Supporting Information for DOI: 10.1055/s-0029-1217531
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Supporting Information

Platinum and Palladium-Catalyzed Sequential Reactions: Regioselective Synthesis of 9-Fluorenylidenes from 9-Ethynylfluoren-9-yl Carboxylates and Furans

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1. General

All solvents were dried by the usual methods and distilled before use. Organic reagents were used as purchased and used without further purification. All catalytic reactions were carried out under an inert atmosphere (N2) using standard Schlenk techniques and a glovebox. Flash column chromatographies were performed on silica gel (230-400 mesh). Analytical TLC was performed on ready-made plates coated with silica gel on glass. The NMR spectra were measured for solutions in CDCl3 with Me4Si as an internal standard for (1H and 13C) at 25 °C. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

2. Typical Procedure for Synthesis of Substrates 1

The preparation of 9-ethynyl-9-fluorenyl acetate 1a has been reported. Benzoate 1b, pivalate 1c and octanoate 1d were prepared from 9-trimethylsilylthynyl-9-fluorenol with acid halide or acid anhydride. To a solution of 9-trimethylsilylthynyl-9-fluorenol (1.4 g, 5.0 mmol) and N,N-dimethylaminopyridine (12 mg, 0.10 mmol) in CH2Cl2 (10 mL) and triethylamine (1.5 mL) was slowly added pivaloyl chloride (0.75 mL, 5.8 mmol) at 0 °C under nitrogen. The resulting mixture was allowed to warm up to room temperature and stirred for 2 h. The resulting solution was poured into ice water (30 mL). The organic layer was separated and the aqueous layer was extracted by CH2Cl2 (10 mL x 2). The combined organic solution was washed with brine (10 mL) and dried over MgSO4. The crude product (ca. 97% yield) was dissolved in MeOH (10 mL) and to the solution was added K2CO3 (1.4 g, 10 mmol) at room temperature. After stirring for 1 h at room temperature, the mixture was poured into ice water (30 mL). The aqueous layer was extracted with AcOEt (20 mL x 3) and the combined organic layer was dried over MgSO4. The organic solvent was removed in vacuo and the residue was recrystallized from AcOEt/hexane to give 1c (1.2 g, 4.3 mmol, 85% for 2 steps) as a pale yellow solid.

1b: a white solid; mp = 108.8-109.8 °C. IR (KBr): 3284 (C≡C-H), 2127 (C≡C), 1730 (C=O) cm⁻¹. 1H NMR (400 MHz, CDCl3): δ 2.66 (s, 1H), 7.34-7.46 (m, 6H), 7.51 (dd, J = 7.2, 7.2 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 74.0, 79.1, 80.7, 120.1, 125.9, 128.2, 128.5, 129.7, 130.0, 130.1, 133.0, 134.7, 164.7. HRMS (FAB): m/z calcd for C22H14O2 [M]+: 310.0094; found: 310.1000.

1c: a pale yellow solid; mp = 131.5-133.0 °C. IR (neat): 3256 (C≡C-H), 2114 (C≡C), 1729 (C=O) cm⁻¹. 1H NMR (400 MHz, CDCl3): δ 1.17 (s, 9H), 2.55 (s, 1H), 7.33 (dd, J = 7.8, 7.8 Hz, 2H), 7.41 (dd, J = 7.8, 7.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 26.9, 39.1, 73.2, 81.0, 120.1, 125.4, 128.4, 129.9, 139.9, 144.0, 144.0, 176.5. HRMS (FAB): m/z calcd for C20H18O2 [M]+: 290.1307; found: 290.1322.

1d: a pale yellow oil; IR (neat): 3289 (C=C-H), 2119 (C=C), 1748 (C=O) cm⁻¹. 1H NMR (400 MHz, CDCl3): δ 0.83-0.90 (m, 3H), 1.15-1.36 (m, 8H), 1.50-1.63 (m, 2H), 2.29 (t, J = 7.6 Hz, 2H), 2.60 (s, 1H), 7.33 (dd, J = 7.2, 7.2 Hz, 2H), 7.41 (dd, J = 7.2, 7.6 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H). 13C NMR (75 MHz, CDCl3): δ 14.0, 22.5, 24.8, 28.8, 28.8, 31.6, 34.7, 73.6, 78.5, 80.8, 120.0, 125.8, 128.4, 130.0, 139.8, 143.8, 172.0. HRMS (FAB): m/z calcd for C23H24O2 [M]+: 332.1776; found: 332.1779.

