Supporting Information

Catalyst-free thiolation of indoles with sulfonyl hydrazides for the synthesis of 3-sulfenylindoles in water

Yu Yang, Sheng Zhang, Lin Tang, Yanbin Hu, Zhenggen Zha and Zhiyong Wang

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei, 230026, P. R. China. Fax: (+86) 551-360-3185; E-mail: zwang3@ustc.edu.cn.

Contents:

General remarks........................................................................................................S2

General procedures for the synthesis of Arylsulfonyl Hydrazides ......................S2

Characterization data of products............................................................................S2

Reference..................................................................................................................S12

NMR Spectra of products.......................................................................................S12
General Remarks

All substrates were purchased commercially without further purification. The yields were determined based on indoles. ¹H and ¹³C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass).

General procedures for the synthesis of Arylsulfonyl Hydrazides

Arylsulfonyl hydrazides 2b-2s were prepared according to the literature procedure.[1] To a solution of an arylsulfonyl chloride (3.0 mmol) in tetrahydofuran (15 mL), was added hydrazine monohydrate (375 mg, 7.5 mmol) dropwise under nitrogen at 0 °C. After vigorous stirring for 30 min at 0 °C, the reaction mixture was added ethyl acetate (60 mL), and washed with saturated brine (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and added to hexane (12 mL) over 5 min. The mixture was filtered, and the collected solid was dried in vacuum.

Characterization data of products

3-(p-tolylthio)-1H-indole (3aa).[1] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 87% yield; mp = 125–126 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 6.95 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 7.12 (t, J = 7.9 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 135.5, 134.6, 130.4, 129.5, 129.1, 126.3, 122.9, 120.8, 119.7, 111.5, 103.5, 20.8.

3-(4-methoxyphenylthio)-1H-indole (3ab).[1] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a
yellow solid: 93% yield, mp = 111–113 °C; 1H NMR (400 MHz, CDCl₃) δ 3.76 (s, 3H), 6.78 (d, J = 8.8 Hz, 2H), 7.18 (m, 3H), 7.28 (t, J = 7.8 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 2.2 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 8.38 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 157.8, 136.5, 130.1, 129.5, 129.0, 128.6, 123.0, 120.8, 119.6, 114.5, 111.6, 104.5, 55.4.

3-(4-propynylphenylthio)-1H-indole (3ac). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 89% yield; mp = 109–111 °C; 1H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.3 Hz, 3H), 1.56 (m, 2H), 2.47 (t, J = 7.3 Hz, 3H), 6.97 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 2.5 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 8.39 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 139.5, 136.4, 135.8, 130.5, 129.2, 128.9, 126.1, 122.9, 120.8, 119.7, 111.5, 103.4, 37.4, 24.5, 13.8; HRMS [M+H]+ calcd. for C₁₇H₁₈NS: 268.1155, found 268.1154.

3-(4-tert-butylphenylthio)-1H-indole (3ad).[2] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 91% yield; mp = 185–187 °C; 1H NMR (400 MHz, CDCl₃) δ 1.24 (s, 9H), 7.04 (d, J = 8.4 Hz, 2H), 7.17 (m, 3H), 7.24 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.44 (d, J = 2.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 8.37 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 148.0, 136.5, 135.7, 130.6, 129.3, 125.9, 125.8, 123.0, 120.8, 119.7, 111.5, 103.4, 34.3, 31.3.

3-(phenylthio)-1H-indole (3ae).[1] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 91% yield; mp = 151–152 °C; 1H NMR (400 MHz, CD₂COCD₃) δ 7.11 (m, 7H), 7.55 (m, 2H), 7.68 (m, 1H), 10.84 (s, 1H); 13C NMR (100 MHz, CD₂COCD₃) δ 139.8, 137.2, 131.9, 129.2, 128.7, 125.6, 124.6, 122.4, 120.3, 118.7, 112.2, 100.9.
3-((trifluoromethoxy)phenylthio)-1H-indole (3af). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 70% yield; ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.42 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 138.2, 136.5, 130.9, 128.8, 126.9, 123.3, 121.7 (q, J = 255.1 Hz), 121.5, 121.1, 119.5, 111.7, 102.3.

