

Lewis Acid–Promoted Annulation of Electron-Deficient Indoles toward Indoloindoles and Higher Fused Architectures

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1. General Information

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure; dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using activated neutral alumina and mixtures of hexane-ethyl acetate were used for elution. Melting points were determined on a Buchi melting point apparatus and are uncorrected. ^1H and $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance spectra were recorded on a Bruker AMX 500 spectrophotometer (DMSO- d_6 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signals of DMSO- d_6 (δ 2.50 ppm) & CDCl_3 (7.26 ppm). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (double doublet); m (multiplet). Coupling constants are reported as J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signals of DMSO- d_6 (δ 39.52 ppm) & CDCl_3 (77.16 ppm). The diffraction data of **5a** single crystal were collected using Rigaku xtaLab synergy- S instrument using Mo/Cu source with HuPix HE detector. The data was collected and analysed using CrysAlis pro software with olex program. Single-crystal XRD data of **3a** were collected on a Bruker D8 Focus diffractometer equipped with a two-circle goniometer and scintillation detector. Mass spectra were recorded using ThermoFinnigan MAT95XL, LTQ Orbitrap Velos, or Agilent 6890 GC-MS systems. All the optimizations, electronic structure, and reactivity parameters were calculated using the M062X/6-311G(d,p) level of density functional theory using Gaussian 16 suite of programs.¹⁻² All the *N*-Ts-3-nitro-indole derivatives were prepared following the literature procedure.³

2. Optimization studies for the synthesis of indolo[3,2-*b*]indole

Optimization studies were performed using **1a** and **2a** as model substrates (Table S1). Our investigation commenced with a systematic screening of various Lewis and Brønsted acid catalysts to identify the most effective promoter for the annulation. From the different Lewis and Brønsted acids such as $\text{Sc}(\text{OTf})_3$, $\text{Y}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, $\text{Zn}(\text{OTf})_2$, $\text{In}(\text{OTf})_3$, AgOTf , Amberlyst-15, $\text{BF}_3\cdot\text{OEt}_2$, FeCl_3 , AlCl_3 , and PTSA, the $\text{Y}(\text{OTf})_3$ catalyzed annulation afforded **3a** in 70% yield (Table 1, entries 1-11). Most importantly, the reaction failed in the absence of a Lewis acid (Table S1, entry 12). Among the solvents tested, toluene was found to be the

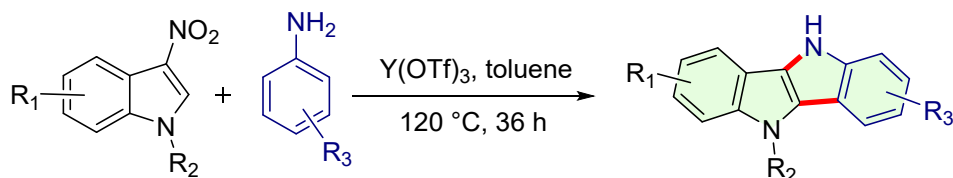
better medium for the Lewis acid catalyzed annulation (Table S1, entries 2, 13-15). An increase in the yield of **3a** to 76% was observed by starting with 1.6 equiv. of **2a** (Table S1, entry 16). Finally, changing the amount of catalyst or the temperature did not affect the reaction outcome (Table 1, entries 17-20).

Table S1. Optimization of the annulation of *N*-Ts-3-nitro-indole **1a** and 1-naphthylamine **2a**

SI No.	Catalyst (mol%)	Solvent	Yield of 3a (%)
1	Sc(OTf) ₃	Toluene	61
2	Y(OTf) ₃	Toluene	70
3	Yb(OTf) ₃	Toluene	55
4	Zn(OTf) ₂	Toluene	53
5	In(OTf) ₃	Toluene	39
6	AgOTf	Toluene	12
7	Amberlyst-15	Toluene	15
8	BF ₃ ·OEt ₂	Toluene	14
9	FeCl ₃	Toluene	12
10	AlCl ₃	Toluene	12
11	PTSA	Toluene	NR
12	-	Toluene	NR
13	Y(OTf) ₃	Xylene	59
14	Y(OTf) ₃	DMSO	NR
15	Y(OTf) ₃	1,4-dioxane	47
16^b	Y(OTf)₃	Toluene	76^b
17 ^c	Y(OTf) ₃	Toluene	70
18 ^d	Y(OTf) ₃	Toluene	68
19 ^e	Y(OTf) ₃	Toluene	70
20 ^f	Y(OTf) ₃	Toluene	NR

^aReaction conditions: **1a** (1.0 equiv.), **2a** (1.2 equiv.), Lewis acid (10 mol%), solvent (2.0 mL), 120 °C, 12 h; ^b **2a** (1.6 equiv.); ^c Lewis acid (5 mol%); ^d Lewis acid (15 mol%); ^e 140 °C; ^f 100 °C;

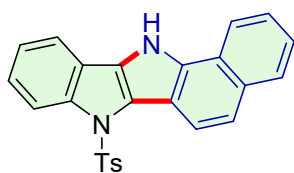
3. General procedure for the synthesis of indolo[3,2-*b*]indole



A mixture of 3-nitroindole (100 mg, 1.0 equiv.), substituted anilines (1.6 equiv.) and Y(OTf)₃ (10 mol%) was weighed into a dry reaction tube. Toluene (2.0 mL) was added under an argon atmosphere and allowed to stir at 120 °C in an oil bath for 12 hours. After completion of reaction as indicated from the TLC, the solvent was removed under vacuum. The residue was then purified by column chromatography (activated neutral alumina, eluent: EtOAc/hexane) to afford the corresponding indolo[3,2-*b*]indole products.

4. Experimental data of indolo[3,2-*b*]indole derivatives

7-tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole (**3a**)

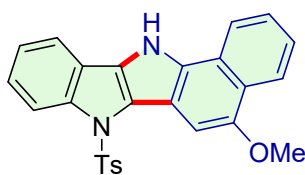


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 1-naphthylamine **2a** (72 mg, 0.51 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3a** as a pale-brown solid (99 mg, 76%).

Analytical data of **3a**: **Mp**: 256-258 °C. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 12.72 (s, 1H), 8.43 (d, *J* = 9.0 Hz, 2H), 8.26-8.25 (m, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.78-7.76 (m, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.55-7.50 (m, 3H), 7.43-7.42 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 3H) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 145.1, 139.9, 134.6, 132.9, 130.1, 129.9, 128.5, 128.1, 126.2, 126.0, 124.6, 123.1, 122.4, 120.8, 120.7, 120.4, 118.9, 118.1, 115.8, 111.3, 20.8 ppm. **HRMS (ESI-Orbitrap) m/z**: (M⁺) calculated for C₂₅H₁₈N₂O₂S 433.0981 found 433.0995.

5-methoxy-7-tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole (**3b**)

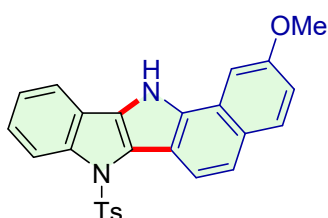
The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-methoxynaphthalen-1-amine **2b** (88 mg, 0.51 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue



was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3b** as a pale-brown solid (134 mg, 96%).

Analytical data of **3b**: **Mp**: 190-192 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.50 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.27-8.24 (m, 2H), 7.86 (s, 1H), 7.73 (broad, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55-7.50 (m, 3H), 7.41-7.40 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 3H), 2.14 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 149.6, 145.0, 140.1, 132.8, 129.84, 129.80, 128.2, 126.7, 126.3, 124.6, 124.5, 124.2, 123.2, 123.0, 122.8, 122.7, 120.7, 120.6, 117.9, 115.9, 110.6, 96.4, 55.6, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M + Na)⁺ calculated for C₂₆H₂₀N₂O₃S 463.1087 found 463.1106.

2-methoxy-7-tosyl-7,12-dihydrobenzo[g]indolo[3,2-*b*]indole (**3c**)

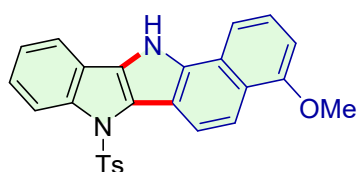


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 7-methoxynaphthalen-1-amine **2c** (88 mg, 0.51 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours.

After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3c** as a pale-brown solid (117 mg, 84%).

Analytical data of **3c**: **Mp**: 222-224 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.59 (s, 1H), 8.28-8.25 (m, 2H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.87 (s, 1H), 7.76-7.74 (m, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.43-7.42 (m, 2H), 7.16-7.13 (m, 3H), 3.98 (s, 3H), 2.14 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 157.7, 145.2, 140.1, 134.5, 133.0, 130.2, 129.9, 128.2, 126.3, 125.1, 124.7, 123.5, 123.1, 120.7, 120.5, 118.1, 116.3, 116.2, 116.0, 111.7, 100.7, 55.4, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₆H₂₀N₂O₃S 463.1087 found 463.1093.

5-methoxy-7-tosyl-7,12-dihydrobenzo[g]indolo[3,2-*b*]indole (**3d**)



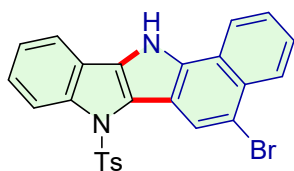
The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 5-methoxynaphthalen-1-amine **2d** (88 mg, 0.51 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours.

After solvent removal, the residue was purified by column chromatography (activated neutral

alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3d** as a brown solid (100 mg, 72%).

Analytical data of **3d**: **Mp**: 232-234 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.64 (s, 1H), 8.39 (d, *J* = 9.0 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 6.5 Hz, 1H), 7.58-7.53 (m, 3H), 7.43-7.42 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 4.02 (s, 3H), 2.15 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 155.8, 145.2, 140.1, 134.7, 132.9, 130.0, 128.4, 126.6, 126.3, 124.8, 124.7, 123.4, 123.0, 121.2, 120.4, 118.2, 118.0, 115.9, 114.3, 113.1, 111.8, 104.1, 55.7, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M⁺) calculated for C₂₆H₂₀N₂O₃S 463.1087 found 463.1100.

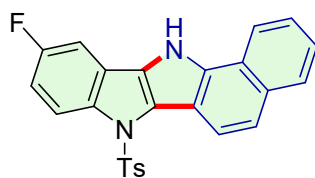
5-bromo-7-tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole (**3e**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-bromonaphthalen-1-amine **2e** (112 mg, 0.51 mmol) and Y(OTf)₃ (17 mg, 0.032 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3e** as a pale-brown solid (82 mg, 53%).

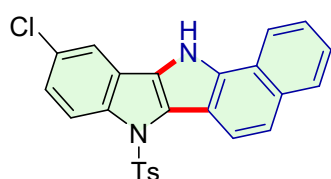
Analytical data of **3e**: **Mp**: **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.96 (s, 1H), 8.75 (s, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 7.78-7.75 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.47-7.44 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 2.16 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.3, 140.0, 134.3, 132.6, 130.0, 128.9, 127.6, 127.4, 127.2, 126.3, 125.2, 124.9, 123.3, 122.7, 122.5, 122.2, 121.5, 120.1, 118.5, 113.6, 111.6, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₅H₁₇BrN₂O₂S 511.0086, found 511.0085.

10-fluoro-7-tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole (**3f**)



The reaction was performed according to the general procedure with 5-fluoro-3-nitro-1-tosyl-1*H*-indole **1b** (100 mg, 0.30 mmol), 1-naphthylamine **2a** (143 mg, 0.48 mmol) and Y(OTf)₃ (16 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3f** as a white solid (82 mg, 64%).

Analytical data of **3f**: **Mp**: 290-292 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.70 (s, 1H), 8.41-8.38 (m, 2H), 8.26-8.23 (m, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.66 (t, *J* = 8.5 Hz, 1H), 7.56-7.52 (m, 3H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.17 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 159.5 (d, *J* = 238.4), 145.3, 136.3, 135.1, 132.6, 130.3, 130.0, 128.6, 127.4 (d, *J* = 3.4 Hz), 126.3, 126.1, 125.0, 124.7, 122.3, 121.5 (d, *J* = 10.6 Hz), 121.1-120.8, 118.9, 117.4 (d, *J* = 9.8 Hz), 111.8 (d, *J* = 25.0 Hz), 111.2, 104.0 (d, *J* = 25.4), 20.9 ppm. **¹⁹F NMR (DMSO-*d*₆, 470 MHz)**: δ -117.5 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₅H₁₇FN₂O₂S 451.0887, found 451.0887.

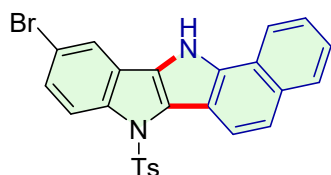


10-chloro-7-tosyl-7,12-dihydrobenzo[g]indolo[3,2-*b*]indole (3g)

The reaction was performed according to the general procedure with 5-chloro-3-nitro-1-tosyl-1*H*-indole **1c** (100 mg, 0.28 mmol), 1-naphthylamine **2a** (65 mg, 0.46 mmol) and Y(OTf)₃ (15 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3g** as a white solid (76 mg, 60%).

Analytical data of **3g**: **Mp**: 281-283 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.71 (s, 1H), 8.42-8.37 (m, 2H), 8.24 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 15.43 (d, *J* = 9.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56-7.52 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.15 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.4, 138.3, 135.1, 132.7, 130.3, 130.0, 129.0, 128.6, 126.8, 126.2, 126.1, 125.0, 124.4, 124.2, 122.3, 121.6, 121.1, 120.7, 118.8, 117.4, 117.3, 111.0, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M-H)⁻ calculated for C₂₅H₁₇ClN₂O₂S 443.0627, found 443.0618.

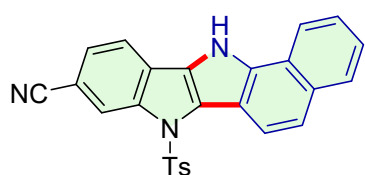
10-bromo-7-tosyl-7,12-dihydrobenzo[g]indolo[3,2-*b*]indole (**3h**)



The reaction was performed according to the general procedure with 5-bromo-3-nitro-1-tosyl-1*H*-indole **1d** (100 mg, 0.25 mmol), 1-naphthylamine **2a** (58 mg, 0.40 mmol) and Y(OTf)₃ (14 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3h** as a white solid (88 mg, 71%).

Analytical data of **3h**: **Mp**: 278-280 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.69 (s, 1H), 8.40 (d, *J* = 9.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.88 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.58-7.53 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.4, 138.7, 135.1, 132.7, 130.3, 130.0, 128.6, 126.9, 126.6, 126.23, 126.16, 125.0, 124.2, 122.3, 122.0, 121.1, 120.7, 120.4, 118.8, 117.7, 117.0, 111.0, 20.9 ppm. **HRMS (ESI-Orbitrap) *m/z***: (*M*+*Na*)⁺ calculated for C₂₅H₁₇BrN₂O₂S 511.0086, found 511.0088.

7-tosyl-7,12-dihydrobenzo[*g*]indolo[3,2-*b*]indole-9-carbonitrile (**3i**)

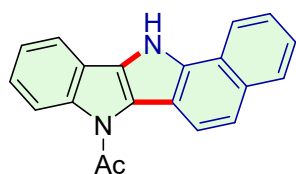


The reaction was performed according to the general procedure with 3-nitro-1-tosyl-1*H*-indole-6-carbonitrile **1e** (100 mg, 0.29 mmol), 1-naphthylamine **2a** (67 mg, 0.47 mmol) and Y(OTf)₃ (16 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours.

After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3i** as a white solid (60 mg, 47%)

Analytical data of **3i**: **Mp**: 297-299 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.94 (s, 1H), 8.58 (s, 1H), 8.42 (d, *J* = 8.5 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69-7.66 (m, 3H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.18 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.8, 138.6, 136.3, 132.7, 130.7, 130.2, 128.7, 128.3, 126.8, 126.5, 126.4, 125.9, 125.6, 123.1, 122.3, 121.5, 121.0, 119.6, 119.2, 118.9, 110.5, 105.8, 21.0 ppm. **HRMS (ESI-Orbitrap) *m/z***: (*M*+*Na*)⁺ calculated for C₂₆H₁₇N₃O₂S 458.0934, found 458.0940.

1-(benzo[*g*]indolo[3,2-*b*]indol-7(12*H*)-yl)ethan-1-one (**3k**)



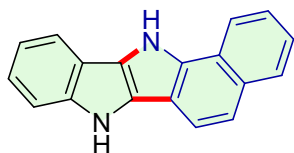
The reaction was performed according to the general procedure with 1-(3-nitro-1*H*-indol-1-yl)ethan-1-one **1f** (100 mg, 0.49 mmol), 1-naphthylamine **2a** (112mg, 0.78 mmol) and Y(OTf)₃ (26 mg, 0.05 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent

removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3k** as a brown solid (111mg, 76%).

Analytical data of **3k**: **Mp**: 250-252 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.67 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 6.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.45-7.39

(m, 2H), 2.96 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 168.3, 138.6, 134.5, 130.0, 128.4, 126.7, 125.6, 124.6, 124.4, 124.2, 123.4, 122.3, 121.7, 120.8, 119.51, 119.46, 118.0, 116.2, 111.9, 26.4 ppm. HRMS (ESI-Orbitrap) m/z : (M+Na) $^+$ calculated for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$ 321.0998 found 321.1007.

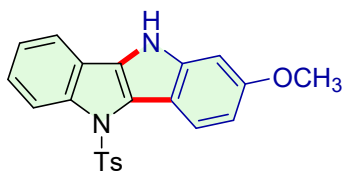
7,12-dihydrobenzo[g]indolo[3,2-*b*]indole (3l)



The reaction was performed according to the general procedure with tert-butyl 3-nitro-1*H*-indole-1-carboxylate **1g** (100 mg, 0.38 mmol), 1-naphthylamine **2a** (87 mg, 0.61 mmol) and $\text{Y}(\text{OTf})_3$ (20 mg, 0.04 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **3l** as a brown solid (32 mg, 33%).

Analytical data of **3l**: **Mp**: 285-287 °C. ^1H NMR (500 MHz, DMSO- d_6 , TMS): δ 12.08 (s, 1H), 11.12 (s, 1H), 8.45 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 7.43 (t, J = 8.5 Hz, 1H), 7.18 (t, J = 7.0 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 140.5, 134.3, 129.8, 128.6, 126.8, 125.4, 124.0, 123.6, 122.7, 121.2, 120.8, 118.6, 118.3, 118.1, 117.2, 114.9, 112.1, 109.4 ppm. HRMS (ESI-Orbitrap) m/z : (M) $^+$ calculated for $\text{C}_{18}\text{H}_{12}\text{N}_2$ 256.1000, found 256.1002.

2-methoxy-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (5a)



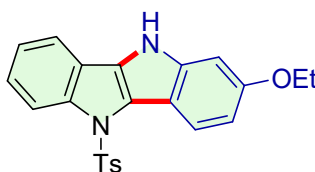
The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), *m*-anisidine **4a** (123 μL , 0.63 mmol) and $\text{Y}(\text{OTf})_3$ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5a** as a pale-brown solid (114 mg, 92%).

Analytical data of **5a**: **Mp**: 208-210 °C. ^1H NMR (500 MHz, DMSO- d_6 , TMS): δ 11.61 (s, 1H), 8.18-8.14 (m, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.38-7.33 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.04 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H), 2.18 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 156.4, 145.0, 141.2, 139.3, 133.0, 129.9, 128.4, 126.2, 124.4, 124.2, 121.7, 120.4, 119.7, 117.9, 115.6, 110.3, 110.1, 95.9, 55.3, 20.9 ppm. HRMS (ESI-Orbitrap) m/z : (M + Na) $^+$ calculated for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ 413.0930, found 413.0945.

Procedure for the scale up of 5a

A mixture of 3-nitro-*N*-tosyl indole **1a** (1.0 g, 3.16 mmol), *m*-anisidine **4a** (0.71 mL, 6.32 mmol) and Y(OTf)₃ (170 mg, 0.32 mmol) was weighed into a dry reaction tube. Toluene (20 mL) was added and allowed to stir at 120 °C for 18 hours. After completion of the reaction as indicated from the TLC, the solvent was removed under vacuum. The residue was then purified by column chromatography (activated neutral alumina, eluent: 7% EtOAc/hexane) to afford **5a** (1.11 g, 90%).

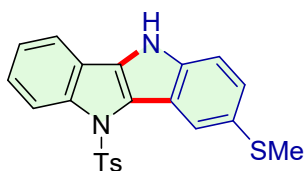
2-ethoxy-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5b**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 3-ethoxyaniline **4b** (87 mg, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5b** as a white solid (92 mg, 72%).

Analytical data of **5b**: **Mp**: 150-152 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.58 (s, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.37-7.33 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 155.7, 145.1, 141.2, 139.3, 133.0, 129.9, 128.4, 126.2, 124.4, 124.1, 121.7, 120.5, 119.7, 117.9, 115.6, 110.4, 110.3, 96.5, 63.2, 20.9, 14.8 ppm. **HRMS (ESI-Orbitrap) m/z**: (M + Na)⁺ calculated for C₂₃H₂₀N₂O₃S 427.1087, found 427.1096.

3-(methylthio)-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5c**)

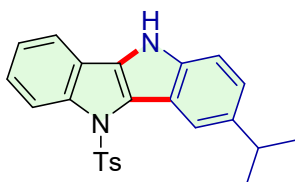


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-(methylthio)aniline **4c** (88 mg, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5c** as a brown solid (94 mg, 73%).

Analytical data of **5c**: **Mp**: 184-186 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.85 (s, 1H), 8.24 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.53-7.50 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H),

2.56 (s, 3H), 2.19 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO-}d_6$): δ 145.1, 140.1, 138.5, 132.8, 130.3, 129.9, 128.1, 126.2, 125.2, 124.5, 123.4, 120.7, 120.0, 118.6, 118.0, 116.4, 115.8, 113.6, 20.9, 17.3 ppm. HRMS (ESI-Orbitrap) m/z : $(\text{M-H})^-$ calculated for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2$ 405.0737, found 405.0730.

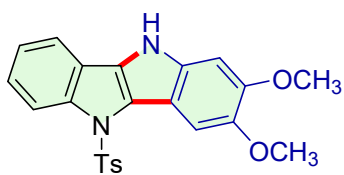
3-isopropyl-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (5d)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), aniline **4d** (86 μL , 0.63 mmol) and $\text{Y}(\text{OTf})_3$ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 $^\circ\text{C}$ for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5d** as a white solid (88 mg, 69%).

Analytical data of **5d**: **Mp**: 158-160 $^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 11.66 (s, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 8.15 (s, 1H), 7.68 (d, $J = 7.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 1H), 7.42-7.35 (m, 2H), 7.19-7.17 (m, 3H), 3.10-3.05 (m, 1H), 2.18 (s, 3H), 1.34 (d, $J = 7.0$ Hz, 6H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO-}d_6$): δ 145.0, 140.1, 140.0, 138.8, 133.1, 129.9, 129.7, 126.2, 124.8, 124.4, 121.8, 121.4, 120.3, 118.3, 115.9, 115.8, 115.7, 112.6, 33.7, 24.7, 20.9 ppm. HRMS (ESI-Orbitrap) m/z : $(\text{M}+\text{Na})^+$ calculated for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$ 425.1294, found 425.1306.

2,3-dimethoxy-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (5e)

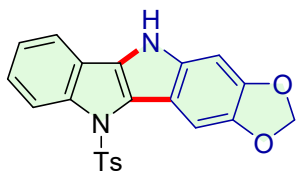


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 3,4-dimethoxyaniline **4e** (97 mg, 0.63 mmol) and $\text{Y}(\text{OTf})_3$ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 $^\circ\text{C}$ for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5e** as a pale-brown solid (124 mg, 93%).

Analytical data of **5e**: **Mp**: 242-244 $^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, TMS): δ 11.48 (s, 1H), 8.18-8.16 (m, 1H), 7.77 (s, 1H), 7.64-7.62 (m, 1H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.34-7.33 (m, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.07 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.18 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $\text{DMSO-}d_6$): δ 147.5, 145.0, 144.8, 139.5, 134.9, 132.9, 129.9, 128.2, 126.3, 124.4, 124.0, 121.9, 120.7, 117.7, 115.7, 108.6, 101.3, 96.2, 55.9, 55.7, 20.9 ppm.

HRMS (ESI-Orbitrap) m/z: (M+Na)⁺ calculated for C₂₃H₂₀N₂O₄S 443.1036, found 443.1048.

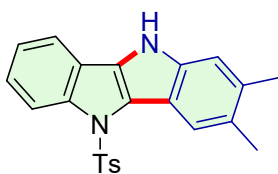
5-tosyl-5,10-dihydro-[1,3]dioxolo[4,5-f]indolo[3,2-b]indole (**5f**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), benzo[*d*][1,3]dioxol-5-amine **4f** (87 mg, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5f** as a pale-brown solid (96 mg, 75%).

Analytical data of **5f**: **Mp**: 244-246 °C. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 11.65 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 7.67 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.36-7.32 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (s, 1H), 6.07 (s, 2H), 2.18 (s, 3H) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 145.02, 144.95, 142.8, 139.5, 135.4, 132.8, 129.9, 128.5, 126.2, 124.5, 124.1, 121.9, 120.6, 117.8, 115.7, 109.5, 100.8, 97.5, 93.6, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z:** (M+Na)⁺ calculated for C₂₂H₁₆N₂O₄S 427.0723 found 427.0737.

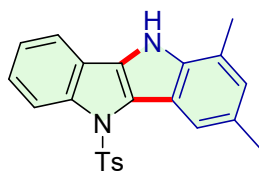
2,3-dimethyl-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5g**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 3,4-dimethylaniline **4g** (77 mg, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5g** as a pale-brown solid (98 mg, 80%).

Analytical data of **5g**: **Mp**: 220-222 °C. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 11.51 (s, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.04 (s, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.39-7.33 (m, 2H), 7.32 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H), 2.18 (s, 3H) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 145.0, 139.8, 139.2, 132.9, 131.7, 129.8, 129.0, 128.2, 126.2, 124.5, 124.4, 121.3, 120.5, 119.0, 118.1, 115.7, 114.3, 113.1, 20.9, 20.3, 20.2 ppm. **HRMS (ESI-Orbitrap) m/z:** (M+Na)⁺ calculated for C₂₃H₂₀N₂O₂S 411.1138, found 411.1153.

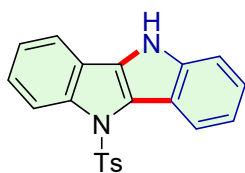
1,3-dimethyl-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5h**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 2,4-dimethylaniline **4h** (85 μ L, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5h** as a pale-brown solid (85 mg, 69%).

Analytical data of **5h**: **Mp**: 232-235 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.50 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.92 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 2.49 (s, 3H), 2.46 (s, 3H), 2.17 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.4, 140.4, 138.4, 133.4, 130.3, 130.2, 129.1, 126.7, 125.6, 125.2, 124.9, 122.1, 121.9, 121.0, 118.8, 116.7, 116.2, 22.0, 21.4, 17.3 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₃H₂₀N₂O₂S 411.1138, found 411.1138.

5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5i**)

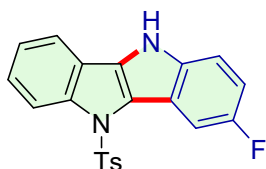


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), aniline **4i** (58 μ L, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5i** as a brown solid (65 mg, 57%)

Analytical data of **5i**: **Mp**: 185-187 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.83 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44-7.37 (m, 2H), 7.30-7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.1, 140.1, 140.0, 133.0, 129.9, 129.6, 126.2, 125.0, 124.5, 122.8, 121.5, 120.2, 120.1, 119.0, 118.5, 115.82, 115.75, 112.9, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₁H₁₆N₂O₂S 383.0825, found 383.0840.

3-fluoro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5j**)

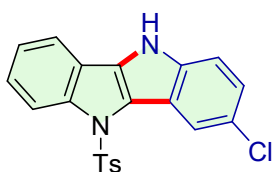
The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-fluoroaniline **4j** (105 μ L, 1.11 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent removal, the residue was purified by



column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5j** as a white solid (75 mg, 63%).

Analytical data of **5j**: **Mp**: 208-210 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.95 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 10.0 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.58-7.56 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 9.0 Hz, 1H), 2.18 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 157.2 (d, *J* = 231.1), 145.2, 140.1, 136.7, 132.7, 131.5, 130.0, 126.3, 125.6, 124.6, 121.2, 119.8, 115.8, 115.6 (d, *J* = 11.2 Hz), 113.9 (d, *J* = 9.9 Hz), 110.8 (d, *J* = 26.2), 103.8 (d, *J* = 26.0 Hz), 20.9 ppm. **¹⁹F NMR (DMSO-*d*₆, 470 MHz)**: δ -122.91. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₁H₁₅FN₂O₂S 401.0730, found 401.0745.

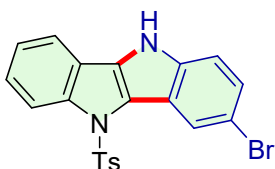
3-chloro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5k**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-chloroaniline **4k** (141 mg, 1.11 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5k** as a white solid (79 mg, 63%).

Analytical data of **5k**: **Mp**: 238-240 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.07 (s, 1H), 8.25 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 9.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.19 (t, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.7, 140.6, 138.9, 133.2, 131.6, 130.5, 126.7, 126.1, 125.1, 125.0, 123.1, 121.1, 120.3, 119.3, 118.4, 117.0, 116.2, 114.9, 21.4 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₁H₁₅ClN₂O₂S 417.0435, found 417.0443.

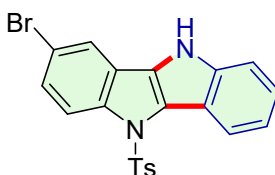
3-bromo-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5l**)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), 4-bromoaniline **4l** (190 mg, 1.11 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5l** as a white solid (75 mg, 54%).

Analytical data of **5l**: **Mp**: 240-242 °C. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 12.09 (s, 1H), 8.40 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.41-7.38 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 2.19 (s, 3H) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 145.3, 140.1, 138.7, 132.6, 131.0, 130.0, 126.2, 125.7, 125.1, 124.7, 120.9, 120.4, 119.8, 118.9, 117.2, 115.8, 114.9, 112.4, 20.9 ppm. HRMS (ESI-Orbitrap) *m/z*: (M+Na)⁺ calculated for C₂₁H₁₅BrN₂O₂S 460.9930, found 460.9946.

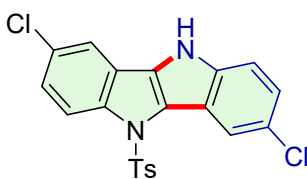
3-bromo-10-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5m**)



The reaction was performed according to the general procedure with 5-bromo-3-nitro-1-tosyl-1*H*-indole **1d** (100 mg, 0.25 mmol), aniline **4i** (46 μL, 0.51 mmol) and Y(OTf)₃ (14 mg, 0.025 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5m** as a pale-brown solid (73 mg, 66%).

