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Supporting Information for

Cu-Catalyzed First Direct Access towards 3-Sulfenylindoles from Aryl Halides

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3-Phenylsulfanyl-1*H***-indole (Table 2, Entry 1)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.08-7.12 (m, 1H, Ar), 7.13-7.17 (m, 2H, Ar), 7.18-7.23 (m, 3H, Ar), 7.30-7.34 (m, 1H, Ar),

7.48 (d, 1H, J = 7.6 Hz, Ar), 7.52 (d, 1H, J = 2.8 Hz, =CHN), 7.66 (d, 1H, J = 8.0 Hz, Ar), 8.42 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.8, 111.6, 119.7, 120.9, 123.1, 124.8, 125.9, 128.7, 129.1, 130.7, 136.5, 139.2. Anal. Calcd for (C₁₄H₁₁NS): C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.72; H, 4.88; N, 6.26; S, 14.14.

3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 2): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.28 (s, 3H, CH₃), 7.01 (d, 2H, *J*= 8.4 Hz, Ar), 7.07 (d, 2H, *J* = 8.4 Hz, Ar), 7.19 (t, 1H, *J* = 7.4 Hz, Ar), 7.28-7.32 (m, 1H, Ar), 7.46 (d, 1H, *J* = 8.0 Hz, Ar), 7.50 (d, 1H, *J* = 2.4 Hz, Ar), 7.65 (d, 1H, *J* = 8.0 Hz, Ar), 8.41 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.9, 103.5, 111.5, 119.7, 120.8, 123.0, 126.2, 129.1, 129.5, 130.4, 134.6, 135.4, 136.4. Anal. Calcd for (C₁₅H₁₃NS): C, 75.28; H, 5.48; N, 5.85; S, 13.40. Found: C, 75.18; H, 5.52; N, 5.92; S, 13.38.

3-((4-Methoxyphenyl)thio)-1*H***-indole (Table 2, Entry 3):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.76 (s, 3H, OCH₃), 6.77 (d, 2H, *J* = 8.8 Hz, Ar), 7.15-7.20 (m, 3H, Ar), 7.45 (d, 1H, *J* = 8.4 Hz, Ar), 7.50 (d, 1H, *J* = 2.8 Hz, Ar), 7.62-7.68 (m, 2H, Ar), 8.44 (s, 1H, NH). Anal. Calcd for (C₁₅H₁₃NOS): C, 70.56; H, 5.13; N, 5.49; S, 12.56. Found: C, 70.42; H, 5.19; N, 5.59; S, 12.64.

3-(*o*-**Tolylthio**)-1*H*-indole (Table 2, Entry 4): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.55 (s, 3H, CH₃), 6.77 (d, 1H, J = 7.6 Hz, Ar), 6.93-6.97 (m, 1H, Ar), 7.01-7.05 (m, 1H, Ar), 7.18-7.23 (m, 2H, Ar), 7.29-7.34 (m, 1H, Ar), 7.47-7.49 (m, 2H, Ar), 7.64 (d, 1H, J = 7.6 Hz, Ar), 8.44 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 19.9, 102.2, 111.7, 119.7, 120.9, 123.0, 124.5, 125.2, 126.3, 129.2, 129.9, 130.9, 134.3, 136.5, 138.3. Anal. Calcd for (C₁₅H₁₃NS): C, 75.28; H, 5.48; N, 5.85; S, 13.40. Found: C, 75.17; H, 5.57; N, 5.90; S, 13.36.

3-((4-Chlorophenyl)thio)-1*H***-indole (Table 2, Entry 5):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.06 (d, 2H, J = 8.4 Hz, Ar), 7.16 (d, 2H, J = 8.4 Hz, Ar), 7.22 (t, 1H, J = 7.6 Hz, Ar), 7.32 (t, 1H, J = 7.6 Hz, Ar), 7.48 (d, 1H, J = 8.0 Hz, Ar), 7.52 (d, 1H, J = 2.4 Hz, Ar), 7.61 (d, 1H, J = 8.0 Hz, Ar), 8.45 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.4, 111.7, 119.5, 121.1, 123.2, 126.5, 127.1, 128.8, 130.5, 130.7, 136.5, 137.8. Anal. Calcd for (C₁₄H₁₀ClNS): C, 64.74; H, 3.88; N, 5.39; S, 12.34. Found: C, 64.64; H, 3.95; N, 5.30; S, 12.45.

3-((2-Chlorophenyl)thio)-1*H***-indole (Table 2, Entry 6):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.69 (d, 1H, *J* = 7.6 Hz, Ar), 6.94-7.04 (m, 2H, Ar), 7.22 (t, 1H, *J* = 7.6 Hz, Ar), 7.31-7.37 (m, 2H, Ar), 7.51 (d, 1H, *J* = 8.0 Hz, Ar), 7.55 (d, 1H, *J* = 2.8 Hz, Ar), 7.63 (d, 1H, *J* = 8.0 Hz, Ar), 8.56 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 101.2, 111.7, 119.6, 121.1, 123.2, 125.4, 126.3, 126.9, 129.0, 129.2, 130.0, 131.3, 136.6, 138.5. Anal. Calcd for (C₁₄H₁₀CINS): C, 64.74; H, 3.88; N, 5.39; S, 12.34. Found: C, 64.60; H, 3.93; N, 5.28; S, 12.40.

