Supplementary Material (ESI) for Green Chemistry

Supporting Information

A reusable $FeCl_3 \cdot 6H_2O$/cationic 2,2'-bipyridyl catalytic system for the coupling of aryl iodides with thiols in water under aerobic conditions

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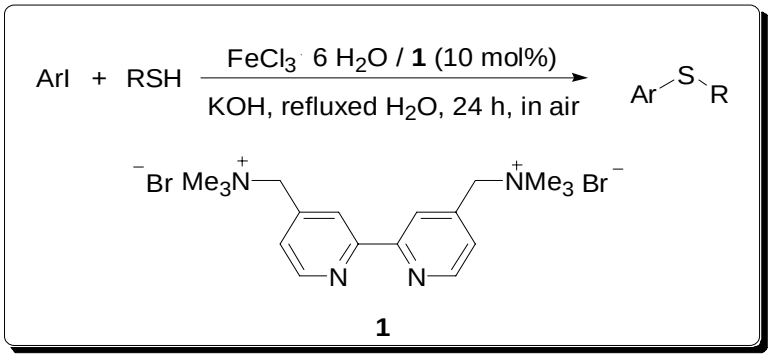

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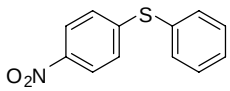
Experimental Section

General

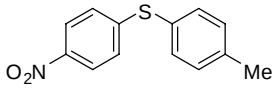
Chemicals were purchased from commercial supplier and were used without further purification. Cationic 2,2-bipyridyl ligand **1** was prepared according to the published procedure.[1] For column chromatography, 70-230 mesh silica gel (Merck Ltd.) was employed. Melting points were recorded using melting point apparatus and were uncorrected. All ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 ^{o}C on a Varian 200 NMR spectrometer. Chemical shifts were reported in ppm using tetramethylsilane (TMS) as internal standard.

General procedure for iron-catalyzed carbon-sulfur bond formation reaction

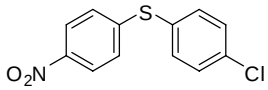
A 20 mL reactor equipped with a condenser was charged with $FeCl_3 \cdot 6H_2O$ (54 mg, 0.2 mmol), ligand **1** (92 mg, 0.2 mmol) and H_2O (5 mL). After the stirring of this solution at 50 ^{o}C for 0.5 h, aryl iodide **2** (3.0 mmol), thiol **3** (2.0 mmol), KOH (4.0 mmol) were added to the solution. The reaction mixture was then heated to reflux under air for 24 h. After cooling the reaction to room temperature the aqueous solution was extracted with hexane three times. The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum. Column chromatography on silica gel afforded the desired product.



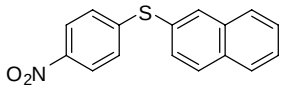
4-Nitrophenyl phenyl sulfide (4a); Mp 54–55 ^{o}C (lit.[2] 54–55 ^{o}C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.07 (dt, *J* = 9.0 Hz, 1.9 Hz, 2H), 7.57−7.52 (m, 2H), 7.47−7.44 (m, 3H), 7.18 (dt, *J* = 9.0 Hz, 1.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.4, 145.4, 134.7 (2C), 130.5, 130.0 (2C), 129.6, 126.7 (2C), 124.0 (2C).



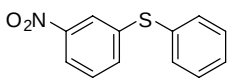
4'-Nitrophenyl-4-tolyl sulfide (4b); Mp 78–79 °C (lit.[3] 78–78.5 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H),7.14 (d, *J* = 8.7 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 149.2, 145.2, 140.1, 135.0 (2C), 130.8 (2C), 126.6, 126.2 (2C), 123.9 (2C), 21.3.



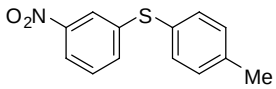
4'-Chlorophenyl-4-nitrophenyl sulfide (4c); Mp 89–90 °C (lit.[4] 88–88.5 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.11−8.06 (m, 2H), 7.46−7.44 (m, 4H), 7.21−7.17 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.5, 145.6, 136.0, 135.7 (2C), 130.2 (2C), 129.2, 126.9 (2C), 124.1 (2C).