Analytical data of **5m**: **Mp**: 221-223 °C. ¹H NMR (500 MHz, DMSO-*d*₆, TMS): δ 11.74 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.88 (s, 1H), 7.60-7.53 (m, 4H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H) ppm. ¹³C{¹H} NMR (125 MHz, DMSO-*d*₆): δ 145.4, 140.3, 138.7, 132.8, 130.0, 128.1, 127.3, 126.2, 123.4, 122.6, 121.8, 120.8, 120.3, 119.2, 117.6, 116.9, 115.4, 113.1, 20.9 ppm. HRMS (ESI-Orbitrap) *m/z*: (M+Na)⁺ calculated for C₂₁H₁₅BrN₂O₂S 460.9930, found 460.9928.

3,8-dichloro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5n**)

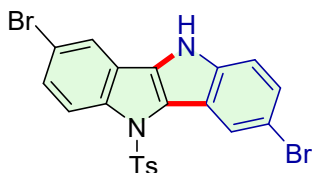


The reaction was performed according to the general procedure with 5-chloro-3-nitro-1-tosyl-1*H*-indole **1c** (100 mg, 0.28 mmol), 4-chloroaniline **4k** (127 mg, 1.0 mmol) and Y(OTf)₃ (15 mg, 0.028 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent

removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5n** as a white solid (72 mg, 59%).

Analytical data of **5n**: **Mp**: 245-247 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.99 (s, 1H), 8.26 (s, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.75 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.5, 138.7, 138.5, 132.5, 130.1, 129.8, 129.0, 126.2, 125.2, 124.7, 123.2, 121.9, 121.0, 118.3, 118.1, 117.2, 116.2, 114.7, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M-H)⁻ calculated for C₂₁H₁₄Cl₂N₂O₂S 427.0080, found 427.0073

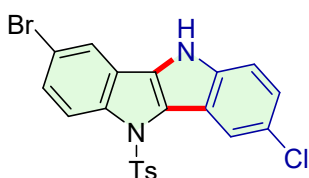
3,8-dibromo-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5o**)



The reaction was performed according to the general procedure with 5-bromo-3-nitro-1-tosyl-1*H*-indole **1d** (100 mg, 0.25 mmol), 4-bromoaniline **4l** (152 mg, 0.89 mmol) and Y(OTf)₃ (14 mg, 0.025 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5o** as a pale-brown solid (77 mg, 59%).

Analytical data of **5o**: **Mp**: 249-251 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 12.00 (s, 1H), 8.40 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.90 (s, 1H), 7.59 (s, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.18 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 145.6, 138.9, 138.8, 132.4, 130.1, 129.5, 128.0, 126.2, 125.8, 121.5, 121.4, 121.3, 121.1, 117.6, 117.1, 116.8, 115.1, 112.6, 20.9 ppm. **HRMS (ESI-Orbitrap) m/z**: (M+Na)⁺ calculated for C₂₁H₁₄Br₂N₂O₂S 538.9035, found 538.9039.

8-bromo-3-chloro-5-tosyl-5,10-dihydroindolo[3,2-*b*]indole (**5p**)

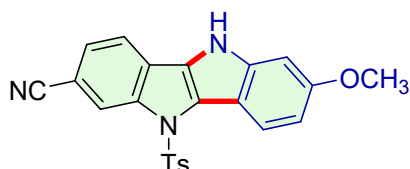


The reaction was performed according to the general procedure with 5-bromo-3-nitro-1-tosyl-1*H*-indole **1d** (100 mg, 0.25 mmol), 4-chloroaniline **4k** (113 mg, 0.89 mmol) and Y(OTf)₃ (14 mg, 0.025 mmol) in toluene (2.0 mL) at 140 °C for 72 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5p** as a white solid (54 mg, 45%).

Analytical data of **5p**: **Mp**: 235-237 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 11.98 (s, 1H), 8.25 (s, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 7.90 (s, *J* = 0.5 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H),

7.60-7.58 (m, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.34-7.32 (m, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.19 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 145.5, 138.8, 138.6, 132.5, 130.1, 129.6, 128.0, 126.2, 124.7, 123.2, 121.7, 121.5, 121.2, 118.1, 117.6, 117.0, 116.2, 114.7, 20.9 ppm. HRMS (ESI-Orbitrap) m/z : (M+Na) $^+$ calculated for C₂₁H₁₄BrClN₂O₂S 494.9540, found 494.9554.

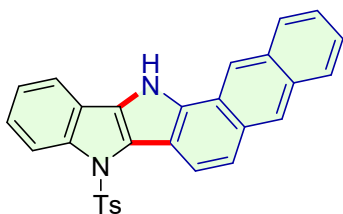
7-methoxy-10-tosyl-5,10-dihydroindolo[3,2-*b*]indole-2-carbonitrile (5q)



The reaction was performed according to the general procedure with 3-nitro-1-tosyl-1*H*-indole-6-carbonitrile **1e** (100 mg, 0.29 mmol), *m*-anisidine **4a** (66 μL , 0.59 mmol) and Y(OTf)₃ (16 mg, 0.029 mmol) in toluene (2.0 mL) at 120 °C for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 10% EtOAc/hexane) to afford the desired product **5q** as a pale-brown solid (56 mg, 46%)

Analytical data of **5q**: Mp: 272-274 °C. ^1H NMR (500 MHz, DMSO- d_6 , TMS): δ 11.80 (s, 1H), 8.50 (s, 1H), 8.20 (d, $J = 9.0$ Hz, 1H), 7.82-7.75 (m, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.08 (s, 1H), 6.95 (d, $J = 9.0$ Hz, 1H), 3.86 (s, 3H), 2.20 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 157.5, 145.7, 142.4, 137.9, 132.7, 130.2, 128.0, 127.1, 126.4, 124.9, 122.9, 120.4, 119.6, 118.9, 118.7, 111.0, 109.4, 105.1, 95.8, 55.4, 21.0 ppm. HRMS (ESI-Orbitrap) m/z : (M + Na) $^+$ calculated for C₂₃H₁₇N₃O₃S 438.0883 found 438.0896.

8-tosyl-8,13-dihydroindolo[3,2-*b*]naphtho[2,3-*g*]indole (7)

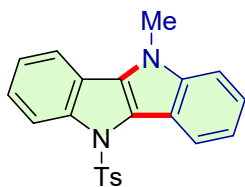


The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), anthracen-1-amine **6** (122 mg, 0.63 mmol) and Y(OTf)₃ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 120 °C for 12 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 15% EtOAc/hexane) to afford the desired product **7** as a pale-brown solid (124 mg, 85%).

Analytical data of **7**: Mp: 262-264 °C. ^1H NMR (500 MHz, DMSO- d_6 , TMS): δ 13.02 (s, 1H), 8.97 (s, 1H), 8.64 (s, 1H), 8.43 (d, $J = 9.0$ Hz, 1H), 8.26-8.25 (m, 1H), 8.13-8.12 (m, 2H), 7.83 (d, $J = 9.0$ Hz, 1H), 7.80-7.78 (m, 1H), 7.59-7.52 (m, 4H), 7.44-7.42 (m, 2H), 7.16 (d, J

= 8.0 Hz, 2H), 2.15 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO- d_6): δ 145.1, 139.9, 133.6, 133.0, 131.1, 130.4, 129.9, 129.2, 128.2, 127.6, 127.5, 126.9, 126.2, 125.9, 125.1, 124.7, 124.5, 123.8, 122.2, 121.3, 120.4, 119.7, 118.3, 117.9, 115.8, 109.8, 20.9 ppm. HRMS (ESI-Orbitrap) m/z : (M-H) $^-$ calculated for $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ 459.1173, found 459.1165.

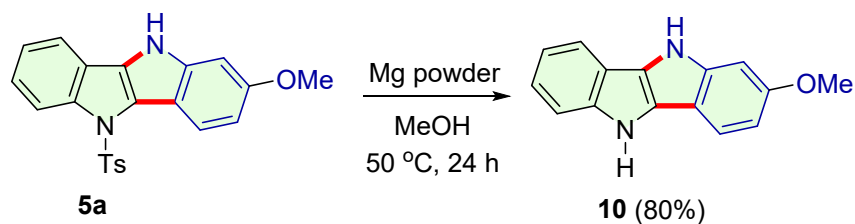
5-methyl-10-tosyl-5,10-dihydroindolo[3,2-*b*]indole (9)



The reaction was performed according to the general procedure with 3-nitro-*N*-tosyl indole **1a** (100 mg, 0.32 mmol), *N*-methylaniline **8** (122 μL , 1.12 mmol) and $\text{Y}(\text{OTf})_3$ (17 mg, 0.03 mmol) in toluene (2.0 mL) at 140 $^\circ\text{C}$ for 18 hours. After solvent removal, the residue was purified by column chromatography (activated neutral alumina, eluent: 5% EtOAc/hexane) to afford the desired product **9** as a white solid (38 mg, 32%).

Analytical data of **9**: Mp: 207-209 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3 , TMS): δ 8.54 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.5 Hz, 1H), 7.38-7.35 (m, 2H), 7.33-7.29 (m, 2H), 7.00 (d, J = 8.0 Hz, 2H), 4.03 (s, 3H), 2.21 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 144.5, 141.3, 140.8, 134.3, 131.0, 129.6, 124.8, 124.0, 122.9, 122.0, 120.7, 120.5, 120.3, 117.7, 116.5, 109.6, 31.5, 21.6 ppm. HRMS (ESI-Orbitrap) m/z : (M+H) $^+$ calculated for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ 375.1162, found 375.1163.

5. Synthesis and characterization of 2-methoxy-5,10-dihydroindolo[3,2-*b*]indole (10)⁴



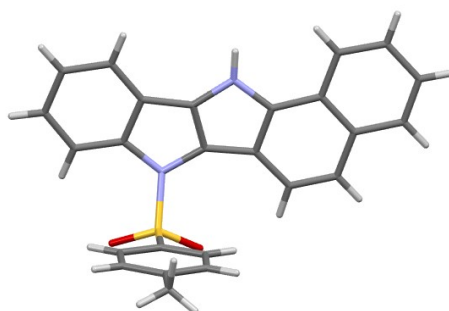
To a stirred solution of **5a** (100 mg, 0.26 mmol, 1.0 equiv.) in MeOH (4 mL) at 50 $^\circ\text{C}$ magnesium powder (2.3 mmol, 9.0 equiv.) was added and allowed to stir the resulting reaction mixture vigorously for 24 h at the same temperature. After the complete consumption of the starting materials, it was quenched with saturated NH_4Cl solution and the reaction mixture was extracted with EtOAc. All organic layers were separated, dried over Na_2SO_4 and concentrated in rotary evaporator under reduced pressure. The residue was purified by column

chromatography (activated neutral alumina, eluent: 20% EtOAc/hexane) to afford the desired product **10** as a white solid (48 mg, 80%).

Analytical data of **10**: **Mp**: 265-267 °C. **¹H NMR (500 MHz, DMSO-*d*₆, TMS)**: δ 10.98 (s, 1H), 10.90 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 3H) ppm. **¹³C{¹H} NMR (125 MHz, DMSO-*d*₆)**: δ 155.7, 141.4, 139.7, 125.4, 124.2, 120.5, 118.0, 117.9, 116.8, 114.9, 112.0, 109.4, 107.5, 95.8, 55.2 ppm. **HRMS (ESI-Orbitrap) m/z**: (M)⁺ calculated for C₁₅H₁₂N₂O 236.0950, found 236.0940.

6. Single crystal X-ray analysis of **3a** and **5a**

Single crystals of **3a** successfully obtained from the slow evaporation of ethylacetate.



Crystallographic data for the compound **3a** (CCDC: 2531953).

Table S2. Crystal data and structure refinement for **3a**

Compound	3a
Formula	C ₂₅ H ₁₈ N ₂ O ₂ S
CCDC Nos.	2531953
Formula Wt.	410.47
Crystal habit	Block
Crystal colour	Colourless
Crystal system	monoclinic
Space group	<i>P12₁/n1</i>

a (Å)	8.0257(2)
b (Å)	17.3835(4)
c (Å)	14.1011(3)
α (°)	90
β (°)	97.5030(10)
γ (°)	90
V (Å ³)	1950.47(8)
Z	4
D_{calc} (g cm ⁻³)	1.398
T (K)	298
(λ) Mo $K\alpha$	0.71073
μ (mm ⁻¹)	0.192
2θ range (°)	56.648
Total Reflns.	42921
Unique Reflns	4852
Reflns. Used	4376
No. Parameters	272
GOF on F^2	1.033
Final $R1, wR2$	0.0400, 0.1045

Single crystals of **5a** successfully obtained from the slow evaporation of ethylacetate.
 Crystallographic data for the compound **5a** (CCDC: 2531770).

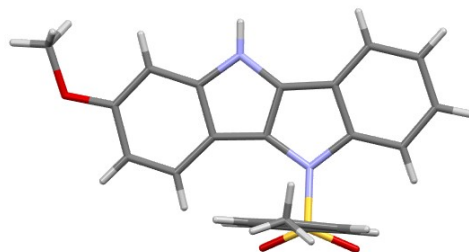


Table S3. Crystal data and structure refinement for **5a**

Compound	5a
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Formula	2(C ₂₂ H ₁₈ N ₂ O ₃ S)
CCDC Nos.	2531770
Formula Wt.	780.89
Crystal habit	Block
Crystal colour	Colourless
Crystal system	monoclinic
Space group	<i>P12₁/c1</i>
<i>a</i> (Å)	19.8915(2)
<i>b</i> (Å)	8.63860(10)
<i>c</i> (Å)	23.0531(3)
α (°)	90
β (°)	110.4310(10)
γ (°)	90
<i>V</i> (Å ³)	3712.13(8)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.397
<i>T</i> (K)	298
(λ)Mo K α	1.54184
μ (mm ⁻¹)	1.771
2 θ range (°)	153.806
Total Reflns.	44566
Unique Reflns	7630
Reflns. Used	6376
No. Parameters	509
GOF on <i>F</i> ²	1.037
Final <i>R</i> 1, <i>wR</i> 2	0.0383, 0.1064

7. References

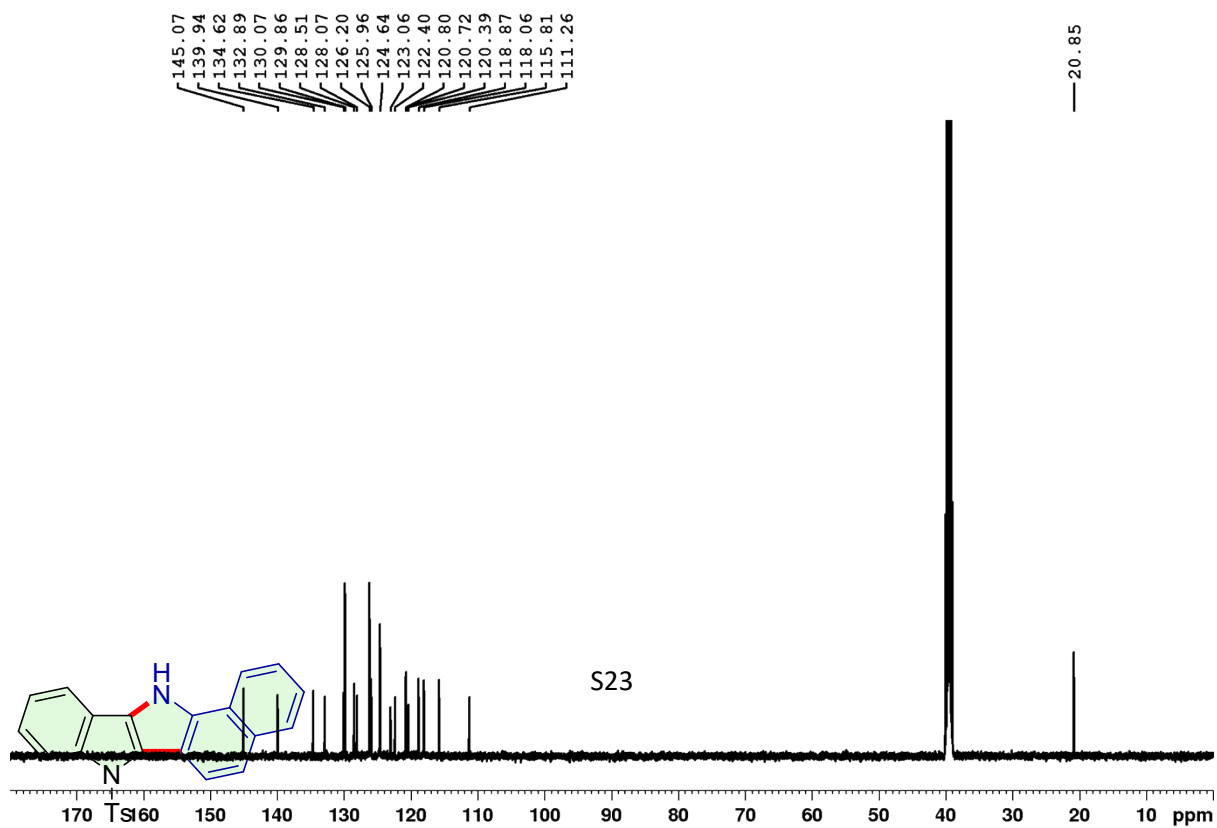
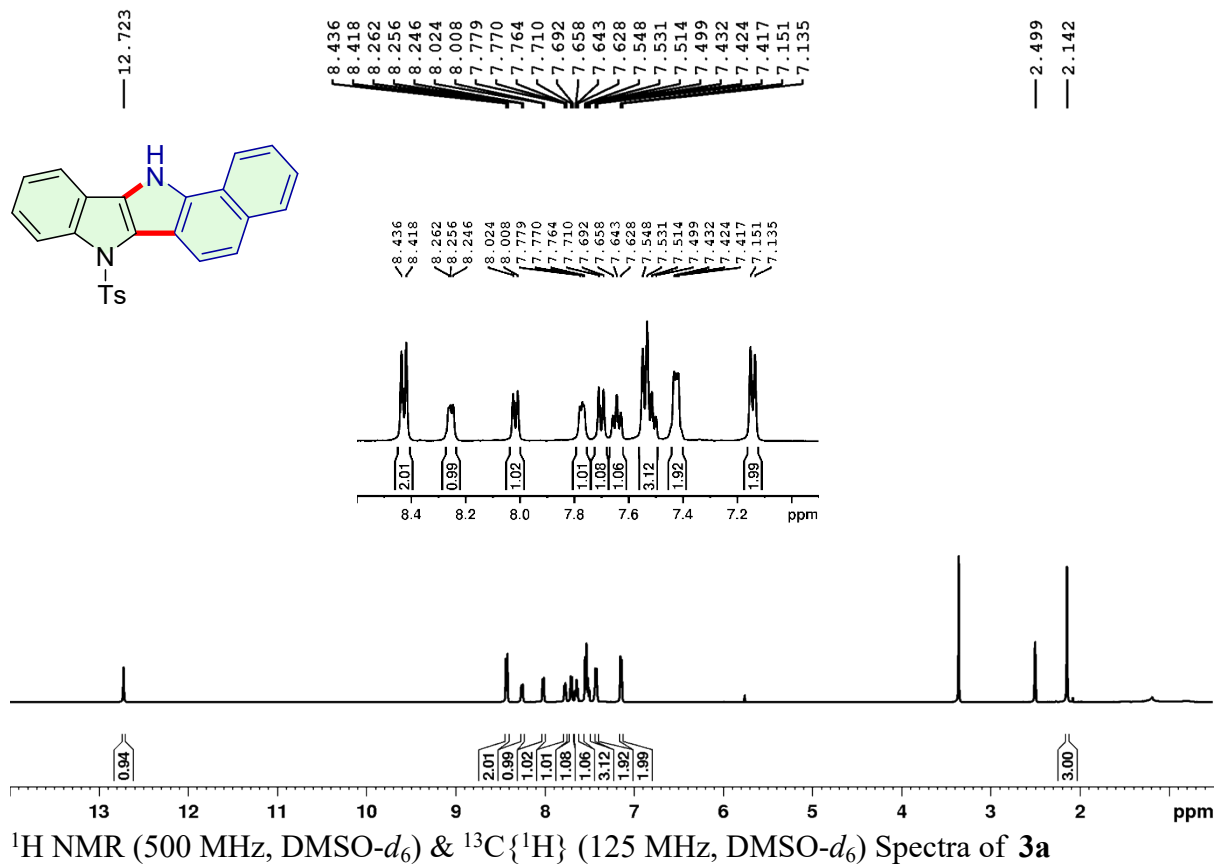
1 Y. Zhao and D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

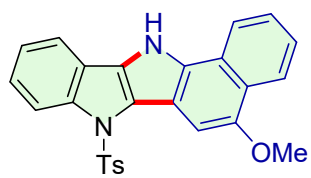
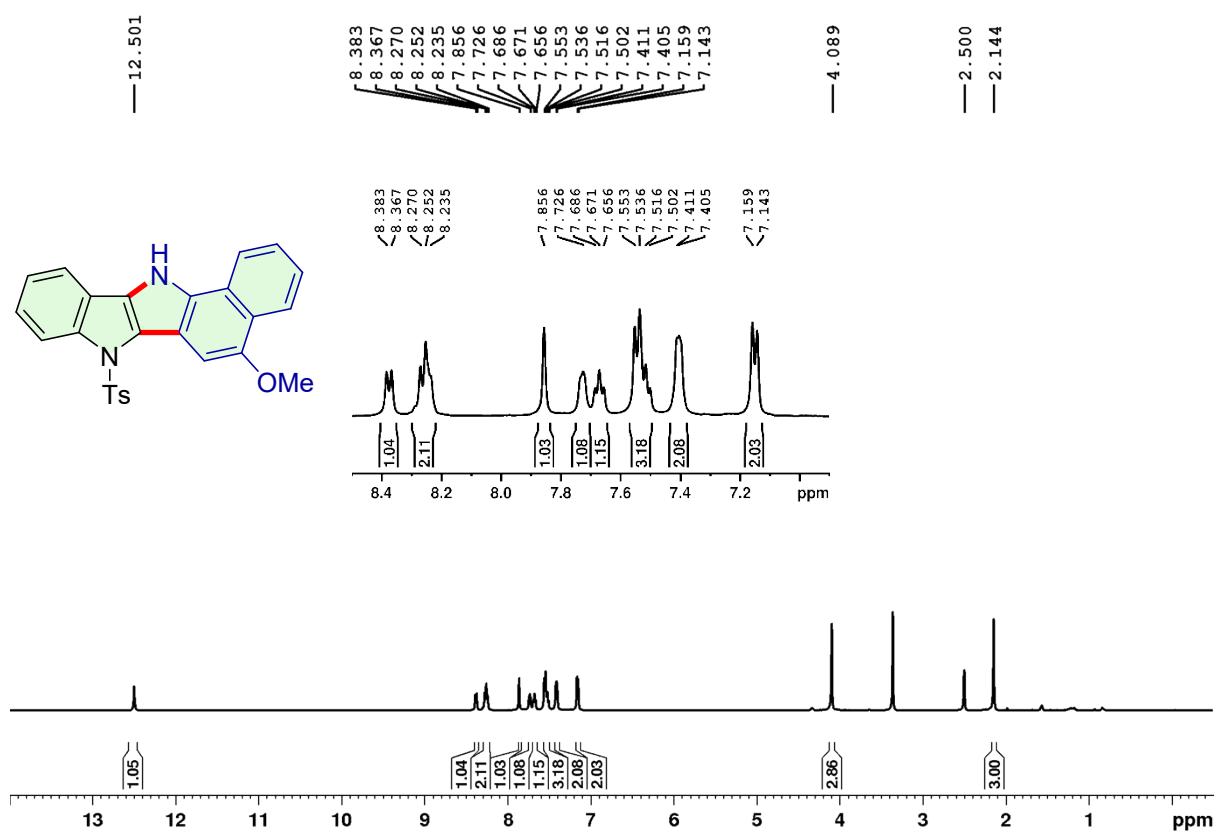
2 Gaussian 16, Revision B.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2016**.

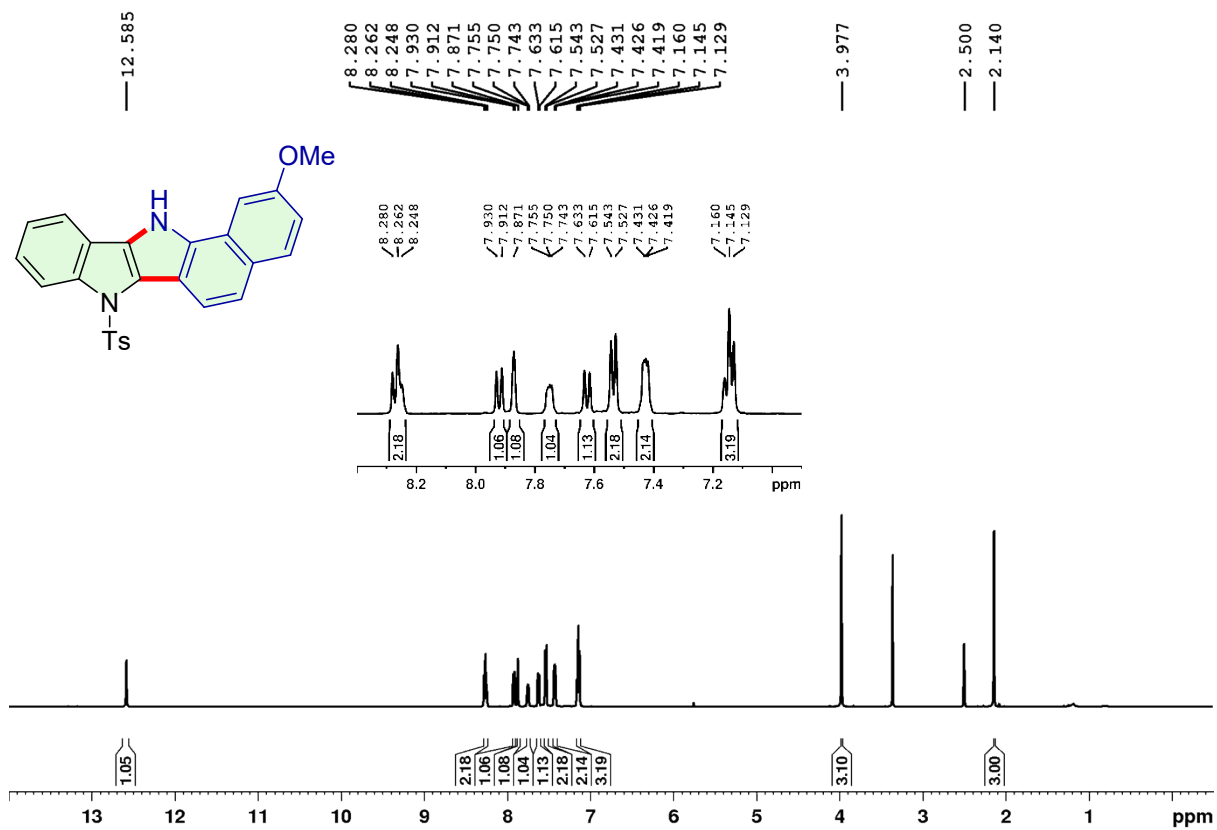
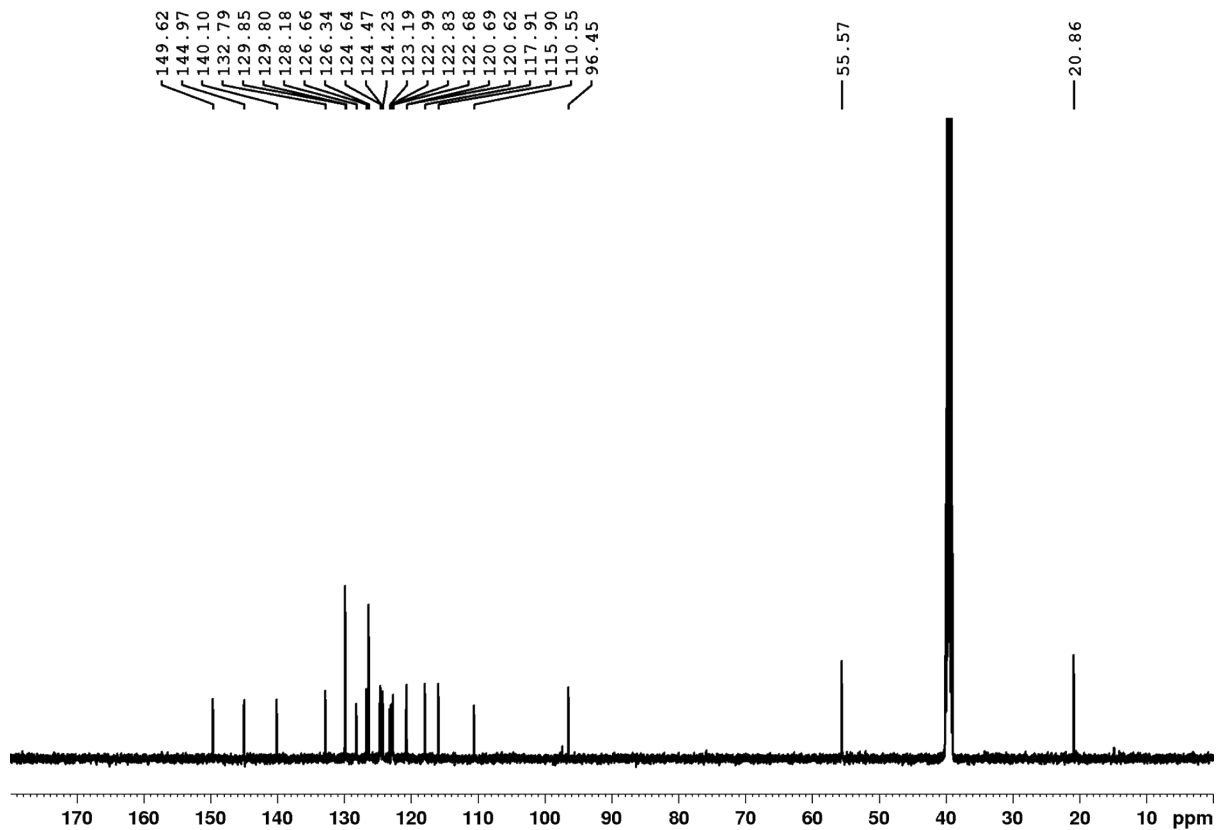
3 Pelkey, E. T.; Gribble, G. W. *Synthesis*, **1999**, 1117–1122.

