Supporting Information

Total synthesis of (–)-Blepharocalyxin D

Haye Min Ko,^a Dong Gil Lee,^a Min Ah Kim,^a Hak Joong Kim,^a Jaejoon Park,^b
Myoung Soo Lah,^b and Eun Lee^{a*}

^aDepartment of Chemistry, College of Natural Sciences,
Seoul National University NS60, Seoul 151-747, Korea

^bDepartment of Chemistry and Applied Chemistry, Hanyang University, 1271 Sa-1-
dong, Ansan, Kyunggi-do 426-791, Korea

General Information

¹H- and ¹³C-NMR spectra were obtained on Bruker DPX-300 (300 MHz), Bruker Avance-600 (600 MHz) and JEOL ECX-400 (400 MHz). Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. Mass spectra were recorded on a JEOL JMS 600W spectrometer using electron impact (EI) or chemical ionization (CI), and JEOL JMS AX505WA spectrometer using fast atom bombardment (FAB) method. Significant fragments are reported in the following fashion: *m/z* (relative intensity). Optical rotation data were obtained on a JASCO P-1030 automatic polarimeter.

The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV light and/or by charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of methanol), KMnO₄ solution (3 g of KMnO₄, 20 g of K₂CO₃, and 5 mL of 5% NaOH solution in 300 mL of water), or phosphomolybdic acid solution (250 mg phosphomolybdic acid in 50 mL ethanol). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using hexane-EtOAc(v/v) or hexane-acetone(v/v). The solvents were simple distilled unless otherwise noted.

Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the organic extracts over anhydrous MgSO₄ or Na₂SO₄ and evaporating under reduced pressure using a rotary evaporator.

All solvents used in reactions were dried under nitrogen atmosphere. THF was

distilled from Na-benzophenone and CH_2Cl_2 was distilled from P_2O_5 . Et_2O was distilled from LAH. CH_3CN was distilled from CaH_2 and stored over 4 Å molecular sieves. Pyridine and TEA was distilled over KOH and stored over 4 Å molecular sieves.

Enantiomeric excesses were calculated from chiral HPLC using a chiralcel OD-H column (flow rate 0.5 mL/min), or from ^1H NMR spectra of the (*O*)-acetyl-(*S*)-mandelate derivatives.

Homoallylic alcohol **4**

TEA (14.7 mL, 105 mmol) and $\text{SO}_3 \cdot \text{pyridine}$ (8.38 g, 52.6 mmol) were added to a solution of alcohol **2** (4.37 g, 26.3 mmol) in $\text{DMSO}-\text{CH}_2\text{Cl}_2$ (1:1, 50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 20 min at this temperature. The reaction was quenched by addition of saturated NH_4Cl solution (40 mL) at 0 °C. The reaction mixture was extracted with CH_2Cl_2 (40 mL $\times$ 3). The organic extracts were washed with brine (40 mL), dried over MgSO_4 , filtered and concentrated. Purification of the residue by flash column chromatography (Hex-EtOAc, 2:1) gave aldehyde **2A** (4.14 g, 96%). R_f 0.68 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 9.82 (s, 1H), 7.12 (d, 2H, $J = 8.5$ Hz), 6.84 (d, 2H, $J = 8.5$ Hz), 3.79 (s, 3H), 2.91 (t, 2H, $J = 7.3$ Hz), 2.75 (t, 2H, $J = 7.3$ Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 201.7, 157.9, 132.2, 129.1, 113.8, 55.0, 45.3, 27.1. IR (neat): $\nu_{\text{max}} = 3001, 2935, 2835, 2725, 1724, 1612, 1583, 1514, 1466, 1408, 1389, 1248, 1034 \text{ cm}^{-1}$. MS m/z (CI, relative intensity): 165 ($\text{M}^+ + 1$, 15), 149 (23), 141 (34), 121 (100), 85 (9), 71 (8). HRMS (CI) calcd. for $\text{C}_{10}\text{H}_{13}\text{O}_2$ ($\text{M}^+ + 1$) 165.0915, found 165.0915.

$\text{Ti}(\text{O}^i\text{Pr})_4$ (0.804 mL, 2.70 mmol) was added to a solution of TiCl_4 (0.099 mL, 0.90 mmol) in CH_2Cl_2 (18 mL) at 0 °C under Ar. The reaction mixture was allowed to warm to room temperature and stirred for 1 h at this temperature. Ag_2O (0.417 g, 1.80 mmol) was added at room temperature and the whole reaction mixture was stirred for 5 h with exclusion of direct light. The reaction mixture was diluted with CH_2Cl_2 (36 mL) and treated with (*R*)-BINOL (1.03 g, 3.60 mmol) at room temperature for 2 h to furnish chiral catalyst **3** in CH_2Cl_2 solvent. Chiral catalyst **3** generated in situ in CH_2Cl_2 was cooled to -15 °C and treated with aldehyde **2A** (2.96 g, 18.0 mmol) in CH_2Cl_2 (1 mL)

and allyltributylstannane (11 mL, 36 mmol). The reaction mixture was allowed to warm to 0 °C and stirred for 7 h. The reaction was quenched with saturated NaHCO₃ (40 mL) and the reaction mixture was extracted with ether (40 mL × 3). The organic extracts were dried over Na₂SO₄ and concentrated. Flash chromatography of the residue on silica gel (Hex-EtOAc, 2:1) gave homoallylic alcohol **4** (3.5 g, 94%, 92% e.e.). R_f 0.44 (Hex-EtOAc, 2:1). The enantiomeric excess was determined by chiral HPLC (Chiralcel OD-H, 10% isopropanol/hexane, 0.5 mL/min): R_t = 10.0 min (*S*-isomer), 10.9 min (*R*-isomer). ¹H NMR (300 MHz, CDCl₃): δ 7.12 (d, 2H, *J* = 8.4 Hz), 6.83 (d, 2H, *J* = 8.4 Hz), 5.82 (ddt, 1H, *J* = 16.9, 10.1, 7.1 Hz), 5.14 (d, 2H, *J* = 12.6 Hz), 3.78 (s, 3H), 3.71-3.62 (m, 1H), 2.80-2.58 (m, 2H), 2.30 and 2.19 (ABX₂, 2H, *J*_{AB} = 13.3, *J*_{AX} = 7.0, *J*_{BX} = 7.2 Hz), 1.79-1.67 (m, 2H), 1.57 (d, 1H, *J* = 4.2 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 157.7, 134.6, 134.0, 129.3, 118.3, 113.8, 69.8, 55.2, 42.0, 38.6, 31.1. IR (neat): ν_{max} = 3348, 3072, 3032, 3003, 2927, 1612, 1514, 1469, 1454, 1335, 1300, 1246, 1034 cm⁻¹. MS *m/z* (EI, relative intensity): 206 (M⁺, 22), 188 (5), 147 (20), 122 (11), 121 (100), 91 (4), 70 (4). HRMS (EI) calcd. for C₁₃H₁₈O₂ (M⁺) 206.1307, found 206.1307. [α]_D¹¹ -19.5 (c 0.55, CHCl₃).

