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Supporting information

Nano-Pd catalyzed synthesis of sulfoxides and sulfones from symmetrical and unsymmetrical sulfides obtained *via* the reaction of diazonium tetrafluoroborate with Na₂S·9H₂O

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1 General

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. Deuterated solvents were purchased from Sigma-Aldrich. Column chromatography was performed on silica gel (200-300 mesh) with petroleum ether (solvent A)/ethyl acetate (solvent B) gradients, unless otherwise specified. The microwave reactions were carried out by using MC8S-3 microwave instrument. All yields were referred to isolated yields (average of two runs) of compounds. The known compounds were partly characterized by melting points (for solid samples), ¹H NMR, and compared to authentic samples or the literature data. Melting points were measured with a RD-II digital melting point apparatus and are uncorrected. ¹H NMR data were acquired at 300 K on a Bruker Advance 600 III MHz spectrometer or Avarian Inova 500 MHz spectrometer using CDCl₃ as a solvent. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (¹H NMR TMS at 0.00 ppm, CHCl₃ at 7.26 ppm; ¹³C{¹H} NMR CDCl₃ at 77.16 ppm). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. New compounds were further characterized by HRMS. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer.

2 General procedures

2.1 General procedure for the preparation of the nano-Pd catalyst

A mixture of $Pd(PPh_3)_4$ (260 mg, 0.225 mmol), tetra(ethylene glycol) (418 mg, 2.20 mmol), 1butanol (3 mL, 32.7 mmol), and aluminum tri-sec-butoxide (9.50 g, 38.5 mmol) was stirred at 110 °C for 10 h. Then water was dropwise added and the system was stirred at 110 °C for another 0.5 h to form a black gel. Subsequently, filtering, washing with acetone, and drying the gel gave the nano-Pd catalyst **1** at room temperature as dark greyish-green powder (See Scheme 1).



Scheme 1. Preparation of the palladium nanoparticles catalyst 1.

2.2 General procedure for the synthesis of symmetrical sulfides under microwave

The mixture of phenyl diazonium tetreafluoroborate (38.5 mg, 0.2 mmol), and Na₂S·9H₂O (53.2 mg, 1.1 equiv.) in water (1.0 mL) was heated under microwave irradiation (300 W, 100 °C) until the starting material was consumed which was determined by TLC. The reaction system was then extracted with ethyl acetate (3×10 mL), and the combined organic phase was dried over anhydrous Na₂SO₄. At last, the organic extracts were concentrated in vacuum and the resulting mixture was purified by column chromatography on silica gel with petroleum ether as an eluent to afford the pure product **3a**.

2.3 General procedure for the synthesis of symmetrical disulfides promoted by FeCl₃

To the mixture system of phenyl diazonium tetrafluoroborate (38.5 mg, 0.2 mmol) and FeCl₃ (39.1 mg, 0.24 mmol, 1.2 equiv) in CH₃OH (1.0 mL) was added Na₂S·9H₂O (53.2 mg, 1.1 equiv.) slowly at 0 °C. The reaction mixture was then stirred, and the temperature rose to room temperature naturally. The stirring continued until no substrate could be detected by TLC. After the solvent CH₃OH was removed under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether as an eluent to afford the direct cross-coupling product diphenyl disulfide **4a**.

2.4 General procedure for the synthesis of asymmetrical sulfides via the cross-coupling of

disulfides with aryl diazonium tetrafluoroborate

To the mixture system of *p*-MeO-phenyl diazonium tetrafluoroborate (44.5 mg, 0.2 mmol) and K_2CO_3 (27.7 mg 0.2 mmol) in CH₃CN (1.0 mL) was added diphenyl disulfide (39.3 mg, 0.18 mmol) under N₂ atmosphere at 25 °C. The reaction mixture was then stirred until no substrate could be detected by TLC. The resulting mixture was purified by column chromatography on

silica gel with petroleum ether as an eluent to afford the direct cross-coupling product (4-methoxyphenyl)(phenyl)sulfide **5a**.

2.5 General procedure for oxidation of symmetric sulfides to sulfoxides with H₂O₂

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), symmetric diphenyl sulfide (0.2 mmol) and 30% H_2O_2 (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 60 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting product was purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product **6a**.

2.6 General procedure for oxidation of asymmetric sulfides to sulfoxides with H₂O₂

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), asymmetric sulfide (0.2 mmol), 30% H_2O_2 (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 60 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting mixture was purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product 7.

2.7 General procedure for the symmetrical and asymmetric sulfides to sulfones

The mixture of nano Pd catalyst (4.1 mg, 0.12 mol% Pd), diphenyl disulfide (10 mol%) symmetric or asymmetric sulfide (0.2 mmol), 30% H₂O₂ (0.2 mL, 10 equiv.) in methanol (1.0 mL) was stirred at 100 °C until the starting material was consumed which was determined by TLC. After the solvent CH₃OH was removed under reduced pressure, the resulting mixture was purified by column chromatography on silica gel with ethyl acetate and petroleum ether as eluents to afford the pure product **8**.

