

Supporting Information

Palladium-Catalyzed Multiple Arylation of Thiophenes

Toru Okazawa, Tetsuya Satoh, Masahiro Miura,* and Masakatsu Nomura

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

Typical Experimental Procedure [Reaction of *N*-(2-Thienoyl)aniline (**2a**) with Bromobenzene

(1a)]: In a 100 cm³ two-necked flask was placed Cs₂CO₃ (6 mmol, 1.95 g), which was then dried at 150 °C in vacuo for 2 h. Then, Pd(OAc)₂ (0.1 mmol, 22.4 mg), P(*o*-biphenyl)(*t*-Bu)₂ (L1) (0.2 mmol, 59.6 mg), **1a** (6 mmol, 942 mg), **2a** (1 mmol, 203 mg), 1-methylnaphthalene (internal standard, ca. 100 mg) and *o*-xylene (5 cm³) were added. The resulting mixture was stirred under N₂ at 160 °C (bath temperature) for 24 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over Na₂SO₄. Analysis by GC and GC-MS confirmed formation of compound **3** (300 mg, 96%) and triphenylamine (201 mg, 82%). Purification by column chromatography on alumina using hexane-diethyl ether (99.8:0.2, v/v) as eluent gave a white solid of **3** (259 mg, 83%): mp 142.5-144 °C (lit,¹⁶ 143 -144 °C); ¹H NMR (CDCl₃, 400MHz) δ 7.25-7.34 (m, 11H), 7.37 (s, 1H), 7.40 (t, 2H, *J* = 7.6 Hz), 7.65 (d, 2H, *J* = 7.6 Hz); ¹³C NMR (100MHz) δ 125.59, 126.49, 127.00, 127.42, 127.61, 128.39, 128.45, 128.93, 129.06, 129.13, 134.09, 134.20, 136.59, 137.98, 138.98, 142.55; MS *m/z* 312 (M⁺). From the second fraction was obtained a white solid of triphenylamine (174 mg, 71%).

Products: The characterization data of new compounds are given below. Compounds **9**,¹⁷ **10**,¹⁷ **12**,¹⁷ **15**,¹⁸ and **16**¹⁸ are known and were compared with those authentic specimens. The substitution patterns of 2,3- and 2,5-disubstituted and 2,3,5-trisubstituted thiophenes were unambiguously determined by 2D NMR. It was reported that a small amount of 2,4-di(4-anisyl)-3-cyanothiophene (5%) was produced in the reaction of **2g** with 4-iodoanisole using Pd(OAc)₂-Bu₄NBr and K₂CO₃ as an example of 2,4-diarylation of 3-substituted thiophene.^{8c} However, the product data seem to be consistent with the 2,5-dianisyl derivative **19b**.

2,3,5-Tris(4-methoxyphenyl)thiophene (4): mp 94-95 °C; ¹H NMR (CDCl₃, 400MHz) δ 3.80 (s, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 6.81 (d, 2H, *J* = 8.7 Hz), 6.84 (d, 2H, *J* = 8.7 Hz), 6.93 (d, 2H, *J* = 8.7 Hz), 7.20 (s, 1H), 7.25 (d, 2H, *J* = 8.7 Hz), 7.26 (d, 2H, *J* = 8.7 Hz), 7.55 (d, 2H, *J* = 8.7 Hz); ¹³C NMR (100MHz) δ 55.21, 55.23, 55.36, 113.79, 113.89, 114.31, 125.40, 126.81, 126.95, 127.13, 129.29, 130.10, 130.27, 136.13, 137.82, 141.57, 158.52, 158.87, 159.19; MS *m/z* 402 (M⁺). Anal. Calcd for C₂₅H₂₂O₃S: C, 74.60; H, 5.51; S, 7.96. Found: C, 74.33; H, 5.55; S, 7.85.

2,3,5-Tris(4-fluorophenyl)thiophene (5): mp 120-121 °C; ¹H NMR (CDCl₃, 400MHz) δ 6.96-7.02 (m, 4H), 7.08-7.12 (m, 2H), 7.23-7.28 (m, 5H), 7.57-7.60 (m, 2H); ¹³C NMR (100MHz) δ 162.49 (d, *J* = 248.2 Hz), 162.30 (d, *J* = 247.3 Hz), 162.03 (d, *J* = 247.3 Hz), 141.59, 138.04, 136.73, 132.23 (d, *J* = 3.7 Hz), 130.83 (d, *J* = 8.3 Hz), 130.60 (d, *J* = 8.3 Hz), 130.16 (d, *J* = 3.7 Hz), 129.94 (d, *J* = 3.7 Hz), 127.31 (d, *J* = 8.3 Hz), 126.17, 115.99 (d, *J* = 21.1 Hz), 115.65 (d, *J* = 22.1 Hz), 115.50 (d, *J* = 22.1 Hz); HRMS Calcd for C₂₂H₁₃F₃S: *m/z* (M⁺) 366.0707. Found: M, 366.0702.

