***N*-Sulfinyl β -Amino Weinreb Amides: Synthesis of Enantiopure β -Amino Carbonyl Compounds. Asymmetric Synthesis of (+)-Sedridine and (-)-Allosedridine**

Franklin A. Davis,* Kavirayani R. Prasad, M. Brad Nolt, and Yongzhong Wu,
Department of Chemistry, Temple University, Philadelphia, PA 19122

Supporting Information

Experimental

General Procedures. Column chromatography was performed on silica gel, Merck grade 60 (230-400 mesh). TLC plates were visualized with UV, in an iodine chamber, or with phosphomolybdic acid, unless noted otherwise. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter and IR spectra were recorded, using NaCl plates or as KBr disks, on a Mattson 4020 FTIR. ^1H NMR and ^{13}C NMR spectra were recorded on a GE Omega 500, operating at 500 and 125 MHz, respectively. HRMS were performed in the Department of Chemistry, Drexel University, Philadelphia, PA, using a Fissions ZAB HF double-focusing mass spectrometer. Elemental analyses were performed in the Department of Chemistry, University of Pennsylvania, Philadelphia, PA.

Dichloromethane was distilled over calcium hydride under an inert atmosphere. THF and ether were freshly distilled under argon from a purple solution of sodium and benzophenone ketyl. Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. (*S*)-(+)-*N*-Benzylidene-*p*-toluenesulfinamide (**2**),¹ (*S_S*,*R*)-(+)-methyl *N*-(*p*-toluenesulfinyl)-3-amino-3-phenylpropanoate (**4**),² and 5-chlorovaleraldehyde³ were prepared as previously described.

(*S_S*,3*R*)-(+)-*N*-(*p*-Toluenesulfinyl)-3-amino *N*-methoxy-*N*-methyl-3-phenylpropionamide (3**).** In an oven-dried, 100-mL, two-neck, round-bottom flask equipped with a magnetic stirring bar and argon balloon was placed *N*-methoxy-*N*-methyl acetamide (0.16 mL, 1.5 mmol) in THF (25 mL). The solution was cooled to -78°C , KHMDS (1.5 mmol, 3 mL of 0.5 M solution in toluene) was added, and the solution was as stirred at this temperature for 1 h. At this time a solution of (+)-**2** (0.24 g, 1 mmol) in THF (10 mL) was added, the reaction mixture was stirred for 1 h, and was quenched at -78°C by addition of sat. aqueous NH_4Cl (10 mL). After warming to rt the solution was poured into water (50 mL) and extracted with ether (2 x 30 mL). The combined organic phases were washed with brine (25 mL), dried (MgSO_4), and concentrated. Chromatography (EtOAc: Hexane 90: 10) gave 0.26 g (76%) of a 78:22 ratio of diastereomers as a thick viscous mass. Careful crystallization from *n*-hexane/ether afforded a that was a 1:1 mixture of diastereoisomers. Evaporation of the organic phase gave 0.18 g (52% based on starting material) of diastereomerically pure (*S_S*,3*R*)-(+)-**3** as a viscous mass. The spectral properties are identical to (+)-**3** prepared from (*S_S*,3*R*)-(+)-**4** (see below).

Preparation of (*S_S*,3*R*)-(+)-*N*-(*p*-Toluenesulfinyl)-3-amino-*N*-methoxy-*N*-methyl-3-phenylpropionamide (3**) from (*S_S*,*R*)-(+)-methyl-*N*-(*p*-toluenesulfinyl)-3-amino-3-phenylpropanoate (**4**).** In an oven-dried, 50-mL, round-bottom flask equipped with a magnetic stirring bar, rubber septum, and argon balloon was placed *N*,*O*-

