SUPPORTING INFORMATION

Cu(OAc)₂-catalyzed N-Arylations of Sulfoximines and Aryl Boronic Acids

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¹H and ¹³C NMR (300 or 400 and 75 or 100 MHz, respectively) spectra were recorded in CDCl₃ using TMS 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, capillaries or in CHCl₃. Dichloromethane was distilled over CaH₂ and MeOH was distilled over magnesium and stored over 3 Å molecular sieves.

General procedure for the N-arylations of sulfoximines with aryl boronic acids:

The aryl boronic acid (0.7 mmol, 2.3 equiv), the NH-free sulfoximine (0.3 mmol, 1.0 equiv) and the copper salt (0.03 mmol, 0.1 equiv) are placed in 10 mL test tube equipped with magnetic stirrer. Solvent (1.0 mL) is added and the test tube is then placed into a 250 mL flask capped with a CaCl₂-drying tube. The reaction is vigorously stirred for 6-12 h. Purification by column chromatography using silica gel and a pentane/acetone-mixture as eluent (usually in a ratio of 5:1) affords the N-arylated product.

***rac*-N-Phenyl-S-phenyl-S-methylsulfoximine (3aa):**¹ Yield: 65 mg (93%); white solid. mp. 100-101 °C; *R_f* 0.28 (petroleum ether / ethyl acetate = 1 : 1); ¹H NMR (300 MHz, CDCl₃): δ 7.98-7.94 (m, 2 H), 7.62-7.49 (m, 3 H), 7.11 (m_c, 2 H), 7.01 (m_c, 2 H), 6.86 (m_c, 1 H), 3.23 (s, 3 H); ¹³C-NMR (75 MHz, CDCl₃): δ 144.9, 139.4, 133.2, 129.5, 128.9, 128.6, 123.2, 121.6, 46.0. IR (KBr): ν = 3060, 3021, 2921, 1592, 1484 cm⁻¹; MS (EI), *m/z* (relative intensity): 231.3 ([M]⁺, 100%); Calcd. for C₁₃H₁₃NOS: 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-phenyl-S-methylsulfoximine (3ab):**¹ Yield: 55 mg (75%); white solid. mp. 61-62 °C; *R_f* 0.21 (pentane / acetone 5:1); ¹H-NMR (300 MHz, CDCl₃): δ 8.00-7.96 (m, 2 H), 7.61-7.49 (m, 3 H), 7.12 (m, 1 H), 7.01 (dd, *J* = 7.9, 1.2 Hz, 1 H), 6.95-6.87 (m, 1 H), 6.81 (td, *J* = 7.4, 1.5 Hz, 1 H), 3.21 (s, 3 H), 2.37 (s, 3 H); ¹³C-NMR (75 MHz, CDCl₃): δ 143.4, 139.9, 133.1, 132.2, 130.3, 129.4, 128.3, 126.2, 121.8, 121.7, 45.5, 18.6. IR (KBr): ν = 3014, 2926 1486, 1442, 1294, 1268, 1209, 1192, 1090, 1022, 770, 739 cm⁻¹; MS (EI), *m/z* (relative intensity): 245.0 ([M]⁺, 100%), 104.0 ([M-C₆H₅SOCH₃], 18); Calcd. for C₁₄H₁₅NOS: C, 68.54; H, 6.16; N, 5.71; found C, 68.59; H, 6.07; N, 5.45.

***rac*-N-[(4-Methyl)-phenyl]-S-phenyl-S-methylsulfoximine (3ac):** Yield: 68 mg (92%); white solid. mp. 112-114 °C; *R_f* 0.16 (pentane / acetone 5:1); ¹H-NMR (300 MHz, CDCl₃): δ 7.99-7.95 (m, 2 H), 7.59-7.47 (m, 3 H), 6.92 (m_c, 4 H), 3.21 (s, 3 H), 2.19 (s, 3 H); ¹³C-NMR (75 MHz, CDCl₃): δ 142.1, 139.5, 133.0, 130.9, 129.5, 129.4, 128.6, 123.1, 45.8,

