Supporting Information

An Efficient Synthesis of Fused Bicyclic Glutarimides. Its Application to the Synthesis of Alloyohimbane and Louisianin D

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General Methods.

Before use, tetrahydrofuran were distilled from a deep blue solution resulting from sodium and benzophenone under nitrogen. All other reagents and solvents were obtained from commercial sources and used without further purification. Thin-layer chromatography (TLC) analysis was performed with precoated silica gel (60 f₂₅₄ plates), and column chromatography was carried out on silica (70-230 mesh). Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvent were dried with anhydrous magnesium sulfate before concentration in vacuo. All report melting temperature were uncorrected.

General procedure of [3+3] annulation to fused bicyclic glutarimides (3). A solution of α -sulfonyl acetamide **1** (2.0 g, 3.3 mmol) in THF (10 mL) was added to a stirred suspension of sodium hydride (396 mg, 9.9 mmol, 60%) in dry THF (40 mL). After the reaction mixture was stirred at room temperature for 15 min., a solution of α,β -unsaturated esters **2** (6.6 mmol) in THF (20 mL) was added. The mixture was refluxed for 8 h, quenched with saturated ammonium chloride solution (2 mL) in an

ice bath, and concentrated under reduced pressure. The residue was diluted with water (20 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic extracts were washed with brine, dried, filtered and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 4:1–1:1) to afford glutarimides ($\pm$)-**3**.

2-Benzyl-4-(toluene-4-sulfonyl)hexahydro-[2]-pyrindine-1,3-dione ($\pm$)-(3a).

Colorless solid: mp 138-141 °C; 88% yield; FT-IR (CH₂Cl₂) ν_{max} 3054, 1725, 1677, 1598, 1265, 1149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.37-7.30 (m, 7H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.07 (d, *J* = 14.0 Hz, 1H), 4.79 (d, *J* = 14.0 Hz, 1H), 4.13 (s, 1H), 3.51 (dt, *J* = 3.5, 8.0 Hz, 1H), 3.16-3.10 (m, 1H), 2.42 (s, 3H), 2.29-2.21 (m, 1H), 2.19-2.12 (m, 1H), 2.09-2.03 (m, 1H), 1.65-1.59 (m, 2H), 1.35-1.24 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): 174.54, 164.21, 145.63, 136.46, 133.45, 129.77 (2C), 129.09 (2C), 128.87 (2C), 128.32 (2C), 127.53, 69.87, 44.00, 43.08, 32.98, 31.90, 31.55, 22.97, 21.76; LRMS (EI) C₂₂H₂₃NO₄S *m/z* (%) = 91 (100), 397; (*M*⁺, 1); HRMS (ESI) calcd for C₂₂H₂₄NO₄S (*M* + *H*)⁺ 398.1426, found 398.1427.

2-Benzyl-4-(toluene-4-sulfonyl)hexahydroisoquinoline-1,3-dione ($\pm$)-(3b).

Colorless solid: mp 122-125 °C; 83% yield; FT-IR (CH₂Cl₂) ν_{max} 3054, 1725, 1678, 1597, 1265, 1147, 1168 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.53 (d, *J* = 8.5 Hz, 2H), 7.35-7.27 (m, 7H), 5.07 (d, *J* = 14.0 Hz, 1H), 4.96 (d, *J* = 14.0 Hz, 1H), 3.83 (s, 1H), 3.55 (s, 1H), 3.07-3.02 (m, 1H), 2.60-2.55 (m, 1H), 2.45 (s, 3H), 1.78-1.72 (m, 1H), 1.66-1.52 (m, 3H), 1.45-1.36 (m, 1H), 1.16-1.03 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 172.41, 164.34, 145.63, 136.66, 134.88, 129.77 (2C), 128.95 (2C), 128.48 (2C), 128.33 (2C), 127.40, 72.37, 43.53, 39.09, 32.14, 29.46, 25.93, 25.20, 21.79, 21.76; LRMS (FAB) C₂₃H₂₆NO₄S *m/z* (%) = 91 (93), 154 (85), 412 (*M*+*H*⁺, 21); HRMS (ESI) calcd for C₂₃H₂₆NO₄S (*M* + *H*)⁺ 412.1582, found 412.1582.

