Electronic Supplementary Information (ESI):

Catalytic Enantioselective Tishchenko Reaction of meso-Dialdehyde: Synthesis of (S)-Cedarmycins

Ismiyarto, a Nobuki Kishi, b Yuki Adachi, a Rui Jiang, a Takahiro Doi, a Da-Yang Zhou, a Kaori Asano, a Yasushi Obora, b Takayoshi Suzuki, a Hiroaki Sasai, a and Takeyuki Suzuki a

a The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

b Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials, and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

E-mail: suzuki-t@sanken.osaka-u.ac.jp

Table of Contents

1. General................................................................................................................................................................................. S2
2. Experimental Section.............................................................................................................................................................. S2
3. CSI-MS of the Ir complex..................................................................................................................................................... S5
4. Determination of the structure by X-ray Crystallography..................................................................................................... S8
5. HPLC Chart.......................................................................................................................................................................... S11
6. NMR Spectra........................................................................................................................................................................ S14
Experimental Procedures

1. General

Melting points were obtained with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 spectrometer. 1H NMR spectra were recorded on JEOL JNM-ECS400 NMR or JEOL JNM-ECA600 NMR or Bruker Avance III 700 NMR spectrometer. The chemical shifts are reported in ppm on the δ scale downfield from tetramethylsilane or relative to the residual solvent signals (CDCl3: 7.26 ppm for 1H NMR and 77.16 for 13C NMR, CD2Cl2: 5.32 ppm for 1H NMR and 53.84 for 13C NMR, CD3OD: 3.31 ppm for 1H NMR and 49.00 for 13C NMR), and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad peak. 13C NMR spectra were measured on a JEOL JNM-ECA600 NMR spectrometer at 151 MHz or Bruker Avance III 176 NMR spectrometer at 176 MHz. APCI or ESI mass spectra were recorded on a THERMO LTQ Orbitrap XL spectrometer. CSI mass spectra were recorded on a Bruker microTOF II spectrometer. X-ray crystallographic analyses were conducted on a Rigaku E-AXIS RAPID 191R diffractometer system equipped with a Rigaku FR-E++ SuperBright (Cu) X-ray generator or a Rigaku XtaLAB PRO MM007 DW diffractometer system equipped with a MicroMax007HF-MW(Cu/Mo) X-ray generator and a HyPix-6000HE detector. Optical rotations were measured with JASCO P-2300 polarimeter. HPLC analyses were performed on SHIMADZU HPLC system (SHIMADZU LC20 AD pump and SPD-M20A DPA detector). Anhydrous THF and methanol were purchased from Kanto Chemicals and used without any purification. Other solvents were purified prior to use by standard techniques. 5% Pd/C (N.E.Chemical NX type) was purchased and used without any purification.

2. Experimental Section

Intramolecular Tishchenko Reaction of Aromatic Dialdehyde (Table 1)

The mixture of 6 (0.15 mmol), K2CO3 (4.1 mg, 0.03 mmol, 20 mol %), 0.6 M i-PrOH in CH2Cl2 solution (0.05 mL, 0.03 mmol, 20 mol %), and 5a (0.81 mg, 0.015 mmol, 1 mol %) in CH2Cl2 (1 mL) was stirred at 30 °C for 7 h under Ar atmosphere. The mixture was passed through a short silica gel column (ethyl acetate) to remove the catalyst and concentrated under reduced pressure. Chemical yield was determined using 1,1,2,2-tetrachloroethane as an internal standard. The crude mixture was purified by silica gel column chromatography (hexane/ ethyl acetate = 1/1) to give the desired product.

- **phthalide (7a)**
  - White solid 19.5 mg, 97%.
  - 1H-NMR (700MHz, CDCl3) δ: 7.93 (d, J = 7.7 Hz, 1H), 7.70 (td, J = 7.4, 1.0 Hz, 1H), 7.55 (td, J = 7.5, 0.9 Hz, 1H), 7.52 (dt, J = 7.7, 0.9 Hz, 1H), 5.34 (s, 2H).
  - 13C-NMR (176MHz, CDCl3) δ: 171.3, 146.6, 134.1, 129.1, 125.81, 125.78, 122.2, 69.8.

