Electronic Supplementary Information (ESI)

Switchable regioselection of C-H thiolation of indoles using different TMS counterions

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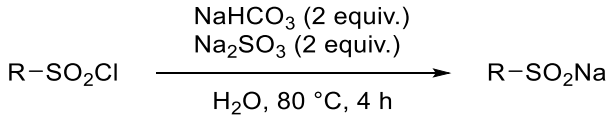
1. General Information

Unless otherwise noted, all reactants or reagents including solvents were obtained from commercial suppliers and used without further purification. TLC plates were visualized by exposure to ultra violet light (UV). High-resolution mass spectra (HRMS) were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained by using a Bruker Avance III 400 MHz NMR or a JNM-ECZ400S/L1 400 MHz NMR spectrometer. Chemical shifts for protons are reported in parts per million (δ scale) and are referenced to residual protium in the NMR solvents [$CDCl_3$: δ 7.26]. Chemical shifts for carbon resonances are reported in parts per million (δ scale) and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant in Hertz (Hz).

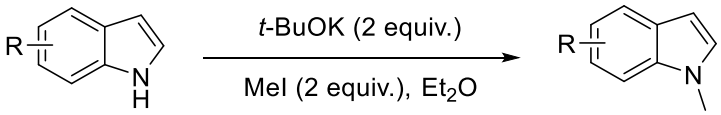
2. General Procedures for the Preparation of Sodium Arylsulfinates 2[1]

Sodium sulfite (20 mmol, 2 equiv), sodium bicarbonate (20 mmol, 2 equiv) and the corresponding R-sulfonyl chloride (10 mmol, 1 equiv) were dissolved in distilled water (10 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling to rt, water was removed by rotary evaporator. Then the remaining solid was extracted and recrystallized by ethanol to get a white solid - the required compound.

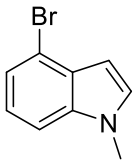


3. General Procedures for the Preparation of *N*-substituted Indoles 1[2,3]

General procedure for the preparation of *N*-methyl indoles. [2] To a stirred solution of the corresponding indole (2 mmol, 1 equiv) in ether (2 mL) was slowly added potassium *tert*-butanolate (4 mmol, 2 equiv) and iodomethane (4 mmol, 2 equiv) at 0 °C, after 24 hours the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with ether (5 mL) three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100–200 mesh, elution 3% ethyl acetate in petroleum ether). The product was identified by NMR and HRMS spectra.

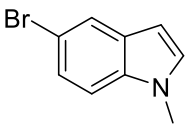


4-Bromo-1-methyl-1*H*-indole (1b)



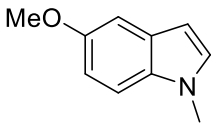
Cyan oil, 303.7 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.15–7.13 (m, 2H), 6.60 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.8, 129.2, 128.9, 122.2, 122.0, 114.6, 108.3, 101.1, 33.0; HRMS (ESI) m/z: Calcd for C_9H_9BrN $[M+H]^+$: 209.9913. Found: 209.9915.

5-Bromo-1-methyl-1*H*-indole (1c)



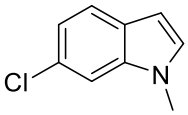
Cyan oil, 332.8 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.2, 130.0, 129.9, 124.1, 123.1, 112.5, 110.5, 100.4, 32.8; HRMS (ESI) m/z: Calcd for C_9H_9BrN $[M+H]^+$:209.9913. Found: 209.9917.

5-Methoxy-1-methyl-1*H*-indole (1d)



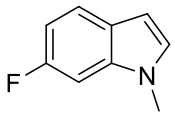
Pale yellow solid; 192.0 mg, 59.6% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.43 (d, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 132.0, 129.2, 128.6, 111.7, 109.8, 102.3, 100.2, 55.7, 32.8; HRMS (ESI) m/z: Calcd for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0913. Found: 162.0911.

6-Chloro-1-methyl-1*H*-indole (1e)



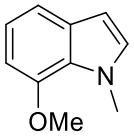
Pale yellow oil, 174.9 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.09 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.47 (dd, *J* = 3.1, 0.6 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9, 129.4, 127.3, 126.8, 121.5, 119.8, 109.1, 101.0, 32.6; HRMS (ESI) m/z: Calcd for C_9H_9ClN $[M+H]^+$: 166.0418. Found: 166.0426.

6-Fluoro-1-methyl-1*H*-indole (1f)



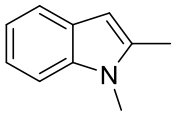
Yellow solid; 134.1 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56–7.52 (m, 1H), 7.04–6.99 (m, 2H), 6.92–6.86 (m, 1H), 6.48 (t, *J* = 2.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7 (d, $J_{C\text{-}F}$ = 237.1 Hz), 136.6 (d, $J_{C\text{-}F}$ = 12.0 Hz), 129.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 124.8, 121.4 (d, $J_{C\text{-}F}$ = 10.1 Hz), 107.9 (d, $J_{C\text{-}F}$ = 24.5 Hz), 100.9, 95.5 (d, $J_{C\text{-}F}$ = 26.2 Hz), 32.6; HRMS (ESI) m/z: Calcd for C_9H_9FN $[M+H]^+$: 150.0714. Found: 150.0721.

7-Methoxy-1-methyl-1*H*-indole (1g)



Cyan solid; 289.8 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 3.1 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 4.09 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 130.8, 129.7, 119.7, 113.7, 102.1, 100.9, 55.3, 36.5; HRMS (ESI) m/z: Calcd for $C_{10}H_{12}NO$ $[M+H]^+$: 162.0913. Found: 162.0917.

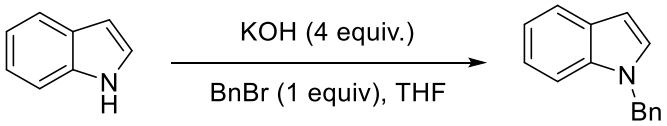
1,2-Dimethyl-1*H*-indole (1h)



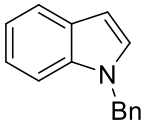
Red solid; 173.4 mg, 59.8% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), 3.68 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 136.6, 127.8, 120.3, 119.5, 119.1, 108.6, 99.4, 29.1, 12.6; HRMS (ESI) m/z: Calcd for $C_{10}H_{12}N$ $[M+H]^+$: 146.0964. Found: 146.0972.

General procedure for the preparation of *N*-benzyl indole.[2] To a stirred solution of 1*H*-indole (2 mmol) in THF (2 mL) was slowly added potassium hydroxide (8 mmol) and benzyl bromide (2 mmol) at 0 °C. After 24 hours, the mixture was poured into saturated aqueous $NaHCO_3$ solution (5 mL) and

extracted with ether (5 mL) three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100–200 mesh, elution 5% ethyl acetate in petroleum ether). The product was identified by NMR and HRMS spectra.

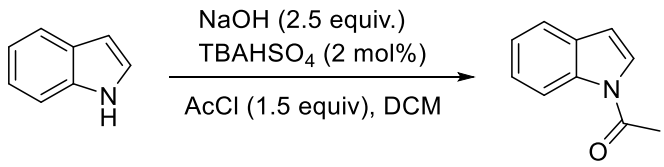


1-Benzyl-1*H*-indole (1i)

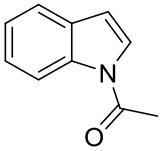


Cyan solid; 393.2 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.8 Hz, 1H), 7.34–7.28 (m, 4H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.16–7.13 (m, 4H), 6.59 (d, *J* = 3.0 Hz, 1H), 5.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 136.2, 128.6, 128.2, 127.5, 126.7, 121.6, 120.9, 119.4, 109.6, 101.6, 49.9; HRMS (ESI) m/z: Calcd for $C_{15}H_{14}N$ $[M+H]^+$: 208.1121. Found: 208.1128.

General procedure for the preparation of 1-(1*H*-Indol-1-yl)ethan-1-one.[3] To a flask charged with indole (2 mmol), sodium hydroxide (5 mmol), and tetrabutylammonium hydrogensulfate (0.04 mmol) was added DCM (5 mL). A solution of acetyl chloride (3 mmol) in DCM (3 mL) was then added dropwise. The reaction mixture was stirred at room temperature for 16 h, filtered through a plug of silica and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100–200 mesh, elution 6% ethyl acetate in petroleum ether). The product was identified by NMR and HRMS spectra.



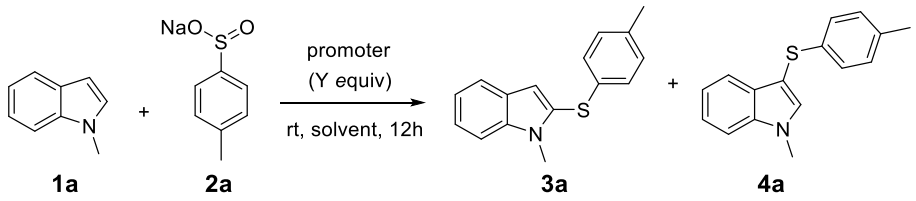
1-(1*H*-Indol-1-yl)ethan-1-one (1j)



Colorless oil; 270.3 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 3.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 3.7 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 135.4, 130.3, 125.1, 125.0, 123.5, 120.7, 116.4, 109.0, 23.8; HRMS (ESI) m/z: Calcd for $C_{10}H_{10}NO$ $[M+H]^+$: 160.0557. Found: 160.0563.

4. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions of **3a**[a]



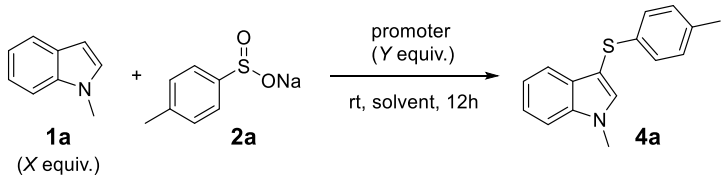
1a **2a** **3a** **4a**

Entry	Promoter (*Y* equiv)	Solvent	Yield (%)[b]	
			3a	**4a**
1[c]	TMSOTf (4.0)	CH_2Cl_2	23	N.D.
2[d]	TMSOTf (4.0)	CH_2Cl_2	N.D.	N.D.
3[e]	TMSOTf (4.0)	CH_2Cl_2	70	N.D.
4[f]	**TMSOTf (4.0)**	**CH_2Cl_2**	**80 (78[h])**	**N.D.**
5[g]	TMSOTf (4.0)	CH_2Cl_2	80	N.D.
6[f]	TfOH (4.0)	CH_2Cl_2	60	N.D.
7[f]	TMSCl (4.0)	CH_2Cl_2	N.D.	83
8[f]	$TMSCF_3$ (4.0)	CH_2Cl_2	N.R.	N.R.
9[f]	BF_3•Et_2O (4.0)	CH_2Cl_2	N.D.	N.D.
10[f]	*p*-TsOH (4.0)	CH_2Cl_2	N.D.	28
11[f]	TMSOTf (4.0)	$(ClCH_2)_2$	76	N.D.
12[f]	TMSOTf (4.0)	$MeNO_2$	67	N.D.
13[f]	TMSOTf (4.0)	MeCN	50	N.D.
14[f]	TMSOTf (4.0)	THF	N.D.	30
15[f]	TMSOTf (4.0)	1,4-dioxane	N.D.	30
16[f]	TMSOTf (1.0)	CH_2Cl_2	N.D.	N.D.
17[f]	TMSOTf (2.0)	CH_2Cl_2	N.D.	N.D.
18[f]	TMSOTf (2.5)	CH_2Cl_2	26	N.D.
19[f]	TMSOTf (3.0)	CH_2Cl_2	55	N.D.
20[f]	TMSOTf (3.5)	CH_2Cl_2	64	N.D.
21[f]	TMSOTf (4.5)	CH_2Cl_2	80	N.D.
22[f,h,i]	TMSOTf (4.0)	CH_2Cl_2	68	N.D.

[a] General conditions: **1a** (0.2–0.6 mmol), **2a** (0.2 mmol), and promoter (0.2–0.8 mmol) in solvent (1.0 mL) at 25 °C for 12 h. [b] The yield was determined by ^{1}H NMR spectroscopy using 0.2 mmol of CH_2Br_2 as a standard. [c] 0.3 mmol of **1a**. [d] 0.2 mmol of **1a**. [e] 0.4 mmol of **1a**. [f] 0.5 mmol of **1a**. [g] 0.6 mmol of **1a**. [h] Isolated yield. [i] Reaction was carried out at 10.7 g scale of **2a** (60.0 mmol). N.D. = no detection. N.R. = no reaction.

The reaction of 1-methyl-1*H*-indole (**1a**) with sodium 4-methylbenzenesulfinate (**2a**) was used as a probe for evaluating the reaction conditions, and the representative results are summarized in Table S1. Reaction of 1-methyl-1*H*-indole (**1a**) with sodium 4-methylbenzenesulfinate (**2a**) in the presence of TMSOTf (4.0 equiv) at room temperature (25 °C) for 12 h afforded 1-methyl-2-(*p*-tolylthio)-1*H*-indole (**3a**) in 23% yield (entry 1). The yield of **3a** was further increased up to 80% when the loading of indole **1a** was increased from 1.0 equivalent to 2.5 equivalents (entries 1–4). No further increase was observed when the loading of indole **2a** exceeded 2.5 equivalents (entries 4–5). A series of other promoters such as TfOH, TMSCl, $TMSCF_3$, BF_3•Et_2O and *p*-TsOH were further investigated for this reaction, but no better results were obtained in comparison to that with the use of TMSOTf as the promoter (entries 4 and 6–10). To our surprised, another product C3-thioindole **4a** was also gained in 83% and 28% yields in the presence of TMSCl and *p*-TsOH, respectively. (entries 7 and 10). The solvent played an important role in this reaction. With the use of $(ClCH_2)_2$, $MeNO_2$, MeCN, THF and 1,4-dioxane in comparison to CH_2Cl_2, lower yields of **3a** were observed (entries 4 and 11–15). Further parameters optimization of **3a** identified the most effective TMSOTf loading as 4.0 equivalents (entries 4 and 16–21). Furthermore, scaling up sodium 4-methylbenzenesulfinate (**2a**) to 10.7 g (60.0 mmol) the reaction provided the yield of **3a** at an excellent level (entry 22).

Table S2. Optimization of the reaction conditions of **4a**[a]



Entry	*X*	Promoter (*Y* equiv)	Solvent	**4a** Yield (%)[b]
1	**2.5**	**TMSCl (*Y* = 4.0)**	**CH_2Cl_2**	**83 (80[c])**
2	2.5	Me_2SiHCl (*Y* = 4.0)	CH_2Cl_2	75
3	2.5	Et_3SiH (*Y* = 4.0)	CH_2Cl_2	N.R.
4	2.5	Ph_3SiH (*Y* = 4.0)	CH_2Cl_2	N.R.
5	2.5	$TMSCF_3$ (*Y* = 4.0)	CH_2Cl_2	N.R.
6	2.5	TMSCl (*Y* = 4.0)	$(ClCH_2)_2$	62
7	2.5	TMSCl (*Y* = 4.0)	$MeNO_2$	73
8	2.5	TMSCl (*Y* = 4.0)	MeCN	71
9	2.5	TMSCl (*Y* = 4.0)	THF	51
10	2.5	TMSCl (*Y* = 4.0)	$CHCl_3$	62
11	2.5	TMSCl (*Y* = 4.0)	1,4-dioxane	15
12	2.5	TMSCl (*Y* = 4.0)	toluene	29
13	2.5	TMSCl (*Y* = 1.0)	CH_2Cl_2	N.D.
14	2.5	TMSCl (*Y* = 2.0)	CH_2Cl_2	63
15	2.5	TMSCl (*Y* = 2.5)	CH_2Cl_2	73
16	2.5	TMSCl (*Y* = 3.0)	CH_2Cl_2	76
17	2.5	TMSCl (*Y* = 3.5)	CH_2Cl_2	78
18	2.5	TMSCl (*Y* = 4.5)	CH_2Cl_2	83
19	1.0	TMSCl (*Y* = 4.0)	CH_2Cl_2	42
20	1.2	TMSCl (*Y* = 4.0)	CH_2Cl_2	45
21	1.5	TMSCl (*Y* = 4.0)	CH_2Cl_2	58
22	2.0	TMSCl (*Y* = 4.0)	CH_2Cl_2	76
23	3.0	TMSCl (*Y* = 4.0)	CH_2Cl_2	83
24[c,d]	2.5	TMSCl (*Y* = 4.0)	CH_2Cl_2	71

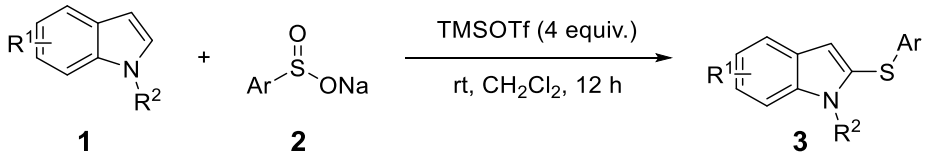
[a] General conditions: **1a** (0.2–0.6 mmol), **2a** (0.2 mmol), and promoter (0.2–2 mmol) in solvent (1.0 mL) at 25 °C for 12 h. [b] The yield of **4a** was determined by ^{1}H NMR spectroscopy using 0.2 mmol of CH_2Br_2 as a standard. [c] Isolated yield. [d] Reaction was carried out at 10.7 g scale of **2a** (60.0 mmol). N.R. = no reaction. N.D. = no detection.

The reaction of 1-methyl-1*H*-indole (**1a**) with sodium 4-methylbenzenesulfinate (**2a**) was used as a probe for evaluating the reaction conditions, and the representative results are summarized in Table S2. Reaction of 1-methyl-1*H*-indole (**1a**) with sodium 4-methylbenzenesulfinate (**2a**) in the presence of TMSCl (4.0 equiv) at room temperature (25 °C) for 12 h

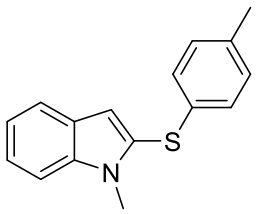
afforded 1-methyl-3-(*p*-tolylthio)-1*H*-indole (**4a**) in 83% yield (entry 1). A series of other promoters such as Me_2SiHCl, Et_3SiH, Ph_3SiH and $TMSCF_3$ were further investigated for this reaction, but no better results were obtained in comparison to that with the use of TMSCl as the promoter (entries 1–5). The solvent played an important role in this reaction. With the use of $(ClCH_2)_2$, $MeNO_2$, MeCN, THF, $CHCl_3$, 1,4-dioxane and toluene in comparison to CH_2Cl_2, lower yields of **4a** were observed (entries 1 and 6–12). Further parameters optimization of **4a** identified the most effective TMSCl loading as 4.0 equivalents (entries 1 and 13–18). The yield of **4a** was further increased up to 83% when the loading of indole **1a** was increased from 1.0 equivalent to 2.5 equivalents (entries 19–22). No further increase was observed when the loading of indole **2a** exceeded 2.5 equivalents (entries 22–23). Furthermore, scaling up sodium 4-methylbenzenesulfinate (**2a**) to 10.7 g (60.0 mmol) the reaction provided the yield of **4a** at an excellent level (entry 24)

5. General Procedures for the Preparation of C2-Thioindoles 3

The mixture of a sodium arylsulfinate (0.2 mmol, 1 equiv), an indole (0.5 mmol, 2.5 equiv) and TMSOTf (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the desired C2-thioindoles **3.** In addition, disubstituted products **5** were also gained for some examples.

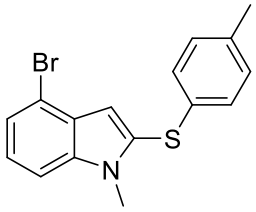


1-Methyl-2-(*p*-tolylthio)-1*H*-indole (3a)



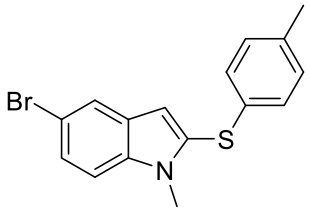
White solid, m.p. = 50–52 °C; 39.5 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* =7.9 Hz, 1H), 7.38–7.33 (m, 2H), 7.24–7.20 (m, 1H), 7.10 (d, *J* =8.3 Hz, 2H), 7.07 (d, *J* =8.5 Hz, 2H), 7.00 (s, 1H), 3.74 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5, 135.7, 133.2, 129.8, 127.8, 127.2, 127.0, 122.7, 120.7, 119.8, 111.2, 109.7, 29.8, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{16}NS$ $[M+H]^+$: 254.0998. Found: 254.0994.

4-Bromo-1-methyl-2-(*p*-tolylthio)-1*H*-indole (3b)



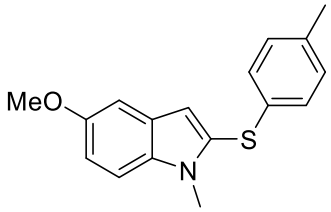
Pale yellow oil, 29.8 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J* =7.6 Hz, 1H), 7.24 (d, *J* =8.3 Hz, 1H), 7.11 (t, *J* =7.9 Hz, 1H), 7.06 (d, *J* =8.4 Hz, 2H), 7.02 (d, *J* =8.4 Hz, 2H), 6.94 (s, 1H), 3.67 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 136.2, 132.3, 129.9, 129.3, 127.9, 127.5, 123.4, 122.7, 114.6, 111.0, 108.8, 30.3, 20.9; FTIR (film): 2917, 2850, 1492, 1447, 1327, 1194, 1085, 802, 755 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}BrNS$ $[M+H]^+$: 332.0103. Found: 332.0106.

5-Bromo-1-methyl-2-(*p*-tolylthio)-1*H*-indole (3c)



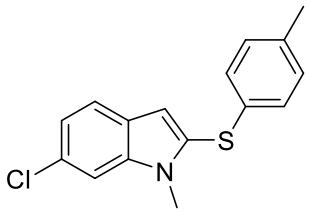
Pale yellow oil, 44.4 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.35 (d, *J* =8.2 Hz, 1H), 7.17 (d, *J* =8.7 Hz, 1H), 7.07 (d, *J* =7.9 Hz, 2H), 7.02 (d, *J* =8.0 Hz, 2H), 6.85 (s, 1H), 3.67 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 136.1, 132.4, 129.9, 128.6, 127.4, 126.2, 125.4, 123.0, 113.0, 111.1, 110.2, 30.0, 20.9; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}BrNS$ $[M+H]^+$: 332.0103. Found: 332.0109.

5-Methoxy-1-methyl-2-(*p*-tolylthio)-1*H*-indole (3d)



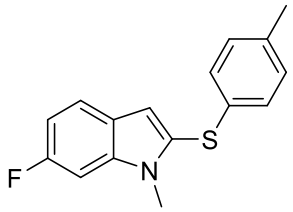
White solid, m.p. = 78–80 °C; 30.0 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* =8.9 Hz, 1H), 7.09 (d, *J* =2.3 Hz, 1H), 7.04 (d, *J* =8.2 Hz, 2H), 7.00–6.94 (m, 3H), 6.84 (s, 1H), 3.87 (s, 3H), 3.66 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.2, 135.7, 134.0, 133.3, 129.8, 127.9, 127.4, 126.9, 113.5, 110.7, 110.5, 101.8, 55.8, 29.9, 20.8; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104. Found: 284.1112.

6-Chloro-1-methyl-2-(p-tolylthio)-1*H*-indole (3e)



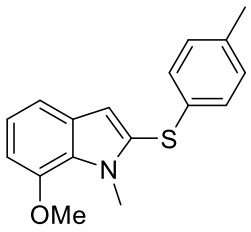
White solid, m.p. = 43–45 °C; 42.5 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* =8.4 Hz, 1H), 7.32 (s, 1H), 7.13 (dd, *J* =8.4, 1.0 Hz, 1H), 7.07 (d, *J* =8.0 Hz, 2H), 7.01 (d, *J* =8.1 Hz, 2H), 6.90 (s, 1H), 3.65 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 136.0, 132.6, 129.9, 129.0, 128.8, 127.2, 125.6, 121.5, 120.5, 111.2, 109.7, 29.9, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}ClNS$ $[M+H]^+$: 288.0608. Found: 288.0613.

6-Fluoro-1-methyl-2-(*p*-tolylthio)-1*H*-indole (3f)



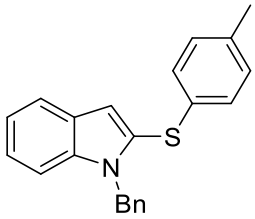
Pale yellow oil, 39.6 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (dd, *J* =8.6, 5.5 Hz, 1H), 7.06 (d, *J* =8.1 Hz, 2H), 7.02–6.98 (m, 3H), 6.95–6.90 (m, 2H), 3.64 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.4 (d, J_{C-F} = 239.8 Hz), 138.7 (d, J_{C-F} = 12.2 Hz), 135.9, 133.0, 129.9, 128.1 (d, J_{C-F} = 3.6 Hz), 127.0, 123.6, 121.7 (d, J_{C-F} = 10.1 Hz), 111.5, 108.8 (d, J_{C-F} = 24.8 Hz), 96.1 (d, J_{C-F} = 26.2 Hz), 30.0, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}FNS$ $[M+H]^+$: 272.0904. Found: 272.0909.

7-Methoxy-1-methyl-2-(*p*-tolylthio)-1*H*-indole (3g)



Pale yellow oil, 14.1 mg, 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 8.0 Hz, 1H), 7.05–6.97 (m, 5H), 6.88 (s, 1H), 6.67 (d, *J* = 7.8 Hz, 1H),3.99 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.4, 135.6, 133.4, 129.8, 129.1, 128.0, 126.9, 126.0, 120.0, 113.5, 111.7, 103.3, 55.3, 33.1, 20.9; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104. Found: 284.1108.

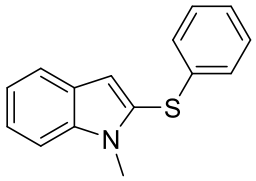
1-Benzyl-2-(*p*-tolylthio)-1*H*-indole (3h)



Yellow oil; 49.4 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* =7.9 Hz, 1H), 7.24–7.13 (m, 6H), 7.04–6.94 (m, 7H), 5.40 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 137.6, 136.0, 132.8, 129.7, 128.4, 127.5, 127.0,

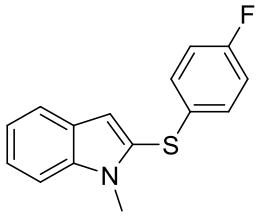
126.3, 122.9, 120.7, 120.0, 111.9, 110.5, 47.0, 20.8; HRMS (ESI) m/z: Calcd for $C_{22}H_{20}NS$ $[M+H]^+$: 330.1311. Found: 330.1338.

1-Methyl-2-(phenylthio)-1*H*-indole (3j)



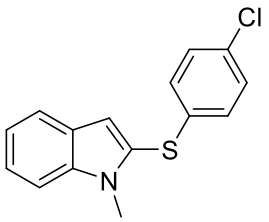
Yellow solid, m.p. = 76.0–78.0 °C; 20.1 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* =7.9 Hz, 1H), 7.39–7.32 (m, 2H), 7.28–7.24 (m, 2H), 7.22–7.15 (m, 2H), 7.10 (d, *J* =7.6 Hz, 2H), 7.00 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 137.0, 129.0, 127.2, 127.0, 126.5, 125.7, 122.9, 120.8, 119.9, 111.7, 109.8, 29.8; HRMS (ESI) m/z: Calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841. Found: 240.0849.

2-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole (3k)



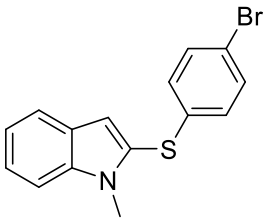
Pale yellow oil, 27.2 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* =7.9 Hz, 1H), 7.35–7.30 (m, 2H), 7.20–7.17 (m, 1H), 7.12–7.08 (m, 2H), 6.98–6.94 (m, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4 (d, $J_{C\text{-}F}$ = 245.9 Hz), 138.6, 131.8 (d, $J_{C\text{-}F}$ = 2.9 Hz), 128.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.4, 127.1, 123.0, 120.8, 119.9, 116.2 (d, $J_{C\text{-}F}$ = 22.2 Hz), 111.5, 109.8, 29.8; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}FNS$ $[M+H]^+$: 258.0747. Found: 258.0752.

2-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole (3l)



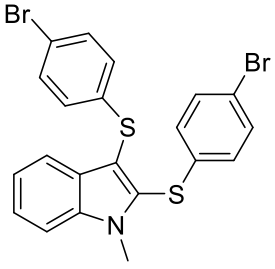
White solid, m.p. = 58–60 °C; 25.1 mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* =7.5 Hz, 1H), 7.36–7.30 (m, 2H), 7.21–7.17 (m, 3H), 7.01–6.98 (m, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 135.6, 131.6, 129.1, 127.7, 127.1, 126.3, 123.1, 120.9, 120.0, 112.0, 109.9, 29.8; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}ClNS$ $[M+H]^+$: 274.0452. Found: 274.0459.

2-((4-Bromophenyl)thio)-1-methyl-1*H*-indole (3m)



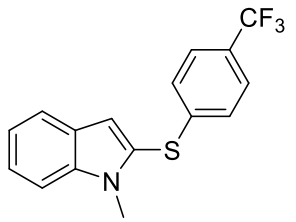
White solid, m.p. = 57–59 °C; 23.4 mg, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.9 Hz, 1H), 7.36–7.30 (m, 4H), 7.20–7.16 (m, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 136.4, 132.1, 127.9, 127.1, 126.1, 123.1, 120.9, 120.0, 119.4, 112.0, 109.9, 29.8; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}BrNS$ $[M+H]^+$: 317.9947. Found: 317.9951.

2,3-Bis((4-bromophenyl)thio)-1-methyl-1*H*-indole (5m)



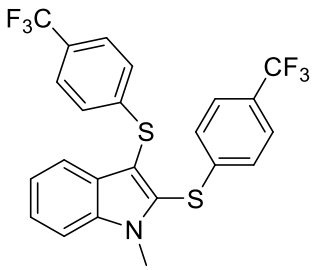
White solid, m.p. = 115–117 °C; 14.0 mg, 14% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.0 Hz, 1H), 7.43–7.36 (m, 2H), 7.30–7.22 (m, 5H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 137.5, 134.8, 133.6, 132.2, 131.6, 128.9, 128.8, 128.0, 124.3, 121.4, 120.1, 118.7, 110.7, 110.3, 31.1; HRMS (ESI) m/z: Calcd for $C_{21}H_{16}Br_2NS_2$ $[M+H]^+$:503.9085. Found: 503.9089.

1-Methyl-2-((4-(trifluoromethyl)phenyl)thio)-1*H*-indole (3n)



White solid, m.p. = 66–68 °C; 17.2 mg, 28% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.38–7.32 (m, 2H), 7.21–7.17 (m, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.01 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 138.8, 127.8 (q, J_{C-F} = 32.6 Hz), 127.1, 125.9 (q, J_{C-F} = 3.7 Hz), 125.7, 124.9, 124.0 (q, J_{C-F} = 271.9 Hz), 123.4, 121.0, 120.2, 112.6, 110.0, 29.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{13}F_3NS$ $[M+H]^+$: 308.0715. Found: 308.0722.

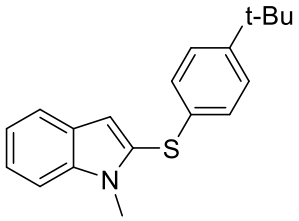
1-Methyl-2,3-bis((4-(trifluoromethyl)phenyl)thio)-1*H*-indole (5n)



White solid, m.p. = 107–109 °C; 21.3 mg, 22% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.45–7.40 (m, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.28–7.25 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J*

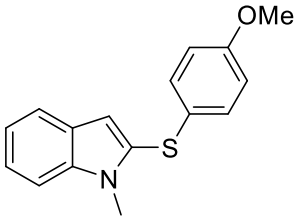
= 8.3 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.54, 143.53, 140.86, 140.85, 138.6, 132.8, 128.9, 128.4 (q, J_{C-F} = 32.7 Hz), 127.2 (q, J_{C-F} = 31.8 Hz), 126.5, 126.1 (q, J_{C-F} = 3.8 Hz), 125.8, 125.5 (q, J_{C-F} = 3.6 Hz), 124.6, 124.1 (q, J_{C-F} = 271.8 Hz), 123.8 (q, J_{C-F} = 271.7 Hz), 121.7, 120.2, 110.5, 110.2, 31.2; HRMS (ESI) m/z: Calcd for $C_{23}H_{16}F_6NS_2$ $[M+H]^+$:484.0623. Found: 484.0628.

2-((4-(*tert*-Butyl)phenyl)thio)-1-methyl-1*H*-indole (3o)



Colorless oil, 51.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.9 Hz, 1H), 7.37–7.32 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.97 (s, 1H), 3.75 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 138.6, 133.3, 127.7, 127.2, 126.6, 126.1, 122.7, 120.7, 119.8, 111.3, 109.7, 34.3, 31.2, 29.9; HRMS (ESI) m/z: Calcd for $C_{19}H_{22}NS$ $[M+H]^+$: 296.1467. Found:296.1469.

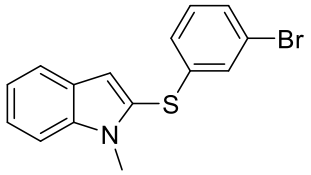
2-((4-Methoxyphenyl)thio)-1-methyl-1*H*-indole (3p)



White solid, m.p. = 50–52 °C; 50.0 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.64 (d, *J* = 7.9 Hz, 1H), 7.32–7.25 (m, 2H), 7.17–7.12 (m, 3H), 6.89 (s, 1H), 6.83–6.79 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 138.5, 129.6, 129.1, 127.2, 126.8, 122.6, 120.6, 119.8, 114.8, 110.4,

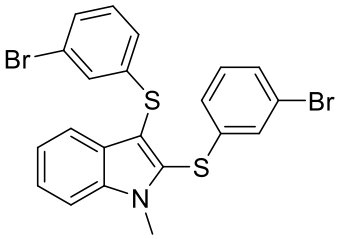
109.6, 55.3, 29.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947. Found: 270.0953.

2-((3-Bromophenyl)thio)-1-methyl-1*H*-indole (3q)



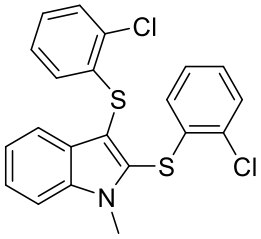
Pale yellow oil, 16.5 mg, 26% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.0 Hz, 1H), 7.37–7.30 (m, 2H), 7.28–7.24 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 138.8, 130.4, 128.9, 128.8, 127.1, 125.6, 124.8, 123.2, 123.1, 121.0, 120.0, 112.3, 109.9, 29.8; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}BrNS$ $[M+H]^+$: 317.9947. Found: 317.9951.

2,3-Bis((3-bromophenyl)thio)-1-methyl-1*H*-indole (5q)



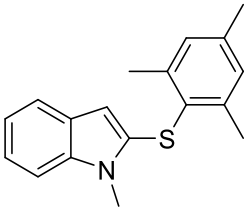
Pale yellow oil, 25.2 mg, 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.9 Hz, 1H), 7.45–7.38 (m, 2H), 7.24–7.15 (m, 5H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.99 (s, 1H), 6.98 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 138.5, 137.8, 133.4, 130.4, 129.9, 129.7, 129.4, 129.0, 128.8, 128.1, 125.7, 124.9, 124.4, 123.1, 122.7, 121.4, 120.2, 110.4, 110.4, 31.2; HRMS (ESI) m/z: Calcd for $C_{21}H_{16}Br_2NS_2$ $[M+H]^+$:503.9085. Found: 503.9091.

2,3-Bis((2-chlorophenyl)thio)-1-methyl-1*H*-indole (5r)



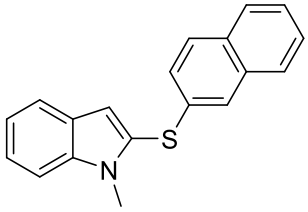
White solid, m.p. = 137–139 °C; 19.9 mg, 24% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42–7.38 (m, 1H), 7.32 (dd, *J* =7.9, 1.2 Hz, 1H), 7.29 (dd, *J* =7.9, 1.2 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.04 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.00–6.94 (m, 2H), 6.90 (dt, *J* = 7.7, 1.3 Hz, 1H), 6.61 (dd, *J* =7.9, 1.5 Hz, 1H), 6.55 (dd, *J* =7.8, 1.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 137.5, 135.0, 133.4, 131.2, 130.5, 129.7, 129.3, 129.0, 127.6, 127.3, 126.9, 126.7, 126.5, 125.5, 124.3, 121.4, 120.3, 110.4, 110.0, 31.1; HRMS (ESI) m/z: Calcd for $C_{21}H_{16}Cl_2NS_2$ $[M+H]^+$:416.0096. Found: 416.0091.

2-(Mesitylthio)-1-methyl-1*H*-indole (3s)



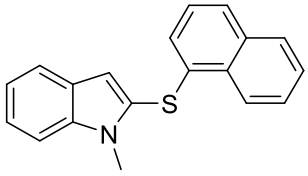
Pale yellow oil, 6.1 mg, 11% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 2H), 5.94 (s, 1H), 3.74 (s, 3H), 2.45 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.7, 139.0, 137.9, 134.2, 129.5, 127.9, 126.9, 120.6, 119.4, 119.1, 108.6, 101.5, 30.0, 21.6, 21.0; HRMS (ESI) m/z: Calcd for $C_{18}H_{20}NS$ $[M+H]^+$: 282.1311. Found: 282.1316.

1-Methyl-2-(naphthalen-2-ylthio)-1*H*-indole (3t)



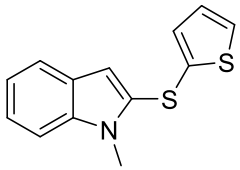
White solid, m.p. = 85–87 °C; 42.2 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.52 (s, 1H), 7.47–7.41 (m, 2H), 7.37–7.31 (m, 2H), 7.26–7.19 (m, 2H), 7.05 (s, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.7, 134.4, 133.7, 131.6, 128.8, 127.7, 127.2, 127.0, 127.0, 126.6, 125.6, 124.8, 124.6, 122.9, 120.8, 119.9, 111.8, 109.8, 29.9; HRMS (ESI) m/z: Calcd for $C_{19}H_{16}NS$ $[M+H]^+$: 290.0998. Found: 290.0994.

1-Methyl-2-(naphthalen-1-ylthio)-1*H*-indole (3u)



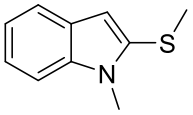
Pale yellow oil, 22.0 mg, 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.40–7.34 (m, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.07 (s, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 134.2, 133.7, 130.7, 128.5, 127.3, 126.6, 126.3, 126.3, 126.3, 125.8, 124.6, 123.8, 122.8, 120.7, 119.9, 111.9, 109.8, 29.8; HRMS (ESI) m/z: Calcd for $C_{19}H_{16}NS$ $[M+H]^+$: 290.0998. Found: 290.1003.

1-Methyl-2-(thiophen-2-ylthio)-1*H*-indole (3v)



Pale yellow oil, 7.3 mg, 15% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.9 Hz, 1H), 7.30–7.23 (m, 3H), 7.14–7.10 (m, 2H), 6.94 (dd, *J* = 5.3, 3.6 Hz, 1H), 6.86 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 134.4, 131.2, 130.1, 128.7, 127.4, 127.0, 122.8, 120.8, 119.9, 109.7, 109.5, 30.0; HRMS (ESI) m/z: Calcd for $C_{13}H_{12}NS_2$ $[M+H]^+$: 246.0406. Found: 246.0412.

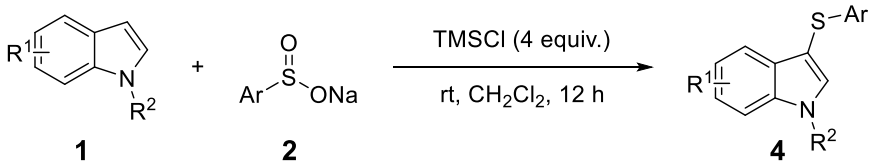
1-Methyl-2-(methylthio)-1*H*-indole (3w)



Pale yellow oil, 11.0 mg, 31% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 6.1 Hz, 1H), 7.14 (t, *J* = 6.6 Hz, 1H), 6.61 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0, 134.0, 127.6, 121.6, 119.7, 119.6, 109.0, 104.6, 29.7, 19.0; HRMS (ESI) m/z: Calcd for $C_{10}H_{12}NS$ $[M+H]^+$: 178.0685. Found: 178.0691.

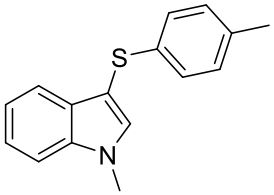
6. General Procedures for the Preparation of C3-Thioindoles 4

The mixture of a sodium arylsulfinates (0.2 mmol, 1 equiv), an indole (0.5 mmol, 2.5 equiv) and TMSCl (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the desired **4**.



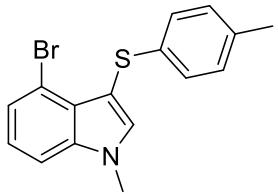
1 **2** **4**

1-Methyl-3-(*p*-tolylthio)-1*H*-indole (4a)



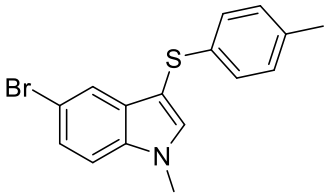
White solid, m.p. = 116–118 °C; 40.5 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* =7.9 Hz, 1H), 7.39 (d, *J* =8.2 Hz, 1H), 7.33–7.29 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 135.8, 134.7, 134.4, 129.7, 129.3, 126.0, 122.4, 120.3, 119.6, 109.6, 101.0, 33.0, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{16}NS$ $[M+H]^+$: 254.0998. Found: 254.1001.

4-Bromo-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4b)



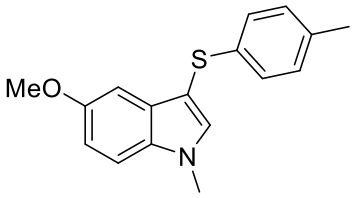
Pale yellow oil, 45.0 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.31 (m, 3H), 7.11 (t, *J* =7.9 Hz, 1H), 7.04–6.99 (m, 4H), 3.80 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.5, 137.6, 137.2, 134.3, 129.3, 126.8, 126.0, 125.2, 123.2, 114.6, 109.1, 102.0, 33.2, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}BrNS$ $[M+H]^+$: 332.0103. Found: 332.0106.

5-Bromo-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4c)



Yellow solid, m.p. = 99.1–101.1 °C; 45.0 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* =1.4 Hz, 1H), 7.36 (dd, *J* =8.6, 1.6 Hz, 1H), 7.30 (s, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.03–6.98 (m, 4H), 3.80 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.1, 135.9, 135.3, 134.7, 131.5, 129.5, 126.1, 125.4, 122.1, 114.1, 111.2, 101.0, 33.2, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}BrNS$ $[M+H]^+$: 332.0103. Found: 332.0108.

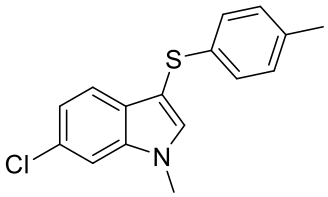
5-Methoxy-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4d)



Pale yellow oil, 44.1 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 1H), 7.30 (d, *J* =8.0 Hz, 1H), 7.12 (d, *J* =2.4 Hz, 1H), 7.08 (d, *J* =8.3 Hz, 2H), 7.03 (d,

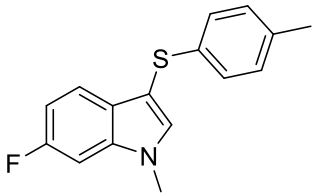
J =8.3 Hz, 2H), 6.99 (dd, *J* =8.8, 2.4 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.8, 136.0, 135.2, 134.3, 132.5, 130.5, 129.3, 125.8, 112.9, 110.5, 100.8, 100.1, 55.7, 33.1, 20.7; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104. Found: 284.1106.

6-Chloro-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4e)



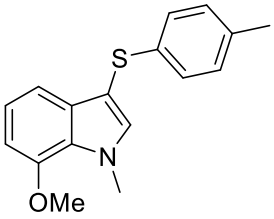
Pale yellow oil, 44.8 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* =8.4 Hz, 1H), 7.37 (s, 1H), 7.30 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 135.3, 135.2, 134.7, 129.4, 128.6, 128.2, 126.2, 121.0, 120.6, 109.7, 101.9, 33.0, 20.8; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}ClNS$ $[M+H]^+$: 288.0608. Found: 288.0615.

6-Fluoro-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4f)



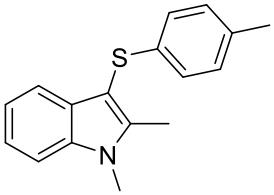
White solid, m.p. = 58–60 °C; 49.9 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (dd, *J* =8.6, 5.3 Hz, 1H), 7.30 (s, 1H), 7.07–7.04 (m, 3H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.94 (dt, *J* = 9.5, 2.2 Hz, 1H), 3.77 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2 (d, $J_{C\text{-}F}$ = 239.1 Hz), 137.4 (d, $J_{C\text{-}F}$ = 12.2 Hz), 135.4, 135.0 (d, $J_{C\text{-}F}$ = 3.4 Hz), 134.6, 129.4, 126.1, 126.0, 120.6 (d, $J_{C\text{-}F}$ = 10.2 Hz), 109.1 (d, $J_{C\text{-}F}$ = 24.6 Hz), 101.6, 96.2 (d, $J_{C\text{-}F}$ = 26.4 Hz), 33.0, 20.7; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}FNS$ $[M+H]^+$: 272.0904. Found: 272.0908.

7-Methoxy-1-methyl-3-(*p*-tolylthio)-1*H*-indole (4g)



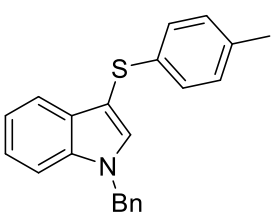
Pale yellow oil, 41.9 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, *J* =7.9 Hz, 1H), 7.22 (s, 1H), 7.10–7.06 (m, 3H), 7.02 (d, *J* =8.2 Hz, 2H), 6.71 (d, *J* =7.7 Hz, 1H), 4.11 (s, 3H), 3.98 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 135.9, 135.7, 134.2, 132.2, 129.3, 127.0, 125.9, 120.8, 112.3, 103.0, 100.7, 55.3, 36.7, 20.7; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NOS$ $[M+H]^+$: 284.1104. Found: 284.1107.

1,2-Dimethyl-3-(*p*-tolylthio)-1*H*-indole (4h)



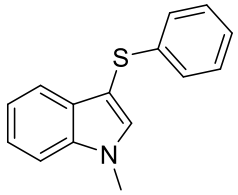
Yellow solid, m.p. = 118.0–120.0 °C; 51.3 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* =7.8 Hz, 1H), 7.35 (d, *J* =8.1 Hz, 1H), 7.25 (t, *J* =7.5 Hz, 1H), 7.15 (t, *J* =7.4 Hz, 1H), 7.00–6.95 (m, 4H), 3.76 (s, 3H), 2.53 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.6, 137.0, 136.1, 134.1, 129.7, 129.3, 125.6, 121.6, 120.3, 118.9, 108.9, 98.5, 30.2, 20.7, 10.8; HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NS$ $[M+H]^+$: 268.1154. Found: 268.1159.

1-Benzyl-3-(*p*-tolylthio)-1*H*-indole (4i)



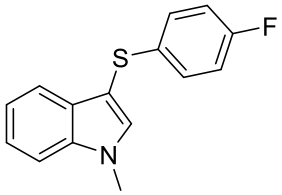
Yellow oil; 55.9 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* =7.8 Hz, 1H), 7.45 (s, 1H), 7.41–7.34 (m, 4H), 7.32–7.28 (m, 1H), 7.25–7.22 (m, 3H), 7.12 (dd, *J* =8.1, 1.6 Hz, 2H), 7.05 (d, *J* =7.9 Hz, 2H), 5.38 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 136.6, 135.7, 134.4, 134.1, 129.9, 129.4, 128.8, 127.8, 126.9, 126.0, 122.6, 120.5, 119.8, 110.1, 101.9, 50.3, 20.8; HRMS (ESI) m/z: Calcd for $C_{22}H_{20}NS$ $[M+H]^+$: 330.1311. Found: 330.1317.

1-Methyl-3-(phenylthio)-1*H*-indole (4k)



White solid, m.p. = 84–87 °C; 43.9 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* =7.9 Hz, 1H), 7.42 (d, *J* =8.2 Hz, 1H), 7.35–7.31 (m, 2H), 7.22–7.13 (m, 5H), 7.09–7.06 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6, 137.4, 135.0, 129.7, 128.6, 125.6, 124.6, 122.5, 120.4, 119.6, 109.6, 100.4, 33.0; HRMS (ESI) m/z: Calcd for $C_{15}H_{14}NS$ $[M+H]^+$: 240.0841. Found: 240.0844.

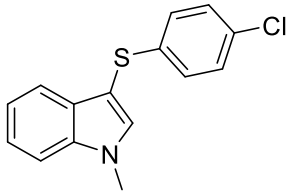
3-((4-Fluorophenyl)thio)-1-methyl-1*H*-indole (4l)



White solid, m.p. = 68–70 °C; 44.2 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* =8.4 Hz, 1H), 7.41 (d, *J* =8.2 Hz, 1H), 7.34–7.31 (m, 2H), 7.20 (t, *J* =7.4 Hz, 1H), 7.13–7.10 (m, 2H), 6.89 (t, *J* = 8.7 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8 (d, $J_{C\text{-}F}$ = 243.7 Hz), 137.4, 134.8, 134.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.5, 127.7 (d, $J_{C\text{-}F}$ = 7.6 Hz), 122.5, 120.5, 119.5, 115.6 (d,

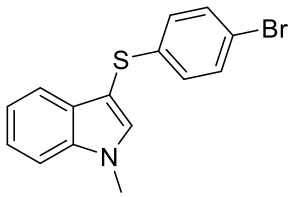
$J_{C\text{-}F}$ = 22.0 Hz), 109.7, 100.9, 33.0; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}FNS$ $[M+H]^+$: 258.0747. Found: 258.0749.

3-((4-Chlorophenyl)thio)-1-methyl-1*H*-indole (4m)



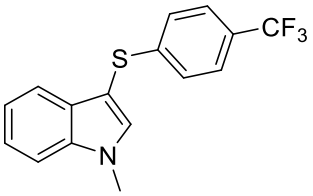
White solid, m.p. = 128–129 °C; 47.0 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, *J* =7.9 Hz, 1H), 7.42 (d, *J* =8.2 Hz, 1H), 7.36–7.32 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 137.5, 135.0, 130.3, 129.4, 128.6, 126.9, 122.6, 120.5, 119.4, 109.7, 99.9, 33.0; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}ClNS$ $[M+H]^+$: 274.0452. Found: 274.0455.

3-((4-Bromophenyl)thio)-1-methyl-1*H*-indole (4n)



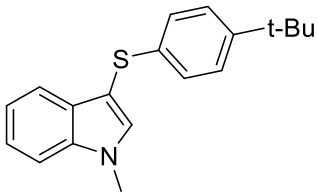
White solid, m.p. = 146–148 °C; 46.3 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.36–7.32 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.9, 137.5, 135.0, 131.5, 129.4, 127.2, 122.6, 120.6, 119.5, 118.1, 109.7, 99.8, 33.1; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}NaNS$ $[M+H]^+$: 317.9947. Found: 317.9949.

1-Methyl-3-((4-(trifluoromethyl)phenyl)thio)-1*H*-indole (4o)



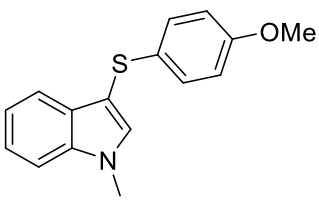
White solid, m.p. = 117–119 °C; 52.8 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.7 Hz, 1H), 7.44–7.32 (m, 5H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.1, 137.6, 135.2, 129.4, 126.6 (q, J_{C-F} = 32.6 Hz), 125.4 (q, J_{C-F} = 3.6 Hz), 125.1, 124.3 (q, J_{C-F} = 271.4 Hz), 122.8, 120.7, 119.4, 109.9, 98.8, 33.1; HRMS (ESI) m/z: Calcd for $C_{16}H_{13}F_3NS$ $[M+H]^+$: 308.0715. Found: 308.0718.

3-((4-(*tert*-Butyl)phenyl)thio)-1-methyl-1*H*-indole (4p)



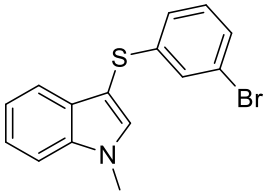
Colorless oil, 56.0 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33–7.29 (m, 2H), 7.20–7.17 (m, 3H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.84 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.7, 137.4, 136.1, 134.9, 129.9, 125.6, 125.6, 122.4, 120.3, 119.7, 109.6, 101.0, 34.2, 33.0, 31.2; HRMS (ESI) m/z: Calcd for $C_{19}H_{22}NS$ $[M+H]^+$: 296.1467. Found:296.1469.

3-((4-Methoxyphenyl)thio)-1-methyl-1*H*-indole (4q)



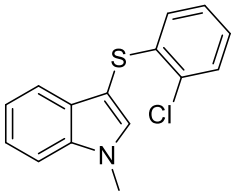
White solid, m.p. = 63–65 °C; 42.0 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31–7.27 (m, 2H), 7.19–7.13 (m, 3H), 6.75 (d, *J* = 7.8 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 137.4, 134.4, 129.9, 129.6, 128.3, 122.4, 120.3, 119.6, 114.4, 109.6, 102.2, 55.2, 33.0; HRMS (ESI) m/z: Calcd for $C_{16}H_{16}NOS$ $[M+H]^+$: 270.0947. Found: 270.0951.