3-(Naphthalen-2-ylthio)-1*H***-indole (Table 2, Entry 7): ¹H-NMR** (400 MHz, CDCl₃) δ (ppm): 7.18 (t,1H, *J* = 7.0 Hz, Ar), 7.31-7.33 (m, 2H, Ar), 7.36-7.43 (m, 3H, Ar), 7.52 (s, 1H, Ar), 7.59-7.61 (m, 2H, Ar), 7.64-7.69 (m, 2H, Ar), 7.74-7.76 (m, 1H, Ar), 8.50 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.8, 111.6, 119.7, 121.0, 123.1, 123.5, 124.7, 125.0, 126.3, 126.9, 127.7, 128.2, 129.1, 130.7, 131.3, 133.7, 136.5, 136.7. Anal. Calcd for (C₁₈H₁₃NS): C, 78.51; H, 4.76; N, 5.09; S, 11.64. Found: C, 78.61; H, 4.69; N, 5.15; S, 11.55.

2-Methyl-3-phenylsulfanyl-1*H***-indole (Table 2, Entry 8)**: ¹H-NMR (400MHz, CDCl₃) δ (ppm): 2.44 (s, 3H, CH₃), 6.95-6.97 (m, 3H, Ar), 7.03-7.18 (m, 4H, Ar), 7.27 (d, 1H, *J* = 8.0 Hz, Ar), 7.47 (d, 1H, *J* = 8.0 Hz, Ar), 8.16 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.2, 99.3, 110.6, 119.0, 120.7, 122.2, 124.4, 125.4, 128.6, 130.2, 135.4, 139.3, 141.1. Anal. Calcd for (C₁₅H₁₃NS): C, 75.28; H, 5.48; N, 5.85; S, 13.40. Found: C, 75.00; H, 5.55; N, 5.97; S, 13.48.

2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 9): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.36 (s, 3H, CH₃), 2.53 (s, 3H, CH₃), 7.09 (d, 4H, *J* = 3.6 Hz, Ar), 7.25-7.33 (m, 2H, Ar), 7.37(d, 1H, *J* = 7.6 Hz, Ar), 7.70 (t, 1H, *J* = 5.8 Hz, Ar), 8.10 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.1, 20.9, 99.7, 110.9, 119.0, 120.7, 122.2, 125.9, 129.6, 130.4, 134.5, 135.5, 135.8, 141.2. Anal. Calcd for (C₁₆H₁₅NS): C, 75.85; H, 5.97; N, 5.53; S, 12.65. Found: C, 75.70; H, 5.88; N, 5.67; S, 12.75.

3-(4-Methoxyphenylthio)-2-methyl-1*H***-indole (Table 2, Entry 10)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.53 (s, 3H, CH₃), 3.76 (s, 3H, OCH₃), 6.77 (d, 2H, *J* = 8.8 Hz, Ar), 7.09 (d, 2H, *J* = 8.8 Hz, Ar), 7.15-7.24 (m, 2H, Ar), 7.33 (d, 1H, *J* = 8.0 Hz, Ar), 7.62 (d, 1H, *J* = 7.6 Hz, Ar), 8.21 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.1, 55.3, 100.7,

110.7, 114.5, 118.9, 120.6, 122.1, 127.9, 129.9, 130.3, 135.4, 140.8, 157.5. Anal. Calcd for (C₁₆H₁₅NOS): C, 71.34; H, 5.61; N, 5.20; S, 11.90. Found: C, 71.22; H, 5.69; N, 5.13; S, 11.82.

2-Methyl-3-(*o*-tolylthio)-1*H*-indole (Table 2, Entry 11): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.53 (s, 6H, CH₃), 6.61 (d, 1H, *J*= 8.0 Hz, Ar), 6.91 (t, 1H, *J*= 7.2 Hz, Ar), 6.97 (t, 1H, *J*= 3.8 Hz, Ar), 7.13-7.17 (m, 2H, Ar), 7.21-7.25 (m, 1H, Ar), 7.39 (d, 1H, *J*= 8.0 Hz, Ar), 7.54 (d, 1H, *J*= 8.0 Hz, Ar), 8.32 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.2, 19.9, 98.7, 110.6, 119.0, 120.6, 122.1, 124.1, 124.5, 126.2, 129.8, 130.4, 134.2, 135.5, 138.8, 141.2. Anal. Calcd for (C₁₆H₁₅NS): C, 75.85; H, 5.97; N, 5.53; S, 12.65. Found: C, 75.69; H, 5.89; N, 5.67; S, 12.75.

