SUPPORTING INFORMATION

Copper-mediated cross coupling reactions of *N*-unsubstituted sulfoximines and aryl halides

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The NMR spectra were recorded in CDCl₃ or in acetone-D₆ on a Varian Mercury 300 (¹H NMR at 300 MHz; ¹³C NMR at 75 MHz; ³¹P NMR at 121 MHz) or a Varian Inova 400 (¹H NMR at 400 MHz; ¹³C NMR at 100 MHz; ³¹P NMR at 162 MHz) spectrometer using TMS or residual solvent peaks (at 7.26 ppm for ¹H NMR or 77 ppm for ¹³C NMR) as internal standard. Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. IR spectra were recorded as KBr discs, in capillaries or in CHCl₃. DMSO was degassed against a positive argon flow without distillation or drying. Unless otherwise noted all reactions were performed under argon using standard Schlenk and vacuum line techniques.

Preparation of *N*-(2-bromo-4-nitro-phenyl)-acetamide (2q) and *N*-(2-bromo-6-nitro-phenyl)-acetamide (2r) starting from 2-bromoaniline:

A. Synthesis of *N*-(2-bromo-phenyl)-acetamide: At 0 °C under atmospheric pressure 2-bromoaniline (10 g, 0.06 mol) was treated with acetic anhydride (13 mL, 0.12 mol). After heating to 70 °C for 20 min, the excess of acetic anhydride was evaporated under reduced pressure. Purification by column chromatography on silica gel (dichloromethane) afforded 12.5 g of *N*-(2-bromo-phenyl)-acetamide as a white solid. Yield: 100%; mp. 96 °C; *R_f* 0.69 (dichloromethane : methanol = 99 : 1); ¹H NMR (300 MHz, CDCl₃): δ 8.38 (d, ³*J* = 7.9 Hz, 1H), 7.66 (br s, NH), 7.59 (d, ³*J* = 7.9 Hz, 1H), 7.36 (t, ³*J* = 7.9 Hz, 1H), 7.03 (d, ³*J* = 7.9 Hz, 1H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.0 (CO), 136.0 (C), 132.3 (CH), 128.4 (CH), 125.2 (CH), 122.0 (CH), 113.0 (CH), 24.9 (CH₃); IR (KBr): ν 3279, 1661, 1531, 1295 cm⁻¹; MS (EI), *m/z* (relative intensity): 212.9, 214.9 ([M]⁺, 22 %); Calcd. for C₈H₈BrNO: C, 44.89; H, 3.77; N, 6.54; found C, 45.06; H, 3.76; N, 6.52.

B. Synthesis of *N*-(2-bromo-4-nitro-phenyl)-acetamide (2q) and *N*-(2-bromo-6-nitro-phenyl)-acetamide (2r): A cooled freshly prepared solution of 0.3 mL of HNO₃ (65%)

and 0.4 mL of conc. H_2SO_4 was slowly added to *N*-(2-bromo-phenyl)-acetamide (0.5 g, 2.3 mmol). The mixture was stirred at room temperature for 7 h. Then, water was added and the aqueous layer was extracted with dichloromethane three times. The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure to give the crude product as a mixture of *N*-(2-bromo-4-nitro-phenyl)-acetamide (**2q**) and *N*-(2-bromo-6-nitro-phenyl)-acetamide (**2r**), which were separated and purified by column chromatography on silica gel (dichloromethane).

***N*-(2-Bromo-4-nitro-phenyl)-acetamide (2q)**: 178 mg as a yellow solid. Yield: 30%; mp. 129 °C; R_f 0.17 (dichloromethane); ^1H NMR (300 MHz, CDCl_3): δ 8.7 (d, $^3J = 9.2$ Hz, 1H), 8.49 (d, $^4J = 2.7$ Hz, 1H), 8.23 (dd, $^3J = 9.2$ Hz, $^4J = 2.7$ Hz, 1H), 7.95 (br s, NH), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 168.6(CO), 143.2 (C), 141.4 (C), 127.9 (CH), 124.2 (CH), 120.2 (CH), 111.9 (C), 25.2 (CH_3); IR (KBr): ν 3261, 1677, 1534, 1508, 1342 cm^{-1} ; MS (EI), m/z (relative intensity): 257.9, 259.9 ($[\text{M}]^+$, 28 %); Calcd. for $\text{C}_8\text{H}_7\text{BrN}_2\text{O}_3$: C, 37.09; H, 2.72; N, 10.81; found C, 36.93; H, 3.05; N, 10.86.

