Supporting Information

Iridium-Catalyzed Reaction of Aryl Chlorides with Internal Alkynes to Produce Substituted Naphthalenes and Anthracenes

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Typical Experimental Procedure [Reaction of Benzoyl Chloride (1a**) with 4-Octyne (**2a**), entry **5** in Table 1]:** A mixture of **1a** (1 mmol, 141 mg), **2a** (3 mmol, 331 mg), [IrCl(cod)]₂ (0.01 mmol, 6.7 mg), and 1-methylnaphthalene (ca 100 mg) as an internal standard was stirred in refluxing *o*-xylene (5 cm³) under nitrogen for 16 h. After cooling, the reaction mixture was poured into water, extracted with diethyl ether, and dried over sodium sulfate. 1,2,3,4-Tetrapropylnaphthalene (**3a**) (275 mg, 93%) was isolated by column chromatography on silica gel using hexane as eluent. Naphthalene **3a** was an oil;⁷ ¹H NMR (CDCl₃, 400 MHz) δ 7.98 (dd, 2H, *J* = 3.3, 6.6 Hz), 7.39 (dd, 2H, *J* = 3.3, 6.6 Hz), 3.03-2.98 (m, 4H), 2.75-2.71 (m, 4H), 1.73-1.54 (m, 8H), 1.13-1.08 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz) δ 136.9, 134.1, 131.2, 124.5, 124.4, 32.6, 31.3, 24.9, 24.4, 15.1, 14.9; MS *m/z* 296 (M⁺). Anal. Calcd for C₂₂H₃₂: C, 89.12; H, 10.88. Found: C, 88.93; H, 10.83. The characterization data of other products are given below. Phenanthrenes **14** and **15** were not characterized, since the yields were very low.

6-Methyl-1,2,3,4-tetrapropylnaphthalene (3b): oil; ¹H NMR δ 7.88 (d, 1H, *J* = 8.8 Hz), 7.73 (s, 1H), 7.22 (d, 1H, *J* = 8.8 Hz), 3.00-2.96 (m, 4H), 2.73-2.69 (m, 4H), 2.50 (s, 3H), 1.72-1.53 (m, 8H), 1.14-1.07 (m, 12H); ¹³C NMR δ 137.0, 136.0, 134.0, 133.7, 133.5, 131.3, 129.3, 126.5, 124.5, 123.6, 32.6, 32.5, 31.3, 31.2, 25.0, 24.9, 24.6, 24.5, 21.9, 15.1 (overlapped), 14.9, 14.9; MS *m/z* 310 (M⁺). Anal. Calcd for C₂₃H₃₄: C, 88.96; H, 11.04. Found: C, 88.69; H, 10.90.

6-tert-Butyl-1,2,3,4-tetrapropylnaphthalene (3c): oil; ¹H NMR δ 7.94-7.92 (m, 2H), 7.50-7.48 (m, 1H), 3.04-2.96 (m, 4H), 2.75-2.69 (m, 4H), 1.73-1.65 (m, 4H), 1.61-1.52 (m, 4H), 1.41 (s,

9H), 1.05-1.13 (m, 12H); ^{13}C NMR δ 146.6, 136.9, 136.2, 134.0, 133.8, 130.8, 129.2, 124.3, 123.1, 119.6, 34.8, 32.6, 32.5, 31.3, 31.3, 31.3, 25.0 (overlapped), 24.6, 24.4, 15.0 (overlapped), 15.0, 14.9; MS m/z 352 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{40}$: C, 88.57; H, 11.43. Found: C, 88.33; H, 11.39.

6-Methoxy-1,2,3,4-tetrapropyl naphthalene (3d): oil; ^1H NMR δ 7.90 (d, 1H, $J = 9.5$ Hz), 7.28 (d, 1H, $J = 9.5$ Hz), 7.09 (dd, 1H, $J = 2.6, 9.5$ Hz), 3.91 (s, 3H), 2.99-2.94 (m, 4H), 2.74-2.68 (m, 4H), 1.74-1.53 (m, 8H), 1.14-1.07 (m, 12H); ^{13}C NMR δ 156.5, 137.6, 134.6, 134.2, 132.9, 132.3, 126.6, 126.3, 116.1, 103.9, 55.2, 32.7, 32.4, 31.5, 31.4, 25.0, 24.9, 24.7, 24.0, 15.1, 15.0, 15.0, 14.9; MS m/z 326 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{34}\text{O}$: C, 84.60; H, 10.49. Found: C, 84.55; H, 10.47.

5-Methoxy-1,2,3,4-tetrapropyl naphthalene (3e): mp 62-63 °C; ^1H NMR δ 7.58 (dd, 1H, $J = 1.1, 8.8$ Hz), 7.28 (dd, 1H, $J = 7.7, 8.8$ Hz), 6.77 (d, 1H, $J = 7.7$ Hz), 3.91 (s, 3H), 3.19-2.93 (m, 4H), 2.73-2.69 (m, 4H), 1.69-1.52 (m, 8H), 1.12-1.06 (m, 12H); ^{13}C NMR δ 157.8, 137.7, 137.4, 135.1, 133.7, 133.5, 124.3, 124.1, 117.3, 104.9, 55.5, 34.3, 32.8, 32.3, 32.0, 25.7, 25.0, 24.8, 24.2, 15.1, 15.1, 15.1, 14.9; MS m/z 326 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{34}\text{O}$: C, 84.60; H, 10.49. Found: C, 84.33; H, 10.46.

