

**Iodophor-Catalyzed Sulfenylation of Indoles with Sulfonyl
Hydrazides for the Synthesis of 3-Sulfenylindoles**
Supporting Information

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Characterization data of the products

[3-(phenylthio)-1H-indole] [3a]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.44 (dd, J = 13.2, 5.3 Hz, 2H), 7.26 (dd, J = 13.3, 5.3 Hz, 1H), 7.15 (ddd, J = 18.1, 11.7, 4.9 Hz, 5H), 7.05 (t, J = 7.0 Hz, 1H).

[3-((4-Fluorophenyl)thio)-1H-indole] [3b]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.10 (dd, J = 8.9, 5.1 Hz, 2H), 6.87 (t, J = 8.8 Hz, 2H).

[3-((4-Bromophenyl)thio)-1H-indole] [3c]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.24 (dd, J = 10.2, 3.6 Hz, 3H), 7.16 (t, J = 7.5 Hz, 1H), 6.94 (dd, J = 8.7, 2.2 Hz, 2H).

[3-((4-(Trifluoromethyl)phenyl)thio)-1H-indole] [3d]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.49 (s), 7.59 (d, J = 7.9 Hz), 7.51 (d, J = 2.6 Hz), 7.48 (d, J = 8.2 Hz), 7.40 (d, J = 8.3 Hz), 7.32 (t, J = 7.6 Hz), 7.21 (t, J = 7.5 Hz), 7.16 (d, J = 8.2 Hz).

[3-((4-(Trifluoromethoxy)phenyl)thio)-1H-indole] [3e]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 2.6 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 8.2 Hz, 2H).

[3-((4-Nitrophenyl)thio)-1H-indole] [3f]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.02 – 7.97 (m, 1H), 7.53 (dd, J = 14.3, 6.6 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.19 (d, J = 7.1 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H).

[3-(p-tolylthio)-1H-indole] [3g]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H).

[3-((4-Methoxyphenyl)thio)-1H-indole] [3h]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 2.5 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.25 (t, J = 7.0 Hz, 1H), 7.16 – 7.12 (m, 3H), 6.74 (d, J = 8.9 Hz, 2H), 3.72 (s, 3H).

[3-(o-tolylthio)-1H-indole] [3i]^[2]

¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 8.6

Hz, 2H), 7.26 (d, $J = 17.6$ Hz, 2H), 7.14 (dd, $J = 15.2, 7.5$ Hz, 2H), 6.96 (t, $J = 6.8$ Hz, 1H), 6.88 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 2.49 (s, 3H).

[3-((2-fluorophenyl)thio)-1H-indole] [3j]^[2]

¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.61 (s, 1H), 7.51 (d, $J = 3.6$ Hz, 1H), 7.44 (d, $J = 3.7$ Hz, 1H), 7.25 (s, 1H), 7.21-7.17 (m, 1H), 7.03 (d, $J = 6.5$ Hz, 1H), 6.87 – 6.82 (m, 1H), 6.81 – 6.75 (m, 1H).

[3-((3-bromophenyl)thio)-1H-indole] [3k]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.44 (d, $J = 2.5$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.21-7.12 (m, 3H), 6.96 (d, $J = 5.1$ Hz, 2H).

[3-((2,5-Dimethylphenyl)thio)-1H-indole] [3l]^[3]

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.52 (d, $J = 7.9$ Hz, 1H), 7.40-7.35 (m, 2H), 7.20 (dt, $J = 5.8, 3.0$ Hz, 1H), 7.11-7.06 (m, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.71 (d, $J = 8.3$ Hz, 1H), 6.50 (s, 1H), 2.38 (s, 3H), 1.97 (s, 3H).

[3-((2,4-dichlorophenyl)thio)-1H-indole] [3m]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.42 (d, $J = 2.5$ Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 1H), 7.26 (d, $J = 2.0$ Hz, 1H), 7.24-7.19 (m, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.81 (d, $J = 8.6$ Hz, 1H), 6.48 (d, $J = 8.6$ Hz, 1H).

[3-((5-bromo-2-fluorophenyl)thio)-1H-indole] [3n]

¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.51 (d, $J = 7.9$ Hz, 1H), 7.43 (d, $J = 2.5$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.15 – 7.09 (m, 2H), 6.89 (d, $J = 8.4$ Hz, 1H), 6.54 (t, $J = 8.3$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 136.32, 131.05, 128.83, 128.80, 128.63, 127.37, 127.34, 123.16, 121.04, 119.20, 118.59, 118.35, 111.58, 99.90. HRMS (APCI): m/z calcd for C₁₄H₉BrFNS₂(M-H)⁺ 320.9623, found: 320.9623.

[Methyl 3-(phenylthio)-1H-indole-4-carboxylate] [4a]^[1]

¹H NMR (400 MHz, CDCl₃) δ 9.06 (s, 1H), 7.39 (s, 1H), 7.38 (d, $J = 1.7$ Hz, 1H), 7.31 (d, $J = 2.7$ Hz, 1H), 7.14 (t, $J = 7.8$ Hz, 1H), 7.03 (d, $J = 7.2$ Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 3.50 (s, 1H).

[4-Nitro-3-(phenylthio)-1H-indole] [4b]^[1]

¹H NMR (400 MHz, CDCl₃) δ 9.07 (s, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.2$ Hz, 1H), 7.51 (s, 1H), 7.20 (dd, $J = 13.2, 5.4$ Hz, 2H), 7.08 (d, $J = 7.2$ Hz, 2H), 7.02 (dd, $J = 12.8, 5.0$ Hz, 3H).

[3-(Phenylthio)-1H-indole-4-carbonitrile] [4c]^[1]

¹H NMR (400 MHz, DMSO-*d*₆) δ 12.32 (d, $J = 9.5$ Hz, 1H), 8.04 (d, $J = 2.8$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.56 (d, $J = 6.6$ Hz, 1H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.25 – 7.18 (m, 1H), 7.08 (t, $J = 7.3$ Hz, 1H), 7.03 (d, $J = 7.2$ Hz, 2H).

[7-Methyl-3-(phenylthio)-1*H*-indole] [4d]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 2.6 Hz, 1H), 7.08 – 6.92 (m, 7H), 2.38 (s, 3H).

[7-Methoxy-3-(phenylthio)-1*H*-indole] [4e]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.12 (dd, *J* = 8.0 Hz, 1H), 7.08- 6.93 (m, 6H), 6.61 (d, *J* = 7.7 Hz, 1H), 3.87 (s, 3H).

[5-methyl-3-(phenylthio)-1*H*-indole] [4f]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.33 (s, 2H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.10-6.94 (m, 6H), 2.32 (s, 3H).

[5-Chloro-3-(phenylthio)-1*H*-indole] [4g]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.09 (d, *J* = 6.7 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 3H).

[6-Bromo-3-(phenylthio)-1*H*-indole] [4h]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.15-7.09 (m, 2H), 7.03 (d, *J* = 8.2 Hz, 3H).

[6-Fluoro-3-(phenylthio)-1*H*-indole] [4i]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.51 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.20 – 7.06 (m, 6H), 6.96-6.89 (m, 1H).

[2-Methyl-3-(phenylthio)-1*H*-indole] [4j]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.00 (m, 4H), 6.98 – 6.90 (m, 3H), 2.37 (s, 3H).

[5-Chloro-2-methyl-3-(phenylthio)-1*H*-indole] [4k]^[1]

¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.17-7.13 (m, 1H), 7.06 (dt, *J* = 8.5, 4.7 Hz, 3H), 6.99-6.92 (m, 3H), 2.41 (s, 3H).

[1-Methyl-3-(phenylthio)-1*H*-indole] [4l]^[1]

¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 8.2 Hz, 1H), 7.23 – 7.10 (m, 7H), 3.81 (s, 3H).

[3-(Phenylthio)-1*H*-pyrrolo (2,3-*b*) pyridine] [4m]^[1]

¹H NMR (400 MHz, CDCl₃) δ 11.69 (s, 1H), 8.41 (d, *J* = 3.4 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.71 (s, 1H), 7.21-7.14 (m, 3H), 7.06-7.12 (m, 3H).

[5-nitro-3-(phenylthio)-1*H*-indole][4n]

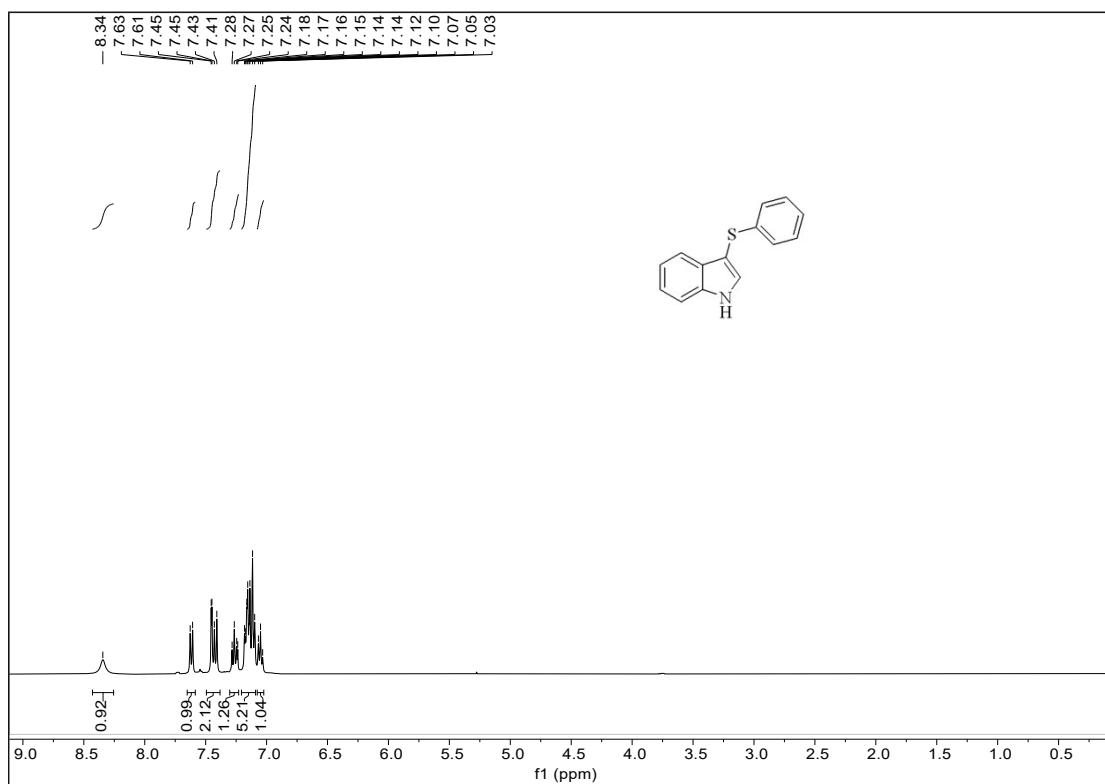
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References

