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# Crystal structure of ( $\pm$ )-(1*SR*,5*SR*,6*SR*,7*SR*,10*SR*,11*SR*,13*SR*)-13-benzyloxy-7-methoxymethoxy-11,15,18,18-tetramethyl-3-oxo-2,4-dioxatetracyclo[12.3.1.0<sup>1,5</sup>.0<sup>6,11</sup>]octadeca-14,16-dien-10-yl benzoate

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In the title compound, C<sub>36</sub>H<sub>42</sub>O<sub>8</sub>, the dioxolane ring adopts a twist conformation; the two adjacent C atoms deviate alternately from the mean plane of other atoms by  $-0.287(5)$  and  $0.174(5)$  Å. The cyclohexane, cyclohexadiene and central cyclooctane rings show chair, half-chair and boat-chair forms, respectively. As a result of the strained ring system, the tetrasubstituted olefin in the cyclohexadiene is skewed from an ideal planar structure. In the crystal, C—H $\cdots$ O hydrogen bonds connect the molecules into a sheet parallel to (100). The sheets are further linked by other weak C—H $\cdots$ O and C—H $\cdots\pi$  interactions, forming a three-dimensional network.

## 1. Chemical context

Paclitaxel is a well-known natural diterpenoid containing a taxane framework (tricyclo[9.3.1.0<sup>3,8</sup>]pentadecane; Fig. 1), with a potent antitumor activity (Wall & Wani, 1995). The complicated structure and significant bioactivity have attracted chemical and medicinal interest. Previously, we have reported the crystal structures of the precursor for cyclization to build the taxane skeleton (Oishi, Yamaguchi *et al.*, 2015), and cyclized compounds (Oishi, Fukaya *et al.*, 2015) obtained in the synthetic study of paclitaxel. The title compound was afforded by further manipulation of functional groups of the cyclized compounds (Fukaya *et al.*, 2015).

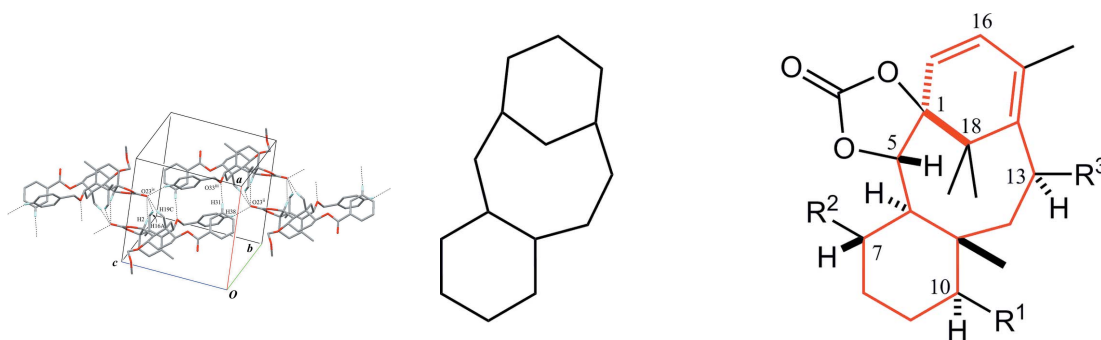
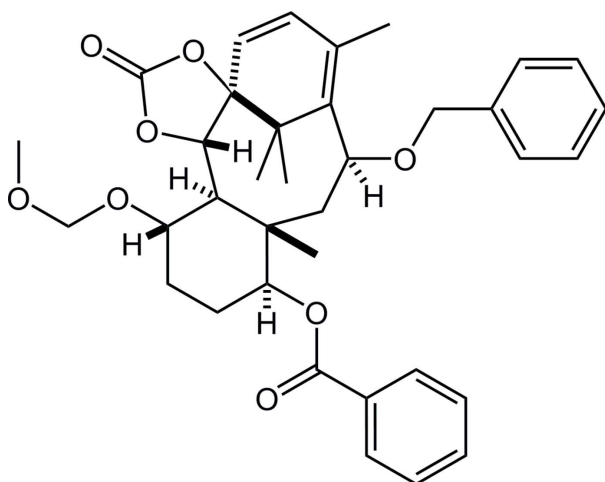


Figure 1

Left: Structure of the tricyclo[9.3.1.0<sup>3,8</sup>]pentadecane (taxane) skeleton; Right: The title compound, indicating the taxane skeleton with red lines.  $R^1 = \text{OC}(=\text{O})\text{Ph}$ ,  $R^2 = \text{OCH}_2\text{OCH}_3$ ,  $R^3 = \text{OCH}_2\text{Ph}$ .