6-Chloro-1,2,3,4-tetrapropyl naphthalene (3f): oil; ^1H NMR δ 7.93 (d, 1H, $J = 2.2$ Hz), 7.90 (d, 1H, $J = 8.8$ Hz), 7.32 (dd, 1H, $J = 2.2, 9.2$ Hz), 2.99-2.92 (m, 4H), 2.74-2.69 (m, 4H), 1.71-1.52 (m, 8H), 1.13-1.08 (m, 12H); ^{13}C NMR δ 138.3, 137.3, 134.3, 133.5, 132.2, 130.4, 129.5, 126.3, 125.1, 123.5, 32.7, 32.5, 31.3, 31.2, 24.9 (overlapped), 24.6, 24.5, 15.0 (overlapped), 14.8 (overlapped); MS m/z 330, 332 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{Cl}$: C, 79.85; H, 9.44; Cl, 10.71. Found: C, 79.59; H, 9.30; Cl, 10.56.

6-Bromo-1,2,3,4-tetrapropyl naphthalene (3g): oil; ^1H NMR δ 8.10 (d, 1H, $J = 1.8$ Hz), 7.84 (d, 1H, $J = 9.2$ Hz), 7.45 (dd, 1H, $J = 1.8, 8.8$ Hz), 2.98-2.92 (m, 4H), 2.74-2.69 (m, 4H), 2.98-1.53 (m, 8H), 1.13-1.08 (m, 12H); ^{13}C NMR δ 138.3, 137.5, 134.4, 133.5, 132.7, 129.7, 127.6, 126.8, 126.4, 118.8, 32.6, 32.6, 31.2, 31.1, 24.8, 24.8, 24.6, 24.5, 15.0 (overlapped), 14.8 (overlapped); MS m/z 374, 376 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{Br}$: C, 70.39; H, 8.32; Br, 21.29. Found: C, 70.24; H, 8.21; Br, 21.03.

6-Iodo-1,2,3,4-tetrapropyl naphthalene (3h): mp 85-86 °C; ^1H NMR δ 8.32 (d, 1H, $J = 1.5$ Hz), 7.69 (d, 1H, $J = 9.2$ Hz), 7.61 (dd, 1H, $J = 1.5, 9.2$ Hz), 2.97-2.91 (m, 4H), 2.73-2.68 (m, 4H), 1.68-1.52 (m, 8H), 1.13-1.07 (m, 12H); ^{13}C NMR δ 138.0, 137.7, 134.3, 133.6, 133.2, 133.2, 132.8,

130.0, 126.4, 90.6, 32.6, 32.6, 31.1, 31.0, 24.8, 24.8, 24.6, 24.5, 15.0 (overlapped), 14.8 (overlapped); MS m/z 422 (M^+). Anal. Calcd for $C_{22}H_{31}I$: C, 62.56; H, 7.40; I, 30.04. Found: C, 62.69; H, 7.40; I, 29.75.

1,2,3,4-Tetrabutyl-naphthalene (4): oil; 1H NMR δ 7.99 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.39 (dd, 2H, $J = 3.3, 6.6$ Hz), 3.05-3.01 (m, 4H), 2.78-2.74 (m, 4H), 1.68-1.47 (m, 16H), 1.03 (t, 12H $J = 7.3$ Hz); ^{13}C NMR δ 136.9, 134.2, 131.2, 124.5, 124.4, 33.7, 33.5, 29.9, 28.7, 23.6, 23.5, 14.0, 13.9; MS m/z 352 (M^+). Anal. Calcd for $C_{26}H_{40}$: C, 88.57; H, 11.43. Found: C, 88.16; H, 11.33.

1,2,3,4-Tetra(3-methylbutyl)naphthalene (5): oil; 1H NMR δ 7.98 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.39 (dd, 2H, $J = 3.3, 6.6$ Hz), 3.04-2.99 (m, 4H), 2.77-2.72 (m, 4H), 1.86-1.71 (m, 4H), 1.58-1.45 (m, 8H), 1.04 (t, 24H, $J = 7.0$ Hz); ^{13}C NMR δ 136.8, 134.2, 131.2, 124.4, 124.4, 40.7, 40.3, 29.2, 29.1, 27.9, 26.8, 22.6, 22.5; MS m/z 408 (M^+). Anal. Calcd for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 87.88; H, 11.68.

1,2,3,4-Tetraphenyl-naphthalene (6):^{6b} mp 203-205 °C; 1H NMR δ 7.64 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.39 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.26-7.14 (m, 10H), 6.88-6.80 (m, 10H); ^{13}C NMR δ 140.5, 139.6, 138.9, 138.4, 132.0, 131.3 (overlapped), 127.5, 127.0, 126.5, 126.4, 125.8, 125.3; MS m/z 432 (M^+).