dimethylhydroxyamine hydrochloride (0.31 g, 3.15 mmol) in THF (5 mL). The solution was stirred, cooled to -78°C , and *n*-BuLi (3.15 mL, 2.0 M in cyclohexane, 6.30 mmol) was added dropwise via syringe. After stirring at this temperature for 5 min, the cooling bath was removed for ca. 15 min, the solution cooled to -78°C , and (*S_S*,*R*)-(+)-**4** (0.20 g, 0.63 mmol) in THF (8 mL) was added via syringe. After stirring at this temperature for 2 h, the reaction mixture was quenched by addition of sat. aq. NH_4Cl (2 mL) and warmed to rt. Water (5 mL) was added and the solution was extracted with Et_2O (20 mL) and EtOAc (3×20 mL). The combined organic phases were washed with brine (5 mL), dried (MgSO_4), and concentrated to give a slightly yellow oil. Flash chromatography (*n*-hexane-EtOAc, 1:1) afforded 0.17 g (78%) of a colorless oil of (+)-**3** and 0.02 g (10%) of (+)-**4**; $[\alpha]_{\text{D}}^{20} +88.6$ (*c* 1.4, CHCl_3); IR (neat) cm^{-1} 3221 (NH), 3029, 2936, 1657, 1453, 1387, 1090; ^1H NMR (CDCl_3) δ 2.32 (s, 3 H), 2.88-2.92 (m, 2 H), 3.02 (s, 3 H), 3.49 (s, 3 H), 4.82-4.86 (m, 1 H), 5.47 (d, *J* = 4.7 Hz, 1 H), 7.19-7.25 (m, 3 H), 7.29-7.32 (m, 2 H), 7.37-7.39 (m, 2 H), 7.52 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (CDCl_3) δ 22.0, 32.6, 40.1, 55.9, 61.9, 126.0, 128.1, 128.6, 129.4, 130.2, 141.7, 141.9, 143.4, 172.2. HRMS Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3\text{SNa}$ (*M*+*Na*) 346.1351, found 346.1346.

(*S_S*,*3R*)-(+)-*N*-(*p*-toluenesulfinyl)-**3-amino-3-phenylpropionaldehyde (5a)**. In an oven-dried, 50-mL, round-bottom flask equipped with a magnetic stirring bar, rubber septum and argon balloon was placed (*S_S*,*3R*)-(+)-**(3)** (0.08g, 0.25 mmol) in THF (20mL). The solution was cooled to -78°C and DIBAL-H (1.25 mmol, 1.25 mL of 1 M solution in CH_2Cl_2) was introduced. After stirring at this temperature for 1 h the reaction mixture was quenched with sat. aq. NH_4Cl (10 mL) and poured into water (15 mL). The solution was extracted with EtOAc (2 x 25 mL), the combined organic phases were washed with brine (20 mL), dried (MgSO_4), and concentrated. Chromatography (EtOAc:hexane, 85:15) gave 0.06 g (84%) of a thick colorless oil; $[\alpha]_{\text{D}} +175.1$ (*c* 0.41, CHCl_3); ^1H NMR δ 9.53 (t, *J* 1.6, 1H), 7.50 (d, *J* 8.4, 2H), 7.35-7.28 (m, 4H), 7.25-7.21 (m, 3H), 4.90 (q, *J* 6.4, 1H), 4.66 (d, *J* 5.2, 1H), 2.87 (dd, *J* 1.2, 6.4, 2H), 2.33 (s, 3H). ^{13}C NMR 200.17, 142.33, 142.03, 140.76, 130.05, 129.34, 128.60, 127.75, 125.80, 53.40, 51.34, 21.78. HRMS Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_2\text{SNa}$ (*M*+*Na*) 310.0878, found 310.0884.

Typical procedure for the addition of Grignard reagents to β -sulfinylamino Weinreb amide (+)-3**.** (*S_S*,*3R*)-(+)-*N*-(*p*-Toluenesulfinyl)-**3-amino-1,3-diphenylpropan-1-one (5c)**. In an oven-dried, 250-mL, round-bottom flask equipped with a magnetic stirring bar, a rubber septum, and argon balloon was placed (*S_S*, *3R*)-(+)-**(3)** (0.66 g, 1.9 mmol) in THF (50 mL). The solution was cooled to -78°C , PhMgBr (9.6 mL of a 1 M solution in ether, 9.6 mmol) was added, and the reaction mixture was warmed to rt. After stirring for 2.5 h, the solution was cooled -78°C and quenched by addition of sat. aq. NH_4Cl (20 mL). The reaction mixture was poured into water (20 mL), extracted with EtOAc (3×20 mL), and the combined organic phases were washed with brine (20 mL), dried (MgSO_4), and concentrated. Chromatography (EtOAc:hexane 70:30) gave 0.64 g (92%) of a white solid mp $94-96^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} + 80.08$ (*c* 1.25, CHCl_3); IR (CHCl_3) 3017, 1683, 1464 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.73 (d, *J* 7.2, 2H), 7.51-7.49 (m, 2H), 7.42-7.38 (m, 3H), 7.31-7.26 (m, 4H), 7.20-7.14 (m, 3H), 3.42 (d, *J* 6.5, 2H), 5.04 (q, *J* 6.0, 1H), 5.11 (d, *J* 4.9, 1H), 2.28 (s, 3H); ^{13}C (CDCl_3) δ 198.21, 142.84, 141.75, 141.25, 136.81, 133.93, 129.97, 129.21, 129.07, 128.50, 128.42, 128.03, 125.82, 55.13, 47.03, 21.53; HRMS calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{SNa}$ (*M* + *Na*) 386.1191; found 386.1198.