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## 2. Structural commentary

The molecular structure of the title compound is shown in Fig. 2. The dioxolane ring (C1/C2/O20/C21/O22) adopts a twist form with puckering parameters of  $Q(2) = 0.272(2)$  Å and

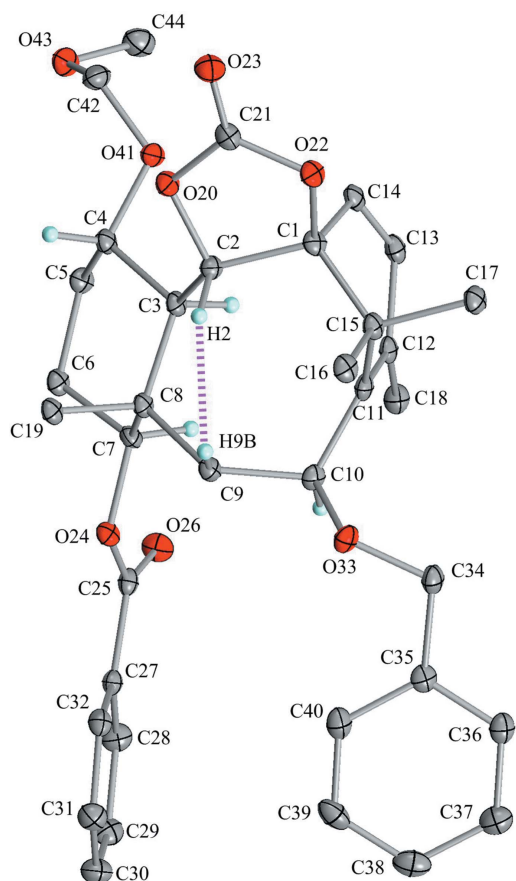


Figure 2

The molecular structure of the title compound with the atom labeling. Displacement ellipsoids are drawn at the 30% probability level. The purple dotted line indicates the intramolecular short contact. For clarity, only the H atoms attached to the chiral C atoms and related to the short contact are shown.

Table 1

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C35–C40 benzene ring.

| $D-H\cdots A$             | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|-------|-------------|-------------|---------------|
| $C34-H34A\cdots O43^i$    | 0.99  | 2.42        | 3.377 (3)   | 163           |
| $C38-H38\cdots O23^{ii}$  | 0.95  | 2.44        | 3.295 (3)   | 149           |
| $C31-H31\cdots O33^{iii}$ | 0.95  | 2.49        | 3.426 (3)   | 168           |
| $C2-H2\cdots O23^{iv}$    | 1.00  | 2.51        | 3.433 (3)   | 153           |
| $C16-H16A\cdots O23^{iv}$ | 0.98  | 2.53        | 3.357 (3)   | 142           |
| $C19-H19C\cdots O23^{iv}$ | 0.98  | 2.54        | 3.477 (3)   | 160           |
| $C18-H18C\cdots Cg^v$     | 0.98  | 2.89        | 3.492 (3)   | 121           |

Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $x, y+1, z-1$ ; (iii)  $-x+1, -y+1, -z+1$ ; (iv)  $-x+1, -y, -z+2$ ; (v)  $-x, -y+1, -z+1$ .