3 Characterization data for the corresponding products

Part 1: symmetric sulfides

Diphenyl sulfide^[1, 2, 3] (**3a**, **5a**) Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.35-7.33 (m, 4H, Ar-H), 7.31 (t, *J* = 7.4 Hz, 4H, Ar-H), 7.25 (tt, *J* = 7.1, 2.1 Hz, 2H, Ar-H) ppm.



Di-p-tolylsulfide^[1, 2, 3] (**3b**)

White solid; M.p.: 57 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.23 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.15 (d, *J* = 8.0 Hz, 4H, Ar-H), 2.32 (s, 6H, Me-H) ppm.



Di-*m*-tolylsulfide^[3] (3c)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.20-7.17 (m, 4H, Ar-H), 7.13 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.05 (d, *J* = 7.6 Hz, 2H, Ar-H), 2.31 (d, *J* = 6.4 Hz, 6H, Me-H) ppm.



Di-*o***-tolylsulfide**^[1, 2] (**3d**)

White solid; M.p.: 64 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.24 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.18 (td, *J* = 7.3, 1.4 Hz, 2H, Ar-H), 7.11 (td, *J* = 8.1, 1.2 Hz, 2H, Ar-H), 7.06 (dd, *J* = 7.7, 2.0 Hz, 2H, Ar-H), 2.38 (s, 6H, Me-H) ppm.



White solid; M.p.: 44 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.28-7.26 (m, 4H, Ar-H), 6.85 (d, *J* = 8.8 Hz, 4H, Ar-H), 3.79 (s, 6H, OMe-H) ppm.

Bis(3-methoxyphenyl)sulfide^[1, 3] (3f)

White solid; M.p.: 45-47 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.22-7.19 (m, 2H, Ar-H), 6.94-7.92 (m, 2H, Ar-H), 6.90-6.89 (m, 2H, Ar-H), 6.80-6.78 (m, 2H, Ar-H), 3.76 (s, 6H, OMe-H) ppm.



Bis(2-methoxyphenyl)sulfide^[1, 3] (**3g**)

White solid; M.p.: 73-74 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.27-7.22 (m, 2H, Ar-H), 7.07 (dd,

J = 7.7, 1.7 Hz, 2H, Ar-H), 6.93-6.90 (m, 2H, Ar-H), 6.89 (td, *J* = 7.5, 1.2 Hz, 2H, Ar-H), 3.87 (s, 6H, OMe-H) ppm.



Bis(4-nitrophenyl)sulfide^[1, 2] (**3h**)

White solid; M.p.: 156 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 8.07 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.55-7.53 (m, 2H, Ar-H), 7.46-7.45 (m, 2H, Ar-H), 7.18 (d, *J* = 9.0 Hz, 2H, Ar-H) ppm.



Bis(3-nitrophenyl)sulfide^[7] (3i)

White solid; M.p.: 42 °C; ¹H NMR (400 MHz, CDCl₃): *δ* = 8.37 (t, *J* = 4.0 Hz, 2H, Ar-H), 8.12-8.10 (m, *J* = 8.4 Hz, 2H, Ar-H), 7.83-7.80 (m, *J* = 8.0 Hz, 2H, Ar-H), 7.53 (t, *J* = 16.0 Hz, 2H, Ar-H) ppm.



Bis(2-nitrophenyl)sulfide^[1, 8] (3j)

Yellow solid; M.p.: 123-124 °C; ¹H NMR (400 MHz, CDCl₃); *δ* = 8.06-8.09 (m, 2H, Ar-H), 7.79-7.84 (m, 2H, Ar-H), 7.63-7.76 (m, 2H, Ar-H), 7.56-7.60 (m, 2H, Ar-H) ppm.



Bis(4-fluorophenyl)sulfide^[1, 3] (3k)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.32-7.29 (m, 4H, Ar-H), 7.02-6.99 (m, 4H, Ar-H) ppm.

Bis(3-fluorophenyl)sulfide^[3] (3l)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.31-7.27 (m, 2 H, Ar-H), 7.14-7.12 (m, 2H, Ar-H), 7.05 (dt, *J* = 9.1, 2.2 Hz, 2H, Ar-H), 6.99-6.95 (m, 2H, Ar-H) ppm.

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Bis(2-fluorophenyl)sulfide^[12] (3m)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.30-7.24 (m, 4 H, Ar-H), 7.12-7.08 (m, 4H, Ar-H) ppm.

Bis(4-clorophenyl)sulfide^[1, 8] (3n)

White solid; M.p.: 88-89 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.29-7.23 (m, 8H, Ar-H) ppm.

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Bis(3-fluorophenyl)sulfide^[8] (30)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.32-7.31 (m, 2H, Ar-H), 7.25-7.24 (m, 4H, Ar-H), 7.22-7.21 (m, 2H, Ar-H) ppm.



