Electronic Supplementary Material (ESI) for ChemComm.

Rhodium(II) Catalysed Domino Synthesis of Azepino Fused Diindoles from Isatin Tethered *N*-sulfonyl-1,2,3-triazoles and Indoles

Nilesh Kahar,[a] Pankaj Jadhav,[a] Dr. R. V. Ramana Reddy,[b] and Dr. Sudam Dawande*[a]

Supporting Information

Contents

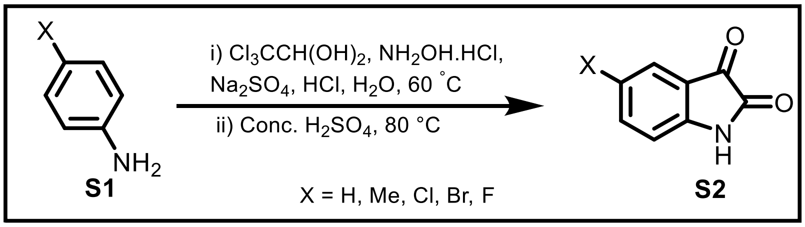
1. General methods

All the reactions were performed in oven-dried glassware under nitrogen atmosphere. Solvents were dried using standard methods. Chloroform, dichloromethane, 1,2-dichloroethane and toluene were distilled over calcium hydride. Unless otherwise stated, all the commercial reagents were used as received. Progress of the reaction was monitored by thin layer chromatography (Merck Silica gel 60 F-254, pre-coated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). Melting points were recorded on a digital melting point apparatus and are uncorrected. Spectroscopic characterizations were carried at the Central Instrumentation Facility (CIF), Institute of Chemical Technology Mumbai, and Indian Institute of Science Education and Research (IISER) Bhopal. ^{1}H-NMR spectra were recorded on BrukerAvance III FT-NMR spectrometers at 500 MHz and Agilent 400MHz. ^{13}C-NMR spectra were recorded at 101 MHz, 126 MHz.^{1}H-NMR chemical shifts are reported in ppm relative to the TMS (= 0) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad). ^{13}C-NMR chemical shifts are reported in ppm relative to the residual $CDCl_3$ signal (= 77.16). HRMS data was obtained on a Bruker microTOF-QII or Agilent 5975C high resolution mass spectrometers. Single crystal XRD data was collected on aBruker D8 VENTURE diffract meter equipped with CMOS Photon 100 detector and Mo-Kα (λ = 0.71073 Å) radiation was used.

2 Preparation of starting materials

2.1. Preparation of isatin derived *N*-Sulfonyl-1,2,3-triazole:

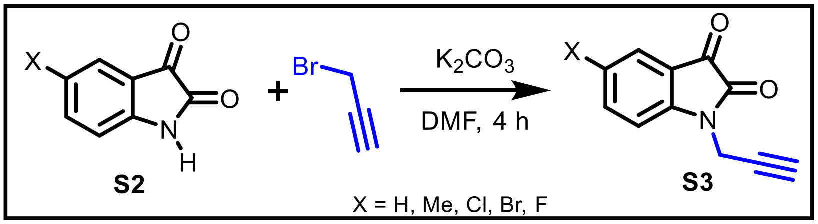
2.1.1. General procedure for the preparation of isatin: Prepared by literature procedure.[1a]



Step-I: To a stirred solution of chloral hydrate (2 g, 16.5 mmol) in deionized water (30 mL), anhydrous sodium sulfate (13 g, 91 mmol) was added. The reaction was stirred at 35 °C, then, the aqueous solution of aniline (10 mmol), concentrated hydrochloric acid (1.2 mL), and hydroxylamine hydrochloride (2.5 g, 37 mmol) were sequentially added. The mixture was stirred at 80 °C for 2 h. After 1 h, the mixture was cooled to 60 °C, during which a precipitate was formed. After filtration and washing with water, the crude product was used next step without purification.

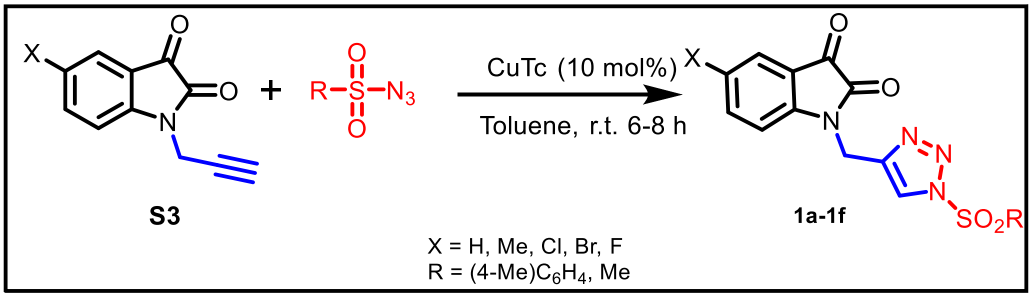
Step-II: To the above crude product Conc. H_2SO_4 was added and reaction mixture was stirred at 80 °C for 30 min. After cooling to room temperature ice cold water (100 mL) was added. Then the mixture was kept standing at 0–5 °C for 1 h, to form precipitate, which was then filtered and washed with water, the crude product was dissolved in aqueous NaOH solution at 60 °C followed by neutralization using acetic acid. Then the mixture was allowed to cool to room temperature to form solid product. The product was then filtered, washed with water and 10% ethanol. The crude product was purified by silica gel chromatography.

2.1.2. General procedure for the preparation of compound *N*-propargyl isatin: Prepared by literature procedure.[1b]

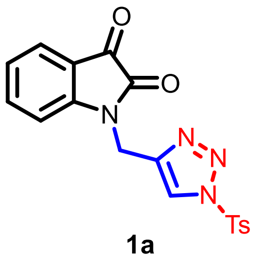


To a solution of isatin (13.6 mmol) in DMF (15 mL) was added potassium carbonate (20.0 mmol) followed by propargyl bromide (16.3 mmol). The mixture was stirred for 4 h at room temperature (the progress of the reaction was monitored by TLC). After completion of the reaction the mixture was diluted with water (25 mL) followed by EtOAc (25 mL) and stirred for 10 min. The organic layer separated was collected and the aqueous layer was extracted with additional EtOAc (2 x 25 mL). The organic layers were collected, combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel (100-200 mesh) column chromatography using hexane/ethyl acetate to afford the desired product.

2.1.3. Preparation of isatin tethered *N*-Sulphonyl-1,2,3-triazoles (1a-1f):

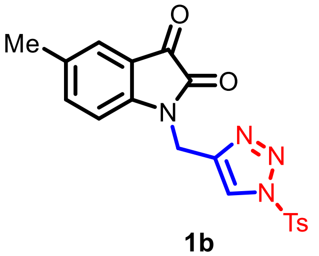


To a stirred solution of *N*-propargyl isatin (5 mmol, 925 mg) in toluene (10 ml) was added sulphonyl azide (5 mmol, 986 mg) followed by CuTc (10 mol%, 95 mg). The resulting solution was stirred for 6 to 8 hrs (progress of rection was monitored by TLC) after complition of the reaction saturated solution of NH_4Cl (25 ml) was added, the resulting solution was extracted by EtOAc (3x30 ml) combined organic layer was dried over Na_2SO_4 and concentrated under vaccume. The resulting solid was washed with a 5% solution of dichloromethane/pet-ether to obtain product **1a** as a yellowish solid.



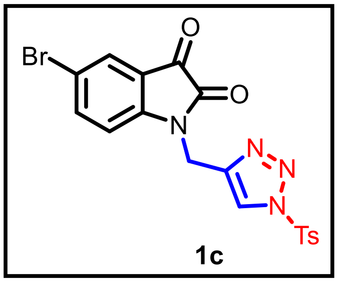
1a

1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1a): Obtained as a pale yellow solid. Yield = 93%; m. p.=136-138°C; R_f = 0.6(Ethyl Acetate/Hexane : 50/50); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.93 (s, 1H), 7.93 (d, *J*=7.7, 2H), 7.72 – 7.24 (m, 4H), 7.12 – 7.06 (m, 1H), 7.03 (d, *J*=7.6, 1H), 4.98 (s, 2H), 2.36 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 182.64, 157.86, 149.63, 147.71, 142.63, 137.78, 132.04, 130.77, 128.13, 124.32, 123.67, 123.27, 117.77, 110.72, 34.66, 21.17; **HRMS (ESI)** calculated for $C_{18}H_{15}N_4O_4S$ $(M+H)^+$ 383.0814, found 383.0821.



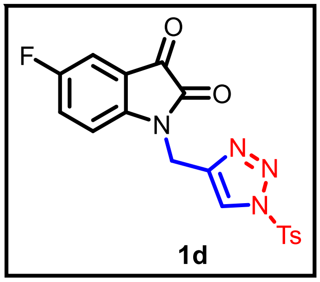
1b

5-methyl-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1b): Obtained as an orange solid. Yield = 95%; m. p.=122-124°C; R_f = 0.6(Ethyl Acetate/Hexane : 50/50); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.92 (s, 1H), 7.93 (d, *J*=7.7, 2H), 7.48 (d, *J*=7.6, 2H), 7.40-7.23 (m, 2H), 6.92 (d, *J*=7.5, 1H), 4.95 (s, 2H), 2.36 (s, 3H), 2.22 (3, 1H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 182.86, 157.90, 147.68, 147.49, 142.65, 138.07, 132.69, 132.06, 130.76, 128.13, 124.55, 123.67, 117.70, 110.59, 34.64, 21.17, 19.95; **HRMS (ESI)** calculated for $C_{19}H_{17}N_4O_4S$ $(M+H)^+$397.0964, found 397.0970.



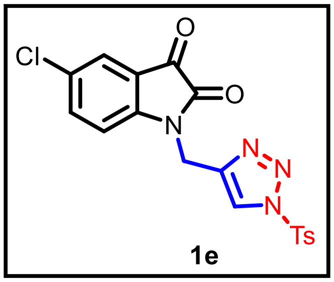
1c

5-bromo-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1c): Obtained as a pale yellow solid. Yield = 90 %; m. p.=156-168°C; R_f = 0.5(Ethyl Acetate/Hexane : 50/50); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.92 (s, 1H), 7.93 (d, *J*=8.2, 2H), 7.75 – 7.61 (m, 2H), 7.49 (d, *J*=8.1, 2H), 7.03 (d, *J*=8.3, 2H), 4.99 (s, 2H), 2.38 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 181.39, 157.47, 148.48, 147.72, 142.45, 139.46, 132.04, 130.78, 128.14, 126.56, 123.66, 119.58, 115.06, 112.90, 39.51, 34.74, 21.19; **HRMS (ESI)** calculated for $C_{18}H_{14}BrN_4O_4S$ $(M+H)^+$ 460.9914, found 460.9916.



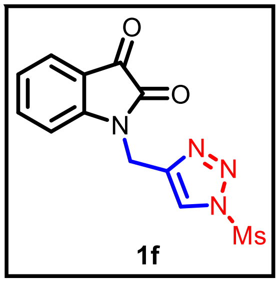
1d

5-fluoro-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1d): Obtained as a pale yellow solid. Yield = 93 %; m. p.=128-130°C; R_f = 0.5(Ethyl Acetate/Hexane : 50/50); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.92 (s, 1H), 7.93 (d, *J*=7.7, 2H), 7.58 – 7.17 (m, 4H), 7.07 (d, *J*=5.1, 1H), 4.99 (s, 2H), 2.37 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 182.03, 159.67, 157.59 (d, *J*=63.5), 147.72, 145.82, 142.54, 132.04, 130.77, 128.14, 123.61 (d, *J*=9.3), 123.57, 118.73 (d, *J*=7.2), 112.15 (d, *J*=7.4), 111.35 (d, *J*=24.9), 34.73, 21.16; **HRMS (ESI)** calculated for $C_{18}H_{14}FN_4O_4S$ $(M+H)^+$401.0714, found 401.0715.



1e

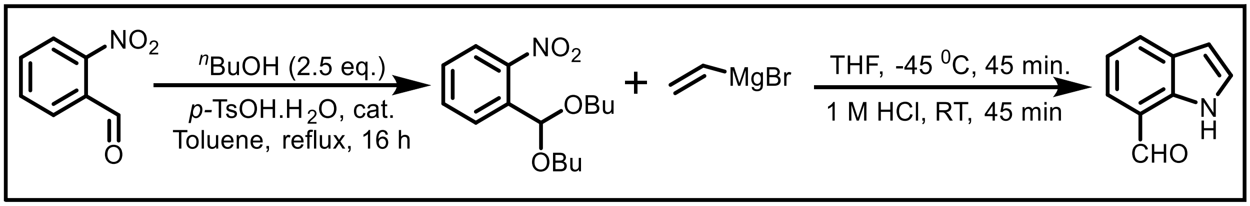
5-chloro-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1e): Obtained as a pale yellow solid. Yield = 92 %; m. p.=130-132°C; R_f = 0.5(Ethyl Acetate/Hexane : 50/50); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.19 (s, 1H), 7.97 (d, *J*=8.1, 2H), 7.67-7.46 (m, 2H), 7.38 (d, *J*=8.1, 2H), 7.19 (s, 1H), 4.99 (s, 2H), 2.44 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 181.81, 157.47, 148.22, 147.91, 141.24, 138.08, 132.58, 130.70, 130.21, 129.02, 125.44, 122.98, 118.48, 112.74, 35.14, 22.00; **HRMS (ESI)** calculated for $C_{18}H_{14}ClN_4O_4S$ $(M+H)^+$ 417.0414, found 417.0415.



1f

1-((1-(methylsulfonyl)-1H-1,2,3-triazol-4-yl)methyl)indoline-2,3-dione (1f): Obtained as a pale yellow solid. Yield = 88 %; m. p.=132-134 °C; R_f = 0.6 (Ethyl Acetate/Hexane : 50/50); ^{1}H NMR **(400 MHz, DMSO-D_6)** δ 7.99 (s, 1H), 7.81 – 7.32 (m, 2H), 7.07 (s, 2H), 4.96 (s, 2H), 2.47 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D_6)** δ = 182.69, 157.48, 149.82, 141.79, 137.73, 124.12, 123.03, 117.27, 110.76, 110.58, 41.93, 34.53; **HRMS (ESI)** calculated for $C_{12}H_{11}N_4O_4S$ $(M+H)^+$ 307.0510, found 307.0512.

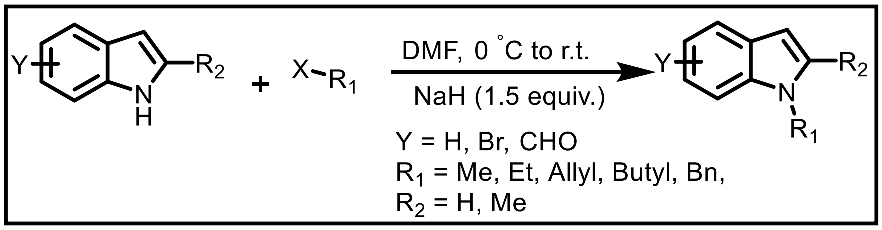
2.2Preparation of 7-formyl Indole: Prepared by following literature procedure[2]



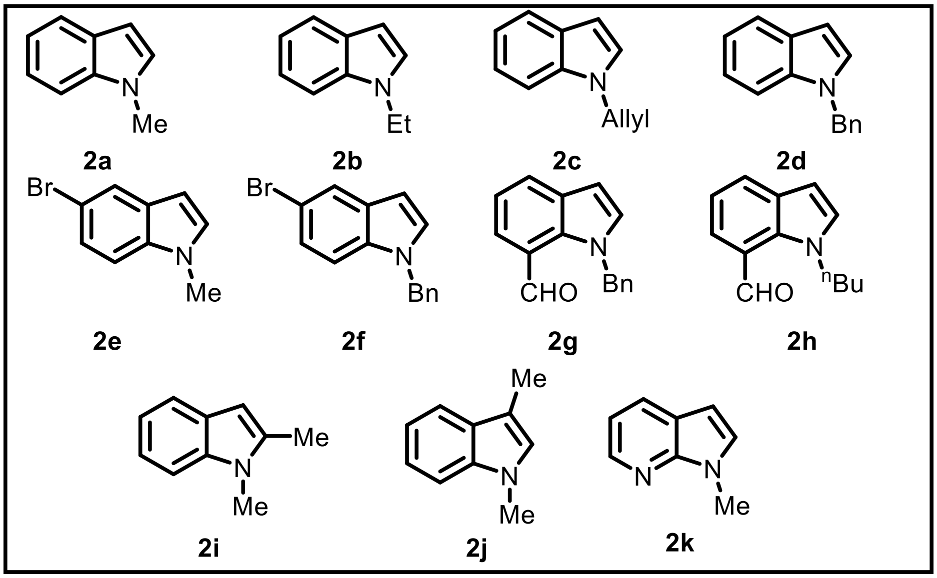
Step 1: Aldehyde (10 mmol, 1 equiv.) was dissolved in toluene (5 mL). Butan-1-ol (2.29 mL, 25 mmol, 2.5 equiv.) was added, followed by *p*-TsOH.H_2O (5.6 mg, 0.03 mmol, 0.003 equiv.), and the resulting mixture was refluxed overnight in a flask equipped with a Dean-Stark apparatus. After cooling back to room temperature, the reaction was quenched with saturated $NaHCO_3$solution (20 mL). The mixture was then extracted with EtOAc (3x20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel (petroleum ether: EtOAc), affording the desired compound as an oil.

Step 2: The acetal prepared *via* step 1 (9 mmol, 1 equiv.) was placed in a flask under argon and dissolved in dry THF (30 mL). The solution was cooled down to about -45 °C. Vinylmagnesium bromide in THF (1 M, 30 mL, 30 mmol, 3.3 equiv.) was added drop wise (2 mL/min). The mixture was then stirred for 45 minutes at about -45 °C. The mixture was allowed to warm to room temperature at which point 1M HCl (aq.) (30 mL, 3.3 equiv.) was carefully added and the resulting mixture was stirred for 45 minutes. The reaction was then quenched with sat. $NaHCO_3$ (aq.) (30 mL) then extracted with Et_2O (3x30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under vacuum. The crude compound was purified by column chromatography on silica gel (petroleum ether: DCM, 7:3) affording the desired indole as a solid.

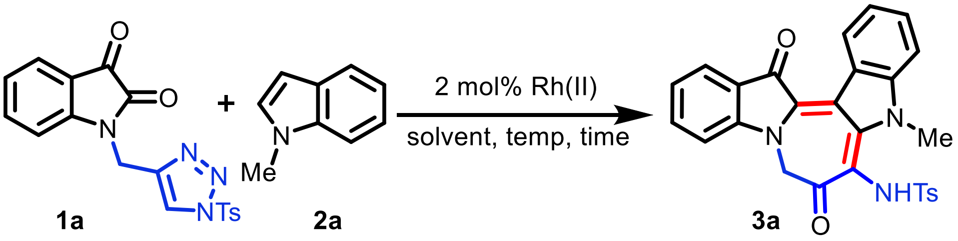
2.3 Preparation of *N*-alkyl indoles: Prepared by following literature procedure[3]



To the solution of indole (10 mmol) in DMF (10 ml), NaH (15 mmol, 60% in mineral oil) was added portion wise at 0 °C then the mixture was stirred for 30 minutes. The alkyl halide (15 mmol) was added drop wise and then reaction mixture was allowed to warm to room temperature with constant stirring. The reaction progress was monitored by TLC. After completion of the reaction water was added, and extracted with EtOAc. The combined organic layer was washed with water, brine and then dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure to obtain crude product which was then purified by column chromatography EtOAc/Pet. ether as eluent.



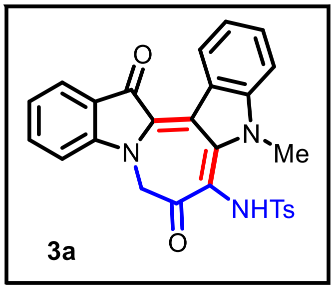
3. Optimization of Rhodium (II) catalyzed synthesis of azepino fused diindoles:



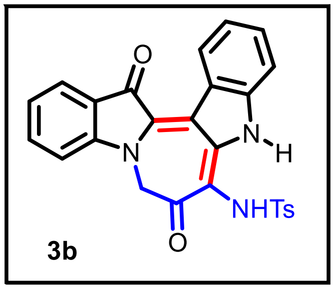
Entry	Catalyst (X mol%)	Solvent	Temp. ˚C	Time Hrs.	Yield %
1	$Rh_2(OAc)_4$ (2)	DCM	50	12	10
2	$Rh_2(OAc)_4$ (2)	DCE	80	6	28
3	$Rh_2(OAc)_4$ (5)	DCE	80	6	55
4	$Rh_2(esp)_2$ (5)	DCE	80	6	72
5	**$Rh_2(Oct)_4$** (5)	**DCE**	**80**	**6**	**78**
6	$Rh_2(TFA)_4$ (5)	DCE	80	6	-
7	$Rh_2(Oct)_4$ (5)	$CHCl_3$	80	6	65
8	$Rh_2(Oct)_4$ (5)	Toluene	80	6	60
9	$Rh_2(Oct)_4$ (5)	EtOAc	80	6	56
10	$Rh_2(Oct)_4$ (5)	DCE	120	6	54

Conditions: In a 10 mL round bottom flask fitted with reflux condenser**,** was added Rh(II)-catalyst (X mol%), isatin derived *N*-sulfonyl-1,2,3-triazole **1a** (0.11 mmol), indole **2a (**0.10 mmol) and solvent 2 mL. Then reaction mixture was heated as mentioned in Table-1 (entry 1-10). The products were isolated by column chromatography.

4. General procedure for Rhodium(II) catalyzed synthesis of azepino fused diindoles: To an oven dried 10 ml round bottom flask equipped with reflux condenser added $Rh_2(Oct)_4$ catalyst (5 mol%), isatin derived *N*-sulfonyl-1,2,3-triazole **1** (0.22 mmol) and indole **2** (0.2 mmol) followed by 4 ml of 1,2-dichloroethane (DCE) as solvent. The reaction mixture was heated to 80 °C with constant stirring for 6 hrs. On completion of reaction (monitored by TLC) the crude reaction mixture was purified by silica gel (100-200 mesh) flash column chromatography using ethyl acetate/petroleum ether as eluent to obtain product **3** as a blue solid.

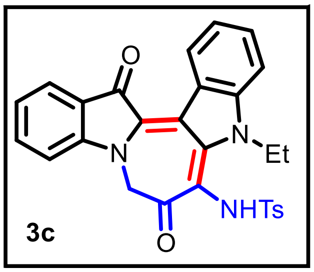


4-methyl-*N*-(5-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)benzenesulfonamide (3a): Obtained as a blue solid. Yield = 78 %; m. p.=156-158 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.72 (d, *J*=7.7, 1H), 7.81 (d, *J*=7.4, 1H), 7.52 (t, *J*=7.7, 1H), 7.47 (t, *J*=7.5, 1H), 7.29 – 7.14 (m, 5H), 7.09 (bs, 1H), 6.78 (d, *J*=8.0, 1H), 6.56 (d, *J*=7.7, 2H), 4.00 (s, 2H), 3.86 (s, 3H), 1.82 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 184.78, 175.94, 151.69, 150.37, 145.20, 143.66, 136.88, 136.23, 134.06, 130.45, 128.24, 127.81, 125.81, 125.74, 123.97, 122.65, 122.27, 122.26, 117.12, 115.50, 110.17, 109.36, 50.17, 34.19, 21.40; **HRMS (ESI)** calculated for $C_{27}H_{22}N_3O_4S$ $(M+H)^+$ 484.1326, found 484.1332.



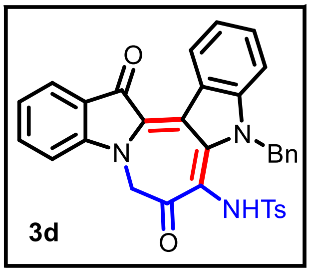
***N*-(7, 14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfon-amide (3b):** Obtained as a blue solid. Yield = 75 %; m. p.=162-164 °C; R_f = 0.3 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 11.12 (s, 1H), 8.77 (s, 1H), 8.59

(d, *J*=7.7, 1H), 7.74 (d, *J*=7.0, 1H), 7.66 (t, *J*=7.2, 1H), 7.40 – 7.32 (m, 3H), 7.28 (d, *J*=7.7, 1H), 7.19 (t, *J*=7.2, 1H), 7.11 (d, *J*=8.1, 1H), 7.06 (t, *J*=7.5, 1H), 6.87 (d, *J*=7.6, 2H), 4.14 (s, 2H), 2.16 (s, 3H); **^{13}C NMR (126 MHz, DMSO-D$_6$)** δ = 185.00, 178.35, 153.02, 151.20, 143.33, 142.34, 138.24, 136.46, 136.10, 129.88, 128.24, 128.20, 127.11, 125.66, 124.93, 123.22, 122.30, 121.83, 120.13, 115.58, 114.15, 110.90, 51.14, 20.99; **HRMS (ESI)** calculated for $C_{26}H_{21}N_3O_4S$ $(M+H)^+$ 470.1175, found 470.1155.

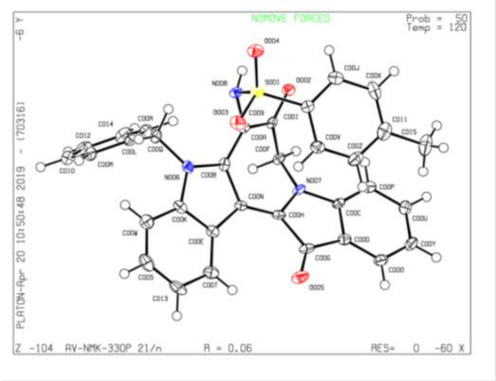


3c

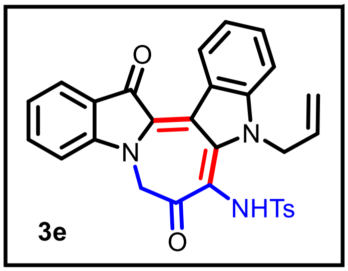
***N*-(5-ethyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3c):** Obtained as a blue solid. Yield = 73 %; m. p.=180-182 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 8.72 (d, *J*=7.8, 1H), 7.82 (d, *J*=7.4, 1H), 7.59 – 7.50 (m, 1H), 7.49 – 7.43 (m, 1H), 7.28 – 7.16 (m, 6H), 6.78 (d, *J*=8.0, 1H), 6.57 (d, *J*=8.0, 2H), 5.32-4.31 (m, 2H) 4.00(s, 2H), 1.86 (s, 3H), 1.24 (t, *J*=7.2, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)**δ 184.64, 176.15, 150.36, 150.25, 144.40, 143.67, 136.96, 136.16, 134.00, 130.34, 128.26, 127.80, 125.85, 125.75, 123.98, 122.68, 122.64, 122.11, 117.70, 115.51, 110.20, 109.63, 50.17, 39.70, 21.43, 12.50; **HRMS (ESI)** calculated for $C_{28}H_{24}N_3O_4S$ $(M+H)^+$ 498.1482, found 498.1475.



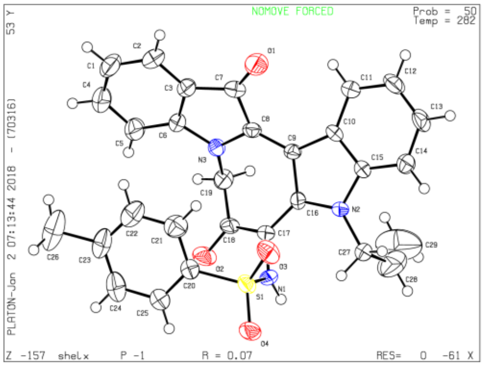
3d



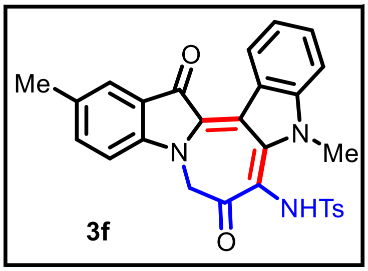
***N*-(5-benzyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3d):** Obtained as a blue solid. Yield = 76 %; m. p.=164-166 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.77 (d, *J*=7.9, 1H), 7.83 (d, *J*=7.3, 1H), 7.57 – 7.50 (m, 1H), 7.48 – 7.42 (m, 1H), 7.26 – 7.15 (m, 8H), 7.09 (s, 1H), 7.07 – 7.01 (m, 2H), 6.77 (d, *J*=8.0, 1H), 6.59 (d, *J*=8.0, 2H), 5.71 (s, 2H), 3.93 (s, 2H), 1.83 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 184.53, 175.77, 150.28, 150.14, 145.05, 143.79, 136.71, 136.55, 136.16, 134.01, 130.52, 128.84, 128.30, 127.82, 127.66, 126.84, 125.91, 125.77, 124.06, 122.74, 122.45, 122.30, 117.61, 116.27, 110.15, 110.04, 50.13, 47.95, 21.42; **HRMS (ESI)** calculated for $C_{33}H_{26}N_3O_4S$ $(M+H)^+$ 560.1639, found 560.1641 **(CCDC 1911349)**.



3e

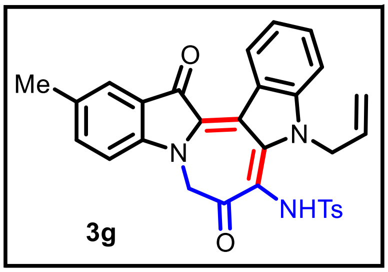


***N*-(5-allyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3e):** Obtained as a blue solid. Yield = 81 %; m. p.=122-124 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 8.74 (d, *J* =7.9, 1H), 7.83 (d, *J*= 7.1, 1H), 7.55 (t, *J* =7.5, 1H), 7.46 (t, *J* =7.3, 1H), 7.32 – 7.10 (m, 6H), 6.79 (d, *J* =7.6, 1H), 6.59 (d, *J* =7.5, 2H), 5.91 – 5.75 (m, 1H), 5.38 – 5.02 (m, 4H), 4.01 (s, 2H), 1.86 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 184.59, 176.13, 150.63, 150.22, 144.67, 143.74, 136.87, 136.18, 134.01, 131.70, 130.36, 128.29, 127.81, 125.82, 125.78, 124.05, 122.72, 122.52, 122.24, 117.82, 117.54, 115.96, 110.20, 110.05, 50.19, 47.31, 21.44; **HRMS (ESI)** calculated for $C_{29}H_{24}N_3O_4S$ $(M+H)^+$ 510.1484, found 510.1482 **(CCDC 1911350)**.



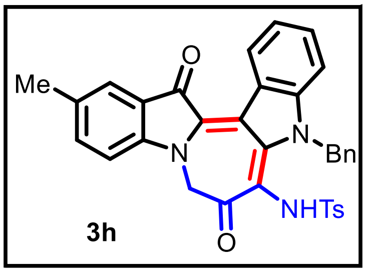
3f

***N*-(5,12-dimethyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methyl benzenesulfonamide (3f):** Obtained as a blue solid. Yield = 80 %; m. p.=174-176°C; R$_f$ = 0.5 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.71 (d, *J*=7.3, 1H), 7.61 (s, 1H), 7.48 (t, *J*=7.2, 1H), 7.33 (d, *J*=7.2, 1H), 7.25 – 7.16 (m, 4H), 7.11 (s, 1H), 6.68 (d, *J*=7.5, 1H), 6.58 (d, *J*=7.2, 2H), 4.00 (s, 2H), 3.87 (s, 3H), 2.42 (s, 3H), 1.85 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 184.93, 175.71, 151.61, 148.42, 145.04, 143.46, 137.18, 137.15, 136.81, 134.17, 134.02, 130.20, 128.24, 127.82, 125.83, 125.68, 122.81, 122.35, 122.19, 116.54, 109.99, 109.32, 77.16, 50.25, 34.15, 21.33, 20.92; **HRMS (ESI)** calculated for $C_{28}H_{24}N_3O_4S$ $(M+H)^+$ 498.1479, found 498.1482.



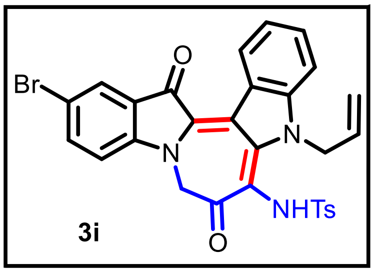
3g

***N*-(5-allyl-12-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3g):** Obtained as a blue solid. Yield = 67 %; m. p.=176-178 °C; R_f= 0.5(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz,CDCl$_3$)** δ = 8.69 (d, *J*=6.9, 1H), 7.59 (s, 1H), 7.43 (t, *J*=7.5, 1H), 7.31 (d, *J*=7.9, 1H), 7.25-7.16 (m, 4H), 7.13 (s, 1H), 6.66 (d, *J*=7.9, 1H), 6.56 (d, *J*=7.3, 2H), 5.87 – 5.75 (m, 1H), 5.37 – 5.00 (m, 4H), 3.94 (s, 2H), 2.40 (s, 3H), 1.84 (s, 3H);**^{13}C NMR (101 MHz, CDCl$_3$)** δ = 184.76, 175.80, 150.59, 150.56, 148.26, 144.51, 143.54, 137.13, 136.76, 134.09, 131.76, 130.09, 128.28, 127.79, 125.86, 125.68, 122.85, 122.57, 122.15, 117.73, 116.91, 115.77, 110.02, 109.99, 50.20, 47.29, 21.35, 20.91; **HRMS (ESI)** calculated for $C_{30}H_{26}N_3O_4S$ (M+H)$^+$ 524.1644, found 524.1652.



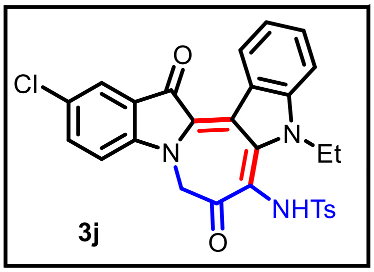
3h

***N*-(5-benzyl-12-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3h):** Obtained as a blue solid. Yield = 72 %; m. p.=188-190 °C; R_f= 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.73 (d, *J*=7.3, 1H), 7.61 (d, *J*=5.1, 1H), 7.48 – 7.40 (m, 1H), 7.31 (d, *J*=7.9, 1H), 7.27 – 7.14 (m, 7H), 7.11 – 7.01 (m, 3H), 6.71 – 6.63 (m, 1H), 6.61 – 6.56 (m, 2H), 3.88 (s, 2H), 2.41 (s, 3H), 1.83 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 184.72, 175.42, 150.27, 148.19, 144.87, 143.59, 137.00, 136.76, 136.60, 134.14, 134.11, 130.25, 128.81, 128.29, 127.81, 127.61, 126.83, 125.86, 125.82, 125.78, 122.88, 122.52, 122.22, 116.98, 116.06, 110.00, 50.13, 47.95, 21.32, 20.91; **HRMS (ESI)** calculated for $C_{34}H_{28}N_3O_4S$ (M+H)$^+$ 574.1795, found 574.1795.



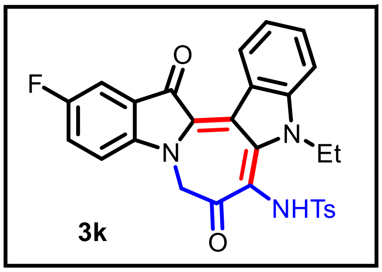
3i

***N*-(5-allyl-12-bromo-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3i):** Obtained as a blue solid. Yield = 59 %; m. p.=180-182 °C; R_f= 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.68 (d, *J*=7.1, 1H), 7.89 (d, *J*=1.3, 1H), 7.60 (d, *J*=6.7, 1H), 7.45 (t, *J*=7.5, 1H), 7.26 – 7.15 (m, 5H), 6.67 (d, *J*=8.4, 1H), 6.60 (d, *J*=7.4, 2H), 5.88 – 5.73 (m, 1H), 5.38 – 4.84 (m, 4H), 3.98 (s, 2H), 1.90 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 182.99, 176.15, 150.30, 148.69, 144.90, 143.77, 138.29, 136.06, 134.24, 131.59, 130.86, 128.33, 127.85, 126.00, 124.42, 122.35, 122.30, 122.29, 118.57, 117.91, 116.76, 116.61, 111.68, 110.14, 50.22, 47.30, 21.45; **HRMS (ESI)** calculated for $C_{29}H_{23}BrN_3O_4S$ $(M+H)^+$ 588.0587, found 588.0585.



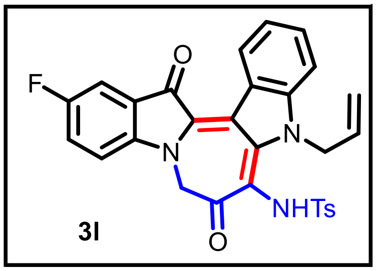
3j

***N*-(12-chloro-5-ethyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3j):** Obtained as a blue solid. Yield = 69 %; m. p.= 180-182 °C; R_f= 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.67 (d, *J* = 7.6 Hz, 1H), 7.75 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.17 (m, 5H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 4.82 (bs, 2H), 3.99 (s, 2H), 1.91 (s, 3H), 1.21 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 183.19, 176.20, 148.34, 144.67, 143.69, 135.48, 134.26, 130.86, 129.84, 129.66, 128.33, 127.88, 126.60, 126.04, 125.40, 124.06, 122.45, 122.24, 118.78, 116.21, 111.27, 109.76, 50.32, 39.73, 21.45, 12.52; **HRMS (ESI)** calculated for $C_{28}H_{23}ClN_3O_4S$ $(M+H)^+$ 532.1092, found 532.1089.



3k

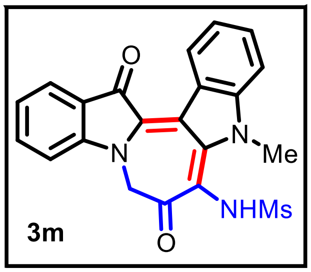
***N*-(5-ethyl-12-fluoro-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3k):** Obtained as a blue solid. Yield = 64 %; m. p.=138-140°C; R_f= 0.5(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.68 (d, *J*=7.1, 1H), 7.53 – 7.42 (m, 2H), 7.34 – 7.10 (m, 6H), 6.73 (d, *J*=6.9, 1H), 6.61 (d, *J*=6.1, 2H), 3.98 (s, 2H), 1.92 (s, 3H), 1.86-1.51 (m, 2H), 1.21 (t, *J*=6.8, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 183.56, 176.17, 160.78, 158.34, 150.00, 146.25, 144.60, 143.60, 137.00, 134.23, 130.71, 128.30, 127.88, 125.90, 122.82, 122.53 (d, *J*=9.1), 122.17, 118.60, 116.14, 112.21 (d, *J*=24.2), 111.27 (d, *J*=7.5), 109.72, 50.42, 39.72, 21.47, 12.51; **HRMS (ESI)** calculated for $C_{28}H_{22}FN_3NaO_4$ $(M+Na)^+$ 538.1207, found 538.1208.



3l

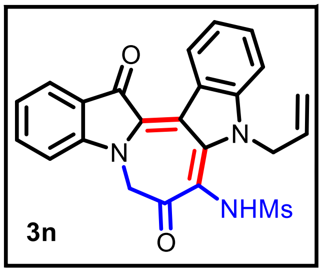
***N*-(5-allyl-12-fluoro-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3l):** Obtained as a blue solid. Yield = 60 %; m. p.=174-176°C; R_f= 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.71 (d, *J*=7.6, 1H), 7.53 –

7.45 (m, 2H), 7.29 – 7.15 (m, 6H), 6.76 (d, *J*=7.3, 1H), 6.64 (d, *J*=6.9, 2H), 5.89 – 5.76 (m, 1H), 5.35 – 5.06 (m, 4H), 4.00 (s, 2H), 1.93 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 183.50, 176.11, 160.56, 158.60, 150.23, 146.19, 144.84, 143.67, 136.89, 134.18, 131.61, 130.73, 128.32, 127.86, 125.85, 123.89 (d, *J*=7.5), 122.72 (d, *J*=25.0),122.31 (d, *J*=4.4), 118.38, 117.88, 116.54, 112.24 (d, *J*=24.3), 111.26 (d, *J*=7.7), 110.12, 50.41, 47.29, 21.49; **HRMS (ESI)** calculated for $C_{29}H_{23}FN_3O_4S$ $(M+H)^+$ 528.1388, found 528.1386.



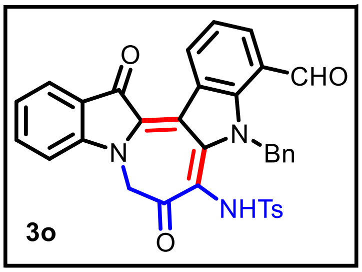
3m

***N*-(5-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)methanesulfonamide (3m):** Obtained as a blue solid. Yield = 71 %; m. p.=170-172°C; R_f= 0.5(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.81 (d, *J*=7.8, 1H), 7.79 (d, *J*=7.6, 1H), 7.61 (t, *J*=7.7, 1H), 7.45 (t, *J*=7.5, 1H), 7.26 – 7.09 (m, 4H), 6.63 (s, 1H), 4.35 (s, 2H), 3.84 (s, 3H), 2.79 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 185.24, 177.86, 153.53, 150.59, 145.10, 138.31, 136.58, 130.36, 125.97, 125.74, 124.34, 122.68, 122.52, 117.28, 114.49, 114.47, 110.52, 109.31, 51.10, 38.27, 34.49; **HRMS (ESI)** calculated for $C_{21}H_{18}N_3O_4S$ $(M+H)^+$ 408.1018, found 408.1016.



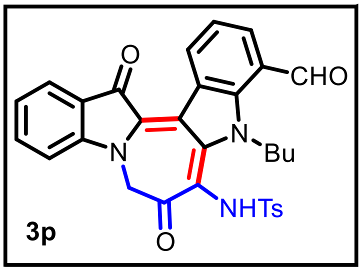
3n

***N*-(5-allyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)methanesulfonamide (3n):** Obtained as a blue solid. Yield = 69 %; m. p.=176-178°C; R_f= 0.5(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 8.80 (d, *J*=7.1, 1H), 7.79 (d, *J*=7.7, 1H), 7.61 (t, *J*=6.1, 1H), 7.42 (t, *J*=7.8, 1H), 7.30 – 7.12 (m, 4H), 6.61 (s, 1H), 5.94 – 5.84 (m, 1H), 5.35 – 4.89 (m, 4H), 4.32 (s, 2H), 2.82 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 185.06, 178.20, 152.91, 150.48, 144.66, 138.42, 136.56, 131.85, 130.29, 126.00, 125.72, 124.43, 122.76, 122.75, 122.53, 117.62, 117.59, 114.88, 110.54, 109.97, 51.18, 47.63, 38.71; **HRMS (ESI)** calculated for $C_{23}H_{20}N_3O_4S$ $(M+H)^+$ 434.1172, found 434.1175.



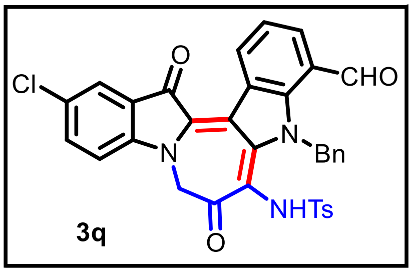
3o

***N*-(5-benzyl-4-formyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3o):** Obtained as a blue solid. Yield = 65 %; m. p.=190-192°C; R_f = 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 10.23 (s, 1H), 8.94 (d, *J*=6.2, 1H), 7.84 (d, *J*=18.5, 2H), 7.55 (t, *J*=7.4, 1H), 7.34 (t, *J*=9.0, 1H), 7.28 – 7.09 (m, 7H), 6.86 – 6.74 (m, 3H), 6.58 (d, *J*=4.8, 2H), 6.01 (bs, 2H), 3.92 (s, 2H), 1.81 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 188.84, 184.10, 175.11, 151.31, 149.89, 144.42, 143.90, 136.56, 136.40, 136.34, 134.50, 134.18, 131.28, 128.68, 128.47, 127.69, 127.59, 126.78, 125.88, 124.49, 124.33, 122.73, 122.53, 121.74, 119.45, 116.18, 110.24, 53.62, 50.05, 21.35; **HRMS (ESI)** calculated for $C_{34}H_{26}N_3O_5S$ $(M+H)^+$ 588.1588, found 588.1586.