3-((3-Bromophenyl)thio)-1-methyl-1*H*-indole (4r)



Colorless oil, 58.3 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.37–7.34 (m, 2H), 7.28–7.20 (m, 3H), 7.06–7.01 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 137.5, 135.2, 129.8, 129.5, 128.0, 127.6, 124.1, 122.7, 122.6, 120.6, 119.4, 109.8, 99.3, 33.1; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}NaNS$ $[M+H]^+$: 317.9947. Found: 317.9950.

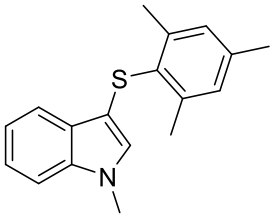
3-((2-Chlorophenyl)thio)-1-methyl-1*H*-indole (4s)



White solid, m.p. = 130–132 °C; 39.9 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35–7.32 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.8, 137.6, 135.5, 129.8, 129.6, 129.1, 126.8, 126.2, 125.2, 122.7, 120.6, 119.6, 109.8,

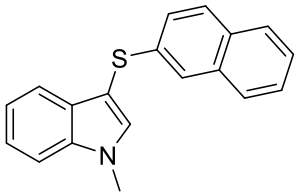
98.7, 33.1; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}ClNS$ $[M+H]^+$: 274.0452. Found: 274.0457.

3-(Mesitylthio)-1-methyl-1*H*-indole (4t)



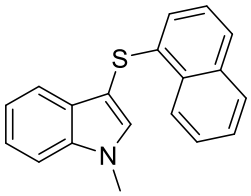
Pale yellow oil, 47.2 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.22 (dt, *J* = 7.53, 0.99 Hz, 1H), 7.13–7.09 (m, 1H), 6.92 (s, 3H), 3.72 (s, 3H), 2.56 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.1, 137.6, 136.9, 130.5, 130.3, 129.1, 128.7, 121.9, 119.5, 119.5, 109.3, 105.7, 32.8, 22.1, 20.9; HRMS (ESI) m/z: Calcd for $C_{18}H_{20}NS$ $[M+H]^+$: 282.1311. Found: 282.1317.

1-Methyl-3-(naphthalen-2-ylthio)-1*H*-indole (4u)



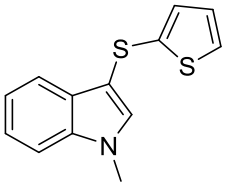
White solid, m.p. = 113–115 °C; 50.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 (s, 1H), 7.43–7.29 (m, 6H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.5, 137.1, 135.0, 133.7, 131.2, 129.7, 128.1, 127.6, 126.8, 126.2, 124.9, 124.6, 123.2, 122.5, 120.5, 119.7, 109.7, 100.4, 33.1; HRMS (ESI) m/z: Calcd for $C_{19}H_{16}NS$ $[M+H]^+$: 290.0998. Found: 290.0992.

1-Methyl-3-(naphthalen-1-ylthio)-1*H*-indole (4v)



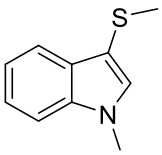
White solid, m.p. = 149–151 °C; 50.3 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, *J* = 8.3 Hz, 1H),7.86 (d, *J* = 8.1 Hz, 1H), 7.63–7.53 (m, 4H), 7.44–7.40 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6, 136.6, 135.2, 133.6, 130.6, 129.7, 128.3, 126.0, 125.9, 125.6, 124.9, 123.8, 123.1, 122.5, 120.4, 119.7, 109.7, 99.6, 33.0; HRMS (ESI) m/z: Calcd for $C_{19}H_{16}NS$ $[M+H]^+$: 290.0998. Found: 290.0991.

1-Methyl-3-(thiophen-2-ylthio)-1*H*-indole (4w)



Pale yellow oil, 30.4 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.7 Hz, 1H), 7.35–7.28 (m, 3H), 7.26–7.22 (m, 1H), 7.18–7.12 (m, 2H), 6.90–6.88 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 137.1, 133.6, 129.5, 129.1, 127.1, 127.1, 122.4, 120.3, 119.4, 109.6, 104.3, 32.9; HRMS (ESI) m/z: Calcd for $C_{13}H_{12}NS_2$ $[M+H]^+$: 246.0406. Found: 246.0411.

1-Methyl-3-(methylthio)-1*H*-indole (4x)



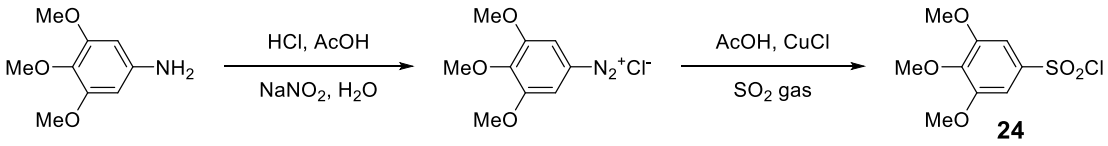
Pale yellow oil, 18.8 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.31–7.27 (m, 1H), 7.24–7.20 (m, 1H),

7.18 (s, 1H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2, 132.4, 129.3, 122.1, 119.8, 119.2, 109.5, 106.0, 32.8, 20.6; HRMS (ESI) m/z: Calcd for $C_{10}H_{12}NS$ $[M+H]^+$: 178.0685. Found: 178.0689.

7. Synthesis of C3-Thioindole 4y

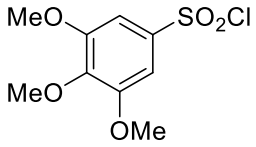
General procedure for the preparation of 3,4,5-trimethoxybenzenesulfonyl chloride (24).[4] To a stirred solution of concentrated (37%) HCl (20 mL), glacial acetic acid (4 mL) and CH_3CN (20 mL) was added 2,4,5-trimethoxyaniline (5.5 g, 30 mmol, 1.0 equiv) at room temperature, the mixture was stirred at 50 °C for 20 min, and after cooling to 0 °C, a solution of $NaNO_2$ (2.3 g, 33 mmol, 1.1 equiv) in H_2O (4 mL) was added dropwise. After the addition, the mixture was allowed to stir for another 45 min at -10 °C to form the diazonium salt.

In a 250 mL round bottom flask containing glacial acetic acid (50 mL), SO_2 gas was bubbled through a diffusion apparatus until saturation of the solution. Then CuCl (0.74 g, 7.5 mmol, 0.25 equiv) was added to the colourless solution, which became greenish–yellow. SO_2 gas was allowed to bubble for an additional 30–45 min until the solution became blue–green showing that the CuCl was dissolved. The mixture was chilled in an ice bath at +10 °C and the diazonium salt previously formed was added dropwise in a rate to keep the temperature below 30 °C, and then stirred for 1 h at room temperature. Then water (100 mL) and ether (100 mL) were added. The aqueous phase was extracted with ether three times. The combined organic layers were washed with saturated aq. $NaHCO_3$, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (100–200 mesh, elution 15% ethyl acetate in petroleum ether) to afford the sulfonyl chloride **24**.



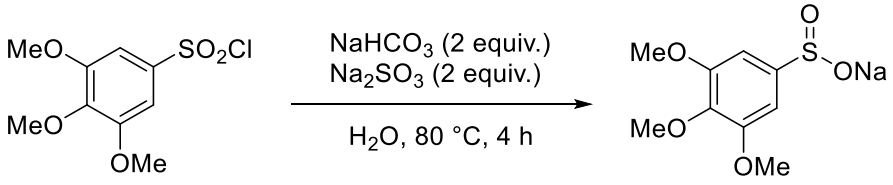
24

3,4,5-Trimethoxybenzenesulfonyl chloride (24)



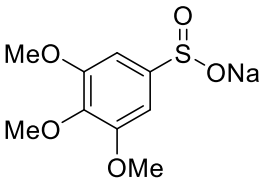
White solid, 1.6 g, 20% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.89 (s, 1H), 7.86 (d, J = 2.6 Hz, 1H), 7.56 (s, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.30 (dd, J = 8.6, 1.8 Hz, 1H), 6.39 (s, 2H), 3.59 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 153.1, 135.4, 135.2, 133.9, 133.2, 130.4, 124.6, 120.3, 114.4, 112.7, 103.5, 99.8, 59.9, 55.7; HRMS (ESI) m/z: Calcd for $C_9H_{12}ClO_5S$ $[M+H]^+$: 267.0088. Found: 267.0093.

General procedure for the preparation of sodium 3,4,5-trimethoxybenzenesulfinate (2b). [1] Sodium sulfite (0.96 g, 8 mmol, 2 equiv), sodium bicarbonate (0.68 g, 8 mmol, 2 equiv) and the 3,4,5-trimethoxybenzenesulfonyl chloride (1.07 g, 4 mmol, 1 equiv) were dissolved in distilled water (5 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling to rt, water was removed by rotary evaporator. Then the remaining solid was extracted and recrystallized by ethanol to get the compound **2b**.



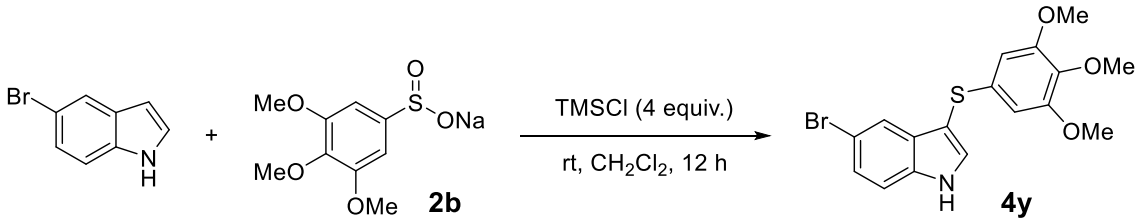
24 **2b**

Sodium 3,4,5-trimethoxybenzenesulfinate (2b)

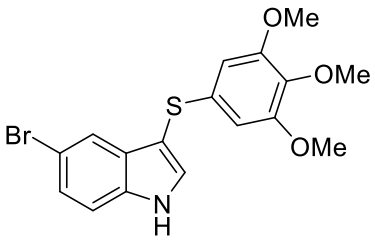


White solid, 0.64 g, 63% yield; ^{1}H NMR (400 MHz, D_2O) δ: 6.89 (s, 2H), 3.82 (s, 6H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ: 152.6, 150.1, 137.9, 100.8, 60.8, 56.1.

The mixture of sodium 3,4,5-trimethoxybenzenesulfinate (127 mg, 0.5 mmol, 1 equiv), 5-bromo-1*H*-indole (248 mg, 1.25 mmol, 2.5 equiv) and TMSCl (254 μL, 2.0 mmol, 4 equiv) in CH_2Cl_2 (2.0 mL) was stirred at 25 °C for 12 h, then water (10 mL) and dichloromethane (20 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 10% → 25% ethyl acetate in petroleum ether) to afford the desired **4y**.



5-Bromo-3-((3,4,5-trimethoxyphenyl)thio)-1*H*-indole (4y)



White solid, m.p. = 153–155 °C; 62.8 mg, 32% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.89 (s, 1H), 7.86 (d, *J* = 2.6 Hz, 1H), 7.56 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.30 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.39 (s, 2H), 3.59 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 153.1, 135.4, 135.2, 133.9, 133.2, 130.4, 124.6, 120.3,

114.4, 112.7, 103.5, 99.8, 59.9, 55.7; HRMS (ESI) m/z: Calcd for $C_{17}H_{17}BrNO_3S$ $[M+H]^+$: 394.0107. Found: 394.0115. ^{1}H- and ^{13}C-NMR data are matching with the literature known spectra.[5]

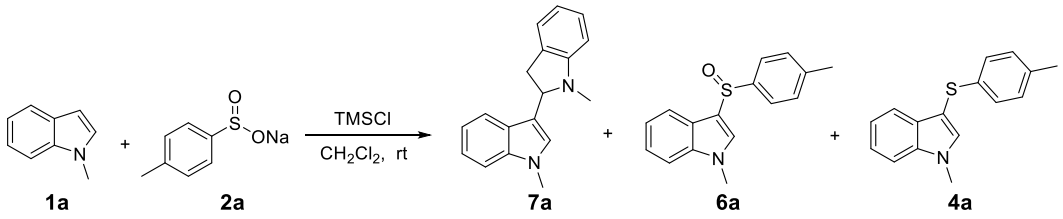
8. Gram-Scale Experimental Procedure for Thioindoles 3a and 4a

To a stirred solution of a sodium 4-methylbenzenesulfinate (**2a**, 10.7 g, 60.0 mmol, 1 equiv), a 1-methyl-1*H*-indole (**1a**, 18.8 mL, 150.0 mmol, 2.5 equiv) in CH_2Cl_2 (100.0 mL) was slowly added TMSOTf (43.5 mL, 240.0 mmol, 4 equiv) at 0 °C, the reaction was allowed to warm to room temperature and stirred for 12 h, then water (100 mL) and dichloromethane (100 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the desired C2-thioindole **3a** (yield 68%, 10.3g)**.**

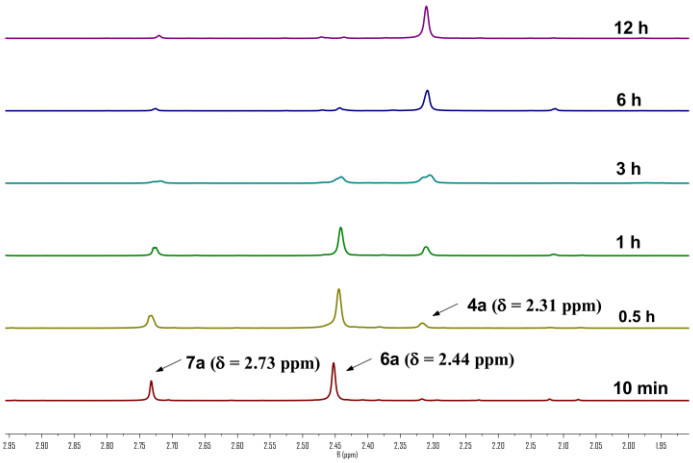
To a stirred solution of a sodium 4-methylbenzenesulfinate (**2a**, 10.7 g, 60.0 mmol, 1 equiv), a 1-methyl-1*H*-indole (**1a**, 18.8 mL, 150.0 mmol, 2.5 equiv) in CH_2Cl_2 (100.0 mL) was slowly added TMSCl (30.4 mL, 240.0 mmol, 4 equiv) at 0 °C, the reaction was allowed to warm to room temperature and stirred for 12 h, then water (100 mL) and dichloromethane (100 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the desired C3-thioindole **4a** (yield 71%, 10.7g)**.**

9. Mechanistic Control Experiments

Progress of the reaction of 1a with 2a, for up to 12 h. The mixture of a sodium 4-methylbenzenesulfinate (**2a**, 0.2 mmol, 1 equiv), a 1-methyl-1*H*-indole (**1a**, 0.5 mmol, 2.5 equiv) and TMSCl (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 10 min-12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The reaction was closely monitored by ^1H NMR spectroscopy using CH_2Br_2 as an internal standard.

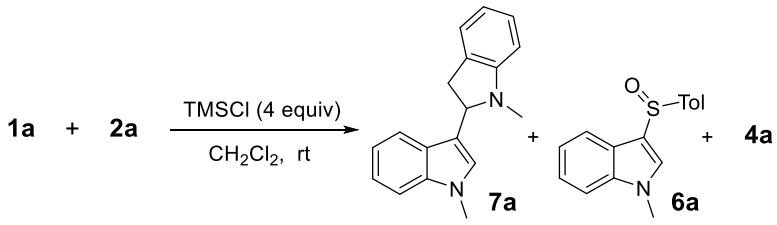


During the 12 h reaction process, three peaks including those for sulfoxide **6a** (δ = 2.44 ppm), C3-thioindole **4a** (δ = 2.31 ppm) and indole dimer **7a** (δ = 2.73 ppm) were observed (Scheme S1), and the representative results are summarized in Table S3. Sulfoxide **6a** and indole dimer **7a** were obtained in 90% and 32% yields, respectively when the reaction time was 10 min (entry 1). C3-thioindole **4a** was obtained in 13% yield when the reaction time was 0.5 h (entry 2). Obviously, the yield of C3-thioindole **4a** was increasing up to 75% with the yield of sulfoxide **6a** decreasing from 90% to 13% (entries 1–5). Finally, C3-thioindole **4a** was obtained in 83% yield when the reaction time was 12 h, and sulfoxide **6a** was disappeared at this time (entry 6). The results indicated that sulfoxide **6a** might be a reaction intermediate in the synthesis of C3-thioindole **4a**.



Scheme S1. Progress of the reaction of **1a** with **2a**, for up to 12 h.

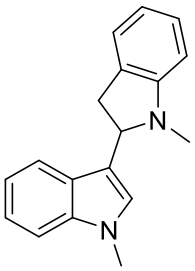
Table S3. Progress of the reaction of **1a** with **2a**, for up to 12 h[a]



Entry	Time	**7a**	**6a**	**4a**
1	10 min	32%	90%	0
2	0.5 h	24%	83%	13%
3	1 h	16%	67%	23%
4	3 h	9%	34%	48%
5	6 h	7%	13%	75%
6	12 h	< 5%	0	83%

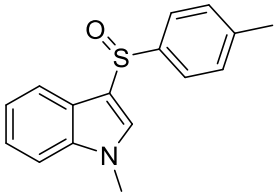
[a] General conditions: **1a** (0.5 mmol), **2a** (0.2 mmol), and TMSCl (0.8 mmol) in solvent (1.0 mL) at 25 °C. The yields of **4a**, **6a** and **7a** were determined by ^{1}H NMR spectroscopy using 0.2 mmol of CH_2Br_2 as a standard.

1-Methyl-3-(1-methylindolin-2-yl)-1*H*-indole (7a)



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22–7.10 (m, 4H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 4.67 (dd, *J* = 11.1, 8.8 Hz, 1H), 3.82 (s, 3H), 3.36 (dd, *J* = 15.5, 8.8 Hz, 1H), 3.25 (dd, *J* = 15.5, 11.2 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 137.4, 129.1, 127.4, 127.2, 126.7, 123.9, 121.7, 120.1, 118.9, 117.7, 115.0, 109.3, 107.1, 64.6, 37.8, 34.0, 32.6; HRMS (ESI) m/z: Calcd for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543. Found: 263.1548.

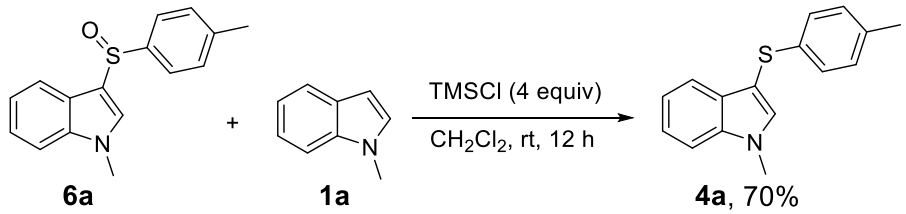
1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (6a)



White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H),7.34–7.24 (m, 4H), 7.12–7.08 (m, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 140.3, 137.6, 132.5, 129.5, 124.8, 124.3, 123.2, 121.3, 119.8, 116.5, 110.0, 33.2, 21.2; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}NaNOS$ $[M+Na]^+$: 292.0767. Found: 292.0765.

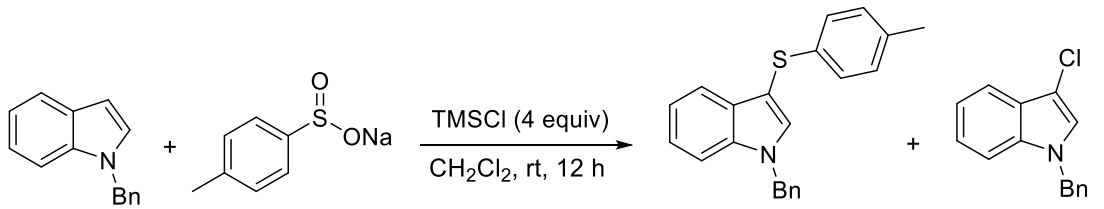
Several control experiments for the C3–H thiolation. The mixture of a sulfoxide (**6a**, 0.2 mmol, 1 equiv), a 1-methyl-1*H*-indole (**1a**, 0.2 mmol, 1 equiv) and TMSCl (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane

(3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, elution 5% ethyl acetate in petroleum ether) to afford the C3-thioindole **4a** in 70% yield.



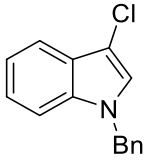
6a **1a** **4a**, 70%

The mixture of a sodium 4-methylbenzenesulfinate (**2a**, 0.2 mmol, 1 equiv), a 1-benzyl-1*H*-indole (**1i**, 0.5 mmol, 2.5 equiv) and TMSCl (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the C3-thioindole **4i** in 85% yield. In addition, 1-benzyl-3-chloro-1*H*-indole (**9a**) was also gained in 26% yield based on indole **1i**.



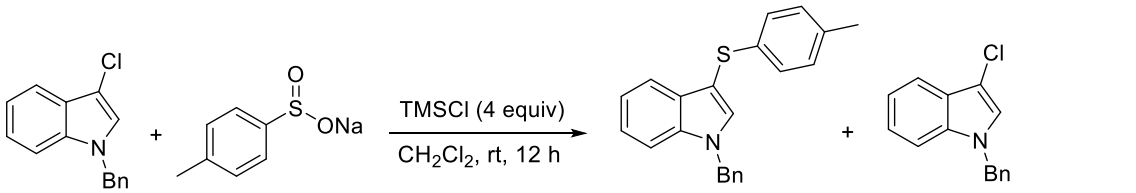
1i **2a** **4i**, 85% **9a**, 26%

1-Benzyl-3-chloro-1*H*-indole (9a)



Pale yellow oil, 31.3 mg, 26% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 7.8 Hz, 1H), 7.34–7.28 (m, 4H), 7.25–7.17 (m, 2H), 7.14–7.12 (m, 2H), 7.10 (s, 1H), 5.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.7, 135.4, 128.8, 127.8, 126.8, 125.9, 124.5, 122.8, 120.1, 118.4, 109.9, 105.2, 50.1; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}ClN$ $[M+H]^+$: 242.0731. Found: 242.0738.

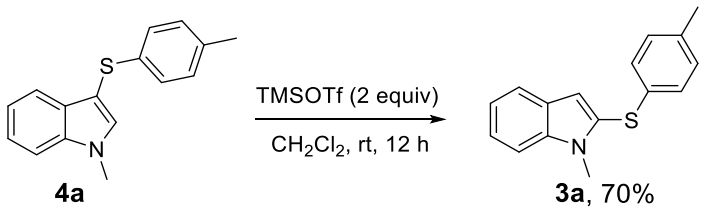
The mixture of a sodium 4-methylbenzenesulfinate (**2a**, 0.2 mmol, 1 equiv), a 1-Benzyl-3-chloro-1*H*-indole (**9a**, 0.5 mmol, 2.5 equiv) and TMSCl (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the the starting materials **9a** in 92% yield, and the C3-thioindole **4i** was not found.



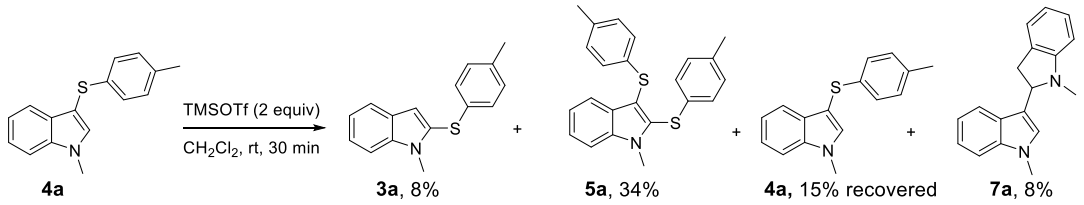
9a **2a** **4i**, 0% **9a**, 92% recovered

Several control experiments for the C2–H thiolation. The mixture of a C3-thioindole (**4a**, 0.2 mmol, 1 equiv) and TMSOTf (0.4 mmol, 2 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous

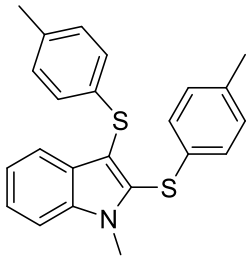
Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 5% ethyl acetate in petroleum ether) to afford the C2-thioindole **3a** in 70% yield.



The mixture of a C3-thioindole (**4a**, 0.2 mmol, 1 equiv) and TMSOTf (0.4 mmol, 2 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 30 min, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the C2-thioindole **3a**, 2,3-bis-thioindole **5a** and dimer **7a** in 8%, 34% and 70% yields, respectively. In addition, C3-thioindole **4a** was also recovered in 15% yield.

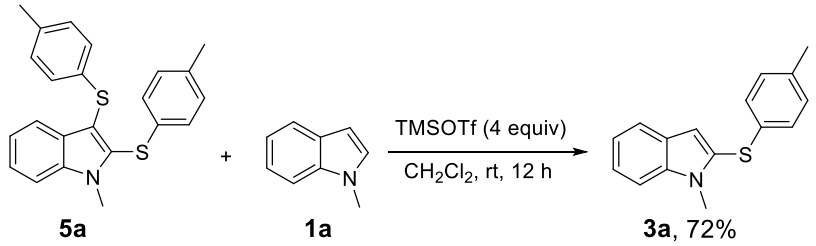


1-Methyl-2,3-bis(*p*-tolylthio)-*1H*-indole (5a)



Pale yellow oil, 25.5 mg, 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.0 Hz, 1H), 7.40–7.31 (m, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.99–6.94 (m, 6H), 3.80 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 136.2, 134.8, 134.8, 134.7, 132.1, 129.9, 129.4, 129.1, 127.8, 126.9, 123.8, 120.9, 120.3, 111.2, 110.0, 31.0, 20.9, 20.9; HRMS (ESI) m/z: Calcd for $C_{23}H_{22}NS_2$ $[M+H]^+$: 376.1188. Found: 376.1191.

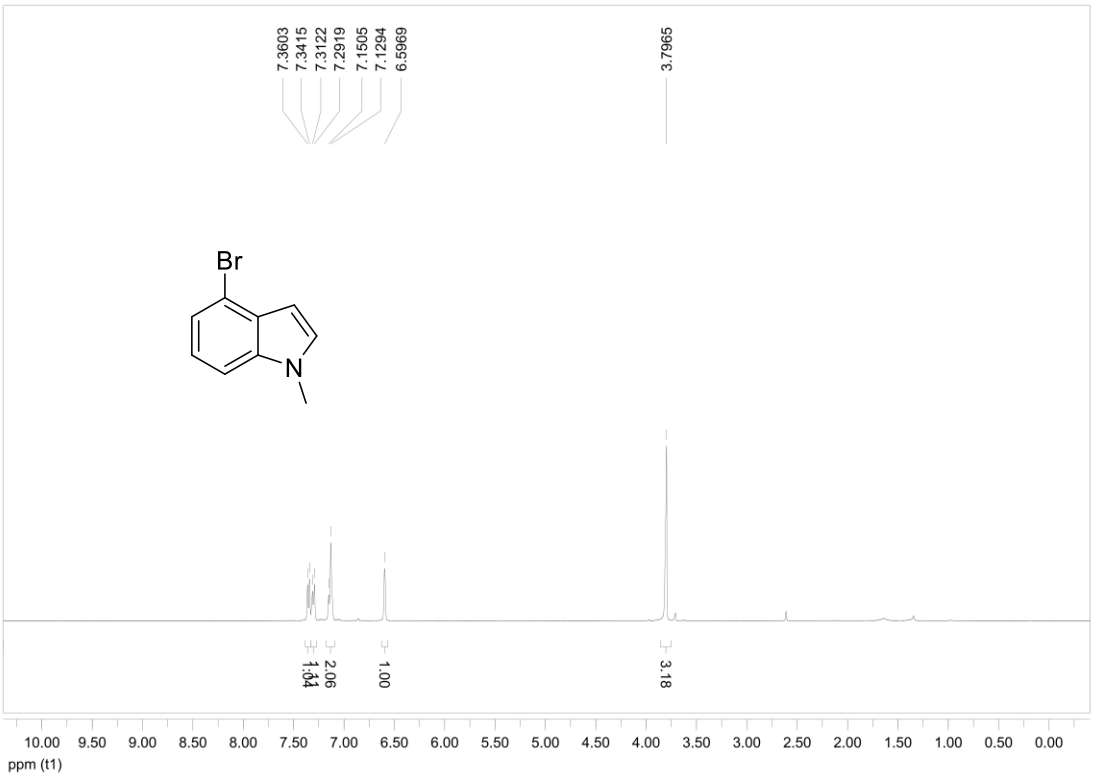
The mixture of a 2,3-bis-thioindole (**5a**, 0.2 mmol, 1 equiv), a 1-methyl-1*H*-indole (**1a**, 0.24 mmol, 1.2 equiv) and TMSOTf (0.8 mmol, 4 equiv) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 12 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, gradient elution 2% → 5% ethyl acetate in petroleum ether) to afford the C2-thioindole **3a** in 72% yield.



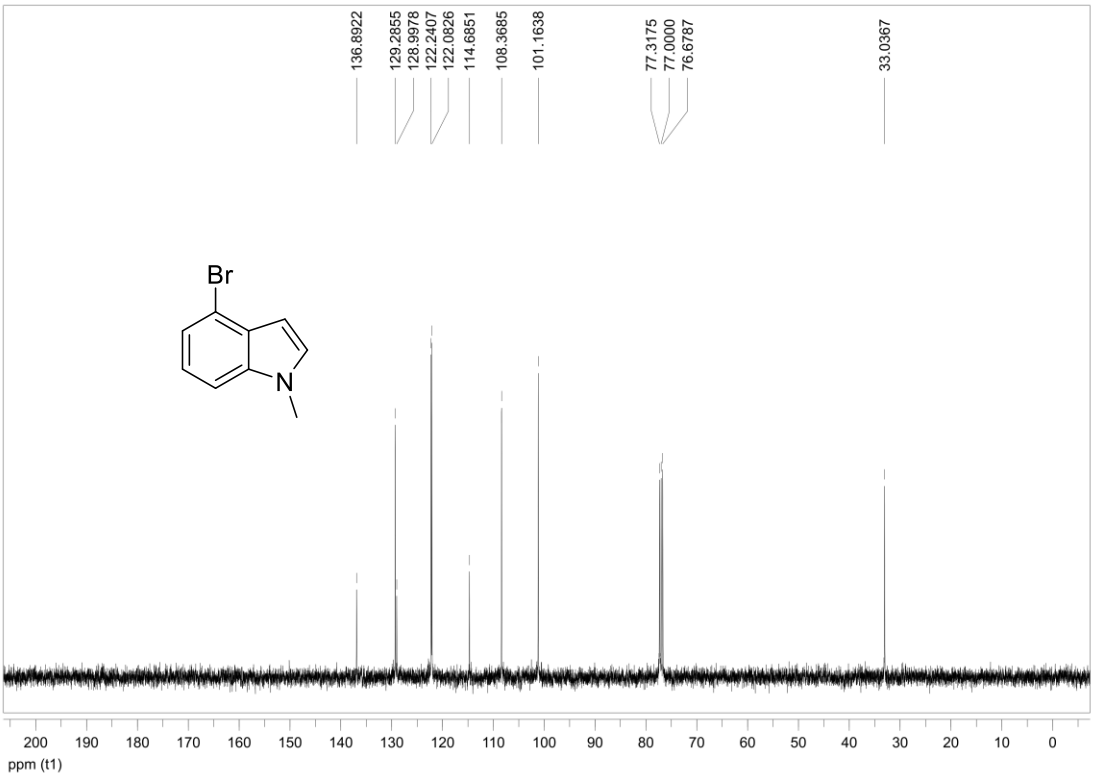
5a + **1a** → **3a**, 72%

10. NMR Spectra

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

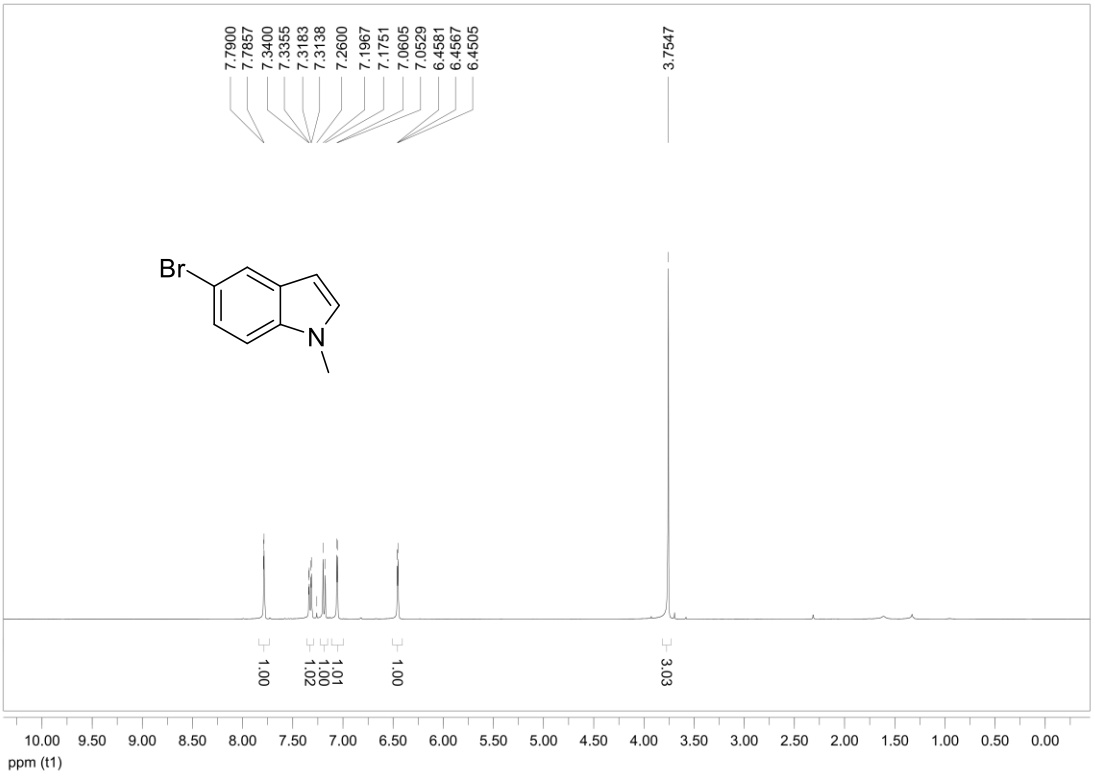


^{13}C NMR (100 MHz, $CDCl_3$)

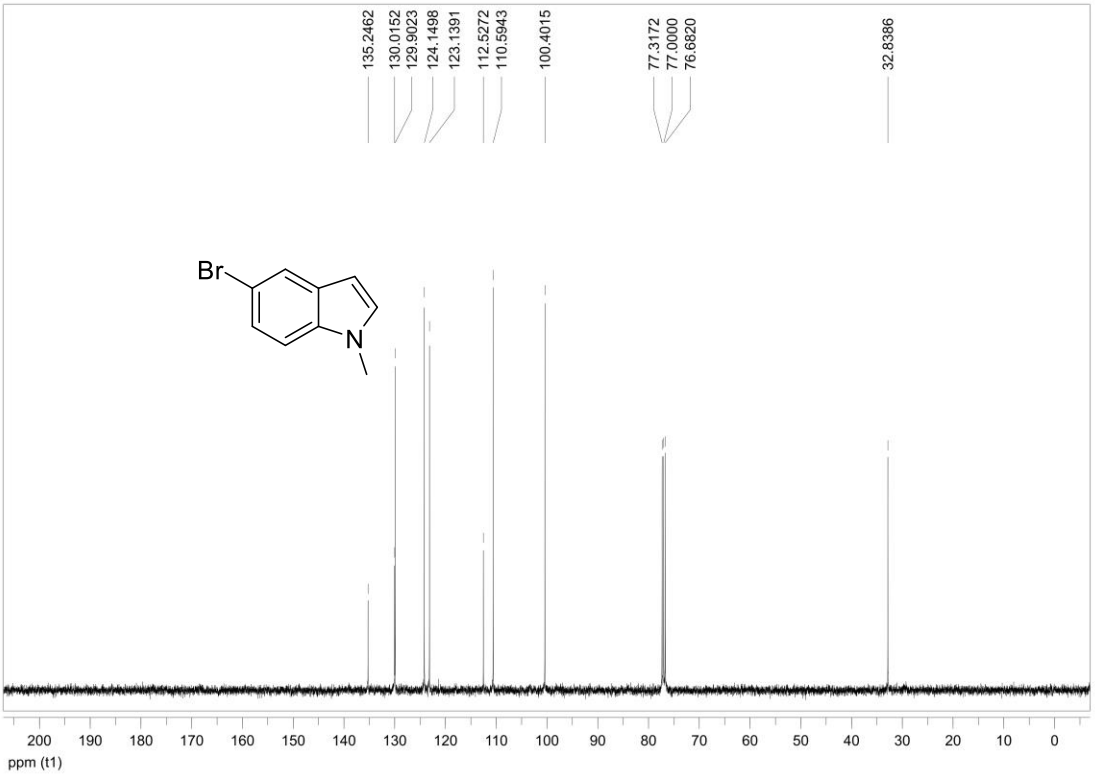


Indole **1c**

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

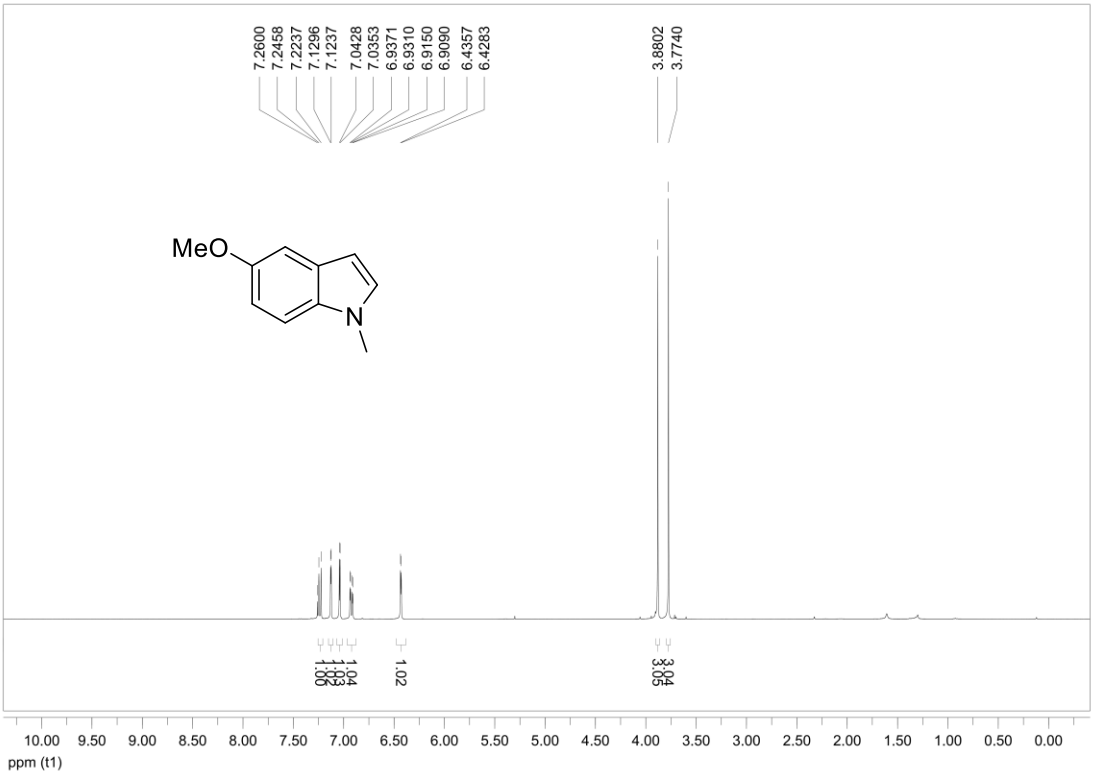


^{13}C NMR (100 MHz, $CDCl_3$)

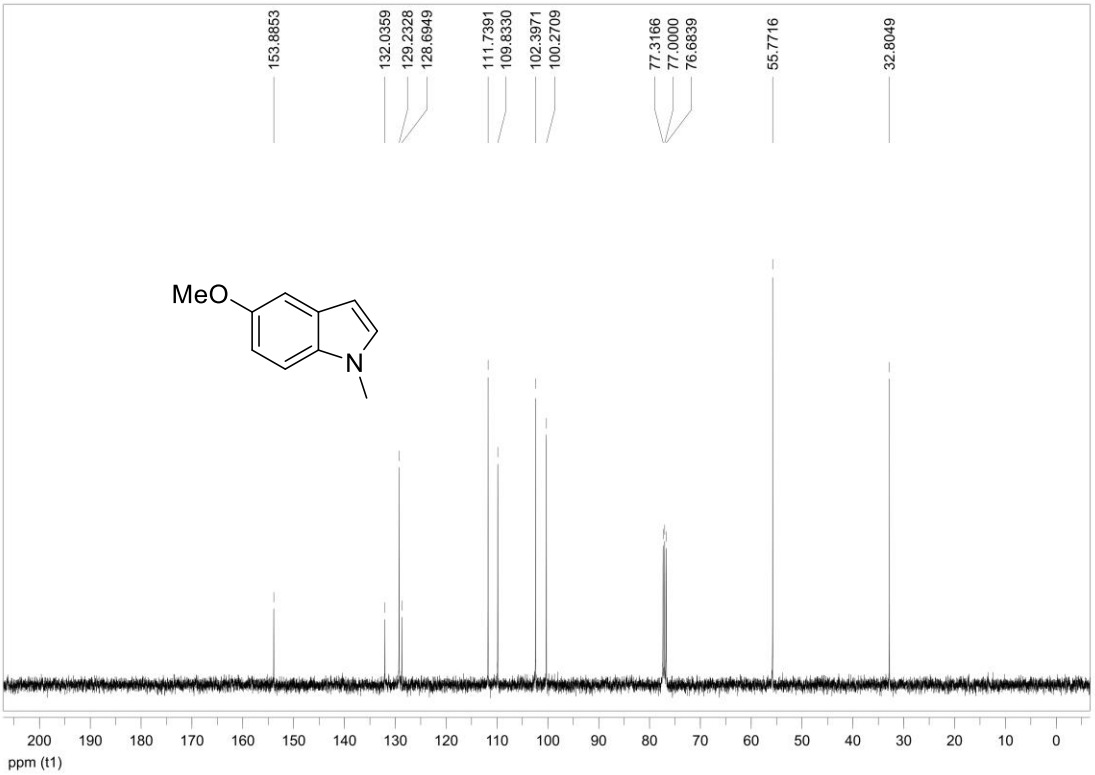


Indole **1d**

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

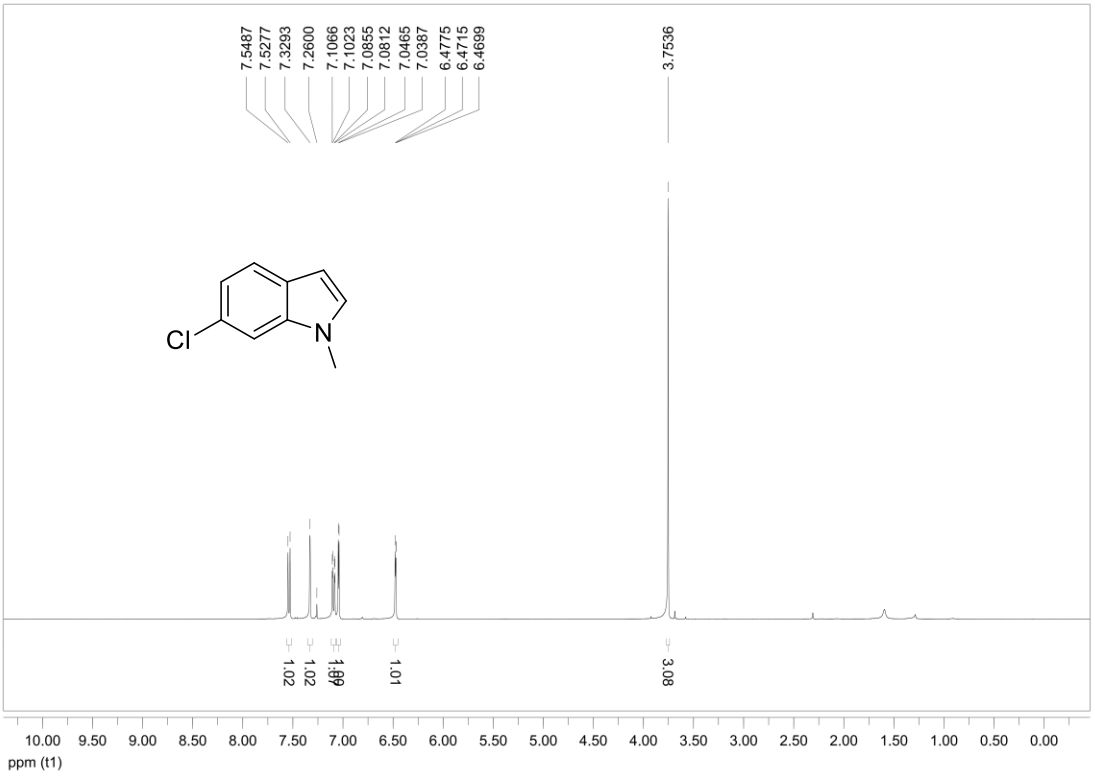


^{13}C NMR (100 MHz, $CDCl_3$)

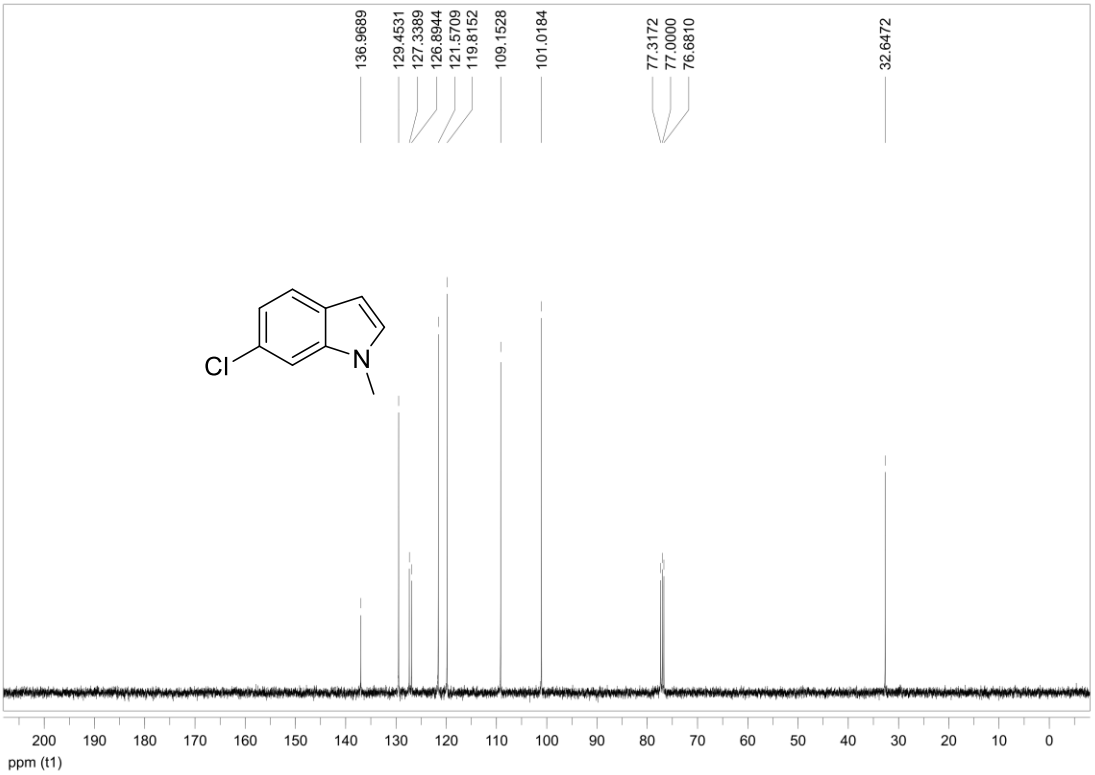


Indole **1e**

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

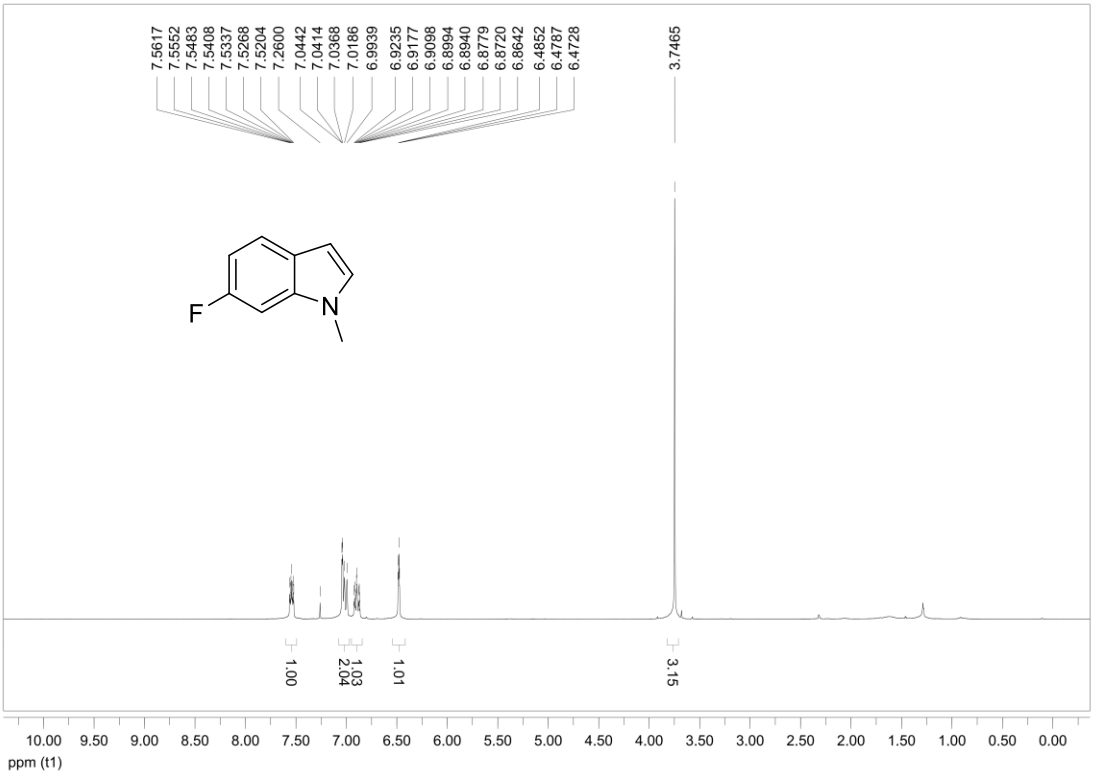


^{13}C NMR (100 MHz, $CDCl_3$)