Bis(2-clorophenyl)sulfide^[3] (3p)

White solid; M.p.: 68-70 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.47 (dd, *J* = 7.9, 1.3 Hz, 2H, Ar-H), 7.25 (td, *J* = 7.8, 1.7 Hz, 2H, Ar-H). 7.21 (td, *J* = 7.8, 1.3 Hz, 2H, Ar-H), 7.15 (dd, *J* = 7.8, 1.7 Hz, 2H, Ar-H) ppm.



Bis(4-bromophenyl)sulfide^[1, 2] (3q)

White solid; M.p.: 110-111 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.44-7.42 (m, 4H, Ar-H), 7.20-7.17 (m, 4H, Ar-H) ppm.

Part 2: symmetric disulfides



Diphenyldisulfide^[4, 5] (4a)

White solid; M.p.: 58-60 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.51-7.49 (m, 4H, Ar-H), 7.31-7.29

(m, 4H, Ar-H), 7.24 (tt, *J* = 7.3, 1.8 Hz, 2H, Ar-H) ppm.



Di(p-methylphenyl)disulfide^[4, 5] (4b)

White solid; M.p.: 48-50 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.43 (d, *J* = 8.1 Hz, 4 H, Ar-H), 7.16 (q, *J* = 7.7 Hz, 4 H, Ar-H), 2.34 (s, 6H, Me-H) ppm.



Di(*m*-methylphenyl)disulfide^[4] (4c)

White solid; M.p.: 112-113 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.38 (t, *J* = 6.8 Hz, 4 H, Ar-H), 7.19 (t, *J* = 7.7 Hz, 4 H, Ar-H), 7.08 (d, *J* = 7.6 Hz, 2 H, Ar-H), 2.32 (s, *J* = 6.4 Hz, 6H, Me-H) ppm.



Di(*o*-methylphenyl)disulfide^[4, 5] (4d)

White solid; M.p.: 40 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.16-7.18 (m, Ar-H), 7.13-7.15 (m, Ar-H), 7.08 (td, *J* = 6.0, 1.2 Hz, 2H, Ar-H), 7.04 (dd, *J* = 6.0, 1.8 Hz, 2H, Ar-H), 2.37 (s, 6H, Me-H) ppm.



Di(4-methoxyphenyl)disulfide^[5, 6] (4e)

White solid; M.p.: 45-47 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.28-7.26 (m, 4 H, Ar-H), 6.84-6.82 (m, 4 H, Ar-H), 3.78 (s, 6 H, OMe-H) ppm.



Di(3-methoxyphenyl)disulfide^[5, 6] (4f)

White solid; M.p.: 106-107 °C; ¹H NMR (400 MHz, CDCl₃); *δ* = 7.12-7.16 (m, 2H, Ar-H), 6.99-7.03 (m, 2H, Ar-H), 6.82-6.88 (m, 2H, Ar-H), 6.67-6.73 (m, 2H, Ar-H), 3.69 (s, 6H, OMe-H) ppm.



Di(2-methoxyphenyl)disulfide^[13, 14] (**4g**)

White solid; M.p.: 120-121 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.53 (d, 2 H, *J* = 1.6 Hz, Ar-H), 7.19-7.17 (m, 2 H, Ar-H), 6.92-6.89 (m, 2 H, Ar-H), 6.86-6.83 (m, 2 H, Ar-H), 3.89 (s, 6 H, OMe-H) ppm.



Bis(4-fluorophenyl)disulfide^[4, 5] (4h)

White solid; M.p.: 50-52 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.32-7.29 (m, 4 H, Ar-H), 7.02-6.99 (m, 4 H, Ar-H) ppm.



Bis(3-fluorophenyl)disulfide^[6] (4i)

Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): δ = 7.31-7.27 (m, 2 H, Ar-H), 7.14-7.12 (m, 2 H, Ar-H), 7.05 (dt, *J* = 9.1, 2.2 Hz, 2H, Ar-H), 6.99-6.95 (m, 2H, Ar-H) ppm.



Bis(2-fluorophenyl)disulfide^[14] (4j)

Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.60 (td, 2 H, *J* = 7.7, 1.7 Hz, Ar-H), 7.28-7.25 (m, 2H, Ar-H), 7.13 (td, 2 H, *J* = 7.7, 1.2 Hz, Ar-H), 7.08-7.04 (m, 2H, Ar-H) ppm.



Bis(4-clorophenyl)disulfide^[4, 5, 6] (4k)

White solid; M.p.: 68-70 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.41-7.39 (m, 4 H, Ar-H), 7.29-7.27 (m, 4 H, Ar-H) ppm.



White solid; M.p.: 80-82 °C; ¹H NMR (400 MHz, CDCl₃): *δ* = 7.31 (s, 2 H, Ar-H), 7.24-7.22 (m, 6H, Ar-H) ppm.