3p

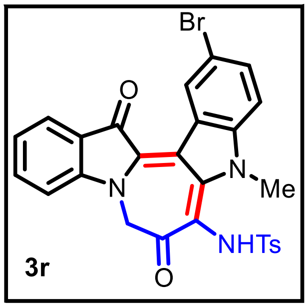
***N*-(5-butyl-4-formyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3p):** Obtained as a blue solid. Yield = 62 %; m. p.=202-204°C; R_f = 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 10.43 (s, 1H), 8.90 (d, *J*=7.3, 1H), 7.96 (d, *J*=7.5, 1H), 7.82 (d, *J*=7.1, 1H), 7.57 (t, *J*=7.6, 1H), 7.38 – 7.17 (m, 5H), 6.86 (d, *J*=7.7, 1H), 6.58 (d, *J*=7.4, 2H), 4.09 (s, 2H), 1.81 (s, 3H), 1.71 (s, 2H), 1.49 – 1.45 (m, 2H), 1.08 (dd, *J*=14.5, 7.1, 2H), 0.79 (t, *J*=6.9, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 188.84, 184.09, 175.07, 150.94, 149.85, 143.99, 143.87, 136.48, 136.33, 134.17, 133.77, 131.27, 128.46, 127.57, 125.88, 124.47, 124.42, 122.75, 122.48, 121.53, 119.00, 116.26, 110.24, 50.06, 49.61, 29.48, 21.36, 19.79, 13.78; **HRMS (ESI)** calculated for $C_{31}H_{27}N_3NaO_5S$ $(M+Na)^+$ 576.1564, found 576.1561.



3q

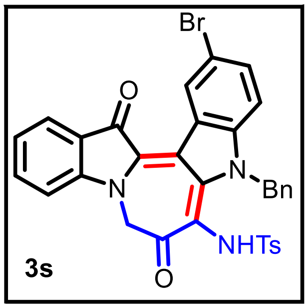
***N*-(5-benzyl-12-chloro-4-formyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3q):** Obtained as a blue solid. Yield = 64 %; m. p.=146-148°C; R_f= 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 10.20 (s, 1H), 8.90 (d, *J*=7.7, 1H), 7.87 (d, *J*=7.6, 1H), 7.78 (d, *J*=8.1, 1H), 7.75 (d, *J*=1.6, 1H), 7.48 (dd, *J*=8.3, 1.5, 1H), 7.34 (t, *J*=7.7, 2H), 7.26 – 7.15 (m, 3H), 7.15 – 7.07 (m, 2H), 6.78 (d, *J*=8.0, 2H), 6.62

(d, *J*=7.9, 2H), 5.99 (s, 2H), 3.94 (s, 2H), 1.88 (s, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 188.83, 182.72, 175.18, 151.04, 147.94, 144.51, 143.93, 136.26, 135.67, 135.02, 134.33, 131.40, 130.18, 129.79, 128.68, 128.52, 127.72, 127.59, 126.77, 126.51, 125.46, 124.03, 122.57, 121.83, 120.02, 117.06, 111.39, 53.59, 50.08, 21.32; **HRMS (ESI)** calculated for $C_{34}H_{25}ClN_3O_5S$ $(M+H)^+$ 622.1198, found 622.1196.



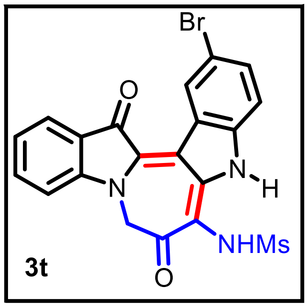
3r

***N*-(2-bromo-5-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3r):** Obtained as a blue solid. Yield = 76 %; m. p.=128-130°C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 8.91 (d, *J*=1.9, 1H), 7.83 (dd, *J*=7.5, 0.6, 1H), 7.63 – 7.51 (m, 2H), 7.22 (dt, *J*=7.4, 3.0, 3H), 7.10 (s, 1H), 7.06 (d, *J*=8.6, 1H), 6.80 (d, *J*=8.0, 1H), 6.59 (d, *J*=7.9, 2H), 4.06 (s, 2H), 3.85 (s, 3H), 1.84 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 184.74, 175.60, 151.33, 150.37, 143.98, 143.78, 137.14, 136.42, 134.04, 132.95, 128.29, 128.25, 127.80, 125.91, 124.36, 123.94, 122.52, 116.04, 115.68, 114.93, 110.62, 110.25, 50.22, 34.36, 21.42; **HRMS (ESI)** calculated for $C_{27}H_{21}BrN_3O_4S$ $(M+H)^+$ 562.0431, found 562.0441.



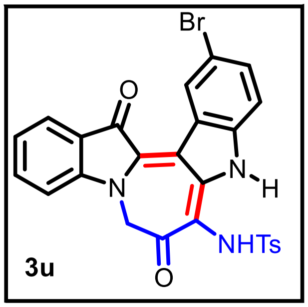
3s

***N*-(5-benzyl-2-bromo-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3s):** Obtained as a blue solid. Yield = 70 %; m. p.=164-166°C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 8.92 (d, *J*=1.9, 1H), 7.83 (d, *J*=6.9, 1H), 7.79 (d, *J*=8.3, 1H), 7.57 – 7.51 (m, 2H), 7.29 (d, *J*=8.0, 1H), 7.25 – 7.19 (m, 4H), 7.13 – 7.09 (m, 2H), 7.03 (d, *J*=2.0, 1H), 7.01 (d, *J*=1.3, 1H), 6.80 (d, *J*=8.0, 1H), 6.59 (d, *J*=8.0, 2H), 5.80 (bs, 2H), 3.94 (s, 2H), 1.83 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 184.52, 175.34, 150.09, 150.04, 143.92, 143.70, 137.02, 136.41, 136.13, 133.89, 132.91, 129.81, 128.90, 128.32, 127.79, 127.73, 126.74, 126.52, 125.89, 124.46, 124.12, 122.50, 116.64, 115.95, 114.93, 111.40, 110.32, 50.06, 48.18, 21.40; **HRMS (ESI)** calculated for $C_{33}H_{25}BrN_3O_4S$ $(M+H)^+$ 638.0744, found 638.0748.



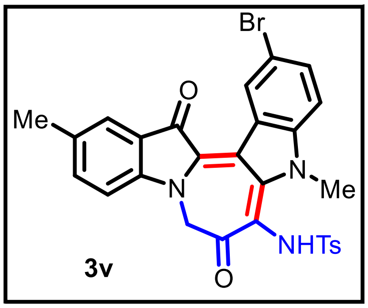
3t

***N*-(2-bromo-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)methanesulfonamide (3t):** Obtained as a blue solid. Yield = 73 %; m. p.=154-156°C; R_f = 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 11.05 (s, 1H), 8.81 (s, 1H), 8.69 (s, 1H), 7.76 – 7.68 (m, 2H), 7.48 (dd, *J*=13.8, 8.4, 2H), 7.26 – 7.15 (m, 2H), 4.40 (s, 2H), 2.95 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 185.37, 179.18, 154.00, 151.33, 141.98, 139.46, 136.79, 131.84, 127.49, 125.00, 124.60, 123.58, 121.81, 113.81, 113.41, 112.65, 111.78, 111.23, 51.58, 40.79; **HRMS (ESI)** calculated for $C_{20}H_{15}BrN_3O_4S$ $(M+H)^+$ 471.9967, found 471.9965.



3u

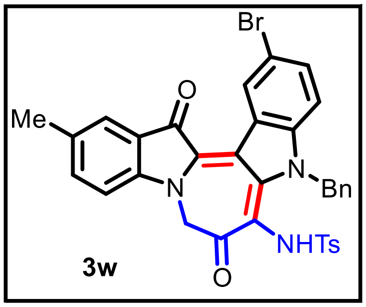
***N*-(2-bromo-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenze–nesulfonamide (3u):** Obtained as a blue solid. Yield = 68 %; m. p.=138-140°C; R_f = 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, DMSO-D$_6$)** δ = 11.23 (s, 1H), 8.86 (s, 1H), 8.75 (d, *J*=1.6, 1H), 7.73 (d, *J*=7.4, 1H), 7.65 (t, *J*=7.7, 1H), 7.50 (dd, *J*=8.5, 1.8, 1H), 7.34 (d, *J*=8.1, 2H), 7.25 – 7.15 (m, 2H), 7.13 (d, *J*=8.0, 1H), 6.87 (d, *J*=8.1, 2H), 4.13 (s, 2H), 2.14 (s, 3H); **^{13}C NMR (126 MHz, DMSO-D$_6$)** δ = 185.23, 178.10, 152.83, 151.23, 142.39, 142.19, 138.94, 136.66, 136.13, 131.93, 128.27, 127.58, 127.12, 125.08, 124.33, 123.54, 121.76, 114.44, 113.85, 112.61, 111.63, 111.04, 51.15, 20.97; **HRMS (ESI)** calculated for $C_{26}H_{19}BrN_3O_4S$ $(M+H)^+$ 548.0280, found 548.0283.



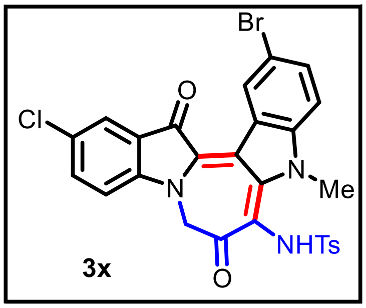
3v

***N*-(2-bromo-5,12-dimethyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3v):** Obtained as a blue solid. Yield = 67 %; m. p.=218-220 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.74 (d, *J*=2.8, 1H), 8.31 (s, 1H), 7.62-7.56 (m, 2H), 7.49 (d, *J*=7.9, 1H), 7.35 (d, *J*=8.9, 1H), 7.04 (d, *J*=7.4, 2H), 6.91 (d, *J*=7.8, 1H), 6.57 (d, *J*=7.1, 2H), 4.12 (s, 2H), 3.70 (s, 3H), 2.39 (s, 3H), 1.93 (s, 3H); **^{13}C** NMR

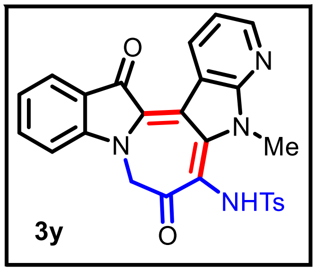
(101 MHz, DMSO-D$_6$) δ = 184.88, 175.28, 152.19, 148.10, 143.30, 142.43, 137.36, 137.05, 134.85, 133.55, 131.53, 127.90, 126.79, 126.63, 125.16, 123.65, 121.90, 115.14, 113.47, 112.64, 111.03, 110.82, 49.72, 33.94, 20.75, 20.18; **HRMS (ESI)** calculated for $C_{28}H_{23}BrN_3O_4S$ $(M+H)^+$ 576.0593, found 576.0596.



***N*-(5-benzyl-2-bromo-12-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3w):** Obtained as a blue solid. Yield = 71 %; m. p.=178-180°C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 8.90 (s, 1H), 7.62 (s, 1H), 7.53 (d, *J*=7.5, 1H), 7.34 (d, *J*=7.5, 1H), 7.26 – 7.16 (m, 5H), 7.11 (d, *J*=9.0, 2H), 7.01 (d, *J*=6.2, 2H), 6.68 (d, *J*=7.7, 1H), 6.60 (d, *J*=7.5, 2H), 3.89 (s, 2H), 2.43 (s, 3H), 1.84 (s, 3H)(benzyl proton missing); **^{13}C NMR (101 MHz, CDCl$_3$)** δ = 184.69, 175.05, 149.99, 148.17, 143.73, 143.61, 137.27, 136.96, 136.23, 134.60, 134.05, 132.74, 128.91, 128.87, 128.35, 128.20, 127.79, 126.76, 126.03, 124.23, 122.72, 116.53, 115.44, 114.92, 111.37, 110.12, 50.15, 48.20, 21.34, 20.96; **HRMS (ESI)** calculated for $C_{34}H_{26}BrN_3NaO_4S$ $(M+H)^+$ 674.0720, found 674.0723.

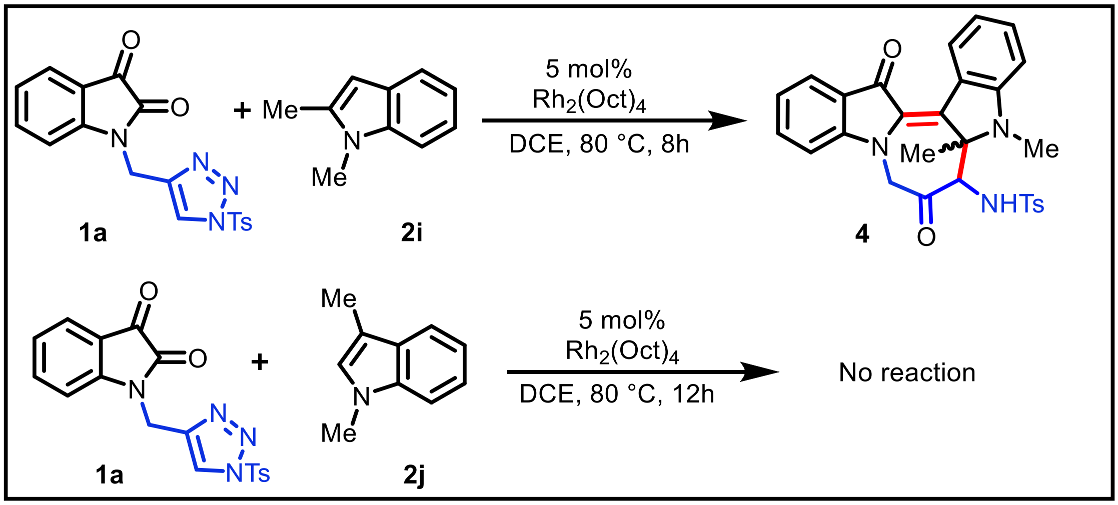


***N*-(2-bromo-12-chloro-5-methyl-7,14-dioxo-5,7,8,14-tetrahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (3x):** Obtained as a blue solid. Yield = 66 %; m. p.=124-126°C; R_f = 0.3(Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (400 MHz, DMSO-D$_6$)** δ = 8.82 (s, 1H), 8.77 (d, *J*=1.2, 1H), 8.31 (s, 1H), 7.83 (d, *J*=2.0, 1H), 7.77 – 7.69 (m, 1H), 7.64 (dd, *J*=8.6, 1.8, 1H), 7.36 (d, *J*=8.7, 1H), 7.08 (d, *J*=7.9, 2H), 6.64 (d, *J*=7.8, 2H), 4.19 (s, 2H), 3.70 (s, 3H), 1.96 (s, 3H); **^{13}C NMR (101 MHz, DMSO-D$_6$)** δ = 183.42, 175.93, 152.01, 148.50, 143.70, 142.47, 136.89, 135.68, 135.00, 132.13, 128.00, 127.93, 127.03, 126.76, 125.55, 124.48, 123.41, 115.99, 114.99, 112.69, 112.66, 111.18, 49.80, 33.96, 20.73; **HRMS (ESI)** calculated for $C_{27}H_{20}BrClN_3O_4S$ $(M+H)^+$ 596.0041, found 596.0045.



4-methyl-N-(5-methyl-7,14-dioxo-5,7,8,14-tetrahydropyrido[3'',2'':4',5']pyrrolo[3',2':3,4] azepino[1,2-a]indol-6-yl)benzenesulfonamide (3y): Obtained as a blue solid. Yield = 54 %; m. p.=188-190°C; R_f= 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, CDCl$_3$)** δ = 8.98 (dd, *J*=7.8, 1.5, 1H), 8.42 (dd, *J*=4.9, 1.5, 1H), 7.86 – 7.80 (m, 2H), 7.62 – 7.52 (m, 1H), 7.33 – 7.21 (m, 3H), 7.16 (dd, *J*=7.8, 4.9, 1H), 7.06 (s, 1H), 6.81 (d, *J*=8.0, 1H), 6.61 (d, *J*=8.0, 2H), 4.07 (s, 1H), 3.99 (s, 3H), 1.90 (s, 3H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ = 185.09, 176.63, 155.71, 150.71, 149.39, 143.71, 137.83, 136.51, 133.61, 129.87, 128.32, 127.86, 126.61, 125.96, 124.26, 122.47, 117.97, 116.77, 115.92, 114.11, 110.29, 50.53, 32.70, 21.46; **HRMS (ESI)** calculated for $C_{26}H_{21}N_4O_4S$ $(M+H)^+$ 485.1278, found 485.1257.

5. Reaction of isatin tethered *N*-sulfonyl-1,2,3-triazole (1a) with 1,2-dimethylindole and 1,3-dimethyl indole:



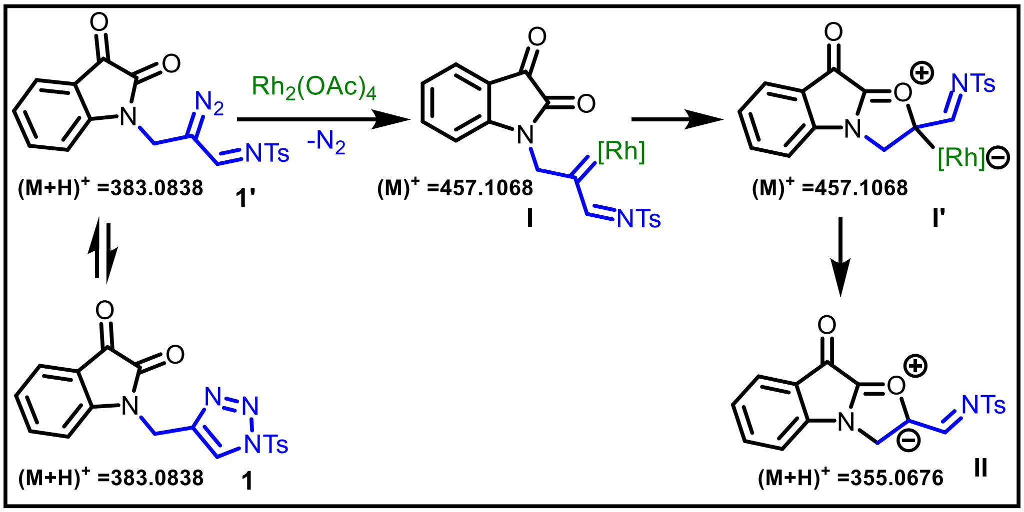
To an oven dried 10 ml round bottom flask equipped with reflux condenser added $Rh_2(Oct)_4$ catalyst (5 mol%), isatin derived N-sulfonyl-1,2,3-triazole **1a** (0.22 mmol) and indole **2i** (0.2 mmol) followed by 4 ml of 1,2-dichloroethane (DCE) as solvent. The reaction mixture was heated to 80 °C with constant stirring for 8 hrs. After completion of reaction the crude reaction mixture was purified by silica gel (100-200 Mesh) flash column chromatography using ethyl acetate/petroleum ether as eluent to obtain product **4** as a white solid.

(In the case of 1,3-dimethylindole the reaction failed to give product)

***N*-(5,5a-dimethyl-7,14-dioxo-5,5a,6,7,8,14-hexahydroazepino[1,2-a:4,3-b']diindol-6-yl)-4-methylbenzenesulfonamide (4):** Obtained as a white solid. Yield = 88 %; m. p.=120-122 °C; R_f = 0.4 (Ethyl Acetate/Hexane : 40/60); **^{1}H NMR (500 MHz, $CDCl_3$)** δ = 7.82 – 7.72 (m, 7H), 7.70 – 7.60 (m, 2H), 7.59 – 7.52 (m, 2H), 7.35 – 7.28 (m, 5H), 7.23 (t, *J*=7.7, 2H), 7.14 (t, *J*=7.6, 2H), 7.06 (t, *J*=8.6, 2H), 7.00 (dd, *J*=17.9, 7.6, 2H), 6.93 (d, *J*=8.1, 1H), 6.87 (t, *J*=6.8, 1H), 5.05 (d, *J*=9.1, 1H), 4.32 (dd, *J*=28.2, 11.9, 1H), 4.24 (d, *J*=9.2, 1H), 4.13 – 4.04 (m, 2H), 3.87 (d, *J*=17.8, 1H), 3.65 (s, 3H), 3.60 (s, 3H), 2.73 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H); **^{13}C NMR**

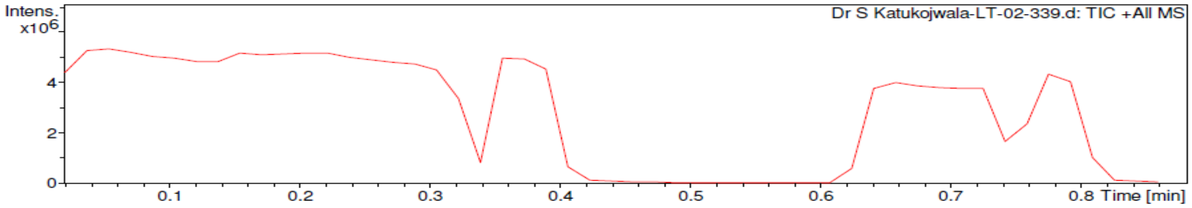
(126 MHz, CDCl$_3$) δ = 208.51, 206.14, 198.70, 198.47, 161.88, 160.75, 144.21, 143.92, 138.37, 137.86, 137.77, 137.44, 136.90, 136.88, 136.15, 135.61, 129.88, 129.70, 127.80, 127.39, 126.53, 126.36, 126.14, 125.69, 123.09, 121.81, 121.56, 121.28, 121.13, 120.69, 120.60, 120.30, 120.14, 119.96, 111.86, 111.47, 109.10, 109.05, 103.48, 100.95, 78.09, 75.02, 66.26, 63.56, 53.88, 52.81, 29.79, 29.57, 21.75, 21.71, 14.80, 11.79; **HRMS (ESI)** calculated for $C_{28}H_{25}N_3KO_4S$ $(M+K)^+$ 538.1203, found 538.1194.

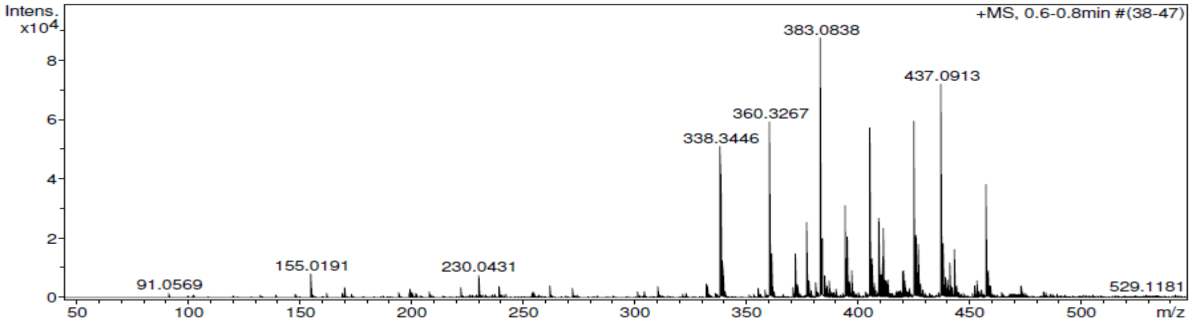
6. ESI-MS analysis of intermediates: To predict the possible mechanism of domino reaction the intermediates formed were analyzed by ESI-MS technique. For this the $Rh_2(OAc)_4$ catalyzed denitrogenative decomposition of isatin tethered *N*-sulfonyl-1,2,3-triazole was carried out at 80 °C for 30 minutes in absence of indole using DCE as solvent. Then the reaction mixture was cooled to room temperature, filtered through a celite pad and diluted with methanol. The diluted reaction mixture was subjected for ESI-MS analysis. The spectra obtained clearly indicates the formation of intermediates **I/I’** and **II** along with starting isatin tethered *N*-sulfonyl-1,2,3-triazole.(as shown below)

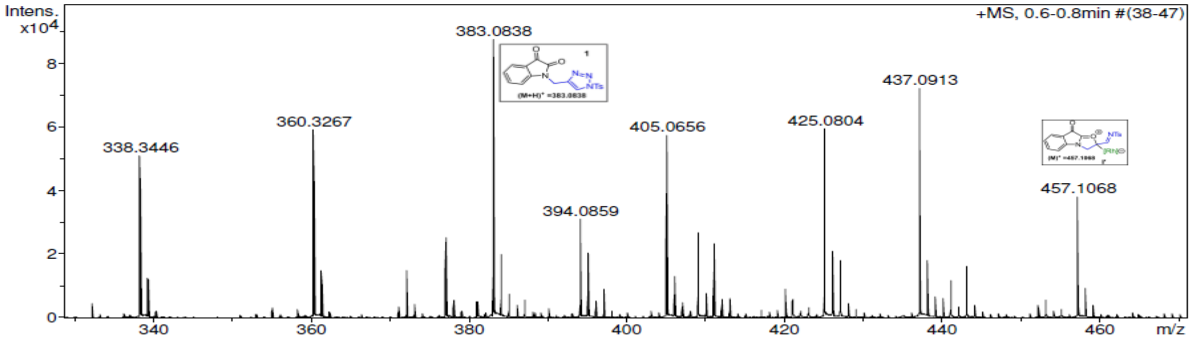


Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste



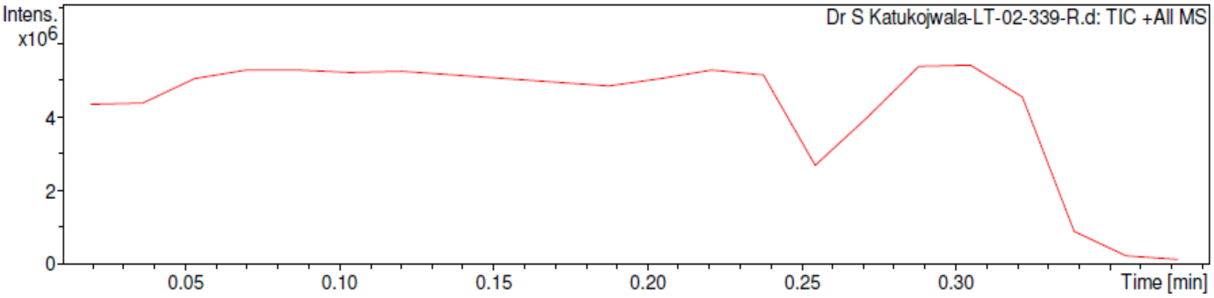


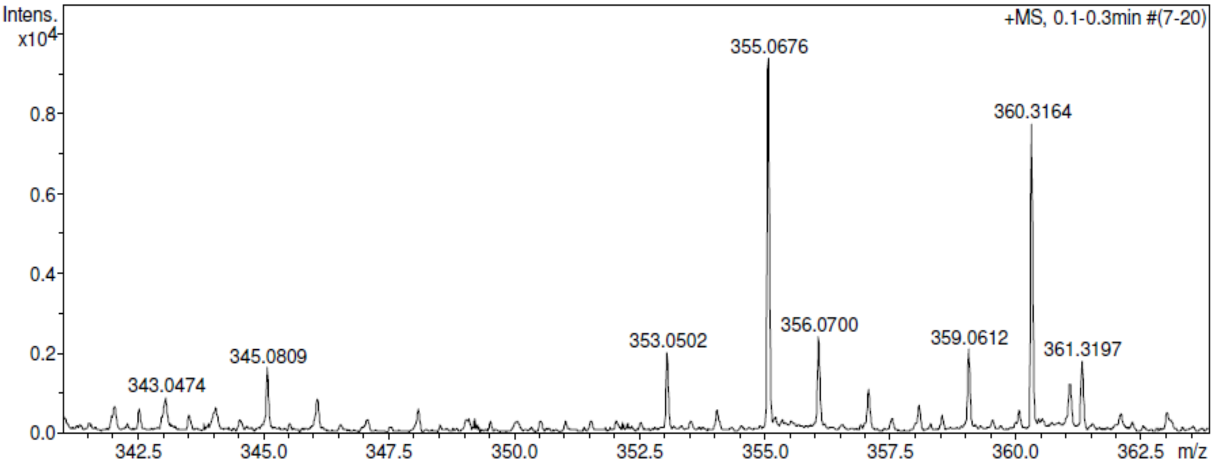


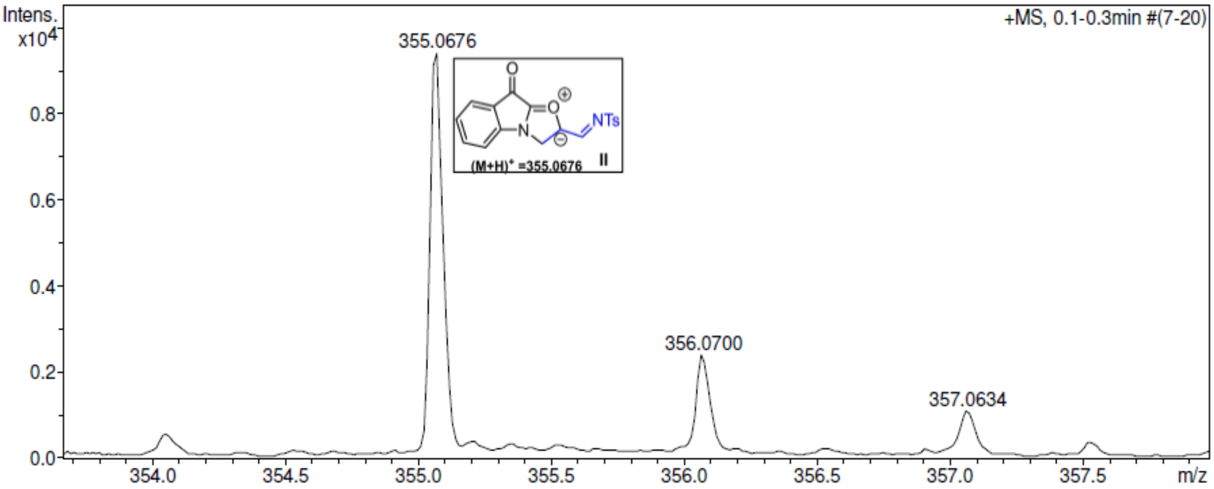
Bruker Compass DataAnalysis 4.0 printed: 9/6/2019 12:42:05 PM Page 1 of 1

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste

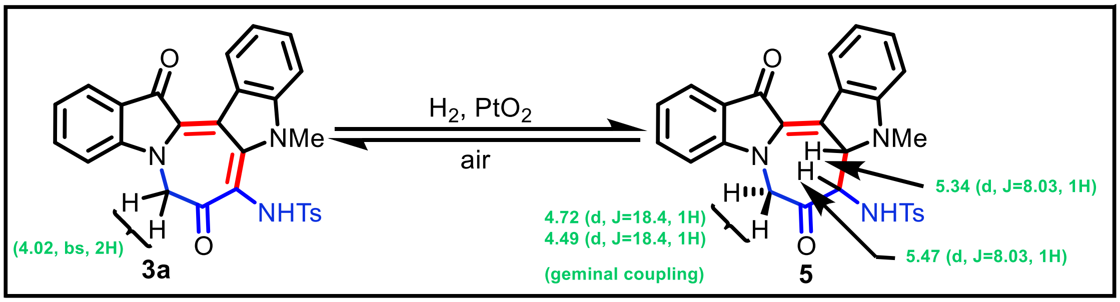




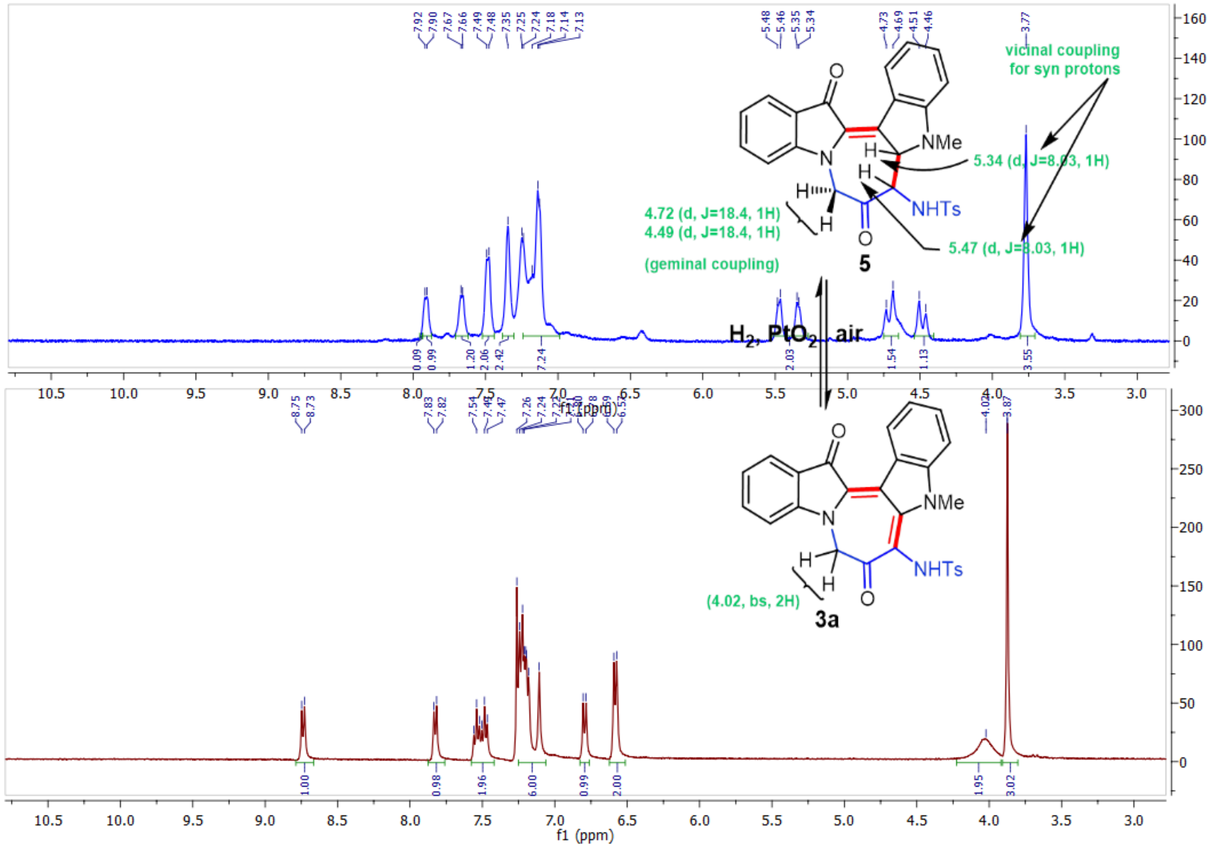


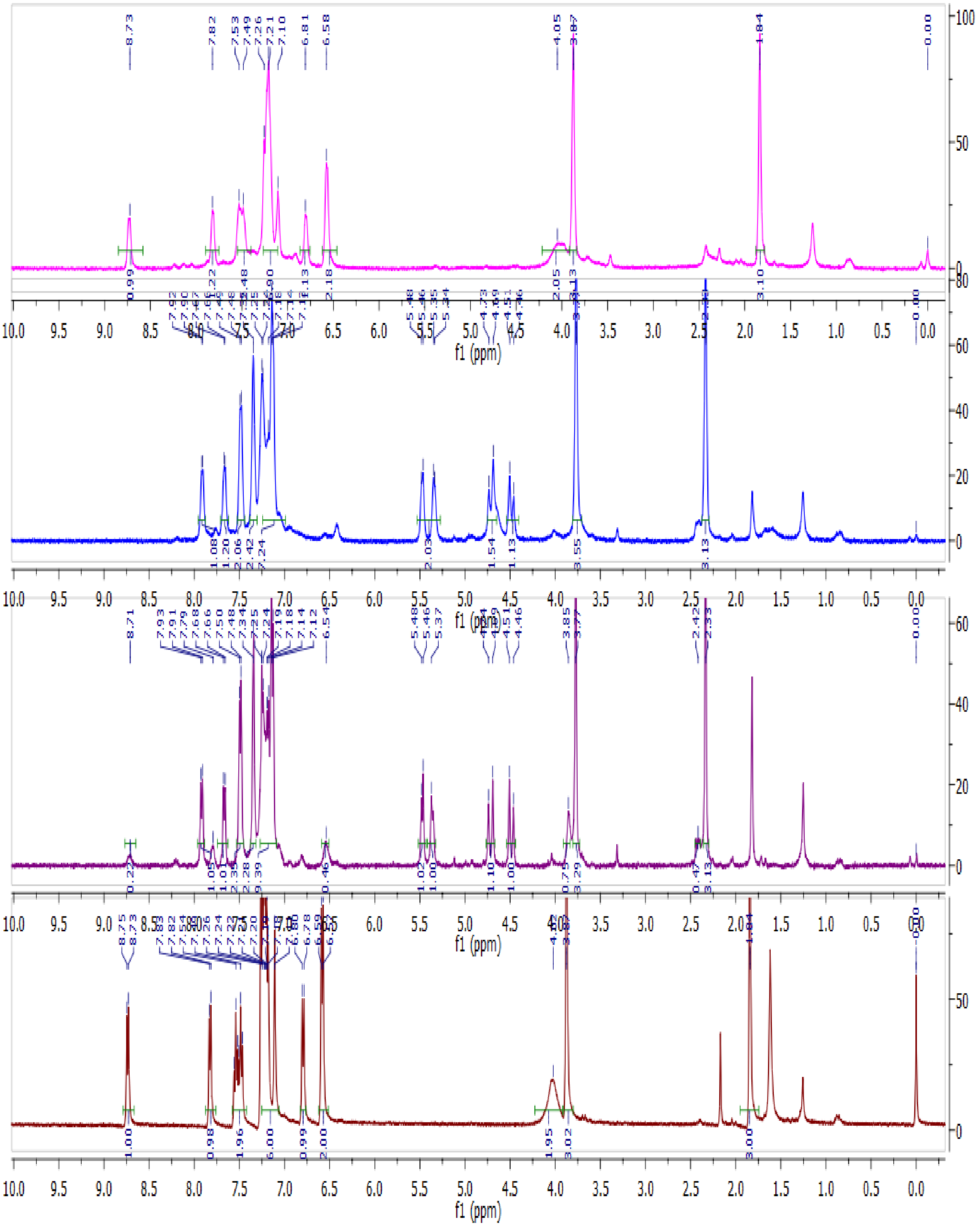
Bruker Compass DataAnalysis 4.0 printed: 9/6/2019 4:19:25 PM Page 1 of 1

7. Hydrogenation studies on azepino fused diindoles:

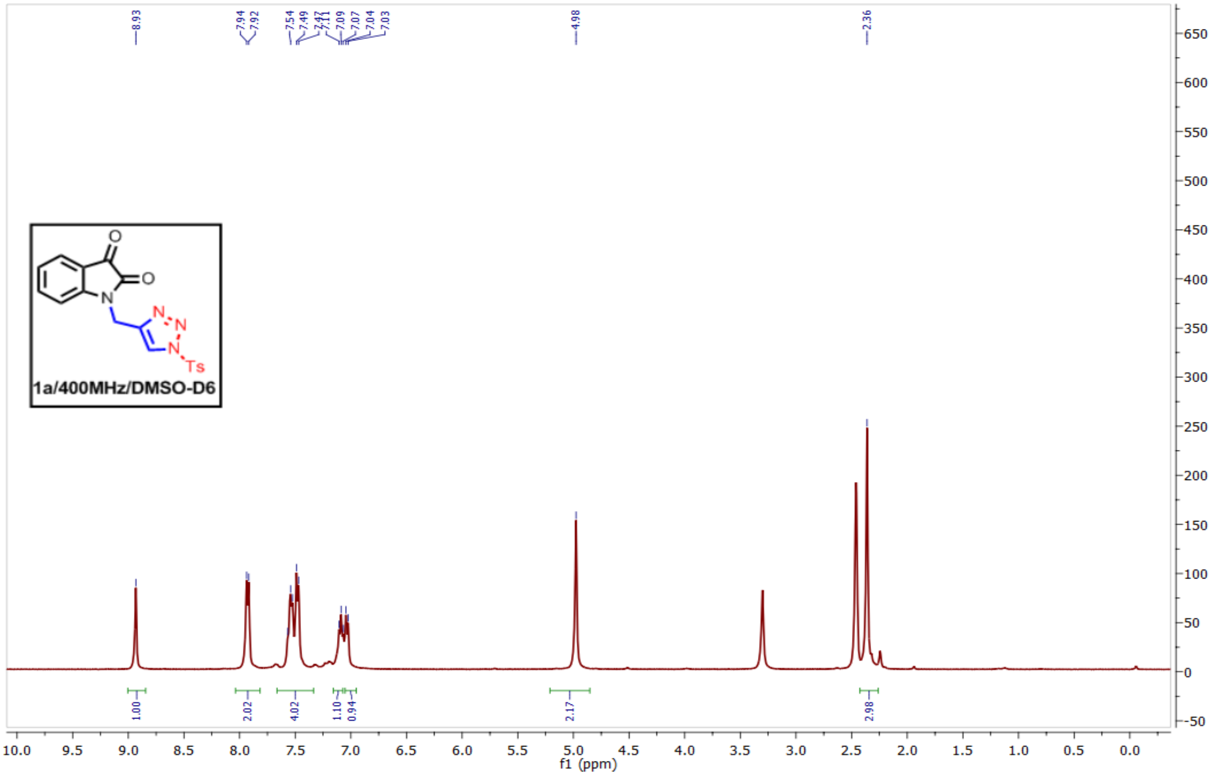


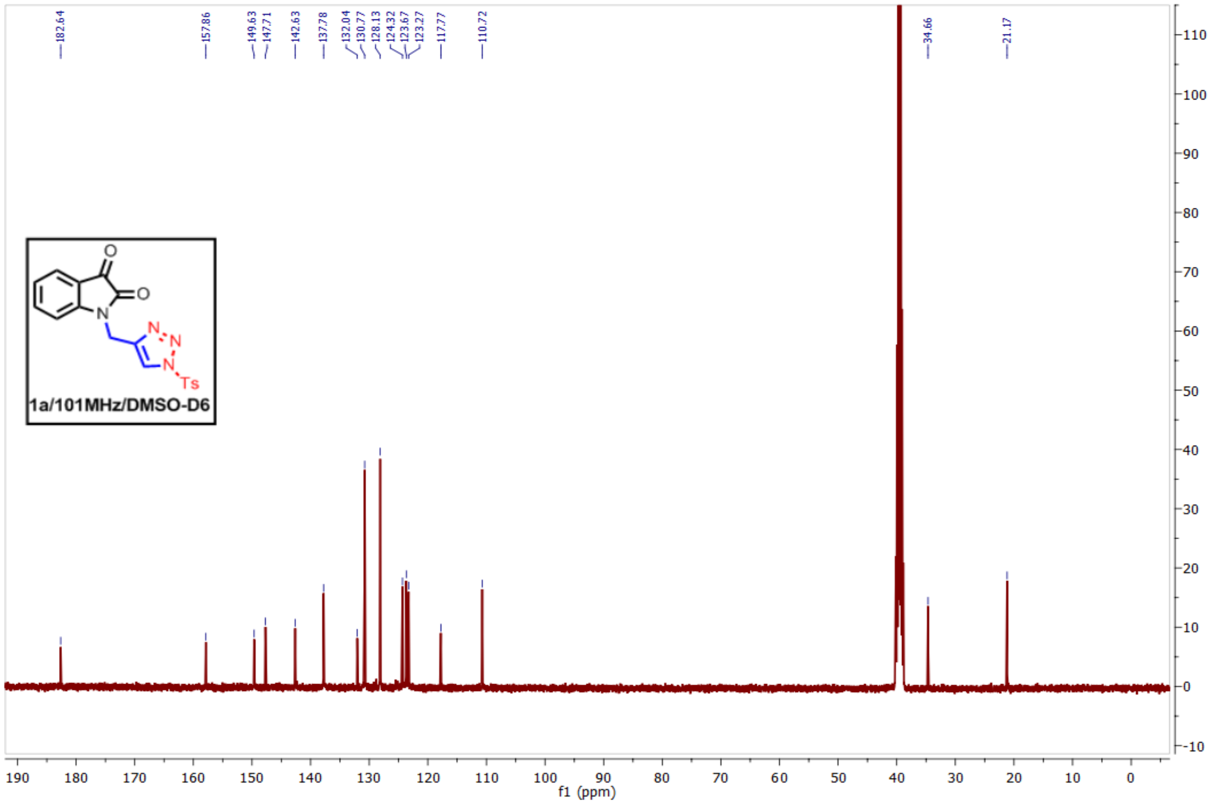
When hydrogenation reactions were carried out on azepino fused diindole **3a** using 10 mol% PtO_2 catalyst in 2 ml $CDCl_3$, it resulted in hydrogenated product **5.** When **5** was exposed to air it underwent rapid reversible oxidation to reproduce **3a**. The redox reaction was repeated, and results were reproduced. The products were analyzed by ^1H NMR spectroscopic analysis. The appearance of ^1H NMR signals at δ = 4.72 (d, *J*=18.4, 1H), 4.49 (d, *J* = 18.4, 1H); and 5.47 (d, *J*=8.03,1H), 5.34 (d, *J* = 8.03,1H) confirms formation of hydrogenated product **5**.

