Supplementary Information

Selenium Dioxide-promoted Selective Synthesis of Mono- and Bis-sulfenylindoles

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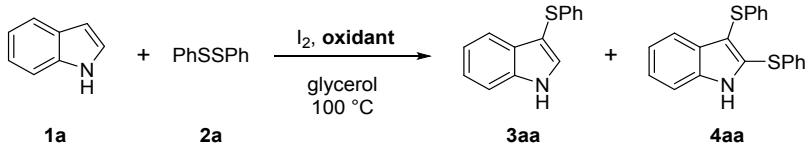
General Information

The reactions were monitored by TLC on Merk silica gel (60 F_{254}) visualized with UV light or with 5% of vanillin in 10% H_2SO_4 with heating. Merck silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^1H NMR spectra were obtained at 400 MHz on a Bruker DPX 400 spectrometer. The spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, referenced against tetramethylsilane (TMS) as the internal standard. ^1H coupling patterns are described as singlet (s), doublet (d), triplet (t) and multiplet (m). Coupling constants (*J*) are reported in Hz. ^{13}C NMR spectra were obtained at 100 MHz on the above-mentioned instrument. The chemical shifts are reported in ppm, referenced to the solvent peak ($CDCl_3$). Low-resolution mass spectra were obtained on a Shimadzu GC-MS-QP2010 mass spectrometer. GC analyses were performed using a RESTEC RTX-5MS capillary column (30m, 0.25 mm id, 0.25 µm film thickness) using products dissolved in ethyl acetate under the following conditions: Injected sample volume, 1.0 µL; flow rate, 54.1 mL/min; initial inlet temperature, 40 °C ramped to 72 °C at 10 °C/min followed by a 5 °C/min ramp to 100 °C (held for 10 min) and 10 °C/min to 280 °C and held for 20 min (total run time: 56.8 min). High-resolution mass spectra were obtained on a Bruker Daltonics micrOTOF-Q II instrument equipped with an ESI and APCI source operating in both positive and negative modes. The samples were dissolved in HPLC-grade acetonitrile and injected into the APCI source by means of a syringe pump at a flow rate of 5.0 µL/min. The Compass 1.3 for micrOTOF-Q II software (Bruker daltonics, USA) was used for data acquisition, processing, and isotopic simulations.

Table S1. Preliminary studies on the preparation of **3aa**.[a]



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

Entry	Oxidant (20 mol%)	I_2(mol%)	Time(h)	% of 3aa[b]	% of 4aa[b]
1	-	10	24	57	-
2	-	-	24	19	-
3[c]	H_2O_2	10	3	76	24
4[d]	H_2O_2	10	3	traces	-
5	SeO_2	10	1	84	-
6[e]	SeO_2	10	1	52	48
7[e,f]	SeO_2	10	1	-	100
8[g]	SeO_2	10	1	100	-
9	SeO_2	10[h]	3	25	-

[a]Reaction conditions: A mixture of **1a** (0.5 mmol), **2a** (0.3mmol), SeO_2 (20 mol%, 0.011 g), I_2 (10 mol%, 0.0076 g), and glycerol (1.0 mL) was stirred at 100 °C and the reaction progress was followed by TLC. [c]Conversion values obtained by GC-MS. [c]0.01 mL of a 30% w/w H_2O_2 aqueous solution was added (0.1 mmol). [d]1.0 mL of 30% w/w aqueous H_2O_2 solution (10 mmol) was added without additional solvent. [e]1.0 equiv. (0.055 g) with respect to indole **1a**. [f]0.6 mmol of **2a** (1.2 equiv) was added. [g]0.6 mmol of **2a** (2.4 equiv.) was added. [h]Br_2 was used as catalyst in replacement to I_2.

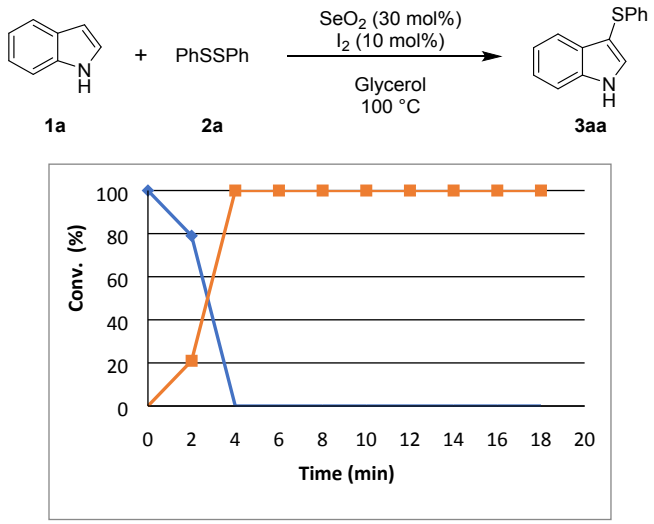
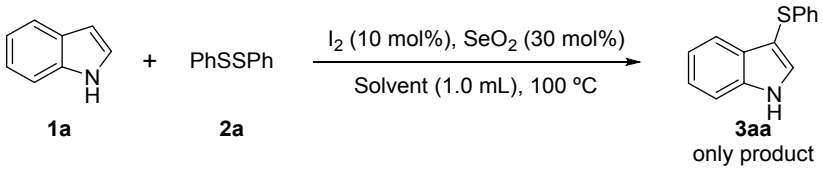


Figure S1: Reaction time studies for the preparation of **3aa**. Blue line (♦): **1a**, red line (■): **3aa**. [**1a** (0.5mmol), **2a** (0.3 mmol), SeO_2 (30 mol%, 0.016 g), I_2 (10 mol%, 0.0076 g) and glycerol (1.0 mL)].

Table S2: Studies on the solvent effect during the formation of mono-sulfenylindole **3aa**.



Entry	Solvent	Time for 100% of conversion to **3aa**[a]
1	Glycerol	4 min
2	H_2O	4 min
3	PEG-400	1 h
4	DMF	12 min
5	THF[b]	24 h

[a] Conversion values obtained by GC-MS. [b] A sealed vial was used.

Control Experiments

Procedure #1

Indole (**1a**) (0.5 mmol, 0.058 g), SeO_2 (0.5 mmol, 0.055 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred for 20 h at 100 °C (oil bath), after which the reaction mixture poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #2

Indole (**1a**) (0.5 mmol, 0.058 g), SeO_2 (0.5 mmol, 0.055 g), molecular iodine (10 mol%, 0.05 mmol, 0.0127), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred at 100 °C (oil bath) and followed by TLC. After 15 min, the reaction mixture poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #3

3,3'-Di-indolyl selenide (**5**) (0.25 mmol, 0.0778 g), the diorganyl disulfide **2a** (0.3 mmol, 0.0655 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred at 100 °C (oil bath) and followed by TLC. After 1 h, the reaction mixture poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #4

Diphenyl disulfide (**2a**) (0.3 mmol, 0.0655g), indole **1a** (0.5 mmol, 0,0586 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred at 100 °C (oil bath) and followed by TLC. After 24 h, the reaction mixture poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #5

Diphenyl disulfide (**2a**) (0.3 mmol, 0.0655g), indole **1a** (0.5 mmol, 0,0586 g), SeO_2 (30 mol%, 0.015 mmol, 0.0166 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred under argon at 100 °C (oil bath). After 4 min, the reaction mixture was poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #6

Diphenyl disulfide (**2a**) (0.3 mmol, 0.0655g), indole **1a** (0.5 mmol, 0,0586 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred under argon on at 100 °C (oil bath). After 24 h, the reaction mixture was poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Procedure #7

Diphenyl disulfide (**2a**) (0.3 mmol, 0.0655g), indole **1a** (0.5 mmol, 0,0586 g), I_2 (0.3 mmol, 0.0761 g), and glycerol (1.0 mL) were added to a round-bottomed flask. The resulting solution was stirred at 100 °C (oil bath). After 4 min, the reaction mixture was poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was then analyzed by GC-MS.

Mechanistic studies through monitoring short-live intermediates by HRMS

For mechanistic studies, the short-live intermediates were analyzed by HRMS. Aliquots which were sampled directly from the reaction experiments and immediately dissolved in MeOH and injected into the ESI or APCI source at a constant flow rate of 3.0 µL/min. The presence of the selenium atom in the intermediates was confirmed its characteristic isotope pattern, which comprises six stable and abundant isotopes. Peaks attributed to intermediates were better detected using the APCI source.

Experimental procedure: Diphenyl disulfide (**2a**) (0.3 mmol, 0.0655g), indole **1a** (0.5 mmol, 0,0586 g), SeO_2 (30 mol%, 0.015 mmol, 0.0166 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and water* (1.0 mL), In a 20 mL vial were added respectively. The resulting solution was stirred at 100 °C (oil bath). After 2 min, a 50 µL aliquot was removed with an infusion syringe and immediately dissolved in MeOH and injected into the ESI source. The recorded spectra and expanded regions, including simulated peaks, are displayed below.

*water was used instead glycerol because glycerol self-polymerizes to generate a large number of peaks.

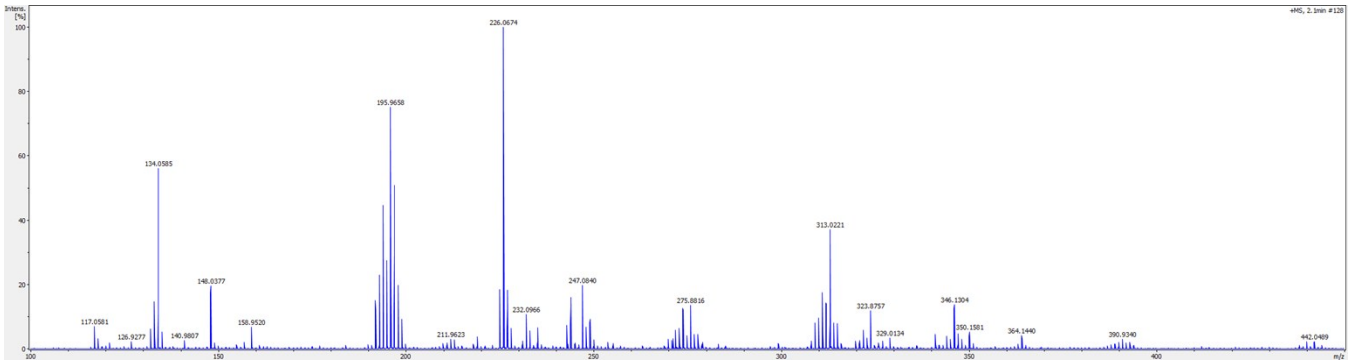


Figure S2. Expanded region between *m/z* 100 and 450 of the HRMS spectrum (APCI source) obtained from Experiment #1.

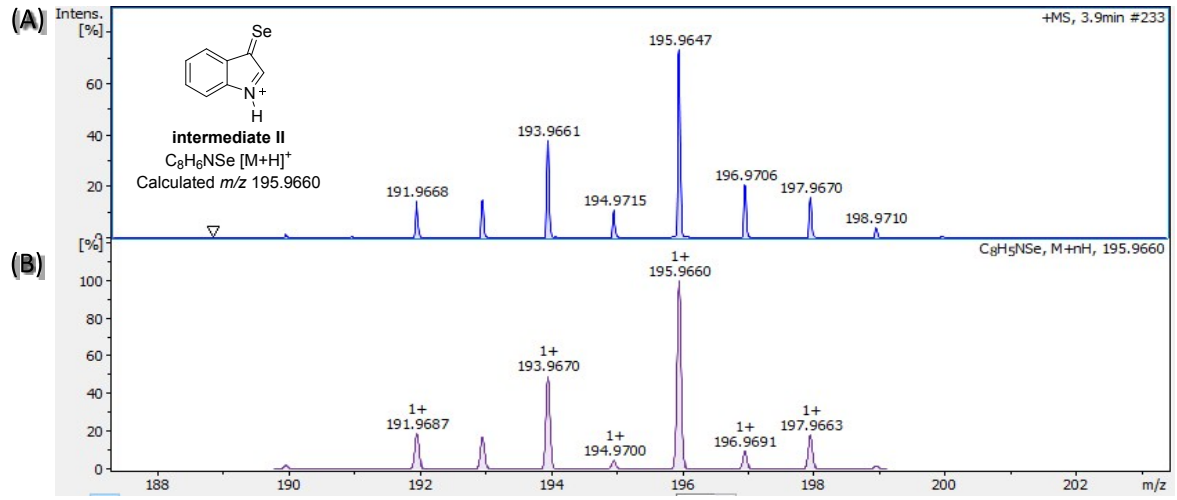


Figure S3. Expanded region of the experiment #1 spectra (Figure S2) showing the peak with *m/z* of 195.9647 attributed to intermediate **II** (A), and the simulated *m/z* and isotope pattern for the molecular formula C_8H_5NSe $[M+H]^+$ (B).

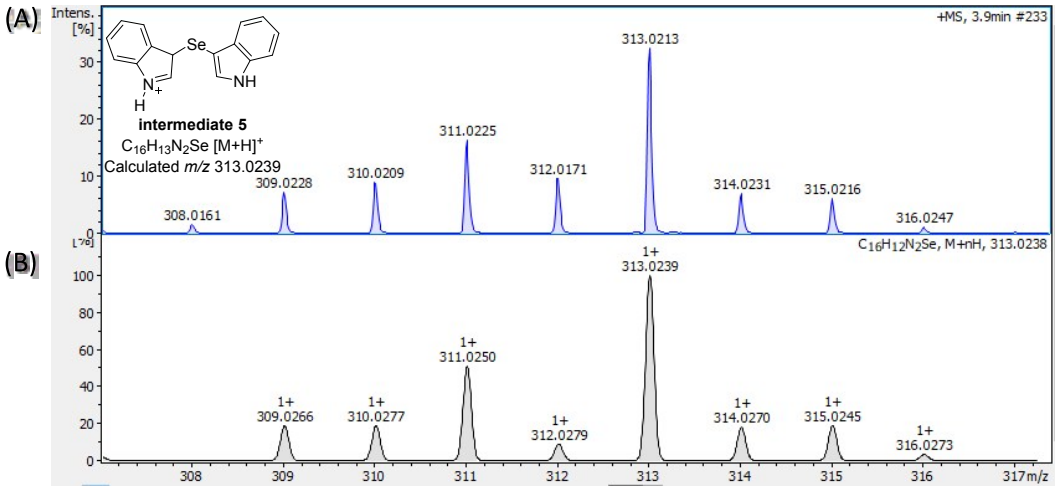


Figure S4. Expanded region of the experiment #1 spectra (Figure S2) showing the peak with *m/z* of 313.0213 attributed to intermediate **5** (A), and the simulated *m/z* and isotope pattern for the molecular formula $C_{16}H_{13}N_2Se$ $[M+H]^+$ (B).

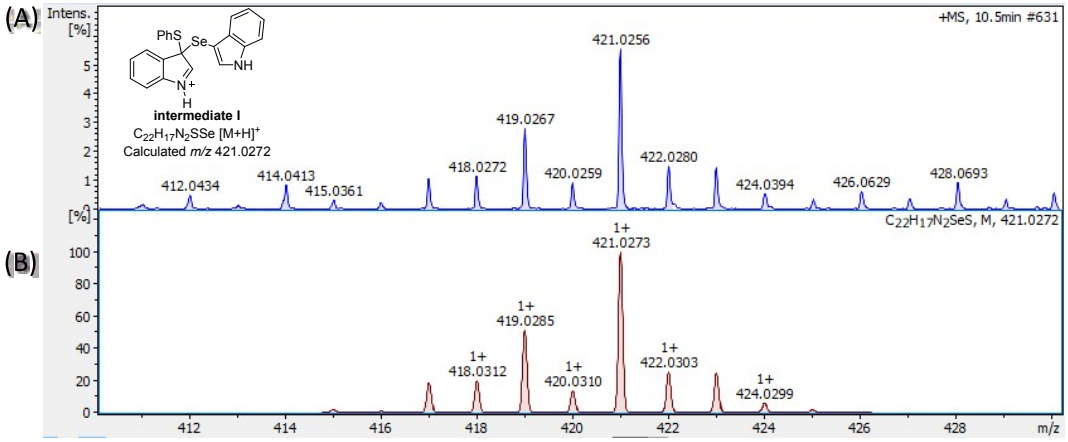


Figure S5. Expanded region of the experiment #1 spectra (Figure S2) showing the peak with *m/z* of 421.0256 attributed to intermediate **I** (A), and the simulated *m/z* and isotope pattern for the molecular formula $C_{22}H_{17}N_2SSe$ $[M+H]^+$ (B).

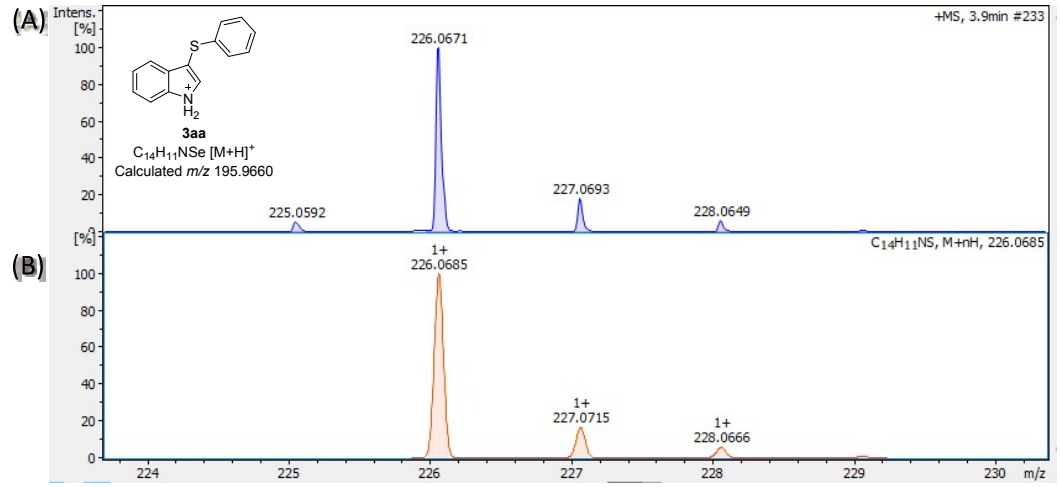


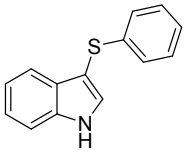
Figure S6. Expanded region of the experiment #1 spectra (Figure S2) showing the peak with *m/z* of 226.00671 corresponding to the product **3aa** (A), and the simulated *m/z* and isotope pattern for the molecular formula $C_{14}H_{11}NSe$ $[M+H]^+$ (B).

General Procedure for the Synthesis of the 3-(Thioaryl)-1*H*-indoles 3

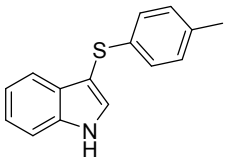
The diorganyl disulfide **2a-j** (0.3 mmol), indole **1a-c** (0.5 mmol), SeO_2 (30 mol%, 0.15 mmol, 0.0166 g), I_2 (10 mol%, 0.03 mmol, 0.0076 g), and glycerol (1 mL) were added to a round-bottomed flask. The resulting solution was stirred at 100 °C (oil bath) for the time indicated in Table 2, after which the reaction mixture was poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica-gel chromatography column with hexane/ethyl acetate as the eluent.

General Procedure for the Synthesis of the 2,3-bis(thioaryl)-1*H*-indoles 4

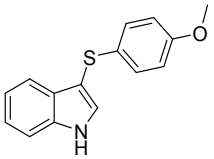
The diorganyl disulfide **2a-g** (0.6 mmol), indole **1a-c** (0.5 mmol), SeO_2 (60 mol%, 0.3 mmol, 0.0333 g), I_2 (10 mol%, 0.06 mmol, 0.0152 g), and glycerol (1 mL) were added to a round-bottomed flask. The resulting mixture was stirred at 100 °C (oil bath) for the time indicated in Table 4, after which the reaction mixture was poured into water (20 mL), extracted with ethyl acetate (3 x 10 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica-gel chromatography column with hexane/ethyl acetate as the eluent.



3-(Phenylthio)-1*H*-indole (3aa):[1] Yield: 0.191 g (85%); Brown solid; mp 149-151 °C (Lit.[1]: 150-151 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.55 - 7.41 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14 - 7.02 (m, 5H), 6.99 (t, *J* = 7.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 136.0, 130.6, 128.1, 127.6, 124.7, 123.6, 121.3, 119.2, 117.9, 111.2, 99.6. **MS (relativeintensity) *m/z*:** 225 (100), 193 (19), 148 (9), 121 (8), 89 (4), 77 (13), 63 (3).

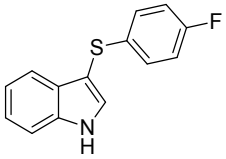


3-(*p*-Tolylthio)-1*H*-indole (3ab):[1] Yield: 0.0905 g (76%); Beige solid; mp 124-126 °C (Lit.[1]: 123-124°C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.11 (bs, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.29 - 7.22 (m, 2H), 7.16 - 7.10 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 2.13 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.4, 135.4, 134.7, 130.4, 129.5, 129.1, 126.3, 122.9, 120.8, 119.6, 111.5, 103.5, 20.7. **MS (relative intensity) *m/z*:** 239 (100), 223 (23), 148 (11), 121 (13), 117 (5), 77 (21), 65 (10).