Bis(4-bromophenyl)disulfide^[6, 8] (4n)

White solid; M.p.: 110-111 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.43-7.41 (m, 4 H, Ar-H), 7.34-7.32 (m, 4 H, Ar-H) ppm.



Slight yellow solid; M.p.: 185-186 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.19 (d, *J* = 8.8 Hz, 4 H, Ar-H), 7.61 (d, *J* = 9.2 Hz, 4 H, Ar-H) ppm.



Bis(3-nitrophenyl)disulfide^[8] (4p)

Yellow solid; M.p.: 78-80 °C; ¹H NMR (600 MHz, CDCl₃); δ = 8.36 (t, *J* = 1.8 Hz, 2H, Ar-H), 8.09 (dt, *J* = 6.0, 1.2 Hz, 2H, Ar-H), 7.79 (dq, *J* = 5.4, 0.6 Hz, 2H, Ar-H), 7.51 (t, *J* = 7.8 Hz, 2H, Ar-H) ppm.



Bis(2-nitrophenyl)disulfide^[5] (4q)

Yellow solid; M.p.: 193-194 °C; ¹H NMR (400 MHz, CDCl₃); *δ* = 8.33 (d, *J* = 8,0 Hz, 2H, Ar-H), 7.86 (dd, *J* = 7.2, 1.2 Hz, 2H, Ar-H), 7.60 (td, *J* = 6.0, 1.2 Hz, 2H, Ar-H), 7.42 (td, *J* = 7.2, 1.2 Hz, 2H, Ar-H) ppm.

Part 3: asymmetric sulfides



(4-Methoxyphenyl)(phenyl)sulfide^[1, 2] (5b, 5n)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.42 (d, J = 8.7 Hz, 2H, Ar-H), 7.25-7.21 (m,

2H, Ar-H), 7.18-7.16 (m, 2H, Ar-H), 7.14-7.11 (m, 1H, Ar-H), 6.90 (d, *J* = 8.8 Hz, 2H, Ar-H), 3.81 (s, 3H, OMe-H) ppm.



(2-Methoxyphenyl)(phenyl)sulfide^[11] (5c, 5o)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.36-7.34 (m, 2H, Ar-H), 7.32-7.29 (m, 2 H, Ar-H), 7.26-7.22 (m, 2H, Ar-H), 7.09-7.07 (m, 1H, Ar-H), 6.91 (dd, *J* = 8.2, 1.1 Hz, 1H, Ar-H), 6.88 (td, *J* = 7.6, 1.3 Hz, 1 H, Ar-H), 3.87 (s, 3H, OMe-H) ppm.



Phenyl(*p*-tolyl)sulfide^[1, 2] (5d)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.31 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.26 (d, *J* = 4.4 Hz, 4H, Ar-H), 7.20-7.17 (m, 1H, Ar-H), 7.14 (d, *J* = 8.5 Hz, 2H, Ar-H), 2.34 (s, 3H, Me-H) ppm.



Phenyl(*m*-tolyl)sulfide^[15] (5e)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.20-7.17 (m, 4 H, Ar-H), 7.13 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.05 (d, *J* = 7.6 Hz, 2H, Ar-H), 2.31 (d, *J* = 6.4 Hz, 3H, Me-H) ppm.



(4-Fluorophenyl)(phenyl)sulfide^[9] (5f)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.50-7.49 (m, 2 H, Ar-H), 7.39-7.36 (m, 1 H, Ar-H), 7.32-7.27 (m, 4H, Ar-H), 7.24-7.22 (m, 2H, Ar-H) ppm.



(3-Fluorophenyl)(phenyl)sulfide^[10] (5g)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.51-7.49 (m, 1H, Ar-H), 7.43-7.42 (m, 2H, Ar-H), 7.43-7.42 (m, 2H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.24-7.21 (m, 1H, Ar-H), 7.05 (dq, *J* = 7.9, 1.1 Hz, 1H, Ar-H), 6.94 (dt, *J* = 9.4, 2.4 Hz, Ar-H), 6.90 (tq, *J* = 8.5, 1.0 Hz, 2H, Ar-H) ppm.



(2-Fluorophenyl)(phenyl)sulfide^[10] (5h)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.35-7.30 (m, 4H, Ar-H), 7.27-7.24 (m, 3H, Ar-H), 7.12-7.06 (m, 2H, Ar-H) ppm.



(4-Nitrophenyl)(phenyl)sulfide^[2, 9] (5i, 5p)

Slight yellow solid; M.p.: 56-57 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 8.07 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.00 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H, Ar-H), 7.50-7.46 (m, 3H, Ar-H), 7.42-7.39 (m, 4H, Ar-H) ppm.



