Supporting information

$In(OTf)_3$-Catalyzed Formal (4 + 3) Cycloaddition Reactions of 3-Benzylideneindoline-2-thiones with 2-Indolylmethanols

Xue-Long Wang, Yi Yang and Yan Jiang*

Key Laboratory of Green Chemistry of Sichuan Institutes of Higher Education, College of Chemistry and Environmental Engineering, Sichuan University of Science & Engineering, Zigong 643000, China

E-mail: jiangyan199@126.com

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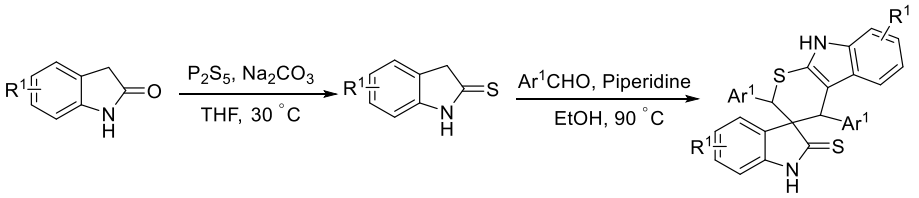
General Information

All starting materials and solvents were of the highest commercially available grade and used without further purification. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Silica gel column chromatography was performed using the silica gel of particle size 200-300 mesh. ^{1}H NMR spectra were recorded on 600 MHz in $CDCl_3$ or DMSO-d_6 and ^{13}C NMR spectra were recorded on 150 MHz in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ = 7.26 ppm or DMSO-d_6, δ = 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.16 ppm or DMSO-d_6, δ = 39.52 ppm). High-resolution mass spectra were obtained on waters G2-XS-TOF MS.

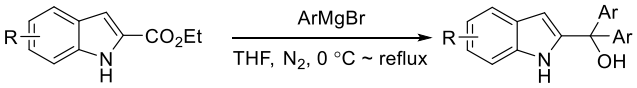
General Procedure for the Preparation of 3-Benzylideneindoline-2-thiones 1[1]



A 100 mL round bottom flask was charged with P_2S_5 (10 mmol, 2.22 g), Na_2CO_3 (10 mmol, 1.06 g) and anhydrous THF (20 mL). The suspension was stirred at 0 °C for 30 min. Then indolin-2-one (5 mmol) was dissolved in 10 mL THF and added dropwise. The mixture was allowed to reaction at 30 °C overnight. The reaction mixture was poured into stirred ice-cold water and the solid was precipitated, filtered, dried to give pure indoline-2-thione.

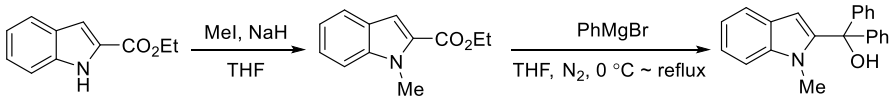
A reaction mixture of indoline-2-thione (2 mmol), aromatic aldehyde (2 mmol) and piperidine (2 drops) in ethanol (6 mL) was stirred in an oil bath at 90 °C for 3-5 h. Upon completion (as determined by TLC analysis), if the product precipitated, the residue was filtered, dried to give 3-benzylideneindoline-2-thione **1**, otherwise the solvent was removed under vacuum and the precipitate was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give 3-benzylideneindoline-2-thione **1**. 3-Benzylideneindoline-2-thione **1** is known to exist as an unsymmetrical dimer.

General Procedure for the Preparation of 2-Indolylmethanols 2a, 2c-g[2]



ArMgBr (20 mL, 20 mmol) (1 M in THF) was added dropwise to the solution of indole-2-carboxylate (5 mmol) in THF (20 mL) at 0 ºC under nitrogen atmosphere. The resulting mixture was warmed to room temperature and stirred at 70 °C in an oil bath under nitrogen atmosphere until the reaction was complete. After the completion of the reaction (monitored by TLC), the mixture was quenched with saturated NH_4Cl and extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 8:1) to give 2-indolylmethanols **2**.

General Procedure for the Preparation of 2-Indolylmethanol 2b

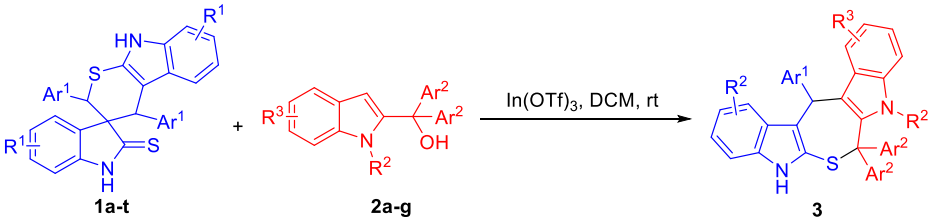


NaH (0.48 g, 12 mmol) (60% in mineral oil) was added in portions to a solution of ethyl 1*H*-indole-2-carboxylate (1.89 g, 10 mmol) in THF (30 mL) at 0 ºC under nitrogen atmosphere. The resulting reaction mixture was stirred at 0 ºC for 15 min under nitrogen atmosphere. MeI (0.62 mL, 10 mmol) was then added dropwise to the reaction mixture dropwise. The resulting mixture was warmed to room temperature and stirred until the reaction was complete. Upon completion (as determined by TLC analysis), the mixture was quenched with saturated NH_4Cl and extracted with EtOAc (3 × 30 mL). The combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 15:1) to ethyl 1-methyl-1*H*-indole-2-carboxylate.

PhMgBr (20 mL, 20 mmol) (1 M in THF) was added dropwise to the solution of ethyl 1-methyl-1*H*-indole-2-carboxylate (1.02 g, 5 mmol) in THF (20 mL) at 0 ºC under nitrogen atmosphere. The resulting mixture was warmed to room temperature and stirred at 70 °C in an oil bath under nitrogen atmosphere until the reaction was complete. After the completion of the reaction (monitored by TLC), the mixture was quenched with saturated NH_4Cl and extracted with EtOAc (3 × 15 mL). The

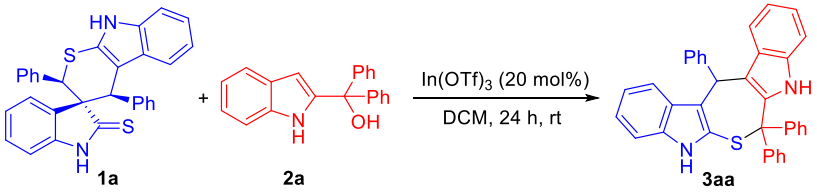
combined organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give 2-indolylmethanols **2b**.

General Procedure for the $In(OTf)_3$-Catalyzed (4 + 3) Cycloaddition Reactions of 3-Benzylideneindoline-2-thiones with 2-Indolylmethanols



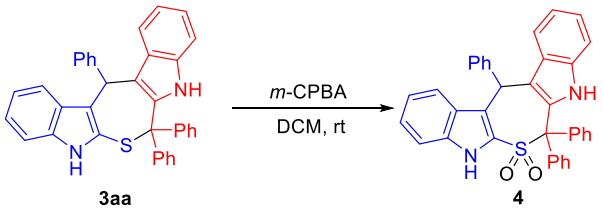
To the mixture of 3-benzylideneindoline-2-thiones **1** (0.1 mmol), 2-indolylmethanols **2** (0.2 mmol) and $In(OTf)_3$ (22.5 mg, 0.04 mmol), 2 mL DCM was added at room temperature. The reaction was stirred at room temperature for 24-72 h. If the product precipitated, the residue was filtered and dried to give the product **3**, otherwise, the resulting mixture was directly purified by silica gel column chromatography to afford the desired compounds **3**.

Gram-Scale Reaction to Synthesize 3aa



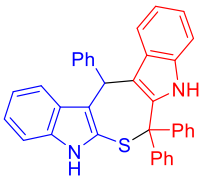
To the mixture of 3-benzylideneindoline-2-thione **1a** (0.712 g, 1.5 mmol) and 2-indolylmethanol **2a** (0.898 g, 3 mmol), DCM (30 mL) was added at room temperature. Under stirring, $In(OTf)_3$ (0.337 g, 0.6 mmol) was added. The reaction was stirred at room temperature for 24 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) to give the desired compound **3aa** as a pink solid (1.25 g, yield: 80%).

Experiment Procedure for the Synthetic Transformation to Sulfone 4

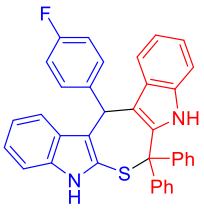


To the solution of **3aa** (0.2 mmol, 103.7 mg) in DCM (2 mL), m-CPBA (0.44 mmol, 89.3 mg, 85 wt %, 2.2 equiv) was added at 0 °C. The resulting mixture was then allowed to warm to ambient temperature. Upon completion (as determined by TLC analysis), the reaction was diluted with DCM, washed with 5% aq. K_2CO_3 and 5% aq. $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo, and the residue was purified by carefully column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give sulfone **4** as a purple solid (39.6 mg, yield: 36%), mp 231.3-232.6 °C.

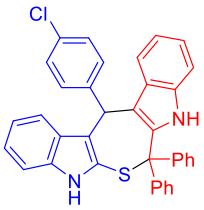
Experiment Data for the compounds 3, 4



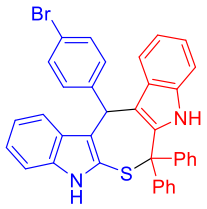
7,7,13-Triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3aa): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1) as a pink solid, mp 129.3-130.7 °C, 95.4 mg, 92% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.04 (s, 1H), 9.92 (s, 1H), 7.95 (dd, J = 6.4, 2.8 Hz, 1H), 7.70 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.38 – 7.31 (m, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.13 (t, J = 7.7 Hz, 2H), 7.11 – 7.02 (m, 4H), 7.01 – 6.97 (m, 2H), 6.97 – 6.91 (m, 1H), 6.10 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.5, 142.9, 142.3, 139.4, 135.6, 134.4, 129.4, 128.9, 128.6, 128.2, 128.0, 127.9, 127.6, 127.4, 127.1, 126.9, 125.6, 124.3, 123.2, 121.6, 121.6, 119.1, 118.9, 118.7, 118.0, 111.4, 111.3, 111.0, 63.0, 38.3. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{36}H_{26}N_2SNa$, 541.1709; Found, 541.1713.



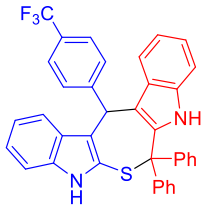
13-(4-Fluorophenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ba): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 258.2-259.7 ℃, 101.2 mg, 94% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.06 (s, 1H), 9.94 (s, 1H), 7.96 (dt, J = 7.0, 3.4 Hz, 1H), 7.69 (dd, J = 8.7, 5.7 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.36 – 7.31 (m, 2H), 7.28 (d, J = 8.1 Hz, 1H), 7.18 – 7.11 (m, 4H), 7.11 – 7.01 (m, 5H), 7.01 – 6.93 (m, 3H), 6.11 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.4 (d, J = 241.6 Hz), 142.8, 142.6 (d, J = 3.0 Hz), 142.2, 139.4, 135.6, 134.4, 129.3, 129.2, 129.1, 128.9, 128.6, 128.1, 128.1, 127.4, 127.1, 126.8, 124.3, 123.0, 121.7, 121.6, 119.0 (d, J = 22.7 Hz), 118.8, 118.0, 114.6 (d, J = 21.1 Hz), 114.5, 111.3, 111.0, 63.0, 37.4. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{36}H_{25}FN_2SNa$, 559.1615; Found, 559.1616.



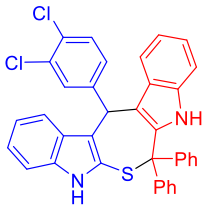
13-(4-Chlorophenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ca): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 184.2-186.1 ℃, 97.5 mg, 88% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.09 (s, 1H), 9.98 (s, 1H), 8.00 – 7.94 (m, 1H), 7.65 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 7.19 – 7.09 (m, 5H), 7.08 – 7.05 (m, 2H), 7.03 – 6.94 (m, 3H), 6.13 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 145.4, 142.8, 142.2, 139.5, 135.6, 134.4, 130.1, 129.3, 129.3, 128.9, 128.6, 128.0, 128.0, 127.8, 127.4, 127.1, 126.8, 124.4, 122.8, 121.7, 121.7, 119.0, 119.0, 118.9, 118.0, 111.5, 111.0, 110.9, 63.0, 37.4. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{36}H_{25}ClN_2SNa$, 575.1319; Found, 575.1317.



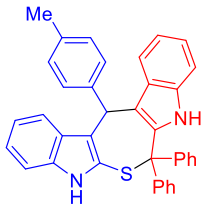
13-(4-Bromophenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3da): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 189.7-191.5 ℃, 100.7 mg, 84% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.09 (s, 1H), 9.98 (s, 1H), 7.96 (dt, J = 6.9, 3.4 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.33 (d, J = 7.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.17 – 7.09 (m, 5H), 7.08 – 7.03 (m, 2H), 7.02 – 6.93 (m, 3H), 6.10 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 145.8, 142.8, 142.2, 139.5, 135.6, 134.4, 130.8, 129.7, 129.3, 128.9, 128.6, 128.1, 128.0, 127.4, 127.1, 126.8, 124.5, 122.7, 121.7, 121.7, 119.0, 118.9, 118.6, 118.0, 111.5, 111.0, 110.8, 63.0, 37.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{36}H_{25}BrN_2SNa$, 619.0814; Found, 619.0812.



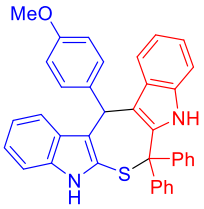
7,7-Diphenyl-13-(4-(trifluoromethyl)phenyl)-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ea): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) as a white solid, mp 193.2-194.9 ℃, 83.0 mg, 71% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.12 (s, 1H), 10.02 (s, 1H), 8.04 – 7.99 (m, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.41 (dd, J = 8.4, 6.1 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.30 (d, J = 8.1 Hz, 1H), 7.19 – 7.10 (m, 5H), 7.10 – 7.04 (m, 2H), 7.04 – 6.99 (m, 2H), 6.99 – 6.95 (m, 1H), 6.23 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.0, 142.7, 142.1, 139.6, 135.6, 134.4, 129.3, 129.0, 128.6, 128.2, 128.1, 128.0, 127.4, 127.1, 126.8, 126.3 (q, J = 31.7 Hz), 124.9 (q, J = 4.5 Hz), 124.7, 124.5 (q, J = 271.8 Hz), 122.4, 121.8, 121.7, 119.1, 119.0, 118.9, 118.0, 111.5, 111.1, 110.4, 63.0, 37.8. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{37}H_{25}F_3N_2SK$, 625.1322; Found, 625.1326.



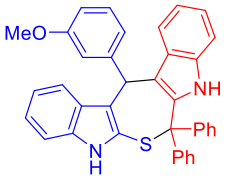
13-(3,4-Dichlorophenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3fa): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a red solid, mp 260.3-262.1 ℃, 56.2 mg, 48% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.15 (s, 1H), 10.04 (s, 1H), 8.02 (dd, J = 6.6, 2.6 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.52 – 7.44 (m, 3H), 7.41 (dd, J = 8.4, 6.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.30 (d, J = 8.1 Hz, 1H), 7.17 – 7.10 (m, 5H), 7.10 – 7.04 (m, 2H), 7.04 – 6.97 (m, 3H), 6.17 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 147.5, 142.6, 142.1, 139.6, 135.6, 134.4, 130.3, 130.2, 129.3, 129.2, 128.8, 128.6, 128.1, 127.9, 127.9, 127.4, 127.1, 126.7, 124.6, 122.2, 121.9, 121.8, 119.1, 119.0, 118.9, 118.0, 111.6, 111.1, 110.3, 63.0, 37.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{24}Cl_2N_2SK$, 625.0669; Found, 625.0665.



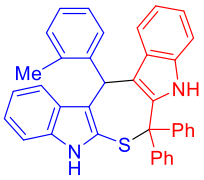
7,7-Diphenyl-13-(p-tolyl)-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ga): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 183.7-185.2 ℃, 102.8 mg, 97% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.03 (s, 1H), 9.91 (s, 1H), 7.96 – 7.90 (m, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 7.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.15 – 7.10 (m, 3H), 7.09 – 7.03 (m, 2H), 7.03 – 6.97 (m, 4H), 6.95 (dd, J = 11.4, 4.3 Hz, 1H), 6.06 (s, 1H), 2.18 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.5, 142.9, 142.3, 139.3, 135.6, 134.5, 134.4, 129.4, 128.9, 128.6, 128.5, 128.2, 128.0, 127.5, 127.4, 127.1, 126.9, 124.3, 123.4, 121.6, 121.6, 119.2, 118.9, 118.7, 118.0, 111.5, 111.4, 111.0, 63.0, 37.9, 20.6. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{37}H_{28}N_2SNa$, 555.1865; Found, 555.1868.



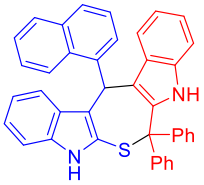
13-(4-Methoxyphenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ha): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale violet solid, mp 248.3-249.6 ℃, 97.5 mg, 89% yield. ^{1}H NMR (600 MHz, DMSO) δ 11.01 (s, 1H), 9.89 (s, 1H), 7.92 (dd, J = 6.1, 3.1 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.33 (d, J = 7.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.13 (t, J = 7.7 Hz, 2H), 7.11 – 7.01 (m, 3H), 7.00 – 6.92 (m, 3H), 6.78 (d, J = 8.8 Hz, 2H), 6.03 (s, 1H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.2, 142.9, 142.3, 139.2, 138.7, 135.6, 134.4, 129.4, 128.9, 128.6, 128.5, 128.2, 128.0, 127.4, 127.1, 126.9, 124.1, 123.4, 121.6, 121.5, 119.2, 118.8, 118.7, 118.0, 113.3, 111.7, 111.4, 111.0, 63.0, 54.9, 37.5. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{37}H_{28}N_2OSNa$, 571.1815; Found, 571.1819.



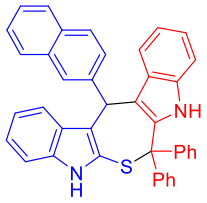
13-(3-Methoxyphenyl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ia): Reaction for 24 h. The product precipitated from the reaction mixture. The solid was filtered and dried to gain the desired product as a purple solid, mp 248.1-249.8 ℃, 90.7 mg, 83% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.07 (s, 1H), 9.93 (s, 1H), 7.94 (dd, J = 6.2, 3.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.27 (d, J = 8.0 Hz, 1H), 7.18 – 7.12 (m, 5H), 7.11 – 7.02 (m, 3H), 7.00 – 6.93 (m, 3H), 6.65 (dd, J = 8.1, 2.2 Hz, 1H), 6.05 (s, 1H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.0, 148.1, 142.8, 142.2, 139.3, 135.6, 134.4, 129.3, 128.9, 128.8, 128.6, 128.2, 128.1, 127.4, 127.1, 126.9, 124.3, 122.9, 121.6, 121.6, 120.1, 119.2, 118.9, 118.7, 118.0, 113.9, 111.4, 111.4, 111.0, 110.4, 63.0, 54.8, 38.4. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{37}H_{28}N_2OSNa$, 571.1815; Found, 571.1819.



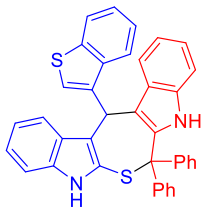
7,7-Diphenyl-13-(o-tolyl)-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ja): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale yellow solid, mp 190.2-192.1 ℃, 96.1 mg, 90% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.93 (s, 1H), 9.85 (s, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.93 – 7.83 (m, 1H), 7.58 – 7.34 (m, 6H), 7.27 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.09 – 6.98 (m, 9H), 6.95 (qd, J = 7.0, 3.6 Hz, 3H), 6.23 (s, 1H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.4, 142.9, 142.3, 139.0, 135.5, 135.3, 134.4, 130.0, 129.4, 129.3, 129.0, 128.7, 128.0, 127.6, 127.1, 126.9, 126.5, 125.7, 125.1, 124.9, 122.2, 121.6, 121.5, 118.9, 118.8, 118.5, 118.4, 112.0, 111.4, 110.9, 63.3, 35.0, 21.1. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{37}H_{28}N_2SNa$, 555.1865; Found, 555.1873.



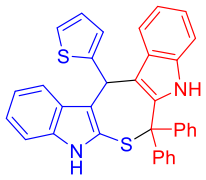
13-(Naphthalen-1-yl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ka): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 205.1-206.3 ℃, 102.3 mg, 90% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.95 (s, 1H), 9.90 (s, 1H), 9.11 (d, J = 8.6 Hz, 1H), 8.44 – 8.35 (m, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.49 – 7.41 (m, 5H), 7.38 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.1 Hz, 1H), 7.13 – 7.02 (m, 5H), 7.02 – 6.94 (m, 3H), 6.94 – 6.90 (m, 1H), 6.88 (s, 1H), 6.85 – 6.81 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 142.9, 142.3, 141.7, 139.3, 135.6, 134.4, 133.5, 130.9, 129.3, 129.1, 128.7, 128.7, 128.1, 127.9, 127.2, 127.0, 126.7, 126.6, 126.3, 125.6, 125.4, 125.2, 125.0, 124.3, 122.6, 121.6, 121.5, 119.0, 118.7, 118.7, 118.6, 112.3, 111.5, 110.9, 63.4, 34.4. HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ Calcd for $C_{40}H_{28}N_2SNa$, 591.1865; Found, 591.1868.



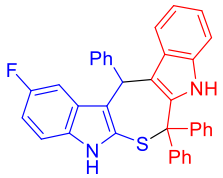
13-(Naphthalen-2-yl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3la): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 261.5-263.1 ℃, 107.1 mg, 94% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.08 (s, 1H), 10.01 (s, 1H), 8.13 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.76 (t, J = 8.2 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.46 – 7.35 (m, 5H), 7.31 (d, J = 8.1 Hz, 1H), 7.19 (d, J = 7.7 Hz, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.09 (dd, J = 17.3, 7.7 Hz, 2H), 7.07 – 6.97 (m, 3H), 6.93 (t, J = 7.5 Hz, 1H), 6.30 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.9, 142.9, 142.3, 139.5, 135.7, 134.5, 132.8, 131.6, 129.4, 129.0, 128.6, 128.2, 128.1, 127.7, 127.5, 127.4, 127.3, 127.1, 126.9, 125.9, 125.2, 124.9, 124.5, 122.9, 121.7, 121.6, 119.1, 119.0, 118.8, 118.1, 111.5, 111.1, 111.0, 63.1, 38.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{40}H_{28}N_2SNa$, 591.1865; Found, 591.1874.



