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Supporting Information

Site-Selective Synthesis of Indanyl-Substituted Indole Derivatives via 1,3-Dithiane induced Nazarov cyclization

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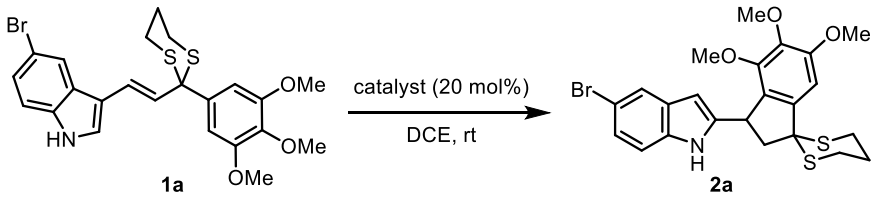
1. General information

All the commercially available chemicals and solvents were purchased from Energy Chemical, Bidepharm, J&K Scientific, Leyan.com, Sigma-Aldrich, Acros Organics and used as received. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reactions requiring heating were carried out using an oil bath. Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (GF254). The products were purified by Flash chromatography using petroleum/ethyl acetate as eluents. Compounds were either visualised under UV-light at 254 nm or dipped the plates either in an aqueous phosphomolybdic solution followed by heating. ^{1}H and ^{13}C NMR spectra were collected on a JEOL JNM-ECS 400MHz, Bruker AVANCE III 400MHz and Agilent-NMR-inova 600 MHz spectrometer at room temperature and and were calibrated using TMS (0.00 ppm) or residual non-deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR and DMSO-*d6*: 2.50 ppm for ^{1}H NMR and 49.50 ppm for ^{13}C NMR). ^{19}F NMR spectra were collected on Bruker AVANCE III 400 MHz spectrometers at room temperature. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiplet and/or multiple resonances, brs = broad signal), integration, coupling constant (*J*) in Hertz, and assignment. High resolution mass (HRMS) data were obtained using an Agilent UPLC-IMQTOF instrument with ESI source. Optical rotations were measured on an AUTOPOL IV Automatic polarimeter (Rudolph Research Analytical). The X-RAY was measured on Rigaku Oxford Diffraction. The melting points were determined on a microscopic apparatus and were uncorrected.

2. The process of optimizing reaction conditions[1]

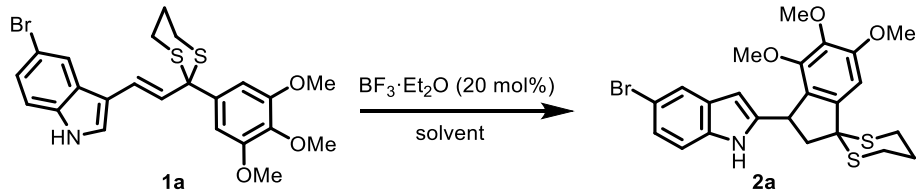
Table S1. Screening of various acids.[a]



entry	catalyst	yield (%)[b]
1	Tf_2NH	nd
2	HOTf	nd
3	CSA	nd
4	$TiCl_4$	nd
5	$SnCl_2$	nd
6	TFA	15
7	TMSCl	30
8	TMSOTf	48
9	$CuCl_2$	nd
10	$AlCl_3$	nd
11	BCl_3	nd
12	BEt_3	nr
13	**$BF_3{\cdot}Et_2O$**	**86**
14	$BF_3{\cdot}2CH_3CO_2H$	20
15	$BF_3{\cdot}CH_3CN$	72
16	$B(C_6F5)_3$	58

[a]Reaction conditions: **1a** (101 mg, 0.2 mmol) and Lewis acid dissolved in DCE (5.0 mL) at room temperature for 10 h. [b]Isolated yields. nd = not detected. nr = no reaction.

Table S2. Screening of other reaction parameters.[a]

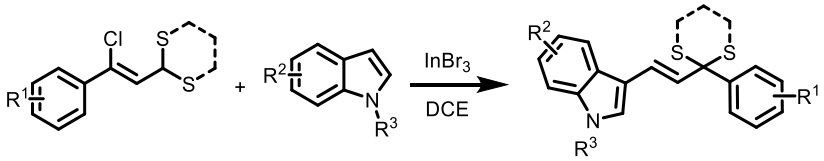


entry	solvent	yield (%)[b]
1	DCE	**86**
2	DCM	80
3	$CHCl_3$	70
4	THF	nr
5	1,4-Dioxane	nr
6	CH_3CN	nd
7	Toluene	66
8	DMF	nr

[a]Reaction conditions: **1a** (101 mg, 0.20 mmol) and $BF_3 \cdot Et_2O$ (20 mmol%) dissolved in solvent (5.0 mL) at room temperature for 10 h. [b]Isolated yields. nd = not detected. nr = no reaction.

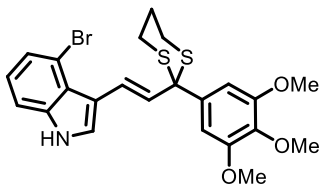
3. Synthesis of substrates

General procedure for the synthesis of alkenyl dithiane derivatives [2]



To a magnetically-stirred solution of β-chlorovinyl dithianes (0.4 mmol, 1.0 equiv) and indole derivatives (0.5 mmol, 1.25 equiv) in DCE (30 mL) were added $InBr_3$ (213 mg, 0.6 mmol 1.5 equiv). The resulting mixture was vigorously stirred at room temperature for 8-48 h under N_2 conditions until the disappearance of β-chlorovinyl dithianes as determined by TLC analysis. The mixture was quenched with 1M $NaHCO_3$ (10 mL) and extracted with EtOAc (15 mL). The organic layer was separated, and the aqueous phase was re-extracted with EtOAc (15 x 3 mL). The combined organic extracts were washed with brine (15 x 3 mL), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the pure desired alkenyl indole products. It is worth noting that some of the purified alkenyl compounds were directly used in site-selective cyclization studies.

(*E*)-4-bromo-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1b)



Colorless oil, R_f = 0.24 (PE/EA = 10:1). 152 mg, isolated yield 75%.

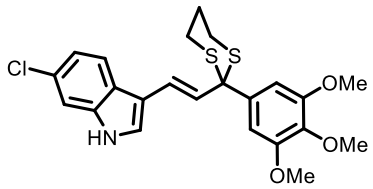
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (brs, 1H), 7.55 (d, *J* = 15.6 Hz, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.31 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 (s, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.17 (d, *J* = 15.7 Hz, 1H), 3.88 (s, 6H), 3.87 (s, 3H), 3.09 – 3.00 (m,

2H), 2.86 – 2.79 (m, 2H), 2.08 – 1.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 137.5, 137.4, 129.5, 127.4, 124.9, 124.7, 123.3, 122.3, 115.6, 114.3, 110.9, 106.1, 61.0, 60.0, 56.3, 28.9, 24.7.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508,0434; found: 506.0449, 508.0429.

(*E*)-6-chloro-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1c)



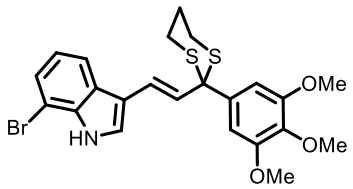
Colorless oil, R_f = 0.42 (PE/EA = 5:1). 148 mg, isolated yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (brs, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.28 (d, *J* = 2.6 Hz, 1H), 7.19 (s, 2H), 7.16 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 6H), 3.05 – 2.94 (m, 2H), 2.86 – 2.76 (m, 2H), 2.05 – 1.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 137.4, 137.4, 137.2, 129.5, 128.7, 126.7, 124.9, 124.2, 121.4, 121.2, 114.4, 111.5, 106.2, 61.0, 60.1, 56.3, 29.1, 24.6.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}ClNO_3S_2$ $[M+H]^+$: 462.0959, found: 462.0963.

(*E*)-7-bromo-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1d)



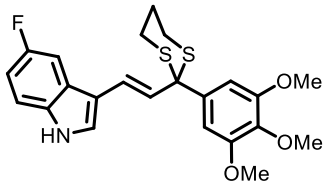
Colorless oil, R_f = 0.20 (PE/EA = 10:1). 148 mg, isolated yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (brs, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.19 (s, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 15.8 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 6H), 3.05 – 2.93 (m, 2H), 2.87 – 2.74 (m, 2H), 2.12 – 1.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 137.5, 137.4, 135.6, 129.8, 126.8, 126.8, 125.2, 124.7, 121.8, 119.6, 115.5, 106.2, 105.2, 61.0, 60.1, 56.3, 29.1, 24.6.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508,0434; found: 506.0455, 508.0438.

(*E*)-5-fluoro-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1f)



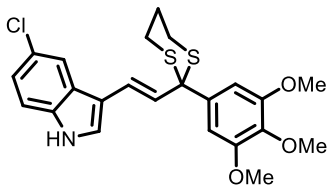
Colorless oil, R_f = 0.28 (PE/EA = 10:1). 116 mg, isolated yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (brs, 1H), 7.54 (dd, *J* = 9.9, 2.5 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.19 (s, 2H), 7.06 – 6.93 (m, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 6H), 3.04 – 2.94 (m, 2H), 2.88 – 2.76 (m, 2H), 2.12 – 1.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (d, *J* = 235.8 Hz), 153.1, 137.5, 137.4, 133.3, 129.0, 126.8, 126.0, 125.9 (d, *J* = 9.8 Hz), 114.4 (d, *J* = 4.7 Hz), 112.2 (d, *J* = 9.6 Hz), 111.2 (d, *J* = 26.3 Hz), 106.1, 105.5 (d, *J* = 24.0 Hz), 61.0, 60.1, 56.3, 29.1, 24.6.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}FNO_3S_2$ $[M+H]^+$: 446.1254, found: 446.1248.

(*E*)-5-chloro-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1g)



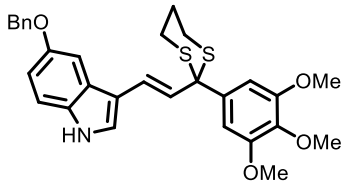
Colorless oil, R_f = 0.46 (PE/EA = 5:1). 140 mg, isolated yield 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 46.3 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.22 – 7.15 (m, 3H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 6H), 3.05 – 2.94 (m, 2H), 2.87 – 2.76 (m, 2H), 2.11 – 1.96 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 137.5, 135.2, 129.1, 126.7, 126.6, 126.3, 125.8, 123.1, 119.7, 119.7, 113.8, 112.6, 106.1, 61.0, 60.1, 56.3, 29.0, 24.6.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}ClNO_3S_2$ $[M+H]^+$: 462.0959, found: 462.0962.

(*E*)-5-(benzyloxy)-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1l)



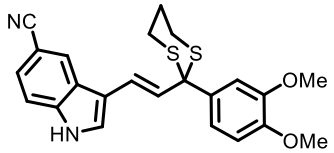
Colorless oil, R_f = 0.40 (PE/EA = 10:1). 128 mg, isolated yield 60%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (brs, 1H), 7.49 – 7.46 (m, 2H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.26 (m, 3H), 7.19 (s, 2H), 6.98 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.40 – 6.31 (m, 1H), 5.13 (s, 2H), 3.87 (s, 3H), 3.85 (s, 6H), 3.05 – 2.97 (m, 2H), 2.85 – 2.76 (m, 2H), 2.08 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.0, 137.6, 137.4, 132.1, 128.7, 128.5, 128.3, 128.0, 127.8, 127.4, 126.0, 125.2, 114.1, 113.3, 112.2, 106.1, 104.3, 71.1, 61.0, 60.2, 56.3, 29.1, 24.7.

HRMS: m/z (ESI) calcd. for $C_{30}H_{32}NO_4S_2$ $[M+H]^+$: 534.1767, found: 534.1772.

(*E*)-3-(2-(2-(3,4-dimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole-5-carbonitrile (1o)



Colorless oil, R_f = 0.34 (PE/EA = 5:1). 104 mg, isolated yield 62%.

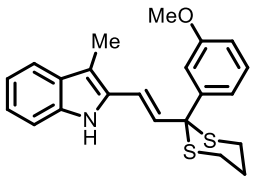
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 8.21 (s, 1H), 7.51 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.40 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.91 (d, *J* = 1.6 Hz, 6H), 3.03 – 2.92 (m, 2H), 2.87 – 2.77 (m, 2H), 2.10 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 148.7, 138.4, 133.8, 131.2, 125.9, 125.8, 125.7, 125.5, 125.4, 121.4, 120.7, 115.2, 112.5, 112.2, 110.7, 103.8, 59.5, 56.1, 56.0, 29.0,

24.6.

HRMS: m/z (ESI) calcd. for $C_{23}H_{23}N_2O_2S_2$ $[M+H]^+$: 423.1195, found: 423.1183.

(*E*)-2-(2-(2-(3-methoxyphenyl)-1,3-dithian-2-yl)vinyl)-3-methyl-1*H*-indole (1aa)



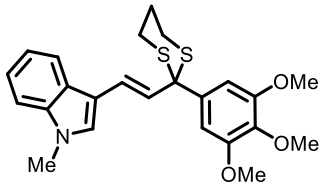
Colorless oil, R_f = 0.24 (PE/EA = 5:1). 108 mg, isolated yield 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.34 – 7.29 (m, 1H), 7.23 (s, 1H), 7.22 – 7.13 (m, 1H), 7.12 – 7.04 (m, 1H), 6.87 – 6.79 (m, 2H), 6.14 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.01 – 2.90 (m, 2H), 2.83 – 2.73 (m, 2H), 2.31 (s, 3H), 2.11 – 1.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 143.1, 136.5, 130.9, 129.7, 129.5, 129.4, 123.4, 122.9, 121.0, 119.6, 119.2, 114.6, 113.5, 112.9, 110.6, 59.2, 55.5, 28.9, 24.6, 8.9.

HRMS: m/z (ESI) calcd. for $C_{22}H_{24}NOS_2$ $[M+H]^+$: 382.1294, found: 382.1281.

(*E*)-1-methyl-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-1*H*-indole (1bd)



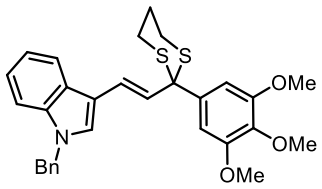
Colorless oil, R_f = 0.38 (PE/EA = 3:1). 102 mg, isolated yield 58%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.20 (s, 2H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.15 (s, 1H), 6.83 (d, *J* = 15.7 Hz, 1H), 6.43 (dd, *J* = 15.9, 1.2 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 6H), 3.76 (s, 3H), 3.04 – 2.96 (m, 2H), 2.83 – 2.73 (m, 2H), 2.05 – 1.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 137.7, 137.4, 129.1, 127.9, 127.3, 126.1, 122.4, 120.4, 120.3, 112.6, 109.7, 106.1, 60.9, 60.3, 56.2, 33.0, 29.1, 24.7.

HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_3S_2$ $[M+H]^+$: 442.1505, found: 442.1501.

(*E*)-1-benzyl-3-(2-(2-(3,4,5-trimethoxyphenyl)-1,3-dithian-2-yl)vinyl)-indole (1be)



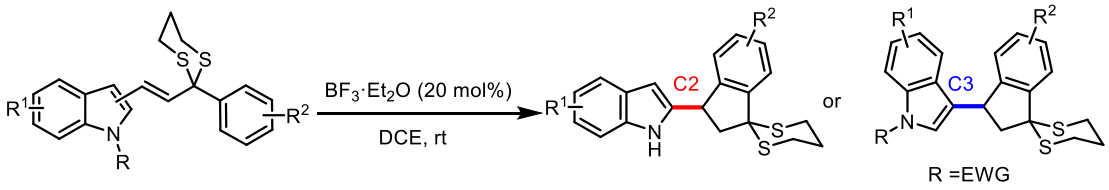
Colorless oil, R_f = 0.40 (PE/EA = 3:1). 107 mg, isolated yield 52%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.0 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.26 – 7.16 (m, 4H), 7.19 – 7.11 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.28 (s, 2H), 3.87 (s, 3H), 3.85 (s, 6H), 3.06 – 2.94 (m, 2H), 2.86 – 2.71 (m, 2H), 2.11 – 1.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 137.6, 137.5, 137.4, 137.0, 129.0, 128.5, 128.4, 128.0, 127.1, 127.1, 126.4, 122.6, 120.5, 113.3, 110.2, 106.3, 60.9, 60.3, 56.3, 50.3, 29.1, 24.7.

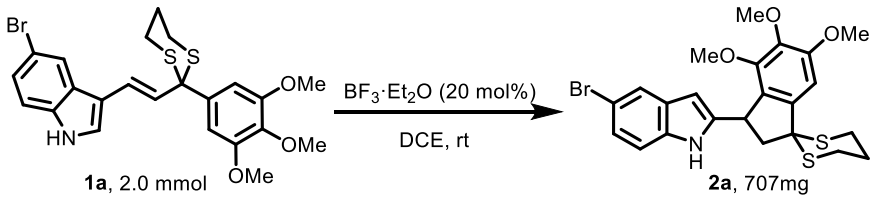
HRMS: m/z (ESI) calcd. for $C_{30}H_{32}NO_3S_2$ $[M+H]^+$: 518.1818, found: 518.1815.

4. General procedure of the C2 and C3 indanyl-substituted indoles



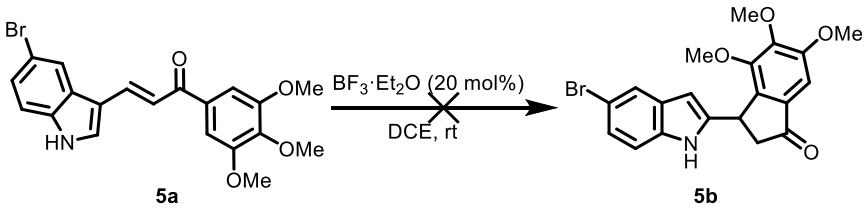
To a magnetically-stirred solution of alkenyl indole (0.2 mmol, 1.0 equiv) and in DCE (5 mL) were added 20 mol% of $BF_3 \cdot Et_2O$. The resulting mixture was vigorously stirred at room temperature for 8-48 h until the disappearance of alkenyl indole as determined by TLC analysis. The mixture was quenched with 1M $NaHCO_3$ (10 mL) and extracted with EtOAc (10 x 3 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the pure desired product.

5. Gram-scale reaction



To a magnetically-stirred solution of alkenyl indole **1a** (1.01 g, 2.0 mmol, 1.0 equiv) and in DCE (50 mL) were added $BF_3{\cdot}Et_2O$ (51 μL, 20 mol%). The resulting mixture was vigorously stirred at room temperature for 24 h. The mixture was quenched with 1M $NaHCO_3$ (100 mL) and extracted with EtOAc (50 x 3 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel with petroleum/ethyl acetate (PE/EA = 50:1 ~ 20:1) to give the pure desired product **2a** (707 mg, 70%) as a white solid.

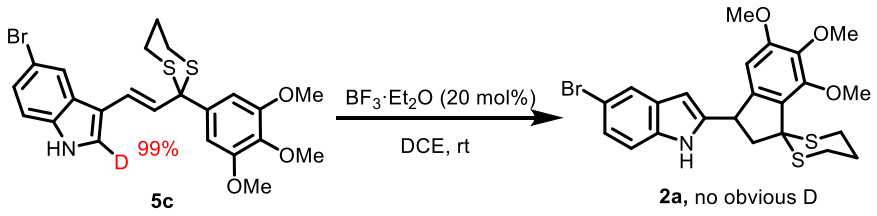
6. Indole enone 5a for C2-cyclization[3]



5a were prepared according to the literature procedure.[4] Prepared following the general procedure outlined above using alkenyl indole **5a** (101 mg, 0.2 mmol, 1.0 equiv), $BF_3{\cdot}Et_2O$ (5 μL, 20 mol%), and DCE (5 mL). After 10 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. The C2-selective indanone product **5b** was not detected and formed.

7. Deuterium incorporation experiments

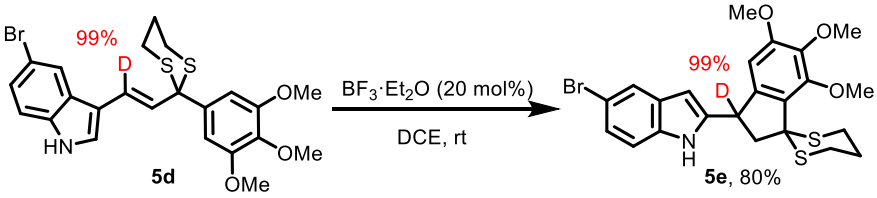
Deuterium incorporation experiments A



Prepared following the general procedure outlined above using [2D]-alkenyl indole **5c** (101 mg, 0.2 mmol, 99% D, 1.0 equiv), $BF_3{\cdot}Et_2O$ (5 μL, 20 mol%), and DCE (5 mL). After 10 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (PE/EA = 50:1 ~ 20:1) gave the **2a** (80 mg, isolated yield 80%) as a white solid.

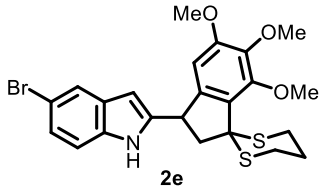
*Found no deuterium incorporation at the product **2a**.*

Deuterium incorporation experiments B



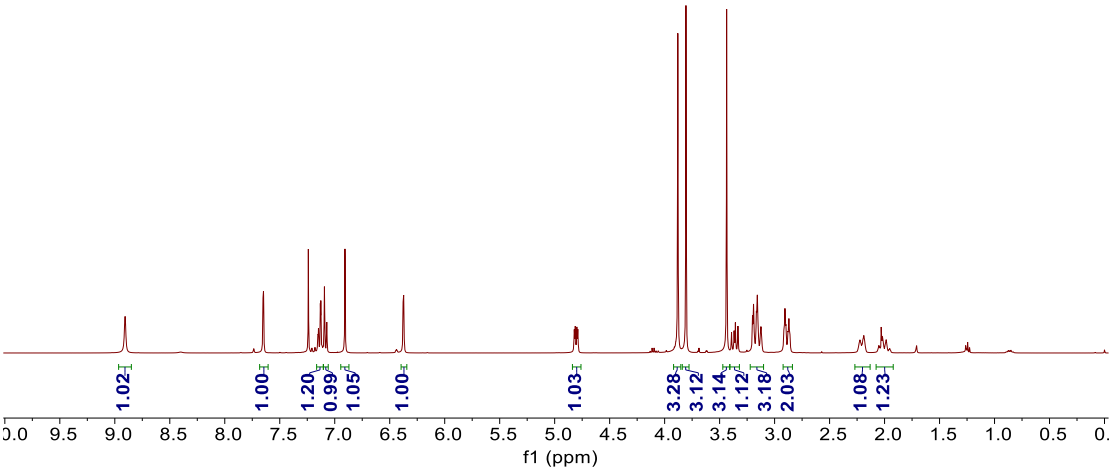
Prepared following the general procedure outlined above using [D]-alkenyl indole **5d** (101 mg, 0.2 mmol, 99% D, 1.0 equiv), $BF_3{\cdot}Et_2O$ (5 μL, 20 mol%), and DCE (5 mL). After 10 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (PE/EA = 50:1 ~ 20:1) gave the **5e** (80 mg, isolated yield 80%) as a white solid.

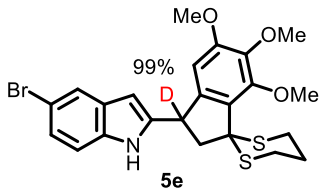
*Found 99% deuterium incorporation in product **5e**.*



2e

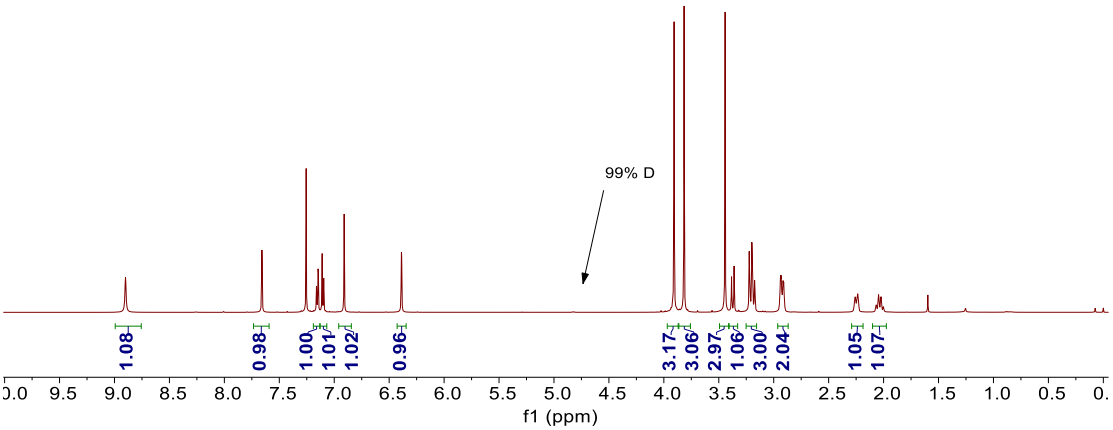
^{1}H NMR (400 MHz, $CDCl_3$)



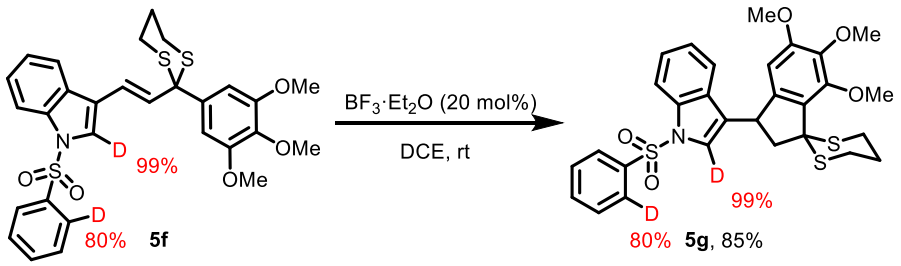


5e

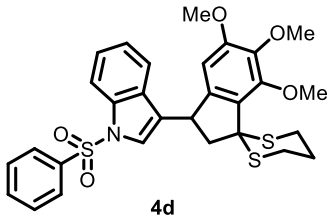
^{1}H NMR (600 MHz, $CDCl_3$)



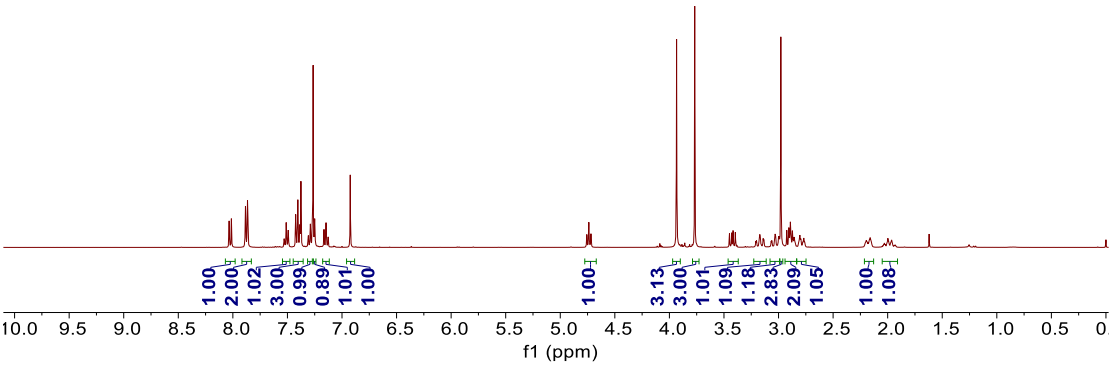
Deuterium incorporation experiments C

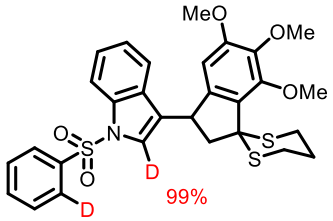


Prepared following the general procedure outlined above using [D]-alkenyl indole **5f** (114 mg, 0.2 mmol, 1.0 equiv), $BF_3{\cdot}Et_2O$ (5 μL, 20 mol%), and DCE (5 mL). After 12 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure. Purification by flash column chromatography (PE/EA = 50:1 ~ 20:1) gave the **5g** (94 mg, isolated yield 80%) as a colorless oil.

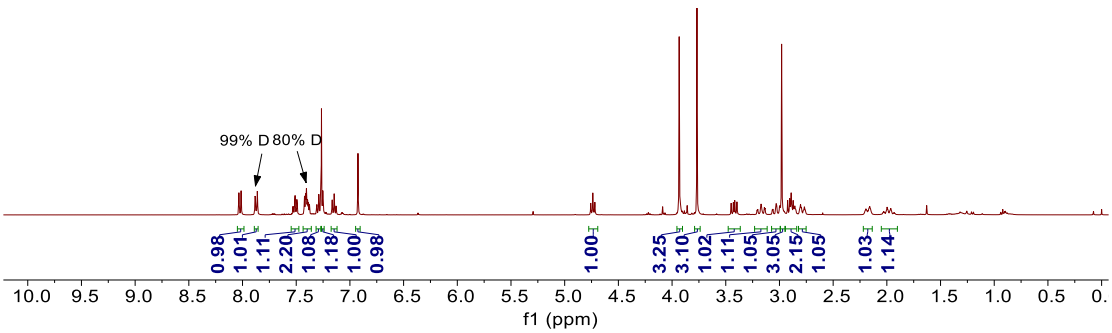

MeO
OMe
OMe
O
S
O
N
S
S

4d

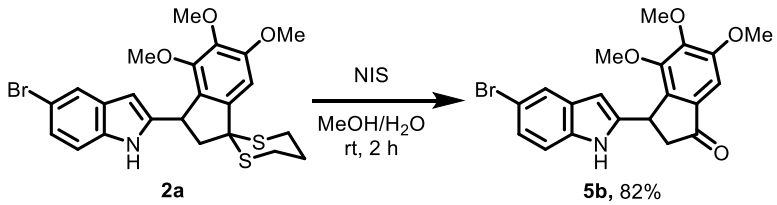

1.00 2.00 1.02 3.00 0.93 0.89 1.01 1.00 1.00 3.13 3.00 1.01 1.09 1.18 2.83 2.09 1.05 1.00 1.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


MeO
OMe
OMe
O
S
O
N
D
S
S
D
99%
80%

5g

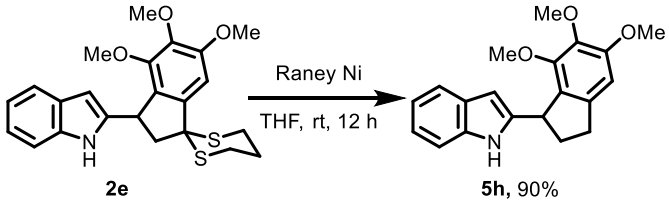

99% D
80% D
0.98 1.01 1.11 2.20 1.08 1.18 1.00 0.98 1.00 3.25 3.10 1.02 1.11 1.05 3.05 2.15 1.05 1.03 1.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

8. Representative synthetic applications



2a **5b,** 82%

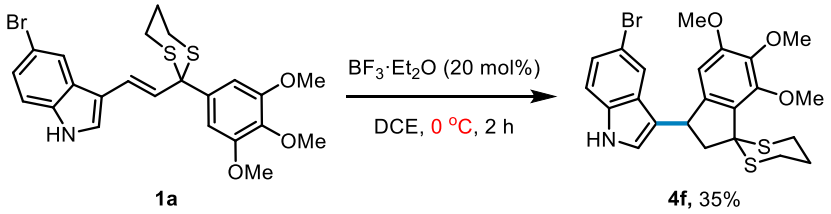
To a stirred solution of **2a** (51 mg, 0.1 mmol, 1.0 equiv) in MeOH/H_2O = 5:1 (3 mL) was added NIS (23 mg, 0.1 mmol, 1.0 equiv).[5] The resulting mixture was vigorously stirred at room temperature for 2 h. The mixture was diluted with DCM (10 mL), washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel to give the **5b** (34 mg, isolated yield 82%) as a yellow oil.



2e **5h,** 90%

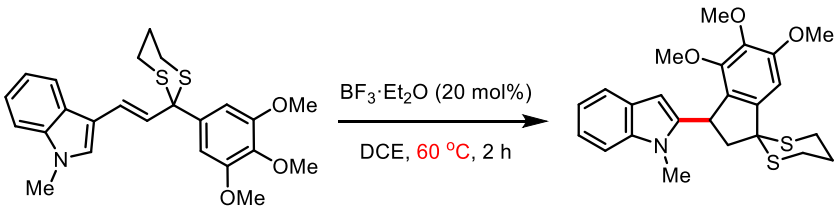
To a solution of **2e** (43 mg, 0.1 mmol) in THF (10 mL) was added Raney-nickel (1 g, Aldrich-2800 50% slurry in water).[6] The reaction mixture was stirred at room temperature for 12 h, then was filtered through a Celite pad and washed with THF. The organic solution was dried over Na_2SO_4 and concentrated in vacuum to afford a crude residue that was purified by flash column chromatography to give the **5h** (29 mg, isolated yield 90%) as a yellow oil.

9. Kinetic and thermodynamic control



1a **4f,** 35%

To a magnetically-stirred solution of alkenyl indole **1a** (101 mg, 0.2 mmol, 1.0 equiv) and in DCE (5 mL) were added 20 mol% of $BF_3{\cdot}Et_2O$. The resulting mixture was vigorously stirred at 0 °C for 2 h. The mixture was quenched with 1M $NaHCO_3$ (10 mL) and extracted with EtOAc (10 x 3 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EA = 50:1 ~ 20:1) to give the gave the **4f** (35 mg, isolated yield 35%) and compound **1a** (20 mg, 20% recovery).



1bd **2v,** 42%

To a magnetically-stirred solution of alkenyl indole **1bd** (88 mg, 0.2 mmol, 1.0 equiv) and in DCE (5 mL) were added 20 mol% of $BF_3{\cdot}Et_2O$. The resulting mixture was vigorously stirred at 60 °C for 2 h. The mixture was quenched with 1M $NaHCO_3$ (10 mL) and extracted with EtOAc (10 x 3 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and purified by flash column chromatography on silica gel (PE/EA = 50:1 ~ 20:1) to give the gave the **2v** (37 mg, isolated yield 42%) and compound **1bd** (16 mg, 18% recovery).

10. Sample preparation and crystal data of 2b

The compound **2b** (10 mg) was dissolved in a 10:1 mixture of petroleum and dichloromethane (5.0 mL) and kept at room temperature for slow evaporation to obtain crystals (about 2 days). Block shaped colorless crystals were formed, which were subjected to X-ray diffraction. A suitable crystal was selected and tested on Rigaku Oxford Diffraction. The crystal was kept at 302.74(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization.

Solid-state structure of compound **2b** (CCDC 2106586), thermal ellipsoids drawn at the 30% probability level. H-atoms omitted for clarity.

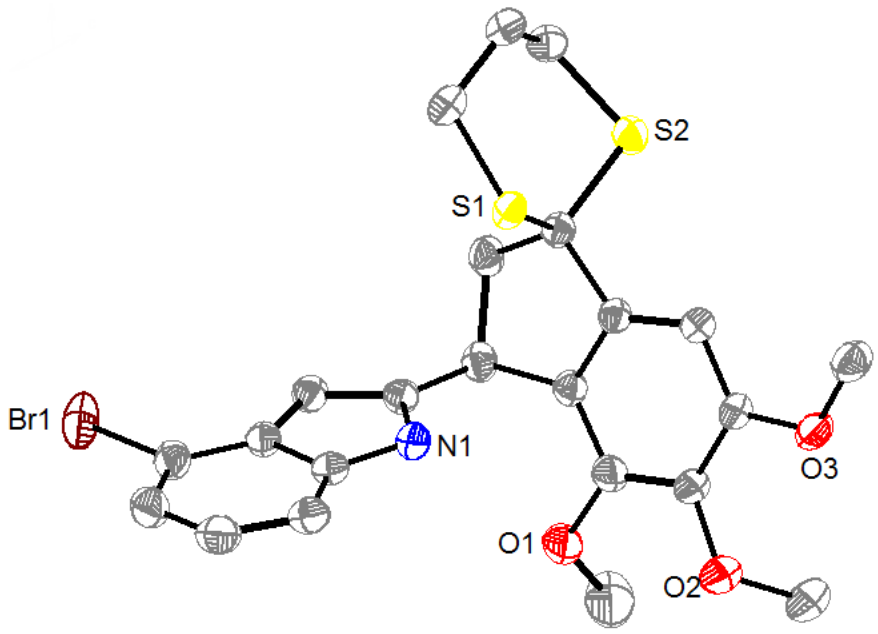


Table S3 Crystal data and structure refinement for Compound 2b

Empirical formula	$C_{46}H_{48}Br_2N_2O_6S_4$
Formula weight	1012.92
Temperature/K	302.74(10)
Crystal system	triclinic

Space group	P-1
a/Å	13.3806(2)
b/Å	13.8640(2)
c/Å	15.8118(2)
α/°	114.8860(10)
β/°	90.4100(10)
γ/°	117.9530(10)
Volume/$Å^3$	2272.66(6)
Z	2
$\rho_{calc}g/cm^3$	1.480
μ/mm^{-1}	4.384
F(000)	1040.0
Crystal size/mm^3	0.11 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.372 to 152.592
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	74877
Independent reflections	9090 [R_{int} = 0.0455, R_{sigma} = 0.0268]
Data/restraints/parameters	9090/0/548
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.1002
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.1039
Largest diff. peak/hole / e $Å^{-3}$	0.76/-0.79

11. References

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2. Li, J.; Dong, K.; Deng, X.; Li, R.-P.; Liu, J.; Wang, X.; Tang, S., C–H Alkenylation of Indoles through a Dual 1,3-Sulfur Migration Process. *Org. Lett.* **2022,** *24*, 7742-7746.
3. Saito, A.; Umakoshi, M.; Yagyu, N.; Hanzawa, Y., Novel One-Pot Approach to Synthesis of Indanones through Sb(V)-Catalyzed Reaction of Phenylalkynes with Aldehydes. *Org. Lett.* **2008,** *10*, 1783-1785.
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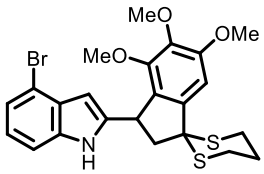
5. Li, R.-P.; Chen, X.; Xu, X.; Tang, Y.; Wang, H.; Tang, S., Stereoselective Synthesis of Highly Substituted 1,3-Dienes through Dual 1,3-Sulfur Rearrangement of Dithianes with Alkynylsilanes. *Org. Lett.* **2024,** *26*, 581-585.
6. Chen, X.; Li, R.-p.; Long, P.; Tang, Y.; Li, J.; Tang, S., Indium-catalyzed inter- and intramolecular dithianyl–alkyne metathesis reactions. *Chem. Commun.,* **2024,** *60*, 1285-1288.

12. Characterization of synthesized compounds

4-bromo-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2b)



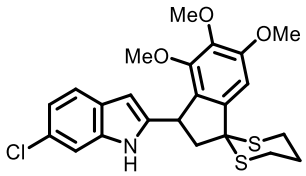
White solid, R_f = 0.58 (PE/EA = 5:1). 81 mg, isolated yield 80%, m.p. = 51.2-52.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (brs, 1H), 7.17 (dd, *J* = 16.4, 7.9 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.50 (d, *J* = 2.1 Hz, 1H), 4.83 (dd, *J* = 9.2, 3.9 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.46 (s, 3H), 3.37 (dd, *J* = 13.9, 9.3 Hz, 1H), 3.21 – 3.09 (m, 3H), 2.88 (d, *J* = 14.5 Hz, 2H), 2.24 – 2.14 (m, 1H), 2.04 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 150.0, 143.2, 141.8, 139.5, 136.3, 129.1, 128.0, 122.3, 122.0, 113.8, 110.0, 103.5, 100.4, 60.8, 60.6, 58.6, 56.3, 50.5, 40.8, 29.6, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508,0434; found: 506.0453, 508.0431.

6-chloro-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2c)



Colorless oil, R_f = 0.67 (PE/EA = 5:1). 70 mg, isolated yield 76%.

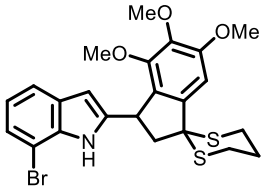
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.01 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.91 (s, 1H), 6.41 (d, *J* = 2.0 Hz, 1H), 4.82 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.46 (s, 3H), 3.38 (dd, *J* = 13.9, 9.4 Hz, 1H),

3.24 – 3.14 (m, 3H), 2.93 (dd, *J* = 14.1, 3.5 Hz, 2H), 2.33 – 2.19 (m, 1H), 2.11 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 150.1, 143.3, 141.9, 139.5, 136.6, 128.3, 127.0, 126.9, 120.9, 120.2, 110.8, 103.6, 100.1, 60.9, 60.7, 58.8, 56.4, 50.5, 40.9, 29.8, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}ClNO_3S_2$ $[M+H]^+$: 462.0959, found: 462.0961.

7-bromo-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2d)



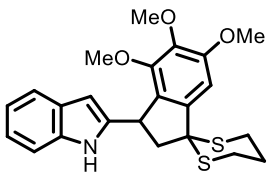
White solid, R_f = 0.56 (PE/EA = 5:1). 80 mg, isolated yield 79%, m.p. = 64.4-66.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (brs, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.96 – 6.87 (m, 2H), 6.51 (d, *J* = 2.2 Hz, 1H), 4.84 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.54 (s, 3H), 3.40 – 3.35 (m, 1H), 3.32 – 3.13 (m, 3H), 2.94 (t, *J* = 15.2 Hz, 2H), 2.33 – 2.15 (m, 1H), 2.08 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 150.1, 143.3, 141.8, 139.3, 135.1, 129.6, 128.3, 123.5, 120.6, 119.2, 104.3, 103.6, 101.2, 60.9, 60.8, 58.8, 56.4, 50.2, 40.8, 29.8, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508,0434; found: 506.0455, 508.0438.

2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2e)



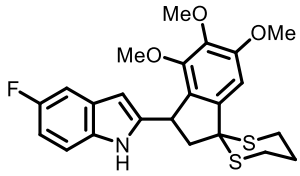
White solid, R_f = 0.52 (PE/EA = 5:1). 57 mg, isolated yield, 67%. m.p, = 65.3-66.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (brs, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.00 (m, 2H), 6.92 (s, 1H), 6.45 (s, 1H), 4.85 (dd, *J* = 9.4, 3.7 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.43 (s, 3H), 3.43 – 3.35 (m, 1H), 3.27 – 3.13 (m, 3H), 2.97 – 2.87 (m, 2H), 2.31 – 2.20 (m, 1H), 2.11 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 150.2, 143.4, 141.1, 139.6, 136.3, 128.7, 128.5, 121.2, 120.2, 119.5, 110.8, 103.7, 100.2, 60.9, 60.8, 58.9, 56.4, 50.8, 41.0, 29.8, 29.3, 24.9.

HRMS: m/z (ESI) calcd. for $C_{23}H_{26}NO_3S_2$ $[M+H]^+$: 428.1349, found: 428.1341.

5-fluoro-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2f)



Colorless oil, R_f = 0.46 (PE/EA = 5:1). 72 mg, isolated yield 81%.

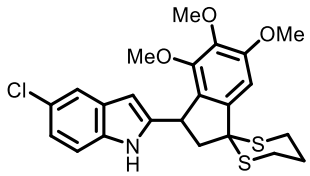
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (brs, 1H), 7.18 (dd, *J* = 9.8, 2.5 Hz, 1H), 7.13 (dd, *J* = 8.8, 4.6 Hz, 1H), 6.91 (s, 1H), 6.87 – 6.77 (m, 1H), 6.41 (d, *J* = 1.4 Hz, 1H), 4.82 (dd, *J* = 9.4, 3.7 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.46 (s, 3H), 3.39 (dd, *J* = 13.9, 9.4 Hz, 1H), 3.26 – 3.14 (m, 3H), 2.92 (d, *J* = 15.0 Hz, 2H), 2.28 – 2.20 (m, 1H), 2.09 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.92 (d, *J* = 233.3 Hz), 156.8, 155.0, 150.1, 143.4, 143.0, 139.5, 132.8, 128.79 (d, *J* = 10.2 Hz), 128.4, 111.29 (d, *J* = 9.7 Hz), 109.35 (d, *J* = 26.2 Hz), 104.94 (d, *J* = 23.4 Hz), 103.6, 100.36 (d, *J* = 4.5 Hz), 60.9, 60.7, 58.8, 56.4, 50.6, 41.0, 29.8, 29.3, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -125.34.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}FNO_3S_2$ $[M+H]^+$: 446.1254, found: 446.1248.

5-chloro-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2g)



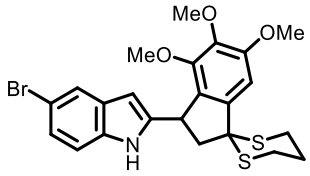
White solid, R_f= 0.66 (PE/EA = 5:1). 70 mg, isolated yield 77%, m.p. =76.5-78.5°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.91 (s, 1H), 6.39 (d, *J* = 1.8 Hz, 1H), 4.82 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.45 (s, 3H), 3.38 (dd, *J* = 13.9, 9.4 Hz, 1H), 3.22 (dd, *J* = 13.9, 3.6 Hz, 3H), 2.92 (d, *J* = 13.0 Hz, 2H), 2.28 – 2.18 (m, 1H), 2.09 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 150.0, 143.3, 142.6, 139.5, 134.5, 129.5, 128.3, 125.0, 121.3, 119.4, 111.8, 103.6, 99.8, 60.9, 60.6, 58.7, 56.3, 50.5, 40.9, 29.7, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}ClNO_3S_2$ $[M+H]^+$: 462.0959, found: 462.0960.

5-bromo-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2a)



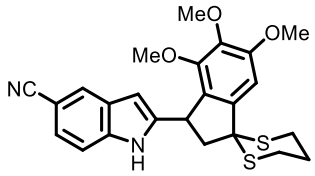
White solid, R_f= 0.48 (PE/EA = 5:1). 87 mg, isolated yield 86%, m.p. = 86.3-88.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.65 (d, J = 1.8 Hz, 1H), 7.14 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.91 (s, 1H), 6.37 (d, *J* = 2.1 Hz, 1H), 4.81 (dd, *J* = 9.3, 3.7 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.44 (s, 3H), 3.36 (dd, *J* = 13.9, 9.3 Hz, 1H), 3.22 – 3.10 (m, 3H), 2.96 – 2.84 (m, 2H), 2.26 – 2.13 (m, 1H), 2.08 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 150.0, 143.2, 142.4, 139.5, 134.8, 130.1, 128.2, 123.9, 122.5, 112.6, 112.2, 103.5, 99.7, 60.8, 60.6, 58.7, 56.3, 50.5, 40.8, 29.7, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508,0434; found: 506.0453, 508.0435.