3-((4-Chlorophenyl)thio)-2-methyl-1*H***-indole (Table 2, Entry 12)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.53 (s, 3H, CH₃), 7.04 (d, 2H, *J* = 6.8 Hz, Ar), 7.19 (d, 2H, *J* = 8.4 Hz, Ar), 7.26 (t, 1H, *J* = 3.8 Hz, Ar), 7.30 (t, 1H, *J* = 6.6 Hz, Ar), 7.38 (d, 1H, *J* = 8.0 Hz, Ar), 7.63(d, 1H, *J* = 7.6 Hz, Ar), 8.23 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.1, 98.8, 110.9, 118.8, 120.9, 122.4, 126.8, 128.8, 130.0, 130.3, 135.5, 138.0, 141.4. Anal. Calcd for (C₁₅H₁₂ClNS): C, 65.81; H, 4.42; N, 5.12; S, 11.71. Found: C, 65.94; H, 4.30; N, 5.04; S, 11.61.

3-((2-Chlorophenyl)thio)-2-methyl-1*H***-indole (Table 2, Entry 13)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.53 (s, 3H, CH₃), 6.56-6.58 (m, 1H, Ar), 6.94-7.00 (m, 2H, Ar), 7.15-7.18 (m, 1H, Ar), 7.22-7.28 (m, 1H, Ar), 7.34-7.40 (m, 2H, Ar), 7.54 (d, 1H, *J* = 8.0 Hz, Ar), 8.34 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.1, 97.7, 110.7, 118.9, 120.9, 122.4, 125.2, 125.8, 126.9, 129.3, 130.0, 130.1, 135.5, 138.3, 141.7. Anal. Calcd for (C₁₅H₁₂CINS): C, 65.81; H, 4.42; N, 5.12; S, 11.71. Found: C, 65.91; H, 4.32; N, 5.00; S, 11.64.

2-(2-Methyl-1*H***-indol-3-ylsulfanyl)-phenylamine (Table 2, Entry 14**): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.45 (s, 3H, CH₃), 4.10 (s, 2H, NH₂), 6.47-6.51 (m, 1H, Ar), 6.59 (d, 1H, *J* = 6.8 Hz, Ar), 6.85-6.90 (m, 2H, Ar), 7.02-7.11 (m, 2H, Ar), 7.22 (d, 2H, *J* = 7.6 Hz, Ar), 8.12 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.3, 110.6, 115.3, 118.8, 118.9, 120.6, 122.0, 126.9, 129.8, 130.1, 131.4, 135.2, 137.7, 140.3, 144.6. Anal. Calcd for (C₁₅H₁₄N₂S): C, 70.83; H, 5.55; N, 11.01; S, 12.60. Found: C, 70.69; H, 5.67; N, 10.89; S, 12.75.

5-Bromo-3-(phenylthio)-1*H***-indole (Table 2, Entry 15)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.10-7.13 (m, 3H, Ar), 7.22 (t, 2H, J = 7.6 Hz, Ar), 7.33 (d, 1H, J = 8.8 Hz, Ar), 7.37-7.40 (m, 1H, Ar), 7.50 (d, 1H, J = 2.4 Hz, Ar), 7.79 (d, 1H, J = 1.6 Hz, Ar), 8.47 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.6, 113.1, 114.5, 122.2, 125.0, 125.8, 126.1, 128.8, 131.0, 131.9, 135.1, 138.7. Anal. Calcd for (C₁₄H₁₀BrNS): C, 55.28; H, 3.31; N, 4.60; S, 10.54. Found: C, 55.40; H, 3.21; N, 4.52; S, 10.66.

5-Bromo-3*-p***-tolylsulfanyl-1***H***-indole (Table 2, Entry 16)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.29 (s, 3H, CH₃), 7.01-7.08 (m, 4H, Ar), 7.29 (d, 1H, *J* = 8.8 Hz, Ar), 7.34-7.37 (m, 1H, Ar), 7.46 (d, 1H, *J* = 2.4 Hz, =CHN), 7.79 (s, 1H, Ar), 8.55 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.9, 103.1, 113.1, 113.6, 114.3, 122.2, 126.2, 129.6, 130.0, 130.9, 131.7, 135.0, 135.1. Anal. Calcd for (C₁₅H₁₂BrNS): C, 56.61; H, 3.80; N, 4.40; S, 10.07. Found: C, 56.48; H, 3.92; N, 4.30; S, 10.18.

5-Bromo-3-((4-methoxyphenyl)thio)-1*H***-indole (Table 2, Entry 17)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.82 (s, 3H, OCH₃), 6.87 (d, 2H, *J*= 8.8 Hz, Ar), 7.38 (d, 2H, *J*= 8.8 Hz, Ar), 7.45 (d, 1H, *J*= 8.0 Hz, Ar), 7.49 (d, 1H, *J*= 2.8 Hz, Ar), 7.61 (d, 1H, *J*= 7.6 Hz, Ar), 7.66 (d, 1H, *J*= 7.6 Hz, Ar), 8.41 (s, 1H, NH). Anal. Calcd for (C₁₅H₁₂BrNOS): C, 53.90; H, 3.62; N, 4.19; S, 9.59. Found: C, 53.77; H, 3.77; N, 4.10; S, 9.62.