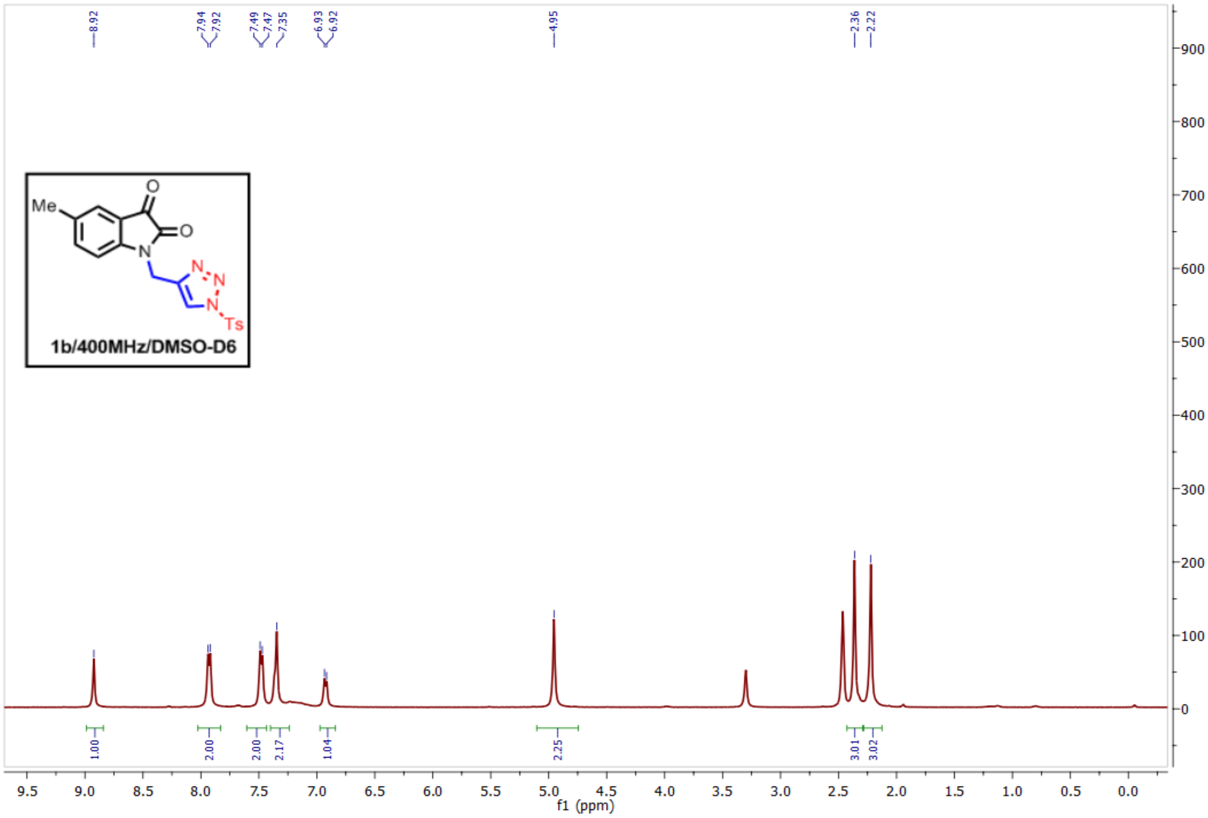


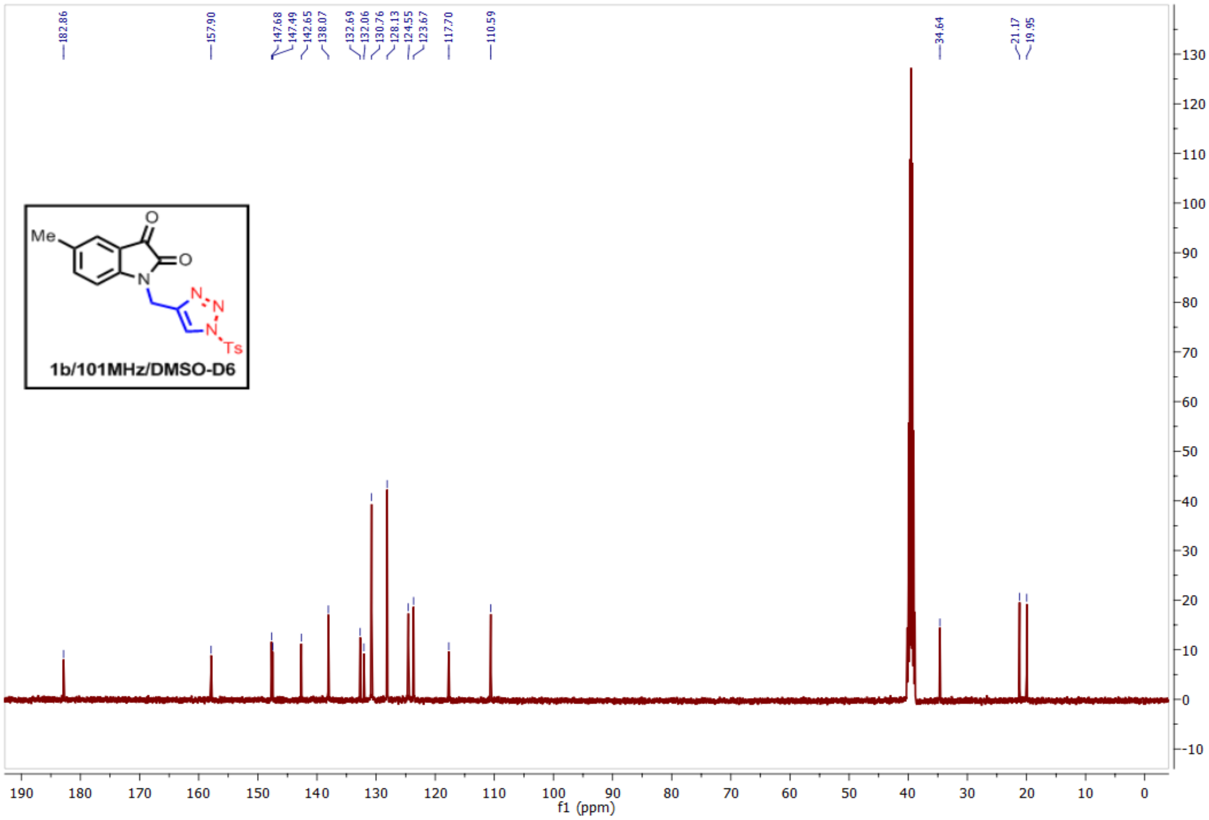

8.73
7.82
7.53
7.49
7.26
7.21
7.10
6.81
6.58
4.05
3.87
1.84
0.00
0.99
1.22
2.48
6.00
1.13
2.18
2.05
3.13
3.10
100
50
0
7.92
7.90
7.67
7.66
5.48
5.46
5.35
5.34
4.73
4.69
4.51
4.46
0.00
1.08
1.20
2.06
2.42
7.24
2.03
1.54
1.13
3.55
3.13
80
60
40
20
0
8.71
7.93
7.91
7.79
7.68
7.66
7.50
7.48
7.34
7.25
7.24
7.19
7.18
7.14
7.12
6.54
5.48
5.46
5.37
4.51
4.46
3.85
3.77
2.42
2.33
0.00
0.22
1.05
1.01
2.36
2.28
9.39
0.46
1.02
1.00
1.10
1.00
0.75
3.29
0.47
3.13
60
40
20
0
8.75
8.73
7.83
7.82
6.80
6.78
6.59
1.84
0.00
1.00
0.98
1.96
6.00
0.99
2.00
1.95
3.02
3.00
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

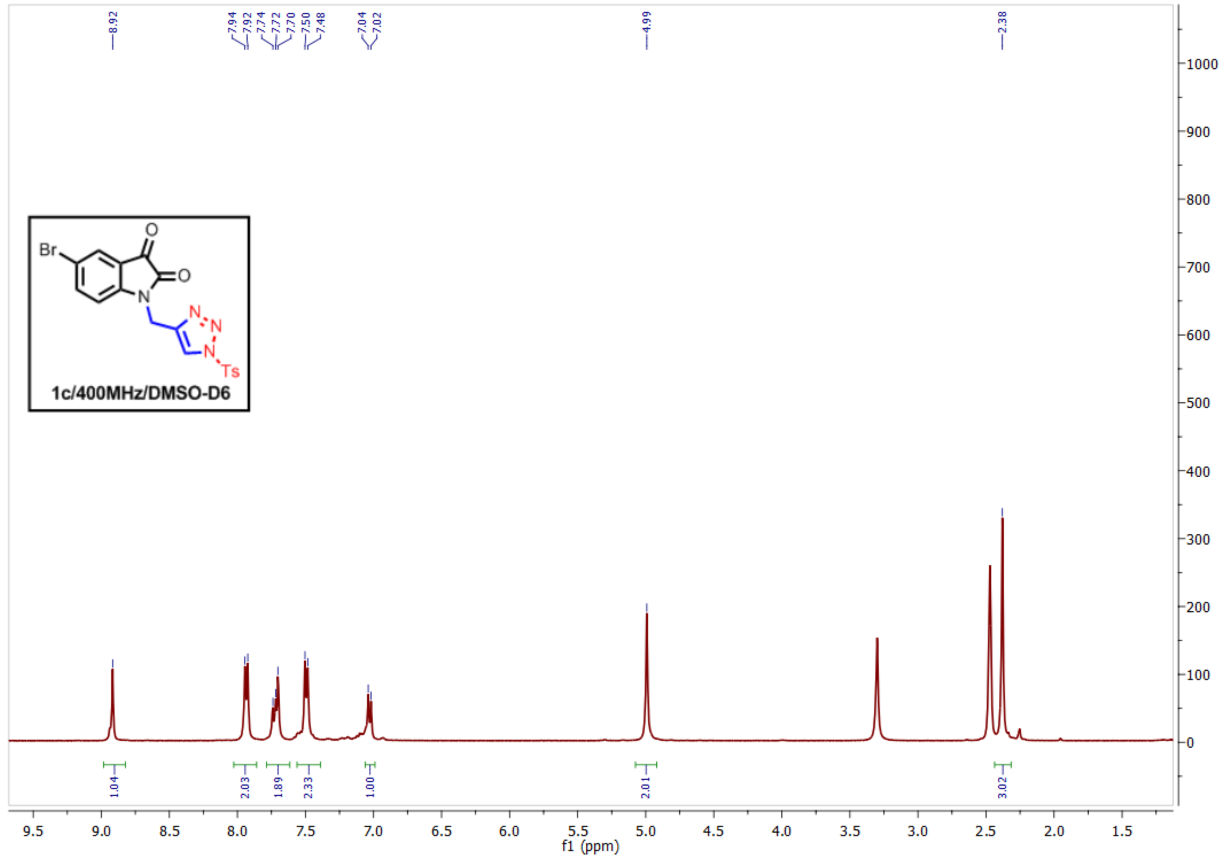
8. NMR spectra:

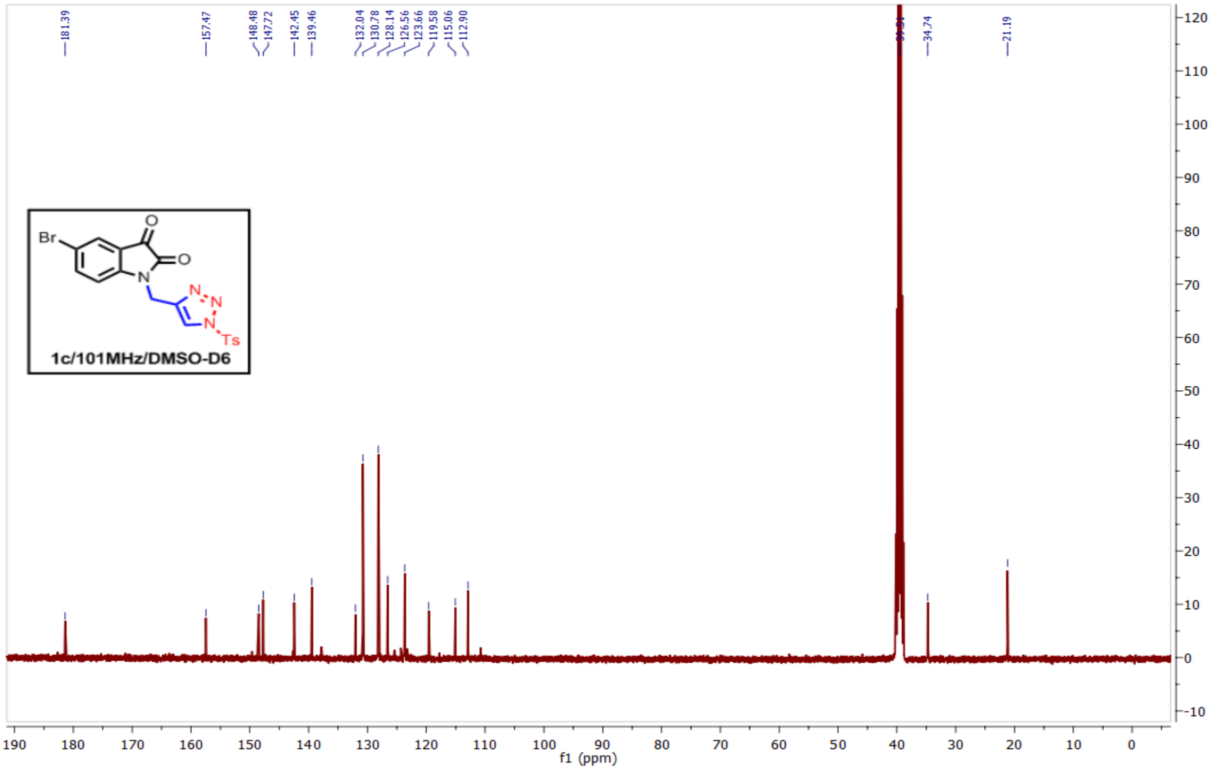


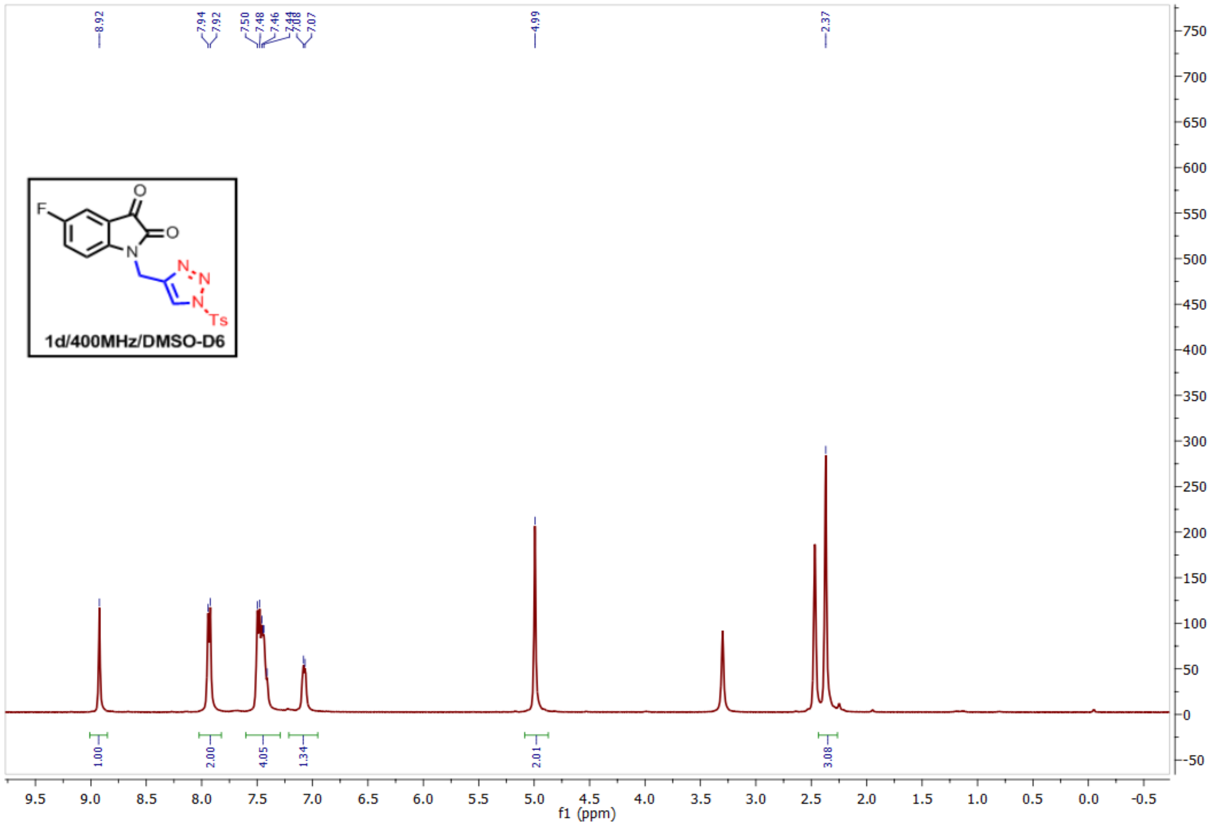


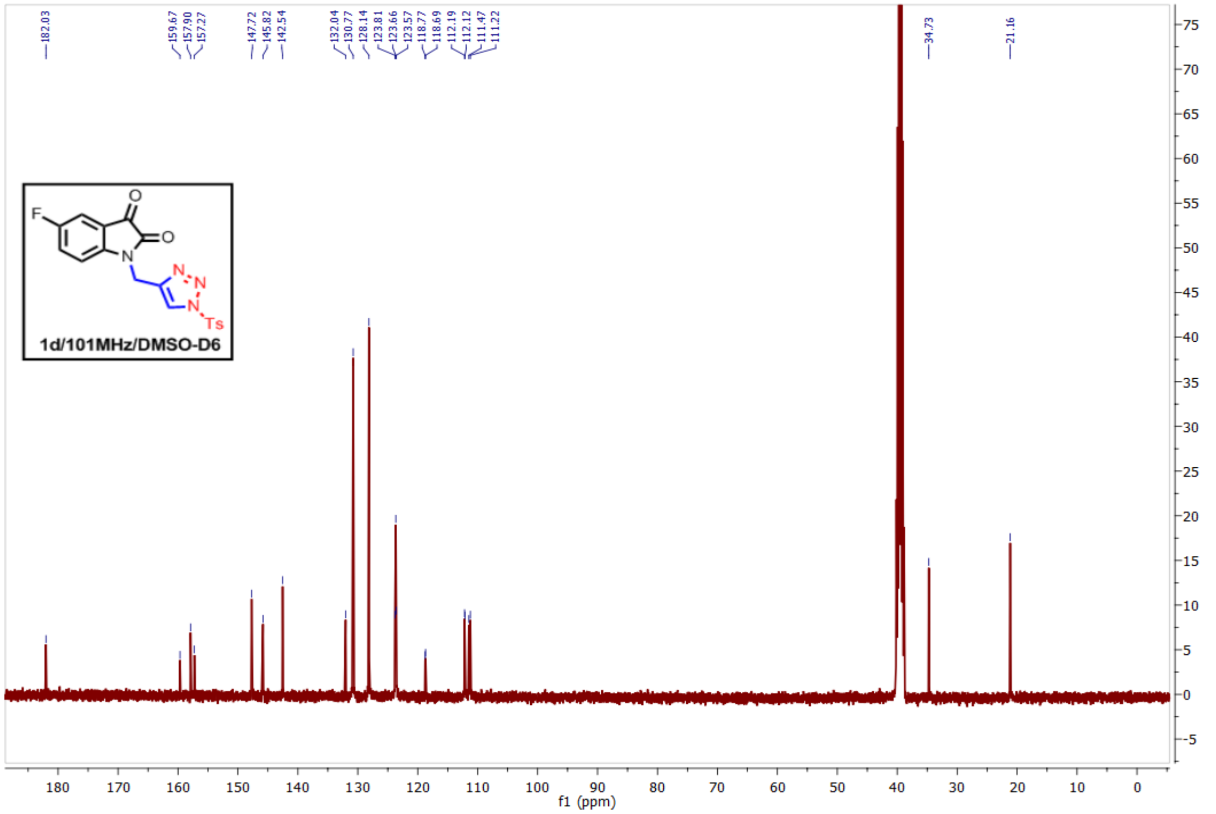

8.92
7.94
7.92
7.49
7.47
7.35
6.93
6.92
4.95
2.36
2.22
Me
O
O
N
N
N
N
Ts
1b/400MHz/DMSO-D6
1.00
2.00
2.00
2.17
1.04
2.25
3.01
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
900
800
700
600
500
400
300
200
100
0

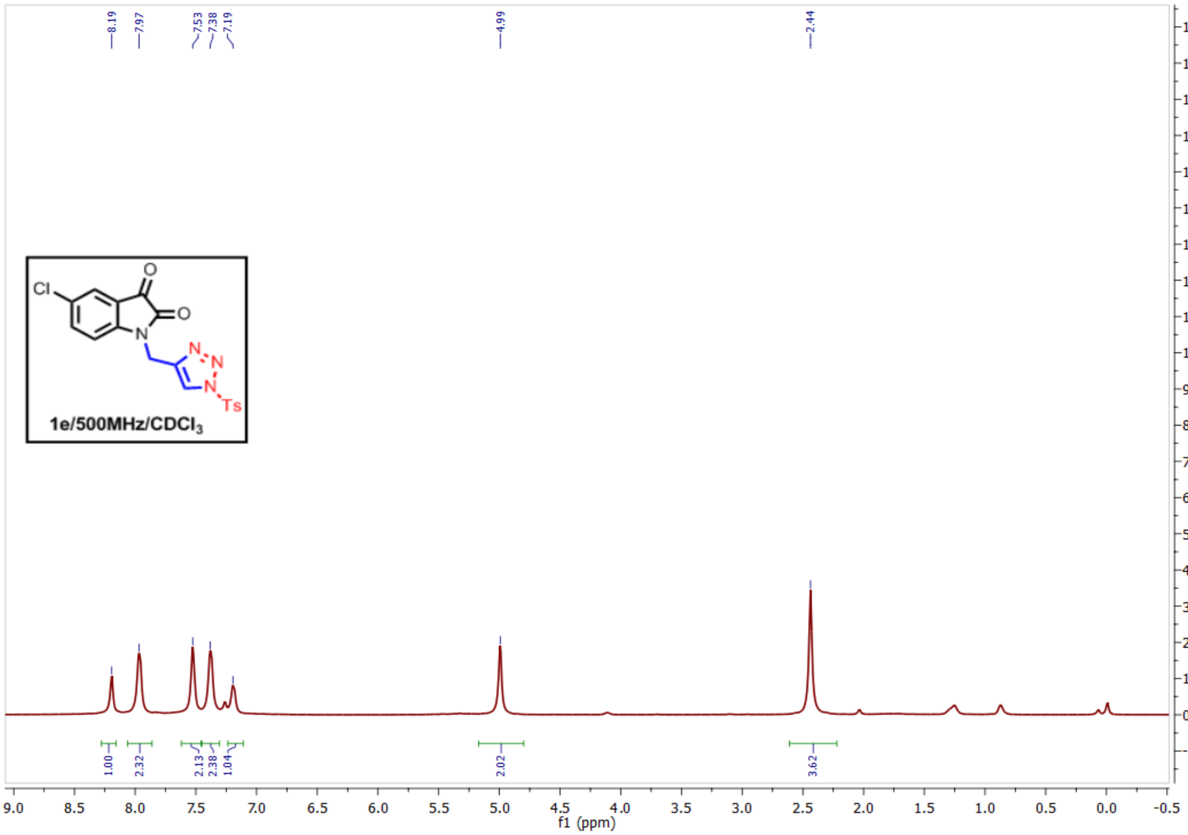

182.86
157.90
147.68
147.49
142.65
138.07
132.69
132.06
130.76
128.13
124.55
123.67
117.70
110.59
34.64
21.17
19.95
Me
O
O
N
N
N
N
Ts
1b/101MHz/DMSO-D6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

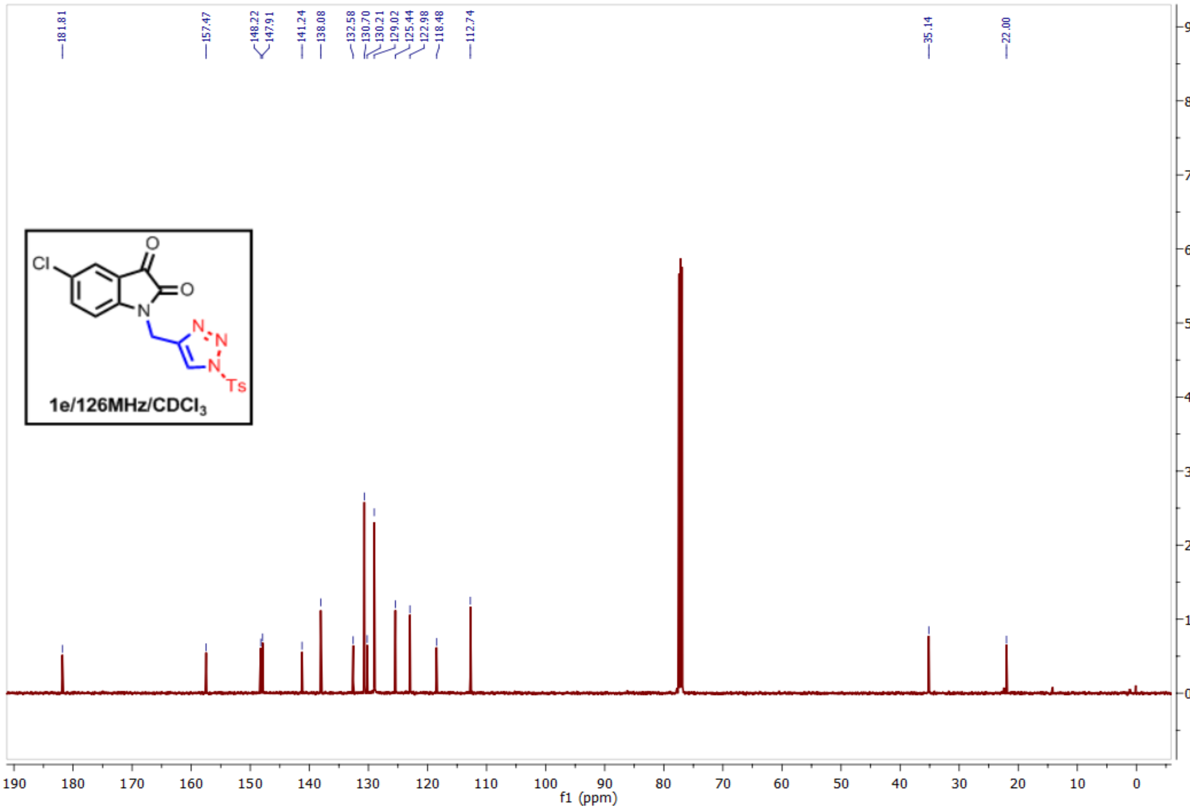

8.92
7.94
7.92
7.74
7.72
7.70
7.50
7.48
7.04
7.02
4.99
2.38
1.04
2.03
1.89
2.33
1.00
2.01
3.02
Br
O
O
N
N
N
N
Ts
1c/400MHz/DMSO-D6
1000
900
800
700
600
500
400
300
200
100
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

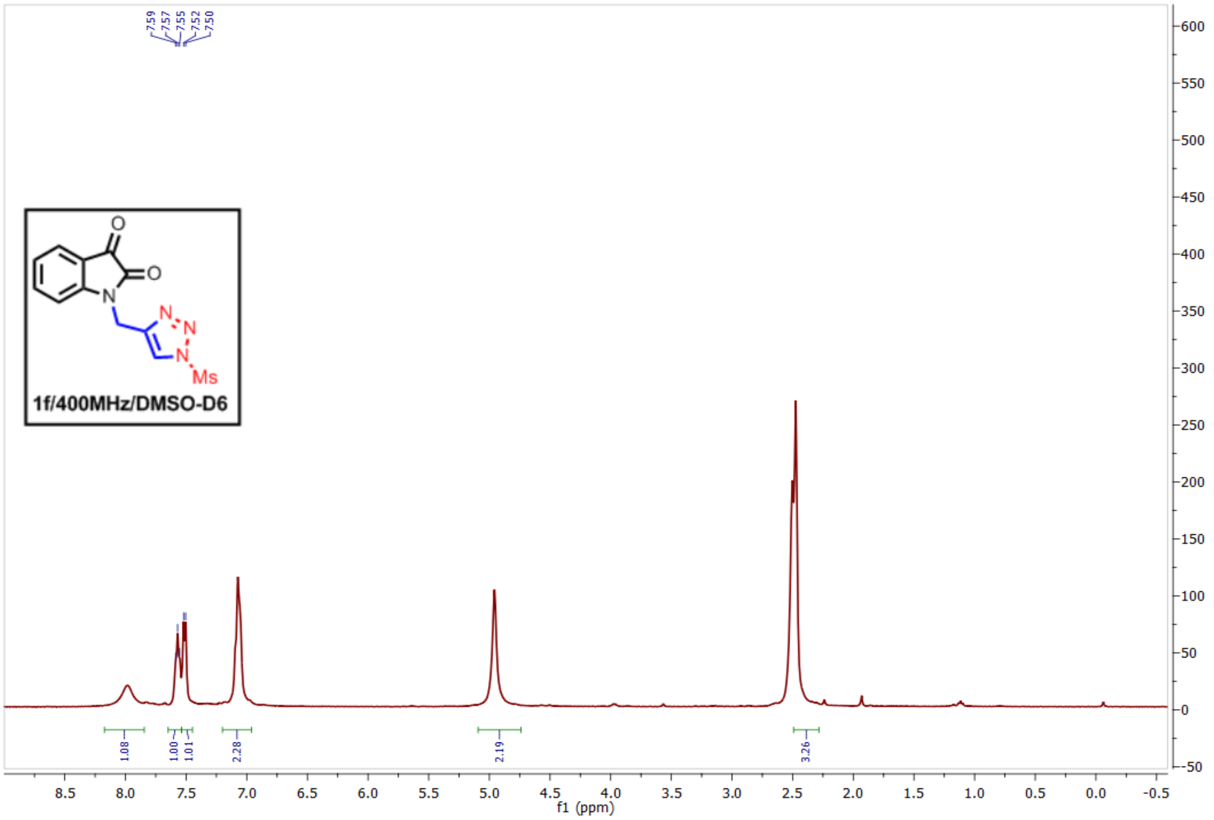

181.39
157.47
148.48
147.72
142.45
139.46
132.04
130.78
128.14
126.56
123.66
119.58
115.06
112.90
34.74
21.19
Br
O
O
N
N
N
N
Ts
1c/101MHz/DMSO-D6
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

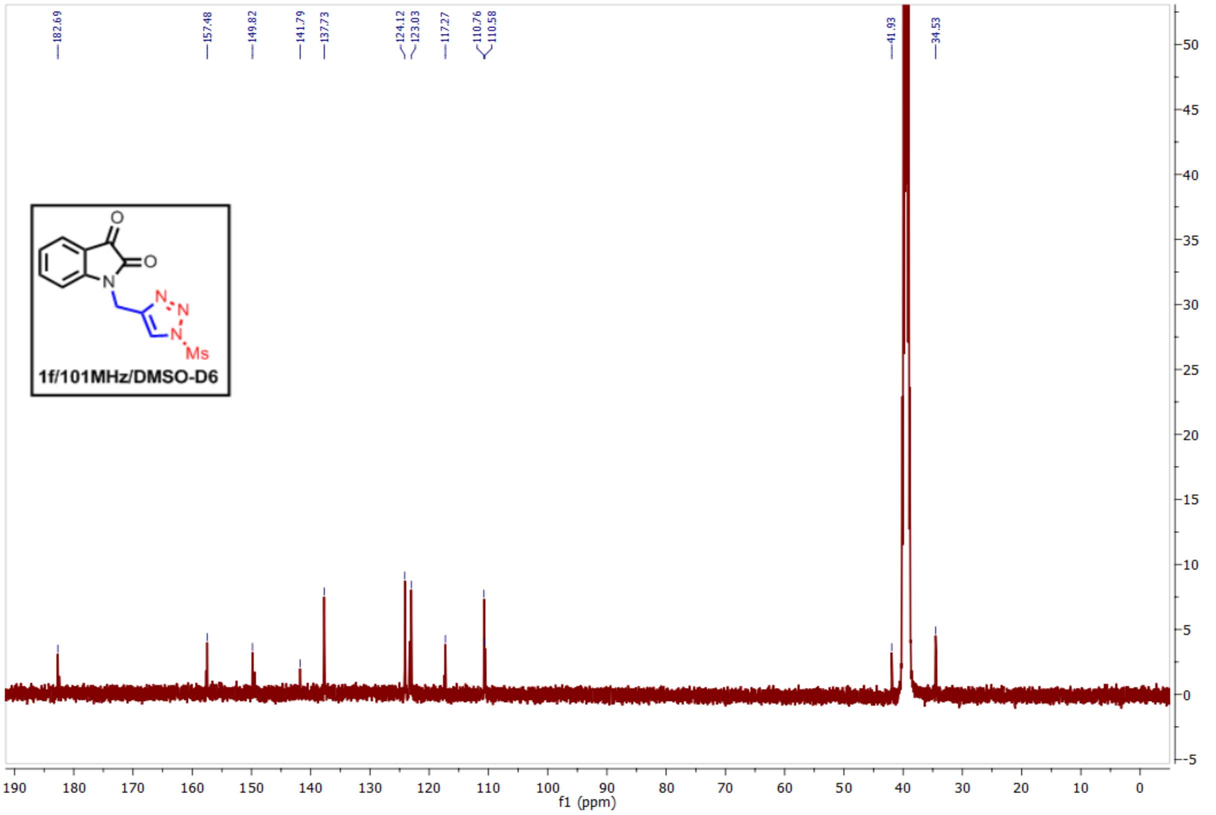

8.92
7.94
7.92
7.50
7.48
7.46
7.44
7.08
7.07
4.99
2.37
F
O
O
N
N
N
N
Ts
1d/400MHz/DMSO-D6
1.00
2.00
4.05
1.34
2.01
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

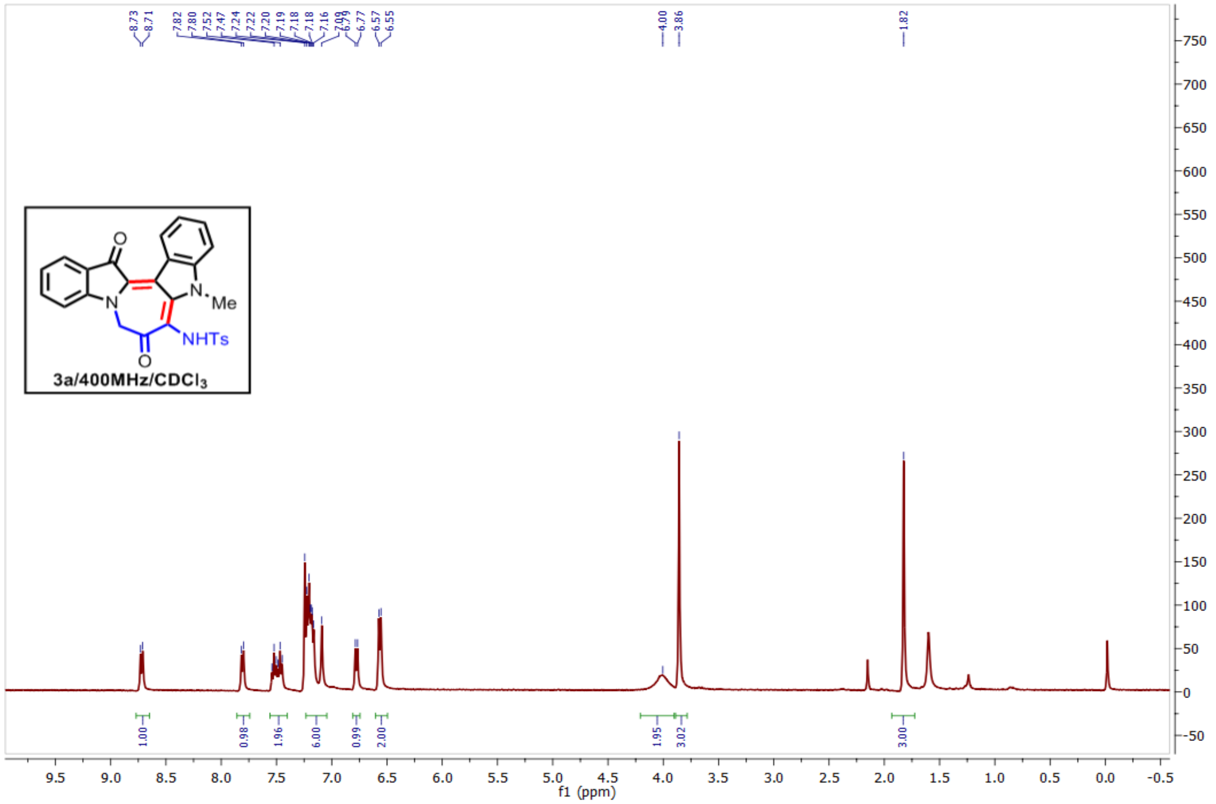

182.03
159.67
157.90
157.27
147.72
145.82
142.54
132.04
130.77
128.14
123.81
123.66
123.57
118.77
118.69
112.19
112.12
111.47
111.22
34.73
21.16
F
O
O
N
N
N
N
Ts
1d/101MHz/DMSO-D6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5


8.19
7.97
7.53
7.38
7.19
4.99
2.44
Cl
O
O
N
N
N
N
Ts
1e/500MHz/CDCl$_3$
1.00
2.32
2.13
2.38
1.04
2.02
3.62
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

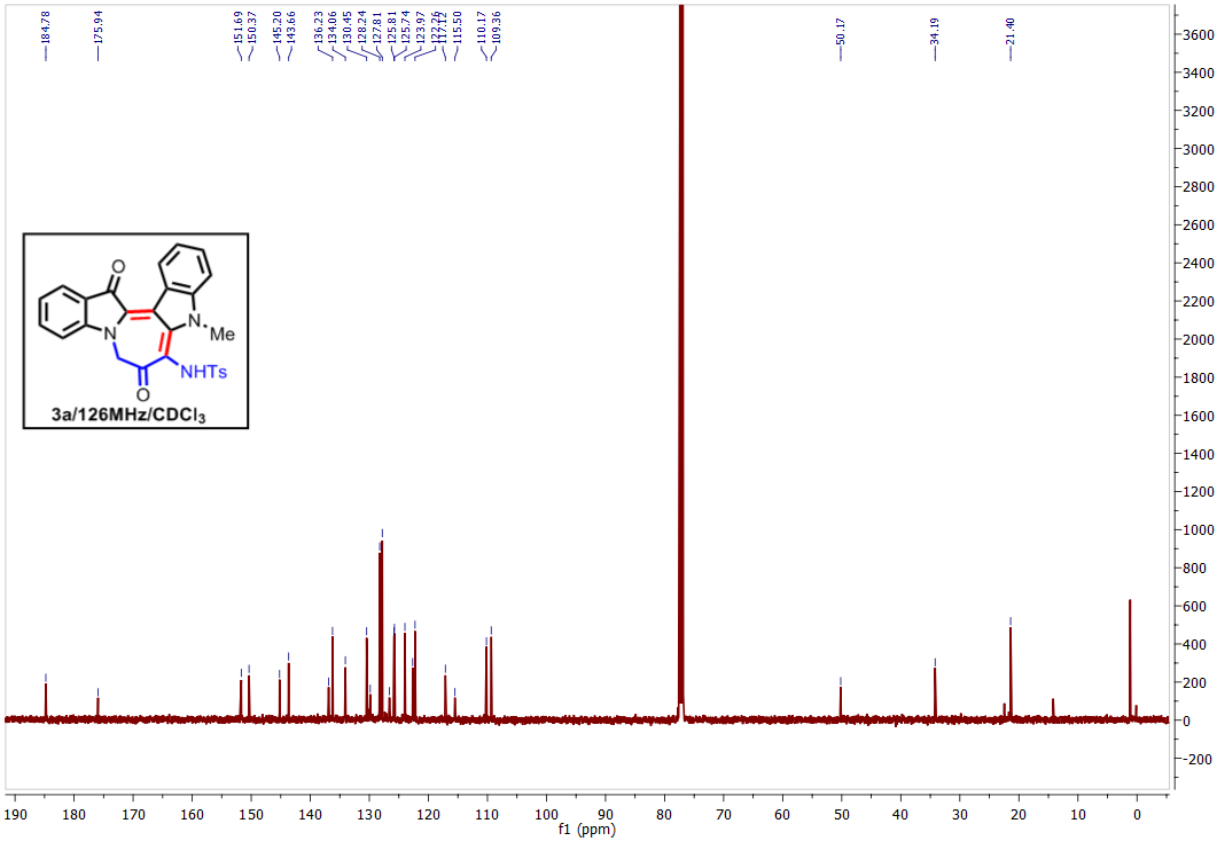

181.81
157.47
148.22
147.91
141.24
138.08
132.58
130.70
130.21
129.02
125.44
122.98
118.48
112.74
35.14
22.00
Cl
O
O
N
N
N
N
Ts
1e/126MHz/CDCl$_3$
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0


7.59
7.57
7.55
7.52
7.50
1f/400MHz/DMSO-D6
Ms
1.08
1.00
1.01
2.28
2.19
3.26
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
600 550 500 450 400 350 300 250 200 150 100 50 0 -50

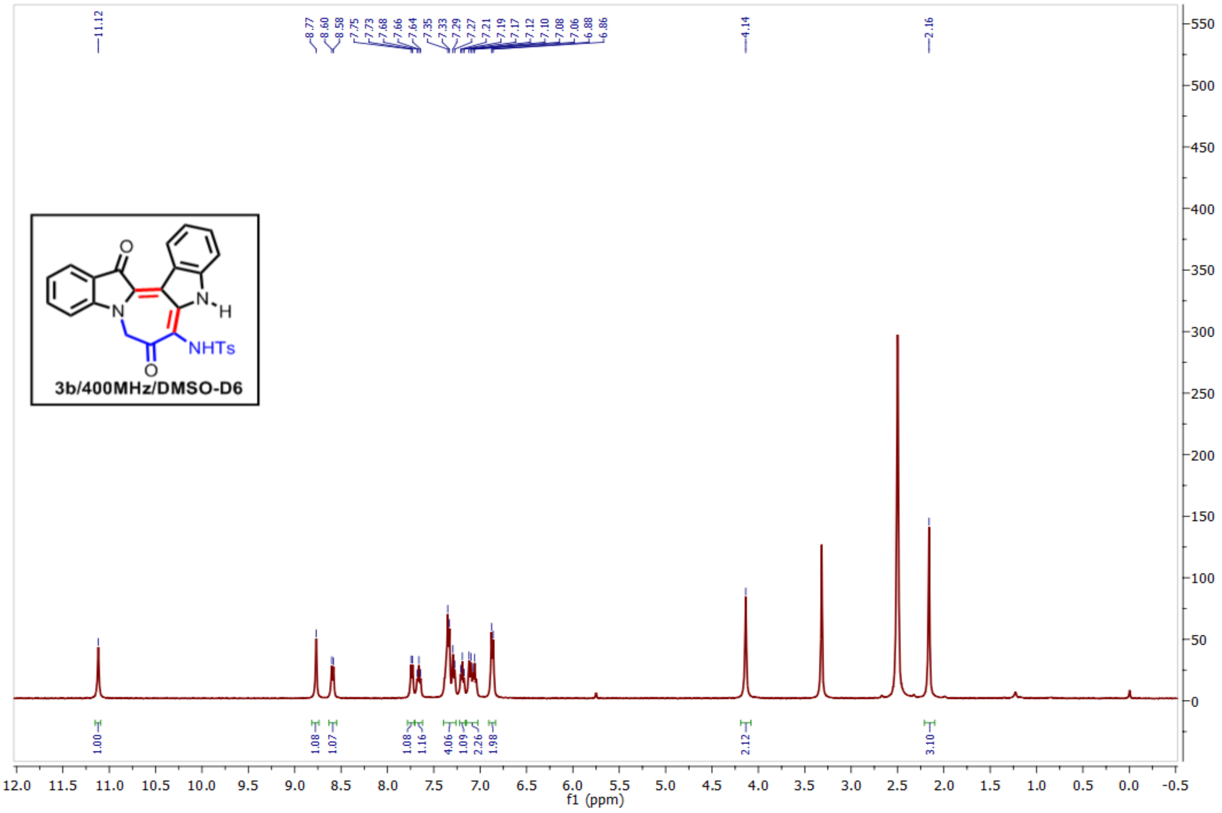

182.69
157.48
149.82
141.79
137.73
124.12
123.03
117.27
110.76
110.58
41.93
34.53
1f/101MHz/DMSO-D6
Ms
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
50 45 40 35 30 25 20 15 10 5 0 -5