$\varphi(2) = 58.3(5)^\circ$ . Atoms C1 and C2 deviate from the mean plane of the other atoms by  $-0.287(5)$  and  $0.174(5)$  Å, respectively. The cyclohexane ring (C3–C8) adopts a chair form with puckering parameters of  $Q = 0.590(2)$  Å,  $\theta = 10.97(19)^\circ$ ,  $\varphi = 294.8(12)^\circ$ ,  $Q(2) = 0.110(2)$  Å and  $Q(3) = 0.579(2)$  Å. The large substituents (C3–C2, C7–O24 and C8–C9) are in equatorial positions, while the methoxymethoxy group (C4–O41) is slightly tilted from the ideal equatorial position with an angle to the Cremer & Pople plane of  $59.01(14)^\circ$ .

The cyclohexadiene ring (C1/C14/C13/C12/C11/C15) adopts a half-boat form with puckering parameters of  $Q = 0.598(2)$  Å,  $\theta = 115.68(19)^\circ$ ,  $\varphi = 131.4(3)^\circ$ ,  $Q(2) = 0.539(2)^\circ$  and  $Q(3) = 0.259(2)^\circ$ . The tetrasubstituted olefin (C10/C15/C11=C12/C13/C18) is skewed from an ideal planar structure as a result of the strain in the fused-ring system, the C10–C11=C12–C18, C15–C11=C12–C13, C10–C11=C12–C13 and C15–C11=C12–C18 torsion angles being  $-19.5(3)$ ,  $-18.4(3)$ ,  $150.34(18)$  and  $171.80(18)^\circ$ , respectively. The dihedral angle between the C10/C11/C15 and C18/C12/C13 planes is  $26.4(3)^\circ$ . The other olefin (C12/C13=C14/C1) slightly deviates from planarity with a C12–C13=C14–C1 torsion angle of  $9.1(3)^\circ$ . The diene moiety shows a

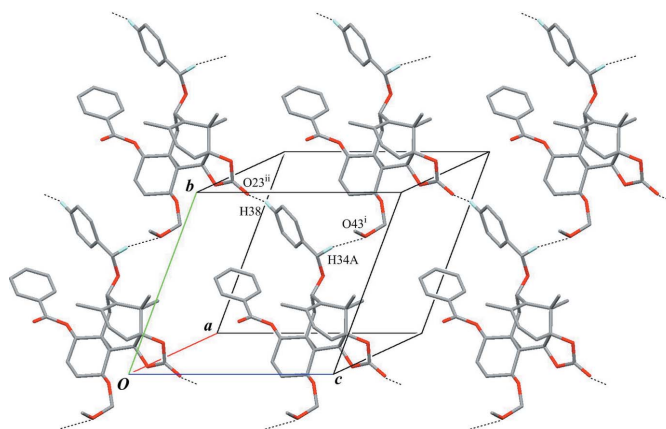
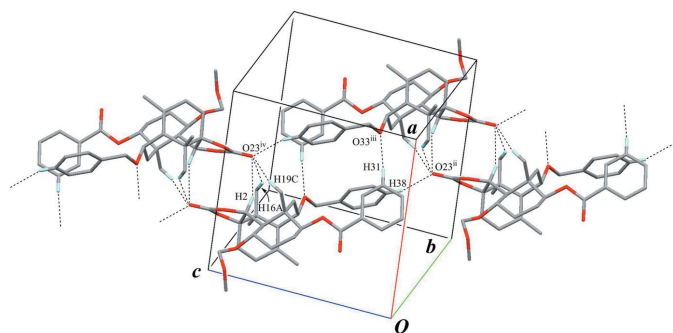


Figure 3

A partial packing view showing a sheet parallel to (100). Black dashed lines indicate the intermolecular C–H $\cdots$ O interactions. Only H atoms involved in hydrogen bonds are shown for clarity. [Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $x, y+1, z-1$ .]



**Figure 4**

A packing diagram showing the connections between enantiomers. Black dashed lines indicate the intermolecular C—H...O interactions. Only H atoms involved in hydrogen bonds are shown for clarity. [Symmetry codes: (ii)  $x, y + 1, z - 1$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y, -z + 2$ .]

