Selective 6-endo-Cyclization of the Acyl Radicals onto the Nitrogen of Imine and Oxazoline C-N Bonds

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General information. ^1H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in CDCl_3 . Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer or JEOL AL-400 (100 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. Infrared spectra were obtained on a JASCO FT/IR 4100 spectrometer; absorption data are reported in reciprocal centimeters. Conventional and high-resolution mass spectra were obtained on a JEOL MS700 spectrometer. Products were purified by flash chromatography on silica gel (nacalai tesque int. Silica Gel 60, 230-400 mesh) and if necessary, were further purified by recycling preparative HPLC (JAI LC-908) equipped with a GPC column using CHCl_3 as eluent.

1-Ethylpropyl (4-phenylselenylbutylidene)amine (1a).

4-(Phenylseleno)butanal (8.9 mmol, 2.01 g) was added to 3-aminopentane (11.1 mmol, 920 mg) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. The mixture dried over Na_2SO_4 . After filtration, the solvent was evaporated. The residue was distilled under reduced pressure to give 1.56 g (60%) of **1a** (122-123 °C/ 0.3 mmHg). ^1H NMR (500 MHz, CDCl_3) δ 0.75 (t, J = 7.3 Hz, 6H, H -7), 1.41-1.57 (m, 4H, H -6), 1.93 (qui, J = 7.3 Hz, 2H, H -3), 2.34-2.38 (m, 2H, H -4), 2.59 (sept, J = 4.1 Hz, 1H, H -5), 2.93 (t, J = 7.3 Hz, 2H, H -2), 7.19-7.25 (m, 3H, H -1, -Ph), 7.45-7.48 (m, 2H, H -Ph), 7.53 (t, J = 4.8 Hz, 1H, H -Ph); ^{13}C NMR (125 MHz, CDCl_3) δ 11.01 (C -7), 27.14, 27.23, 28.69, 35.80, 76.91 (C -5), 126.84 (C -Ph), 129.11 (C -Ph), 130.27 (C -Ph), 132.56 (C -Ph), 162.07 (C -1); IR (neat) 3057, 2961, 2930, 2872, 2833, 1666, 1579, 1478, 1456, 1438; MS (EI) m/z (rel intensity) 297 (M^+ , 12), 157 (14), 140 (10), 113 (95), 84 (100); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{23}\text{NSe}$ (M^+) 297.0996, found 297.0992.

1-Ethylpropyl-((1-prop-2-ynylcyclohexyl)methylene) amine (1d).

1-Prop-2-ynyl-cyclohexanecarbaldehyde (9.1 mmol, 1.37 g) was added to 3-aminopentane (9.1 mmol, 1.1 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. The mixture dried over Na_2SO_4 . After filtration, the solvent was evaporated. The residue was distilled

under reduced pressure to give 1.00 g (50%) of **1e** (62-63 °C/ 0.3 mmHg). ¹H NMR (500 MHz, CDCl₃) δ 0.76 (t, *J* = 7.3 Hz, 6H, *H*-11), 1.22-1.30 (m, 1H), 1.40- 1.56 (m, 11H), 1.80-1.86 (m, 2H), 1.92 (t, *J* = 2.8 Hz, 1H, *H*-5), 2.25 (d, *J* = 2.8 Hz, 2H, *H*-3), 2.62 (sep, *J* = 4.4 Hz, 1H, *H*-9), 7.46 (s, 1H, *H*-1); ¹³C NMR (125 MHz, CDCl₃) δ 11.22 (*C*-11), 22.40, 25.91, 28.86, 29.55, 33.57, 41.69, 70.31 (*C*-5), 75.42 (*C*-2), 81.34 (*C*-4), 168.22 (*C*-1); IR (neat) 3312, 2118, 1664; MS (EI) *m/z* (rel intensity) 219 (*M*⁺, 4), 150 (100); HRMS (EI) *m/z* calcd for C₁₅H₂₅N (*M*⁺) 219.1987, found 219.1996.

1-Ethylpropyl (4-iodo-2,2-dimethyl-3-butenylidene) amine (**1j**).

The mixture of (*Z*)-4-iodo-2,2-dimethyl-3-butenal (4.5 mmol, 1.0 g), 3-aminopentane (5.1 mmol, 0.6 mL) and K₂CO₃ (10 g) in Et₂O (50 mL) was stirred at room temperature for 19.5 h. After filtration, the solvent was evaporated. The residue was distilled under reduced pressure to give 0.4 g (30%) of **1j** (82 °C/2 mmHg). ¹H NMR (400 MHz, CDCl₃) δ 0.80 (t, *J* = 7.4 Hz, 6H, *H*-8), 1.37 (s, 6H, *H*-5), 1.49-1.60 (m, 4H, *H*-7), 2.72 (sex, *J* = 4.9 Hz, 1H, *H*-6), 6.31 (d, *J* = 8.3 Hz, 1H, *H*-3), 6.82 (d, *J* = 8.3 Hz, 1H, *H*-4), 7.72 (s, 1H, *H*-1); ¹³C NMR (100 MHz, CDCl₃) δ 11.13 (*C*-8), 25.71 (*C*-5), 28.56 (*C*-7), 42.41 (*C*-2), 74.39 (*C*-6), 77.86 (*C*-4), 146.18 (*C*-3), 167.43 (*C*-1); IR (neat) 1662, 1602, 1460; MS (EI) *m/z* (rel intensity) 293 (*M*⁺, 7), 264 (6), 226 (16), 195(21), 166 (35), 153 (23), 98 (43), 84 (49), 71 (100); HRMS (EI) *m/z* calcd for C₁₁H₂₀NI (*M*⁺) 293.0640, found 293.0633.

