A Synthesis of (-)-Sedinine by Allene Cyclisation and Iminium Ion Chemistry: Experimental Section

Roderick W. Bates and Yongna Lu

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371

roderick@ntu.edu.sg

General Methods

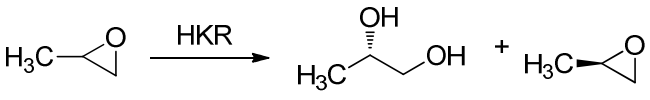
All reactions requiring anhydrous conditions were carried out under a nitrogen atmosphere using oven-dried glassware (120 °C), which was cooled under vacuum. Anhydrous tetrahydrofuran was distilled from sodium metal and benzophenone under nitrogen. Anhydrous dichloromethane and acetonitrile were dried by distillation from CaH_2 immediately prior to use under nitrogen. Anhydrous methanol was distilled from activated magnesium under nitrogen. All other solvents and reagents were used as received.

^{1}H NMR spectra were recorded at 300, 400 or 500 MHz in $CDCl_3$ solutions. ^{13}C NMR spectra were recorded at the corresponding frequency on the same instruments at 75, 100 or 125 MHz. Chemical shifts are recorded in ppm and coupling constants *J* are recorded in Hz.

Melting points are uncorrected. Optical rotations are given with units of 10^{-1}degcm^{2}g^{-1}. The rotations were measured at a wavelength of 589 nm.

Enantiomeric excess was determined by chiral HPLC analysis, using Chiralcel OD-H column or OJ-H columns, eluting with IPA/hexane.

(*S*)-Propane-1,2-diol[1]

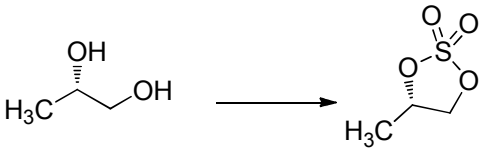


Acetic acid (0.57 mmol, 33 μL) was added to a solution of (1*R*,2*R*)-(-)-1,2-cyclohexanediamino-*N*,*N*'-bis(3,5-di-*t*-butylsalicylidene)cobalt(II) (0.2 mol%, 0.17 g) in toluene (1.5 mL) at room temperature. The reaction mixture

was stirred open to the air for an hour at room temperature. The color changed from red to dark-brown. After concentration *in vacuo*, the catalyst was obtained as a brown solid. Racemic propylene oxide (142.7 mmol, 10.0 mL) was added in one portion at room temperature. The reaction mixture was cooled to 0 ºC and water (78.5 mmol, 1.4 mL) was added dropwise over 15 min. The reaction mixture was then warmed to room temperature and was stirred for a further 14 h. (*R*)-Propylene oxide was removed by evaporation and the residue was distilled under reduced pressure, giving (*S*)-propylene glycol (4.4 g, 41%) as a colorless oil.

$[\alpha]_D^{22.3}$ +23.9 (*c* 7.5, H_2O) [ref. 2 $[\alpha]_D^{23}$ +20.7 (*c* 7.5, H_2O)]

(*S*)-4-methyl-1,3,2-dioxathiolane 2,2-dioxide (4)[3]



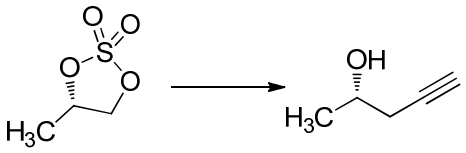
Thionyl chloride (11.5 mL, 0.16 mol) was added dropwise to a solution of (*S*)-propylene glycol (10 g, 0.13 mol) in CH_2Cl_2 (80 mL) at room temperature. After completion of addition, the reaction mixture was heated at reflux for 1 h and then cooled to 0 ºC. Acetonitrile (50 mL), water (80 mL), ruthenium trichloride trihydrate (27 mg, 0.13 mmol) and sodium periodate (42 g, 0.2 mol) were added sequentially. The reaction mixture was warmed to room temperature and stirred for a further 1 h. After extraction with Et_2O (3 x 20 mL), the combined organic layers were washed with sat. $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give the crude product as a yellowish oil. The crude product was purified by distillation (80 ºC (oil bath), 0.5 mmHg) to give cyclic sulfate **4** (16.3 g, 90%) as a

colorless oil.

$[\alpha]_D^{24.5}$ +20.0 (*c* 3.7, CH_2Cl_2) [ref 3 $[\alpha]_D^{23}$ +16.5 (*c* 0.16, CH_2Cl_2)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18- 5.07 (1H, m), 4.73 (1H, dd, *J* = 8.5, 5.8 Hz), 4.31 (1H, t, *J* = 8.5 Hz), 1.61 (3H, d, *J* = 6.3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.6, 74.0, 17.7.

All data are consistent with those reported.[3]

(*S*)-Pent-4-yn-2-ol (5)[3,4]



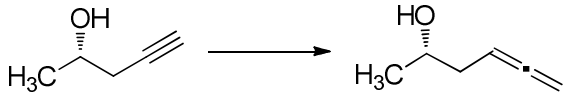
Acetylene gas was bubbled through THF (130 mL) at -78 ºC for 0.5 h. *n*-BuLi in hexane (1.6 M, 87.0 mmol) was added dropwise over 0.5 h at -78 ºC under nitrogen. After addition, the clear solution was stirred for 1 h at -78 ºC. Then, cyclic sulphate **4** (10 g, 72.5 mmol) in THF (30 ml) was added *via* cannula. The reaction mixture was stirred at -78 ºC for 1.5 h, then allowed to warm to room temperature and stirred for a further 1 h. Concentrated sulfuric acid (1.2 mL) and water (1.2 mL) were added and the cloudy, opaque mixture was stirred for 0.5 h. Powdered $NaHCO_3$ and water (2 mL) were added to neutralize the acidic solution. The reaction mixture was dried over anhydrous Na_2SO_4 and filtered through celite, washing with Et_2O (3 x 20 mL). Removal of the solvent by simple distillation at atmospheric pressure and subsequent distillation under reduced pressure [*ca* 45 ºC (oil bath), 6 mmHg] gave (*S*)-pent-4-yn-2-ol **5** (4.80 g, 79%) as a colorless oil.

