Supporting Information
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General Remarks: Nuclear magnetic resonance (\(^1\)H NMR (400 MHz), \(^{13}\)C NMR (100 MHz)) spectra were determined on a JEOL-ECS400 instrument or a JEOL-ECZ400S instrument unless otherwise noted. Chemical shifts for \(^1\)H NMR are reported in parts per million (ppm) downfields from tetramethylsilane (\(\delta\)) as the internal standard or relative to the singlet at 7.26 ppm for residual chloroform, and coupling constants are in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, m = multiplet. Chemical shifts for \(^{13}\)C NMR were reported in ppm relative to the center line of a triplet at 77.0 ppm for deuteriochloroform. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrophotometer and were reported in wavenumbers (cm\(^{-1}\)). High resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LP AccuTOF LC-plus either in positive electrospray ionization (ESI) method with sodium trifluoroacetate as the internal standard. Optical rotations were measured on JASCO P-2200 Polarimeter at room temperature using the sodium D line. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F\(_{254}\). Preparative TLC separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F\(_{254}\) unless otherwise noted. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 N (spherical, neutral, 40-50 mesh) unless otherwise noted. Reagents were commercial grades and were used without any purification unless otherwise noted. Chlorotrimethylsilane (TMSCl) was purified by distillation from calcium hydride. Dehydrated tetrahydrofuran, diethyl ether, toluene, and dichloromethane were purchased from Kanto Chemicals Co., Inc., and were purified using a Glass Contour Solvent System. Dehydrated acetonitrile was purchased from Wako Pure Chemical Industries, Ltd., and stored over activated MS3A*. All reactions sensitive to oxygen or moisture were conducted under an argon atmosphere.

(R)-2-(Hydroxymethyl)-5-methylcyclohex-2-enone (13)

\[
\begin{align*}
\text{Me} & \quad \text{aq HCHO, DMAP} \\
\text{H}_2\text{O, rt} & \quad \text{Me} \\
75\% & \quad \text{OH}
\end{align*}
\]

To a solution of hexadecyltrimethylammonium bromide (18.6 mg) in H\(_2\)O (47 mL) was added enone 12 (2.6 g, 22.0 mmol) and formalin (37%, 3.8 mL, 47.2 mmol) at rt. Then, DMAP (288.4 mg, 2.36 mmol) was added to the reaction mixture, which was stirred for 1 h. The reaction mixture was diluted with water and extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 1:1) to give allyl alcohol 13 (2.3 g, 16 mmol, 75%) as a pale yellow oil. [\(\alpha\)\(_D\)\(^{21}\)] = −70.9\(^\circ\) (c 0.96, CHCl\(_3\)); IR (film, cm\(^{-1}\)): 3426, 2955, 2926, 2873, 1668, 1456, 1429, 1395, 1335, 1237, 1137, 1065, 1042, 1005, 916, 903; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.90 (m, 1H), 4.25 (d, \(J = 5.2\) Hz, 2H), 2.55 (m, 1H), 2.51 (m, 1H), 2.47 (m, 1H), 2.24 (m, 1H), 2.15 (m, 1H), 2.09 (m,

* Molecular sieves were “activated” in the following manner: A round-bottom flask containing molecular sieves was heated in a regular microwave for 1.5-2.0 minute and the flask was immediately evacuated. When cooled to room temperature, the flask was backfilled with argon. The above procedure was repeated three times.
1H), 1.08 (d, J = 6.4 Hz, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 200.9 (C), 146.3 (CH), 137.9 (C), 62.0 (CH\(_2\)), 46.3 (CH\(_3\)), 33.9 (CH\(_2\)), 30.3 (CH), 21.1 (CH\(_3\)); HRMS (ESI\(+\)): 163.0738 (calcd for C\(_9\)H\(_{12}\)NaO\(_2\) 163.0735). [SW02084]

\((R)-[4\text{-Methyl-6-oxocyclohex-1-en-1-yl}]\text{methyl acetate (14)}\)