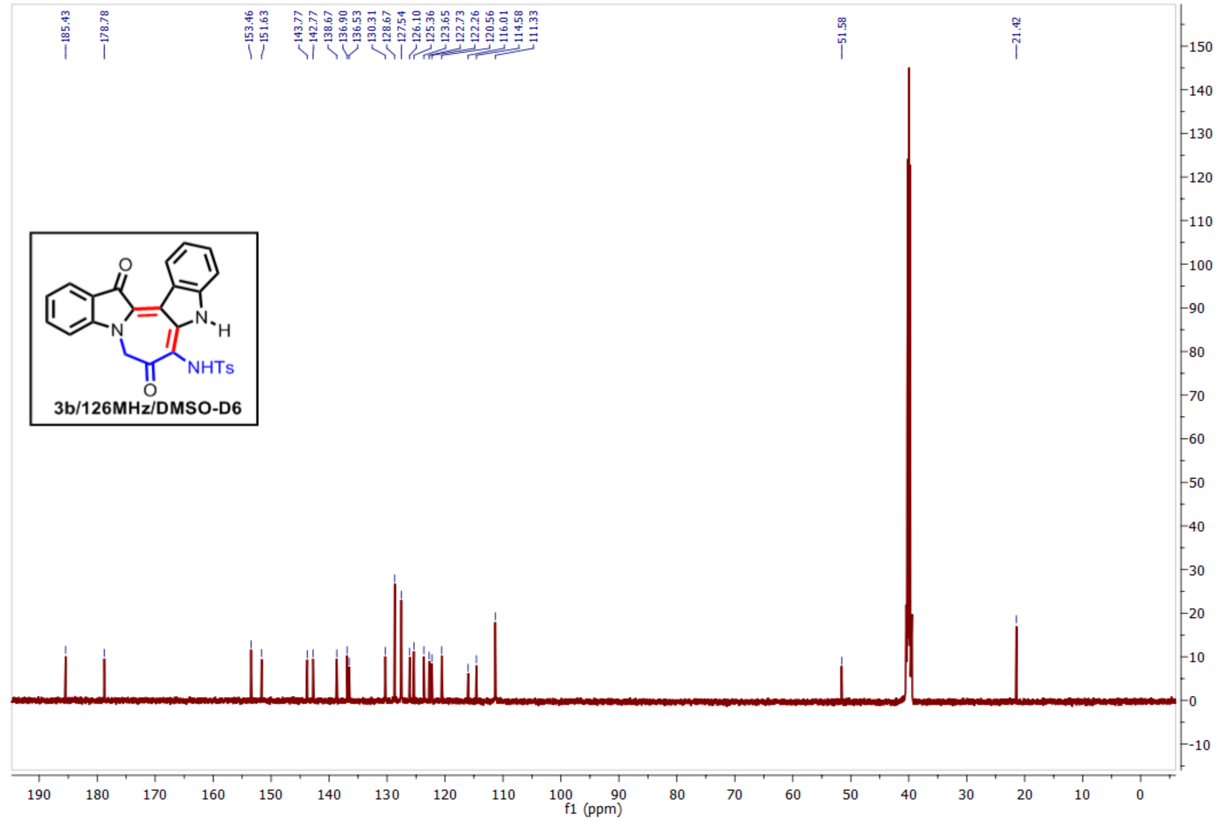


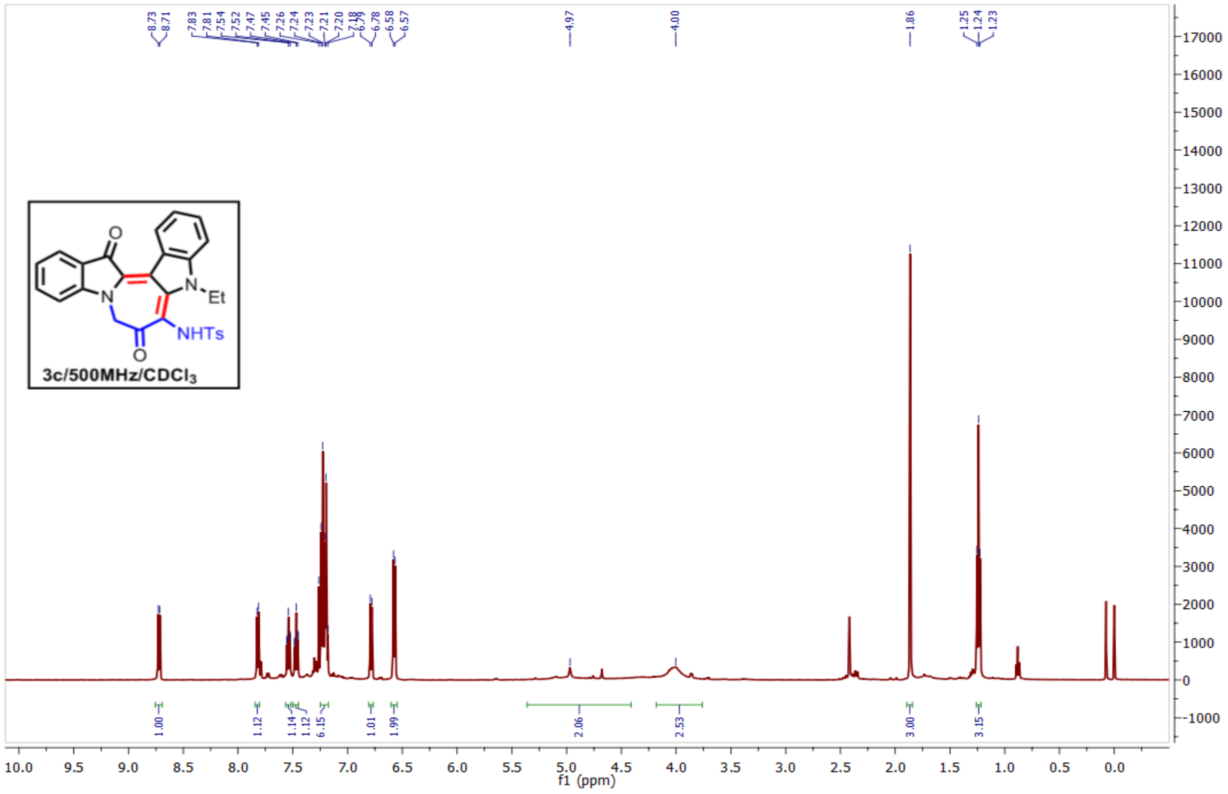
8.73
8.71
7.82
7.80
7.52
7.47
7.24
7.22
7.20
7.19
7.18
7.18
7.16
7.09
6.79
6.77
6.57
6.55
4.00
3.86
1.82
O
N
N
Me
NHTs
O
3a/400MHz/CDCl$_3$
1.00
0.98
1.96
6.00
0.99
2.00
1.95
3.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

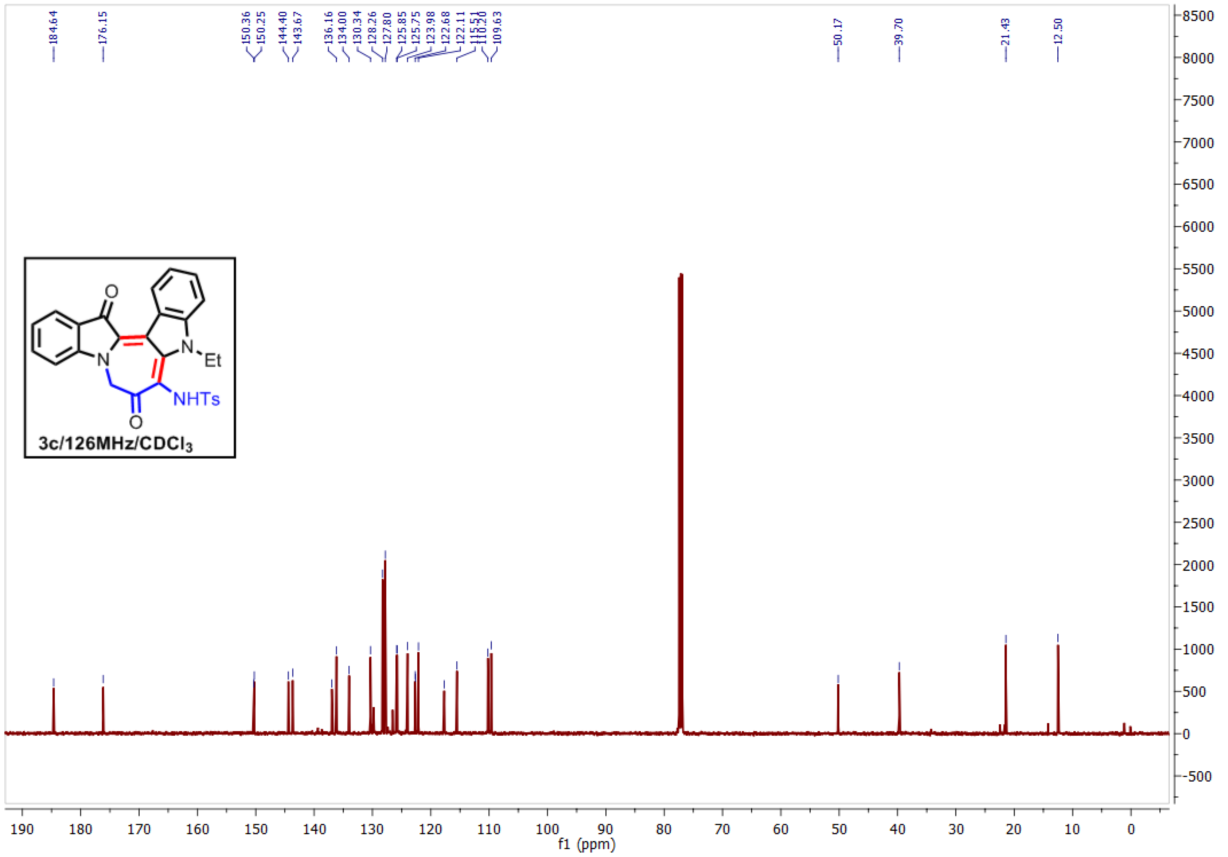


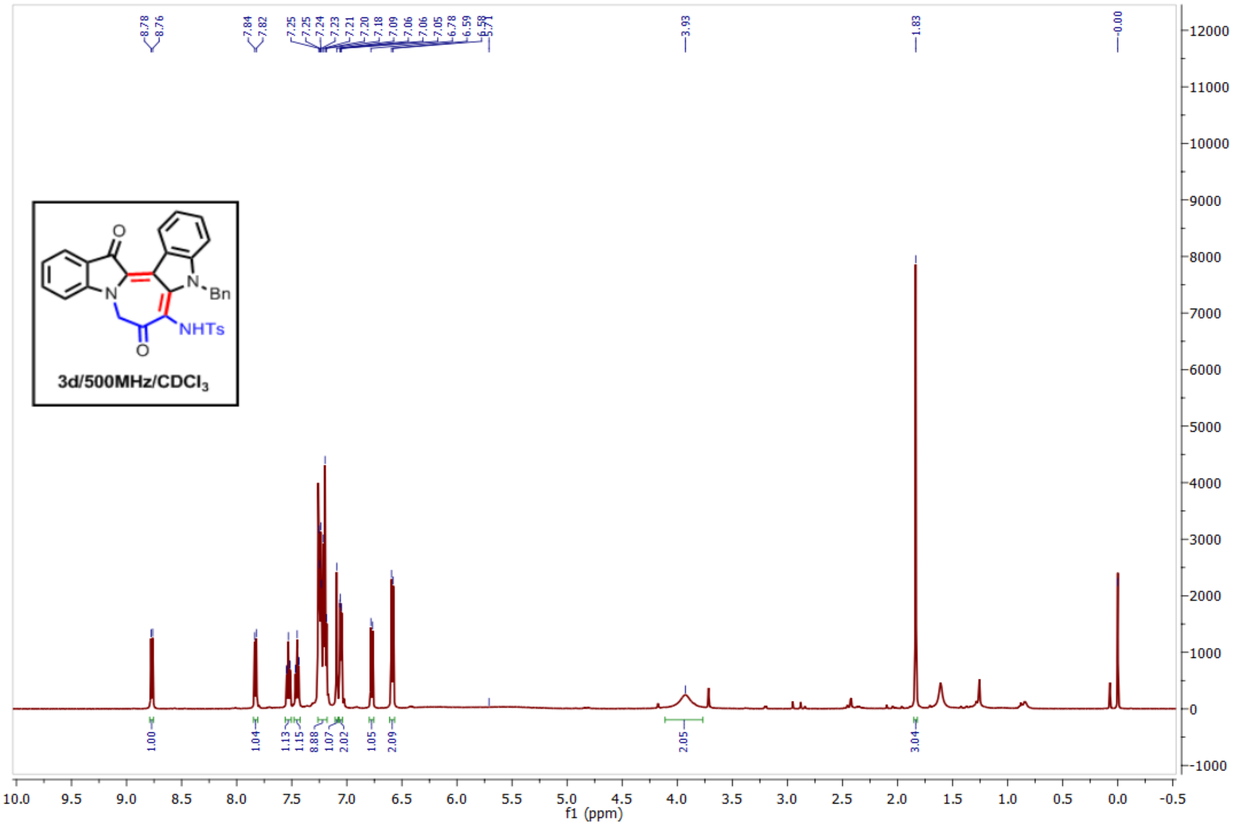
184.78
175.94
151.69
150.37
145.20
143.66
136.23
134.06
130.45
128.24
127.81
125.81
125.74
123.97
122.26
117.12
115.50
110.17
109.36
50.17
34.19
21.40
O
N
N
Me
NHTs
O
3a/126MHz/CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


11.12
8.77
8.60
8.58
7.75
7.73
7.68
7.66
7.64
7.35
7.33
7.29
7.27
7.21
7.19
7.17
7.12
7.10
7.08
7.06
6.88
6.86
4.14
2.16
1.00
1.08
1.07
1.08
1.16
4.06
1.09
2.26
1.98
2.12
3.10
O
N
N
H
NHTs
O
3b/400MHz/DMSO-D6
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0

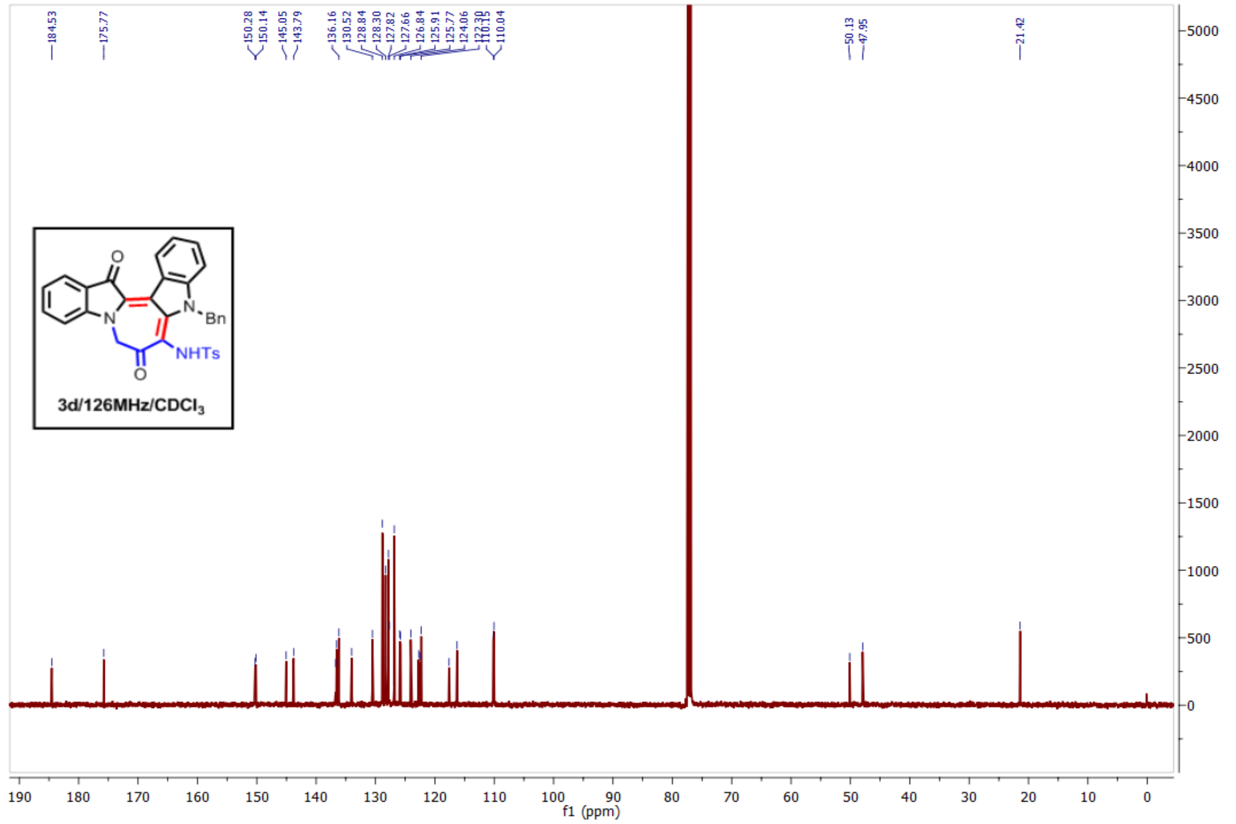

185.43
178.78
153.46
151.63
143.77
142.77
138.67
136.90
136.53
130.31
128.67
127.54
126.10
125.36
123.65
122.73
122.26
120.56
116.01
114.58
111.33
51.58
21.42
O
N
N
H
NHTs
O
3b/126MHz/DMSO-D6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.73
8.71
7.83
7.81
7.54
7.52
7.47
7.45
7.26
7.24
7.23
7.21
7.20
7.18
6.79
6.78
6.58
6.57
4.97
4.00
1.86
1.25
1.24
1.23
3c/500MHz/CDCl$_3$
NHTs
N
Et
O
1.00
1.12
1.14
1.12
6.15
1.01
1.99
2.06
2.53
3.00
3.15
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

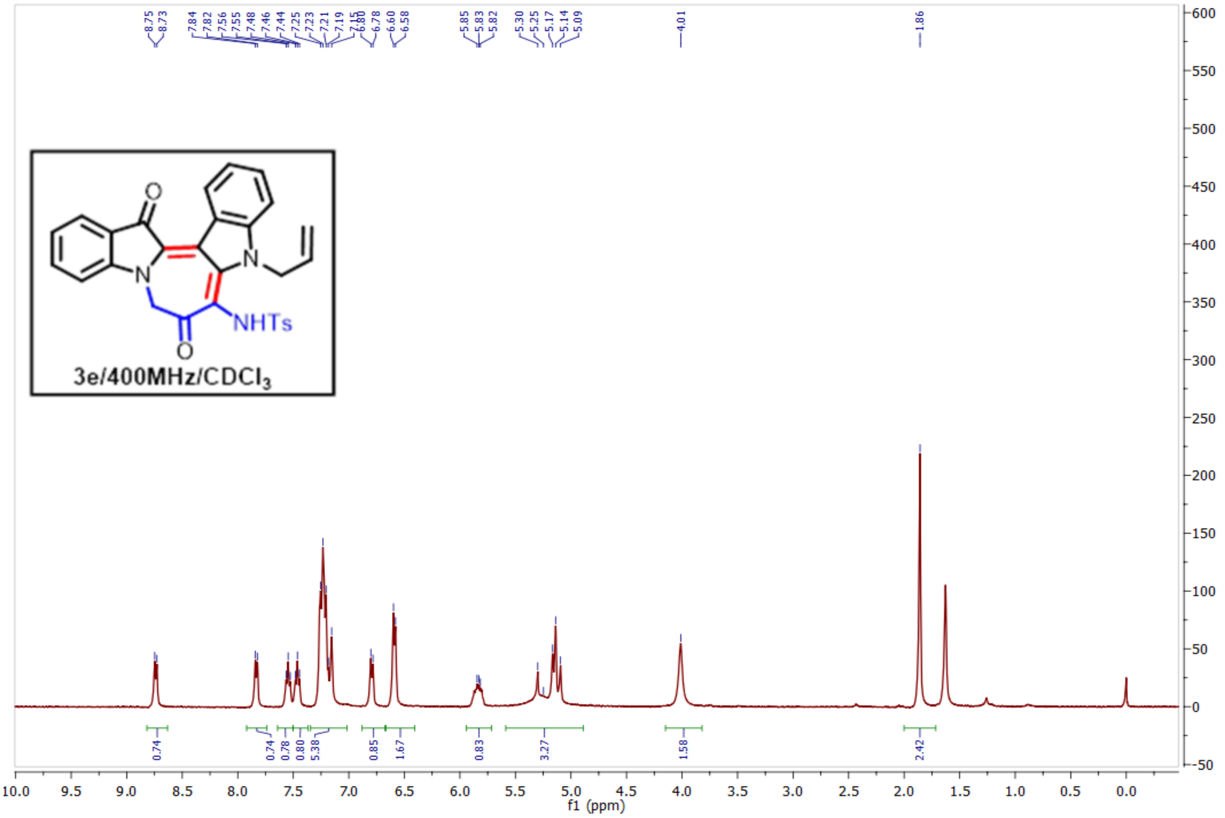

184.64
176.15
150.36
150.25
144.40
143.67
136.16
134.00
130.34
128.26
127.80
125.85
125.75
123.98
122.68
122.11
115.51
110.20
109.63
50.17
39.70
21.43
12.50
3c/126MHz/CDCl$_3$
NHTs
N
Et
O
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

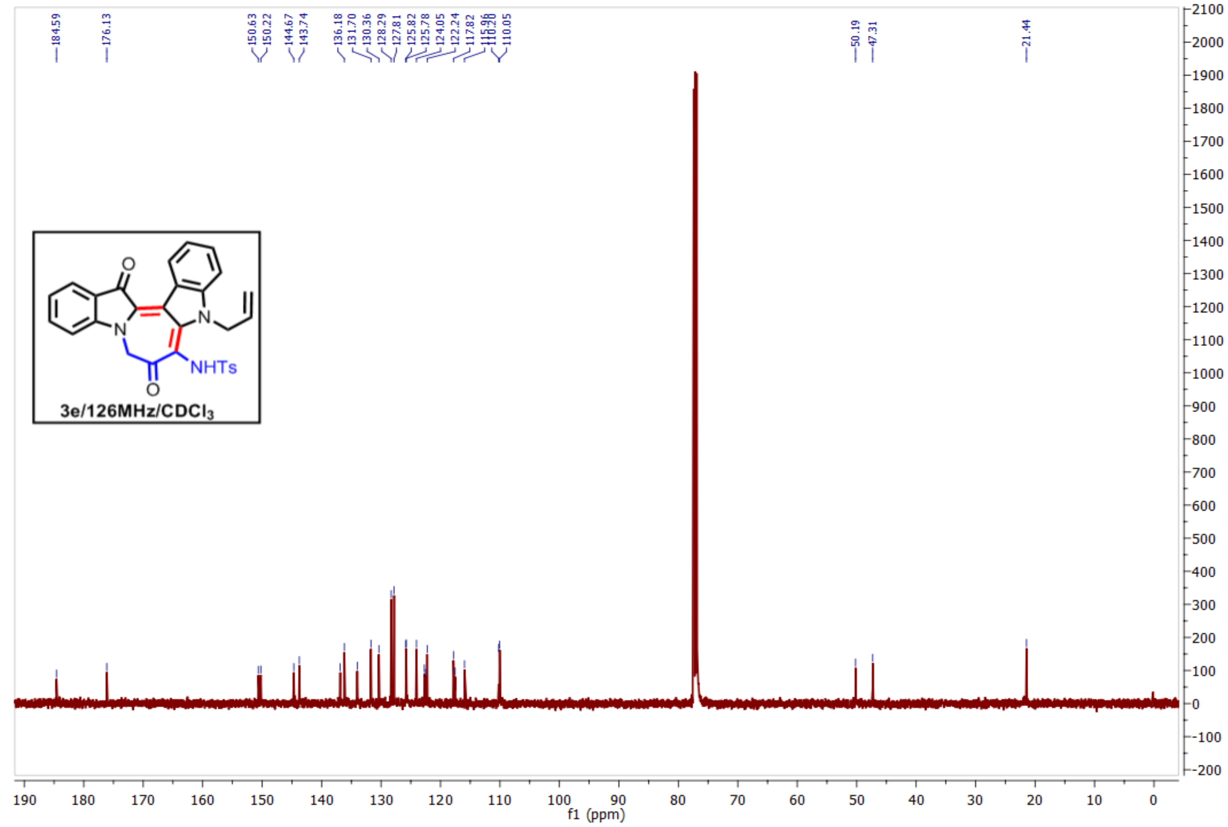


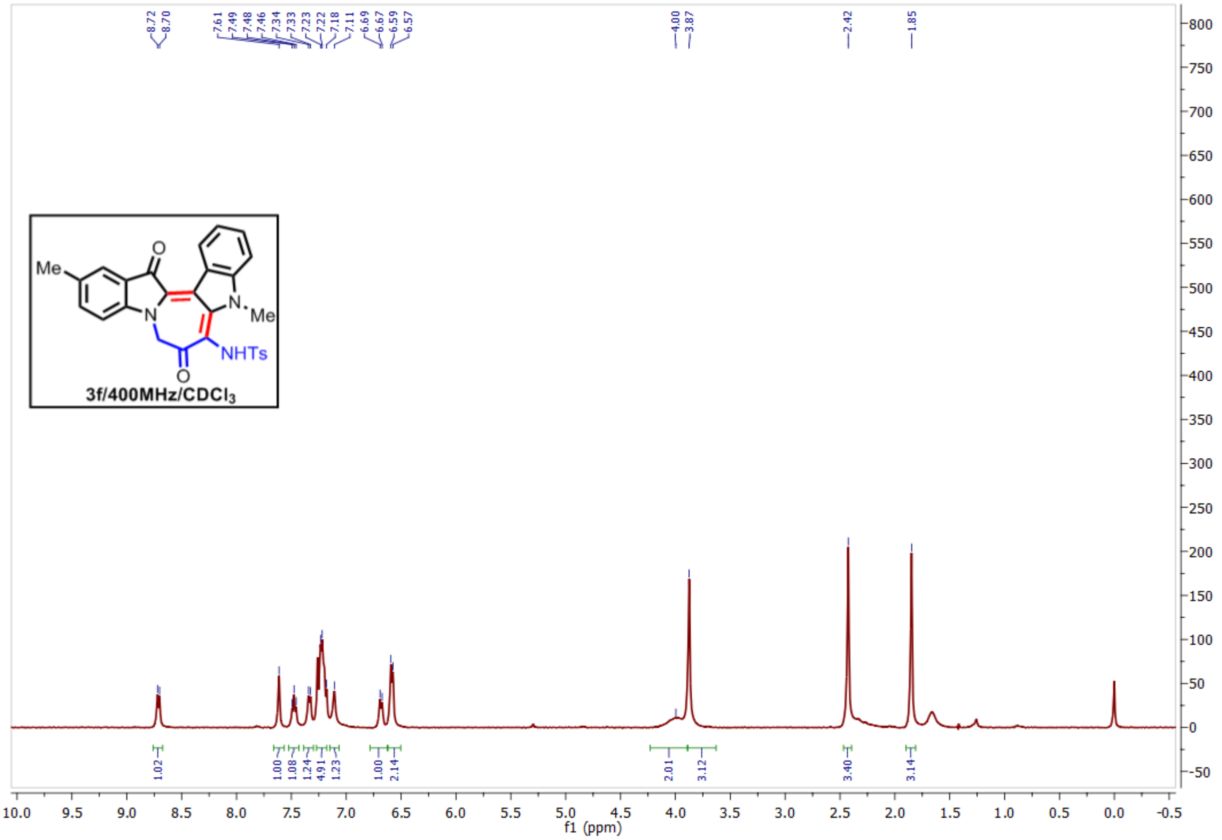
8.78
8.76
7.84
7.82
7.25
7.25
7.24
7.23
7.21
7.20
7.18
7.09
7.06
7.06
7.05
6.78
6.59
6.58
5.71
3.93
1.83
0.00
O
N
N
Bn
NHTs
O
3d/500MHz/CDCl$_3$
1.00
1.04
1.13
1.15
8.88
1.07
2.02
1.05
2.09
2.05
3.04
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

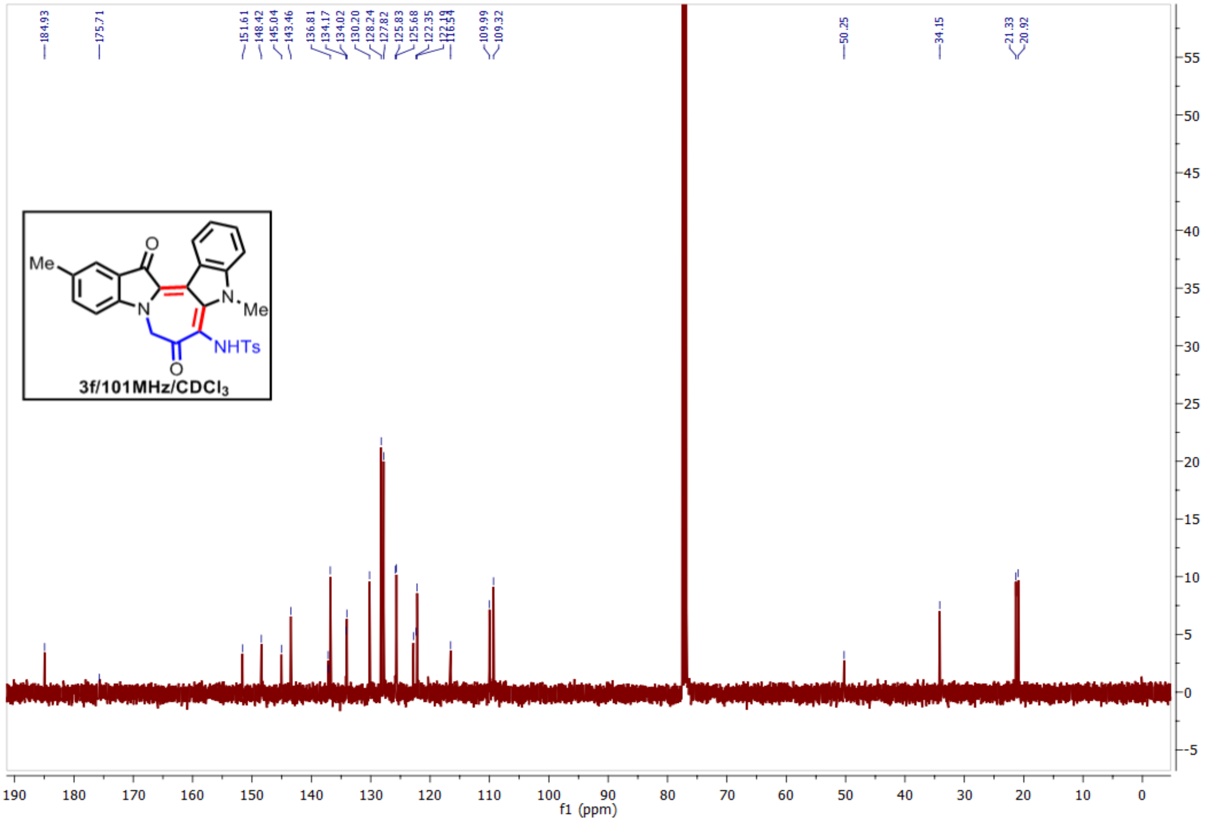


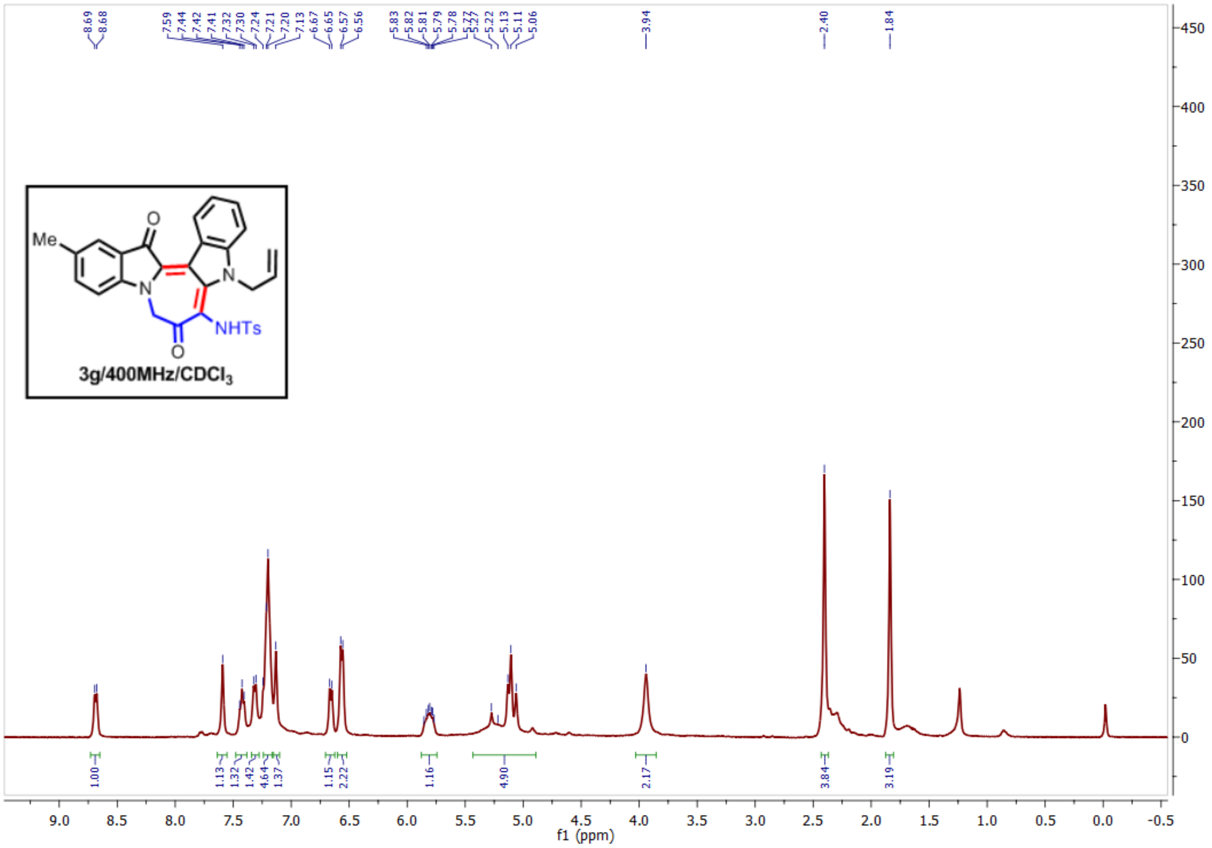
184.53
175.77
150.28
150.14
145.05
143.79
136.16
130.52
128.84
128.30
127.82
127.66
126.84
125.91
125.77
124.06
122.30
110.15
110.04
50.13
47.95
21.42
O
N
N
Bn
NHTs
O
3d/126MHz/CDCl$_3$
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

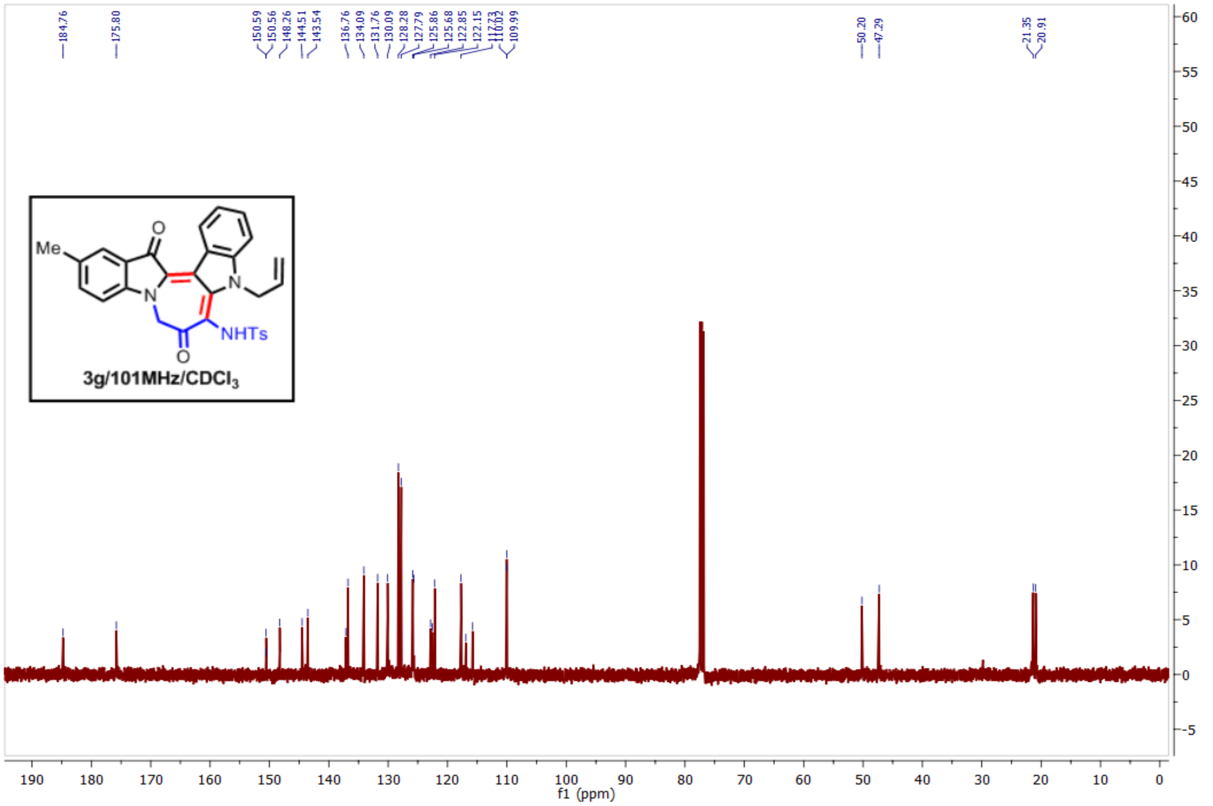

8.75
8.73
7.84
7.82
7.56
7.55
7.48
7.46
7.44
7.25
7.23
7.21
7.19
7.15
6.80
6.78
6.60
6.58
5.85
5.83
5.82
5.30
5.25
5.17
5.14
5.09
4.01
1.86
O
N
N
NHTs
O
3e/400MHz/CDCl3
0.74
0.74
0.78
0.80
5.38
0.85
1.67
0.83
3.27
1.58
2.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

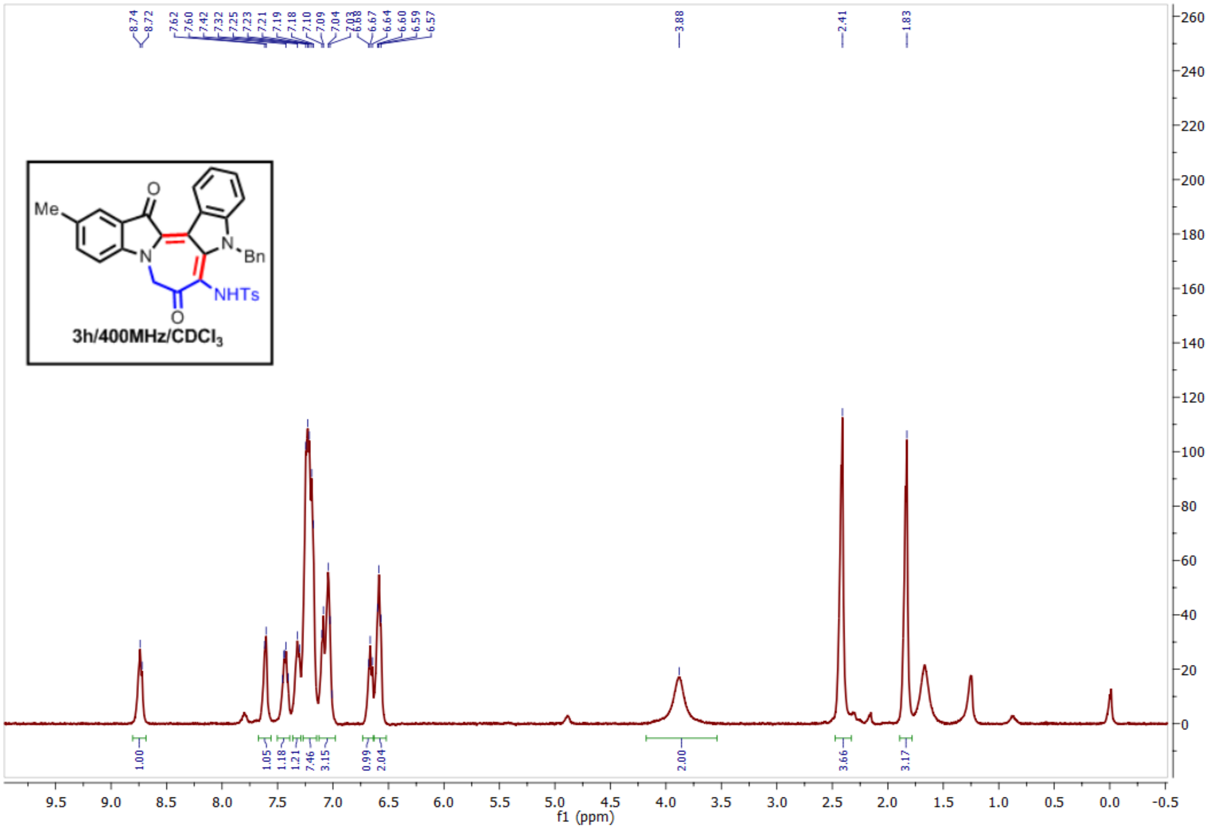

184.59
176.13
150.63
150.22
144.67
143.74
136.18
131.70
130.36
128.29
127.81
125.82
125.78
124.05
122.24
117.82
115.96
110.20
110.05
50.19
47.31
21.44
O
N
N
NHTs
O
3e/126MHz/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

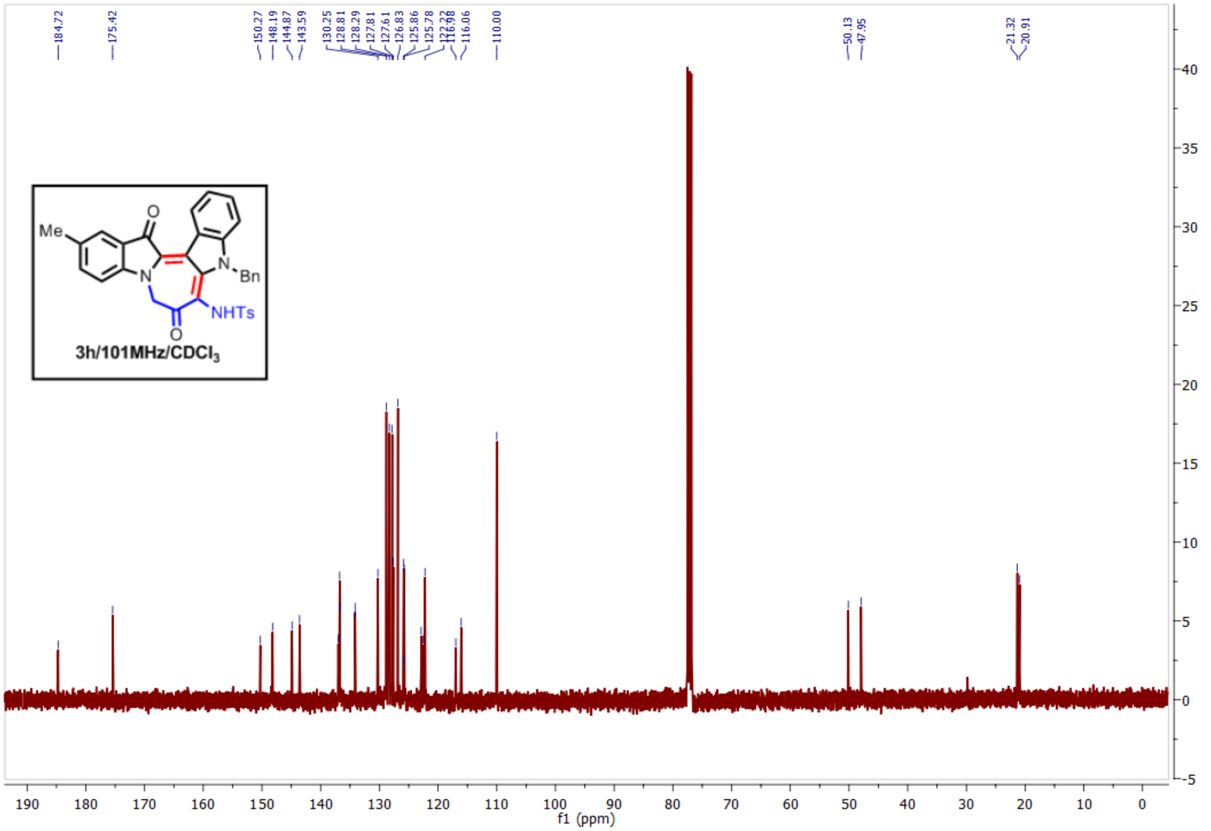

8.72
8.70
7.61
7.49
7.48
7.46
7.34
7.33
7.23
7.22
7.18
7.11
6.69
6.67
6.59
6.57
4.00
3.87
2.42
1.85
1.02
1.00
1.08
1.24
4.91
1.23
1.00
2.14
2.01
3.12
3.40
3.14
Me
O
N
N
Me
NHTs
O
3f/400MHz/CDCl3
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

