

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

**(+)-(1*S*,5*R*,10*S*)-11,11-Dimethyl-4-oxatricyclo[8.4.0.0<sup>1,5</sup>]tetradecane-3,12-dione**

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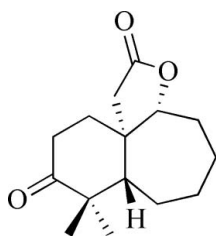
Received 20 November 2007; accepted 7 December 2007

Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.026;  $wR$  factor = 0.057; data-to-parameter ratio = 6.8.

The title compound,  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , was prepared *via* amino-acid-promoted Robinson annulation followed by tandem Pd/C-mediated hydrogenation and oxidative cyclization. This product was instrumental in determining the feasibility of a stereocontrolled hydrogenation in which the directing hydroxyl group is adjacent to the 6–7-ring network and its olefinic component. The asymmetric unit consists of a single molecule with normal geometric parameters. The absolute configuration was assigned based on the known enantiomeric precursor. Intermolecular C–H $\cdots$ O interactions link each molecule with four neighboring molecules.

## Related literature

For related chemistry, see: Brown (1987); Crabtree & Davis (1986); Inomata *et al.* (2005), Nagamine *et al.* (2007); Peng *et al.* (2004); Stork & Kahne (1983). For related literature on geometry, see: Allen *et al.* (1987); Desiraju & Steiner (1999); Steiner & Saenger (1992); Taylor & Kennard (1982).



## Experimental

## Crystal data

$\text{C}_{15}\text{H}_{22}\text{O}_3$   
 $M_r = 250.33$   
 Trigonal,  $P6_5$   
 $a = 7.6239$  (10) Å  
 $c = 38.064$  (5) Å  
 $V = 1916.0$  (4) Å<sup>3</sup>

$Z = 6$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 $0.35 \times 0.27 \times 0.19$  mm

## Data collection

Nonius KappaCCD diffractometer  
 Absorption correction: none  
 23396 measured reflections  
 1130 independent reflections  
 1023 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.057$   
 $S = 1.06$   
 1130 reflections  
 165 parameters  
 1 restraint  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.11$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.14$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
C10—H10 $\cdots$ O1 <sup>i</sup>	1.00	2.70	3.596 (2)	149
C14—H14A $\cdots$ O1 <sup>i</sup>	0.99	2.70	3.562 (3)	146
C2—H2A $\cdots$ O2 <sup>ii</sup>	0.99	2.62	3.449 (2)	141
C9—H9B $\cdots$ O2 <sup>ii</sup>	0.99	2.66	3.454 (2)	138
C5—H5 $\cdots$ O2 <sup>iii</sup>	1.00	2.58	3.194 (2)	119

Symmetry codes: (i)  $x - y + 1, x, z - \frac{1}{6}$ ; (ii)  $y, -x + y + 1, z + \frac{1}{6}$ ; (iii)  $y + 1, -x + y + 1, z + \frac{1}{6}$ .

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

The authors thank Professor E. A. Meyers for his assistance in the preparation of the manuscript.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SQ2007).

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin 2*, pp. S1–S19.
- Brown, J. M. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 190–203.
- Bruker (1999). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Crabtree, R. H. & Davis, M. W. (1986). *J. Org. Chem.* **51**, 2655–2661.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. IUCr Monographs on Crystallography, 9. Oxford University Press.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Inomata, K., Barragué, M. & Paquette, L. A. (2005). *J. Org. Chem.* **70**, 533–539.
- Nagamine, T., Inomata, K., Endo, Y. & Paquette, L. A. (2007). *J. Org. Chem.* **72**, 123–131.
- Nonius (1997–2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Peng, X., Bondar, D. & Paquette, L. A. (2004). *Tetrahedron*, **60**, 9589–9598.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Steiner, T. & Saenger, W. (1992). *J. Am. Chem. Soc.* **114**, 10146–10154.
- Stork, G. & Kahne, D. E. (1983). *J. Am. Chem. Soc.* **105**, 1072–1073.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

**supplementary materials**

*Acta Cryst.* (2008). E64, o287 [ doi:10.1107/S1600536807066159 ]

**(+)-(1*S*,5*R*,10*S*)-11,11-Dimethyl-4-oxatricyclo[8.4.0.0<sup>1,5</sup>]tetradecane-3,12-dione**

**J. C. Gallucci, K. Inomata, R. D. Dura and L. A. Paquette**

**Comment**

The capability of *L*-amino acids to promote the enantioselective intramolecular aldolization of prochiral substrates (I) and (II) has projected the related Hajos-Parrish (III) and Wieland-Miescher ketones (IV) into favored positions as starting materials for targeted synthesis (see Fig. 1). Most notably, the selection of these particular synthons has resulted in the rather direct preparation of numerous terpenoids and steroids (Inomata *et al.*, 2005).