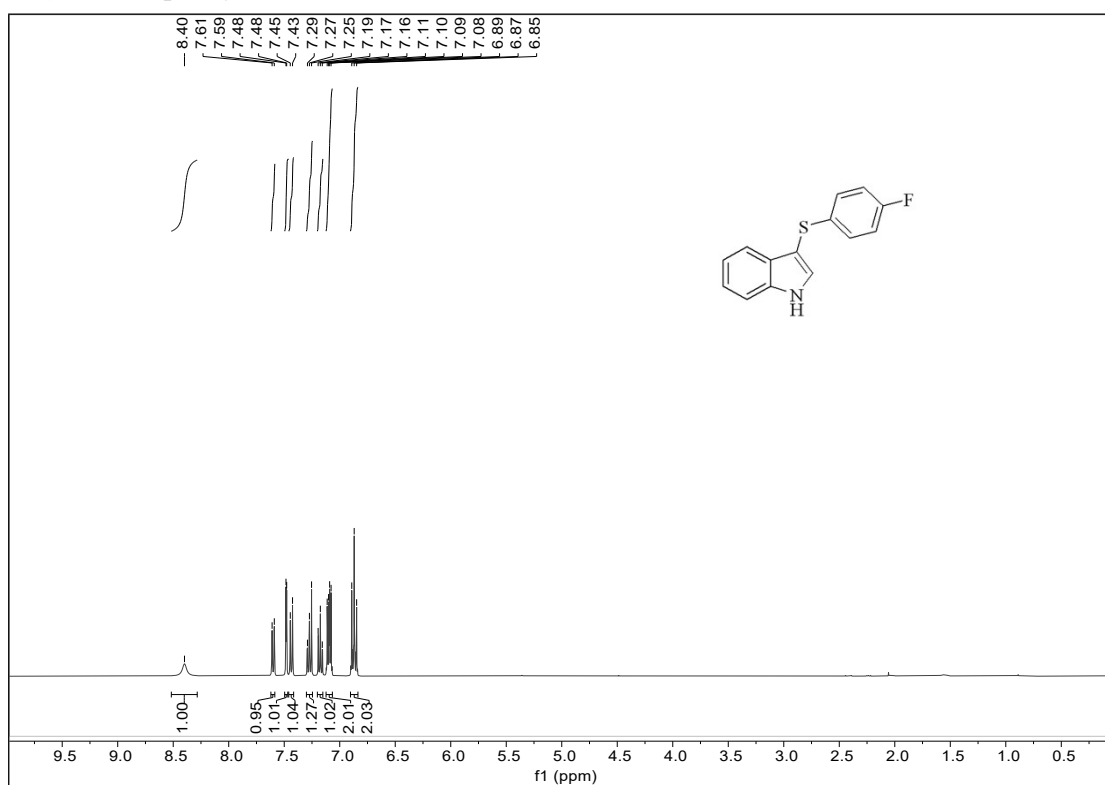
- [1] L. Chen, J. Zhang, Y. Wei, Z. Yang, P. Liu, J. Zhang and Dai B. *Tetrahedron*. 2019, **75**, 130664.
- [2] F. L. Yang and S. K. Tian, *Angew. Chem., Int. Ed.*, 2013, **52**, 4929.
- [3] G. Kumaraswamy, R. Raju and Narayanarao V. *RSC Adv.*, 2015, **5**, 22718.

NMR spectra

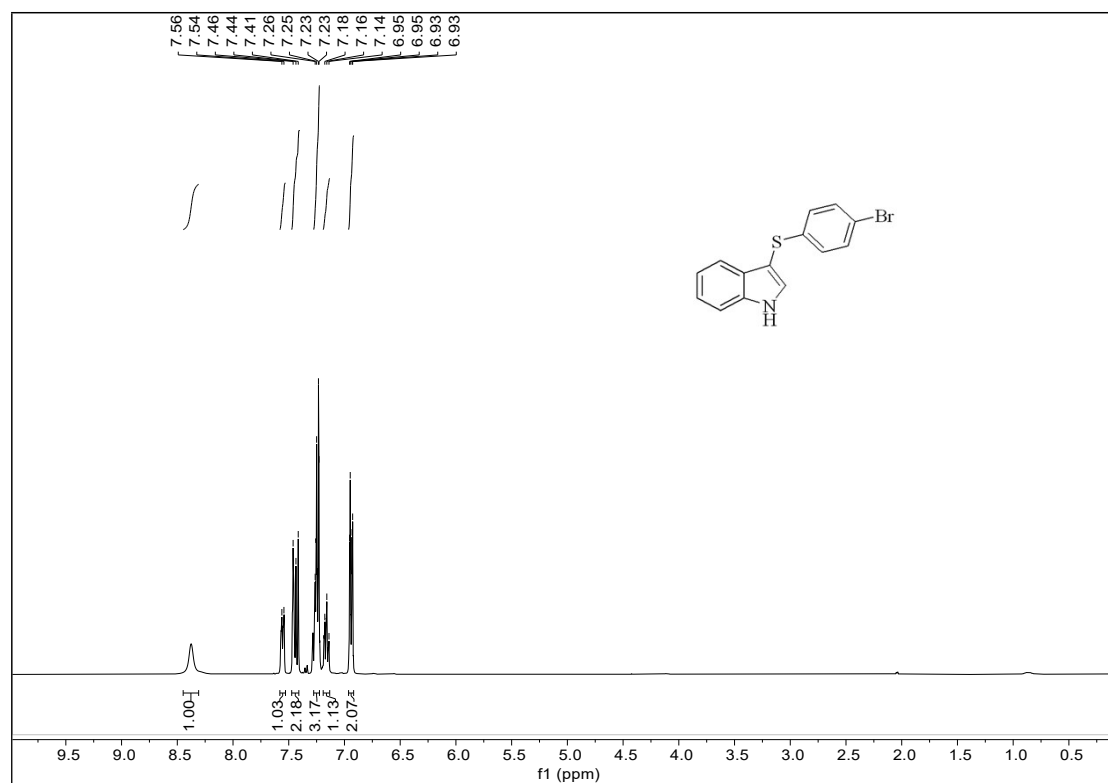
[3-(phenylthio)-1H-indole] [3a] ^1H NMR (400 MHz, CDCl_3)



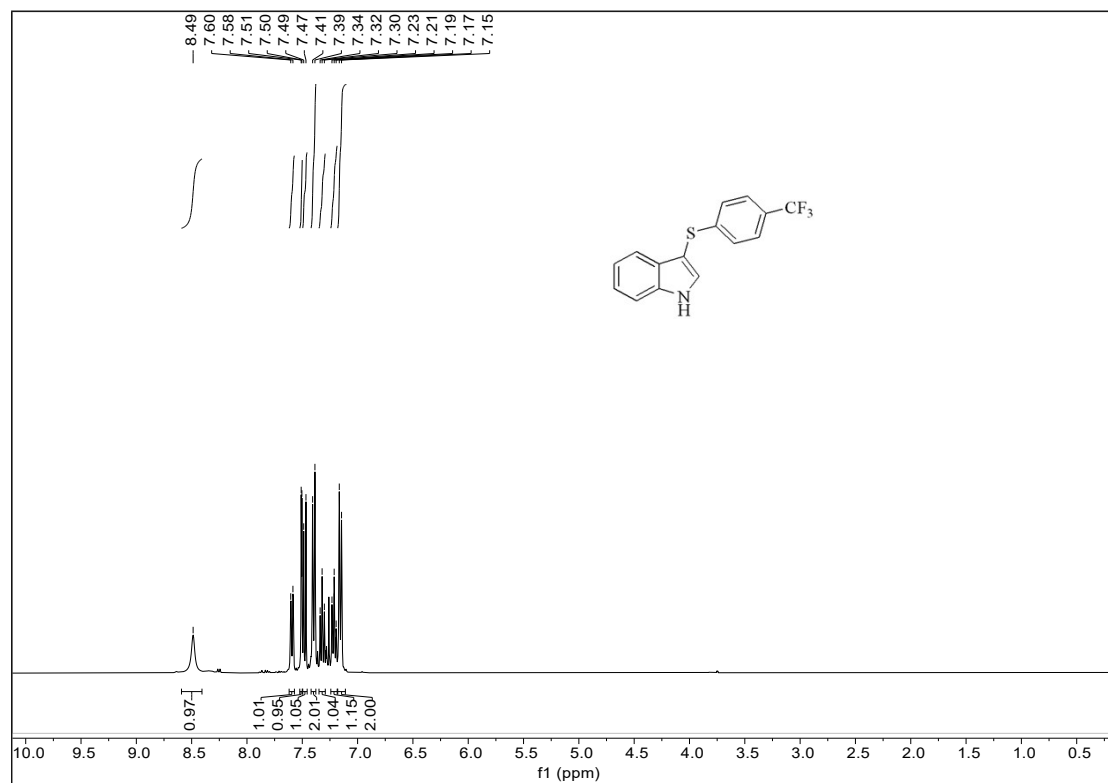
[3-((4-Fluorophenyl)thio)-1H-indole] [3b] ^1H NMR (400 MHz, CDCl_3)



