Supporting Information.

Heteroaromatic Annulation of 2-Methyl/2-Cyanomethylbenzimidazole Dianions with -oxoketene Dithioacetals : A Highly Regiospecific Synthetic Protocol for 1,2- and 2,3-Substituted/Annulated pyrido[1,2-*a*]benzimidazoles`

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Table of Contents.

1. NOE Characterization data for products **11a** and **17a**.
2. Characterization data for products **7b**, **7d**, **20A**, **5c**, **14b**, **30**, **6c**, **6d**, **16b**, **31**, **8b**, and **35**.

NOE Results

The methyl hydrogens in **17a** showed a positive NOE effect (87%) on H-5 proton.

The H-3 hydrogen in **11a** showed positive NOE effect (85%) on H-2 and methyl hydrogens.

2-[4-Bis(methylthio)-2-hydroxy-2-methylbut-3-ene-1-yl]benzimidazole (7b). Yield 92% (2.16g); brown crystals (chloroform-hexane); mp 175 °C; R_f 0.3 (9:1 hexane-EtOAc); IR (KBr): 3353, 3169, 2956, 2919, 1578 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 1.47 (s, 3H, CH_3), 2.18 (s, 3H, SCH_3), 2.36 (s, 3H, SCH_3), 3.21 (d, $J = 15.1$ Hz, 1H, CH), 3.34 (d, $J = 15.1$ Hz, 1H, CH_2), 6.03 (s, 1H, ArH), 7.22-7.25 (m, 2H, ArH), 7.55-7.57 (m, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): 16.8, 17.6, 29.3, 42.0, 74.0, 122.3, 133.9, 137.3, 141.9, 151.6, 148.0, 156.0, 157.0; MS (m/z , %): 228 (100), 213 (95).

2-[4-Bis(methylthio)-2-hydroxy-3-methyl-2-phenylbut-3-ene-1-yl]benzimidazole (7d). Yield 90% (2.66g); brown crystals (chloroform-hexane); mp 142 °C, R_f 0.6 (9:1 hexane-EtOAc); IR (KBr): 3056, 2988, 2919, 1660, 1586 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.05 (s, 3H, CH_3), 2.20 (s, 3H, SCH_3), 2.35 (s, 3H, SCH_3), 2.65 (s, 2H, CH_2), 7.20-7.22 (m, 2H, ArH), 7.42-7.49 (m, 3H, ArH), 7.54-7.58 (m, 3H, ArH), 7.86-7.88 (m, 1H, ArH), 9.51 (brs, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): 14.5, 16.0, 17.0, 19.9, 92.5, 114.3, 122.3, 128.1, 128.6, 128.6, 128.9, 129.5, 133.1, 133.5, 136.0, 137.8, 143.3, 151.2.

2-[[4-Bis(methylthio)methylene]-1-hydroxy-1-[2-benzimidazolymethyl]-1,2,3,4-tetrahydronaphthalene (20A). Yield 91% (2.78g); yellow low melting solid; R_f 0.3 (9:1 hexane-EtOAc); IR (CCl_4): 3316, 3062, 2929, 2791, 1640 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.17 (s, 3H, SCH_3), 2.22 (s, 3H, SCH_3), 2.81-2.88 (m, 2H, CH_2), 2.95-3.02 (m, 1H, CH_2), 3.08-3.15 (m, 1H, CH_2), 3.38 (d, $J = 14.4$ Hz, 1H, CH_2), 3.64 (d, $J = 14.4$ Hz, 1H, CH_2), 7.08-7.15 (m, 3H, ArH), 7.19-7.22 (m, 2H, ArH), 7.49-7.50 (m, 2H, ArH); ^{13}C

NMR (100 MHz, CDCl₃): 16.7, 17.9, 29.3, 32.1, 44.0, 122.2, 122.4, 125.5, 126.5, 127.3, 127.7, 128.0, 136.2, 149.6, 150.1, 122.7, 123.2, 141.1; MS (*m/z*, %): 250 (52), 235 (98).

