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Experimental Section

General. ^{1}H NMR spectra were recorded at the indicated field strength as solutions in $CDCl_3$ unless otherwise indicated. Chemical shifts are expressed in parts per million (ppm, δ) downfield from TMS and are referenced to $CHCl_3$ (7.26 ppm) as internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, braod. ^{13}C NMR spectra were recorded at the indicated field strength as solutions in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in parts per million (ppm, d) downfield from TMS and are referenced to the center line of $CDCl_3$ (77.0 ppm) as internal standard. Carbon signals were assigned by a DEPT pulse sequence, q = methyl, t = methyleme, d = methine, and s = quaternary.

(5*R*,6*S*)-(-)-5-Acetoxy-6-(acetoxymethyl)-1-(phenylmethyl)-2-piperidone

To a stirred solution of (-)-**4**[4] (1.44 g, 6.13 mmol) in pyridine (10 mL) was added Ac_2O (6 mL, 63.59 mmol) at 0 °C, then the resulting mixture was stirred at room temperature for 18 h. The solvent was evaporated, and the residue was chromatographed on SiO_2 (50 g, hexane:acetone=4:1) to give the diacetate (1.72 g, 88%) as a colorless oil.

IR (neat) cm^{-1}: 3063, 3030, 2960, 1738, 1650, 1469, 1454, 1416, 1367, 1236, 1187, 1055, 724; ^{1}H NMR (500 MHz) δ: 1.83 & 2.06 (each 3H, each s), 1.95-2.01 (1H, m), 2.13-2.20 (1H, m), 2.52 (1H, ddd, *J* = 18.0, 7.5, 2.1 Hz), 2.63 (1H, ddd, *J* = 18.0, 11.0, 7.5 Hz), 3.56-3.60 (1H, m), 3.88 (1H, d, *J* = 15.0 Hz), 4.10 (1H, dd, *J* = 11.9, 7.5 Hz), 4.20 (1H, dd, *J* = 11.9, 4.0 Hz), 5.05-5.07 (1H, m), 5.46 (1H, d, *J* = 15.0 Hz), 7.22-7.30 (5H, m); ^{13}C NMR (75 MHz) δ: 20.62 (q), 20.71 (q), 21.93 (t), 26.91 (t), 47.86 (t), 57.32 (d), 61.98 (t), 67.12 (d), 127.49 (d), 128.05 (d), 128.48 (d), 136.60 (s), 169.18 (s), 169.83 (s), 170.23 (s); MS: 320 (M^++1), 319 (M^+), 91 (100); HRMS: Calcd. for $C_{17}H_{21}NO_5$: 319.1419, Found: 319.1390; $[\alpha]^{26}_D$ -55.0 (*c* 2.15, $CHCl_3$).

(5*R*,6*S*)-(-)-5-Acetoxy-6-(acetoxymethyl)-1-(phenylmethyl)-2-piperidinethione

To a stirred solution of the diacetate (1.54 g, 4.83 mmol) in THF (20 mL) was added Lawesson's reagent (1.2 g, 2.90 mmol), then the resulting suspension was refluxed for 2 h. After cooling, the solvent was evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (50 g, hexane:acetone=10:1) to give the thiolactam (1.59 g, 99%) as a colorless oil.

IR (neat) cm^{-1}: 3062, 3029, 2946, 1746, 1596, 1495, 1454, 1413, 1367, 1300, 1235, 1173, 1123, 1050, 959, 923, 731, 704; ^{1}H NMR (500 MHz) δ: 1.82 & 2.10 (each 3H, each s), 1.86-1.95 (1H, m), 2.13-2.20 (1H, m), 3.19 (1H, ddd, *J* = 19.5, 7.5, 4.0 Hz), 3.27 (1H, ddd, *J* = 19.5, 9.6, 7.1 Hz), 3.79-3.82 (1H, m), 4.22 (1H, dd, *J* = 12.6, 7.0 Hz), 4.26 (1H, dd, *J* = 12.6, 4.5 Hz), 4.28 (1H, d, *J* = 15.0 Hz), 5.14 (1H, q-like, *J* = 2.2 Hz), 6.61 (1H, d, *J* = 15.0 Hz), 7.27-7.36 (5H, m); ^{13}C NMR (75 MHz) δ: 20.65 (q), 20.71 (q), 22.32 (t), 36.89 (t), 55.33 (t), 59.28 (d), 61.64 (t), 67.47 (d), 127.93 (d), 128.13 (d), 128.63 (d), 134.88 (s), 169.82 (s), 170.12 (s), 201.47 (s); MS: 336 (M^++1), 335 (M^+), 91 (100); HRMS: Calcd. for $C_{17}H_{21}NO_4S$: 335.1191, Found: 335.1149; $[\alpha]^{26}_D$ -137.0 (*c* 1.71, $CHCl_3$).

Methyl (5*R*,6*S*)-(+)-5-Acetoxy-6-(acetoxymethyl)-1-(phenylmethyl)-2-piperidinylidenethanoate (5)

To a stirred solution of the thiolactam (1.61 g, 4.83 mmol) in MeCN (20 mL) was added $BrCH_2CO_2Me$ (0.55 mL, 5.77 mmol), then the resulting mixture was stirred at room temperature for 24 h. To the

reaction mixture was added Ph_3P (1.51 g, 5.77 mmol) and Et_3N (2.0 mL, 14.48 mmol), then the resulting suspension was refluxed for 24 h. Ahter cooling, the solvent was evaporated, and the residue was chromatographed on SiO_2 (70 g, hexane:acetone=50:1~12:1) to give (+)-**5** (1.66 g, 92%) as a colorless oil.