To a solution of allyl alcohol 13 (2.2 g, 15.7 mmol) in CH\(_2\)Cl\(_2\) (16 mL) was added pyridine (3.2 mL, 39 mmol) and Ac\(_2\)O (3.0 mL, 31 mmol) sequentially at rt. After stirring for 7.5 h, the reaction mixture was diluted with water and a 1 N HCl. Then the mixture was extracted with EtOAc and washed with saturated aqueous NaHCO\(_3\). The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 3:1) to give ester 14 (2.76 g, 16.4 mmol, 97%) as a pale yellow oil. IR (film, cm\(^{-1}\)): 2957, 1744, 1680, 1370, 1058, 1025; \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.97 (m, 1H), 4.74 (s, 2H), 2.53 (ddd, \(J = 15.2, 2.8, 1.2\) Hz, 1H), 2.49 (m, 1H), 2.23 (m, 1H), 2.15 (dd, \(J = 16.4, 11.6\) Hz, 1H), 2.12 (m, 1H), 2.07 (s, 3H), 1.07 (d, \(J = 6.4\) Hz, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.2 (C), 170.7 (C), 148.0 (CH), 134.1 (C), 61.2 (CH\(_2\)), 46.2 (CH\(_2\)), 34.0 (CH\(_2\)), 30.3 (CH), 21.1 (CH\(_3\)), 21.0 (CH\(_3\)); HRMS (ESI\(+\)): 205.0843 (calcd for C\(_{10}\)H\(_{14}\)NaO\(_3\) 205.0841). [SW02086]

\(\text{Methyl 2-}([5(15R)]-3-\{(tert-butylidimethylsilyl)oxy\}-5\text{-methyl-2-methylenecyclohex-3-en-1-yl})\text{acetate (17)}\)