2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole-5-carbonitrile (2h)



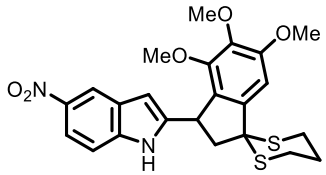
White solid, R_f = 0.25 (PE/EA = 5:1). 60 mg, isolated yield 66%, m.p. = 111.3-113.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (brs, 1H), 7.88 (d, *J* = 0.8 Hz, 1H), 7.34 – 7.28 (m, 2H), 6.92 (s, 1H), 6.52 (d, *J* = 2.1 Hz, 1H), 4.86 (dd, *J* = 9.4, 3.3 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.51 (s, 3H), 3.40 (dd, *J* = 14.0, 9.4 Hz, 1H), 3.29 – 3.16 (m, 3H), 2.98 – 2.90 (m, 2H), 2.31 – 2.21 (m, 1H), 2.12 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 150.0, 143.6, 143.3, 139.5, 138.0, 128.2, 127.8, 125.6, 124.4, 121.1, 111.7, 103.7, 102.6, 100.8, 61.0, 60.8, 58.8, 56.4, 50.3, 40.8, 30.0, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{24}H_{25}N_2O_3S_2$ $[M+H]^+$: 453.1300, found: 453.1303.

5-nitro-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2i)



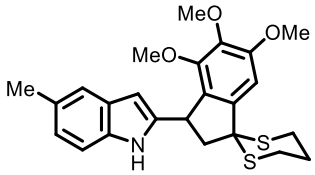
White solid, R_f = 0.40 (PE/EA = 5:1). 66 mg, isolated yield 70%, m.p. = 146.6-148.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (brs, 1H), 8.50 (d, *J* = 2.2 Hz, 1H), 8.01 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.92 (s, 1H), 6.62 (s, 1H), 4.87 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.53 (s, 3H), 3.41 (dd, *J* = 14.0, 9.4 Hz, 1H), 3.33 – 3.18 (m, 3H), 2.97 (dd, *J* = 9.2, 5.3 Hz, 2H), 2.32 – 2.23 (m, 1H), 2.13 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 150.0, 144.6, 143.3, 141.8, 139.5, 139.4, 127.8, 127.7, 117.3, 117.2, 110.7, 103.7, 102.2, 61.0, 60.8, 58.8, 56.4, 50.1, 40.8, 30.0, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}N_2O_5S_2$ $[M+H]^+$: 473.1199, found: 473.1202.

5-methyl-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2j)



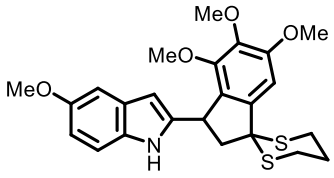
Colorless oil, R_f = 0.48 (PE/EA = 10:1). 64 mg, isolated yield 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.57 (m, 1H), 7.33 (s, 1H), 7.13 (d, *J* = 8.2 Hz, 1H), 6.93 – 6.83 (m, 2H), 6.36 (d, *J* = 1.2 Hz, 1H), 4.83 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.42 (s, 3H), 3.40 – 3.33 (m, 1H), 3.24 – 3.14 (m, 3H), 2.95 – 2.87 (m, 2H), 2.41 (s, 3H), 2.28 – 2.19 (m, 1H), 2.06 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.2, 143.4, 141.2, 139.5, 134.6, 128.8, 128.7, 128.6, 122.7, 119.8, 110.5, 103.6, 99.7, 60.9, 60.7, 58.8, 56.4, 50.8, 41.0, 29.7, 29.3, 24.9, 21.5.

HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_3S_2$ $[M+H]^+$: 442.1505, found: 442.1499.

5-methoxy-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2k)



Colorless oil, R_f = 0.65 (PE/EA = 10:1). 65 mg, isolated yield 71%.

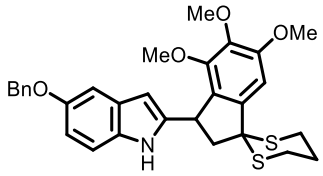
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.91 (s, 1H), 6.74 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 4.81 (dd,

J = 9.3, 3.8 Hz, 1H), 3.90 (s, 3H), 3.82 (d, *J* = 3.0 Hz, 6H), 3.44 (s, 3H), 3.38 (dd, *J* = 13.9, 9.3 Hz, 1H), 3.23 – 3.13 (m, 3H), 2.94 – 2.83 (m, 2H), 2.27 – 2.17 (m, 1H), 2.07 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 154.1, 150.2, 143.4, 141.9, 139.5, 131.4, 128.9, 128.7, 111.4, 111.1, 103.6, 102.2, 100.1, 60.9, 60.7, 58.8, 56.4, 55.9, 50.8, 41.0, 29.8, 29.3, 24.9.

HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_4S_2$ $[M+H]^+$: 458.1454, found:458. 1455.

5-(benzyloxy)-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2l)



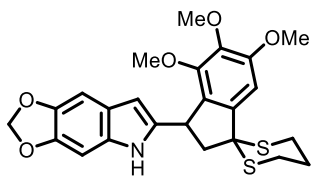
White solid, R_f = 0.65 (PE/EA = 5:1). 69 mg, isolated yield 65%, m.p. = 98.3-100.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 1H), 7.50 – 7.43 (m, 2H), 7.42 – 7.33 (m, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.91 (s, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.36 (s, 1H), 5.08 (s, 2H), 4.82 (dd, *J* = 9.4, 3.7 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.45 (s, 3H), 3.39 (dd, *J* = 13.9, 9.4 Hz, 1H), 3.26 – 3.14 (m, 3H), 2.96 – 2.86 (m, 2H), 2.25 (d, *J* = 14.7 Hz, 1H), 2.08 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 153.3, 150.2, 143.4, 142.0, 139.5, 138.0, 131.7, 128.9, 128.7, 128.6, 127.8, 127.7, 111.9, 111.5, 103.9, 103.6, 100.1, 71.0, 61.0, 60.8, 58.9, 56.4, 50.8, 41.1, 29.8, 29.3, 24.9.

HRMS: m/z (ESI) calcd. for $C_{30}H_{32}NO_4S_2$ $[M+H]^+$: 534,1767, found: 534.1770.

6-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-5*H*-[1,3]dioxolo[4,5-f]indole (2m)



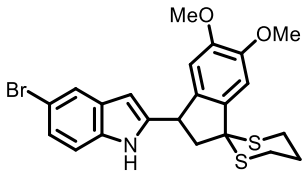
White solid, R_f = 0.48 (PE/EA = 10:1). 62 mg, isolated yield 65%, m.p. = 110.2-112.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 6.72 (s, 1H), 6.30 (brs, 1H), 5.87 (s, 2H), 4.78 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.45 (s, 3H), 3.37 (dd, *J* = 13.9, 9.3 Hz, 1H), 3.24 – 3.13 (m, 3H), 2.92 (d, *J* = 14.4 Hz, 2H), 2.29 – 2.19 (m, 1H), 2.08 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.2, 144.2, 143.4, 142.7, 139.5, 131.0, 128.8, 122.2, 103.6, 100.4, 98.9, 92.1, 60.9, 60.8, 58.8, 56.4, 50.8, 41.0, 29.8, 29.3, 24.9.

HRMS: m/z (ESI) calcd. for $C_{24}H_{26}NO_5S_2$ $[M+H]^+$: 472.1247, found:472.1254.

5-bromo-2-(5,6-dimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2n)



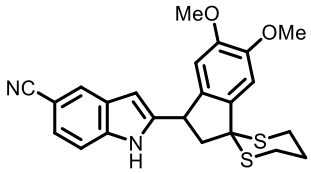
Colorless oil, R_f = 0.33 (PE/EA = 10:1). 58 mg, isolated yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (brs, 1H), 7.59 (d, *J* = 0.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.11 (s, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.56 (s, 1H), 4.77 – 4.70 (m, 1H), 3.93 (s, 3H), 3.70 (s, 3H), 3.55 (dd, *J* = 12.8, 7.3 Hz, 1H), 3.27 – 3.08 (m, 2H), 2.92 – 2.82 (m, 2H), 2.79 (dd, *J* = 12.9, 9.2 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.08 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.2, 137.2, 136.1, 135.3, 128.6, 125.1, 123.4, 121.9, 117.7, 112.9, 112.8, 107.5, 107.1, 58.1, 56.3, 56.2, 52.6, 40.0, 30.4, 28.7, 25.2.

HRMS: m/z (ESI) calcd. for $C_{22}H_{23}BrNO_2S_2$ $[M+H]^+$:476.0348, 478.0328. found: 476.0337, 478.0321.

2-(5,6-dimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole-5-carbonitrile (2o)



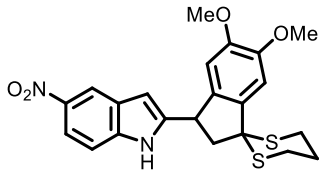
Colorless oil, R_f = 0.43 (PE/EA = 5:1). 38 mg, isolated yield 45%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (brs, 1H), 7.77 (s, 1H), 7.50 – 7.37 (m, 2H), 7.22 (s, 1H), 7.13 (s, 1H), 6.51 (s, 1H), 4.78 (t, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.70 (s, 3H), 3.63 – 3.50 (m, 1H), 3.28 – 3.07 (m, 2H), 2.96 – 2.78 (m, 3H), 2.28 – 2.18 (m, 1H), 2.10 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 149.5, 138.5, 136.5, 136.3, 126.6, 125.3, 124.4, 120.8, 119.1, 112.4, 107.4, 107.2, 102.7, 58.0, 56.3, 56.2, 52.7, 40.1, 30.4, 28.7, 25.1.

HRMS: m/z (ESI) calcd. for $C_{23}H_{23}N_2O_2S_2$ $[M+H]^+$: 423.1195, found: 423.1182.

2-(5,6-dimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-5-nitro-1*H*-indole (2p)



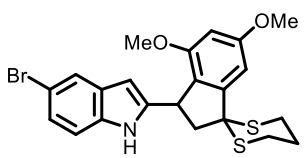
Yellow oil, R_f = 0.58 (PE/EA = 2:1). 48 mg, isolated yield 55%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (brs, 1H), 8.51 (d, *J* = 2.2 Hz, 1H), 8.13 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.13 (s, 1H), 6.58 (d, *J* = 1.0 Hz, 1H), 4.84 (t, *J* = 8.1 Hz, 1H), 3.95 (s, 3H), 3.72 (s, 3H), 3.63 (dd, *J* = 12.9, 7.5 Hz, 1H), 3.31 – 3.19 (m, 1H), 3.20 – 3.09 (m, 1H), 2.96 – 2.77 (m, 3H), 2.28 – 2.18 (m, 1H), 2.10 – 1.95 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.4, 141.7, 139.6, 136.5, 136.4, 126.4, 125.2, 121.1, 118.0, 116.6, 111.5, 107.4, 107.2, 58.0, 56.3, 56.2, 52.9, 39.8, 30.4, 28.7, 25.1.

HRMS: m/z (ESI) calcd. for $C_{22}H_{23}N_2O_4S_2$ $[M+H]^+$: 443.1094, found: 443.1079.

5-bromo-2-(4,6-dimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (2q)



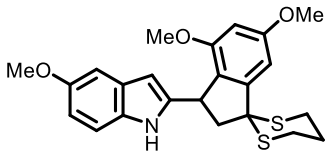
Colorless oil, R_f = 0.58 (PE/EA =10:1). 68 mg, isolated yield 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (brs, 1H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.14 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 2.1 Hz, 1H), 6.35 (dd, *J* = 11.7, 2.1 Hz, 2H), 4.76 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.83 (s, 3H), 3.64 (s, 3H), 3.36 (dd, *J* = 13.9, 9.3 Hz, 1H), 3.26 – 3.10 (m, 3H), 2.97 – 2.85 (m, 2H), 2.27 – 2.17 (m, 1H), 2.09 – 1.97 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 157.1, 146.6, 142.7, 134.7, 130.3, 123.7, 122.9, 122.5, 112.5, 112.2, 100.5, 100.2, 99.6, 58.8, 55.9, 55.7, 50.7, 40.4, 29.7, 29.0, 24.9.

HRMS: m/z (ESI) calcd. for $C_{22}H_{23}BrNO_2S_2$ $[M+H]^+$: :476.0348, 478.0328. found: 476.0334, 478.0311.

2-(4,6-dimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-5-methoxy-1*H*-indole (2r)



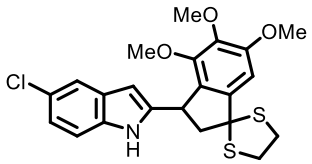
Colorless oil, R_f = 0.50 (PE/EA =10:1). 52 mg, isolated yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (brs, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.75 – 6.70 (m, 2H), 6.37 (d, *J* = 2.1 Hz, 1H), 6.32 (d, *J* = 2.1 Hz, 1H), 4.76 (dd, *J* = 9.4, 3.4 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.65 (s, 3H), 3.37 (dd, *J* = 13.8, 9.3 Hz, 1H), 3.25 – 3.11 (m, 3H), 2.94 – 2.85 (m, 2H), 2.28 – 2.15 (m, 1H), 2.10 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 157.1, 154.0, 146.7, 142.2, 131.4, 129.0, 123.3, 111.4, 110.9, 102.2, 100.5, 100.3, 99.8, 58.8, 56.0, 55.9, 55.7, 50.9, 40.5, 29.6, 29.1, 25.0.

HRMS: m/z (ESI) calcd. for $C_{23}H_{26}NO_3S_2$ $[M+H]^+$:428.1349, found:428.1341.

5-chloro-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithiolan]-3-yl)-1*H*-indole (2s)



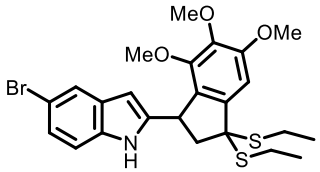
Colorless oil, R_f = 0.65 (PE/EA =10:1). 56 mg, isolated yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (brs, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.91 (s, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 4.68 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.66 (s, 3H), 3.60 – 3.39 (m, 4H), 3.20 (dd, *J* = 14.0, 8.4 Hz, 1H), 3.05 (dd, *J* = 14.1, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 149.1, 142.6, 142.2, 140.4, 134.5, 129.5, 127.6, 125.1, 121.4, 119.5, 111.7, 103.8, 99.7, 72.4, 61.0, 60.9, 56.3, 54.2, 41.4, 41.2, 40.2.

HRMS: m/z (ESI) calcd. for $C_{22}H_{23}ClNO_3S_2$ $[M+H]^+$: 448.0802, found: 448.0807.

2-(3,3-bis(ethylthio)-5,6,7-trimethoxy-2,3-dihydro-1H-inden-1-yl)-5-bromo-1*H*-indole (2t)



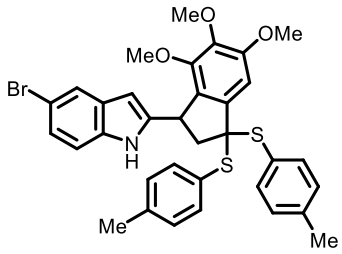
Colorless oil, R_f = 0.68 (PE/EA =10:1). 42 mg, isolated yield 40%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.51 (d, *J* = 1.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.81 (s, 1H), 4.78 (t, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.30 (s, 3H), 2.98 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.66 – 2.55 (m, 3H), 1.28 – 1.09 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 150.7, 142.5, 140.5, 135.2, 128.6, 128.5, 124.8, 123.1, 122.0, 118.6, 112.8, 112.6, 103.1, 65.5, 61.0, 60.2, 56.5, 51.5, 38.1, 25.5, 25.4, 14.2, 14.0.

HRMS: m/z (ESI) calcd. for $C_{24}H_{29}BrNO_3S_2$ $[M+H]^+$:522.0767, 524.0747. found: 522.0761, 524.0743.

5-bromo-2-(5,6,7-trimethoxy-3,3-bis(p-tolylthio)-2,3-dihydro-1*H*-inden-1-yl)-1H-indole (2u)



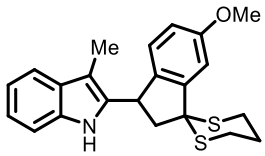
Colorless oil, R_f = 0.66 (PE/EA =10:1). 74 mg, isolated yield 58%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (brs, 1H), 7.25 – 7.22 (m, 4H), 7.20 – 7.16 (m, 2H), 7.13 (d, *J* = 1.6 Hz, 1H), 7.09 – 7.05 (m, 2H), 7.04 – 6.97 (m, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.52 (s, 1H), 4.50 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.21 (s, 3H), 2.74 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.57 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 150.2, 142.4, 140.1, 139.5, 139.3, 137.0, 136.2, 135.1, 129.7, 129.4, 129.4, 129.3, 128.9, 128.5, 124.8, 123.0, 121.9, 118.4, 112.6, 112.5, 104.1, 70.7, 61.1, 60.2, 56.0, 48.3, 37.8, 21.5, 21.4.

HRMS: m/z (ESI) calcd. for $C_{34}H_{33}BrNO_3S_2$ $[M+H]^+$:646.1080, 648.1060. found: 646.1071, 648.1052.

2-(6-methoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-3-methyl-1*H*-indole (3a)



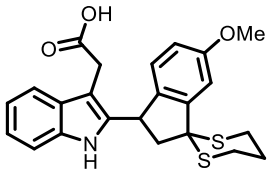
Colorless oil, R_f = 0.45 (PE/EA =5:1). 50 mg, isolated yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (brs, 1H), 7.56 – 7.50 (m, 1H), 7.20 – 7.15 (m, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.91 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.85 (t, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 3.49 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.27 – 3.10 (m, 2H), 2.98 – 2.83 (m, 3H), 2.37 (s, 3H), 2.28 – 2.19 (m, 1H), 2.13 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 145.9, 135.7, 135.7, 135.7, 129.2, 126.2, 121.6, 119.1, 118.5, 116.9, 110.7, 109.2, 108.2, 58.2, 55.8, 51.3, 39.8, 29.8, 29.0, 25.1, 8.8.

HRMS: m/z (ESI) calcd. for $C_{22}H_{24}NOS_2$ $[M+H]^+$: 382.1294, found: 382.1277.

2-(2-(6-methoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)acetic acid (3b)



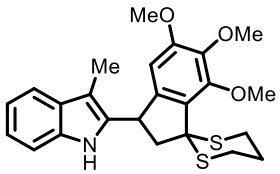
Colorless oil, R_f = 0.40 (PE/EA =1:1). 66 mg, isolated yield 77%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (brs, 1H), 7.60 – 7.54 (m, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.06 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.90 – 4.77 (m, 1H), 3.86 (d, *J* = 1.7 Hz, 2H), 3.81 (s, 3H), 3.58 – 3.42 (m, 1H), 3.23 – 3.09 (m, 2H), 2.94 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.91 – 2.75 (m, 2H), 2.24 – 2.14 (m, 1H), 2.07 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 160.3, 146.0, 138.2, 135.6, 135.1, 128.0, 126.4, 122.1, 119.8, 118.5, 117.0, 111.0, 109.3, 104.7, 58.2, 55.8, 51.4, 39.9, 30.3, 29.6, 29.0, 24.9.

HRMS: m/z (ESI) calcd. for $C_{23}H_{24}NO_3S_2$ $[M+H]^+$: 426.1192, found: 426.1186.

3-methyl-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (3c)



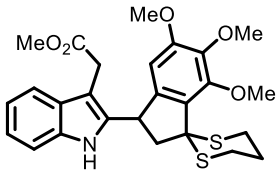
Colorless oil, R_f = 0.25 (PE/EA =10:1). 57 mg, isolated yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (brs, 1H), 7.55 – 7.48 (m, 1H), 7.21 – 7.14 (m, 1H), 7.10 – 7.01 (m, 2H), 6.92 (s, 1H), 4.95 (dd, *J* = 9.7, 3.3 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.40 (dd, *J* = 14.0, 9.7 Hz, 1H), 3.30 (s, 3H), 3.21 – 3.12 (m, 3H), 2.92 (dd, *J* = 14.2, 3.9 Hz, 2H), 2.40 (s, 3H), 2.27 – 2.18 (m, 1H), 2.08 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 150.1, 143.4, 139.2, 136.2, 135.4, 129.3, 129.0, 121.1, 118.8, 118.3, 110.6, 106.9, 103.4, 60.8, 60.3, 59.1, 56.3, 50.6, 38.3, 29.8, 29.2, 24.8, 8.7.

HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_3S_2$ $[M+H]^+$:442.1505, found: 442.1516.

methyl 2-(2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)acetate (3d)



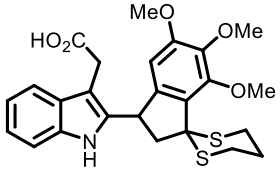
Colorless oil, R_f = 0.45 (PE/EA =2:1). 71 mg, isolated yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (brs, 1H), 7.60 – 7.52 (m, 1H), 7.20 – 7.18 (m, 1H), 7.11 – 7.06 (m, 2H), 6.92 (s, 1H), 4.98 (dd, *J* = 9.8, 3.1 Hz, 1H), 4.00 – 3.84 (m, 5H), 3.79 (s, 3H), 3.71 (s, 3H), 3.44 (dd, *J* = 14.2, 9.8 Hz, 1H), 3.32 (s, 3H), 3.24 – 3.13 (m, 3H), 2.99 – 2.88 (m, 2H), 2.29 – 2.18 (m, 1H), 2.09 – 2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 155.0, 150.1, 143.3, 139.4, 138.3, 135.3, 128.7, 128.1, 121.5, 119.4, 118.5, 110.9, 104.2, 103.4, 60.8, 60.4, 59.1, 56.4, 52.0, 50.6, 38.4, 30.1, 29.9, 29.2, 24.8.

HRMS: m/z (ESI) calcd. for $C_{26}H_{30}NO_5S_2$ $[M+H]^+$: 500.1560, found: 500.1550.

2-(2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)acetic acid (3f)



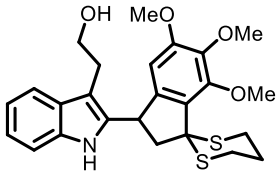
Colorless oil, R_f = 0.35 (PE/EA =1:1). 78 mg, isolated yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (brs, 1H), 7.57 – 7.54 (m, 1H), 7.21 – 7.15 (m, 1H), 7.09 – 7.05 (m, 2H), 6.91 (s, 1H), 4.94 (dd, *J* = 9.7, 3.2 Hz, 1H), 4.03 – 3.85 (m, 5H), 3.77 (s, 3H), 3.40 (dd, *J* = 14.2, 9.7 Hz, 1H), 3.33 (s, 3H), 3.19 – 3.10 (m, 3H), 2.87 (d, *J* = 14.7 Hz, 2H), 2.23 – 2.15 (m, 1H), 2.04 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.3, 155.0, 149.9, 143.2, 139.4, 138.5, 135.3, 128.4, 128.0, 121.7, 119.5, 118.4, 110.9, 103.5, 103.4, 60.8, 60.4, 59.0, 56.3, 50.5, 38.4, 30.2, 29.8, 29.1, 24.8.

HRMS: m/z (ESI) calcd. for $C_{25}H_{28}NO_5S_2$ $[M+H]^+$: 486.1403, found: 486.1409.

2-(2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)ethan-1-ol (3f)



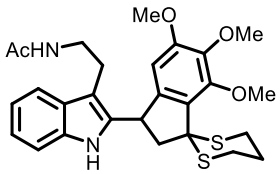
Colorless oil, R_f = 0.28 (PE/EA =2:1). 56 mg, isolated yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.13 – 7.05 (m, 2H), 6.94 (s, 1H), 5.04 (dd, *J* = 9.5, 4.3 Hz, 1H), 3.93 (s, 5H), 3.79 (s, 3H), 3.43 (dd, *J* = 13.9, 9.5 Hz, 1H), 3.31 (s, 3H), 3.21 – 3.10 (m, 4H), 3.03 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.43 (brs, 1H), 2.23 (d, *J* = 14.2 Hz, 1H), 2.09 – 1.98 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 149.8, 143.2, 139.9, 138.2, 135.8, 128.2, 128.2, 121.6, 119.3, 118.3, 110.9, 108.2, 103.6, 63.2, 60.9, 60.4, 58.9, 56.4, 51.2, 38.4, 29.6, 29.4, 28.0, 24.9.

HRMS: m/z (ESI) calcd. for $C_{25}H_{30}NO_4S_2$ $[M+H]^+$: 472.1611, found: 472.1620.

N-(2-(2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)ethyl)acetamide (3g)



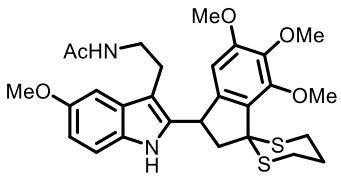
Yellow solid, R_f = 0.45 (DCM/MeOH = 10:1). 74 mg, isolated yield 73%, m.p. = 81.1-83.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.6 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.20 (d, *J* = 6.4 Hz, 1H), 7.14 – 7.04 (m, 2H), 6.96 (s, 1H), 6.42 (brs, 1H), 4.91 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.92 (s, 4H), 3.79 (s, 3H), 3.48 – 3.33 (m, 2H), 3.26 (s, 3H), 3.18 – 3.07 (m, 3H), 3.01 – 2.92 (m, 2H), 2.92 – 2.85 (m, 2H), 2.27 – 2.15 (m, 1H), 2.06 – 1.95 (m, 1H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 155.0, 149.7, 143.3, 140.2, 137.3, 135.7, 128.1, 128.0, 121.7, 119.4, 118.3, 110.8, 109.1, 103.8, 60.8, 60.3, 58.7, 56.4, 51.2, 40.3, 38.4, 29.5, 29.4, 24.8, 24.3, 23.0.

HRMS: m/z (ESI) calcd. for $C_{27}H_{33}N_2O_4S_2$ $[M+H]^+$: 513.1876, found: 513.1871.

N-(2-(5-methoxy-2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indol-3-yl)ethyl)acetamide (3h)



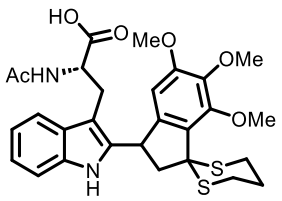
Yellow solid, R_f = 0.48 (DCM/MeOH = 10:1). 82 mg, isolated yield 75%, m.p. = 94.1-96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 3.0 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.95 (s, 1H), 6.75 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.50 (brs, 1H), 4.88 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.91 (s, 4H), 3.84 (s, 3H), 3.79 (s, 3H), 3.48 – 3.33 (m, 2H), 3.26 (s, 3H), 3.24 – 3.05 (m, 3H), 3.00 – 2.85 (m, 4H), 2.33 – 2.14 (m, 1H), 2.05 – 1.96 (m, 1H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 154.9, 153.9, 149.6, 143.2, 140.1, 138.1, 130.7, 128.4, 128.0, 111.5, 111.4, 108.9, 103.8, 100.4, 60.8, 60.3, 58.6, 56.3, 55.9, 51.2, 40.1, 38.4, 29.5, 29.3, 24.8, 24.3, 23.0.

HRMS: m/z (ESI) calcd. for $C_{28}H_{34}N_2NaO_5S_2$ $[M+Na]^+$:565.1801, found:565.1800.

(2S)-2-acetamido-3-(2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3] dithian]-3-yl)-1*H*-indol-3-yl)propanoic acid (3i)



Yellow oil, R_f (Isomer-1) = 0.58 (DCM/MeOH = 10:1), R_f (Isomer-2) = 0.43 (DCM/MeOH = 10:1). 74 mg, isolated yield 67% (Isomer-1: Isomer-2 = 1.2:1).

Isomer – 1: ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.72 (brs, 1H), 10.50 (s, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 6.98 – 6.89 (m, 2H), 6.88 (s, 1H), 4.78 – 4.71 (m, 1H), 4.68 – 4.59 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.52 (dd, J = 13.0, 7.5 Hz, 1H), 3.26 – 3.19 (m, 3H), 3.16 (s, 3H), 3.14 – 3.08 (m, 1H), 2.94 – 2.82 (m, 2H), 2.65 (dd, J = 13.1, 8.9 Hz, 1H), 2.19 – 2.12 (m, 1H), 1.86 – 1.78 (m, 1H), 1.73 (s, 3H).

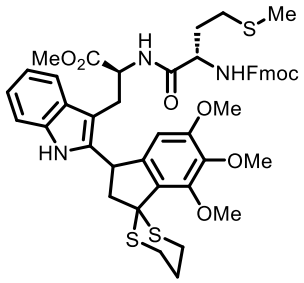
^{13}C NMR (151 MHz, DMSO-d_6) δ 173.4, 168.8, 154.0, 149.5, 142.7, 140.7, 137.7, 135.8, 128.0, 120.3, 118.2, 118.0, 110.9, 106.3, 103.4, 60.2, 59.8, 57.9, 56.1, 52.7, 51.4, 38.1, 29.3, 27.7, 26.7, 24.5, 22.4.

Isomer – 2:^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (brs, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.96 (s, 1H), 6.80 (d, J = 5.5 Hz, 1H), 4.95 – 4.87 (m, 2H), 3.93 (s, 3H), 3.78 (s, 3H), 3.53 (dd, J = 14.9, 5.4 Hz, 1H), 3.46 (s, 3H), 3.43 (dd, J = 14.1, 9.6 Hz, 1H), 3.33 (dd, J = 14.9, 9.6 Hz, 1H), 3.22 – 3.15 (m, 2H), 3.10 (dd, J = 14.0, 3.7 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.30 – 2.19 (m, 1H), 2.09 (s, 1H), 2.07 – 1.98 (m, 2H), 1.94 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.3, 171.9, 155.2, 149.7, 143.3, 139.7, 138.5, 135.7, 128.2, 127.7, 122.0, 119.8, 118.6, 110.9, 105.6, 104.0, 61.0, 60.8, 58.9, 56.5, 53.6, 51.1, 38.2, 29.8, 29.3, 26.5, 24.8, 22.6.

HRMS: m/z (ESI) calcd. for $C_{28}H_{33}N_2O_6S_2$ $[M+H]^+$:557.1775, found:557.1765.

methyl (2S)-2-((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-4-(methylthio)butanamido)-3-(2-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1H-indol-3-yl)propanoate (3j)



Yellow oil, R_f (Isomer-1) = 0.35 (PE/EA = 2:1), R_f (Isomer-2) = 0.25 (PE/EA = 2:1). 97 mg, isolated yield 55% (Isomer-1: Isomer-2 = 1:1).

Isomer – 1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.42 – 7.33 (m, 3H), 7.31 – 7.27 (m, 2H), 7.19 – 7.14 (m, 1H), 7.12 – 7.02 (m, 2H), 6.93 (s, 1H), 5.60 (d, *J* = 8.1 Hz, 1H), 5.11 (dd, *J* = 9.0, 4.7 Hz, 1H), 4.84 (dd, *J* = 9.3, 4.9 Hz, 1H), 4.33 – 4.21 (m, 3H), 4.16 (t, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.69 (s, 3H), 3.58 (dd, *J* = 15.0, 4.4 Hz, 1H), 3.42 – 3.32 (m, 1H), 3.30 (s, 3H), 3.15 – 3.02 (m, 2H), 2.91 (dd, *J* = 13.8, 4.9 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.54 – 2.36 (m, 2H), 2.16 (d, *J* = 14.4 Hz, 1H), 2.11 – 2.04 (m, 1H), 2.01 (s, 3H), 1.95 (d, *J* = 13.6 Hz, 1H), 1.87 – 1.77 (m, 1H).

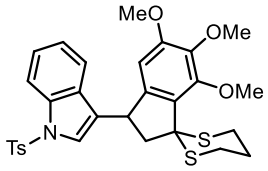
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 171.2, 155.6, 155.3, 149.4, 144.1, 144.0, 143.7, 141.4, 140.2, 138.8, 135.5, 128.5, 127.8, 127.2, 125.3, 121.9, 120.1, 120.0, 119.7, 118.3, 110.9, 105.6, 104.2, 67.0, 61.0, 60.8, 58.8, 56.5, 54.1, 53.1, 52.5, 51.2, 47.3, 38.7, 32.8, 29.8, 29.5, 26.8, 24.8, 15.3.

Isomer – 2:^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.75 (dd, *J* = 7.6, 4.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.33 – 7.25 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.10 – 6.95 (m, 2H), 6.92 (s, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 5.35 (d, *J* = 8.3 Hz, 1H), 4.94 (t, *J* = 6.9 Hz, 1H), 4.88 (dd, *J* = 9.6, 3.4 Hz, 1H), 4.41 – 4.28 (m, 3H), 4.17 (t, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 3.79 (d, *J* = 2.8 Hz, 6H), 3.53 (dd, *J* = 14.8, 5.8 Hz, 1H), 3.43 (dd, *J* = 14.0, 9.6 Hz, 1H), 3.38 – 3.25 (m, 4H), 3.20 (dd, *J* = 14.0, 3.4 Hz, 2H), 2.98 – 2.81 (m, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 2.24 (d, *J* = 13.8 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.92 (s, 4H), 1.85 – 1.72 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 170.9, 155.7, 155.2, 149.9, 144.0, 143.8, 143.4, 141.4, 139.4, 138.8, 135.6, 128.4, 128.0, 127.8, 127.2, 125.2, 125.1, 121.9, 120.1, 119.6, 118.1, 111.1, 105.3, 103.7, 66.9, 61.0, 60.5, 59.1, 56.4, 53.4, 53.1, 52.6, 50.7, 47.3, 38.3, 32.5, 29.9, 29.6, 29.2, 26.8, 24.8, 15.1.

HRMS: m/z (ESI) calcd. for $C_{47}H_{52}N_3O_8S_3$ $[M+H]^+$:882.2911, found: 882.2895.

1-tosyl-3-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-2-yl)-1H-indole (4a)



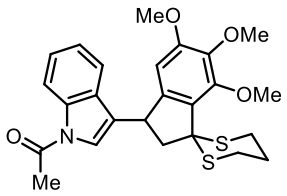
Colorless oil, R_f = 0.35 (PE/EA = 10:1). 99 mg, isolated yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.38 (s, 1H), 7.29 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 4.74 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 3.42 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.22 – 3.11 (m, 1H), 3.01 (s, 4H), 2.92 – 2.84 (m, 2H), 2.78 (d, *J* = 14.1 Hz, 1H), 2.32 (s, 3H), 2.22 – 2.11 (m, 1H), 2.03 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.1, 144.7, 142.8, 140.1, 135.6, 135.4, 130.1, 129.7, 128.1, 126.9, 125.2, 124.6, 123.5, 123.0, 120.1, 113.9, 103.3, 60.8, 59.7, 58.5, 56.3, 51.1, 38.3, 29.8, 28.8, 24.9, 21.6.

HRMS: m/z (ESI) calcd. for $C_{30}H_{32}NO_5S_3$ $[M+H]^+$: 582.1437, found: 582.1427.

1-(3-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-2-yl)-1*H*-indol-1-yl)ethan-1-one (4b)



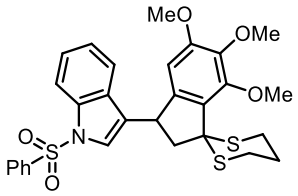
Colorless oil, R_f = 0.55 (PE/EA = 5:1). 56 mg, isolated yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.23 – 7.16 (m, 2H), 6.95 (s, 1H), 4.86 – 4.71 (m, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 3.49 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.35 (s, 3H), 3.26 – 3.15 (m, 1H), 3.15 – 3.01 (m, 1H), 2.98 (dd, *J* = 13.3, 7.1 Hz, 1H), 2.93 – 2.79 (m, 2H), 2.57 (s, 3H), 2.25 – 2.15 (m, 1H), 2.06 – 1.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 154.7, 150.3, 143.0, 140.3, 136.4, 129.8, 128.2, 125.3, 125.1, 123.5, 122.5, 119.6, 116.9, 103.4, 60.9, 60.3, 58.7, 56.4, 51.4, 38.4, 30.0, 29.1, 25.1, 24.2.

HRMS: m/z (ESI) calcd. for $C_{25}H_{28}NO_4S_2$ $[M+H]^+$: 470.1454, found: 470.1446.

1-(phenylsulfonyl)-3-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-2-yl)-1*H*-indole (4c)



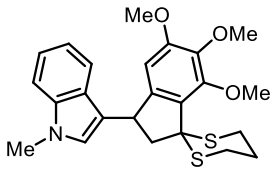
Colorless oil, R_f = 0.40 (PE/EA = 10:1). 98 mg, isolated yield 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.55 – 7.47 (m, 1H), 7.44 – 7.36 (m, 3H), 7.32 – 7.28 (m, 1H), 7.25 (s, 1H), 7.17 – 7.12 (m, 1H), 6.92 (s, 1H), 4.74 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 3.42 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.23 – 3.11 (m, 1H), 3.09 – 2.97 (m, 1H), 2.98 (s, 3H), 2.93 – 2.84 (m, 2H), 2.84 – 2.75 (m, 1H), 2.23 – 2.11 (m, 1H), 2.05 – 1.89 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 150.2, 142.8, 140.1, 138.3, 135.7, 133.7, 130.1, 129.2, 128.0, 126.9, 125.5, 124.7, 123.5, 123.2, 120.2, 114.0, 103.2, 60.8, 59.8, 58.5, 56.3, 51.0, 38.3, 29.9, 28.9, 25.0.

HRMS: m/z (ESI) calcd. for $C_{29}H_{29}NNaO_5S_3$ $[M+Na]^+$: 590.1100, found: 590.1083.

1-methyl-3-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (4d)



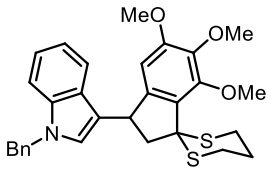
Colorless oil, R_f = 0.50 (PE/EA = 10:1). 72 mg, isolated yield 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.14 (m, 1H), 7.06 – 6.99 (m, 1H), 6.94 (s, 1H), 6.89 (s, 1H), 4.87 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.51 (dd, *J* = 13.3, 8.2 Hz, 1H), 3.24 (s, 3H), 3.22 – 3.16 (m, 1H), 3.15 – 3.03 (m, 1H), 2.99 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.92 – 2.77 (m, 2H), 2.24 – 2.13 (m, 1H), 2.07 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 150.5, 143.0, 140.1, 137.3, 129.8, 127.1, 126.7, 121.4, 119.5, 118.7, 117.3, 109.3, 103.3, 60.9, 60.1, 58.7, 56.3, 52.6, 38.7, 32.8, 30.0, 29.0, 25.2.

HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_3S_2$ $[M+H]^+$: 442.1505, found: 442.1501.

1-benzyl-3-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (4e)



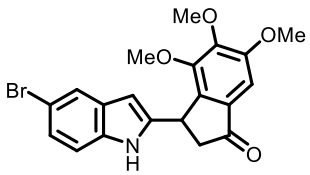
Colorless oil, R_f = 0.61 (PE/EA = 10:1). 81 mg, isolated yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.07 (m, 3H), 7.05 – 7.01 (m, 1H), 6.99 (s, 1H), 6.94 (s, 1H), 5.26 (s, 2H), 4.87 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.78 (s, 3H), 3.51 (dd, *J* = 13.3, 8.0 Hz, 1H), 3.21 (s, 4H), 3.15 – 3.04 (m, 1H), 3.01 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.93 – 2.75 (m, 2H), 2.25 – 2.13 (m, 1H), 2.07 – 1.93 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 150.5, 143.0, 140.1, 138.0, 137.0, 129.8, 128.8, 127.6, 127.4, 126.8, 126.2, 121.7, 119.7, 119.0, 117.9, 109.8, 103.2, 60.9, 60.1, 58.7, 56.3, 52.4, 50.0, 38.8, 30.1, 29.0, 25.2.

HRMS: m/z (ESI) calcd. for $C_{30}H_{32}NO_3S_2$ $[M+H]^+$: 518.1818, found: 518.1811.

3-(5-bromo-1H-indol-2-yl)-4,5,6-trimethoxy-2,3-dihydro-1*H*-inden-1-one (5b)



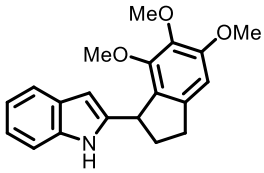
Colorless oil, R_f = 0.25 (PE/EA = 10:1). 34 mg, isolated yield 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (brs, 1H), 7.64 – 7.59 (m, 1H), 7.21 – 7.13 (m, 2H), 7.02 (s, 1H), 6.24 (d, *J* = 2.0 Hz, 1H), 4.81 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 3.17 (dd, *J* = 19.1, 8.0 Hz, 1H), 2.91 (dd, *J* = 19.1, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 155.3, 150.1, 148.6, 141.7, 141.5, 134.9, 131.8, 130.1, 124.5, 122.7, 113.0, 112.2, 101.2, 99.1, 61.2, 61.1, 56.3, 44.0, 35.0.

HRMS: m/z (ESI) calcd. for $C_{20}H_{19}BrNO_4$ $[M+H]^+$: 416.0492, 418.0472. found: 416.0482, 418.0461.

2-(5,6,7-trimethoxy-2,3-dihydro-1H-inden-1-yl)-1*H*-indole (5h)



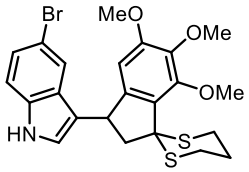
Colorless oil, R_f = 0.45 (PE/EA = 10:1). 29 mg, isolated yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (brs, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.03 (m, 1H), 7.06 – 6.98 (m, 1H), 6.59 (s, 1H), 6.27 (s, 1H), 4.64 (t, *J* = 5.4 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.17 – 3.05 (m, 1H), 2.93 – 2.82 (m, 1H), 2.54 – 2.44 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 149.4, 142.2, 140.7, 139.6, 136.3, 129.3, 128.5, 121.1, 119.9, 119.5, 110.7, 104.3, 97.8, 61.1, 61.1, 56.3, 41.5, 32.2, 32.1.

HRMS: m/z (ESI) calcd. for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$: 346.1414, found: 346.1419.

5-bromo-3-(5,6,7-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-1*H*-indole (4f)



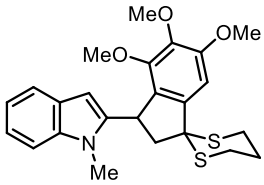
Colorless oil, R_f = 0.30 (PE/EA = 5:1). 35mg, isolated yield 35%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.02 (s, 1H), 7.37 – 7.29 (m, 2H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.14 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.86 (s, 1H), 4.76 (t, *J* = 7.7 Hz, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 3.50 (dd, *J* = 13.5, 8.2 Hz, 1H), 3.24 (d, *J* = 12.3 Hz, 1H), 3.18 (s, 3H), 3.16 – 3.04 (m, 1H), 2.93 – 2.82 (m, 2H), 2.79 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.14 (d, *J* = 13.7 Hz, 1H), 1.82 (q, *J* = 13.1 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 153.5, 149.9, 142.3, 140.1, 135.1, 129.2, 127.9, 124.4, 123.1, 120.7, 116.6, 113.5, 110.7, 103.1, 60.3, 59.6, 58.0, 56.0, 52.2, 38.0, 28.9, 28.0, 24.5.

HRMS: m/z (ESI) calcd. for $C_{23}H_{25}BrNO_3S_2$ $[M+H]^+$: 506.0454, 508.0434; found: 506.0452, 508.0433.

methyl-2-(4,5,6-trimethoxy-2,3-dihydrospiro[indene-1,2'-[1,3]dithian]-3-yl)-indole (2v)



Colorless oil, R_f = 0.60 (PE/EA = 5:1). 37 mg, isolated yield 42%.

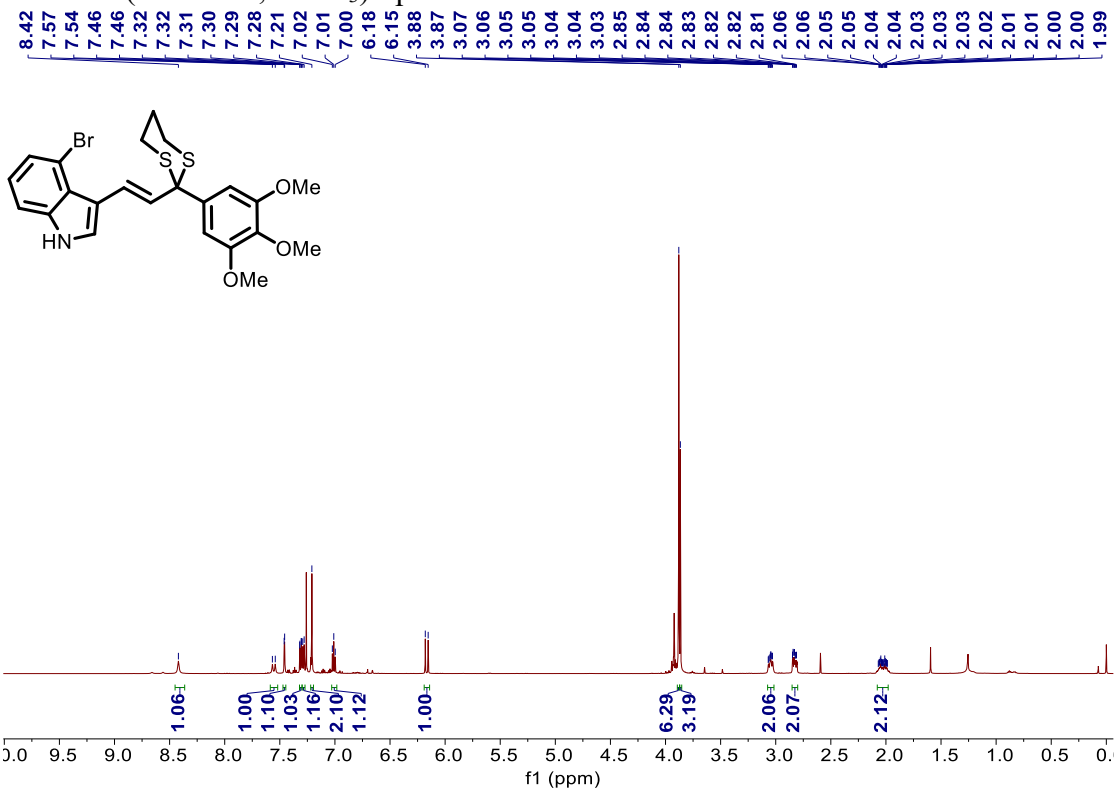
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.12 (m, 1H), 7.10 – 6.99 (m, 1H), 6.92 (s, 1H), 6.29 (s, 1H), 4.80 (t, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 3.53 (dd, *J* = 13.3, 8.0 Hz, 1H), 3.23 (s, 3H), 3.22 – 3.08 (m, 2H), 2.99 (dd, *J* = 13.3, 7.9 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.29 – 2.16 (m, 1H), 2.07 – 1.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 150.1, 143.3, 139.6, 137.6, 129.2, 127.9, 120.8, 120.2, 119.4, 108.9, 103.4, 99.8, 60.9, 60.3, 58.4, 56.4, 51.9, 39.1, 30.3, 30.2, 28.9, 25.1.