4 M. Munda, R. Nandi, V. R. Gavit, S. Kundu, S. Niyogi and A. Bisai, *Chem. Sci.*, **2022**, 13, 11666–11671.

8. Copies of ^1H & $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of indolo[3,2-*b*]indole derivatives

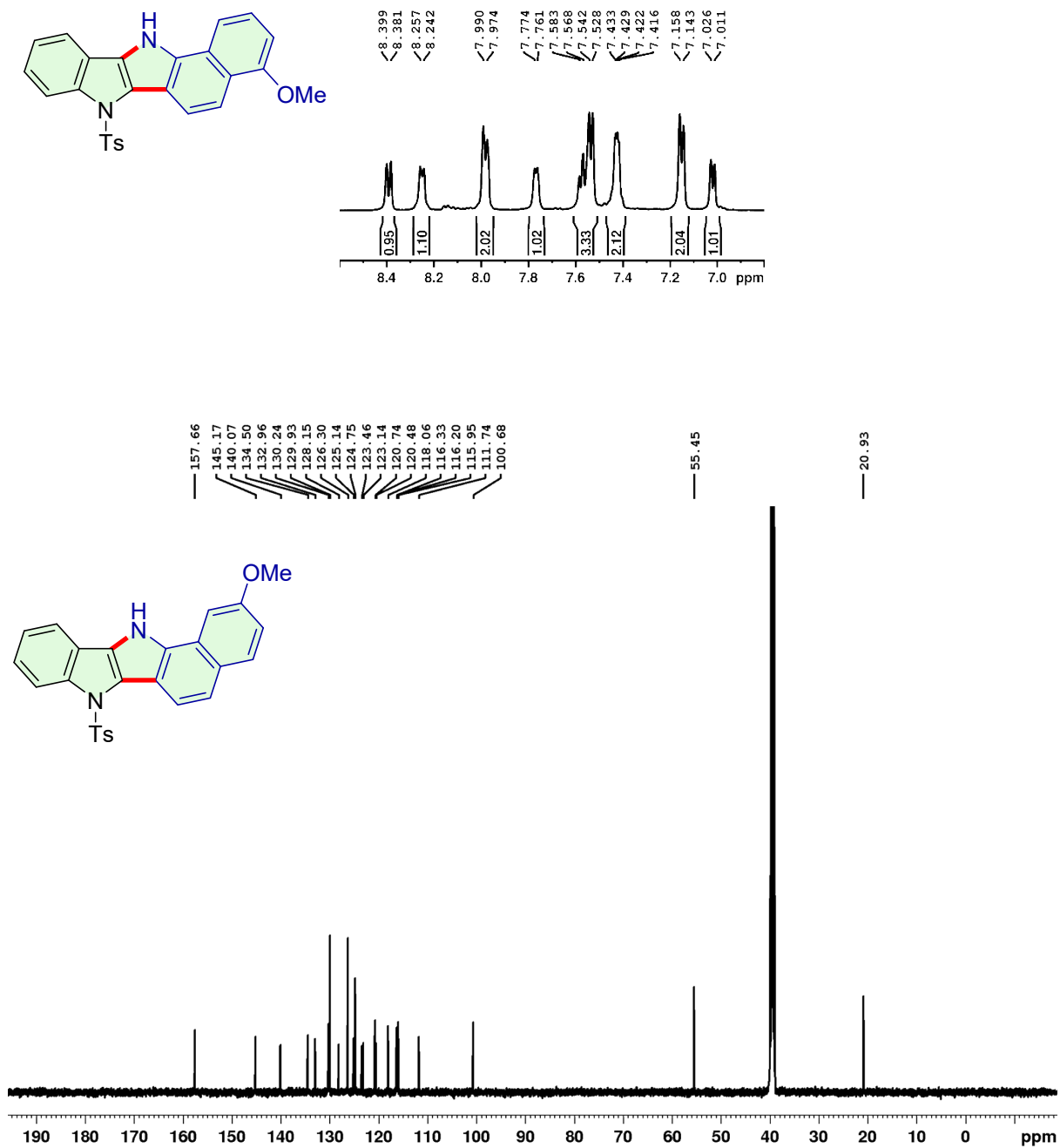


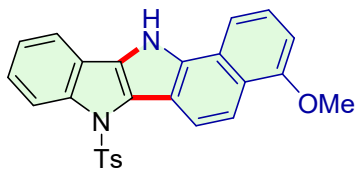
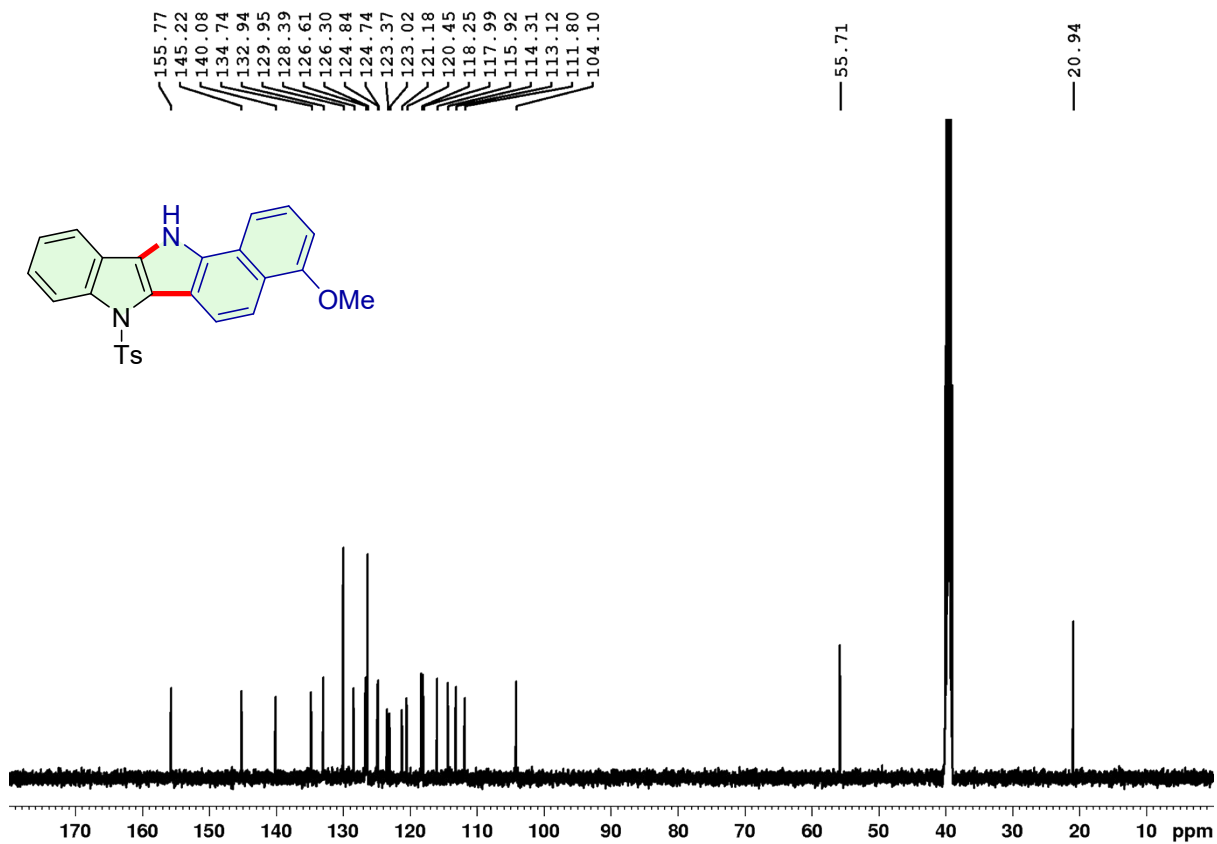
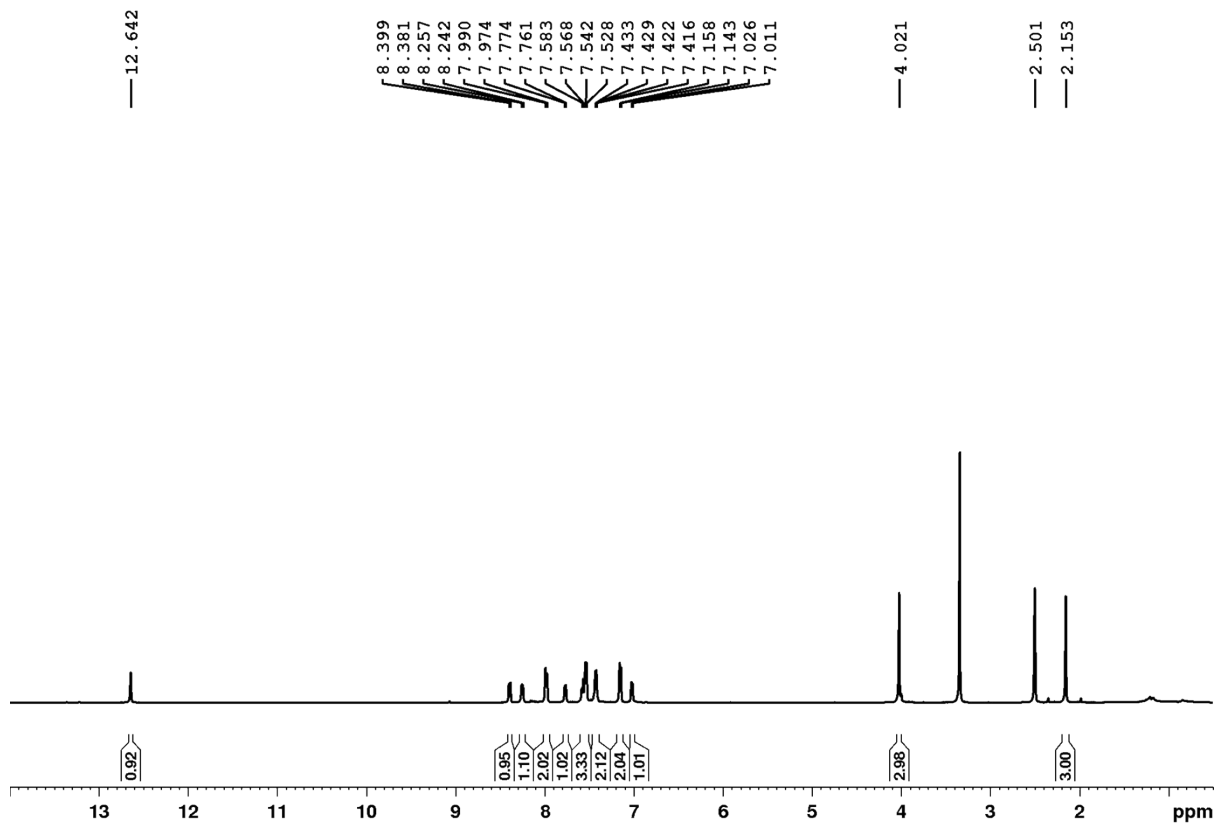


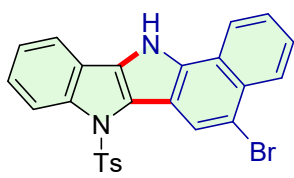
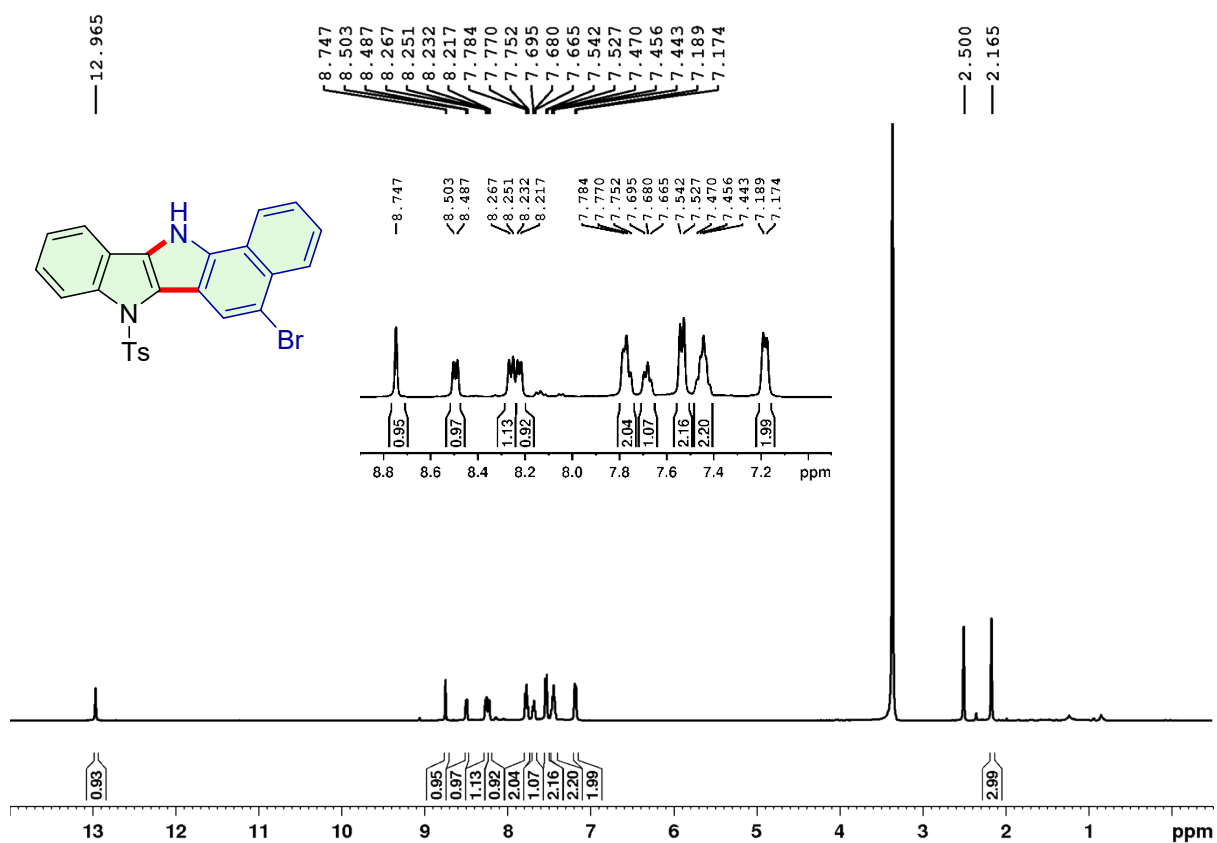


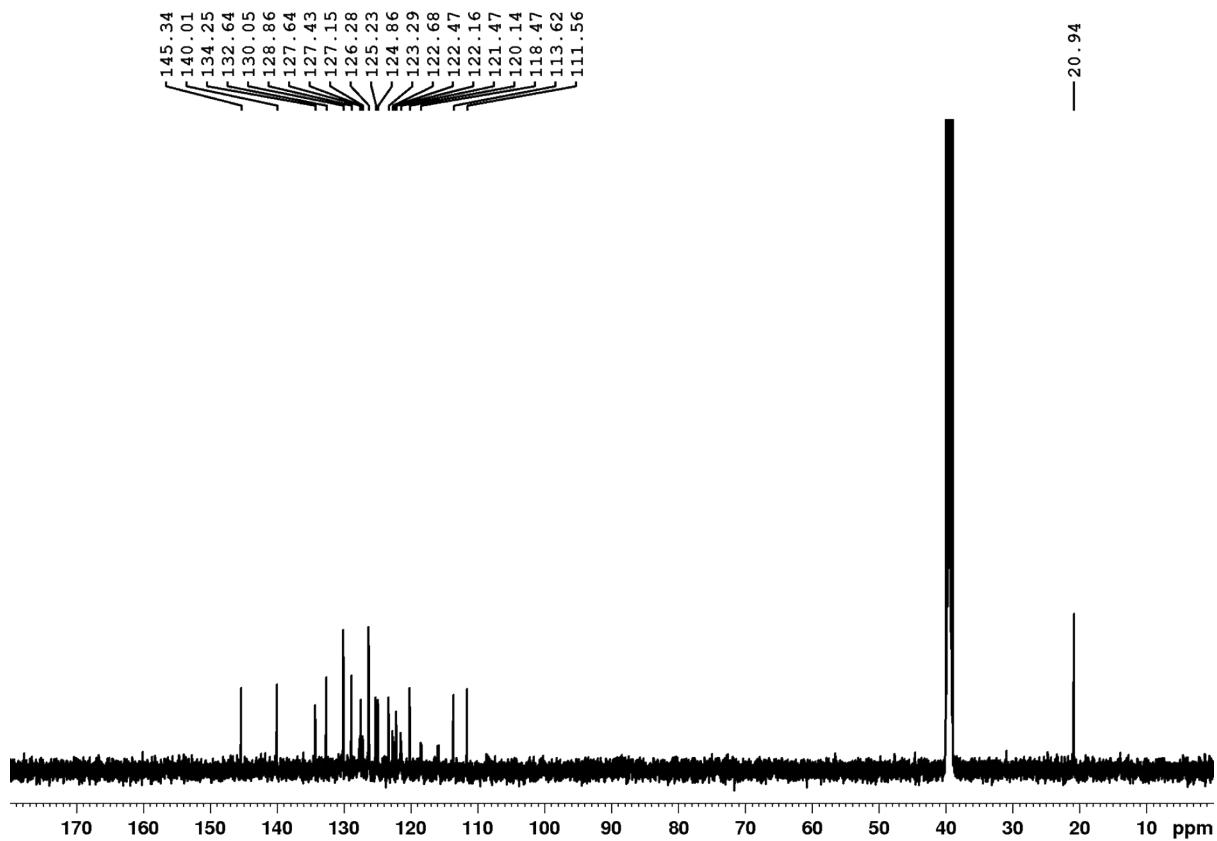
¹H NMR (500 MHz, DMSO-*d*₆) & ¹³C{¹H} (125 MHz, DMSO-*d*₆) Spectra of 3c

^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **3d**

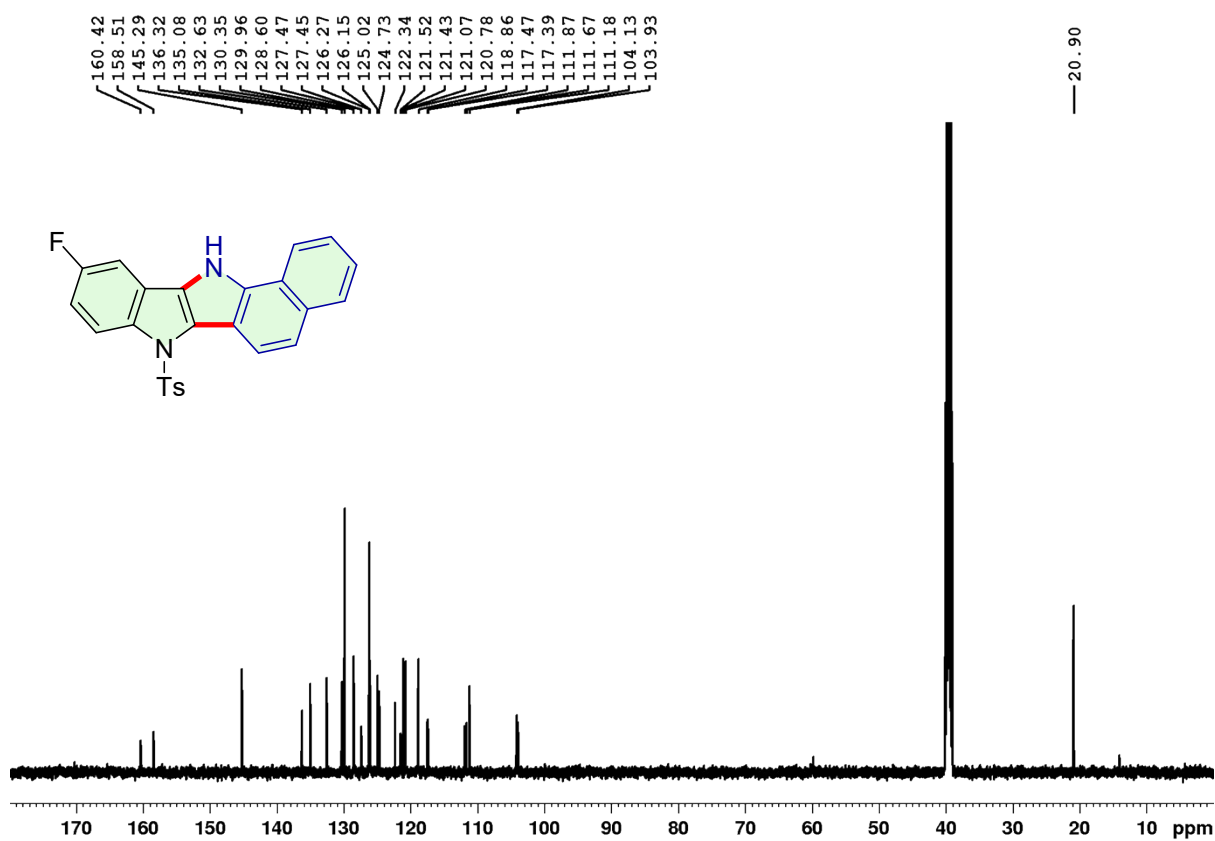
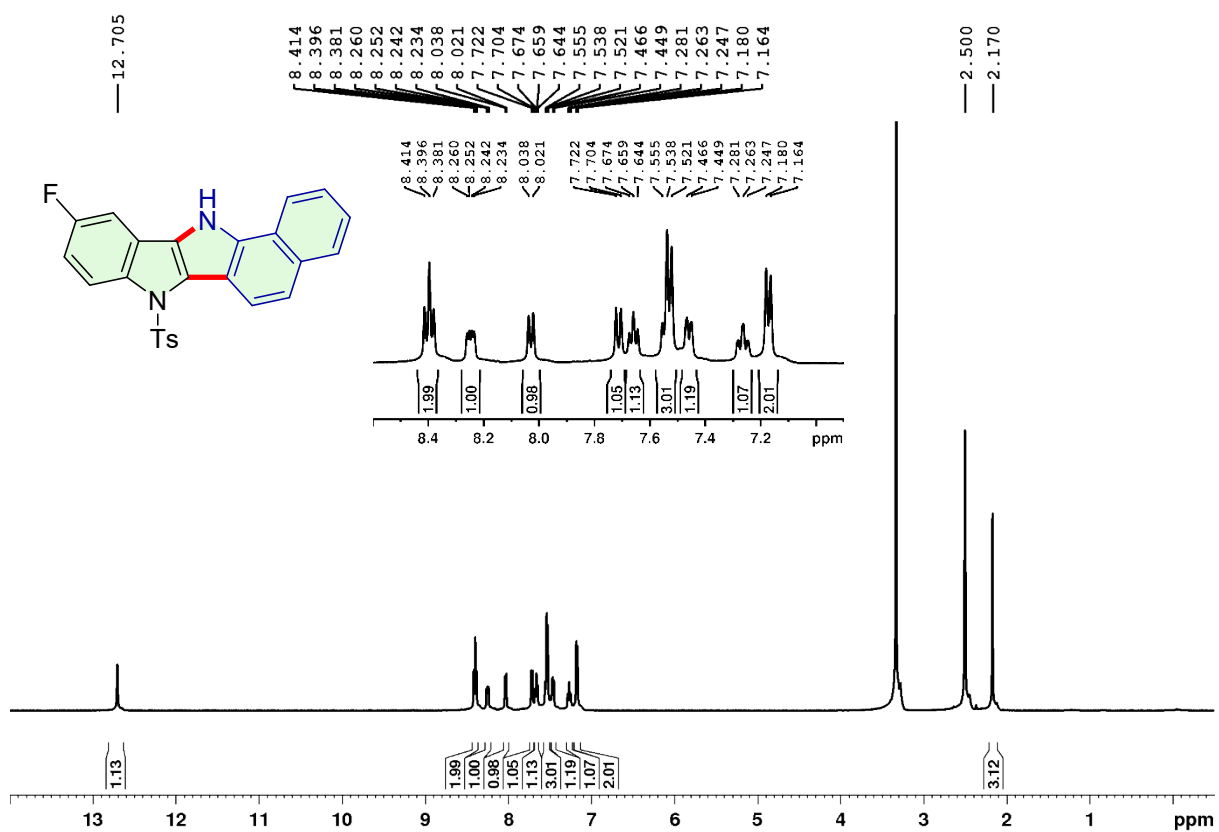




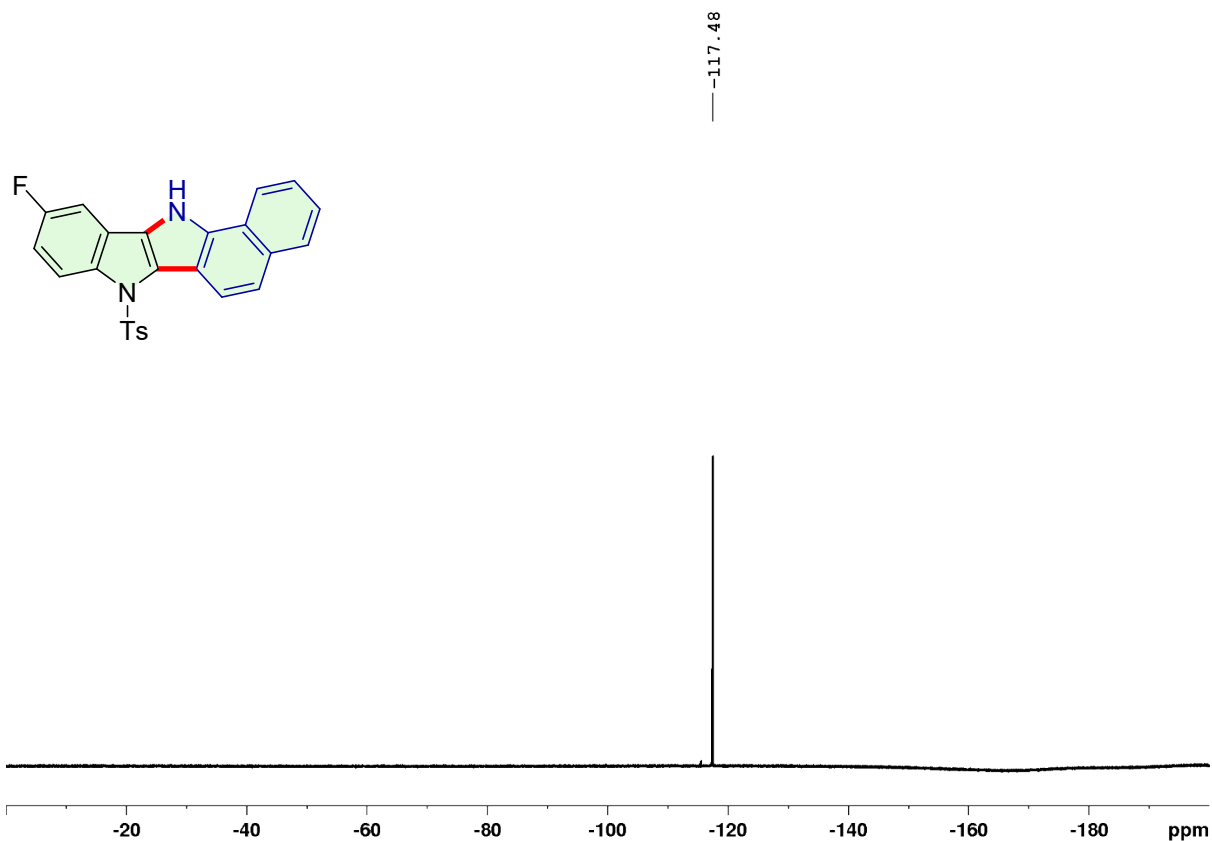




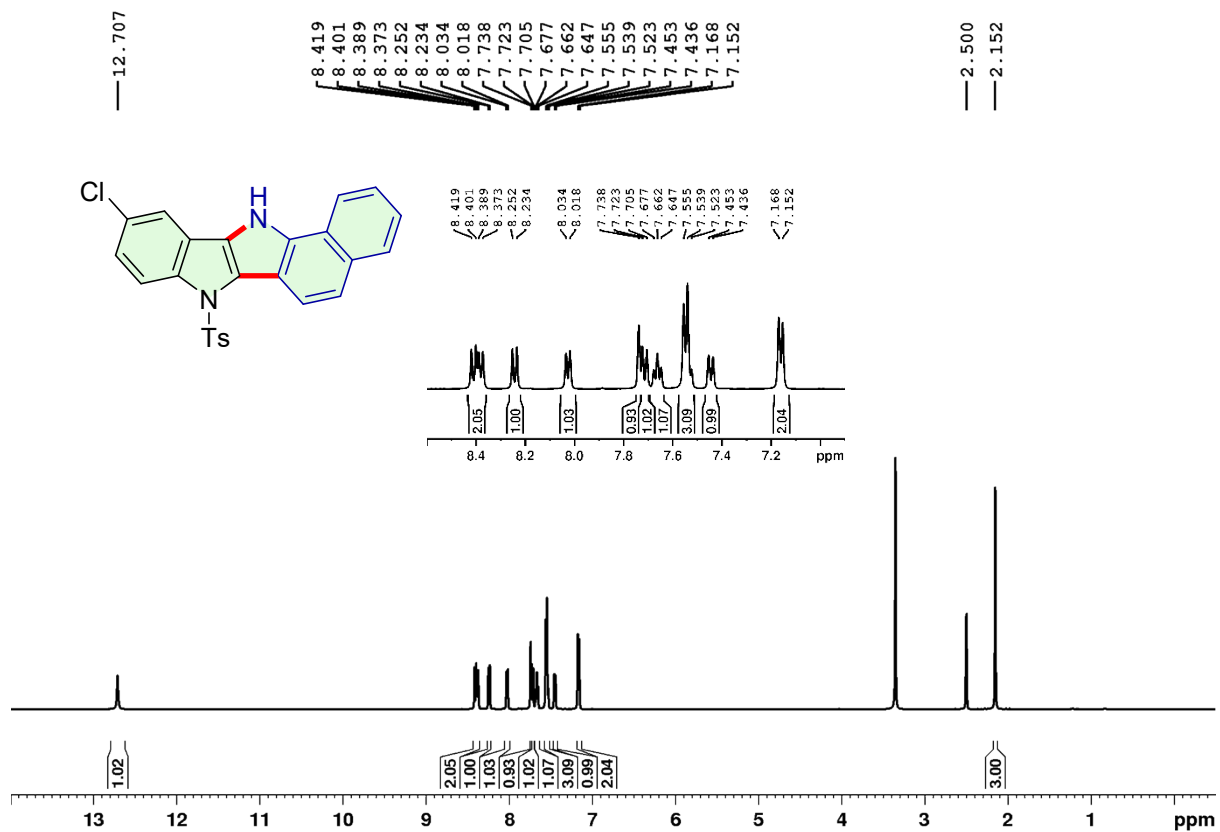
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$), ^{19}F (470 MHz, DMSO-