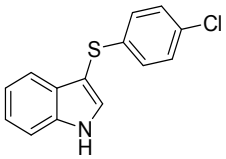


3-((4-Methoxyphenyl)thio)-1*H*-indole (3ac):[1] Yield: 0.1036 g (84%); Brown solid; mp 111-113°C (Lit.[1]: 112-114 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.57 – 7.46 (m, 1H), 7.32 – 7.20 (m, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.08 – 6.96 (m, 3H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 136.4, 130.0, 129.5,

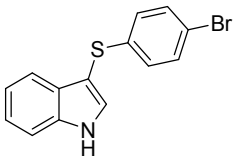
129.00, 128.6, 122.9, 120.7, 119.6, 114.5, 111.5, 104.6, 55.3. **MS (relative intensity) *m/z*:** 255 (100), 240 (42), 223 (16), 148 (6), 139 (4), 89 (4), 77(10), 63 (6).



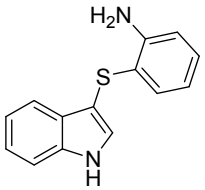
3-((4-Fluorophenyl)thio)-1*H*-indole (3ad):[1] Yield: 0.086 g (71%); Beige solid; mp 134-137 °C (Lit.[1]: 133-134 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.47 (d, *J* = 2.6 Hz, 1H), 7.44 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.32 - 7.25 (m, 1H), 7.23 - 7.17 (m, 1H), 7.15 - 7.08 (m, 2H), 6.93 - 6.85 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.9 (d, J^1(C-F) = 244.1 Hz), 136.5, 134.0 (d, J^4(C-F) = 3.0 Hz), 130.5, 128.8, 127.9 (d, J^3(C-F) = 7.9 Hz), 123.1, 120.9, 119.5, 115.7 (d, J^2(C-F) = 22.0 Hz), 111.6, 103.3. **MS (relative intensity) *m/z*:** 243 (100), 211 (29), 183 (11), 148 (15), 121 (17), 89 (7), 77 (16), 63 (6), 45 (9).



3-((4-Chlorophenyl)thio)-1*H*-indole (3ae):[1] Yield: 0.086 g (67%); Yellow solid; mp 135-137 °C (Lit.[1]: 134-135 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.63 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.47 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.35 - 7.30 (m, 1H), 7.25 - 7.20 (m, 1H), 7.18 - 7.14 (m, 2H), 7.11 - 7.02 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 136.4, 130.7, 130.5, 128.7, 128.7, 127.1, 123.2, 121.0, 119.4, 111.6, 102.3. **MS (relative intensity) *m/z*:** 259 (100), 224 (66), 148 (23), 121 (19), 111 (32), 77 (31), 63 (12), 45 (17).

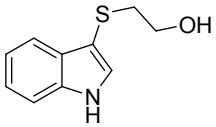


3-((4-Bromophenyl)thio)-1*H*-indole (3af):[2] Yield: 0.0345 g (23%); Orange solid; mp 141-144 °C(Lit.[2]: 144-146 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.91 (s, 1H), 7.50 - 7.42 (m, 3H), 7.25 - 7.14 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.5, 136.3, 131.0, 130.7, 128.1, 126.6, 121.7, 119.6, 118.1, 117.1, 111.5, 99.4. **MS (relative intensity) *m/z*:** 305 (75), 224 (100), 148 (34), 89 (15), 77 (41), 45 (23).

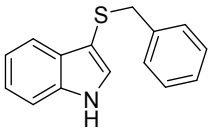


2-((1*H*-Indol-3-yl)thio)aniline (3ag):[2] Yield: 0.0797 g (66%); Black solid; mp 94-97 °C (Lit.[2]: 93-94 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.35 - 7.28 (m, 2H), 7.28 - 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 7.04 (td, *J* = 7.9, 1.5 Hz, 1H), 6.70 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.65 (td, *J* = 7.5, 1.3 Hz, 1H), 4.19 (s, 2H). **^{13}C NMR**

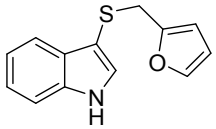
(100 MHz, $CDCl_3$) δ 145.6, 136.3, 131.9, 129.0, 128.7, 128.0, 122.8, 120.8, 120.6, 119.3, 118.9, 115.4, 111.5, 104.1. **MS (relative intensity) *m/z***: 240 (100), 223 (16), 148 (8), 117(71), 90 (14), 77 (12), 45 (5).



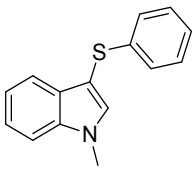
2-((1*H*-Indol-3-yl)thio)ethanol (3ah): Yield: 0.140 g (93%); Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.78 - 7.72 (m, 1H), 7.36 - 7.31 (m, 1H), 7.29 - 7.14 (m, 3H), 3.62 (t, *J* = 5.9 Hz, 2H), 2.85 (t, *J* = 5.9 Hz, 2H), 2.31 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.4, 129.9, 129.2, 122.8, 120.6, 119.1, 111.6, 104.1, 60.5, 39.1. **MS (relative intensity) *m/z*:** 302 (92), 282 (13), 145 (12), 78 (100), 51 (56). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{10}H_{11}NOS$ $[M+H]^+$ 194.0634, found 194.0634.



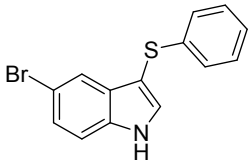
3-(Benzylthio)-1*H*-indole (3ai):[2] Yield: 0.100 g (84%); Orange solid; mp 79-81 °C (Lit.[2]: 84-85 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.23 - 7.13 (m, 5H), 7.06 - 7.042 (m, 2H), 6.91 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ138.9, 136.1, 129.8, 129.1, 128.9, 128.1, 126.7, 122.5, 120.4, 119.2, 111.4, 105.0, 40.9. **MS (relative intensity) *m/z*:** 239 (78), 206 (18), 148 (100), 121 (10), 104 (8), 91 (92), 77 (16).



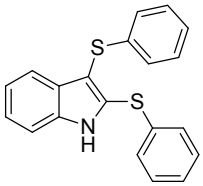
3-((Furan-2-ylmethyl)thio)-1*H*-indole (3aj): Yield: 0.072 g (31%); Brown solid; mp 77-79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.31 - 7.24 (m, 2H), 7.22 - 7.12 (m, 2H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.26 - 6.09 (m, 1H), 5.86 (d, *J* = 3.1 Hz, 1H), 3.85 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 141.8, 136.3, 130.0, 129.3, 122.7, 120.5, 119.3, 111.4, 110.3, 107.6, 105.5, 33.5. **MS (relative intensity) *m/z*:** 229 (16), 196 (10), 148 (29), 121 (8), 81 (100), 77 (16), 53 (11). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{13}H_{11}NOS$ 230.0634 $[M+H]^+$, found 230.0634.



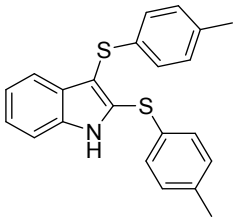
1-Methyl-3-(phenylthio)-1*H*-indole (3ba):[1] Yield: 0.076 g (64%); Yellow solid; mp 83-85 °C (Lit.[1]: 85-87 °C). **^{1}H NMR (**400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.29 - 7.22 (m, 2H), 7.17 - 7.05 (m, 5H), 7.03 - 6.97 (m, 1H), 3.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.6, 137.5, 135.0, 129.8, 128.6, 125.7, 124.6, 122.5, 120.4, 119.7, 109.7, 100.5, 33.0. **MS (relative intensity) *m/z*:** 239 (100), 224 (18), 162 (10), 128 (4), 91 (2), 77 (13).



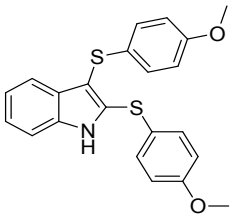
5-Bromo-3-(phenylthio)-1*H*-indole (3ca):[1] Yield: 0.075 g (52%); White solid; mp 121-123°C (Lit.[1]: 121-123 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (bs, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.32 (dd,*J* = 8.6, 1.8 Hz, 1H), 7.27 - 7.22 (m, 1H), 7.16 (dd, *J* = 8.1, 6.9 Hz, 2H), 7.10 - 7.03 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 135.1, 131.8, 130.9, 128.8, 126.1, 125.9, 125.0, 122.2, 114.4, 113.1, 102.8. **MS (relative intensity) *m/z*:** 305 (100), 224 (91), 191 (21), 165 (9), 88 (4), 77 (9).



2,3-Bis(phenylthio)-1*H*-indole (4aa):[3] Yield: 0.1421 g (85%); Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.55 (s, 1H), 7.37 (s, 1H), 7.31 - 6.92 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.1, 137.3, 135.4, 132.5, 129.6, 128.9, 128.4, 128.4, 126.3, 126.2, 124.7, 123.3, 120.5, 119.4, 111.6, 108.9. **MS (relative intensity) *m/z*:** 333 (54), 254 (3), 224 (100), 197 (4), 146 (5), 121 (6), 77 (8).

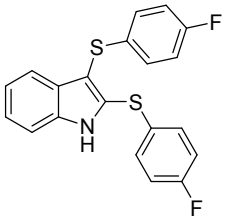


2,3-Bis(*p*-tolylthio)-1*H*-indole (4ab):[3] Yield: 0.135 g (75%); Orange oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (bs, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.32 - 7.23 (m, 4H), 7.22 - 7.16 (m, 1H), 7.15 - 7.06 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6, 136.7, 134.8, 134.4, 130.5, 130.2, 130.1, 130.1, 129.4, 127.0, 123.4, 121.0, 119.7, 110.9, 108.5, 20.9, 20.8. **MS (relative intensity) *m/z*:** 361 (67), 238 (100), 223 (86), 205 (16), 121 (5), 91 (7), 65 (10), 40 (6). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{22}H_{18}NS_2$ $[M + H]^+$ 362.1032, found 362.1032.

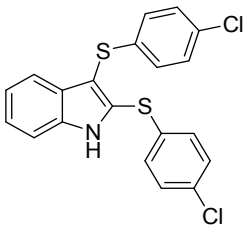


2,3-Bis((4-methoxyphenyl)thio)-1*H*-indole (4ac):[4]Yield: 0.086 g (44%); Yellow solid; mp 127-130 °C.(Lit.[4]: 134-137 °C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (bs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.30 - 7.13 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.79 - 6.73 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8,

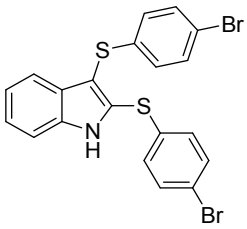
157.9, 136.6, 135.5, 133.5, 130.2, 129.3, 128.6, 123.5, 123.2, 121.0, 119.4, 115.1, 114.5, 110.8, 108.0, 55.4, 55.3. **MS (relative intensity) *m/z*:** 393 (45), 254 (100), 223 (60), 210 (19), 139 (10), 77 (6).



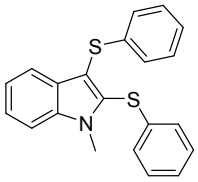
2,3-Bis((4-fluorophenyl)thio)-1*H*-indole (4ad):[3] Yield: 0.113 g (62%); Brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.26 - 7.11 (m, 4H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.02 - 6.92 (m, 2H), 6.83 (t, *J* = 8.6 Hz, 2H), 6.74 (t, *J* = 8.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.2 (, J^1(C-F) = 248.2 Hz), 161.0 (d, J^1(C-F) = 244.8 Hz), 136.7, 133.7, 132.8 (d, J^4(C-F) = 3.2 Hz), 132.2 (d, J^3(C-F) = 8.3 Hz), 129.8, 129.1 (d, J^4(C-F) = 3.3 Hz), 128.7 (d, J^3(C-F) = 7.9 Hz), 124.0, 121.3, 119.7, 116.5 (d, J^2(C-F) = 22.2 Hz), 115.7 (d, J^2(C-F) = 22.1 Hz), 111.2, 109.5. **MS (relative intensity) *m/z*:** 369 (52), 272 (3), 242 (100), 146 (7), 120 (8), 102 (8), 75 (7), 45 (2). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{20}H_{13}F_2NS_2[M + H]^+$ 370.0530, found 370.0530.



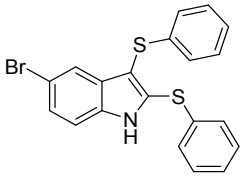
2,3-Bis((4-chlorophenyl)thio)-1*H*-indole (4ae): Yield: 0.0782 g (39%); Yellow solid; mp 68-72 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (bs, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.23 - 7.14 (m, 1H), 7.13 - 6.96 (m, 7H), 6.90 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8, 136.4, 133.4, 132.9, 132.8, 131.0, 130.7, 129.7, 129.4, 128.8, 127.9, 124.3, 121.5, 119.8, 111.3, 109.6. **MS (relative intensity) *m/z*:** 401 (19), 258 (19), 223 (100), 178 (4), 120 (6), 102 (6), 75 (7), 69 (3). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{20}H_{13}Cl_2NS_2$ $[M + H]^+$ 401.9940, found 401.9940.



2,3-Bis((4-bromophenyl)thio)-1*H*-indole (4af): Yield: 0.130 g (53%); Beige solid; mp 109-112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (bs, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.42 - 7.16 (m, 7H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.1, 136.8, 133.6, 132.6, 132.4, 131.7, 130.8, 129.7, 128.2, 124.3, 121.6, 121.3, 119.9, 118.9, 111.3, 109.6. **MS (relative intensity) *m/z*:** 491 (3), 303 (3), 255 (4), 223 (100), 146 (4), 120 (4), 76 (5). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{20}H_{13}Br_2NS_2$ $[M + H]^+$ 491.8906, found 491.8908.



1-Methyl-2,3-bis(phenylthio)-1*H*-indole (4ba): Yield: 0.171 g (99%); Beige solid. mp 92-94°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.37 (m, 2H), 7.29 - 7.14 (m, 8H), 7.14 - 7.07 (m, 3H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) 138.4 (2C), 135.8, 134.2, 129.1, 128.6, 127.3, 126.5, 126.1, 124.9, 123.9, 121.0, 120.3, 111.0, 110.1, 31.0. **MS (relative intensity) *m/z*:** 347 (100), 238 (92), 223 (83), 205 (5), 165 (4), 121 (4), 77 (11). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{21}H_{17}S_2N_1$ $[M]^+$ 347.0802, found: 347.0801.



5-Bromo-2,3-bis(phenylthio)-1*H*-indole (4ca): Yield: 0.1589 g (77%); Brown solid; mp 151-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.28 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.25 - 7.09 (m, 7H), 7.07 - 6.96 (m, 3H). Missing one signal, *N*-*H*. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6, 134.9, 133.7, 133.3, 129.8, 127.8, 127.4, 127.1, 125.3, 124.6, 123.7, 119.9, 112.5, 112.3, 106.0. **MS (relative intensity) *m/z*:** 413 (23), 303 (4), 255 (5), 223 (100), 207 (10), 119 (4), 77 (5). **HRMS** (APCI-TOF) *m/z*: calculated for $C_{20}H_{14}BrNS_2$ $[M + H]^+$ 411.9825, found 411.9824.

Supporting Information References

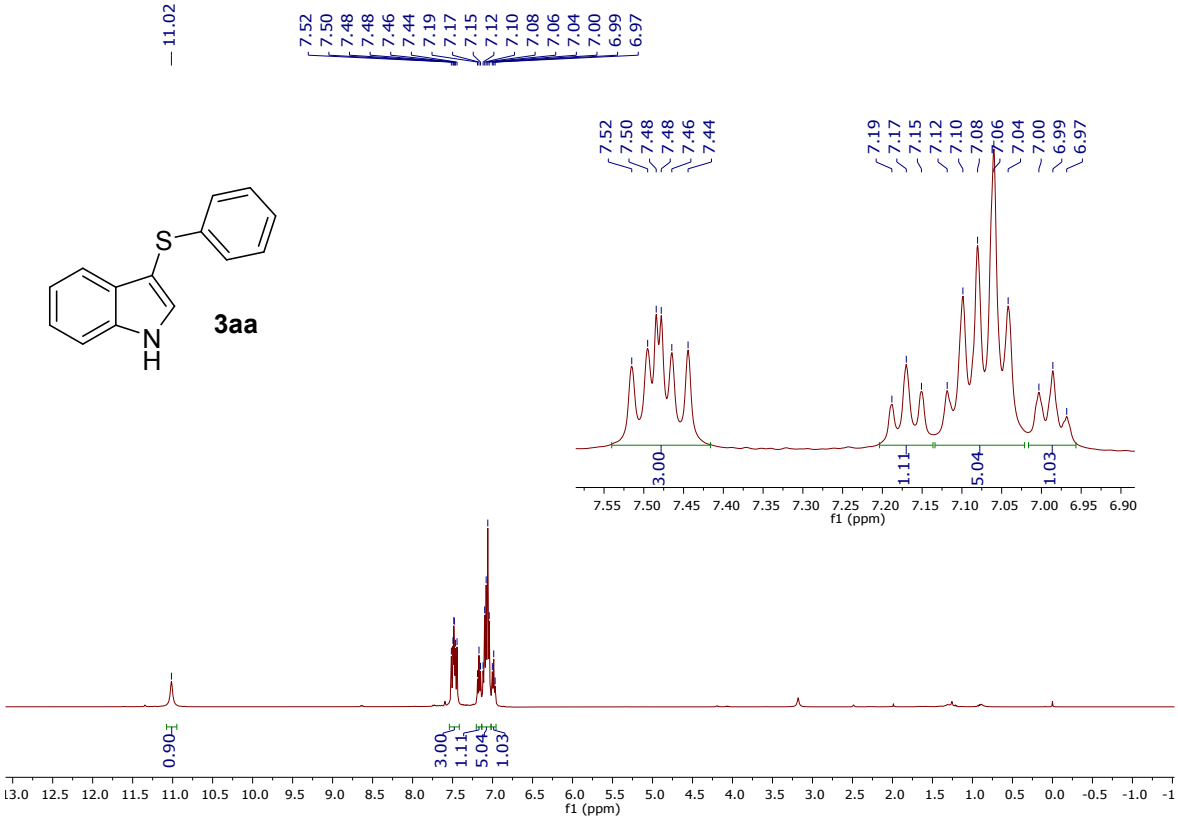
1 X. Fang, R. Tang, P. Zhong, J. Li, *Synthesis*, 2009, 4183.

2 W. Ge, Y. Wei, *Green Chem.*, 2012, **14**, 2066.

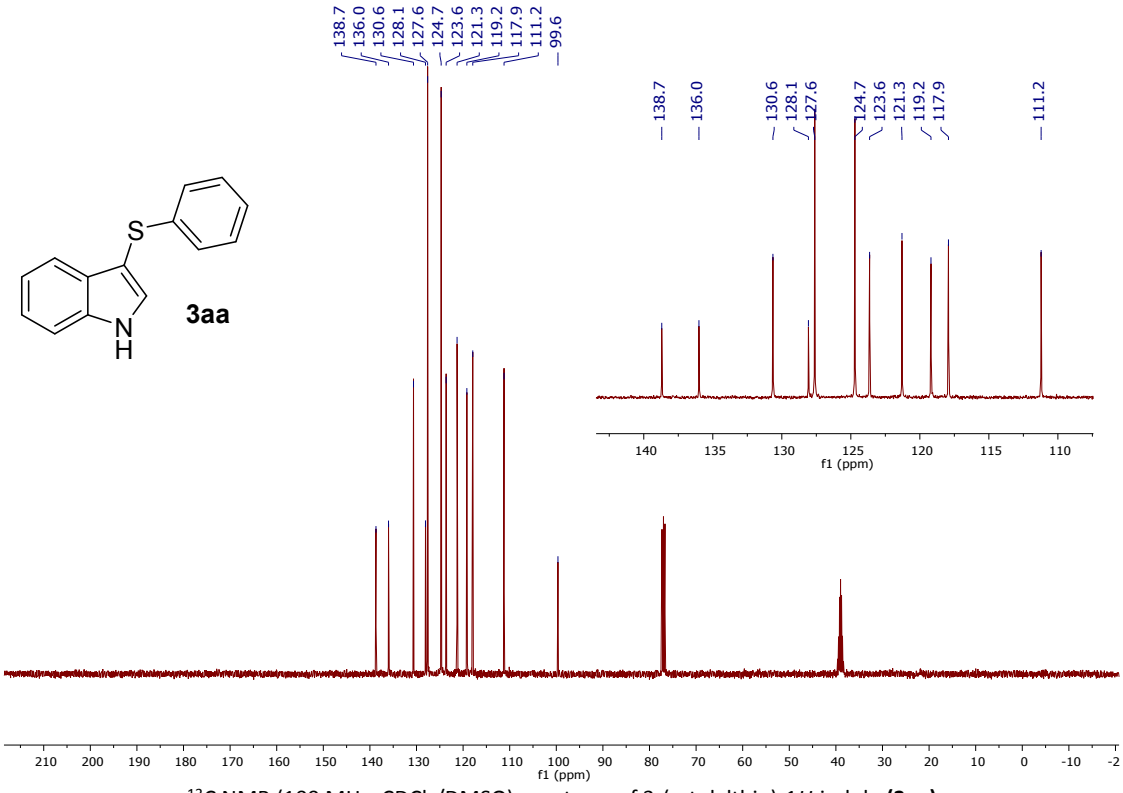
3 H. Zhang, X. Bao, Y. Song, J. Qu, B. Wang, *Tetrahedron*, 2015, **71**, 8885.