5-Bromo-3-((4-chlorophenyl)thio)-1*H***-indole (Table 2, Entry 18)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.00-7.04 (m, 2H, Ar), 7.15-7.19 (m, 2H, Ar), 7.34-7.41 (m, 2H, Ar), 7.53 (d, 1H, *J* = 2.8 Hz, Ar), 7.74 (d, 1H, *J* = 1.6 Hz, Ar), 8.54 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.2, 113.2, 114.6, 122.0, 126.3, 127.1, 128.9, 130.7, 130.8, 132.0, 135.1, 137.3. Anal. Calcd for (C₁₄H₉BrClNS): C, 49.65; H, 2.68; N, 4.14; S, 9.47. Found: C, 49.56; H, 2.75; N, 4.00; S, 9.35.

5-Bromo-3-(naphthalen-2-ylthio)-1*H***-indole (Table 2, Entry 19): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.27-7.30 (m, 1H, Ar), 7.37-7.43 (m, 4H, ArH), 7.49 (d, 1H, J = 1.2 Hz, Ar), 7.57 (d, 1H, J = 2.4 Hz, Ar), 7.61-7.63 (m, 1H, Ar), 7.70 (d, 1H, J = 8.8 Hz, Ar), 7.76-7.78 (m, 1H, Ar), 7.80 (d, 1H, J = 1.2 Hz, Ar), 8.50 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 113.1, 114.5, 122.2, 123.6, 124.7, 125.2, 126.2, 126.4, 126.9, 127.7, 128.4, 128.9, 131.0, 131.4, 131.9, 133.7, 135.1, 136.1. Anal. Calcd for (C₁₈H₁₂BrNS): C, 61.03; H, 3.41; N, 3.95; S, 9.05. Found: C, 61.12; H, 3.31; N, 4.08; S, 8.88. HRMS (EI+) calcd for C₁₈H₁₂BrNS: 352.9874; found: 352.9869.**

3-Phenylsulfanyl-1*H***-indole (Table 2, Entry 20)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.08-7.12 (m, 1H, Ar), 7.14-7.16 (m, 2H, Ar), 7.18-7.23 (m, 3H, Ar), 7.29-7.33 (m, 1H, Ar), 7.48 (d, 1H, *J* = 8.0 Hz, Ar), 7.52 (d, 1H, *J* = 2.4 Hz, =CHN), 7.66 (d, 1H, *J* = 7.6 Hz, Ar), 8.42 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.6, 111.3, 119.4, 120.7, 122.8, 124.5, 125.6, 128.4, 128.8, 130.4, 136.2, 139.0. Anal. Calcd for (C₁₄H₁₁NS): C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.74; H, 4.80; N, 6.37; S, 14.09.

3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 21): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.26 (s, 3H, CH₃), 6.98 (d, 2H, *J*= 8.4 Hz, Ar), 7.04 (d, 2H, *J* = 8.4 Hz, Ar), 7.17 (t, 1H, *J* = 7.4 Hz, Ar), 7.25-7.28 (m, 1H, Ar), 7.44 (d, 1H, *J* = 8.0 Hz, Ar), 7.47 (d, 1H, *J* = 2.4 Hz, Ar), 7.63 (d, 1H, *J* = 8.0 Hz, Ar), 8.38 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.8, 103.4, 111.4, 119.6, 120.7, 122.9, 126.1, 129.0, 129.4, 130.3, 134.5, 135.4, 136.4. Anal. Calcd for (C₁₅H₁₃NS): C, 75.28; H, 5.48; N, 5.85; S, 13.40. Found: C, 75.13; H, 5.55; N, 5.74; S, 13.58.

3-((4-Chlorophenyl)thio)-1*H***-indole (Table 2, Entry 22):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.99 (d, 2H, J = 8.4 Hz, Ar), 7.09 (d, 2H, J = 8.4 Hz, Ar), 7.15 (t, 1H, J = 7.6 Hz, Ar), 7.22-7.27 (m, 1H, Ar), 7.42 (d, 1H, J = 8.0 Hz, Ar), 7.45 (d, 1H, J = 2.4 Hz, Ar), 7.55 (d, 1H, J = 8.0 Hz, Ar), 8.39 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.3, 111.6, 119.5, 121.0, 123.2, 125.7, 127.0, 128.7, 130.5, 130.7, 136.4, 137.8. Anal. Calcd for (C₁₄H₁₀ClNS): C, 64.74; H, 3.88; N, 5.39; S, 12.34. Found: C, 64.60; H, 4.00; N, 5.49; S, 12.22.