Imines **1b**, **1c** and **1i** were prepared by a similar procedure from the corresponding amines and aldehydes. Azaenyne **1e**, **1f**, **1g** and **1h** were prepared from a corresponding amines and hex-5-yn-2-one by azeotropic distillation using Dean-Stark tube (solvent C₆H₆).

(*R*)-4-Phenyl-2-(3-phenylselenenylpropyl)-4,5-dihydrooxazole (**1m**).

¹H NMR (500 MHz, CDCl₃) δ 2.10 (qui, *J* = 7.3 Hz, 2H, *H*-7), 2.51-2.54 (m, 2H, *H*-8), 3.02 (t, *J* = 7.3 Hz, 2H, *H*-6), 4.05 (t, *J* = 8.3 Hz, 1H, *H*-5), 4.58 (t, *J* = 9.2 Hz, 1H, *H*-5), 5.15 (t, *J* = 9.2 Hz, 1H, *H*-4), 7.20 (m, 6H, *Ph*), 7.31 (m, 2H, *Ph*), 7.49 (m, 2H, *Ph*); ¹³C NMR (100 MHz, CDCl₃) δ 26.40 (*C*-6 or 7 or 8), 27.01 (*C*-6 or 7 or 8), 27.79 (*C*-6 or 7 or 8), 69.53 (*C*-4 or 5), 74.43 (*C*-4 or 5), 126.46, 126.79, 127.45, 128.64, 129.00, 132.55, 142.32, 167.82 (*C*-2); IR (neat) 1665, 1578; MS (EI) *m/z* (rel intensity) 345 (*M*⁺, 12), 188 (12), 161 (100), 120 (11), 91 (11); HRMS (EI) *m/z* calcd for C₁₈H₁₉NOS₂ (*M*⁺) 345.0632, found 345.0623.

Typical procedure for radical carbonylation. A magnetic stirring bar, AIBN (2,2'-azobisisobutyronitrile, 17.3 mg, 0.1 mmol), benzene (17 mL), imine **1a** (143.6 mg, 0.48 mmol) and Bu₃SnH (186.1 mg, 0.64 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 80 atm of CO and then heated 90 °C

for 1 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc = 1/1) to give **2a** (66.3 mg, 81%).

1-(1-ethylpropyl)piperidin-2-one (**2a**).

(R_f = 0.28, hexane/EtOAc = 1/1). ^1H NMR (500 MHz, CDCl_3) δ 0.83 (t, J = 7.3 Hz, 6H, H -9), 1.36-1.51 (m, 4H, H -8), 1.73-1.79 (m, 4H, H -4, 5), 2.43 (t, J = 6.9 Hz, 2H, H -3), 3.03 (t, J = 6.0 Hz, 2H, H -6), 4.53 (sept, J = 5.0 Hz, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 10.79 (C-9), 21.05, 23.22, 24.68, 32.44, 40.39 (C-6), 54.92 (C-7), 170.42 (C-2); IR (neat) 1636; MS (EI) m/z (rel intensity) 169 (M^+ , 18), 140 (100), 112 (13); HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{19}\text{NO}$ (M^+) 169.1467, found 169.1465.

Typical procedure for the stannylcarbonylation of alkynyl imine and subsequent protodestannylation. A magnetic stirring bar, AIBN (2,2'-azobisisobutyronitrile, 16.8 mg, 0.1 mmol), benzene (17 mL), alkynyl imine **1b** (78.6 mg, 0.52 mmol) and Bu_3SnH (212.6 mg, 0.73 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 85 atm. of CO and then heated 90 °C for 8 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was dissolved into MeOH (3.5 mL), and TMSCl (0.42 mL) was added. The solution was stirring at room temperature for 5 min, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc = 2/1) to give **2b** (67.2 mg, 71%).

1-(1-Ethylpropyl)-3-methylene-piperidin-2-one (**2b**).

(R_f = 0.35, hexane/EtOAc = 2/1). ^1H NMR (500 MHz, CDCl_3) δ 0.86 (td, J = 7.3, 1.3 Hz, 6H, H -10), 1.40- 1.56 (m, 4H, H -9), 1.86 (qui, J = 6.4, 5.7 Hz, 2H, H -5), 2.58 (td, J = 6.4, 1.4 Hz, 2H, H -4), 3.14 (t, J = 5.7 Hz, 2H, H -6), 4.60 (m, 1H, H -8), 5.29 (t, J = 1.8 Hz, 1H, H -7), 6.24 (t, J = 1.8 Hz, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 10.92 (C-10), 23.34 (C-5), 24.92 (C-9), 29.97 (C-4), 41.18 (C-6), 55.86 (C-8), 121.78 (C-7), 137.95 (C-3), 164.86 (C-2); IR (neat) 1653, 1614; MS (EI) m/z (rel intensity) 181 (M^+ , 19), 153 (40), 152 (100), 149 (23), 136 (25), 107 (31), 106 (23), 105 (19), 89 (34), 78 (24), 77 (70), 69 (26), 57 (31), 55 (31), 51 (22); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{19}\text{NO}$ (M^+) 181.1467, found 181.1463.

1-(1-Ethylproryl)-5,5-dimethyl-3-methylene-piperidin-2-one (**2c**).

(R_f = 0.14, hexane/EtOAc = 5/1). ^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, J = 7.3 Hz, 6H, H -11), 1.01 (s, 6H, H -8) 1.36- 1.53 (m, 4H, H -10), 2.35 (s, 2H, H -4), 2.85 (s, 2H, H -6), 4.57 (broad, 1H, H -9), 5.27 (qua-like, J = 1.8 Hz, 1H, H -7), 6.26 (t-like, J = 1.8 Hz, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 11.03 (C -11), 24.80, 26.26, 30.14, 43.32, 52.96, 55.89, 122.97 (C -7), 136.77 (C -3), 164.49 (C -2); IR (neat) 1659, 1615; MS (EI) m/z (rel intensity) 209 (M^+ , 12), 180 (100), 166 (6); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{23}\text{NO}$ (M^+) 209.1780, found 209.1772.