4 C. D. Prasad, S. Kumar, M. Sattar, A. Adhikary, S. Kumar, *Org. Biomol. Chem*., 2013, **11**, 8036.

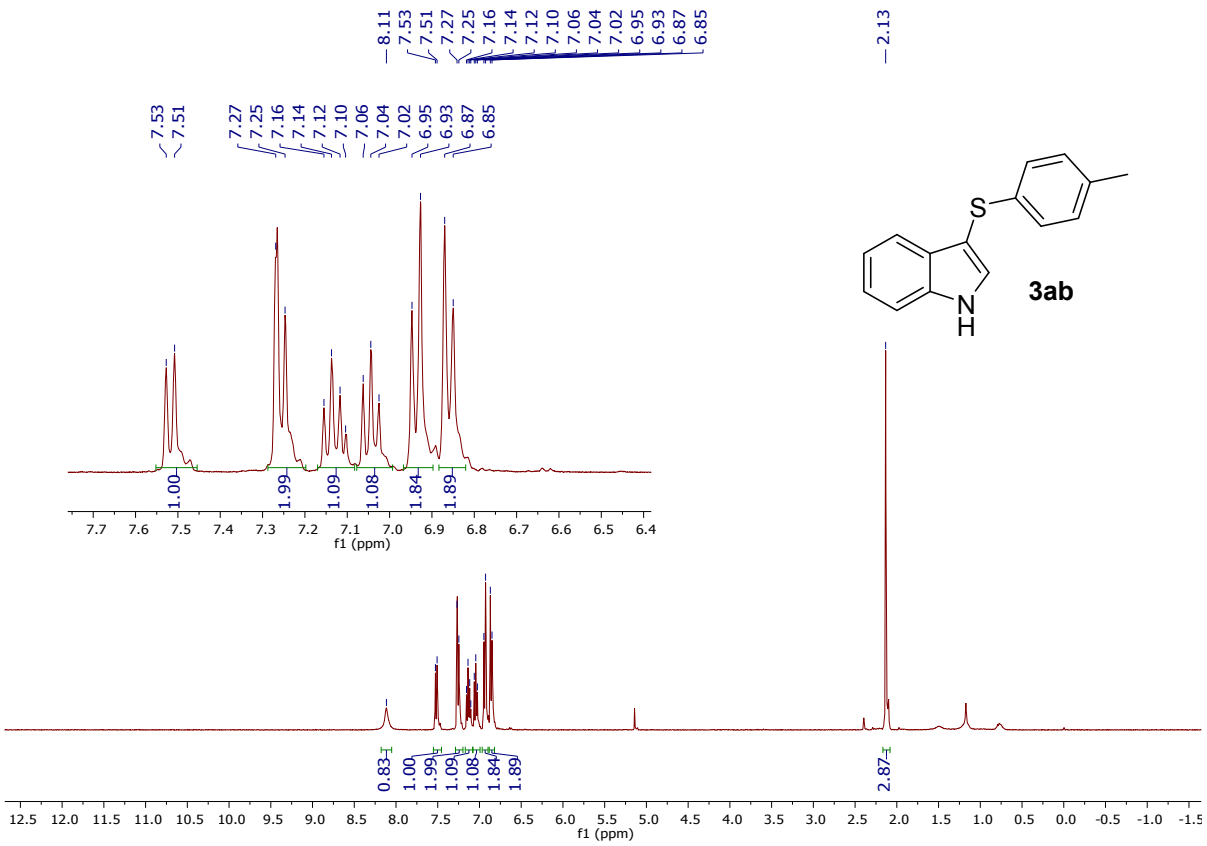
Selected Spectra



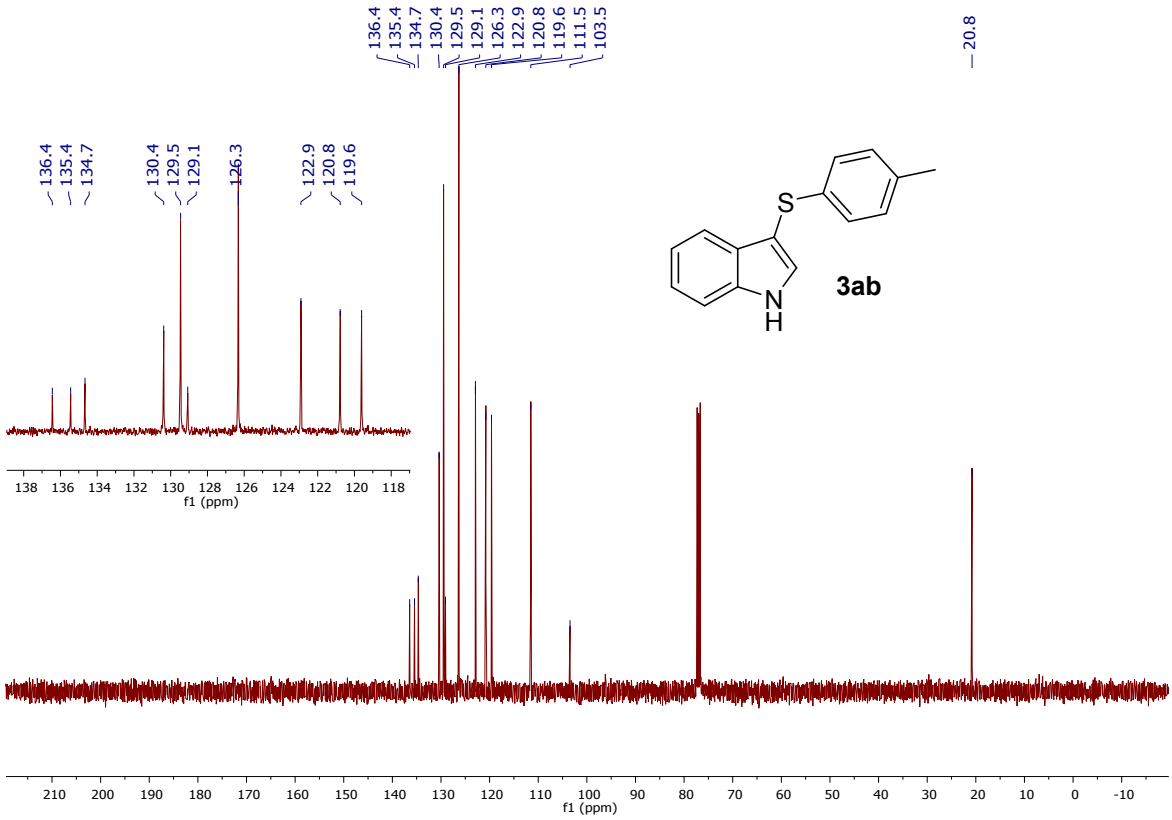
^{1}H NMR (400 MHz, $CDCl_3$/DMSO) spectrum of 3-(*p*-tolylthio)-1*H*-indole **(3aa)**



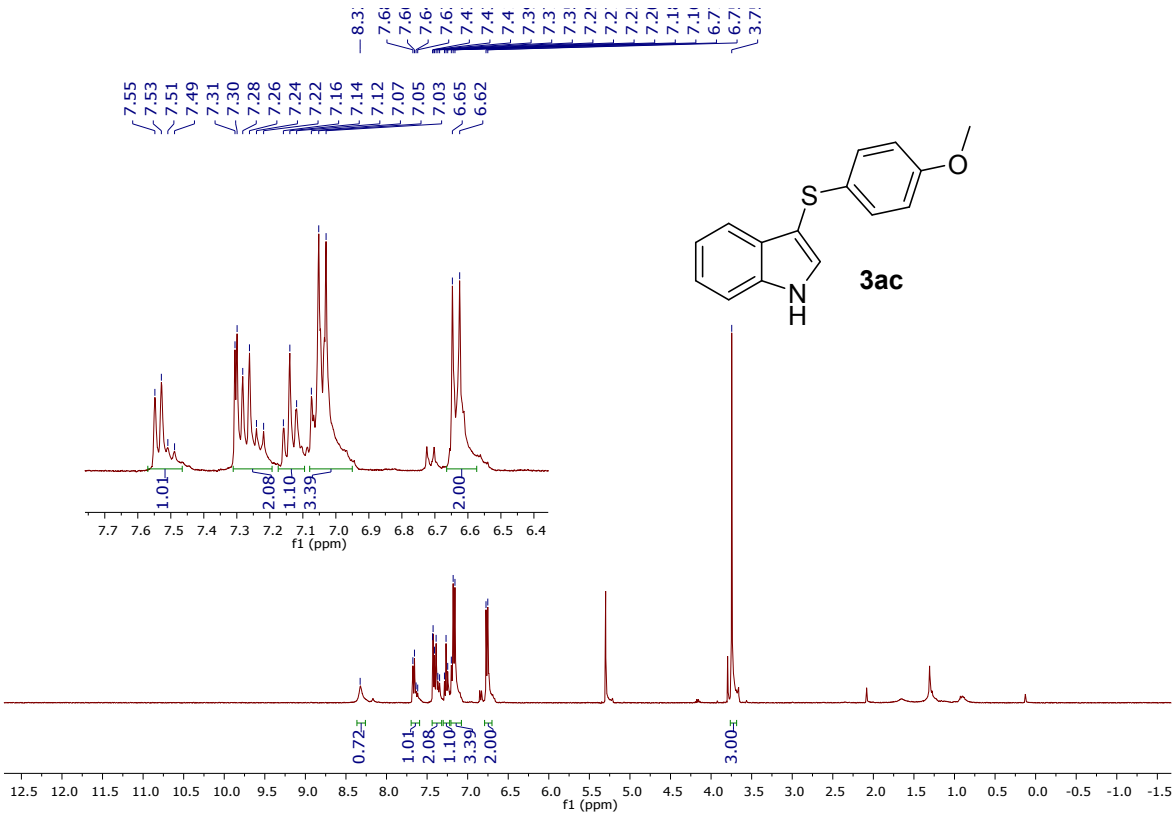
^{13}C NMR (100 MHz, $CDCl_3$/DMSO) spectrum of 3-(*p*-tolylthio)-1*H*-indole **(3aa)**



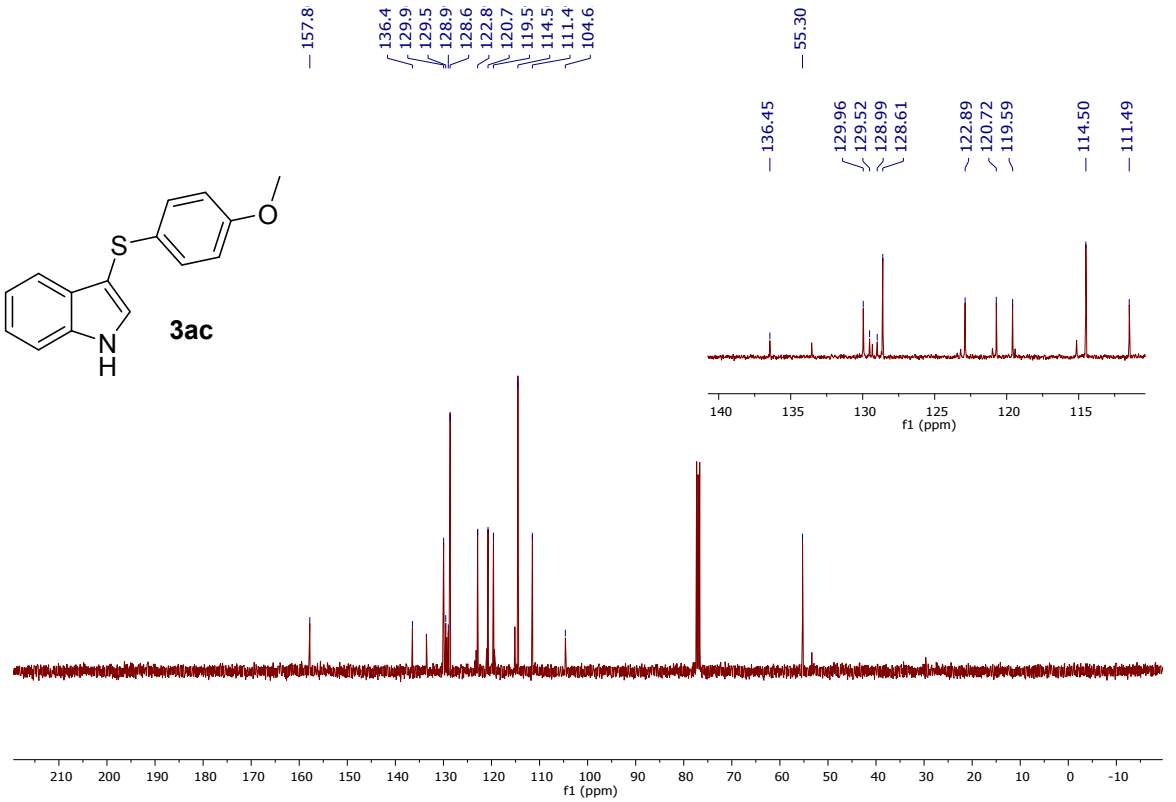
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of3-(*p*-tolylthio)-1*H*-indole (**3ab)**



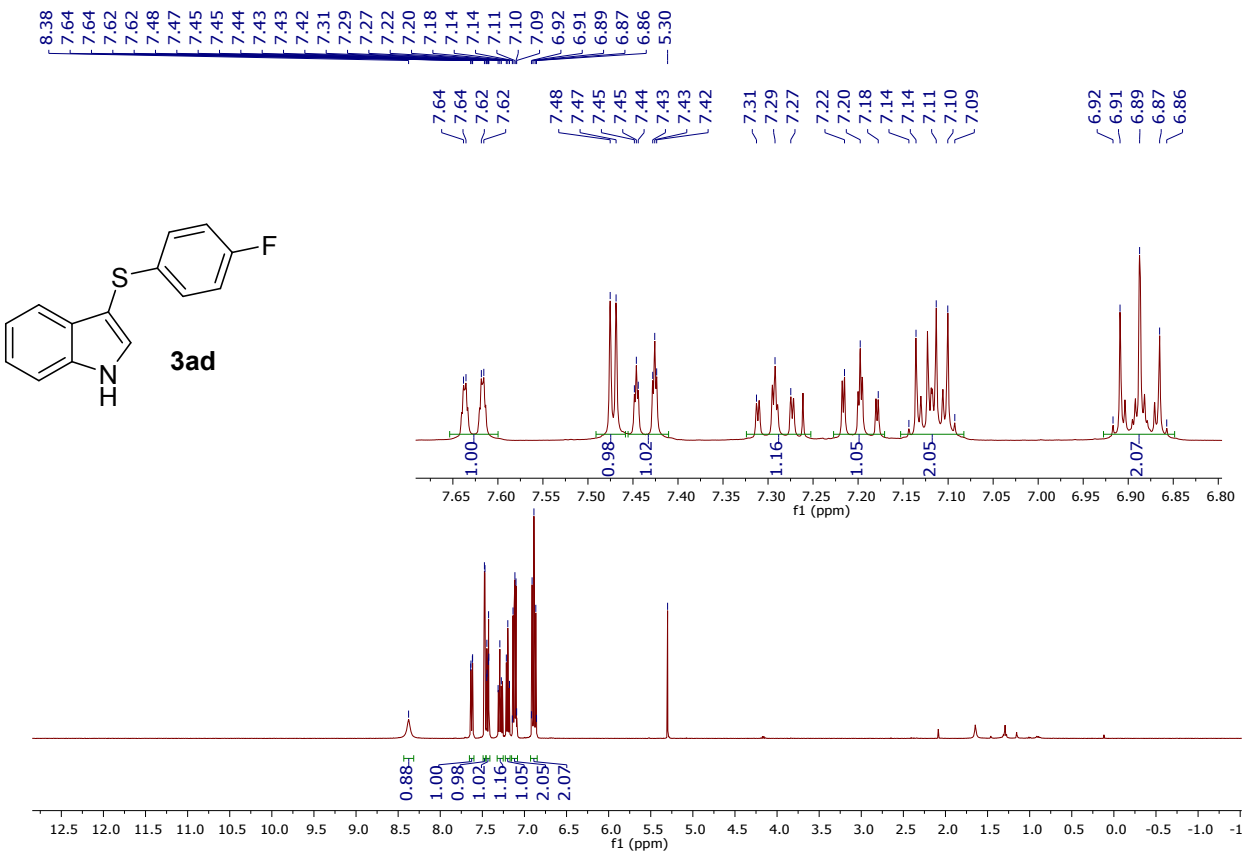
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of3-(*p*-tolylthio)-1*H*-indole (**3ab)**



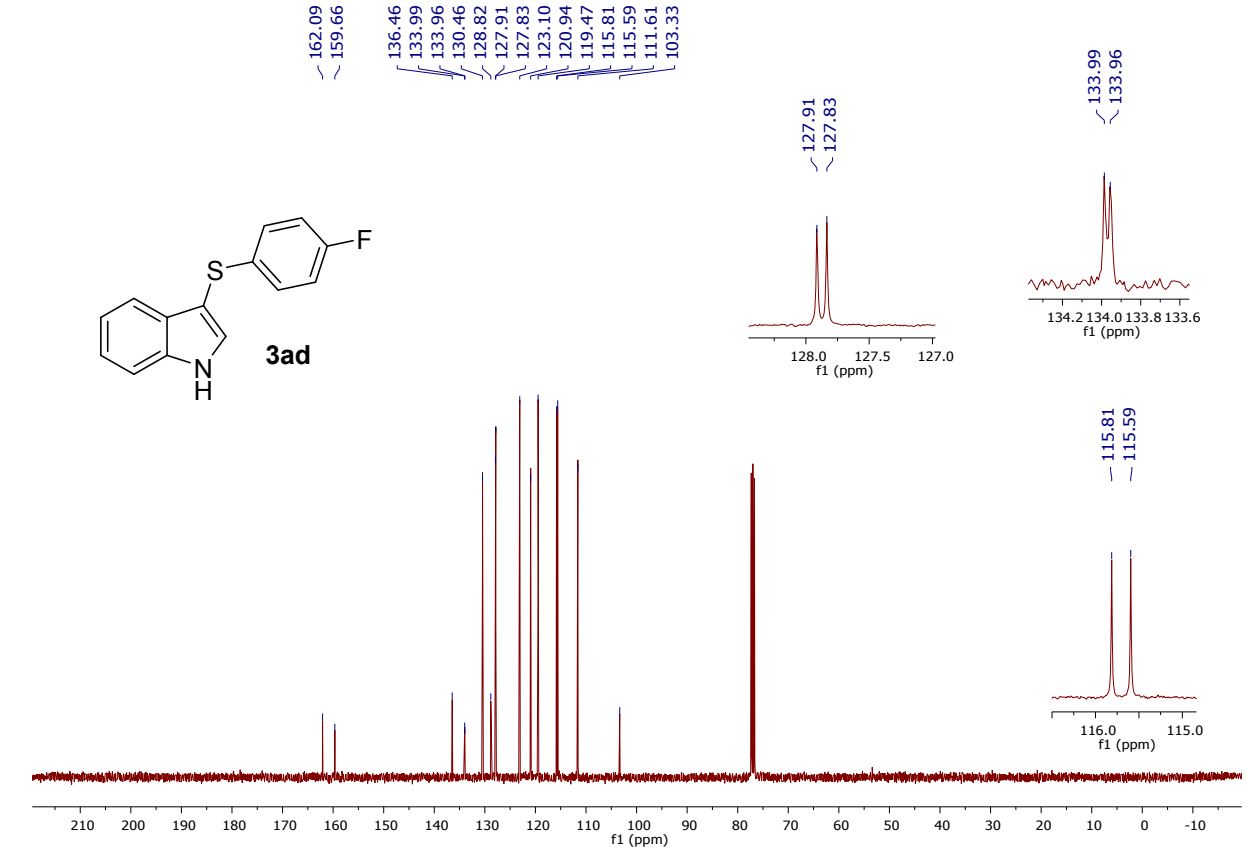
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((4-methoxyphenyl)thio)-1*H*-indole **(3ac)**