To a solution of ketone 14 (1.6 g, 8.8 mmol) in Et\(_2\)O (12 mL) was added Et\(_3\)N (2.4 mL, 18 mmol) at \(-20^\circ\)C. Then TBSOTf (3.6 mL, 16 mmol) was added to the reaction mixture, which was stirred for 2 h at the same temperature. Then, the reaction mixture was filtrated through an alumina column. The solvent was removed under reduced pressure to give a crude material. This material was used without further purification. To a solution of NaHMDS (1.9 M in THF, 9.3 mL, 18 mmol) in THF (7.5 mL) at \(-78^\circ\)C was added a solution of the crude material in THF (28 mL). Then, TMSCI (2.2 mL, 18 mmol) was added dropwise into the reaction mixture. The mixture was stirred for 30 min at \(-78^\circ\)C then allowed to warm to rt. The mixture was heated at 70 \(^\circ\)C for 30 min. The reaction mixture was cool to rt and was quenched with saturated aqueous NH\(_4\)Cl. The reaction mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a crude material. This material was used without further purification. The crude material in Et\(_2\)O (11 mL) and MeOH (3.3 mL) was added trimethylsilyldiazomethane (2.0 M in hexane, 8.8 mL, 2.0 mmol) at 0 \(^\circ\)C. Then, the reaction mixture was allowed to warm to rt and stirred for 30 min. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc:Et\(_3\)N = 300:10:1) to give ester 17 (1.1 g, 3.5 mmol, 40% from allyl ester 14) as a colorless oil. The product contained a small amount of impurities. [\(\alpha\)]\(_D^{21}\) : 32.0° (c 1.00, CHCl\(_3\)); IR (film, cm\(^{-1}\)): 2955, 2929, 2857, 1741, 1637, 1601, 1472, 1461, 1436,
To a solution of ester 17 (1.1 g, 3.5 mmol) in THF (36 mL) was added AcOH (0.35 mL, 6.1 mmol) and TBAF (1.0 M in THF, 4.6 mL, 4.6 mmol) sequentially at rt. After stirring for 10 min, the reaction was quenched with saturated aqueous NH₄Cl. The mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a crude material. This material was used without further purification. The crude material was dissolved in butyl vinyl ether (36 mL), and to the resulting mixture was added Yb(fod)₃ (378 mg, 0.357 mmol) at rt. After stirring for 15 h, the reaction mixture was diluted with water. The reaction mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc:CHCl₃ = 15:1:3) to give cyclic acetal 19 (994 mg, 3.35 mmol, 93% from ester 17) as a yellow oil. The material was obtained as a mixture of two diastereomers. [α]D²¹ = −16.0° (c 0.98, CHCl₃); IR (film, cm⁻¹): 2954, 2872, 1739, 1691, 1456, 1435, 1376, 1348, 1292, 1241, 1158, 1106, 1090, 1051, 983, 936, 887, 859; ¹H-NMR (400 MHz, CDCl₃): δ 4.93 (s, 1H), 3.95 (dt, J = 9.6, 6.9 Hz, 1H), 3.68 (s, 3H), 3.50 (dt, J = 9.6, 6.4 Hz, 1H), 2.56-2.46 (m, 2H), 2.21 (m, 1H), 2.01 (m, 1H), 2.00-1.72 (m, 5H), 1.68 (m, 1H), 1.65-1.47 (m, 3H), 1.41-1.29 (m, 3H), 0.96 (d, J = 6.4 Hz, 3H), 0.91 (t, J = 7.6 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 173.9 (C), 144.4, 144.1 (C), 106.5, 106.2 (C), 96.6 (CH), 67.7, 67.4 (CH₂), 51.5 (CH₃), 38.4, 38.1 (CH₃), 35.7, 35.6 (CH₂), 34.7 (CH), 31.8 (CH₂), 27.2, 27.1 (CH₂), 24.6, 24.4 (CH), 21.7, 21.6 (CH₃), 19.6 (CH₂), 19.2 (CH₂), 13.8, 13.7 (CH₃); HRMS (ESI⁺): 319.1895 (calcld for C₁₇H₂₀NaO₃ 319.1885). [SW02157-2]
Rochelle salt and the mixture was warmed up to rt. After stirring for 30 min, the mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 6:1) to give aldehyde 20 (369 mg, 1.38 mmol, 80%) as a pale yellow oil. This material was obtained as a mixture of two diastereomers. [α]D21: -4.2° (c 1.03, CHCl3); IR (film, cm⁻¹): 2955, 2912, 2871, 1725, 1691, 1456, 1376, 1240, 1163, 1143, 1108, 1052, 1031, 980; ¹H-NMR (400 MHz, CDCl₃): δ 9.78 (m, 1H), 4.94 (m, 1H), 3.75 (m, 1H), 3.50 (m, 1H), 2.62 (m, 1H), 2.55 (m, 1H), 2.40 (m, 1H), 2.03 (m, 1H), 1.95 (m, 1H), 1.92-1.75 (m, 4H), 1.75-1.43 (m, 4H), 1.43-1.30 (m, 3H), 0.96 (d, J = 6.8 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 203.2, 203.1 (CH), 144.5, 144.1 (C), 105.9, 105.6 (C), 96.6 (CH), 67.7, 67.4 (CH₂), 48.1, 47.7 (CH₂), 36.1, 36.0 (CH₂), 35.7, 35.4 (CH₂), 33.0, 32.2 (CH), 31.7 (CH₂), 27.1, 27.0 (CH₂), 24.7, 24.5 (CH), 21.6, 21.4 (CH₃), 20.2, 19.6 (CH₂), 19.3 (CH₂), 13.8 (CH₃); HRMS (ESI⁺): 289.1790 (calcd for C₁₆H₂₆NaO₃ 289.1780). [SW02146]

1-((5S,7R)-2-Butoxy-7-methyl-3,4,5,6,7,8-hexahydro-2H-chromen-5-yl)but-3-yn-2-ol (21)

\[
\begin{align*}
\text{Me,} & \quad \text{O} \\
\text{Me,} & \quad \text{O} \\
\text{H} & \quad \text{MgBr} \\
\text{Me,} & \quad \text{OH} \\
\end{align*}
\]

