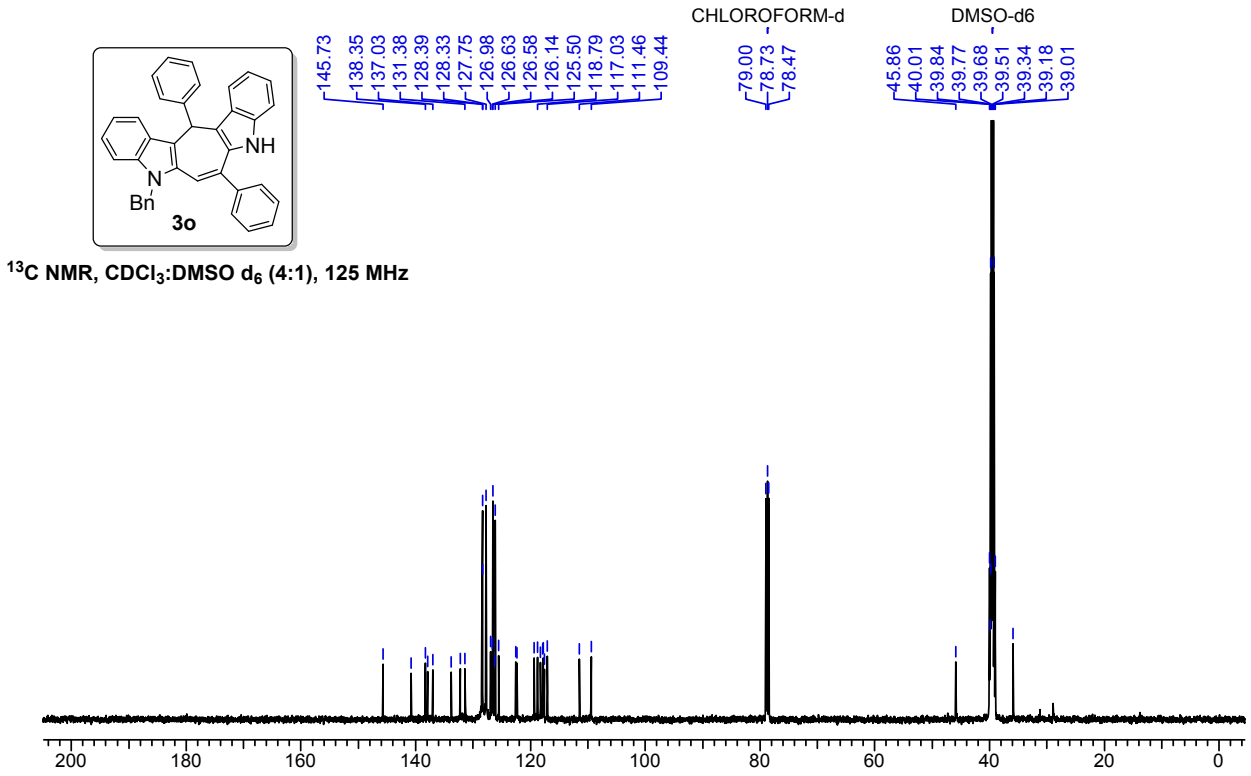
^{1}H NMR, $CDCl_3$, 500 MHz



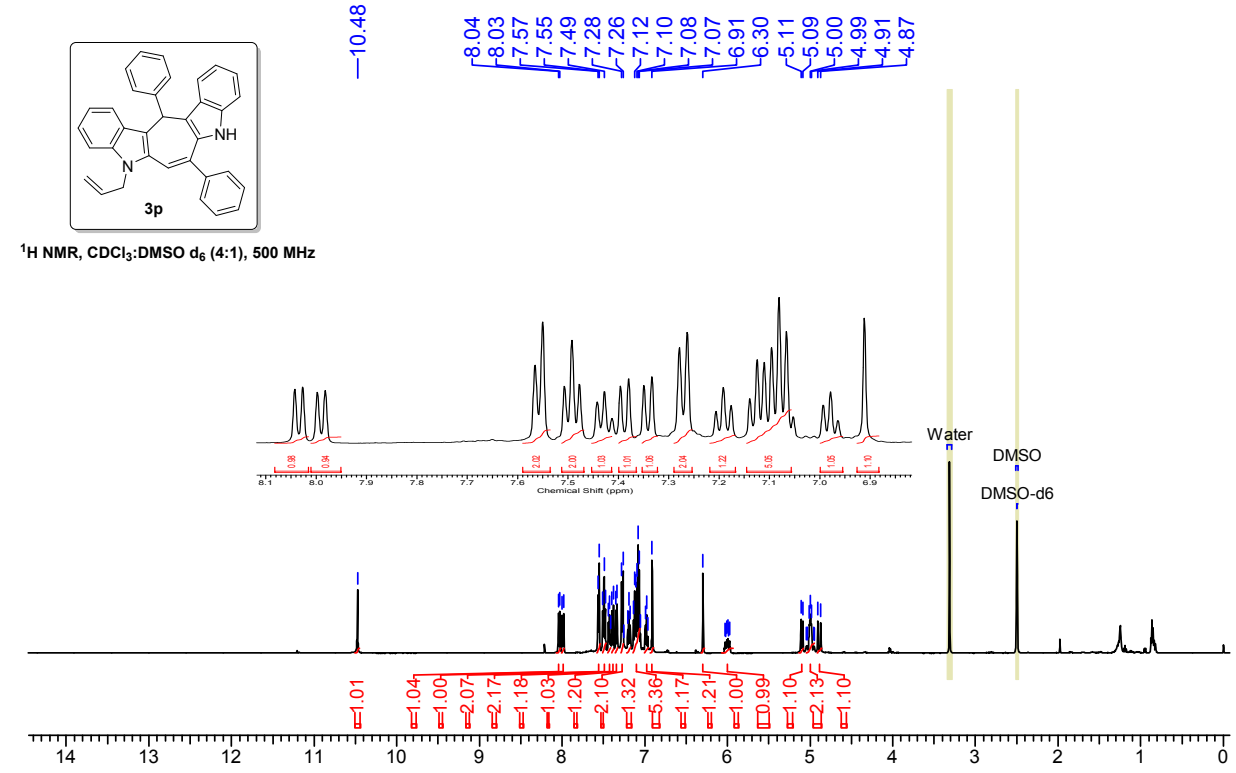
^{13}C NMR, $CDCl_3$, 125 MHz

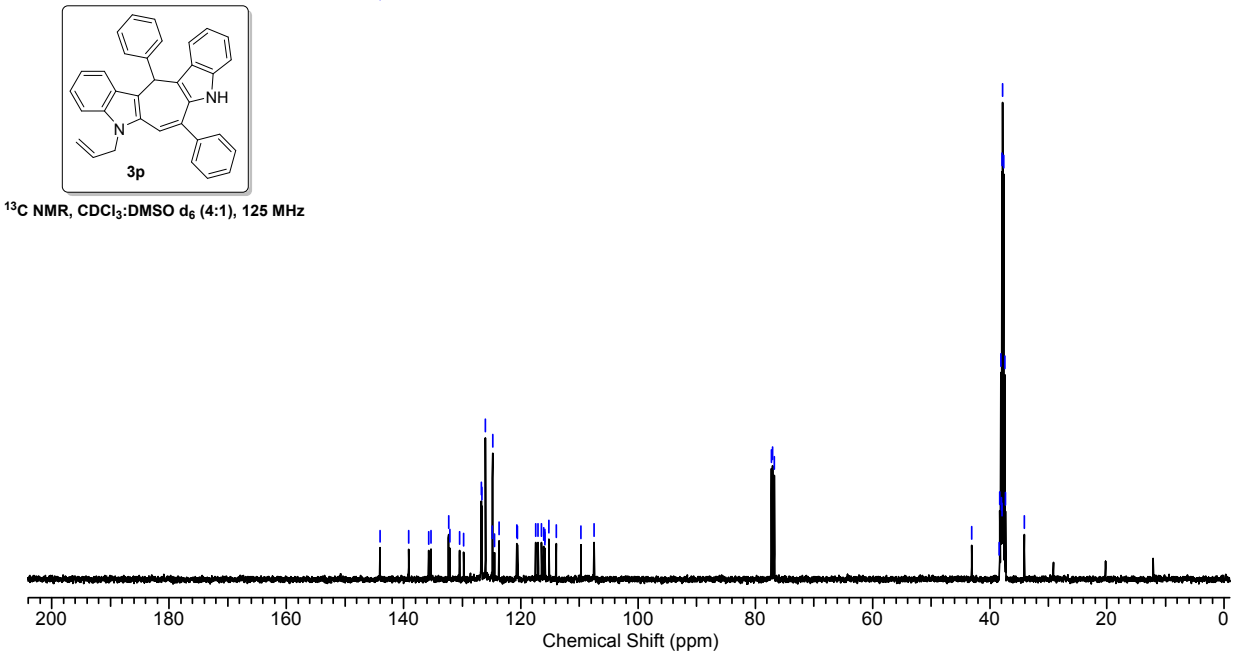


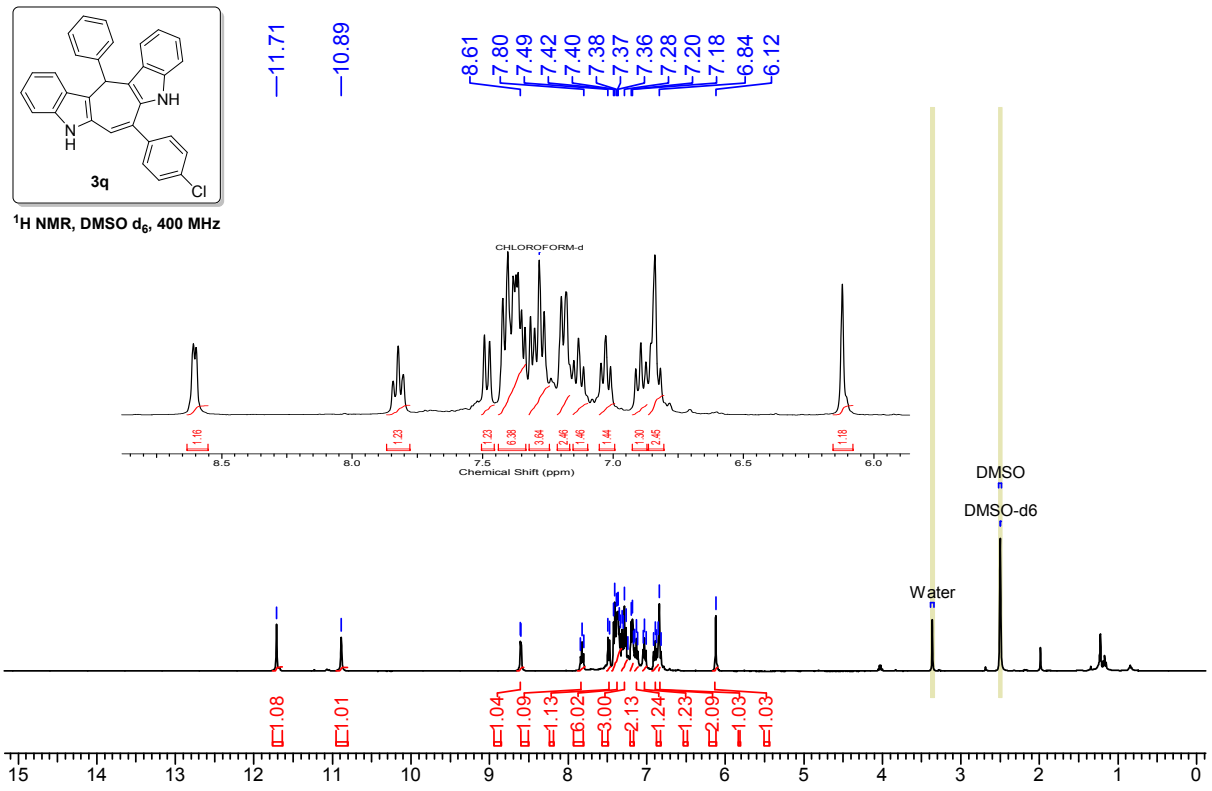
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 500 MHz