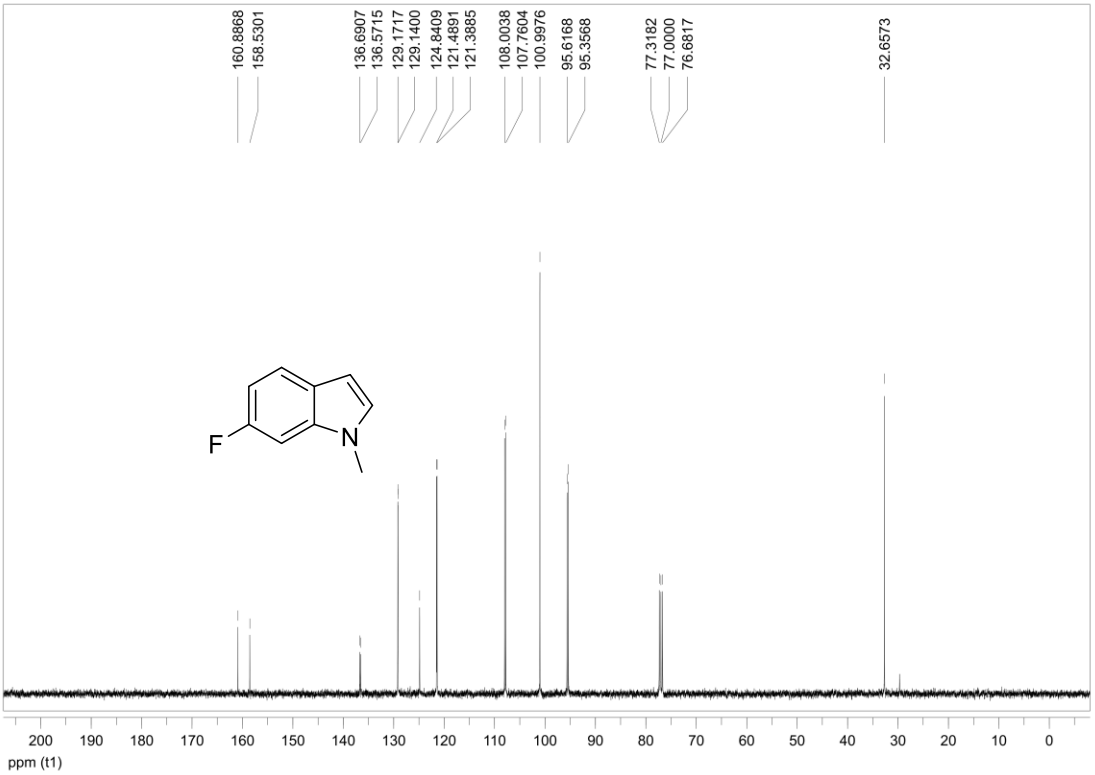


Indole **1f**

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

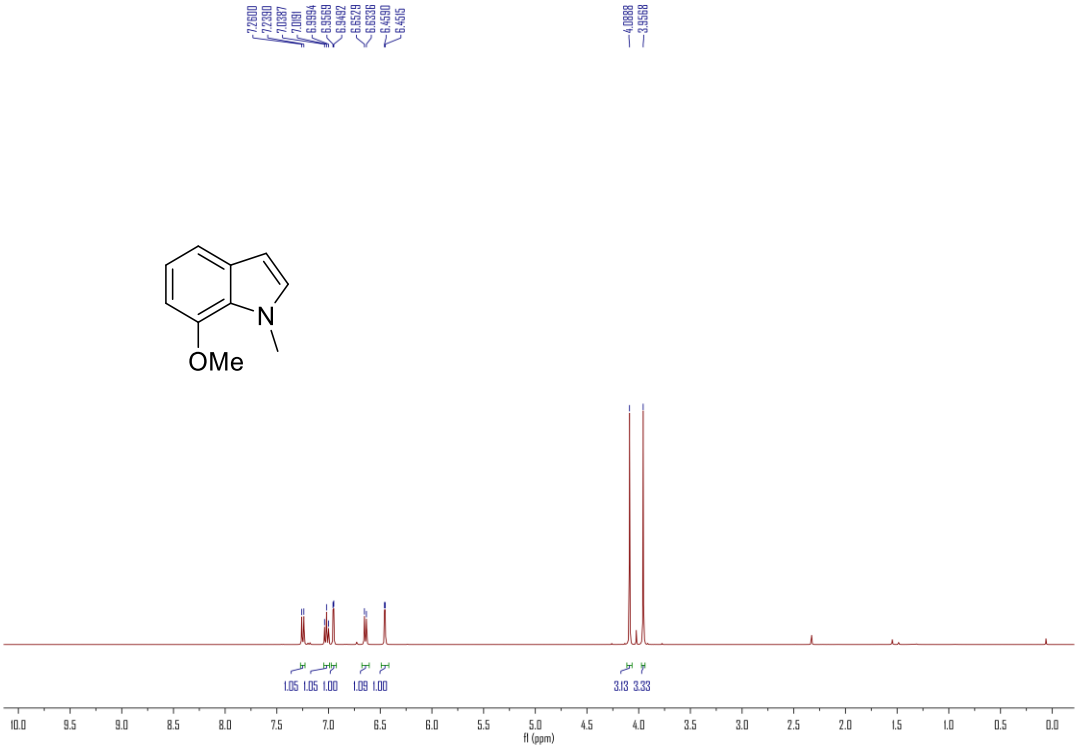


^{13}C NMR (100 MHz, $CDCl_3$)

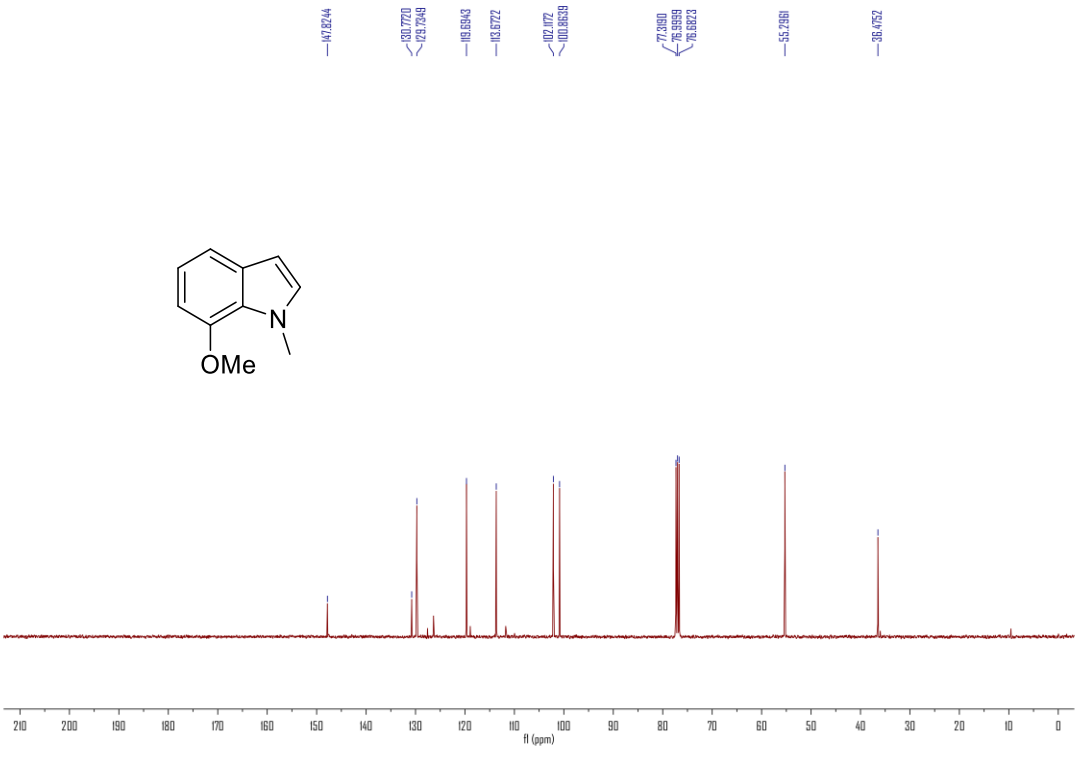


Indole **1g**

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

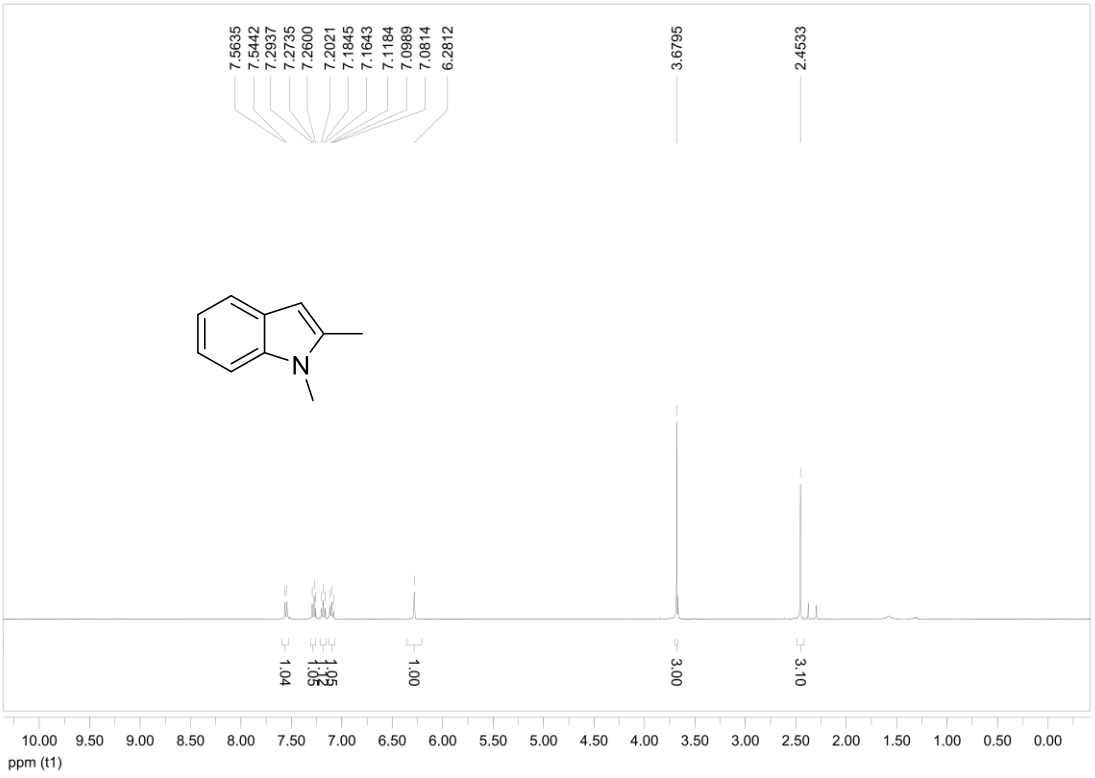


^{13}C NMR (100 MHz, $CDCl_3$)

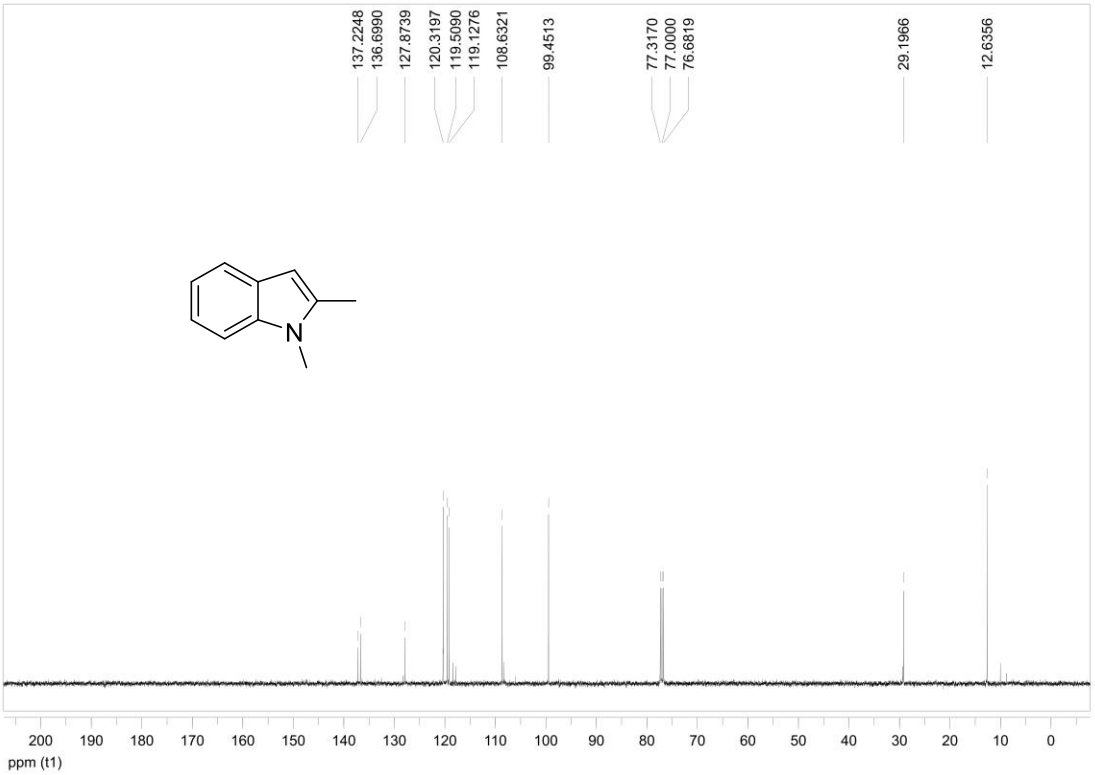


Indole **1h**

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

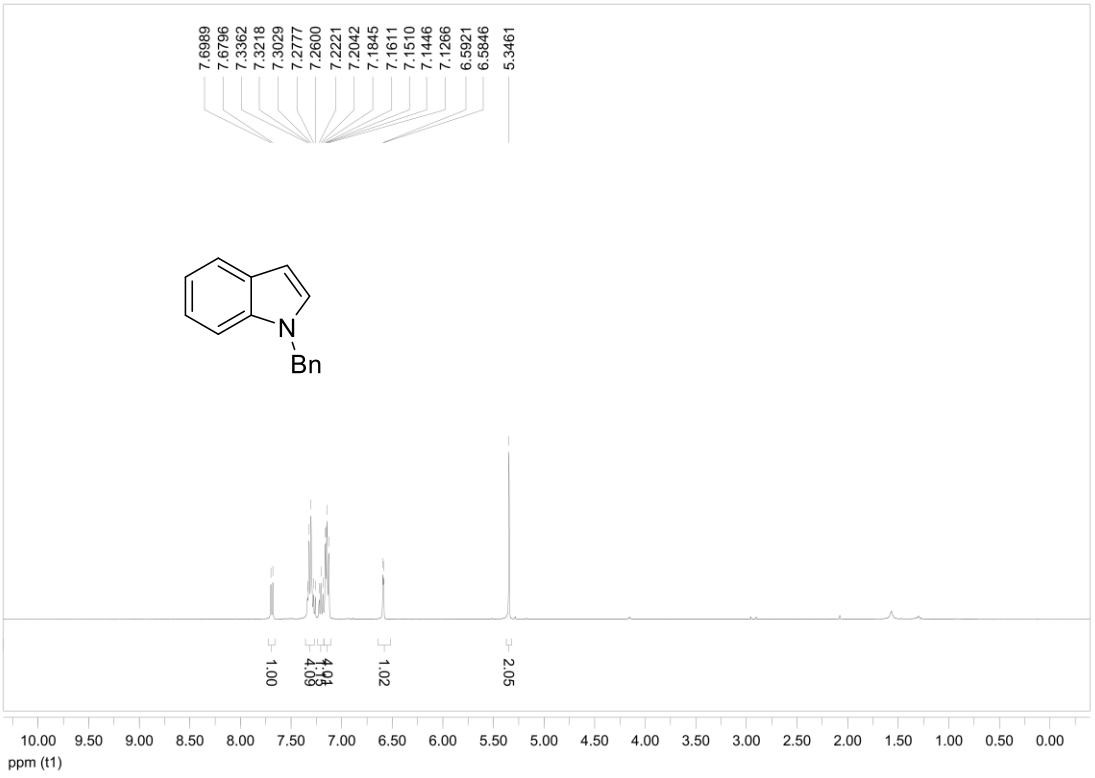


^{13}C NMR (100 MHz, $CDCl_3$)

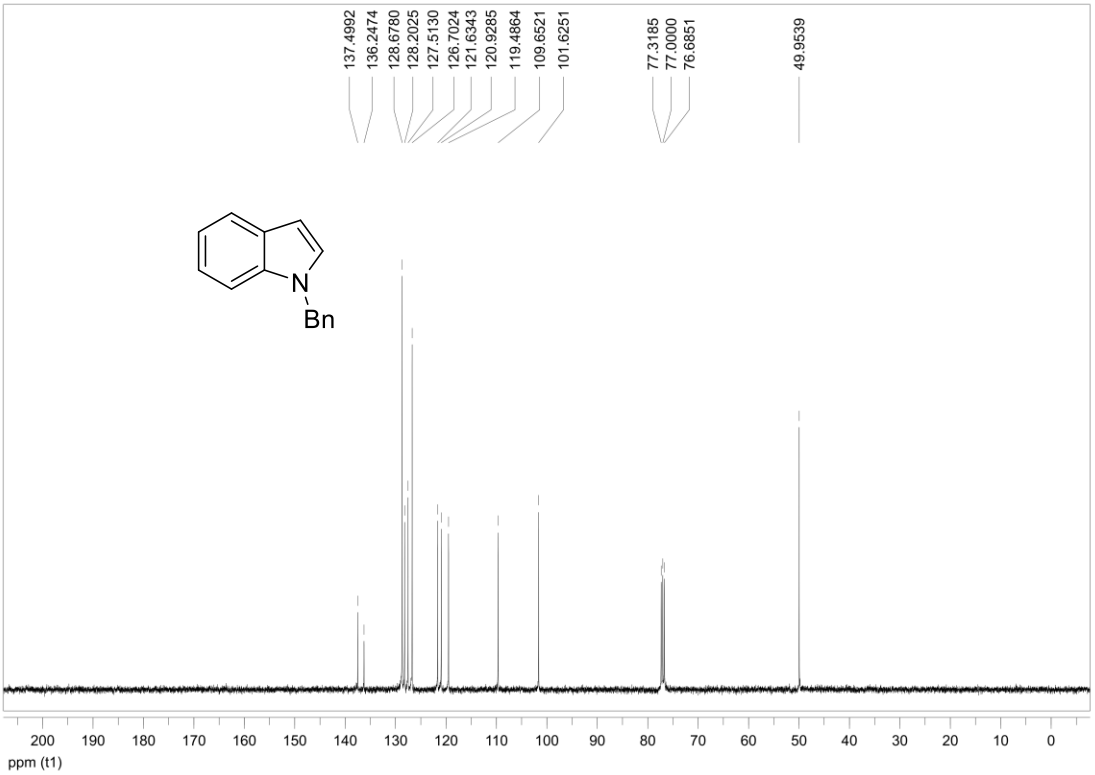


Indole **1i**

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

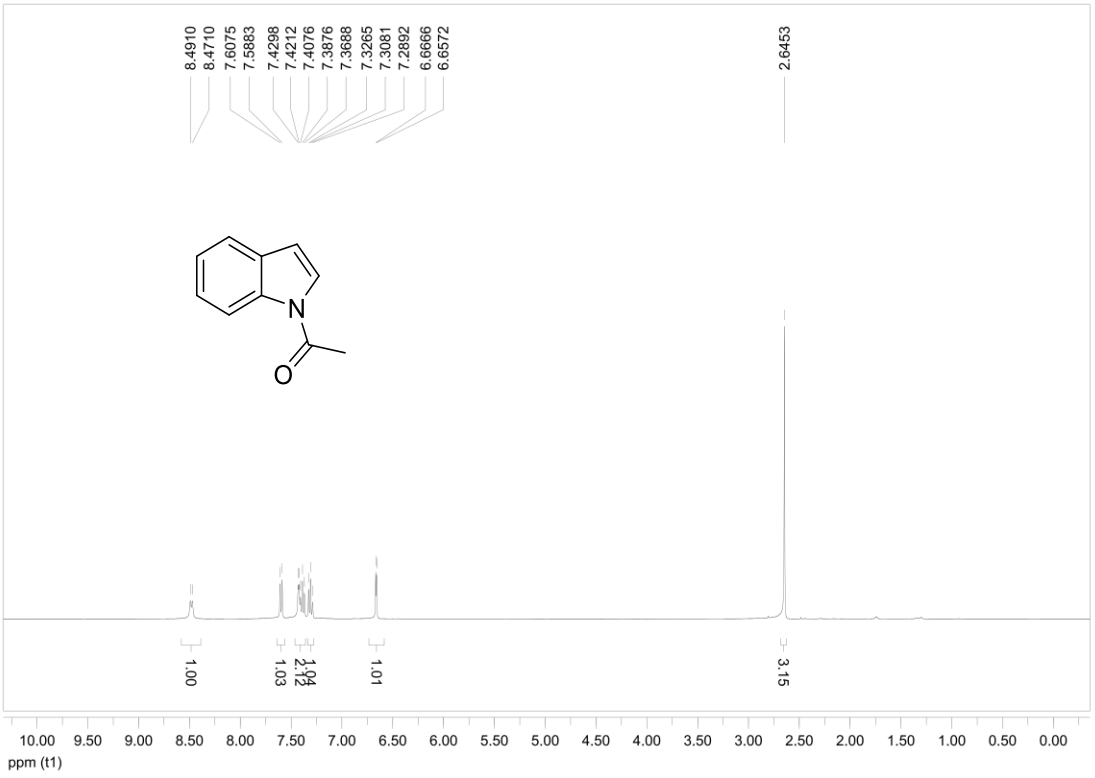


^{13}C NMR (100 MHz, $CDCl_3$)

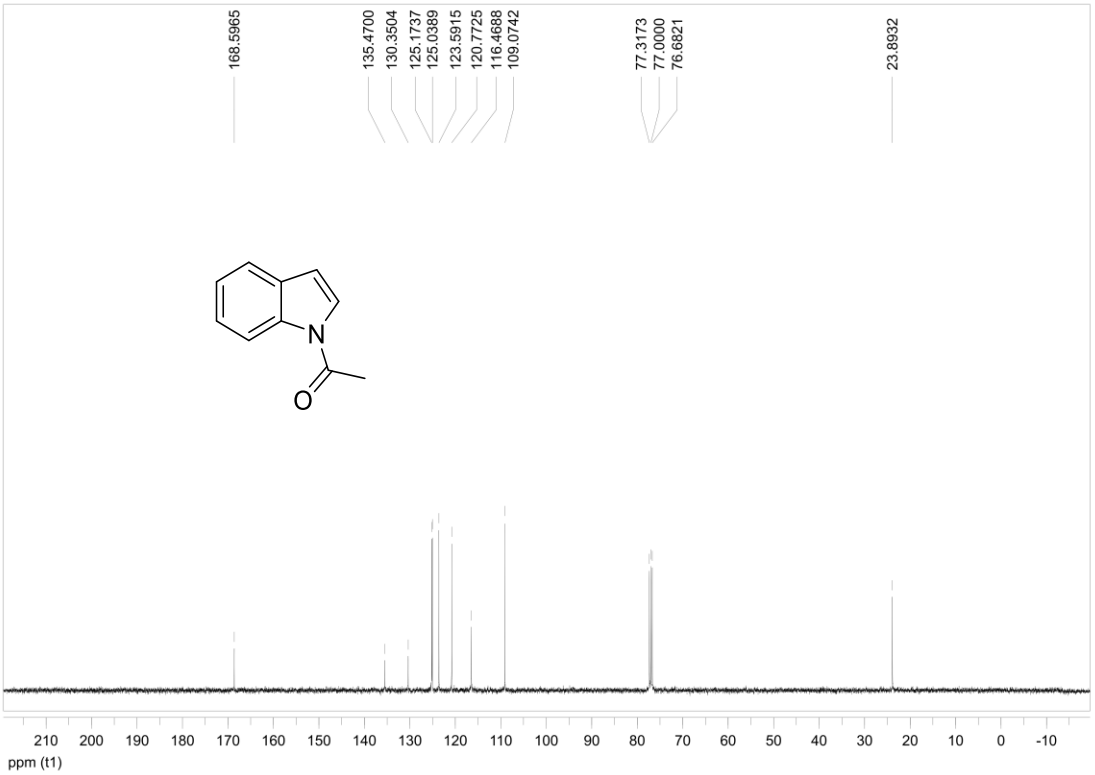


Indole **1j**

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

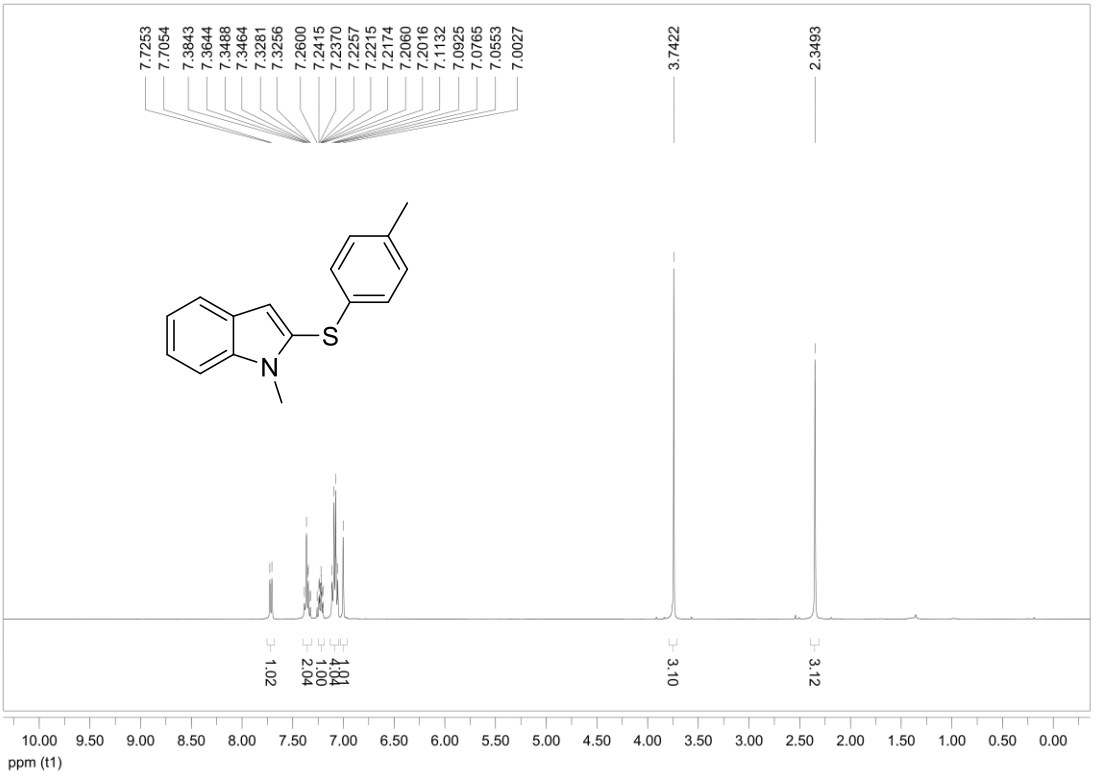


^{13}C NMR (100 MHz, $CDCl_3$)

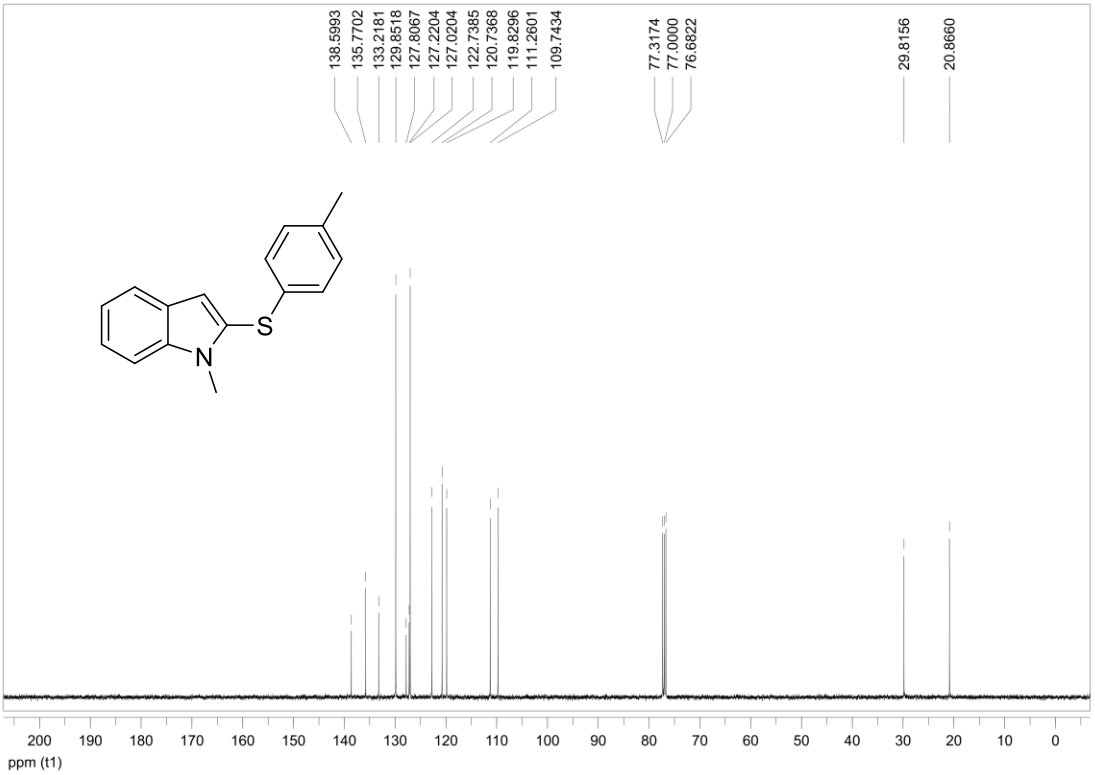


C2-Thioindole **3a**

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

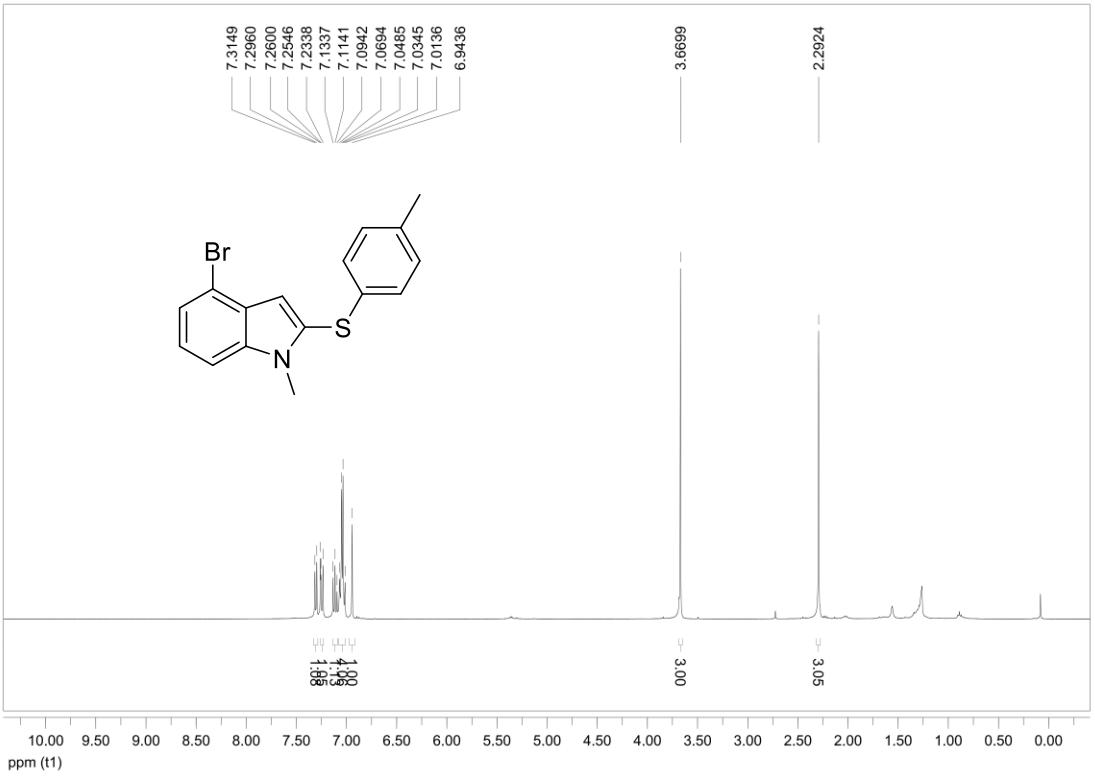


^{13}C NMR (100 MHz, $CDCl_3$)

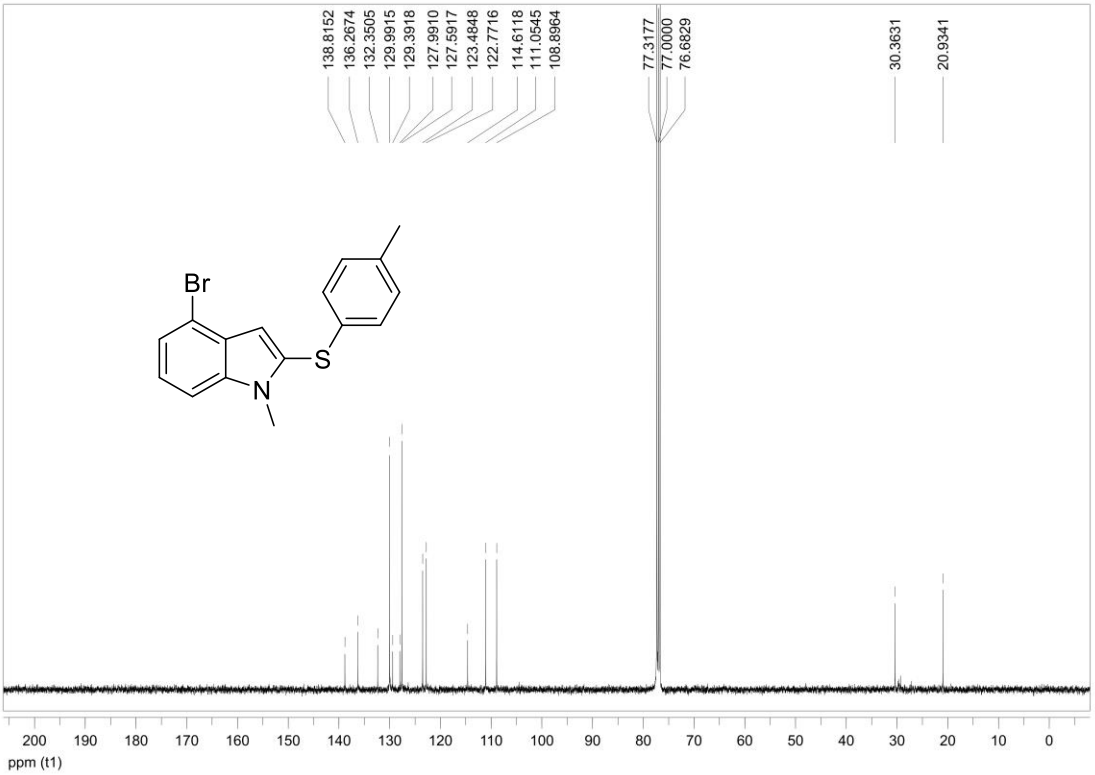


C2-Thioindole **3b**

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

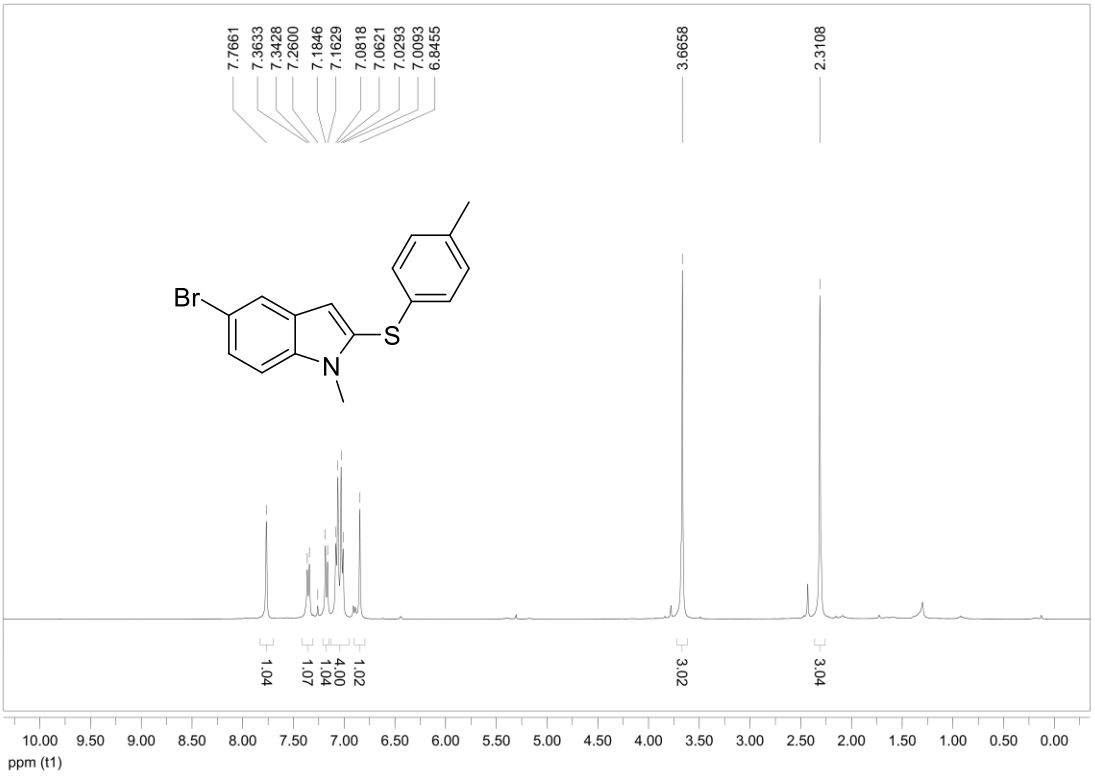


^{13}C NMR (100 MHz, $CDCl_3$)

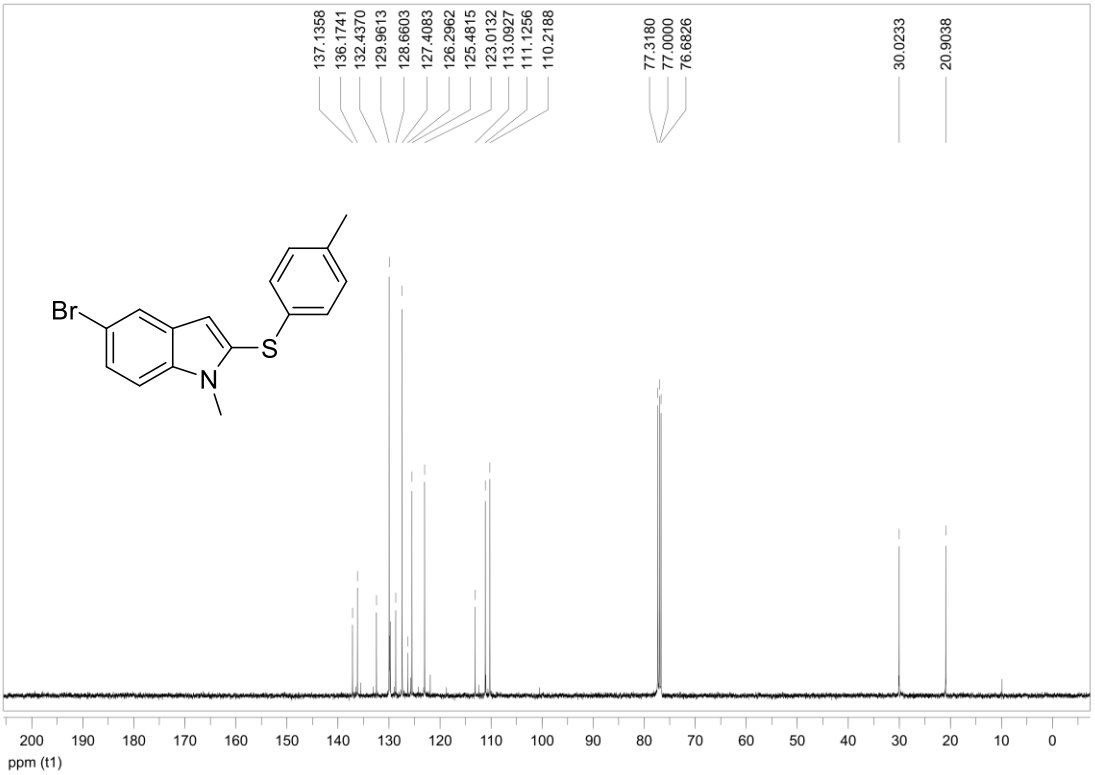


C2-Thioindole **3c**

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

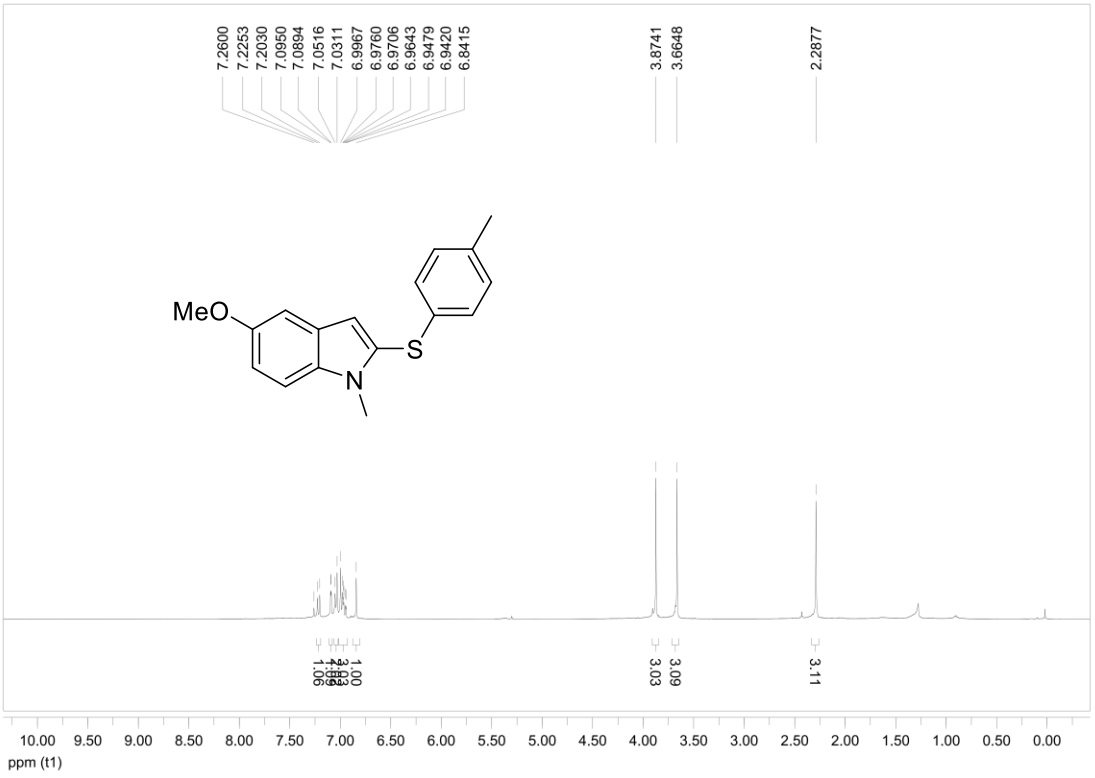


^{13}C NMR (100 MHz, $CDCl_3$)

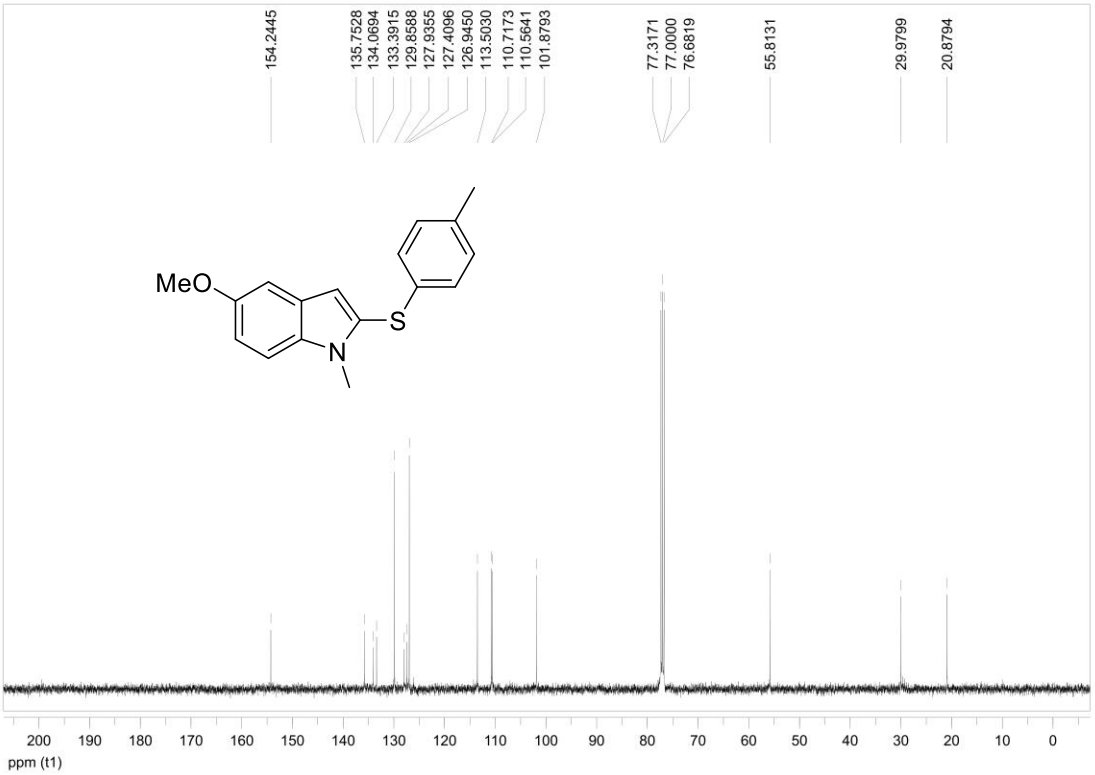


C2-Thioindole **3d**

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

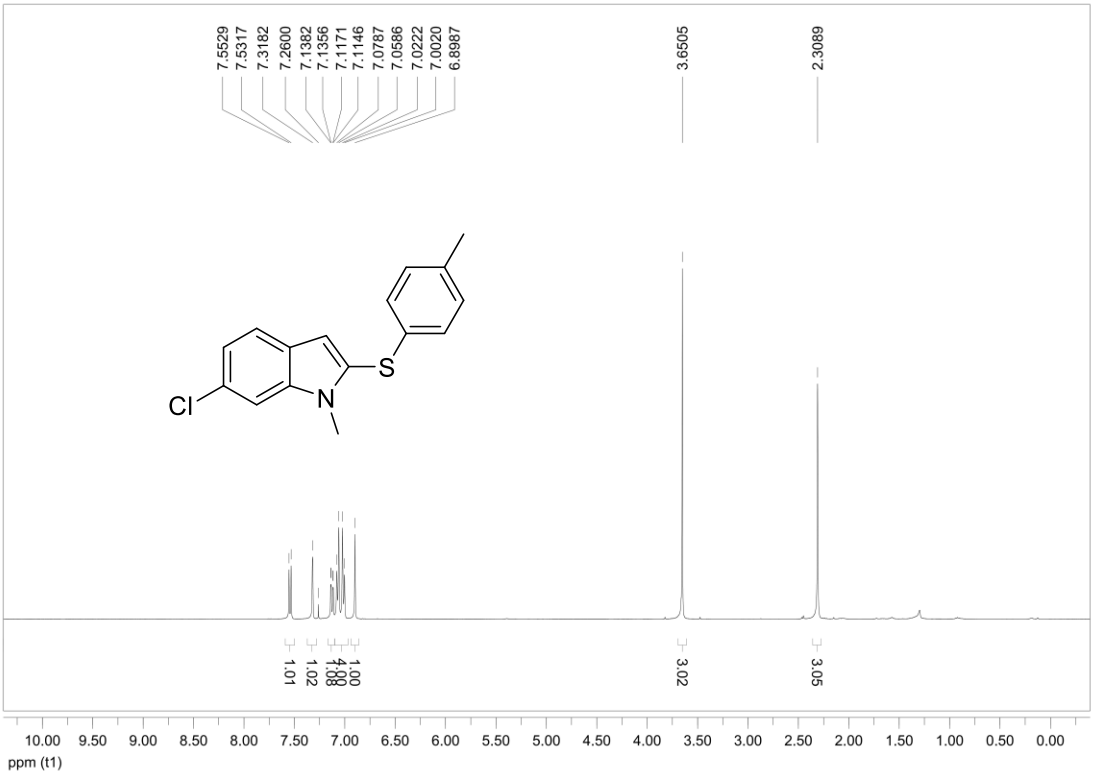


^{13}C NMR (100 MHz, $CDCl_3$)

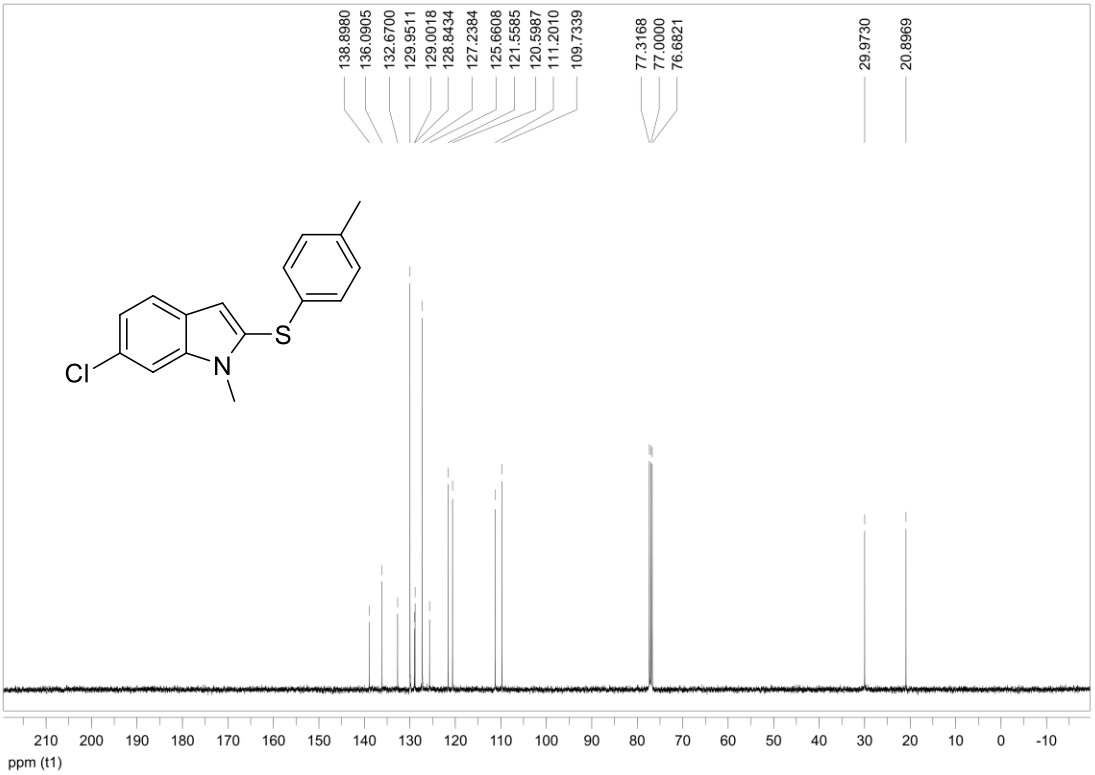


C2-Thioindole **3e**

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

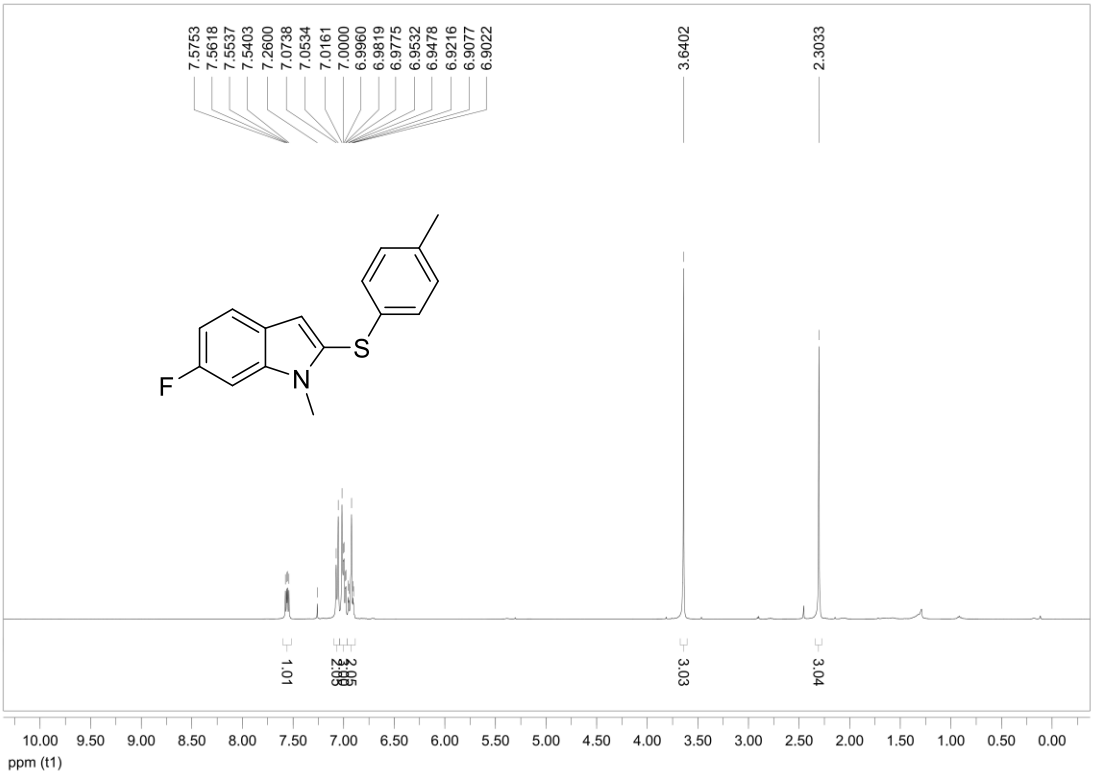


^{13}C NMR (100 MHz, $CDCl_3$)