To a solution of aldehyde 20 (362 mg, 1.36 mmol) in THF (14 mL) was added ethynylmagnesium bromide (0.5 M in THF, 5.4 mL, 2.7 mmol) at −78 °C. Then, the reaction mixture was allowed to warm to rt. After stirring for 40 min, the reaction was quenched with saturated aqueous NH₄Cl. The mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 4:1) to give propargyl alcohol 21 (326 mg, 1.11 mmol, 82%) as a yellow oil. This material was obtained as a mixture of four diastereomers. [α]D21: −6.6° (c 1.03, CHCl₃); IR (film, cm⁻¹): 3426, 3309, 2954, 2870, 1692, 1455, 1375, 1347, 1240, 1185, 1156, 1141, 1107, 1095, 1051, 980, 934; ¹H-NMR (400 MHz, CDCl₃): δ 4.93 (m, 1H), 4.42 (m, 1H), 3.76 (m, 1H), 3.50 (m, 1H), 2.50 (m, 1H), 2.23 (m, 1H), 2.07-1.76 (m, 7H), 1.76-1.51 (m, 5H), 1.42-1.24 (m, 3H), 0.96 (d, J = 7.2 Hz, 3H), 0.91 (t, J = 7.6 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 143.7, 143.6, 143.5 (C), 107.4, 107.3, 107.0, 106.9 (C), 96.7, 96.7, 96.6, 96.6 (CH), 85.4, 84.9, 84.8 (C), 73.5, 73.3, 72.7 (CH), 67.7, 67.6, 67.4 (CH₂), 61.9, 61.7, 60.7, 60.6 (CH), 41.4, 41.3, 41.1, 40.9 (CH₂), 35.8, 35.8 (CH₂), 35.3, 34.9 (CH₂), 34.4, 33.5 (CH), 31.8 (CH₂), 27.2 (CH₂), 24.9, 24.7, 24.6, 24.5 (CH), 21.8, 21.7, 21.6 (CH₂), 20.5, 20.3, 19.6, 19.5 (CH₂), 19.2 (CH₂), 13.8, 13.8 (CH₃); HRMS (ESI⁺): 315.1939 (calcd for C₁₆H₂₆NaO₃ 315.1936). [SW02147]
(3aS,6R,7aS)-3a-(3,3-Dimethoxypropyl)-2-hydroxy-6-methyl-3-methylenehexahydro-1H-inden-4(2H)-one (22)

To a solution of propargyl alcohol 21 (173 mg, 0.591 mmol) in MeOH (6.0 mL) was added the supernatant of a suspension of gold triphenylphosphine chloride and silver hexafluoroantimonate (0.059 M in MeOH, 1.0 mL, 0.059 mmol) at 0 °C. After stirring for 11 h, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 1:1) to give allyl alcohol 22 (113 mg, 0.400 mmol, 67%) as a pale yellow oil. This material was obtained as a 3:2 mixture of two diastereomers, containing a small amount of impurities. [α]D²¹ 39.4° (c 0.97, CHCl₃); IR (film, cm⁻¹): 3445, 2955, 2359, 2249, 1698, 1456, 1383, 1191, 1128, 1053, 910; ¹H-NMR (400 MHz, CDCl₃): δ 5.47 (d, J = 1.4 Hz, (3/5)1H), 5.45 (d, J = 2.3 Hz, (2/5)1H), 5.13 (m, 1H), 4.56 (m, (3/5)1H), 4.40 (m, (2/5)1H), 4.33 (m, 1H), 3.32 (s, (3/5)3H), 3.31 (s, (2/5)3H), 3.30 (s, (3/5)3H), 3.30 (s, (2/5)3H), 2.69 (m, (3/5)1H), 2.50-2.02 (m, 3H+(2/3)1H), 1.93-1.46 (m, 8H+(3/5)1H), 1.41 (m, (2/5)1H), 1.00 (d, J = 6.4 Hz, (2/5)3H), 0.98 (d, J = 6.4 Hz, (3/5)3H); ¹³C-NMR (100 MHz, CDCl₃): δ 211.8, 211.4 (C), 155.2, 154.4 (C), 113.8, 112.2 (CH₂), 104.5, 104.5 (CH), 73.7, 73.4 (CH), 61.0, 60.4 (C), 53.0, 52.8 (CH₂), 46.8, 46.6 (CH₂), 40.2, 40.1 (CH), 38.7, 38.1 (CH₂), 33.6, 33.2 (CH₂), 30.5, 30.4 (CH₂), 28.7, 28.7 (CH), 28.1, 27.9 (CH₂), 21.8, 21.1 (CH₃); HRMS (ESI+): 305.1731 (calcd for C₁₆H₂₀NaO₃ 305.1729). [SW02154]

