**Magnesium-Induced Copper-Catalyzed Synthesis of Unsymmetrical Diaryl
Chalcogenide Compounds from Aryl Iodide via Cleavage of the Se-Se or S-S Bond**

Nobukazu Taniguchi* and Tetsuo Onami

Department of Chemistry, Fukushima Medical University, Fukushima 960-1295 Japan

SUPPORTING INFORMATION

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General Procedure. All reactions were carried out under a nitrogen atmosphere. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ^1H , 67.5 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. IR spectra were measured by Perkin-Elmer Spectrum One FT-IR spectrometer.

References for known compounds:

Diphenyl selenide (entry 1 in Table 2): (a) Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727. (b) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354–1356.

Phenyl 2-tolyl selenide (entry 2 in Table 2): Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727.

2-Methoxyphenyl phenyl selenide (entry 3 in Table 2): Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727.

2-Nitrophenyl phenyl selenide (entry 6 in Table 2): Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727.

Phenyl 4-tolyl selenide (entry 8 in Table 2): Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727.

4-Methoxyphenyl phenyl selenide (entry 9 in Table 2): (a) Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725–1727. (b) Pierini, A. B.; Penénory, A. B.; Rossi, A. R. *J. Org. Chem.* **1984**, *49*, 486–490.

4-Bromophenyl phenyl selenide (entry 10 in Table 2): Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org.*

Lett. **1999**, *1*, 1725–1727

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1-Naphthyl phenyl selenide (entry 13 in Table 2): Pierini, A. B.; Rossi, A. R. *J. Org. Chem.* **1979**, *44*, 4667–4673.

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Phenyl 2-thienyl selenide (entry 16 in Table 2): Gujadhur, R. K.; Venkataruman, D. *Tetrahedron Lett.* **2003**, *44*, 81–84.

Diphenyl sulfide (entry 1 in Table 3): (a) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 1385–1389. (b) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174.

Phenyl 2-tolyl sulfide (entry 2 in Table 3): (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174. (b) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657–3658.

n-Butyl 2-tolyl sulfide (entry 4 in Table 3): Zheng, N.; McWilliams, C.; Fleitz, F. J.; Armstrong III, J. D.; Volante, R. P. *J. Org. Chem.*, **1998**, *63*, 9606–9607.

2-Methoxyphenyl phenyl sulfide (entry 5 in Table 3): (a) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385–1389. (b) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174.

4-Methoxyphenyl phenyl sulfide (entry 8 in Table 3): (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174. (b) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657–3658.

Phenyl 4-tolyl sulfide (entry 10 in Table 3): (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174. (b) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657–3658.

1,4-Bis(phenyl sulfide) benzene (entry 11 in Table 3): Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3611–3612.

Phenyl 4-trifluoromethylphenyl sulfide (entry 12 in Table 3): Petrillo, G.; Novi, M.; Garbarino, G.; Dell'erba, C. *Tetrahedron* **1987**, *43*, 4625–4643.

4-Nitrophenyl phenyl sulfide (entry 15 in Table 3): (a) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657–3658. (b) Cristau, H. J.; Chabaud, B.; Chene, A.; Christol, H. *Synthesis* **1981**, 892–895.

1-Naphthyl phenyl sulfide (entry 16 in Table 3): (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173–3174. (b) Cristau, H. J.; Chabaud, B.; Chene, A.; Christol, H. *Synthesis* **1981**, 892–895.

2-Pyridyl phenyl sulfide (entry 17 in Table 3): Zoltewicz, J. A.; Locko, G. A. *J. Org. Chem.* **1983**, *48*, 4214–4219.

3-Pyridyl phenyl sulfide (entry 18 in Table 3): Amatore, C.; Beugelmans, R.; Bois-Choussy, H.; Combellas, C.; Thiebault, A. *J. Org. Chem.* **1989**, *54*, 5688–5695.