2-(1-Ethylpropyl)-4-methylene-2-aza-spiro[5.5]undecan-3-one (2d).

(R_f = 0.23, hexane/EtOAc = 5/1). ^1H NMR (500 MHz, CDCl_3) δ 0.85 (t, J = 7.3 Hz, 6H, H -10), 1.23- 1.53 (m, 14H, H -1', 2', 3', 4', 5', 9), 2.41 (s, 2H, H -5), 2.89 (s, 2H, H -1), 4.56 (broad, 1H, H -8), 5.27 (t-like, J = 1.8 Hz, 1H, H -7), 6.23 (t-like, J = 1.8 Hz, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 10.99 (C -10), 21.52 (C -2', 4'), 24.89 (C -9), 26.32, 32.42, 34.48, 40.20, 51.25, 55.83 (C -8), 122.86 (C -7), 136.31 (C -4), 164.72 (C -3); IR (neat) 1659, 1616; MS (EI) m/z (rel intensity) 249 (M^+ , 9), 221 (16), 220 (100), 206 (6), 81 (4), 79 (6), 77 (4), 67 (6), 55 (6); HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{27}\text{NO}$ (M^+) 249.2093, found 249.2085.

1-(1-Ethylpropyl)-6-methyl-3-methylene-piperidin-2-one (2e).

(R_f = 0.29, hexane/EtOAc = 2/1). ^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, J = 7.3 Hz, 3H, H -11), 0.92 (t, J = 7.3 Hz, 3H, H -11), 1.25 (d, J = 6.9 Hz, 3H, H -8), 1.51-1.74 (m, 5H, H -5, 10), 1.88-1.95 (m, 1H, H -5), 2.54-2.57 (m, 1H, H -4), 2.71-2.79 (m, 1H, H -4), 3.55 (qui, J = 6.9 Hz, 1H, H -6), 3.91 (broad, 1H, H -9), 5.28 (s, 1H, H -7), 6.25 (s, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 11.56 (C -11), 20.31 (C -8), 24.10 (C -5 or 12), 25.38 (C -5 or 12), 26.17 (C -5 or 12), 29.55 (C -4), 49.97 (C -6), 61.05 (C -9), 121.89 (C -7), 137.70 (C -3), 164.66 (C -2); IR (neat) 1655, 1609; MS (EI) m/z (rel intensity) 196 (M^+ , 23), 195 (100), 180 (21), 167 (39), 166 (100), 152 (11), 126 (11), 124 (5), 110 (7); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{21}\text{NO}$ (M^+) 195.1623, found 195.1614.

1-(1-Cyclohexylethyl)-6-methyl-3-methylene-piperidin-2-one (2f).

(R_f = 0.3, hexane/EtOAc = 5/1). Obtained as a diastereomer mixture. ^1H NMR (500 MHz, CDCl_3) δ 0.73-0.93 (m, 4H), 1.04-1.24 (m, 16H), 1.31 (d, J = 6.9 Hz, 3H), 1.58-1.94 (m, 15H), 2.45-2.55 (m, 2H, H -4), 2.60-2.76 (m, 2H, H -4), 3.14 (broad, 1H, H -9), 3.47 (t, J = 6.9 Hz, 1H, H -6), 3.55 (t, J = 6.4 Hz, 1H, H -6), 4.08 (broad, 1H, H -9), 5.19 (d, J = 0.9 Hz, 1H, H -7), 5.27 (d, J = 1.4 Hz, 1H, H -7), 6.15 (s, 1H, H -7), 6.21 (s, 1H, H -7); ^{13}C NMR (125 MHz, CDCl_3) δ 16.85, 16.90, 19.46, 19.51, 20.80, 20.85, 25.99, 26.13, 26.26, 26.38, 30.53, 30.62, 30.70, 31.02, 40.49, 40.79, 48.69, 54.00, 56.37, 61.91, 121.28 (C-7), 122.12 (C-7), 137.54 (C-3), 138.12 (C-3), 163.73 (C-2), 164.41 (C-2); IR (neat) 1649, 1609; MS (EI) m/z (rel intensity) 235 (M^+ , 8), 153 (13), 152 (100), 126 (27), 83 (11), 81 (20), 70 (10), 67 (14), 55 (62), 54 (13), 53 (17); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{25}\text{NO}$ (M^+) 235.1936, found 235.1939.

6-Methyl-3-methylene-1-(1-phenylethyl)-piperidine-2-one (2g).