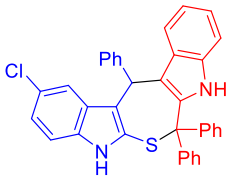
13-(Benzo[b]thiophen-3-yl)-7,7-diphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ma): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale yellow solid, mp 201.5-202.2 ℃, 102.5 mg, 89% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.03 (s, 1H), 9.92 (s, 1H), 8.39 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.79 (s, 1H), 7.53 – 7.39 (m, 6H), 7.34 – 7.24 (m, 3H), 7.08 (t, J = 4.4 Hz, 4H), 7.06 – 7.01 (m, 4H), 6.99 – 6.94 (m, 1H), 6.91 (dd, J = 11.1, 4.0 Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 142.8, 142.2, 140.2, 139.9, 138.9, 138.2, 135.5, 134.4, 129.4, 129.2, 128.7, 128.0, 127.7, 127.3, 127.0, 126.4, 125.2, 123.9, 123.8, 123.8, 123.0, 122.2, 121.6, 121.6, 118.8, 118.6, 118.5, 111.8, 111.5, 111.1, 63.2, 31.9. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{38}H_{26}N_2S_2Na$, 597.1430; Found, 597.1432.



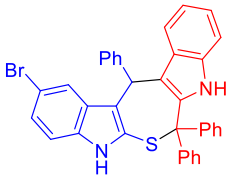
7,7-Diphenyl-13-(thiophen-2-yl)-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3na): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale yellow solid, mp 242.2-243.9 ℃, 93.0 mg, 94% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.12 (s, 1H), 9.96 (s, 1H), 7.88 (dd, J = 6.3, 2.4 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.40 – 7.38 (m, 1H), 7.36 – 7.31 (m, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.19 – 7.10 (m, 6H), 7.10 – 7.05 (m, 3H), 7.04 – 6.96 (m, 3H), 6.82 (dd, J = 5.1, 3.5 Hz, 1H), 6.37 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.0, 142.9, 142.1, 138.5, 135.5, 134.3, 129.4, 128.9, 128.5, 128.0, 127.9, 127.4, 127.1, 126.5, 125.9, 124.7, 123.8, 123.5, 123.0, 121.7, 121.7, 119.1, 118.9, 118.8, 117.8, 112.2, 111.4, 111.1, 62.8, 33.4. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{34}H_{24}N_2S_2Na$, 547.1273; Found, 547.1274.



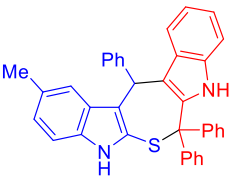
2-Fluoro-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3oa): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 176.7-178.4 ℃, 100.2 mg, 93% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.16 (s, 1H), 9.92 (s, 1H), 7.83 (dd, J = 10.2, 2.2 Hz, 1H), 7.71 (d, J = 7.7 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 7.5 Hz, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.17 – 7.11 (m, 4H), 7.10 – 7.01 (m, 4H), 6.94 (t, J = 7.5 Hz, 1H), 6.83 (td, J = 9.2, 2.4 Hz, 1H), 6.09 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.0 (d, J = 231.0 Hz), 146.4, 142.7, 142.2, 139.1, 134.4, 132.3, 129.3, 128.9, 128.6, 128.2, 128.1, 127.9, 127.6, 127.4, 127.1 (d, J = 10.6 Hz), 127.0, 126.5, 125.6, 123.4 (d, J = 4.5 Hz), 121.6, 119.3, 118.7, 111.9 (d, J = 10.6 Hz), 111.4, 111.4, 109.9 (d, J = 25.7 Hz), 102.9 (d, J = 24.2 Hz), 63.1, 38.2. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{36}H_{25}FN_2SNa$, 559.1615; Found, 559.1621.



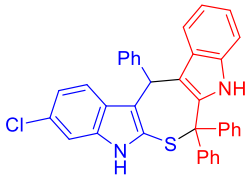
2-Chloro-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3pa): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale violet solid, mp 267.8-269.5 °C, 92.6 mg, 84% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.25 (s, 1H), 9.90 (s, 1H), 8.12 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 7.3 Hz, 2H), 7.26 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.17 – 7.00 (m, 8H), 7.00 – 6.91 (m, 2H), 6.15 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.3, 142.7, 142.1, 139.0, 134.4, 133.9, 129.3, 128.9, 128.6, 128.1, 128.1, 127.9, 127.9, 127.6, 127.4, 127.1, 126.4, 125.6, 123.8, 123.1, 121.6, 119.4, 118.7, 117.4, 112.5, 111.4, 111.2, 63.1, 37.9. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{25}ClN_2SK$, 591.1059; Found, 591.1063.



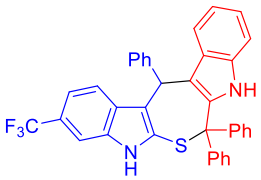
2-Bromo-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3qa): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 256.1-257.8 °C, 107.9 mg, 91% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.27 (s, 1H), 9.91 (s, 1H), 8.28 (d, J = 1.6 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.41 (dd, J = 8.3, 6.3 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.27 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.17 – 7.00 (m, 9H), 6.94 (dd, J = 11.2, 4.0 Hz, 1H), 6.16 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.2, 142.7, 142.1, 139.0, 134.4, 134.2, 129.3, 128.9, 128.6, 128.6, 128.1, 128.1, 127.9, 127.6, 127.4, 127.1, 126.3, 125.6, 124.1, 123.1, 121.6, 120.4, 119.4, 118.7, 112.9, 111.8, 111.4, 111.2, 63.1, 37.8. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{25}BrN_2SK$, 635.0553; Found, 635.0555.



2-Methyl-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ra): Reaction for 24 h. The product precipitated from the reaction mixture. The solid was filtered and dried to gain the desired product as a purple solid, mp 266.7-268.2 ℃, 64.5 mg, 61% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.88 (s, 1H), 9.90 (s, 1H), 7.73 (s, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.16 – 7.10 (m, 4H), 7.10 – 7.02 (m, 3H), 6.99 – 6.93 (m, 2H), 6.81 (dd, J = 8.3, 1.0 Hz, 1H), 6.06 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.5, 142.9, 142.3, 139.4, 134.4, 134.0, 129.4, 128.9, 128.6, 128.2, 128.0, 127.9, 127.6, 127.5, 127.4, 127.1, 127.0, 125.5, 124.2, 123.3, 122.8, 121.6, 119.1, 118.7, 117.5, 111.4, 111.4, 110.8, 63.0, 38.1, 21.3. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{37}H_{28}N_2SK$, 571.1605; Found, 571.1614.

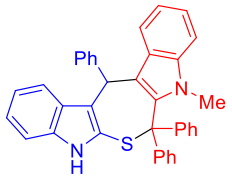


3-Chloro-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3sa): Reaction for 48 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) as a pink solid, mp 236.5-238.1 ℃, 78.8 mg, 71% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.21 (s, 1H), 9.92 (s, 1H), 8.01 (d, J = 8.6 Hz, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.39 – 7.32 (m, 2H), 7.28 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.11 (d, J = 1.8 Hz, 1H), 7.10 – 7.02 (m, 3H), 7.00 (dd, J = 8.6, 1.9 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.11 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.2, 142.6, 142.1, 139.2, 135.8, 134.4, 129.3, 128.9, 128.6, 128.1, 128.0, 127.5, 127.4, 127.1, 126.5, 125.7, 125.6, 123.5, 121.6, 119.6, 119.3, 119.1, 118.8, 111.4, 111.0, 110.4, 63.1, 38.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{25}ClN_2SK$, 591.1059; Found, 591.1060.

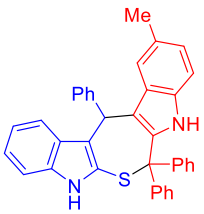


7,7,13-Triphenyl-3-(trifluoromethyl)-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ta): Reaction for 72 h. The partial product precipitated from the reaction mixture. The solid was filtered, dried to give the product 32.1 mg and the residue solution was purified by column chromatography

on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give the desired product 33.2 mg. The product is a pale yellow solid, mp 260.3-262.1 ℃, 65.3 mg, 56% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.58 (s, 1H), 9.96 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.14 (d, J = 4.2 Hz, 4H), 7.11 – 7.03 (m, 3H), 6.99 – 6.94 (m, 1H), 6.20 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.1, 142.6, 142.1, 139.1, 134.5, 134.2, 129.3, 129.1, 129.0, 128.7, 128.4, 128.2, 128.1, 128.0, 127.5, 127.5, 127.2, 125.7, 125.3 (q, J = 271.8 Hz), 123.6, 121.9 (q, J = 30.2 Hz), 121.7, 119.2, 119.1, 118.8, 115.1 (q, J = 3.0 Hz), 111.5, 111.0, 108.1 (q, J = 3.0 Hz), 63.2, 38.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{37}H_{25}F_3N_2SK$, 625.1322; Found, 625.1320.

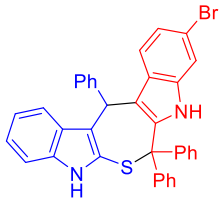


8-Methyl-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ab): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a pale violet solid, mp 152.3-153.9 ℃, 63.7 mg, 60% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.99 – 7.92 (m, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 6.7 Hz, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.26 – 7.15 (m, 7H), 7.13 (t, J = 6.2 Hz, 1H), 7.07 (dd, J = 17.6, 7.5 Hz, 3H), 7.03 – 6.95 (m, 2H), 6.21 (s, 1H), 2.76 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 145.8, 142.4, 140.2, 139.9, 136.0, 135.6, 129.8, 128.8, 128.2, 127.9, 127.8, 127.7, 127.7, 127.4, 127.3, 126.6, 125.5, 124.9, 124.7, 122.2, 121.8, 119.4, 119.2, 118.9, 118.1, 112.7, 111.2, 109.3, 63.0, 37.8, 32.6. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{37}H_{28}N_2SK$, 571.1605; Found, 571.1605.

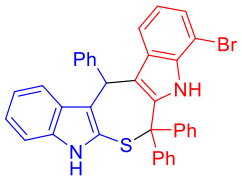


11-Methyl-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ac): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum

ether/ethyl acetate = 5:1) as a white solid, mp 192.3-194.1 ℃, 105.2 mg, 99% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.03 (s, 1H), 9.81 (s, 1H), 7.98 (d, J = 5.7 Hz, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 6.9 Hz, 2H), 7.43 – 7.29 (m, 4H), 7.28 – 7.04 (m, 10H), 7.00 (d, J = 3.3 Hz, 2H), 6.89 (d, J = 7.9 Hz, 1H), 6.09 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.4, 142.9, 142.4, 139.3, 135.6, 132.8, 129.4, 128.9, 128.5, 128.4, 128.0, 127.9, 127.5, 127.3, 127.2, 127.0, 126.9, 125.5, 124.3, 123.5, 123.2, 121.6, 118.9, 118.5, 118.0, 111.2, 111.0, 110.8, 63.0, 38.1, 21.4. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{37}H_{28}N_2SK$, 571.1605; Found, 571.1613.

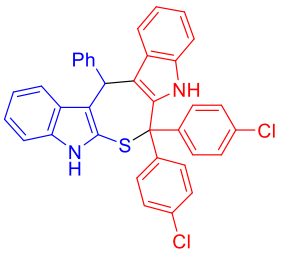


10-Bromo-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ad): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a purple solid, mp 151.6-152.8 ℃, 104.8 mg, 88% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.09 (s, 1H), 10.07 (s, 1H), 7.97 (dd, J = 6.1, 2.7 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.42 (t, J = 7.3 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.19 – 7.13 (m, 4H), 7.13 – 7.03 (m, 4H), 7.03 – 6.95 (m, 1H), 6.11 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.2, 142.6, 141.9, 140.4, 135.6, 135.2, 129.3, 128.8, 128.7, 128.2, 128.0, 127.5, 127.3, 127.2, 126.9, 125.7, 124.2, 122.8, 121.7, 121.6, 121.1, 118.9, 118.1, 114.4, 114.0, 111.8, 111.0, 62.9, 38.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{25}BrN_2SK$, 635.0553; Found, 635.0562.

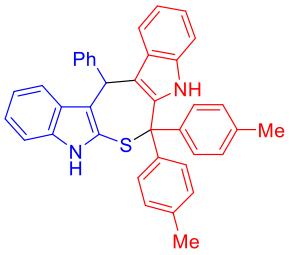


9-Bromo-7,7,13-triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ae): Reaction for 24 h. The product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a white solid, mp 188.6-190.4 ℃, 75.9 mg, 64% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.10 (s, 1H), 10.08 (s, 1H), 7.98 (dd, J = 6.1, 3.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.53 – 7.44 (m, 4H), 7.42 (t, J = 7.3 Hz, 1H), 7.33 (d, J = 7.4 Hz, 2H), 7.21 (t, J = 7.7 Hz, 2H), 7.16 (dt, J = 15.4, 7.8 Hz, 4H), 7.11 – 7.06 (m, 4H), 7.03 – 6.95 (m, 2H), 6.12 (s, 1H). ^{13}C NMR

(151 MHz, DMSO-d_6) δ 146.2, 142.6, 141.9, 140.4, 135.6, 135.2, 129.3, 128.8, 128.7, 128.2, 128.0, 127.5, 127.3, 127.2, 126.9, 125.7, 124.2, 122.8, 121.7, 121.6, 121.1, 118.9, 118.1, 114.4, 114.0, 111.8, 111.0, 62.9, 38.1. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{25}BrN_2SK$, 635.0553; Found, 635.0557.

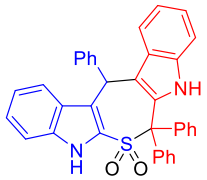


7,7-Bis(4-chlorophenyl)-13-phenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3af): Reaction for 24 h. The product precipitated from the reaction mixture. The solid was filtered and dried to gain the desired product as a light purple solid, mp 261.3-262.7 ℃, 96.9 mg, 82% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.13 (s, 1H), 10.05 (s, 1H), 7.98 (dd, J = 6.4, 2.7 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.57 – 7.53 (m, 3H), 7.34 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.6 Hz, 4H), 7.17 – 7.11 (m, 3H), 7.08 – 7.05 (m, 2H), 7.03 – 7.01 (m, 2H), 6.96 (dd, J = 11.2, 4.0 Hz, 1H), 6.12 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.2, 141.2, 141.1, 138.5, 135.6, 134.5, 132.9, 131.7, 131.1, 130.6, 128.7, 128.1, 128.0, 127.5, 126.8, 125.6, 123.6, 123.3, 121.9, 121.8, 119.2, 119.0, 118.9, 118.1, 111.6, 111.4, 111.0, 61.9, 38.2. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{36}H_{24}Cl_2N_2SK$, 625.0669; Found, 625.0678.



13-Phenyl-7,7-di-p-tolyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole (3ag): Reaction for 24 h. The product precipitated from the reaction mixture. The solid was filtered and dried to gain the desired product as a purple solid, mp 292.5-294.1 ℃, 71.5 mg, 65% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.06 (s, 1H), 9.87 (s, 1H), 7.94 (d, J = 4.4 Hz, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.8 Hz, 1H), 7.34 – 7.16 (m, 7H), 7.14 – 6.89 (m, 10H), 6.07 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 146.6, 140.3, 139.6, 137.2, 136.0, 135.6, 134.3, 129.2, 129.1,

128.8, 128.2, 128.0, 127.9, 127.6, 127.0, 125.5, 124.6, 122.8, 121.5, 121.4, 119.1, 118.8, 118.6, 118.0, 111.4, 111.2, 111.0, 62.5, 38.4, 20.7, 20.5. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{38}H_{30}N_2SK$, 585.1761; Found, 585.1770.



7,7,13-Triphenyl-5,7,8,13-tetrahydrothiepino[2,3-b:6,5-b']diindole 6,6-dioxide (4): The product was obtained by carefully column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) as a purple solid, mp 231.3-232.6 °C, 39.6 mg, 36% yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.90 (s, 1H), 10.03 (s, 1H), 8.15 (s, 1H), 7.67 (s, 4H), 7.55 (s, 3H), 7.40 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 6.8 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.19 (dd, J = 13.9, 6.8 Hz, 3H), 7.16 – 6.99 (m, 8H), 6.94 (t, J = 7.5 Hz, 1H), 6.36 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 144.8, 136.3, 135.6, 135.1, 134.4, 132.1, 131.2, 129.4, 128.9, 128.5, 128.3, 128.2, 127.8, 127.6, 127.5, 125.8, 125.7, 124.9, 122.0, 121.1, 121.0, 120.3, 119.9, 119.1, 112.5, 112.0, 80.8. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{36}H_{26}N_2O_2SNa$, 573.1607; Found, 573.1614.

X-ray Structure Determination

Single Crystal X-ray diffraction data were collected using a Bruker D8 Quest diffractometer (Mo Kα, λ= 0.71073 Å). Indexing was performed using APEX3 (Difference Vectors method). Data integration and reduction were performed using SaintPlus. Absorption correction was performed by multi-scans method implemented in SADABS. Space groups were determined using XPREP implemented in APEX3. Structures were solved using SHELXT (direct methods) and refined using SHELXL-2017 (full-matrix least-squares on F^2) with anisotropic displacement contained in APEX3 program packages. Hydrogen atoms on carbon and nitrogen were calculated in ideal positions with isotropic placement parameters set to 1.2 × U_{eq} of the attached atoms.

Single crystals of **3aa** were obtained by evaporation from hexane/chloroform.

X-ray crystallographic data of compound **3aa** have been deposited in the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/ data_request/cif.) under accession code CCDC 2358829.

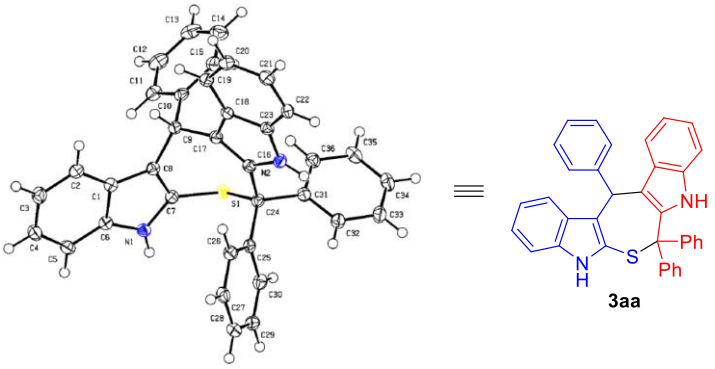


Figure S1. The structure of compound **3** in the crystal. Ellipsoids represent 50% probability levels.

Table 1 Crystal data and structure refinement for 3aa.

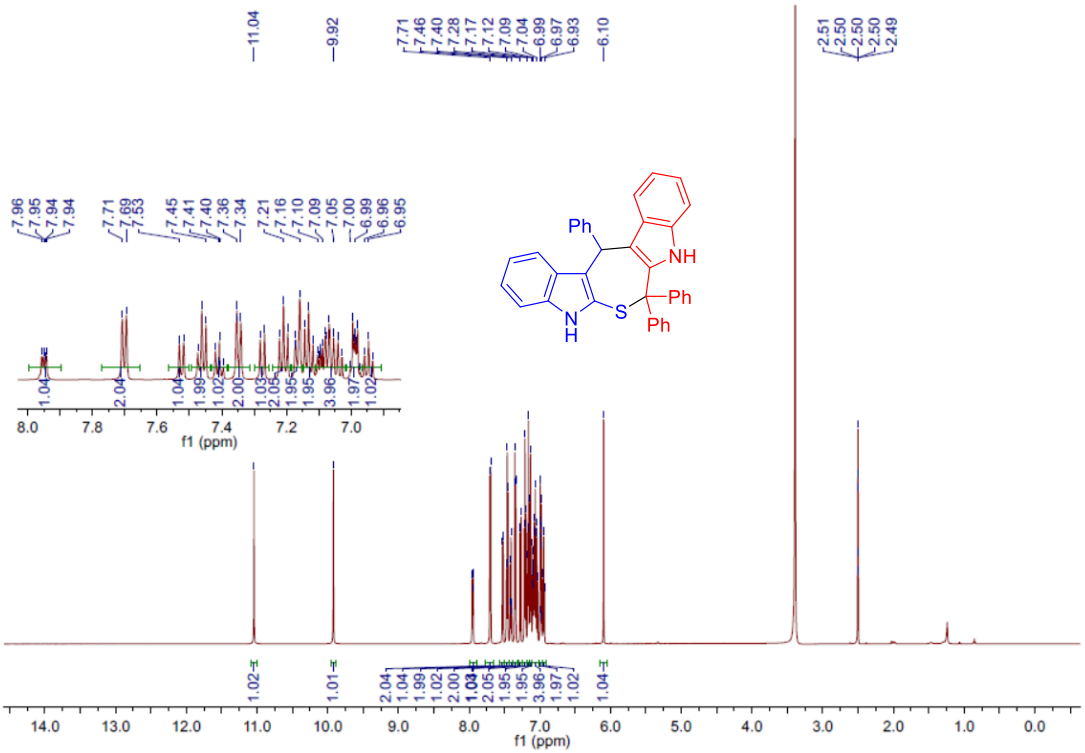
Identification code	**3aa**
Empirical formula	$C_{36}H_{26}N_2S$
Formula weight	518.65
Temperature/K	100.00(16)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.11660(10)
b/Å	13.15070(10)
c/Å	14.17090(10)
α/°	90
β/°	98.7160(10)
γ/°	90
Volume/Å^3	2600.35(3)
Z	4
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	1.318
F(000)	1088.0
Crystal size/mm^3	0.13 × 0.12 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.238 to 148.654
Index ranges	-15 ≤ h ≤ 17, -16 ≤ k ≤ 8, -17 ≤ l ≤ 15
Reflections collected	13984
Independent reflections	5136 [R_{int} = 0.0237, R_{sigma} = 0.0260]
Data/restraints/parameters	5136/0/352
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0999
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.1013
Largest diff. peak/hole / e Å^{-3}	0.63/-0.44

References

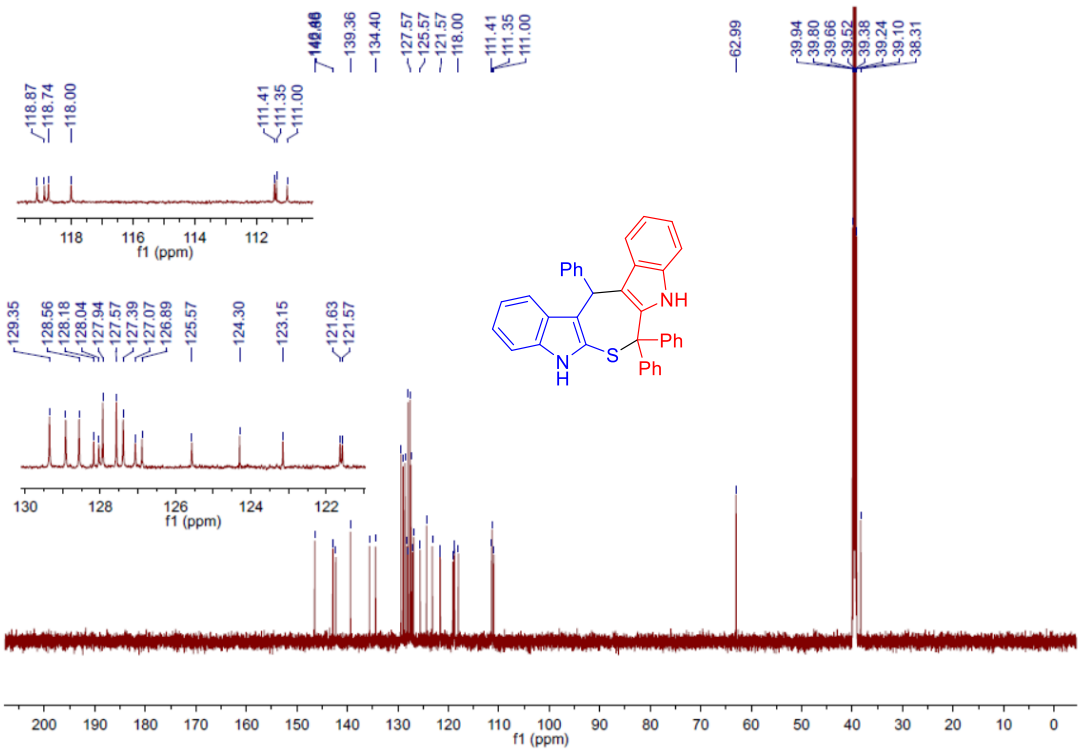
[1] (a) A. M. Thompson, M. Boyd and W. A. Denny, *J. Chem. Soc. Perkin Trans. 1*, 1993, 1835–1837. (b) Y. Jiang, H.-J. Ma, X.-L. Wang and Y. Yang, *J. Org. Chem*. 2023, **88**, 14587–14600. (c) X.-L. Wang, J.-Y. Zeng, Y. Yang, Y. Jiang, *Tetrahedron Lett*. 2024, **135**, 154886.