(*O*)-Acetyl-(*S*)-mandelate **5**

Oxalyl chloride (0.634 mL, 7.30 mmol) was added to a solution of (*S*)-(+)-(*O*)-acetylmandelic acid (141 mg, 0.730 mmol) in CH₂Cl₂ (0.5 mL) at room temperature. The reaction mixture was stirred for 1.5 h and the residual oxalyl chloride was thoroughly evaporated in vacuo. Homoallylic alcohol **4** (15 mg, 0.073 mmol) in CH₂Cl₂ (0.5 mL) and pyridine (0.018 mL, 0.22 mmol) were added to (*O*)-acetyl-(*S*)-mandeloyl chloride. The reaction mixture was stirred for 10 min and concentrated. Flash column chromatography (Hex-EtOAc, 2:1) gave (*O*)-acetyl-(*S*)-mandelate **5**. R_f 0.61 (Hex-EtOAc, 2:1). ¹H NMR (300 MHz, CDCl₃): δ 7.48-7.36 (m, 6H), 7.06 (d, 2H, *J* = 8.4 Hz), 6.81 (d, 2H, *J* = 8.4 Hz), 5.94-5.89 (m, 1H), 5.42 (ddt, 1H, *J* = 16.4, 10, 7.2 Hz), 4.98-4.92 (m, 1H), 4.81 (d, 1H, *J* = 9.5 Hz), 4.78 (d, 1H, *J* = 17.2 Hz), 3.78 (s, 3H), 3.72 (s, 1H), 2.65-2.51 (m, 2H), 2.20 (s, 6H), 1.92-1.79 (m, 2H).

mixture was stirred for 20 min at this temperature. Ylide generated in situ in THF was treated with aldehyde **8** (452 mg, 2.03 mmol) in THF (4 mL). The reaction mixture was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$, warmed to $0\text{ }^{\circ}\text{C}$ over 30 min. The reaction was diluted with ether (10 mL) and quenched by addition of acetone (10 mL). The reaction mixture was filtered through a short pad of silica gel. Concentration of filtrate and purification of the residue by flash chromatography (Hex-EtOAc, 4:1) gave **8A** (86 mg, 19%) and **8B** (172 mg, 39%). **8A**, R_f 0.65 (Hex-EtOAc, 4:1). ^1H NMR (300 MHz, CDCl_3): δ 7.41 (d, 2H, $J = 8.6$ Hz), 6.89 (d, 2H, $J = 8.6$ Hz), 5.53 (ddd, 1H, $J = 17.5, 10.3, 7.4$ Hz), 5.39 (s, 1H), 5.17 (d, 1H, $J = 18.8$ Hz), 5.15 (d, 1H, $J = 9.5$ Hz), 4.21 (dd, 2H, $J = 11.5, 4.7$ Hz), 3.80 (s, 3H), 3.70 (t, 2H, $J = 11.4$ Hz), 2.86-2.80 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 160.0, 133.6, 130.9, 127.4, 118.0, 113.7, 101.2, 71.3, 55.3, 38.9. **8B**, R_f 0.57 (Hex-EtOAc, 4:1). ^1H NMR (300 MHz, CDCl_3): δ 7.41 (d, 2H, $J = 8.6$ Hz), 6.89 (d, 2H, $J = 8.6$ Hz), 6.38 (ddd, 1H, $J = 17.6, 10.2, 7.6$ Hz), 5.50 (s, 1H), 5.28 (d, 1H, $J = 17.4$ Hz), 5.21 (d, 1H, $J = 10.5$ Hz), 4.19-4.10 (m, 4H), 3.80 (s, 3H), 2.19-2.17 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 160.0, 138.3, 131.1, 127.4, 116.0, 113.6, 101.7, 71.0, 55.3, 38.5. IR (neat): $\nu_{\text{max}} = 3070, 2964, 2910, 2850, 1614, 1518, 1464, 1387, 1304, 1248, 1171, 1032\text{ cm}^{-1}$. MS m/z (CI, relative intensity): 221($\text{M}^+ + 1$, 100), 220 (17), 219 (14), 137 (31), 113 (61), 67 (13). HRMS (CI) calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_3$ ($\text{M}^+ + 1$) 221.1178, found 221.1178.

