Supporting Information

Palladium-Catalyzed Selective 2,3-Diarylation of α,α -Disubstituted 3-Thiophenemethanols via Cleavage of C-H and C-C Bonds

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Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, for CDCl_3 solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm x 25 m).

Alcohols **2a-2c** were prepared by the method reported previously, i.e. treatment of the corresponding bromothiophenes with BuLi (1.6 M in hexane) in ether at $-78\text{ }^\circ\text{C}$ followed by addition of benzophenone or acetone.^{9a-c} Other starting materials were commercially available.

The following experimental procedure may be regarded as typical in methodology and scale.

Palladium-Catalyzed Reaction of 2,3-Diphenyl-3-thiophenemethanol (2a) with 4-Bromoanisole (1b) (the first example in Table 2): In a 20 cm³ two-necked flask were added the bromide **1b** (2 mmol, 374 mg), the alcohol **2a** (0.5 mmol, 133 mg), $\text{Pd}(\text{OAc})_2$ (0.05 mmol, 11.2 mg), $\text{P}(\text{biphenyl-2-yl})(t\text{-Bu})_2$ (0.1 mmol, 20.1 mg), Cs_2CO_3 (2 mmol, 652 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and toluene (2.5 cm³) were added. The resulting mixture was stirred under N_2 (balloon) at $135\text{ }^\circ\text{C}$ (bath temperature) for 8 h. After cooling, analysis of the mixture by GC confirmed formation of compound **3b** (127 mg, 86%). The product (89 mg, 60%) was also isolated by filtration of the mixture with a filter paper with ether, evaporation of the solvents, and chromatography on silica gel using hexane-ethyl acetate (98:2, v/v).

Characterization Data of Products.

2,3-Diphenylthiophene (3a)^{8a}: mp $82\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, $J = 5.1\text{ Hz}$, 1H), 7.25-7.31 (m, 10H), 7.32 (d, $J = 5.1\text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 124.1, 126.8, 127.4, 128.3, 128.4, 129.1, 129.3, 130.5, 134.3, 136.6, 138.1, 138.7; MS m/z 236 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{S}$: C, 81.31; H, 5.12. Found: C, 81.16; H, 5.48.

2,3-Bis(4-methoxyphenyl)thiophene (3b)^{2b}: mp $105\text{--}106\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 3.80 (s, 3H), 3.80 (s, 3H), 6.79-6.84 (m, 4H), 7.10 (d, $J = 5.1\text{ Hz}$, 1H), 7.19-7.25 (m, 4H), 7.25 (d, $J = 5.1\text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.2, 55.2,

113.8, 113.9, 123.3, 127.0, 129.2, 130.1, 130.3, 130.5, 137.0, 137.7, 158.4, 158.9; MS m/z 296 (M^+). Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.76; H, 5.26.

2,3-Bis(4-trifluoromethylphenyl)thiophene (3c): mp 93 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 5.1 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 5.1 Hz, 1H), 7.55-7.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.3 (q, J = 272.1 Hz), 121.4 (q, J = 272.1 Hz), 125.5-125.7 (m), 125.8, 129.3 (q, J = 32.2 Hz), 129.4, 129.5, 129.7 (q, J = 32.2), 130.4, 137.5, 137.7, 138.0, 139.7; HRMS m/z (M^+) Calcd for $C_{18}H_{10}F_6S$ 372.0407. Found 372.0410.

2,3-Bis(4-chlorophenyl)thiophene (3d): mp 98-99 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 5.1 Hz, 1H), 7.17-7.22 (m, 4H), 7.24-7.28 (m, 4H), 7.34 (d, J = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.8, 128.7, 128.8, 130.2, 130.3, 130.5, 132.5, 133.0, 133.6, 134.7, 137.2, 137.6; MS m/z 304, 306 (M^+). Anal. Calcd for $C_{16}H_{10}Cl_2S$: C, 62.96; H, 3.30. Found: C, 63.02; H, 3.47.

2,3-Bis(4-fluorophenyl)thiophene (3e): mp 94-95 °C; 1H NMR (400 MHz, $CDCl_3$) δ 6.95-7.00 (m, 4H), 7.11 (d, J = 5.1 Hz, 1H), 7.19-7.25 (m, 4H), 7.31 (d, J = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.4 (d, J = 22.1 Hz), 115.6 (d, J = 22.1 Hz), 124.3, 130.2, 130.6 (d, J = 8.3 Hz), 131.0 (d, J = 8.3 Hz), 133.3, 132.3, 137.2, 137.5, 161.9 (d, J = 246.3 Hz), 162.3 (d, J = 248.2 Hz); MS m/z 272 (M^+). Anal. Calcd for $C_{16}H_{10}F_2S$: C, 70.57; H, 3.70. Found: C, 70.35; H, 3.57.