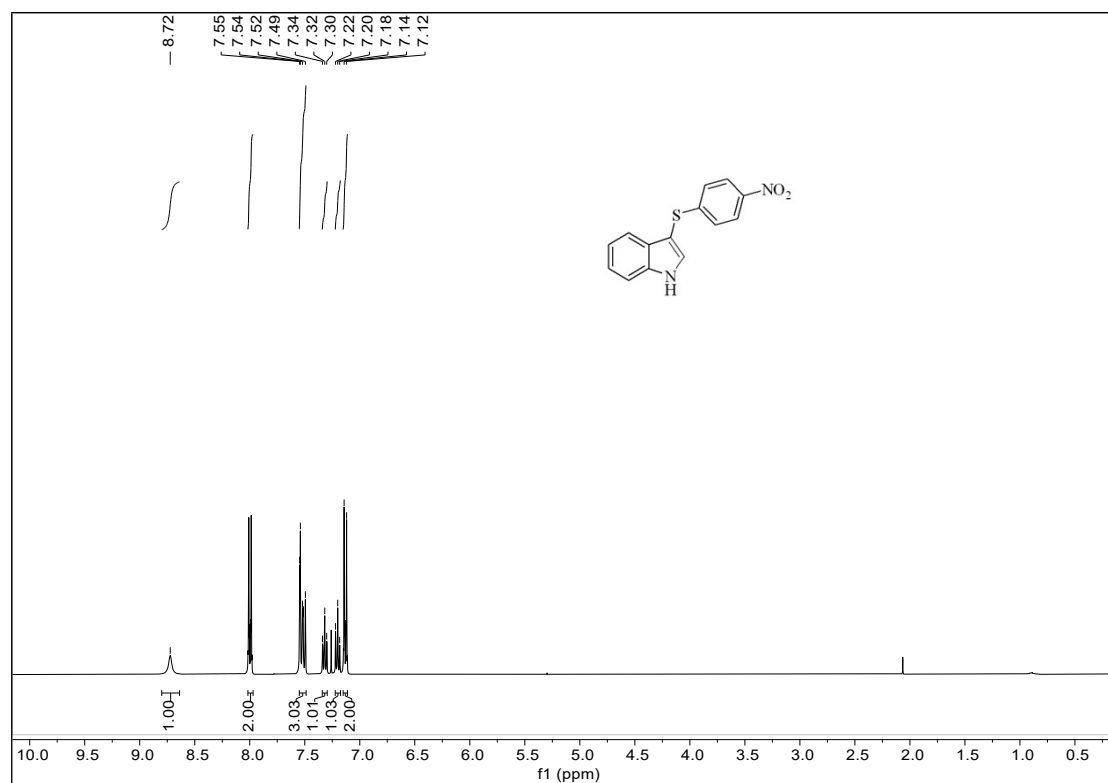
[3-((4-Bromophenyl)thio)-1H-indole] [3c] ^1H NMR (400 MHz, CDCl_3)



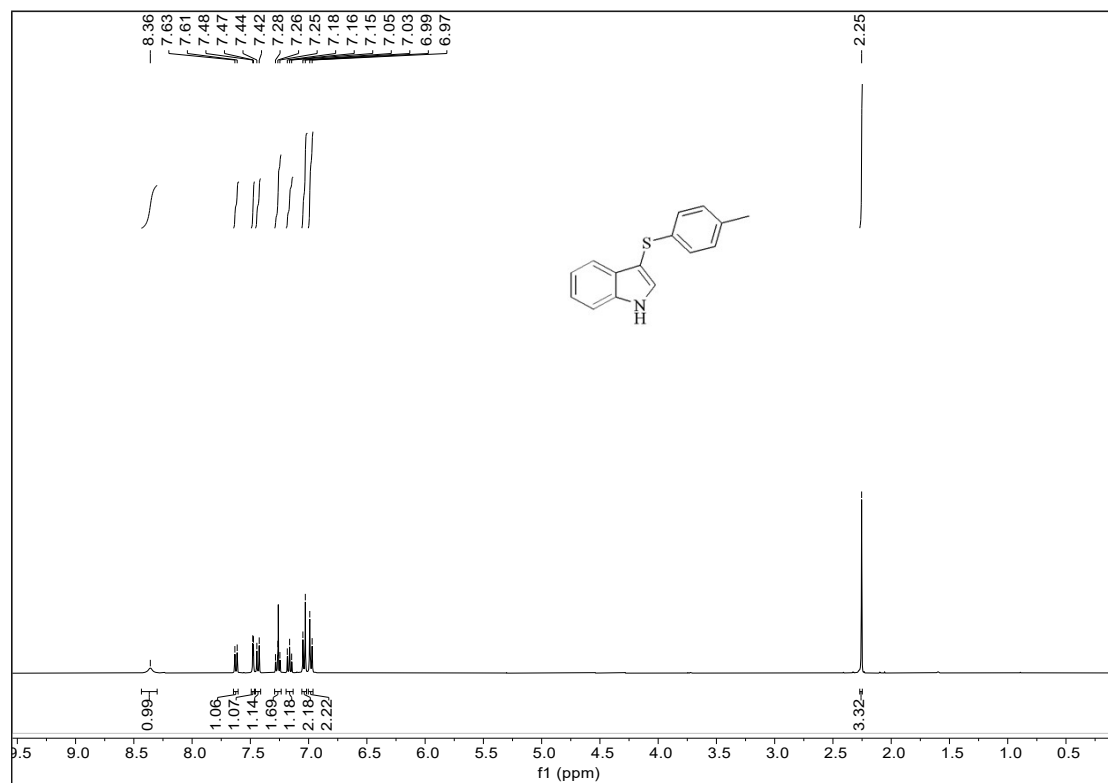
[3-((4-(Trifluoromethyl)phenyl)thio)-1H-indole] [3d] ^1H NMR (400 MHz, CDCl_3)



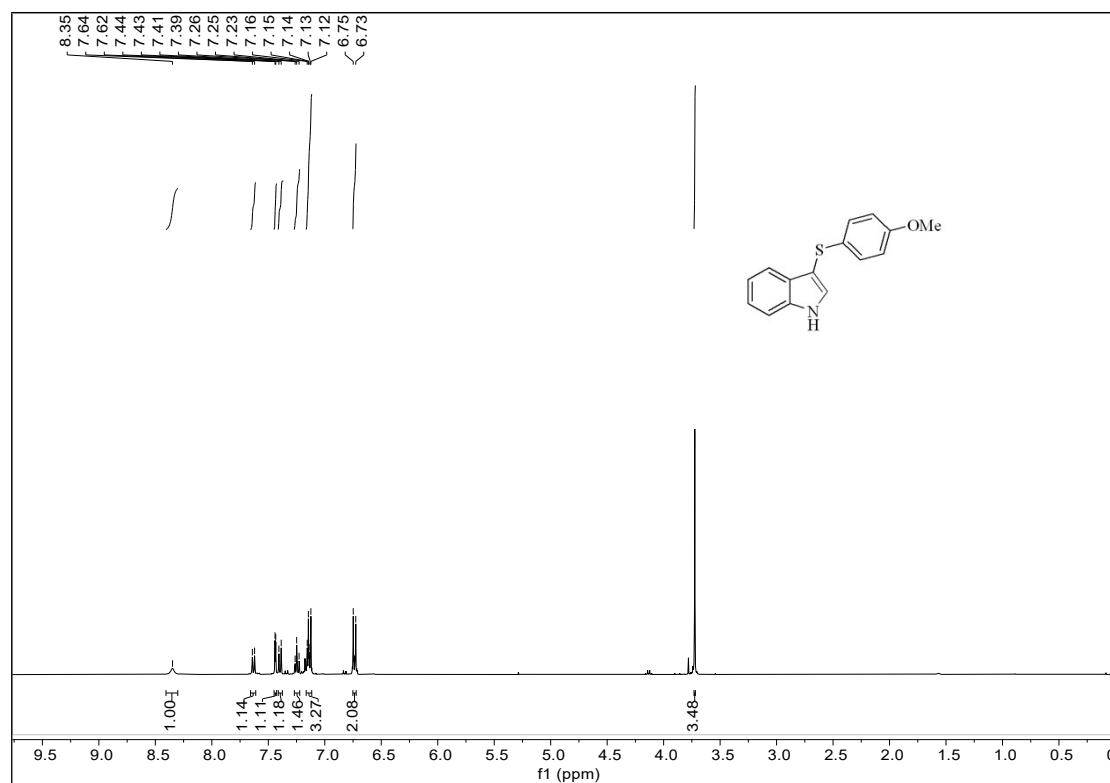
[3-((4-Nitrophenyl)thio)-1H-indole] [3f] $^1\text{H NMR}$ (400 MHz, CDCl_3)



