Supporting Information

Synthesis of Tetra-Substituted Naphthalenes by Palladium-Catalyzed Reaction of Aryl Iodides with Internal Alkynes

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Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. 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 with a CBP-1 capillary column (i. d. 0.5 mm x 25 m). 2-Iodonaphthalene (**1g**) was prepared according to the procedure reported previously.[14] The following

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

Reaction of Iodobenzene (1a) with Diethyl Acetylenedicarboxylate (2a). In a 20 cm^3 two-necked flask was placed Ag_2CO_3 (275 mg, 1 mmol), which was then dried at 150 °C in vacuo for 2 h. Then, **1a** (204 mg, 1 mmol), **2a** (680 mg, 4 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), 1-methylnaphthalene (ca. 100 mg) as internal standard, and DMF (5 cm^3) were added. The resulting mixture was stirred under N_2 at 120 °C for 8 h. After cooling, the solvent was evaporated in vacuo. Organic part of the residue was dissolved in CH_2Cl_2 and subjected to column chromatography on silica gel (hexane-ethyl acetate, 93:7 v/v) to give tetraethyl naphthalene-1,2,3,4-tetracarboxylate (**3a**)[6a] (312 mg, 75%): mp 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, 6H, *J* = 7.3 Hz), 1.42 (t, 6H, *J* = 7.3 Hz), 4.37 (q, 4H, *J* = 7.3 Hz), 4.50 (q, 4H, *J* = 7.3 Hz), 7.68-7.71 (m, 2H), 8.07-8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.0, 62.2, 62.3, 126.1, 127.7, 129.4, 130.0, 133.9, 166.2, 166.8; MS *m/z* 416 (M^+).

Tetraethyl 6-Methylnaphthalene-1,2,3,4-tetracarboxylate (3b): mp 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.44 (m, 12H), 2.55 (s, 3H), 4.33-4.39 (m, 4H), 4.46-4.52 (m, 4H), 7.52 (dd, 1H, *J* = 1.7, 8.8 Hz), 7.83 (s, 1H), 7.97 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C), 14.0 (2C), 22.0, 62.1 (2C), 62.2 (2C), 125.0, 125.9, 126.6, 127.7, 128.2, 130.2, 131.7, 133.1, 133.8, 139.9, 166.3, 166.4, 167.0 (2C); MS *m/z* 430 (M^+). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 64.05; H, 6.09.

Tetraethyl 6-Methoxynaphthalene-1,2,3,4-tetracarboxylate

(3c): mp 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.44 (m, 12H), 3.93 (s, 3H), 4.35 (q, 2H, *J* = 7.3 Hz), 4.36 (q, 2H, *J* = 7.3 Hz), 4.48 (q, 4H, *J* = 7.3 Hz), 7.32 (dd, 1H, *J* = 2.6, 9.2 Hz), 7.41 (d, 1H, *J* = 2.6 Hz), 7.96 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C), 14.0 (2C), 55.4, 62.1 (3C), 62.2, 104.2, 122.2, 124.8, 125.3, 127.7, 129.2, 131.6, 132.1, 134.2, 160.2, 166.2, 166.6, 167.0, 167.0; MS m/z 446 (M^+). Anal. Calcd for $C_{23}H_{26}O_9$: C, 61.88; H, 5.87. Found: C, 61.81; H, 5.72.

Tetraethyl 6-Chloronaphthalene-1,2,3,4-tetracarboxylate (3d): mp 99-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36-1.44 (m, 12H), 4.37 (q, 2H, *J* = 7.3 Hz), 4.37 (q, 2H, *J* = 7.3 Hz), 4.49 (q, 2H, *J* = 7.3 Hz), 4.50 (q, 2H, *J* = 7.3 Hz), 7.63 (dd, 1H, *J* = 2.2, 9.2 Hz), 8.05 (d, 1H, *J* = 9.2 Hz), 8.11 (d, 1H, *J* = 2.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C), 14.0 (2C), 62.4 (2C), 62.5, 62.5, 125.1, 127.8, 127.9, 128.2, 129.3, 130.4, 130.8, 132.7, 133.9, 136.0, 165.9, 166.0, 166.2, 166.4; MS m/z 450, 452 (M^+). Anal. Calcd for $C_{22}H_{23}O_8Cl$: C, 58.61; H, 5.14; Cl, 7.86. Found: C, 58.56; H, 4.94; Cl, 7.77.