[2] J. Mao, H. Zhang, X.-F. Ding, X. Luo, W.-P. Deng, *J. Org. Chem*. 2019, **84**, 11186–11194.

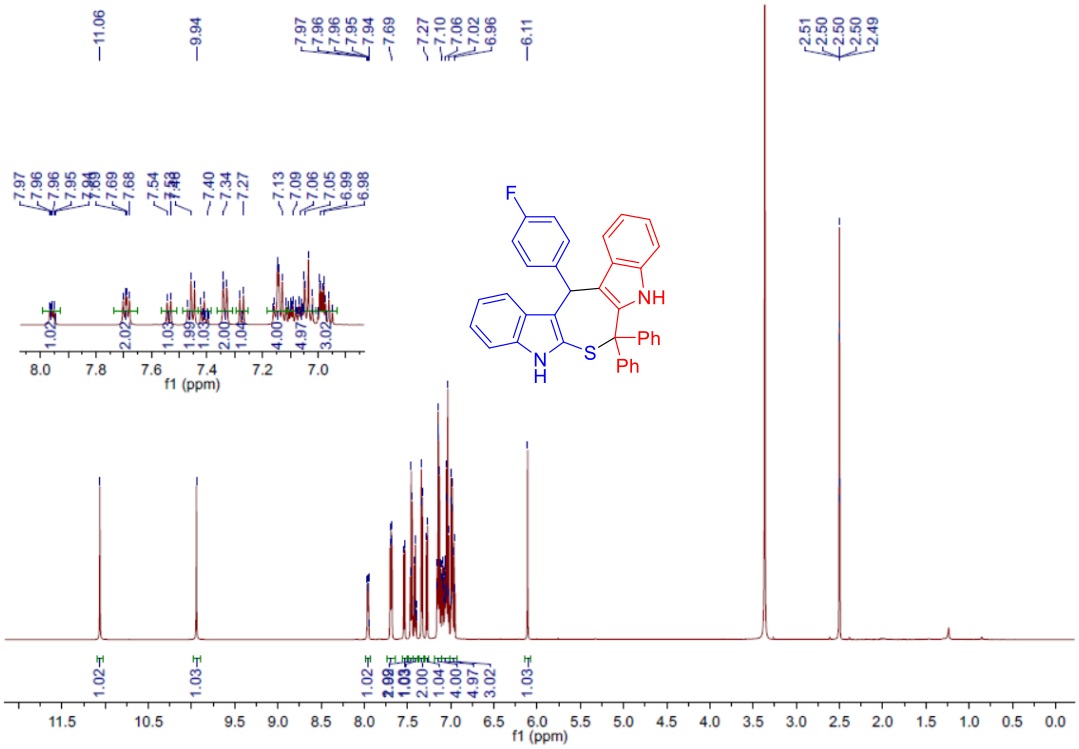
NMR Spectra



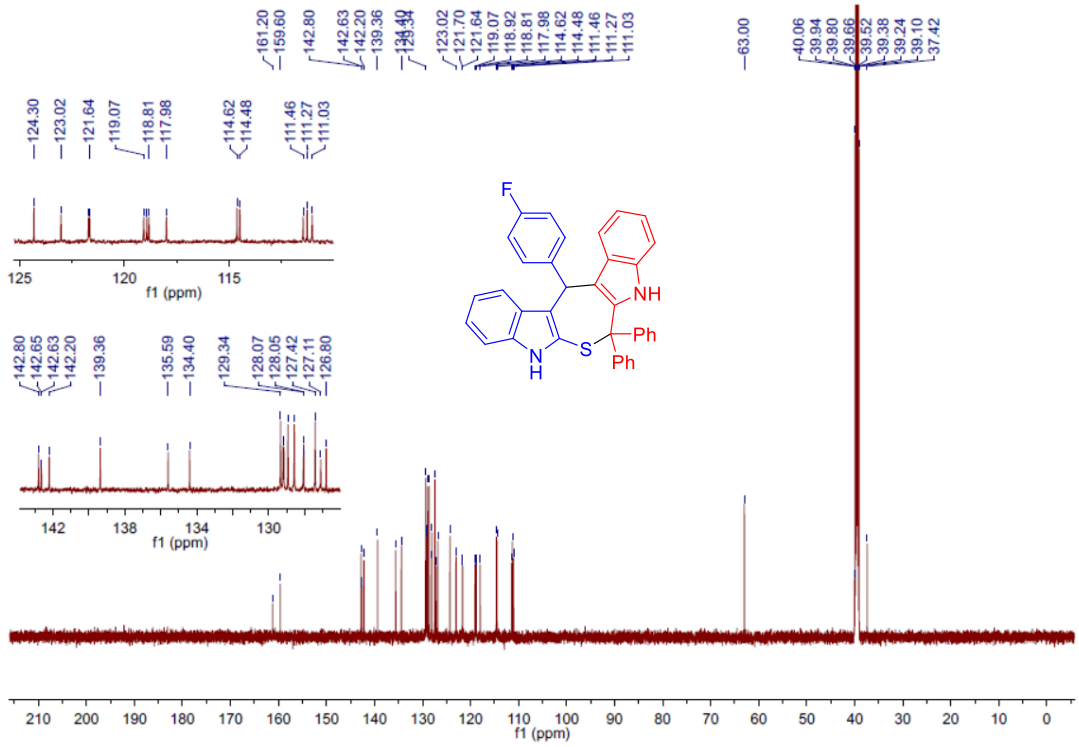
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3aa**



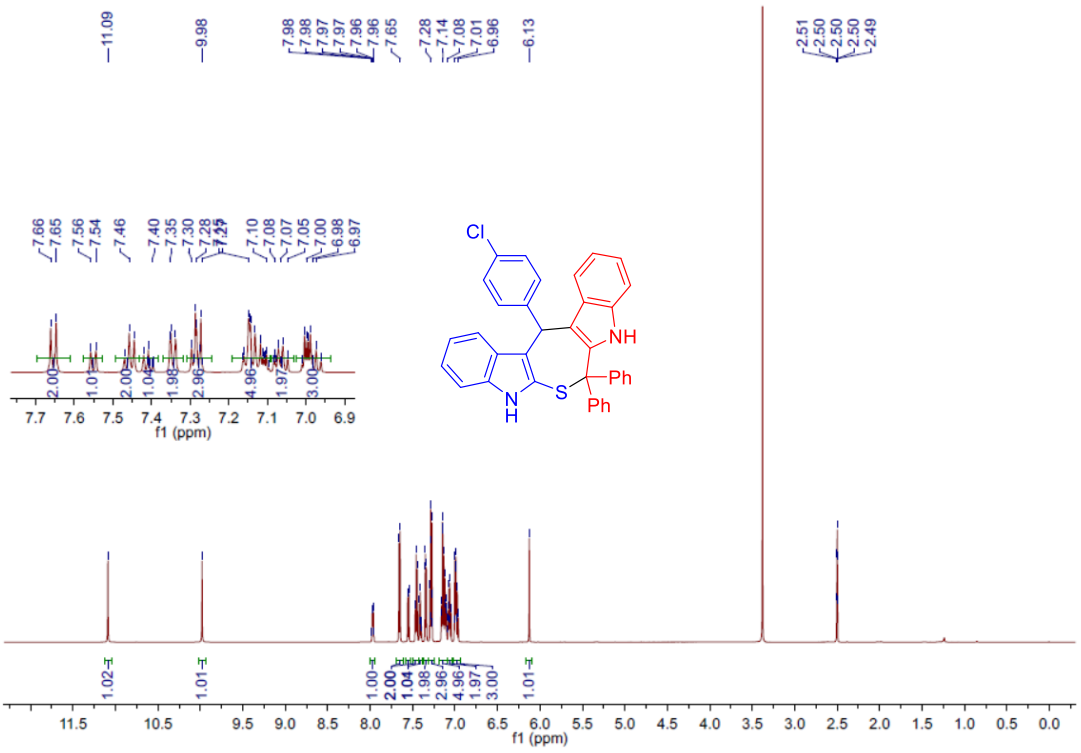
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3aa**



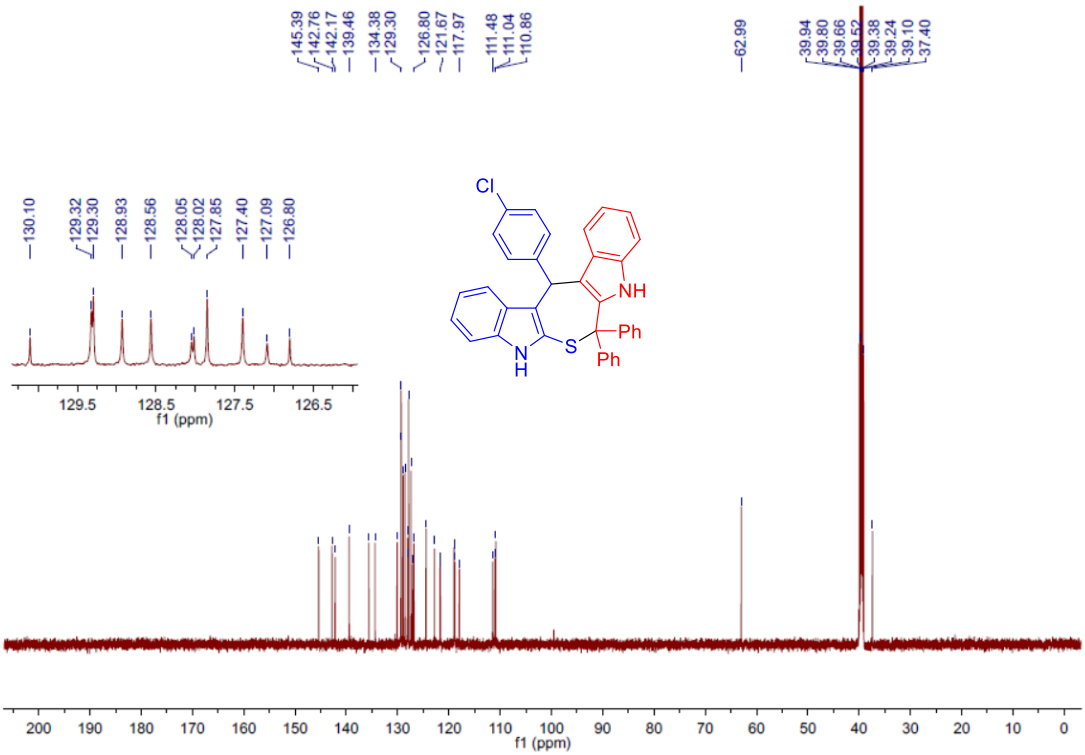
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ba**



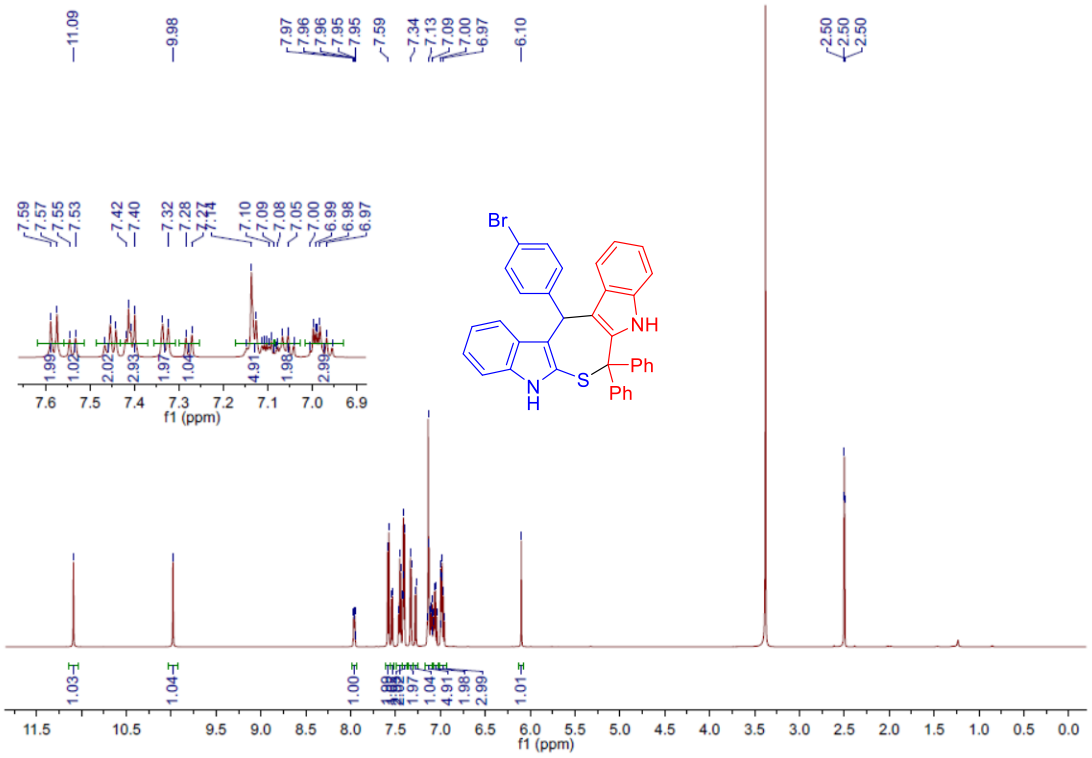
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ba**



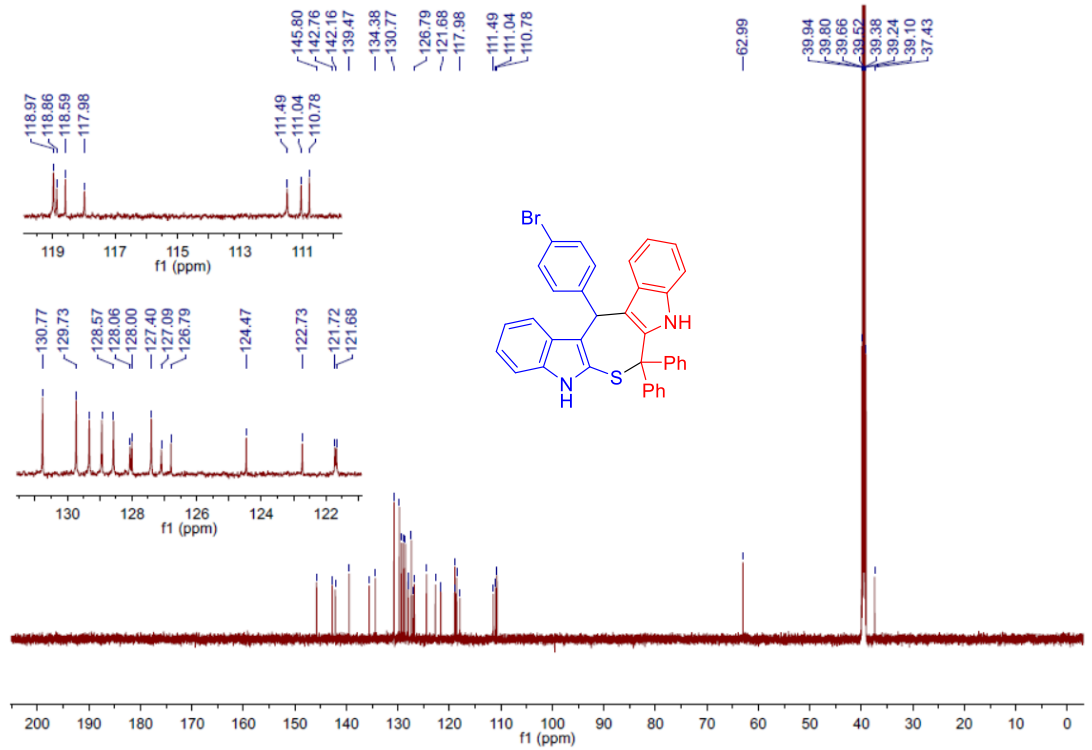
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ca**



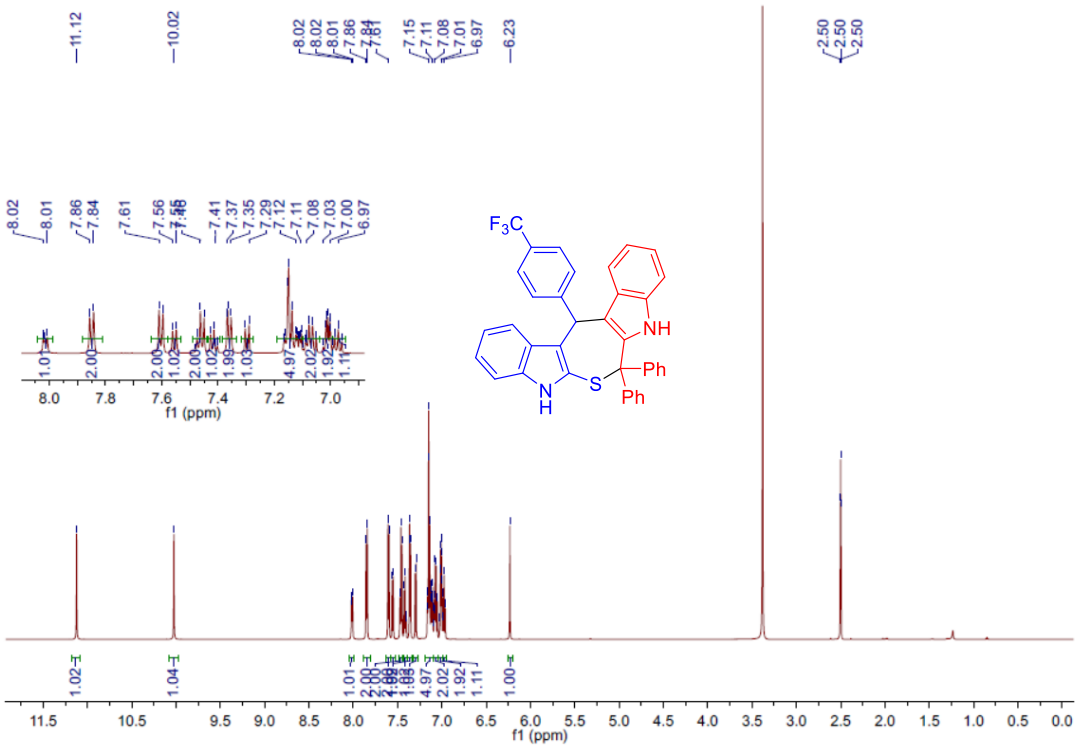
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ca**



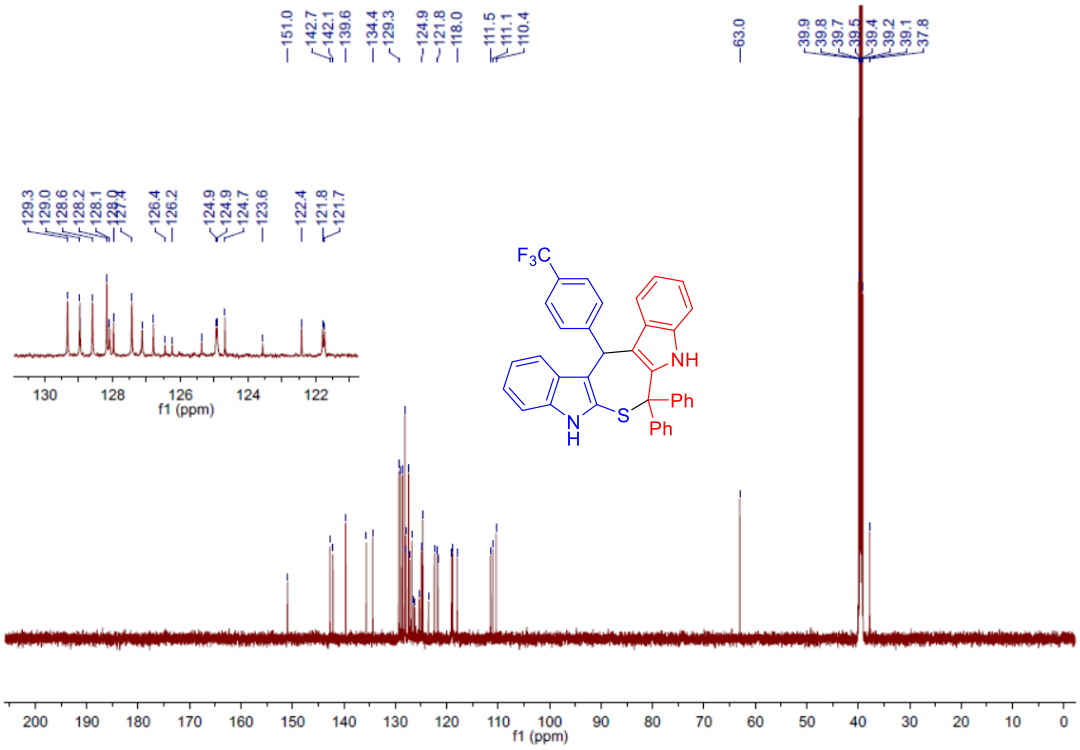
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3da**