***N*-(2-Bromo-6-nitro-phenyl)-acetamide (2r)**: 90 mg as a brown solid. Yield: 15%; mp. 187 °C; R_f 0.68 (dichloromethane : methanol = 99 : 1); ^1H NMR (300 MHz, CDCl_3): δ 7.86-7.78 (m, 2H), 7.62 (m, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.1 (CO), 136.3 (CH), 128.3 (C), 126.2 (CH), 124.0 (C), 123.4 (CH), 120.8 (C), 22.6 (CH_3); IR (KBr): ν 3273, 1533, 1458, 1357 cm^{-1} ; MS (EI), m/z (relative intensity): 257.9, 259.9 ($[\text{M}]^+$, 2 %); Calcd. for $\text{C}_8\text{H}_7\text{BrN}_2\text{O}_3$: C, 37.09; H, 2.72; N, 10.81; found C, 36.75; H, 2.96; N, 10.80.

General procedure for *N*-arylations of sulfoximines: Under an argon atmosphere a dry Schlenk tube was charged with sulfoximine **1** (1.0 equiv), aryl halide (2.0 equiv), CuI (1.0 equiv) and base [2.5 equiv, Cs_2CO_3 (method A) or CsOAc (method B) as indicated in Table 2; in method C the reagents were as follows: sulfoximine **1** (2.0 equiv), aryl halide (1.0 equiv), CuI (1.0 equiv), CsOAc (2.5 equiv)]. The mixture was dissolved in degassed DMSO (1 M). After heating to 90 °C for 12 h, the mixture was cooled to room temperature and neutralized with HCl. The aqueous layer was extracted with dichloromethane three times. The combined organic extracts were dried (MgSO_4), filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel afforded the *N*-arylated sulfoximines.

***rac-N*-(Phenyl)-*S*-methyl-*S*-phenylsulfoximine (3a)**: (Table 1, entry 1) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 78.2 mg, 0.506 mmol) and iodobenzene (**2a**, 204 mg, 1.012 mmol) gave 109 mg of **3a** as a light brown solid. Yield:

94%; mp. 100-101 °C; R_f 0.28 (petroleum ether : ethyl acetate = 1 : 1); ^1H NMR (400 MHz, CDCl_3): δ 7.95-7.99 (m, 2H), 7.54-7.58 (m, 1H), 7.47-7.53 (m, 2H), 7.08-7.14 (m, 2H), 6.99-7.03 (m, 2H), 6.83-6.88 (m, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 144.9 (C), 139.4 (C), 133.2 (CH), 129.5 (2 x CH), 129.0 (2 x CH), 128.6 (2 x CH), 123.3 (2 x CH), 121.7 (CH), 46.1 (CH_3); IR (KBr): ν 3060, 3021, 2921, 1592, 1484 1198, 1095 cm^{-1} ; MS (EI), m/z (relative intensity): 231 ($[\text{M}]^+$, 100 %); Calcd. for $\text{C}_{13}\text{H}_{13}\text{NOS}$: C, 67.50; H, 5.66; N, 6.06; found C, 67.42; H, 5.51; N, 5.84.

***rac-N*-[2-(Methyl)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3b):** (Table 2, entry 1) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 84.1 mg, 0.542 mmol) and 1-iodo-2-methylbenzene (**2b**, 238.1 mg, 1.092 mmol) gave 111 mg of **3b** as a brown solid. Yield: 84%; mp. 61-62 °C; R_f 0.28 (petroleum ether : ethyl acetate = 2 : 1); ^1H NMR (400 MHz, CDCl_3): δ 7.97-8.00 (m, 2H), 7.56-7.61 (m, 1H), 7.50-7.55 (m, 2H), 7.10-7.13 (m, 1H), 6.99-7.02 (m, 1H), 6.88-6.93 (m, 1H), 6.79-6.84 (m, 1H), 3.22 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.0 (C), 132.9 (C), 132.1 (CH), 130.2 (C), 129.3 (CH), 128.2 (2 x CH), 126.1 (2 x CH), 121.7 (2 x CH), 121.6 (2 x CH), 45.4 (CH_3), 18.6 (CH_3); IR (KBr): ν 3012, 2921, 1591, 1486 1263, 1188, 1094 cm^{-1} ; MS (EI), m/z (relative intensity): 245 ($[\text{M}]^+$, 100 %); Calcd. for $\text{C}_{14}\text{H}_{15}\text{NOS}$: C, 68.54; H, 6.16; N, 5.71; found C, 68.71; H, 5.99; N, 5.42.