(4aS,7aS,9R,10aS)-1-Benzyl-9-methyl-5-methylenedodecahydrocyclopenta[e]quinolin-6-ol (24)

To a solution of 22 (111 mg, 0.393 mmol) in acetone (6.6 mL) and H₂O (1.0 mL) was added PPTS (29.6 mg, 0.118 mmol) at rt. Then, the mixture was warmed up to 50 °C. After stirring for 6 h, the solvent was removed under reduced pressure. To the residue was added aqueous sat. NaHCO₃. The mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a crude material. This material was used without further purification. The crude material in MeOH (4.0 mL) was added BnNH₂ (0.05 mL, 0.08 mmol) at 0 °C. Then, NaBH₃CN (61.7 mg, 0.982 mmol) was added to the mixture. After stirring for 30 min, the mixture was warmed up to rt and stirred for 14 h. The reaction was quenched with aqueous sat. NaHCO₃. The reaction mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtOAc = 4:1) to give piperidine 24 (59.5 mg, 0.191 mmol, 48%
from ester 22). This material was obtained as a 3:1 mixture of diastereomers. \([\alpha]_D^{21}: 62.3^\circ\) (c 0.98, CHCl3); IR (film, cm\(^{-1}\)): 3365, 2948, 2850, 2786, 1493, 1454, 1380, 1314, 1127, 1094, 1069, 1041, 1001, 916; \(^1\)H-NMR (400 MHz, CDCl3): \(\delta\) 7.32-7.19 (m, 5H), 6.21 (m, 3/4)1H), 6.19 (m, 1/4)1H), 5.51 (m, 3/4)1H), 5.45 (m, 1/4)1H), 4.64 (m, 3/4)1H), 4.57 (m, 1/4)1H), 4.17 (d, \(J = 13.2\) Hz, 1/4)1H), 4.14 (d, \(J = 13.3\) Hz, 3/4)1H), 2.83 (m, 1H), 2.80 (d, \(J = 13.3\) Hz, 3/4)1H), 2.78 (d, \(J = 13.2\) Hz, 1/4)1H), 2.41 (m, 1H+1/4)1H), 2.04-1.50 (m, 9H), 1.37-1.09 (m, 4H+3/4)1H), 0.99 (d, \(J = 6.8\) Hz, 3H); \(^13\)C-NMR (100 MHz, CDCl3): \(\delta\) 156.3, 156.0 (C), 141.0, 140.9 (C), 128.6 (CH), 128.1 (CH), 115.5, 112.1 (CH3), 75.8, 73.4 (CH), 63.2, 63.0 (CH), 58.2, 58.1 (CH3), 54.8, 54.7 (CH2), 49.6, 49.4 (C), 42.0, 41.3 (CH), 38.4, 38.0 (CH2), 37.1, 36.5 (CH2), 36.2, 35.9 (CH2), 31.5, 31.2 (CH3), 27.1, 26.4 (CH), 21.6, 21.2 (CH2), 20.1, 19.6 (CH3); HRMS (ESI+): 334.2134 (calcd for C21H29NNAO 334.2146). [SW02152]

