Supporting Information

Palladium-Catalyzed C–H Homocoupling of Thiophenes. Facile Construction of Bithiophene Structure

Kentaro Masui, Haruka Ikegami, and Atsunori Mori*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan

Experimental

5,5'-Diformyl-2,2'-bithiophene (2a):¹ To a screw-capped glass tube equipped with a magnetic stirring bar were added a palladium catalyst (5.8 mg, 0.015 mmol), 3 mL of DMSO, and 2-formylthiophene (**1a**, 0.047 mL, 0.5 mmol). To the resulting mixture silver(I) fluoride (127 mg, 1.0 mmol) was added and heated at 60 °C for 5 h. Then, the mixture was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid. Purification by chromatography on silica gel with chloroform as an eluent afforded 38.5 mg of **2a** (69%). ¹H NMR (300 MHz, CDCl₃) δ 7.42 (2H, d, *J* = 3.9 Hz), 7.73 (2H, d, *J* = 3.9 Hz), 9.92 (2H, s). ¹³C NMR (75.5 MHz, CDCl₃) δ 126.7, 136.8, 143.4, 144.8, 182.5. IR (KBr) 3100, 3070, 1655 cm⁻¹.

XRD analysis of the silver residue: The residue on the filter was washed with chloroform repeatedly to leave a black powder, which was subjected to XRD analysis on a glass plate with Rigaku X-ray diffractometer RINT Ultima+/PC (λ = 1.54184 Å), 2θ (rel intensity) 38.150 (2510), 44.380 (910), 64.500 (530), 77.460 (517).

2-Formyl-5-phenylthiophene (4):² To a 25 mL of Schlenk tube equipped with a magnetic stirring bar were added, PdCl₂(dppb) (8.1 mg, 0.015 mmol) and 3 mL of DMSO. To the resulting solution were added **1a** (0.047 mL, 0.5 mmol) and 4-iodobenzene (**3**, 0.112 mL, 1.0 mmol). Then, AgF (127 mg, 1.0 mmol) was added and the resulting suspension was heated with stirring at 60 °C for 5 h. After cooling to room temperature the mixture was filtered off and the residue was repeatedly washed with diethyl ether. The solution was washed with water and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (20 mL x 2). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel to afford 55 mg of **4** as a yellow solid (58%). ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.47 (4H, m), 7.65-7.69 (2H, m), 7.75 (1H, d, *J* = 3.6 Hz), 9.89 (1H, s). ¹³C NMR (75.5 MHz, CDCl₃) δ 124.1, 126.4, 129.2, 129.4, 133.0, 137.4, 142.4, 154.2, 182.8. IR (KBr) 3096, 1700, 1684.

XRD analysis of the silver residue: The analysis was carried out in a similar manner for the synthesis of **2a**; 2θ (rel intensity), 22.300 (309), 23.680 (221), 25.319 (158), 32.709 (89), 39.161 (227), 42.629 (172), 45.579 (31), 46.300 (126), 47.230 (24), 52.000 (16), 59.330 (36), 62.949 (16), 66.470 (30), 71.060 (17), 73.417 (26), 76.069 (19).

Synthesis of the following compounds were carried out in a similar manner to that of **2a**.

5,5'-Di(ethoxycarbonyl)-2,2'-bithiophene (2b):³ ¹H NMR (300 MHz, CDCl₃) δ 1.39 (6H, t, *J* = 7.2 Hz), 4.36 (4H, q, *J* = 7.2 Hz), 7.23 (2H, d, *J* = 4.2 Hz), 7.71 (2H, d, *J* = 4.2 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ 14.3, 61.3, 125.1, 133.4, 133.9, 142.5, 161.7. IR (KBr) 3110, 2926, 3078, 1694 cm⁻¹.

5,5'-Di(1-oxoethyl)-2,2'-bithiophene (2c):⁴ ¹H NMR (300 MHz, CDCl₃) δ 2.57 (6H, s), 7.30 (2H, q, *J* = 4.2 Hz), 7.61 (2H, d, *J* = 4.2 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ

26.6, 125.9, 133.1, 144.0, 144.3, 190.3. IR (KBr) 3085, 3073, 2924, 1657, 1510 cm^{-1} .
5,5'-Dimethyl-2,2'-bithiophene (2d):⁵ ^1H NMR (300 MHz, CDCl_3) δ 2.46 (6H, s), 6.63 (2H, d, $J = 3.3$ Hz), 6.87 (2H, d, $J = 3.3$ Hz).
5,5'-Di(4-methylphenyl)-2,2'-bithiophene (2e):⁶ ^1H NMR (300 MHz, CDCl_3) δ 2.37 (6H, s), 7.14 (2H, d, $J = 3.9$ Hz), 7.18-7.21 (4H, m), 7.50 (2H, d, $J = 8.4$ Hz). IR (KBr) 3067, 3022, 2959, 2853, 1694 cm^{-1} .
2,2'-Bibenzothiophene (2f):⁷ ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.40 (4H, m), 7.52 (2H, s), 7.76-7.83 (4H, m). IR (KBr) 3054, 2363 cm^{-1} .
5,5'-Di(4-methoxyphenyl)-2,2'-bithiazole (6): ^1H NMR (300 MHz, CDCl_3) δ 3.88 (6H, s), 6.98 (4H, d, $J = 9.0$ Hz), 7.86 (2H, s), 7.90 (4H, d, $J = 9.0$ Hz). IR (KBr) 3071, 3017, 2972, 2838, 1607 cm^{-1} . HRMS Found: m/z 380.0645. Calcd for 380.0653.
5,5'-Dibromo-2,2'-bithiophene (8):⁸ ^1H NMR (300 MHz, CDCl_3) δ 6.85 (2H, d, $J = 3.9$ Hz), 6.96 (2H, d, $J = 3.9$ Hz). ^{13}C NMR (75.5 MHz, CDCl_3) δ 111.5, 124.1, 130.7, 137.8. IR (KBr) 3100, 3069, 2921, 1507, 1417 cm^{-1} .

XRD analysis of (a) the silver residue to afford **2a** and (b) authentic Ag.

(a) XRD analysis of the silver residue to afford **4** and (b) the authentic sample of AgI.

¹H NMR spectrum of **6**

- ¹ Wei, Y.; Wang, B.; Tian, J. *Tetrahedron Lett.* **1995**, 36, 665.
- ² Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, 71, 467.
- ³ Itahara, T.; Hashimoto, M.; Yumisashi, H. *Synthesis* **1984**, 255.
- ⁴ Kawase, T.; Ueno, N.; Oda, M. *Tetrahedron Lett.* **1992**, 33, 665.
- ⁵ Marsella, M. J.; Piao, G.; Tham, Fook, S. *Synthesis* **2002**, 1133.
- ⁶ Hotta, S.; Lee, S. A.; Tamaki, T. *J. Heterocyclic. Chem.* **2000**, 37, 25.
- ⁷ Parrish, J. P.; Jung, Y. C.; Floyd, R. J.; Jung, W. *Tetrahedron Lett.* **2002**, 43, 7899.
- ⁸ Available from Aldrich Chemicals Co. Ltd. CAS No. 4805-22-5.