Supporting Information

for

Naphthalenes, Isoquinolines and a Benzazocine from Zirconocene-Copper Mediated Coupling of Benzocyclobutadiene with Nitriles and Alkynes:

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Procedures

Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox. Solvents were dried by standard techniques and stored under dinitrogen over 4 Å molecular sieves or sodium metal. Alkynes and nitriles were purchased from commercial sources, flushed with dinitrogen gas, and stored under dinitrogen over 4 Å molecular sieves. NMR spectra were recorded on a Bruker AMX-250, -300, or 500 spectrometers at ambient probe temperatures. Shifts are given in *ppm* with positive values downfield of TMS.

Naphthalenes and Isoquinolines:

Method 1 (Scheme 2). Two equivalents of CuCl is added to a THF (5 ml) solution of the metallacycle, **4** or **5** (20 mg) and the mixture is stirred for two hours. During this time a Cu mirror is deposited. The reaction mixture is quenched with aqueous NaHCO₃ and extracted with diethyl ether. The crude products are purified over alumina. Yields are given in Table I of the manuscript.

Method 2 (Scheme 3). Two equivalents of R-CC-R' (for naphthalenes) or R-CN (for isoquinolines) is added to 50 mg of Cp₂ZrMe(1-benzocyclobutenyl) **2** in benzene (5ml) and the mixture is heated at 70 °C for 50 minutes. The mixture is allowed to cool. THF (5 ml) and two equivalents of CuCl are then added and the mixture is stirred for a further two hr at room temperature. During this time a Cu mirror forms and/or solid Cu precipitates. After all the volatiles are evaporated, the crude product is extracted into ether and purified over alumina. Yields are given in Table I of the manuscript.

Benzazocene **11**:

Two equivalents of dimethylacetylenedicarboxylate (21 mg) and two equivalents of CuCl (15 mg) are added to 30 mg of zirconacycle **5** (R = t-Bu) in THF (5 ml) at – 30 °C. The mixture is stirred for 3 hours while allowing it to come to room temperature. During this time a Cu mirror forms and/or solid Cu precipitates. The reaction is quenched with aqueous NaHCO₃ and extracted with ether. The crude product is purified over alumina using a mixture of hexane and ether (7:3) to obtain benzazocene **11** in 57% yield.

Compound Data

2,3-diphenylnaphthalene **6**. ¹H NMR (300 MHz, CD₂Cl₂): 7.92-7.89 (m, 3H), 7.54-51 (m, 2H), 7.24 (m, 10H). ¹³C NMR (CD₂Cl₂): 141.9, 139.4, 133.0(C), 130.3, 129.77, 128.1, 128.0, 126.8, 126.6 (CH). See: (a) Crawford, M. *J. Am. Chem. Soc.* **1939**, *61*, 608-610. (b) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246-7. (c) Wenkert, E.; Michelotti, E. L.; Swindell, C. S.; Tingoli, M. *J. Org. Chem.* **1984**, *49*, 4894-9. (d) Nakayama, J.; Kuroda, M.; Hoshino, M. *Heterocycles* **1986**, *24*, 1233-6. (f) Evenzahav, A.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 1835-1841.

2-phenylnaphthalene **7**: ¹H NMR (250 MHz, CDCl₃): 8.03 (s, 1H), 7.92-7.83 (m, 3H), 7.75-7.70 (m, 3H), 7.52-7.44 (m, 3H), 7.37-7.33 (m, 2H). ¹³C NMR (CDCl₃): 141.1, 138.5, 133.6, 132.6 (C), 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.2, 125.9, 125.7, 125.6 (CH). See: (a)

Uozumi, Y.; Nakai, Y. *Org. Lett.* **2002**, *4*(17), 2997-3000. (b) Savarin, C.; Liebeskind, L. S. *Org. Lett.* **2001**, *3*(14), 2149-2152.

