

## Supporting Information

### **PtBr<sub>2</sub>-Catalyzed Consecutive Enyne Metathesis-Aromatization of 1-(1-Methoxy-but-3-enyl)-2-(1-alkynyl)benzenes. Dual Role of the Pt Catalyst**

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**General Information.**  $^1\text{H}$  NMR spectra are reported as follows: chemical shift in ppm ( $\delta$ ) relative to the chemical shift of  $\text{CDCl}_3$  at 7.24 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz).  $^{13}\text{C}$  NMR spectra reported in ppm ( $\delta$ ) relative to the central line of triplet for  $\text{CDCl}_3$  at 77 ppm. IR bands are reported in  $\text{cm}^{-1}$ . Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 100~210  $\mu\text{m}$ ). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F<sub>254</sub>. All manipulations were conducted under an argon atmosphere using standard Schlenk techniques.

### Analytical Data

**1-(1-Methylenebutyl)naphthalene (3a):** Slight yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.4$  Hz, 3H), 1.48-1.39 (m, 2H), 2.49 (t,  $J = 7.4$  Hz, 2H), 5.07 (d,  $J = 2.0$  Hz, 1H), 5.39-5.38 (m, 1H), 7.27 (dd,  $J = 1.2, 6.8$  Hz, 1H), 7.48-7.40 (m, 3H), 7.76-7.74 (m, 1H), 7.86-7.82 (m, 1H), 8.06-8.02 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 21.3, 40.8, 115.1, 124.9, 125.1, 125.5, 125.6, 125.8, 127.0, 128.1, 131.2, 133.6, 141.4, 148.8. IR (neat) 3059-2870, 1636, 1590, 1506, 1463, 903, 801, 778  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{16}$  (196.29): C, 91.78; H, 8.22. Found: C, 92.05; H, 8.13. HRMS (EI) Calcd for  $\text{C}_{15}\text{H}_{16}$  ( $\text{M}^+$ ) 196.1252. Found 196.1248.

**1-(1-Methylenepentyl)naphthalene (3b):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t,  $J = 7.2$  Hz, 3H), 1.45-1.29 (m, 4H), 2.50 (t,  $J = 7.2$  Hz, 2H), 5.05 (d,  $J = 2.0$  Hz, 1H), 5.39-5.37 (m, 1H), 7.28-7.25 (m, 1H), 7.47-7.40 (m, 3H), 7.71-7.70 (m, 1H), 7.86-7.82 (m, 1H), 8.04-8.01 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 30.4, 38.4, 114.9, 124.9, 125.1, 125.5, 125.6, 125.8, 126.9, 128.1, 133.6, 141.5, 149.0. IR (neat) 3059-2859, 1636, 1591, 1507, 1465, 1378, 1252, 901, 801, 777  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{18}$  (210.31): C, 91.37; H, 8.63. Found: C, 91.33; H, 8.50. HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{18}$  ( $\text{M}^+$ ) 210.1409. Found 210.1403.

**1-(1-Methyleneheptyl)naphthalene (3c):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (t,  $J = 6.8$  Hz, 3H), 1.45-1.18 (m, 8H), 2.50 (t,  $J = 7.3$  Hz, 2H), 5.05 (d,  $J = 2.0$  Hz, 1H), 5.38-5.37 (m, 1H), 7.27-7.25 (m, 1H), 7.48-7.40 (m, 3H), 7.76-7.74 (m, 1H), 7.86-7.82 (m, 1H), 8.06-8.01 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 28.1, 29.1, 31.7, 38.7, 114.9, 124.9, 125.1, 125.5, 125.6, 125.8, 126.9, 128.1, 131.2, 133.6, 142.8, 149.1. IR (neat) 3059-2855, 1636, 1591, 1507, 1465, 902, 800, 777  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{22}$  (238.37): C, 90.70; H, 9.30. Found: C,

90.84; H, 9.46. HRMS (EI) Calcd for  $C_{18}H_{22}$  ( $M^+$ ) 238.1721. Found 238.1717.

**1-(1-Cyclopropyl-ethenyl)naphthalene (3d):** Colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.46-0.42 (m, 2H), 0.75-0.70 (m, 2H), 1.81-1.75 (m, 1H), 4.96 (d,  $J = 1.6$  Hz, 1H), 5.31 (m, 1H), 7.23-7.22 (m, 1H), 7.50-7.39 (m, 3H), 7.76-7.74 (m, 1H), 7.84-7.80 (m, 1H), 8.09-8.06 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  7.2, 18.0, 112.1, 124.9, 125.4, 125.51, 125.52, 126.1, 127.1, 127.9, 131.6, 133.3, 139.0, 150.0. IR (neat) 3082-3007, 1626, 1591, 1506, 1205, 1051, 1020, 1005, 945, 897, 800, 779, 739  $cm^{-1}$ . Anal. Calcd for  $C_{15}H_{14}$  (194.27): C, 92.74; H, 7.26. Found: C, 92.63; H, 7.28. HRMS (EI) Calcd for  $C_{15}H_{14}$  ( $M^+$ ) 194.1096. Found 194.1090.

