

## SUPPORTING INFORMATION

### Representative experimental of procedures for reactions with *N*-acyliminium ions.

**Conversion of 3c to 6c.** To a solution of the *N,O*-acetal **3c** (100 mg, 0.64 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) at -78 °C was added allyltrimethylsilane (0.520 mL, 6.4 mmol) followed by SnCl<sub>4</sub> (0.96 mL of a 1.0 M solution in ether, 0.96 mmol). The reaction mixture was warmed up to rt overnight. Then a saturated solution of NaHCO<sub>3</sub> (5 mL) was added, the organic layer was separated, dried over MgSO<sub>4</sub> and concentrated in vacuo to afford the crude product. Purification by column chromatography (silica gel, EtOAc + 1% Et<sub>3</sub>N) afforded 66 mg (58%) of amide **6c**.

**Conversion of 10a to 12.** To a solution of the *N,O*-acetal **10a** (50 mg, 0.27 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) at -78 °C was added Me<sub>3</sub>SiCN (0.360 mL, 2.7 mmol) followed by Me<sub>3</sub>SiOTf (50 μL, 0.27 mmol) and stirred at the same temperature for 2 h. Then a saturated solution of NaHCO<sub>3</sub> (3 mL) was added, the organic layer was separated, dried over MgSO<sub>4</sub> and concentrated in vacuo to afford the crude product. Purification by column chromatography (silica gel, EtOAc + 1% Et<sub>3</sub>N) afforded 33 mg (62%) of hydroxy cyanide **12**.

**Conversion of 15a to 19a.** A solution of enamide **15a** (50 mg, 0.24 mmol) in HCO<sub>2</sub>H (5 mL) was stirred at rt for 17 h and then concentrated in vacuo. The residue was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub> and concentrated in vacuo. The crude residue was dissolved in MeOH/NH<sub>3</sub>, stirred for 30 min and concentrated to give the tricyclic enamide **19a**, which was crystallized from EtOAc.

**Enamide 5b:** IR (film): 1644 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 1.65 (s, 3H), 1.71-1.78 (m, 4H), 2.01 (t, *J* = 5.5 Hz, 2H), 2.41-2.47 (m, 4H), 3.70 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 18.6, 19.4, 21.8, 25.0, 29.3, 32.9, 40.1, 105.2, 129.1, 173.0. HRMS (EI): C<sub>10</sub>H<sub>15</sub>NO (165.1154): found 165.1142.

**Allylated lactam 6c:** IR (film): 1696 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.89 (d, *J* = 7.1 Hz, 3H), 1.56 (m, 1H), 1.83 (m, 1H), 1.94-2.11 (m, 2H), 2.20-2.37 (m, 4H), 2.68 (m, 1H), 2.93 (m, 1H), 3.68 (m, 1H), 5.12 (d, *J* = 5.7 Hz, 1H), 5.16 (s, 1H), 5.77 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 16.1, 25.6, 33.7, 34.1, 37.9, 40.0, 43.6, 72.3, 119.0, 133.4, 175.7. HRMS (FAB): C<sub>11</sub>H<sub>18</sub>NO (180.1388): found 180.1381.

**Cyanide 7a:** IR (film): 2320, 1696 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 1.08 (d, *J* = 6.2 Hz, 3H), 1.34-1.554 (m, 3H), 1.73-1.84 (m, 2H), 1.97 (m, 1H), 2.45 (m, 1H), 2.52-2.63 (m, 2H), 2.80 (dt, *J* = 12.8, 2.8 Hz, 1H, NCH), 4.08-4.14 (m, 1H, NCH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 15.9, 23.7, 29.1, 29.7, 30.4, 38.0, 41.4, 63.8, 117.5, 172.8. HRMS (FAB): C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O (179.1184): found 179.1184.

**Hydroxy cyanide 12:** IR (film): 3402, 2231, 1684  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.36-1.45 (m, 2H), 1.75-1.90 (m, 4H), 2.23 (m, 1H), 2.44-2.54 (m, 2H), 2.68-3.05 (m, 2H), 3.70 (dd,  $J$  = 11.1, 5.6 Hz, 1H), 3.80 (dd,  $J$  = 11.1, 8.1 Hz, 1H), 4.11 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 23.2, 24.5, 29.2, 32.1, 38.1, 47.9, 62.1, 63.9, 117.6, 173.2. HRMS (FAB):  $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2$  (195.1141): found 195.1134.

**Allylated enamide 15a:** IR (film): 1682  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.74-1.80 (m, 2H), 2.0-2.12 (m, 4H), 2.13-2.17 (m, 2H), 2.43-2.47 (m, 2H), 2.58-2.68 (m, 2H), 3.47 (t,  $J$  = 5.9 Hz, 2H), 4.96 (dd,  $J$  = 9.9, 1.3 Hz, 1H), 4.99 (dd,  $J$  = 17.1, 1.5 Hz, 1H), 5.80 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 20.8, 21.1, 25.2, 29.3, 31.1, 31.9, 38.7, 108.8, 114.9, 132.2, 138.1, 175.1. HRMS (FAB):  $\text{C}_{12}\text{H}_{18}\text{NO}$  (192.1388): found 192.1379.