3-(4-fluorophenylthio)-1H-indole (3ag). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 83% yield; mp = 132-133 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.86 (t, J = 8.4 Hz, 2H), 7.08 (m, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 8.40 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 162.1 (d, J̄CF = 242.5 Hz), 136.5, 134.0 (d, J̄CF = 2.9 Hz), 130.5, 128.9, 127.9 (d, J̄CF = 7.7 Hz), 123.1, 121.0, 119.5, 115.8 (d, J̄CF = 21.8 Hz), 111.6, 102.5.

3-(4-chlorophenylthio)-1H-indole (3ah). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 66% yield; mp = 130-131 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 8.43 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 136.5, 130.7, 130.6, 128.8, 128.7, 127.1, 123.2, 121.1, 119.5, 111.7, 102.5.

3-(4-bromophenylthio)-1H-indole (3ai). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 65% yield; mp = 140-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.95 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 1H), 7.27 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 8.44 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 136.5, 131.7, 130.8, 128.8, 127.4, 123.3, 121.1, 119.5, 118.3, 111.7, 102.3.
4-(1H-indol-3-ylthio)benzonitrile (3aj). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light green solid: 74% yield; mp = 184-186 °C; 1H NMR (400 MHz, CDCl3) δ 7.03 (d, J = 8.4 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.23 (m, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.44 (m, 3H), 8.58 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 147.1, 136.6, 132.2, 131.2, 128.5, 125.4, 123.5, 121.3, 119.3, 119.2, 111.9, 107.6, 100.2. HRMS [M]+ calcd. for C15H10N2S: 250.0565, found 250.0564.

3-(4-(trifluoromethyl)phenylthio)-1H-indole (3ak). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 52% yield; 1H NMR (400 MHz, CDCl3) δ 7.17 (d, J = 8.2 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.53 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 8.48 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 144.7, 136.6, 131.1, 128.8-120.3 (q, J = 271.2 Hz), 127.2-126.3 (q, J = 32.2 Hz), 125.5 (q, J = 3.6 Hz), 125.3, 123.4, 123.0, 121.3, 120.3, 119.4, 111.78, 101.2.

3-(4-nitrophénylthio)-1H-indole (3ai). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a yellow solid: 82% yield; mp = 174–175 °C; 1H NMR (400 MHz, CDCl3) δ 7.10 (m, 2H), 7.17 (m, 1H), 7.30 (m, 1H), 7.50 (m, 3H), 7.98 (m, 2H), 8.75 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 150.0, 144.8, 136.6, 131.4, 128.4, 125.1, 123.9, 123.5, 121.4, 119.2, 112.1, 100.0.

3-(3-nitrophénylthio)-1H-indole (3am). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 78% yield; mp = 135–136 °C; 1H NMR (400 MHz, CDCl3) δ 7.18 (t, J = 7.9 Hz, 2H), 7.29 (m, 1H), 7.35 (m, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.55 (m, 2H), 7.88 (m, 1H), 7.91 (m, 1H), 8.62 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 148.6, 142.6, 136.6, 131.3, 129.3, 128.5, 123.5, 121.3, 120.4, 119.7, 119.2, 111.9, 100.8.
3-(3-fluoro-4-methylphenylthio)-1H-indole (3ao). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 82% yield; mp = 138-140 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.15 (s, 3H), 6.72 (m, 1H), 6.82 (t, \(J = 8.0\) Hz, 1H), 7.17 (t, \(J = 7.8\) Hz, 1H), 7.27 (d, \(J = 7.2\) Hz, 1H), 7.44 (d, \(J = 8.0\) Hz, 1H), 7.47 (d, \(J = 2.5\) Hz, 1H), 7.6 (d, \(J = 7.8\) Hz, 1H), 8.45 (s, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.6 (d, \(J_{CF} = 244.8\) Hz), 138.3 (d, \(J_{CF} = 7.6\) Hz), 136.5, 131.4 (d, \(J_{CF} = 5.5\) Hz), 130.7, 128.9, 123.1, 121.3 (d, \(J_{CF} = 3.5\) Hz), 121.2, 121.0, 119.5, 112.7 (d, \(J_{CF} = 24.9\) Hz), 111.6, 102.5, 14.0 (d, \(J_{CF} = 3.5\) Hz); HRMS [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{13}\)FNS: 258.0753, found 258.0749.