**1-(1-Cyclohexyl-ethenyl)naphthalene (3e):** Colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  1.26-1.17 (m, 5H), 1.89-1.64 (m, 5H), 2.32-2.28 (m, 1H), 5.01 (d,  $J = 1.6$  Hz, 1H), 5.34 (t,  $J = 1.6$  Hz, 1H), 7.24-7.22 (m, 1H), 7.47-7.40 (m, 3H), 7.76-7.74 (m, 1H), 7.85-7.81 (m, 1H), 7.97-7.94 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  26.4, 26.7, 32.3, 45.3, 112.8, 125.0, 125.2, 125.4, 125.48, 126.1, 126.8, 128.1, 131.7, 133.5, 141.8, 154.0. IR (neat) 3044-2791, 1634, 1591, 1506, 1448, 1024, 1005, 905, 862, 804, 773, 741  $cm^{-1}$ . Anal. Calcd for  $C_{18}H_{20}$  (236.35): C, 91.47; H, 8.53. Found: C, 91.68; H, 8.71. HRMS (EI) Calcd for  $C_{18}H_{20}$  ( $M^+$ ) 236.1565. Found 236.1561.

**1-(1-Phenyl-ethenyl)naphthalene (3f):**<sup>1</sup> Colorless solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  5.39 (d,  $J = 1.2$  Hz, 1H), 5.98 (d,  $J = 1.2$  Hz, 1H), 7.34-7.22 (m, 6H), 7.51-7.40 (m, 3H), 7.76 (d,  $J = 8.4$  Hz, 1H), 7.87-7.84 (m, 2H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  116.2, 125.3, 125.6, 125.8, 126.3, 126.5, 127.1, 127.6, 127.8, 128.1, 128.3, 131.8, 133.8, 139.7, 140.9, 148.2. IR (neat) 3086-2949, 1591, 1505, 1494, 1444, 1407, 1340, 1253, 1026, 905, 805, 777, 712  $cm^{-1}$ . Anal. Calcd for  $C_{18}H_{14}$  (230.30): C, 93.87; H, 6.13. Found: C, 93.71; H, 6.22. HRMS (EI) Calcd for  $C_{18}H_{14}$  ( $M^+$ ) 230.1096. Found 230.1091.

**1-[1-(4-Trifluoromethyl-phenyl)ethenyl]naphthalene (3g):** Colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  5.55 (d,  $J = 1.2$  Hz, 1H), 6.08 (d,  $J = 1.2$  Hz, 1H), 7.56-7.35 (m, 8H), 7.73-7.71 (m, 1H), 7.91-7.90 (m, 2H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  118.2, 122.7, 125.3, 125.8, 125.99, 126.05, 126.8, 127.3, 128.2, 128.3, 129.4, 129.7, 131.5, 133.7, 138.7, 144.4, 147.1. IR (neat) 3134-3011, 1616, 1404, 1327, 1169, 1124, 1067, 1016, 914, 849, 800, 781  $cm^{-1}$ . Anal. Calcd for  $C_{19}H_{13}F_3$  (298.30): C, 76.50; H, 4.39. Found: C, 76.21; H, 4.62. HRMS (EI) Calcd for

$C_{19}H_{13}F_3$  ( $M^+$ ) 298.0969. Found 298.0966.

**1-[1-(4-methyl-phenyl)ethenyl]naphthalene (3h):** Yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  2.31 (s, 3H), 5.32 (d,  $J = 1.6$  Hz, 1H), 5.94 (d,  $J = 1.6$  Hz, 1H), 7.07-7.05 (m, 2H), 7.21-7.19 (m, 2H), 7.34-7.30 (m, 1H), 7.50-7.40 (m, 3H), 7.77-7.75 (m, 1H), 7.86-7.82 (m, 2H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  21.2, 115.2, 125.3, 125.6, 125.7, 126.38, 126.43, 127.1, 127.7, 128.0, 129.0, 131.8, 133.6, 137.4, 138.1, 139.9, 147.9. IR (neat) 3086-2864, 1608, 1591, 1510, 1400, 1340, 1304, 1254, 1186, 1121, 1018, 903, 827, 802, 779, 735  $cm^{-1}$ . Anal. Calcd for  $C_{19}H_{16}$  (244.33): C, 93.40; H, 6.60. Found: C, 93.17; H, 6.66. HRMS (EI) Calcd for  $C_{19}H_{16}$  ( $M^+$ ) 244.1252. Found 244.1247.