2,3-Dimethyl-1-(methylthio)pyrido[1,2-*a*]benzimidazole (5c). Yield 62% (1.20g); light yellow crystals (chloroform-hexane); mp 115 °C; *R_f* 0.2 (8:2 hexane-EtOAc); IR (KBr): 2922, 2852, 2746, 2358, 2337 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 2.34 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.55 (s, 3H, SCH₃), 7.25 (t, *J* = 8.2 Hz, 1H, ArH), 7.44 (s, 1H, ArH), 7.43 (t, *J* = 7.8 Hz, 1H, ArH), 7.83 (d, *J* = 8.0 Hz, 1H, ArH), 8.96 (d, *J* = 8.56 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 16.5, 17.8, 21.6, 100.7, 106.4, 116.3, 117.5, 119.2, 120.6, 124.9, 132.0, 144.1, 145.0, 125.3; MS (*m/z*, %): 242 (M⁺, 85.5), 227 (100). Anal. Calcd. for C₁₄H₁₄N₂S (242.34): C, 69.39; H, 5.82; N, 11.55 %. Found: C, 69.57; H, 5.60; N, 11.38%.

11-(Methylthio)cyclopenta[*b*]pyrido[1,2-*a*]benzimidazole (14b). Yield 66% (1.34g); brown crystals (chloroform-hexane); mp 125 °C; *R_f* 0.25 (8:2 hexane-EtOAc); IR (KBr): 3372, 2955, 2922, 2850, 1892, 1691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 2.02-2.09 (m, 2H, CH₂), 2.35 (s, 3H, SCH₃), 2.95 (t, *J* = 7.4 Hz, 2H, CH₂), 3.04 (t, *J* = 7.0 Hz, 2H, CH₂), 7.22 (t, *J* = 7.5 Hz, ArH), 7.38 (t, *J* = 8.0 Hz, 1H, ArH), 7.38 (s, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 1H, ArH), 8.83 (d, *J* = 8.2 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 17.5, 25.3, 31.3, 33.2, 112.0, 115.6, 119.2, 120.5, 124.6, 129.2, 130.1, 137.0, 144.8, 148.3, 150.2; MS (*m/z*, %): 254 (M⁺, 100), 239 (81.8). Anal.

Calcd. for C₁₅H₁₄N₂S (254.35): C, 70.83; H, 5.54; N, 11.02%. Found: C, 70.92; H, 5.40; N, 11.04%.

6-(Methylthio)benzimidazo[1,2-*b*]fluorene (30). Yield 68% (1.64g); yellow crystals (chloroform-hexane); mp 120 °C; R_f 0.3 (8:2 hexane-EtOAc); IR (KBr): 3053, 2985, 2927, 2350, cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 2.43 (s, 3H, SCH₃), 4.10 (s, 2H, CH₂), 7.28 (t, *J* = 8.2 Hz, 1H, ArH), 7.32-7.37 (m, 2H, ArH), 7.43 (t, *J* = 7.3 Hz, 1H, ArH), 7.48 (t, *J* = 3.6 Hz, 1H, ArH), 7.79 (t, *J* = 5.12 Hz, 1H, ArH), 7.86 (t, *J* = 3.6 Hz, 2H, ArH), 8.87 (d, *J* = 8.7 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 17.7, 29.6, 105.1, 107.0, 115.6, 119.2, 119.9, 121.1, 121.9, 124.2, 125.1, 125.3, 126.1, 127.5, 129.7, 130.6, 138.8, 140.6, 143.8; MS (*m/z*, %): 302 (M⁺, 32.2), 257 (13.2). Anal. Calcd. for C₁₉H₁₄N₂S (302.39): C, 75.56; H, 4.66; N, 9.26%. Found: C, 75.38; H, 4.89; N, 9.32%.