$[\alpha]_D^{23}$ +17.9 (*c* 1.2, $CHCl_3$) [ref. 4 $[\alpha]_D^{23}$ +17.5 (*c* 0.16, $CHCl_3$)]; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 3.98 (1H, qt, J = 6.2, 5.4), 2.41 (1H, ddd, J = 16.6, 5.0, 2.6 Hz), 2.32 (1H, ddd, J = 16.6, 6.6, 2.6 Hz), 2.07 (1H, t, J = 2.6 Hz), 1.27 (3H, d, J = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.8, 70.8, 66.2, 28.9, 22.2.

All data are consistent with these reported.[3,4]

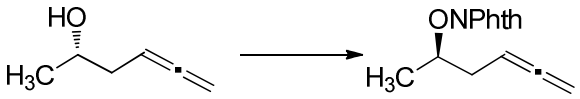
(*S*)-Hexa-4,5-dien-2-ol (6)



Diisopropylamine (13.1 mL, 93.3 mmol) was added to a suspension of (*S*)-pent-4-yn-2-ol **5** (3.92 g ,46.7 mmol), paraformaldehyde (2.80 g, 93.3 mmol) and copper (I) bromide (2.20 g, 15.4 mmol) in 1,4-dioxane (80 mL). The reaction mixture was heated at reflux overnight and then cooled to room temperature. Air was bubbled through the reaction mixture for 0.5 h and the reaction mixture was then filtered through celite, washing with Et_2O (3 x 10 mL). The combined filtrates were concentrated *in vacuo* to give the crude product as a brown oil. The crude product was purified by distillation under reduced pressure [50 ºC (oil bath), 1 mmHg] to give (*S*)-hexa-4,5-dien-2-ol **6** (3.22 g, 68%) as a colorless oil.

$[\alpha]_D^{23}$ +9.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.12 (1H, tt, J = 7.0, 7.0 Hz), 4.72 (2H, dt, J = 7.0, 2.8 Hz), 3.9-3.84 (1H, m), 2.23-2.08 (2H, m), 1.68 (1H, brd) 1.17 (3H, d, J =6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 86.2, 74.8, 67.1, 38.2, 22.6; IR (neat) 2970, 2909, 1956 cm^{-1}; HRMS *m/z calcd*. for $C_6H_{10}ONa$ $[M+Na]^+$ 121.0627, found 121.0629.

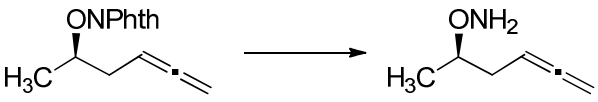
(*R*)-2-(Hexa-4,5-dien-2-yloxy)isoindoline-1,3-dione (7)



A solution of diisopropyl azodicarboxylate (4.6 mL, 23.3 mmol) in THF (10 mL) was added to a solution of (*S*)-hexa-4,5-dien-2-ol **6** (1.9 g, 19.4 mmol), triphenylphosphine (6.1 g, 23.3 mmol) and *N*-hydroxyphthalimide (3.8 g, 23.3 mmol) in THF (60 mL) dropwise at -20 ºC. The reaction mixture was stirred at -20 ºC for 3 h. After evaporation of the solvent, the residue was purified by flash chromatography (EtOAc : Hexane = 1 : 9) to give the *N*-phthaloyl hydroxylamine **7** (4.4 g, 94%) as a colorless solid.

$[\alpha]_D^{23}$ +18.5 (*c* 1.1, $CHCl_3$); m.p.: 60-61 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.82 (2H, m), 7.76-7.74 (2H, m), 5.22 (1H, tt, *J* = 7.0, 7.0 Hz), 4.68 (2H, dt, *J* = 7.0, 2.8 Hz), 4.44 (1H, qt, *J* = 6.2, 6.2 Hz), 2.23-2.08 (2H, m), 2.55-2.32 (2H, m), 1.39 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 164.2 (2C), 134.4 (2C), 128.9 (2C), 123.5 (2C), 85.2, 83.7, 75.0, 33.9, 18.3; IR (neat) 1953, 1729 cm^{-1}; MS *m/z* 244 $[M+H]^+$; HRMS *m/z* calcd. for $C_{14}H_{14}NO_3$ $[M+H]^+$ 244.0975, found 244.0974.

(*R*)-O-(Hexa-4,5-dien-2-yl)hydroxylamine (8)

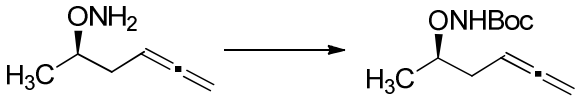


Hydrazine monohydrate (2.0 mL, 41.2 mmol) was added to a solution of the *N*-phthaloyl hydroxylamine **7** (2.5 g, 10.3 mmol) in dichloromethane (30 mL) at room temperature. The reaction mixture was stirred at room temperature for 0.5 h and then

filtered through celite, washing with Et_2O (3 x 10 mL). The filtrate was concentrated *in vacuo* to give the free hydroxylamine **8** (1.1 g, 95%) as a colorless oil, which was used without further purification.

$[\alpha]_D^{23}$ +10.7 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (1H, tt, *J* = 7.0, 7.0 Hz), 4.67 (2H, dt, *J* = 7.0, 2.8 Hz), 3.73 (1H, qt, *J* = 6.2, 6.2 Hz), 2.35-2.11 (2H, m), 1.17 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 86.1, 79.3, 74.4, 33.8, 18.3; IR (neat) 3317, 1956 cm^{-1}; HRMS *m/z* calcd. for $C_6H_{12}NO$ $[M+H]^+$ 114.0919, found 114.0919.

***N-tert*-Butoxycarbonyl (*R*)-hexa-4,5-dien-2-hydroxylamine (9)**

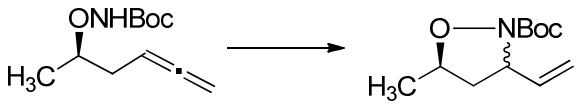


Powered sodium hydroxide (1.02 g, 25.4 mmol) was added to a solution of the free hydroxylamine **8** (1.1 g, 10.6 mmol) and di-*tert*-butyl dicarbonate (2.68 mL, 11.7 mmol) in dichloromethane-water (25 mL-25 mL) at room temperature. The reaction mixture was stirred at room temperature overnight and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product as a light yellow oil. Purification by flash chromatography (EtOAc : Hexane = 1 : 9) provided *N*-protected hydroxylamine **9** as a colorless oil (1.87 g, 90%).