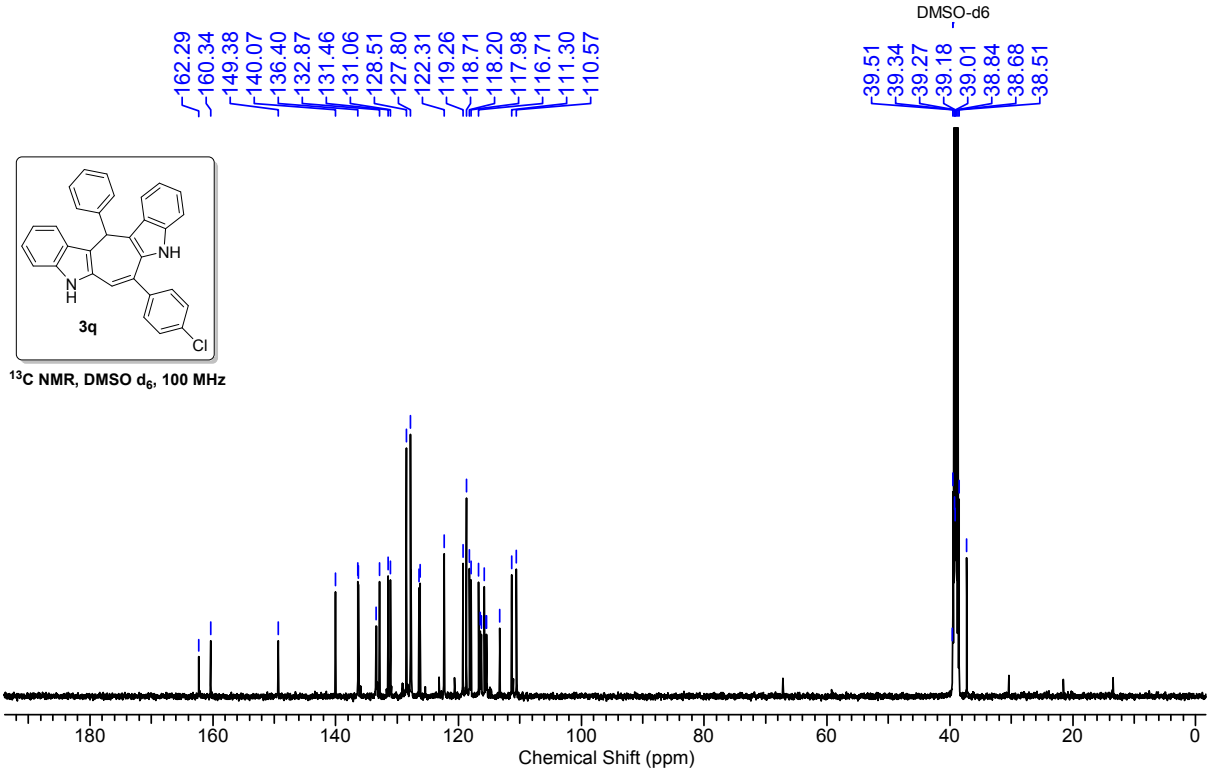


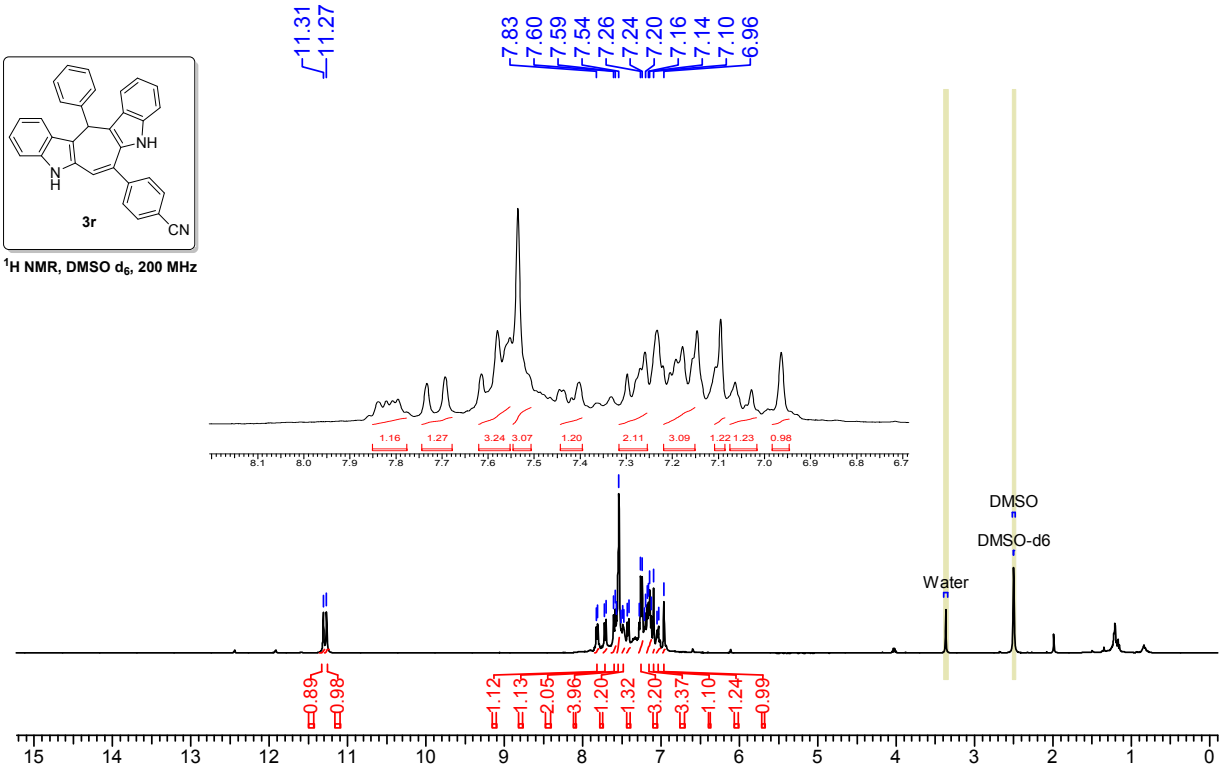
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 125 MHz

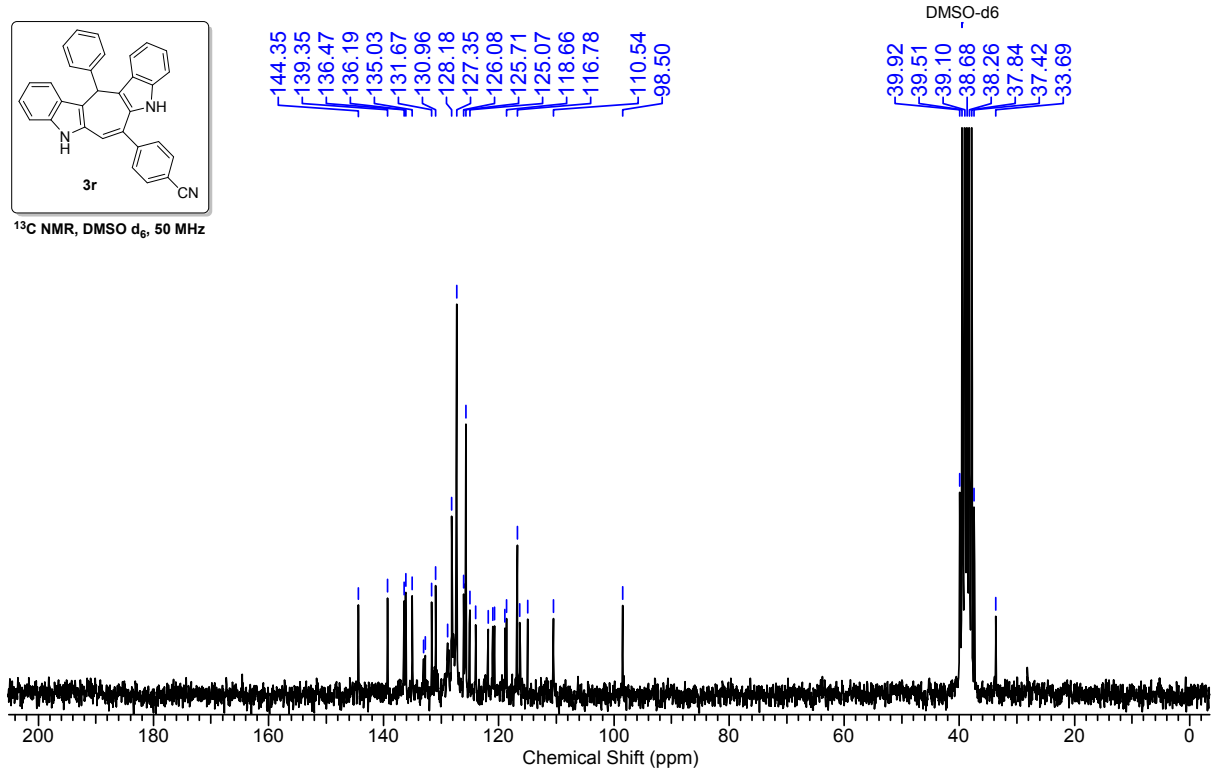

3p
^{1}H NMR, CDCl$_3$:DMSO d$_6$ (4:1), 500 MHz
10.48
8.04
8.03
7.57
7.55
7.49
7.28
7.26
7.12
7.10
7.08
7.07
6.91
6.30
5.11
5.09
5.00
4.99
4.91
4.87
Water
DMSO
DMSO-d6
Chemical Shift (ppm)

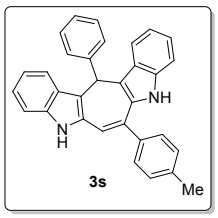

3p
^{13}C NMR, CDCl$_3$:DMSO d$_6$ (4:1), 125 MHz
CHLOROFORM-d
DMSO-d6
144.01
132.34
132.11
126.77
126.66
126.00
124.83
123.74
120.68
117.49
117.04
116.45
115.17
109.75
107.55
77.27
77.00
76.74
43.09
38.28
38.11
38.04
37.95
37.78
37.61
37.44
37.28
34.10
Chemical Shift (ppm)