Copper Catalyzed Synthesis of Diaryl Selenide from Aryl Iodide and Diselenide (Table 2)

A typical procedure (Entry 2): To a mixture of Cu_2O (2.1 mg, 0.015 mmol), magnesium (powder) (14.6 mg, 0.6 mmol), 2,2'-bipyridyl (bpy) (4.6 mg, 0.03 mmol) and DMF (0.5 mL) were added 2-iodotoluene (**1a**) (65.4 mg, 0.3 mmol) and diphenyl diselenide (46.8 mg, 0.15 mmol), and the mixture was stirred at 110 °C for 30 h. After evaporation of the solvent, the residue was dissolved in Et_2O . The solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (Hexane) gave phenyl 2-tolyl selenide (**3a**) (78.1 mg, 92 %). ^1H NMR (CDCl_3) δ 2.39 (s, 3H), 7.06 (t, $J = 7.0$ Hz, 1H), 7.15–7.41 (m, 7H), 7.56–7.62 (m, 1H); ^{13}C NMR (CDCl_3) δ 22.3, 126.7, 127.1, 127.7, 127.8, 129.1, 129.3, 130.2, 131.5, 132.7, 133.6; IR (neat) 3056, 1574, 1474, 1436 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{Se}$: C, 63.16; H, 4.89. Found: C, 63.11; H, 4.87.

Entry 1: ^1H NMR (CDCl_3) δ 7.24–7.26 (m, 6H), 7.44–7.47 (m, 4H); ^{13}C NMR (CDCl_3) δ 127.2, 129.3, 131.1, 132.9.

Entry 3: ^1H NMR (CDCl_3) δ 3.88 (s, 3H), 6.79 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.25–7.36 (m, 3H), 7.56–7.60 (m, 2H); ^{13}C NMR (CDCl_3) δ 55.8, 110.4, 121.6, 121.9, 127.7, 128.0, 128.3, 129.4, 130.8, 135.3, 135.4; IR (neat) 1575, 1473 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OSe}$: C, 59.32; H, 4.60. Found: C, 59.59; H, 4.58.

Entry 6: ^1H NMR (CDCl_3) δ 7.00 (d, $J = 7.2$ Hz, 1H), 7.24–7.32 (m, 3H), 7.42–7.51 (m, 3H), 7.70 (d, $J = 7.2$ Hz, 1H), 8.32 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 125.7, 126.0, 128.1, 129.8, 130.0, 130.2, 133.1, 133.6, 135.8, 137.3. IR (neat) 1588, 1513, 1331, 1304 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_2\text{Se}$: C, 51.81; H, 3.26; N, 5.04. Found: C, 51.80; H, 3.28; N, 5.01.

Entry 8: ^1H NMR (CDCl_3) δ 2.33 (s, 3H), 7.10 (d, $J = 7.9$ Hz, 2H), 7.20–7.27 (m, 3H), 7.40 (d, $J = 7.9$ Hz, 2H), 7.36–7.42 (m, 2H); ^{13}C NMR (CDCl_3) δ 21.1, 126.8, 129.2, 130.0, 130.2, 131.5, 132.0, 133.8, 137.6. IR (neat) 1577, 1488, 1475 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{Se}$: C, 63.16; H, 4.89. Found: C, 63.11; H, 4.90.

Entry 9: ^1H NMR (CDCl_3) δ 3.81 (s, 3H), 6.85 (d, $J = 8.5$ Hz, 2H), 7.19–7.34 (m, 5H), 7.50 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 55.2, 115.1, 119.9, 120.1, 126.4, 129.1, 130.9, 136.5, 159.0. IR (neat) 1577, 1490 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OSe}$: C, 59.32; H, 4.60. Found: C, 59.37; H, 4.63.

Entry 10: ^1H NMR (CDCl_3) δ 7.26–7.31 (m, 5H), 7.35–7.38 (m, 2H), 7.45–7.48 (m, 2H); ^{13}C NMR (CDCl_3) δ 121.4, 127.7, 129.4, 130.3, 132.3, 133.2, 133.3, 134.2. IR (neat) 1577, 1466 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{SeBr}$: C, 46.19; H, 2.91. Found: C, 46.39; H, 3.05.

Entry 12: ^1H NMR (CDCl_3) δ 7.35 (d, $J = 9.0$ Hz, 2H), 7.38–7.50 (m, 3H), 7.61–7.78 (m, 2H), 8.04 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 123.5, 123.9, 129.5, 129.7, 130.0, 131.9, 134.2, 135.8; IR (neat) 1574, 1514, 1342 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_2\text{Se}$: C, 51.81; H, 3.26; N, 5.04. Found: C, 51.78; H, 3.28; N, 5.03.