\((4aS,7aS,9R,10aS)-1\text{-Benzy}-9\text{-methyl}-5\text{-methylene}deca-hydrocyclopenta[e]quinolin-6(5H)\text{-one (25)}\)

\[\text{To a solution of alcohol 24 (58.5 mg, 0.187 mmol) in CH}_2\text{Cl}_2 (19 mL) was added Dess-Martin periodinane (120 mg, 0.282 mmol) at rt. After stirring for 30 min, the reaction was quenched with saturated aqueous NaHCO}_3 and saturated aqueous Na}_2\text{SO}_4. The mixture was extracted with CH}_2\text{Cl}_2. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane:EtoAc = 6:1) to give enone 25 (45.6 mg, 0.147 mmol, 78%).} \([\alpha]_D^{21}: -13.8^\circ\) (c 0.75, CHCl3); IR (film, cm\(^{-1}\)): 2928, 2789, 1724, 1633, 1452, 1384, 1217, 1114, 1097, 954; \(^1\)H-NMR (400 MHz, CDCl3): \(\delta\) 7.34-7.21 (m, 5H), 6.35 (d, \(J = 2.7\) Hz, 1H), 6.33 (d, \(J = 2.7\) Hz, 1H), 4.15 (d, \(J = 12.8\) Hz, 1H), 2.85 (m, 1H), 2.84 (d, \(J = 13.2\) Hz, 1H), 2.65 (dd, \(J = 18.3, 7.4\) Hz, 1H), 2.53 (dd, \(J = 12.4, 4.6\) Hz, 1H), 2.12 (m, 1H), 1.92 (d, \(J = 18.3\) Hz, 1H), 1.95-1.81 (m, 2H), 1.77 (ddd, \(J = 12.4, 4.4, 4.4\) Hz, 1H), 1.70-1.53 (m, 3H), 1.48 (ddd, \(J = 15.0, 5.6, 5.6\) Hz, 1H), 1.39-1.32 (m, 2H), 1.16 (m, 1H), 1.03 (d, \(J = 7.6\) Hz, 3H); \(^13\)C-NMR (100 MHz, CDCl3): \(\delta\) 208.3 (C), 147.3 (C), 140.4 (C), 128.6 (CH), 128.2 (CH), 126.6 (CH), 122.6 (CH2), 63.0 (CH), 58.0 (CH2), 54.3 (CH2), 48.1 (C), 43.0 (CH2), 37.2 (CH), 36.4 (CH2), 36.2 (CH2), 31.3 (CH3), 26.5 (CH), 21.0 (CH2), 19.8 (CH3); HRMS (ESI+): 332.1992 (calcd for C21H27NNAO 332.1990). [SW02153]

\((4aS,6R,7aS,12bS)-4\text{-Benzy}-6\text{-methyl}-1,2,3,4,4a,5,6,7a,8-deca-hydropyrido[2',3':4,5]cyclopenta[1,2-e]quinolin-in-10(9H)\text{-one (26)}\)