$[\alpha]_D^{24.1}$ +40.8 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (1H, brs), 5.13 (1H, tt, *J* = 7.0, 7.0), 4.68 (2H, dt, *J* = 7.0, 2.8 Hz), 3.95 (1H, qt, *J* = 6.2, 6.2 Hz), 2.39-2.33 (1H, m), 2.23-2.18 (1H, m), 1.48 (9H, s), 1.23 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (75

MHz, $CDCl_3$) δ 209.4, 157.1, 85.7, 84.7, 81.6, 81.0, 74.6, 33.6, 28.2 (3C), 18.0; IR (neat) 3319, 2980, 1957, 1716 cm^{-1}; MS *m/z* 236 $[M+Na]^+$; HRMS *m/z* calcd. for $C_{11}H_{19}O_3NNa$ $[M+Na]^+$ 236.1263, found 236.1271.

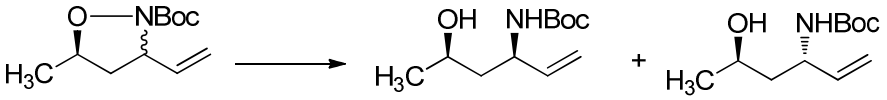
(5*R*)-*tert*-Butyl 5-methyl-3-vinylisoxazolidine-2-carboxylate (10)



$AgBF_4$ (91 mg, 0.47 mmol) was added to a solution of the *N*-protected hydroxylamine **9** (1.0 g, 4.7 mmol) in dried CH_2Cl_2 (25 mL) at room temperature. The reaction mixture was stirred at room temperature in the absence of light for 8 h and was then filtered through celite, washing with Et_2O (3 x 10 mL). The combined filtrates were washed with sat.$NaHCO_3$ solution and brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was then evaporated *in vacuo* to give the residue which was purified by flash chromatography (EtOAc : Hexane = 1 : 9) to afford an inseparable mixture of *trans*-**10** and *cis*-**10** (*trans*-**10**: *cis*-**10** = 1:13, 0.90 g, 90%) as a colorless oil.

cis-**10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 (1H, ddd, *J* = 17.0, 10.1, 6.9 Hz), 5.17 (1H, d, *J* = 17.0 Hz), 5.17 (1H, d, *J* = 10.1 Hz), 4.52 (1H, td, *J* = 7.2, 7.2 Hz), 3.95 (1H, ddq, *J* = 9.9, 6.2, 5.7 Hz), 2.51 (1H, ddd, *J* = 14.0, 8.3, 5.7 Hz), 1.60 (1H, ddd, *J* = 12.0, 9.9, 7.2 Hz), 1.45 (9H, s), 1.27 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 137.9, 115.1, 81.4, 76.9, 62.4, 42.7, 34.4, 27.9 (3C), 17.4; IR (neat) 2979, 2936, 1701cm^{-1}; MS *m/z* 236 $[M+Na]^+$, 114 (42%); HRMS *m/z* calcd. for $C_{11}H_{19}O_3NNa$ $[M+Na]^+$ 236.1263, found 236.1252.

***tert*-Butyl ((3*R*, 5*R*)-5-hydroxyhex-1-en-3-yl)carbamate (*syn*-11a) and *tert*-butyl ((3S,5R)-5-hydroxyhex-1-en-3-yl)carbamate (*anti*-11b)**



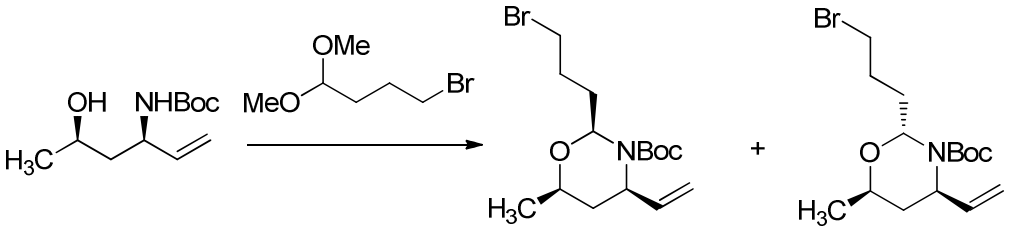
$Mo(CO)_6$ (2.0 g, 7.51 mmol) was added to a solution of isoxazolidines **10** (1.0 g, 4.69 mmol) in CH_3CN-H_2O (49 mL-7 mL). The mixture was stirred at room temperature for 15 min and $NaBH_4$ (90 mg, 2.38 mmol) was added in one portion. The reaction mixture was heated at reflux overnight and cooled to room temperature. The suspension was filtered through celite, washing with Et_2O (3 x 10 mL). The filtrate was then concentrated *in vacuo* to afford the crude product, which was purified by flash chromatography (EtOAc : Hexane = 1 : 9) to give *syn*-**11a** (0.79 g, 78%) and *anti*-**4-11b** (60 mg, 6%).

syn-**4-11a**: $[\alpha]_D^{22}$ -21.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (1H, ddd, *J* = 17.0, 10.5, 6.2 Hz), 5.19 (1H, d, *J* = 17.0), 5.11 (1H, d, *J* = 10.5 Hz), 4.68 (1H, brs), 4.23 (1H, brs), 3.93 (1H, qt, *J* = 6.2, 6.2 Hz), 1.64 (2H, dd, *J* = 6.2, 6.2 Hz), 1.39 (9H, s), 1.23 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 138.8, 114.7, 79.6, 65.7,51.2, 44.3, 28.3 (3C), 23.8; IR (neat) 3333, 2976, 2933, 1683 cm^{-1}; MS *m/z* 238 $[M+Na]^+$, 216 ($[M+1]^+$, 12%), 116 (38%); HRMS *m/z* calcd. for $C_{11}H_{21}NO_3Na$ $[M+Na]^+$ 238.1419, found 238.1412.

anti-**11b**: $[\alpha]_D^{21.4}$ -2.4 (*c* 1.36, $CHCl_3$); m. p.: 52-55 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (1H, ddd, *J* = 17.0, 11.0, 5.3 Hz), 5.19 (1H, d, *J* = 17.0), 5.12 (1H, d, *J* = 11.0

Hz), 4.69 (1H, brs), 4.40 (1H, brs), 3.84 (1H, qt, *J* = 6.2, 6.2 Hz), 1.68-1.61 (2H, m), 1.45 (9H, s), 1.21 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 138.4, 114.4, 79.9, 63.7, 49.4, 45.0, 28.3 (3C), 22.9; IR (neat) 3356, 2976, 2832, 1687 cm^{-1}; MS *m/z* 238 $[M+Na]^+$; HRMS *m/z* calcd. for $C_{11}H_{21}NO_3Na$ $[M+Na]^+$ 238.1419, found 238.1413.

