Supporting Information for:

**Iodine-Mediated Thiolation of Phenol/Phenylamine Derivatives and Sodium Arylsulfinites in Neat Water**

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**General Information**

$^1$H and $^{13}$C NMR spectra were recorded on Bruker Ascend™ 400(400 MHz) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. $^{1f-1g}$ were prepared according to the literature procedure.$^1$ The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Adamas, Aladdin and TCI used as received.

**General Procedure for the Synthesis of the Desired Thioethers 3**

Iodine (76.1 mg, 0.3 mmol) was added to a solution of 2-Naphthol $^2$ (0.3 mmol), sodium benzenesulfinites $^1$ (0.36 mmol) and triphenylphosphine(94.4 mg, 0.36 mmol) in H$_2$O (2 mL), and the reaction mixture was stirred under reflux conditions for 10 h. The reaction mixture was quenched by the addition of saturated sodium thiosulfate solution. Further stirring was followed by extraction with EtOAc (3×20 mL). The combined organic extracts were dried (MgSO$_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography using ethyl acetate / petroleum ether as eluent to afford the corresponding product 3.

**General Procedure for the Synthesis of the Desired Thioethers 5**

Iodine (76.1 mg, 0.3 mmol) was added to a solution of Phenol/Amine $^4$ (0.36 mmol), sodium benzenesulfinites $^1$ (0.3 mmol) and triphenylphosphate(94.4 mg, 0.36 mmol) in H$_2$O (2 mL), and the reaction mixture was stirred under reflux conditions for 8-12 h. The reaction mixture was quenched by the addition of saturated sodium thiosulfate solution. Further stirring was followed by extraction with EtOAc (3×20 mL). The combined organic extracts were dried (MgSO$_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography using ethyl acetate / petroleum ether as eluent to afford the corresponding product 5.

**Analytical Data for the Products Showed in Tables 2 and 3**

![Chemical structure](image)

$^3$a, $^2$ Yellow solid (62.0 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, J = 8.0 Hz, 1H), 7.92 (d, J =
8.0 Hz, 1H), 7.83 (d, J = 4.0 Hz, 1H), 7.52–7.50 (m, 1H), 7.39–7.36 (m, 2H), 7.20 (s, 3H), 7.13–7.12 (m, 1H), 7.07–7.05 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.0, 135.5, 135.4, 132.8, 129.5, 129.2, 128.6, 127.9, 126.4, 125.9, 124.7, 123.8, 116.9, 108.1.

![3b](image)

3b. Yellow solid (71.1 mg, 89% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.30 (d, J = 8.0 Hz, 1H), 7.93–7.91 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.54–7.51 (m, 1H), 7.43–7.39 (m, 2H), 7.23 (d, J = 4.0 Hz, 1H), 7.15 (s, 1H), 7.07–7.03 (m, 1H), 6.91–6.88 (m, 1H), 6.45 (d, J = 8.0 Hz, 1H), 2.64 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.2, 135.6, 135.2, 134.4, 132.8, 130.4, 129.6, 128.7, 127.9, 126.8, 125.5, 124.8, 124.7, 123.9, 116.9, 107.4, 20.9.

![3c](image)

3c. Yellow solid (66.0 mg, 83% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.20 (d, J = 12.0 Hz, 1H), 7.96 (d, J = 12.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.54–7.50 (m, 1H), 7.43–7.39 (m, 2H), 7.15 (s, 1H), 7.07–7.03 (m, 1H), 6.91–6.88 (m, 1H), 6.45 (d, J = 8.0 Hz, 1H), 2.64 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.2, 135.6, 135.2, 134.4, 132.8, 130.4, 129.6, 128.7, 127.9, 126.8, 125.5, 124.8, 124.7, 123.9, 116.9, 107.4, 20.9.

![3d](image)

3d. Yellow solid (72.9 mg, 85% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.16 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.52–7.49 (m, 1H), 7.40–7.33 (m, 2H), 7.15–7.11 (m, 3H), 6.95–6.93 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.0, 135.2, 133.9, 133.1, 131.9, 129.5, 129.3, 128.6, 128.1, 127.6, 124.4, 124.0, 116.9, 107.6.