2'-Naphthalyl-4-nitrophenyl sulfide (4d); Mp 108–110 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10−7.48 (m, 7H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.2, 145.4, 134.5, 133.8, 133.3, 130.6, 129.8, 127.8 (2C), 127.6, 127.4, 127.0, 126.8 (2C), 124.0 (2C). HRMS Calcd for $C_{16}H_{11}NO_2S$: 281.0510. Found: 281.0512.

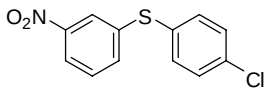


3-Nitrophenyl phenyl sulfide (4e)[2]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95−7.90 (m, 4H), 7.44−7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.2, 133.3, 132.1, 129.8, 129.6 (2C), 128.9, 128.7 (2C), 128.2, 123.1, 120.9.

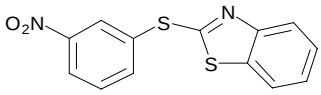


4'-Methylphenyl-3-nitrophenyl sulfide (4f); Mp 60–61 °C (lit.[5] 59–61 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.96−7.95 (m, 2H), 7.45−7.36 (m, 4H), 7.22 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR

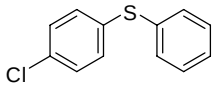
($CDCl_3$, 50 MHz) δ 148.6, 141.5, 139.4, 134.0 (2C), 133.3, 130.6 (2C), 129.4, 127.8, 122.2, 120.3, 21.2.



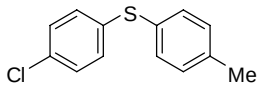
4'-Chlorophenyl-3-nitrophenyl sulfide (4g); Mp 70–71 °C (lit.[6] 70–72 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.06−8.04 (m, 2H), 7.53−7.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.6, 134.5, 134.4 (2C), 130.0 (2C), 129.9, 129.8, 129.2, 128.9, 123.5, 121.3.



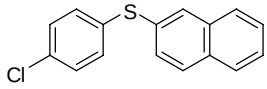
2-(3-Mitrophenylsulfanyl)benzothiazole (4h)[5]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.58 (br, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.6, 153.4, 148.7, 139.6, 135.8, 132.9, 130.4, 128.6, 126.5, 125.1, 124.5, 122.5, 120.0.



4-Chlorophenyl phenyl sulfide (4i)[7]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.34−7.25 (m, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.1, 134.6, 132.9, 132.0 (2C), 131.3 (2C), 129.3 (2C), 129.1, 127.4 (2C).

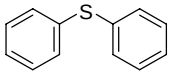


4'-Chlorophenyl-4-tolyl sulfide (4j); Mp 70–71 °C (lit.[8] 71.4 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31−7.18 (m, 4H), 7.17−7.13 (m, 4H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.0, 135.9, 132.4 (2C), 132.3, 130.8 (2C), 130.7, 130.2 (2C), 129.1 (2C), 21.1.

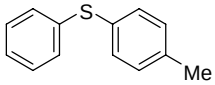


4'-Chlorophenyl-2-Naphthalyl sulfide (4k); Mp 108–110 °C (lit.[9] 106–107 °C); ^{1}H NMR ($CDCl_3$,

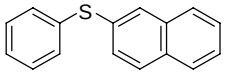
200 MHz) δ 7.84−7.26 (m, 11H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.7, 133.8, 132.4, 132.3, 131.9 (2C), 130.3, 129.3 (2C), 129.0, 128.7, 127.7, 127.4, 126.7, 126.4, 126.2.



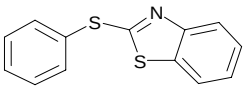
Diphenyl sulfide (4l)[2]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36−7.22 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8 (2C), 131.0 (4C), 129.1 (4C), 126.9 (2C).