Entry 13: ^1H NMR (CDCl_3) δ 7.16–7.19 (m, 3H), 7.32–7.39 (m, 3H), 7.47–7.51 (m, 2H), 7.74–7.84 (m, 3H), 8.31–8.35 (m, 1H). ^{13}C NMR (CDCl_3) δ 126.0, 126.3, 126.7, 126.9, 127.6, 128.5, 129.1, 129.2, 129.3, 129.4, 131.6, 133.8, 134.1, 134.2; IR (neat) 3054, 1561, 1503 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{Se}$: C, 67.85; H, 4.27. Found: C, 67.55; H, 4.47.

Entry 14: ^1H NMR (CDCl_3) δ 6.98–7.04 (m, 2H), 7.34–7.42 (m, 4H), 7.68–7.73 (m, 2H), 8.42–8.45 (m, 1H); ^{13}C NMR (CDCl_3) δ 120.3, 124.2, 128.8, 129.6, 136.1, 136.6, 149.8, 149.9, 158.8; IR (neat) 1570,

1557, 1414 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NSe}$: C, 56.42; H, 3.87; N, 5.98. Found: C, 56.42; H, 4.00; N, 6.01.

Entry 16: ^1H NMR (CDCl_3) δ 7.02–7.05 (m, 1H), 7.17–7.27 (m, 3H), 7.30–7.35 (m, 3H), 7.45 (d, $J = 5.3$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 123.1, 126.7, 128.3, 129.1, 129.9, 131.9, 133.3, 136.9; IR (neat) 3069, 1575, 1475, 1437, 1397 cm^{-1} ; Anal. Calcd for $\text{C}_{10}\text{H}_8\text{SSe}$: C, 50.21; H, 3.37. Found: C, 50.15; H, 3.38.

Copper Catalyzed Synthesis of Diaryl Sulfide from Aryl Iodide and Disulfide (Table 3)

A typical procedure (entry 1): To a mixture of CuI (5.7 mg, 0.03 mmol), magnesium (powder) (14.6 mg, 0.6 mmol), bpy (4.6 mg, 0.03 mmol) and DMF (0.5 mL) were added iodobenzene (61.2 mg, 0.3 mmol) and diphenyl disulfide (**4a**) (31.2 mg, 0.15 mmol), and the mixture was stirred at 110 $^\circ\text{C}$ for 18 h. After evaporation of the solvent, the residue was dissolved in Et_2O . The solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (Hexane) gave diphenyl sulfide (50.3 mg, 90 %): ^1H NMR (CDCl_3) δ 7.23–7.36 (m, 10H); ^{13}C NMR (CDCl_3) δ 127.0, 129.1, 131.0, 135.7.

Entry 2: ^1H NMR (CDCl_3) δ 2.37 (s, 3H), 7.13–7.33 (m, 8H), 7.49 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 20.5, 126.3, 126.7, 127.5, 127.9, 129.0, 129.1, 129.2, 129.6, 130.5, 133.0; IR (neat) 1582, 1476 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{S}$: C, 77.95; H, 6.04. Found: C, 77.98; H, 6.11.

Entry 4: ^1H NMR (CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.42–1.53 (m, 2H), 1.53–1.68 (m, 2H), 2.36 (s, 3H), 2.89 (t, $J = 7.4$ Hz, 2H), 7.06–7.26 (m, 4H); ^{13}C NMR (CDCl_3) δ 13.6, 20.3, 22.0, 31.0, 32.5, 125.2, 126.2, 127.3, 129.9, 136.3, 137.2; IR (neat) 2956, 1582, 1468 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{S}$: C, 73.27; H, 8.94. Found: C, 73.39; H, 8.75.

Entry 5: ^1H NMR (CDCl_3) δ 3.85 (s, 3H), 6.83–6.90 (m, 2H), 7.08 (d, $J = 7.5$ Hz, 1H), 7.19–7.36 (m, 6H); ^{13}C NMR (CDCl_3) δ 55.8, 110.8, 121.2, 124.0, 127.0, 128.3, 129.1, 131.4, 131.6, 134.5, 157.3; IR (neat) 1577, 1431 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$ C, 72.19; H, 5.59. Found: C, 71.74; H, 5.61.