(*S*,3*R*)-(+)-*N*-(*p*-Toluenesulfinyl)-3-amino-1-methyl-3-phenylpropan-1-one (5b). Chromatography (EtOAc:hexane 70:30) afforded 0.48 g (84%) of a colorless viscous mass; $[\alpha]_D^{25} + 94.2$ (*c* 1.0, CHCl₃); IR (neat) 3195, 2921, 1750 cm⁻¹; ¹H NMR (CDCl₃) δ 7.47 (d, *J* 8.2, 2H), 7.33-7.25 (m, 4H), 7.22-7.7.16 (m, 3H), 4.96 (d, *J* 6.0, 1H), 4.81 (q, *J* 6.0, 1H), 2.9 (d, *J* 6.0, 2H), 2.29 (s, 3H), 1.95 (s, 3H); ¹³C (CDCl₃) δ 207.23, 142.74, 141.77, 141.48, 141.10, 130.21, 129.95, 129.17, 128.37, 127.83, 125.76, 54.07, 51.15, 31.01, 22.35; HRMS calcd for C₁₇H₁₉NO₂SNa (M + Na) 324.1034; found 324.1043.

(*S*)-(+)-5-chloro-*N*-(pentylidene)-*p*-toluenesulfonamide (7). In an oven-dried, 250-mL, two-neck, round-bottom flask, equipped with a magnetic stirring bar, a rubber septum and an balloon was placed 5-chlorovaleraldehyde (2.57 g, 10 mmol) in CH₂Cl₂ (100 mL). A solution of (*S*)-(+)-*p*-toluenesulfonamide (6) (1.5 g, 10 mmol) in CH₂Cl₂ (20 mL) and Ti(OEt)₄ (10.5 mL, 50 mmol) were added successively, and the reaction mixture was stirred at rt for 1 h. The reaction mixture was cooled to 0° C, quenched with ice-cold water (50 mL), and filtered through a pad of Celite. The Celite pad was washed with CH₂Cl₂ (3 x 15 mL), the organic phases combined, washed with water (100 mL), brine (50 mL), dried (MgSO₄), and concentrated. Chromatography (*n*-hexane:ether 80:20) gave 1.38 g (54%) of a colorless oil; $[\alpha]_D + 285.5$ (*c* 0.5, CHCl₃); IR 2955, 1621, 1472, 1098, 821 cm⁻¹; ¹H NMR (CDCl₃) δ 8.11 (t, *J* = 4.6, 1H), 7.43 (d, *J* = 8.0, 2H), 7.18 (d, *J* = 8.0, 2H), 3.41-3.37 (m, 2H), 2.42-2.37 (m, 2H), 2.28 (s, 3H), 1.69-1.63 (m, 4H); ¹³C NMR (CDCl₃) δ 166.65, 142.11, 130.21, 124.91, 44.80, 35.36, 30.73, 22.92, 21.55; HRMS calcd for C₁₂H₁₆NOSClNa (M + Na) 280.0539; found 280.0541.