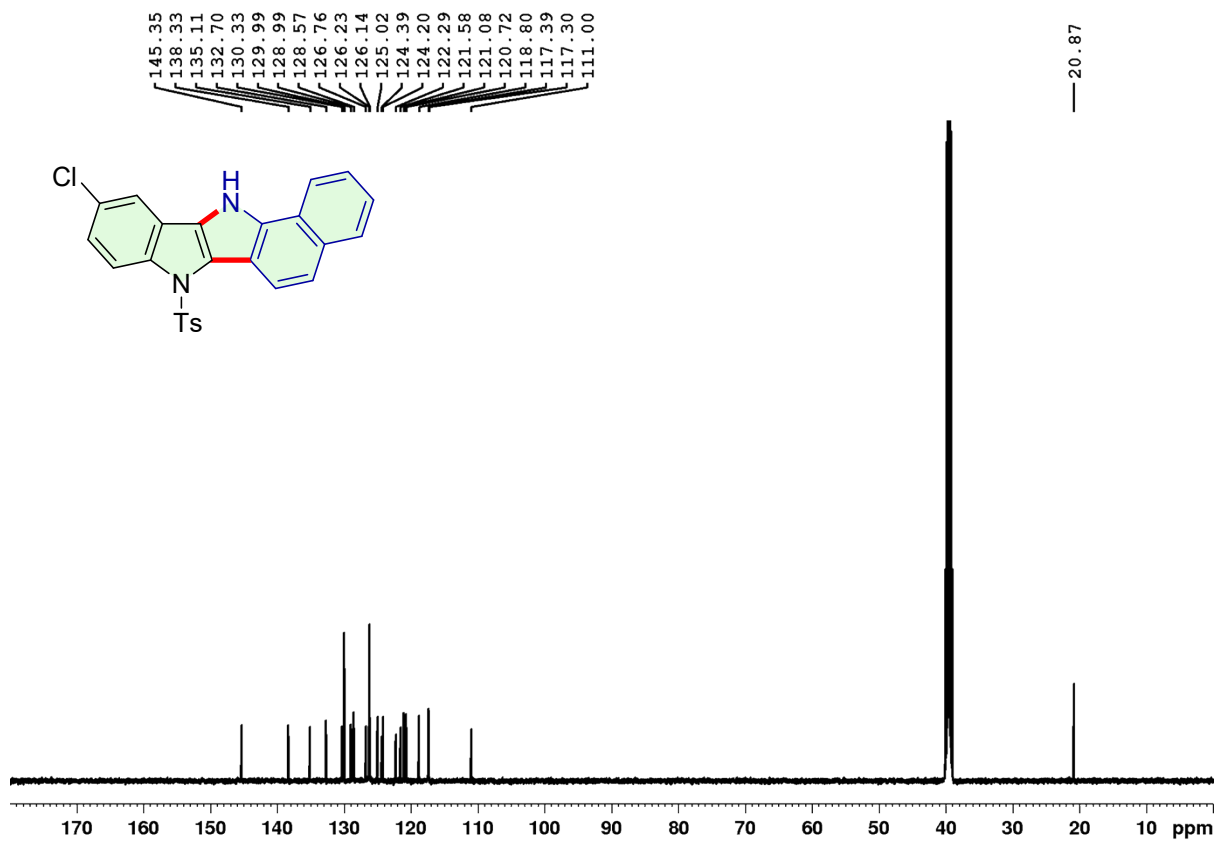


d_6) Spectra of **3f**

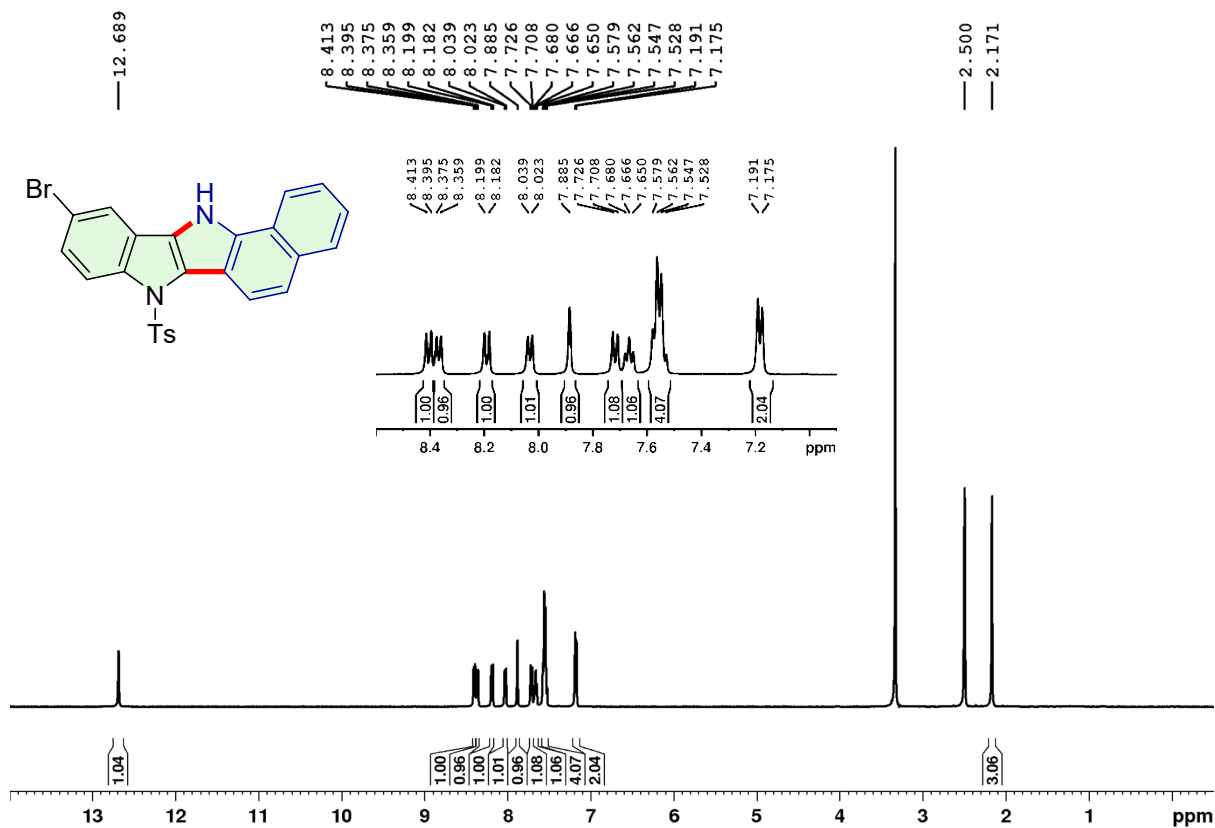


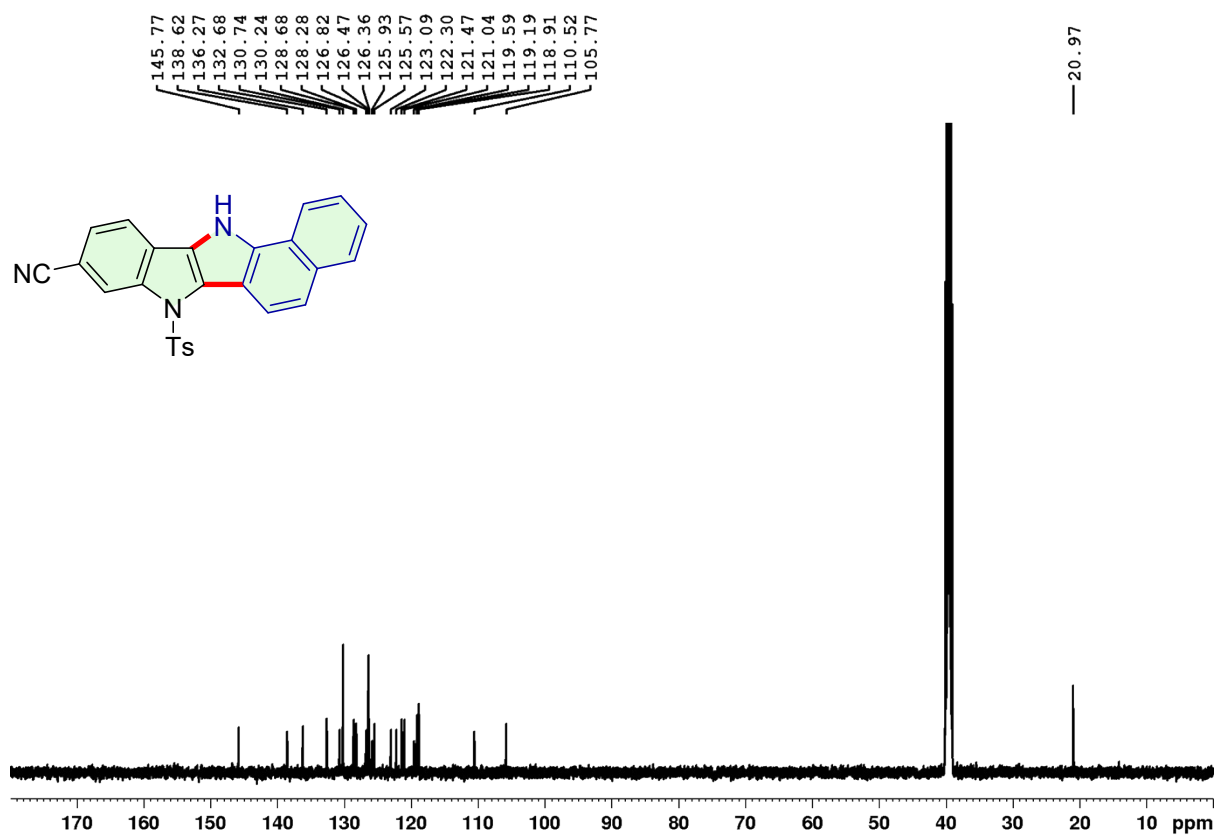
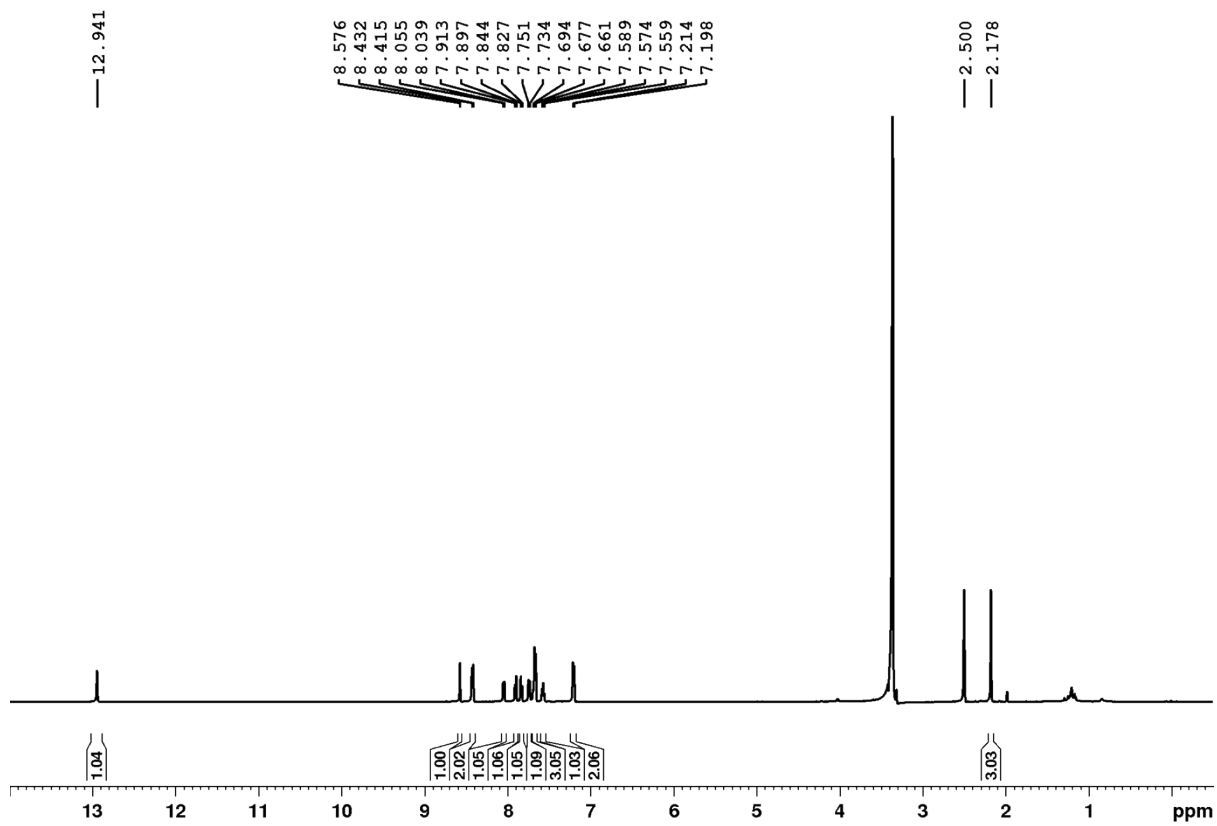
^1H NMR (500 MHz, DMSO- d_6) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, DMSO- d_6) Spectra of 3g

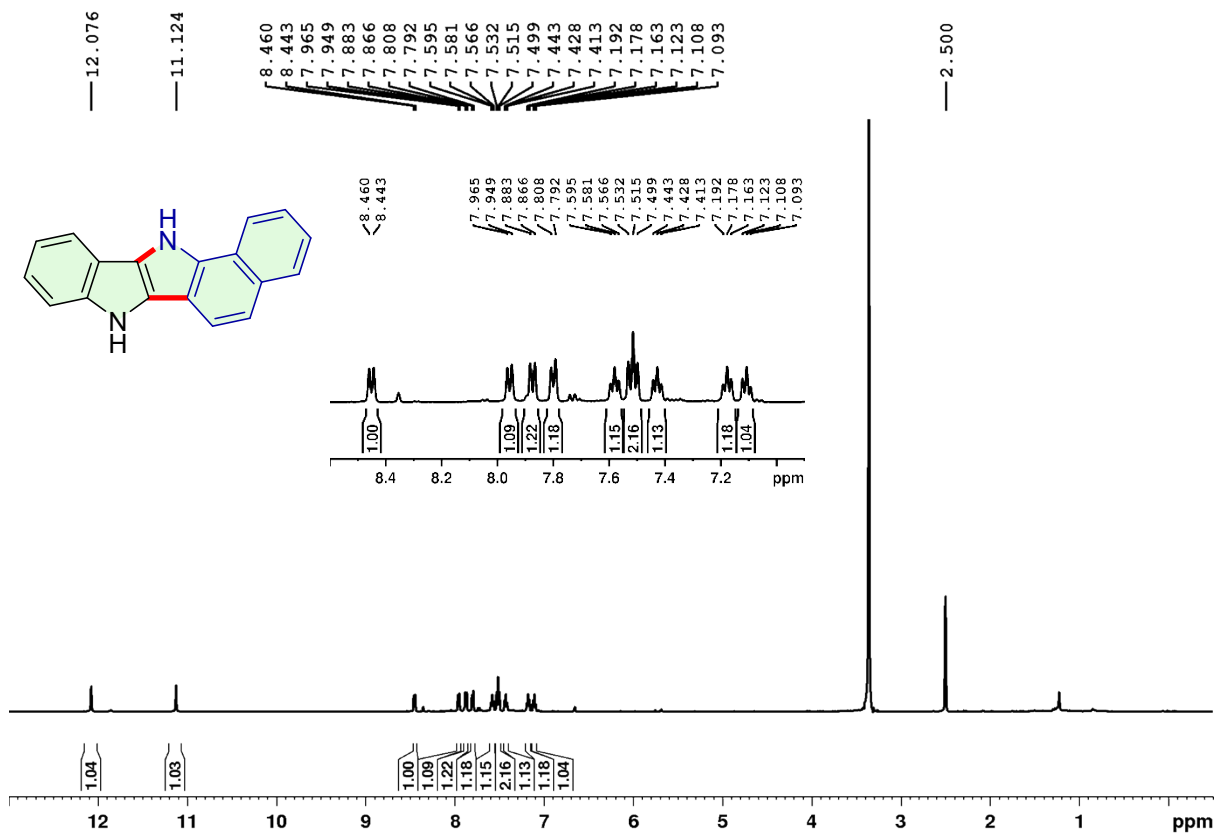


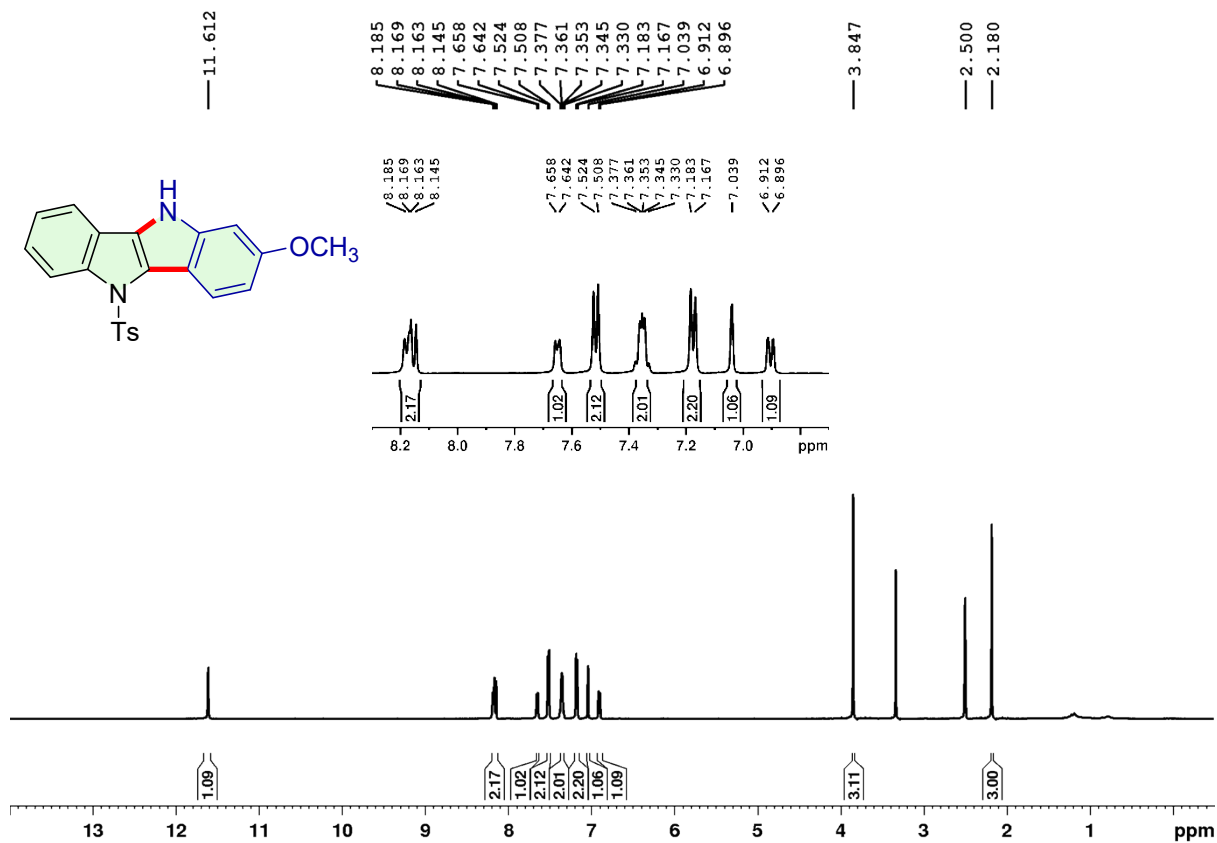
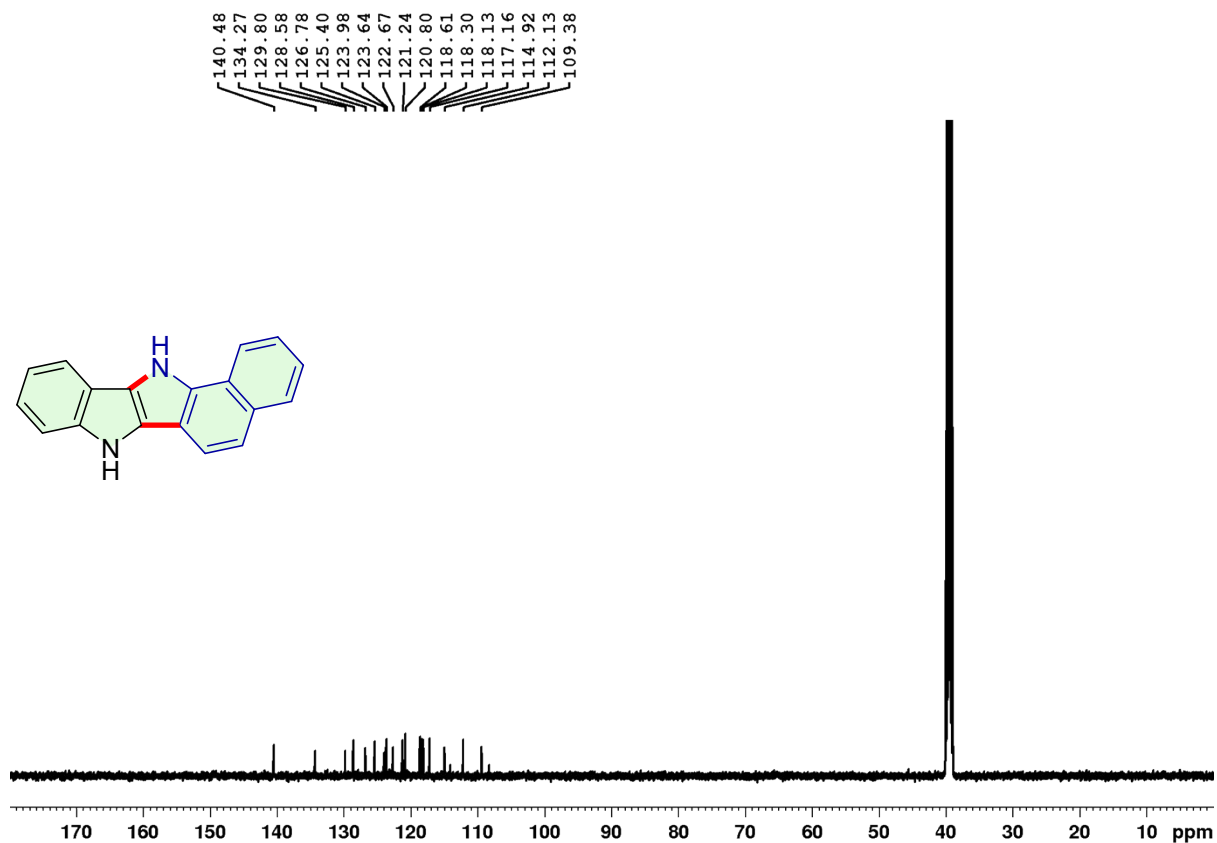


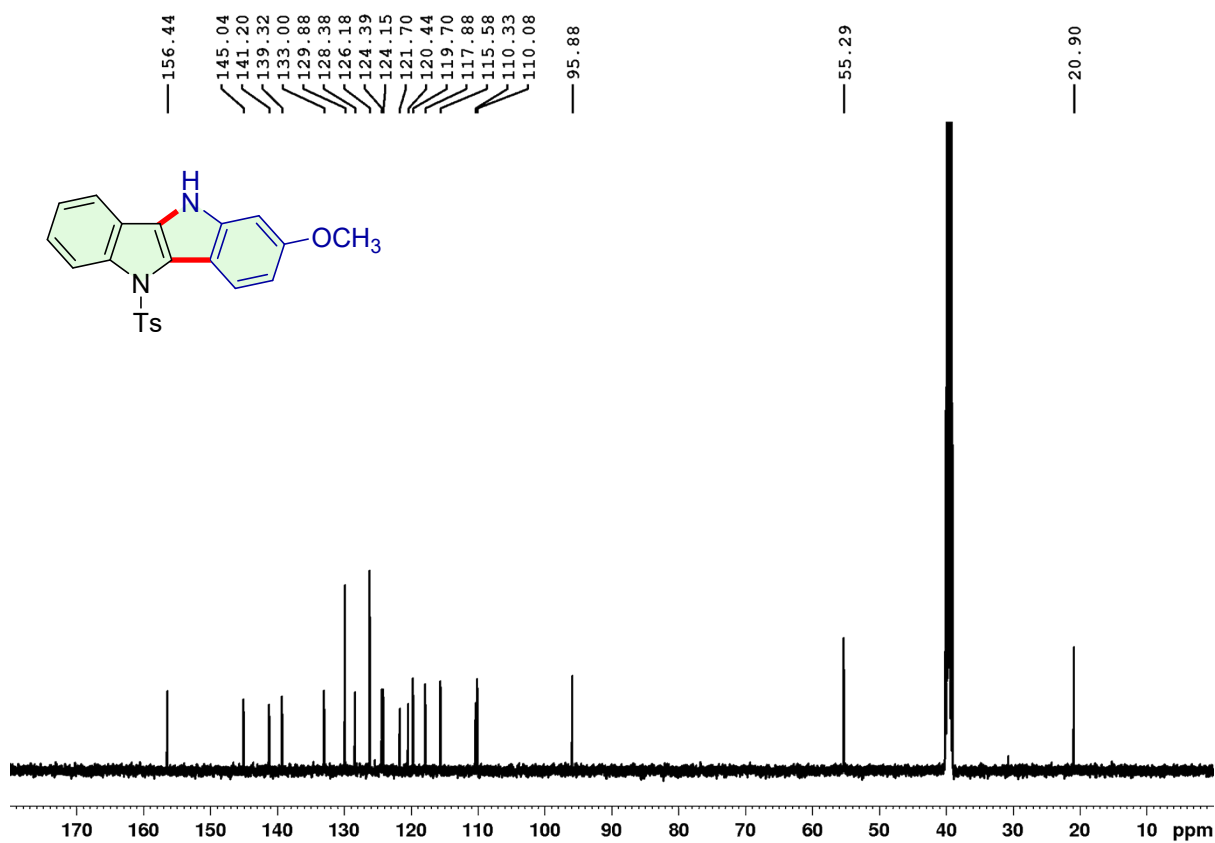
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **3h**



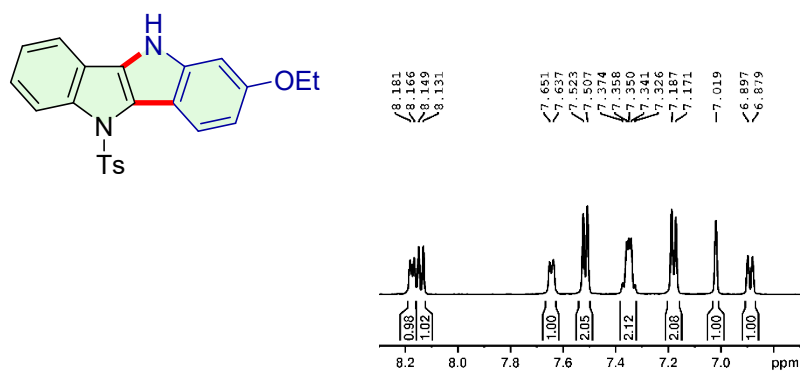


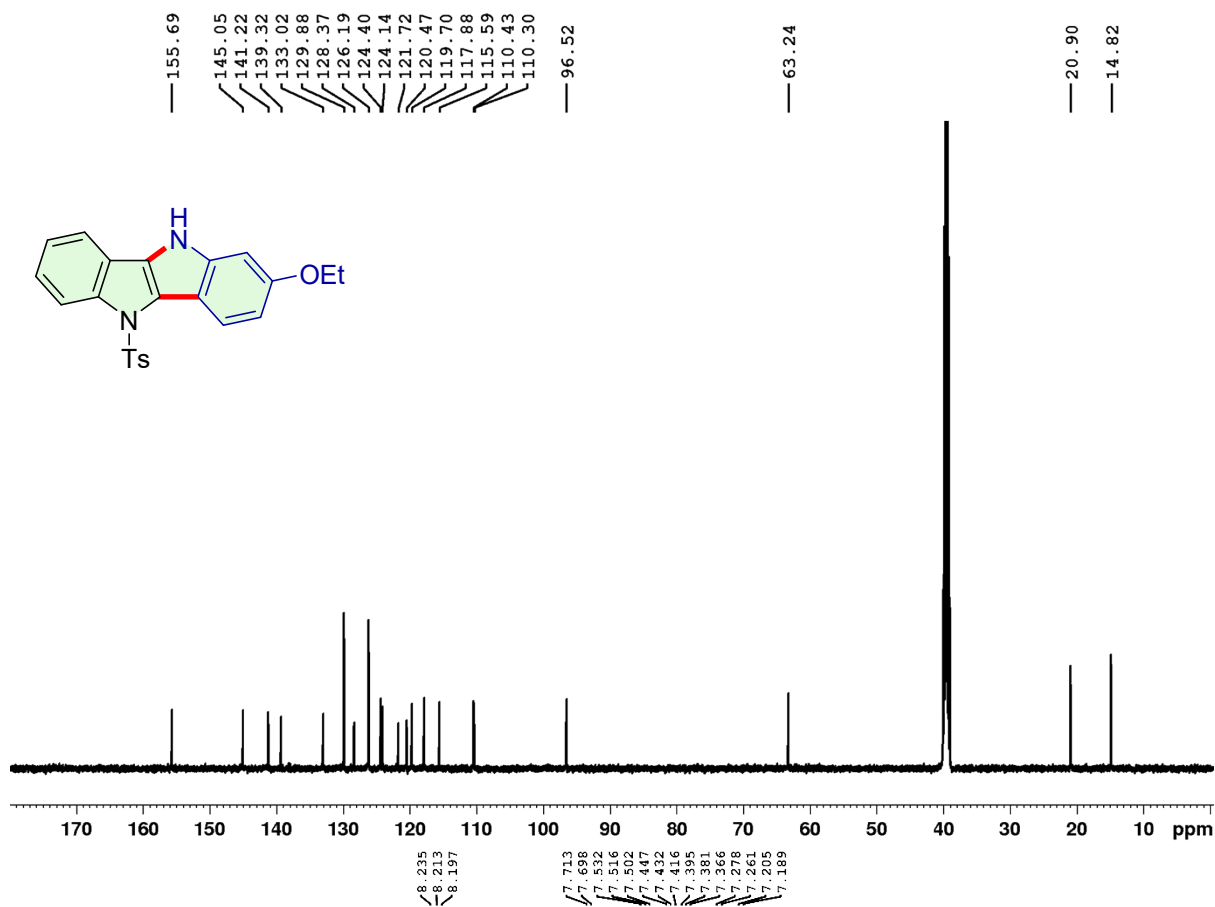
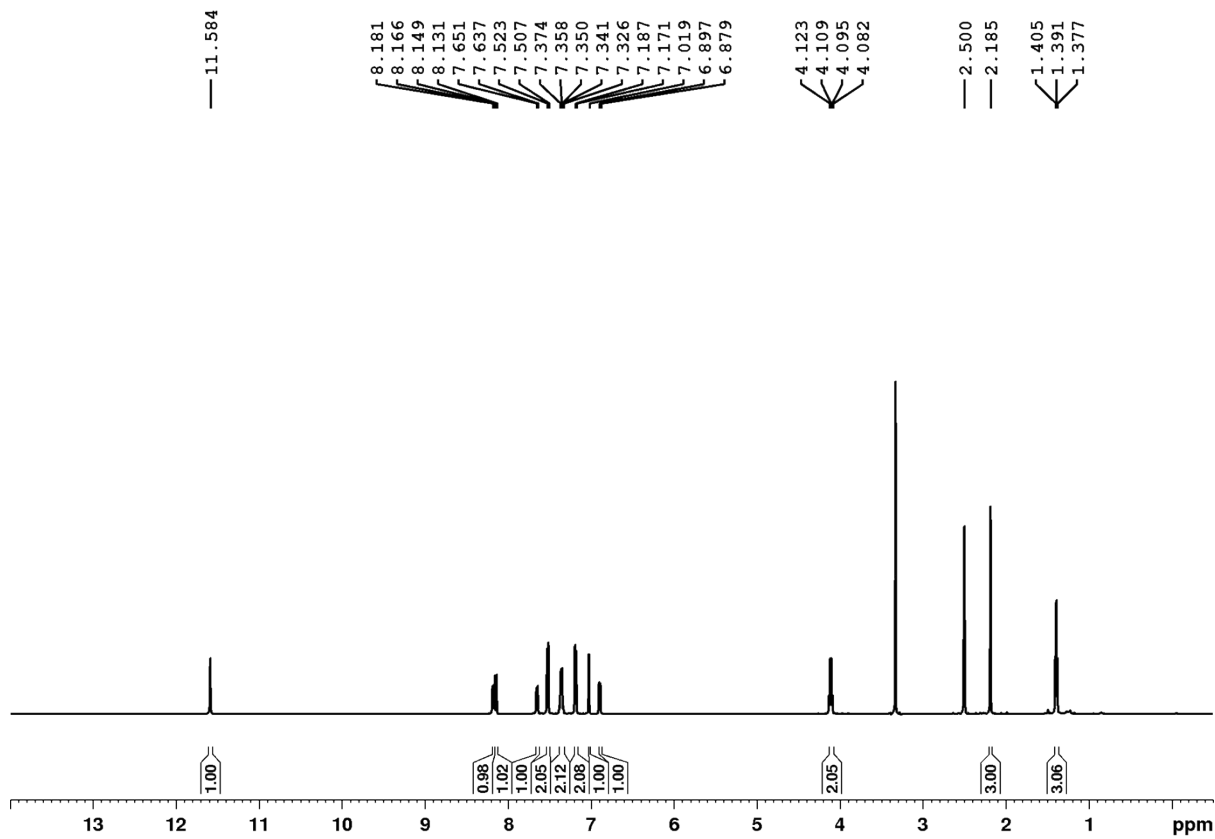