IR (neat) cm^{-1}: 3063, 2947, 1732, 1694, 1682, 1574, 1558, 1496, 1434, 1372, 1242, 1142, 1046, 942, 730, 697; ^1H NMR (500 MHz) δ: 1.85-1.92 (1H, m), 2.02 & 2.04 (each 3H, each s), 2.06-2.13 (1H, m), 3.13 (1H, dt, *J* = 18.0, 6.0 Hz), 3.39 (1H, dddd, *J* = 18.0, 9.0, 6.0, 1.0 Hz), 3.53 (1H, tdd, *J* = 7.0, 2.2, 1.0 Hz), 3.55 (3H, s), 4.17 (1H, d, *J* = 6.0 Hz), 4.28 (1H, d, *J* = 16.0 Hz), 4.59 (1H, d, *J* = 16.0 Hz), 4.72 (1H, br s), 5.10-5.13 (1H, m), 7.21 (2H, d-like, *J* = 8.0 Hz), 7.25 (1H, t-like, J = 8.0 Hz), 7.32 (2H, t-like, *J* = 8.0 Hz); ^{13}C NMR (75 MHz) δ: 20.73 (q), 21.03 (q), 21.73 (t), 21.84 (t), 50.08 (q), 53.80 (t), 60.32 (d), 62.75 (t), 68.65 (d), 86.20 (d), 126.75 (d), 127.41 (d), 128.64 (d), 135.73 (s), 160.36 (s), 168.98 (s), 170.15 (s), 170.41 (s); MS: 375 (M^+), 242 (M^+-133), 91 (100); HRMS: Calcd. for $C_{20}H_{25}NO_6$: 375.1682, Found: 375.1723; $[\alpha]^{26}_D$ +70.3 (*c* 9.59, $CHCl_3$).

Methyl (5*R*,6*S*)-5-Acetoxy-6-(acetoxymethyl)-1-(phenylmethyl)piperidin-2-ethanoate

To a stirred suspension of (+)-**5** (1.60 g, 4.27 mmol) in CH_2Cl_2 (20 mL) and $NaBH_3CN$ (95%, 440 mg, 6.65 mmol) was added dropwise TFA (1.0 mL, 13.0 mmol) at 0 °C, then the resulting suspension was stirred at 0 °C for 2 h. The reaction was quenched with satd. $NaHCO_3$, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL x 4), and the organic extracts were combined, dried, and evaporated to give a colorless oil, which was chromatographed on SiO_2 (50 g, hexane:acetone=11:1) to afford the piperidine (1.34 g, 84%) as a 11:1 mixture of the *trans*(2,6)- and *cis*(2,6)-piperidines as a colorless oil.

(4a*S*,6*R*,8a*R*)-(-)-Hexahydro-6-{2-(hydroxy)ethyl}-2,2-dimethyl-5-(phenylmethyl)-4*H*-1,3-dioxino[5,4-b]pyridine (6)

To a stirred solution of the above mixture (1.0 g, 2.65 mmol) in THF (20 mL) was added $LiAlH_4$ (300 mg, 7.96 mmol) at 0 °C, then the resulting suspension was refluxed for 18 h. After cooling, the reaction was quenched with 10% NaOH, and the residue was extracted with hot $CHCl_3$ (10 mL x 10). The organic extracts were combined, dried, and evaporated to give a colorless oil, which was used directly in the next step. To a stirred solution of the above oil in CH_2Cl_2 (30 mL) was added 2,2-dimethoxypropane (0.66 mL, 5.31 mmol), *p*-TsOH•H_2O (760 mg, 3.98 mmol), and molecular sieves 5A (10 g), then the resulting suspension was stirred at room temperature for 20 h. The reaction was quenched with 15% K_2CO_3, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (30 mL x 5), the organic extracts were combined, dried, and evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (40 g, hexane:acetone=12:1) to give (-)-**6** (606 mg, 75%) as a colorless oil.

IR (neat) cm^{-1}: 3423, 3061, 3027, 2992, 2941, 2874, 1378, 1265, 1202, 1167, 1093, 1040, 735, 700; ^1H NMR (500 MHz) δ: 1.40 & 1.49 (each 3H, each s), 1.42-1.51 (1H, m), 1.59-1.72 (2H, m), 1.78 (1H, dq, *J* = 13.0, 3.0 Hz), 2.00 (1H, tt, *J* = 14.0, 5.0 Hz), 2.11-2.18 (1H, m), 2.88 (1H, q-like, *J* = 6.0 Hz), 2.98 (1H, td, *J* = 10.0, 5.0 Hz), 3.07 (1H, br), 3.46 (1H, ddd, *J* = 11.0, 9.0, 4.5 Hz), 3.63 (1H, dt, *J* = 10.8, 5.0 Hz), 3.68 & 3.76 (2H, ABq, *J* = 13.2 Hz), 3.79 & 3.84 (1H, ABq, *J* = 10.7 Hz), 3.80 & 3.82 (1H, ABq, *J* = 11.0 Hz), 3.90 (1H, td, *J* = 10.0, 4.5 Hz), 7.23-7.34 (5H, m); ^{13}C NMR (75 MHz) δ: 19.33 (q), 24.67 (t), 26.22 (t), 28.59 (t), 29.44 (q), 52.76 (t), 54.68 (d), 55.07 (d),

62.10 (t), 62.89 (t), 69.03 (d), 98.61 (s), 127.17 (d), 128.31 (d), 128.46 (d), 139.57 (s); MS: 305 (M^+), 91 (100); HRMS: Calcd. for $C_{18}H_{27}NO_3$: 305.2088, Found: 305.2045; $[\alpha]^{26}_D$ -20.9 (*c* 0.99, $CHCl_3$).

