Supporting Information

Divergent synthesis of polythioindoles using elemental sulfur as the polysulfur source under metal-free conditions

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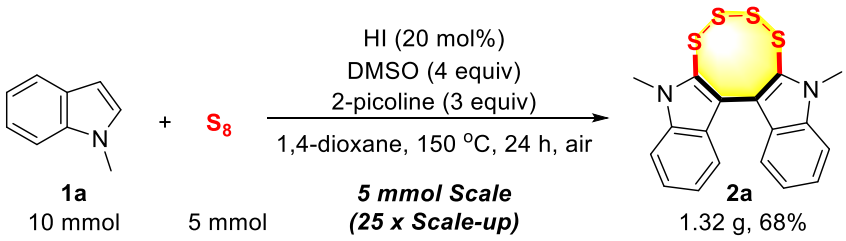
1. General information

All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using silica gel (neutral) (200-300 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100, and 376 MHz, respectively) and Bruker Avance-500 instrument (500, 126, and 471 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Multiplicities are described as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), and the coupling constants (J) are reported in Hertz. High-resolution mass spectra (HRMS) were recorded at a Waters corporation, Acquity UPLC H-Class XEVO G2-XS QTOF instrument. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP 2010 Ultra. Reactions were monitored by thin-layer chromatography. The structures of known compounds were further corroborated by comparing their ^{1}H, ^{13}C, ^{19}F NMR data, and MS data with those of the literature. All reagents were obtained from commercial suppliers and used without further purification. The molecular weight of S_8 is determined to be 256 g/mol unless otherwise noted.

2. The Synthetic Procedure for Compounds 2

Indole derivatives **1** (0.4 mmol), S_8 (51.2 mg, 0.2 mmol), HI (12 μL, 0.04 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), DMSO (60.0 μL, 0.8 mmol), 2-picoline (60.0 μL, 0.6 mmol), and 1,4-dioxane (0.8 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 150 ^{o}C for 12 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with dichloromethane (DCM, 8 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ DCM, v/v) to yield the desired product **2**.

Gram-scale experiment for the synthesis of 2a:



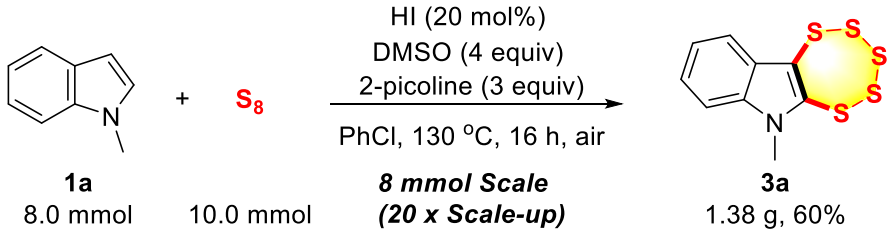
1-Methylindole **1a** (1.31 mL, 10 mmol), S_8 (1.28 g, 5 mmol), HI (300 μL, 1.0 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), DMSO (1.5 mL, 20.0 mmol),

2-picoline (1.5 mL, 15.0 mmol), and 1,4-dioxane (25 mL) were added successfully to a 100 mL oven-dried reaction flask. The sealed reaction flask was stirred at 150 ℃ for 24 h. After cooling to room temperature, the reaction was diluted with DCM (25 mL) and saturated solution of $Na_2S_2O_3$ (40 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (100 mL) three times. The combined organic layer and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/DCM: 80/1) to yield the desired product **3a** (1.32 g, 68%) as a yellow solid.

3. The Synthetic Procedure for Compounds 3

Indole derivatives **1** (0.4 mmol), S_8 (128.0 mg, 0.5 mmol), HI (24 μL, 0.08 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), DMSO (120.0 μL, 1.6 mmol), 2-picoline (120.0 μL, 1.2 mmol), and PhCl (1.0 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 130 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with DCM (8 ml) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ DCM, v/v) to yield the desired product **3**.

Gram-scale experiment for the synthesis of 3a:

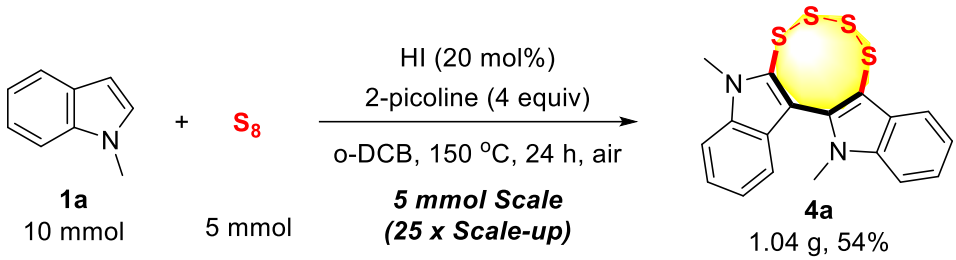


1-Methylindole **1a** (1.0 mL, 8.0 mmol), S_8 (2.56 g, 10 mmol), HI (0.48 mL, 1.6 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), DMSO (2.4 mL, 32.0 mmol), 2-picoline (2.4 mL, 24.0 mmol), and PhCl (30 mL) were added successfully to a 100 mL oven-dried reaction flask. The sealed reaction flask was stirred at 130 ℃ for 16 h. After cooling to room temperature, the reaction was diluted with DCM (40 mL) saturated solution of $Na_2S_2O_3$ (40 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (100 mL) three times. The combined organic layer and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/DCM: 100/1) to yield the desired product **2a** (1.38 g, 60%) as a yellow solid.

4. The Synthetic Procedure for Compounds 4

Indole derivatives **1** (0.4 mmol), S_8 (51.2 mg, 0.2 mmol), HI (12 μL, 0.04 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), 2-picoline (60.0 μL, 0.6 mmol), and 1,2-dichlorobenzene (*o*-DCB, 0.8 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 150 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with DCM (8 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ DCM, v/v) to yield the desired product **4**.

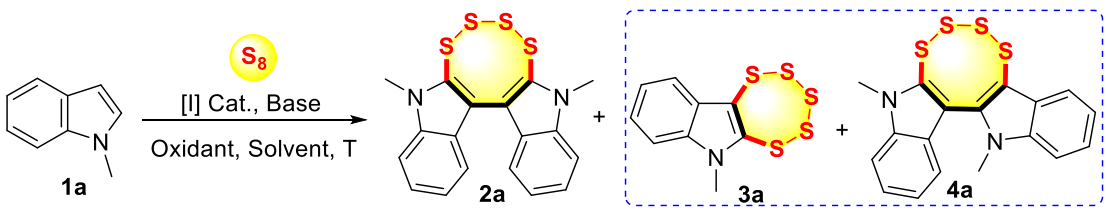
Gram-scale experiment for the synthesis of 4a:



1-Methylindole **1a** (1.31 mL, 10 mmol), S_8 (1.28 g, 5 mmol), HI (300 μL, 1.0 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), 2-picoline (1.5 mL, 15.0 mmol), and 1,2-dichlorobenzene (25 mL) were added successfully to a 100 mL oven-dried reaction flask. The sealed reaction flask was stirred at 150 ℃ for 24 h. After cooling to room temperature, the reaction was diluted with DCM 25 mL and a saturated solution of $Na_2S_2O_3$ (40 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (100 mL) three times. The combined organic layer was brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (PE/DCM: 15/1) to yield the desired product **4a** (1.04 g, 54%) as a yellow solid.

5. Supporting tables S1-S6

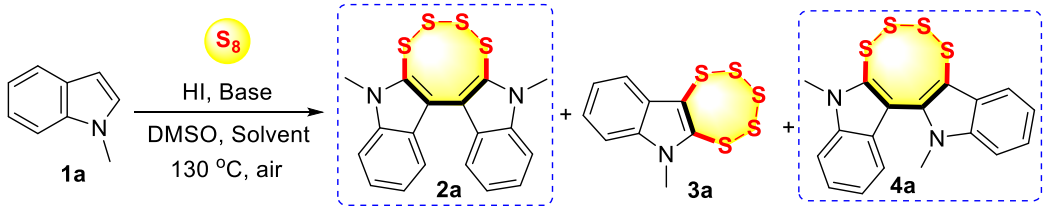
Table S1. Screening the reaction conditions of **2a**[a]



Entry	[I] Cat.	Base	Oxidant	Solvent	T (°C)	Isolated yield (%)
						2a, **3a**, **4a**
1	HI	pyridine	DMSO	1,4-dioxane	150	63, 8, trace
2	**HI**	**2-picoline**	**DMSO**	**1,4-dioxane**	**150**	**73, 5, trace**
3	HI	3-methylpyridine	DMSO	1,4-dioxane	150	62, 8, n trace
4	HI	4-methylpyridine	DMSO	1,4-dioxane	150	60, 7, trace
5	HI	DMAP	DMSO	1,4-dioxane	150	52, 11, trace
6	HI	2,2'-bipyridine	DMSO	1,4-dioxane	150	61, trace, trace.
7	HI	quinoline	DMSO	1,4-dioxane	150	57, 15, trace
8	HI	isoquinoline	DMSO	1,4-dioxane	150	68, trace, trace
9	HI	diethylamine	DMSO	1,4-dioxane	150	trace, n.d. n.d.
10	HI	triethylamine	DMSO	1,4-dioxane	150	23, trace, n.d.
11	HI	pyrrolidine	DMSO	1,4-dioxane	150	21, trace, n.d.
12	HI	piperidine	DMSO	1,4-dioxane	150	39, trace, n.d.
13	HI	morpholine	DMSO	1,4-dioxane	150	45, 11, n.d.
14	HI	2-picoline	DBSO	1,4-dioxane	150	65, 5, trace
15	HI	2-picoline	PhSOMe	1,4-dioxane	150	55, 10, n.d.
16	HI	2-picoline	Ph_2SO	1,4-dioxane	150	13, 19, trace
17	HI	2-picoline	Sulfolane	1,4-dioxane	150	15, 23, trace
18	HI	2-picoline	Ph_2SO_2	1,4-dioxane	150	17, 26, trace
19	HI	2-picoline	DMSO	toluene	150	36, 27, n.d.
20	HI	2-picoline	DMSO	*o*-xylene	150	38, 30, n.d.
21	HI	2-picoline	DMSO	mesitylene	150	31, 26, n.d.
22	HI	2-picoline	DMSO	anisole	150	29, 25, n.d.
23	HI	2-picoline	DMSO	$PhCF_3$	150	42, 22, n.d.
24	HI	2-picoline	DMSO	PhCl	150	68, 9, trace
25	HI	2-picoline	DMSO	*o*-DCB	150	65, trace, 7
26	HI	2-picoline	DMSO	pyridine	150	61, n.d. n.d.
27	HI	2-picoline	DMSO	quinoline	150	59, n.d n.d.
28	HI	2-picoline	DMSO	DMF	150	trace, trace, n.d.
29	HI	2-picoline	DMSO	NMP	150	51, n.d. n.d.
30	HI	2-picoline	DMSO	1,4-dioxane	140	53, 22, 9
31	HI	2-picoline	DMSO	1,4-dioxane	130	9, 51, n.d.
32	HI	---	DMSO	1,4-dioxane	150	n.d. n.d. n.d.
33	HI	2-picoline	----	1,4-dioxane	150	27, n.d. 19
34	---	2-picoline	DMSO	1,4-dioxane	150	n.d. trace, n.d.
35[b]	HI	2-picoline	DMSO	1,4-dioxane	150	70, 6, trace
36[c]	HI	2-picoline	DMSO	1,4-dioxane	150	65, 11, n.d.
37[d]	---	2-picoline	DMSO	1,4-dioxane	150	n.d. 13, n.d.
38[e]	---	2-picoline	DMSO	1,4-dioxane	150	n.d. trace, n.d.

[a] *Conditions*: **1a** (0.4 mmol), S_8 (51.6 mg, 0.2 mmol), [I] catalyst (20 mol%), oxidant (4 equiv), base (3 equiv), solvent (1.0 mL), 150 °C, 12 h, under air atmosphere. Isolated yield based on **1a**. [b] Under Ar. [c] Under O_2. [d] HBr (20 mol%). [e] HCl (20 mol%).

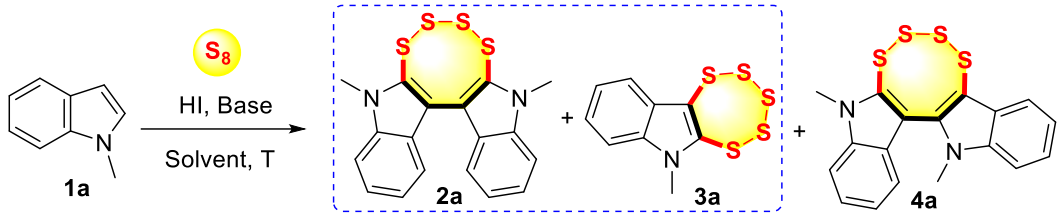
Table S2. Screening the reaction conditions of **3a**[a]



Entry	Base	Solvent	Isolated yield (%)
			2a, **3a**, **4a**
1	pyridine	1,4-dioxane	7, 53, n.d.
2	2-picoline	1,4-dioxane	9, 63, n.d.
3	3-methylpyridine	1,4-dioxane	8, 55, n.d.
4	4-methylpyridine	1,4-dioxane	7, 52, n.d.
5	DMAP	1,4-dioxane	8, 56, n.d.
6	2,2'-bipyridine	1,4-dioxane	9, 48, n.d.
7	quinoline	1,4-dioxane	8, 47, n.d.
8	isoquinoline	1,4-dioxane	8, 57, n.d.
9	2-picoline	toluene	trace, 55, n.d.
10	2-picoline	*o*-xylene	trace, 60, n.d.
11	2-picoline	mesitylene	trace, 57, n.d.
12	2-picoline	$PhCF_3$	trace, 62, n.d.
13	**2-picoline**	**PhCl**	**trace, 71, n.d.**
14	2-picoline	*o*-DCB	n.d. 62, trace
15	2-picoline	pyridine	n.d. 63, n.d.
16	2-picoline	quinoline	trace, 51, n.d.
17	2-picoline	NMP	21, trace, n.d.
18	---	PhCl	n.d. n.d. n.d.
19[b]	2-picoline	PhCl	trace, 70, n.d.
20[c]	2-picoline	PhCl	7, 67, n.d.
21[d]	2-picoline	PhCl	trace, 57, n.d.
22[e]	2-picoline	PhCl	trace, 16, n.d.

[a] *Conditions*: **1a** (0.4 mmol), S_8 (128 mg, 0.5 mmol), HI (20 mol%), oxidant (4 equiv), base (3 equiv), solvent (1.0 mL), 130 °C, 12 h, under air atmosphere. Isolated yield based on **1a**. [b] Under Ar. [c] Under O_2. [d] HBr (20 mol%) instead of HI. [e] HCl (20 mol%) instead of HI.

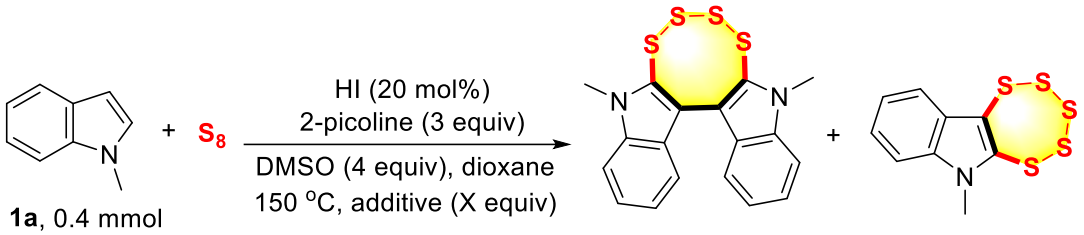
Table S3. Screening the reaction conditions of **4a**[a]



Entry	Base	Solvent	T (°C)	Isolated yield (%)
				2a, **3a**, **4a**
1	pyridine	*o*-DCB	150	7, n.d. 53
2	2-picoline	*o*-DCB	150	trace, n.d. 58
3	3-methylpyridine	*o*-DCB	150	5, n.d. 56
4	4-methylpyridine	*o*-DCB	150	7, n.d. 54
5	DMAP	*o*-DCB	150	6, n.d. 50
6	2,2'-bipyridine	*o*-DCB	150	11, n.d. 52
7	quinoline	*o*-DCB	150	16, n.d. 47
8	isoquinoline	*o*-DCB	150	8, n.d. 57
9	2-picoline	toluene	150	26, trace, n.d.
10	2-picoline	*o*-xylene	150	24, trace, n.d.
11	2-picoline	mesitylene	150	19, trace, n.d.
12	2-picoline	anisole	150	30, trace, n.d.
13	2-picoline	$PhCF_3$	150	37, n.d., trace
14	2-picoline	PhCl	150	13, n.d. 41
15	2-picoline	pyridine	150	53, n.d. n.d.
16	2-picoline	NMP	150	47, n.d. n.d.
17	2-picoline	*o*-DCB	140	13, n.d. 39
18[b]	**2-picoline**	***o*-DCB**	**150**	**trace, n.d. 63**
19[c]	2-picoline	*o*-DCB	150	trace, n.d. 60
20	---	*o*-DCB	150	n.d. trace n.d.
21[d]	2-picoline	*o*-DCB	150	trace, n.d. trace
22[e]	2-picoline	*o*-DCB	150	trace, n.d. trace

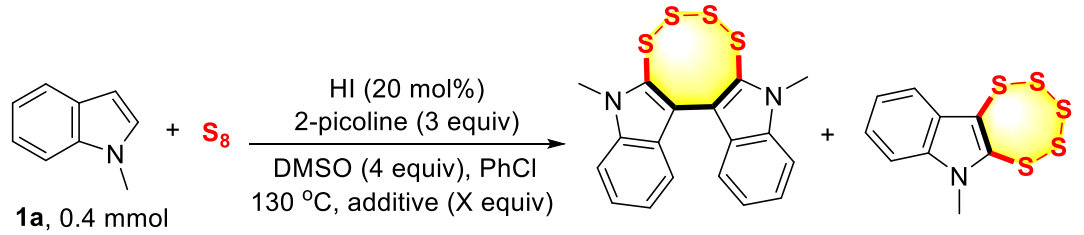
[a] *Conditions*: **1a** (0.4 mmol), S_8 (51.6 mg, 0.2 mmol), HI (20 mol%), base (3 equiv), solvent (1.0 mL), 12 h, under air atmosphere. Isolated yield based on **1a**. [b] 2-Picoline (4 equiv). [c] 2-Picoline (5 equiv). [d] HBr (20 mol%) instead of HI. [e] HCl (20 mol%) instead of HI.

Table S4. Free radical capture experiments



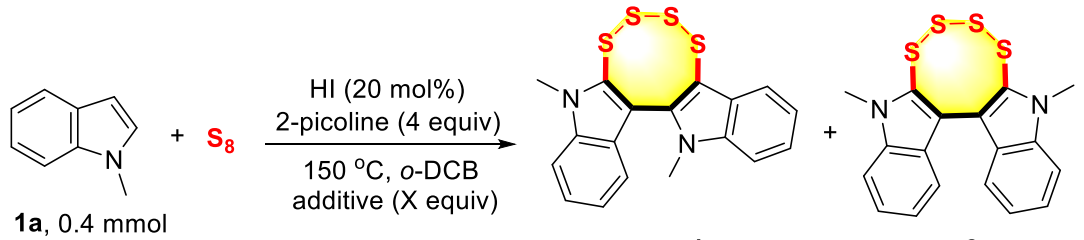
1a, 0.4 mmol

additive (X equiv)	yield: **2a**	**3a**
BHT (1 eq.)	51%	trace
BHT (2 eq.)	19%	n.d.
ethene-1,1-diyldibenzene (1 eq.)	64%	13%
ethene-1,1-diyldibenzene (2 eq.)	53%	trace
TEMPO (1 eq.)	21%	38%
TEMPO (2 eq.)	n.d.	trace



1a, 0.4 mmol

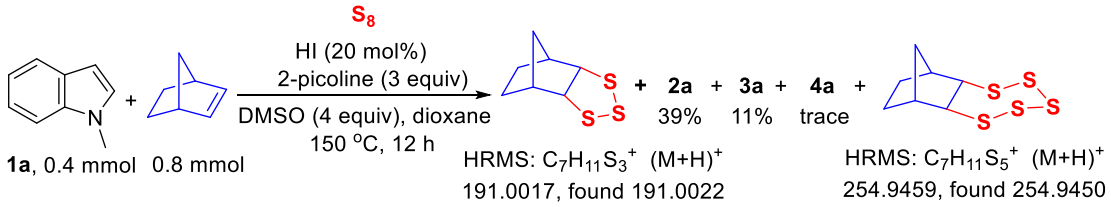
additive (X equiv)	yield: **2a**	**3a**
BHT (1 eq.)	n.d.	trace
BHT (2 eq.)	n.d.	n.d.
ethene-1,1-diyldibenzene (1 eq.)	trace	64%
ethene-1,1-diyldibenzene (2 eq.)	trace	53%
TEMPO (1 eq.)	trace	47%
TEMPO (2 eq.)	n.d.	14%



1a, 0.4 mmol

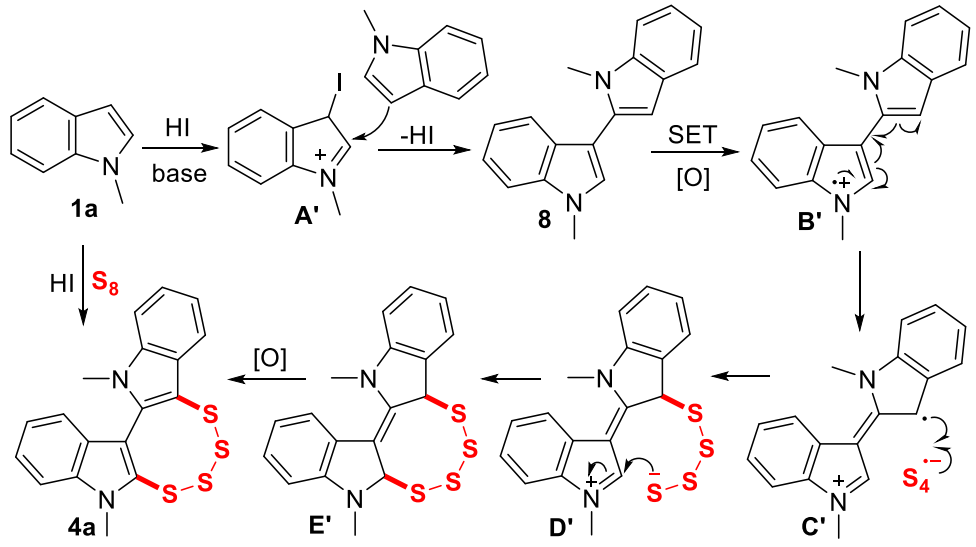
additive (X equiv)	yield: **4a**	**2a**
BHT (1 eq.)	13%	trace
BHT (2 eq.)	n.d.	n.d.
ethene-1,1-diyldibenzene (1 eq.)	20%	trace
ethene-1,1-diyldibenzene (2 eq.)	n.d.	n.d.
TEMPO (0.2 eq.)	19%	11%
TEMPO (0.5 eq.)	n.d.	n.d.

Table S5. Norbornene capture polysulfur radical anion



1-Methylindole **1a** (0.4 mmol), bicyclo[2.2.1]hept-2-ene (norbornene, 0.8 mmol), S_8 (128 mg, 0.5 mmol), HI (12 μL, 0.04 mmol, 20 mol%, 55% w/w aqueous. solution, stab with 1.5% hypophosphorous acid), DMSO (60.0 μL, 0.8 mmol), 2-picoline (60.0 μL, 0.6 mmol), and 1,4-dioxane (1.0 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 150 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with dichloromethane (DCM, 25 mL). (3a*R*, 4*R*, 7*S*, 7a*S*)-Hexahydro-4,7-methanobenzo[*d*][1,2,3]trithiole and (6*R*,9*S*)-hexahydro-6,9-methanobenzo[*f*][1,2,3,4,5] pentathiepine was detected by HRMS, respectively. HRMS (ESI, m/z) calcd for $C_7H_{11}S_3^+$ $[M+H]^+$: 191.0017; found: 191.0022. HRMS (ESI, m/z) calcd for $C_7H_{11}S_5^+$ $[M+H]^+$: 254.9459; found: 254.9450.

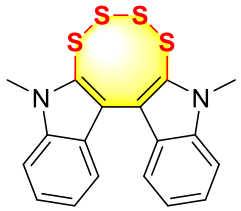
Table S6. Possible reaction mechanism of **4a**



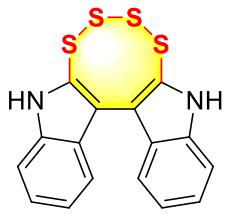
Based on the above experimental observations and related references,[1] We propose a possible mechanism for the formation of asymmetric tetrathiadiindole **4a** by sulfur. Polysulfide radical anion ($S_n^{\cdot-}$) was generated in situ from S_8 under standard conditions.[2] First, the nucleophilic

attack of indole on the iodine atom of HI forms intermediate **A**'. Then, an intermolecular nucleophilic addition reaction of the second indole and the elimination of a molecule of hydrogen iodide were carried out to obtain 2,3'-biindolyl **8**. A nitrogen radical cation **B**' is generated *via* single-electron transfer (SET) promoted by an HI/DMSO oxidation system. This intermediate can further convert into vinyl radical intermediate **C**' *via* an isomerization step. Then **C**' reacts with the tetrasulfide radical anion to form a tetrathioindole intermediate **D**', which undergoes an intramolecular nucleophilic attack to remove the proton to give **E**'. The final desired product **4a** is formed through the oxidation of **E**'.

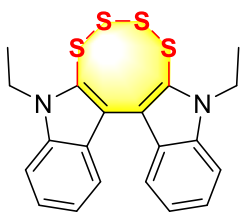
6. Characterization data of products



5,10-Dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2a, CAS: 13637-40-6) [3]**:** Purified by silica gel flash chromatography with petroleum ether and dichloromethane (50:1, v/v) The **2a** was prepared as a yellow solid following the general procedure in 73% yield (56.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.47 (d, J = 8.0 Hz, 2H), 7.44 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.13 – 7.06 (m, 2H), 4.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.5, 128.1, 126.7, 124.8, 121.2, 121.0, 120.4, 110.3, 30.7; HRMS calcd. for $C_{18}H_{14}N_2NaS_4^+$ $(M+Na)^+$ 408.9932, found 408.9926.

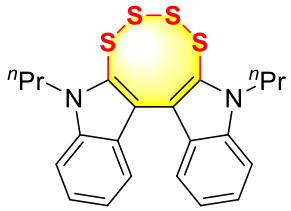


5,10-Dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2b, CAS: 13839-92-4)[4]**:** Purified by silica gel flash chromatography with petroleum ether and dichloromethane (8:1, v/v). The **2b** was prepared as a yellow solid following the general procedure in 55% yield (39.5 mg); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 12.16 (s, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.06 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 136.2, 126.9, 124.8, 124.5, 120.2, 120.1, 119.2, 112.1; HRMS calcd. for $C_{16}H_{11}N_2S_4^+$ $(M+H)^+$ 358.9800, found 358.9803.

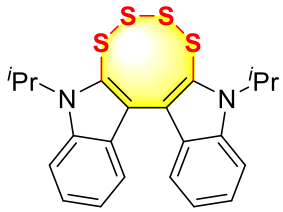


5,10-Diethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2c): Purified by silica

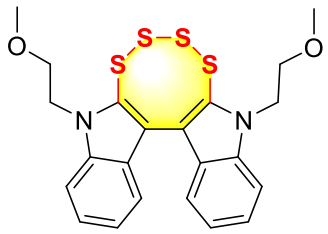
gel flash chromatography with petroleum ether and dichloromethane (50:1, v/v). The **2c** was prepared as yellow solid following the general procedure in 80% yield (66.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.00 (t, J = 7.5 Hz, 2H), 4.57 – 4.45 (m, 2H), 4.43 – 4.32 (m, 2H), 1.38 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.4, 127.2, 126.9, 124.6, 121.5, 121.0, 120.2, 110.2, 39.0, 15.7; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 437.0245, found 437.0248.



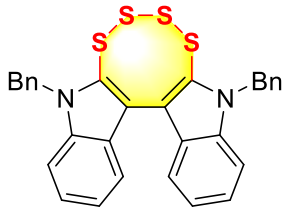
5,10-Dipropyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2d): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (50:1, v/v). The **2d** was prepared as yellow solid following the general procedure in 72% yield (63.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.47 – 7.41 (m, 4H), 7.39 – 7.31 (m, 2H), 7.08 (t, J = 7.5 Hz, 2H), 4.53 – 4.44 (m, 2H), 4.43 – 4.34 (m, 2H), 2.05 – 1.88 (m, 4H), 1.04 (t, J = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 136.9, 127.8, 126.8, 124.6, 121.4, 120.9, 120.2, 110.5, 45.8, 23.9, 11.6; HRMS calcd. for $C_{22}H_{23}N_2S_4^+$ $(M+H)^+$ 443.0739, found 443.0746.



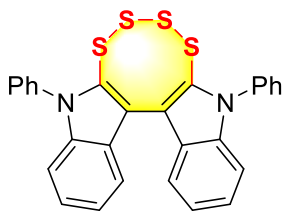
5,10-Dipropyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2e): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (50:1, v/v). The **2e** was prepared as yellow solid following the general procedure in 65% yield (57.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (d, J = 8.5 Hz, 2H), 7.49 – 7.47 (m, 2H), 7.39 – 7.30 (m, 2H), 7.08 – 7.05 (m, 2H), 5.51 – 5.48 (m, 2H), 1.79 (d, J = 7.0 Hz, 6H), 1.72 (d, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.4, 127.9, 127.7, 124.0, 121.8, 121.3, 119.8, 112.2, 48.3, 21.6; HRMS calcd. for $C_{22}H_{23}N_2S_4^+$ $(M+H)^+$ 443.0739, found 443.0736.



5,10-Bis(2-methoxyethyl)-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2f): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (20:1, v/v). The **2f** was prepared as yellow solid following the general procedure in 71% yield (67.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.4 Hz, 2H), 7.46 – 7.44 (m, 2H), 7.38 – 7.34 (m, 2H), 7.13 – 7.05 (m, 2H), 4.77 – 4.69 (m, 2H), 4.66 – 4.58 (m, 2H), 3.80 (t, J = 6.3 Hz, 4H), 3.36 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 137.4, 127.8 126.8, 124.8, 121.3, 121.3, 120.5, 110.7, 71.6, 59.2, 43.9; HRMS calcd. for $C_{22}H_{22}KN_2O_2S_4^+$ $(M+K)^+$ 513.0196, found 513.0205.

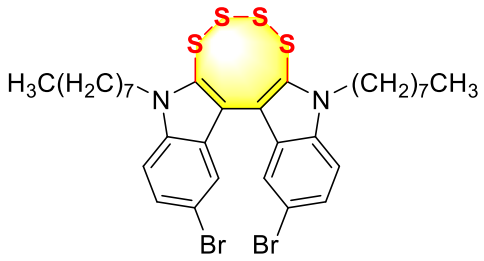


5,10-Dibenzyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2g): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2g** was prepared as yellow solid following the general procedure in 60% yield (64.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54 (d, J = 8.1 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 6H), 7.27 – 7.22 (m, 2H), 7.18 – 7.09 (m, 6H), 5.80 (d, J = 16.5 Hz, 2H), 5.67 (d, J = 16.5 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 137.5, 137.2, 128.7, 128.4, 127.4, 127.0, 126.6, 125.0, 121.4, 121.2, 120.6, 110.9, 47.6; HRMS calcd. for $C_{30}H_{23}N_2S_4^+$ $(M+H)^+$ 539.0739, found 539.0732.

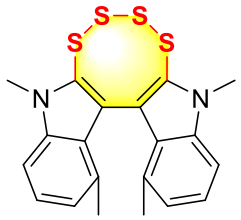


5,10-Diphenyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2h): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2h** was

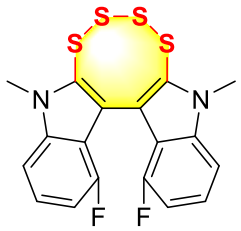
prepared as yellow solid following the general procedure in 41% yield (42.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (d, J = 6.4 Hz, 2H), 7.57 (s, 2H), 7.52 – 7.46 (m, 4H), 7.46 – 7.39 (m, 4H), 7.34 (t, J = 7.0 Hz, 2H), 7.25 – 7.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.1, 136.3, 131.4, 129.9, 129.6, 126.7, 124.3, 122.9, 120.9, 119.8, 110.7, 108.4; HRMS calcd. for $C_{28}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 533.0245, found 533.0240.



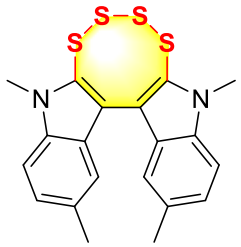
2,13-Dibromo-5,10-dioctyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2i): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (20:1, v/v). The **2i** was prepared as yellow solid following the general procedure in 26% yield (39.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, J = 1.9 Hz, 2H), 7.38 (dd, J = 8.8, 1.9 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 4.44 – 4.08 (m, 4H), 1.81 – 1.64 (m, 4H), 1.40 – 1.17 (m, 20H), 0.98 – 0.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.3, 134.5, 130.5, 127.5, 123.2, 118.1, 115.4, 112.2, 45.5, 31.7, 30.8, 29.1, 29.1, 26.8, 22.6, 14.1; HRMS calcd. For $C_{32}H_{40}Br_2KN_2S_4^+$ $(M+K)^+$ 777.0073, found 777.0066.



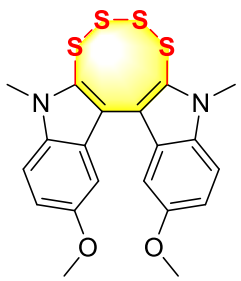
1,5,10,14-Tetramethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2j): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2j** was prepared as yellow solid following the general procedure in 58% yield (48.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 – 7.24 (m, 4H), 6.86 – 6.85 (m, 2H), 3.99 (s, 6H), 1.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 132.9, 130.1, 127.2, 124.6, 121.8, 121.7, 108.0, 30.8, 19.2; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+H)^+$ 437.0245, found 437.0248.



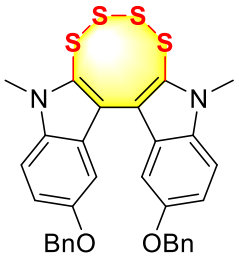
1,14-Difluoro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2k): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2k** was prepared as yellow solid following the general procedure in 50% yield (42.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 – 7.24 (m, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.89 – 6.86 (m, 2H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.1 (d, J = 252.6 Hz), 142.4, 138.9 (d, J = 9.0 Hz), 125.5 (d, J = 7.8 Hz), 117.6 (d, J = 17.7 Hz), 116.8 (d, J = 3.9 Hz), 107.4 (d, J = 18.8 Hz), 106.8 (d, J = 4.4 Hz), 32.1; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -121.4; HRMS calcd. for $C_{18}H_{13}F_2N_2S_4^+$ $(M+H)^+$ 422.9924, found 422.9915.



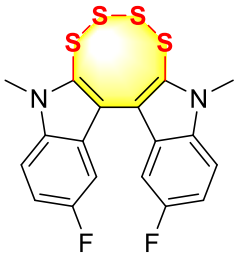
2,5,10,13-Tetramethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2l): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2l** was prepared as yellow solid following the general procedure in 78% yield (64.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (d, J = 8.4 Hz, 2H), 7.25 (s, 2H), 7.21 (d, J = 8.6 Hz, 2H), 3.98 (s, 6H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.9, 129.8, 128.1, 126.9, 126.6, 120.5, 120.4, 110.0, 30.7, 21.4; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 437.0245, found 437.0248.



2,13-Dimethoxy-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2m): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (5:1, v/v). The **2m** was prepared as yellow solid following the general procedure in 68% yield (60.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.34 (d, J = 9.0 Hz, 2H), 7.05 (dd, J = 9.0, 2.1 Hz, 2H), 6.85 (s, 2H), 3.99 (s, 6H), 3.68 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.7, 132.9, 128.2, 126.8, 120.5, 116.2, 111.3, 101.5, 55.8, 30.9; HRMS calcd. for $C_{20}H_{18}N_2NaO_2S_4^+$ $(M+Na)^+$ 469.0143, found 469.0151.

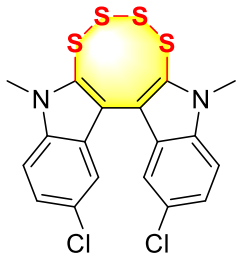


2,13-Bis(benzyloxy)-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2n): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (8:1, v/v). The **2n** was prepared as yellow solid following the general procedure in 52% yield (62.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 – 7.34 (m, 6H), 7.33 – 7.28 (m, 4H), 7.28 – 7.23 (m, 2H), 7.14 (dd, J = 9.0, 2.4 Hz, 2H), 6.93 (d, J = 2.4 Hz, 2H), 4.87 (s, 4H), 4.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.8, 137.1, 133.0, 128.4, 127.8, 127.6, 126.8, 120.3, 116.7, 111.6, 102.9, 70.6, 30.9; HRMS calcd. for $C_{32}H_{27}N_2O_2S_4^+$ $(M+H)^+$ 599.0950, found 599.0953.

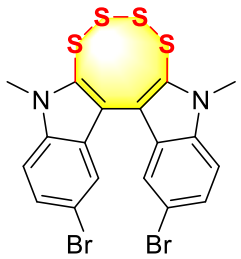


2,13-Difluoro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2o): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (50:1, v/v). The **2o** was prepared as yellow solid following the general procedure in 71% yield (60.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35 (dd, J = 9.0, 4.2 Hz, 2H), 7.13 (td, J = 9.1, 2.5 Hz, 2H),

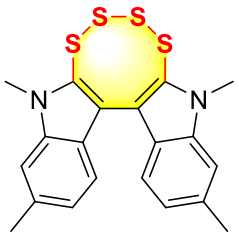
7.06 (dd, J = 9.0, 2.5 Hz, 2H), 3.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.0 (d, J = 237.6 Hz), 134.1, 129.7, 126.6 (d, J = 9.8 Hz), 120.0 (d, J = 5.1 Hz), 113.8 (d, J = 26.8 Hz), 111.4 (d, J = 9.3 Hz), 105.4 (d, J = 23.6 Hz), 31.0; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -122.2; HRMS calcd. for $C_{18}H_{13}F_2N_2S_4^+$ $(M+H)^+$ 422.9924, found 422.9915.



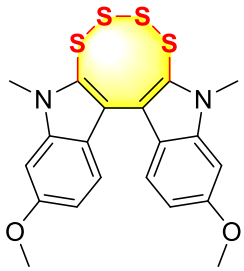
2,13-Dichloro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2p): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2p** was prepared as yellow solid following the general procedure in 67% yield (60.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.67 (d, J = 1.9 Hz, 2H), 7.28 (dd, J = 8.8, 2.0 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.7, 135.0, 129.8, 128.1, 125.2, 120.0, 118.5, 111.8, 31.8; HRMS calcd. for $C_{18}H_{13}Cl_2N_2S_4^+$ $(M+H)^+$ 454.9333, found 454.9333.



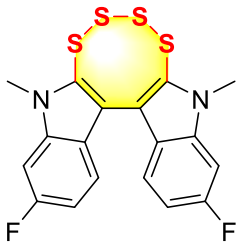
2,13-Dibromo-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2q): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2q** was prepared as yellow solid following the general procedure in 59% yield (64.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 – 7.82 (m, 2H), 7.41 (dd, J = 8.8, 1.9 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 142.5, 135.2, 130.3, 127.7, 123.1, 118.4, 115.6, 112.1, 31.8; HRMS calcd. for $C_{18}H_{13}Br_2N_2S_4^+$ $(M+H)^+$ 542.8323, found 542.8334.



3,5,10,12-Tetramethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2r): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2r** was prepared as yellow solid following the general procedure in 77% yield (63.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 (d, J = 8.2 Hz, 2H), 7.12 (s, 2H), 6.84 (d, J = 8.2 Hz, 2H), 3.87 (s, 6H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.8, 134.9, 127.1, 124.7, 122.3, 121.1, 120.9, 110.0, 30.6, 22.1; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 437.0245, found 437.0248.

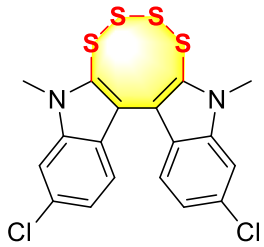


3,12-Dimethoxy-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2s): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (6:1, v/v). The **2s** was prepared as yellow solid following the general procedure in 77% yield (68.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.34 (d, J = 8.7 Hz, 2H), 6.82 (s, 2H), 6.77 (d, J = 8.7 Hz, 2H), 3.96 (s, 6H), 3.91 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 158.7, 138.4, 126.3, 122.1, 121.5, 121.2, 111.2, 92.8, 55.7, 30.7; HRMS calcd. for $C_{20}H_{19}N_2O_2S_4^+$ $(M+H)^+$ 447.0324, found 447.0331.

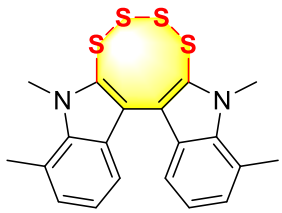


3,12-Difluoro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*'']diindole (2t): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v).

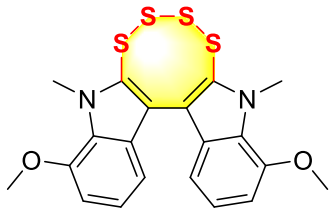
The **2t** was prepared as yellow solid following the general procedure in 73% yield (61.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.34 (m, 2H), 7.10 (dd, J = 9.6, 2.2 Hz, 2H), 6.88 (td, J = 9.1, 2.2 Hz, 2H), 3.96 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6 (d, J = 242.5 Hz), 137.6 (d, J = 12.2 Hz), 128.4 (d, J = 3.5 Hz), 123.1, 122.3 (d, J = 10.4 Hz), 120.8, 109.8 (d, J = 25.1 Hz), 96.5 (d, J = 26.4 Hz), 30.9; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -115.9; HRMS calcd. for $C_{18}H_{13}F_2N_2S_4^+$ $(M+H)^+$ 422.9924, found 422.9915.



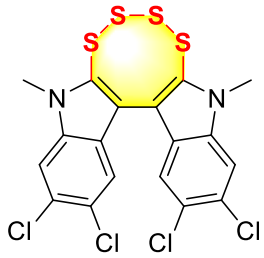
3,12-Dichloro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2u): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2u** was prepared as yellow solid following the general procedure in 68% yield (61.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 (s, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.07 (dd, J = 8.4, 1.7 Hz, 2H), 3.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.7, 131.0, 129.0, 125.0, 121.9, 121.4, 120.4, 110.3, 30.9; HRMS calcd. for $C_{18}H_{13}Cl_2N_2S_4^+$ $(M+H)^+$ 454.9333, found 454.9333.



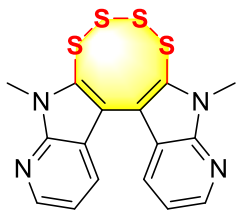
4,5,10,11-Tetramethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindoleiazole (2v): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2v** was prepared as yellow solid following the general procedure in 78% yield (64.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.21 – 7.15 (m, 2H), 6.99 (d, J = 7.2 Hz, 2H), 6.87 (t, J = 7.5 Hz, 2H), 4.24 (s, 6H), 2.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.6, 128.9, 127.5, 122.1, 121.8, 121.6, 120.4, 119.5, 33.8, 20.5; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 437.0245, found 437.0248.



4,11-Dimethoxy-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2w): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2w** was prepared as yellow solid following the general procedure in 65% yield (58.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.00 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.8 Hz, 2H), 6.71 (d, J = 7.5 Hz, 2H), 4.29 (s, 6H), 3.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 147.5, 128.7, 128.5, 127.6, 121.2, 120.5, 113.9, 104.7, 55.6, 34.0; HRMS calcd. for $C_{20}H_{19}N_2O_2NaS_4^+$ $(M+H)^+$ 447.0324, found 447.0331.

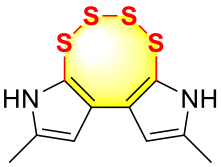


2,3,12,13-Tetrachloro-5,10-dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (2x): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v). The **2x** was prepared as yellow solid following the general procedure in 72% yield (75.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.76 (s, 2H), 7.42 (s, 2H), 3.88 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 143.4, 135.2, 129.1, 128.3, 126.7, 121.6, 118.6, 112.2, 31.9; HRMS calcd. for $C_{18}H_{10}Cl_4KN_2S_4^+$ $(M+K)^+$ 560.8113, found 560.8099.

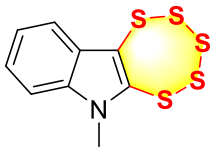


5,10-Dimethyl-5,10-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']bipyrrolo[2,3-*b*]pyridine (2y): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (40:1, v/v).

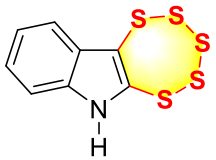
The **2y** was prepared as yellow solid following the general procedure in 61% yield (47.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.54 – 8.50 (m, 2H), 7.73 (dd, J = 7.8, 1.7 Hz, 2H), 7.14 – 7.06 (m, 2H), 4.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.7, 146.5, 128.9, 128.8, 119.5, 118.2, 116.8, 29.5; HRMS calcd. for $C_{16}H_{13}N_4S_4^+$ $(M+H)^+$ 389.0018, found 389.0008.



2,9-Dimethyl-3,8-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']dipyrrole (2z): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (4:1, v/v). The **2z** was prepared as yellow solid following the general procedure in 40% yield (22.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.34 (s, 2H), 6.20 (d, J = 2.9 Hz, 2H), 2.22 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 129.7, 129.0, 128.1, 115.1, 13.2; HRMS calcd. for $C_{10}H_{11}N_2S_4^+$ $(M+H)^+$ 286.9800, found 286.9808.

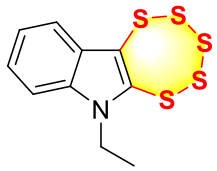


6-Methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3a, CAS: 371970-71-7) [3]: Purified by silica gel flash chromatography with petroleum ether and dichloromethane (100:1, v/v). The **3a** was prepared as yellow solid following the general procedure in 71% yield (82.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.72 – 7.65 (m, 1H), 7.37 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.3, 136.6, 128.9, 124.7, 122.2, 120.6, 119.1, 110.5, 31.5; HRMS calcd. for $C_9H_8NS_5^+$ $(M+H)^+$ 289.9255, found 289.9253.

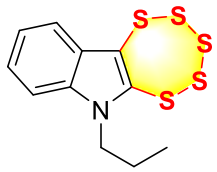


6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3b, CAS: 157984-19-5) [3]: Purified by silica gel flash chromatography with petroleum ether and dichloromethane (6:1, v/v). The **3b** was prepared as a

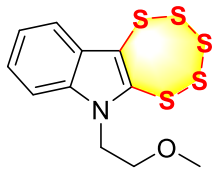
yellow solid following the general procedure in 58% yield (63.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.61 (s, 1H), 7.68 (dd, J = 7.8, 1.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 137.8, 134.9, 129.8, 125.0, 122.3, 120.5, 120.3, 111.6; HRMS calcd. for $C_8H_6NS_5^+$ $(M+H)^+$ 275.9098, found 275.9098.



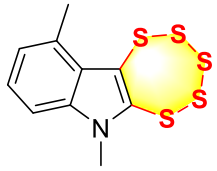
6-Ethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3c): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3c** was prepared as yellow solid following the general procedure in 78% yield (94.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.70 (d, J = 7.9 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.28 – 7.21 (m, 1H), 4.50 – 4.41 (m, 1H), 4.40 – 4.31 (m, 1H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 140.6, 135.5, 129.2, 124.6, 122.1, 120.8, 119.1, 110.4, 40.1, 16.2; HRMS calcd. for $C_{10}H_{10}NS_5^+$ $(M+H)^+$ 303.9411, found 303.9418.



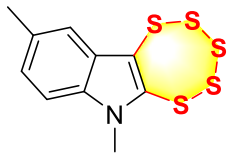
6-Propyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3d): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (200:1, v/v). The **3d** was prepared as yellow solid following the general procedure in 58% yield (73.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.70 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 3.5 Hz, 2H), 7.28 – 7.24 (m, 1H), 4.40 – 4.33 (m, 1H), 4.31 – 4.24 (m, 1H), 1.86 – 1.77 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.2, 135.9, 129.1, 124.5, 122.0, 120.7, 119.0, 110.7, 46.7, 24.1, 11.4; HRMS calcd. for $C_{11}H_{11}NNaS_5^+$ $(M+Na)^+$ 339.9387, found 339.9381.



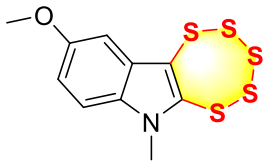
6-(2-Methoxyethyl)-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3f): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (10:1, v/v). The **3f** was prepared as yellow solid following the general procedure in 68% yield (90.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.70 (d, J = 7.9 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.29 – 7.23 (m, 1H), 4.63 – 4.46 (m, 2H), 3.64 (t, J = 5.6 Hz, 2H), 3.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.8, 136.1, 129.1, 124.6, 122.1, 120.6, 119.1, 110.7, 71.4, 59.2, 44.9; HRMS calcd. for $C_{11}H_{12}NOS_5^+$ $(M+H)^+$ 333.9517, found 333.9511.



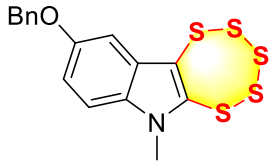
6,10-Dimethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3j): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (100:1, v/v). The **3j** was prepared as yellow solid following the general procedure in 47% yield (57.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.23 – 7.19 (m, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.95 (d, J = 7.1 Hz, 1H), 3.88 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.1, 136.9, 132.1, 126.8, 125.0, 123.9, 119.6, 108.6, 31.7, 20.7; HRMS calcd. for $C_{10}H_{10}NS_5^+$ $(M+H)^+$ 303.9411, found 303.9418.



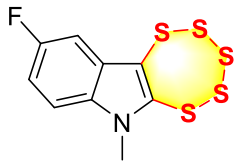
6,9-Dimethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3l): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (100:1, v/v). The **3l** was prepared as yellow solid following the general procedure in 74% yield (89.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.45 (s, 1H), 7.16 – 7.13 (m, 2H), 3.84 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.0, 135.0, 131.8, 129.2, 126.5, 119.9, 118.4, 110.2, 31.5, 21.5; HRMS calcd. for $C_{10}H_{10}NS_5^+$ $(M+H)^+$ 303.9411, found 303.9418.