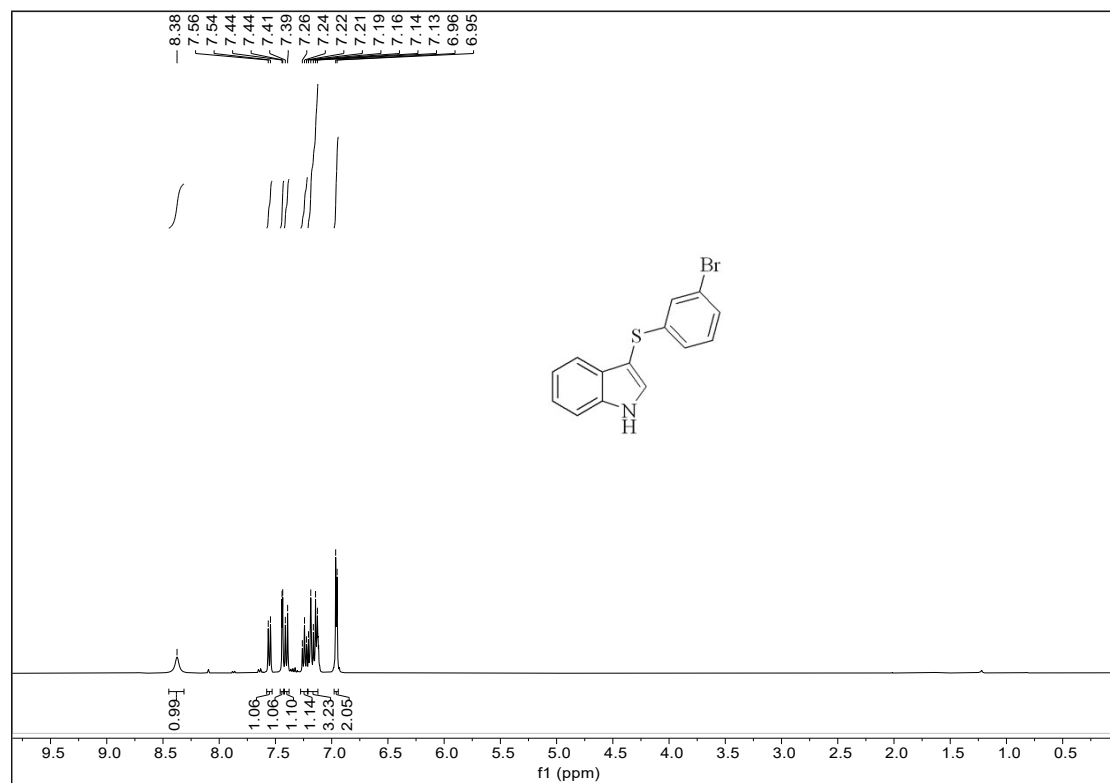
[3-(P-tolylthio)-1H-indole] [3g] $^1\text{H NMR}$ (400 MHz, CDCl_3)



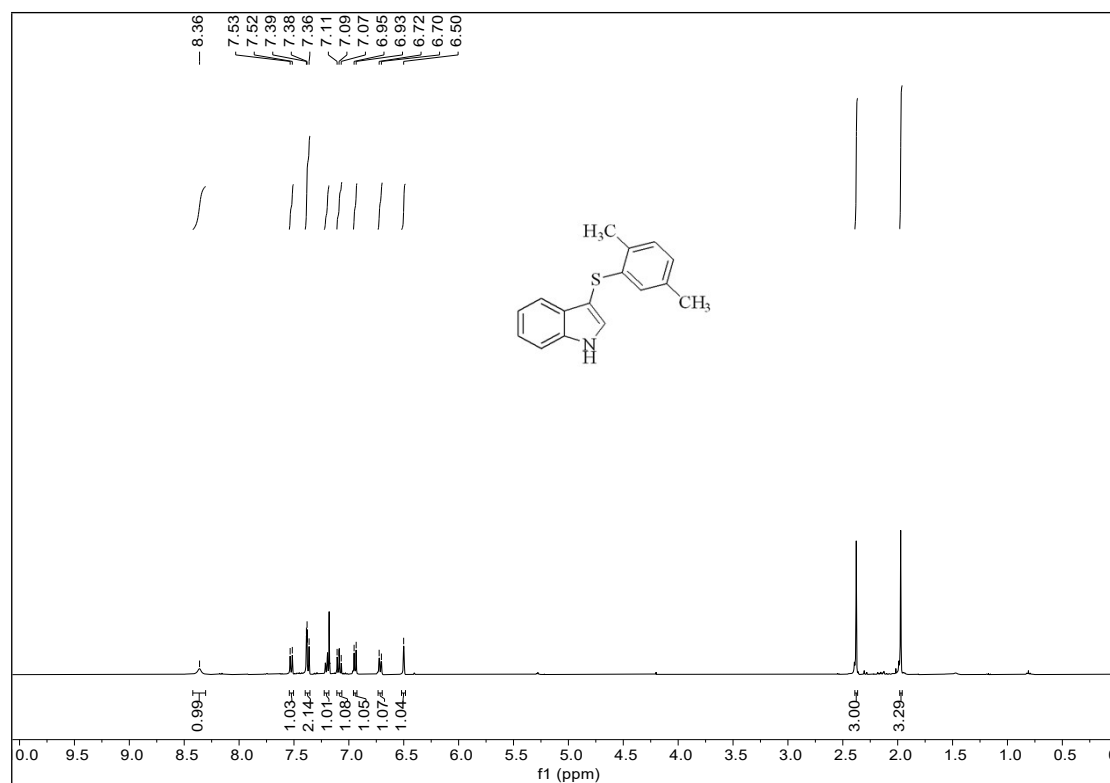
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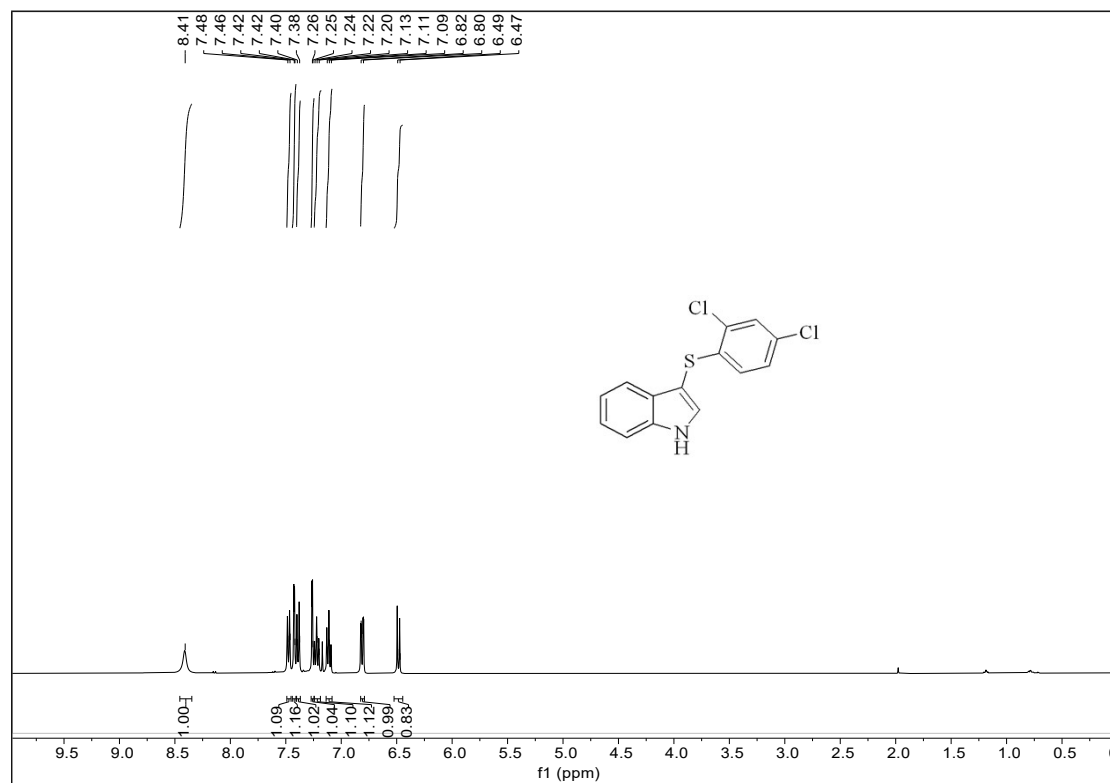
[3-((3-bromophenyl)thio)-1H-indole] [3k] ^1H NMR (400 MHz, CDCl_3)



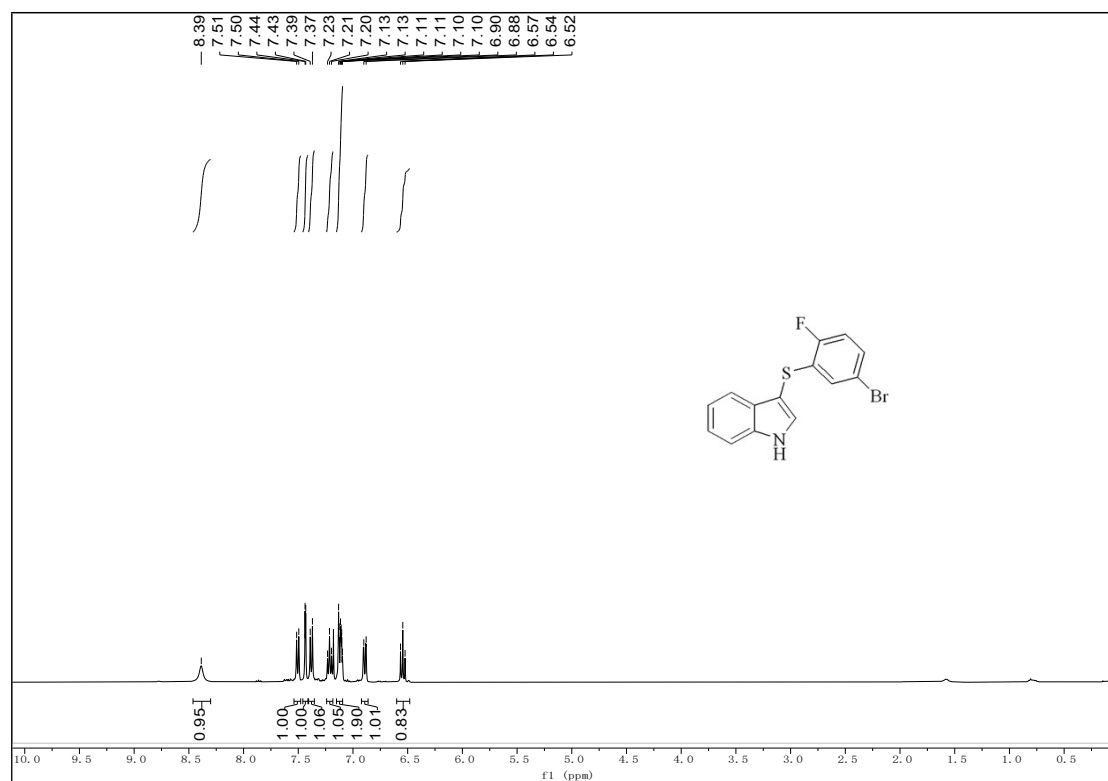
[3-((2,5-Dimethylphenyl)thio)-1H-indole] [3l] ¹H NMR (400 MHz, CDCl₃)