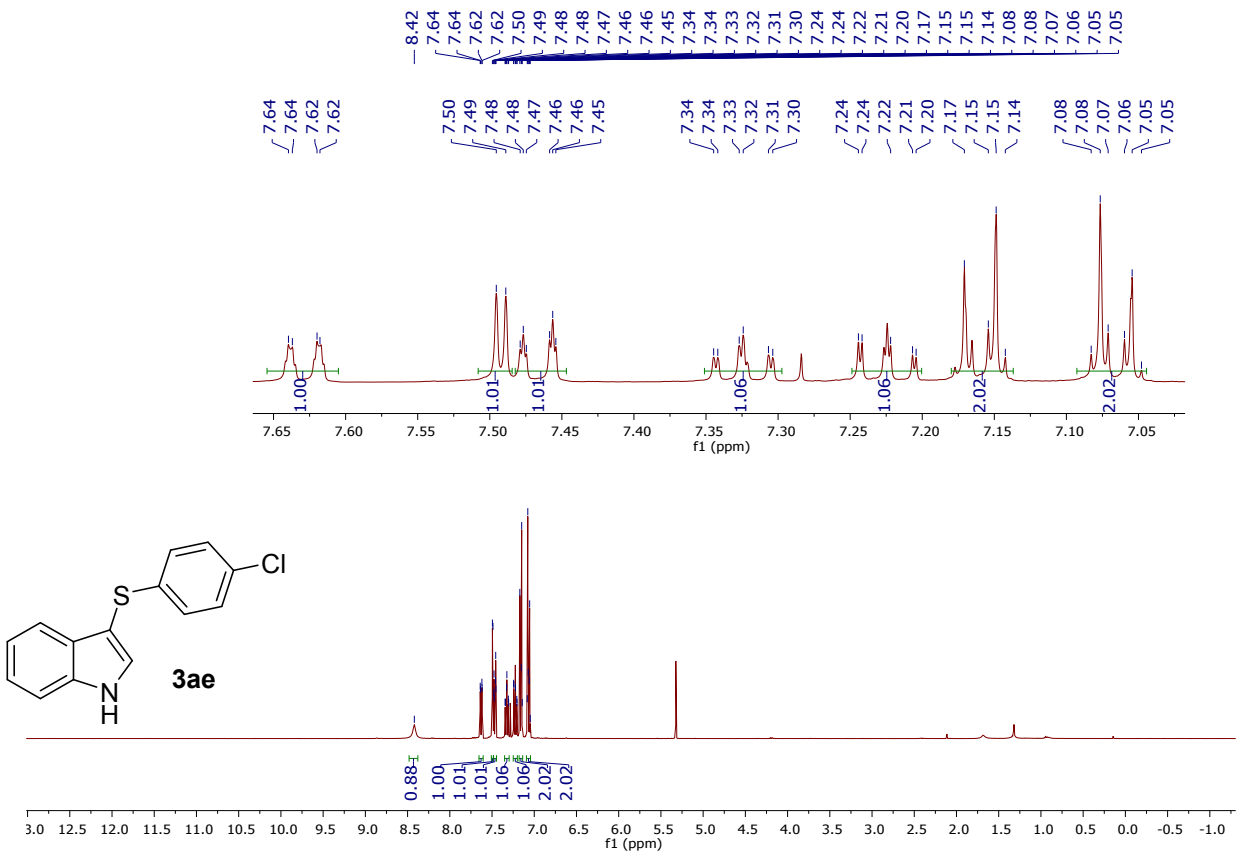
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-((4-methoxyphenyl)thio)-1*H*-indole **(3ac)**



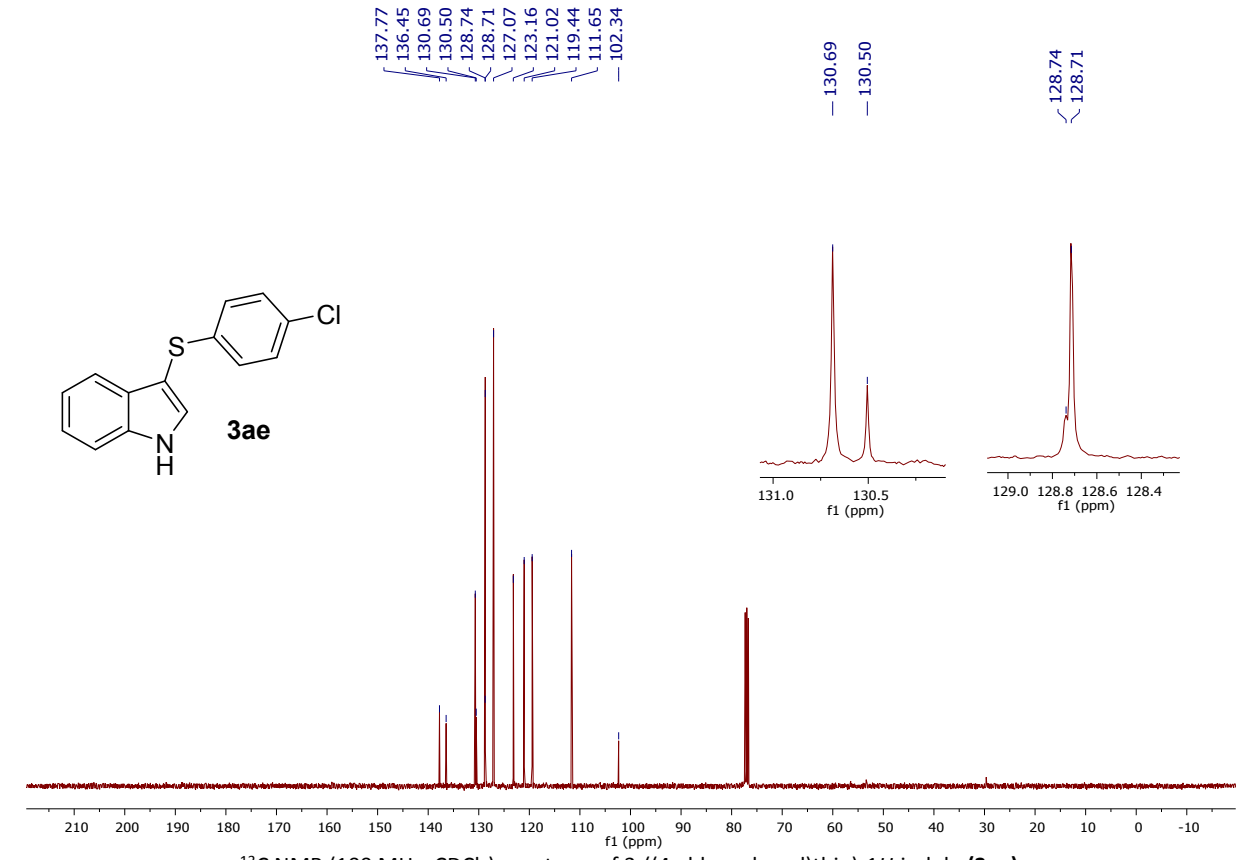
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((4-fluorophenyl)thio)-1*H*-indole **(3ad)**



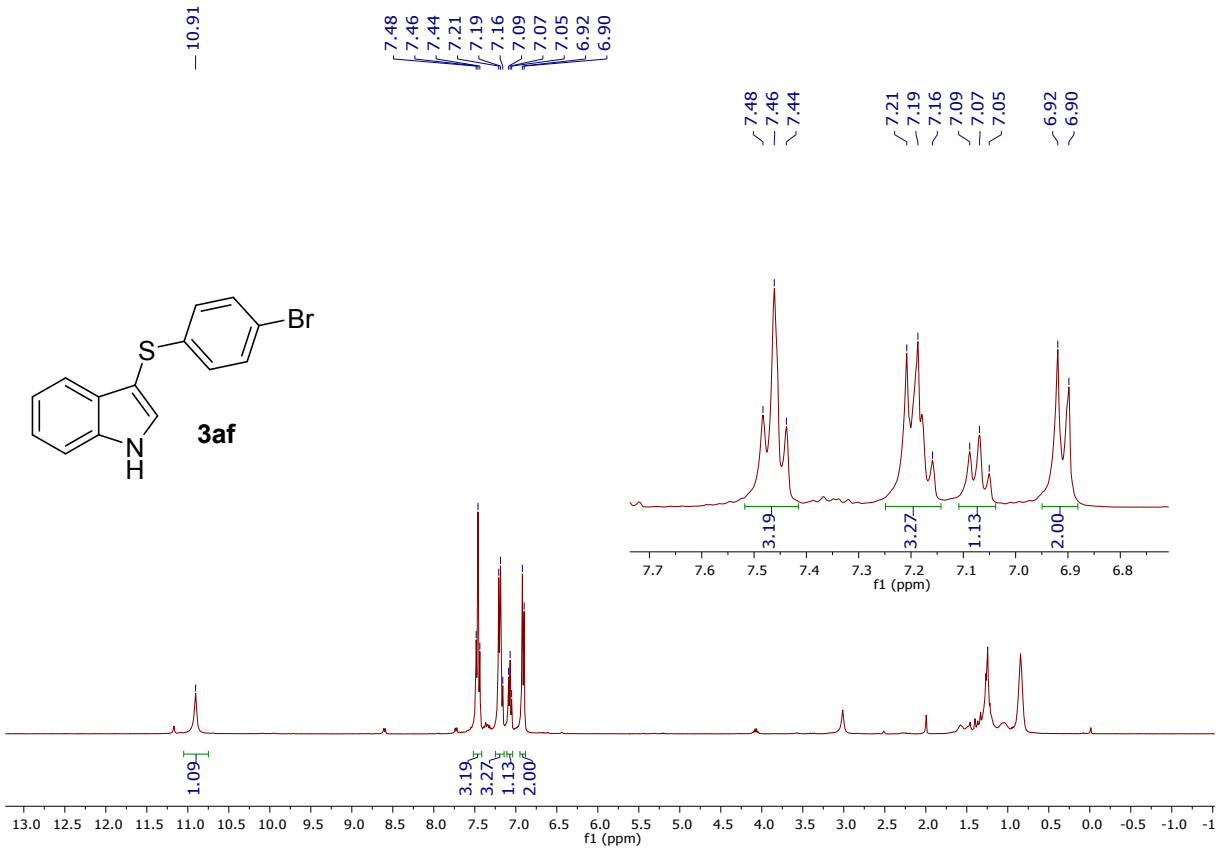
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((4-fluorophenyl)thio)-1*H*-indole **(3ad)**



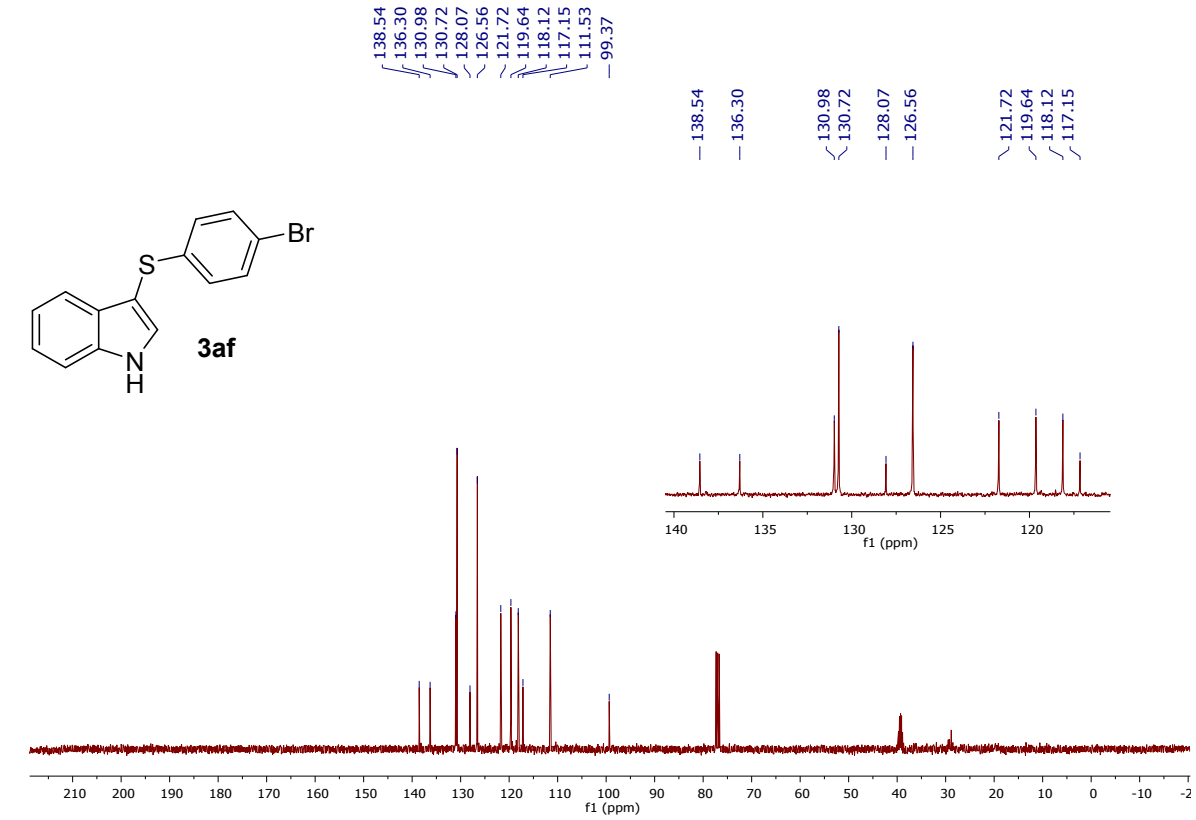
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((4-chlorophenyl)thio)-1*H*-indole **(3ae)**



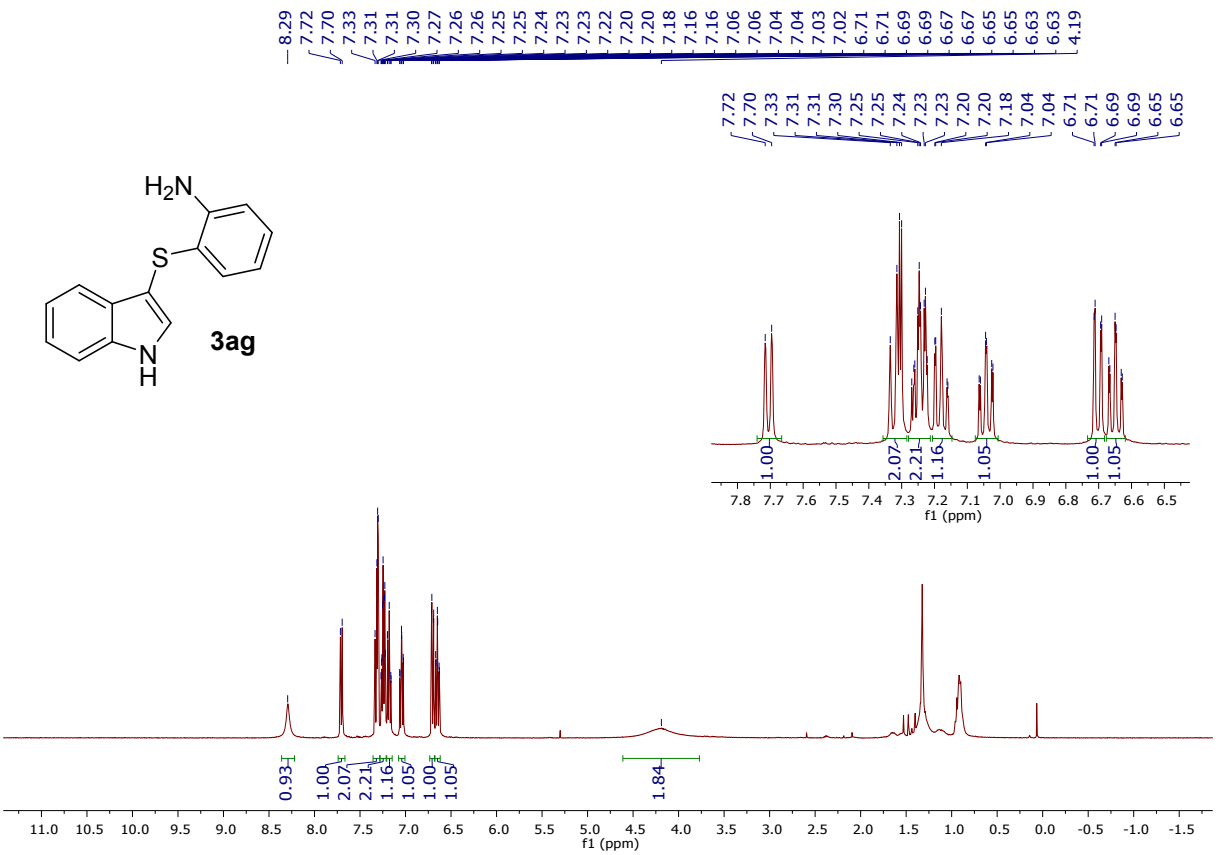
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-((4-chlorophenyl)thio)-1*H*-indole **(3ae)**



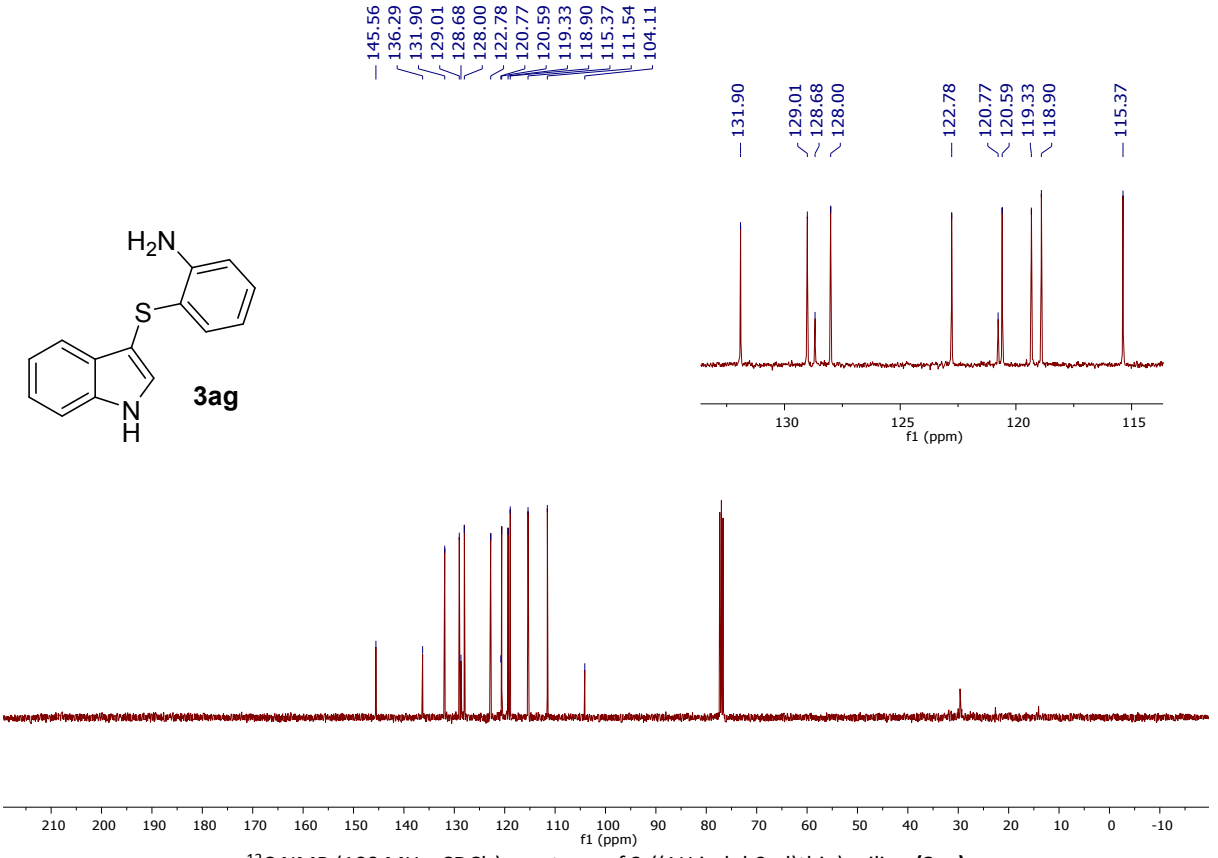
^{1}H NMR (400 MHz, $CDCl_3$/DMSO) spectrum of 3-((4-bromophenyl)thio)-1*H*-indole **(3af)**



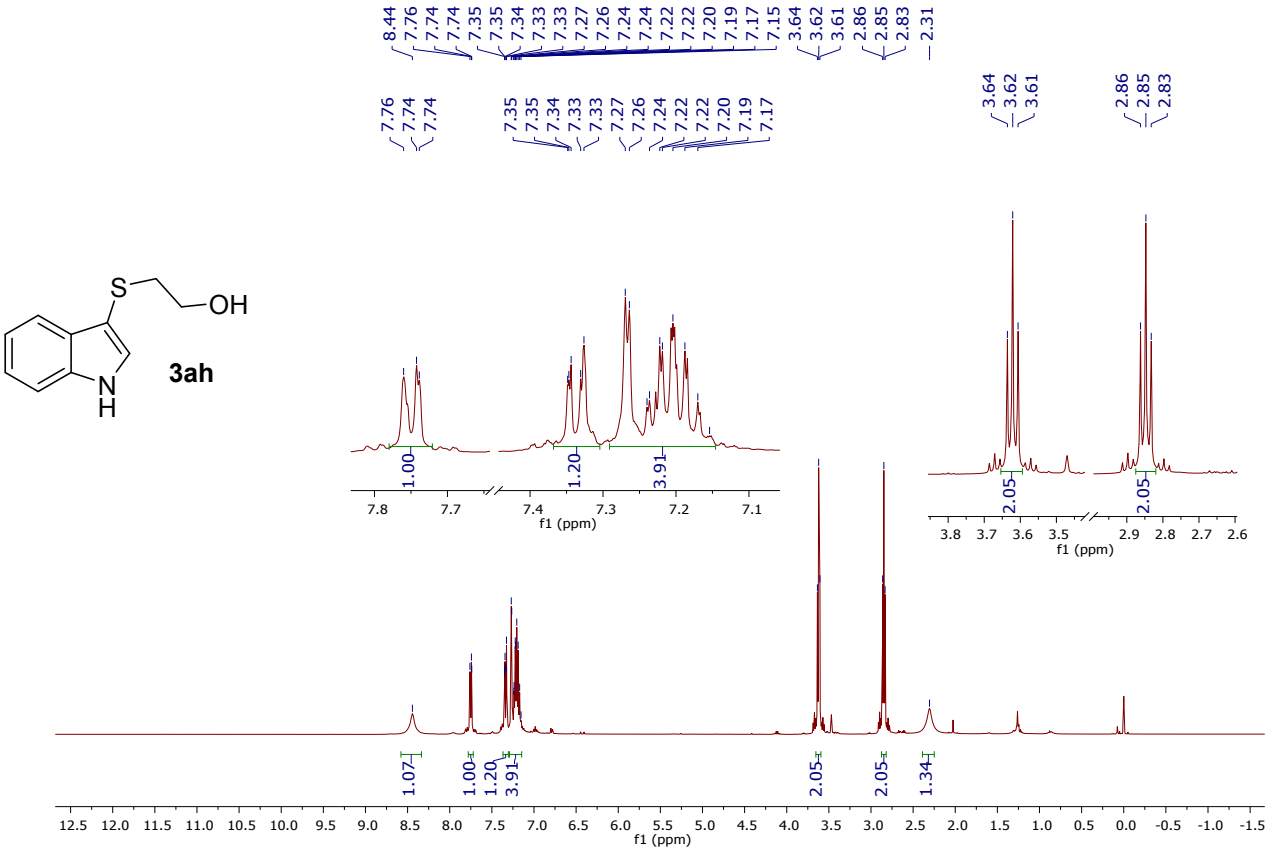
^{13}C NMR (100 MHz, $CDCl_3$/DMSO) spectrum of 3-((4-bromophenyl)thio)-1*H*-indole **(3af)**