3-(4-chloro-3-nitrophenylthio)-1H-indole (3ap). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a yellow solid: 50% yield; mp = 196-198 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.65 (d, \(J = 8.7\) Hz, 1H), 7.23 (m, 4H), 7.44 (d, \(J = 8.0\) Hz, 1H), 7.51 (d, \(J = 2.5\) Hz, 1H), 7.61 (d, \(J = 7.9\) Hz, 1H), 8.01 (d, \(J = 2.1\) Hz, 1H), 8.42 (s, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.8, 136.5, 135.6, 132.3, 130.3, 128.7, 126.5, 124.6, 123.2, 121.0, 119.4, 119.3, 111.7, 103.6; HRMS [M+H]\(^+\) calcd. for C\(_{14}\)H\(_{10}\)ClN\(_2\)O\(_2\)S: 305.0151, found 305.0141.

3-(naphthalen-2-ylthio)-1H-indole (3aq). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 99% yield; mp = 142-143 °C; \(^1\)H NMR (400 MHz, CD\(_2\)COCD\(_3\)) \(\delta\) 7.09 (t, \(J = 7.5\) Hz, 1H), 7.22 (t, \(J = 7.5\) Hz, 1H), 7.28 (d, \(J = 8.6\) Hz, 1H), 7.39 (m, 2H), 7.57 (m, 4H), 7.77 (m, 3H), 10.88 (s, 1H); \(^1\)C NMR (100 MHz, CD\(_2\)COCD\(_3\)) \(\delta\) 137.4, 137.2, 133.9, 132.1, 131.4, 129.2, 128.2, 127.7, 126.7, 126.5, 125.1, 124.5, 123.1, 122.5, 120.3, 118.8, 112.2, 100.8.
3-(naphthalen-1-ylthio)-1H-indole (3ar). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 67% yield; mp = 166-168 °C; 1H NMR (400 MHz, CDCl3) δ 6.95 (dd, J = 7.4 Hz, 10Hz, 1H), 7.13 (m, 1H), 7.15 (d, J = 7.6, 1H), 7.27 (m, 1H), 7.43 (d, J = 8.0, 1H), 7.55 (m, 5H), 7.82 (m, 1H), 8.41 (s, 1H), 8.48 (d, J = 8.0, 1H); 13C NMR (100 MHz, CDCl3) δ 136.6, 136.2, 133.7, 130.9, 130.8, 129.1, 128.5, 126.1, 126.0, 125.7, 125.2, 124.0, 123.4, 123.1, 120.9, 119.7, 116.7, 102.3; HRMS [M+H]+ calcd. for C18H14NS: 276.0841, found 276.0849.

3-(4-methoxyphenylthio)-2-methyl-1H-indole (3bb).[3] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a colorless solid: 68% yield; mp = 115-116 ºC; 1H NMR (400 MHz, CDCl3) δ 2.52 (s, 3H), 3.72 (s, 3H), 6.70 (m, 2H), 7.03 (m, 2H), 7.09 (m, 2H), 7.30 (m, 1H), 7.57 (d, J = 7.8 Hz, 1H), 8.19 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 157.5, 140.6, 135.4, 132.7, 129.9, 127.9, 122.1, 120.6, 119.0, 114.5, 110.6, 101.0, 55.3, 12.2.

