

Switchable C2/C3 positional selectivity of thioisatins in a three-component domino reaction: combined computational and experimental studies

Baolin Liu,[†] Qingsong Deng,[†] Lei Zhang,^{*‡} Xiangtai Meng^{*†}

[†]Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China.

[‡]Tianjin Engineering Technology Center of Chemical Wastewater Source Reduction and Recycling, School of Science Tianjin Chengjian University, Tianjin 300384, P.R. China

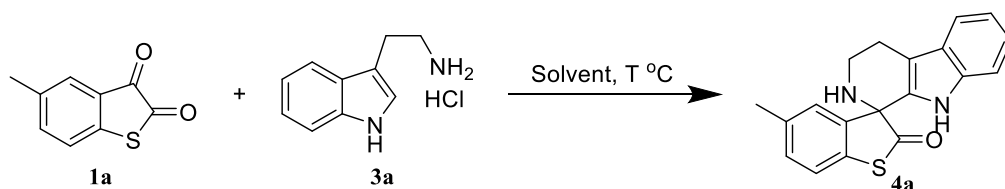
Table of contents:

1. General Experimental Information.....	S2
2. Optimization of Reaction Conditions ^a	S2
3. General procedure for the synthesis of 4	S3
4. General procedure for the synthesis of 5	S3
5. Procedure for gram-scale reaction of 4a	S3
6. Synthetic procedure for 6,7 and 8	S3
7. Characterization of all new compounds.....	S5
8. NMR spectra of all new compounds.....	S17
9. X-ray data collection and structure determinations.....	S48
10. X-ray Crystal Structures.....	S49
11. The results of CO detection by gas chromatography.....	S51
12. Computational Methods.....	S52
13. Computational Details.....	S77
14. References.....	S77

1. General Experimental Information

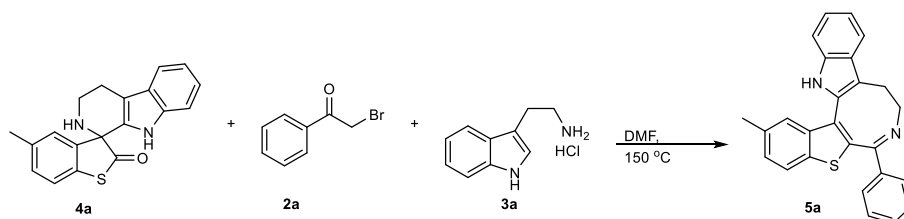
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. The heat source of all reactions that require heating is an oil bath. Unless otherwise stated, all reagents were purchased from commercial suppliers (Aldrich, TCI or Alfa Aesar) and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silicagel. ¹H- and ¹³C-NMR spectrum was recorded at ambient temperature on Bruker 400 instruments. All spectra were referenced to CDCl₃ (¹H NMR δ 7.26 ppm and ¹³C NMR δ 77.00 ppm) and DMSO-d₆ (¹H NMR, δ 2.50 ppm; ¹³C NMR, δ 39.52 ppm). HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. The evolved CO was detected using an online gas chromatography (GC7900, Techcomp) equipped with a 0.5 nm molecular sieve column.

2. Optimization of Reaction Conditions^a



Entry	1a:3a	T (°C)	Solvent	Yield 4a (%) ^b
1	1:2.0	R.T	DMF	N.R
2	1:2.0	60	DMF	42
3	1:2.0	90	DMF	64
4	1:2.0	110	DMF	51
5	1:2.5	90	DMF	89
6	1:3.0	90	DMF	86
7	1:3.5	90	DMF	73
8	1:2.5	90	EA	N.R
9	1:2.5	90	Toluene	N.R
10	1:2.5	90	1,4-dioxane	N.R
11	1:2.5	90	CH ₃ CN	N.R
12	1:2.5	90	THF	N.R
13	1:2.5	90	DCE	N.R
14	1:2.5	90	H ₂ O	N.R
15	1:2.5	90	EtOH	78

^aReaction conditions: **1a** (0.5 mmol) and **3a** (1.25 mmol) in DMF (2 mL) at 90 °C. ^bIsolated yields.



Entry	4a:2a:3a	Yield 5a (%) ^c
1	1.0:2.5:1.0	68
2	1.0:2.5:2.0	72
3	1.0:2.5:3.0	88
4	1.0:2.5:4.0	80
5 ^d	1.0:2.5:3.0	39

Reaction conditions: **4a** (0.3 mmol), **2a** (0.75 mmol) and **3a** (0.9 mmol) in DMF (4 mL) at 150 °C. ^cIsolated yields. ^dHCl replaces **3a**.

3. General procedure for the synthesis of **4**

Under Ar atmosphere, to a solution of **1** (0.50 mmol) in DMF 2 mL was added **3** (1.25 mmol), The reaction mixture was stirred at 90 °C for 4 h. After the mixture was distilled under reduced pressure. The solid was dissolved with DCM and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **4a-p**.

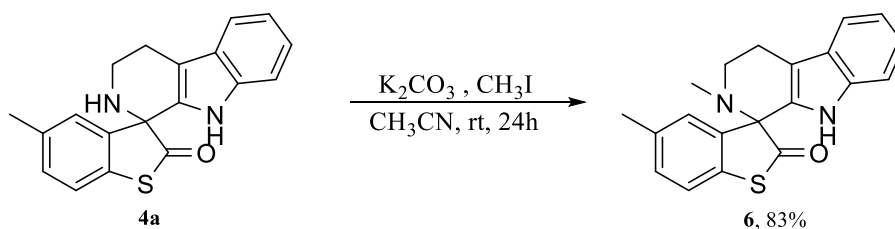
4. General procedure for the synthesis of **5**

Under Ar atmosphere, to a solution of **4** (0.30 mmol) in DMF 5 mL was added **2** (0.75 mmol), and **3a** (0.90 mmol). The reaction mixture was stirred at 150 °C for 6 h. The reaction mixture was extracted with ethyl acetate (25 mL×3). The combined organic layers were dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **5a-l**.

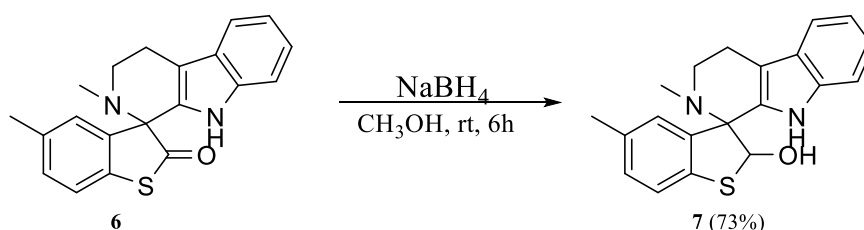
5. Procedure for gram-scale reaction of **4a**

Under Ar atmosphere, to a solution of **1a** (1 g, 5.61 mmol) in DMF 35 mL was added **3a** (2.76 g, 14.03 mmol). The reaction mixture was stirred at 90 °C for 4 h. The reaction mixture was extracted with ethyl acetate (100 mL×3). The combined organic layers were dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:3) to give **4a** (1.41 g, 78%) as yellow solid.

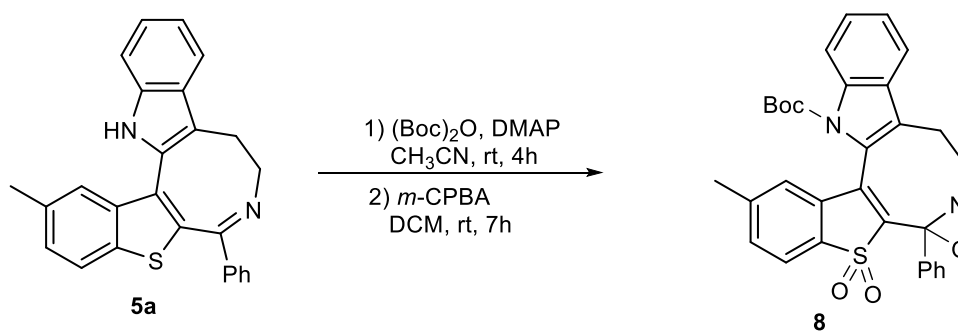
6. Synthetic procedure for **6,7** and **8**



Under Ar atmosphere, to a solution of **4a** (96 mg, 0.30 mmol) and K_2CO_3 (41 mg, 0.30 mmol) in CH_3CN 2 mL was added CH_3I (51 mg, 0.36 mmol). The reaction mixture was stirred at room temperature for 24 h. After the reaction is complete (monitored by TLC), the reaction mixture was extracted with ethyl acetate (25 mL \times 3). The combined organic layers were dried over MgSO_4 and concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) to give **6** (83 mg, 83%) as yellow solid.



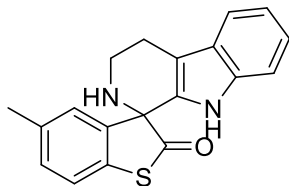
Under Ar atmosphere, to a solution of **6** (100 mg, 0.30 mmol) in CH_3OH 2 mL was added NaBH_4 (11 mg, 0.303 mmol). The reaction mixture was stirred at room temperature for 6 h. After the reaction is complete (monitored by TLC), the solvent was removed in vacuum. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) to give **7** (74 mg, 73%) as yellow solid.



Synthetic procedure for 8: Under Ar atmosphere, to a CH_3CN (2 mL) solution of **5a** (39 mg, 0.1 mmol) was added $(\text{Boc})_2\text{O}$ (65 mg, 0.3 mmol) and DMAP (1.2 mg, 0.01 mmol). The resulting mixture was stirred at room temperature for 4 h. After the reaction completed (monitored by TLC), the solvent was removed under reduce pressure, The crude product was used for the next step without further purification. Under Ar atmosphere, to a dry DCM (4 mL) solution of reaction mixture was added *m*-CPBA (69 mg, 0.4 mmol). The resulting mixture was stirred at room temperature for 7 h. After the reaction completed (monitored by TLC), the residue was dissolved by 50 mL DCM and then washed with saturated sodium bicarbonate solution. The combined organic layers were dried over MgSO_4 and concentrated. The residue was

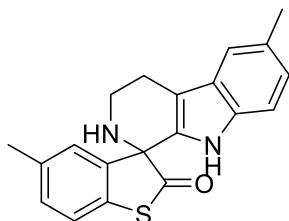
purified by column chromatography (ethyl acetate : petroleum ether = 1:3) to give **8** (29 mg, 54%) as white solid.

7. Characterization of all new compounds



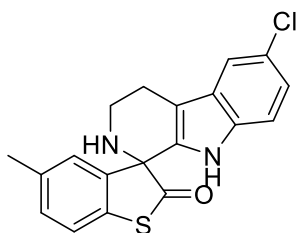
5-methyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4a).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 143 mg (yield 89%); mp 210-212 °C; IR (KBr) 3303, 3078, 2926, 1710, 1456, 1298, 1098, 917, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.6$ Hz, 1H), 7.49 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.24 – 7.11 (m, 4H), 6.97 (s, 1H), 3.91 – 3.73 (m, 1H), 3.35 – 3.24 (m, 1H), 3.11 – 2.98 (m, 1H), 2.97 – 2.88 (m, 1H), 2.31 (s, 1H), 2.25 (s, 3H) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 204.0, 137.9, 137.3, 136.2, 131.2, 130.7, 129.6, 127.4, 126.9, 123.2, 122.8, 119.7, 118.8, 112.6, 111.1, 70.6, 39.3, 21.6, 21.1 ppm.; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{OS}^+$ 321.1056, found 321.1056.



5,6'-dimethyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4b).

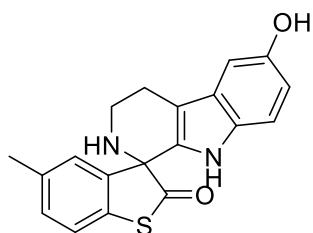
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 119 mg (yield 71%); mp 159-161 °C; IR (KBr) 3319, 2847, 2359, 1697, 1453, 1205, 1073, 813 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37 (s, 2H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.22 – 7.15 (m, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 7.00 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.98 – 6.93 (m, 1H), 3.90 – 3.70 (m, 1H), 3.38 – 3.20 (m, 1H), 3.07 – 2.95 (m, 1H), 2.94 – 2.82 (m, 1H), 2.45 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 204.1, 138.2, 137.3, 134.5, 131.0, 130.6, 129.8, 129.0, 127.4, 127.1, 124.2, 123.1, 118.4, 112.1, 110.7, 70.7, 39.3, 21.6, 21.4, 21.0 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{OS}^+$ 335.1213, found 335.1220.



6'-chloro-5-methyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4c).

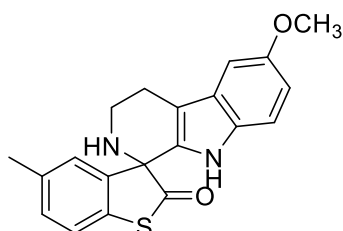
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 103 mg (yield 58%); mp 167-169 °C; IR (KBr) 3314, 2939, 1711, 1450, 1300, 1062, 928, 802 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 2H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.23 – 7.15 (m, 1H), 7.11 (d, $J = 1.2$ Hz, 2H), 7.00 – 6.91 (m, 1H), 3.93 – 3.75 (m, 1H), 3.35 – 3.23 (m, 1H), 3.06 – 2.93 (m, 1H), 2.92 – 2.81 (m, 1H), 2.30 (s, 1H), 2.26 (s, 3H) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 203.9, 137.8,

137.5, 134.5, 131.3, 131.2, 130.7, 128.0, 127.3, 125.5, 123.3, 123.0, 118.4, 112.3, 112.1, 70.6, 39.1, 21.5, 21.1 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{16}ClN_2OS^+$ 355.0666, found 355.0682.



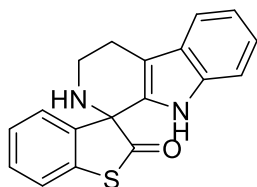
6'-hydroxy-5-methyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4d).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:1) as a yellow solid: 94 mg (yield 56%); mp 155-157 °C; IR (KBr) 3295, 2963, 1714, 1468, 1262, 1075, 1021, 797 cm^{-1} ; 1H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 8.67 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.27 – 7.19 (m, 1H), 6.97 (d, $J = 8.8$ Hz, 1H), 6.91 – 6.84 (m, 1H), 6.77 (d, $J = 2.4$ Hz, 1H), 6.56 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.67 (s, 1H), 3.48 (td, $J = 12.4, 4.0$ Hz, 1H), 3.05 (dd, $J = 12.0, 4.8$ Hz, 1H), 2.85 – 2.72 (m, 1H), 2.66 – 2.57 (m, 1H), 2.22 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO) δ 205.1, 150.5, 139.4, 136.1, 131.2, 130.8, 130.4, 127.2, 126.9, 123.1, 111.7, 111.7, 109.9, 102.1, 70.4, 38.4, 21.4, 20.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{17}N_2O_2S^+$ 337.1005, found 337.1006.



6'-methoxy-5-methyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4e).

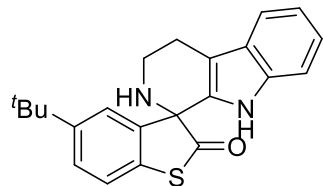
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 112 mg (yield 64%); mp 170-172 °C; IR (KBr) 3293, 2842, 1719, 1470, 1217, 1025, 950, 809 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.22 – 7.17 (m, 1H), 7.10 (d, $J = 8.8$ Hz, 1H), 7.02 (d, $J = 2.4$ Hz, 1H), 6.98 – 6.96 (m, 1H), 6.82 (dd, $J = 8.8, 2.4$ Hz, 1H), 3.86 (s, 3H), 3.85 – 3.79 (m, 1H), 3.33 – 3.21 (m, 1H), 3.07 – 2.96 (m, 1H), 2.93 – 2.83 (m, 1H), 2.30 (s, 1H), 2.25 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 204.1, 154.2, 138.1, 137.3, 131.3, 131.1, 130.6, 130.5, 127.4, 127.3, 123.2, 112.8, 112.3, 111.8, 100.8, 70.7, 56.0, 39.3, 21.7, 21.1 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_2O_2S^+$ 351.1162, found 351.1167.



2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4f).

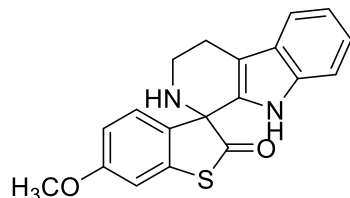
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a white solid: 106 mg (yield 69%); mp 140-142 °C; IR (KBr) 3175, 2931, 1701, 1451, 1298, 1078, 880, 751 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J = 7.2$ Hz, 1H), 7.48 (s, 1H), 7.45 – 7.36 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.16 (dd, $J = 17.2, 8.8$ Hz, 4H), 3.87 – 3.79 (m, 1H), 3.34 – 3.23 (m, 1H), 3.09 – 2.98

(m, 1H), 2.97 – 2.87 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 203.6, 138.2, 136.3, 134.3, 130.3, 129.5, 127.2, 126.9, 123.4, 122.8, 119.7, 118.8, 112.7, 111.1, 70.6, 39.2, 21.6 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2\text{OS}^+$ 307.0900, found 307.0891.



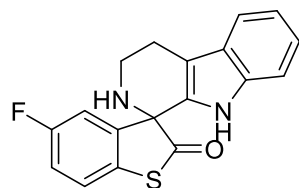
5-(tert-butyl)-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4g).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 145 mg (yield 80%); mp 177-179 °C; IR (KBr) 3309, 2957, 1715, 1456, 1362, 1070, 913, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.57 (m, 1H), 7.49 (s, 1H), 7.44 (dd, J = 8.0, 2.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.24 – 7.11 (m, 4H), 3.98 – 3.73 (m, 1H), 3.40 – 3.23 (m, 1H), 3.16 – 2.99 (m, 1H), 2.98 – 2.86 (m, 1H), 1.23 (s, 9H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 204.3, 150.9, 137.8, 136.3, 130.9, 129.8, 127.7, 127.0, 123.5, 123.0, 122.6, 119.6, 118.7, 112.5, 111.1, 71.0, 39.3, 34.8, 31.3, 21.6 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{OS}^+$ 363.1526, found 363.1522.



6-methoxy-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4h).

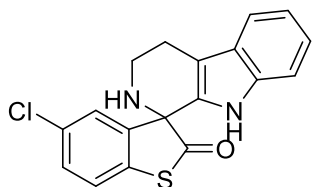
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 122 mg (yield 72%); mp 160-162 °C; IR (KBr) 3150, 2936, 1702, 1574, 1493, 1241, 1032, 751 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 7.6 Hz, 1H), 7.48 (s, 1H), 7.23 – 7.10 (m, 3H), 7.05 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 6.72 (dd, J = 8.4, 2.4 Hz, 1H), 3.83 (s, 3H), 3.86 – 3.78 (m, 1H), 3.35 – 3.23 (m, 1H), 3.06 – 2.97 (m, 1H), 2.94 – 2.87 (m, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 203.6, 161.0, 136.2, 135.5, 129.88, 129.86, 127.7, 127.0, 122.7, 119.7, 118.8, 113.0, 112.7, 111.1, 109.0, 70.2, 55.6, 39.2, 21.6 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_2\text{S}^+$ 337.1005, found 337.1001.



5-fluoro-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4i).

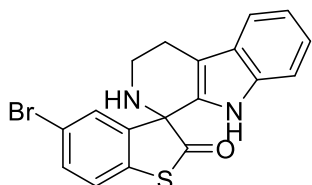
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a white solid: 117 mg (yield 72%); mp 159-161 °C; IR (KBr) 3141, 2932, 1714, 1456, 1264, 1076, 833, 739 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 10.66 (s, 1H), 7.69 (dd, J = 8.8, 5.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 6.8 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.86 (dd, J = 8.8, 2.8 Hz, 1H), 3.90 (s, 1H), 3.60 – 3.45 (m, 1H), 3.19 – 3.05 (m, 1H), 2.97 – 2.81 (m, 1H), 2.74 (dd, J = 15.2, 2.8 Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO) δ 204.8, 161.3 (d, $J_{\text{C-F}}$ = 241.8 Hz), 141.4 (d, $J_{\text{C-F}}$ = 7.5 Hz), 136.4, 130.1, 129.2 (d, $J_{\text{C-F}}$ = 2.8 Hz), 126.2, 125.0 (d, $J_{\text{C-F}}$ = 7.7 Hz), 121.7, 118.6, 118.2, 117.1 (d, $J_{\text{C-F}}$ = 22.5 Hz), 113.9 (d, $J_{\text{C-F}}$ = 23.6 Hz), 111.4, 111.1, 70.7 (d,

$J_{C-F} = 1.9$ Hz), 38.3, 21.2 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{14}FN_2OS^+$ 325.0805, found 325.0810.



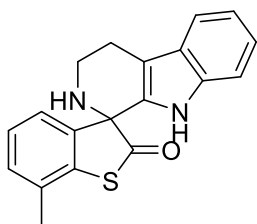
5-chloro-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4j).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a white solid: 120 mg (yield 70%); mp 135-137 °C; IR (KBr) 3195, 2978, 1714, 1450, 1259, 1089, 827, 738 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 7.6$ Hz, 1H), 7.50 (s, 1H), 7.36 (d, $J = 2.0$ Hz, 2H), 7.25 – 7.11 (m, 4H), 3.88 – 3.74 (m, 1H), 3.47 – 3.22 (m, 1H), 3.14 – 2.97 (m, 1H), 2.96 – 2.86 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.9, 139.9, 136.3, 133.2, 132.4, 130.5, 128.8, 127.2, 126.8, 124.5, 123.0, 119.9, 118.9, 112.9, 111.1, 70.9, 39.3, 21.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{14}ClN_2OS^+$ 341.0510, found 341.0515.



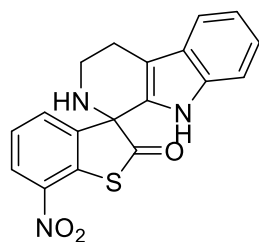
5-bromo-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4k).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 123 mg (yield 64%); mp 150-152 °C; IR (KBr) 3165, 2941, 1675, 1453, 1296, 1077, 842, 754 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 7.2$ Hz, 2H), 7.50 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.30 (d, $J = 2.0$ Hz, 1H), 7.28 (s, 1H), 7.21 – 7.12 (m, 3H), 3.86 – 3.74 (m, 1H), 3.33 – 3.22 (m, 1H), 3.08 – 2.98 (m, 1H), 2.96 – 2.87 (m, 1H), 2.30 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 202.7, 140.1, 136.3, 133.3, 133.1, 129.9, 128.7, 126.7, 124.7, 123.0, 120.7, 119.8, 118.8, 112.9, 111.1, 70.8, 39.2, 21.5 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{14}BrN_2OS^+$ 385.0005, found 385.0013.



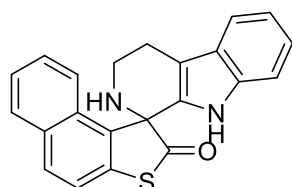
7-methyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4l).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 126 mg (yield 79%); mp 156-158 °C; IR (KBr) 3164, 2938, 1716, 1450, 1298, 1063, 923, 742 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J = 7.6$ Hz, 1H), 7.44 (s, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.10 (m, 3H), 6.98 (d, $J = 7.6$ Hz, 1H), 3.88 – 3.76 (m, 1H), 3.36 – 3.25 (m, 1H), 3.06 – 2.97 (m, 1H), 2.95 – 2.88 (m, 1H), 2.39 (s, 3H), 2.29 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.7, 138.2, 136.3, 134.1, 132.8, 131.1, 129.7, 127.0, 126.9, 123.9, 122.7, 119.7, 118.8, 112.6, 111.1, 71.3, 39.3, 21.7, 20.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{17}N_2OS^+$ 321.1056, found 321.1056.



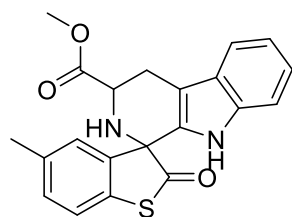
7-nitro-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (4m).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a brown solid: 115 mg (yield 65%); mp 170-172 °C; IR (KBr) 3068, 2921, 1716, 1516, 1441, 1126, 978, 827 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 10.64 (s, 1H), 8.43 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.57 – 7.47 (m, 3H), 7.17 (d, $J = 8.0$ Hz, 1H), 7.10 – 6.98 (m, 2H), 4.10 (s, 1H), 3.60 (td, $J = 12.0, 4.0$ Hz, 1H), 3.14 (dd, $J = 12.0, 5.2$ Hz, 1H), 2.97 – 2.83 (m, 1H), 2.78 (dd, $J = 15.2, 2.8$ Hz, 1H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO) δ 205.3, 142.7, 141.9, 136.3, 133.0, 132.9, 129.7, 127.7, 126.1, 126.0, 121.9, 118.8, 118.3, 111.3, 111.1, 68.5, 38.3, 21.2 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{O}_3\text{S}^+$ 352.0750, found 352.0755.



2',3',4',9'-tetrahydro-2H-spiro[naphtho[2,1-b]thiophene-1,1'-pyrido[3,4-b]indol]-2-one (4n).

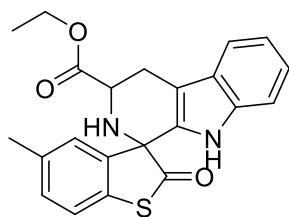
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 137 mg (yield 77%); mp 181-183 °C; IR (KBr) 3266, 2901, 1659, 1508, 1432, 1131, 820, 737 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 10.87 (s, 1H), 9.04 (d, $J = 8.4$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 7.77 – 7.71 (m, 1H), 7.66 – 7.56 (m, 2H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.11 – 7.02 (m, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 4.30 (d, $J = 2.4$ Hz, 1H), 3.49 – 3.39 (m, 1H), 3.03 (td, $J = 11.2, 4.4$ Hz, 1H), 2.88 – 2.70 (m, 2H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO) δ 199.7, 157.2, 137.5, 136.2, 131.07, 131.05, 130.6, 129.9, 129.0, 126.0, 125.7, 123.4, 121.9, 121.8, 120.6, 118.6, 118.0, 111.3, 81.8, 42.6, 21.2 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_3\text{S}^+$ 357.1056, found 357.1063.



methyl-5-methyl-2-oxo-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indole]-3'-carboxylate (4o).

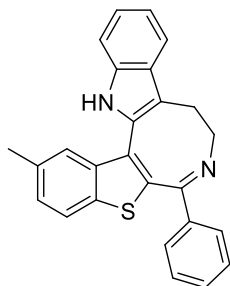
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 152 mg (yield 80%); mp 122-124 °C; IR (KBr) 3389, 2897, 1729, 1445, 1336, 1231, 1143, 1006, 925, 836, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.6$ Hz, 1H), 7.52 (s, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.25 – 7.11 (m, 4H), 7.06 – 6.99 (m, 1H), 4.85 (dd, $J = 11.2, 4.4$ Hz, 1H), 3.82 (s, 3H), 3.36 (dd, $J = 15.6, 4.4$ Hz, 1H), 3.04 (dd, $J = 15.2, 11.2$ Hz, 2H), 2.25 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 204.7, 172.9, 137.5, 137.1, 136.6, 131.4, 130.6, 130.0, 128.0, 126.7, 123.2, 123.0,

120.0, 118.8, 111.5, 111.2, 70.6, 52.4, 51.5, 24.9, 21.1 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{21}H_{19}N_2O_3S^+$ 378.1032, found 378.1032.



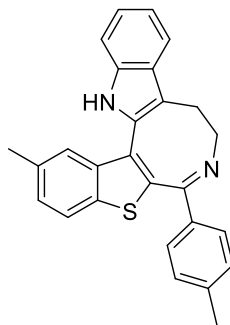
ethyl-5-methyl-2-oxo-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indole]-3'-carboxylate (4p).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 155 mg (yield 79%); mp 96-98 °C; IR (KBr) 3336, 2925, 1711, 1460, 1335, 1274, 1182, 1034, 923, 811, 741 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 7.2$ Hz, 1H), 7.49 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.25 – 7.12 (m, 4H), 7.02 (s, 1H), 4.82 (dd, $J = 10.8, 4.0$ Hz, 1H), 4.32 – 4.24 (m, 2H), 3.36 (dd, $J = 15.6, 4.4$ Hz, 1H), 3.03 (dd, $J = 15.2, 11.2$ Hz, 2H), 2.25 (s, 3H), 1.35 (t, $J = 6.8$ Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 204.7, 172.5, 137.4, 137.1, 136.5, 131.3, 130.5, 130.0, 128.0, 126.7, 123.1, 122.9, 119.9, 118.8, 111.5, 111.2, 70.6, 61.4, 51.4, 24.9, 21.0, 14.2 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{21}N_2O_3S^+$ 393.1267, found 393.1269.



(Z)-2-methyl-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5a).

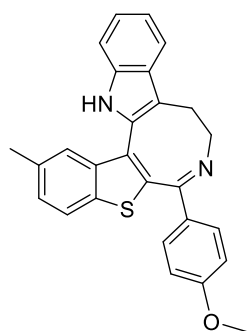
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid: 104 mg (yield 88%); mp 266-268 °C; IR (KBr) 3207, 3046, 2885, 2337, 1699, 1576, 1458, 1296, 1215, 929, 802, 740, 668, 596 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.84 (s, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.71 – 7.66 (m, 2H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.42 – 7.29 (m, 5H), 7.29 – 7.20 (m, 1H), 7.18 – 7.12 (m, 1H), 4.40 – 4.23 (m, 2H), 3.74 – 3.61 (m, 1H), 3.37 – 3.23 (m, 1H), 2.51 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 139.2, 138.2, 137.8, 135.8, 135.2, 133.6, 130.4, 130.0, 129.1, 128.6, 128.0, 127.5, 126.7, 123.7, 123.0, 122.6, 119.7, 119.2, 112.3, 110.6, 51.7, 25.8, 21.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{20}N_2S^+$ 393.1420, found 393.1421.



(Z)-2-methyl-6-(p-tolyl)-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5b).

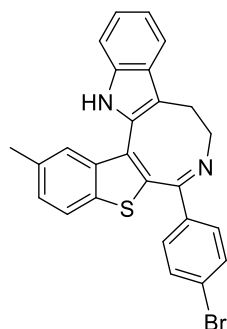
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow

solid: 108 mg (yield 89%); mp 187-189 °C; IR (KBr) 3345, 3149, 2925, 2338, 1592, 1458, 1297, 1122, 1012, 799, 737, 652 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 11.28 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 3H), 7.42 – 7.32 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.09 (m, 1H), 7.07 – 6.98 (m, 1H), 4.25 – 4.20 (m, 1H), 4.07 – 3.97 (m, 1H), 3.51 – 3.40 (m, 1H), 3.24 – 3.15 (m, 1H), 2.46 (s, 3H), 2.29 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, DMSO) δ 162.8, 140.5, 138.0, 136.8, 136.2, 135.7, 134.6, 132.1, 130.4, 128.8, 128.3, 128.0, 127.5, 126.6, 124.4, 122.6, 122.2, 118.8, 118.5, 111.2, 110.1, 51.0, 25.4, 21.6, 20.9 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₇H₂₂N₂S⁺ 407.1576, found 407.1576.



(Z)-6-(4-methoxyphenyl)-2-methyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5c).

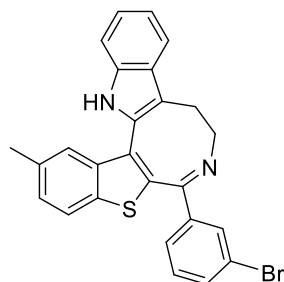
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a white solid: 106 mg (yield 84%); mp 255-257 °C; IR (KBr) 3343, 3149, 2832, 2362, 1595, 1510, 1442, 1259, 1176, 1032, 832, 736, 649 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 7.84 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.57 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.17 – 7.12 (m, 1H), 6.84 – 6.80 (m, 2H) 4.33 – 4.20 (m, 2H), 3.79 (s, 3H), 3.71 – 3.61 (m, 1H), 3.28 (dt, *J* = 16.8, 2.8 Hz, 1H), 2.50 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.3, 161.4, 138.3, 137.7, 135.8, 135.1, 133.7, 132.0, 130.2, 129.8, 129.1, 127.5, 126.8, 123.7, 122.9, 122.5, 119.6, 119.2, 113.3, 112.3, 110.5, 55.3, 51.4, 25.8, 21.6 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₇H₂₂N₂OS⁺ 423.1526, found 423.1527.



(Z)-6-(4-bromophenyl)-2-methyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5d).

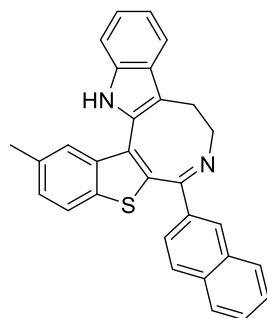
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 114 mg (yield 81%); mp 206-208 °C; IR (KBr) 3403, 3172, 3081, 2885, 2365, 1585, 1486, 1296, 1077, 1008, 924, 802, 738, 609 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.84 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.47 – 7.42 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.18 – 7.14 (m, 1H), 4.36 – 4.31 (m, 1H), 4.30 – 4.22 (m, 1H), 3.71 – 3.61 (m, 1H), 3.31 (dt, *J* = 16.8, 2.8 Hz, 1H), 2.51 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.2, 138.2, 138.0, 137.8, 135.8, 135.3, 132.7, 131.2, 130.2, 130.2, 129.0, 127.7,

126.6, 125.0, 123.8, 123.1, 122.6, 119.8, 119.2, 112.3, 110.6, 51.8, 25.7, 21.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{19}BrN_2S^+$ 471.0525, found 471.0525.



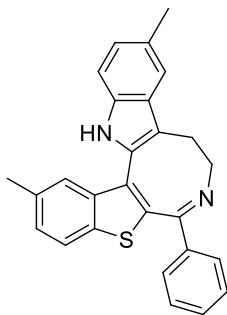
(Z)-6-(3-bromophenyl)-2-methyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5e).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 110 mg (yield 78%); mp 169-171 °C; IR (KBr) 3386, 3152, 3061, 2865, 2351, 1645, 1462, 1314, 1209, 1063, 880, 790, 731, 638 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.87 – 7.80 (m, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.37 – 7.29 (m, 1H), 7.24 (d, $J = 1.2$ Hz, 1H), 7.23 – 7.11 (m, 2H), 4.40 – 4.30 (m, 1H), 4.33 – 4.22 (m, 1H), 3.72 – 3.60 (m, 1H), 3.31 (dt, $J = 16.8, 2.8$ Hz, 1H), 2.51 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9, 141.1, 138.1, 137.8, 135.8, 135.4, 133.2, 132.6, 131.5, 130.4, 129.5, 129.0, 127.7, 127.2, 126.6, 123.8, 123.1, 122.6, 122.4, 119.8, 119.2, 112.3, 110.6, 51.8, 25.7, 21.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{19}BrN_2S^+$ 471.0525, found 471.0525.



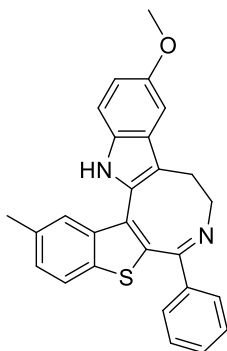
(Z)-2-methyl-6-(naphthalen-2-yl)-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5f).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 105 mg (yield 79%); mp 232-234 °C; IR (KBr) 3343, 3238, 3147, 2926, 2339, 1687, 1524, 1459, 1253, 1190, 1011, 795, 735, 668, 585 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.03 (s, 1H), 7.94 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.88 (s, 1H), 7.84 – 7.78 (m, 3H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.51 – 7.38 (m, 3H), 7.34 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.25 – 7.21 (m, 1H), 7.17 – 7.12 (m, 1H), 4.45 – 4.38 (m, 1H), 4.37 – 4.29 (m, 1H), 3.76 – 3.63 (m, 1H), 3.33 (dt, $J = 16.8, 2.8$ Hz, 1H), 2.53 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 138.3, 137.9, 136.6, 135.9, 135.3, 134.4, 133.6, 132.7, 130.1, 129.7, 129.1, 128.8, 127.8, 127.6, 127.6, 127.1, 126.8, 126.2, 125.1, 123.8, 123.0, 122.6, 119.7, 119.2, 112.4, 110.6, 51.8, 25.8, 21.6 ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{30}H_{22}N_2S^+$ 443.1576, found 443.1577.



