Supplementary Information

Ligand- free Cu-catalyzed odorless synthesis of unsymmetrical sulfides through cross-coupling reaction of aryl/benzyl/alkyl halides with aryl boronic acids/S\textsubscript{8} system as a thiolating agent in PEG

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1. Experimental Sections
1.1. General information
All materials were obtained from commercial sources and used as received. $^1$H NMR and $^{13}$C NMR spectra were recorded on 250 or 400 MHz at ambient temperature with CDCl$_3$ as the solvent. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent (CHCl$_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of the solvent (CDCl$_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

1.2. General procedure for the synthesis of unsymmetrical sulfides using aryl boronic acid and aryl/benzyl/alkyl halides:
A one-necked flask was charged with CuI (20-40 mg, 0.1-0.2 mmol), sodium hydroxide (160 mg, 4.0 mmol), S$_8$ (32 mg, 1 mmol), aryl/benzyl/alkyl halide (1 mmol), aryl boronic acid (1.1 mmol) and PEG200 (2 mL). The mixture was magnetically stirred and heated at 40-60 °C for the appropriate reaction time (Table 2). After completion of the reaction, the reaction mixture was cooled to room temperature and H$_2$O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent and purification by flash column chromatography on silica gel (EtOAc/n-hexane) gave the desired sulfides in 65-98% yields.
2. The Synthetic Procedure and Analytical Data for Table 2

A mixture of CuI (20 mg, 0.1 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), iodobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 40 °C for 4.5 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄. The mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 50:1) to afford the desired product diphenyl sulfide (Table 2, entry 1):¹ ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 7.2-7.3 ppm (m, 10 H); ¹³C NMR (100MHz, CDCl₃, 25 °C, TMS): δ= 127.5, 129.8, 131.6, 135.9 ppm.

A mixture of CuI (20 mg, 0.1 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-iodoanisol (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 9 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 30:1) to afford the desired product 4-methoxy diphenyl sulfide (Table 2, entry 3):² ¹H NMR (250 MHz, CDCl₃, 25 °C, TMS): δ= 4.2(s, 3H), 7.1-7.2 ppm (m, 5H), 7.3-7.6 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃, 25 °C, TMS): δ= 55.3, 116.3, 126.8, 127.4, 128.5, 129.4, 137.4, 138.2, 158.2 ppm.

A mixture of CuI (30 mg, 0.15 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-iodoanisol (1 mmol), p-tolyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 11 h. After the reaction was...
complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 30:1) to afford the desired product (4-methoxy phenyl) p-tolyl- sulfide (Table 4, entry 4):

δ 1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 2.3 ppm (s, 3H), 3.8 (s, 3H), 6.91 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 7.18, (d, J = 8.4 Hz, 2H), 7.41, (d, J = 7.6 Hz, 2H); δ 13C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ= 21.0, 55.3, 114.9, 125.6, 129.4, 129.8, 134.4, 136.1, 159.5 ppm.

A mixture of CuI (20 mg, 0.1 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-methyliodobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 50 °C for 9 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product 4-methyl diphenyl sulfide (Table 2, entry 5):

δ 1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 2.5 ppm (s, 3H), 7.1-7.4(m, 9H); δ 13C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ= 21.2, 126.1, 127.0, 127.7, 129.1, 129.4, 131.0, 133.6, 137.0 ppm.

A mixture of CuI (30 mg, 0.15 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-methyliodobenzene (1 mmol), p-tolylboronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 10 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product di-p-tolyl sulfide (Table 2, entry 6):

δ 1H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 2.25 ppm (s, 6H), 7.25 (d, J= 8, 4H), 7.34 (d, J= 8, 4H); δ 13C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ= 21.0, 128.5, 129.8, 131.1, 137.4 ppm.
A mixture of CuI (20 mg, 0.10 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 2-methyliodobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 12 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product 2-methyl diphenyl sulfide (Table 2, entry 7): ²¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 2.3 ppm (s, 3H), 7.1-7.4 (m, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ= 20.6, 126.3, 127.9, 128.8, 129.6, 130.4, 131.0, 133.0, 135.7, 137.0, 139.9 ppm.

A mixture of CuI (20 mg, 0.10 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-nitroiodobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 40 °C for 1.30 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 20:1) to afford the desired product 4-nitro diphenyl sulfide (Table 2, entry 8): ³¹H NMR (250 MHz, CDCl₃, 25 °C, TMS): δ= 7.0 ppm (d, 2H, J=7.5Hz), 7.3-7.4 (m, 5 H), 7.95 (d, 2H, J= 7.5 Hz); ¹³C NMR (62.9 MHz, CDCl₃, 25 °C, TMS): δ= 124.0, 126.6, 129.6, 130.0, 130.4, 134.7, 145.3, 148.5 ppm.

A mixture of CuI (20 mg, 0.10 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-nitroiodobenzene (1 mmol), p-tolylboronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 40 °C for 3 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was
evaporated under vacuum and purified by flash column chromatography (n-hexane/ethyl acetate 20:1) to afford the desired product (4-nitro phenyl) \( p \)-tolyl sulfide (Table 2, entry 9):\(^5\) \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 2.3 \text{ ppm (s, 3H), 7.14 (d, } J = 7.6 \text{ Hz, 2H) 7.29, (d, } J = 7.6 \text{ Hz, 2H) 7.45, (d, } J = 8 \text{ Hz, 2H) 8.06, (d, } J = 8 \text{ Hz, 2H); } \)\(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 21.3, 124.0, 126.1, 126.4, 130.9, 135.1, 140.2, 145.1, 149.4 \text{ ppm.}\)