![3e](image)

3e. Yellow solid (85.9 mg, 87% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 8.14–8.12 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 12.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.50–7.46 (m, 1H), 7.38–7.31 (m, 2H), 7.28–7.24 (m, 2H), 7.08 (s, 1H), 6.86 (d, J = 4.0 Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 157.0, 135.1, 134.6, 133.1, 132.1, 129.5, 128.6, 128.1, 127.9, 124.4, 124.0, 119.6, 116.9, 107.4.
3f, Yellow solid (68.5 mg, 81% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.30 (d, \(J = 12.0\) Hz, 1H), 7.92 (d, \(J = 8.0\) Hz, 1H), 7.84 (d, \(J = 8.0\) Hz, 1H), 7.55–7.51 (m, 1H), 7.42–7.38 (m, 3H), 7.31 (d, \(J = 4\) Hz, 2H), 7.01 (d, 2H), 2.27 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.5, 156.7, 135.4, 132.5, 129.5, 128.8, 128.5, 127.8, 125.9, 124.7, 123.7, 116.8, 114.9, 109.9, 55.3.

3h, White solid (94.0 mg, 91% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (d, \(J = 12\) Hz, 1H), 7.94 (d, \(J = 12.0\) Hz, 1H), 7.78 (d, \(J = 8.0\) Hz, 1H), 7.54–7.51 (m, 1H), 7.33 (d, \(J = 8.0\) Hz, 1H), 7.20–7.14 (m, 4H), 6.99 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.3, 135.2, 134.1, 131.7, 131.0, 131.0, 130.4, 129.3, 126.6, 126.4, 126.1, 118.0, 117.6, 109.2, 20.9.

3i, White solid (71.0 mg, 88% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84–7.81 (m, 1H), 7.73–7.70 (m, 1H), 7.51 (s, 1H), 7.18–7.10 (m, 4H), 7.00 (m, 3H), 5.14 (s, 1H), 1.63 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.7, 155.6, 137.3, 135.2, 132.7, 132.7, 130.7, 129.2, 126.1, 125.8, 115.3, 114.3, 107.2.

3j, Yellow oil (59.6 mg, 71% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.49–8.47 (d, \(J = 8.0\) Hz, 1H), 7.98 (d, \(J = 8.0\) Hz, 1H), 7.83 (d, \(J = 8.0\) Hz, 1H), 7.52–7.49 (m, 1H), 7.41–7.36 (m, 2H), 7.15–7.02 (m, 4H), 3.98 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.3, 136.3, 132.1, 129.6, 128.7, 128.3, 126.3, 125.5, 124.8, 124.1, 113.4, 56.9, 29.7.

3k, Colourless oil (66.2 mg, 73% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.56–8.54 (d, \(J = 8.0\) Hz, 1H), 7.95 (d, \(J = 8.0\) Hz, 1H), 7.83 (d, \(J = 8.0\) Hz, 1H), 7.58–7.52 (m, 1H), 7.43–7.40 (m, 1H), 7.36–7.32 (m, 1H), 7.17–7.06 (m, 4H), 4.23–4.18 (m, 2H), 1.35–1.31 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.6, 136.4, 135.2, 131.6, 129.5, 128.6, 128.2, 127.5, 126.8, 125.5, 124.8, 124.1, 114.9, 66.5, 14.8.
3l,Colourless oil (40.0 mg, 52% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24–7.21 (m, 3H), 7.14 (d, $J$ = 4Hz,1H), 7.08 (d, $J$ = 8 Hz,2H), 6.78 (s, 1H), 6.24 (s, 1H), 7.77-2.69 (m, 4H), 1.78 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.9, 142.1, 137.0, 136.5, 130.2, 129.1, 126.5,125.8, 115.2, 112.9, 29.6,28.4, 23.2, 22.9.

5aa,white solid (66.3 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.15-7.14 (d, $J$ = 4.0 Hz, 2H), 7.03 (d, $J$ = 7 Hz, 3H), 3.86 (s, 3H), 3.78 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.9, 162.5 , 138.7, 128.5, 125.6, 124.3, 98.7, 91.2, 56.3, 55.4.

5ba,white solid (123.4 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.95 (d, $J$ = 2.0 Hz, 4H), 6.20 (s, 2H), 3.85 (s, 3H), 3.79 (s, 6H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.6, 162.3, 135.0, 134.1, 129.3, 125.9, 99.3, 91.2, 56.3, 55.4, 20.9.