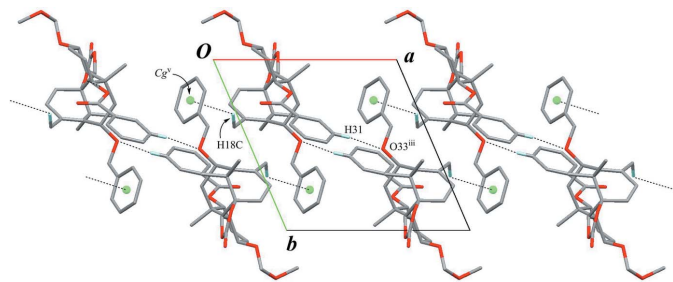
C11=C12—C13=C14 torsion angle of  $-17.7(3)^\circ$ . The central cyclooctane ring (C1—C3/C8—C11/C15) adopts a boat-chair form with puckering parameters of  $Q = 1.182(2) \text{ \AA}$ ,  $Q(2) = 0.897(2) \text{ \AA}$ ,  $\varphi(2) = 179.75(15)^\circ$ ,  $Q(3) = 0.627(2) \text{ \AA}$ ,  $\varphi(3) = 2.7(2)^\circ$  and  $Q(4) = 0.441(2) \text{ \AA}$ . There is an intramolecular short contact of  $1.98 \text{ \AA}$  between atoms H2 and H9B (Fig. 2).

### 3. Supramolecular features

Intermolecular C—H...O interactions (C34—H34A...O43<sup>i</sup> and C38—H38...O23<sup>ii</sup>; Table 1 and Fig. 3) lead to the formation of a sheet parallel to (100). These sheets are further linked through weak intermolecular C—H...O and C—H... $\pi$  interactions (C31—H31...O33<sup>iii</sup>, C2—H2...O23<sup>iv</sup>, C16—H16A...O23<sup>iv</sup>, C19—H19C...O23<sup>iv</sup> and C18—H18C...Cg<sup>v</sup>; Table 1, Figs. 4 and 5) into a three-dimensional network.

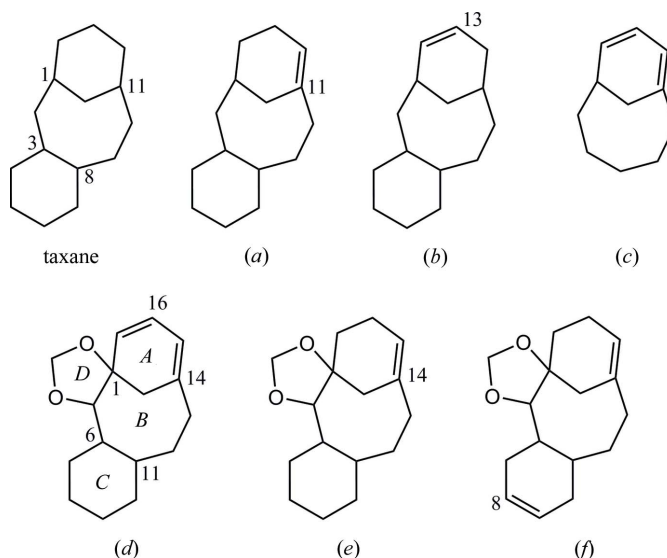
### 4. Database survey

In the Cambridge Structural Database (CSD, Version 5.36, November 2014; Groom & Allen, 2014), 85 structures containing a tricyclo[9.3.1.0<sup>3,8</sup>]pentadec-11-ene skeleton, (a), are registered (Fig. 6). These include a large number of paclitaxels and its analogues, and one compound (NEGBOQ;



**Figure 5**

A packing diagram viewed down the  $c$  axis. Black dashed lines indicate the intermolecular C—H...O and C—H... $\pi$  interactions. Cg is the centroid of the C35—C40 benzene ring. Only H atoms involved in hydrogen bonds are shown for clarity. [Symmetry codes: (iii)  $-x + 1, -y + 1, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ .]