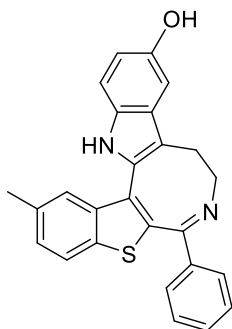
(Z)-2,11-dimethyl-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5g).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 96 mg (yield 79%); mp 226-228 °C; IR (KBr) 3341, 3218, 2927, 2327, 1699, 1591, 1458, 1377, 1265, 1084, 861, 791, 724, 597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.83 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.70 – 7.63 (m, 2H), 7.41 – 7.32 (m, 2H), 7.35 – 7.26 (m, 3H), 7.27 (s, 1H), 7.07 (dd, $J = 8.4, 1.2$ Hz, 1H), 4.37 – 4.21 (m, 2H), 3.69 – 3.56 (m, 1H), 3.27 (dt, $J = 16.8, 2.8$ Hz, 1H), 2.50 (s, 3H), 2.46 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 164.1, 139.2, 138.2, 137.8, 135.2, 134.1, 133.4, 130.3, 130.1, 129.3, 129.0, 128.6, 128.0, 127.5, 126.9, 124.5, 123.8, 122.5, 118.8, 111.9, 110.2, 51.7, 25.8, 21.6, 21.5 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{S}^+$ 407.1576, found 407.1581.



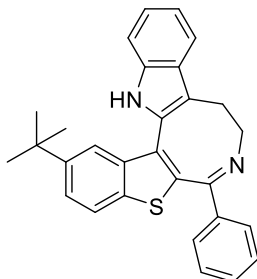
(Z)-11-methoxy-2-methyl-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5h).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 103 mg (yield 81%); mp 231-233 °C; IR (KBr) 3323, 3237, 3035, 2895, 2356, 1869, 1487, 1216, 1087, 964, 808, 667, 597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.84 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.71 – 7.63 (m, 2H), 7.39 – 7.32 (m, 1H), 7.35 – 7.24 (m, 4H), 7.01 (d, $J = 2.4$ Hz, 1H), 6.90 (dd, $J = 8.4, 2.4$ Hz, 1H), 4.38 – 4.21 (m, 2H), 3.87 (s, 3H), 3.68 – 3.54 (m, 1H), 3.26 (dt, $J = 16.8, 2.8$ Hz, 1H), 2.50 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 164.2, 154.2, 139.2, 138.2, 137.8, 135.2, 133.4, 131.0, 130.4, 130.0, 129.5, 128.6, 128.0, 127.6, 127.5, 123.8, 122.5, 113.3, 112.0, 111.4, 100.9, 56.0, 51.6, 25.9, 21.6 ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{OS}^+$ 423.1526, found 423.1530.



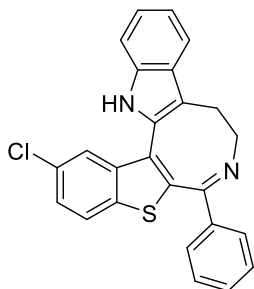
(Z)-2-methyl-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indol-11-ol (5i).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:1) as a brown solid: 80 mg (yield 65%); mp 262-264 °C; IR (KBr) 3344, 3281, 2925, 2632, 2357, 1699, 1559, 1459, 1238, 1085, 881, 792, 667, 596 cm^{-1} ; ^1H NMR (400 MHz, DMSO) δ 10.95 (s, 1H), 8.75 (s, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.77 (s, 1H), 7.65 – 7.58 (m, 2H), 7.46 – 7.34 (m, 5H), 7.15 (d, $J = 8.8$ Hz, 1H), 6.80 (d, $J = 2.4$ Hz, 1H), 6.66 (dd, $J = 8.8, 2.4$ Hz, 1H), 4.28 – 4.19 (m, 1H), 4.02 (td, $J = 12.8, 2.8$ Hz, 1H), 3.30 (dd, $J = 13.2, 4.4$ Hz, 1H), 3.17 – 3.08 (m, 1H), 2.46 (s, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO) δ 150.6, 138.4, 138.0, 136.8, 134.7, 131.5, 130.8, 130.7, 130.6, 129.0, 128.8, 128.3, 128.0, 127.5, 127.0, 124.5, 122.6, 112.6, 111.7, 109.1, 102.2, 51.2, 25.5, 21.2 ppm; HRMS (ESI-TOF) m/z [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{OS}^+$ 409.1369, found 409.1374.



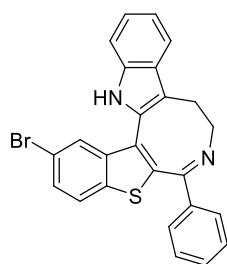
(Z)-2-(tert-butyl)-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5j).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 109 mg (yield 84%); mp 107-109 °C; IR (KBr) 3380, 3148, 2926, 2358, 1689, 1576, 1447, 1277, 1206, 967, 857, 745, 652 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 8.02 (d, $J = 1.6$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.68 – 7.64 (m, 2H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.57 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.18 – 7.13 (m, 1H), 4.38 – 4.24 (m, 2H), 3.74 – 3.64 (m, 1H), 3.32 (dt, $J = 16.8, 2.8$ Hz, 1H), 1.40 (s, 9H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 164.2, 148.8, 139.2, 137.9, 137.9, 136.0, 133.6, 130.44, 130.35, 129.2, 128.6, 128.0, 126.9, 124.3, 122.9, 122.5, 119.8, 119.7, 119.2, 112.5, 110.6, 51.7, 35.0, 31.6, 25.8 ppm; HRMS (ESI-TOF) m/z [$\text{M} + \text{H}$] $^+$ calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{S}^+$ 435.1889, found 435.1887.



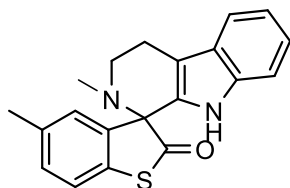
(Z)-2-chloro-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5k).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 92 mg (yield 74%); mp 260-262 °C; IR (KBr) 3344, 3153, 3080, 2763, 2356, 1590, 1458, 1273, 1081, 989, 804, 741, 674 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.20 – 7.11 (m, 1H), 4.37 (dt, *J* = 9.6, 4.0 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.74 – 3.61 (m, 1H), 3.31 (dt, *J* = 16.8, 2.8 Hz, 1H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.5, 139.1, 138.9, 138.6, 136.0, 135.1, 131.7, 130.6, 129.7, 129.1, 128.6, 128.1, 126.3, 125.9, 123.9, 123.6, 123.3, 119.9, 119.3, 112.9, 110.8, 51.7, 25.7 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₇ClN₂S⁺ 413.0874, found 413.0876.



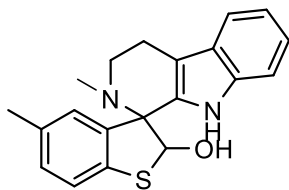
(Z)-2-bromo-6-phenyl-9,14-dihydro-8H-benzo[4',5']thieno[3',2':6,7]azocino[5,4-b]indole (5l).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) as a yellow solid: 106 mg (yield 77%); mp 246-248 °C; IR (KBr) 3344, 3148, 3059, 2822, 2358, 1698, 1576, 1458, 1207, 965, 844, 739, 667 cm⁻¹; ¹H NMR (400 MHz, DMSO) δ 11.34 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.44 – 7.35 (m, 3H), 7.21 – 7.12 (m, 1H), 7.09 – 7.00 (m, 1H), 4.32 – 4.23 (m, 1H), 4.09 – 3.98 (m, 1H), 3.52 – 3.42 (m, 1H), 3.27 – 3.18 (m, 1H) ppm; ¹³C{¹H} NMR (100 MHz, DMSO) δ 162.5, 139.3, 138.5, 138.1, 136.3, 133.7, 130.8, 130.0, 128.7, 128.4, 128.3, 128.0, 126.8, 125.8, 125.1, 122.5, 119.0, 118.6, 118.6, 111.3, 110.7, 51.2, 25.4 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₇BrN₂S⁺ 457.0369, found 457.0368.



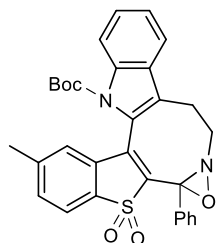
2',5-dimethyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-one (6).

The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 83 mg (yield 83%); mp 176-178 °C; IR (KBr) 3367, 2919, 1700, 1451, 1285, 945, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.53 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.07 (m, 4H), 7.00 (s, 1H), 3.89 – 3.76 (m, 1H), 3.19 – 3.02 (m, 2H), 2.94 (dd, *J* = 15.6, 4.8 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.0, 137.4, 137.1, 136.6, 131.3, 131.0, 130.9, 127.7, 126.7, 123.0, 122.6, 119.7, 118.8, 111.0, 110.9, 75.8, 47.9, 38.7, 21.2, 21.1 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₀H₁₉N₂OS⁺ 335.1213, found 335.1219.



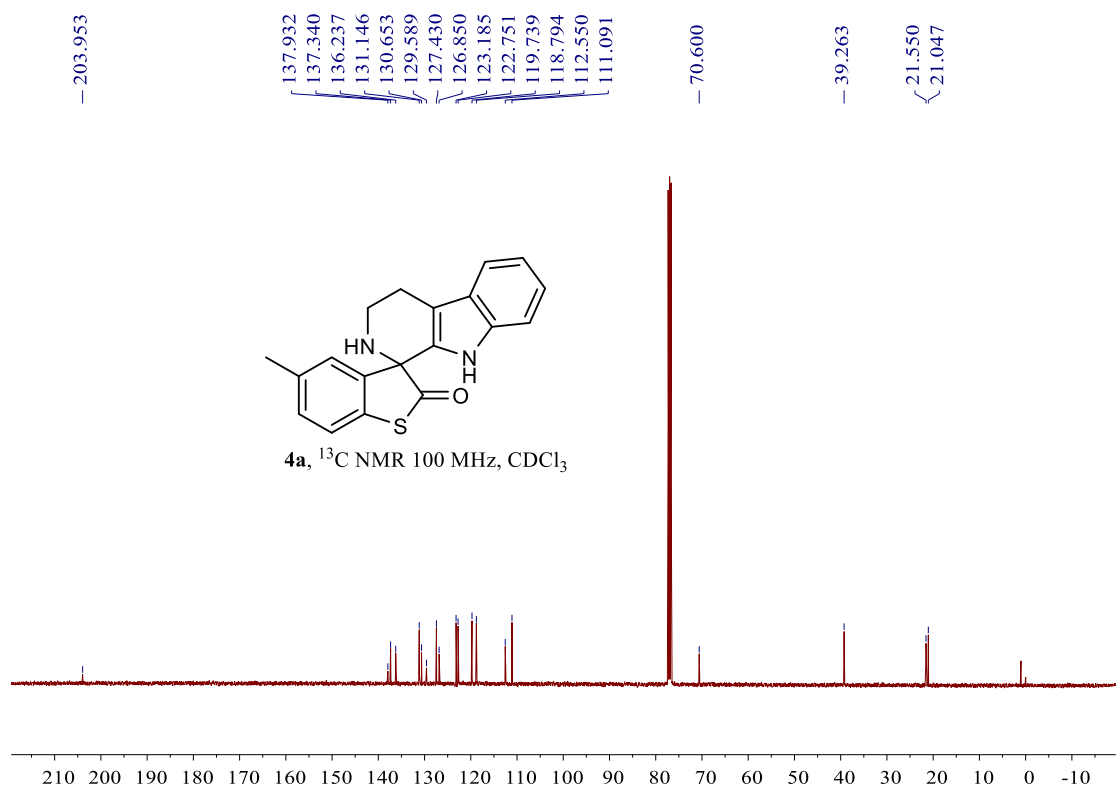
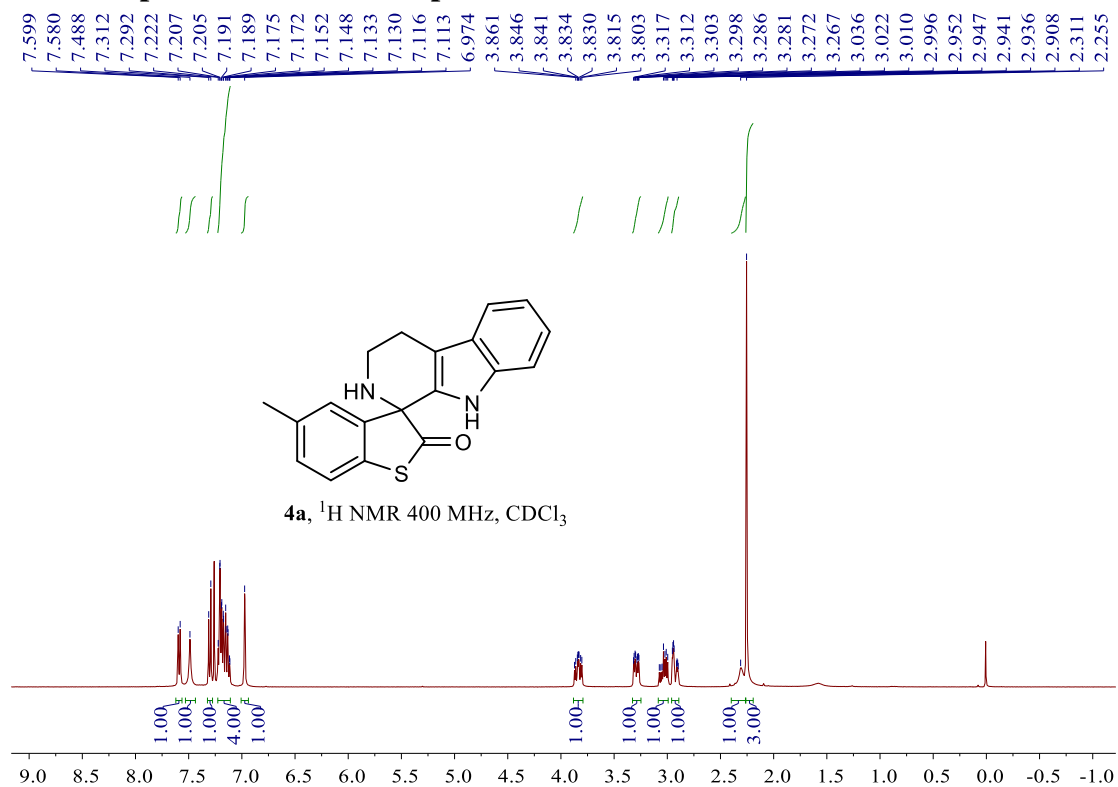
2',5-dimethyl-2',3',4',9'-tetrahydro-2H-spiro[benzo[b]thiophene-3,1'-pyrido[3,4-b]indol]-2-ol (7).

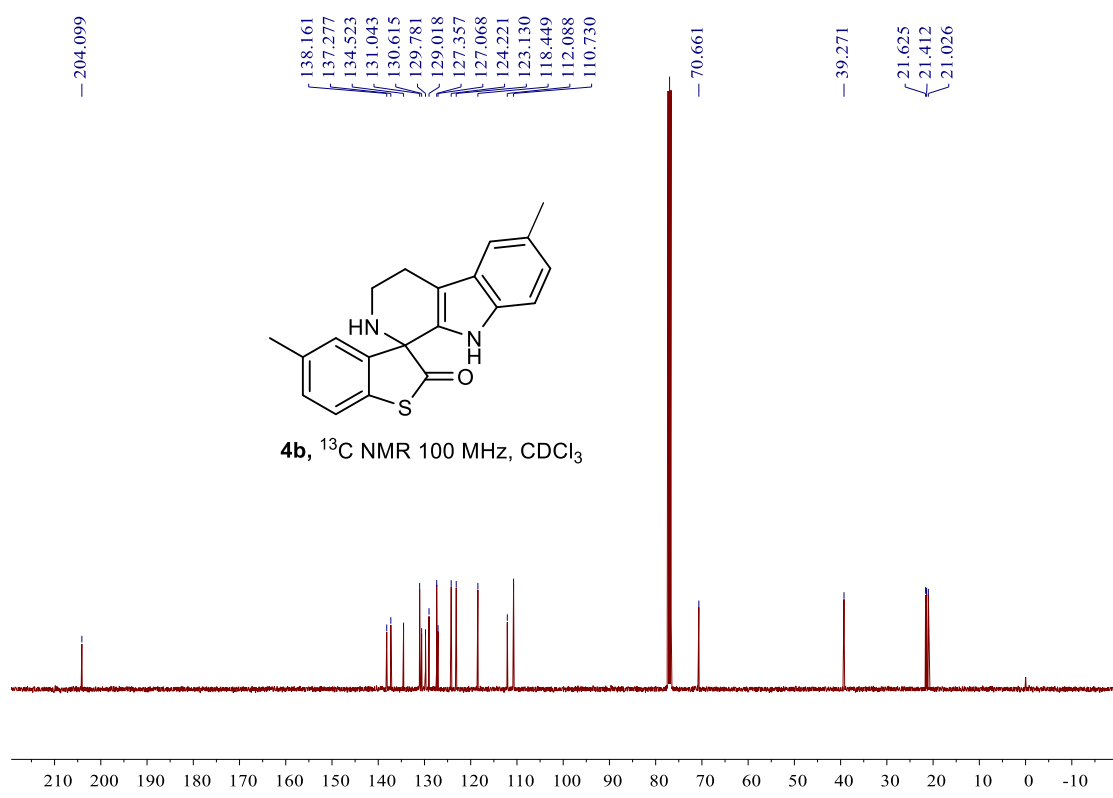
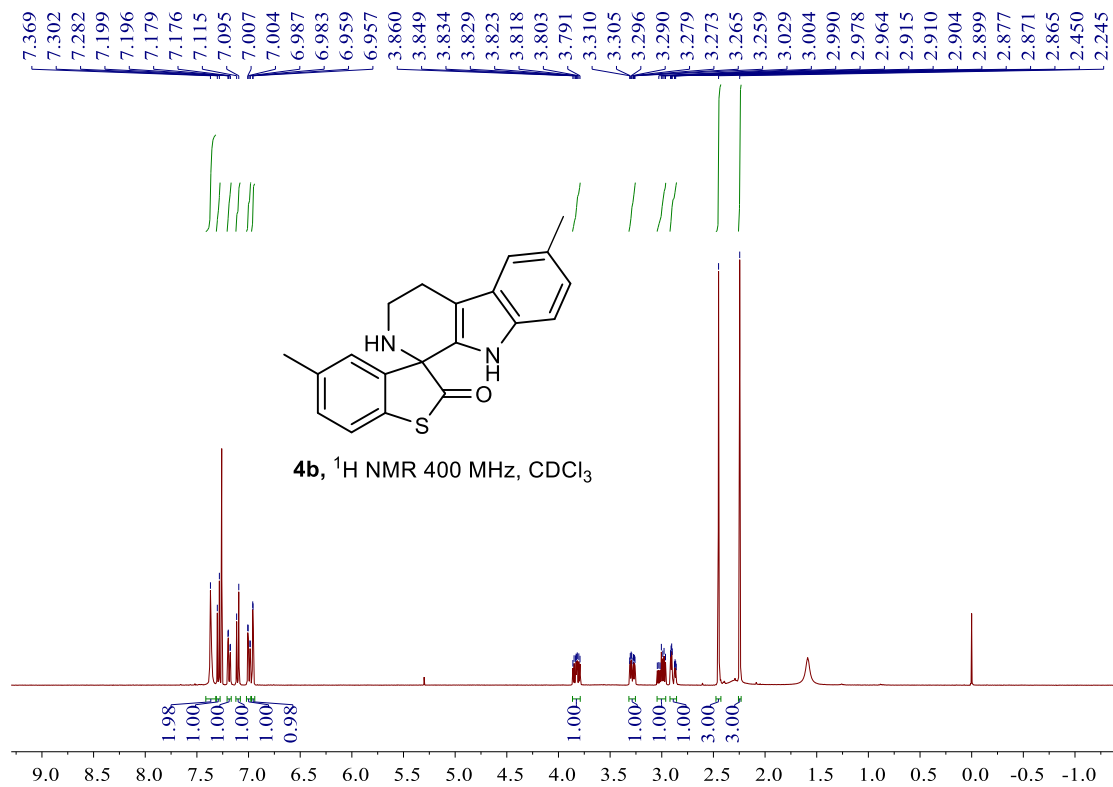
The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 74 mg (yield 73%); mp 190-192 °C; IR (KBr) 3369, 2915, 1710, 1468, 1301, 1095, 752 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.50 (m, 2H), 7.26 – 7.22 (m, 1H), 7.20 – 7.16 (m, 1H), 7.15 – 7.12 (m, 1H), 7.12 – 7.07 (m, 2H), {6.84, 6.73} (s, 1H), 6.18 (s, 1H), 3.22 – 3.14 (m, 1H), 3.09 – 2.95 (m, 2H), 2.89 – 2.82 (m, 1H), {2.44, 2.36} (s, 3H), 2.21 (s, 3H) ppm; ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 137.3, 136.7, 136.1, 134.5, 134.1, 131.1, 127.9, 126.1, 122.8, 122.5, 119.7, 118.4, 113.0, 111.1, 87.3, 72.4, 50.8, 39.8, 21.5, 21.0 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₀H₂₁N₂OS⁺ 337.1369, found 337.1374.

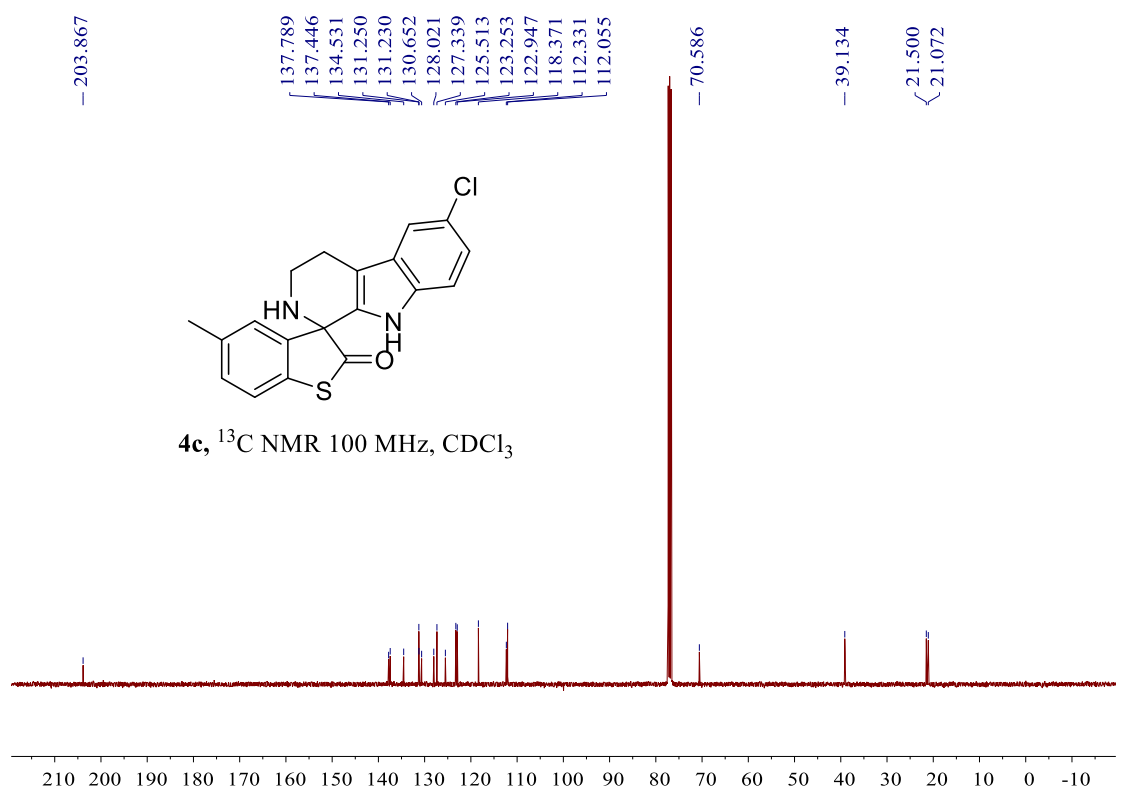
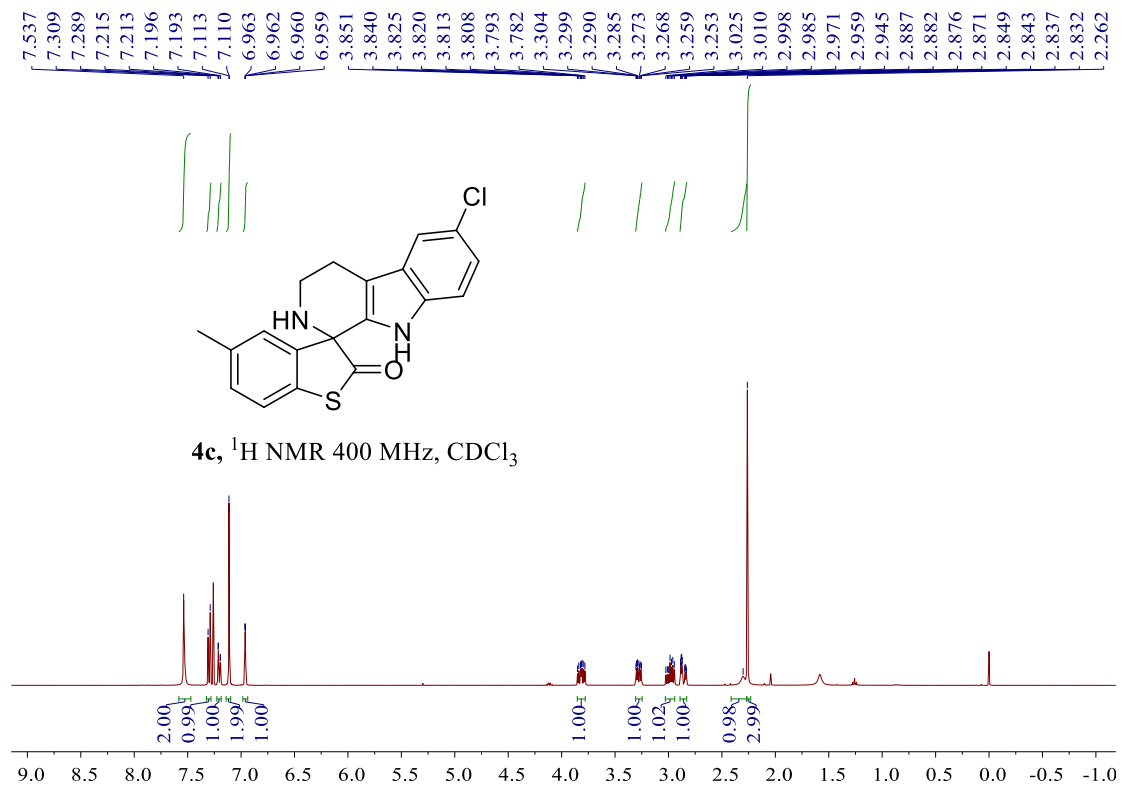


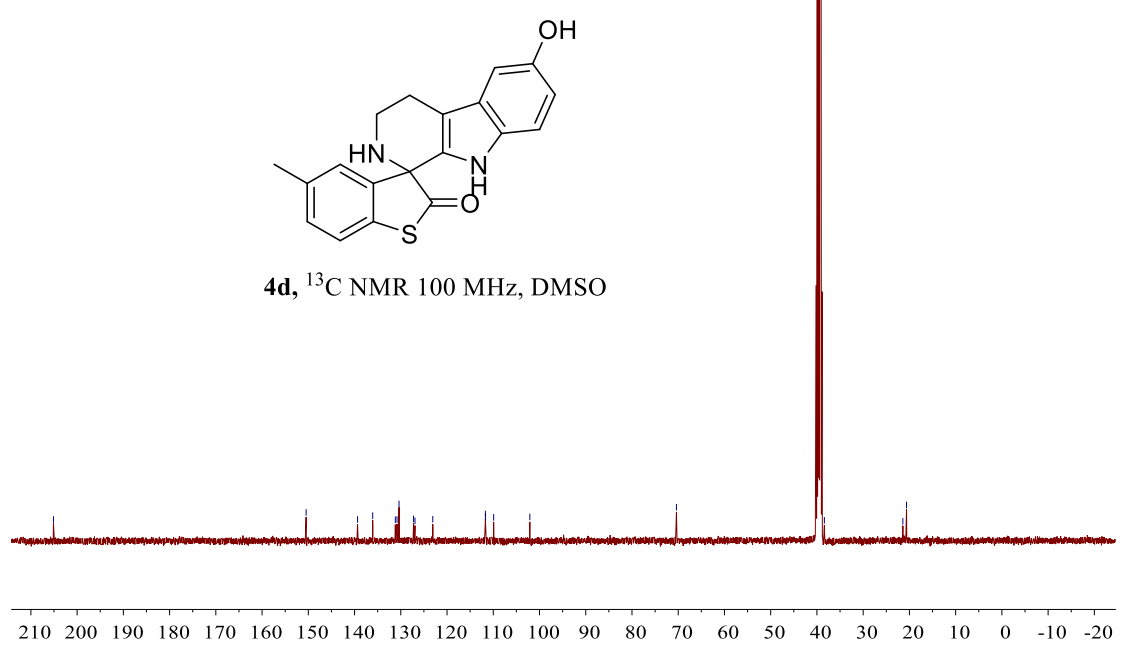
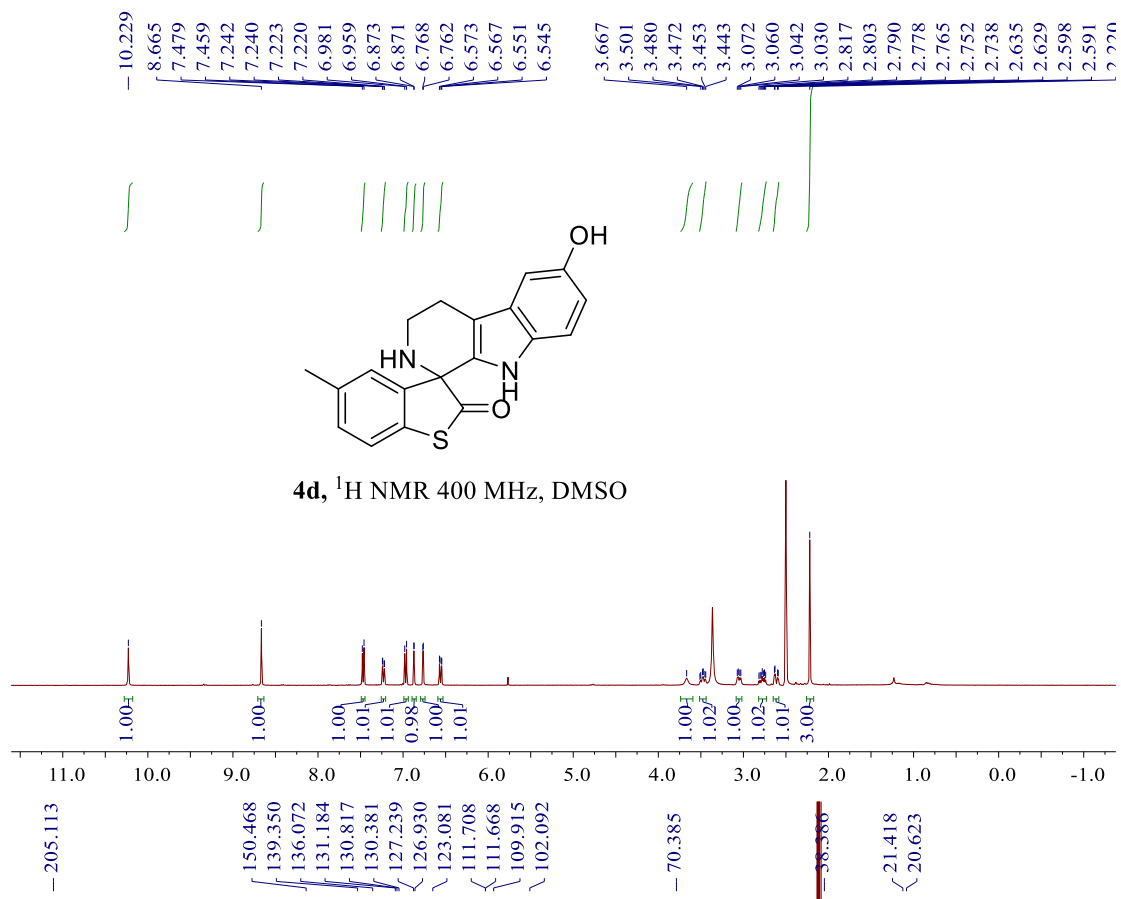
tert-butyl-2-methyl-5b-phenyl-8,9-dihydrobenzo[4',5']thieno[3',2':6,7][1,2]oxazireno[2',3':1,8]azocin of[5,4-b]indole-14(5bH)-carboxylate 5,5-dioxide (8). The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:3) as a yellow solid: 29 mg (yield 54%); mp 190-192 °C; IR (KBr) 3096, 3011, 2840, 2728, 2603, 2352, 2176, 1924, 1717, 1371, 1309, 1158, 810, 654 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.43 (m, 3H), 7.42 – 7.32 (m, 2H), 7.33 – 7.24 (m, 1H), 7.27 – 7.18 (m, 2H), 3.99 – 3.89 (m, 1H), 3.76 – 3.65 (m, 1H), 3.47 – 3.39 (m, 1H), 3.17 (dt, *J* = 18.0, 3.2 Hz, 1H), 2.38 (s, 3H), 1.18 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 144.6, 137.5, 136.3, 135.3, 134.0, 132.4, 131.1, 130.9, 129.82, 128.2, 127.3, 126.9, 124.6, 123.6, 122.9, 121.3, 120.6, 119.2, 115.9, 85.6, 81.2, 52.9, 29.7, 27.5, 22.8, 21.7 ppm; HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₃₁H₂₉N₂O₅S⁺ 541.1792, found 541.1800.