Ethyl (4a*S*,6*R*,8a*R*)-(+)-Hexahydro-2,2-dimethyl-5-(phenylmethyl)-4*H*-1,3-dioxino-[5,4-b]pyridine-6-but-(2*E*)-enoate (7)

To a stirred solution of $(COCl)_2$ (0.19 mL, 2.28 mmol) in CH_2Cl_2 (5 mL) was added DMSO (0.32 mL, 4.56 mmol) at -78 °C, then the resulting mixture was stirred for 5 min. To the mixture was added (-)-**6** (347 mg, 1.14 mmol) in CH_2Cl_2 (5 mL) was added at -78 °C, then the mixture was stirred for 30 min. To the resulting mixture was added Et_3N (0.95 mL, 6.84 mmol) at - 78°C, then the temperature was rised gradually to 0 °C. The reaction was quenched with satd. $NaHCO_3$, and the aqueous layer was extracted with Et_2O (20 mL x3). The organic extracts were combined, dried, and evaporated to give the crude aldehyde as a pale yellow oil. This ladehyde was used directly in the next step. To a stirred suspension of NaH (60%, 68 mg, 1.71 mmol) in THF (10 mL) was added $(EtO)_2P(O)CH_2CO_2Et$ (0.37 mL, 1.82 mmol) at 0 °C, then the reaction mixture was stirred at 0 °C for 30 min. To the mixture was added the above aldehyde in THF (5 mL) at 0 °C, then the mixture was stirred at room temperature for 40 h. The reaction was quenched with H_2O, and the aqueous layer was extracted with CH_2Cl_2 (10 mL x 5). The organic extracts were combined, dried, and evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (20 g, hexane:acetone=50:1) to give (+)-**7** (338 mg, 80%) as a colorless oil.

IR (neat) cm^{-1}: 3062, 3027, 2991, 2942, 2874, 1716, 1652, 1454, 1368, 1319, 1265, 1202, 1174, 1122, 1093, 1041, 985, 927, 868, 737, 700; ^1H NMR (500 MHz) δ: 1.27 (3H, t, *J* = 7.0 Hz), 1.40 & 1.47 (each 3H, each s), 1.52-1.64 (2H, m), 1.68-1.74 (2H, m), 2.47-2.52 (2H, m), 2.69 (1H, td, *J* = 10.5, 4.5 Hz), 2.82-2.86 (1H, m), 3.52 & 3.69 (2H, ABq, *J* = 14.0 Hz), 3.59 (1H, t, *J* = 10.0 Hz), 3.72 (1H, ddd, *J* = 11.0, 9.0, 4.5 Hz), 3.88 (1H, dd, *J* = 10.9, 4.5 Hz), 4.16 (2H, q, *J* = 7.0 Hz), 5.79 (1H, dt-like, *J* = 15.0, 1.0 Hz), 6.72 (1H, dt, *J* = 15.0, 8.0 Hz), 7.22-7.31 (5H, m); ^{13}C NMR (75 MHz) δ: 14.17 (q), 19.17 (q), 25.02 (t), 25.46 (t), 26.25 (t), 29.50 (q), 52.95 (t), 55.18 (d), 55.91 (d), 60.13 (t), 63.93 (t), 72.11 (d), 98.47 (s), 122.89 (d), 126.99 (d), 127.98 (d), 128.29 (d), 139.33 (s), 146.88 (d), 166.19 (s); MS: 373 (M^+), 91 (100); HRMS: Calcd. for $C_{22}H_{31}NO_4$: 373.2251, Found: 373.2232; $[\alpha]^{26}_D$ +62.6 (*c* 1.00, $CHCl_3$).

Trichloroethyl (4a*S*,6*S*,8a*R*)-(-)-Hexahydro-6-{4-(hydroxy)butyl}-2,2-dimethyl-4*H*-1,3-dioxino[5,4-b]pyridine-5-carboxylate (8)

To a stirred solution of (+)-**7** (300 mg, 0.80 mmol) in EtOH (10 mL) was added $Pd(OH)_2$ (20 mg), then the resulting suspension was hydrogenated at 1 atm for 15 h. The catalyst was filtered off, and the filterate was evaporated to give a colorless oil. To a stirred solution of the oil in THF (10 mL) was added $LiAlH_4$ (61 mg, 1.60 mmol), then the resulting suspension was refluxed for 12 h. After cooling, the reaction was quenched with 10% NaOH, and the residue was extracted with hot $CHCl_3$ (10 ml x 6). The organic extracts were combined, dried, and evaporated to afford a colorless oil, which was used directly in the next step. To a stirred solution of the above oil in $CHCl_3$ (20 mL) and H_2O (2 mL) was added K_2CO_3 (220 mg, 1.60 mmol) and TrocCl (0.22 mL, 1.60 mmol) at 0 °C, then the resulting mixture was stirred at room temperature for 8 h. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (10 mL x 5). The organic extracs were combined, dried, and

evaporated to give a colorless oil, which was chromatographed on SiO_2 (15 g, hexane:acetone=11:1) to give (-)-**8** (220 mg, 65%) as a colorless oil.

IR (neat) cm^{-1}: 3446, 2994, 2939, 1717, 1424, 1382, 1266, 1204, 1098, 705; ^1H NMR (500 MHz) δ: 1.39 & 1.51 (each 3H, each s), 1.31-1.42 (2H, m), 1.55-1.70 (6H, m), 1.74-1.88 (3H, m), 3.23 (1H, td, J = 10.0, 4.5 Hz), 3.63 (2H, t-like, J = 6.2 Hz), 3.71 (1H, td, J = 10.5, 4.5 Hz), 4.36 & 4.44 (each 1H, each br), 4.59 (1H, t, J = 11.0 Hz), 4.66 & 4.72 (each 1H, each br); ^{13}C NMR (75 MHz) δ: 19.07 (q), 22.49 (t), 26.03 (t), 26.37 (t), 29.15 (t), 29.39 (q), 32.34 (t), 53.39 (d), 53.46 (d), 62.36 & 62.45 (each t, due to rotamers), 62.52 (t), 70.63 (d), 74.94 (s), 95.41 (s), 98.49 (s), 153.25 (s); $[\alpha]^{26}_D$ -9.3 (*c* 2.24, $CHCl_3$).