2-trimethylsilylnaphthalene **8**: ^1H NMR (250 MHz, CDCl_3): 8.02 (s, 1H), 7.86-7.81 (m, 3H), 7.63-7.59 (m, 2H), 7.49-7.46 (m, 2H), 0.35 (s, 9H). ^{13}C NMR (CDCl_3): 138.0, 134.1, 133.3 (C), 130.2, 128.2, 127.9, 127.1, 126.5, 126.2(CH), -1.05 (SiMe_3). See: (a) Goossen, L. J.; Ferwanah, A.-R. S. *Synlett.* **2000**, *12*, 1801-1803. (b) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, *19*, 1895-1896. (c) Morley, J. A.; Woolsey, N. F. *J. Org. Chem.* **1992**, *57*, 6487-95.

3-phenylisoquinoline **9**: ^1H NMR (250 MHz, CD_2Cl_2): 9.33 (s, 1H) 8.12-8.18 (m, 3H), 7.95 (d, $J = 8.3$ Hz, 1H), 7.91 (d, $J = 8.3$ 1H), 7.68-7.75 (m, 1H), 7.57-7.64 (m, 1H), 7.47-7.55 (m, 2H), 7.38-7.45 (m, 1H). ^{13}C NMR (CD_2Cl_2): 151.3, 139.9, 137.0, 128.2 (C), 152.7, 130.8, 129.0, 128.8, 127.8, 127.4, 127.27, 127.21, 116.5 (CH). See: Bradsher, C. K.; Wallis, T. G. *J. Org. Chem.* **1978**, *43*, 3817-3820.

3-tert-butylisoquinoline **10**: ^1H NMR (250 MHz, CD_2Cl_2): 9.20 (s, 1H), 7.93 (d, $J = 8.23$ Hz, 1H), 7.79 (d, $J = 8.23$ Hz, 1H), 7.65 (t, 1H), 7.62 (s, 1H), 7.50 (t, 1H), 1.44 (s, 9H). ^{13}C NMR (CD_2Cl_2): 126.7, 36.9 (C), 151.2, 129.8, 127.0, 126.4, 126.2, 113.8 (Ar-CH), 29.8 (CH_3). See: Beugelmans, R.; Chastanet, J.; Roussi, G. *Tetrahedron* **1984**, *40*, 311-314.

Azocine **11** : ^1H NMR (300 MHz, CD_2Cl_2): 7.92 (s, 1H), 7.12-7.30 (m, 4H), 5.67 (s, 1H), 3.74 (d, 6H), 1.18 (s, 9H). ^{13}C NMR (250 MHz, CD_2Cl_2): 165.5, 147.7, 136.7, 134.3, 130.6, 129.3, 129.0, 127.3, 105.6, 52.4, 51.7, 37.0, 28.9. (Mass, Ionspray): 328.1535 (M + 1)

2-methyl-3-trimethylsilylnaphthalene **12**: ^1H NMR (300 MHz, CD_2Cl_2): 7.99 (s, J = 7.46 Hz, 1H), 7.82 (d, J = 7.59 Hz, 1H), 7.74 (d, 1H), 7.61 (s, H), 7.48-7.41 (m, 2H), 2.63 (s, 3H), 0.43 (s, 9H). ^{13}C NMR (CD_2Cl_2): 140.4, 138.2, 135.3, 131.6 (C), 128.0, 127.3, 127.0, 126.7, 125.3 (CH), 23.4 (Me), 0.08 (SiMe_3).

2,3-bis(trimethylsilyl)naphthalene **13**: ^1H NMR (250 MHz, CD_2Cl_2): 8.14 (s, 2H), 7.82-7.78 (m, 2H), 7.51-7.47 (m, 2H). 0.44 (s, 18 H). ^{13}C NMR (CD_2Cl_2): 142.5, 132.7 (C), 135.9, 127.9, 126.8 (CH), 2.0 (SiMe_3). See: Kitamura, T.; Fukatsu, N.; Fujiwara, Y. *J. Org. Chem.* **1998**, *63*, 8579-8581.