(R_f = 0.13, hexane/EtOAc = 5/1). Obtained as a diastereomer mixture ^1H NMR (500 MHz, CDCl_3) δ 0.65 (d, J = 6.9 Hz, 3H, H -8), 1.24 (d, J = 6.4 Hz, 3H, H -8), 1.46-1.62 (m, 2H, H -5), 1.57 (d, J = 7.3 Hz, 3H, H -10), 1.61 (d, J = 6.8 Hz, 3H, H -10), 1.63-1.69 (m, 1H, H -5), 1.83-1.90 (m, 1H, H -5), 2.55-2.58 (m, 2H, H -4), 2.69-2.81 (m, 2H, H -4), 3.34-3.37 (m, 1H, H -6), 3.66-3.69 (m, 1H, H -6), 5.32 (d, J = 1.9 Hz, 1H, H -7), 5.35 (d, J = 2.3 Hz, 1H, H -7), 5.94 (q, J = 6.8 Hz, 1H, H -9), 6.07 (q, J = 7.3 Hz, 1H, H -9), 6.32 (s, 1H, H -7), 6.34 (s, 1H, H -7), 7.22-7.41 (m, 10H, H -Ph); ^{13}C NMR (125 MHz, CDCl_3) δ 16.13 (C-10), 17.31 (C-10), 19.71 (C-8), 20.96 (C-8), 24.05 (C-4), 24.23 (C-4), 29.33 (C-5), 29.85 (C-5), 47.76 (C-6), 48.63 (C-6), 51.80 (C-9), 52.11 (C-9), 122.79 (C-2), 123.07 (C-2), 127.37 (C-Ph), 127.42 (C-Ph), 127.45 (C-Ph), 128.00 (C-Ph), 128.37 (C-Ph), 128.46 (C-Ph), 137.15 (C-3), 137.41 (C-3), 140.83 (C-11), 141.02 (C-11), 164.13 (C-2), 164.52 (C-2); IR (neat) 2930, 2970, 2850, 1655, 1610, 1450, 1430; MS (EI) m/z (rel intensity) 229 (M^+ , 83), 214 (22), 172 (73), 105 (100); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ (M^+), 229.1467 found 229.1469.

6-Methyl-3-methylene-1-(1,2,2-trimethylpropyl)-piperidin-2-one (2h).

(R_f = 0.33, hexane/EtOAc = 5/1). For major isomer; ^1H NMR (500 MHz, CDCl_3) δ 0.91 (s, 9H, H -12), 1.17- 1.21 (m, 6H, H -8, 10), 1.66-1.71 (m, 1H, H -5), 1.94-2.02 (m, 1H, H -5), 2.61-2.65 (m, 1H, H -4),

2.76-2.84 (m, 1H, *H*-4), 3.72-3.78 (m, 1H, *H*-6), 4.75-4.80 (m, 1H, *H*-9), 5.28-5.31 (m, 1H, *H*-7), 6.23-6.25 (m, 1H, *H*-7); ^{13}C NMR (125 MHz, CDCl_3) δ 13.27 (*C*-10), 21.09 (*C*-8), 23.32 (*C*-4), 27.47 (*C*-4), 28.00 (*C*-12), 36.61 (*C*-11), 47.78 (*C*-6), 55.38 (*C*-9), 123.15 (*C*-7), 137.20 (*C*-3), 165.55 (*C*-2); IR (neat) 1651, 1610, 1428; MS (EI) m/z (rel intensity) 209 (M^+ , 2), 152 (100), 108 (14), 81 (11); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{23}\text{NO}$ (M^+) 209.1780, found 209.1775. For minor isomer (Minor isomer was obtained as a mixture with major isomer.); ^1H NMR (500 MHz, CDCl_3) δ 0.99 (s, 9H, *H*-12), 1.23-1.25 (m, 3H, *H*-8 or 10), 1.53 (d, $J = 7.3$ Hz, 3H, *H*-8 or 10), 1.60-1.71 (m, 1H, *H*-5), 1.97-2.05 (m, 1H, *H*-5), 2.51-2.57 (m, 1H, *H*-4), 2.65-2.74 (m, 1H, *H*-4), 3.45-3.53 (m, 1H, *H*-6), 4.72-4.78 (m, 1H, *H*-9), 5.22 (s, 1H, *H*-7), 6.20 (s, 1H, *H*-7).

1-Benzyl-8,8-dimethyl-6-methylene-hexahydroindolozin-5-one (2i).

($R_f = 0.13$, hexane/EtOAc = 5/1). diastereomer mixture ^1H NMR (500 MHz, CDCl_3) δ 0.84 (s, 3H, *H*-11 or 12), 1.03 (s, 3H, *H*-11 or 12), 1.07 (s, 3H, *H*-11 or 12), 1.22 (s, 3H, *H*-11 or 12), 1.51-1.64 (m, 1H, *H*-7), 1.68-1.74 (m, 1H, *H*-7), 2.24-2.36 (m, 3H, *H*-4, 7, 9), 2.39-2.47 (m, 2H, *H*-4, 9), 2.61-2.66 (m, 1H, *H*-4), 2.99-3.05 (m, 1H, *H*-4), 3.21 (d, $J = 10.8$ Hz, 1H, *H*-6), 3.42-3.47 (m, 1H, *H*-11), 3.54-3.68 (m, 2H, *H*-6, 11), 5.25 (d, $J = 1.9$ Hz, 1H, *H*-7), 5.25 (s, 1H, *H*-10), 6.22 (s, 1H, *H*-10), 7.10-7.30 (m, 10H, *H*-Ph); ^{13}C NMR (125 MHz, CDCl_3) δ 18.71 (*C*-12 or 13), 21.16 (*C*-12 or 13), 26.22 (*C*-8), 26.69 (*C*-12 or 13), 27.53 (*C*-12 or 13), 29.60 (*C*-8), 33.63 (*C*-7), 34.01 (*C*-7), 40.31 (*C*-4), 42.77 (*C*-4), 43.37 (*C*-11), 44.43 (*C*-11), 45.76 (*C*-9), 48.67 (*C*-9), 62.46 (*C*-5), 66.49 (*C*-5), 70.18 (*C*-6), 71.54 (*C*-6), 121.58 (*C*-10), 121.61 (*C*-10), 126.17 (*C*-Ph), 126.28 (*C*-Ph), 128.46 (*C*-Ph), 128.77 (*C*-Ph), 136.05 (*C*-3), 136.92 (*C*-3), 139.70 (*C*-11), 140.00 (*C*-11), 162.91 (*C*-2), 163.66 (*C*-2); IR (neat) 3027, 2957, 1656, 1616, 1496, 1452; MS (EI) m/z (rel intensity) 269 (M^+ , 5), 178 (83), 152 (10), 84 (100); HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{NO}$ (M^+), 269.1780 found 269.1782.