***rac-N*-[2-(Bromo)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3c):** (Table 2, entry 2) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 81.3 mg, 0.524 mmol) and 1-bromo-2-iodobenzene (**2c**, 67.5 mg, 1.048 mmol) gave 110 mg of **3c** as a light brown solid. Yield: 68%; mp. 63-64 °C; R_f 0.25 (petroleum ether : ethyl acetate = 3 : 1); ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.09 (m, 2H), 7.57-7.63 (m, 1H), 7.48-7.56 (m, 3H), 7.18-7.22 (m, 1H), 7.00-7.05 (m, 1H), 6.73-6.78 (m, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.2 (C), 138.8 (C), 133.3 (CH), 132.8 (CH), 129.3 (2 x CH), 128.4 (2 x CH), 127.7 (CH), 123.4 (CH), 122.9 (CH), 119.1 (C), 45.4 (CH_3); IR (KBr): ν 3011, 2920, 1577, 1197, 1124, 684 cm^{-1} ; MS (EI), m/z (relative intensity): 309, 311 ($[\text{M}]^+$, 84%); Calcd. for $\text{C}_{14}\text{H}_{12}\text{BrNOS}$: C, 50.33; H, 3.90; N, 4.52; found C, 50.18; H, 4.12; N, 4.26.

***rac-N*-[2-(Nitro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3d):** (Table 2, entry 3, 14) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 86.2 mg,

0.555 mmol) and 1-iodo-2-nitro-benzene (**2d**, 276.5 mg, 1.110 mmol) gave 127 mg of **3d** as a yellow solid; yield: 83% (Table 2, entry 3).

The general procedure (method B) using *rac*-*S*-methyl-*S*-phenylsulfoximine (**1a**, 40.4 mg, 0.260 mmol) and 1-bromo-2-nitro-benzene (**2o**, 105 mg, 0.520 mmol) gave 56 mg of **3d** as a yellow oil. Yield: 78%; (Table 2, entry 14) mp. 77-79 °C; R_f 0.41 (petroleum ether : ethyl acetate = 7 : 3); ^1H NMR (300 MHz, CDCl_3): δ 8.15-8.11 (m, 2H), 7.73-7.60 (m, 4H), 7.36-7.26 (m, 2H), 7.03-6.97 (m, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 145.3 (C), 139.1 (C), 138.6 (C), 133.9 (CH), 132.6 (CH), 129.8 (2 x CH), 128.6 (2 x CH), 124.5 (CH), 124.4 (CH), 121.4 (CH), 45.8 (CH_3); IR (CHCl_3): ν 1521, 1287, 1209, 1100, 749 cm^{-1} ; MS (EI), m/z (relative intensity): 276 ($[\text{M}]^+$, 100 %); Calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$: C, 56.51; H, 4.38; N, 10.14; found C, 56.24; H, 4.85; N, 10.22.

***rac*-*N*-[2-(Methoxy)phenyl]-*S*-methyl-*S*-phenylsulfoximine (**3e**):** (Table 2, entry 4)

The general procedure (method A) using *rac*-*S*-methyl-*S*-phenylsulfoximine (**1a**, 81.6 mg, 0.523 mmol) and 1-iodo-2-methoxybenzene (**2e**, 250.6 mg, 1.071 mmol) gave 99 mg of **3e** as a brown oil. Yield: 72%; R_f 0.25 (petroleum ether : ethyl acetate = 1 : 2); ^1H NMR (300 MHz, CDCl_3): δ 8.00-8.05 (m, 2H), 7.46-7.59 (m, 3H), 7.06-7.10 (m, 1H), 6.84-6.91 (m, 1H), 6.78-6.83 (m, 1H), 6.66-6.73 (m, 1H), 3.83 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 153.0 (C), 140.0 (C), 133.8 (C), 133.1 (CH), 129.4 (2 x CH), 128.5 (2 x CH), 124.3 (CH), 122.8 (CH), 120.8 (CH), 111.4 (CH), 55.7 (CH_3), 46.2 (CH_3); IR (capillary): ν 3060, 3004, 2928, 2834, 1586, 1496 1237, 1200, 1122, 1095, 1026 cm^{-1} ; MS (EI), m/z (relative intensity): 261 ($[\text{M}]^+$, 78 %); Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$: HRMS of $[\text{M}]^+$: Calcd. 261.0824; found 261.0827.