3q
^{1}H NMR, DMSO d_6, 400 MHz
11.71
10.89
8.61
7.80
7.49
7.42
7.40
7.38
7.37
7.36
7.28
7.20
7.18
6.84
6.12
CHLOROFORM-d
Chemical Shift (ppm)
DMSO
DMSO-d6
Water
1.08
1.01
1.04
1.09
1.13
6.02
3.00
2.13
1.24
1.23
2.09
1.03
1.03

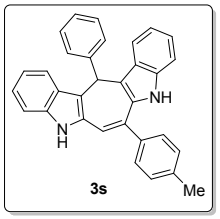

3q
^{13}C NMR, DMSO d_6, 100 MHz
162.29
160.34
149.38
140.07
136.40
132.87
131.46
131.06
128.51
127.80
122.31
119.26
118.71
118.20
117.98
116.71
111.30
110.57
DMSO-d6
39.51
39.34
39.27
39.18
39.01
38.84
38.68
38.51
Chemical Shift (ppm)


11.31
11.27
7.83
7.60
7.59
7.54
7.26
7.24
7.20
7.16
7.14
7.10
6.96
NH
N
H
3r
CN
1H NMR, DMSO d6, 200 MHz
1.16
1.27
3.24
3.07
1.20
2.11
3.09
1.22
1.23
0.98
DMSO
DMSO-d6
Water
0.89
0.98
1.12
1.13
2.05
3.96
1.20
1.32
3.20
3.37
1.10
1.24
0.99
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

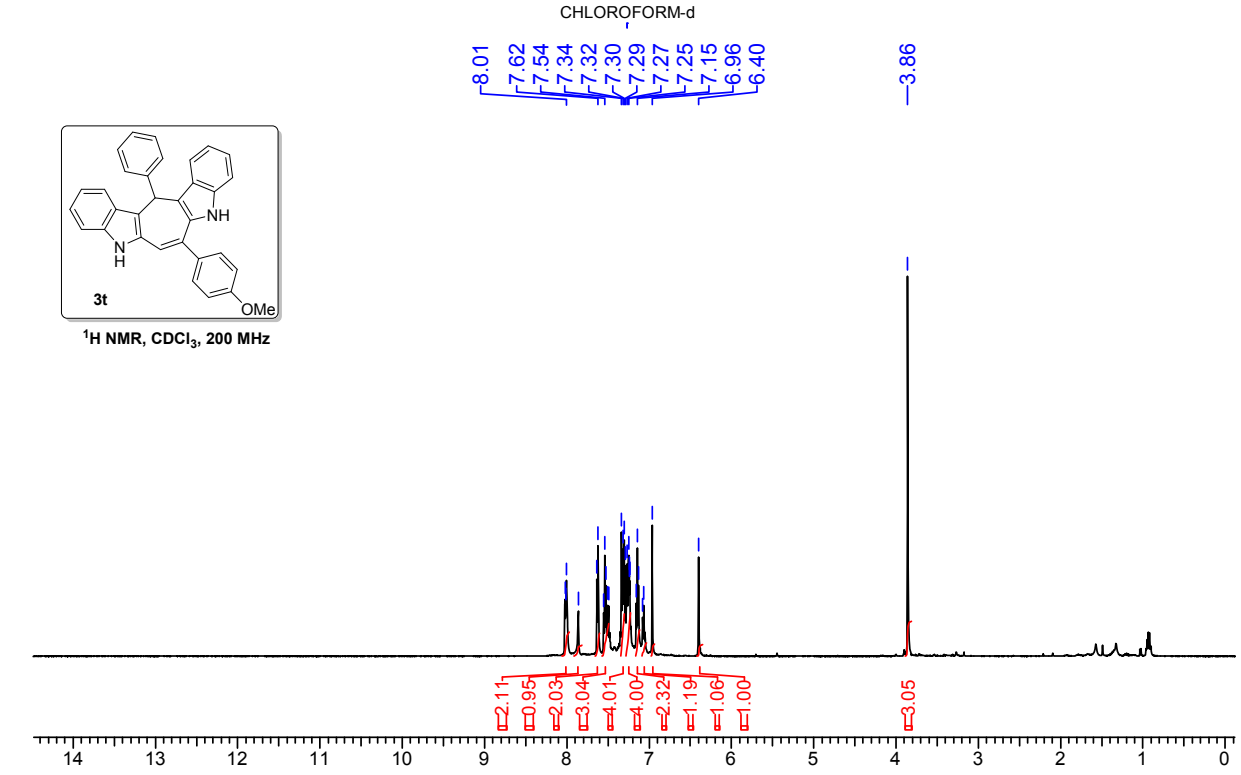

144.35
139.35
136.47
136.19
135.03
131.67
130.96
128.18
127.35
126.08
125.71
125.07
118.66
116.78
110.54
98.50
DMSO-d6
39.92
39.51
39.10
38.68
38.26
37.84
37.42
33.69
NH
N
H
3r
CN
13C NMR, DMSO d6, 50 MHz
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