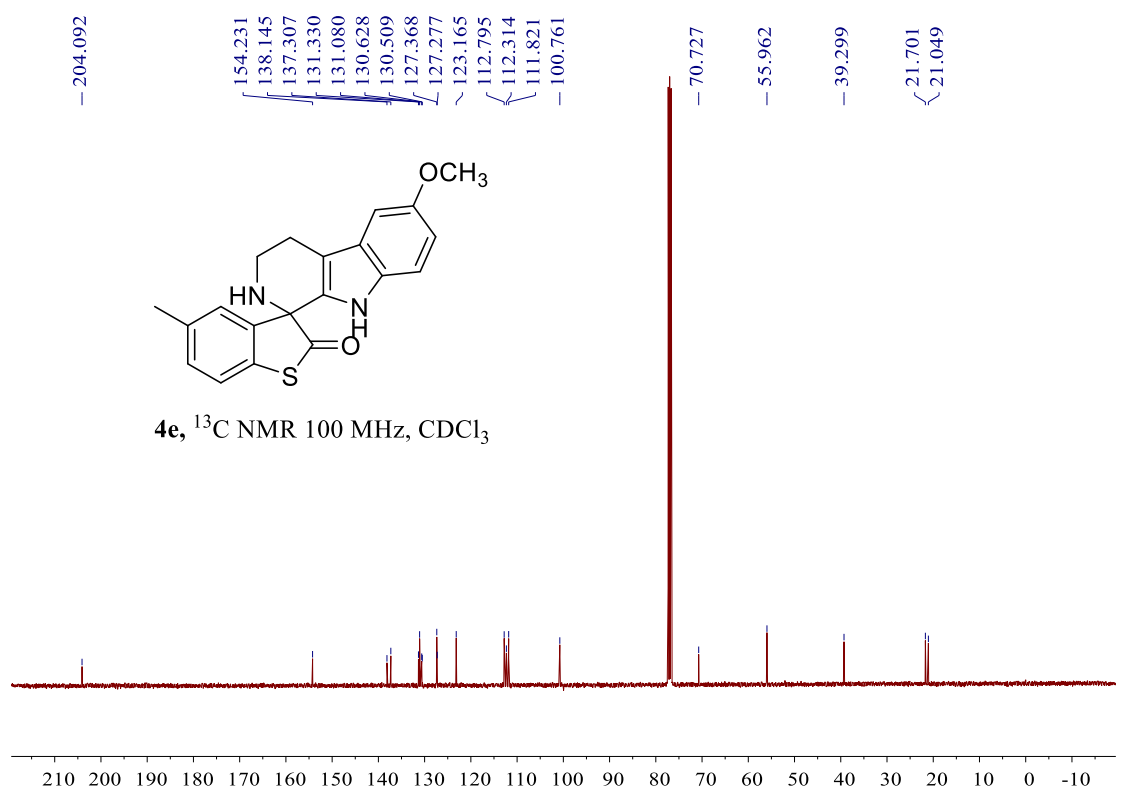
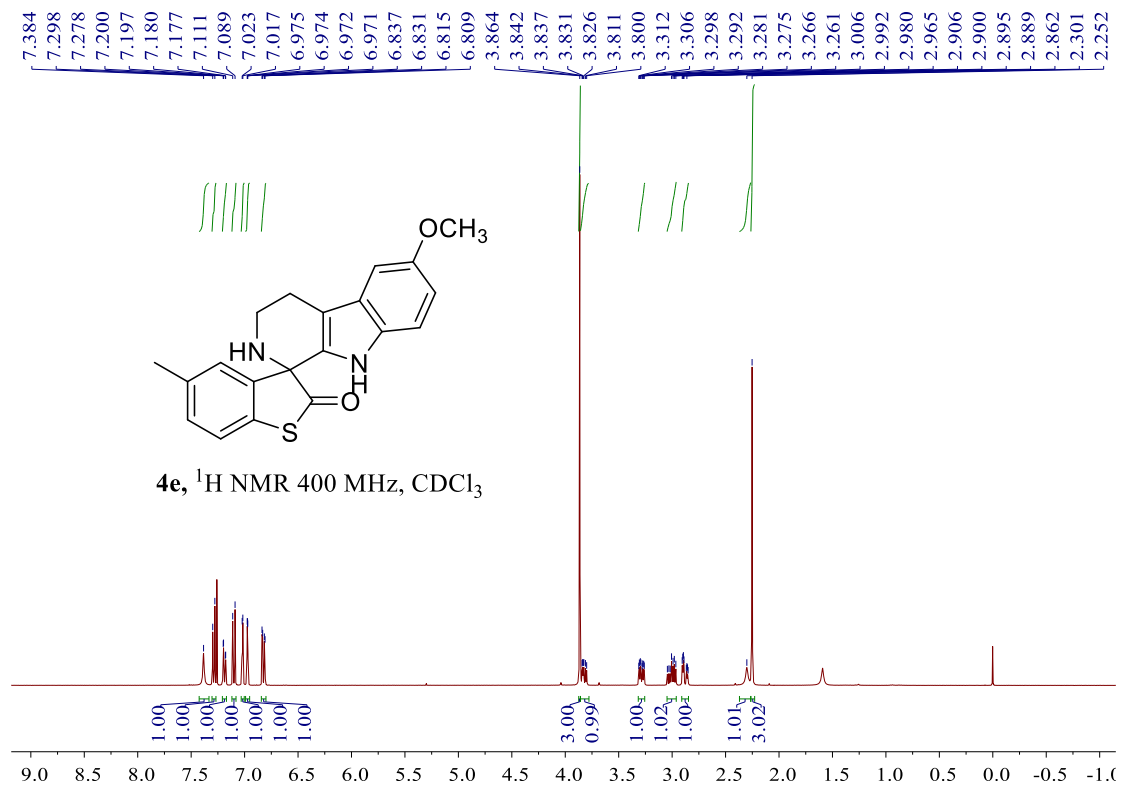
8. NMR spectra of all new compounds

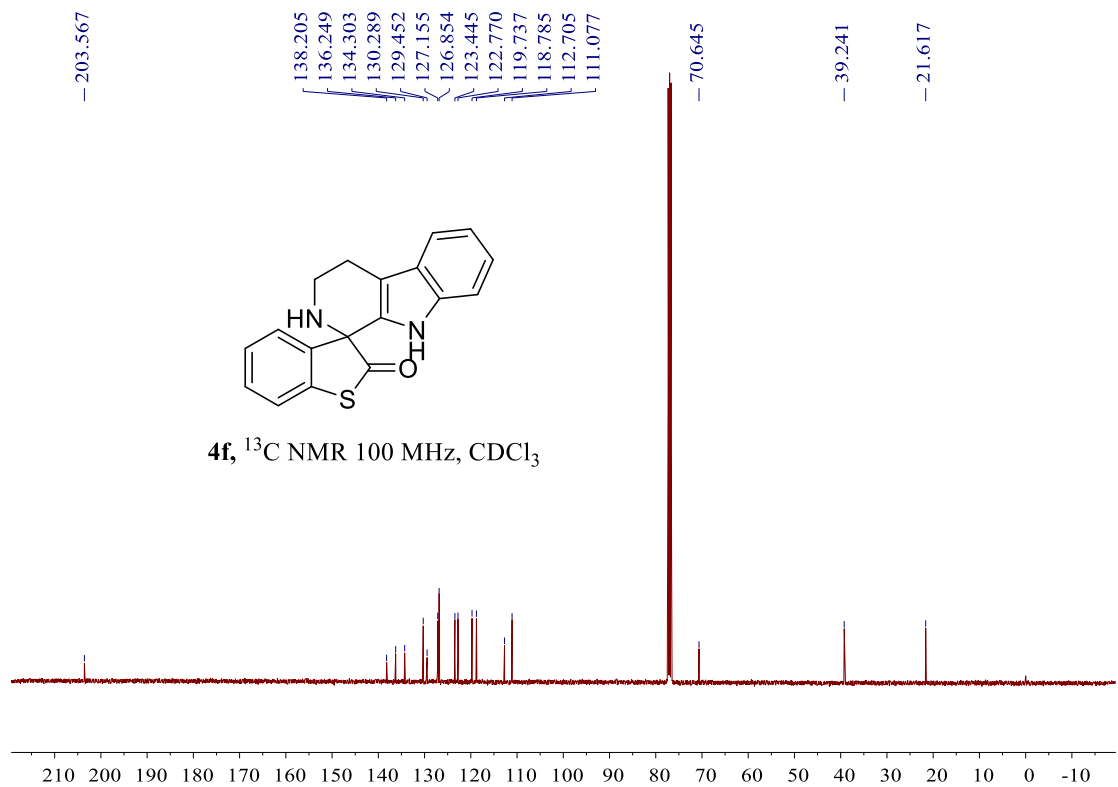
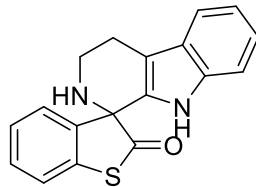
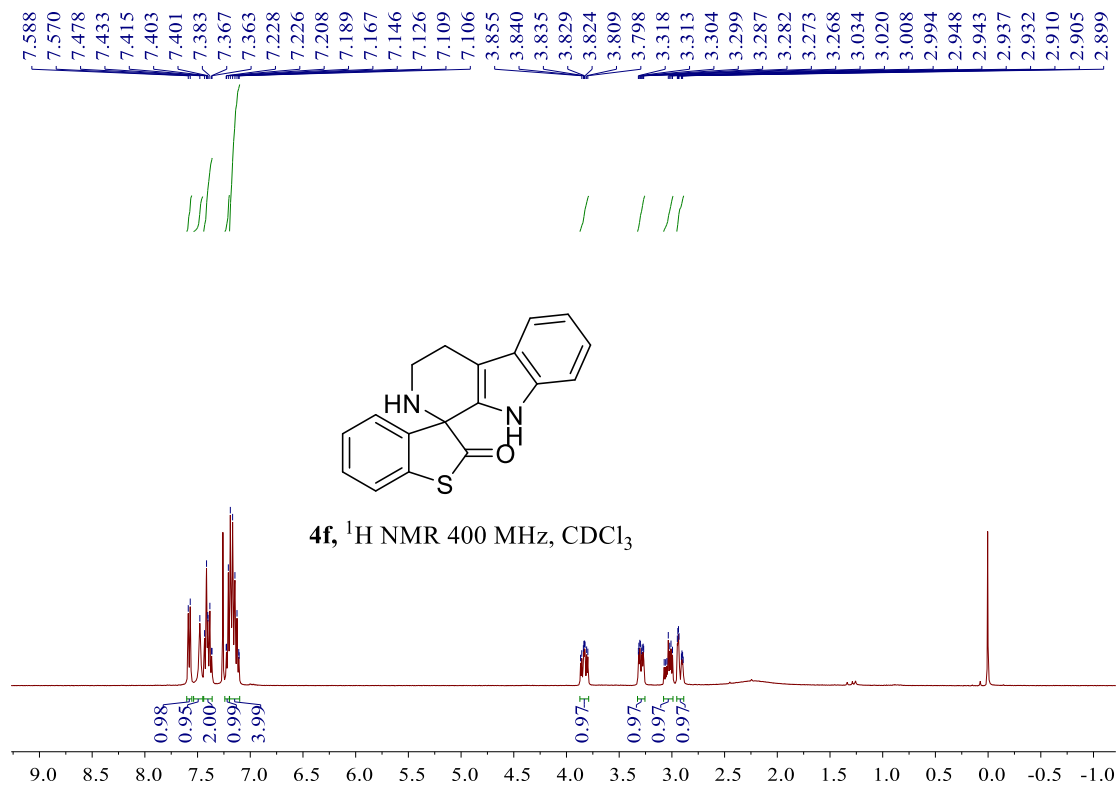


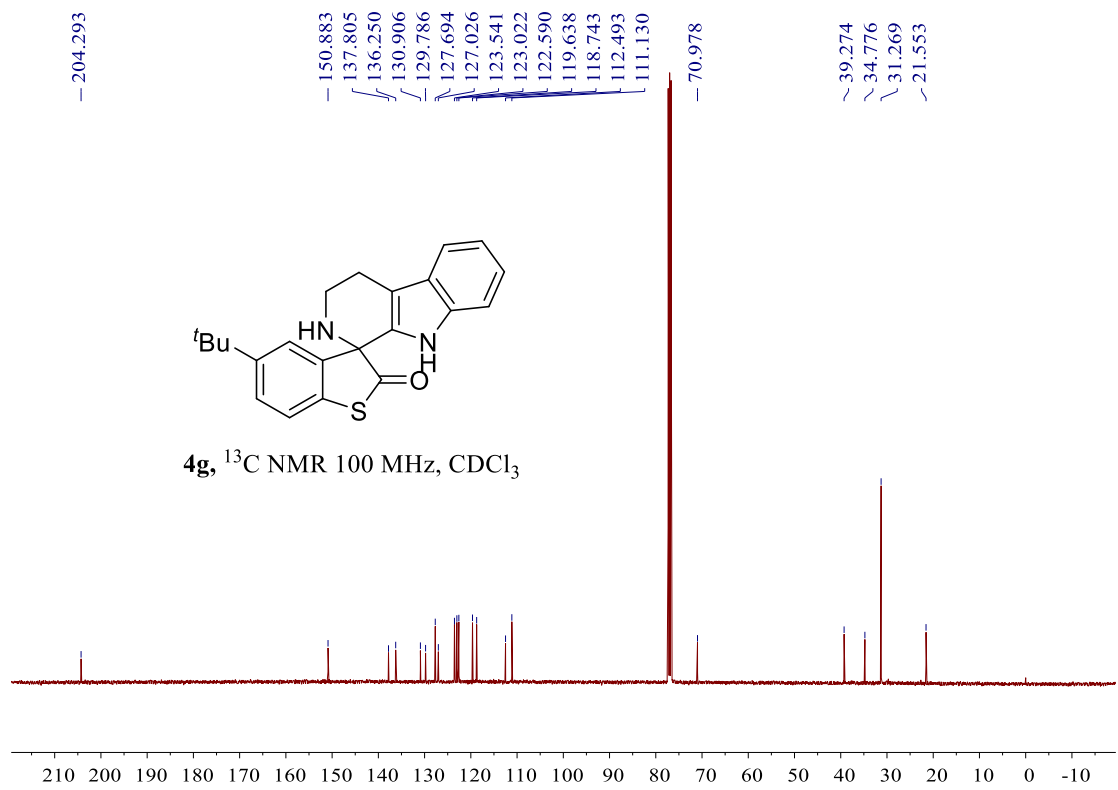
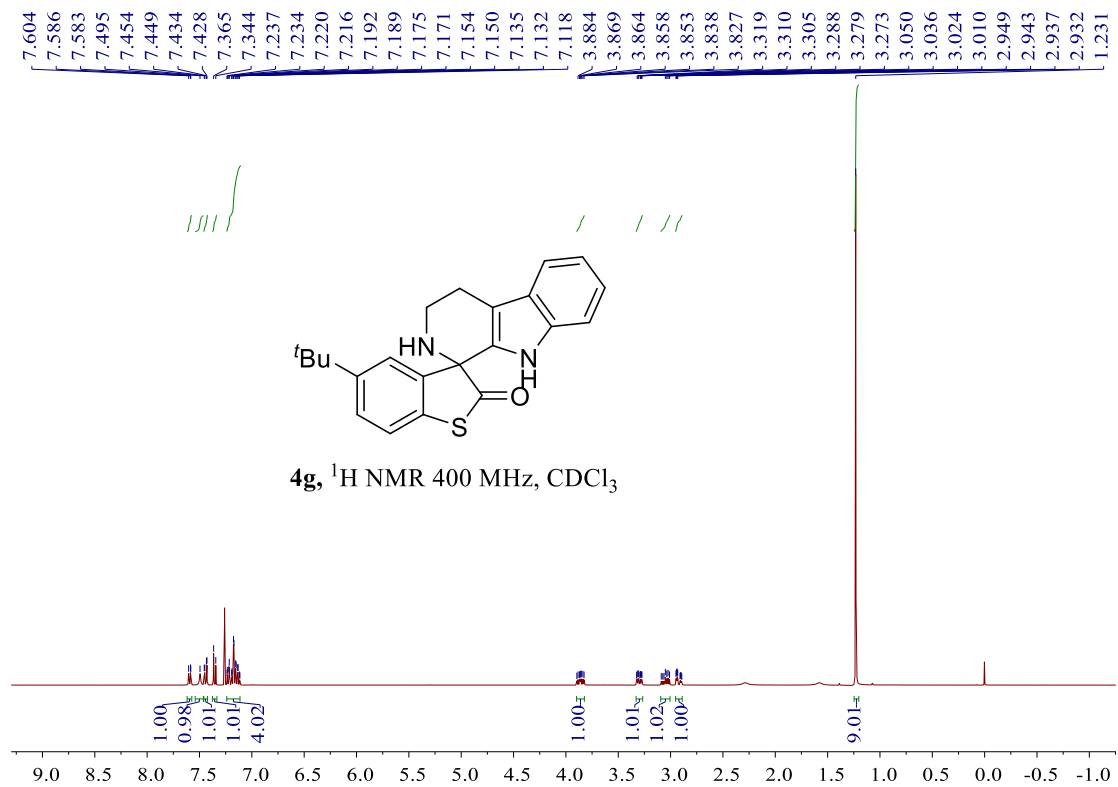


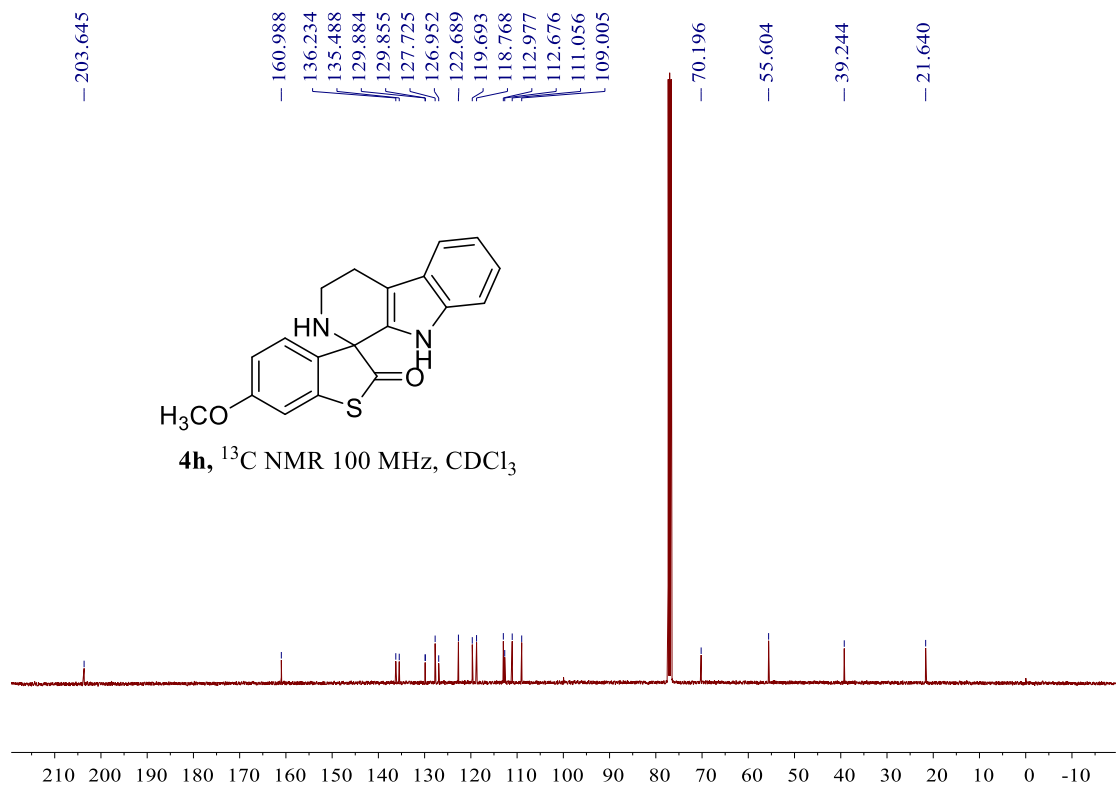
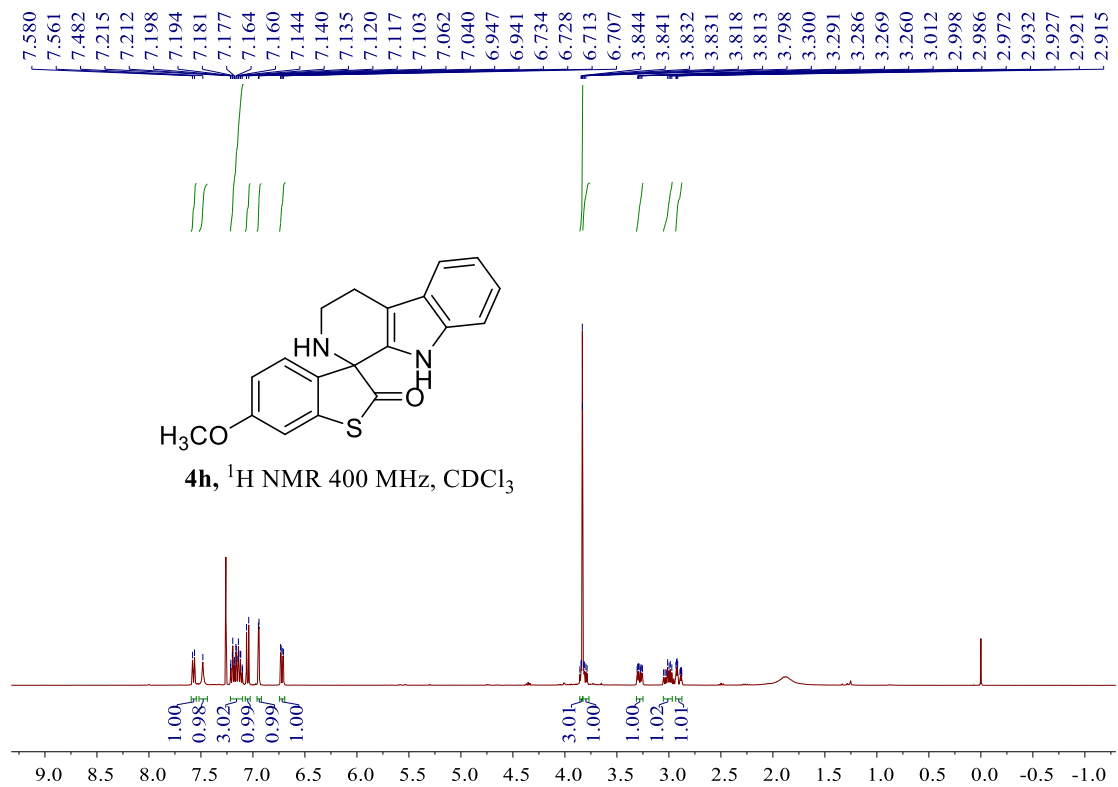


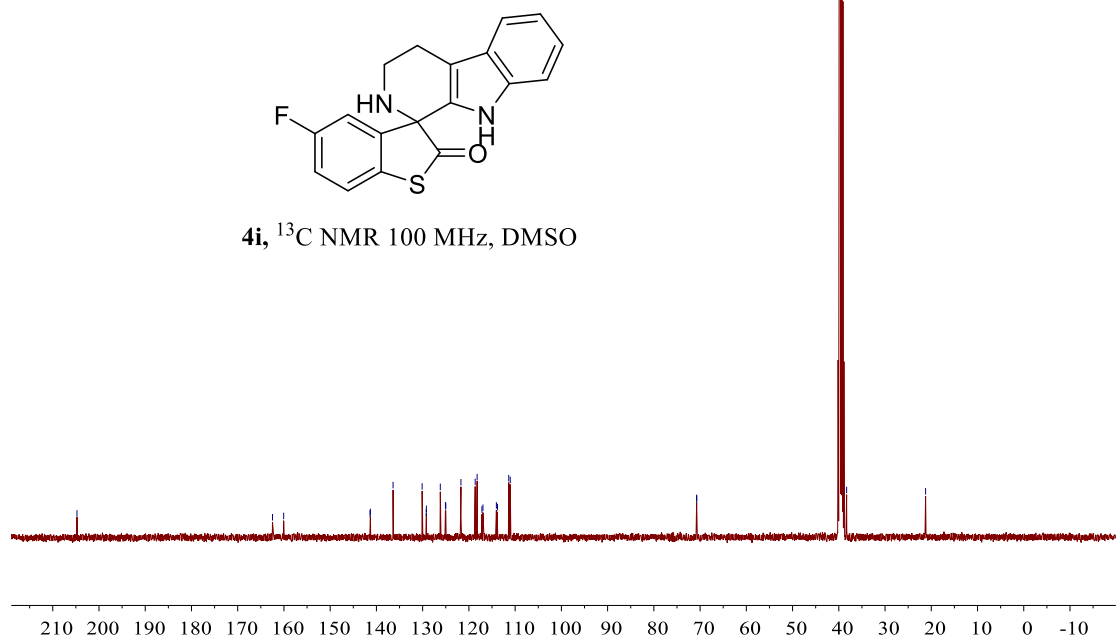
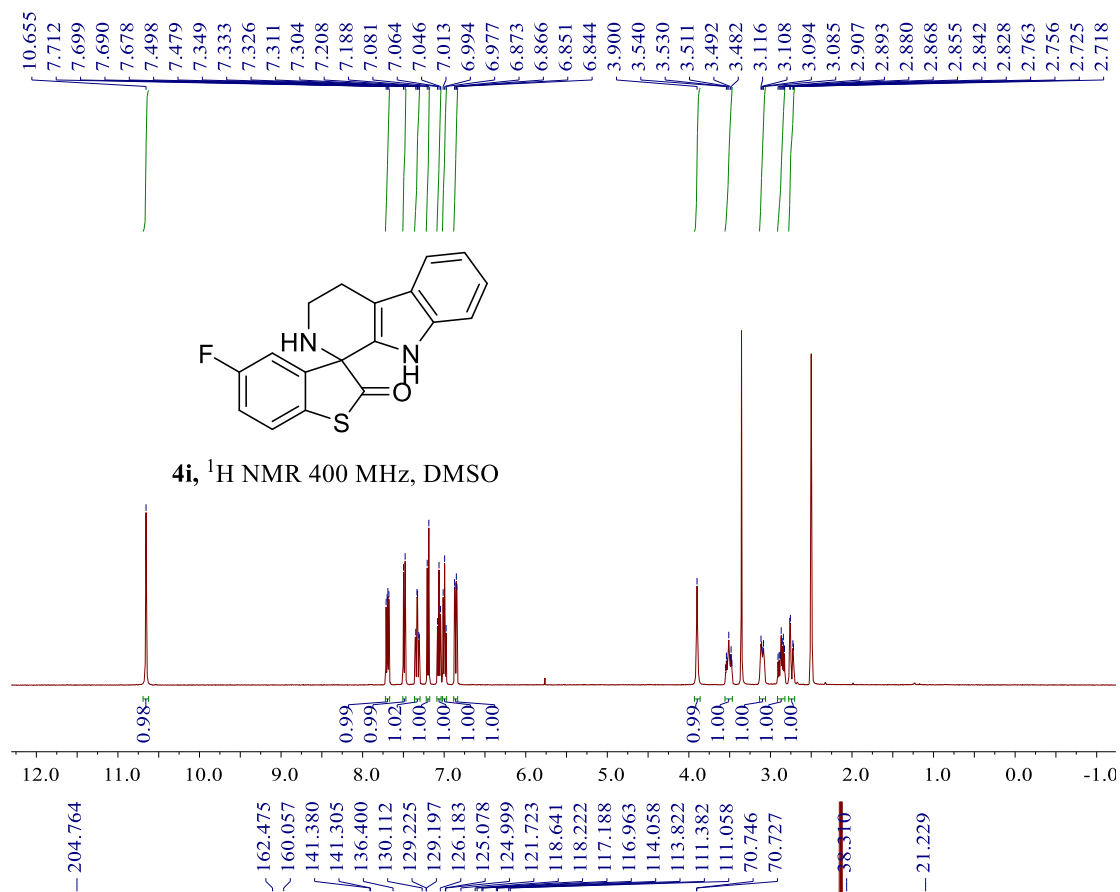


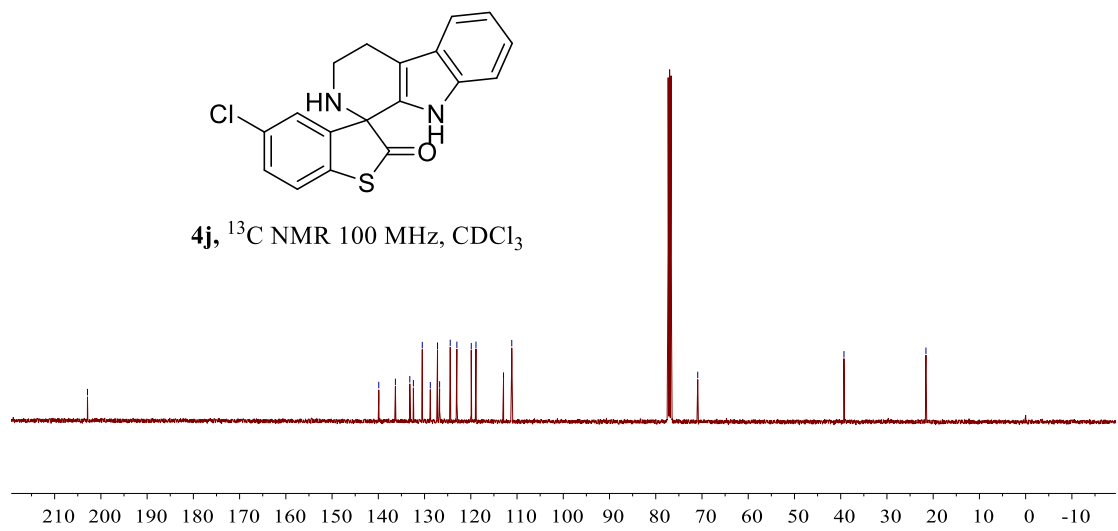
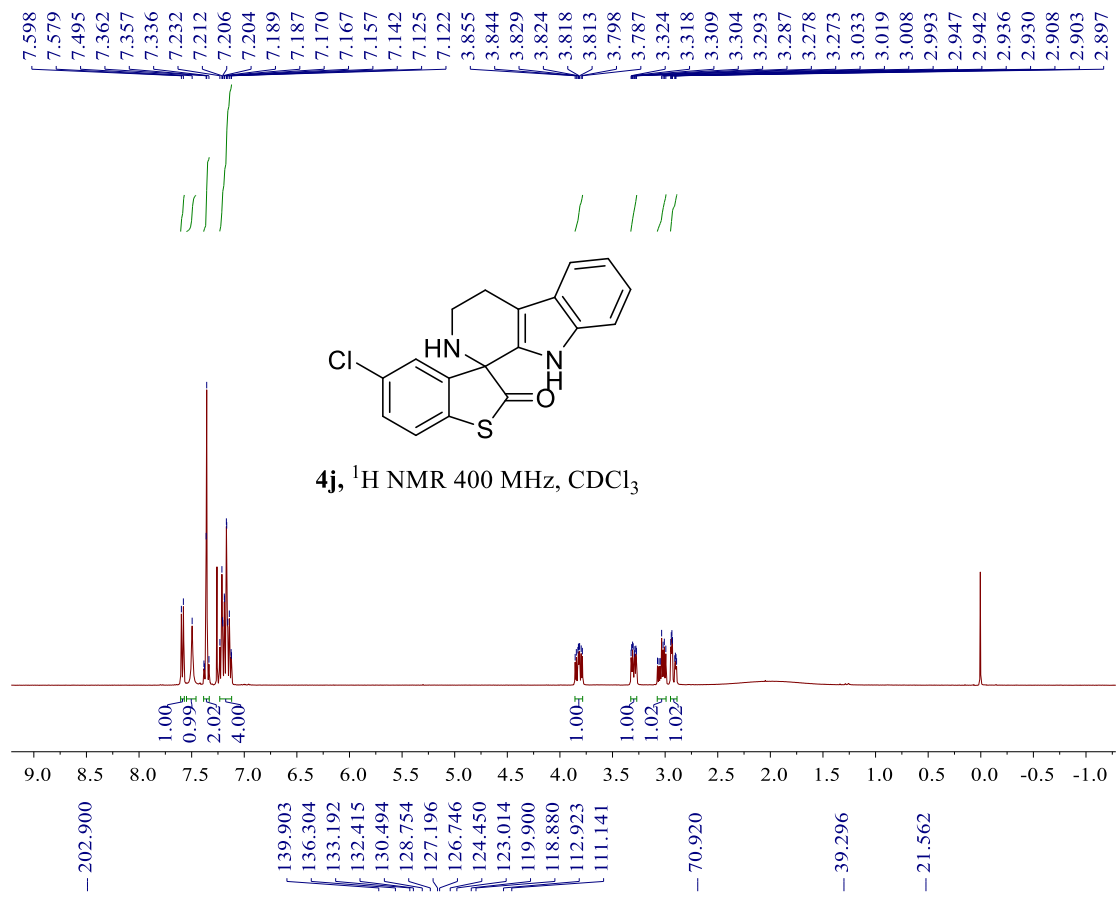


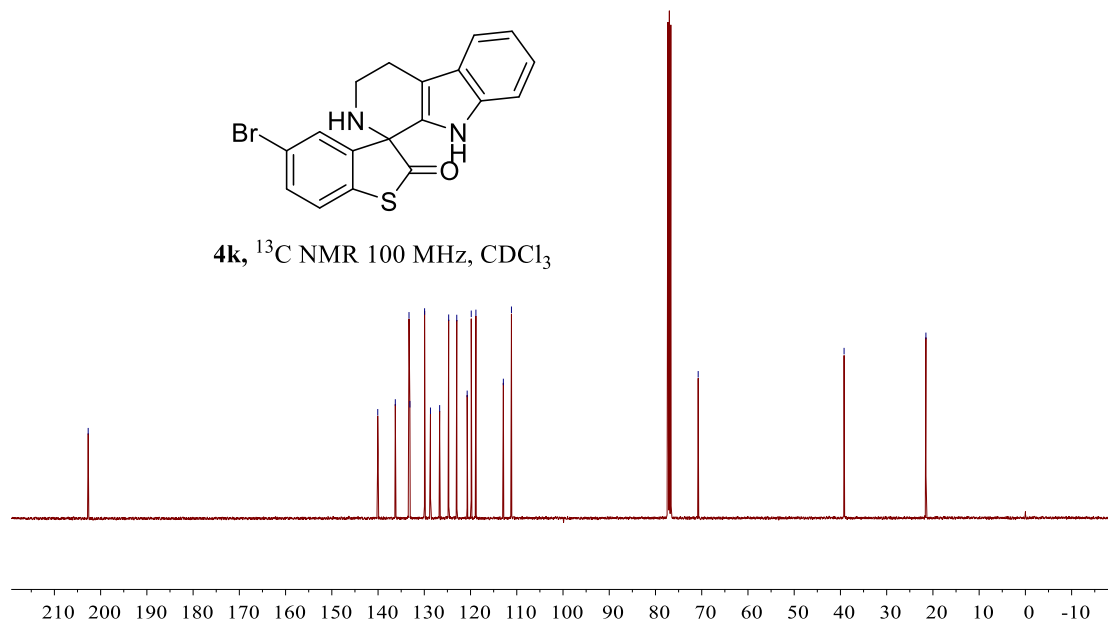
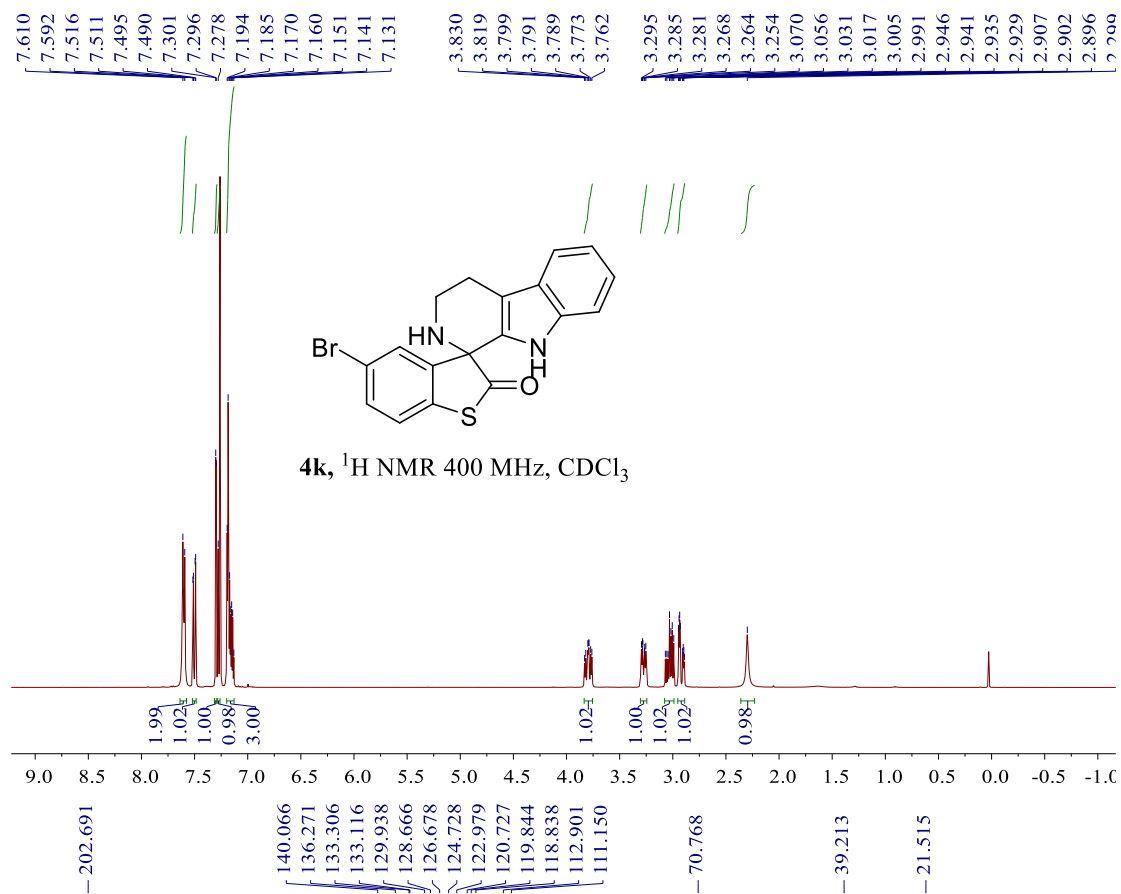


