Supplemental Material

A Novel Sequential Azadiene Diels-Alder Strategy for the Rapid Construction of Kornfeld's Ketone Analogs

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Supporting Information Available: Characterization of all new compounds prepared in this study.

***tert*-Butyl *N*-(2-Bromo-2-propenyl)-*N*-(2-furyl)carbamate (17a).** IR (neat) 2978, 2932, 1720, 1613 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.46 (s, 9 H), 4.39 (s, 2 H), 5.55 (d, *J* = 1.7 Hz, 1 H), 5.77 (dd, *J* = 3.2, 1.7 Hz, 1 H) 6.09 (bs, 1 H), 6.33 (dd, *J* = 3.1, 2.2 Hz, 1 H), 7.17 (d, *J* = 1.7 Hz, 1 H); ^{13}C-NMR (75 MHz) δ 28.3, 56.0, 82.1, 101.8, 109.6, 111.1, 117.5, 128.9, 138.5, 147.8; HRMS Calcd. for $C_{12}H_{16}NO_3Br$ (M+1): 301.0314. Found: 301.0323.

***tert*-Butyl *N*-(2-Bromo-2-propenyl)-*N*-(5-methylfur-2-yl)carbamate (17b).** IR (neat) 2979, 2928, 1721, 1628, 1575 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.45 (s, 9 H), 2.21 (s, 3 H), 4.34 (s, 2 H), 5.54 (dd, *J* = 1.9, 1.0 Hz, 1 H), 5.78 (d, *J* = 1.4 Hz, 1 H), 5.89 (dd, *J* = 1.9, 0.7 Hz, 1 H), 5.94 (bs, 1 H); ^{13}C-NMR (75 MHz) δ 13.8, 28.3, 56.4, 81.9, 103.2, 106.8, 117.4, 129.0, 145.9, 148.3, 153.8; HRMS Calcd. for $C_{13}H_{18}NO_3Br$ (M+): 315.0470. Found: 315.0469.

***tert*-Butyl *N*-(2-Bromo-2-propenyl)-*N*-(3-methylfur-2-yl)carbamate (17c).** IR (neat) 2976, 2920, 1713, 1641 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.40 (bs, 9 H), 1.92 (s, 3 H), 4.33 (bs, 2 H), 5.52 (s, 1 H), 5.81 (s, 1 H), 6.18 (d, *J* = 1.8 Hz, 1 H), 7.11 (d, *J* = 1.7 Hz, 1 H); ^{13}C-NMR (75 MH) δ 10.0, 28.3, 56.1, 81.5, 112.7, 113.3, 118.5, 128.8, 138.6, 143.7, 154.1; HRMS Calcd. for $C_{13}H_{18}NO_3Br$ (M+): 315.0470. Found: 315.0468.

***tert*-Butyl *N*-(2-carboxymethyl-2-propenyl)-*N*-(2-furyl)carbamate (18a).** IR (neat) 1716, 1639, 1614 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.43 (s, 9 H), 3.72 (s, 3 H), 4.43 (t, *J* = 1.6 Hz, 1 H), 5.71 - 5.72 (m, 1 H), 5.99 (bs, 1 H), 6.25 - 6.32 (m, 2 H), 7.12 (dd, *J* = 1.9, 1.0 Hz, 1 H); ^{13}C (75 MHz) δ 28.3, 49.3, 52.1, 81.8, 101.1, 111.1, 125.5, 136.3, 138.2, 148.5, 153.7, 166.5; HRMS Calcd. for $C_{14}H_{19}NO_5$ (M+): 281.1263. Found: 281.1261.

***tert*-Butyl *N*-(2-carboxymethyl-2-propenyl)-*N*-(5-methylfur-2-yl)carbamate (18b).** IR (neat) 1720, 1625, 1575, 1476 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.43 (s, 9 H), 2.20 (s, 3 H), 3.73 (s, 3 H), 4.39 (t, *J* = 1.6 Hz, 2 H), 5.74 (m, 1 H), 5.82 - 5.90 (m, 2 H), 6.29 (m, 1H); ^{13}C-NMR (75 MHz) δ 13.8, 28.3, 49.6, 52.1, 81.6, 102.5, 106.7, 125.5, 136.3, 146.6, 148.0, 154.1, 166.6; HRMS Calcd. for $C_{15}H_{21}NO_5$ (M+): 295.1420. Found: 295.1407.

***tert*-Butyl *N*-(2-carboxymethyl-2-propenyl)-*N*-(3-methylfur-2-yl)carbamate (18c).** IR (neat) 1719, 1646, 1508, 1475 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.40 (s, 9 H), 1.86 (s, 3 H), 3.71 (s, 3 H), 4.37 (bs, 2 H), 5.83 (s, 1 H), 6.16 (d, *J* = 1.9 Hz, 1 H), 6.28 (d, *J* = 1.0 Hz, 1 H), 7.09 (d, *J* = 1.9 Hz, 1 H); ^{13}C-NMR (75 MHz) δ 9.7, 28.3, 49.2, 52.0, 81.2, 112.1, 113.2, 126.8, 136.2, 138.4, 144.3, 154.2, 166.5; HRMS Calcd. for $C_{15}H_{21}NO_5$ (M+): 295.1418. Found: 295.1424.