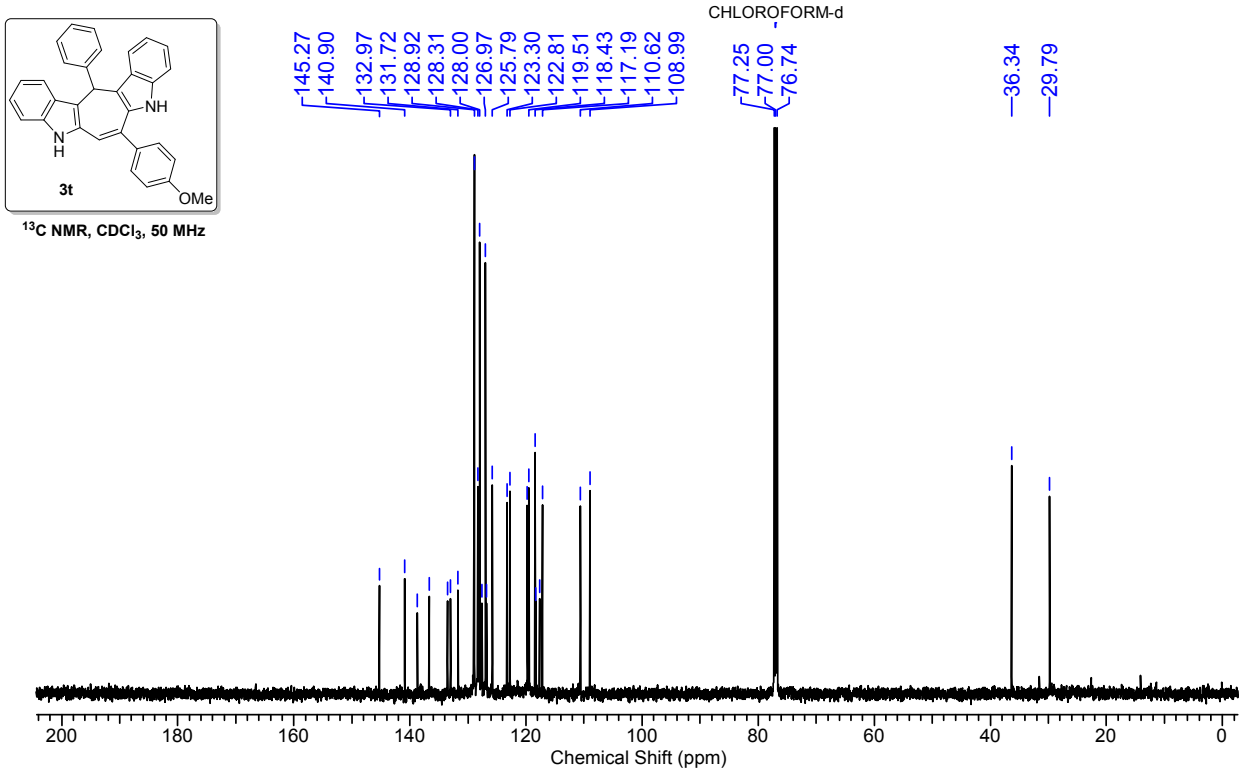
^{1}H NMR, $CDCl_3$, 500 MHz



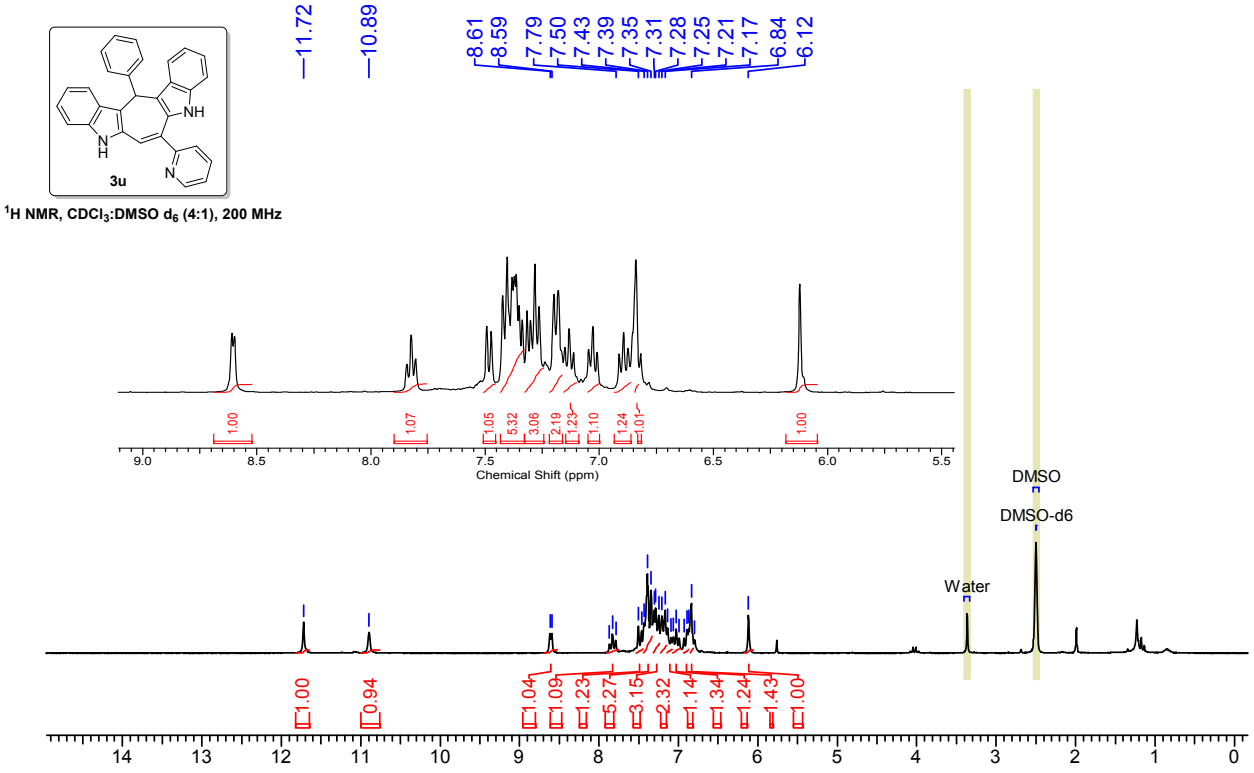
^{13}C NMR, $CDCl_3$, 125 MHz



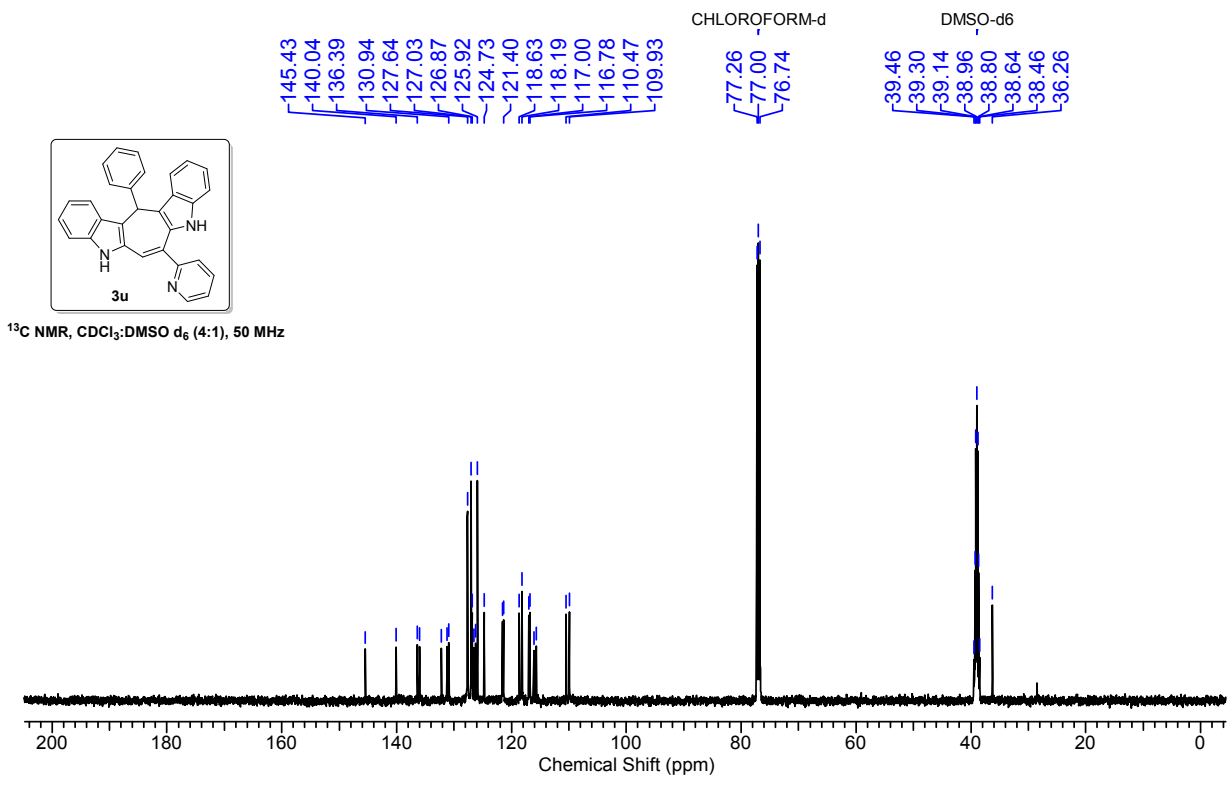
^{1}H NMR, $CDCl_3$, 200 MHz



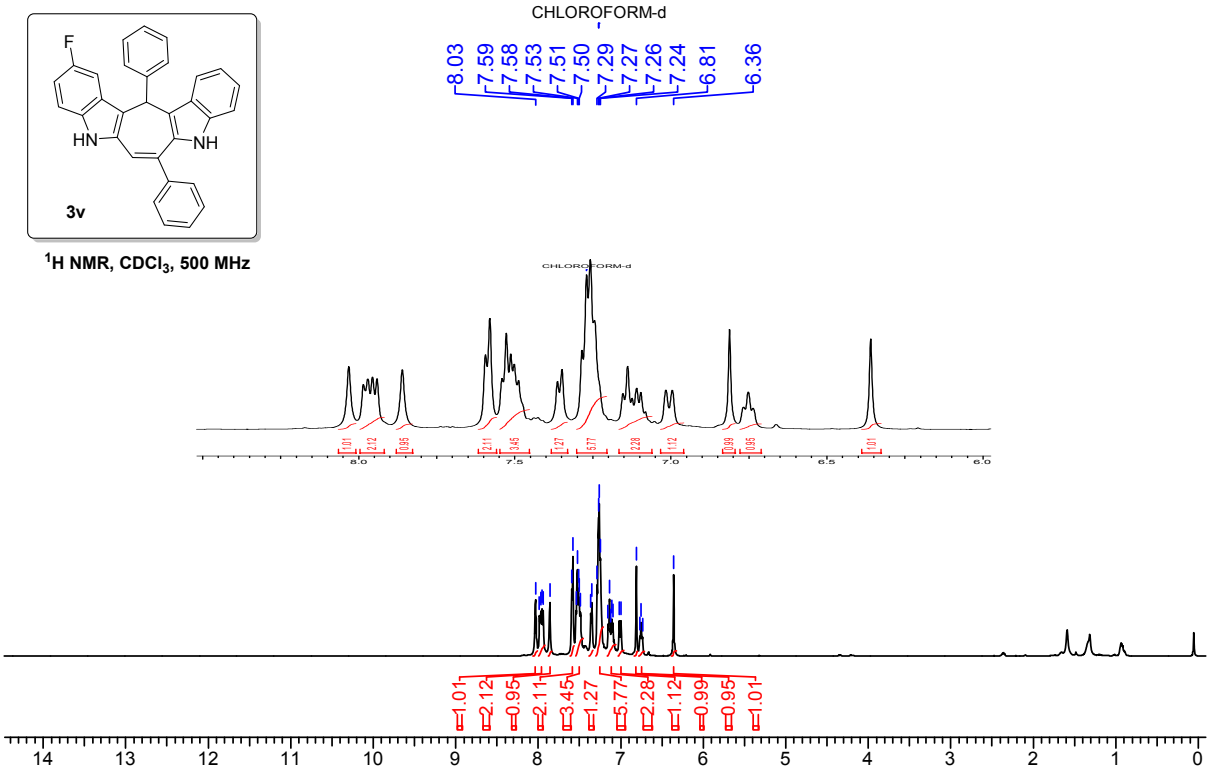
^{13}C NMR, $CDCl_3$, 50 MHz



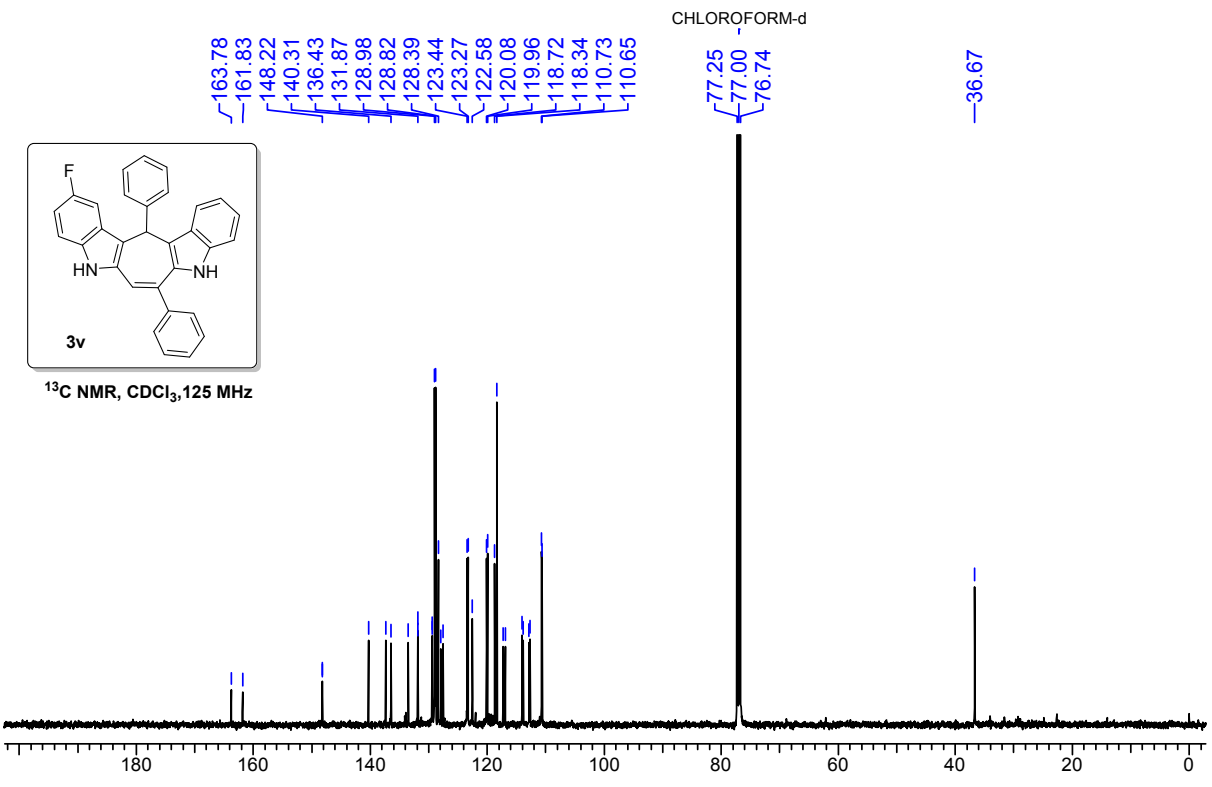
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