3-(4-methoxyphenylthio)-1-methyl-1H-indole (3cb).[4] The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 99% yield; mp = 60-62 ºC; 1H NMR (400 MHz, CDCl3) δ 3.72 (s, 3H), 3.81 (s, 3H), 6.71 (d, J = 8.8 Hz, 2H), 7.13 (m, 3H), 7.29 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.82 - 7.85 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 157.7, 137.5, 134.5, 130.0, 129.7, 128.4, 122.5, 120.4, 119.7, 114.5, 109.7, 102.3, 55.3, 33.1.

3-(4-methoxyphenylthio)-4-methyl-1H-indole (3db). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 56% yield; mp = 117-119 ºC; 1H NMR (400 MHz, CDCl3) δ 2.67 (s, 3H), 3.74 (s, 3H), 6.75 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 7.1 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 7.13 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 7.1 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 8.37 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 157.4, 137.0, 132.1, 132.0, 131.5, 127.6, 126.9, 123.1, 122.4, 114.6, 109.4, 103.8, 55.4, 18.8; HRMS [M+H]+ calcd. for C16H16NOS: 270.0953, found 270.0944.
5-methoxy-3-(4-methoxyphenylthio)-1H-indole (3eb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 72% yield; mp = 57-59 °C; 1H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 3.80 (s, 3H), 6.88 (dd, J = 8.8 Hz, 2.3 Hz, 2H), 7.06 (d, J = 2.3 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 2.3 Hz, 1H), 8.31 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 156.4, 154.0, 130.3, 129.7, 128.8, 128.6, 127.2, 113.4, 112.4, 111.3, 102.8, 99.8, 54.8, 54.3; HRMS [M+H]+ calcd. for C₁₆H₁₆NO₂S: 286.0902, found 286.0896.

6-fluoro-3-(4-methoxyphenylthio)-1H-indole (3fb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 85% yield; mp = 86-88 °C; 1H NMR (400 MHz, CDCl₃) δ 3.73 (s, 3H), 6.75 (d, J = 8.6 Hz, 2H), 6.89 (m, 1H), 7.10 (m, 3H), 7.43 (s, 1H), 7.51 (m, 1H), 8.39 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 161.6 (d, J_{CF} = 237.7 Hz), 157.9, 136.4 (d, J_{CF} = 12.7 Hz), 130.2 (d, J_{CF} = 3.1Hz), 139.0, 128.7, 125.4, 120.6 (d, J_{CF} = 10.1 Hz), 114.5, 109.7 (d, J_{CF} = 24.6 Hz), 105.1, 98.0 (d, J_{CF} = 26.2 Hz), 55.3; HRMS [M+H]+ calcd. for C₁₅H₁₃FNOS: 274.0702, found 274.0701.

4-chloro-3-(4-methoxyphenylthio)-1H-indole (3gb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 74% yield; mp = 77-79 °C; 1H NMR (400 MHz, CDCl₃) δ 3.74 (s, 3H), 6.75 (m, 2H), 7.13 (m, 4H), 7.30 (m, 1H), 7.41 (s, 1H), 8.47 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 157.8, 138.0, 131.8, 130.8, 128.8, 126.9, 125.0, 123.5, 122.1, 114.5, 110.4, 105.0, 55.3; HRMS [M+H]+ calcd. for C₁₅H₁₃ClNOS: 290.0406, found 290.0408.

5-bromo-3-(4-methoxyphenylthio)-1H-indole (3hb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 81% yield; mp = 106-108 °C; 1H NMR (400 MHz, CDCl₃) δ 3.74 (s, 3H), 6.75 (m, 2H), 7.11 (m, 2H), 7.28 (d, J = 8.6 Hz, 1H), 7.31 (dd, J = 8.6 Hz, 1.8 Hz, 1H), 7.45 (d, J
= 2.5 Hz, 1H), 7.76 (d, J = 1.8 Hz, 1H), 8.40 (s, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)) δ 158.0, 135.1, 131.2, 130.9, 128.9, 128.7, 126.0, 122.2, 114.6, 114.3, 113.0, 104.6, 55.4; HRMS [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{13}\)BrNOS: 333.9901, found 333.9904.