2-Methyl-3-phenylsulfanyl-1*H***-indole (Table 2, Entry 23)**: ¹H-NMR (400MHz, CDCl₃) δ (ppm): 2.34 (s, 3H, CH₃), 6.85-6.87 (m, 3H, Ar), 6.93-7.04 (m, 4H, Ar), 7.17 (d, 1H, *J* = 8.0 Hz, Ar), 7.36 (d, 1H, *J* = 8.0 Hz, Ar), 8.05 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.0, 99.1, 110.4, 118.8, 120.5, 122.0, 124.3, 125.2, 128.5, 130.1, 135.2, 139.1, 140.9. Anal. Calcd for (C₁₅H₁₃NS): C, 75.28; H, 5.48; N, 5.85; S, 13.40. Found: C, 75.40; H, 5.56; N, 5.70; S, 13.34.

2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 24): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.29 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 7.02-7.04 (m, 4H, Ar), 7.17-7.26 (m, 2H, Ar), 7.30(d, 1H, *J* = 7.6 Hz, Ar), 7.62 (t, 1H, *J* = 5.8 Hz, Ar), 8.03 (s, 1H, NH). ¹³C-NMR (100

MHz, CDCl₃) δ (ppm): 12.1, 20.9, 99.6, 110.8, 118.9, 120.7, 122.1, 125.8, 129.6, 130.3, 134.4, 135.4, 135.7, 141.1. Anal. Calcd for (C₁₆H₁₅NS): C, 75.85; H, 5.97; N, 5.53; S, 12.65. Found: C, 75.69; H, 6.09; N, 5.38; S, 12.84.

3-((4-Chlorophenyl)thio)-2-methyl-1*H***-indole (Table 2, Entry 25)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.49 (s, 3H, CH₃), 7.01 (d, 2H, *J* = 6.8 Hz, Ar), 7.15 (d, 2H, *J* = 8.4 Hz, Ar), 7.20 (t, 1H, *J* = 3.8 Hz, Ar), 7.24-7.28 (m, 1H, Ar), 7.34 (d, 1H, *J* = 8.0 Hz, Ar), 7.59 (d, 1H, *J* = 7.6 Hz, Ar), 8.19 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 12.0, 98.7, 110.9, 118.7, 120.8, 122.3, 126.7, 128.7, 129.9, 130.2, 135.4, 137.9, 141.3. Anal. Calcd for (C₁₅H₁₂ClNS): C, 65.81; H, 4.42; N, 5.12; S, 11.71. Found: C, 65.93; H, 4.55; N, 5.00; S, 11.60.

5-Bromo-3-(phenylthio)-1*H***-indole (Table 2, Entry 26)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.02-7.05 (m, 3H, Ar), 7.14 (t, 2H, J = 7.6 Hz, Ar), 7.25 (d, 1H, J = 8.8 Hz, Ar), 7.29-7.32 (m, 1H, Ar), 7.42 (d, 1H, J = 2.4 Hz, Ar), 7.71 (d, 1H, J = 1.6 Hz, Ar), 8.39 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.6, 113.0, 114.4, 122.1, 125.0, 125.8, 126.0, 128.8, 130.9, 131.8, 135.0, 138.6. Anal. Calcd for (C₁₄H₁₀BrNS): C, 55.28; H, 3.31; N, 4.60; S, 10.54. Found: C, 55.12; H, 3.43; N, 4.70; S, 10.42.

5-Bromo-3*-p***-tolylsulfanyl-1***H***-indole (Table 2, Entry 27)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.19 (s, 3H, CH₃), 6.91-6.98 (m, 4H, Ar), 7.19 (d, 1H, *J* = 8.8 Hz, Ar), 7.24-7.27 (m, 1H, Ar), 7.36 (d, 1H, *J* = 2.4 Hz, =CHN), 7.69 (s, 1H, Ar), 8.45 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.9, 103.1, 113.1, 113.6, 114.3, 122.1, 125.9, 126.2, 129.6, 130.9, 131.7, 134.9, 135.1. Anal. Calcd for (C₁₅H₁₂BrNS): C, 56.61; H, 3.80; N, 4.40; S, 10.07. Found: C, 56.52; H, 3.92; N, 4.29; S, 9.95.

5-Bromo-3-((4-chlorophenyl)thio)-1*H***-indole (Table 2, Entry 28)**: ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 6.94 (d, 2H, J = 8.8 Hz, Ar), 7.09 (d, 2H, J = 8.8 Hz, Ar), 7.28 (s, 1H, Ar), 7.29-7.32 (d, 1H, Ar), 7.44 (d, 1H, J = 2.4 Hz, Ar), 7.65(d, 1H, J = 1.6 Hz, Ar), 8.45 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.1, 113.1, 114.5, 121.9, 126.2, 127.0, 128.8, 130.6, 130.7, 131.9, 135.0, 137.2. Anal. Calcd for (C₁₄H₉BrClNS): C, 49.65; H, 2.68; N, 4.14; S, 9.47. Found: C, 49.72; H, 2.57; N, 4.20; S, 9.38.