More recently, the discovery has been made that comparable asymmetric Robinson annulation involving (V) and (VII) is accompanied by a striking crossover in enantioselectivity (Nagamine *et al.*, 2007). When the 1,3-cyclohexanedione (V) is involved, the *S* enantiomer defined by (VI) continues to be formed predominantly. On the other hand, progression to the seven-membered triketone homolog (VII) results in the kinetically favored generation of the *R* product (VIII) (see Fig. 2). As a result, our desire to involve 6–7 fused bicyclic systems of type (VIII) as synthetic intermediates now mandates that each ensuing step involving the introduction of a new stereogenic center be carefully evaluated. The present report details such an example.

The hindered nature of the double bond in (IX) causes this intermediate to be unreactive to a broad range of hydrogenation conditions. However, recourse to the use of 10% palladium on carbon in methanol at 550 psi leads to saturation of the olefinic linkage with concomitant loss of the acetonide functionality. The chromatographically inseparable nature of (X) and (XI) was overcome by efficient (93% overall) two-step oxidative cyclization to generate (XII) and (XIII), the ratio of which was shown by NMR analysis to be 56:44 (see Fig. 3). Identification of the less dominant, highly-crystalline product as the *trans*-fused isomer (XIII) was realized by X-ray crystallography, as shown in Fig. 4. The level of production of (XIII) provides suggestive indication that hydroxyl-directed hydrogenation is unable to operate at the heightened levels customarily observed (Brown, 1987; Crabtree & Davis, 1986; Peng *et al.*, 2004; Stork & Kahne, 1983).

The bond distances in (XIII) are in agreement with those that were selected in the critical evaluation of structures in the Cambridge data base (Allen *et al.*, 1987). The presence of intermolecular CH—O hydrogen bonds is indicated by short H to O distances (2.58 Å to 2.70 Å) between the observed O1 and O2 positions and calculated H positions (Taylor & Kennard, 1982; Steiner & Saenger, 1992; Desiraju & Steiner, 1999). Each molecule H-bonds with four adjacent molecules, as shown in Fig. 5, with contact distances and angles given in the table of hydrogen bonds.

**Experimental**

A suspension of (IX) (20 mg) and 10% Pd—C (2 mg) in methanol (1 ml) was pressurized to 550 psi of hydrogen gas in an autoclave and stirred for 15 h at rt. After filtration through Celite and solvent evaporation, the residue was chromatographed on silica gel to afford 11 mg of an inseparable mixture of (X) and (XI). This mixture was dissolved in THF (0.5 ml) and saturated NaHCO<sub>3</sub> solution (0.5 ml), cooled to 0 °C, treated with NaIO<sub>4</sub> (48 mg), and stirred in the cold for 3 h. The mixture was extracted with ethyl acetate and the combined organic layers were dried and evaporated. The residue was dissolved in benzene (1 ml), and Ag<sub>2</sub>CO<sub>3</sub> on Celite (48 mg) was introduced. After being heated at reflux for 2 h, the mixture was filtered

## supplementary materials

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through a Celite pad and the filtrate was evaporated under reduced pressure. Chromatographic purification was performed on silica gel to afford (XII) as a colorless oil (5 mg) and (XIII) as colorless crystals (4 mg) displaying a melting point of 155.5–156 °C after recrystallization from ethyl acetate.

### Refinement

The intensity statistics are non-centrosymmetric and the systematic absences restrict the space group possibilities to  $P6_1$  or  $P6_5$ . The correct enantiomer was chosen based on the known chiral centers at atoms C1 and C5. For the methyl groups, the hydrogen atoms were added at calculated positions using a riding model with  $C-H = 0.98\text{\AA}$  and  $U_{\text{iso}}(H) = 1.5 * U_{\text{eq}}(C)$ . The torsion angle, which defines the orientation of the methyl group about the  $C-C$  bond, was refined. The remaining hydrogen atoms were included at calculated positions using a riding model with  $C-H = 0.99\text{\AA}$  and  $U_{\text{iso}}(H) = 1.2 * U_{\text{eq}}(C)$ .