3-(4-methoxyphenylthio)-5-nitro-1H-indole (3ib). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a yellow solid: 35% yield; mp = 181-183 °C; \[^{1}\text{H}\] NMR (400 MHz, CDCl\(_3\)) δ 3.75 (s, 3H), 6.76 (m, 2H), 7.18 (m, 2H), 7.47 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 8.14 (dd, J = 8.9 Hz, 2.4 Hz, 1H), 8.58 (d, J = 2.0 Hz, 1H), 8.78 (s, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)) δ 157.4, 141.7, 138.4, 131.5, 128.8, 126.8, 126.0, 117.6, 115.9, 113.7, 110.7, 107.9, 55.3; HRMS [M+H]\(^+\) calcd. for C\(_{15}\)H\(_{13}\)N\(_2\)O\(_3\)S: 333.9901, found 333.9904.

3-(4-methoxyphenylthio)-1H-indole-5-carbonitrile (3jb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 56% yield; mp = 236-238 °C; \[^{1}\text{H}\] NMR (400 MHz, CD\(_3\)COCD\(_3\)) δ 3.73 (s, 3H), 6.83 (m, 2H), 7.20 (m, 2H), 7.51 (dd, J = 8.5 Hz, 1.6 Hz, 1H), 7.71 (m, 1H), 7.88 (d, J = 2.5 Hz, 1H), 7.92 (m, 1H), 11.21 (s, 1H); \[^{13}\text{C}\] NMR (100 MHz, CD\(_3\)COCD\(_3\)) δ 158.1, 148.4, 142.9, 130.9, 129.1, 128.4, 125.1, 124.1, 119.8, 114.6, 113.5, 105.1, 103.4, 54.7; HRMS [M]\(^+\) calcd. for C\(_{16}\)H\(_{12}\)N\(_2\)O\(_3\): 280.0670, found 280.0671.

3-(4-methoxyphenylthio)-1H-pyrrolo[2,3-b]pyridine (3kb). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 65% yield; mp = 173-175 °C; \[^{1}\text{H}\] NMR (400 MHz, CDCl\(_3\)) δ 3.12 (s, 3H), 6.78 (d, J = 8.7 Hz, 2H), 7.15 (m, 3H), 7.66 (s, 1H), 7.97 (d, J = 7.8 Hz, 1H), 8.38 (s, 1H), 10.94 (s, 1H); \[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)) δ 158.1, 148.4, 142.9, 130.9, 129.1, 128.8, 128.6, 122.2, 116.7, 114.6, 103.8, 55.3; HRMS [M]\(^+\) calcd. for C\(_{14}\)H\(_{12}\)N\(_2\)OS: 256.0665, found 256.0656.

1,2-dip-tolyldisulfane (4). The title compound was prepared according to the general working
procedure and purified by column chromatography to give the product as a white solid: 25% yield; mp = 45–46 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.31 (s, 6H), 7.10 (d, $J$ = 8.0 Hz, 4H), 7.38 (d, $J$ = 8.0 Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.5, 133.9, 129.8, 128.5, 21.1.

4-methylbenzenesulfonyl acid S-(4-methylphenyl) ester (5).$^{[1]}$ The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 57% yield; mp = 91-93 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.36 (s, 3H), 2.41 (s, 3H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.21 (t, $J$ = 8.0 Hz, 4H), 7.44 (d, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.7, 142.1, 140.4, 136.5, 130.3, 129.4, 127.6, 124.5, 21.7, 21.5.

Reference

NMR Spectra of products