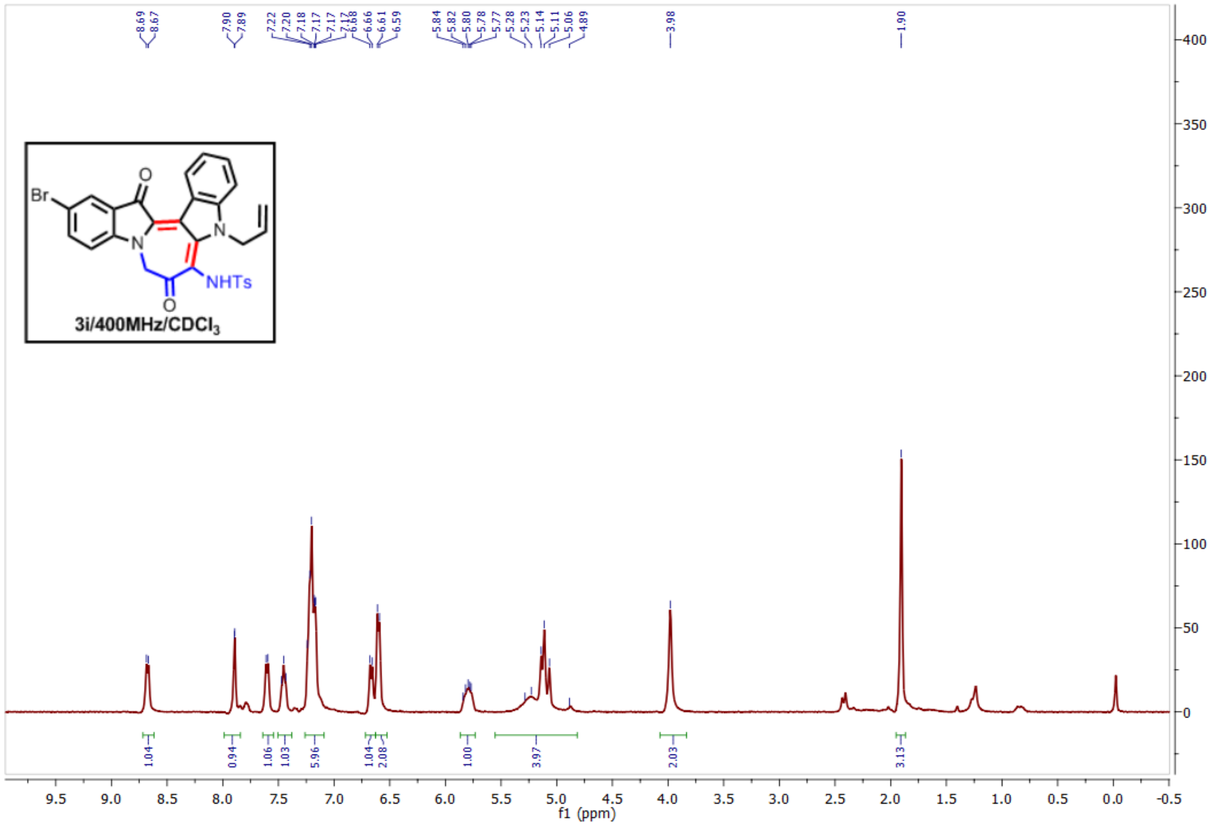

184.93
175.71
151.61
148.42
145.04
143.46
136.81
134.17
134.02
130.20
128.24
127.82
125.83
125.68
122.35
122.19
116.54
109.99
109.32
50.25
34.15
21.33
20.92
Me
O
N
N
Me
NHTs
O
3f/101MHz/CDCl3
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
55
50
45
40
35
30
25
20
15
10
5
0
-5

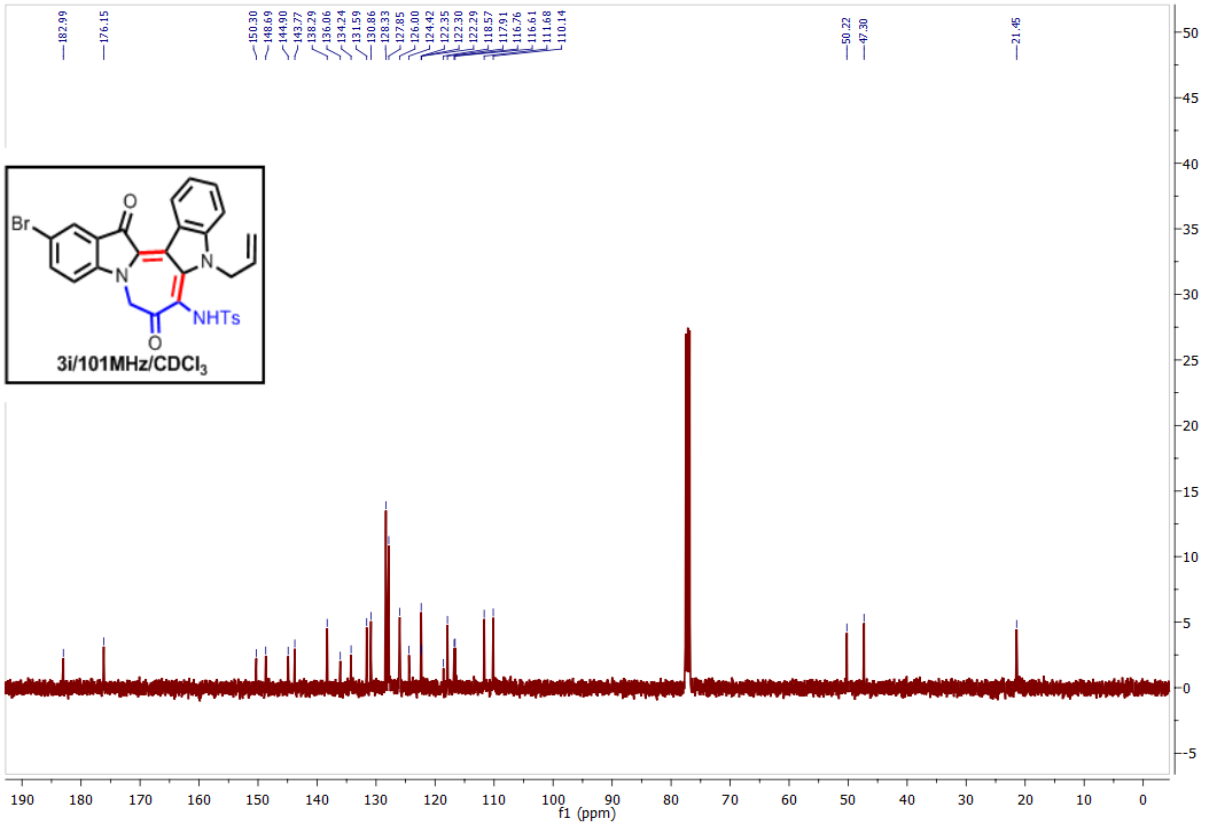

8.69
8.68
7.59
7.44
7.42
7.41
7.32
7.30
7.24
7.21
7.20
7.13
6.67
6.65
6.57
6.56
5.83
5.82
5.81
5.79
5.78
5.77
5.27
5.22
5.13
5.11
5.06
3.94
2.40
1.84
Me
O
N
N
NHTs
O
3g/400MHz/CDCl$_3$
1.00
1.13
1.32
1.42
4.64
1.37
1.15
2.22
1.16
4.90
2.17
3.84
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
450
400
350
300
250
200
150
100
50
0

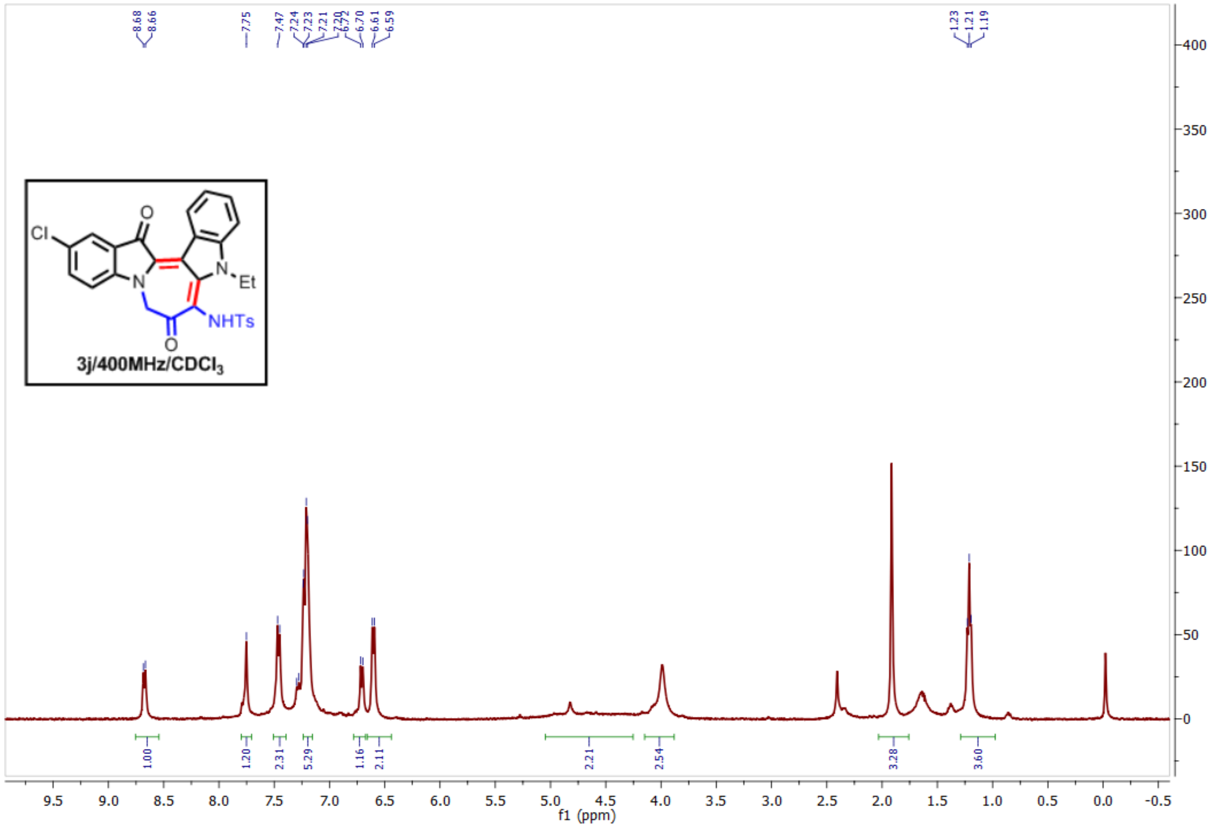

184.76
175.80
150.59
150.56
148.26
144.51
143.54
136.76
134.09
131.76
130.09
128.28
127.79
125.86
125.68
122.85
122.15
117.73
110.02
109.99
50.20
47.29
21.35
20.91
Me
O
N
N
NHTs
O
3g/101MHz/CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

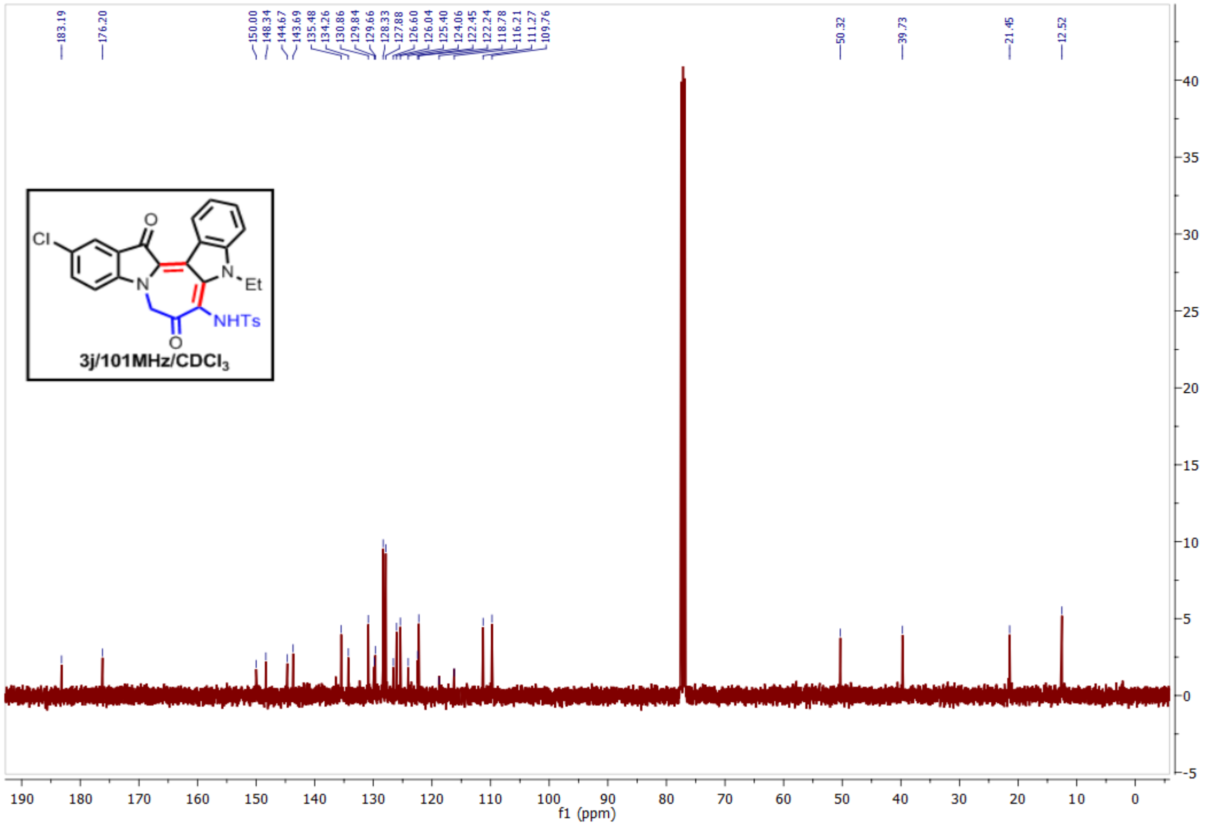

8.74
8.72
7.62
7.60
7.42
7.32
7.25
7.23
7.21
7.19
7.18
7.10
7.09
7.04
7.03
6.68
6.67
6.64
6.60
6.59
6.57
3.88
2.41
1.83
Me
O
N
N
Bn
NHTs
O
3h/400MHz/CDCl$_3$
1.00
1.05
1.18
1.21
7.46
3.15
0.99
2.04
2.00
3.66
3.17
260
240
220
200
180
160
140
120
100
80
60
40
20
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

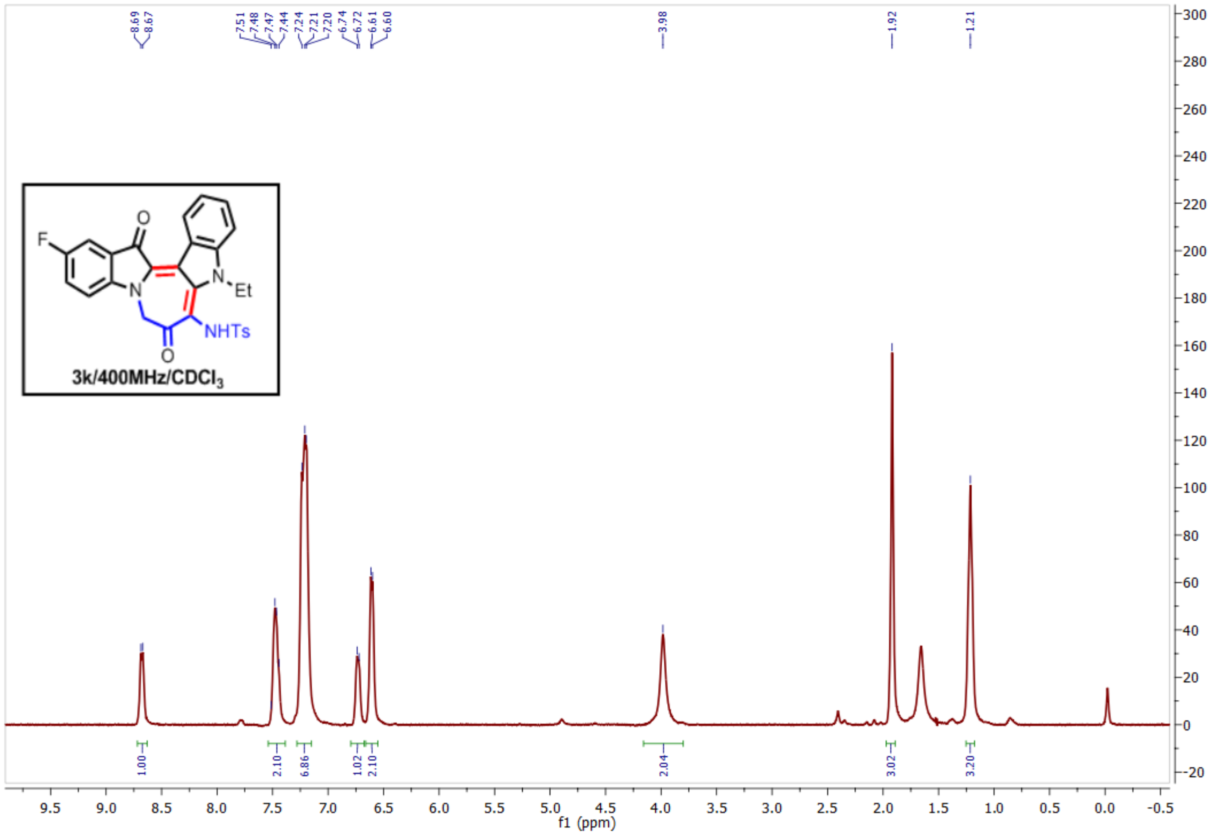

184.72
175.42
150.27
148.19
144.87
143.59
130.25
128.81
128.29
127.81
127.61
126.83
125.86
125.78
122.22
116.98
116.06
110.00
50.13
47.95
21.32
20.91
Me
O
N
N
Bn
NHTs
O
3h/101MHz/CDCl$_3$
40
35
30
25
20
15
10
5
0
-5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

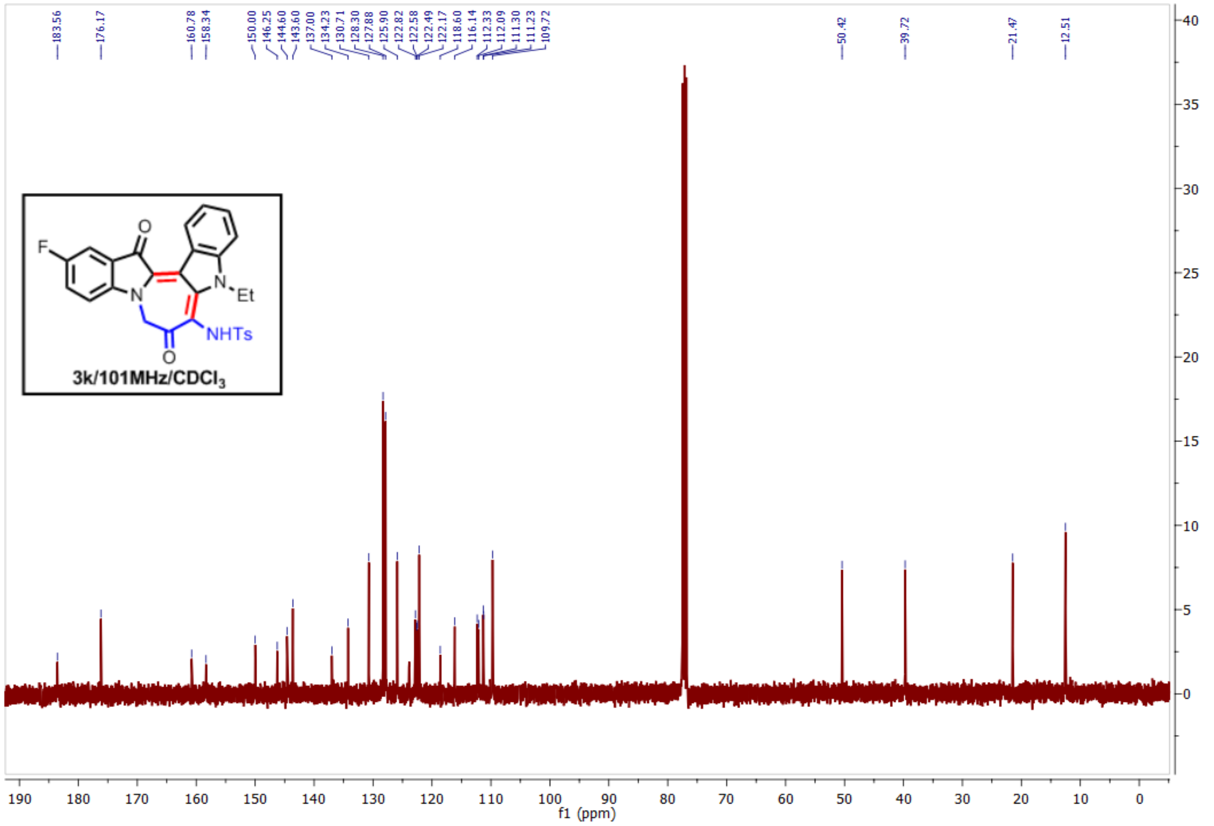

8.69
8.67
7.90
7.89
7.22
7.20
7.18
7.17
7.17
7.17
6.68
6.66
6.61
6.59
5.84
5.82
5.80
5.78
5.77
5.28
5.23
5.14
5.11
5.06
4.89
3.98
1.90
Br
O
N
N
NHTs
O
3i/400MHz/CDCl$_3$
1.04
0.94
1.06
1.03
5.96
1.04
2.08
1.00
3.97
2.03
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
400
350
300
250
200
150
100
50
0

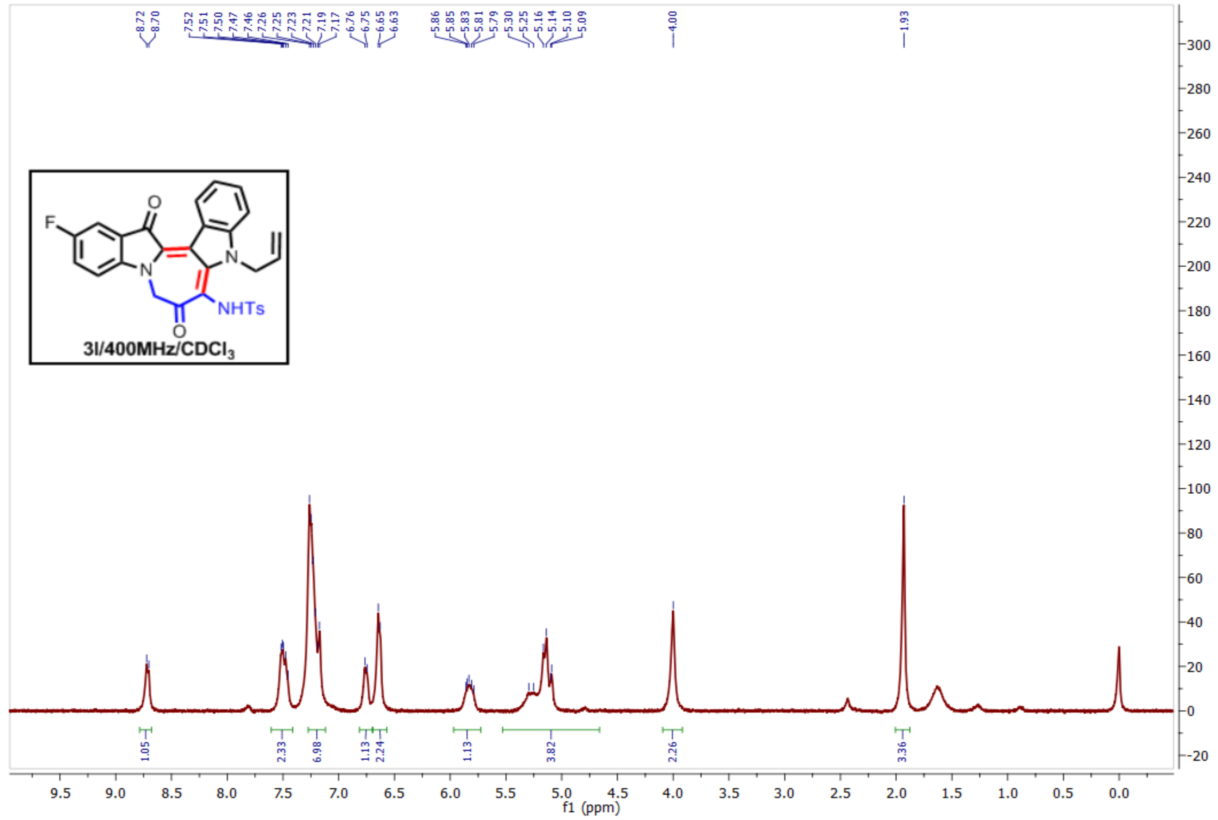

182.99
176.15
150.30
148.69
144.90
143.77
138.29
136.06
134.24
131.59
130.86
128.33
127.85
126.00
124.42
122.35
122.30
122.29
118.57
117.91
116.76
116.61
111.68
110.14
50.22
47.30
21.45
Br
O
N
N
NHTs
O
3i/101MHz/CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
50
45
40
35
30
25
20
15
10
5
0
-5

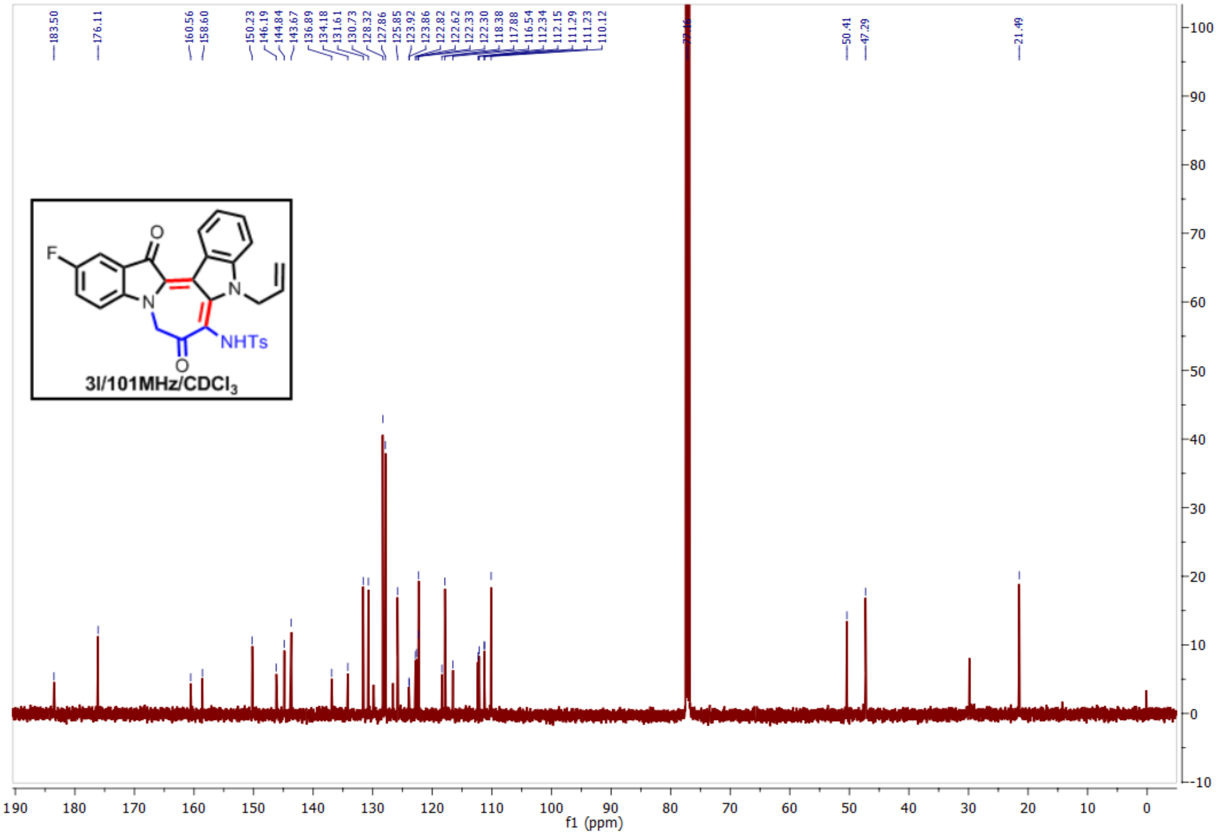

8.68
8.66
7.75
7.47
7.24
7.23
7.21
7.20
6.72
6.70
6.61
6.59
1.23
1.21
1.19
Cl
O
N
N
Et
NHTs
O
3j/400MHz/CDCl$_3$
1.00
1.20
2.31
5.29
1.16
2.11
2.21
2.54
3.28
3.60
f1 (ppm)

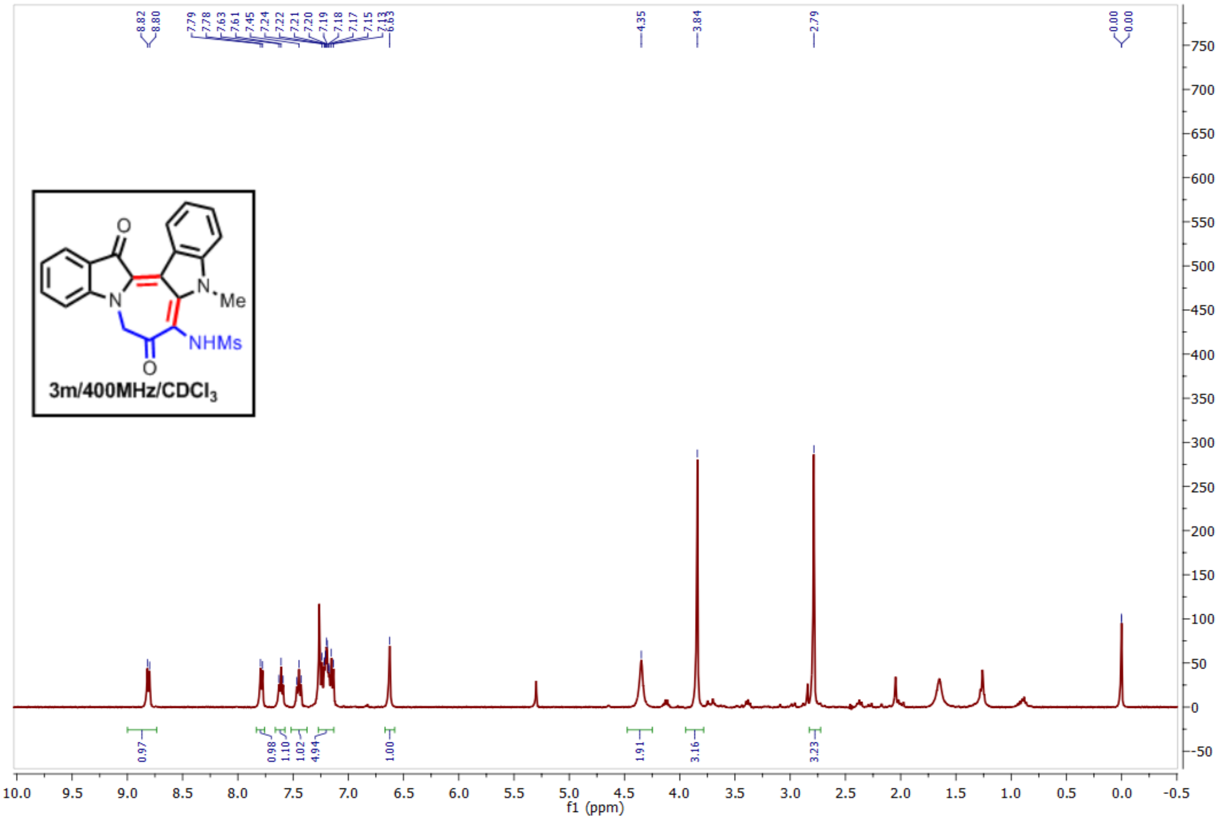

183.19
176.20
150.00
148.34
144.67
143.69
135.48
134.26
130.86
129.84
129.66
128.33
127.88
126.60
126.04
125.40
124.06
122.45
122.24
118.78
116.21
111.27
109.76
50.32
39.73
21.45
12.52
Cl
O
N
N
Et
NHTs
O
3j/101MHz/CDCl$_3$
f1 (ppm)

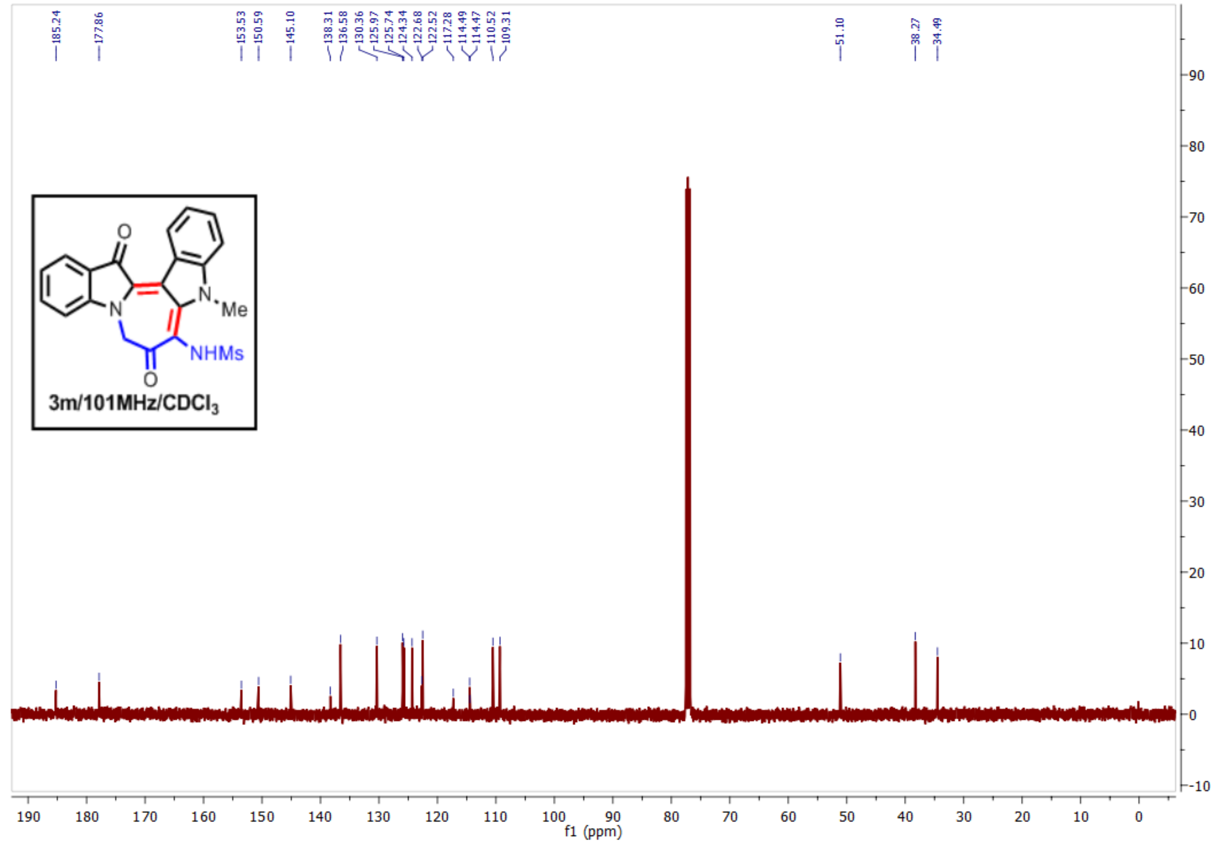

8.69
8.67
7.51
7.48
7.47
7.44
7.24
7.21
7.20
6.74
6.72
6.61
6.60
3.98
1.92
1.21
F
O
N
N
Et
NHTs
O
3k/400MHz/CDCl$_3$
1.00
2.10
6.86
1.02
2.10
2.04
3.02
3.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

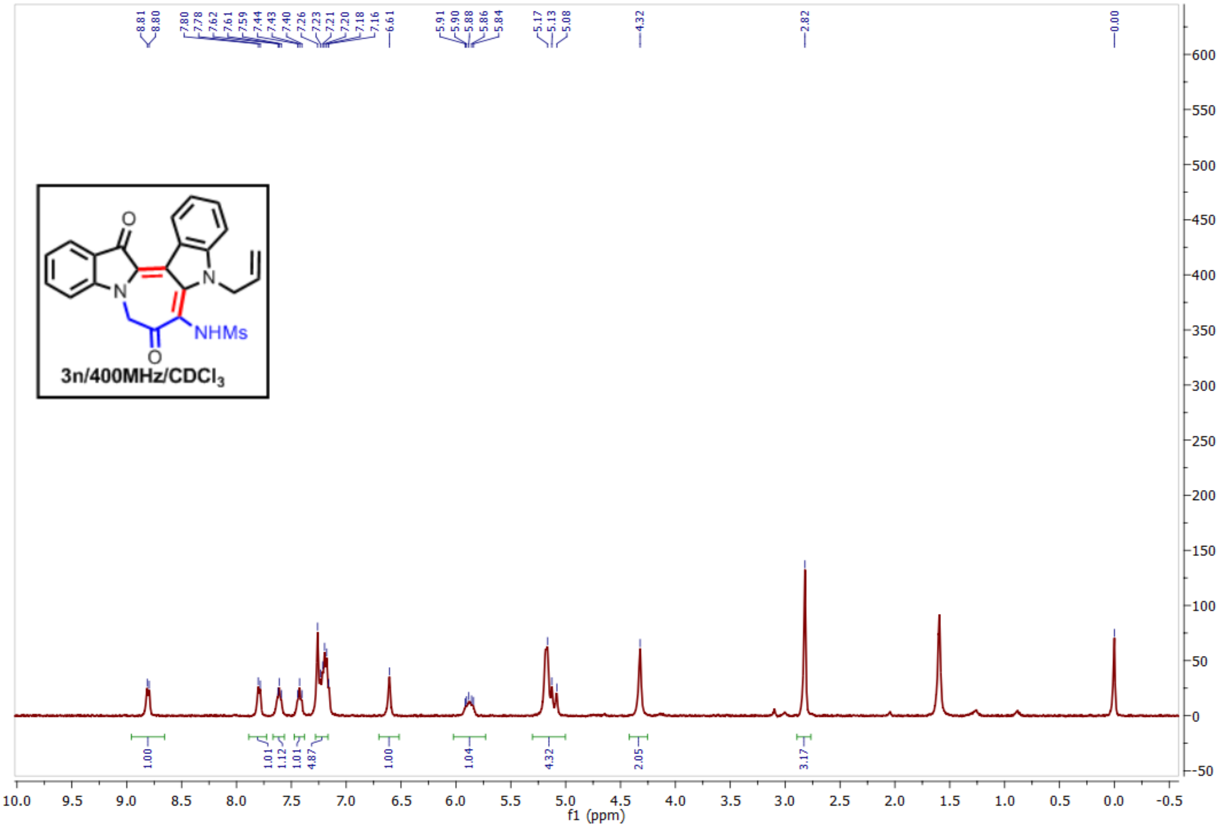

183.56
176.17
160.78
158.34
150.00
146.25
144.60
143.60
137.00
134.23
130.71
128.30
127.88
125.90
122.82
122.58
122.49
122.17
118.60
116.14
112.33
112.09
111.30
111.23
109.72
50.42
39.72
21.47
12.51
F
O
N
N
Et
NHTs
O
3k/101MHz/CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
40
35
30
25
20
15
10
5
0

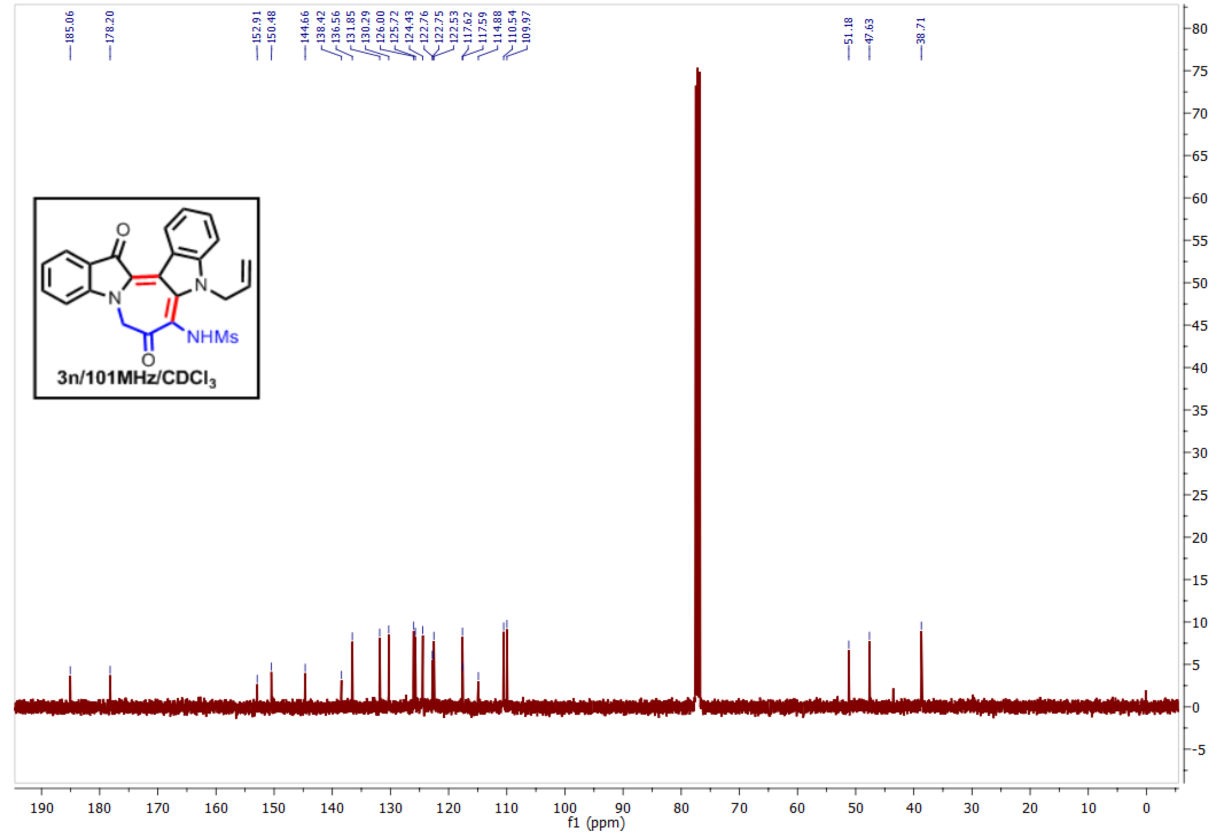

8.72
8.70
7.52
7.51
7.50
7.47
7.46
7.26
7.25
7.23
7.21
7.19
7.17
6.76
6.75
6.65
6.63
5.86
5.85
5.83
5.81
5.79
5.30
5.25
5.16
5.14
5.10
5.09
4.00
1.93
F
O
N
N
NHTs
O
3l/400MHz/CDCl3
1.05
2.33
6.98
1.13
2.24
1.13
3.82
2.26
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