4-Cyano-1,2-dimethyl-3-(methylthio)pyrido[1,2-*a*]benzimidazole (6c). Yield 64% (0.54g); yellow crystals (chloroform-hexane); mp 210 °C; R_f 0.3 (8:2 hexane-EtOAc); IR (KBr): 3210, 2854, 2197, 1590, 1433 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 2.52 (s, 3H, CH₃), 2.76 (s, 3H, CH₃), 3.04 (s, 3H, SCH₃), 7.31 (t, *J* = 7.3 Hz, 1H, ArH), 7.52 (t, *J* = 7.3 Hz, 1H, ArH), 8.02 (d, *J* = 8.2 Hz, 1H, ArH), 8.05 (d, *J* = 8.5 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 15.9, 18.6, 19.3, 101.1, 115.0, 118.5, 120.3, 121.6, 121.7, 125.9, 130.0, 139.8, 145.0, 146.7, 150.2, MS (*m/z*, %): 267 (M⁺, 100), 252 (20.9). Anal. Calcd. for C₁₅H₁₃N₃S (267.35): C, 67.39; H, 4.89; N, 15.71%. Found: C, 67.55; H, 4.85; N, 15.54%.

S5

4-Cyano-2-methyl-3-(methylthio)-1-phenylpyrido[1,2-*a*]benzimidazole (6d). Yield 74% (0.78g); yellow crystals (chloroform-hexane); mp 278 °C; R_f 0.25 (8:2 hexane-

EtOAc); IR (KBr): 2466, 2426, 2272, 2336, 1587 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.20 (s, 3H, CH_3), 2.90 (s, 3H, SCH_3), 5.92 (d, $J = 8.8$ Hz, 1H, ArH), 6.91 (t, $J = 7.5$ Hz, 1H, ArH), 7.37-7.42 (m, 3H, ArH), 7.66-7.72 (m, 3H, ArH), 7.94 (d, $J = 8.2$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): 16.1, 19.0, 114.1, 114.9, 119.3, 120.1, 121.4, 125.9, 128.7, 128.8, 129.7, 130.1, 130.2, 130.6, 132.9, 140.6, 144.8, 151.1; MS (m/z , %): 329 (M^+ , 100), 314 (8.37). Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{N}_3\text{S}$ (329.42): C, 72.92; H, 4.58; N, 12.75%. Found: C, 72.80; H, 4.34; N, 12.98%.

5-Cyano-4-(methylthio)cyclopenta[*a*]pyrido[1,2-*a*] benzimidazole (16b). Yield 65% (0.58g); yellow crystals (chloroform-hexane); mp 240 $^\circ\text{C}$; R_f 0.3 (8:2 hexane-EtOAc); IR (KBr): 3398, 3194, 2924, 2215, 1602 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.38-2.46 (m, 2H, CH_2), 2.88 (s, 3H, SCH_3), 2.99 (t, $J = 7.3$ Hz, 2H, CH_2), 3.54 (t, $J = 7.3$ Hz, 2H, CH_2), 7.28 (t, $J = 8.0$ Hz, 1H, ArH), 7.49 (dd, $J = 7.3, 8.0$ Hz, 1H, ArH), 7.76 (d, $J = 8.0$ Hz, 1H, ArH), 7.93 (d, $J = 7.8$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): 17.5, 21.8, 29.6, 32.1, 112.6, 115.3, 118.9, 119.9, 121.6, 124.4, 126.0, 128.8, 143.5, 144.6, 148.0, 148.4; MS (m/z , %): 279 (M^+ , 100), 264 (16.6). Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_3\text{S}$ (279.36): C, 68.79; H, 4.68; N, 15.04%. Found: C, 68.96; H, 4.34; N, 15.08%.