(*S*,3*S*)-(+)-7-Chloro-*N*-(*p*-toluenesulfinyl)-3-amino-*N*-methoxy-*N*-methylheptanoamide (8). In an oven-dried, two-neck, round-bottom flask equipped with a magnetic stirring bar, a rubber septum, and argon inlet was placed *N*-methoxy, *N*-methyl acetamide (1.5 mL, 1.5 mmol) in THF (50 mL). The reaction mixture was cooled to -78° C and a solution of KHMDS (3 mL of 0.5 M solution in toluene, 1.5 mmol) was added. After stirring at -78° C for 45 min, (+)-7 (0.26 g, 1 mmol) in THF (10 mL) was added and the solution was stirred for 1.5 h, and the reaction progress monitored by TLC. When the reaction was complete sat. aq. NH₄Cl (15 mL) was added, the solution warmed to rt, and diluted with Et₂O (50 mL). The organic phase was washed with H₂O (2 x 50 mL), brine (25 mL), dried (MgSO₄), and concentrated. Chromatography (*n*-hexane:EtOAc 10:90) gave 0.27 g (76%) of an oil (>96% de); $[\alpha]_D = +101.0$ (*c* 0.44, CHCl₃); IR 2930, 2858, 1756, 1733, 1452 cm⁻¹; ¹H NMR (CDCl₃) δ 7.58 (d, *J* = 8.2, 2H), 7.27 (d, *J* = 8.2, 2H), 4.94 (d, *J* = 9.5, 1H), 3.69 (m, 1H), 3.66 (s, 3H), 3.57 (t, *J* = 7.0, 2H), 3.15 (s, 3H), 2.85-2.73 (m, 2H), 2.40 (s, 3H), 1.84-1.63 (m, 6H); ¹³C NMR 172.56, 142.96, 141.59, 129.89, 125.93, 61.67, 53.40, 45.18, 37.92, 35.38, 32.53, 32.38, 23.98, 21.72. HRMS calcd for C₁₆H₂₅N₂O₃SClNa (M + Na) 383.1172; found 383.1188.

(*S*,3*S*)-(+)-8-Chloro-*N*-(*p*-toluenesulfinyl)-3-amino-octane-2-one (9). In an oven-dried, 100-mL, two-necked, round-bottom flask equipped with a magnetic stirring bar and a rubber septa and argon balloon was placed (+)-8 (0.36 g, 1 mmol) in THF (60 mL). The solution was cooled to -78° C and a solution of MeMgBr (1.7 mL of 3 M solution in Et₂O, 5.1 mmol) was added. After stirring at this temperature for 30 min, the reaction mixture was warmed to rt, stirred for 1.5 h, and cooled to -78° C. The reaction mixture was quenched with sat. aq. NH₄Cl (10 mL), warmed to rt, and diluted with Et₂O

(60 mL). The organic phase was washed with H₂O (2 x 50 mL), brine (25 mL), dried (MgSO₄), and concentrated. Chromatography (*n*-hexane:EtOAc 1:1) afforded 0.24 g (77%) of a viscous mass; [α]_D = +95.9 (0.44, CHCl₃); IR 3209, 2941, 1713, 1436, 1089 cm⁻¹; ¹H NMR δ 7.43 (d, *J* 8.0, 2H), 7.15 (d, *J* = 8.0, 2H), 4.33 (d *J* = 9.2, 1H), 3.50 (m, 1H), 3.42 (t, *J* = 6.4, 2H), 2.77 (s, 3H), 2.64 (d, *J* = 5.1, 2H), 2.02 (s, 3H), 1.62-1.32 (m, 6H); ¹³C NMR 207.87, 142.73, 141.79, 52.77, 49.52, 45.27, 35.34, 32.42, 31.23, 23.92, 21.74. HRMS calcd for C₁₅H₂₂NSO₂ClNa (M + Na) 338.0957; found 338.0970.

anti-(S_S,2S,3S)-(+)-8-Chloro-*N*-(*p*-toluenesulfinyl)-3-aminooctan-2-ol (10). In an oven-dried, 100-mL, two-necked, round-bottom flask equipped with a magnetic stirring bar and rubber septum and argon balloon was placed (+)-**9** (0.16 g, 0.5 mmol) in CH₂Cl₂ (50 mL). The reaction mixture was cooled to -78° C, Super-Hydride (3 mL of 1 M solution in THF, 3 mmol) was added via syringe, and the solution was stirred for 2.5 h. At this time the reaction was quenched by addition of MeOH (5 mL) and sat. aq. NH₄Cl (5 mL). The reaction mixture was warmed to rt, stirred for 2 h, poured into H₂O (25 mL), and extracted with ether (2 x 40 mL). The combined organic phases were washed with brine (25 mL), dried (MgSO₄), and concentrated. Chromatography (ether: *n*-hexane 75:25) afforded 0.117 g (74%) of a oil; [α]_D +86.5 (*c* 0.52, CHCl₃), IR 3415-3329, 3019, 2932, 1452, 1216, 1047 cm⁻¹; ¹H NMR δ 7.55 (d, *J* 8.2, 2H), 7.24 (d, *J* 8.2, 2H), 4.01-3.94 (m, 2H), 3.60-3.48 (m, 3H), 2.35 (s, 3H), 1.81-1.62 (m, 4H), 1.51 (m, 2H), 1.40 (ddd, *J* 2.6, 9.6, 14.5, 1H), 1.13 (d, *J* 6.3, 3H); ¹³C NMR δ 142.42, 142.09, 130.07, 125.79, 63.86, 53.97, 45.41, 45.11, 37.01, 32.60, 24.01, 23.80, 21.80. HRMS calcd for C₁₅H₂₅NO₂ClS (M+H) 318.1295; found 318.1301.