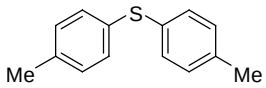
4-Tolyl phenyl sulfide (4m)[2]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.27 (d, J = 8.3 Hz, 2H), 7.24−7.16 (m, 5H), 7.12 (d, J = 8.3 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.5, 137.0, 132.2 (2C), 131.4, 130.0 (2C), 129.8 (2C), 129.0 (2C), 126.4, 21.1.



2'-Naphthalyl phenyl sulfide (4n); Mp 50−51 ^{o}C (lit.[10] 50 ^{o}C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.84−7.71 (m, 4H), 7.49−7.25 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 135.8, 133.8, 133.0, 132.2, 130.9 (2C), 129.8, 129.2 (2C), 128.8, 128.7, 127.7, 127.4, 127.0, 126.5, 126.1.

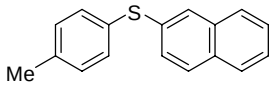


2-Phenylsulfanyl-benzothiazole (4o)[5]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.88 (d, J = 8.2 Hz, 1H), 7.74 (td, J = 7.0, 1.6 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.52−7.46 (m, 3H), 7.40 (dt, J = 8.0, 1.4 Hz, 1H), 7.25 (dt, J = 8.0, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.8, 135.4, 135.2 (2C), 132.6, 130.3, 129.8 (2C), 126.0, 124.4, 124.2, 121.8, 120.7.

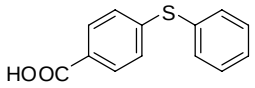


Di-*p*-tolylsulfide (4p); Mp 55–56 ^{o}C (lit.[8] 56.1 ^{o}C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.15 (d, J = 7.3

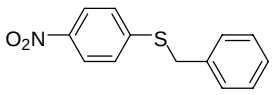
Hz, 4H), 7.02 (d, *J* = 7.3 Hz, 4H), 2.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 136.8 (2C), 132.6 (2C), 131.0 (4C), 129.8 (4C), 21.0 (2C).



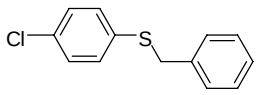
2'-Naphthalyl-4-tolyl sulfide (4q); Mp 66–67 °C (lit.[9] 66–67 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.73−7.05 (m, 11H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.3, 133.5, 132.5, 132.1, 130.0 (2C), 128.9 (2C), 128.4, 127.9, 127.7, 127.4, 126.7, 126.6, 126.2, 125.7, 21.1.



4-(phenylthio)benzoic acid (4r); Mp 173–174 °C (lit.[7] 172–173 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.51−7.49 (m, 2H), 7.40−7.38 (m, 3H),7.19 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.2, 145.8, 133.9, 131.7 (2C), 130.5 (2C), 129.6 (2C), 128.8 (2C), 127.0, 126.2.



Benzyl 4-nitrophenyl sulfide (4s)[11]; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10 (d, *J* = 9.2 Hz, 2H), 7.34 (d, *J* = 9.2 Hz, 2H), 7.37−7.30 (m, 5H), 4.25 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.1, 145.3, 135.4, 128.8 (2C), 128.6 (2C), 127.7, 126.7 (2C), 123.8 (2C), 37.1.



Benzyl 4-chlorophenyl sulfide (4t); Mp 50–51 °C (lit.[12] 47–49 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26−7.20 (m, 9H), 4.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 137.1, 134.6, 132.4, 131.4 (2C), 128.9 (2C), 128.7 (2C), 128.4 (2C), 127.2, 39.4.

