Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. $^1$H and $^{13}$C NMR spectra were taken on a Varian Gemini 300 or Unity Plus 500 spectrometer. $^1$H NMR spectra were recorded at the indicated field strength as solutions in CDCl$_3$ unless otherwise indicated. Chemical shifts are given 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, broad. $^{13}$C NMR spectra were recorded at the indicated field strength as solutions in CDCl$_3$ unless otherwise indicated. Chemical shifts are given in parts per million (ppm, δ) 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 = methylene, d = methine, and s = quaternary carbons. Infrared spectra (IR) were measured with a Perkin-Elmer 1600 series FT-IR spectrophotometer. Mass spectra (MS) and high-resolution mass spectra (HRMS) were measured on a JEOL JMS-AX505HAD mass spectrometer. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Column chromatography was performed on Merck silica gel 60 (No 7734-5B) or (No 9385).

**Dimethyl (2R,3S,6S)-(+) -6-(t-Butyldiphenylsilyloxymethyl)-3-vinyl-piperidine-1,2-dicarboxylate (2)**

To a stirred suspension of CuI (1.71 g, 9.00 mmol) in Et$_2$O (15 mL) was added a solution of vinyl lithium, prepared from tetravinyltin (0.37 mL, 4.50 mmol) and MeLi (1.0 M in Et$_2$O, 18 mL, 18.0 mmol) in Et$_2$O (15 mL) at 0 °C for 30 min, at –78 °C, and the resulting suspension was warmed to –35 °C for 20 min. The resulting suspension was re-cooled to –78 °C, and a solution of $^{15}$ (1.05 g, 2.25 mmol) in Et$_2$O (5 mL) was added to the resulting suspension. The reaction mixture was warmed to -30 °C for 1 h, and the reaction was quenched with satd. NH$_4$Cl (aq). The aqueous mixture was diluted with CH$_2$Cl$_2$ (100 mL),
and the resulting suspension was filtered. The filtrate was separated, and the aqueous layer was extracted with CH₂Cl₂ (20 mL x 2). The organic layer and extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (40 g, hexane:acetone=40:1-30:1) to give 2 (1.07 g, 96%) as a colorless oil.

IR (neat) 3071, 2935, 2890, 1750, 1705, 1113 cm⁻¹; ¹H NMR (500 MHz) δ 1.05 (9H, s), 1.41-1.43 (1H, m), 1.59 (1H, br), 1.74-1.81 (1H, br m), 1.85-1.88 (1H, m), 3.00 (1H, br), 3.45 (3H, s), 3.65 (3H, s), 3.67-3.70 (1H, m), 4.28 (1H, br), 4.78 (1H, br), 5.09-5.30 (2H, m), 5.81-5.88 (1H, m), 7.36-7.44 (6H, m), 7.65-7.67 (4H, m); ¹³C NMR (125 MHz) δ 18.68 (t), 19.56 (s), 21.03 (t), 27.15 (q), 37.06 (d), 52.27 (d), 52.34 (q), 53.19 (q), 56.05 (d), 62.34 (t), 115.56 (t), 127.74 (d), 129.72 (d), 133.76 (s), 135.63 (d), 138.91 (d), 157.63 (s), 172.66 (s); MS: 495 (M⁺); HRMS: Calcd for C₂₈H₃₇NO₅Si 495.2441; Found 495.2464; [α]D²⁶ +2.1 (c 1.57, CHCl₃).

Methyl (9S)-(−)-3-Oxo-1,7,8,8a-tetrahydrooxazolo[3,4-a]pyridine-5-carboxylate (3)

To a stirred solution of 1 (3.93 g, 8.42 mmol) in THF (50 mL) was added a solution of TBAF (1M in THF, 9.3 mL, 9.3 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. The reaction was quenched with satd NH₄Cl (aq), and the aqueous mixture was extracted with CHCl₃ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (50 g, hexane:acetone=15:1-3:1) to give dimethyl (6S)-(−)-6-hydroxymethyl-5,6-dihydro-4H-pyridine-1,2-dicarboxylate (1.74 g, 90%) as colorless oil.

IR (neat) 3484, 1714, 1647, 1241 cm⁻¹; ¹H NMR (500 MHz) δ 1.78-1.83 (1H, m), 1.88-1.95 (1H, br m), 2.10-2.22 (2H, m), 2.48 (1H, br), 3.47-3.52 (1H, br m), 3.56-3.61 (1H, br m), 3.71 (3H, s), 3.76 (3H, s), 4.45-4.52 (1H, br m), 6.15 (1H, t, J = 3.8 Hz); ¹³C NMR (125 MHz) δ 20.15 (t), 23.71 (t), 52.53 (q), 53.55 & 53.63 (each q), 53.72 (d), 61.13 (t), 123.98
To a stirred solution of dimethyl (6S)-(-)-6-hydroxymethyl-5,6-dihydro-4H-pyridine-1,2-dicarboxylate (55 mg, 0.24 mmol) in THF (3 mL) was added NaH (60%, 11 mg, 0.26 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 0.5 h. The reaction was quenched with 10% AcOH (aq) and the aqueous mixture was extracted with CH₂Cl₂ (5 mL x 4). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (10 g, hexane:acetone=3:1) to give 3 (45 mg, 95%) as colorless solid (mp 85-86 °C).

IR (KBr) 1761, 1645, 1219 cm⁻¹; ¹H NMR (500 MHz) δ 1.71-1.80 (1H, m), 1.96-2.00 (1H, m), 2.25-2.34 (1H, m), 2.38-2.44 (1H, m), 3.80 (1H, s), 3.79-3.85 (1H, m), 4.10 (1H, dd, J = 9, 2.7 Hz), 4.55 (1H, t, J = 8.4 Hz), 6.28-6.30 (1H, m); ¹³C NMR (125 MHz) δ 22.56 (t), 26.30 (t), 52.33 (q), 52.53 (d), 67.50 (t), 124.25 (d), 128.93 (s), 155.01 (s), 163.18 (s); MS: 197 (M⁺); HRMS: Calcd for C₉H₁₁NO₄ 197.0688; Found 197.0659; [α]D²⁶ –18.2 (c 2.05, CHCl₃).

Methyl (5S,6R,9S)-(+) -3-Oxo-6-vinylhexahydrooxazolo[3,4-a]pyridine-5-carboxylate (4)

To a stirred suspension of CuI (1.39 g, 7.31 mmol) in Et₂O (8 mL) was added a solution of vinyl lithium, prepared from tetravinyltin (0.30 mL, 3.65 mmol) and MeLi (1.0 M in Et₂O, 15 mL, 15.0 mmol) in Et₂O (6 mL) at 0 °C for 30 min, at −78 °C, and the resulting suspension was warmed to −35 °C for 20 min. The resulting suspension was re-cooled to −78 °C, and a solution of 3 (360 mg, 1.83 mmol) in Et₂O (2 mL) and THF (2 mL) was added to the resulting suspension. The reaction mixture was warmed to -30 °C for 1 h, and the
reaction was quenched with satd. \( \text{NH}_2\text{Cl} \) (aq). The aqueous mixture was diluted with \( \text{CH}_2\text{Cl}_2 \) (80 mL), and the resulting suspension was filtered. The filtrate was separated, and the aqueous layer was extracted with \( \text{CH}_2\text{Cl}_2 \) (10 mL \( \times \) 2). The organic layer and extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on \( \text{SiO}_2 \) (20 g, hexane:acetone=15:1-10:1) to give 4 (319 mg, 78%) as colorless oil.