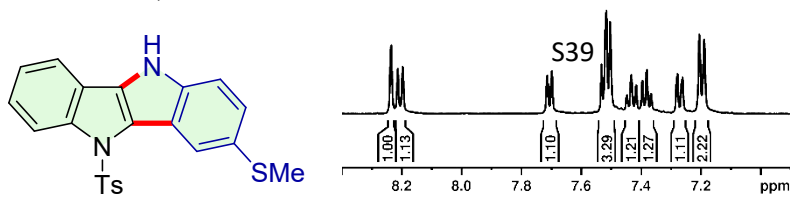
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5b**

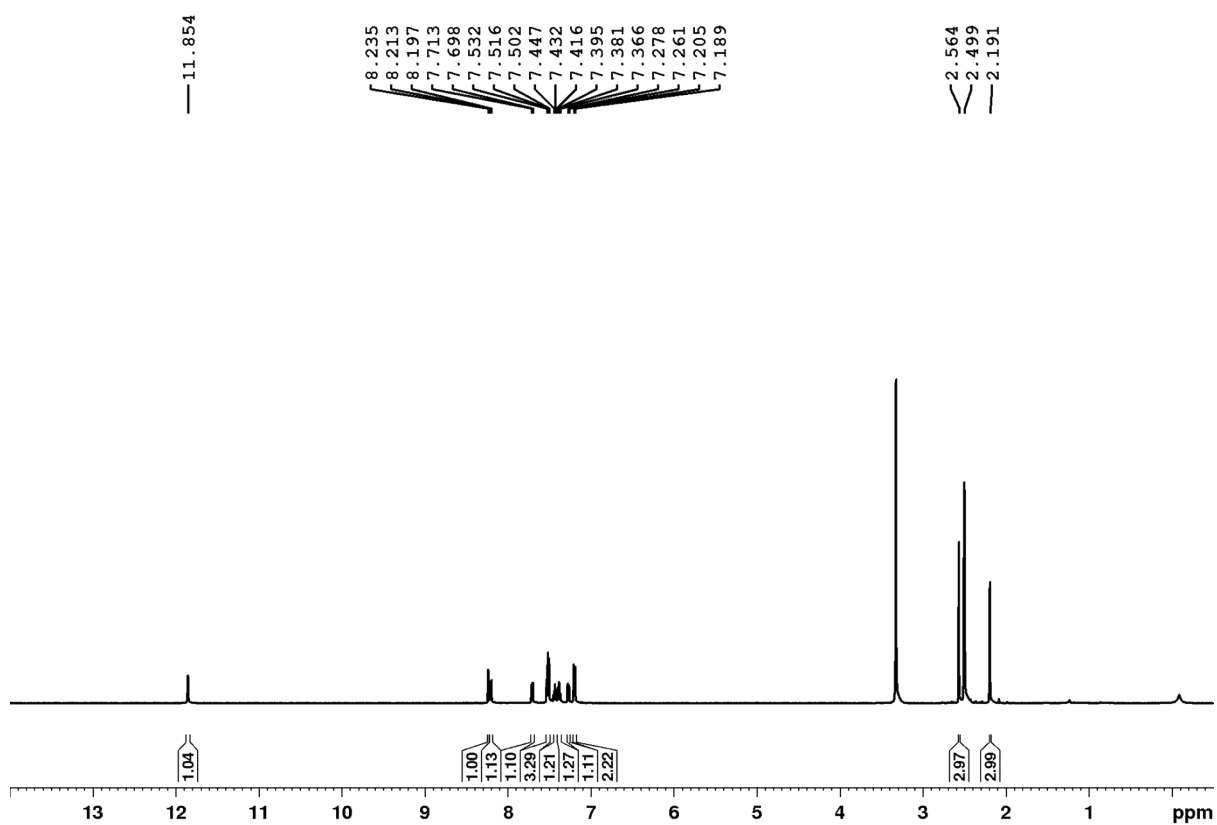




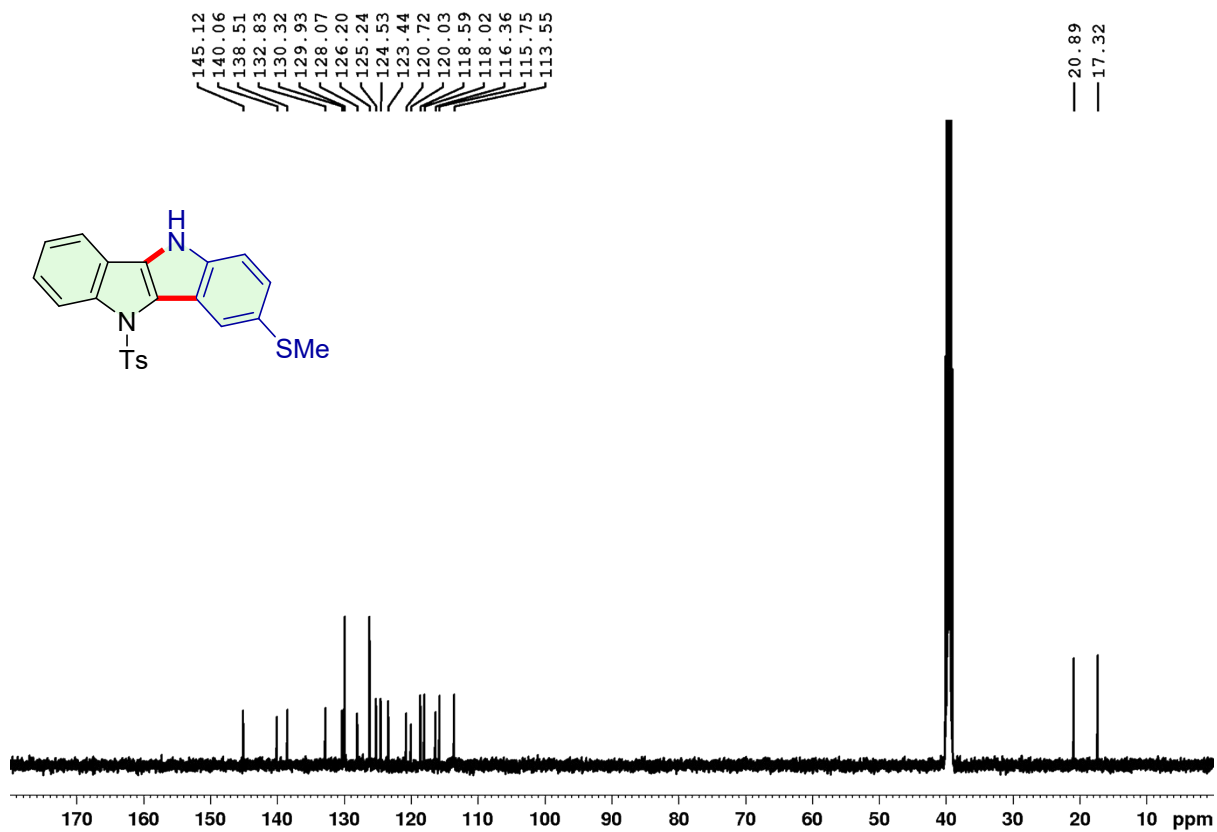
^1H NMR (500 MHz,

DMSO- d_6) & $^{13}\text{C}\{^1\text{H}\}$ (125

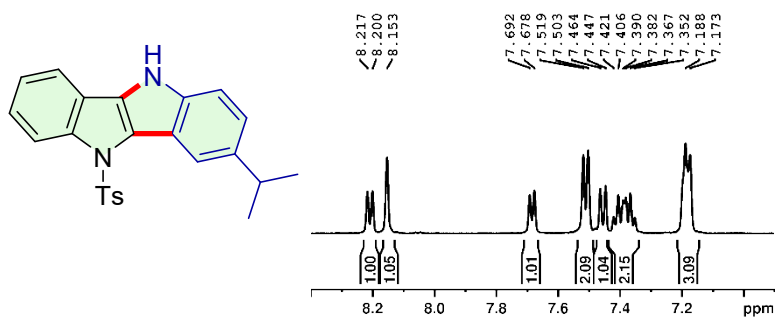


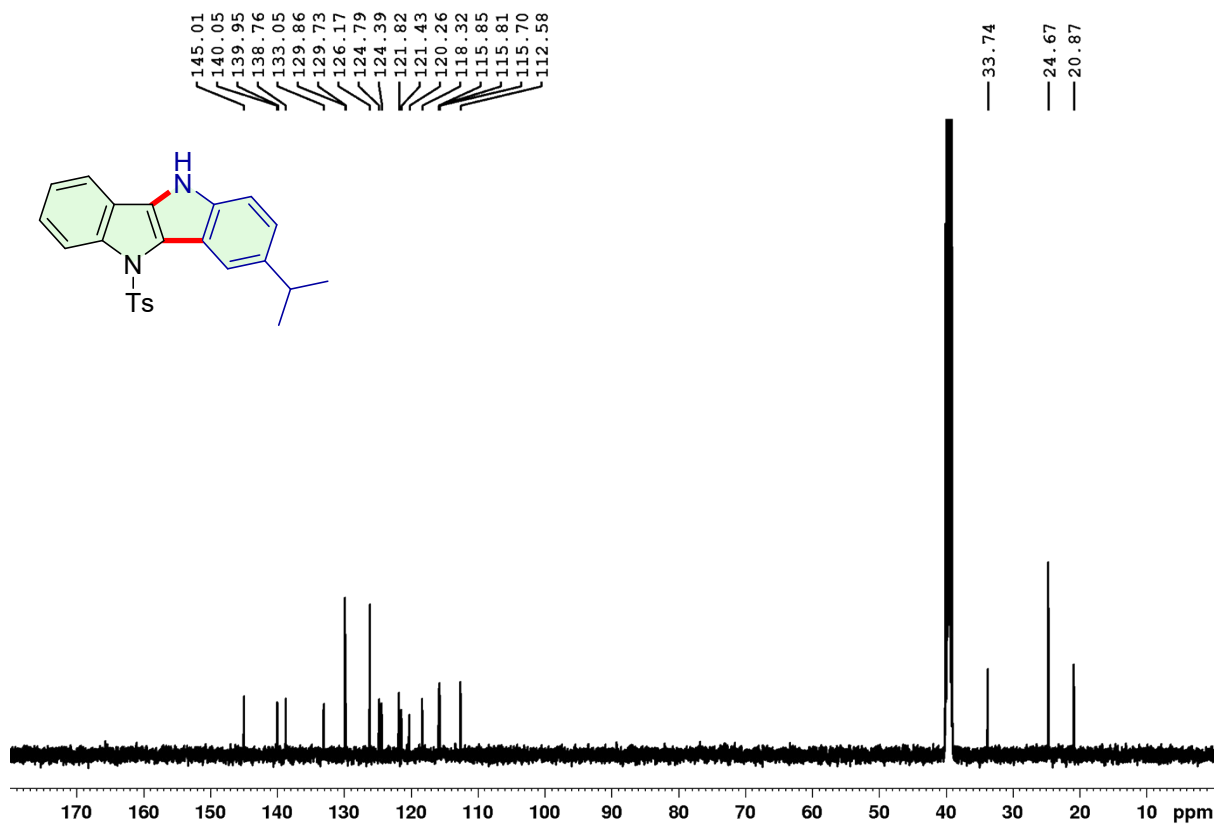
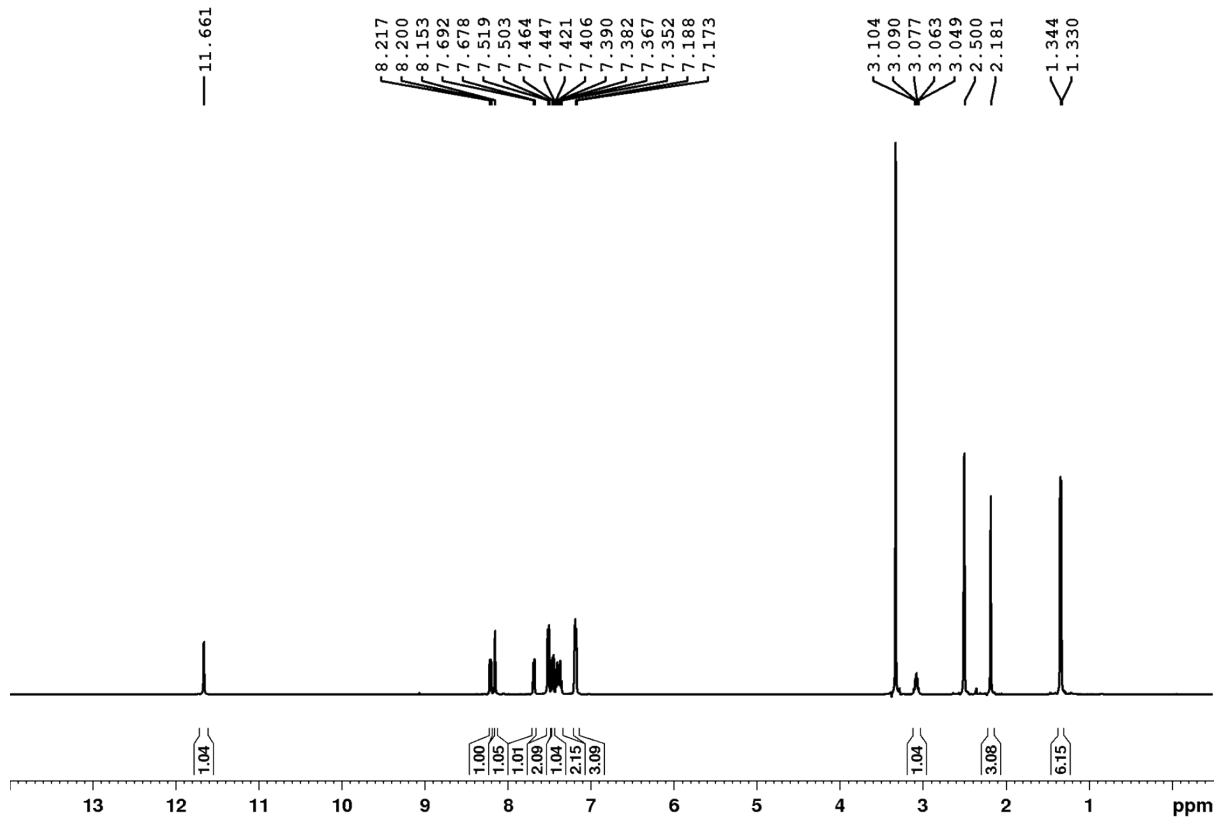


MHz, DMSO- d_6) Spectra of **5c**

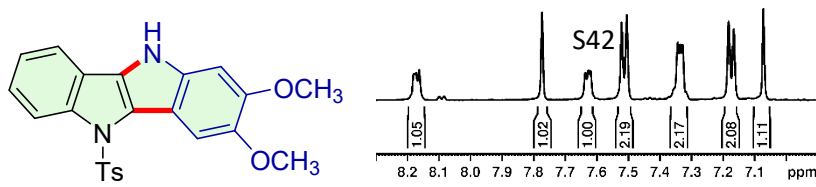


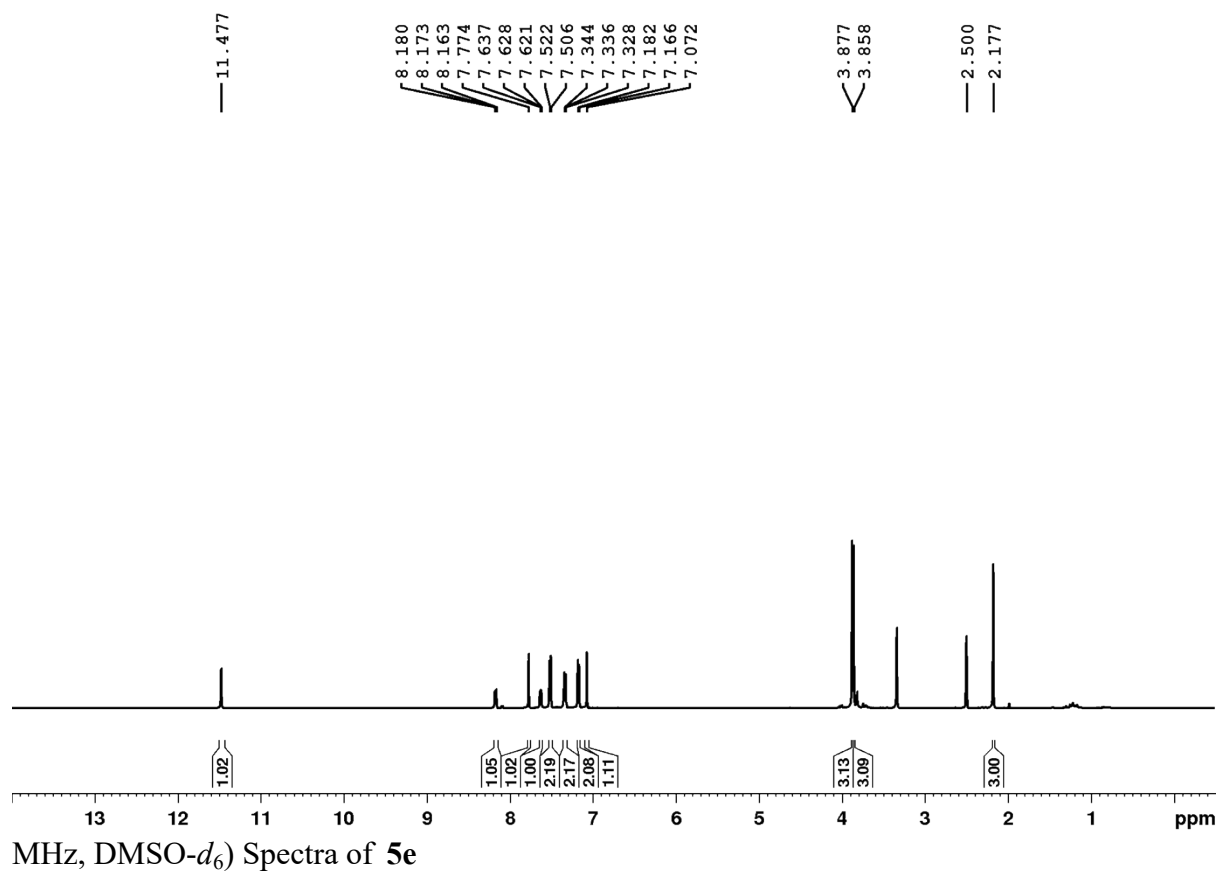
^1H NMR (500 MHz, DMSO- d_6) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, DMSO- d_6) Spectra of **5d**

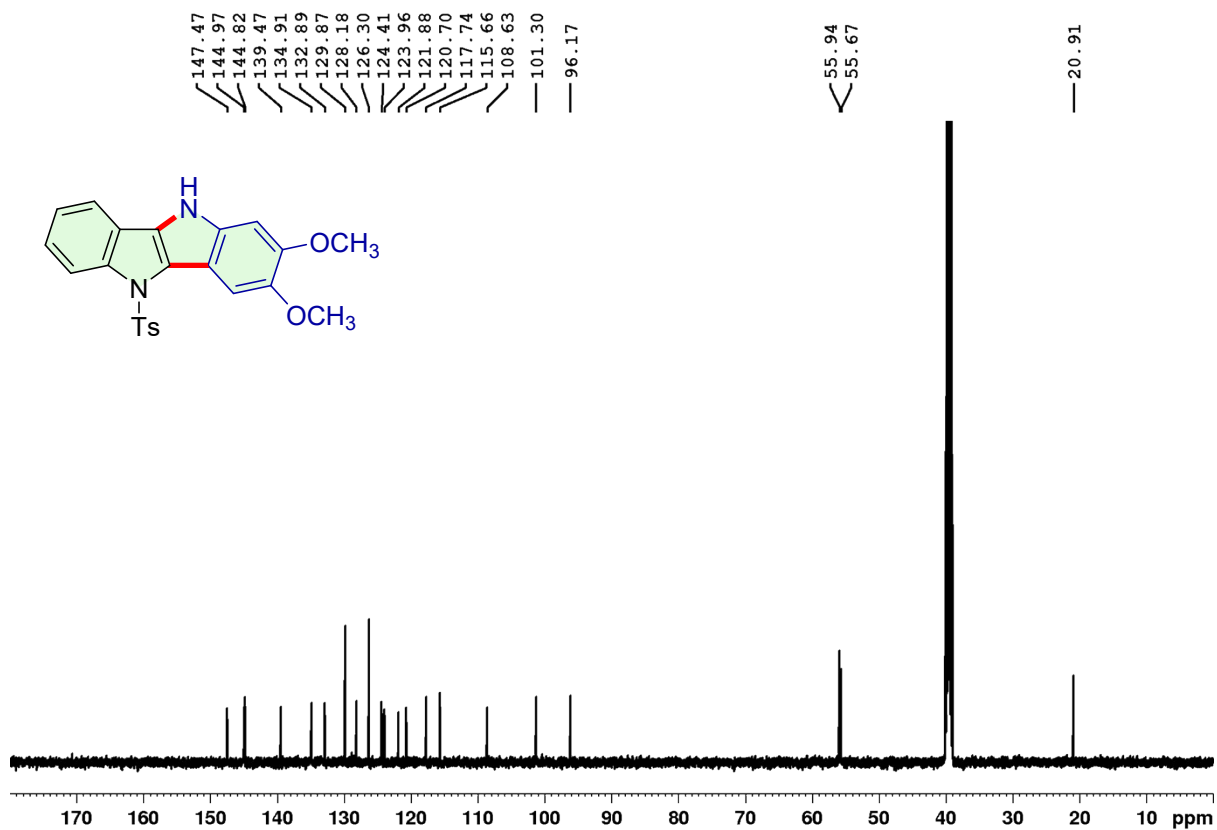




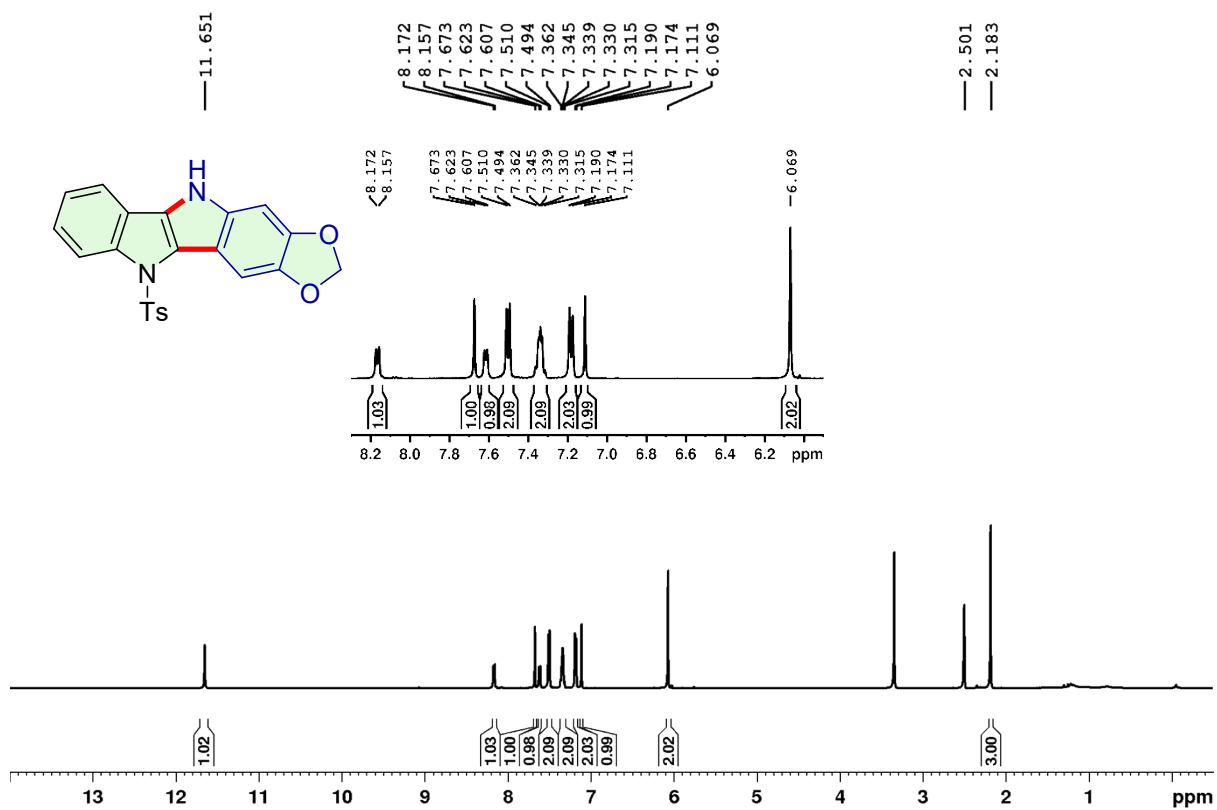
^1H NMR (500 MHz, DMSO- d_6) & ^{13}C NMR (125 MHz, DMSO- d_6)