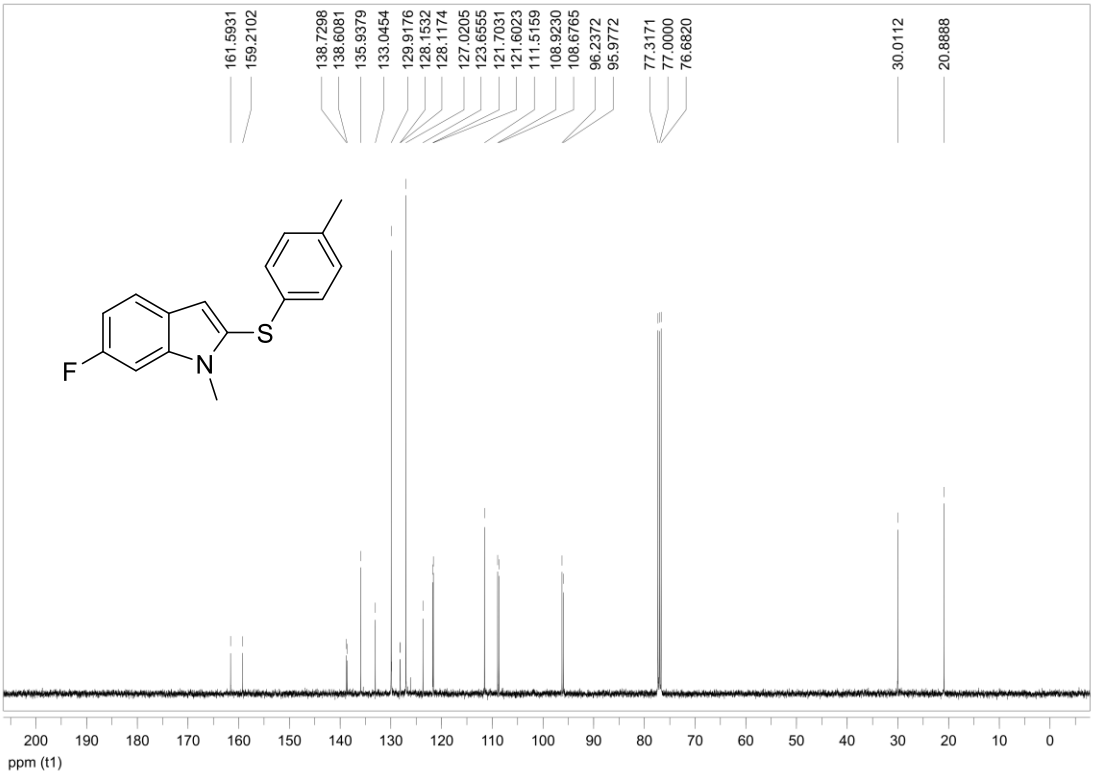


C2-Thioindole **3f**

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

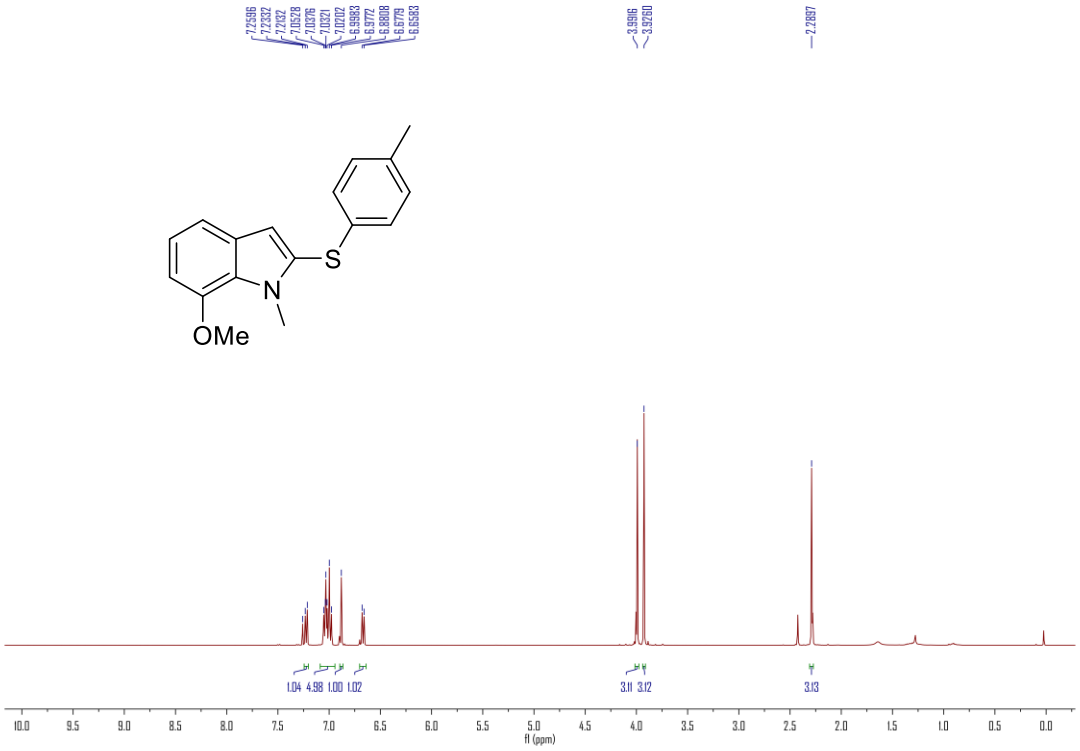


^{13}C NMR (100 MHz, $CDCl_3$)

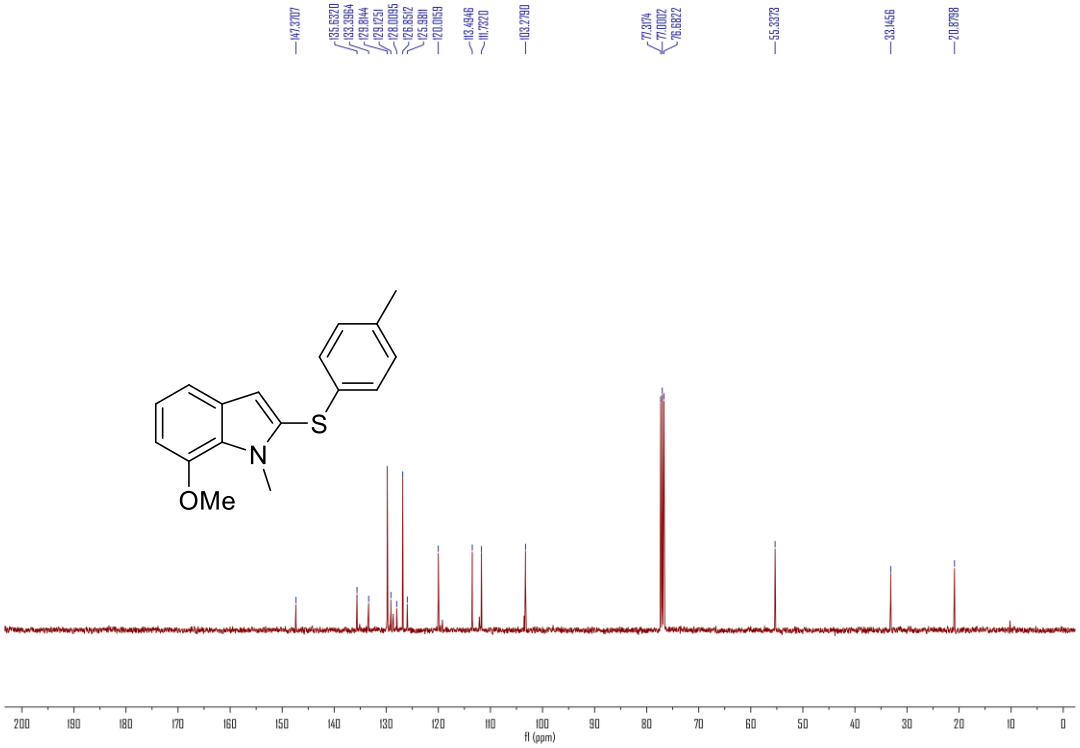


C2-Thioindole **3g**

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

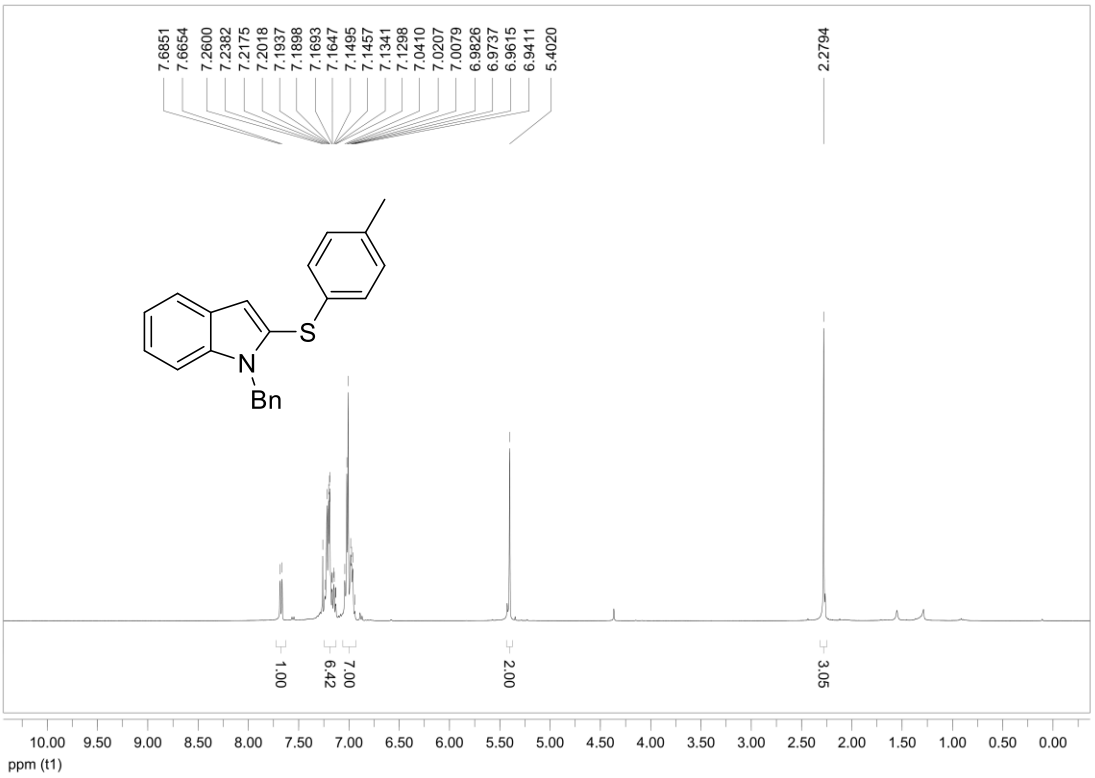


^{13}C NMR (100 MHz, $CDCl_3$)

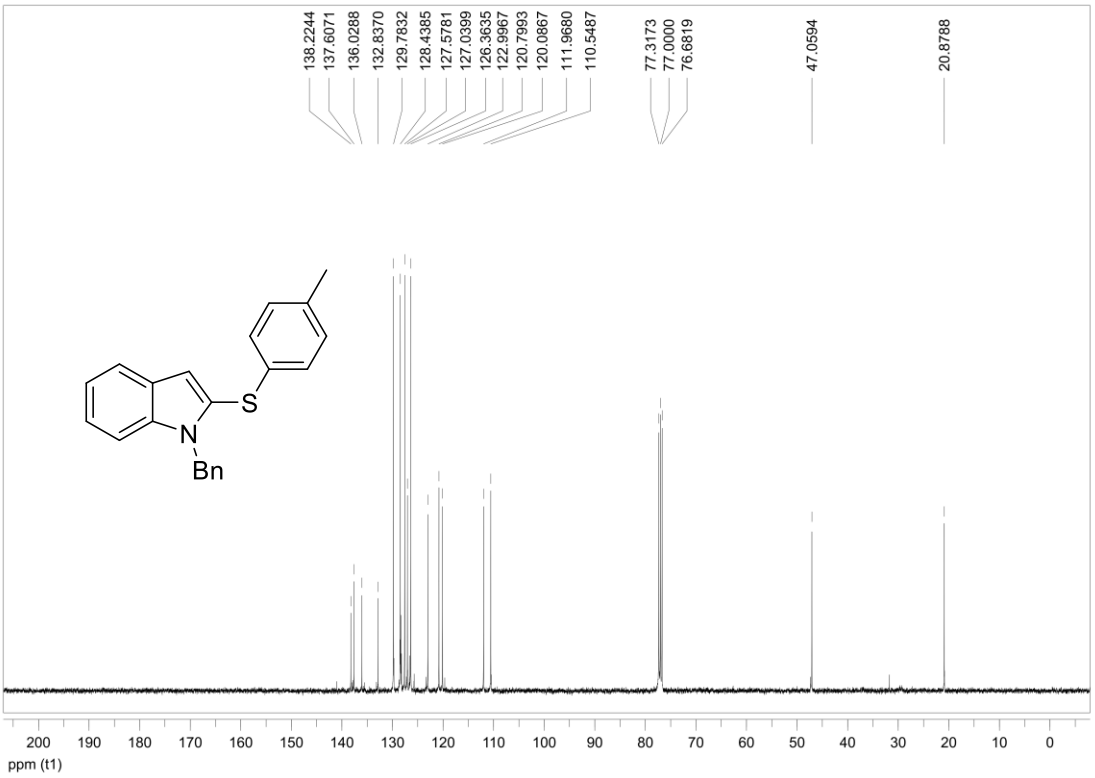


C2-Thioindole **3h**

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

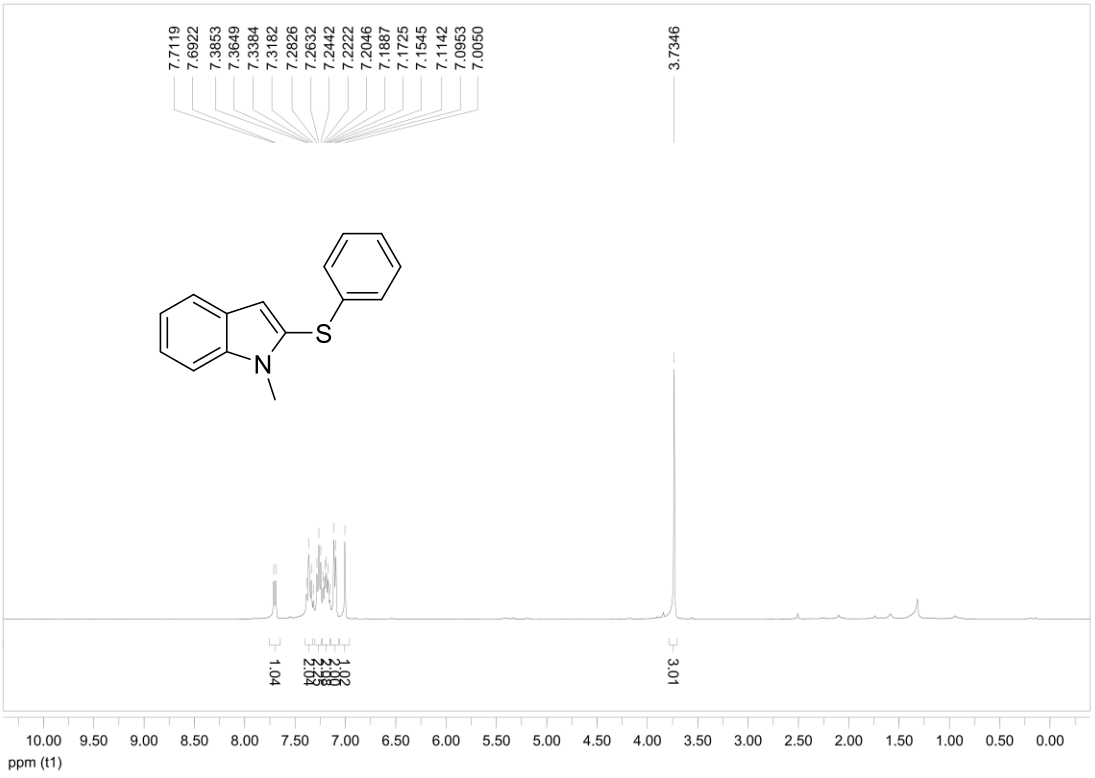


^{13}C NMR (100 MHz, $CDCl_3$)

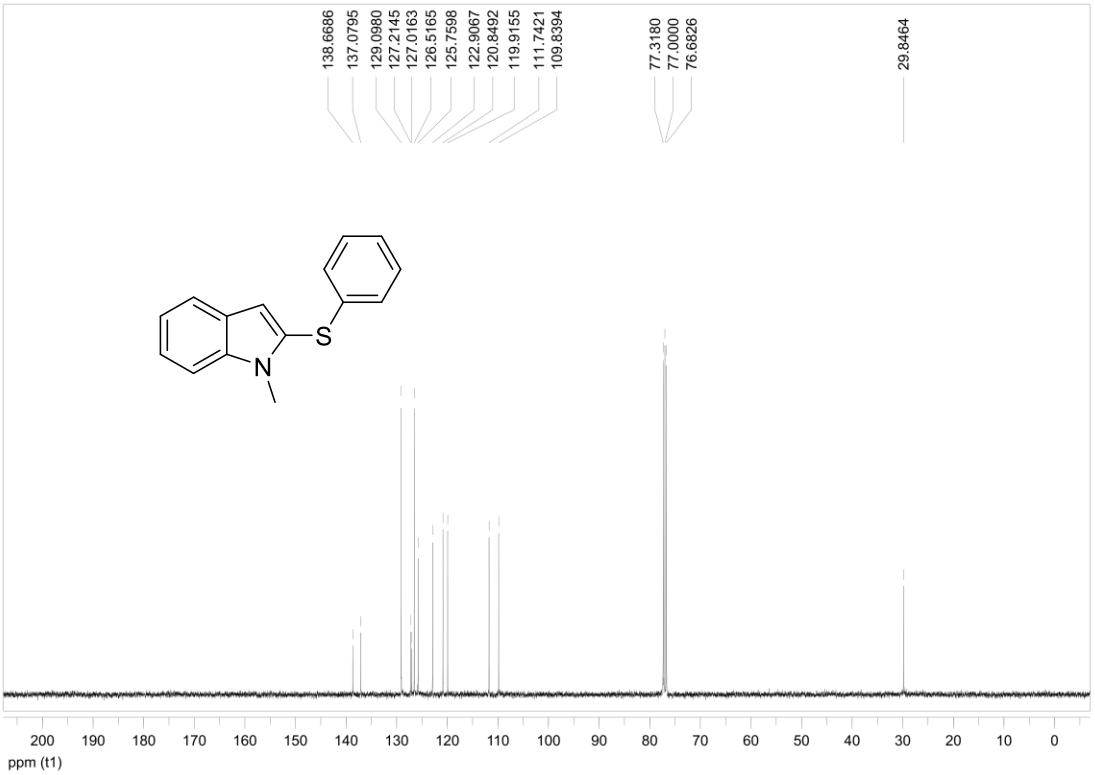


C2-Thioindole **3j**

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

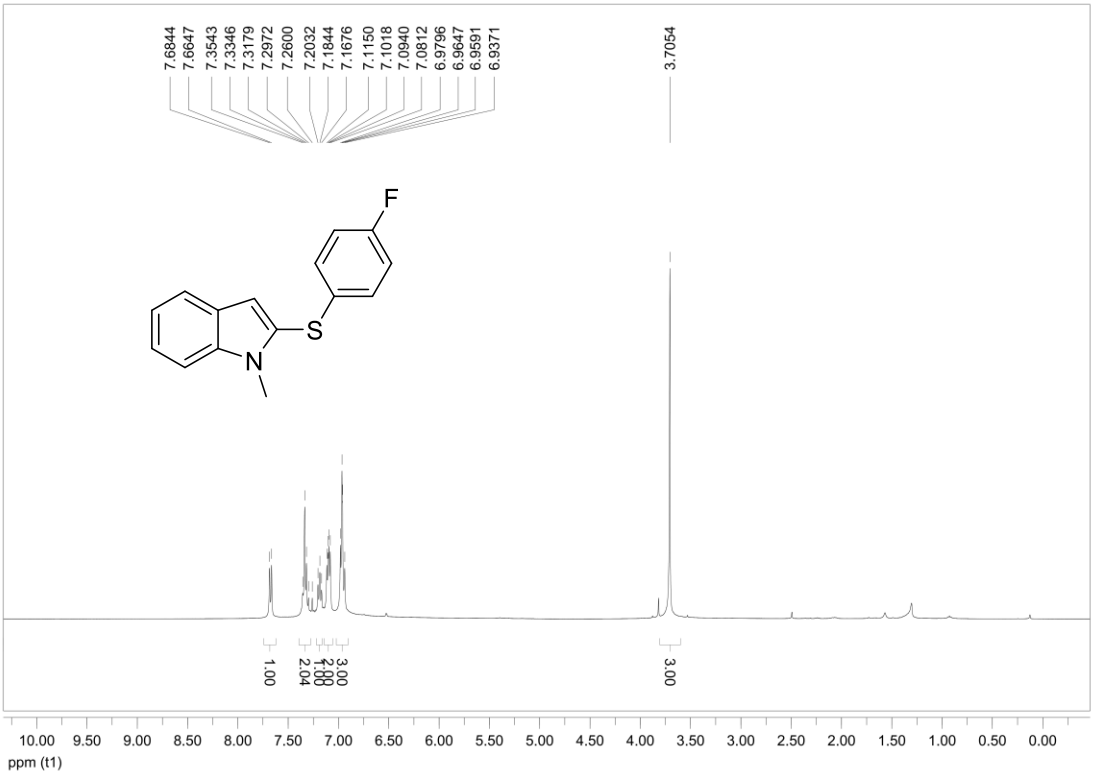


^{13}C NMR (100 MHz, $CDCl_3$)

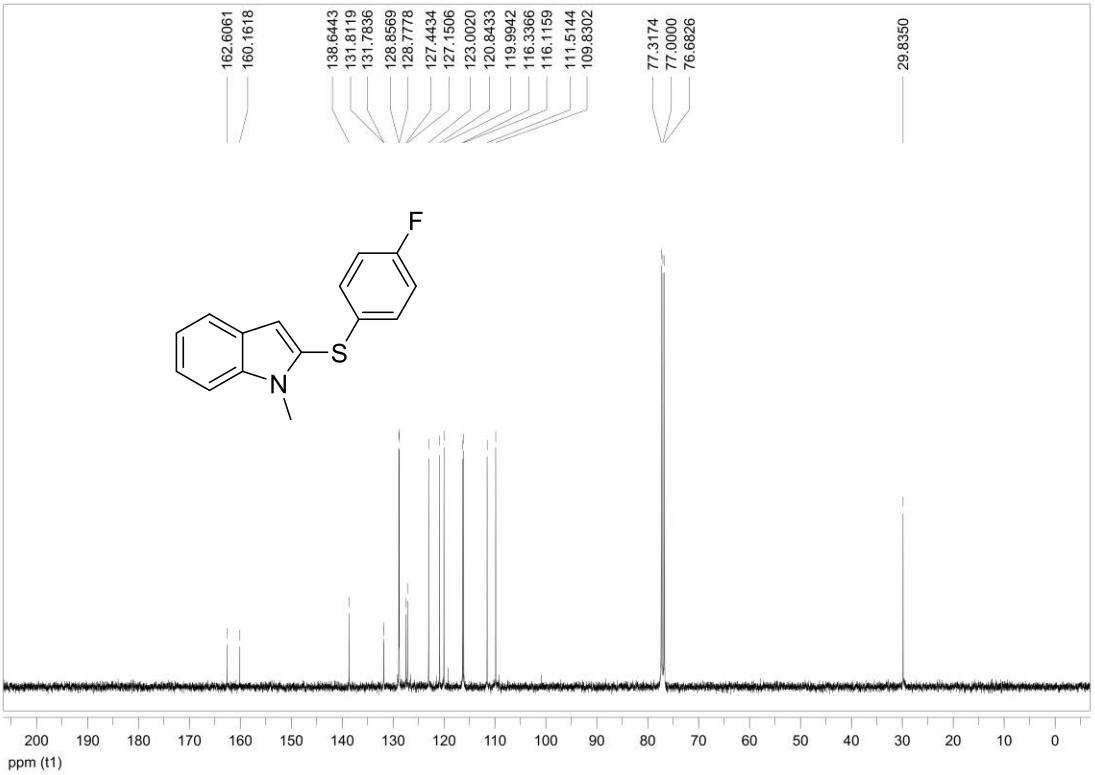


C2-Thioindole **3k**

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

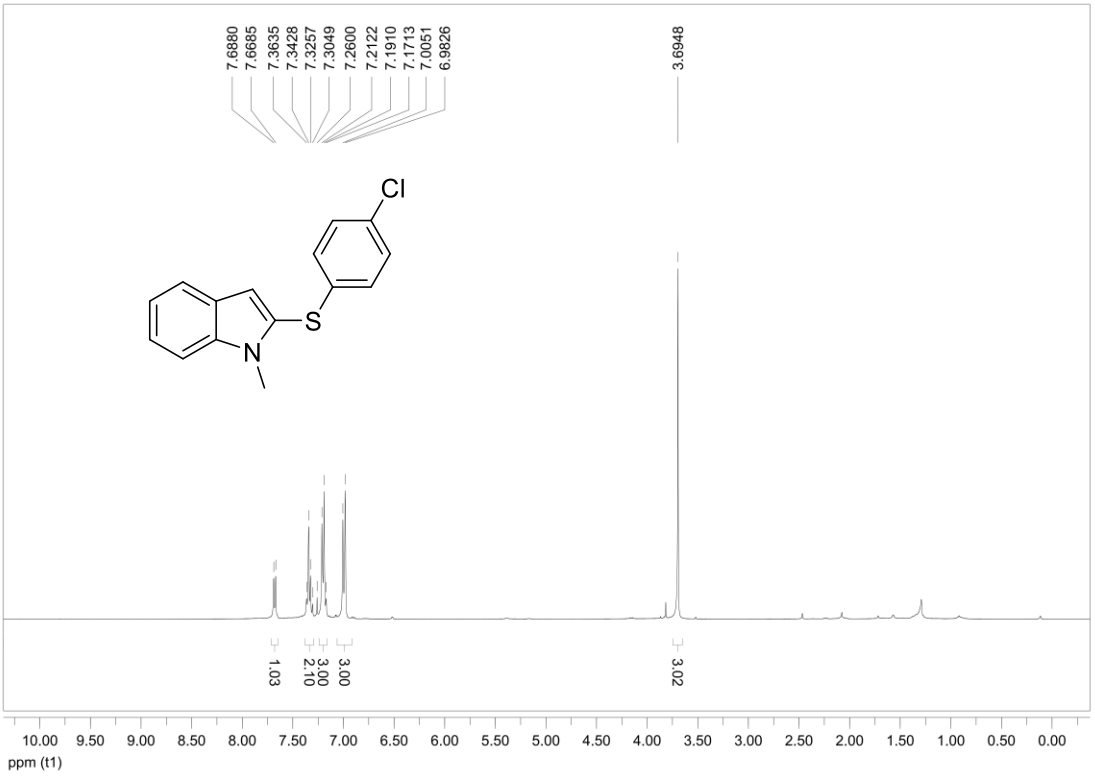


^{13}C NMR (100 MHz, $CDCl_3$)

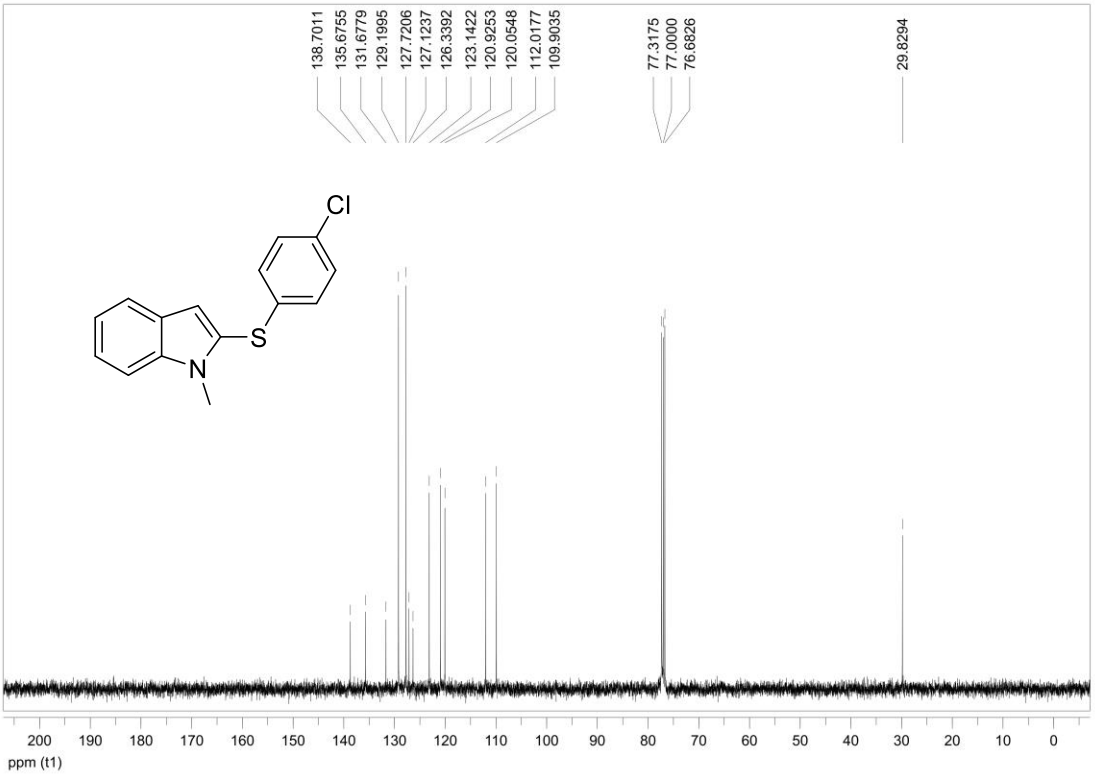


C2-Thioindole **3l**

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

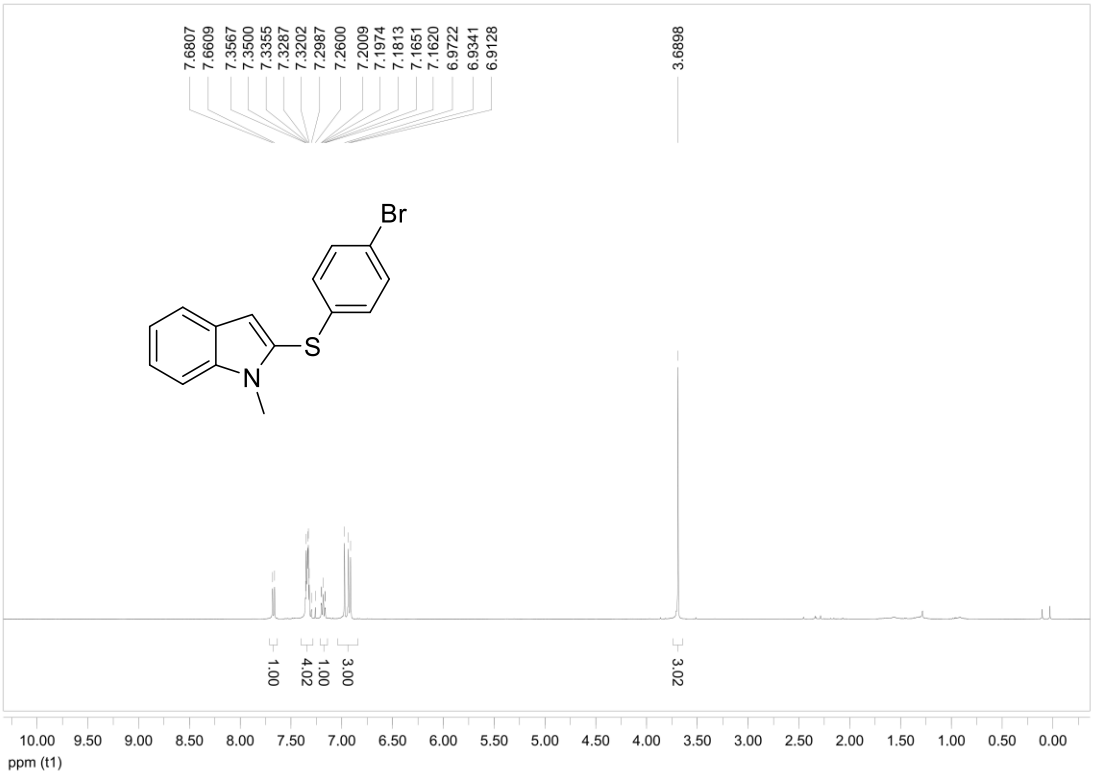


^{13}C NMR (100 MHz, $CDCl_3$)

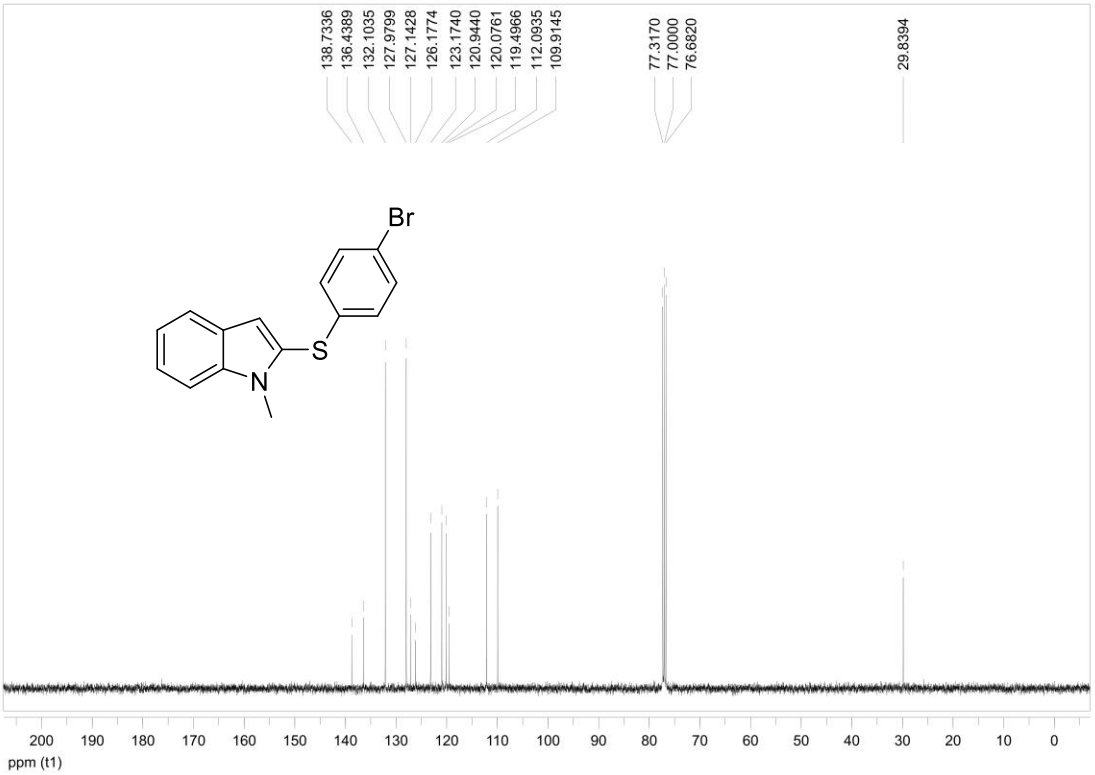


C2-Thioindole **3m**

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

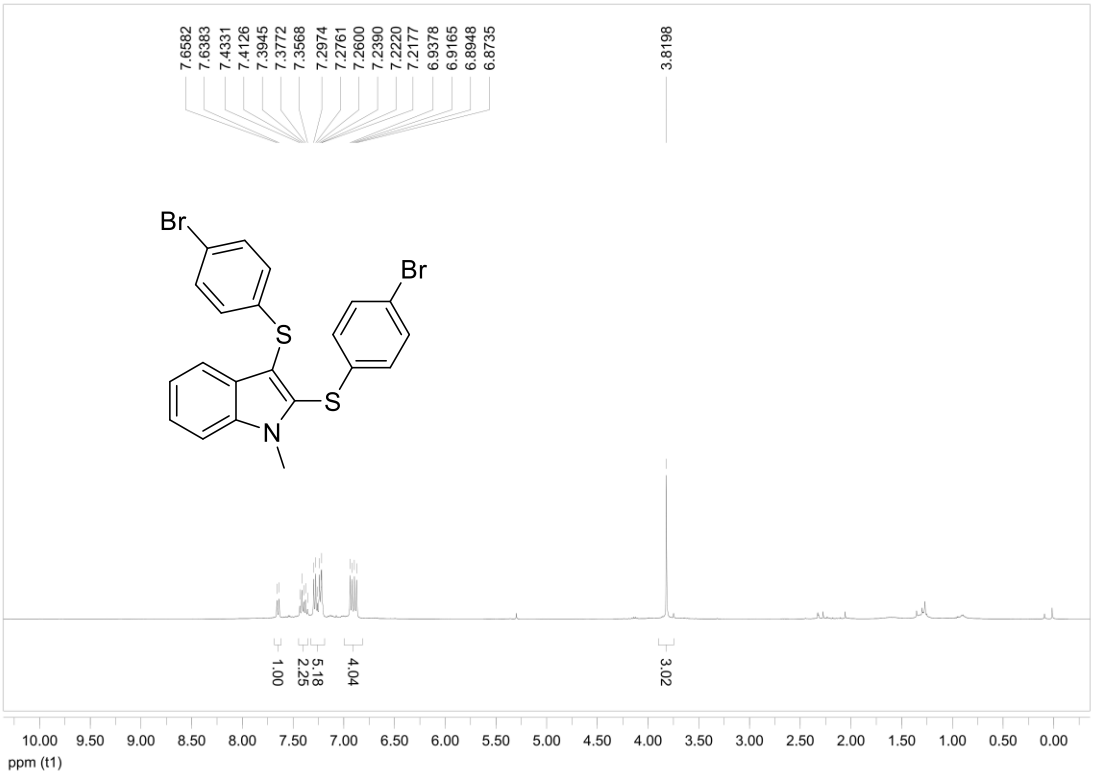


^{13}C NMR (100 MHz, $CDCl_3$)

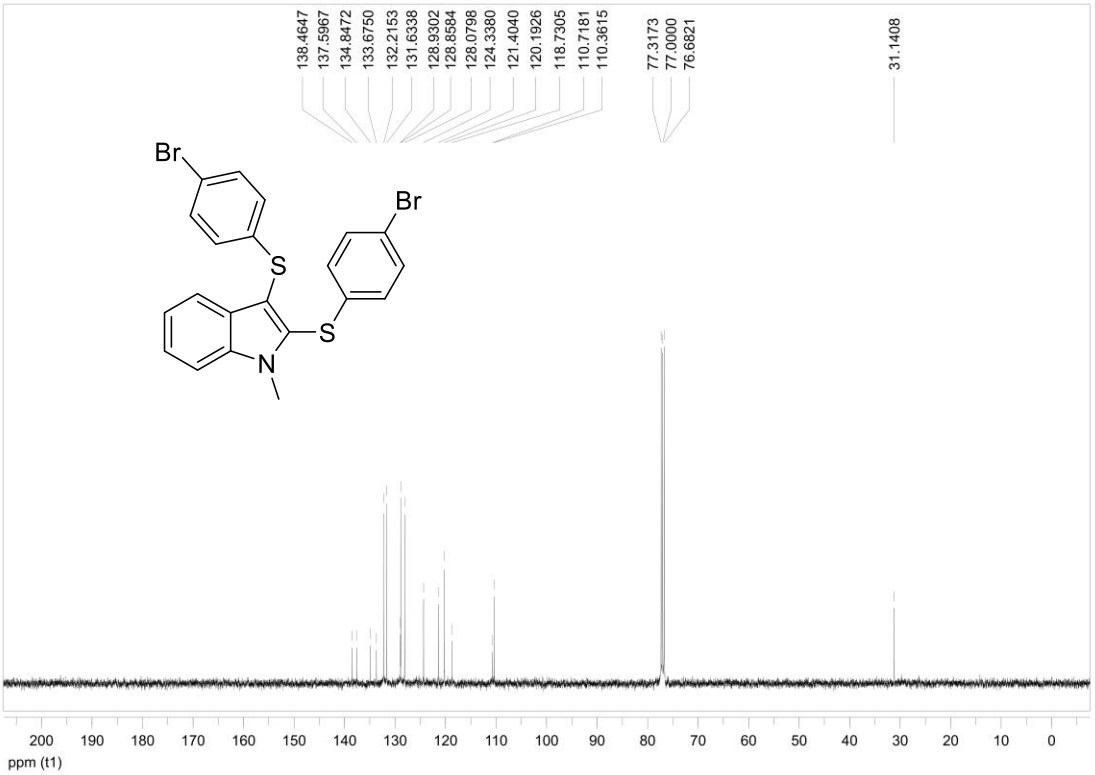


2,3-bis-Thioindole **5m**

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

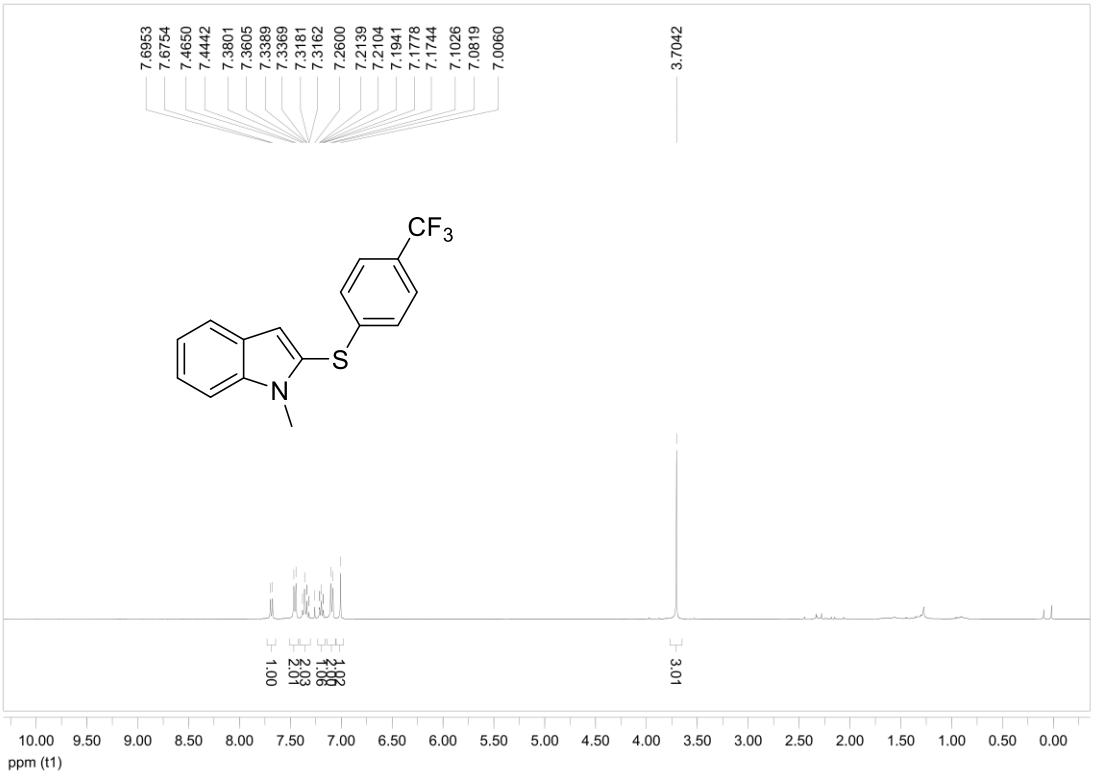


^{13}C NMR (100 MHz, $CDCl_3$)

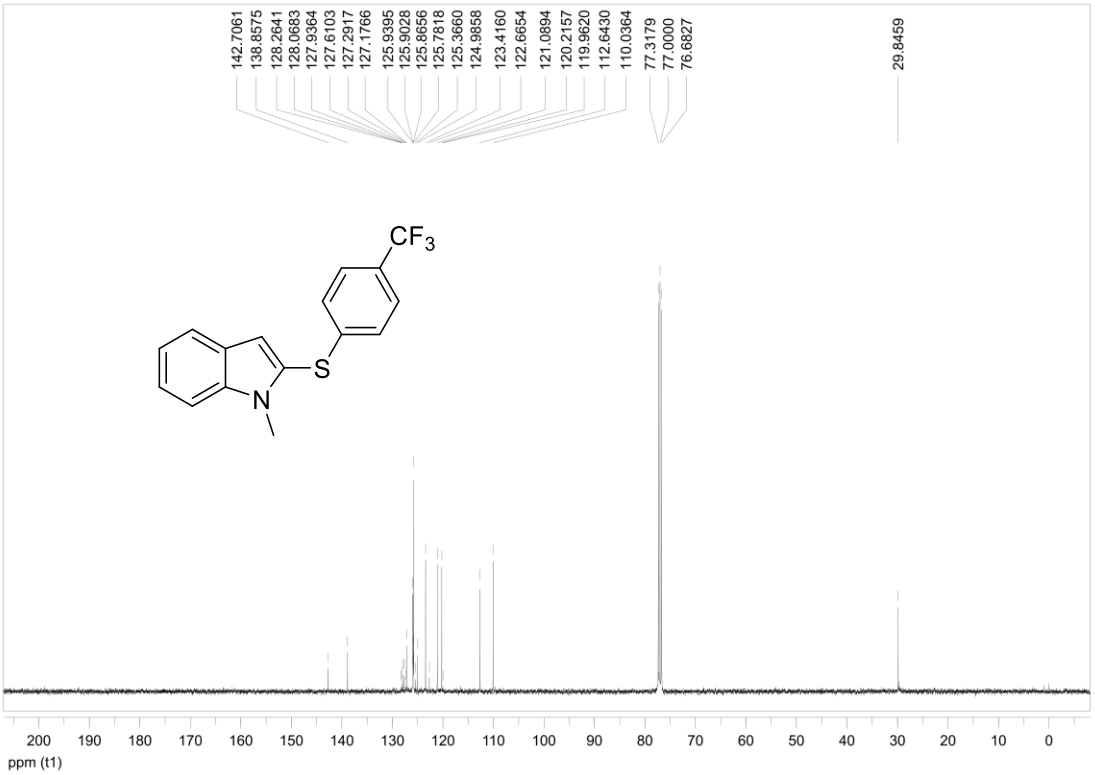


C2-Thioindole **3n**

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

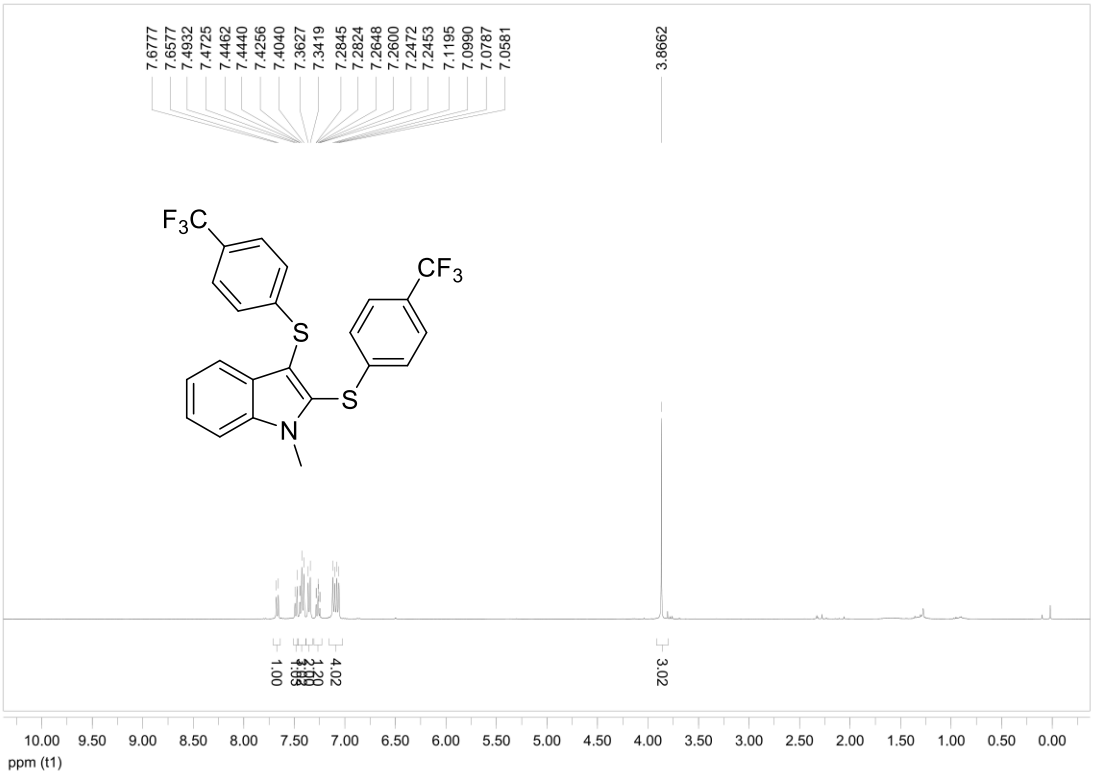


^{13}C NMR (100 MHz, $CDCl_3$)

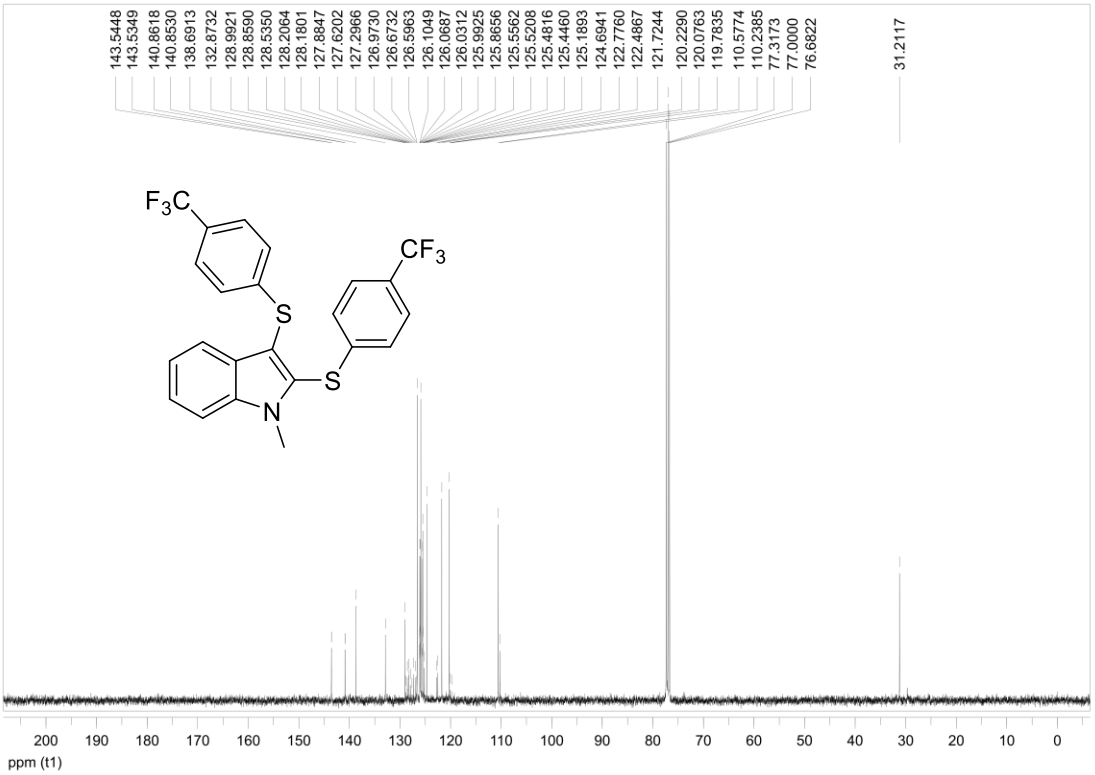


2,3-bis-Thioindole **5n**

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

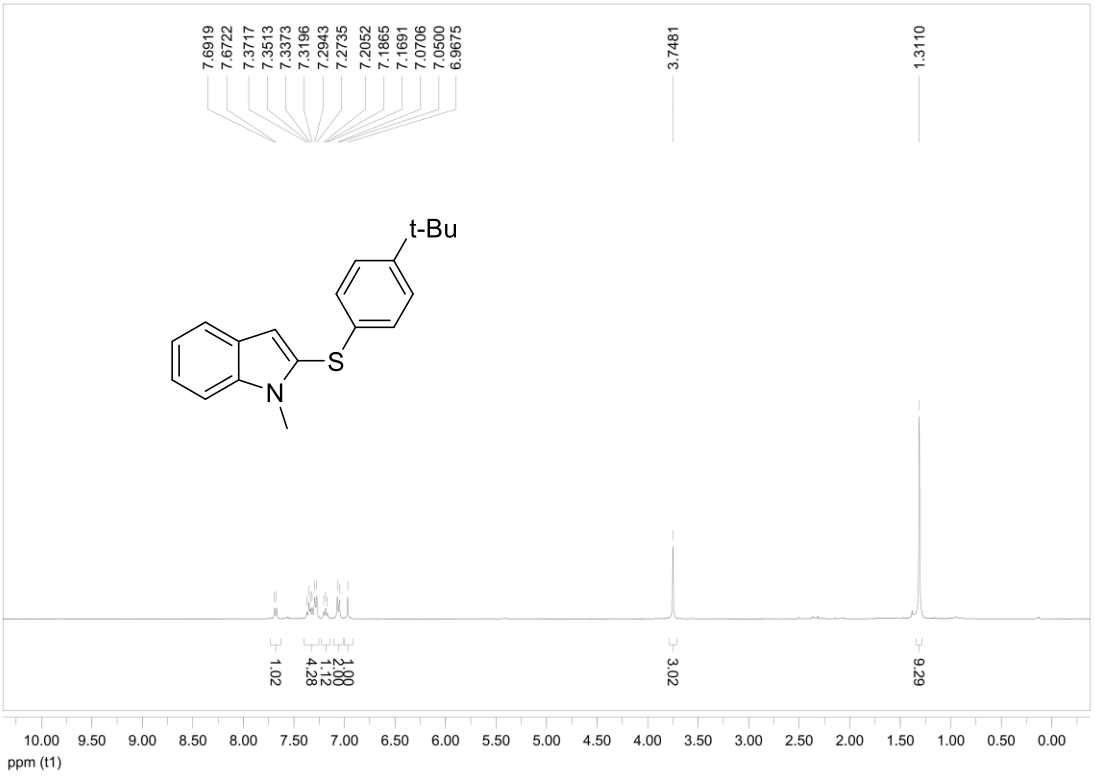


^{13}C NMR (100 MHz, $CDCl_3$)