Phenyl sluphone (-)-(9)

To a stirred solution of $(COCl)_2$ (0.103 mL, 1.22 mmol) in CH_2Cl_2 (2 mL) was added DMSO (0.17 mL, 2.44 mmol) at -78 °C, then the resulting mixture was stirred for 5 min. To the mixture was added (-)-**8** (255 mg, 0.61 mmol) in CH_2Cl_2 (2 mL) was added at -78 °C, then the mixture was stirred for 30 min. To the resulting mixture was added Et_3N (0.51 mL, 3.66 mmol) at - 78°C, then the temperature was rised gradually to 0 °C. The reaction was quenched with H_2O, and the aqueous layer was extracted with Et_2O (20 mL x3). The organic extracts were combined, dried, and evaporated to give the crude aldehyde as a pale yellow oil. This aldehyde was used directly in the next step. To a stirred suspension of NaH (60%, 27 mg, 0.67 mmol) in THF (5 mL) was added $(EtO)_2P(O)CH_2SO_2Ph$ (214 mg, 0.73 mmol) at 0 °C, then the reaction mixture was stirred at 0 °C for 30 min. To the mixture was added the above aldehyde in THF (5 mL) at 0 °C, then the mixture was stirred at room temperature for 3 h. The reaction was quenched with H_2O, and the aqueous layer was extracted with CH_2Cl_2 (10 mL x 5). The organic extracts were combined, dried, and evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (20 g, hexane:acetone=15:1) to give (-)-**9** (266 mg, 80%) as a colorless oil.

IR (neat) cm^{-1}: 2995, 2945, 2868, 1715, 1446, 1384, 1307, 1266, 1234, 1204, 1147, 1096, 753, 688; ^1H NMR (500 MHz) δ: 1.37 & 1.48 (each 3H, each s), 1.40-1.51 (3H, m), 1.55-1.64 (2H, m), 1.73-1.86 (3H, m), 2.26 (2H, q, J = 7.0 Hz), 3.14 (1H, td, J = 10.0, 4.5 Hz), 3.65-3.72 (1H, m), 4.29 (1H, br), 4.39 (1H, br), 4.56 (1H, br t-like, J = 11.0 Hz), 4.52-4.66 (1H, br), 4.71 (1H, d-like, J = 11.0 Hz), 6.30 (1H, dd-like, J = 14.0, 1.0 Hz), 6.93 (1H, dtd, J = 14.0, 6.5, 1.0 Hz), 7.52 (2H, tm, J = 8.0 Hz), 7.59 (1H, tm, J = 8.0 Hz), 7.84 (2H, dm, J = 8.0 Hz); ^{13}C NMR (125 MHz) δ: 19.01 (q), 22.53 (t), 24.18 (t), 25.95 & 26.46 (each t, due to rotamers), 28.66 & 29.34 (each t, due to rotamers), 29.34 (q), 30.97 & 31.45 (each t, due to rotamers), 52.93 (d), 53.37 (d), 62.20 (t), 70.40 (d), 74.75 (t), 95.47 (s), 98.45 (s), 127.45 (d), 129.20 (d), 130.84 (d), 133.25 (d), 140.38 (s), 145.98 (d); $[\alpha]^{26}_D$ -3.77 (*c* 4.10, $CHCl_3$).

Quinolizidine (-)-10

To a stirred solution of (-)-**9** (278 mg, 0.50 mmol) in THF (6 mL) and 1N NH_4OAc (6 mL) was added 10% Cd-Pb (440 mg), then the resulting suspension was stirred at room temperature for 24 h. To the suspension was added an addiional 10% Cd-Pb (440 mg), then the suspension was stirred an additional 24 h. The insoluble material was removed through the celite pad, and the the aqueous layer was extracted with $CHCl_3$ (15 mL x 4). The organic extracts were combined, dried, and evaporated to give a colorless oil, which was recrystallized from *i*-Pr_2O-benzene-hexane to afford (-)-**10** (127 mg, 67%) as

a colorless needle (mp 194~195 °C). The mother liquor was evaporated, and the residue was chromatographed on SiO_2 (10 g, hexane:acetone=17:1) to give (-)-**10** (48 mg, 25%) as an additional crops.

IR (KBr) cm^{-1}: 3062, 2991, 2972, 2942, 2914, 2887, 2867, 1300, 1291, 1268, 1201, 1173, 1148, 1138, 1092, 1034, 865, 753; ^1H NMR (500 MHz) δ: 0.95 (1H, dm, *J* = 13.5 Hz), 1.00 (1H, tt, *J* = 14.0, 5.0 Hz), 1.25 (2H, tm, *J* = 17.0 Hz), 1.32-1.46 (2H, m), 1.38 & 1.44 (each 3H, each s), 1.48 & 1.53 (1H, each dt, *J* = 14.0, 4.0 Hz), 1.72 (1H, dm, *J* = 13.5 Hz), 1.75-1.89 (2H, m), 2.65 (1H, dm, *J* = 12.2 Hz), 2.78 (1H, td-like, *J* = 9.5, 4.5 Hz), 3.14 (1H, dd, *J* = 15.0, 5.0 Hz), 3.23 (1H, ddd, *J* = 11.0, 9.0, 4.2 Hz), 3.40 (1H, br dt-like, *J* = 8.0, 4.0 Hz), 3.48 (1H, t, *J* = 11.0 Hz), 3.74 (1H, dd, *J* = 14.0, 8.0 Hz), 3.90 (1H, dd, *J* = 11.0, 4.5 Hz), 7.56 (2H, t-like, *J* = 8.0, 1.0 Hz), 7.65 (1H, tt-like, *J* = 8.0, 1.1 Hz), 7.92 (2H, dm, *J* = 8.0 Hz); ^{13}C NMR (125 MHz) δ: 19.07 (q), 20.48 (t), 21.33 (t), 22.23 (t), 25.59 (t), 27.82 (t), 29.42 (q), 48.42 (d), 49.21 (d), 52.79 (d), 57.27 (t), 62.60 (t), 71.84 (d), 98.09 (s), 127.86 (d), 128.86 (d), 133.20 (d), 140.67 (s); MS: 379 (M^+), 138 (100); HRMS: Calcd. for $C_{20}H_{29}NO_4S$: 379.1817, Found: 379.1839; $[\alpha]^{26}_D$ -44.5 (*c* 1.06, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(-)-6-{(2,2-Dimethylethyldiphenylsiloxy)methyl}-7-hydroxy-4-(phenylsulfonylmehyl)octahydro-2*H*-quinolizine (11)