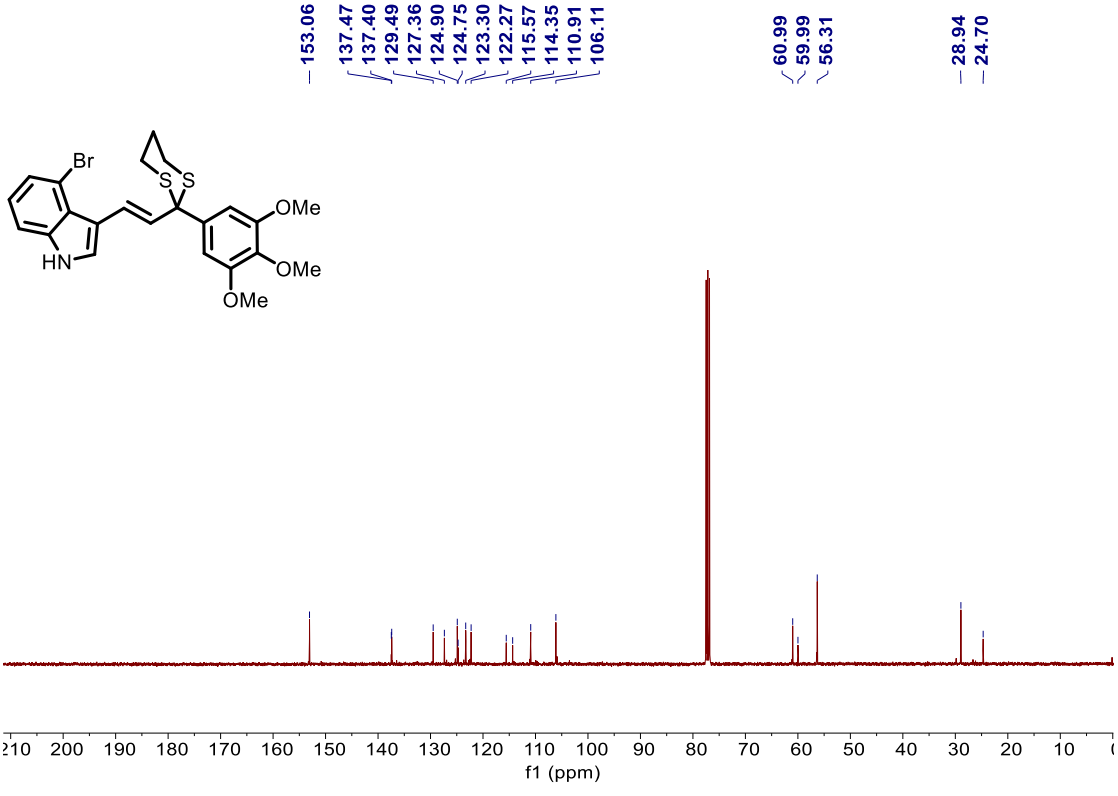
HRMS: m/z (ESI) calcd. for $C_{24}H_{28}NO_3S_2$ [M+H]+: 442.1505, found: 442.1500.

13. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra

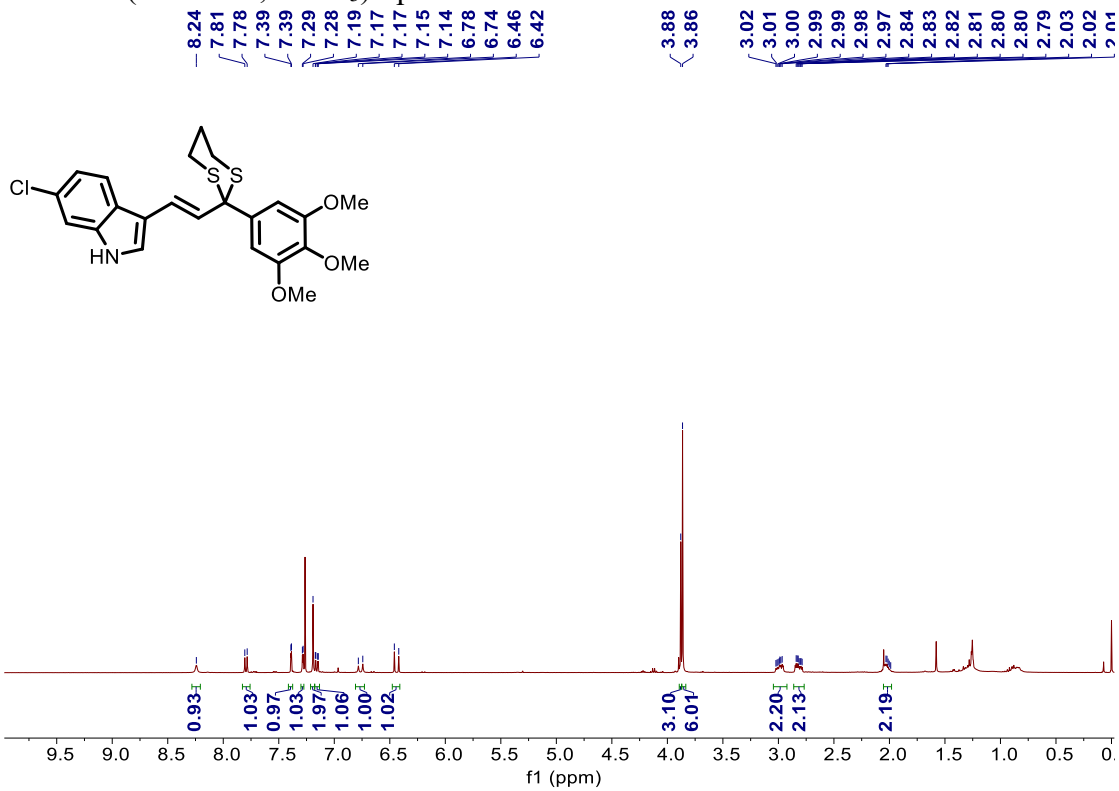
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **1b**



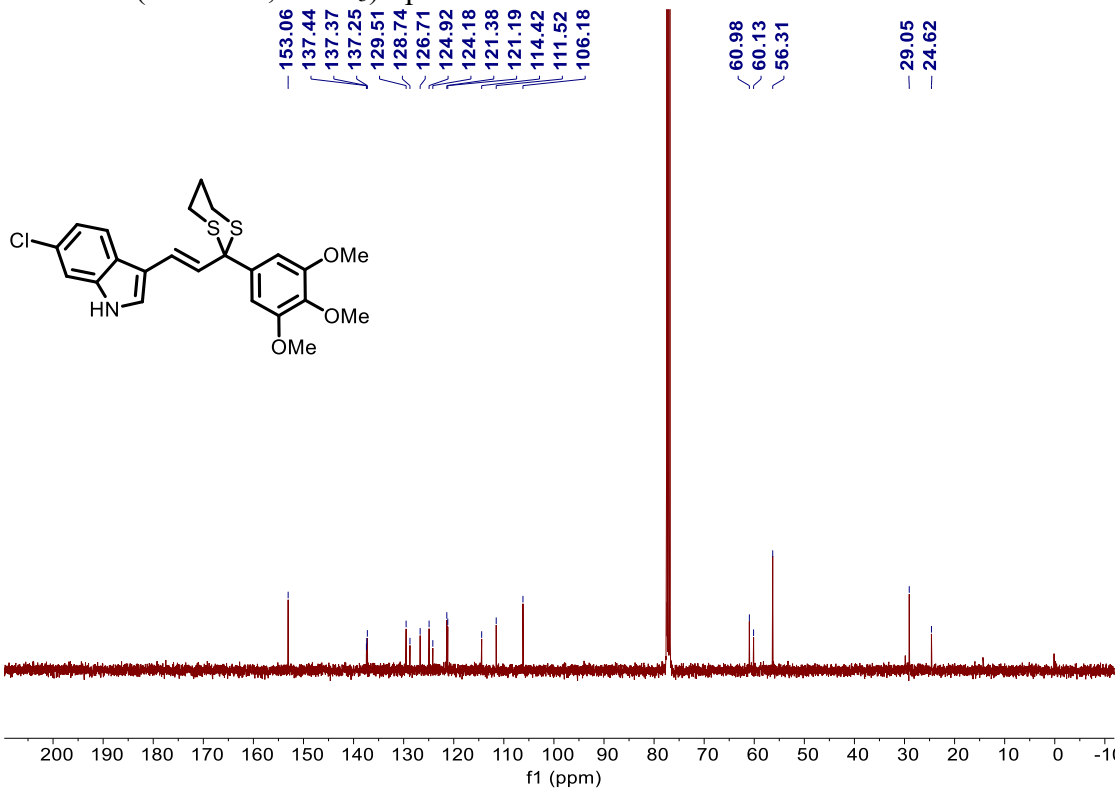
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1b**



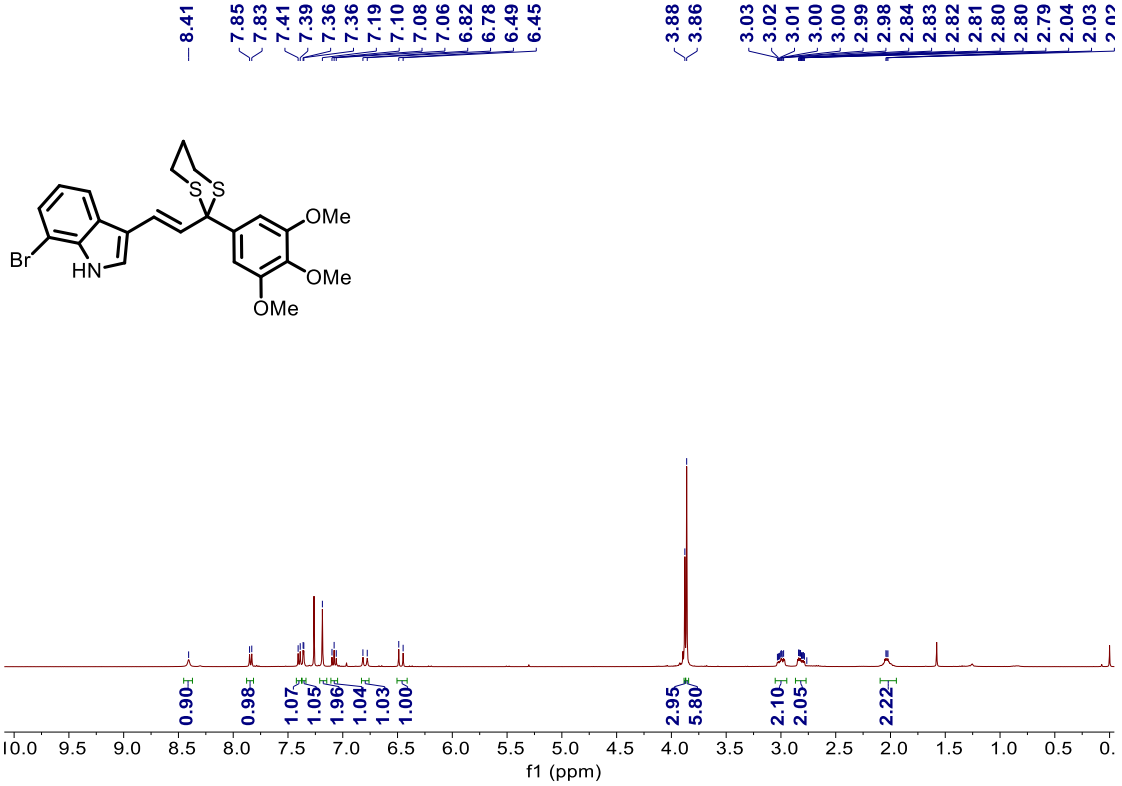
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1c**



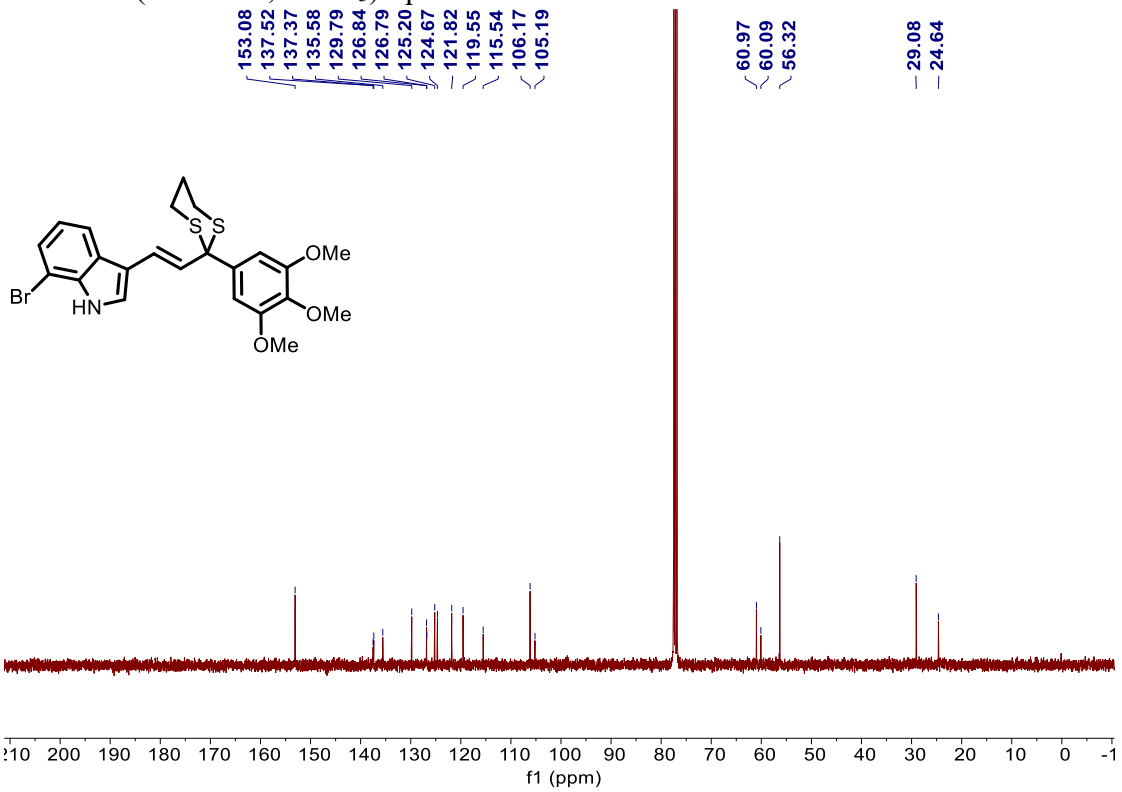
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1c**



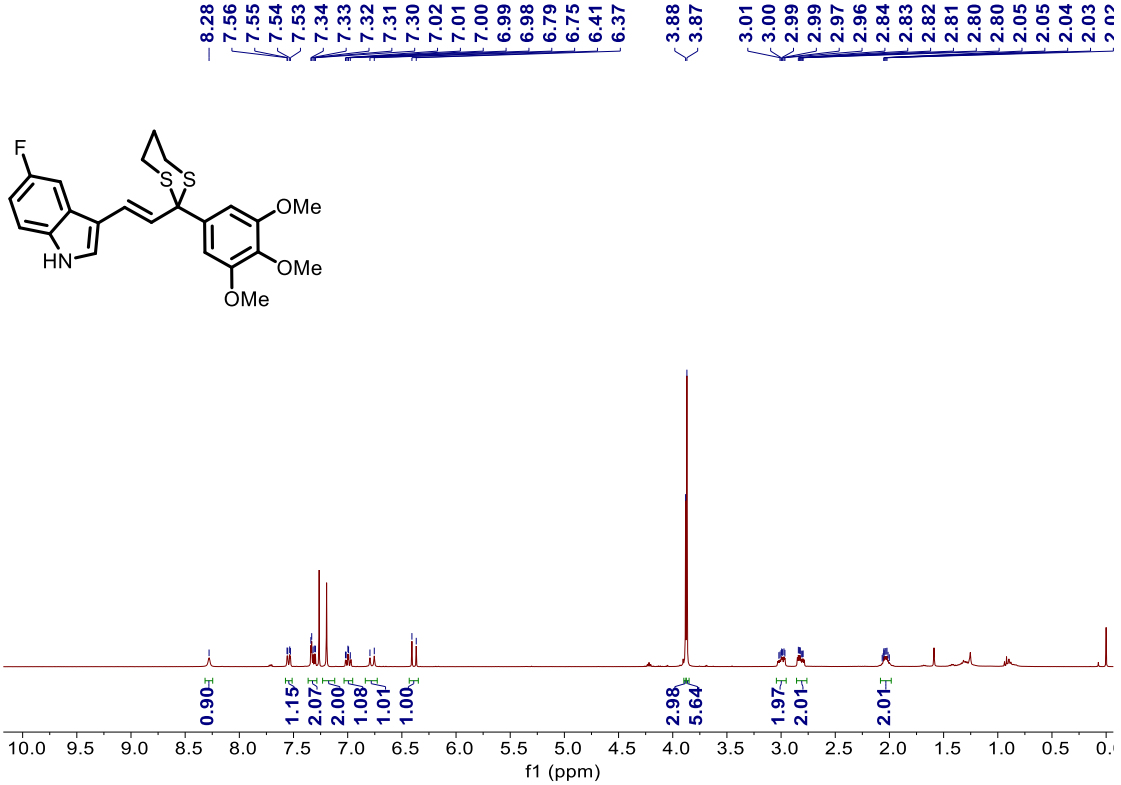
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1d**



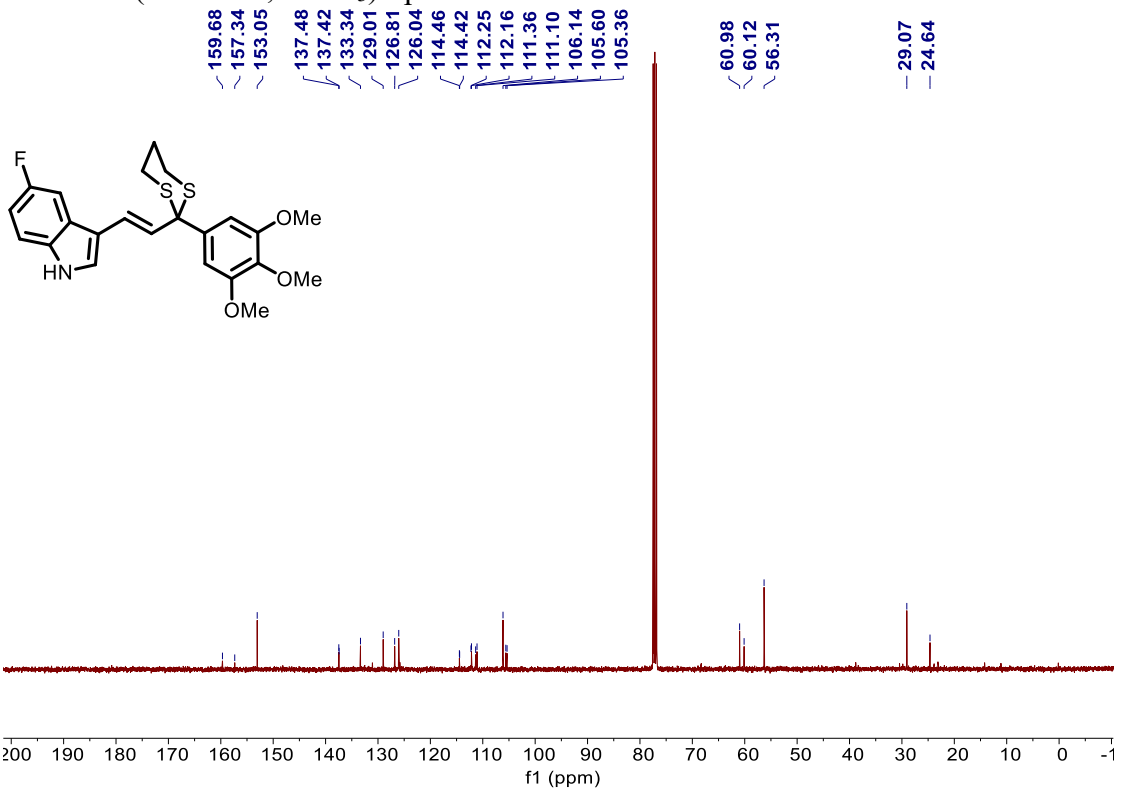
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1d**



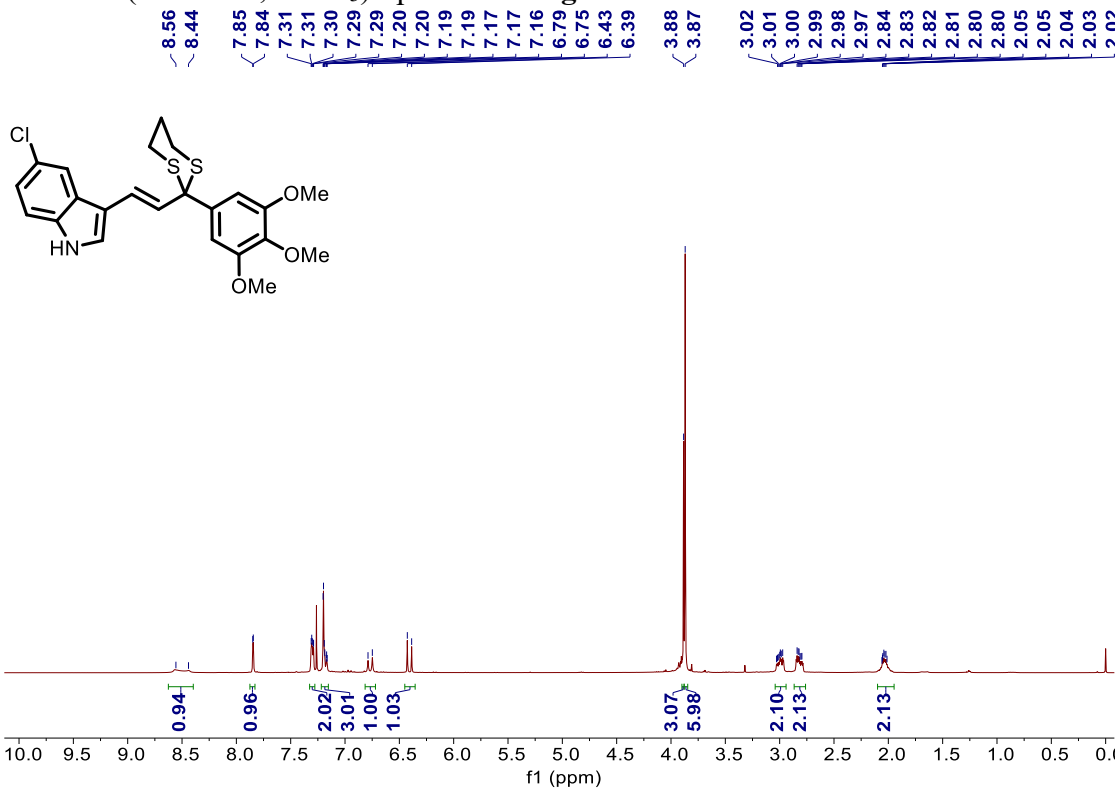
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1f**



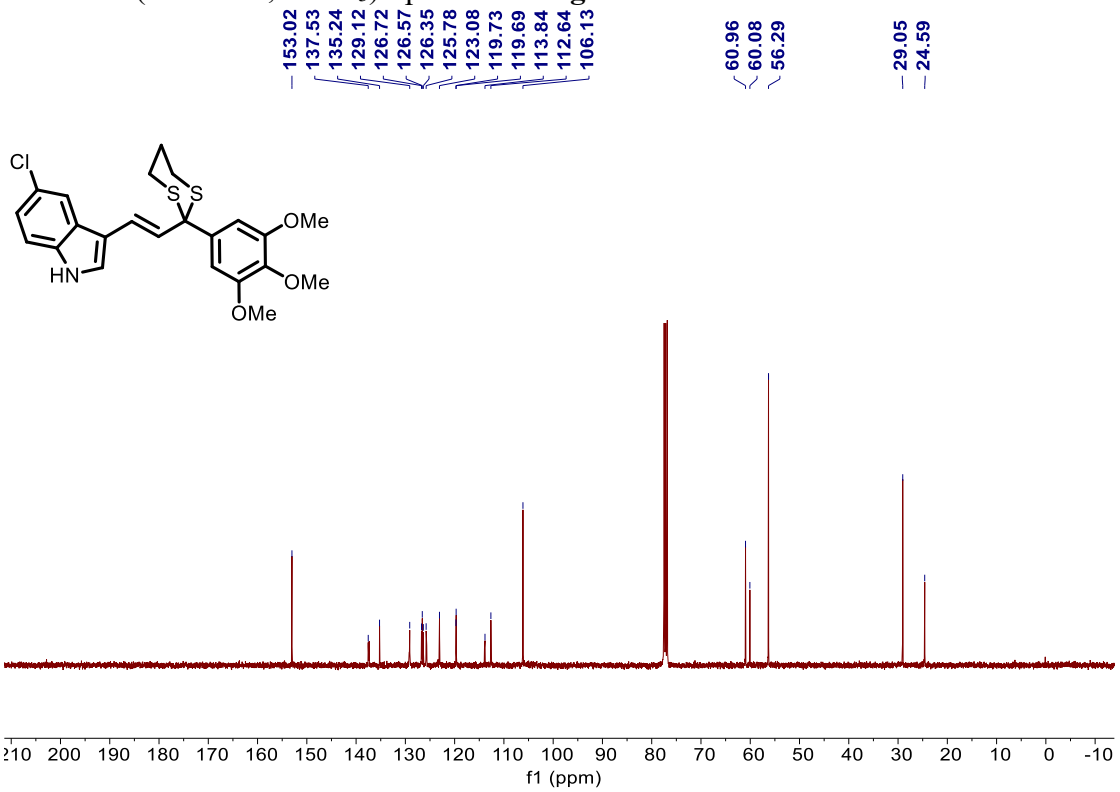
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1f**



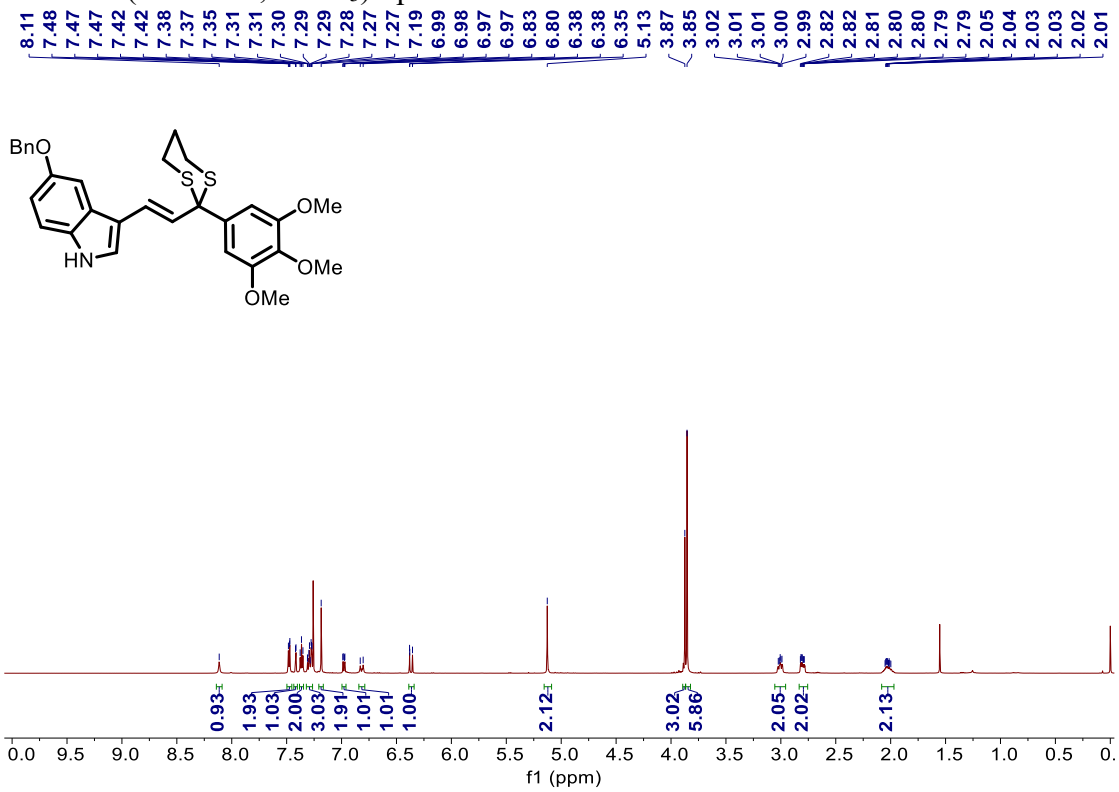
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1g**



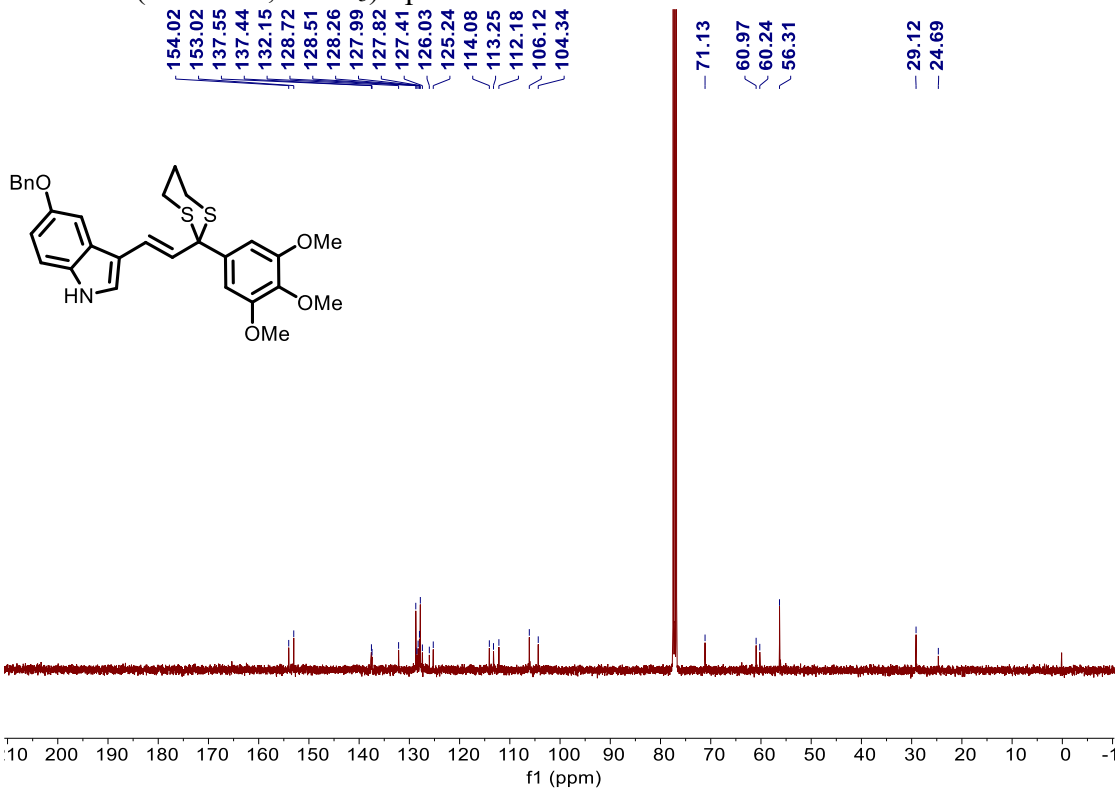
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1g**



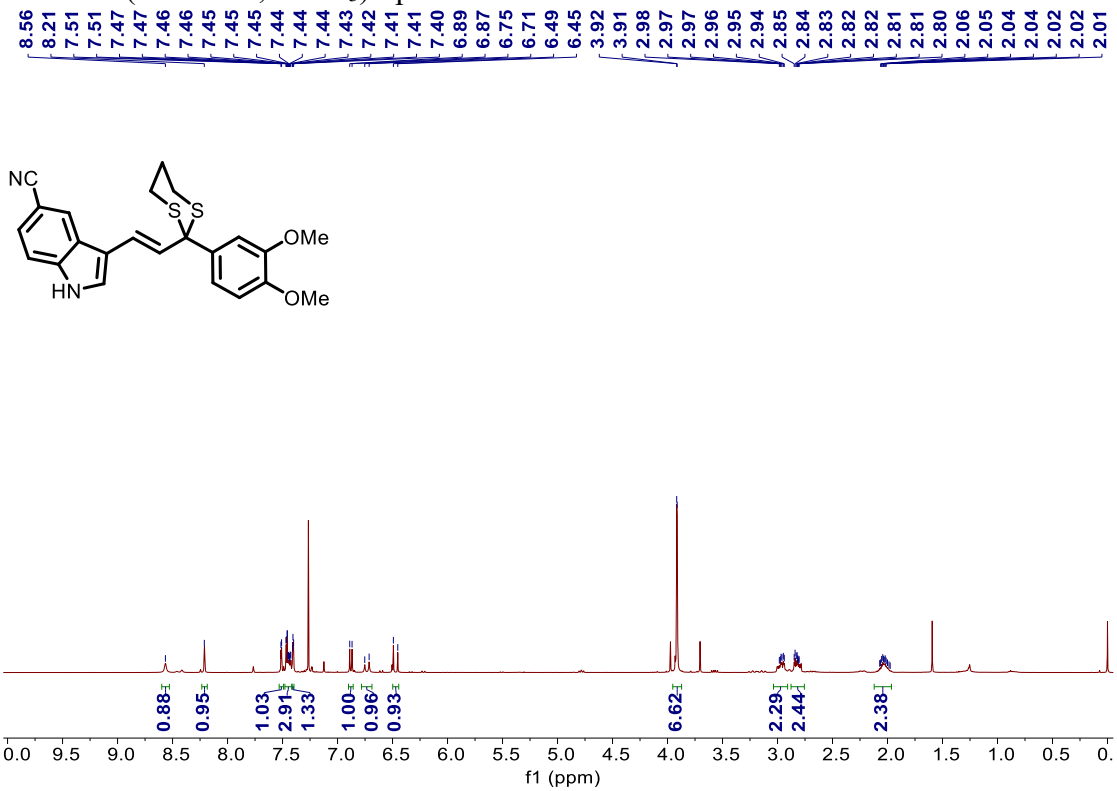
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **1l**



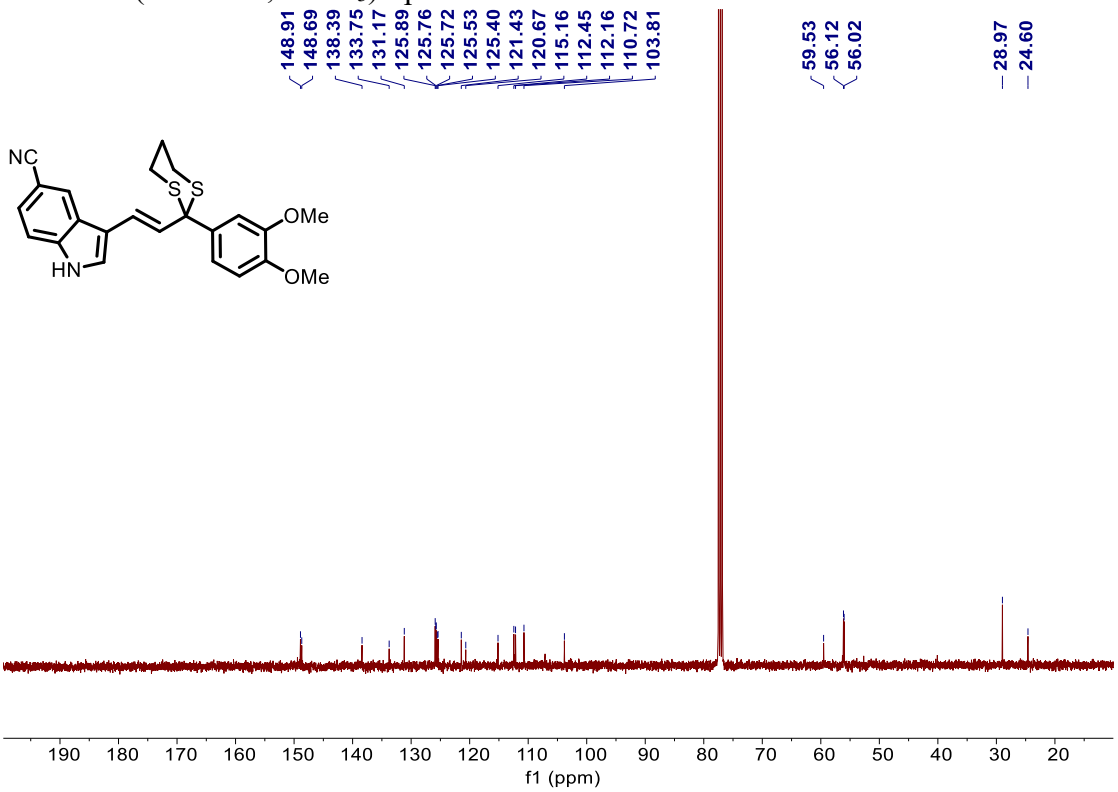
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1l**



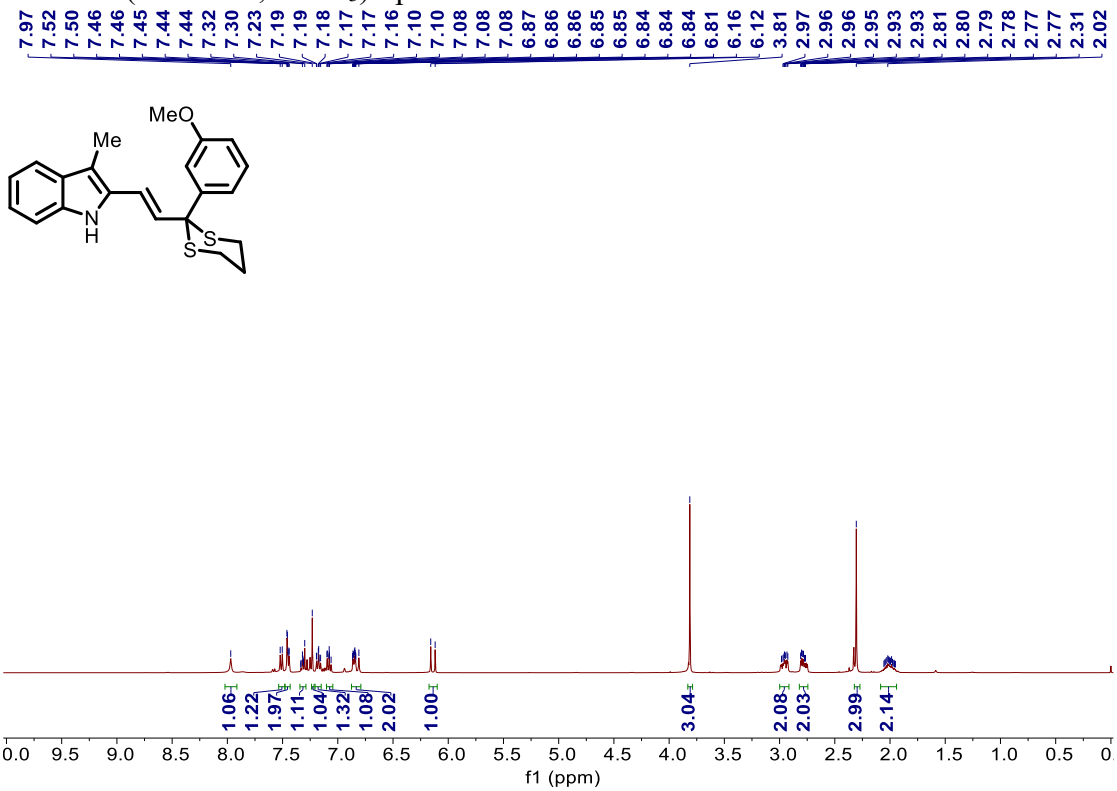
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1o**



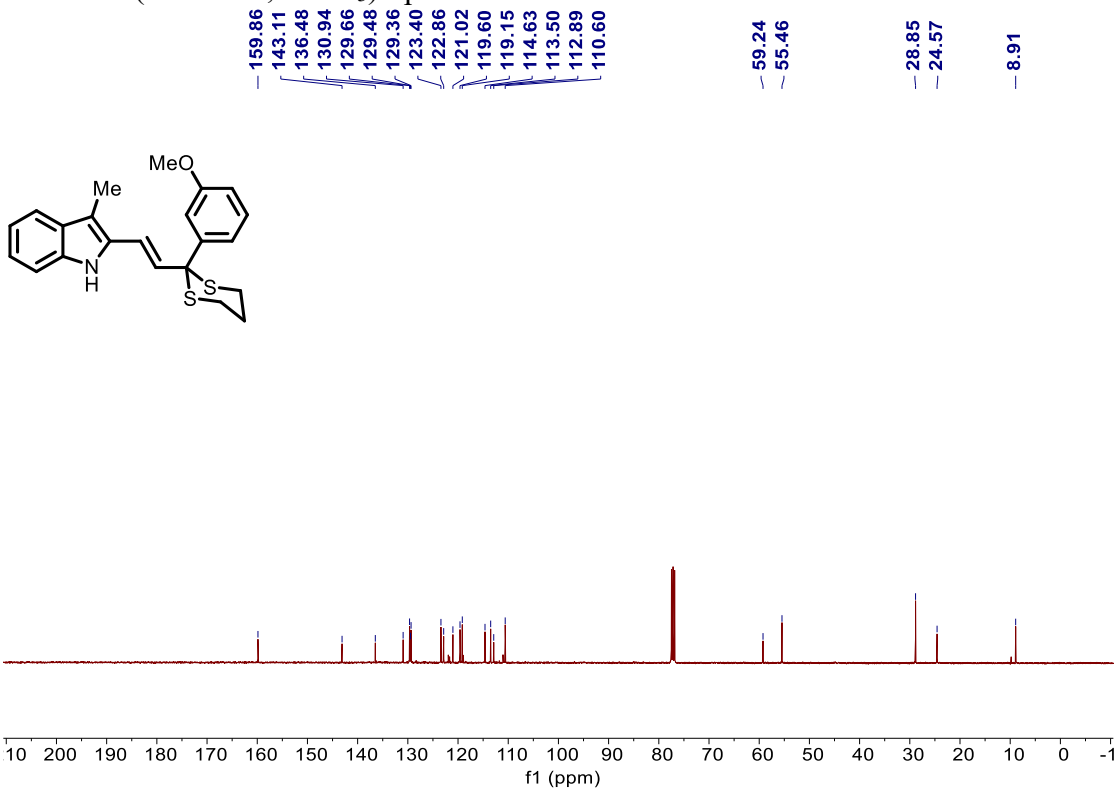
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1o**



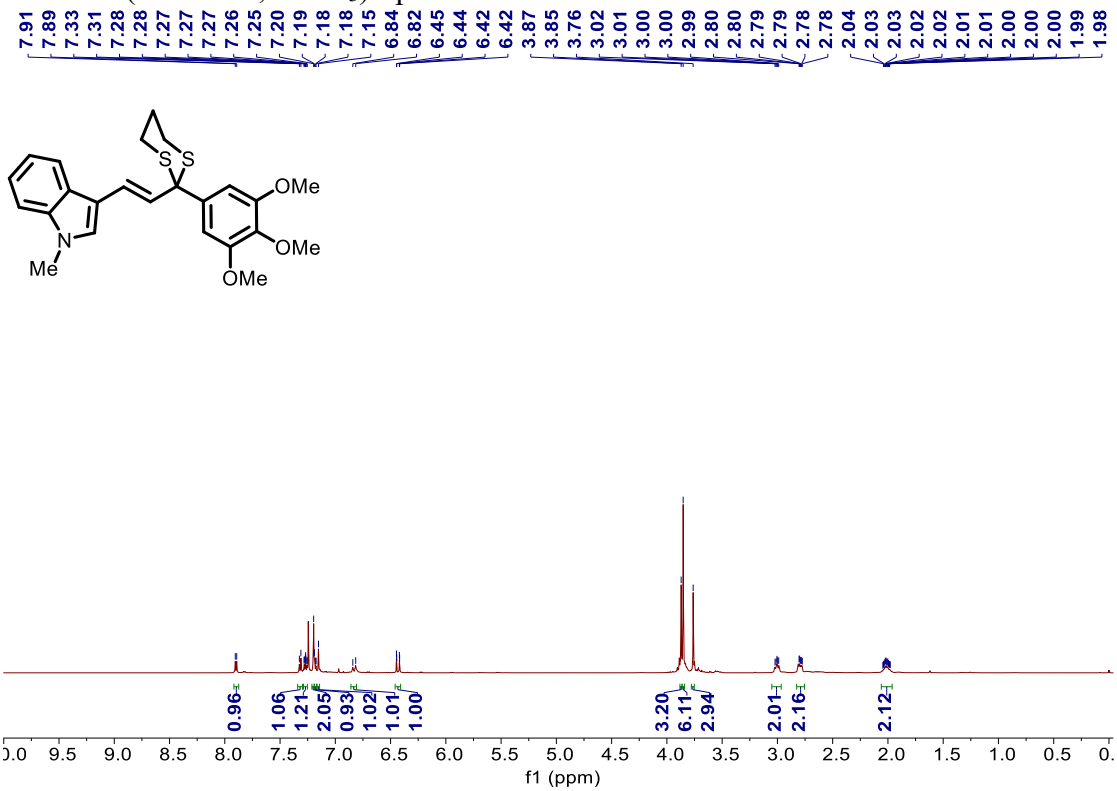
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **1aa**



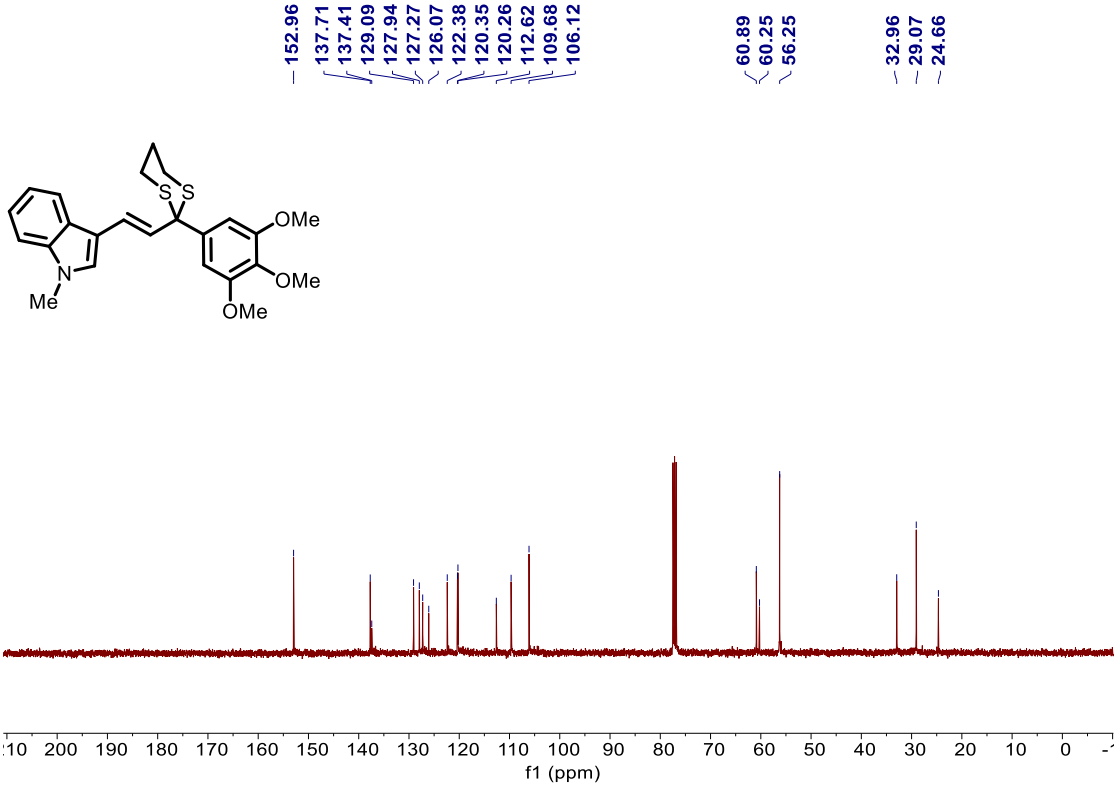
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1aa**