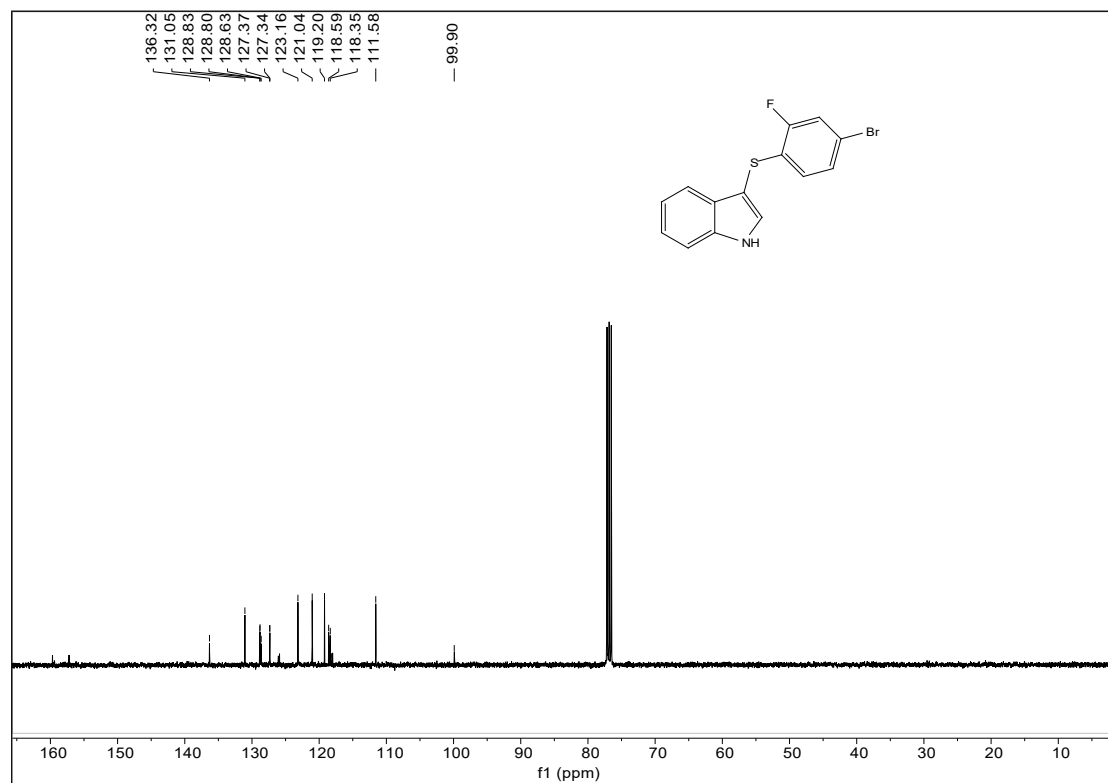
[3-((2,4-dichlorophenyl)thio)-1H-indole] [3m] ¹H NMR (400 MHz, CDCl₃)



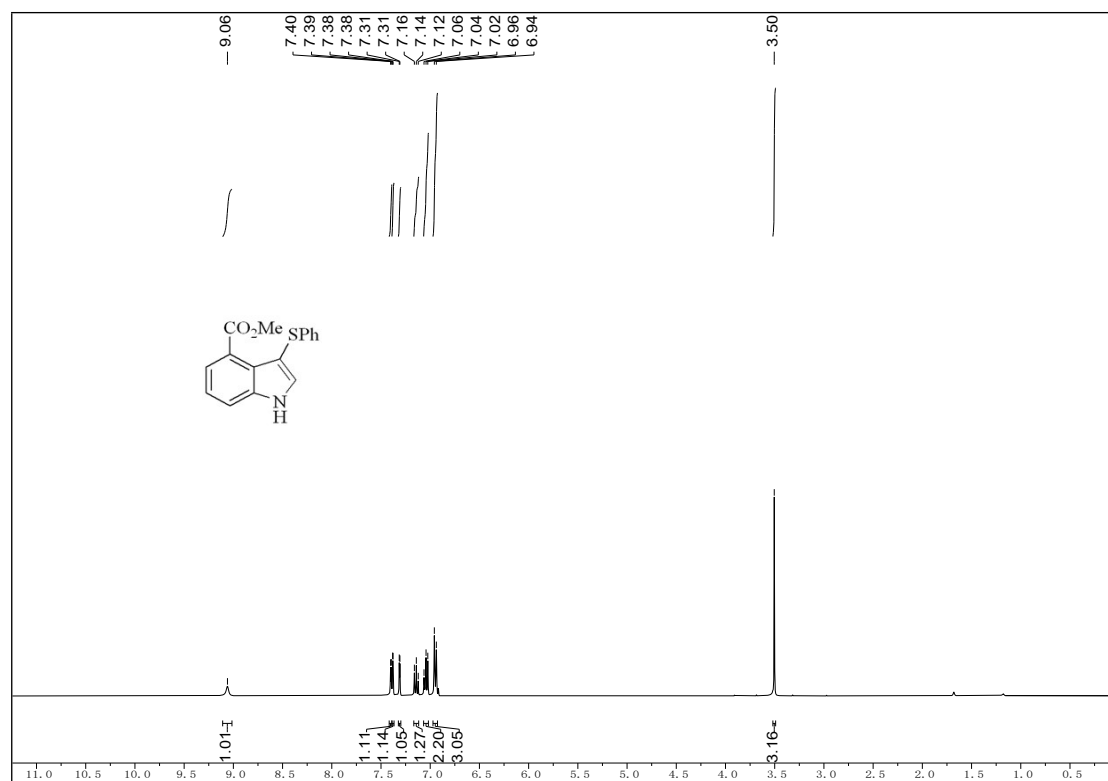
[3-((5-bromo-2-fluorophenyl)thio)-1H-indole] [3n] ¹H NMR (400 MHz, CDCl₃)



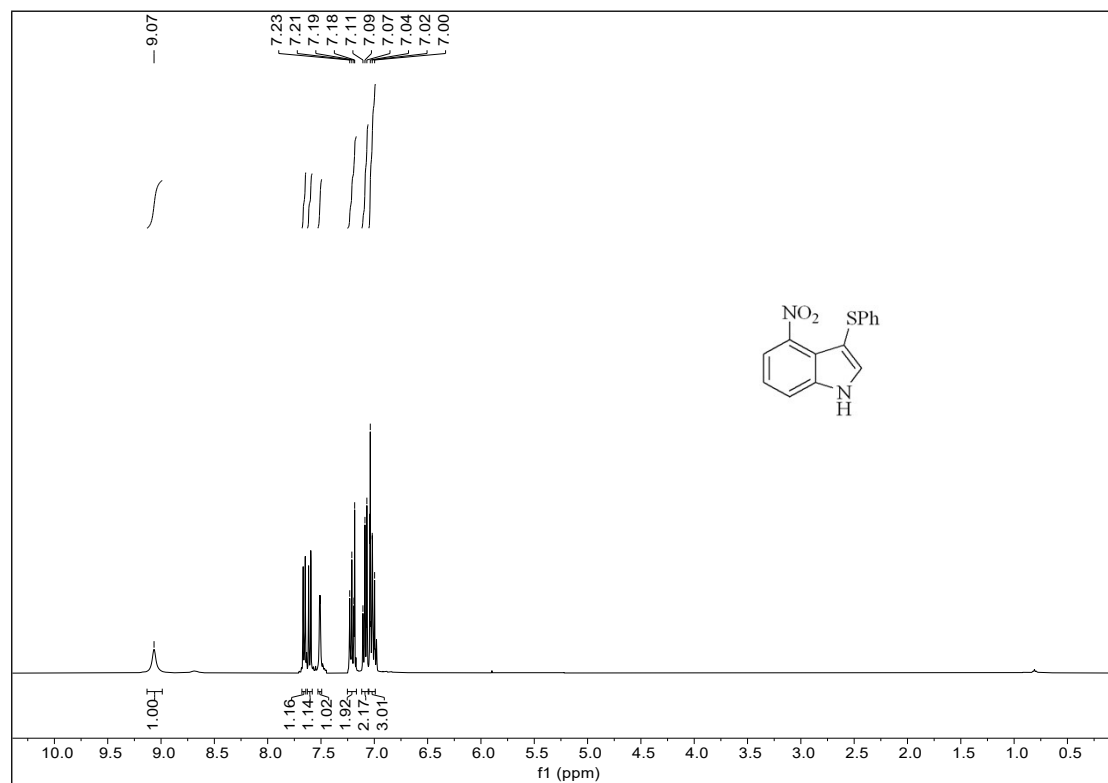
[3-((5-bromo-2-fluorophenyl)thio)-1H-indole] [3n] ¹³C NMR (101 MHz, CDCl₃)