9-Methoxy-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3m): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **3m** was prepared as yellow solid following the general procedure in 68% yield (86.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.18 (d, J = 9.0 Hz, 1H), 7.07 (d, J = 2.5 Hz, 1H), 6.97 (dd, J = 9.0, 2.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.9, 141.1, 131.8, 129.7, 118.4, 116.1, 111.6, 100.6, 55.7, 31.7; HRMS calcd. for $C_{10}H_9NNaOS_5^+$ $(M+H)^+$ 341.9180, found 341.9181.

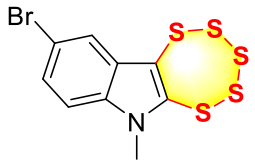


9-(Benzyloxy)-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3n): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (20:1, v/v). The **3n** was prepared as yellow solid following the general procedure in 62% yield (98.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.51 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.22 – 7.16 (m, 2H), 7.06 (dd, J = 9.0, 2.5 Hz, 1H), 5.13 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.1, 141.3, 136.9, 132.0, 130.0, 128.6, 128.0, 127.7, 118.4, 116.6, 111.7, 102.2, 70.6 31.7; HRMS calcd. for $C_{16}H_{14}NOS_5^+$ $(M+H)^+$ 395.9673, found 395.9659.

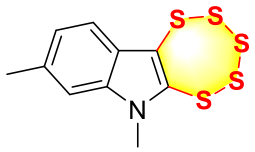


9-Fluoro-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3o): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3o** was prepared as yellow solid following the general procedure in 80% yield (98.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.33 (dd, J = 8.9, 2.5 Hz, 1H), 7.23 (dd, J = 9.0, 4.1 Hz, 1H), 7.08 (td, J = 9.0, 2.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 159.1 (d, J = 239.8 Hz), 142.8, 133.2, 129.5 (d,

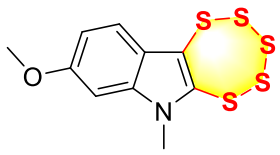
J = 10.4 Hz), 118.8 (d, *J* = 3.6 Hz), 113.7 (d, *J* = 26.8 Hz), 111.7 (d, *J* = 9.3 Hz), 105.4 (d, *J* = 24.5 Hz), 31.8; ^{19}F NMR (471 MHz, $CDCl_3$, ppm) δ -119.9; HRMS calcd. for $C_9H_7FNS_5^+$ $(M+H)^+$ 307.9161, found 307.9169.



9-Bromo-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3q): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (100:1, v/v). The **3q** was prepared as yellow solid following the general procedure in 60% yield (88.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.21 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.1, 136.8, 130.9, 127.4, 123.0, 121.7, 119.5, 110.5, 31.7; HRMS calcd. for $C_9H_7BrNS_5^+$ $(M+H)^+$ 367.8360, found 367.8359.

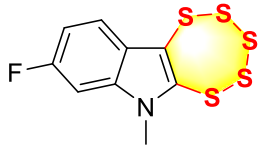


6,8-Dimethyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3r): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3r** was prepared as yellow solid following the general procedure in 78% yield (94.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.10 – 7.07 (m, 2H), 3.85 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 140.5, 136.9, 135.0, 127.0, 124.1, 120.2, 119.2, 110.2, 31.4, 22.0; HRMS calcd. for $C_{10}H_{10}NS_5^+$ $(M+H)^+$ 303.9411, found 303.9418.

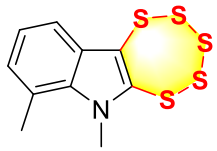


8-Methoxy-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3s): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (10:1, v/v). The **3s** was prepared as yellow solid following the general procedure in 61% yield (77.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.54 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 6.68 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H);

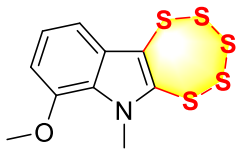
^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 158.4, 139.5, 137.4, 123.4, 121.5, 119.8, 113.0, 92.9, 55.7, 31.5; HRMS calcd. for $C_{10}H_9NNaOS_5^+$ $(M+H)^+$ 341.9180, found 341.9181.



8-Fluoro-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3t): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3t** was prepared as yellow solid following the general procedure in 71% yield (87.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.65 – 7.58 (m, 1H), 7.07 – 7.00 (m, 1H), 6.97 (dt, J = 9.4, 1.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.2 (d, J = 243.4 Hz), 141.6 (d, J = 3.6 Hz), 136.6 (d, J = 12.0 Hz), 125.4, 122.0 (d, J = 10.3 Hz), 119.6, 111.4 (d, J = 25.0 Hz), 96.8 (d, J = 26.7 Hz), 31.7; ^{19}F NMR (471 MHz, $CDCl_3$, ppm) δ -115.88; HRMS calcd. for $C_9H_7FNS_5^+$ $(M+H)^+$ 307.9161, found 307.9169.

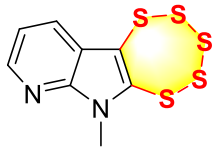


6,7-Dimethyl-6H-[1,2,3,4,5]pentathiepino[6,7-*b*]indole (3v): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3v** was prepared as yellow solid following the general procedure in 80% yield (97.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.52 (d, J = 8.0 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 4.17 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.0, 135.7, 129.8, 127.4, 122.1, 122.1, 119.4, 118.7, 34.9, 20.2; HRMS calcd. for $C_{10}H_{10}NS_5^+$ $(M+H)^+$ 303.9411, found 303.9418.

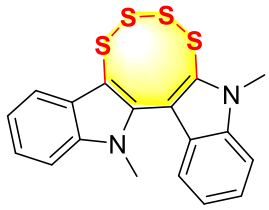


7-Methoxy-6-methyl-6*H*-[1,2,3,4,5]pentathiepino[6,7-b]indole (3w): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (30:1, v/v). The **3w** was prepared as yellow solid following the general procedure in 75% yield (95.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$,

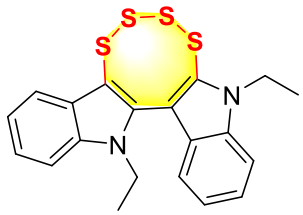
ppm) δ 7.24 (d, J = 7.8 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 4.16 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 147.5, 141.8, 131.0, 126.7, 122.4, 119.2, 112.9, 104.5, 55.6, 35.1; HRMS calcd. for $C_{10}H_{10}NOS_5^+$ $(M+H)^+$ 319.9360, found 319.9367.



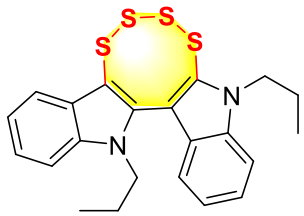
6-Methyl-6*H*-[1,2,3,4,5]pentathiepino[6',7':4,5]pyrrolo[2,3-*b*]pyridine (3y): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (150:1, v/v). The **3y** was prepared as yellow solid following the general procedure in 46% yield (53.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.44 (dd, J = 4.6, 1.5 Hz, 1H), 7.99 (dd, J = 7.9, 1.6 Hz, 1H), 7.25 – 7.17 (m, 1H), 4.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 146.5, 146.1, 142.3, 128.9, 122.0, 118.2, 117.1, 30.2; HRMS calcd. for $C_8H_7N_2S_5^+$ $(M+H)^+$ 290.9207, found 290.9203.



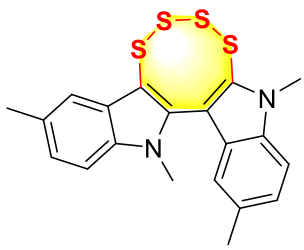
9,14-Dimethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4a): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4a** was prepared as yellow solid following the general procedure in 63% yield (49.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.92 (d, J = 7.9 Hz, 1H), 7.48 – 7.35 (m, 4H), 7.36 – 7.29 (m, 2H), 7.22 – 7.15 (m,1H), 4.02 (s, 3H), 3.65 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.7, 137.8, 137.3, 131.7, 129.3, 126.4, 124.8, 123.4, 121.5, 121.4, 120.7, 119.7, 114.9, 110.8, 109.8, 108.7, 31.9, 30.8; HRMS calcd. for $C_{18}H_{15}N_2S_4^+$ $(M+H)^+$ 387.0113, found 387.0117.



9,14-Dipropyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4c): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4c** was prepared as yellow solid following the general procedure in 74% yield (61.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.93 (d, J = 7.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.35 (m, 3H), 7.34 – 7.29 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 4.69 – 4.43 (m, 2H), 4.27 – 4.00 (m, 2H), 1.51 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.9, 136.6, 136.3, 131.5, 129.6, 126.5, 124.7, 123.3, 121.3, 121.2, 120.7, 119.8, 115.0, 110.7, 110.0, 109.5, 40.2, 39.2, 15.6, 15.6; HRMS calcd. for $C_{20}H_{18}N_2NaS_4^+$ $(M+Na)^+$ 437.0245, found 437.0248.

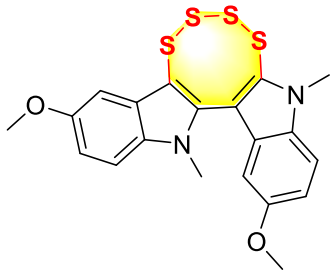


9,14-Dipropyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4d): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4d** was prepared as yellow solid following the general procedure in 63% yield (55.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.92 (d, J = 7.1 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.39 – 7.29 (m, 4H), 7.16 (t, J = 7.5 Hz, 1H), 4.55 – 4.37 (m, 2H), 4.24 – 3.87 (m, 2H), 1.95 (q, J = 7.5 Hz, 2H), 1.58 (q, J = 7.4 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H), 0.61 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.3, 136.9, 136.6, 132.0, 129.6, 126.3, 124.6, 123.2, 121.3, 121.8, 120.6, 119.8, 115.1, 111.0, 110.2, 109.4, 46.8, 45.9, 23.7, 23.0, 11.5, 11.3; HRMS calcd. for $C_{22}H_{23}N_2S_4^+$ $(M+H)^+$ 443.0739, found 443.0746.

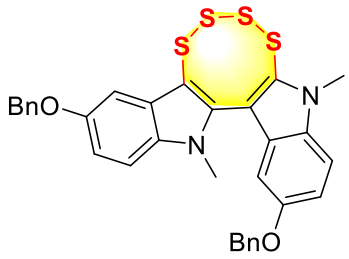


3,9,12,14-Tetramethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (4l): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4l** was prepared as yellow solid following the general procedure in 63% yield (52.3 mg); ^{1}H NMR

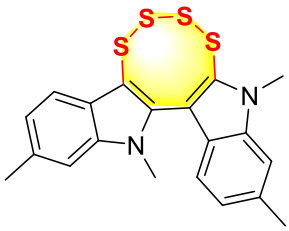
(500 MHz, $CDCl_3$, ppm) δ 7.70 (s, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.08 (s, 1H), 3.98 (s, 3H), 3.63 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.9, 136.2, 135.8, 131.5, 131.1, 130.9, 129.5, 126.7, 126.7, 124.9, 120.0, 119.4, 114.5, 110.5, 109.5, 108.1, 32.0, 30.8, 21.6, 21.5; HRMS calcd. for $C_{20}H_{18}KN_2S_4^+$ $(M+K)^+$ 452.9984, found 452.9989.



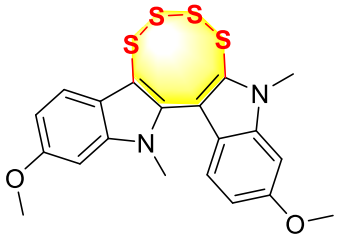
3,12-Dimethoxy-9,14-dimethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:8,7-*b*']diindole (4m): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (8:1, v/v). The **4m** was prepared as yellow solid following the general procedure in 59% yield (52.7 mg); ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.37 – 7.30 (m, 3H), 7.06 – 7.03 (m, 2H), 6.67 (s, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.75 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.7, 155.5, 143.1, 132.9, 132.6, 131.8, 130.0, 126.8, 116.1, 114.4, 113.8, 111.8, 110.7, 108.2, 101.1, 101.0, 56.0, 55.9, 31.9, 30.9; HRMS calcd. for $C_{20}H_{18}N_2NaO_2S_4^+$ $(M+Na)^+$ 469.0143, found 469.0151.



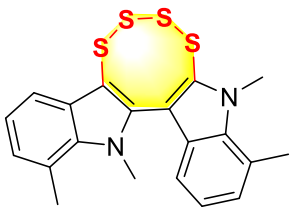
3,12-Bis(benzyloxy)-9,14-dimethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4n): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4n** was prepared as yellow solid following the general procedure in 52% yield (62.3 mg); ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.52 (d, J = 7.5 Hz, 2H), 7.47 (s, 1H), 7.44 – 7.28 (m, 10H), 7.17 – 7.07 (m, 2H), 6.72 (s, 1H), 5.21 – 5.20 (m, 2H), 5.00 (q, J = 11.8 Hz, 2H), 4.00 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.8, 154.4, 143.1, 137.5, 137.1, 133.1, 132.7, 131.8, 130.0, 128.6, 128.6, 127.9, 127.9, 127.7, 127.4, 126.7, 116.7, 114.5, 114.4, 111.8, 110.7, 108.1, 102.8, 102.7, 71.0, 70.7, 31.8, 30.9; HRMS calcd. for $C_{32}H_{27}N_2O_2S_4^+$ $(M+H)^+$ 599.0950, found 599.0948.



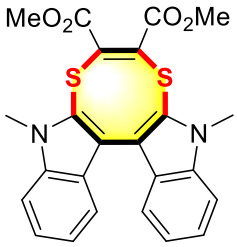
2,9,11,14-Tetramethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4r): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4r** was prepared as yellow solid following the general procedure in 71% yield (58.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 8.1 Hz, 1H), 7.22 (d, J = 7.4 Hz, 2H), 7.16 (dd, J = 17.7, 8.8 Hz, 2H), 7.02 – 7.00 (m, 1H), 3.96 (s, 3H), 3.60 (s, 3H), 2.55 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 142.3, 138.1, 137.6, 135.0, 133.3, 130.8, 127.1, 124.4, 123.4, 123.0, 120.3, 119.3, 115.0, 110.5, 109.7, 108.3, 31.8, 30.6, 26.9, 22.0; HRMS calcd. for $C_{20}H_{18}KN_2S_4^+$ $(M+K)^+$ 452.9984, found 452.9989.



2,11-Dimethoxy-9,14-dimethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4s): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (6:1, v/v). The **4s** was prepared as yellow solid following the general procedure in 58% yield (51.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.78 (d, J = 8.6 Hz, 1H), 7.20 (d, J = 8.6 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.88 – 6.85 (m, 3H), 3.97 (s, 3H), 3.92 (s, 3H), 3.92 (s, 3H), 3.61 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 158.6, 157.6, 141.8, 138.5, 138.3, 130.0, 123.5, 121.6, 120.9, 120.4, 115.6, 112.3, 111.0, 108.4, 93.5, 93.2, 55.9, 55.7, 31.9, 30.7; HRMS calcd. for $C_{20}H_{18}N_2NaO_2S_4^+$ $(M+Na)^+$ 469.0143, found 469.0151.

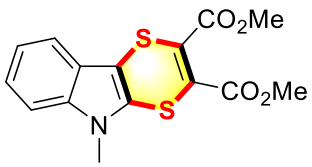


1,9,10,14-Tetramethyl-9,14-dihydro-[1,2,3,4]tetrathiocino[5,6-*b*:7,8-*b*']diindole (4v): Purified by silica gel flash chromatography with petroleum ether and dichloromethane (15:1, v/v). The **4v** was prepared as yellow solid following the general procedure in 60% yield (49.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.76 (d, J = 7.9 Hz, 1H), 7.19 – 7.12 (m, 2H), 7.09 – 7.05 (m, 3H), 4.32 (s, 3H), 3.88 (s, 3H), 2.86 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 143.7, 136.7, 136.5, 132.4, 130.2, 127.6, 127.4, 126.4, 122.3, 121.7, 121.6, 121.4, 118.9, 117.9, 115.7, 109.0, 35.3, 33.9, 20.5, 20.1; HRMS calcd. for $C_{20}H_{18}KN_2S_4^+$ $(M+K)^+$ 452.9984, found 452.9989.



Dimethyl-(*Z*)-5,10-dimethyl-5,10-dihydro-[1,4]dithiocino[5,6-*b*:8,7-*b*']diindole-7,8-dicarboxylate (5): A solution of triphenylphosphine (4 mmol) in dichloromethane (3 mL) was added dropwise to a stirred solution of **2a** (1 mmol) and dimethyl but-2-ynedioate (3 mmol) in dichloromethane (10 mL). The reaction vessel was stirred at 50 °C for 4 h under an air atmosphere, solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to yield the desired product **5** as a yellowish solid (63% yield).

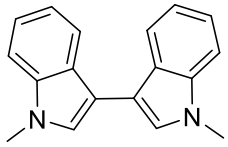
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.72 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.22 – 7.17 (m, 2H), 3.99 (s, 6H), 3.86 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 166.0, 138.9, 132.6, 125.3, 124.2, 121.8, 120.8, 120.6, 120.5, 110.5, 53.4, 31.0.



Dimethyl 5-methyl-5*H*-[1,4]dithiino[2,3-*b*]indole-2,3-dicarboxylate (6, CAS: 913618-45-8) [5]: A solution of triphenylphosphine (4 mmol) in dichloromethane (3 mL) was added dropwise to a stirred solution of **3a** (1 mmol) and dimethyl but-2-ynedioate (3 mmol) in dichloromethane (10

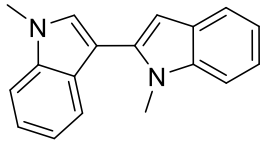
mL) at room temperature. The reaction mixture was stirred for 1 h, solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 8:1) to yield the desired product **6** as a red solid (85% yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.45 (d, J = 7.9 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.17 – 7.11 (m, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 163.9, 162.4, 140.6, 140.5, 130.1, 128.0, 124.9, 122.7, 120.7, 117.7, 109.8, 102.5, 53.3, 30.8.



1,1'-Dimethyl-1*H*,1'*H*-3,3'-biindole (7, CAS: 13637-39-3) [6]: The reaction was conducted with 1-methylindole **1a** (0.4 mmol), S_8 (51.2 mg, 0.2 mmol), HI (12 μL, 0.04 mmol, 20 mol %), DMSO (60.0 μL, 0.8 mmol), 2-picoline (60.0 μL, 0.6 mmol), and 1,4-dioxane (1 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 150 ^{o}C for 1 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with dichloromethane 8 mL and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 15:1) to yield the desired product **7** as white solid (13% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.92 – 7.75 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.23 (m, 4H), 7.19 – 7.12 (m, 2H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.1, 127.1, 126.0, 121.8, 120.2, 119.2, 109.5, 109.3, 32.8.



1,1'-Dimethyl-1*H*,1'*H*-2,3'-biindole (8, CAS: 63955-66-8) [1b]: The reaction was conducted with 1-methylindole **1a** (0.4 mmol), S_8 (51.2 mg, 0.2 mmol), HI (12 μL, 0.04 mmol, 20 mol %), 2-picoline (60.0 μL, 0.6 mmol), and 1,2-dichlorobenzene (1 mL) were added successfully to a 10 mL oven-dried reaction vessel. The reaction vessel was stirred at 150 ^{o}C for 1 h under an air atmosphere. After cooling to room temperature, the reaction was diluted with dichloromethane 8

mL and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 10:1) to yield the desired product **8** as white solid (8% yield).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.66 (dd, J = 30.5, 7.9 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.10 (m, 4H), 6.61 (s, 1H), 3.80 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 138.0, 136.9, 135.2, 128.4, 128.4, 127.6, 122.3, 121.0, 120.3, 120.2, 120.0, 119.5, 109.5, 109.3, 107.3, 101.2, 32.9, 30.9.

7. References

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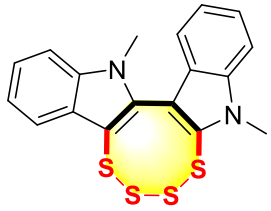
8. Crystal data and structure refinement for 4a



4a

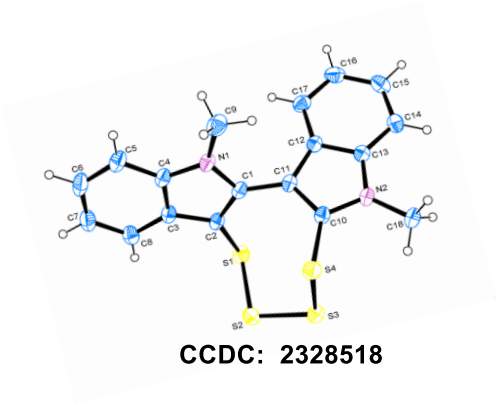


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Table 1. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	C18 H14 N2 S4	
Formula weight	386.55	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.1086(5) Å	α= 90 °.
	b = 15.8046(8) Å	β= 90 °.
	c = 22.2013(10) Å	γ = 90 °.
Volume	3546.9(3) $Å^3$	
Z	8	
Density (calculated)	1.448 Mg/m^3	
Absorption coefficient	0.537 mm^{-1}	
F(000)	1600	
Crystal size	0.220 x 0.180 x 0.180 mm^3	
Theta range for data collection	1.835 to 28.864 °.	
Index ranges	-13<=h<=13, -20<=k<=21, -30<=l<=18	
Reflections collected	22226	
Independent reflections	4594 [R(int) = 0.0340]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4594 / 0 / 219	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0883	
R indices (all data)	R1 = 0.0616, wR2 = 0.1003	

Extinction coefficient	n/a
Largest diff. peak and hole	0.244 and -0.217 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(4)	3199(1)	2018(1)	5178(1)	49(1)
S(3)	1940(1)	985(1)	5177(1)	57(1)
S(2)	356(1)	1334(1)	4660(1)	55(1)
S(1)	1048(1)	1372(1)	3783(1)	47(1)
N(1)	3057(2)	3469(1)	3561(1)	41(1)
N(2)	5364(2)	1378(1)	4588(1)	38(1)
C(6)	148(3)	4675(2)	3033(1)	60(1)
C(5)	1462(2)	4557(1)	3168(1)	52(1)
C(4)	1828(2)	3756(1)	3375(1)	40(1)
C(1)	2934(2)	2647(1)	3756(1)	37(1)
C(11)	4061(2)	2167(1)	3981(1)	38(1)
C(12)	5207(2)	1912(1)	3648(1)	38(1)
C(13)	5986(2)	1421(1)	4040(1)	37(1)
C(14)	7171(2)	1051(1)	3855(1)	46(1)
C(15)	7562(2)	1192(1)	3271(1)	53(1)
C(3)	914(2)	3101(1)	3446(1)	38(1)
C(2)	1635(2)	2393(1)	3687(1)	38(1)
C(10)	4197(2)	1834(1)	4553(1)	38(1)
C(18)	5927(2)	997(1)	5127(1)	46(1)
C(16)	6810(2)	1685(2)	2876(1)	54(1)
C(17)	5635(2)	2045(1)	3056(1)	47(1)
C(9)	4228(2)	3993(1)	3612(1)	58(1)
C(8)	-415(2)	3240(1)	3302(1)	46(1)
C(7)	-775(2)	4030(2)	3098(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for **4a**.

S(4)-C(10)	1.7409(19)
S(4)-S(3)	2.0690(9)

S(3)-S(2)	2.0467(8)
S(2)-S(1)	2.0686(8)
S(1)-C(2)	1.7332(19)
N(1)-C(1)	1.375(2)
N(1)-C(4)	1.386(2)
N(1)-C(9)	1.449(3)
N(2)-C(13)	1.371(2)
N(2)-C(10)	1.385(2)
N(2)-C(18)	1.455(2)
C(6)-C(5)	1.374(3)
C(6)-C(7)	1.390(3)
C(6)-H(6)	0.9300
C(5)-C(4)	1.397(3)
C(5)-H(5)	0.9300
C(4)-C(3)	1.396(3)
C(1)-C(2)	1.382(3)
C(1)-C(11)	1.457(2)
C(11)-C(10)	1.381(3)
C(11)-C(12)	1.433(3)
C(12)-C(17)	1.399(3)
C(12)-C(13)	1.409(2)
C(13)-C(14)	1.394(3)
C(14)-C(15)	1.374(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.398(3)
C(15)-H(15)	0.9300
C(3)-C(8)	1.398(3)
C(3)-C(2)	1.439(2)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(16)-C(17)	1.376(3)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(8)-C(7)	1.378(3)

C(8)-H(8)	0.9300
C(7)-H(7)	0.9300
C(10)-S(4)-S(3)	102.94(7)
S(2)-S(3)-S(4)	105.63(3)
S(3)-S(2)-S(1)	105.71(3)
C(2)-S(1)-S(2)	104.99(7)
C(1)-N(1)-C(4)	108.75(16)
C(1)-N(1)-C(9)	126.12(16)
C(4)-N(1)-C(9)	124.70(16)
C(13)-N(2)-C(10)	108.34(15)
C(13)-N(2)-C(18)	124.81(16)
C(10)-N(2)-C(18)	126.49(16)
C(5)-C(6)-C(7)	121.8(2)
C(5)-C(6)-H(6)	119.1
C(7)-C(6)-H(6)	119.1
C(6)-C(5)-C(4)	116.8(2)
C(6)-C(5)-H(5)	121.6
C(4)-C(5)-H(5)	121.6
N(1)-C(4)-C(3)	108.50(16)
N(1)-C(4)-C(5)	129.18(19)
C(3)-C(4)-C(5)	122.28(19)
N(1)-C(1)-C(2)	109.03(16)
N(1)-C(1)-C(11)	121.94(17)
C(2)-C(1)-C(11)	129.03(17)
C(10)-C(11)-C(12)	106.71(16)
C(10)-C(11)-C(1)	126.28(17)
C(12)-C(11)-C(1)	126.94(17)
C(17)-C(12)-C(13)	119.41(18)
C(17)-C(12)-C(11)	133.91(18)
C(13)-C(12)-C(11)	106.67(16)
N(2)-C(13)-C(14)	129.41(17)
N(2)-C(13)-C(12)	108.69(16)
C(14)-C(13)-C(12)	121.89(18)
C(15)-C(14)-C(13)	117.26(19)
C(15)-C(14)-H(14)	121.4
C(13)-C(14)-H(14)	121.4
C(14)-C(15)-C(16)	121.7(2)
C(14)-C(15)-H(15)	119.2

C(16)-C(15)-H(15)	119.2
C(4)-C(3)-C(8)	119.64(17)
C(4)-C(3)-C(2)	106.48(16)
C(8)-C(3)-C(2)	133.85(19)
C(1)-C(2)-C(3)	107.24(16)
C(1)-C(2)-S(1)	125.60(14)
C(3)-C(2)-S(1)	126.68(15)
C(11)-C(10)-N(2)	109.58(16)
C(11)-C(10)-S(4)	127.74(15)
N(2)-C(10)-S(4)	122.38(14)
N(2)-C(18)-H(18A)	109.5
N(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(16)-C(15)	121.2(2)
C(17)-C(16)-H(16)	119.4
C(15)-C(16)-H(16)	119.4
C(16)-C(17)-C(12)	118.53(19)
C(16)-C(17)-H(17)	120.7
C(12)-C(17)-H(17)	120.7
N(1)-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(8)-C(3)	118.1(2)
C(7)-C(8)-H(8)	121.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

S(4)	58(1)	51(1)	38(1)	-2(1)	2(1)	11(1)
S(3)	57(1)	55(1)	60(1)	20(1)	11(1)	11(1)
S(2)	48(1)	54(1)	65(1)	10(1)	10(1)	6(1)
S(1)	52(1)	33(1)	56(1)	-2(1)	-1(1)	-1(1)
N(1)	47(1)	33(1)	43(1)	6(1)	-6(1)	0(1)
N(2)	43(1)	37(1)	36(1)	2(1)	-7(1)	4(1)
C(6)	75(2)	47(1)	59(1)	6(1)	-8(1)	24(1)
C(5)	69(1)	36(1)	51(1)	5(1)	-5(1)	7(1)
C(4)	52(1)	35(1)	34(1)	1(1)	-5(1)	6(1)
C(1)	47(1)	32(1)	32(1)	1(1)	-3(1)	3(1)
C(11)	42(1)	34(1)	38(1)	2(1)	-5(1)	2(1)
C(12)	40(1)	36(1)	38(1)	2(1)	-5(1)	-3(1)
C(13)	38(1)	35(1)	37(1)	-2(1)	-4(1)	-3(1)
C(14)	39(1)	49(1)	50(1)	-2(1)	-7(1)	1(1)
C(15)	37(1)	66(1)	57(1)	-9(1)	2(1)	-4(1)
C(3)	48(1)	35(1)	32(1)	-4(1)	-4(1)	8(1)
C(2)	47(1)	31(1)	35(1)	0(1)	-4(1)	4(1)
C(10)	43(1)	34(1)	37(1)	0(1)	-3(1)	4(1)
C(18)	52(1)	46(1)	40(1)	6(1)	-11(1)	5(1)
C(16)	50(1)	69(1)	43(1)	1(1)	6(1)	-12(1)
C(17)	50(1)	51(1)	40(1)	6(1)	-4(1)	-7(1)
C(9)	62(1)	44(1)	68(2)	10(1)	-13(1)	-11(1)
C(8)	47(1)	49(1)	43(1)	-8(1)	-5(1)	9(1)
C(7)	53(1)	60(1)	55(1)	0(1)	-9(1)	19(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4a**.

	x	y	z	U(eq)
H(6)	-131	5202	2896	72
H(5)	2079	4989	3123	62
H(14)	7675	724	4116	55
H(15)	8347	952	3135	64
H(18A)	6182	425	5042	70
H(18B)	5280	1002	5444	70
H(18C)	6690	1315	5251	70

H(16)	7109	1771	2485	65
H(17)	5137	2369	2790	56
H(9A)	4956	3655	3751	87
H(9B)	4066	4442	3894	87
H(9C)	4439	4229	3226	87
H(8)	-1038	2811	3344	55
H(7)	-1655	4134	3001	67

Table 6. Torsion angles [°] for **4a**.

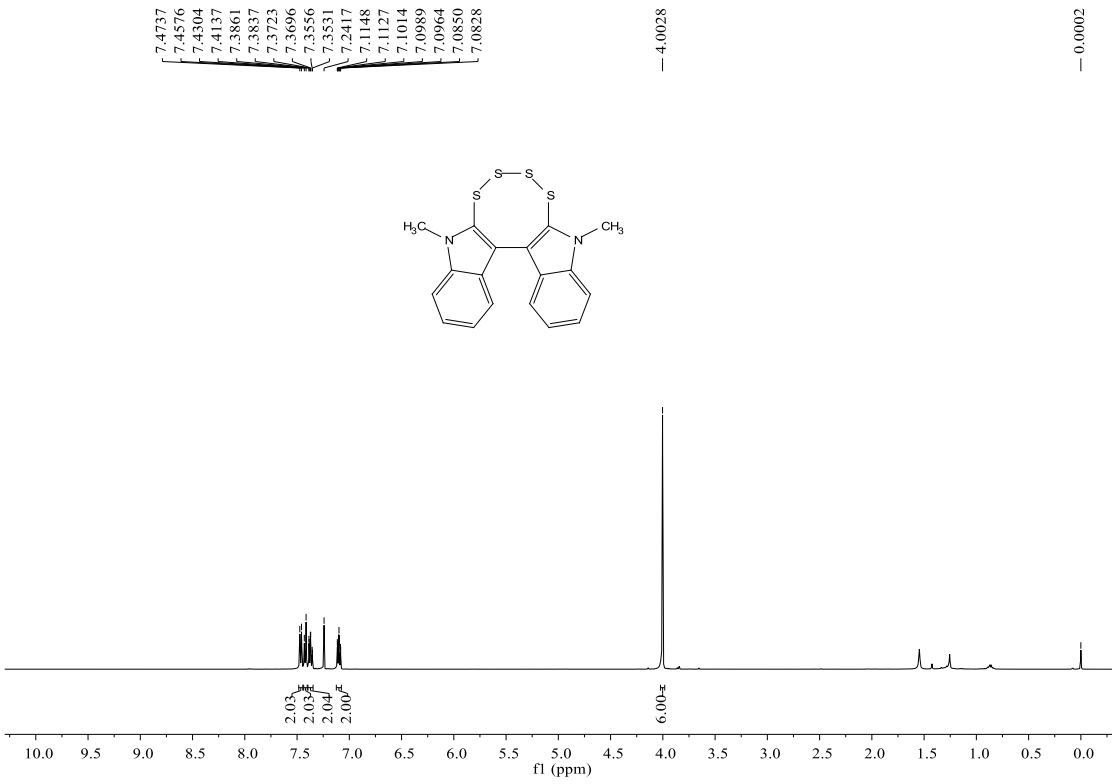
C(7)-C(6)-C(5)-C(4)	-0.2(3)
C(1)-N(1)-C(4)-C(3)	-0.7(2)
C(9)-N(1)-C(4)-C(3)	-173.46(19)
C(1)-N(1)-C(4)-C(5)	177.0(2)
C(9)-N(1)-C(4)-C(5)	4.2(3)
C(6)-C(5)-C(4)-N(1)	-177.5(2)
C(6)-C(5)-C(4)-C(3)	-0.1(3)
C(4)-N(1)-C(1)-C(2)	1.0(2)
C(9)-N(1)-C(1)-C(2)	173.63(19)
C(4)-N(1)-C(1)-C(11)	179.97(17)
C(9)-N(1)-C(1)-C(11)	-7.4(3)
N(1)-C(1)-C(11)-C(10)	118.5(2)
C(2)-C(1)-C(11)-C(10)	-62.8(3)
N(1)-C(1)-C(11)-C(12)	-64.8(3)
C(2)-C(1)-C(11)-C(12)	113.9(2)
C(10)-C(11)-C(12)-C(17)	179.7(2)
C(1)-C(11)-C(12)-C(17)	2.5(3)
C(10)-C(11)-C(12)-C(13)	0.7(2)
C(1)-C(11)-C(12)-C(13)	-176.47(17)
C(10)-N(2)-C(13)-C(14)	-178.81(19)
C(18)-N(2)-C(13)-C(14)	7.7(3)
C(10)-N(2)-C(13)-C(12)	0.0(2)
C(18)-N(2)-C(13)-C(12)	-173.48(17)
C(17)-C(12)-C(13)-N(2)	-179.63(17)
C(11)-C(12)-C(13)-N(2)	-0.5(2)
C(17)-C(12)-C(13)-C(14)	-0.7(3)
C(11)-C(12)-C(13)-C(14)	178.48(17)

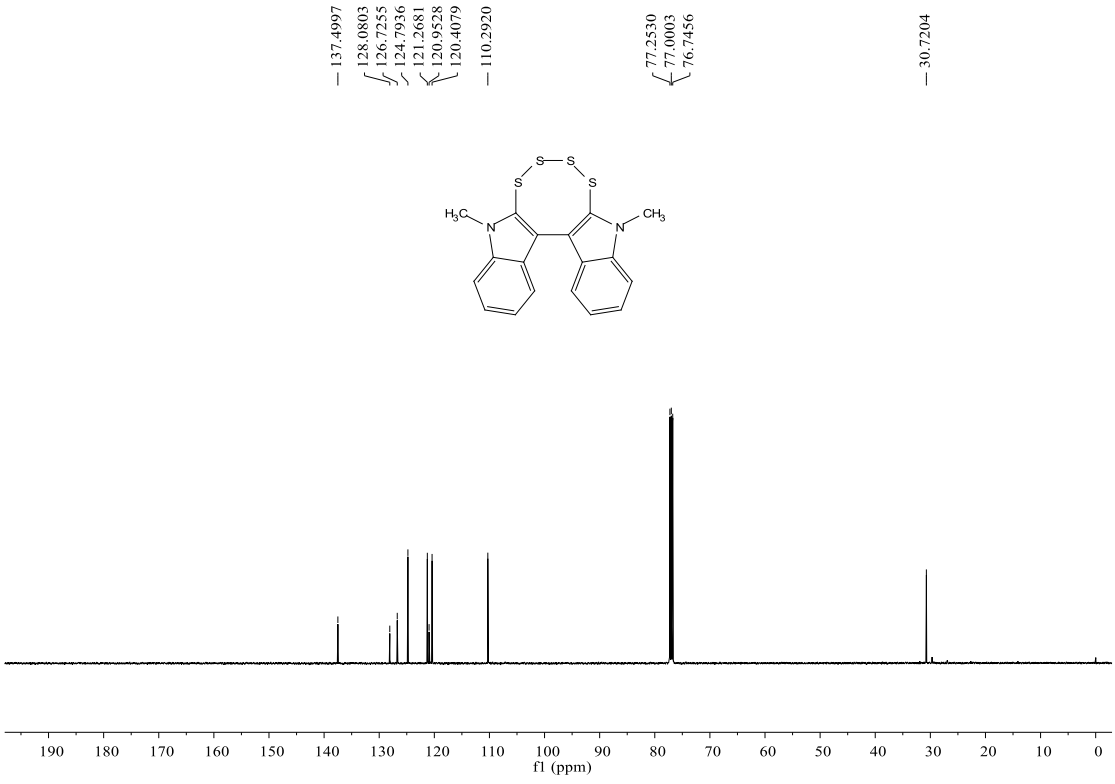
N(2)-C(13)-C(14)-C(15)	179.24(18)
C(12)-C(13)-C(14)-C(15)	0.5(3)
C(13)-C(14)-C(15)-C(16)	0.1(3)
N(1)-C(4)-C(3)-C(8)	178.33(17)
C(5)-C(4)-C(3)-C(8)	0.5(3)
N(1)-C(4)-C(3)-C(2)	0.1(2)
C(5)-C(4)-C(3)-C(2)	-177.73(18)
N(1)-C(1)-C(2)-C(3)	-0.9(2)
C(11)-C(1)-C(2)-C(3)	-179.77(18)
N(1)-C(1)-C(2)-S(1)	171.57(14)
C(11)-C(1)-C(2)-S(1)	-7.3(3)
C(4)-C(3)-C(2)-C(1)	0.5(2)
C(8)-C(3)-C(2)-C(1)	-177.4(2)
C(4)-C(3)-C(2)-S(1)	-171.90(14)
C(8)-C(3)-C(2)-S(1)	10.3(3)
S(2)-S(1)-C(2)-C(1)	95.50(17)
S(2)-S(1)-C(2)-C(3)	-93.49(17)
C(12)-C(11)-C(10)-N(2)	-0.7(2)
C(1)-C(11)-C(10)-N(2)	176.50(17)
C(12)-C(11)-C(10)-S(4)	173.03(14)
C(1)-C(11)-C(10)-S(4)	-9.8(3)
C(13)-N(2)-C(10)-C(11)	0.4(2)
C(18)-N(2)-C(10)-C(11)	173.81(17)
C(13)-N(2)-C(10)-S(4)	-173.70(13)
C(18)-N(2)-C(10)-S(4)	-0.3(3)
S(3)-S(4)-C(10)-C(11)	97.50(18)
S(3)-S(4)-C(10)-N(2)	-89.49(15)
C(14)-C(15)-C(16)-C(17)	-0.6(3)
C(15)-C(16)-C(17)-C(12)	0.5(3)
C(13)-C(12)-C(17)-C(16)	0.2(3)
C(11)-C(12)-C(17)-C(16)	-178.7(2)
C(4)-C(3)-C(8)-C(7)	-0.4(3)
C(2)-C(3)-C(8)-C(7)	177.2(2)
C(3)-C(8)-C(7)-C(6)	0.1(3)
C(5)-C(6)-C(7)-C(8)	0.3(4)

Symmetry transformations used to generate equivalent atoms:

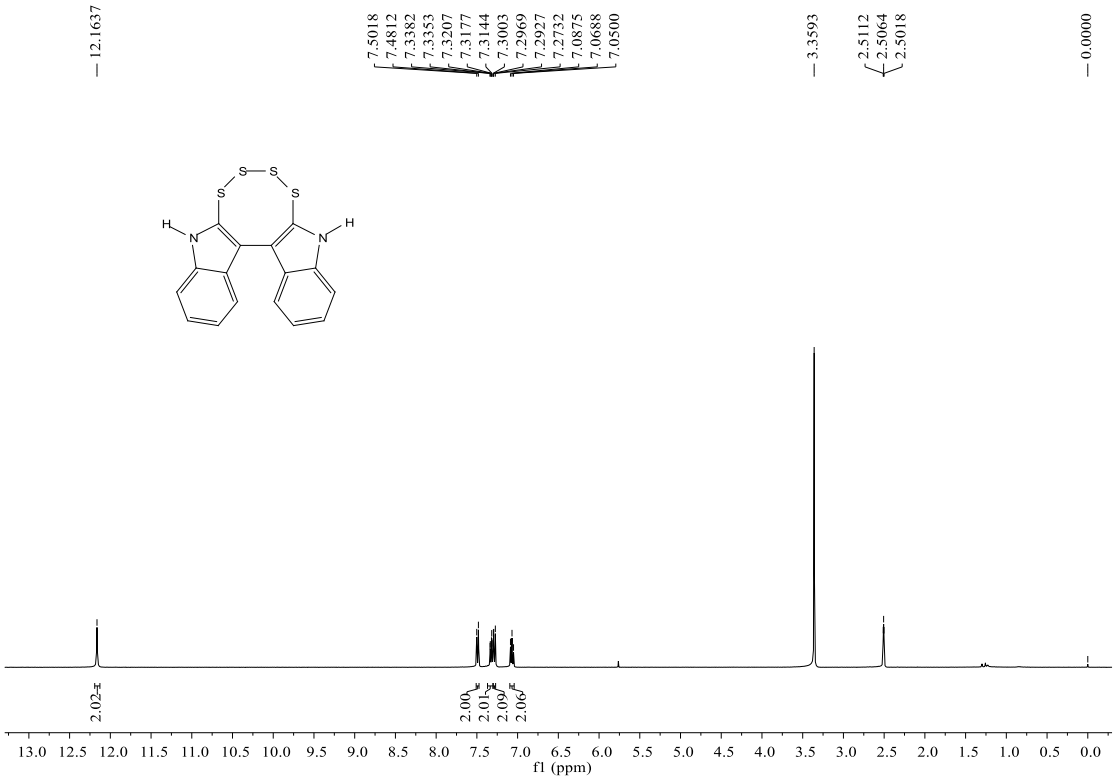
9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of all products