(±)-3c

2-Benzyl-6-methyl-4-(toluene-4-sulfonyl)hexahydro-[2,6]-naphthyridine-1,3-dione (±)-(3c). **Yellow oil:** 64% yield; FT-IR (CH₂Cl₂) ν_{max} 3064, 1727, 1597, 1271, 1257, 1167, 1150 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.53 (d, J = 8.0 Hz, 2H), 7.35-7.26 (m, 7H), 5.08 (d, J = 14.0 Hz, 1H), 4.95 (d, J = 14.0 Hz, 1H), 3.86 (s, 1H), 3.46-3.50 (m, 1H), 3.30-3.25 (m, 1H), 2.69-2.62 (m, 2H), 2.51-2.48 (m, 1H), 2.45 (s, 3H), 2.18 (s, 3H), 1.93-1.86 (m, 1H), 1.80-1.70 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 171.95, 164.00, 145.78, 136.44, 134.52, 129.82 (2C), 128.99 (2C), 128.58 (2C), 128.32 (2C), 127.50, 69.72, 57.11, 52.23, 46.29, 43.66, 36.93, 31.00, 25.95, 21.77; LRMS (FAB) C₂₃H₂₇N₂O₄S m/z (%) = 154 (82), 427 (M+H⁺, 8); HRMS (ESI) calcd for C₂₃H₂₇N₂O₄S (M + H)⁺ 427.1691, found 427.1693.

(±)-3d

7-Benzyl-2-(4-methoxybenzyl)-4-(toluene-4-sulfonyl)hexahydro-[2,7]-naphthyridine-1,3-dione (±)-(3d). **Yellow oil:** 64% yield; FT-IR (CH₂Cl₂) ν_{max} 3063, 1728, 1679, 1612, 1597, 1265, 1176, 1156 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.51 (d, J = 8.5 Hz, 2H), 7.33-7.21 (m, 9H), 6.84 (d, J = 8.5 Hz, 2H), 5.03 (d, J = 14.0 Hz, 1H), 4.97 (d, J = 14.0 Hz, 1H), 3.85 (s, 1H), 3.80 (s, 3H), 3.76 (d, J = 11.5 Hz, 1H), 3.64 (d, J = 13.5 Hz, 1H), 3.44-3.39 (m, 2H), 3.03-2.99 (m, 1H), 2.80-2.75 (m, 1H), 2.45 (s, 3H), 2.30 (dd, J = 3.0, 11.5 Hz, 1H), 2.01 (dt, J = 2.0, 11.5 Hz, 1H), 1.51-1.58 (m, 1H), 1.40-1.32 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): 171.24, 164.06, 158.87, 145.73, 137.94, 134.54, 130.21 (2C), 129.80 (2C), 128.94, 128.92(2C), 128.78 (2C), 128.13 (2C), 127.07, 113.57, 71.64, 62.39, 55.22, 53.63, 51.74, 43.00, 39.41, 30.12, 29.00, 21.77; LRMS (FAB) C₃₀H₃₃N₂O₅S m/z (%) = 91 (81), 154 (51), 533 (M+H⁺, 4); HRMS (ESI) calcd for C₃₀H₃₃N₂O₅S (M + H)⁺ 533.2110, found 533.2106.

2-[2-(1H-Indol-3-yl)ethyl]-4-(toluene-4-sulfonyl)hexahydroisoquinoline-1,3-dione (±)-(3e). **Brown oil:** 35% yield; FT-IR (CH₂Cl₂) $\nu_{\max}$ 3469, 3055, 1725, 1677, 1598, 1256, 1163, 1148 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 7.96 (br s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20-7.17 (m, 1H), 7.14-7.11 (m, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 4.23-4.17 (m, 1H), 4.13-4.07 (m, 1H), 3.83 (s, 1H), 3.46 (s, 1H), 3.02-2.97 (m, 3H), 2.54 (d, *J* = 14.5 Hz, 1H), 2.47 (s, 3H), 1.66-1.49 (m, 4H), 1.40-1.30 (m, 1H), 1.07-0.94 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 172.21, 164.41, 145.68, 136.14, 135.33, 129.87 (2C), 128.96 (2C), 127.54, 122.34, 122.05, 119.48, 119.19, 112.49, 110.96, 72.44, 40.81, 39.00, 32.09, 29.19, 25.90, 25.21, 23.40, 21.79, 21.62; LRMS (FAB) C₂₆H₂₉N₂O₄S *m/z* (%) = 143 (100), 154 (71), 465 (M+H⁺, 5); HRMS (ESI) calcd for C₂₆H₂₉N₂O₄S (M + H)⁺ 465.1848, found 465.1845.

