Supporting Information.

[4 + 2] Cycloaromatization of 4-Bis(methylthio)-3-buten-2-one with Active Methylene Ketones: A Simple and Facile Phenol Annulation

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Characterization data for products **4c**, **4g**, **4l**, **4o**, **5f** and **5h**

7-Hydroxy-1-methyl-5-(methylthio)-1,2,3,4-tetrahydronaphthalene (4c). Yield 72% (0.89g); Yellow liquid; R_f 0.22 (9:1 hexane-EtOAc); IR (KBr): 3325, 2932, 1592, 1436 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.18 (d, $J = 7$ Hz, 3H, CH_3), 1.40-1.46 (m, 1H, CH), 1.60-1.82 (m, 3H, CH_2), 2.34 (s, 3H, SCH_3), 2.38-2.52 (m, 2H, CH_2), 2.75-2.78 (m, 1H, CH), 4.92 (brs, 1H, OH), 6.40 (d, $J = 2.4$ Hz, 1H, ArH), 6.42 (d, $J = 2.4$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 15.0, 20.0, 22.8, 26.3, 30.6, 32.9, 108.6, 111.0, 126.0, 139.1, 143.8, 153.6; MS (m/z , %): 208 (M^+ , 100), 193 (98). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{OS}$ (208.33): C, 69.18; H, 7.74%. Found: C, 69.49; H, 7.93%.

3-Hydroxy-1-(methylthio)-5,6,7,8,9,10-hexahydrobenzocyclooctene (4g). Yield 72% (0.96g); White solid (chloroform-hexane); mp 99-100 $^\circ\text{C}$; R_f 0.21 (9:1 hexane-EtOAc); IR (KBr): 3403, 2922, 1599, 1577 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.26-1.32 (m, 2H, CH_2), 1.35-1.40 (m, 2H, CH_2), 1.61-1.69 (m, 4H, CH_2), 2.39 (s, 3H, SCH_3), 2.67 (t, $J=6.1\text{Hz}$, 2H, CH_2), 2.85 (t, $J = 6.3$ Hz, 2H, CH_2), 4.96 (s, 1H, OH), 6.39 (d, $J = 2.6$ Hz, 1H, ArH), 6.54 (d, $J = 2.6$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 15.7, 26.1, 27.1, 27.1, 29.2, 32.3, 33.4, 109.8, 112.8, 130.4, 138.3, 143.6, 153.8; MS (m/z , %): 222 (M^+ , 27.0), 207 (8). Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{OS}$ (222.35): C, 70.22; H, 8.15%. Found: C, 70.53, H, 8.27%.

3-Hydroxy-7-methoxy-1-(methylthio)-9,10-dihydrophenanthrene (4l). White low melting solid (chloroform-hexane); Yield 71% (1.16g); R_f 0.23 (9:1 hexane-EtOAc); IR (KBr): 3375, 2927, 1599, 1439 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.39 (s, 3H, SCH_3), 2.76-2.83 (m, 4H, CH_2), 3.80 (s, 3H, OCH_3), 4.80 (brs, 1H, OH), 6.62 (d, $J = 2.2$ Hz, 1H, ArH), 6.74-6.76 (m, 2H, ArH), 6.95 (d, $J = 2.2$ Hz, 1H, ArH), 7.47 (dd, $J = 9.3, 3.2$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 15.6, 24.4, 29.2, 55.3, 107.2, 110.8, 112.3,

113.2, 125.4, 126.5, 127.0, 135.9, 138.1, 139.0, 154.6, 159.2; MS (m/z , %): 272 (M^+ , 100), 257 (19.5). Anal. Calcd for $C_{16}H_{16}O_2S$ (272.58): C, 63.12; H, 5.29%. Found: 63.47; H, 5.34%.

3-Hydroxy-3-(methylthio)-4'-(methoxy)biphenyl (4o). Yield 63% (0.93g); Red viscous liquid; R_f 0.23 (9:1 hexane-EtOAc); IR (CCl_4): 3409, 2933, 1599, 1492 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H, SCH_3), 3.82 (s, 3H, OCH_3), 6.13 (brs, 1H, OH), 6.69 (s, 1H, ArH), 6.78 (s, 1H, ArH), 6.92 (d, $J = 8.3$ Hz, 2H, ArH), 6.97 (s, 1H, ArH), 7.44 (d, $J = 8.3$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.6, 55.3, 110.8, 111.5, 113.8, 113.8, 114.1, 117.1, 128.1, 132.9, 140.2, 142.7, 156.5, 159.3; MS (m/z , %): 246 (M^+ , 65), 231 (4). Anal. Calcd for $C_{14}H_{14}O_2S$ (246.33): C, 68.26; H, 5.72%. Found: C, 68.43; H, 5.87%.

2-Hydroxy-6,7,8,9-tetrahydro-5H-benzocycloheptene (5f). Yield 83% (0.67g, Method A), 62% (0.60g, from 6); White solid (chloroform-hexane); mp 57-58 °C; R_f 0.30 (9:1 hexane-EtOAc); IR (KBr): 3339, 2847, 1502, 1449 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 1.51-1.54 (m, 4H, CH_2), 1.68-1.74 (m, 2H, CH_2), 2.59-2.63 (m, 4H, CH_2), 4.67 (brs, 1H, OH), 6.44-6.47 (m, 1H, ArH), 6.51 (t, $J = 2.4$ Hz, 1H, ArH), 6.85 (d, $J = 8.0$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2, 28.6, 32.6, 35.7, 36.7, 112.0, 116.1, 130.0, 135.8, 145.0, 153.3; MS (m/z , %): 162 (M^+ , 100), 147 (48). Anal. Calcd for $C_{11}H_{14}O$ (162.23): C, 81.43; H, 8.69%. Found: C, 81.52; H, 8.86%.

2-Hydroxy-5,6,7,8,9,10,11,12,13,14-decahydrobenzocyclododecene (5h). Yield 89% (1.03g, with Raney Ni), 64% (0.89g, from 6); White solid (chloroform-hexane); mp 59-60 °C; R_f 0.31 (9:1 hexane-EtOAc); IR (KBr): 3053, 2986, 1503, 1422 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 1.34-1.43 (m, 8H, CH_2), 1.49-1.52 (m, 3H, CH_2), 1.62-1.72 (m, 5H,

CH₂), 2.55-2.60 (m, 4H, CH₂), 5.33 (brs, 1H, OH), 6.53 (dd, $J = 2.9, 8.1$ Hz, 1H, ArH), 6.57 (d, $J = 2.6$ Hz, 1H, ArH), 6.93 (d, $J = 8.3$ Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 22.8, 22.9, 25.3, 25.6, 26.0, 26.2, 28.6, 29.4, 29.6, 30.1, 113.0, 115.9, 130.6, 133.2, 142.5, 153.2; MS (m/z , %): 232 (M⁺, 100), 233 (24.1). Anal. Calcd for C₁₆H₂₄O (232.37): C, 82.70; H, 10.41%. Found: C, 82.88; H, 10.68%.