(*S*)-*N*-[2-(Diphenylphosphanoxid)phenyl]-*S*-methyl-*S*-phenyl-sulfoximine (3f**):**

(Table 2, entry 5) The general procedure (method B) using (*S*)-*S*-methyl-*S*-phenylsulfoximine [(*S*)-**1a**, 155 mg, 1.00 mmol] and 2-diphenylphosphanoxid-iodobenzene (**2f**, 808 mg, 2.00 mmol) gave 306 mg of (*S*)-**3f** as a white solid. Yield: 71%, mp. 206 °C; R_f 0.21 (ethyl acetate); $[\alpha]_D^{20} = -124.5$ ($c = 0.42$, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.65-7.89 (m, 6H), 7.33-7.53 (m, 10H), 7.24 (m, 1H), 7.05 (dd, $J = 7.5, 5.0$ Hz, 1H), 6.88 (mc, $J = 7.5, 2.4, 0.9$ Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.5 (d, $J_{\text{CP}} = 3.8$ Hz), 138.7, 135.5, 134.5 (d, $J_{\text{CP}} = 9.9$ Hz), 134.0 (d, $J_{\text{CP}} = 19.5$ Hz), 133.3, 133.2, 131.8 (d, $J_{\text{CP}} = 9.7$ Hz), 131.7 (d, $J_{\text{CP}} = 9.7$ Hz), 131.2 (d, $J_{\text{CP}} = 2.2$ Hz), 130.9 (d, $J_{\text{CP}} = 2.2$ Hz), 129.1, 128.5, 128.4, 128.1, 127.9, 125.8, 124.4, 122.2 (d, $J_{\text{CP}} = 7.7$ Hz), 121.1 (d, $J_{\text{CP}} = 12.5$ Hz), 44.9; IR (KBr): ν 3428, 3054, 2988, 2909, 1582, 1466, 1439, 1299, 1260, 1205, 1184, 1097, 1015, 777, 745, 710, 610, 542

cm⁻¹; MS (EI), *m/z* (relative intensity): 431 ([M]⁺, 21 %); Calcd. for C₂₅H₂₂NO₂PS: C, 69.59; H, 5.14; N, 3.25; found C, 69.38; H, 5.43; N, 3.10.

***rac-N*-[3-(Cyano)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3g):** (Table 2, entry 6) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 82.1 mg, 0.529 mmol) and 3-iodo-benzonitrile (**2g**, 241.8 mg, 1.060 mmol) gave 127 mg of **3g** as a light brown solid. Yield: 94%; mp. 74-76 °C; *R_f* 0.19 (petroleum ether : ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 7.93-7.98 (m, 2H), 7.60-7.67 (m, 1H), 7.52-7.60 (m, 2H), 7.10-7.27 (m, 4H), 3.28 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 146.1 (C), 138.4 (C), 133.7 (CH), 129.8 (2 x CH), 129.8 (CH), 128.5 (2 x CH), 127.6 (CH), 126.1 (CH), 125.0 (CH), 119.0 (C), 112.7 (C), 46.2 (CH₃); IR (capillary): ν 3064, 3022, 2928, 2579, 1732, 1590, 1211, 1095 cm⁻¹; MS (EI), *m/z* (relative intensity): 256 ([M]⁺, 95 %); Calcd. for C₁₄H₁₂N₂OS: C, 65.60; H, 4.72; N, 10.93; found C, 65.36; H, 4.85; N, 10.69.

***rac-N*-[4-(Methyl)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3h):** (Table 2, entry 7) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 103.4 mg, 0.662 mmol) and 1-iodo-4-methylbenzene (**2h**, 291.3 mg, 1.340 mmol) gave 151 mg of **3h** as a light yellow solid. Yield: 93%; mp. 113-114 °C; *R_f* 0.28 (petroleum ether : ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 7.95-8.00 (m, 2H), 7.47-7.61 (m, 3H), 6.92-6.93 (m, 4H), 3.22 (s, 3H), 2.20 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 142.1 (C), 139.4 (C), 133.1 (CH), 131.0 (C), 129.6 (2 x CH), 129.5 (2 x CH), 128.6 (2 x CH), 123.2 (2 x CH), 45.8 (CH₃), 20.7 (CH₃); IR (KBr): ν 3023, 2999, 2920, 1609, 1506, 1189, 1088 cm⁻¹; MS (EI), *m/z* (relative intensity): 245 ([M]⁺, 100 %); Calcd. for C₁₄H₁₅NOS: C, 68.54; H, 6.16; N, 5.71; found C, 68.61; H, 6.36; N, 5.54.