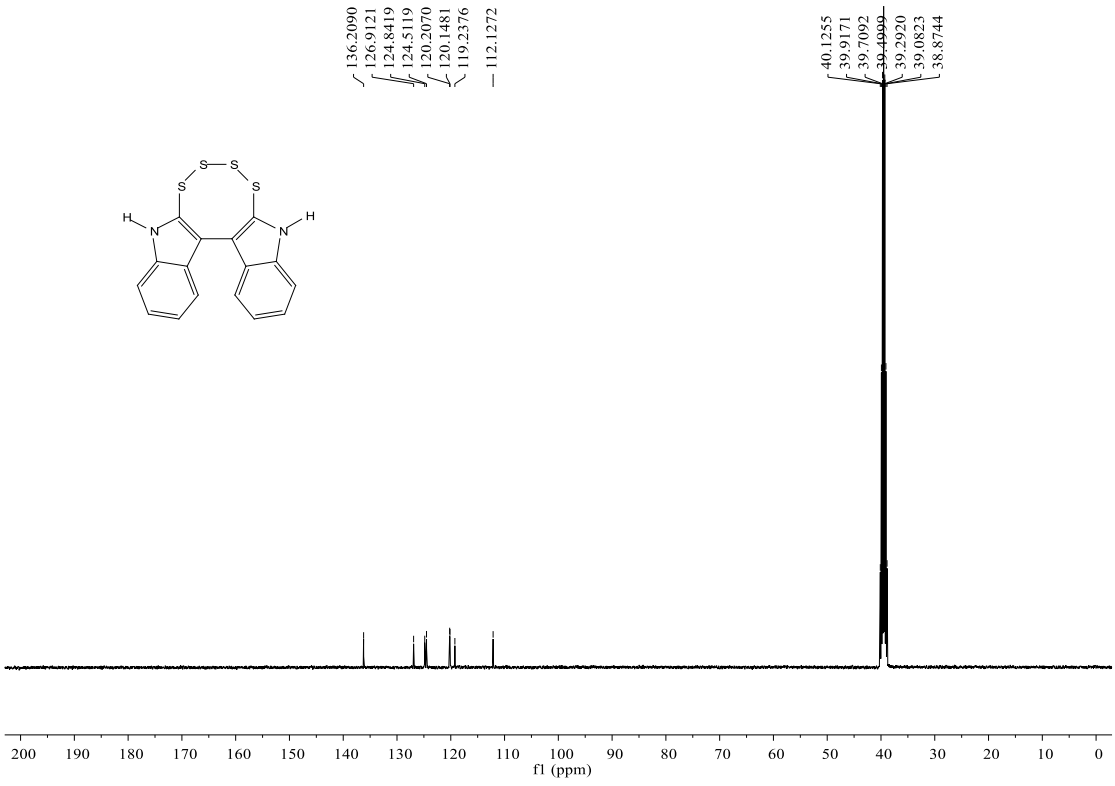
^{1}H and ^{13}C NMR spectra of **2a**



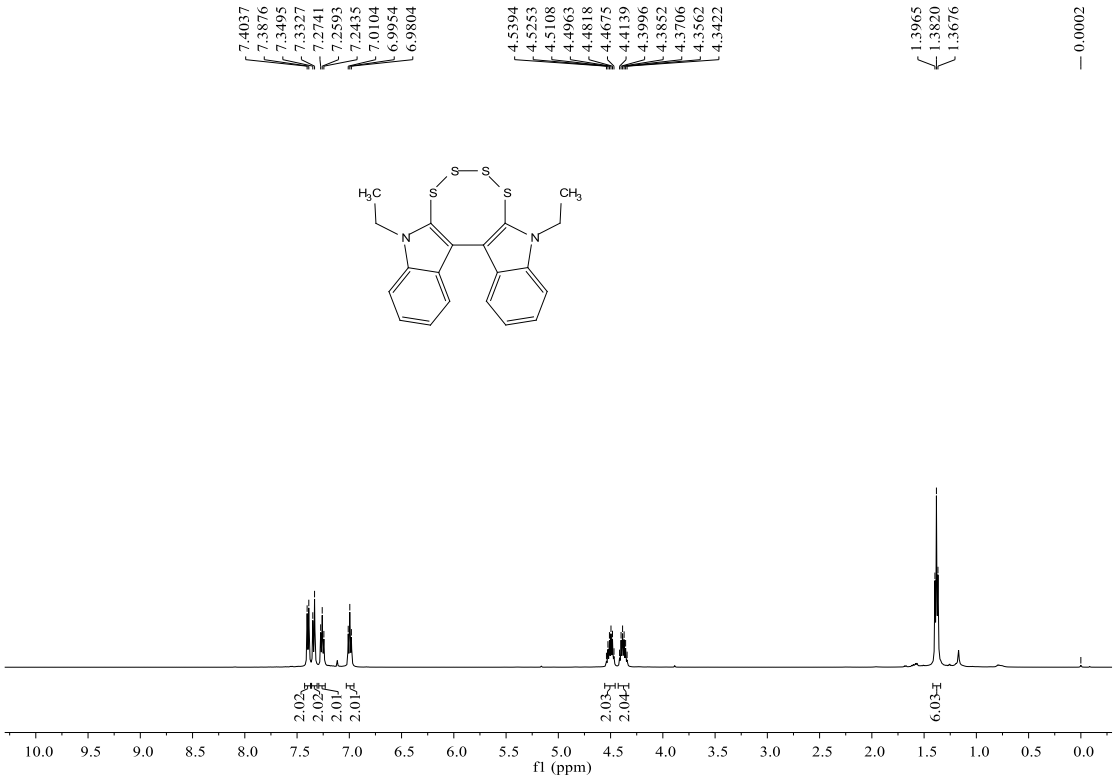


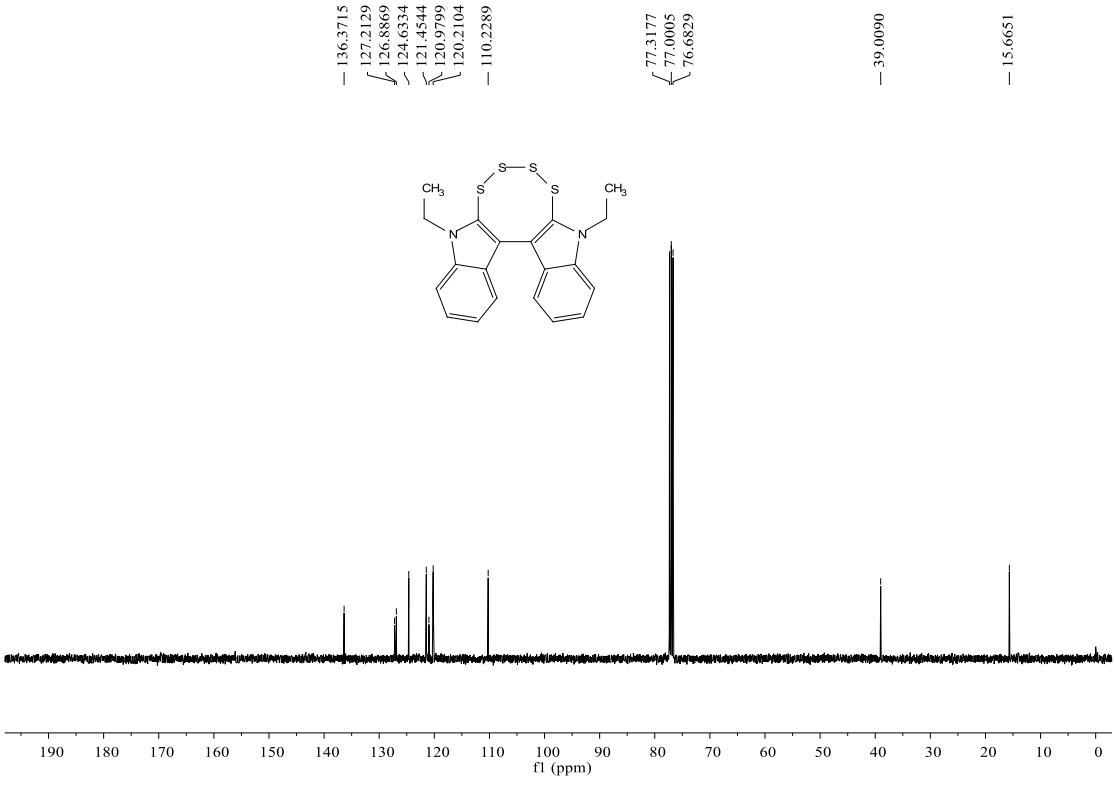
^{1}H and ^{13}C NMR spectra of **2b**



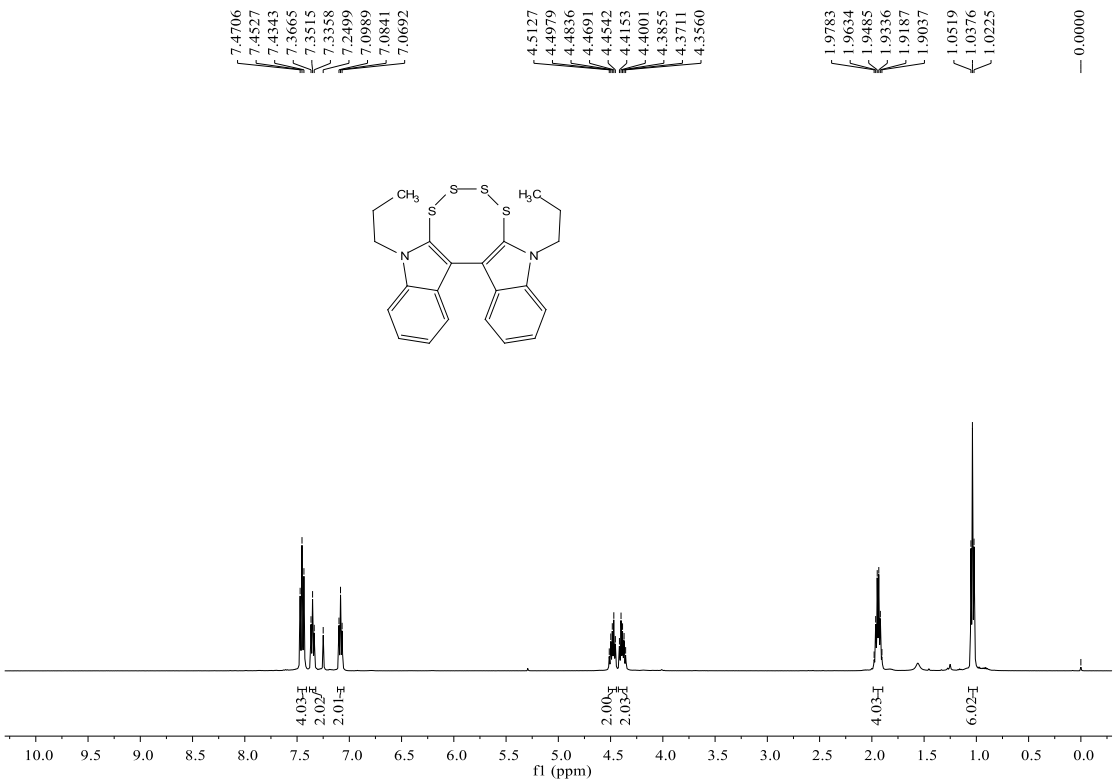


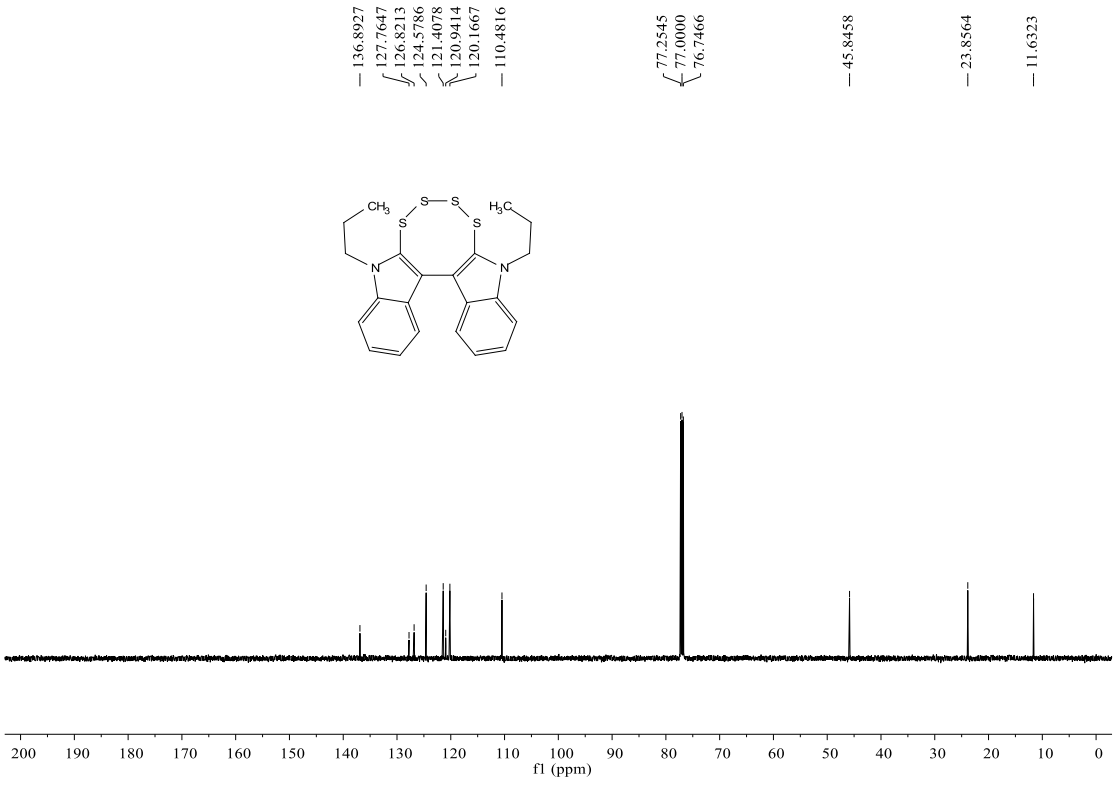
^{1}H and ^{13}C NMR spectra of **2c**



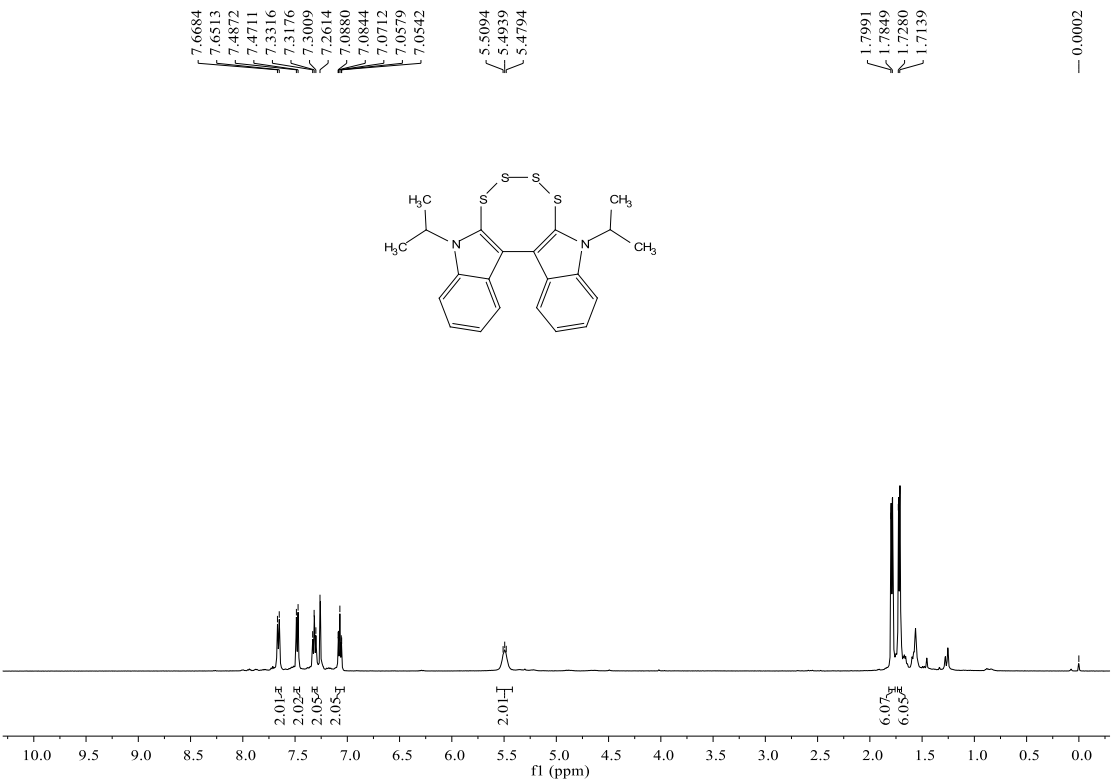


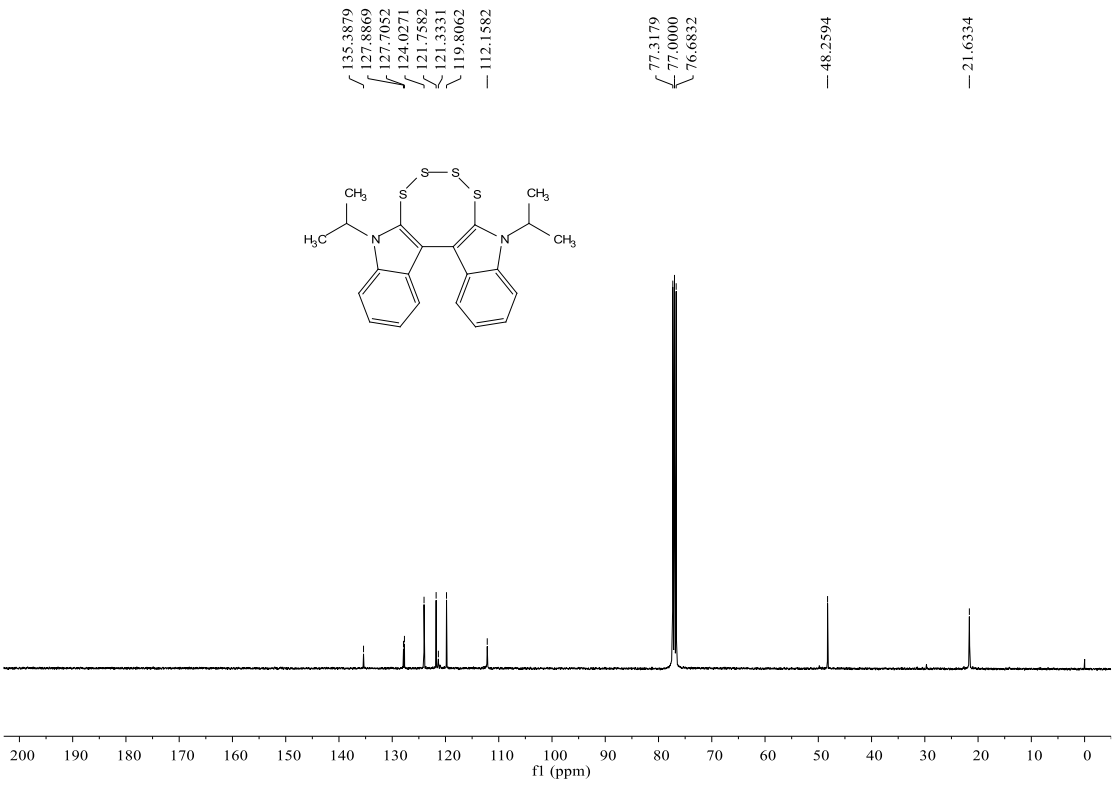
^{1}H and ^{13}C NMR spectra of **2d**



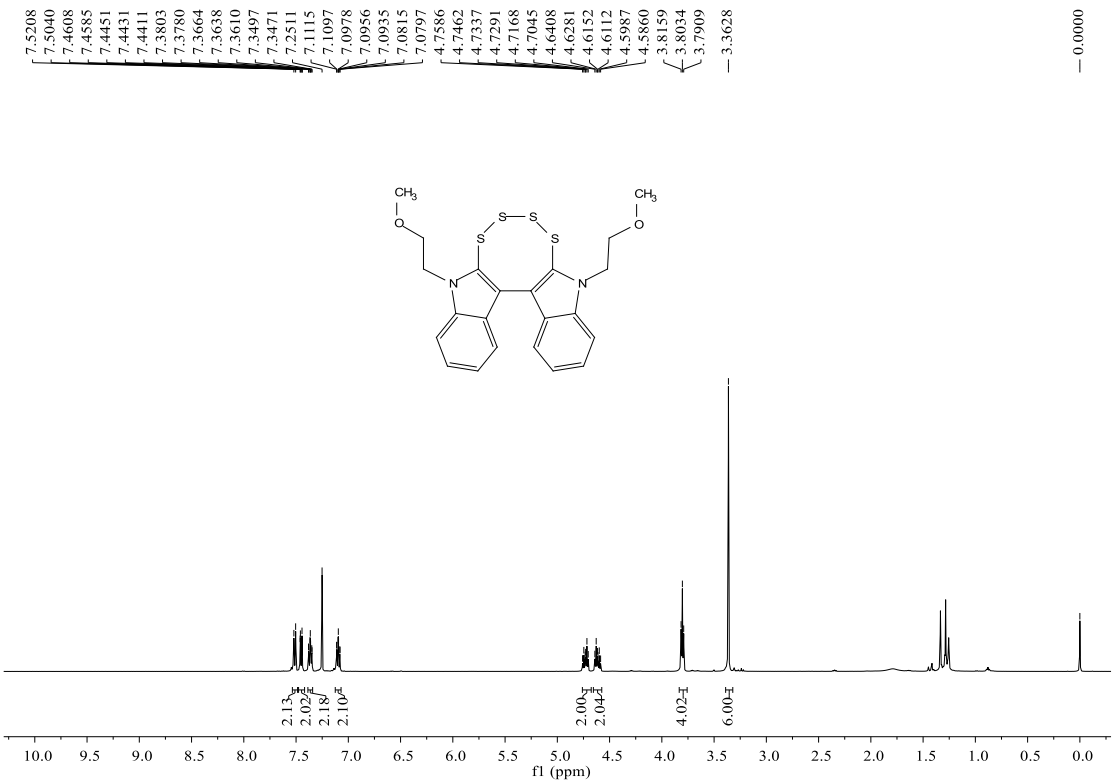


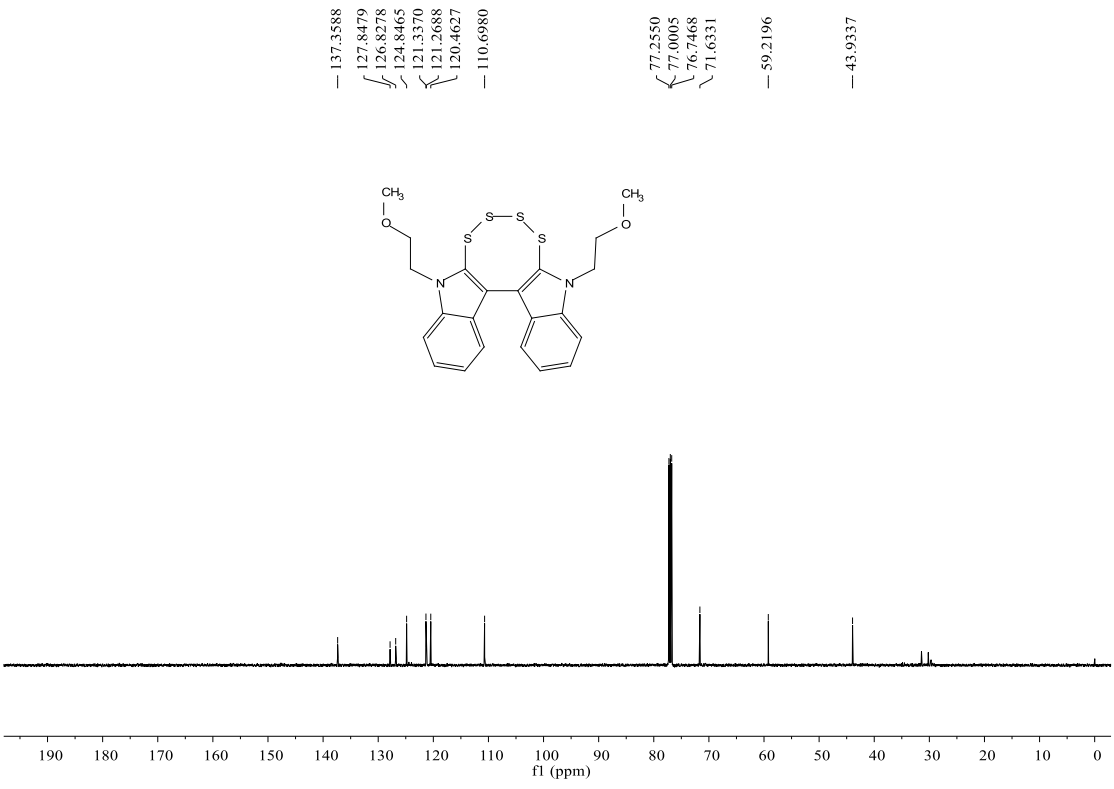
^{1}H and ^{13}C NMR spectra of **2e**



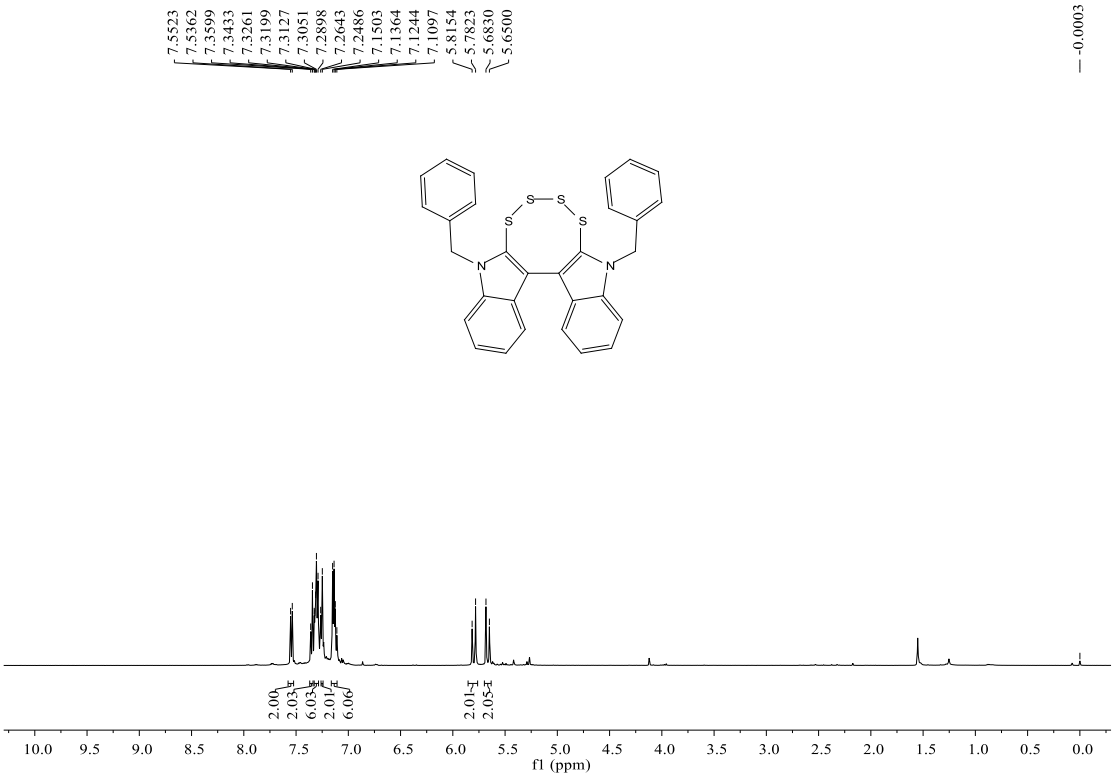


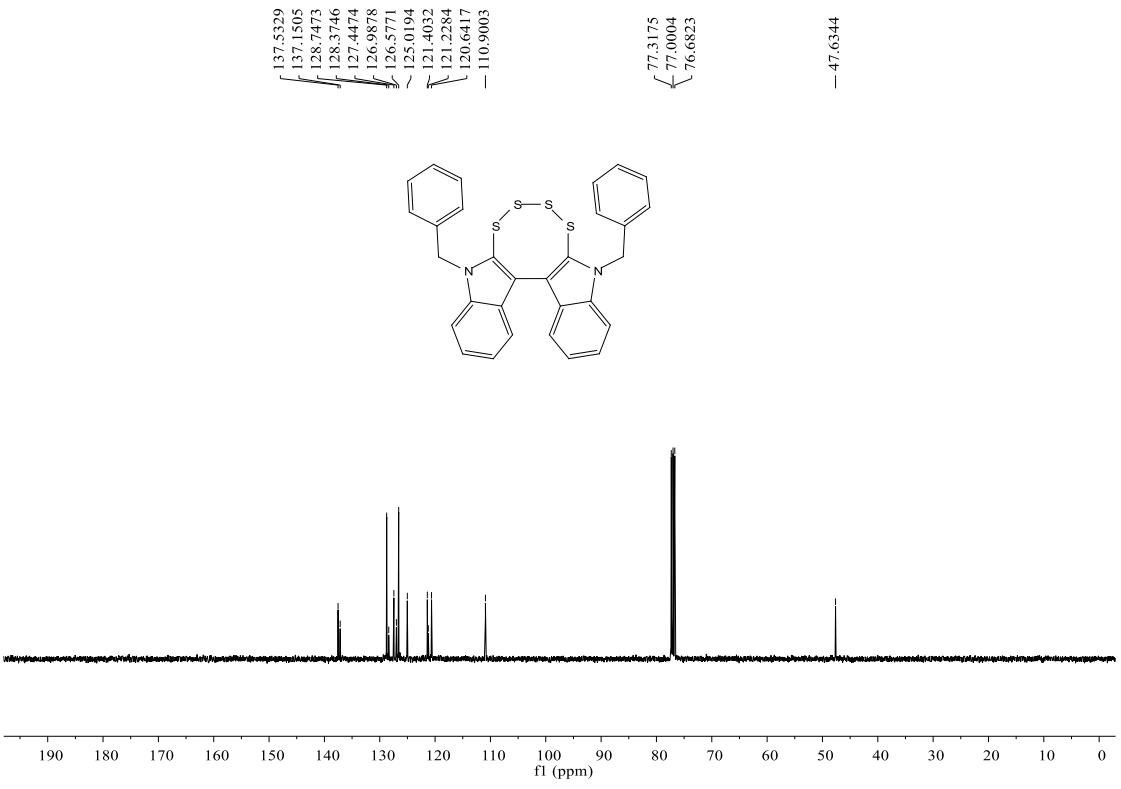
^{1}H and ^{13}C NMR spectra of **2f**



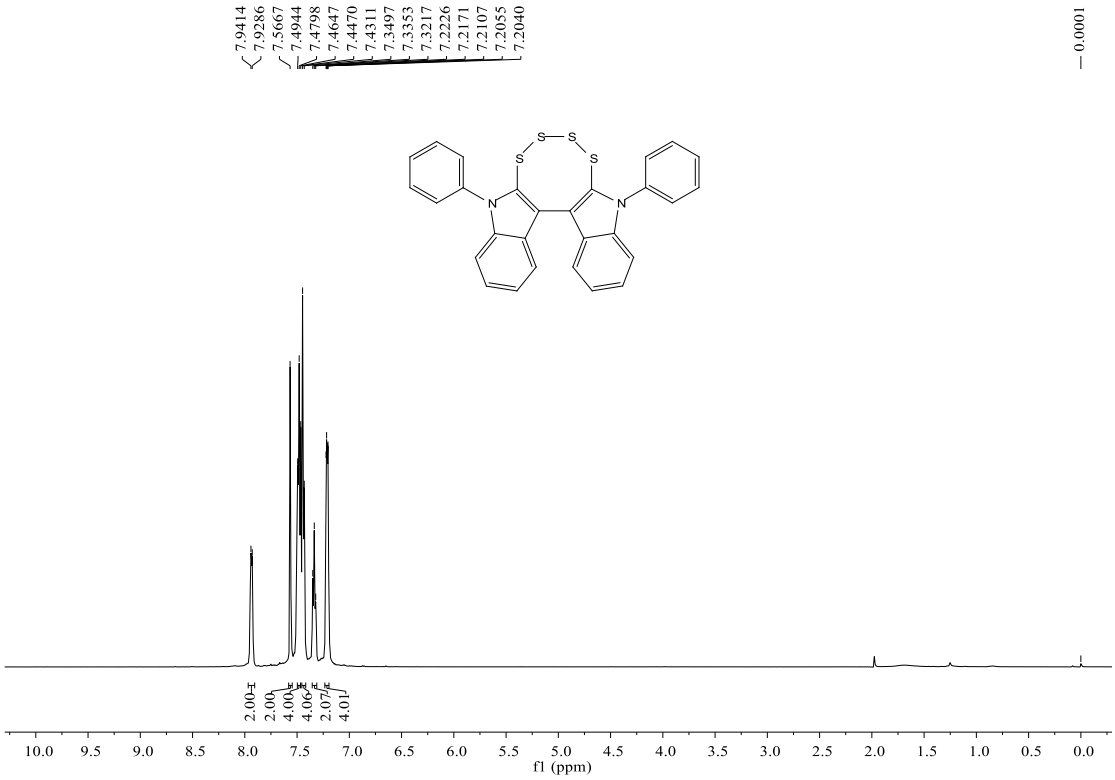


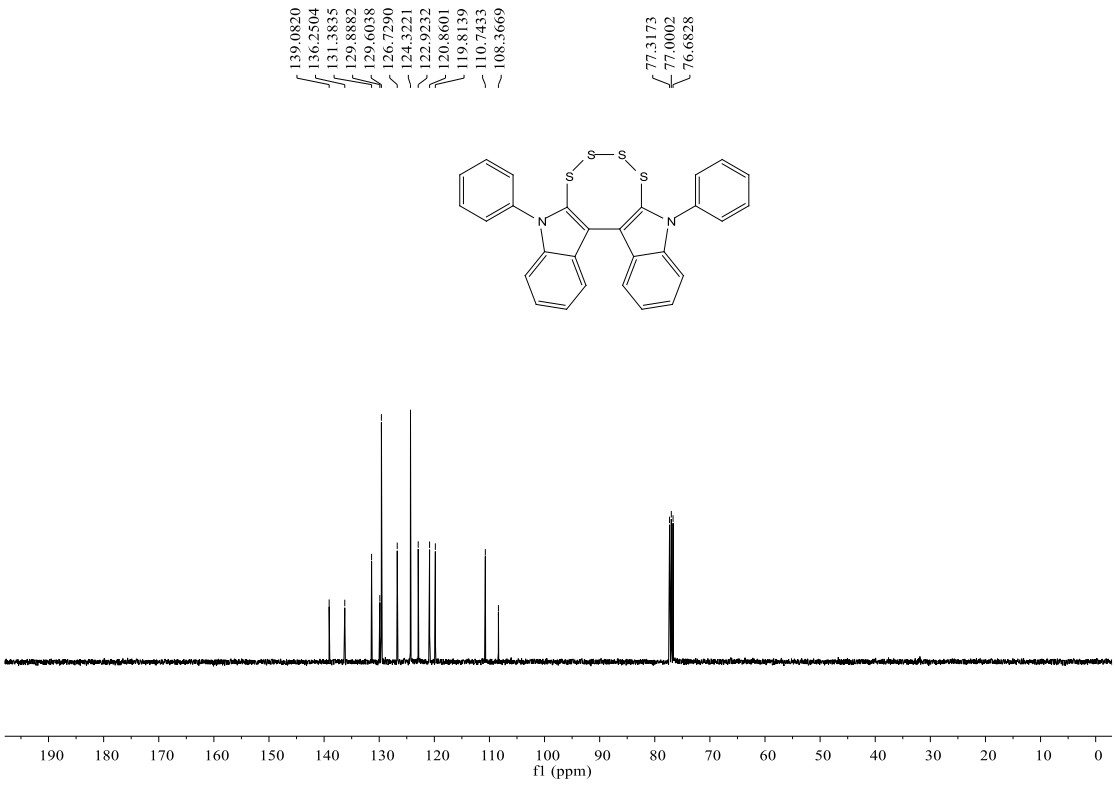
^{1}H and ^{13}C NMR spectra of **2g**



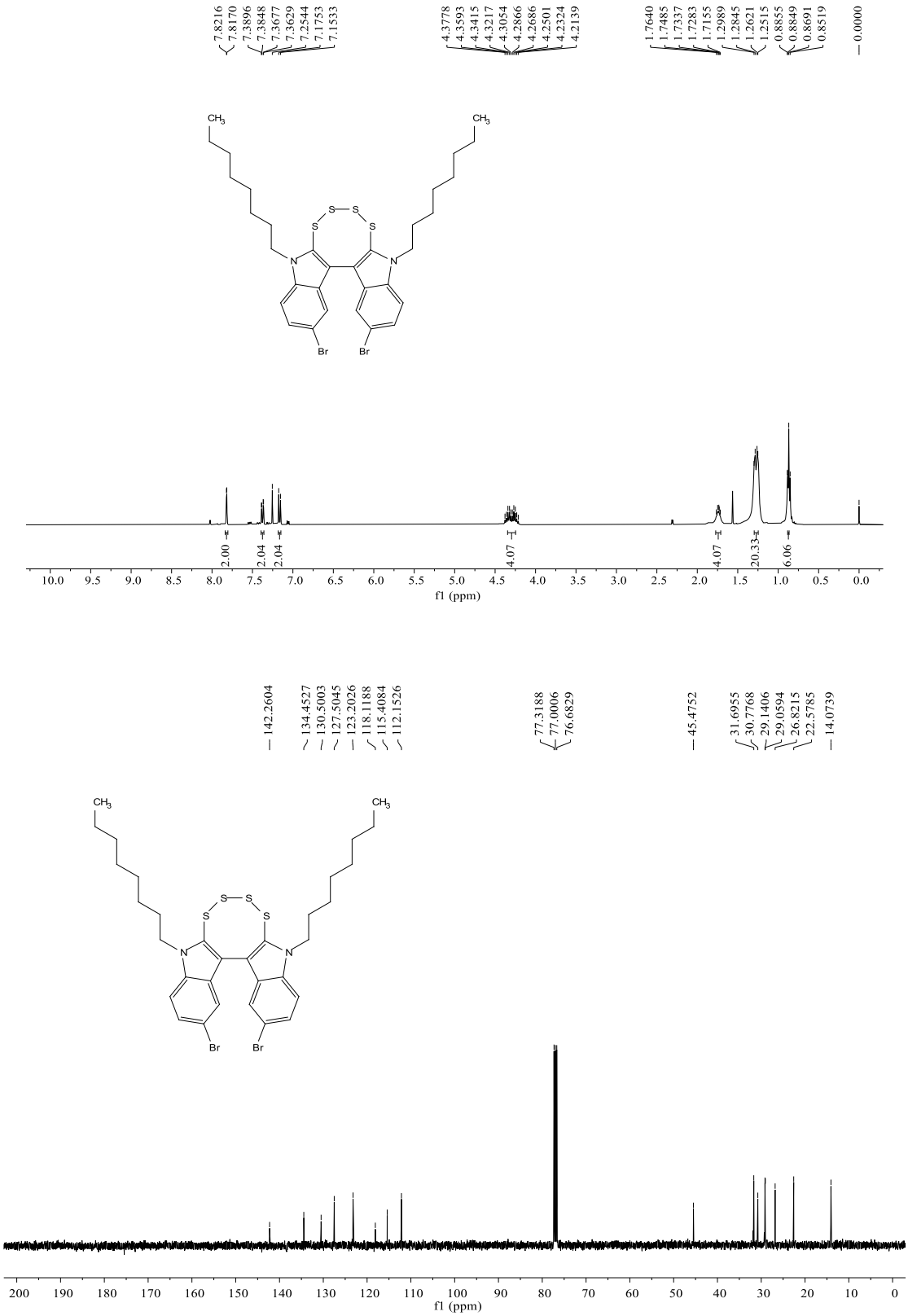


^{1}H and ^{13}C NMR spectra of **2h**

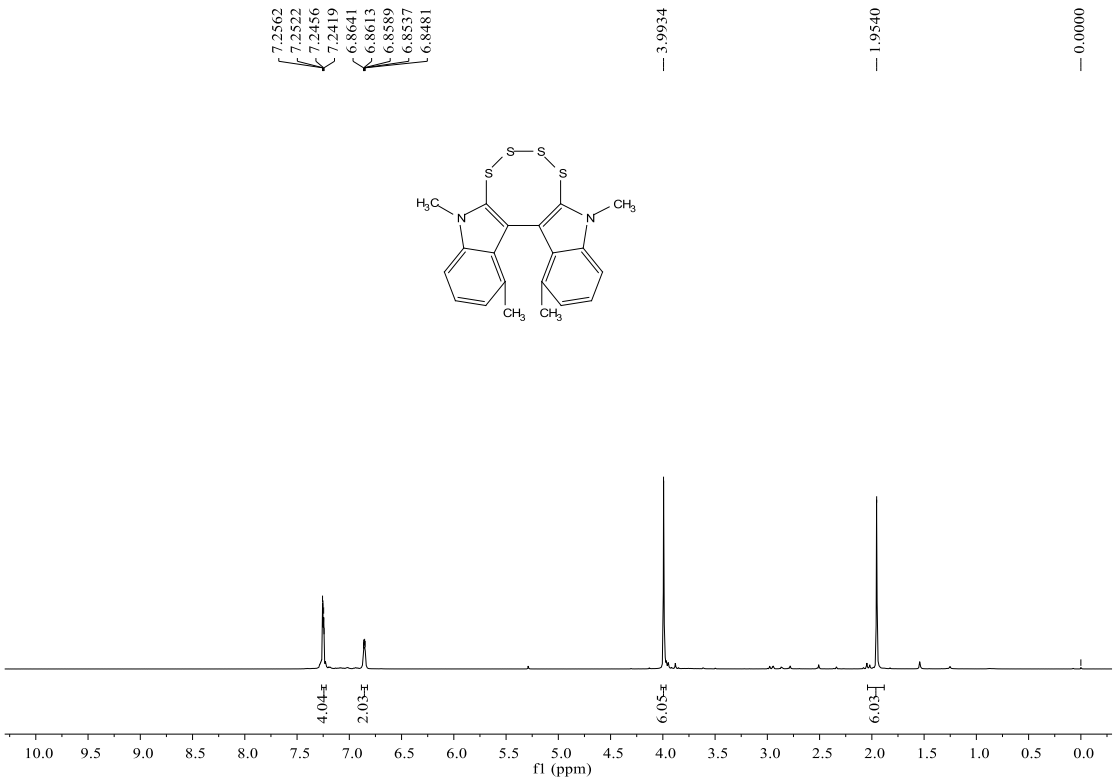


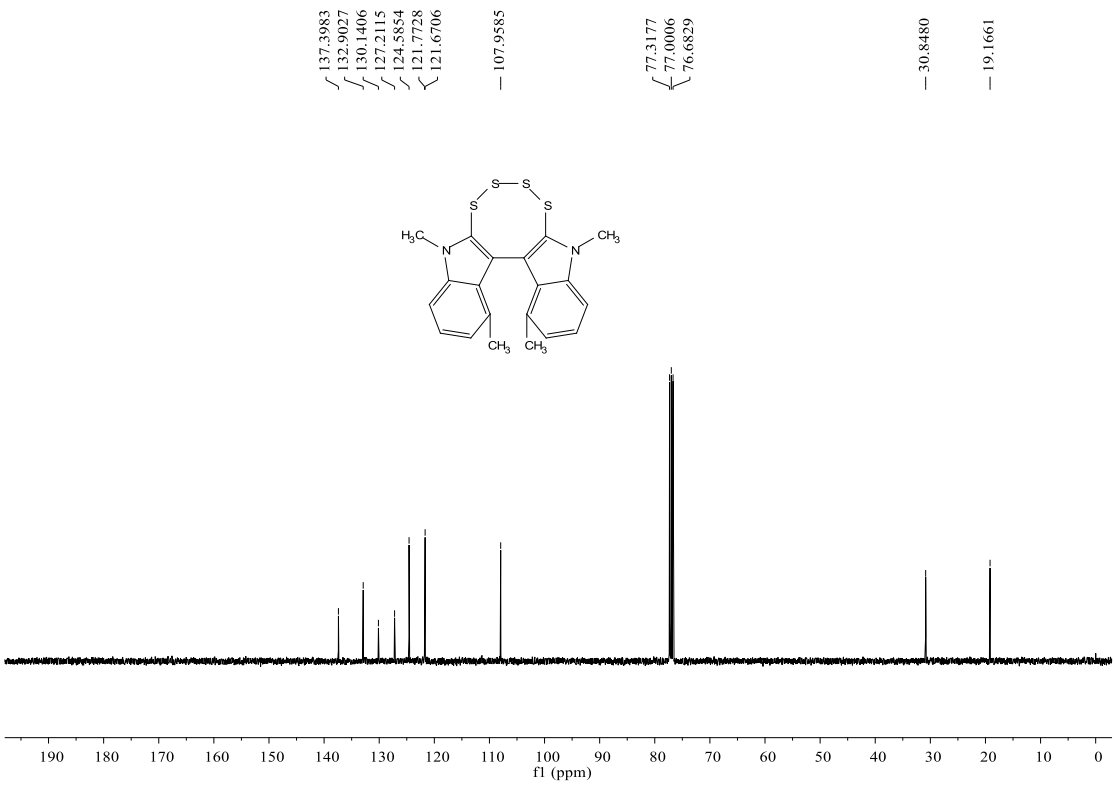


^{1}H and ^{13}C NMR spectra of **2i**

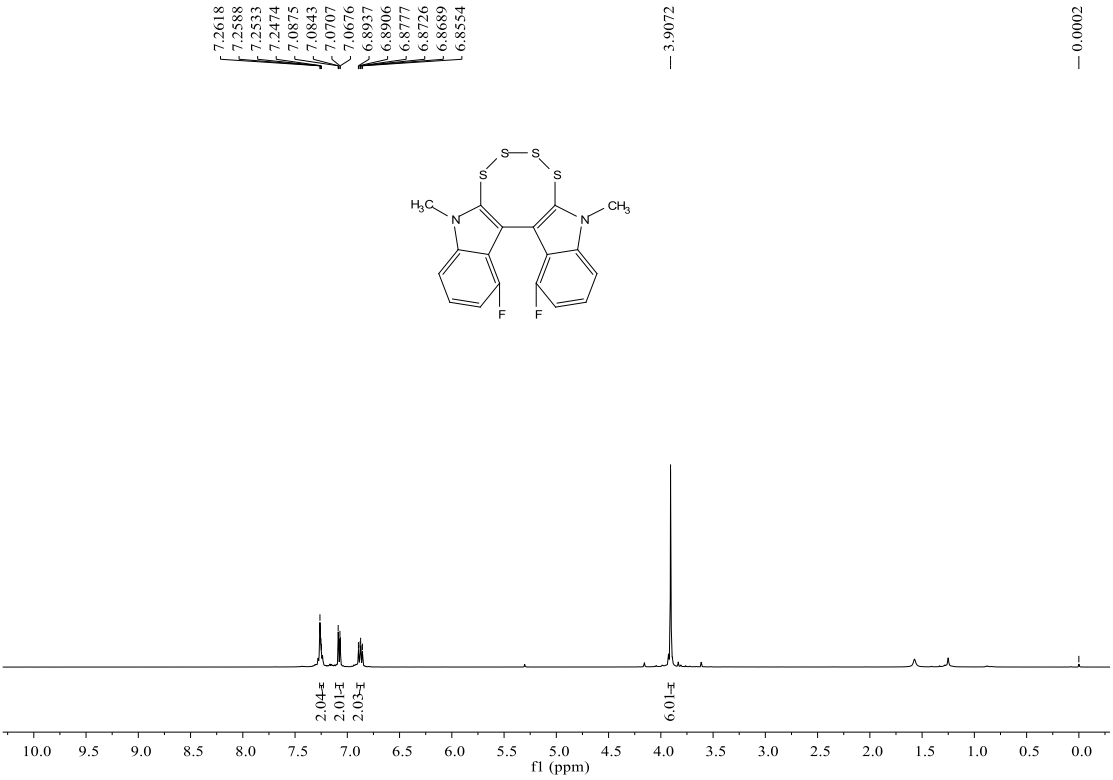


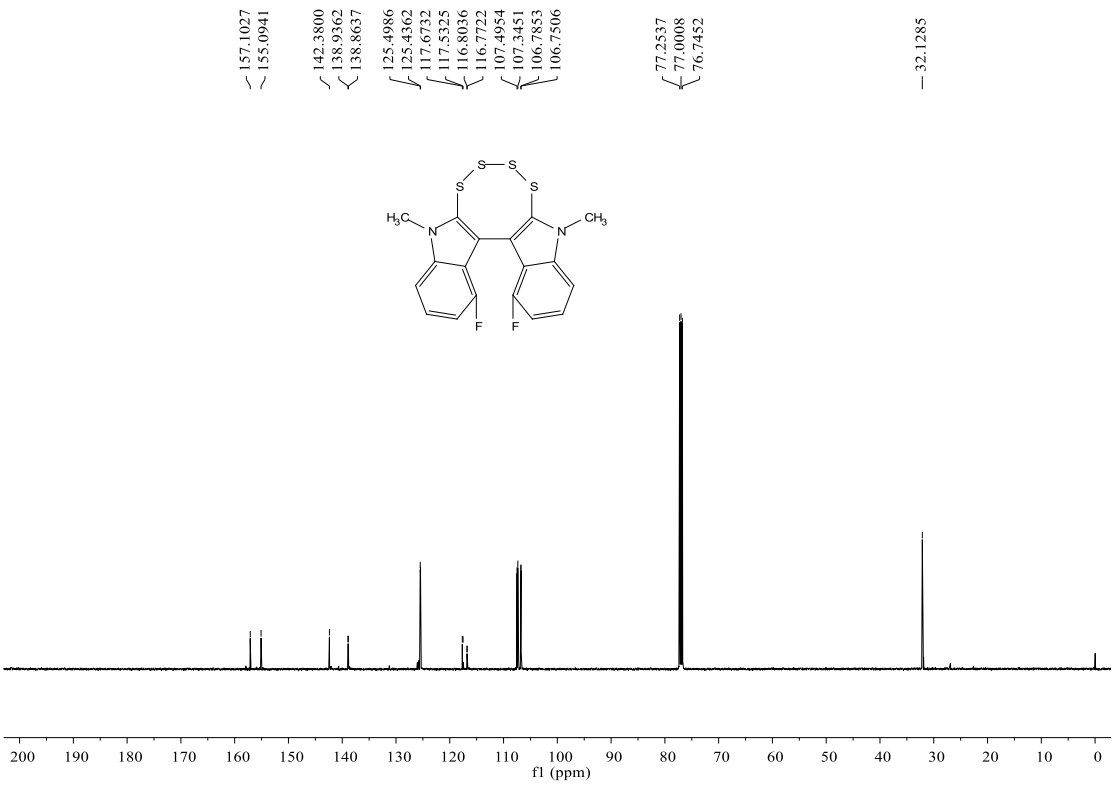
^{1}H and ^{13}C NMR spectra of **2j**

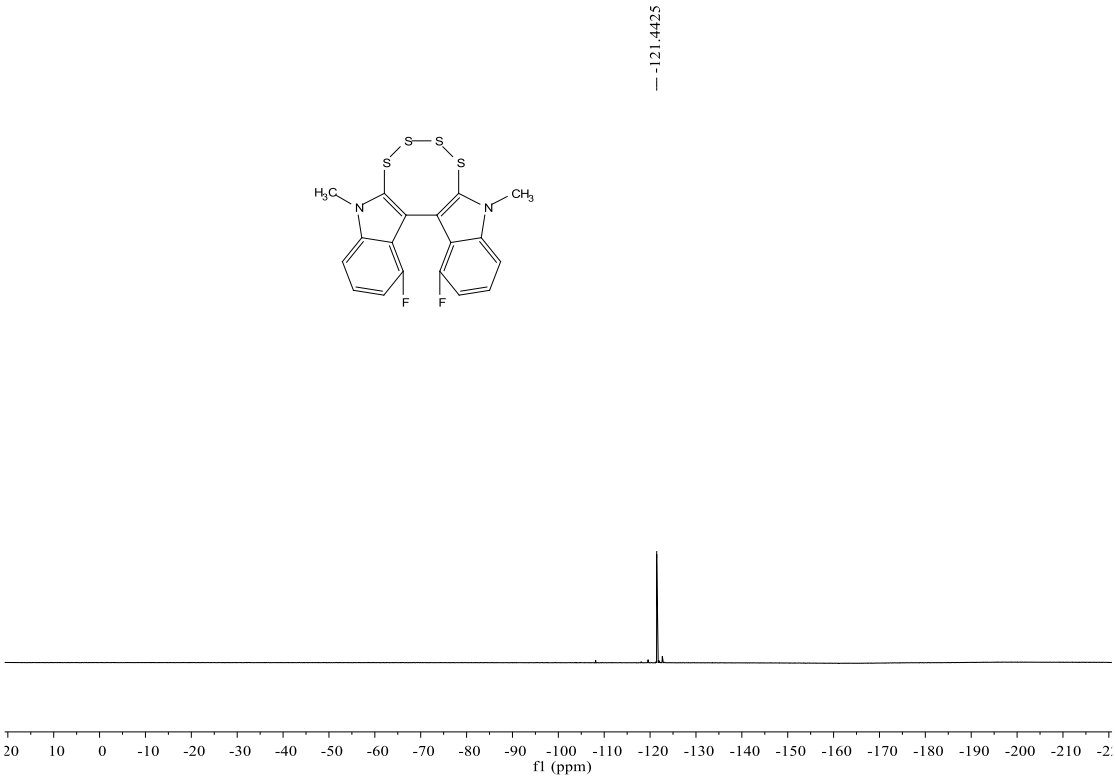




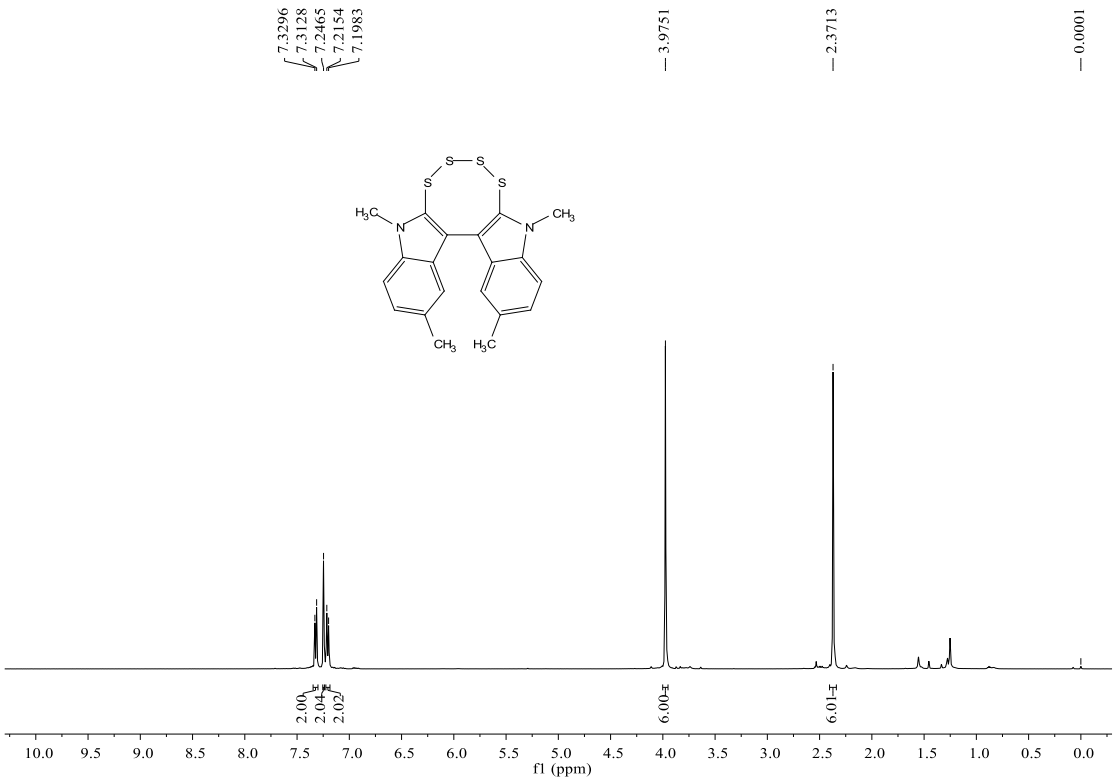
^{1}H, ^{13}C and ^{19}F NMR spectra of **2k**