1-(1-Ethylpropyl)-5,5-dimethyl-5,6-dihydro-1H-pyridin-2-one (2j).

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 7.3$ Hz 6H, *H*-10), 1.11 (s, 6H, *H*-7), 1.35-1.53 (m, 4H, *H*-9), 2.95 (s, 2H, *H*-6), 4.42 (sex, $J = 5.0$ Hz, 2H, *H*-6), 5.81 (d, $J = 9.6$ Hz, 1H, *H*-4), 6.23 (d, $J = 9.6$ Hz, 1H, *H*-3); ^{13}C NMR (125 MHz, CDCl_3) δ 11.20 (*C*-10), 24.83 (*C*-7 or 9), 26.11 (*C*-7 or 9), 32.52 (*C*-6), 51.09 (*C*-8), 55.02 (*C*-5), 123.24 (*C*-4), 148.71 (*C*-3), 164.44 (*C*-2); IR (neat) 1659, 1608, 1476, 1430; MS (EI) m/z (rel intensity) 195 (M^+ , 9), 166 (100), 83 (23); HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{21}\text{NO}$ (M^+), 195.1623 found 195.1614.

5-Oxo-3,3-dimethyl-6-methylene-2,7,8,8a-hexahydro-5H-oxazolo[3,2-a]pyridine (2k).

(R_f = 0.13, hexane/EtOAc = 5/1). ^1H NMR (500 MHz, CDCl_3) δ 1.55 (d, J = 3.67 Hz, 6H, H -11), 1.57-1.68 (m, 1H, H -8), 2.27 (dq, J = 11.91, 3.52 Hz, 1H, H -8), 2.41-2.49 (m, 1H, H -7), 2.71 (dt, J = 16.50, 3.67 Hz, 1H, H -7), 3.62 (d, J = 8.71 Hz, 1H, H -2), 3.88 (d, J = 8.71 Hz, 1H, H -2), 4.82 (dd, J = 10.08, 3.21 Hz, 1H, H -9), 5.32 (s, 1H, H -10), 6.24 (t, J = 2.06 Hz, 1H, H -10); ^{13}C NMR (125 MHz, CDCl_3) δ 23.42 (C -11), 24.59 (C -11), 25.74 (C -7), 29.00 (C -8), 60.30 (C -3), 79.36 (C -2), 88.90 (C -9), 121.57 (C -10), 137.10 (C -6), 161.31 (C -5); IR (neat) 1663, 1616; MS (EI) m/z (rel intensity) 181 (M^+ , 74), 180 (49), 166 (100), 149 (28), 138 (30), 77 (24), 54 (25); HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ (M^+) 181.1103, found 181.1102.

(3S,8aR)-5-Oxo-3-isopropyl-6-methylene-2,3,7,8,8a-hexahydro-5H-oxazolo[3,2-a]pyridine (2l).

(R_f = 0.33, hexane/EtOAc = 2/1). ^1H NMR (500 MHz, CDCl_3) δ 0.90 (d, J = 6.9 Hz, 3H, H -12 or 13), 0.92 (d, J = 6.9 Hz, 3H, H -12 or 13), 1.48-1.56 (m, 1H, H -8), 2.16-2.32 (m, 2H, H -8, 11), 2.40-2.49 (m, 1H, H -7), 2.65 (dt, J = 15.6, 3.7 Hz, 1H, H -7), 3.73 (dd, J = 8.7, 6.9 Hz, 1H, H -2), 4.07 (t-like, J = 8.3 Hz, 1H, H -2), 4.25 (q, J = 6.9 Hz, 1H, H -3), 4.84 (dd, J = 9.6, 4.6 Hz, 1H, H -9), 5.36 (s, 1H, H -10), 6.24 (s, 1H, H -10); ^{13}C NMR (125 MHz, CDCl_3) δ 17.00 (C -12 or 13), 19.03 (C -12 or 13), 25.44 (C -4), 28.78 (C -5 or 11), 29.76 (C -5 or 11), 59.63 (C -3), 66.87 (C -2), 88.06 (C -6), 121.59 (C -10), 136.73 (C -6), 162.60 (C -5); IR (neat) 1664, 1620, 1445; MS (EI) m/z (rel intensity) 195 (M^+ , 23), 152 (100), 124 (54); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{17}\text{NO}$ (M^+) 195.1259, found 195.1260.

(3S,8aS)-5-Oxo-3-isopropyl-6-methylene-2,3,7,8,8a-hexahydro-5H-oxazolo[3,2-a]pyridine (2l).

(R_f = 0.33, hexane/EtOAc = 2/1). ^1H NMR (500 MHz, CDCl_3) δ 0.76 (d, J = 6.9 Hz, 3H, H -12 or 13), 0.91 (d, J = 6.9 Hz, 3H, H -12 or 13), 1.54-1.73 (m, 1H, H -11), 2.24-2.27 (m, 1H, H -8), 2.46-2.52 (m, 1H, H -8), 2.46-2.52 (m, 1H, H -7), 2.75-2.86 (m, 1H, H -7), 3.80 (dd, J = 9.4, 7.1 Hz, 1H, H -2), 4.00-4.07 (m, 1H, H -2), 4.07-4.10 (m, 1H, H -3), 4.75 (dd, J = 10.3, 3.0 Hz, 1H, H -9), 5.37 (s, 1H, H -10), 6.27 (s, 1H, H -10); IR (neat) 1655, 1459; MS (EI) m/z (rel intensity) 195 (M^+ , 29), 152 (100), 124 (57); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{17}\text{NO}$ (M^+) 195.1259, found 195.1250.