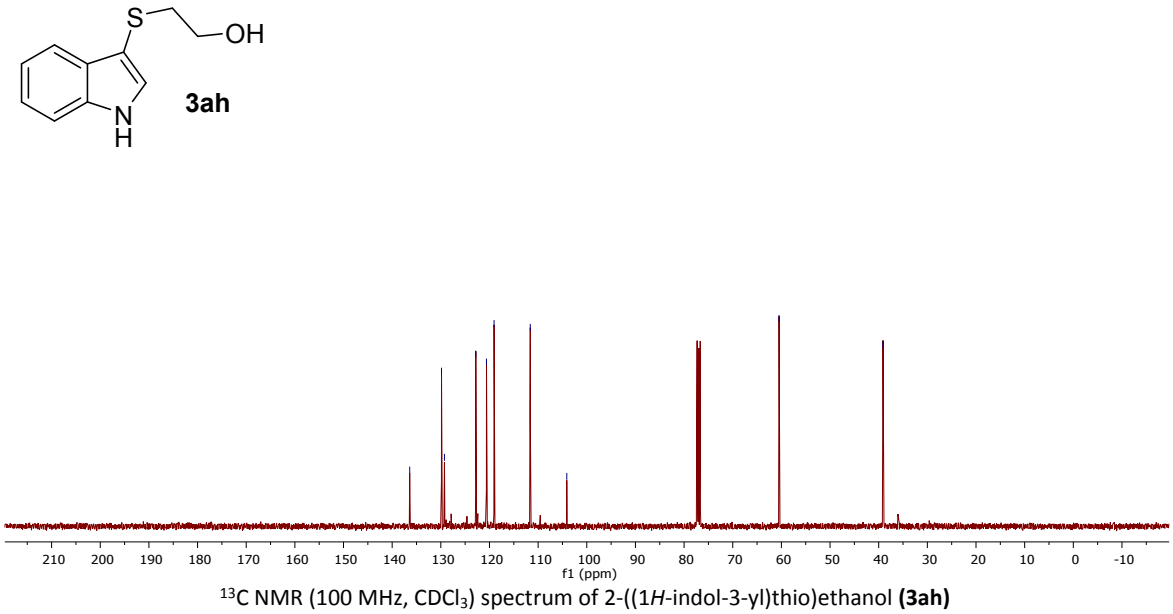
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-((1*H*-indol-3-y)thio)aniline **(3ag)**



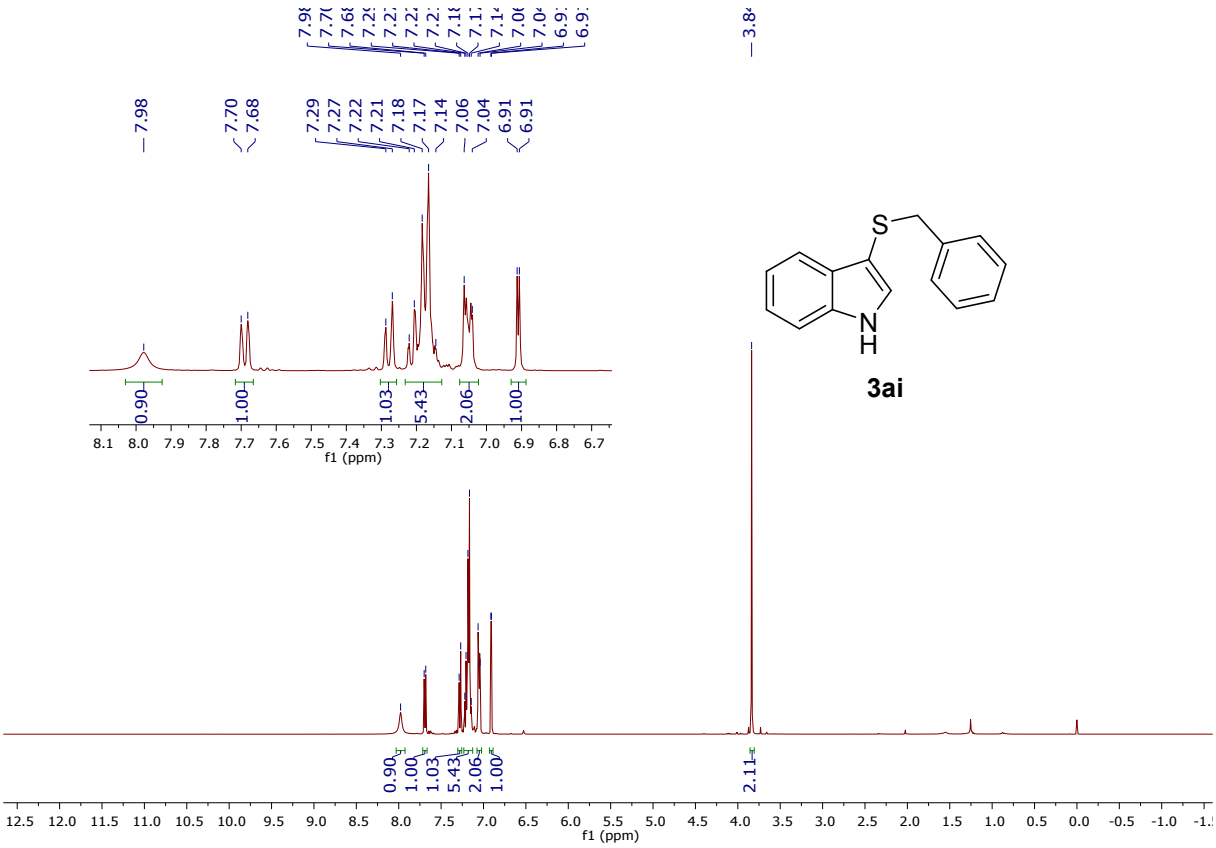
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-((1*H*-indol-3-yl)thio)aniline **(3ag)**



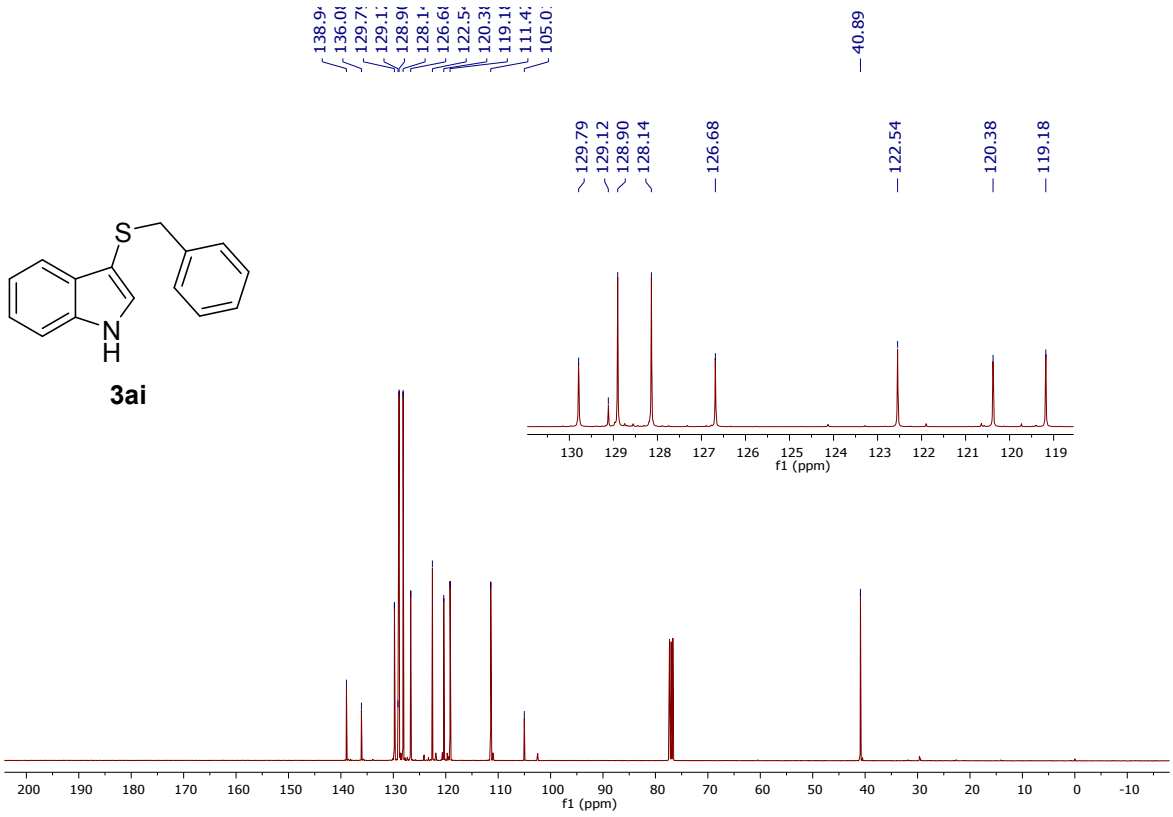
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-((1*H*-indol-3-yl)thio)ethanol **(3ah)**



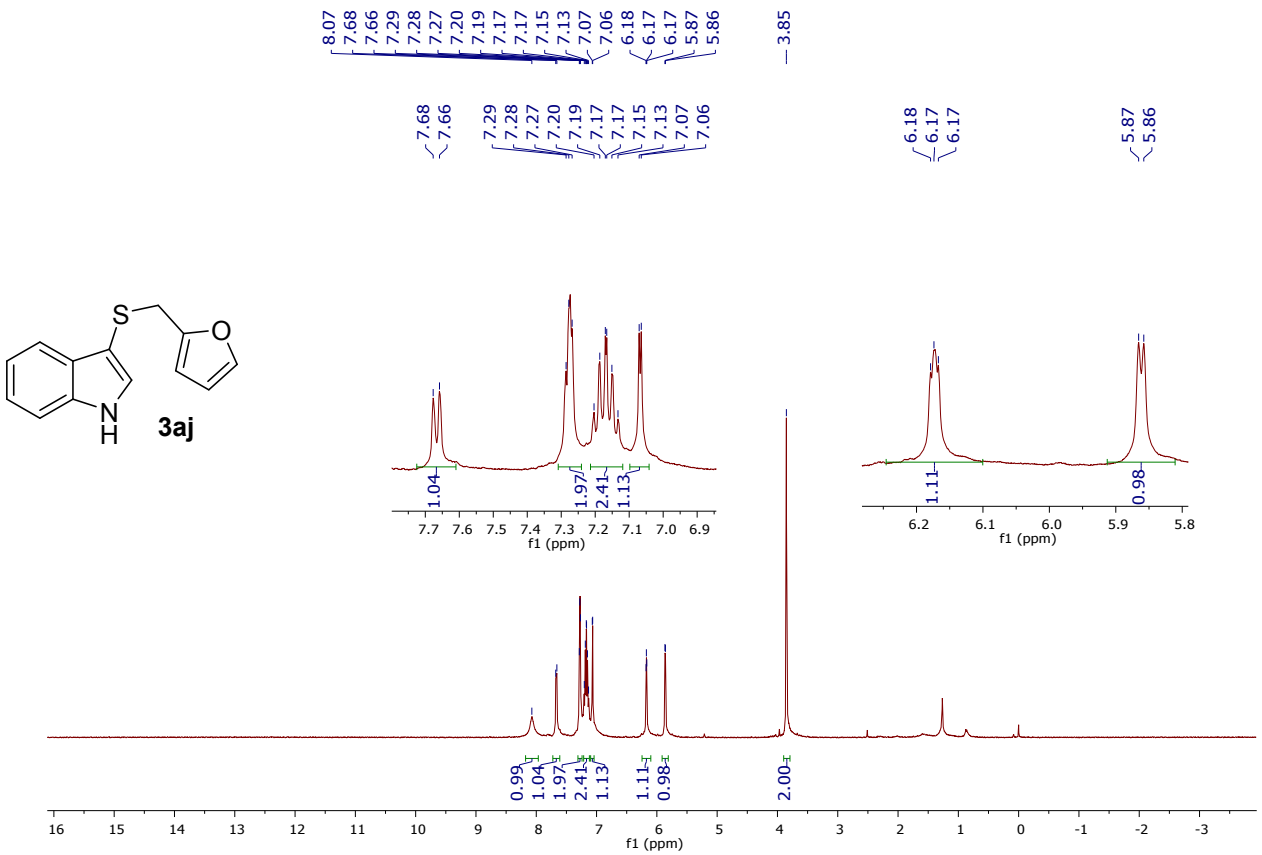
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-((1*H*-indol-3-yl)thio)ethanol **(3ah)**



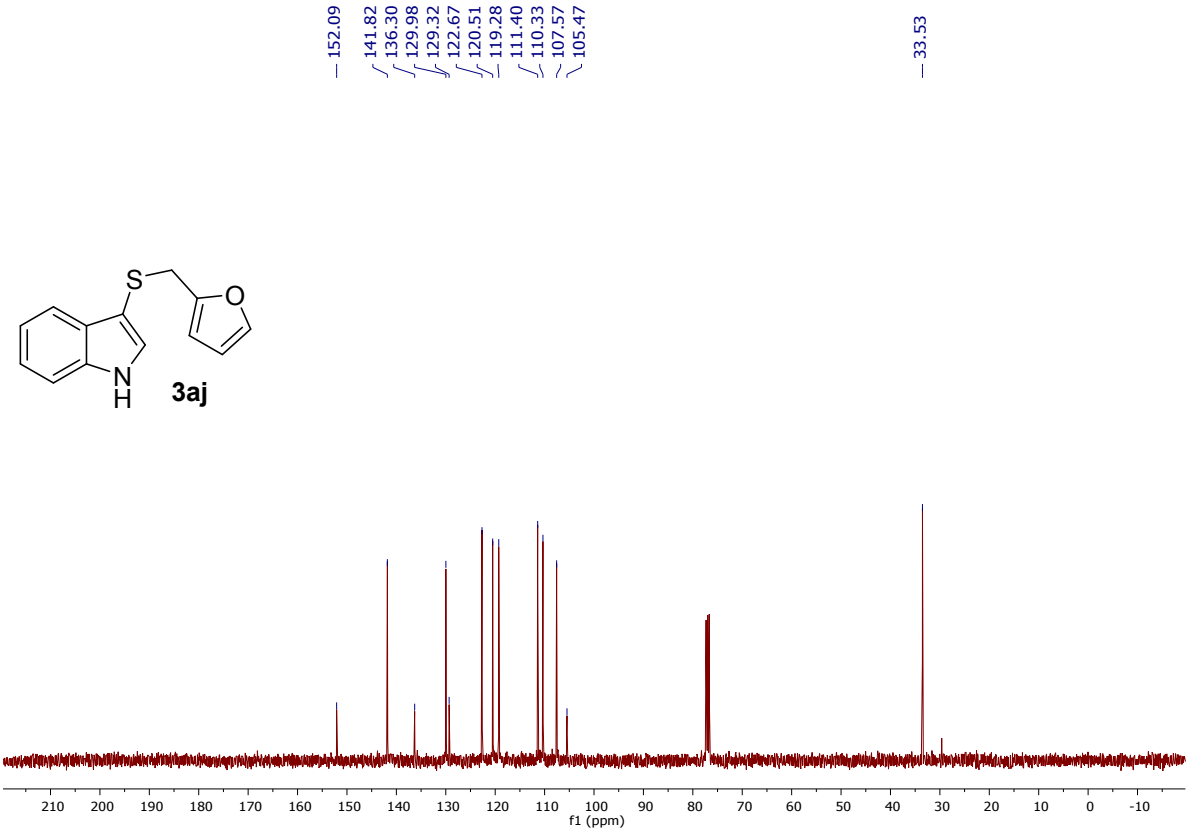
^{1}H NMR (100 MHz, $CDCl_3$) spectrum of 3-(benzylthio)-1H-indole (**3ai**)



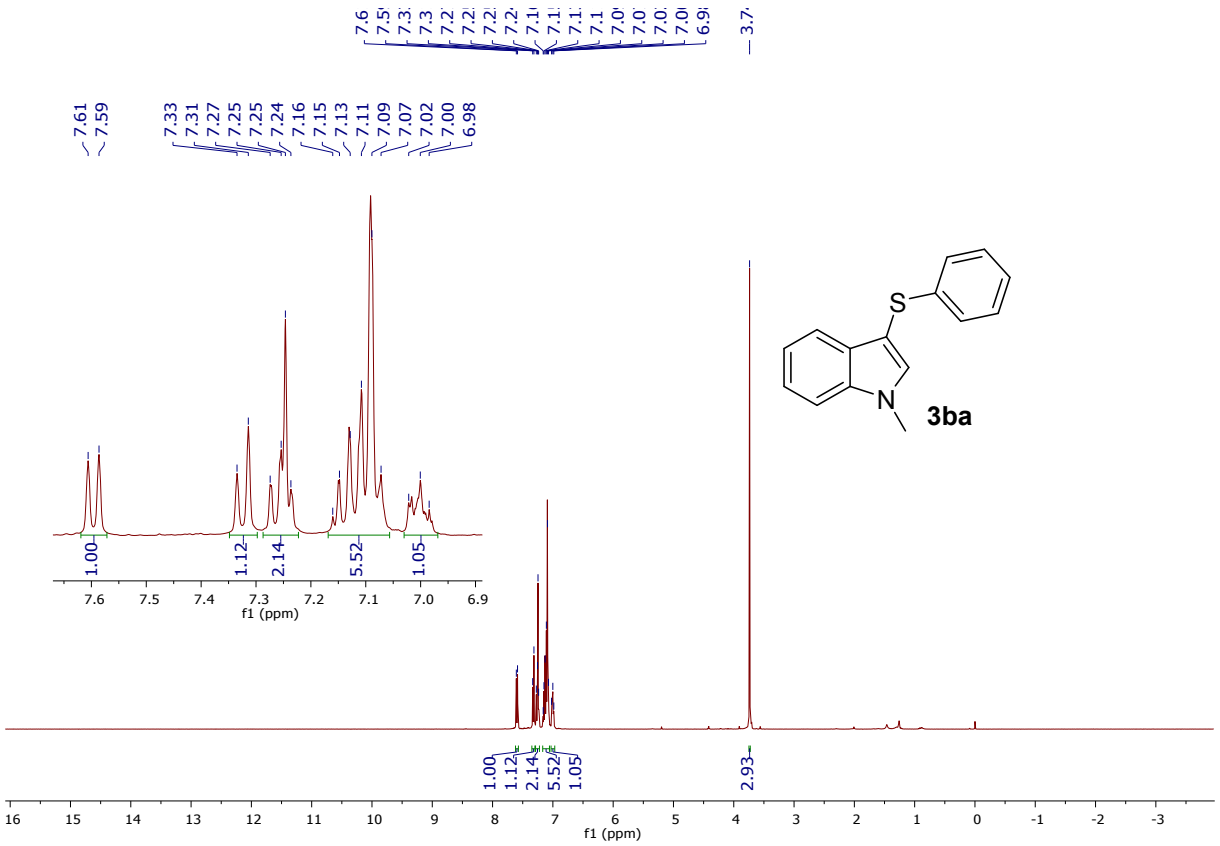
^{13}C NMR (100 MHz, $CDCl_3$) spectrum 3-(benzylthio)-1H-indole (**3ai**)