To a stirred solution of (-)-**10** (583 mg, 1.54 mmol) in EtOH (40 mL) was added 10% HCl (3 mL), then the resulting mixture was refluxed for 30 min. After coolling, the solvent was evaporated, and the residue was disolved in $CHCl_3$ (30 mL). To the solution was added K_2CO_3 (3 g), then the suspension was stirred at room temperature for 1 h. Filteration and the evaporation of the filterate gave a colorless oil, which was used directly in the next step. To a stirred solution of the oil in DMF (5 mL) was added imidazole (160 mg, 2.35 mmol) and TBDPSCl (0.41 mL, 1.58 mmol), then the resulting solution was stirred at 80 °C for 40 min. After cooling, the reaction mixture was diluted with $CHCl_3$ (20 mL) and 15% K_2CO_3 (5 mL), and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (10 mL x 5), and the organic extracts were combined, dried over K_2CO_3, and evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (20 g, hexane:acetone=10:1) to give (-)-**11** (755 mg, 85%) as a colorless solid (mp 160~163 °C).

IR (KBr) cm^{-1}: 3501, 3070, 2935, 2891, 2857, 1589, 1448, 1428, 1300, 1289, 1144, 1113, 1085, 1058, 806, 746, 703, 689; ^1H NMR (500 MHz) δ: 0.93 (1H, , *J* = 13.0, 4.5 Hz), 1.06 (9H, s), 1.19 (1H, dm, *J* = 13.0 Hz), 1.24-1.34 (2H, m), 1.39 (1H, qm, *J* = 13.0 Hz), 1.50 (1H, qt-like, *J* = 12.0, 4.5 Hz), 1.59 (1H, dq, *J* = 13.0, 4.5 Hz), 1.67-1.77 (3H, m), 2.61 (1H, dm, *J* = 11.0 Hz), 2.89 (1H, q-like, *J* = 7.5 Hz), 3.18 (1H, dd, *J* = 14.0, 5.5 Hz), 3.20 (1H, br s), 3.18-3.25 (1H, m), 3.61 (1H, dd, *J* = 15.0, 7.0 Hz), 3.69-3.75 (1H, br), 3.71 (1H, dd, *J* = 11.0, 5.5 Hz), 3.88 (1H, dd, *J* = 11.0, 5.0 Hz), 7.34 (2H, t-ike, *J* = 7.5 Hz), 7.42-7.49 (7H, m), 7.70-7.74 (6H, m); ^{13}C NMR (125 MHz) δ: 19.03 (s), 20.34 (t), 22.99 (t), 23.70 (t), 26.74 (q), 26.86 (t), 27.63 (t), 49.48 (d), 49.94 (d), 58.38 (t), 60.44 (d), 66.84 (t), 71.45 (d), 127.81 (d), 127.86 (d), 128.82 (d), 129.92 (d), 129.97 (d), 132.62 (s), 132.81 (s), 133.09 (d), 135.63 (d), 135.65 (d), 140.25 (s); MS: 577 (M^+), 520 (M^+-57), 69 (100); HRMS: Calcd. for $C_{33}H_{43}NO_4S_1Si$: 577.2700, Found: 577.2658; $[\alpha]^{26}_D$ -1.01 (*c* 1.02, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(-)-6-{(2,2-Dimethylethyldiphenylsiloxy)methyl}-7-(methoxymethoxy)-4-(phenylsulfonylmethyl)octahydro-2*H*-quinolizine (12)

To a stirred solution of (-)-**11** (755 mg, 1.31 mmol) in $CHCl_3$ (15 mL) was added MOMCl (0.31 mL, 4.08 mmol) and $(i\text{-Pr})_2EtN$ (0.83 mL, 4.74 mmol), then the resulting solution was refluxed for 40 min. After cooling, the solven was evaporated to give an orange oil, which was chromatographed on SiO_2 (20 g, hexane:acetone=12:1) to give (-)-**12** (753 mg, 93%) as a colorless oil.