Synthesis of the precursor of (-)-coniine.

A magnetic stirring bar, AIBN (28.8 mg, 0.18 mmol), benzene (20 mL), oxazoline **1m** (173.1 mg, 0.50 mmol) and (TMS)₃SiH (189 mg, 0.77 mmol) were placed in a 50 mL stainless steel autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 71 atm of CO and then heated 90 °C for 10 h. Excess CO was discharged at room temperature. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane/EtOAc = 1/1 to EtOAc) to give cis isomer **2m** (53.4 mg, 49%). Trans isomer was further purified by preparative HPLC (17.4 mg, 16%).

(3R,8aR)-5-Oxo-3-phenyl-2,3,7,8,8a-hexahydro-5H-oxazolo[3,2-a]pyridine (**2m**).

(*R_f* = 0.17, EtOAc). ¹H NMR (500 MHz, CDCl₃) δ 1.72-1.80 (m, 2H, *H*-7 or 8) 2.01-2.06 (m, 1H, *H*-7 or 8), 2.24-2.31 (m, 1H, *H*-6 or 7 or 8), 2.35-2.41 (m, 2H, *H*-6, 7 or 8), 4.01 (dd, *J* = 8.9, 1.1 Hz, 1H, *H*-2 or 3), 4.15 (dd, *J* = 9.2, 6.9 Hz, 1H, *H*-2 or 3), 4.85 (dd, *J* = 9.4, 3.4 Hz, 1H, *H*-2 or 3), 4.92 (d, *J* = 6.9 Hz, 1H, *H*-9), 7.22-7.36 (m, 5H, *H*-Ph); ¹³C NMR (100 MHz, CDCl₃) δ 17.78 (*C*-7), 28.20 (*C*-8), 30.99 (*C*-6), 58.74 (*C*-3), 73.78 (*C*-2), 88.86 (*C*-9), 126.32 (*C*-11), 127.45 (*C*-13), 128.50 (*C*-12), 141.47 (*C*-10), 167.31 (*C*-2); This product is a known compound and was identified by NMR with comparison of literature data (Amat, M. *et al. J. Org. Chem.* **2000**, 65, 3074.).

(3R,8aS)-5-Oxo-3-phenyl-2,3,7,8,8a-hexahydro-5H-oxazolo[3,2-a]pyridine (**2m**).

(*R_f* = 0.1, hexane/EtOAc = 1/2). ¹H NMR (500 MHz, CDCl₃) δ 1.51-1.60 (m, 1H, *H*-7 or 8), 1.73-1.83 (m, 1H, *H*-7 or 8), 1.95-2.01 (m, 1H, *H*-7 or 8), 2.31-2.40 (m, 2H, *H*-6, 7 or 8), 2.53 (dd, *J* = 17.9, 6.0 Hz, 1H, *H*-6), 3.77 (dd, *J* = 9.2, 7.8 Hz, 1H, *H*-2 or 3), 4.48-4.51 (m, 1H, *H*-2 or 3), 5.03 (dd, *J* = 9.2, 4.6 Hz, 1H, *H*-2 or 3), 5.28 (t, *J* = 7.8 Hz, 1H, *H*-9), 7.25-7.36 (m, 5H, *H*-Ph); ¹³C NMR (100 MHz, CDCl₃) δ 17.16 (*C*-7), 28.48 (*C*-8), 31.38 (*C*-6), 58.08 (*C*-3), 72.45 (*C*-2), 88.67 (*C*-9), 126.09 (*C*-11), 127.59 (*C*-13), 128.80 (*C*-12), 139.62 (*C*-10), 168.87 (*C*-2) This product is a known compound and was identified by NMR with comparison of literature data (Amat, M. *et al. J. Org. Chem.* **2000**, 65, 3074.).

Computational Chemistry

All density functional (DFT) calculations were carried out on a DACS XJ-3000 computer using the Gaussian 98 program.¹ Geometry optimizations were performed using standard gradient techniques² at the BHandHLYP level of theory. All calculations were performed using standard basis sets. BHandHLYP/cc-pVDZ Gaussian Archive entries and imaginary frequencies for the optimized structures in this study and BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ calculated single-point energies are listed below.

Figure S1. Reaction profile of 5-exo and 6-endo cyclization of 2-methylene-6-aza-5-hexenoyl radical. Energies (in kJ/mol) are calculated on the BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ.