3. Typical Procedure for Synthesis of Furans

Furan, 2-methylfuran, 2-methoxyfuran, and 2-acetylfuran were purchased and used without further purification. 2-Phenylfuran, 2-(p-methoxyphenyl)furan, 2-(p-trifluoromethylphenyl)furan, 2-(1-naphthyl)furan, and 2-benzylfuran were known compounds. We prepared these compounds by using Suzuki-Miyaura coupling reaction.
To an aryl bromide (4.0 mmol) and 2-furylboronic acid (0.45 g, 6.0 mmol) in THF (3 mL) and toluene (3 mL) were successively added Na₂CO₃ (0.37 g, 3.5 mmol) in water (3.0 mL) and Pd(PPh₃)₄ (0.12 g, 0.10 mmol) at room temperature in a flame-dried Schlenk tube. The reaction mixture was heated at 90 °C for 6 h and the resulting mixture was poured into ice water (10 mL) and the aqueous layer was extracted with AcOEt (5 mL x 2). The combined organic layer was dried over MgSO₄, and the organic solvent was removed in vacuo. The crude product was subjected to column chromatography on SiO₂ with hexane to give the corresponding 2-arylfuran and 2-benzylfuran in 60-95% yield.

3. Typical Procedure for Synthesis of Fluorenylidenes

In a flame-dried Schlenk tube, PtCl₂ (1.3 mg, 0.0050 mmol) and PdCl₂ (0.9 mg, 0.0050 mmol) were dispersed in toluene (2.5 mL). To this solution were added 1a (124 mg, 0.50 mmol) and 2-methylfuran (50 μL, 0.55 mmol) at room temperature. The mixture was stirred at 50 °C for 7 h. The yellow suspension was cooled and the solvent was removed under reduced pressure to give EE-2a in 99% yield without further purification. For the reactions using other furans, the resulting mixture was washed with hexane by using centrifuge to give EE-2. If necessary, the volume of the hexane solution was reduced under vacuo and the residue was purified by column chromatography on SiO₂ with hexane/AcOEt (v/v = 4/1) to give EE-2.

EE-2b: a yellow solid; mp = 251.8-252.4 °C. IR (KBr): 2924, 2852, 1750 (C=O), 1715, 1622, 1446, 1196, 1181, 727 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 2.54 (s, 3H), 3.90 (s, 3H), 6.78 (d, J = 11.7, 14.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 1.50 Hz, 1H), 7.24-7.43 (m, 2H), 7.60-7.84 (m, 4H), 8.01 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 21.2, 55.5, 113.9, 119.9, 120.2, 125.3, 127.4, 127.7, 127.9, 128.8, 129.1, 130.8, 130.9, 131.5, 132.4, 135.6, 136.7, 140.4, 142.3, 145.1, 163.6, 168.3. HRMS (FAB): m/z calcd for C₂₂H₁₉O₄ [M+H]+: 347.1283; found: 347.1290.

EE-2c: a yellow solid; decomposition temp. = 185 °C. IR (KBr): 3056, 2814, 2736, 1753 (C=O), 1665, 1193, 1118, 728 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 2.52 (s, 3H), 6.32 (dd, J = 7.7, 15.2 Hz, 1H), 6.73 (dd, J = 11.3, 15.2 Hz, 1H), 7.24-7.41 (m, 5H), 7.64-7.81 (m, 5H), 9.66 (d, J = 7.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 21.1, 119.9, 120.2, 125.2, 125.4, 127.3, 127.8, 129.0, 129.4, 130.3, 131.7, 133.1, 133.6, 135.5, 136.6, 140.4, 141.0, 144.5, 149.8, 168.2, 193.2. HRMS (FAB): m/z calcd for C₂₁H₁₇O₃ [M+H]+: 317.1178; found: 317.1190.