- **naphtho[2,3-c]furan-1(3H)-one (7b)**
  - White solid 26.8 mg, 97%.
  - 1H-NMR (700MHz, CDCl3) δ: 8.52 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.92 (s, 1H), 7.68-7.66 (m, 1H), 7.62-7.60 (m, 1H), 5.50 (s, 2H).
  - 13C-NMR (176MHz, CDCl3) δ: 171.2, 140.1, 136.4, 133.2, 130.1, 129.2, 128.3, 127.2, 127.1, 123.5, 121.0, 69.8.

(1R,7S,8S,9R)-4,4-diphenyl-3,5-dioxabicyclo[5.2.0]nonane-8,9-diol (9)

- cis-3-Cyclobutene-1,2-dimethanol ββββ(1.385 g, 12.1 mmol) and diphenyl diazomethane (2.361 g, 12.1 mmol) in 96 mL of 1,2-dichloroethane were slowly added to a solution of 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ) (2.758 g, 12.1 mmol) in 55 mL of 1,2-dichloroethane at room temperature. The mixture was stirred for 1 h and the reaction mixture was concentrated in vacuo. The concentrate was dissolved in toluene and the solution was washed with saturated NaHCO3. The organic layer was washed with short column silica gel and concentrated in vacuo in order to give crude acetal product as a yellow oil (3.378 g crude product). To a cooled (0 °C) solution of crude acetal (12.1 mmol) in acetone–H2O (10:1, 125 mL) was added N-methylmorpholine-N-oxide (4.27 g, 36.5 mmol) and a solution of osmium tetroxide in BuOH (0.04 M, 15.2 mL, 0.607 mmol). The reaction mixture was allowed to warm to ambient temperature over 10 min and attired at 30 °C for 30 min and the reaction was quenched by the addition of saturated aqueous Na2SO3 7.18 g (36.5 mmol). After stirring for 20 min, the layers were separated and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na2SO4, and concentrated in vacuo. The resulting oil was purified by flash chromatography (30:70 EtOAc–hexanes) to afford 9 as a white solid (2.21 g, 58% in two steps).

MP 178°C

- 1H-NMR (700MHz, CDCl3) δ: 7.59-7.55 (m, 4H), 7.28 (t, J = 7.7 Hz, 4H), 7.21-7.20 (m, 2H), 4.17 (s, 2H), 3.82 (dd, J = 12.9, 6.5 Hz, 2H), 3.65-3.63 (br m, 2H), 3.11 (d, J = 3.4 Hz, 2H), 2.48-2.48 (m, 2H).
Synthesis of meso-Dialdehyde 10

To a vigorously stirred suspension of silica gel-supported NaOAc\textsuperscript{H} (666 mg, 0.448mmol, 2 equiv) was added a solution of the diol 9 (70 mg, 0.224 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2.24 mL, 0.1 M). The reaction was monitored by TLC until disappearance of the starting material (generally 10-30 min). The mixture was filtered through a sintered glass funnel, and the silica gel was thoroughly washed with CH\textsubscript{2}Cl\textsubscript{2} to total volume 10 mL. The reaction was filtered through a short silica gel column (ethyl acetate) to remove the catalyst and concentrated under reduced pressure.

\textsuperscript{1}H-NMR (700MHz, CD\textsubscript{3}Cl) δ: 9.75 (s, 2H), 7.56 (d, J = 7.3 Hz, 2H), 7.47 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 4.12 (s, 4H), 3.01 (s, 2H).

\textsuperscript{13}C-NMR (176MHz, CD\textsubscript{3}Cl) δ: 200.3 (2C), 143.3, 143.1, 128.57 (2C), 128.55 (2C), 128.20, 128.16, 126.5 (2C), 126.3 (2C), 104.7, 61.0 (2C), 52.8 (2C).

IR(KBr): 3330cm\textsuperscript{-1}

ESI-HRMS. Calcd for C\textsubscript{10}H\textsubscript{16}O\textsubscript{4} [M+Na]\textsuperscript{+}: 333.1103. Found: 333.1097.

Enantioselective Tishchensko reaction of 10 (Table 2, entry 4)

To a 0.14 M solution of 10 in CH\textsubscript{2}Cl\textsubscript{2} (0.0644 mmol) was added 5b (4.5mg, 0.0065mmol, 10 mol %), K\textsubscript{2}CO\textsubscript{3} (3.6 mg, 0.0261 mmol, 40 mol %), (PhO)\textsubscript{2}PO\textsubscript{2}H (6.4 mg, 0.0256 mmol, 40 mol %) and 0.6 M i-PrOH in CH\textsubscript{2}Cl\textsubscript{2} solution (0.0214 mL, 0.0128 mmol, 20 mol %) and then the mixture was stirred at 30 °C for 24 h under Ar atmosphere. The mixture was passed through a short silica gel column (ethyl acetate) to remove the catalyst and concentrated under reduced pressure. Then crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate = 85/15) to give the lactone as a white solid (15.6 mg, 78% and 91% ee). The optically pure lactone was prepared from the recrystallization from hexane and ethyl acetate.