***rac-N*-[4-Formyl(phenyl)]-*S*-methyl-*S*-phenylsulfoximine (3i):** (Table 2, entry 8) The general procedure (method C) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 152.3 mg, 0.981 mmol) and 4-iodobenzaldehyde (**2i**, 115.7 mg, 0.499 mmol) gave 151 mg of **3i** as a light yellow solid. Yield: 85%; mp. 92-94 °C; *R_f* 0.28 (petroleum ether : ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 9.78 (br s, 1H), 7.94-7.99 (m, 2H), 7.61-7.67 (m, 3H), 7.52-7.59 (m, 2H), 7.05-7.11 (m, 2H), 3.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 191.1 (CH), 151.9 (C), 138.5 (C), 133.9 (CH), 131.2 (2 x CH), 130.1 (C), 129.8 (2 x CH), 128.4 (2 x CH), 122.9 (2 x CH), 46.5 (CH₃); IR (KBr): ν 3001, 2921, 2836, 1688, 1595 cm⁻¹; MS (EI), *m/z* (relative

intensity): 259 ($[M]^+$, 100 %); Calcd. for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40; found C, 64.71; H, 4.93; N, 5.20.

***rac-N*-[4-(Ethylloxycarbonyl)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3j):** (Table 2, entry 9) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 85.2 mg, 0.549 mmol) and 4-iodobenzoic acid ethylester (**2j**, 313.5 mg, 1.136 mmol) gave 147 mg of **3j** as a white solid. Yield: 88%; mp. 125 °C; R_f 0.28 (petroleum ether : ethyl acetate = 1 : 1); 1H NMR (300 MHz, $CDCl_3$): δ 7.94-7.97 (m, 2H), 7.78-7.84 (m, 2H), 7.59-7.65 (m, 1H), 7.51-7.59 (m, 2H), 6.99-7.05 (m, 2H), 4.29 (q, $^3J = 7.2$ Hz, 2H), 1.33 (t, $^3J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (C), 149.8 (C), 138.3 (C), 133.6 (CH), 130.8 (2 x CH), 129.7 (2 x CH), 128.5 (2 x CH), 123.4 (C), 122.4 (2 x CH), 60.5 (CH_2), 46.3 (CH_3), 14.4 (CH_3); IR (KBr): ν 3061, 2971, 1708, 1599, 1502, 1270, 1198, 1168, 1097 cm^{-1} ; MS (EI), m/z (relative intensity): 303 ($[M]^+$, 100 %); Calcd. for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62; found C, 63.35; H, 5.65; N, 4.35.

***rac-N*-[4-(Nitro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3k):** (Table 2, entry 10) The general procedure (method A) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 71.3 mg, 0.459 mmol) and 1-iodo-4-nitrobenzene (**2k**, 227.7 mg, 0.914 mmol) gave 104 mg of **3k** as an orange solid. Yield: 82%; mp. 151-154 °C; R_f 0.22 (petroleum ether : ethyl acetate = 1 : 1); 1H NMR (300 MHz, $CDCl_3$): δ 7.93-8.03 (m, 4H), 7.63-7.70 (m, 1H), 7.54-7.61 (m, 2H), 6.99-7.05 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6 (C), 141.7 (C), 138.2 (C), 134.0 (CH), 129.9 (2 x CH), 128.4 (2 x CH), 125.2 (2 x CH), 122.4 (2 x CH), 46.6 (CH_3); IR (KBr): ν 3078, 3006, 2922, 1585, 1499, 1336, 1269 cm^{-1} ; MS (EI), m/z (relative intensity): 276 ($[M]^+$, 100 %); Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; found C, 56.66; H, 4.68; N, 9.96.