(3-Nitrophenyl)(phenyl)sulfide^[16] (5j, 5q)

Slight yellow solid; M.p.: 42-44 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 8.03 (t, *J* = 8.9 Hz, 2H, Ar-H), 7.55-7.54 (m, 2H, Ar-H), 7.46-7.45 (m, 3H, Ar-H), 7.18-7.17 (m, 2H, Ar-H) ppm.



(4-Clorophenyl)(phenyl)sulfide^[1, 2] (5k)

White solid; M.p.: 64-66 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.35-7.30 (m, 4H, Ar-H), 7.28-7.24 (m, 5H, Ar-H) ppm.



(4-Bromophenyl)(phenyl)sulfide^[2] (5l)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.42-7.39 (m, 2H, Ar-H), 7.36-7.32 (m, 4H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.18-7.16 (m, 2H, Ar-H) ppm.



(2-Naphyl)(phenyl)sulfide^[9] (5m)

White solid; M.p.: 41-42 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.38-8.37 (m, 1H, Ar-H), 7.88-7.85

(m, 2H, Ar-H), 7.67 (dd, *J* = 7.1, 1.1 Hz, 1 H, Ar-H), 7.52 (q, *J* = 3.2 Hz, 2H, Ar-H), 7.44 (t, *J* = 7.7 Hz, 1H, Ar-H), 7.23-7.20 (m, 2H, Ar-H), 7.19-7.17 (m, 2H, Ar-H), 7.16-7.13 (m, 1H, Ar-H) ppm.

Ethyl(phenyl)sulfane^[18, 26] (5r)

Slight yellow liquid; ¹H NMR (400 MHz, CDCl₃); *δ* = 7.32 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.18-7.15 (t, *J* = 7.2 Hz, 1H, Ar-H), 2.97 (q, *J* = 7.6 Hz, 2 H, CH₂), 1.33 (t, *J* = 7.6 Hz, 3H, CH₃) ppm.



(3-Methylbut-2-en-1-yl)(phenyl)sulfane^[19, 26] (5s)

Slight yellow liquid; ¹H NMR (400 MHz, CDCl₃); δ = 7.87 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.68-7.63 (m, 1H, Ar-H), 7.58-7.54 (m, 2H, Ar-H), 5.85-5.74 (m, 1H), 5.35 (dd, *J* = 9.2, 1.2 Hz, 1H), 5.18 (dd, *J* = 16, 1.2 Hz, 1H, CH₂-H), 3.82 (d, *J* = 7.6 Hz, 2 H, CH₂) ppm.

Part 4: symmetric sulfoxides

Diphenyl-sulfoxide^[20, 22] (6a)

White solid; M.p.: 72-74 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.66-7.64 (m, 4H, Ar-H), 7.47-7.43 (m, 6H, Ar-H) ppm.

Di-p-tolylsulfoxide^[20] (6b)

White solid; M.p.: 93-94 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.52 (d, *J* = 8.2 Hz, 4H, Ar-H), 7.26 (t, *J* = 8.0 Hz, 4H, Ar-H), 2.36 (s, 6H, Me-H) ppm.

Di-m-tolylsulfoxide^[12] (6c)

Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): δ = 7.48 (s, 2 H, Ar-H), 7.42 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.34 (t, *J* = 7.7 Hz, 2H, Ar-H), 7.23 (d, *J* = 7.6 Hz, 2H, Ar-H), 2.37 (s, 6H, Me-H) ppm.



Di-*o***-tolylsulfoxide**^[12] (6d)

Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): δ = 7.70 (dd, *J* = 7.0, 2.2 Hz, 2H Ar-H), 7.38-7.33 (m, 4H, Ar-H), 7.20 (dd, *J* = 6.9, 1.6 Hz, 2H, Ar-H), 2.41 (s, 6H, Me-H) ppm.



Bis(4-methoxyphenyl)sulfoxide^[20] (6e)

White solid; M.p.: 200-202 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.54-7.52 (m, 4H, Ar-H), 6.97–6.94 (m, 4H, Ar-H), 3.82 (s, 6H, OMe-H) ppm.



Bis(2-methoxyphenyl)sulfoxide^[12] (6f)

White solid; M.p.: 96-97 °C; ¹H NMR (400 MHz, CDCl₃): *δ* = 7.66 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.39 (t, *J* = 7.6 Hz, 2H, Ar-H), 7.05 (t, *J* = 7.5 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.81 (s, 6H, OMe-H) ppm.



Bis(4-fluorophenyl)sulfoxide^[20] (6g)

Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): δ = 7.64-7.61 (m, 4H, Ar-H), 7.18 (t, *J* = 8.6 Hz, 4H, Ar-H) ppm.



Bis(3-fluorophenyl)sulfoxide^[12] (6h)

White solid; M.p.: 136-138 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.48-7.42 (m, 4H, Ar-H), 7.40 (dt, *J* = 7.9, 2.0 Hz, 2H, Ar-H), 7.16 (tq, *J* = 8.2, 1.0 Hz, 2H, Ar-H) ppm.