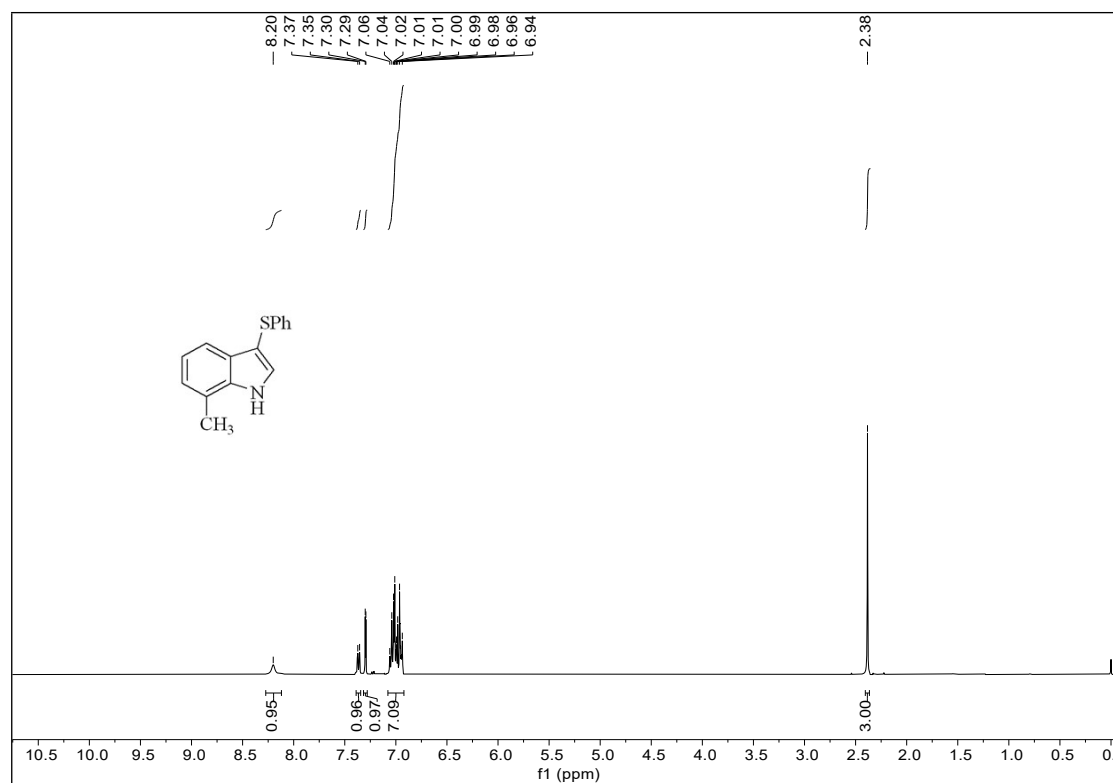
[Methyl 3-(phenylthio)-1H-indole-4-carboxylate] [4a] ^1H NMR (400 MHz, CDCl_3)



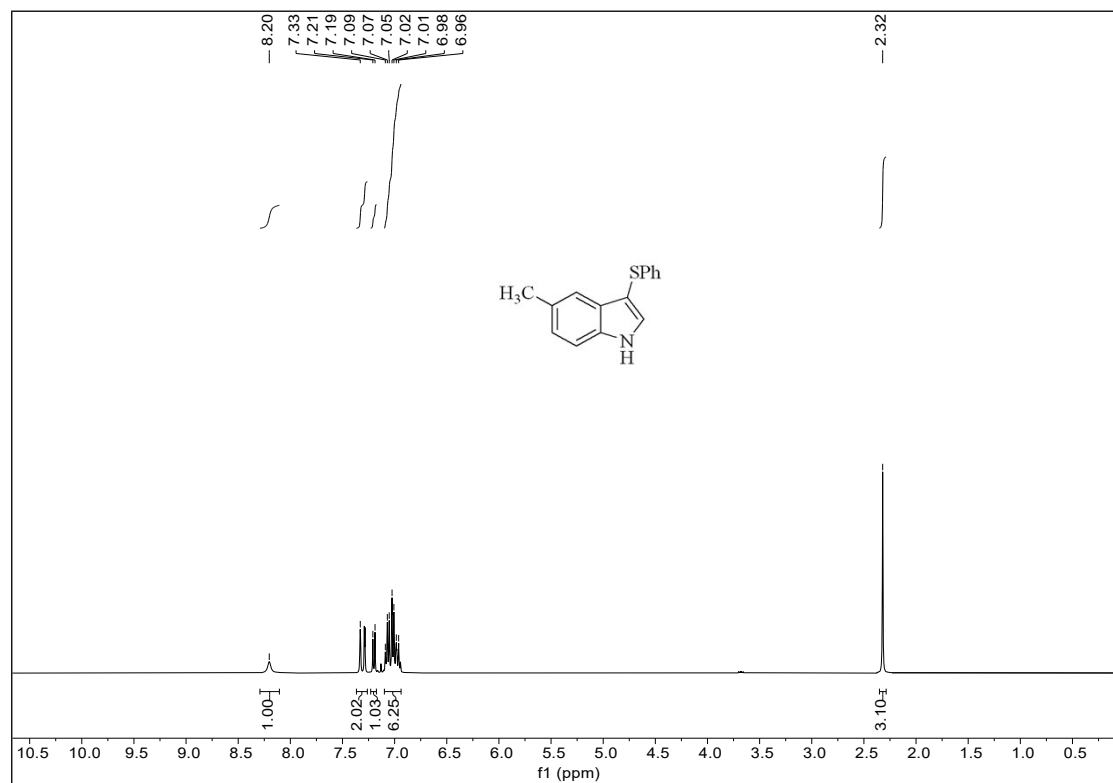
[4-Nitro-3-(phenylthio)-1H-indole] [4b] ^1H NMR (400 MHz, CDCl_3)



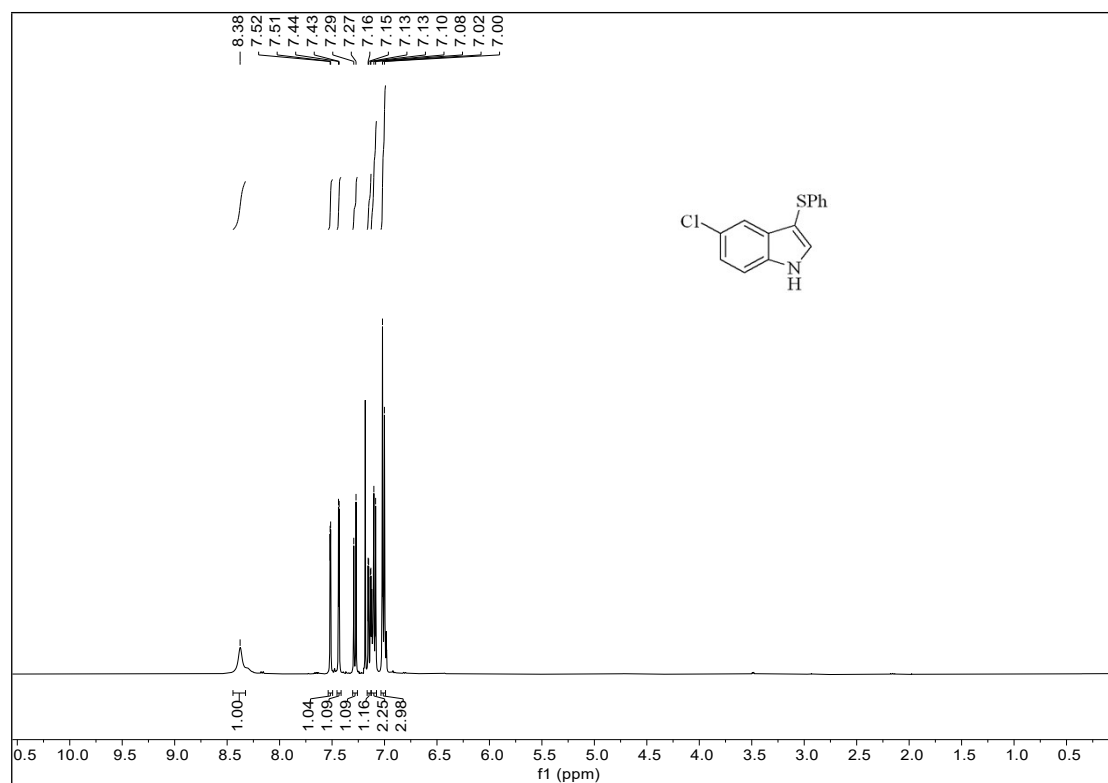
[7-Methyl-3-(phenylthio)-1H-indole] [4d] ^1H NMR (400 MHz, CDCl_3)