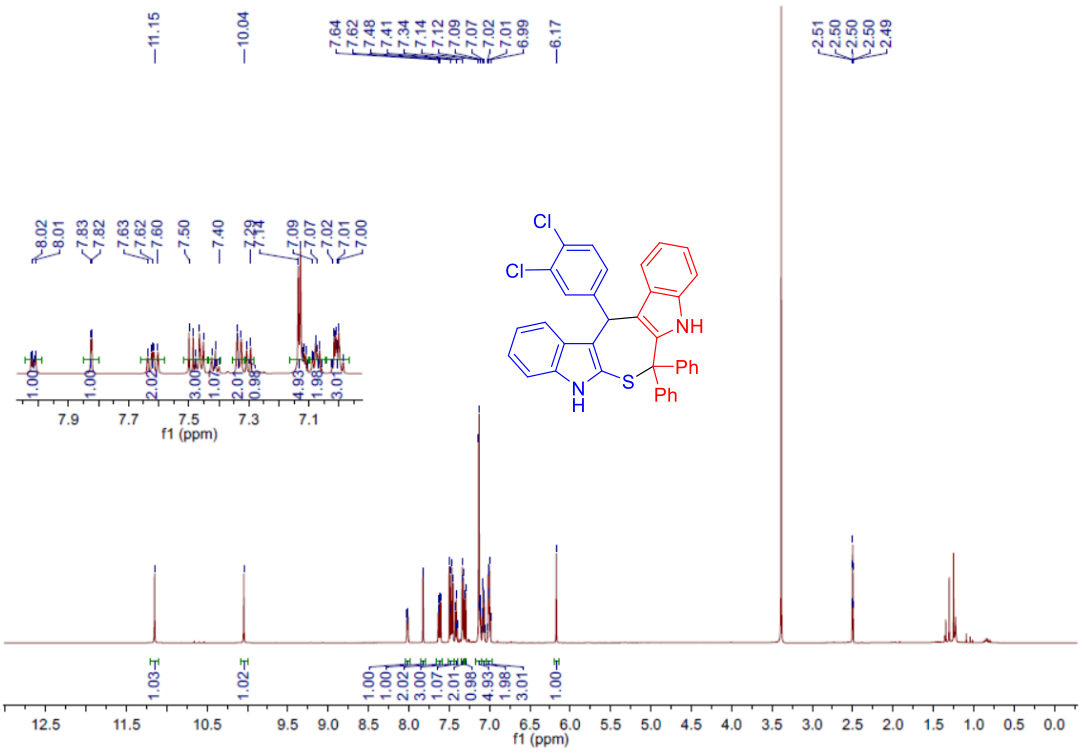
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3da**



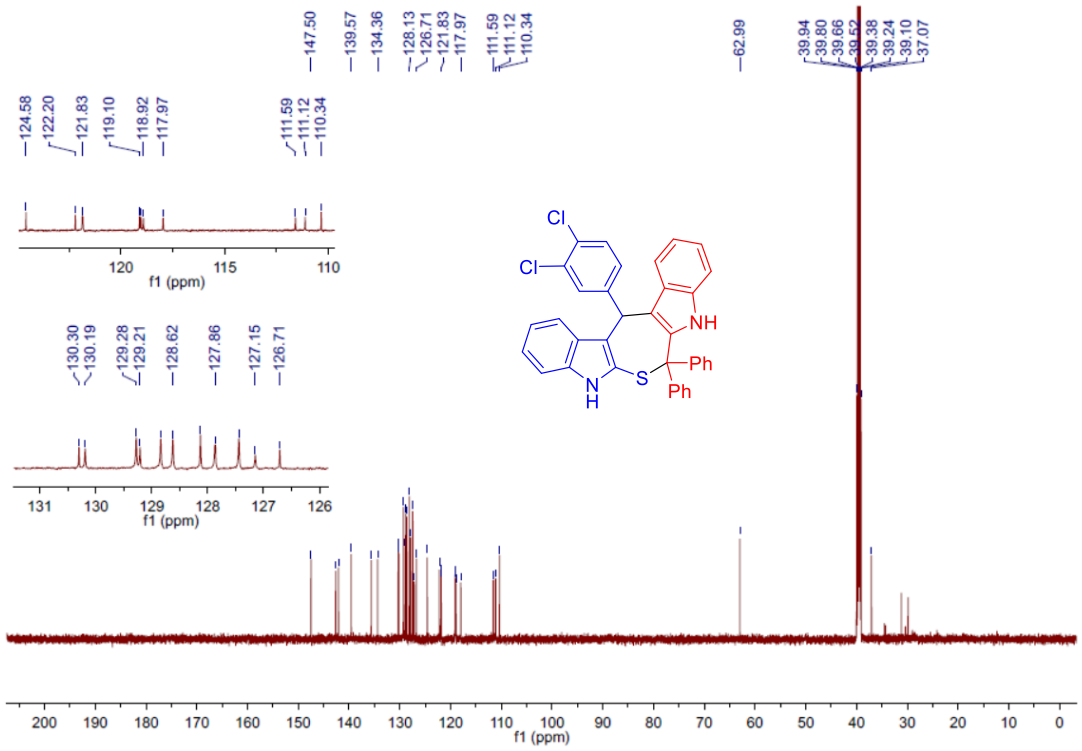
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ea**



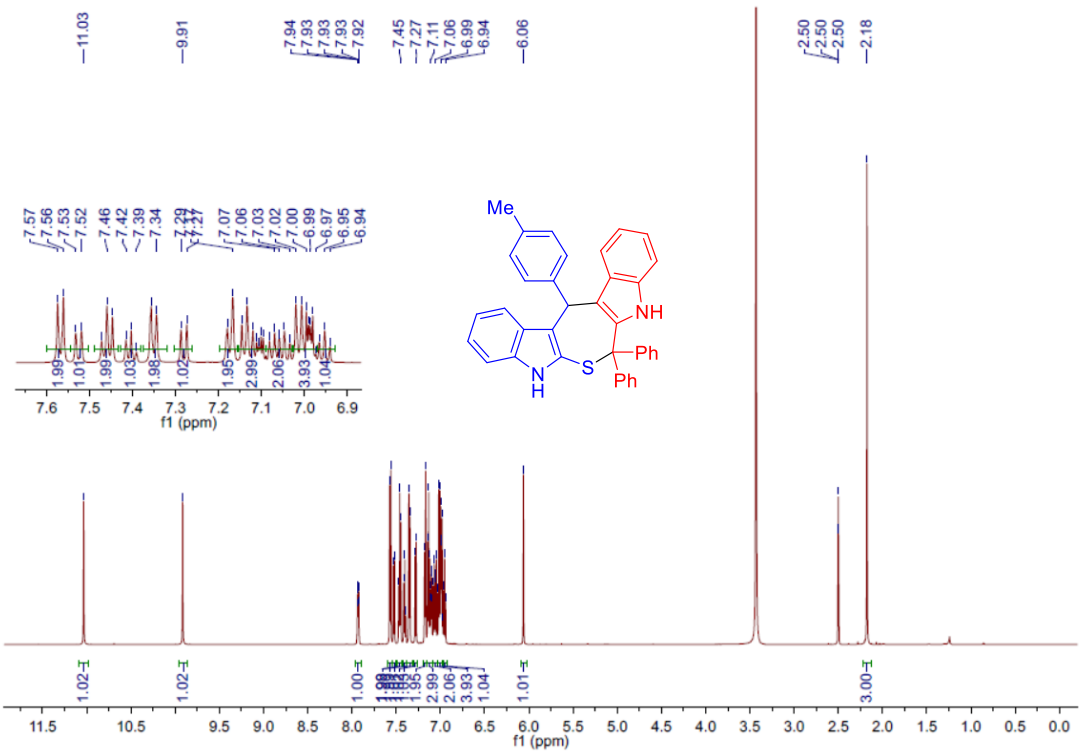
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ea**



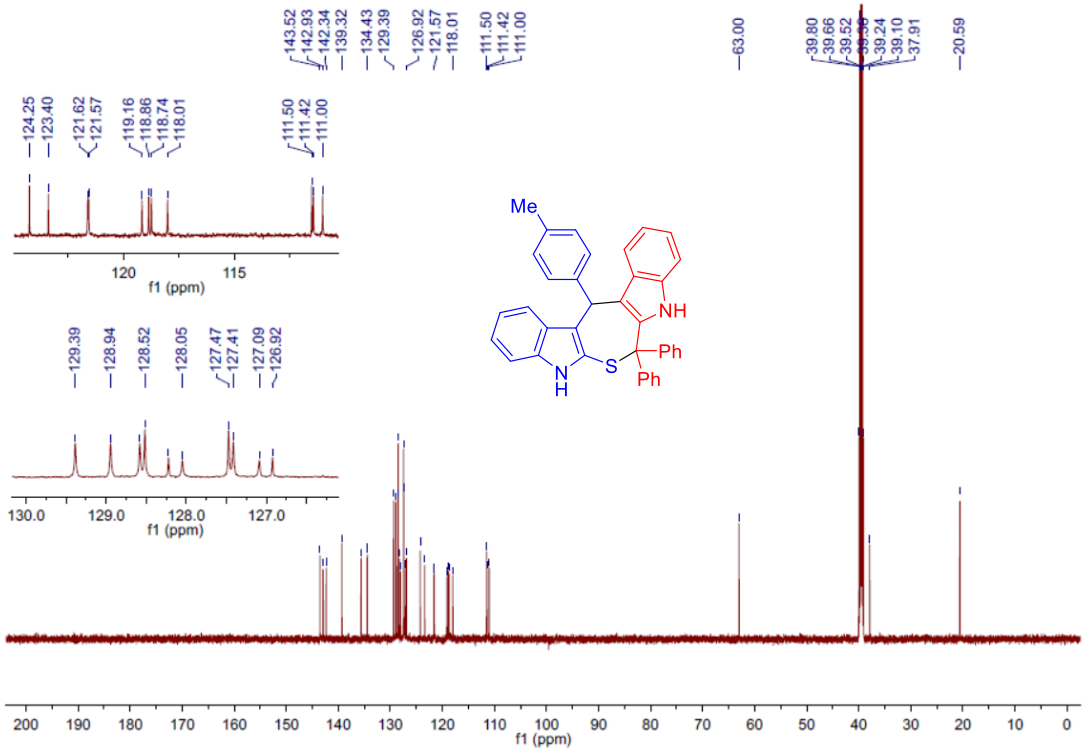
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3fa**



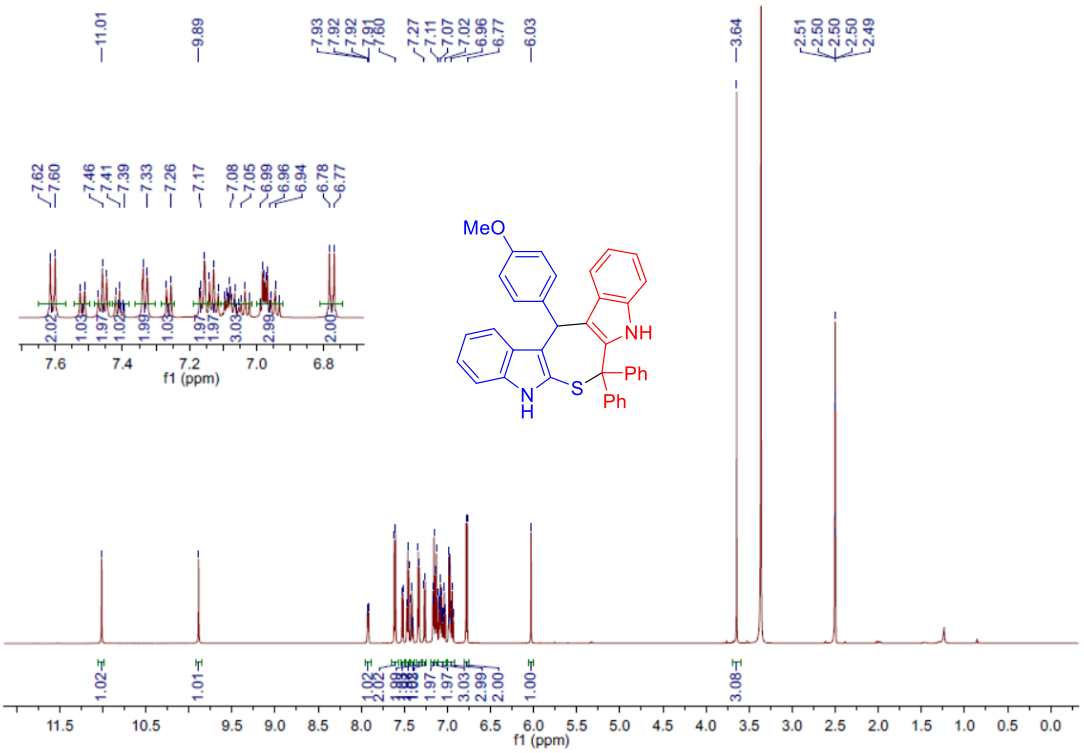
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3fa**



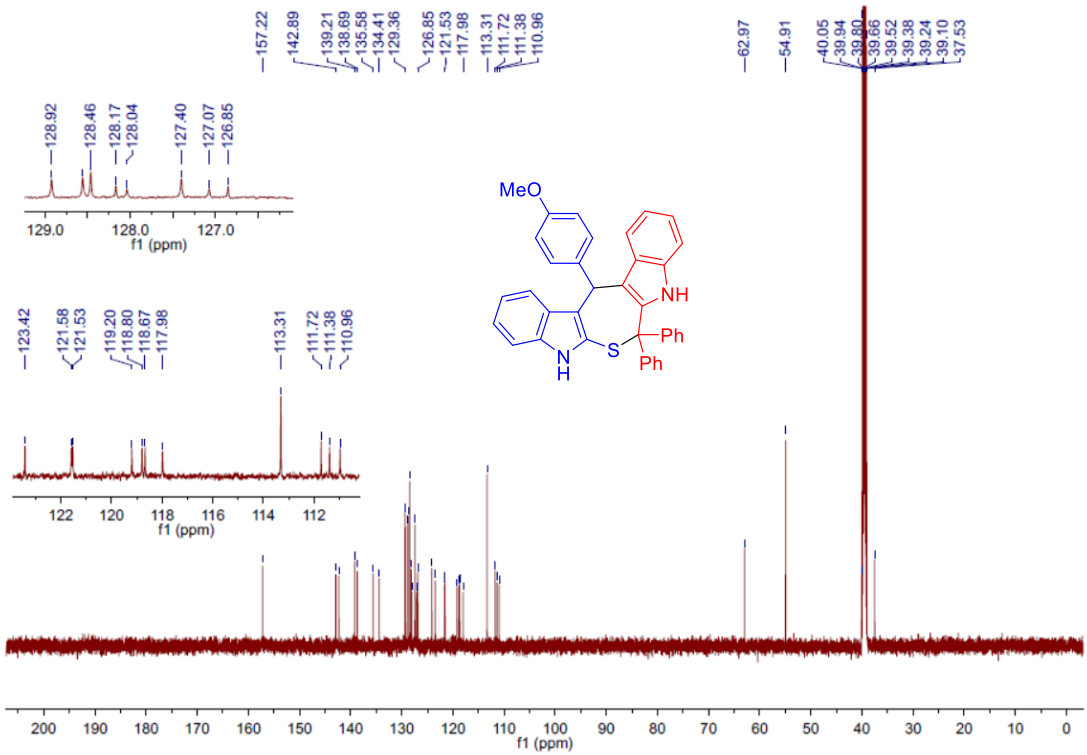
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ga**



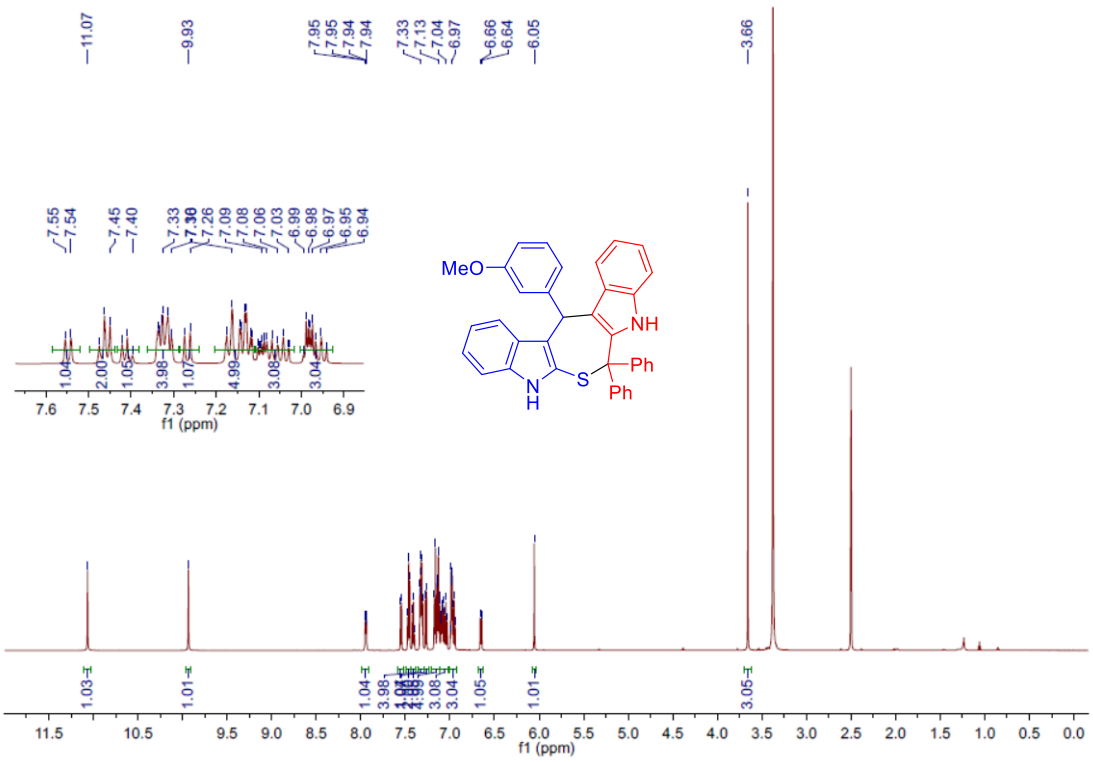
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ga**



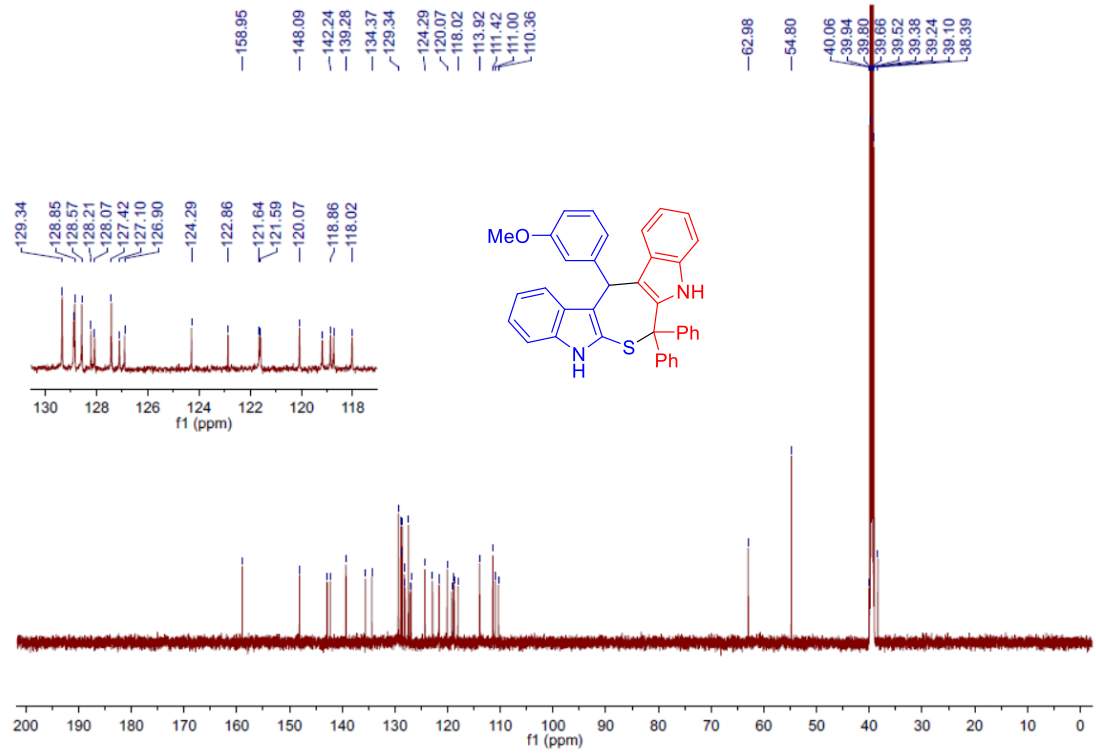
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ha**



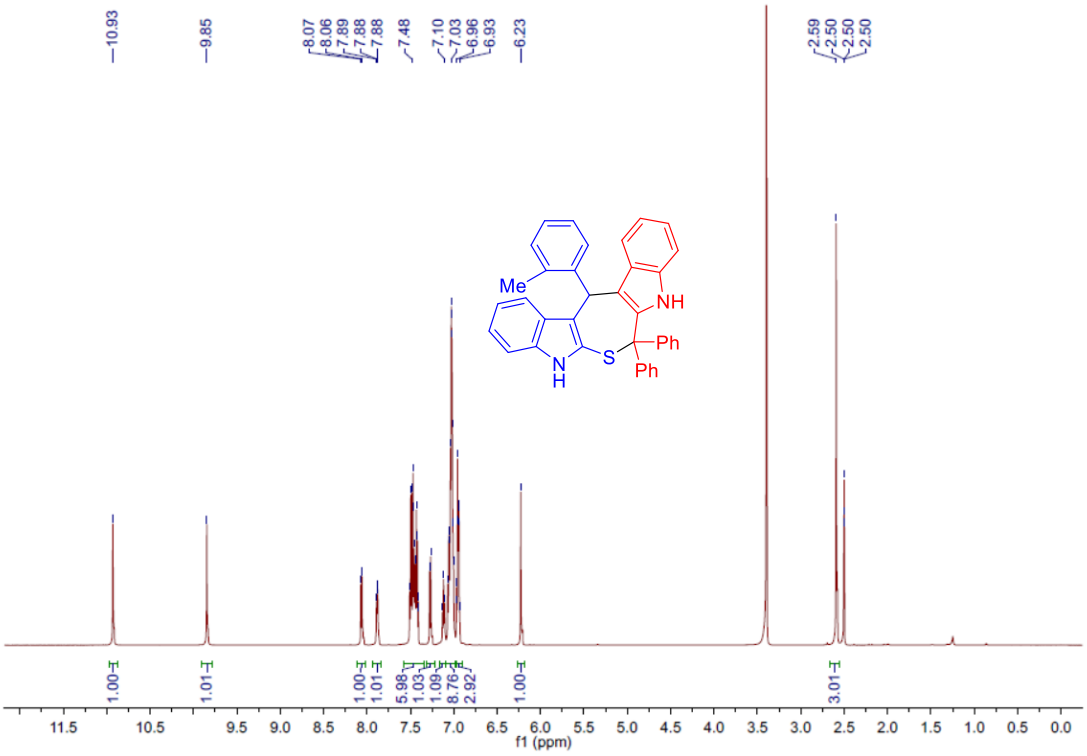
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ha**