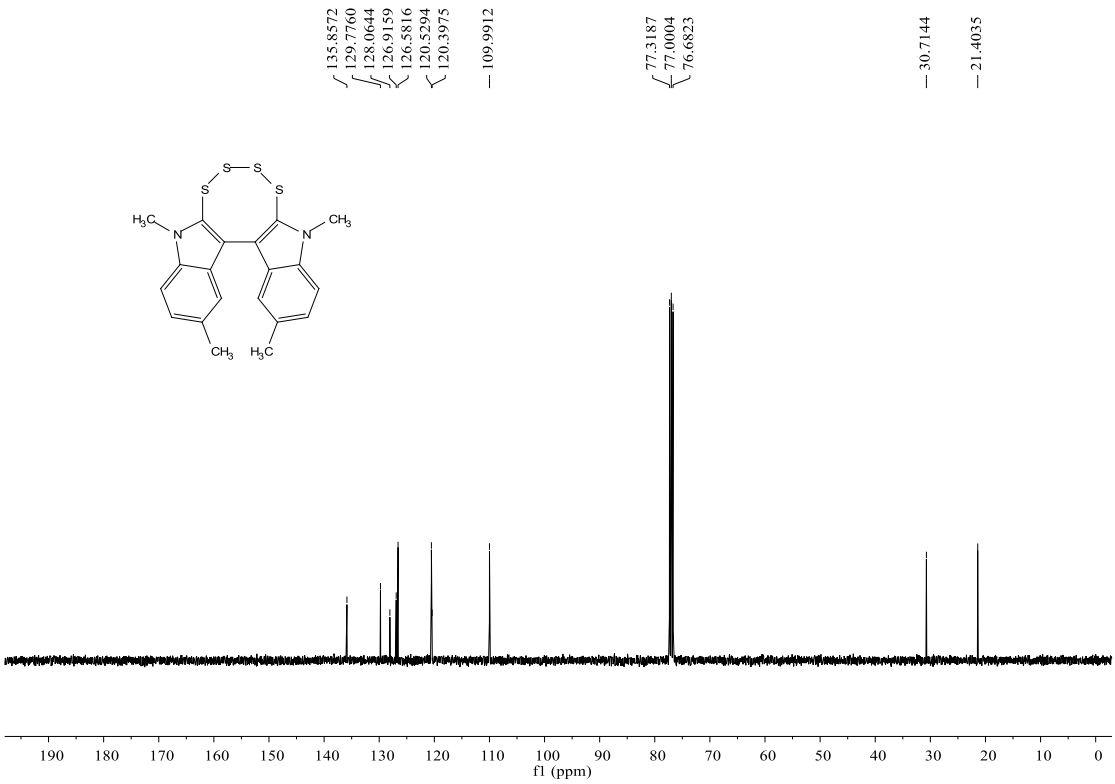




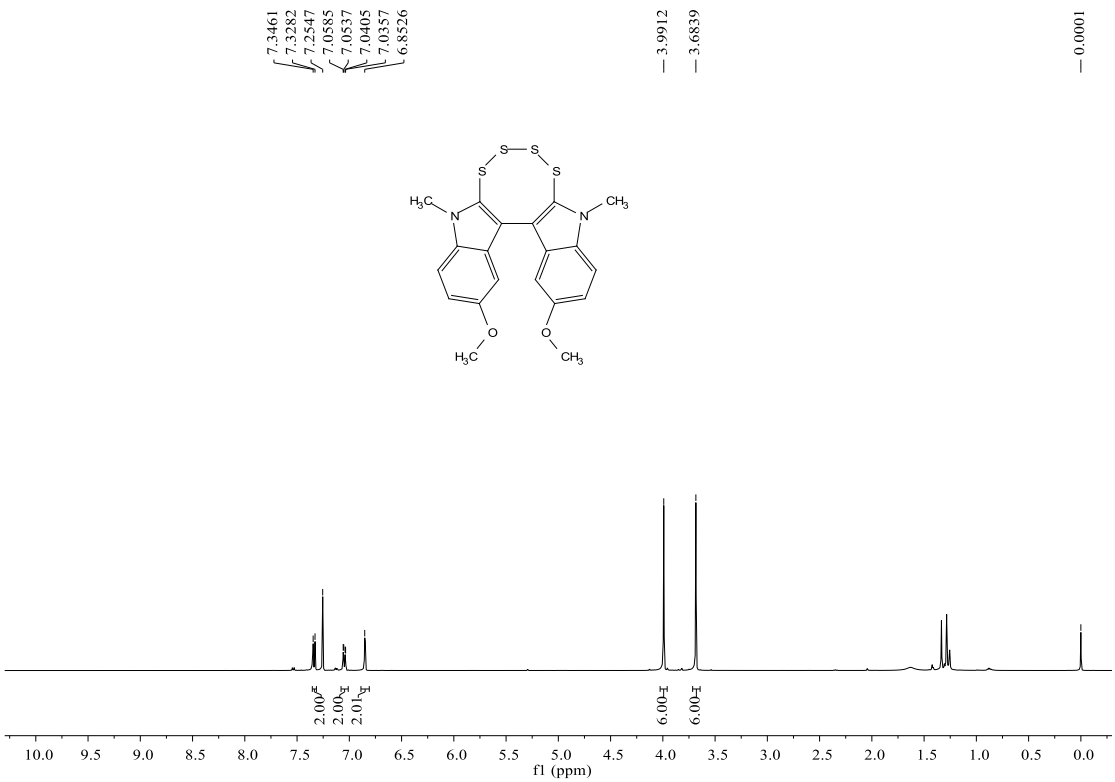


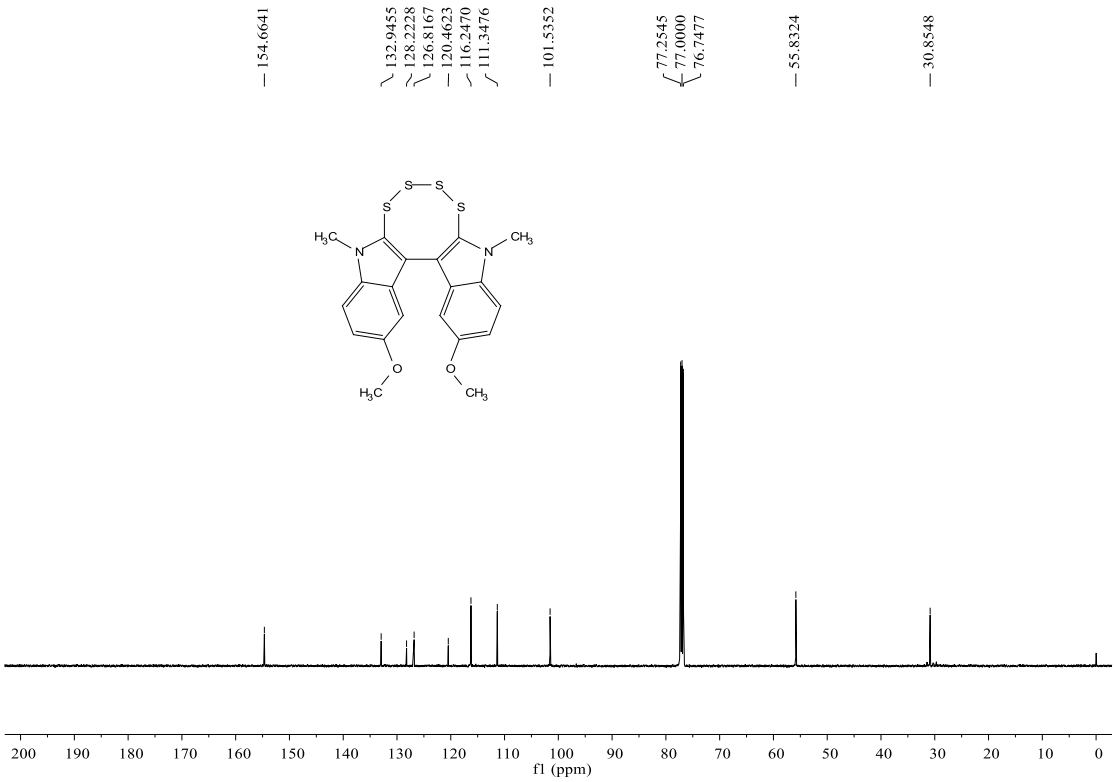
^{1}H and ^{13}C NMR spectra of **2l**



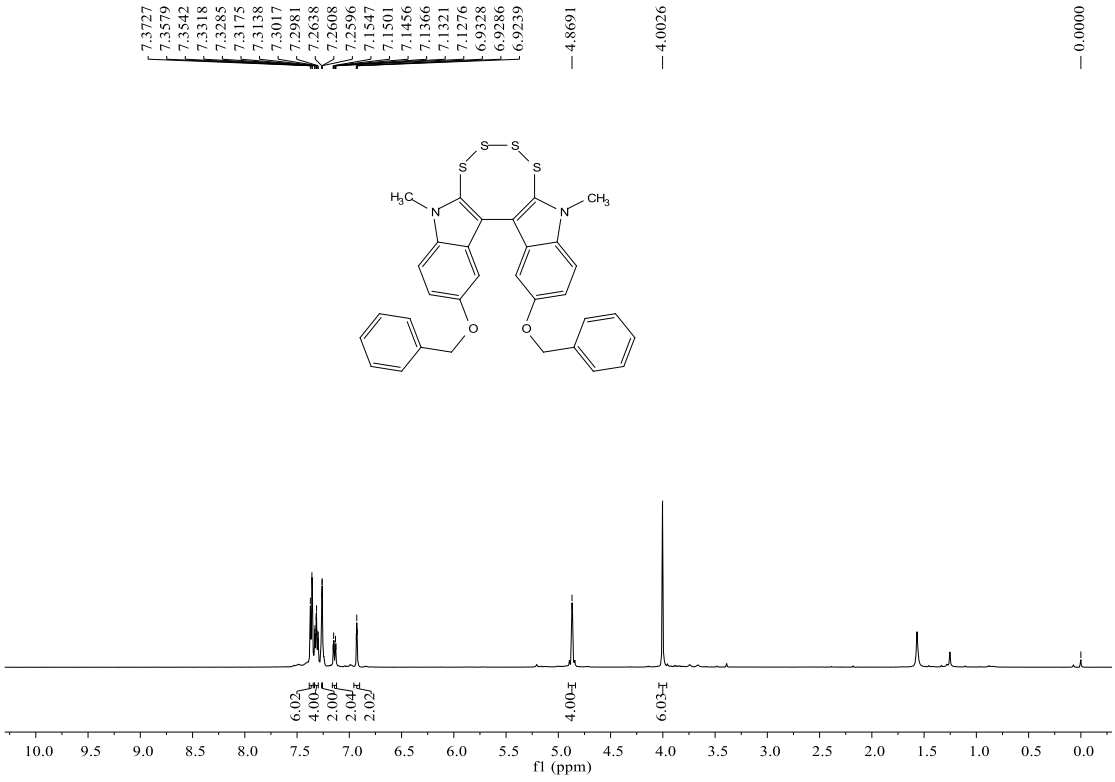


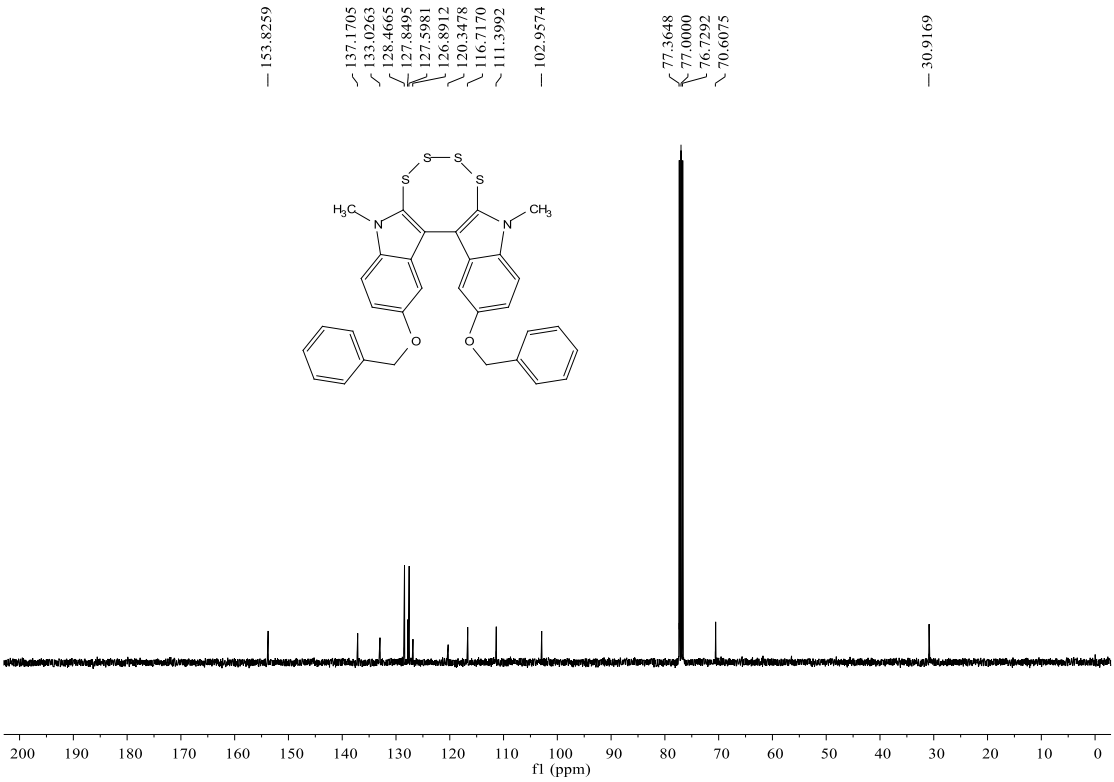
^{1}H and ^{13}C NMR spectra of **2m**



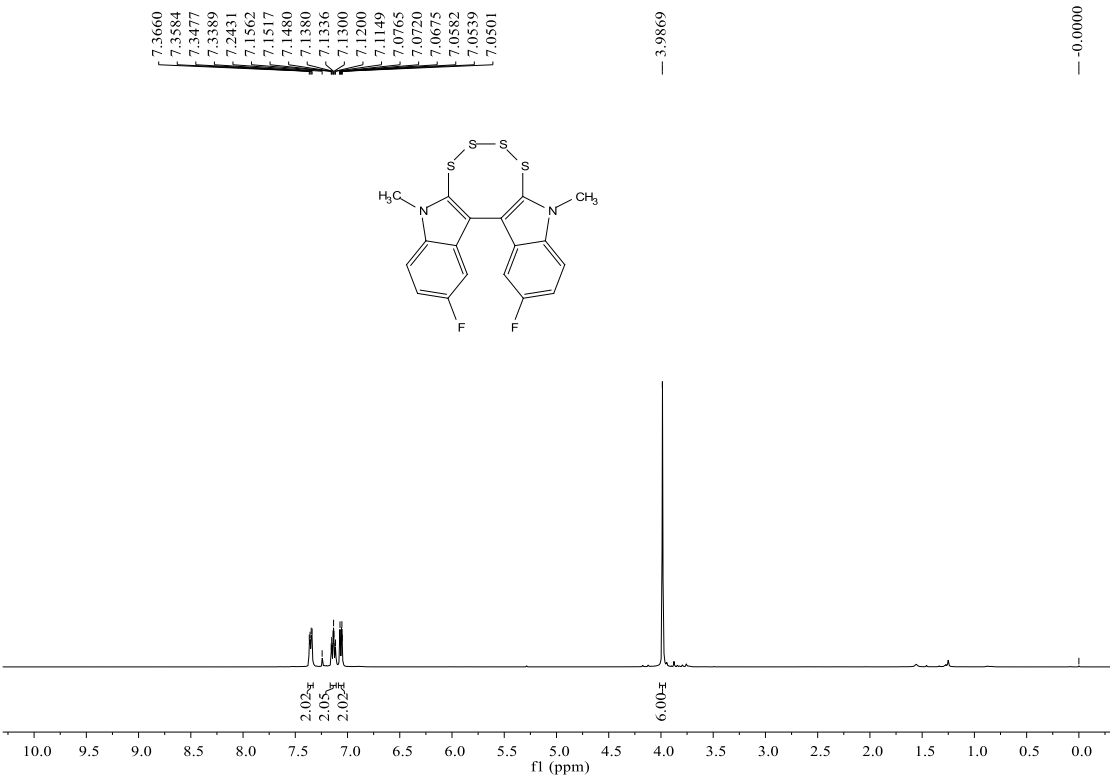


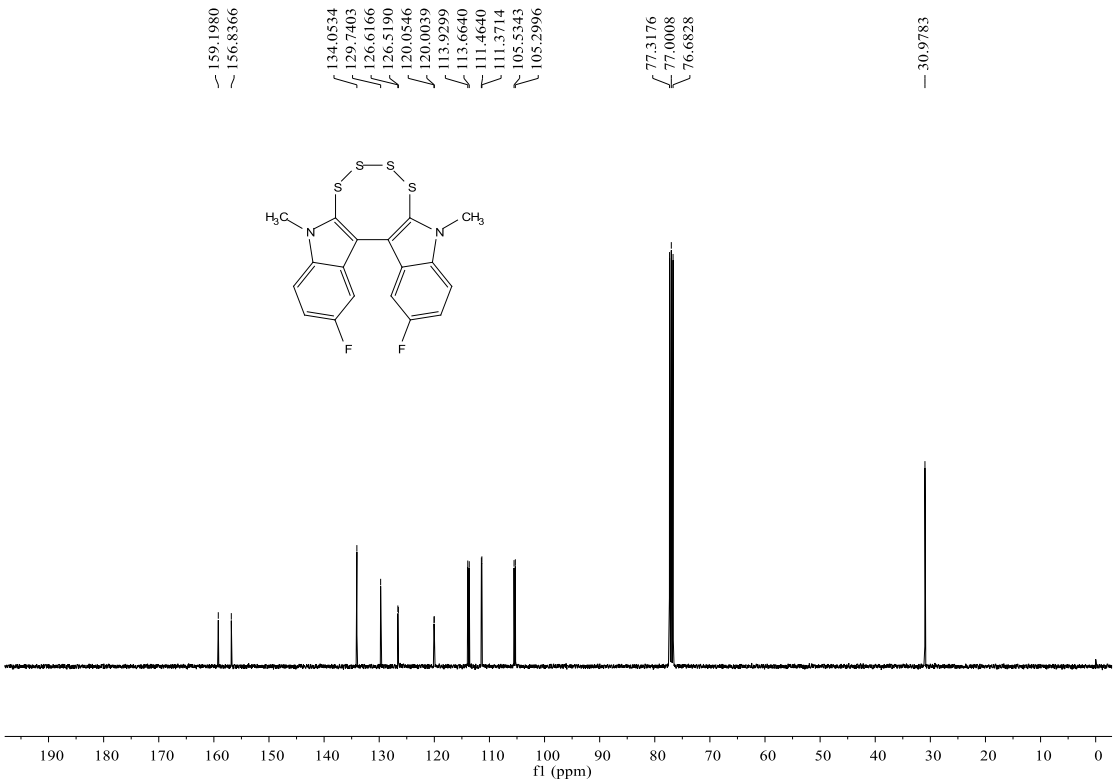
^{1}H and ^{13}C NMR spectra of **2n**





^{1}H, ^{13}C and ^{19}F NMR spectra of **2o**

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134.0534
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105.2996
77.3176
77.0008
76.6828
30.9783
S
S
S
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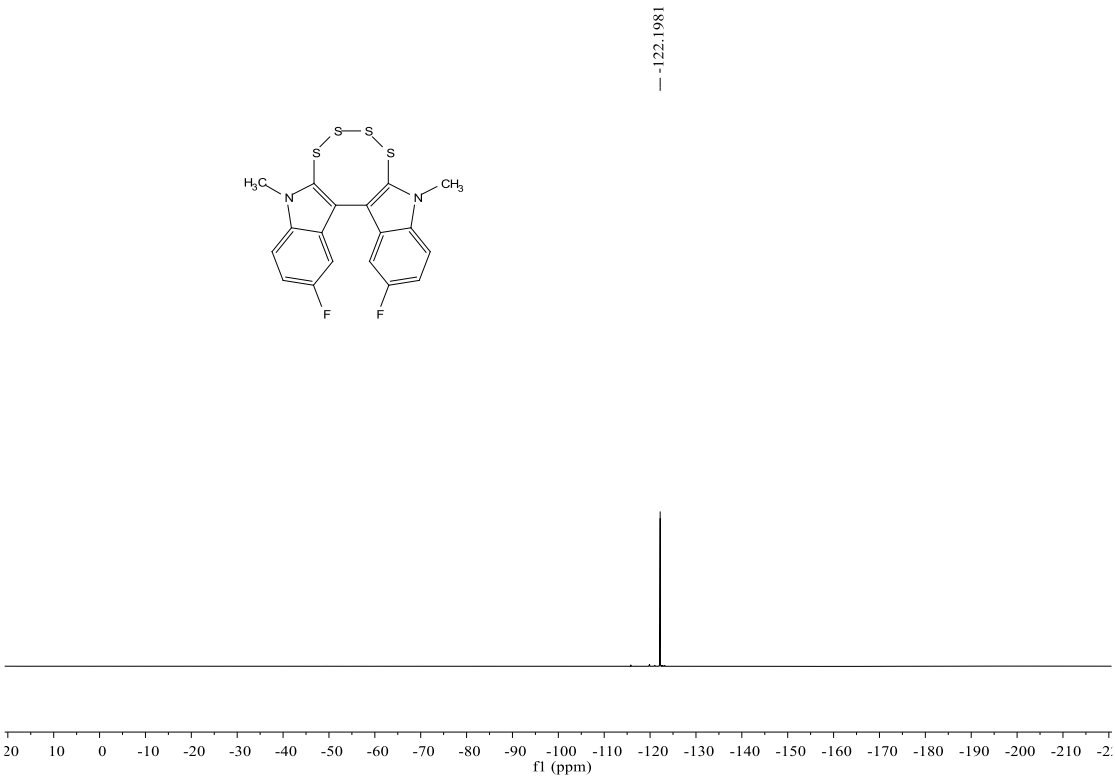
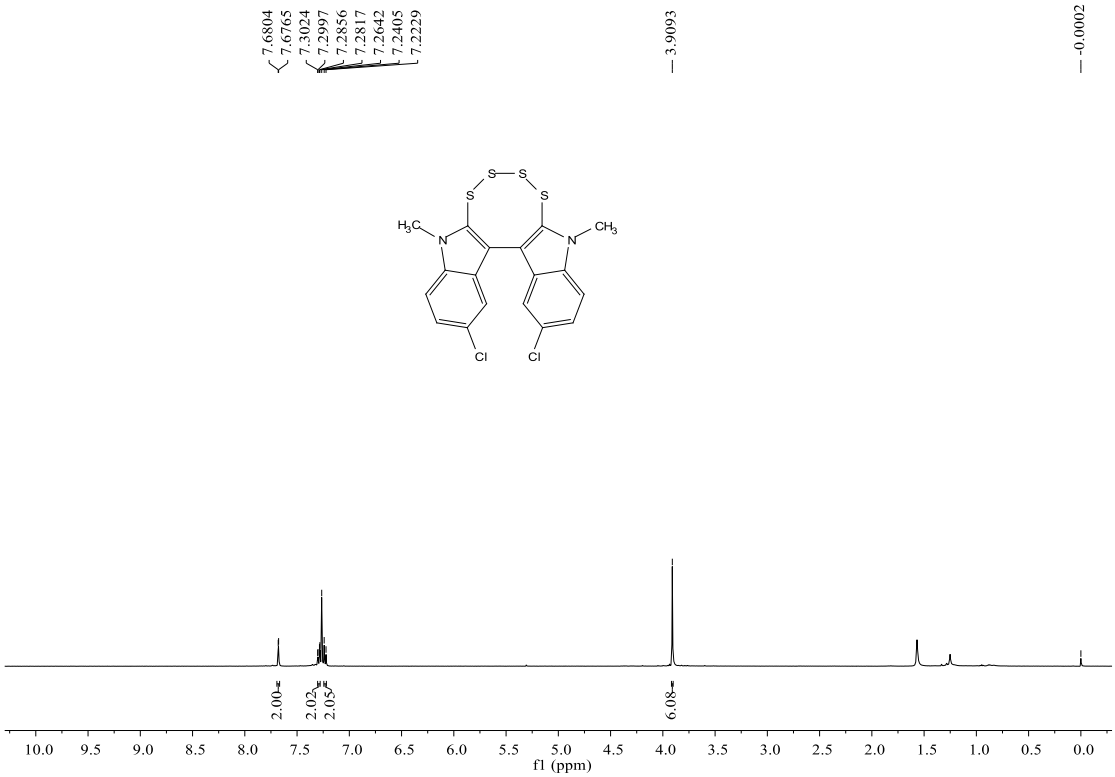
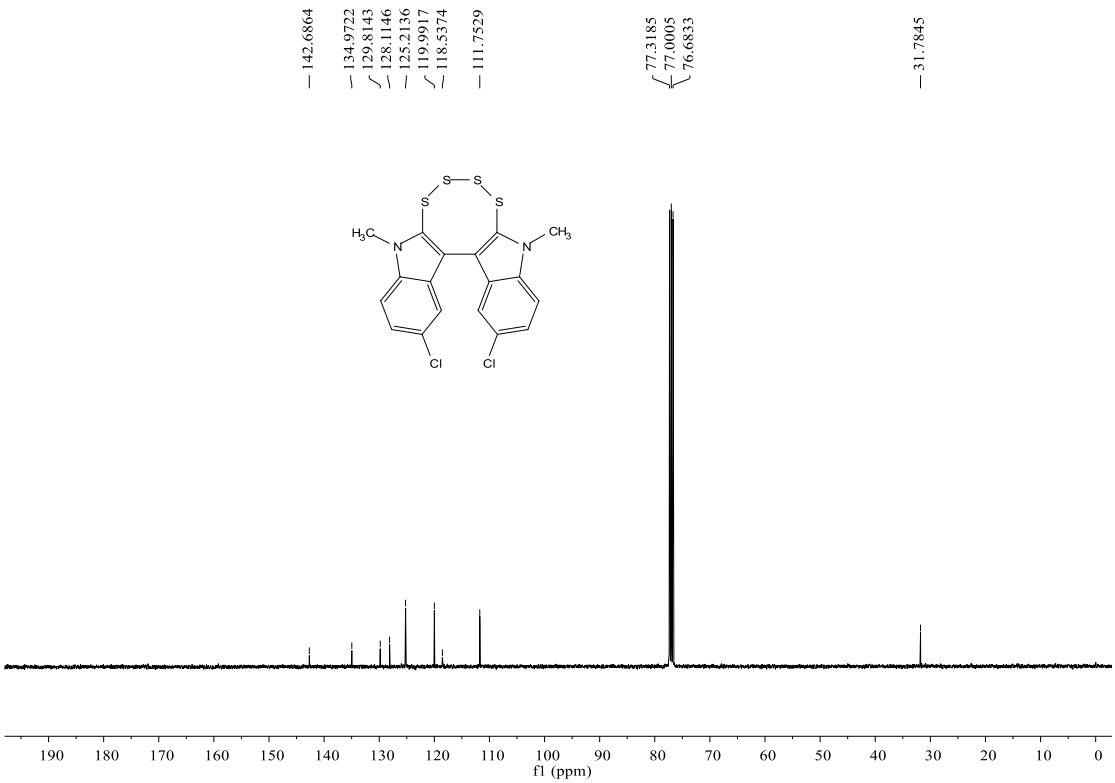
H3C
N
N
CH3
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

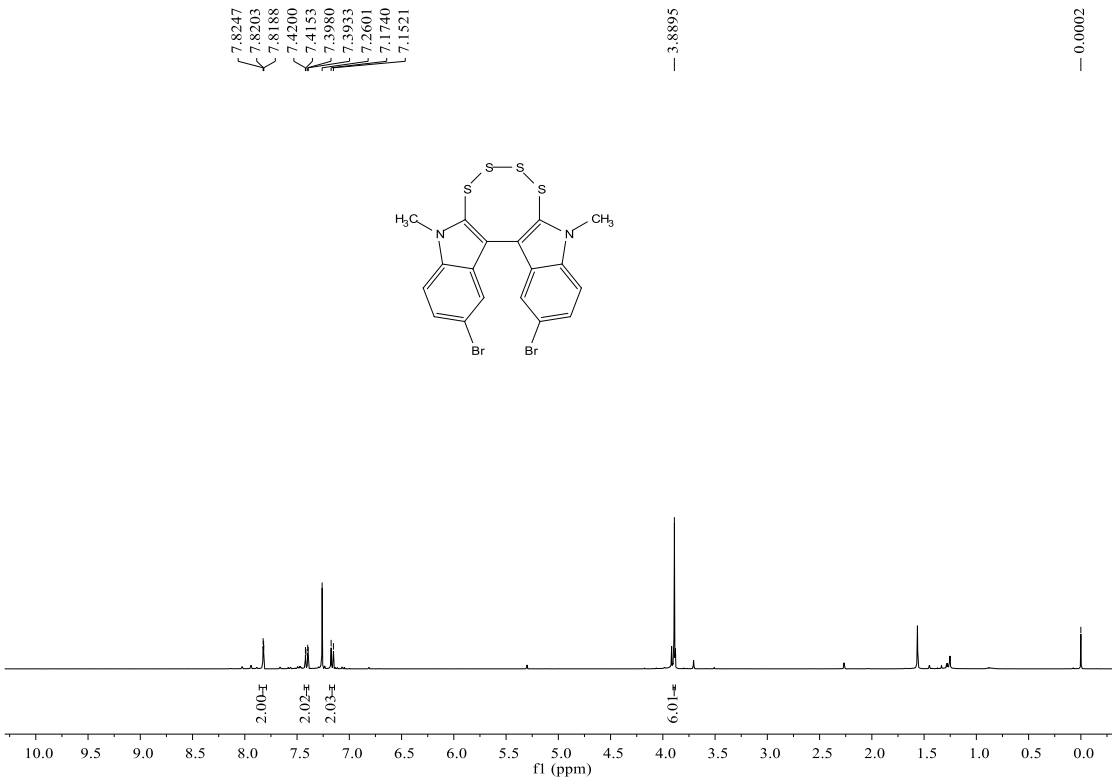

-122.1981
S
S
S
S
H3C
N
N
CH3
F
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

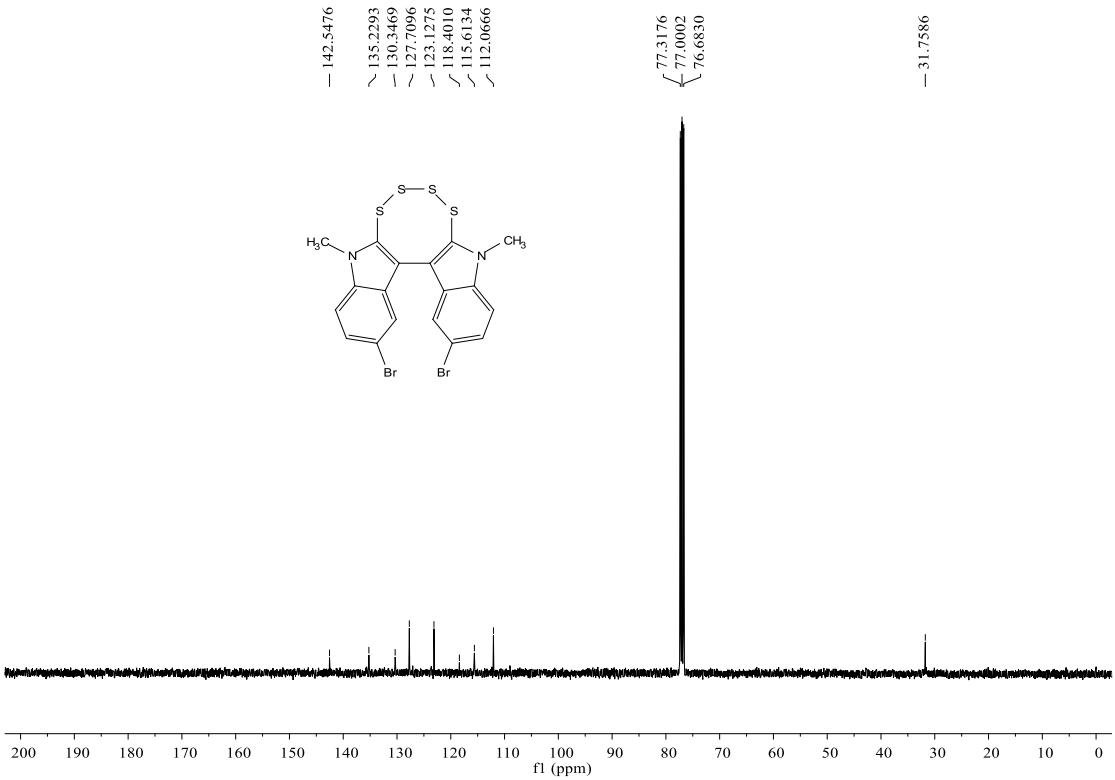
^{1}H and ^{13}C NMR spectra of **2p**



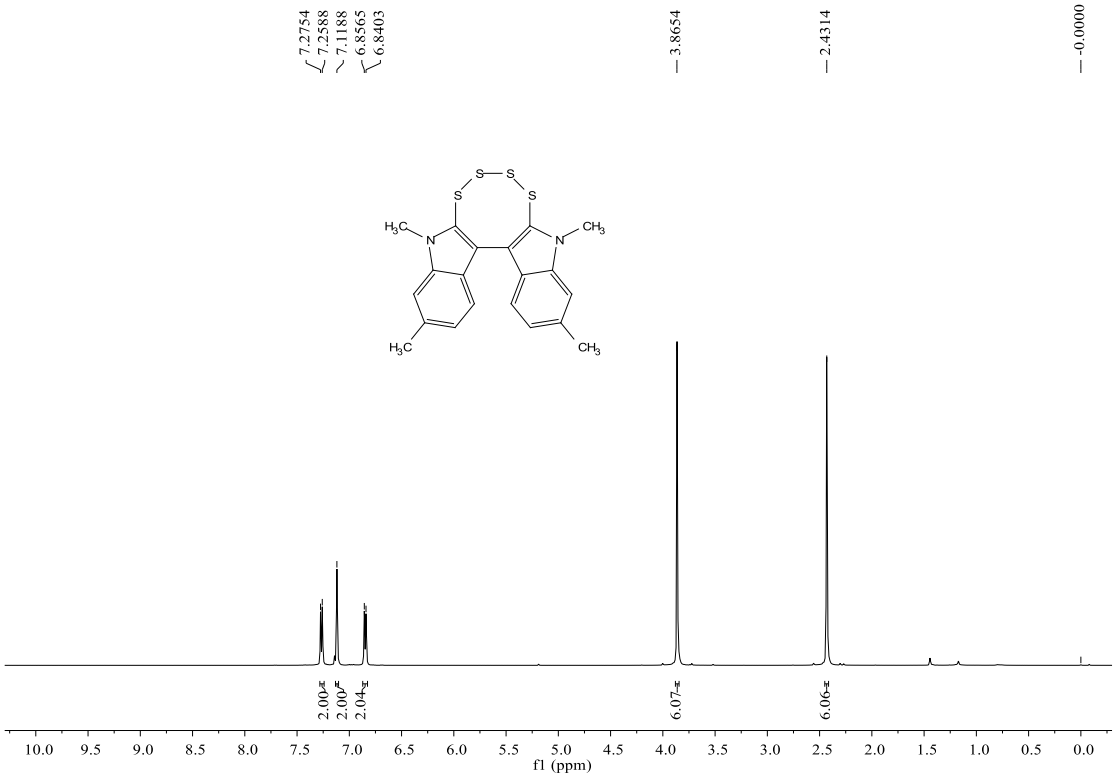


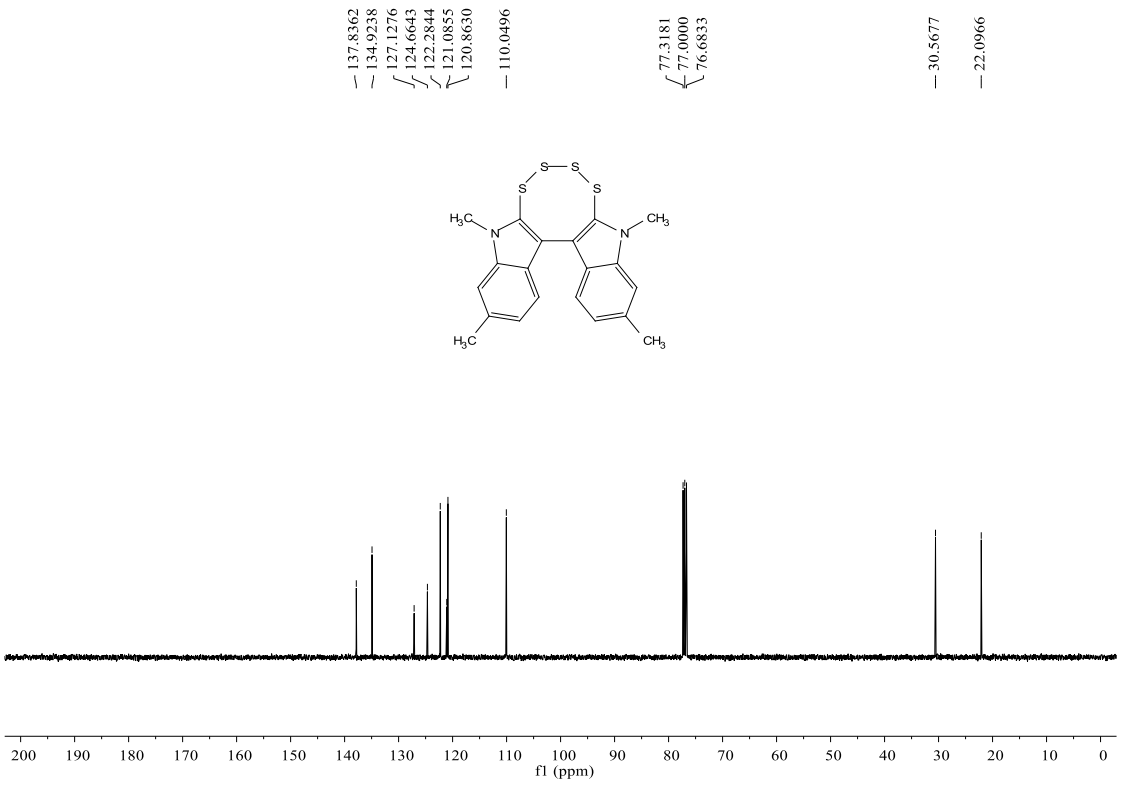
^{1}H and ^{13}C NMR spectra of **2q**



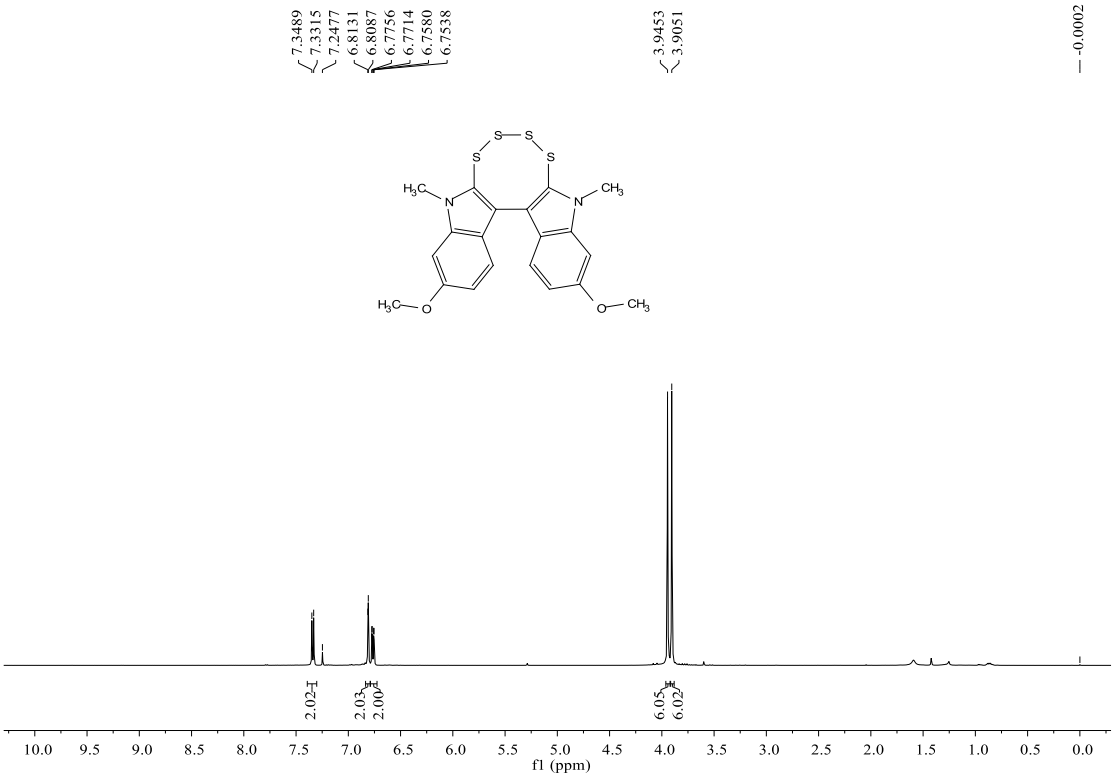


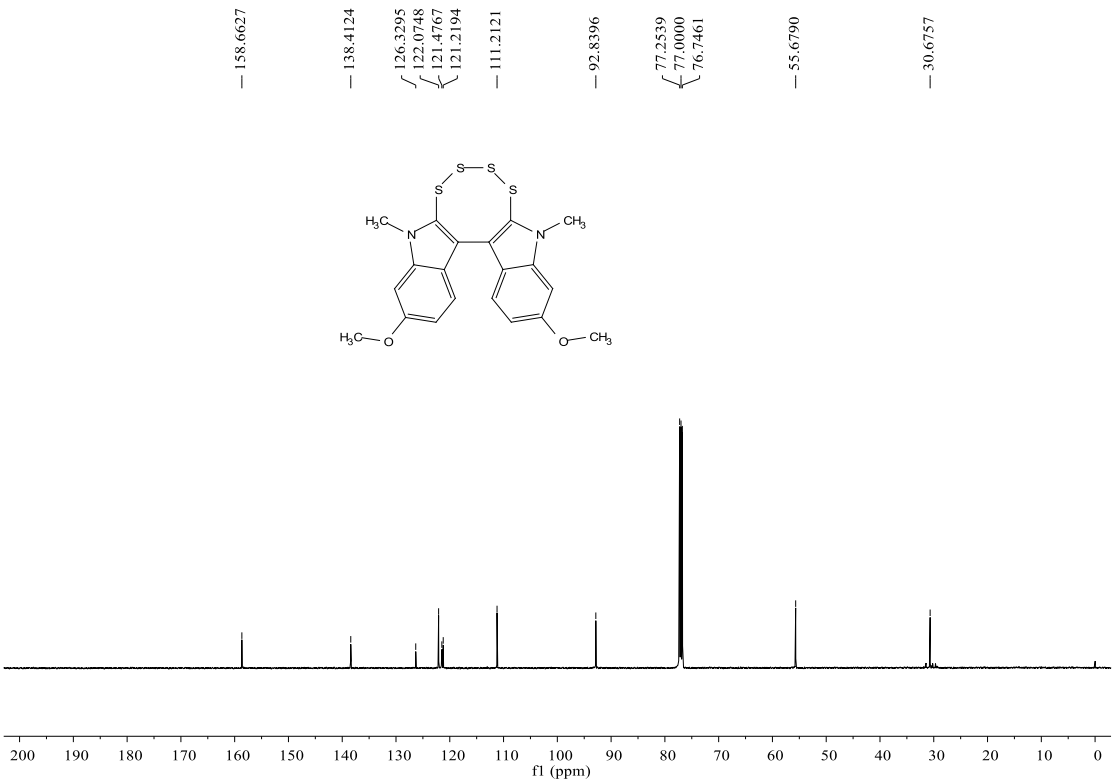
^{1}H and ^{13}C NMR spectra of **2r**



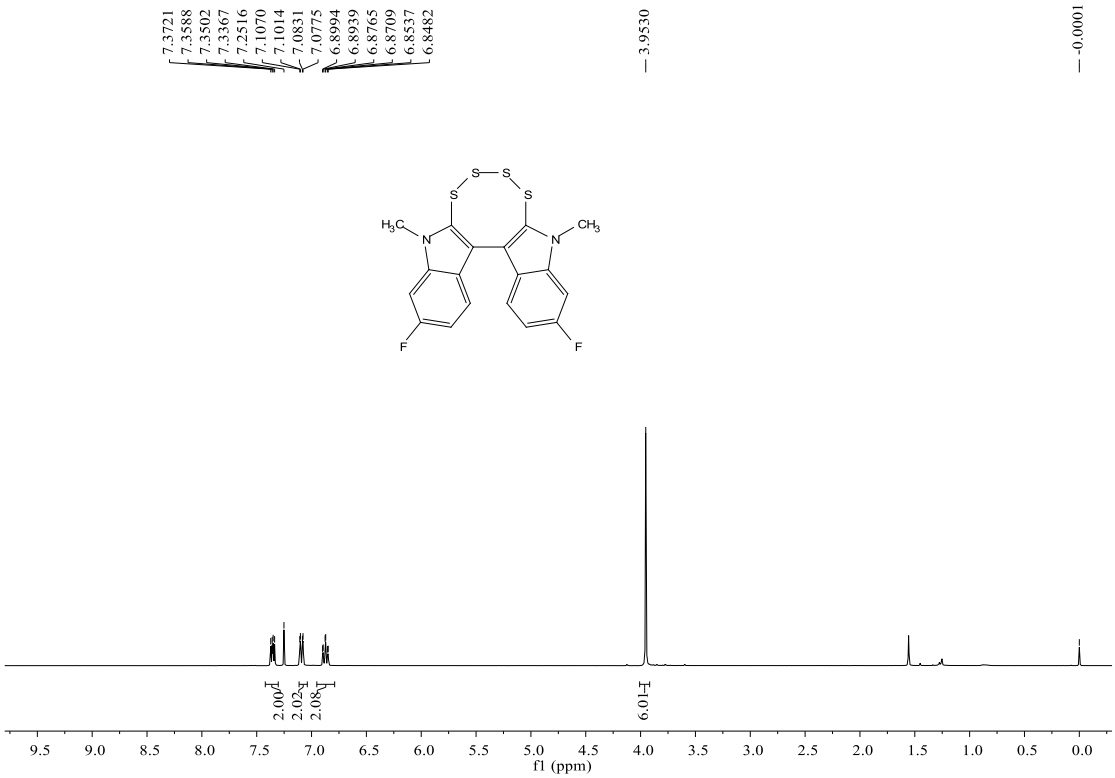


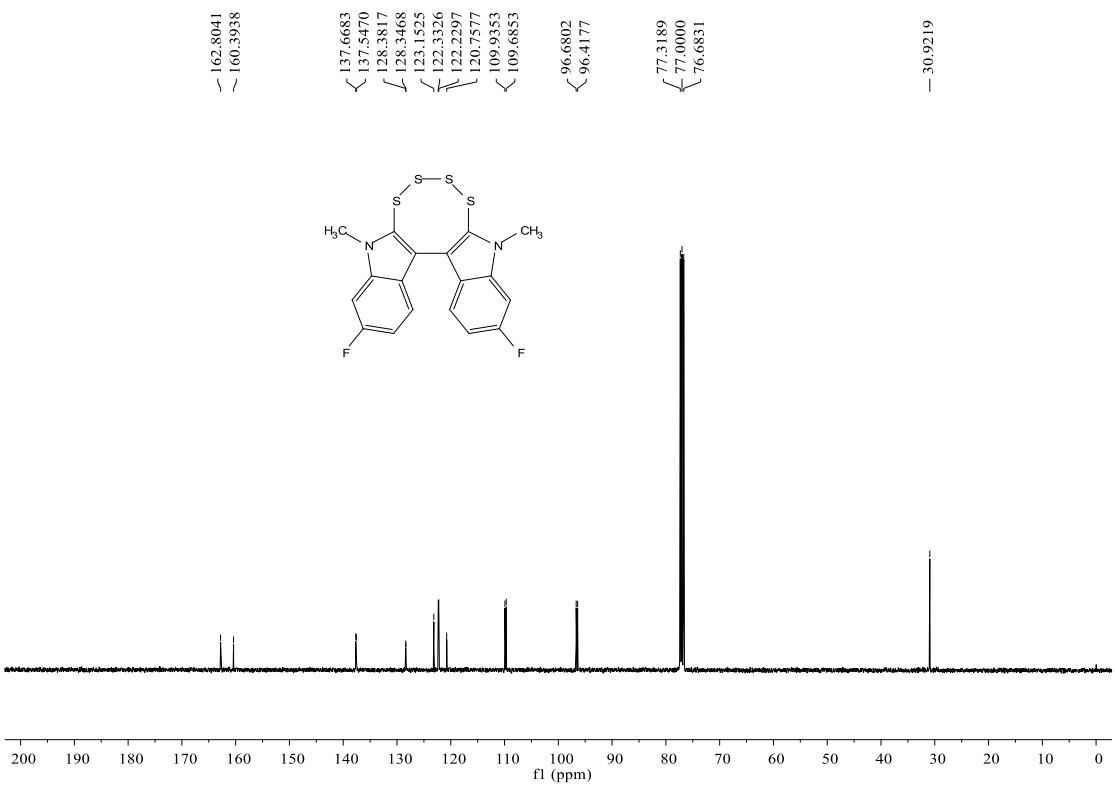
^{1}H and ^{13}C NMR spectra of **2s**

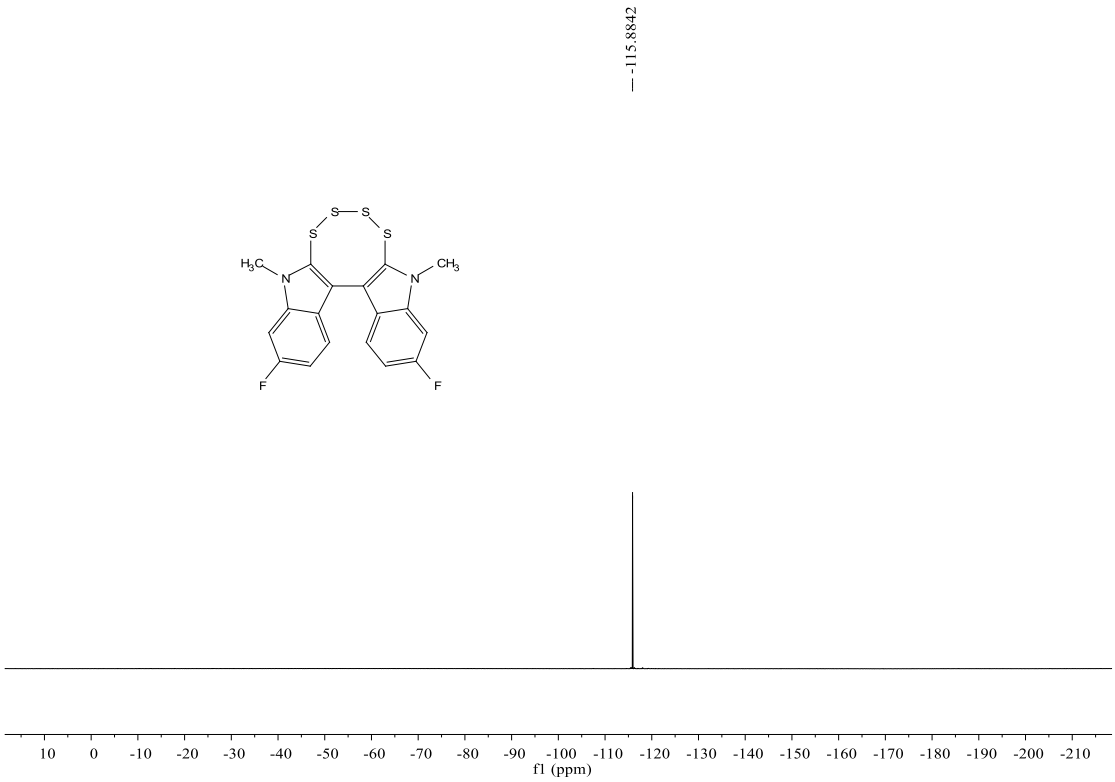




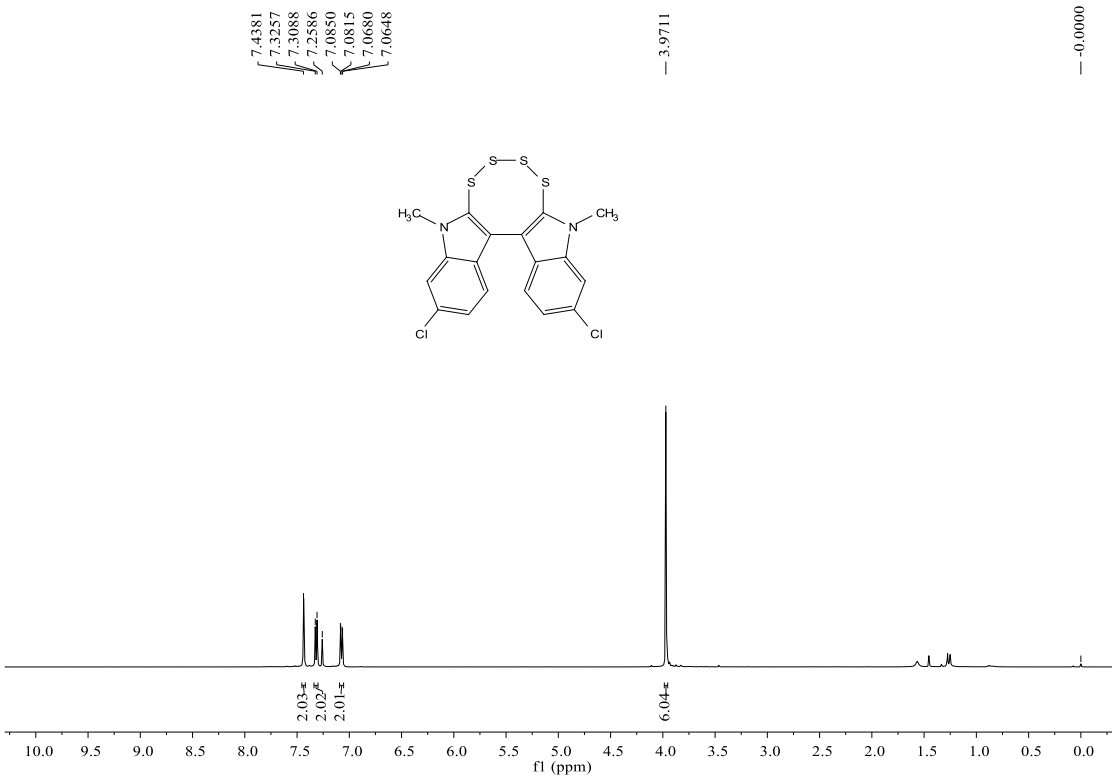
^{1}H, ^{13}C and ^{19}F NMR spectra of **2t**