N-(3-Phenyl-2-thenoyl)aniline (6): mp 117-118.5 °C; ¹H NMR (CDCl₃, 400MHz) δ 7.04 (1H, t, *J* = 7.3 Hz), 7.07 (1H, d, *J* = 4.8 Hz), 7.14 (2H, d, *J* = 7.7 Hz), 7.20-7.26 (2H, m), 7.32 (1H, s), 7.51-7.56 (6H, m); ¹³C NMR (100MHz) δ 119.29, 124.17, 128.93, 129.04, 129.31, 129.44, 129.63, 130.84, 135.28, 135.55, 137.51, 142.09, 159.95; MS *m/z* 279 (M⁺). Anal. Calcd for C₁₇H₁₃NOS: C, 73.09; H, 4.69; N, 5.01; S, 11.48. Found: C, 73.06; H, 4.79; N, 4.90; S, 11.24.

N-(3,5-Diphenyl-2-thenoyl)aniline (7): mp 142-144 °C; ¹H NMR (CDCl₃, 400MHz) δ 7.04 (1H, t, *J* = 7.3 Hz), 7.15 (2H, d, *J* = 7.6 Hz), 7.23 (2H, t, *J* = 7.3 Hz), 7.27 (1H, s), 7.33 (1H, s), 7.36 (1H, t, *J* = 7.3 Hz), 7.42 (2H, t, *J* = 7.3 Hz), 7.56-7.56 (5H, m), 7.67 (2H, d, *J* = 7.3 Hz); ¹³C NMR (100MHz) δ 119.25, 124.12, 126.06, 126.66, 128.73, 128.93, 129.10, 129.17, 129.38 (overlapped), 133.26, 134.22, 135.36, 137.56, 142.88, 147.92, 159.85; MS *m/z* 355 (M⁺). Anal. Calcd for C₂₃H₁₇NOS: C, 77.72; H, 4.82; N, 3.94; S, 9.02. Found: C, 77.44; H, 4.70; N, 3.91; S, 8.82.

N-(5-Phenyl-2-thenoyl)piperidine (13): mp 100-101 °C; ¹H NMR (CDCl₃, 400MHz) δ 1.64-1.70 (6H, m), 3.70 (4H, t, *J* = 4.7 Hz), 7.21 (1H, d, *J* = 3.6 Hz), 7.24 (1H, d, *J* = 3.6 Hz), 7.32 (1H, t, *J* =

7.3 Hz), 7.39 (2H, t, $J = 7.3$ Hz), 7.61 (2H, d, $J = 7.6$ Hz); ^{13}C NMR (100MHz) δ 24.6, 26.1, 47.1, 122.5, 126.1, 128.2, 129.0, 129.4, 133.6, 136.6, 147.16, 163.24; MS m/z 271 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NOS}$: C, 70.82; H, 6.31; N, 5.20; S, 11.81. Found: C, 70.53; H, 6.17; N, 5.16; S, 11.67.

***N*-(3,5-Diphenyl-2-thenoyl)piperidine (14)**: mp 129-130.5 °C; ^1H NMR (CDCl_3 , 400MHz) δ 0.90-1.60 (6H, m), 3.04 (2H, m), 3.60 (2H, m), 7.32-7.42 (7H, m), 7.50 (2H, d, $J = 7.0$ Hz), 7.62 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100MHz) δ 24.27, 25.21, 48.22, 123.63, 125.94, 127.85, 128.04, 128.12, 128.68, 129.00, 130.86, 133.56, 135.48, 140.88, 144.75, 163.73; MS m/z 347 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{NOS}$: C, 76.05; H, 6.09; N, 4.03; S, 9.23. Found: C, 75.79; H, 6.15; N, 3.95; S, 9.11.

3-Benzoyl-2,5-diphenylthiophene (17): oil; ^1H NMR (CDCl_3 , 400MHz) δ 7.20-7.22 (m, 3H), 7.28-7.38 (m, 5H), 7.39-7.45 (m, 3H), 7.49 (s, 1H), 7.64 (d, 2H, $J = 7.3$ Hz), 7.79 (d, 2H, $J = 7.6$ Hz); ^{13}C NMR (100MHz) δ 125.65, 125.80, 128.09, 128.17, 128.31, 128.43, 129.04 (overlapped), 129.93, 132.85, 133.03, 133.37, 137.42, 137.48, 143.11, 146.52, 192.91; HRMS Calcd for $\text{C}_{23}\text{H}_{16}\text{OS}$: m/z (M^+) 340.0938. Found: M, 340.0935.