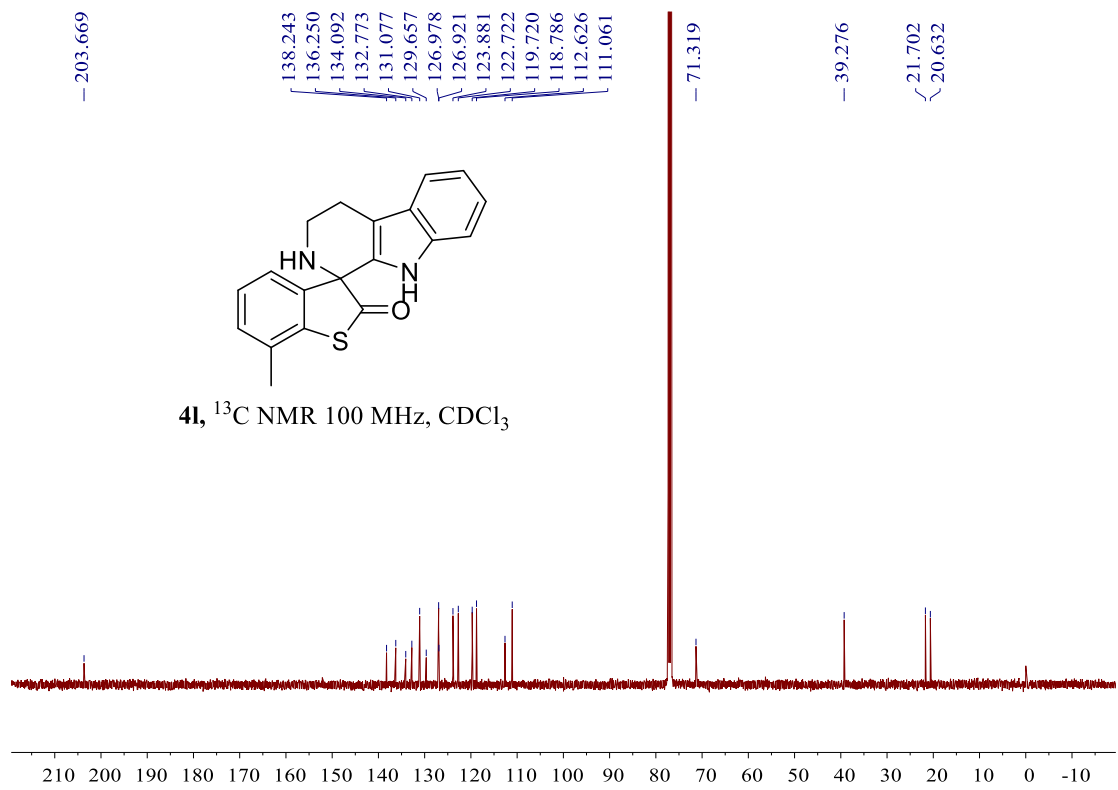
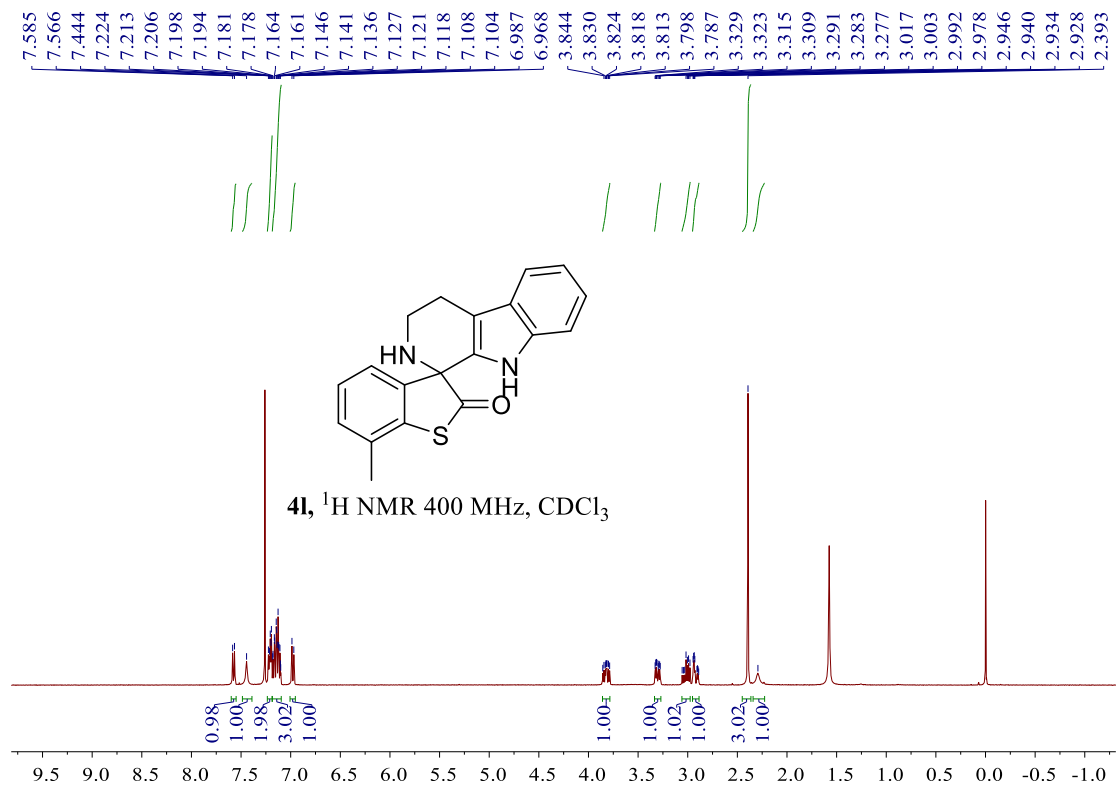


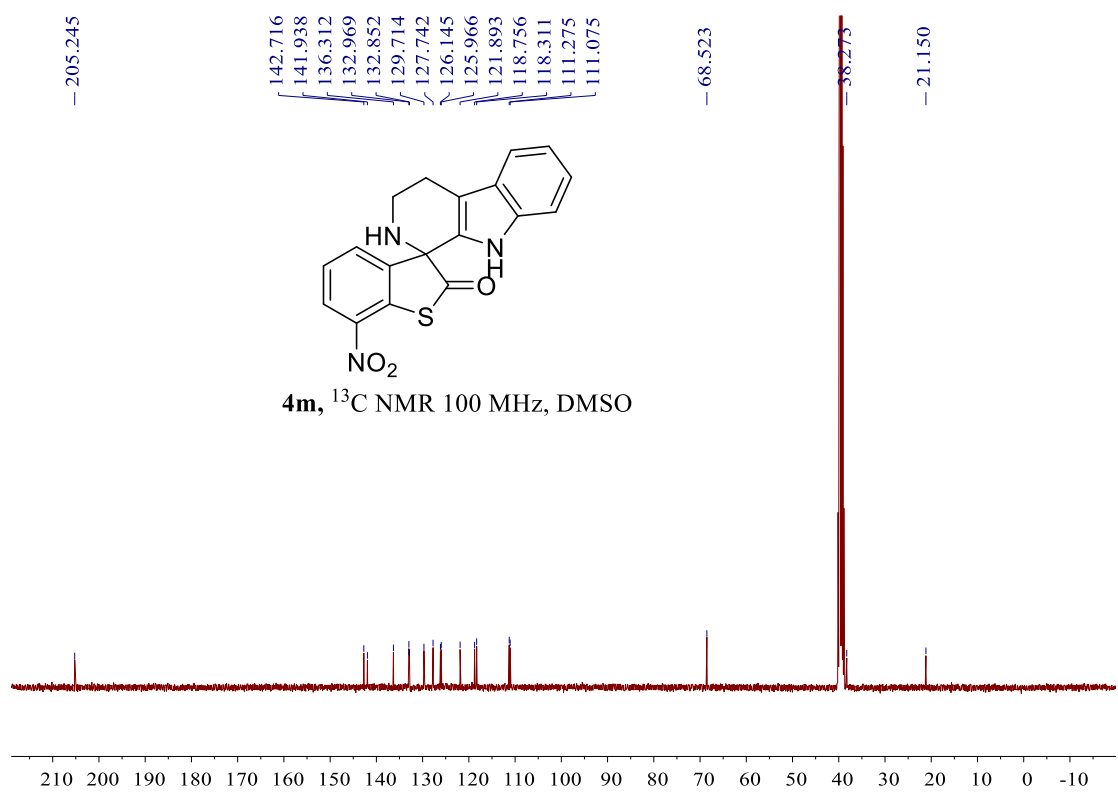
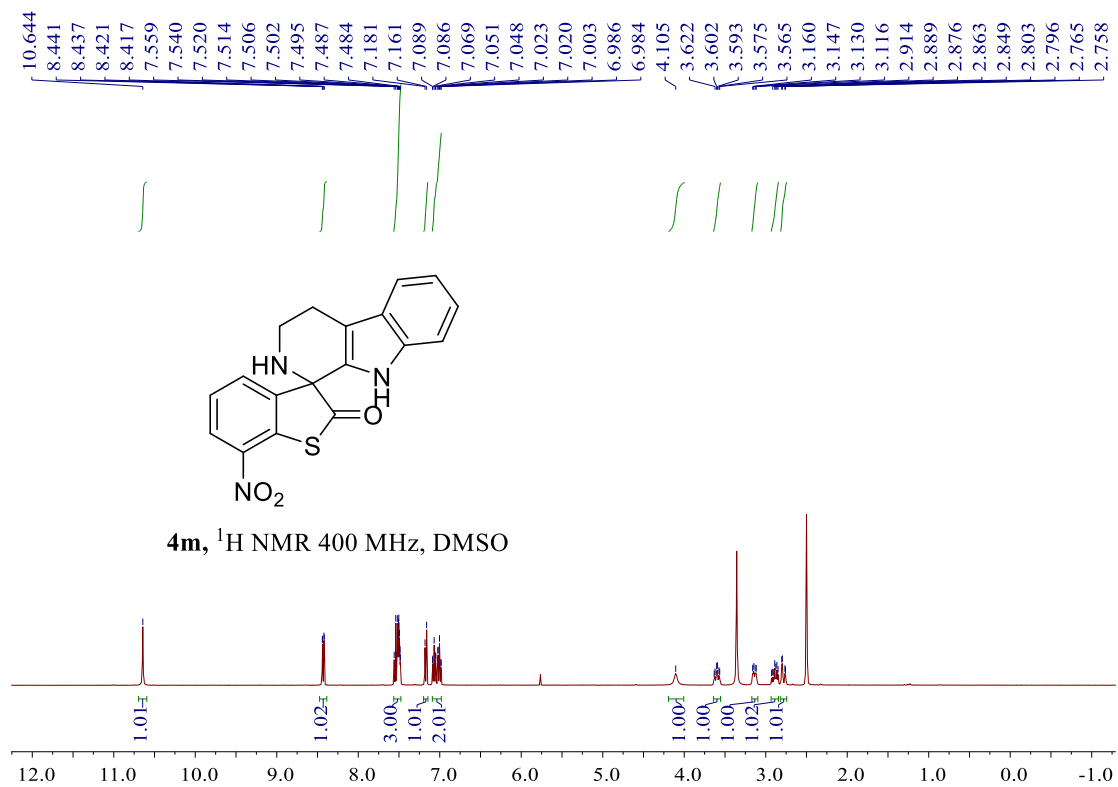


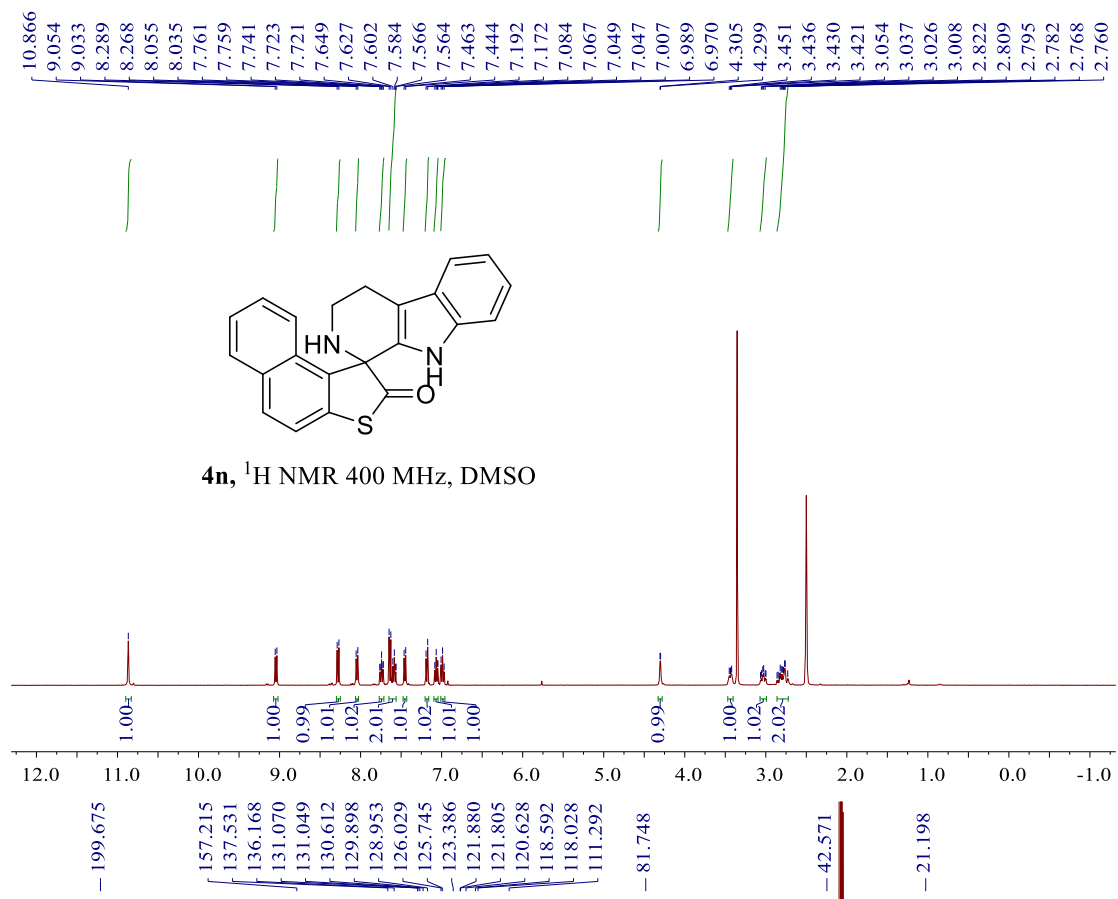




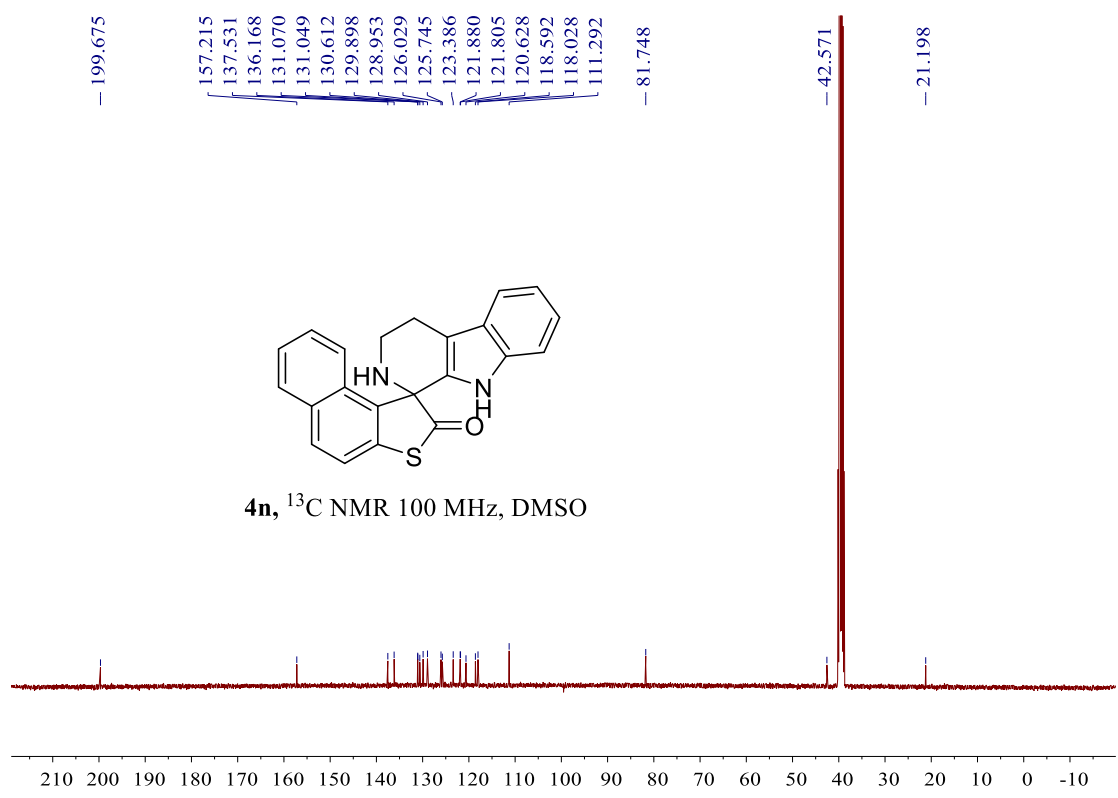




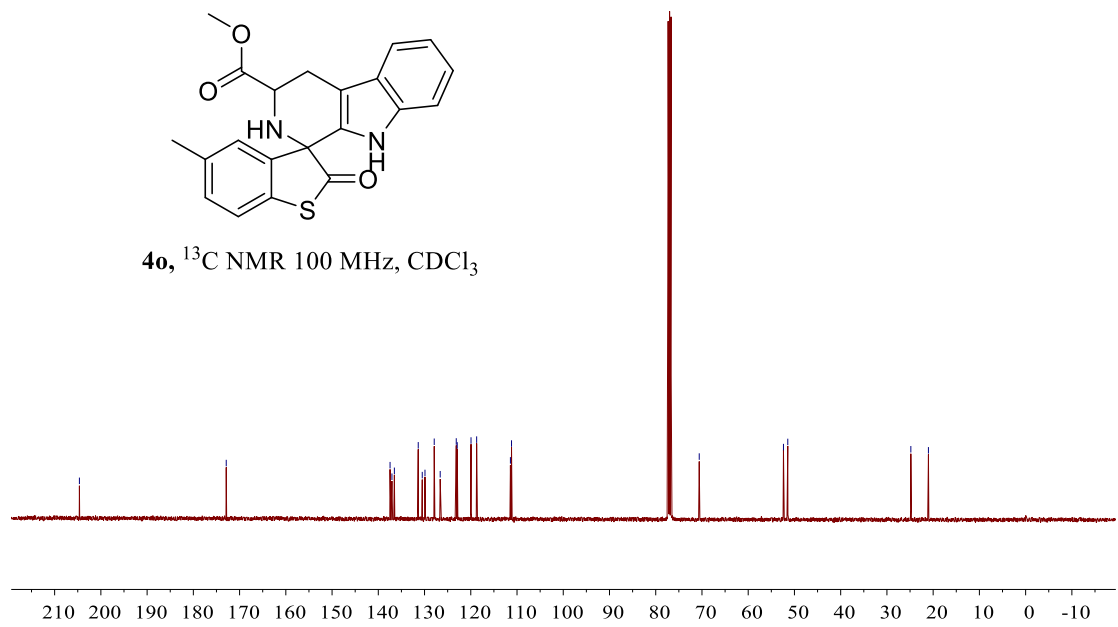
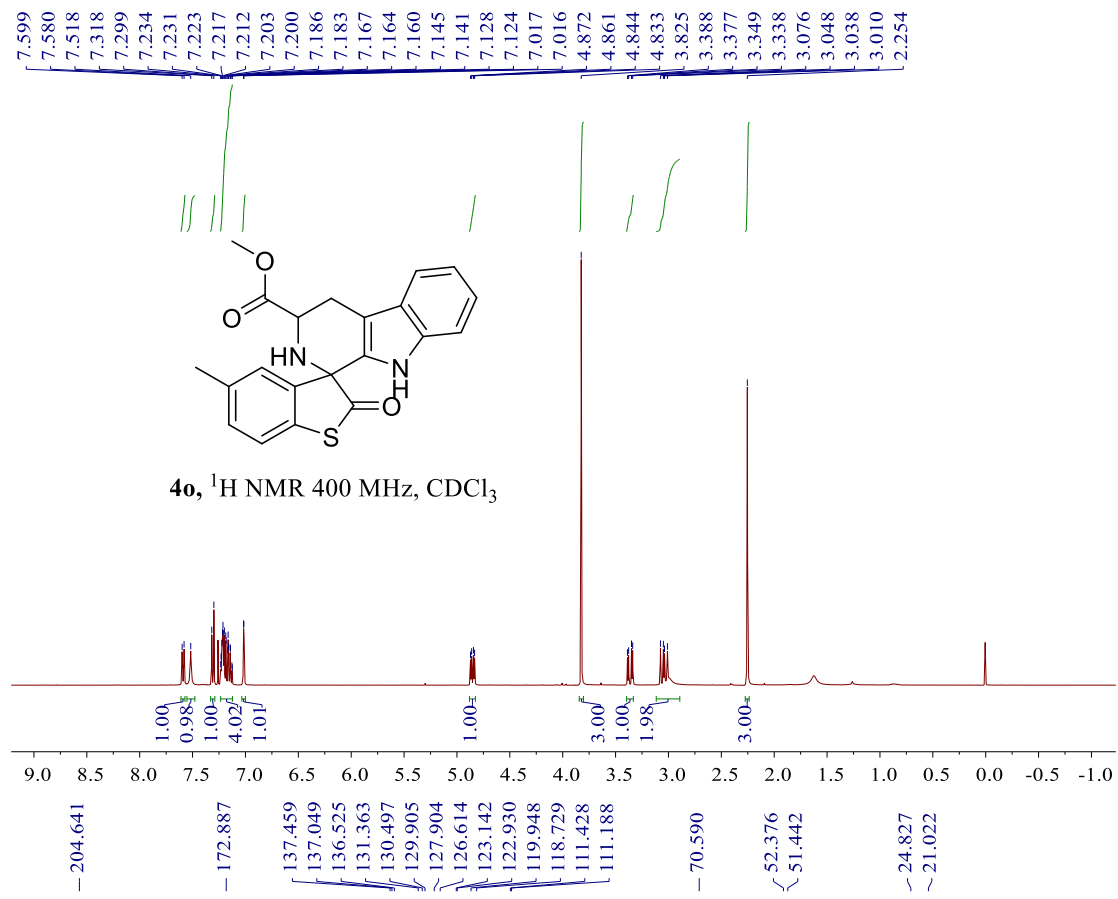


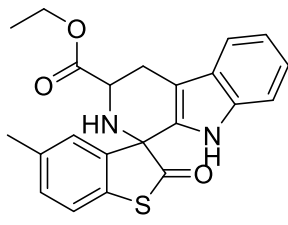
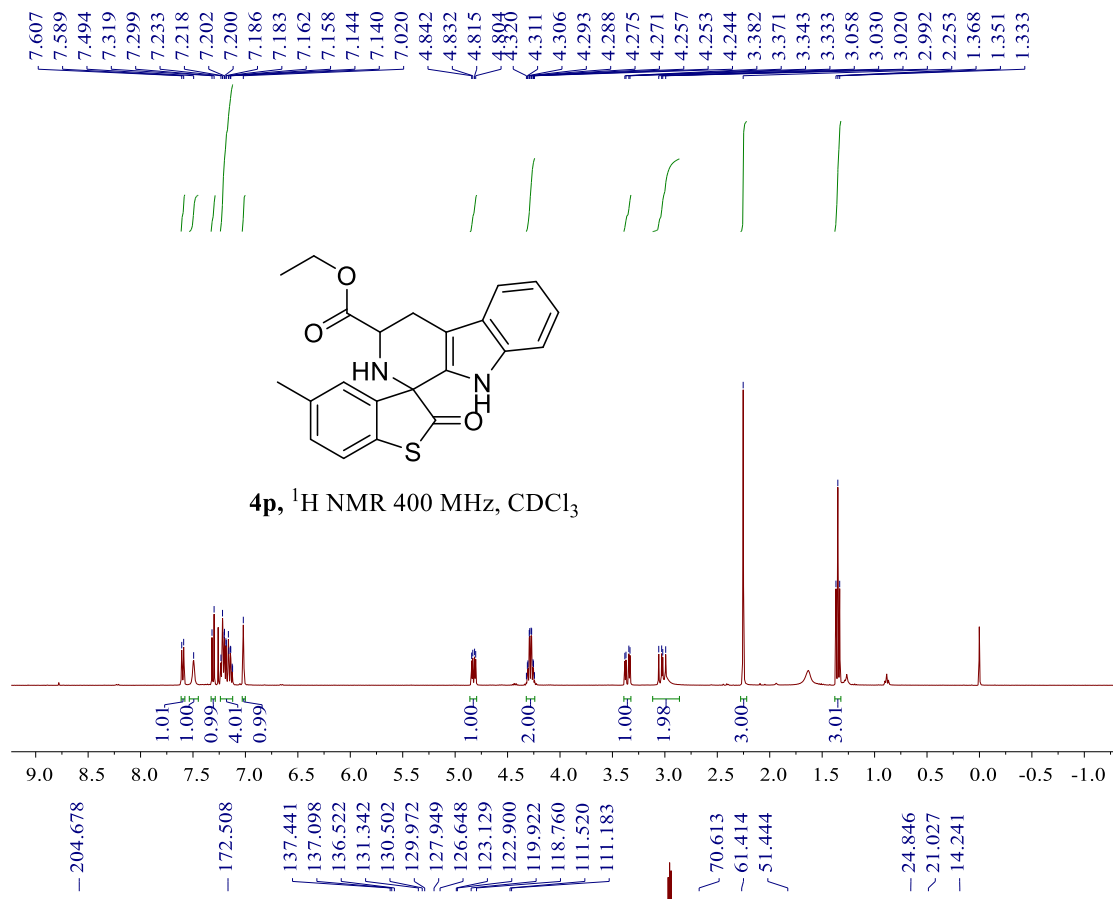


4n, ¹H NMR 400 MHz, DMSO

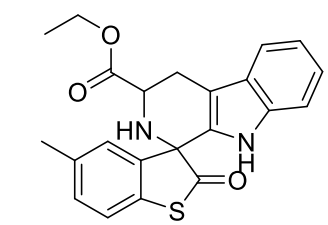
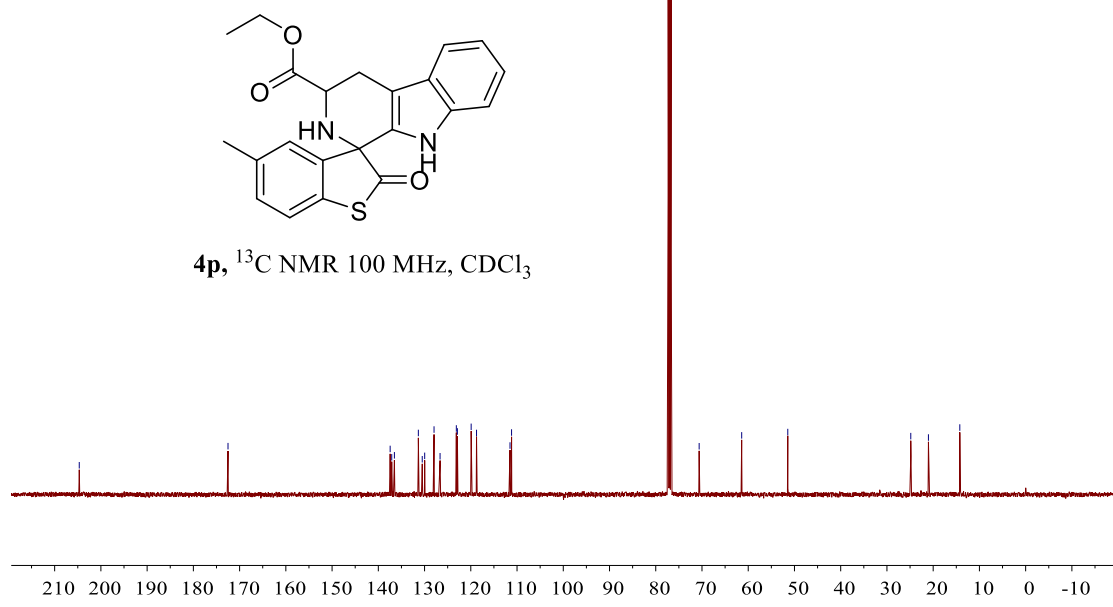


4n, ¹³C NMR 100 MHz, DMSO

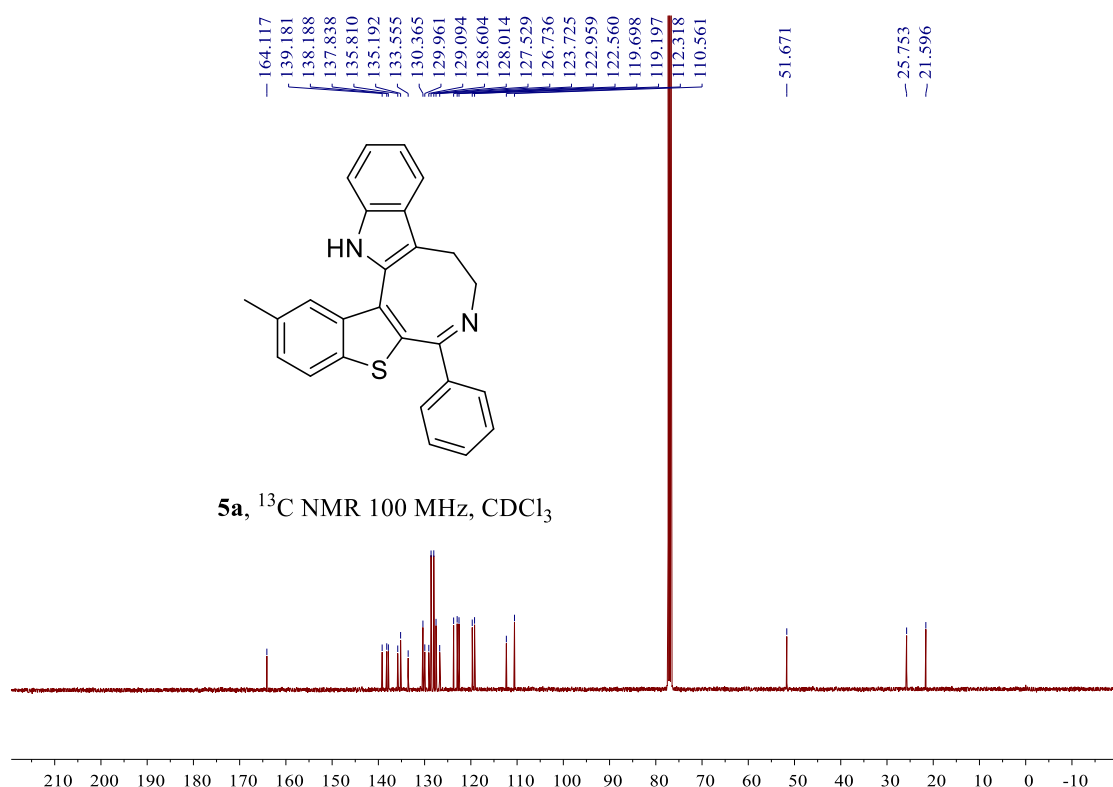
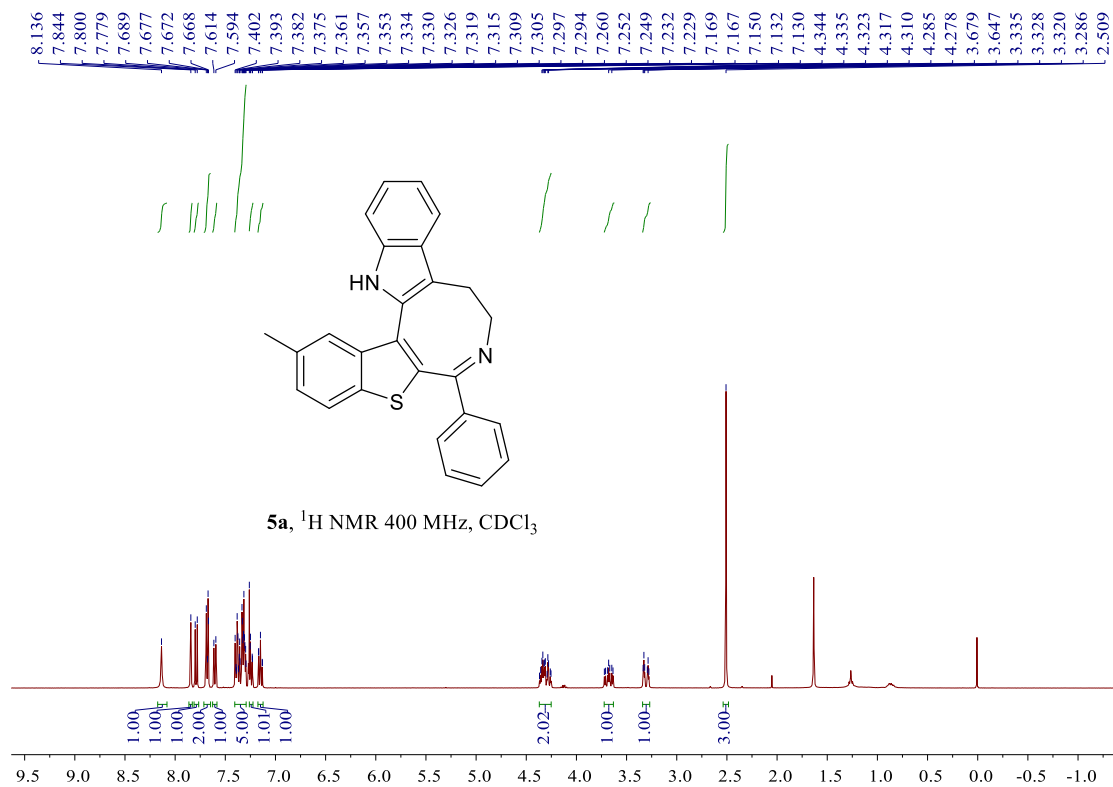