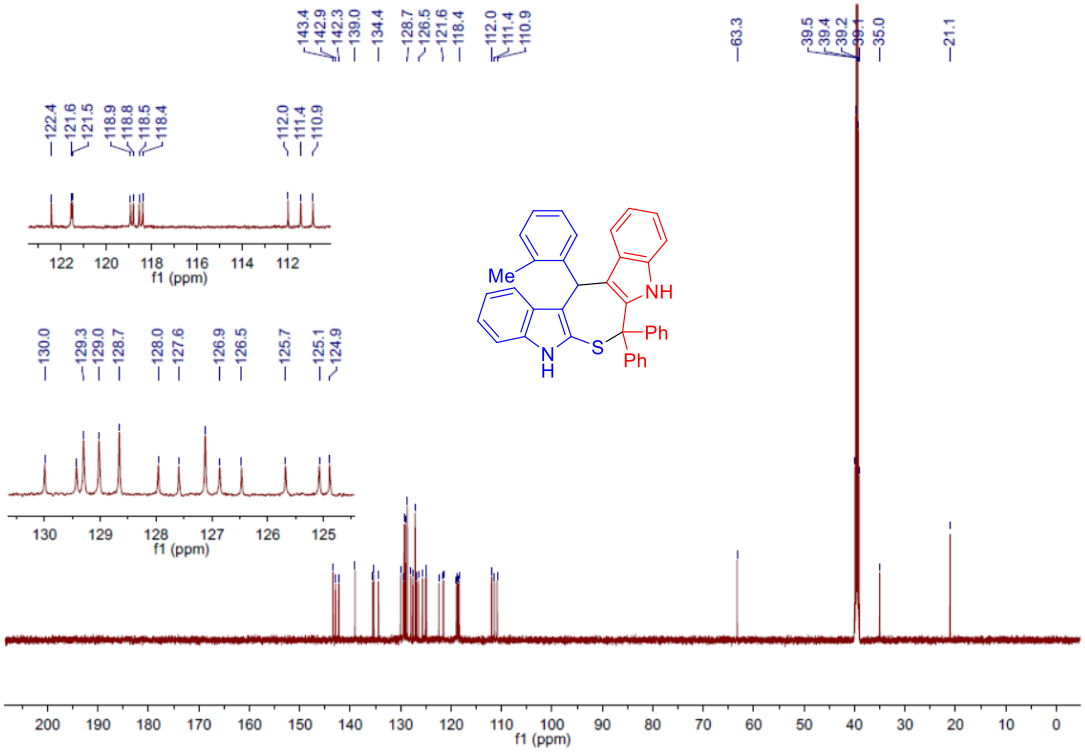
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ia**



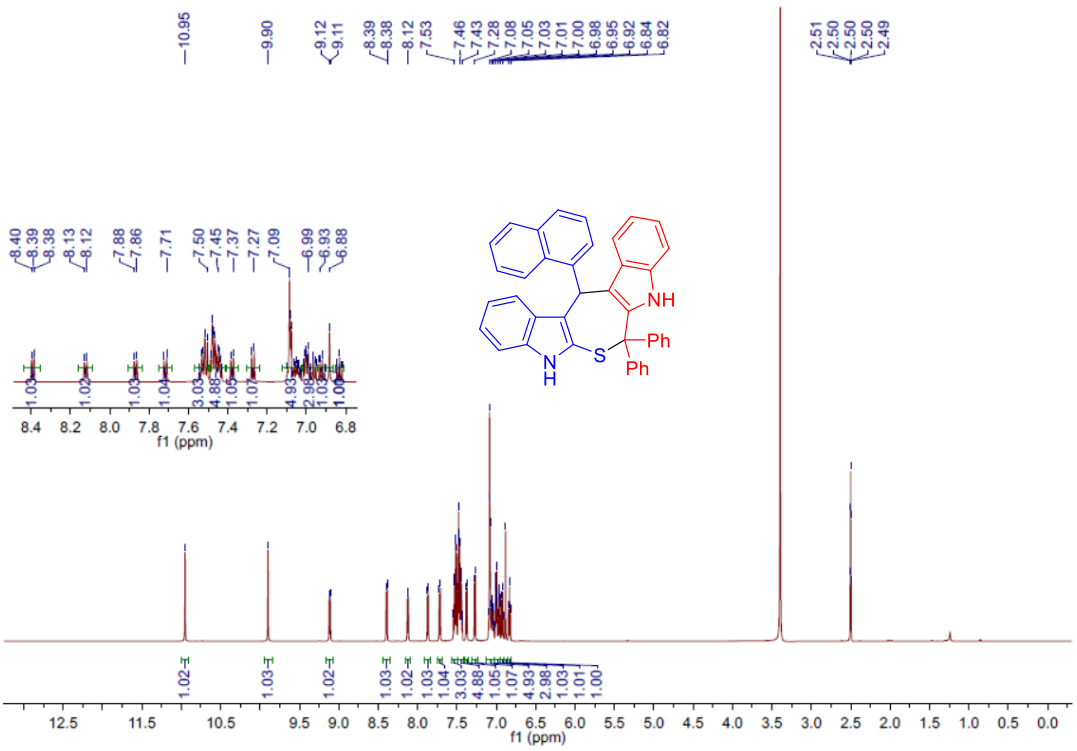
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ia**



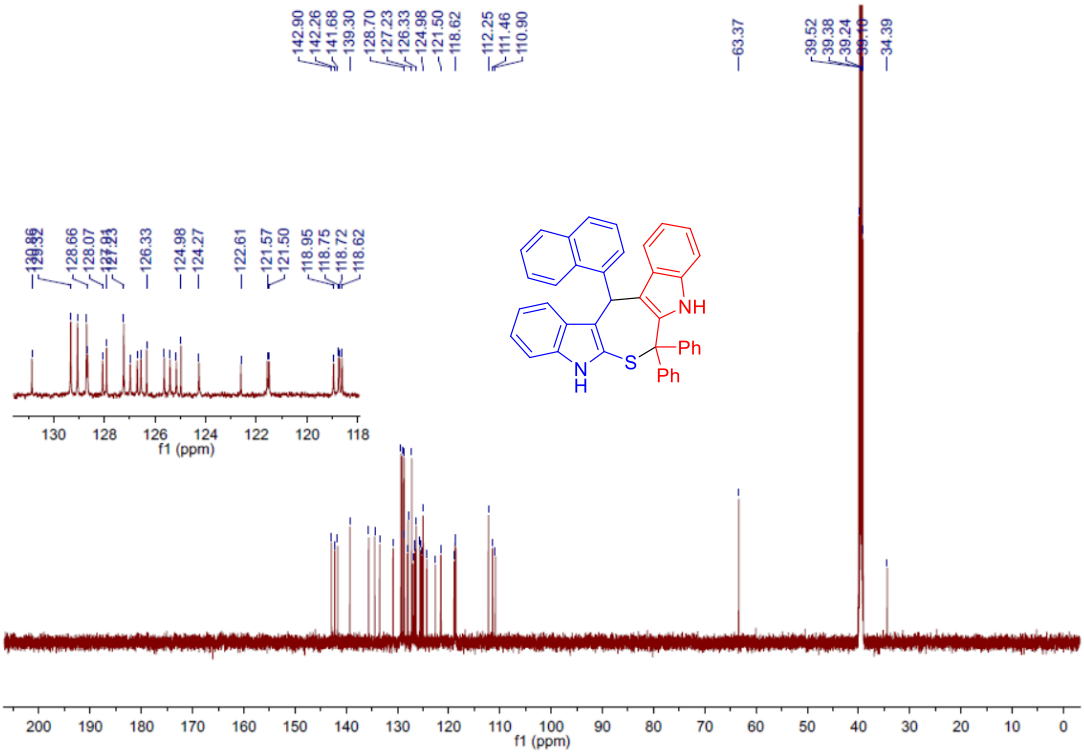
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ja**



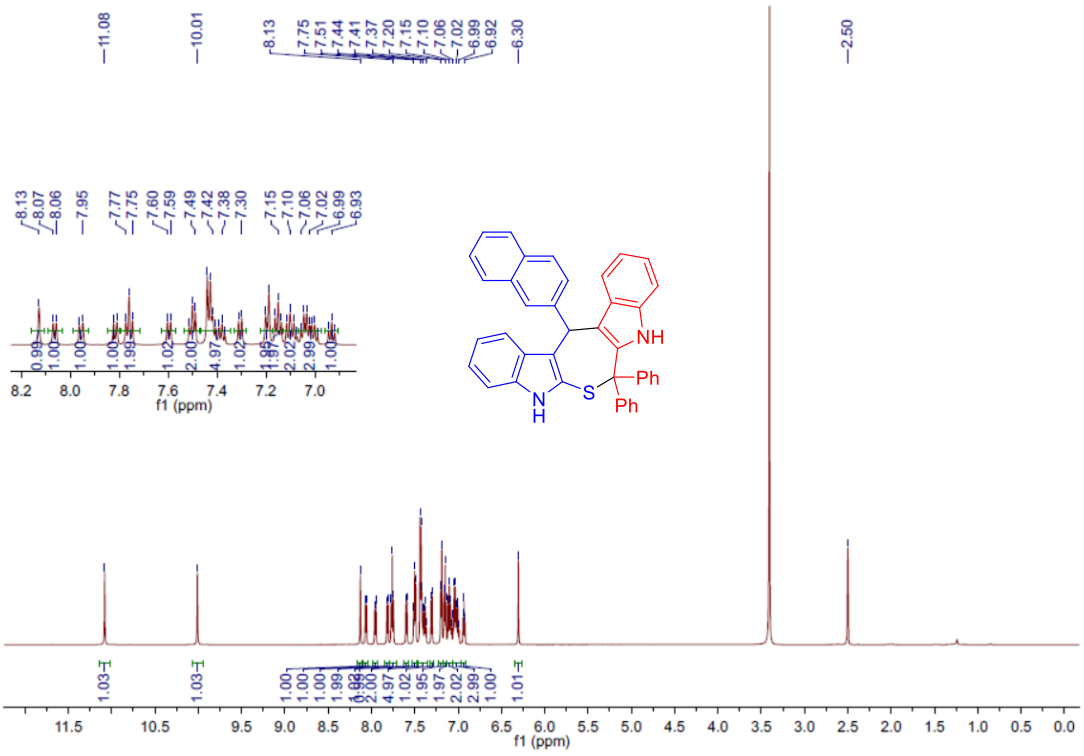
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ja**



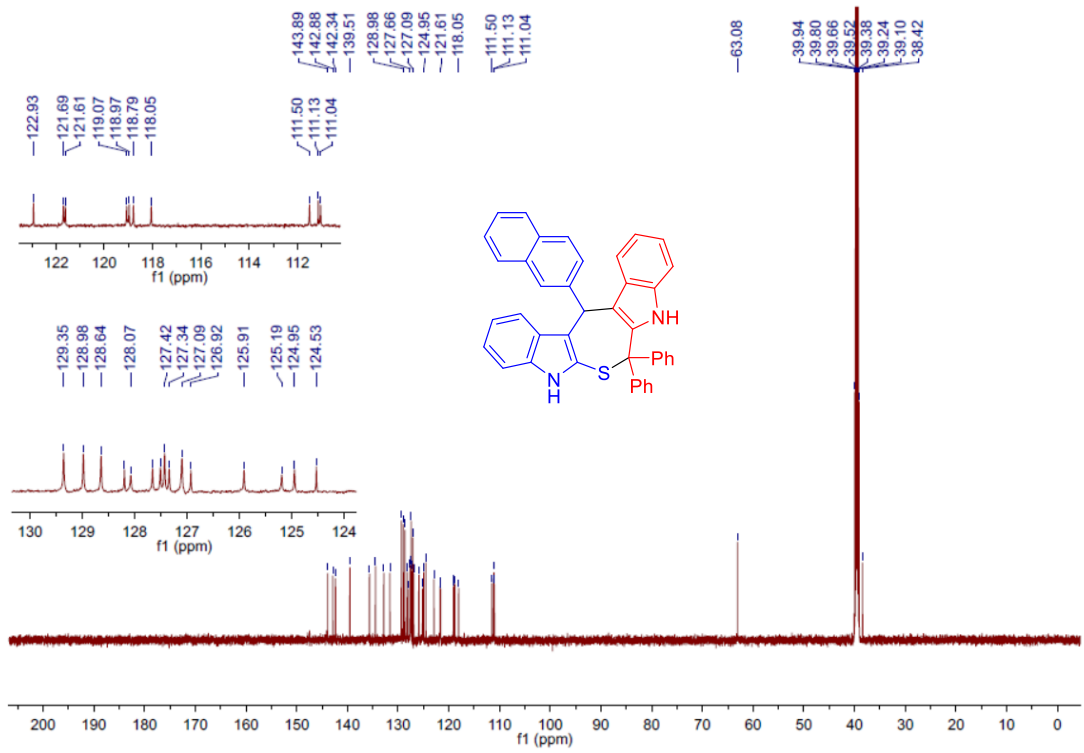
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ka**



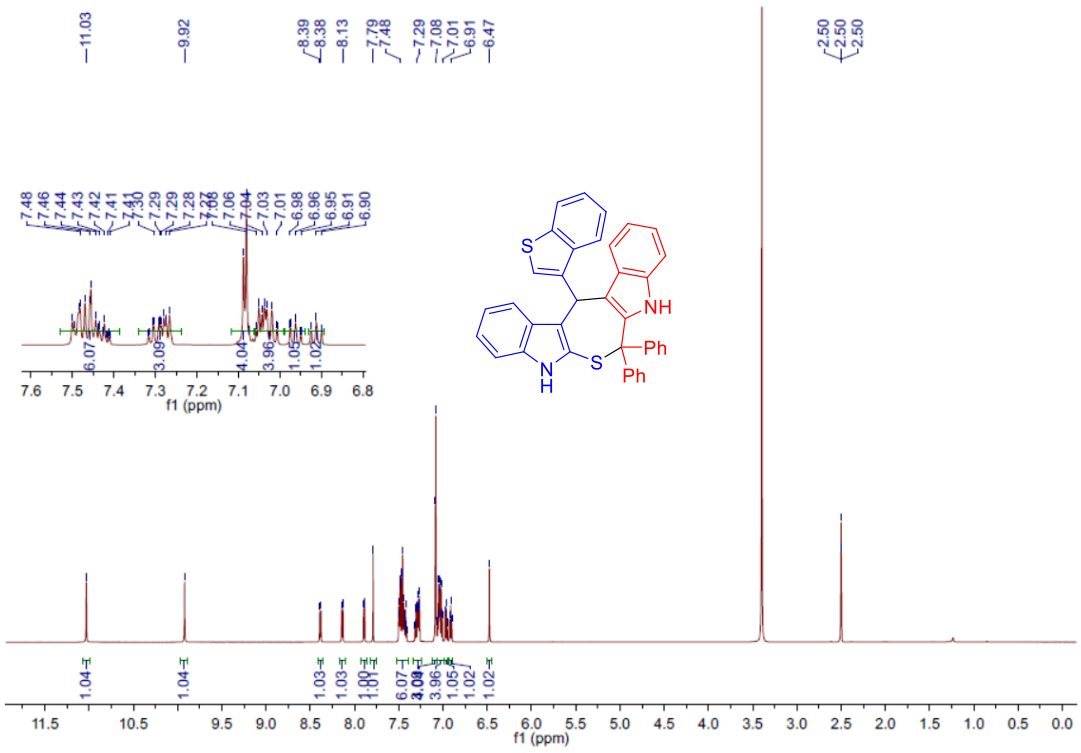
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ka**



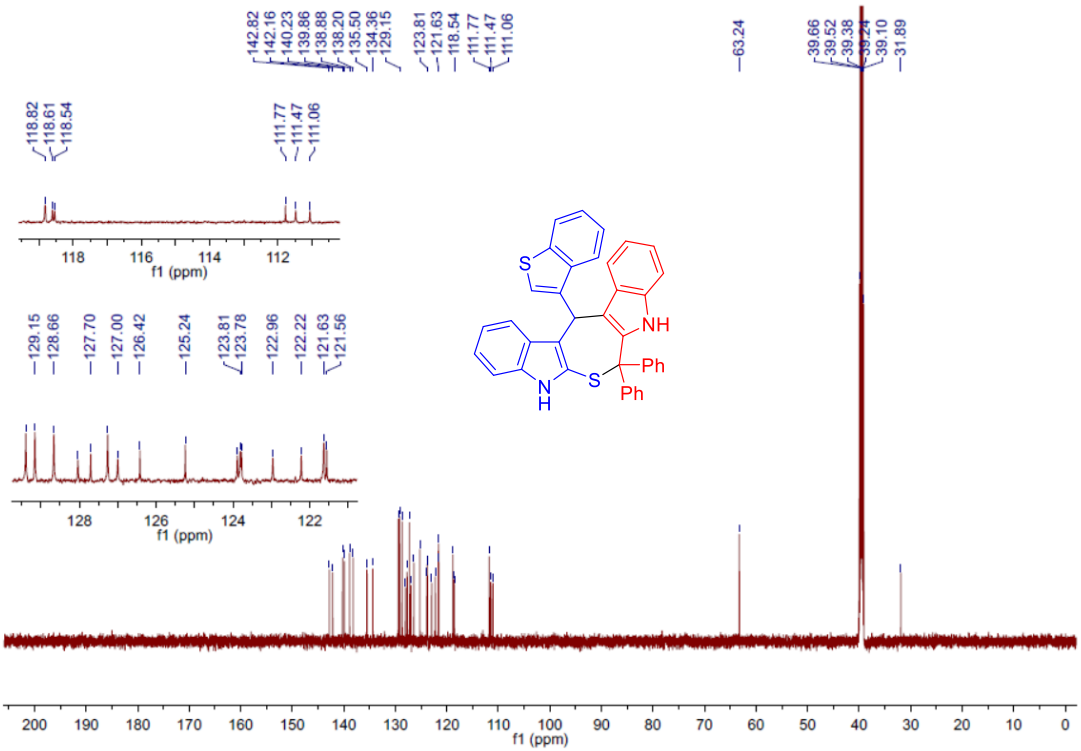
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3la**



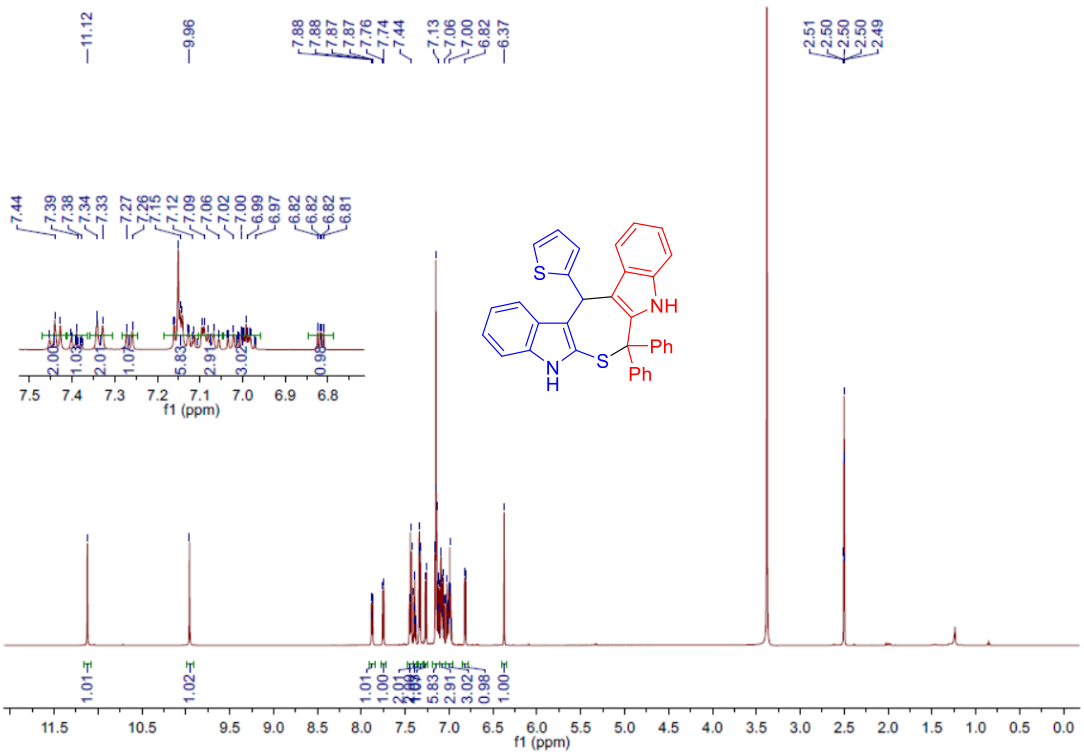
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3la**



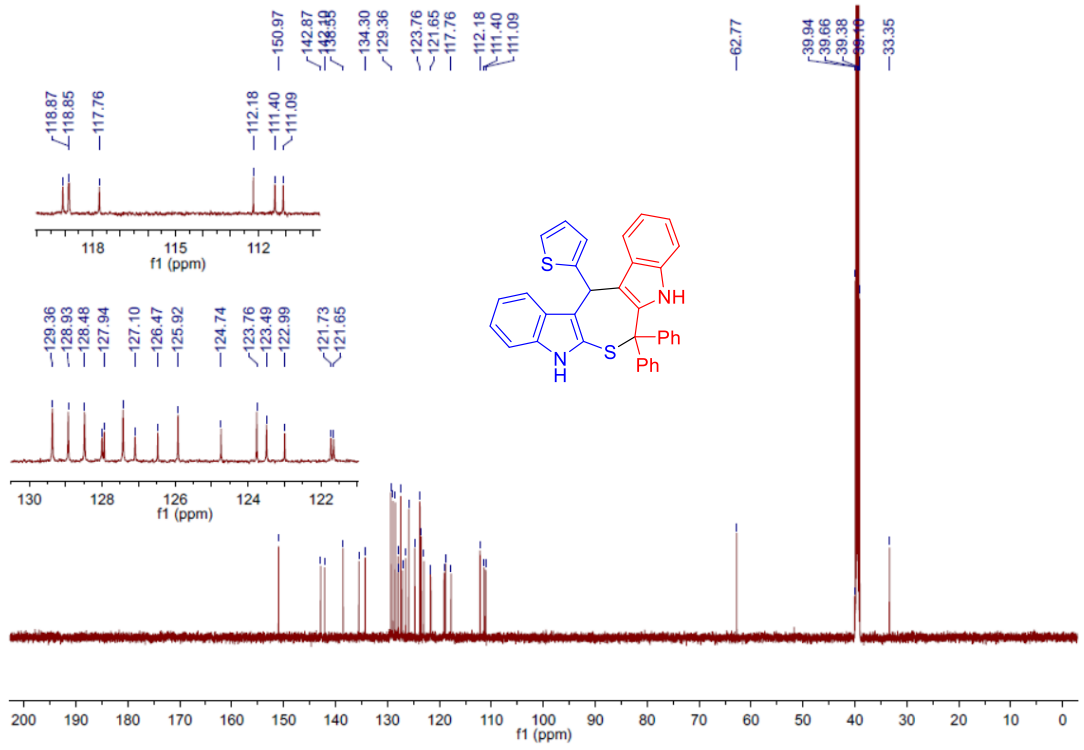
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ma**