(*2S,4R,6R*)-*tert*-Butyl2-(3-bromopropyl)-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (*cis*-12a) and (2*R*,4*R*,6*R*)-*tert*-butyl 2-(3-bromopropyl)-6-methyl-4- vinyl 1,3-oxazinane-3-carboxylate (*trans*-12b)



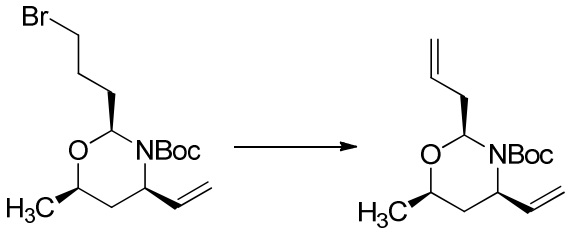
A mixture of protected amino alcohol *syn*-**11a** (0.4 g, 1.86 mmol), 4-bromo-1,1-dimethoxybutane (1.1 g, 5.58 mmol) and PPTS-resin (50% by weight) in anhydrous toluene was heated at 105 ºC for 3.0 h. The reaction mixture was cooled to room temperature and filtered through celite, washing with Et_2O (3 x 8 mL). The combined filtrates were removed *in vacuo* to give a pale yellow oil. The residue was purified by flash chromatography (EtOAc: Hexane = 5: 95) to afford *cis*-**12a** (0.39 g, 60 %) and *trans*-**12b** (65 mg, 10 %) both as colorless oils.

cis-**12a**: $[\alpha]_D^{22}$ -23.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (1H, ddd, *J* = 17.1, 10.3, 6.8 Hz), 5.16 (1H, dd, *J* = 6.2, 3.8 Hz); 5.12 (1H, d, *J* = 17.1 Hz), 5.06 (1H, *J* = 10.3 Hz), 4.67-4.62 (1H, m), 3.57 (1H, ddq, *J* = 10.3, 6.3, 6.3 Hz), 3.41-3.31 (2H, m), 2.10-2.07 (1H, m), 1.96-1.85 (3H, m), 1.75-1.65 (1H, m), 1.61-1.55 (1H, m), 1.47

(9H, s), 1.22 (3H, d, J = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 140.9, 114.7, 85.0, 80.3, 68.1, 50.8, 36.2, 36.0, 33.6, 28.8, 28.4 (3C), 22.1; IR (neat) 1689 cm^{-1}; MS *m/z* 370 $[M+Na]^+$, 348 ($[M+H]^+$, 60%), 248 (100%); HRMS *m/z* calcd. for $C_{15}H_{26}NO_3BrNa$ $[M+Na]^+$ 370.0994, found 370.0998.

tran-**12b**: $[\alpha]_D^{22}$ +2.8 (*c* 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.01 (1H, ddd, J = 17.1, 10.3, 6.2 Hz), 5.35 (1H, dd, J = 8.9, 3.5 Hz), 5.06 (1H, d, J = 17.1 Hz), 5.02 (1H, J = 10.3 Hz), 4.28 (1H, dt, J = 6.2, 6.2 Hz), 4.03 (1H, qdd, J = 6.3, 6.3, 6.3 Hz), 3.53-3.40 (2H, m), 2.10-1.92 (5H, m), 1.66-1.57 (1H, m), 1.43 (9H, s), 1.22 (3H, d, J = 6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 140.3, 113.0, 82.5, 80.2, 63.3, 52.7, 35.9, 33.5, 30.1, 28.9, 28.4 (3C), 22.8; IR (neat) 1687 cm^{-1}; MS *m/z* 370 $[M+Na]^+$, 348 ($[M+H]^+$, 60%), 248 (100%); HRMS *m/z* calcd. for $C_{15}H_{26}NO_3BrNa$ $[M+Na]^+$ 370.0994, found 370.1008.

(2*S*,4*R*,6*R*)-*tert*-Butyl 2-allyl-6-methyl-4-vinyl-1,3-oxazinane-3-carboxylate (13)

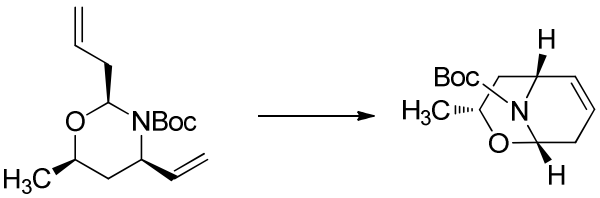


KO*t*-Bu (0.20 g, 1.77 mmol) was added to a solution of compound **12a** (0.41 g, 1.18 mmol) in THF (10 mL) at 0 ºC. The mixture was allowed to warm to room temperature and was stirred for 2.0 h further. The mixture was then quenched with saturated NH_4Cl solution and extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered through celite

and concentrated *in vacuo* to afford the crude product. The crude product was purified by flash chromatography (EtOAc : Hexane = 5 : 95) to provide diene **13** (0.28 g, 89%) as a colorless oil.

$[\alpha]_D^{22}$ -14.5 (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (1H, ddd, *J* = 17.3, 10.3, 6.7 Hz), 5.83 (1H, ddt, *J* = 17.2, 10.2, 7.1 Hz), 5.21 (1H, dd, *J* = 7.8, 4.3 Hz); 5.14-5.04 (4H, m), 4.75-4.71 (1H, m), 3.66 (1H, ddq, *J* = 10.3, 6.3, 6.3 Hz), 2.54-2.52 (1H, m), 2.46-2.41 (1H, m), 2.19 (1H, ddd, *J* = 13.8, 9.1, 4.7 Hz), 1.96-1.85 (3H, m), 1.75-1.65 (1H, m), 1.61-1.55 (1H, m), 1.46 (9H, s), 1.23 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 141.1, 134.0, 117.2, 114.5, 85.5, 80.2, 68.2, 50.8, 42.0, 36.4, 28.4 (3C), 22.1; IR (neat) 1694 cm^{-1}; MS *m/z* 267 $[M]^+$; HRMS *m/z* calcd. for $C_{15}H_{25}NO_3Na$ $[M+Na]^+$ 290.1732, found 290.1732.