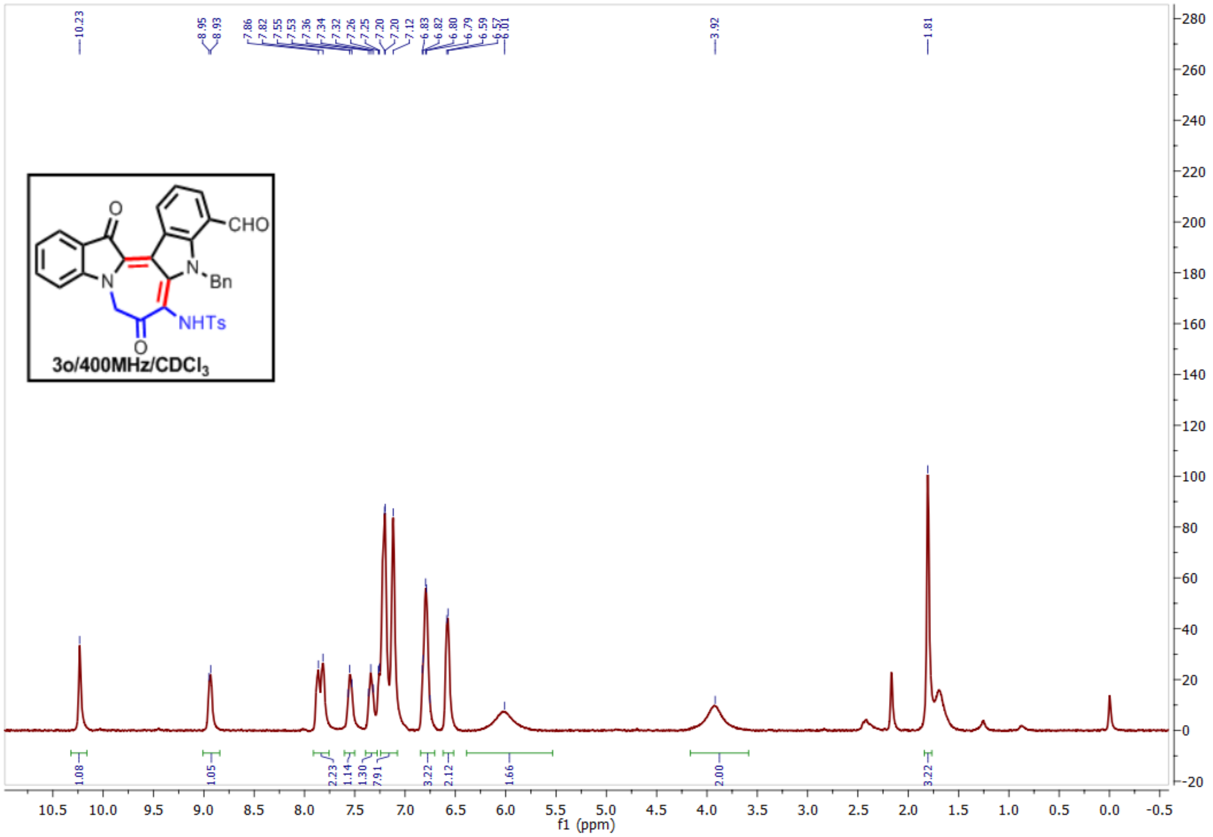

183.50
176.11
160.56
158.60
150.23
146.19
144.84
143.67
136.89
134.18
131.61
130.73
128.32
127.86
125.85
123.92
123.86
122.82
122.62
122.33
122.30
118.38
117.88
116.54
112.34
112.15
111.29
111.23
110.12
77.16
50.41
47.29
21.49
F
O
N
N
NHTs
O
3l/101MHz/CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
100
90
80
70
60
50
40
30
20
10
0
-10


8.82
8.80
7.79
7.78
7.63
7.61
7.45
7.24
7.22
7.21
7.20
7.19
7.18
7.17
7.15
7.13
6.63
4.35
3.84
2.79
0.00
0.00
O
N
N
Me
NHMs
O
3m/400MHz/CDCl$_3$
0.97
0.98
1.10
1.02
4.94
1.00
1.91
3.16
3.23
f1 (ppm)

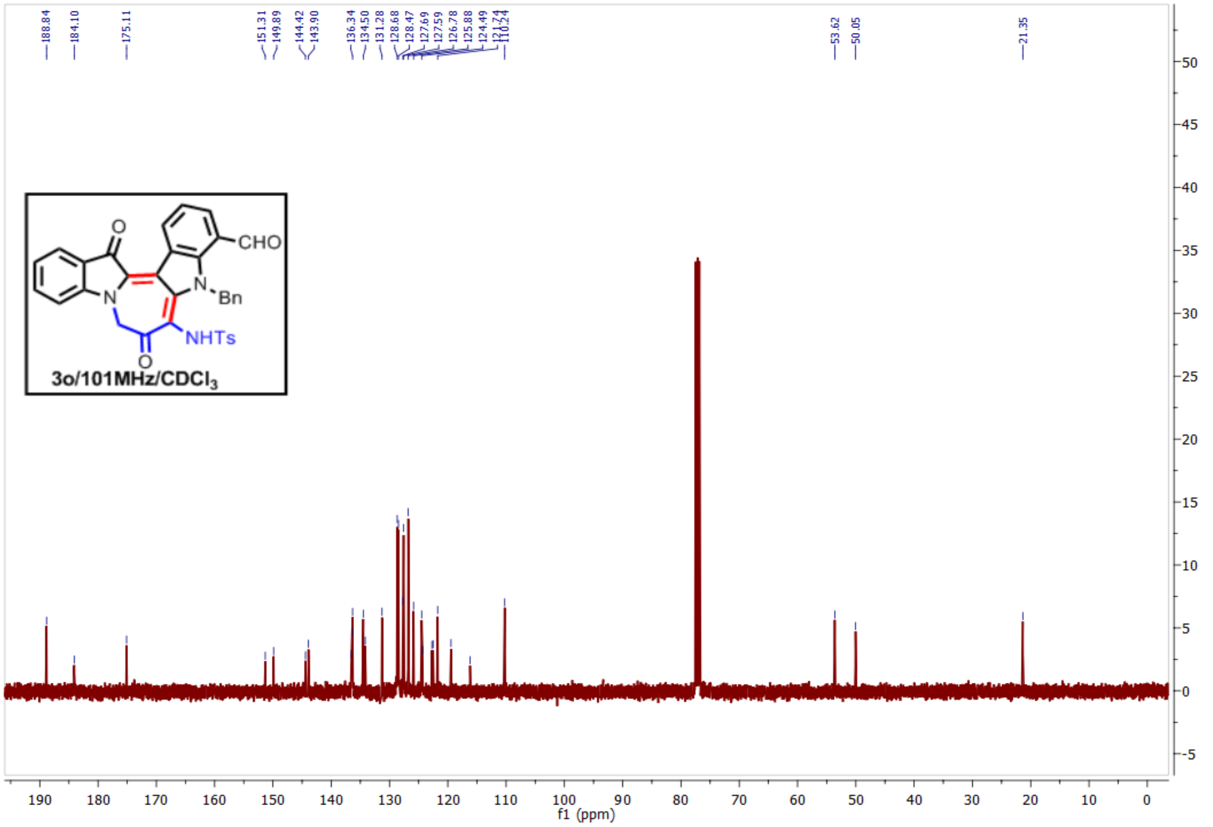

185.24
177.86
153.53
150.59
145.10
138.31
136.58
130.36
125.97
125.74
124.34
122.68
122.52
117.28
114.49
114.47
110.52
109.31
51.10
38.27
34.49
O
N
N
Me
NHMs
O
3m/101MHz/CDCl$_3$
f1 (ppm)


8.81
8.80
7.80
7.78
7.62
7.61
7.59
7.44
7.43
7.40
7.26
7.23
7.21
7.20
7.18
7.16
6.61
5.91
5.90
5.88
5.86
5.84
5.17
5.13
5.08
4.32
2.82
0.00
O
N
N
NHMs
O
3n/400MHz/CDCl$_3$
1.00
1.01
1.12
1.01
4.87
1.00
1.04
4.32
2.05
3.17
f1 (ppm)

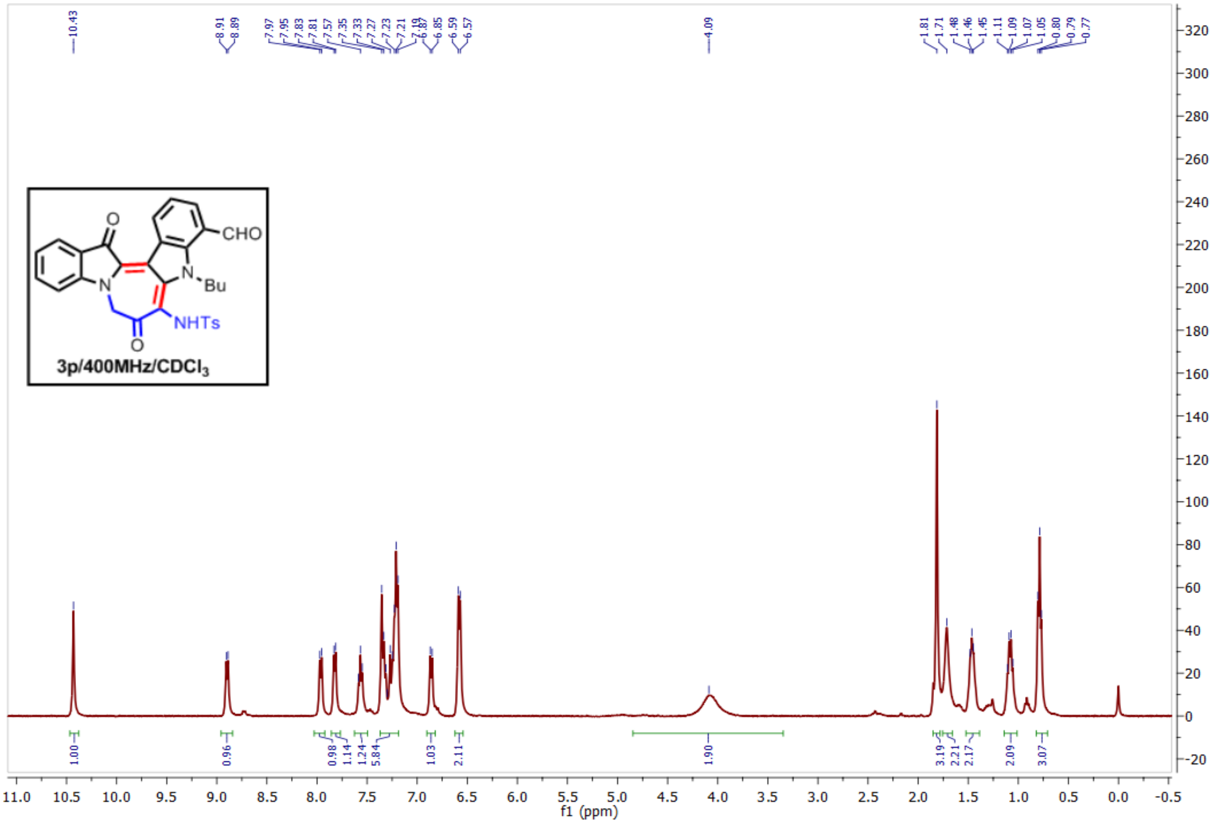

185.06
178.20
152.91
150.48
144.66
138.42
136.56
131.85
130.29
126.00
125.72
124.43
122.76
122.75
122.53
117.62
117.59
114.88
110.54
109.97
51.18
47.63
38.71
O
N
N
NHMs
O
3n/101MHz/CDCl$_3$
f1 (ppm)

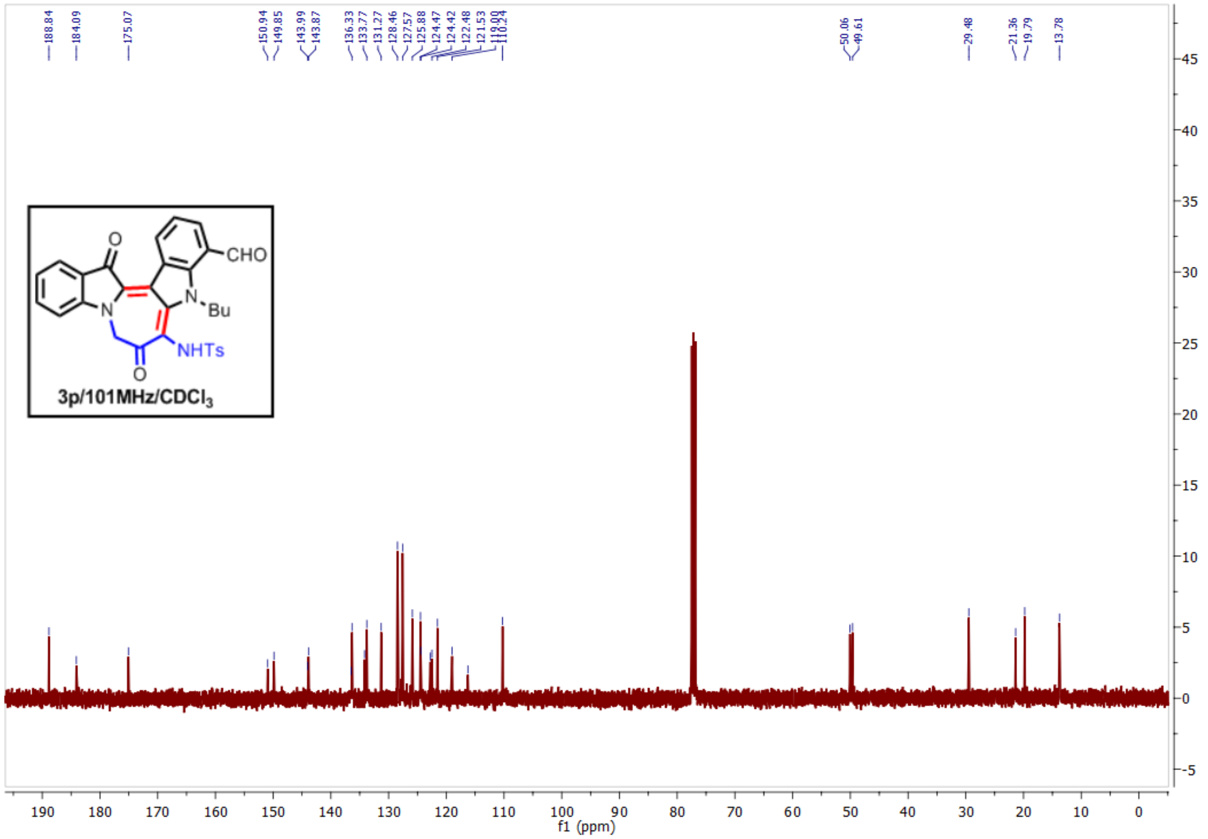


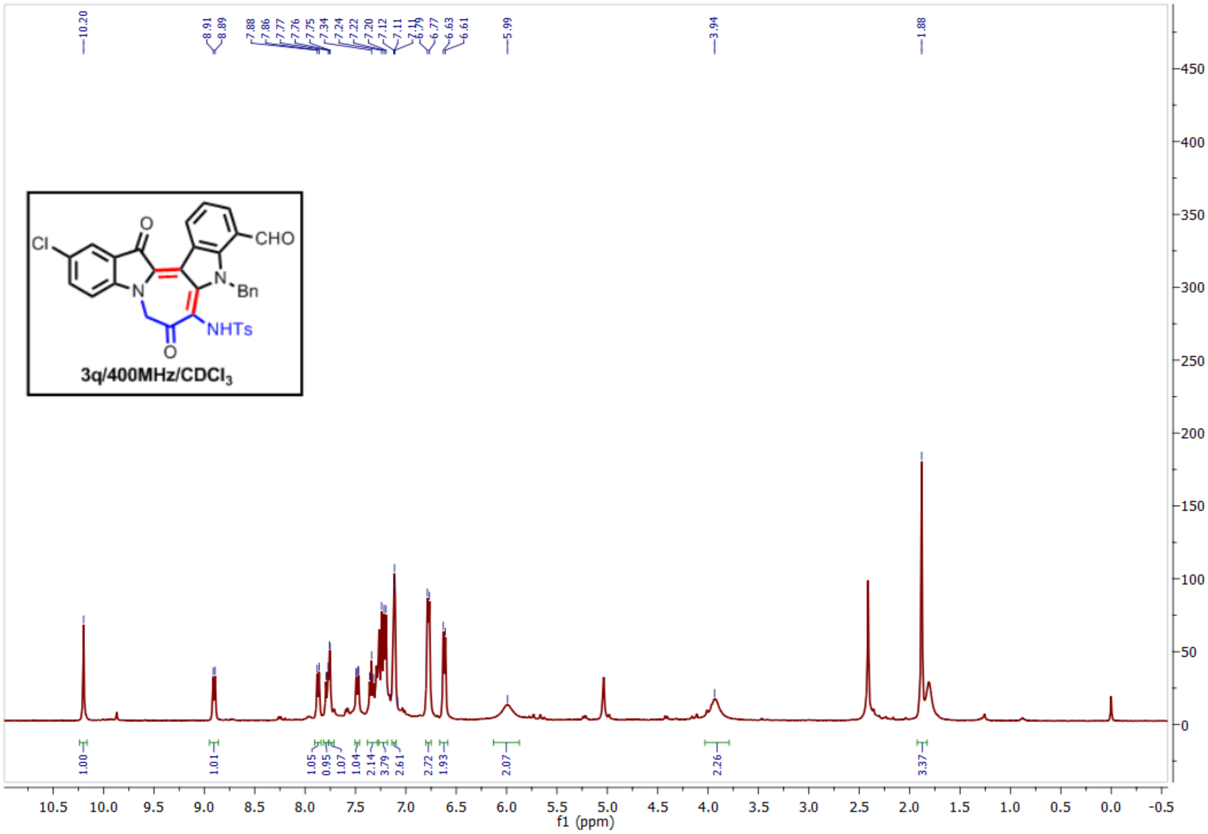
10.23
8.95
8.93
7.86
7.82
7.55
7.53
7.36
7.34
7.32
7.26
7.25
7.20
7.20
7.12
6.83
6.82
6.80
6.79
6.59
6.57
6.01
3.92
1.81
CHO
O
N
Bn
NHTs
3o/400MHz/CDCl$_3$
1.08
1.05
2.23
1.14
1.30
7.91
3.22
2.12
1.66
2.00
3.22
f1 (ppm)

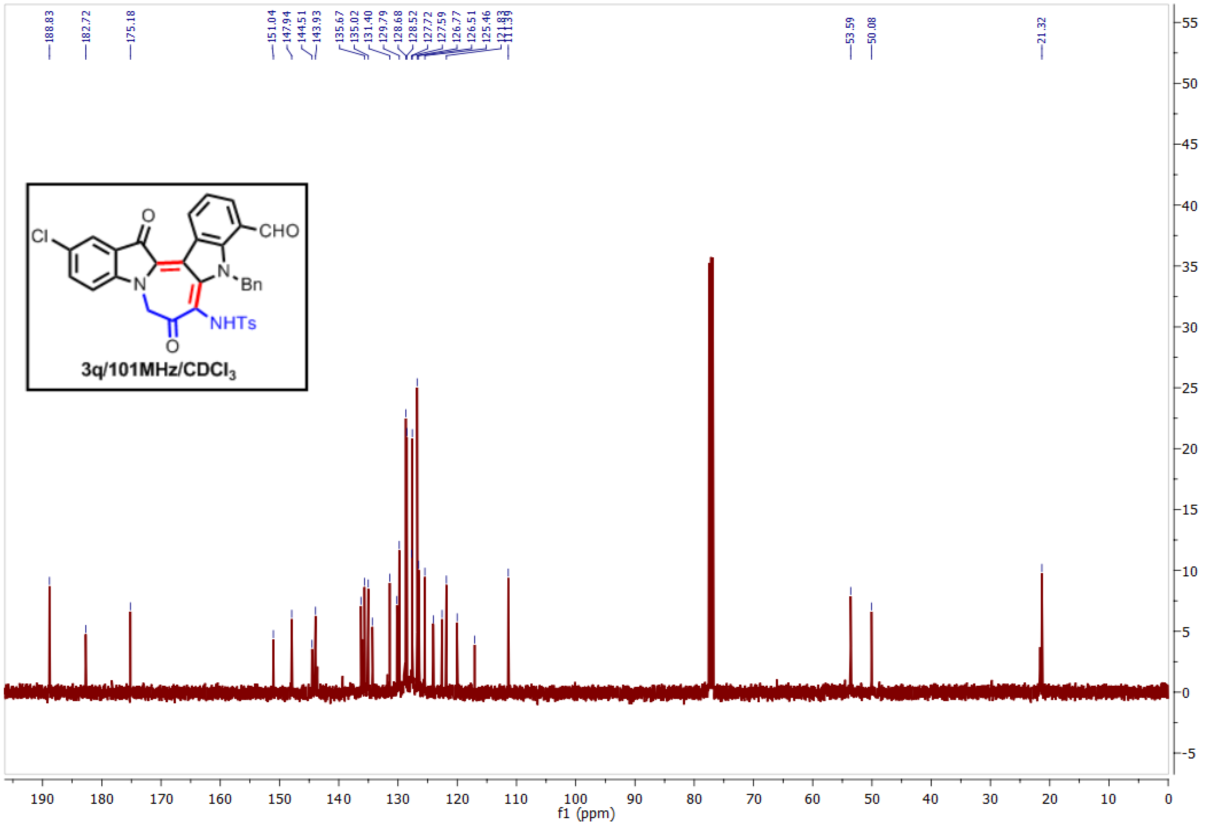


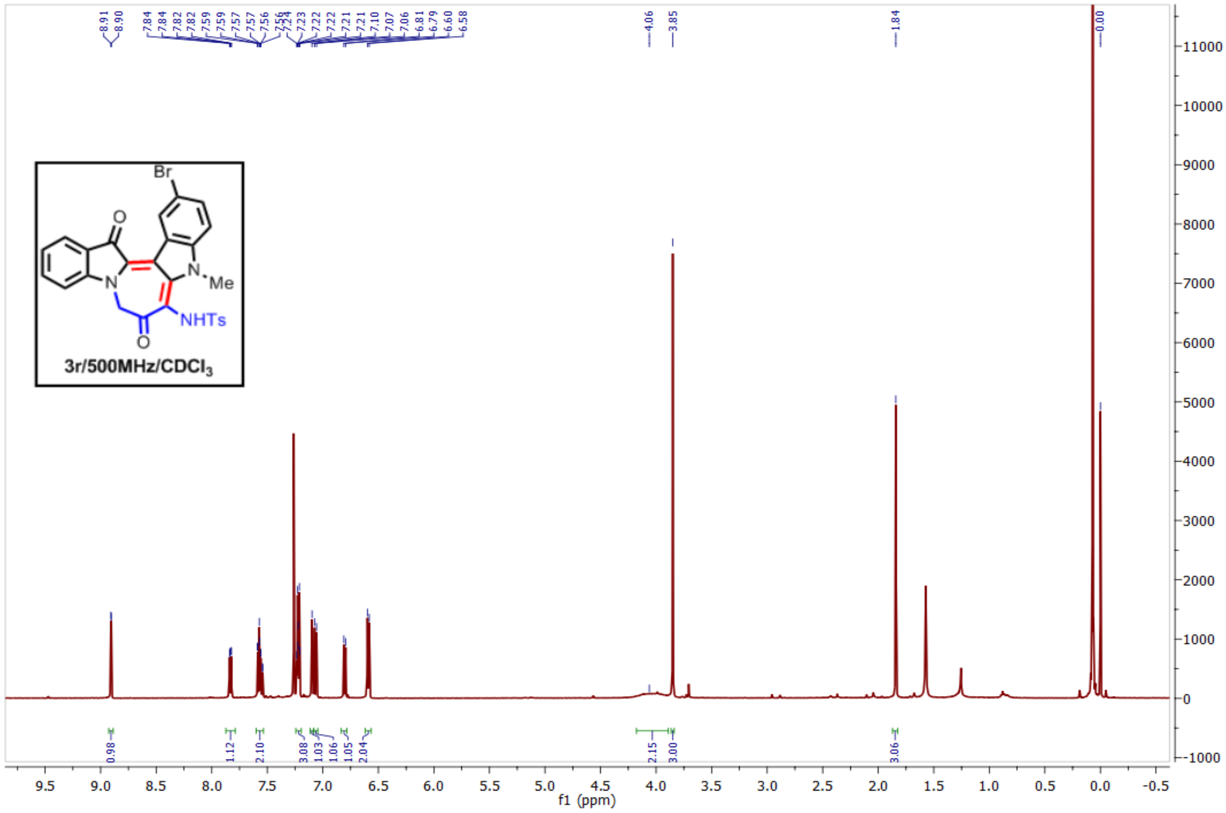
188.84
184.10
175.11
151.31
149.89
144.42
143.90
136.34
134.50
131.28
128.68
128.47
127.69
127.59
126.78
125.88
124.49
121.74
110.24
53.62
50.05
21.35
CHO
O
N
Bn
NHTs
3o/101MHz/CDCl$_3$
f1 (ppm)

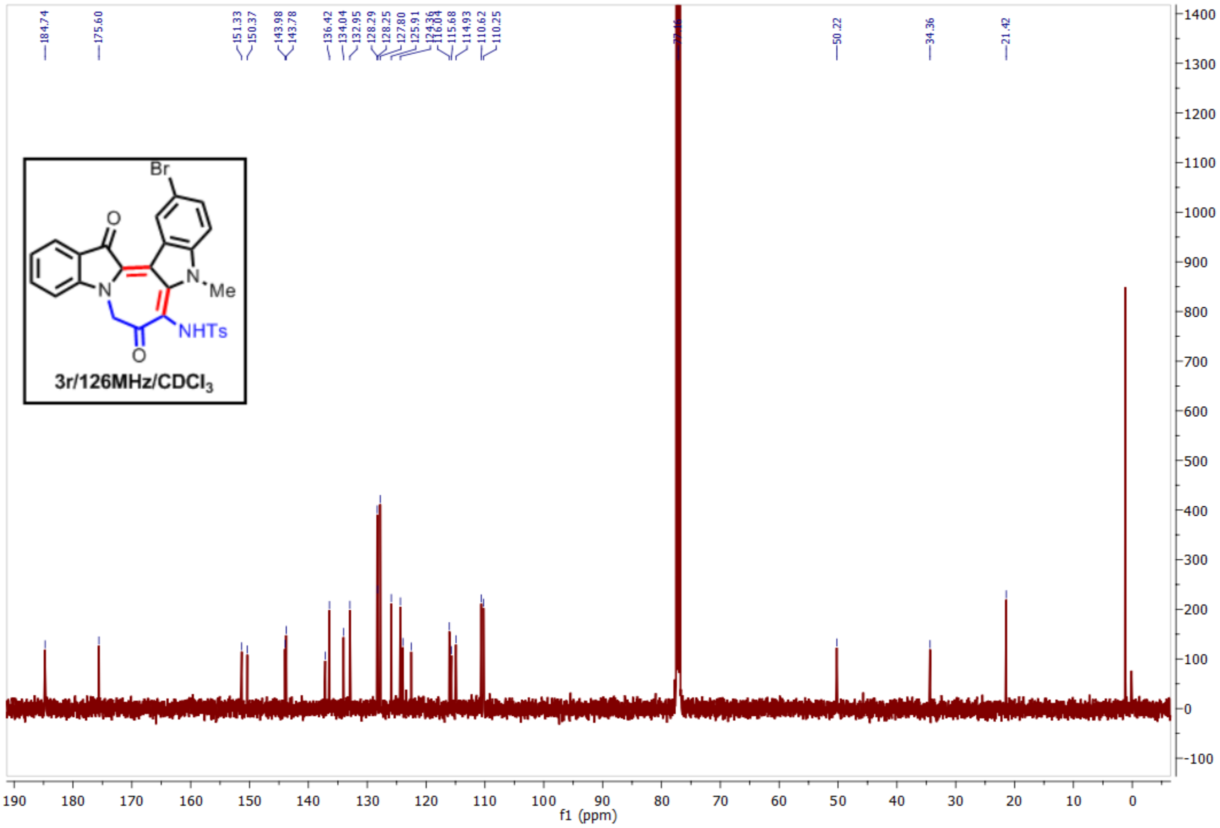

3p/400MHz/CDCl$_3$
CHO
N
Bu
NHTs
O
O
N
10.43
8.91
8.89
7.97
7.95
7.83
7.81
7.57
7.35
7.33
7.27
7.23
7.21
7.19
6.87
6.85
6.59
6.57
4.09
1.81
1.71
1.48
1.46
1.45
1.11
1.09
1.07
1.05
0.80
0.79
0.77
1.00
0.96
0.98
1.14
1.24
5.84
1.03
2.11
1.90
3.19
2.21
2.17
2.09
3.07
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

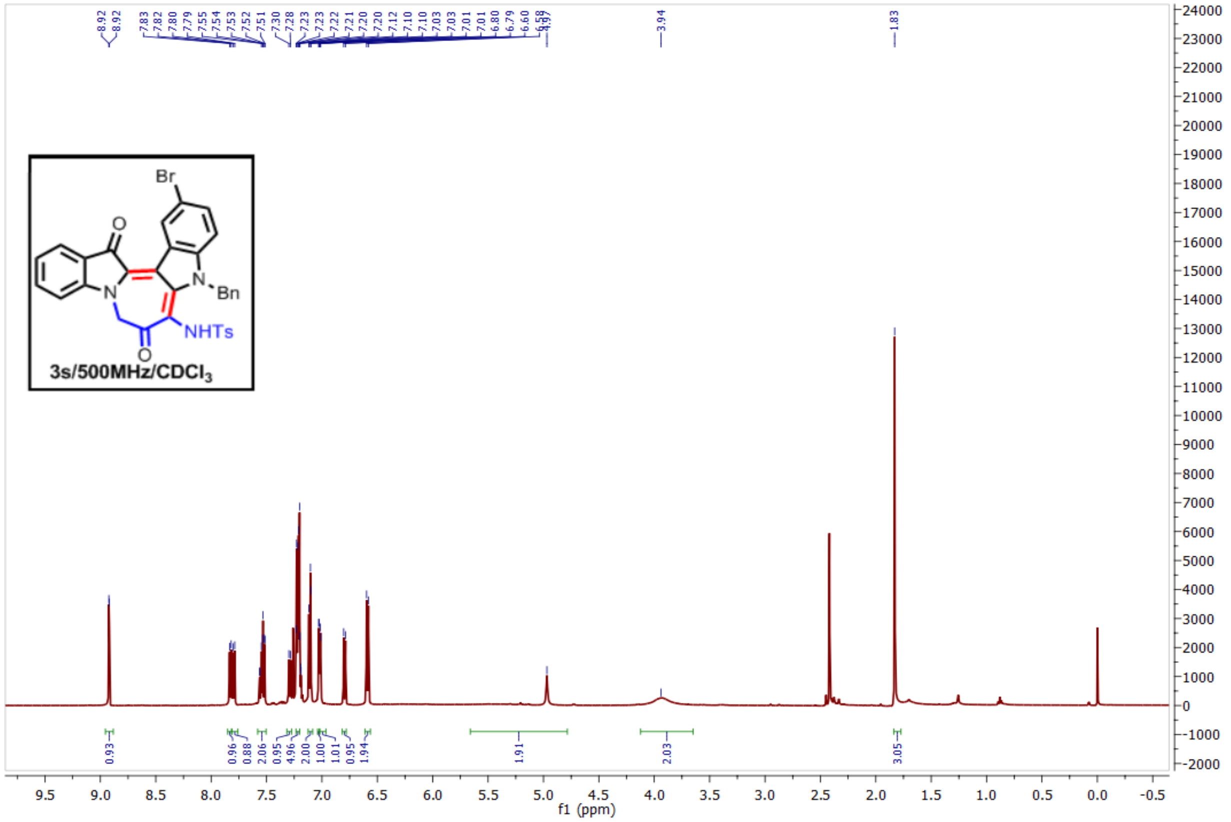

3p/101MHz/CDCl$_3$
CHO
N
Bu
NHTs
O
O
N
188.84
184.09
175.07
150.94
149.85
143.99
143.87
136.33
133.77
131.27
128.46
127.57
125.88
124.47
124.42
122.48
121.53
119.00
110.24
50.06
49.61
29.48
21.36
19.79
13.78
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
45
40
35
30
25
20
15
10
5
0
-5

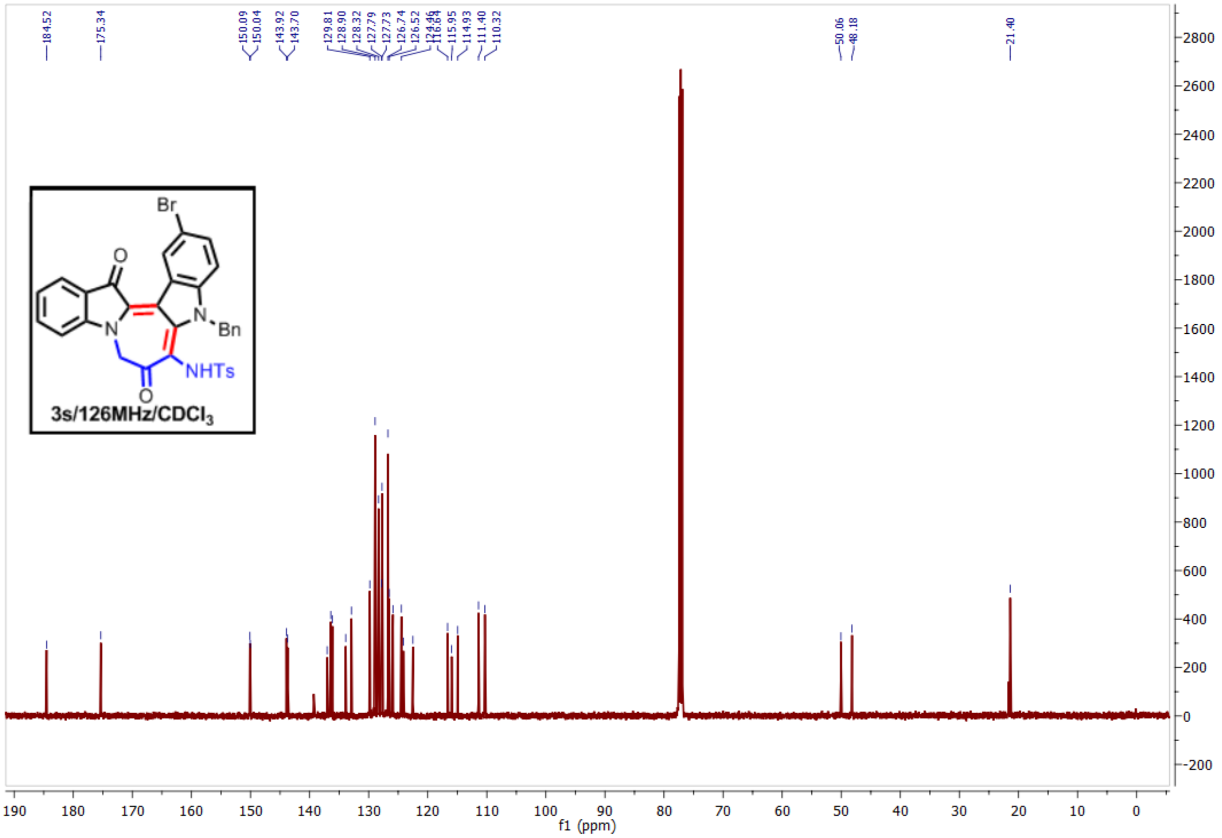

10.20
8.91
8.89
7.88
7.86
7.77
7.76
7.75
7.34
7.24
7.22
7.20
7.12
7.11
7.11
6.79
6.77
6.63
6.61
5.99
3.94
1.88
Cl
O
CHO
N
N
Bn
NHTs
O
3q/400MHz/CDCl$_3$
1.00
1.01
1.05
0.95
1.07
1.04
2.14
3.79
2.61
2.72
1.93
2.07
2.26
3.37
450
400
350
300
250
200
150
100
50
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

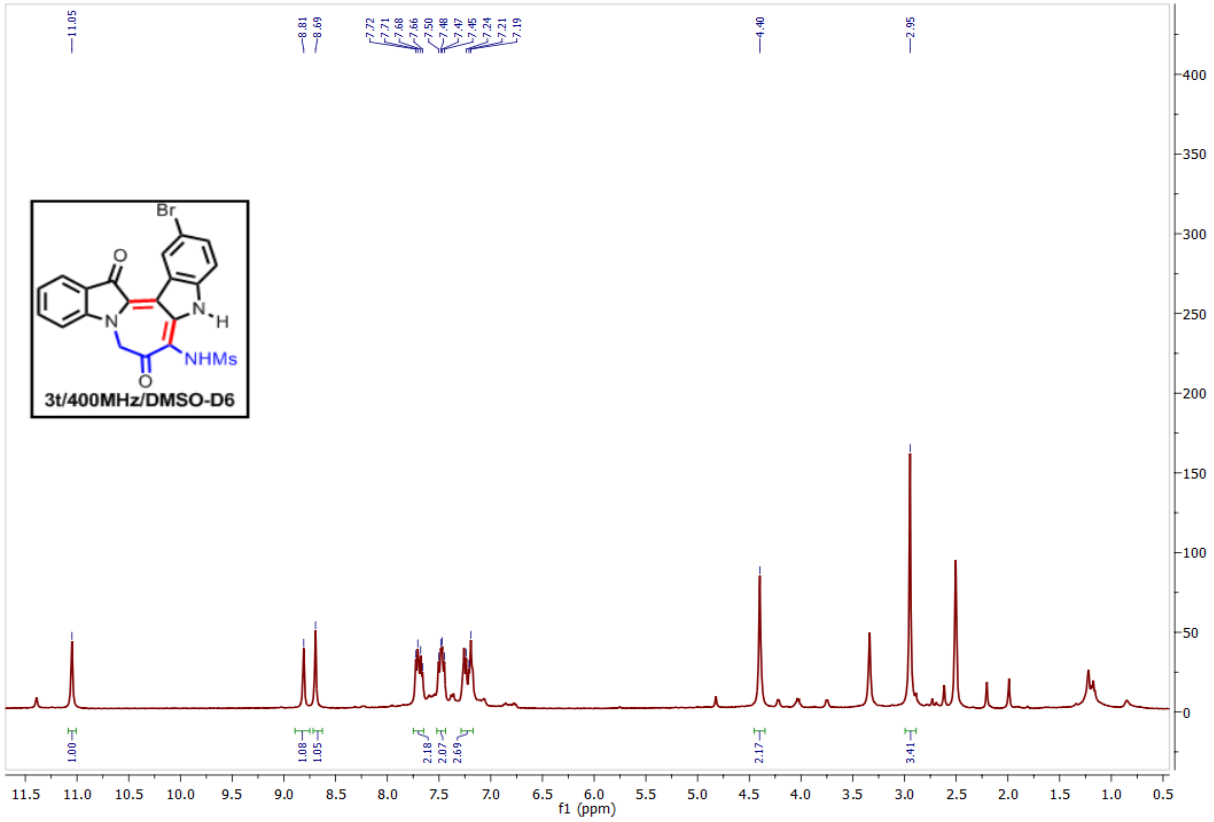

188.83
182.72
175.18
151.04
147.94
144.51
143.93
135.67
135.02
131.40
129.79
128.68
128.52
127.72
127.59
126.77
126.51
125.46
121.83
111.39
53.59
50.08
21.32
Cl
O
CHO
N
N
Bn
NHTs
O
3q/101MHz/CDCl$_3$
55
50
45
40
35
30
25
20
15
10
5
0
-5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

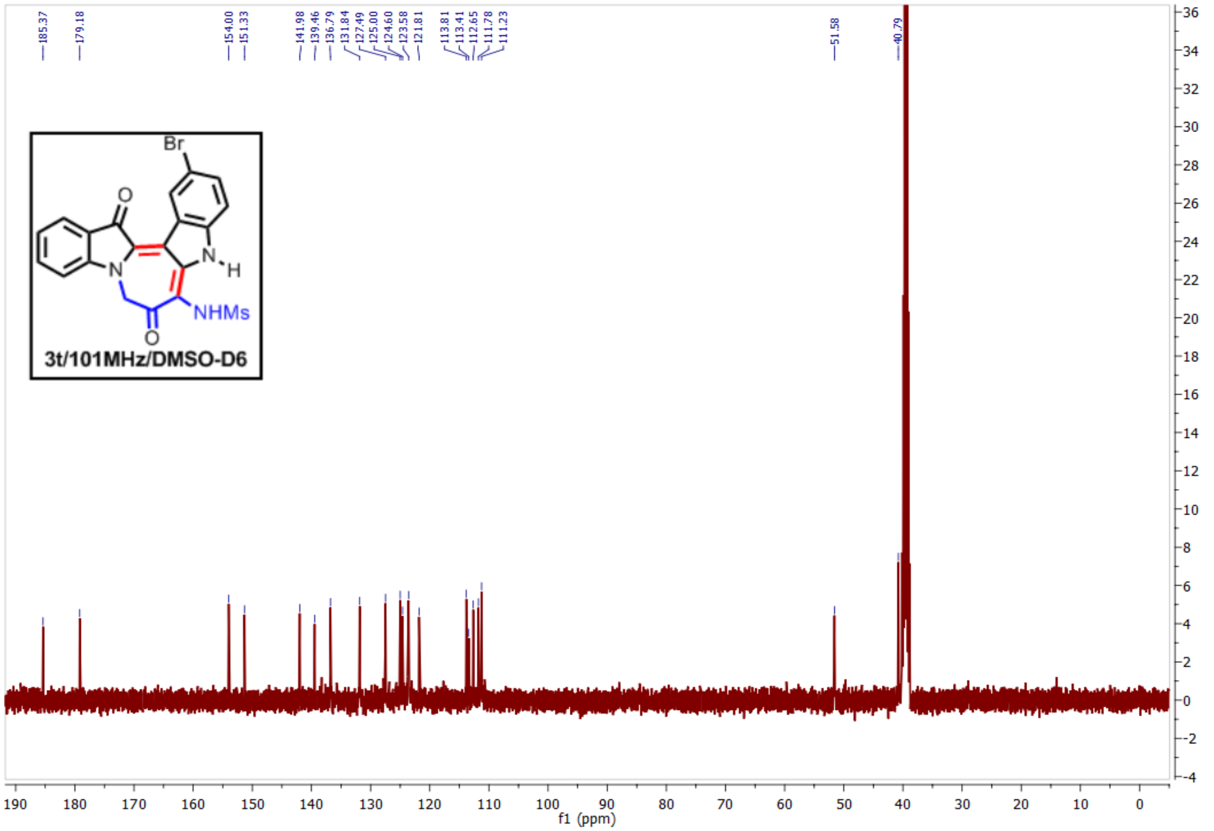

8.91
8.90
7.84
7.84
7.82
7.82
7.59
7.59
7.57
7.57
7.56
7.56
7.24
7.23
7.22
7.22
7.21
7.21
7.10
7.07
7.06
6.81
6.79
6.60
6.58
4.06
3.85
1.84
0.00
Br
O
N
N
Me
NHTs
O
3r/500MHz/CDCl$_3$
0.98
1.12
2.10
3.08
1.03
1.06
1.05
2.04
2.15
3.00
3.06
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

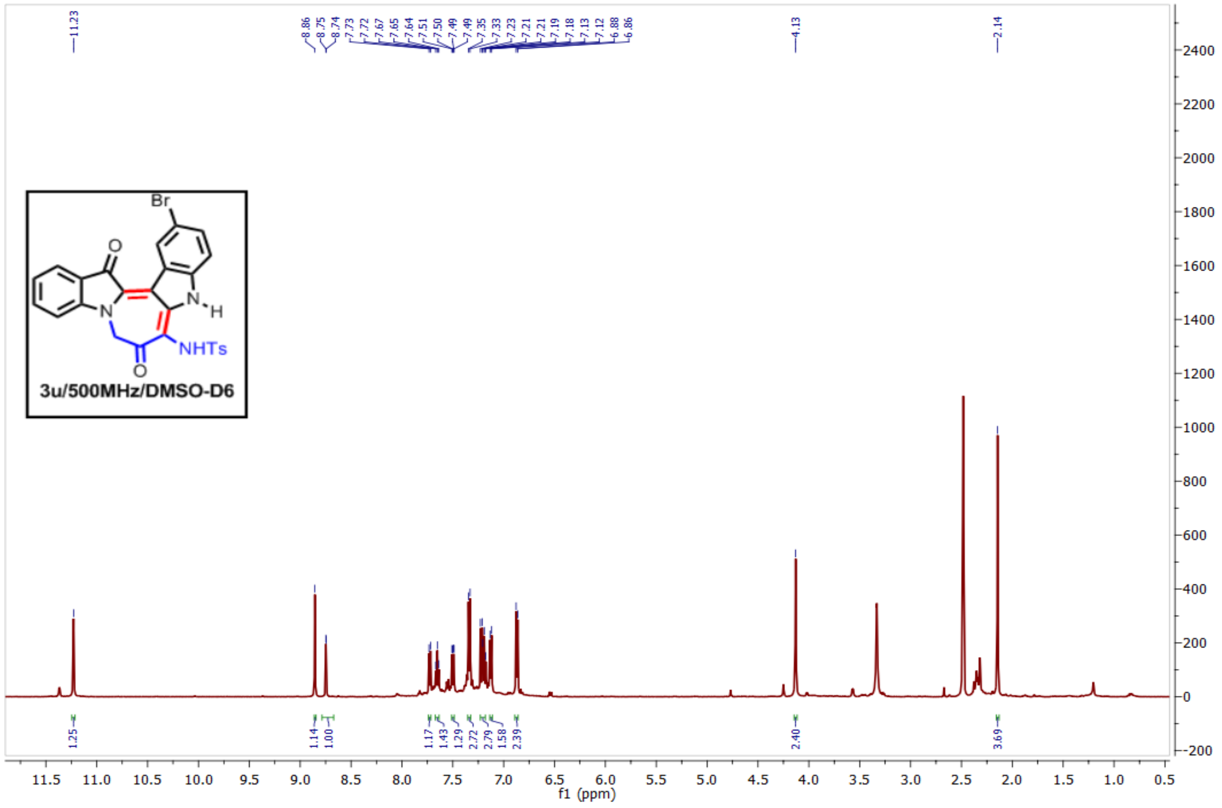

184.74
175.60
151.33
150.37
143.98
143.78
136.42
134.04
132.95
128.29
128.25
127.80
125.91
124.36
116.04
115.68
114.93
110.62
110.25
77.16
50.22
34.36
21.42
Br
O
N
N
Me
NHTs
O
3r/126MHz/CDCl$_3$
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