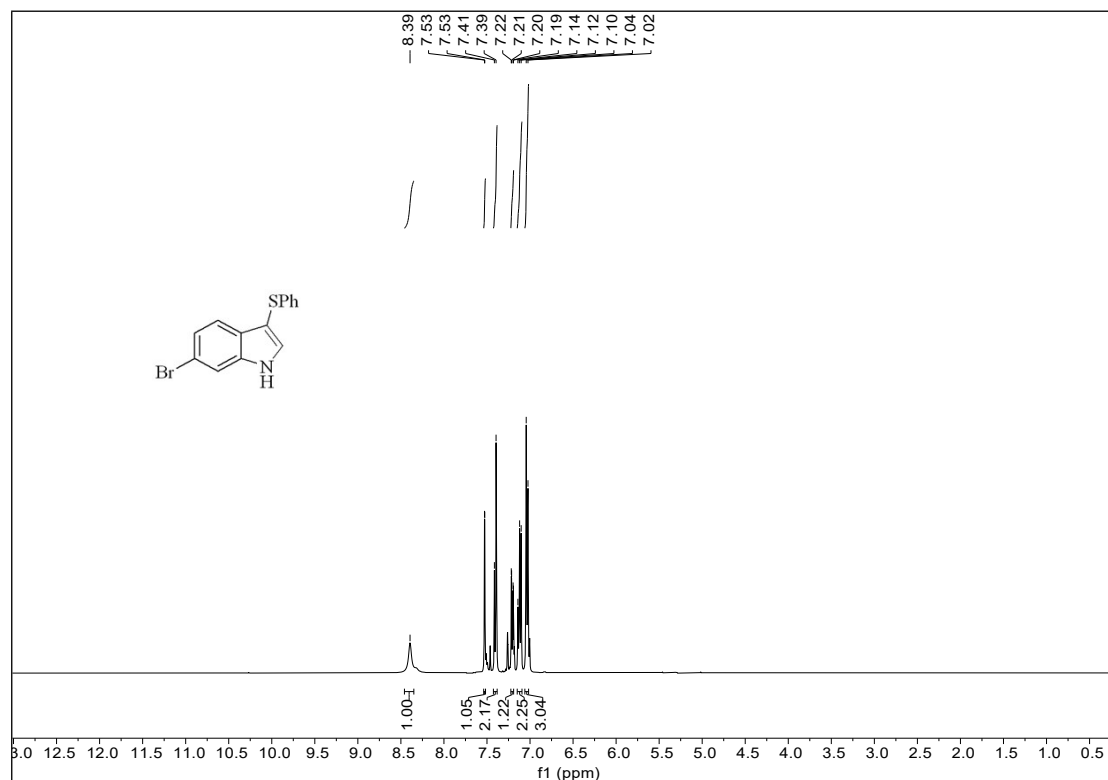
[5-methyl-3-(phenylthio)-1H-indole] [4f] ^1H NMR (400 MHz, CDCl_3)



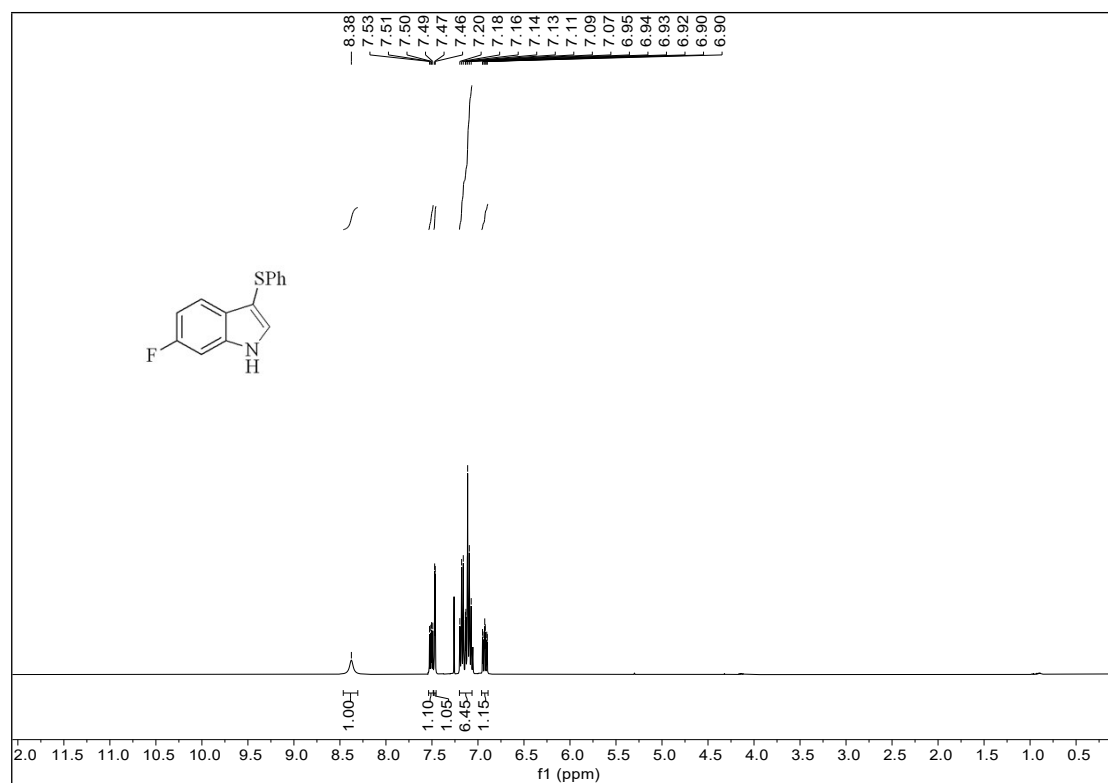
[5-Chloro-3-(phenylthio)-1H-indole] [4g] ¹H NMR (400 MHz, CDCl₃)



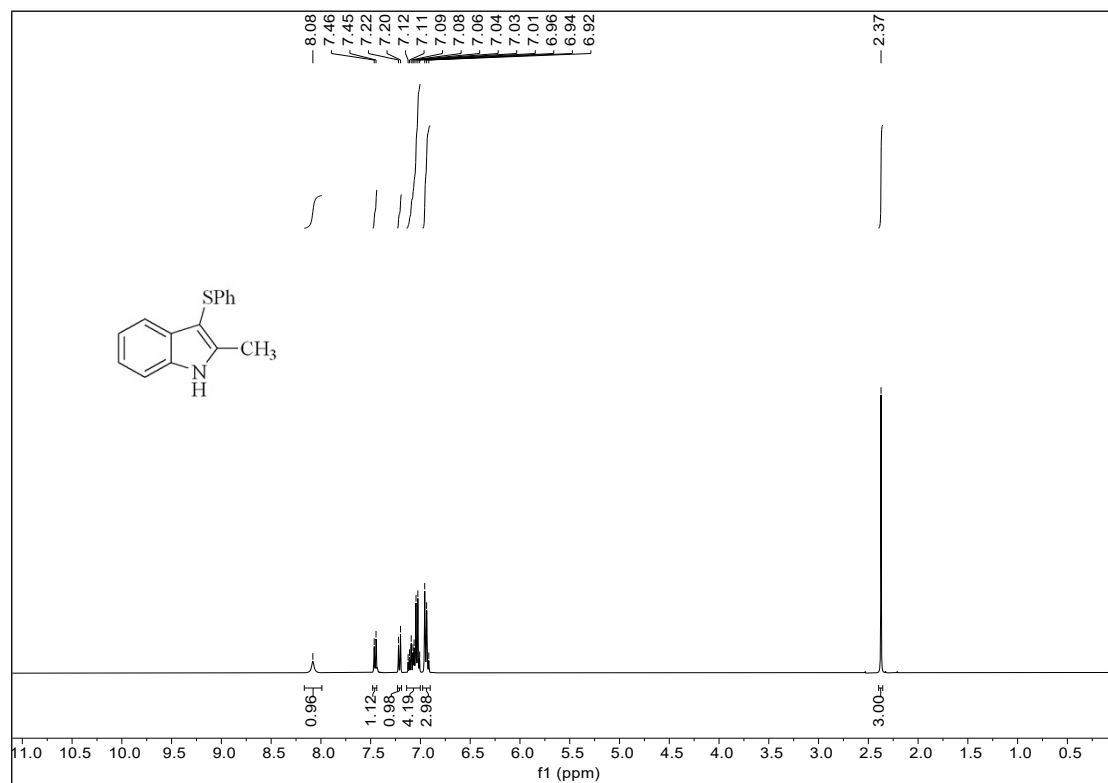
[6-Bromo-3-(phenylthio)-1H-indole] [4h] ¹H NMR (400 MHz, CDCl₃)



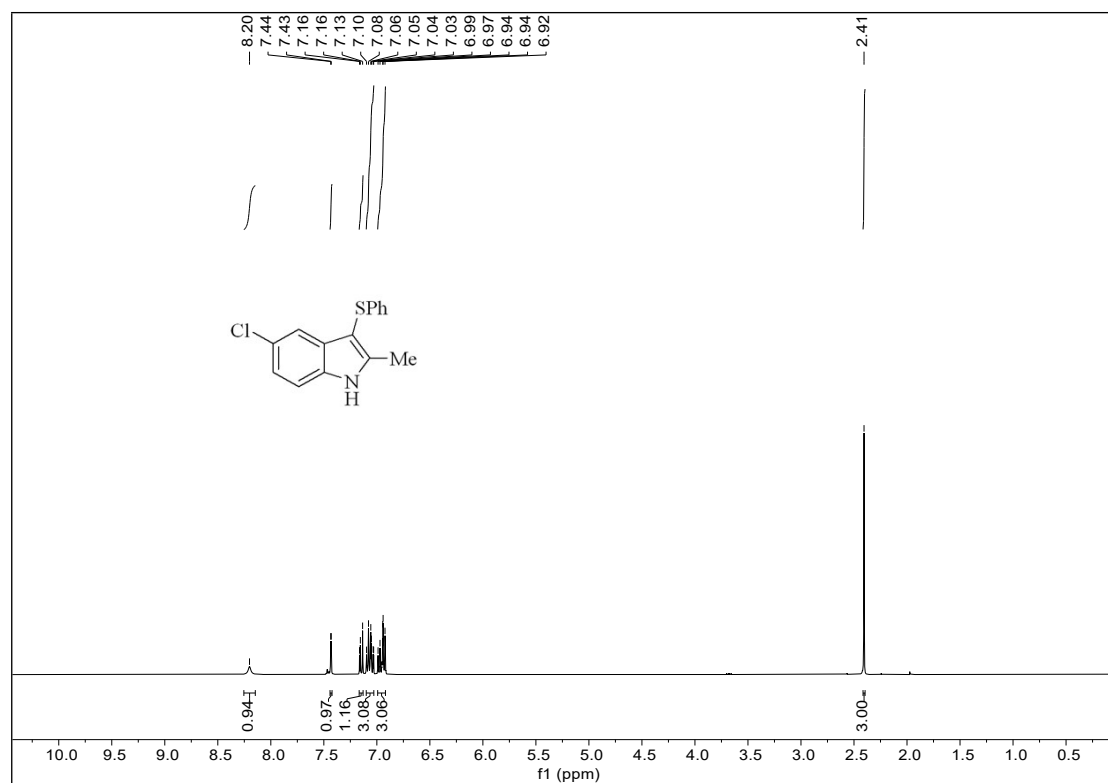
[6-Fluoro-3-(phenylthio)-1H-indole] [4i] ^1H NMR (400 MHz, CDCl_3)