\[\text{To a solution of enone 25 (27.4 mg, 0.088 mmol), LiCl (37.5 mg, 0.885 mmol) and 2-(phenylsulfinyl)acetamide (5,}
64.5 mg, 0.354 mmol) in MeCN (1.0 mL) was added DBU (0.13 mL, 0.88 mmol) at rt. Then, the mixture was warmed up to 60 °C and stirred for 3 h. After cooling to rt, hydrogen chloride in MeOH (5~10%, 2.0 mL) was added to the mixture. The mixture was warmed up to 80 °C and stirred for 42 h. Then, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was extracted with EtOAc. The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by PTLC (CH₂Cl₂:MeOH = 19:1) to give pyridone 26 (11.8 mg, 0.034 mmol, 39%). [α]₀²¹: −23.7° (c 0.59, CHCl₃); IR (film, cm⁻¹): 2926, 2859, 2790, 1652, 1604, 1551, 1467, 1093, 832; ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, J = 9.2 Hz, 1H), 7.38-7.23 (m, 5H), 6.38 (d, J = 9.2 Hz, 1H), 4.18 (d, J = 13.0 Hz, 1H), 3.32 (dd, J = 17.4, 7.3 Hz, 1H), 2.91 (m, 1H), 2.81 (d, J = 13.0 Hz, 1H), 2.52 (dd, J = 11.6, 5.2 Hz, 1H), 2.42 (d, J = 17.4 Hz, 1H), 2.29 (m, 1H), 1.88 (ddd, J = 12.0, 12.0, 3.2 Hz, 1H), 1.71-1.32 (m, 8H), 1.23 (m, 1H). 0.92 (d, J = 6.4 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 166.1 (C), 150.1 (C), 143.1 (CH), 140.3 (C), 128.9 (CH), 128.3 (CH), 126.7 (CH), 125.1 (C), 114.9 (CH), 62.6 (CH), 58.0 (CH₂), 54.1 (CH₂), 49.2 (C), 43.3 (CH), 39.1 (CH₂), 36.8 (CH₂), 36.0 (CH₂), 33.1 (CH₃), 24.6 (CH), 22.1 (CH₃), 21.8 (CH₂); HRMS (ESI+): 371.2099 (calcd for C₂₃H₂₈N₂NaO 371.2099). [SW02155] 

Lycoposerramine-R (1)

![Diagram of Lycoposerramine-R (1)](image)

To a solution of 26 (11.8 mg, 0.033 mmol) in i-PrOH (1.0 mL) was added 20% Pd(OH)₂/C (47.5 mg, 0.033 mmol) at rt. The mixture was stirred for 4.5 h at rt under 1.0 atm pressure of hydrogen atmosphere. The mixture was filtrated through a pad of NH₂ silica gel. The solvent was removed under reduced pressure. The crude product was purified by PTLC (CH₂Cl₂:MeOH = 19:1) to give lycoposerramine-R (1, 8.6 mg, 0.033 mmol, quant). [α]₀²¹: −28.6° (c 0.43, CHCl₃); IR (film, cm⁻¹): 2925, 2851, 2801, 1650, 1600, 1550, 1466, 1437, 1093, 832, 753; ¹H-NMR (400 MHz, CDCl₃): δ 8.32 (d, J = 9.2 Hz, 1H), 6.34 (d, J = 9.2 Hz, 1H), 3.21 (dd, J = 16.8, 6.4 Hz, 1H), 3.17 (m, 1H), 2.90 (dd, J = 12.0, 4.8 Hz, 1H), 2.79 (ddd, J = 11.6, 11.6, 3.2 Hz, 1H), 2.33 (d, J = 16.8 Hz, 1H), 2.19 (ddd, J = 6.9, 6.9, 6.9 Hz, 1H), 1.78 (m, 1H), 1.68 (m, 1H), 1.60 (m, 1H), 1.52 (m, 1H), 1.46 (m, 1H), 1.45 (m, 2H), 1.43 (m, 1H), 1.24 (m, 1H), 1.18 (m, 1H), 0.97 (d, J = 7.6 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 166.1 (C), 150.3 (C), 143.3 (CH), 124.5 (C), 114.7 (CH), 57.1 (CH), 49.3 (C), 48.0 (CH₂), 41.7 (CH), 38.1 (CH₂), 36.1 (CH₂), 36.0 (CH₂), 34.8 (CH₂), 25.6 (CH), 22.9 (CH₂), 20.5 (CH₃); HRMS (ESI+): 281.1623 (calcd for C₁₆H₂₂N₂NaO 281.1629). [SW02159]
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**Sample Details**