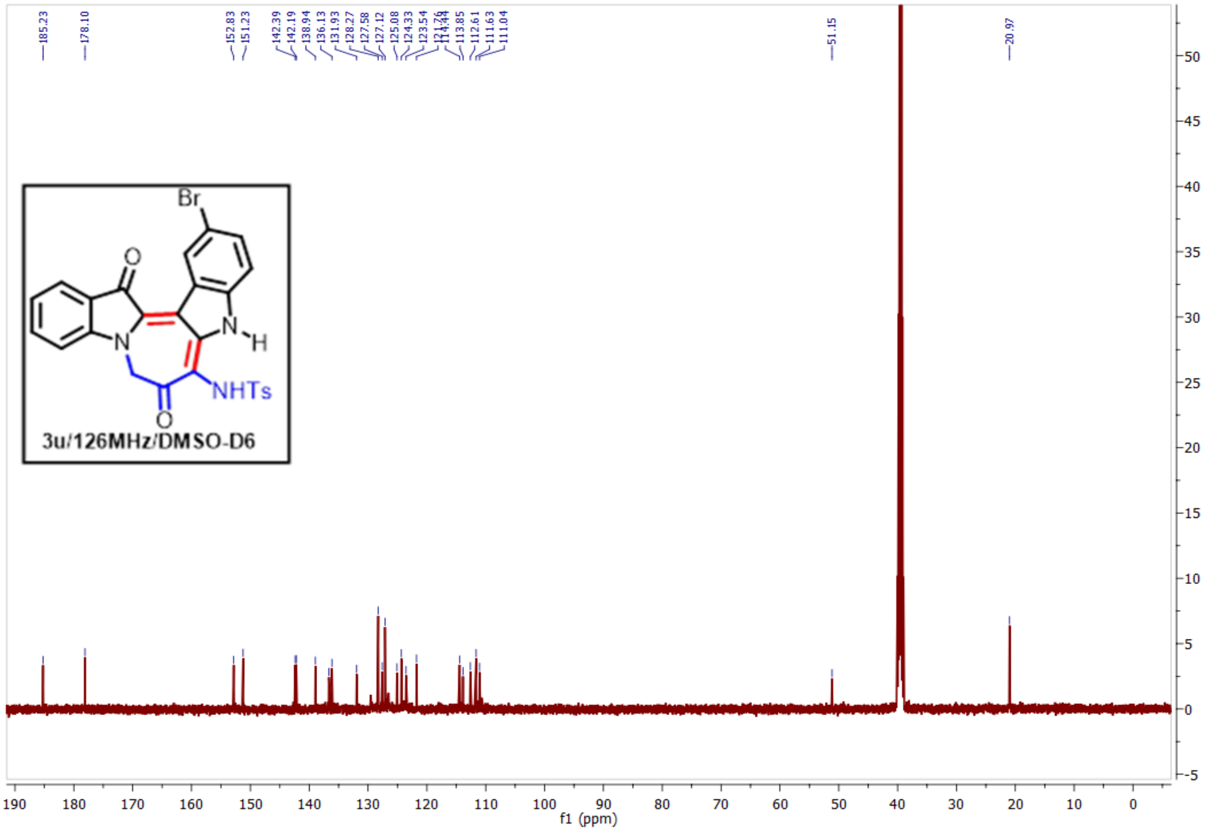

8.92
8.92
7.83
7.82
7.80
7.79
7.55
7.54
7.53
7.52
7.51
7.30
7.28
7.23
7.23
7.22
7.21
7.20
7.20
7.12
7.10
7.10
7.03
7.03
7.01
7.01
6.80
6.79
6.60
6.58
4.97
3.94
1.83
Br
O
N
N
Bn
NHTs
O
3s/500MHz/CDCl$_3$
0.93
0.96
0.88
2.06
0.95
4.96
2.00
1.00
1.01
0.95
1.94
1.91
2.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

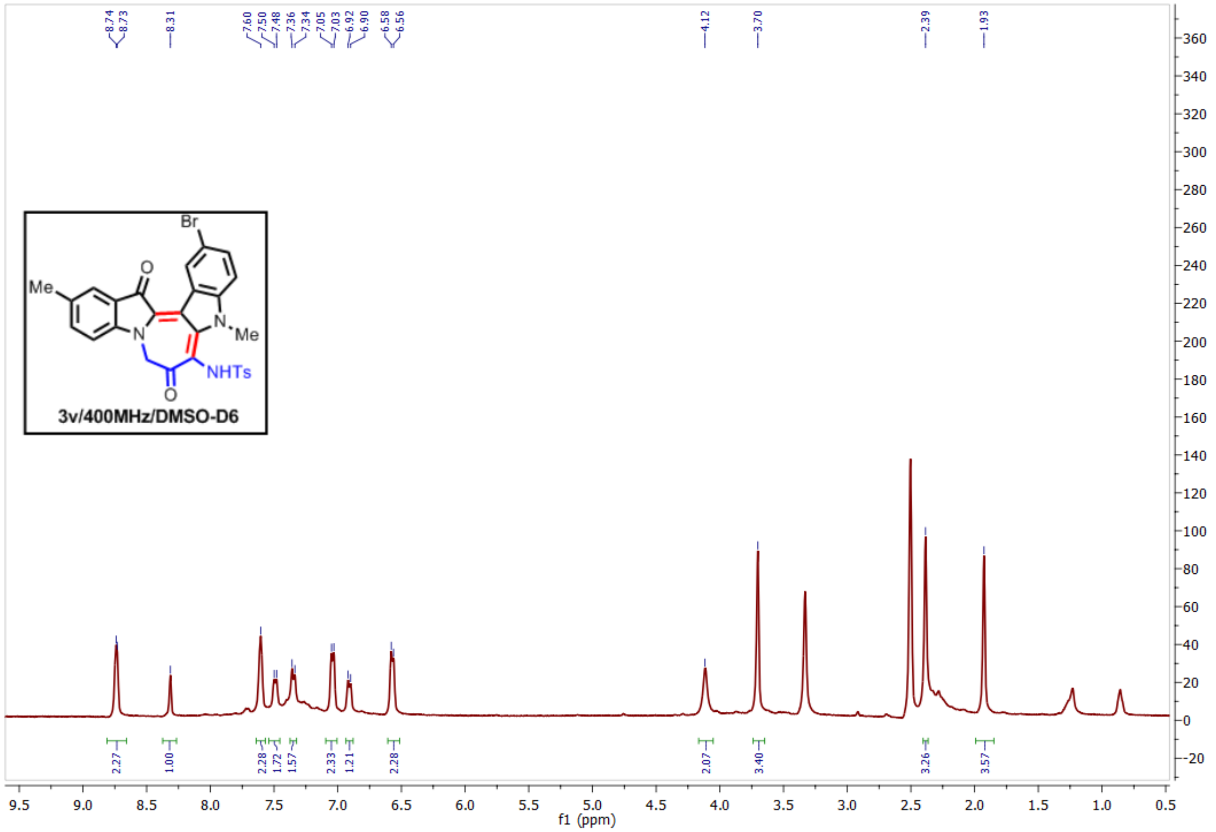

184.52
175.34
150.09
150.04
143.92
143.70
129.81
128.90
128.32
127.79
127.73
126.74
126.52
124.46
116.64
115.95
114.93
111.40
110.32
50.06
48.18
21.40
Br
O
N
N
Bn
NHTs
O
3s/126MHz/CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

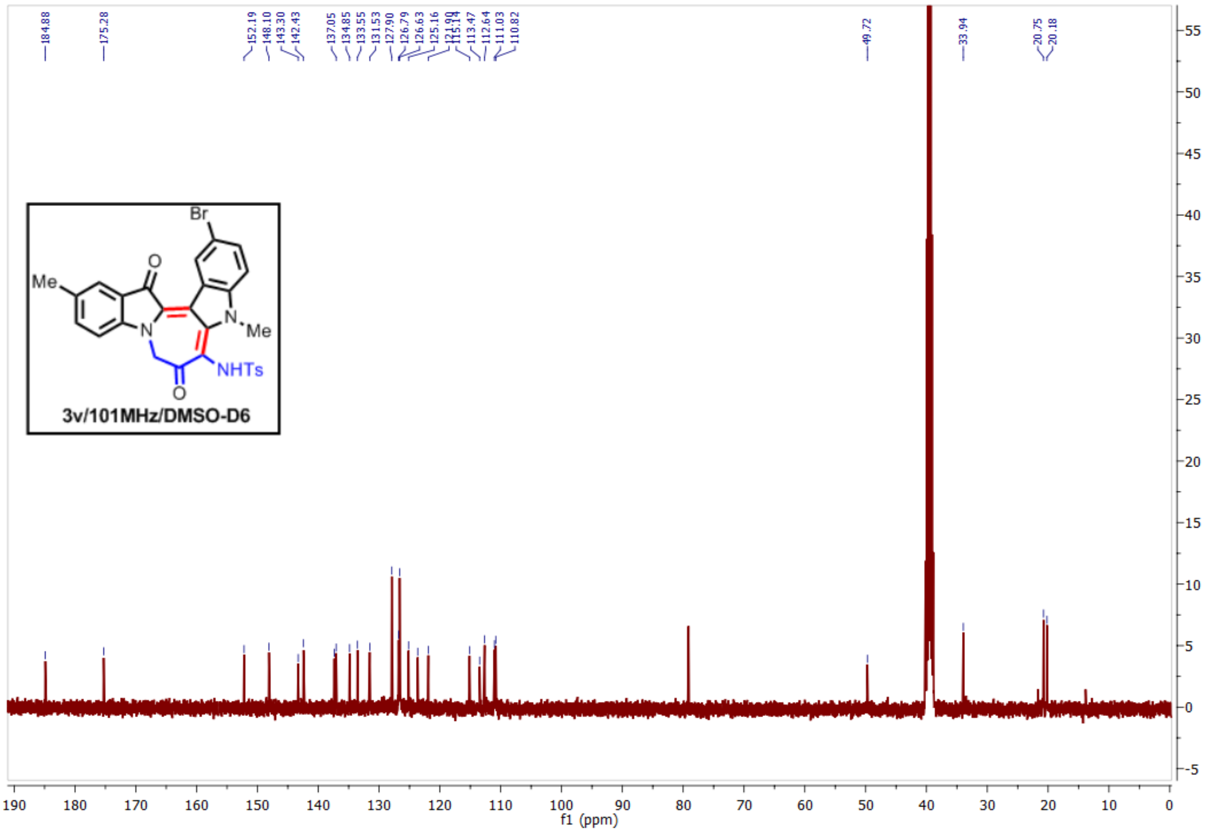

11.05
8.81
8.69
7.72
7.71
7.68
7.66
7.50
7.48
7.47
7.45
7.24
7.21
7.19
4.40
2.95
Br
O
N
N
H
NHMs
O
3t/400MHz/DMSO-D6
1.00
1.08
1.05
2.18
2.07
2.69
2.17
3.41
400
350
300
250
200
150
100
50
0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

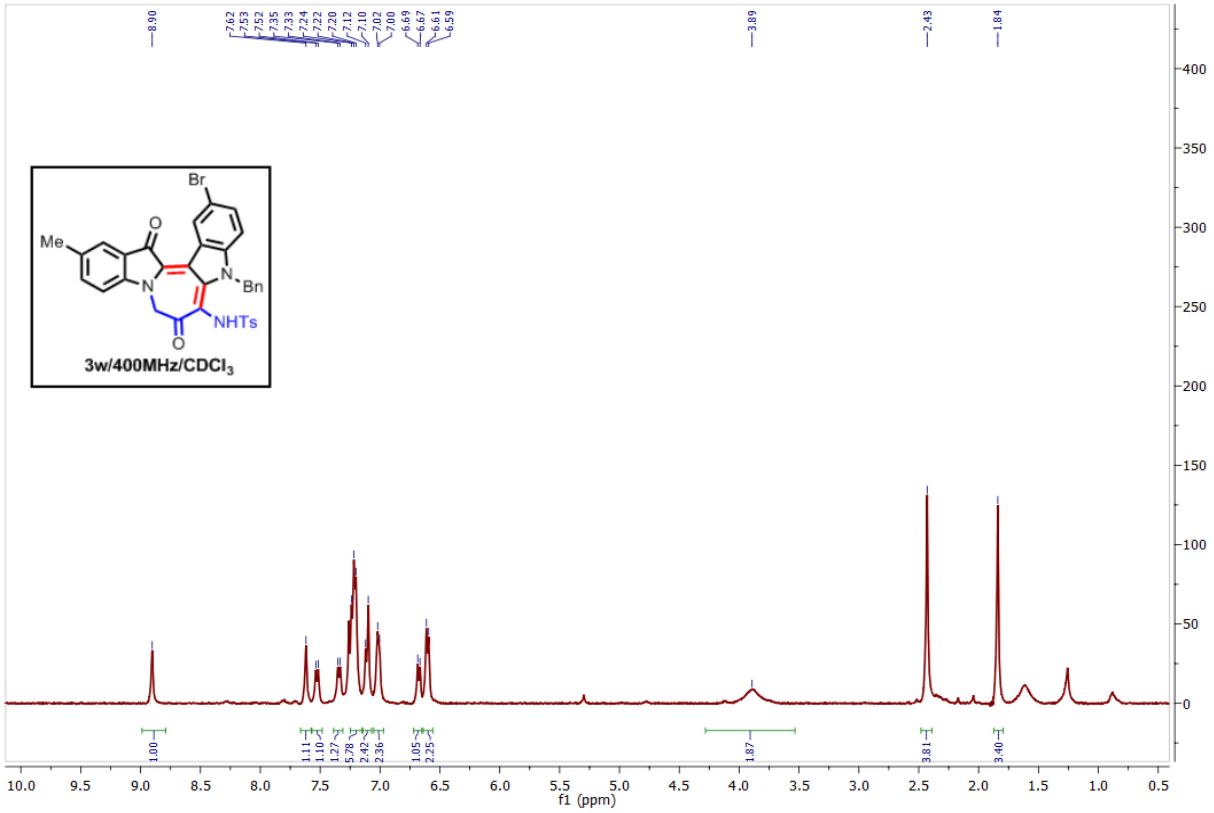

185.37
179.18
154.00
151.33
141.98
139.46
136.79
131.84
127.49
125.00
124.60
123.58
121.81
113.81
113.41
112.65
111.78
111.23
51.58
40.79
Br
O
N
N
H
NHMs
O
3t/101MHz/DMSO-D6
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

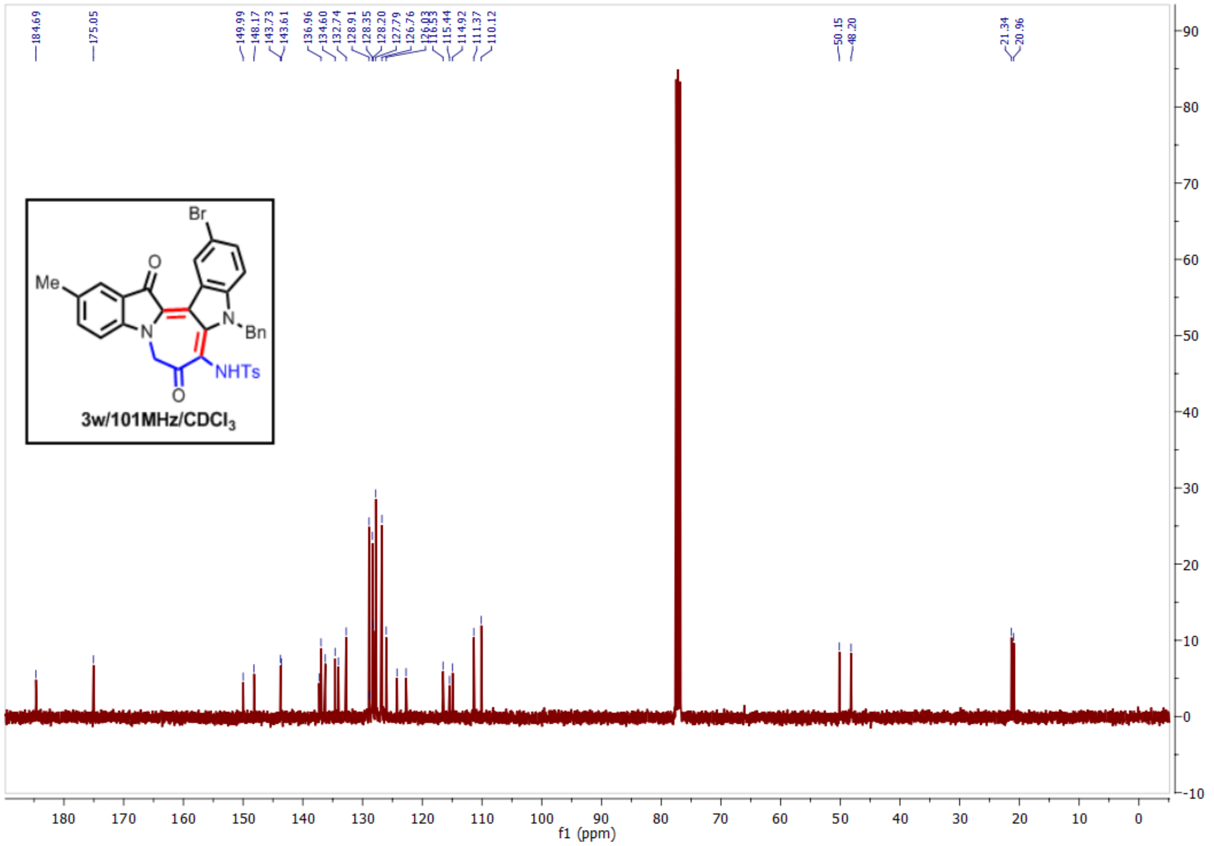

11.23
8.86
8.75
8.74
7.73
7.72
7.67
7.65
7.64
7.51
7.50
7.49
7.49
7.35
7.33
7.23
7.21
7.21
7.19
7.18
7.13
7.12
6.88
6.86
4.13
2.14
Br
O
N
N
H
NHTs
O
3u/500MHz/DMSO-D6
1.25
1.14
1.00
1.17
1.43
1.29
2.72
2.79
1.58
2.39
2.40
3.69
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

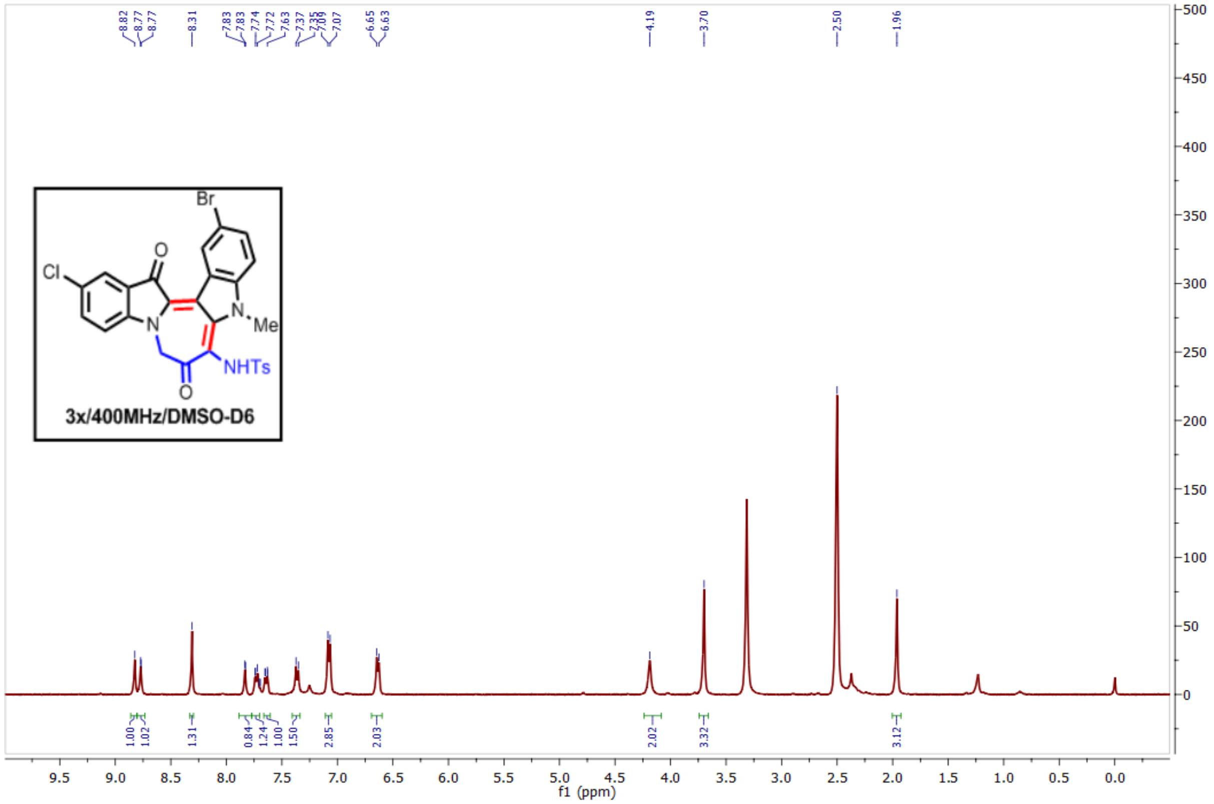

185.23
178.10
152.83
151.23
142.39
142.19
138.94
136.13
131.93
128.27
127.58
127.12
125.08
124.33
123.54
121.76
114.44
113.85
112.61
111.63
111.04
51.15
20.97
Br
O
N
N
H
NHTs
O
3u/126MHz/DMSO-D6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
50
45
40
35
30
25
20
15
10
5
0
-5

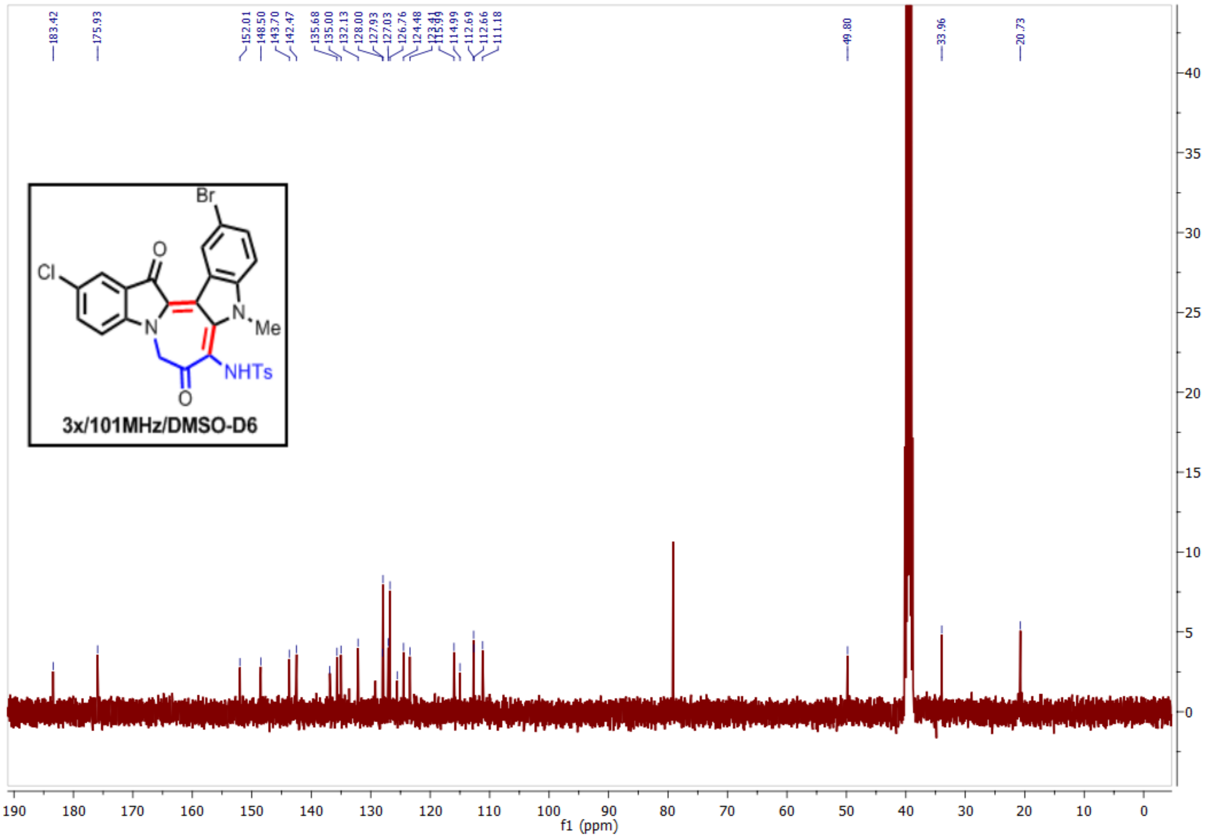

8.74
8.73
8.31
7.60
7.50
7.48
7.36
7.34
7.05
7.03
6.92
6.90
6.58
6.56
4.12
3.70
2.39
1.93
2.27
1.00
2.28
1.72
1.57
2.33
1.21
2.28
2.07
3.40
3.26
3.57
Br
Me
O
N
N
Me
NHTs
O
3v/400MHz/DMSO-D6
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

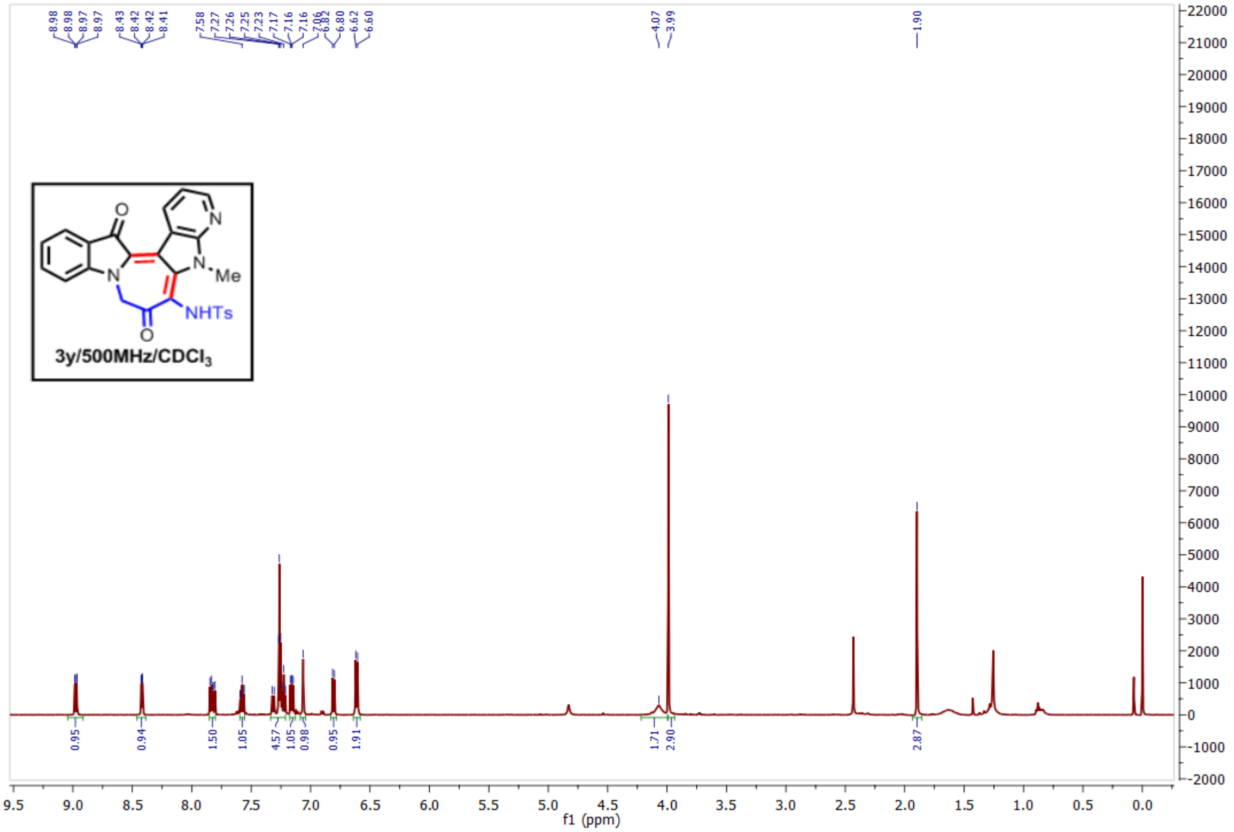

184.88
175.28
152.19
148.10
143.30
142.43
137.05
134.85
133.55
131.53
127.90
126.79
126.63
125.16
121.90
115.14
113.47
112.64
111.03
110.82
49.72
33.94
20.75
20.18
Br
Me
O
N
N
Me
NHTs
O
3v/101MHz/DMSO-D6
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
55
50
45
40
35
30
25
20
15
10
5
0
-5

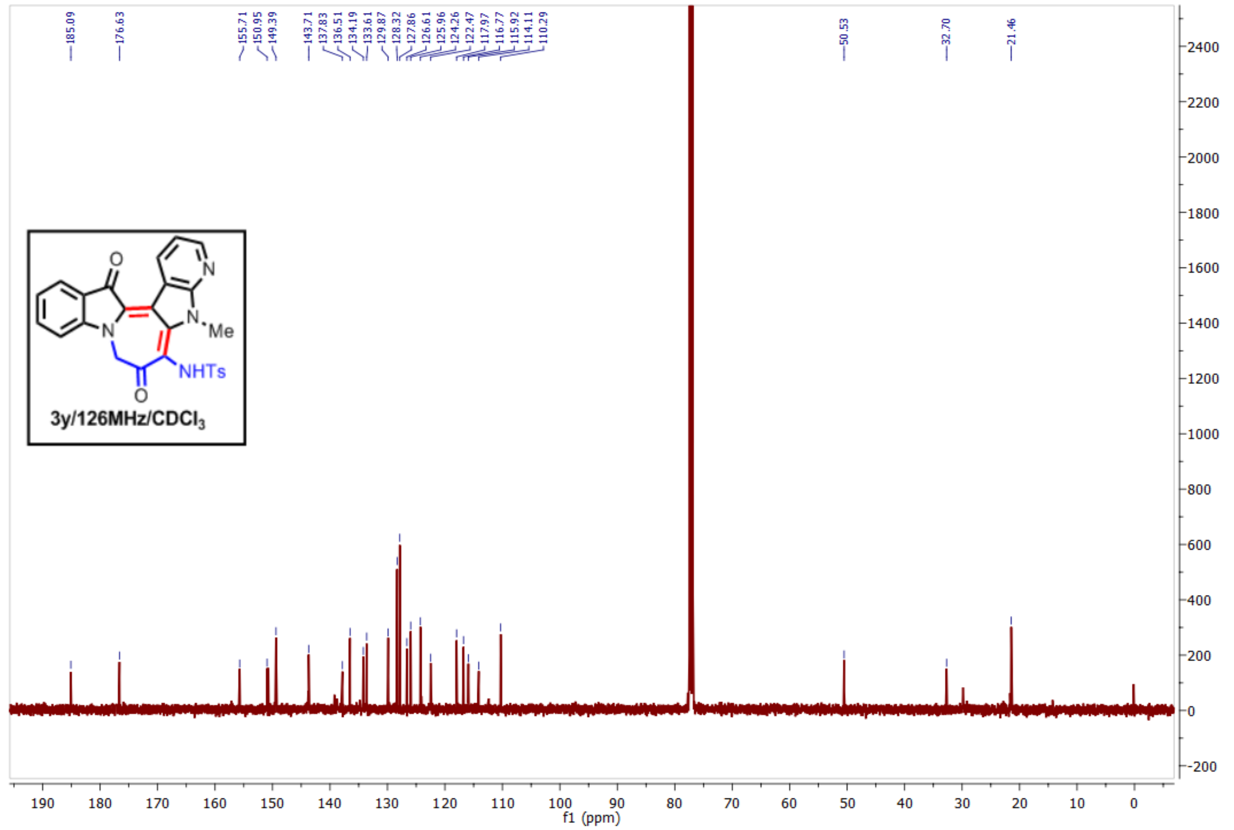

8.90
7.62
7.53
7.52
7.35
7.33
7.24
7.22
7.20
7.12
7.10
7.02
7.00
6.69
6.67
6.61
6.59
3.89
2.43
1.84
1.00
1.11
1.10
1.27
5.78
2.42
2.36
1.05
2.25
1.87
3.81
3.40
400
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
Br
O
Me
N
N
Bn
NHTs
O
3w/400MHz/CDCl$_3$

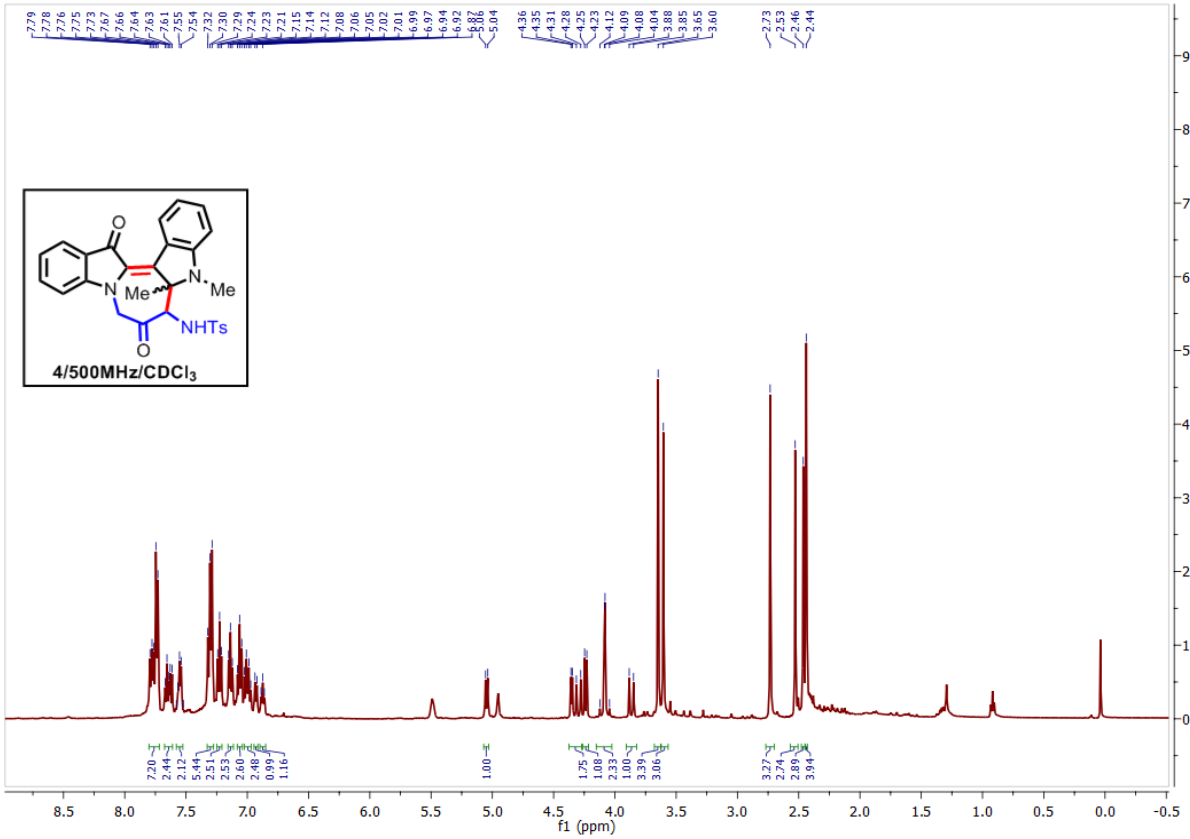

184.69
175.05
149.99
148.17
143.73
143.61
136.96
134.60
132.74
128.91
128.35
128.20
127.79
126.76
126.03
116.53
115.44
114.92
111.37
110.12
50.15
48.20
21.34
20.96
90
80
70
60
50
40
30
20
10
0
-10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Br
O
Me
N
N
Bn
NHTs
O
3w/101MHz/CDCl$_3$

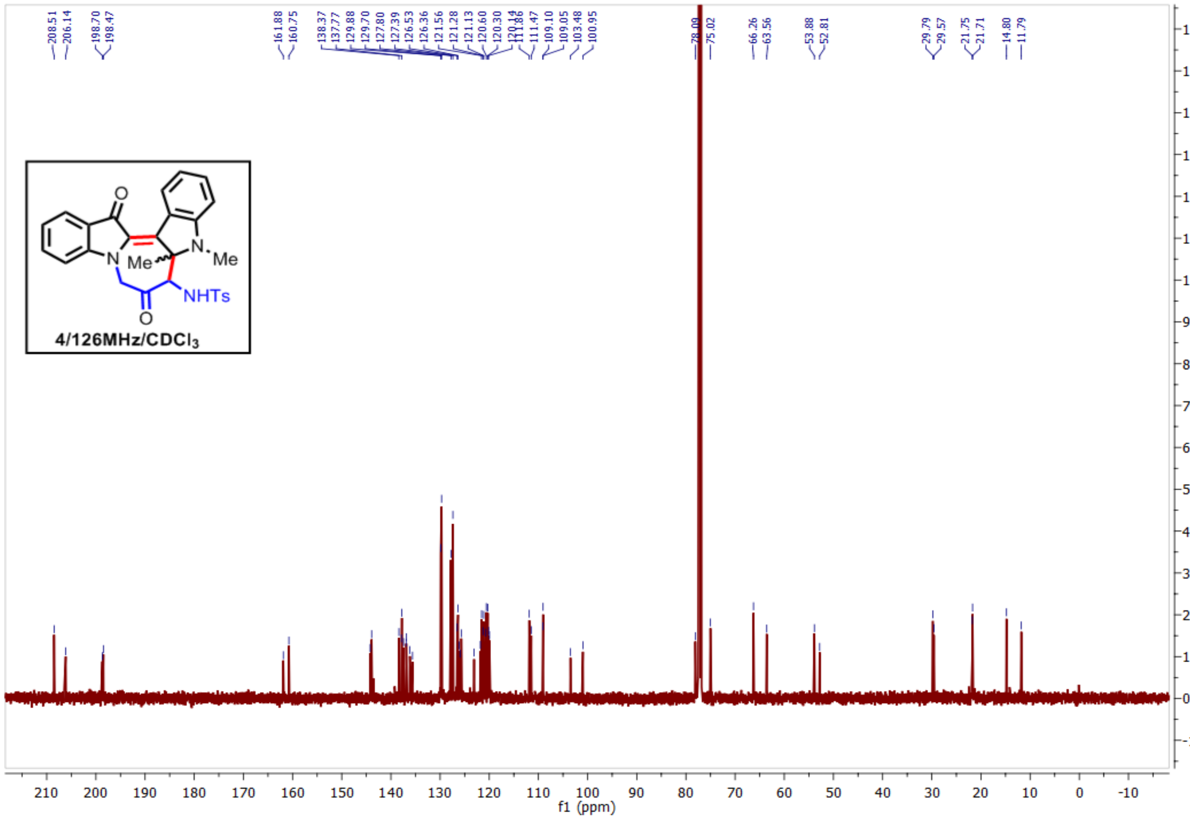

8.82
8.77
8.77
8.31
7.83
7.83
7.74
7.72
7.63
7.37
7.35
7.09
7.07
6.65
6.63
4.19
3.70
2.50
1.96
Br
O
Cl
N
N
Me
NHTs
O
3x/400MHz/DMSO-D6
1.00
1.02
1.31
0.84
1.24
1.00
1.50
2.85
2.03
2.02
3.32
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0


183.42
175.93
152.01
148.50
143.70
142.47
135.68
135.00
132.13
128.00
127.93
127.03
126.76
124.48
123.41
115.99
114.99
112.69
112.66
111.18
49.80
33.96
20.73
Br
O
Cl
N
N
Me
NHTs
O
3x/101MHz/DMSO-D6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
40
35
30
25
20
15
10
5
0


8.98
8.98
8.97
8.97
8.43
8.42
8.42
8.41
7.58
7.27
7.26
7.25
7.23
7.17
7.16
7.16
7.06
6.82
6.80
6.62
6.60
4.07
3.99
1.90
O
N
N
N
Me
NHTs
O
3y/500MHz/CDCl$_3$
0.95
0.94
1.50
1.05
4.57
1.05
0.98
0.95
1.91
1.71
2.90
2.87
f1 (ppm)


185.09
176.63
155.71
150.95
149.39
143.71
137.83
136.51
134.19
133.61
129.87
128.32
127.86
126.61
125.96
124.26
122.47
117.97
116.77
115.92
114.11
110.29
50.53
32.70
21.46
O
N
N
N
Me
NHTs
O
3y/126MHz/CDCl$_3$
f1 (ppm)


7.79
7.78
7.76
7.75
7.73
7.67
7.66
7.64
7.63
7.61
7.55
7.54
7.32
7.30
7.29
7.24
7.23
7.21
7.15
7.14
7.12
7.08
7.06
7.05
7.02
7.01
6.99
6.97
6.94
6.92
6.87
5.06
5.04
4.36
4.35
4.31
4.28
4.25
4.23
4.12
4.09
4.08
4.04
3.88
3.85
3.65
3.60
2.73
2.53
2.46
2.44
O
N
Me
N
Me
NHTs
O
4/500MHz/CDCl$_3$
7.20
2.44
2.12
5.44
2.51
2.53
2.60
2.48
0.99
1.16
1.00
1.75
1.08
2.33
1.00
3.39
3.06
3.27
2.74
2.89
3.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0


208.51
206.14
198.70
198.47
161.88
160.75
138.37
137.77
129.88
129.70
127.80
127.39
126.53
126.36
121.56
121.28
121.13
120.60
120.30
120.14
111.86
111.47
109.10
109.05
103.48
100.95
78.09
75.02
66.26
63.56
53.88
52.81
29.79
29.57
21.75
21.71
14.80
11.79
O
N
Me
N
Me
NHTs
O
4/126MHz/CDCl$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

9. Photophysical properties

Steady state absorption: UV-*vis*-NIR absorption spectra were recorded at room temperature on a PerkinElmer's LAMBDA 35 UV/Vis Spectrophotometer. Quartz cell with optical path length of 10 mm was used for all steady-state measurements. Solvents cyclohexane, toluene, THF, $CHCl_3$, MeCN, MeOH and DMSO obtained from Spectrochem (spectroscopic grade) were used.

Steady-state fluorescence emission studies and fluorescence decay measurements: Emission spectra were measured on a fluoromax-4P fluorimeter from HoribaYovin (model: FM-100) at room temperature. Spectroscopic-grade solvents were used for measuring optical properties. Quartz cell with optical path length of 10 mm was used for all steady-state measurements. The measurements of spontaneous fluorescence decay were done on time- correlated single photon counting system from Horiba (Fluorocube-01-NL).All samples were excited using a picosecond diode laser source at 280 nm and all the molecules were probed at their emission maxima. The full width at half-maximum (FWHM) of the instrument response function of our setup was ~140 ps. The data analysis was performed using IBH DAS version 6 decay analysis software. The decays were fitted with a multi-exponential function.

$$I(t) = \sum_{i=1}^{n} a_i \, exp\left(\frac{-t}{\tau_i}\right) \qquad (1)$$

Here, *I(t)* denotes normalized fluorescence decay and $\alpha_i$is the normalized amplitude of decay components τ_i, respectively. The average lifetime was obtained from the equation

$$\langle \tau \rangle = \sum_{i=1}^{n} a_i \, \tau_i \qquad (2)$$

The quality of the fit was judged by reduced chi square (χ^2) values and corresponding residual distribution. The acceptable fit has a χ^2 near unity.

Quantum yields were calculated according to the following formula and relative to quinine sulfate (H_2SO_4, 0.5 M), Φ_{ref}= 0.546 as a reference.

$$QY = QY_{ref} \frac{I A_{ref} \, \eta^2}{A I_{ref} \, \eta_{ref}^2} \qquad (3)$$

where, *QY* = quantum yield; *ref* = reference (quinine sulphate); *A* = Absorbance; *I* = integrated fluorescence intensity; η = refractive index of the solvent.