3-(Phenylthio)-1*H***-indole-5-carbonitrile (Table 2, Entry 29):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.11-7.15 (m, 3H, Ar), 7.22 (t, 2H, *J* = 7.4 Hz, Ar), 7.51-7.56 (m, 2H, Ar),

7.65 (d, 1H, J = 2.4 Hz, Ar), 7.98 (s, 1H, Ar), 8.83 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 103.9, 104.5, 112.3, 119.8, 125.0, 125.1, 125.7, 126.0, 128.6, 128.7, 132.2, 137.5, 137.9. Anal. Calcd for (C₁₅H₁₀N₂S): C, 71.97; H, 4.03; N, 11.19; S, 12.81. Found: C, 71.89; H, 4.11; N, 11.27; S, 12.73.

3-(*p*-Tolylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 30): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.30 (s, 3H, CH₃), 7.03-7.07 (m, 4H, Ar), 7.53 (d, 2H, *J* = 8.0 Hz, Ar), 7.63(d, 1H, *J* = 2.4 Hz, Ar), 7.97 (s, 1H, Ar), 8.73 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.9, 104.2, 105.7, 112.5, 120.2, 125.4, 126.0, 126.9, 128.9, 129.7, 132.2, 134.0, 135.5, 138.2. Anal. Calcd for (C₁₆H₁₂N₂S): C, 72.70; H, 4.58; N, 10.60; S, 12.13. Found: C, 72.60; H, 4.44; N, 10.73; S, 12.23.

3-((4-Methoxyphenyl)thio)-1*H***-indole-5-carbonitrile (Table 2, Entry 31):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 3.79 (s, 3H, OCH₃), 6.79-6.81 (m, 2H, Ar), 7.18-7.20 (m, 2H, Ar), 7.50 (d, 2H, *J*= 1.2 Hz, Ar), 7.61 (d, 1H, *J*= 2.8 Hz, Ar), 7.99 (s, 1H, Ar), 8.70 (s, 1H, NH). Anal. Calcd for (C₁₆H₁₂N₂OS): C, 68.55; H, 4.31; N, 9.99; S, 11.44. Found: C, 68.42; H, 4.40; N, 9.88; S, 11.53.

3-(Phenylthio)-1*H***-indole-5-carbonitrile (Table 2, Entry 32):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.10-7.14 (m, 3H, Ar), 7.21 (t, 2H, *J* = 7.4 Hz, Ar), 7.49-7.55 (m, 2H, Ar), 7.64 (d, 1H, *J* = 2.4 Hz, Ar), 7.97 (s, 1H, Ar), 8.81 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 104.2, 104.9, 112.6, 120.2, 125.3, 125.5, 126.0, 126.3, 128.9, 129.0, 132.6, 137.8, 138.2. Anal. Calcd for (C₁₅H₁₀N₂S): C, 71.97; H, 4.03; N, 11.19; S, 12.81. Found: C, 71.88; H, 4.12; N, 11.08; S, 12.92.

6-Fluoro-3-(phenylthio)-1*H***-indole (Table 2, Entry 33):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.09 (t, 1H, *J*= 7.2 Hz, Ar), 7.15 (d, 1H, *J*= 7.2 Hz, Ar), 7.18-7.23 (m, 3H, Ar), 7.29-7.33 (m, 1H, Ar), 7.48 (d, 1H, *J*= 8.4 Hz, Ar), 7.51 (d, 1H, *J*= 2.8 Hz, Ar), 7.66 (d, 1H, *J*= 8.0 Hz, Ar), 8.42 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.7, 111.6, 119.7, 120.9, 123.1, 124.8, 125.8, 128.7, 129.1, 130.7, 136.5, 139.2. Anal. Calcd for (C₁₄H₁₀FNS): C, 69.11; H, 4.14; N, 5.76; S, 13.18. Found: C, 69.00; H, 4.21; N, 5.66; S, 13.27.

6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 34): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.29 (s, 3H, CH₃), 7.01 (d, 2H, *J* = 8.0 Hz, Ar), 7.07 (d, 2H, *J* = 8.4 Hz, Ar), 7.20 (t, 1H, *J* = 7.4 Hz, Ar), 7.46 (d, 1H, *J* = 8.4 Hz, Ar), 7.50 (d, 1H, *J* = 2.4 Hz, Ar), 7.66 (d, 1H, *J*

= 8.0 Hz, Ar), 8.39 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.7, 103.2, 111.4, 119.5, 120.7, 122.8, 126.1, 128.9, 129.4, 130.4, 134.5, 135.3, 136.3. Anal. Calcd for (C₁₅H₁₂FNS): C, 70.01; H, 4.70; N, 5.44; S, 12.46. Found: C, 70.11; H, 4.82; N, 5.30; S, 12.38.