\((5S,8aR)-3,3\text{-diphenyltetrahydro-1H,6H-furo[3,4-e][1,3]dioxepin-6-one (11)}\)

\textsuperscript{1}H-NMR (700MHz, CD\textsubscript{3}Cl) δ: 7.58-7.53 (m, 4H), 7.32-7.26 (m, 4H), 7.25-7.20 (m, 2H), 4.28 (dd, J = 9.5, 6.5 Hz, 1H), 4.23 (d, J = 12.7 Hz, 1H), 3.99 (m, 1H), 3.93 (dd, J = 12.7, 3.2 Hz, 1H), 3.79 (dd, J = 12.5, 4.7 Hz, 1H), 3.68 (dd, J = 12.5, 10.8 Hz, 1H). 2.95-2.93 (m, 1H), 2.80-2.80 (m, 1H).

\textsuperscript{13}C-NMR (176MHz, CD\textsubscript{3}Cl)δ: 176.5, 142.9, 142.7, 128.38 (2C), 128.32 (2C), 128.0, 127.9, 126.37 (2C), 126.35 (2C), 104.6, 67.5, 61.9, 59.6, 44.5, 39.1.

IR(KBr): 1777cm\textsuperscript{-1}

APCI-HRMS. Calcd for C\textsubscript{19}H\textsubscript{16}O\textsubscript{4} [M+Na]\textsuperscript{+}: 333.1103. Found: 333.1097.

\([\text{d}]\textsubscript{20}\textsuperscript{R} = -165.1^{+} (c = 1.0, \text{CHCl}_3, >99\% ee).\]

Preparation of meso-Diol 12

To a CH\textsubscript{2}Cl\textsubscript{2} solution of meso-dialdehyde 10 (99.3 mg, 0.320 mmol) was added MeOH (1.4 mL), then NaBH\textsubscript{4} (16mg, 0.422 mmol) was added and stirred at the 30 °C for 24 h. The mixture was quenched by sat. NaHCO\textsubscript{3} and extracted with AcOEt, then the organic layer was washed with sat. NaHCO\textsubscript{3} and brine, dried over Na\textsubscript{2}SO\textsubscript{4}. The organic layer was evaporated under reduced pressure to give the desired product 12 as a colorless liquid (88.6 mg, 88% yield).

\textsuperscript{1}H-NMR (600MHz, CD\textsubscript{3}Cl) δ: 7.56-7.54 (m, 4H), 7.30-7.26 (m, 4H), 7.21 (t, J = 6.9 Hz, 2H), 3.80 (m, 8H), 2.66 (s, 2H), 2.14 (m, 2H).

\textsuperscript{13}C-NMR (150MHz, CD\textsubscript{3}Cl)δ: 143.66, 143.60, 128.20 (2C), 128.1 (2C), 127.58, 127.54, 126.16 (2C), 126.01 (2C), 103.9, 64.5 (2C), 62.6 (2C), 43.24 (2C).

IR(KBr): cm\textsuperscript{-1} 3273 cm\textsuperscript{-1}

APCI-HRMS. Calcd for C\textsubscript{18}H\textsubscript{20}O\textsubscript{2} [M+Na]\textsuperscript{+}: 337.1416. Found: 337.1411.

Enantioselective Oxidative Lactonization of meso-Diol 12

A mixture of Ir complex 5b (36.3 mg, 0.0525 mmol, 5 mol %), K\textsubscript{2}CO\textsubscript{3} (14.5 mg, 0.105 mmol) and diol 12 (329.7 mg, 1.05 mmol) in acetone (5.3 mL) was stirred at 30 °C. After 86 h the resulting solution was passed through a short column chromatography (SiO\textsubscript{2}, AcOEt) and evaporated, and the residue was purified by column chromatography (SiO\textsubscript{2}, hexane/AcOEt, 1:1) to give 11 (300 mg, 92% as a white solid).