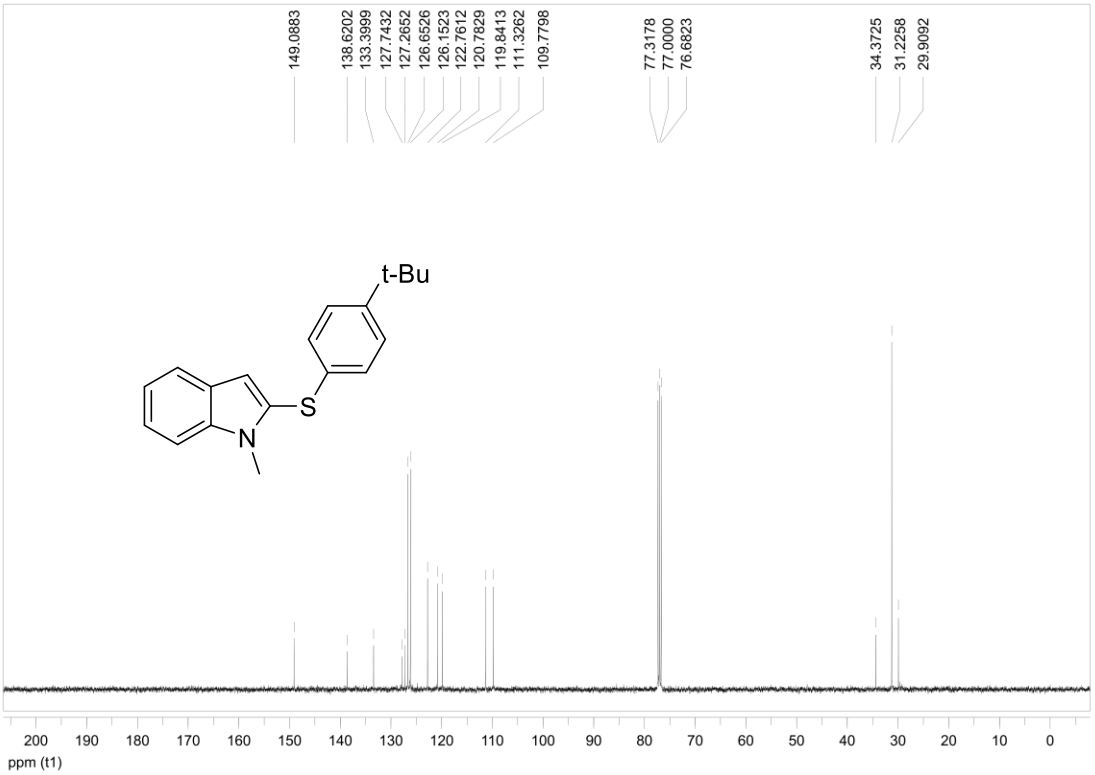


C2-Thioindole **3o**

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

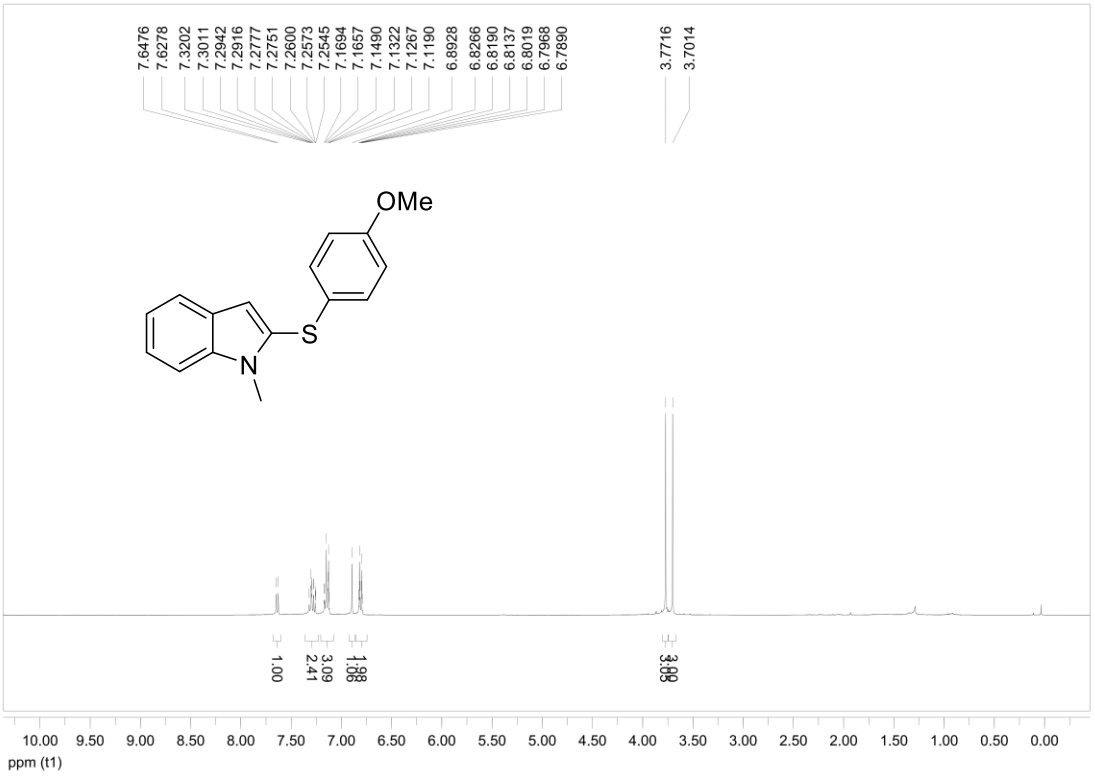


^{13}C NMR (100 MHz, $CDCl_3$)

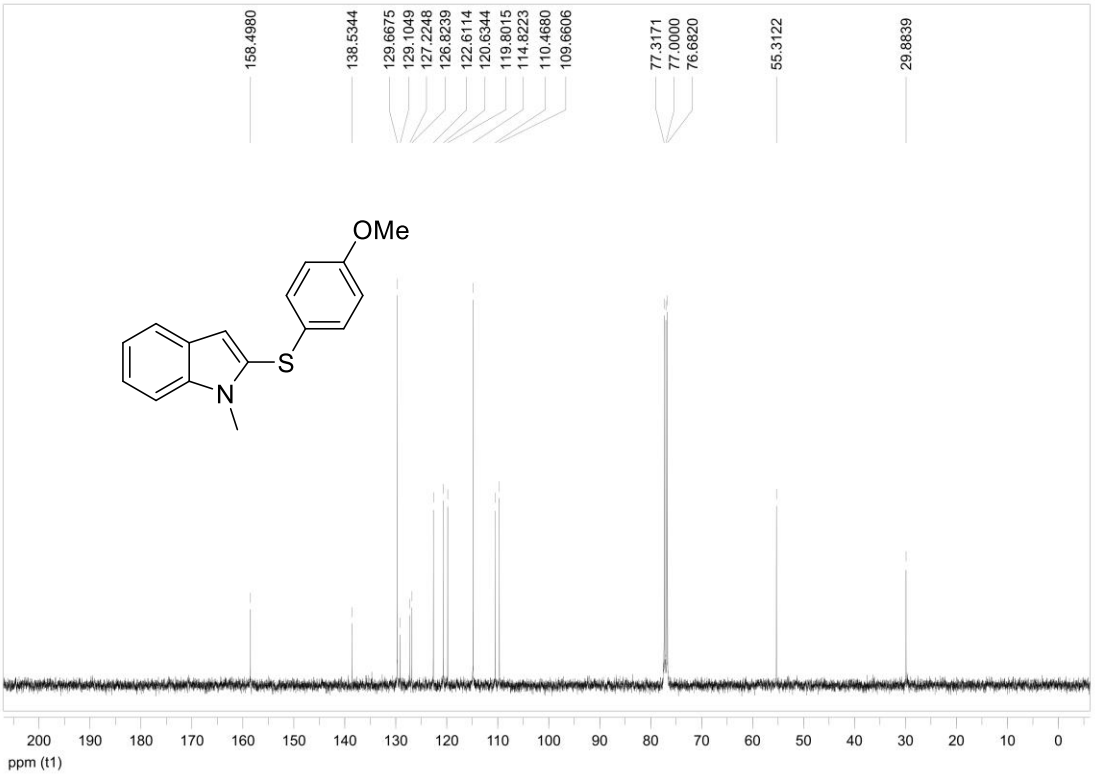


C2-Thioindole **3p**

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

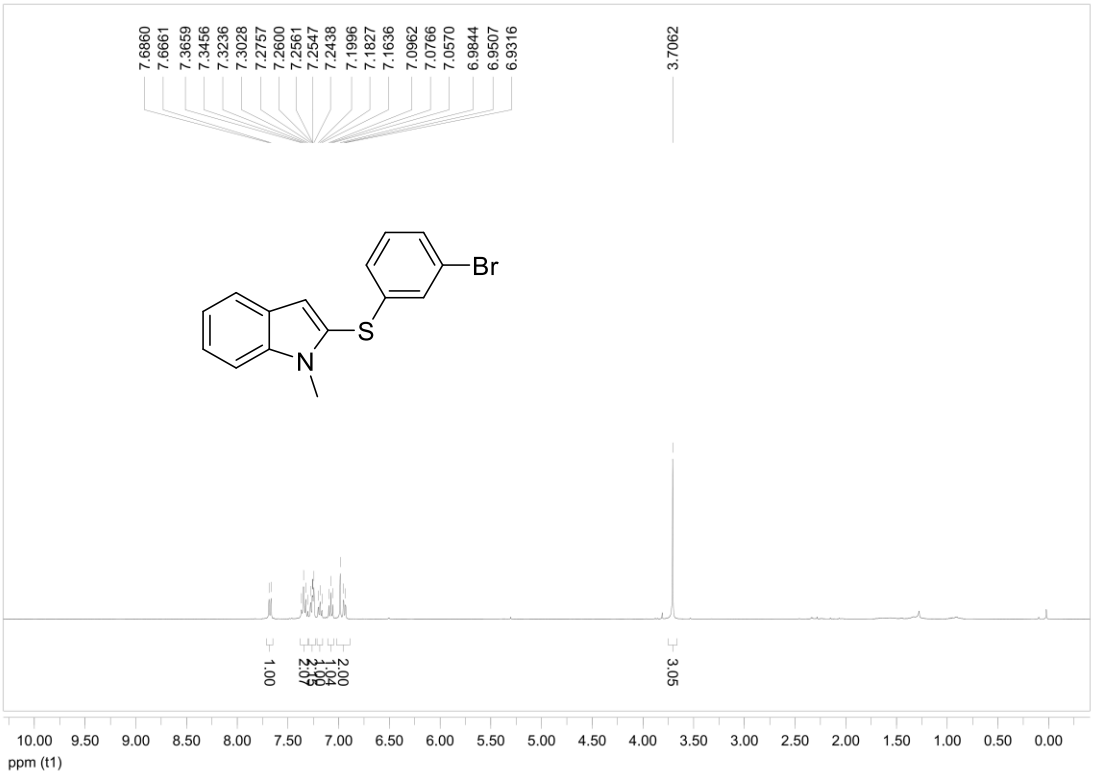


^{13}C NMR (100 MHz, $CDCl_3$)

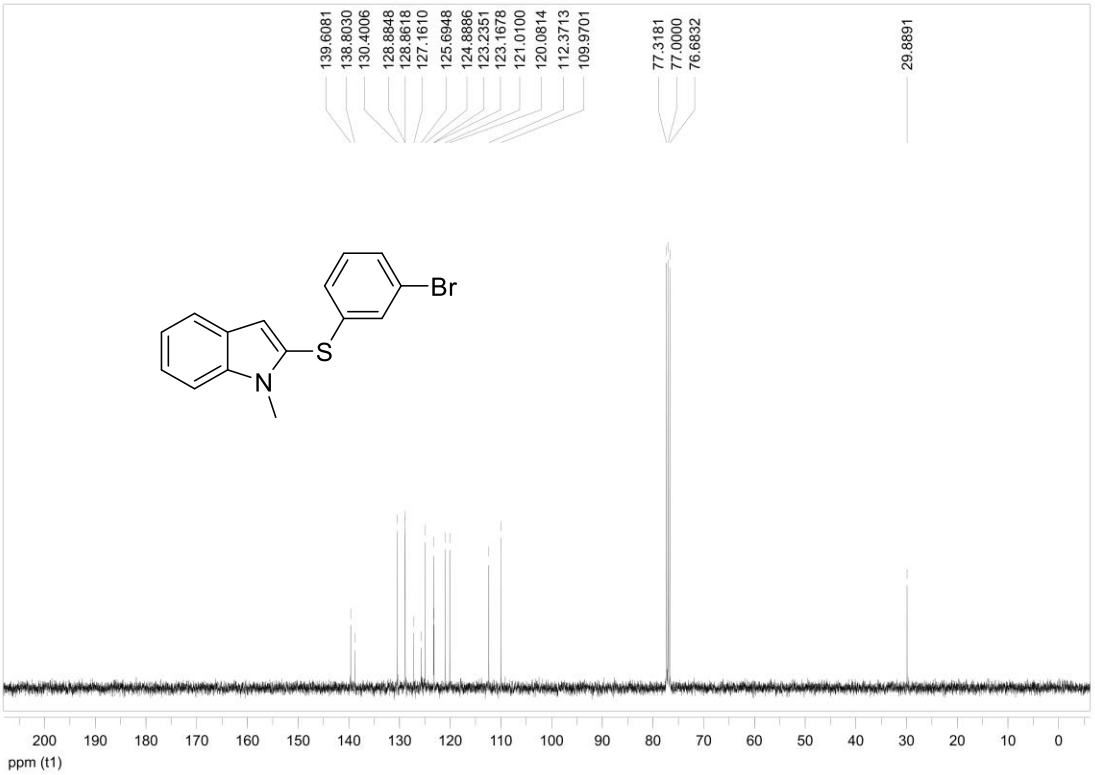


C2-Thioindole **3q**

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

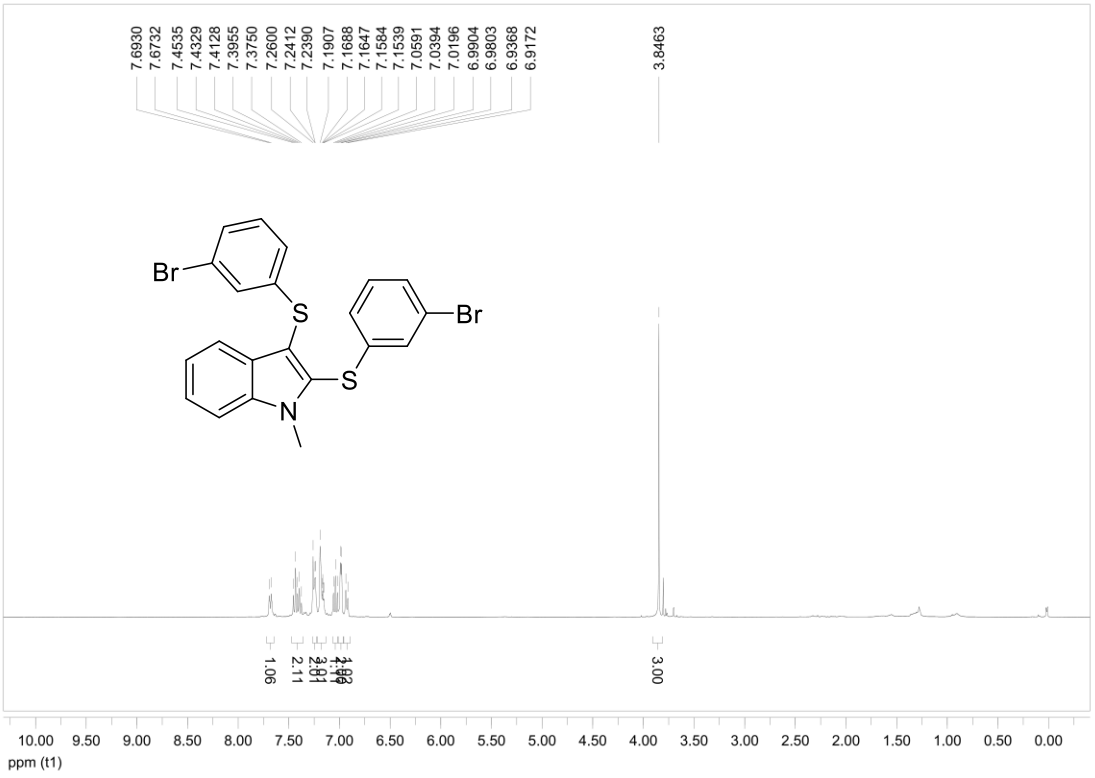


^{13}C NMR (100 MHz, $CDCl_3$)

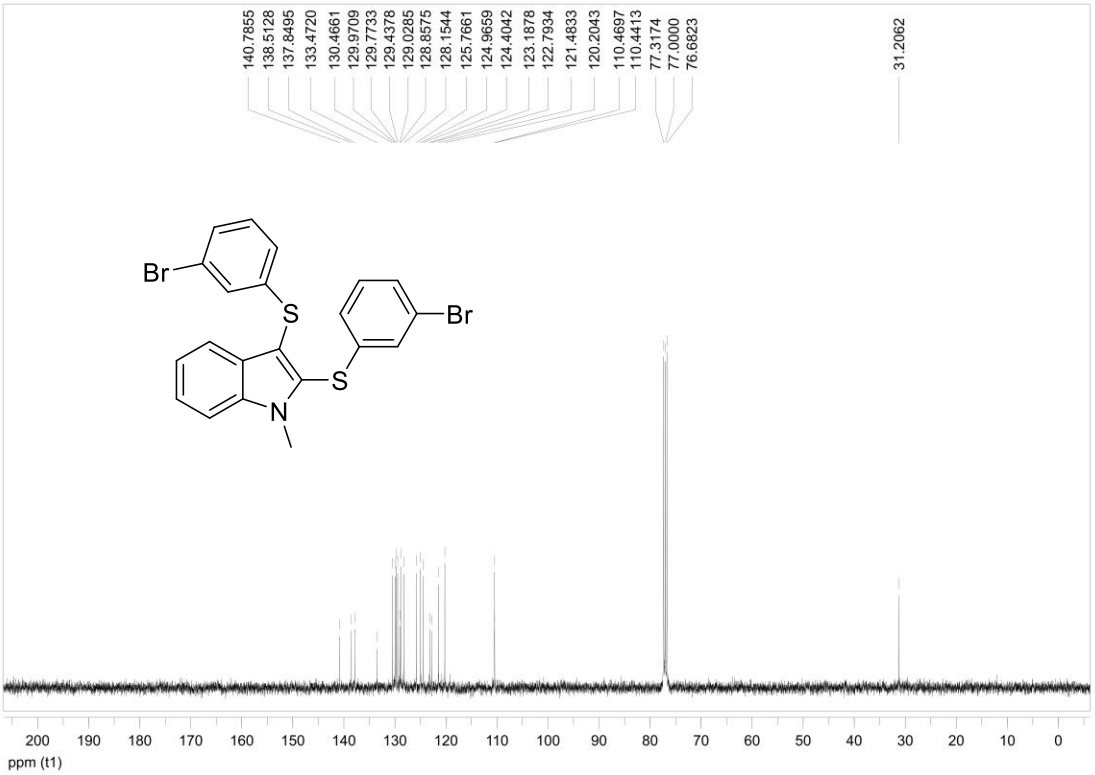


2,3-bis-Thioindole **5q**

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

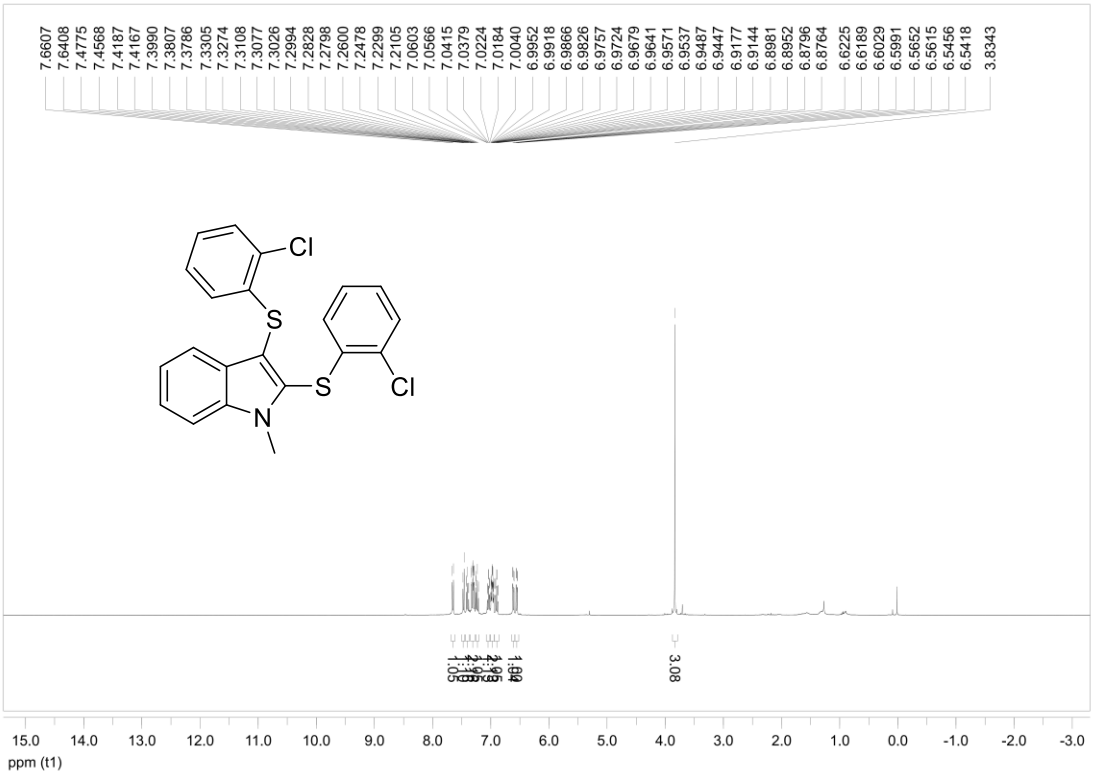


^{13}C NMR (100 MHz, $CDCl_3$)

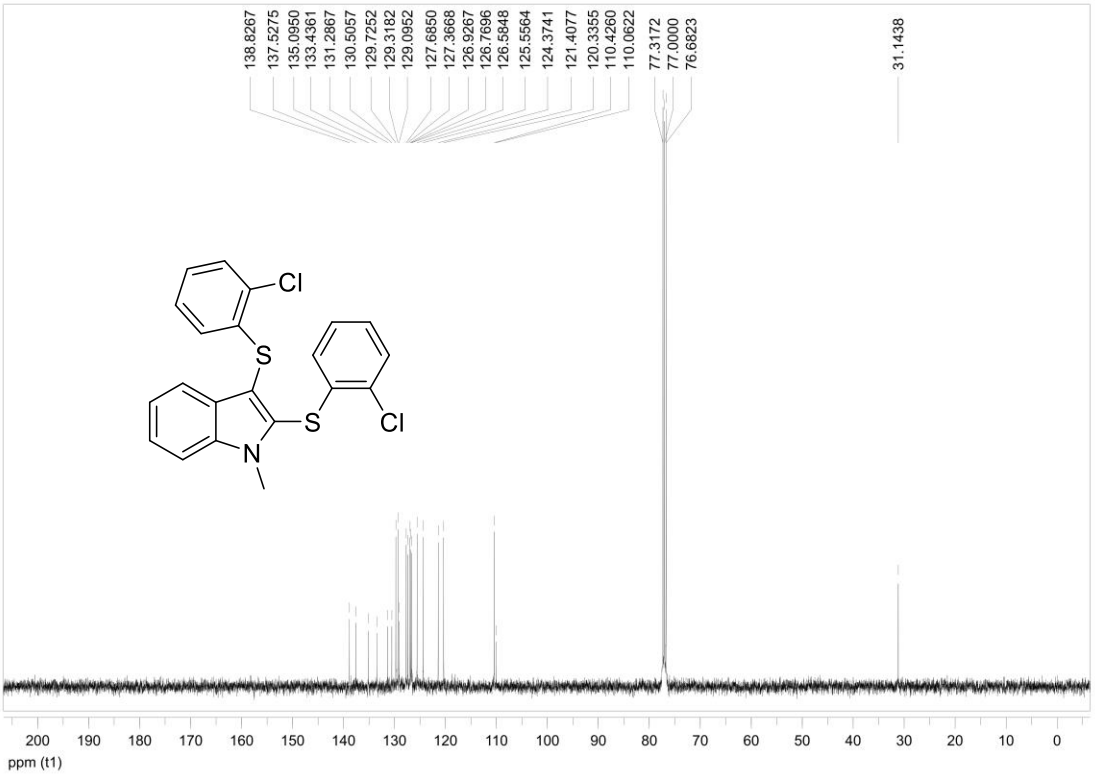


2,3-bis-Thioindole **5r**

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

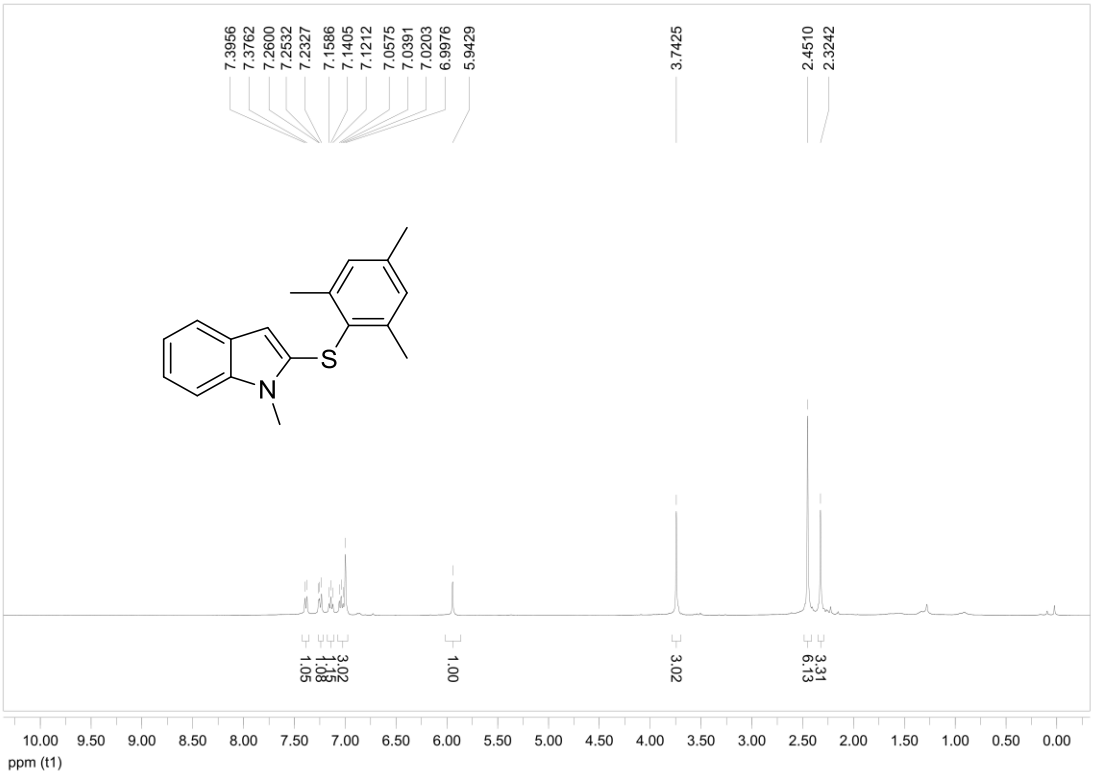


^{13}C NMR (100 MHz, $CDCl_3$)

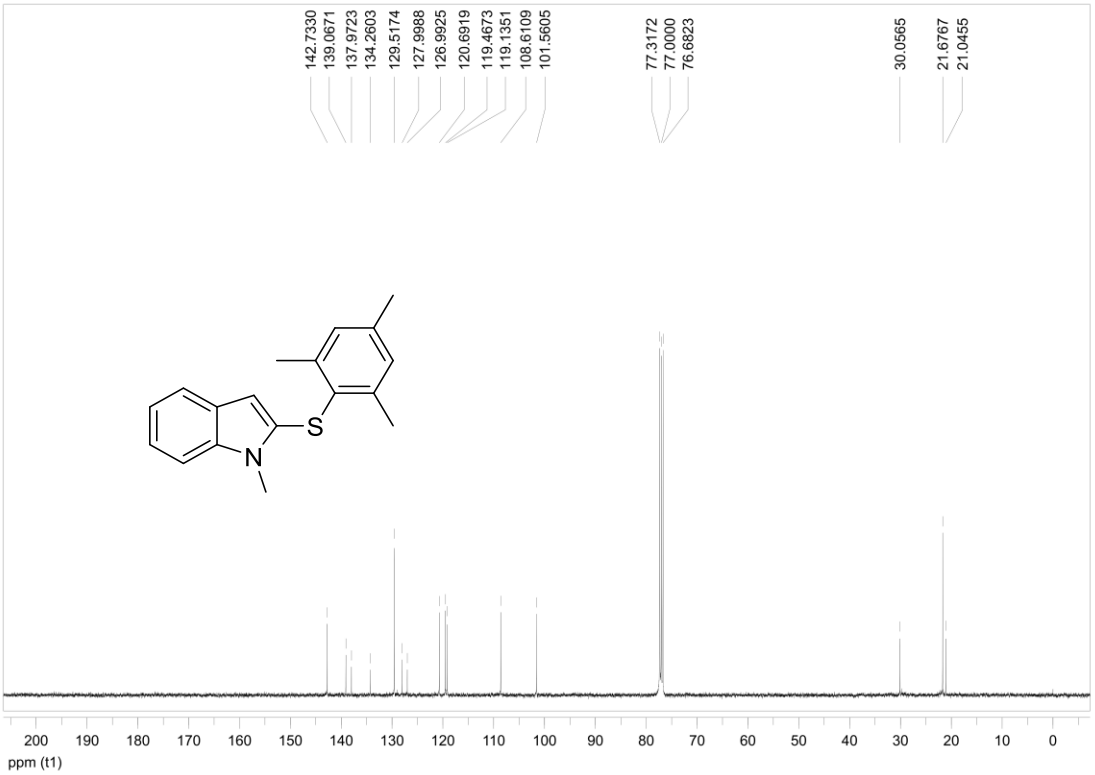


C2-Thioindole **3s**

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

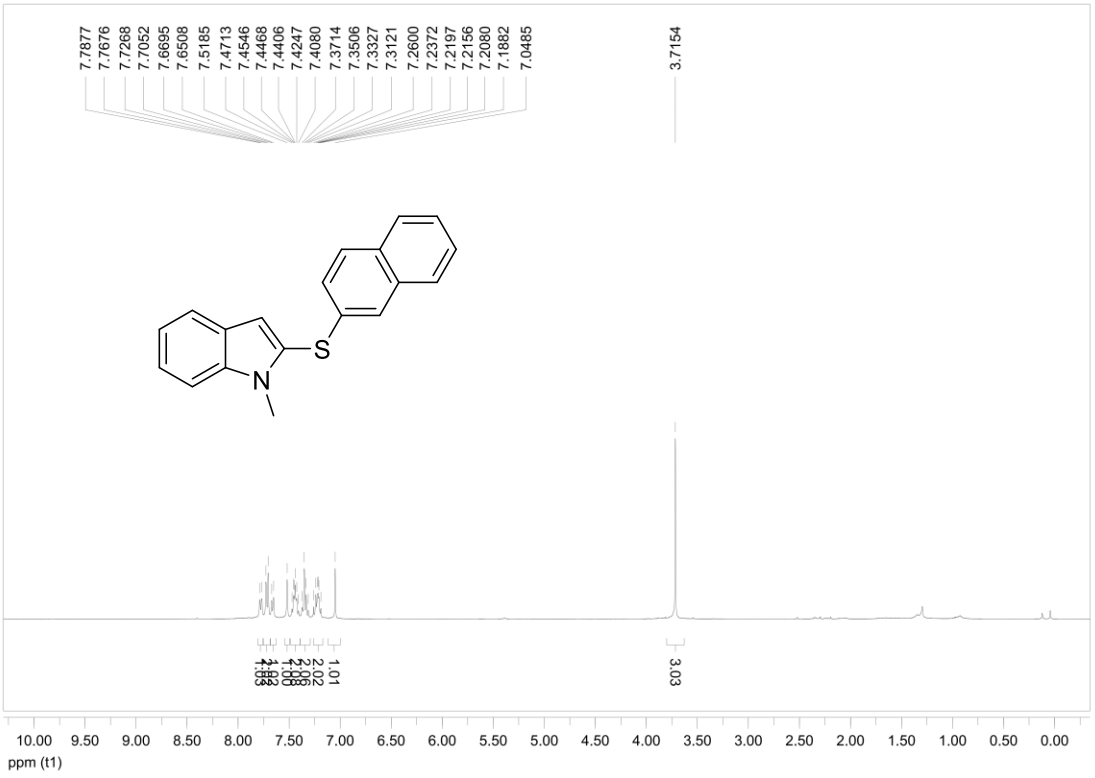


^{13}C NMR (100 MHz, $CDCl_3$)

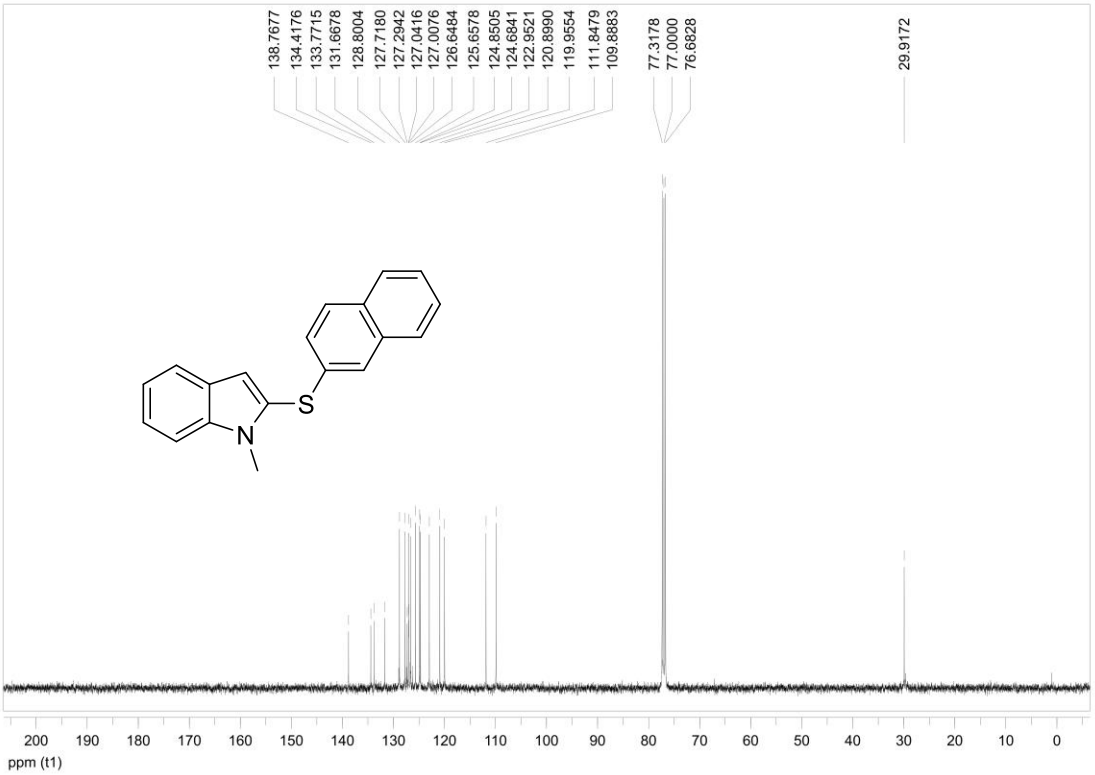


C2-Thioindole **3t**

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



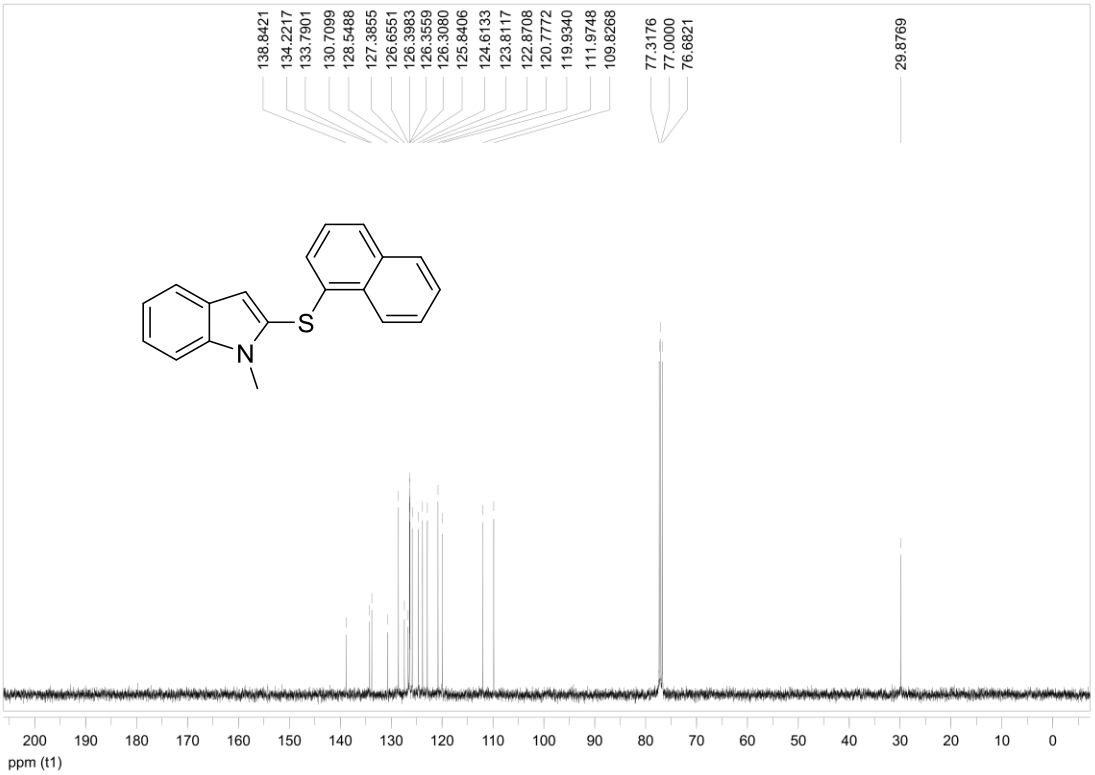
^{13}C NMR (100 MHz, $CDCl_3$)



C2-Thioindole **3u**

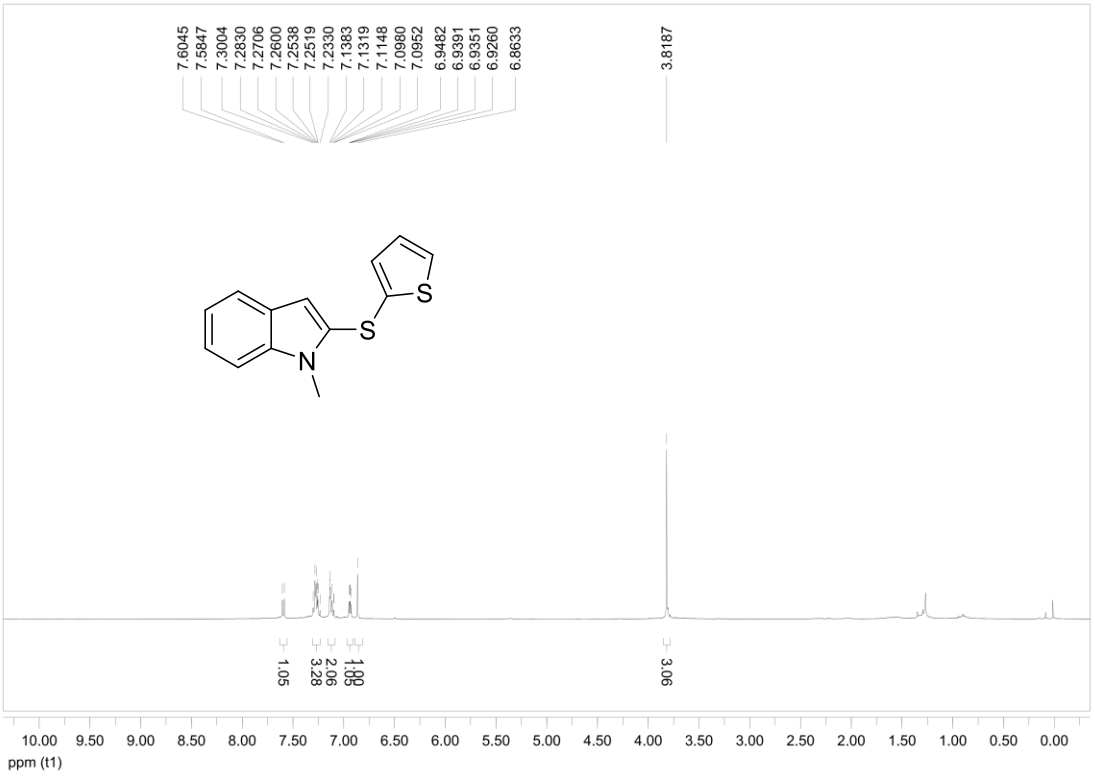
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)

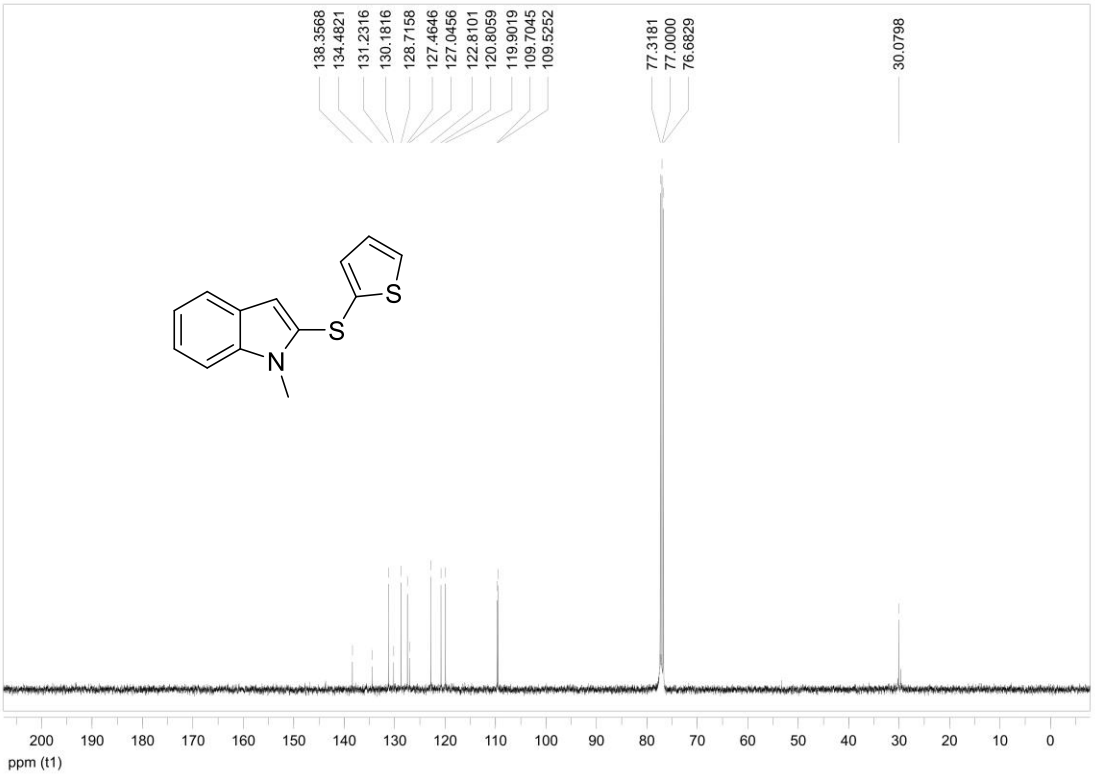


C2-Thioindole **3v**

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

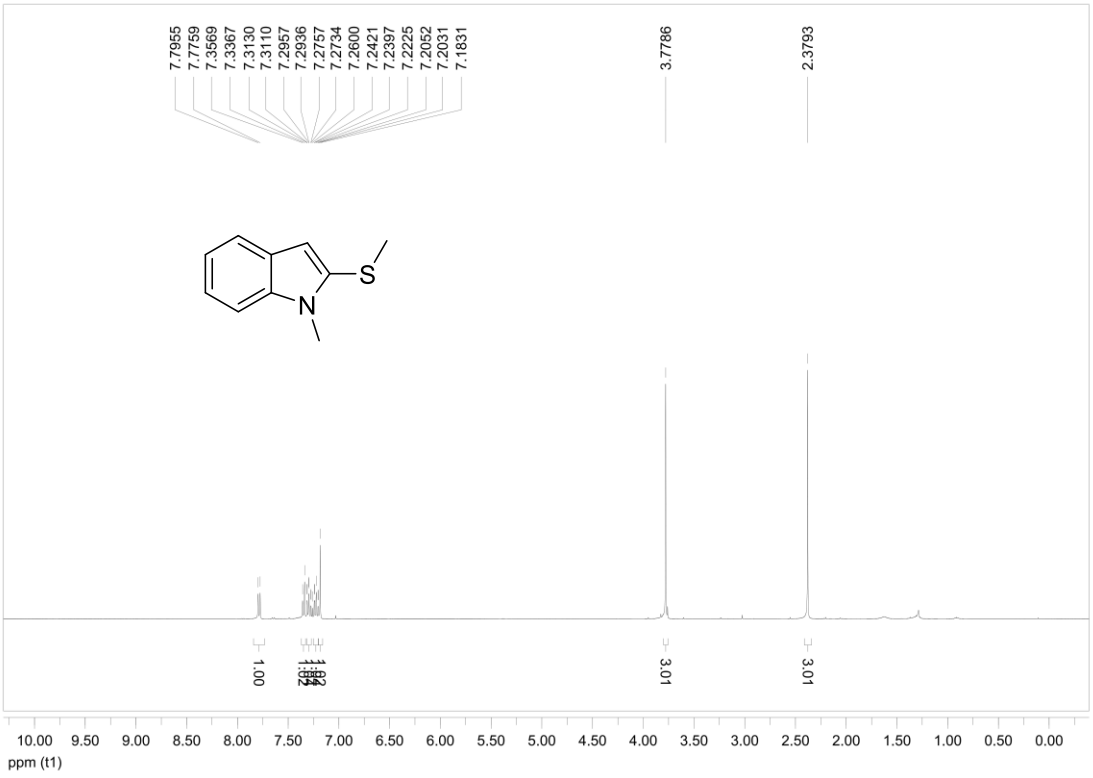


^{13}C NMR (100 MHz, $CDCl_3$)

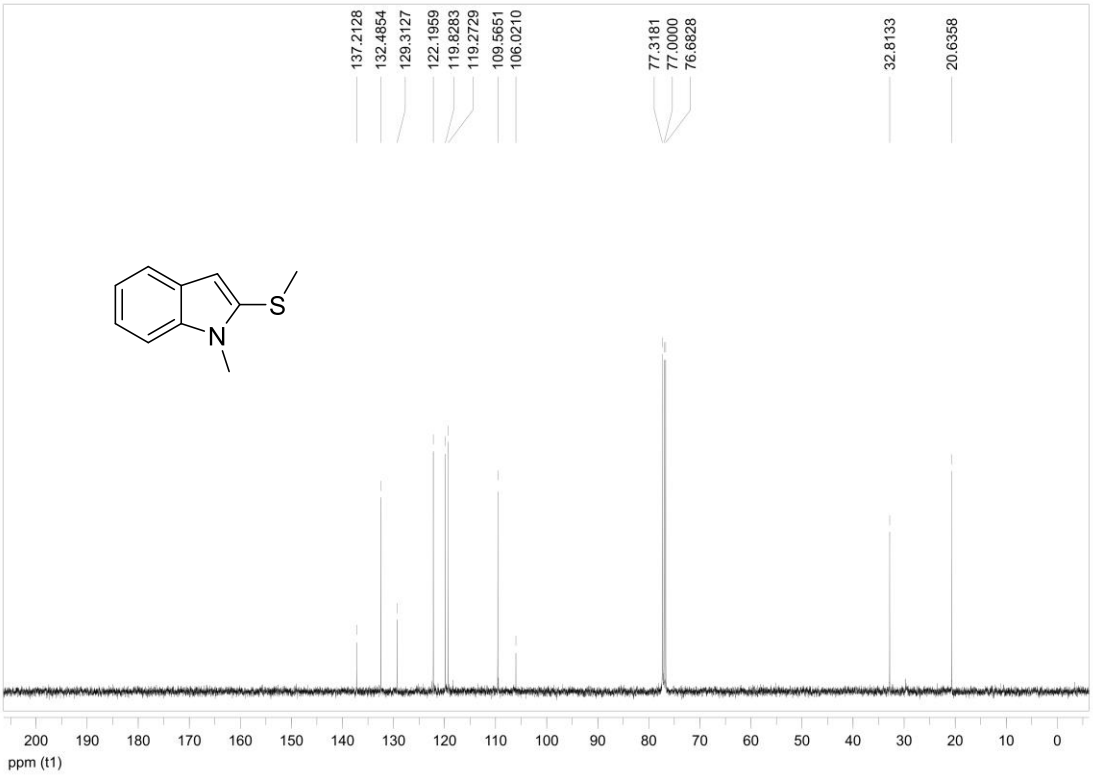


C2-Thioindole **3w**

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

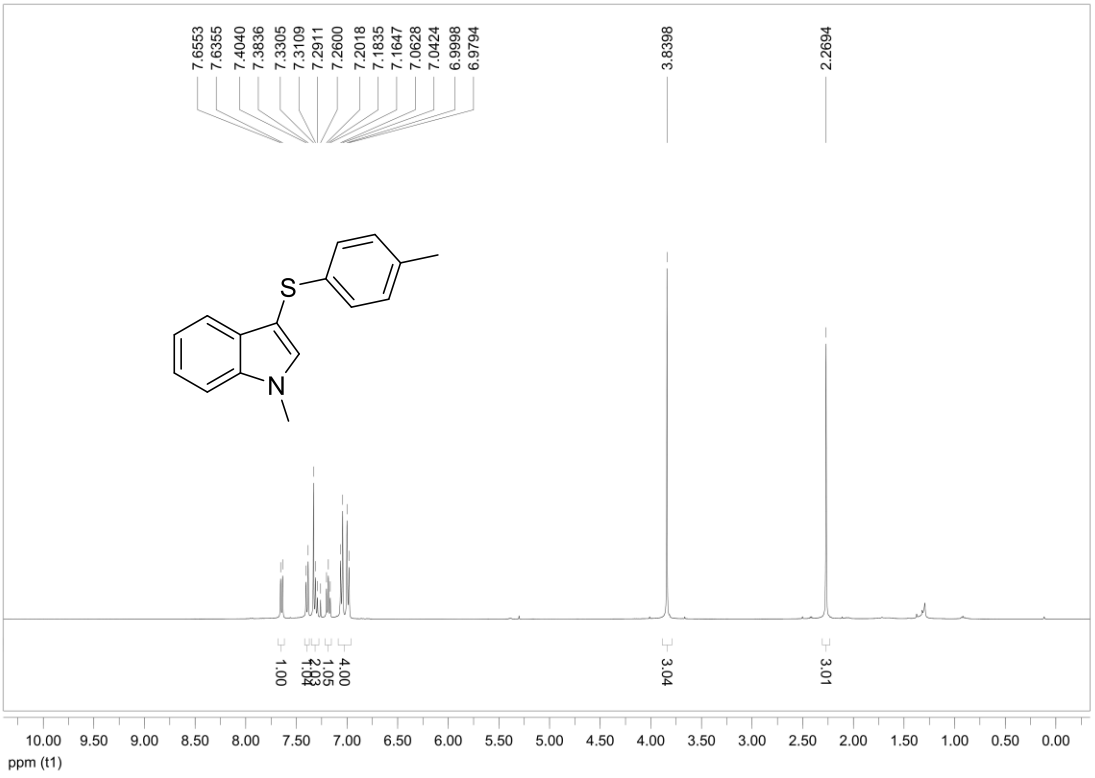


^{13}C NMR (100 MHz, $CDCl_3$)