2-[2-(1H-Indol-3-yl)ethyl]-4-(toluene-4-sulfonyl)octahydroisoquinolin-3-one (6). A solution of glutarimide **3e** (280 mg, 0.6 mmol) in THF (10 mL) was added to a stirred solution of triethylamine (134 mg, 1.3 mmol) in THF (5 mL). After the reaction mixture was stirred at room temperature for 30 min., lithium aluminum hydride (193 mg, 4.8 mmol) was added. The resulting mixture was refluxed for 6 h, quenched with saturated ammonium chloride solution (0.5 mL) in an ice bath, filtered and concentrated under reduced pressure. The residue was diluted with water (5 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 2:1) to afford 3-sulfonyl lactam **6** as brown oil (189 mg, 0.4 mmol, 70 %): FT-IR (CH₂Cl₂) $\nu_{\max}$ 3469, 3055, 1646, 1256, 1145 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): 8.02 (br s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 1H), 7.15-7.11 (m, 2H), 3.76-3.71 (m, 1H), 3.63 (d, *J* = 3.0 Hz, 1H), 3.58-3.53 (m, 1H), 3.19-3.13 (m, 2H), 3.06-3.03 (m, 2H), 2.91-2.87 (m, 1H), 2.63-2.56 (m, 1H),

2.44 (s, 3H), 1.62-1.18 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3): 161.08, 144.61, 136.61, 136.26, 129.46 (2C), 128.95 (2C), 127.29, 126.61, 122.03, 119.40, 118.66, 112.74, 111.18, 71.12, 49.60, 48.90, 38.80, 29.64, 27.72, 26.58, 24.49, 22.81, 21.71, 20.90; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 451.2055, found 451.2053.

2-[2-(1H-Indol-3-yl)ethyl]octahydroisoquinolin-3-one (7). A solution of 3-sulfonyl lactam **6** (189 mg, 0.4 mmol), disodium hydrogen phosphate (40 mg), and sodium amalgam (1.5 g, 6%) in methanol (10 mL) was stirred at room temperature under nitrogen for 12 h. The mercury was removed, and the solvent was stripped off under reduced pressure. Water (20 mL) was added to the residue, which was then extracted with ethyl acetate (3 $\times$ 25 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 2:1) to afford 4, 5-annulated lactam **7** as brown oil (118 mg, 0.4 mmol, 95 %): ^1H NMR (500 MHz, CDCl_3): 8.11 (br s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.06 (br s, 1H), 3.78-3.72 (m, 1H), 3.63-3.57 (m, 1H), 3.24-3.10 (m, 2H), 3.07-3.03 (m, 2H), 2.46-2.34 (m, 2H), 2.04-1.96 (m, 1H), 1.96-1.88 (m, 1H), 1.59-1.28 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3): 169.51, 136.25, 127.49, 122.13, 121.98, 119.33, 118.78, 113.14, 111.15, 51.21, 48.22, 35.17, 32.91, 32.41, 28.30, 26.42, 23.02, 22.45, 22.61; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 297.1967, found 297.1966.