5ca,white solid (76.3 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.10 (d, $J$ = 8.0 Hz, 2H), 6.94 (d, $J$ = 12 Hz, 2H), 6.20 (s, 2H), 3.86 (s, 3H), 3.80 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.1, 162.4, 137.7, 130.4, 128.5, 126.9, 110.3, 91.2, 56.2, 55.4.

5da,white solid (85.0 mg, 80% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24 (d, $J$ = 8 Hz, 2H), 6.86 (d, $J$ = 8 Hz, 2H), 6.19 (s, 2H), 3.85 (s, 3H), 3.79 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.0, 162.4, 138.1, 131.4, 127.2, 117.8, 98.0, 91.2, 56.3, 55.4.

5ea,white solid (75.3 mg, 82% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06 (d, $J$ = 4 Hz, 2H), 6.72 (d, $J$ = 8.0 Hz, 2H), 6.18 (s,2H), 3.83(s, 3H), 3.80 (s,6H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 152.6, 152.3, 157.5, 129.2, 128.6, 114.2, 91.2, 56.3, 55.4, 55.3.
5fa, yellow solid (75.1 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 6.22 (s, 2H), 3.87 (s, 3H), 3.79 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.4, 152.4, 149.5, 144.6, 124.8, 123.7, 95.9, 91.3, 56.3, 55.5.

5ab, gray solid (58.9 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40 (d, $J = 8$ Hz, 1H), 7.25-7.11 (m, 2H), 7.05 (d, $J = 1.0$, 8 Hz, 2H), 6.59 (d, $J = 8$ Hz, 2H), 6.47 (d, $J = 8$ Hz, 1H) 5.37 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.5, 158.4, 138.1, 136.0, 133.0, 130.0, 126.7, 109.3, 108.1, 102.5.

5bb, brown solid (64.1 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (d, $J = 8$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.63 (s, 1H), 6.56 (d, $J = 2.5$ Hz, 1H), 6.45 (m, 1H), 5.48 (s, 1H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.1, 158.4, 138.1, 136.0, 133.0, 130.0, 126.7, 109.3, 108.1, 102.5, 20.9.

5db, brown solid (78.1 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.25 (m, 3H), 6.89 (d, $J = 4.0$ Hz, 2H), 6.57 (s, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 5.49 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.6, 158.5, 138.2, 135.8, 132.1, 127.7, 119.6, 109.5, 106.6, 102.6.

5eb, white solid (64.7 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.25 (m, 3H), 6.89 (d, $J = 4.0$ Hz, 2H), 6.57 (s, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 5.49 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 158.9, 158.3, 137.7, 129.4, 128.9, 127.1, 114.9, 109.0, 102.3, 55.4.

5ac, yellow solid (57.0 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40 (d, $J = 4.0$ Hz, 2H), 7.21 (d, $J = 8$ Hz, 2H), 7.10 (d, $J = 4.0$ Hz, 3H), 6.71 (d, $J = 4.0$ Hz, 2H), 3.00 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 139.9, 136.1, 128.7, 126.8, 124.9, 117.1, 112.9, 40.3.
5bc, yellow solid (72.9 mg, 87% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37-7.35 (m, 2H), 7.13 (d, \(J = 8.5\) Hz, 2H), 7.04 (d, \(J = 4.0\) Hz, 4H), 6.69 (m, 2H), 3.97 (s, 6H), 2.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.4, 138.1, 135.5, 129.5, 127.7, 118.5, 112.9, 40.2, 20.8.

5dc, white solid (77.4 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36 (d, \(J = 8.0\) Hz, 2H), 7.29 (d, \(J = 8.0\) Hz, 2H), 6.94 (d, \(J = 8.0\) Hz, 2H), 6.69 (d, \(J = 8.0\) Hz, 2H), 2.99 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.7, 139.9, 136.2, 131.6, 128.2, 118.4, 117.9, 112.9, 40.2.

5ec, yellow oil (63.7 mg, 82% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.33 (d, \(J = 8.0\) Hz, 2H), 7.21 (d, \(J = 8.0\) Hz, 2H), 6.81 (d, \(J = 8.0\) Hz, 2H), 6.68 (d, \(J = 8.0\) Hz, 2H), 3.77 (s, 3H), 2.96 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.3, 150.1, 134.3, 133.7, 132.7, 130.9, 114.6, 113.0, 55.3, 40.4.

References

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