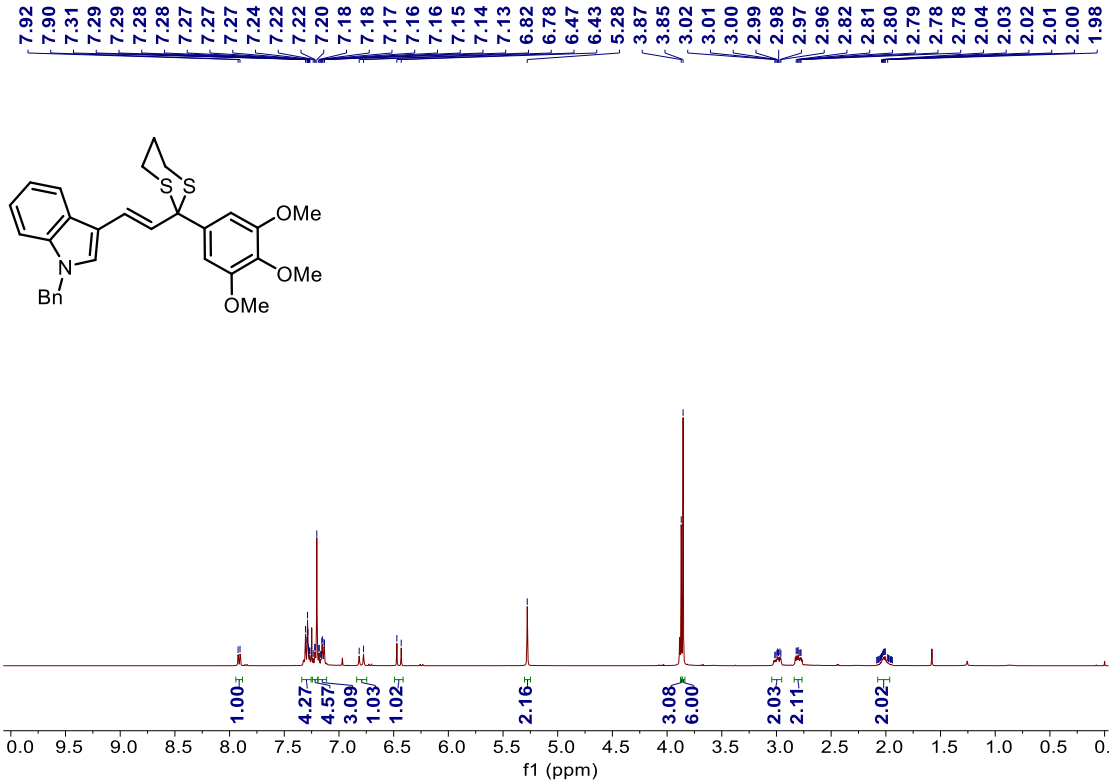
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **1bd**



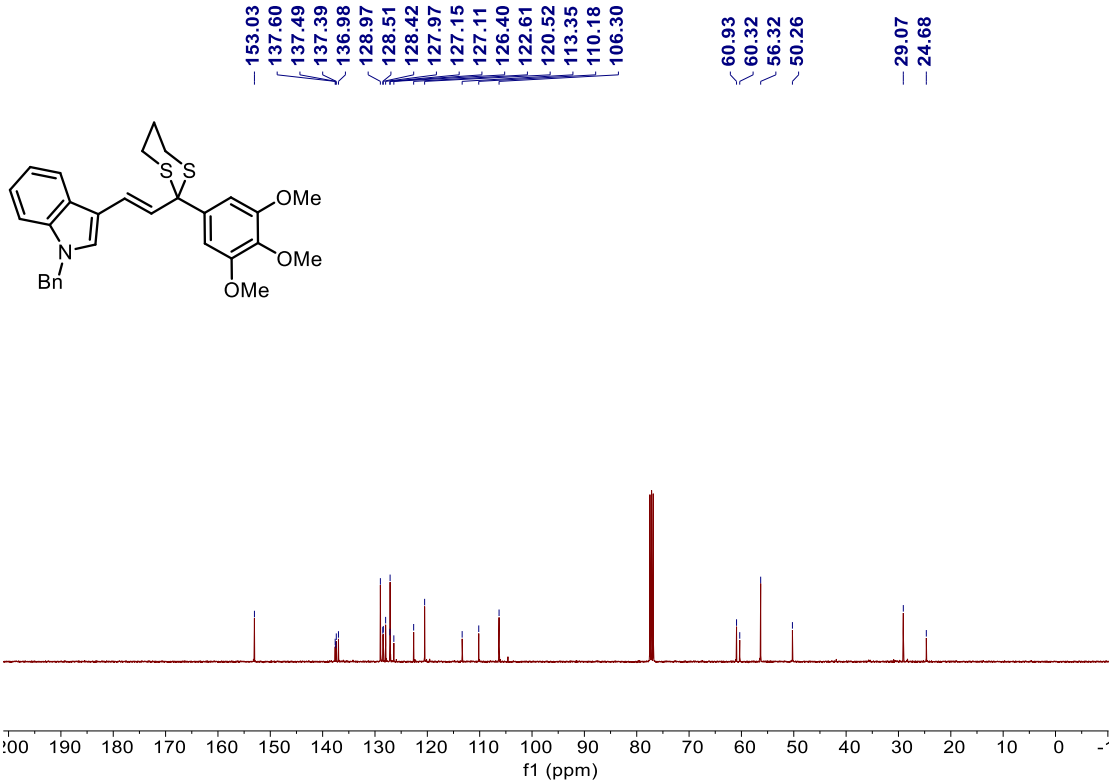
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **1bd**



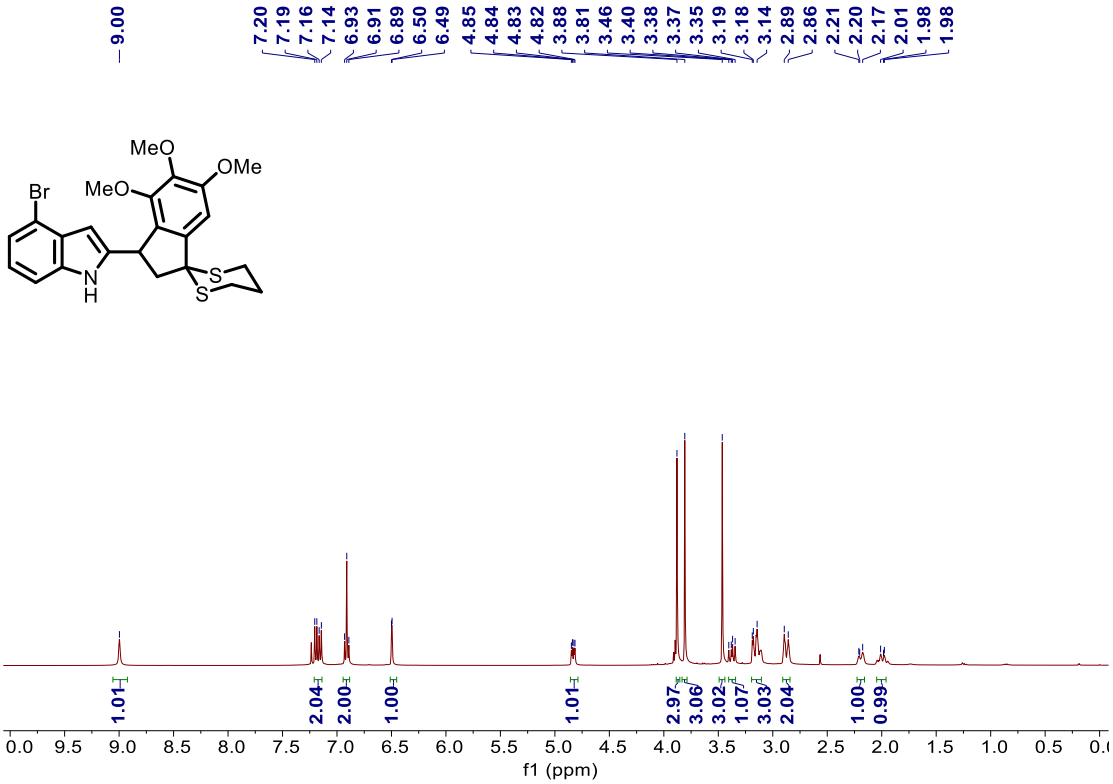
1H NMR (400 MHz, CDCl3) Spectrum of **1be**



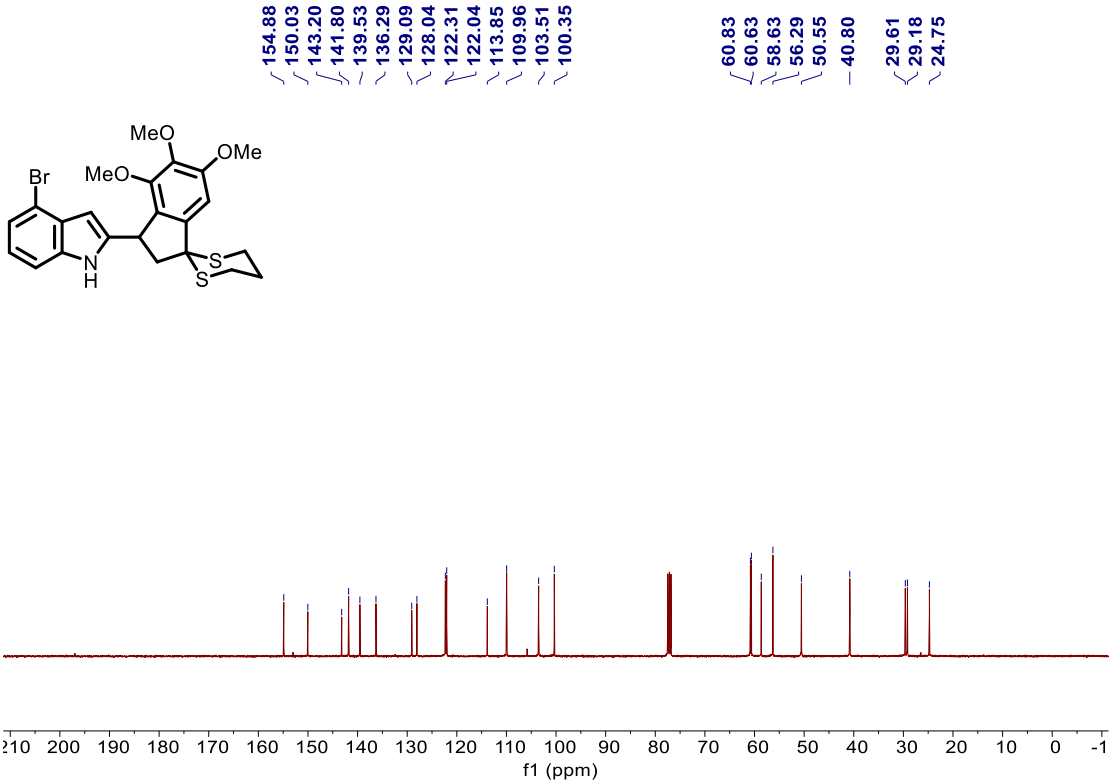
13C NMR (101 MHz, CDCl3) Spectrum of **1be**



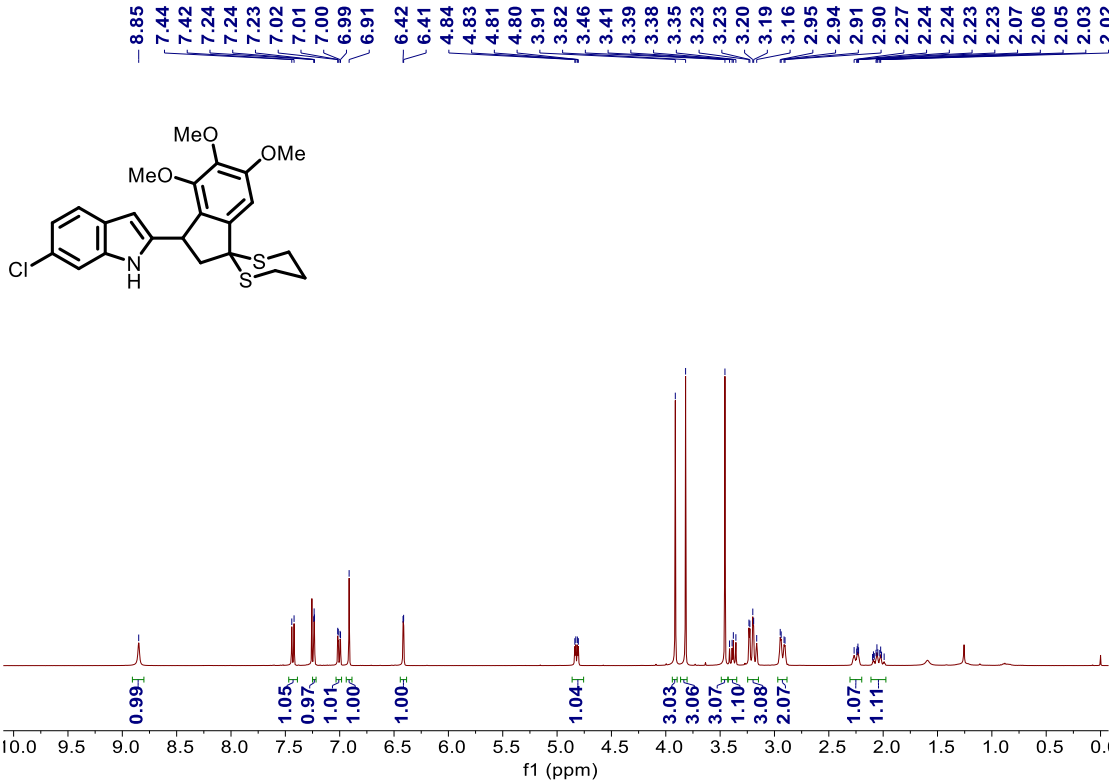
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2b**



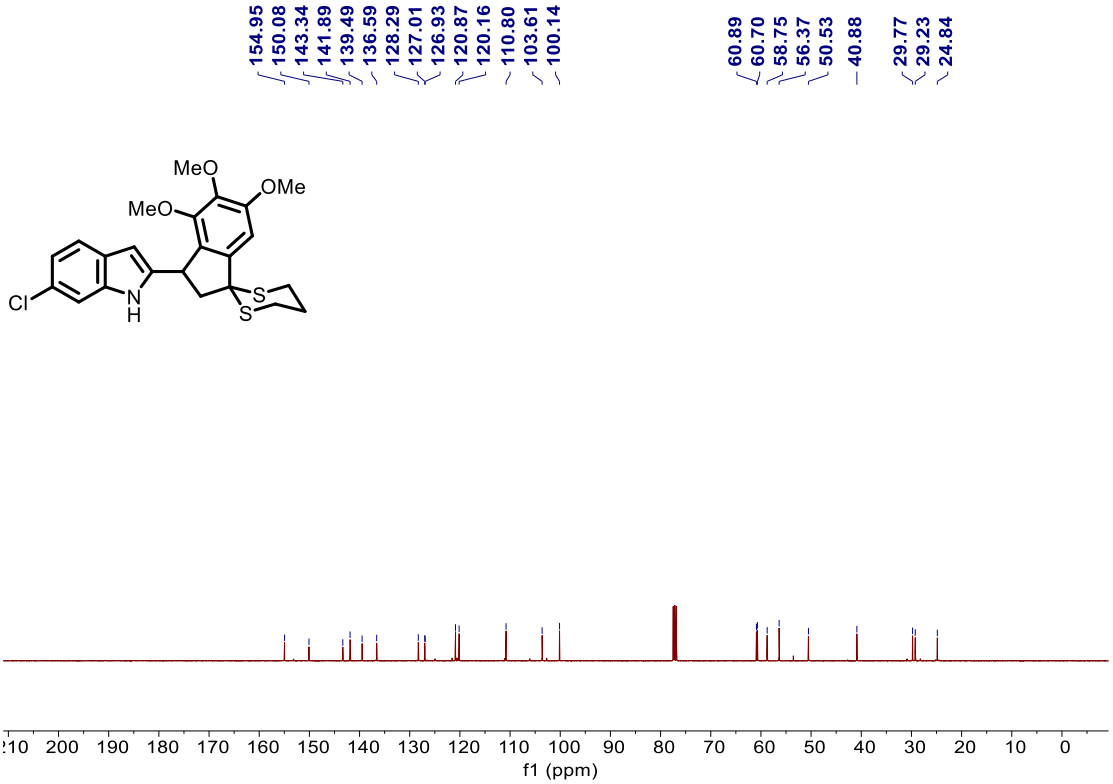
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2b**



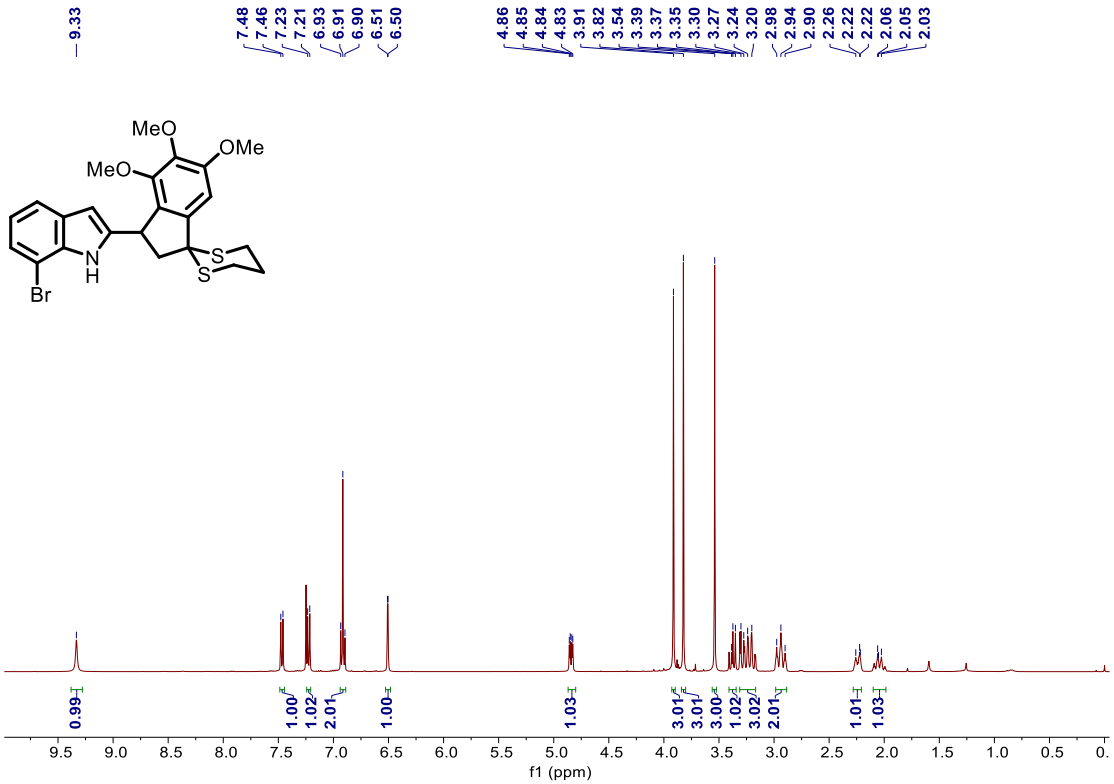
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2c**



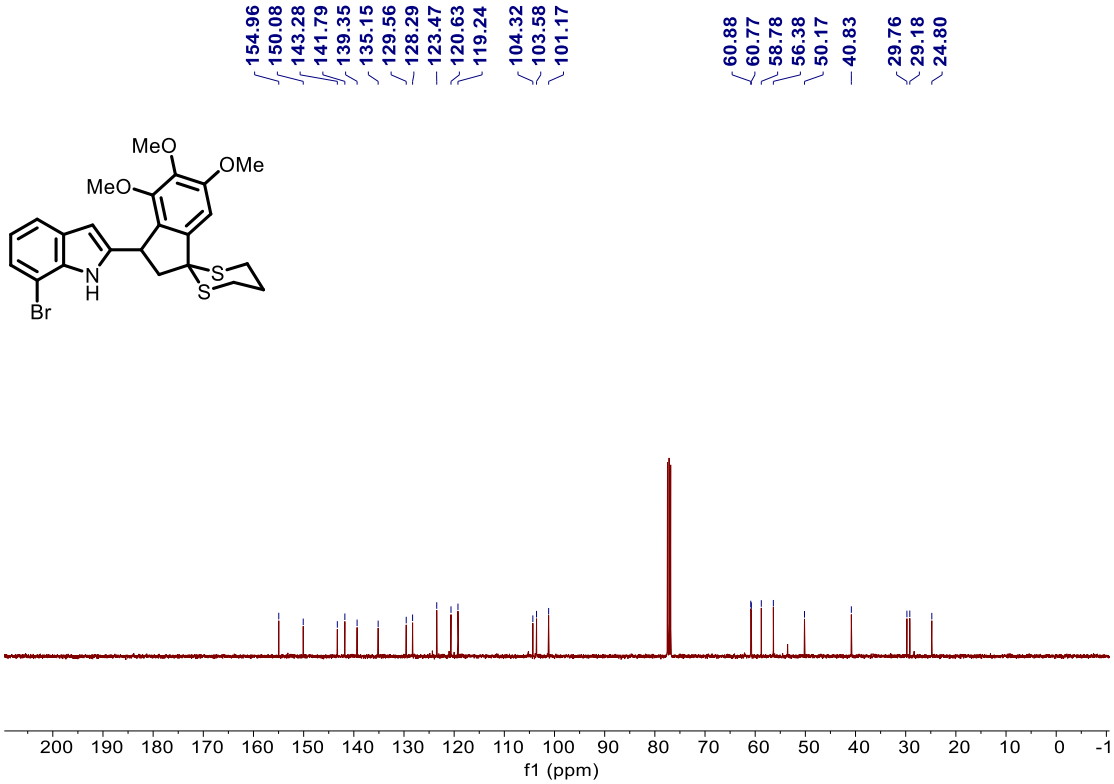
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2c**



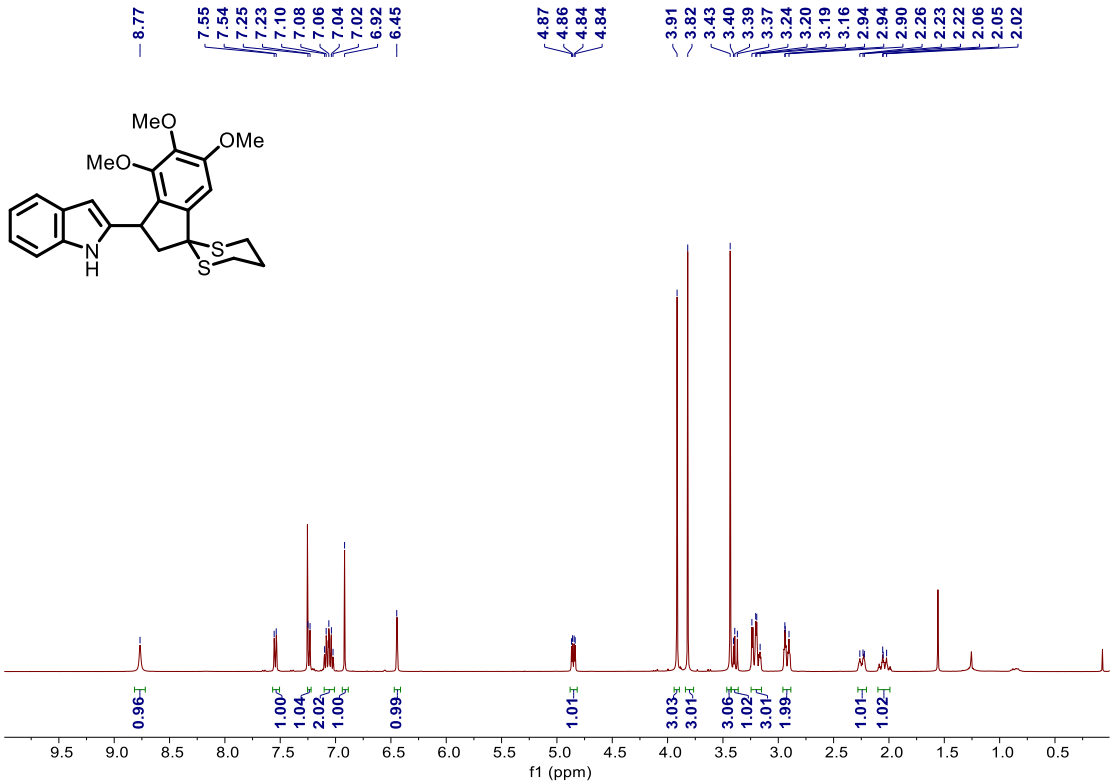
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2d**



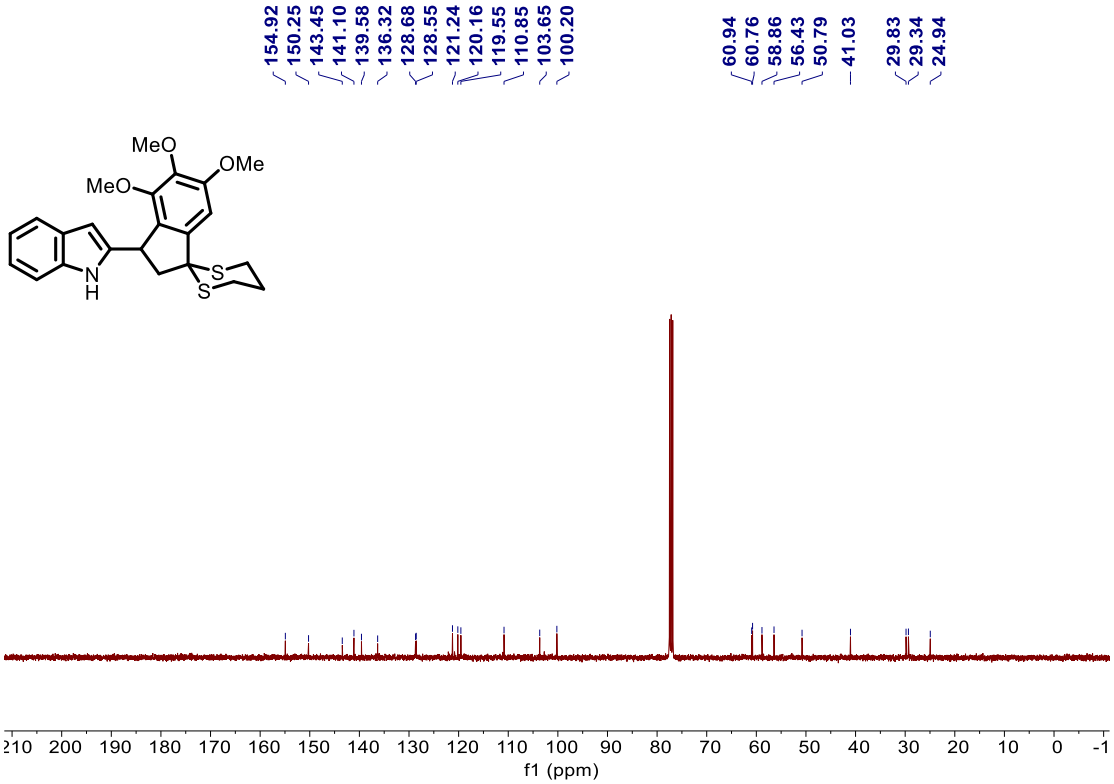
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2d**



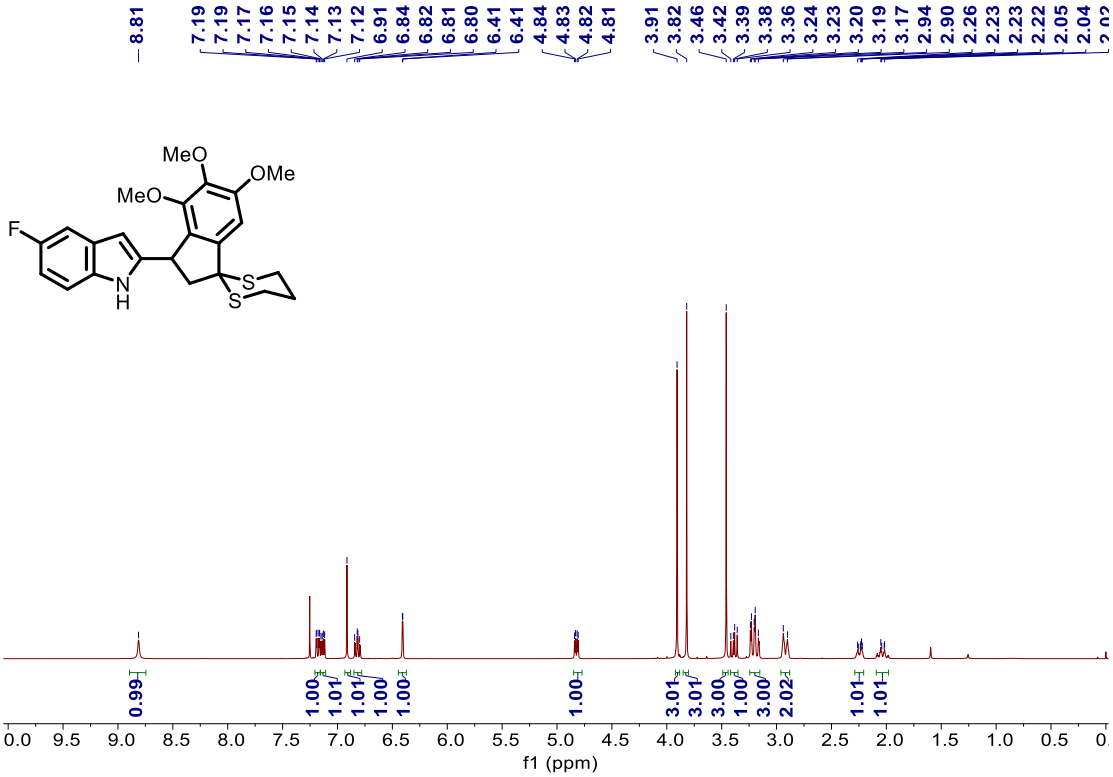
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2e**



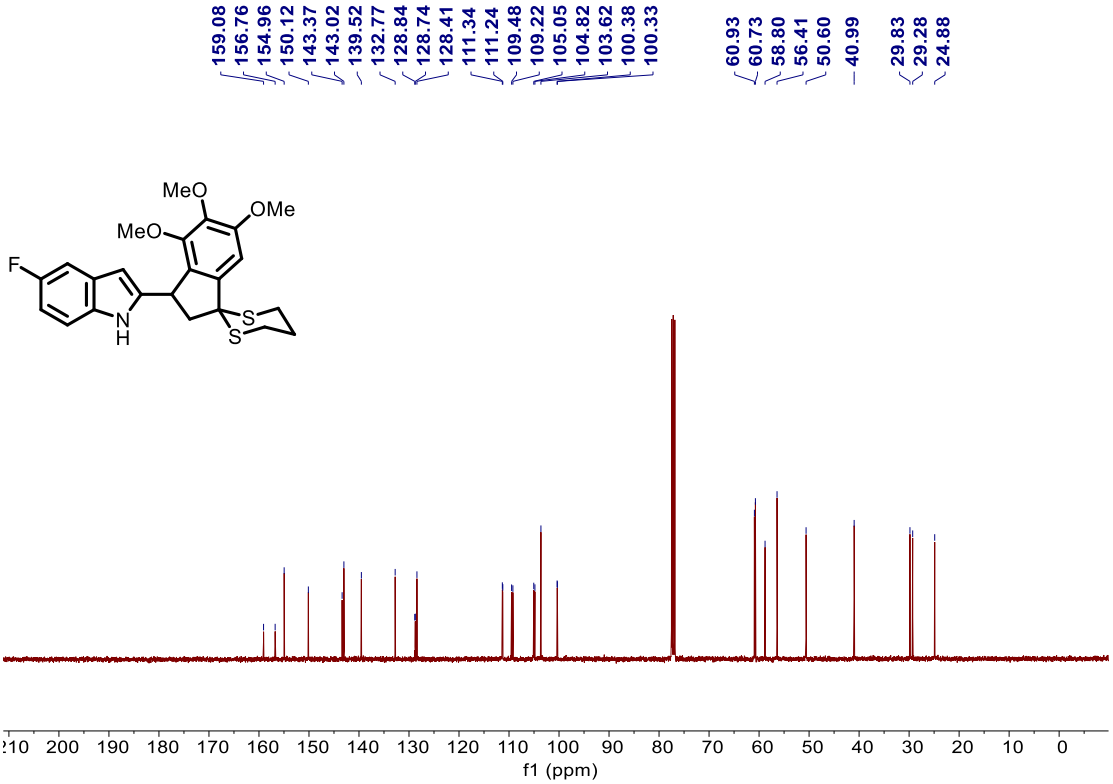
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2e**



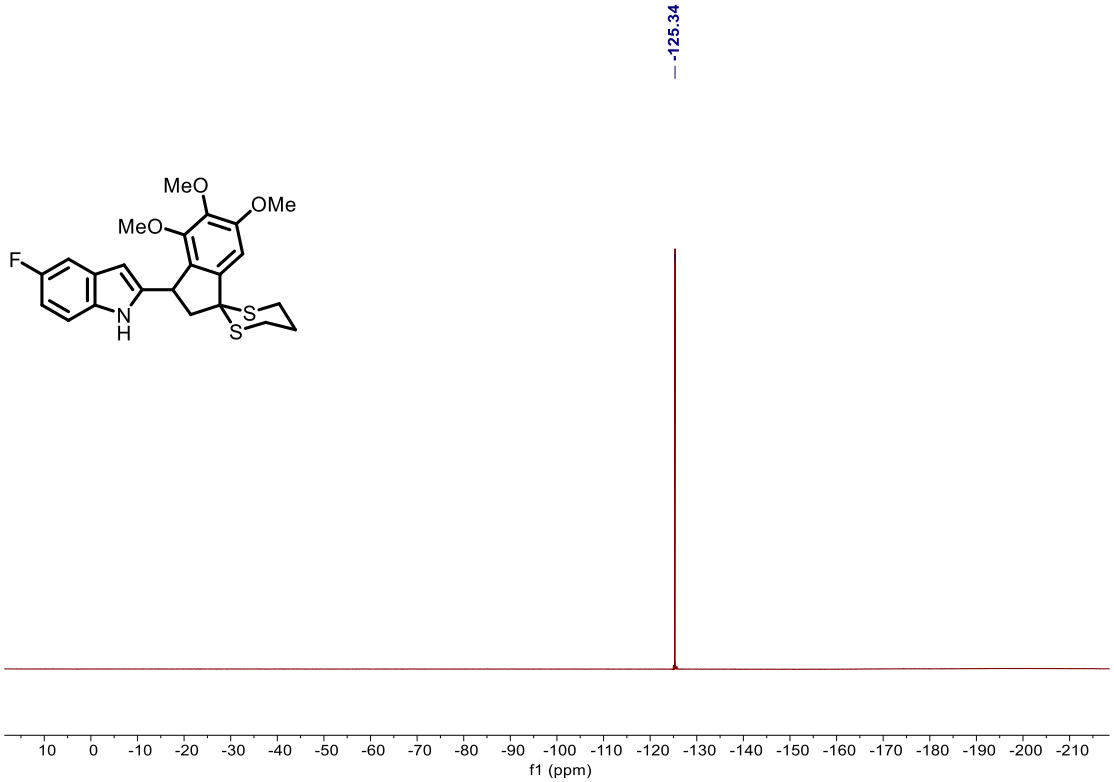
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2f**



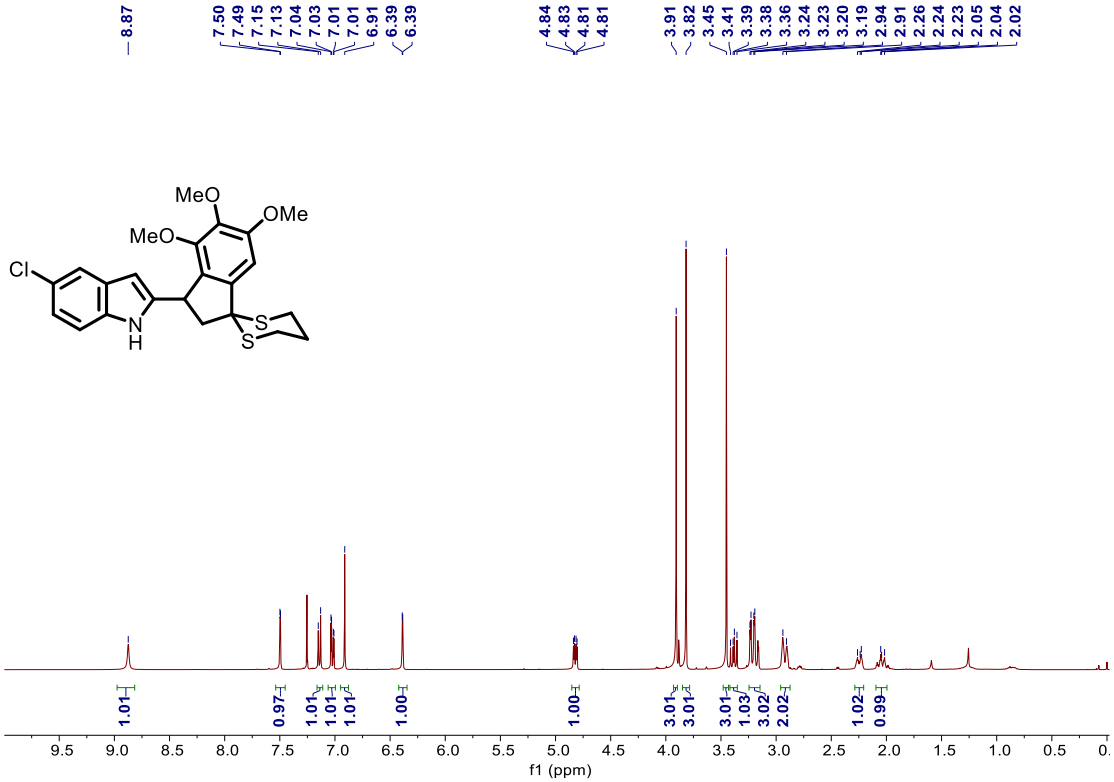
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2f**



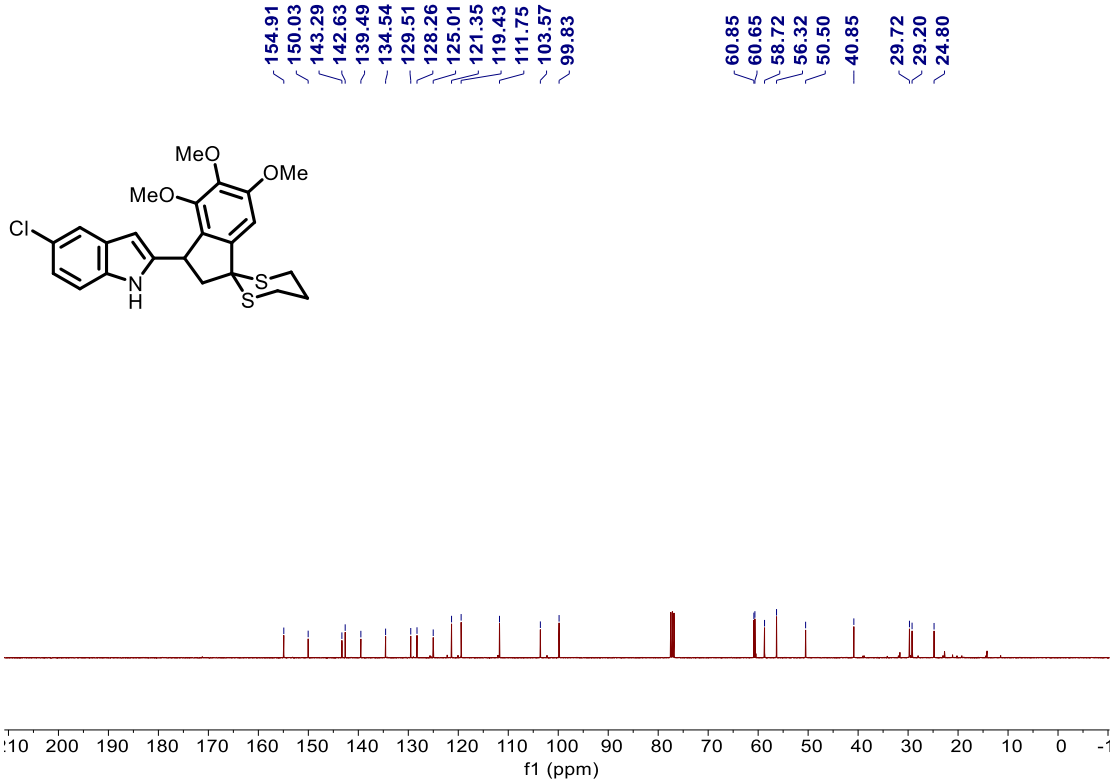
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **2f**



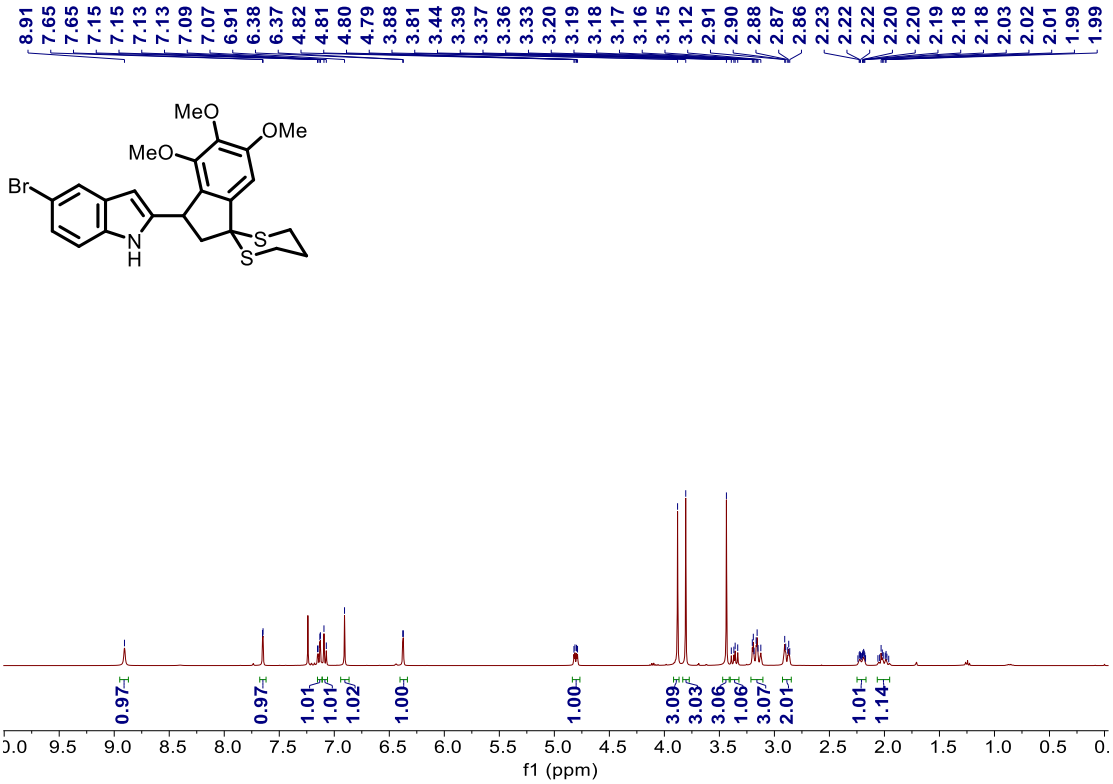
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2g**



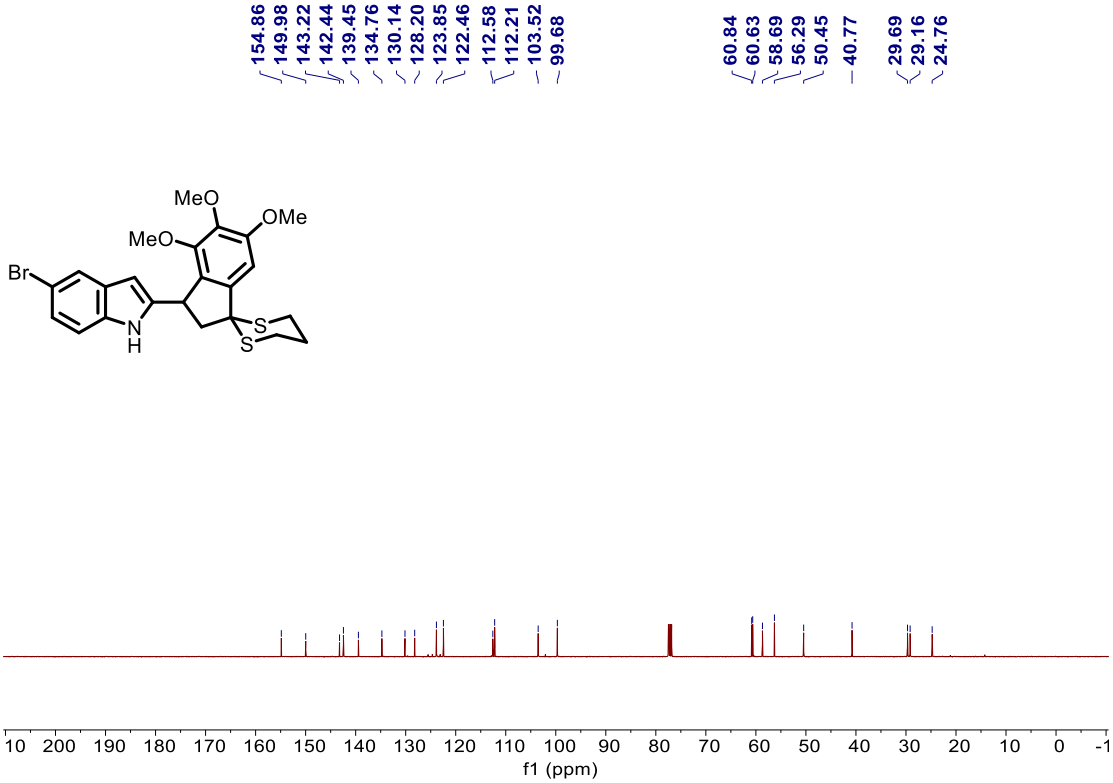
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2g**