### Figures

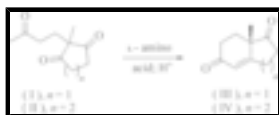


Fig. 1. Chemical schemes for (I), (II), (III), and (IV). Hydrogen atoms are not shown

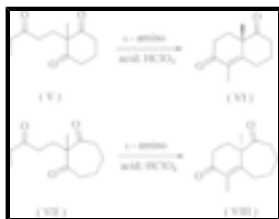


Fig. 2. Chemical schemes for (V), (VI), (VII), and (VIII). Hydrogen atoms are not shown



Fig. 3. Chemical schemes for (IX), (X), (XI), (XII), and (XIII).

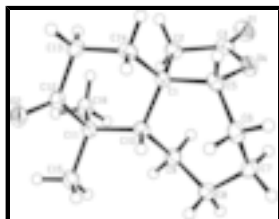


Fig. 4. The molecular structure is drawn with 50% probability displacement ellipsoids for the non-hydrogen atoms. The hydrogen atoms are drawn with an artificial radius.

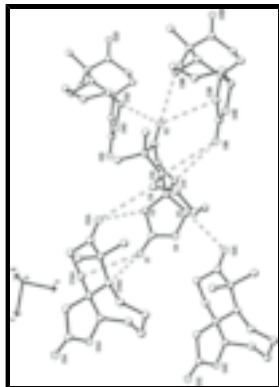


Fig. 5. A portion of the intermolecular hydrogen bond network. The symmetry operations for the molecules related to the central molecule are as follows: A:  $y, -x + y + 1, 1/6 + z$ ; B:  $x - y + 1, x, z - 1/6$ ; C:  $y + 1, -x + y + 1, 1/6 + z$ ; D:  $x - y, x - 1, z - 1/6$ .

**(+)-(1*S*,5*R*,10*S*)-11,11-dimethyl-4-oxatricyclo[8.4.0.0<sup>1,5</sup>]tetradecane-3,12-dione**

*Crystal data*

$C_{15}H_{22}O_3$

$M_r = 250.33$

Trigonal,  $P6_5$

Hall symbol: P 65

$a = 7.6239 (10) \text{ \AA}$

$b = 7.6239 (10) \text{ \AA}$

$c = 38.064 (5) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 1916.0 (4) \text{ \AA}^3$

$Z = 6$

$F_{000} = 816$

$D_x = 1.302 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2164 reflections

$\theta = 2.0\text{--}25.0^\circ$

$\mu = 0.09 \text{ mm}^{-1}$

$T = 150 (2) \text{ K}$

Chunk, colorless

$0.35 \times 0.27 \times 0.19 \text{ mm}$

*Data collection*

Nonius KappaCCD  
diffractometer

Monochromator: graphite

Detector resolution: 9 pixels  $\text{mm}^{-1}$

$T = 150(2) \text{ K}$

$\omega$  scans

Absorption correction: none

23396 measured reflections

1130 independent reflections

1023 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 3.1^\circ$

$h = -9 \rightarrow 9$

$k = -7 \rightarrow 7$

$l = -44 \rightarrow 44$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

# supplementary materials

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$wR(F^2) = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.1114P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1130 reflections	$(\Delta/\sigma)_{\max} = 0.001$
165 parameters	$\Delta\rho_{\max} = 0.11 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.14 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

## Special details

**Experimental.** The data collection crystal was a clear, colorless chunk, which was cut from a cluster of crystals. Initial examination of the diffraction pattern on a Nonius Kappa CCD diffractometer indicated a trigonal or hexagonal crystal system. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Omega scans with a frame width of 1.0 degree were used for data collection. Data integration was done with *DENZO* (Otwinowski & Minor, 1997) and scaling and merging of the data was done with *SCALEPACK* (Otwinowski & Minor, 1997).

The Laue group was determined to be  $6/m$  by *XPREP* (Bruker Nonius, 2003). The intensity statistics are non-centrosymmetric and the systematic absences restrict the space group possibilities to  $P6_1$  or  $P6_5$ . The structure was solved by the direct methods procedure in *SHELXS86* (Sheldrick, 1990). Full-matrix least-squares refinements based on  $F^2$  were performed in *SHELXL97* (Sheldrick, 1997), as incorporated in the *WinGX* package (Farrugia, 1999). The correct enantiomer was chosen based on the known chiral centers at atoms C(1) and C(5).