20.6; IR (KBr): ν 3063, 3015, 2924, 1505, 1445, 1292, 1264, 1191, 815, 502 cm^{-1} ; MS (EI), m/z (relative intensity): 245.0 ($[\text{M}]^+$, 100%), 104.0 ($[\text{M}-\text{C}_6\text{H}_5\text{SOCH}_3$, 18); Calcd. for $\text{C}_{14}\text{H}_{15}\text{NOS}$: C, 68.54; H, 6.16; N, 5.71; found C, 68.35; H, 6.04; N, 5.53.

rac-N-[(2-Chlor)-phenyl]-S-phenyl-S-methylsulfoximine (3ad): Yield: 72 mg (90%); white solid. mp. R_f 0.29 (pentane / acetone 5:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.06-8.02 (m, 2H), 7.62-7.50 (m, 3 H), 7.31 (dd, $J = 8.0, 1.7$ Hz, 1 H), 7.19 (dd, $J = 8.0, 1.4$ Hz, 1 H), 6.97 (td, $J = 7.7, 1.4$ Hz, 1 H), 6.82 (td, $J = 7.7, 1.7$ Hz, 1 H), 3.25 (s, 3 H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 141.9, 138.9, 133.3, 129.7, 129.4, 128.4, 127.0, 123.8, 122.6, 45.6; IR (KBr): ν 3019, 2927, 1472, 1441, 1297, 1206, 1093, 1021, 771, 741 cm^{-1} ; MS (EI), m/z (relative intensity): 264.9 ($[\text{M}]^+$, 100%), Calcd. for $\text{C}_{13}\text{H}_{12}\text{ClNOS}$: C, 58.75; H, 4.55; N, 5.27; found C, 58.97; H, 4.59; N, 5.36.

rac-N-[(4-Chlor)-phenyl]-S-phenyl-S-methylsulfoximine (3ae):² Yield: 74 mg (93%); white solid. mp. 64-66 $^\circ\text{C}$; R_f 0.29 (pentane / acetone 5:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.96-7.92 (m, 2 H), 7.62-7.52 (m, 3 H), 7.06 (m_c, 2 H), 6.93 (m_c, 2 H), 3.24 (s, 3 H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 143.5, 138.7, 133.3, 129.5, 128.8, 128.5, 126.7, 124.3, 46.01; IR (KBr): ν 3064, 3014, 2926, 1592, 1487, 1402, 1371, 1291, 1198, 1091, 1016, 828, 738, 681 cm^{-1} ; MS (EI), m/z (relative intensity): 264.9 ($[\text{M}]^+$, 100%).

rac-N-[(2-Methoxy)-phenyl]-S-phenyl-S-methylsulfoximine (3af):¹ Yield: 57 mg (73%); brown oil; R_f 0.05 (pentane / acetone 5:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.04-8.00 (m, 2 H), 7.58-7.48 (m, 3 H), 7.07 (dd, $J = 8.0, 1.7$ Hz, 1 H), 6.87 (td, $J = 8.0, 1.7$ Hz, 1 H), 6.81 (dd, $J = 8.0, 1.7$ Hz, 1 H), 6.70 (td, $J = 7.7, 1.7$ Hz, 1 H), 3.84 (s, 3 H), 3.26 (s, 3 H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 152.8, 139.9, 133.7, 132.9, 129.2, 128.4, 124.0, 122.5, 120.6, 111.2, 55.6, 46.2; IR (KBr): ν 3060, 3007, 2930, 2834, 1495, 1451, 1295, 1266, 1236, 1201, 1026, 749 cm^{-1} ; MS (EI), m/z (relative intensity): 261.0 ($[\text{M}]^+$, 100%); Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$: C, 64.34; H, 5.79; N, 5.36; found C, 64.42; H, 5.88; N, 5.81.

rac-N-[(4-Bromo)phenyl]-S-phenyl-S-methylsulfoximine (3ag): Yield: 66 mg (71%); white solid. mp. 109-111 $^\circ\text{C}$; R_f 0.26 (pentane / acetone 5:1); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.96-7.91 (m, 2 H), 7.63-7.50 (m, 3 H), 7.20 (m_c, 2 H), 6.88 (m_c, 2 H), 3.23 (s, 3 H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 144.2, 138.8, 133.4, 131.8, 129.6, 128.5, 124.8, 114.3, 46.0; IR (CHCl_3): $\nu = 3063, 3017, 2928, 1483, 1289, 1206, 1095, 1023, 753$ cm^{-1} ; MS (EI), m/z (relative intensity): 310.9 ($[\text{M}]^+$, 100%); Calcd. for $\text{C}_{13}\text{H}_{12}\text{BrNOS}$: C, 50.33; H, 3.90; N, 4.52; found C, 50.31; H, 4.19; N, 4.51.