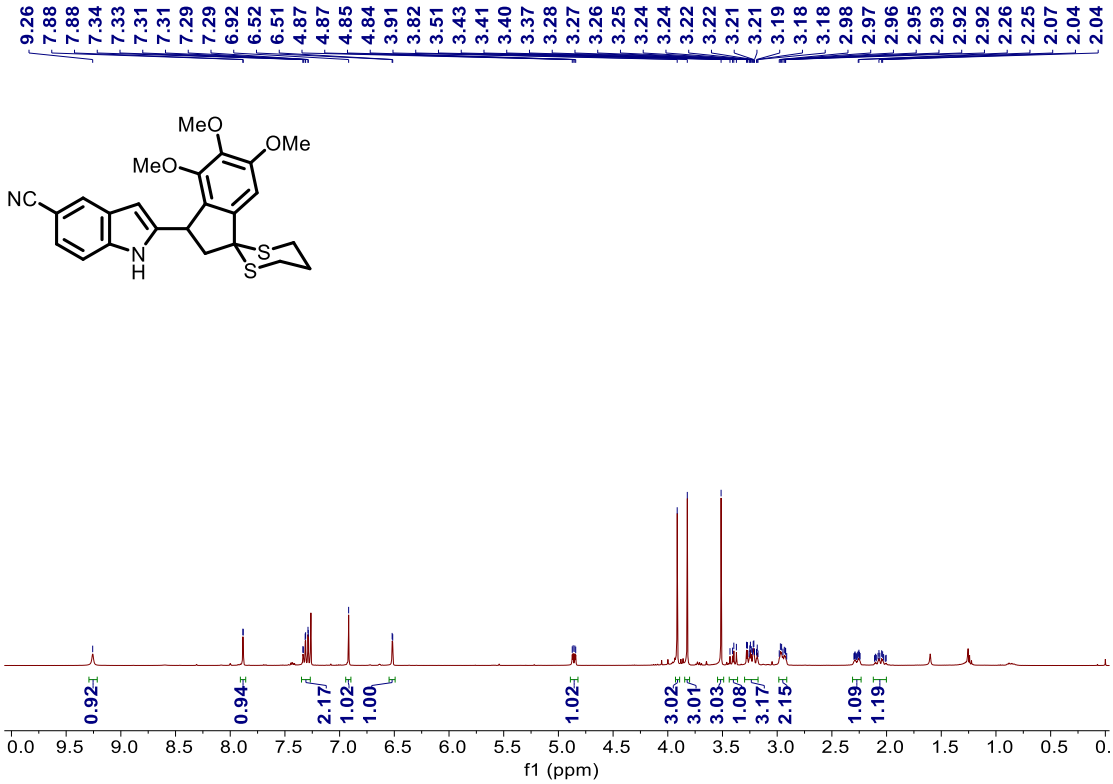
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2a**



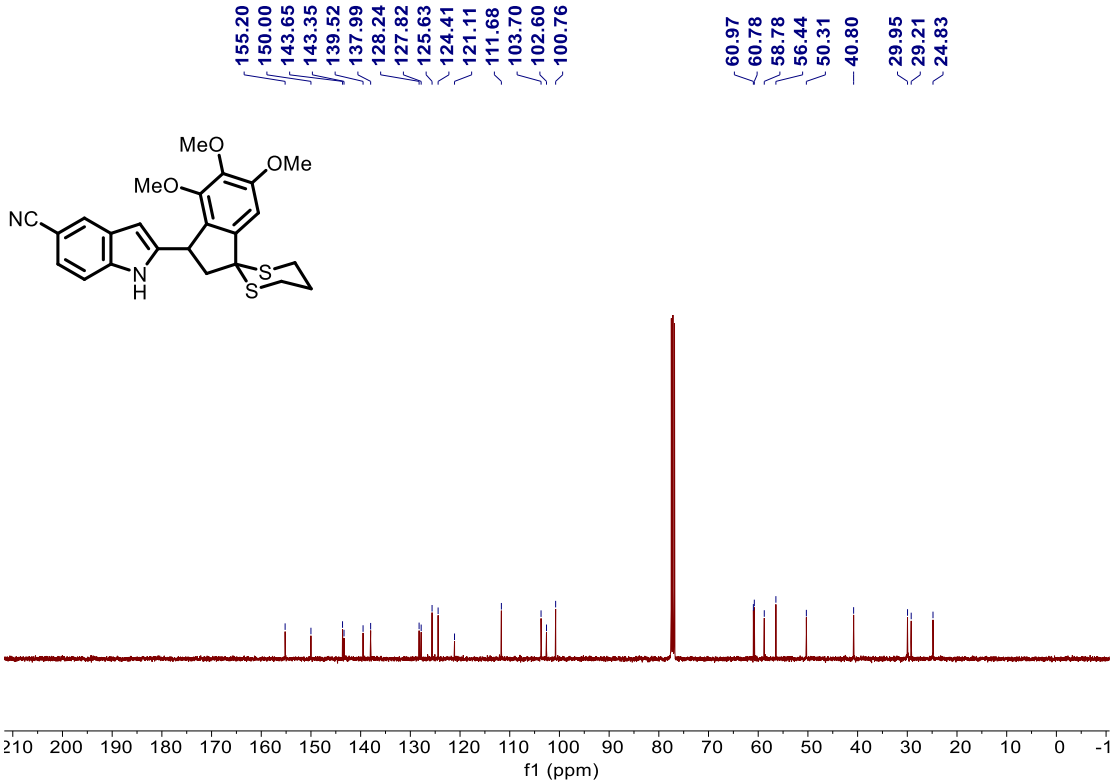
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2a**



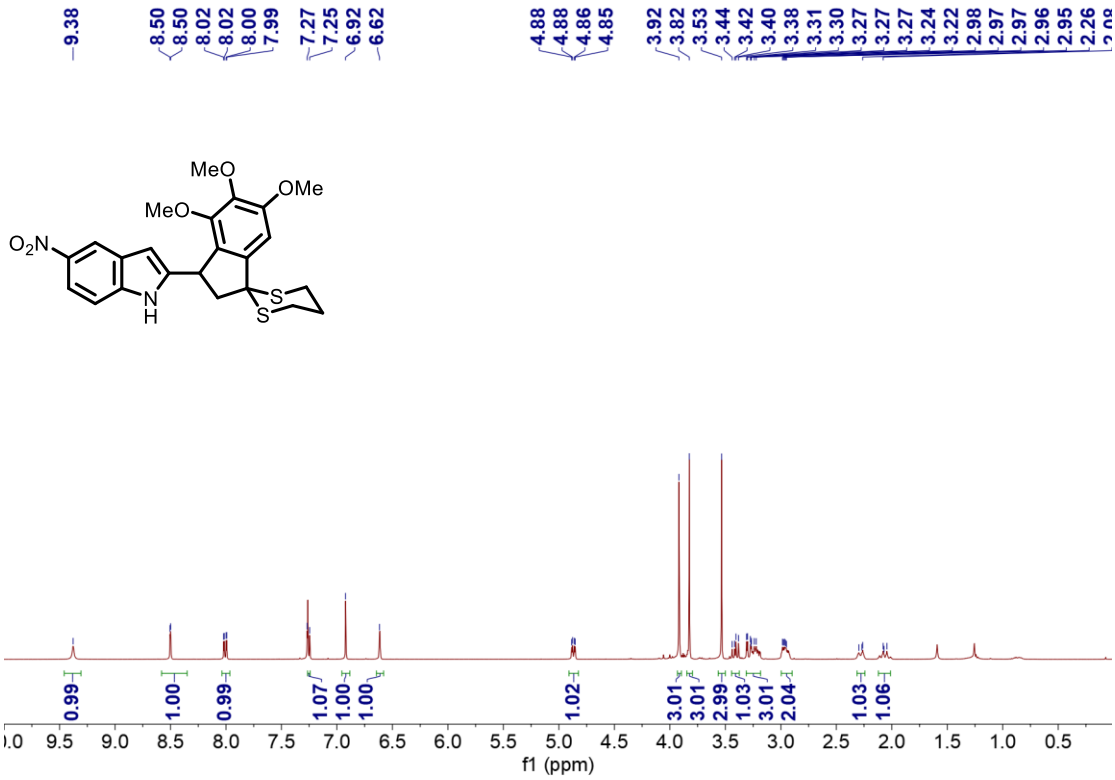
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2h**



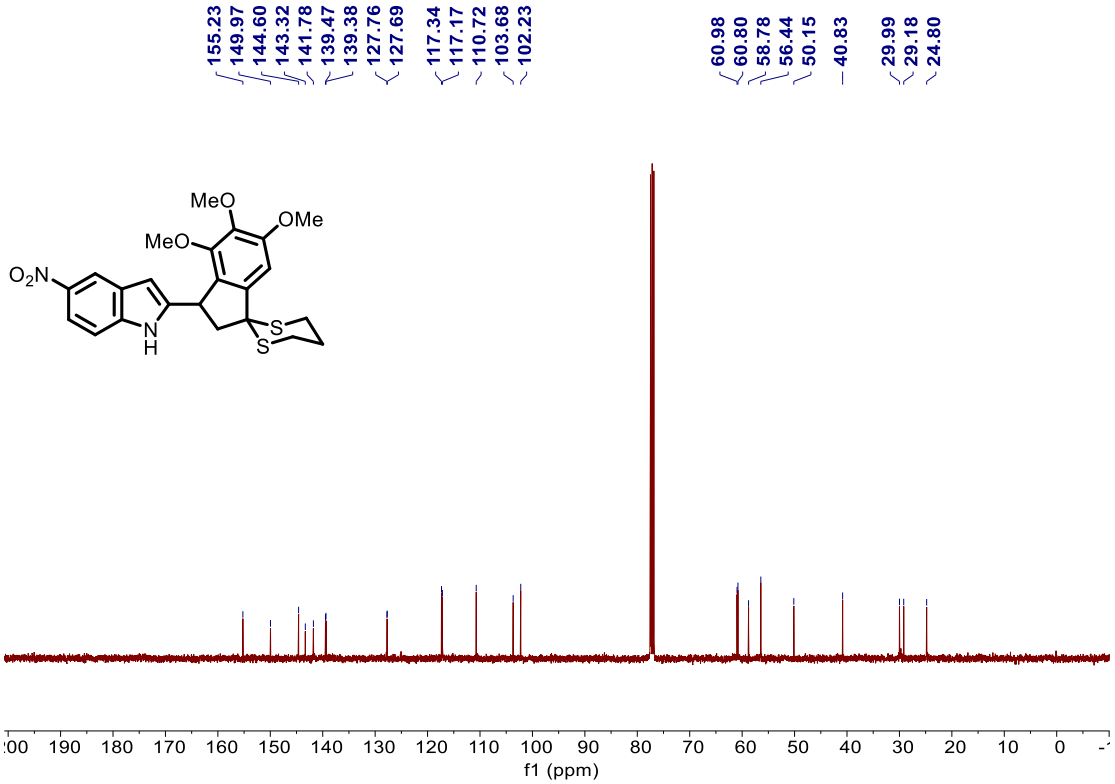
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2h**



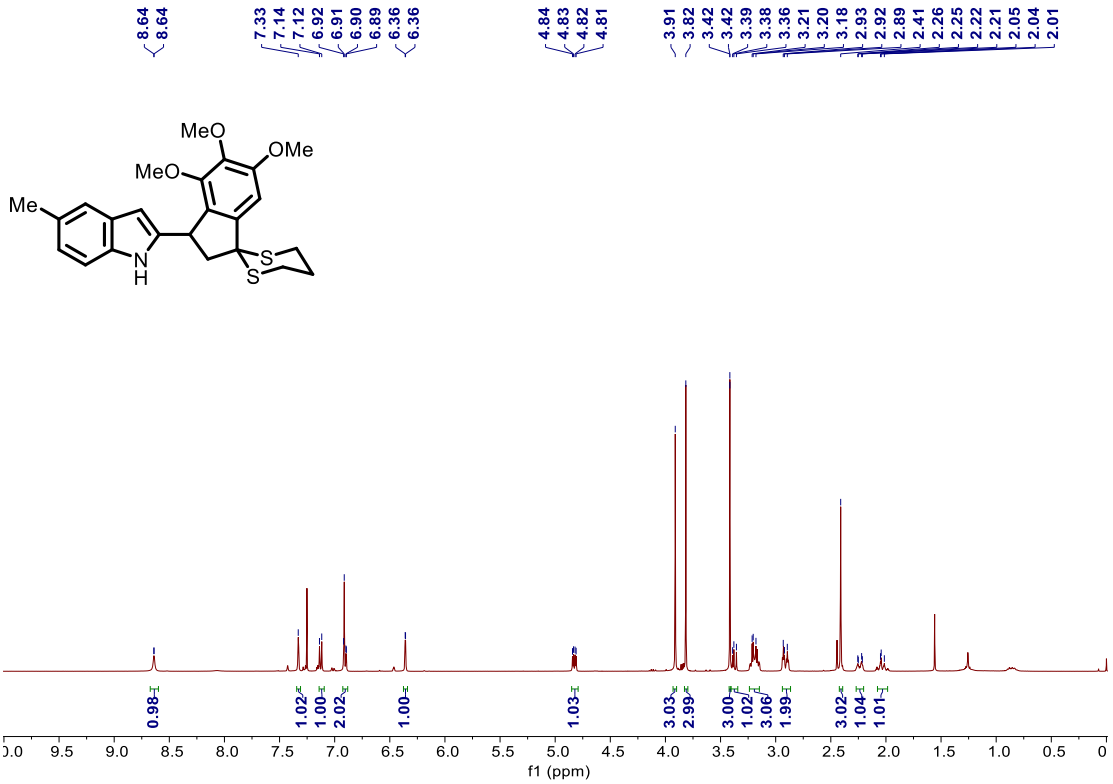
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2i**



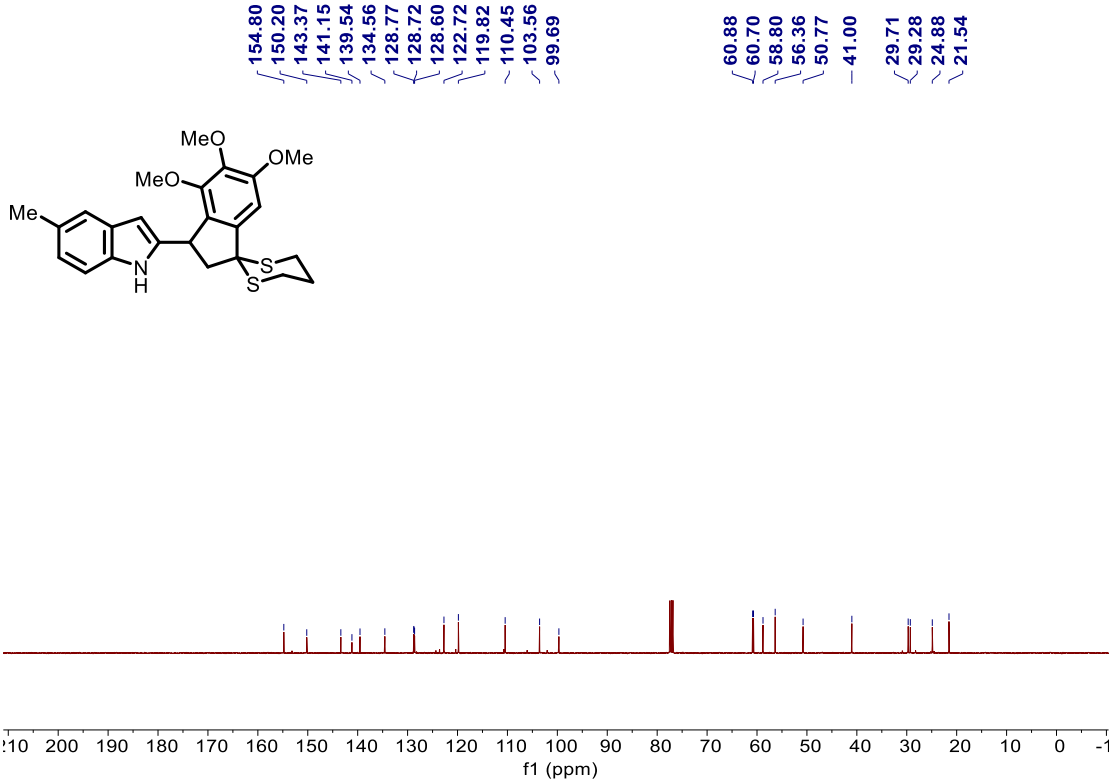
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2i**



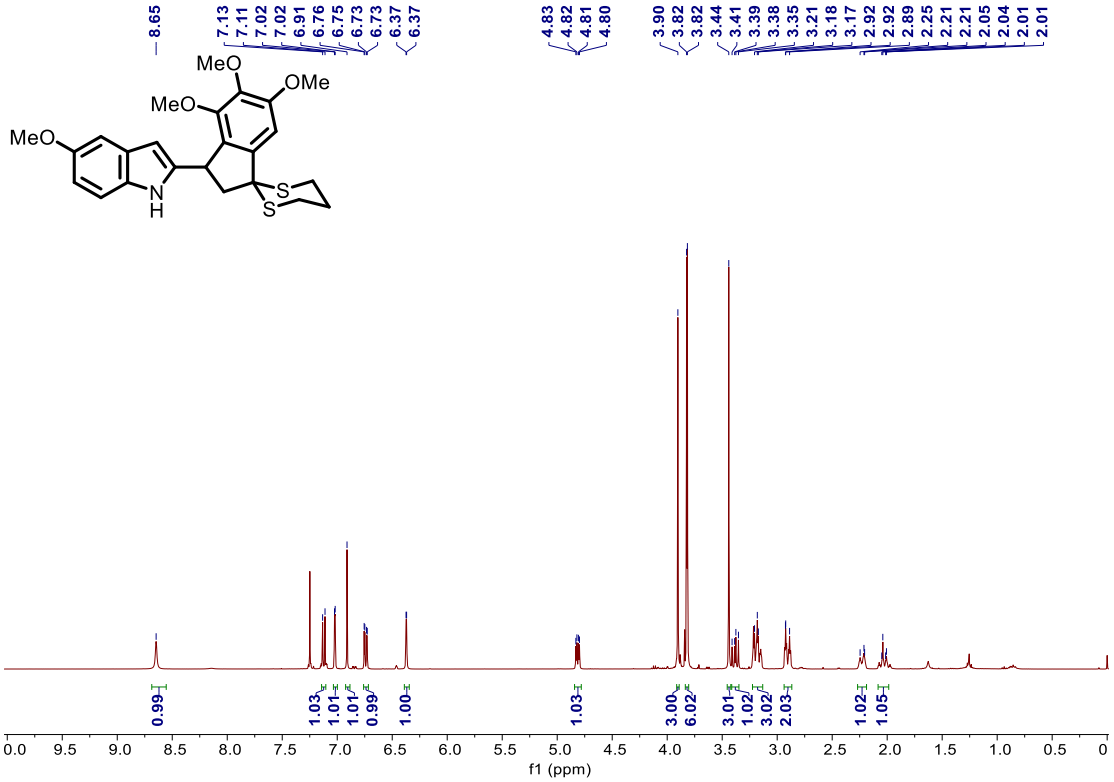
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2j**



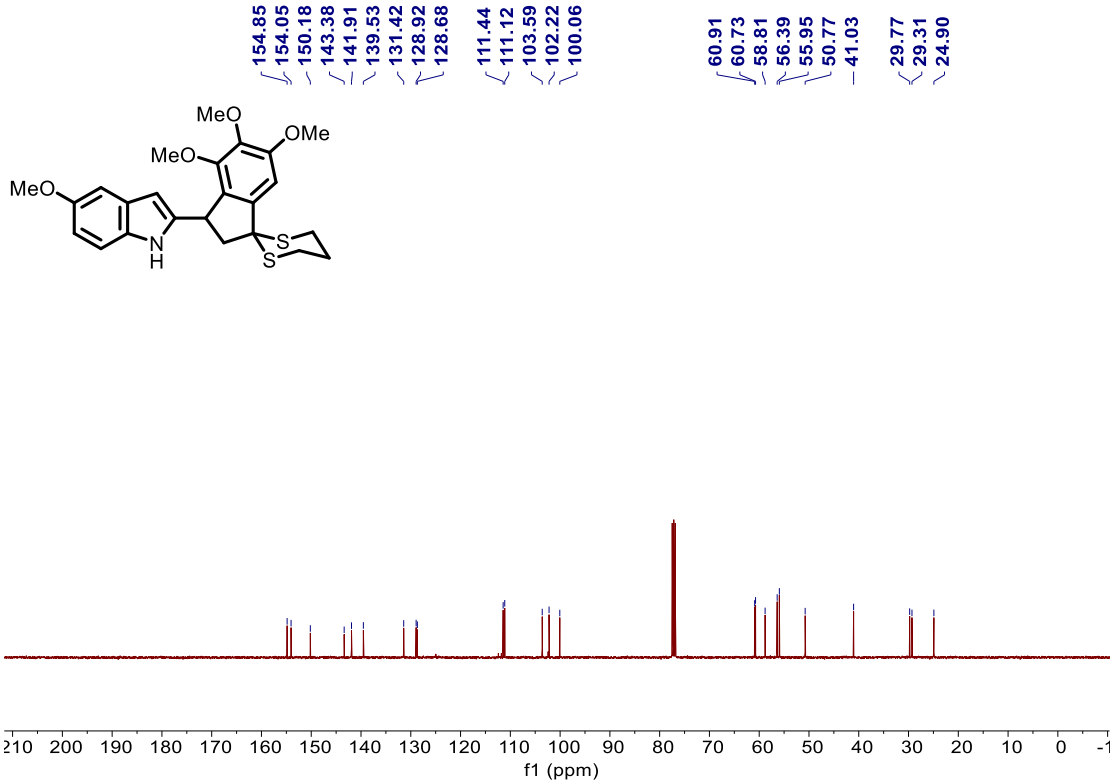
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2j**



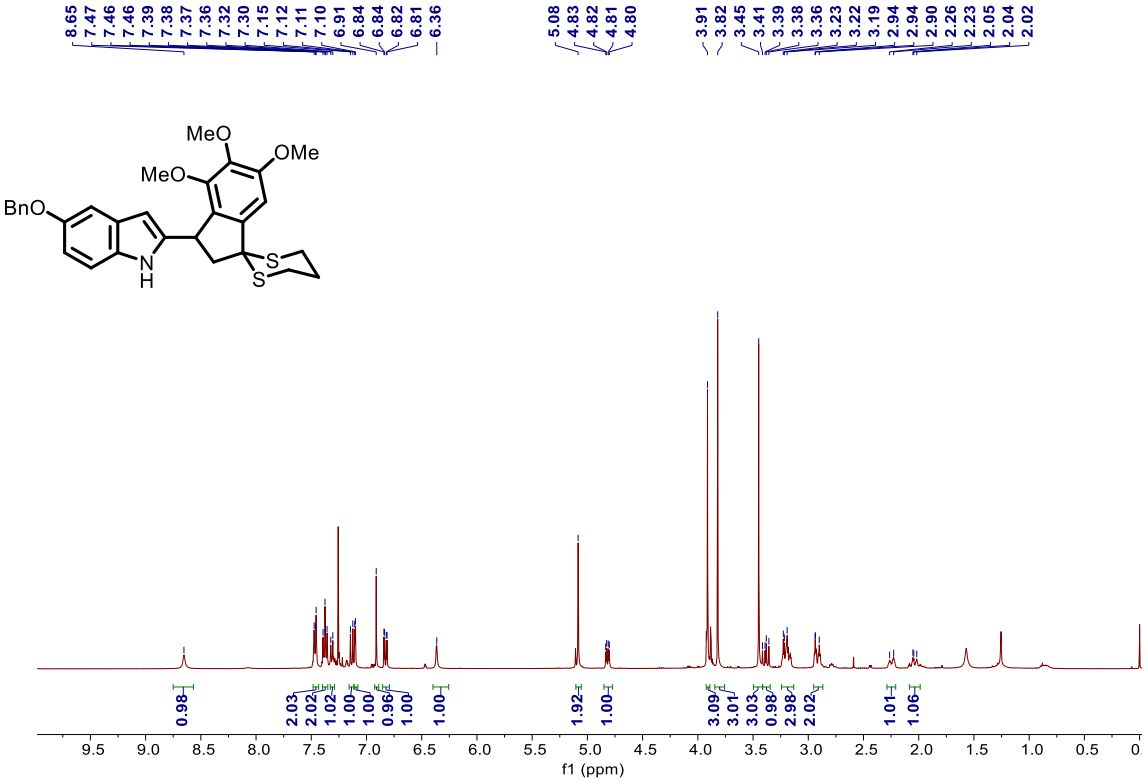
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2k**



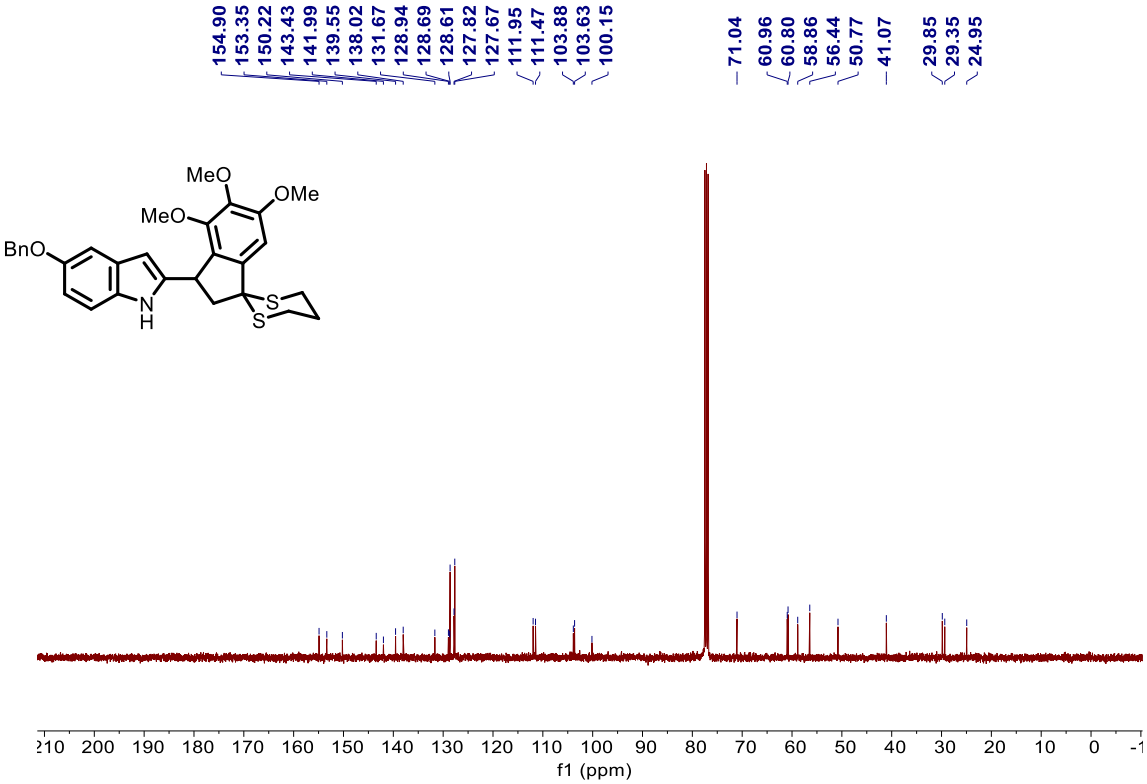
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2k**



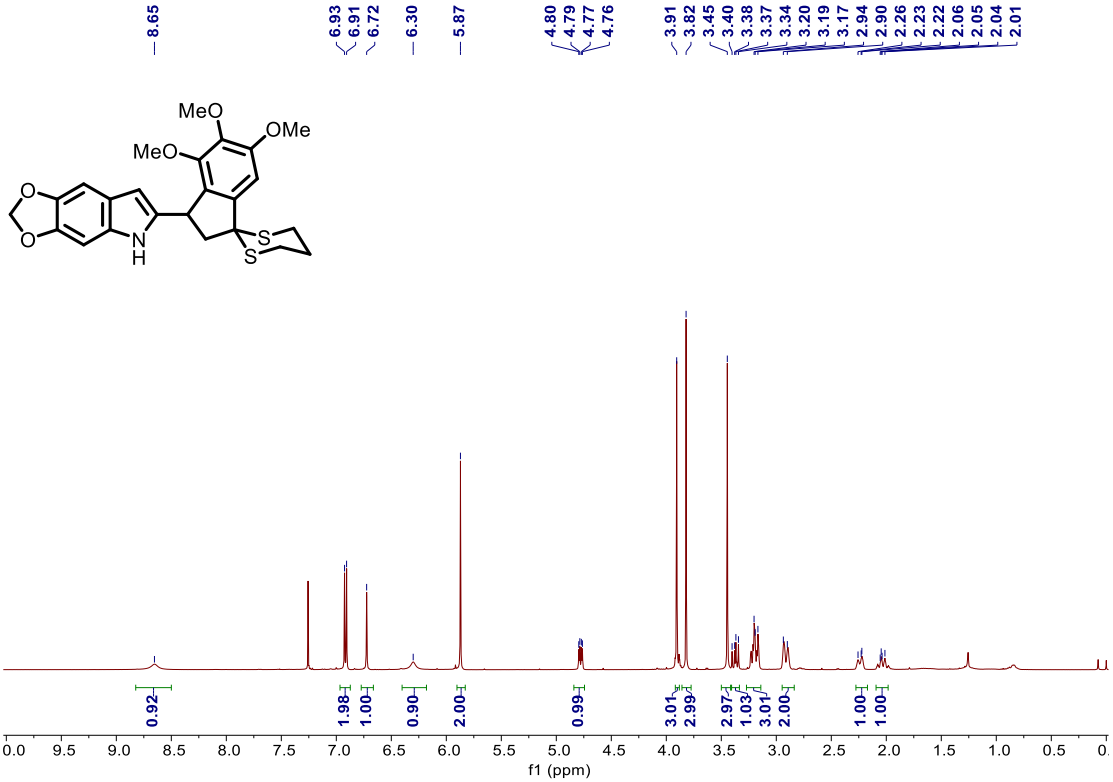
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2l**



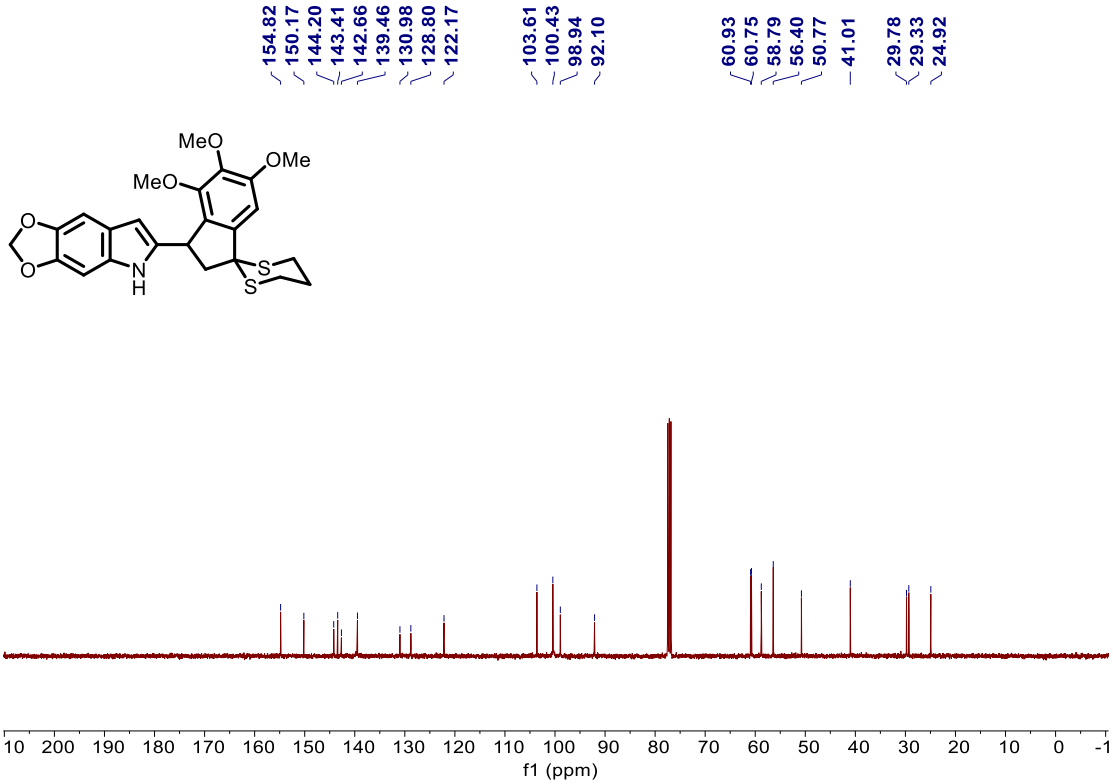
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2l**



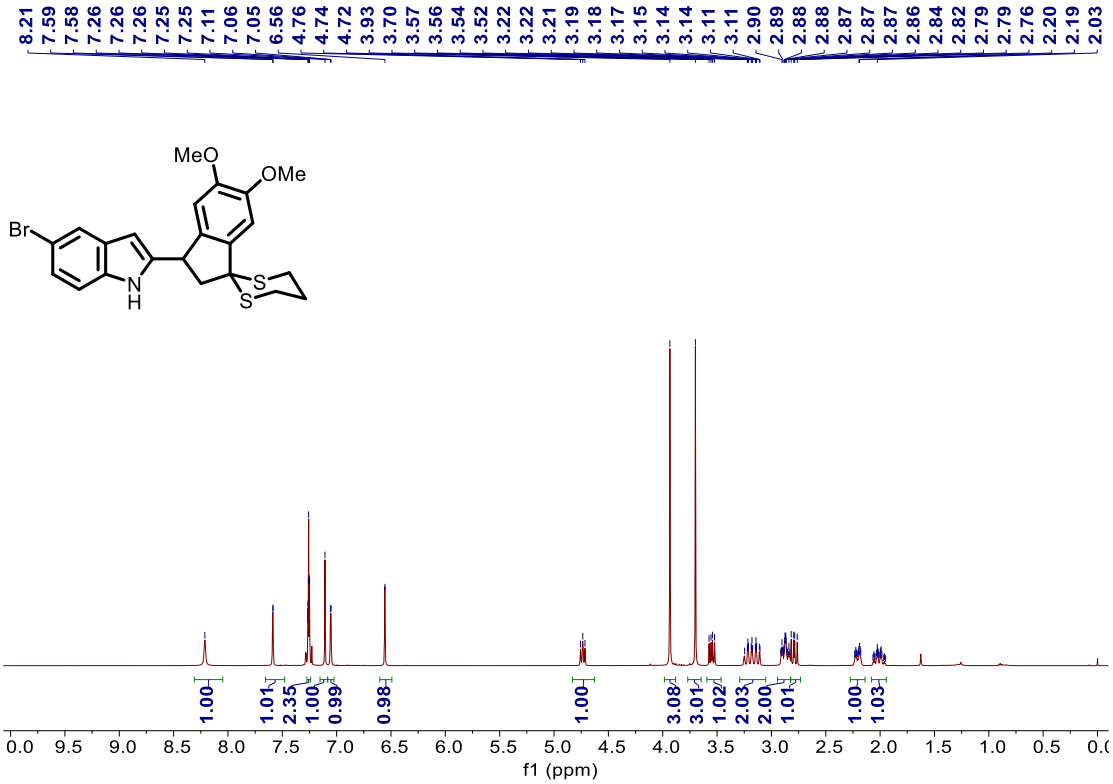
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2m**



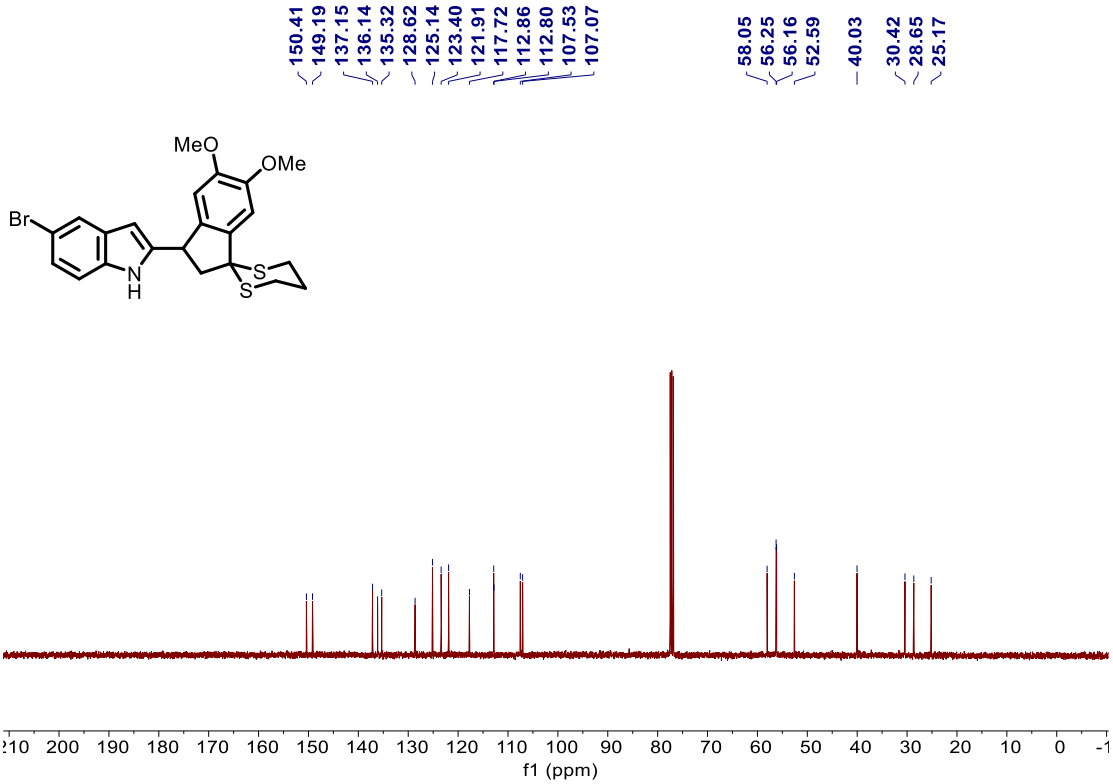
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2m**



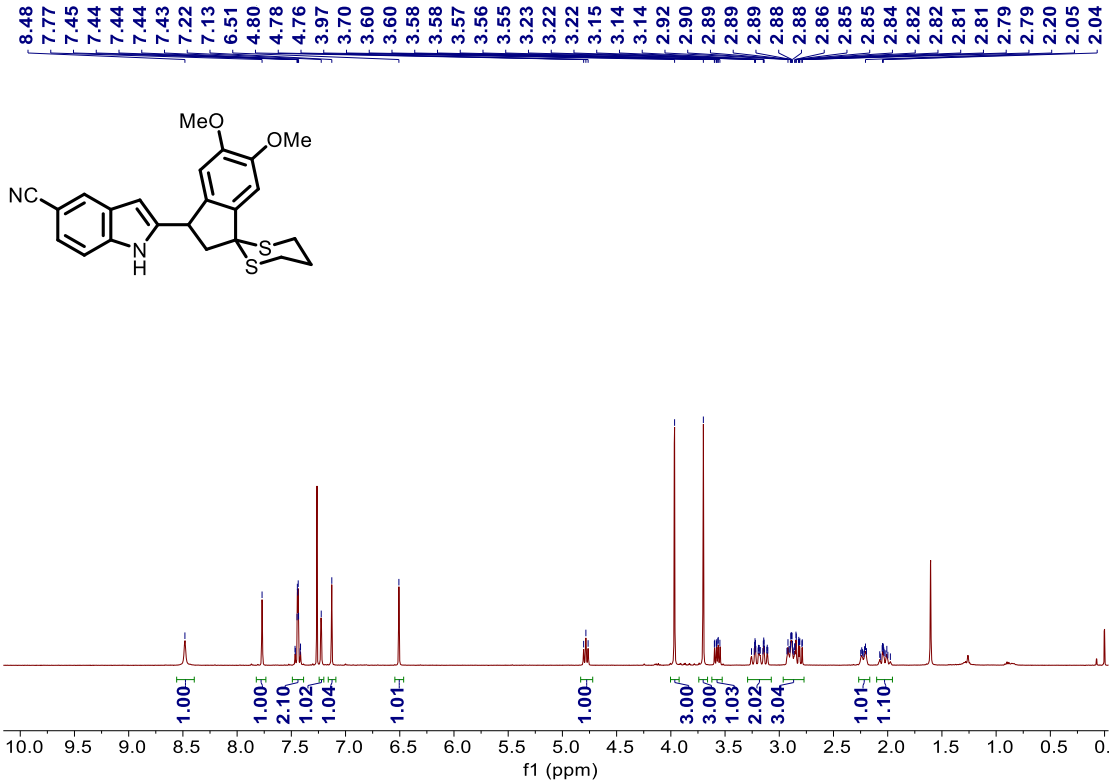
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2n**



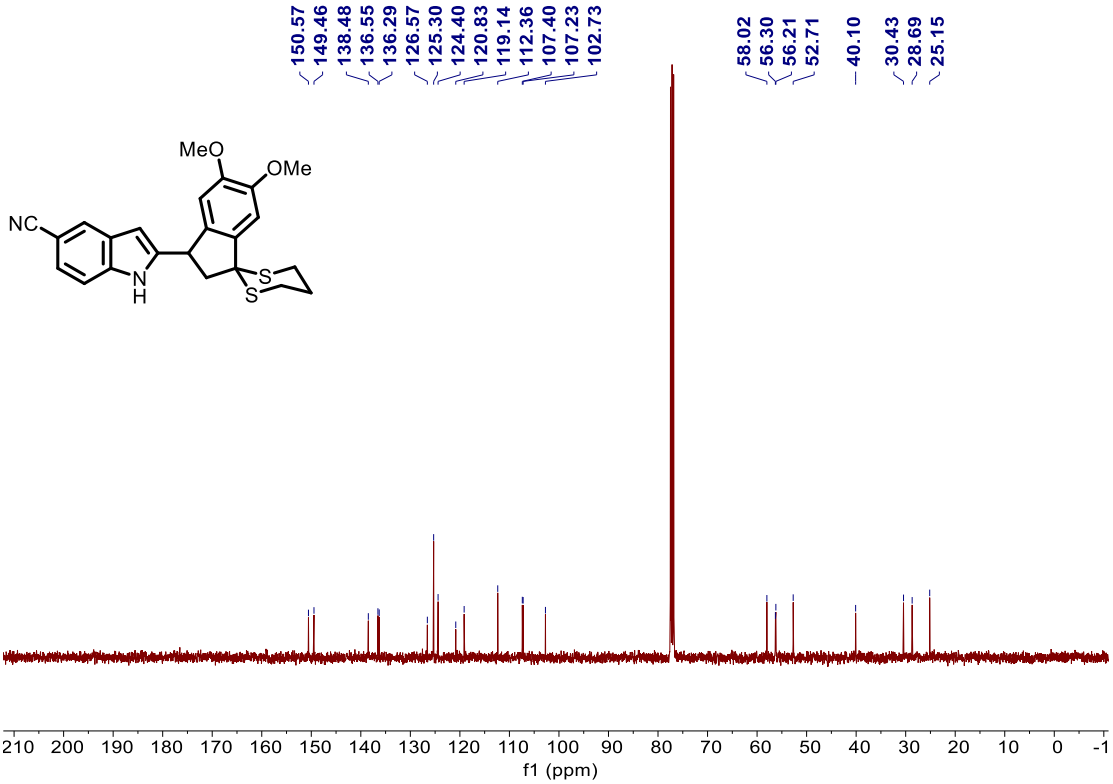
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2n**



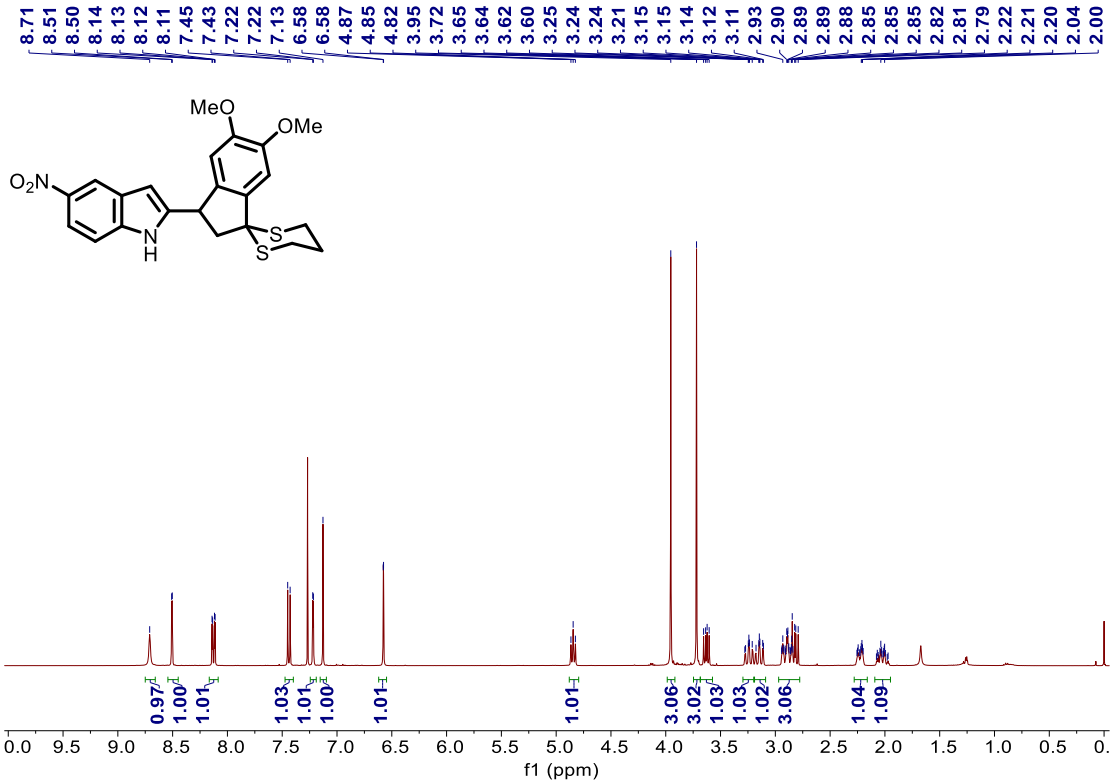
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2o**