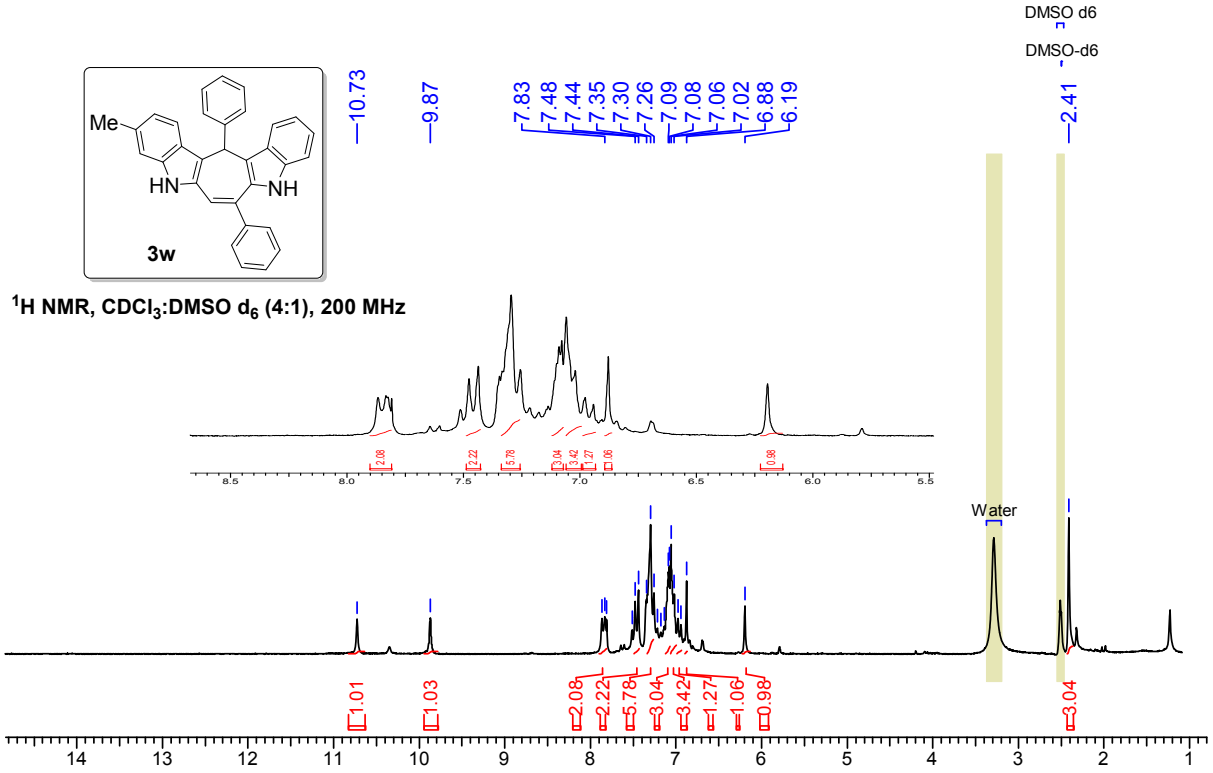
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



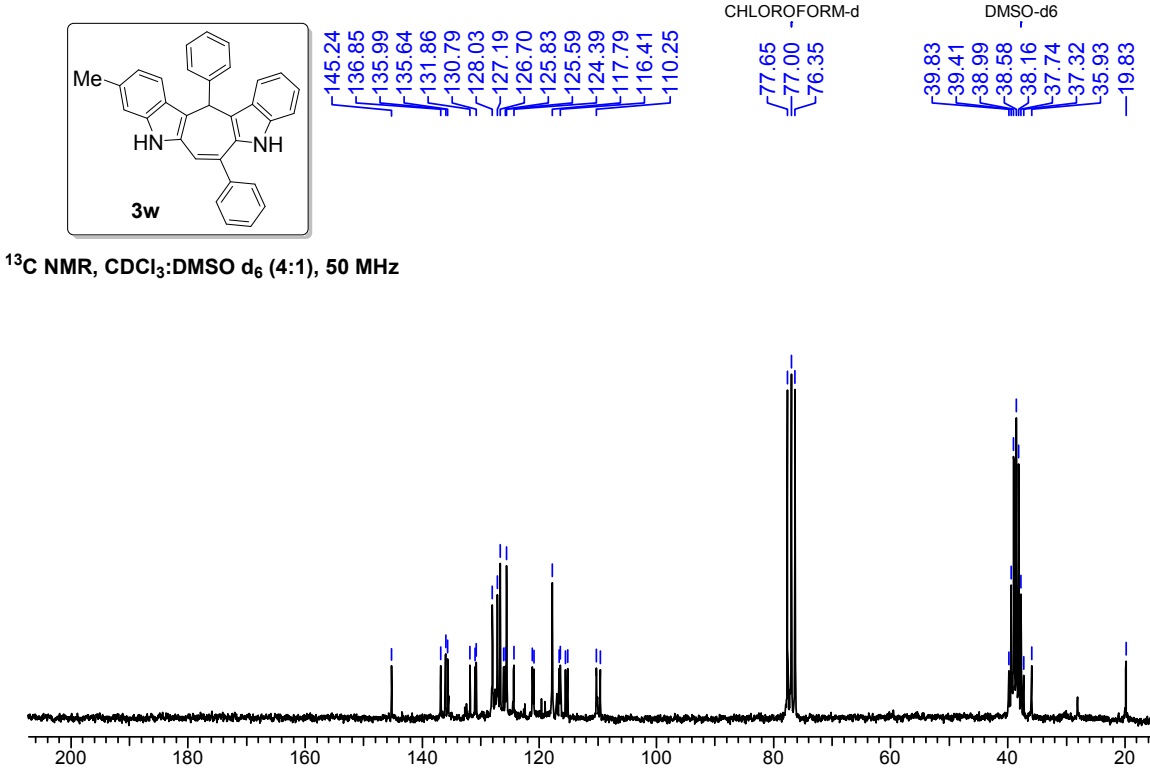
^{1}H NMR, $CDCl_3$, 500 MHz



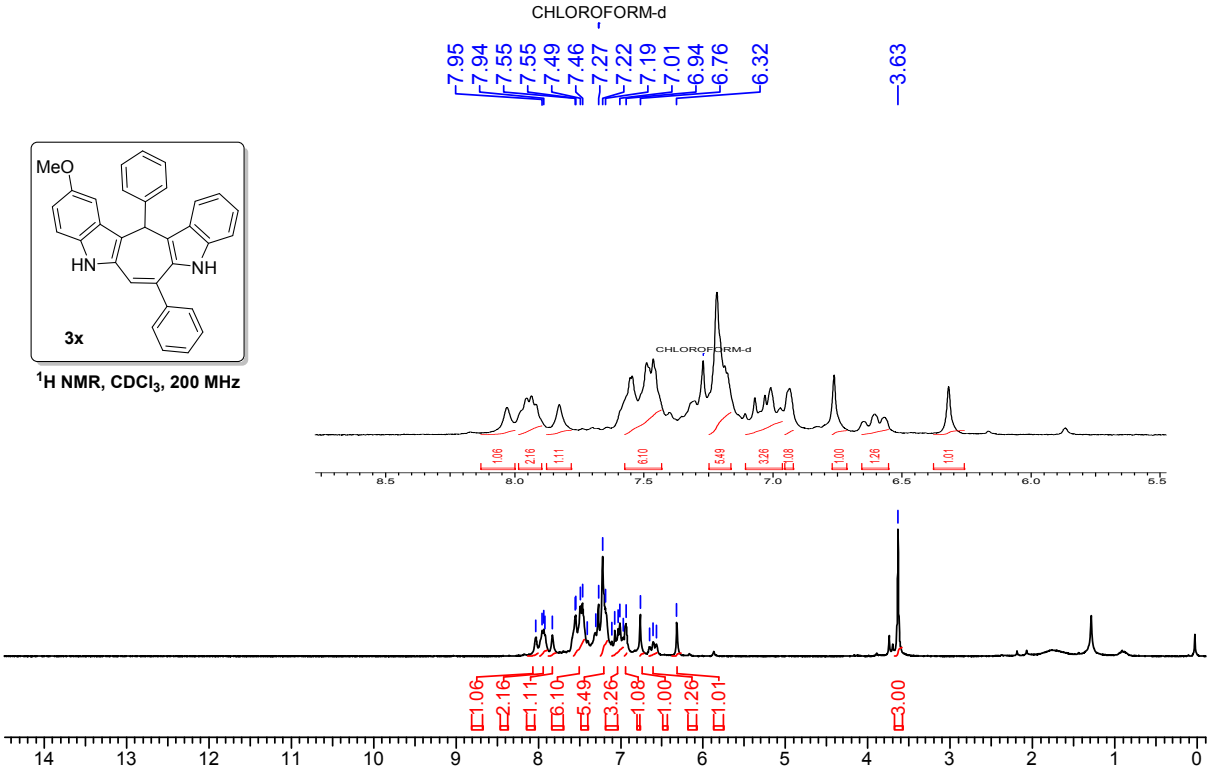
^{13}C NMR, $CDCl_3$,125 MHz



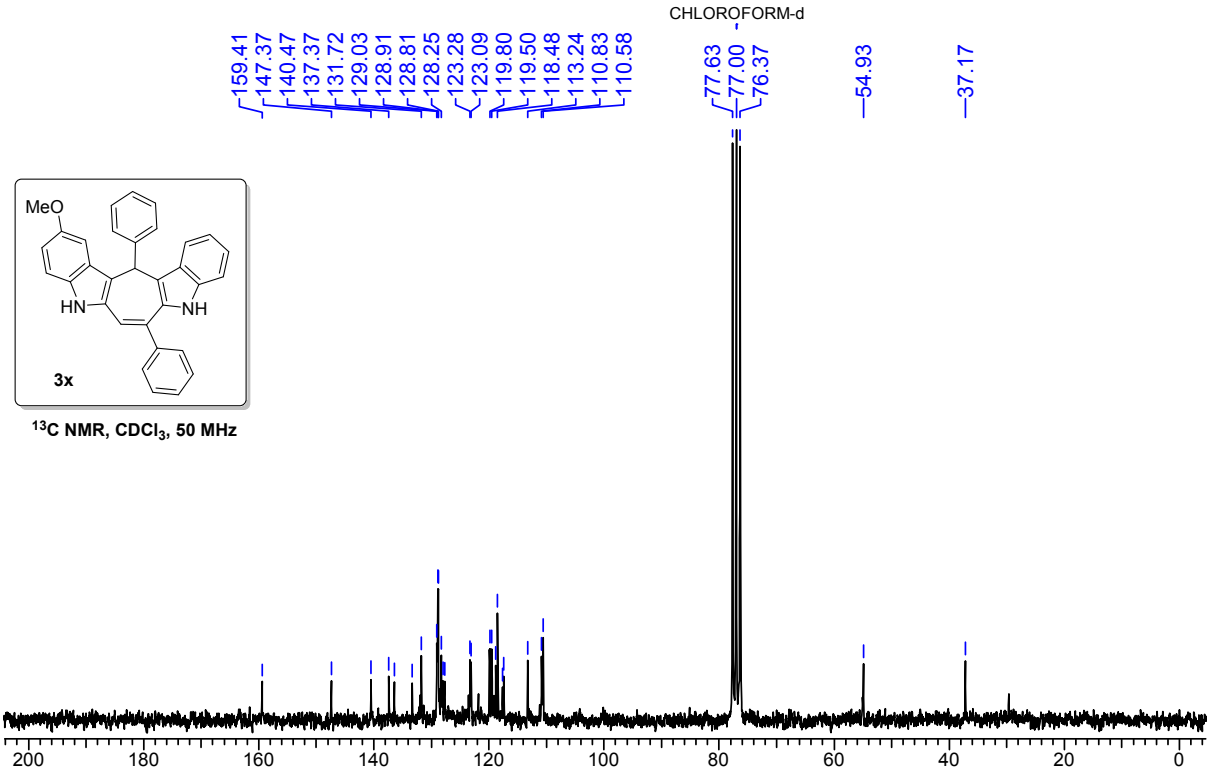
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