syn-(S_S,2R,3S)-(+)-8-Chloro-*N*-(*p*-toluenesulfinyl)-3-aminooctan-2-ol (11). Similar reduction of (+)-**9** with LiAl(O-*t*-Bu)₃H gave 0.053 g (34%) of an oil following chromatography (ether:hexane 75:25); [α]_D +61.04 (*c* 0.24, CHCl₃); ¹H NMR δ 7.51 (d, *J* = 8.2, 2H), 7.21 (d, *J* = 8.0, 2H), 4.42 (d, *J* = 6.6, 1H), 3.93 (m, 1H), 3.64 (bm, 1H), 3.52-3.46 (m, 3H), 2.33 (s, 3H), 1.88 (bs, 1H), 1.79-1.68 (m, 2H), 1.61-1.43 (m, 4H), 1.08 (d, *J* = 6.3, 3H). ¹³C NMR 142.46, 141.97, 130.02, 125.80, 67.63, 56.09, 45.35, 37.21, 32.68, 24.79, 23.20, 21.77. HRMS calcd for C₁₅H₂₅NO₂ClS (M+H) 318.1295; found 318.1303.

(S_S,2S-(2S)-(+)-(1-*p*-Toluenesulfinyl-piperidin-2-yl)propan-2-ol (12a).

Typical cyclization procedure. In an oven-dried, 100-mL, one-neck, round-bottom flask equipped with a magnetic stirring bar, rubber septum, and argon balloon was placed (+)-(*S*_S,2*S*,3*S*)-**10** (0.23 g, 0.73 mmol) in THF (25 mL). The solution was cooled to 0° C; 18-crown-6 (0.08 g, 0.3 mmol) and NaH (0.17 g of 60% suspension in oil, 4.3 mmol) were added successively. After stirring at this temperature for 1.5 h, the reaction mixture was cautiously quenched by addition of sat. aq. NH₄Cl (5 mL), poured into water (25 mL), and extracted with Et₂O (2 x 35 mL). The combined organic phases were washed with brine (25 mL), dried (MgSO₄), and concentrated. Chromatography (*n*-hexane:ether 30:70) gave 0.15 g (72%) of an oil; [α]_D = +91.87 (*c* 0.8, CHCl₃); IR (neat) 3397, 2938, 1492, 1083 cm⁻¹; ¹H NMR δ 7.57 (d, *J* 8.0, 2H), 7.31 (d, *J* 8.0, 2H), 3.74 (m, 2H), 3.10-3.03 (m, 3H), 2.97 (dt, *J* 4.4, 13.6, 1H), 2.34 (s, 3H), 2.09 (dt, *J* 8.6, 14.4, 1H), 2.0-1.85 (m, 2H), 1.68-1.55 (m, 8H), 1.10 (d, *J* 6.2, 3H). ¹³C NMR 141.43, 140.71, 129.86, 126.58, 64.74, 54.24, 42.07, 39.74, 31.61, 26.41, 24.23, 21.67, 19.97. HRMS calcd for C₁₅H₂₃NO₂SNa (M+Na) 304.1347; found 304.1340.

(S_S,2R-(2S)-(+)-(1-*p*-Toluenesulfinyl-piperidin-2-yl)propan-2-ol (13a). Chromatography (hexane:ether 30:70) gave 71% of an oil: $[\alpha]_D +63.63$ (*c* 0.55, CHCl₃); ¹H NMR δ 7.46 (d, *J* 7.9, 2 H), 7.23 (d, *J* 7.8, 2 H), 3.73 (bm, 2 H), 3.11-3.0 (m, 2 H), 2.94-2.86 (m, 1H), 2.34 (s, 3 H), 2.09-2.00 (m, 1H), 1.84-1.77 (m, 1H), 1.58-1.46 (m, 4H), 1.35-1.27 (m, 1H), 1.09 (d, *J* 6.2, 3H); δ ¹³C NMR 141.55, 141.01, 129.94, 126.67, 66.43, 56.89, 41.74, 40.70, 31.17, 27.05, 24.65, 21.76, 19.78. HRMS Calcd for C₁₅H₂₄NO₂S (M+H) 282.1528; found 282.1523.