IR (neat) 1743, 1641, 1262 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \( \delta \) 1.53-1.58 (1H, m), 1.63-1.70 (2H, m), 1.81 (1H, d-like, \( J = 13 \) Hz), 3.00 (1H, br), 3.77 (3H, s), 3.90 (1H, t, \( J = 8.2 \) Hz), 4.00-4.10 (1H, m), 4.51 (1H, t, \( J = 8.2 \) Hz), 4.59 (1H, br s), 5.19-5.24 (2H, m), 5.83-5.90 (1H, m); \(^{13}\)C NMR (125 MHz) \( \delta \) 24.79 (t), 24.99 (t), 37.42 (d), 51.88 (d), 52.79 (q), 55.46 (d), 69.27 (t), 116.61 (t), 137.28 (d), 157.31 (s), 170.73 (s); MS: 225 (\( M^+ \)); HRMS: Calcd for \( \text{C}_{11}\text{H}_{15}\text{NO}_4 \) 225.1001; Found 225.0981; \([\alpha]_D^{26} +36.7 \) (\( c 2.23, \text{CHCl}_3 \)).

**Methyl (2S,3S,6S)-(-)-6-(t-Butyldiphenylsilyloxymethyl)-2-{(methoxy-carbonyl)methyl}-3-vinylpiperidine-1-carboxylate (5)**

To a stirred solution of 2 (2.93 g, 5.92 mmol) in MeOH (15 mL) and H\(_2\)O (5 mL) was added LiOH•H\(_2\)O (501 mg, 11.8 mmol), and the resulting solution was refluxed for 2 h. After cooling, the MeOH was evaporated and the residue was acidified with 10% HCl solution (aq). The aqueous mixture was extracted with EtOAc (20 mL \( \times \) 5). The organic extracts were combined, dried, and evaporated to give colorless paste, which was used directly in the next step. To a stirred solution of the above oil in THF (50 mL) were added Cl\(\text{CO}_2\)Et (0.62 mL, 6.51 mmol) and Et\(_3\)N (0.91 mL, 6.51 mmol) at 0 °C, and the resulting suspension was stirred at 0 °C for 1 h. The reaction mixture was diluted with Et\(_2\)O (50 mL) and Et\(_3\)N•HCl was filtered off. The filtrate was evaporated to give colorless oil, which was used directly in the next step. To a stirred solution of the above oil in Et\(_2\)O (20 mL) was added a solution of CH\(_2\)N\(_2\) in Et\(_2\)O at 0 °C, and the reaction mixture was stirred at room temperature for 15 h.
The solvent was evaporated to give pale yellow oil, which was dissolved in MeOH (50 mL). To the MeOH solution were added AgCO\textsubscript{2}Ph (136 mg, 0.59 mmol) and Et\textsubscript{3}N (1.7 mL, 11.8 mmol), and the resulting suspension was stirred at room temperature for 9 h. The reaction mixture was diluted with Et\textsubscript{2}O and the insoluble material was filtered off. The filtrate was evaporated to give pale yellow oil, which was chromatographed on SiO\textsubscript{2} (50 g, hexane:acetone=60:1−50:1) to give 5 (2.4 g, 80%) as colorless oil.

IR (neat) 1739, 1698, 1109 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz) \(\delta\) 1.06 (9H, s), 1.37-1.40 (1H, br m), 1.65-1.69 (2H, br), 1.78-1.82 (1H, m), 2.28 (1H, br), 2.38-2.47 (2H, m), 3.58-3.60 (2H, br), 3.61 (3H, s), 3.64 (3H, s), 4.34 (1H, br), 4.58 (1H, br), 5.07-5.10 (2H, m), 5.81-5.87 (1H, m), 7.39-7.45 (6H, m), 7.67-7.68 (4H, m); \textsuperscript{13}C NMR (125 MHz) \(\delta\) 19.09 (t), 19.27 (s), 19.92 (t), 26.89 (q), 39.50 (d), 39.79 (t), 50.70 (d), 51.28 (d), 51.68 (q), 52.72 (q), 63.93 (t), 115.11 (t), 127.60 (d), 129.60 (d), 133.30 (s), 135.46 (d), 139.71 (d), 156.63 (s), 171.33 (s); MS: 509 (M\textsuperscript{+}); HRMS: Calcd for C\textsubscript{29}H\textsubscript{39}NO\textsubscript{5}Si 509.2598; Found 509.2608; [\(\alpha\)]\textsubscript{D}\textsuperscript{26} –35.3 (c 3.04, CHCl\textsubscript{3}).

**Methyl (5R,6R,9S)-(+-)(3-Oxo-6-vinylhexahydrooxazolo[3,4-a]pyridin-5-yl)acetate (6)**

To a stirred solution of 4 (1.28 g, 5.69 mmol) in MeOH (12 mL) and H\textsubscript{2}O (4 mL) was added LiOH•H\textsubscript{2}O (477 mg, 11.4 mmol), and the resulting mixture was refluxed for 1.5 h. After cooling, the MeOH was evaporated and the aqueous residue was acidified with 10% HCl (aq). The aqueous layer was extracted with EtOAc (20 mL x 5), and the organic extracts were combined, dried, and evaporated to give pale yellow solid, which was used directly in the next step. To a stirred solution of the above solid in THF (40 mL) were added ClCO\textsubscript{2}Et (0.6 mL, 6.26 mmol) and Et\textsubscript{3}N (0.87 mL, 6.26 mmol) at 0 °C, and the resulting suspension was stirred at 0 °C for 1 h. The insoluble Et\textsubscript{3}N•HCl was filtered off, washed with Et\textsubscript{2}O, and the filtrate and washing were combined and evaporated to give colorless oil, which was used
directly in the next step. To a stirred solution of the above oil in Et₂O (5 mL) was added a solution of CH₂N₂ in Et₂O at 0 °C, and the reaction mixture was stirred at room temperature for 8 h. The solvent was evaporated to give pale yellow oil, which was dissolved in MeOH (40 mL). To the MeOH solution were added AgCO₂Ph (130 mg, 0.57 mmol) and Et₃N (1.6 mL, 11.4 mmol), and the resulting suspension was stirred at room temperature for 12 h. The insoluble material was filtered off, and the filtrate was evaporated to give pale brown oil, which was chromatographed on SiO₂ (40 g, hexane:acetone=15:1-10:1) to give 6 (795 mg, 59%) as colorless oil.

IR (neat) 1744, 1642, 1172 cm⁻¹; ¹H NMR (500 MHz) δ 1.53-1.61 (1H, m), 1.65-1.69 (1H, m), 1.76 (1H, dq, J = 14, 3.5 Hz), 1.85 (1H, tt, J = 13, 5 Hz), 2.39-2.40 (1H, br), 2.59 (1H, dd, J = 14, 7 Hz), 2.68 (1H, dd, J = 14, 8 Hz), 3.69 (3H, s), 3.80-3.90 (2H, br m), 4.41 (1H, quint, J = 8 Hz), 5.14-5.30 (2H, m), 5.83-5.90 (1H, m); ¹³C NMR (125 MHz) δ 23.55 (t), 25.64 (t), 36.23 (t), 38.90 (d), 50.23 (d), 50.44 (d), 52.22 (q), 68.74 (t), 116.29 (t), 138.28 (d), 156.84 (s), 170.77 (s); MS: 239 (M⁺), 208 (100); HRMS: Calcd for C₁₂H₁₇NO₄ 239.1158; Found 239.1175; [α]D²⁶ +9.5 (c 4.47, CHCl₃).