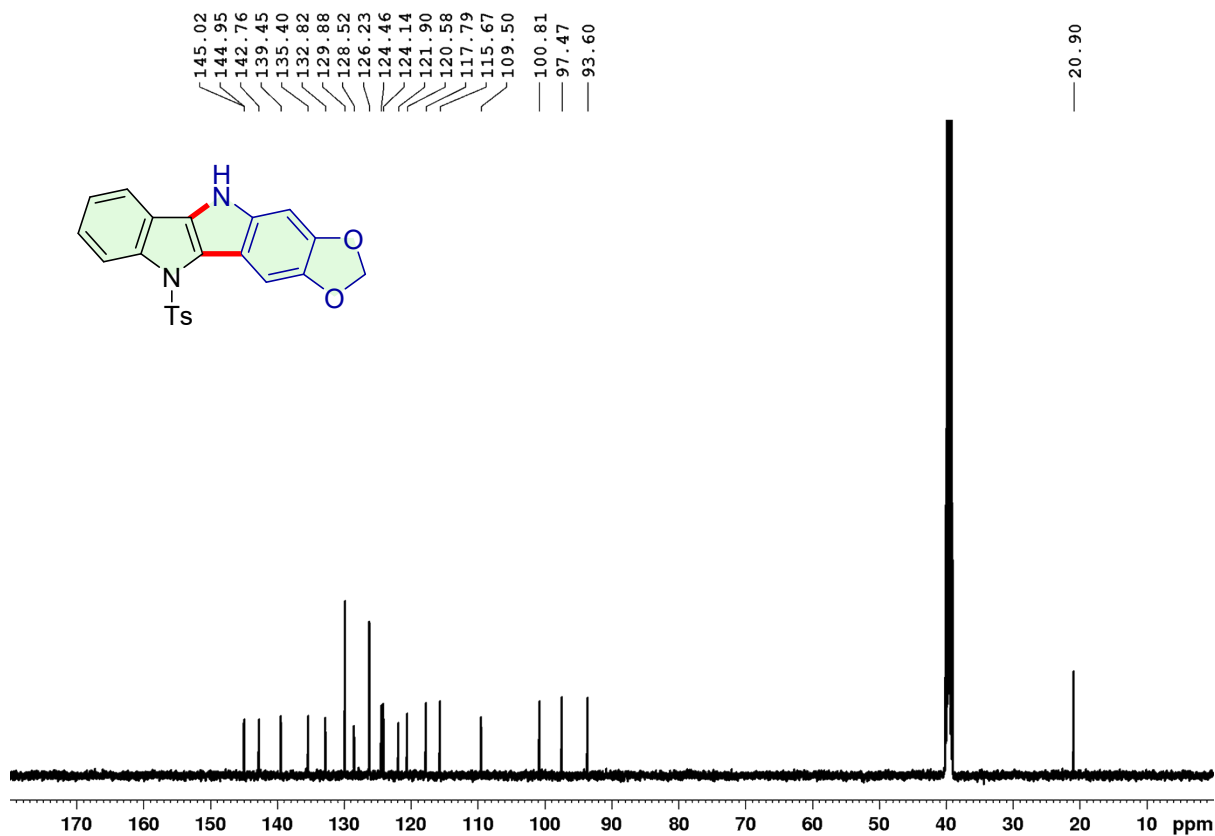




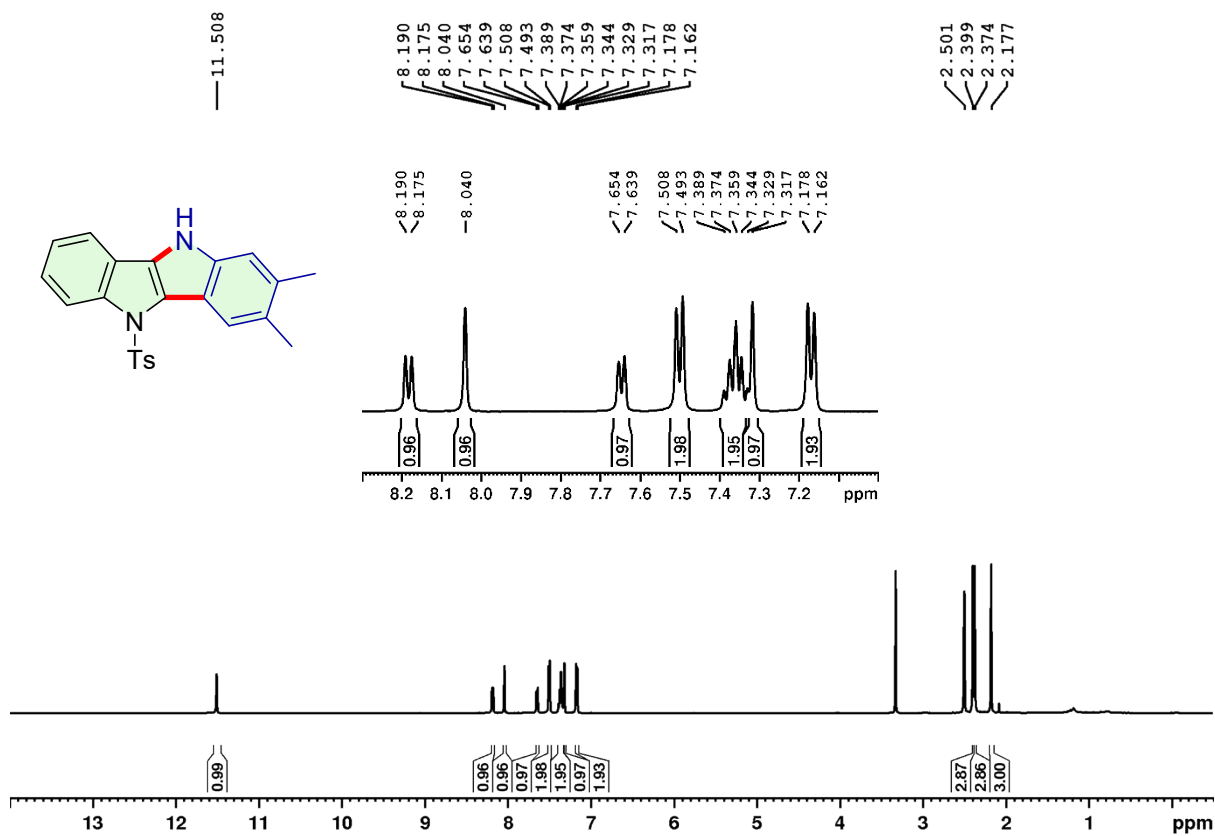


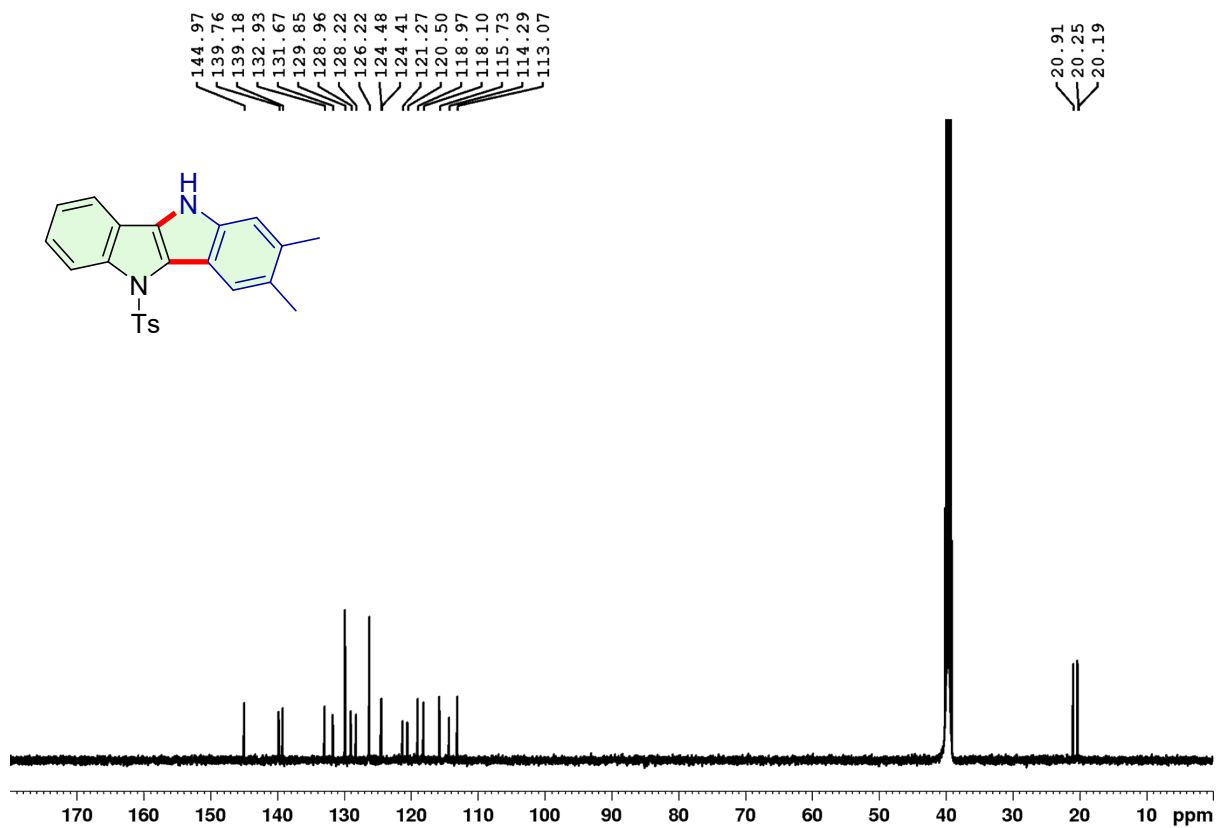
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5f**



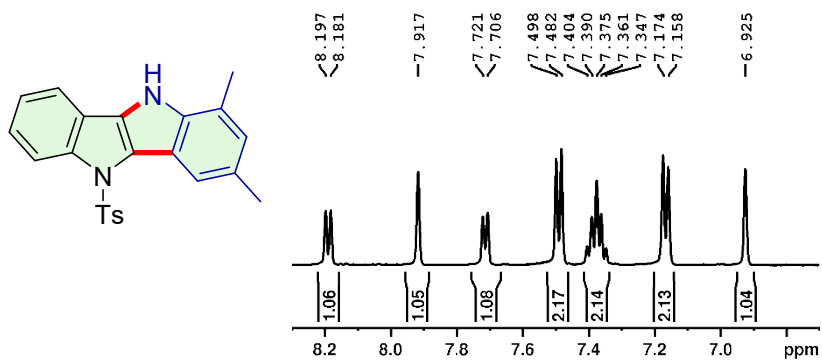


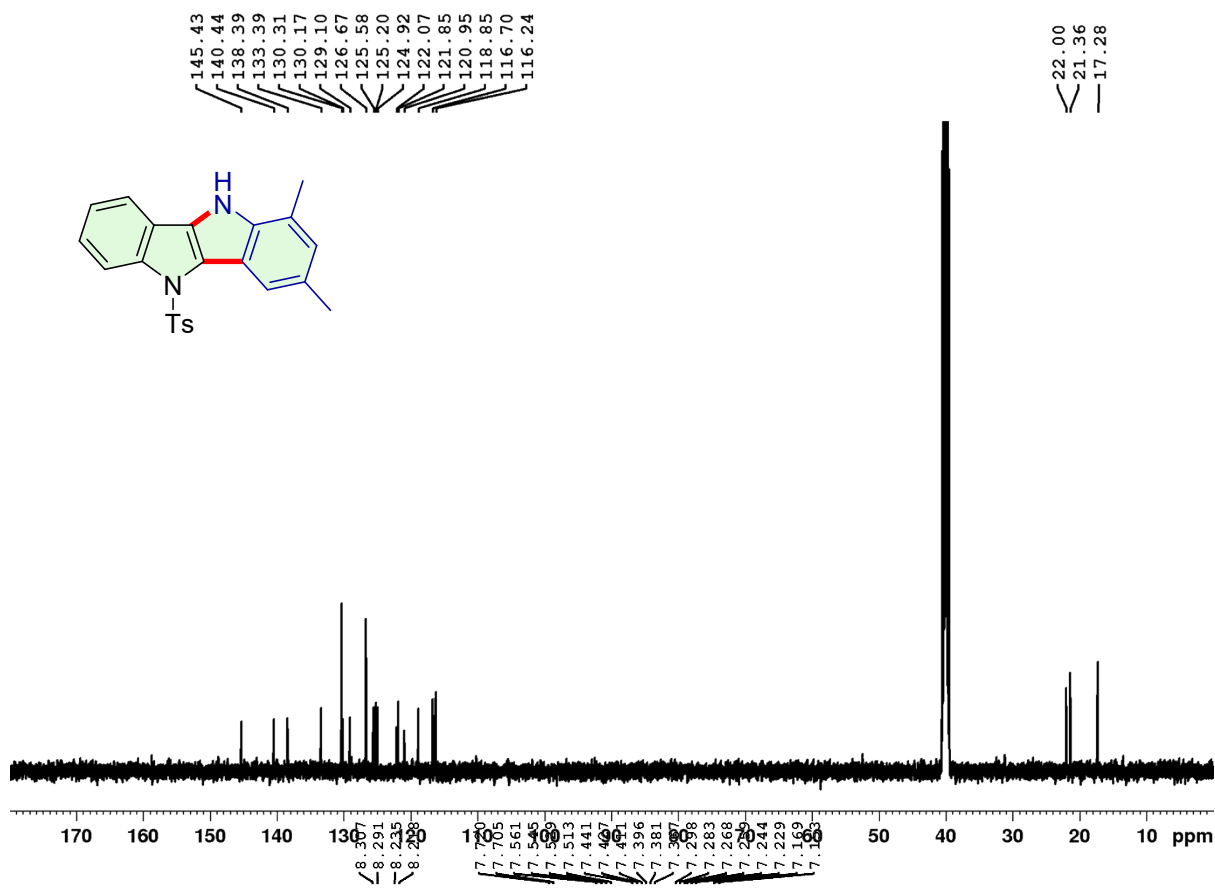
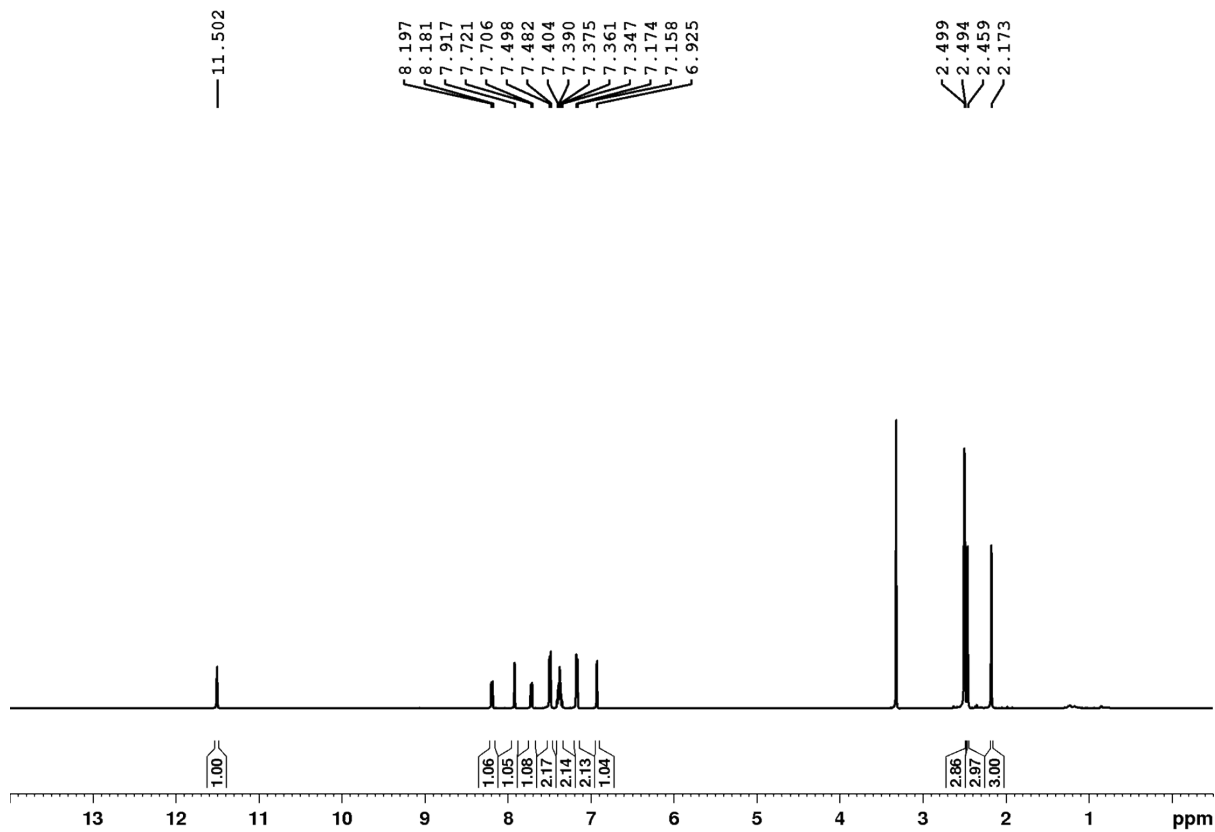
¹H NMR (500 MHz, DMSO-*d*₆) & ¹³C{¹H} (125 MHz, DMSO-*d*₆) Spectra of **5g**





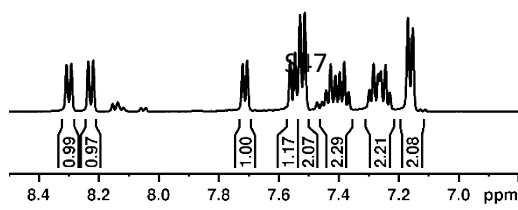
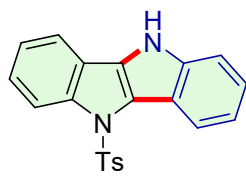
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5h**



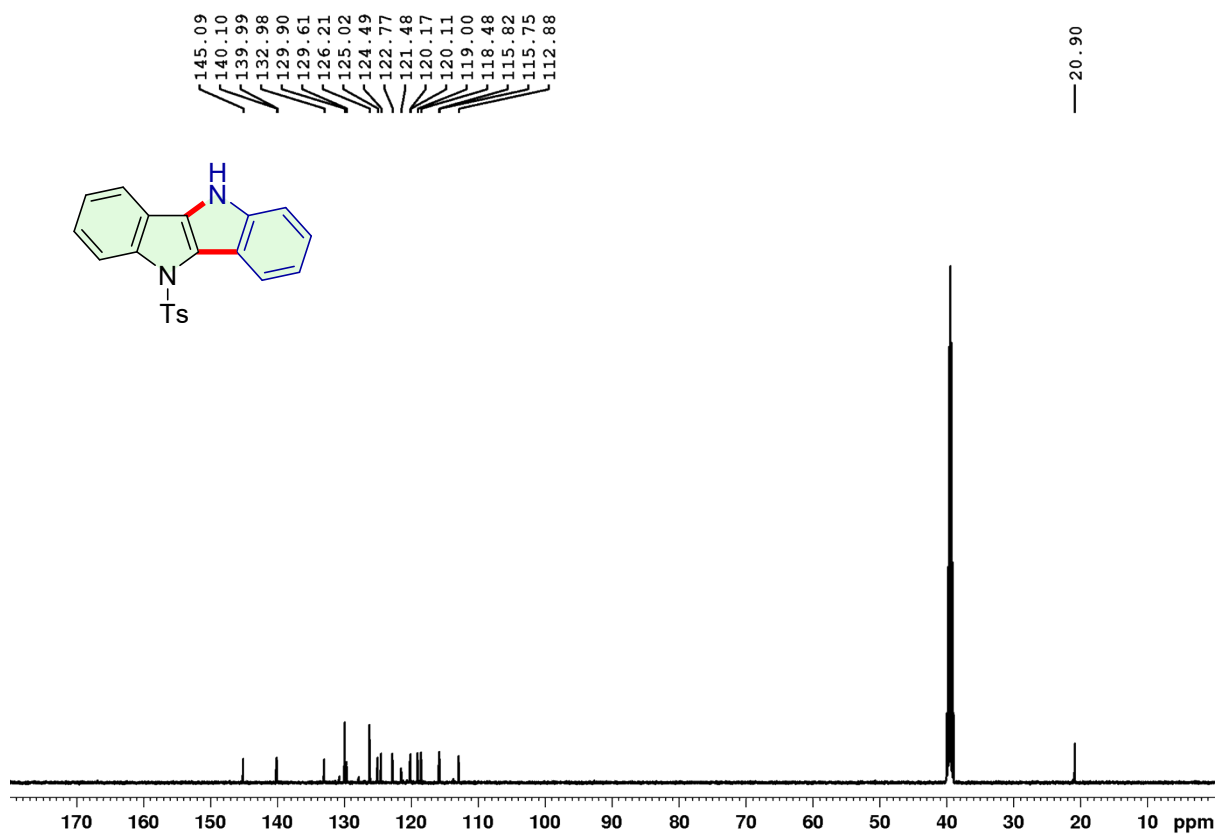
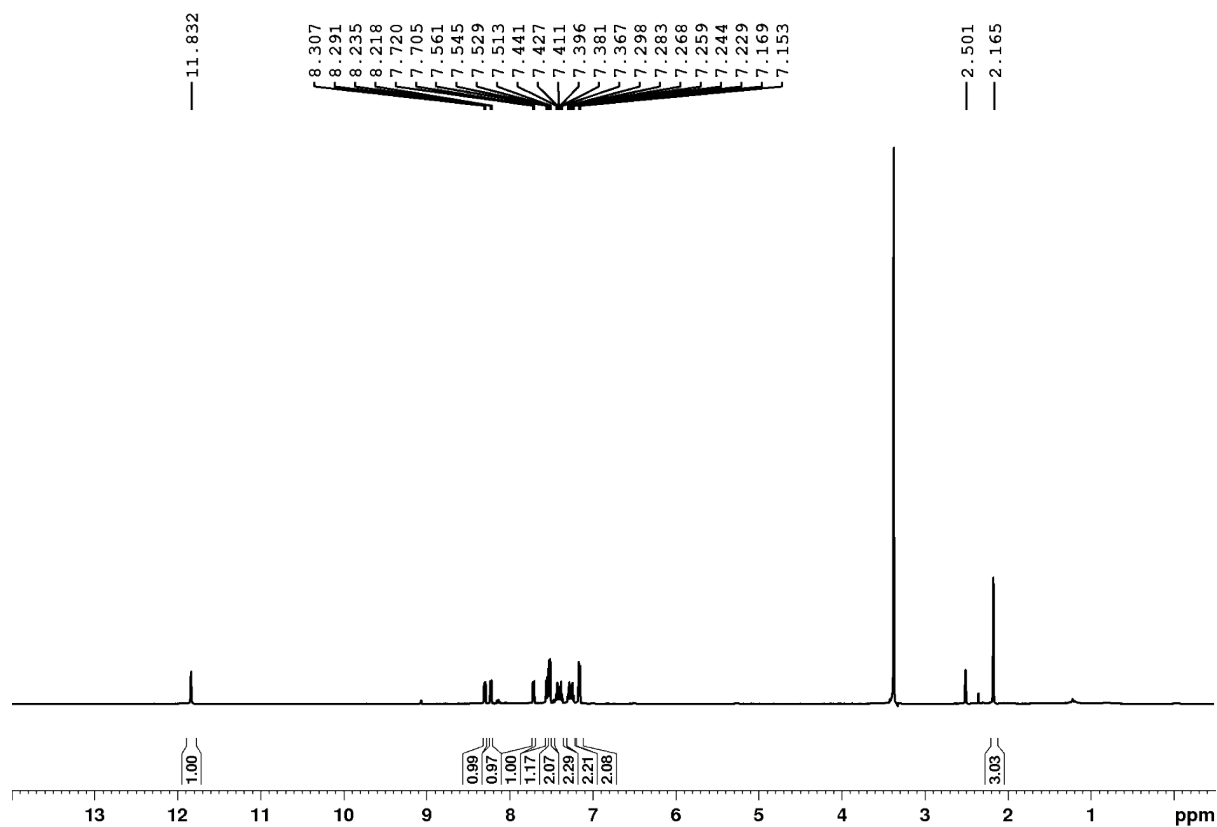


$^1\text{H NMR}$ (500 MHz,

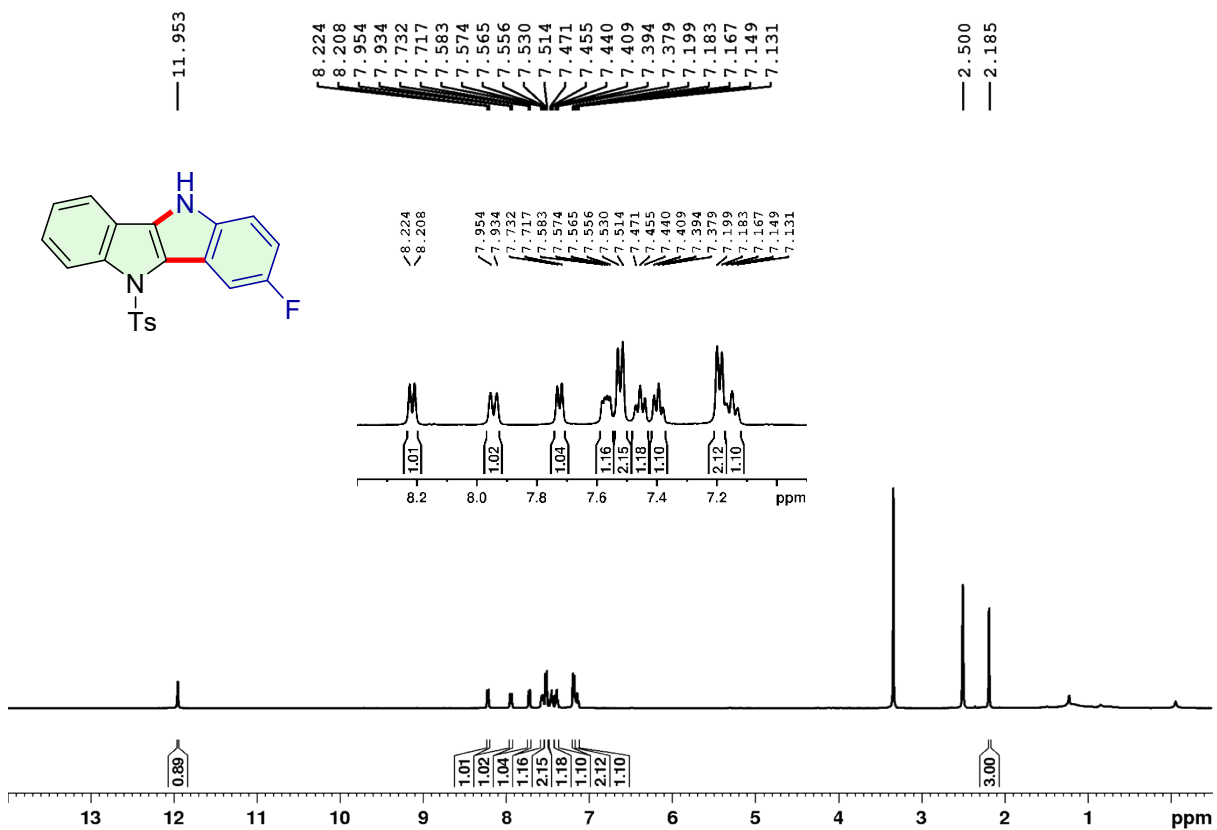
$\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125



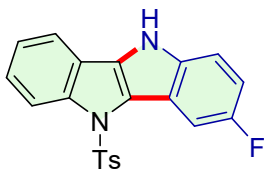
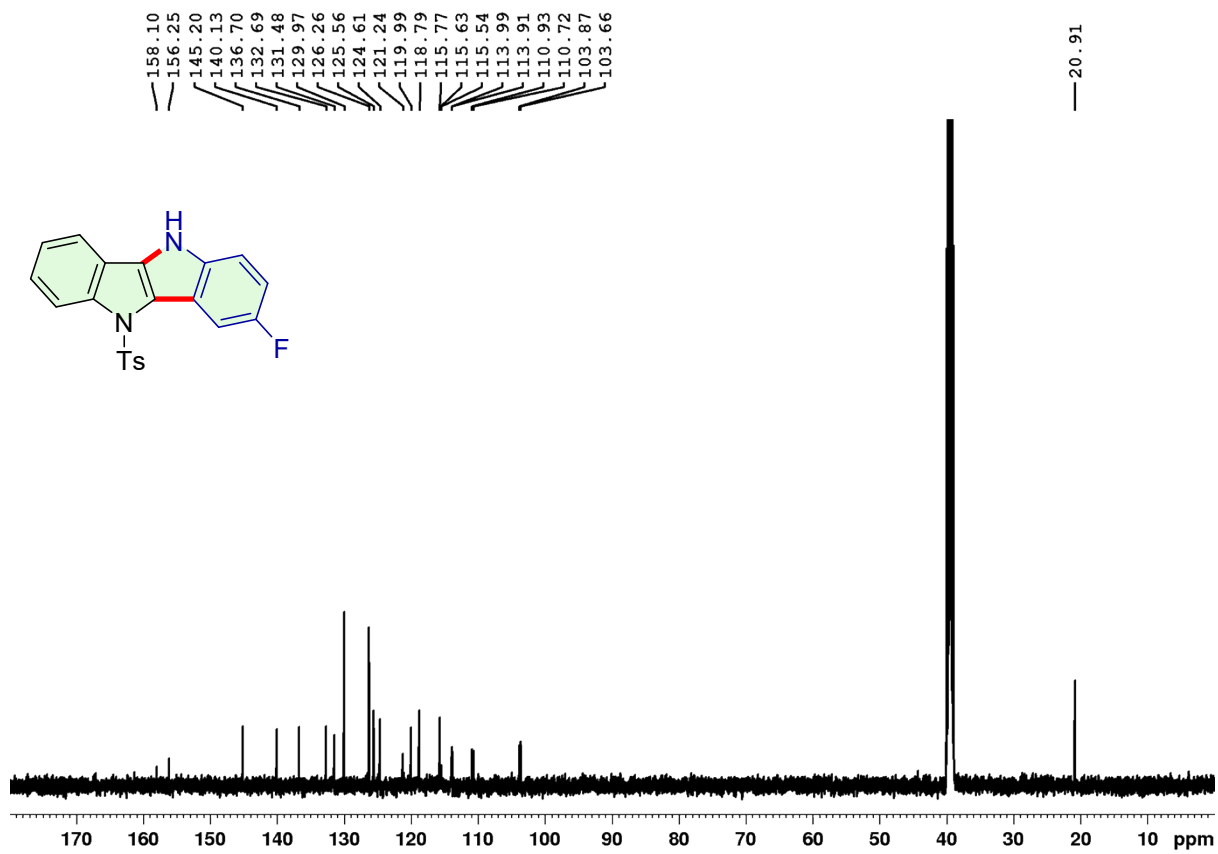
MHz, DMSO-*d*₆) Spectra of **5i**