\((3R,4S)-3,4\text{-bis(hydroxymethyl)}\text{dihydrofuran-2(3H)-one (cis-14)}\)
To a solution of \( \text{cis-14} \) (35 mg, 0.11 mmol) in CHCl\(_3\) (0.7 mL) and CF\(_3\)CH\(_2\)OH (0.7 mL) was added 5% Pd/C (24 mg, 0.011 mmol) and stirred at 15 °C for 6 h under H\(_2\) (0.6 MPa). The mixture was filtered by membrane and concentrated under reduced pressure at less than 30 °C. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 1/2, then 0/1) to give the desired product \( \text{14} \) (15.7 mg, 95%, as a colorless oil).

\( ^1H\)-NMR (700MHz, CD\(_3\)OD) \( \delta \): 4.36 (dd, \( J = 8.7, 7.2 \) Hz, 1H), 4.26 (dd, \( J = 9.0, 3.8 \) Hz, 1H), 3.92 (dd, \( J = 11.3, 4.0 \) Hz, 1H), 3.85 (dd, \( J = 11.3, 7.1 \) Hz, 1H), 3.80 (dd, \( J = 11.1, 5.0 \) Hz, 1H), 3.71 (dd, \( J = 11.1, 6.3 \) Hz, 1H), 2.92-2.91 (m, 1H), 2.81-2.77 (m, 1H).

\( ^{13}C\)-NMR (175MHz, CD\(_3\)OD) \( \delta \): 180.0, 71.6, 61.0, 59.2, 45.3, 40.8.

IR(KBr): 3377, 1759cm\(^{-1}\). APCI-HRMS. Calcd for \( \text{C}_6\text{H}_9\text{O}_3\text{M}^+ \): 147.0657. Found: 147.0649. [% e] \( ^{2} \text{D} = +34.2 \) (c 0.63, AcOEt).

**Synthesis of cedarmicine A (15a)**

To a solution of \( \text{14} \) (8.4 mg, 0.0575 mmol) in 0.15 mL DCM was added 2.6-lutidine (26.6 \( \mu \)L, 0.23 mmol), DMAP (4.21 mg, 0.0345 mmol) and 5-methylhexanoilchloride\(^{[6]}\) (35.5 \( \mu \)L, 0.23 mmol) and stirred at 30 °C for 24 h, then DBU (43 \( \mu \)L, 0.288mmol) was added and stirred for 20 h. The mixture was quenched by NH\(_4\)Cl, then extracted with EtOAc. After dried with Na\(_2\)SO\(_4\) and evaporated, the crude product was purified by preparative thin layer column chromatography (hexane/ethyl acetate) to give Cedarminic A (15a) 10.5 mg (76% yield).

To a solution of \( \text{14} \) (9.5 mg, 0.065 mmol) in 0.15 mL DCM was added 2.6-lutidine (30 \( \mu \)L, 0.26 mmol), DMAP (4.8 mg, 0.039 mmol) and hexanoilchloride (36 \( \mu \)L, 0.26 mmol) and stirred at 30 °C for 20 h, then DBU (49 \( \mu \)L, 0.33 mmol) was added and stirred for 4 h. The mixture was quenched by NH\(_4\)Cl, then extracted with EtOAc. After dried with Na\(_2\)SO\(_4\) and evaporated, the crude product was purified by preparative thin layer column chromatography (hexane/ethyl acetate) to give Cedarminic B (15b) 12.5 mg (85% yield).

**References**

1. P.-C. Qian, Y. Liu, R.-J. Song, M. Hu, X.-H. Yang, J.-N. Xiang and J.-H. Li, *Eur. J. Org. Chem.*, 2015, 2015, 1680-1684.
2. Y. H. Zhang, B. F. Shi and J. Q. Yu, *Angew. Chem. Int. Ed. Engl.*, 2009, 48, 6097-6100.
3. (a) J. I. Brauman and W. G. Archie, *J. Am. Chem. Soc.*, 1972, 94, 4262-4265; (b) F. Binns, R. Hayes, S. Ingham, S. T. Saengchattara, R. W. Turner and T. W. Wallace, *Tetrahedron*, 1992, 48, 515-530; (c) N. Gauvry, C. Comoy, C. Lescop and F. Huet, *Synthesis*, 1999, 1999, 574-576.
4. Y. L. Zhong and T. K. Shing, *J. Org. Chem.*, 1997, 62, 2622-2624.
5. R. A. Coats, S. L. Lee, K. A. Davis, K. M. Patel, E. K. Rhoads and M. H. Howard, *J. Org. Chem.*, 2004, 69, 1734-1737.
6. T. Sasaki, Y. Igarashi, N. Saito and T. Furumai, *J. Antibiot.*, 2001, 54, 567-572.
3. CSI-MS of the Ir complex.