**M e t h y l (2S,3S,6S)-(-)-6-(t-Butyldiphenylsilyloxymethyl)-2-{(methoxy-methylcarbamoyl)methyl}-3-vinylpiperidine-1-carboxylate (7)**

To a stirred solution of 5 (870 mg, 1.71 mmol) in MeOH (3 mL) and H₂O (1 mL) was added LiOH•H₂O (148 mg, 3.52 mmol), and the resulting solution was refluxed for 1 h. After cooling, the MeOH was evaporated and the residue was acidified with 10% HCl solution (aq). The aqueous mixture was extracted with EtOAc (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless paste, which was used directly in the next step. To a stirred solution of the above paste in CH₂Cl₂ (5 mL) was added 1,1’-carbonyldiimidazole (372 mg, 2.29 mmol) at 0 °C, and the resulting solution was stirred for
To the reaction mixture were added MeON(Me)H•HCl (224 mg, 2.29 mmol) and Et₃N (0.32 mL, 2.29 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated and the residue was chromatographed on SiO₂ (30 g, hexane:acetone=15:1) to give 7 (741 mg, 81%) as colorless paste.

IR (neat) 1695, 1444, 1109 cm⁻¹; ¹H NMR (500 MHz) δ 1.05 (9H, s), 1.39-1.42 (1H, br m), 1.64-1.83 (3H, br m), 2.17-2.63 (3H, br), 3.11 (3H, br s), 3.52 (3H, br s), 3.57-3.61 (2H, m), 3.65 (3H, br s), 4.40 (1H, br), 4.65 (1H, br), 5.06-5.12 (2H, m), 5.84-5.91 (1H, m), 7.37-7.45 (6H, m), 7.68-7.70 (4H, m); ¹³C NMR (125 MHz) δ 18.91 (t), 19.20 (s), 19.56 (t), 26.77 (q), 32.07 (q), 36.97 (t), 38.73 (d), 50.29 (d), 51.10 (d), 52.57 (q), 53.39 (t), 61.07 (q), 63.81 (t), 114.82 (t), 127.51 (d), 129.49 (d), 133.24 (s), 135.31 (d), 139.89 (d), 156.58 (s), 171.58 (s); MS: 538 (M⁺); HRMS: Calcd for C₃₀H₄₂N₂O₅Si 538.2863; Found 538.2817; [α]D²⁶ –34.2 (c 1.21, CHCl₃).

(5R,6R,9S)-(+)–N-Methoxy-N-methyl-2-(3-oxo-6-vinylhexahydro-oxazolo[3,4-a]pyridin-5-yl)acetamide (8)

To a stirred solution of 6 (464 mg, 1.94 mmol) in MeOH (6 mL) and H₂O (2 mL) was added LiOH•H₂O (163 mg, 3.88 mmol), and the resulting solution was refluxed for 2 h. After cooling, the MeOH was evaporated and the residue was acidified with 10% HCl solution (aq). The aqueous mixture was extracted with EtOAc (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless solid, which was used directly in the next step. To a stirred solution of the above solid in CH₂Cl₂ (15 mL) was added 1,1’-carbonyldiimidazole (409 mg, 2.52 mmol) at 0 °C, and the resulting solution was stirred for 0.5 h. To the reaction mixture were added MeON(Me)H•HCl (246 mg, 2.52 mmol) and Et₃N (0.35 mL, 2.52 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 20 h. The solvent was evaporated and the residue was chromatographed on
SiO₂ (30 g, hexane:acetone=8:1-4:1) to give 8 (480 mg, 92%) as colorless solid (mp 101-102 °C).

IR (KBr) 1738, 1651, 1271, 1190 cm⁻¹; ¹H NMR (500 MHz) δ 1.54-1.59 (1H, m), 1.65-1.68 (1H, m), 1.74-1.77 (1H, m), 1.91 (1H, tt, J = 14, 4 Hz), 2.48 (1H, br), 2.70 (1H, dd, J = 14, 8 Hz), 2.77-2.81 (1H, m), 3.17 (3H, br s), 3.84-3.92 (2H, m), 4.41-4.44 (2H, m), 5.14-5.21 (2H, m), 5.85-5.92 (1H, m); ¹³C NMR (125 MHz) δ 23.42 (t), 25.51 (t), 32.30 (q), 34.15 (t), 34.70 (q), 38.63 (d), 49.76 (d), 50.61 (d), 61.43 (q), 61.52 (q), 68.69 (t), 115.84 (t), 129.28 (s), 138.60 (d), 156.79 (s), 170.90 (s); MS: 268 (M⁺), 166 (100); HRMS: Calcd for C₁₃H₂₀N₂O₄ 268.1423; Found 268.1392; [α]D²⁶ +29.6 (c 2.03, CHCl₃).

M e t h y l (2S,3S,6S)-(−)-6-(t-Butyldiphenylsilyloxy)methyl)-2-(2-oxopropyl)-3-vinylpiperidine-1-carboxylate (9)

To a stirred solution of 7 (1.04 g, 1.93 mmol) in THF (20 mL) was added a solution of MeMgBr (0.9 M in THF, 3.2 mL, 2.90 mmol) at 0 °C, and the resulting solution was stirred at room temperature for 1 h. The reaction was quenched with satd. NH₄Cl (aq), and the aqueous mixture was extracted with CH₂Cl₂ (20 mL x 3). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (30 g, hexane:acetone=20:1) to give 9 (910 mg, 96%) as colorless oil.

IR (neat) 1696, 1109 cm⁻¹; ¹H NMR (500 MHz) δ 1.06 (9H, s), 1.27-1.39 (1H, m), 1.63-1.65 (2H, br), 1.76-1.81 (1H, m), 2.09 (3H, s), 2.17-2.24 (1H, br), 2.48-2.50 (2H, m), 3.56-3.57 (2H, m), 3.63 (3H, s), 4.34 (1H, br), 4.56 (1H, br), 5.06-5.09 (2H, m), 5.85-5.89 (1H, m), 7.39-7.45 (6H, m), 7.65-7.67 (4H, m); ¹³C NMR (125 MHz) δ 19.20 (t), 19.42 (s), 19.92 (t), 27.04 (q), 30.10 (q), 39.53 (d), 49.34 (t), 49.95 (d), 51.39 (d), 52.80 (q), 64.05 (t), 115.25 (t), 127.78 (d), 129.82 (d), 133.38 (s), 135.59 (d), 139.91 (d), 156.82 (s), 206.28 (s); MS: 493
(M⁺); HRMS: Calcd for C₂₉H₃₉NO₄Si 493.2648; Found 493.2621; [α]D²⁶ –51.5 (c 3.27, CHCl₃).

(5R,6R,9S)-(−)-5-(2-Oxopropyl)-6-vinylhexahydrooxazolo[3,4-a]pyridin-3-one (10)

To a stirred solution of 8 (110 mg, 0.41 mmol) in THF (4 mL) was added a solution of MeMgBr (0.9 M in THF, 0.69 mL, 0.62 mmol) at 0 °C, and the resulting solution was stirred at room temperature for 1 h. The reaction was quenched with satd NH₄Cl (aq), and the aqueous mixture was extracted with CH₂Cl₂ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (15 g, hexane:acetone=5:1) to give 10 (85.3 mg, 93%) as colorless solid (mp 82-83 °C).