2-Benzyl-4-(toluene-4-sulfonyl)-2,4,4a,5,6,7-hexahydro[2]pyrindin-3-one (9). A suspension of sodium hydride (302 mg, 7.5 mmol, 60% dispersion in oil, was washed 3 times with dry hexane) in dry THF (100 mL) was added glutarimide **3a** (2.5 g, 6.29 mmol) at 25 $^\circ\text{C}$ and stirred for 30 min.. LAH (9.4 mmol) was added to the mixture at 0 $^\circ\text{C}$ and stirred for 1 h, then quenched with ammonium chloride solution (5 mL). The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 $\times$ 15

mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. Without purification, crude **8** was treated with boron trifluoride (catalyst) in 20 mL of CH₂Cl₂ at 4 °C for 1 day and quenched with saturated aqueous sodium bicarbonate. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash chromatography (hexane/ethyl acetate = 4:1) to afford dehydration product **9** as yellow oil (1.8 g, 4.7 mmol, 75 %).

2-Benzyl-4-propenyl-2,5,6,7-tetrahydro[2]pyrindin-3-one (10). A suspension of sodium hydride (288 mg, 7.2 mmol, 60% dispersion in oil, was washed 3 times with dry hexane) in dry THF (100 mL) was added enlactam **9** (2.5 g, 6.6 mmol) at 25 °C and stirred for 30 min.. Allyl bromide (7.2 mmol) was added, the mixture was stirred for 1.5 h and then quenched with saturated ammonium chloride solution (5 mL). The organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried, filtered, and concentrated. Without purification, the residue was dissolved in *tert*-butyl alcohol, potassium *tert*-butoxide was added (808 mg, 7.2 mmol) and the resulting mixture was refluxed for 12 h and quenched with water. The mixture was separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 4:1) to afford dehydrosulfonated product **10** as colorless oil (1.4 g, 5.3 mmol, 80 %): FT-IR (CH₂Cl₂) ν_{max} 3054, 1662, 1598, 1271, 1259 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.37-7.27 (m, 5H), 7.02 (s, 1H), 6.79 (qd, J = 6.5, 16.0 Hz, 1H), 6.48 (dd, J = 1.5, 16.0 Hz, 1H), 5.13 (s, 2H), 2.87 (t, J = 7.5 Hz, 2H), 2.66 (dt, J = 1.5, 7.5 Hz, 2H), 2.01 (tt, J = 7.5, 7.5 Hz, 2H), 1.91 (dd, J = 1.5, 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 161.35, 154.06, 137.19, 131.00, 128.73 (2C), 128.02 (2C), 127.67, 127.62, 125.27, 123.29, 122.60, 52.31, 32.66, 29.20, 25.68, 19.73; LRMS (FAB) C₁₈H₂₀NO m/z (%) = 91 (100), 154 (55), 266 (M+H⁺, 2).

3-Chloro-4-propenyl-6,7-dihydro-5H-[2]pyrindine (11). A suspension of 2-pyridone **10** (530 mg, 2.0 mmol) and POCl₃ (3.0 g, 20.0 mmol) in toluene was refluxed for 12 h, and allowed to cool to 0 °C. The mixture was neutralized with saturated sodium bicarbonate solution and then extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 2:1) to afford 2-chloropyridine **11** as colorless oil (232 mg, 1.2 mmol, 60 %): FT-IR (CH₂Cl₂) ν_{max} 3054, 2926, 1577, 1421, 1367, 1185, 1156 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.96 (dd, 3H, *J* = 2.0, 6.5 Hz), 2.11 (p, 2H, *J* = 7.5 Hz), 2.91 (t, 2H, *J* = 7.5 Hz), 2.98 (t, 2H, *J* = 7.5 Hz), 6.11 (dq, 1H, *J* = 6.5, 16.5 Hz), 6.59 (dd, 1H, *J* = 16.5 Hz), 8.06 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 19.30, 25.73, 29.94, 33.79, 125.81, 128.95, 133.25, 140.07, 142.04, 147.25, 154.31; HRMS (ESI) calcd for C₁₁H₁₃NCl⁺ (*M* + *H*) 194.0736, found 194.0735.