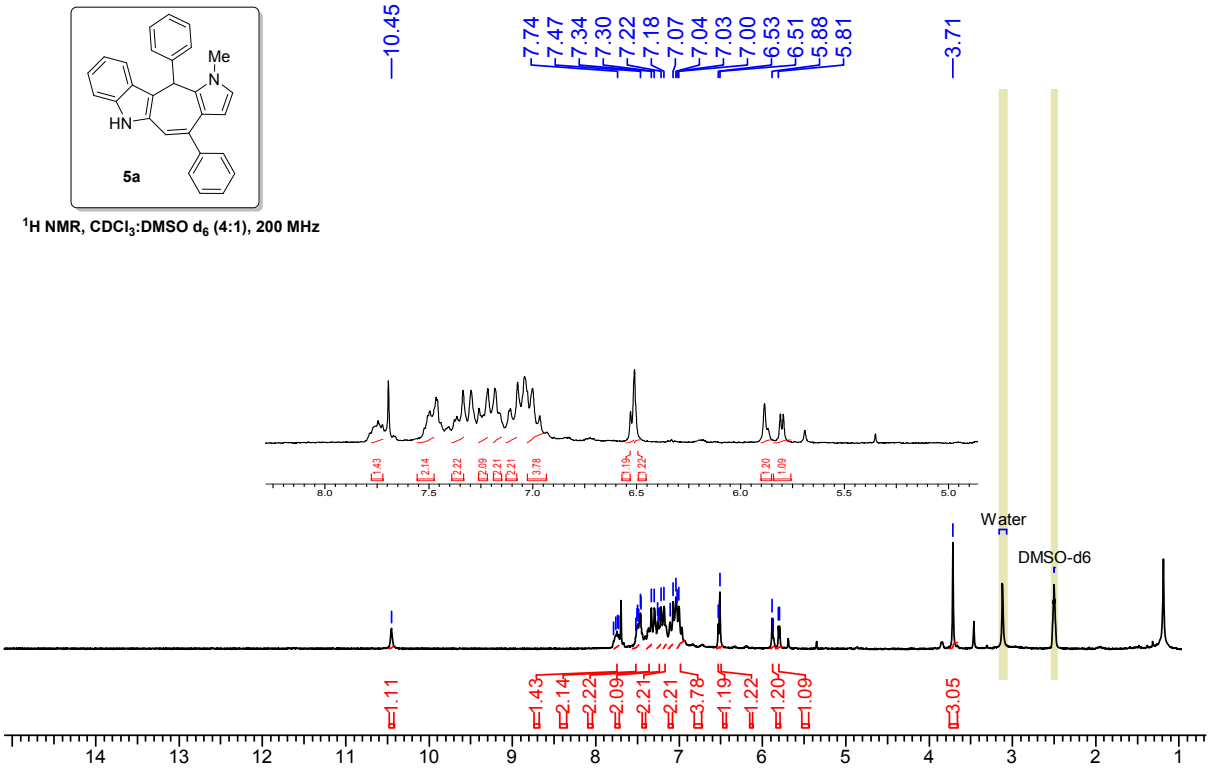
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



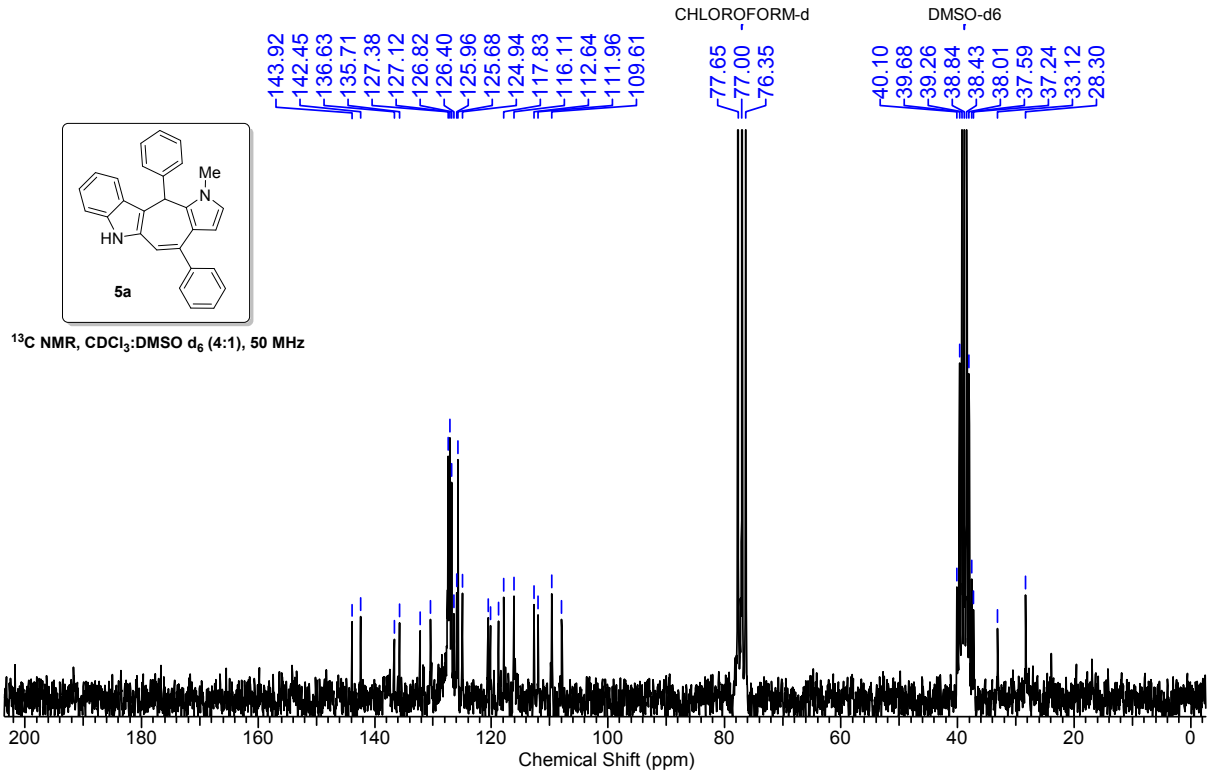
^{1}H NMR, $CDCl_3$, 200 MHz



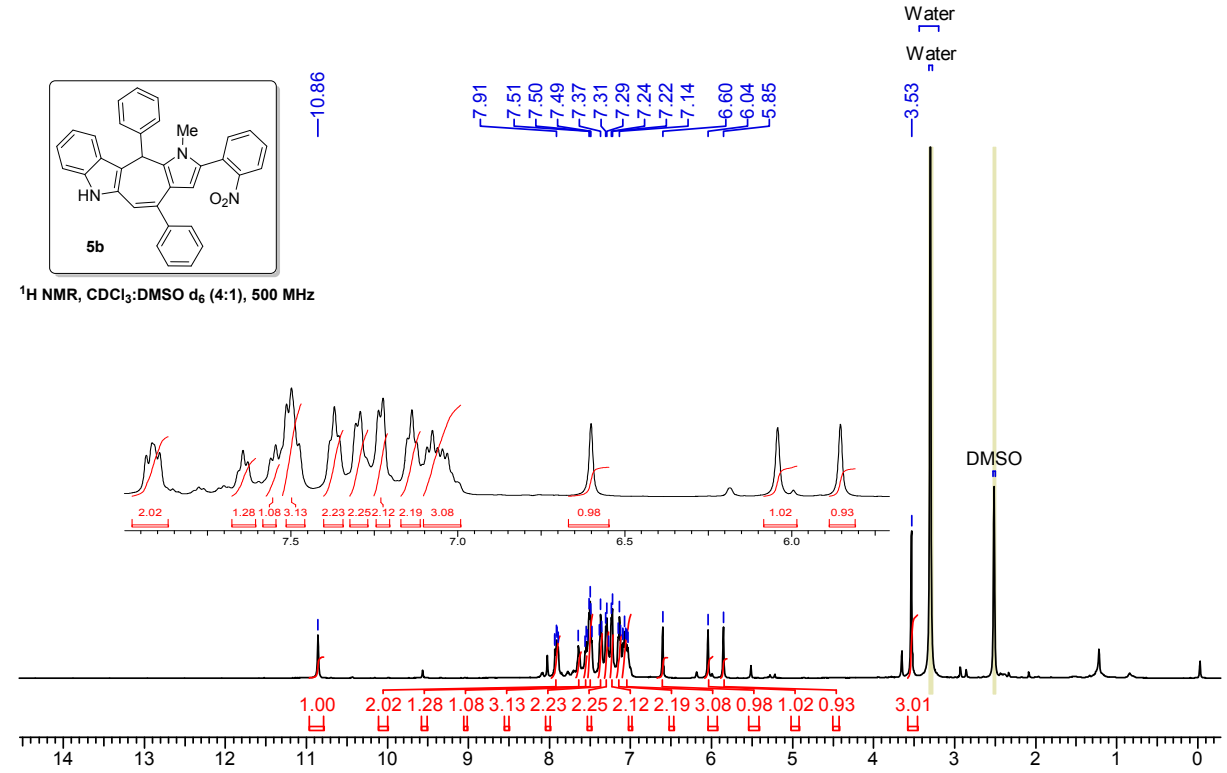
^{13}C NMR, $CDCl_3$, 50 MHz



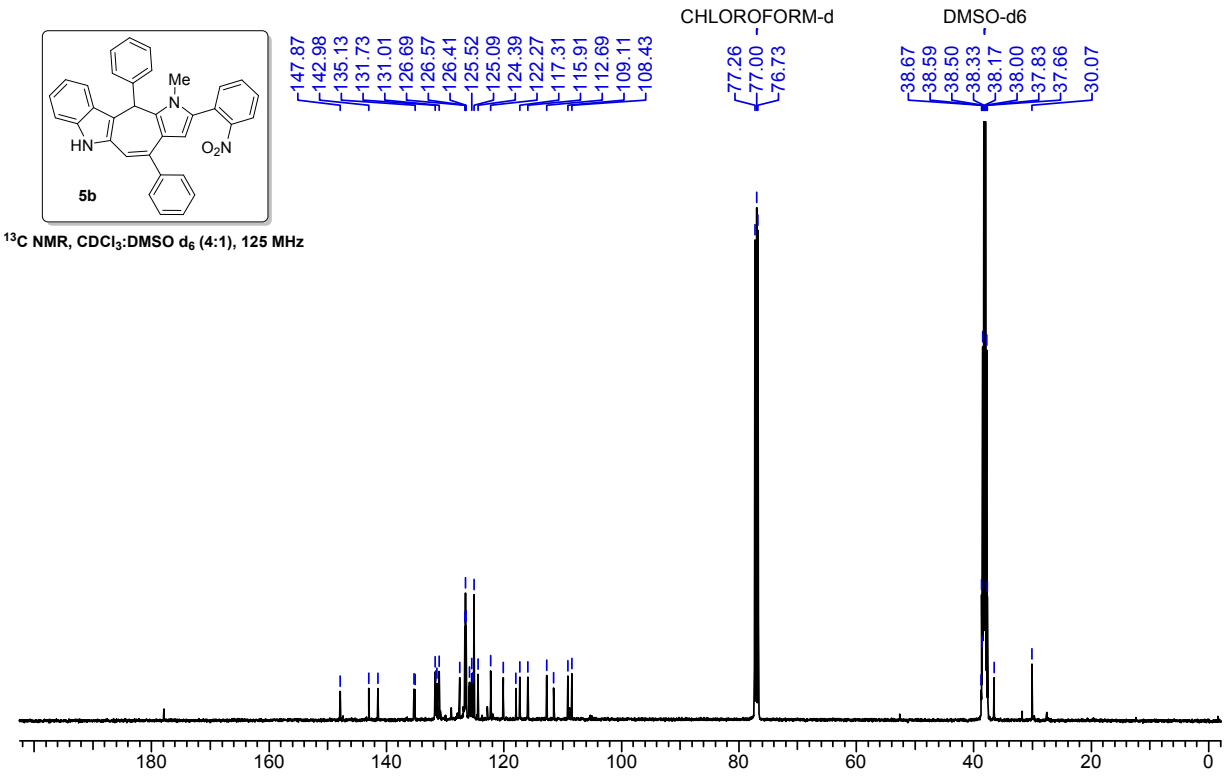
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 200 MHz