**Figure 6**

Core structures for database survey; tricyclo[9.3.1.0<sup>3,8</sup>]pentadecane (taxane) and its (a) 11-ene and (b) 13-ene derivatives, (c) bicyclo[5.3.1]undeca-7,9-diene, (d) the tetracyclic core of the title compound with ring labelling and (e) its dihydro derivative and (f) the regioisomer of olefin. The ring-fusion geometries are similar to the title compound in each of the related structures, as *cis*-AB, *trans*-BC and *trans*-BD.

Poujol *et al.*, 1997) containing a 2,4-dioxatetracyclo[12.3.1.0<sup>1,5</sup>.0<sup>6,11</sup>]octadec-14-ene skeleton, (e), which is a dihydro derivative for the tetracyclic core of the title compound, (d). Another related structure (SOJWOD; Paquette & Zhao, 1998) containing a tricyclo[9.3.1.0<sup>3,8</sup>]pentadec-13-ene skeleton, (b), has also been reported.

On the other hand, there are two related structures (GOQBET and GOQBIX; Keil *et al.*, 1994) containing a bicyclo[5.3.1]undeca-7,9-diene skeleton, (c). Additionally, related tetracyclic taxoid (ILIQUP; Ohba *et al.*, 2003) and cyclic precursors for a taxane framework (NOTROF; Oishi, Yamaguchi *et al.*, 2015) were obtained in our previous study. Furthermore, the structures of the three related tetracyclic compounds have been reported (Oishi, Fukaya *et al.*, 2015). There are other crystalline compounds, closely related to the title compound with 2,4-dioxatetracyclo[12.3.1.0<sup>1,5</sup>.0<sup>6,11</sup>]octadeca-8,14-diene skeleton, (f) (Nicolaou, Ueno *et al.*, 1995; Nicolaou, Yang *et al.*, 1995), but they have not been deposited in the CSD.

### 5. Synthesis and crystallization

The title compound was provided in a synthetic study on paclitaxel (Fukaya *et al.*, 2015). The cyclohexadiene unit (C1/C14/C13/C12/C11/C15) was synthesized according to the reported procedure (Nicolaou, Liu *et al.*, 1995), and coupled with the substituted cyclohexane unit (C3—C8) prepared from 3-methylanisole by a Shapiro reaction (Nicolaou, Liu *et al.*, 1995). A cyclization reaction followed by further manipulations of the functional groups afforded the title compound. Purification was carried out by silica gel chromatography, and

**Table 2**  
Experimental details.

|                                                                                                                |                                                |
|----------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| Crystal data                                                                                                   |                                                |
| Chemical formula                                                                                               | C <sub>36</sub> H <sub>42</sub> O <sub>8</sub> |
| <i>M<sub>r</sub></i>                                                                                           | 602.69                                         |
| Crystal system, space group                                                                                    | Triclinic, <i>P</i> $\bar{1}$                  |
| Temperature (K)                                                                                                | 90                                             |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)                                                                             | 10.9358 (6), 11.6121 (6),<br>13.6833 (7)       |
| $\alpha$ , $\beta$ , $\gamma$ (°)                                                                              | 72.148 (2), 86.447 (2), 66.766 (2)             |
| <i>V</i> (Å <sup>3</sup> )                                                                                     | 1516.36 (14)                                   |
| <i>Z</i>                                                                                                       | 2                                              |
| Radiation type                                                                                                 | Mo <i>K</i> α                                  |
| $\mu$ (mm <sup>-1</sup> )                                                                                      | 0.09                                           |
| Crystal size (mm)                                                                                              | 0.32 × 0.27 × 0.16                             |
| Data collection                                                                                                |                                                |
| Diffraction                                                                                                    | Broker D8 Venture                              |
| Absorption correction                                                                                          | Multi-scan ( <i>SADABS</i> ; Bruker, 2014)     |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>                                                                | 0.97, 0.98                                     |
| No. of measured, independent and<br>observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                          | 27885, 5346, 4078                              |
| <i>R<sub>int</sub></i>                                                                                         | 0.052                                          |
| (sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )                                                      | 0.595                                          |
| Refinement                                                                                                     |                                                |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.047, 0.120, 1.04                             |
| No. of reflections                                                                                             | 5346                                           |
| No. of parameters                                                                                              | 402                                            |
| H-atom treatment                                                                                               | H-atom parameters constrained                  |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )                                     | 0.59, -0.23                                    |

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006), *pubCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

colorless crystals were obtained from a benzene solution under a pentane-saturated atmosphere by slow evaporation at ambient temperature.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically with C–H = 0.95–1.00 Å, and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ .

## Acknowledgements

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## References

- Bruker (2014). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Fukaya, K., Sugai, T., Yamaguchi, Y., Watanabe, A., Sato, T. & Chida, N. (2015). In preparation.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Keil, J. M., Massa, W., Riedel, R., Seitz, G. & Wocadlo, S. (1994). *Tetrahedron Lett.* **35**, 7923–7926.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nicolaou, K. C., Liu, J.-J., Yang, Z., Ueno, H., Sorensen, E. J., Claiborne, C. F., Guy, R. K., Hwang, C.-K., Nakada, M. & Nantermet, P. G. (1995). *J. Am. Chem. Soc.* **117**, 634–644.
- Nicolaou, K. C., Ueno, H., Liu, J.-J., Nantermet, P. G., Yang, Z., Renaud, J., Paulvannan, K. & Chadha, R. (1995). *J. Am. Chem. Soc.* **117**, 653–659.
- Nicolaou, K. C., Yang, Z., Liu, J.-J., Nantermet, P. G., Claiborne, C. F., Renaud, J., Guy, R. K. & Shibayama, K. (1995). *J. Am. Chem. Soc.* **117**, 645–652.
- Ohba, S., Chinen, A., Matsumoto, Y. & Chida, N. (2003). *Acta Cryst. E* **59**, o1476–o1477.
- Oishi, T., Fukaya, K., Yamaguchi, Y., Sugai, T., Watanabe, A., Sato, T. & Chida, N. (2015). *Acta Cryst. E* **71**, 466–472.
- Oishi, T., Yamaguchi, Y., Fukaya, K., Sugai, T., Watanabe, A., Sato, T. & Chida, N. (2015). *Acta Cryst. E* **71**, 8–11.
- Paquette, L. A. & Zhao, M. (1998). *J. Am. Chem. Soc.* **120**, 5203–5212.
- Poujol, H., Ahond, A., Al Mourabit, A., Chiaroni, A., Poupat, C., Riche, C. & Potier, P. (1997). *Tetrahedron*, **53**, 5169–5184.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
- Wall, M. E. & Wani, M. C. (1995). *ACS Symp. Ser.* **583**, 18–30.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

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**Crystal structure of  $(\pm)$ -(1*SR*,5*SR*,6*SR*,7*SR*,10*SR*,11*SR*,13*SR*)-13-benzyloxy-7-methoxymethoxy-11,15,18,18-tetramethyl-3-oxo-2,4-dioxatetracyclo-[12.3.1.0<sup>1,5</sup>.0<sup>6,11</sup>]octadeca-14,16-dien-10-yl benzoate**

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**Computing details**

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

**$(\pm)$ -(1*SR*,5*SR*,6*SR*,7*SR*,10*SR*,11*SR*,13*SR*)-13-Benzyloxy-7-methoxymethoxy-11,15,18,18-tetramethyl-3-oxo-2,4-dioxatetracyclo[12.3.1.0<sup>1,5</sup>.0<sup>6,11</sup>]octadeca-14,16-dien-10-yl benzoate**

*Crystal data*

$C_{36}H_{42}O_8$   
 $M_r = 602.69$   
 Triclinic, *P* $\bar{1}$   
 $a = 10.9358$  (6) Å  
 $b = 11.6121$  (6) Å  
 $c = 13.6833$  (7) Å  
 $\alpha = 72.148$  (2)°  
 $\beta = 86.447$  (2)°  
 $\gamma = 66.766$  (2)°  
 $V = 1516.36$  (14) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 644$   
 $D_x = 1.320$  Mg m<sup>-3</sup>  
 Melting point: 465.2 K  
 Mo *K* $\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 9212 reflections  
 $\theta = 2.2$ – $25.0^\circ$   
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 90$  K  
 Prism, colorless  
 $0.32 \times 0.27 \times 0.16$  mm