(1*S*,3*R*,5*R*)-*tert*-Butyl 3-methyl-2-oxa-9-azabicyclo[3.3.1]non-6-ene-9-carboxylate (14)

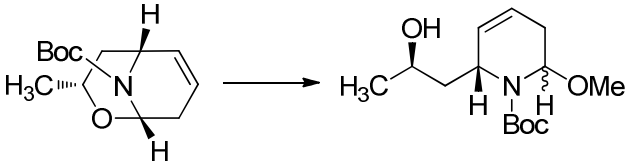


A solution of Grubbs I catalyst (43 mg, 5 mol%) in CH_2Cl_2 (5 mL) was added to a solution of diene **13** (0.28 g, 1.05 mmol) in CH_2Cl_2 at reflux (5 mL) in four portions via syringe over 0.5 h. The mixture was heated at reflux for an additional 3.5 h and then concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc : Hexane = 1 : 9) to provide bicyclic *N*,*O*-acetal **14** (0.21 g, 84%) as a colorless oil.

$[\alpha]_D^{20.7}$ -146.2 (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93-5.60 (3H, m),

4.53 (1H, ddd, *J* = 16.5, 9.6, 5.4 Hz), 3.58 (1H, ddq, *J* = 11.0, 5.5, 5.5 Hz), 2.35-2.07 (3H, m), 1.48 (9H, s), 1.41-1.30 (1H, m), 1.16 (d, *J* = 5.5 Hz) and 1.15 (d, *J* = 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 and 153.7, 130.4 and 129.8, 121.3 and 120.8, 80.1 and 80.0, 78.4, 63.2 and 62.9, 45.3 and 43.7, 36.6 and 35.8, 32.0 and 31.9, 28.2 and 28.1 (3C), 20.7 and 20.6; IR (neat) 1632 cm^{-1}; MS *m/z* 239 $[M]^+$, 207 (100%), 179 (95%); HRMS *m/z* calcd. for $C_{13}H_{21}NO_3Na$ $[M+Na]^+$ 262.1419, found 262.1429.

(2*R*)-*tert*-Butyl 5,6-dihydro-2-((*R*)-2-hydroxypropyl)-6-methoxypyridine-1(2H)-carboxylate (15)

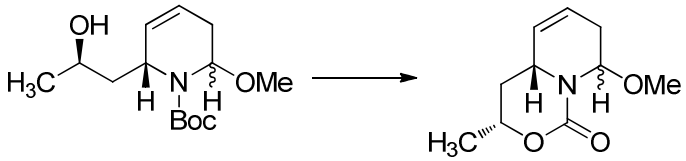


PPTS (79 mg, 0.31 mmol) was added to a solution of *N*,*O*-acetal **14** (0.15 g, 0.63 mmol) in MeOH (10 mL) at -10 ºC. The reaction mixture was warmed to 0 ºC and stirred at 0 ºC for 5 h. the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc : Hexane = 2 : 8) to afford semicyclic *N*,*O*-acetal **15** (0.15 g, 88%) as a colorless oil.

$[\alpha]_D^{20.3}$-185.5 (*c* 1.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78-5.38 (3H, m), 4.46 (1H, brs), 3.87 (1H, brs), 3.25 (3H, s), 2.37-2.28 (2H, m), 1.74 (1H, dd, *J* = 6.0, 6.0 Hz), 1.45 (9H, s), 1.15 (3H, d, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 126.7 and 126.1, 120.1 and 119.3, 80.7 and 80.3, 79.5, 65.5 and 64.7, 55.3 and 55.0, 48.8, 45.3, 30.4, 28.3 (3C), 24.0; IR (neat) 1660 cm^{-1}; MS *m/z* 294 $[M+Na]^+$; HRMS

m/z calcd. for $C_{14}H_{25}NO_4Na$ $[M+Na]^+$ 294.1681, found 294.1668.

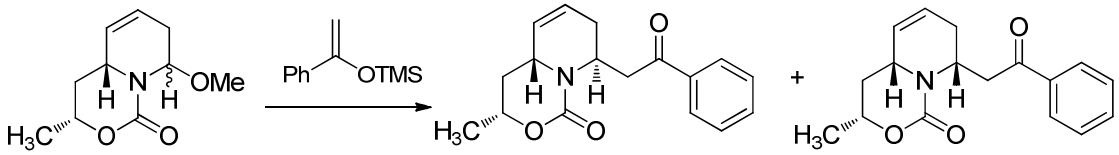
(3*R*,4*aR*)-4,4a,7,8-Tetrahydro-8-methoxy-3-methylpyrido[1,2-c][1,3]oxazin-1(3H) -one (16)



KO*t*-Bu (75 mg, 0.66 mmol) was added to a solution of compound **15** (0.18 g, 0.66 mmol) in THF (10 mL) at -10 ºC and was stirred at this temperature for 10 min. The mixture was then quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo* to afford the crude product. The crude product was purified by flash chromatography (EtOAc : Hexane = 1 : 1) to provide product **16** (65 mg, 50%) as a colorless oil.

$[\alpha]_D^{22}$ -41.1 (*c* 2.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02-5.98 (1H, m) 5.77 (1H, dt, *J* = 9.6, 2.4 Hz), 5.55 (1H, t, *J* = 3.3 Hz), 4.58 (1H, ddq, *J* = 11.2, 6.2, 6.2 Hz), 3.99-3.94 (1H, m), 3.39 (3H, s), 2.58 (1H, ddd, *J* = 16.2, 6.9, 2.3 Hz), 2.28-2.22 (1H, m), 2.14 (1H, ddd, *J* = 13.4, 2.3, 2.3 Hz), 1.73 (1H, aq.q, *J* = 12.0 Hz), 1.43 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 126.8, 125.2, 82.0, 75.5, 56.7, 49.7, 37.4, 29.4, 22.0; IR (neat) 1670 cm^{-1}; MS *m/z* 220 $[M+Na]^+$, 179 (100%); HRMS *m/z* calcd. for $C_{10}H_{15}NO_3Na$ $[M+Na]^+$ 220.0950, found 220.0944.