4-Propenyl-6,7-dihydro-5H-[2]pyrindine (12). A suspension of 2-chloropyridine **11** (232 mg, 1.2 mmol) and zinc (1.2 g, 18.0 mmol) in acetic acid (10 mL) was refluxed for 12 h under nitrogen and then allowed to cool down to room temperature. Sodium hydroxide (10%) was added to neutralize the mixture and then extracted with dichloromethane (3x20mL). The combined organic extracts were washed with water, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 2:1) to afford bicyclic pyridine **12** as colorless oil (182 mg, 1.14 mmol, 95 %): FT-IR (CH₂Cl₂) ν_{max} 3052, 2967, 1584, 1435, 1170, 1131 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.92 (dd, 3H, *J* = 1.5, 6.5 Hz), 2.10 (p, 2H, *J* = 7.5 Hz), 2.93 (t, 4H, *J* = 7.5 Hz), 6.25 (dq, 1H, *J* = 7.0, 16.0 Hz), 6.40 (dd, 1H, *J* = 1.5, 16 Hz), 8.29 (s, 1H), 8.39 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 18.98, 24.56, 30.33, 31.70, 126.48, 128.97, 129.93, 139.76, 143.33, 144.60, 150.02; HRMS (ESI) calcd for C₁₁H₁₄N⁺ (*M* + *H*)⁺ 160.1126, found 160.1125.

4-Propenyl-6,7-dihydro-5H-[2]pyrindin-5-ol (13). LHMDs (12.6 mL, 1 M) was added to a solution of bicyclic pyridine **12** (210 mg, 1.31 mmol) in dry THF (20 mL) at 0 °C and the mixture was stirred for 2 h. Oxygen was bubbled through the mixture until the reaction completed as monitored by TLC and then quenched with water. The organic layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 1:1) to afford hydroxyl bicyclic pyridine **13** as colorless oil (185 mg, 1.05 mmol, 80 %): FT-IR (CH₂Cl₂) ν_{max} 3592, 3054, 2969, 1654, 1578, 1447, 1419, 1174, 1045 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.93 (dd, 3H, *J* = 1.5, 6.5 Hz), 2.11–2.05 (m, 1H), 2.44–2.37 (m, 1H), 2.85–2.72 (m, 2H), 3.10 (p, 1H, *J* = 7.5 Hz), 5.38 (dd, 1H, *J* = 3.5, 7.0 Hz), 6.38 (dq, 1H, *J* = 6.5, 16.0 Hz), 6.68 (dd, 1H, *J* = 1.5, 16.0 Hz), 8.28 (s, 1H), 8.45 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 19.03, 27.68, 34.88, 74.53, 125.03, 130.15, 130.59, 139.02, 143.95, 144.70, 149.24; HRMS (ESI) calcd for C₁₁H₁₄NO⁺ (*M* + *H*) 176.1075, found 176.1076.

4-Propenyl-6,7-dihydro[2]pyrindin-5-one, Loisianin D (5). A solution of oxalyl chloride (268 mg, 2.11 mmol) in CH₂Cl₂ (10 mL) was mixed with dimethyl sulfoxide (412 mg, 5.28 mmol) together carefully at -78 °C. The solution was warmed to -40 °C for 5 min and recooled to -78 °C, and then a solution of **13** (185 mg, 1.05 mmol) in CH₂Cl₂ (10 mL) was added dropwise. The mixture was stirred at -78 °C for 1 h followed by excess triethylamine (1.1 g, 10.56 mmol) for 10 min. The reaction mixture was warmed to room temperature and then poured into saturated aqueous ammonium chloride solution (1 mL), concentrated. The residue was diluted with water (15 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried, filtered, and concentrated. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 2:1) to afford Loisianin D (**5**) as colorless solid (155 mg, 0.89 mmol, 80 %): mp 164–167 °C; ¹H

NMR (500 MHz, CDCl₃): δ 1.98 (dd, 3H, J = 2.0, 6.5 Hz), 2.73-2.71 (m, 2H), 3.15 (t, 2H, J = 6.0 Hz), 6.56 (dq, 1H, J = 7.0, 16.0 Hz), 7.41 (dd, 1H, J = 1.5, 16.0 Hz), 8.71 (s, 1H), 8.82 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 19.07, 23.04, 36.48, 123.59, 131.12, 132.63, 137.29, 144.66, 146.58, 147.90, 207.40; HRMS (ESI) calcd for C₁₁H₁₂NO⁺ (M + H)⁺ 174.0919, found 174.0920.

X-ray structure of (±)-3a

X-ray structure of 3b