CAN (6.8 g, 12 mmol) was added to a solution of **8A** and **8B** (544 mg, 2.47 mmol) in $\text{CH}_3\text{CN-H}_2\text{O}$ (9:1, 56 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to warm to room temperature and stirred for 20 min. The reaction mixture was diluted with EtOAc and treated with saturated NaHCO_3 (40 mL) at $0\text{ }^{\circ}\text{C}$. The mixture was extracted with EtOAc (40 mL $\times$ 3) and the organic extracts were dried over Na_2SO_4 , filtered, and concentrated. Purification of the residue by flash chromatography (Hex-EtOAc, 1:1) gave diol **9** (205 mg, 81%). R_f 0.11 (Hex-EtOAc, 1:1). ^1H NMR (300 MHz, CDCl_3): δ 5.77-5.65 (m, 1H), 5.21 (dd, 1H, $J = 11, 0.7$ Hz), 5.20 (d, 1H, $J = 16.9$ Hz), 3.76 (d, 4H, $J = 6.2$ Hz), 2.54 (dqui, 1H, $J = 6.4, 6.4$ Hz), 2.21 (br, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 135.6, 118.1, 64.7, 47.5. IR (neat): $\nu_{\text{max}} = 3400, 2927, 1643, 1425, 1032\text{ cm}^{-1}$. MS m/z (CI, relative intensity): 103 ($\text{M}^+ + 1$, 16), 89 (21), 85 (69), 67 (100), 57 (58), 55 (46), 54 (20). HRMS (CI) calcd. for $\text{C}_5\text{H}_{11}\text{O}_2$ ($\text{M}^+ + 1$) 103.0759, found 103.0759.

Olefin **10**

Ac₂O (0.16 mL, 1.7 mmol), TEA (0.38 mL, 2.8 mmol) and DMAP (4.2 mg, 0.035 mmol) were added to a solution of diol **9** (70.6 mg, 0.690 mmol) in CH₂Cl₂ (7 mL) at room temperature. The reaction mixture was stirred for 1 h, and quenched with saturated NH₄Cl (10 mL) and extracted with CH₂Cl₂ (10 mL × 3). The organic extracts were dried over MgSO₄, concentrated. Flash column chromatography (Hex-EtOAc, 2:1) gave olefin **10** (107 mg, 83%). R_f 0.57 (Hex-EtOAc, 2:1). ¹H NMR (300 MHz, CDCl₃): δ 5.72 (ddd, 1H, *J* = 17.6, 10, 7.7 Hz), 5.193 (d, 1H, *J* = 16 Hz), 5.186 (d, 1H, *J* = 11.8 Hz), 4.18-4.07 (m, 4H), 2.75 (dqui, 1H, *J* = 6.5, 6.5 Hz), 2.06 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 170.9, 134.6, 118.2, 63.9, 41.8, 20.8. IR (neat): ν_{max} = 3084, 2958, 1745, 1645, 1427, 1381, 1367, 1227, 1039 cm⁻¹. MS *m/z* (CI, relative intensity): 187 (M⁺+1, 2), 127 (100), 89 (6), 85 (4), 67 (12), 61 (4). HRMS (CI) calcd. for C₉H₁₅O₄ (M⁺+1) 187.0970, found 187.0970.

Alcohol **12**

Olefin **10** (20 mg, 0.11 mmol) and homoallylic alcohol **4** (11 mg, 0.053 mmol) were added to a solution of Hoveyda-Grubbs 2nd generation catalyst **11** (2 mg, 5 mol%) in CH₂Cl₂ (1 mL) at room temperature under Ar. The reaction mixture was stirred for 24 h at this temperature. Concentration and purification of the residue by flash column chromatography (Hex-EtOAc, 2:1) gave alcohol **12** (13 mg, 67%). R_f 0.22 (Hex-EtOAc, 2:1). ¹H NMR (300 MHz, CDCl₃): δ 7.12 (d, 2H, *J* = 8.5 Hz), 6.83 (d, 2H, *J* = 8.6 Hz), 5.70-5.56 (m, 1H), 5.42 (dd, 1H, *J* = 15.5, 8.0 Hz), 4.15-4.02 (m, 4H), 3.79 (s, 3H), 3.62 (br, 1H), 2.79-2.58 (m, 3H), 2.27 and 2.15 (ABX₂, 2H, *J*_{AB} = 13.5, *J*_{AX} = 6.3, *J*_{BX} = 7.1 Hz), 2.04 (s, 6H), 1.77-1.69 (m, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 170.94, 170.92, 157.7, 133.9, 130.1, 130.0, 129.2, 113.7, 69.8, 64.15, 64.11, 55.2, 41.2, 40.8, 38.6, 31.0, 20.8. IR (neat): ν_{max} = 3464, 2935, 1739, 1612, 1583, 1514, 1466, 1367, 1246, 1178, 1038 cm⁻¹. MS *m/z* (CI, relative intensity): 365 (M⁺+1, 5), 305 (29), 287 (49), 227 (100), 147 (18), 140 (18), 121 (61). HRMS (CI) calcd. for C₂₀H₂₉O₆ (M⁺+1) 365.1964, found 365.1964. [α]_D²⁷ -4.6 (c 0.78, CHCl₃).

Oxane **13**

Anisaldehyde (0.0053 mL, 0.047 mmol) and TMSOAc (0.0060 mL, 0.039 mmol) were added to a solution of homoallylic alcohol **12** (14 mg, 0.039 mmol) in AcOH (0.090 mL, 1.6 mmol) at room temperature. TESOTf (0.040 mL, 0.16 mmol) was added dropwise to the resulting solution at the same temperature. The reaction mixture was stirred for 1 h, diluted with CH₂Cl₂ (2 mL), and treated with TEA (0.1 mL). Concentration and purification of the residue by flash column chromatography (Hex-EtOAc, 1:1) gave oxane **13** (13 mg, 60%). *R*_f 0.57 (Hex-EtOAc, 1:1). ¹H NMR (300 MHz, CDCl₃): δ 7.27 (d, 2H, *J* = 9.3 Hz), 7.03 (d, 2H, *J* = 8.6 Hz), 6.91 (d, 2H, *J* = 8.6 Hz), 6.80 (d, 2H, *J* = 8.6 Hz), 5.02 (td, 1H, *J* = 10.8, 4.7 Hz), 4.24 (d, 1H, *J* = 10.5 Hz), 4.10 (dd, 1H, *J* = 11, 7.9 Hz), 3.96 (dd, 1H, *J* = 11, 7.0 Hz), 3.87 (d, 2H, *J* = 6.0 Hz), 3.82 (s, 3H), 3.78 (s, 3H), 3.51-3.41 (m, 1H), 2.69-2.52 (m, 2H), 2.25-2.20 (m, 1H), 2.14 (t, 1H, *J* = 11.3 Hz), 2.08 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.94-1.89 (m, 1H), 1.87-1.80 (m, 1H), 1.75-1.64 (m, 1H), 1.43 (q, 1H, *J* = 11.4 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 170.5, 170.0, 159.7, 157.8, 133.8, 131.8, 129.3, 129.0, 114.1, 113.7, 81.1, 74.3, 72.3, 64.4, 62.0, 55.3, 55.2, 45.8, 37.8, 37.3, 36.2, 30.4, 21.4, 20.8. IR (neat): *v*_{max} = 2952, 2837, 1739, 1612, 1585, 1514, 1464, 1367, 1246, 1178, 1036 cm⁻¹. MS *m/z* (FAB, relative intensity): 542 (M⁺, 4), 483 (10), 282 (11), 154 (60), 121 (100), 69 (64), 55 (76), 43 (61). HRMS (FAB) calcd. for C₃₀H₃₈O₉ (M⁺) 542.2516, found 542.2523. [α]_D¹³ -22.6 (c 0.55, CHCl₃).