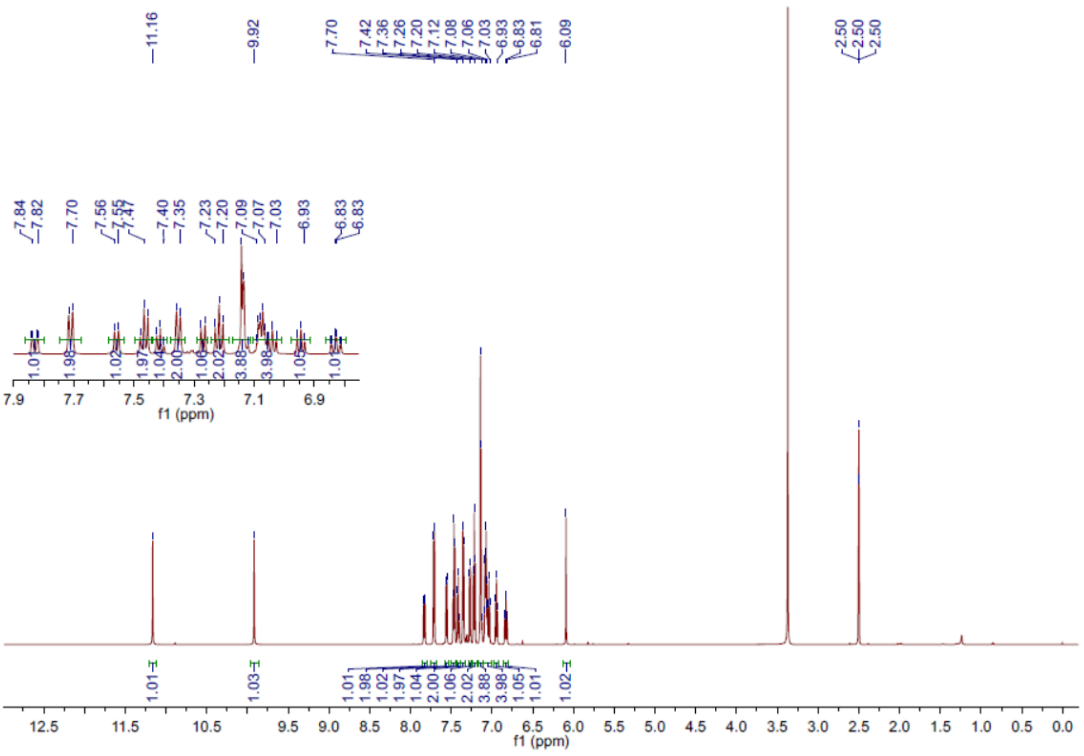
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ma**



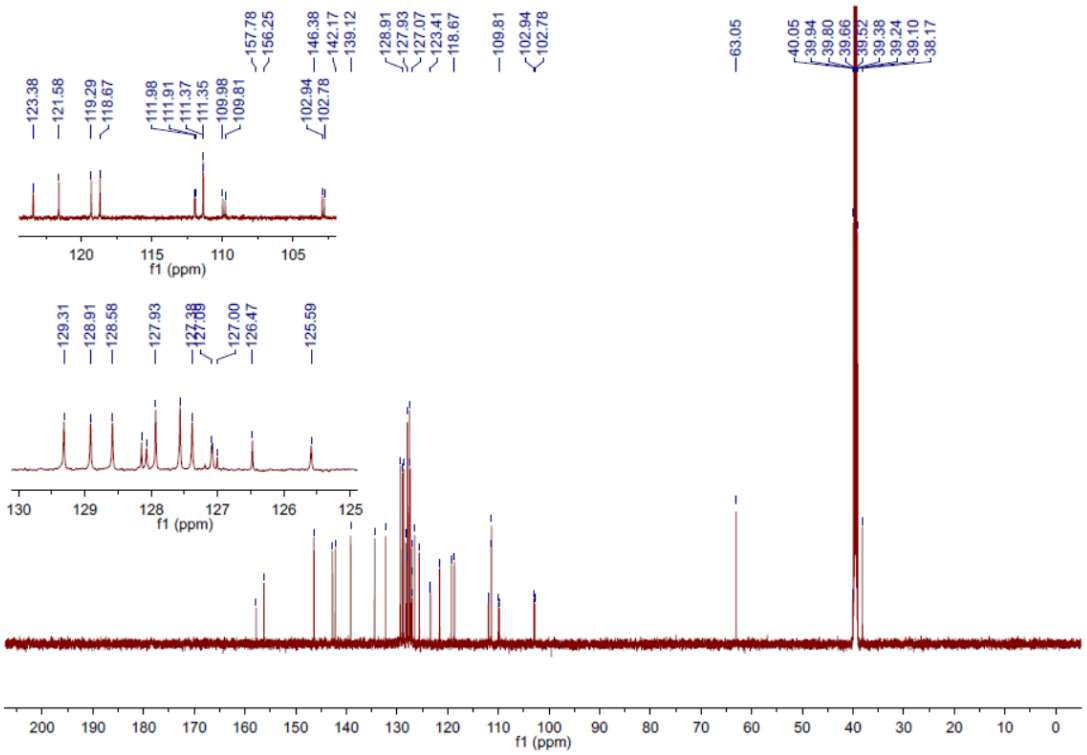
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3na**



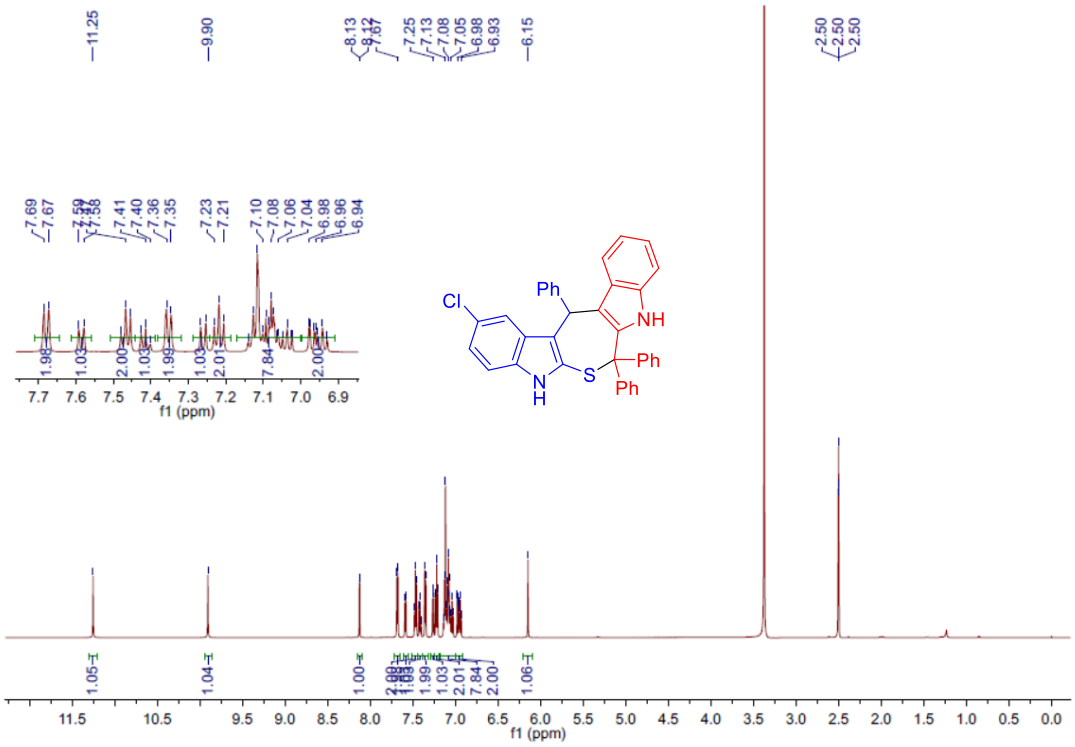
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3na**



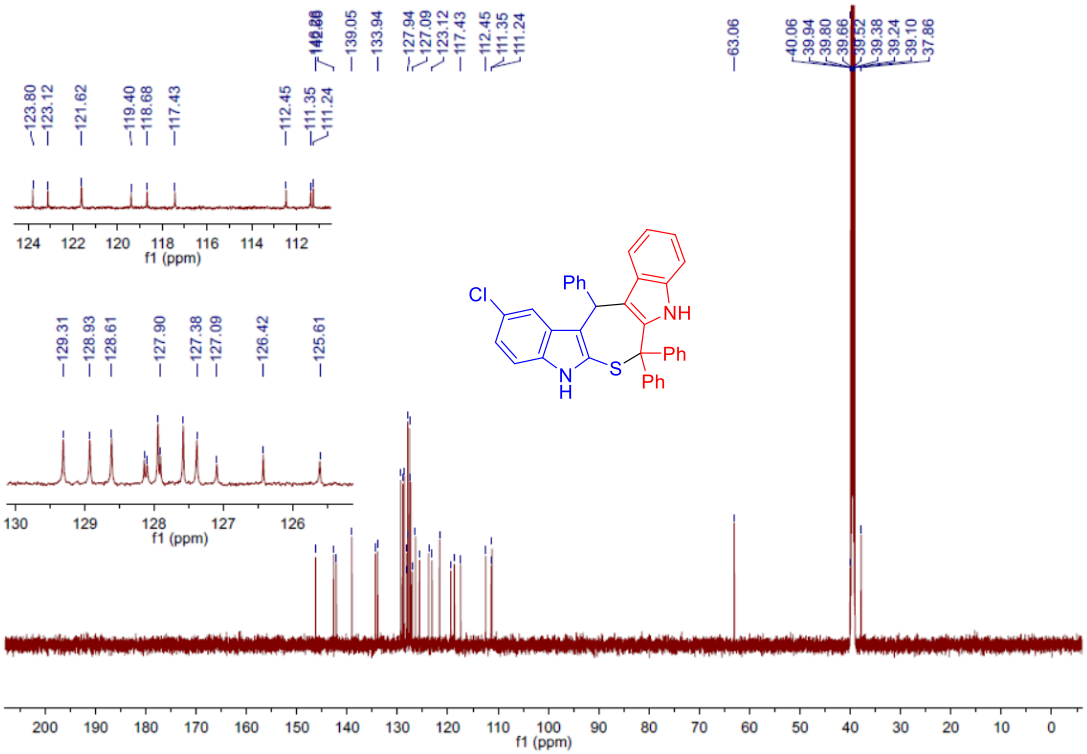
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3oa**



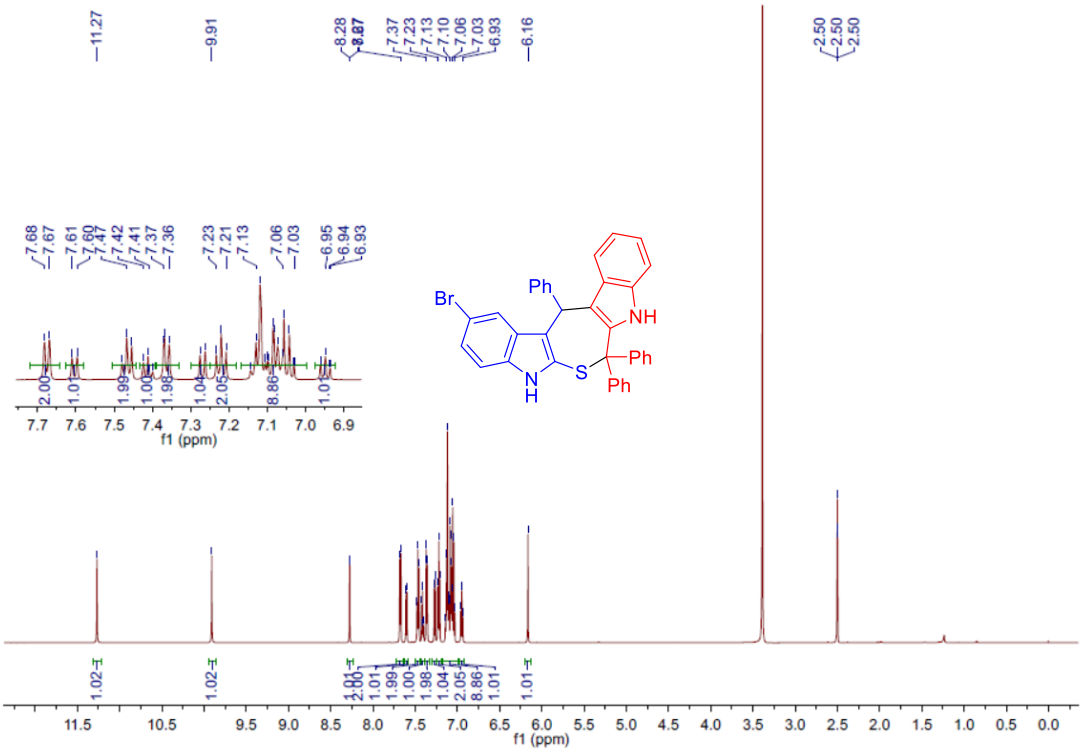
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3oa**



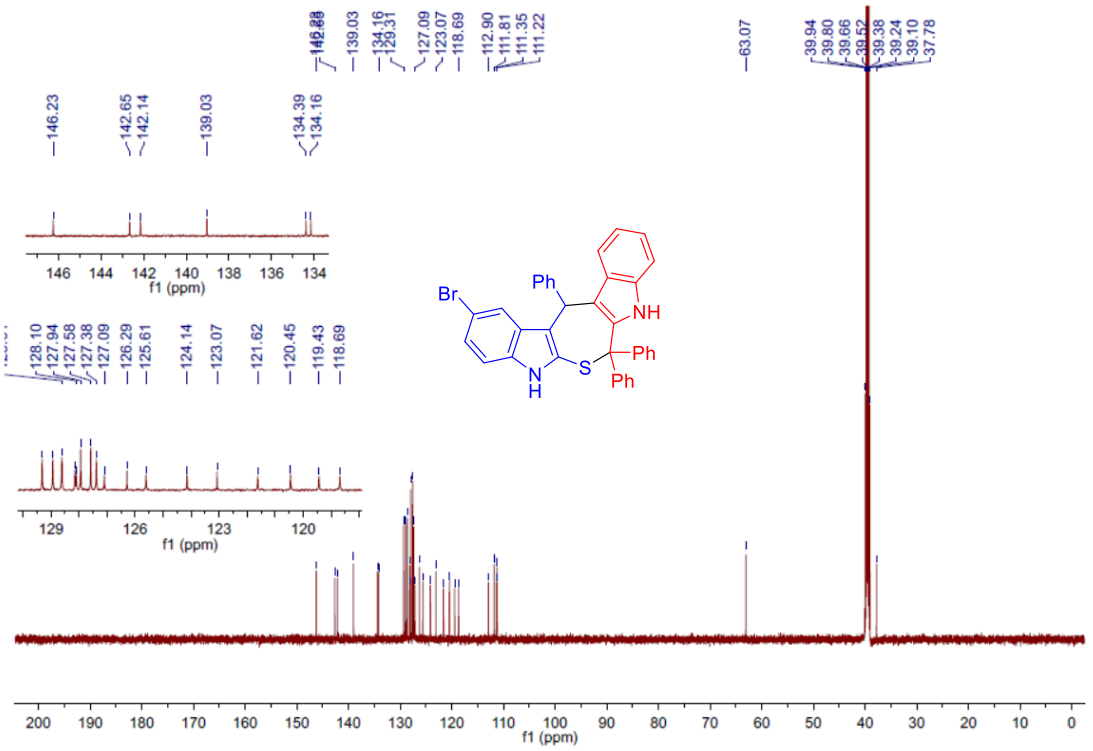
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3pa**



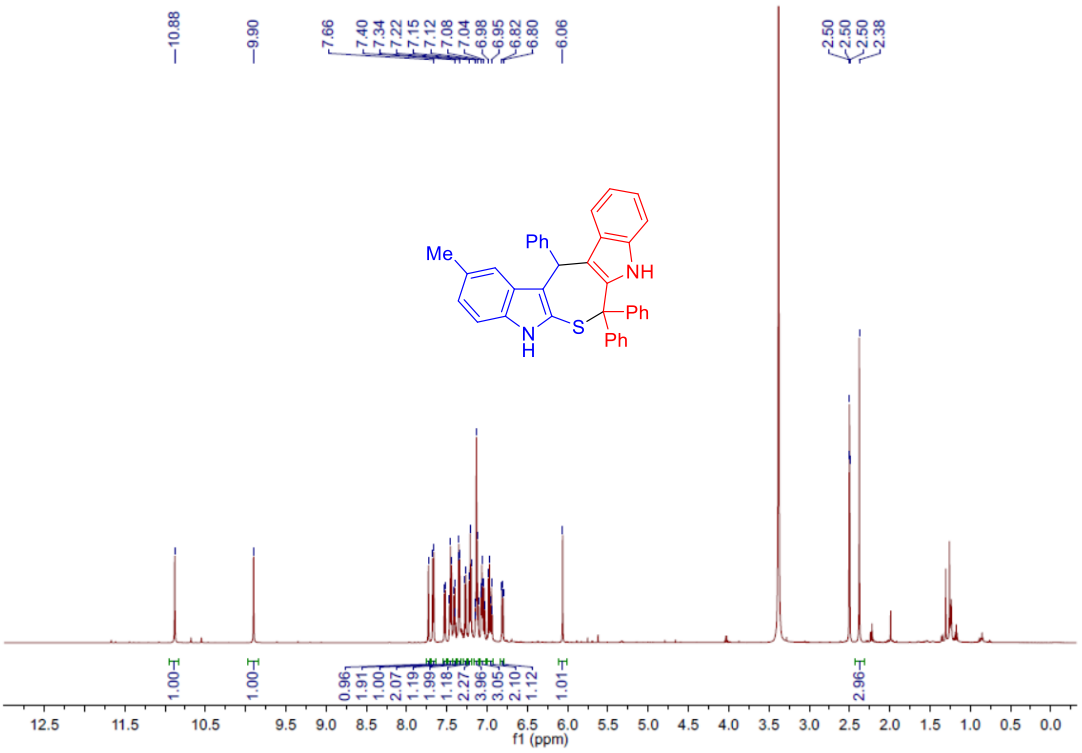
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3pa**



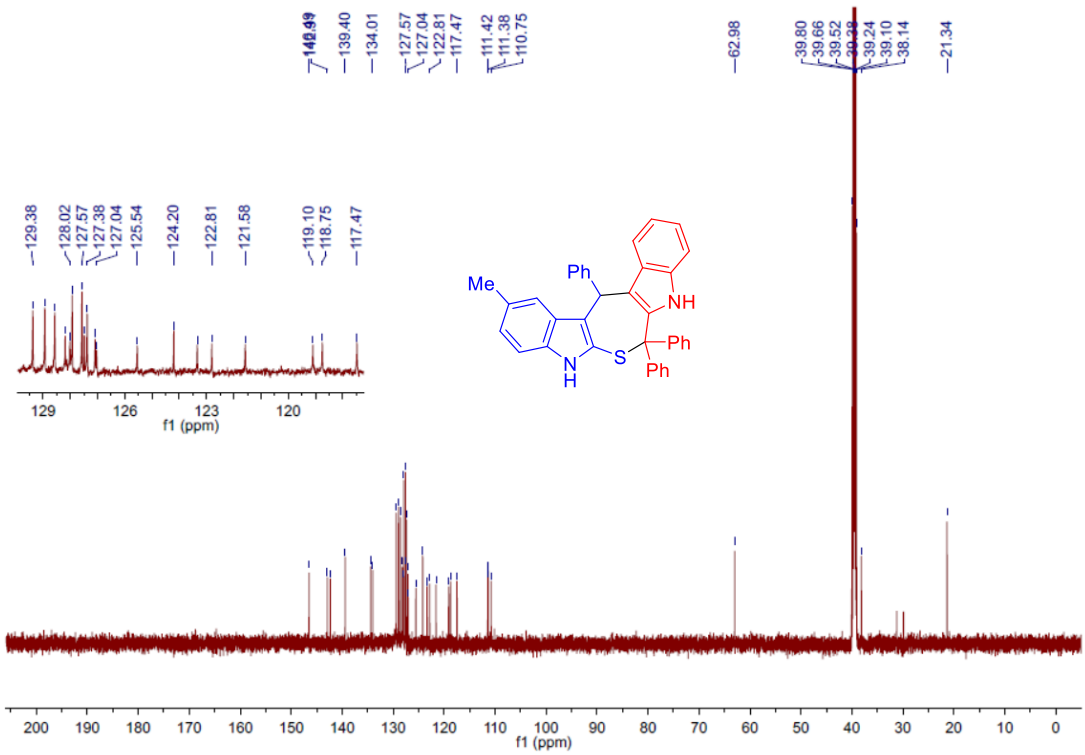
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3qa**