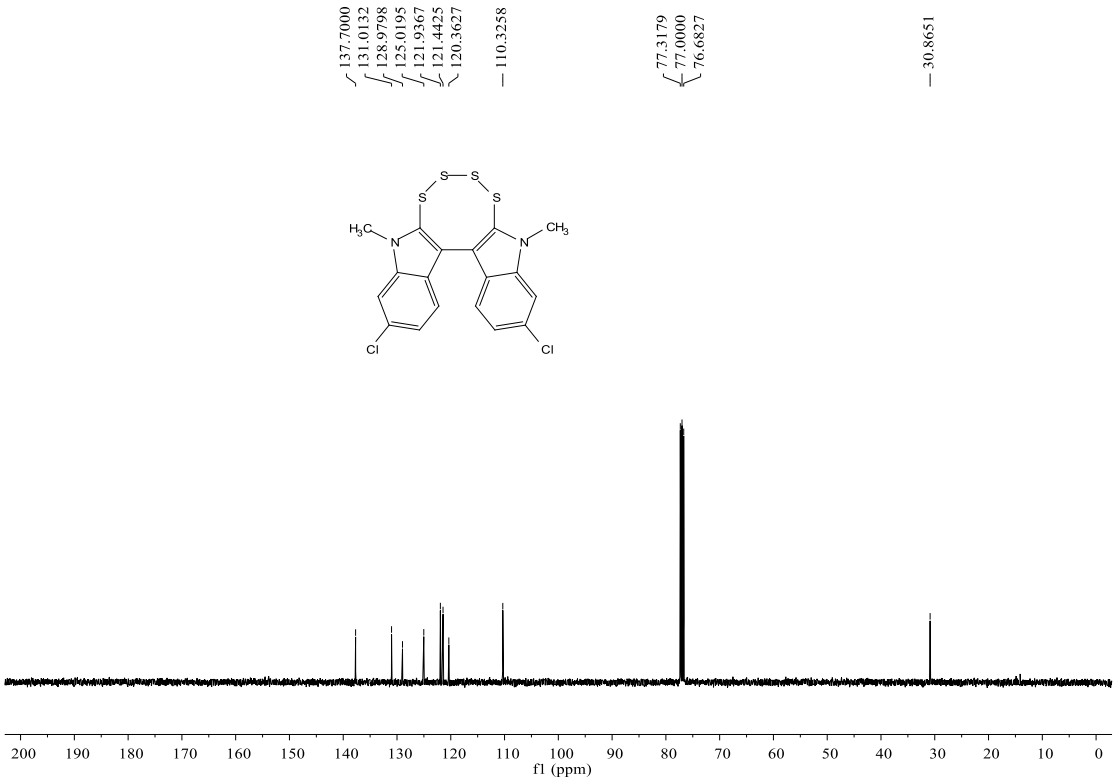




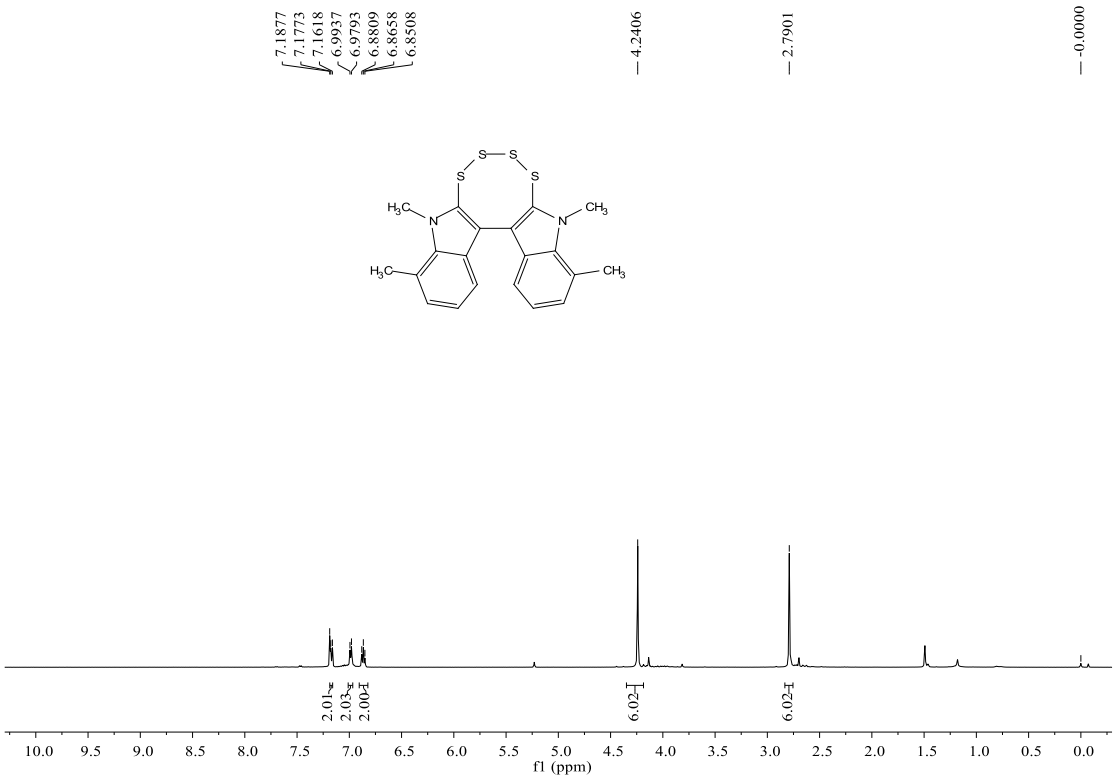


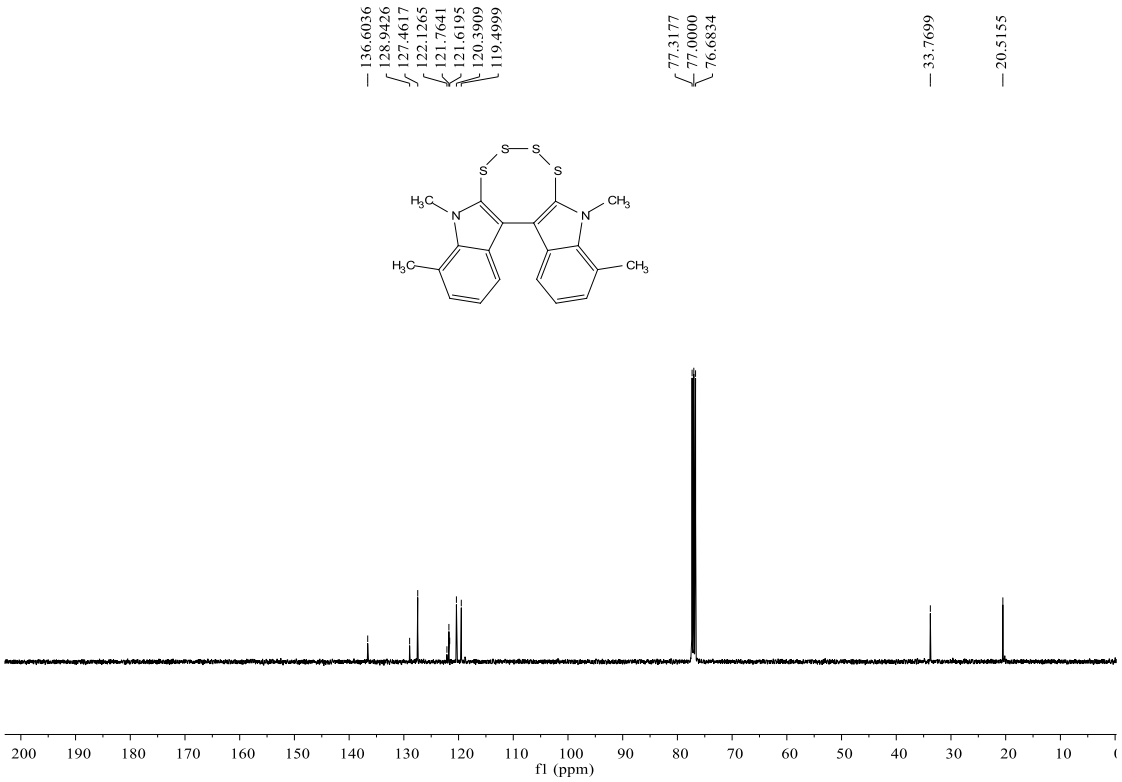
H and ^{13}C NMR spectra of **2u**



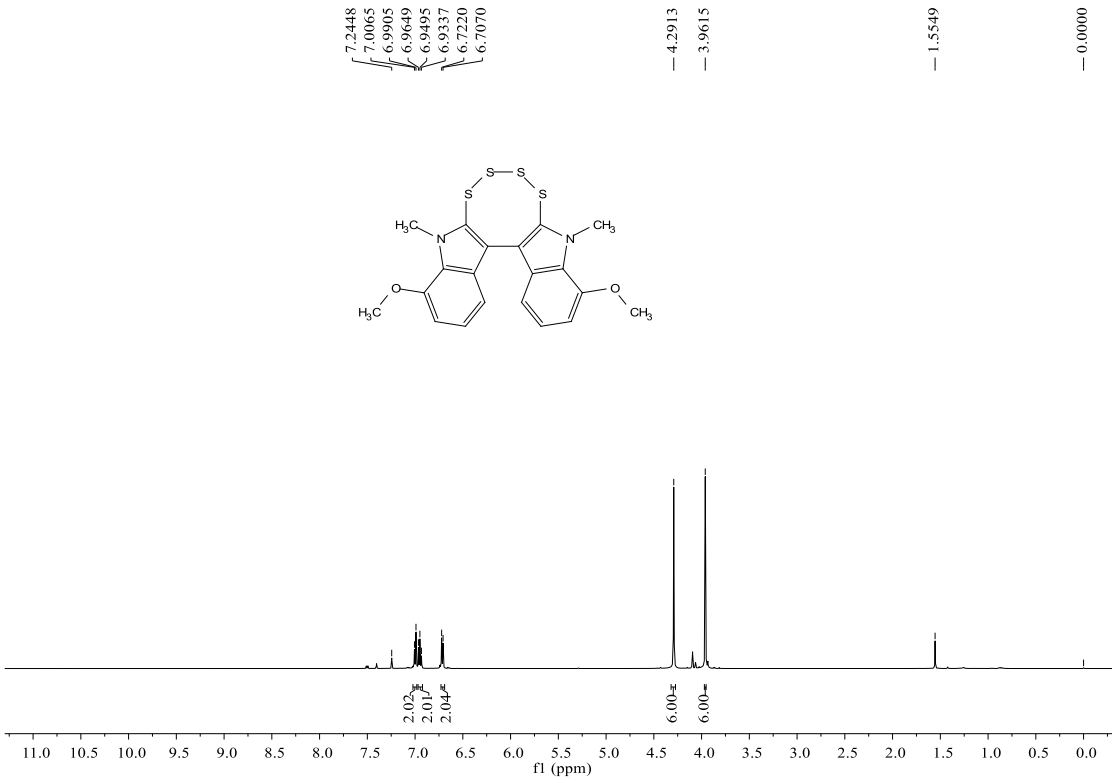


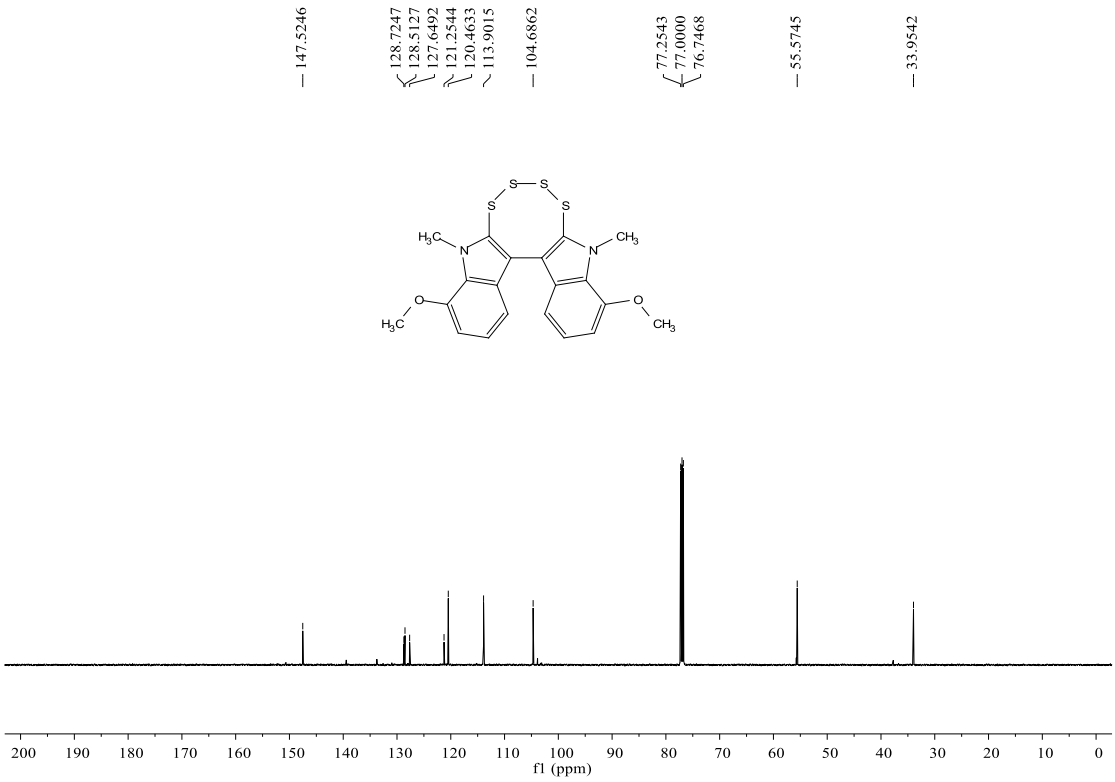
^{1}H and ^{13}C NMR spectra of **2v**



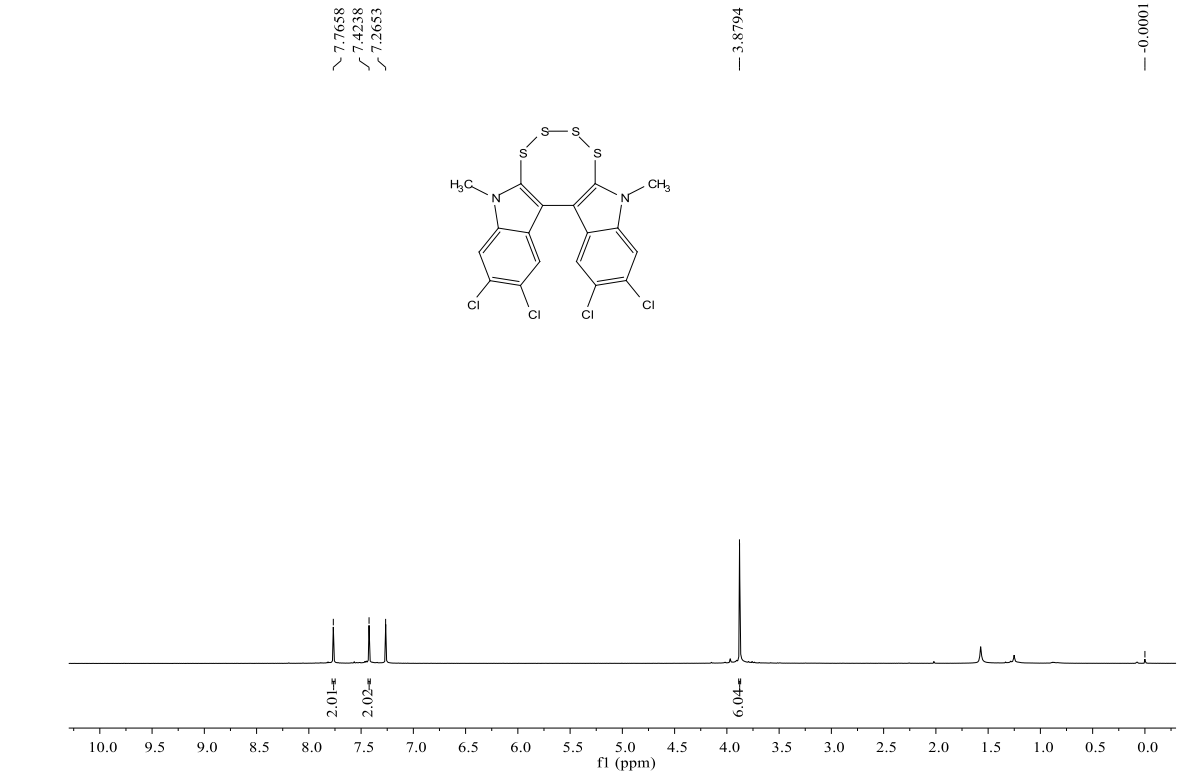


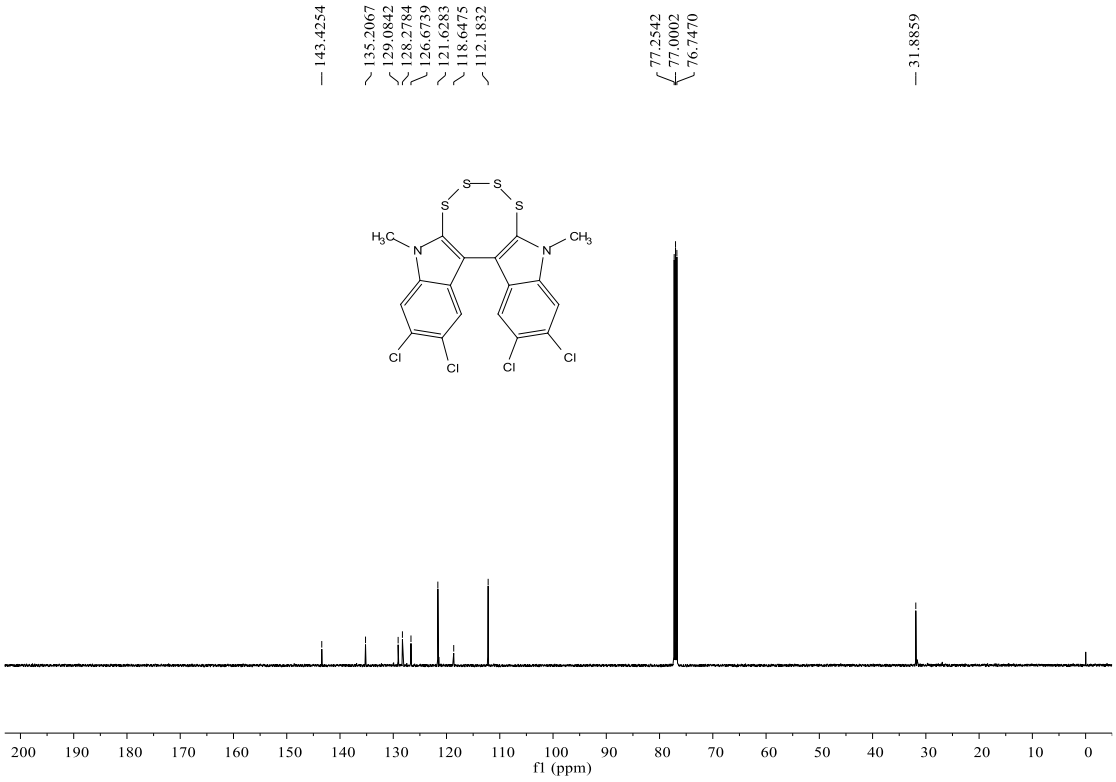
^{1}H and ^{13}C NMR spectra of **2w**



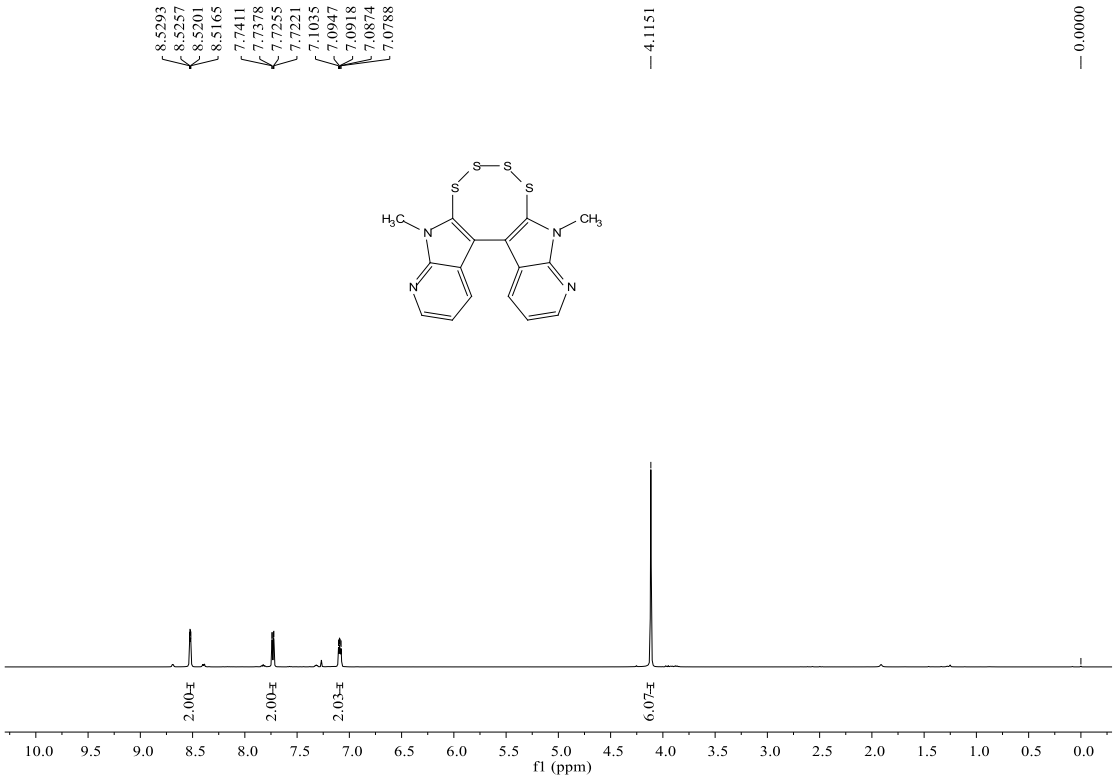


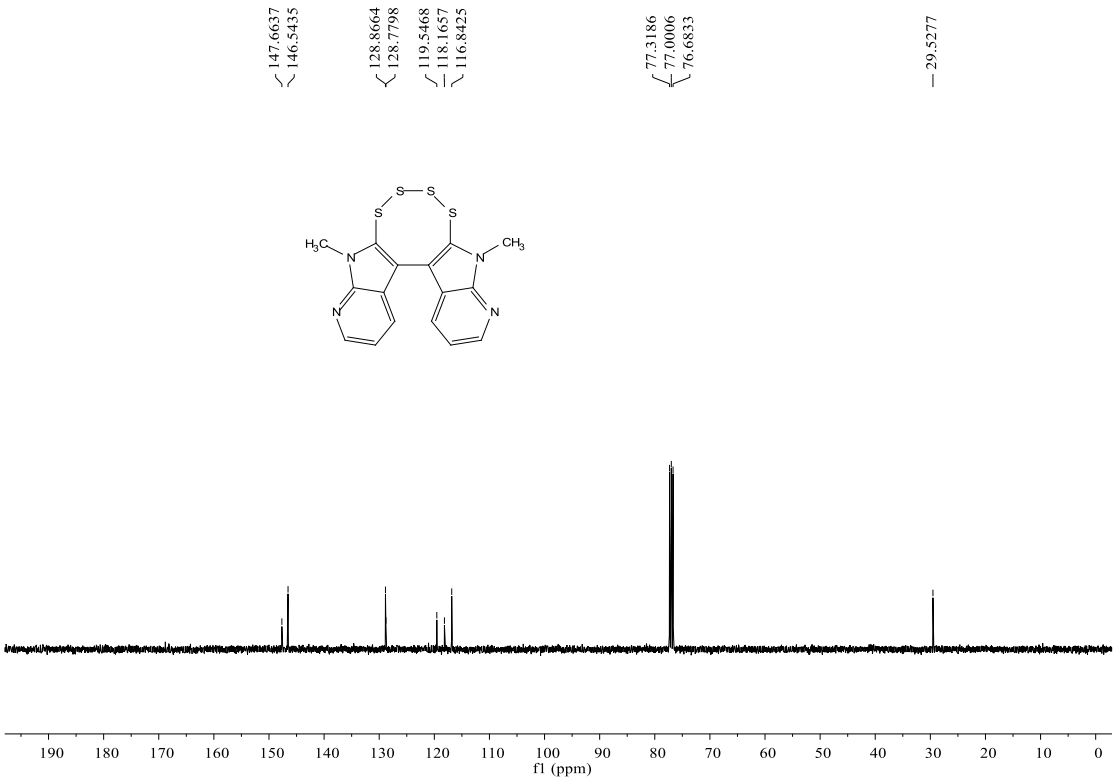
^{1}H and ^{13}C NMR spectra of **2x**



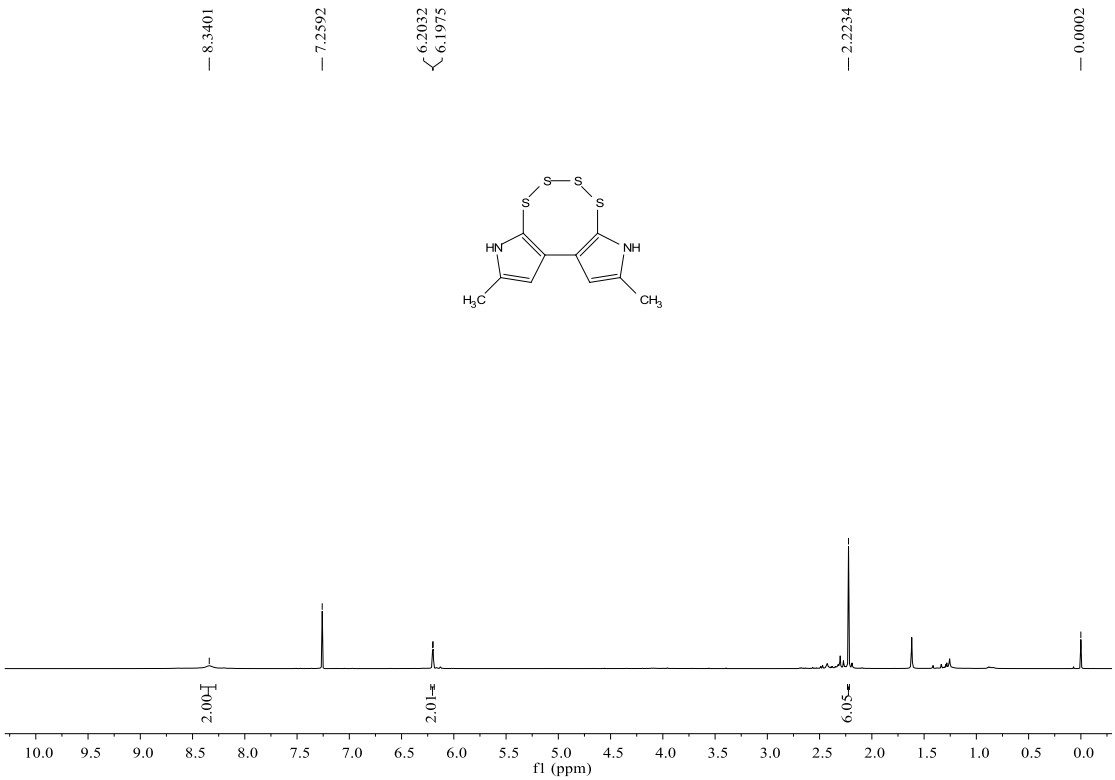


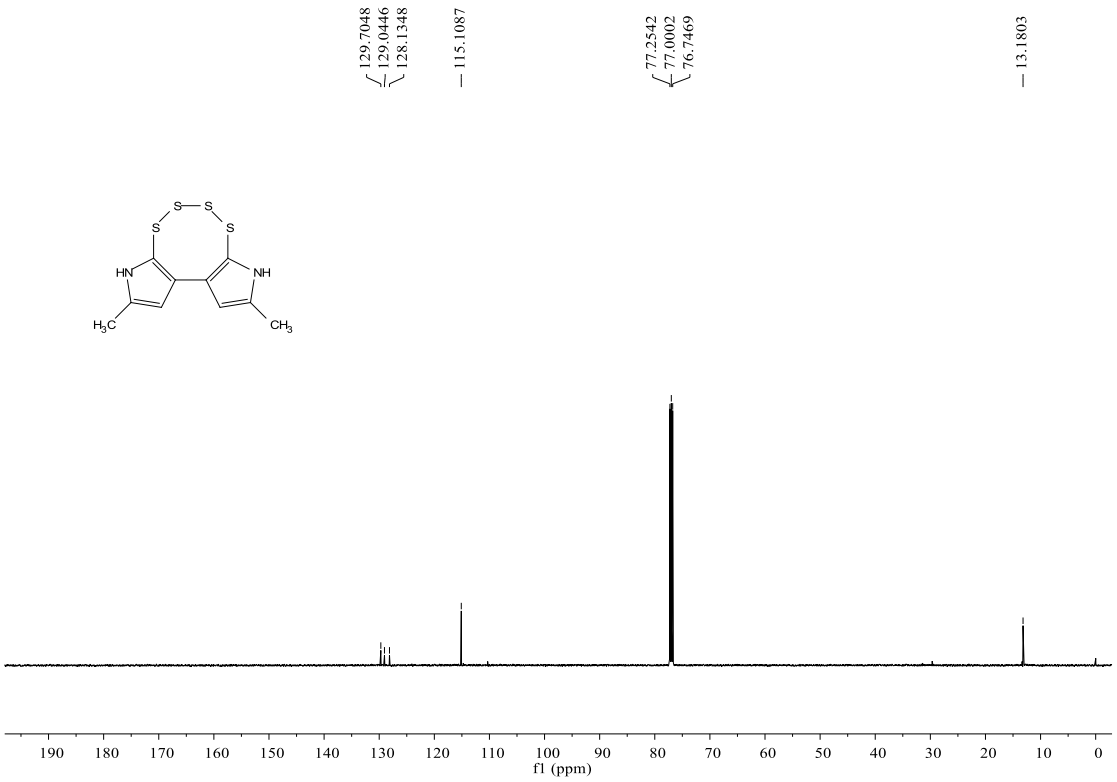
^{1}H and ^{13}C NMR spectra of **2y**



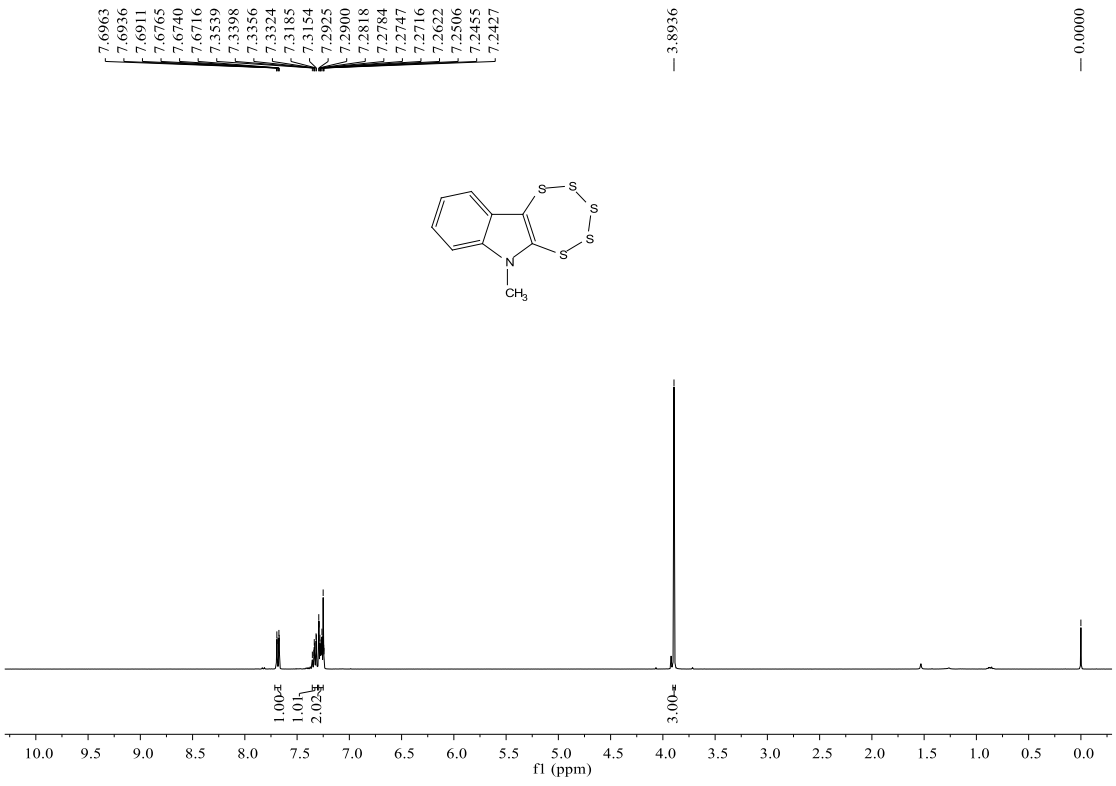


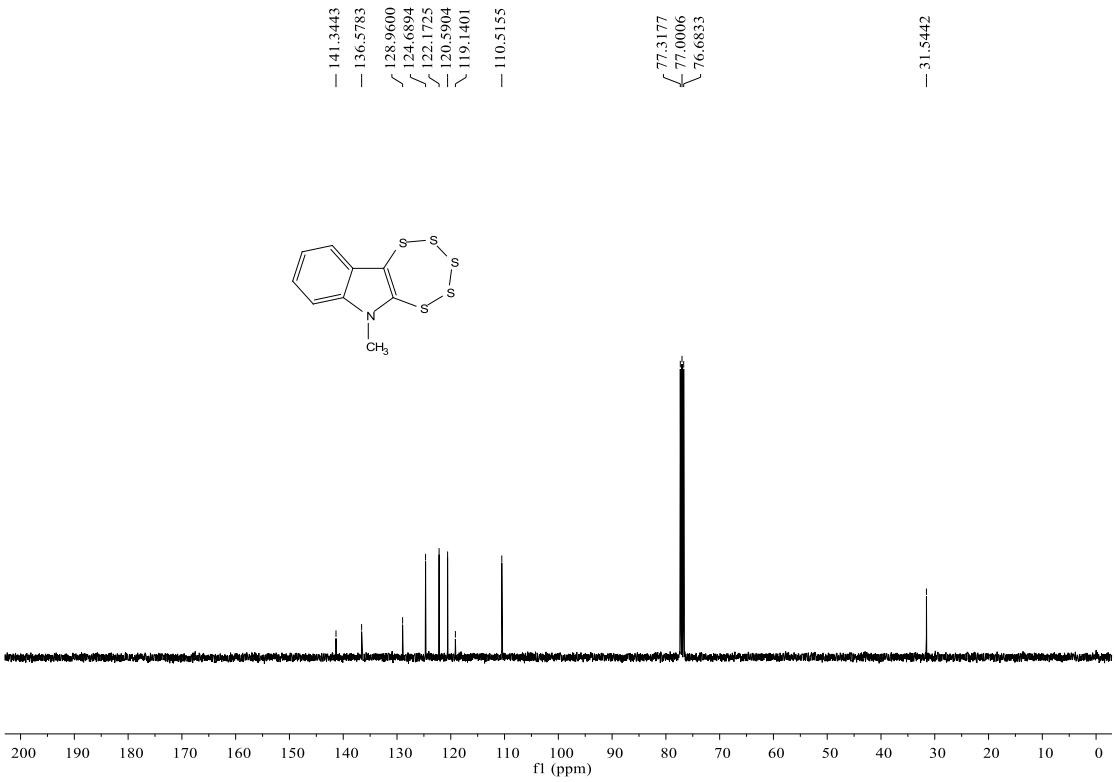
^{1}H and ^{13}C NMR spectra of **2z**



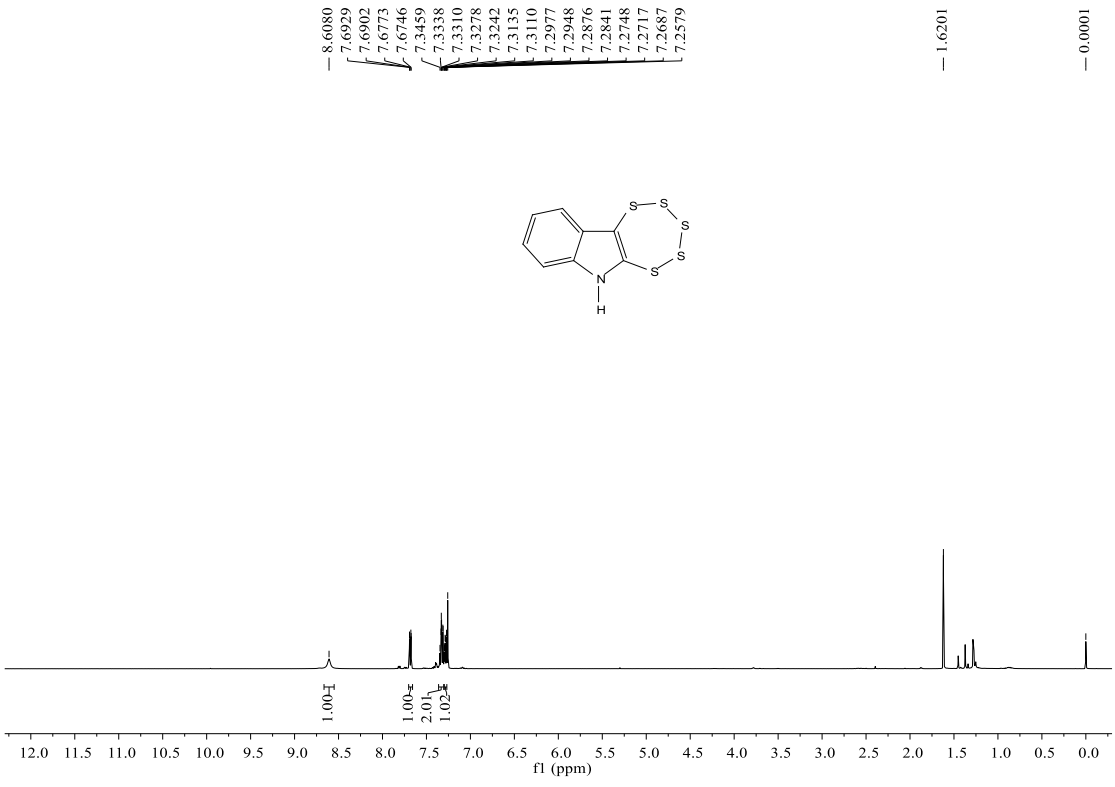


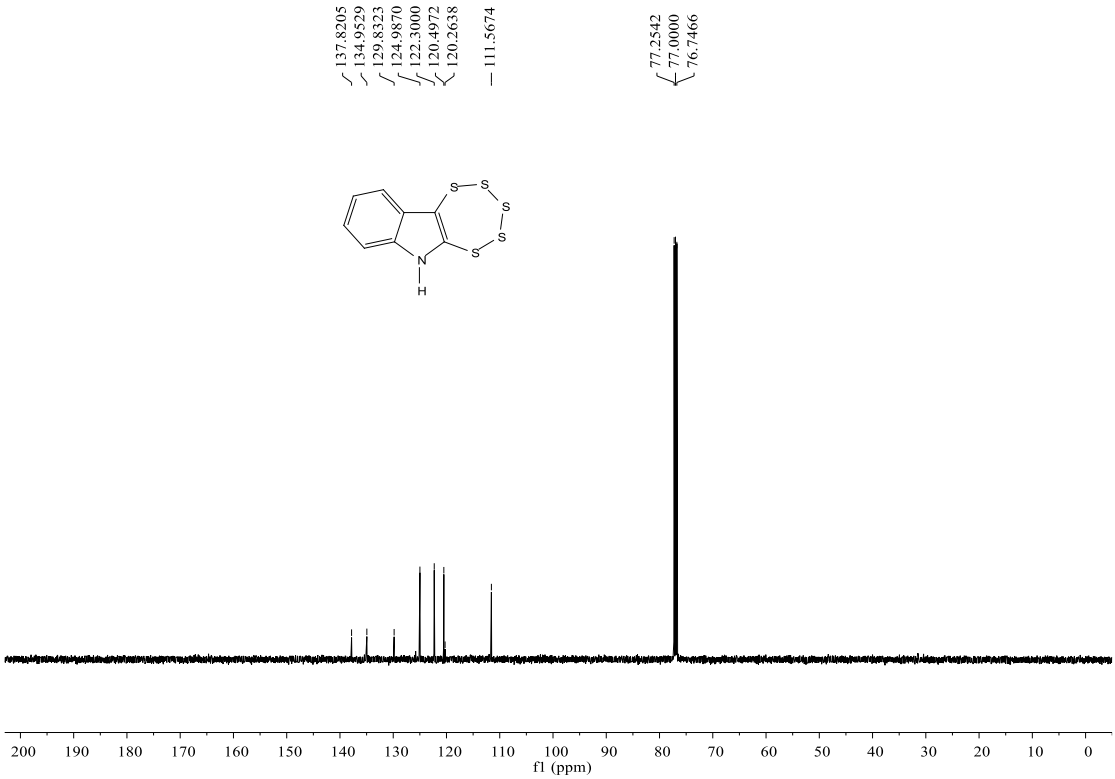
^{1}H and ^{13}C NMR spectra of **3a**



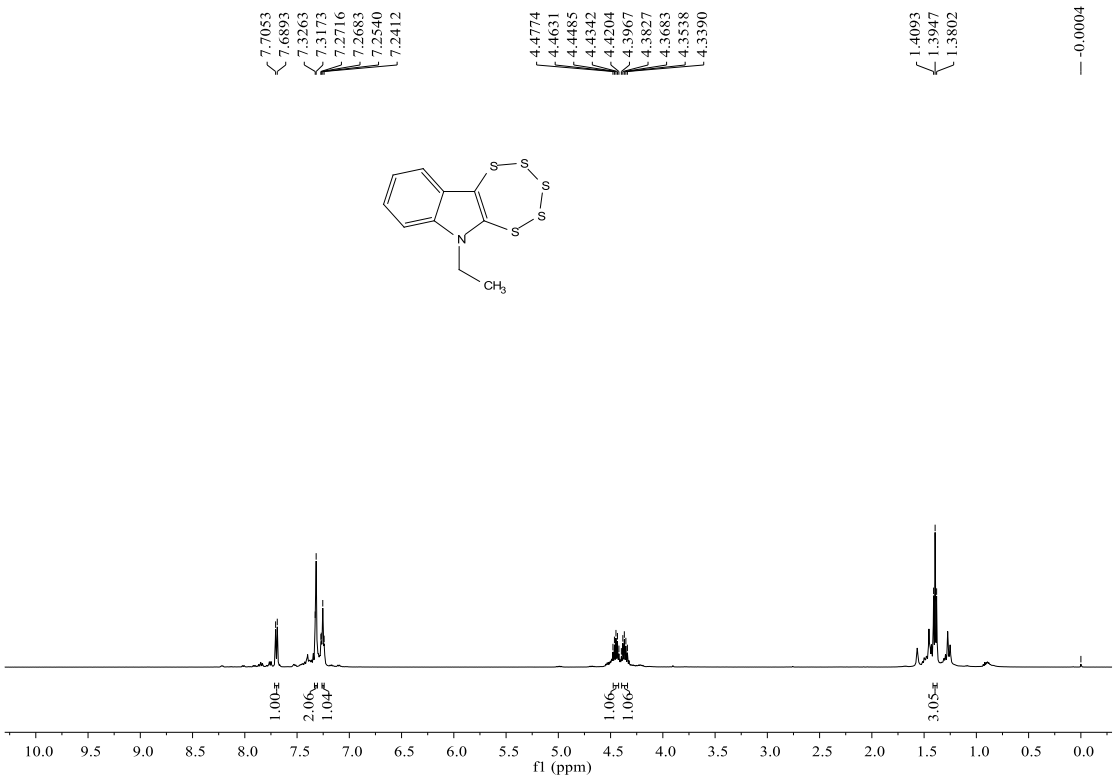


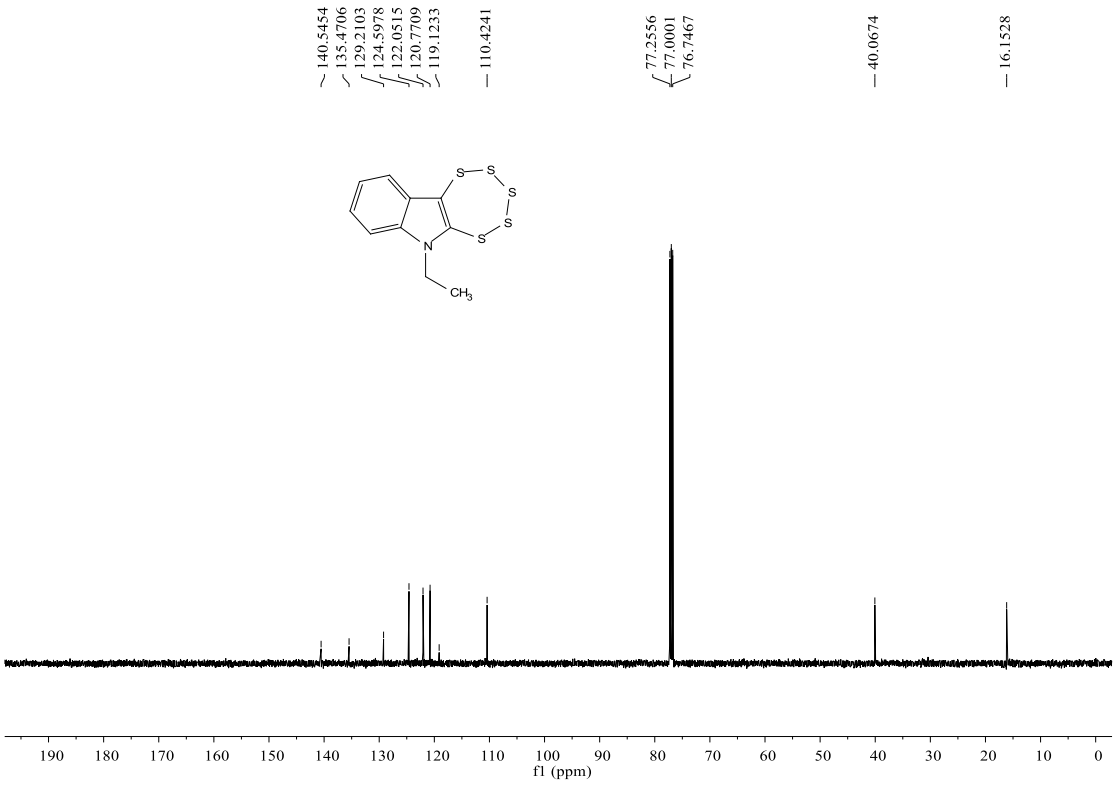
^{1}H and ^{13}C NMR spectra of **3b**



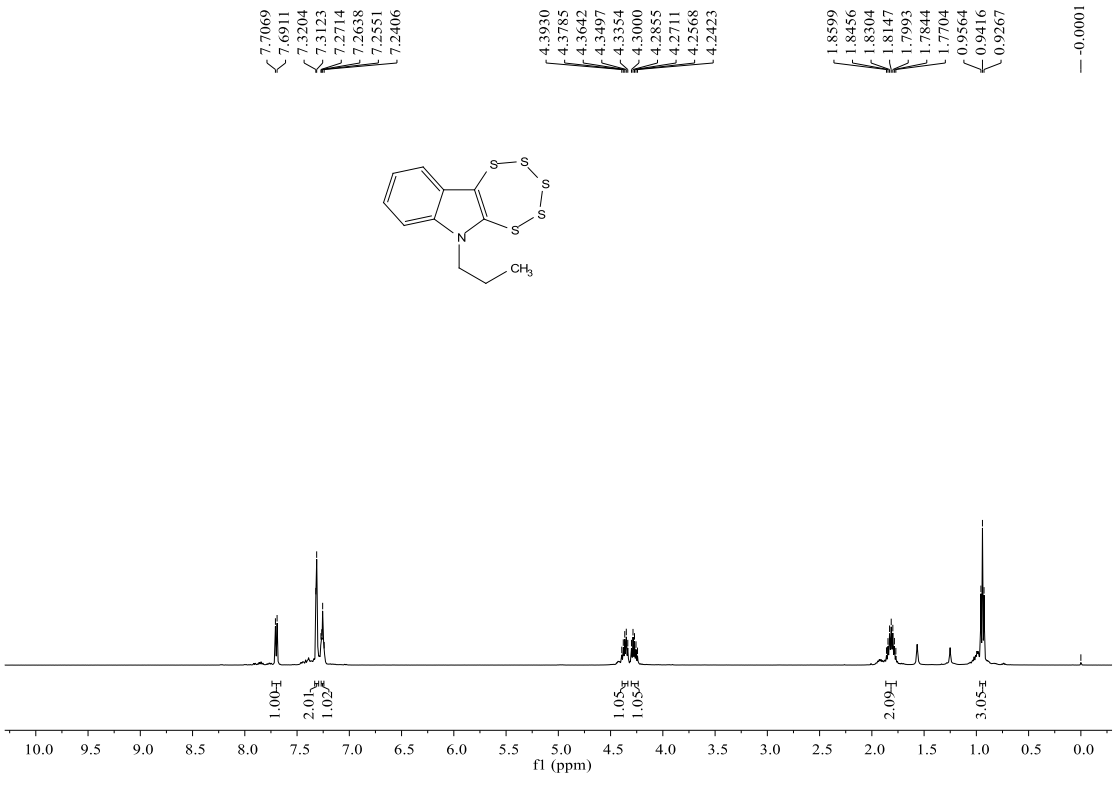


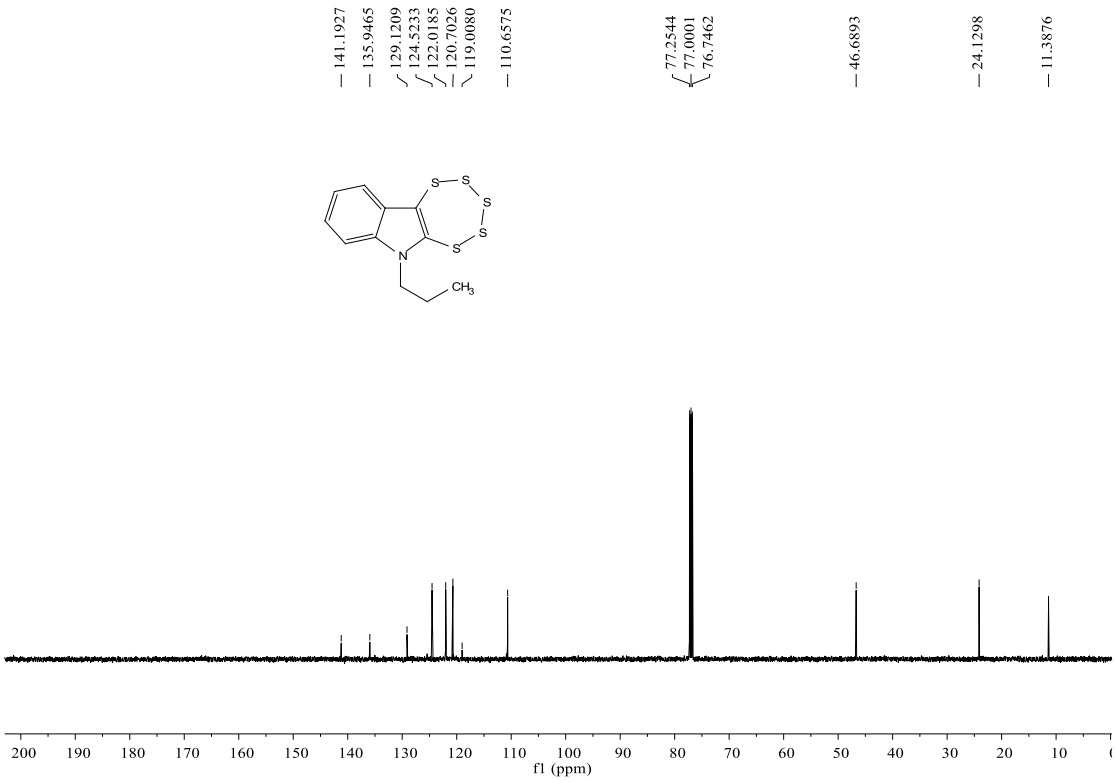
^{1}H and ^{13}C NMR spectra of **3c**



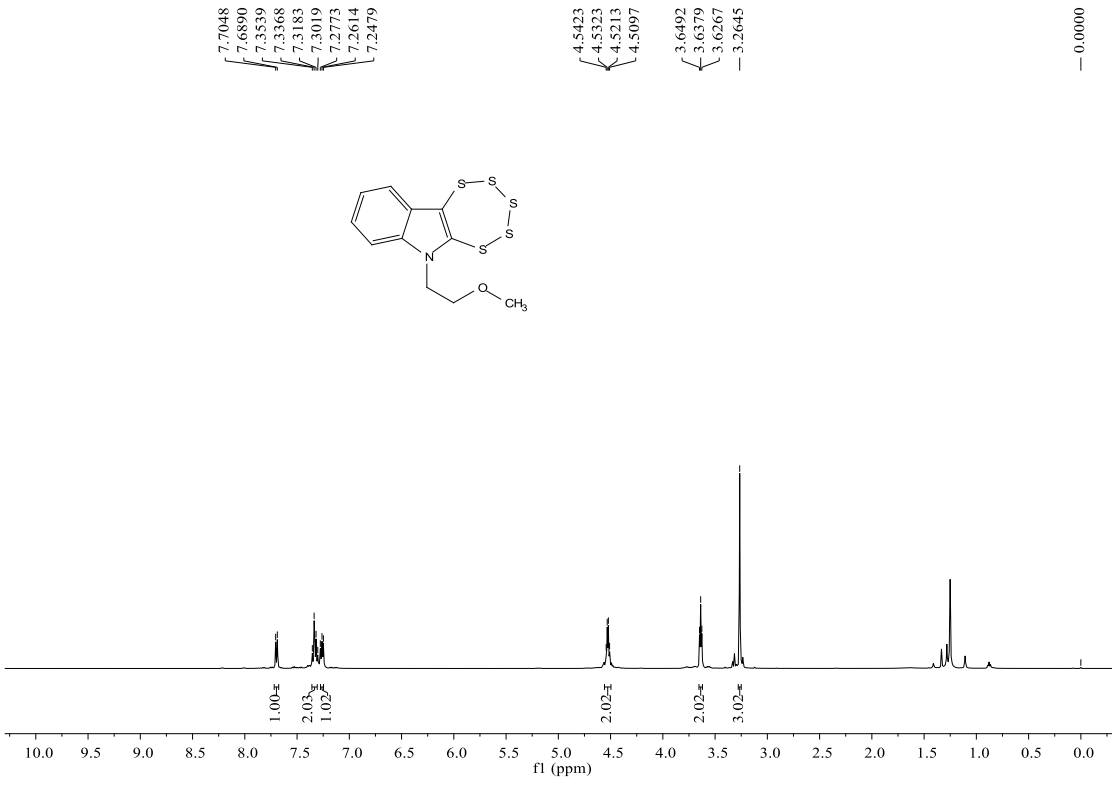