IR (neat) cm^{-1}: 2925, 1654, 1648, 1560, 1458, 1448, 1429, 1305, 1036, 742; ^1H NMR (500 MHz) δ: 0.81 (1H, tt, J = 14.0, 4.5 Hz), 1.05 (9H, s), 1.22-1.44 (4H, m), 1.56 (1H, q, J = 12.5, 4.0 Hz), 1.66-1.76 (2H, m), 1.82 (1H, qd, J = 12.5, 4.0 Hz), 2.18 (1H, tt, J = 14.0, 4.9 Hz), 2.64 (1H, dm, J = 11.5 Hz), 2.75 (1H, td, J = 10.0, 4.5 Hz), 3.02 (3H, s), 3.06 (1H, dd, J = 9.0, 6.0 Hz), 3.26 (1H, dd, J = 14.5, 5.5 Hz), 3.79 (1H, dd, J = 10.0, 6.0 Hz), 3.81 (1H, dd, J = 14.0, 7.5 Hz), 3.98 (1H, d, J = 11.0 Hz), 4.23 & 4.39 (2H, ABq, J = 7.0 Hz), 4.46-4.53 (1H, m), 7.36-7.46 (5H, m), 7.54 (1H, tt, J = 7.5, 1.2 Hz), 7.74 (2H, dm, J = 7.5 Hz), 7.81-7.84 (2H, m), 7.88 (2H, dm, J = 7.5 Hz); ^{13}C NMR (125 MHz) δ: 19.11 (s), 20.65 (t), 22.59 (t), 22.63 (t), 22.97 (t), 25.70 (t), 26.69 (q), 26.91 (t), 31.56 (t), 49.31 (d), 50.63 (d), 55.42 (q), 58.22 (t), 61.64 (d), 65.69 (t), 74.61 (d), 95.26 (t), 127.46 (d), 127.70 (d), 127.95 (d), 128.75 (d), 129.44 (d), 129.56 (d), 132.92 (d), 133.37 (s), 133.47 (s), 135.80 (d), 135.85 (t), 141.24 (s); MS: 621 (M^+), 564 (M^+-57), 352 (100); HRMS: Calcd. for $C_{35}H_{47}NO_5S_1Si$: 621.2973, Found: 621.2932; $[\alpha]^{26}_D$ -4.58 (*c* 1.24, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(-)-6-(Hydroxymethyl)-7-(methoxymethoxy)-4-(phenylsulfonylmethyl)octahydro-2*H*-quinolizine (13)

To a stirred solution of (-)-**12** (753 mg, 1.21 mmol) in THF (15 mL) was added pyridine (3.6 mL, 44.5 mmol) and 47% HF (0.91 mL) at 0 °C, then the resulting solution was stirred at room temperature for 1.5 h. The reaction was quenched with 30% K_2CO_3, and the aqueous layer was extracted with $CHCl_3$ (10 mL x 8). The organic extracts were combined, dried over K_2CO_3, and evaporated to give a colorless oil, which was chromatographed on SiO_2 (15 g, hexane:acetone=5:1) to give (-)-**13** (443 mg, 95%) as a colorless oil.

IR (neat) cm^{-1}: 3502, 3064, 2937, 1447, 1405, 1301, 1212, 1144, 1049, 967, 915, 881, 750, 688; ^1H NMR (500 MHz) δ: 0.89-1.00 (2H, m), 1.14 (1H, br d, J = 14.5 Hz), 1.20 (1H, dq, J = 14.0, 3.0 Hz), 1.41 (1H, qm, J = 12.0 Hz), 1.49 (1H, qt, J = 13.0, 4.5 Hz), 1.70 (1H, dm, J = 14.0 Hz), 1.73-1.84 (3H, m), 2.65-2.70 (2H, br m), 3.08 (1H, dd, J = 14.0, 3.0 Hz), 3.35 (1H, br), 3.38 (3H, s), 3.55 (1H, ddd, J = 11.0, 9.0, 4.5 Hz), 3.82-4.00 (4H, m), 4.70 & 4.72 (2H, ABq, J = 6.5 Hz), 7.55 (2H, tm, J = 8.0 Hz), 7.62 (1H, tt, J = 8.0, 1.2 Hz), 7.94 (2H, dm, J = 8.0 Hz); ^{13}C NMR (125 MHz) δ: 20.60 (t), 21.70 (t), 22.71 (t), 25.79 (t), 26.84 (t), 48.72 (d), 49.06 (d), 55.49 (q), 57.16 (t), 59.10 (d), 73.36 (d), 96.13 (t), 127.83 (d), 129.07 (d), 133.41 (d), 140.67 (s); MS: 383 (M^+), 352 (100); HRMS: Calcd. for $C_{19}H_{29}NO_5S$: 383.1730, Found: 383.1751; $[\alpha]^{26}_D$ -3.06 (*c* 1.18, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(+)-6-(Iodomethyl)-7-(methoxymethoxy)-4-(phenylsulfonylmethyl)octahydro-2*H*-quinolizine (14)

To a stirred solution of (-)-**13** (443 mg, 1.16 mmol) in benzene (20 mL) was added imidazole (195 mg, 2.87 mmol), Ph_3P (757 mg, 2.89 mmol) and I_2 (584 mg, 2.30 mmol), then the resulting suspension was stirred at room temperature for 20 min. The reaction was quenched with 10% $Na_2S_2O_3$ in satd. $NaHCO_3$, and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 1, 10 mL x 5). The organic extracts were combined, dried over K_2CO_3, and evaporated to give a pale yellow oil, which was

chromatographed on SiO_2 (20 g, hexane:acetone=15:1) to give (+)-**14** (510 mg, 89%) as a pale yellow oil.