**Allylated enamide 15b:** IR (film): 1642  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.70-1.79 (m, 4H), 2.03-2.15 (m, 6H), 2.46 (m, 4H), 3.68 (m, 2H), 4.95 (dd,  $J$  = 9.4, 1.9 Hz, 1H), 4.99 (dd,  $J$  = 15.6, 1.7 Hz, 1H), 5.79 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 19.6, 21.7, 24.9, 27.3, 32.4, 32.5, 32.9, 40.3, 114.3, 114.9, 130.1, 138.1, 168.5. HRMS (FAB):  $\text{C}_{13}\text{H}_{20}\text{NO}$  (206.1545): found 206.1548.

**Ketone 16a:** IR (film): 1714, 1680  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.74 (q,  $J$  = 6.0 Hz, 2H), 1.97 (t,  $J$  = 6.0 Hz, 2H), 2.12 (s, 3H), 2.22 (t,  $J$  = 7.3 Hz, 2H), 2.42 (dd,  $J$  = 7.2, 5.3 Hz, 2H), 2.49 (t,  $J$  = 7.3 Hz, 2H), 2.61 (m, 2H), 3.43 (t,  $J$  = 5.9 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 20.6, 20.9, 24.9, 25.6, 29.1, 30.0, 38.6, 41.4, 107.4, 132.8, 174.1, 208.2. HRMS (FAB):  $\text{C}_{12}\text{H}_{18}\text{NO}_2$  (208.1338): found 208.1330.

**Ketone 17a:** IR (film): 1704, 1679  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.28-1.31 (m, 1H), 1.61-2.09 (m, 10H), 2.27-2.71 (m, 8H), 3.37-3.53 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 20.7, 21.3, 25.0, 25.3, 27.9, 29.2, 31.4, 33.5, 38.7, 42.1, 48.7, 106.8, 133.4, 174.1, 212.8. HRMS (FAB):  $\text{C}_{15}\text{H}_{22}\text{NO}_2$  (248.1651): found 248.1650.

**Tricyclic lactam 19a:** IR (film): 3375, 1659  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.34-1.87 (m, 13H), 2.10 (m, 1H), 2.33 (dd,  $J$  = 10.1, 3.2 Hz, 1H), 2.43 (m, 1H), 2.52 (m, 1H), 3.76 (m, 1H), 4.02 (dd,  $J$  = 13.4, 4.8 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 24.9, 25.3, 25.5, 29.3, 29.5, 31.3, 36.3, 36.8, 41.5, 62.7, 68.3, 172.6. HRMS (FAB):  $\text{C}_{12}\text{H}_{20}\text{NO}_2$  (210.1494): found 210.1491.

**Tricyclic lactam 19b:** IR (film): 3380, 1606  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.41-1.54 (m, 6H), 1.65-1.91 (m, 7H), 1.96 (m, 2H), 2.15 (m, 1H), 2.35-2.47 (m, 2H), 2.59 (dt,  $J$  = 13.6, 2.4 Hz, 1H), 3.81 (m, 1H), 5.00 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 16.2, 25.2, 25.6, 26.3, 29.5, 32.5, 33.4, 36.6, 36.7, 41.5, 60.1, 67.4, 170.1. HRMS (FAB):  $\text{C}_{13}\text{H}_{22}\text{NO}_2$  (224.1651): found 224.1652.

**Bicyclic enamide 23:** IR (film): 3375, 1681  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.87 (t,  $J$  = 6.5 Hz, 3H), 1.29 (m, 9H), 1.48 (m, 2H), 1.85 (m, 2H), 2.01-2.18 (m, 5H), 2.40-2.64 (m, 4H), 4.12 (m, 1H), 4.95 (d,  $J$  = 10.1 Hz, 1H), 4.99 (dd,  $J$  = 17.1, 1.5 Hz, 1H), 5.76 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.02, 21.2, 21.4, 22.6, 23.4, 25.8, 29.2, 29.4, 31.1, 31.2, 31.7, 32.0, 47.6, 108.0, 114.8, 131.5, 138.2, 173.8. HRMS (FAB):  $\text{C}_{18}\text{H}_{30}\text{NO}$  (276.2327): found 276.2333.

**Tricyclic lactam 24:** IR (film): 3380, 1657  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.85 (t,  $J$  = 7.3 Hz, 3H), 1.26-1.96 (m, 25H), 2.14 (t,  $J$  = 9.3 Hz, 1H), 2.25 (dd,  $J$  = 9.7, 1.4 Hz, 1H), 2.46 (m, 1H), 4.16 (q,  $J$  = 7.1 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 14.0, 21.4, 22.6, 25.8, 27.2, 27.6, 29.3, 29.4, 29.7, 31.8, 32.5, 34.6, 39.8, 43.1, 48.0, 63.3, 68.7, 173.4. HRMS (EI):  $\text{C}_{18}\text{H}_{31}\text{NO}_2$  (293.2355): found 293.2345.