IR (KBr) 1729, 1423, 1265 cm⁻¹; ¹H NMR (500 MHz) δ 1.55-1.66 (2H, m), 1.75 (1H, dm, J = 10.9 Hz), 1.81-1.87 (1H, m), 2.22 (3H, s), 2.36 (1H, br), 2.69-2.77 (2H, br m), 3.77-3.83 (1H, m), 3.87 (1H, dd, J = 8.5, 6.4 Hz), 4.38-4.45 (2H, m), 5.16 (1H, d-like, J = 10.5 Hz), 5.20 (1H, d-like, J = 17 Hz), 5.85-5.91 (1H, m); ¹³C NMR (125 MHz) δ 23.42 (t), 25.52 (t), 29.97 (q), 38.90 (d), 45.17 (t), 49.44 (d), 50.49 (d), 68.83 (t), 116.10 (t), 138.34 (d), 156.85 (s), 205.80 (s); MS: 223 (M⁺), 179 (100); HRMS: Calcd for C₁₂H₁₇NO₃ 223.1208; Found 223.1202; [α]D²⁶ –17.0 (c 1.46, CHCl₃).

Methyl (2S,3R,6S)-(−)-6-(t-Butyldiphenylsilyloxymethyl)-3-formyl-2-(2-oxopropylpiperidine-1-carboxylate (11)

To a stirred solution of 9 (300 mg, 0.61 mmol) in dioxane (3.5 mL) and H₂O (3.5 mL) was added a solution of OsO₄ (13 drops, 4% aqueous solution) at room temperature, and the reaction mixture was stirred at room temperature for 10 min. To the reaction mixture was added NaIO₄ (130 mg, 0.61 mmol) and the resulting mixture was stirred for 1 h. Additional sodium metaperiodate (130 mg, 0.61 mmol) was added to the reaction mixture and the
stirring was continued for additional 1 h. After 3 h, a solution of OsO$_4$ (2 drops) was added to the reaction mixture and the stirring was continued for 3 h. The reaction was quenched with 10% Na$_2$S$_2$O$_3$ in satd NaHCO$_3$ (aq), and the aqueous mixture was extracted with CH$_2$Cl$_2$ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give pale yellow oil, which was chromatographed on SiO$_2$ (15 g, hexane:acetone=15:1) to give 11 (218 mg, 79%) and 9 (29 mg, 9.7%) as colorless oil, respectively.

IR (neat) 1697, 1109 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 1.06 (9H, s), 1.56 (2H, m), 1.71-1.72 (1H, m), 1.92 (1H, br), 2.09 (3H, br s), 2.37-2.66 (3H, br), 3.56 (2H, br d-like, $J$ = 7.8 Hz), 3.64 (3H, br s), 4.23 (1H, br), 5.11 (1H, br), 7.41-7.47 (6H, m), 7.66-7.67 (4H, m), 9.68 (1H, s); $^{13}$C NMR (125 MHz) $\delta$ 14.62 (t), 19.29 (s), 20.57 (t), 26.93 (q), 30.25 (q), 45.04 (d), 47.98 (t), 48.89 (d), 51.02 (d), 52.88 (q), 53.56 (t), 63.59 (t), 127.75 (d), 129.78 & 129.82 (each d), 133.05 & 133.13 (each s), 135.48 (d), 156.38 (s), 202. 45 (s), 205.99 (s); MS: 495 (M$^+$), 454 (100); HRMS: Calcd for C$_{28}$H$_{37}$NO$_5$Si 495.2441; Found 495.2453; $\left[\alpha\right]_D^{26}$ –69.2 ($c$ 0.99, CHCl$_3$).

(5R,6S,9S)-(+)-6-Formyl-5-(2-oxopropyl)hexahydrooxazolo[3,4-a]pyridin-3-one (12)

To a stirred solution of 10 (364 mg, 1.63 mmol) in dioxane (7 mL) and H$_2$O (7 mL) was added a solution of OsO$_4$ (14 drops, 4% aqueous solution) at room temperature, and the reaction mixture was stirred at room temperature for 15 min. To the reaction mixture was added NaIO$_4$ (350 mg, 1.63 mmol) and the resulting mixture was stirred for 1 h. Additional sodium metaperiodate (350 mg, 1.63 mmol) was added to the reaction mixture and the stirring was continued for additional 3 h. The reaction was quenched with 10% Na$_2$S$_2$O$_3$ in satd NaHCO$_3$ (aq), and the aqueous mixture was extracted with CH$_2$Cl$_2$ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give pale yellow oil, which was
chromatographed on SiO$_2$ (25 g, hexane:acetone=4:1) to give 12 (320 mg, 87%) as colorless solid (mp 96-98 °C).

IR (KBr) 1743, 1419 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 1.31-1.38 (1H, m), 1.66-1.77 (2H, m), 2.22 (3H, s), 2.27 (1H, d-like, $J = 15.4$ Hz), 2.54 (1H, br), 2.78 (1H, dd, $J = 16$, 5.5 Hz), 2.79-2.84 (1H, m), 2.89 (1H, dd, $J = 16$, 9.2 Hz), 3.71-3.77 (1H, m), 3.79-3.82 (1H, m), 4.38 (1H, t-like, $J = 8$ Hz), 4.92-4.95 (1H, m), 9.72 (1H, s); $^{13}$C NMR (125 MHz) $\delta$ 17.98 (t), 26.59 (t), 30.36 (q), 43.94 (t), 44.94 (d), 48.26 (d), 50.46 (d), 68.69 (t), 156.33 (s), 201.51 (s); MS: 225 (M$^+$), 140 (100); HRMS: Calcd for C$_{11}$H$_{15}$NO$_4$ 225.1001; Found 225.0992; $[\alpha]_D$ $^{26}$ +75.1 (c 2.20, CHCl$_3$).

Methyl (2$S$,4$aR$,8$aS$)-(-)-2-(t-Butyldiphenylsilyloxymethyl)-7-oxo-3,4,4$a$,8$a$-hexahydro-2$H$-quinoline-1-carboxylate (13) and Methyl (2$S$,4$aS$,8$aS$)-(−)-2-(t-Butyldiphenylsilyloxymethyl)-7-oxo-3,4,4$a$,8$a$-hexahydro-2$H$-quinoline-1-carboxylate (13’)

To a stirred solution of 11 (640 mg, 1.29 mmol) in benzene (40 mL) was added DBU (0.77 mL, 5.17 mmol), and the resulting solution was refluxed for 48 h using Dean-Stark apparatus. After cooling, the reaction mixture was diluted with benzene (10 mL) and the organic layer was washed with 10% HCl (aq) and H$_2$O successively, dried, and evaporated to give pale yellow oil, which was chromatographed on SiO$_2$ (30 g, hexane:acetone=25:1-20:1) to give the 4$a$,8$a$-trans enone (28.3 mg, 4.6%) and 13 (321 mg, 52%) as colorless form, respectively.

4$a$,8$a$-trans-enone 13’:

IR (neat) 1687 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 1.05 (9H, s), 1.60 (1H, br m), 1.82-1.91 (2H, m), 2.08-2.11 (1H, m), 2.13 (1H, dd, $J = 16.6$, 12.5 Hz), 2.25-2.37 (1H, br), 2.60 (1H, t-like, $J = 13.2$ Hz), 3.26 (1H, dd, $J = 16.6$, 3.2 Hz), 3.63-3.75 (2H, m), 3.67 (3H, s), 4.40-4.45 (1H,
(3aS,5aS,9aR)-(−)-3a,4,5,5a,9,9a-Hexahydro-3H-oxazolo[3,4-a]quinoline-1,8-dione (14)

To a stirred solution of 12 (57 mg, 0.25 mmol) in benzene (10 mL) was added DBU (0.15 mL, 1.01 mmol), and the resulting solution was refluxed for 48 h using Dean-Stark apparatus. After cooling, the reaction mixture was diluted with benzene (10 mL) and the organic layer was washed with 10% HCl (aq) and H₂O successively, dried, and evaporated to give pale yellow oil, which was chromatographed on SiO₂ (10 g, hexane:acetone=6:1-5:1) to give 14 (26.6 mg, 51%) as colorless oil.