***rac-N*-[4-(Fluoro)-2-(nitro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3l):** (Table 2, entry 11) The general procedure (method B) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 14.7 mg, 0.095 mmol) and 4-fluoro-1-iodo-2-nitrobenzene (**2l**, 50.7 mg, 0.190 mmol) gave 26.4 mg of **3l** as a yellow solid. Yield: 95%; mp. 81 °C; R_f 0.37 (dichloromethane : methanol = 99 : 1); 1H NMR (300 MHz, $CDCl_3$): δ 7.98-7.85 (m, 2H), 7.61-7.47 (m, 3H), 7.33-7.30 (m, 1H), 7.22-7.18 (m, 1H), 6.95-6.89 (m, 1H), 3.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4 (CF, d, $^1J_{CF} = 241$ Hz), 142.0 (C), 138.4 (C), 135.5 (C), 133.9 (CH), 129.8 (2 x CH), 128.6 (2 x CH), 125.7 (CH, d, $^3J_{CF} = 8$ Hz), 119.9 (CH, d, $^2J_{CF} = 24$ Hz), 111.8 (CH, d, $^2J_{CF} = 24$ Hz), 45.8

(CH₃); IR (KBr): ν 1532, 1485, 1214 cm⁻¹; MS (EI), m/z (relative intensity): 294 ([M]⁺, 100 %); Calcd. for C₁₃H₁₁FN₂O₃S: C, 53.05; H, 3.77; N, 9.52; found C, 52.67; H, 4.13; N, 9.20.

***rac-N*-[4-(Methoxy)-2-(nitro)phenyl]- *S*-methyl-*S*-phenylsulfoximine (3m):** (Table 2, entry 12) The general procedure (method B) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 139.7 mg, 0.900 mmol) and 1-iodo-4-methoxy-2-nitrobenzene (**2m**, 502.2 mg, 1.800 mmol) gave 220 mg of **3m** as an orange oil. Yield: 80%; R_f 0.30 (dichloromethane : methanol = 99 : 1); ¹H NMR (300 MHz, CDCl₃): δ 8.00-7.97 (m, 2H), 7.59-7.46 (m, 3H), 7.17 (d, ³ J = 9.1 Hz, 1H), 7.13 (d, ⁴ J = 3.1 Hz, 1H), 6.79 (dd, ³ J = 9.1 Hz, ⁴ J = 3.1 Hz, 1H), 3.69 (s, 3H), 3.19 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 154.2 (C), 145.2 (C), 138.7 (C), 133.8 (CH), 132.0 (C), 129.7 (2 x CH), 128.7 (2 x CH), 126.1 (CH), 119.8 (CH), 109.0 (CH), 55.9 (CH₃), 45.4 (CH₃); IR (CHCl₃): ν 2828, 1524, 1494, 1278, 1225, 1098 cm⁻¹; MS (EI), m/z (relative intensity): 306 ([M]⁺, 100 %); Calcd. for C₁₄H₁₄N₂O₄S: C, 54.89; H, 4.61; N, 9.14; found C, 54.87 ; H, 4.24; N, 9.28.

***rac-N*-[2,4,6-(Trichloro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3n):** (Table 2, entry 13) The general procedure (method B) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 77.6 mg, 0.500 mmol) and 1,3,5-trichloro-2-iodo-benzene (**2n**, 307 mg, 1.000 mmol) gave 100 mg of **3n** as a white solid. Yield: 60%; mp. 101-103 °C; R_f 0.21 (petroleum ether : ethyl acetate = 4 : 1); ¹H NMR (300 MHz, CDCl₃): δ 8.22-8.18 (m, 2H), 7.70-7.56 (m, 3H), 7.32 (s, 2H), 3.21 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 140.1 (C), 137.8 (C), 133.6 (CH), 132.7 (2 x C), 129.4 (2 x CH), 128.4 (2 x CH), 128.3 (C), 128.1 (2 x CH), 45.1 (CH₃); IR (capillary): ν 1444, 1298, 1218, 743 cm⁻¹; MS (EI), m/z (relative intensity): 334.9 ([M]⁺, 88 %); Calcd. for C₁₀H₁₀Cl₃NOS: C, 46.66; H, 3.01; N, 4.19; found C, 46.38; H, 3.03; N, 3.99.

***rac-N*-[2-(Nitro)-4-(trifluoromethyl)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3p):** (Table 2, entry 15) The general procedure (method B) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 40.4 mg, 0.260 mmol) and 1-bromo-2-nitro-4-trifluoromethylbenzene (**2p**, 140.4 mg, 0.520 mmol) gave 74 mg of **3p** as a yellow oil. Yield: 83%; R_f 0.39 (petroleum ether : ethyl acetate = 7 : 3); ¹H NMR (300 MHz, CDCl₃): δ 8.01-7.96 (m, 2H), 7.81 (d, ⁴ J = 2.2 Hz, 1H), 7.63-7.49 (m, 3H), 7.36 (dd, ³ J = 8.7 Hz, ⁴ J = 2.2 Hz, 1H), 7.26 (d, ³ J = 8.7 Hz, 1H), 3.24 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 144.5 (C), 142.7 (C), 138.0 (C), 134.3 (CH), 130.0 (2 x CH), 129.1 (CH), 128.5 (2 x CH), 124.1 (CH), 123.4 (CF₃, q, ¹ J_{CF} = 272 Hz), 123.0 (C, q, ² J_{CF} = 35 Hz), 121.5 (CH), 46.5 (CH₃); IR (CHCl₃): ν 1623, 1534, 1324, 1215, 1125 cm⁻¹.