IR (neat) cm^{-1}: 3061, 2934, 1448, 1302, 1199, 1036, 968, 917, 750, 719, 688; ^1H NMR (500 MHz) δ: 1.09 (1H, br d, J = 12.0 Hz), 1.22-1.32 (1H, br m), 1.39-1.55 (3H, m), 1.61-1.81 (4H, m), 1.86-1.93 (1H, br m), 2.16 (1H, br d, J = 8.0 Hz), 2.82 (1H, br d, J = 12.0 Hz), 3.12-3.19 (2H, m), 3.33-3.39 (1H, m), 3.36 (3H, s), 3.43 (1H, br d, J = 10.0 Hz), 3.70 (1H, d-like, J = 10.0 Hz), 3.73 (1H, dd, J = 13.0, 11.0 Hz), 4.64 & 4.69 (2H, ABq, J = 6.8 Hz), 7.55 (2H, t-like, J = 7.5 Hz), 7.63 (1H, t-like, J = 7.5 Hz), 7.93 (2H, d-like, J = 7.5 Hz); ^{13}C NMR (125 MHz) δ: 11.08 (t), 19.77 (t), 19.78 (t), 23.49 (t), 24.93 (t), 27.64 (t), 48.41 (d), 50.24 (d), 55.77 (q), 56.06 (d), 58.71 (t), 76.75 (d), 95.58 (t), 128.06 (d), 129.29 (d), 133.63 (d), 139.94 (s); MS: 493 (M^+), 366 (100); HRMS: Calcd. for $C_{19}H_{28}INO_4S$: 493.0747, Found: 493.0787; $[\alpha]^{26}_D$ +30.9 (*c* 2.78, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(-)-7-(Methoxymethoxy)-6-methyl-4-(phenylsulfonylmethyl)-octahydro-2*H*-quinolizine (15)

To a stirred solution of (+)-**14** (510 mg, 1.03 mmol) in toluene (15 mL) was added *n*-Bu_3SnH (0.35 mL, 1.24 mmol) and AIBN (34 mg, 0.21 mmol), then the resulting solution was refluxed for 16 h. After cooling, the solvent was evaporaed, and the residue was disolved with MeCN (25 mL), and the solution was washed with hexane (6 mL x 8), then the solvent was evaporated. The residue was chromatographed on SiO_2 (15 g, hexane:acetone=14:1) to give (-)-**15** (358 mg, 94%) as a colorless oil.

IR (neat) cm^{-1}: 3061, 2935, 1447, 1304, 1148, 1106, 1086, 1036, 750, 689; ^1H NMR (500 MHz) δ: 0.89-0.94 (1H, m), 0.99 (1H, tt, J = 15.0, 5.0 Hz), 1.04 (3H, d, J = 5.9 Hz), 1.22-1.37 (3H, m), 1.54 (1H, tt, J = 13.0, 4.0 Hz), 1.67-1.83 (4H, m), 2.61 (1H, dm, J = 12.5 Hz), 2.72-2.78 (1H, m), 2.82 (1H, tt, J = 11.0, 4.5 Hz), 3.26 (1H, dd, J = 14.5, 6.0 Hz), 3.35 (3H, s), 3.63 (1H, dd, J = 14.5, 7.0 Hz), 3.82 (1H, br q, J = 5.5 Hz), 4.56 & 4.68 (2H, ABq, J = 7.0 Hz), 7.53 (2H, t-like, J = 8.0 Hz), 7.60 (1H, tt-like, J = 8.0, 1.0 Hz), 7.91 (2H, dm, J = 8.0 Hz); ^{13}C NMR (125 MHz) δ: 15.39 (q), 20.45 (t), 20.97 (t), 22.23 (t), 25.82 (t), 27.70 (t), 48.93 (d), 49.15 (d), 53.02 (d), 55.54 (q), 58.13 (t), 79.31 (d), 95.58 (t), 128.07 (d), 128.84 (d), 133.16 (d), 140.53 (s); MS: 367 (M^+), 212 (100); HRMS: Calcd. for $C_{19}H_{29}NO_4S$: 367.1796, Found: 367.1830; $[\alpha]^{26}_D$ -10.95 (*c* 0.81, $CHCl_3$).

(4*S*,6*S*,7*R*,9a*S*-*cis*)-(-)-4-(Deca-7,9-dienyl)-7-(methoxymethoxy)-6-methyloctahydro-2*H*-quinolizine (16)

To a stirred solution of (-)-**15** (76 mg, 0.21 mmol) in THF (2 mL) was added *n*-BuLi (0.15 mL, 0.23 mmol) at -80 °C, then the resulting solution was stirred for 10 min. To the solution was added *trans*-2-nonenal (0.07 mL, 0.42 mmol) at -80 °C, then the reaction mixture was stirred at -50 °C for 1 h. The reaction was quenched with 15 % K_2CO_3, and the aqueous layer was extracted with $CHCl_3$ (10 mL x 5). The organic extracts were combined, dried over K_2CO_3, and evaporated to give a pale yellow oil, which was used directly in he next step. To a stirred solution of the above oil in MeOH (5 mL) was added Na_2HPO_4 (220 mg, 1.55 mmol) and 5% Na-Hg (1.8 g), then he resulting suspension was stirred at room emperature for 2 h. The reaction was quenched with 15% K_2CO_3, and the aqueous layer was extracted with $CHCl_3$ (10 mL x 4). The organic exracts were combined, dried over K_2CO_3, and evaporated to give a pale yellow oil, which was chromatographed on SiO_2 (15 g, hexane:acetone=20:1) to give (-)-**16** (38 mg, 53%) as a colorless oil.