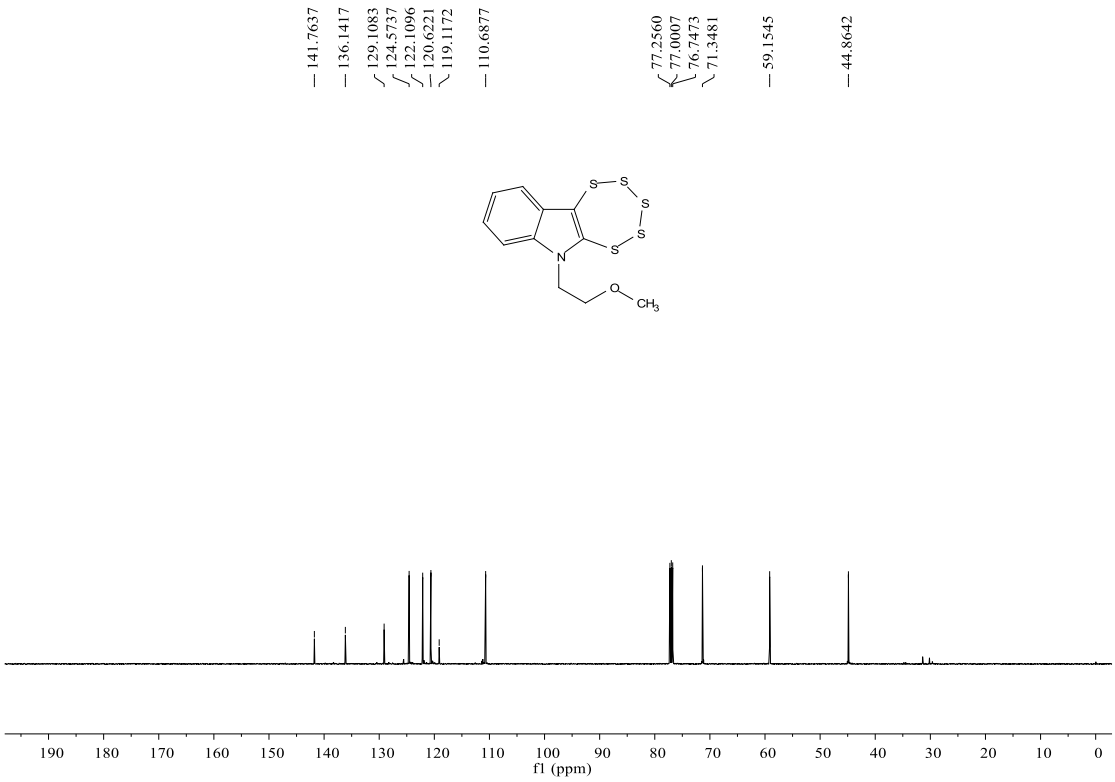
^{1}H and ^{13}C NMR spectra of **3d**



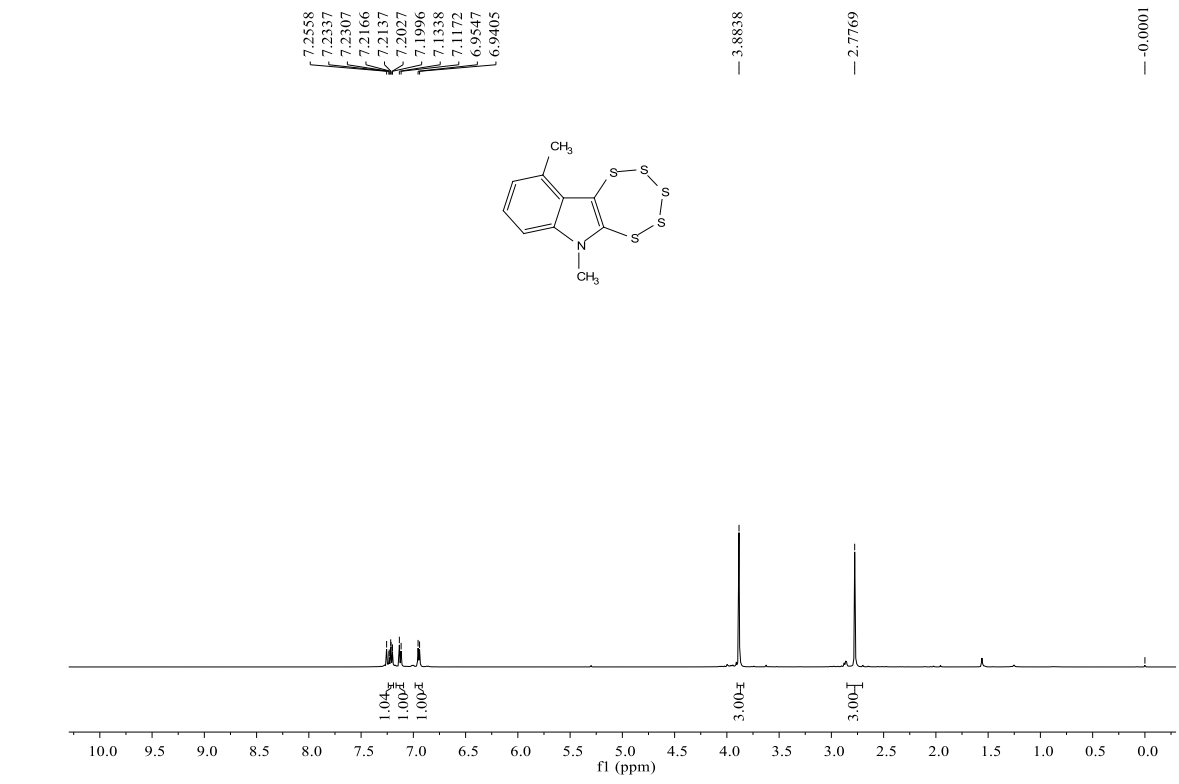


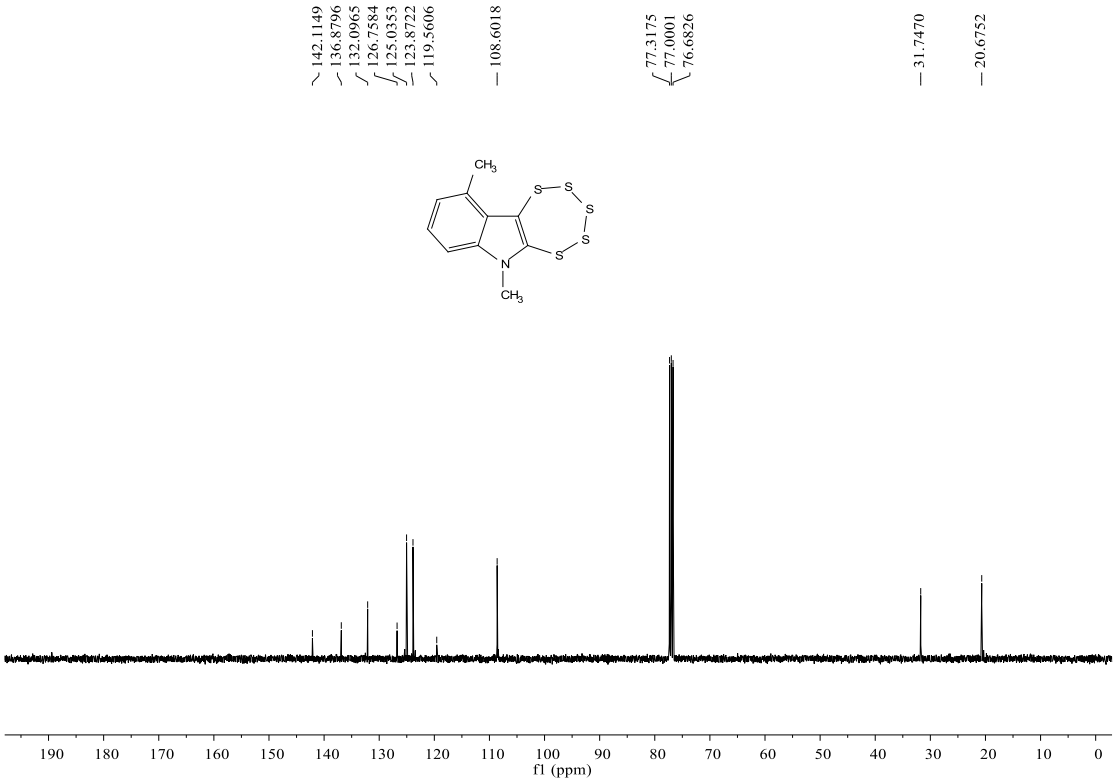
^{1}H and ^{13}C NMR spectra of **3f**



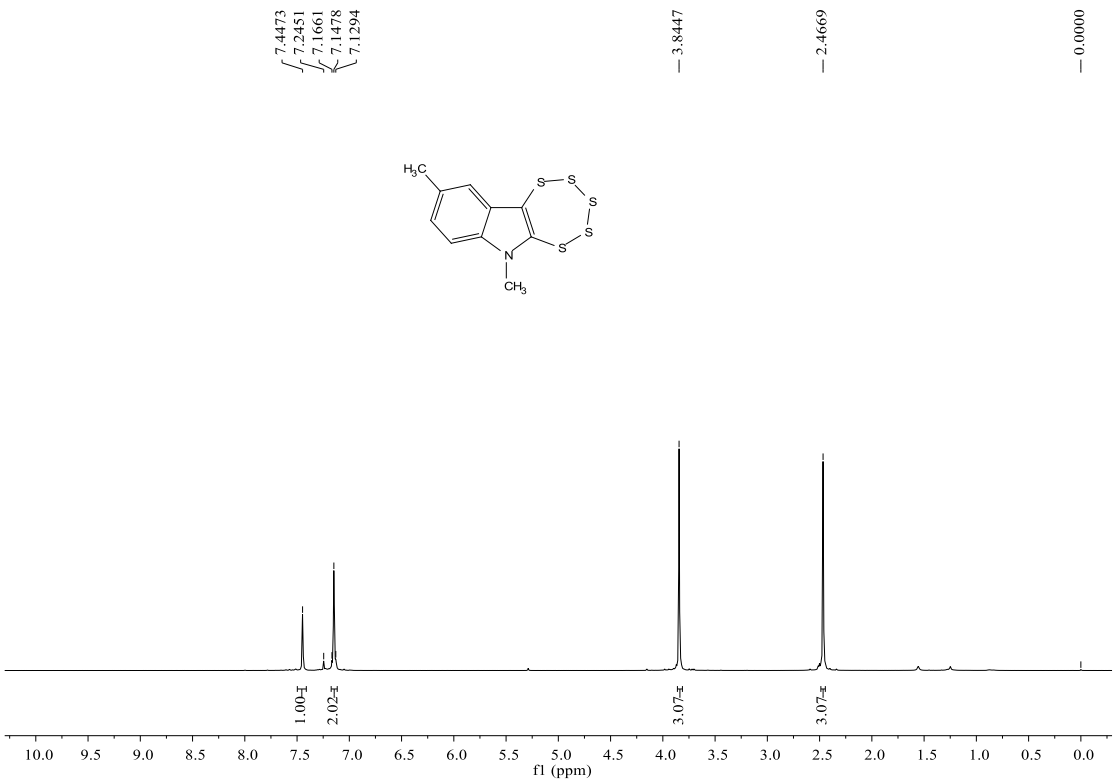


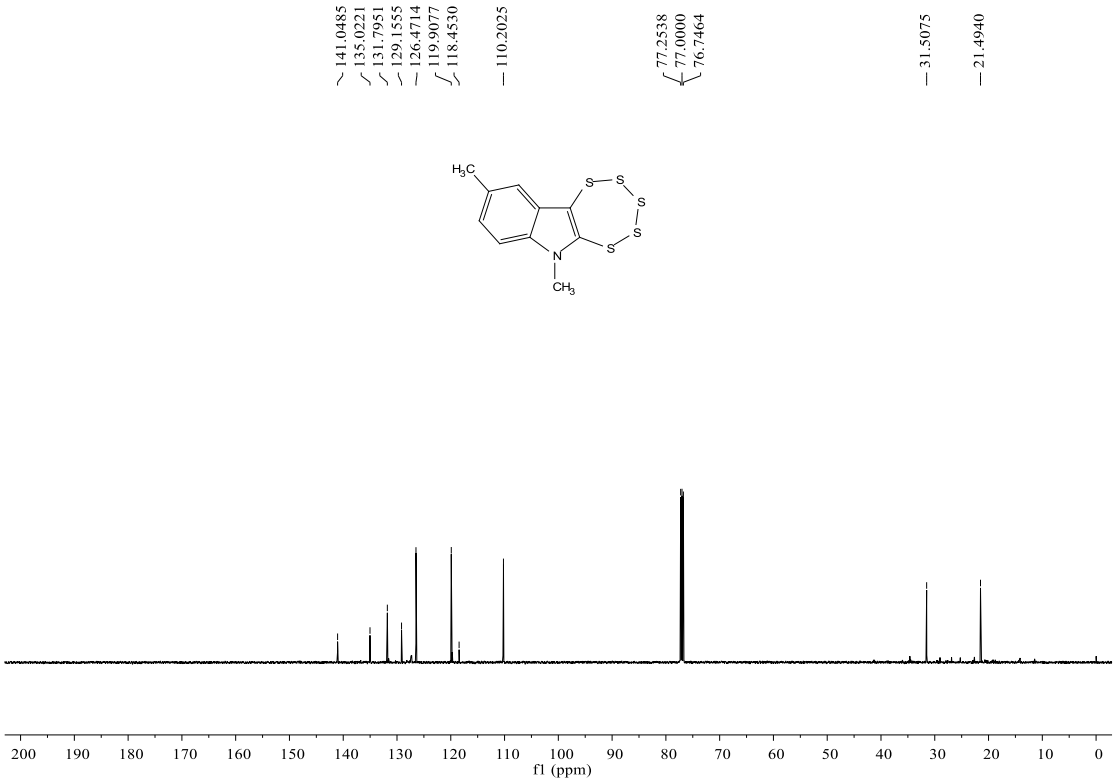
^{1}H and ^{13}C NMR spectra of **3j**



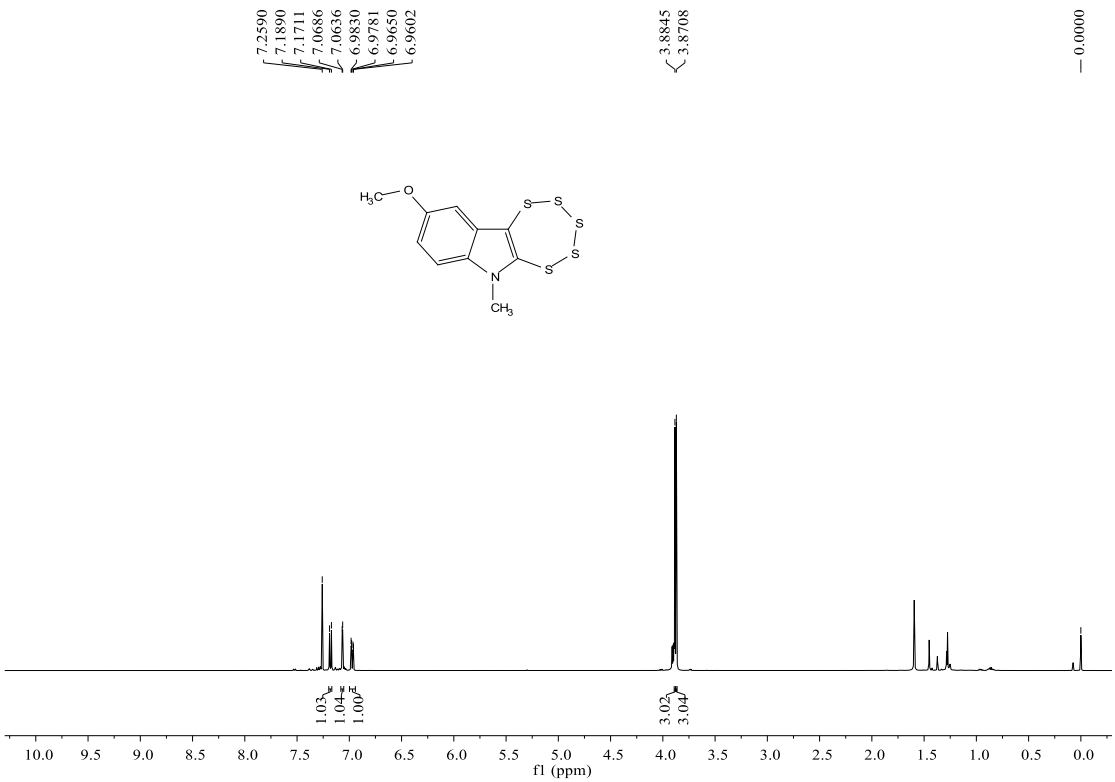


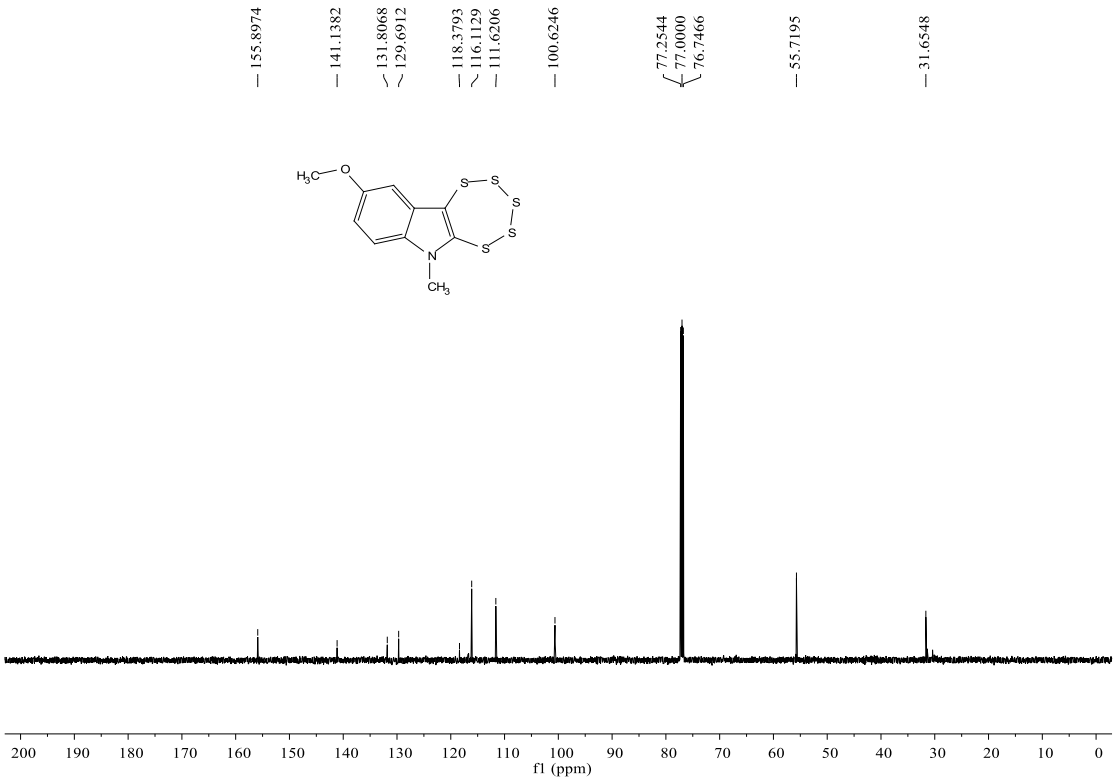
^{1}H and ^{13}C NMR spectra of **3l**



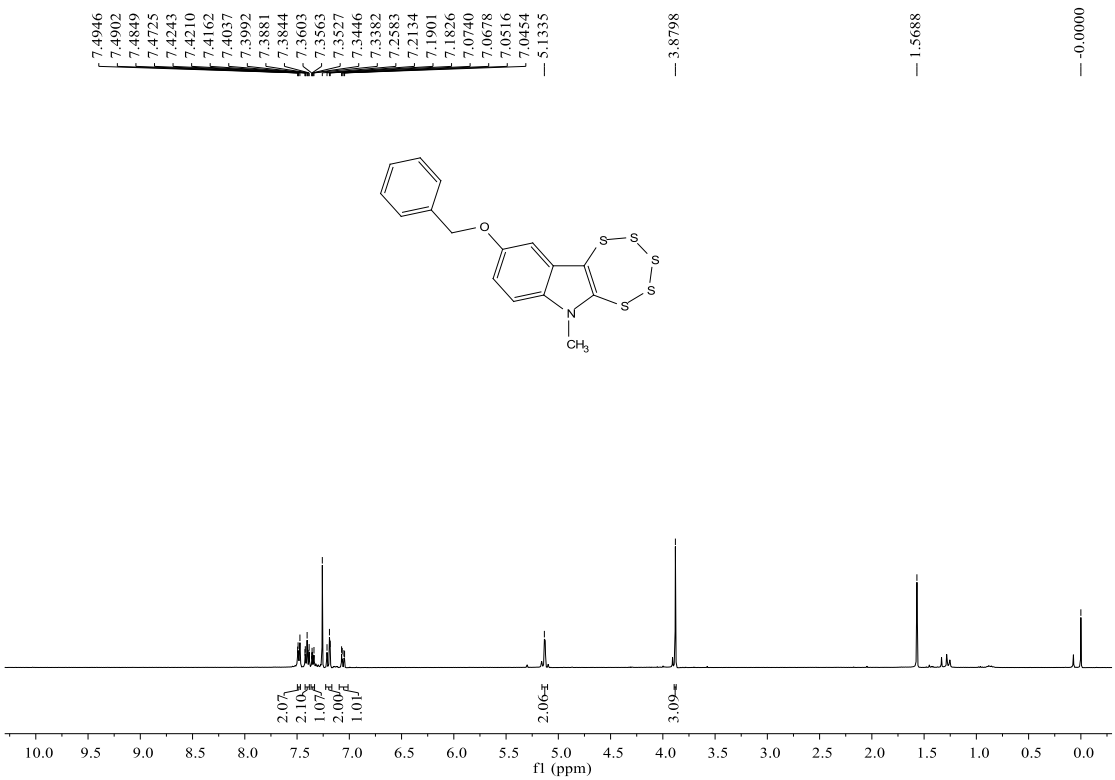


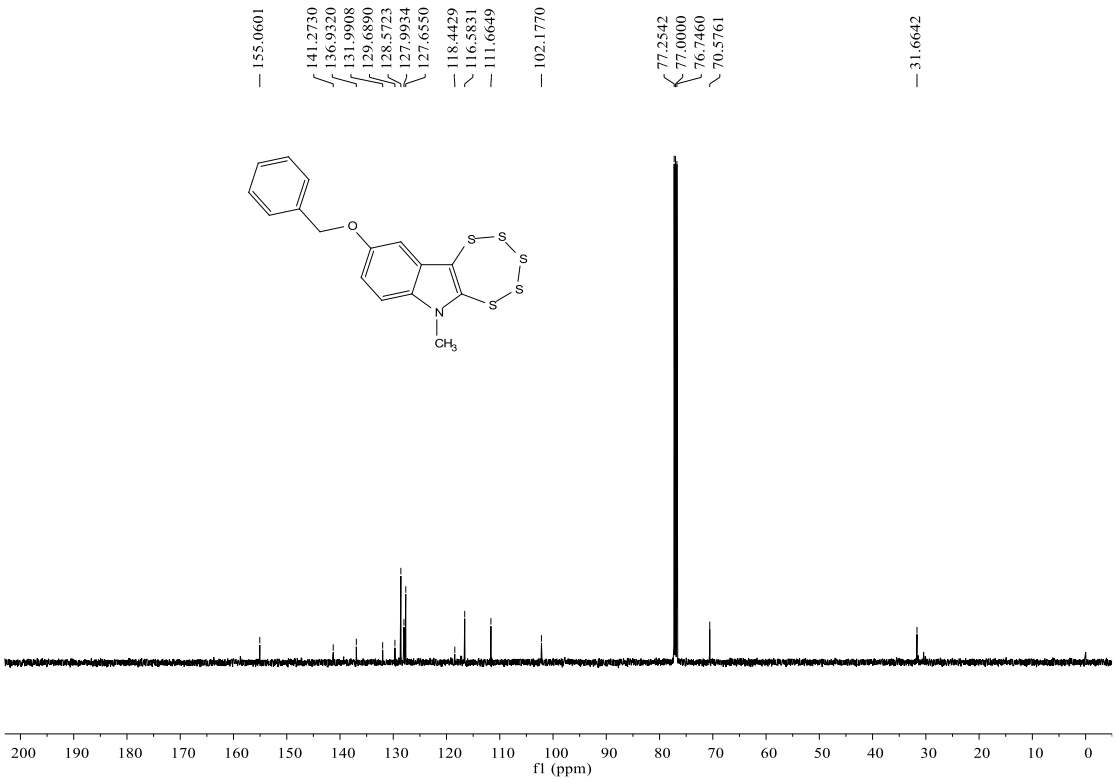
^{1}H and ^{13}C NMR spectra of **3m**



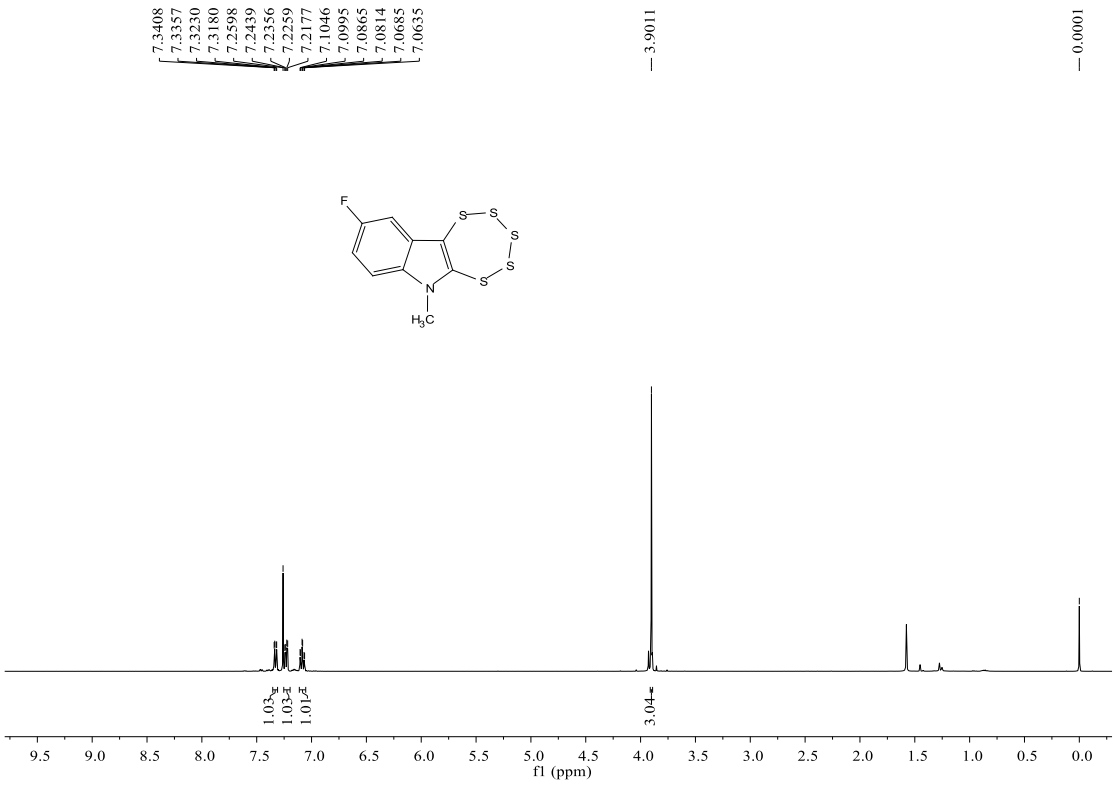


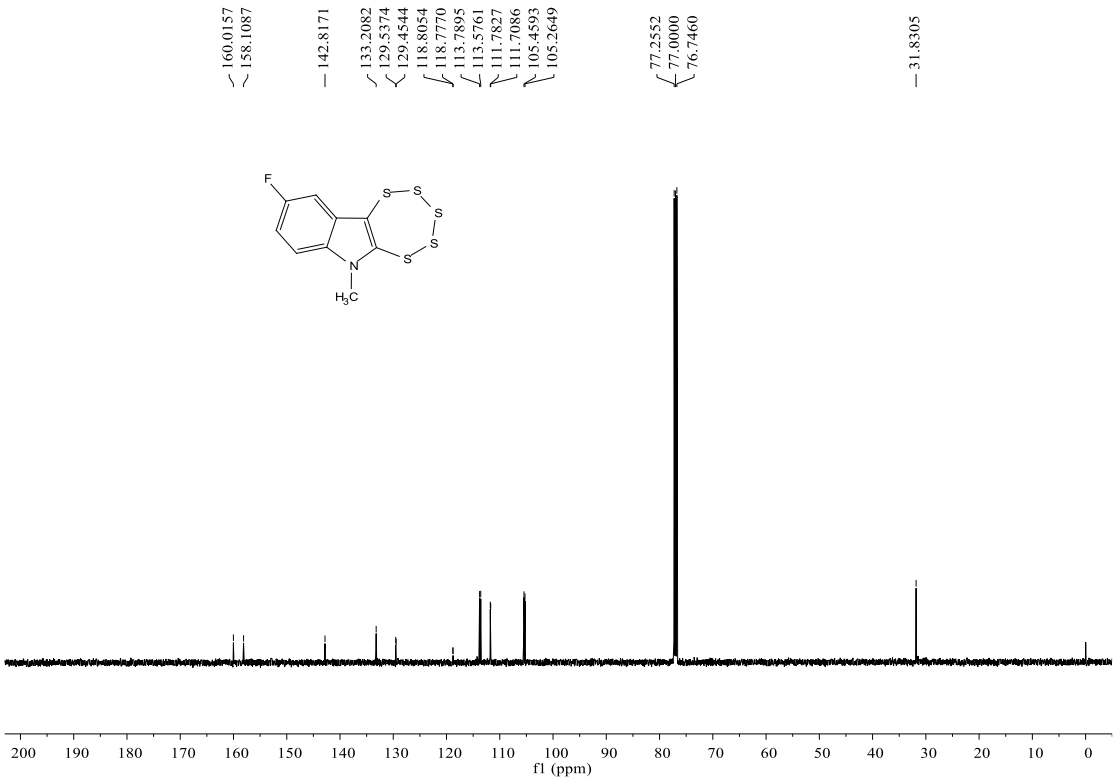
^{1}H and ^{13}C NMR spectra of **3n**





^{1}H, ^{13}C and ^{19}F NMR spectra of **3o**

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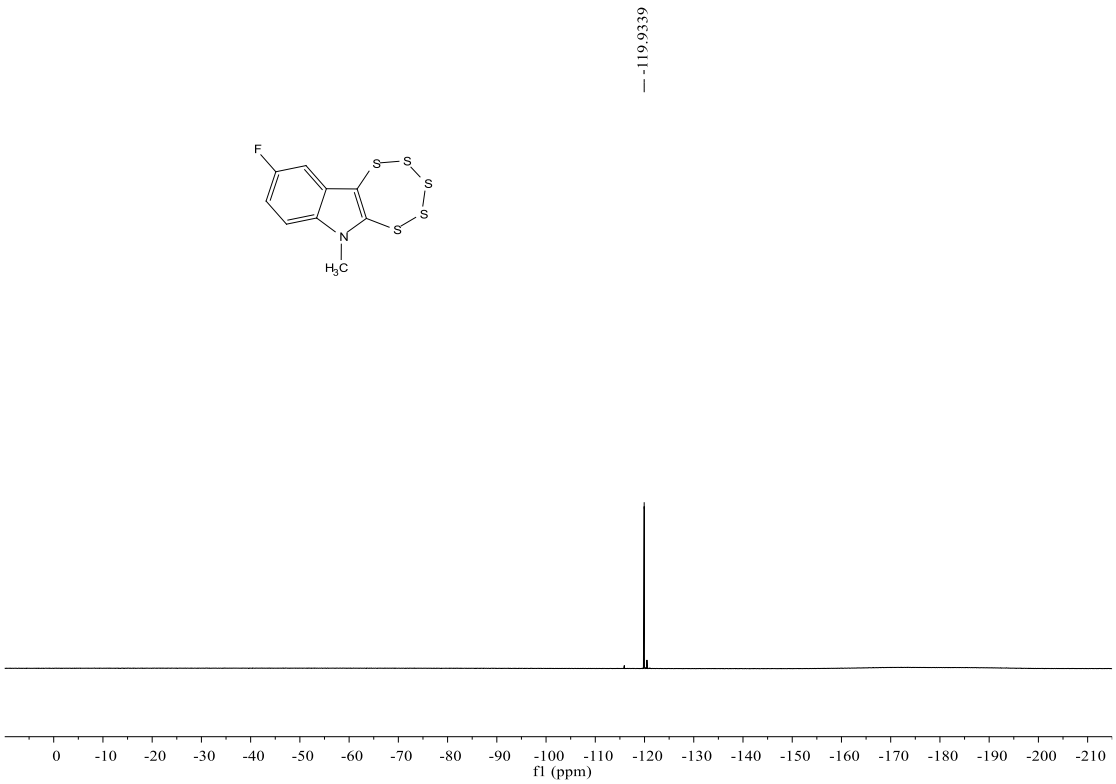
111.7827
111.7086
105.4593
105.2649
77.2552
77.0000
76.7460
31.8305
F
S
S
S
S
S
S
N
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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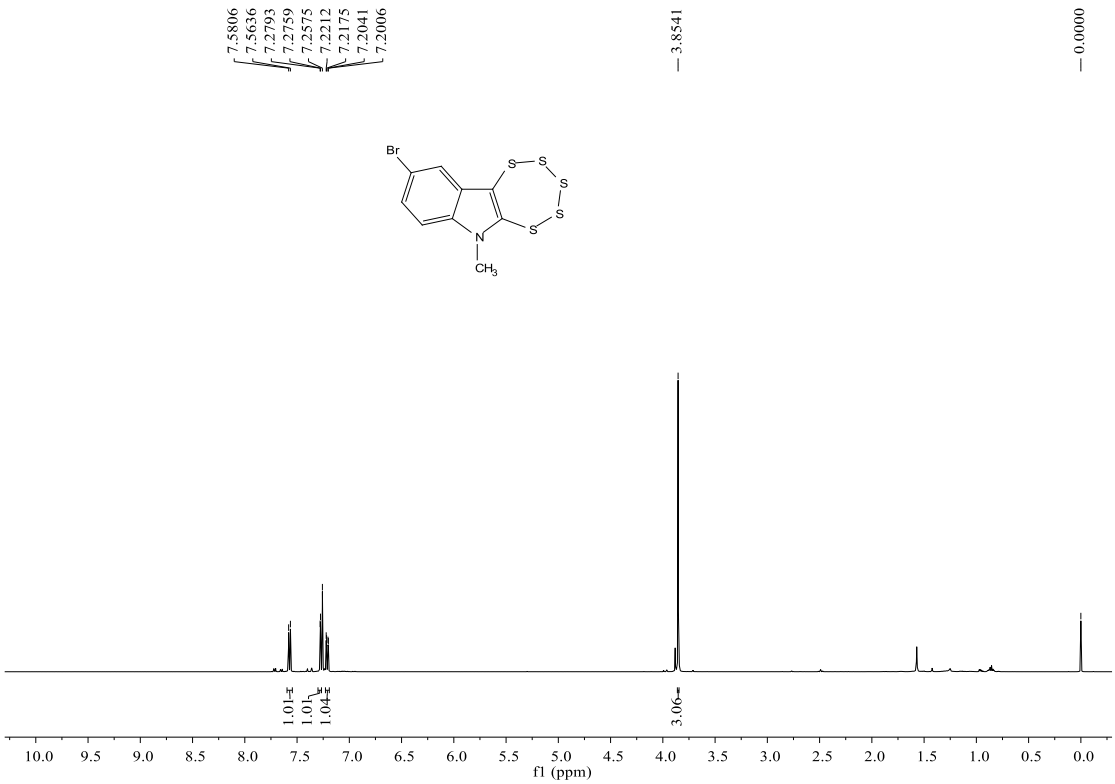
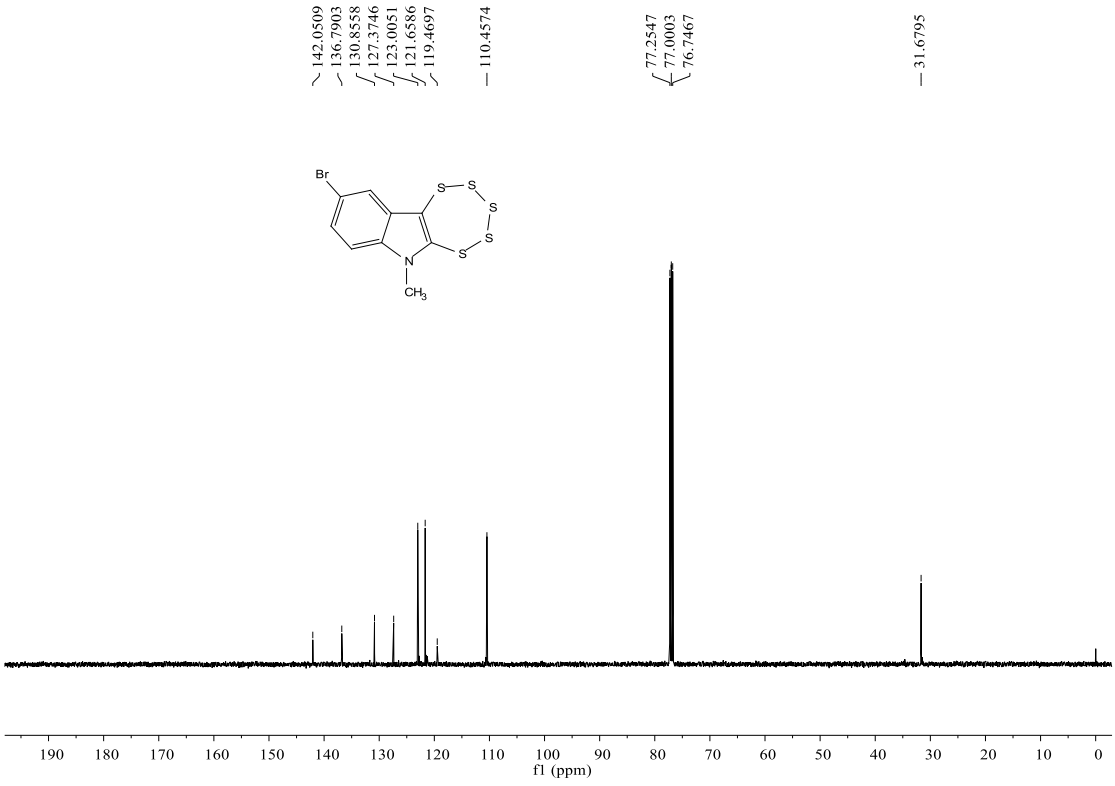
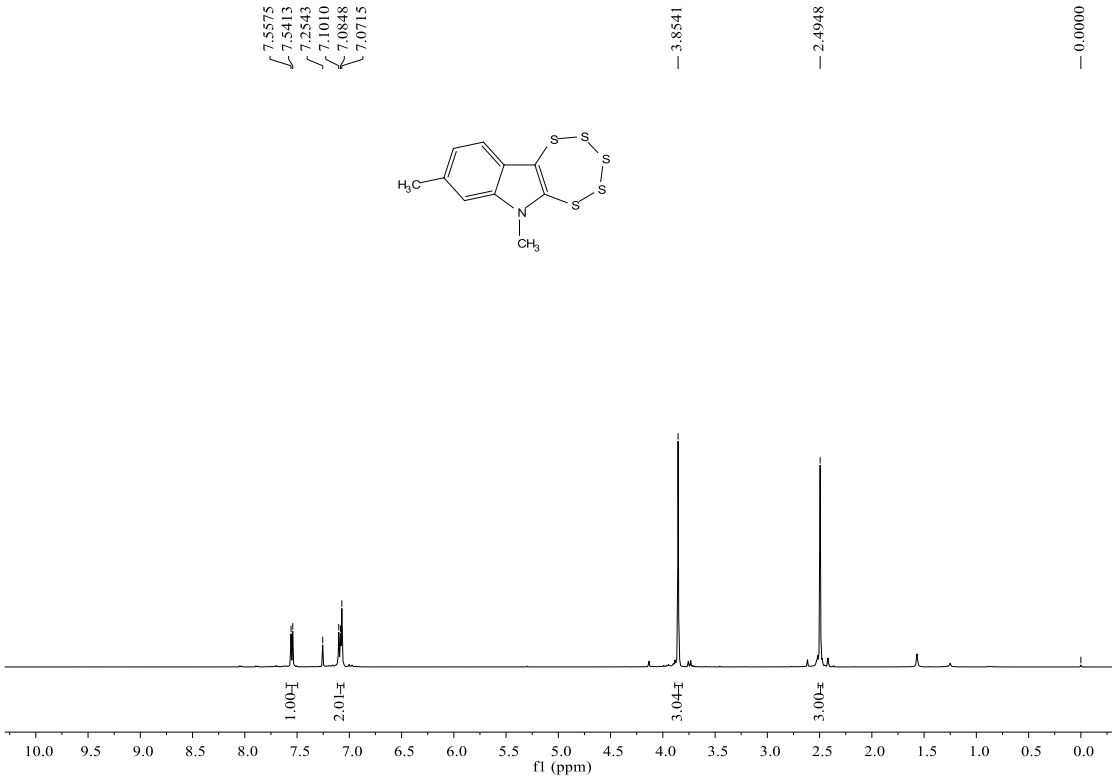
F
S
S
S
S
S
S
N
H3C
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