¹; MS (EI), *m/z* (relative intensity): 344 ([M]⁺, 100 %); Calcd. for C₁₄H₁₁F₃N₂O₃S: C, 48.84; H, 3.22; N, 8.14; found C, 48.91; H, 3.29; N, 8.12.

***rac-N*-[2-(Acetylamino)-5-(nitro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3q):** (Table 2, entry 16) The general procedure (method C) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 31.0 mg, 0.200 mmol) and *N*-(2-bromo-4-nitro-phenyl)-acetamide (**2q**, 25.9 mg, 0.100 mmol) gave 43 mg of **3q** as a yellow solid. Yield: 65%; mp. 184 °C, *R_f* 0.27 (dichloromethane : methanol = 98 : 2); ¹H NMR (400 MHz, CDCl₃): δ 8.59 (br s, NH), 8.44 (d, ³*J* = 9.1 Hz, 1H), 7.86-7.83 (m, 2H), 7.70 (dd, ³*J* = 9.1 Hz, ⁴*J* = 2.5 Hz, 1H), 7.63-7.51 (m, 3H), 7.60 (d, ⁴*J* = 2.5 Hz, 1H), 3.33 (s, 3H), 3.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 168.5 (CO), 142.6 (C), 137.7 (C), 137.2 (C), 134.4 (CH), 133.3 (C), 130.3 (2 x CH), 128.2 (2 x CH), 118.3 (CH), 118.0 (CH), 114.9 (CH), 46.4 (CH₃), 25.4 (CH₃); IR (KBr): ν 3361, 1702, 1508, 1335, 1231, 1101 cm⁻¹; MS (EI), *m/z* (relative intensity): 333 ([M]⁺, 100 %); Calcd. for C₁₅H₁₅N₃O₄S: C, 54.04; H, 4.54; N, 12.60; found C, 53.66; H, 4.57; N, 12.64.

***rac-N*-[2-(Acetylamino)-3-(nitro)phenyl]-*S*-methyl-*S*-phenylsulfoximine (3r):** (Table 2, entry 17) The general procedure (method C) using *rac-S*-methyl-*S*-phenylsulfoximine (**1a**, 60.5 mg, 0.390 mmol) and *N*-(2-bromo-6-nitro-phenyl)-acetamide (**2r**, 50.5 mg, 0.195 mmol) gave 62 mg of **3r** as a white solid. Yield: 48%; mp. 156 °C ; *R_f* 0.18 (dichloromethane : methanol = 98 : 2); ¹H NMR (400 MHz, CDCl₃): δ 8.15 (br s, NH), 8.02-8.00 (m, 2H), 7.71-7.59 (m, 3H), 7.43 (dd, ³*J* = 8.2 Hz, ⁴*J* = 1.4 Hz, 1H), 7.19 (dd, ³*J* = 8.2, ⁴*J* = 1.4 Hz, 1H), 7.00 (t, ³*J* = 8.2 Hz, 1H), 3.37 (s, 3H), 2.28 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 168.4 (CO), 145.0 (C), 140.5 (C), 138 (C), 134.0 (CH), 129.9 (2 x CH), 128.4 (2 x CH), 125.5 (CH), 125.3 (CH), 124 (C), 117.6 (CH), 46.1 (CH₃), 23.9 (CH₃); IR (CHCl₃): ν 3350, 3018, 1688, 1532, 1443, 1224, 1098, 752 cm⁻¹; MS (EI), *m/z* (relative intensity): 333 ([M]⁺, 80%); Calcd. for C₁₅H₁₅N₃O₄S: C, 54.04; H, 4.54; N, 12.60; found C, 54.17; H, 4.31; N, 12.91.