IR (neat) cm^{-1}: 2926, 1654, 1560, 1543, 1508, 1459, 1104, 1040, 990; ^1H NMR (500 MHz) δ: 0.88 (3H, t, J = 7.0 Hz), 1.12 (3H, d, J = 6.5 Hz), 1.24-1.31 (7H, m), 1.36 (2H, quint-like, J = 7.0 Hz), 1.45-1.56 (3H, m), 1.57-1.64 (2H, m), 1.70-1.76 (2H, m), 1.87 (1H, tt-like, J = 12.5, 3.8 Hz), 1.91-1.99 (1H, m), 2.05 (2H, br q, J = 6.5 Hz), 3.18-3.23 (1H, m), 3.27-3.33 (1H, m), 3.35 (3H, s), 3.39 (1H, q, J = 4.0 Hz), 3.84 (1H, td, J = 8.0, 3.0 Hz), 4.61 (2H, s), 5.52 (1H, dd, J = 14.0, 7.5 Hz), 5.58 (1H, dt, J = 14.0, 7.1 Hz), 6.03 (1H, dd, J = 14.0, 10.0 Hz), 6.09 (1H, dd, J = 14.0, 10.0 Hz); ^{13}C NMR (125 MHz) δ: 14.10 (q), 17.12 (q), 19.68 (t), 22.05 (t), 22.59 (t), 25.92 (t), 28.91 (t), 29.32 (t), 29.38 (t), 31.24 (t), 31.72 (t), 32.63 (t), 49.13 (d), 52.95 (d), 55.27 (q), 57.64 (d), 75.44 (d), 94.42 (t), 130.13 (d), 131.01 (d), 133.35 (d), 136.26 (d); MS: 349 (M^+), 334 (100); HRMS: Calcd. for $C_{22}H_{39}NO_2$: 349.3018, Found: 349.3001; $[\alpha]^{26}_D$ -20.7 (*c* 0.81, $CHCl_3$).

(+)-clavepictine B (2)

To a stirred solution of (-)-**16** (38 mg, 0.11 mmol) in MeOH (2 mL) was added c. HCl (2 drops), then the resulting solution was refluxed for 4 h. After cooling, the reaction was quenched with 15 % K_2CO_3, and the solvent was evaporated. The residue was extracted with hot $CHCl_3$ (5 mL x 10), and the organic extracts were combined, evaporated to give a colorless oil, which was chromatographed on SiO_2 (10 g, $CHCl_3$:MeOH=10:1) to give (+)-**2** (27 mg, 82%) as a colorless solid (mp 70~72 °C, lit[1] mp 70~72 °C).

IR (KBr) cm^{-1}: 3202, 3019, 2923, 2855, 1659, 1443, 1368, 1340, 1278, 1202, 1151, 1055, 1039, 1029, 990, 950; ^1H NMR (500 MHz, C_5D_5N) δ: 0.81 (3H, t, J = 7.0 Hz), 1.15-1.27 (7H, br m), 1.29 (3H, d, J = 6.5 Hz), 1.29-1.35 (2H, m), 1.36-1.43 (1H, m), 1.48-1.59 (2H, m), 1.60-1.72 (3H, m), 1.77-1.86 (2H, m), 1.90-1.96 (1H, m), 2.05 (2H, q, J = 7.0 Hz), 3.11-3.16 (1H, m), 3.32 (1H, quint, J = 6.0 Hz), 3.62 (1H, quint-like, J = 5.0 Hz), 4.04 (1H, br q, J = 5.0 Hz), 5.65 (1H, dt, J = 15.0, 7.0 Hz), 5.78 (1H, d, J = 5.5 Hz), 5.87 (1H, dd, J = 15.0, 7.0 Hz), 6.22 (1H, dd, J = 15.0, 10.0 Hz), 6.38 (1H, dd, J = 15.0, 10.0 Hz); ^{13}C NMR (125 MHz, C_5D_5N) δ: 14.24 (q), 16.79 (q), 20.60 (t), 22.84 (t), 26.07 (t), 27.87 (t), 28.10 (t), 29.12 (t), 29.34 (t), 29.70 (t), 31.92 (t), 32.95 (t), 49.47 (d), 56.67 (d), 57.21 (d), 71.87 (d), 130.87 (d), 131.23 (d), 133.02 (d), 137.03 (d); $[\alpha]^{26}_D$ +25.7 (*c* 0.61, CH_2Cl_2).

(-)-clavepictine A (1)

To a stirred solution of (+)-**2** (25 mg, 0.082 mmol) in pyridine (0.3 mL) was added Ac_2O (0.1 mL), then the resulting solution was stirred at room temperature for 5 h. The volatile was evaporated, and the residue was chromatographed on SiO_2 (10 g, hexane:acetone=16:1) to give (-)-**1** (26 mg, 90%) as a colorless oil.

IR (neat) cm^{-1}: 3016, 2928, 2856, 1736, 1654, 1560, 1458, 1376, 1246, 1162, 1108, 1029, 990, 962; ^1H NMR (500 MHz, C_5D_5N) δ: 0.80 (3H, t, J = 7.1 Hz), 0.95 (1H, dq-like, J = 12.6, 3.0 Hz), 1.10 (3H, d, J = 7.1 Hz), 1.12-1.24 (6H, m), 1.26-1.35 (3H, m), 1.42-1.50 (4H, br m), 1.58 (1H, dm, J = 13.0 Hz), 1.75 (1H, dq, J = 13.0, 4.0 Hz), 1.84 (1H, tt, J = 11.0, 4.0 Hz), 1.93 (1H, qd-like, J = 13.0, 4.0 Hz), 2.04 (2H, q-like, J = 6.0 Hz), 2.15 (3H, s), 3.11 (1H, dm, J = 10.0 Hz), 3.50 (1H, qd-like, J = 7.0, 2.5 Hz), 3.85 (1H, td, J = 8.0, 3.0 Hz), 4.70 (1H, q, J = 3.0 Hz), 5.66 (1H, dd, J = 15.0, 7.0 Hz), 5.73 (1H, dt, J = 15.0, 7.0 Hz), 6.17 (1H, dd, J = 15.0, 10.5 Hz), 6.31 (1H, dd, J = 15.0, 10.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.10 (q), 17.20 (q), 19.68 (t), 20.59 (t), 21.60 (t),

22.59 (t), 25.68 (q), 28.96 (t), 29.29 (t), 31.72 (t), 32.63 (t), 49.00 (d), 52.89 (d), 58.01 (d), 73.29 (d), 129.97 (d), 130.95 (d), 133.58 (d), 136.15 (d), 170.34 (s); $[\alpha]^{26}_{D}$ -74.5 (*c* 0.55, CH_2Cl_2).