Supporting Information

Copper-mediated cascade synthesis of diaryl sulfones via the Sandmeyer reaction

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**General experimental procedures**

All reactions were carried out under nitrogen atmosphere. Proton and carbon magnetic resonance spectra (1H NMR and 13C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl₃ as the internal standard (1H NMR: TMS at 0.00 ppm, CDCl₃ at 7.26 ppm; 13C NMR: CDCl₃ at 77.0 ppm) or tetramethylsilane (TMS) in the solvent of DMSO-d₆ as the internal standard (1H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; 13C NMR: DMSO at 40.0 ppm).

**Synthesis of compounds 2a-e.** Sodium arylsulfinate (5 mmol) was dissolved in the water (15 mL), and then the concentrated hydrochloric acid was dropped into the aqueous solution until pH = 2~3. The resulting solution was extracted with EtOAc three times (3 × 8 mL). The combined organic layer was dried over anhydrous NaSO₄, and the solvent was removed under reduced pressure to provide the compounds 2a-e.

**General procedure for synthesis of compounds 3a-u.** Arylamine (1) (0.5 mmol), Cu powder (1.5 mmol, 96 mg), arylsulfinic acid (2) (1.5 mmol) and acetonitrile (1 mL) were added to a dry Schlenk tube equipped with a magnetic stir bar, and then isoamyl nitrite (1.5 mmol, 175.5 mg) in 1 mL of acetonitrile was injected slowly into the tube at 0 °C under nitrogen atmosphere. After a 1 h stirring at this temperature, the tube was kept at room temperature for 11-23 h under nitrogen atmosphere. The resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel to provide the desired product (3a-u).

**Characterization data of compounds 3a-u**

**Sulfonyldibenzene (3a).** Eluent: petroleum ether/ethyl acetate (15:1). Yield 75 mg (69%). White solid, mp 123-125 °C (lit1. 122-124 °C). 1H NMR (CDCl₃, 300 MHz) δ 7.96 (m, 4H), 7.52 (m, 6H). 13C NMR (CDCl₃, 75 MHz) δ 141.6, 133.3, 129.4, 127.7. MS (ESI) [M+Na]⁺ m/z 241.2.
1-Methyl-4-(phenylsulfonyl)benzene (3b). Eluent: petroleum ether/ethyl acetate (15:1). Yield 83 mg (72%). White solid, mp 127-129 °C (lit.1 127-129 °C). 1H NMR (CDCl3, 400 MHz) δ 7.92 (d, 2H, J = 7.4 Hz), 7.82 (d, 2H, J = 8.3 Hz), 7.50 (m, 3H), 7.28 (d, 2H, J = 8.2 Hz), 2.38 (s, 3H). 13C NMR (CDCl3, 100 MHz) δ 144.3, 142.1, 138.7, 133.1, 130.0, 129.3, 127.8, 127.6, 127.2, 21.6. MS (ESI) [M+Na]+ m/z 255.1.

1-Methyl-2-(phenylsulfonyl)benzene (3c). Eluent: petroleum ether/ethyl acetate (15:1). Yield 59 mg (51%). Light yellow solid, mp 124-126 °C (lit.2 125-127 °C). 1H NMR (CDCl3, 400 MHz) δ 8.22 (m, 1H), 7.86 (m, 2H), 7.49 (m, 5H), 7.24 (m, 1H), 2.44 (s, 3H). 13C NMR (CDCl3, 100 MHz) δ 141.4, 138.9, 138.0, 133.7, 133.1, 132.7, 129.5, 129.1, 127.7, 126.6, 20.3. MS (ESI) [M+Na]+ m/z 255.0.

1-(tert-Butyl)-4-(phenylsulfonyl)benzene (3d). Eluent: petroleum ether/ethyl acetate (15:1). Yield 100 mg (74%). Light yellow solid, mp 123-124 °C (lit.1 127-128 °C). 1H NMR (CDCl3, 400 MHz) δ 7.94 (m, 2H), 7.84 (m, 2H), 7.49 (m, 5H), 7.24 (m, 1H), 35.3, 31.1. MS (ESI) [M+Na]+ m/z 297.4.

1-Methoxy-4-(phenylsulfonyl)benzene (3e). Eluent: petroleum ether/ethyl acetate (7:1). Yield 77 mg (62%). Light yellow solid, mp 86-87 °C (lit.1 92-93 °C). 1H NMR (CDCl3, 400 MHz) δ 7.87 (m, 4H), 7.47 (m, 2H), 6.93 (d, 1H, J = 9.1 Hz), 3.80 (s,
1-Fluoro-4-(phenylsulfonyl)benzene (3f). Eluent: petroleum ether/ethyl acetate (15:1). Yield 72 mg (61%). White solid, mp 114-115 °C (lit.1 112-113 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.95 (m, 4H), 7.53 (m, 3H), 7.17 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.5 (J = 254.5 Hz), 141.5, 137.8, 133.4, 130.5 (J = 9.5 Hz), 129.5, 127.6, 116.6 (J = 21.9 Hz). MS (ESI) [M+Na]+ m/z 259.1.