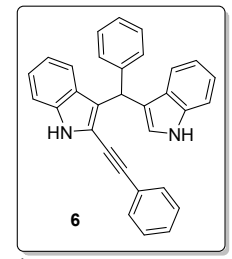
^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 50 MHz



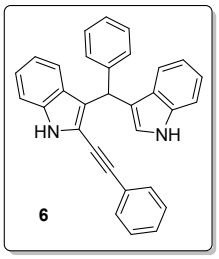
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 500 MHz



^{13}C NMR, $CDCl_3$:DMSO d_6 (4:1), 125 MHz

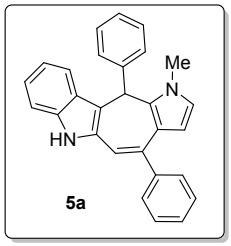


^{1}H NMR, $CDCl_3$, 200 MHz



^{13}C NMR, $CDCl_3$, 50 MHz

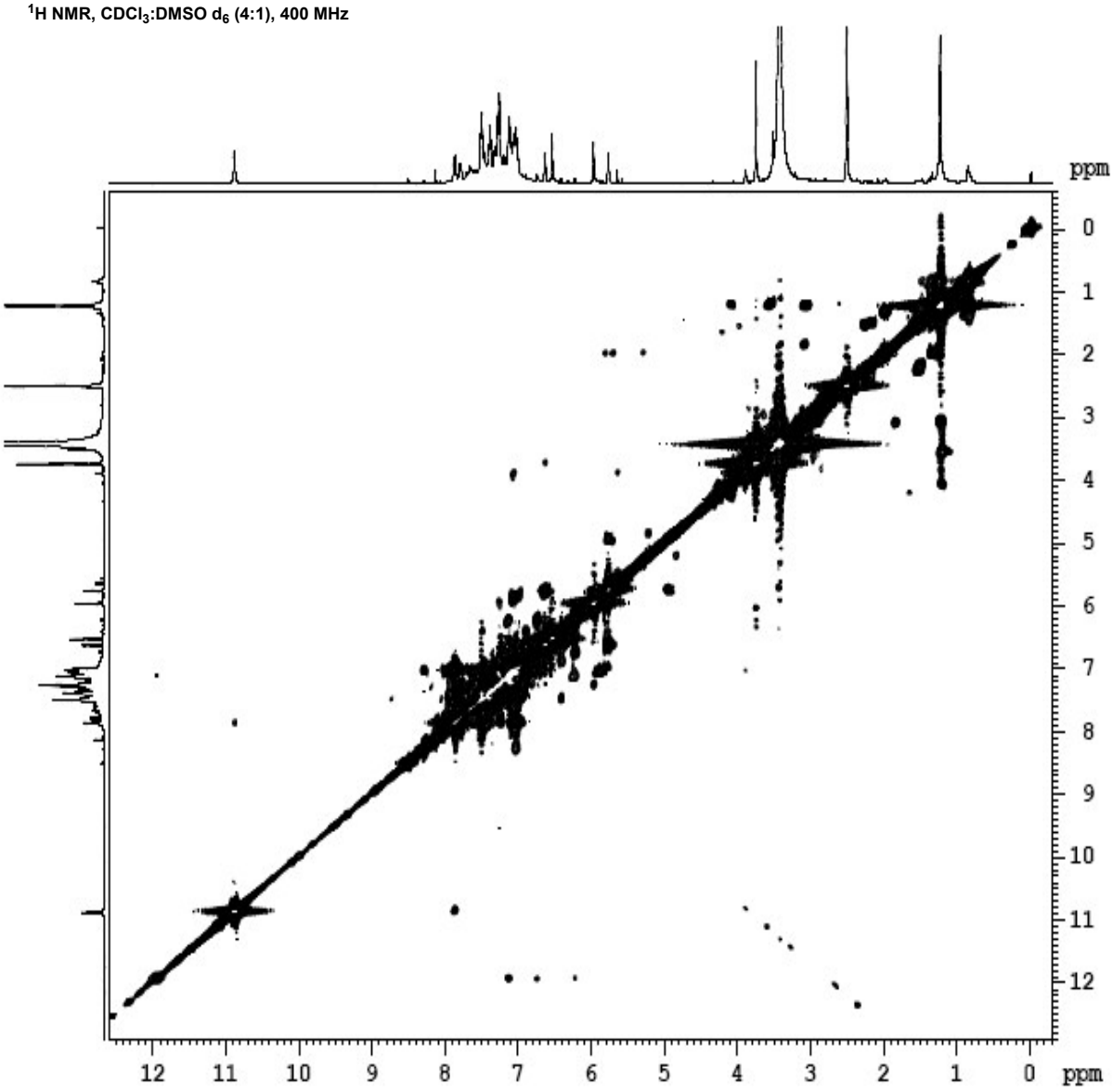
4. 2D NMR spectrum for 5a



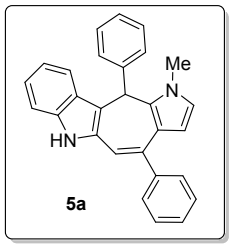
5a

^{1}H-^{1}H COSY spectrum for 5a

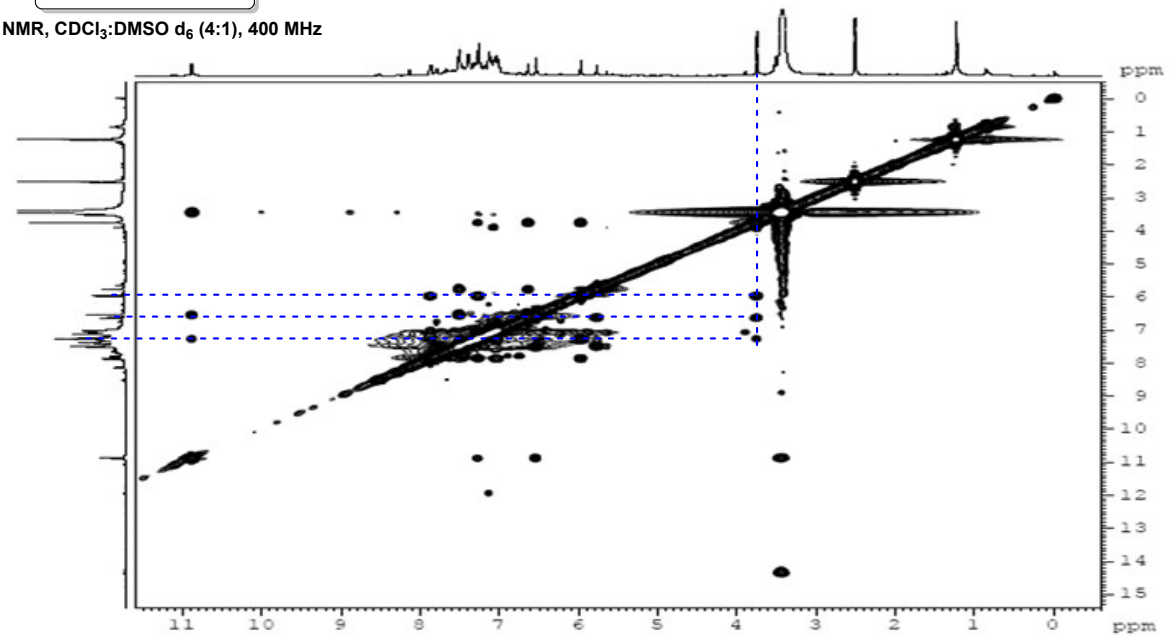
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 400 MHz