***rac-N*-(Phenyl)-*S*-benzyl-*S*-phenylsulfoximine (3s):** The general procedure (method A) using *S*-benzyl-*S*-phenylsulfoximine (**1b**, 109.2 mg, 0.472 mmol) and phenyl iodide (**2a**, 200.5 mg, 0.983 mmol) gave 91.2 mg of **3s** as a light brown solid. Yield: 63%; mp. 148-151 °C; *R_f* 0.50 (petroleum ether : ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 7.60-7.63 (m, 2H), 7.44-7.52 (m, 1H), 7.07-7.40 (m, 10H), 6.99-7.07 (m, 2H), 4.58 (d, ²*J* = 13.9 Hz, 1H), 4.52 (d, ²*J* = 13.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 144.5 (C), 136.1 (C), 133.1 (CH), 131.1 (2 x CH), 129.6 (2 x CH), 128.8 (2 x CH), 128.8 (2 x CH), 128.6 (CH), 128.1 (2

x CH), 127.9 (C), 123.2 (2 x CH), 121.6 (CH), 63.2 (CH₂); IR (KBr): ν 3060, 2922, 1595, 1489, 1289, 1263 1207, 1088 cm⁻¹; MS (EI), m/z (relative intensity): 307 ([M]⁺, 45 %); Calcd. for C₁₉H₁₇NOS: C, 74.23; H, 5.57; N, 4.56; found C, 74.34; H, 5.52; N, 4.24.

rac-N-(Phenyl)-S-4-bromo-phenyl-S-methylsulfoximine (3t): The general procedure (method A) using *S*-4-bromo-phenyl-*S*-methylsulfoximine (**1c**, 117.0 mg, 0.502 mmol) and phenyl iodide (**2a**, 210.0 mg, 1.030 mmol) gave 82.0 mg of **3t** as a yellow oil. Yield: 53%; R_f 0.50 (petroleum ether : ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 7.82-7.79 (m, 2H), 7.65-7.61 (m, 2H), 7.13-7.08 (m, 2H), 6.98-6.95 (m, 1H), 6.89-6.85 (m, 1H), 3.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.5 (C), 138.4 (C), 132.8 (2 x CH), 130.2 (2 x CH), 129.0 (2 x CH), 128.4 (C), 123.2 (2 x CH), 121.9 (CH), 46.0 (CH₃); IR (KBr): ν 3022, 2926, 1593, 1487, 1292, 1204, 1093 cm⁻¹; MS (EI), m/z (relative intensity): 309, 311 ([M]⁺, 50.1 %); Calcd. for C₁₃H₁₂BrNOS: C, 50.33; H, 3.90; N, 4.52; found C, 50.11; H, 4.02; N, 4.80.

(S,S)-N,N'-[Naphthalene]-1,8-bis-(S-methyl-S-phenylsulfoximine) (6): Under an argon atmosphere a dry Schlenk tube was charged with (*S*)-*S*-methyl-*S*-phenylsulfoximine [(*S*)-**1a**, 161.4 mg, 1.04 mmol, 4.0 equiv], CsOAc (399 mg, 2.08 mmol, 8.0 equiv) and CuI (99 mg, 0.52 mmol, 2.0 equiv). Degassed DMSO (1 mL) followed by 1,8-dibromo-naphthalene (**4**)¹ (74 mg, 0.26 mmol, 1.0 equiv) was then added to the mixture. After heating to 90 °C for 12 h, the mixture was cooled to room temperature and neutralized with HCl. The aqueous layer was extracted with dichloromethane three times. The combined organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel afforded 63 mg of (*S,S*)-**6** as a grey solid. Yield: 56%; mp. 110 °C; R_f 0.37 (ethyl acetate : petroleum ether = 3 : 1); ¹H NMR (acetone-D₆): δ 8.31-8.29 (m, 4H), 7.59-7.50 (m, 6H), 7.21-7.16 (m, 4H), 7.03-6.99 (m, 2H), 3.49 (s, 6H); ¹³C NMR (CDCl₃): δ 142.1 (2 x C), 139.0 (C), 137.1 (C), 133.0 (2 x CH), 131.1 (2 x C), 129.5 (4 x CH), 129.3 (4 x CH), 125.6 (2 x CH), 123.1 (2 x CH), 119.9 (2 x CH), 45.9 (CH₃); IR (KBr): ν 2924, 1296, 1210, 1089, 745 cm⁻¹; MS (EI), m/z (relative intensity): 434 ([M]⁺, 100 %); Calcd. for C₂₄H₂₂N₂O₂S₂•H₂O: C, 63.69; H, 5.34; N, 6.19; found C, 66.33; H, 5.10; N, 6.45.

Reference

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