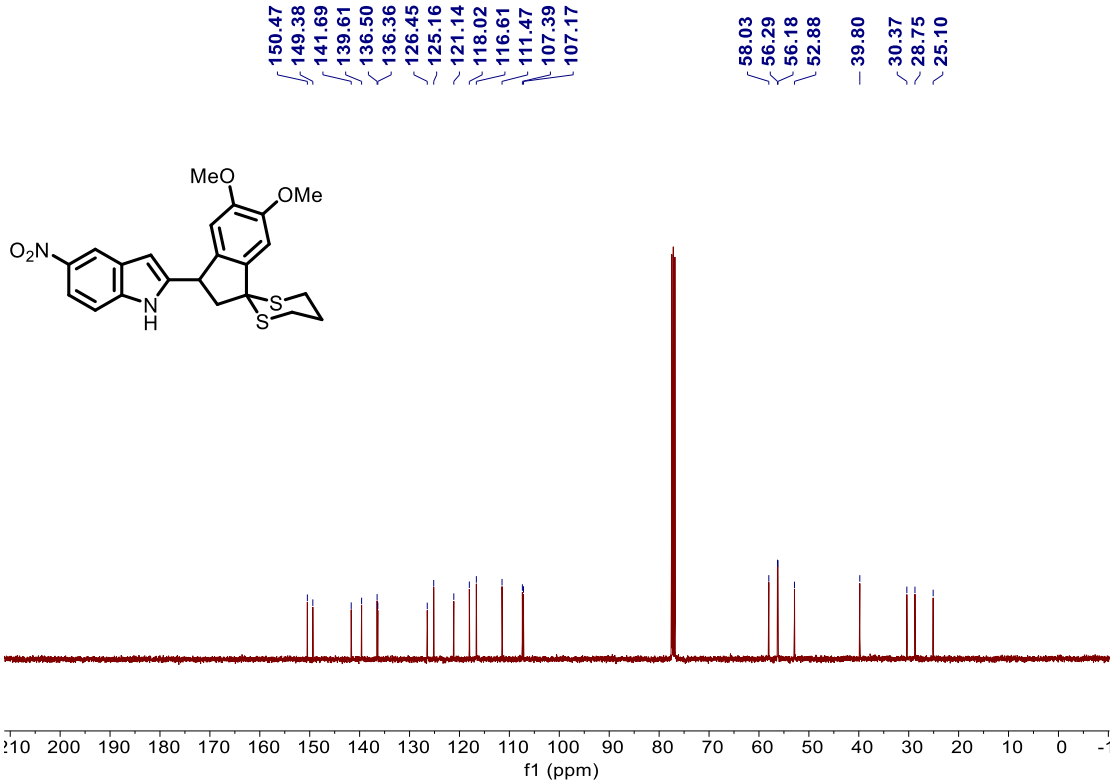
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2o**



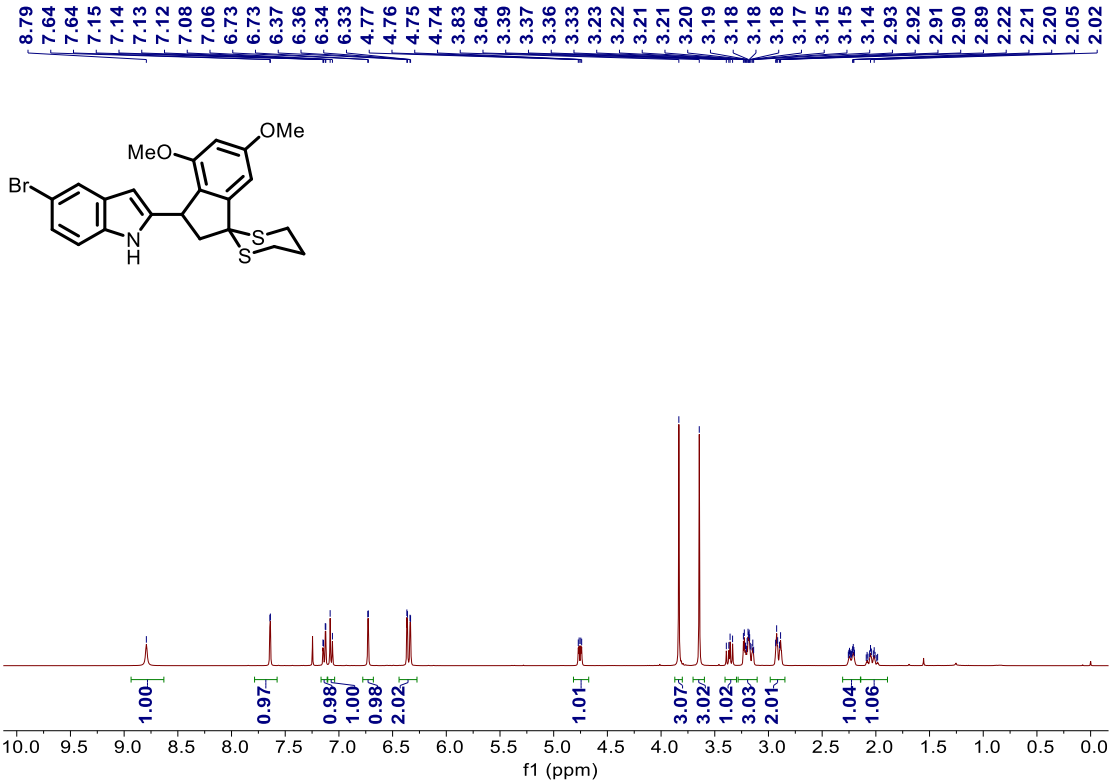
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2p**



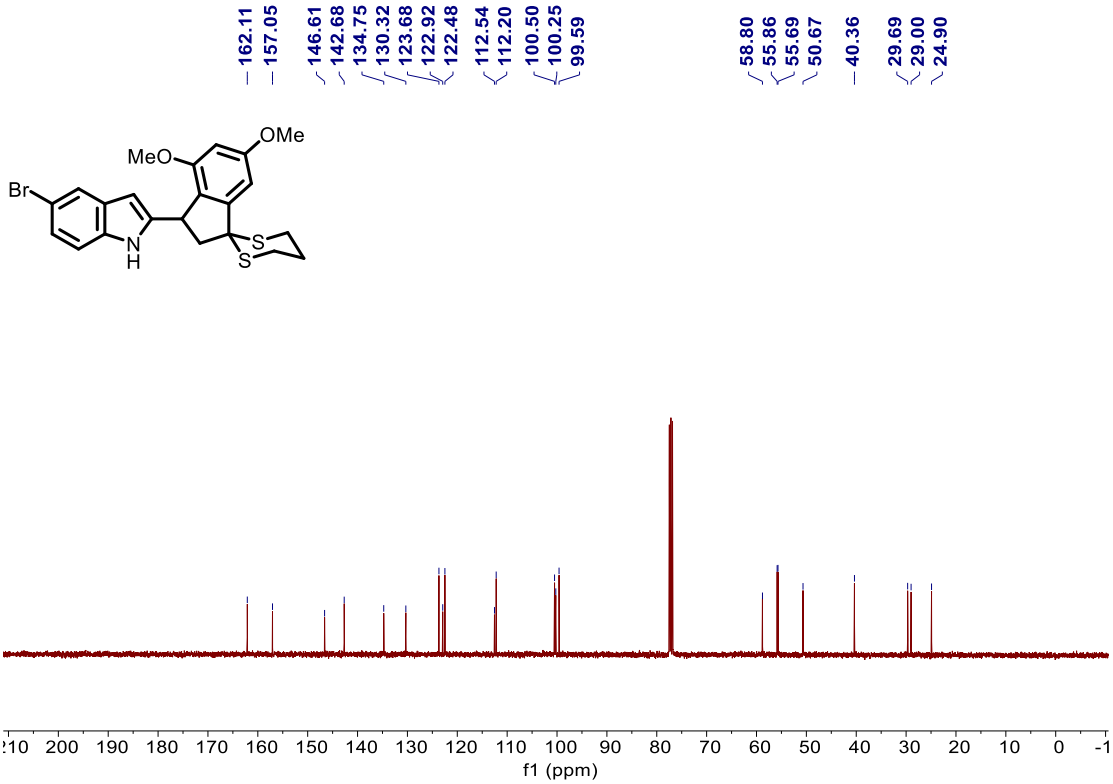
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2p**



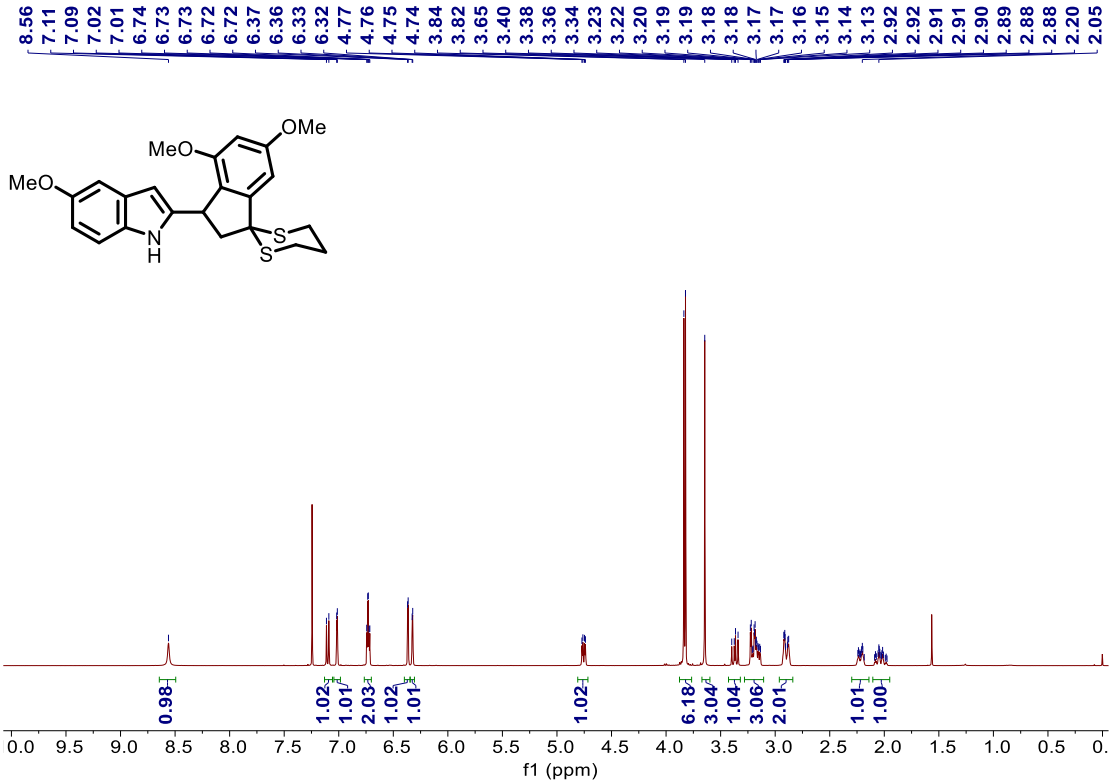
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2q**



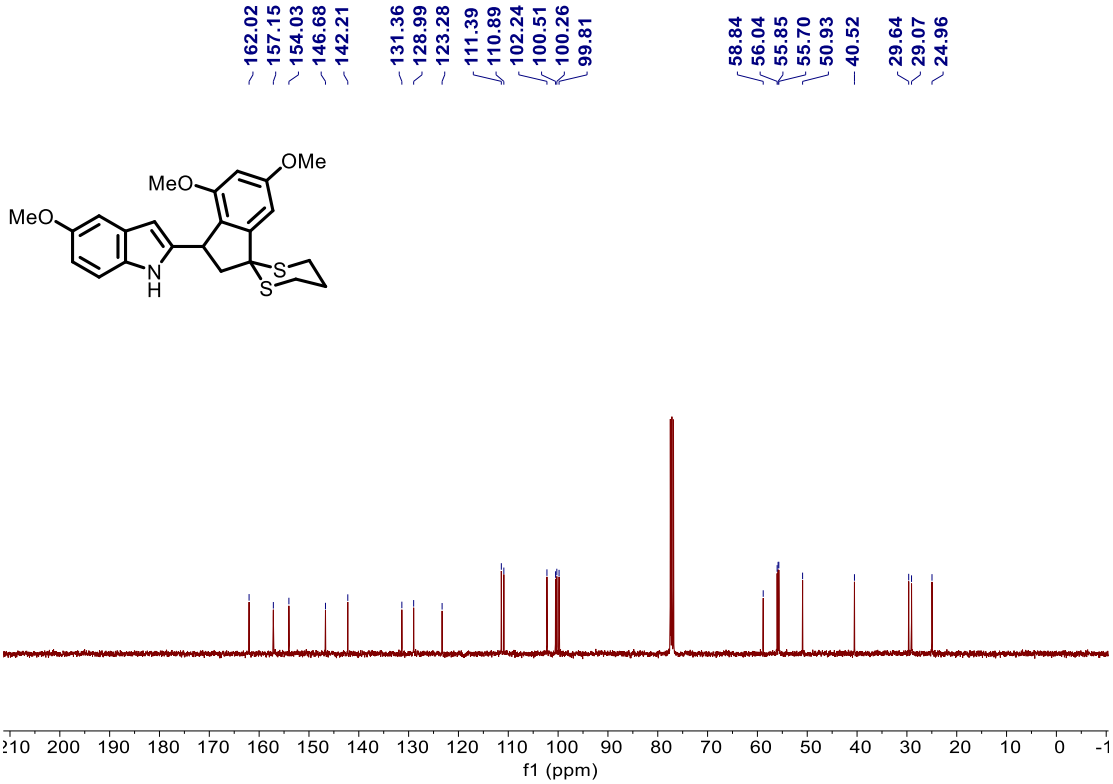
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2q**



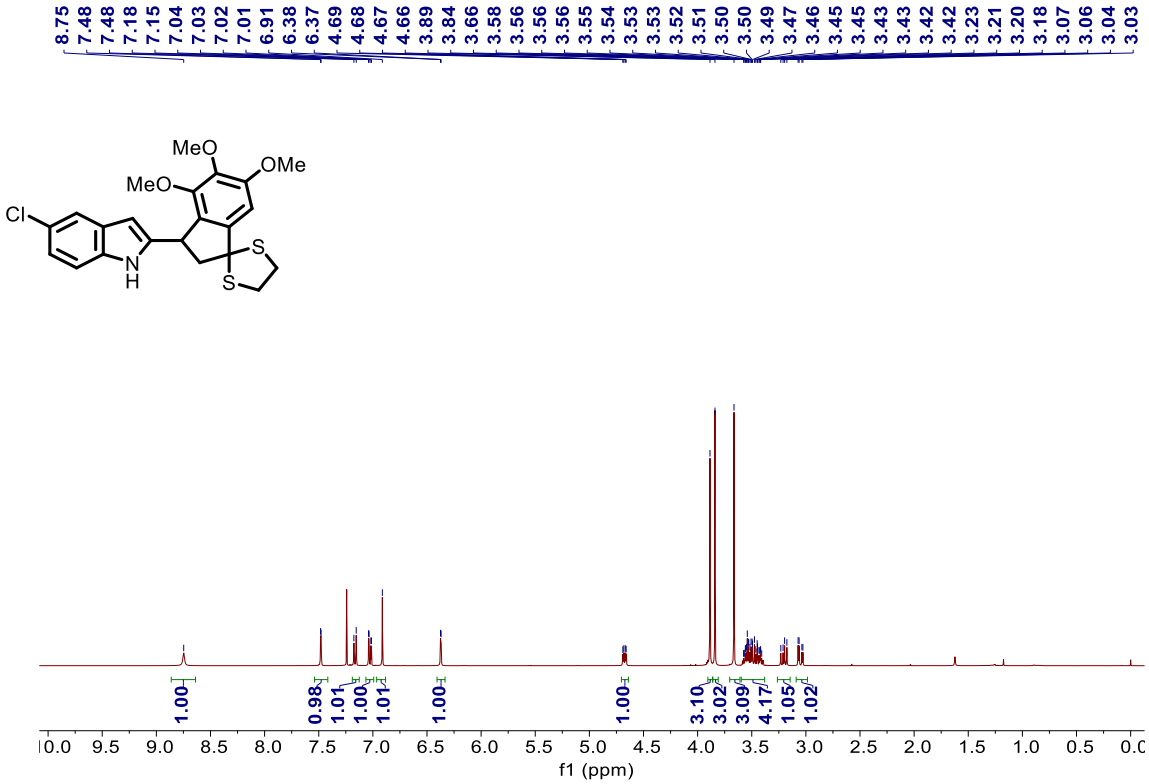
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2r**



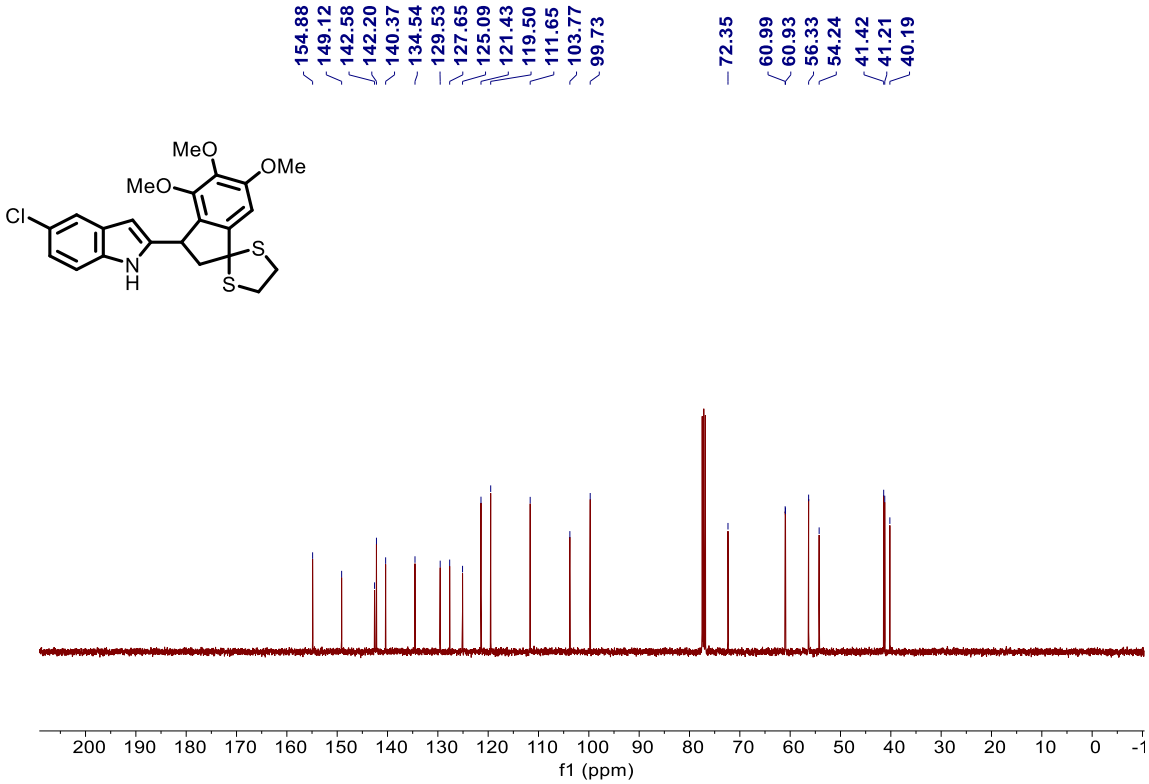
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2r**



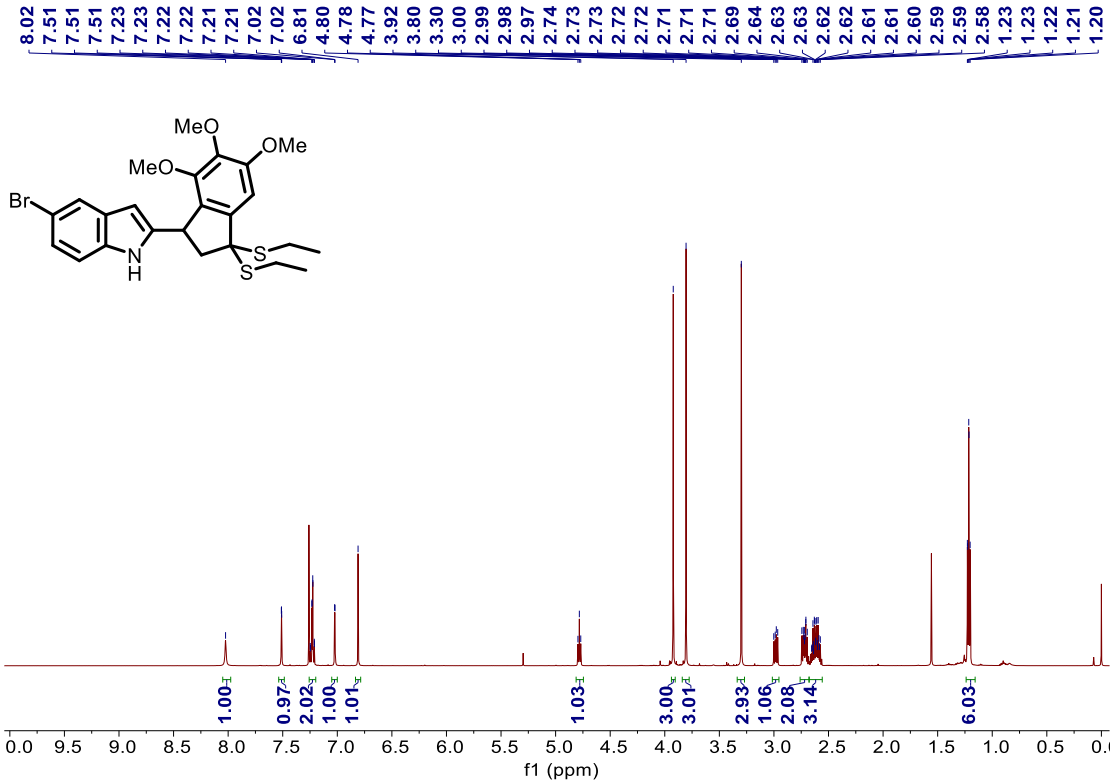
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2s**



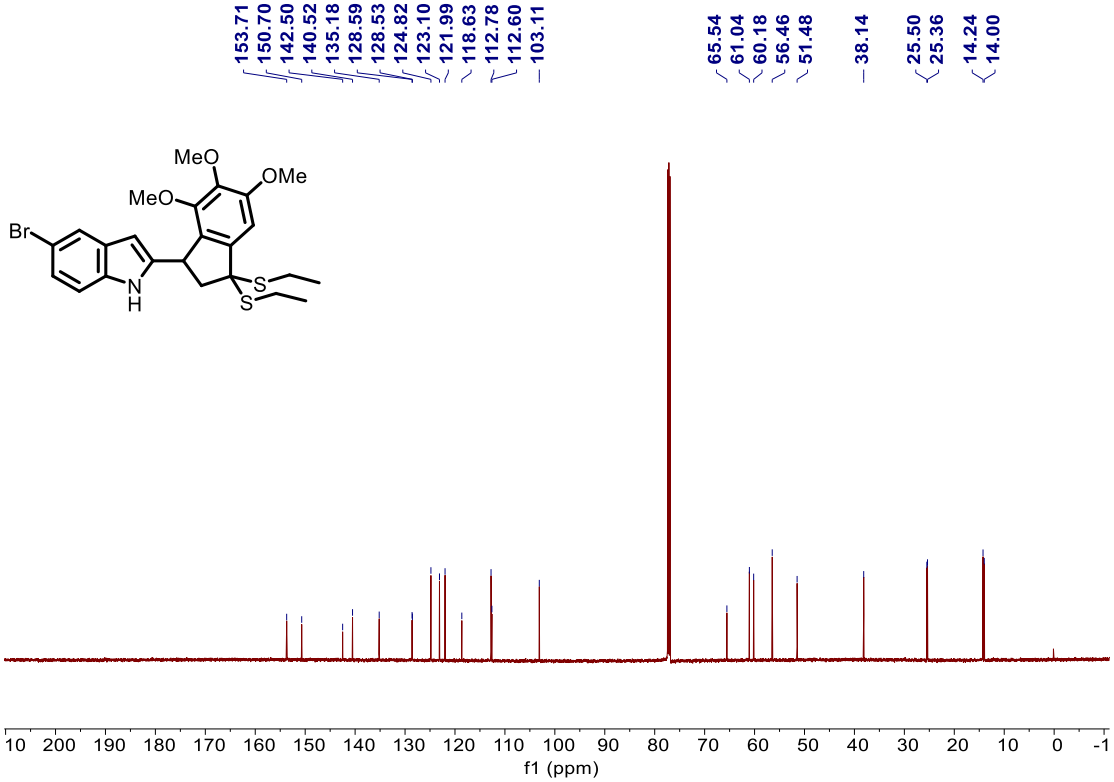
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2s**



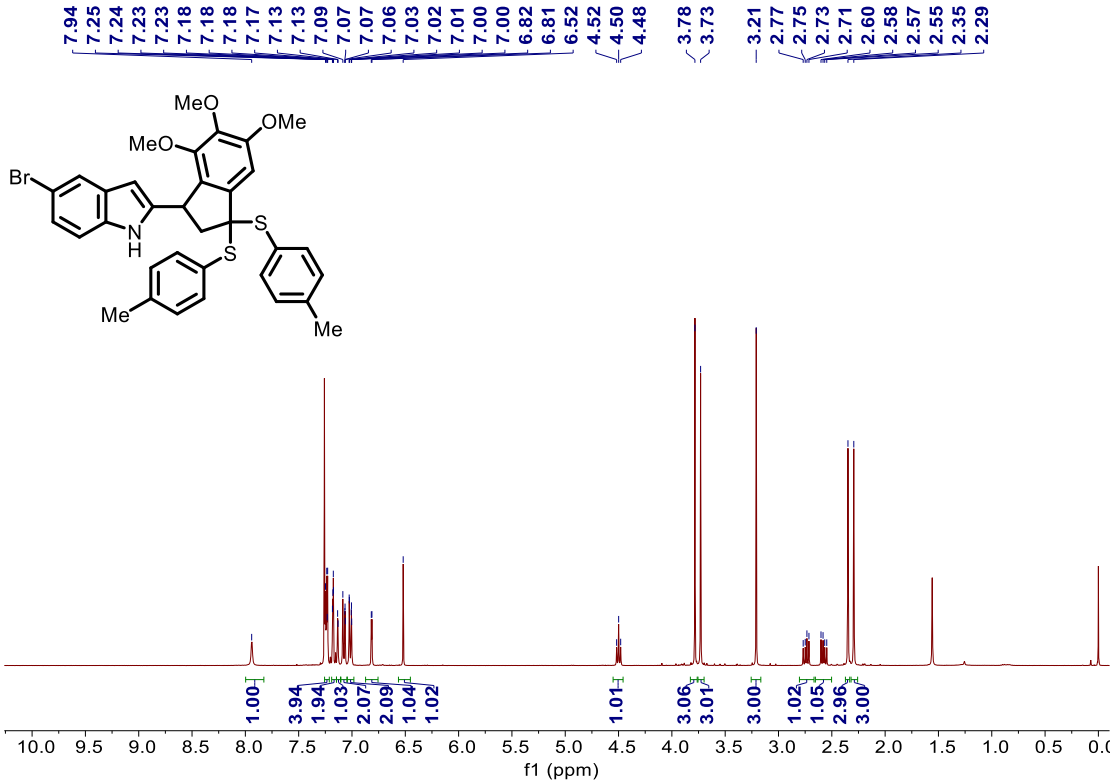
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2t**



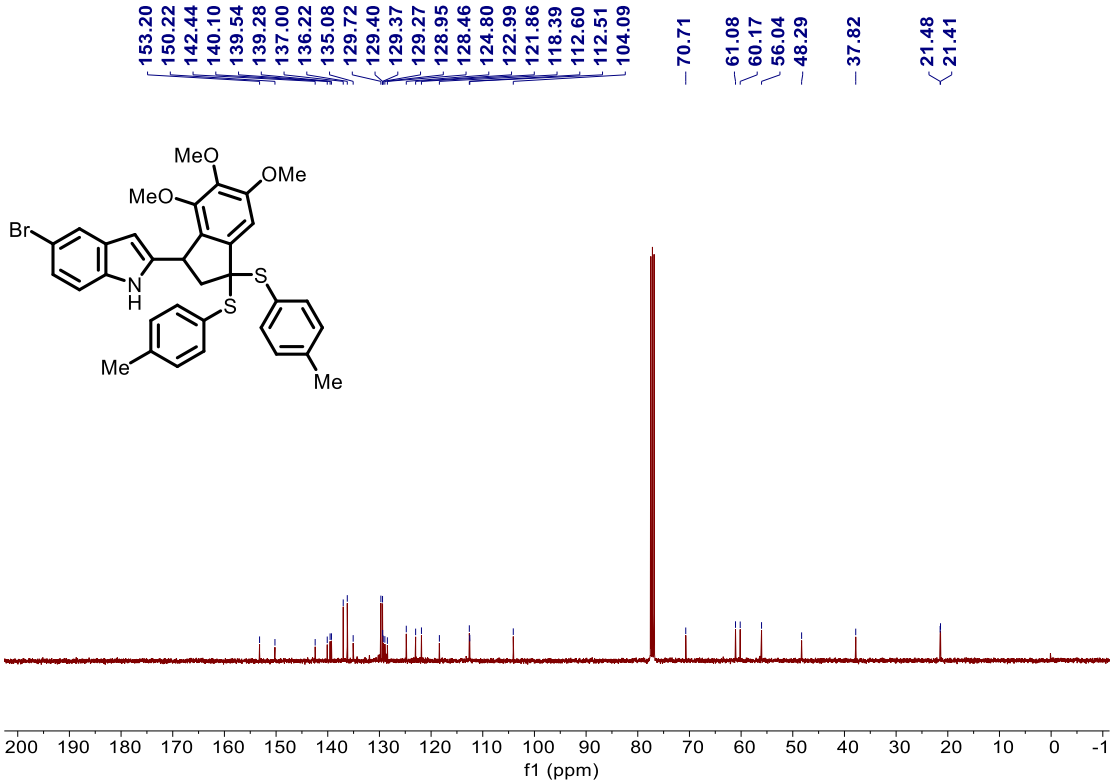
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2t**



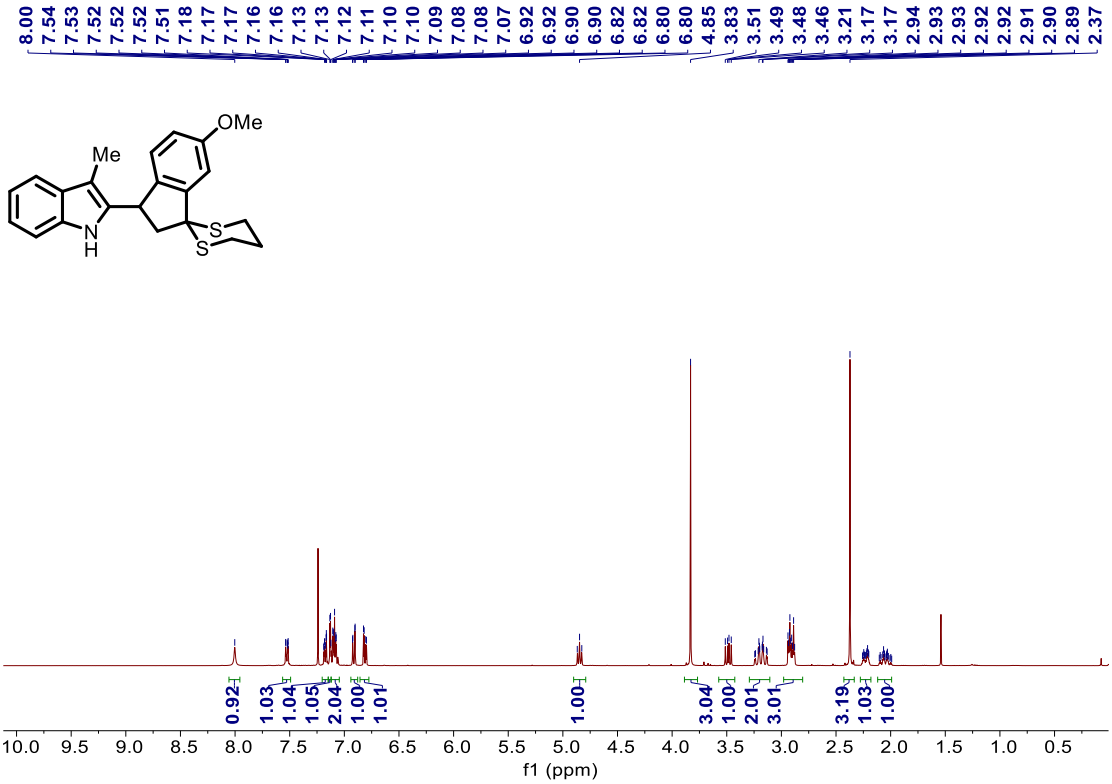
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2u**



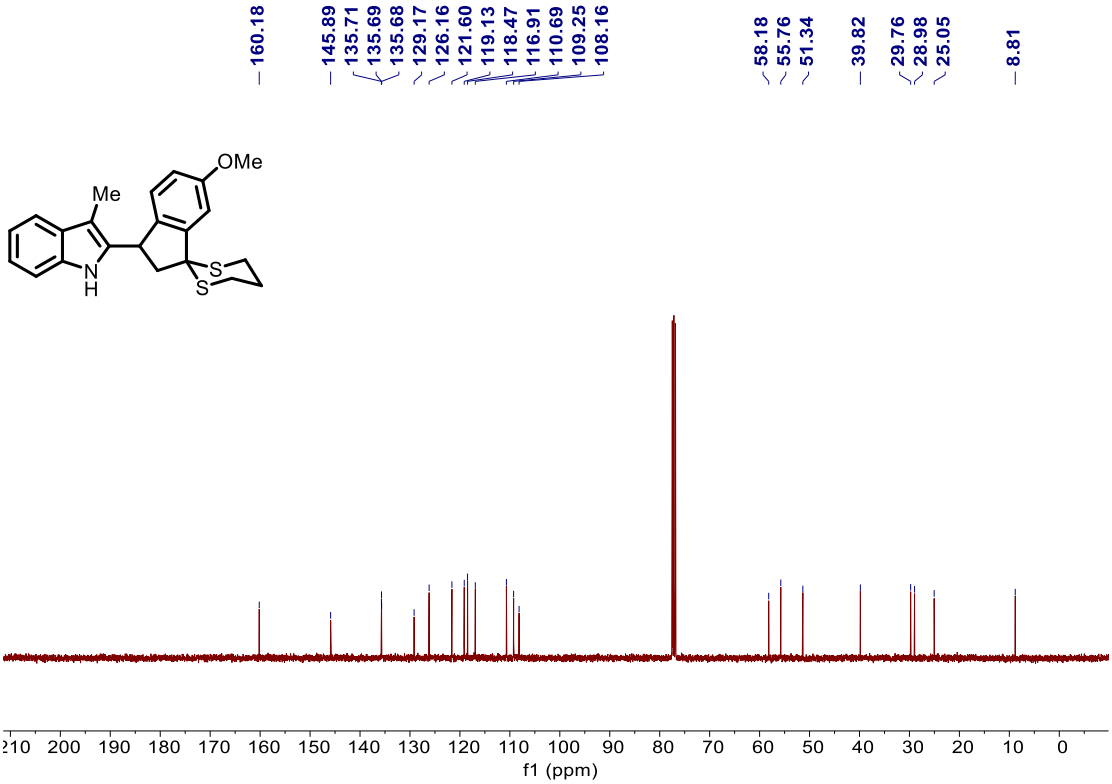
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2u**



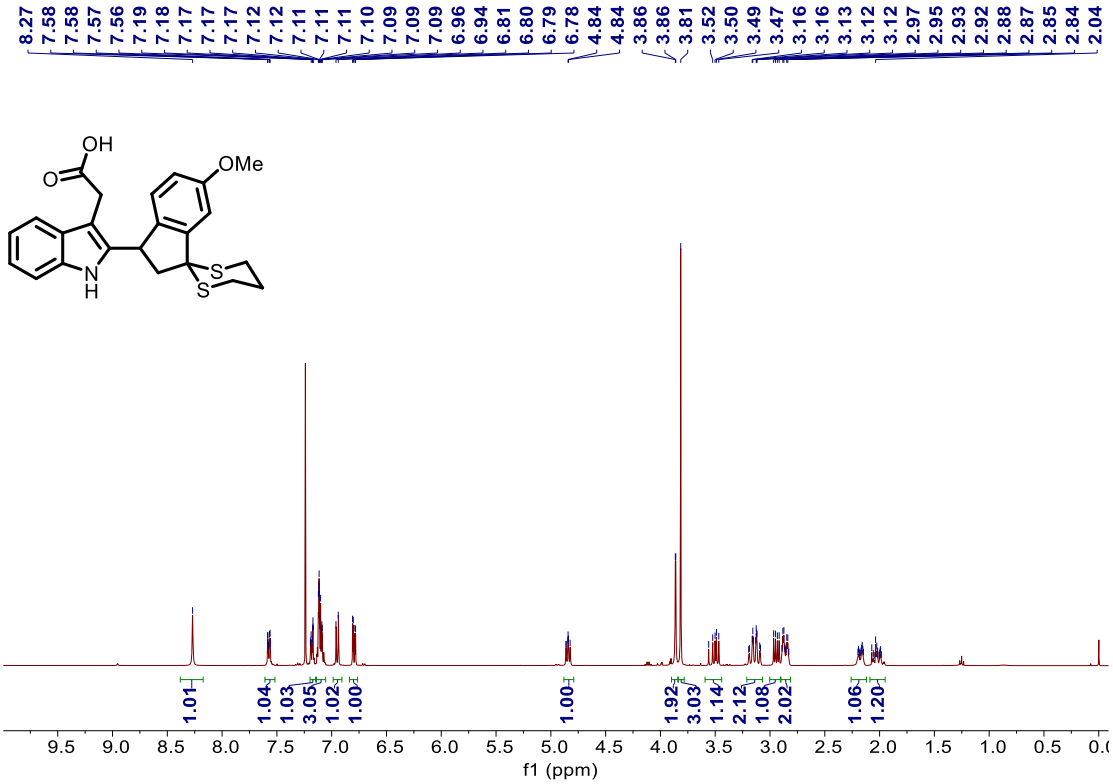
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3a**



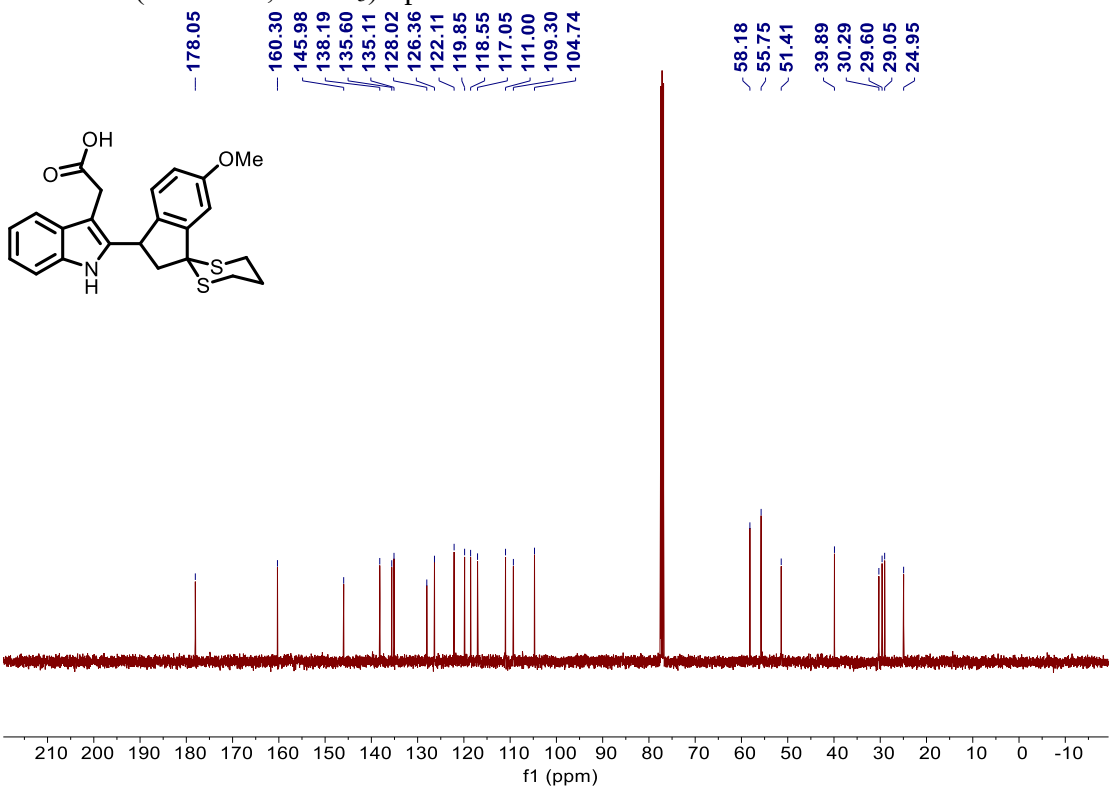
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3a**



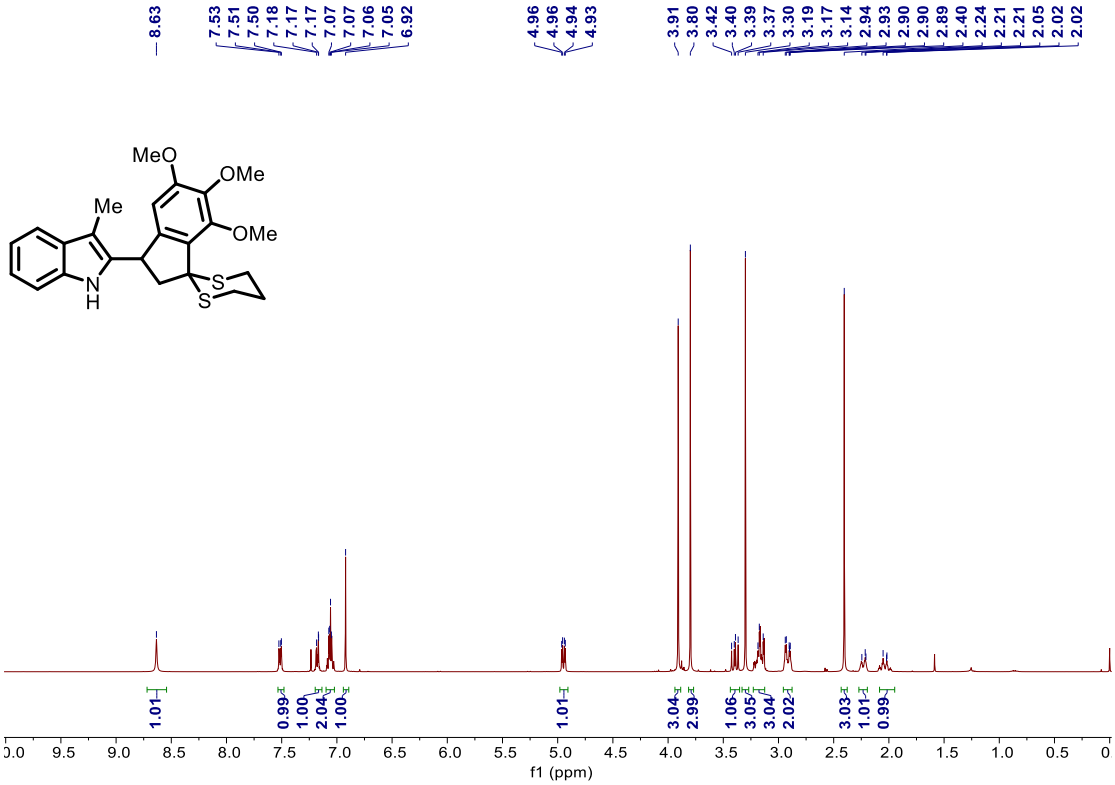
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3b**



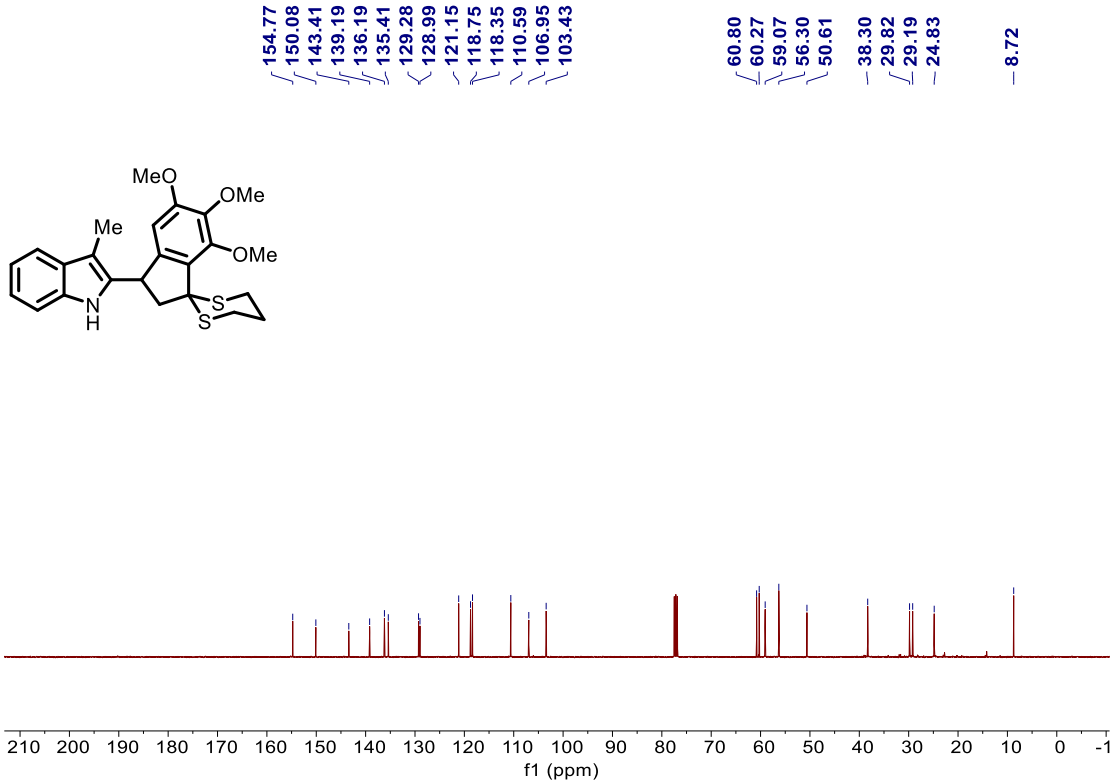
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3b**