Thionocarbonate **14**

K_2CO_3 (1.53 g, 11.1 mmol) was added to a solution of oxane **13** (602 mg, 1.11 mmol) in MeOH (30 mL) at room temperature. The reaction mixture was stirred for 3 h and concentrated, and diluted with H_2O (20 mL). The reaction mixture was extracted with ether (20 mL $\times$ 3), and the organic extracts were dried over MgSO_4 and filtered. Concentration and purification of the residue by flash chromatography (Hex-Acetone, 1:1) gave triol **13A** (392 mg, 85%). R_f 0.26 (Hex-Acetone, 1:1). ^1H NMR (300 MHz, CDCl_3): δ 7.24 (d, 2H, $J = 8.0$ Hz), 7.04 (d, 2H, $J = 8.6$ Hz), 6.87 (d, 2H, $J = 8.6$ Hz), 6.79 (d, 2H, $J = 8.6$ Hz), 4.98 (br, 1H), 4.31 (br, 1H), 4.11 (d, 1H, $J = 10.4$ Hz), 3.78 (s, 3H), 3.76 (s, 3H), 3.69 (br, 2H), 3.60 (d, 1H, $J = 8.3$ Hz), 3.41-3.34 (m, 2H), 3.20 (br, 1H), 2.68-2.52 (m, 2H), 2.02 (dd, 1H, $J = 12.0, 3.6$ Hz), 1.93-1.81 (m, 1H), 1.77-1.65 (m, 2H), 15.9-1.58 (m, 1H), 1.42 (q, 1H, $J = 11.5$ Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 159.4, 157.7, 134.0, 132.7, 129.3, 129.0, 114.0, 113.7, 81.6, 74.5, 68.2, 64.0, 60.2, 55.22, 55.20, 51.5, 41.1, 40.8, 37.4, 30.4. IR (neat): $\nu_{\text{max}} = 3334, 2937, 1612, 1585, 1514, 1464, 1369, 1300, 1248, 1178, 1034\text{ cm}^{-1}$. MS m/z (FAB, relative intensity): 417 ($\text{M}^+ + 1$, 6), 399 (10), 191 (12), 154 (25), 121 (100), 55 (24), 43 (17). HRMS (FAB) calcd. for $\text{C}_{24}\text{H}_{33}\text{O}_6$ ($\text{M}^+ + 1$) 417.2277, found 417.2290. $[\alpha]_D^{13} -50.9$ (c 0.56, CHCl_3).

Phenyl chlorothionoformate (0.0061 mL, 0.044 mmol) and pyridine (0.0060 mL, 0.073 mmol) were added to a solution of triol **13A** (15 mg, 0.037 mmol) in CH_2Cl_2 (3 mL) at 0°C . The reaction mixture was allowed to warm to room temperature and stirred for 20 min. Concentration and purification of the residue by flash chromatography (Hex-Acetone, 1:1) gave thionocarbonate **14** (16 mg, 80%). R_f 0.42 (Hex-Acetone, 1:1).

^1H NMR (300 MHz, CDCl_3): δ 7.40 (t, 2H, $J = 7.7$ Hz), 7.29 (d, 1H, $J = 7.0$ Hz), 7.27 (d, 2H, $J = 6.8$ Hz), 7.07 (d, 2H, $J = 8.4$ Hz), 7.04 (d, 2H, $J = 7.5$ Hz), 6.90 (d, 2H, $J = 8.6$ Hz), 6.81 (d, 2H, $J = 8.5$ Hz), 4.81-4.70 (m, 1H), 4.42 (dd, 1H, $J = 10.9, 5.9$ Hz), 4.13 (d, 1H, $J = 10.4$ Hz), 4.04-3.99 (m, 1H), 3.84-3.76 (m, 8H), 3.48-3.41 (m, 1H), 3.03 (br, 1H), 2.63 (t, 2H, $J = 7.5$ Hz), 2.17 (br, 1H), 2.09-2.02 (m, 2H), 1.97-1.84 (m, 1H), 1.81-1.69 (m, 2H), 1.52 (q, 1H, $J = 11.9$ Hz).