7-Cyano-6-(methylthio)benzimidazo[1,2-*a*]fluorene (31). Yield 66% (0.69g);

S6

yellow crystals (chloroform-hexane); mp 215 $^\circ\text{C}$; R_f 0.3 (8:2 hexane-EtOAc); IR (KBr): 3055, 2957, 2303, 2199, 1675 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 2.88 (s, 3H, SCH_3),

3.93 (s, 2H, CH₂), 7.34 (t, *J* = 7.8 Hz, 1H, ArH), 7.48-7.53 (m, 3H, ArH), 7.65 (t, *J* = 7.8 Hz, 1H, ArH), 7.99 (d, *J* = 8.0 Hz, 1H, ArH), 8.44 (d, *J* = 8.5 Hz, 1H, ArH), 8.49 (d, *J* = 8.52 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 17.8, 29.6, 102.8, 114.5, 115.4, 120.7, 121.2, 123.2, 125.6, 126.3, 127.0, 127.3, 129.2, 129.6, 135.1, 142.0, 144.7, 145.2, 146.4, 149.7; MS (*m/z*, %): 327 (M⁺, 100), 312 (9.9). Anal. Calcd. for C₂₀H₁₃N₃S (327.40): C, 73.37; H, 4.00; N, 12.83%. Found: C, 73.53; H, 4.04; N, 12.60%.

3-Methyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazole (8b). Yield 74% (0.68g); off white crystals (chloroform-hexane); mp 118 °C; R_f 0.25 (8:2 hexane-EtOAc); IR (KBr): 3049, 2951, 2862, 1674, 1648 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 1.16 (d, *J* = 6.5 Hz, 3H, CH₃), 1.68-1.79 (m, 1H, CH), 2.07-2.15 (m, 2H, CH₂), 2.56-2.63 (m, 1H, CH₂), 3.14-3.20 (m, 1H, CH₂), 3.86-3.93 (m, 1H, CH₂), 4.14-4.19 (m, 1H, CH₂), 7.17-7.31 (m, 3H, ArH), 7.66-7.70 (m, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 20.9, 27.4, 30.3, 33.3, 41.4, 108.6, 118.7, 121.5, 121.8, 134.3, 142.9, 151.6; MS (*m/z*, %): 186 (M⁺, 100), 171 (17.3). Anal. Calcd. for C₁₂H₁₄N₂ (186.25): C, 77.38; H, 7.57; N, 15.03%. Found: C, 77.14; H, 7.74; N, 15.16%

7-(Methylthio)benzimidazo[1,2-*e*]fluoranthene (35). Yield 62% (0.67g); red Crystals (chloroform-hexane); mp 253°C; R_f 0.2 (8:2 hexane-EtOAc); IR (KBr): 2360, 791, 762, 536 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): 2.66 (s, 3H, SCH₃), 7.33 (s, 1H, ArH), 7.33-7.37 (m, 1H, ArH), 7.51 (t, *J* = 7.8 Hz, 1H, ArH), 7.58 (t, *J* = 7.3 Hz, 1H, ArH), 7.67 (t, *J* = 7.8 Hz, 1H, ArH), 7.80(d, *J* = 8.2 Hz, 1H, ArH), 7.89 (d, *J* = 7.3 Hz, 1H, ArH), 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 8.33 (d, *J* = 7.0 Hz, 1H, ArH), 8.61 (d, *J* = 8.0 Hz, 1H, ArH), 8.71 (d, *J* = 7.3 Hz, 1H, ArH); ¹³C NMR (100 MHz, CDCl₃): 29.6, 113.8,

115.2, 123.1, 125.6, 126.2, 126.5, 126.9, 127.0, 127.4, 128.2, 128.3, 128.5, 129.0, 129.1, 130.5, 132.4, 140.4, 143.0, 145.0, 146.0, 148.4; MS (m/z , %): 338 (M^+ , 100%), 323 (11.2). Anal. Calcd. for $C_{22}H_{14}N_2S$ (338.43): C, 78.08; H, 4.16; N, 8.27%. Found: C, 78.14; H, 4.19; N, 8.14%.