F O F S Bis(2-fluorophenyl)sulfoxide^[12] (6i)

White solid; M.p.: 127-129 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.85-7.82 (m, 2H, Ar-H), 7.48-7.45 (m, 2H, Ar-H) 7.34 (t, *J* = 7.6 Hz, 2 H, Ar-H) ppm.



Bis(4-clorophenyl)sulfoxide^[20] (6j)

White solid; M.p.: 143-145 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.58-7.55 (m, 4H, Ar-H), 7.46-7.44 (m, 4H, Ar-H) ppm.



Bis(3-clorophenyl)sulfoxide^[21] (6k)

Colorless liquid; ¹H NMR (400 MHz, CDCl₃); δ = 7.64-7.66 (m, 2H, Ar-H), 7.51-7.53 (m, 3H, Ar-H), 7.41-7.44 (m, 3H, Ar-H) ppm.



Bis(2-chlorophenyl)sulfoxide^[12] (61)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.46 (dd, *J* = 7.9, 1.4 Hz, 2H, Ar-H), 7.24 (td, *J* = 7.8, 1.2 Hz, 2 H, Ar-H), 7.20 (td, *J* = 7.5, 1.4 Hz, 2H, Ar-H), 7.15 (dd, *J* = 7.7, 1.7 Hz, 2H, Ar-H) ppm.



Bis(4-bromophenyl)sulfoxide^[20] (6m)

White solid; M.p.: 150 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.62-7.59 (m, 4H, Ar-H), 7.50-7.48 (m, 4H, Ar-H) ppm.

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4,4'-Thiodiphenol^[22] (**6n**)

White solid; M.p.: 201 °C; ¹H NMR (600 MHz, CD₃OD): *δ* = 7.45-7.42 (m, 4H, Ar-H), 6.91-6.88 (m, 4H, Ar-H) , 4.83 (s, 2H, OH-H) ppm.

NH₂ O NH₂

2,2'-Sulfinyldianiline^[33] (60)

Colorless liquid; ¹H NMR (400 MHz, CDCl₃); δ = 7.26 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.24 (t, *J* = 2.4 Hz, 2H, Ar-H), 6.75 (t, *J* = 7.6 Hz, 2H, Ar-H), 6. 68 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.81 (s, 4H) ppm.

Dibenzylsulfoxide^[23] (6p)

White solid; M.p.: 130-132 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.39-7.34 (m, 6H, Ar-H), 7.30-7.28 (m, 4H, Ar-H), 3.93 (q, *J* = 8.8 Hz, 4H, CH₂-H) ppm.

Part 5: asymmetric sulfoxides



White solid; M.p.: 63-64 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.92 (dt, *J* = 3.6, 1.2 Hz, 2H, Ar-H), 7.88 (dd, *J* = 4.8, 2.0 Hz, 2H, Ar-H), 7.55-7.50 (m, 1H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 6.98 (dt, *J* = 4.8, 2.4 Hz, 2H), 3.81 (s, 3H, OMe-H) ppm.



Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.91 (d, *J* = 1.7 Hz, 1 H, Ar-H), 7.72-7.71 (m, 2 H, Ar-H), 7.42-7.40 (m, 4 H, Ar-H), 7.17 (td, *J* = 7.6, 0.7 Hz, 1 H, Ar-H), 6.86 (d, *J* = 8.2 Hz, 1 H, Ar-H), 3.81 (s, 3H, OMe-H) ppm.



White solid; M.p.: 63-65 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.64-7.62 (m, 2 H, Ar-H), 7.45-



Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.66-7.63 (m, 4 H, Ar-H), 7.49-7.46 (m, 3 H, Ar-H), 7.17 (t, *J* = 8.7 Hz, 2 H, Ar-H) ppm.



Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ = 7.65-7.63 (m, 2 H, Ar-H), 7.60 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.47-7.46 (m, 3 H, Ar-H), 7.44 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm.



Light yellow solid; M.p.: 84-86 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.33 (d, J = 8.9 Hz, 2 H, Ar-H), 7.85 (d, J = 8.9 Hz, 2 H, Ar-H), 7.69-7.67 (m, 2 H, Ar-H), 7.51-7.50 (m, 3H, Ar-H) ppm.



Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 8.23-8.21 (m, 2 H, Ar-H), 7.98 (d, *J* = 8.2 Hz, 1 H, Ar-H), 7.69-7.67 (m, 2 H, Ar-H), 7.67 (t, *J* = 7.3 Hz, 1 H, Ar-H), 7.55-7.52 (m, 2 H, Ar-H), 7.40-7.38 (m, 3 H, Ar-H) ppm.

O S Methyl(phenyl)sulfoxide^[27] (7h)

White solid; M.p.: 35-37 °C; ¹H NMR (400 MHz, CDCl₃): *δ* = 7.57 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.46 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.44 (d, *J* = 2.4 Hz, 2H, Ar-H), 2.65 (s, 3H) ppm.