1-*tert*-Butyloxycarbonyl-2*a*-carboxymethyl-5-keto-1,2,2*a*,3,4,5-hexahydrobenz-[*cd*]indole (21a). mp 166 - 167 ˚C; IR (film) 1733, 1706, 1689, 1614, 1596 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.79 (s, 9 H), 2.12 - 2.24 (m, 1 H), 2.63 - 2.71 (m, 3 H), 3.67 (s, 3 H), 3.76 (d, *J* = 11.1 Hz, 1 H), 4.62 (bd, *J* = 11.1 Hz), 7.34 (t, *J* = 7.9 Hz, 1 H), 7.47 (dd, *J* = 7.9, 0.8 Hz, 1 H), 7.89 (bs, 1 H); ^{13}C-NMR (75 MHz) δ 28.6, 32.3, 35.8, 49.6, 53.3, 59.8, 81.9, 119.3, 119.5, 130.2, 136.5, 141.9, 152.2, 173.3, 195.9. Anal. Calcd. for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.02; H, 6.44; N, 4.12.

1-*tert*-Butyloxycarbonyl-2*a*-carboxymethyl-5-keto-6-methyl-1,2,2*a*,3,4,5-hexahydro-benz[*cd*]indole (21c). mp 127 - 127.5 ˚C; IR (neat) 1731, 1705, 1680, 1608, 1585 cm^{-1};

^{1}H-NMR (300 MHz) δ 1.54 (s, 9 H), 2.11 - 2.19 (m, 1 H), 2.56 (s, 3 H), 2.60 - 2.68 (m, 3 H), 3.66 (s, 3 H), 3.72 (d, *J* = 11.2 Hz, 1 H), 4.58 (bd, *J* = 11.2 Hz, 1 H), 7.11 (d, *J* = 8.2 Hz, 1 H), 7.78 (bs, 1 H) ; ^{13}C-NMR (75 MHz) δ 20.7, 28.3, 31.5, 36.6, 49.9, 52.9, 59.3, 81.4, 118.9, 127.9, 132.7, 133.6, 137.0, 139.9, 151.9, 173.4, 196.8. Anal. Calcd. for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 66.14; H, 6.63; N, 4.05.

1-*tert*-Butyloxycarbonyl-2*a*-carboxymethyl-5-keto-8-methyl-1,2,2*a*,3,4,5-hexahydro-benz[*cd*]indole (21c). mp 133 - 134 ˚C; IR (film) 1727, 1712, 1685, 1614, 1590 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.50 (s, 9 H), 1.88 - 1.99 (m, 1 H), 2.36 (s, 3 H), 2.57 - 2.82 (m, 3 H), 3.65 (s, 1 H), 3.70 (d, *J* = 11.8 Hz, 1 H), 4.81 (d, *J* = 11.8 Hz, 1 H), 7.18 (dd, *J* = 8.2, 0.5 Hz, 1 H), 7.51 (d, *J* = 8.2 Hz, 1 H); ^{13}C-NMR (75 MHz) δ 20.1, 28.2, 30.6, 35.6, 50.0, 52.9, 63.2, 81.4, 121.7, 127.5, 132.4, 135.3, 140.9, 141.9, 153.7, 172.5, 196.0. Anal. Calcd. for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.94; H, 6.84; N, 4.24.

1-*tert*-Butyloxycarbonyl-2*a*-carboxymethyl-5-[(trifluoromethane)sulfonyl]-1,2,2*a*,3-tetrahydrobenz[*cd*]indole (25). mp 132 - 133 ˚C; IR (film) 1736, 1706, 1634, 1619, 1583 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.55 (s, 9 H), 2.64 (dd, *J* = 16.8, 2.2 Hz, 1 H), 3.14 - 3.28 (m, 1 H), 3.62 (s, 3 H), 3.80 (d, *J* = 11.5 Hz, 1 H), 4.49 (bs, 1 H), 5.91 (bd, *J* = 5.0 Hz, 1 H), 6.95 (d, *J* = 7.9 Hz, 1 H), 7.29 (t, *J* = 7.9 Hz, 1 H), 7.70 (bs, 1 H); ^{13}C (75 MHz) δ 28.5, 32.0, 47.5, 53.2, 60.1, 82.1, 114.7, 116.1, 117.1, 118.8 (q, *J* = 320.7), 126.7, 128.6, 130.5, 141.9, 146.5, 152.2, 173.8; ^{19}F (282 MHz) δ -74.58 (s, 3 F). Anal. Calcd. for $C_{19}H_{20}F_3NO_7S$: C, 49.24; H, 4.35; N, 3.02. Found: C, 49.23; H, 4.31; N, 2.96.