**1-[1-(4-Methoxy-phenyl)ethenyl]naphthalene (3i):** Light pale yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  3.75 (s, 3H), 5.26 (d,  $J = 1.6$  Hz, 1H), 5.87 (d,  $J = 1.2$  Hz, 1H), 6.79-6.75 (m, 2H), 7.49-7.21 (m, 6H), 7.84-7.75 (m, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  55.2, 113.6, 114.2, 125.3, 125.5, 125.7, 126.4, 127.0, 127.7, 128.0, 131.8, 133.57, 133.62, 139.9, 147.5, 159.1. IR (neat) 3044-2835, 1605, 1574, 1506, 1462, 1441, 1290, 1248, 1178, 1034, 899, 837, 804, 781, 746  $cm^{-1}$ . Anal. Calcd for  $C_{19}H_{16}O$  (260.33): C, 87.66; H, 6.19. Found: C, 87.42; H, 6.39. HRMS (EI) Calcd for  $C_{19}H_{16}O$  ( $M^+$ ) 260.1201. Found 260.1198.

**1-(1-Methylenebutyl)-6-trifluoromethyl naphthalene (3j):** Slight yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.92 (t,  $J = 7.2$  Hz, 3H), 1.48-1.38 (m, 2H), 2.48 (t,  $J = 7.6$  Hz, 2H), 5.07 (d,  $J = 2.0$  Hz, 1H), 5.43-5.42 (m, 1H), 7.40-7.38 (m, 1H), 7.62-7.50 (m, 2H), 7.85-7.83 (m, 1H), 8.16-8.14 (m, 2H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  13.9, 21.3, 40.8, 115.8, 121.2, 123.0, 125.8, 126.5, 126.96, 126.99, 127.2, 127.6, 127.8, 132.4, 141.6, 148.0. IR (neat) 3080-2874, 1635, 1595, 1470, 1379, 1344, 1310, 1194, 1171, 1153, 1126, 1070, 895, 833, 800, 760, 739  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{15}F_3$  (264.29): C, 72.71; H, 5.72. Found: C, 72.74; H, 5.82. HRMS (EI) Calcd for  $C_{16}H_{15}F_3$  ( $M^+$ ) 264.1126. Found 264.1122.

**4-Methoxy-1-propyl-2,2a,3,4-tetrahydro-cyclobuta[a]naphthalene (11a):** Colorless oil.  $^1H$  NMR (594 MHz,  $CDCl_3$ )  $\delta$  0.94 (t,  $J = 7.4$  Hz, 3H), 1.52 (dd,  $J = 7.7, 14.8$  Hz, 1H), 1.55-1.47 (m, 2H), 2.21-2.17 (m, 1H), 2.28-2.24 (m, 2H), 2.62 (ddd,  $J = 4.2, 8.9, 10.7$  Hz, 1H), 2.70-2.66 (m, 2H), 3.48 (s, 3H), 4.54 (dd,  $J = 4.8, 11.3$  Hz, 1H), 7.21-7.19 (m, 2H), 7.30-7.28 (m, 1H), 7.57-7.56 (m, 1H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  14.1, 20.9, 31.7, 34.3, 34.6, 35.6, 55.8, 77.5,

124.1, 126.62, 126.63, 127.0, 131.5, 138.0, 139.0, 139.2. IR (neat) 3063-2822, 1470, 1252, 1192, 1184, 1155, 1111, 1094, 762, 741  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{O}$  (228.33): C, 84.16; H, 8.83. Found: C, 83.87; H, 8.69. HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{20}\text{O}$  ( $\text{M}^+$ ) 228.1514. Found 228.1509.

**1-Methoxy-4-(1-methylenebutyl)-1,2-dihydronaphthalene (2a):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.4$  Hz, 3H), 1.46-1.37 (m, 2H), 2.30-2.17 (m, 2H), 5.09 (t,  $J = 5.4$  Hz, 2H), 3.33 (s, 3H), 4.26 (t,  $J = 5.6$  Hz, 1H), 5.02 (d,  $J = 1.2$  Hz, 1H), 5.07 (d,  $J = 1.2$  Hz, 1H), 5.84 (t,  $J = 4.4$  Hz, 1H), 7.36-7.21 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 21.2, 29.4, 38.0, 56.1, 76.3, 113.8, 121.9, 125.4, 126.6, 127.3, 127.9, 133.6, 134.7, 140.0, 148.7. IR (neat) 3070-2818, 1630, 1450, 1354, 1196, 1126, 1095, 901, 852, 775, 758  $\text{cm}^{-1}$ . GCMS Calcd for  $\text{C}_{16}\text{H}_{20}\text{O}$  ( $\text{M}^+$ ) 228. Found 228.

## References

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