4,5,6,7-Tetrapropylbenzo[*b*]thiophene (8): oil; 1H NMR δ 7.33 (d, 1H, $J = 5.5$ Hz), 7.28 (d, 1H, $J = 5.5$ Hz), 2.90-2.80 (m, 4H), 2.69-2.65 (m, 4H), 1.78-1.51 (m, 8H), 1.09-1.04 (m, 12H); ^{13}C NMR δ 138.6, 137.2, 135.4, 135.3, 133.4, 132.1, 124.0, 123.1, 35.3, 33.1, 31.9, 31.7, 25.3, 25.2, 24.7, 23.0, 15.0 (overlapped), 14.9, 14.8; MS m/z 302 (M^+). Anal. Calcd for $C_{20}H_{30}S$: C, 79.40; H, 10.00; S, 10.60. Found: C, 79.16; H, 10.21; S, 10.40.

1,2,3,4-Tetrapropylanthracene (10): mp 112-113 °C; 1H NMR δ 8.51 (s, 2H), 7.97 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.40 (dd, 2H, $J = 3.3, 6.6$ Hz), 3.17-3.13 (m, 4H), 2.80-2.75 (m, 4H), 1.83-1.73 (m, 4H), 1.67-1.58 (m, 4H), 1.18 (t, 6H, $J = 7.3$ Hz), 1.12 (t, 6H, $J = 7.3$ Hz); ^{13}C NMR δ 136.6, 133.6, 130.7, 130.3, 128.2, 124.7, 122.8, 32.8, 31.5, 24.9, 24.4, 15.1, 15.0; MS m/z 346 (M^+). Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89. Found: C, 89.87; H, 9.87.

1,2,3,4-Tetra(3-methylbutyl)anthracene (11): oil; 1H NMR δ 8.51 (s, 2H), 7.97 (dd, 2H, $J = 3.3, 6.6$ Hz), 7.40 (dd, 2H, $J = 3.3, 6.6$ Hz), 3.17-3.13 (m, 4H), 2.81-2.76 (m, 4H), 1.92-1.75 (m, 4H), 1.67-1.61 (m, 4H), 1.55-1.49 (m, 4H), 1.10 (d, 12H, $J = 6.6$ Hz), 1.05 (d, 12H, $J = 6.6$ Hz); ^{13}C

NMR δ 136.5, 133.6, 130.7, 130.3, 128.2, 124.7, 122.6, 40.6, 40.2, 29.2, 29.2, 28.1, 27.0, 22.6, 22.5; MS m/z 458 (M^+). Anal. Calcd for $C_{34}H_{50}$: C, 89.01; H, 10.99. Found: C, 88.62; H, 10.88.

6-Methoxy-1,2,3,4-tetrapropylantracene (12): oil; 1H NMR δ 8.43 (s, 1H), 8.36 (s, 1H), 7.55 (d, 1H, $J = 9.2$ Hz), 7.19 (d, 1H, $J = 1.8$ Hz), 7.09 (dd, 1H, $J = 9.2, 2.2$ Hz), 3.97 (s, 3H), 3.14-3.10 (m, 4H), 2.78-2.74 (m, 4H), 1.81-1.74 (m, 4H), 1.65-1.59 (m, 4H), 1.21-1.10 (m, 12H); ^{13}C NMR δ 156.8, 136.7, 135.6, 133.7, 133.0, 131.6, 130.7, 129.9, 128.8, 127.3, 122.9, 120.9, 119.8, 103.7, 55.2, 32.8, 32.7, 31.6, 31.5, 24.9, 24.9, 24.5, 24.3, 15.1 (overlapped), 15.0, 15.0; MS m/z 376 (M^+). Anal. Calcd for $C_{27}H_{36}O$: C, 86.12; H, 9.64. Found: C, 85.85; H, 9.77.

1,2,3,4-Tetrapropylphenanthrene (13): oil; 1H NMR δ 8.49 (dd, 1H, $J = 4.4, 8.8$ Hz), 7.88 (d, 1H, $J = 9.1$ Hz), 7.83-7.81 (m, 1H), 7.60 (d, 1H, $J = 9.4$ Hz), 7.51-7.49 (m, 2H), 3.20-3.00 (m, 4H), 2.89-2.78 (m, 4H), 2.04-1.95 (m, 2H), 1.81-1.52 (m, 6H), 1.20-1.09 (m, 12H); ^{13}C NMR δ 139.7, 137.8, 135.5, 134.8, 132.8, 131.1, 130.2, 129.8, 128.0, 127.7, 125.7, 125.3, 124.5, 123.4, 35.1, 32.5 (overlapped), 31.8, 25.3, 25.0, 24.9, 24.7, 15.1, 15.1, 14.9, 14.4; HRMS m/z (M^+) calcd for $C_{26}H_{34}$ 346.2660, found 346.2678.