2,3-Bis(4-ethoxycarbonylphenyl)thiophene (3f): mp 126-127 °C; 1H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 4.36 (q, J = 7.0 Hz, 2H), 4.37 (q, J = 7.0 Hz, 2H), 7.19 (d, J = 5.1 Hz, 1H), 7.32-7.35 (m, 4H), 7.41 (d, J = 5.1 Hz, 1H), 7.93-7.98 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 14.3, 61.0, 61.0, 125.6, 129.0, 129.1, 129.5, 129.8, 129.8, 130.4 (overlapped), 138.2, 138.5, 138.6, 140.8, 166.2, 166.4; MS m/z 380 (M^+). Anal. Calcd for $C_{22}H_{20}O_4S$: C, 69.45; H, 5.30. Found: C, 69.38; H, 5.27.

2,3-Bis(biphenyl-4-yl)thiophene (3g): mp 172-173 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 5.1 Hz, 1H), 7.33 (t, J = 7.3 Hz, 2H), 7.36 (d, J = 5.5 Hz, 1H), 7.39-7.45 (m, 8H), 7.51-7.56 (m, 4H), 7.58-7.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 126.9 (overlapped), 127.1, 127.1, 127.3, 127.4, 128.8, 128.8, 129.5, 129.7, 130.6, 133.4, 135.6, 137.7, 138.4, 139.6, 140.1, 140.4, 140.6; MS m/z 388 (M^+). Anal. Calcd for $C_{28}H_{20}S$: C, 86.56; H, 5.19. Found: C, 86.35; H, 5.22.

2,3,5-Triphenylthiophene (4)^{8a}: mp 144-145 °C; 1H NMR (400 MHz, $CDCl_3$) δ

7.25-7.34 (m, 11H), 7.37 (s, 1H), 7.40 (t, $J = 7.7$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 125.6, 126.5, 127.0, 127.4, 127.6, 128.4, 128.5, 128.9, 129.1, 129.1, 134.1, 134.2, 136.6, 138.0, 139.0, 142.6; MS m/z 312 (M^+).

2,3-Diphenyl-benzo[*b*]thiophene (5a)¹⁰: mp 117-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.27 (m, 3H), 7.30-7.42 (m, 9H), 7.57-7.62 (m, 1H), 7.85-7.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 122.0, 123.3, 124.4, 124.5, 127.4, 127.7, 128.3, 128.6, 129.6, 130.4, 133.2, 134.2, 135.5, 138.8, 139.5, 140.9; MS m/z 286 (M^+).

2,3-Bis(4-methoxyphenyl)benzo[*b*]thiophene (5b)¹¹: mp 128-129 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 3H), 3.85 (s, 3H), 6.79 (d, $J = 8.8$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 8.8$ Hz, 2H), 7.26 (d, $J = 8.8$ Hz, 2H), 7.29-7.35 (m, 2H), 7.54-7.59 (m, 1H), 7.81-7.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.2, 55.2, 113.8, 114.1, 122.0, 123.1, 124.2, 124.3, 126.8, 127.9, 130.7, 131.5, 132.0, 138.5, 139.0, 141.2, 158.8, 159.1; MS m/z 346 (M^+).

2,3-Bis(4-ethoxycarbonylphenyl)benzo[*b*]thiophene (5f): mp 123-124 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.38 (t, $J = 7.0$ Hz, 3H), 1.42 (t, $J = 7.0$ Hz, 3H), 4.36 (q, $J = 7.0$ Hz, 2H), 4.41 (q, $J = 7.0$ Hz, 2H), 7.34-7.43 (m, 6H), 7.58-7.60 (m, 1H), 7.89-7.94 (m, 3H), 8.08-8.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 14.3, 61.0, 61.9, 122.2, 123.3, 124.9, 125.2, 129.5, 129.7, 129.7 (overlapped), 130.0, 130.4, 133.4, 138.3, 139.1, 139.1, 139.9, 140.2, 166.1, 166.33; MS m/z 430 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}$: C, 72.54; H, 5.15. Found: C, 72.38; H, 5.13.

1,1',2-Triphenyl-3-thiophenemethanol: mp 115-116 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 6.32 (s, 1H), 6.59 (d, $J = 5.5$ Hz, 1H), 7.01-7.24 (m, 15H), 7.40 (d, $J = 5.5$ Hz, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 79.1, 123.2, 126.6, 126.9, 127.2, 127.3, 127.5, 130.0, 131.5, 135.0, 140.3, 143.4, 148.1; HRMS m/z (M^+) Calcd for $\text{C}_{23}\text{H}_{18}\text{OS}$ 342.1078. Found 342.1073.

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1,1,2-Triphenyl-3-thiophenemethanol

No.	ppm	Hz	Height
1	148.06	14884.1	33.81
2	143.36	14411.1	11.50
3	140.29	14102.9	11.42
4	134.96	13566.5	11.61
5	131.48	13217.1	18.72
6	129.95	13063.0	37.57
7	127.50	12817.3	99.42
8	127.34	12801.3	88.22
9	127.24	12790.6	40.94
10	126.93	12760.1	20.28
11	126.57	12723.5	39.07
12	123.18	12382.4	20.17
13	79.14	7955.1	15.86