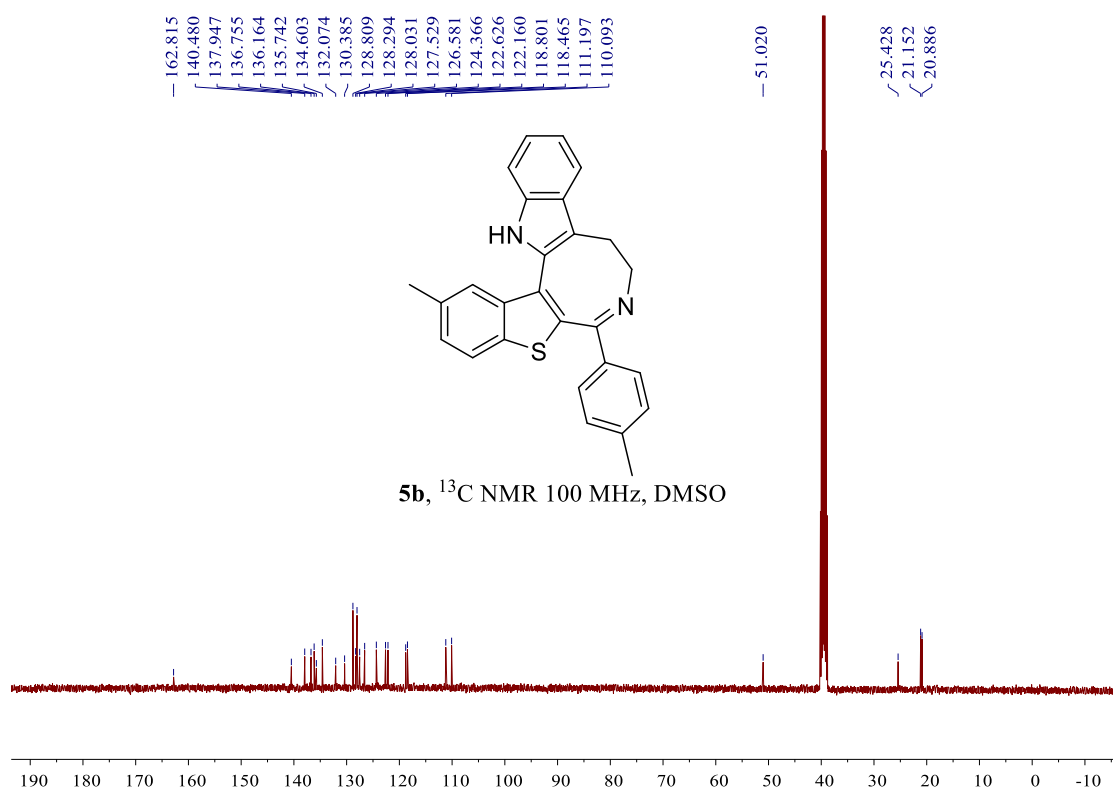
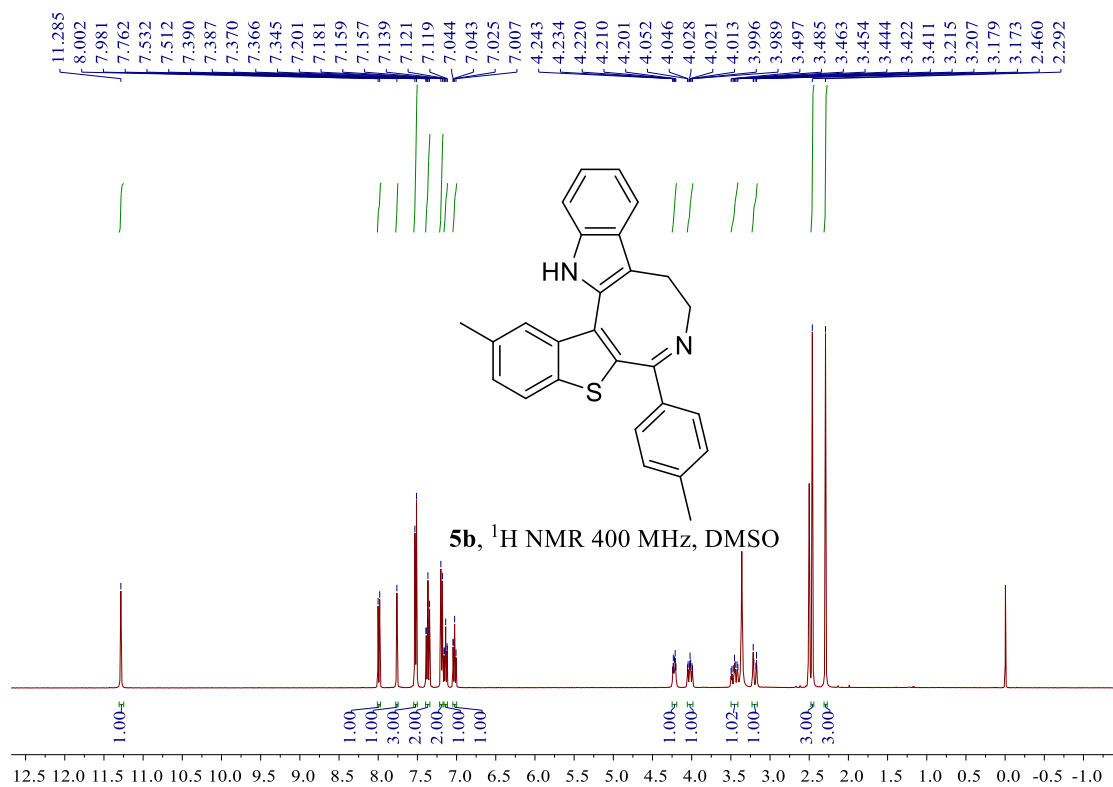


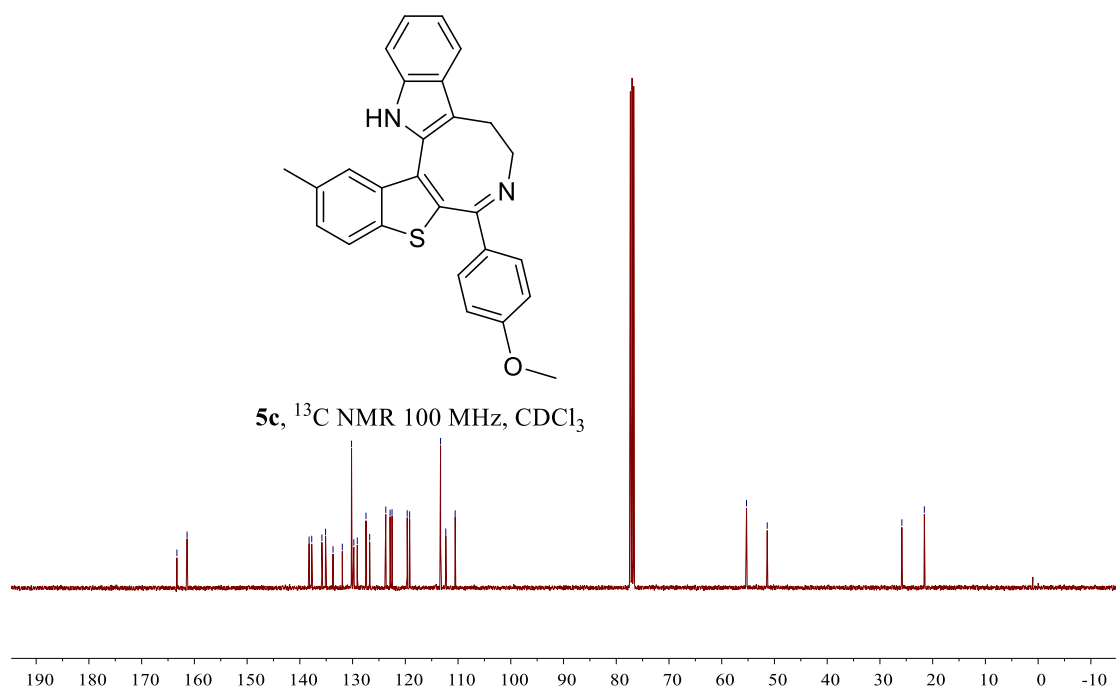
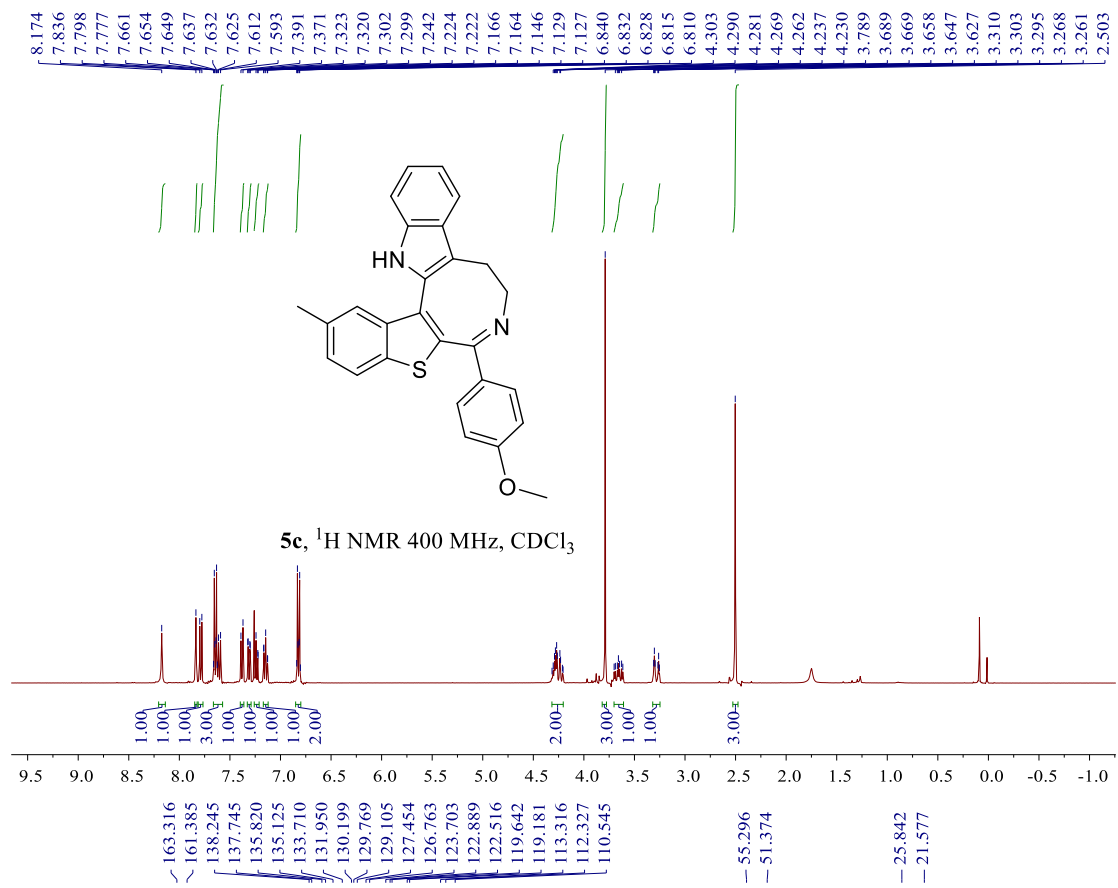
4p, ^1H NMR 400 MHz, CDCl_3

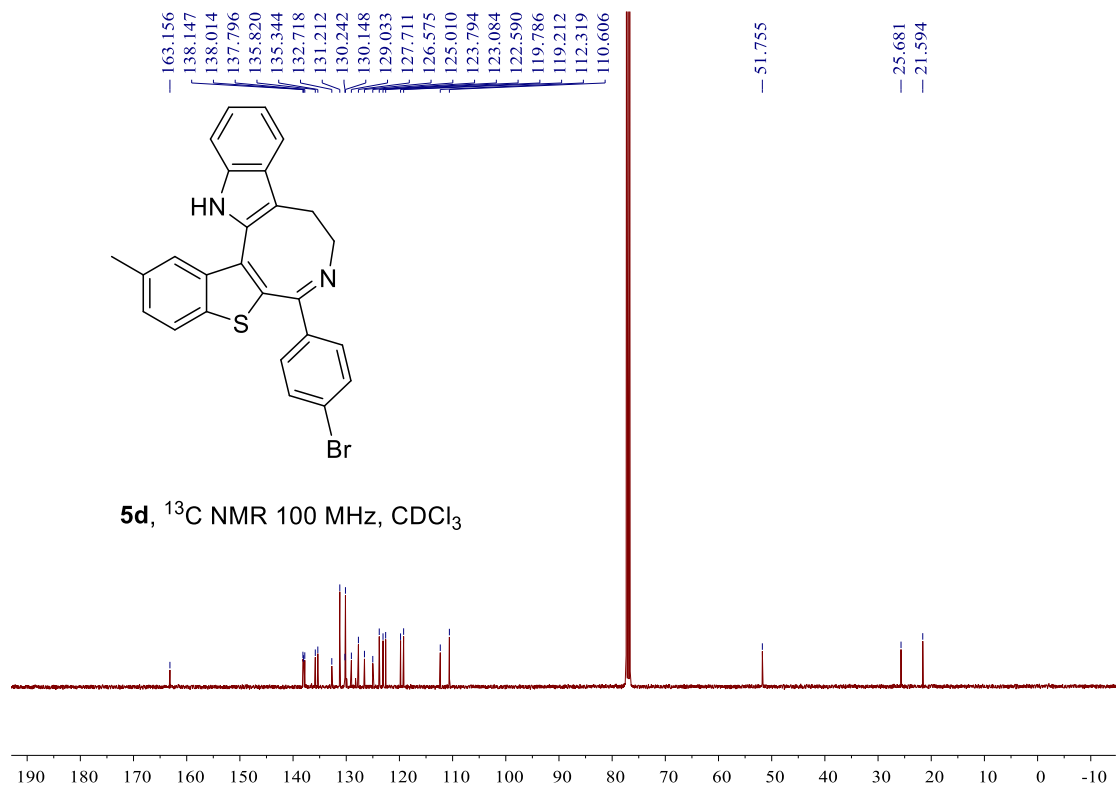
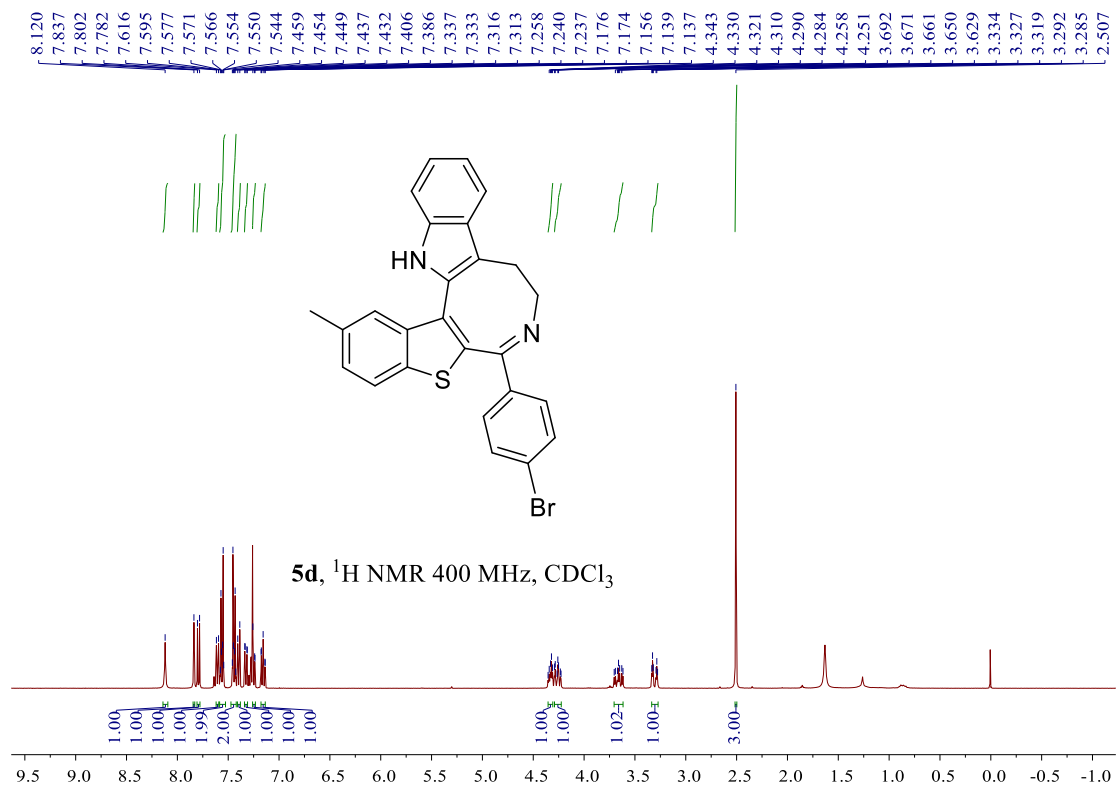


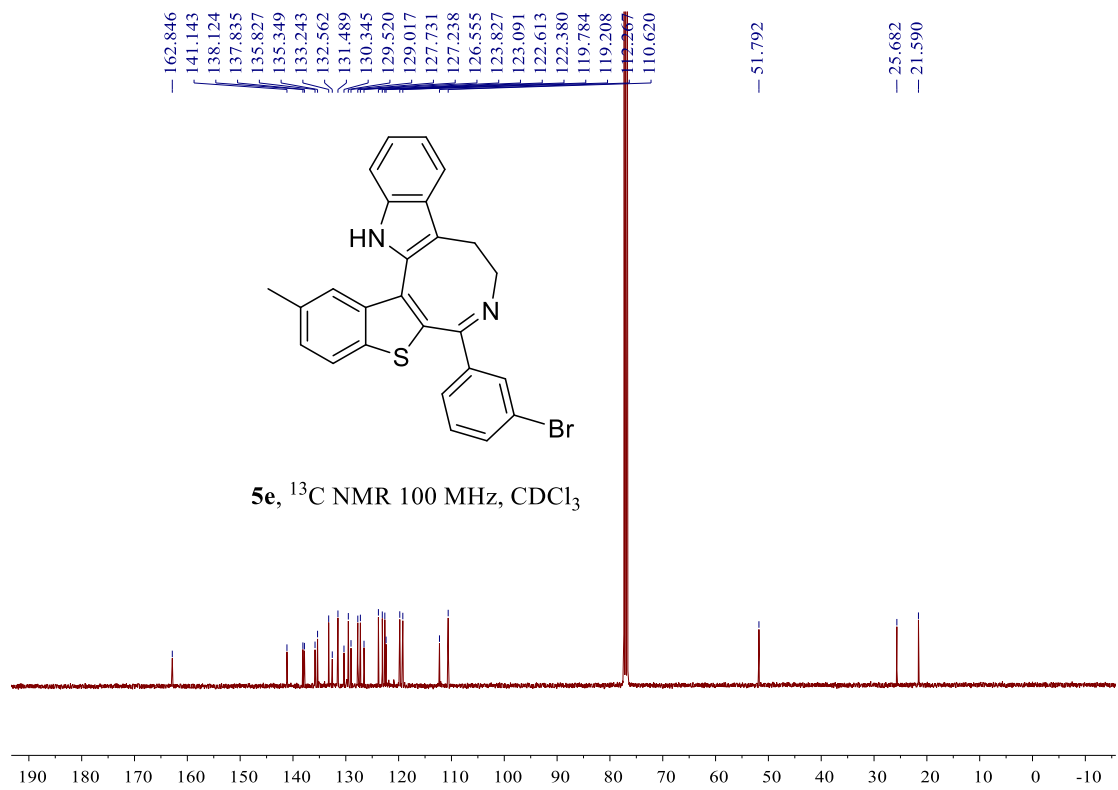
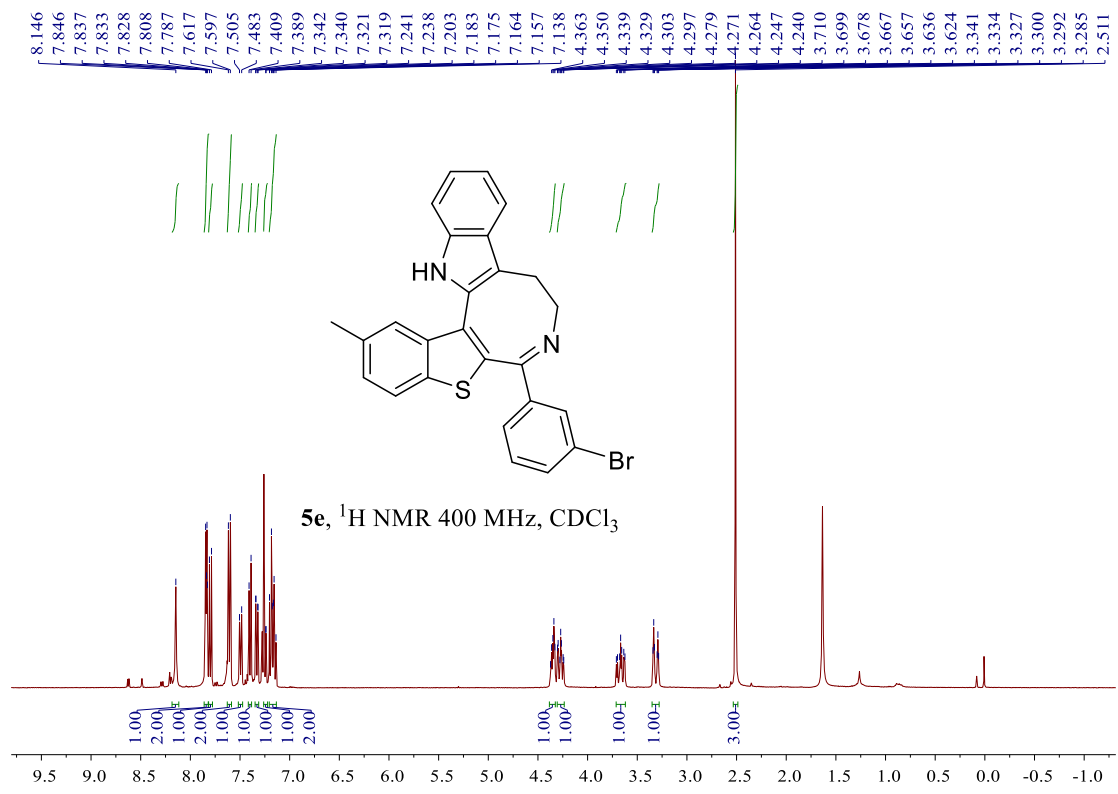
4p, ^{13}C NMR 100 MHz, CDCl_3

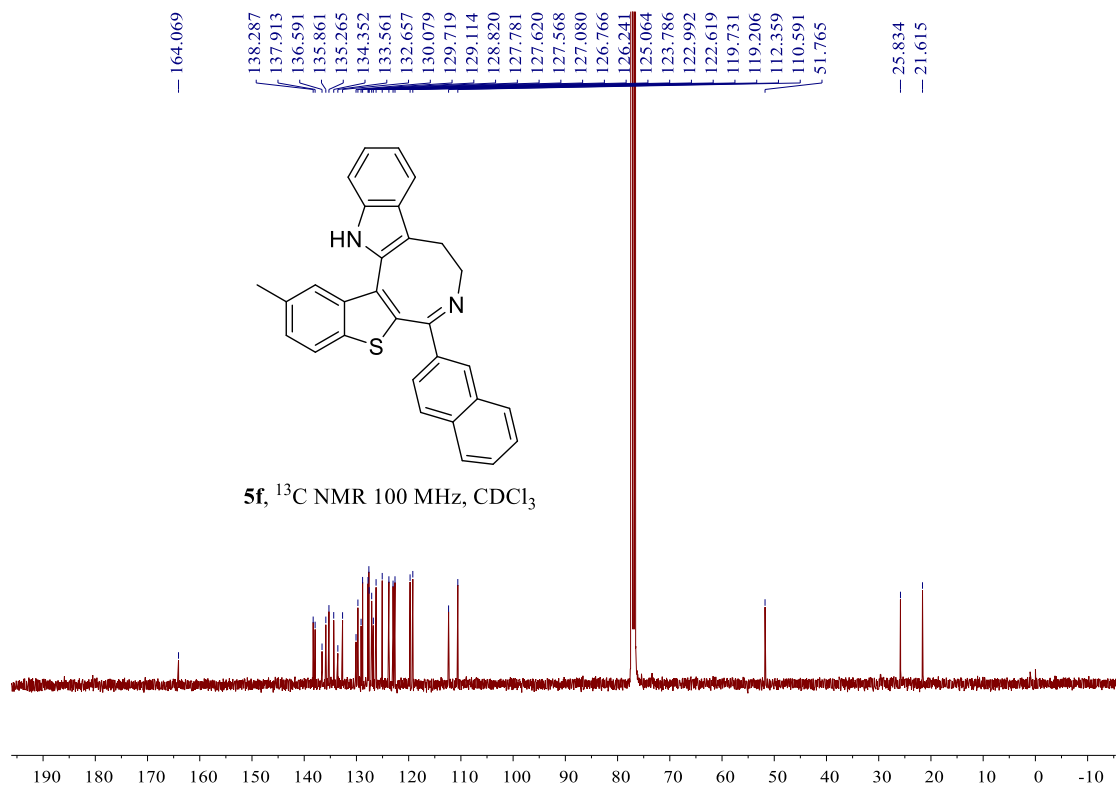
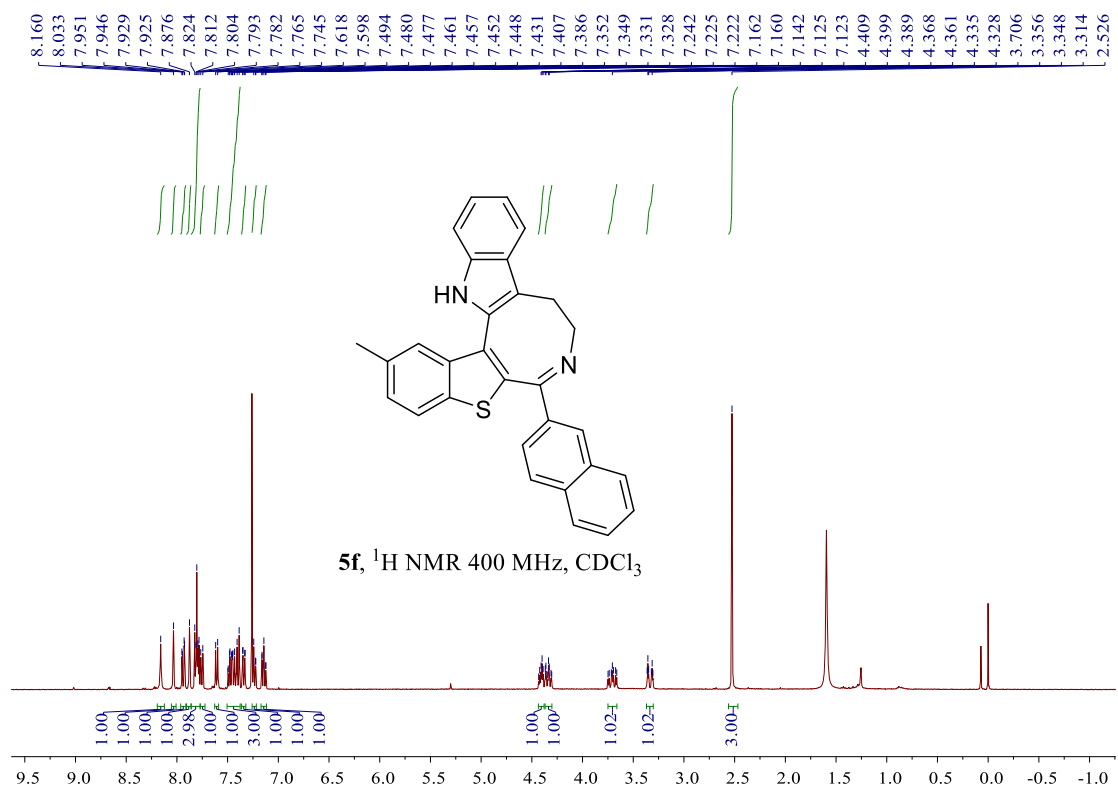


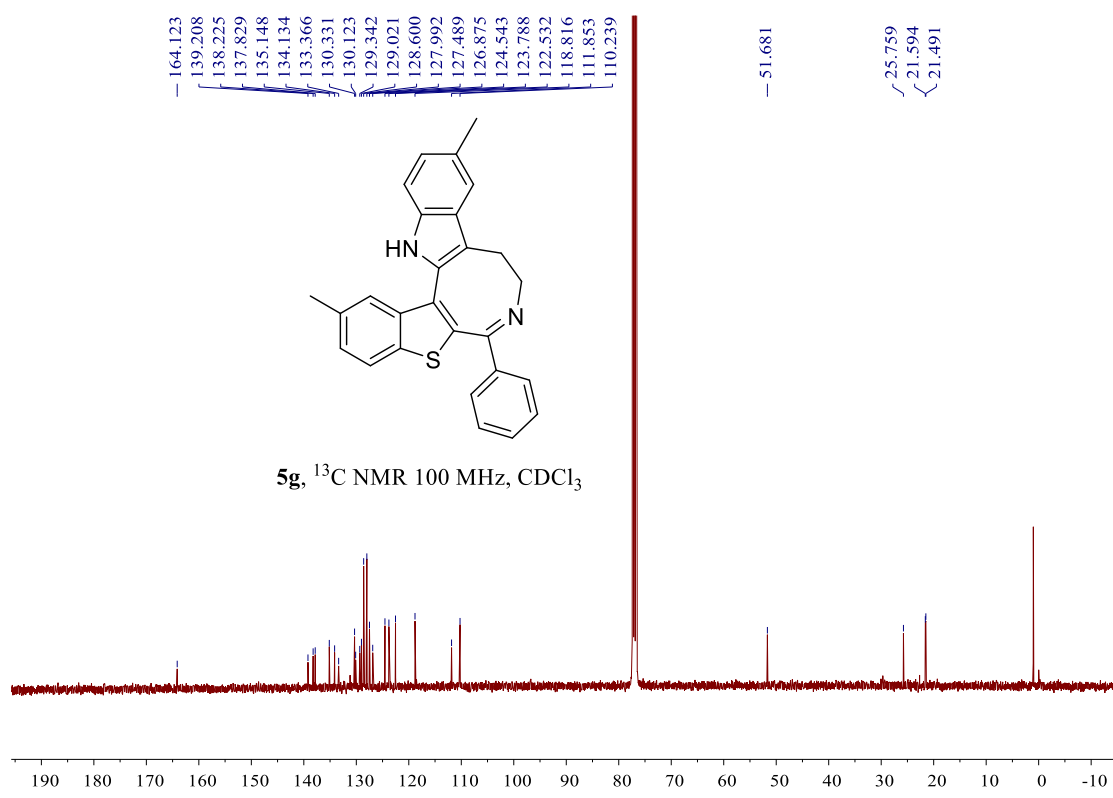
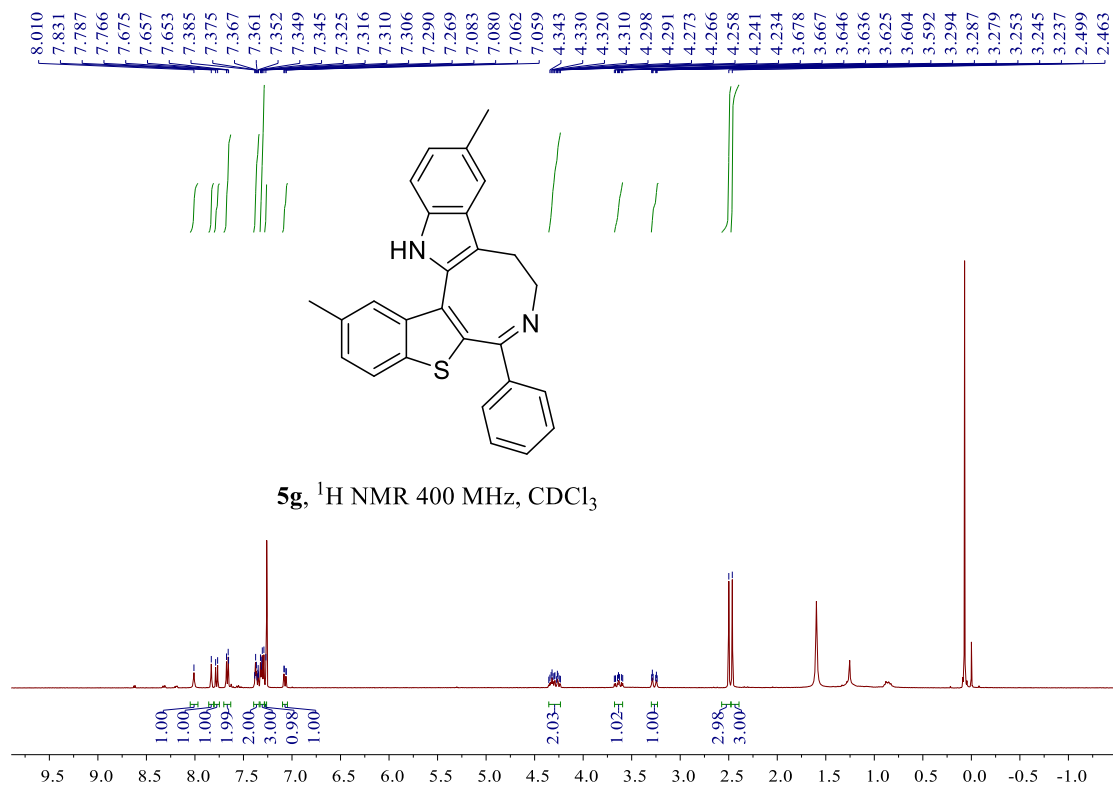


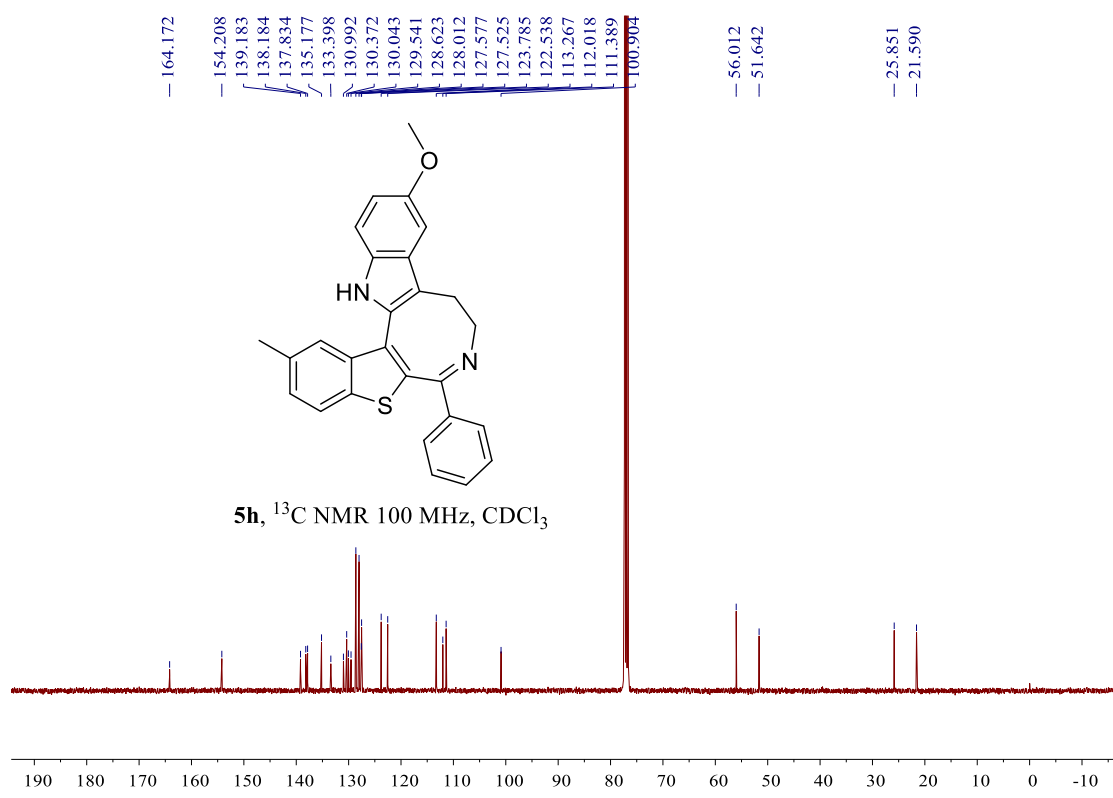
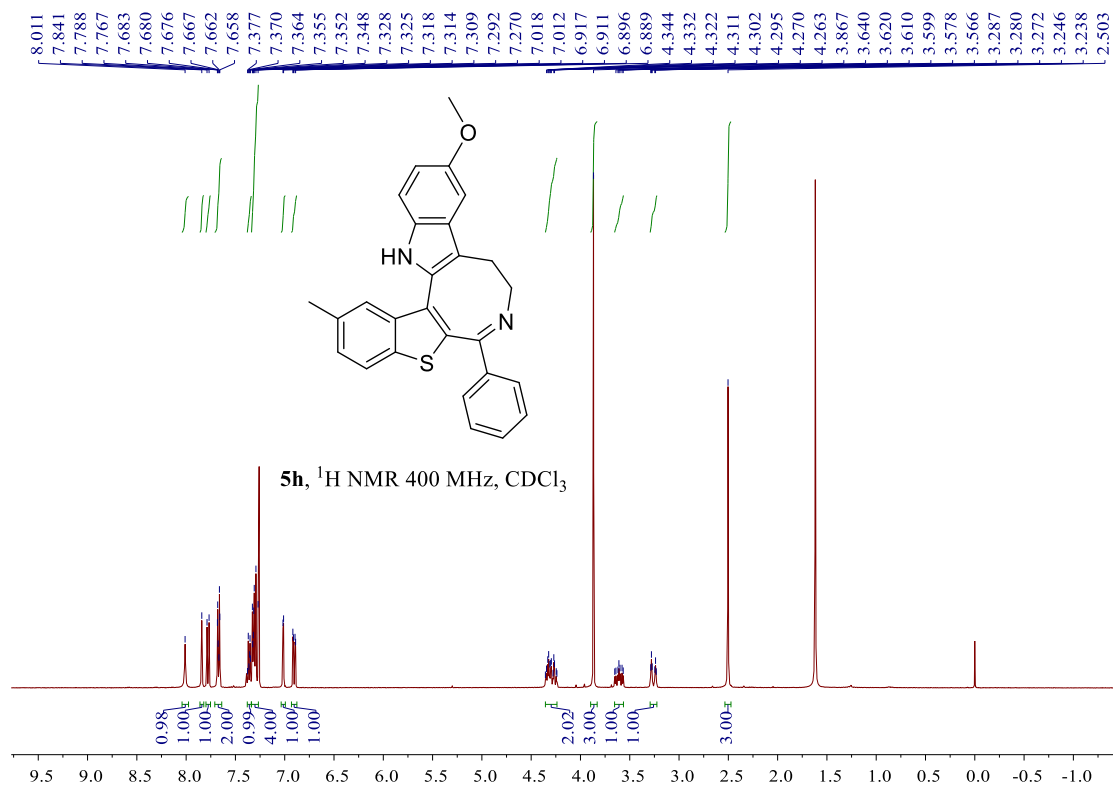