EE-2d: a yellow solid; mp = 236.0-237.2 °C. IR (KBr): 3052, 1746 (C=O), 1601, 1254, 1019, 726 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.53 (s, 3H), 6.77 (dd, J = 11.7, 14.6 Hz, 1H), 7.17 (d, J = 14.6 Hz, 1H), 7.24-7.40 (m, 5H), 7.50 (dd, J = 7.6, 7.6 Hz, 2H), 7.59 (dd, J = 7.3, 7.3 Hz, 1H), 7.63-7.73 (m, 4H), 7.75-7.85 (m, 2H), 7.99 (d, J = 8.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 21.2, 119.9, 120.2, 125.3, 125.4, 127.4, 127.7, 127.9, 128.4, 128.7, 128.9, 129.2, 130.9, 131.3, 132.9, 132.9, 135.6, 136.7, 137.9, 140.4, 140.9, 143.0, 145.0, 168.2, 190.0. HRMS (FAB): m/z calcd for C₂₇H₂₁O₃ [M+H]+: 393.1491; found: 393.1497.

EE-2f: a yellow solid; mp = 226.7-227.0 °C. IR (KBr): 2930, 1749 (C=O), 1603, 1254, 1170, 1021, 728 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 2.54 (s, 3H), 3.89 (s, 3H), 6.73-6.83 (m, 1H), 6.98 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 15.1 Hz, 1H), 7.24-7.40 (m, 4H), 7.62-7.73 (m, 4H), 7.75-7.82 (m, 2H), 8.00 (d, J = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 21.2, 55.5, 113.9, 119.9, 120.1, 125.3, 125.4, 127.4, 127.6, 127.9, 128.8, 129.1, 130.7, 130.8, 130.9, 131.5, 132.4, 135.6, 136.7, 140.4, 140.9, 142.3, 145.1, 163.6, 168.2, 188.2. HRMS (FAB): m/z calcd for C₂₈H₂₃O₄ [M+H]+: 423.1596; found: 423.1609.
1H NMR (300 MHz, CDCl3): δ 2.48 (s, 3H), 3.87 (s, 2H), 6.38 (d, J = 15.3 Hz, 1H), 6.56 (dd, J = 11.3, 14.6 Hz, 1H), 7.20-7.38 (m, 9H), 7.47 (dd, J = 11.3, 15.3 Hz, 1H), 7.60 (d, J = 14.6 Hz, 1H), 7.64-7.70 (m, 2H), 7.75 (dd, J = 7.7, 7.7 Hz, 2H).  13C NMR (100 MHz, CDCl3): δ 21.1, 119.9, 120.1, 124.5, 125.2, 125.3, 125.6, 126.5, 127.3, 127.3, 127.6, 128.4, 129.2, 130.4, 131.0, 131.1, 131.8, 132.7, 132.8, 133.8, 135.5, 136.6, 136.7, 140.3, 140.9, 143.8, 144.8, 168.2, 195.0.  HRMS (FAB): m/z calcd for C25H25O3 [M+H]+: 373.1804; found: 373.1803.

EE-2a: a white solid; mp = 211.1-211.9 °C. IR (KBr): 3056, 2916, 1736 (C=O), 1656, 1446, 1263, 1215, 1174, 1022, 992, 780, 730, 703 cm−1.  1H NMR (400 MHz, CDCl3): δ 2.28 (s, 3H), 6.21 (d, J = 15.7 Hz, 1H), 6.65 (dd, J = 11.4, 14.6 Hz, 1H), 7.06 (dd, J = 7.3, 7.3 Hz, 1H), 7.17 (dd, J = 7.3 Hz, 1H), 7.22-7.42 (m, 4H), 7.59-7.79 (m, 6H), 7.86 (d, J = 7.7 Hz, 1H), 8.35 (d, J = 7.7 Hz, 2H).  13C NMR (100 MHz, CDCl3): δ 27.8, 119.8, 120.2, 125.2, 125.5, 127.3, 127.8, 128.2, 128.5, 128.9, 129.0, 129.1, 130.4, 131.1, 132.3, 132.6, 134.4, 135.7, 136.6, 140.2, 141.0, 141.5, 144.9, 164.0, 197.9.  HRMS (FAB): m/z calcd for C27H25O2 [M+H]+: 393.1491; found: 393.1507.

References