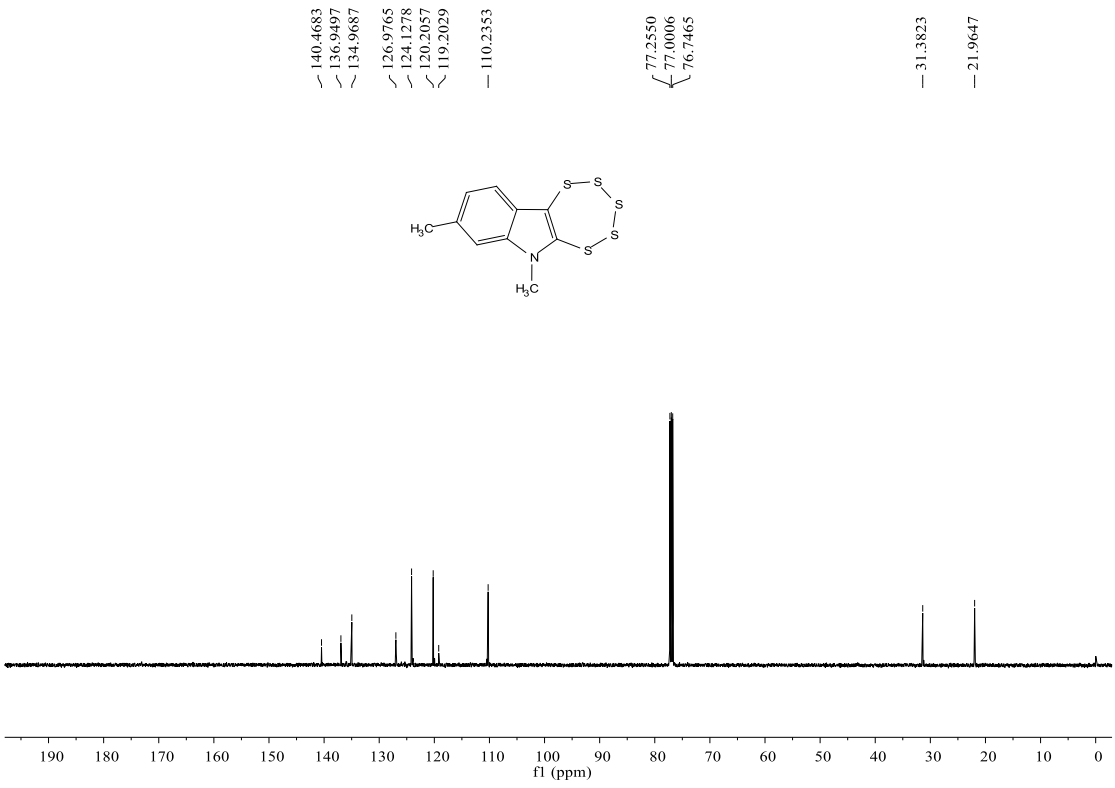
^{1}H and ^{13}C NMR spectra of **3q**



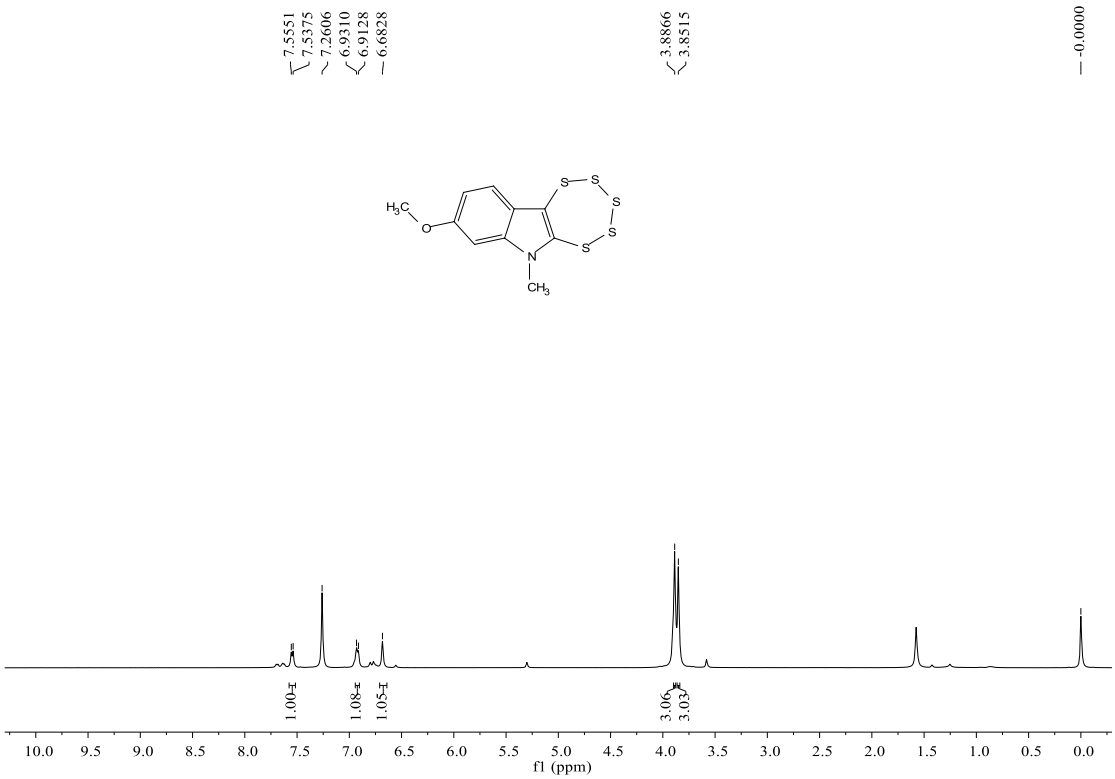


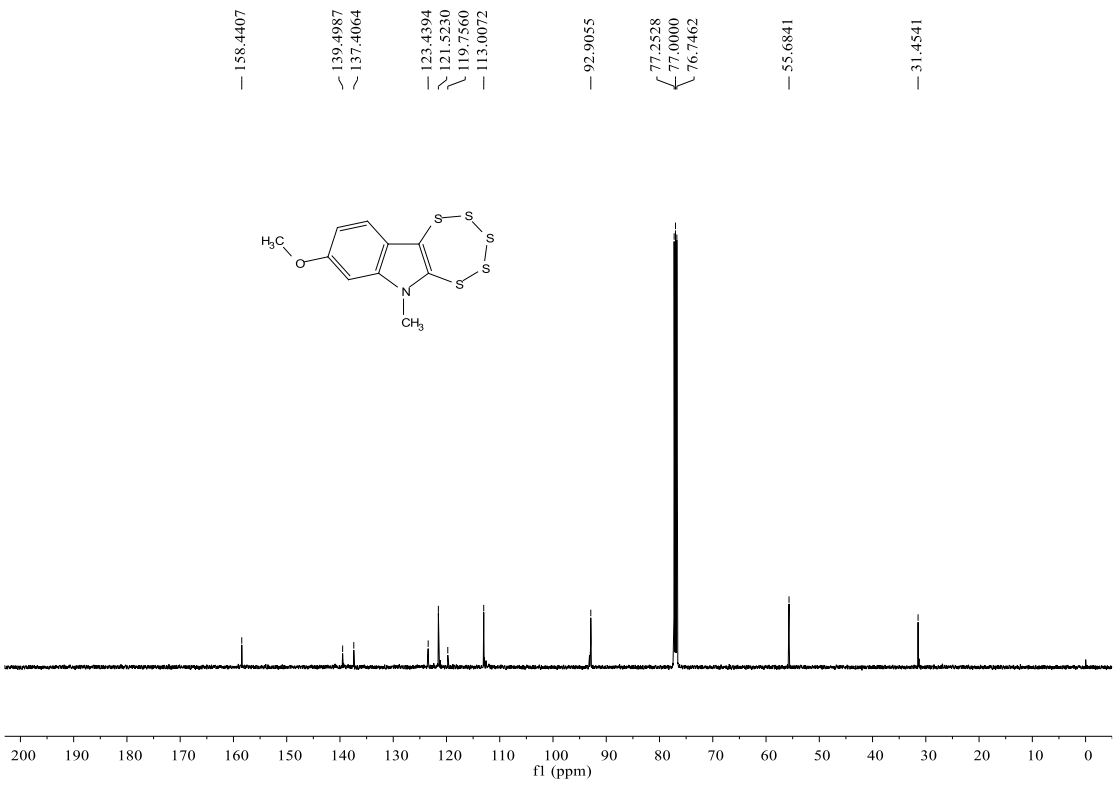
^{1}H and ^{13}C NMR spectra of **3r**



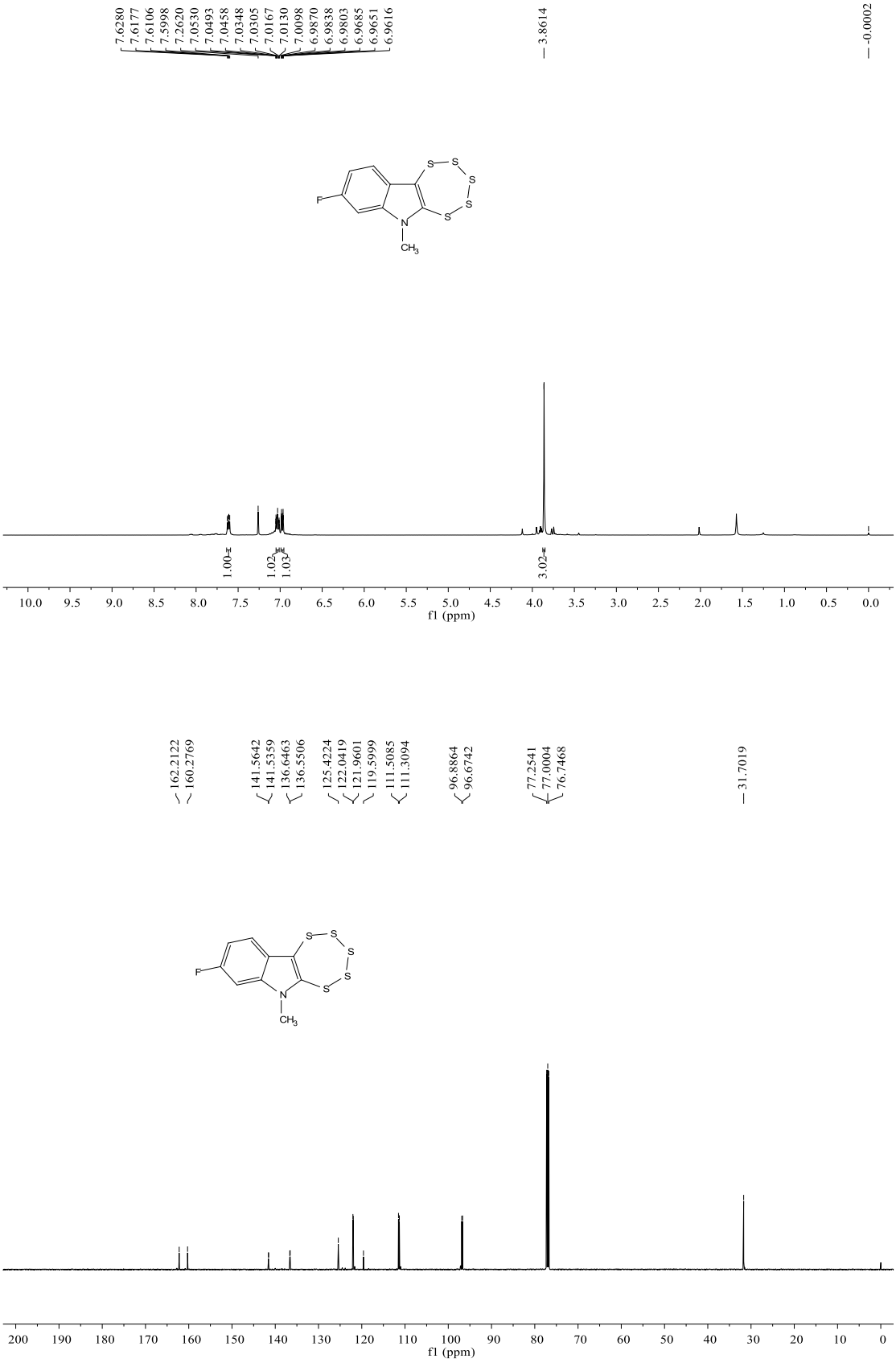


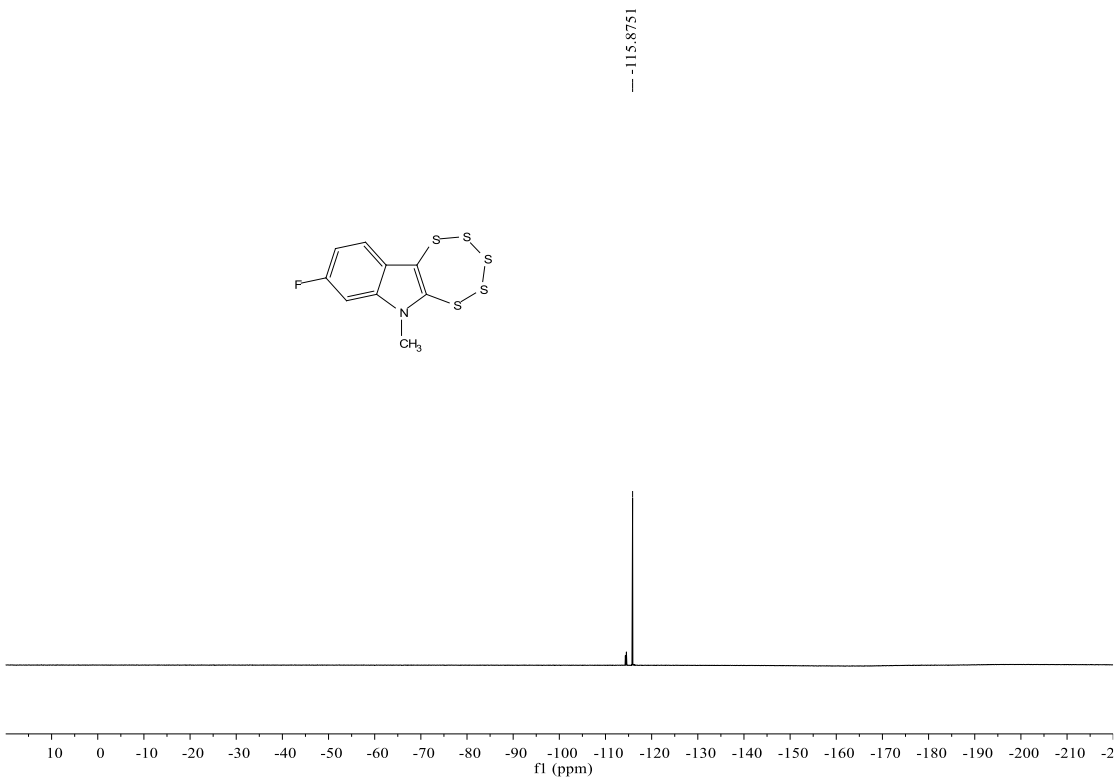
^{1}H and ^{13}C NMR spectra of **3s**



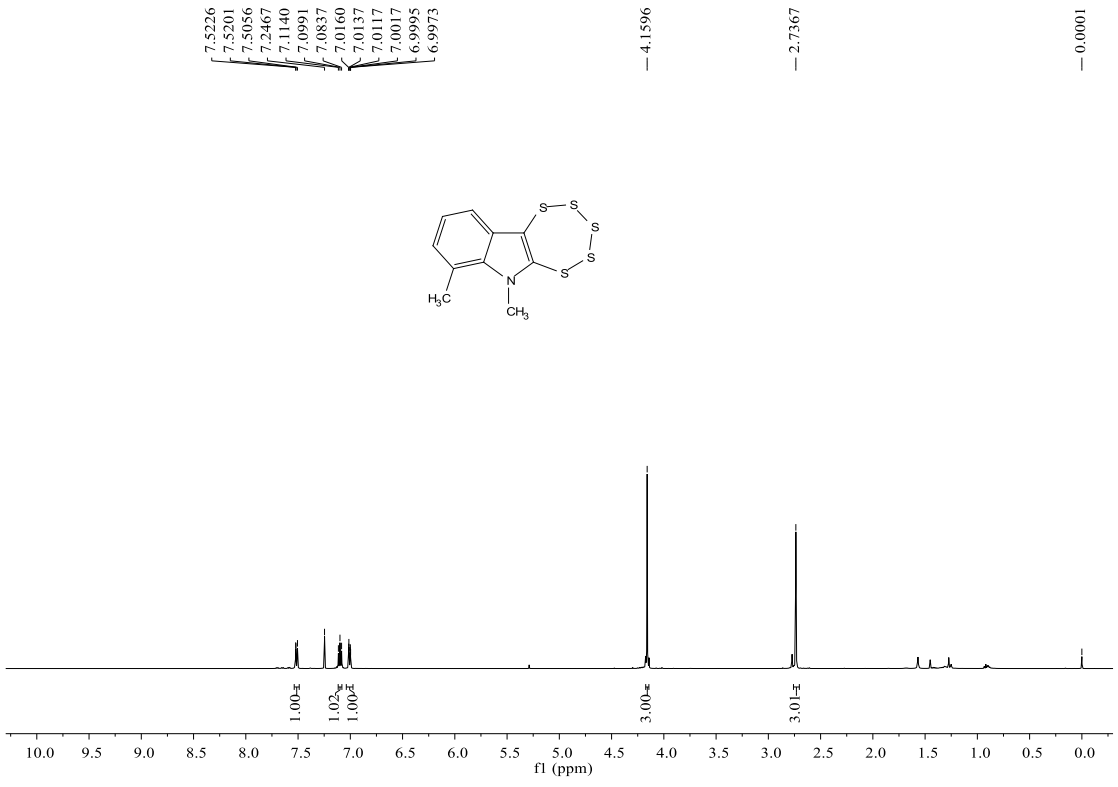


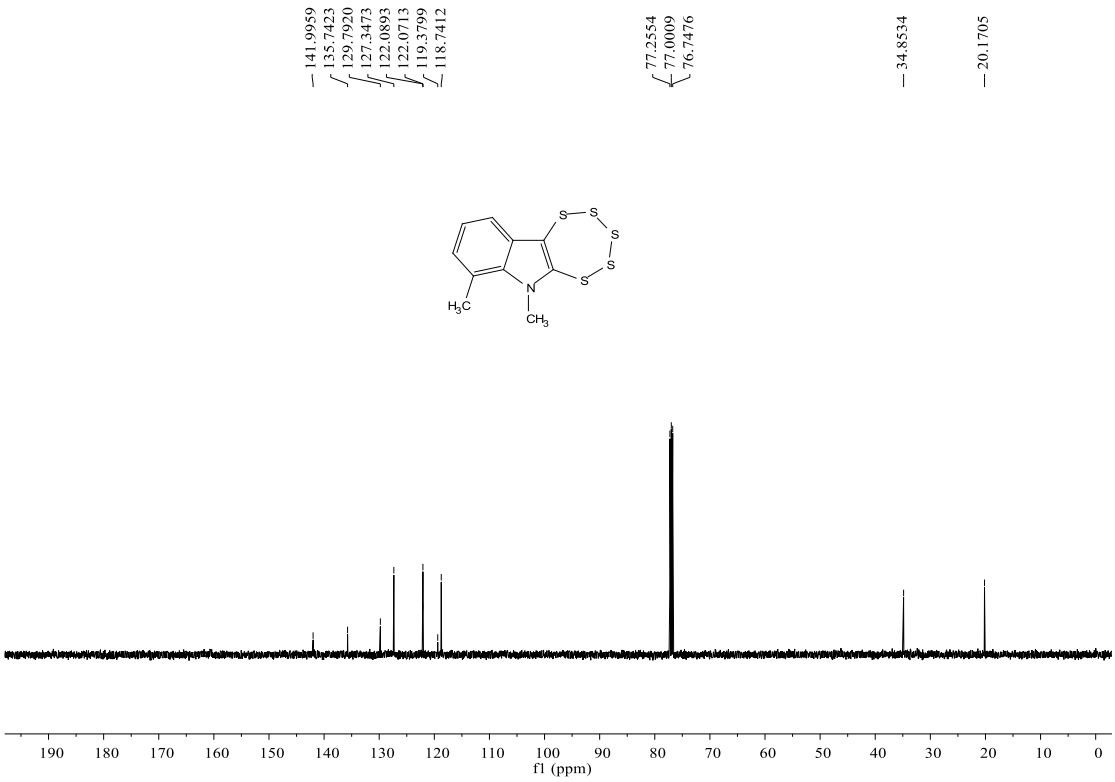
^{1}H, ^{13}C and ^{19}F NMR spectra of **3t**



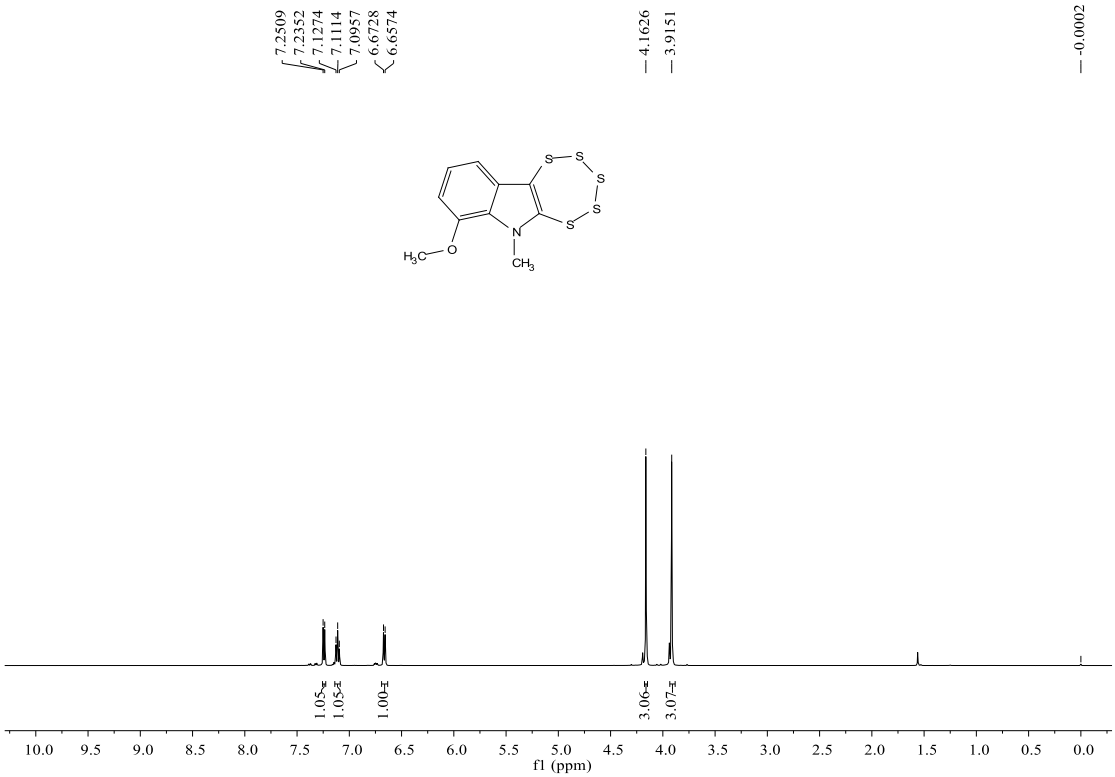


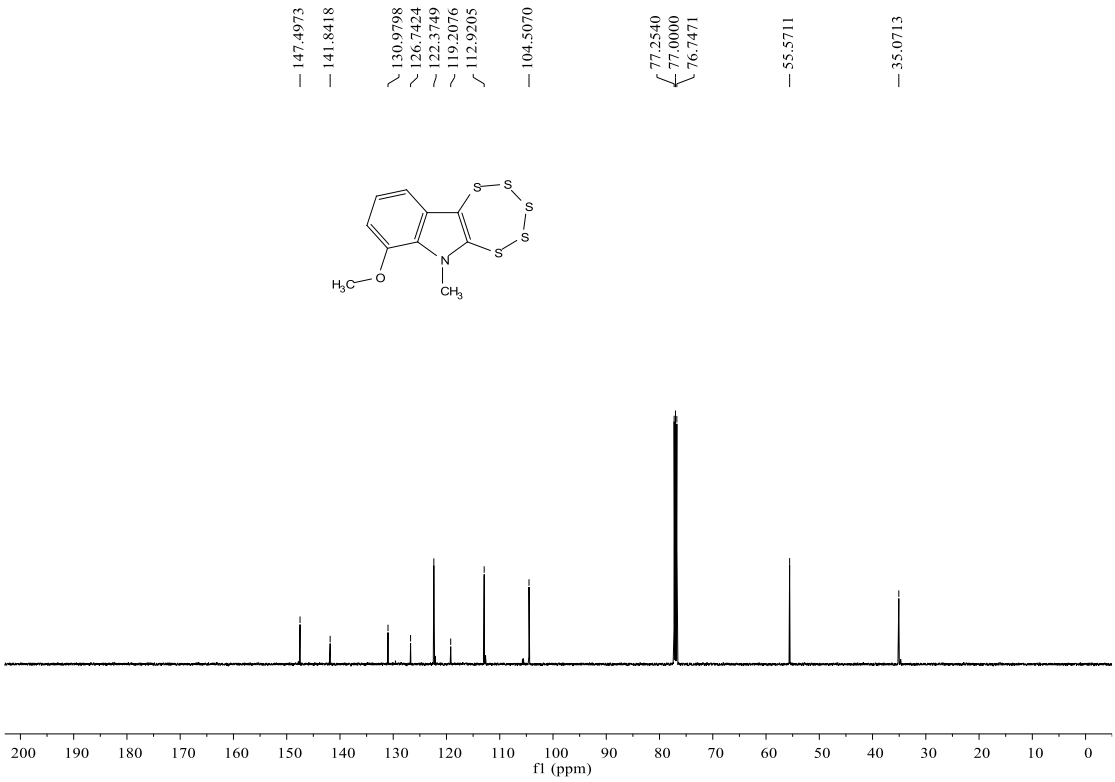
^{1}H and ^{13}C NMR spectra of **3v**



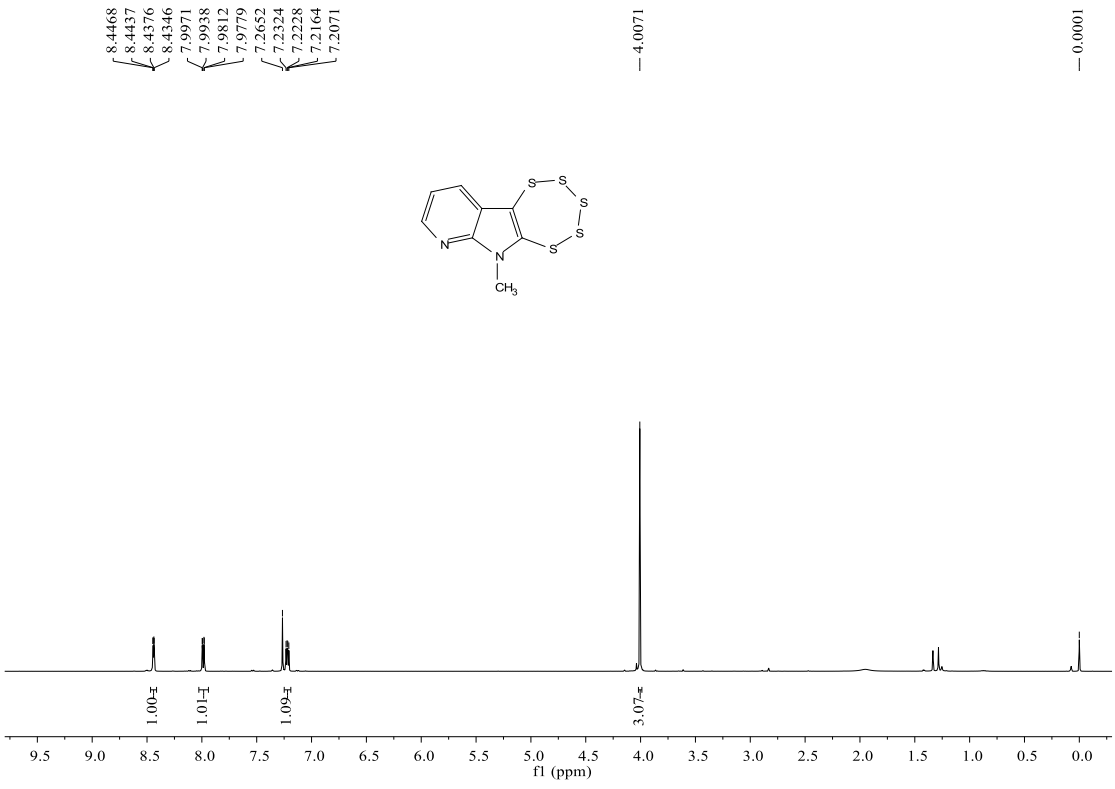


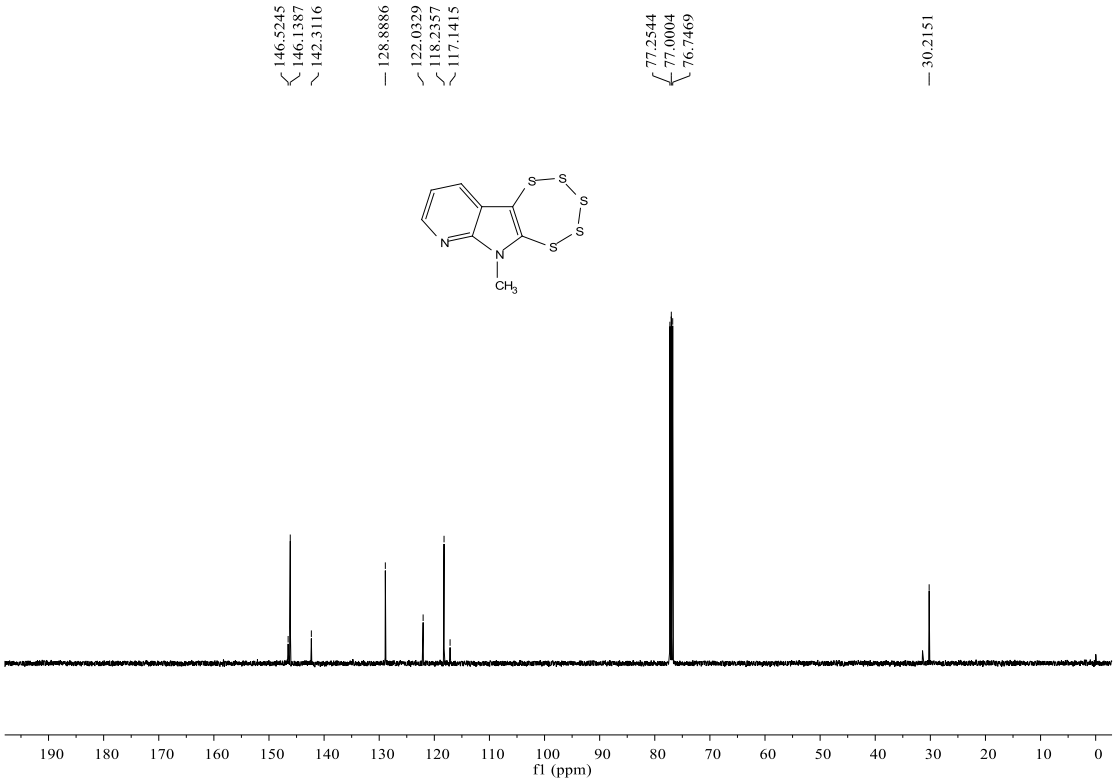
^{1}H and ^{13}C NMR spectra of **3w**



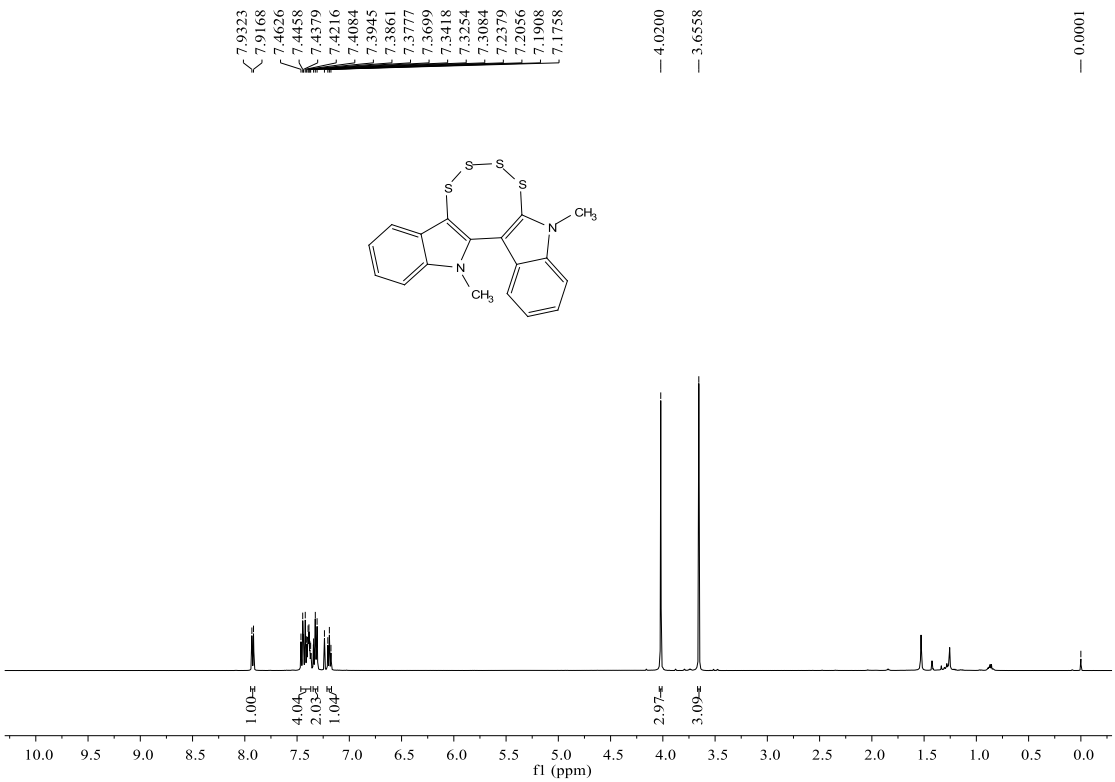


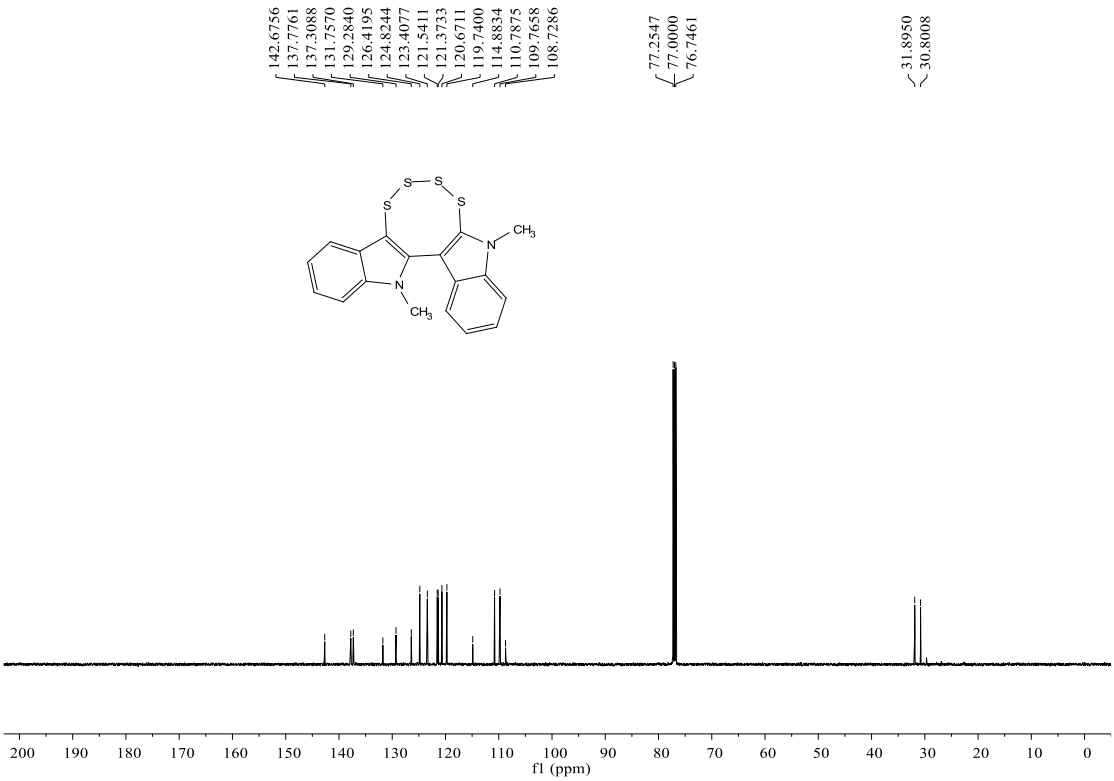
^{1}H and ^{13}C NMR spectra of **3y**



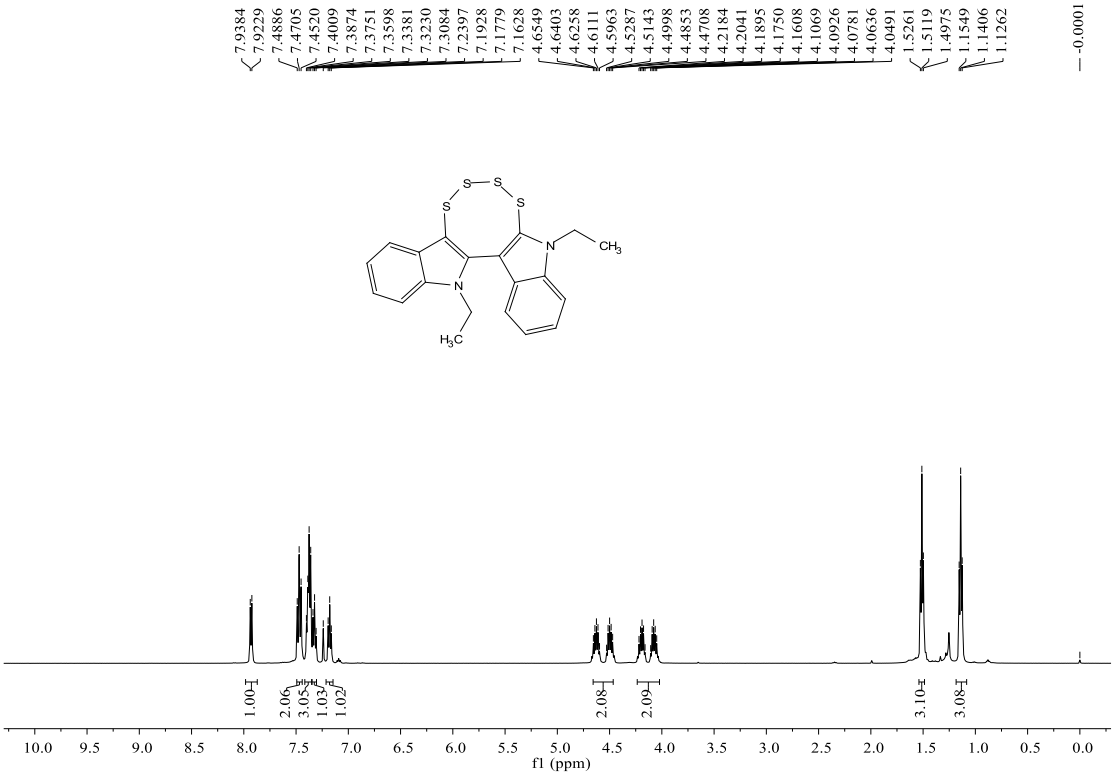


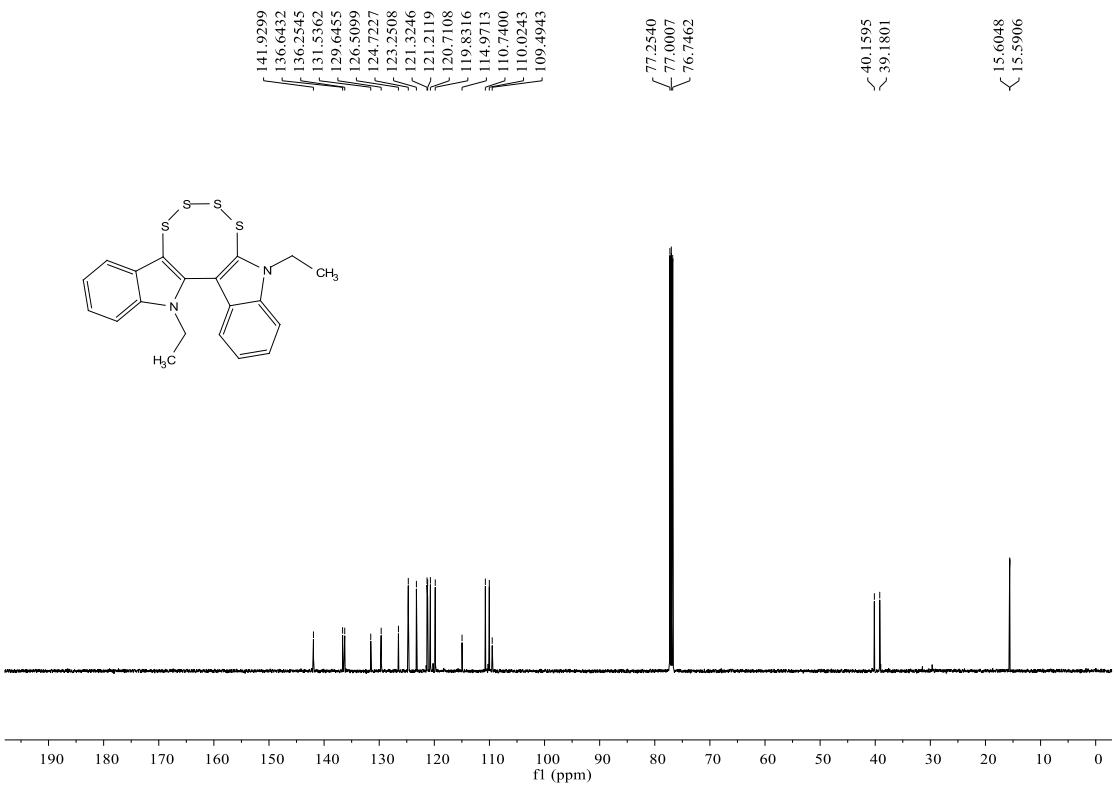
^{1}H and ^{13}C NMR spectra of **4a**



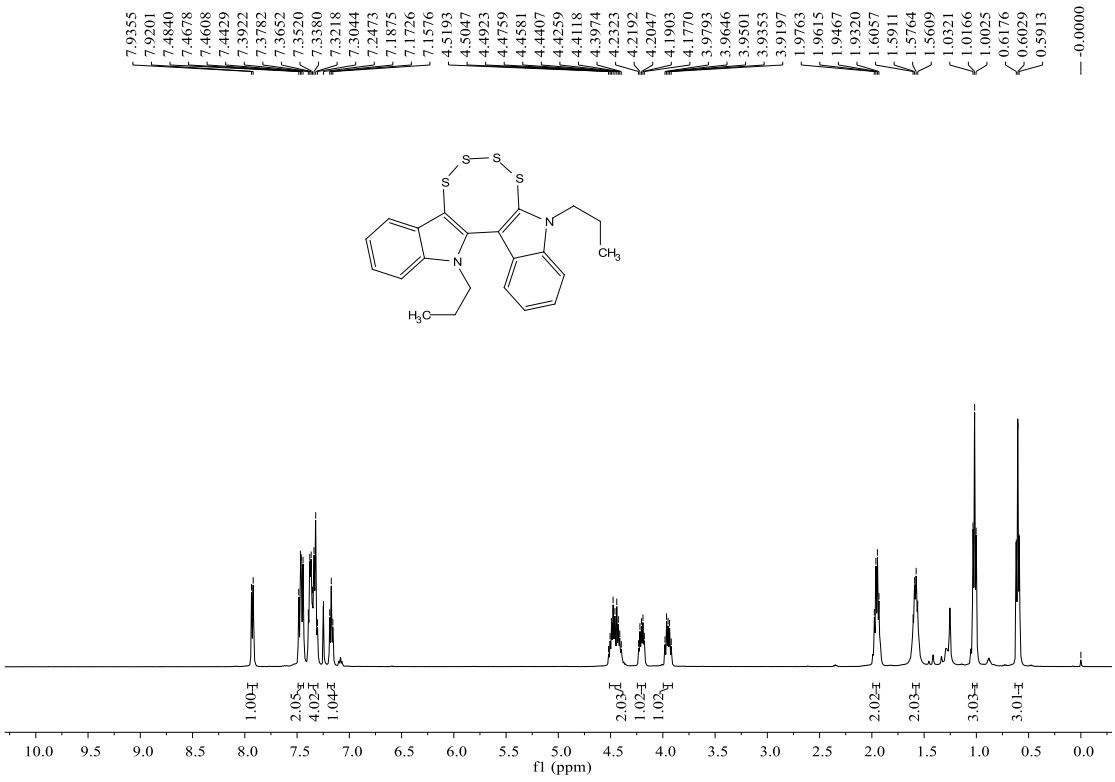


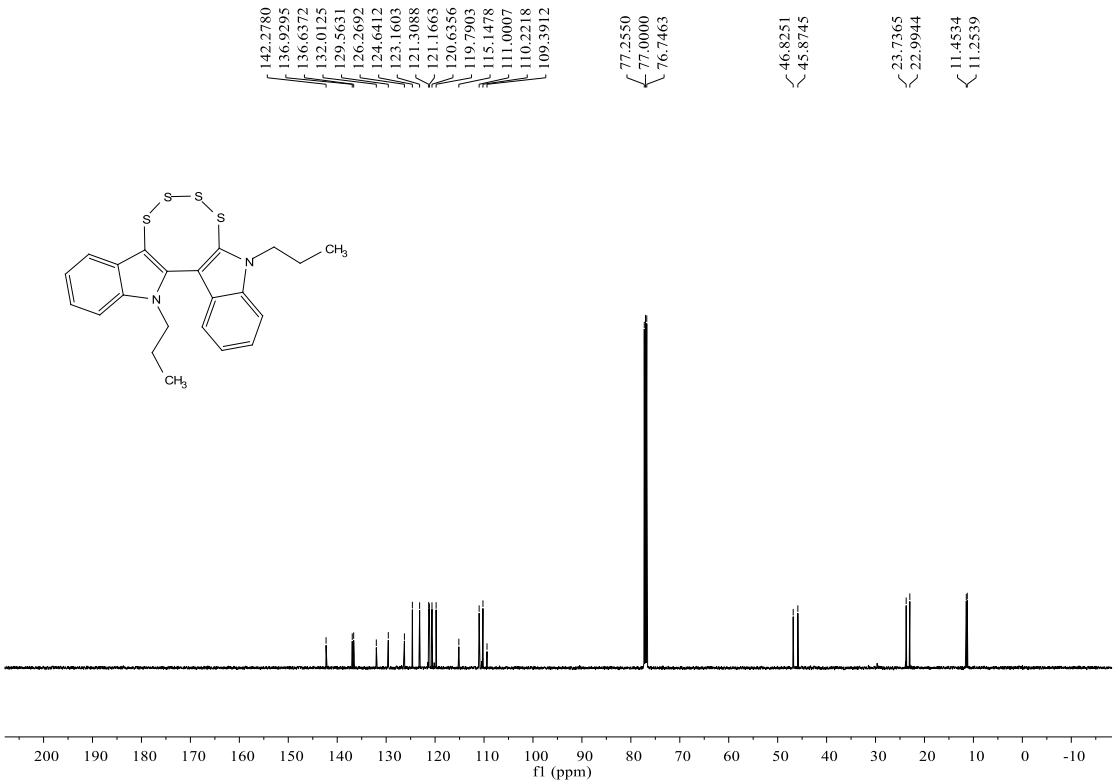
^{1}H and ^{13}C NMR spectra of **4c**





^{1}H and ^{13}C NMR spectra of **4d**





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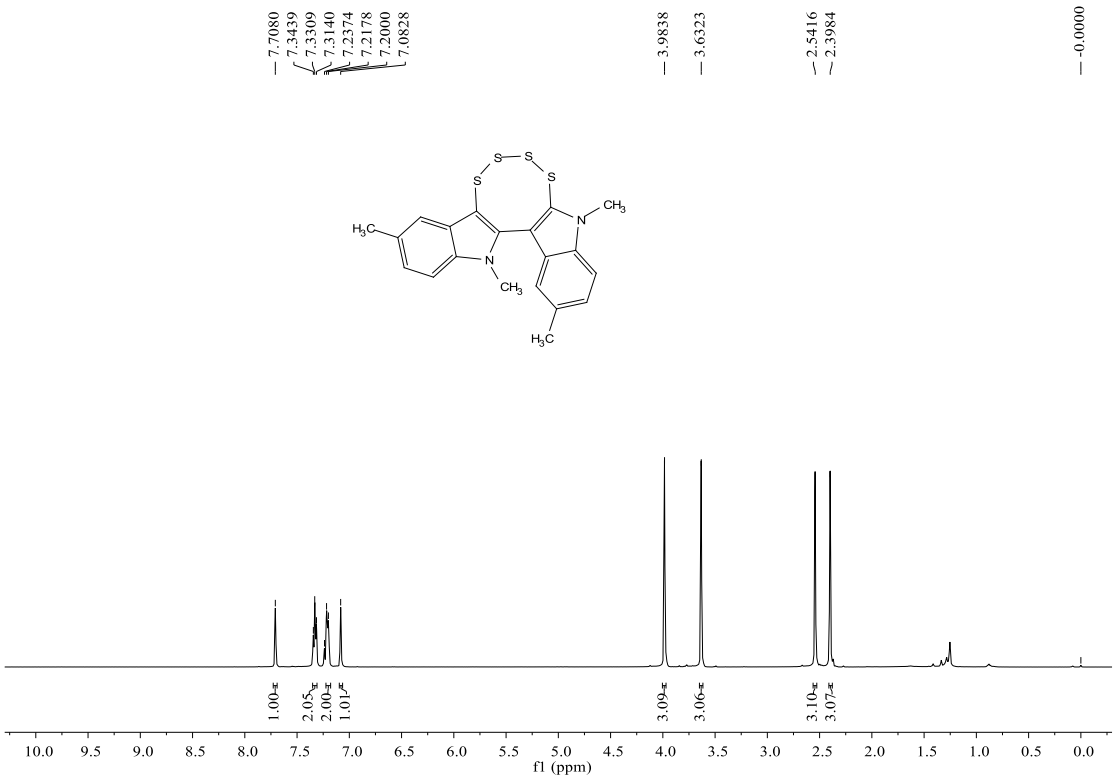
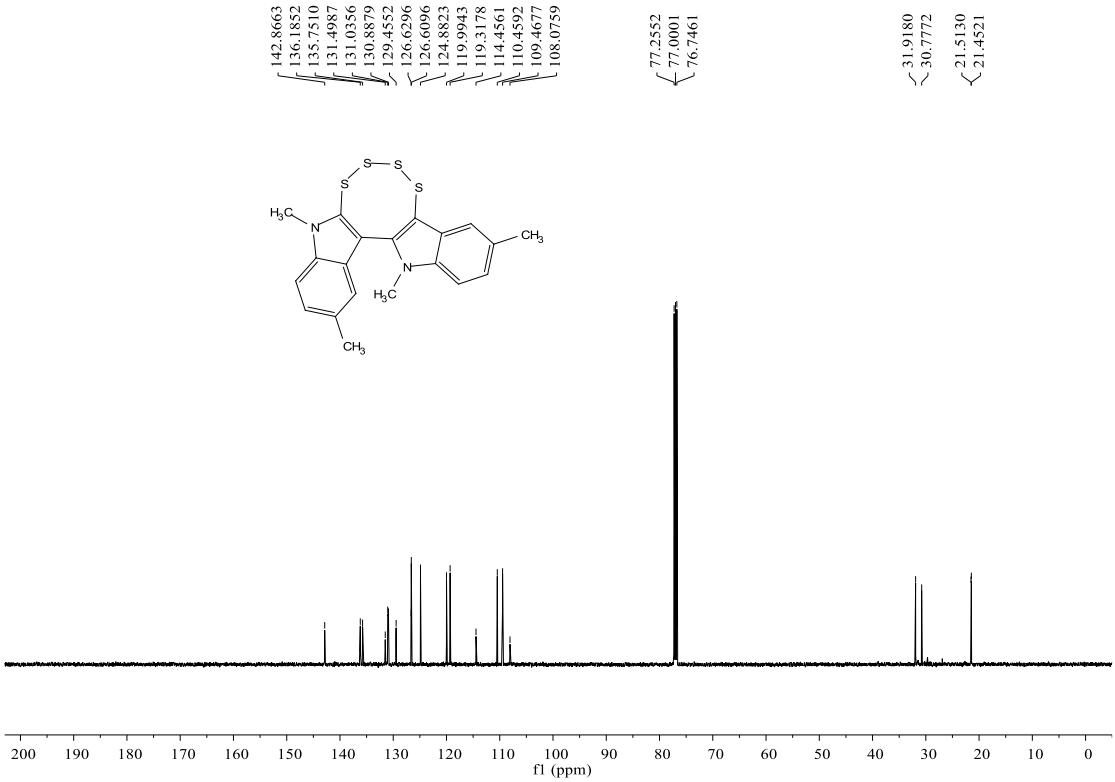
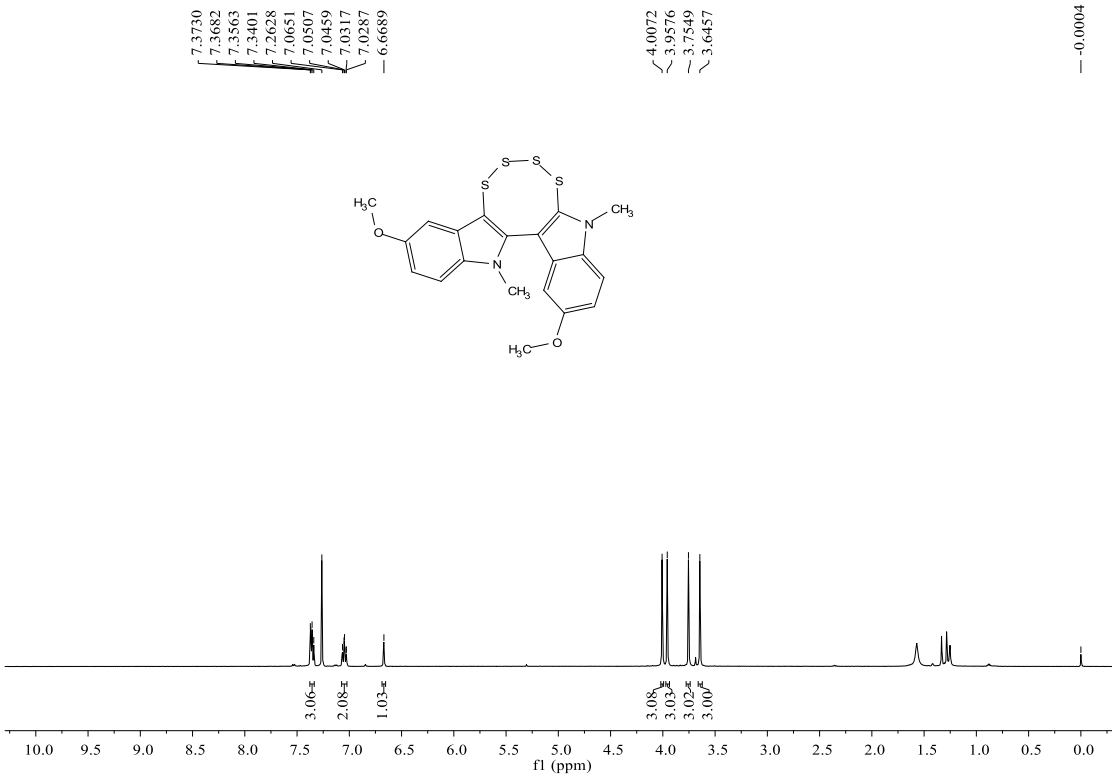
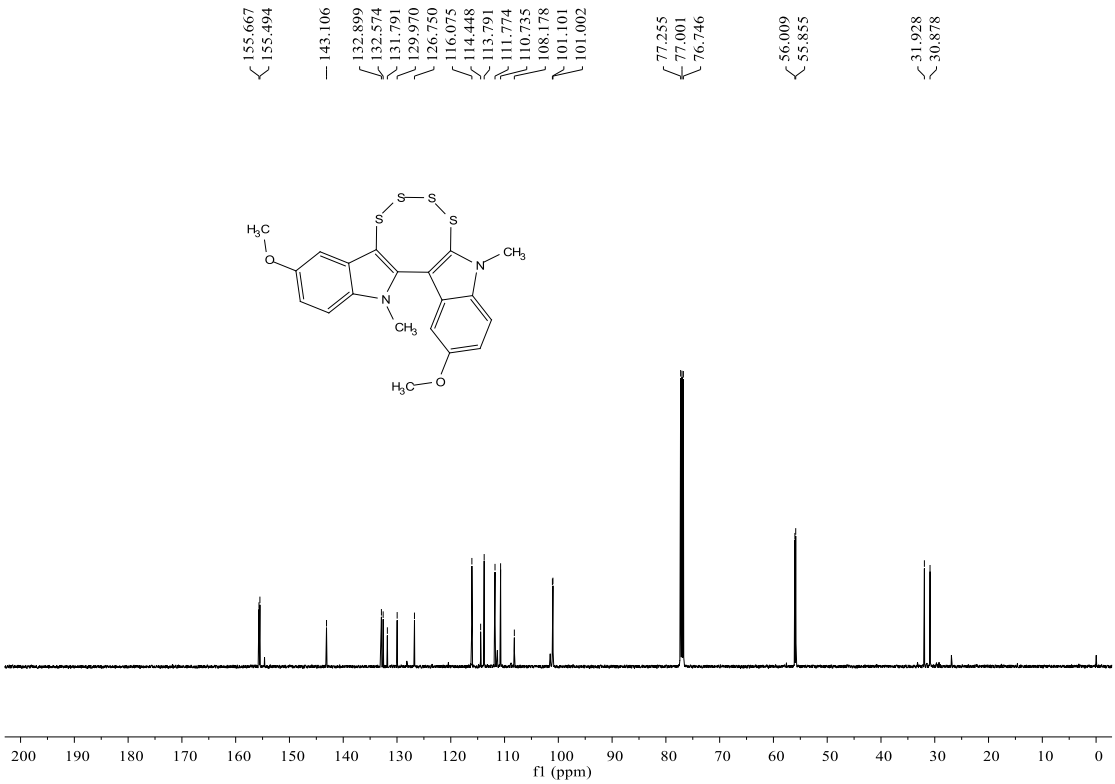
^{1}H and ^{13}C NMR spectra of **4l**