IR (neat) 1743, 1676 cm⁻¹; ¹H NMR (500 MHz) δ 1.41-1.55 (2H, m), 1.92-1.96 (1H, m), 2.01-2.04 (1H, m), 2.47-2.56 (2H, m), 2.66 (1H, dd, J = 16, 14 Hz), 3.79-3.84 (1H, m), 3.97 (1H, dd, J = 9, 6 Hz), 4.42-4.47 (2H, m), 6.04 (1H, d, J = 10 Hz), 6.92 (1H, dd, J = 10, 6 Hz); ¹³C NMR (125 MHz) δ 24.23 (t), 29.70 (t), 35.46 (d), 37.08 (t), 48.03 (d), 50.33 (d), 68.22 (t), 129.43 (d), 151.14 (d), 156.38 (s), 196.69 (s); MS: 207 (M⁺), 206 (100); HRMS: Calcd for C₁₁H₁₃NO₃ 207.0895; Found 207.0927; [α]D²⁶ −97.7 (c 5.36, CHCl₃).
**Methyl (2S,3S,6S)-(-)-6-(Hydroxymethyl)-2-(2-oxopropyl)-3-vinylpiperidine-1-carboxylate (15)**

To a stirred solution of 9 (1.91 g, 3.87 mmol) in THF (28 mL) was added a solution of TBAF (1 M in THF, 4.3 mL, 4.3 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. The reaction was quenched with satd. NH₄Cl (aq), and the aqueous mixture was extracted with CHCl₃ (15 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (40 g, hexane:acetone=10:1-3:1) to give 15 (847 mg, 86%) as colorless oil.

IR (neat) 3445, 3077, 1690, 1447, 1360, cm⁻¹; ¹H NMR (500 MHz) δ 1.38-1.44 (2H, br m), 1.72-1.87 (1H, m), 2.19 (1H, br), 2.23 (3H, s), 2.54 (1H, dd, J = 14, 6.5 Hz), 2.79 (1H, dd, J = 14, 4.5 Hz), 3.63 (2H, br), 3.64 (3H, s), 4.31 (1H, br), 4.56 (1H, br), 5.06-5.09 (2H, m), 5.78-5.85 (1H, m); ¹³C NMR (125 MHz) δ 20.42 (t), 21.63 (t), 30.44 (q), 41.76 (d), 49.48 (t), 50.97 (d), 52.07 (d), 52.93 (q), 64.66 (t), 115.38 (t), 139.66 (d), 157.66 (s), 208.44 (s); MS: 255 (M⁺); HRMS: Calcd for C₁₃H₂₁NO₄ 255.1469; Found 255.1487; [α]D²⁶ +16.1 (c 2.77, CHCl₃).

**(5R,6R,9S)-(+-)-5-(2-oxopropyl)-6-vinylhexahydrooxazolo[3,4-a]pyridin-3-one (16)**

To a stirred solution of 15 (847 mg, 3.32 mmol) in THF (20 mL) was added NaH (60%, 146 mg, 3.65 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 0.5 h. The reaction was quenched with 10% AcOH (aq), and the aqueous mixture was extracted with CH₂Cl₂ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (30 g, hexane:acetone=8:1-5:1) to give 16 (575 mg, 78%) as a colorless oil.

IR (neat) 1744, 1642, 1279 cm⁻¹; ¹H NMR (500 MHz) δ 1.44-1.48 (2H, br m), 1.82-1.89 (2H, br m), 2.04-2.07 (1H, m), 2.19 (3H, s), 2.62 (1H, dd, J = 17, 3 Hz), 3.49 (1H, dd, J =
17. 9.6 Hz), 3.56 (1H, dt, J = 10, 3.2 Hz), 3.66-3.68 (1H, br), 3.80 (1H, dd, J = 8.1, 6 Hz),
4.32 (1H, t, J = 8.1 Hz), 5.06-5.14 (2H, m), 5.43-5.51 (1H, m); 13C NMR (125 MHz) δ 29.80 (t), 29.98 (q), 30.76 (t), 42.64 (t), 46.13 (d), 54.28 (d), 56.61 (d), 66.95 (t), 117.74 (t), 138.59 (d), 156.16 (s), 206.04 (s); MS: 223 (M+); HRMS: Calcd for C_{12}H_{17}NO_{3} 223.1208; Found 223.1229; [α]_{D}^{26} –9.73 (c 2.39, CHCl_{3}).

(5S,6R,9S)-(+) -6-Formyl-5-(2-oxopropyl)hexahydrooxazolo[3,4-a]pyridin-3-one (17)

To a stirred solution of 16 (85 mg, 0.38 mmol) in dioxane (2 mL) and H_{2}O (2 mL) was added a solution of OsO_{4} (5 drops, 4% aqueous solution) at room temperature, and the reaction mixture was stirred at room temperature for 15 min. To the reaction mixture was added NaIO_{4} (82 mg, 0.38 mmol) and the resulting mixture was stirred for 1 h. Additional sodium metaperiodate (82 mg, 0.38 mmol) was added to the reaction mixture and the stirring was continued for additional 4 h. The reaction was quenched with 10% Na_{2}S_{2}O_{3} in satd NaHCO_{3} (aq), and the aqueous mixture was extracted with CH_{2}Cl_{2} (10 mL x 5). The organic extracts were combined, dried, and evaporated to give pale yellow oil, which was chromatographed on SiO_{2} (10 g, hexane:acetone=4:1) to give 17 (54 mg, 63%) as colorless solid (mp 104-105 °C).

IR (KBr) 1742, 1650, 1427 cm\(^{-1}\); 1H NMR (500 MHz) δ 1.47-1.62 (2H, br m), 1.94-1.98 (1H, m), 2.15-2.19 (1H, m), 2.20 (3H, s), 2.56 (1H, dd, J = 11, 3.3 Hz), 2.72 (1H, dd, J = 18, 3.7 Hz), 3.54 (1H, dd, J = 18, 9 Hz), 3.67-3.71 (1H, m), 3.84 (1H, dd, J = 8.5, 5.9 Hz), 3.98-4.02 (1H, m), 4.36 (1H, t, J = 8.5 Hz), 9.57 (1H, s); 13C NMR (125 MHz) δ 24.62 (t), 29.08 (t), 30.05 (q), 42.48 (t), 50.65 (d), 52.33 (d), 56.31 (d), 67.02 (t), 156.14 (s), 200.93 (s); MS: 225 (M+), 168 (100); HRMS: Calcd for C_{11}H_{13}NO_{4} 225.1001; Found 225.1027; [α]_{D}^{26} –17.5 (c 1.48, CHCl_{3}).
(5S,6S,9S)-(−)-5-(Methoxycarbonylmethyl)-6-vinylhexahydrooxazolo[3,4-a]pyridin-3-one (19)

To a stirred solution of 5 (1.28 g, 2.52 mmol) in THF (10 mL) was added a solution of TBAF (1 M in THF, 2.8 mL, 2.8 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. The reaction was quenched with satd. NH₄Cl (aq), and the aqueous mixture was extracted with CH₂Cl₂ (15 mL × 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (20 g, hexane:acetone=30:1-5:1) to give methyl (2S,3S,6S)-(−)-6-(hydroxymethyl)-2-methoxycarbonylmethyl-3-vinyl-piperidine-1-carboxylate (543 mg, 80%) as colorless oil.