Figure S1. CSI-MS spectrum of Cp*IrTsDPEN in DCM/CH3CN.

Figure S2. CSI-MS spectrum of Cp*IrTsDPEN in iPrOH.
Figure S3. CSI-MS spectrum of a mixture of Cp*IrTsDPEN, (PhO)$_2$PO$_2$H (1 equiv), K$_2$CO$_3$ (1 equiv) in DCM/ i-PrOH.
4. Determination of the structure by X-ray Crystallography

The CS Analysis of diol 9

Diol 3 (in dichloromethane and hexane) was treated with a single crystal of [(ZnI₂₂)(tpt)₂] complex [CS crystal; tpt = 2,4,6-tris(4-pyridyl)triazine], 9 and the guest-absorbed CS crystal was subjected to a diffraction study. ORTEP diagram of the asymmetric unit is shown in Figure S1.

CCDC 2019330 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Figure S1. Asymmetric unit of the 9[(ZnI₂₂)(tpt)₂] inclusion complex. Solvent (dichloromethane) and hydrogens have been removed for clarity.

Figure S2. Diol 9; ellipsoids are at 50% probability

Experimental. A Single colourless rod-shaped crystals was attached to a capton film on an Rigaku XtaLAB PRO diffractometer. The crystal was kept at a steady T = 100.15 K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of ShelXL (Sheldrick, 2015) using Least Squares minimisation.

| Formula | C₁₆₆.₂₅H₄₆.₅Cl₂.₅I₆N₁₂O₄Zn₃ |
|---------|---------------------------------|
| Dcalc/g cm⁻³ | 1.703 |
| μ/μm⁻¹ | 20.865 |
| Formula Weight | 2000.69 |
| Colour | colourless |
| Shape | rod |
| Size/mm³ | 0.15×0.08×0.06 |
| T/K | 100.15 |
| Crystal System | monoclinic |
| Space Group | P2₁/c |
| a/Å | 34.9669(3) |
| b/Å | 14.81360(10) |
| c/Å | 30.7587(2) |
| α/° | 90 |
| β/° | 101.5970(10) |
| γ/° | 90 |
| V/Å³ | 15607.3(2) |
| Z | 8 |
| Z’ | 2 |
| Wavelength/Å | 1.54184 |
| Radiation type | CuKα |
| θmax/° | 80.472 |
| θmin/° | 2.580 |
| Measured Refl. | 320208 |
| Independent Refl. | 32630 |
| Reflections with I > 2(I) | 25738 |
| Rint | 0.0879 |
| Parameters | 1680 |
| Restraints | 923 |
| Largest Peak | 1.993 |
| Deepest Hole | -1.209 |
| Goof | 1.225 |
| wR2 (all data) | 0.03029 |
| wR2 | 0.2857 |
| R1 (all data) | 0.0976 |
| R1 | 0.0884 |

Structure Quality Indicators

| Reflections: | d min (Cu) 0.78 | Rint 8.79% |
|--------------|-----------------|------------|
| Refinement:  | Shift 0.001 | Max Peak 2.0 | Goof 1.225 |
A colorless rod-shaped crystal with dimensions 0.15×0.08×0.06 mm$^3$ was attached to a Kapton film. Data were collected using a Rigaku XtaLAB PRO diffractometer operating at $T = 100.15$ K.

Data were measured using $\omega$ scans using CuK$_{\alpha}$ radiation. The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.35a, 2018) The maximum resolution that was achieved was $\theta = 80.472^\circ$ (0.78 Å).

The diffraction pattern was indexed. The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.35a, 2018) and the unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.35a, 2018) on 97276 reflections, 30% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.35a, 2018). The final completeness is 100.00 % out to 80.472° in $\theta$. A gaussian absorption correction was performed using CrysAlisPro 1.171.40.35a (Rigaku Oxford Diffraction, 2018)Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonicsas implemented in SCALE3 ABSPACK. The absorption coefficient $\mu$ of this material is 20.865 mm$^{-1}$ at this wavelength ($\lambda = 1.542$Å) and the minimum and maximum transmissions are 0.005 and 0.156.