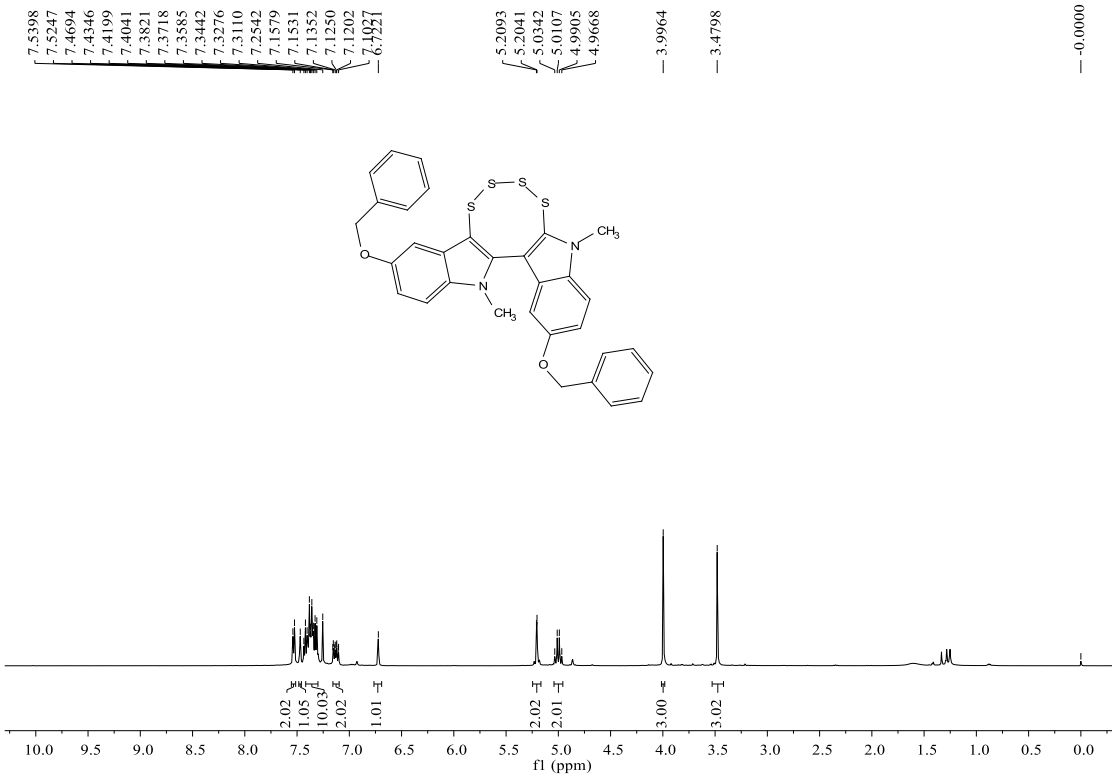


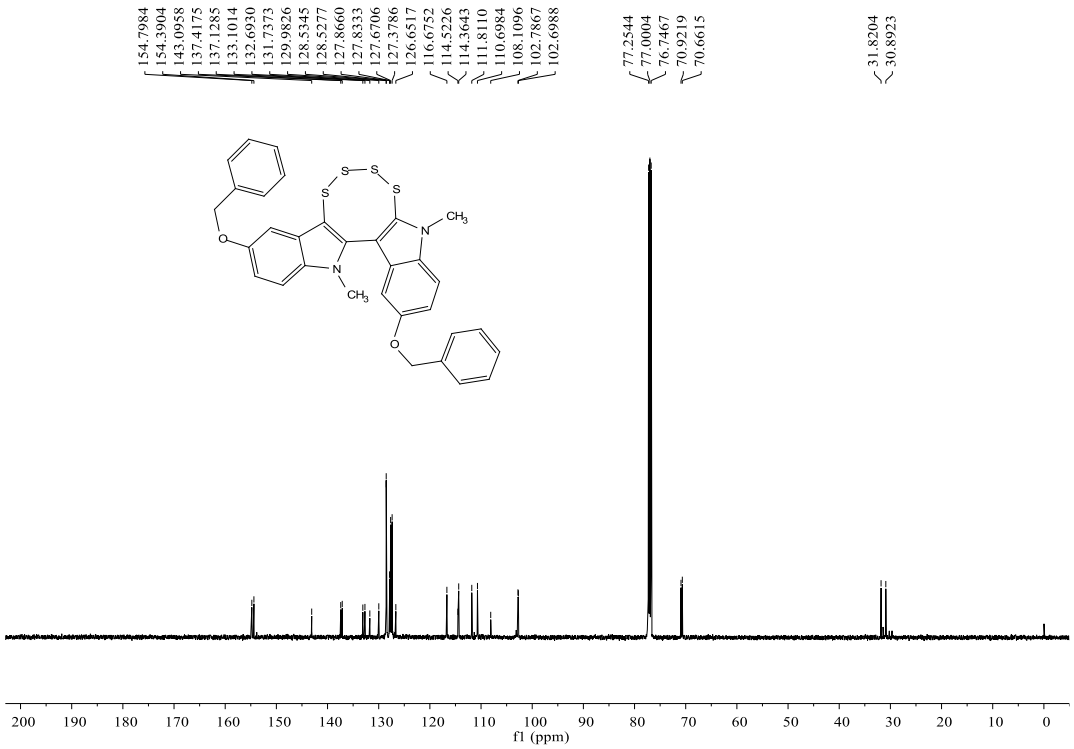
^{1}H and ^{13}C NMR spectra of **4m**



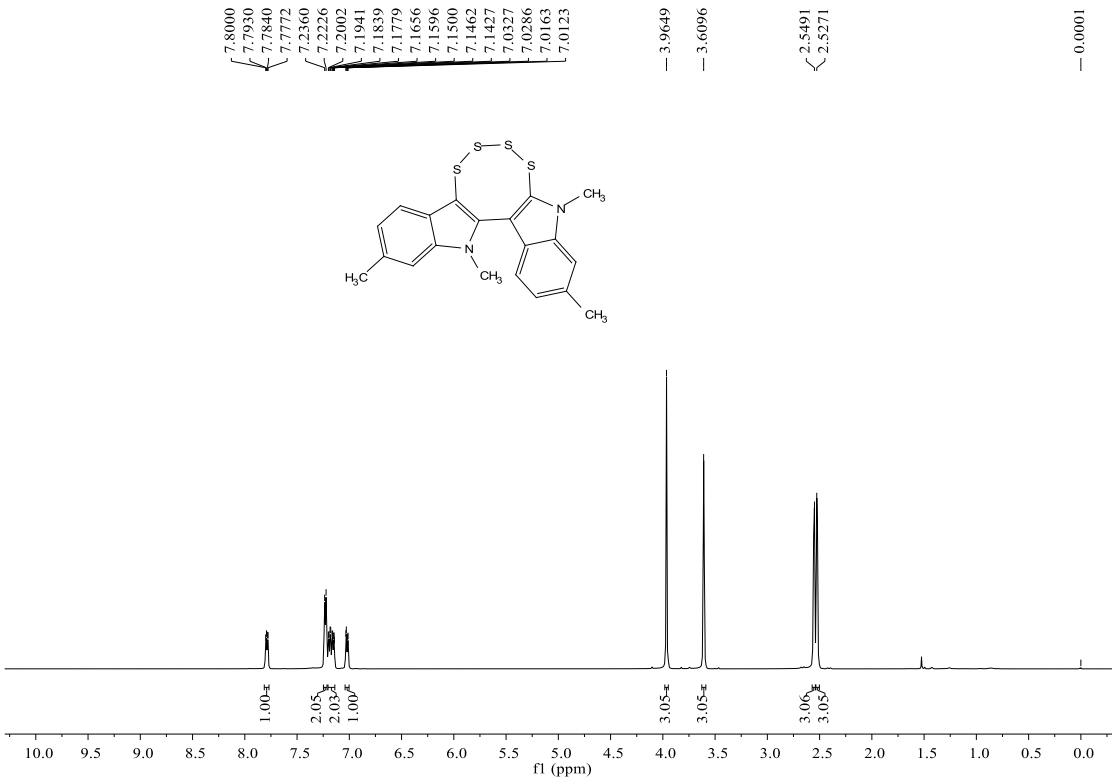


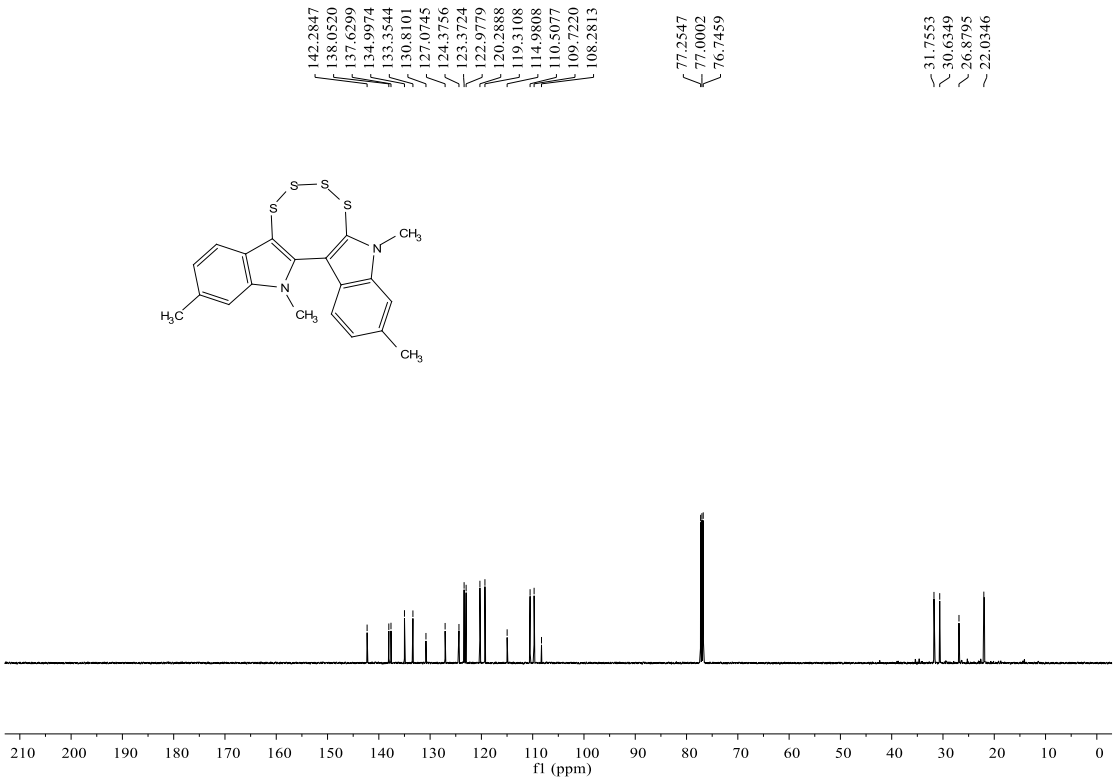
^{1}H and ^{13}C NMR spectra of **4n**



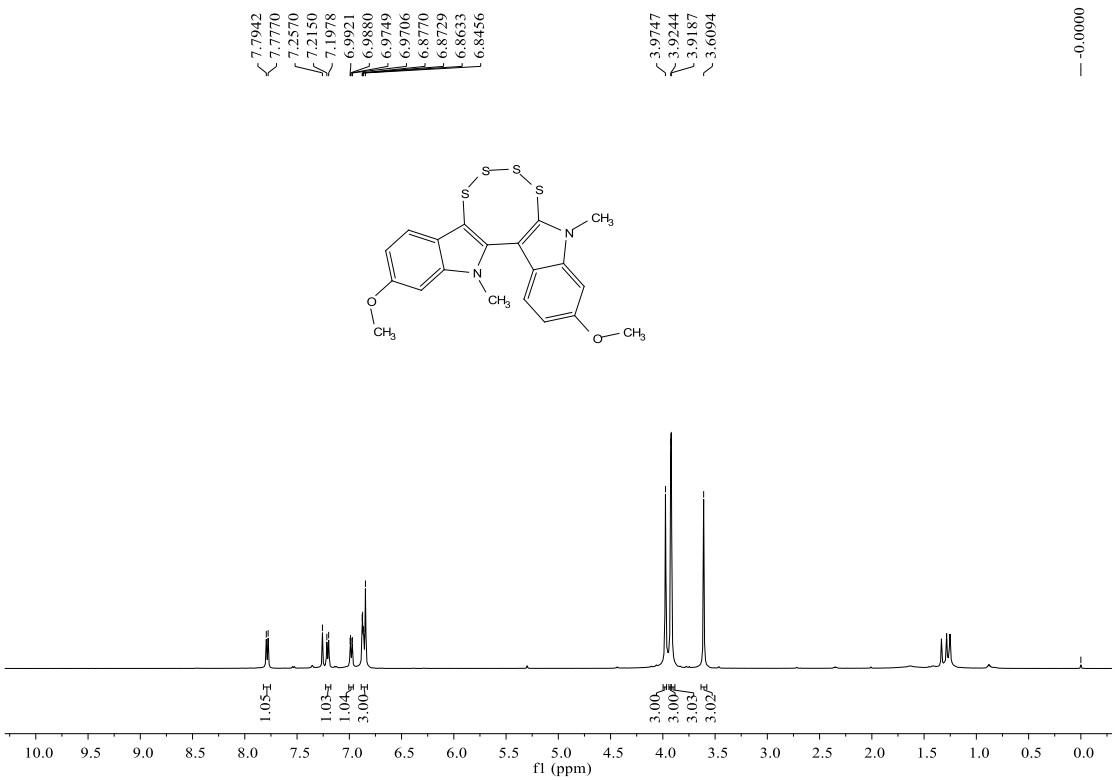


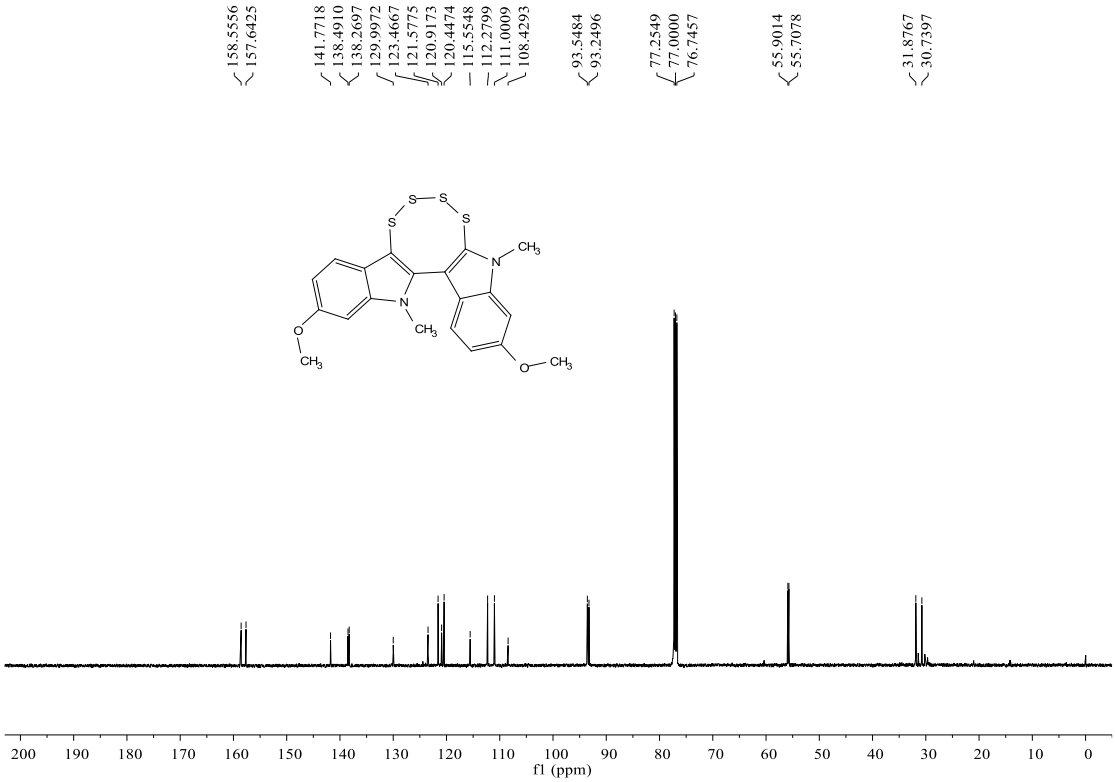
^{1}H and ^{13}C NMR spectra of **4r**



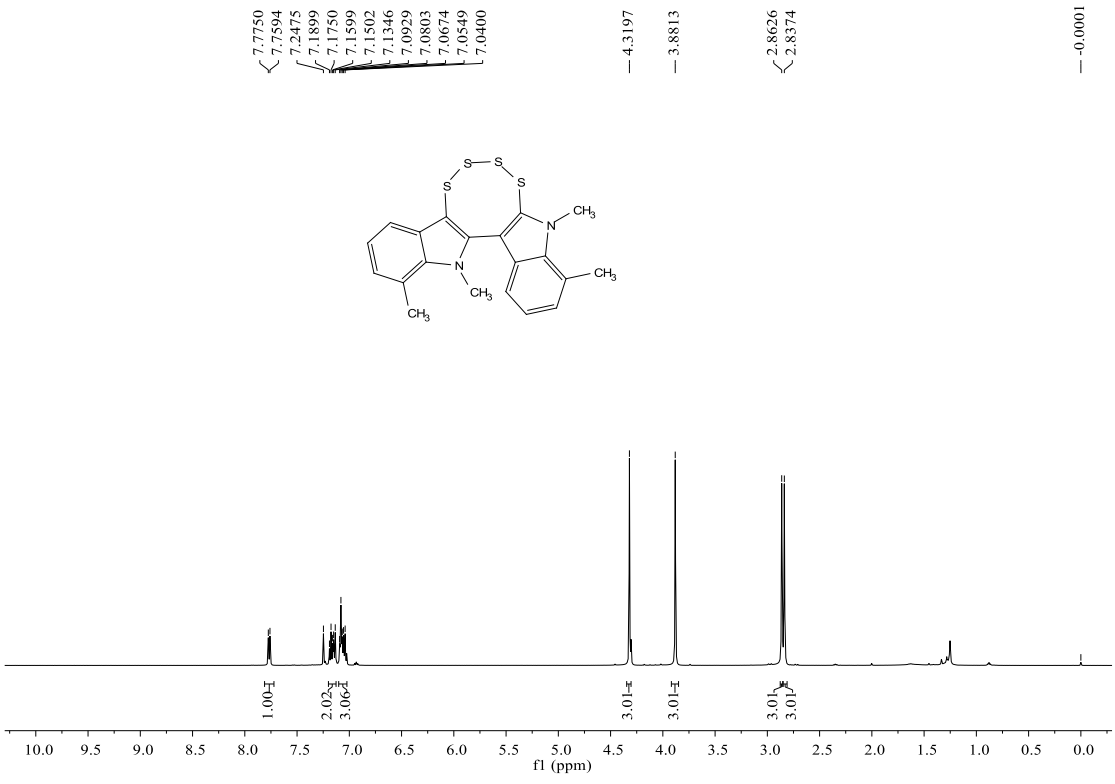


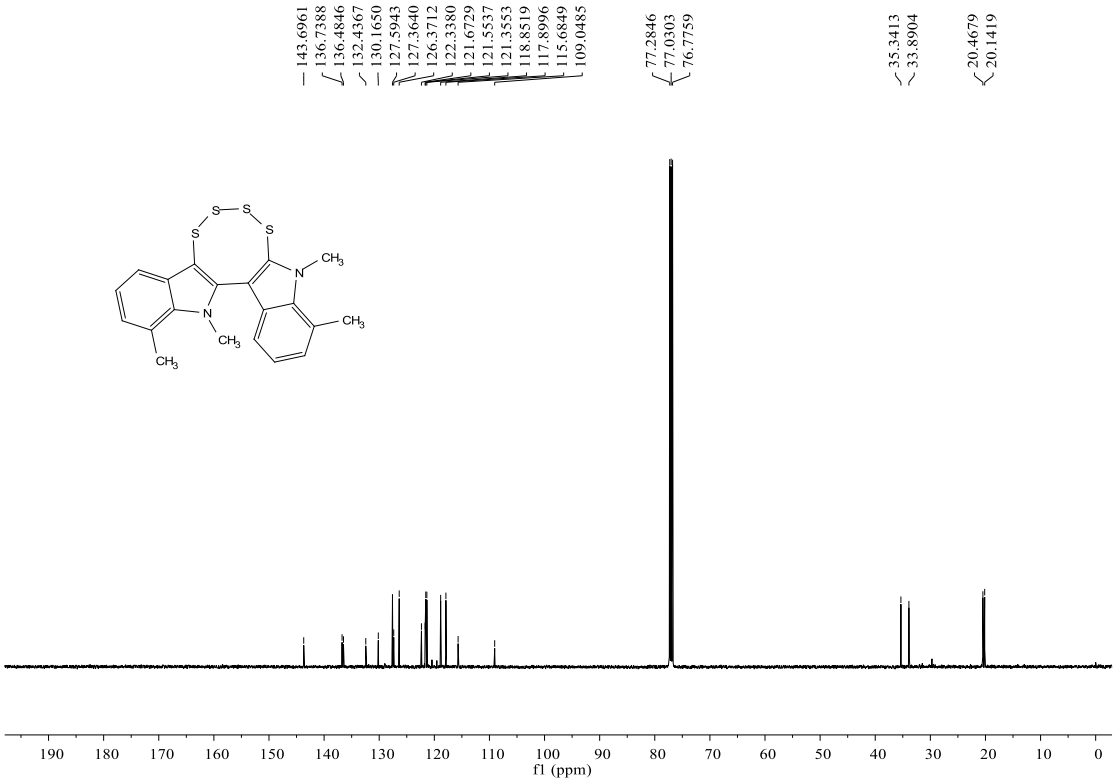
^{1}H and ^{13}C NMR spectra of **4s**



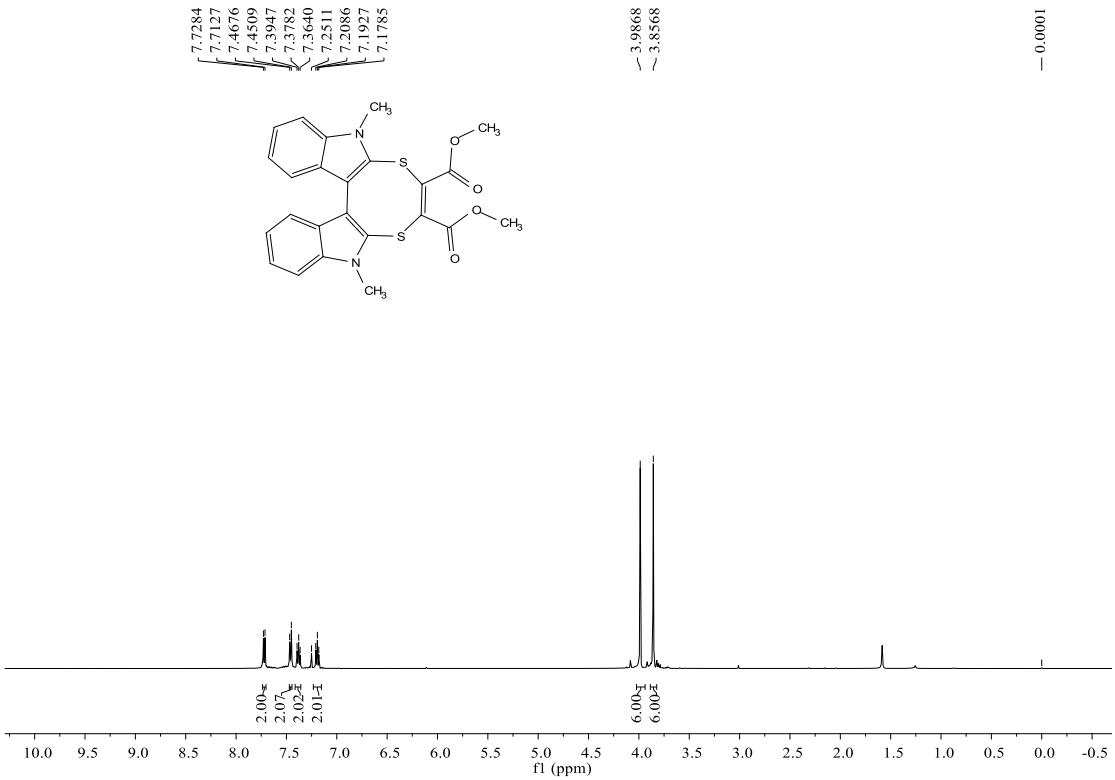


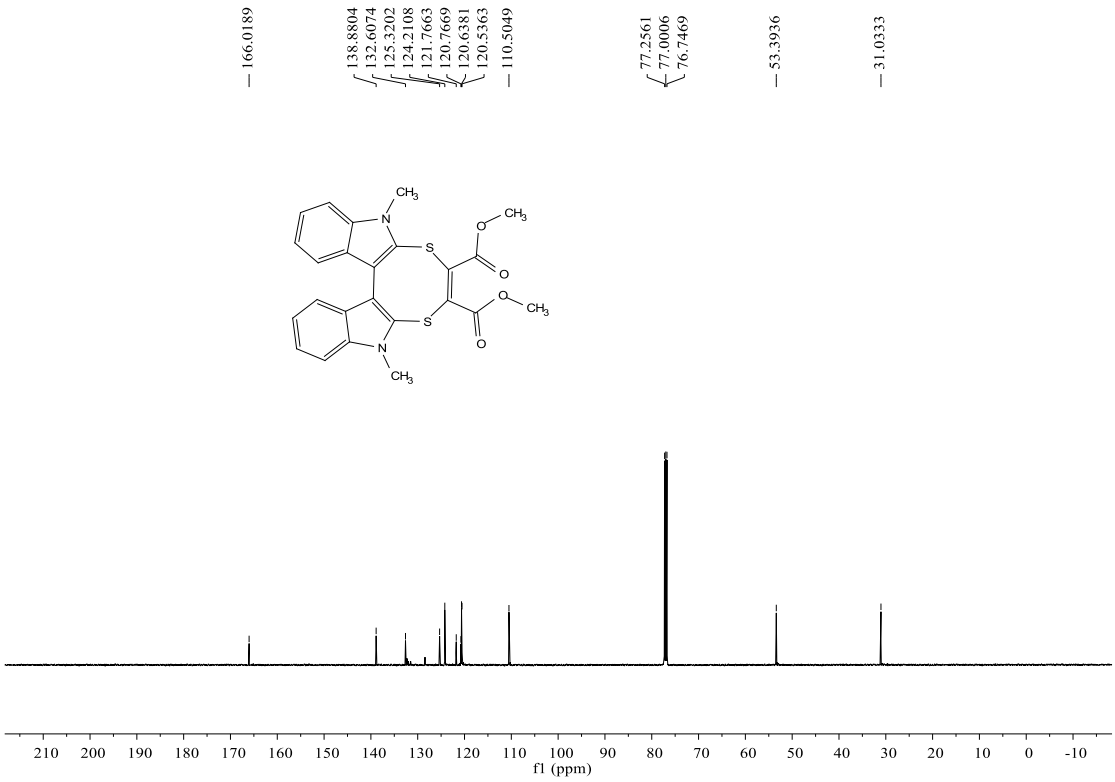
^{1}H and ^{13}C NMR spectra of **4v**



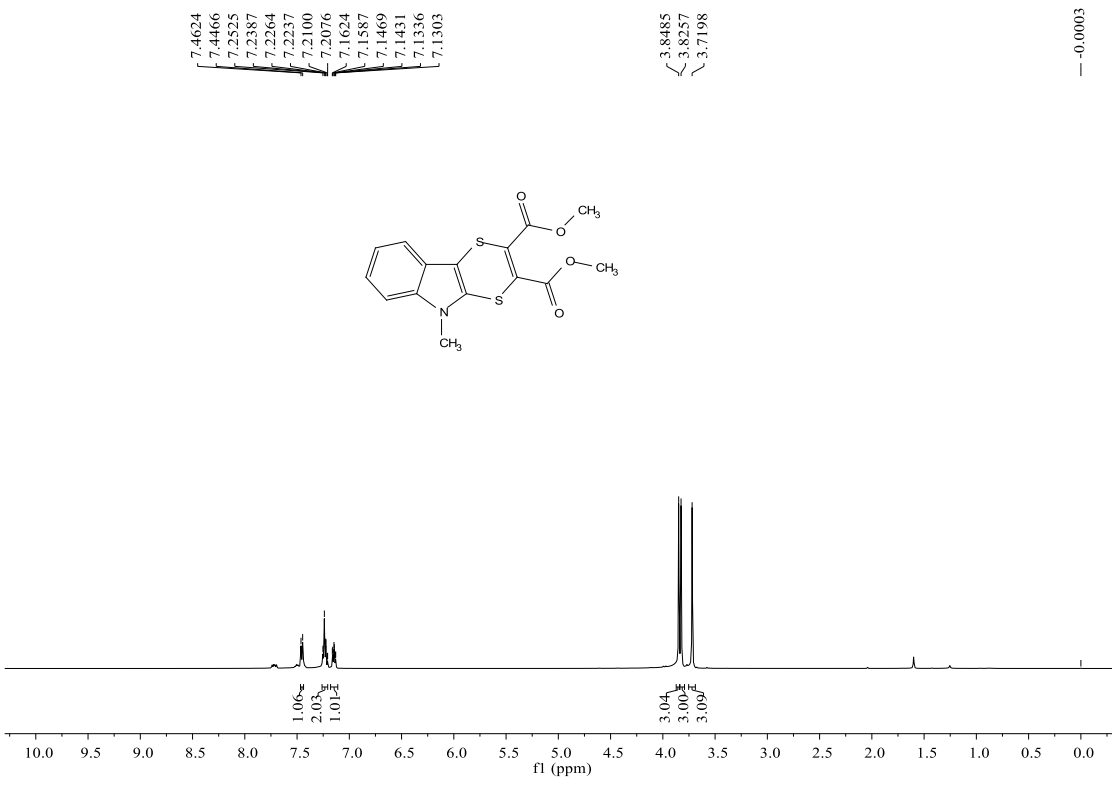


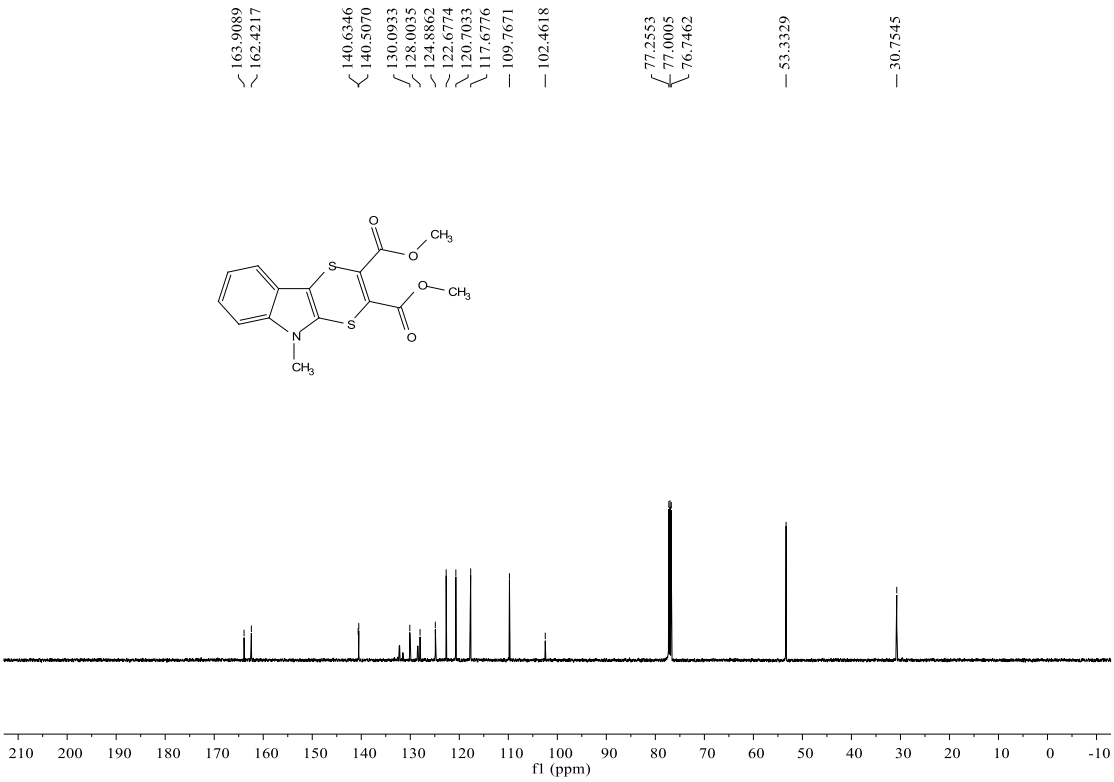
^{1}H and ^{13}C NMR spectra of **5**



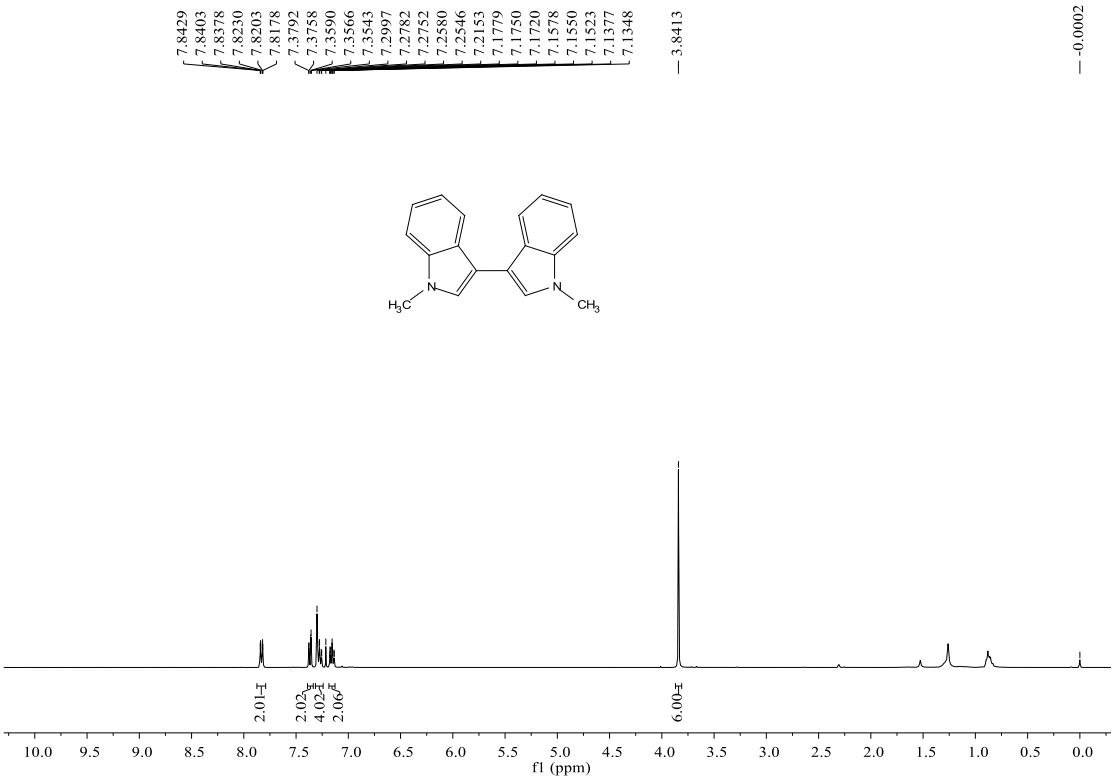


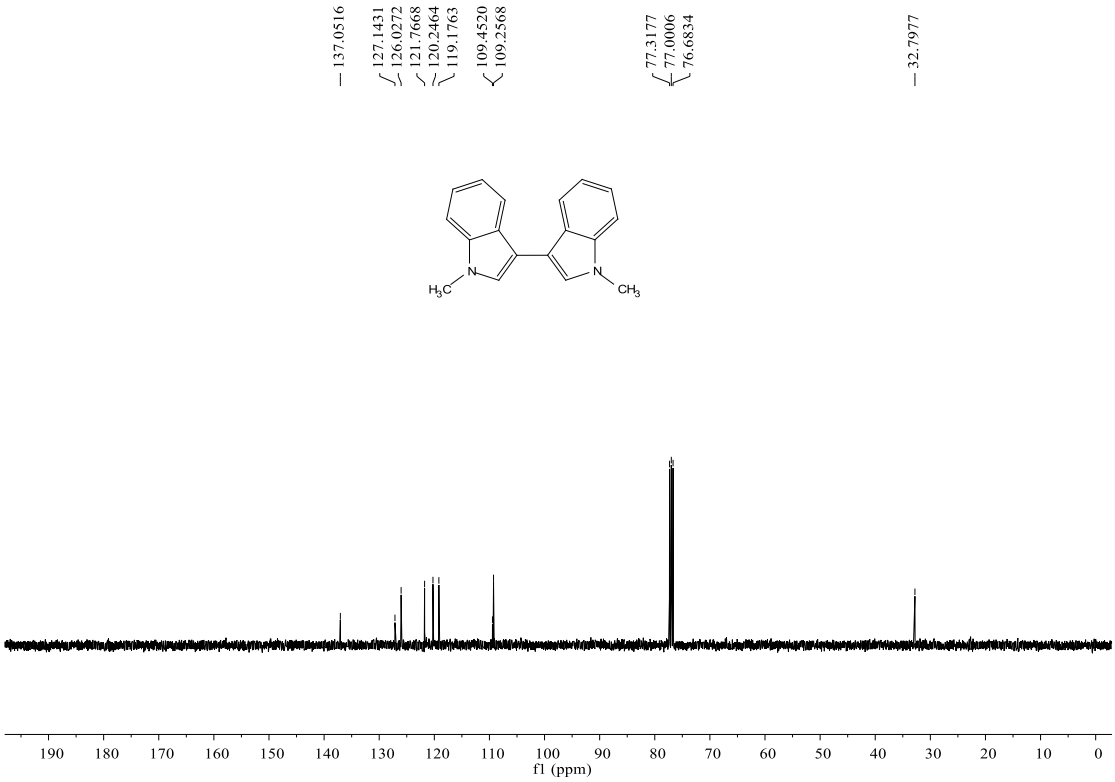
^{1}H and ^{13}C NMR spectra of **6**



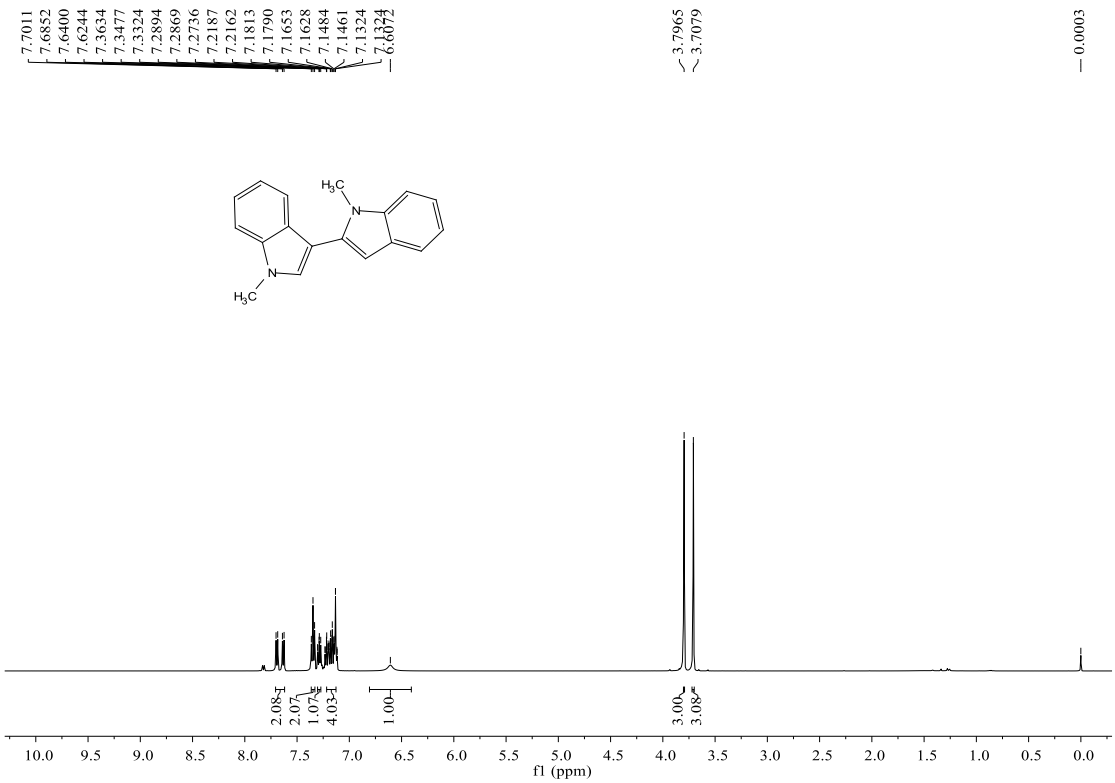


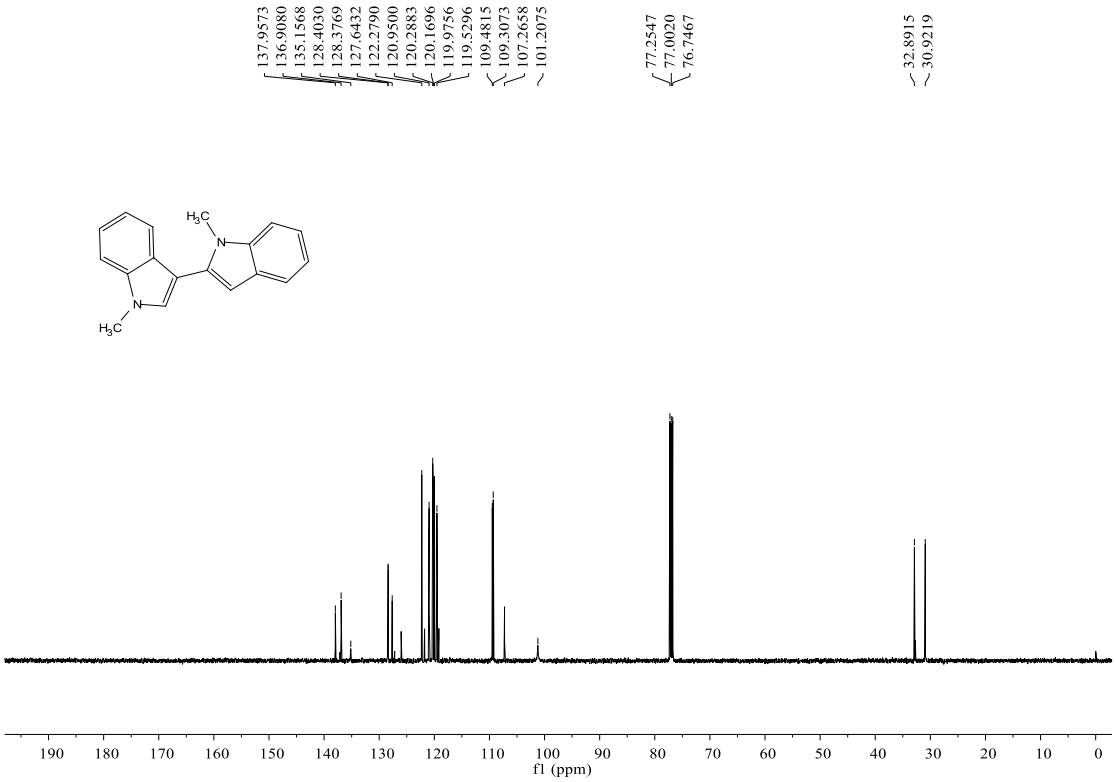
^{1}H and ^{13}C NMR spectra of **7**





^{1}H and ^{13}C NMR spectra of **8**

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30.9219
H3C
N
N
H3C
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f1 (ppm)