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

## Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.1237 (3)	0.6294 (3)	0.84987 (5)	0.0200 (4)
C2	0.9527 (3)	0.4864 (3)	0.87492 (5)	0.0248 (5)
H2A	0.8387	0.5136	0.8738	0.03*
H2B	0.9017	0.3435	0.8682	0.03*
C3	1.0397 (3)	0.5250 (3)	0.91134 (5)	0.0245 (5)
C5	1.3134 (3)	0.7149 (3)	0.87446 (5)	0.0236 (4)
H5	1.3852	0.6387	0.8688	0.028*
C6	1.4721 (3)	0.9388 (3)	0.87398 (6)	0.0273 (5)
H6A	1.5073	0.9816	0.8492	0.033*
H6B	1.5958	0.956	0.8856	0.033*
C7	1.4117 (3)	1.0810 (3)	0.89168 (6)	0.0276 (5)
H7A	1.3505	1.023	0.9148	0.033*

H7B	1.536	1.2123	0.8961	0.033*
C8	1.2636 (3)	1.1208 (3)	0.87107 (5)	0.0266 (5)
H8A	1.3305	1.1937	0.8492	0.032*
H8B	1.2318	1.2105	0.8851	0.032*
C9	1.0656 (3)	0.9300 (3)	0.86149 (5)	0.0234 (5)
H9A	0.9685	0.9697	0.8525	0.028*
H9B	1.0067	0.8479	0.883	0.028*
C10	1.0931 (3)	0.7992 (3)	0.83360 (5)	0.0196 (4)
H10	1.2246	0.8928	0.8218	0.024*
C11	0.9294 (3)	0.7288 (3)	0.80369 (5)	0.0204 (4)
C12	0.9724 (3)	0.6034 (3)	0.77757 (5)	0.0207 (4)
C13	0.9882 (3)	0.4299 (3)	0.79298 (5)	0.0243 (5)
H13A	1.0177	0.3585	0.7742	0.029*
H13B	0.8586	0.3322	0.8043	0.029*
C14	1.1584 (3)	0.5144 (3)	0.82012 (5)	0.0235 (5)
H14A	1.2879	0.6068	0.8082	0.028*
H14B	1.1702	0.4012	0.8303	0.028*
C15	0.9500 (3)	0.9168 (3)	0.78510 (6)	0.0289 (5)
H15A	0.8683	0.8756	0.7636	0.043*
H15B	1.0924	1.0085	0.7791	0.043*
H15C	0.9024	0.9865	0.8007	0.043*
C16	0.7081 (3)	0.5997 (3)	0.81654 (6)	0.0280 (5)
H16A	0.6841	0.4669	0.8243	0.042*
H16B	0.6153	0.582	0.7973	0.042*
H16C	0.6847	0.6685	0.8362	0.042*
O1	0.9541 (2)	0.4526 (2)	0.93853 (4)	0.0347 (4)
O2	1.0008 (2)	0.6444 (2)	0.74647 (4)	0.0259 (3)
O4	1.2389 (2)	0.6617 (2)	0.91052 (3)	0.0268 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0192 (11)	0.0211 (10)	0.0205 (10)	0.0106 (9)	0.0003 (8)	0.0024 (8)
C2	0.0243 (11)	0.0238 (11)	0.0249 (12)	0.0110 (9)	0.0024 (9)	0.0042 (9)
C3	0.0293 (11)	0.0244 (11)	0.0253 (12)	0.0176 (9)	0.0048 (10)	0.0057 (9)
C5	0.0249 (11)	0.0296 (11)	0.0183 (10)	0.0152 (9)	0.0027 (8)	0.0048 (9)
C6	0.0189 (10)	0.0322 (12)	0.0288 (12)	0.0113 (10)	-0.0025 (9)	0.0015 (9)
C7	0.0230 (11)	0.0247 (11)	0.0277 (12)	0.0063 (9)	-0.0020 (9)	-0.0001 (9)
C8	0.0309 (12)	0.0228 (11)	0.0241 (11)	0.0119 (9)	-0.0014 (9)	-0.0025 (9)
C9	0.0267 (11)	0.0262 (11)	0.0205 (11)	0.0157 (9)	0.0013 (9)	0.0002 (9)
C10	0.0182 (10)	0.0204 (10)	0.0199 (10)	0.0095 (8)	0.0012 (8)	0.0022 (8)
C11	0.0213 (10)	0.0243 (10)	0.0181 (10)	0.0132 (9)	0.0003 (8)	0.0008 (8)
C12	0.0139 (9)	0.0225 (11)	0.0218 (11)	0.0061 (9)	-0.0036 (8)	-0.0017 (8)
C13	0.0282 (11)	0.0238 (11)	0.0230 (11)	0.0145 (9)	0.0017 (9)	-0.0030 (9)
C14	0.0266 (11)	0.0232 (10)	0.0247 (11)	0.0155 (9)	0.0024 (9)	0.0037 (9)
C15	0.0376 (13)	0.0335 (11)	0.0235 (11)	0.0236 (10)	-0.0037 (9)	-0.0009 (9)
C16	0.0211 (11)	0.0372 (12)	0.0261 (12)	0.0149 (9)	-0.0028 (9)	-0.0034 (9)
O1	0.0416 (9)	0.0421 (9)	0.0235 (9)	0.0231 (8)	0.0099 (7)	0.0100 (7)