3-Benzoyl-2,4,5-triphenylthiophene (18): mp 162-164 °C; ^1H NMR (CDCl_3 , 400MHz) δ 7.10 (s, 5H), 7.18-7.26 (m, 10H), 7.35 (t, 1H, $J = 7.3$ Hz), 7.43-7.45 (m, 2H), 7.69-7.71 (m, 2H); ^{13}C NMR (100MHz) δ 127.23, 127.62, 128.13 (overlapped), 128.18, 128.43, 128.59, 128.64, 129.17, 129.68, 130.09, 132.98, 133.06, 133.37, 135.08, 137.48, 138.58, 138.81, 139.38, 142.00, 195.42; HRMS Calcd for $\text{C}_{29}\text{H}_{20}\text{OS}$: m/z (M^+) 416.1252. Found: M, 416.1243.

3-Cyano-2,5-diphenylthiophene (19a): mp 60.5-62 °C; ^1H NMR (CDCl_3 , 400MHz) δ 7.37-7.51 (m, 7H), 7.60 (d, 2H, $J = 7.7$ Hz), 7.80 (d, 2H, $J = 7.7$ Hz); ^{13}C NMR (100MHz) δ 106.58, 115.80, 125.52, 125.89, 127.54, 128.81, 129.23, 129.26, 129.76, 131.35, 132.31, 144.15, 152.46; MS m/z 261 (M^+). Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{NS}$: C, 78.13; H, 4.24; N, 5.36; S, 12.27. Found: C, 77.90; H, 4.04; N, 5.25; S, 12.19.

3-Cyano-2,5-bis(4-methoxyphenyl)thiophene (19b): mp 134-135.5 °C (lit,^{8c} 137.5 °C); ^1H NMR

(CDCl₃, 400MHz) δ 3.85 (s, 3H), 3.87 (s, 3H), 6.95 (d, 2H, J = 8.8 Hz), 6.99 (d, 2H, J = 8.8 Hz), 7.27 (s, 1H), 7.50 (d, 2H, J = 8.8 Hz), 7.73 (d, 2H, J = 8.8 Hz); ¹³C NMR (100MHz) δ 55.41, 55.43, 105.39, 114.56, 114.61, 116.22, 124.12, 124.17, 125.20, 127.15, 128.86, 143.06, 151.77, 160.03, 160.70; MS m/z 321 (M⁺). Anal. Calcd for C₁₉H₁₅NO₂S: C, 71.01; H, 4.70; N, 4.36; S, 9.98. Found: C, 71.01; H, 4.70; N, 4.34; S, 9.88.

3-Cyano-2,4,5-triphenylthiophene (20a): mp 160-162 °C; ¹H NMR (CDCl₃, 400MHz) δ 7.21-7.28 (m, 5H), 7.36-7.37 (m, 5H), 7.46-7.52 (m, 3H), 7.83 (d, 2H, J = 7.3 Hz); ¹³C NMR (100MHz) δ 108.80, 115.89, 127.81, 128.31, 128.35, 128.67, 128.69, 129.07, 129.25, 129.77, 129.83, 131.45, 132.33, 133.31, 139.33, 140.06, 152.39; MS m/z 337 (M⁺). Anal. Calcd for C₂₃H₁₅NS: C, 81.87; H, 4.48; N, 4.15; S, 9.50. Found: C, 81.66; H, 4.46; N, 4.13; S, 9.44.

3-Cyano-2,4,5-tris(4-methoxyphenyl)thiophene (20b): mp 156.5-158 °C; ¹H NMR (CDCl₃, 400MHz) δ 3.79 (s, 3H), 3.83 (s, 3H), 3.87 (s, 3H), 6.79 (d, 2H, J = 8.8 Hz), 6.90 (d, 2H, J = 8.4 Hz), 7.01 (d, 2H, J = 8.8 Hz), 7.15 (d, 2H, J = 8.8 Hz), 7.27 (d, 2H, J = 8.8 Hz), 7.76 (d, 2H, J = 8.8 Hz); ¹³C NMR (100MHz) δ 55.21, 55.25, 55.42, 107.87, 114.10, 114.13, 114.61, 116.47, 124.20, 125.02, 125.87, 129.08, 130.22, 131.01, 137.71, 138.76, 151.65, 159.41, 159.45, 160.72; MS m/z 427 (M⁺). Anal. Calcd for C₂₆H₂₁NO₃S: C, 73.05; H, 4.95; N, 3.28; S, 7.50. Found: C, 72.77; H, 4.81; N, 3.25; S, 7.42.

3-Cyano-2,4,5-tris(3-trifluoromethylphenyl)thiophene (20d): mp 94-95.5 °C; ¹H NMR (CDCl₃, 400MHz) δ 7.38 (d, 1H, J = 8.1 Hz), 7.42-7.46 (m, 2H), 7.55-7.59 (m, 4H), 7.67-7.71 (m, 2H), 7.77 (d, 1H, J = 7.3 Hz), 8.03 (s, 1H), 8.07 (d, 1H, J = 7.7 Hz); MS m/z 541 (M⁺). Anal. Calcd for C₂₆H₁₂NF₉S: C, 57.68; H, 2.23; N, 2.59. Found: C, 57.28; H, 2.24; N, 2.57.

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