rac-N-[(4-*t*-Butyl-dimethylsilyloxy)phenyl]-S-phenyl-S-methylsulfoximine (3ah): Yield: 96 mg (88%); white solid. mp. 85-87 $^\circ\text{C}$; R_f 0.17 (pentane / acetone 5:1); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.99-7.92 (m, 2 H), 7.60-7.47 (m, 3 H), 6.87 (d, $J = 8.9$ Hz, 2 H), 6.61 (d, $J = 8.9$ Hz, 2 H), 3.20 (s, 3 H), 0.93 (s, 9 H), 0.11 (s, 6 H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 150.4, 139.4, 138.3, 133.0, 129.3, 128.6, 124.2, 120.3, 45.6, 25.6, 18.1, -4.6; IR (KBr): $\nu = 3056, 3036, 2933, 1501, 1245, 1095, 907, 837$ cm^{-1} ; MS (EI), m/z (relative intensity) = 361.1 ($[\text{M}]^+$, 100%); Calcd. for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$: C, 63.11; H, 7.53; N, 3.87; found C, 63.03; H, 7.41; N, 3.75.

rac-N-[(4-Phenyl)-phenyl]-S-phenyl-S-methylsulfoximine (3ai): Yield: 68 mg (74%); white solid. mp. 140-141 $^\circ\text{C}$; R_f 0.10 (pentane / acetone 6:1); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.01-7.97 (m, 2 H), 7.59-7.45 (m, 5 H), 7.39-7.31 (m, 4 H), 7.26-7.20 (m, 1 H), 7.07 (m_c, 2 H), 3.23 (s, 3 H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 144.4, 140.8, 139.3, 134.3,

133.2, 129.5, 128.5, 127.5, 126.5 123.4, 46.0; IR (KBr): ν 3065, 3019, 2923, 1599, 1510, 1481, 1281, 1192, 1095, 836, 502 cm^{-1} ; MS (EI), m/z (relative intensity): 307.0 ($[\text{M}]^+$, 100%); Calcd. for $\text{C}_{19}\text{H}_{17}\text{NOS}$: C, 74.23; H, 5.57; N, 4.56; found C, 74.28; H, 5.76; N, 4.56.

rac-N-[1-Naphthyl]-S-phenyl-S-methylsulfoximine (3aj):³ Yield: 52 mg (62%); white solid. mp. 90-93 °C; R_f 0.17 (pentane / acetone 6:1); $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 8.54 (m_c , 1 H), 8.02-7.98 (m, 2 H), 7.76-7.72 (m, 1 H), 7.58-7.36 (m, 6 H), 7.20-7.09 (m, 2 H), 3.30 (s, 3 H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 141.5, 139.3, 134.5, 133.2, 130.0, 129.5, 128.4, 127.7, 126.0, 125.8, 125.0, 123.9, 121.5, 116.5, 45.9; IR (KBr): ν 3065, 3019, 2923, 1511, 1481, 1282, 1191 cm^{-1} ; Calcd. for $\text{C}_{17}\text{H}_{15}\text{NOS}$: C, 72.57; H, 5.37; N, 4.98; found C, 72.56; H, 5.07; N, 4.82.

rac-N-(Phenyl)-S-[4-(Bromo)phenyl]-S-methylsulfoximine (3ba): Yield: 80 mg (86%); white solid. mp. 109-111 °C; R_f 0.26 (pentane / acetone 5:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.82 (m_c , 2 H), 7.65 (m_c , 2 H), 7.11 (m_c , 2 H), 6.99 (m_c , 2 H), 6.89 (m_c , 1 H), 3.23 (s, 3 H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 144.4, 138.3, 132.7, 130.1, 129.0, 128.4, 123.2, 121.9, 46.1; IR (CHCl_3): ν 3488, 3442, 3050, 3020, 2928, 1569, 1483, 1289, 1267, 1204, 1039, 778, 538, 505 cm^{-1} ; MS (EI), m/z (relative intensity) = 310.9 ($[\text{M}]^+$, 83%), 308.9 ($[\text{M}]^+$, 76%), 167.0 (100%); Calcd. for $\text{C}_{13}\text{H}_{12}\text{BrNOS}$: C, 50.33; H, 3.90; N, 4.52; found C, 50.09; H, 4.06; N, 4.29.