Transition state involved in the 6-endo cyclization

BHandHLYP/cc-pVDZ

1\1\GINC-G98\FTSUBH\HandHLYP\CC-pVDZ\C6H8N1O1(2)\MATSU\04-Aug-2004\1\1\#BHANDHLYP/CC-PVDZ SCF =DIRECT FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(TS,NOEIGENTEST,Z-MATRIX,READFC,MAX CYCLE=100) NOSYMM\TS for 6-endo cyclization\0,2\C\N,1,r1\C,2,r2,1,a1\C,3,r3,2,a2,1,d1,0\C,4,r4,3,a3,2,d2,0\C,1,r5,2,a4,3,d3,0\O,1,r6,2,a5,3,d4,0\H,2,r7,3,a6,4,d5,0\H,3,r8,2,a7,1,d6,0\H,4,r10,3,a9,2,d8,0\H,4,r11,3,a10,2,d9,0\H,5,r12,4,a11,3,d10,0\H,5,r13,4,a12,3,d11,0\C,6,r14,5,a13,4,d12,0\H,14,r15,6,a14,1,d13,0\H,14,r16,6,a15,1,d14,0\vr1=1.97882429vr2=1.26149624vr3=1.48926628vr4=1.52301771vr5=1.3703798vr6=1.17943117vr7=1.01436957vr8=1.09400737vr10=1.09524173vr11=1.09917451vr12=1.09686563vr13=1.09140959vr14=1.40269171vr15=1.08186648vr16=1.0824963\vr17=1.2205211881vr18=1.20420266vr19=1.1136213781vr20=1.0250267173vr21=1.0584412235vr22=1.1708467117vr23=1.2228658887vr24=1.0917873105vr25=1.0745743995vr26=1.0805284133vr27=1.0869058759vr28=1.2011712423vr29=1.2134583792vr30=1.1998129928vr31=23.16482539vd1=17.52848836vd2=-29.1693359vd3=-211.21004475vd4=176.68240468vd5=204.63123962vd6=140.54122141vd7=-104.56647447vd8=66.56305262vd9=181.69080994vd10=-131.83215814vd11=-0.08018392vd12=179.62172293\Version=x86-Linux-G98RevA.9\HF=-363.1274887\S2=0.78771\S2-1=0.\S2A=0.75033\RMSD=9.170e-09\RMSF=1.034e-05\Dipole=0.8298419,0.1159162,2.021128\PG=C01 [X(C6H8N1O1)]\@\

Imaginary frequency: -287.4418 cm⁻¹.

BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ

HF=-363.1514607

Transition state involved in the 5-exo cyclization

BHandHLYP/cc-pVDZ

1\1\GINC-G98\FTSUBH\HandHLYP\CC-pVDZ\C6H8N1O1(2)\MATSU\04-Aug-2004\1\1\#BHANDHLYP/CC-PVDZ SCF =DIRECT FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(TS,NOEIGENTEST,Z-MATRIX,READFC,MAX CYCLE=100) NOSYMM\TS for 5-exo cyclization\0,2\O\C,1,r2\C,2,r3,1,a2\C,3,r4,2,a3,1,d2,0\C,2,r5,3,a4,4,d3,0\C,3,r6,2,a5,1,d4,0\H,4,r7,3,a6,2,d5,0\H,4,r8,3,a7,2,d6,0\C,5,r9,2,a8,3,d7,0\N,5,r10,2,a9,1,d8,0\H,6,r11,3,a10,2,d9,0\H,6,r12,3,a11,2,d10,0\H,9,r13,5,a12,2,d11,0\H,9,r14,5,a13,2,d12,0\H,5,r15,2,a14,1,d13,0\H,10,r16,5,a15,2,d14,0\vr2=1.17200165vr3=1.48555496vr4=1.32885288vr5=2.15634876vr6=1.49724536vr7=1.08459367vr8=1.08576552vr9=1.51469248vr10=1.30089783vr11=1.09168634vr12=1.09738928vr13=1.09501398vr14=1.09603986vr15=1.09569512vr16=1.02114858vr17=1.13144449002vr18=1.1942682209vr19=98.88546252vr20=112.10575635vr21=120.19728616vr22=121.76355403vr23=90.97756483vr24=108.55191618vr25=111.53212626vr26=109.15689121vr27=109.12561244vr28=108.97573494vr29=90.12970196vr30=109.44405919vd1=7.61679803vd2=-169.22500056vd3=-174.6994397vd4=-2.01437046vd5=177.82518814vd6=16.75857567vd7=-31.68971986vd8=-156.090153vd9=86.00912363vd10=-157.63919679vd11=-85.51506156vd12=85.27255209vd13=-89.18042924\Version=x86-Linux-G98RevA.9\HF=-363.114503\S2=0.812741\S2-1=0.\S2A=0.750612\RMSD=8.137e-09\RMSF=3.248e-05\Dipole=1.3974668,0.070167,1.3132957\PG=C01 [X(C6H8N1O1)]\@\

Imaginary frequency: -383.1360 cm⁻¹.

BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ

HF=-363.1391292

2-Methylene-5-aza-5-hexenyl radical

BHandHLYP/cc-pVDZ

1\1\GINC-G98\POpt\UBH\HandHLYP\CC-pVDZ\C6H8N1O1(2)\MATSU\04-Aug-2004\1\1\#BHANDHLYP/CC-PVDZ SCF =DIRECT FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOSYMM\acyl radical\0,2\C\X,1,1.\O,1,r1,2,90.\C,1,r2,2,a1,3,d1,0\C,4,r3,1,a2,3,d2,0\C,4,r4,1,a3,3,d3,0\C,6,r5,4,a4,1,d4,0\C,7,r6,6,a5,4,d5,0\N,8,r7,7,a6,6,d6,0\H,9,r8,8,a7,7,d7,0\H,5,r9,4,a8,1,d8,0\H,5,r10,4,a9,1,d9,0\H,6,r11,4,a10,1,d10,0\H,6,r12,4,a11,1,d11,0\H,7,r13,6,a12,4,d12,0\H,7,r14,6,a13,4,d13,0\H,8,r15,7,a14,6,d14,0\vr1=1.17497241vr2=1.495388vr3=1.33087243vr4=1.49813274vr5=1.53189597vr6=1.49646858vr7=1.26051555vr8=1.01820478vr9=1.08414637vr10=1.08591666vr11=1.09437239vr12=1.09580212vr13=1.09281309vr14=1.09709962vr15=1.10042025vr16=39.17331708vr17=117.79042773vr18=116.73910276vr19=112.57838981vr20=112.08008224vr21=121.56699612vr22=110.54608986vr23=120.43592986vr24=121.51811854vr25=109.15730962vr26=108.98997774vr27=110.56818607vr28=108.90692489vr29=115.33392017vd1=171.77418693vd2=-4.9081405vd3=175.9191716vd4=-65.88867675vd5=180.39161648vd6=241.22339868vd7=179.72351888vd8=1.06232786vd9=