(3*R*,4a*R*,8*S*)-3-Methyl-8-(2-oxo-2-phenylethyl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (*trans*-17a) and **(3*R*,4a*R*,8*R*)-3-methyl-8-(2-oxo-2-phenylethyl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (*cis*-17b)**



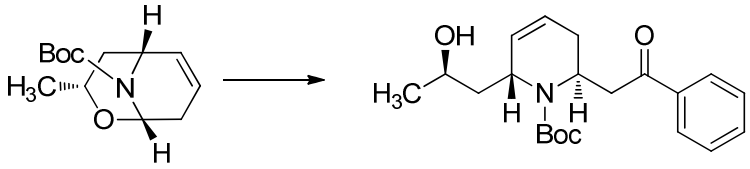
$SnCl_4$ (1 M in CH_2Cl_2, 36 μL, 0.036 mmol) was added to a cooled (-78 ºC) solution of *N*,*O*-acetal **16** (6 mg, 0.03 mmol) and (1-phenylvinyloxy)trimethylsilane (20 μL, 0.09 mmol) in CH_2Cl_2 (3 mL) *via* syringe. After stirring at -78 ºC for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution at this temperature and then allowed to warm to room temperature. The reaction mixture was then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo* to afford the crude product. The crude product was purified by flash chromatography (EtOAc : Hexane = 2 : 8) to provide *trans*-**17a** (3 mg, 34%) as a colorless oil and *cis*-**4-17b** (3 mg, 34%) as a colorless solid.

trans-**17a**: m.p.: 147-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 7.6 Hz), 7.56 (1H, t, J = 7.6 Hz), 7.46 (2H, t, J = 7.6 Hz), 5.83 (1H, dd, J = 10.1, 6.0 Hz), 5.59 (1H, d, J = 10.1 Hz), 5.32 (1H, dt, J = 6.8, 6.8 Hz), 4.68 (1H, app. d, J = 11.8 Hz), 4.37 (1H, qt, J = 6.2, 6.2 Hz), 3.27 (1H, dd, J = 14.8, 8.4 Hz), 3.19 (1H, dd, J = 14.8, 6.6 Hz), 2.56 (1H, dd, J = 6.2, 2.3 Hz), 2.07-2.04 (2H, m), 1.60-1.51 (1H, m), 1.36 (3H, d, J = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 152.9, 136.6, 133.3, 128.7 (2C), 128.2 (2C), 125.9, 124.0, 71.9, 48.8, 45.5, 40.3, 35.9, 28.2, 21.0; IR (neat) 1670

cm^{-1}; MS *m/z* 286 $[M+H]^+$; HRMS *m/z* calcd. for $C_{17}H_{20}NO_3$ $[M+H]^+$ 286.1443, found 286.1434.

cis-**17b**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (2H, d, J = 7.4 Hz), 7.55 (1H, t, J = 7.4 Hz), 7.45 (2H, t, J = 7.4 Hz), 5.87-5.92 (1H, m), 5.66 (1H, d, J = 9.7 Hz), 4.38 (1H, qt, J = 6.2, 6.2 Hz), 4.22-4.17 (2H, m), 3.94 (1H, dd, J = 17.3, 5.0 Hz), 3.38 (1H, dd, J = 17.3, 8.2 Hz), 2.57-2.51 (1H, m), 2.18 (2H, dd, J = 13.5, 4.6 Hz), 1.58-1.51 (1H, m), 1.35 (3H, d, J = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 153.6, 136.9, 133.1, 128.6 (2C), 128.5, 128.3 (2C), 127.4, 71.5, 54.0, 52.0, 41.9, 36.7, 28.8, 20.6; IR (neat) 1673 cm^{-1}; MS *m/z* 286 $[M+H]^+$; HRMS *m/z* calcd. for $C_{17}H_{20}NO_3$ $[M+H]^+$ 286.1443, found 286.1439.

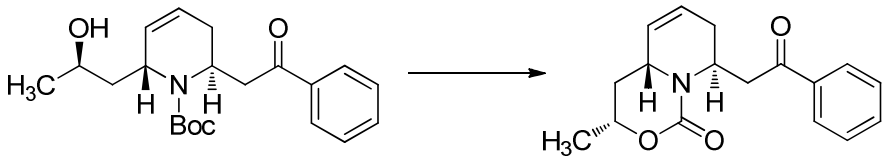
(2*R*,6*S*)-*tert*-Butyl 2-((R)-2-hydroxypropyl)-6-(2-oxo-2-phenylethyl)-5,6-dihydro pyridine-1(2H)-carboxylate (19)



$SnCl_4$ (1 M in CH_2Cl_2, 0.55 mL, 0.55 mmol) *via* syringe was added to a cooled (-78 ºC) solution of cyclic *N*,*O*-acetal **14** (110 mg, 0.46 mmol) and (1-phenylvinyloxy)trimethylsilane (0.56 mL, 2.8 mmol) in CH_2Cl_2 (8 mL). After stirring at -78 ºC for 0.5 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution and then allowed to warm to room temperature. The reaction mixture was then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in*

vacuo to afford the crude product, which was purified with flash chromatography (EtOAc : Hexane = 2 : 8) to provide ketone **19** (100 mg, 60%) as a colorless oil. $[\alpha]_D^{19.5}$ -101.4 (*c* 1.27, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (2H, d, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.46 (2H, t, *J* = 7.5 Hz), 5.97 (1H, dd, *J* = 9.4, 4.5 Hz), 5.82 (1H, dt, *J* = 9.4, 4.4 Hz), 4.46-4.42 (2H, m), 3.94-3.87 (1H, m), 3.37 (1H, brs), 3.28 (H, dd, *J* = 41.7, 8.8 Hz), 2.28-2.21 (2H, m), 2.01 (1H, ddd, *J* = 14.2, 9.3, 5.2 Hz), 1.66 (1H, ddd, *J* = 13.7, 7.4, 3.1 Hz), 1.45 (9H, s), 1.20 (3H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 155.2, 136.8, 133.0, 130.3, 128.5 (2C), 128.0 (2C), 124.1, 80.2, 66.0, 51.4, 48.1, 44.9, 42.4, 28.3(3C), 28.2, 24.1; IR (neat) 1674, 1597, 1580, 1449 cm^{-1}; MS *m/z* 382 $[M+Na]^+$, 360 ([M+H], 47%); HRMS *m/z* calcd. for $C_{21}H_{29}NO_4Na$ $[M+Na]^+$ 382.1994, found 382.1980.