rac-N-Phenyl-S-phenyl-S-cyclopentylsulfoximine (3ca): Yield: 54 mg (81%); white solid. mp. 75-77 °C; R_f 0.37 (pentane / acetone 6:1); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.91-7.86 (m, 2 H), 7.57-7.46 (m, 3 H), 7.10-7.05 (m, 2 H), 7.02-6.98 (m, 2 H), 6.90-6.79 (m, 1 H), 3.72 (m_c , 1 H), 2.39-2.31 (m, 1 H), 2.16-1.96 (m, 2 H), 1.82-1.52 (m, 5 H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 145.4, 137.9, 132.7, 129.5, 129.2, 128.7, 123.2, 121.0, 65.8, 27.5, 27.4, 25.8, 25.7; IR (KBr): ν 3069, 2951, 2865, 1589, 1483, 1444, 1261, 1181, 1012, 767, 694, 541 cm^{-1} ; MS (EI), m/z (relative intensity): 287.8 ($[\text{M}]^+$, 26%), 91.9 (100 %); Calcd. for $\text{C}_{17}\text{H}_{19}\text{NOS}$: C, 71.54; H, 6.71; N, 4.91; found C, 71.47; H, 6.84; N, 5.00.

References:

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Compound **3ab**:

ppm (f1)

4	9	0	2	3	4	3	2	8	7	2	0	8	3	9
.	.	.	.	.	.	.	.	.	.	4	0	5	5	5
3	9	3	2	0	9	8	6	1	1	.	.	.	5	.
4	3	3	3	3	2	2	2	2	2	7	7	6	5	8
1	1	1	1	1	1	1	1	1	1	7	7	7	4	1

ppm (f1)

Compound **3ac**:

ppm (f1)

ppm (f1)

Compound **3ad**:

ppm (f1)

ppm (f1)

Compound **3ae**:

ppm (t1)

6	9	3	5	9	5	7	3
3	6	3	9	8	8	6	4
4	3	3	2	2	2	2	2
1	1	1	1	1	1	1	1

2	0	7
4	0	5
7	7	6
7	7	7

2
0
6
4

ppm (f1)

Compound **3af**:

ppm (t1)

ppm (t1)

Compound **3ag**:

ppm (t1)

2	8	3	8	5	5	8	2
.	.	.	.	.	.	.	.
4	8	3	1	9	8	4	4
4	3	3	3	2	2	2	1
1	1	1	1	1	1	1	1

2	0	7
4	0	5
.	.	.
7	7	6
7	7	7

2
0
.
6
4

ppm (t1)

Compound **3ah**:

ppm (t1)

4	3	3	0	3	6	1	3
.	.	9	8	.	9	8	.
0	9	8	3	9	8	4	0
5	3	3	3	2	2	2	2
1	1	1	1	1	1	1	1

2	0	7
4	0	5
.	.	.
7	7	6
7	7	7

6
5
.
5
4

1	5
6	0
.	.
5	8
2	1

5
5
.
4
-

ppm (t1)

Compound **3ai**:

ppm (t1)

ppm (t1)

Compound **3aj**:

ppm (t1)

ppm (t1)

Compound **3ba**:

ppm (t1)

ppm (t1)

Compound **3ca**:

ppm (t1)

3	8	7	5	1	6	1	0
.	.	.	.	.	.	.	.
5	7	2	9	9	8	3	1
4	3	3	2	2	2	2	2
1	1	1	1	1	1	1	1

1	0	8	2
3	0	6	8
.	.	.	.
7	7	6	5
7	7	7	6

6	4	9	7
4	3	7	6
.	.	.	.
7	7	5	5
2	2	2	2

ppm (t1)