White solid; M.p.: 126-128 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.47-7.45 (m, 1H, Ar-H), 7.44-7.41 (m, 2 H, Ar-H), 7. 38-7.36 (m, 2H, Ar-H), 7.29-7.28 (m, 1H, Ar-H), 7.26-7.24 (m, 2H, Ar-H), 6.98 (t, *J* = 7.1 Hz, 2H, Ar-H), 4.11 (q, *J* = 12.6 Hz, 2H, CH₂-H) ppm.



White solid; M.p.: 88-89 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.68-7.66 (m, 2H, Ar-H), 7.54-7.51 (m, 2H, Ar-H), 2.72 (s, Me-H) ppm.



Slight yellow oil; ¹H NMR (600 MHz, CDCl₃): δ = 7.96 (dd, *J* = 7.8, 1.6 Hz, 1H, Ar-H), 7.60-7.56 (m, 2H, Ar-H), 7.39 (td, *J* = 7.6, 1.6 Hz, 1H, Ar-H), 2.82 (s, Me-H) ppm.

Slight yellow oil; ¹H NMR (600 MHz, CD₃Cl): *δ* = 7.43 (dd, *J* = 1.2, 0.8 Hz, 1H, Ar-H), 6.41-6.39 (m, 2 H, Ar-H), 2.52 (s, 3 H, Me-H) ppm.

2-((methylsulfinyl)methyl)furan^[31] (7m)

Slight yellow liquid; ¹H NMR (400 MHz, CDCl₃); δ = 7.44 (s, 1H), 6.41 (d, *J* = 3.2 Hz, 1H), 6.39 (t, *J* = 2 Hz, 1H), 4.01 (q, *J* = 14 Hz, 2H), 2.53 (s, 3H) ppm.

S O **3-(methylsulfinyl)prop-1-ene**^[32] (**7n**) Slight yellow oil; ¹H NMR (400 MHz, CDCl₃): *δ* = 5.96 (td, J = 10.0, 7.6 Hz, 1H), 5.48-5.38 (m, 2H), 3.54-3.41 (m, 2H), 2.56 (s, 3H) ppm.

Part 6: sulfones



Diphenyl sulfone^[34, 37] (8a)

White solid; M.p.: 122-124 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.96 (dt, *J* = 10.6, 1.7 Hz, 4 H, Ar-H), 7.59 (tt, *J* = 11.0, 4.2 Hz, 2 H, Ar-H), 7.53-7.48 (m, 4 H, Ar-H) ppm.



4, 4'-sulfonyldiphenol^[34] (8b)

White solid; M.p.: 240-242 °C; ¹H NMR (600 MHz, CD₃OD): *δ* = 7.73 (d, *J* = 8.8 Hz, 4 H, Ar-H), 6.89 (d, *J* = 8.8, 4 H, Ar-H) ppm.



Bis(methoxy)dipheney sulfone^[34, 35] (8c)

White solid; M.p.: 129-130 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.86 (d, *J* = 13.4 Hz, 4 H, Ar-H), 6.97 (d, *J* = 22.3, 4 H, Ar-H) 3.83 (s, 6 H, OMe-H) ppm.



Bis(cloro)diphenyl sulfone^[35, 36] (8d)

White solid; M.p.: 148-150 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.87 (d, *J* = 13.0 Hz, 4 H, Ar-H), 7.50 (d, *J* = 13.0, 4 H, Ar-H) ppm.



Bis(bromo)diphenyl sulfone^[35] (8e)

White solid; M.p.: 158-160 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.80 (d, *J* = 20.0 Hz, 4 H, Ar-H), 7.67 (d, *J* = 13.1, 4 H, Ar-H) 3.83 (s, 6 H, OMe-H) ppm.



2-Methoxyphenyl phenyl sulfone^[37] (8g)

White solid; M.p.: 120-122 °C; ¹H NMR (600 MHz, CDCl₃): δ = 8.17 (dd, J = 11.8, 2.6 Hz, 1 H, Ar-H), 7.99-7.96 (m, 2 H, Ar-H), 7.59-7.52 (m, 2 H, Ar-H), 7.50-7.46 (m, 2 H, Ar-H), 7.13 (td, J = 11.8, 1.3 Hz, 1 H, Ar-H), 6.91 (d, J = 12.4 Hz, 1 H, Ar-H), 3.75 (s, 3 H, OMe-H) ppm.



4-Methyl diphenyl sulfone^[36, 37] (8h)

White solid; M.p.: 120-122 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.94-7.92 (m, 2 H, Ar-H), 7.84 (d, *J* = 12.4 Hz, 2 H, Ar-H), 7.56-7.52 (m, 1 H, Ar-H), 7.30 (d, *J* = 12.2 Hz, 2 H, Ar-H), 2.39 (s, 3 H, Me-H) ppm.