Entry 8: ^1H NMR (CDCl_3) δ 3.81 (s, 3H), 6.88 (d, $J = 8.6$ Hz, 2H), 7.12–7.25 (m, 5H), 7.41 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 55.3, 114.9, 124.3, 125.7, 128.2, 128.9, 135.3, 138.5, 159.8; IR (neat) 1592, 1493, 1246 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$ C, 72.19; H, 5.59. Found: C, 72.36; H, 5.79.

Entry 10: ^1H NMR (CDCl_3) δ 2.34 (s, 3H), 7.17–7.33 (m, 9H); ^{13}C NMR (CDCl_3) δ 21.1, 126.3, 127.1, 127.5, 129.0, 129.1, 129.7, 130.0, 132.2; IR (neat) 1581, 1476 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{S}$ C, 77.95; H, 6.04. Found: C, 77.69; H, 6.22.

Entry 11: mp 80–81 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 7.21 (s, 4H), 7.24–7.37 (m, 10H); ^{13}C NMR (CDCl_3) δ 127.3, 129.2, 131.0, 131.1, 131.3, 131.4, 134.9, 135.0; IR (CHCl_3) 1581, 1474, 1439 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{S}_2$ C, 73.43; H, 4.79. Found: C, 73.13; H, 4.81.

Entry 12: ^1H NMR (CDCl_3) δ 7.26 (d, $J = 8.2$ Hz, 2H), 7.36–7.47 (m, 5H), 7.48 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 125.6, 125.7, 125.8, 125.9, 128.2, 128.6, 129.6, 132.4, 133.5; IR (neat) 1606, 1326 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{S}$ C, 61.41; H, 3.57. Found: C, 61.70; H, 3.83.

Entry 15: ^1H NMR (CDCl_3) δ 7.18 (d, $J = 8.0$ Hz, 2H), 7.18–7.25 (m 3H), 7.43–7.60 (m, 2H), 8.05 (d, $J = 8.0$ Hz, 2H); IR (neat) 1574, 1514, 1475, 1337 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_9\text{NO}_2\text{S}$: C, 62.32; H, 3.92; N, 6.06. Found: C, 62.24; H, 4.13; N, 6.06.

Entry 16: ^1H NMR (CDCl_3) δ 7.13–7.24 (m, 5H), 7.38–7.53 (m, 3H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.82–7.83 (m, 2H), 8.35–8.39 (m, 1H); ^{13}C NMR (CDCl_3) δ 125.6, 125.8, 126.1, 126.4, 126.9, 128.5,

128.9, 129.0, 129.1, 131.2, 132.5, 133.5, 134.2, 136.9; IR (neat) 1582, 1502, 1477, 1438 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{S}$ C, 81.31; H, 5.12. Found: C, 81.02; H, 5.35.

Entry 17: ^1H NMR (CDCl_3) δ 6.88 (d, $J = 8.2$ Hz, 1H), 6.98 (dd, $J = 7.2$ and 5.7 Hz, 1H), 7.40–7.47 (m, 4H), 7.58–7.61 (m, 2H), 8.41–8.43 (m, 1H); ^{13}C NMR (CDCl_3) δ 119.8, 121.3, 129.0, 129.5, 131.0, 134.9, 136.6, 149.5, 161.5. IR (neat) 1574, 1447, 1417 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NS}$ C, 70.55; H, 4.84; N, 7.48. Found: C, 70.20; H, 4.99; N, 7.21.

Entry 18: ^1H NMR (CDCl_3) δ 7.20 (dd, $J = 7.9$ and 4.6 Hz, 1H), 7.28–7.39 (m, 5H), 7.58 (dt, $J = 7.9$ and 2.3 Hz, 1H), 8.45 (d, $J = 4.6$ Hz, 1H), 8.56 (d, $J = 2.3$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 123.8, 127.8, 129.8, 131.7, 133.5, 133.9, 137.8, 147.8, 151.0; IR (neat) 1582, 1566, 1476, 1405 cm^{-1} ; Anal. Calcd for $\text{C}_{11}\text{H}_9\text{NS}$ C, 70.55; H, 4.84; N, 7.48. Found: C, 70.17; H, 5.10; N, 7.38.