IR (neat) 3421, 1732, 1694, cm⁻¹; ¹H NMR (500 MHz) δ 1.41-1.48 (2H, br m), 1.75-1.89 (2H, br m), 2.23 (1H, br), 2.55 (2H, d, J = 7.3 Hz), 3.60-3.65 (1H, m), 3.66 (3H, s), 3.67 (3H, s), 4.32-4.33 (1H, br), 4.55-4.58 (1H, br), 5.05-5.09 (2H, m), 5.77-5.84 (1H, m); ¹³C NMR (125 MHz) δ 20.15 (t), 21.27 (t), 40.32 (t), 41.17 (d), 51.35 (d), 52.05 (q), 52.05 (d), 52.90 (q), 64.63 (t), 115.35 (t), 139.60 (d), 157.67 (s), 172.55 (s); MS: 271 (M⁺); HRMS: Calcd for C₁₅H₂₁NO₅ 271.1418; Found 271.1429; [α]D²⁶ +0.16 (c 2.18, CHCl₃).

To a stirred solution of methyl (2S,3S,6S)-(−)-6-(hydroxymethyl)-2-methoxycarbonylmethyl-3-vinyl-piperidine-1-carboxylate (543 mg, 2 mmol) in THF (5 mL) was added NaH (60%, 88 mg, 2.2 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with 10% AcOH (aq), and the aqueous mixture was extracted with CH₂Cl₂ (10 mL × 4). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (20 g, hexane:acetone=30:1-6:1) to give 19 (408 mg, 85%) as a colorless oil.

IR (neat) 1745, 1641, cm⁻¹; ¹H NMR (500 MHz) δ 1.43-1.54 (2H, br m), 1.82-1.88 (1H, m), 1.89-1.92 (1H, m), 2.09-2.15 (1H, m), 2.77 (1H, dd, J = 17, 4 Hz), 3.27 (1H, dd, J = 17. 9
(5S,6S,9S)-5-(2-Hydroxyethyl)-6-vinylhexahydrooxazolo[3,4-a]pyridin-3-one (20)

To a stirred solution of **19** (239 mg, 1 mmol) in THF (8 mL) was added a solution of Super-Hydride (1 M in THF, 2.2 mL, 2.2 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with satd. NaHCO₃ (aq), and the aqueous mixture was extracted with CH₂Cl₂ (10 mL x 5). The organic extracts were combined, drie, and evaporated to give colorless oil, which was chromatographed on SiO₂ (15 g, hexane:acetone=60:1-2:1) to give **20** (205 mg, 97%) as colorless oil.

IR (neat) 3423, 1741, cm⁻¹; ¹H NMR (500 MHz) δ 1.38-1.63 (2H, br m), 1.76-1.83 (1H, m), 1.85-1.92 (1H, m), 2.00-2.11 (1H, m), 2.13-2.21 (2H, m), 2.55-2.66 (1H, m), 3.13 (1H, td, J = 10.1, 3.3 Hz), 3.57-3.65 (1H, m), 3.73-3.77 (2H, m), 3.86 (1H, dd, J = 8.5, 4.1 Hz), 4.31 (1H, t-like, J = 8.5 Hz), 5.06-5.15 (2H, m), 5.49-5.61 (1H, m); ¹³C NMR (125 MHz) δ 29.47 (t), 31.12 (t), 31.44 (t), 46.00 (d), 57.71 (d), 57.92 (d), 60.21 (t), 66.99 (t), 116.92 (t), 138.79 (s), 156.54 (s); MS: 211 (M⁺); HRMS: Calcd for C₁₁H₁₇NO₃ 211.1207; Found 211.1205.

(5S,6S,9S)-(−)-5-(2-Oxobut-3-enyl)-6-vinylhexahydrooxazolo[3,4-a]pyridin-3-one (21)

To a stirred solution of (COCl)₂ (0.22 mL, 2.47 mmol) in CH₂Cl₂ (5 mL) was added DMSO (0.35 mL, 4.94 mmol) at −78 °C, and the resulting mixture was stirred at −78 °C for 10 min. To the mixture was added a solution of **20** (344 mg, 1.63 mmol) in CH₂Cl₂ (4 mL) at −78 °C, and the reaction mixture was stirred at −78 °C for 30 min. To the reaction mixture was added Et₃N (1.02 mL, 7.31 mmol) at −78 °C, and the reaction temperature was gradually
increased to 0 °C for 1 h with stirring. The reaction was quenched with H₂O, and the aqueous mixture was extracted with Et₂O (15 mL x 3). The organic extracts were combined, dried, and evaporated to give pale yellow oil, which was used directly in the next step.

To a stirred solution of the above aldehyde in THF (8 mL) was added a solution of vinylmagnesium bromide (1 M in THF, 2.5 mL, 2.5 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched with satd. NH₄Cl (aq), and the aqueous mixture was extracted with CH₂Cl₂ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give pale yellow oil, which was used directly in the next step.

To a stirred solution of the above alcohol in CH₂Cl₂ (10 mL) were added PCC (420 mg, 1.94 mmol) and NaOAc (320 mg, 3.89 mmol), and the resulting suspension was stirred at room temperature for 16 h. The insoluble material was filtered off and washed with Et₂O. The filtrate and washings were combined and evaporated to give orange oil, which was chromatographed on SiO₂ (20 g, hexane:acetone=10:1-8:1) to give 21 (258 mg, 67%) as colorless oil.

IR (neat) 1743, cm⁻¹; ¹H NMR (500 MHz) δ 1.45-1.54 (2H, m), 1.81-1.85 (1H, m), 1.87-1.93 (1H, m), 2.09-2.15 (1H, m), 2.76 (1H, dd, J = 17, 3 Hz), 3.64-3.69 (2H, m), 3.70-3.77 (1H, m), 3.81-3.83 (1H, m), 4.31 (1H, t-like, J = 8 Hz), 5.06-5.15 (2H, m), 5.45-5.52 (1H, m), 5.79 (1H, d, J = 10.6 Hz), 6.23 (1H, d, J = 17.5 Hz), 6.37 (1H, dd, J = 17.5, 10.6 Hz); ¹³C NMR (125 MHz) δ 29.70 (t), 30.85 (t), 39.22 (t), 46.23 (d), 54.44 (d), 56.78 (d), 66.91 (t), 117.77 (t), 127.86 (t), 136.42 (d), 138.59 (d), 156.16 (s), 197.65 (s); MS: 235 (M⁺), 166 (100); HRMS: Calcd for C₁₃H₁₇NO₃ 235.1207; Found 235.1201; [α]D 26 +15.9 (c 0.88, CHCl₃).
(3S,5aS,9aS)-(−)-3a,4,5,5a,9,9a-Hexahydro-3H-oxazolo[3,4-a]quinoline-1,8-dione (18)

To a stirred solution of 21 (236 mg, 1 mmol) in CH₂Cl₂ (15 mL) was added benzylidenebis(tricyclohexylphosphine)dichlororuthenium (83 mg, 0.1 mmol), and the resulting mixture was stirred at room temperature for 15 h. The solvent was evaporated to give brown oil, which was chromatographed on SiO₂ (20 g, hexane:acetone=10:1-4:1) to give 18 (200 mg, 96%) as colorless solid (mp 172-173 °C).