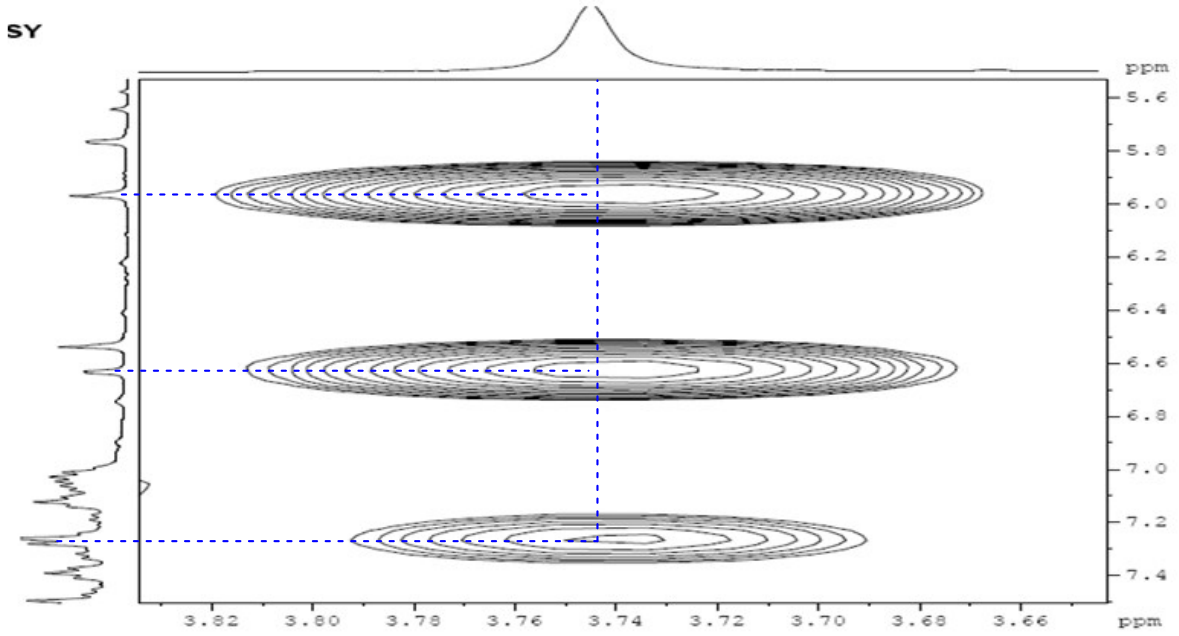
NOESY spectrum for 5a



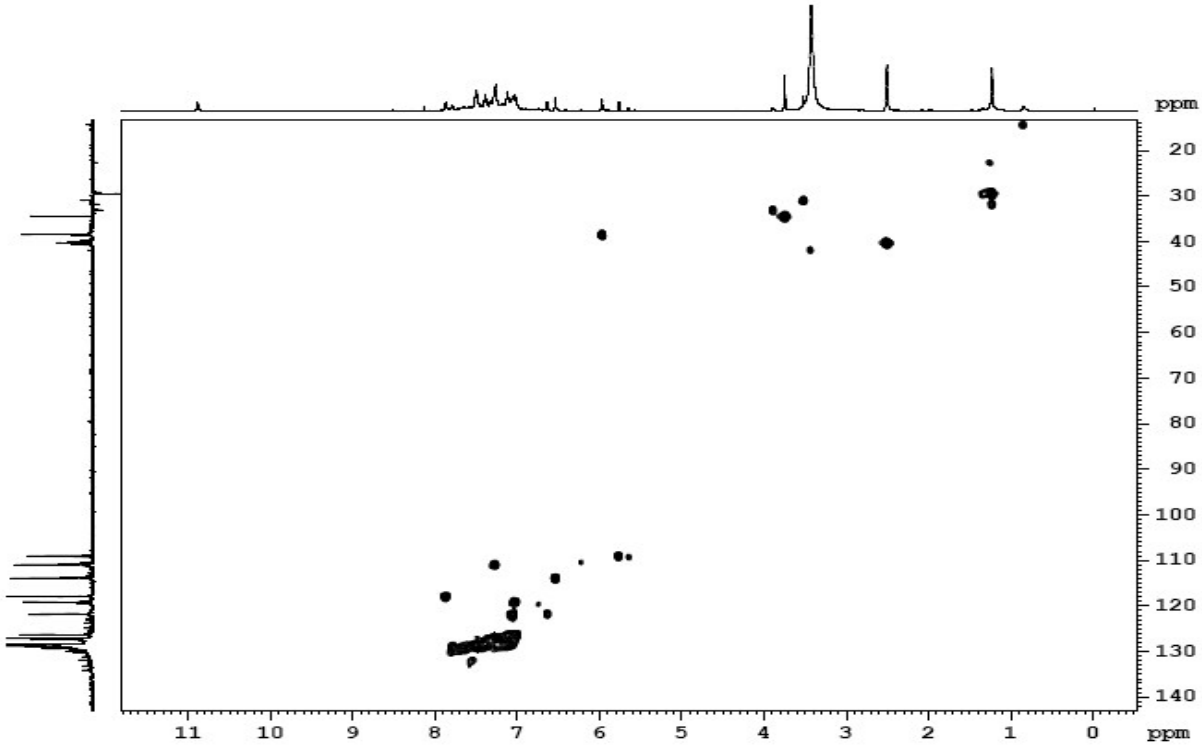
^{1}H NMR, $CDCl_3$:DMSO d_6 (4:1), 400 MHz



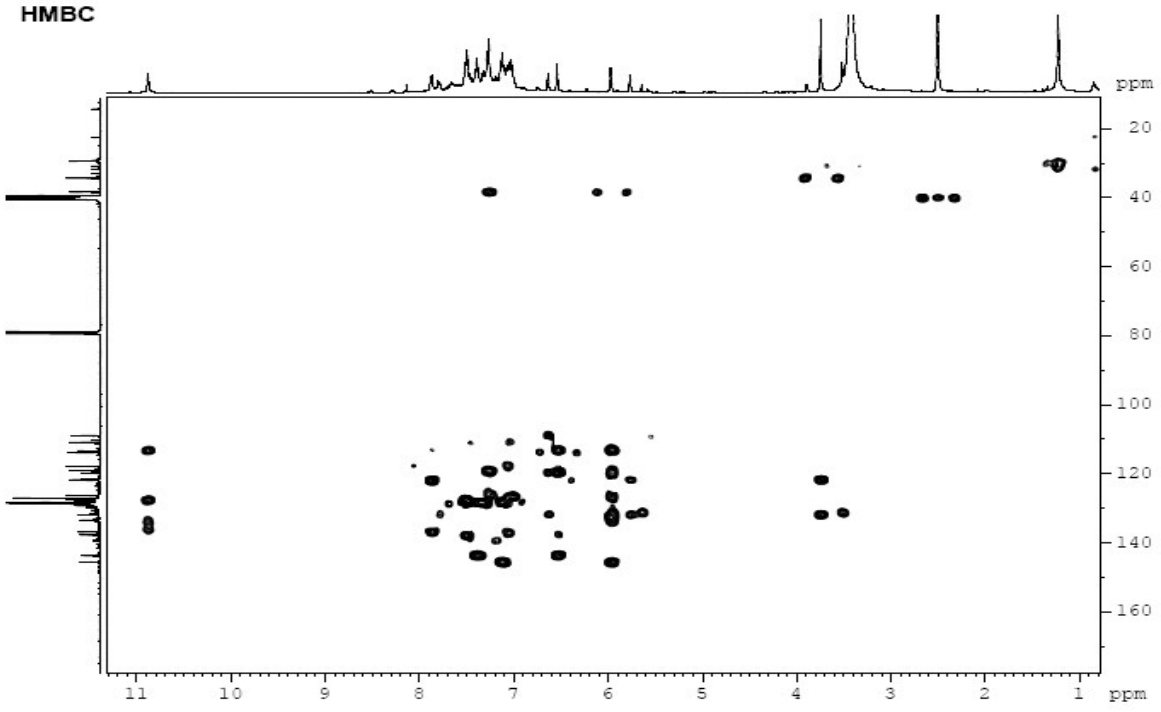
Enlarged NOESY spectrum for 5a



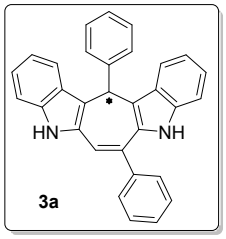
HSQC spectrum for 5a

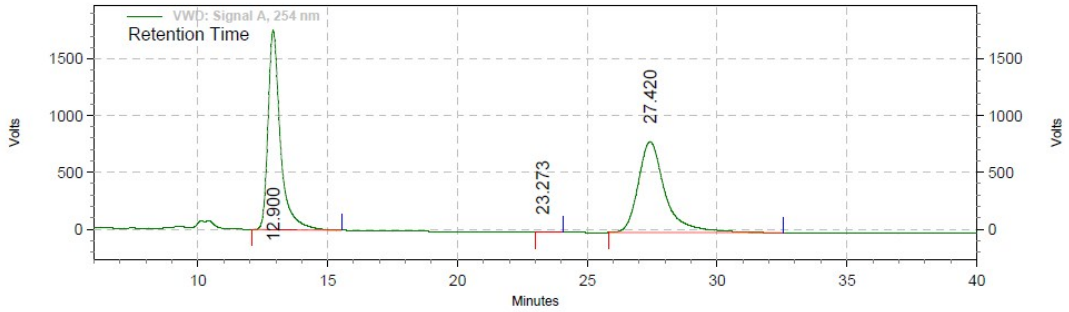


HMBC spectrum for 5a



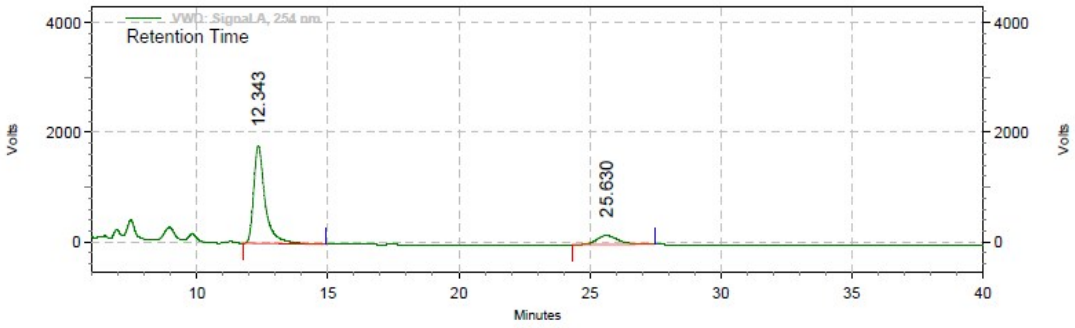
5. HPLC Analysis of 3a





VWD: Signal A,
254 nm Results

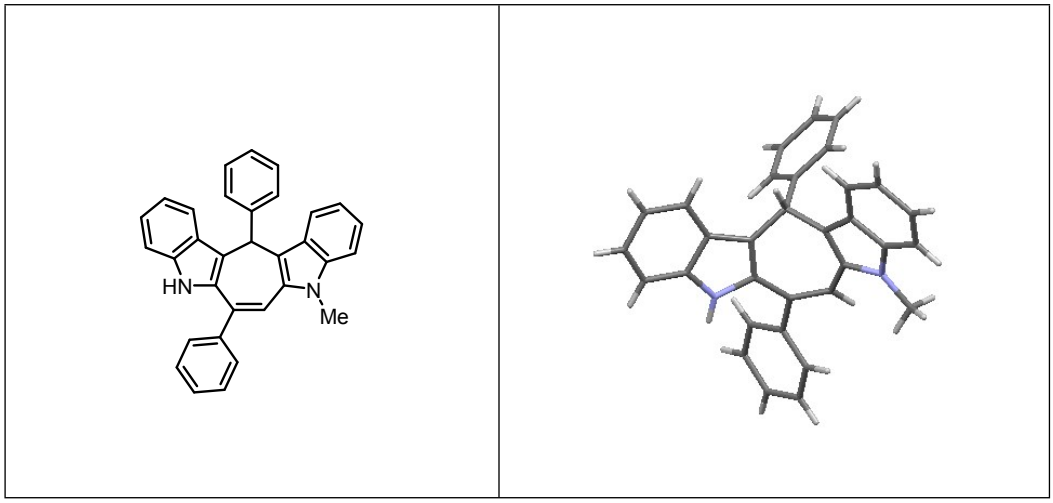
Retention Time	Area	Area %	Height	Height %
12.900	977934116	50.12	29425417	68.64
23.273	175720	0.01	4315	0.01
27.420	973108178	49.87	13440626	31.35
Totals	1951218014	100.00	42870358	100.00



VWD: Signal A,
254 nm Results

Retention Time	Area	Area %	Height	Height %
12.343	904400473	84.89	29868549	91.56
25.630	160947152	15.11	2753249	8.44
Totals	1065347625	100.00	32621798	100.00

6. ORTEP diagram for “3n” (CCDC No. 1503514):



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[2] M. Rueping, B. J. Nachtsheim, R. M. Koenigs and W. Ieawsuwan, *Chem. Eur. J.,* 2010, **16**, 13116.

[3] M.-H. Zhuo, Y.-J. Jiang, Y.-S. Fan, Y. Gao, S. Liu and S. Zhang, *Org. Lett*., 2014, **16**, 1096.

[4] M. Nagamochi, Y.-Q. Fang and M. Lautens, *Org. Lett.,* 2007, **9**, 2955.