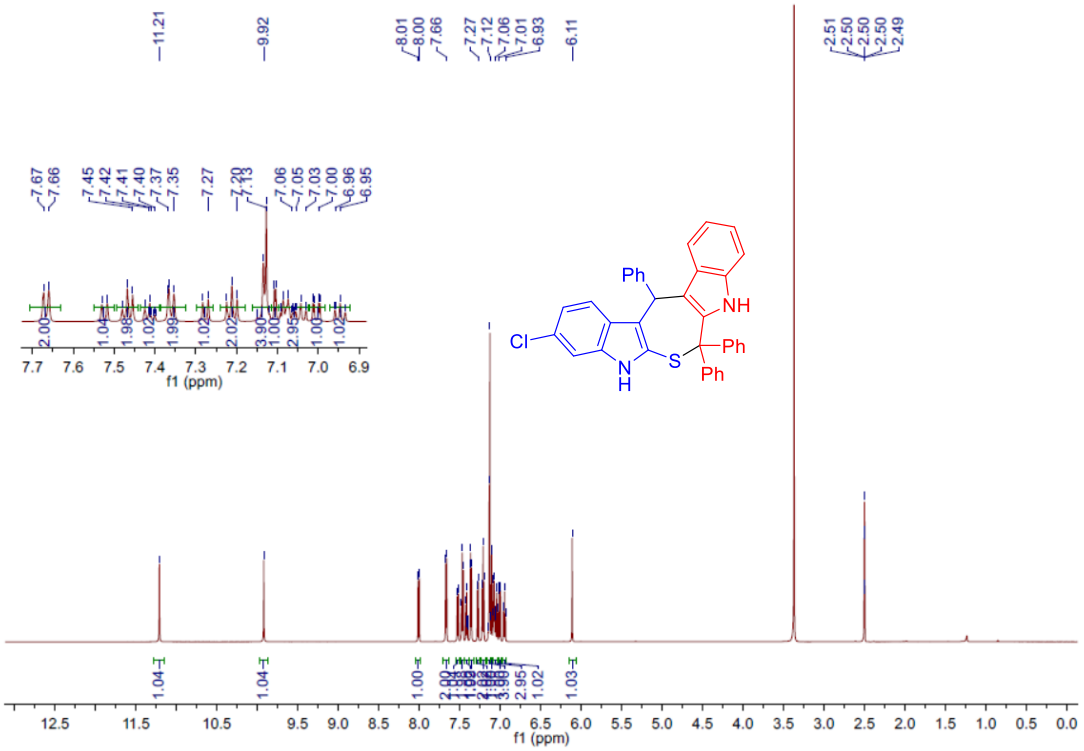
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3qa**



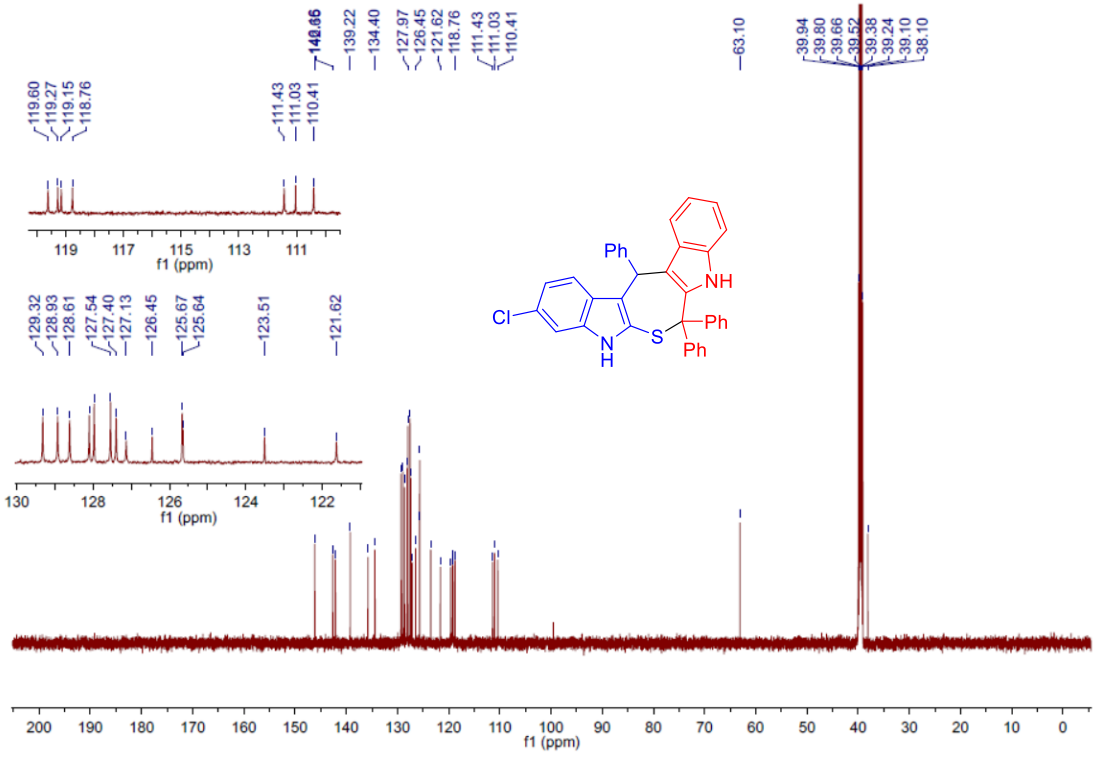
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ra**



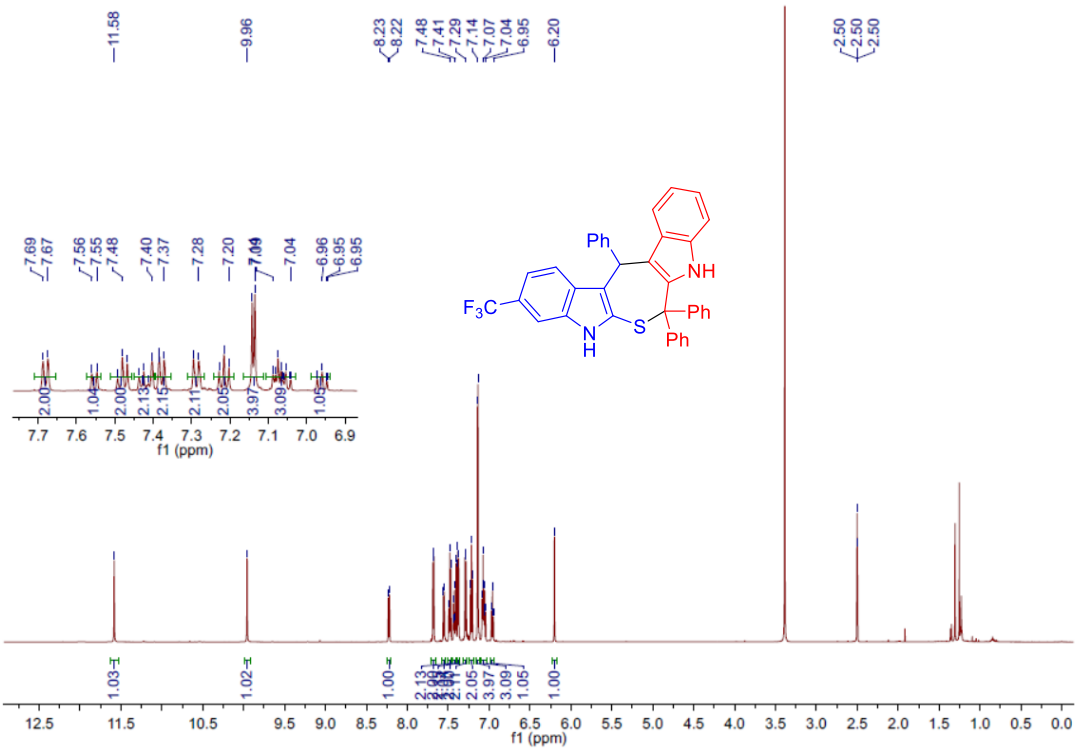
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ra**



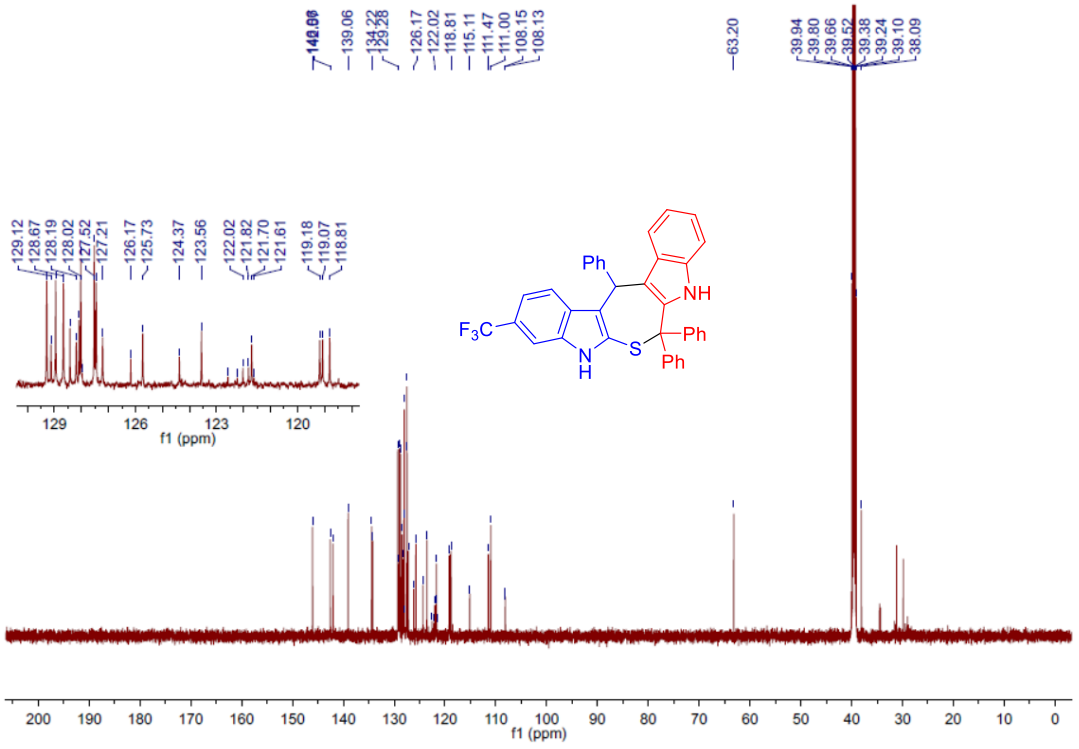
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3sa**



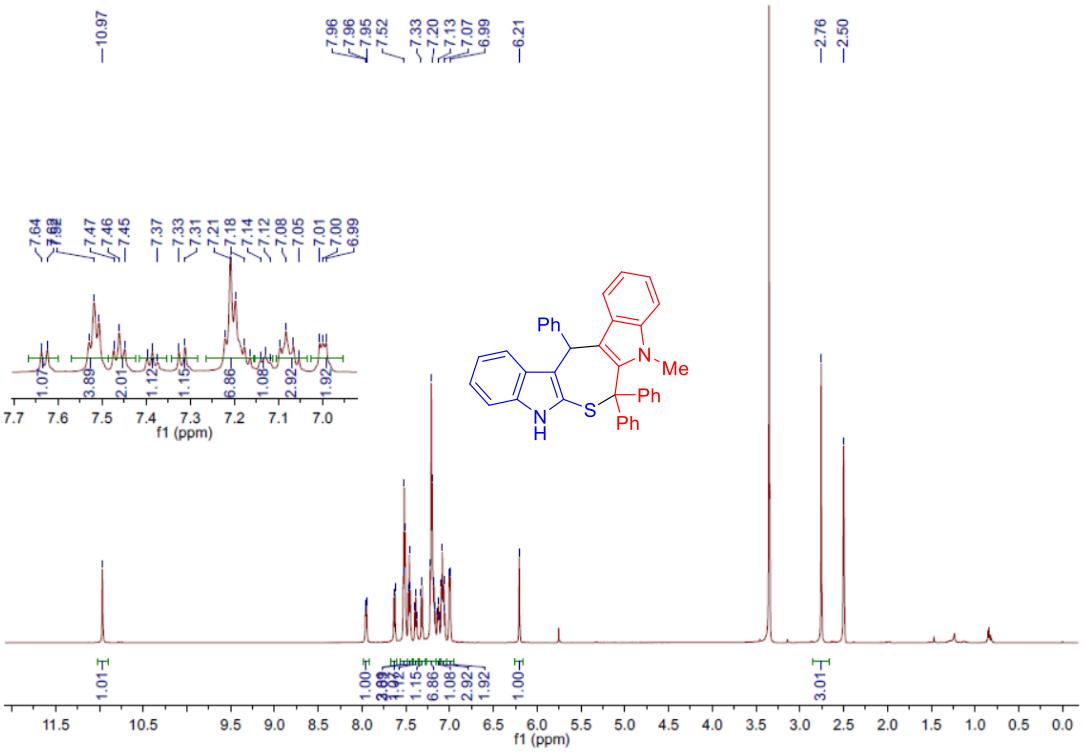
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3sa**



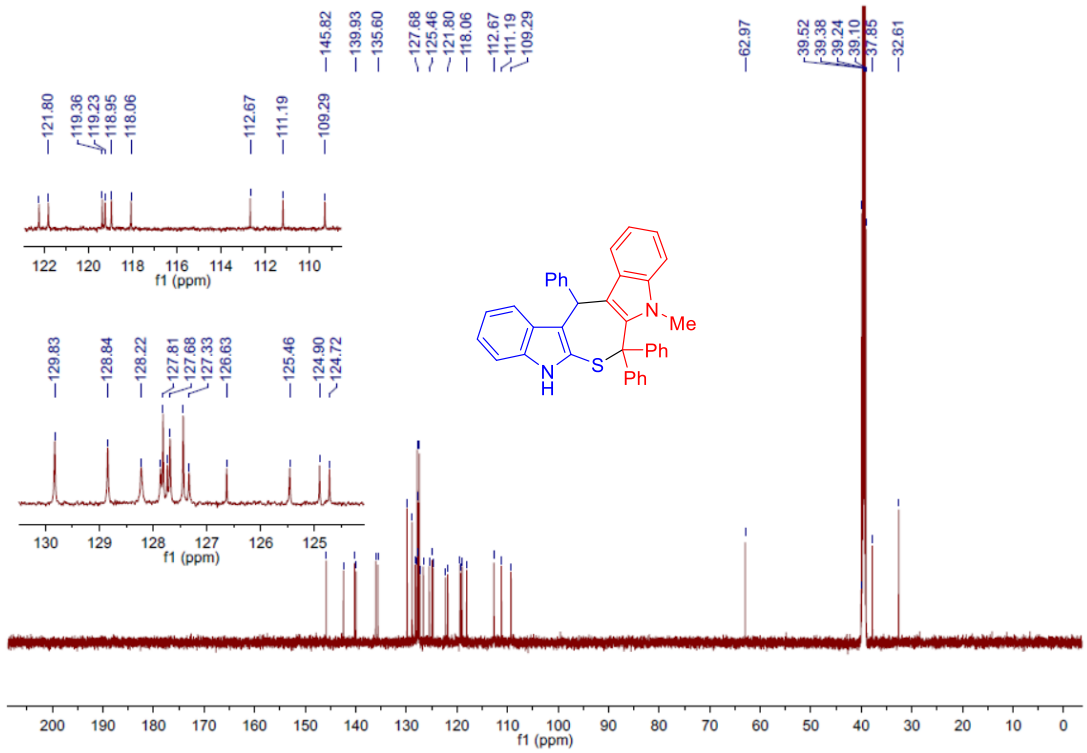
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ta**



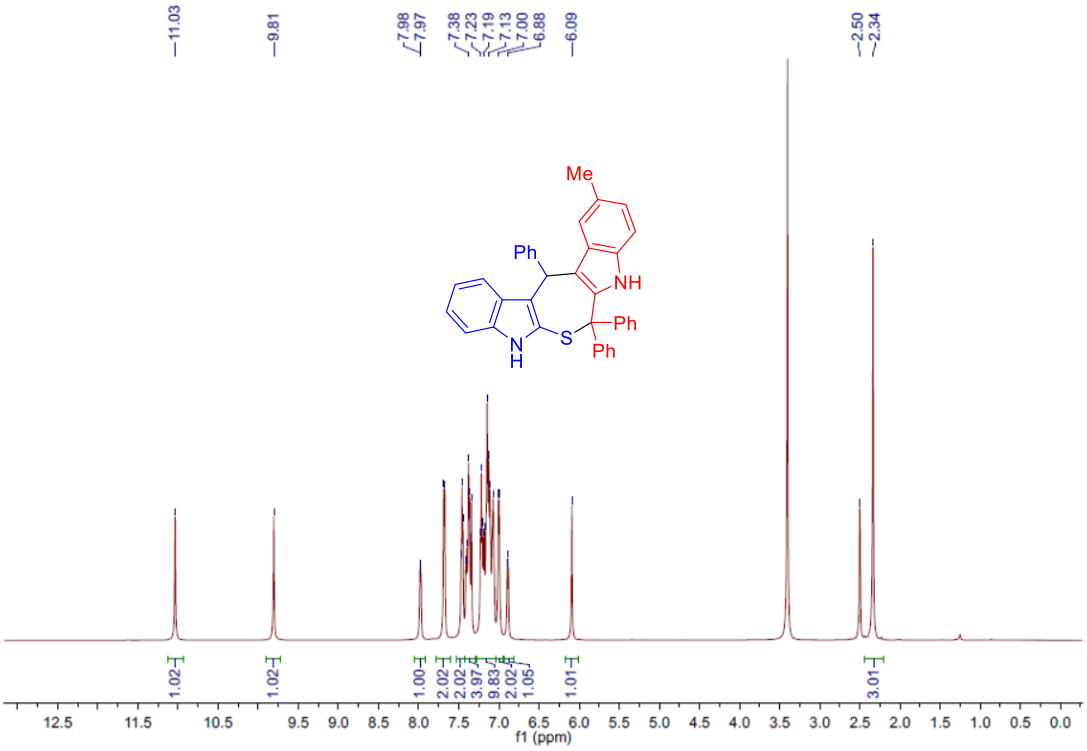
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ta**



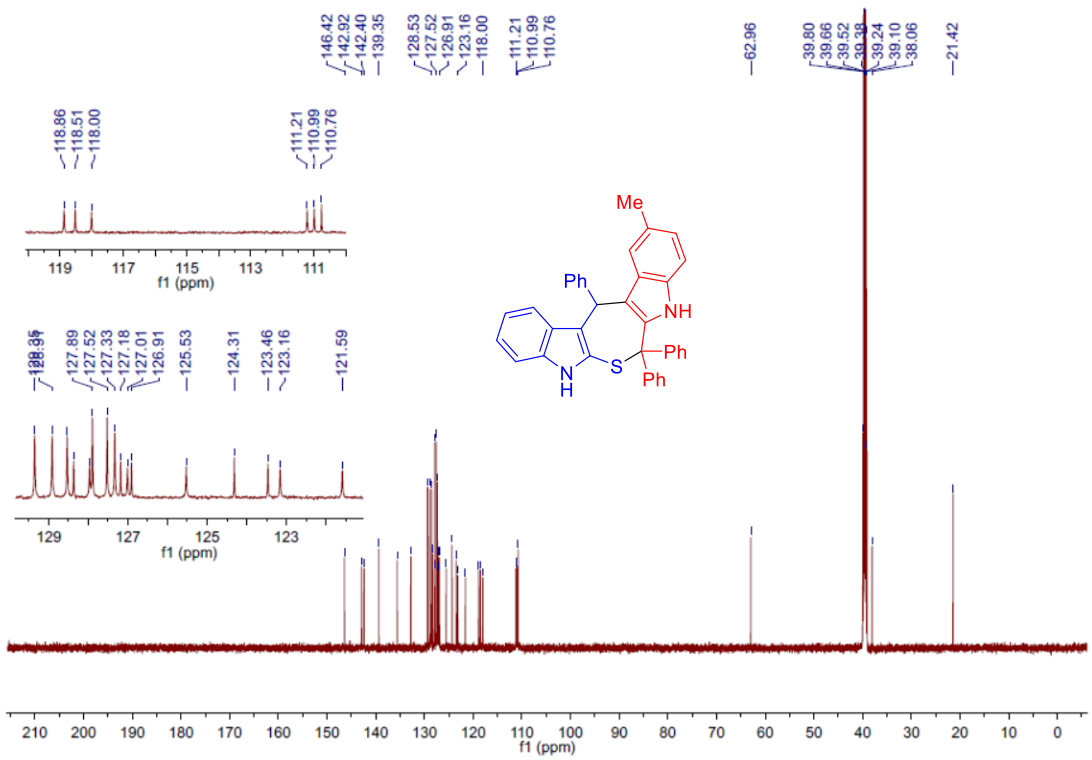
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ab**



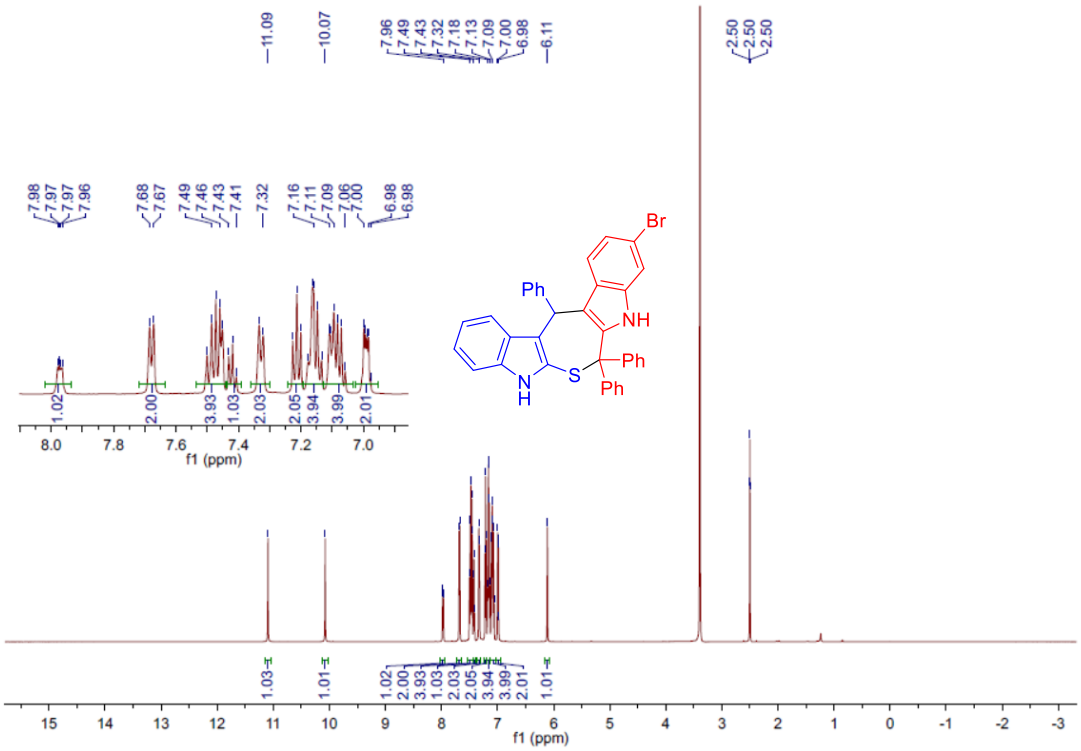
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ab**