IR (KBr) 1743, 1670, cm⁻¹; ¹H NMR (500 MHz) δ 1.44 (1H, qd, J = 13, 3.5 Hz), 1.64 (1H, qd, J = 13, 3.5 Hz), 1.96 (1H, dq, J = 13, 3 Hz), 2.16 (1H, dq, J = 13, 3 Hz), 2.42 (1H, tm, J = 11 Hz), 3.19 (1H, dd, J = 16.5, 14 Hz), 3.33 (1H, ddd, J = 15, 10, 4 Hz), 3.43 (1H, dd, J = 16.5, 4 Hz), 3.66 (1H, m), 3.89 (1H, dd, J = 8.5, 6 Hz), 4.38 (1H, td, J = 8.5 Hz), 6.04 (1H, dd, J = 9.5, 3 Hz), 6.63 (1H, dd, J = 9.5, 1.8 Hz); ¹³C NMR (125 MHz) δ 28.80 (t), 29.95 (t), 40.13 (d), 40.95 (t), 56.60 (d), 57.25 (d), 67.26 (t), 129.99 (d), 149.99 (d), 156.01 (s), 197.17 (s); MS: 207 (M⁺); HRMS: Calcd for C₁₁H₁₃NO₃ 207.0895; Found 207.0899; [α]D²⁶ −105.7 (c 0.67, CHCl₃).

Methyl (2S,4aR,5S,8aS)-(−)-2-(t-Butyldiphenylsilyloxy)methyl)-5-methyl-7-oxo-octahydroquinoline-1-carboxylate (22)

To a stirred suspension of CuI (120 mg, 0.63 mmol) in Et₂O (3 mL) was added a solution of MeLi (1M in Et₂O, 1.3 mL, 1.3 mmol) at −78 °C, and the reaction mixture was allowed to warm to −35 °C for 30 min. To the reaction mixture was added a solution of 13 (58 mg, 0.12 mmol) in Et₂O (6 mL) at −78 °C, and the reaction mixture was allowed to warm to −30 °C for 1 h. The reaction was quenched with satd. NH₄Cl (aq), and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (10 mL x 3), and the organic layer and extracts were combined, dried, and evaporated to give colorless oil, which was
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chromatographed on SiO$_2$ (15 g, hexane:acetone=25:1) to give 22 (58 mg, 96%) as colorless oil.

IR (neat) 1699, 1590, 1276 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 1.01 (3H, d, $J = 6.9$ Hz), 1.06 (9H, s), 1.18-1.30 (1H, br m), 1.40 (1H, br d, $J = 12$ Hz), 1.50-1.59 (1H, m), 1.62-1.73 (2H, m), 2.02-2.08 (2H, m), 2.11-2.20 (1H, br), 2.38 (2H, ddd-like, $J = 15$, 6.4 Hz), 3.64 & 3.66 (3H, each s), 4.37 (1H, br m), 4.52 (1H, br m), 7.37-7.45 (6H, m), 7.64-7.66 (4H, m); $^{13}$C NMR (125 MHz) $\delta$ 19.44 (s), 20.43 (q), 21.15 (t), 24.73 (t), 27.11 (q), 34.63 (d), 40.67 (d), 43.63 (t), 44.17 (t), 49.18 (d), 51.57 (d), 52.88 (q), 63.88 (t), 127.81 (d), 129.85 (d), 133.23 (s), 133.41 (s), 135.64 (d), 156.19 (s), 208.87 (s); MS: 493 (M$^+$), 478 (100); HRMS: Calcd for C$_{29}$H$_{39}$NO$_4$Si 493.2648; Found 493.2663; $[\alpha]_{D}^{26}$ –19.3 (c 2.70, CHCl$_3$).

**Methyl (2S,4aR,5S,8aS)-(−)-2-(Hydroxymethyl)-5-methyl-7-oxooctahydro-quinoline-1-carboxylate (23)**

To a stirred solution of 22 (58 mg, 0.12 mmol) in THF (3 mL) was added a solution of TBAF (1M in THF, 0.13 mL, 0.13 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 1.5 h. The reaction was quenched with satd NH$_4$Cl (aq), and the aqueous mixture was extracted with CHCl$_3$ (10 mL x 5). The organic extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO$_2$ (15 g, hexane:acetone=3:1) to give 23 (20 mg, 67%) as colorless oil.

IR (neat) 3420, 2955, 1680, 1192 cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 1.01 (3H, d, $J = 6.9$ Hz), 1.53 (1H, br d, $J = 12$ Hz), 1.73 (1H, br), 1.82 (1H, t-like, $J = 14$ Hz), 1.97 (1H, d-like, $J = 13$ Hz), 2.08 (2H, m), 2.39-2.54 (4H, m), 3.58-3.68 (2H, m), 3.70 (3H, s), 4.30 (1H, br), 4.52-4.55 (1H, br); $^{13}$C NMR (125 MHz) $\delta$ 20.24 (q), 21.18 (t), 24.93 (t), 34.43 (d), 40.52 (d), 43.38 (t), 44.03 (t), 49.17 (d), 51.70 (d), 53.01 (q), 64.51 (t), 208.65 (s); MS: 255 (M$^+$), 225
(3aS,5aS,6R,9aR)-(-)-6-Methyloctahydrooxazolo[3,4-a]quinoline-1,8-dione (24)

To a stirred suspension of CuI (184 mg, 0.97 mmol) in Et₂O (5 mL) was added a solution of MeLi (1M in Et₂O, 1.9 mL, 1.9 mmol) at –78 °C, and the reaction mixture was allowed to warm to –35 °C for 30 min. To the reaction mixture was added a solution of 14 (40 mg, 0.19 mmol) in Et₂O (1 mL) and THF (1 mL) at –78°C, and the reaction mixture was allowed to warm to –30 °C and stirring was continued for 1 h. The reaction was quenched with satd. NH₄Cl (aq), and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (10 mL x 4), and the organic layer and extracts were combined, dried, and evaporated to give colorless oil, which was chromatographed on SiO₂ (15 g, hexane:acetone=6:1) to give 24 (41 mg, 96%) as colorless oil.

IR (neat) 1743 cm⁻¹; ¹H NMR (500 MHz) δ 1.02 (3H, d, J = 6 Hz), 1.47 (1H, q-like, J = 11 Hz), 1.76-1.85 (3H, br m), 2.09 (2H, d-like, J = 12 Hz), 2.42-2.61 (3H, m), 3.73-3.84 (1H, m), 3.91-3.94 (1H, m), 4.37-4.44 (2H, m); ¹³C NMR (125 MHz) δ 20.31 (q), 24.83 (t), 30.78 (t), 34.10 (d), 39.52 (t), 40.36 (t), 43.30 (t), 48.47 (d), 50.37 (d), 68.33 (t), 156.27 (s), 207.87 (s); MS: 223 (M⁺), 166 (100); HRMS: Calcd for C₁₂H₁₇NO₃ 223.1208; Found 223.1213; [α]D²⁶ −25.7 (c 1.00, CHCl₃).