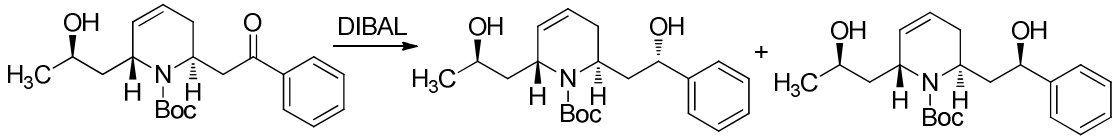
(3*R*,4*aR*,8*S*)-3-methyl-8-(2-oxo-2-phenylethyl)-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (*trans*-17a)



KO*t*-Bu (9 mg, 0.075 mmol) was added to a solution of compound **19** (18 mg, 0.05 mmol) in THF (5 mL) at 0 ºC and the mixture was warmed to room temperature. The mixture was stirred at room temperature for 1 h, then quenched with saturated NH_4Cl solution and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo* to afford the crude product. The crude product was purified by flash chromatography (EtOAc : Hexane = 1 : 1) to provide product (5 mg, 35%) as a

colorless solid. The NMR data is consistent with that of *trans*-**17a** (See above).

(2*R*,6*S*)-*tert*-Butyl 6-((*S*)-2-hydroxy-2-phenylethyl)-2-((*R*)-2-hydroxypropyl)-5,6-dihydropyridine-1 (2H)-carboxylate (*anti*-21a) and **(2*R*,6*S*)-*tert*-butyl 6-((*R*)-2-hydroxy-2-phenylethyl)-2-((*R*)-2-hydroxypropyl)-5,6-dihydropyridine-1(2H)-carboxylate (*syn*-21b)**



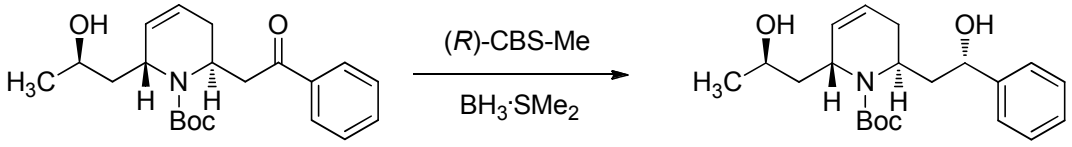
DIBAL (1M in cyclohexane, 0.97 mmol, 0.97 mL) was slowly added to a solution of compound (70 mg, 0.19 mmol) in CH_2Cl_2 (mL) at -78 ºC *via* syringe over 5 min. The reaction mixture was stirred at -78 ºC for 2 h and then warmed to -40 ºC for 0.5 h. Then methanol (0.5 mL) and water (0.5 mL) were added subsequently to quench the reaction. It was allowed to warm to room temperature for 0.5 h, dried over anhydrous Na_2SO_4 and stirred for 10 min further. After filtration through celite and evaporation, the residue was purified with flash chromatography (EtOAc : Hexane = 2 : 8) to provide *anti*-**21a** (56 mg, 82%) and *syn*-**21b** (14 mg, 18%) as colorless oils.

anti-**21a**: $[\alpha]_D^{20.2}$ -118.9 (*c* 1.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.21 (5H, m), 5.89 (1H, ddd, *J* = 9.9, 4.6, 1.2 Hz, 5.81 (1H, dt, *J* = 9.9, 4.1 Hz), 4.65 (1H, dt, *J* = 9.4, 3.7 Hz), 4.36 (1H, dt, *J* = 5.9, 5.9 Hz), 4.01 (1H, ddt, *J* = 8.3, 4.2, 4.2 Hz), 3.87-3.83 (1H, m), 3.31 (1H, brs), 2.80 (1H, brs), 2.26-2.21 (2H, m), 2.07-1.98 (2H, m), 1.90 (1H, ddd, *J* = 14.0, 9.1, 5.1 Hz), 1.58 (1H, ddd, *J* = 14.0, 7.4, 3.3 Hz), 1.48

(9H, s), 1.18 (3H, d, J = 6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 144.8, 130.5, 128.4 (2C), 127.3, 125.7 (2C), 124.4, 80.5, 72.3, 66.2, 51.7, 49.4, 44.7, 44.3, 28.5 (3C), 28.0, 24.1; IR (neat) 3393, 1652, 1475, 1454, 1400 cm^{-1}; MS *m/z* 362 $[M+H]^+$, 384 ([M+Na], 48%); HRMS *m/z* calcd. for $C_{21}H_{32}NO_4$ $[M+H]^+$ 362.2331, found 362.2332.

syn-**21b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.21 (5H, m), 5.84-5.81 (2H, m), 4.63 (1H, dd, J = 10.4, 2.6 Hz), 4.50-4.46 (1H, m), 4.13-4.05 (1H, m), 4.03-3.93 (1H, m), 2.30 (1H, ddd, J = 13.7, 10.3, 2.8 Hz), 2.20-2.15 (1H, m), 2.06-1.95 (1H, m), 1.82-1.59 (3H, m), 1.44 (9H, s), 1.21 (3H, d, J = 6.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 144.6 (Ar), 129.9, 128.3 (2C), 127.1, 125.7, 125.6 (2C), 80.8, 70.4, 67.1, 53.1, 48.5, 43.9, 43.6, 29.6, 28.5 (3C), 24.3; IR (neat) 3365, 1666, 1454, 1400 cm^{-1}; MS *m/z* 362 $[M+H]^+$, 384 ([M+Na], 38%); HRMS *m/z* calcd. for $C_{21}H_{32}NO_4$ $[M+H]^+$ 362.2331, found 362.2321.

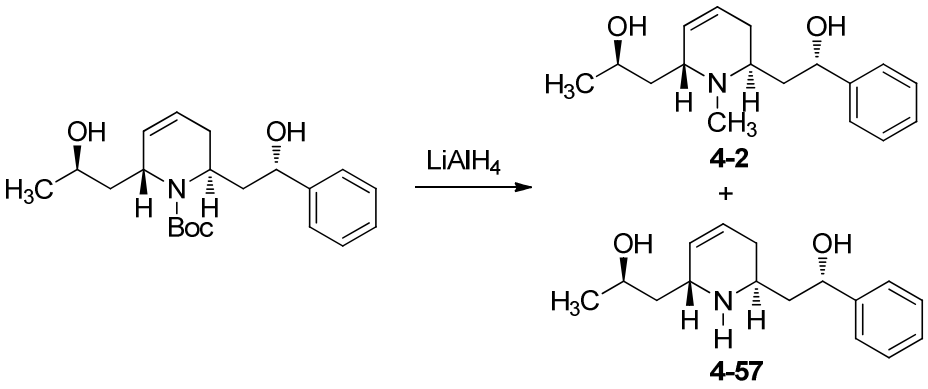
(2*R*,6*S*)-*tert*-Butyl6-((*S*)-2-hydroxy-2-phenylethyl)-2-((R)-2-hydroxypropyl)-5,6-dihydropyridine-1(2H)-carboxylate (*anti*-21a)