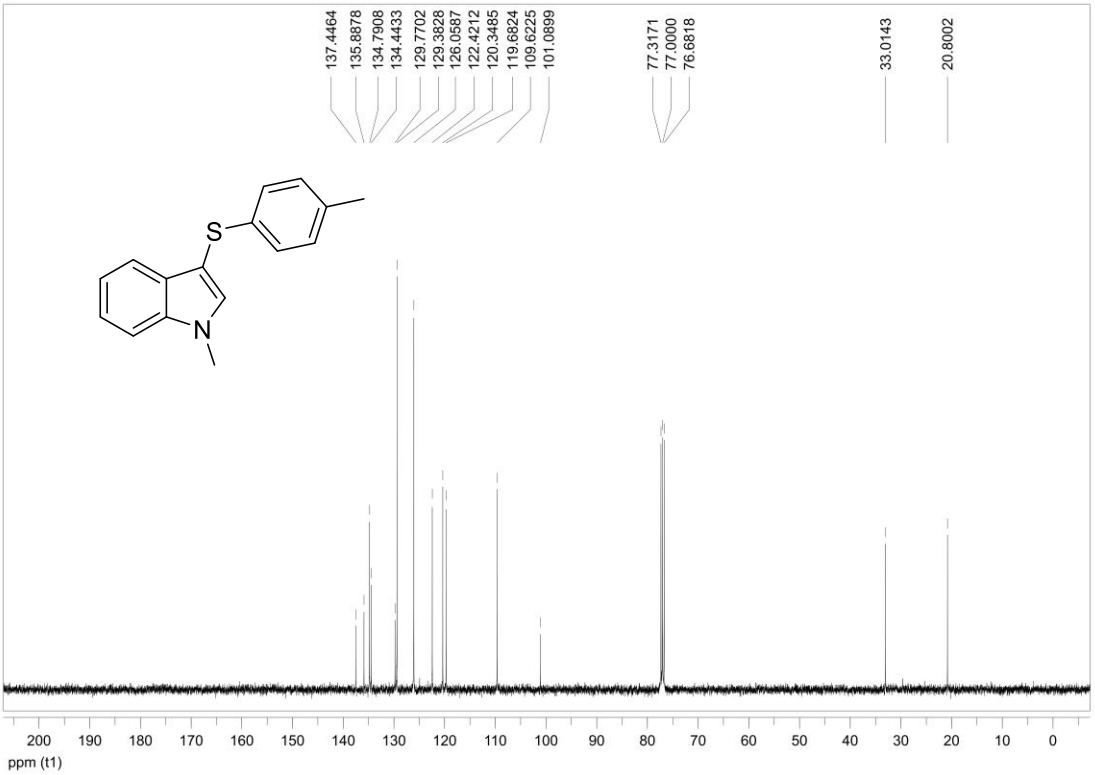


C3-Thioindole **4a**

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

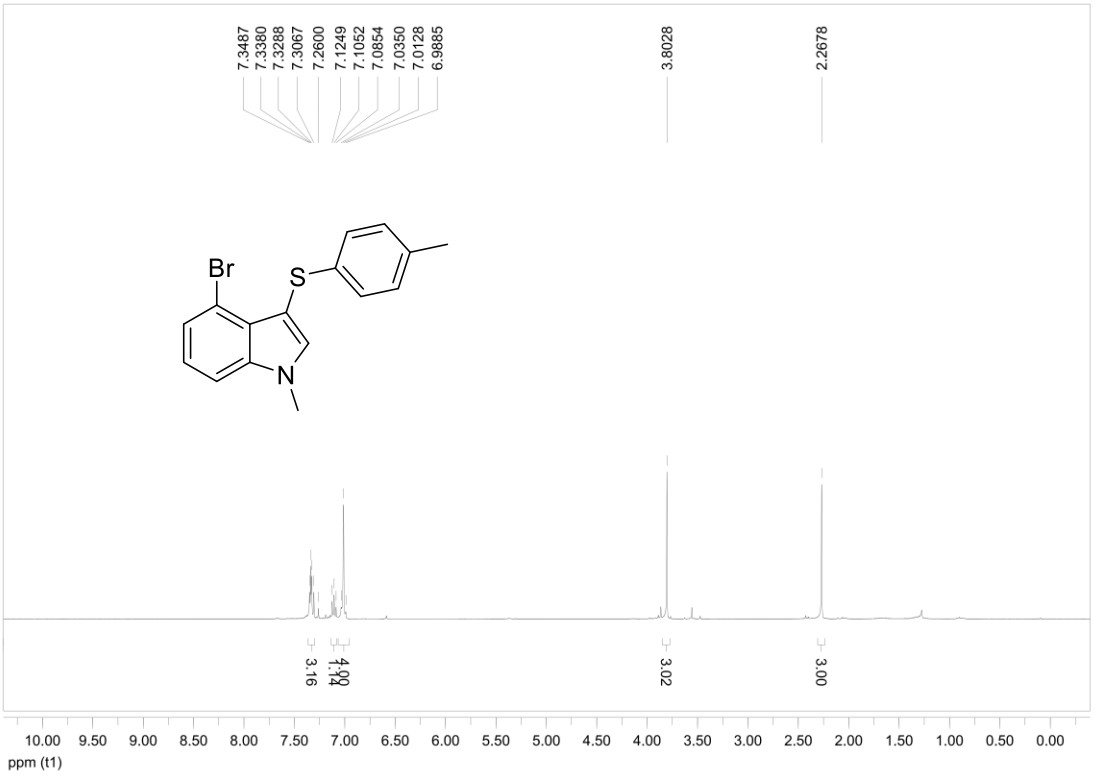


^{13}C NMR (100 MHz, $CDCl_3$)

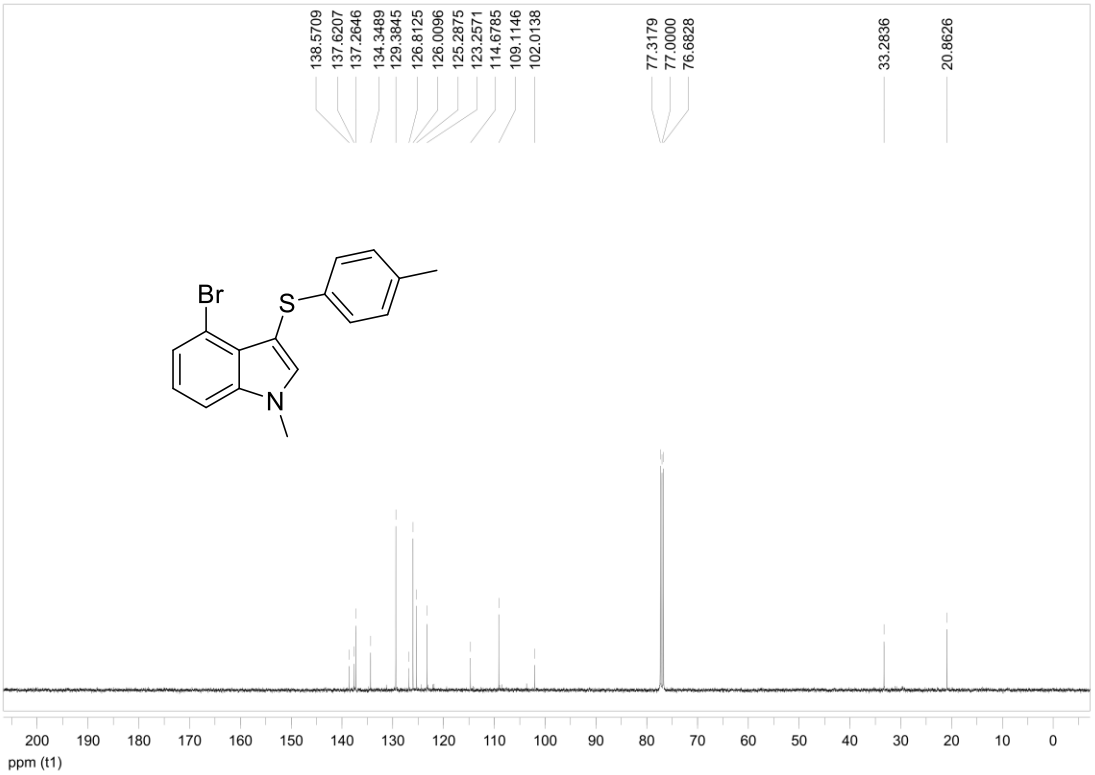


C3-Thioindole **4b**

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

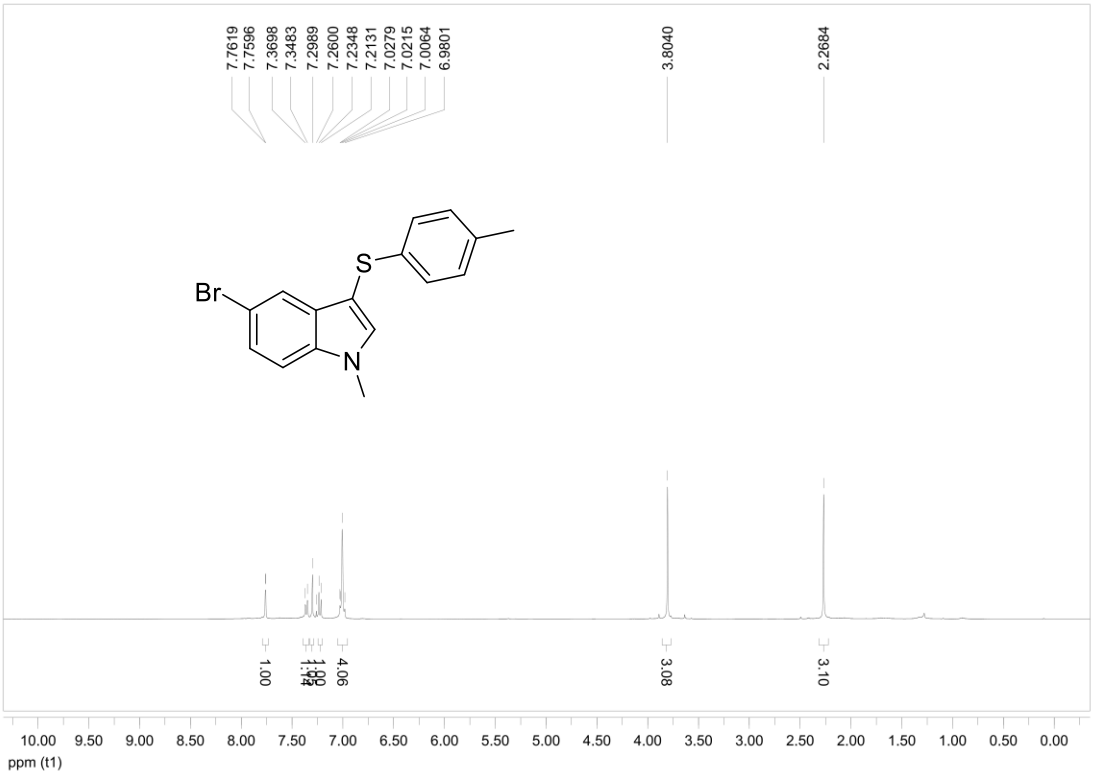


^{13}C NMR (100 MHz, $CDCl_3$)

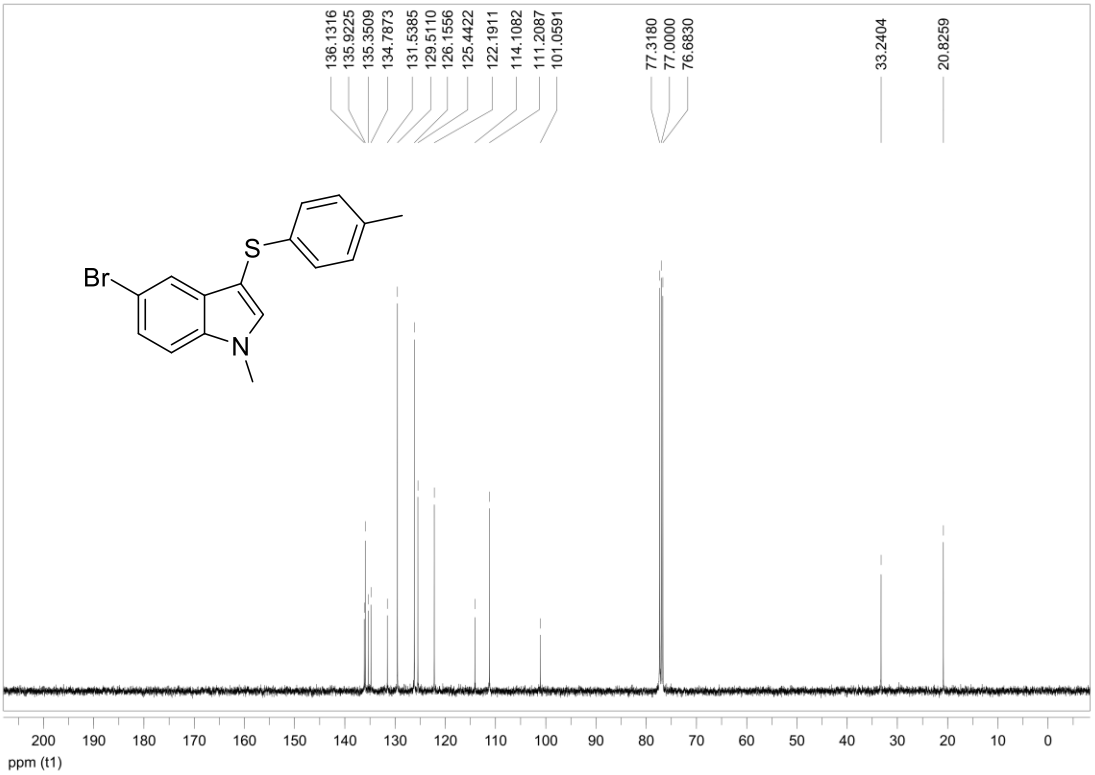


C3-Thioindole **4c**

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

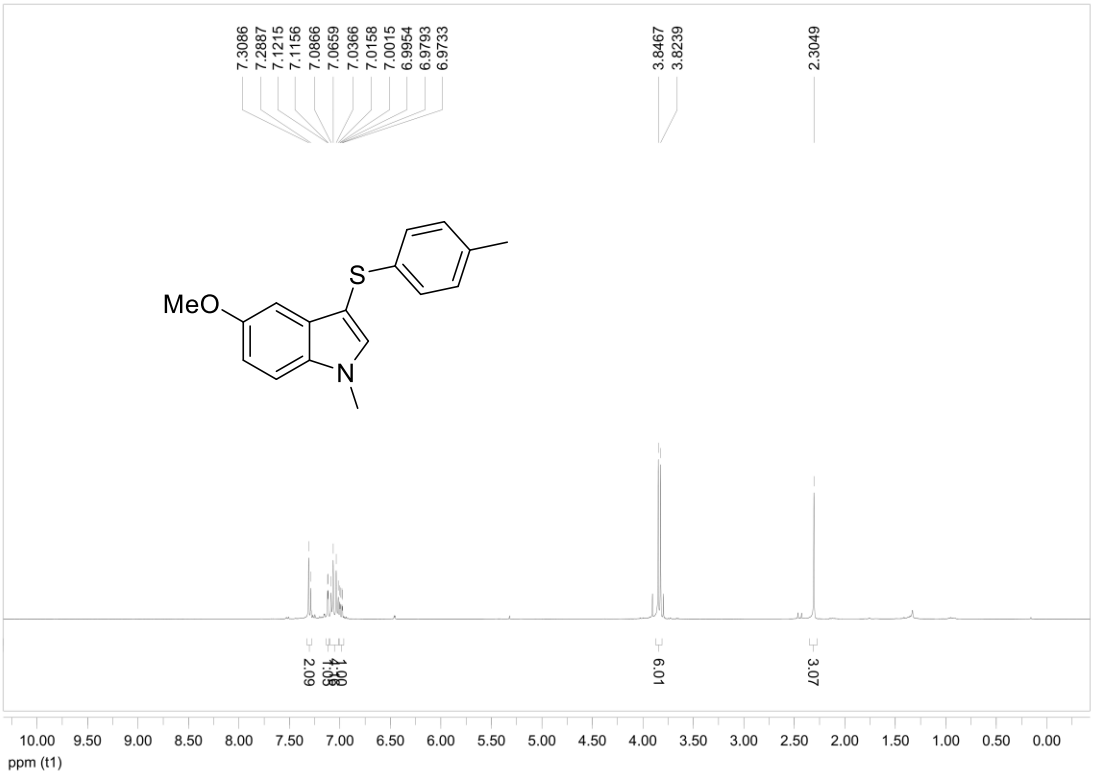


^{13}C NMR (100 MHz, $CDCl_3$)

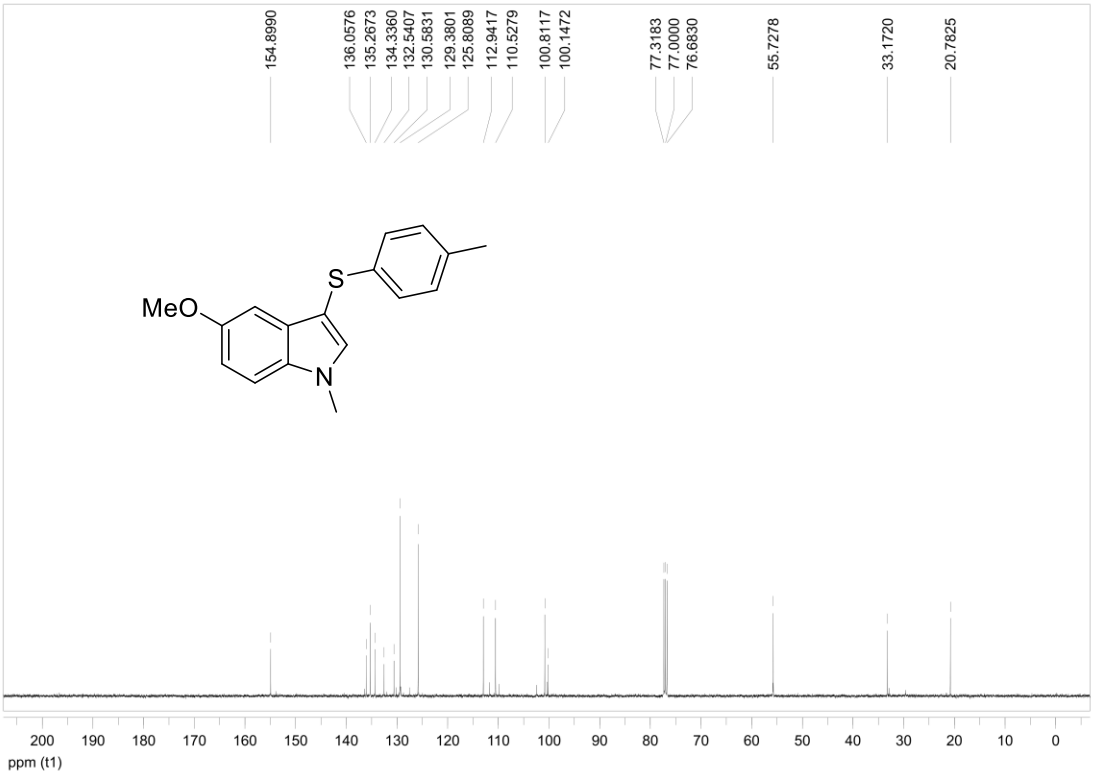


C3-Thioindole **4d**

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

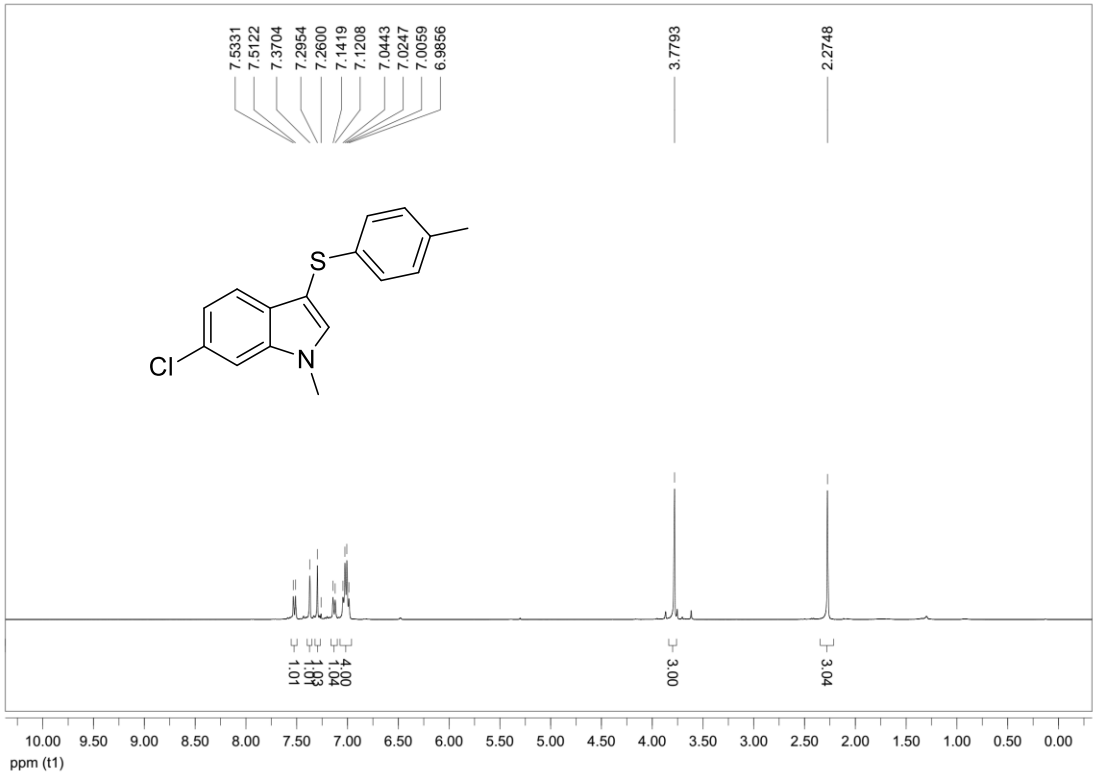


^{13}C NMR (100 MHz, $CDCl_3$)

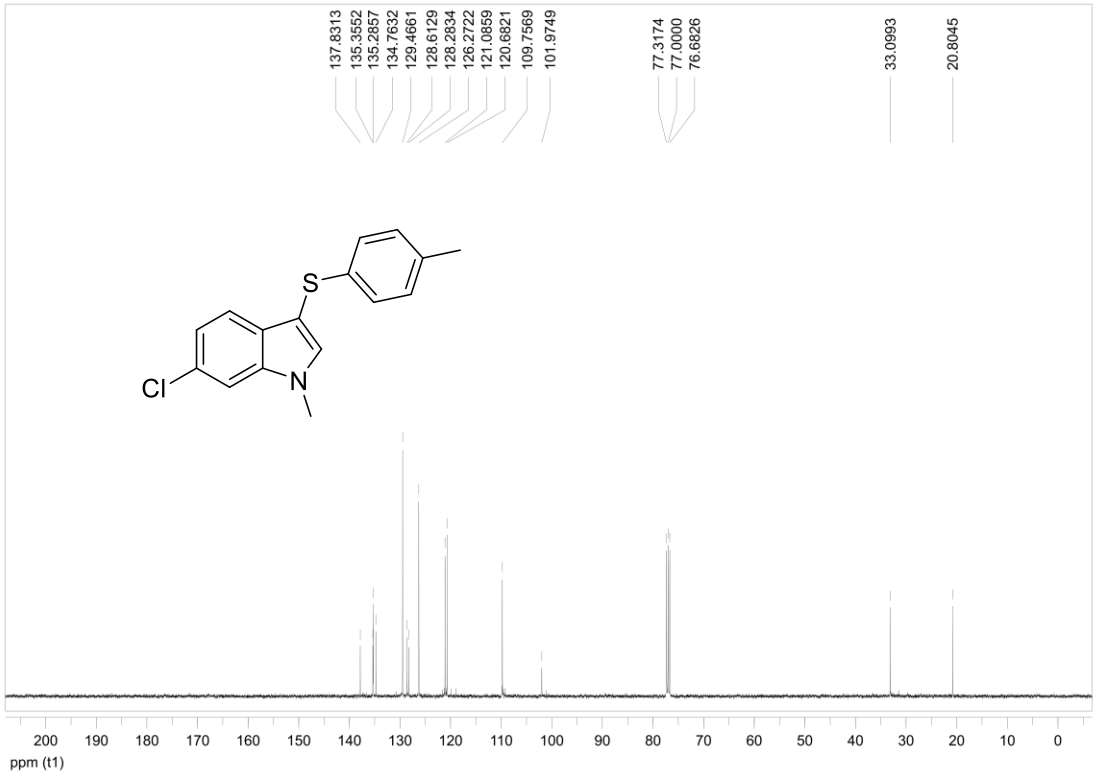


C3-Thioindole **4e**

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

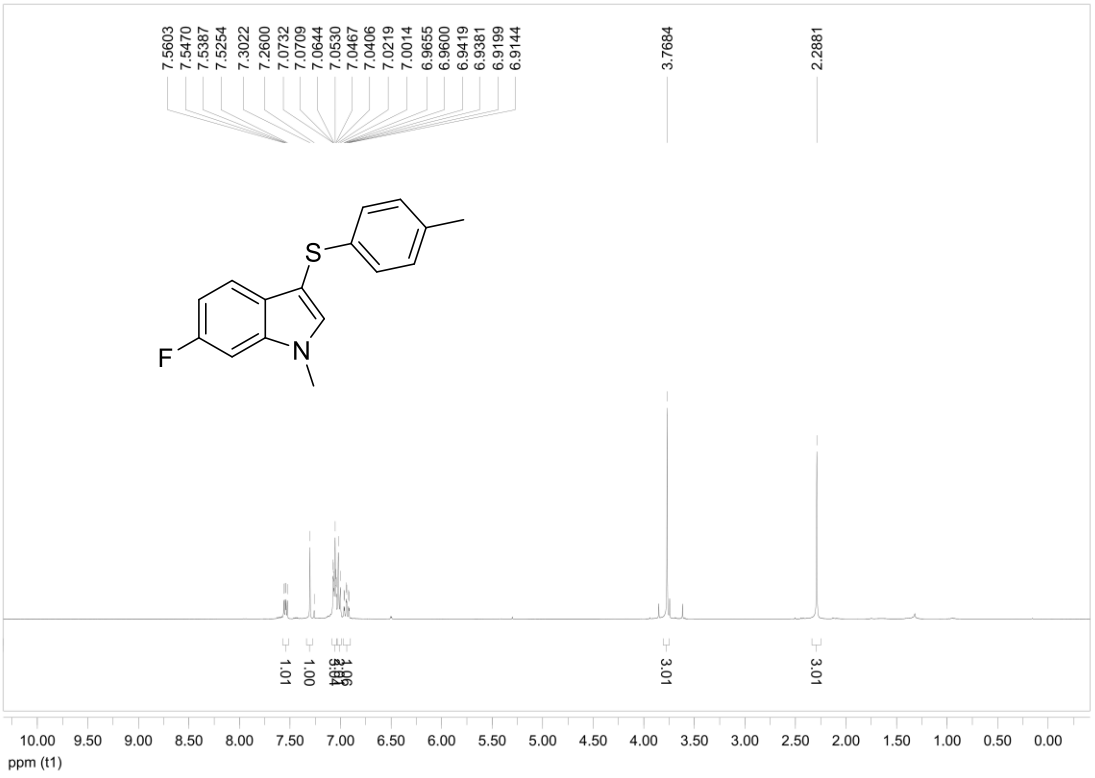


^{13}C NMR (100 MHz, $CDCl_3$)

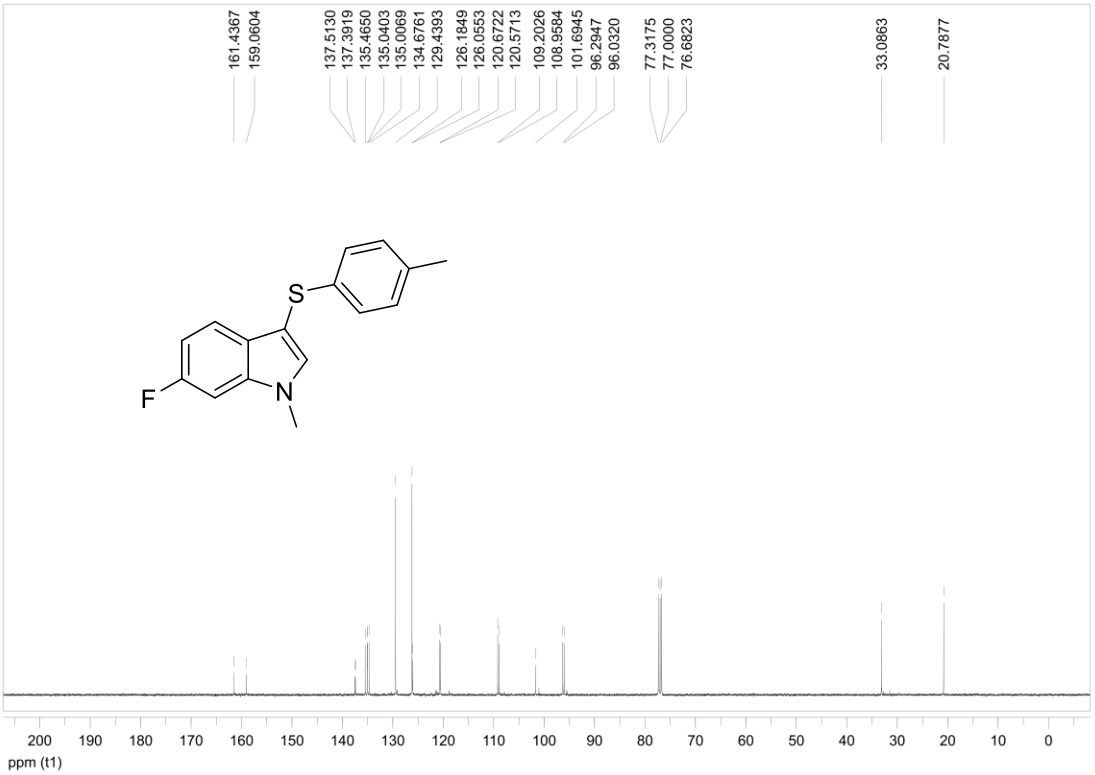


C3-Thioindole **4f**

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

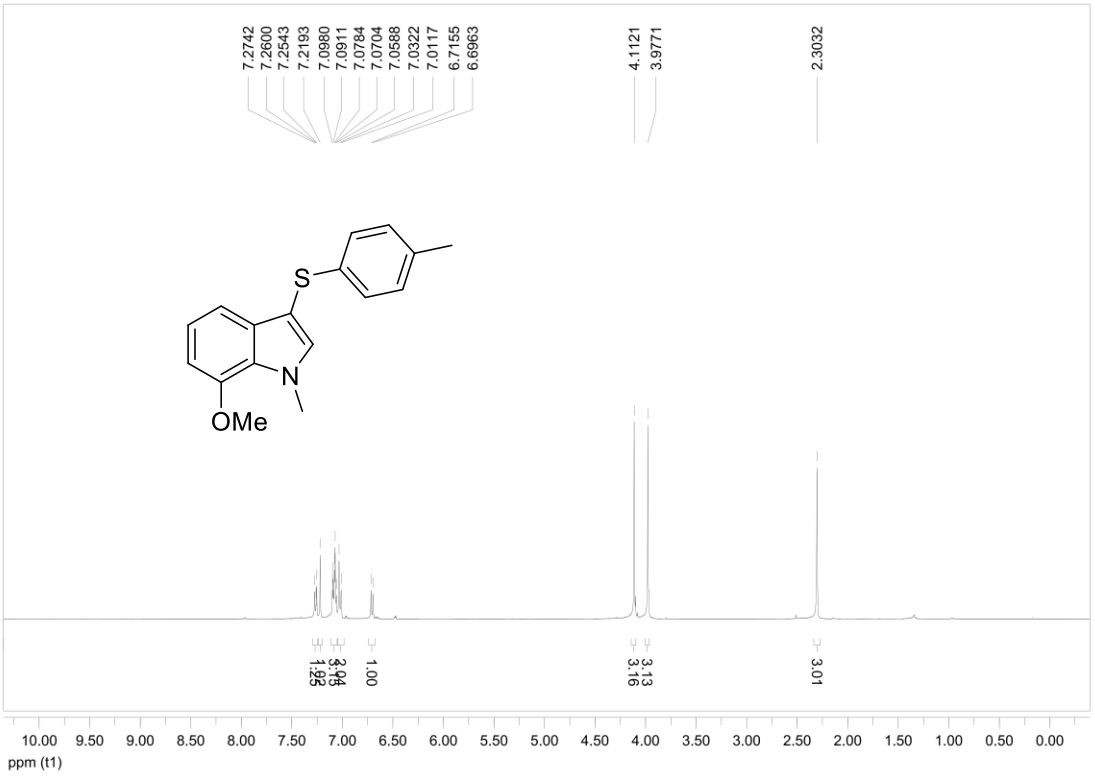


^{13}C NMR (100 MHz, $CDCl_3$)

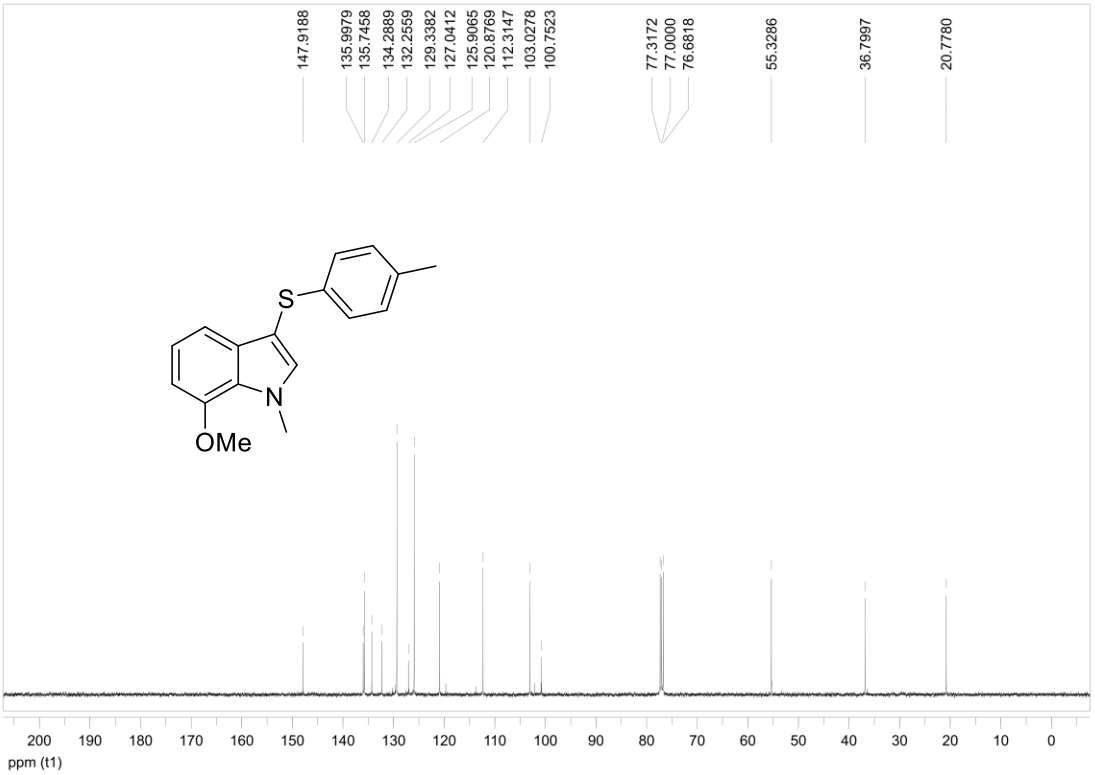


C3-Thioindole **4g**

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

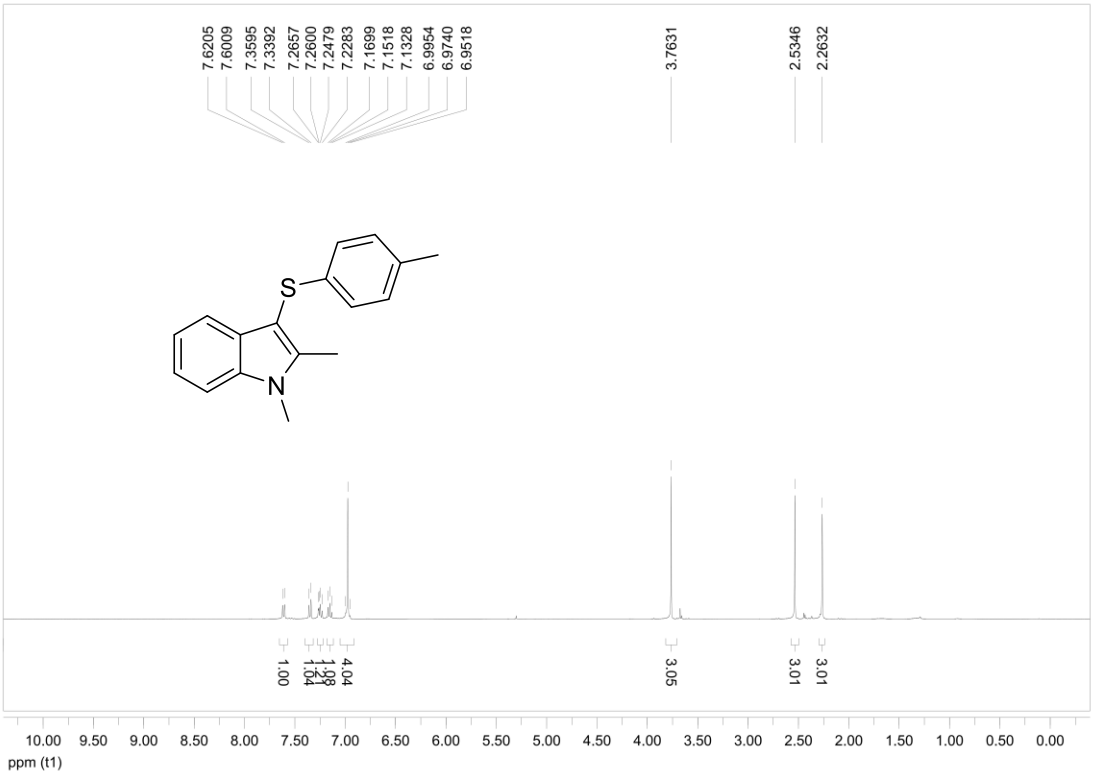


^{13}C NMR (100 MHz, $CDCl_3$)

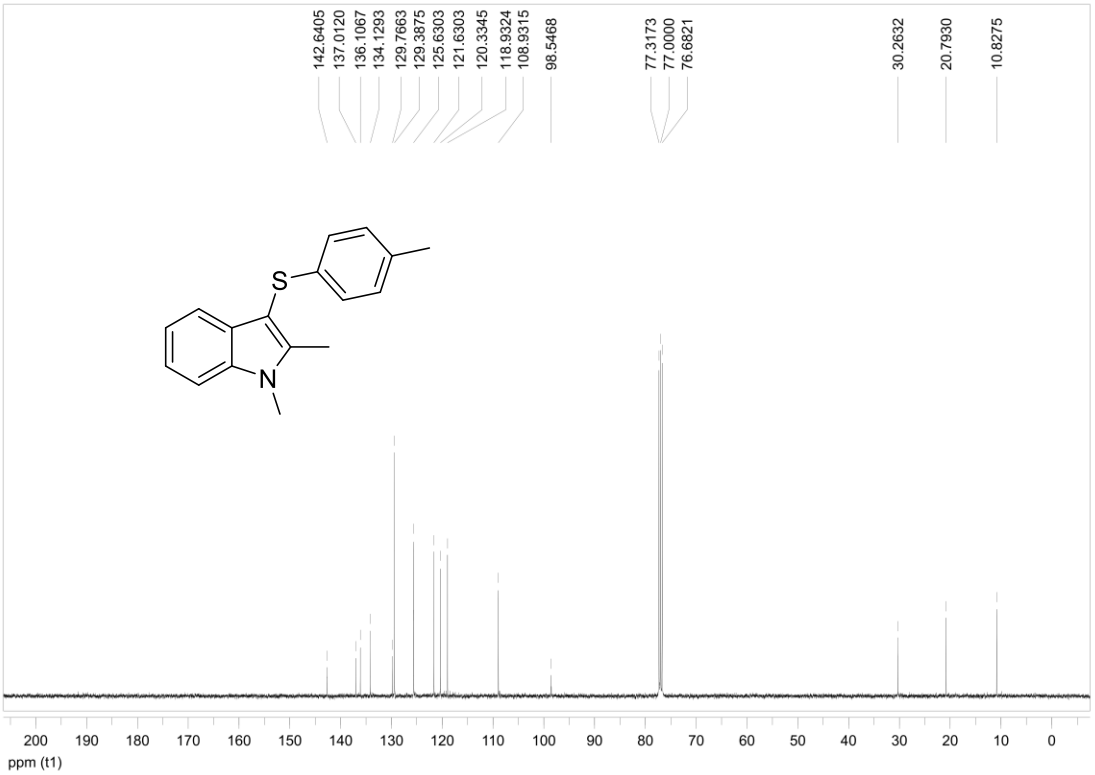


C3-Thioindole **4h**

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

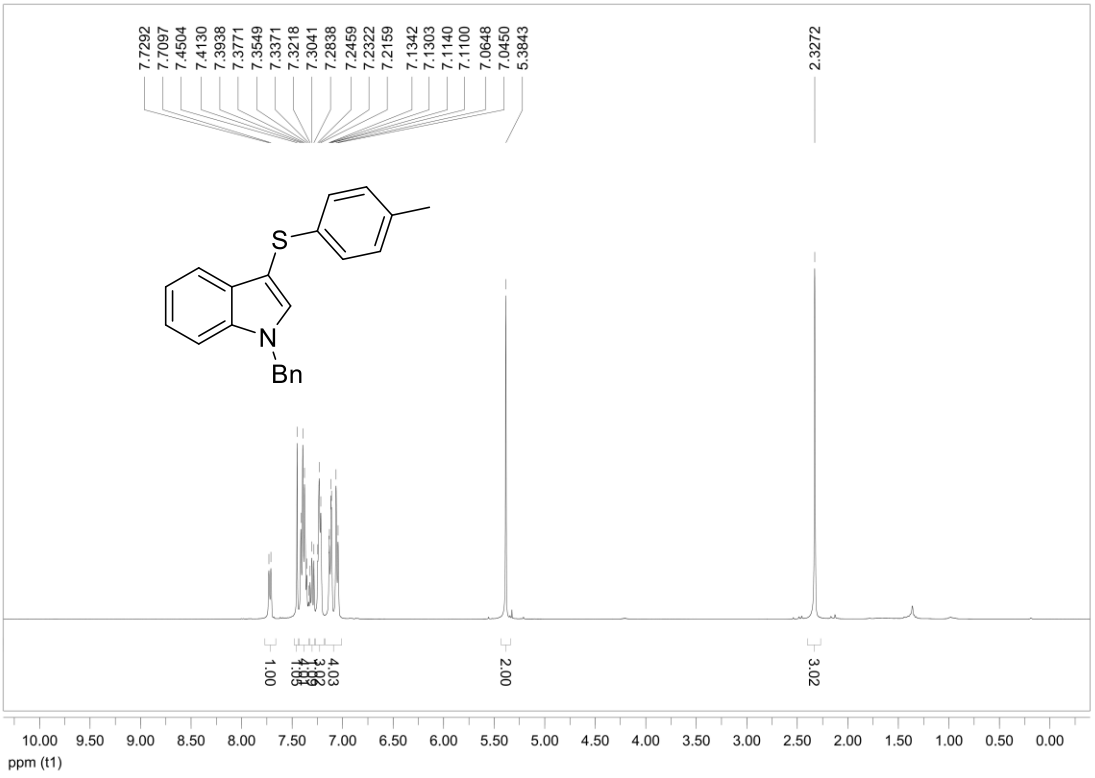


^{13}C NMR (100 MHz, $CDCl_3$)

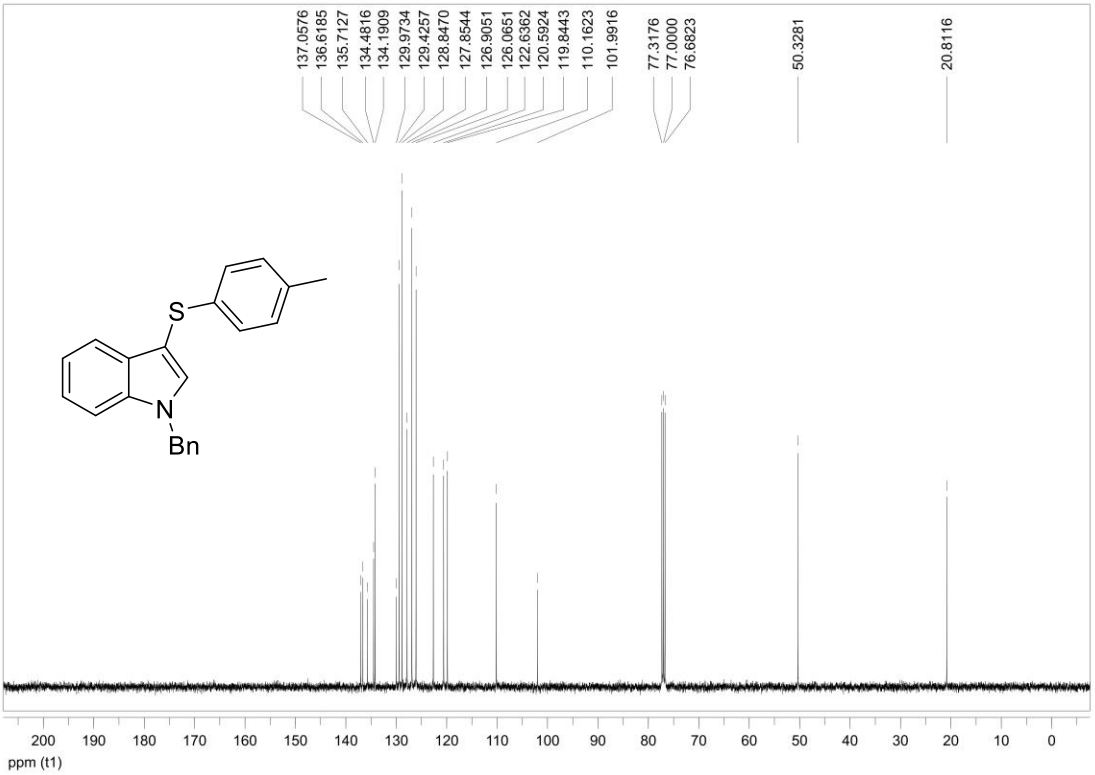


C3-Thioindole **4i**

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

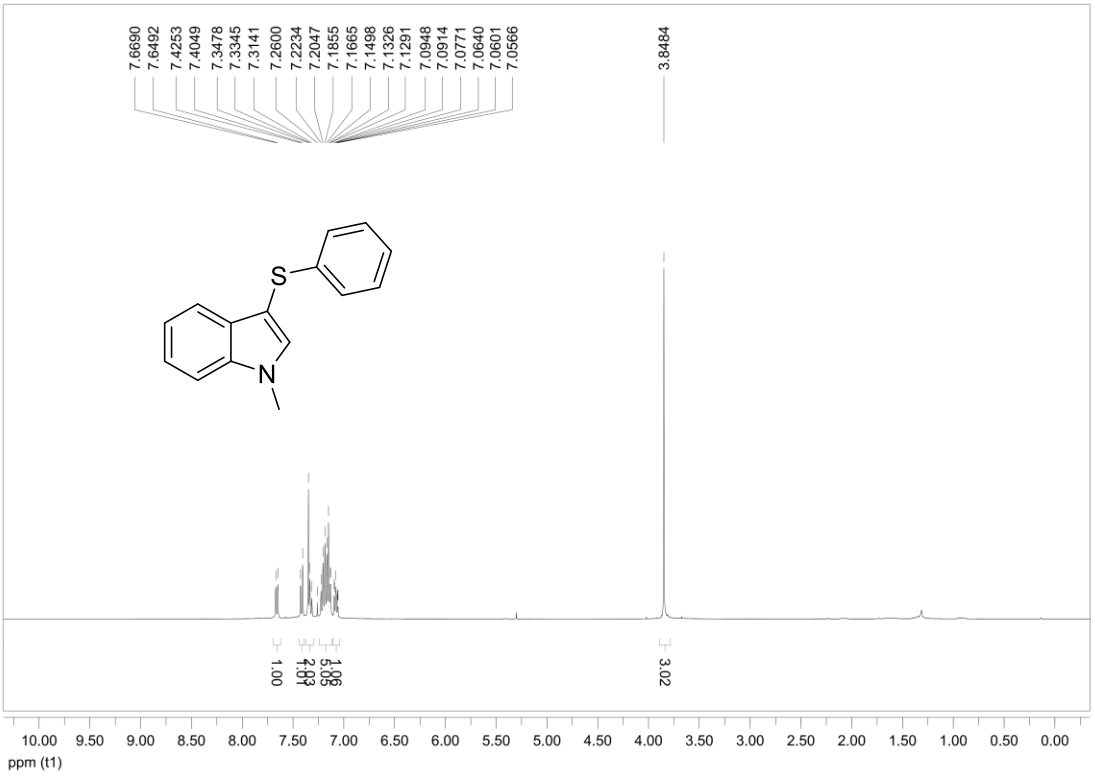


^{13}C NMR (100 MHz, $CDCl_3$)

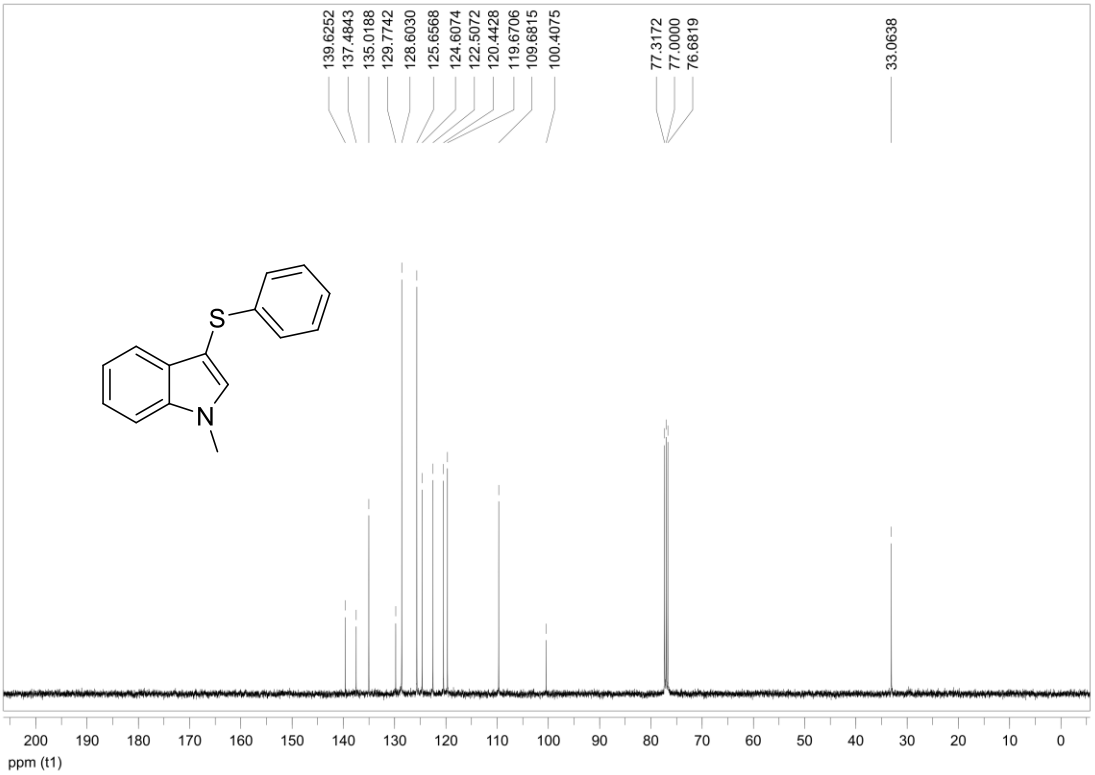


C3-Thioindole **4k**

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

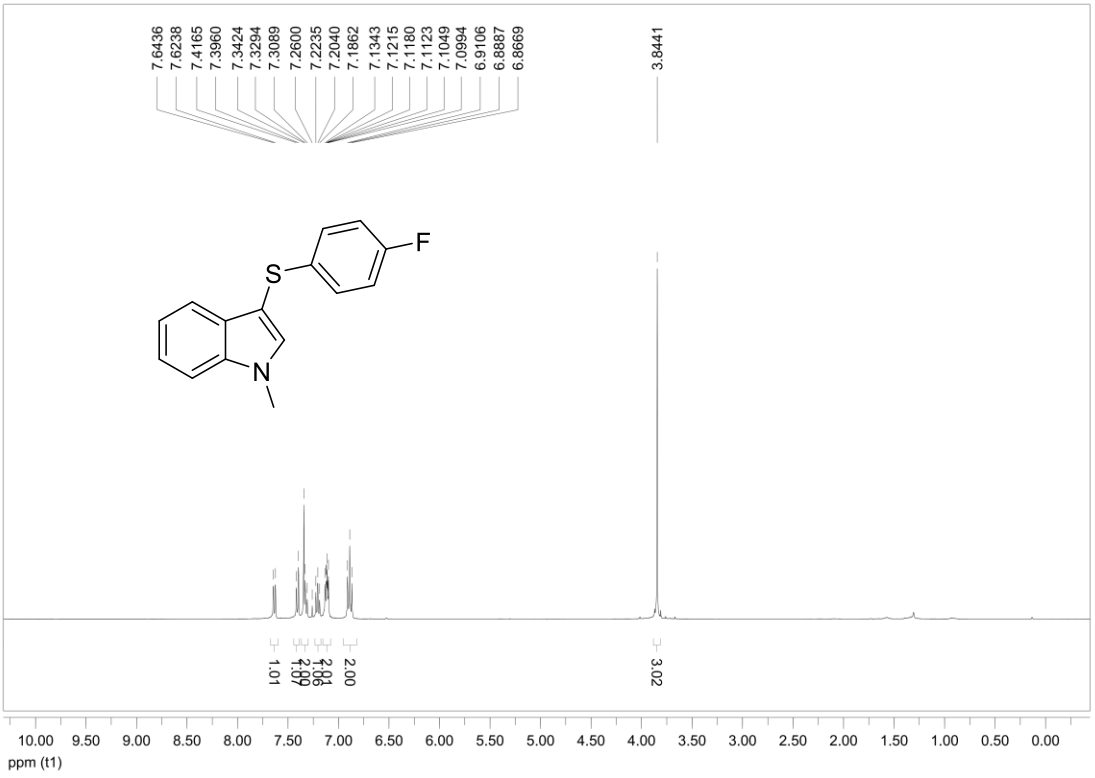


^{13}C NMR (100 MHz, $CDCl_3$)