A mixture of CuI (20 mg, 0.10 mmol), sodium hydroxide (160 mg, 4.0 mmol), \( S_8 \) (32 mg, 1 mmol), 4-nitryliodobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 40 °C for 2.30 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H\(_2\)O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na\(_2\)SO\(_4\). The mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane/ethyl acetate 20:1) to afford the desired product 4-nitryl diphenyl sulfide (Table 2, entry 6):\(^4\) \(^1\)H NMR (250 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 6.5-7.06 \text{ ppm (m, 5H), 7.31-7.9 (m, 4H); } \)\(^{13}\)C NMR (62.9 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 108.5, 118.8, 127.3, 129.4, 129.9, 130.8, 132.3, 132.8, 134.4, 145.7 \text{ ppm.}\)

A mixture of CuI (20 mg, 0.10 mmol), sodium hydroxide (160 mg, 4.0 mmol), \( S_8 \) (32 mg, 1 mmol), 4-nitryliodobenzene (1 mmol), \( p \)-tolylboronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 40 °C for 4 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H\(_2\)O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na\(_2\)SO\(_4\). The mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane/ethyl acetate 50:1) to afford the desired product (4-nitryl phenyl) \( p \)-tolyl sulfide (Table 2, entry 11):\(^3\) \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 2.4 \text{ ppm (s, 3H), 7.13 (d, } J = 8.4 \text{ Hz, 2H) 7.27 (d, } J = 8.4 \text{ Hz, 2H) 7.43-7.49, (m, 4H); } \)\(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 21.3, 108.2, 118.9, 126.6, 130.7, 132.6, 133.4, 134.9, 140.0, 146.6 \text{ ppm.}\)
A mixture of CuI (30 mg, 0.15 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), 4-chloro bromobenzene (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 21 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product 4-chloro diphenyl sulfide (Table 2, entry 20):

^1^H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ= 7.1-7.4 ppm (m, 9H); ^1^C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ= 125.6, 127.1, 127.4, 129.0, 131.0, 132.0, 135.7, 137.0 ppm.

A mixture of CuI (40 mg, 0.2 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), benzyl bromide (1 mmol), phenyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 11 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 50:1) to afford the desired product Benzyl (phenyl) sulfide (Table 2, entry 21):

^1^H NMR (250 MHz, CDCl₃, 25 °C, TMS): δ= 4.01 ppm (s, 2H), 7.18-7.22 (m, 10H). ^1^C NMR (62.9 MHz, CDCl₃, 25 °C, TMS): δ= 39.1, 126.5, 127.3, 127.5, 128.5, 128.9, 129.4, 129.8, 136.9, 137.7 ppm.

A mixture of CuI (40 mg, 0.2 mmol), sodium hydroxide (160 mg, 4.0 mmol), S₈ (32 mg, 1 mmol), benzyl bromide (1 mmol), p-tolyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 14 h. After the reaction was complete, the reaction mixture was cooled to room temperature and H₂O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na₂SO₄, the mixture was
evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product benzyl (p-tolyl) sulfide (Table 2, entry 22):$^6$ $^1$HNMR (250 MHz, CDCl$_3$, 25 °C, TMS): δ= 2.1 ppm (s, 3H), 3.94 (s, 2H), 6.96-6.92 (d, J= 8, 2H), 7.22-7.08 (m, 7H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, 25 °C, TMS): δ= 21.16, 39.79, 127.16, 128.51, 128.92, 129.10, 129.70, 130.71, 132.57, 136.58 ppm.

A mixture of CuI (40 mg, 0.2 mmol), sodium hydroxide (160 mg, 4.0 mmol), S$_8$ (32 mg, 1 mmol), 1-bromobutane (1 mmol), boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 12h. After the reaction was complete, the reaction mixture was cooled to room temperature and H$_2$O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na$_2$SO$_4$, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product butyl (phenyl) sulfide (Table 2, entry 23):$^6$ $^1$HNMR (250 MHz, CDCl$_3$, 25 °C, TMS): δ=0.79-0.85 ppm (t, J= 7.5, 3H), 1.32-1.36 (m, 2H), 1.39-1.57 (m, 2H), 2.79-2.95 (t, J= 7.25, 3H), 7.01 -7.25 (m, 5H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, 25 °C, TMS): δ=13.67, 21.99, 31.23, 33.23, 125.6, 128.81, 128.81, 137.07 ppm.

A mixture of CuI (40 mg, 0.2 mmol), sodium hydroxide (160 mg, 4.0 mmol), S$_8$ (32 mg, 1 mmol), 1-bromobutane (1 mmol), p-tolyl boronic acid (1.1 mmol) and PEG200 (2 mL) in a one-necked flask was heated at 60 °C for 14h. After the reaction was complete, the reaction mixture was cooled to room temperature and H$_2$O (4 mL) was added. The product was extracted with EtOAc (3×4 mL) and dried over anhydrous Na$_2$SO$_4$, the mixture was evaporated under vacuum and purified by flash column chromatography (n-hexane /ethyl acetate 40:1) to afford the desired product hexyl (4-methoxyphenyl) sulfide (Table 2, entry 24):$^6$ $^1$HNMR (250 MHz, CDCl$_3$, 25 °C, TMS): 0.83-0.78 (t, J= 7.25, 3H), 1.53-1.31 (m, 4H), 2.20 (s, 3H), 2.80-2.74 (t, J= 7.25, 2H), 6.99-6.96 (d, J= 8, 2H), 7.162-7.130 (d, J= 8, 2H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, 25 °C, TMS):, 13.69, 21.01, 21.97, 22.10, 31.37, 34.02, 129.62, 129.75, 133.22, 135.76.
References

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