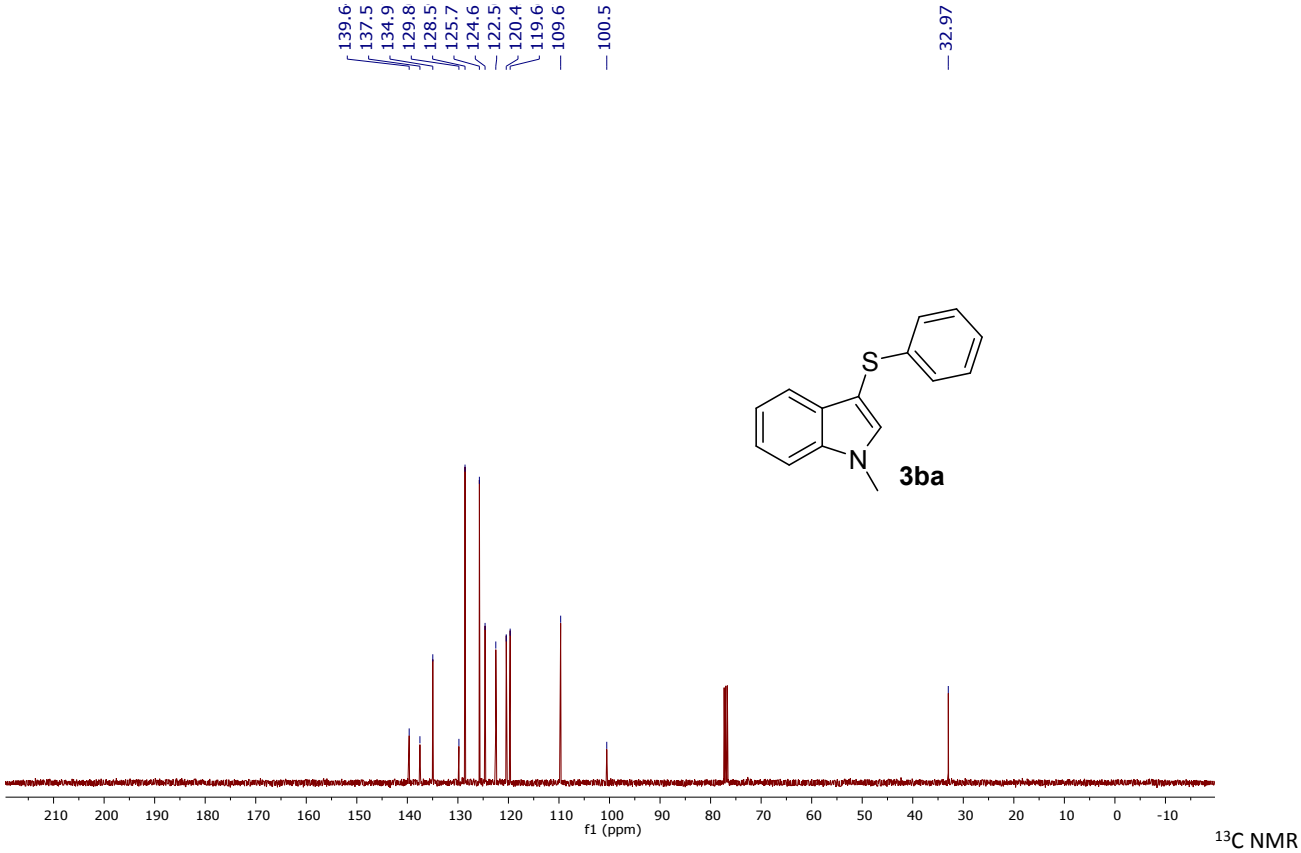
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-((furan-2-ylmethyl)thio)-1*H*-indole **(3aj)**



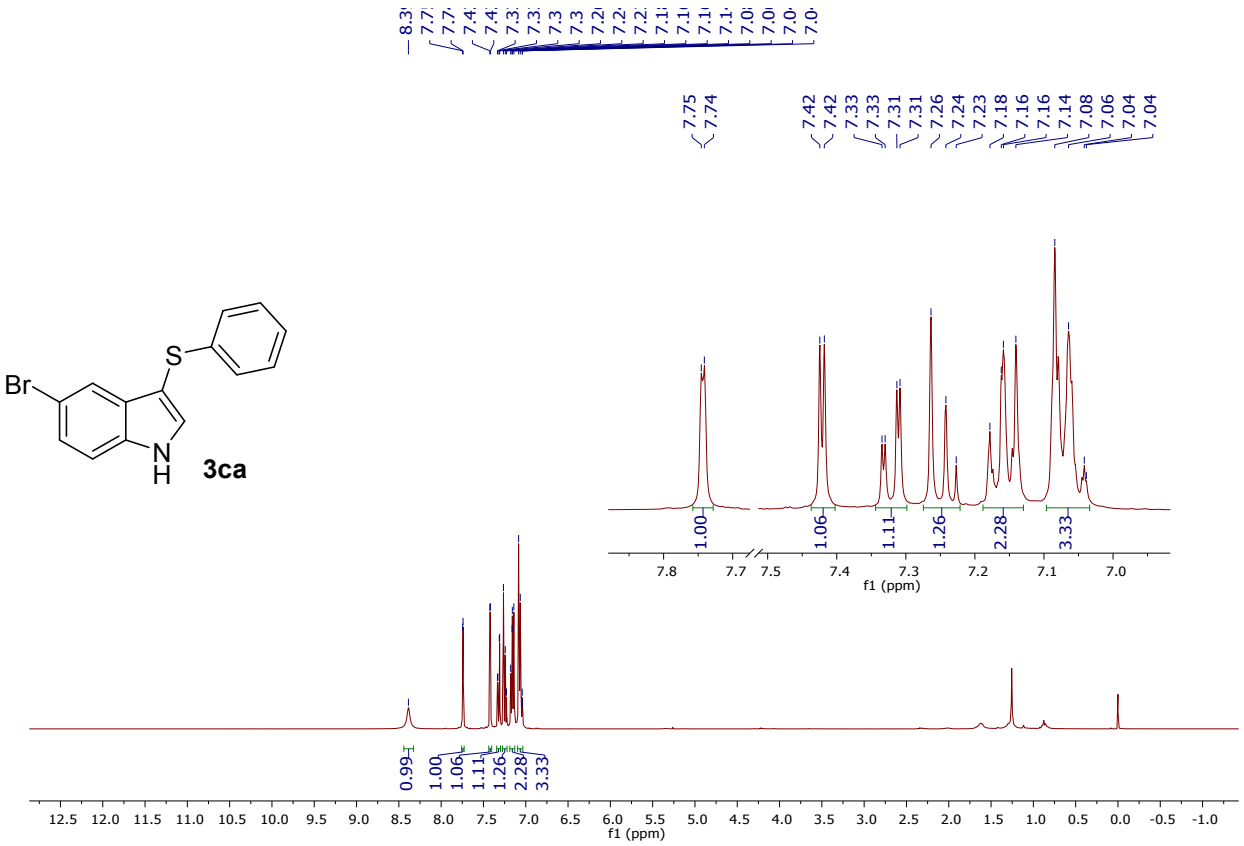
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-((furan-2-ylmethyl)thio)-1*H*-indole **(3aj)**



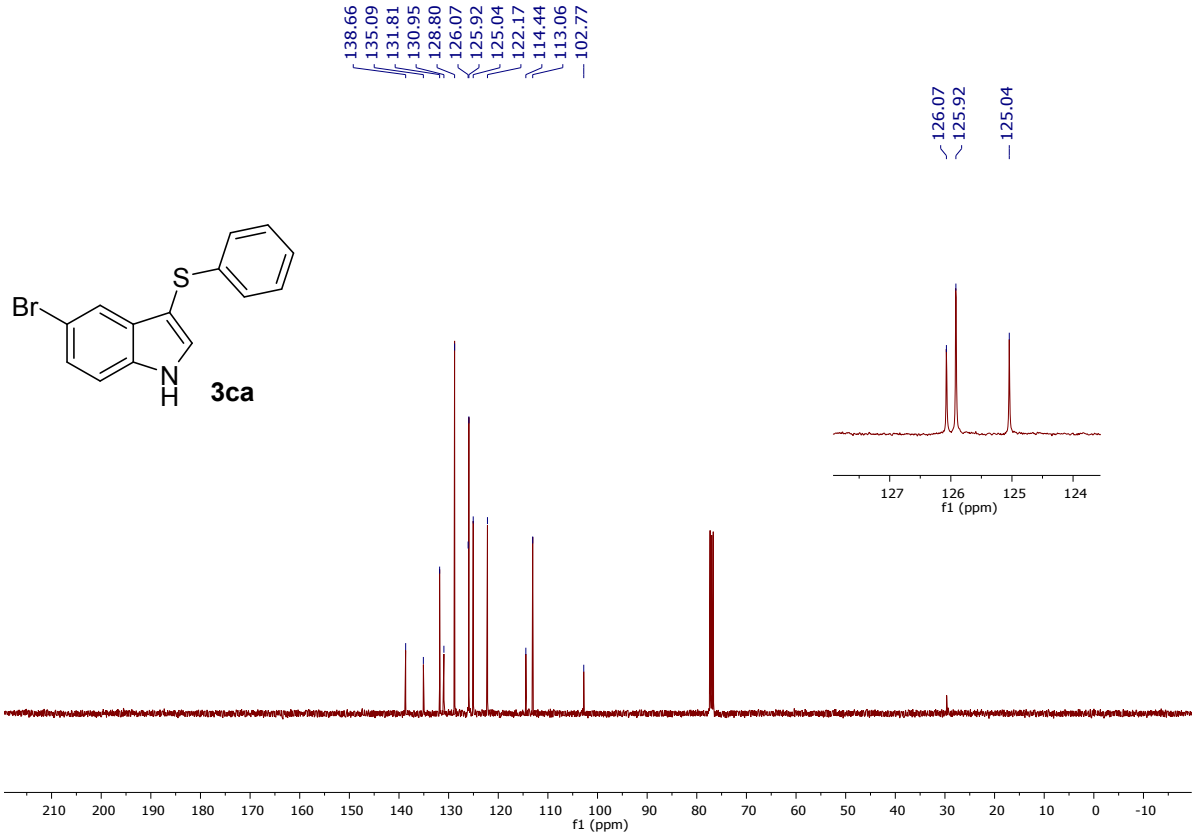
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-methyl-3-(phenylthio)-1*H*-indole **(3ba)**



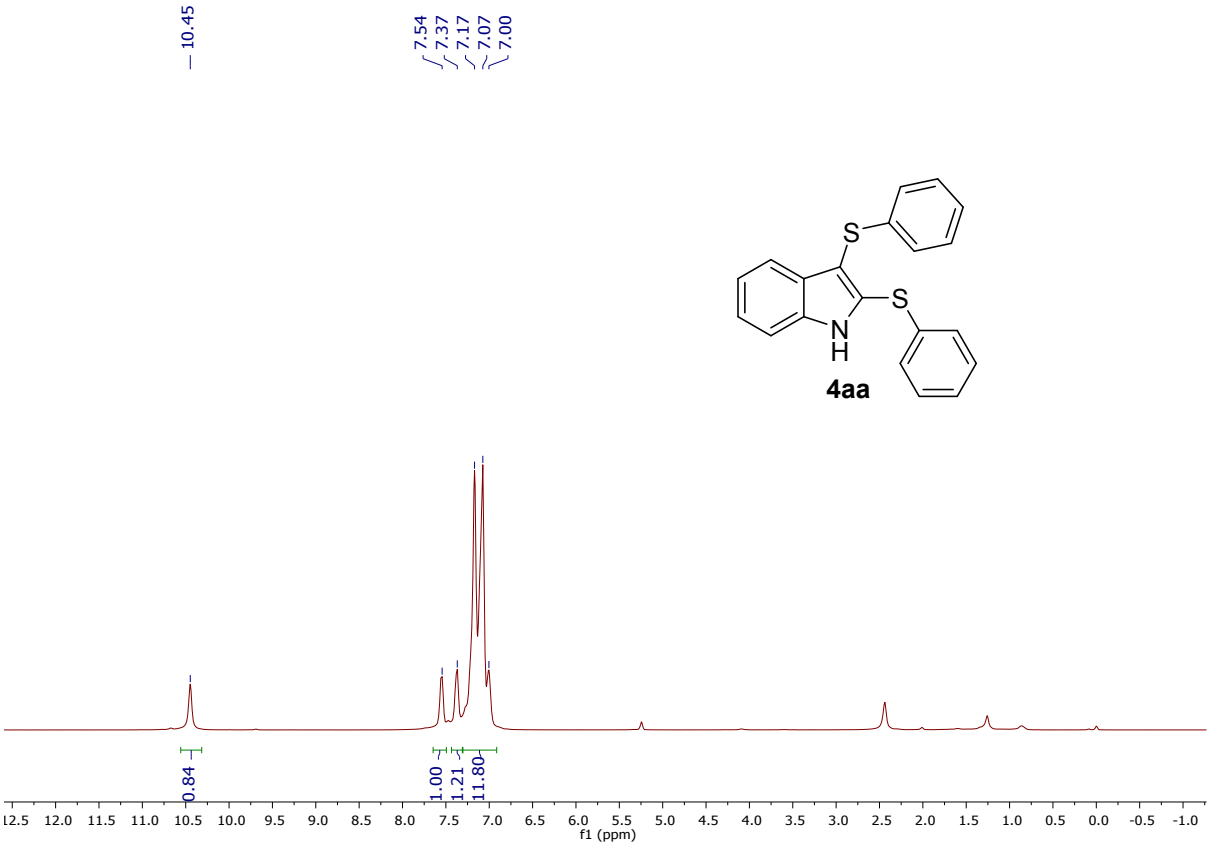
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1-methyl-3-(phenylthio)-1*H*-indole **(3ba)**



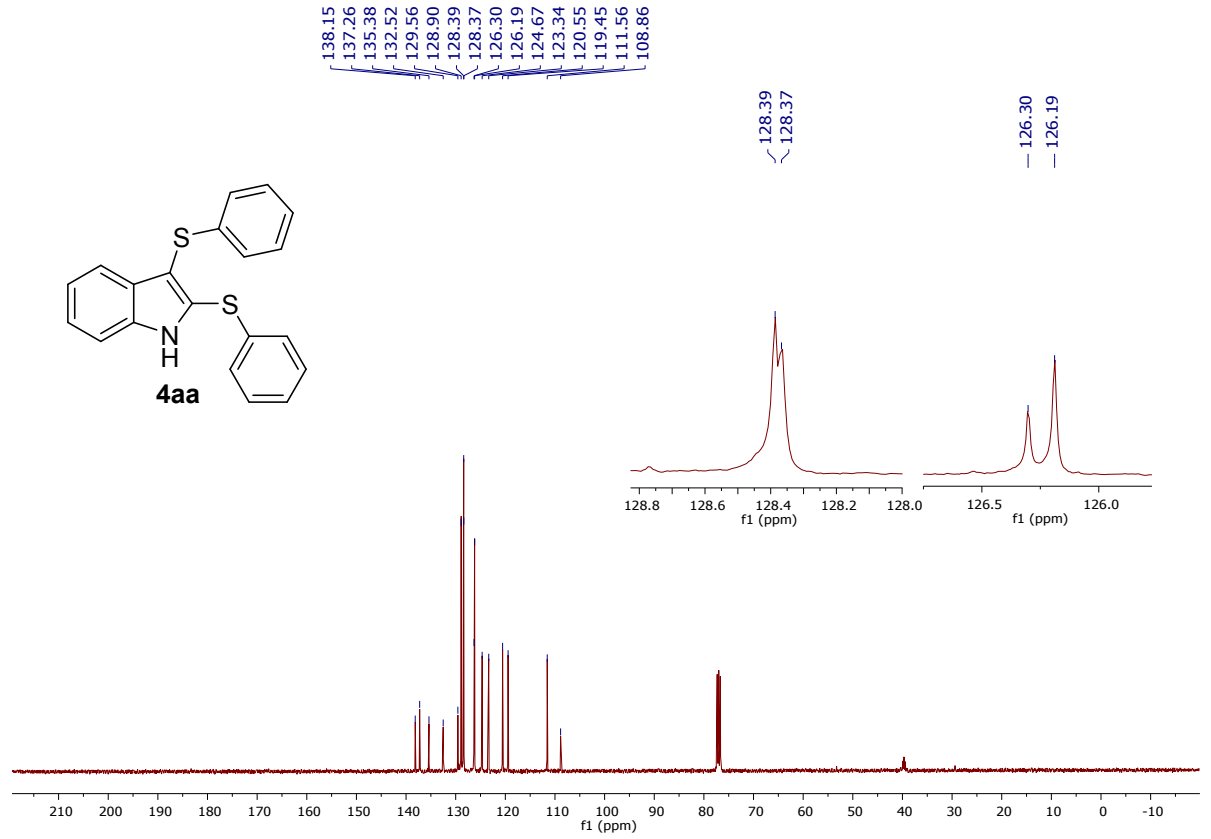
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-bromo-3-(phenylthio)-1*H*-indole **(3ca)**



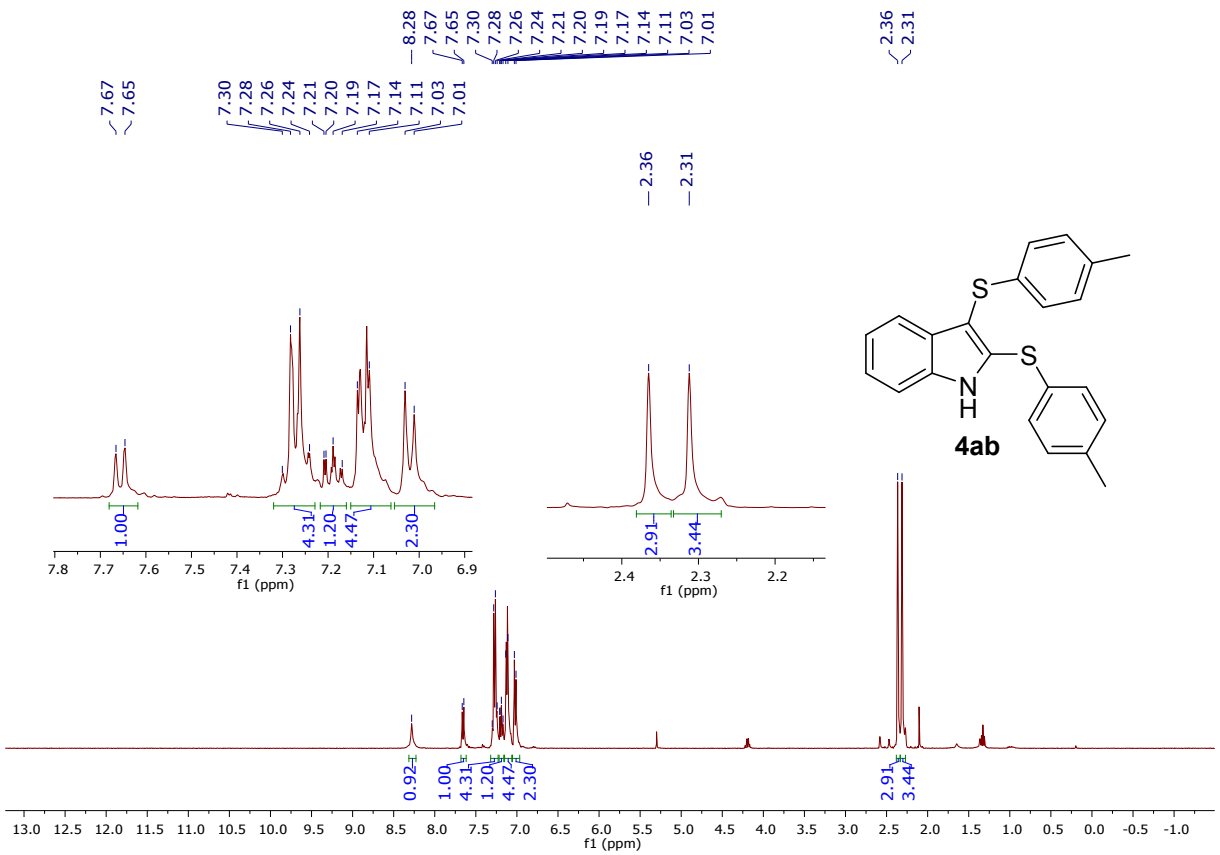
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5-bromo-3-(phenylthio)-1*H*-indole **(3ca)**



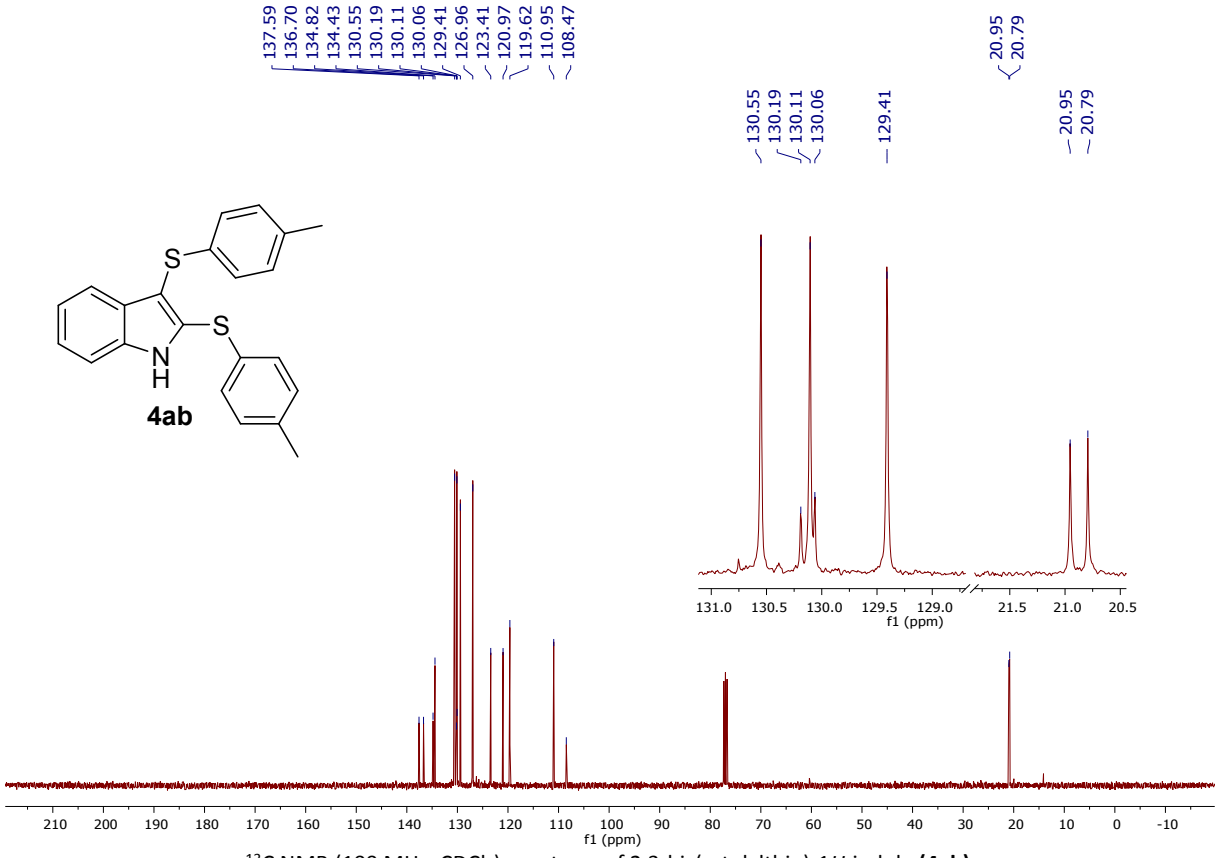
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,3-bis(phenylthio)-1*H*-indole **(4aa)**