4-Florophenyl phenyl sulfone^[37, 38] (8i)

White solid; M.p.: 110-112 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.98-7.92 (m, 4 H, Ar-H), 7.60 (tt, *J* = 11.0, 4.0 Hz, 1 H, Ar-H), 7.54-7.49 (m, 2 H, Ar-H), 7.20 (t, *J* = 12.7 Hz, 2 H, Ar-H) ppm.



3-florophenyl phenyl sulfone^[38] (8j)

Colorless liquid; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.97-7.94 (m, 2 H, Ar-H), 7.76 (dq, *J* = 11.8, 1.5 Hz, 1 H, Ar-H), 7.66 (dt, *J* = 11.5, 3.6 Hz, 1 H, Ar-H), 7.62 (tt, *J* = 11.0, 3.8 Hz, 1 H, Ar-H), 7.55-7.52 (m, 2 H, Ar-H), 7.51-7.47 (m, 1 H, Ar-H), 7.28-7.23 (m, 1 H, Ar-H) ppm.



2-florophenyl phenyl sulfone^[39] (8k)

White solid; M.p.: 95-97 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 8.14 (td, *J* = 11.7, 2.7 Hz, 1 H, Ar-H), 8.03-8.00 (m, 2 H, Ar-H), 7.64-7.60 (m, 1 H, Ar-H), 7.59-7.56 (m, 1 H, Ar-H), 7.55 (t, *J* = 11.9 Hz, 2 H, Ar-H), 7.34 (td, *J* = 11.6, 1.5 Hz, 1 H, Ar-H), 7.13-7.08 (m, 1 H, Ar-H) ppm.



Benzyl phenyl sulfone^[36] (8l)

White solid; M.p.: 146-148 °C; ¹H NMR (600 MHz, CDCl₃): *δ* = 7.64 (dd, *J* = 12.4, 1.6 Hz, 2 H, Ar-H), 7.60 (d, *J* = 11.2 Hz, 1 H, Ar-H), 7.46 (t, *J* = 11.8 Hz, 2 H, Ar-H), 7.34 (tt, *J* = 11.0, 7.7 Hz, 1 H, Ar-H), 7.27-7.23 (m, 2 H, Ar-H), 7.09-7.07 (m, 2 H, Ar-H), 4.31 (s, 2 H, CH₂-H) ppm.

Phenyl methyl sulfone^[36] (8m)

White solid; M.p.: 85-87 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.97-7.95 (m, 2 H, Ar-H), 7.69 (tt, J = 11.1, 3.3 Hz, 1 H, Ar-H), 7.60-7.57 (t, J = 11.8 Hz, 2 H, Ar-H), 3.06 (s, 3 H, CH₃-H) ppm.



Yellow liquid; ¹H NMR (400 MHz, CDCl₃); $\delta = 6.03-5.92$ (m, 1H), 5.51 (d, J = 12.0 Hz, 1H), 5.46 (d, J = 16.0 Hz, 1H), 3.73 (d, J = 7.6 Hz, 2H), 2.88 (s, 3H) ppm.

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4 ¹H and ¹³C NMR spectra

Part 1: symmetric sulfides



































S35





























S43









































7.573 7.566 7.566 7.562 7.558 7.461 7.457 457 457 454 7.454 454 7.454 67 454 7.453

NAME 2 EXPNO PROCNO Date_ Time INSTRUM PROBHD 9 PULPROG TD SOLVENT NS DS CRUU	20140926wangqi 3 20140926 16.47 5 mm PADUL 13C 2g30 65536 CDCl3 4 2225 526	ngyu
SWH	12335.526	HZ
FIDRES	2 6564426	HZ
RG	2.0304420	sec
DW	40.533	usec
DE	6.50	usec
TE	298.3	К
D1	1.00000000	sec
NUC1 P1 SI SF WDW SSB LB GB PC	CHANNEL f1 ===- 1H 14.00 32768 600.1300163 0 -0.10 0 1.00	usec MHz Hz











Part 5: asymmetric sulfoxides



















STRUM						s	pe	ect		
OBHD	5	mm	P	AD	U	L	1	.3C		
LPROG							zc	130		
						6	55	36		
LVENT						С	DC	:13		
								4		
								2		
H			1	23	3	5		26	Hz	
DRES				Ο.	1	8	82	25	Hz	
			2	. 6	5	6	44	26	se	C
							2	203		
					4	0	. 5	533	use	ec
							6.	50	use	ec
						2	89	.8	K	
		1	ι.	00	0	0	00	000	se	С
	~ -			_						
	CF	IAN	VE.	L	İ	1	-		===:	==
C1								1H		
						1	4.	00	use	ec
		~			~	3	2	68		
		60	00	• 1	.3	0	01	.48	MH:	Z
W								GM		
В								0		
						-	υ.	TO	ΗZ	
							_ (.1		
							Τ.	00		









Part 6: sulfones

