## supplementary materials

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O2	0.0265 (8)	0.0292 (8)	0.0196 (8)	0.0120 (7)	-0.0007 (6)	-0.0011 (6)
O4	0.0269 (8)	0.0324 (8)	0.0193 (7)	0.0135 (7)	0.0000 (6)	0.0046 (6)

### *Geometric parameters (Å, °)*

C1—C14	1.534 (3)	C9—C10	1.541 (3)
C1—C2	1.542 (3)	C9—H9A	0.99
C1—C10	1.554 (3)	C9—H9B	0.99
C1—C5	1.565 (3)	C10—C11	1.573 (3)
C2—C3	1.501 (3)	C10—H10	1
C2—H2A	0.99	C11—C12	1.524 (3)
C2—H2B	0.99	C11—C15	1.534 (3)
C3—O1	1.201 (2)	C11—C16	1.547 (3)
C3—O4	1.345 (2)	C12—O2	1.216 (2)
C5—O4	1.463 (2)	C12—C13	1.505 (3)
C5—C6	1.521 (3)	C13—C14	1.527 (3)
C5—H5	1	C13—H13A	0.99
C6—C7	1.530 (3)	C13—H13B	0.99
C6—H6A	0.99	C14—H14A	0.99
C6—H6B	0.99	C14—H14B	0.99
C7—C8	1.524 (3)	C15—H15A	0.98
C7—H7A	0.99	C15—H15B	0.98
C7—H7B	0.99	C15—H15C	0.98
C8—C9	1.527 (3)	C16—H16A	0.98
C8—H8A	0.99	C16—H16B	0.98
C8—H8B	0.99	C16—H16C	0.98
C14—C1—C2	112.26 (16)	C10—C9—H9B	109
C14—C1—C10	108.82 (16)	H9A—C9—H9B	107.8
C2—C1—C10	114.16 (16)	C9—C10—C1	112.96 (15)
C14—C1—C5	106.98 (16)	C9—C10—C11	112.20 (15)
C2—C1—C5	101.73 (15)	C1—C10—C11	115.38 (15)
C10—C1—C5	112.57 (16)	C9—C10—H10	105
C3—C2—C1	107.32 (16)	C1—C10—H10	105
C3—C2—H2A	110.3	C11—C10—H10	105
C1—C2—H2A	110.3	C12—C11—C15	109.38 (15)
C3—C2—H2B	110.3	C12—C11—C16	108.37 (16)
C1—C2—H2B	110.3	C15—C11—C16	108.06 (16)
H2A—C2—H2B	108.5	C12—C11—C10	107.64 (14)
O1—C3—O4	121.31 (18)	C15—C11—C10	108.80 (15)
O1—C3—C2	128.34 (18)	C16—C11—C10	114.52 (16)
O4—C3—C2	110.34 (16)	O2—C12—C13	121.53 (18)
O4—C5—C6	107.62 (16)	O2—C12—C11	122.68 (17)
O4—C5—C1	107.19 (15)	C13—C12—C11	115.72 (16)
C6—C5—C1	120.72 (16)	C12—C13—C14	108.53 (16)
O4—C5—H5	106.9	C12—C13—H13A	110
C6—C5—H5	106.9	C14—C13—H13A	110
C1—C5—H5	106.9	C12—C13—H13B	110
C5—C6—C7	115.98 (17)	C14—C13—H13B	110
C5—C6—H6A	108.3	H13A—C13—H13B	108.4