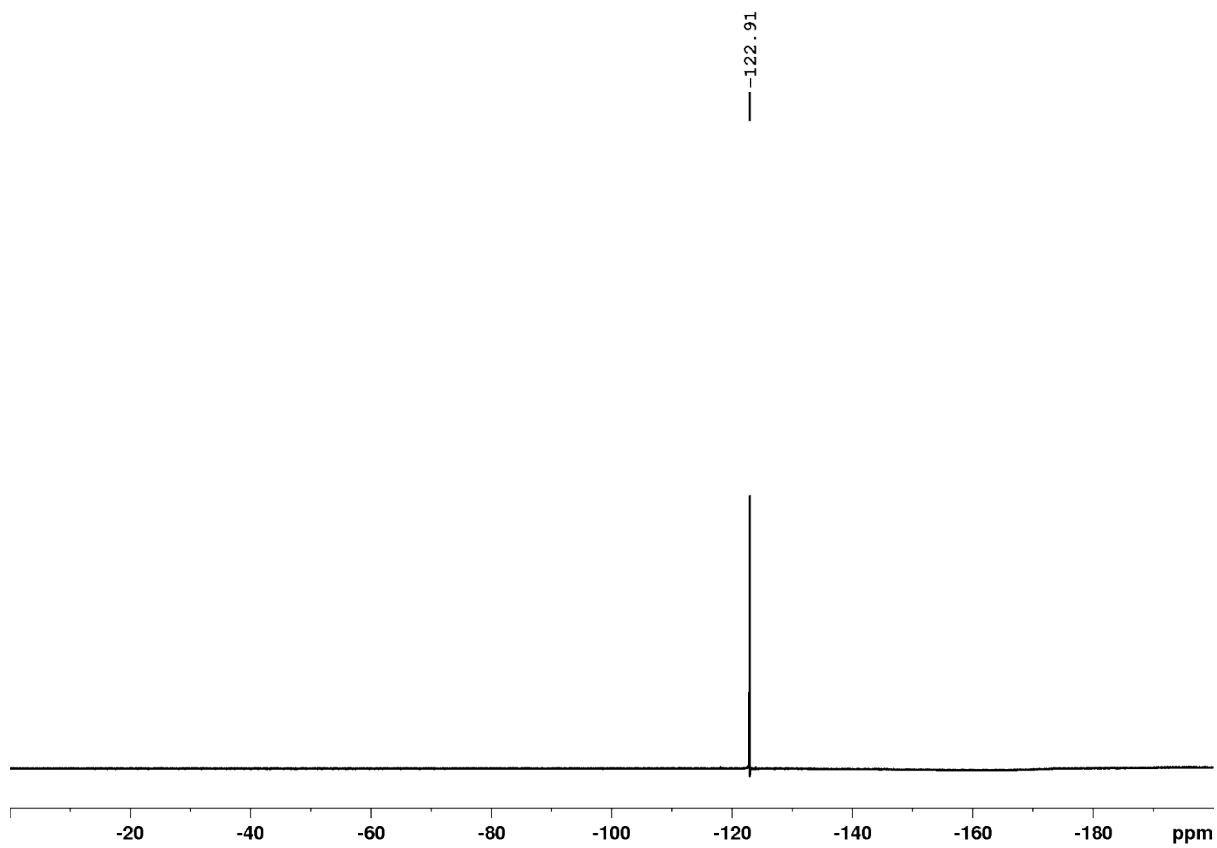


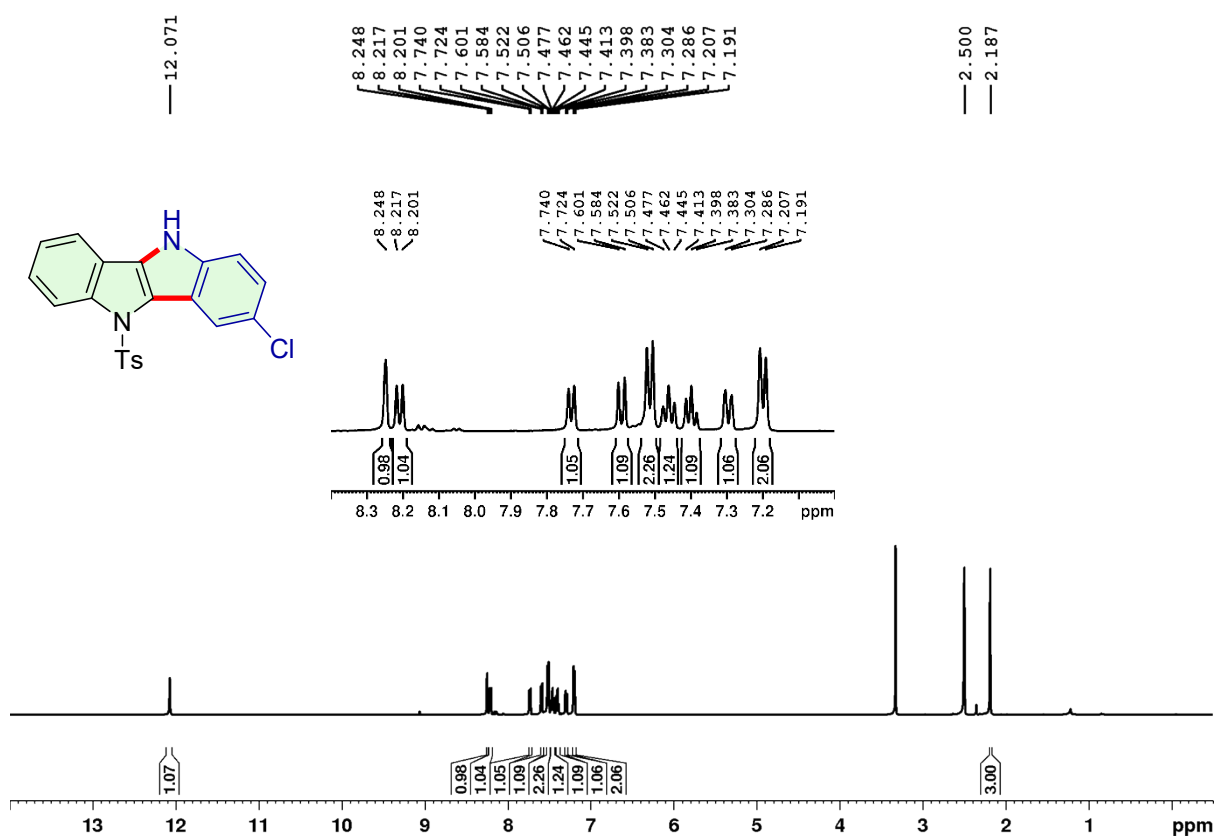
^1H NMR (500 MHz, $\text{DMSO-}d_6$), $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$), ^{19}F (470 MHz, $\text{DMSO-}d_6$)



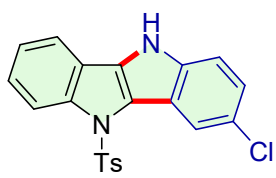
Spectra of **5j**

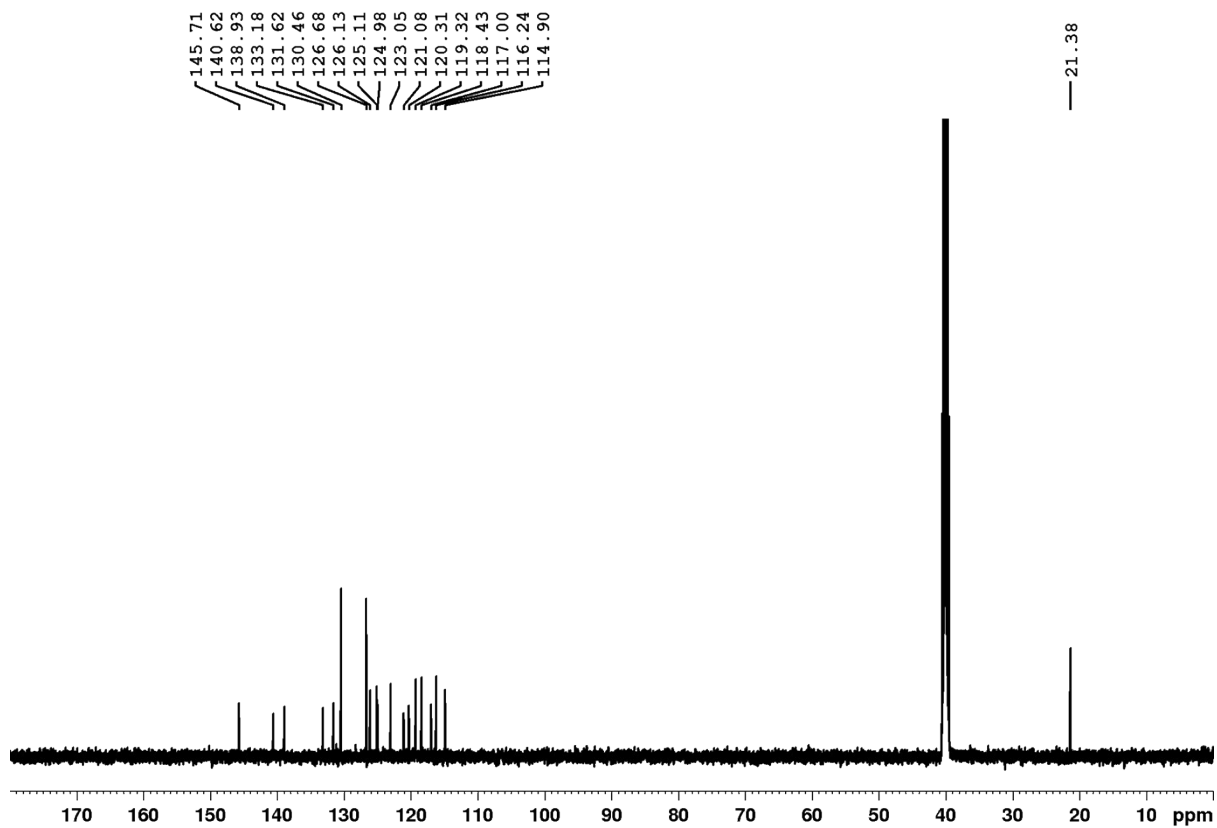




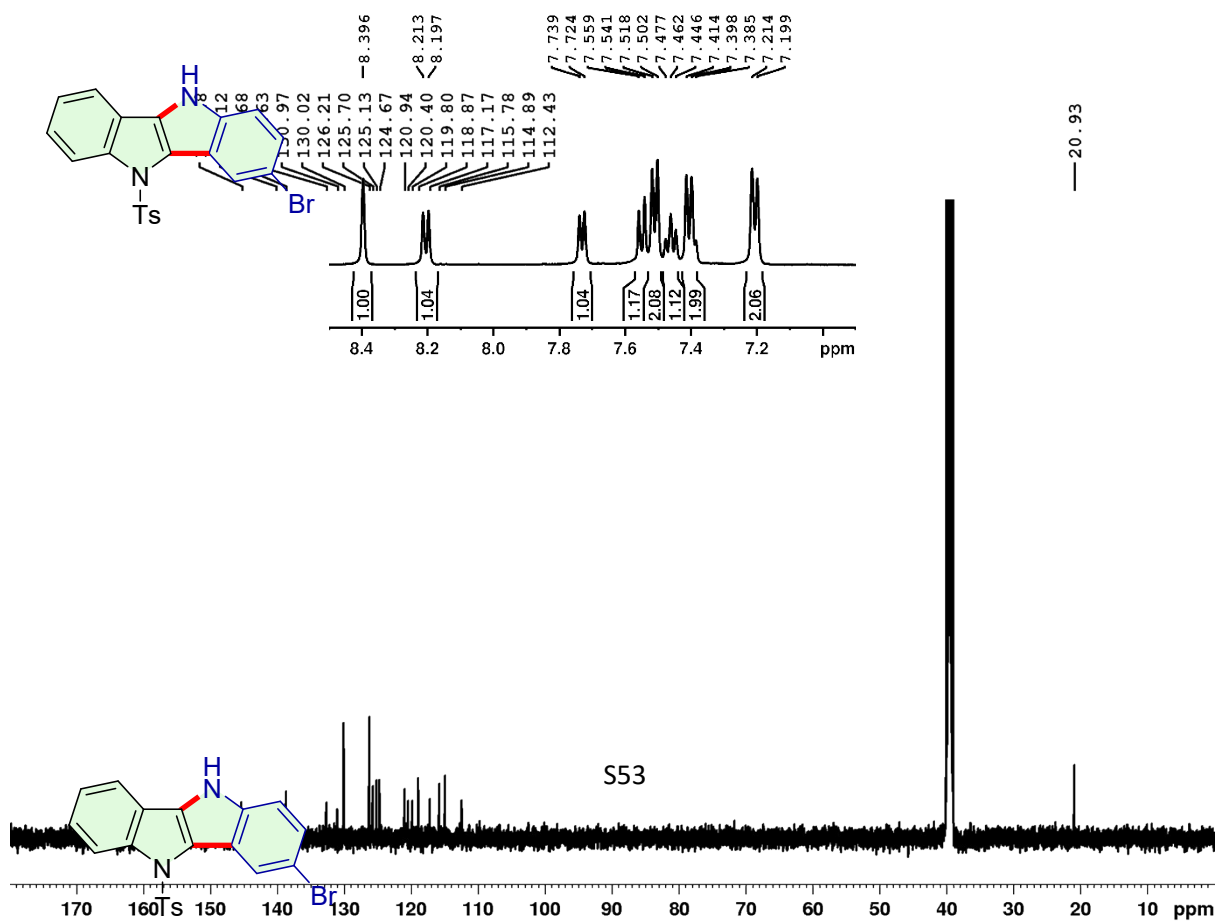


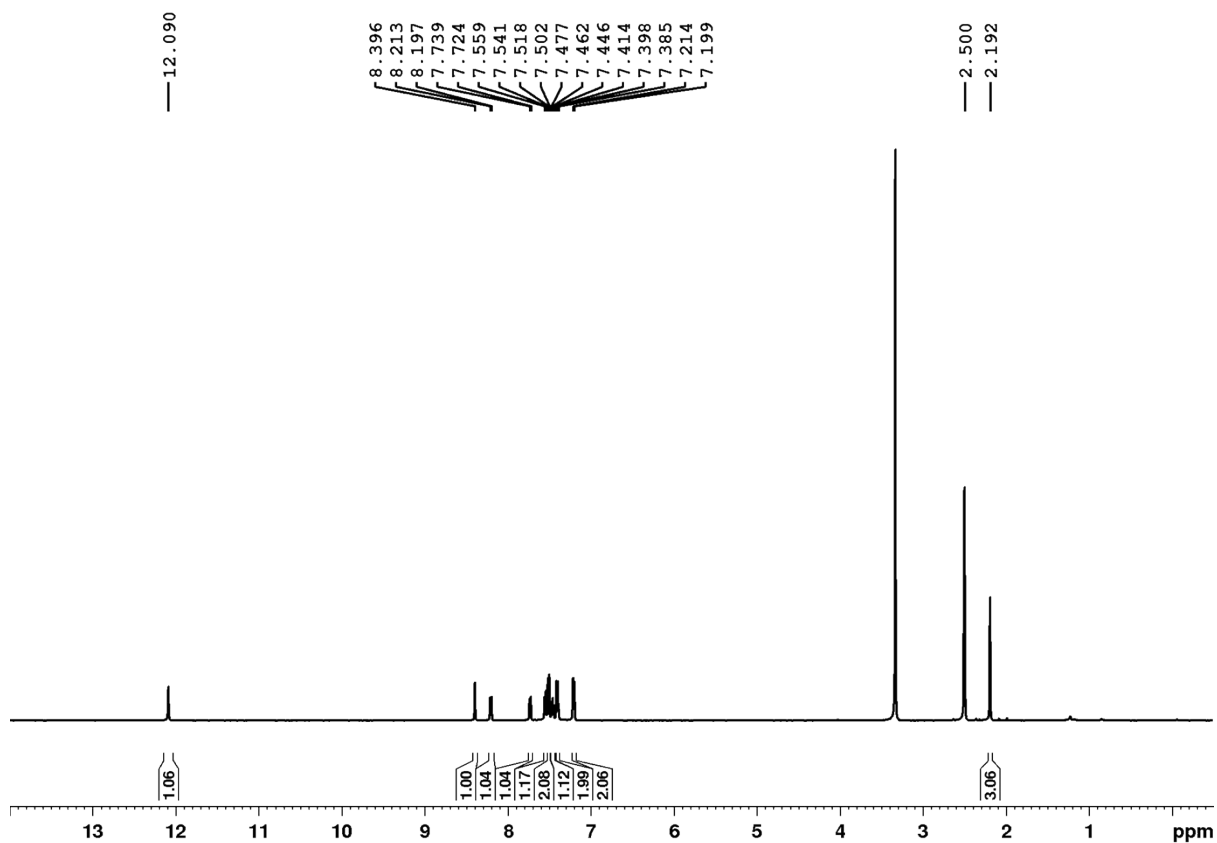
¹H NMR (500 MHz, DMSO-*d*₆) & ¹³C{¹H} (125 MHz, DMSO-*d*₆) Spectra of **5k**



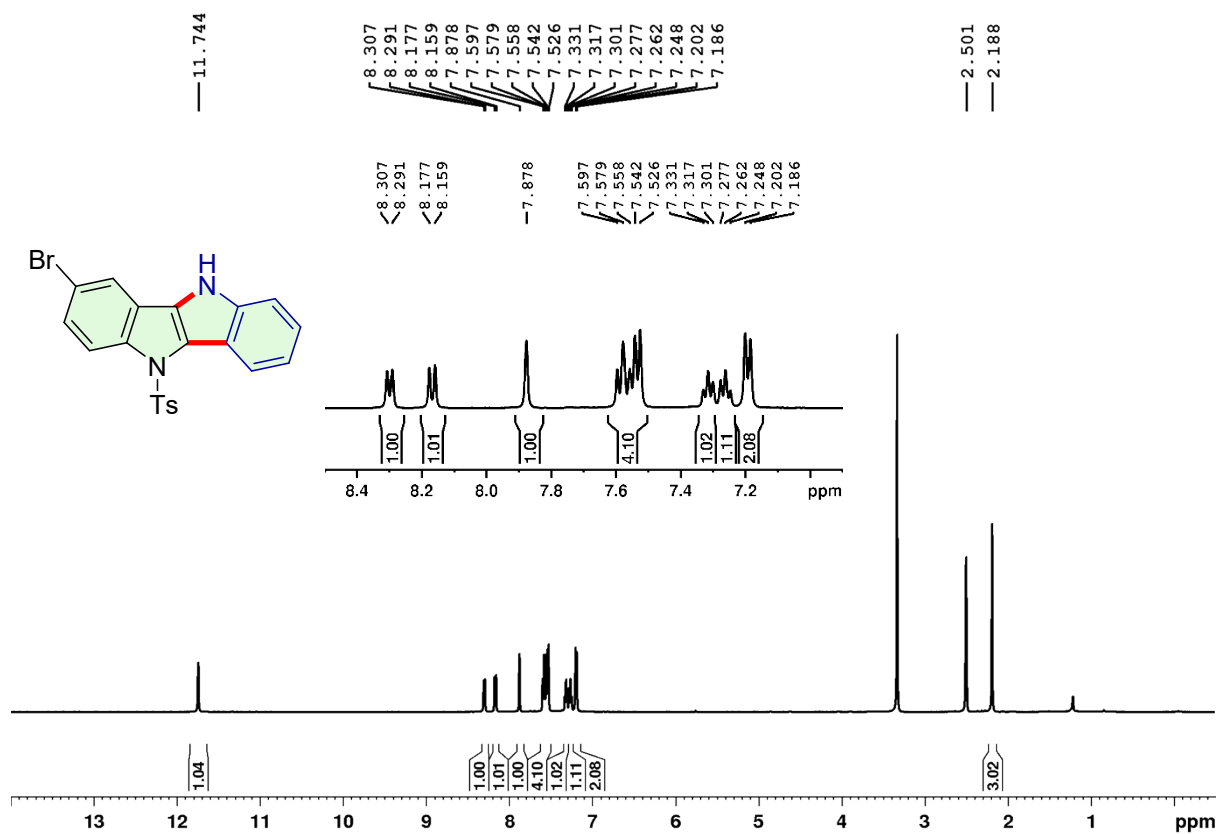


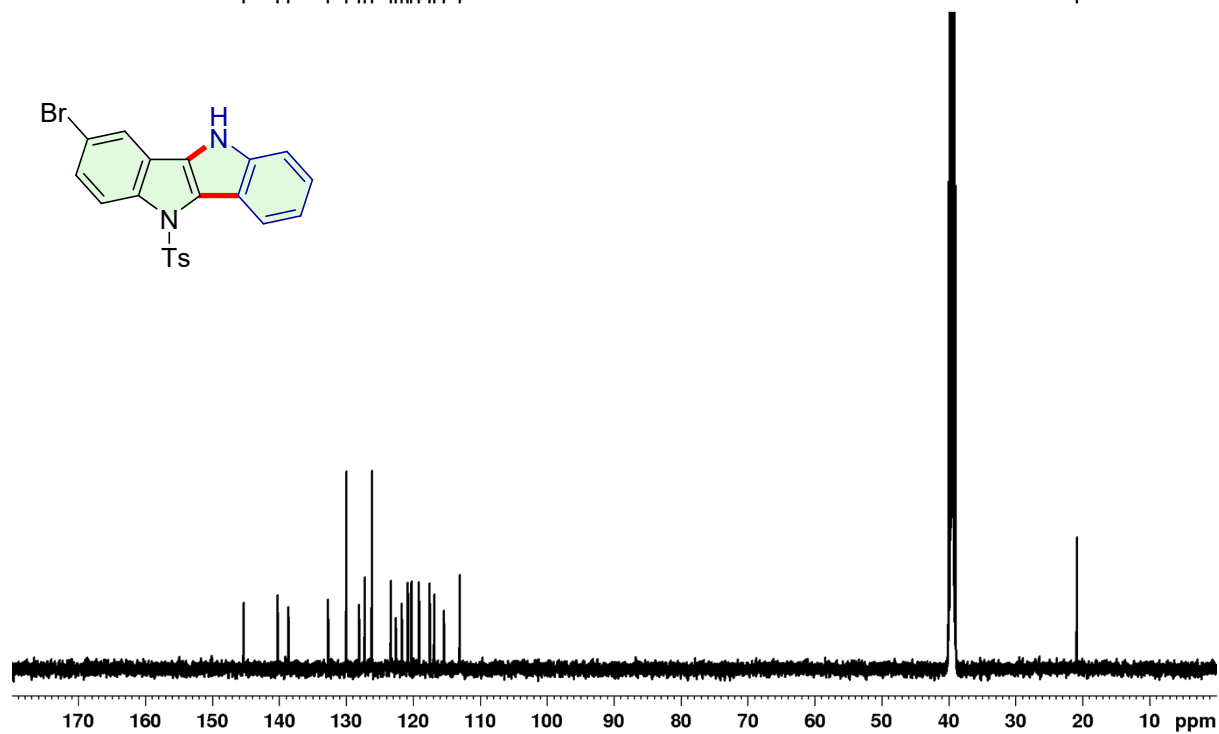
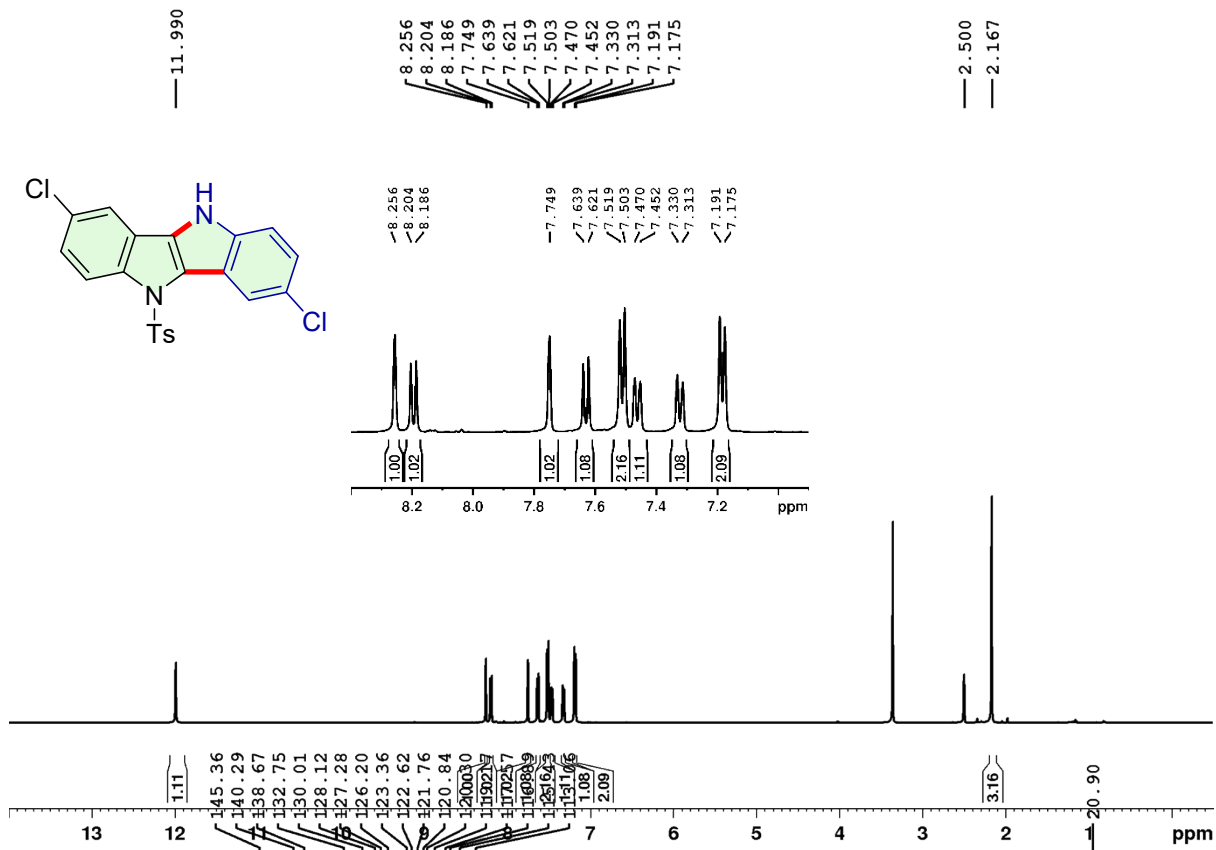
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **51**





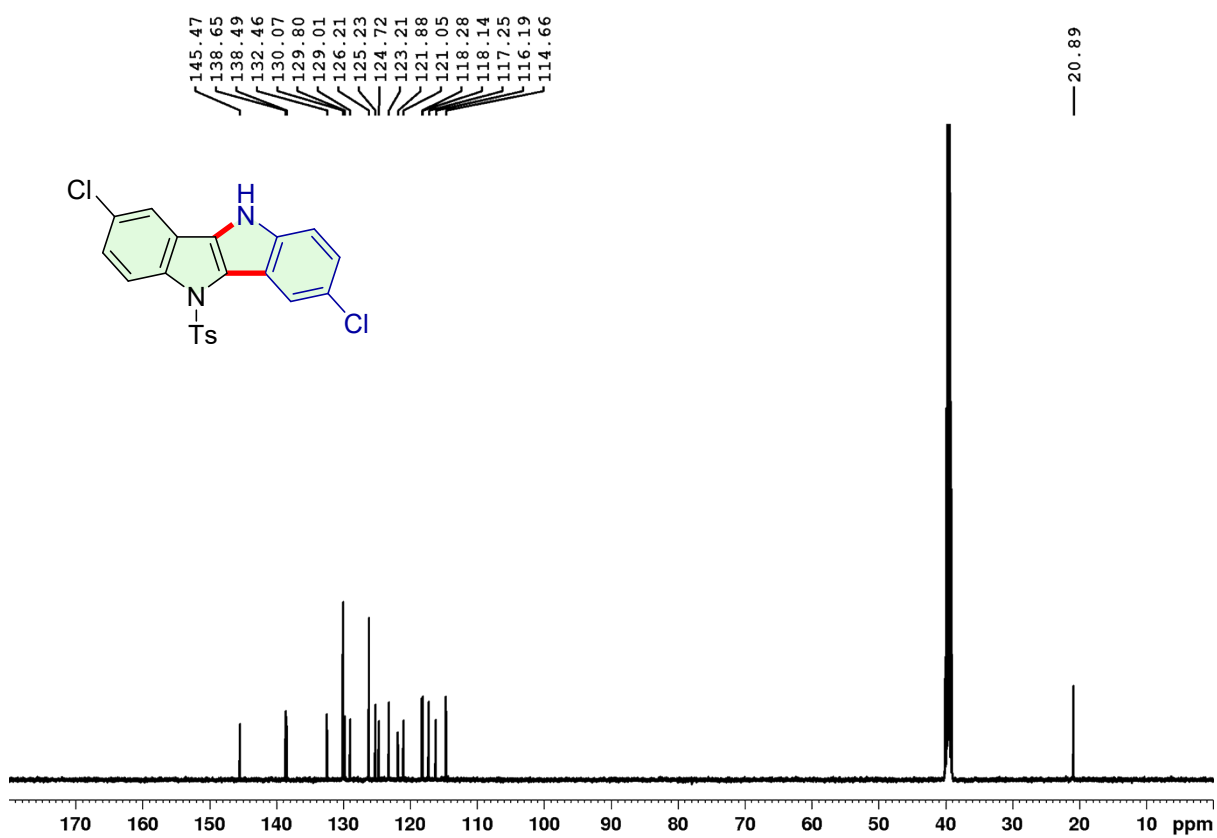
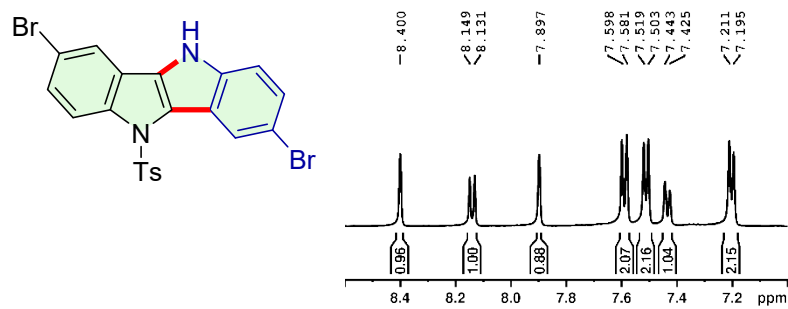
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5m**