(3aS,5aS,6S,9aS)-(-)-6-Methyloctahydrooxazolo[3,4-a]quinoline-1,8-dione (25) and (3aS,5aS,6R,9aS)-(-)-6-Methyloctahydrooxazolo[3,4-a]quinoline-1,8-dione (26)

To a stirred suspension of CuI (380 mg, 2.0 mmol) in Et₂O (12 mL) was added a solution of MeLi (1.14 M in Et₂O, 3.6 mL, 4.1 mmol) at –78 °C, and the resulting mixture was stirred at –35°C for 30 min. To a stirred solution of 18 (42 mg, 0.2 mmol) in Et₂O (130 mL) was
added a solution of Me₂CuLi in Et₂O prepared above at –50 °C. The reaction mixture was stirred at –50-0 °C for 2 h, and quenched with satd. NH₄Cl (aq). The organic layer was separated and the aqueous mixture was extracted with CH₂Cl₂ (10 mL x 5). The organic layer and extracts were combined, dried, and evaporated to give pale yellow oil, which was chromatographed on SiO₂ (10 g, hexane:acetone=9:1-8:1) to give 25 (27 mg, 60%) and 26 (9 mg, 20%) as colorless solid, respectively. (mp 25: 72-73 °C, 26: 98-100 °C)

**25:** IR (KBr) 1751, 1709 cm⁻¹; ¹H NMR (500 MHz) δ 0.87 (3H, d, J = 7.3 Hz), 1.51-1.55 (2H, m), 1.82-1.85 (1H, m), 1.88-1.95 (2H, m), 2.22-2.25 (1H, m), 2.28 (1H, d, J = 13.7 Hz), 2.64 (1H, dd, J = 14, 6 Hz), 3.16 (1H, t-like, J = 15 Hz), 3.32-3.38 (2H, m), 3.53-3.59 (1H, m), 3.85 (1H, t-like, J = 8.5 Hz), 4.34 (1H, t-like, J = 8.5 Hz); ¹³C NMR (125 MHz) δ 14.09 (q), 27.65 (t), 29.61 (t), 33.30 (d), 42.89 (d), 44.09 (t), 48.98 (t), 54.48 (d), 56.99 (d), 67.11 (t), 156.57 (s), 208.31 (s); MS: 223 (M⁺), 208 (100); HRMS: Calcd for C₁₂H₁₇NO₃ 223.1208; Found 223.1211; [α]D²⁶ –50.0 (c 0.90, CHCl₃).

**26:** IR (KBr) 1751, 1709 cm⁻¹; ¹H NMR (500 MHz) δ 1.05 (3H, d, J = 6 Hz), 1.14 (1H, ddt, J = 13.5, 11.5, 4 Hz), 1.42-1.57 (3H, br m), 1.90 (1H, dq, J = 13.5, 3.5 Hz), 2.18 (1H, t-like, J = 13.5 Hz), 2.26 (1H, dq, J = 13.5, 3.5 Hz), 2.37 (1H, ddd, J = 14.5, 4, 2.5 Hz), 3.05-3.11 (1H, m), 3.24 (1H, ddd, J = 14.5, 4.5, 2.5 Hz), 3.36 (1H, t-like, J = 13.5 Hz), 3.59-3.64 (1H, m), 3.87 (1H, dd, J = 8, 5.5 Hz), 4.35 (1H, t-like, J = 8 Hz); ¹³C NMR (125 MHz) δ 19.30 (q), 27.78 (t), 29.59 (t), 34.80 (d), 43.86 (t), 45.52 (d), 49.43 (t), 57.37 (d), 59.01 (d), 66.94 (t), 156.12 (s), 207.55 (s); MS: 223 (M⁺), 208 (100); HRMS: Calcd for C₁₂H₁₇NO₃ 223.1208; Found 223.1205; [α]D²⁶ –84.6 (c 0.35, CHCl₃).

**Methyl (2S,4aS, 8aS)-(-)-2-(t-Butyldiphenylsilyloxymethyl)-5-methyl-7-oxo-3,4,4a,7,8,8a-hexahydro-2H-quinoline-1-carboxylate (27)**

To a stirred suspension of CuI (144 mg, 0.76 mmol) in THF (0.5 mL) was added a solution of MeLi (1 M in Et₂O, 1.5 mL, 1.5 mmol) at 0 °C, and the resulting mixture was stirred at 0
°C for 20 min. The reaction mixture was cooled to –78 °C, and then a solution of TMSCl (0.12 mL, 0.94 mmol), HMPA (0.16 mL, 0.94 mmol) and 13 (90 mg, 0.19 mmol) in THF (2 mL) was added to the reaction mixture. The resulting mixture was stirred at –78 °C for 1 h, and then the reaction was quenched with Et₃N (2 mL) at –78 °C. The reaction mixture was diluted with EtOAc (20 mL), and H₂O (10 mL), and the organic layer was separated. The organic layer was washed with brine, dried, and evaporated to give pale yellow oil, which was used directly in the next step.

To a stirred solution of the above oil in MeCN (5 mL) was added Pd(OAc)₂ (42.4 mg, 0.19 mmol), and the resulting mixture was stirred at room temperature for 40 h. The insoluble material was filtered off, and the filtrate was evaporated to give pale yellow oil, which was chromatographed on SiO₂ (15 g, hexane:acetone=10:1) to give 27 (74 mg, 80%) as colorless oil.

IR (neat) 1663, 1170 cm⁻¹; ¹H NMR (500 MHz) δ 1.05 (9H, s), 1.26-1.42 (1H, br m), 1.61-1.68 (1H, m), 1.77 (1H, m), 1.98 (1H, br s), 2.10-2.17 (2H, br m), 2.20-2.24 (1H, m), 2.41-2.50 (1H, br m), 3.62-3.70 (2H, br), 3.67 (3H, s), 4.34-4.64 (2H, br), 5.85 (1H, s), 7.37-7.43 (6H, m), 7.65-7.66 (4H, m); ¹³C NMR (125 MHz) δ 19.24 (t), 19.69 (s), 22.70 (q), 24.40 (t), 26.88 (q), 38.98 (t), 41.87 (d), 48.73 (d), 51.05 (d), 52.75 (q), 63.30 (t), 126.31 (d), 127.61 (d), 129.65 (d), 132.95 & 133.09 (each s), 135.39 (d), 163.46 (s), 197.15 (s); MS: 491 (M⁺), 438 (100); HRMS: Calcd for C₂₉H₃₇NO₄Si 491.2492; Found 491.2491; [α]D²⁶ –1.51 (c 3.71, CHCl₃).
Methyl (2S,4aR, 5R, 8aS)-(−)-2-(t-Butyldiphenylsilyloxymethyl)-5-methyl-7-oxooctahydroquinoline-1-carboxylate (28)

To a stirred solution of 27 (66 mg, 0.13 mmol) in MeOH (5 mL) was added Pd(OH)_2 (5 mg), and the resulting suspension was stirred under hydrogen atmosphere for 13 h. The catalyst was filtered off, and the filtrate was evaporated to give 28 (67 mg, quant) as colorless oil.

IR (neat) 1687, 1153 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \(\delta\) 1.01 (3H, d-like, \(J = 6.6\) Hz), 1.06 (9H, s), 1.13-1.18 (1H, m), 1.21-1.36 (1H, m), 1.41-1.53 (1H, m), 1.57-1.68 (1H, br m), 1.76 (1H, br), 1.98-2.01 (2H, m), 2.04-2.17 (2H, m), 2.26 (1H, t-like, \(J = 13\) Hz), 2.36-2.50 (1H, m), 3.60 & 3.66 (3H, each s), 4.20-4.31 (1H, m), 4.41-4.49 (1H, m), 7.37-7.45 (6H, m), 7.64-7.68 (4H, m); \(^1^3\)C NMR (125 MHz) \(\delta\) 12.84 & 12.94 (each t), 18.64 (q), 19.12 (s), 24.33 (t), 26.78 (q), 32.77 & 33.11 (each d), 40.21 & 40.32 (each d), 42.98 & 43.84 (each t), 44.25 (t), 51.17 & 51.59 (each d), 52.18 (d), 52.59 (q), 63.72 & 63.89 (each t), 127.67 & 127.70 (each d), 129.68 & 129.74 (each d), 133.09 (s), 135.46 & 135.50 (each d), 156.10 (s), 207.93 & 208.45 (each s); MS: 493 (M\(^+\)); HRMS: Calcd for C\(_{29}\)H\(_{39}\)NO\(_4\)Si 493.2648; Found 493.2641; \([\alpha]_D^{26}\) –14.5 (c 3.33, CHCl\(_3\)).