(2S-(2S)-(+)-(1-*p*-Toluenesulfonyl-piperidin-2-yl)propan-2-ol (12b): Typical oxidation procedure. In an oven-dried, 50-mL, round-bottom flask equipped with a magnetic stirring bar was placed (+)-**12a** (0.1 g, 0.36 mmol) in CH₂Cl₂ (50 mL). The solution was cooled to 0°C, *m*-CPBA (0.12 g, 0.72 mmol, 77%) was added, and the reaction mixture was stirred at this temperature for 1.5 h. At this time sat. aq. NaHCO₃ (20 mL) was added and the solution was vigorously stirred for 30 min. The organic phase was separated, washed with H₂O (20 mL), brine (20 mL), dried (MgSO₄), and concentrated. Chromatography (ether:*n*-hexane 1:1) gave 0.084 g (79%) of a viscous mass; $[\alpha]_D = -16.8$ (*c* 1.0, EtOH); ¹H NMR δ 7.68 (d, *J* = 8.0, 2H), 7.23 (d, *J* = 8.0, 2H), 4.14 (bm, 1H), 3.92 (bm, 1H), 3.81 (bdd, *J* = 2.8, 14.8, 1H), 3.39 (bs, 1H), 2.91 (dt, *J* = 2.4, 13.6, 1H), 1.40-1.22 (m, 4H), 1.16 (d, *J* = 6.1, 3H) super imposed on 0.95-1.17 (m, 5H); ¹³C NMR 143.58, 139.10, 130.59, 127.14, 63.66, 50.07, 41.23, 39.72, 28.19, 24.31, 23.05, 21.92, 19.08.

(2R-(2S)-(+)-(1-*p*-Toluenesulfonyl-piperidin-2-yl) propan-2-ol (13b). Similarly oxidation of (+)- **13a** afforded 0.078 g (74%) of a viscous mass; $[\alpha]_D = -30.5$ (*c* 0.54, EtOH); ¹H NMR δ 7.66 (d, *J* = 8.0, 2H), 7.21 (d, *J* = 8.0, 2H), 4.13 (bm, 1H), 3.84 (bm, 1H), 3.72 (bm, 1H), 2.98 (t, *J* = 14, 1H), 1.88-1.81 (m, 1H), 1.47-1.24 (m, 6H), 1.16 (d, *J* = 6.1, 3H) super imposed on 1.07-1.17 (m, 4H); ¹³C NMR 412.76, 138.04, 129.83, 126.73, 66.11, 50.62, 40.54, 38.78, 27.46, 23.81, 23.37, 21.18, 18.14.

(+)-Sedridine (14) and (-)-allosedridine (15) by deprotection of *N*-(*p*-toluenesulfonyl) sedridine (12b) and allosedridine (13b). General Procedure. A 50-ml, two-neck, round-bottom flask equipped with a magnetic stirring bar and a rubber septum was cooled to -78°C. Liq. NH₃ (25 mL) was collected into the flask by standard ammonia cooling device. A solution of (+)-**12b** (0.074g, 0.25 mmol) in THF (5 mL) was added via syringe, followed by small pieces of freshly cut sodium until a permanent deep blue color persisted. The solution was stirred for 1.5 h and cautiously quenched by addition of a large excess of solid NH₄Cl (~ 50g). The ammonia was allowed to evaporate, the solid residue was washed with EtOAc (50 mL) and decanted. Evaporation of the solvent gave 0.03 g (84%) of an oil, which was purified by sublimation (Kuegelrohr bath temp 90°C /1mmHg), mp 73-75° C [lit⁴ mp 83-84° C]; $[\alpha]_D +30.0$ (*c* 1.0, EtOH), [lit⁴ $[\alpha]_D +28.36$ (*c* 1.13, EtOH)]. Spectral properties were identical to literature values.³

(-)-Allosedridine (15). Similarly reaction of (+)-**13b** gave 0.025 (70%) of allosedridine as a crystalline solid. An analytically pure sample was obtained by sublimation (Kuegelrohr- bath temp 100° C/1mmHg); mp 57-59° C [lit³ 60-61° C]; $[\alpha]_D = -10$ (*c* 0.8, MeOH), [lit³ $[\alpha]_D = -16.18$ (*c* 1.55, MeOH)]. Spectral properties were identical to literature values.³

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