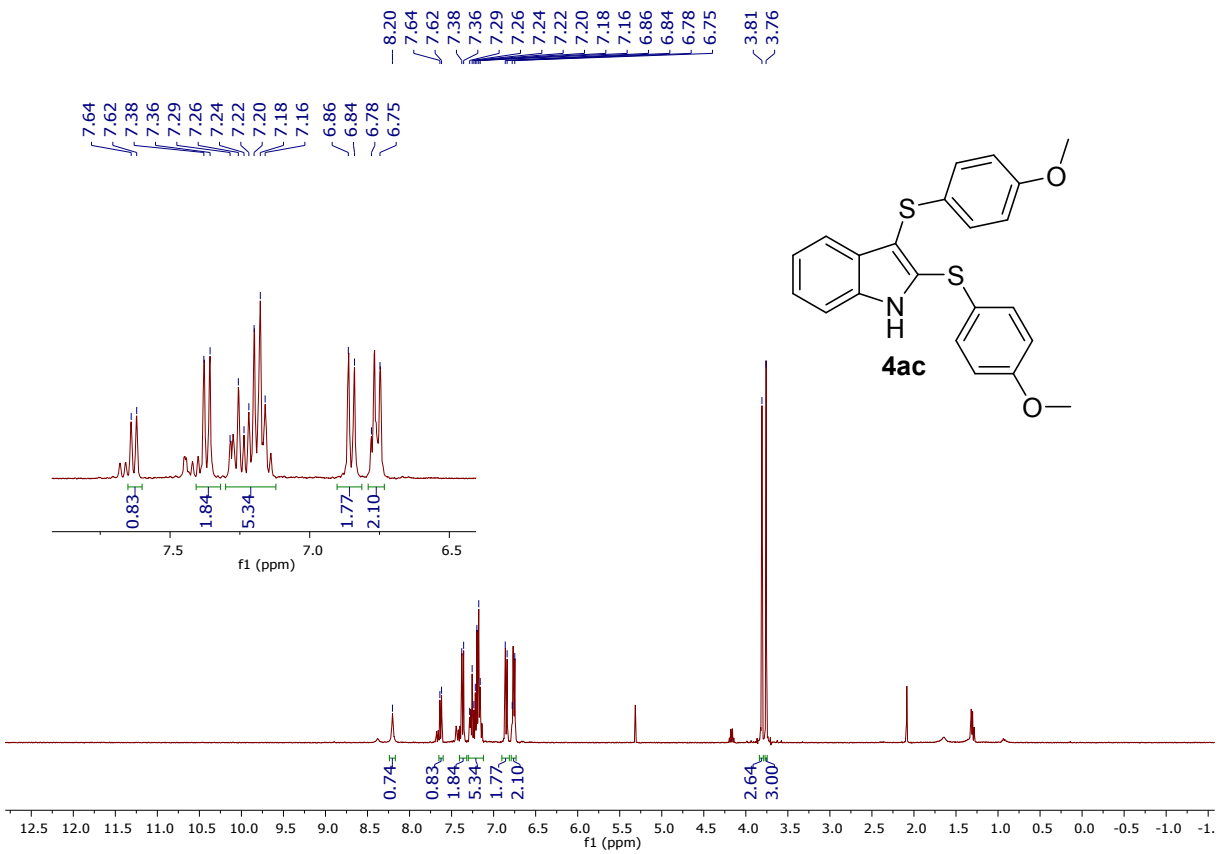
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,3-bis(phenylthio)-1*H*-indole **(4aa)**



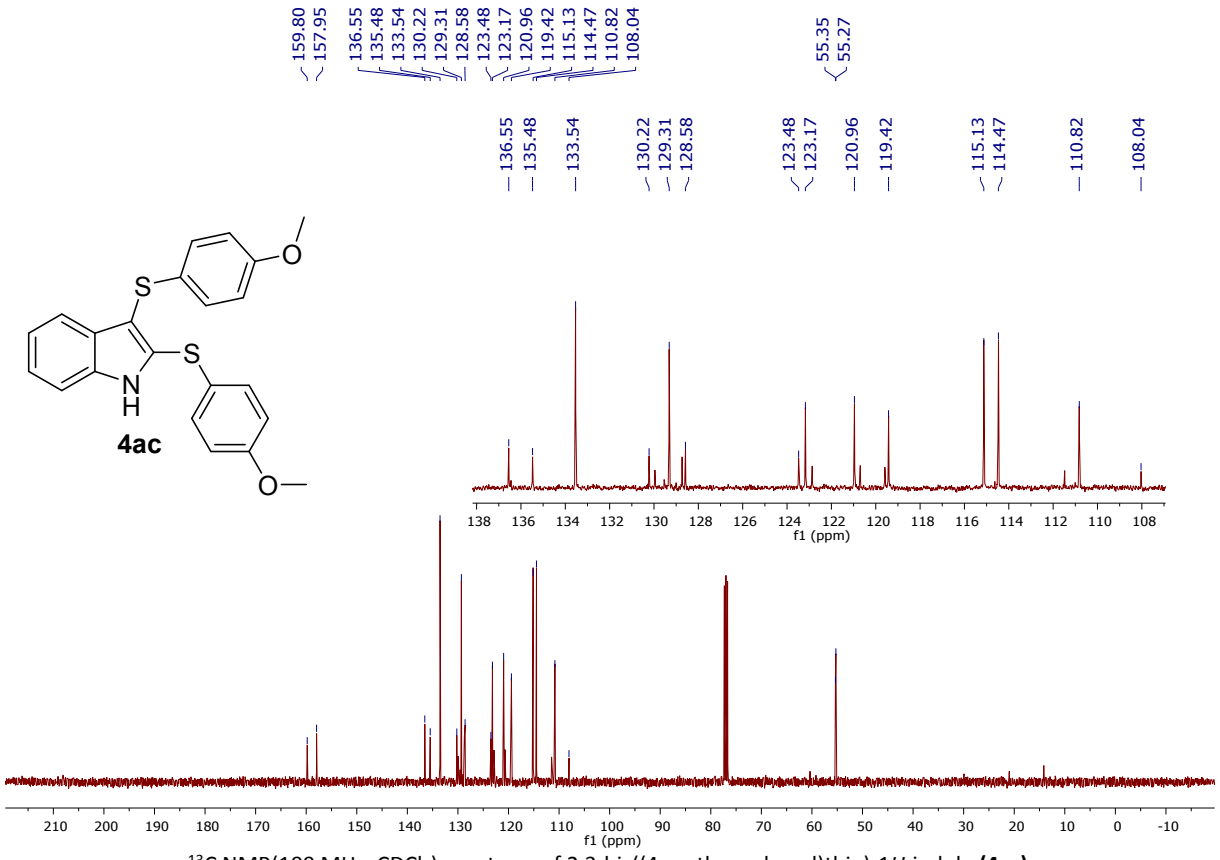
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,3-bis(*p*-tolylthio)-1*H*-indole **(4ab)**



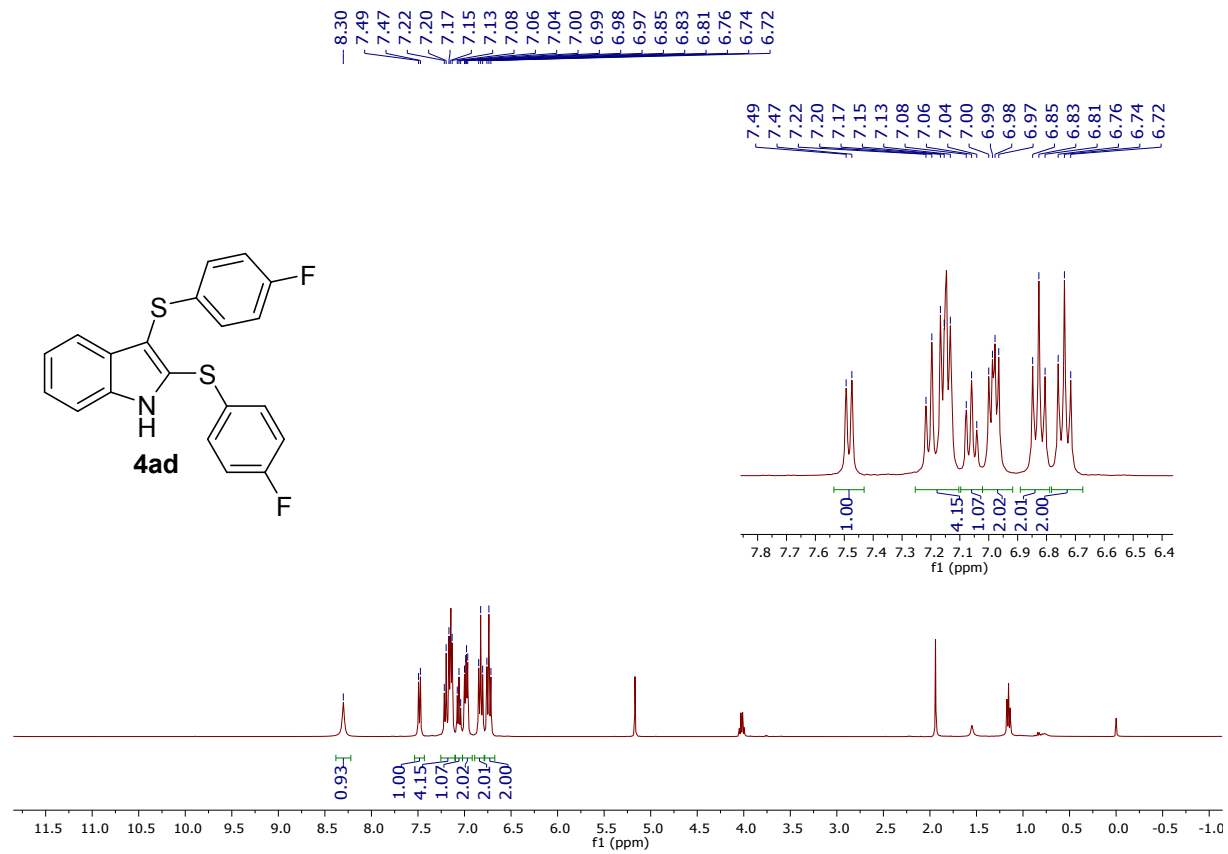
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,3-bis(*p*-tolylthio)-1*H*-indole **(4ab)**



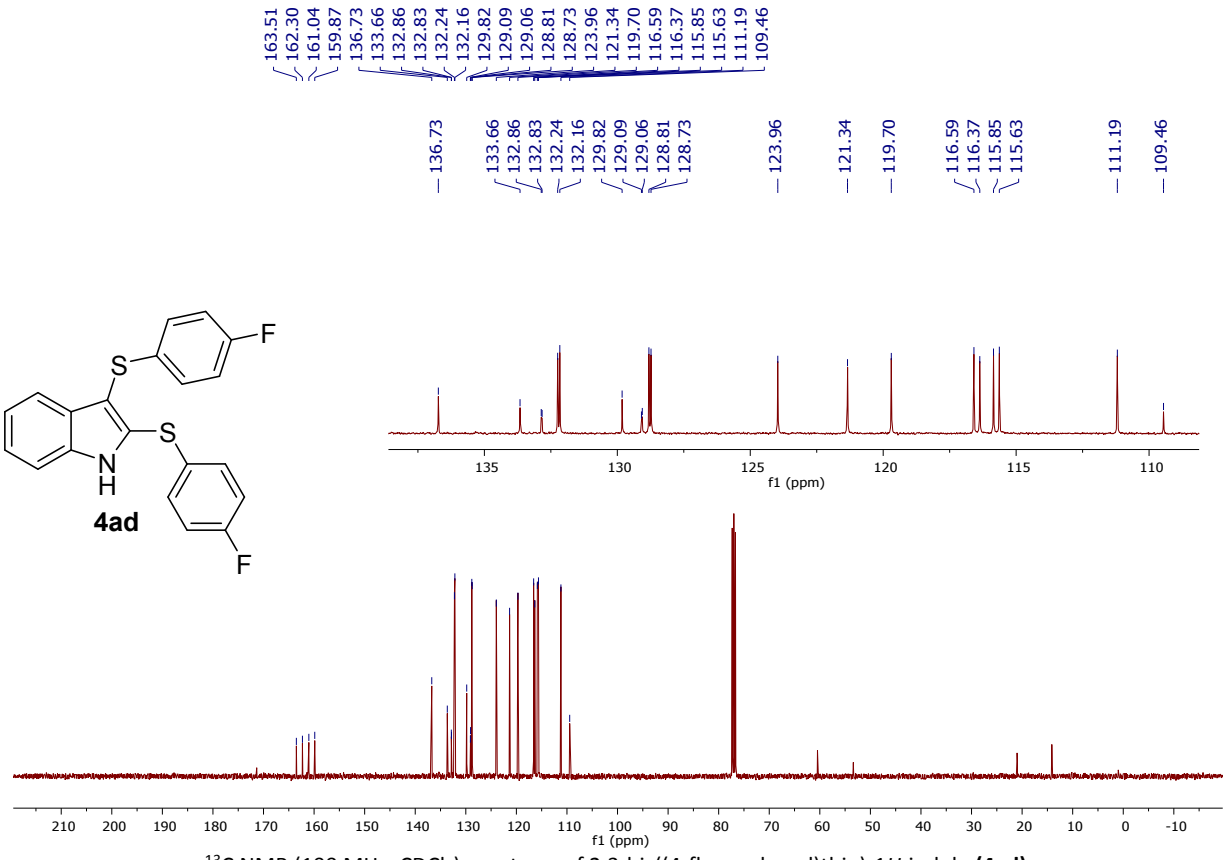
^{1}H NMR(400 MHz, $CDCl_3$) spectrum of 2,3-bis((4-methoxyphenyl)thio)-1*H*-indole **(4ac)**



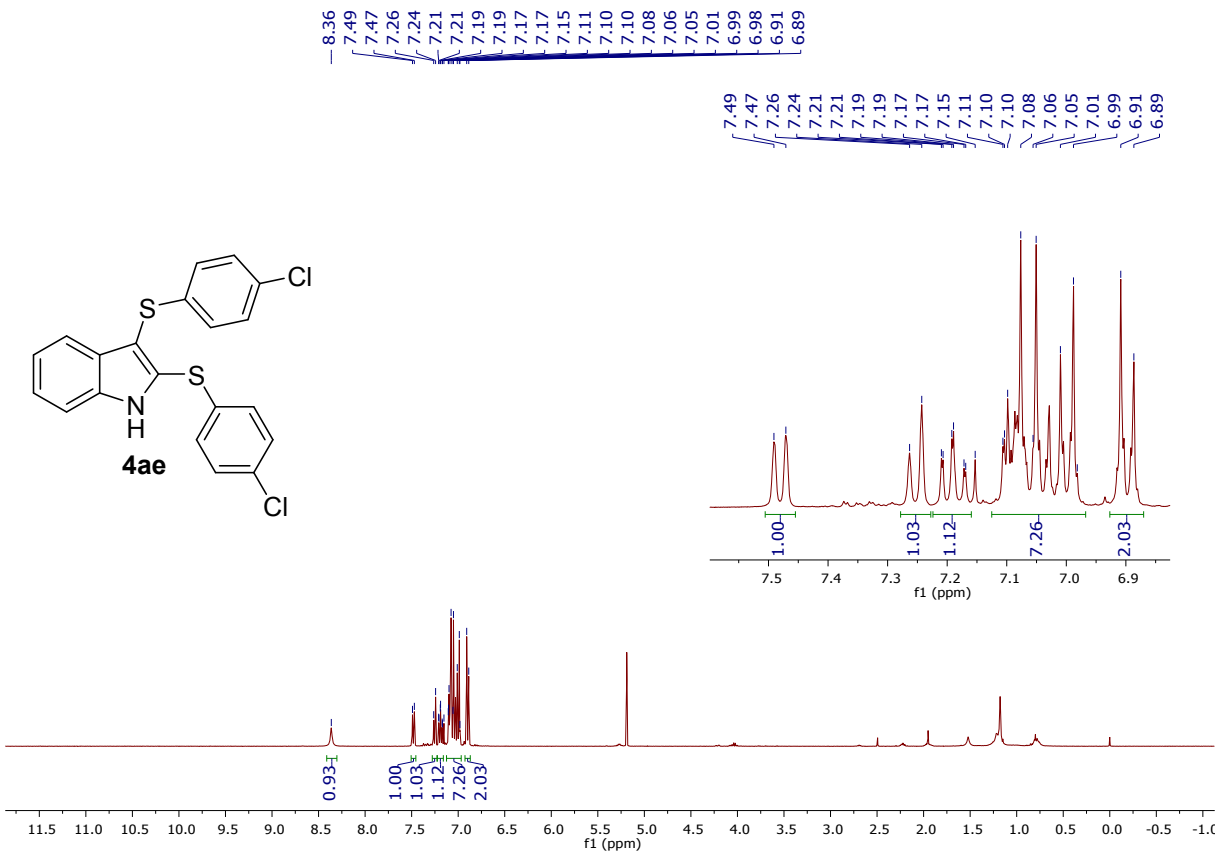
^{13}C NMR(100 MHz, $CDCl_3$) spectrum of 2,3-bis((4-methoxyphenyl)thio)-1*H*-indole **(4ac)**



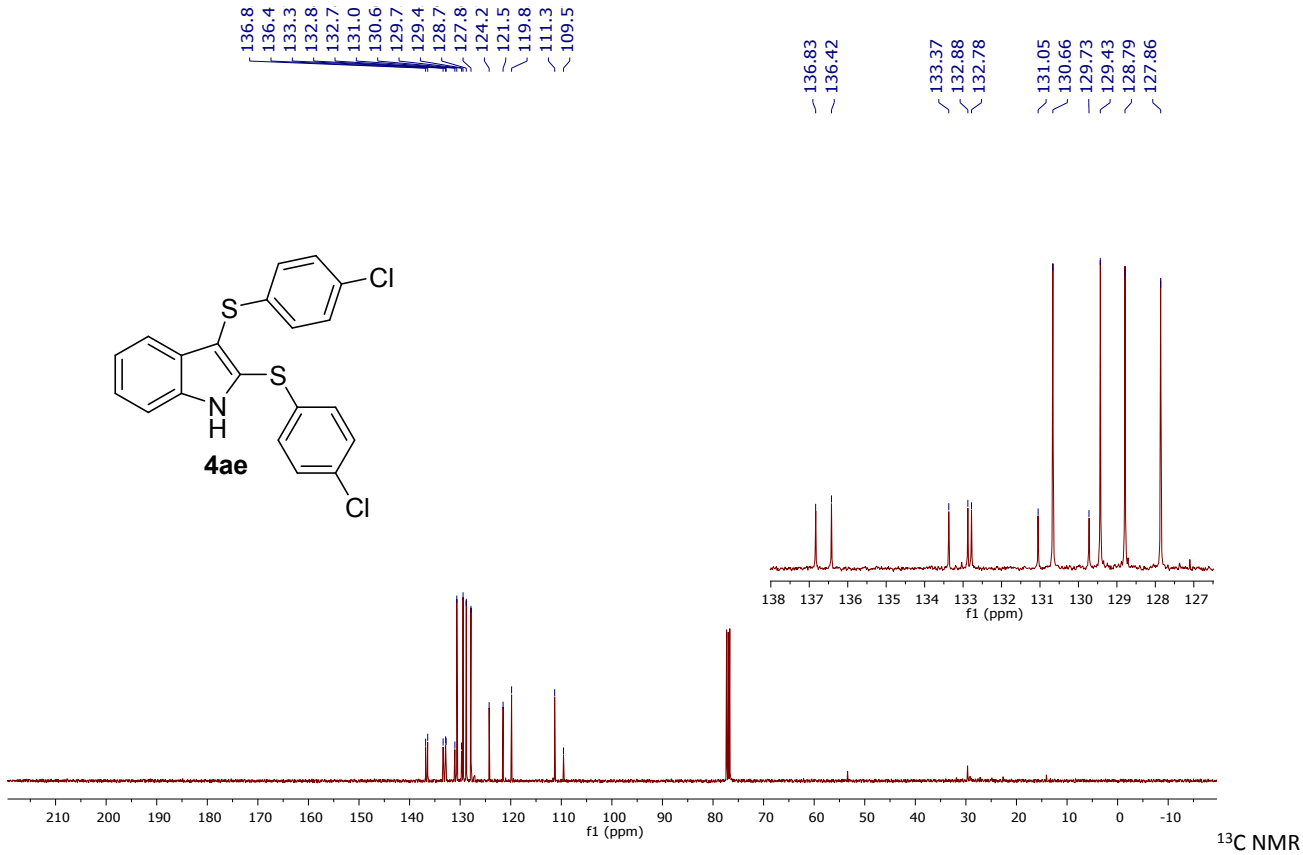
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,3-bis((4-fluorophenyl)thio)-1*H*-indole **(4ad)**