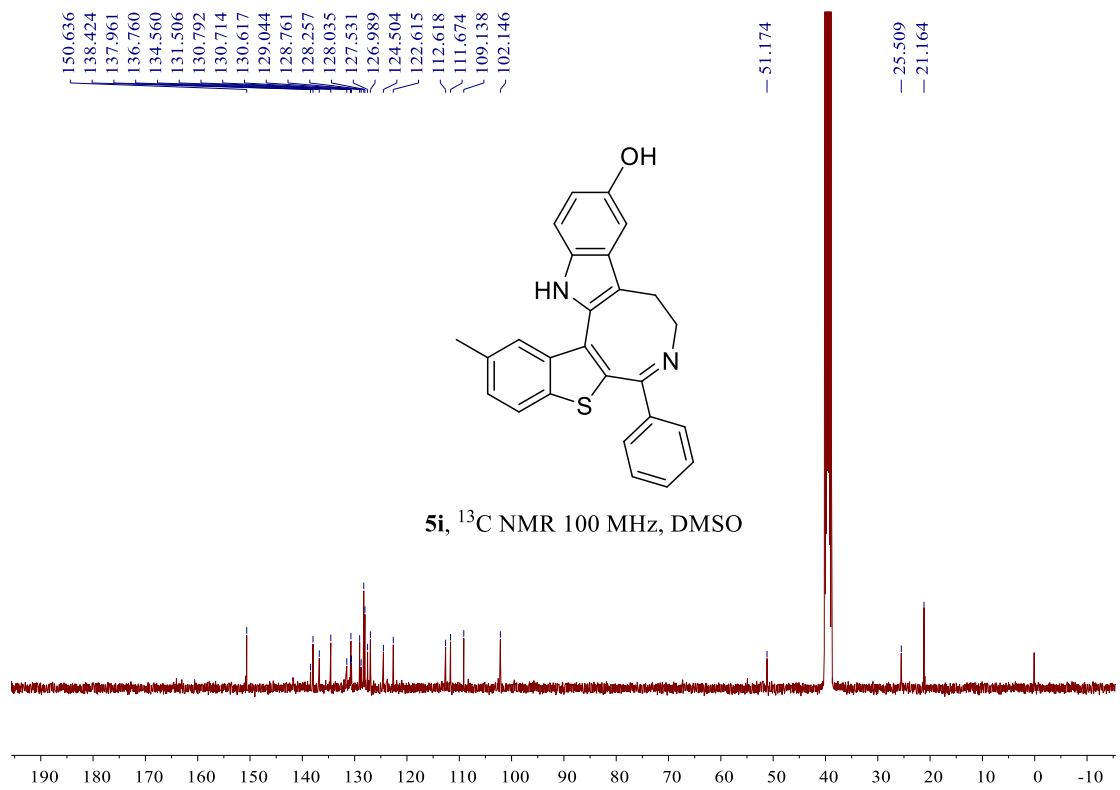
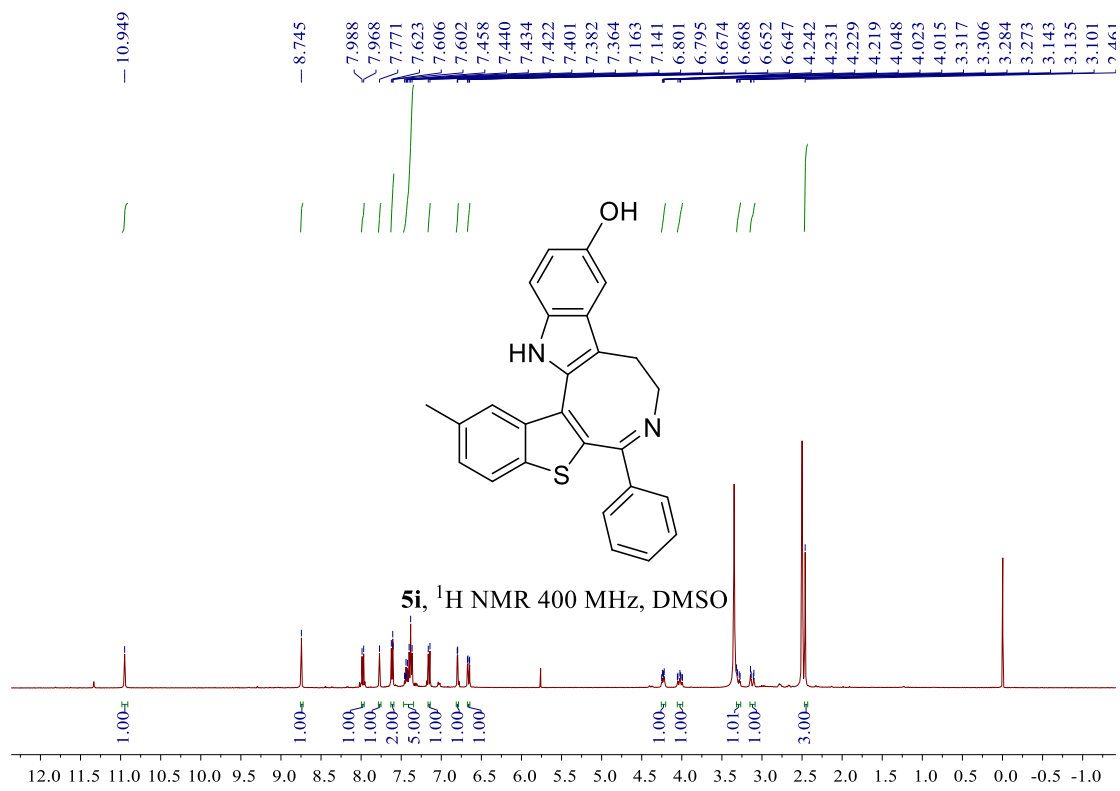


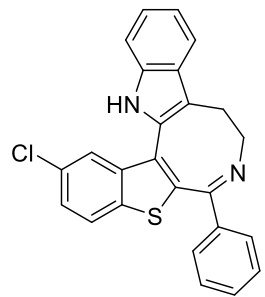
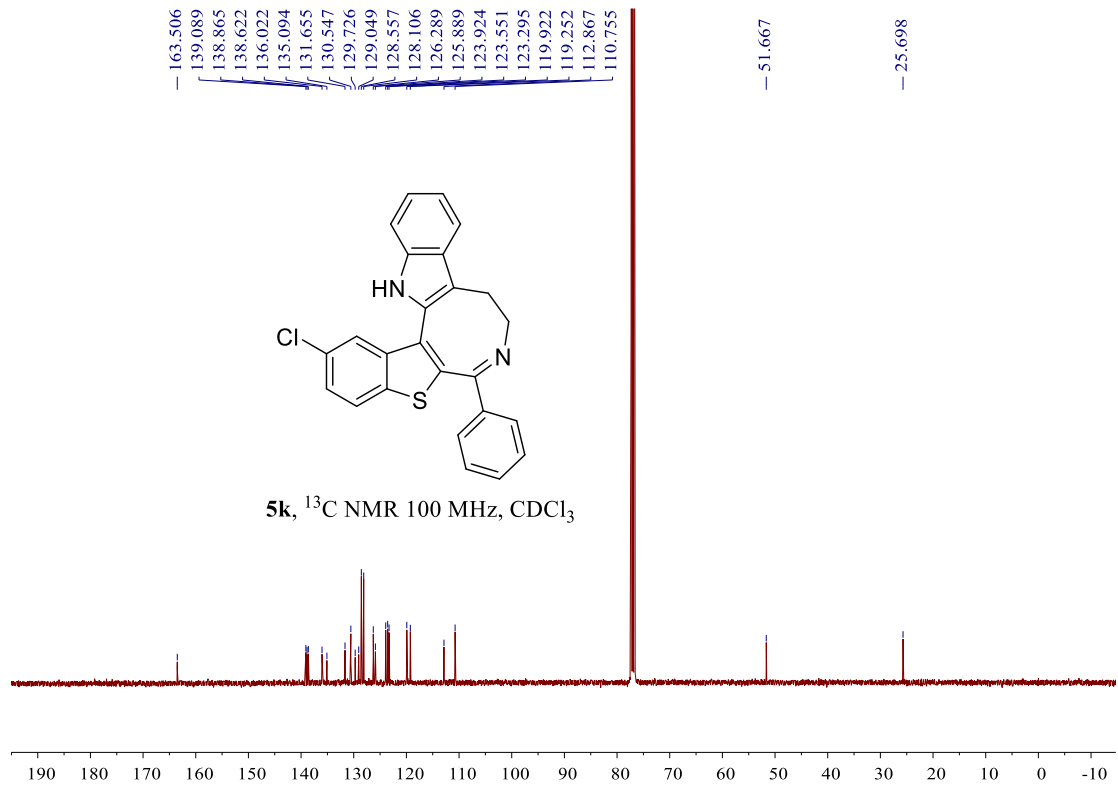
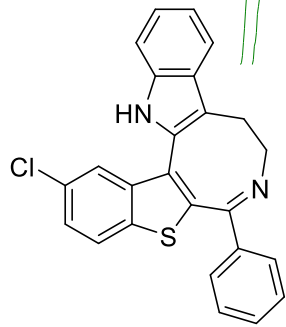
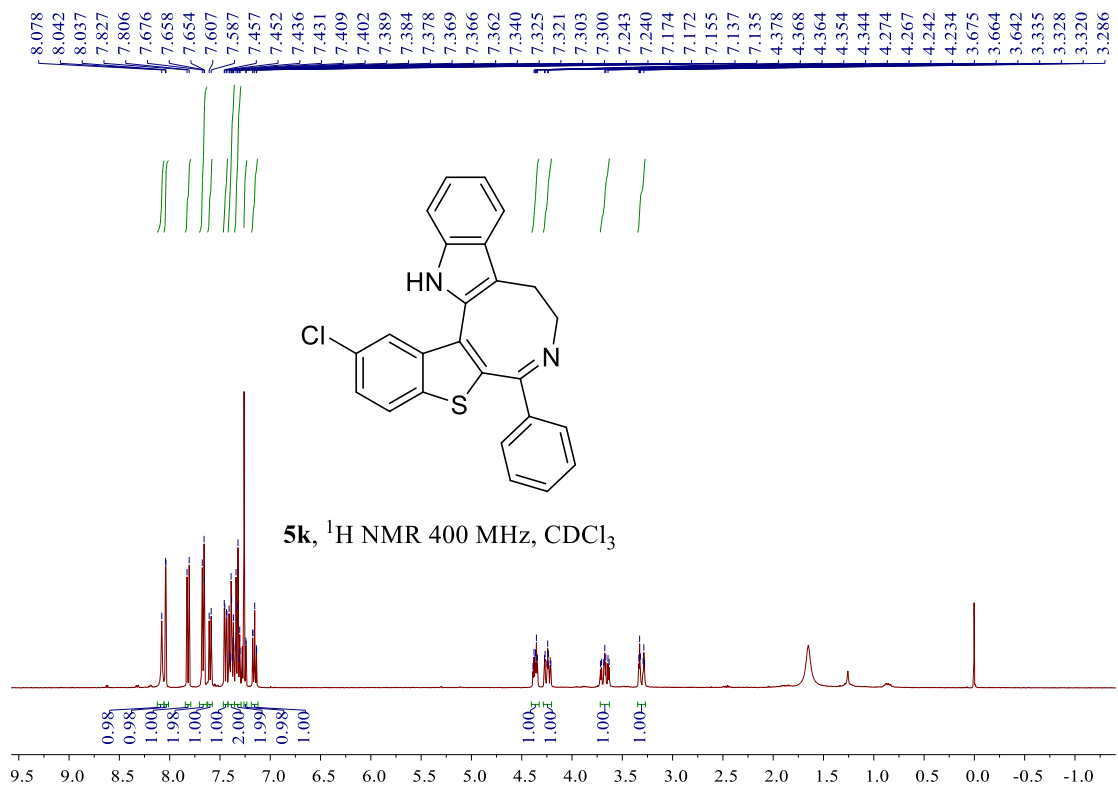


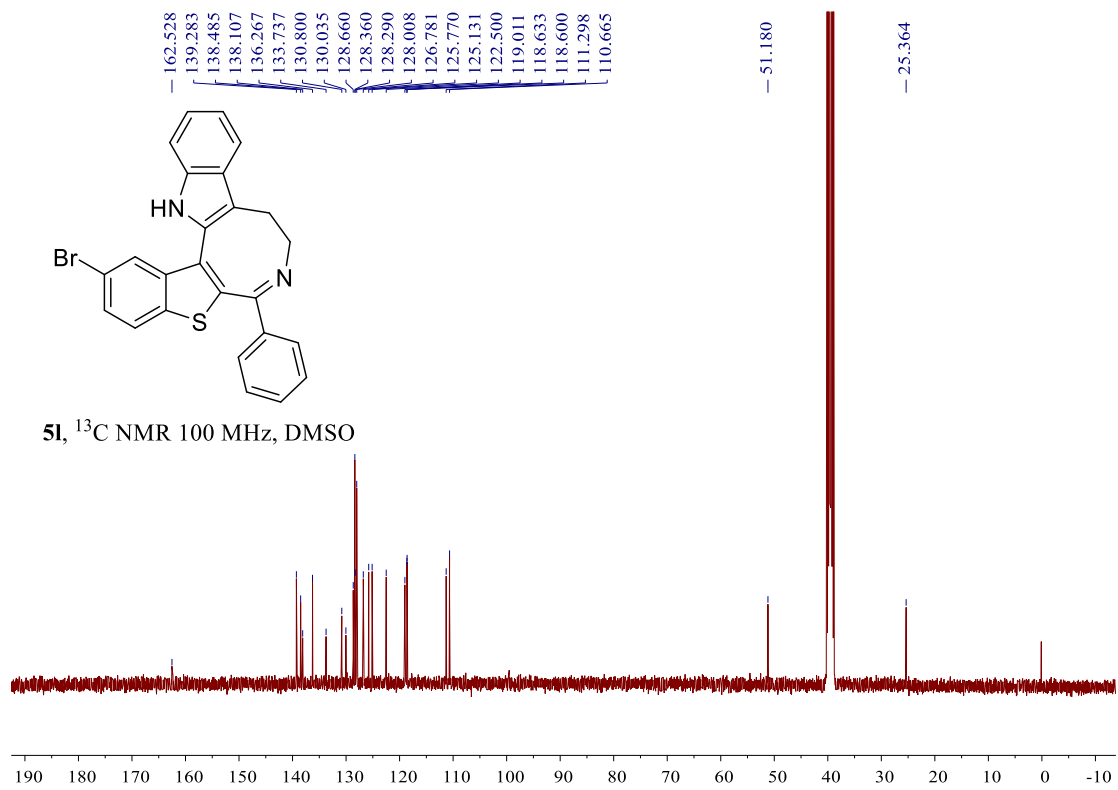
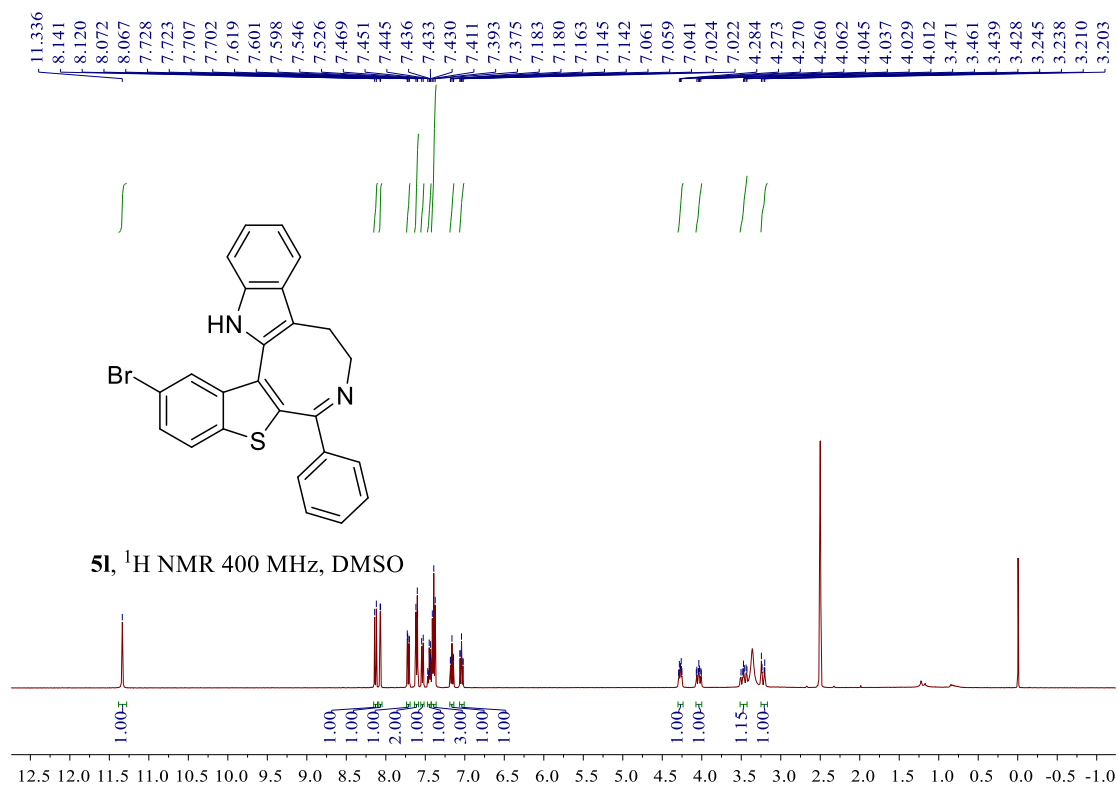


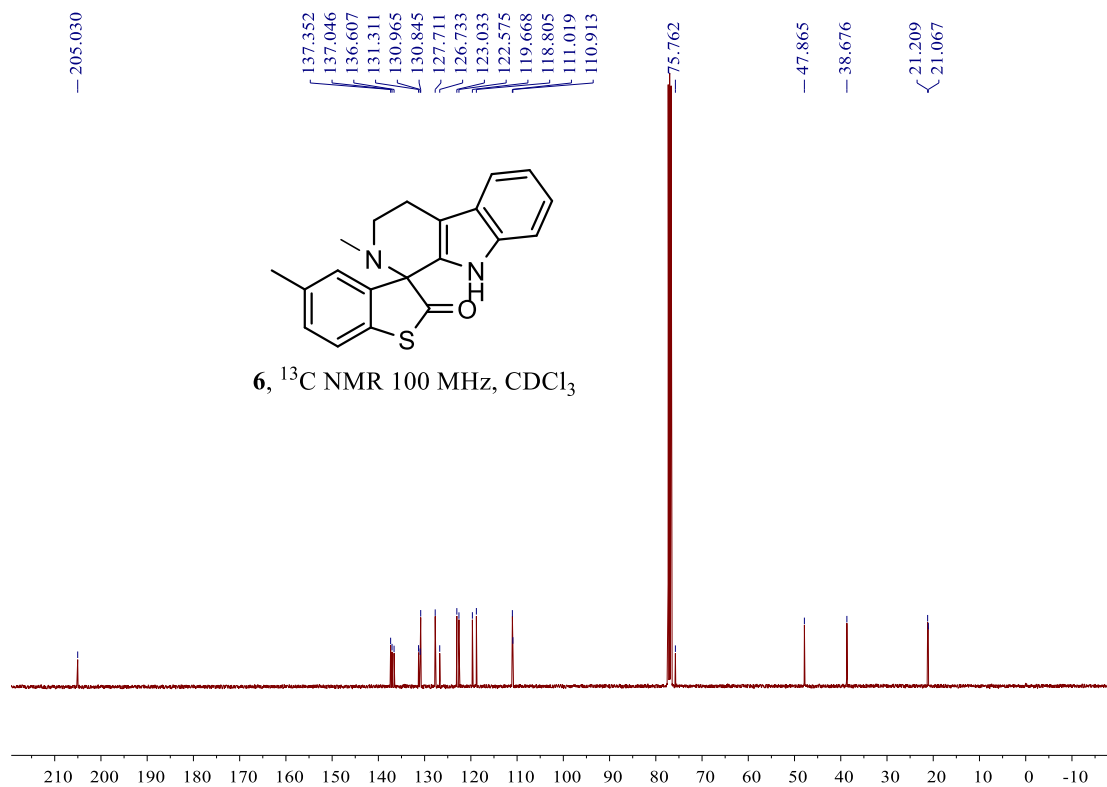
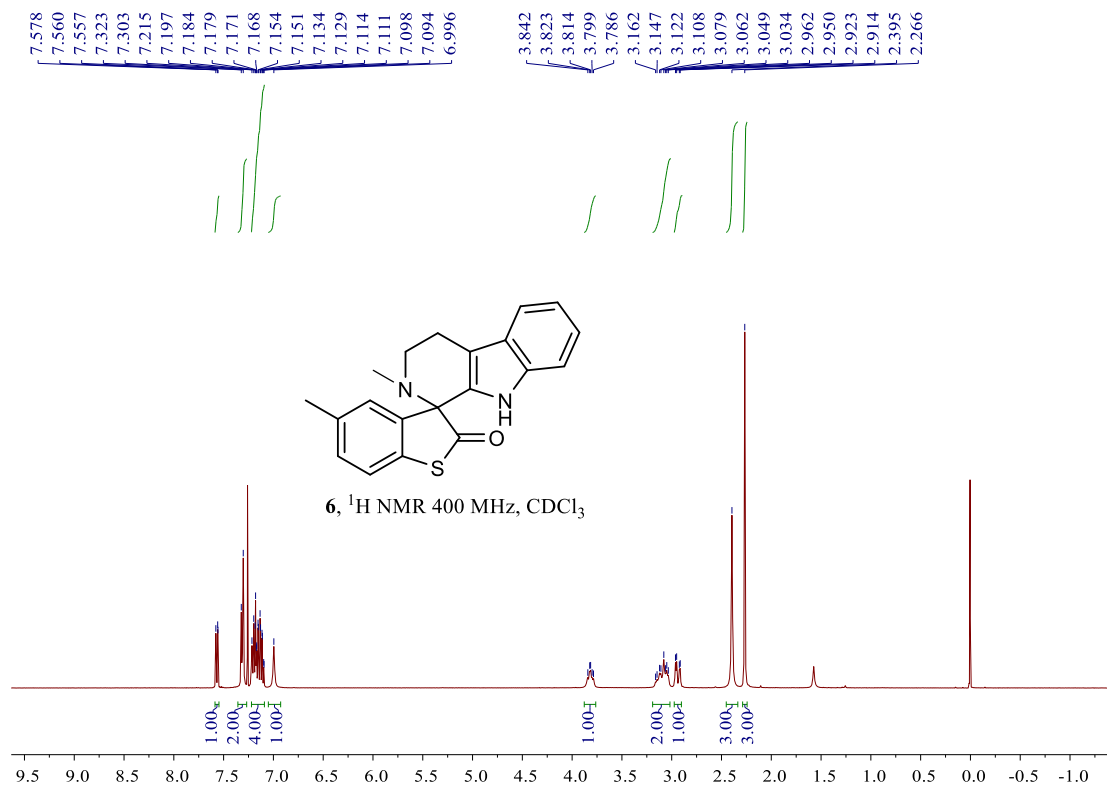


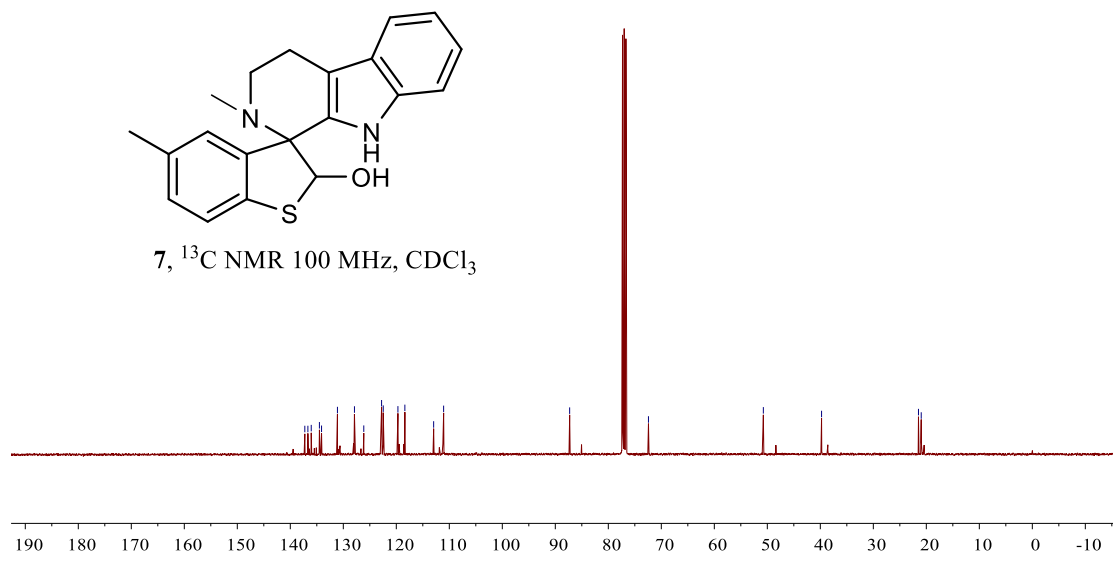
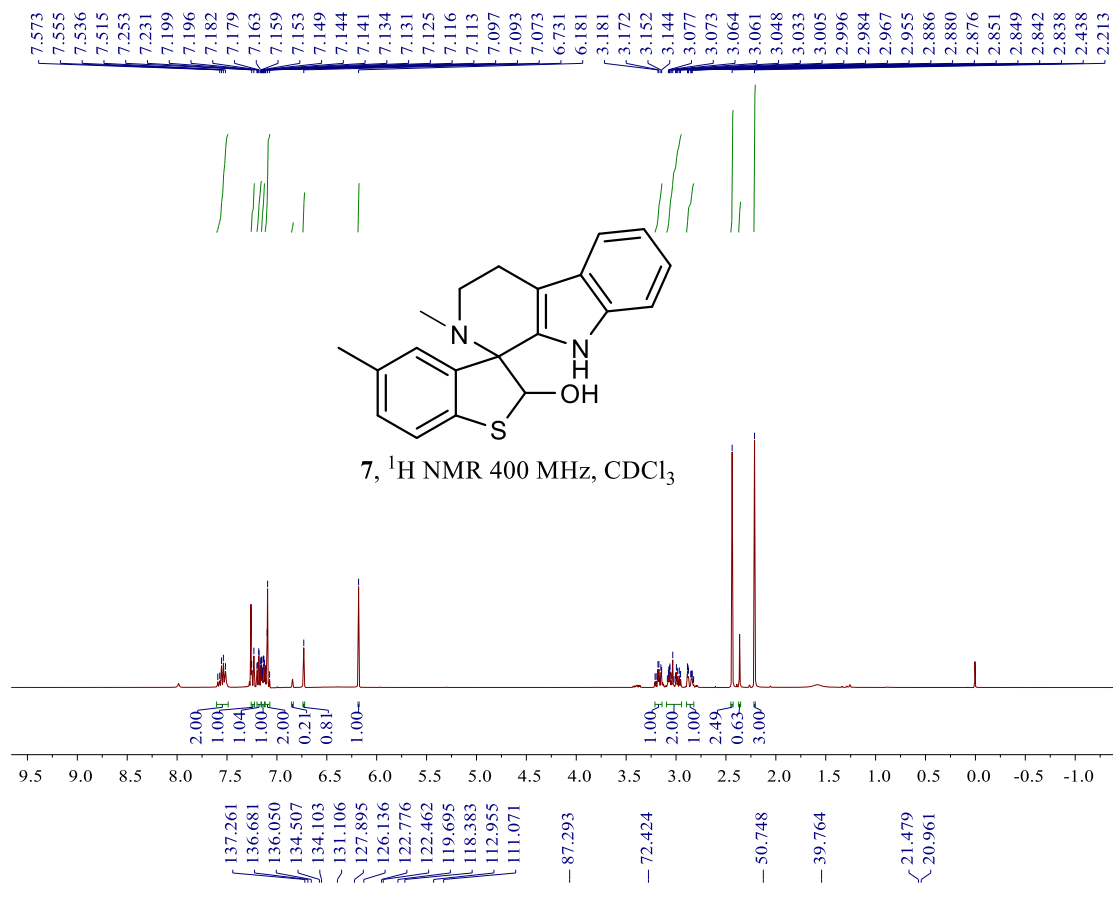


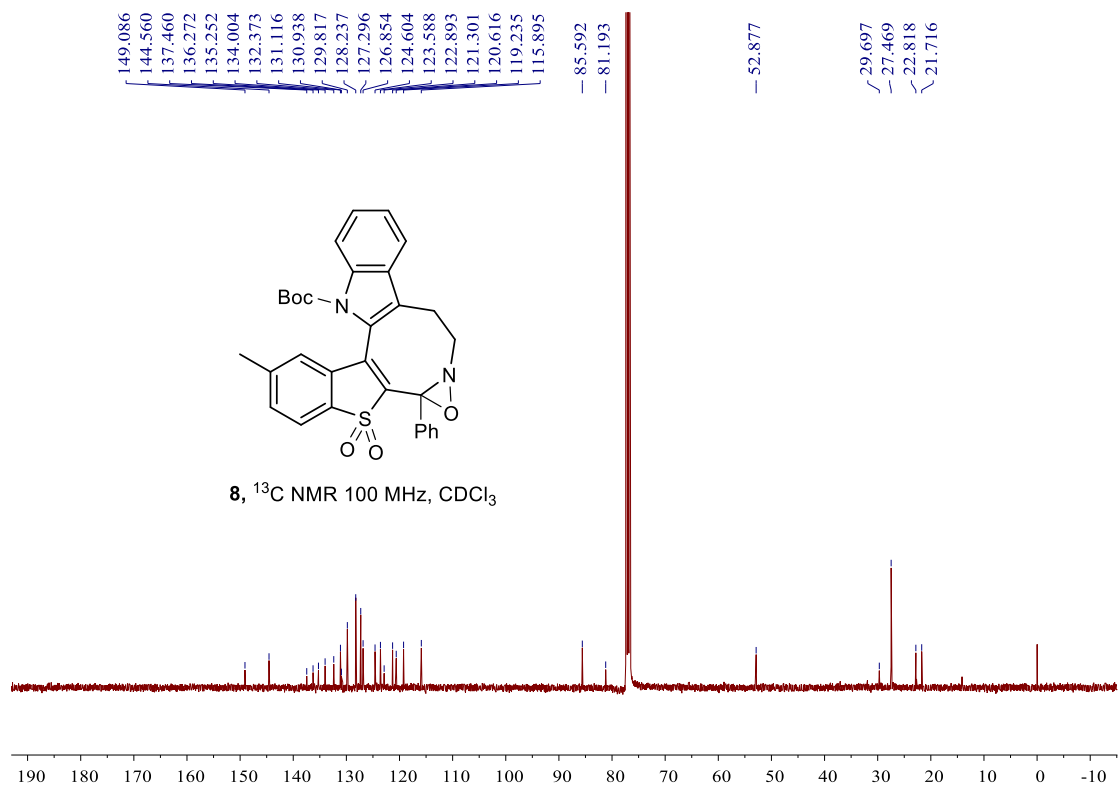
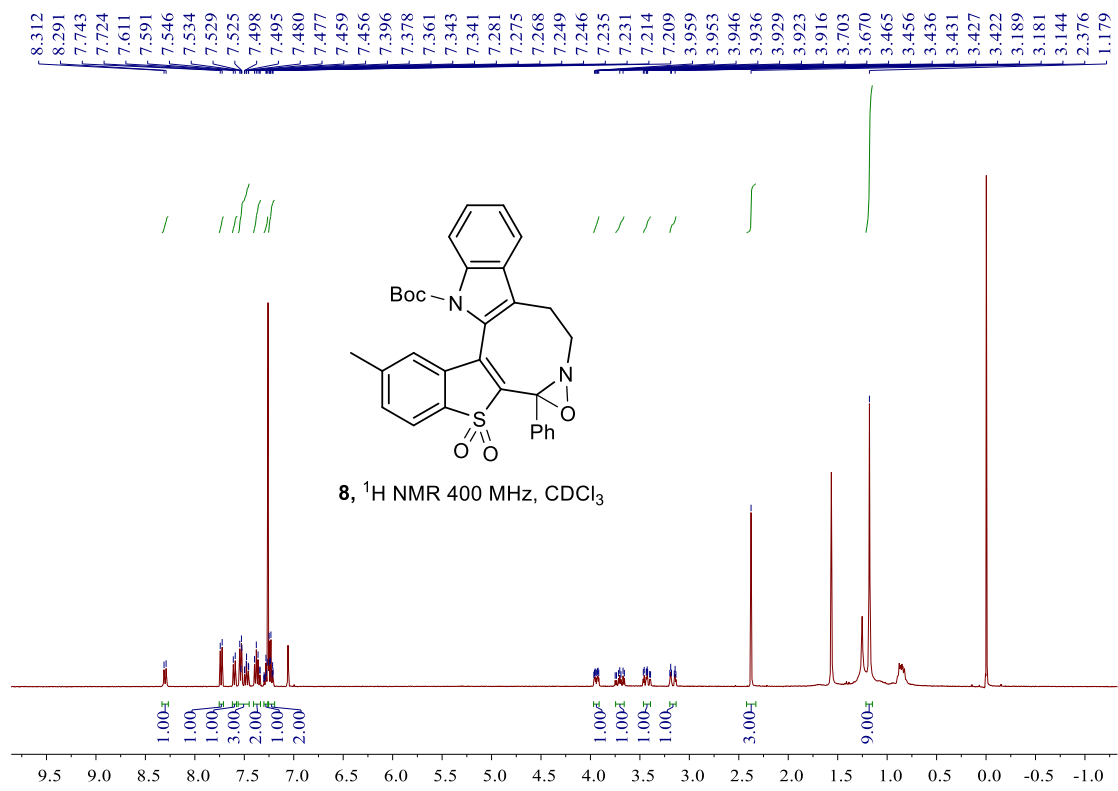












9. X-ray data collection and structure determinations

Table Crystal Data and Structure Refinements for **4a**, **5j**, **6**, **7**, **8**

	4a	5j
Chemical formula	C ₁₉ H ₁₆ N ₂ OS	C ₂₉ H ₂₆ N ₂ S
Formula weight	320.40	434.60
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
<i>a</i> (Å)	9.94330(10)	10.57330(10)
<i>b</i> (Å)	17.21630(10)	25.8833(3)
<i>c</i> (Å)	18.86940(10)	11.55000(10)
<i>V</i> (Å ³)	3230.19(4)	3100.97(5)
α (°)	90	90
β (°)	90	101.1760(10)
γ (°)	90	90
<i>Z</i>	4	4
F(000)	1344.0	1252.0
<i>GOF</i>	1.043	1.025
<i>D/g cm</i> ⁻³	1.318	1.293
μ (mm ⁻¹)	1.817	4.267
<i>T/K</i>	293	293
<i>R</i> _a / <i>R</i> _b	0.0313/0.0861	0.0720/0.2124