1-Chloro-4-(phenylsulfonyl)benzene (3g). Eluent: petroleum ether/ethyl acetate (15:1). Yield 66 mg (53%). White solid, mp 94-96 °C (lit.1 96-97 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.91 (m, 4H), 7.52 (m, 5H). ¹³C NMR (CDCl₃, 100 MHz) δ 141.3, 140.2, 139.9, 133.5, 129.7, 129.5, 129.2, 127.7. MS (ESI) [M+Na]+ m/z 275.1.

4,4'-Sulfonylbis(methylbenzene) (3h). Eluent: petroleum ether/ethyl acetate (15:1). Yield 101 mg (82%). White solid, mp 158-160 °C (lit.2 158-159 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.80 (d, 1H, J = 8.7 Hz), 7.27 (d, 1H, J = 7.8 Hz), 2.38 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 144.0, 139.1, 129.9, 127.6, 21.6. MS (ESI) [M+Na]+ m/z 269.2.

1-(tert-Butyl)-4-tosylbenzene (3i). Eluent: petroleum ether/ethyl acetate (15:1). Yield 98 mg (68%). White solid, mp 80-81 °C (lit.4 78-79 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.83 (m, 4H), 7.48 (m, 2H), 7.28 (d, 2H, J = 8.2 Hz), 2.38 (s, 3H), 1.30 (s, 9H). ¹³C
NMR (CDCl₃, 100 MHz) δ 156.9, 144.0, 139.0, 129.9, 127.7, 127.4, 126.5, 114.9, 35.2, 31.1, 21.6. MS (ESI) [M+H]+ m/z 289.6.

1-Methoxy-4-tosylbenzene (3j). Eluent: petroleum ether/ethyl acetate (7:1). Yield 106 mg (81%). White solid, mp 102-103 °C (lit.² 101 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (m, 2H), 7.79 (m, 2H), 7.27 (m, 2H), 6.94 (m, 2H), 3.82 (s, 3H), 2.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 163.3, 143.8, 139.5, 133.6, 129.9, 129.8, 127.4, 114.5, 55.7, 21.6. MS (ESI) [M+Na]+ m/z 285.2.

1-Fluoro-4-tosylbenzene (3k). Eluent: petroleum ether/ethyl acetate (15:1). Yield 61 mg (49%). White solid, mp 85-87 °C (lit.³ 83-85 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.94 (m, 2H), 7.81 (m, 2H), 7.30 (d, 2H, J = 8.3 Hz), 7.15 (m, 2H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.4(J = 253.6 Hz), 144.4, 138.6, 138.2, 130.3(J = 9.5 Hz), 130.1, 127.7, 127.2, 116.5(J = 22.9 Hz), 21.6. MS (ESI) [M+Na]+ m/z 273.1.

1-Chloro-4-tosylbenzene (3l). Eluent: petroleum ether/ethyl acetate (15:1). Yield 102 mg (77%). Light yellow solid, mp 118-120 °C (lit.⁴ 119-120 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.84 (m, 4H), 7.44 (m, 2H), 7.29 (d, 2H, J = 8.2 Hz), 2.39 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 145.1, 141.1, 140.2, 138.8, 130.6, 130.1, 129.5, 128.2, 22.1. MS (ESI) [M+Na]+ m/z 289.0.

1-(tert-Butyl)-4-((4-chlorophenyl)sulfonyl)benzene (3m). Eluent: petroleum
ether/ethyl acetate (15:1). Yield 106 mg (69%). White solid, mp 140-142 °C. ¹H NMR (CDCl₃, 400 MHz) δ 7.86 (m, 4H), 7.51 (d, 2H, J = 8.3 Hz), 6.97 (d, 2H, J = 8.2 Hz), 1.31 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 157.5, 140.6, 139.7, 138.2, 129.6, 129.1, 127.6, 126.5, 35.3, 31.1. MS (ESI) [M+Na]⁺ m/z 331.1.

![3n](image)

1-Chloro-4-((4-methoxyphenyl)sulfonyl)benzene (3n). Eluent: petroleum ether/ethyl acetate (7:1). Yield 91 mg (65%). Light yellow solid, mp 99-100 °C (lit.⁶ 103-104 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (m, 4H), 7.45 (m, 2H), 6.97 (m, 2H), 3.84 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 163.7, 141.0, 139.5, 132.7, 129.9, 129.6, 128.9, 114.7, 55.8. MS (ESI) [M+Na]⁺ m/z 305.1.

![3o](image)

1-Chloro-4-((4-fluorophenyl)sulfonyl)benzene (3o). Eluent: petroleum ether/ethyl acetate (15:1). Yield 85 mg (63%). White solid, mp 114-115 °C (lit.⁵ 113 °C). ¹H NMR (CDCl₃, 400 MHz) δ 7.96 (m, 2H), 7.90 (m, 2H), 7.48 (m, 2H), 7.19 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.6(J = 255.5 Hz), 140.1, 137.4, 130.5(J = 9.5 Hz), 129.8, 129.1, 116.8(J = 21.9 Hz). MS (ESI) [M+Na]⁺ m/z 293.1.