C7—C6—H6A	108.3	C13—C14—C1	112.81 (15)
C5—C6—H6B	108.3	C13—C14—H14A	109
C7—C6—H6B	108.3	C1—C14—H14A	109
H6A—C6—H6B	107.4	C13—C14—H14B	109
C8—C7—C6	115.44 (17)	C1—C14—H14B	109
C8—C7—H7A	108.4	H14A—C14—H14B	107.8
C6—C7—H7A	108.4	C11—C15—H15A	109.5
C8—C7—H7B	108.4	C11—C15—H15B	109.5
C6—C7—H7B	108.4	H15A—C15—H15B	109.5
H7A—C7—H7B	107.5	C11—C15—H15C	109.5
C7—C8—C9	114.27 (17)	H15A—C15—H15C	109.5
C7—C8—H8A	108.7	H15B—C15—H15C	109.5
C9—C8—H8A	108.7	C11—C16—H16A	109.5
C7—C8—H8B	108.7	C11—C16—H16B	109.5
C9—C8—H8B	108.7	H16A—C16—H16B	109.5
H8A—C8—H8B	107.6	C11—C16—H16C	109.5
C8—C9—C10	113.03 (17)	H16A—C16—H16C	109.5
C8—C9—H9A	109	H16B—C16—H16C	109.5
C10—C9—H9A	109	C3—O4—C5	111.59 (15)
C8—C9—H9B	109		
C14—C1—C2—C3	124.11 (17)	C5—C1—C10—C11	169.82 (15)
C10—C1—C2—C3	-111.44 (18)	C9—C10—C11—C12	179.42 (16)
C5—C1—C2—C3	10.1 (2)	C1—C10—C11—C12	-49.3 (2)
C1—C2—C3—O1	175.8 (2)	C9—C10—C11—C15	61.0 (2)
C1—C2—C3—O4	-3.3 (2)	C1—C10—C11—C15	-167.71 (16)
C14—C1—C5—O4	-131.22 (17)	C9—C10—C11—C16	-60.0 (2)
C2—C1—C5—O4	-13.32 (19)	C1—C10—C11—C16	71.3 (2)
C10—C1—C5—O4	109.29 (17)	C15—C11—C12—O2	-5.6 (2)
C14—C1—C5—C6	105.2 (2)	C16—C11—C12—O2	112.0 (2)
C2—C1—C5—C6	-136.86 (18)	C10—C11—C12—O2	-123.67 (19)
C10—C1—C5—C6	-14.2 (3)	C15—C11—C12—C13	171.40 (17)
O4—C5—C6—C7	-49.0 (2)	C16—C11—C12—C13	-71.0 (2)
C1—C5—C6—C7	74.4 (2)	C10—C11—C12—C13	53.3 (2)
C5—C6—C7—C8	-74.9 (2)	O2—C12—C13—C14	118.03 (19)
C6—C7—C8—C9	56.7 (2)	C11—C12—C13—C14	-59.0 (2)
C7—C8—C9—C10	-69.9 (2)	C12—C13—C14—C1	59.0 (2)
C8—C9—C10—C1	93.9 (2)	C2—C1—C14—C13	71.8 (2)
C8—C9—C10—C11	-133.64 (17)	C10—C1—C14—C13	-55.6 (2)
C14—C1—C10—C9	-177.66 (16)	C5—C1—C14—C13	-177.43 (16)
C2—C1—C10—C9	56.1 (2)	O1—C3—O4—C5	174.92 (18)
C5—C1—C10—C9	-59.3 (2)	C2—C3—O4—C5	-5.8 (2)
C14—C1—C10—C11	51.4 (2)	C6—C5—O4—C3	143.75 (16)
C2—C1—C10—C11	-74.9 (2)	C1—C5—O4—C3	12.5 (2)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10 $\cdots$ O1 <sup>i</sup>	1	2.70	3.596 (2)	149

## supplementary materials

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C14—H14A···O1 <sup>i</sup>	0.99	2.70	3.562 (3)	146
C2—H2A···O2 <sup>ii</sup>	0.99	2.62	3.449 (2)	141
C9—H9B···O2 <sup>ii</sup>	0.99	2.66	3.454 (2)	138
C5—H5···O2 <sup>iii</sup>	1	2.58	3.194 (2)	119

Symmetry codes: (i)  $x-y+1, x, z-1/6$ ; (ii)  $y, -x+y+1, z+1/6$ ; (iii)  $y+1, -x+y+1, z+1/6$ .