^a*R*= $\sum||F_o| - |F_c||/\sum|F_o|$. ^b*R*_w= $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

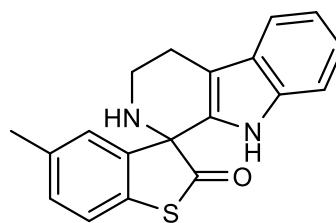
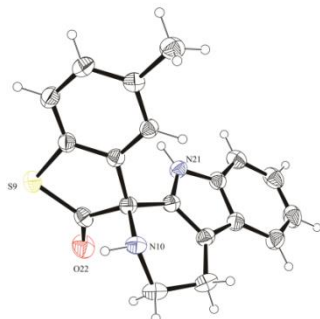
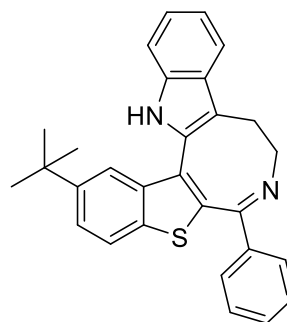
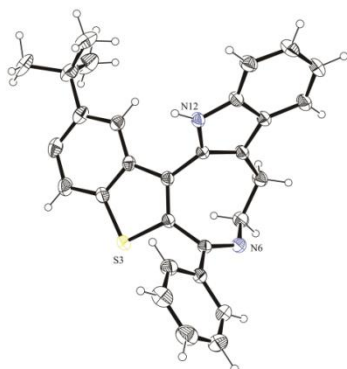
	6	7
Chemical formula	C ₂₀ H ₁₈ N ₂ OS	C ₂₀ H ₂₀ N ₂ OS
Formula weight	334.42	336.13
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁
<i>a</i> (Å)	13.5789(2)	11.4056(3)
<i>b</i> (Å)	7.1947(10)	7.6851(1)
<i>c</i> (Å)	18.2456(3)	13.5446(3)
<i>V</i> (Å ³)	1710.87(5)	1095.81(5)
α (°)	90	90
β (°)	106.301(2)	112.632(3)
γ (°)	90	90
<i>Z</i>	4	2
F(000)	704.0	472.0
<i>GOF</i>	1.089	1.059
<i>D/g cm</i> ⁻³	1.298	1.381
μ (mm ⁻¹)	1.737	4.789
<i>T/K</i>	293	293
<i>R</i> _a / <i>R</i> _b	0.0369/0.1058	0.0537/0.1561

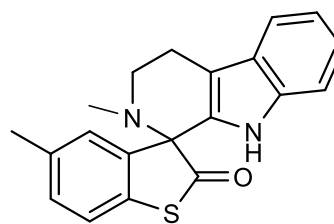
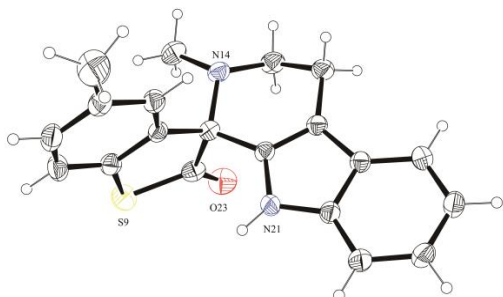
^a*R*= $\sum||F_o| - |F_c||/\sum|F_o|$. ^b*R*_w= $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

8

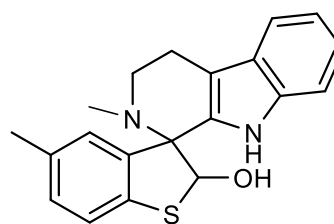
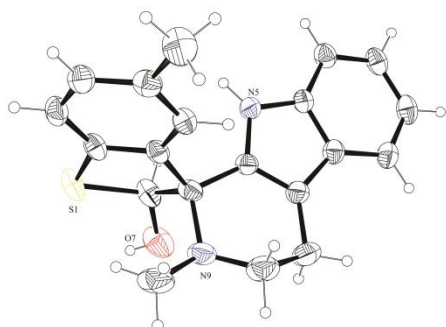
Chemical formula	C ₃₁ H ₂₈ N ₂ O ₅ S
Formula weight	540.61
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	16.3292(10)
<i>b</i> (Å)	9.8454(6)
<i>c</i> (Å)	18.1637(10)
<i>V</i> (Å ³)	2750.43(3)
α (°)	90
β (°)	109.633(6)
γ (°)	90
<i>Z</i>	4
F(000)	1136.0
<i>GOF</i>	1.074
<i>D</i> /g cm ⁻³	1.306
μ (mm ⁻¹)	1.402
<i>T</i> /K	293
<i>R</i> _a / <i>R</i> _b	0.0635/0.1857

$${}^aR = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^bR_w = \frac{[\sum [w(F_o^2 - F_c^2)^2]]}{\sum w(F_o^2)^2}^{1/2}.$$

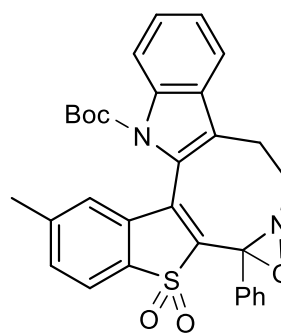
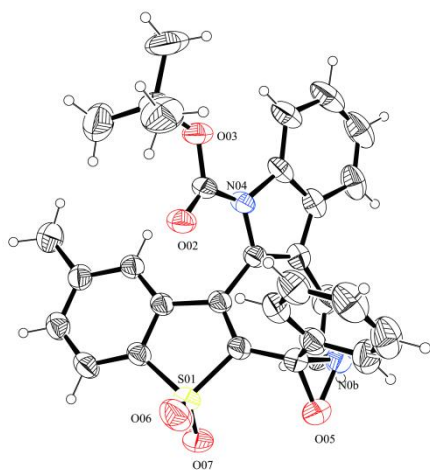
10. X-ray Crystal Structures**4a** (CCDC 2205447)**5j** (CDCC 2205448)



6 (CDCC 2205449)

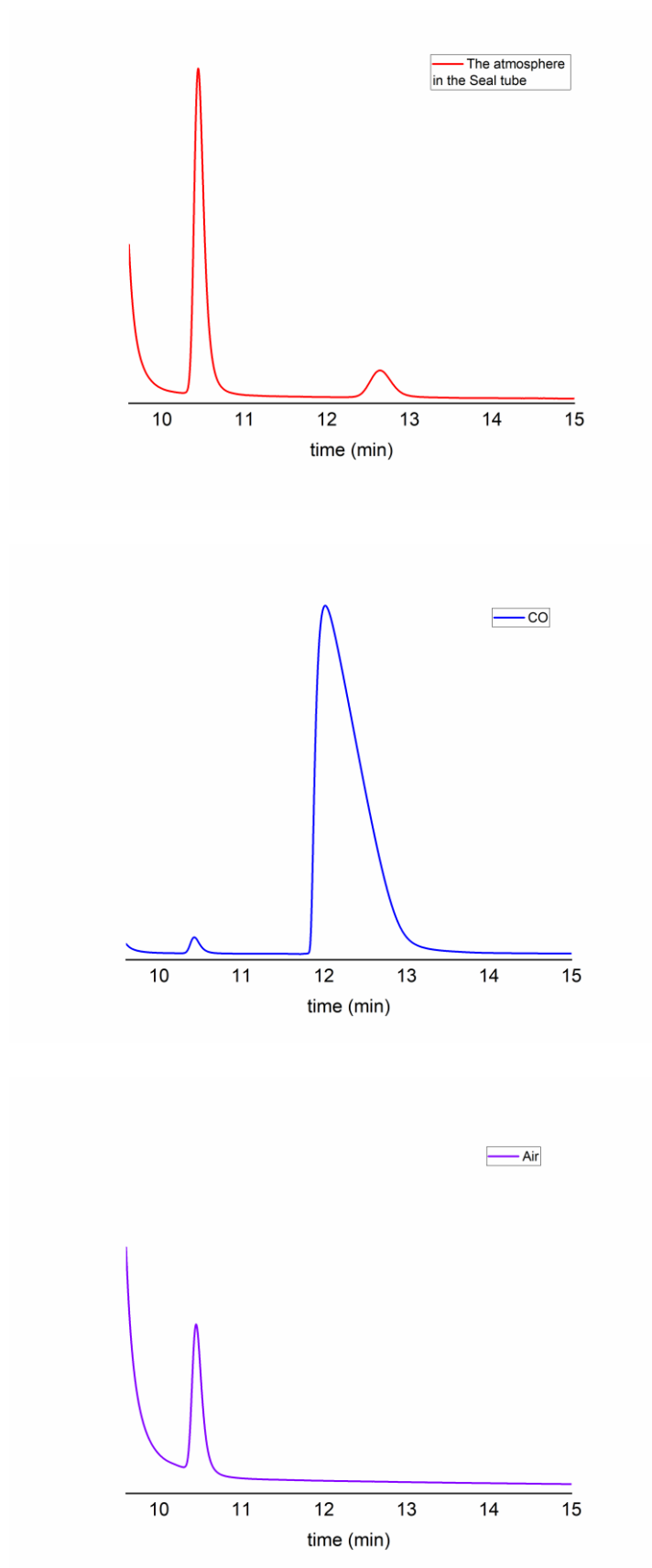


7 (CDCC 2205450)



8 (CDCC 2205451)

11. The results of CO detection by gas chromatography



12. Computational materials

Table. Cartesian coordinates of the optimized stationary points

Names	Cartesian coordinates			
1a	6	-0.521734000	-0.757387000	0.000053000
	6	-0.407094000	0.645310000	-0.000033000
	6	-1.553390000	1.450687000	0.000127000
	6	-2.809367000	0.845309000	0.000302000
	6	-2.910259000	-0.553219000	0.000339000
	6	-1.769470000	-1.369448000	0.000212000
	6	1.960441000	-0.101434000	-0.000133000
	6	0.973941000	1.118497000	-0.000357000
	1	-1.448588000	2.531880000	0.000051000
	1	-3.708130000	1.453946000	0.000393000
	1	-3.890908000	-1.020661000	0.000486000
	1	-1.866186000	-2.450635000	0.000275000
	16	1.039902000	-1.640142000	0.000002000
	8	1.398992000	2.259095000	-0.000304000
	8	3.163129000	-0.001864000	-0.000233000
2a	6	1.819946000	-1.168594000	-0.000260000
	6	1.368667000	0.164562000	-0.000147000
	6	2.310225000	1.209951000	0.000140000
	6	3.675008000	0.930216000	0.000179000
	6	4.117343000	-0.398474000	0.000242000
	6	3.188189000	-1.443404000	0.000003000
	1	1.122065000	-1.998822000	-0.000372000
	1	1.956400000	2.235893000	0.000118000
	1	4.394418000	1.744394000	0.000252000
	1	5.181562000	-0.617947000	0.000298000
	1	3.529099000	-2.474913000	-0.000019000
	6	-0.082899000	0.517681000	-0.000281000
	8	-0.467187000	1.678729000	-0.000315000
	6	-1.055066000	-0.656787000	-0.000195000
	1	-0.908296000	-1.276922000	-0.885934000
1	-0.908109000	-1.276867000	0.885547000	
35	-2.933660000	-0.134159000	0.000130000	
3a	6	-2.567124000	0.603881000	-0.372971000
	6	-1.510552000	-0.194938000	0.151392000
	6	-1.795102000	-1.507207000	0.577473000
	6	-3.099732000	-1.982978000	0.474645000
	6	-4.132469000	-1.172192000	-0.050041000
	6	-3.881400000	0.128813000	-0.480132000
	6	-0.674250000	1.823347000	-0.415415000
	6	-0.309972000	0.606229000	0.116759000

	1	-1.009673000	-2.141582000	0.981541000
	1	-3.331094000	-2.993695000	0.801138000
	1	-5.141278000	-1.570994000	-0.119304000
	1	-4.675001000	0.752357000	-0.883542000
	1	-0.083696000	2.707692000	-0.612702000
	7	-2.025644000	1.826885000	-0.705677000
	1	-2.527584000	2.603796000	-1.112137000
	6	1.049885000	0.151493000	0.577236000
	1	0.958359000	-0.317321000	1.567324000
	1	1.439060000	-0.625705000	-0.095235000
	6	2.064277000	1.289296000	0.659808000
	1	1.753417000	2.058055000	1.370387000
	1	2.235979000	1.754726000	-0.313004000
	7	3.401578000	0.774752000	1.114533000
	1	3.338137000	0.303847000	2.022127000
	1	3.821311000	0.089226000	0.419506000
	1	4.074650000	1.539514000	1.220363000
	17	4.626736000	-1.226226000	-0.914175000
	6	3.928869000	-0.159027000	0.371448000
	6	2.958594000	-0.154683000	-0.644070000
	6	3.140297000	-0.924973000	-1.795471000
	6	4.286437000	-1.714849000	-1.912287000
	6	5.240102000	-1.724382000	-0.886274000
	6	5.074686000	-0.941581000	0.264451000
	6	2.069248000	1.532724000	0.937183000
	6	1.823185000	0.743479000	-0.373116000
	1	2.394418000	-0.899605000	-2.584428000
	1	4.439349000	-2.320465000	-2.800355000
	1	6.129906000	-2.340085000	-0.982911000
	1	5.828596000	-0.942362000	1.045643000
	16	3.568332000	0.940365000	1.735711000
	8	1.361774000	2.414089000	1.362108000
	6	-4.295221000	-0.289887000	0.812396000
	6	-3.383475000	-1.027321000	0.002235000
	6	-3.626858000	-1.116981000	-1.383074000
	6	-4.744751000	-0.481583000	-1.916955000
	6	-5.632303000	0.248133000	-1.093062000
	6	-5.421078000	0.352747000	0.279783000
	6	-2.688183000	-1.126074000	2.147889000
	6	-2.362012000	-1.554353000	0.879179000
	1	-2.953989000	-1.675214000	-2.029779000
	1	-4.940449000	-0.544436000	-2.984415000
	1	-6.495877000	0.735351000	-1.538482000
	1	-6.104110000	0.911217000	0.914626000
TS-1				

	7	-3.841998000	-0.368745000	2.112679000
	1	-4.287263000	0.049514000	2.917535000
	6	-1.173496000	-2.386628000	0.487573000
	1	-0.788895000	-2.926759000	1.361803000
	1	-1.468994000	-3.150133000	-0.244908000
	6	-0.016356000	-1.579376000	-0.146747000
	7	0.585853000	-0.596982000	0.766824000
	1	-0.373128000	-1.029906000	-1.024265000
	1	-2.188055000	-1.314808000	3.088963000
	1	1.083969000	-1.052169000	1.533072000
	8	1.060695000	1.173514000	-1.278547000
	1	0.141271000	2.134112000	-1.131300000
	1	0.774705000	-2.261647000	-0.470296000
	1	-0.135145000	0.001043000	1.177032000
	17	-0.929557000	3.145146000	-1.237082000
	6	3.999534000	0.148317000	0.337218000
	6	2.935961000	-0.408987000	-0.387587000
	6	3.175805000	-1.482388000	-1.247827000
	6	4.463292000	-2.020512000	-1.336356000
	6	5.507815000	-1.474431000	-0.583452000
	6	5.288100000	-0.374510000	0.253290000
	6	1.879960000	1.518953000	0.766689000
	6	1.625075000	0.312764000	-0.212716000
	1	2.375460000	-1.888052000	-1.858269000
	1	4.650648000	-2.859510000	-1.999348000
	1	6.506729000	-1.894560000	-0.657118000
	1	6.106938000	0.064361000	0.814761000
	16	3.570732000	1.593236000	1.298605000
	8	0.993876000	2.262047000	1.122023000
	6	-4.176524000	-0.065514000	0.909100000
	6	-3.359126000	-0.965187000	0.166597000
	6	-3.721905000	-1.276121000	-1.159040000
	6	-4.862964000	-0.692148000	-1.701484000
	6	-5.654428000	0.203767000	-0.946756000
	6	-5.323981000	0.528238000	0.366361000
	6	-2.492195000	-0.734197000	2.242210000
	6	-2.284538000	-1.380124000	1.040616000
	1	-3.123944000	-1.962401000	-1.753927000
	1	-5.151337000	-0.924606000	-2.723352000
	1	-6.537805000	0.646668000	-1.399281000
	1	-5.932607000	1.214745000	0.949065000
	7	-3.619602000	0.052795000	2.166289000
	1	-3.981154000	0.620767000	2.919953000
	6	-1.162438000	-2.329190000	0.722698000
INT-1				

	1	-0.730587000	-2.726999000	1.649538000
	1	-1.534427000	-3.195865000	0.162050000
	6	-0.039351000	-1.722374000	-0.136264000
	7	0.583398000	-0.550267000	0.581512000
	1	-0.408411000	-1.341015000	-1.088257000
	1	-1.926565000	-0.793051000	3.163164000
	1	1.019201000	-0.880595000	1.450762000
	8	1.089078000	0.679850000	-1.412899000
	1	0.342088000	1.363594000	-1.368401000
	1	0.749721000	-2.452844000	-0.312396000
	1	-0.180441000	0.081352000	0.872740000
	17	-1.151410000	2.627365000	-1.827455000
	6	-3.528384000	-0.802080000	-0.202558000
	6	-2.445378000	-0.344205000	0.564426000
	6	-2.585762000	-0.217436000	1.947467000
	6	-3.792127000	-0.583030000	2.553916000
	6	-4.852440000	-1.065813000	1.780685000
	6	-4.732969000	-1.172925000	0.390300000
	6	-1.613695000	-0.128264000	-1.760094000
	6	-1.229085000	-0.024828000	-0.256201000
	1	-1.773490000	0.176131000	2.549723000
	1	-3.903216000	-0.485963000	3.629546000
	1	-5.786105000	-1.350175000	2.257420000
	1	-5.565040000	-1.527295000	-0.210140000
	16	-3.238412000	-0.813462000	-1.966018000
	8	-0.859410000	0.192531000	-2.651953000
	6	4.588744000	-0.158784000	-0.632236000
	6	3.756102000	-0.339716000	0.510405000
	6	3.974363000	0.469534000	1.643559000
	6	4.991273000	1.419995000	1.611244000
	6	5.801110000	1.583647000	0.463901000
	6	5.612693000	0.797553000	-0.670427000
	6	3.134229000	-1.816838000	-1.080233000
	6	2.831294000	-1.407051000	0.200611000
	1	3.361417000	0.353985000	2.534270000
	1	5.167794000	2.048356000	2.480541000
	1	6.586986000	2.334568000	0.467734000
	1	6.238082000	0.919321000	-1.551207000
	7	4.182668000	-1.072239000	-1.582519000
	1	4.593250000	-1.191449000	-2.498042000
	6	1.745621000	-1.958035000	1.084360000
	1	1.405977000	-2.924404000	0.692472000
	1	2.134494000	-2.145230000	2.093711000
	6	0.522969000	-1.033586000	1.237638000
TS-2				

	7	-0.095023000	-0.802570000	-0.074271000
	1	0.820228000	-0.084825000	1.704906000
	1	2.686171000	-2.600911000	-1.676868000
	1	0.588873000	-0.697998000	-0.823517000
	8	-0.927133000	1.498533000	0.011543000
	1	-0.186993000	1.781133000	-0.564464000
	1	-1.808146000	2.281076000	-0.131155000
	1	-0.208829000	-1.518129000	1.889514000
	17	-2.937022000	3.407855000	-0.293408000
	6	2.375582000	1.409926000	0.065105000
	6	1.433789000	0.579574000	-0.603623000
	6	0.344371000	1.183384000	-1.266161000
	6	0.220903000	2.568464000	-1.270867000
	6	1.165494000	3.364690000	-0.611132000
	6	2.250444000	2.790339000	0.065749000
	6	3.080446000	-1.006251000	0.331334000
	6	1.796701000	-0.806632000	-0.493764000
	1	-0.411326000	0.588113000	-1.760006000
	1	-0.617170000	3.029672000	-1.782464000
	1	1.058682000	4.445252000	-0.617430000
	1	2.974770000	3.417518000	0.574734000
	16	3.711208000	0.549223000	0.878285000
	8	3.553156000	-2.100561000	0.542519000
	6	-2.637666000	0.039133000	1.259120000
	6	-2.513681000	-0.680265000	0.035849000
	6	-3.322647000	-0.306822000	-1.056297000
	6	-4.212856000	0.753183000	-0.906207000
	6	-4.316262000	1.452099000	0.317847000
	6	-3.532992000	1.104434000	1.416304000
	6	-1.090493000	-1.567602000	1.552536000
	6	-1.516636000	-1.704785000	0.245487000
	1	-3.261084000	-0.838252000	-2.003032000
	1	-4.842439000	1.048000000	-1.741682000
	1	-5.021952000	2.273999000	0.405140000
	1	-3.615233000	1.637560000	2.359717000
	7	-1.754410000	-0.526635000	2.158113000
	1	-1.631756000	-0.242751000	3.120495000
	6	-1.027479000	-2.711111000	-0.748191000
	1	-0.652506000	-3.606508000	-0.240758000
	1	-1.843769000	-3.041365000	-1.401876000
	6	0.086169000	-2.198284000	-1.710355000
	7	1.318801000	-1.914788000	-0.978938000
	1	-0.224076000	-1.313073000	-2.260178000
	1	-0.364744000	-2.150165000	2.104800000

INT-2

	1	1.867365000	-2.739217000	-0.710422000
	1	0.330802000	-2.982727000	-2.430381000
TS-3	6	-2.566747000	-0.927460000	0.409413000
	6	-2.201531000	0.320305000	-0.123332000
	6	-3.049199000	0.955211000	-1.036302000
	6	-4.252953000	0.346167000	-1.398615000
	6	-4.603304000	-0.897393000	-0.859712000
	6	-3.761565000	-1.547054000	0.050170000
	6	-0.319618000	-0.163228000	1.398515000
	6	-0.889673000	0.822987000	0.361518000
	1	-2.777160000	1.910909000	-1.477533000
	1	-4.913258000	0.838335000	-2.105822000
	1	-5.538427000	-1.368294000	-1.148418000
	1	-4.038961000	-2.509194000	0.469556000
	16	-1.390652000	-1.587492000	1.571887000
	8	0.704604000	-0.012690000	2.025040000
	6	2.058686000	-0.955097000	-0.910643000
	6	2.554149000	0.328472000	-0.501660000
	6	3.886568000	0.447489000	-0.023972000
	6	4.671601000	-0.684562000	0.021362000
	6	4.159658000	-1.948032000	-0.395357000
	6	2.863222000	-2.107089000	-0.855607000
	6	0.358648000	0.525378000	-1.151008000
	6	1.515337000	1.259120000	-0.689003000
	1	4.275666000	1.411789000	0.288812000
	1	5.696028000	-0.623013000	0.375281000
	1	4.812045000	-2.815519000	-0.349433000
	1	2.485054000	-3.075328000	-1.167232000
	7	0.762972000	-0.810584000	-1.310108000
	1	0.199516000	-1.533268000	-1.739770000
	6	1.434542000	2.676828000	-0.289643000
	1	2.410171000	3.075082000	0.001823000
	1	1.029345000	3.297332000	-1.095109000
	6	0.457991000	2.808608000	0.947554000
7	-0.804122000	2.159112000	0.676032000	
1	-1.508806000	2.748625000	0.244371000	
1	0.264247000	3.863207000	1.147532000	
1	-0.323484000	0.919271000	-1.896443000	
1	0.934804000	2.357854000	1.818350000	
INT-3	6	-2.751519000	-0.726692000	0.486241000
	6	-2.121290000	0.185117000	-0.373334000
	6	-2.749372000	0.547486000	-1.566337000
	6	-3.998230000	0.004370000	-1.887044000
	6	-4.614144000	-0.902628000	-1.018595000

	6	-3.993827000	-1.278861000	0.177803000
	6	-0.477788000	-0.031945000	1.454678000
	6	-0.793412000	0.712819000	0.121173000
	1	-2.277771000	1.247459000	-2.252550000
	1	-4.485715000	0.287450000	-2.814948000
	1	-5.582732000	-1.324075000	-1.271712000
	1	-4.472331000	-1.984309000	0.850260000
	16	-1.824273000	-1.091955000	1.962816000
	8	0.546702000	0.108884000	2.084550000
	6	2.148737000	-1.064938000	-0.704144000
	6	2.671066000	0.255884000	-0.426582000
	6	4.050475000	0.420930000	-0.094907000
	6	4.848704000	-0.693545000	-0.061027000
	6	4.311901000	-1.991005000	-0.349141000
	6	2.985604000	-2.200940000	-0.666738000
	6	0.396239000	0.397521000	-0.924446000
	6	1.624204000	1.154228000	-0.556084000
	1	4.448118000	1.408249000	0.116704000
	1	5.902414000	-0.606555000	0.182933000
	1	4.982874000	-2.844697000	-0.314813000
	1	2.599237000	-3.192085000	-0.878930000
	7	0.831779000	-0.979572000	-0.969311000
	1	0.263138000	-1.738550000	-1.325625000
	6	1.524670000	2.601293000	-0.287729000
	1	2.460735000	3.014650000	0.097203000
	1	1.267135000	3.134354000	-1.211956000
	6	0.359070000	2.840006000	0.740976000
	7	-0.863363000	2.130016000	0.401256000
	1	-1.439026000	2.622995000	-0.274913000
	1	0.127980000	3.906466000	0.776779000
	1	0.011699000	0.710205000	-1.902074000
	1	0.703565000	2.530946000	1.730000000
INT-3-1	6	-2.926819000	-0.501365000	0.359567000
	6	-1.807610000	-0.303846000	-0.462246000
	6	-1.688340000	-1.054789000	-1.634940000
	6	-2.691846000	-1.963387000	-1.988860000
	6	-3.810146000	-2.133708000	-1.165411000
	6	-3.933352000	-1.407027000	0.024050000
	6	-1.309220000	1.183852000	1.454482000
	6	-0.831498000	0.767311000	0.011831000
	1	-0.811833000	-0.941074000	-2.266072000
	1	-2.596041000	-2.542917000	-2.902624000
	1	-4.586761000	-2.841702000	-1.441329000
	1	-4.792617000	-1.551635000	0.672448000

	16	-2.907737000	0.469230000	1.858337000
	8	-0.705933000	1.916860000	2.201878000
	6	2.407239000	-0.898887000	0.631489000
	6	2.824950000	0.130010000	-0.263504000
	6	4.184887000	0.214664000	-0.619545000
	6	5.080800000	-0.708817000	-0.086872000
	6	4.643954000	-1.721335000	0.797743000
	6	3.304971000	-1.830694000	1.168261000
	6	0.597782000	0.308765000	0.060884000
	6	1.648431000	0.883573000	-0.611771000
	1	4.530828000	0.989874000	-1.299123000
	1	6.133193000	-0.653290000	-0.353297000
	1	5.365989000	-2.428805000	1.197279000
	1	2.970211000	-2.609773000	1.848265000
	7	1.045451000	-0.764069000	0.815190000
	1	0.471515000	-1.381275000	1.373304000
	6	1.460008000	2.051403000	-1.534366000
	1	1.746494000	2.993523000	-1.044920000
	1	2.089108000	1.954095000	-2.428196000
	6	-0.012818000	2.108333000	-1.953394000
	7	-0.886698000	2.029599000	-0.767015000
	1	-1.852000000	2.199753000	-1.041953000
	1	-0.217744000	1.306605000	-2.681183000
	1	-0.238590000	3.061008000	-2.442611000
TS-4	6	-2.536225000	-0.928938000	0.222392000
	6	-2.056268000	0.249217000	-0.419168000
	6	-2.790390000	0.790061000	-1.497582000
	6	-3.958446000	0.194806000	-1.960579000
	6	-4.435292000	-0.958421000	-1.324415000
	6	-3.740429000	-1.496717000	-0.246418000
	6	-0.909997000	0.289843000	2.130953000
	6	-0.814452000	0.972232000	-0.038460000
	1	-2.406686000	1.673426000	-2.000540000
	1	-4.485799000	0.620074000	-2.809656000
	1	-5.351331000	-1.434435000	-1.664781000
	1	-4.125478000	-2.378653000	0.257340000
	16	-1.744025000	-1.662923000	1.618982000
	8	-0.345072000	0.440860000	3.146576000
	6	2.187074000	-1.051143000	-0.538066000
	6	2.764998000	0.224632000	-0.244997000
	6	4.170740000	0.353560000	-0.221872000
	6	4.950263000	-0.766777000	-0.476677000
	6	4.356833000	-2.022319000	-0.759717000
	6	2.975931000	-2.182146000	-0.797119000

	6	0.512819000	0.396428000	-0.193863000
	6	1.678298000	1.126873000	-0.032457000
	1	4.633455000	1.313162000	-0.006112000
	1	6.033740000	-0.684829000	-0.460115000
	1	4.996182000	-2.879524000	-0.953350000
	1	2.523983000	-3.145265000	-1.017630000
	7	0.818619000	-0.912902000	-0.519199000
	1	0.151124000	-1.672079000	-0.553698000
	6	1.611573000	2.576531000	0.344657000
	1	1.596659000	2.685553000	1.439226000
	1	2.480579000	3.134904000	-0.018980000
	6	0.343434000	3.185890000	-0.266289000
	7	-0.834770000	2.320723000	-0.081335000
	1	-1.736103000	2.775902000	-0.010606000
	1	0.490582000	3.342855000	-1.343981000
	1	0.114329000	4.152381000	0.188351000
	6	2.472123000	-0.898656000	-0.566518000
	6	2.145142000	0.270886000	0.187248000
	6	3.026639000	0.774153000	1.172509000
	6	4.206056000	0.110510000	1.483488000
	6	4.518394000	-1.072405000	0.791123000
	6	3.675956000	-1.557785000	-0.200936000
	6	0.885847000	1.003481000	-0.009419000
	1	2.749818000	1.668836000	1.725286000
	1	4.862442000	0.491731000	2.260074000
	1	5.433541000	-1.611530000	1.025496000
	1	3.947769000	-2.457888000	-0.745428000
	16	1.528716000	-1.453091000	-1.937569000
	6	-2.110049000	-0.976385000	0.487187000
	6	-2.673997000	0.262577000	0.038909000
	6	-4.076808000	0.378820000	-0.094073000
	6	-4.866218000	-0.719586000	0.205408000
	6	-4.286962000	-1.940464000	0.641278000
	6	-2.914536000	-2.086968000	0.791743000
	6	-0.422602000	0.441564000	0.118564000
	6	-1.584020000	1.150073000	-0.177579000
	1	-4.523904000	1.311869000	-0.426065000
	1	-5.946067000	-0.652387000	0.107567000
	1	-4.936983000	-2.782190000	0.864483000
	1	-2.478349000	-3.022733000	1.128975000
	7	-0.748433000	-0.830998000	0.554475000
	1	-0.084418000	-1.587194000	0.655712000
	6	-1.499081000	2.557394000	-0.689368000
	1	-1.478597000	2.555821000	-1.789117000
INT-4				

	1	-2.365041000	3.155372000	-0.388560000
	6	-0.234119000	3.213975000	-0.126592000
	7	0.934150000	2.314253000	-0.220138000
	1	1.847229000	2.738591000	-0.345387000
	1	-0.373546000	3.461778000	0.934322000
	1	0.016032000	4.129478000	-0.664453000
	6	0.157565000	1.888215000	0.478697000
	6	-0.769394000	1.707844000	-0.578445000
	6	-1.083491000	2.762733000	-1.451315000
	6	-0.477029000	4.010389000	-1.302998000
	6	0.448102000	4.203591000	-0.271125000
	6	0.760556000	3.159513000	0.597552000
	6	-1.472671000	0.413691000	-0.801594000
	1	-1.796578000	2.600175000	-2.255938000
	1	-0.722564000	4.817681000	-1.986616000
	1	0.928301000	5.170311000	-0.143148000
	1	1.476877000	3.317022000	1.398443000
	16	0.527610000	0.627901000	1.664289000
	6	-4.884949000	0.528587000	0.394626000
	6	-4.739893000	-0.867641000	0.101598000
	6	-5.812522000	-1.749210000	0.375863000
	6	-6.978440000	-1.229470000	0.910018000
	6	-7.105330000	0.159887000	1.181131000
	6	-6.074104000	1.052756000	0.930001000
	6	-2.841338000	0.220844000	-0.458684000
	6	-3.441031000	-1.038116000	-0.446166000
	1	-5.721099000	-2.811015000	0.164966000
	1	-7.815136000	-1.887695000	1.125736000
	1	-8.037068000	0.531572000	1.598713000
	1	-6.177485000	2.112645000	1.142653000
	7	-3.715628000	1.161571000	0.064856000
	1	-3.539793000	2.155379000	0.133041000
	6	-2.644535000	-2.247188000	-0.837486000
	1	-2.229246000	-2.721667000	0.063698000
	1	-3.261963000	-3.001555000	-1.335064000
	6	-1.525754000	-1.828544000	-1.800687000
	7	-0.843287000	-0.591531000	-1.370377000
	1	-1.942065000	-1.630484000	-2.797461000
	6	1.845924000	-1.314811000	0.675506000
	1	2.194518000	-1.420469000	1.688501000
	1	0.890116000	-1.739080000	0.424890000
	6	2.476393000	-0.381368000	-0.284985000
	8	1.946804000	-0.196869000	-1.395281000
	6	3.750100000	0.309600000	0.065458000

TS-5

	6	4.482281000	0.026062000	1.232816000
	6	4.214516000	1.313192000	-0.802739000
	6	5.654232000	0.727608000	1.516547000
	1	4.158083000	-0.749304000	1.918147000
	6	5.386381000	2.013214000	-0.518487000
	1	3.645655000	1.535392000	-1.699573000
	6	6.110489000	1.720983000	0.642686000
	1	6.214080000	0.495629000	2.418303000
	1	5.733289000	2.786809000	-1.198166000
	1	7.024021000	2.265095000	0.867440000
	35	2.995869000	-3.273357000	-0.048291000
	1	0.169411000	-0.488544000	-1.554999000
	1	-0.766941000	-2.606315000	-1.897813000
INT-5	6	-0.494399000	-2.039116000	0.306572000
	6	0.434590000	-1.768489000	-0.720174000
	6	0.650798000	-2.712321000	-1.734956000
	6	-0.039969000	-3.926332000	-1.733918000
	6	-0.952093000	-4.203033000	-0.715116000
	6	-1.178334000	-3.263104000	0.293668000
	6	1.222741000	-0.503898000	-0.786681000
	1	1.357882000	-2.492125000	-2.530029000
	1	0.138356000	-4.647261000	-2.526046000
	1	-1.492765000	-5.144936000	-0.703225000
	1	-1.889915000	-3.475954000	1.085187000
	16	-0.745155000	-0.973077000	1.733897000
	6	4.636029000	-0.974635000	0.311314000
	6	4.573238000	0.452729000	0.191413000
	6	5.700448000	1.231071000	0.547872000
	6	6.839630000	0.582866000	0.990137000
	6	6.885522000	-0.834675000	1.087476000
	6	5.799401000	-1.628875000	0.751317000
	6	2.603443000	-0.443992000	-0.453819000
	6	3.280986000	0.766868000	-0.302585000
	1	5.668568000	2.314042000	0.468847000
	1	7.717706000	1.159242000	1.266729000
	1	7.799089000	-1.308417000	1.436065000
	1	5.841832000	-2.711026000	0.830876000
	7	3.425775000	-1.492949000	-0.067060000
	1	3.195992000	-2.476406000	-0.121971000
	6	2.553250000	2.061194000	-0.507273000
	1	2.196567000	2.437267000	0.462944000
	1	3.205903000	2.835897000	-0.922155000
	6	1.379380000	1.852068000	-1.473019000
	7	0.642487000	0.600336000	-1.202028000