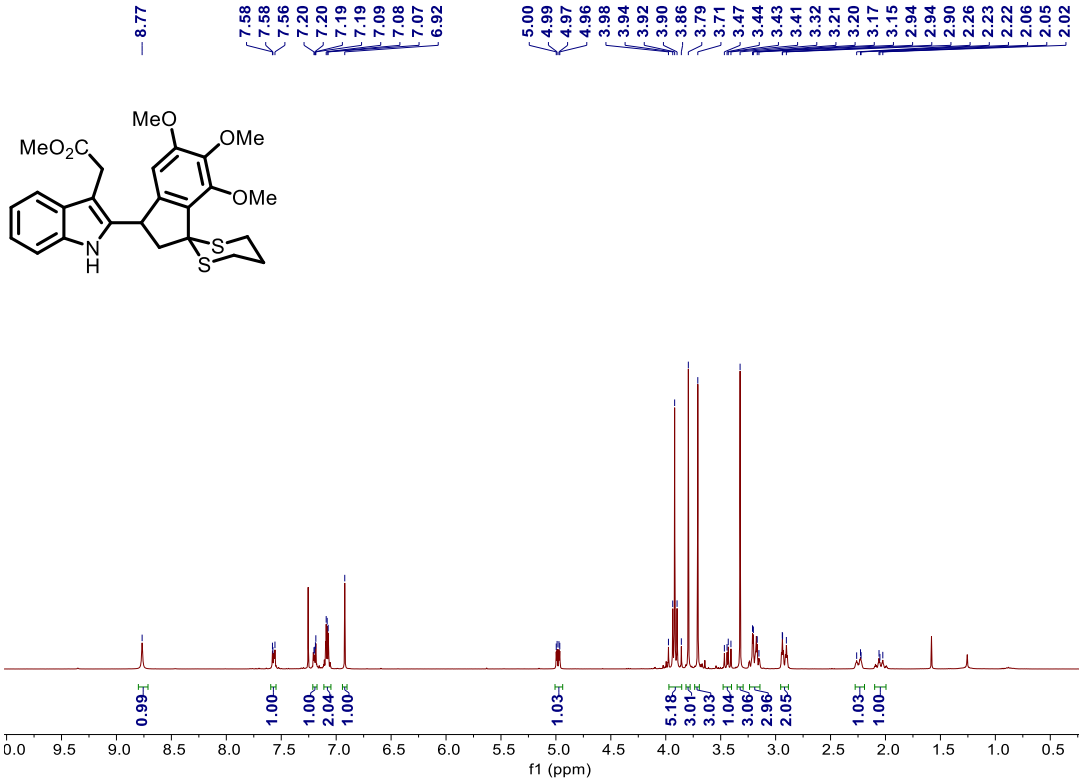
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3c**



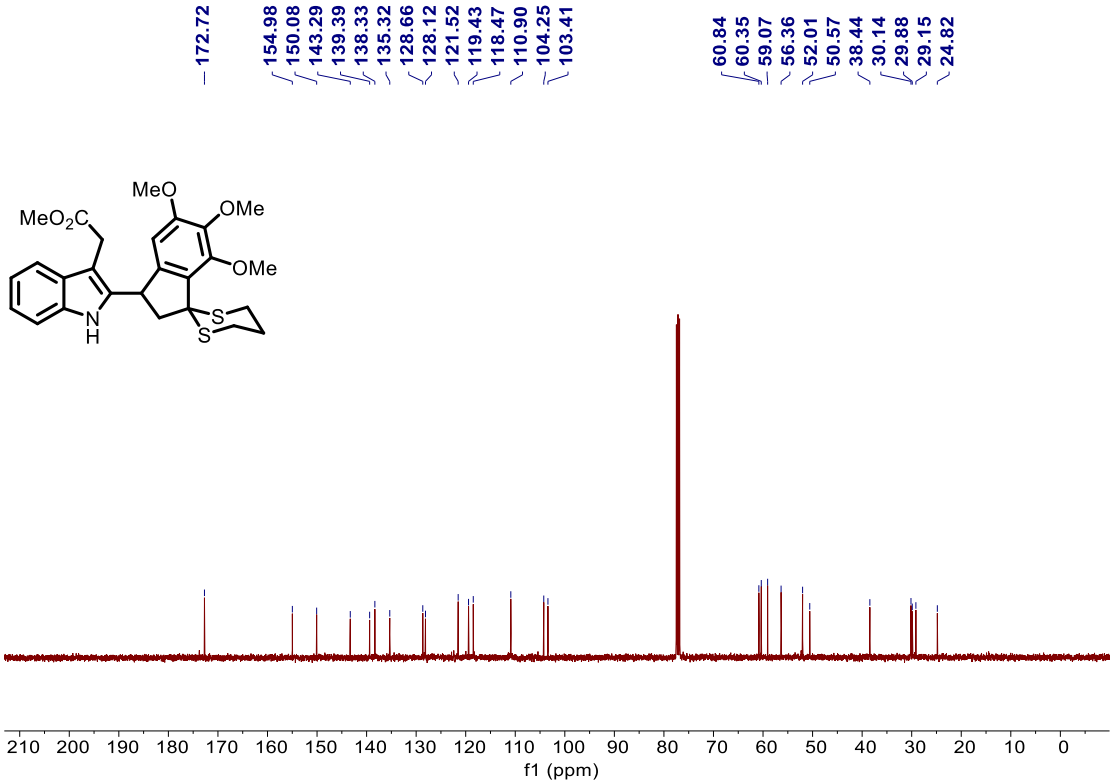
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3c**



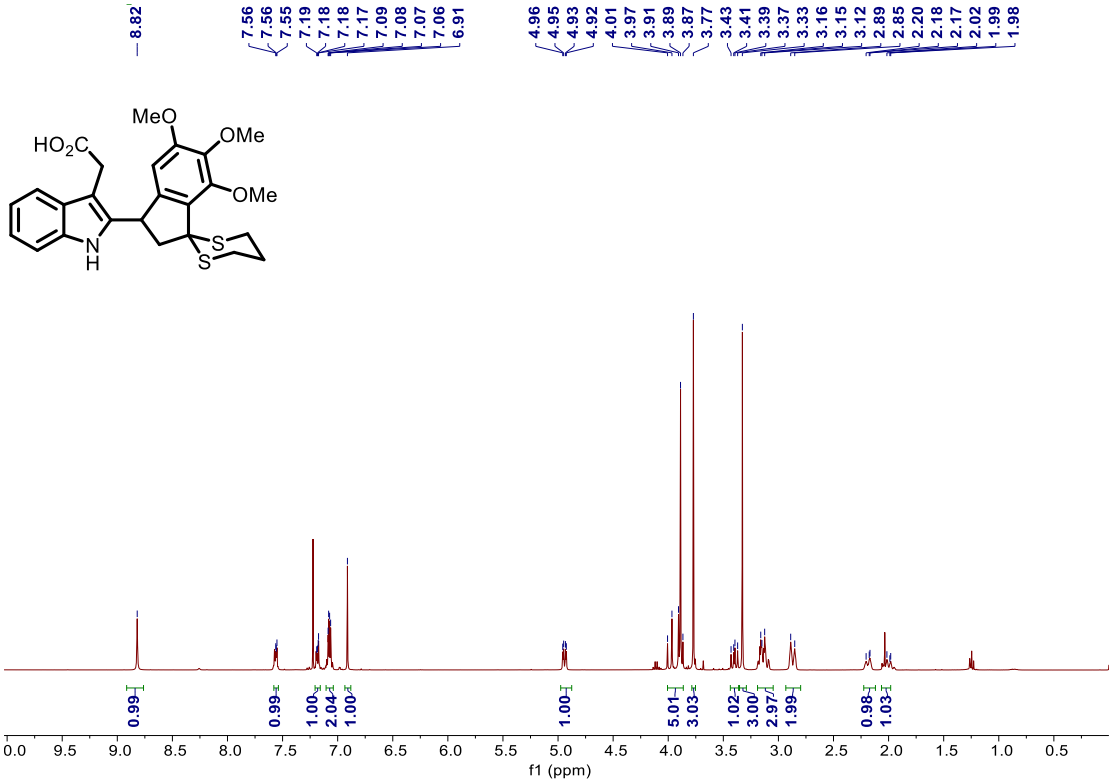
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3d**



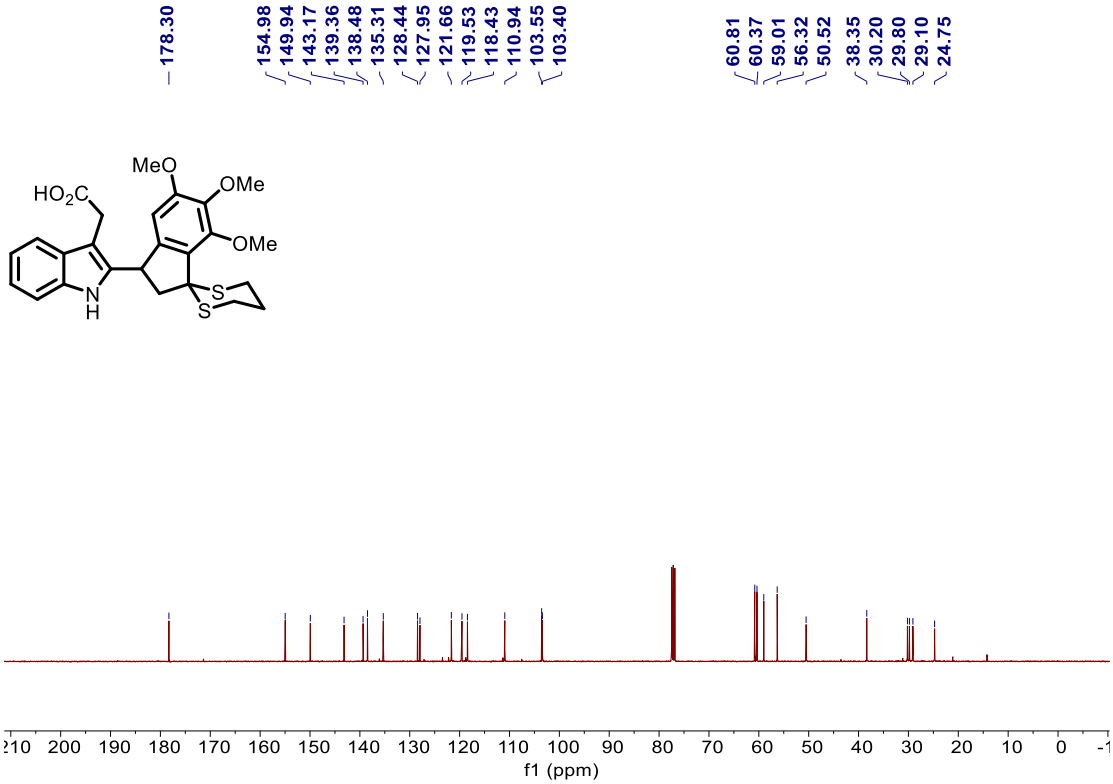
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3d**



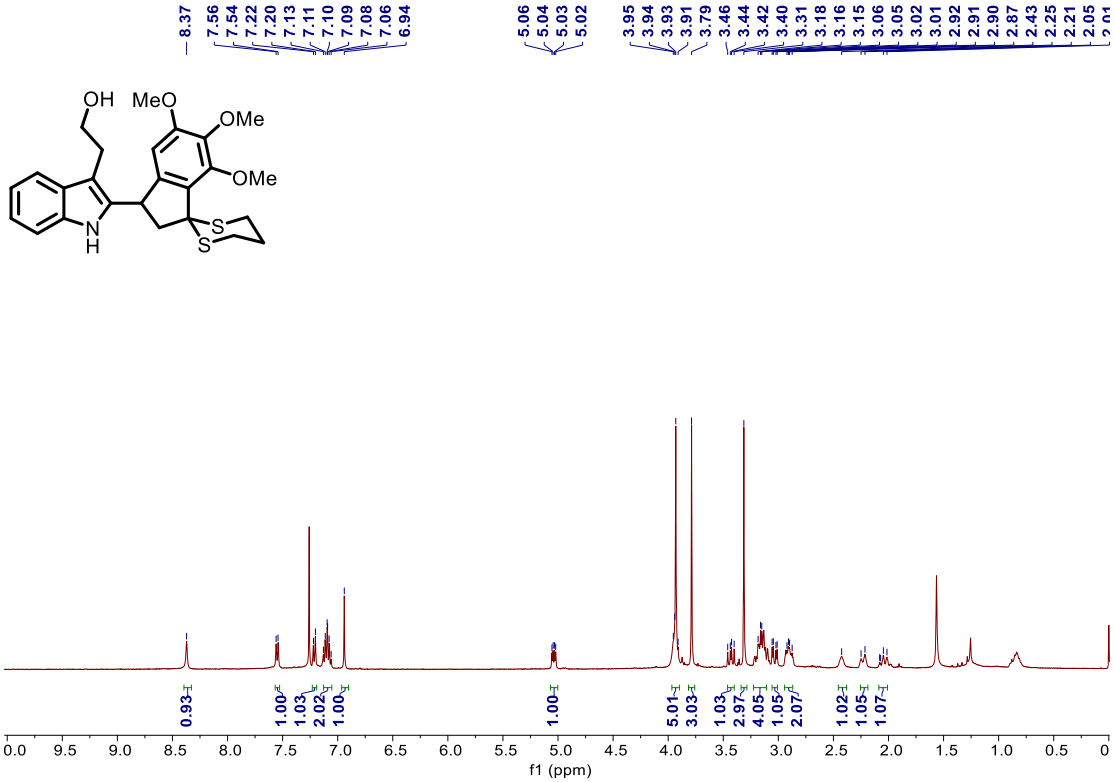
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3e**



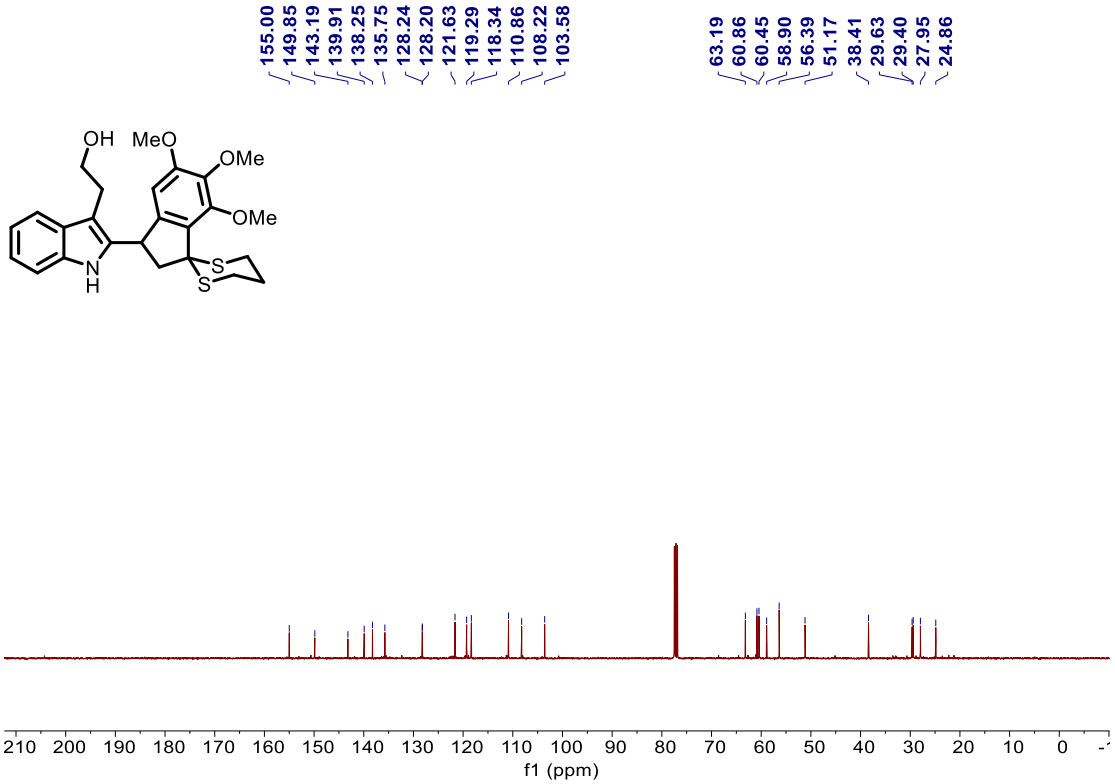
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3e**



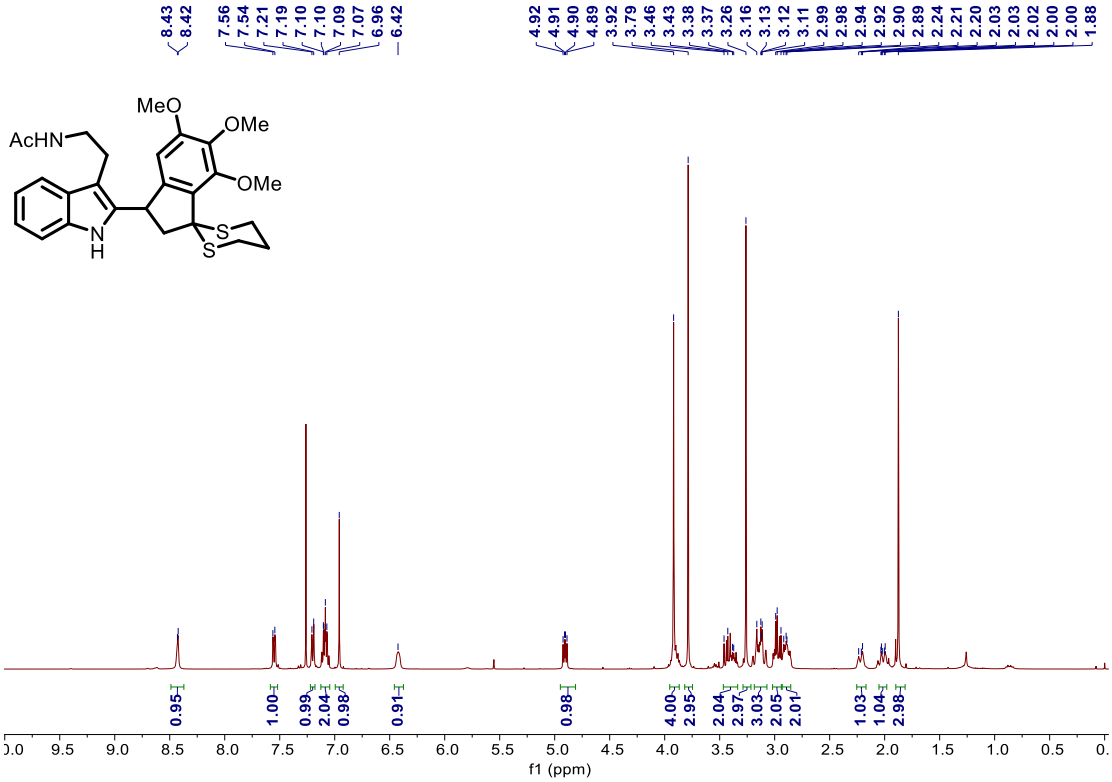
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3f**



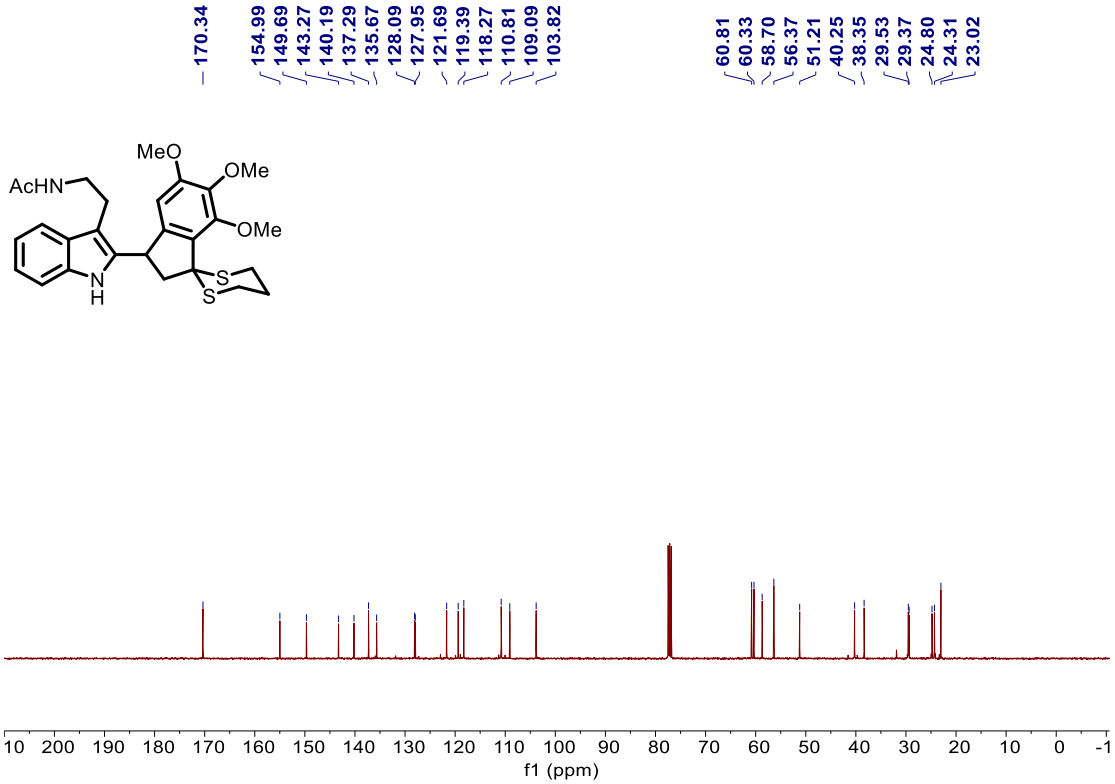
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3f**



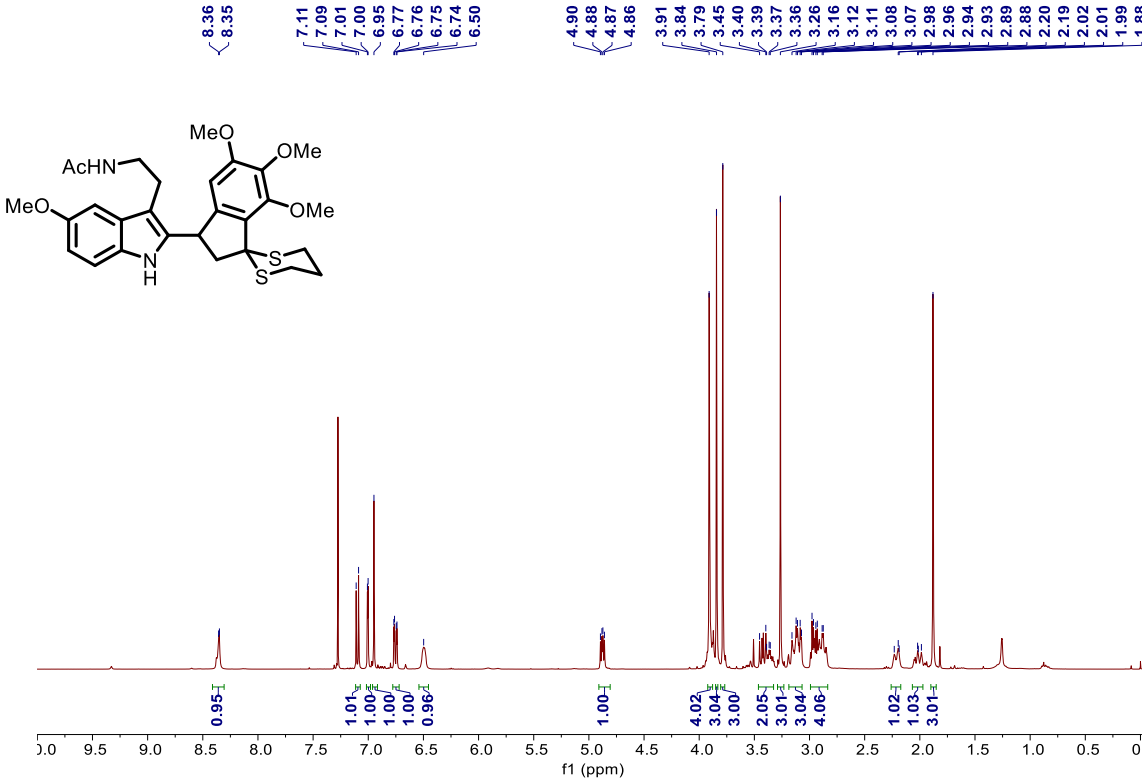
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3g**



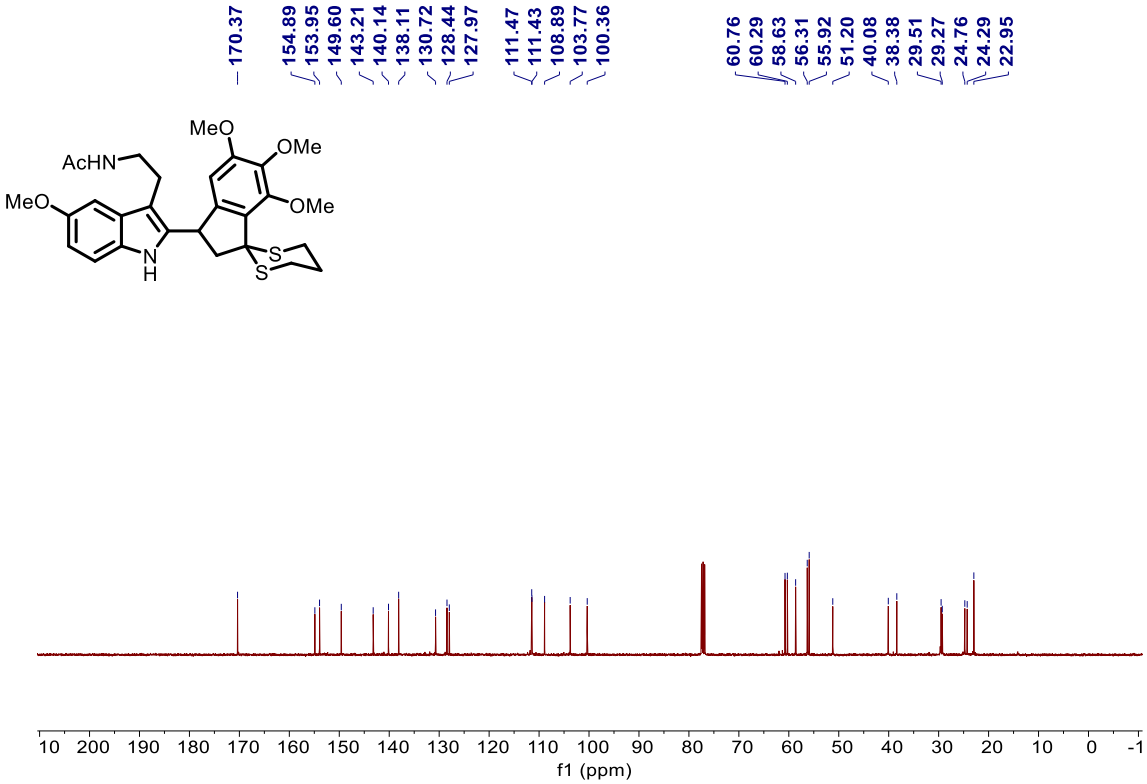
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3g**



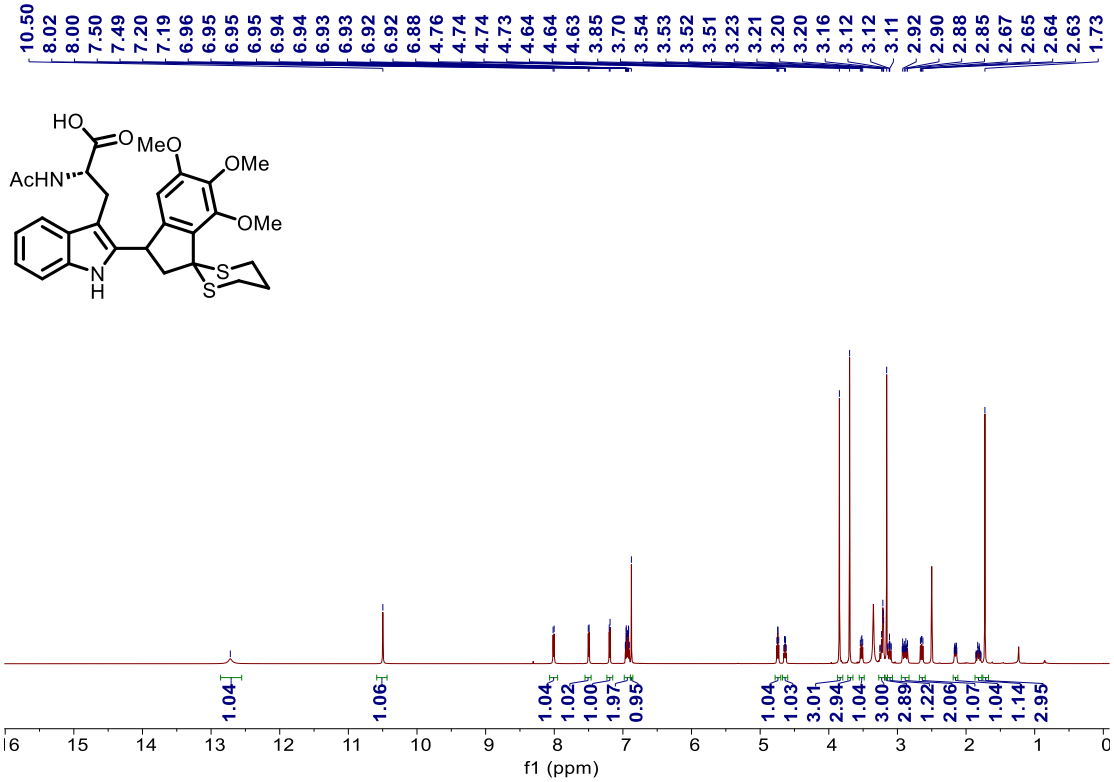
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3h**



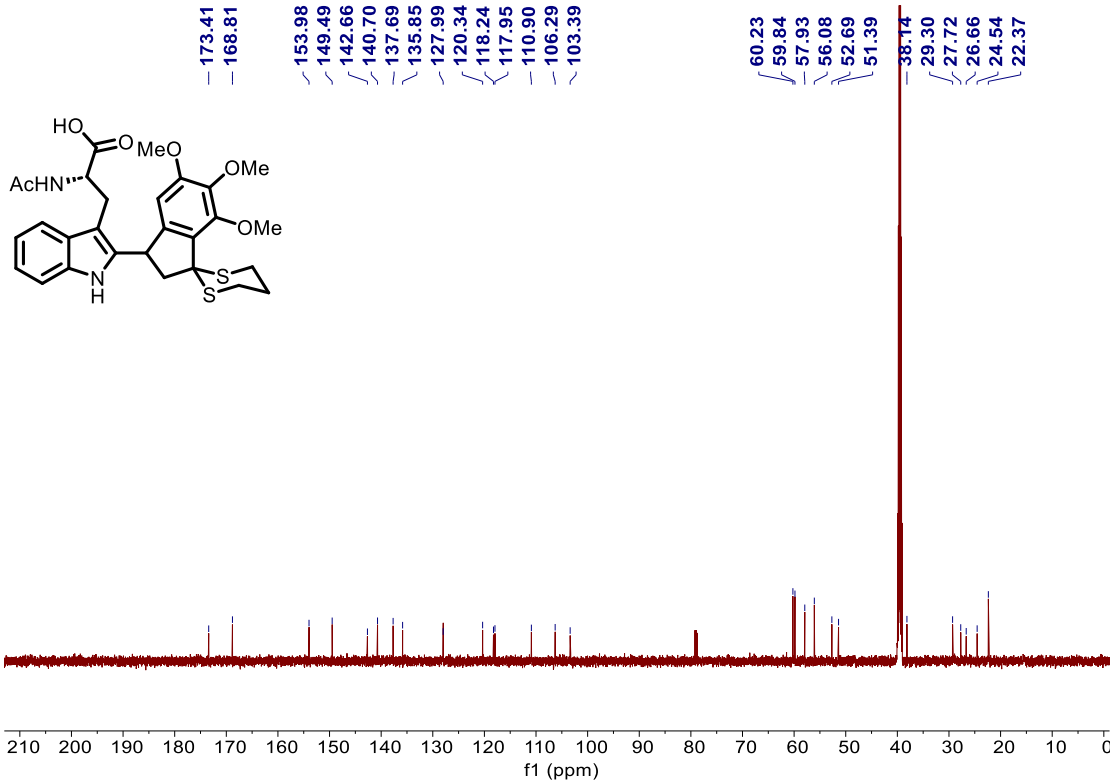
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3h**



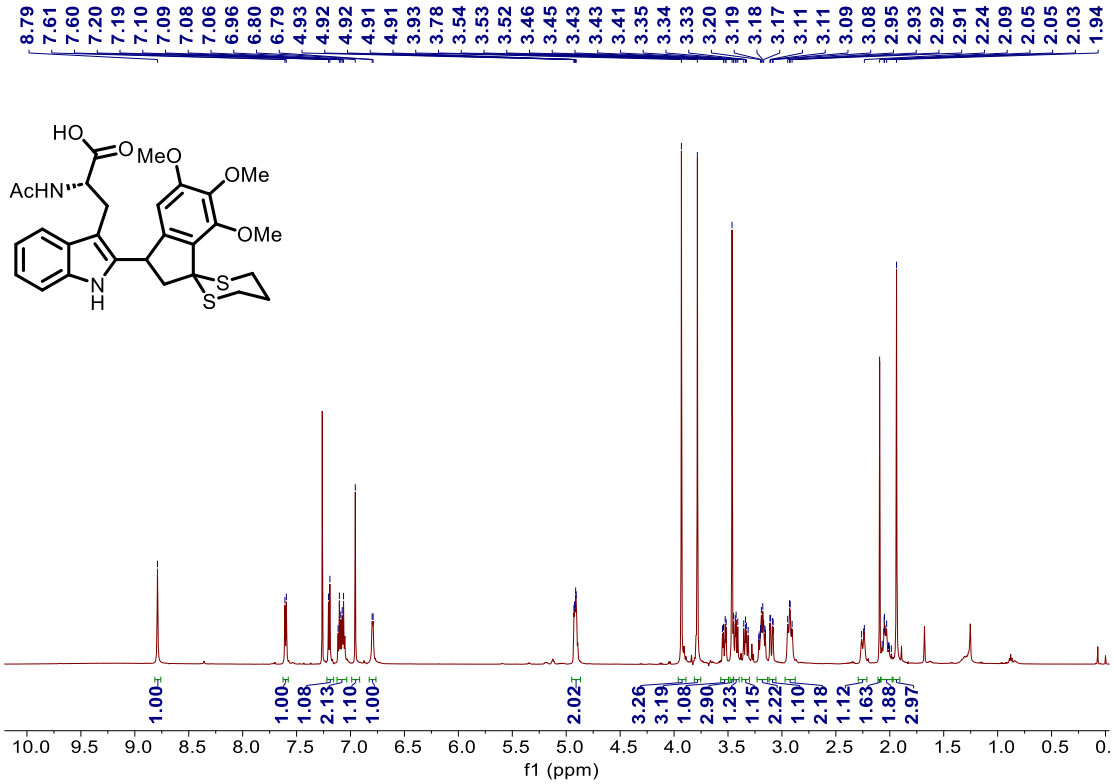
Isomer – 1: ^{1}H NMR (600 MHz, DMSO-d_6) Spectrum of **3i**



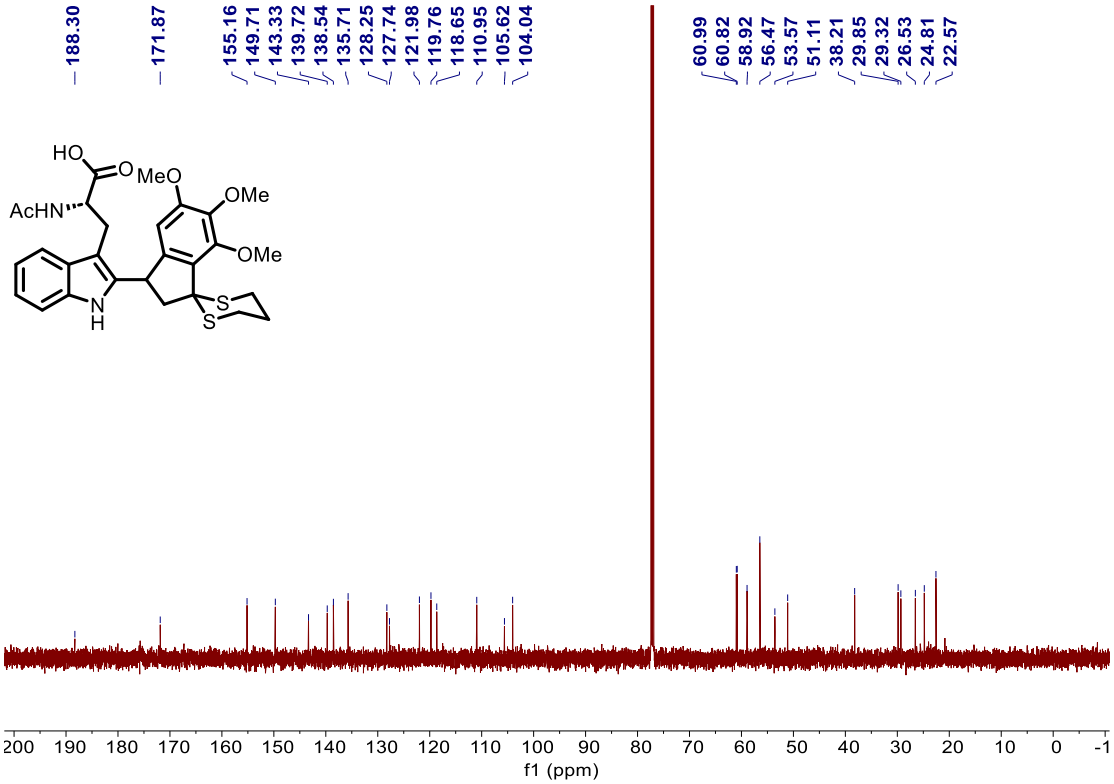
Isomer – 1: ^{13}C NMR (151 MHz, DMSO-d_6) Spectrum of **3i**



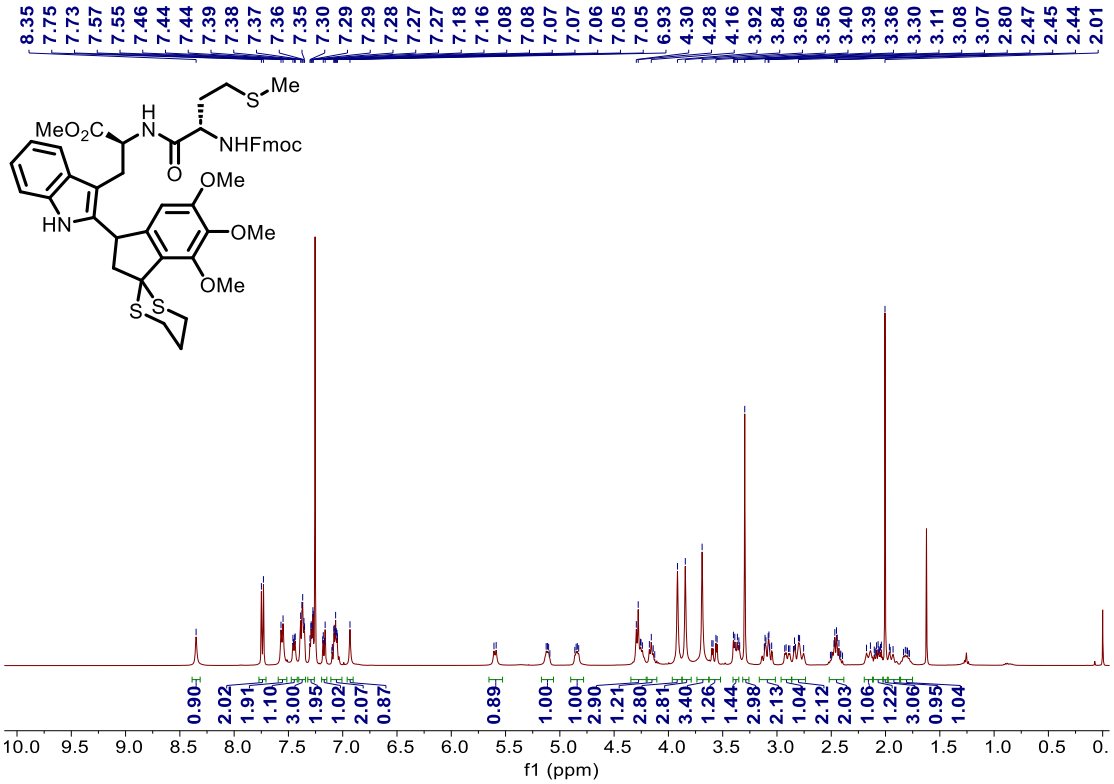
Isomer – 2: ^{1}H NMR (600 MHz, $CDCl_3$)



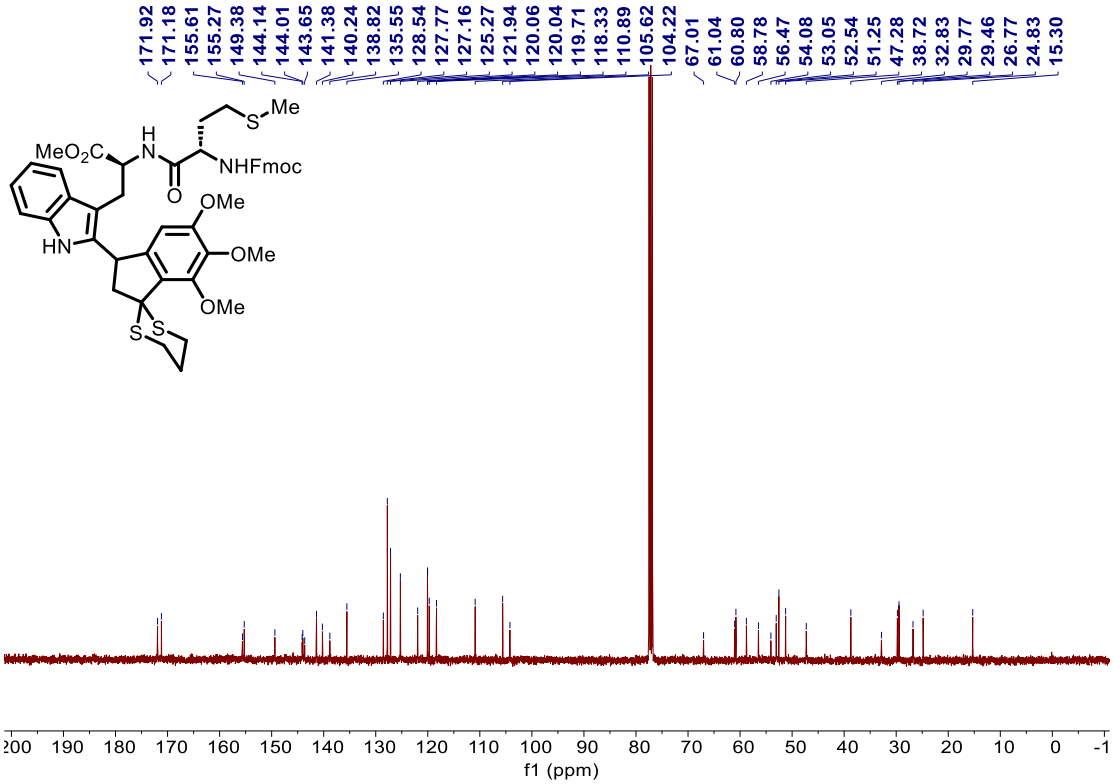
Isomer – 2: ^{13}C NMR (151 MHz, $CDCl_3$)



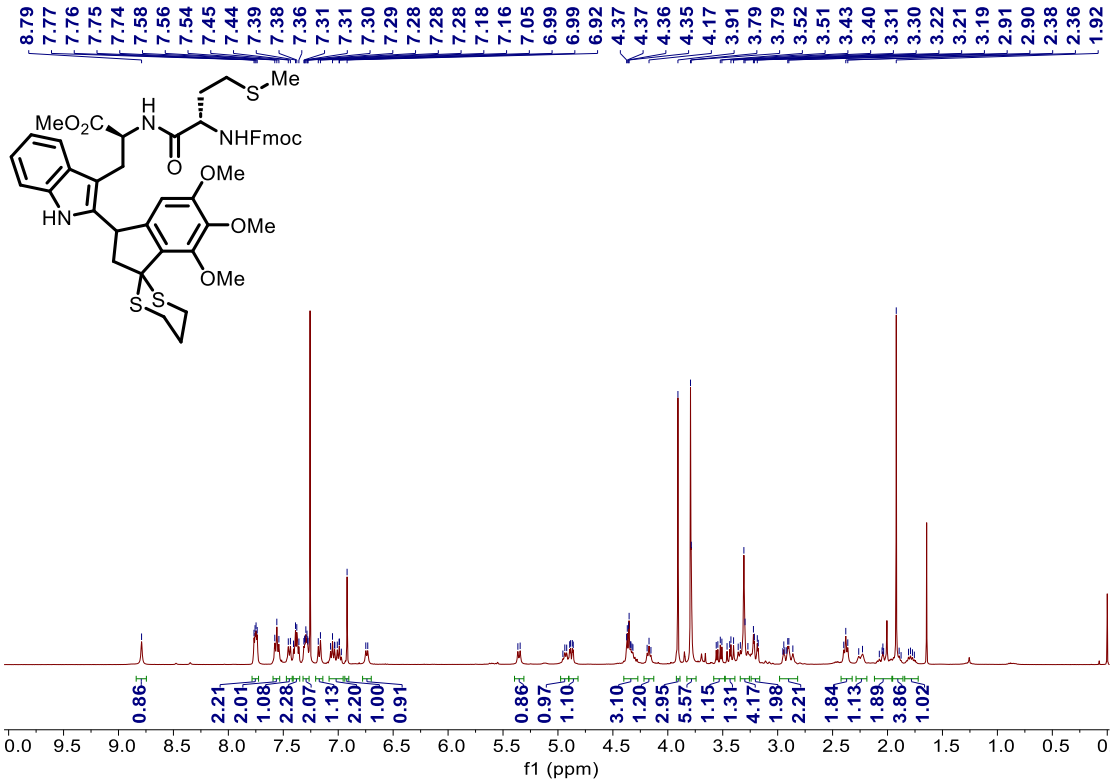
Isomer – 1: ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **3j**