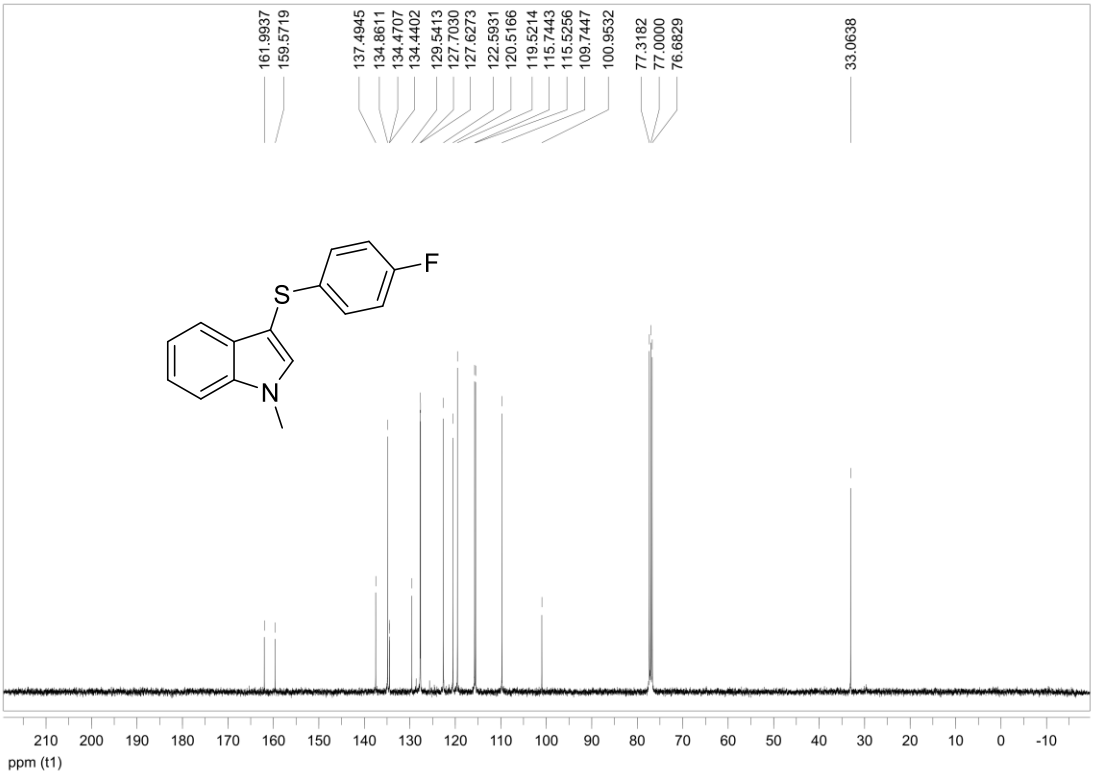


C3-Thioindole **4l**

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

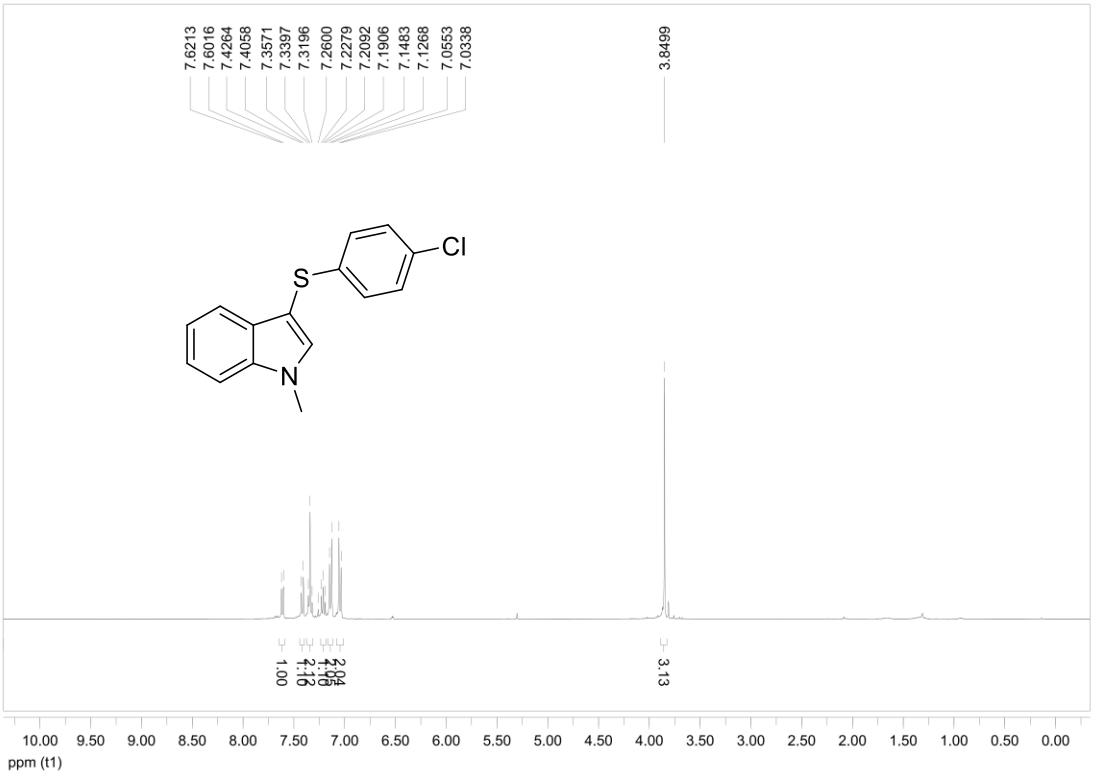


^{13}C NMR (100 MHz, $CDCl_3$)

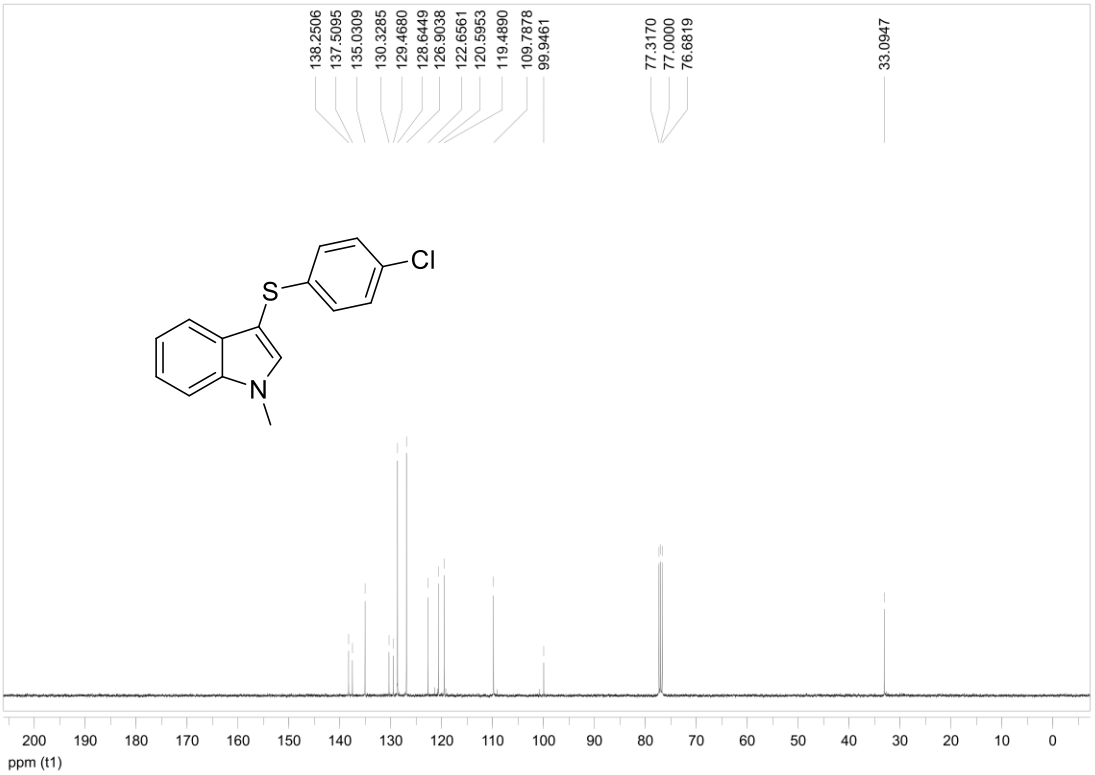


C3-Thioindole **4m**

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

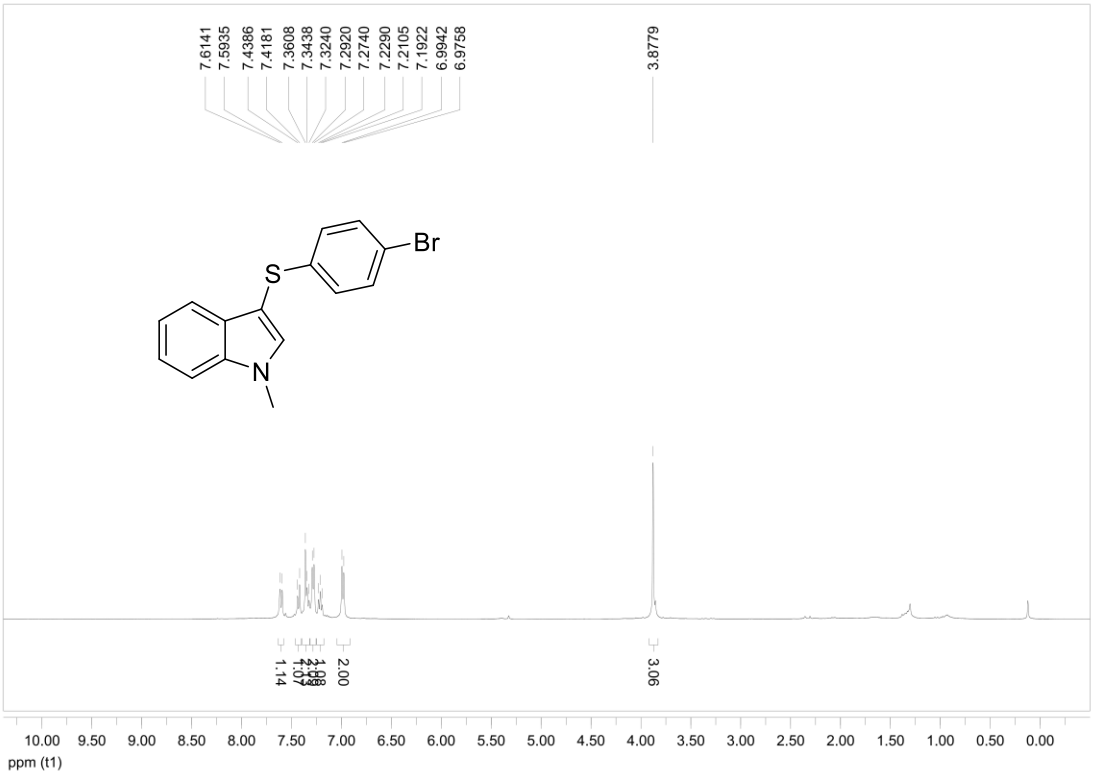


^{13}C NMR (100 MHz, $CDCl_3$)

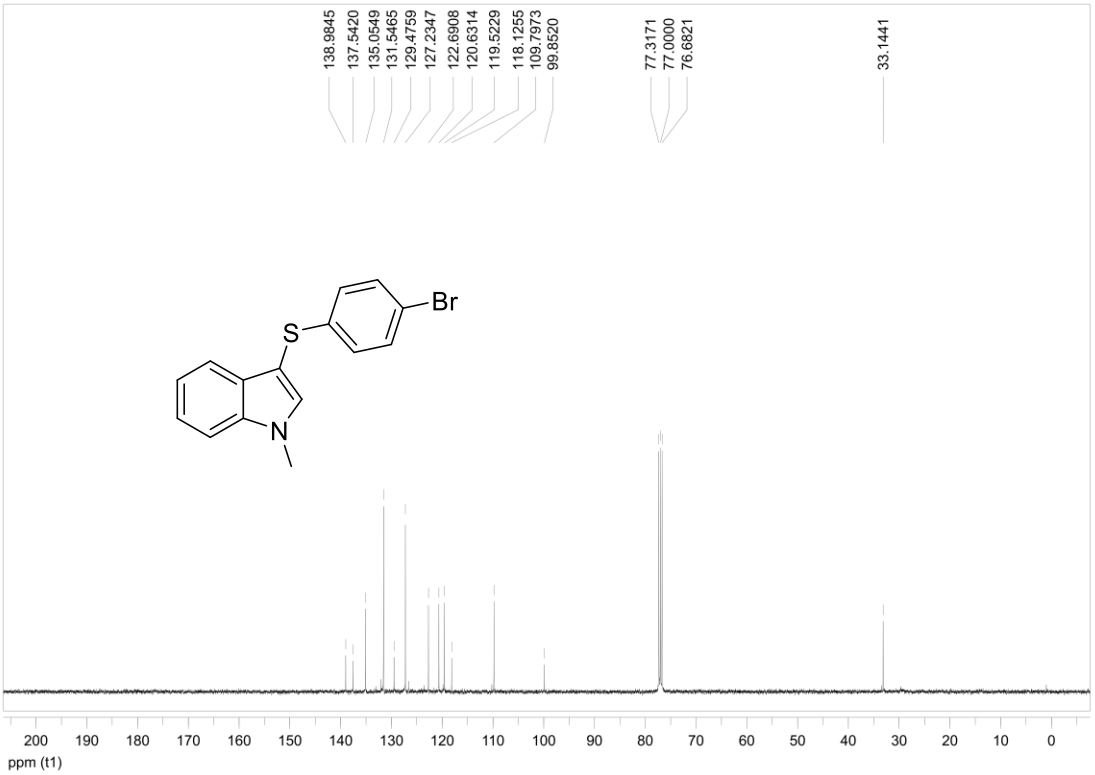


C3-Thioindole **4n**

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

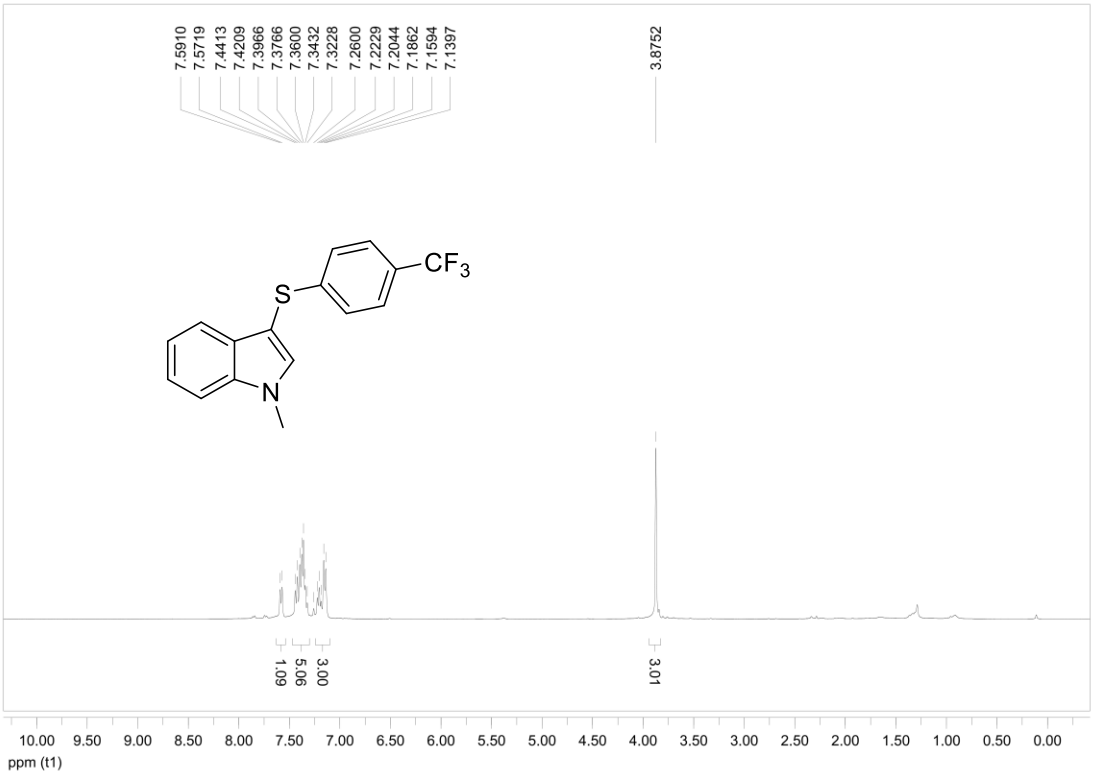


^{13}C NMR (100 MHz, $CDCl_3$)

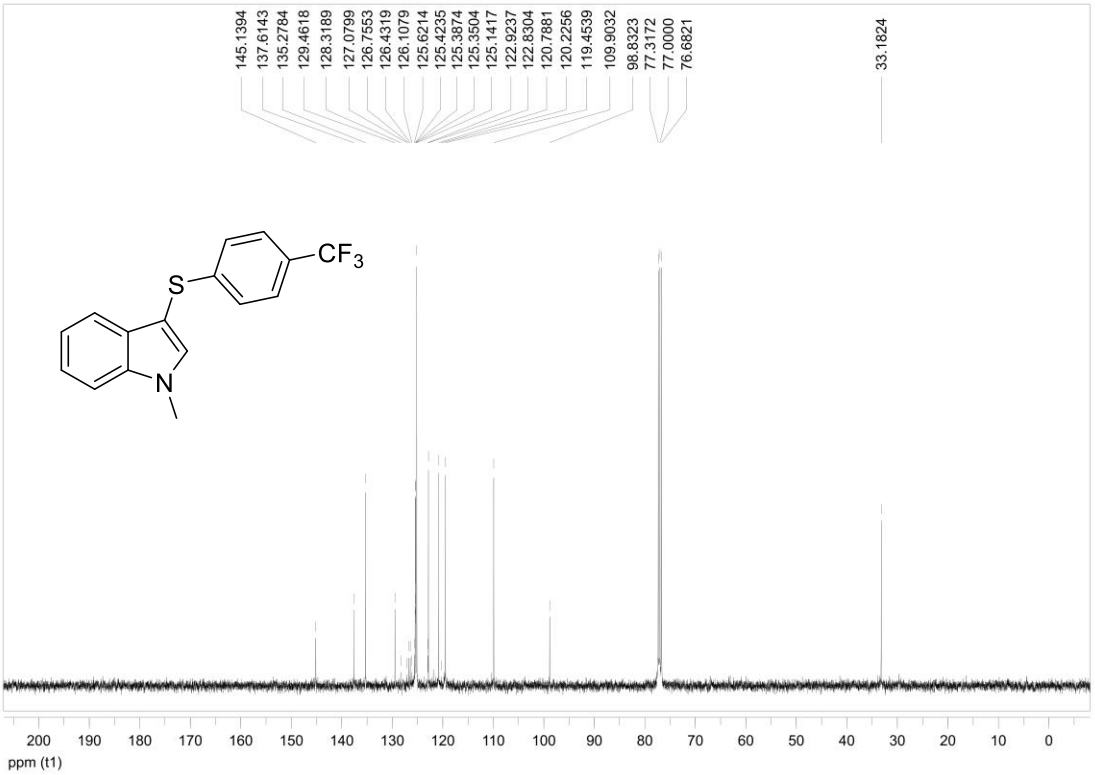


C3-Thioindole **4o**

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

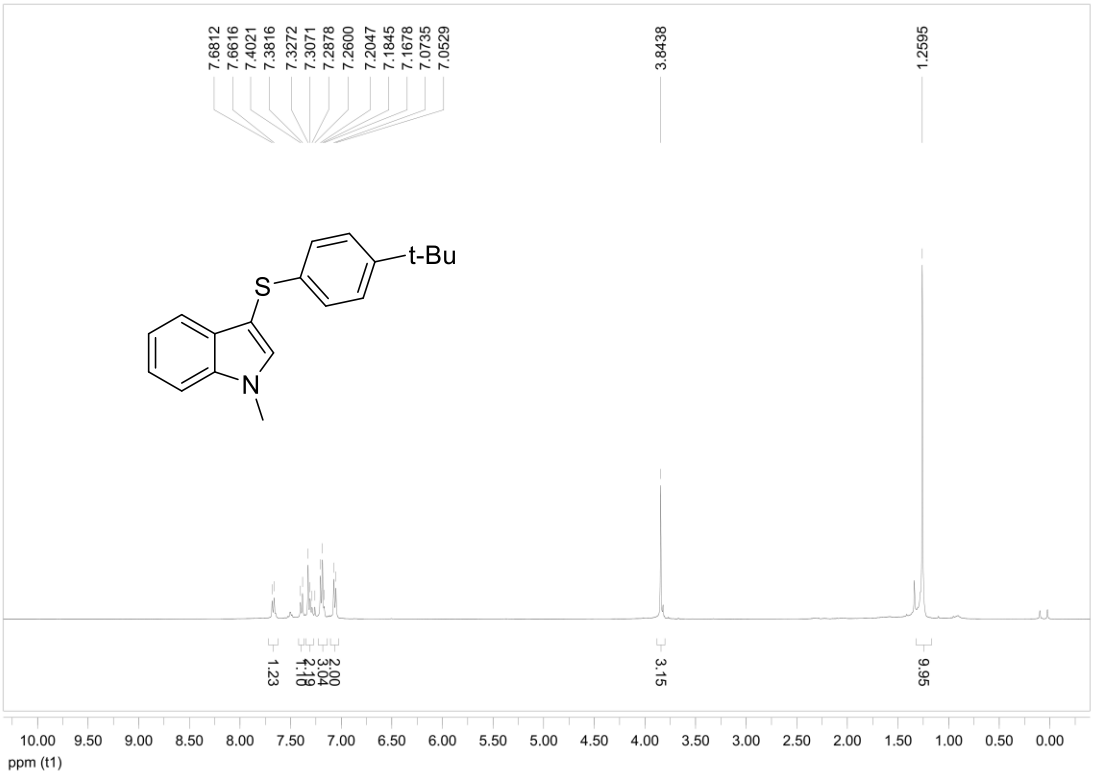


^{13}C NMR (100 MHz, $CDCl_3$)

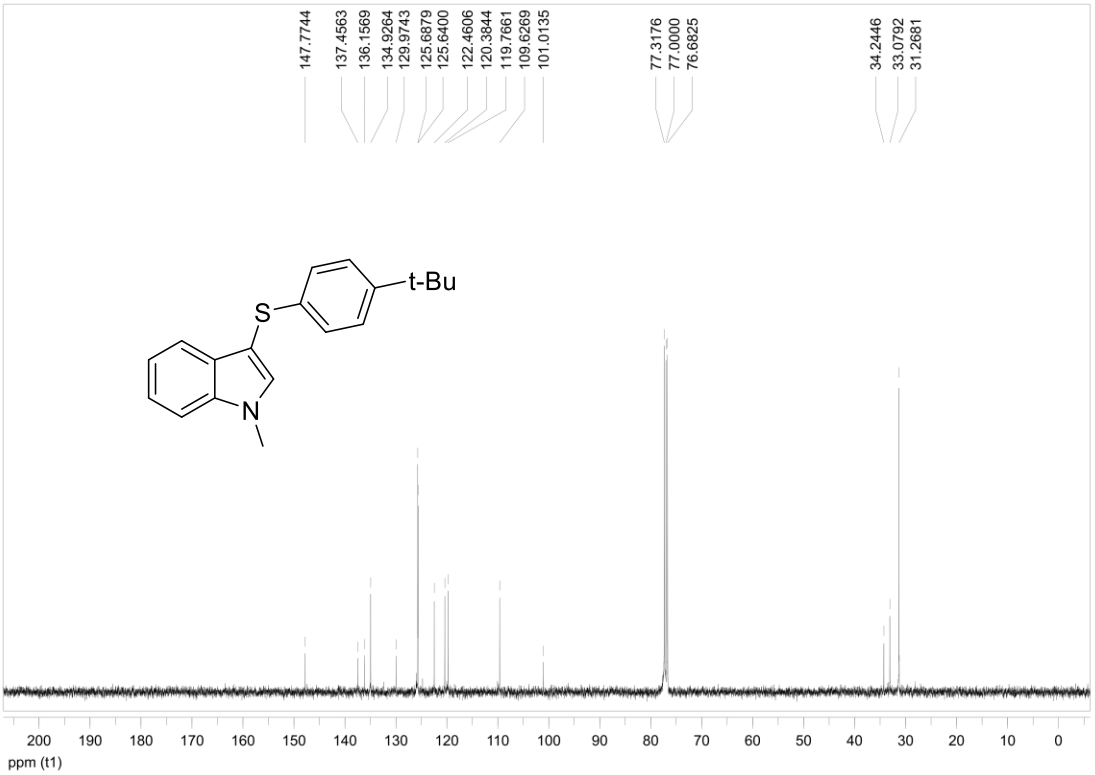


C3-Thioindole **4p**

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

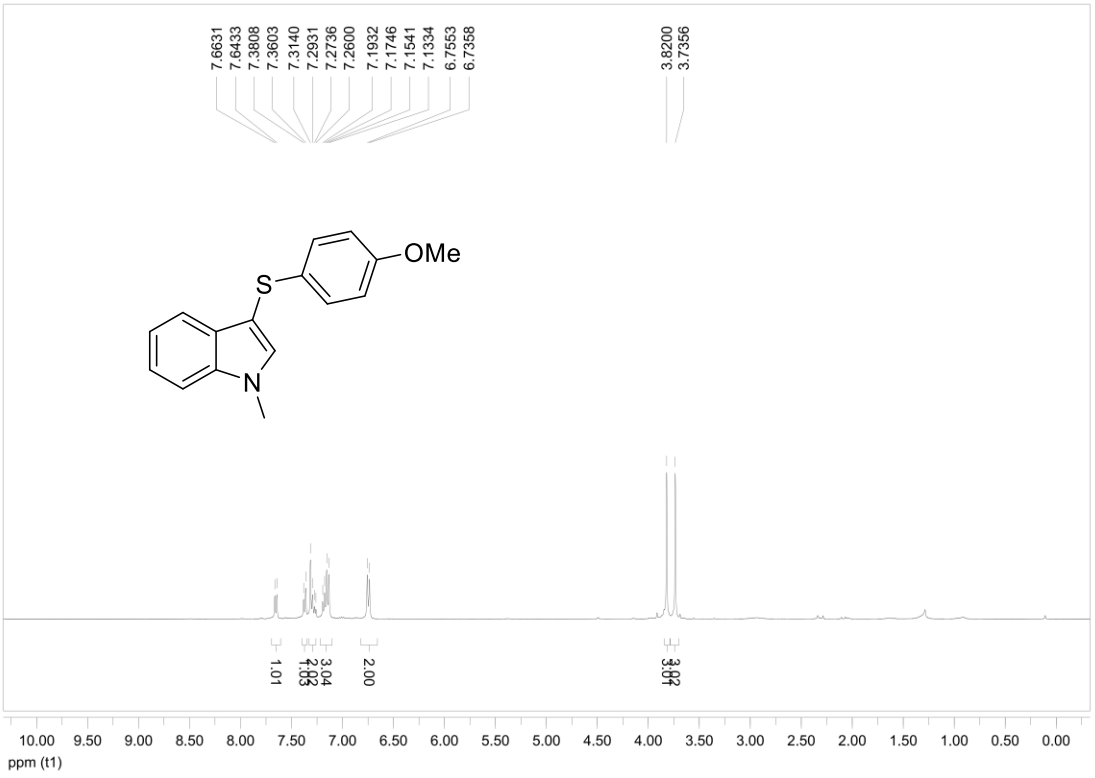


^{13}C NMR (100 MHz, $CDCl_3$)

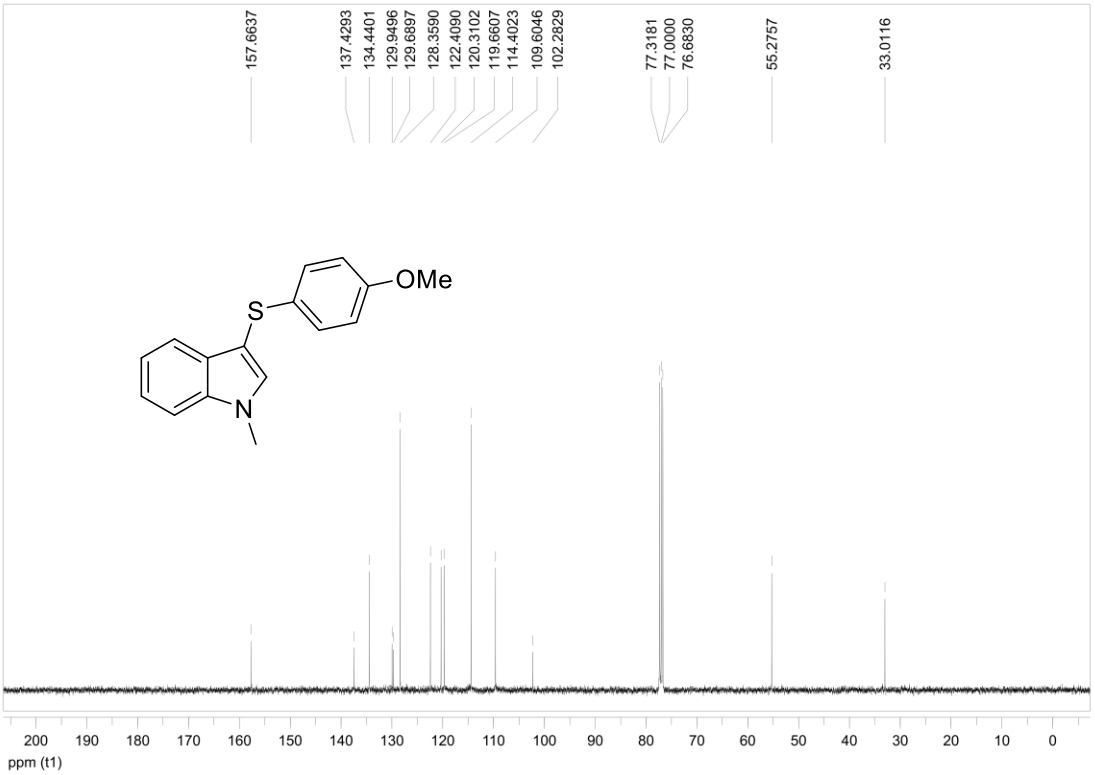


C3-Thioindole **4q**

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

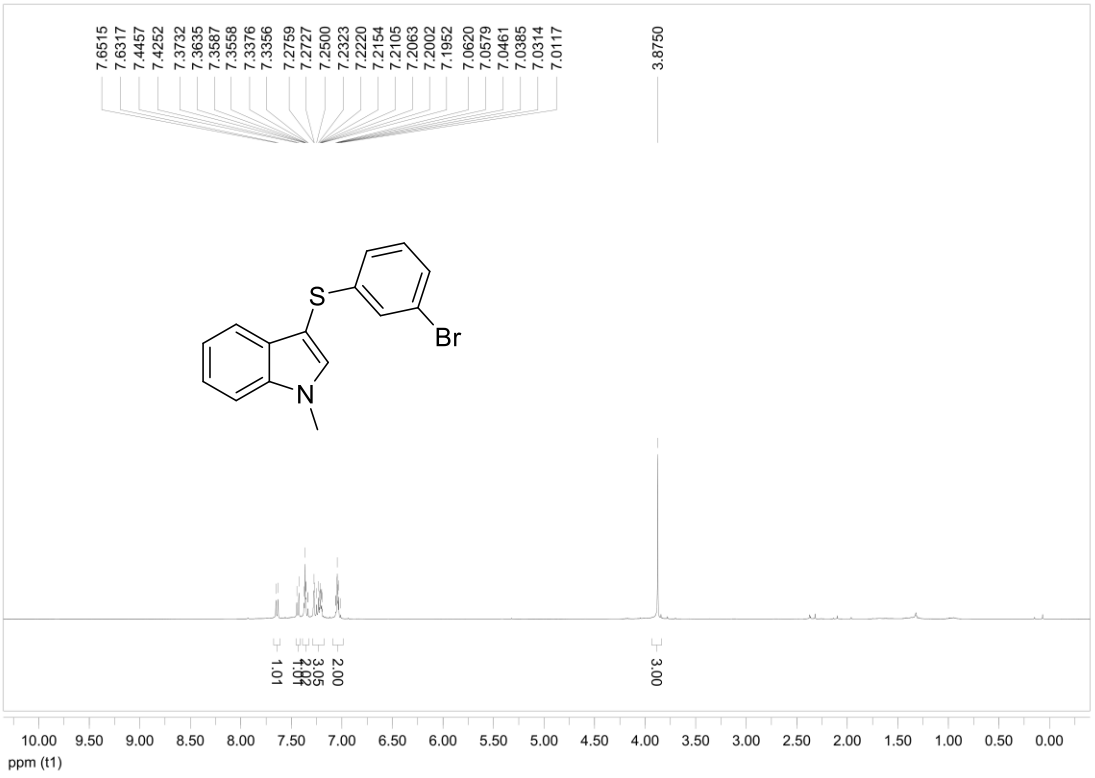


^{13}C NMR (100 MHz, $CDCl_3$)

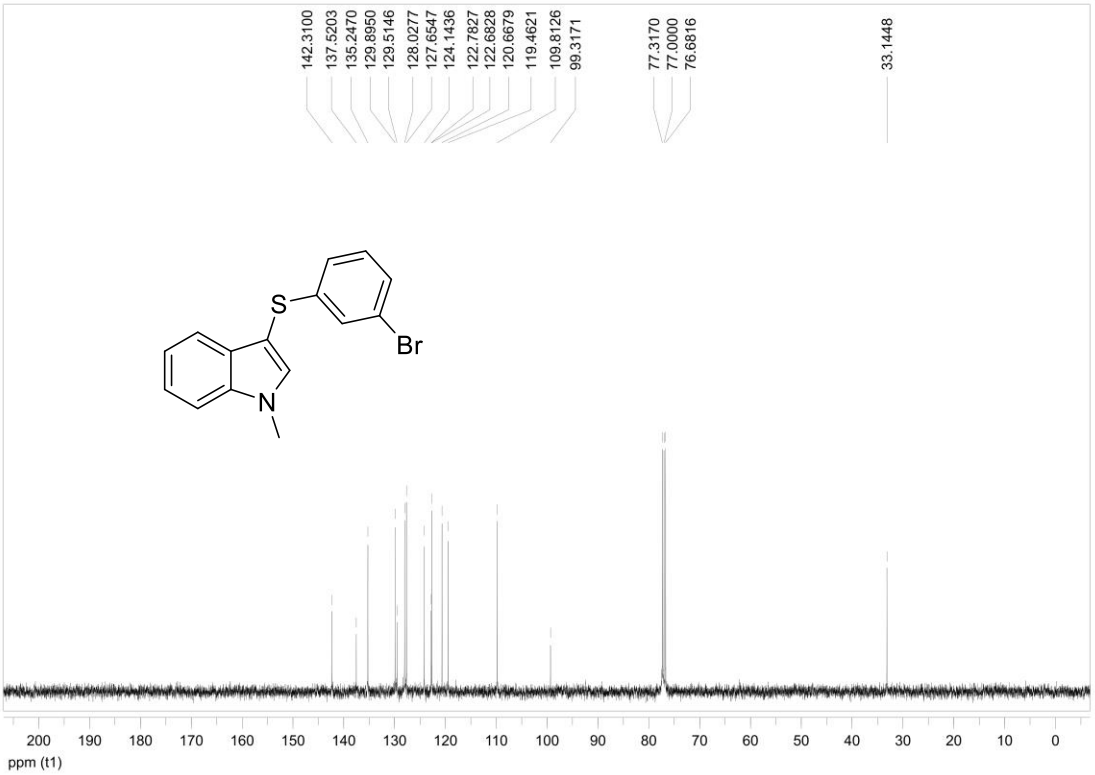


C3-Thioindole **4r**

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

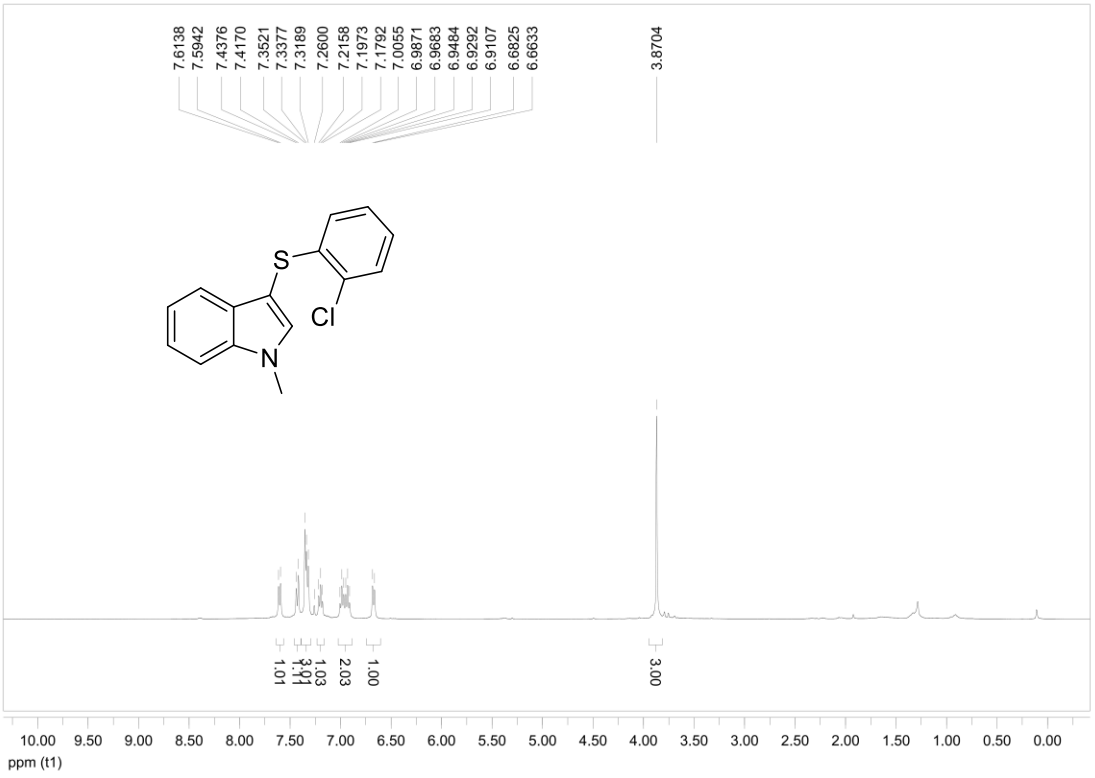


^{13}C NMR (100 MHz, $CDCl_3$)

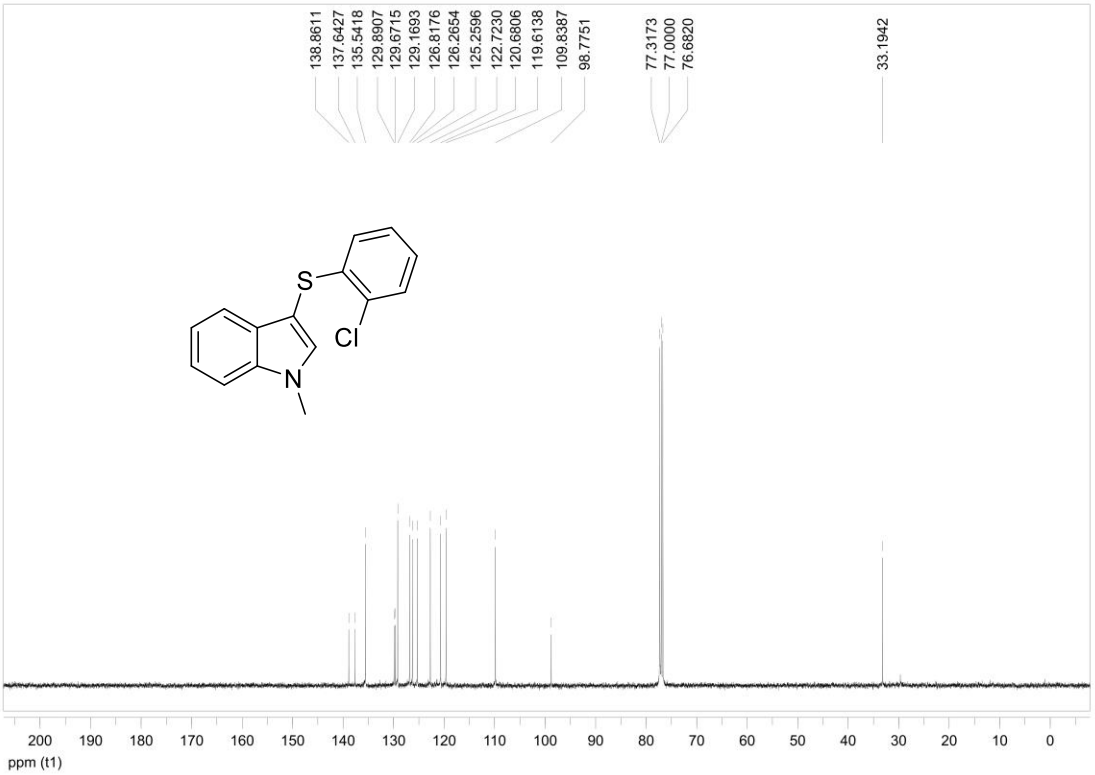


C3-Thioindole **4s**

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

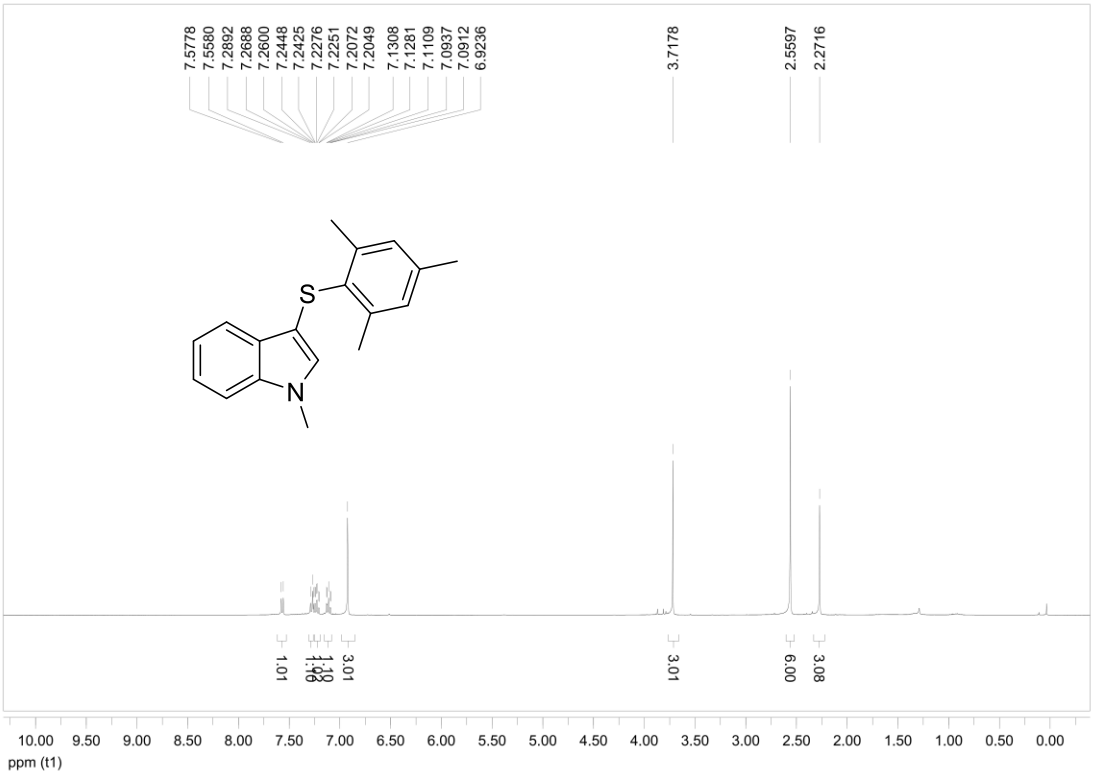


^{13}C NMR (100 MHz, $CDCl_3$)

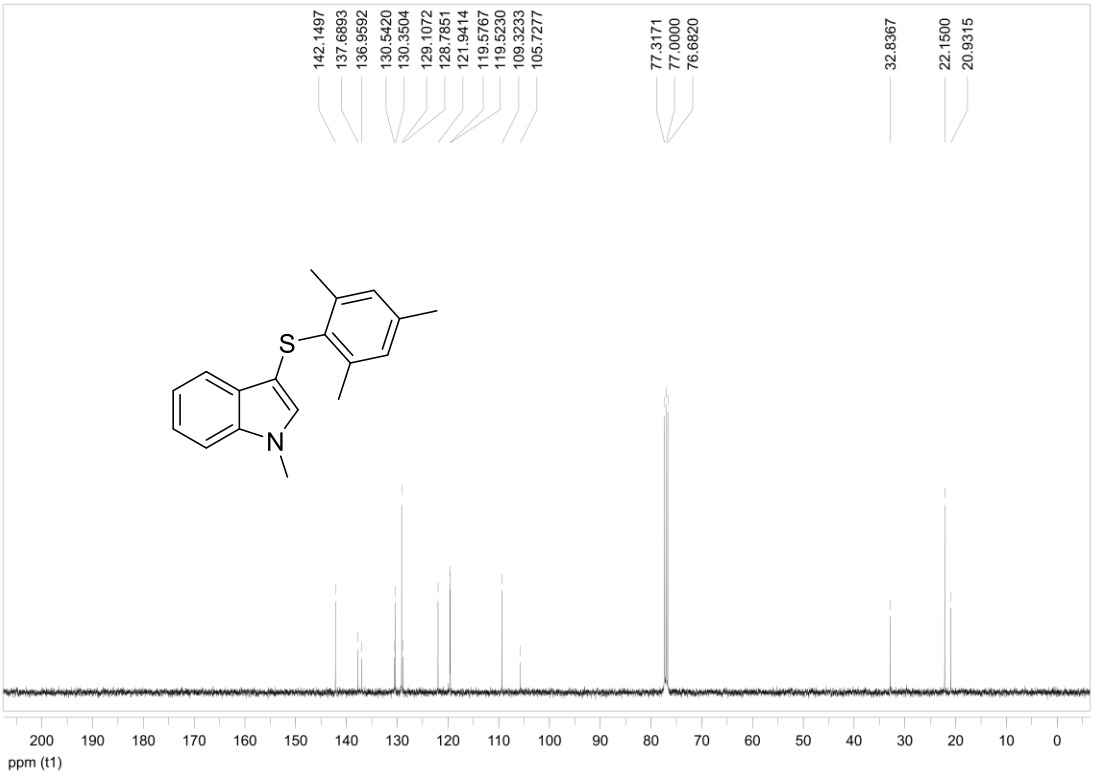


C3-Thioindole **4t**

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

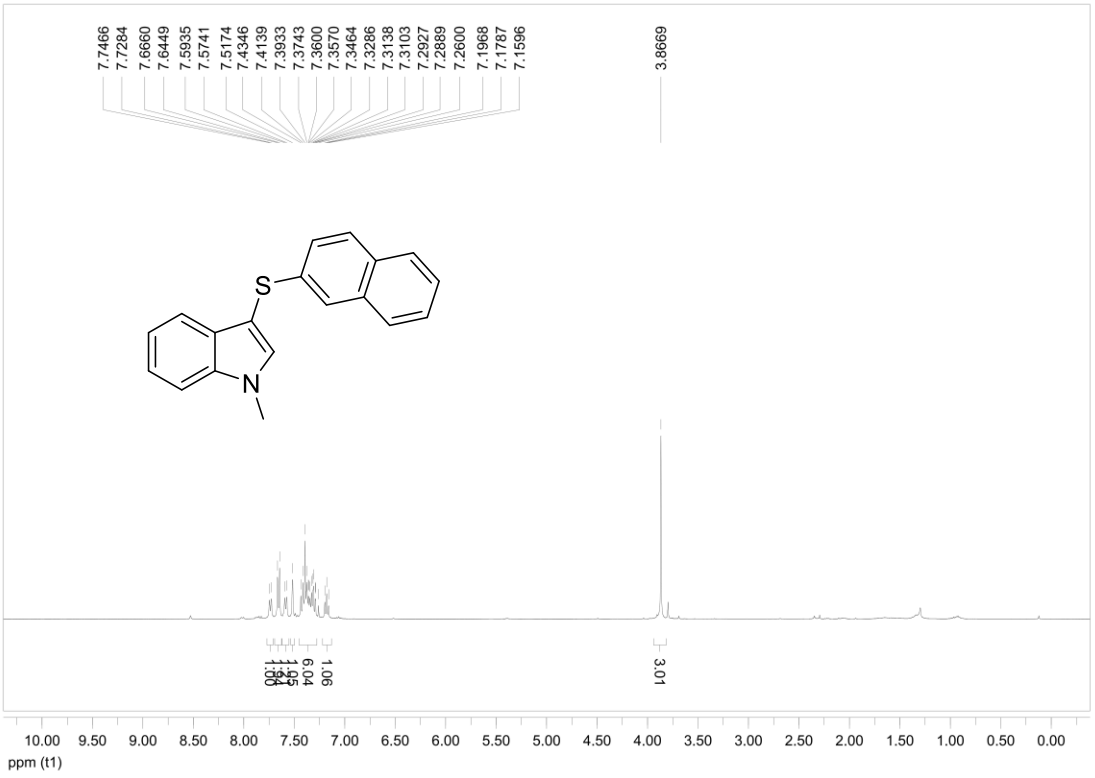


^{13}C NMR (100 MHz, $CDCl_3$)

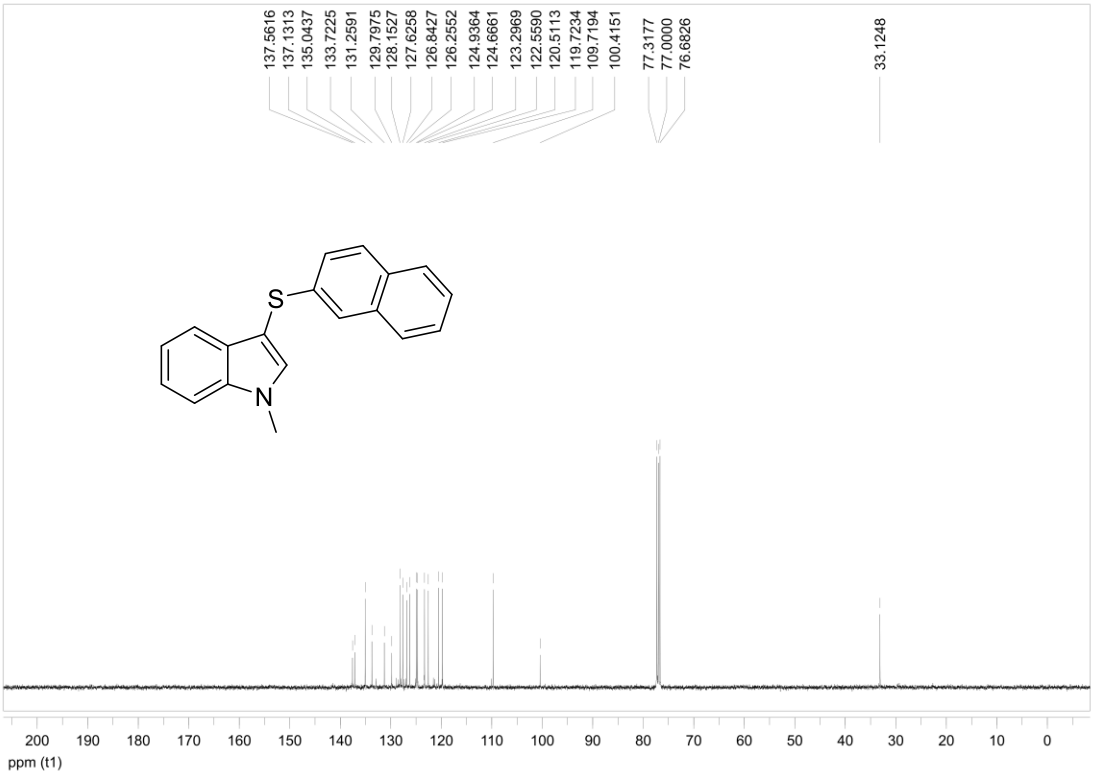


C3-Thioindole **4u**

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

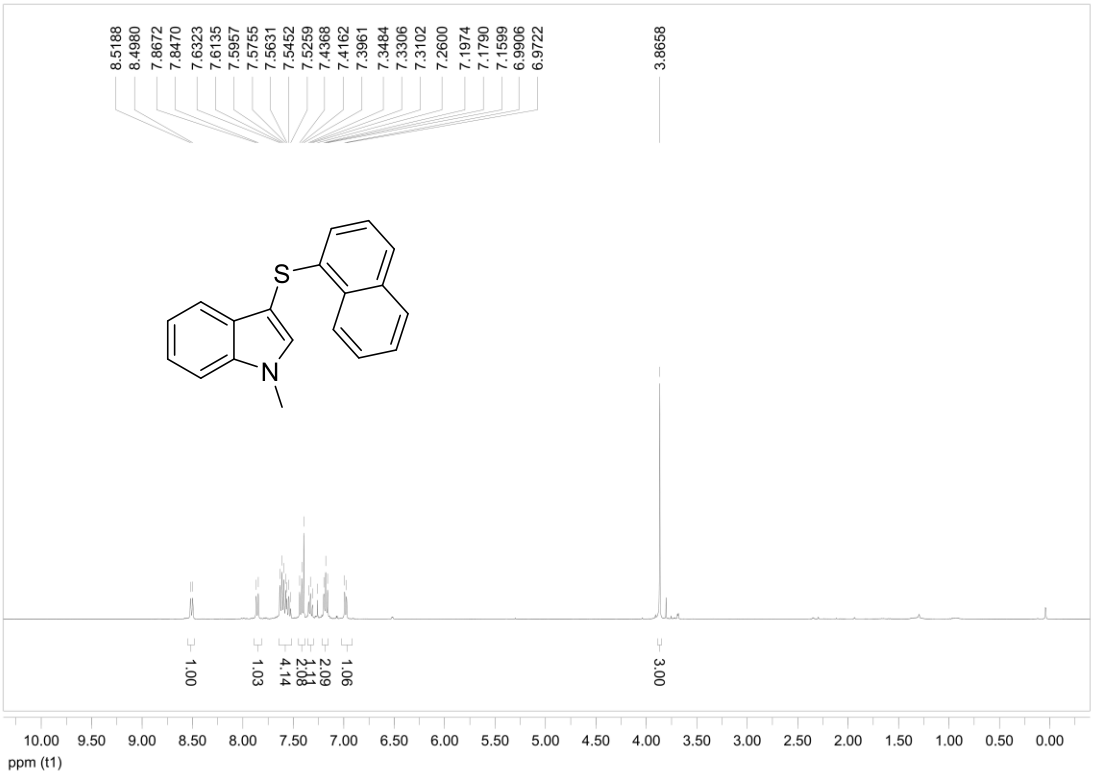


^{13}C NMR (100 MHz, $CDCl_3$)