Acetal **16**

1-Methylimidazole (0.134 mL, 1.72 mmol) was added dropwise to a solution of thionyl chloride (0.123 mL, 1.72 mmol) in CH_3CN (0.2 mL) at room temperature. The reaction mixture was stirred for 12 h and concentrated. Residual CH_3CN , thionyl chloride, and 1-methylimidazole were removed in vacuo at 150°C . The ionic liquid **15** generated was diluted with CH_2Cl_2 (3 mL). Aldehyde **2A** (24 mg, 0.15 mmol) and thionocarbonate **14** (68 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) were added to the resulting solution. The mixture was heated under reflux for 90 min and treated with H_2O (6 mL). The reaction mixture was extracted with ether (6 mL $\times$ 3), and the organic extracts were dried over Na_2SO_4 . Concentration and purification of the residue by flash

chromatography (Hex-EtOAc, 2:1) gave **14A** (60 mg, 69%). R_f 0.44 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 7.38 (t, 2H, $J = 7.8$ Hz), 7.30-7.23 (m, 3H), 7.12-7.00 (m, 6H), 6.89 (d, 2H, $J = 8.5$ Hz), 6.83 (d, 2H, $J = 8.3$ Hz), 6.81 (d, 2H, $J = 8.4$ Hz), 4.50 (t, 1H, $J = 5.1$ Hz), 4.31 (t, 1H, $J = 10.4$ Hz), 4.07 (dd, 1H, $J = 13.3, 2.8$ Hz), 3.97 (d, 1H, $J = 10.2$ Hz), 3.86-3.78 (m, 11H), 3.63 (dd, 1H, $J = 10.3, 4.5$ Hz), 3.44-3.37 (m, 1H), 2.70-2.62 (m, 4H), 2.07-2.00 (m, 1H), 1.96-1.87 (m, 3H), 1.82-1.73 (m, 2H), 1.66-1.52 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 194.2, 159.7, 157.8, 157.7, 153.3, 133.9, 133.7, 131.8, 129.4, 129.3, 129.0, 126.4, 121.9, 114.1, 113.8, 113.7, 105.9, 82.7, 79.0, 74.6, 73.9, 66.9, 55.3, 55.2, 50.2, 39.3, 39.1, 37.4, 36.4, 30.4, 29.9. IR (neat): $\nu_{\text{max}} = 2951, 2835, 1612, 1585, 1512, 1464, 1379, 1298, 1246, 1201, 1136, 1036\text{ cm}^{-1}$. MS m/z (FAB, relative intensity): 698 (M^+ , 2), 535 (9), 399 (8), 173 (15), 121 (100), 55 (20), 43 (13). HRMS (FAB) calcd. for $\text{C}_{41}\text{H}_{46}\text{O}_8\text{S}$ (M^+) 698.2913, found 698.2928.

NaHCO_3 (0.61 mg, 7.2 mmol) was added to a solution of **14A** (1.01 g, 1.44 mmol) in diphenyl ether (20 mL). The reaction mixture was heated under reflux for 3 h. Flash chromatography (Hex-EtOAc, 2:1) gave the cyclic acetal **16** (619 mg, 79%). R_f 0.49 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 7.24 (d, 2H, $J = 8.3$ Hz), 7.08 (d, 4H, $J = 8.2$ Hz), 6.83 (t, 6H, $J = 8.2$ Hz), 4.96 (s, 1H), 4.77 (s, 1H), 4.63 (t, 1H, $J = 5.5$ Hz), 4.39 (d, 1H, $J = 10.7$ Hz), 4.21 and 4.07 (ABq, 2H, $J = 12.6$ Hz), 3.78 (s, 9H), 3.54-3.41 (m, 2H), 2.71-2.62 (m, 5H), 2.08 (dd, 1H, $J = 12.8, 3.1$ Hz), 1.99-1.87 (m, 3H), 1.80-1.69 (m, 1H), 1.56 (q, 1H, $J = 11.8$ Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 159.2, 157.8, 157.7, 145.4, 134.0, 133.7, 132.4, 129.4, 129.3, 129.2, 116.6, 113.84, 113.79, 113.74, 113.65, 100.2, 80.7, 79.9, 74.8, 74.6, 55.24, 55.19, 51.9, 38.3, 37.5, 37.4, 30.5, 30.0.

Aldehyde **17**

Acetal **16** (619 mg, 1.14 mmol) in CH_2Cl_2 (20 mL) was cooled to $-55\text{ }^\circ\text{C}$ and treated dropwise with $\text{BF}_3\cdot\text{OEt}_2$ (0.173 mL, 1.36 mmol). The reaction mixture was

stirred for 3 h at the same temperature, allowed to warm to $-20\text{ }^{\circ}\text{C}$, and stirred for 15 min. The reaction was quenched with saturated NH_4Cl (20 mL), and the reaction mixture was extracted with CH_2Cl_2 (20 mL $\times$ 3). The organic extracts were dried over Na_2SO_4 . Purification by flash chromatography (Hex-EtOAc, 2:1) gave aldehyde **17** (526 mg, 85%). R_f 0.51 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 9.68 (s, 1H), 7.23 (d, 2H, $J = 7.1$ Hz), 7.07 (d, 4H, $J = 8.5$ Hz), 6.87 (d, 2H, $J = 6.8$ Hz), 6.81 (d, 4H, $J = 8.6$ Hz), 4.65 (d, 1H, $J = 10.5$ Hz), 3.84-3.75 (m, 10H), 3.60-3.53 (m, 1H), 3.44-3.35 (m, 1H), 2.76-2.53 (m, 4H), 2.32 (t, 1H, $J = 4.2$ Hz), 2.06-2.01 (m, 1H), 1.99-1.94 (m, 1H), 1.91-1.80 (m, 1H), 1.78-1.73 (m, 3H), 1.66-1.62 (m, 1H), 1.55-1.43 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 203.3, 159.5, 157.8, 157.7, 134.1, 134.0, 131.7, 129.33, 129.26, 128.5, 114.0, 113.80, 113.76, 78.5, 75.0, 74.3, 72.7, 55.3, 55.2, 49.1, 45.7, 38.6, 38.0, 37.8, 31.8, 30.7, 30.5. IR (neat): $\nu_{\text{max}} = 2935, 2835, 1720, 1612, 1583, 1514, 1464, 1300, 1246, 1178, 1068, 1036\text{ cm}^{-1}$. MS m/z (FAB, relative intensity): 545 ($\text{M}^+ + 1$, 11), 307 (25), 289 (12), 154 (100), 121 (70), 107 (21), 89 (16). HRMS (FAB) calcd. for $\text{C}_{34}\text{H}_{41}\text{O}_6$ ($\text{M}^+ + 1$) 545.2903, found 545.2894. $[\alpha]_D^{16} -32.1$ (c 0.23, CHCl_3).