	1	1.743666000	1.783387000	-2.506945000
	6	-1.674985000	0.520920000	1.115969000
	1	-2.178010000	0.896773000	2.007893000
	1	-0.973514000	1.280680000	0.774784000
	6	-2.630085000	0.201514000	-0.017791000
	8	-2.199161000	0.257211000	-1.175755000
	6	-4.028816000	-0.219663000	0.248914000
	6	-4.569558000	-0.281502000	1.546435000
	6	-4.837321000	-0.578693000	-0.847713000
	6	-5.889623000	-0.691026000	1.740344000
	1	-3.972917000	-0.014985000	2.411838000
	6	-6.154429000	-0.984121000	-0.652198000
	1	-4.416021000	-0.533392000	-1.846512000
	6	-6.683522000	-1.041486000	0.643935000
	1	-6.297269000	-0.734997000	2.746144000
	1	-6.769550000	-1.257354000	-1.504935000
	1	-7.711556000	-1.358298000	0.797592000
	35	-1.341978000	4.014886000	-0.207862000
	1	-0.372484000	0.573126000	-1.386856000
	1	0.657680000	2.667940000	-1.398475000
INT-5-1	6	-0.771455000	2.740369000	-0.259829000
	6	-2.091316000	2.491902000	0.171068000
	6	-2.822383000	3.505239000	0.814967000
	6	-2.227442000	4.738793000	1.076425000
	6	-0.906823000	4.973466000	0.678445000
	6	-0.188870000	3.988128000	-0.000972000
	6	-2.726017000	1.159895000	-0.013692000
	1	-3.840748000	3.309675000	1.138899000
	1	-2.791052000	5.511410000	1.590503000
	1	-0.441448000	5.935026000	0.875674000
	1	0.818665000	4.191836000	-0.350760000
	16	0.044085000	1.494325000	-1.251568000
	6	-1.219065000	-1.442214000	1.996163000
	6	-2.080849000	-2.208832000	1.145164000
	6	-2.094470000	-3.619313000	1.257408000
	6	-1.277081000	-4.216753000	2.199844000
	6	-0.436343000	-3.436966000	3.039777000
	6	-0.395555000	-2.052829000	2.956634000
	6	-2.320826000	-0.011221000	0.679686000
	6	-2.776140000	-1.283473000	0.327563000
	1	-2.737175000	-4.217501000	0.617745000
	1	-1.270828000	-5.297877000	2.304267000
	1	0.193429000	-3.941352000	3.767551000
	1	0.252534000	-1.465392000	3.599947000

	7	-1.368537000	-0.116500000	1.682176000
	1	-0.941360000	0.655850000	2.175930000
	6	-3.732060000	-1.441259000	-0.814385000
	1	-3.164594000	-1.618410000	-1.739313000
	1	-4.397347000	-2.299036000	-0.676499000
	6	-4.590062000	-0.175460000	-0.925970000
	7	-3.767618000	1.049588000	-0.822710000
	1	-5.327407000	-0.139433000	-0.113061000
	6	1.572112000	1.286279000	-0.373595000
	1	1.620861000	1.744424000	0.607051000
	6	2.600735000	0.551453000	-0.852623000
	8	2.538473000	-0.116887000	-2.049098000
	6	3.895655000	0.413587000	-0.146653000
	6	4.375063000	1.402221000	0.734470000
	6	4.682559000	-0.734075000	-0.358148000
	6	5.591763000	1.237201000	1.397564000
	1	3.806361000	2.315525000	0.885593000
	6	5.904146000	-0.893229000	0.300119000
	1	4.328172000	-1.499174000	-1.040950000
	6	6.363380000	0.088558000	1.183948000
	1	5.945977000	2.014479000	2.069942000
	1	6.495633000	-1.788428000	0.124873000
	1	7.314830000	-0.034532000	1.694700000
	1	-4.061787000	1.869450000	-1.344079000
	1	1.704164000	-0.655098000	-2.131698000
	35	0.073767000	-2.180991000	-2.258782000
	1	-5.120735000	-0.131285000	-1.877619000
TS-6	6	-1.399241000	2.255089000	-1.020057000
	6	-0.875299000	2.093759000	0.265856000
	6	-0.868694000	3.184975000	1.145014000
	6	-1.374049000	4.421252000	0.737456000
	6	-1.882620000	4.573108000	-0.558322000
	6	-1.897955000	3.492927000	-1.443024000
	6	-0.217660000	0.783698000	0.668838000
	1	-0.455271000	3.066073000	2.143211000
	1	-1.368496000	5.261145000	1.425946000
	1	-2.278347000	5.532717000	-0.879366000
	1	-2.309697000	3.606494000	-2.442142000
	16	-1.437934000	0.808612000	-2.059852000
	6	3.274427000	1.038181000	-0.425595000
	6	3.426999000	0.216536000	0.731999000
	6	4.713154000	-0.234742000	1.090170000
	6	5.799434000	0.147610000	0.311302000
	6	5.627357000	0.975871000	-0.823475000

	6	4.369028000	1.433583000	-1.205669000
	6	1.246603000	0.749197000	0.491576000
	6	2.119975000	0.043303000	1.290712000
	1	4.852702000	-0.870481000	1.960924000
	1	6.797737000	-0.192673000	0.573417000
	1	6.496615000	1.260235000	-1.410682000
	1	4.240605000	2.067645000	-2.078821000
	7	1.932930000	1.329183000	-0.563341000
	1	1.548784000	1.998548000	-1.217011000
	6	1.618045000	-0.744187000	2.460797000
	1	1.410172000	-1.780665000	2.161406000
	1	2.358178000	-0.786016000	3.267868000
	6	0.350038000	-0.066185000	2.987217000
	7	-0.598610000	0.257506000	1.903897000
	1	0.630825000	0.853999000	3.522260000
	6	-0.815455000	-0.324542000	-0.800934000
	1	0.133737000	-0.757496000	-1.110101000
	6	-1.682665000	-1.357613000	-0.279681000
	8	-1.120486000	-2.453592000	0.142801000
	6	-3.124113000	-1.303929000	-0.053083000
	6	-3.842000000	-0.091630000	0.031856000
	6	-3.820508000	-2.524019000	0.113850000
	6	-5.211160000	-0.103698000	0.287925000
	1	-3.338270000	0.860449000	-0.066388000
	6	-5.192333000	-2.528112000	0.341441000
	1	-3.278887000	-3.460381000	0.043150000
	6	-5.891029000	-1.317726000	0.432302000
	1	-5.748512000	0.836332000	0.369672000
	1	-5.717962000	-3.472038000	0.450711000
	1	-6.961731000	-1.321159000	0.616472000
	1	-1.501410000	0.575967000	2.235462000
	1	-0.174945000	-0.717922000	3.691020000
	35	1.735425000	-2.950744000	-0.895152000
	1	-0.146776000	-2.576835000	-0.166194000
INT-6	6	-1.380971000	2.180494000	-1.251063000
	6	-0.762429000	2.071788000	-0.000264000
	6	-0.629002000	3.216203000	0.793360000
	6	-1.126293000	4.442052000	0.342595000
	6	-1.748335000	4.532147000	-0.909269000
	6	-1.877726000	3.401272000	-1.719204000
	6	-0.242121000	0.677825000	0.375828000
	1	-0.133674000	3.157164000	1.757879000
	1	-1.025352000	5.326118000	0.965429000
	1	-2.133570000	5.486315000	-1.258028000

	1	-2.360338000	3.468879000	-2.690083000
	16	-1.448375000	0.659099000	-2.177898000
	6	3.372455000	0.815890000	-0.351107000
	6	3.414590000	0.291129000	0.974288000
	6	4.663765000	0.002092000	1.556115000
	6	5.821862000	0.244848000	0.822134000
	6	5.756770000	0.774637000	-0.486859000
	6	4.534999000	1.068447000	-1.089656000
	6	1.259750000	0.638806000	0.397706000
	6	2.052367000	0.184915000	1.424002000
	1	4.723485000	-0.405297000	2.562471000
	1	6.792578000	0.025393000	1.259233000
	1	6.677492000	0.955956000	-1.035381000
	1	4.486485000	1.473215000	-2.097213000
	7	2.046315000	1.011376000	-0.679788000
	1	1.716519000	1.439699000	-1.534368000
	6	1.471171000	-0.292808000	2.718819000
	1	1.397598000	-1.389700000	2.739872000
	1	2.098482000	-0.000716000	3.569950000
	6	0.083129000	0.330349000	2.879783000
	7	-0.736224000	0.135073000	1.664381000
	1	0.194980000	1.395053000	3.135801000
	6	-0.765787000	-0.315293000	-0.770912000
	1	0.093080000	-0.858486000	-1.165534000
	6	-1.706115000	-1.379195000	-0.224671000
	8	-1.242364000	-2.572276000	-0.155924000
	6	-3.105552000	-1.229988000	0.150390000
	6	-3.752285000	0.024468000	0.208605000
	6	-3.841745000	-2.393572000	0.477920000
	6	-5.085222000	0.111052000	0.595494000
	1	-3.225906000	0.937049000	-0.039112000
	6	-5.177549000	-2.300999000	0.849479000
	1	-3.358843000	-3.362444000	0.431365000
	6	-5.801526000	-1.048880000	0.913503000
	1	-5.567458000	1.082369000	0.643961000
	1	-5.732958000	-3.201391000	1.093372000
	1	-6.844663000	-0.977320000	1.208181000
	1	-1.670247000	0.495795000	1.843708000
	1	-0.465306000	-0.147451000	3.697583000
	35	1.598839000	-3.042213000	-1.070917000
	1	-0.248650000	-2.701324000	-0.467482000
INT-6-1	6	-1.322667000	3.171274000	0.068481000
	6	-1.912218000	2.066523000	-0.565124000
	6	-3.233153000	2.159763000	-1.017559000

6	-3.928434000	3.364596000	-0.892419000
6	-3.314575000	4.470379000	-0.289769000
6	-2.012697000	4.379621000	0.206159000
6	-1.031265000	0.823463000	-0.610017000
1	-3.733699000	1.295902000	-1.443206000
1	-4.950563000	3.436191000	-1.251607000
1	-3.859729000	5.404747000	-0.188816000
1	-1.548402000	5.229303000	0.697931000
16	0.300016000	2.872394000	0.707282000
6	-2.654611000	-1.734795000	1.490694000
6	-2.808433000	-2.352970000	0.216515000
6	-3.464332000	-3.595989000	0.132572000
6	-3.943650000	-4.183188000	1.300278000
6	-3.780606000	-3.551565000	2.554391000
6	-3.136024000	-2.321676000	2.667802000
6	-1.716839000	-0.395881000	-0.049165000
6	-2.205025000	-1.472446000	-0.750016000
1	-3.594252000	-4.089939000	-0.827155000
1	-4.452015000	-5.142507000	1.250369000
1	-4.165545000	-4.034482000	3.448693000
1	-3.011799000	-1.836539000	3.632293000
7	-1.987532000	-0.540936000	1.296874000
1	-1.719270000	0.106301000	2.025577000
6	-2.039176000	-1.645578000	-2.230552000
1	-1.259163000	-2.388100000	-2.450786000
1	-2.958557000	-2.018381000	-2.697382000
6	-1.689915000	-0.311907000	-2.891495000
7	-0.656015000	0.427636000	-2.071694000
1	-2.555411000	0.343518000	-2.981982000
6	0.286628000	1.200183000	0.072039000
6	1.349254000	0.365061000	0.142910000
8	1.208638000	-0.880866000	-0.400176000
6	2.641001000	0.683242000	0.805193000
6	3.451234000	1.736683000	0.356352000
6	3.064325000	-0.098830000	1.893508000
6	4.670269000	2.003346000	0.985576000
1	3.140107000	2.330207000	-0.498761000
6	4.276464000	0.177709000	2.527297000
1	2.440849000	-0.916671000	2.244865000
6	5.083156000	1.227328000	2.072940000
1	5.297996000	2.812491000	0.622115000
1	4.593482000	-0.428376000	3.371727000
1	6.030840000	1.436147000	2.562158000
1	-0.362979000	1.276910000	-2.564101000

	1	2.101770000	-1.282790000	-0.627982000
	35	3.882915000	-2.171993000	-1.438273000
	1	0.178467000	-0.173202000	-1.973164000
	1	-1.250955000	-0.445333000	-3.882145000
TS-7	6	1.421186000	3.302725000	-0.329918000
	6	2.073994000	2.077487000	-0.071239000
	6	3.480800000	2.021012000	-0.094384000
	6	4.206110000	3.176821000	-0.355008000
	6	3.539966000	4.395403000	-0.592810000
	6	2.148688000	4.470975000	-0.586363000
	6	1.155237000	0.978472000	0.201665000
	1	3.986614000	1.076444000	0.083540000
	1	5.291138000	3.142604000	-0.377459000
	1	4.119062000	5.291597000	-0.797584000
	1	1.643593000	5.411337000	-0.785218000
	16	-0.325662000	3.157784000	-0.315589000
	6	2.118975000	-2.191980000	-1.313757000
	6	2.449851000	-2.521017000	0.029664000
	6	2.977150000	-3.797130000	0.309376000
	6	3.161694000	-4.694686000	-0.738752000
	6	2.828981000	-4.343177000	-2.067327000
	6	2.306558000	-3.088856000	-2.373964000
	6	1.623554000	-0.419238000	-0.006321000
	6	2.135914000	-1.374820000	0.847625000
	1	3.235704000	-4.080009000	1.326847000
	1	3.566321000	-5.682901000	-0.535817000
	1	2.983249000	-5.065201000	-2.865001000
	1	2.049473000	-2.817998000	-3.394569000
	7	1.630972000	-0.905400000	-1.307907000
	1	1.280879000	-0.406767000	-2.114540000
	6	2.288574000	-1.308452000	2.341516000
	1	1.451892000	-1.832389000	2.829632000
	1	3.195585000	-1.842990000	2.649401000
	6	2.368043000	0.119340000	2.879137000
	7	1.238611000	0.901122000	2.358753000
	1	3.287149000	0.610412000	2.543269000
	6	-0.204260000	1.392672000	-0.029610000
	6	-1.326587000	0.569387000	-0.054352000
	8	-1.144749000	-0.727715000	0.113826000
	6	-2.701797000	1.057976000	-0.307453000
	6	-3.239985000	2.146287000	0.401680000
	6	-3.491620000	0.397870000	-1.267389000
6	-4.545938000	2.569223000	0.148884000	
1	-2.656538000	2.639723000	1.172635000	

	6	-4.786754000	0.840658000	-1.531110000
	1	-3.086630000	-0.447309000	-1.814483000
	6	-5.316729000	1.925726000	-0.824545000
	1	-4.959913000	3.399589000	0.713698000
	1	-5.384332000	0.335522000	-2.284551000
	1	-6.329691000	2.263024000	-1.026267000
	1	1.276358000	1.880098000	2.639553000
	1	0.338564000	0.519867000	2.652126000
	1	-1.999095000	-1.261920000	0.241357000
	35	-3.468906000	-2.689640000	0.693069000
	1	2.374216000	0.115733000	3.977431000
INT-7	6	2.358867000	2.936342000	-0.411411000
	6	0.949290000	2.800620000	-0.351596000
	6	0.161052000	3.965936000	-0.225563000
	6	0.778601000	5.205383000	-0.144614000
	6	2.185408000	5.316325000	-0.189561000
	6	2.985828000	4.188397000	-0.331625000
	6	0.512010000	1.427920000	-0.497492000
	1	-0.921602000	3.884272000	-0.206066000
	1	0.173992000	6.103016000	-0.051137000
	1	2.649880000	6.296052000	-0.120862000
	1	4.067242000	4.274710000	-0.379644000
	16	3.144820000	1.392378000	-0.630795000
	6	-2.886815000	0.273052000	-1.180757000
	6	-3.083618000	0.756450000	0.144189000
	6	-4.377682000	0.696079000	0.701303000
	6	-5.413430000	0.150673000	-0.050447000
	6	-5.189009000	-0.336377000	-1.360673000
	6	-3.925601000	-0.282451000	-1.941725000
	6	-0.911207000	1.049143000	-0.416654000
	6	-1.814473000	1.245670000	0.620435000
	1	-4.564027000	1.061315000	1.708117000
	1	-6.414106000	0.098214000	0.371224000
	1	-6.017899000	-0.759871000	-1.922150000
	1	-3.749943000	-0.651270000	-2.949058000
	7	-1.568770000	0.482340000	-1.502154000
	1	-1.077876000	0.058103000	-2.277559000
	6	-1.529496000	1.806721000	1.989463000
	1	-0.847218000	2.661243000	1.914396000
	1	-2.458998000	2.203495000	2.420544000
	6	-0.902362000	0.821101000	2.997053000
	1	-0.022367000	0.350474000	2.543808000
	7	-1.832426000	-0.251316000	3.385618000
	1	-1.356614000	-0.911090000	4.000007000

	6	2.785356000	-3.023372000	-0.944088000
	6	3.692666000	-3.928915000	-0.399703000
	6	4.322998000	-3.641753000	0.817878000
	6	4.048763000	-2.443686000	1.485680000
	6	3.158497000	-1.522487000	0.932728000
	6	2.513452000	-1.808007000	-0.285308000
	1	2.292014000	-3.237518000	-1.887009000
	1	3.909788000	-4.857022000	-0.920741000
	1	5.025606000	-4.352023000	1.245195000
	1	4.528017000	-2.226482000	2.435912000
	1	2.939448000	-0.602622000	1.464655000
	6	1.519066000	-0.887603000	-0.887614000
	8	0.596526000	-1.343901000	-1.596439000
	6	1.586031000	0.565402000	-0.668338000
	1	-2.597883000	0.139566000	3.935291000
	1	-0.375169000	-2.498439000	-0.868862000
	35	-1.344610000	-3.244820000	-0.029919000
	1	-0.547054000	1.407200000	3.861710000
INT-7-1	6	-2.377646000	2.886258000	0.213958000
	6	-1.125289000	2.367224000	0.625357000
	6	-0.071442000	3.270673000	0.884066000
	6	-0.277660000	4.632705000	0.713856000
	6	-1.528016000	5.126580000	0.285362000
	6	-2.588830000	4.261593000	0.039286000
	6	-1.142276000	0.923766000	0.775558000
	1	0.887713000	2.898362000	1.231227000
	1	0.531687000	5.328133000	0.917397000
	1	-1.668167000	6.195880000	0.153998000
	1	-3.555757000	4.641943000	-0.276845000
	16	-3.560164000	1.616142000	0.006609000
	6	1.337831000	-1.171619000	2.455127000
	6	2.149342000	-0.700641000	1.382749000
	6	3.502507000	-1.102280000	1.322915000
	6	3.992550000	-1.954292000	2.307707000
	6	3.164360000	-2.418830000	3.356097000
	6	1.829918000	-2.033532000	3.445620000
	6	0.062920000	0.163888000	1.156419000
	6	1.317985000	0.144947000	0.559379000
	1	4.158487000	-0.751320000	0.528898000
	1	5.032506000	-2.268846000	2.274369000
	1	3.578356000	-3.085265000	4.108315000
	1	1.193609000	-2.383393000	4.254224000
	7	0.090427000	-0.616064000	2.301796000
	1	-0.755719000	-0.914685000	2.771847000

	6	1.723060000	0.795927000	-0.736988000
	1	1.153553000	1.714620000	-0.906817000
	1	2.779615000	1.086173000	-0.706570000
	6	1.485589000	-0.076996000	-1.978489000
	1	0.449263000	-0.413423000	-2.044021000
	7	2.354089000	-1.306445000	-1.955953000
	1	2.157000000	-1.923955000	-2.748609000
	6	-4.576200000	-2.681431000	0.006066000
	6	-5.403318000	-3.303825000	-0.926399000
	6	-5.378631000	-2.896513000	-2.266720000
	6	-4.527923000	-1.862447000	-2.669309000
	6	-3.712780000	-1.222548000	-1.733195000
	6	-3.729814000	-1.627923000	-0.386690000
	1	-4.583010000	-2.994387000	1.045560000
	1	-6.066206000	-4.105376000	-0.612627000
	1	-6.019899000	-3.386289000	-2.994601000
	1	-4.498049000	-1.553806000	-3.710450000
	1	-3.047037000	-0.428663000	-2.056202000
	6	-2.827009000	-1.021955000	0.633711000
	8	-2.454936000	-1.680486000	1.610887000
	6	-2.387329000	0.391440000	0.492629000
	1	3.368632000	-1.022543000	-2.005010000
	35	5.341759000	0.012986000	-2.011394000
	1	1.748287000	0.463490000	-2.890539000
	1	2.212685000	-1.849008000	-1.096929000
TS-8	6	-0.708197000	3.638556000	-0.340359000
	6	-1.660534000	2.588588000	-0.381557000
	6	-3.030921000	2.908751000	-0.502073000
	6	-3.411588000	4.238476000	-0.600333000
	6	-2.447413000	5.270580000	-0.569027000
	6	-1.093574000	4.983992000	-0.434440000
	6	-1.049901000	1.287646000	-0.261166000
	1	-3.772827000	2.115817000	-0.520137000
	1	-4.462964000	4.492630000	-0.699427000
	1	-2.767799000	6.305759000	-0.646457000
	1	-0.356215000	5.780489000	-0.401931000
	16	0.916599000	3.030879000	-0.132135000
	6	-3.260516000	-1.608304000	-0.618852000
	6	-2.884832000	-1.760117000	0.747255000
	6	-3.431420000	-2.826645000	1.489364000
	6	-4.309934000	-3.704447000	0.861723000
	6	-4.659242000	-3.539656000	-0.498956000
	6	-4.141416000	-2.492140000	-1.256527000
	6	-1.820913000	0.047029000	-0.102132000

	6	-1.969673000	-0.691756000	1.059156000
	1	-3.168923000	-2.965474000	2.535343000
	1	-4.735882000	-4.532044000	1.423037000
	1	-5.346734000	-4.242668000	-0.962025000
	1	-4.412583000	-2.362317000	-2.300872000
	7	-2.616760000	-0.488713000	-1.101969000
	1	-2.623972000	-0.178755000	-2.064247000
	6	-1.306962000	-0.375621000	2.370489000
	1	-1.109074000	0.700385000	2.418893000
	1	-1.979550000	-0.606762000	3.205328000
	6	0.019806000	-1.129827000	2.605738000
	1	0.605708000	-0.618860000	3.375769000
	7	0.828283000	-1.204297000	1.374180000
	1	1.752661000	-1.587284000	1.574944000
	6	3.733445000	0.269010000	-0.826909000
	6	5.061936000	0.556988000	-0.509048000
	6	5.386995000	1.078385000	0.745956000
	6	4.377713000	1.326156000	1.685382000
	6	3.049635000	1.052641000	1.369177000
	6	2.717492000	0.510033000	0.113963000
	1	3.486400000	-0.116821000	-1.810025000
	1	5.840349000	0.373832000	-1.243913000
	1	6.422699000	1.294646000	0.992891000
	1	4.626866000	1.729103000	2.662653000
	1	2.270685000	1.231079000	2.104255000
	6	1.302086000	0.279480000	-0.265395000
	8	1.014918000	-0.566531000	-1.227636000
	6	0.324559000	1.364715000	-0.136520000
	1	0.392100000	-1.855970000	0.721284000
	1	1.626067000	-1.387824000	-1.241276000
	35	2.540308000	-3.233349000	-1.043763000
	1	-0.183175000	-2.147553000	2.967934000
INT-8	6	-0.875322000	3.470133000	-0.497644000
	6	-1.809828000	2.418954000	-0.354169000
	6	-3.184556000	2.735237000	-0.335682000
	6	-3.586270000	4.057019000	-0.488462000
	6	-2.638058000	5.086864000	-0.651073000
	6	-1.275551000	4.804544000	-0.649746000
	6	-1.165573000	1.119638000	-0.208147000
	1	-3.925103000	1.953815000	-0.197685000
	1	-4.645077000	4.299935000	-0.477875000
	1	-2.972072000	6.113618000	-0.771709000
	1	-0.541716000	5.597560000	-0.760255000
	16	0.767159000	2.879893000	-0.411299000

	6	-3.611881000	-1.598203000	-0.317924000
	6	-2.891171000	-1.990894000	0.846230000
	6	-3.298664000	-3.143763000	1.547247000
	6	-4.388502000	-3.866950000	1.074569000
	6	-5.084420000	-3.463023000	-0.089004000
	6	-4.708202000	-2.326527000	-0.799499000
	6	-1.947337000	-0.105499000	0.003289000
	6	-1.842811000	-1.024125000	1.036538000
	1	-2.769488000	-3.465642000	2.440701000
	1	-4.712849000	-4.758576000	1.604557000
	1	-5.931272000	-4.050192000	-0.434128000
	1	-5.244592000	-2.014667000	-1.691495000
	7	-3.028116000	-0.445387000	-0.797827000
	1	-3.269990000	0.012871000	-1.665873000
	6	-0.764884000	-0.990262000	2.078162000
	1	-0.578046000	0.044353000	2.386444000
	1	-1.065399000	-1.536519000	2.978241000
	6	0.538214000	-1.629019000	1.571468000
	1	1.400877000	-1.377342000	2.188057000
	7	0.849629000	-1.244163000	0.150674000
	1	1.605022000	-1.882496000	-0.201977000
	6	3.828092000	0.585255000	-0.114520000
	6	4.962023000	0.951462000	0.616550000
	6	4.851293000	1.311499000	1.961251000
	6	3.592826000	1.324470000	2.570302000
	6	2.460983000	0.958871000	1.840604000
	6	2.567117000	0.567512000	0.495976000
	1	3.938883000	0.324221000	-1.159653000
	1	5.932375000	0.955759000	0.127847000
	1	5.734941000	1.594740000	2.526560000
	1	3.487655000	1.624953000	3.608925000
	1	1.489433000	1.011591000	2.322462000
	6	1.315496000	0.171302000	-0.300756000
	8	1.553856000	0.003370000	-1.676523000
	6	0.208580000	1.219050000	-0.211710000
	1	0.024266000	-1.462597000	-0.422524000
	1	2.204827000	-0.732202000	-1.816056000
	35	3.212149000	-2.790712000	-1.467009000
	1	0.446576000	-2.717923000	1.540688000
TS-9	6	-1.183430000	2.761251000	-0.803322000
	6	0.144580000	2.337643000	-0.567871000
	6	1.156549000	3.314524000	-0.464739000
	6	0.825065000	4.660183000	-0.575602000
	6	-0.507680000	5.061484000	-0.797745000

6	-1.522262000	4.116259000	-0.919198000
6	0.262372000	0.887984000	-0.536383000
1	2.188334000	3.016150000	-0.307643000
1	1.604408000	5.412922000	-0.493618000
1	-0.746656000	6.118273000	-0.879761000
1	-2.549632000	4.421018000	-1.097641000
16	-2.273092000	1.398430000	-0.921651000
6	3.616983000	-0.233577000	0.349331000
6	3.396709000	-1.044463000	-0.803118000
6	4.418865000	-1.917290000	-1.226982000
6	5.606727000	-1.970095000	-0.502739000
6	5.797905000	-1.165266000	0.643927000
6	4.809173000	-0.287028000	1.083080000
6	1.550291000	0.207483000	-0.437297000
6	2.076391000	-0.738553000	-1.291782000
1	4.283186000	-2.544477000	-2.104857000
1	6.400635000	-2.641752000	-0.819463000
1	6.734497000	-1.230356000	1.191749000
1	4.958291000	0.335438000	1.961621000
7	2.493720000	0.544745000	0.527666000
1	2.265405000	1.040303000	1.379686000
6	1.374703000	-1.338522000	-2.473951000
1	0.855237000	-0.566773000	-3.056503000
1	2.120304000	-1.783742000	-3.143303000
6	0.371839000	-2.448830000	-2.110398000
1	0.223692000	-3.086006000	-2.988254000
7	-0.993345000	-2.006919000	-1.757140000
1	-1.595698000	-2.825229000	-1.782974000
6	-3.253284000	-1.298446000	1.063827000
6	-4.600812000	-1.492585000	1.373126000
6	-5.524085000	-1.779221000	0.363277000
6	-5.087598000	-1.869824000	-0.960192000
6	-3.736047000	-1.691383000	-1.271154000
6	-2.800371000	-1.420689000	-0.259645000
1	-2.561598000	-1.052592000	1.862249000
1	-4.928928000	-1.407545000	2.405506000
1	-6.573113000	-1.925775000	0.605734000
1	-5.795315000	-2.079166000	-1.757682000
1	-3.418809000	-1.748640000	-2.307084000
6	-1.307479000	-1.231898000	-0.595196000
8	-0.497309000	-1.718571000	0.595557000
6	-0.948297000	0.255074000	-0.689001000
1	-0.822680000	-2.595576000	0.876052000
35	-0.082740000	0.020696000	2.947510000

	1	0.805318000	-3.077855000	-1.320372000
	1	-0.326500000	-0.939357000	1.660450000
INT-9	6	-1.328202000	2.759920000	-0.379135000
	6	-0.014934000	2.327553000	-0.067031000
	6	0.972514000	3.297341000	0.220984000
	6	0.631618000	4.641079000	0.206869000
	6	-0.684184000	5.050040000	-0.100911000
	6	-1.670478000	4.119299000	-0.406107000
	6	0.131668000	0.892717000	-0.158751000
	1	1.991224000	2.992121000	0.437011000
	1	1.386947000	5.389872000	0.426272000
	1	-0.930032000	6.108117000	-0.104405000
	1	-2.679342000	4.436091000	-0.652129000
	16	-2.386984000	1.421583000	-0.738743000
	6	3.378352000	-0.331819000	0.963003000
	6	3.250474000	-1.053346000	-0.260335000
	6	4.300764000	-1.901827000	-0.669090000
	6	5.421118000	-2.020777000	0.144135000
	6	5.519097000	-1.307082000	1.362912000
	6	4.504246000	-0.455745000	1.788774000
	6	1.387051000	0.193965000	0.052166000
	6	1.975608000	-0.704974000	-0.819023000
	1	4.233576000	-2.457562000	-1.600865000
	1	6.237088000	-2.672870000	-0.155555000
	1	6.408148000	-1.423292000	1.976916000
	1	4.583473000	0.096916000	2.720827000
	7	2.246647000	0.440041000	1.114335000
	1	2.002552000	0.953456000	1.950652000
	6	1.351440000	-1.136554000	-2.111701000
	1	0.842575000	-0.292591000	-2.589968000
	1	2.116640000	-1.474969000	-2.819320000
	6	0.383262000	-2.301327000	-1.944240000
	1	-0.121301000	-2.532482000	-2.890766000
	7	-0.694616000	-2.144184000	-0.931786000
	1	-1.071654000	-3.053491000	-0.672282000
	6	-3.053460000	-0.987042000	1.430748000
	6	-4.216789000	-1.411764000	2.068650000
	6	-5.041182000	-2.368207000	1.464166000
6	-4.695054000	-2.909950000	0.222226000	
6	-3.519527000	-2.508003000	-0.411518000	
6	-2.691071000	-1.539196000	0.187337000	
1	-2.412074000	-0.250754000	1.904587000	
1	-4.481019000	-0.996715000	3.036675000	
1	-5.953805000	-2.687478000	1.959315000	

	1	-5.341022000	-3.640147000	-0.255939000
	1	-3.268924000	-2.914313000	-1.387657000
	6	-1.417018000	-1.142468000	-0.465008000
	6	-1.065600000	0.264778000	-0.504451000
	1	0.926181000	-3.195924000	-1.629335000

Table. Electronic energies (E^{B3} , a.u.), Gree free energies (G^{B3} , a.u), number and values of imaginary frequencies (NIF/VIF, cm^{-1}) calculated at the B3LYP/6-31+G* level of theory, and electronic energies (E^{m06} , a.u.) calculated at the m06/6-311++g(3df,2p) level of theory.

Name	E^{B3}	G^{B3}	E^{m06}	NIF	VIF
1a	-855.920655	-855.8738051	-855.7502479	0	
3a	-958.671124	-958.5145877	-958.4273454	0	
3a-LB	-497.821701	-497.6744627	-497.5879962	0	
TS-1	-1814.553723	-1814.323285	-1814.15449	1	-624.1 i
INT-1	-1814.572835	-1814.331256	-1814.174951	0	
TS-2	-1814.547789	-1814.314716	-1814.155287	1	-606.1 i
ClH2O	-536.82118	-536.8364296	-536.8096731	0	
INT-2	-1277.743806	-1277.522602	-1277.353211	0	
TS-3	-1277.726128	-1277.502548	-1277.339756	1	-278.6 i
INT-3	-1277.731652	-1277.507126	-1277.346582	0	
HClH2O	-537.243123	-537.2503394	-537.2382266	0	
INT-3-1	-1277.31365	-1277.101997	-1276.9296	0	
TS-4	-1277.271041	-1277.064094	-1276.880158	1	-270.7 i
CO	-113.318098	-113.3418975	-113.2943126	0	
INT-4	-1163.976688	-1163.772642	-1163.602247	0	
2a	-2956.040156	-2955.964597	-2958.161626	0	
TS-5	-4120.014475	-4119.701222	-4121.762171	1	-377.4 i
INT-5	-4120.049762	-4119.735674	-4121.805508	0	
INT-5-1	-4120.034572	-4119.722174	-4121.792517	0	
TS-6	-4120.006561	-4119.691585	-4121.775099	1	-339.8 i
INT-6	-4120.014606	-4119.698204	-4121.783182	0	
INT-6-1	-4120.030913	-4119.710574	-4121.799684	0	
TS-7	-4120.017718	-4119.705075	-4121.783698	1	-186.2 i
INT-7	-4120.024827	-4119.718502	-4121.792582	0	
INT-7-1	-4120.069162	-4119.753733	-4121.830643	0	
TS-8	-4120.025539	-4119.709783	-4121.794602	1	-135.8 i
INT-8	-4120.046386	-4119.725048	-4121.817061	0	
TS-9	-4120.009035	-4119.696405	-4121.782205	1	-620.3 i
INT-9	-1471.694912	-1471.395777	-1471.168634	0	
BrH2O	-2648.342485	-2648.359366	-2650.636228	0	

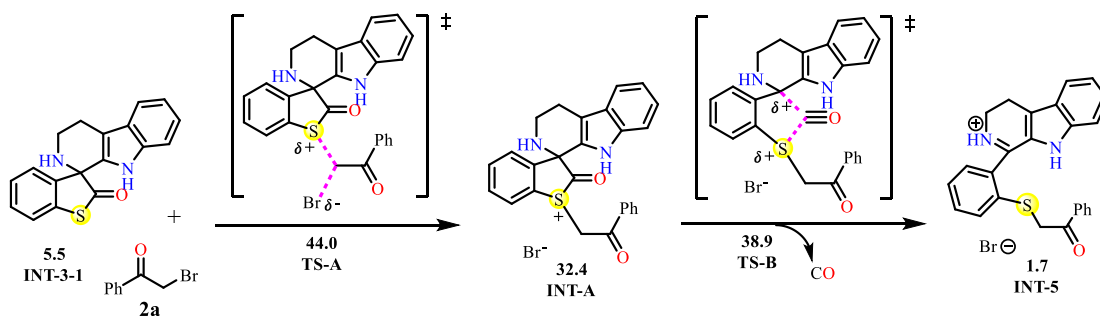


Figure S1. The mechanism in which alkylation of sulfur is prior to decarbonylation. However, this mechanism is quite inaccessible, because **TS-A** involves a free-energy barrier of 44.0 kcal/mol. It is understandable that the sulfur atom close to an electron-withdrawing carbonyl group is a poor nucleophile.

13. Computational Details

All calculations were finished under the Gaussian 16 computational program.^[1] Geometries were optimized using the B3LYP density functional method^[2] and the 6-31+g* basis sets for all atoms, in which the solvation effect of DMF was simulated by the default PCM option.^[3] Frequency analyses were performed at the same level of theory, in order for Gibbs free-energy calculations (423.15 K and 1 atm) and to ensure that all the optimized stationary points resided at the minima or first-order saddle points. Single-point energy corrections were carried out using the m06 density functional method^[4] and the 6-311++g(3df,2p) basis sets for all atoms with the same solvation model.

14. References

- [1] *Gaussian 16, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2016.
 [2] (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) P. J. Stephens, F. J. Devlin, C. F. N. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623-11627.
 [3] G. Scalmani and M. J. Frisch, *J. Chem. Phys.* 2010, **132**, 114110.
 [4] Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* 2006, **125**, 194101.