![3p](image)

1-(Phenylsulfonyl)-4-(trifluoromethyl)benzene (3p). Eluent: petroleum ether/ethyl acetate (15:1). Yield 100 mg (70%). White solid, mp 91-92 °C (lit.¹ 90-91 °C). ¹H NMR (CDCl₃, 400 MHz) δ 8.08 (d, 2H, J = 8.2 Hz), 7.96 (m, 2H), 7.76 (d, 2H, J = 8.2 Hz), 7.58 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 145.8, 141.1, 135.2(J = 32.4 Hz), 134.3, 130.1, 128.8, 128.4, 126.9(J = 3.8 Hz), 123.6(J = 271.7 Hz). MS (ESI) [M+Na]⁺ m/z 309.1.
1-Methyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)benzene (3q). Eluent: petroleum ether/ethyl acetate (15:1). Yield 74 mg (49%). White solid, mp 114-115 °C (lit. 105-107 °C). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.05 (d, 2H, \(J = 8.2\) Hz), 7.84 (d, 2H, \(J = 7.8\) Hz), 7.75 (d, 2H, \(J = 8.2\) Hz), 7.32 (d, 2H, \(J = 8.3\) Hz), 2.41 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 146.2, 145.5, 138.2, 135.1 (\(J = 33.4\) Hz), 130.7, 128.6, 128.5, 126.9 (\(J = 2.9\) Hz), 123.7 (\(J = 271.7\) Hz), 22.1. MS (ESI) [M+Na]+ m/z 323.1.

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1-(tert-Butyl)-4-((4-(trifluoromethyl)phenyl)sulfonyl)benzene (3r). Eluent: petroleum ether/ethyl acetate (15:1). Yield 80 mg (47%). White solid, mp 133-135 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.08 (d, 2H, \(J = 8.2\) Hz), 7.88 (m, 2H), 7.76 (d, 2H, \(J = 7.4\) Hz), 7.55 (m, 2H), 1.31 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 158.1, 145.8, 137.7, 134.9 (\(J = 32.4\) Hz), 128.4, 128.0, 126.8, 126.6 (\(J = 3.8\) Hz), 123.4 (\(J = 276.5\) Hz), 35.5, 31.2. MS (ESI) [M+Na]+ m/z 365.1.

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1-Methoxy-4-((4-(trifluoromethyl)phenyl)sulfonyl)benzene (3s). Eluent: petroleum ether/ethyl acetate (7:1). Yield 82 mg (52%). White solid, mp 100-101 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.04 (d, 2H, \(J = 8.2\) Hz), 7.89 (d, 2H, \(J = 8.7\) Hz), 7.74 (d, 2H, \(J = 8.7\) Hz), 6.99 (m, 2H), 3.85 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 163.8, 145.9, 134.3 (\(J = 33.4\) Hz), 131.8, 130.1, 127.8, 126.3 (\(J = 3.8\) Hz), 123.1 (\(J = 276.5\) Hz), 114.7, 55.7. MS (ESI) [M+Na]+ m/z 339.1.

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1-Fluoro-4-((4-(trifluoromethyl)phenyl)sulfonyl)benzene (3t). Eluent: petroleum ether/ethyl acetate (15:1). Yield 79 mg (49%). White solid, mp 125-126 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.10 (d, 2H, \(J = 8.2\) Hz), 7.88 (d, 2H, \(J = 8.7\) Hz), 7.75 (d, 2H, \(J = 8.2\) Hz), 7.32 (d, 2H, \(J = 8.3\) Hz), 2.41 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 146.2, 145.5, 138.2, 135.1 (\(J = 33.4\) Hz), 130.7, 128.6, 128.5, 126.9 (\(J = 2.9\) Hz), 123.7 (\(J = 271.7\) Hz), 22.1. MS (ESI) [M+Na]+ m/z 324.1.

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ether/ethyl acetate (15:1). Yield 110 mg (73%). White solid, mp 116-117 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.07 (d, 2H, J = 8.2 Hz), 7.98 (m, 2H), 7.77 (d, 2H, J = 8.2 Hz), 7.21 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 166.3 (J = 255.5 Hz), 145.6, 137.2 (J = 2.9 Hz), 135.5(J = 32.4 Hz), 131.3(J = 10.5 Hz), 128.7, 127.0(J = 3.8 Hz), 123.6(J = 271.7 Hz), 117.4 (J = 22.9 Hz). MS (ESI) [M+Na]⁺ m/z 327.1.

1-Fluoro-4-((4-nitrophenyl)sulfonyl)benzene (3u). Eluent: petroleum ether/ethyl acetate (10:1). Yield 85 mg (61%). Yellow solid, mp 149-151 °C. ¹H NMR (CDCl₃, 400 MHz) δ 8.35 (m, 2H), 8.13 (m, 2H), 8.01 (m, 2H), 7.24 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 166.1 (J = 256.5 Hz), 150.5, 147.2, 136.1, 131.0 (J = 10.5 Hz), 129.0, 124.9, 117.2(J = 22.9 Hz). MS (ESI) [M+Na]⁺ m/z 304.1.

References

The $^1$H and $^{13}$C NMR spectra of compounds 3a-u