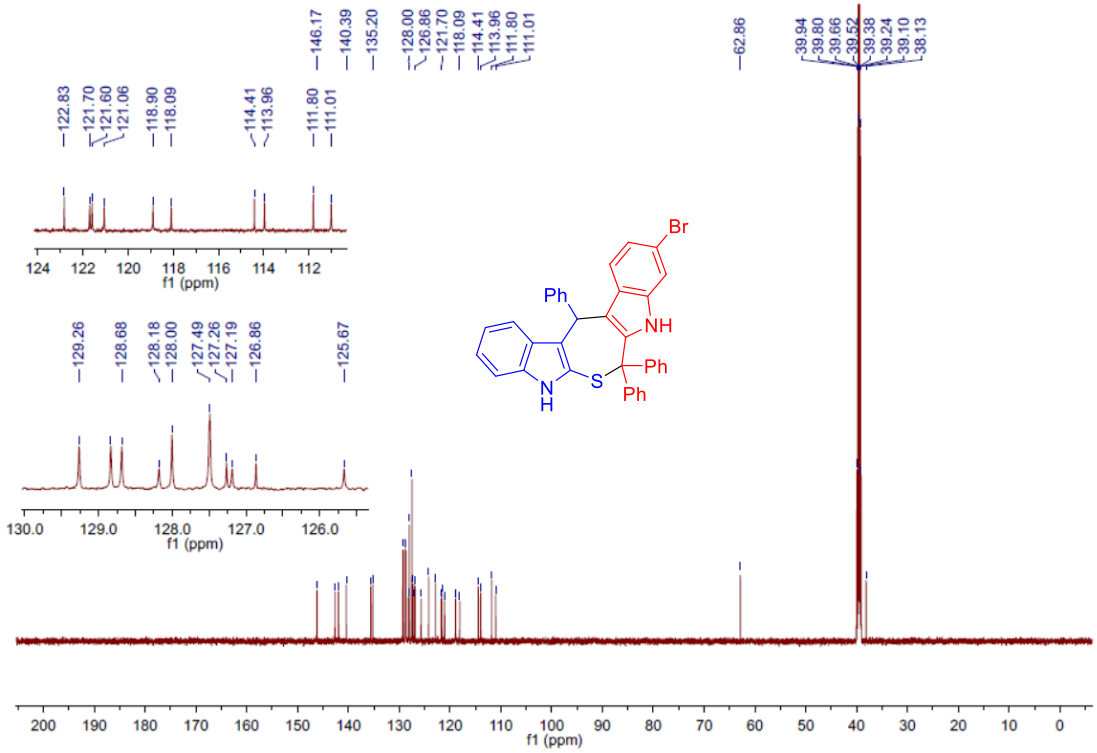
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ac**



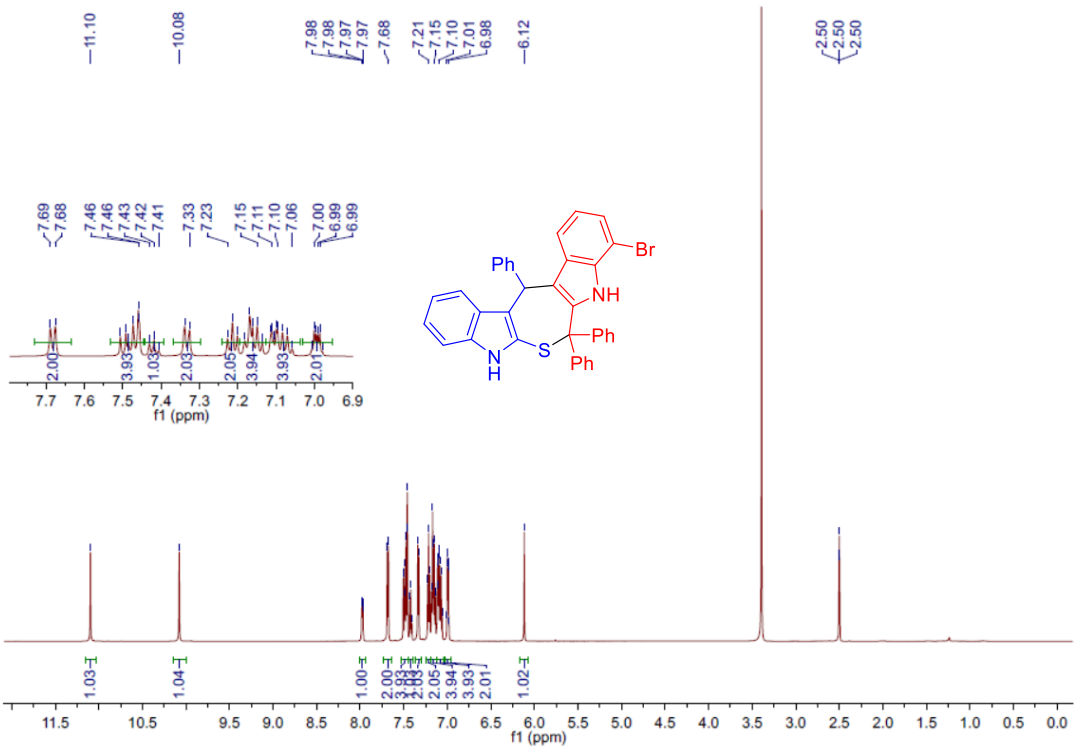
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ac**



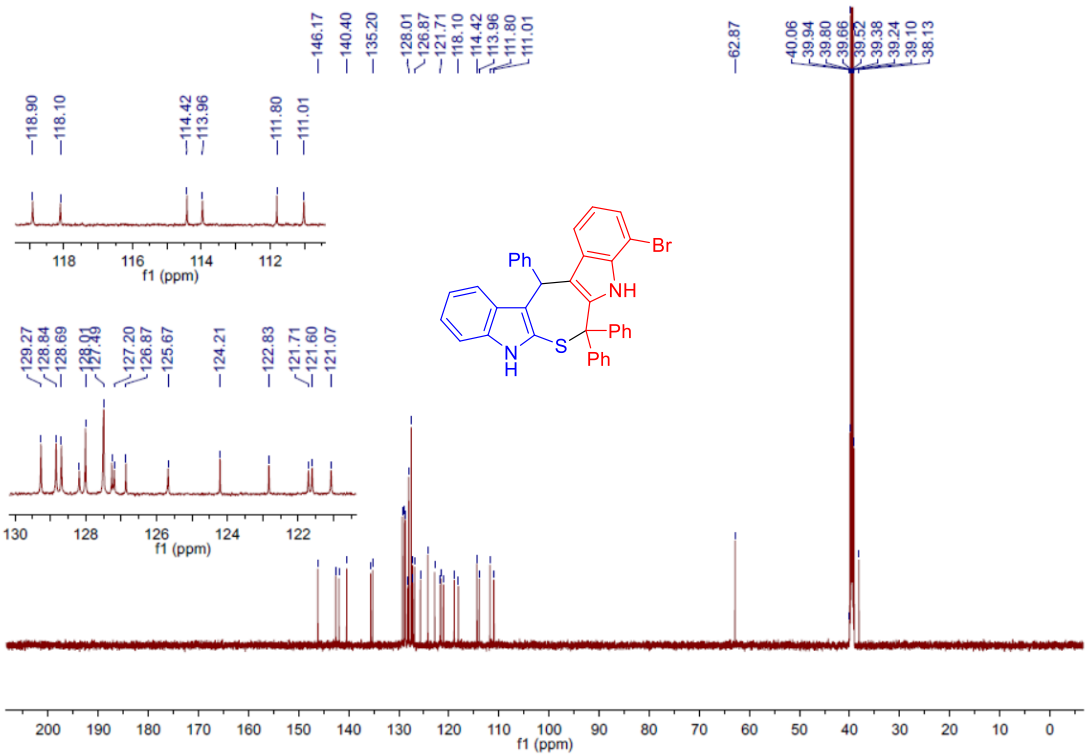
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ad**



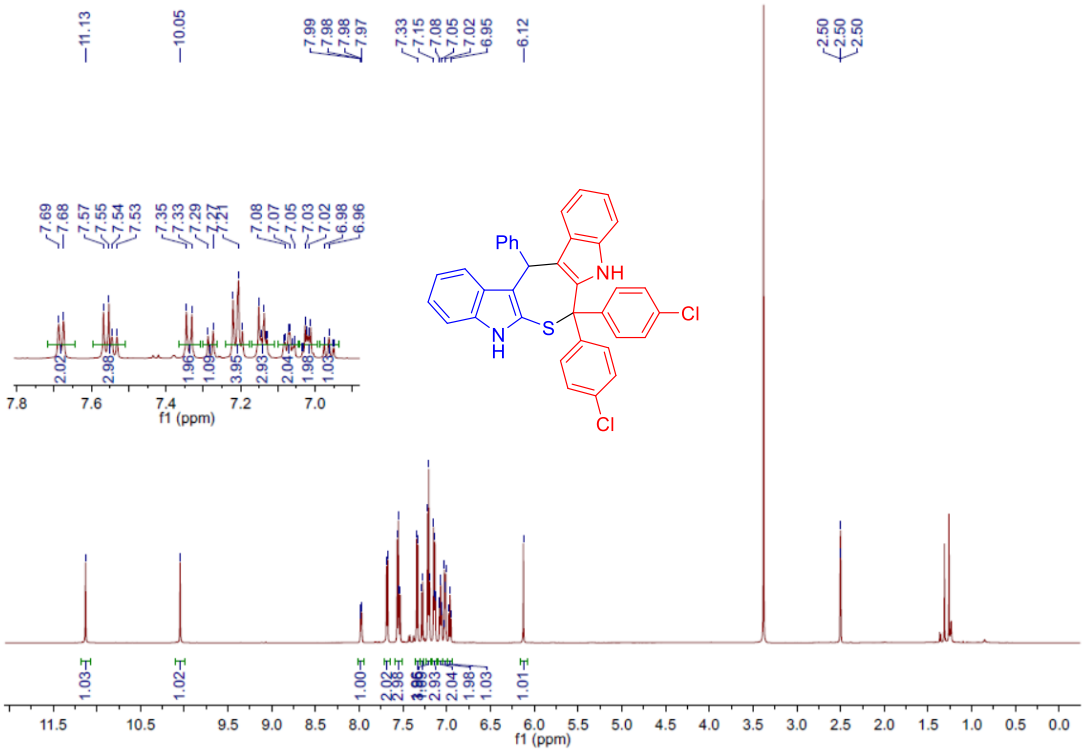
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ad**



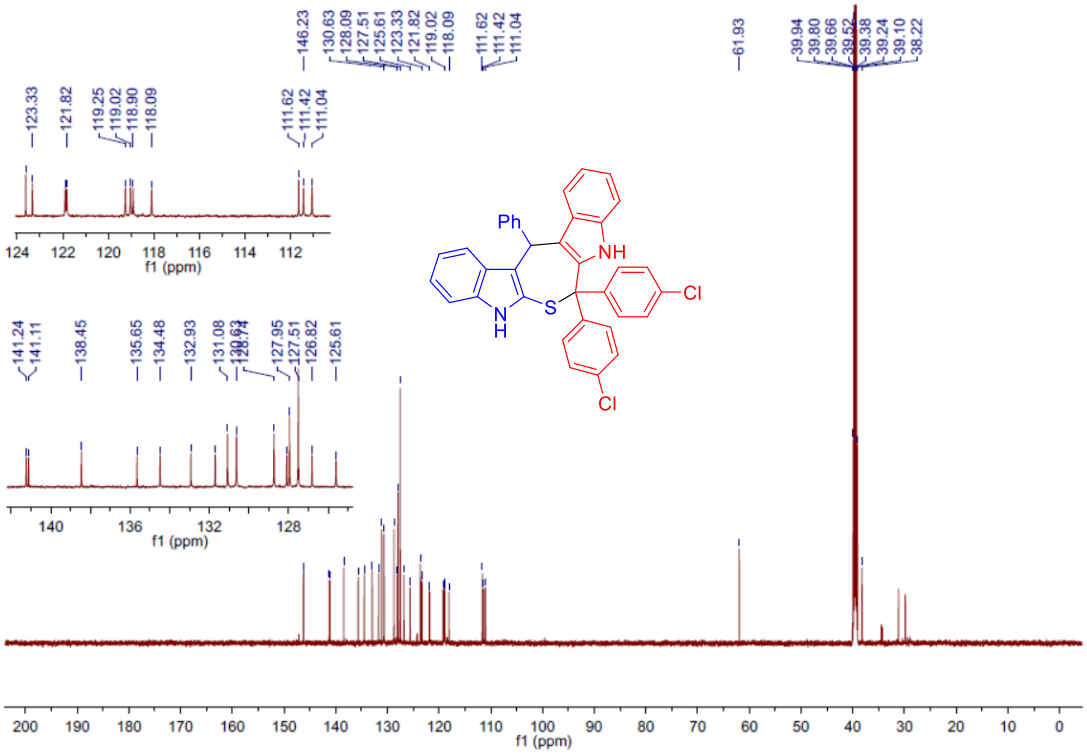
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ae**



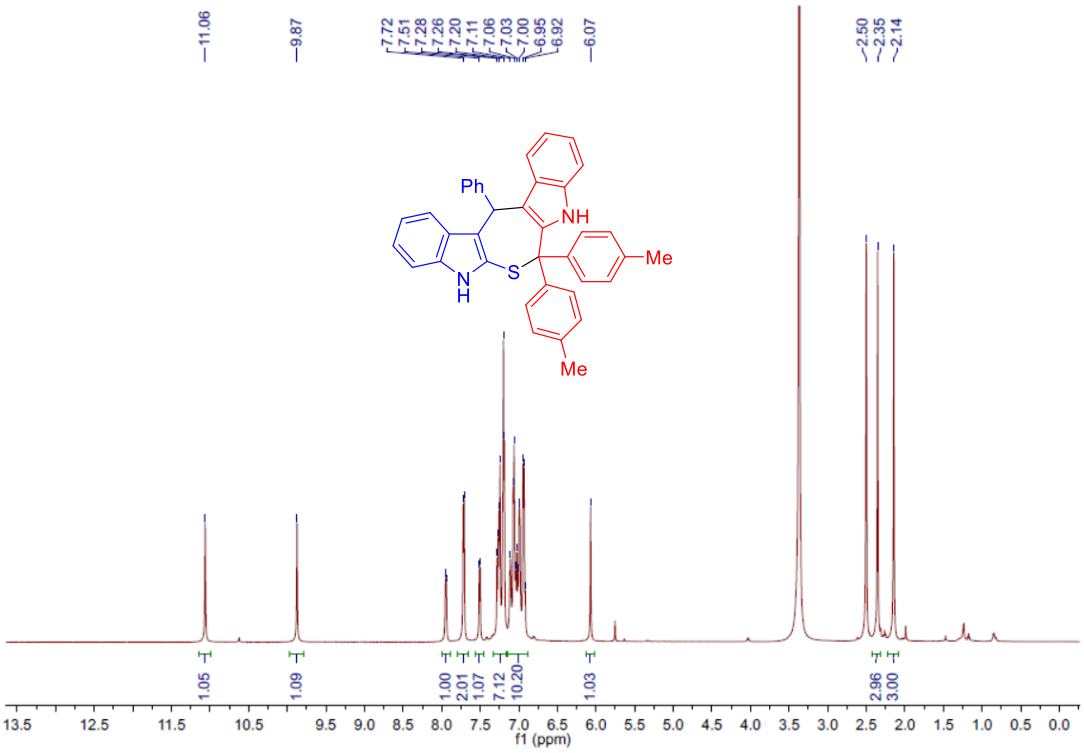
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ae**



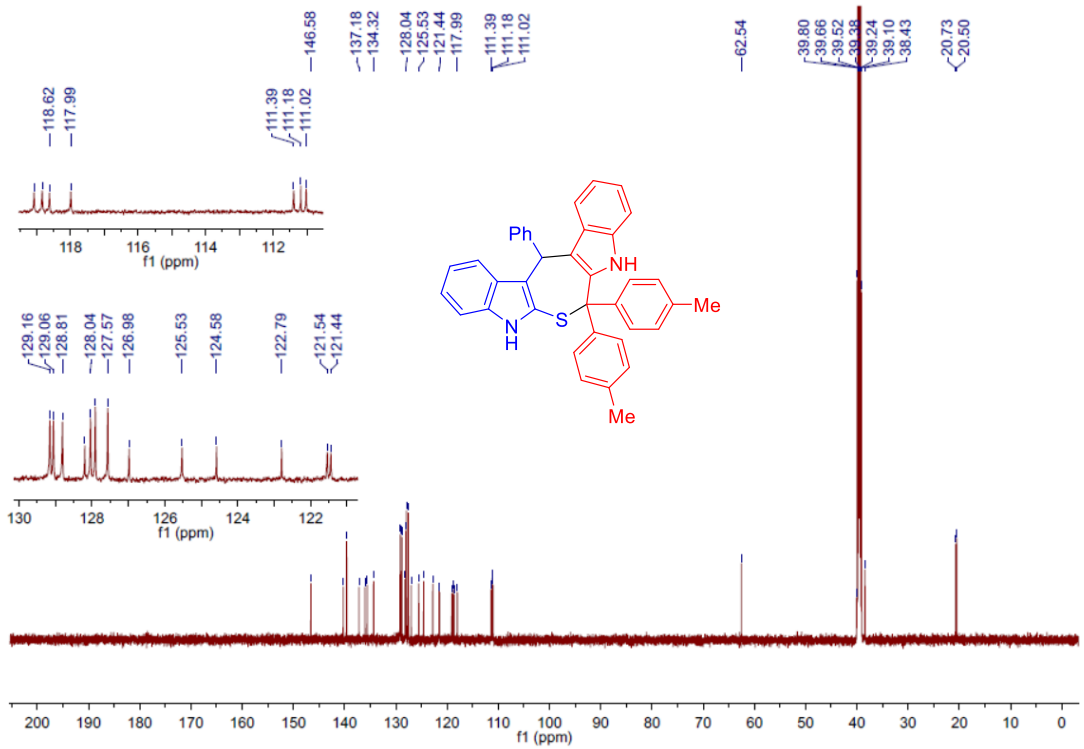
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3af**



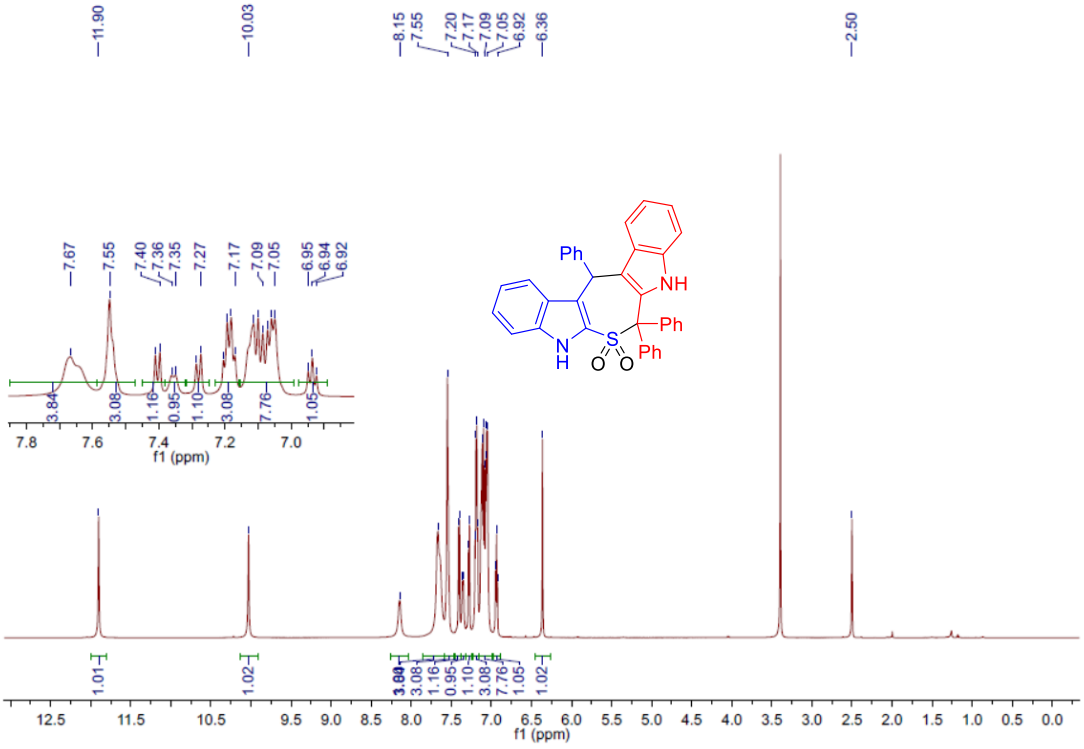
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3af**



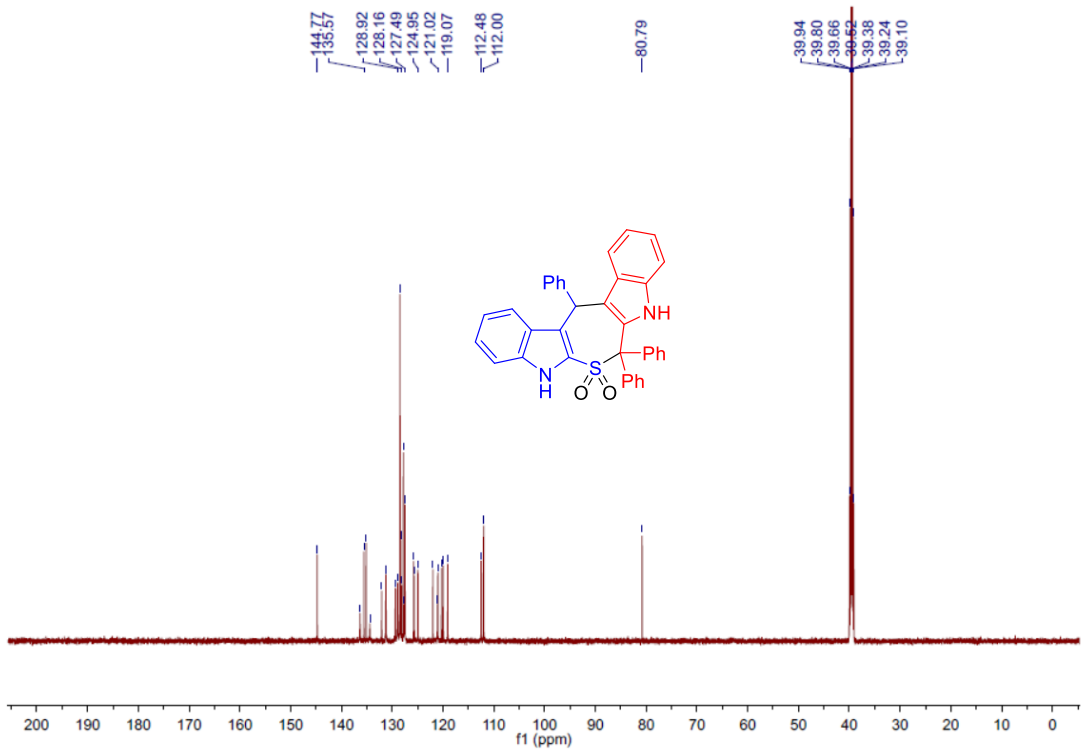
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3ag**



^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **3ag**



^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4**



^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **4**