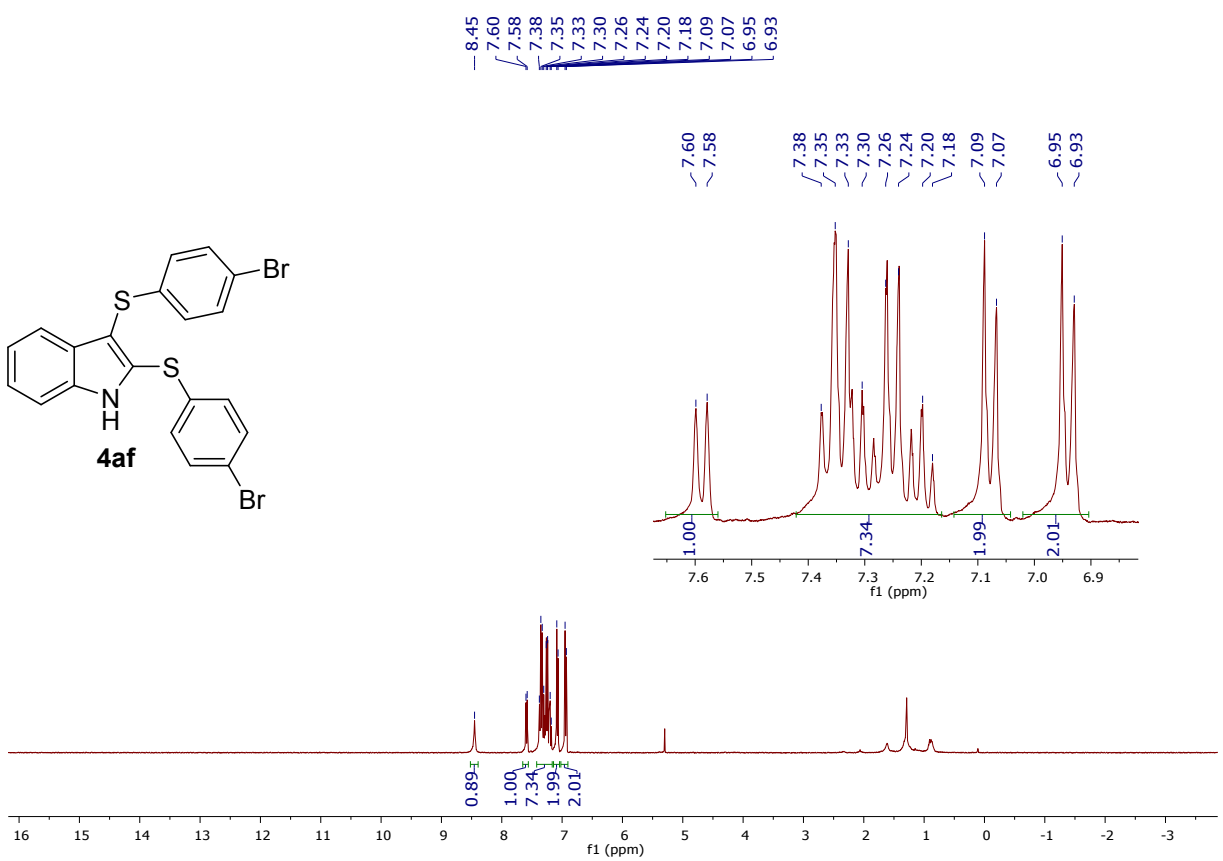
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,3-bis((4-fluorophenyl)thio)-1*H*-indole **(4ad)**



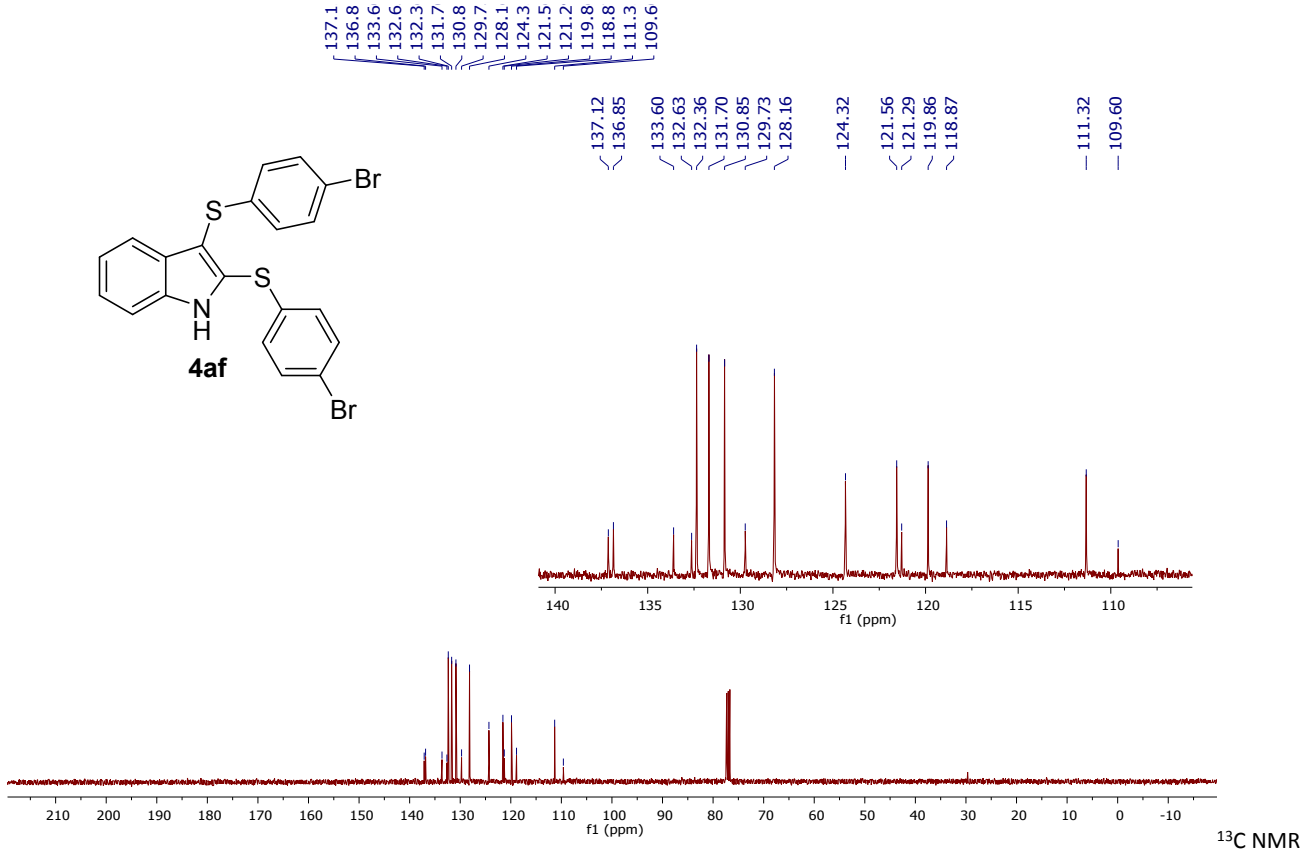
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,3-bis((4-chlorophenyl)thio)-1*H*-indole **(4ae)**



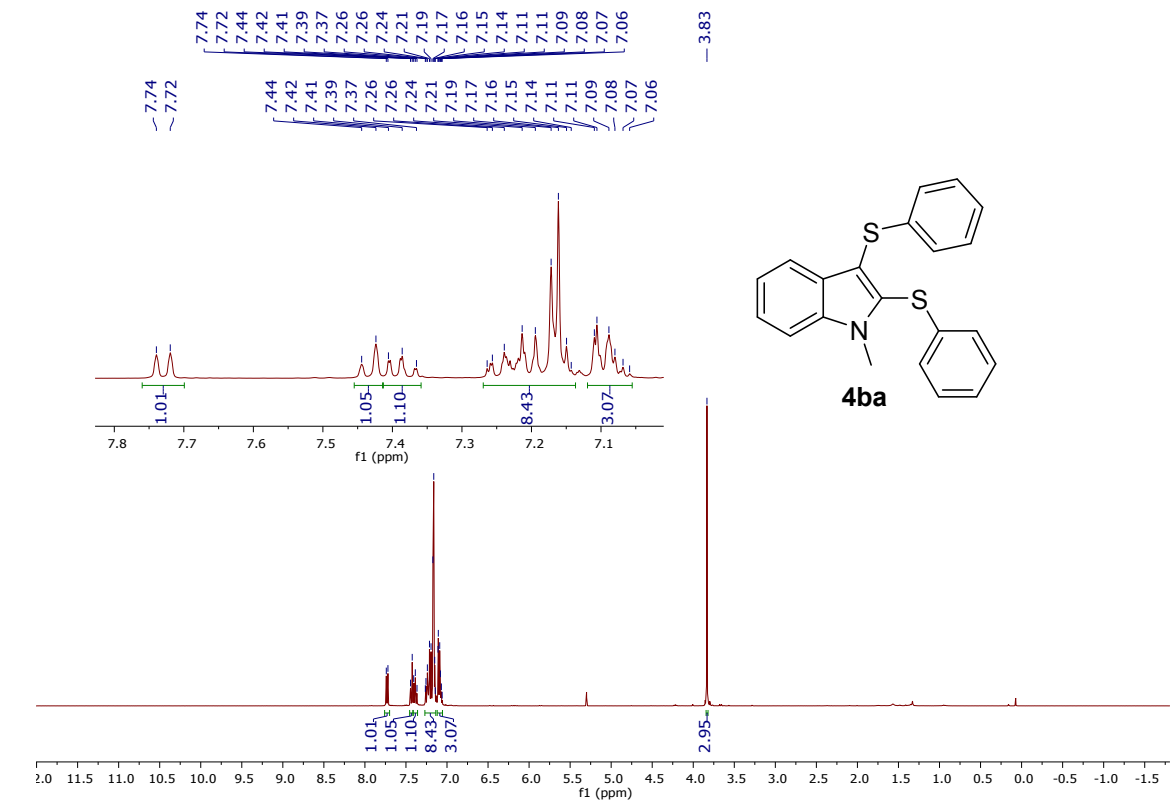
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,3-bis((4-chlorophenyl)thio)-1*H*-indole **(4ae)**



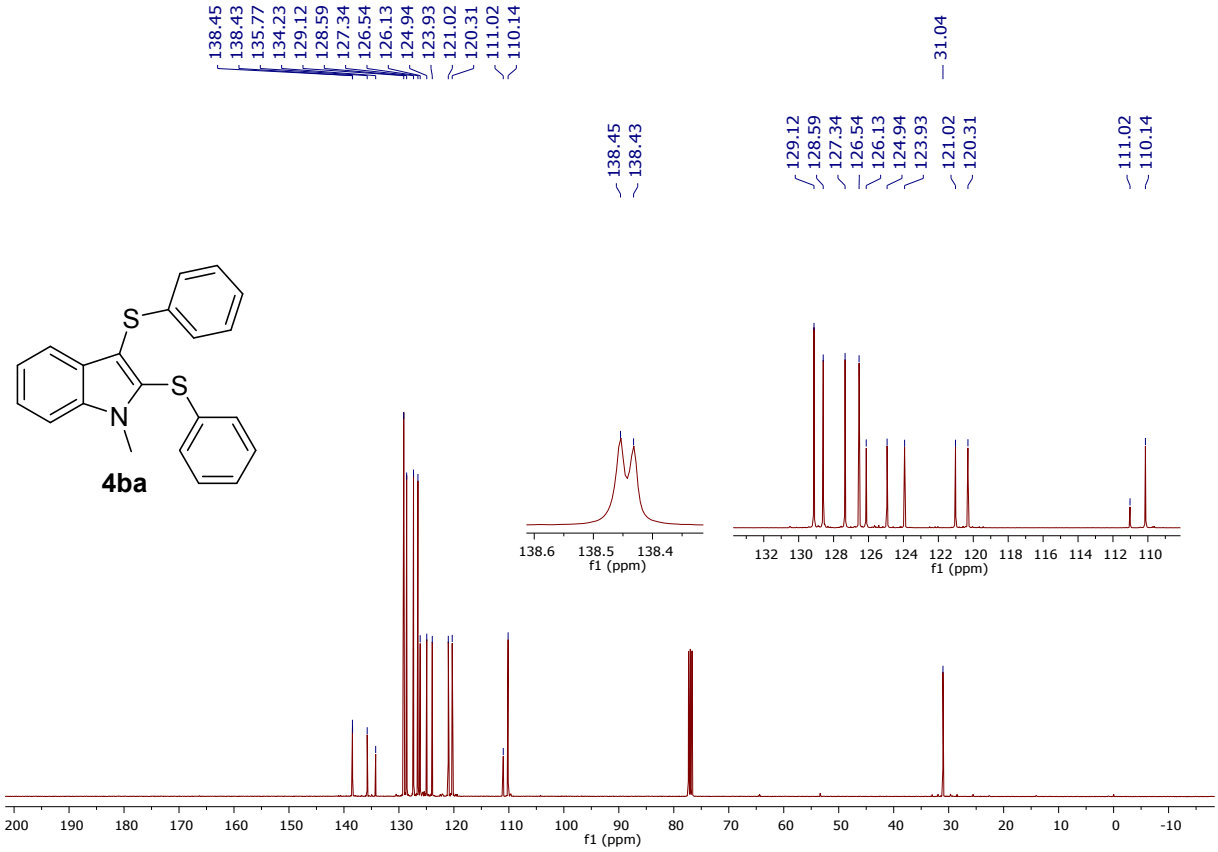
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2,3-bis((4-bromophenyl)thio)-1*H*-indole **(4af)**



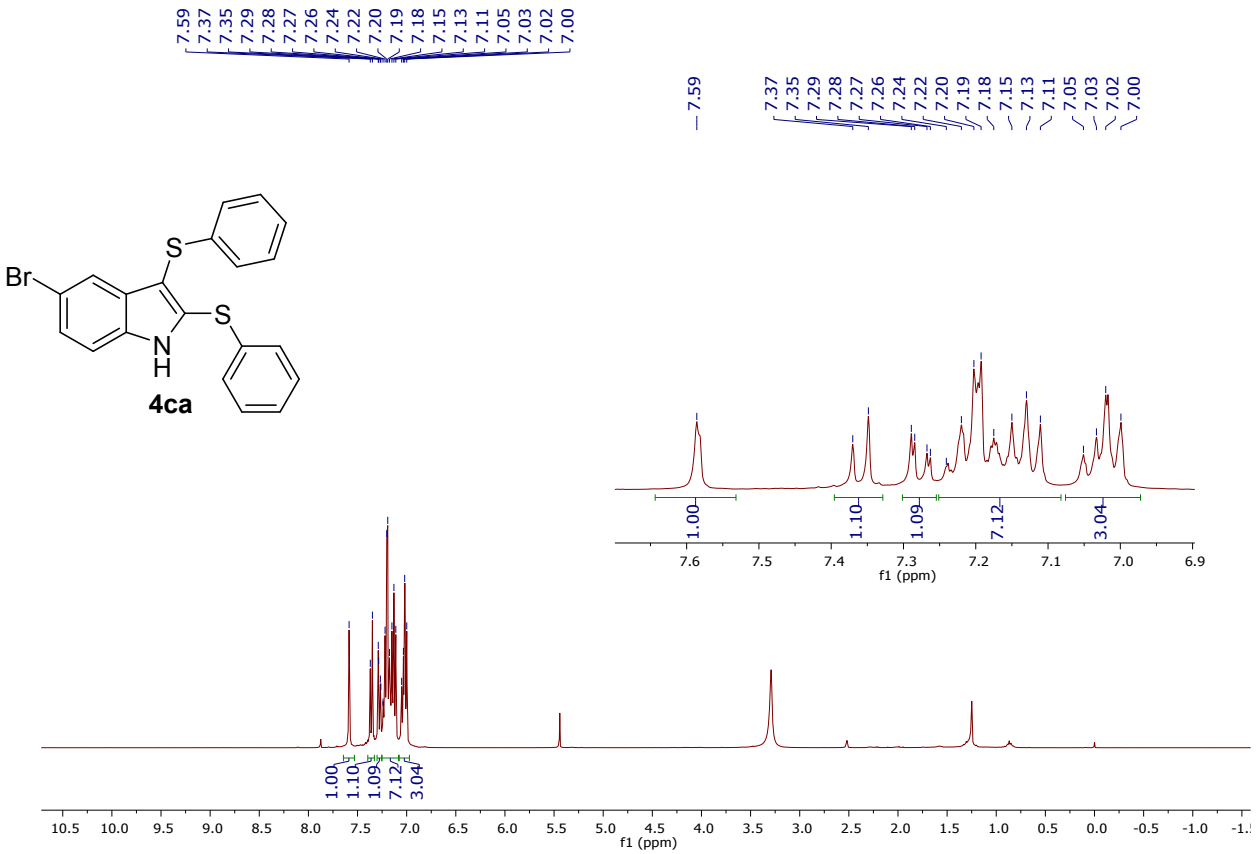
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2,3-bis((4-bromophenyl)thio)-1*H*-indole **(4af)**



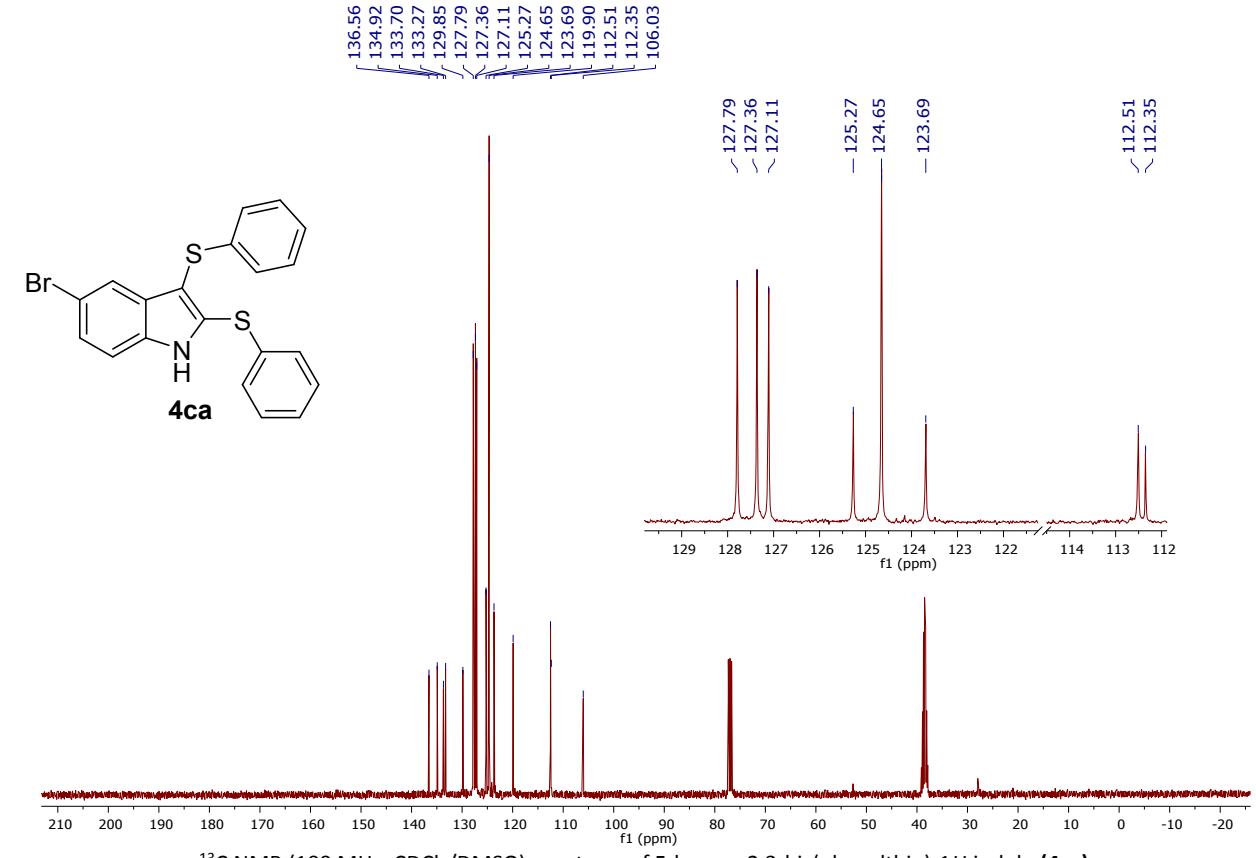
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-methyl-2,3-bis(phenylthio)-1*H*-indole **(4ba)**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1-methyl-2,3-bis(phenylthio)-1*H*-indole **(4ba)**



^{1}H NMR (400 MHz, $CDCl_3$/DMSO) spectrum of 5-bromo-2,3-bis(phenylthio)-1*H*-indole **(4ca)**



^{13}C NMR (100 MHz, $CDCl_3$/DMSO) spectrum of 5-bromo-2,3-bis(phenylthio)-1*H*-indole **(4ca)**