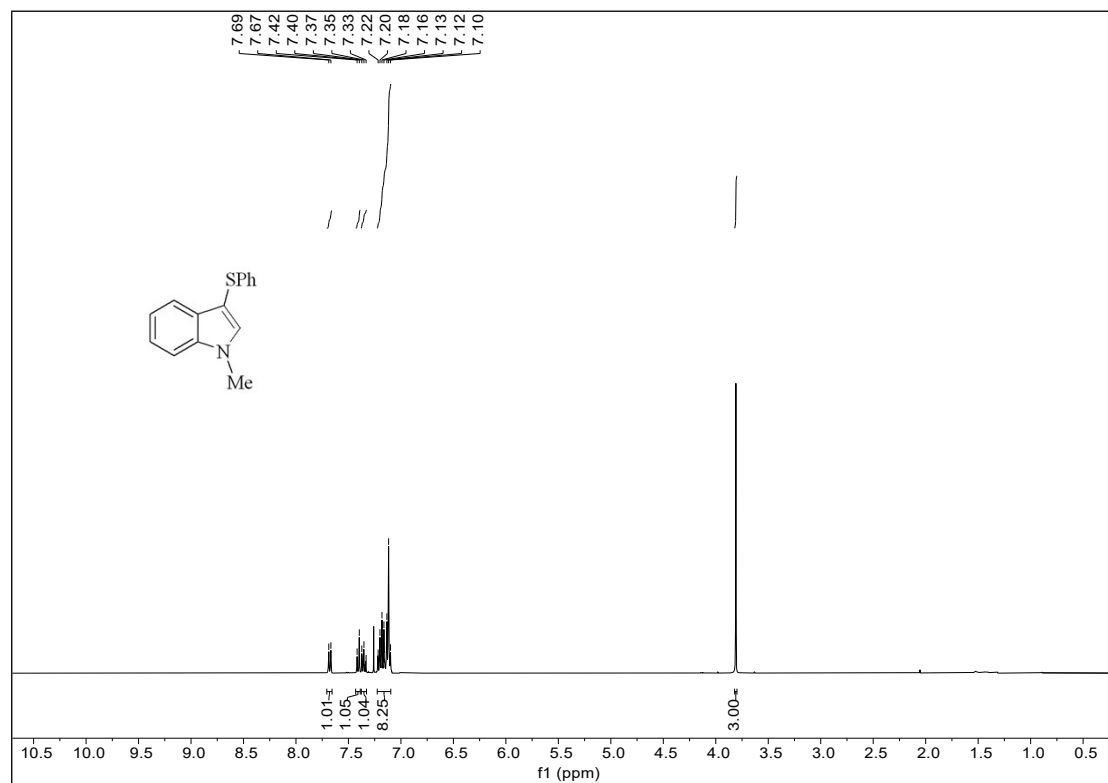
[2-Methyl-3-(phenylthio)-1H-indole] ^1H NMR (400 MHz, CDCl_3)



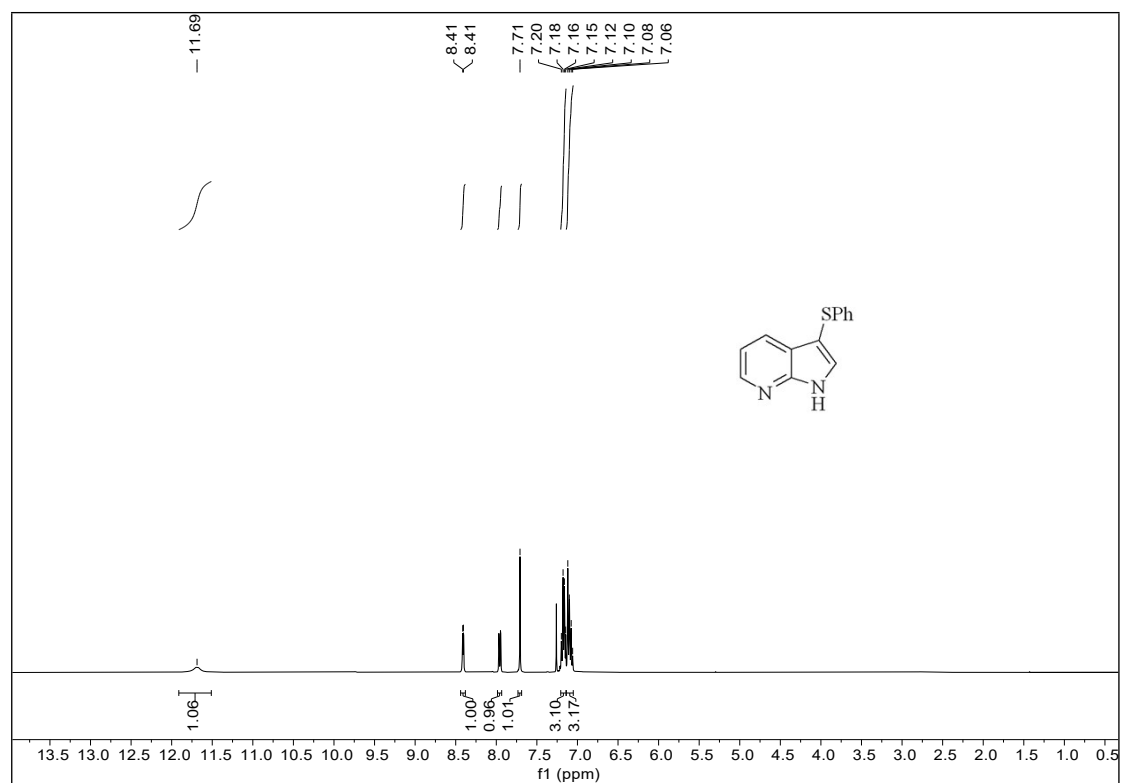
[5-Chloro-2-methyl-3-(phenylthio)-1H-indole] ¹H NMR (400 MHz, CDCl₃)



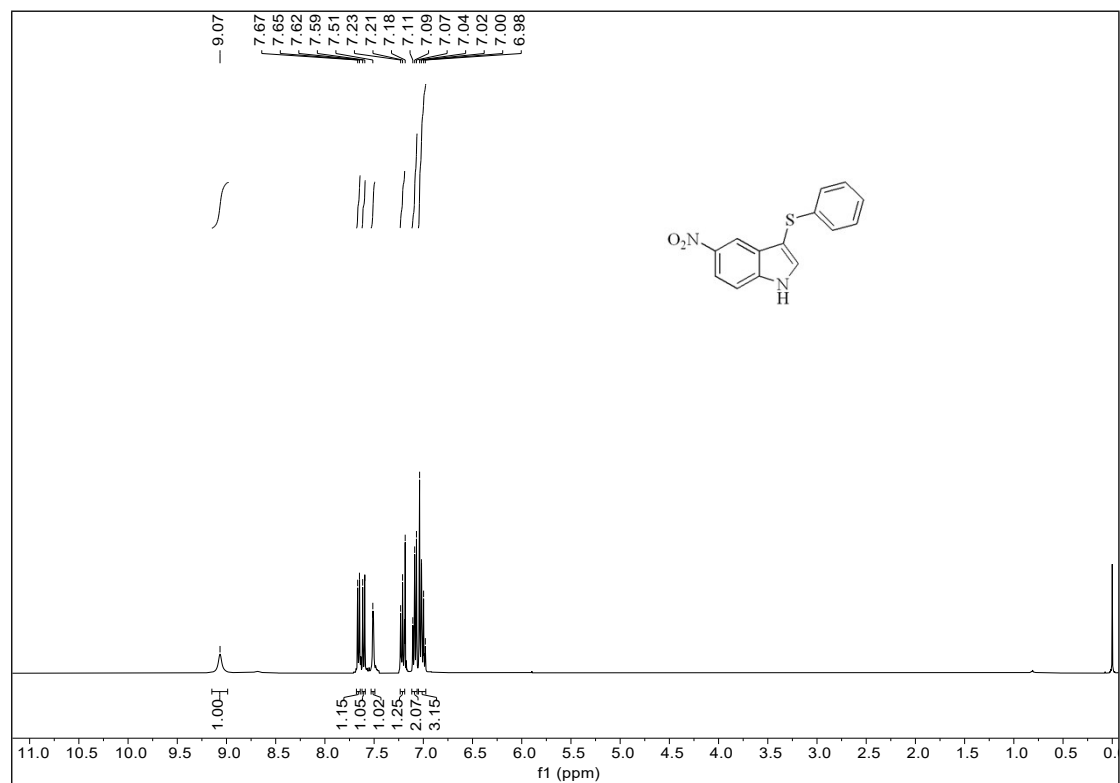
[1-Methyl-3-(phenylthio)-1H-indole] [4] ¹H NMR (400 MHz, CDCl₃)



[3-(Phenylthio)-1H-pyrrolo (2,3-b) pyridine] [4m] ¹H NMR (400 MHz, CDCl₃)



[5-nitro-3-(phenylthio)-1H-indole][4n] ¹H NMR (400 MHz, CDCl₃)



[5-nitro-3-(phenylthio)-1H-indole][4n] ¹³C NMR (101 MHz, CDCl₃)