Fig. 1

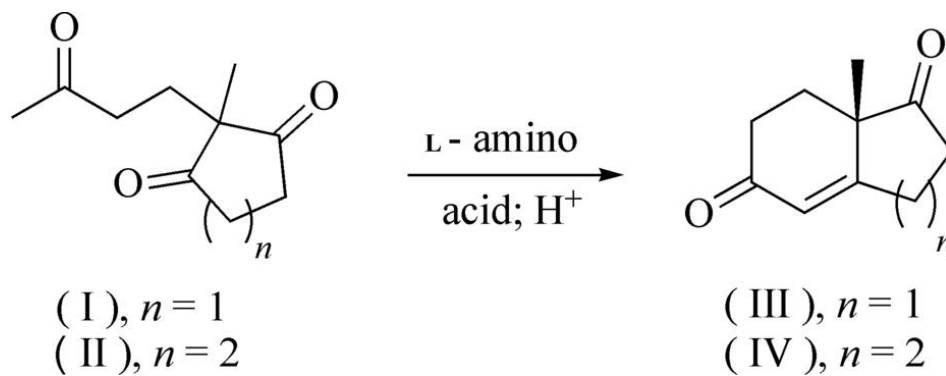


Fig. 2

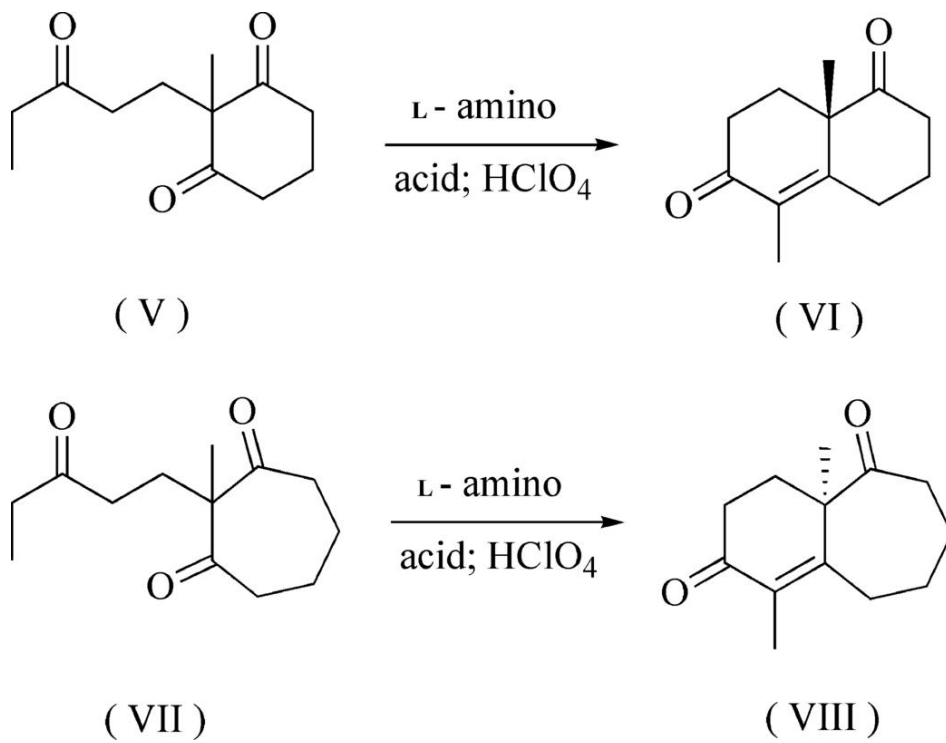