- **Filename**: SW02084_single_pulse-2-3.jdf
- **Author**: delta
- **Experiment**: single_pulse.jxp
- **Sample_Id**: SW02084 Fr22-32
- **Solvent**: CHLOROFORM-D
- **Creation_Time**: 29-JAN-2018 05:42:
- **Revision_Time**: 26-JUL-2018 12:34:
- **Current_Time**: 26-JUL-2018 12:36:
- **Comment**: single_pulse
- **Data_Format**: 1D COMPLEX
- **Dim_Size**: 1310
- **Dim_Title**: Proton
- **Dim_Units**: ppm
- **Dimensions**: X
- **Spectrometer**: JNM-ECZ400S/L1
- **Field_Strength**: 9.389766[T] (400[MHz])
- **X_Acq_Duration**: 2.18628096[s]
- **X_Domain**: Proton
- **X_Freq**: 399.78219838[MHz]
- **X_Offset**: 5[ppm]
- **X_Points**: 16384
- **X_Prescans**: 1
- **X_Resolution**: 0.45739775[Hz]
- **X_Sweep**: 7.4940048[kHz]
- **X_Sweep_Clipped**: 5.99520384[kHz]
- **Irr_Domain**: Proton
- **Irr_Freq**: 399.78219838[MHz]
- **Irr_Offset**: 5[ppm]
- **Tri_Domain**: Proton
- **Tri_Freq**: 399.78219838[MHz]
- **Tri_Offset**: 5[ppm]
- **Blanking**: 2[us]
- **Clipped**: FALSE
- **Decimation_Reg**: r: 1668(1667),q:
- **Total_Scans**: 8
- **Relaxation_Delay**: 5[s]
- **Recvr_Gain**: 50
- **Temp_Get**: 20.5[dC]
- **X_90_Width**: 6.3[us]
- **X_Acq_Time**: 2.18628096[s]
- **X_Angle**: 45[deg]
- **X_Atn**: 1.6[db]
- **K_Pulse**: 3.15[us]
- **Irr_Mode**: Off
- **Tri_Mode**: Off
- **Comment_1**: *** Pulse ***

**Chemical Structure**

1H-NMR (400 MHz, CDCl₃)
$^{13}$C-NMR (100 MHz, CDCl$_3$)

$^{13}$C-NMR

Ke - parts per Million : Carbon13
13C-NMR (100 MHz, CDCl₃)

OTBS

Me₃C

OMe
$^{13}C$-NMR (100 MHz, CDCl$_3$)
$\text{Filename} = \text{SW02147_non-data-1-54.jdf}$
$\text{Author} = \text{delta}$
$\text{Experiment} = \text{proton.jxp}$
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$\text{Creation_Time} = \text{10-MAR-2018 14:29:45}$
$\text{Revision_Time} = \text{9-AUG-2018 12:30:08}$
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$\text{Comment_1} = ***\text{ Pulse ***}$

$\text{H-NMR} (400\text{ MHz, CDCl}_3)$
$^{13}$C-NMR (100 MHz, CDCl$_3$)

$^{13}$C-NMR spectrum of a molecule showing the chemical shifts of various carbon atoms in parts per million (ppm) range.
<table>
<thead>
<tr>
<th>ppm</th>
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<tbody>
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<td>143.0842</td>
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**NMR Spectrogram**

![NMR Spectrogram](image)

- **Sample Id**: SW02155
- **Solvent**: CHLOROFORM-D
- **Field Strength**: 9.389766 [T]
- **X Freq**: 100.52530333 [MHz]
- **X_Offset**: 100 [ppm]
- **X_Points**: 32768
- **X_Resolution**: 0.95846665 [Hz]
- **X_Sweep**: 31.40703518 [kHz]
- **X_90_Width**: 8.6 [us]
- **X_Acq_Time**: 1.04333312 [s]
- **X_Angle**: 30 [deg]
- **X_Atn**: 4 [dB]
- **X_Pulse**: 2.86666667 [us]
- **Decoupling**: TRUE
- **Initial_Wait**: 1 [s]
- **Noe**: TRUE
- **Noe_Time**: 1.5 [s]

**Chemical Shift Table**

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<th>ppm</th>
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<tbody>
<tr>
<td>166.0721</td>
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**Reference**: 13C-NMR (100 MHz, CDCl₃)
lycoperosamine-R (1)

1H-NMR
(400 MHz, CDCl₃)