References

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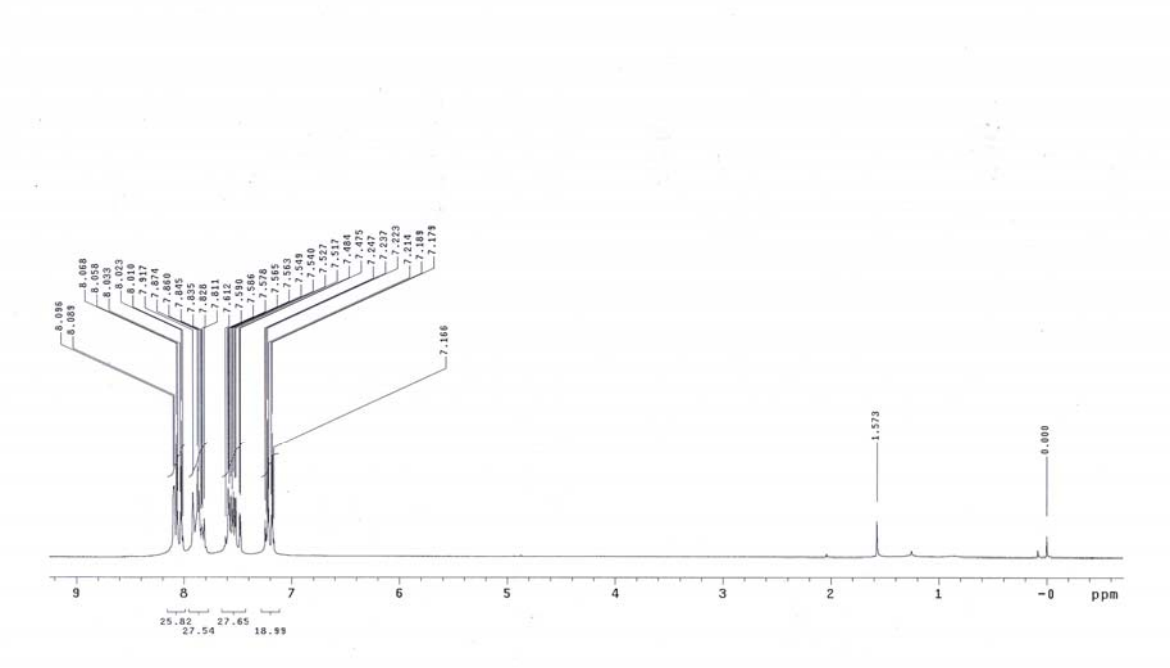
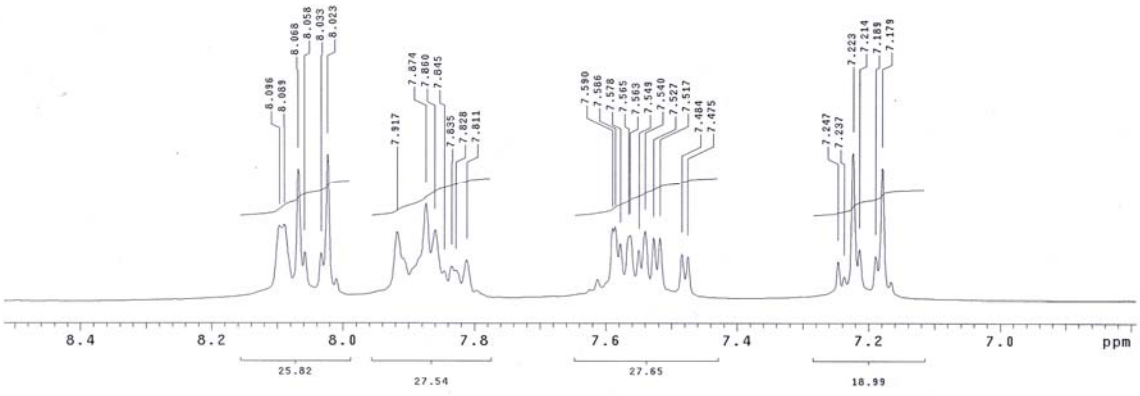
^{1}H NMR spectrum of 2'-Naphthalyl-4-nitrophenyl sulfide **(4d)**





^{13}C NMR spectrum of 2'-Naphthalyl-4-nitrophenyl sulfide **(4d)**