Fig. 3

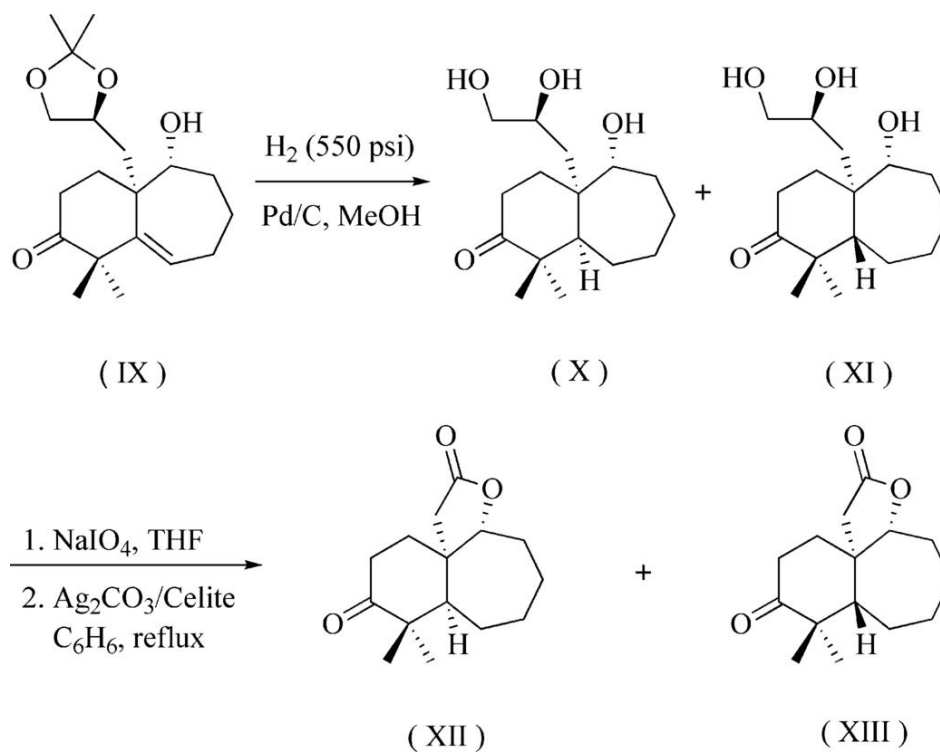


Fig. 4

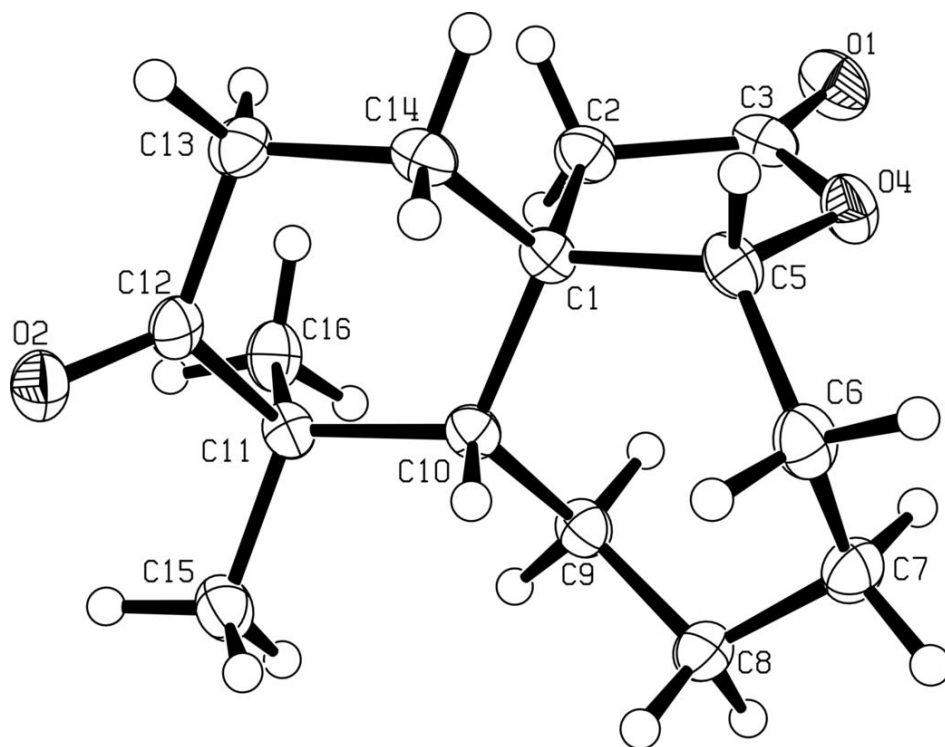


Fig. 5