Aldehyde **18**

NaOH solution (2 N, 15 mL) was added to a solution of aldehyde **17** (526 mg, 0.970 mmol) in THF (15 mL). The reaction mixture was heated under reflux for 4 h, and treated with saturated NH_4Cl (20 mL). The mixture was extracted with ether (20 mL $\times$ 3), and the organic extracts were washed with brine (20 mL), dried over MgSO_4 , filtered, and concentrated. Purification of the residue by flash chromatography (Hex-EtOAc, 2:1) gave aldehyde **18** (272 mg, 52%). R_f 0.37 (Hex-EtOAc, 2:1). Aldehyde **17** (133 mg, 25%) was also recovered. ^1H NMR (300 MHz, CDCl_3): δ 8.38 (d, 1H, $J = 4.7$ Hz), 7.21 (br, 2H), 7.10-7.06 (m, 4H), 6.86-6.80 (m, 6H), 3.91 (d, 1H, $J = 9.6$ Hz), 3.79 (s, 9H), 3.58-3.51 (m, 1H), 3.36-3.28 (m, 2H), 2.75-2.57 (m, 4H), 2.24-2.13 (m, 1H), 2.06 (dd, 1H, $J = 12.2, 2.1$ Hz), 2.01-1.87 (m, 2H), 1.85-1.77 (m, 2H), 1.74-1.61 (m, 2H), 1.50-

1.41 (m, 1H), 1.31 (q, 1H, $J = 11.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3): δ 200.0, 160.1, 157.83, 157.75, 134.0, 133.7, 131.0, 129.33, 129.30, 113.8, 113.7, 82.0, 77.9, 75.2, 74.7, 55.25, 55.21, 49.7, 47.6, 37.9, 37.73, 37.65, 32.2, 30.5, 30.4. IR (neat): $\nu_{\text{max}} = 2937$, 2837, 1720, 1612, 1583, 1512, 1464, 1300, 1246, 1176, 1132, 1034 cm^{-1} . MS m/z (EI, relative intensity): 544 (M^+ , 20), 526 (14), 366 (24), 323 (11), 147 (14), 121 (100). HRMS (EI) calcd. for $\text{C}_{34}\text{H}_{40}\text{O}_6$ (M^+) 544.2825, found 544.2825. $[\alpha]_{\text{D}}^{16} -30.0$ (c 0.34, CHCl_3).

Sulfone **19**

A solution of BTSH (3.03 g, 18.1 mmol) and DEAD (2.85 mL, 18.1 mmol) in THF (20 mL) was added to a solution of alcohol **19A** (1.81 mL, 14.5 mmol) and PPh_3 (4.75 g, 18.1 mmol) in THF (20 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was concentrated and purified by flash chromatography (Hex-EtOAc, 2:1) to give sulfide **19B** (4.16 g, quant.). R_f 0.71 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 7.89 (d, 1H, $J = 8.1$ Hz), 7.72 (dd, 1H, $J = 8.0$, 0.6 Hz), 7.43-7.33 (m, 3H), 7.30-7.23 (m, 1H), 6.86-6.82 (m, 2H), 4.54 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 166.5, 159.1, 153.1, 135.2, 130.3, 127.9, 126.0, 124.2, 121.4, 120.9, 114.0, 55.2, 37.2. IR (neat): $\nu_{\text{max}} = 3047$, 2962, 2927, 2837, 1614, 1516, 1456, 1427, 1309, 1257, 1037 cm^{-1} . MS m/z (CI, relative intensity): 288 ($\text{M}^+ + 1$, 34), 410 (12), 409 (27), 408 (100), 289 (8), 287 (21), 121 (44). HRMS (CI) calcd. for $\text{C}_{15}\text{H}_{14}\text{NOS}_2$ ($\text{M}^+ + 1$) 288.0517, found 288.0517.

m -CPBA (9.45 g, 54.8 mmol) and NaHCO_3 (9.20 g, 110 mmol) were added to a solution of sulfide **19B** (3.32 g, 11.0 mmol) in CH_2Cl_2 (40 mL) at room temperature. The reaction mixture was stirred for 5 h and treated with aqueous solution saturated with NaHCO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ (30 mL). The reaction mixture was extracted with EtOAc (40 mL $\times$ 3). The organic extracts were washed with brine (40 mL), dried over Na_2SO_4 , filtered, and concentrated. Purification of the residue by flash chromatography (Hex-EtOAc, 2:1) gave sulfone **19** (3.50 g, quant.). R_f 0.43 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 8.25 (d, 1H, $J = 7.9$ Hz), 7.96-7.93 (m, 1H), 7.67-7.55 (m, 2H), 7.18 (d, 2H, $J = 8.7$ Hz), 6.79 (d, 2H, $J = 8.7$ Hz), 4.70 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (75 MHz,

CDCl₃): δ 165.5, 160.3, 152.6, 137.1, 132.3, 127.9, 127.6, 125.4, 122.3, 118.1, 114.4, 60.4, 55.2. IR (neat): $\nu_{\max}$ = 3020, 2974, 2927, 2843, 1610, 1514, 1466, 1325, 1257, 1147, 1026 cm⁻¹. MS m/z (CI, relative intensity): 320 ($M^+ + 1$, 14), 440 (32), 257 (13), 256 (77), 122 (9), 121 (100). HRMS (CI) calcd. for C₁₅H₁₄NO₃S₂ ($M^+ + 1$) 320.0415, found 320.0415.