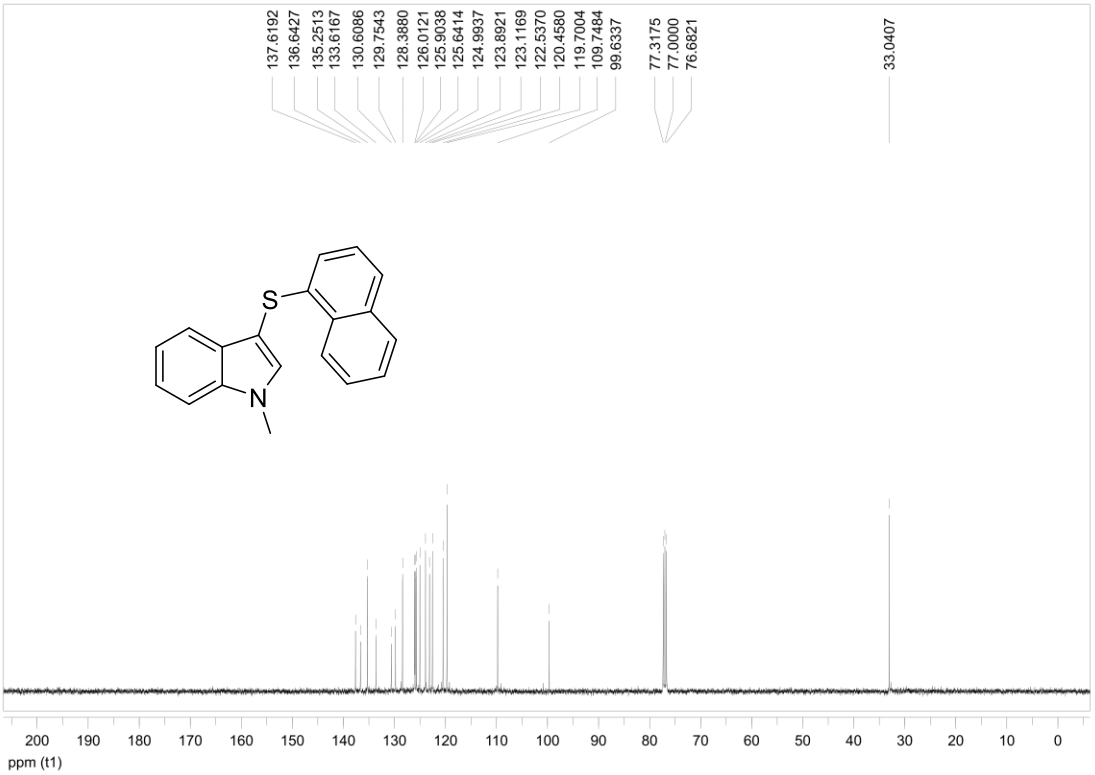


C3-Thioindole **4v**

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

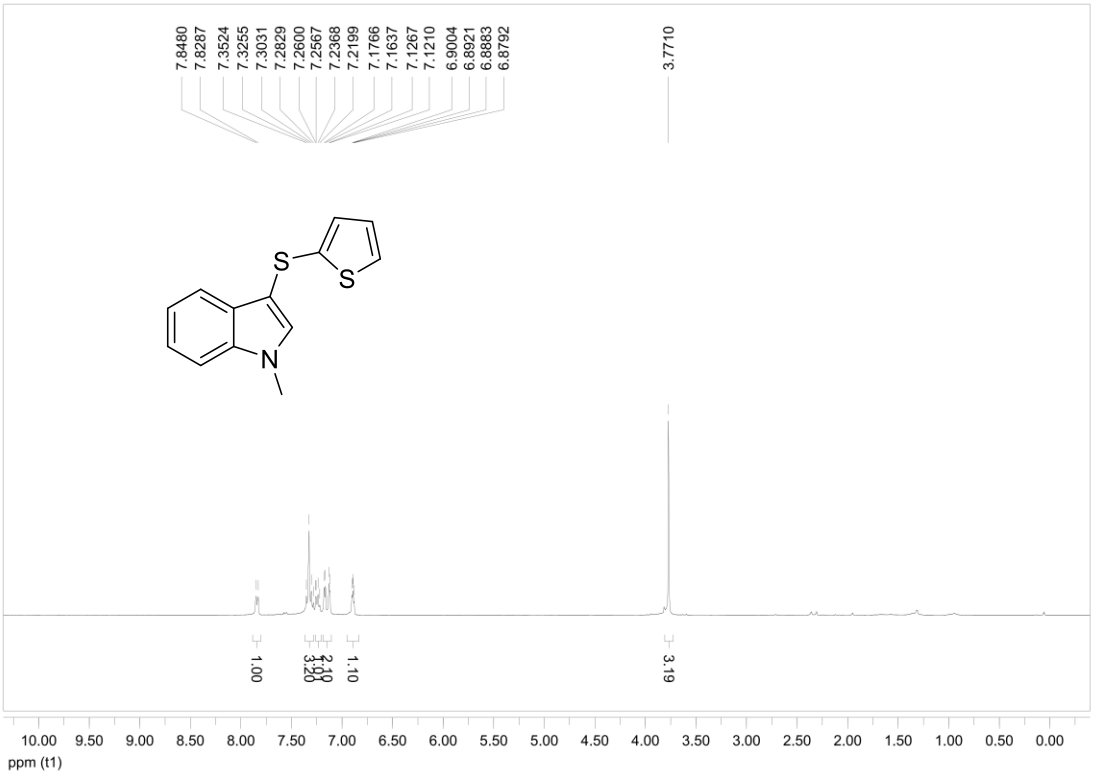


^{13}C NMR (100 MHz, $CDCl_3$)

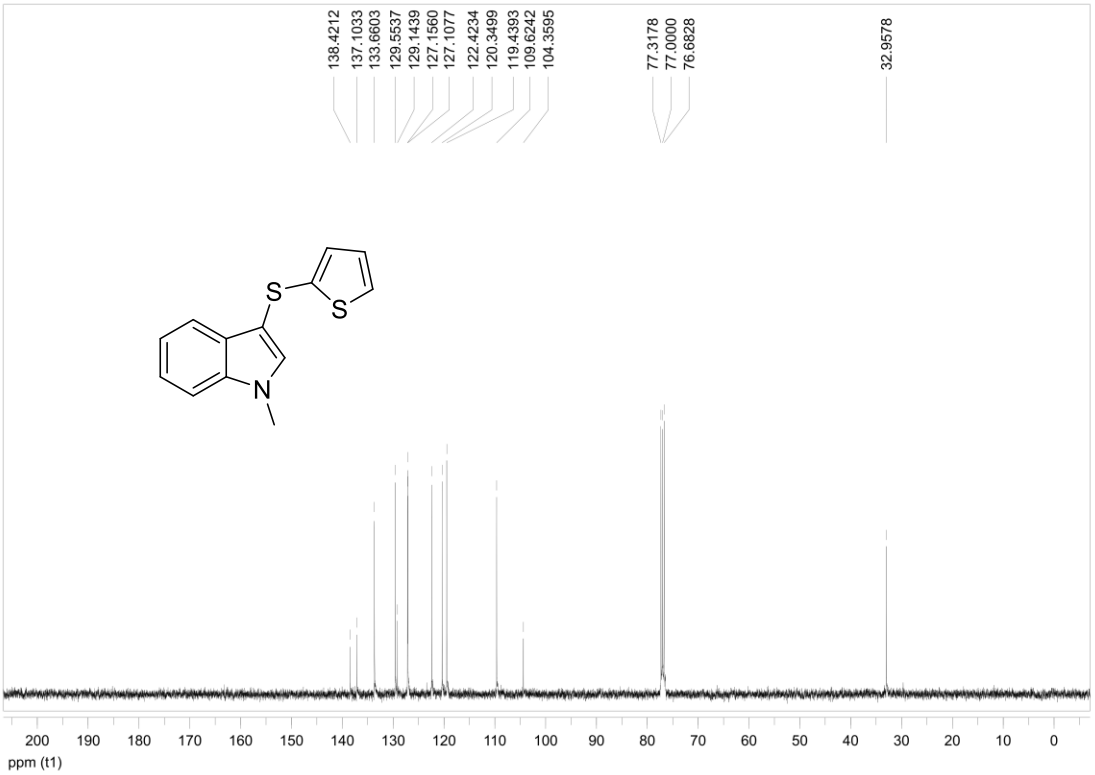


C3-Thioindole **4w**

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

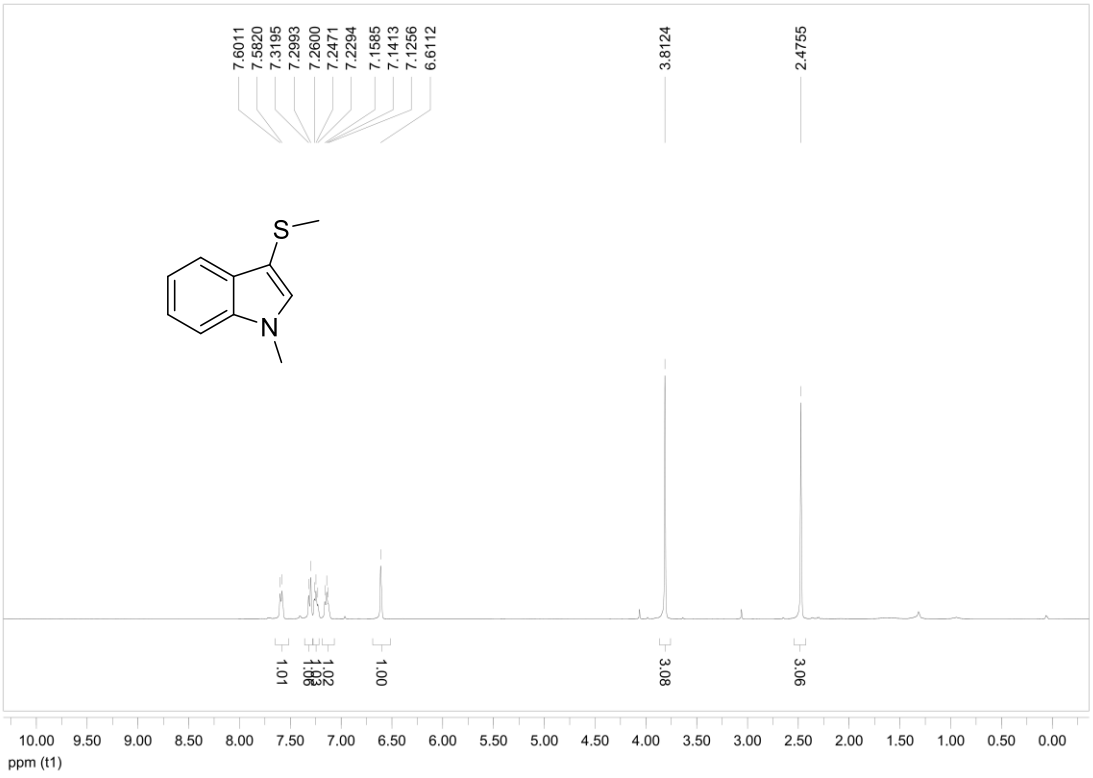


^{13}C NMR (100 MHz, $CDCl_3$)

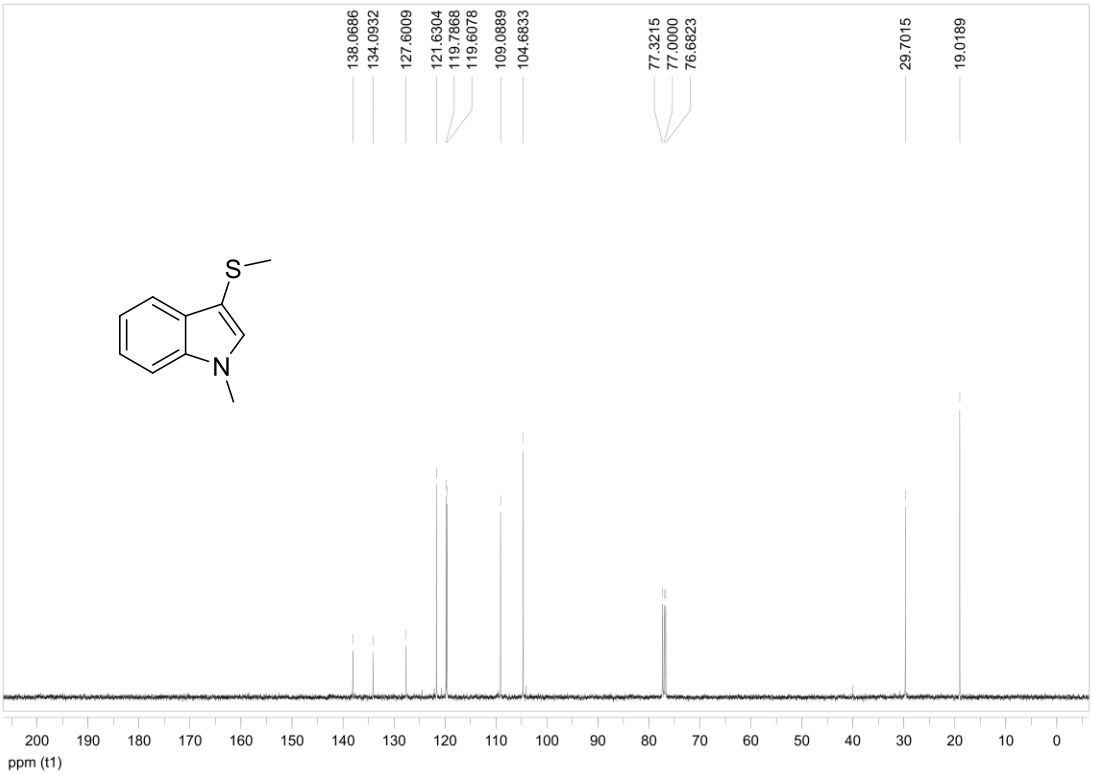


C3-Thioindole **4x**

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

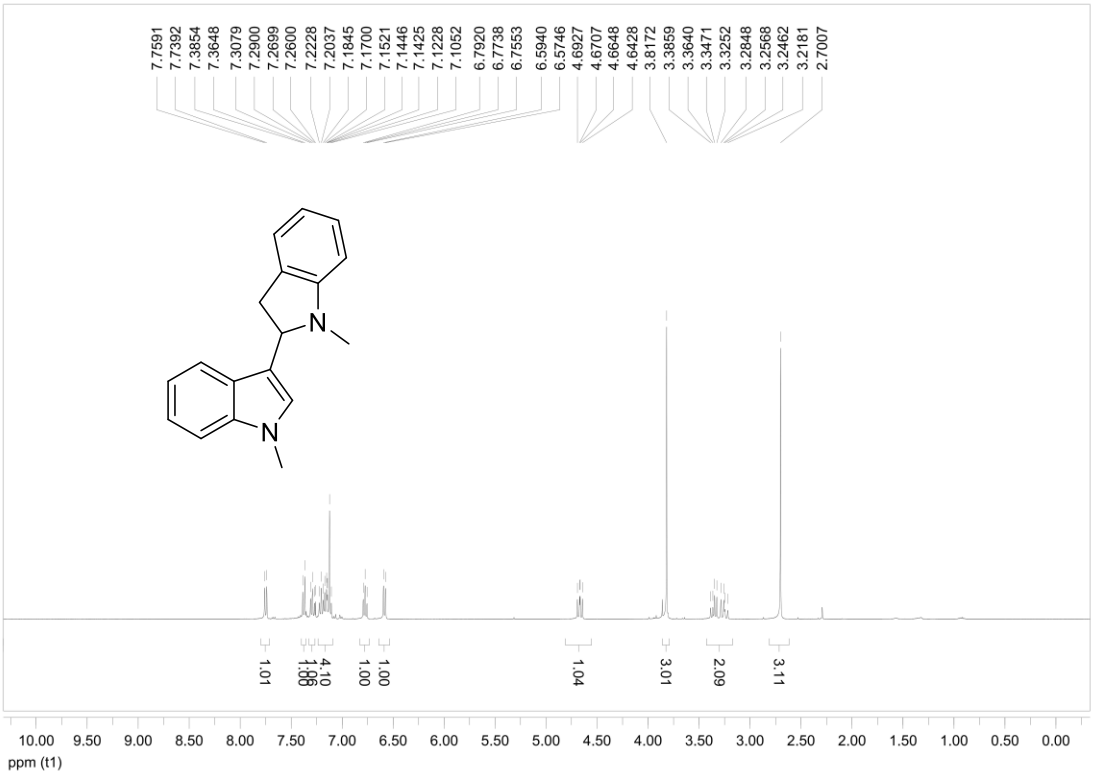


^{13}C NMR (100 MHz, $CDCl_3$)

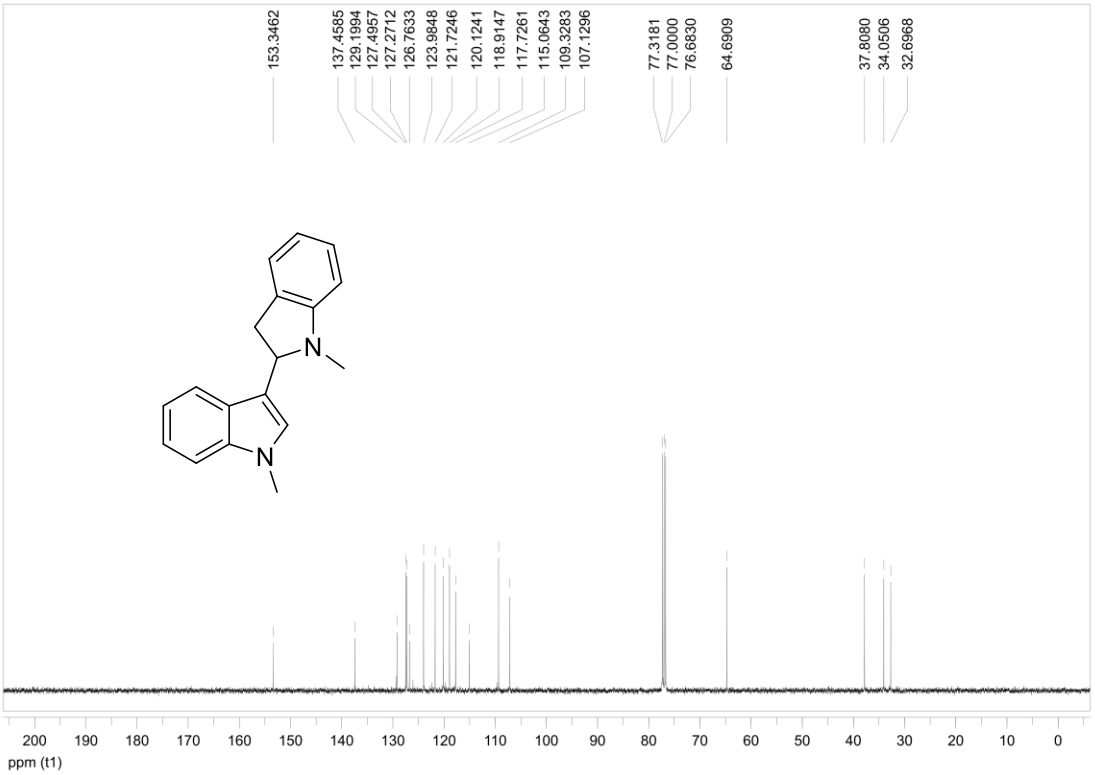


Indole dimer **7a**

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

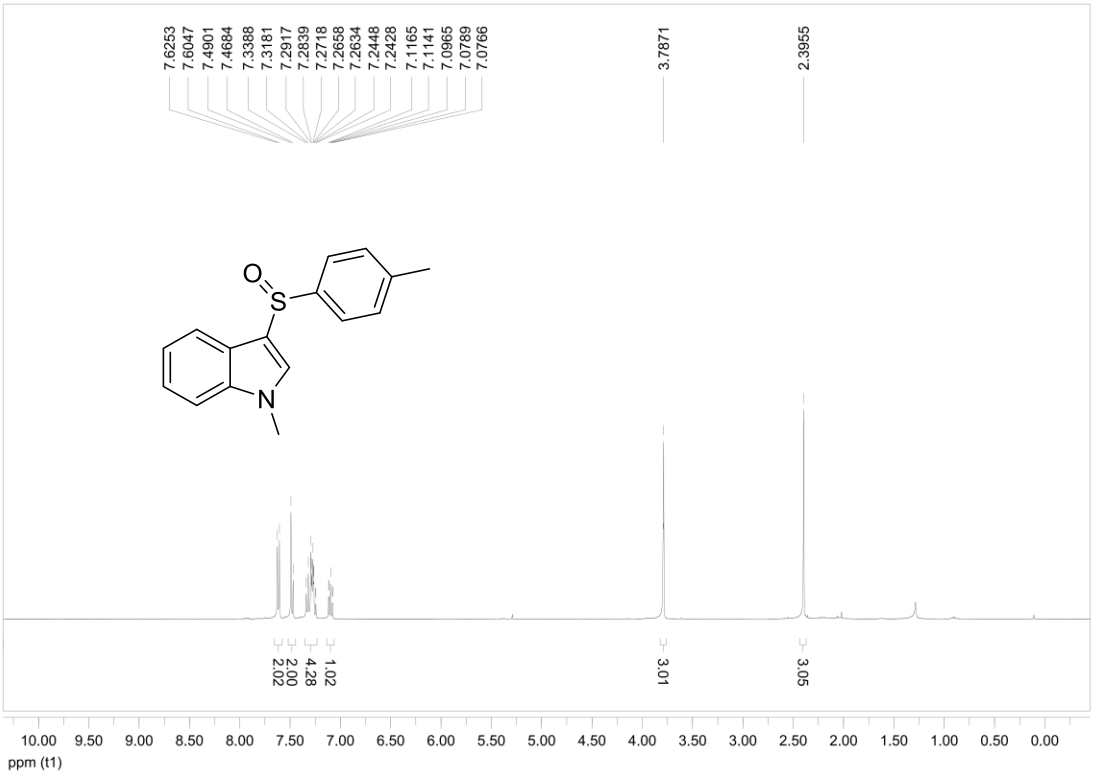


^{13}C NMR (100 MHz, $CDCl_3$)

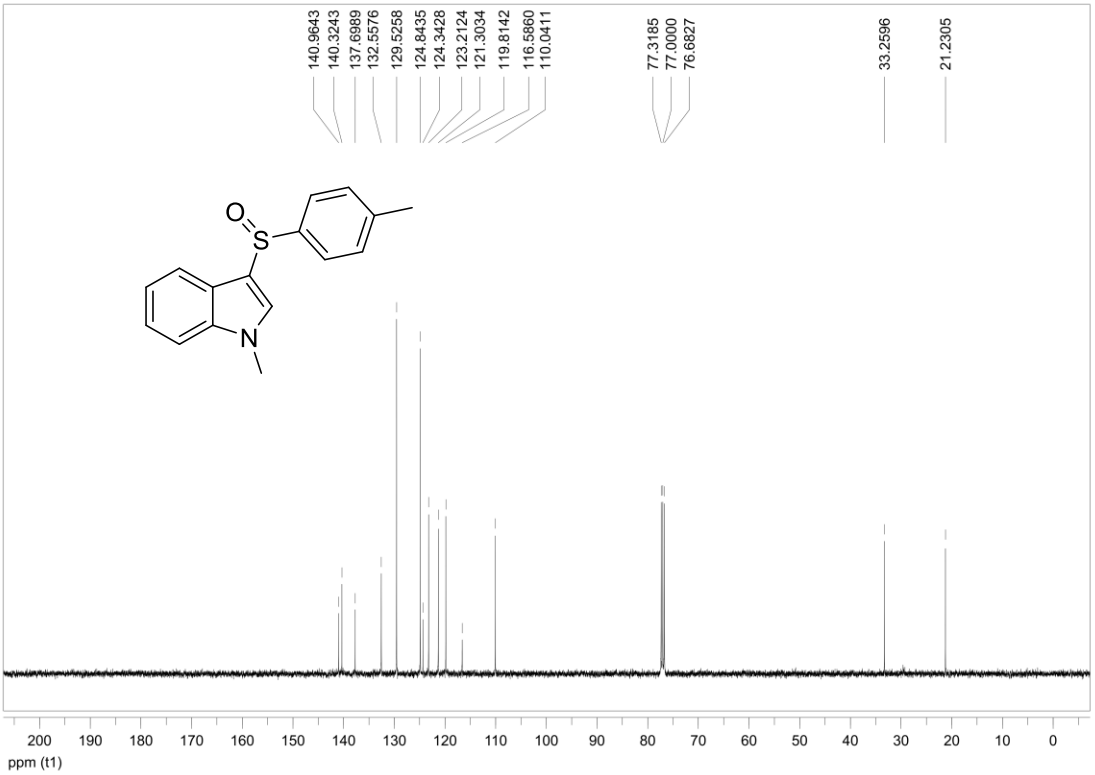


Sulfoxide **6a**

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

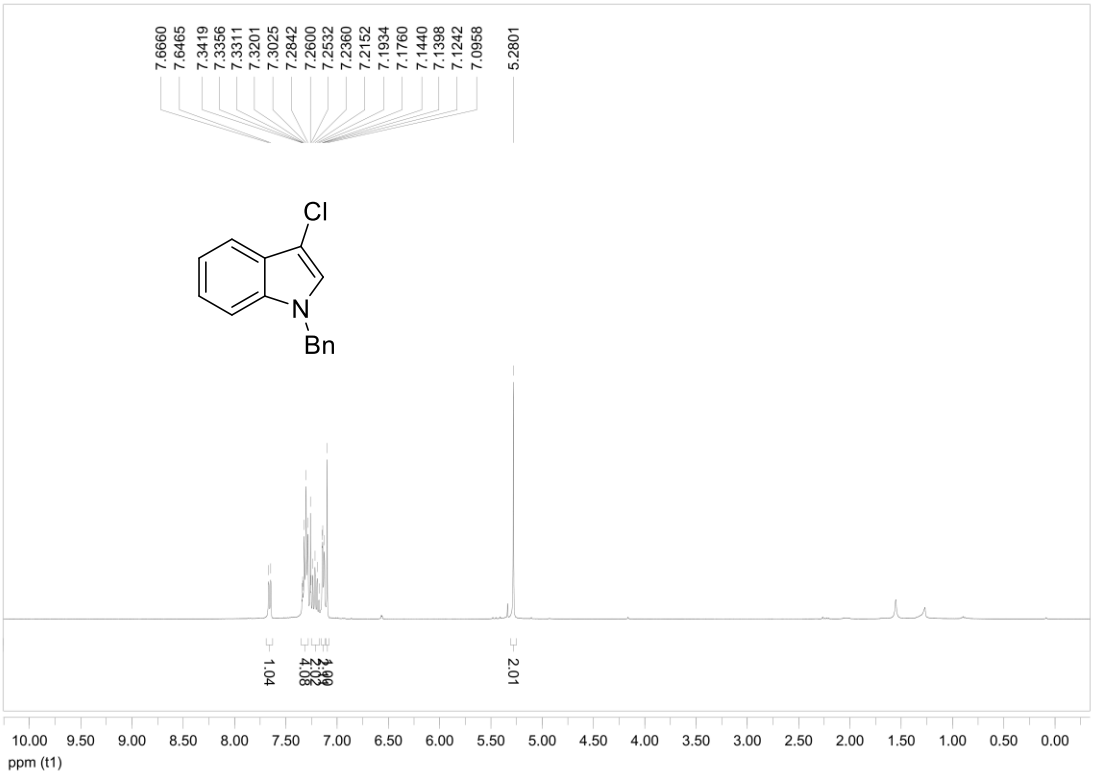


^{13}C NMR (100 MHz, $CDCl_3$)

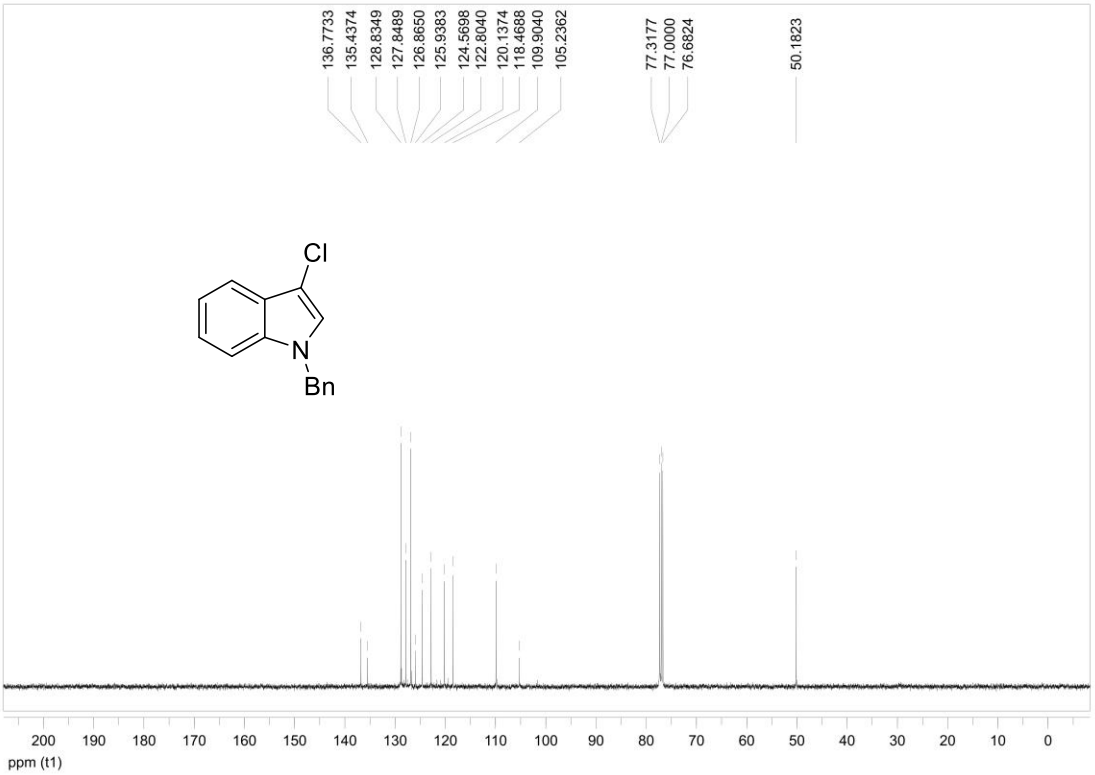


Compound **9a**

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

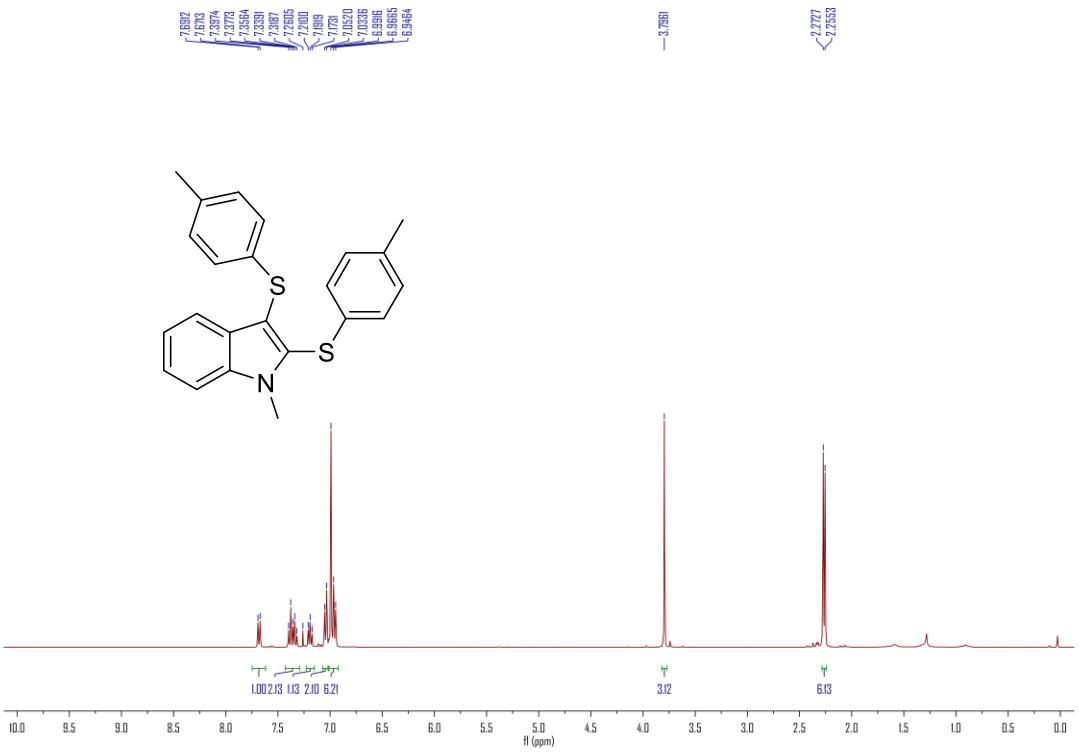


^{13}C NMR (100 MHz, $CDCl_3$)

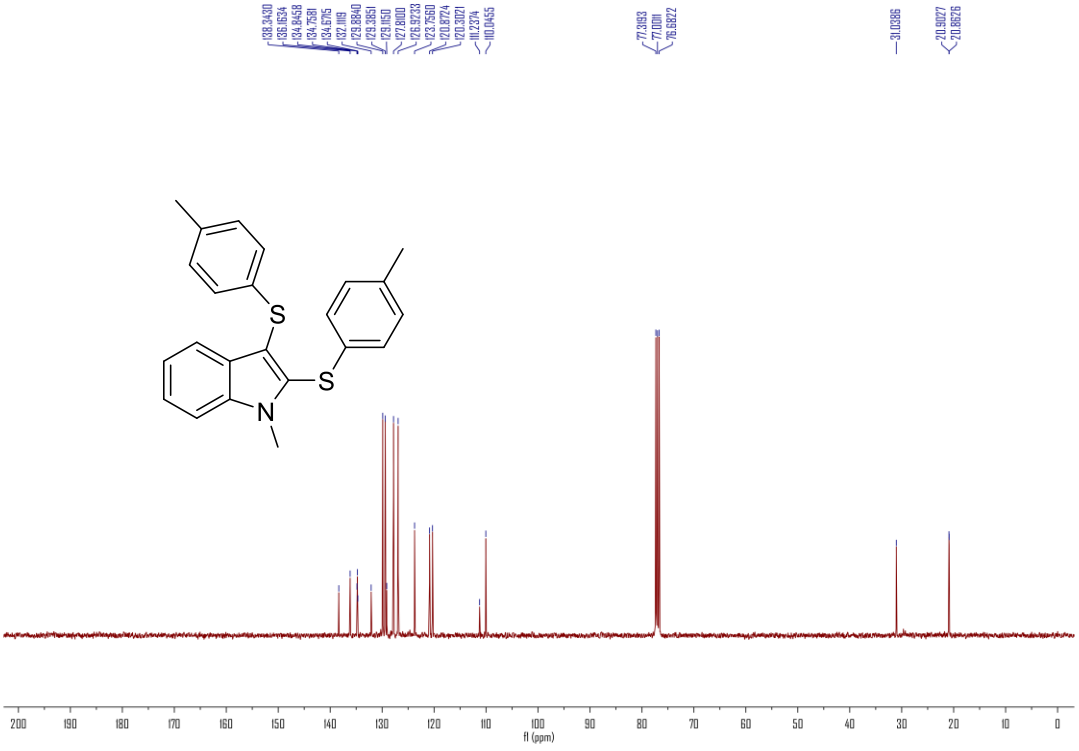


Compound **5a**

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

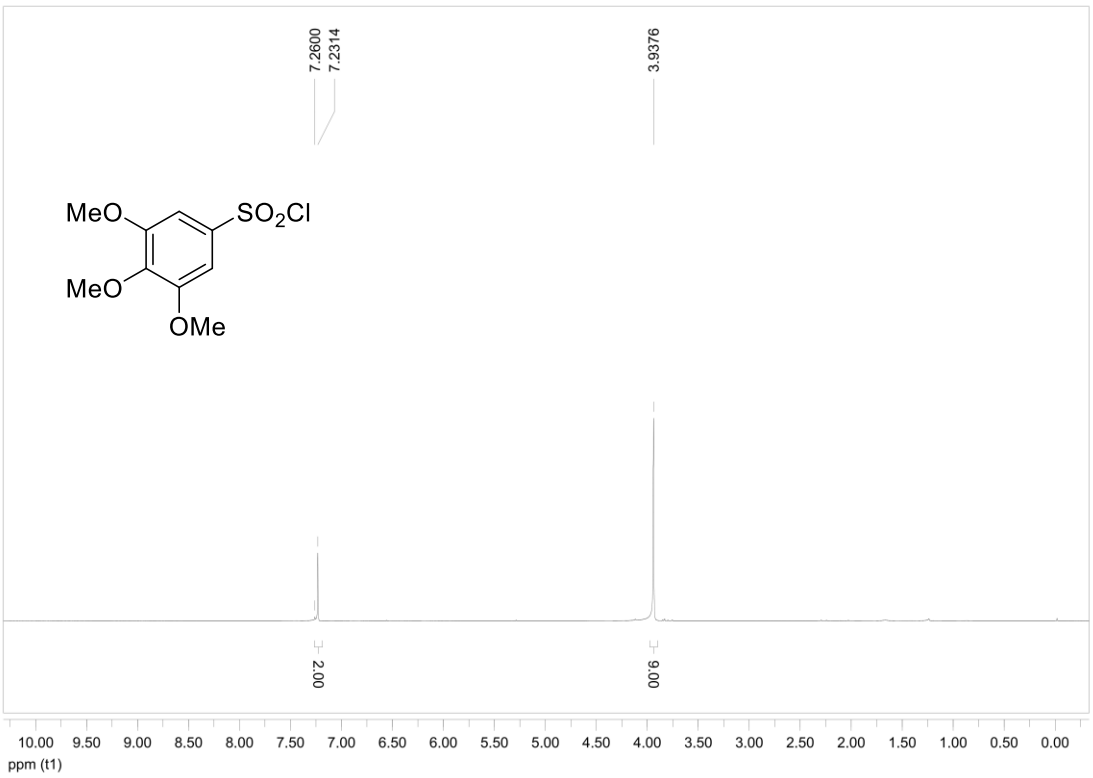


^{13}C NMR (100 MHz, $CDCl_3$)

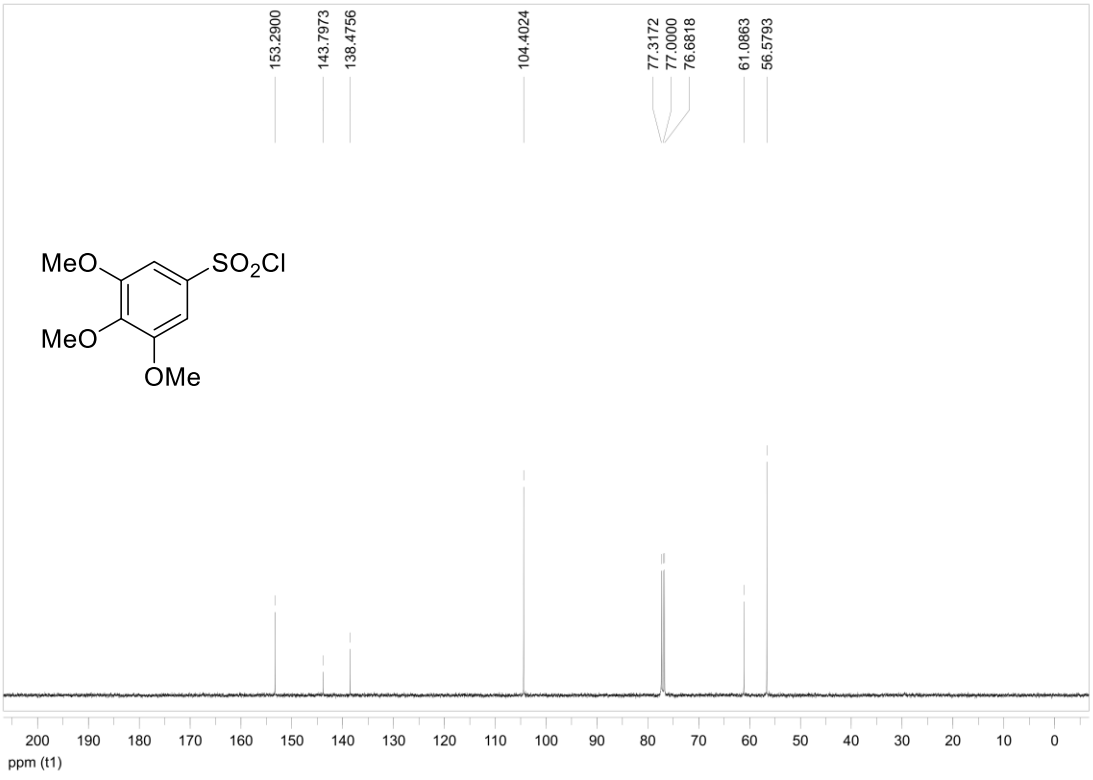


Compound **24**

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

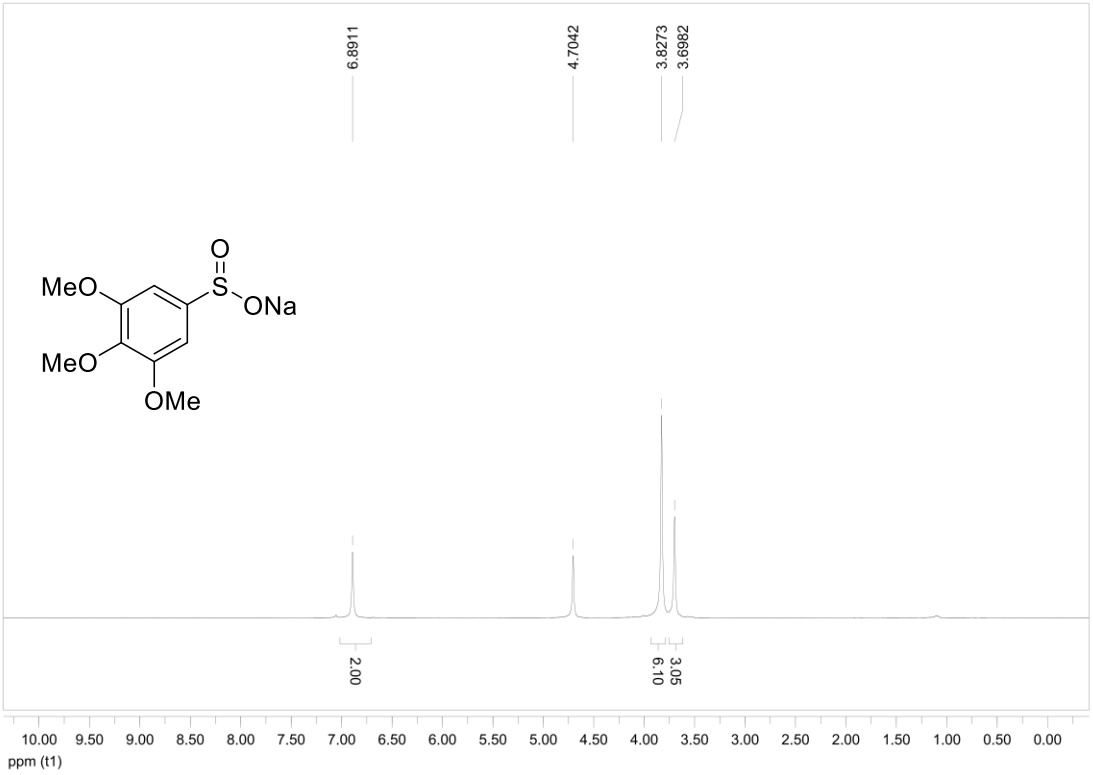


^{13}C NMR (100 MHz, $CDCl_3$)

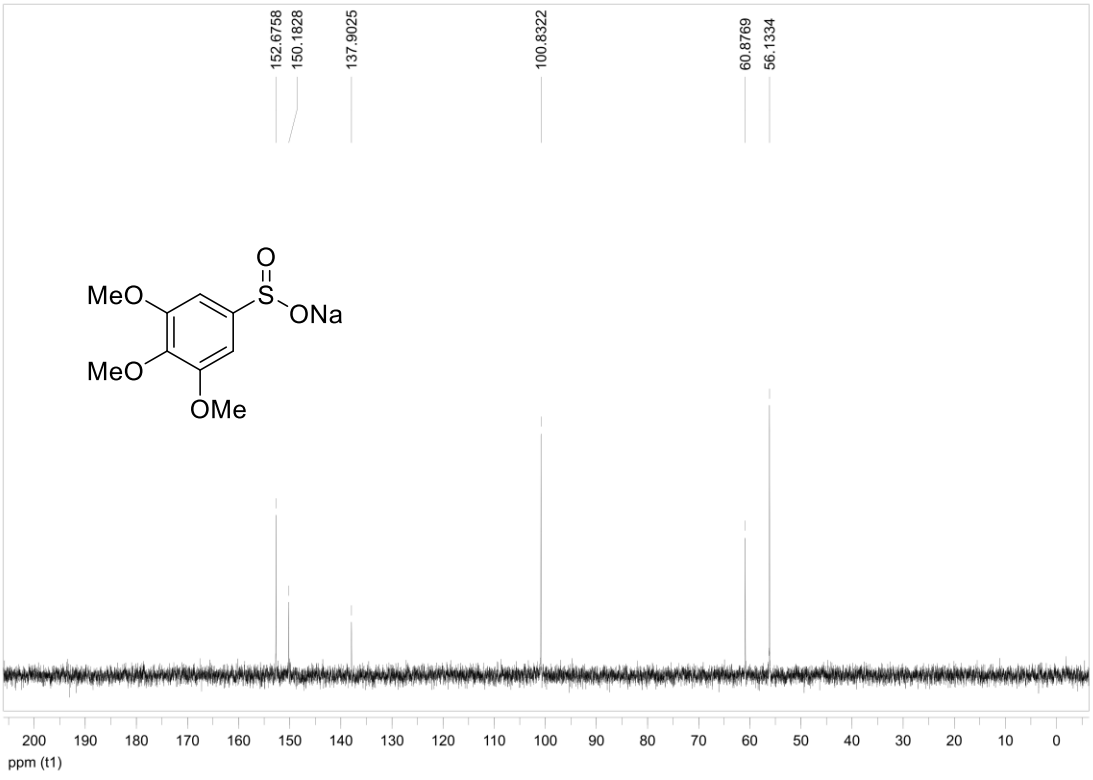


Compound **2b**

^{1}H NMR (400 MHz, D2O)

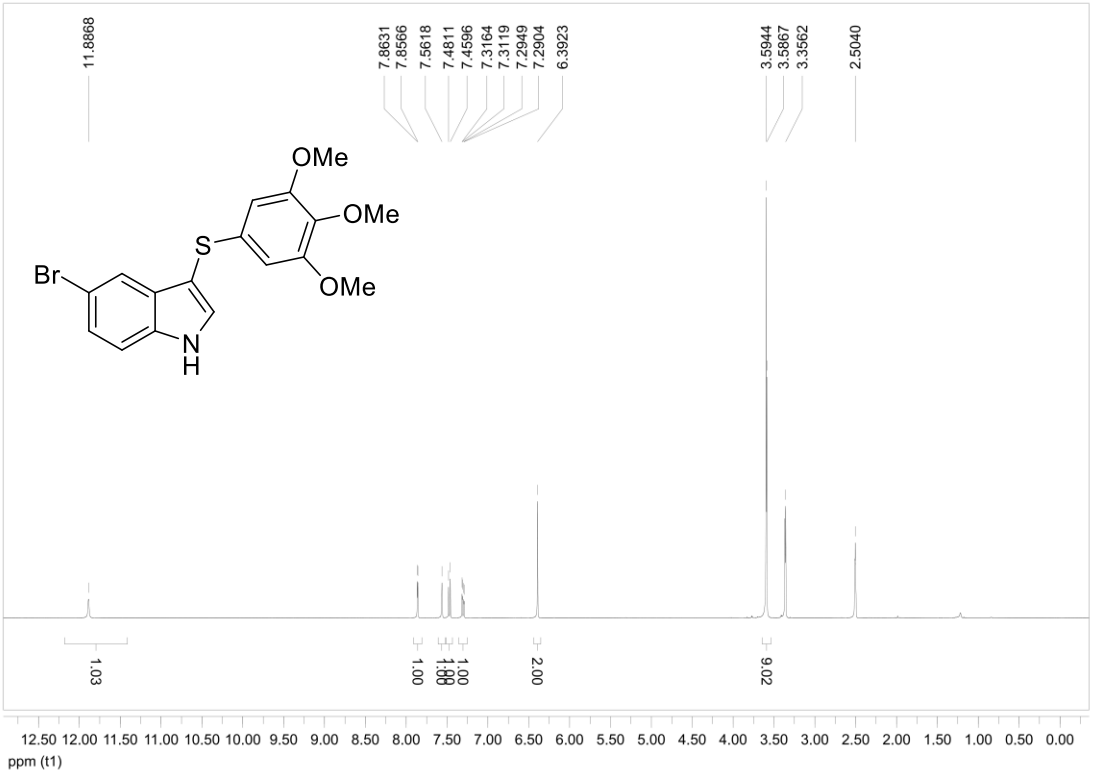


^{13}C NMR (100 MHz, D2O)

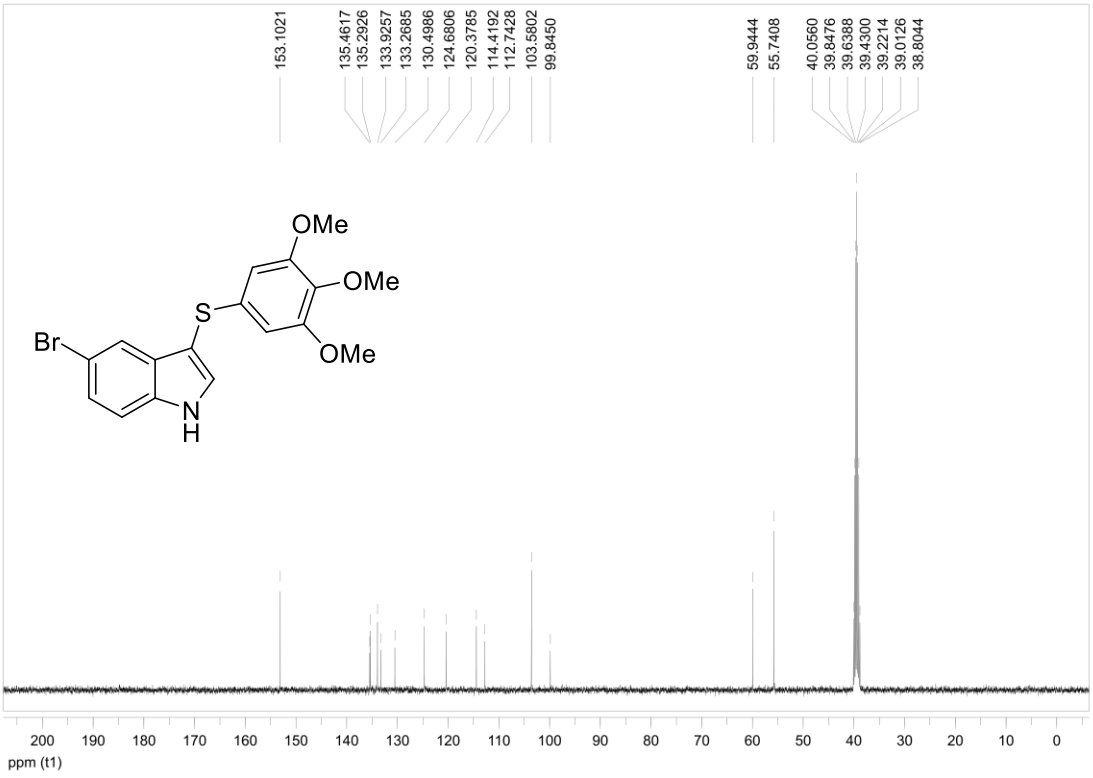


Compound **4y**

^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)



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