6-Fluoro-3-(phenylthio)-1*H***-indole (Table 2, Entry 35):** ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.04 (t, 1H, *J*= 7.2 Hz, Ar), 7.09 (d, 1H, *J*= 7.2 Hz, Ar), 7.13-7.17 (m, 3H, Ar), 7.26-7.28 (m, 1H, Ar), 7.42 (d, 1H, *J*= 8.4 Hz, Ar), 7.46 (d, 1H, *J*= 2.8 Hz, Ar), 7.61 (d, 1H, *J*= 8.0 Hz, Ar), 8.37 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 102.4, 111.3, 119.3, 120.6, 122.7, 124.4, 125.5, 128.4, 128.7, 130.4, 136.1, 138.9. Anal. Calcd for (C₁₄H₁₀FNS): C, 69.11; H, 4.14; N, 5.76; S, 13.18. Found: C, 69.00; H, 4.22; N, 5.65; S, 13.30.

6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 36): ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 2.18 (s, 3H, CH₃), 6.91 (d, 2H, J = 8.0 Hz, Ar), 6.97 (d, 2H, J = 8.4 Hz, Ar), 7.10 (t, 1H, J = 7.4 Hz, Ar), 7.36 (d, 1H, J = 8.4 Hz, Ar), 7.40 (d, 1H, J = 2.4 Hz, Ar), 7.55(d, 1H, J = 8.0 Hz, Ar), 8.29 (s, 1H, NH). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 20.9, 103.3, 111.6, 119.7, 120.8, 123.0, 126.2, 129.1, 129.5, 130.5, 134.7, 135.5, 136.5. Anal. Calcd for (C₁₅H₁₂FNS): C, 70.01; H, 4.70; N, 5.44; S, 12.46. Found: C, 70.13; H, 4.82; N, 5.31; S, 12.35.



¹H-NMR of 3-Phenylsulfanyl-1*H*-indole (Table 2, Entry 1)



Expansion of the ¹H-NMR of 3-Phenylsulfanyl-1*H*-indole (Table 2, Entry 1)



¹³C-NMR of 3-Phenylsulfanyl-1*H*-indole (Table 2, Entry 1)



¹H-NMR of 3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 2)



Expansion of the ¹H-NMR of **3**-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 2)



¹³C-NMR of 3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 2)



¹H-NMR of 3-((4-Methoxyphenyl)thio)-1*H*-indole (Table 2, Entry 3)



Expansion of the ¹H-NMR of 3-((4-Methoxyphenyl)thio)-1*H*-indole (Table 2, Entry 3)



¹H-NMR of 3-(*o*-Tolylthio)-1*H*-indole (Table 2, Entry 4)



Expansion of the ¹H-NMR of 3-(*o*-Tolylthio)-1*H*-indole (Table 2, Entry 4)



¹³C-NMR of 3-(*o*-Tolylthio)-1*H*-indole (Table 2, Entry 4)



¹H-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 5)



Expansion of the ¹H-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 5)



¹³C-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 5)



¹H-NMR of 3-((2-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 6)



Expansion of the ¹H-NMR of 3-((2-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 6)



¹³C-NMR of 3-((2-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 6)



¹H-NMR of 3-(Naphthalen-2-ylthio)-1*H*-indole (Table 2, Entry 7)



¹³C-NMR of 3-(Naphthalen-2-ylthio)-1*H*-indole (Table 2, Entry 7)



¹H-NMR of 2-Methyl-3-phenylsulfanyl-1*H*-indole (Table 2, Entry 8)



¹³C-NMR of 2-Methyl-3-phenylsulfanyl-1*H*-indole (Table 2, Entry 8)



¹H-NMR of 2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 9)



¹³C-NMR of 2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 9)



¹H-NMR of 3-(4-Methoxyphenylthio)-2-methyl-1*H*-indole (Table 2, Entry 10)



¹³C-NMR of 3-(4-Methoxyphenylthio)-2-methyl-1*H*-indole (Table 2, Entry 10)



¹H-NMR of 2-Methyl-3-(o-tolylthio)-1H-indole (Table 2, Entry 11)



¹³C-NMR of 2-Methyl-3-(o-tolylthio)-1H-indole (Table 2, Entry 11)


¹H-NMR of 3-((4-Chlorophenyl)thio)-2-methyl-1*H*-indole (Table 2, Entry 12)



¹³C-NMR of 3-((4-Chlorophenyl)thio)-2-methyl-1*H*-indole (Table 2, Entry 12)



¹H-NMR of 3-(2-Chlorophenylthio)-2-methyl-1*H*-indole (Table 2, Entry 13)



¹³C-NMR of 3-(2-Chlorophenylthio)-2-methyl-1*H*-indole (Table 2, Entry 13)



¹H-NMR of 2-(2-Methyl-1*H*-indol-3-ylsulfanyl)-phenylamine (Table 2, Entry 14)



¹³C-NMR of 2-(2-Methyl-1*H*-indol-3-ylsulfanyl)-phenylamine (Table 2, Entry 14)