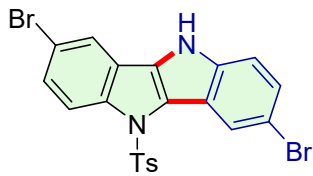
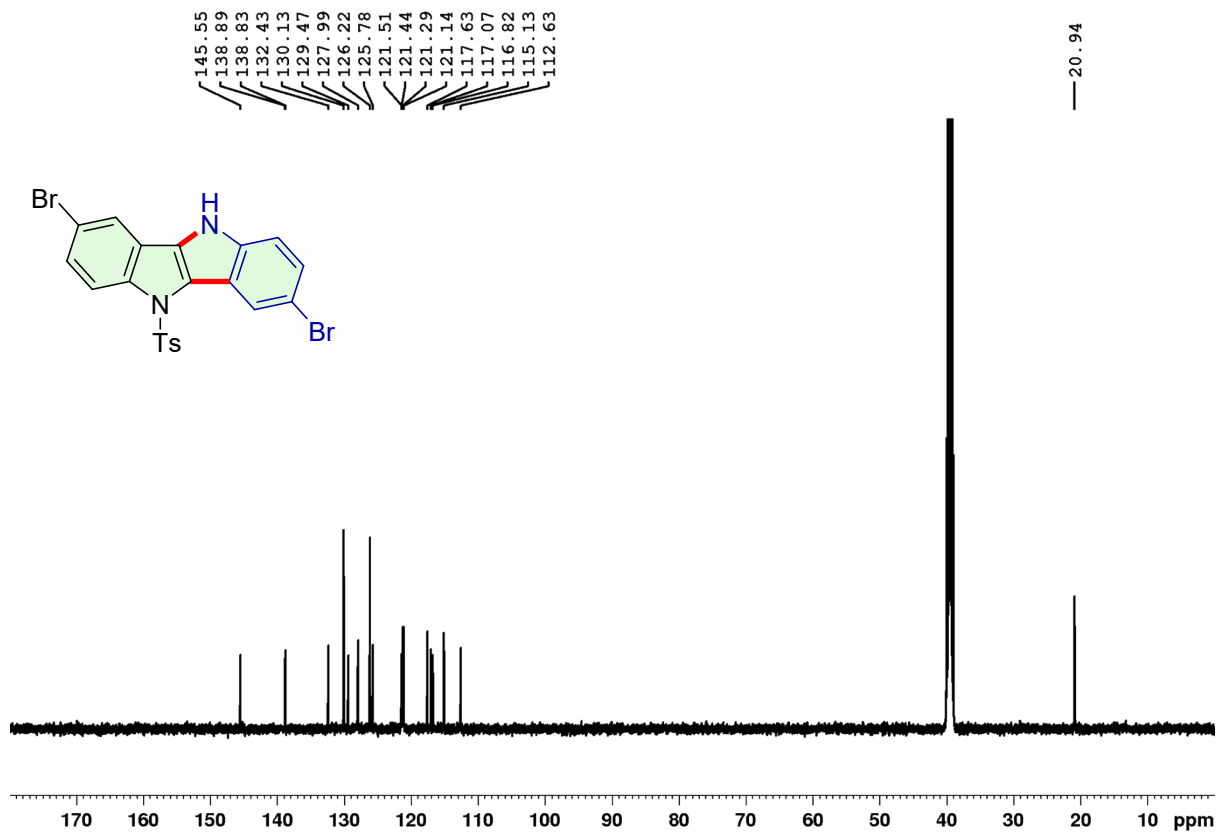
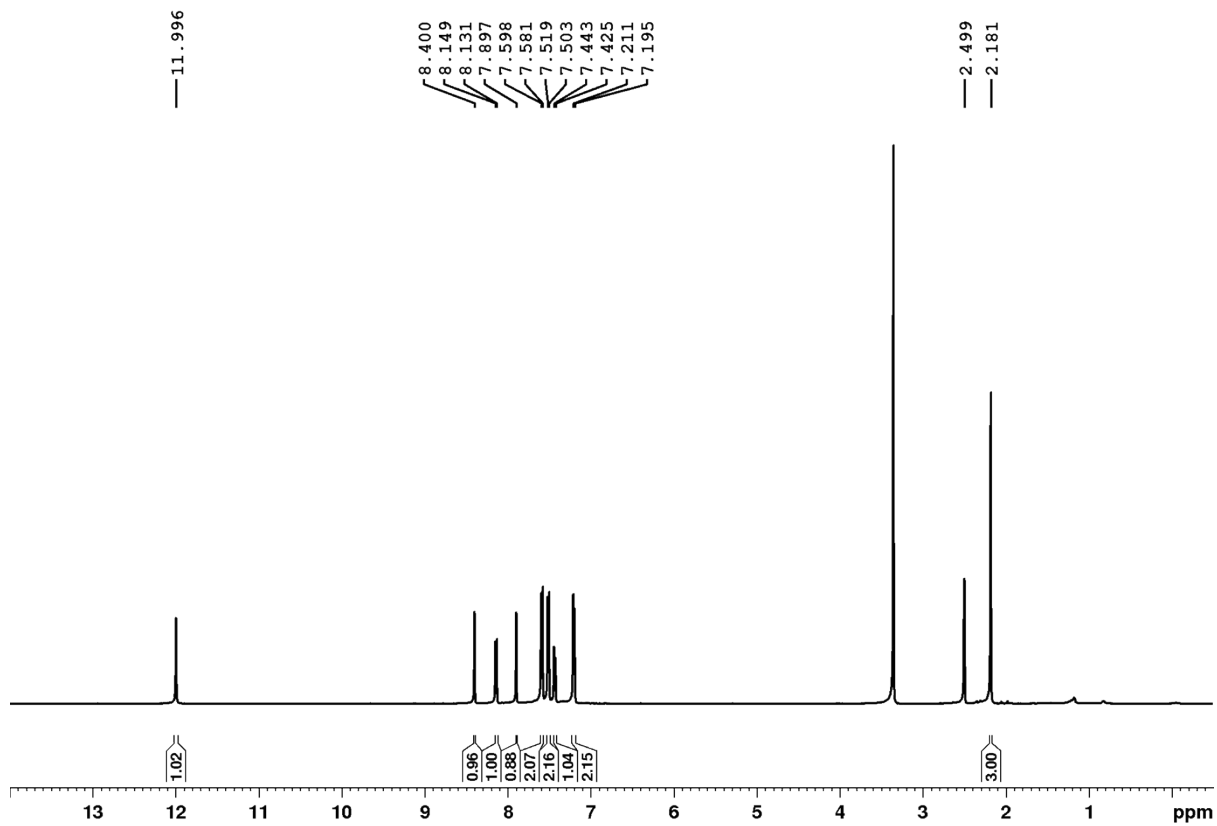


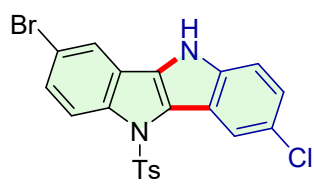
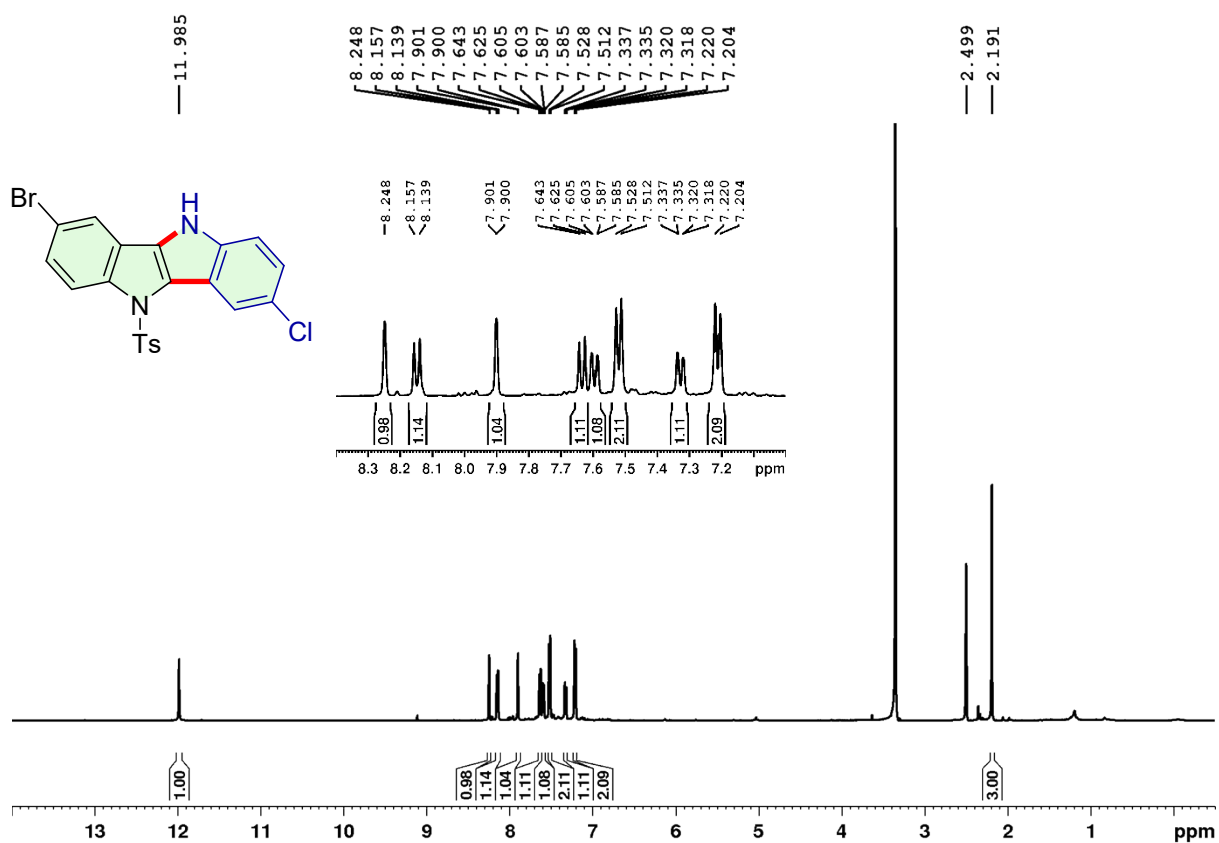


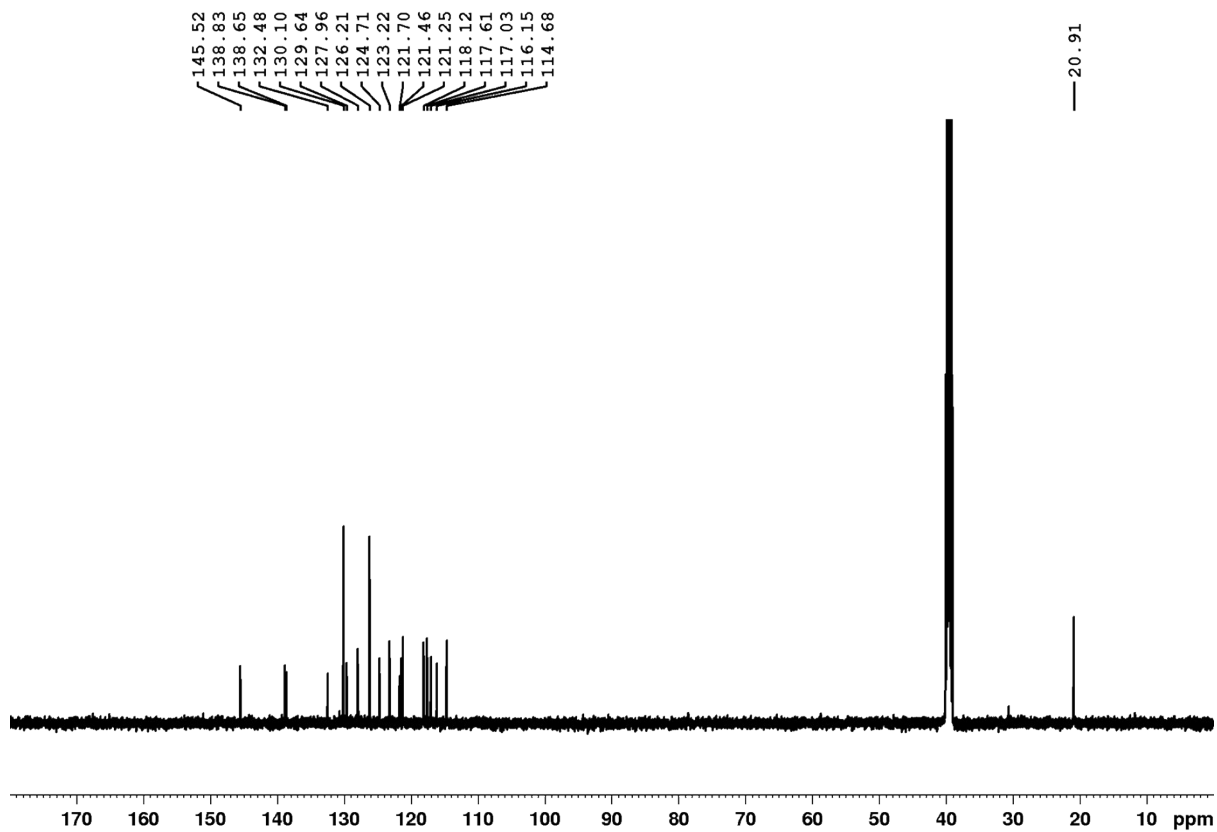
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of 5n

^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5o**

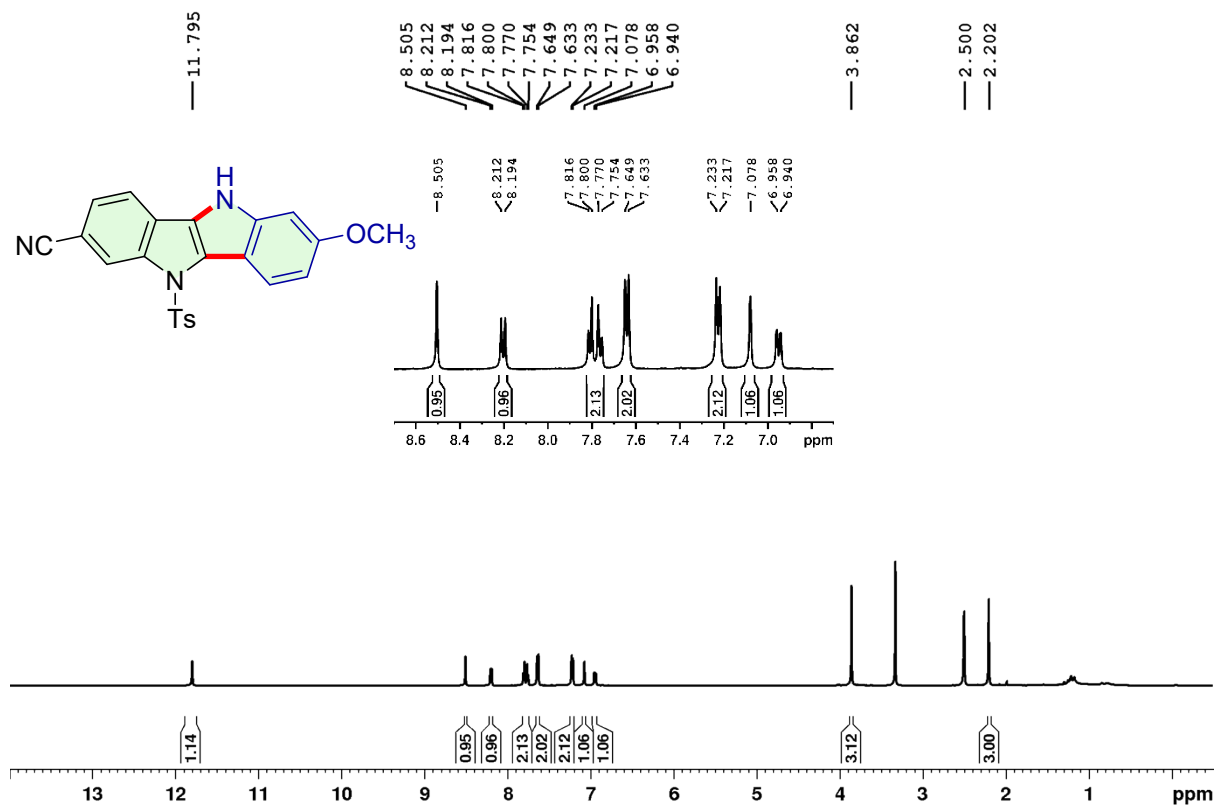


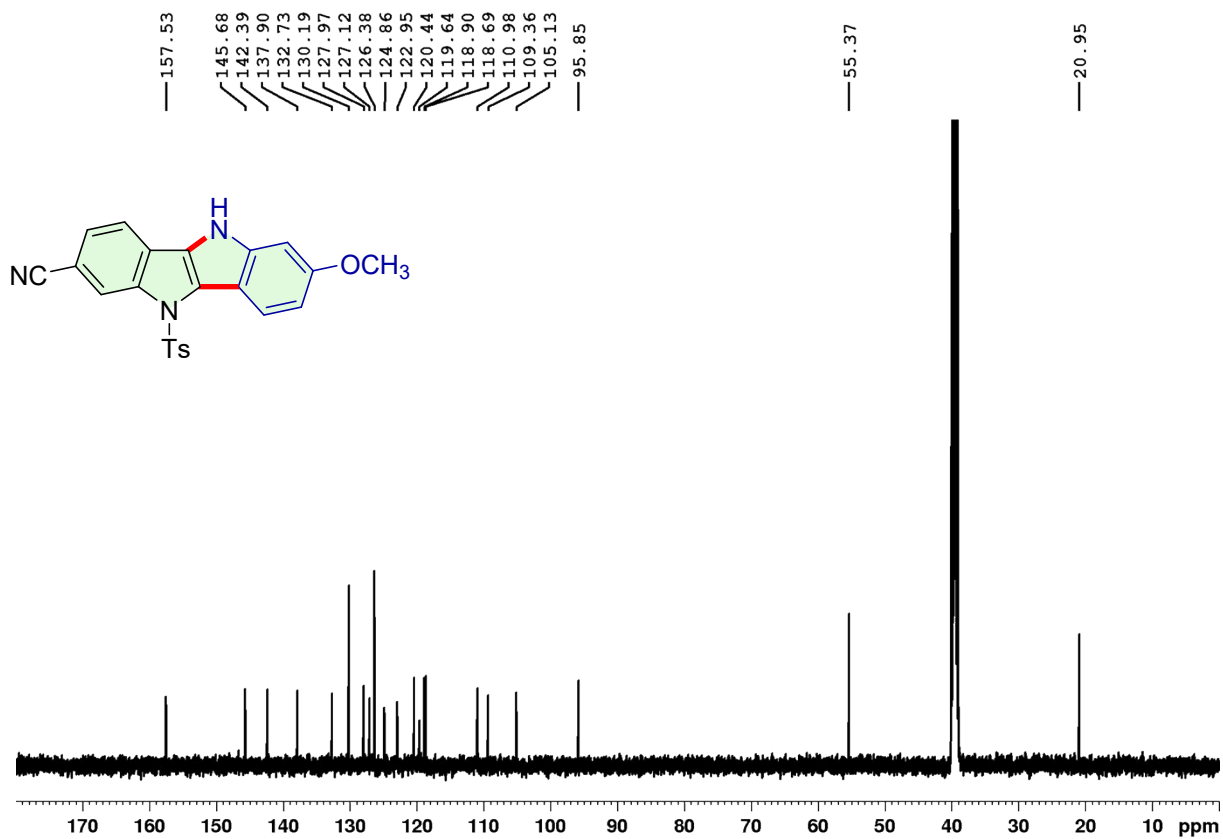




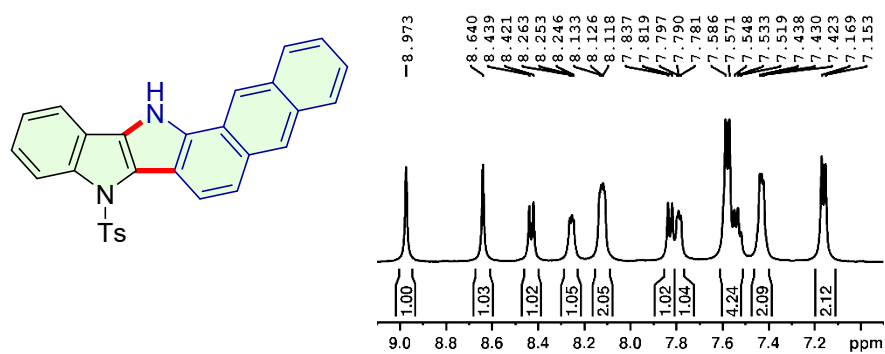


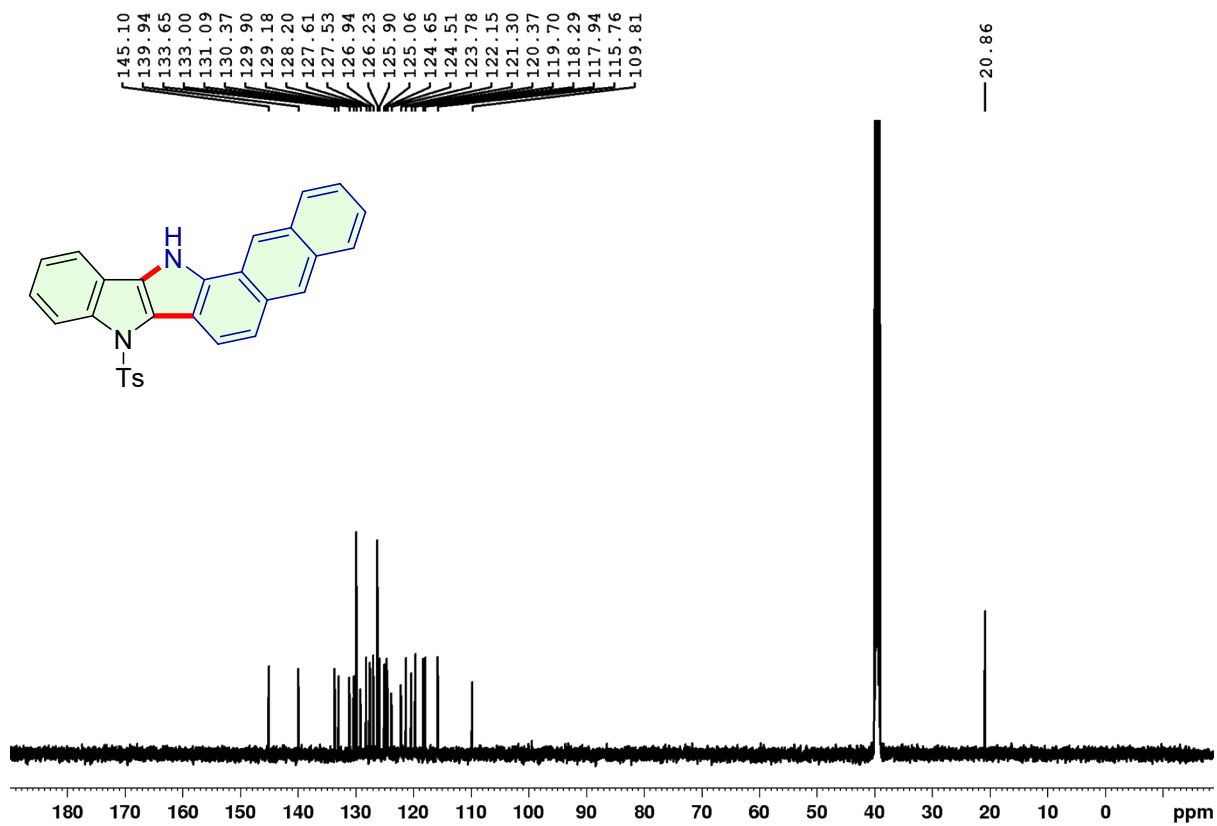
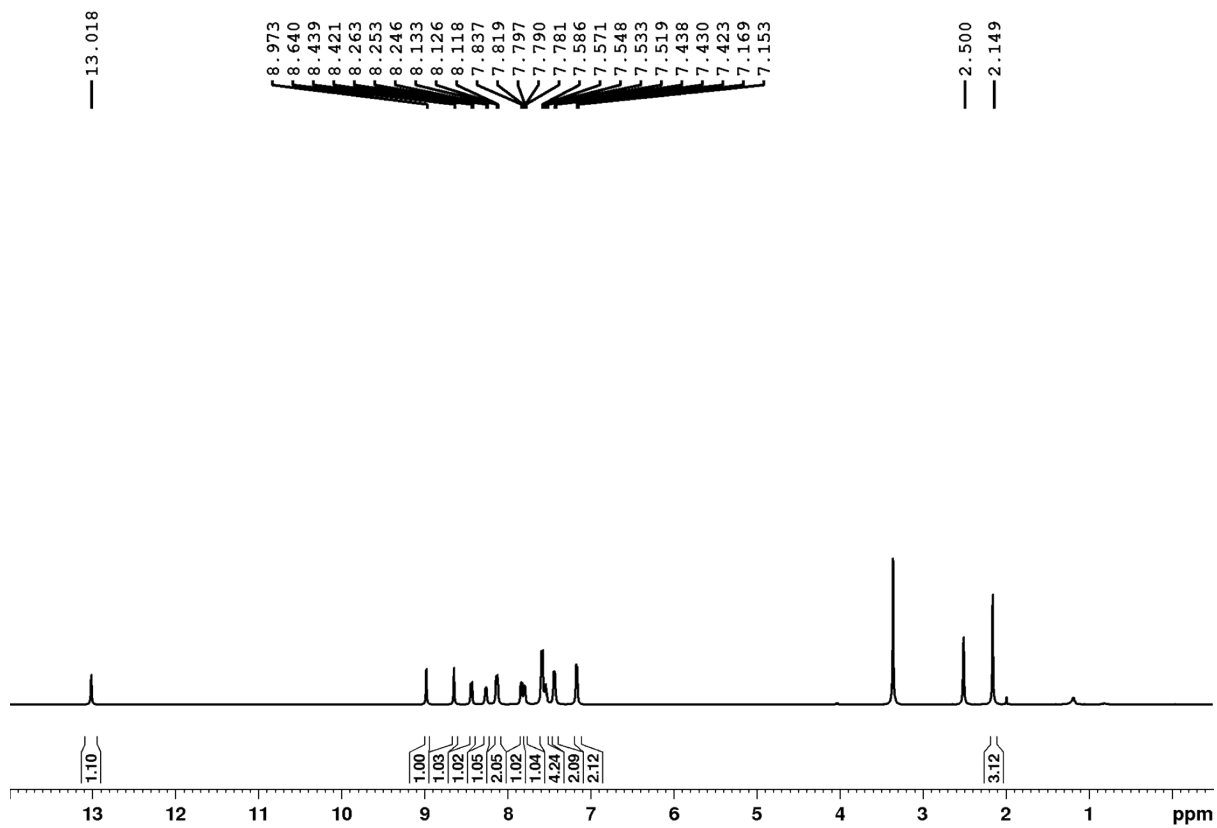
^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **5q**



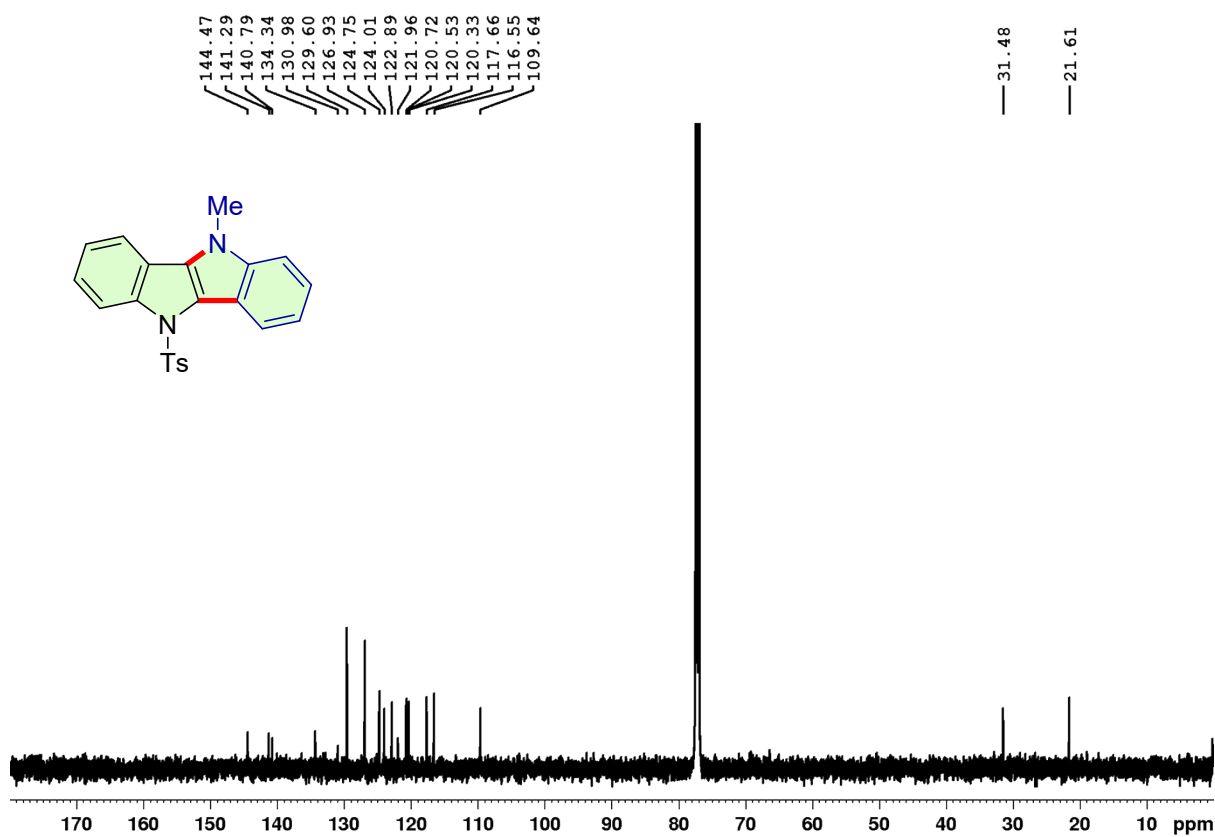
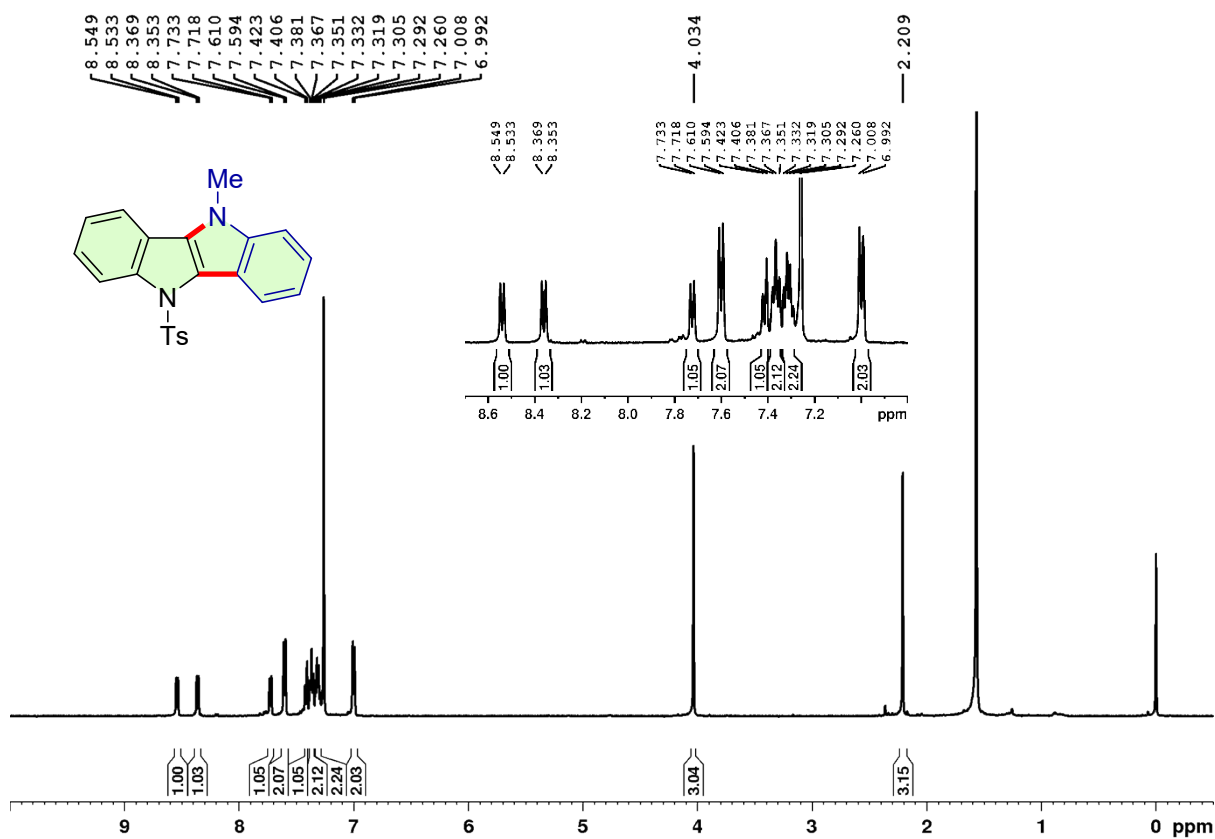


^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of 7





^1H NMR (500 MHz, CDCl_3) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3) Spectra of **9**



^1H NMR (500 MHz, $\text{DMSO-}d_6$) & $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, $\text{DMSO-}d_6$) Spectra of **10**