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BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ
HF=-363.1567105

2-Aza-4-methylene-3-oxocyclohexyl radical (product of the 6-endo cyclization)

BHandHLYP/cc-pVDZ

1\\GINC-G98\\FOpt\\UBHandHLYP\\CC-pVDZ\\C6H8N1O1(2)\\MATSU\\26-Aug-2004\\I\\#BHANDHLYP\\CC-PVDZ SCF=\\DIRECT\\FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOS YMM\\product of 6-endo cyclization\\0,2\\C\\N,1,r1\\C,2,r2,1,a1\\C,3,r3,2,a2,1,d1,0\\C,4,r4,3,a3,2,d2,0\\C,1,r5,2,a4,3,d3,0\\O,1,r6,2,a5,3,d4,0\\H,2,r7,3,a6,4,d5,0\\H,3,r8,2,a7,1,d6,0\\H,4,r10,3,a9,2,d8,0\\H,4,r11,3,a10,2,d9,0\\H,5,r12,4,a11,3,d10,0\\H,5,r13,4,a12,3,d11,0\\C,6,r14,5,a13,4,d12,0\\H,14,r15,6,a14,1,d13,0\\H,14,r16,6,a15,1,d14,0\\r1=1.37010576\\r2=1.38350123\\r3=1.485449\\r4=1.52648282\\r5=1.49474885\\r6=1.21184022\\r7=1.00659195\\r8=1.08197211\\r10=1.0931298\\r11=1.10334221\\r12=1.09745737\\r13=1.09232953\\r14=1.32799684\\r15=1.08346818\\r16=1.08498895\\a1=127.11464757\\a2=117.2669017\\a3=109.83043476\\a4=115.3901974\\a5=120.65518891\\a6=119.37292381\\a7=115.7949156\\a9=109.90942246\\a10=110.57497743\\a11=108.43949898\\a12=111.21475702\\a13=124.6922384\\a14=119.89246535\\a15=121.42174472\\d1=-11.98693557\\d2=39.93069688\\d3=-2.82647069\\d4=-182.99831036\\d5=168.11728275\\d6=190.81095775\\d8=162.16424751\\d9=-80.31957722\\d10=66.34810796\\d11=183.95064073\\d12=-139.57987246\\d13=0.79464027\\d14=180.44315459\\Version=x86-Linux-G98RevA.9\\HF=-363.1888631\\S2=0.761323\\S2-1=0.\\S2A=0.750073\\RMSD=9.478e-09\\RMSF=8.562e-05\\Dipole=0.99509,-0.0477085,0.8475058\\PG=C01 [X(C6H8N1O1)]\\@

BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ
HF=-363.2116084

3-Methylene-2-oxocyclopentylaminyl radical (product of the 5-exo cyclization)

BHandHLYP/cc-pVDZ

1\\GINC-G98\\FOpt\\UBHandHLYP\\CC-pVDZ\\C6H8N1O1(2)\\MATSU\\26-Aug-2004\\I\\#BHANDHLYP\\CC-PVDZ SCF=\\DIRECT\\FREQ=NORAMAN GEOM=CHECK GUESS=READ OPT=(Z-MATRIX,READFC,MAXCYCLE=100) NOS YMM\\product of 5-exo cyclization\\0,2\\O\\C,1,r2\\C,2,r3,1,a2\\C,3,r4,2,a3,1,d2,0\\C,2,r5,3,a4,4,d3,0\\C,3,r6,2,a5,1,d4,0\\H,4,r7,3,a6,2,d5,0\\H,4,r8,3,a7,2,d6,0\\C,5,r9,2,a8,3,d7,0\\N,5,r10,2,a9,1,d8,0\\H,6,r11,3,a10,2,d9,0\\H,6,r12,3,a11,2,d10,0\\H,9,r13,5,a12,2,d11,0\\H,9,r14,5,a13,2,d12,0\\H,5,r15,2,a14,1,d13,0\\H,10,r16,5,a15,2,d14,0\\r2=1.19971586\\r3=1.48933584\\r4=1.32682139\\r5=1.52962744\\r6=1.50674476\\r7=1.08499349\\r8=1.08495625\\r9=1.52828811\\r10=1.42539441\\r11=1.09141743\\r12=1.09697891\\r13=1.09056821\\r14=1.09451387\\r15=1.10772633\\r16=1.02619384\\a2=127.6632467\\a3=121.80899895\\a4=107.6367376\\a5=108.09233062\\a6=119.38212964\\a7=122.35321506\\a8=103.87517873\\a9=115.07594247\\a10=112.88836655\\a11=109.62841842\\a12=112.87521349\\a13=108.21633894\\a14=104.53380157\\a15=105.51611752\\d2=1.53956075\\d3=-177.00213819\\d4=-180.62290135\\d5=-1.62774352\\d6=178.09823293\\d7=19.95474129\\d8=-30.95133204\\d9=-144.32921595\\d10=96.34259576\\d11=-156.05918035\\d12=84.80023957\\d13=87.06401517\\d14=35.56600321\\Version=x86-Linux-G98RevA.9\\HF=-363.1526232\\S2=0.754949\\S2-1=0.\\S2A=0.750018\\RMSD=4.889e-09\\RMSF=1.133e-05\\Dipole=0.670358,-0.3865409,0.8966926\\PG=C01 [X(C6H8N1O1)]\\@

BHandHLYP/aug-cc-pVDZ//BHandHLYP/cc-pVDZ
HF=-363.1766876

References

- 1 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.;

- Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.9; Gaussian, Inc., Pittsburgh PA, 1998.
- 2 Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, P. A. *Ab Initio Molecular Orbital Theory* Wiley: New York, 1986.