Tetraethyl 6-Bromonaphthalene-1,2,3,4-tetracarboxylate (3e): mp 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36-1.44 (m, 12H), 4.36 (q, 2H, *J* = 7.3 Hz), 4.37 (q, 2H, *J* = 7.3 Hz), 4.48 (q, 2H, *J* = 7.3 Hz), 4.50 (q, 2H, *J* = 7.3 Hz), 7.76 (dd, 1H, *J* = 1.8, 9.2 Hz), 7.97 (d, 1H, *J* = 9.2 Hz), 8.28 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (2C), 14.0 (2C), 62.4 (2C), 62.5, 62.6, 124.5, 127.7, 128.0, 128.4, 128.5, 129.2, 131.0, 132.6, 132.9, 134.0, 165.9, 166.0, 166.2, 166.4; MS m/z 494, 496 (M^+). Anal. Calcd for $C_{22}H_{23}O_8Br$: C, 53.35; H, 4.68; Br, 16.13. Found: C, 53.30; H, 4.46; Br, 15.90.

Tetraethyl Benzo[*b*]thiophene-4,5,6,7-tetracarboxylate (3f): mp 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36-1.47 (m, 12H), 4.34-4.52

(m, 8H), 7.68 (d, 1H, *J* = 5.8 Hz), 7.77 (d, 1H, *J* = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 13.9, 14.1 (2C), 62.1, 62.3, 62.3, 62.7, 123.0, 125.1, 128.1, 130.6, 131.0, 133.4, 138.8, 142.6, 164.7, 166.2, 166.2, 167.1; MS m/z 422 (M^+); Anal. Calcd for $C_{20}H_{22}O_8S$: C, 56.86, H, 5.25, S, 7.59. Found: C, 56.85, H, 5.12, S, 7.42.

Tetraethyl Anthracene-1,2,3,4-tetracarboxylate (3g) : mp 214-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, 6H, *J* = 7.3 Hz), 1.46 (d, 6H, *J* = 7.3 Hz), 4.39 (q, 4H, *J* = 7.3 Hz), 4.57 (q, 4H, *J* = 7.3 Hz), 7.58-7.60 (m, 2H), 8.02-8.04 (m, 2H), 8.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 62.2, 62.4, 126.0, 126.5, 126.7, 127.6, 128.6, 133.1, 134.5, 166.3, 167.0; HRMS m/z (M^+) calcd for $C_{26}H_{26}O_8$ 466.1627, found: 466.1646. Anal. Calcd for $C_{26}H_{26}O_8$: C, 66.94; H, 5.62. Found: C, 66.82; H, 5.67.

Tetraethyl Phenanthrene-1,2,3,4-tetracarboxylate (4): mp 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33-1.45 (m, 12H), 4.36-4.43 (m, 4H) , 4.46-4.54 (m, 4H), 7.60 (dt, 1H, *J* = 1.5, 8.4 Hz), 7.67-7.71 (m, 1H), 7.83 (d, 1H, *J* = 8.8 Hz), 7.90 (d, 1H, *J* = 8.8 Hz), 7.93 (d, 1H, *J* = 8.4 Hz), 8.36 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.9, 13.9, 14.0, 62.3, 62.3, 62.4, 62.6, 123.0, 126.2, 126.9, 127.3, 128.5, 128.5, 128.9, 128.9, 129.9,130.3, 131.0, 132.7, 133.4, 134.0, 165.9, 167.0, 167.3, 169.6; HRMS m/z (M^+) calcd for $C_{26}H_{26}O_8$ 466.1627, found: 466.1635. Anal. Calcd for $C_{26}H_{26}O_8$: C, 66.94; H, 5.62. Found: C, 66.54; H, 5.62.

Diethyl Acenaphtylene-1,2-dicarboxylate (5): mp 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, 6H, *J* = 7.3 Hz), 4.48 (q, 4H, *J* = 7.3 Hz), 7.65 (dd, 2H, *J* = 7.3, 8.1 Hz) 7.97 (d, 2H, *J* = 8.1 Hz), 8.13 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 61.3, 127.9, 128.0, 128.3, 128.5, 130.1, 134.6, 135.3, 164.7; MS *m*/*z* 296 (M^+). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.76; H, 5.36.

Tetramethyl Naphthalene-1,2,3,4-tetracarboxylate (6): mp 151-153 °C (ref[4b] 147 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 6H), 4.02 (s, 6H), 7.69-7.73(m, 2H), 8.06-8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 126.2, 127.5, 129.7, 130.0, 133.9, 166.6, 167.2; MS *m/z* 360 (M^+).

1,2,3,4-Tetraphenylnaphthalene (7): mp 209-210 °C (ref[15] 205-206 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80-6.88 (m, 10H), 7.17-7.26 (m, 10H), 7.38-7.40 (m, 2H), 7.63-7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 125.8, 126.4, 126.5 (2C), 127.0, 127.5 (2C), 131.3 (4C), 132.0, 138.4, 138.9, 139.6, 140.5; MS *m/z* 432 (M^+).

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