Photophysical properties of 3e, **3l**, and **3i:**

The photophysical properties of **3e**, **3l**, and **3i** were evaluated using UV−vis-NIR absorption and photoluminescence (PL) spectroscopies. The spectra are shown in Figure S2-S3, and photophysical data are summarized in Table S1. All of the compounds exhibited almost identical spectra with a relatively broad and intense absorption in the UV-vis-NIR region. The sharp absorption bands between 280−450 nm are ascribed to the π−π* transitions of the conjugated systems, the broad bands in the range of 450−860 nm are assigned to the intramolecular charge transfer (ICT). However, the molar absorption coefficients of the compounds are different. These results indicate that the different substituents on the isatin moiety has little influence on the absorption maxima. Additionally, The TD-DFT calculations revealed that the longest-wavenumber absorptions in **3e**, **3l** and **3i** (673 to 680 nm) are attributed to the allowed HOMO–LUMO transitions (see Figure S8-S13, Table S2-S4).

In the PL spectra, the shapes of emission peaks were almost the same and exhibited an emission maximum in the 405−432 nm region for all derivatives. The quantum yields (Φ) in solution were observed 0.48−0.53%, respectively and the excited state lifetime (τ) of **3l**, **3i** were observed in a narrow range from 1.517 to 1.751 ns, while it was higher for **3e** (25.434 ns) (see Figure S7). The absorption and emission investigations were carried out in different solvents like cyclohexane (CH), toluene, tetrahydrofuran (THF), chloroform, acetonitrile (MeCN), methanol (MeOH), and dimethyl sulfoxide (DMSO) and noticed the identical spectra in these solvents except in DMSO (see Figure S4-S6).

Table S1. Photophysical properties of **3e, 3l,** and **3i**.

Compound	λ_{abs} [a] **(nm)**	**ε[a] (M^{-1} cm^{-1})**	λ_{em}[a] **(nm)**	**Φ_{fl}[b] (%)**	**τ_{fl}[c] (ns)**
3e	299	2459	432	0.48	25.434
3l	308	4097	431	0.53	1.517
3i	312	4095	406	0.49	1.751

[a] In $CHCl_3$ (200 μM). [b] Measured relative quinine sulfate (H_2SO_4, 0.5 M), Φ_{ref}= 0.546. [c] Fluorescence lifetime.

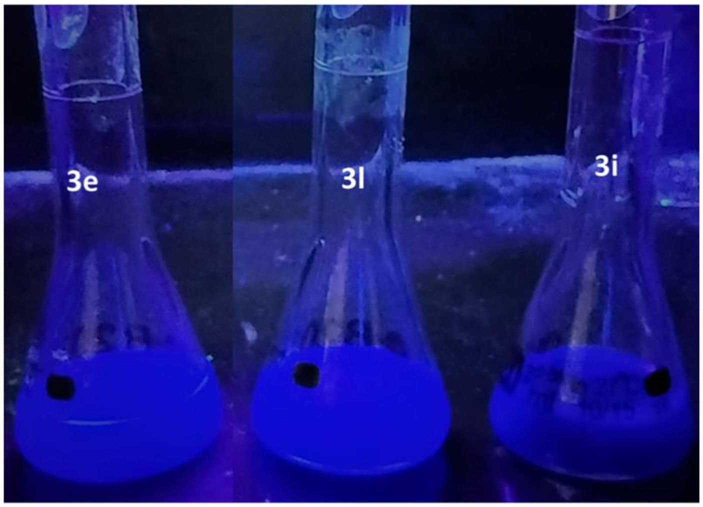


Figure S1. Solutions of compound **3e, 3l** and **3i** under UV-Vis light source**.**

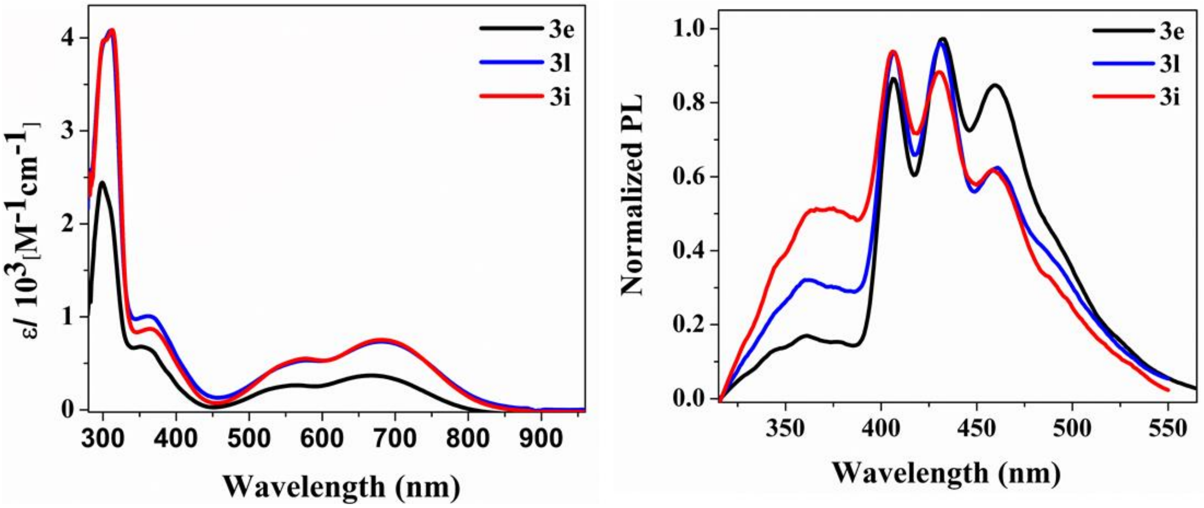


Figure S2. UV-*vis*-NIR absorption (left side) and photoluminescence (PL) (right side) spectra of **3e, 3l** & **3i** in $CHCl_3$ with concentration of 20×10^{-5} M.

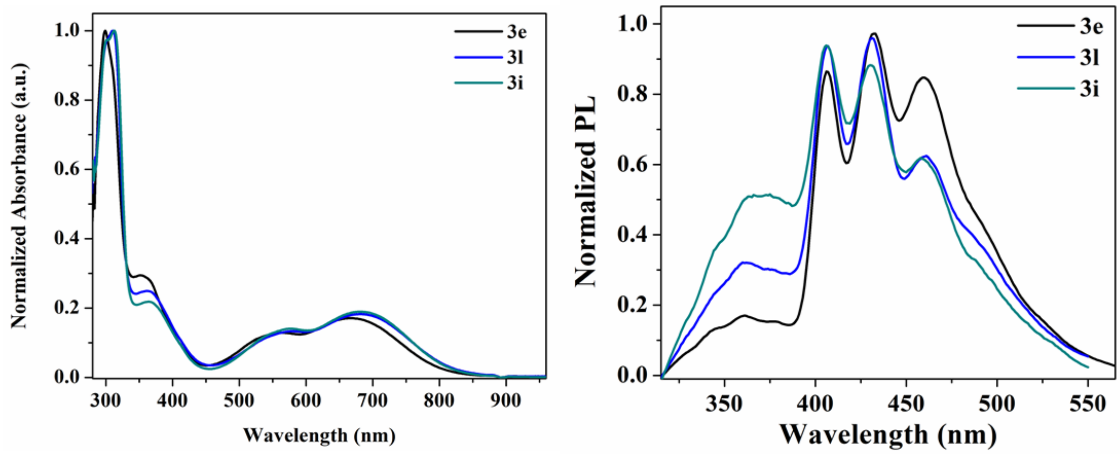


Figure S3. Normalized UV-*vis*-NIR absorption (left side) and fluorescence (right side) spectra of **3e, 3l** & **3i** in $CHCl_3$.

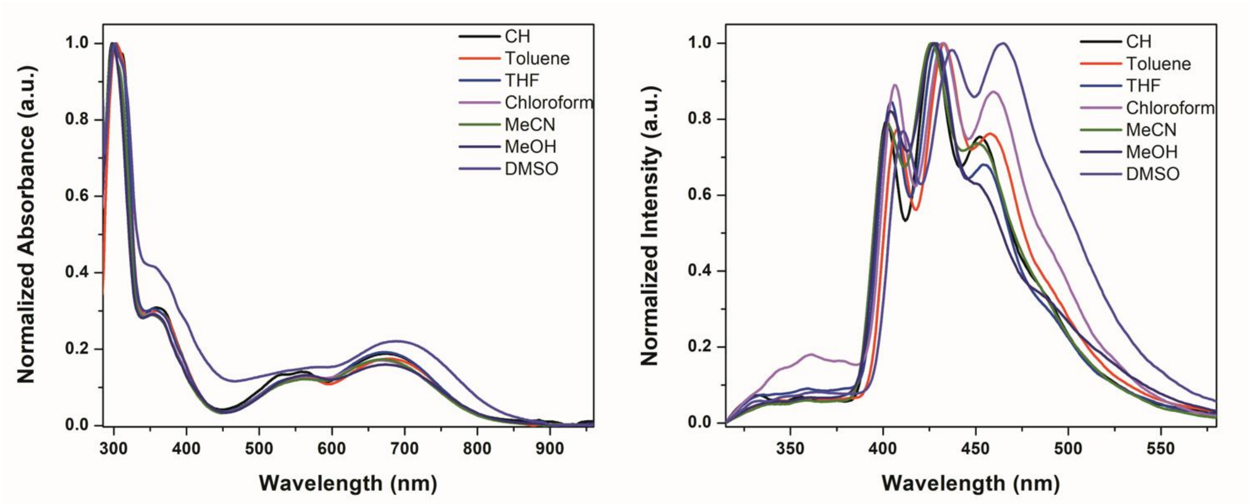


Figure S4. Normalized absorption (left side) and emissions (right side) of **3e** in cyclohexane (CH), toluene, tetrahydrofuran (THF), chloroform, acetonitrile (MeCN), methanol (MeOH), and dimethyl sulfoxide (DMSO).

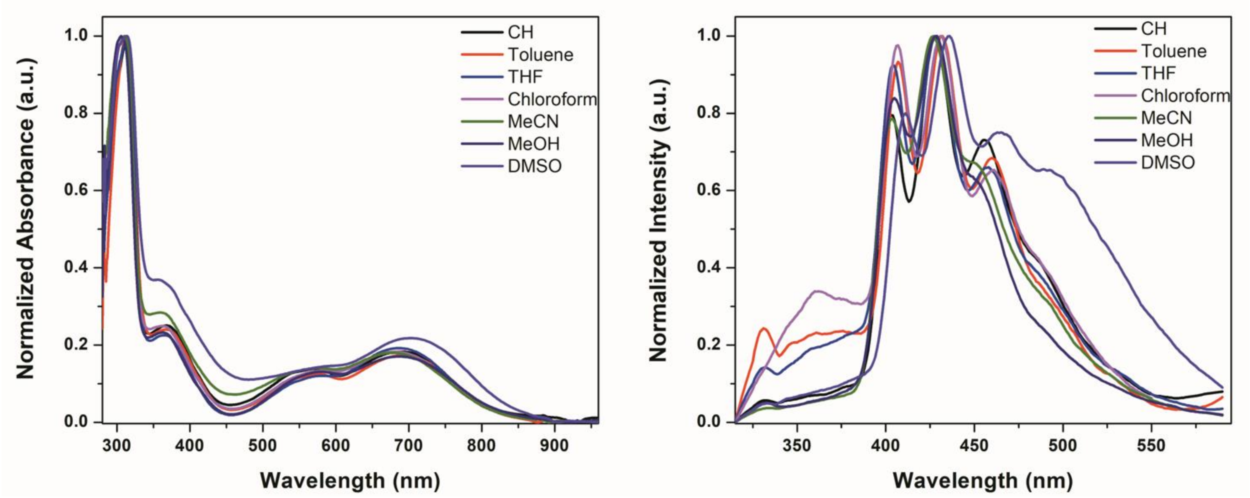


Figure S5. Normalized absorption (left side) and emissions (right side) of **3l** in cyclohexane (CH), toluene, tetrahydrofuran (THF), chloroform, acetonitrile (MeCN), methanol (MeOH), and dimethyl sulfoxide (DMSO).

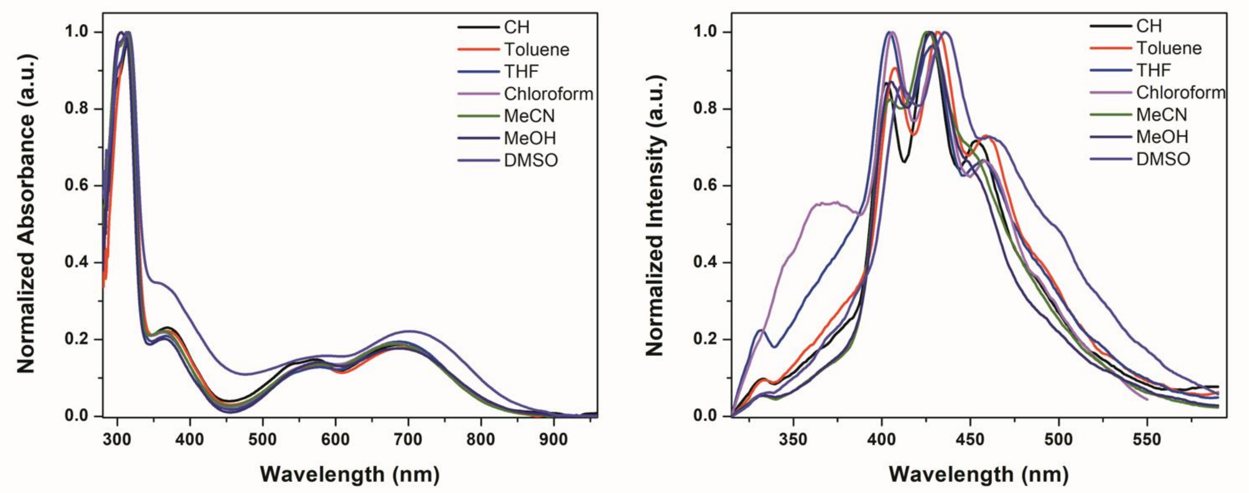


Figure S6. Normalized absorption (left side) and emissions (right side) of **3i** in cyclohexane (CH), toluene, tetrahydrofuran (THF), chloroform, acetonitrile (MeCN), methanol (MeOH), and dimethyl sulfoxide (DMSO).

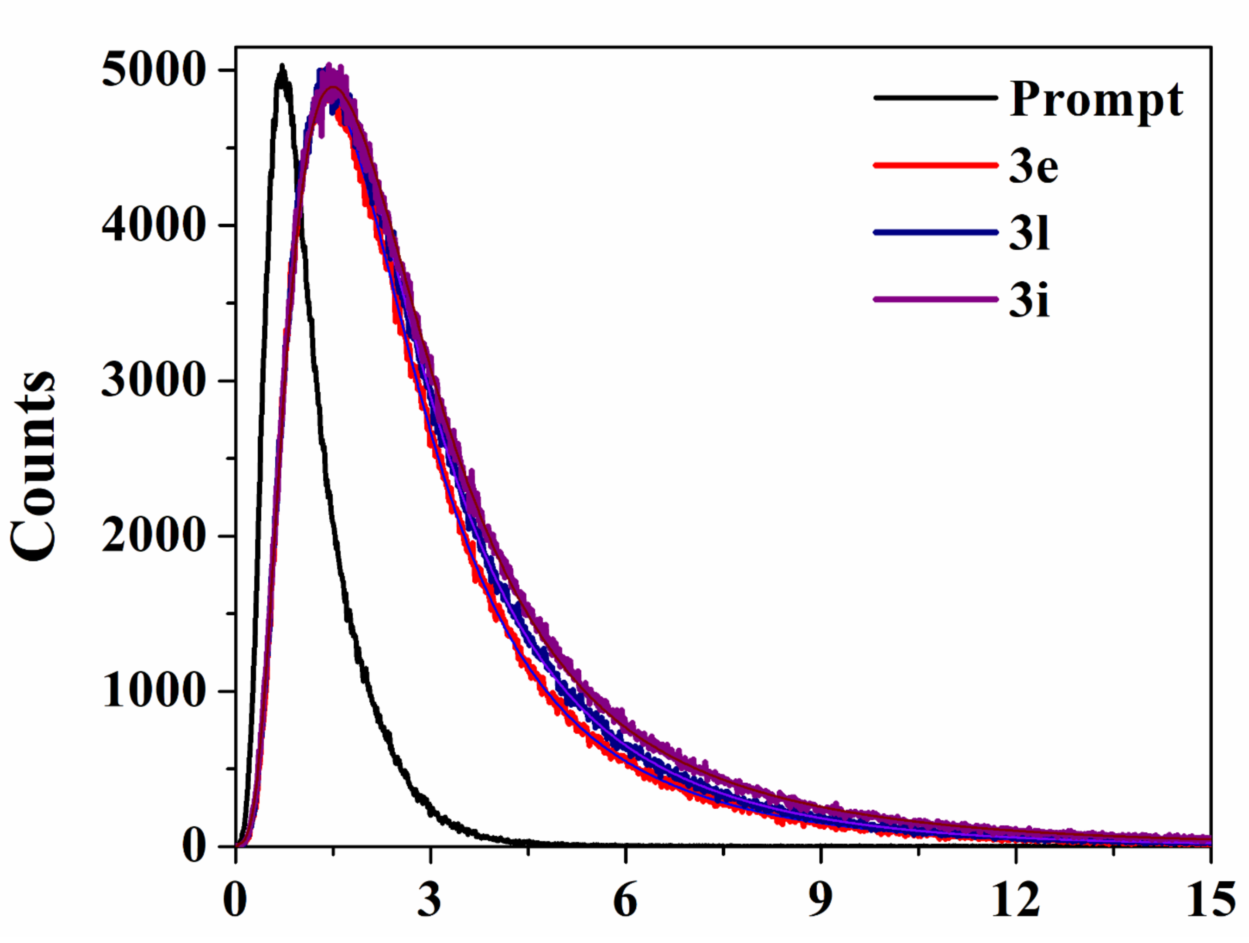


Figure S7. Fluorescence decay profile of **3e**, **3l**, & **3i** in $CHCl_3$ (λ_{exc} 280 nm).

10. DFT calculations of 3e, 3l, & 3i

Theoretical calculations were performed with the Gaussian09 program suite.[4] All calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-311G(d,p) basis set for all atoms.[5] While the –NTs, p-tolyl group were replaced with methyl group to simplify the calculations. Solvent effects were calculated using the polarized continuum model (PCM).[6] In all calculations, $CHCl_3$ was used as the solvent. To simulate the ground-state absorption spectra, the time-dependent(PCM-TDDFT) calculationswere employed with B3LYP/6-311G(d,p) level for the first 50 states. Visualization of the results was performed by use of GaussView 5.0 software.

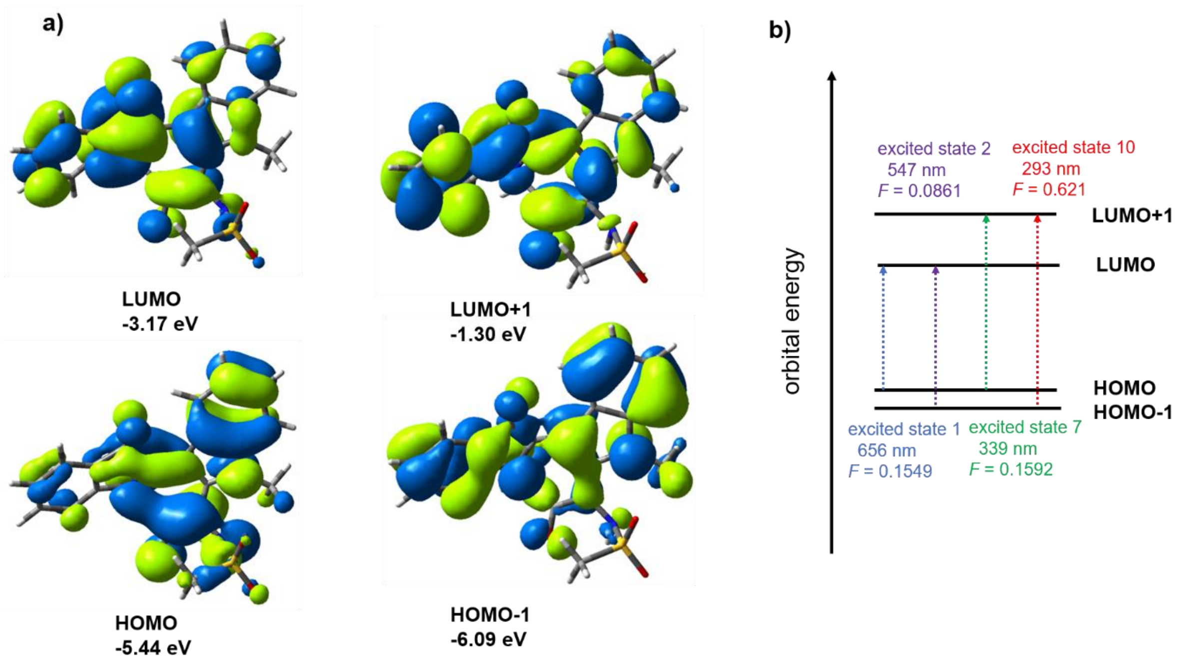


Figure S8. Pictorial representations of the frontier MOs of **3e** and energy diagrams and, calculated at the B3LYP/6-311G(d,p) level of theory.

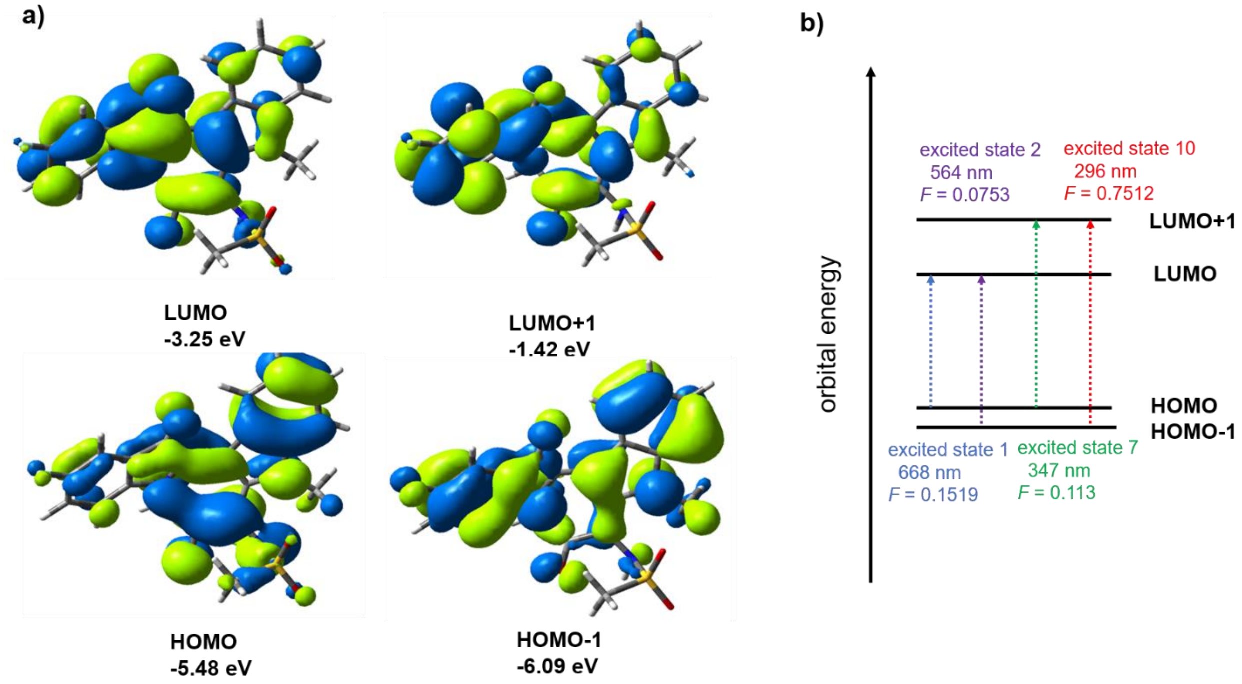


Figure S9. Pictorial representations of the frontier MOs of **3l** and energy diagrams and, calculated at the B3LYP/6-311G(d,p) level of theory.

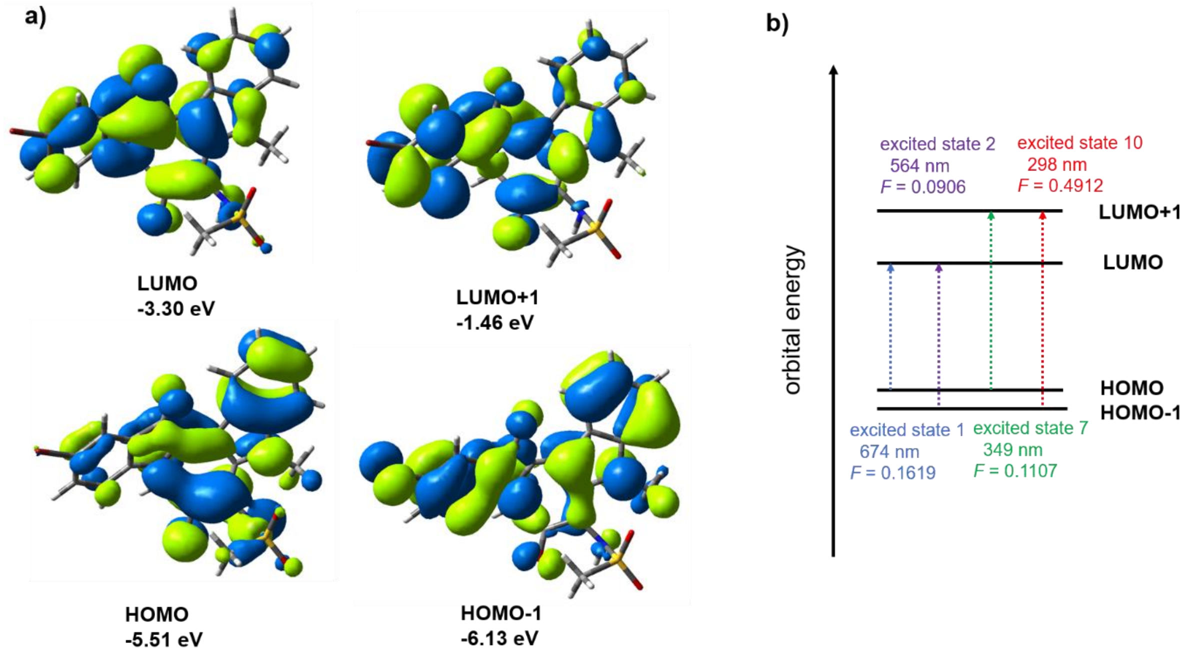


Figure S10. Pictorial representations of the frontier MOs of **3i** and energy diagrams and, calculated at the B3LYP/6-311G(d,p) level of theory.

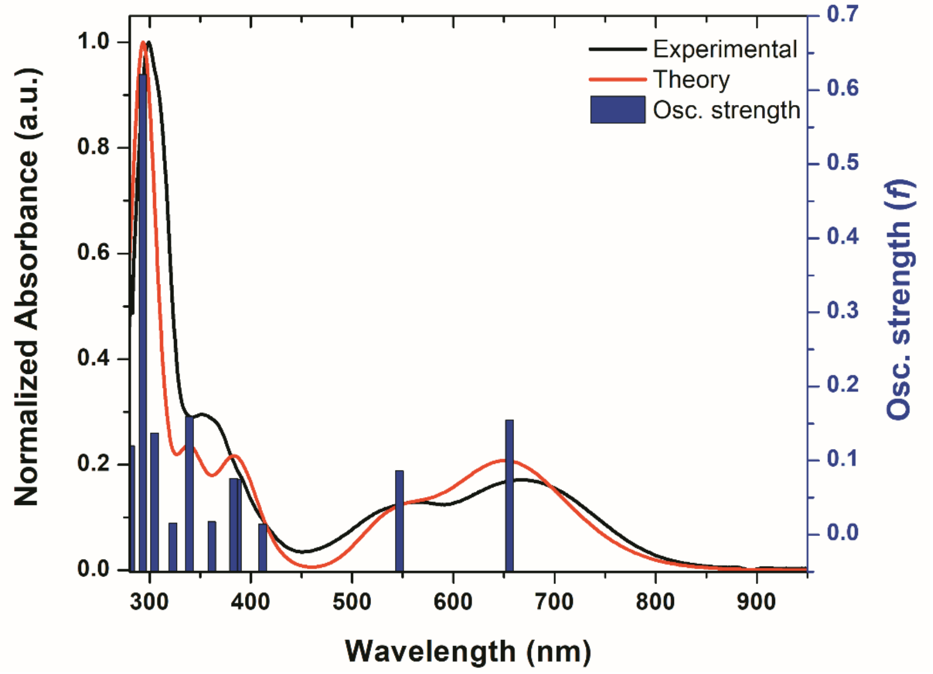


Figure S11. Experimental (black) calculated (red) UV-*vis*-NIR spectra of **3e** and oscillator strengths are shown as blue vertical lines.

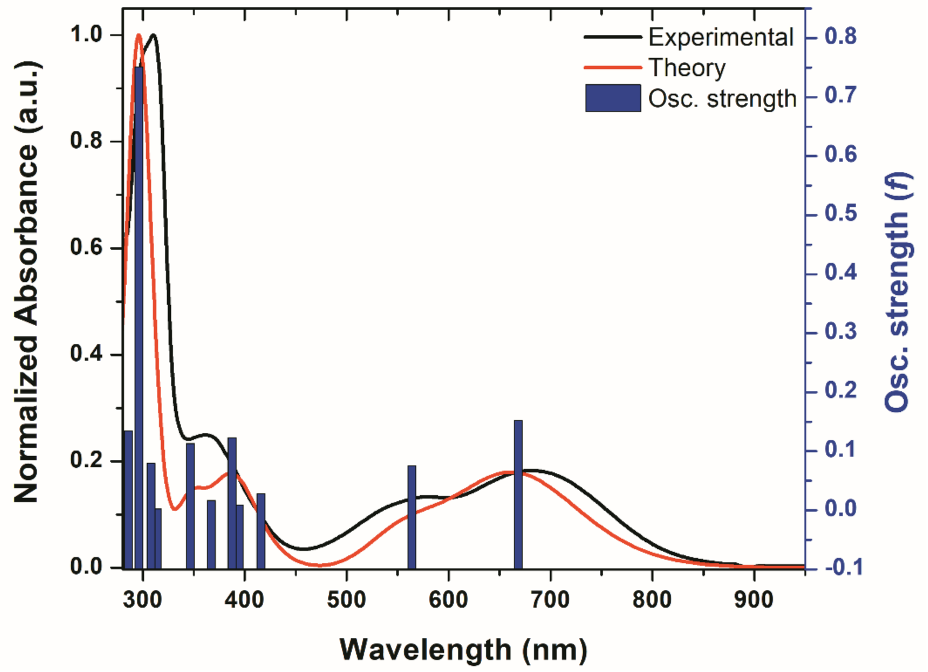


Figure S12. Experimental (black) calculated (red) UV-vis-NIR spectra of **3l** and oscillator strengths are shown as blue vertical lines.

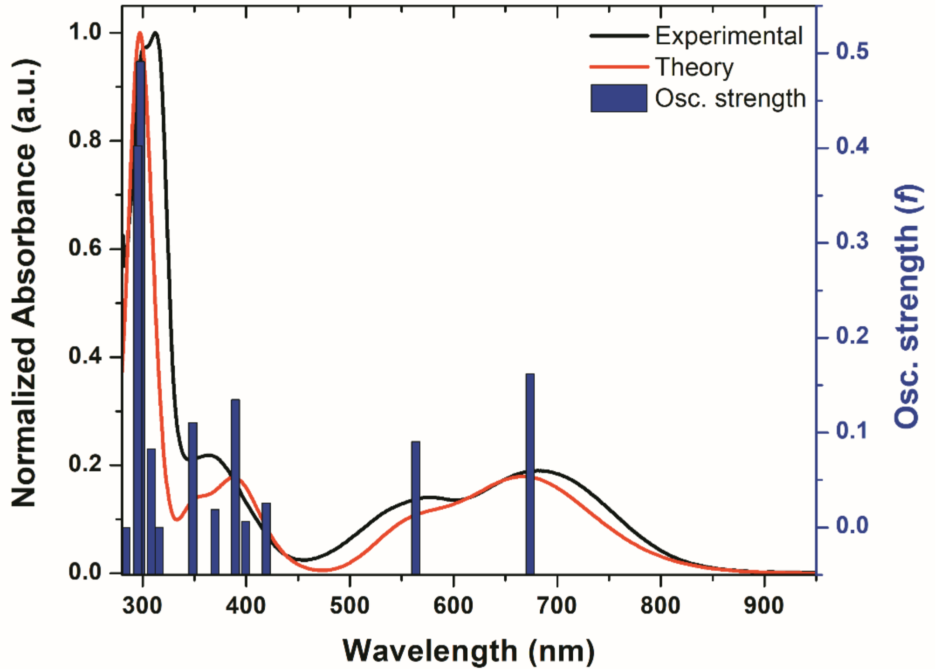


Figure S13. Experimental (black) calculated (red) UV-vis-NIR spectra of **3i** and oscillator strengths are shown as blue vertical lines.

TableS2. Selected TD-DFT (B3LYP/6-311G(d,p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **3e**.

Excited state	Energy(eV)	Wavelength(nm)	Osc. Strength	Major contribs
1	1.8914	655.51	0.1549	HOMO->LUMO (99%)
2	2.2677	546.73	0.0861	H-1->LUMO (95%)
3	3.0128	411.52	0.0141	H-5->LUMO (52%), H-2->LUMO (44%)
4	3.2056	386.77	0.0749	H-5->LUMO (14%), H-4->LUMO (16%)
5	3.2387	382.82	0.0759	H-5->LUMO (22%), H-3->LUMO (50%)
6	3.4303	361.43	0.0176	H-4->LUMO (61%), HOMO->L+1 (22%)
7	3.6579	338.94	0.1592	H-4->LUMO (16%), HOMO->L+1 (72%)
8	3.8388	322.97	0.0154	H-6->LUMO (90%)
9	4.0709	304.56	0.1372	H-1->L+1 (18%), HOMO->L+2 (77%)
10	4.2303	293.08	0.621	H-1->L+1 (72%), HOMO->L+2 (16%)

Table S3. Selected TD-DFT (B3LYP/6-311G(d,p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **3l**.

Excited state	Energy (eV)	Wavelength (nm)	Osc. Strength	Major contribs
1	1.8557	668.12	0.1519	HOMO->LUMO (99%)
2	2.1983	564.00	0.0753	H-1->LUMO (96%)
3	2.9817	415.81	0.0279	H-5->LUMO (42%), H-2->LUMO (55%)
4	3.1425	394.53	0.0092	H-3->LUMO (88%)
5	3.2000	387.45	0.123	H-5->LUMO (49%), H-2->LUMO (40%)
6	3.3766	367.18	0.0168	H-4->LUMO (60%), HOMO->L+1 (26%)
7	3.5774	346.57	0.113	H-4->LUMO (21%), HOMO->L+1 (70%)
8	3.9447	314.30	0.0023	H-6->LUMO (72%), H-1->L+1 (21%)
9	4.0281	307.79	0.0795	HOMO->L+2 (64%)
10	4.1859	296.19	0.7512	H-1->L+1 (53%), HOMO->L+2 (26%)

Table S4. Selected TD-DFT (B3LYP/6-311G(d,p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **3i**.

Excited state	Energy (eV)	Wavelength (nm)	Osc. Strength	Major contribs
1	1.8407	673.57	0.1619	HOMO->LUMO (99%)
2	2.2001	563.53	0.0906	H-1->LUMO (96%)
3	2.9576	419.20	0.0258	H-5->LUMO (39%), H-2->LUMO (57%)
4	3.1052	399.27	0.0066	H-3->LUMO (82%)
5	3.1825	389.58	0.1348	H-5->LUMO (49%), H-2->LUMO (32%)
6	3.3512	369.96	0.019	H-4->LUMO (61%), HOMO->L+1 (24%)
7	3.5580	348.46	0.1107	H-4->LUMO (20%), HOMO->L+1 (71%)
8	3.9279	315.65	0.0002	H-6->LUMO (75%), H-1->L+1 (19%)
9	4.0189	308.50	0.0829	H-1->L+1 (22%), HOMO->L+2 (66%)
10	4.1647	297.70	0.4912	H-7->LUMO (26%), H-1->L+1 (37%)

Cartesian coordinates of optimized structures

3e:

-2.394287	-2.546403	-1.021133
0.186947	-3.078851	1.619875
2.228251	2.639396	-1.115986
-2.696563	-1.327552	-1.770918
-3.392168	-3.613311	-0.922235
-2.088103	-2.083229	0.584839
-2.007599	-2.931926	1.144237
-2.346026	0.841899	0.642731
1.832649	-0.245415	0.829954
5.645958	-0.257810	-0.846415
6.626377	-0.221326	-1.305586
4.725275	0.762100	-1.079179
4.967078	1.610606	-1.709030
3.473492	0.669812	-0.480185
2.320260	1.582131	-0.519240
1.260217	0.891312	0.316988
-0.083776	1.185136	0.437962

-1.142773	0.188283	0.722087
-0.997985	-1.201626	0.862737
-0.874248	-3.236987	-1.689424
-2.154787	2.177961	0.291649
-0.775205	2.436966	0.159725
5.304867	-1.337093	-0.023200
6.029164	-2.126305	0.144032
4.052390	-1.434743	0.591053
3.808469	-2.286987	1.212307
3.145084	-0.411829	0.346756
1.269302	-0.967307	1.959053
0.918174	-0.243341	2.701629
2.034356	-1.592497	2.411690
0.139520	-1.853914	1.464077
-0.353589	3.742264	-0.121394
0.696750	3.965583	-0.226179
-1.308466	4.739988	-0.296010
-0.988152	5.749368	-0.526903
-2.673515	4.453915	-0.189036
-3.402048	5.242179	-0.342218
-3.117378	3.167301	0.110246
-4.175197	2.952614	0.187561
-3.660781	0.308169	0.983098
-3.565299	-0.461437	1.742693
-4.154201	-0.112907	0.105537
-4.264197	1.121080	1.385767
-1.083986	-3.504027	-2.725926
-0.095969	-2.476169	-1.648177
-0.599672	-4.116490	-1.109930

3l:

-2.488626	-2.609365	-1.086777
-0.071648	-3.051506	1.709704
1.953553	2.696660	-0.979422
-2.666653	-1.395636	-1.882668
-3.533340	-3.634322	-1.062101
-2.313287	-2.119595	0.531055
-2.271157	-2.955692	1.112749

-2.651971	0.791265	0.560635
1.535910	-0.186013	0.965017
5.378581	-0.135605	-0.557935
4.474144	0.872606	-0.848009
4.745238	1.709756	-1.479655
3.206795	0.750734	-0.289225
2.037385	1.643681	-0.375439
0.962289	0.934728	0.420032
-0.392728	1.195680	0.476852
-1.437293	0.170857	0.708730
-1.262055	-1.213114	0.868238
-0.942528	-3.378131	-1.589736
-2.477821	2.132121	0.219507
-1.100491	2.427975	0.161129
5.060422	-1.220712	0.254063
5.813061	-1.978088	0.436088
3.788489	-1.332725	0.819331
3.543302	-2.184818	1.439872
2.869078	-0.330056	0.533553
0.939434	-0.909387	2.076016
0.534566	-0.186309	2.791665
1.697400	-1.509233	2.572565
-0.142318	-1.830399	1.537277
-0.698087	3.744195	-0.097200
0.350100	3.995196	-0.146490
-1.667806	4.717541	-0.319028
-1.362474	5.735618	-0.531059
-3.028717	4.395608	-0.283549
-3.768429	5.165530	-0.472231
-3.454531	3.097257	-0.010076
-4.509280	2.856420	0.011765
-3.970047	0.222811	0.823229
-3.900507	-0.546295	1.585721
-4.401608	-0.207945	-0.082113
-4.617154	1.018763	1.190465
-1.064998	-3.677118	-2.631413
-0.141750	-2.645362	-1.501077
-0.757847	-4.243808	-0.956542

6.625172	-0.072437	-1.088834

3i:

-3.252927	-2.580516	-1.192989
-1.024677	-3.063937	1.764886
1.253818	2.662438	-0.787085
-3.376067	-1.361297	-1.990667
-4.306938	-3.595314	-1.229855
-3.161228	-2.101603	0.435102
-3.160969	-2.941638	1.012757
-3.462933	0.812508	0.457107
0.681810	-0.213439	1.131781
4.656944	-0.141582	-0.041106
3.760718	0.852481	-0.418384
4.058410	1.696237	-1.028112
2.448935	0.725667	0.022294
1.289551	1.615562	-0.168000
0.154792	0.912325	0.544565
-1.197147	1.186799	0.506419
-2.268227	0.175964	0.674292
-2.120905	-1.210242	0.837979
-1.689706	-3.361810	-1.615595
-3.251126	2.151775	0.130061
-1.868930	2.428851	0.151057
4.262015	-1.219337	0.757412
4.981402	-1.978774	1.035982
2.944554	-1.336671	1.204528
2.654733	-2.182503	1.814707
2.044610	-0.349723	0.821508
0.003788	-0.942927	2.191383
-0.432850	-0.225834	2.894338
0.722429	-1.562455	2.720845
-1.057527	-1.843269	1.580762
-1.434879	3.739956	-0.081227
-0.382366	3.976841	-0.071751
-2.377249	4.726720	-0.355058
-2.046786	5.740813	-0.547515
-3.742205	4.423609	-0.396148

-4.459596	5.203960	-0.623852
-4.200134	3.130798	-0.149988
-5.257802	2.904840	-0.184717
-4.800789	0.261038	0.645739
-4.783653	-0.503722	1.415648
-5.184193	-0.170500	-0.280515
-5.458342	1.067125	0.969148
-1.754499	-3.645684	-2.666715
-0.886428	-2.640947	-1.471018
-1.552501	-4.238525	-0.985322
6.482135	-0.039550	-0.634206

----

11. Crystallographic data of 3d and 3e

Table S6. Crystallographic data and structure refinement detail for **3d** and **3e.**

	3d	**3e**
CCDC No.	1911349	1911350
Formula	$C_{33}H_{24}N_3O_4S$	$C_{29}H_{23}N_3O_4S$
Formula weight (g/mol)	558.61	509.56
Temperature/K	120(2)	282(2)
λ/Å	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P\ 2_1/n$	P -1
a/Å	9.2400(18)	10.8543(11)
b/Å	12.733(3)	11.7730(11)
c/Å	22.312(5)	11.9282(10)
α/°	90	106.799(4)
β/°	96.380(7)	100.940(4)
γ/°	90	116.237(4)
Volume/Å ^{3}	2608.9(9)	1216.1(2)
Z	4	2

D_{calc}g / cm^3	1.422	1.392
μ/mm^{-1}	0.171	0.176
F(000)	1164	532
Crystal size/mm^3	0.06×0.03×0.01	0.30×0.175×0.120
2θ range for data collection/°	2.304 to 25.956	2.251 to 25.177
Index ranges	-10<=h<=11, -15<=k<=15, -27<=l<=27	-12<=h<=12, -14<=k<=14, -14<=l<=14
Reflections collected / unique	51039/ 5003 [R(int) = 0.1771]	17413/ 4336 [R(int) = 0.1709]
Data / restraints / parameters	5003 / 0 / 371	4336 / 0 / 336
Goodness-of-fit on F^2	1.064	1.016
Final R indices [I>2σ(I)]	R1 = 0.0623, wR2 = 0.101	R1 = 0.0725, wR2 = 0.1299
R indices (all data)	R1 = 0.1244, wR2 = 0.1183	R1 = 0.1673, wR2 = 0.1617
Largest diff. peak and hole/ e Å^{-3}	0.617and -0.444	0.354 and -0.424

12. References

1. a) Y.-Y. Gui, J. Yang, L.-W. Qi, X. Wang, F. Tian, X.-N. Li, L.Peng and L.-X. Wang, *Org. Biomol. Chem.,* 2015, **13**, 6371; b) D. Rambabu, S. K. Kumar, B. Y. Sreenivas, S. Sandra, A. Kandale, P. Misra, M.V.B. Rao and M. Pal, *Tetraheron Lett.*, 2013, **54**, 495.

2. M. Giardinetti, X. Moreau, V. Coeffard and C. Greck, *Adv. Synth. Catal.*, 2015, **357**, 3501.

3. X.-H. XU, G.-K. Liu, A. Azuma, E. Tokunaga and N. Shibata, *Org. Lett.*2011, **13**, 4854.

4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Barone, V. Scalmani, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai,

T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Revision D.1; Wallingford, CT, 2009.

5. a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
6. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.