1-*tert*-Butyloxycarbonyl-2*a*,5-dicarboxymethyl-1,2,2*a*,3-tetrahydrobenz[*cd*]indole (27). mp 146 - 146 ˚C; IR (film) 1726, 1702, 1621, 1457 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.56 (bs, 9 H), 2.46 (dd, *J* = 17.3, 2.4 Hz, 1 H), 3.30 (dd, *J* = 17.3, 5.4 Hz, 1 H), 3.60 (s, 3 H), 3.79 (d, *J* =11.5 Hz, 1 H), 3.81 (s, 3 H), 4.33 - 4.54 (m, 1 H), 7.13 (d, *J* = 4.8 Hz), 7.26 (t, *J* = 7.8 Hz, 1 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.67 (bs, 1 H); ^{13}C-NMR (75 MHz) δ. Anal. Calcd. for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.22; H, 6.31; N, 3.69.

4-Bromo-1-*tert*-butyloxycarbonyl-2*a*-carboxymethyl-5-keto-1,2,2*a*,3,4,5-hexahydro-benz[*cd*]indole (22). Major diastereomer: IR (neat) 1734, 1705, 1698, 1615, 1596 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.55 (bs, 9 H), 2.66 (t, *J* = 12.6 Hz, 1 H), 1.74 (dd, *J* = 12.6, 5.8 Hz, 1 H), 3.70 (s, 3 H), 3.77 (d, *J* = 11.0 Hz, 1 H), 4.64 (bd, *J* = 11 Hz, 1 H), 4.99 (dd, *J* = 12.6, 5.8 Hz, 1 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.52 (dd, *J* = 7.8, 0.8 Hz, 1 H), 7.91 (bs, 1 H); ^{13}C-NMR (75 MHz) δ 28.5, 43.5, 48.0, 50.6, 53.7, 59.1, 82.3, 119.7, 120.1, 120.4, 128.7, 130.8, 136.0, 142.4, 152.0, 172.3, 189.5; HRMS Calcd. for $C_{18}H_{20}BrNO_5$ (M+): 409.0525. Found: 409.0531.

Minor diastereomer: mp 144 - 145 ˚C (Et_2O/CH_2Cl_2); IR (film) 1735, 1706, 1694, 1597, 1478, 1461 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.56 (s, 9H), 2.76 (dd, *J* = 15.1, 5.2 Hz, 1 H), 3.26 (d, *J* = 15.1 Hz, 1 H), 3.71 (s, 3 H), 3.76 (d, *J* = 11.3 Hz, 1 H), 4.53 (d, *J* = 11.3 Hz, 1 H), 4. 70 (dd, *J* = 5.2, 1.7 Hz, 1 H), 7.41 (t, *J* = 7.9 Hz, 1 H), 7.59 (dd, *J* = 7.9, 0.7 Hz, 1 H), 7.96 (bs, 1 H); ^{13}C (75 MHz) δ 28.5, 40.6, 44.5, 47.4, 53.7, 61.4, 82.4, 120.2,

120.7, 128.1, 130.7, 136.0, 142.6, 152.1, 174.0, 188.7. Anal. Calcd. for $C_{18}H_{20}BrNO_5$: C, 52.70; H, 4.91; N, 3.41. Found: C, 52.92; H, 4.98; N, 3.43.

1-*tert*-Butyloxycarbonyl-2a-carboxymethyl-5-(*N*-methylpropriolamid-3-yl)-1,2,2*a*,3-tetrahydrobenz[*cd*]indole (26). IR (film) 3295, 2215, 1733, 1701, 1652, 1568, 1538 cm^{-1}; ^{1}H-NMR (300 MHz) δ 1.53 (bs, 9 H), 2.43 (dd, *J* = 17.5, 2.6 Hz, 1 H), 2.85 (d, *J* = 4.8 Hz, 3 H), 3.18 (dd, *J* = 17.5, 6.4 Hz, 1 H), 3.58 (s, 3 H), 3.76 (d, *J* = 11.5, 1 H), 4.43 (bs, 1 H), 6.43 (dd, *J* = 6.4, 2.6 Hz, 1 H), 6.45 - 6.49 (m, 1 H), 7.02 (d, *J* = 8.2 Hz, 1 H), 7.21 (t, *J* = 7.7 Hz, 1 H), 7.62 (bs, 1 H); ^{13}C-NMR (75 MHz) δ 26.8, 28.6, 32.9, 47.2, 53.1, 60.6, 81.2, 81.9, 85.3, 115.1, 117.9, 119.5, 126.7, 129.3, 130.3, 137.6, 141.5, 152.4, 154.2, 173.7; HRMS Calcd. for $C_{22}H_{24}N_2O_5$ (M+): 396.1685. Found: 396.1674.