¹H-NMR of 5-Bromo-3-(phenylthio)-1*H*-indole (Table 2, Entry 15)



Expansion of the ¹H-NMR of 5-Bromo-3-(phenylthio)-1*H*-indole (Table 2, Entry 15)



¹³C-NMR of 5-Bromo-3-(phenylthio)-1*H*-indole (Table 2, Entry 15)



¹H-NMR of 5-Bromo-3-*p*-tolylsulfanyl-1*H*-indole (Table 2, Entry 16)



¹³C-NMR of 5-Bromo-3-*p*-tolylsulfanyl-1*H*-indole (Table 2, Entry 16)



¹H-NMR of 5-Bromo-3-((4-methoxyphenyl)thio)-1*H*-indole (Table 2, Entry 17)



Expansion of the ¹H-NMR of 5-Bromo-3-((4-methoxyphenyl)thio)-1*H*-indole (Table 2, Entry 17)



¹H-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 18)



Expansion of the ¹H-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 18)



¹³C-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 18)



¹H-NMR of 5-Bromo-3-(naphthalen-2-ylthio)-1*H*-indole (Table 2, Entry 19)



Expansion of the ¹H-NMR of 5-Bromo-3-(naphthalen-2-ylthio)-1*H*-indole (Table 2, Entry 19)



¹³C-NMR of 5-bromo-3-(naphthalen-2-ylthio)-1*H*-indole (Table 2, Entry 19)



¹H-NMR of 3-Phenylsulfanyl-1*H*-indole (Table 2, Entry 20)



¹³C-NMR of 3-Phenylsulfanyl-1*H*-indole (Table 2, Entry 20)



¹H-NMR of 3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 21)



Expansion of the ¹H-NMR of **3**-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 21)



¹³C-NMR of 3-(*p*-Tolylthio)-1*H*-indole (Table 2, Entry 21)



¹H-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 22)



Expansion of the ¹H-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 22)



¹³C-NMR of 3-((4-Chlorophenyl)thio)-1*H*-indole (Table 2, Entry 22)



¹H-NMR of 2-Methyl-3-phenylsulfanyl-1*H*-indole (Table 2, Entry 23)



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¹³C-NMR of 2-Methyl-3-phenylsulfanyl-1*H*-indole (Table 2, Entry 23)



¹H-NMR of 2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 24)



¹³C-NMR of 2-Methyl-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 24)



¹H-NMR of 3-((4-Chlorophenyl)thio)-2-methyl-1*H*-indole (Table 2, Entry 25)



Expansion of the ¹H-NMR of 3-((4-Chlorophenyl)thio)-2-methyl-1*H*-indole (Table 2, Entry 25)



¹³C-NMR of 3-((4-Chlorophenyl)thio)-2-methyl-1*H*-indole (Table 2, Entry 25)



¹H-NMR of 5-Bromo-3-(phenylthio)-1*H*-indole (Table 2, Entry 26)



¹³C-NMR of 5-Bromo-3-(phenylthio)-1*H*-indole (Table 2, Entry 26)


¹H-NMR of 5-Bromo-3-*p*-tolylsulfanyl-1*H*-indole (Table 2, Entry 27)



¹³C-NMR of 5-Bromo-3-*p*-tolylsulfanyl-1*H*-indole (Table 2, Entry 27)



¹H-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 28)



Expansion of the ¹H-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 28)



¹³C-NMR of 5-Bromo-3-((4-chlorophenyl)thio)-1*H*-indole (Table 2, Entry 28)



¹H-NMR of 3-(Phenylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 29)



¹³C-NMR of 3-(Phenylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 29)



¹H-NMR of 3-(*p*-Tolylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 30)



¹³C-NMR of 3-(*p*-Tolylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 30)



¹H-NMR of 3-((4-Methoxyphenyl)thio)-1*H*-indole-5-carbonitrile (Table 2, Entry 31)



¹H-NMR of 3-(Phenylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 32)



¹³C-NMR of 3-(Phenylthio)-1*H*-indole-5-carbonitrile (Table 2, Entry 32)



¹H-NMR of 6-Fluoro-3-(phenylthio)-1*H*-indole (Table 2, Entry 33)



¹³C-NMR of of 6-Fluoro-3-(phenylthio)-1*H*-indole (Table 2, Entry 33)



¹H-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 34)



Expansion of the ¹H-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 34)



¹³C-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 34)



¹H-NMR of 6-Fluoro-3-(phenylthio)-1*H*-indole (Table 2, Entry 35)



Expansion of the ¹H-NMR of 6-Fluoro-3-(phenylthio)-1*H*-indole (Table 2, Entry 35)



¹³C-NMR of 6-Fluoro-3-(phenylthio)-1*H*-indole (Table 2, Entry 35)



¹H-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 36)



Expansion of the ¹H-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 36)



¹³C-NMR of 6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (Table 2, Entry 36)