Tetramethyl blepharocalyxin D (**20**)

Sulfone **19** (248 mg, 0.780 mmol) in THF (10 mL) was cooled to -78 °C and treated dropwise with LiHMDS (1.0 M in THF, 1.62 mL) under Ar. The reaction mixture was stirred for 20 min and treated with aldehyde **18** (353 mg, 0.650 mmol) in THF (10 mL). The reaction mixture was stirred for 3 h at the same temperature and allowed to warm to room temperature, stirred for 3 h, and treated with H₂O (15 mL). The reaction mixture was extracted with ether (20 mL $\times$ 3), and the organic extracts were dried over MgSO₄, and concentrated. Purification of the residue by flash chromatography (Hex-EtOAc, 2:1) gave tetramethyl blepharocalyxin D (**20**, 323 mg, 77%). R_f 0.57 (Hex-EtOAc, 2:1). ¹H NMR (300 MHz, CDCl₃): δ 7.14 (br, 1H), 7.08 (t, 5H, J = 8.8 Hz), 6.81 (t, 4H, J = 7.5 Hz), 6.72-6.65 (m, 6H), 5.70 (d, 1H, J = 15.8 Hz), 4.98 (dd, 1H, J = 15.8, 8.8 Hz), 3.94 (d, 1H, J = 9.7 Hz), 3.78 (d, 6H, J = 2.2 Hz), 3.75 (s, 3H), 3.52-3.42 (m, 5H), 3.37-3.29 (m, 1H), 2.75-2.57 (m, 4H), 2.16-2.02 (m, 2H), 1.98-1.86 (m, 1H), 1.84-1.75 (m, 2H), 1.73-1.57 (m, 3H), 1.54-1.50 (m, 1H), 1.29 (q, 1H, J = 12.5 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 159.0, 158.3, 157.62, 157.57, 134.11, 134.08, 133.2, 132.2, 130.4, 129.33, 129.31, 126.9, 126.7, 113.7, 113.6, 113.2, 82.7, 79.1, 75.6, 74.8, 55.2, 54.8, 51.0, 41.9, 40.3, 38.1, 37.8, 37.6, 30.6, 30.4. IR (neat): $\nu_{\max}$ = 2997, 2933, 2835, 1738, 1707, 1610, 1583, 1512, 1464, 1360, 1300, 1246, 1176, 1036 cm⁻¹. MS m/z (EI, relative intensity): 648 (M^+ , 67), 338 (9), 308 (9), 174 (16), 147 (15), 121 (100). HRMS (EI) calcd. for C₄₂H₄₈O₆ (M^+) 648.3451, found 648.3451. $[\alpha]_D^{14}$ -90.4 (c 0.32, CHCl₃).

Blepharocalyxin D (**1**)

n-PrSLi (3 M in HMPA, 1 mL) was added to a solution of **20** (33 mg, 0.05 mmol) in HMPA (1.8 mL). The reaction mixture was heated under reflux for 3 h at 160–180 °C. The reaction was quenched with saturated aqueous NH₄Cl solution (3 mL) and H₂O (2 mL), and the mixture was extracted with EtOAc (5 mL × 3). The organic extracts were dried over Na₂SO₄. Concentration and purification of the residue by flash chromatography (CHCl₃-MeOH, 10:1) gave blepharocalyxin D (**1**, 17 mg, 56%). *R*_f 0.2 (CHCl₃-MeOH, 10:1). ¹H NMR (300 MHz, CD₃OD): δ 7.08 (br, 2H), 6.98 (t, 4H, *J* = 7.8 Hz), 6.70–6.52 (m, 10H), 5.75 (d, 1H, *J* = 15.8 Hz), 5.00 (dd, 1H, *J* = 15.7, 8.6 Hz), 3.97 (d, 1H, *J* = 9.8 Hz), 3.53–3.48 (m, 2H), 3.41–3.34 (m, 1H), 2.70–2.52 (m, 4H), 2.20–2.11 (m, 1H), 2.01–1.97 (m, 1H), 1.88–1.78 (m, 1H), 1.75–1.66 (m, 2H), 1.63–1.56 (m, 2H), 1.54–1.46 (m, 2H), 1.26 (q, 1H, *J* = 12.1 Hz). ¹³C NMR (75 MHz, CD₃OD): δ 158.2, 157.0, 156.38, 156.35, 134.23, 134.19, 133.5, 132.7, 131.0, 130.4, 130.3, 128.6, 128.0, 116.1, 116.0, 115.7, 84.4, 80.6, 77.3, 76.4, 52.2, 43.1, 41.8, 39.4, 39.2, 31.8, 31.6. IR (neat): *v*_{max} = 3375, 3022, 2976, 2931, 1660, 1614, 1514, 1446, 1383, 1230, 1101 cm⁻¹. MS *m/z* (FAB, relative intensity): 591 (*M*⁻1, 3), 306 (57), 266 (56), 199 (35), 153 (100), 113 (73), 46 (32). HRMS (FAB) calcd. for C₃₈H₃₉O₆ (*M*⁻1) 591.2747, found 591.2734.

Tetramethyl blepharocalyxin D (**20**) from **1**

A mixture of blepharocalyxin D (**1**, 1.3 mg, 2.2×10^{-6} mmol), K_2CO_3 (3.0 mg, 2.2×10^{-5} mmol), and MeI (0.01 mL, 2.2×10^{-5} mmol) in acetone (2 mL) was heated under reflux over 4 h. The reaction mixture was filtered to remove K_2CO_3 and concentrated. The residue was dissolved in EtOAc and washed with water. The organic layer was dried over Na_2SO_4 and evaporated at reduced pressure. Purification by flash chromatography (Hex-EtOAc, 2:1) gave tetramethyl blepharocalyxin D (**20**, 1.3 mg, 91%). R_f 0.57 (Hex-EtOAc, 2:1). ^1H NMR (300 MHz, CDCl_3): δ 7.14 (br, 1H), 7.08 (t, 5H, $J = 8.8$ Hz), 6.81 (t, 4H, $J = 7.5$ Hz), 6.72-6.65 (m, 6H), 5.70 (d, 1H, $J = 15.8$ Hz), 4.98 (dd, 1H, $J = 15.8, 8.8$ Hz), 3.94 (d, 1H, $J = 9.7$ Hz), 3.78 (d, 6H, $J = 2.2$ Hz), 3.75 (s, 3H), 3.52-3.42 (m, 5H), 3.37-3.29 (m, 1H), 2.75-2.57 (m, 4H), 2.16-2.02 (m, 2H), 1.98-1.86 (m, 1H), 1.84-1.75 (m, 2H), 1.73-1.57 (m, 3H), 1.54-1.50 (m, 1H), 1.29 (q, 1H, $J = 12.5$ Hz). $[\alpha]_{\text{D}}^{23} -87.8$ (c 0.065, CHCl_3).