The structure was solved and the space group $P2_1/c$ (# 13) determined by the ShelXT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of ShelXL (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

CCDC 2022569 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

A. Crystal Data

| Property               | Value                        |
|------------------------|------------------------------|
| Empirical Formula      | C19H18O4                     |
| Formula Weight         | 310.35                       |
| Crystal Color, Habit   | colorless, block             |
| Crystal Dimensions     | 0.136 X 0.082 X 0.077 mm     |
| Crystal System         | orthorhombic                 |
| Lattice Type           | Primitive                    |
| Lattice Parameters     | $a = 8.91118(16)$ Å          |
|                        | $b = 11.0174(2)$ Å           |
|                        | $c = 15.8907(11)$ Å          |
|                        | $V = 1560.12(12)$ Å$^3$      |
| Space Group            | P212121 (#19)                |
| Z value                | 4                            |
| Dcalc                  | 1.321 g/cm$^3$               |
| F000                    | 656.00                       |
| $\mu$(CuK$\alpha$)     | 7.545 cm$^{-1}$              |

B. Intensity Measurements

| Property               | Value                        |
|------------------------|------------------------------|
| Diffractometer         | R-AXIS RAPID 191R            |
| Radiation              | CuK$\alpha$ ($\lambda = 1.54187$ Å) |
| Voltage, Current       | 45kV, 55mA                   |
| Temperature            | -150.00°C                    |
| Detector Aperture      | 783.0 x 382.0 mm             |
| Data Images            | 56 exposures                 |
| $\omega$ oscillation   | (x=54.0, $\Phi$=0.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
| $\omega$ oscillation   | (x=54.0, $\Phi$=60.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
| $\omega$ oscillation   | (x=54.0, $\Phi$=120.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
| $\omega$ oscillation   | (x=54.0, $\Phi$=180.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
| $\omega$ oscillation   | (x=54.0, $\Phi$=240.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
| $\omega$ oscillation   | (x=54.0, $\Phi$=320.0) 80.0 - 255.00 |
| Exposure Rate          | 3.0 sec./o                   |
ω oscillation Range (x =20.0, Φ=0.0) 80.0 - 255.0°
Exposure Rate 3.0 sec./°
ω oscillation Range (x =20.0, Φ=120.0) 80.0 - 255.0°
Exposure Rate 3.0 sec./°
Detector Position 191.00 mm
Pixel Size 0.100 mm

No. of Reflections Measured
Total: 29839
Unique: 2849 (Rint = 0.0327)
Parsons quotients (Flack x parameter): 1068

C. Structure Solution and Refinement

Structure Solution  Direct Methods (SHELXT Version 2014/5)
Refinement     Full-matrix least-squares on F2
Function Minimized     Σ w (Fo2 - Fc2)2
Least Squares Weights
w = 1/ [ o2(Fo2) + (0.0290 . P)2
+ 0.3245 . P ]
where P = (Max(Fo2,0) + 2Fc2)/3
2θmax cutoff 136.5°
Anomalous Dispersion All non-hydrogen atoms
No. Observations (All reflections) 2849
No. Variables 209
Reflection/Parameter Ratio 13.63
Residuals: R1 (I>2.00σ(I)) 0.0319
Residuals: R (All reflections) 0.0342
Residuals: wR2 (All reflections) 0.0707
Goodness of Fit Indicator 1.090
Flack parameter (Parsons' quotients = 1068) -0.13(6)
Max Shift/Error in Final Cycle 0.000
Maximum peak in Final Diff. Map 0.15 e-/Å3
Minimum peak in Final Diff. Map -0.22 e-/Å3
5. HPLC Chart

\(\text{(5aS,8aR)-3,3-diphenyltetrahydro-1H,6H-furo[3,4-e][1,3]dioxepin-6-one (11)}}\)

\[
\begin{align*}
\text{HPLC conditions: DAICEL CHIRALPAK IA-3, hexane/i-PrOH = 9/1, flow rate = 1.0 mL/min, detection} \\
\text{219 nm, retention time = 9.7 min (5aR,8aS) and 12.0 min (5aS,8aR).}
\end{align*}
\]

\(\text{(5aS,8aR)-11}\)
cedarmicine A (15a)

HPLC conditions: DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 8/2, flow rate = 1.0 mL/min, detection 212 nm, retention time = 23 min (R) and 28 min (S).
Cedarmicine B (15b)

HPLC conditions: DAICEL CHIRALPAK IC-3, hexane/i-PrOH = 8/2, flow rate = 1.0 mL/min, detection 212 nm, retention time = 31 min (R) and 37 min (S).

15b: Cedarmycin B