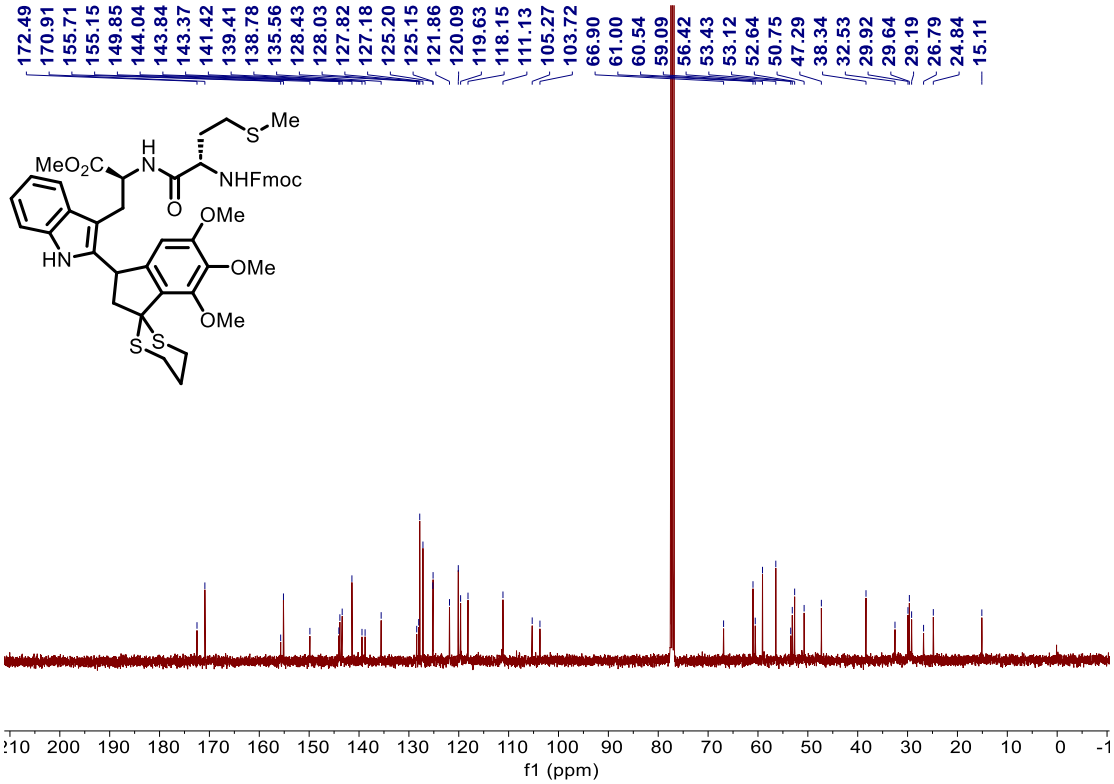
Isomer – 1: ^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **3j**



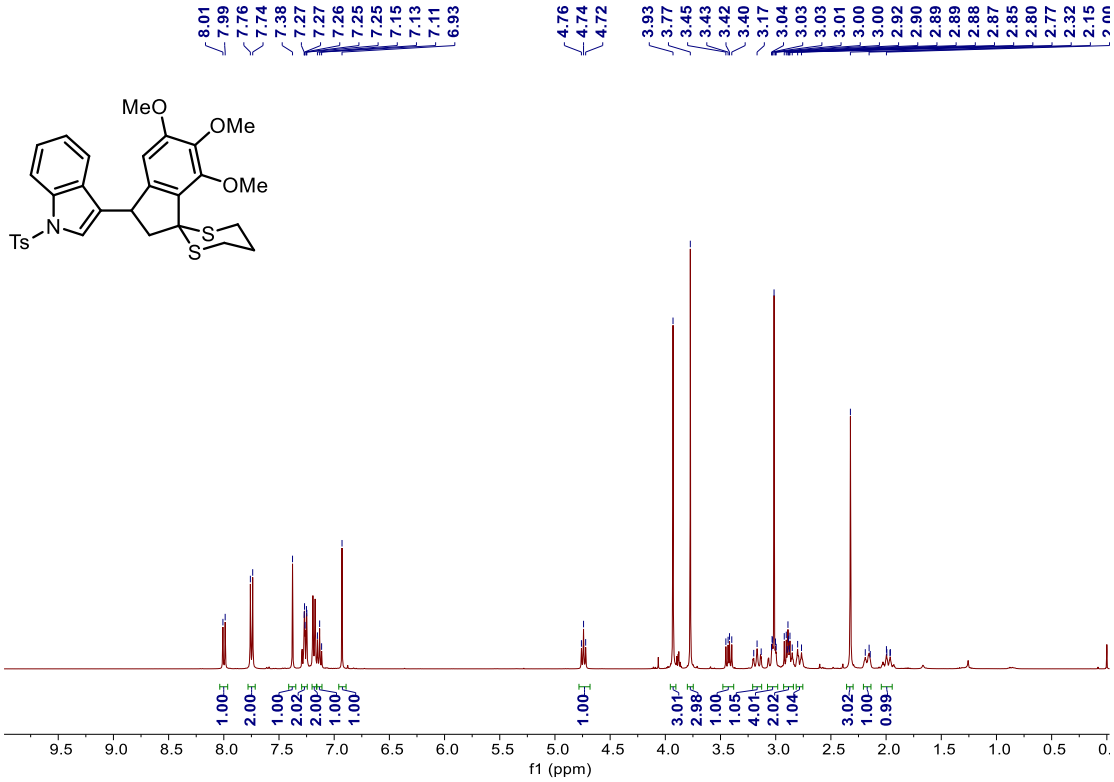
Isomer – 2: ^{1}H NMR (400 MHz, $CDCl_3$)



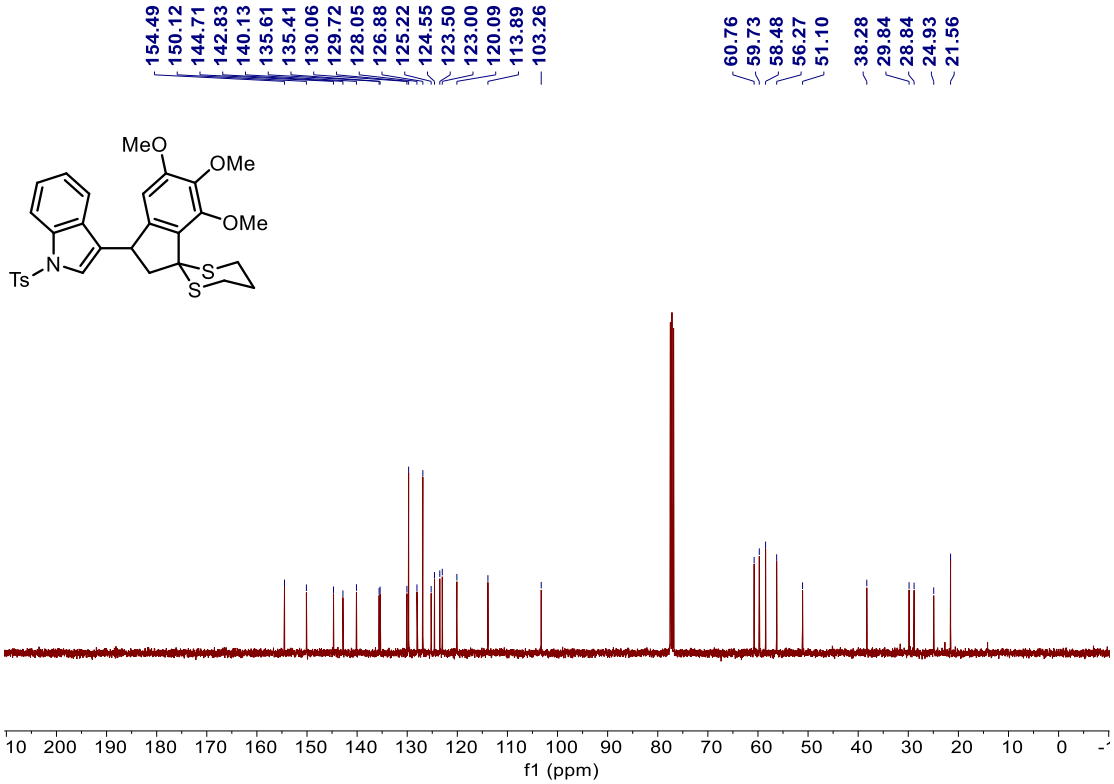
Isomer – 2: ^{13}C NMR (101 MHz, $CDCl_3$)



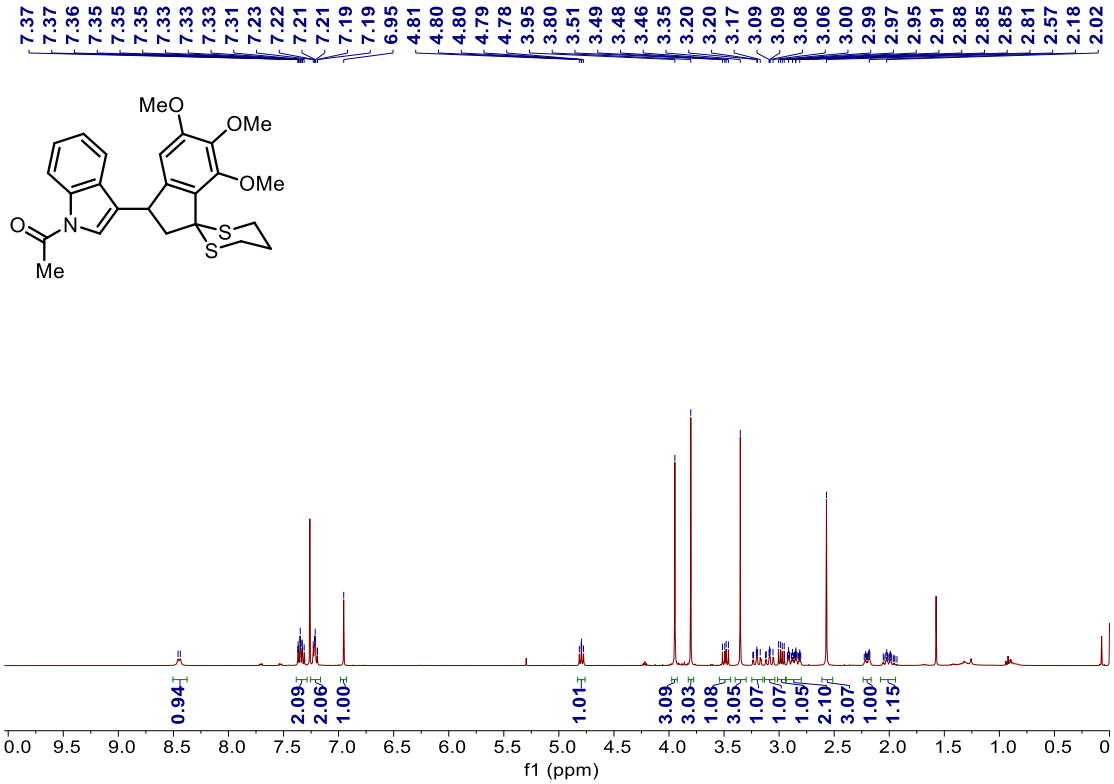
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4a**



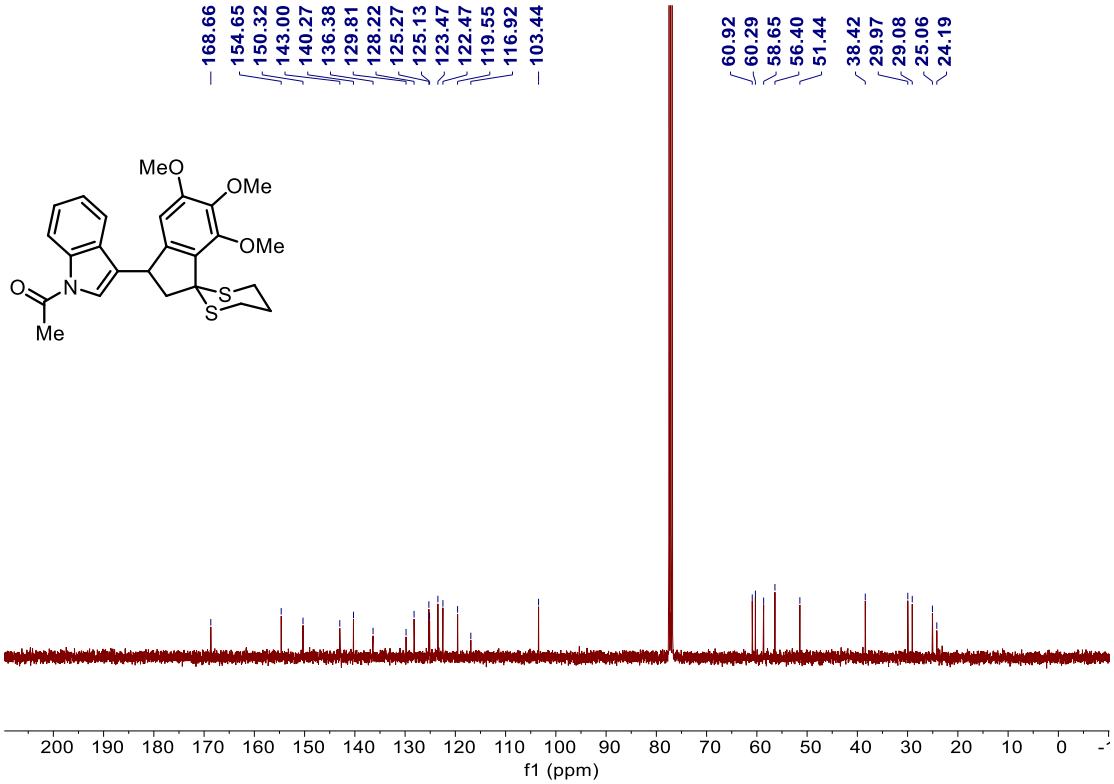
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4a**



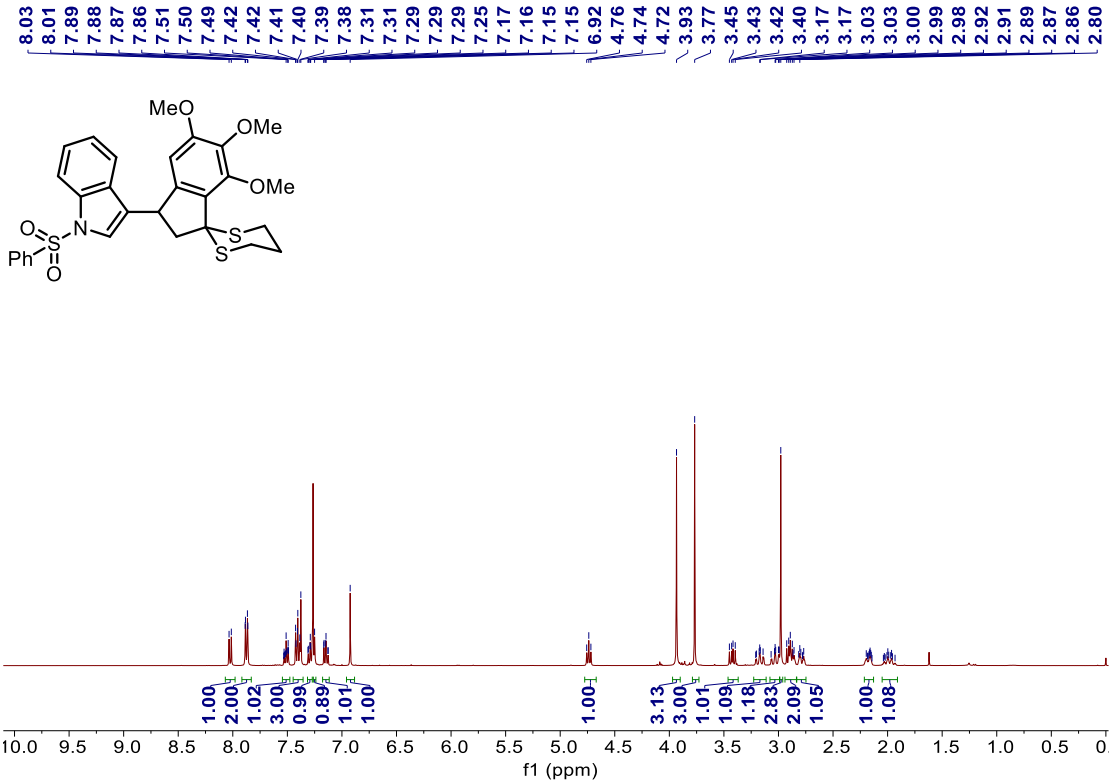
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4b**



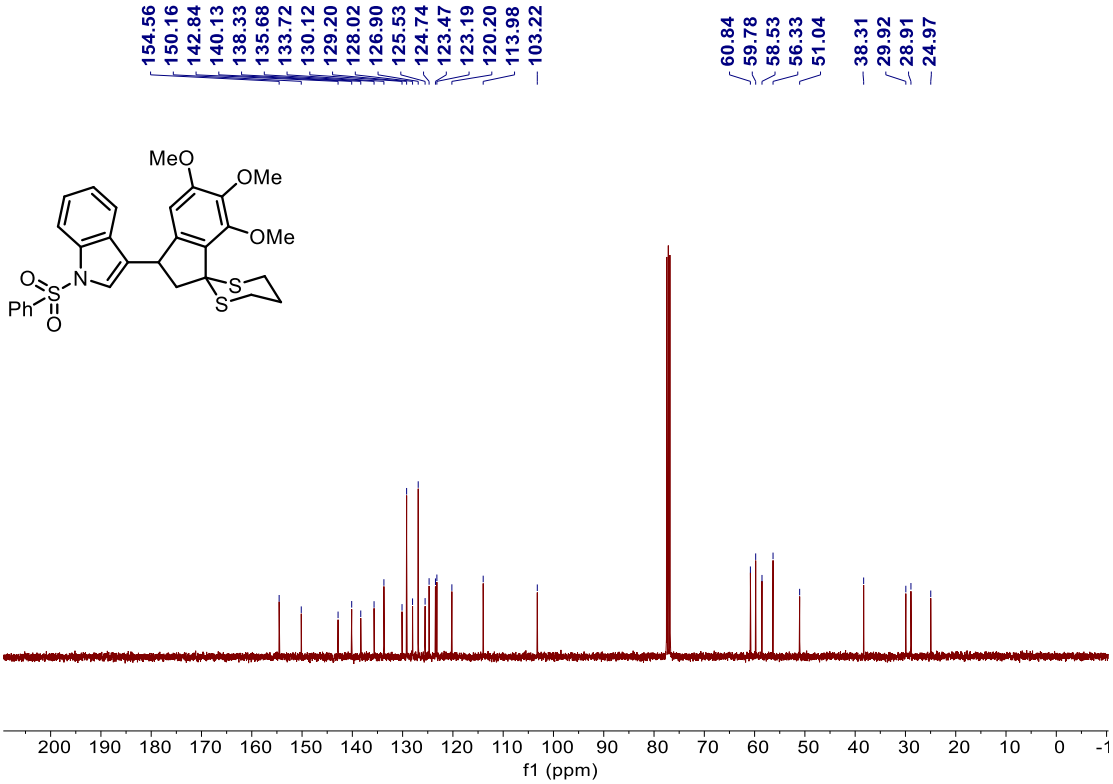
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4b**



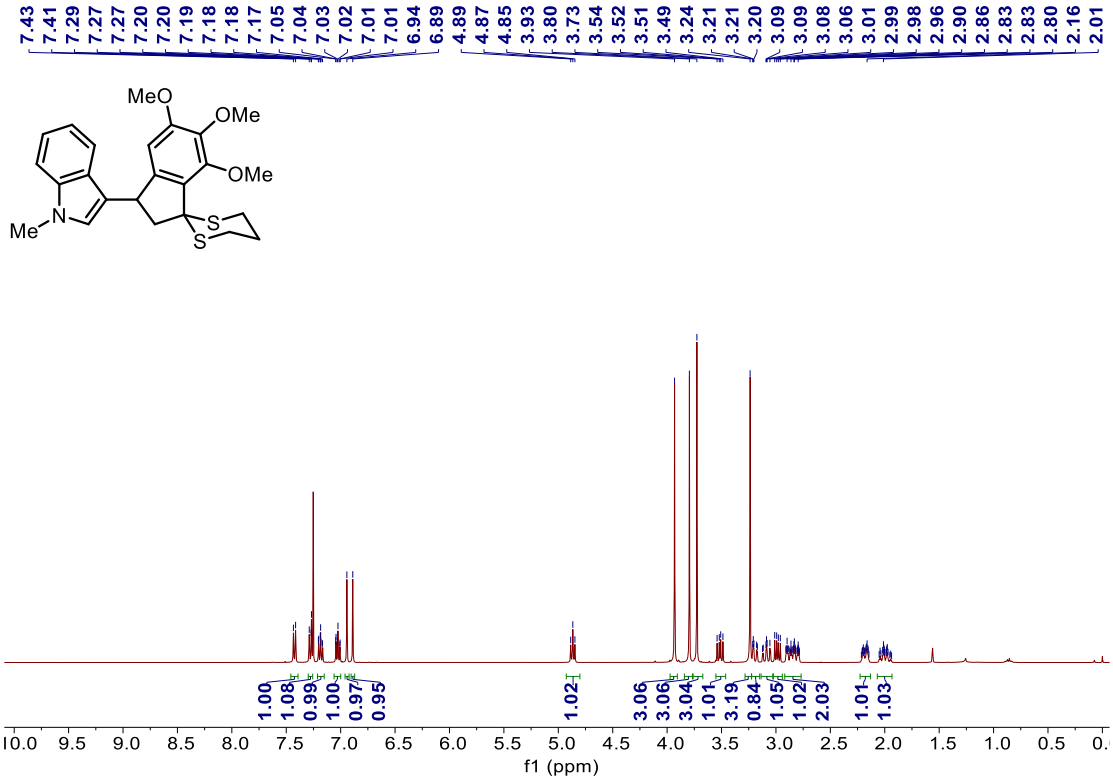
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4c**



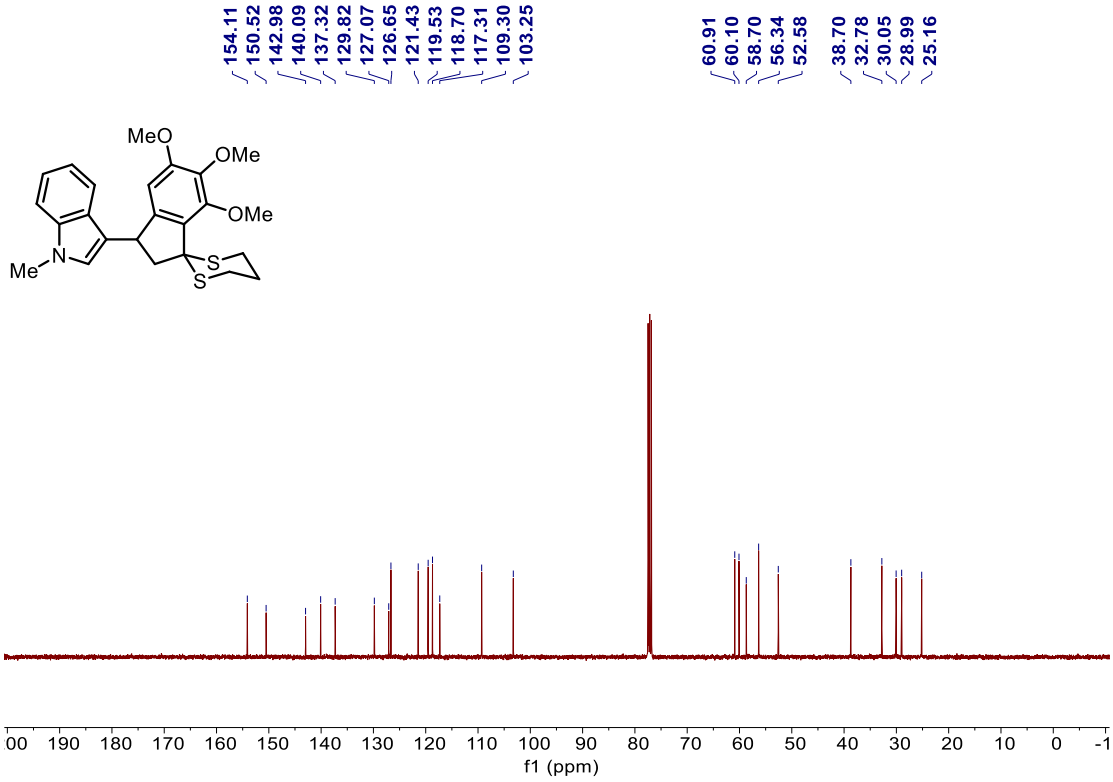
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4c**



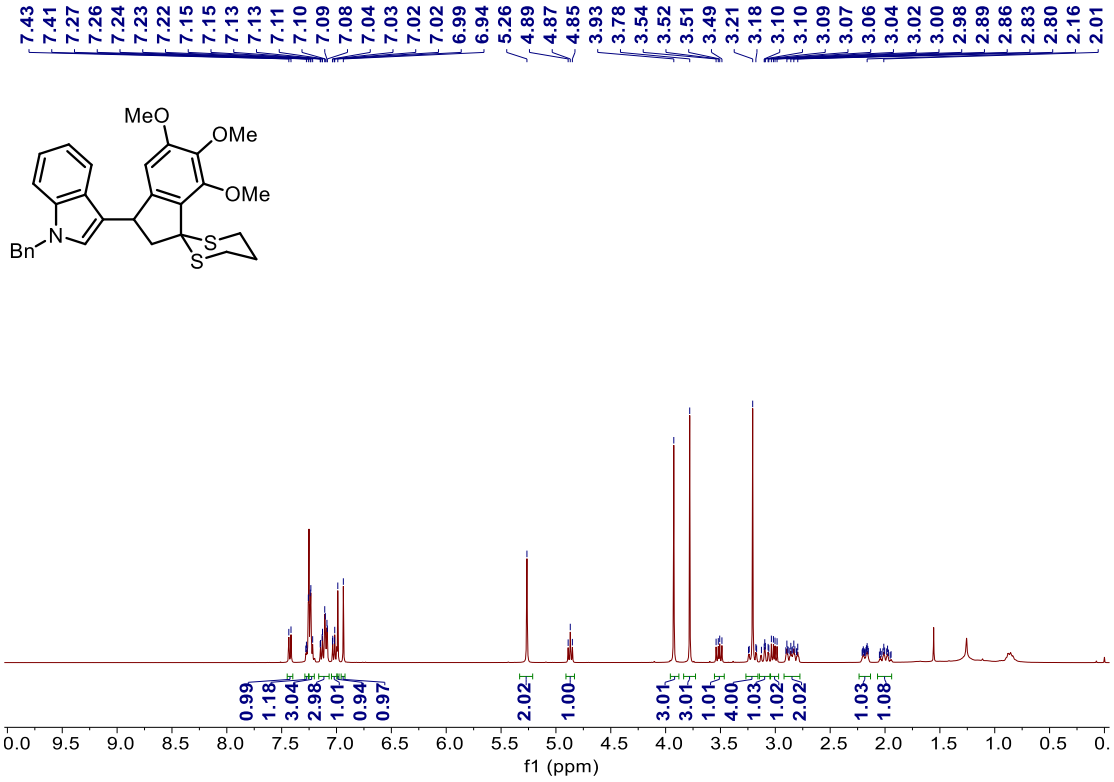
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4d**



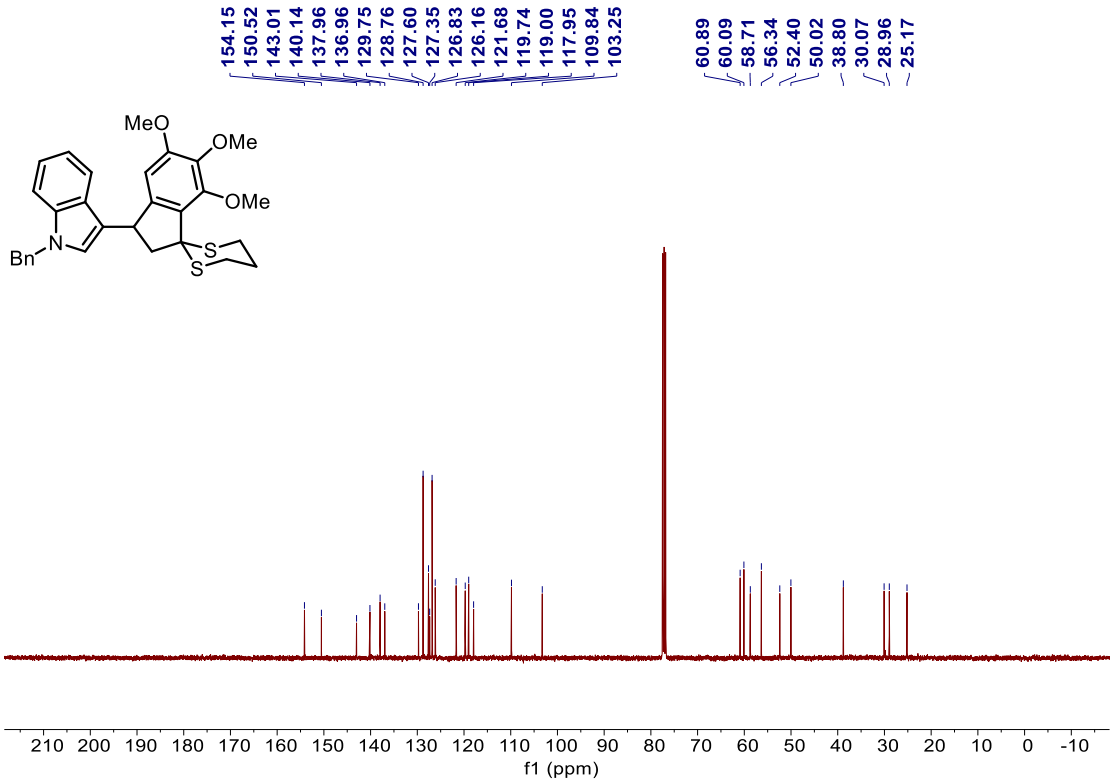
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4d**



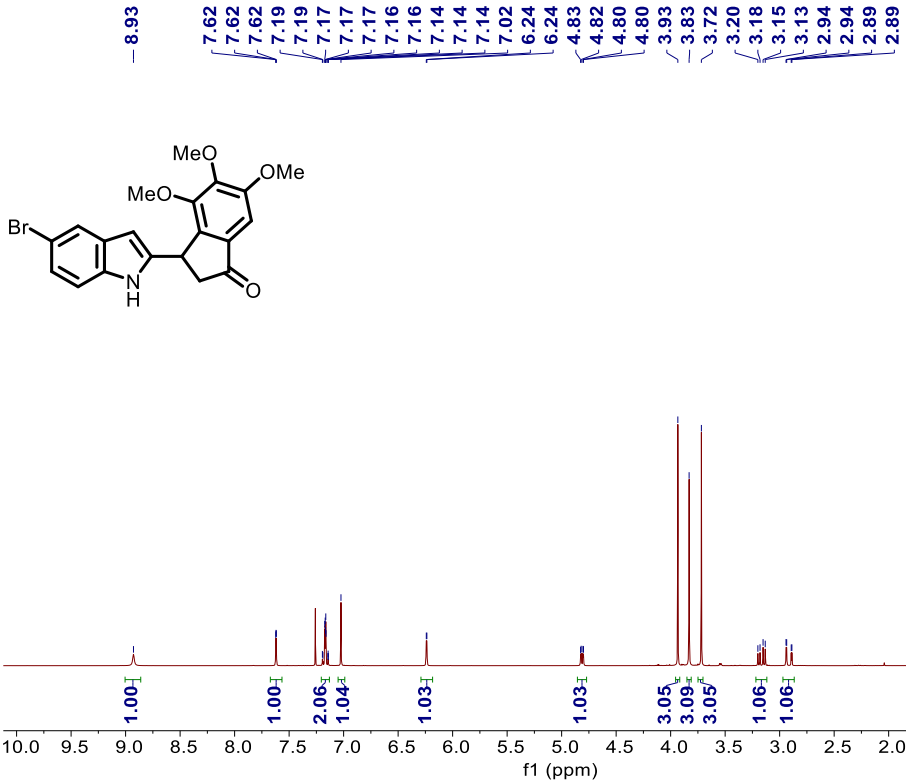
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **4e**



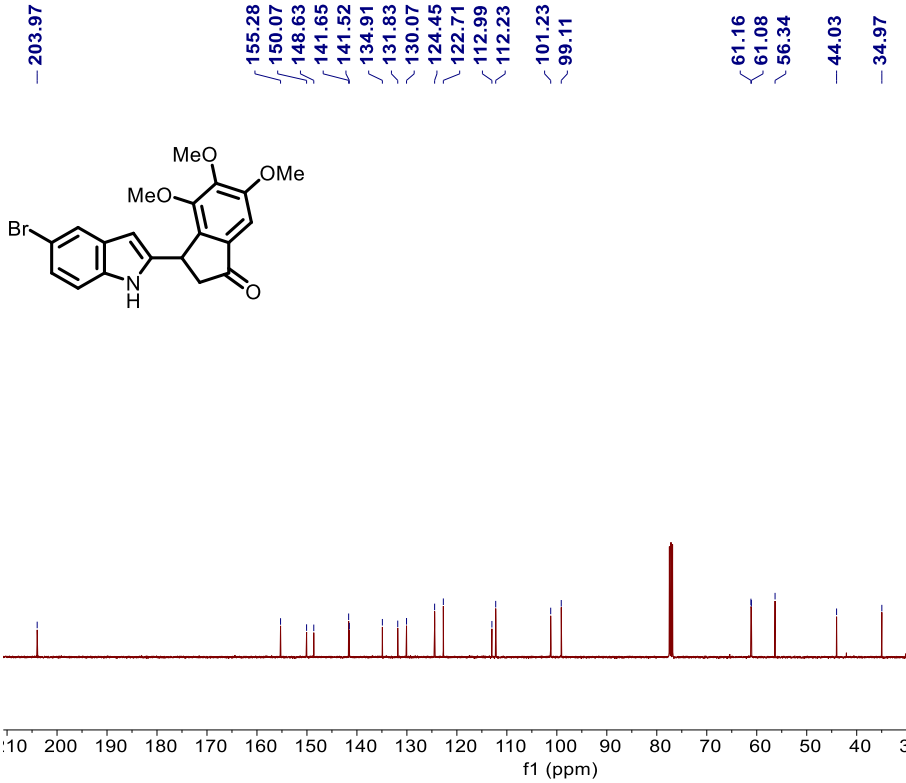
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **4e**



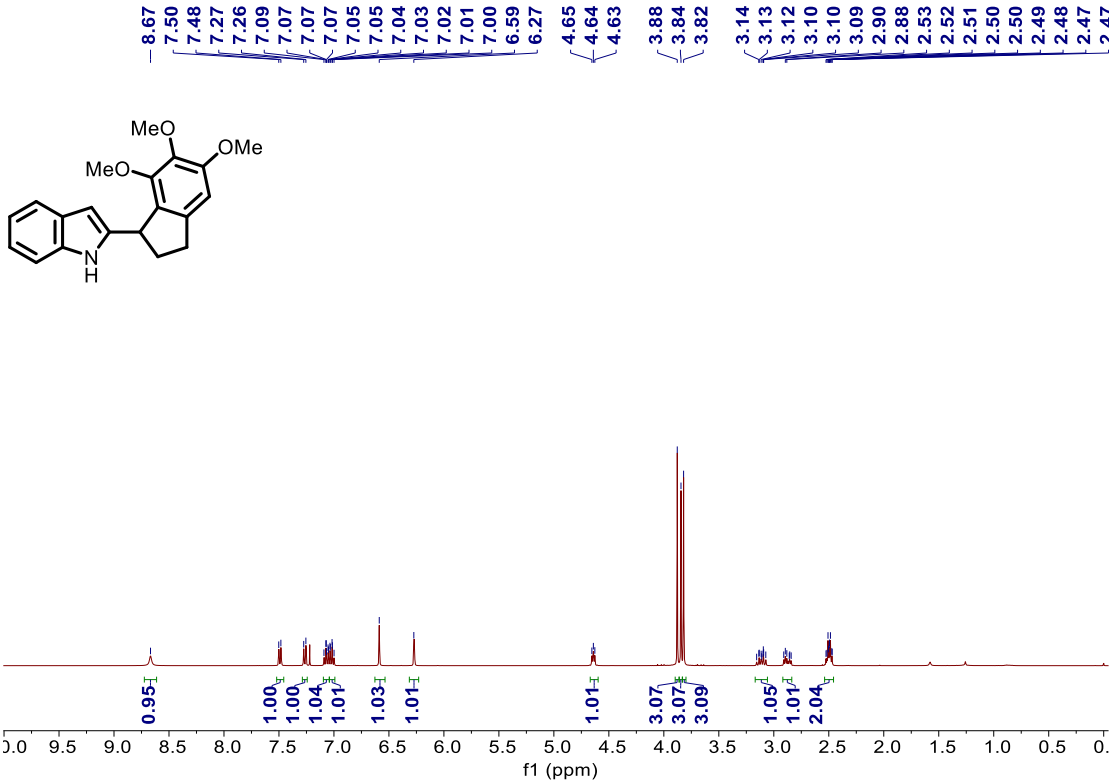
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5b**



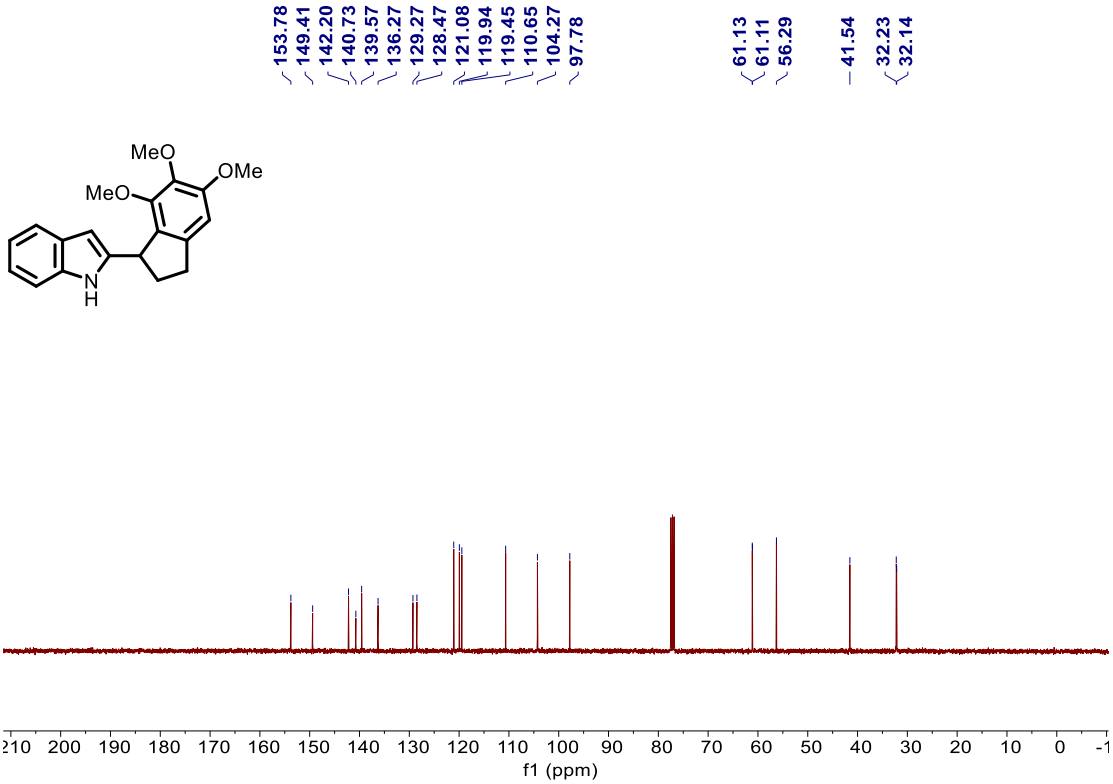
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **5b**



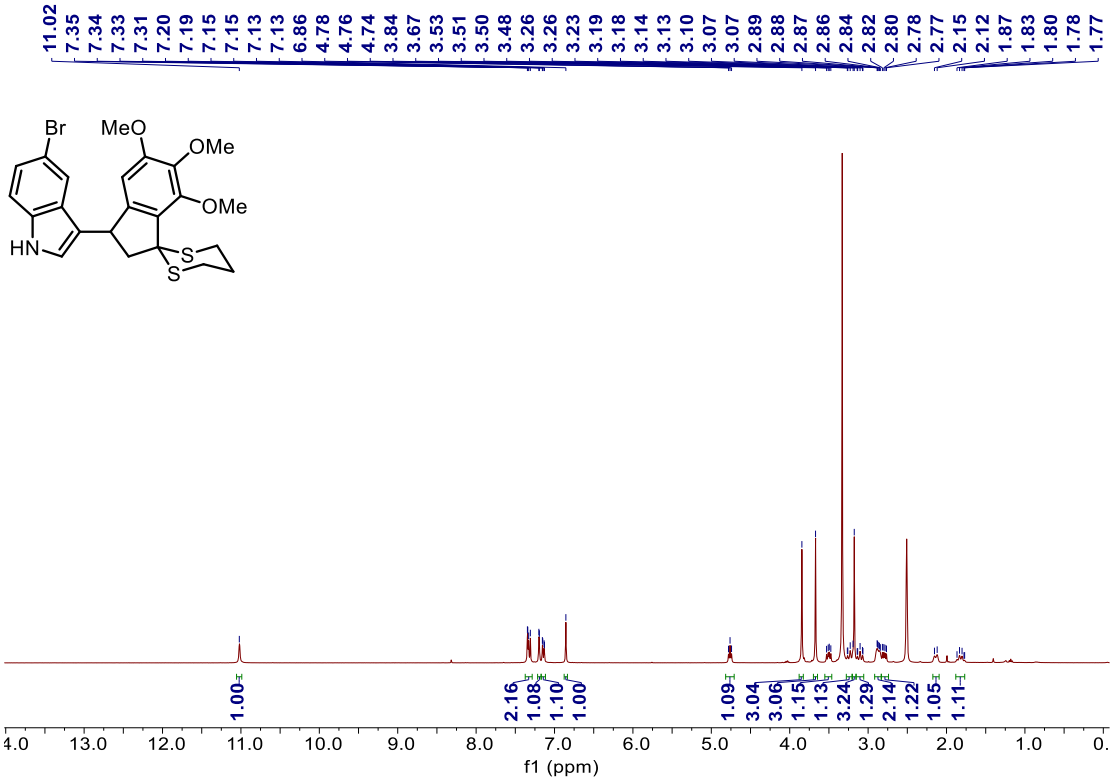
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **5h**



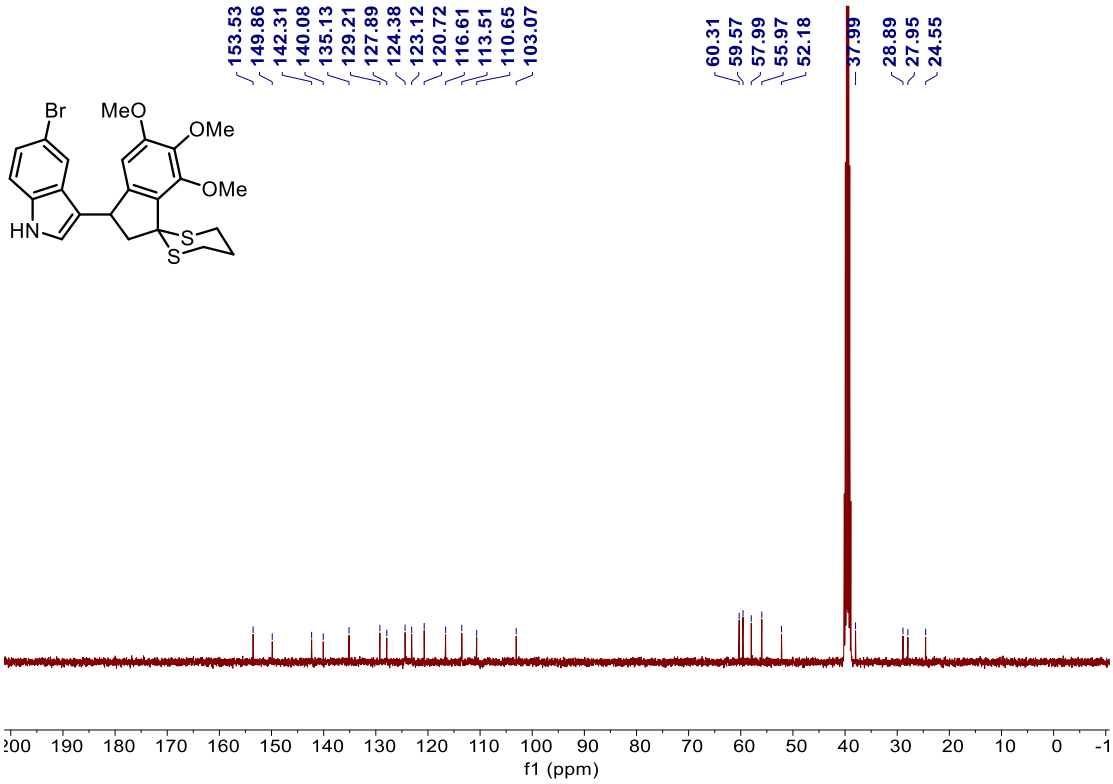
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **5h**



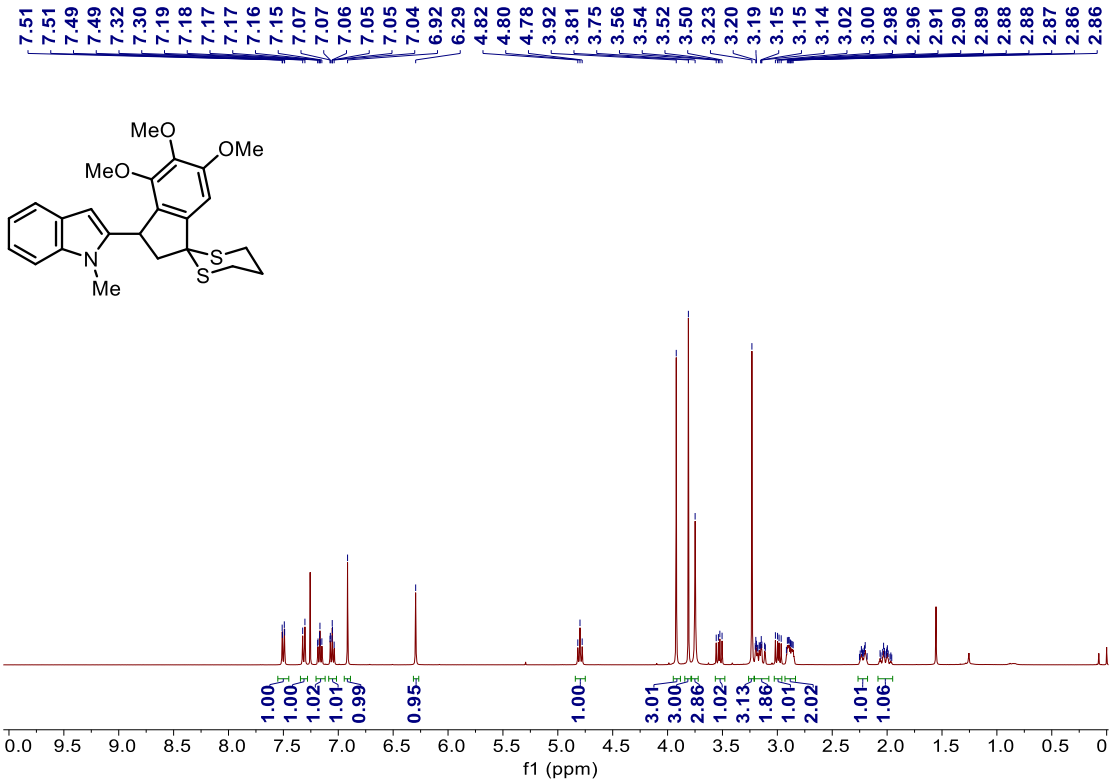
^{1}H NMR (400 MHz, DMSO-*d6*) Spectrum of **4f**



^{13}C NMR (101 MHz, DMSO-*d6*) Spectrum of **4f**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of **2v**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of **2v**