Crystallographic Data Collection and Refinements of Structure for 20

Crystal of appropriate dimensions was mounted on glass fiber in random orientation, Preliminary examination and data collection were performed using a Bruker SMART CCD Detector single crystal X-Ray diffractometer using a graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) source equipped with a sealed tube X-ray source at -100°C for **20**. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ω) scans. A data set collected consists of 1286 frames of intensity data collected with a frame width of 0.3° in ω and counting time of 10 seconds / frame at a crystal to detector distance of 5.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 1997) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of 8130 reflections ($\theta < 28.2^\circ$). Collected data were corrected for absorbance using SADABS based upon the Laue symmetry using equivalent reflections. Structure solution and refinement of the structure were carried out using the SHELXTL-PLUS (5.03) software package (Sheldrick, G. M., Siemens Analytical X-Ray Division, Madison, WI, 1997). The structure was solved by direct method and refined successfully in the space group $P2_12_12_1$. Full matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. One of the phenyl groups was statistically disordered. All non-hydrogen atoms except for the minor part of the disordered phenyl group were refined anisotropically; hydrogen atoms were assigned isotropic displacement coefficients $U(\text{H}) = 1.2U(\text{C})$ or $1.5U(\text{C}_{\text{methyl}})$, and their coordinates were allowed to ride on their respective atoms. Refinement of the structure converged at a final $R1 = 0.0691$, $wR2 = 0.1265$ for 5317 reflections with $I > 2\sigma(I)$, $R1 = 0.1181$, $wR2 = 0.1417$ for all 8308 reflections. The largest difference peak and hole were 0.258 and $-0.245 \text{ e} \cdot \text{\AA}^{-3}$, respectively. A summary of the crystal and intensity data is given in Table S1.

Table S1. Crystal data and structure refinement for **20**.

Empirical formula	C ₄₂ H ₄₈ O ₆	
Formula weight	648.80	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	<i>a</i> = 6.0896(11) Å	$\alpha = 90^\circ$.
	<i>b</i> = 22.401(4) Å	$\beta = 90^\circ$.
	<i>c</i> = 26.176(5) Å	$\gamma = 90^\circ$.
Volume	3570.7(11) Å ³	
<i>Z</i>	4	
Density (calculated)	1.207 Mg/m ³	
Absorption coefficient	0.079 mm ⁻¹	
<i>F</i> (000)	1392	
Crystal size	0.45 x 0.43 x 0.20 mm ³	
Theta range for data collection	1.20 to 28.34°.	
Index ranges	-5 ≤ <i>h</i> ≤ 8, -29 ≤ <i>k</i> ≤ 28, -34 ≤ <i>l</i> ≤ 22	
Reflections collected	21341	
Independent reflections	8308 [<i>R</i> (int) = 0.0461]	
Completeness to theta = 28.34°	96.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9843 and 0.9652	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8308 / 0 / 471	
Goodness-of-fit on <i>F</i> ²	1.057	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0691, <i>wR</i> 2 = 0.1265	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1181, <i>wR</i> 2 = 0.1417	
Absolute structure parameter	-0.2(14)	
Largest diff. peak and hole	0.258 and -0.245 e.Å ⁻³

¹H-NMR (300 MHz, CDCl₃) of **4**

¹³C-NMR (75 MHz, CDCl₃) of **4**

¹H-NMR (300 MHz, CDCl₃) of **10**

¹³C-NMR (75 MHz, CDCl₃) of **10**

^1H -NMR (300 MHz, CDCl_3) of **12**

¹³C-NMR (75 MHz, CDCl₃) of **12**

¹H-NMR (600 MHz, CDCl₃) of **13**

¹³C-NMR (75 MHz, CDCl₃) of **13**

$^1\text{H-NMR}$ (300 MHz, CDCl_3) of **13A**

^{13}C -NMR (75 MHz, CDCl_3) of **13A**

^1H -NMR (300 MHz, CDCl_3) of **14**

¹³C-NMR (75 MHz, CDCl₃) of **14A**

¹H-NMR (300 MHz, CDCl₃) of **16**

¹³C-NMR (75 MHz, CDCl₃) of **16**

¹H-NMR (600 MHz, CDCl₃) of **17**

¹³C-NMR (75 MHz, CDCl₃) of **18**

¹H-NMR (600 MHz, CDCl₃) of **20**

¹³C-NMR (75 MHz, CDCl₃) of **20**

^{13}C -NMR (75 MHz, CD_3OD) of Blepharocalyxin D (1)

^1H -NMR (500 MHz, Acetone- d_6) of Blepharocalyxin D (**1**)

Comparison of ^{13}C NMR data for synthetic and natural samples of blepharocalyxin D (**1**)

position	Natural Blepharocalyxin D (CD ₃ OD)	Synthetic Blepharocalyxin D(1) (CD ₃ OD)
	^{13}C δ	
1	31.74	31.76
2	39.11	39.15
3	76.40	76.40
4	41.76	41.78
5	80.64	80.61
6	52.22	52.20
7	84.39	84.38
8	134.20	134.19
9	130.32	130.34
10	116.10	116.08
11	156.30	156.35
12	133.51	133.50
13	130.36	130.38
14	116.06	116.05
15	158.11	158.15

position	Natural Blepharocalyxin D (CD ₃ OD)	Synthetic Blepharocalyxin D(1) (CD ₃ OD)
	^{13}C δ	
1'	31.61	31.63
2'	39.32	39.37
3'	77.35	77.33
4'	39.32	39.37
5'	43.14	43.15
6'	132.73	132.73
7'	128.64	128.63
8'	134.25	134.23
9'	130.32	130.34
10'	116.10	116.08
11'	156.35	156.38
12'	130.98	130.97
13'	128.03	128.04
14'	115.77	115.74
15'	157.02	157.05