A solution of (*R*)-CBS-Me in toluene (34 µL, 0.034 mmol) was added to a solution of $BH_3{\cdot}SMe_2$ (48 µL, 0.50 mmol) in anhydrous THF (2 mL) at room temperature. The reaction mixture was stirred for 15 min and cooled to -10 ºC for 5 min. A solution of the ketone **19** (60 mg, 0.167 mmol) in THF (2 mL) was added dropwise by cannula. The reaction mixture was stirred at -10 ºC for 20 min and warmed to 0 ºC. The

reaction mixture was stirred at 0 ºC for 0.5 h and quenched with methanol (2 mL) and stirred at room temperature for 15 min. After evaporation, the residue was purified by flash chromatography (EtOAc : Hexane = 2 : 8) to give the alcohol *trans*-**21a** (55 mg, 92%) as a colorless oil.

(-)-sedinine (1) and **(*R*)-1-((2*R*,6*S*)-6-((*S*)-2-hydroxy-2-phenylethyl)-1,2,5,6-tetrahydropyridin-2-yl)propan-2-ol (22)**



$LiAlH_4$ (53 mg, 1.39 mmol) was added to a solution of compound **21a** (50 mg, 0.139 mmol) in anhydrous THF (5 mL) at room temperature. The mixture was heated at reflux for 24 h and was cooled to 0 ºC. Water was added cautiously and dropwise. The mixture was stirred for 15 min further. It was dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo*. The residue was purified by flash chromatography (basic Al_2O_3, EtOAc : Hexane = 3 : 2) to give sedinine **1** (15 mg, 40 %) as a colorless solid and byproduct **22** (7 mg, 20%) as a yellowish oil.

Sedinine 1: $[\alpha]_D^{20.4}$ -97.2 (*c* 0.57, MeOH) [ref. 5 $[\alpha]_D^{20}$ -98 (*c* 1.9, MeOH)]; m.p.: 118-120 ºC [ref. 86: 120-121 ºC]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 7.6 Hz), 7.34 (1H, t, J = 7.6 Hz), 7.27 (2H, t, J = 7.6 Hz), 5.75 (1H, ddd, J = 10.3, 5.3, 1.7

Hz), 5.56 (1H, ddt, *J* = 10.3, 3.9, 1.9 Hz), 4.81 (1H, dd, *J* = 9.3, 4.5 Hz), 4.01 (1H, dqd, *J* = 9.4, 3.2, 3.2 Hz), 3.28 (1H, ddt, *J* = 12.0, 6.0, 6.0 Hz), 3.18 (1H, brd, *J* = 10.3 Hz), 2.35 (3H, s), 2.00-1.92 (2H, m), 1.83 (1H, dt, *J* = 18.0, 4.5 Hz), 1.72-1.65 (2H, m), 1.50 (1H, dt, *J* = 14.5, 3.3 Hz), 1.18 (3H, d, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 128.4 (2C), 127.5, 127.4, 125.9 (2C), 125.0, 73.1, 68.6, 62.7, 49.2, 42.0, 40.6, 34.6, 24.3, 23.8; MS *m/z* 276 $[M+H]^+$, 246 (36%); HRMS *m/z* calcd. for $C_{17}H_{26}NO_2$ $[M+H]^+$ 276.1964, found 276.1961.

Compound **22**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.19 (5H, m), 5.81-5.75 (1H, m), 5.68-5.64 (1H, m), 4.90 (1H, dd, *J* = 9.0, 4.6 Hz), 4.00 (1H, dqd, *J* = 9.3, 6.0, 3.2 Hz), 3.60 (1H, brd, *J* = 9.7 Hz), 3.12 (1H, ddt, *J* = 9.4, 9.4, 4.6 Hz), 2.34-1.47 (6H, m), 1.20 (3H, d, *J* = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 129.8, 128.4 (2C), 127.5, 125.9 (2C), 125.1, 73.0, 68.2, 52.7, 46.4, 44.4, 41.0, 31.0, 24.0; MS *m/z* 262 $[M+H]^+$; HRMS *m/z* calcd. for $C_{16}H_{24}NO_2$ $[M+H]^+$ 262.1807, found 262.1801.

(-)-sedinine (1) and **(*R*)-1-((2*R*,6*S*)-6-((*S*)-2-hydroxy-2-phenylethyl)-1,2,5,6-tetrahydropyridin-2-yl)propan-2-ol (22)**

Red-Al (65% in toluene, 0.75 mmol, 0.24 mL) was added to a solution of compound **21a** (55 mg, 0.15 mmol) in anhydrous toluene (5 mL) at room temperature. The mixture was heated at reflux for 6 h and then cooled to room temperature. Sodium hydroxide (3 mL of 5% w/v aqueous solution) was added and the mixture was stirred for 15 min further. The aqueous phase was extracted with chloroform (3 x 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo*. The residue was purified by flash chromatography (basic

Al_2O_3, EtOAc : Hexane = 3 : 2) to give sedinine **1** (21 mg, 50%) as a colorless solid and byproduct **22** (12 mg, 30%) as a yellowish oil. The NMR data are consistent with those obtained by the reduction with $LiAlH_4$.

(-)-sedinine (1) and **(*R*)-1-((2*R*,6*S*)-6-((*S*)-2-hydroxy-2-phenylethyl)-1,2,5,6-tetrahydropyridin-2-yl)propan-2-ol (22)**

Alane-*N*,*N*-dimethylethylamine complex(0.83 mL, 0.42 mmol, 0.5 M in toluene) was added to a solution of compound **21a** (30 mg, 0.083 mmol) in anhydrous THF (5 mL) at room temperature. The mixture was heated at reflux for 5 h and then cooled to 0 ^{o}C. Water was added cautiously and dropwise. The reaction mixture was extracted with $CHCl_3$ (3 x 5 mL), dried over anhydrous Na_2SO_4, filtered through celite and concentrated *in vacuo*. The residue was purified by flash chromatography (basic Al_2O_3, MeOH : CH_2Cl_2 = 2 : 98) to give sedinine **1** (16 mg, 70 %) as a colorless solid and byproduct **22** (4 mg, 15%) as a yellowish oil.

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