*Data collection*

Bruker D8 Venture  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Multilayered confocal mirror monochromator  
 Detector resolution: 8.333 pixels mm<sup>-1</sup>  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2014)  
 $T_{\min} = 0.97$ ,  $T_{\max} = 0.98$

27885 measured reflections  
 5346 independent reflections  
 4078 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.1^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -13 \rightarrow 13$   
 $l = -16 \rightarrow 16$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$  $wR(F^2) = 0.120$  $S = 1.04$ 

5346 reflections

402 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 1.0416P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$  $\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$ *Special details*

**Experimental.** *M.p.* 462.2–465.2 K (not corrected); IR (film): 2940, 1806, 1716, 1274, 1109, 1043, 713  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (p.p.m.) 8.03 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.61 (tt,  $J = 7.5, 1.2$  Hz, 1H), 7.49 (ddd,  $J = 8.3, 7.5, 1.7$  Hz, 2H), 7.23–7.12 (m, 5H), 6.17 (d,  $J = 9.2$  Hz, 1H), 5.63 (d,  $J = 9.2$  Hz, 1H), 4.94 (d,  $J = 4.9$  Hz, 1H), 4.90 (dd,  $J = 11.3, 5.2$  Hz, 1H), 4.75 (d,  $J = 6.9$  Hz, 1H), 4.65 (dd,  $J = 11.7, 5.4$  Hz, 1H), 4.50 (d,  $J = 6.9$  Hz, 1H), 4.47 (d,  $J = 12.0$  Hz, 1H), 4.24 (d,  $J = 12.0$  Hz, 1H), 3.70 (ddd,  $J = 10.5, 10.5, 4.9$  Hz, 1H), 3.33 (s, 3H), 2.26 (dddd,  $J = 13.4, 5.0, 4.9, 2.6$  Hz, 1H), 2.12 (dd,  $J = 15.9, 5.4$  Hz, 1H), 2.04 (dd,  $J = 10.5, 4.9$  Hz, 1H), 1.99 (dd,  $J = 15.9, 11.7$  Hz, 1H), 1.91–1.85 (m, 1H), 1.84–1.73 (m, 1H), 1.80 (s, 3H), 1.58 (s, 3H), 1.50 (s, 3H), 1.35–1.24 (m, 1H), 1.18 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (p.p.m.) 165.9 (C), 154.6 (C), 138.3 (C), 138.2 (C), 137.8 (C), 135.5 (CH), 133.5 (CH), 130.6 (CH), 130.1 (C), 129.8 (CH), 128.7 (CH), 128.5 (CH), 127.7 (CH), 127.4 (CH), 97.6 ( $\text{CH}_2$ ), 93.1 (C), 79.7 (CH), 74.2 (CH), 74.1 (CH), 73.4 (CH), 69.9 ( $\text{CH}_2$ ), 56.0 ( $\text{CH}_3$ ), 45.7 (CH), 42.8 (C), 39.8 ( $\text{CH}_2$ ), 37.9 (C), 32.5 ( $\text{CH}_2$ ), 29.5 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_2$ ), 19.33 ( $\text{CH}_3$ ), 19.27 ( $\text{CH}_3$ ), 17.7 ( $\text{CH}_3$ ); HRMS (ESI): calcd for  $\text{C}_{36}\text{H}_{42}\text{O}_8\text{Na}^+$   $[M+\text{Na}]^+$  625.2777, found 625.2777.

**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  $F^2 > \sigma(F^2)$  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. Problematic one reflection with  $|I(\text{obs}) - I(\text{calc})|/\sigma W(I)$  greater than 10 (–2 3 1) has been omitted in the final refinement.

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

|     | <i>x</i>   | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|-------------|--------------|----------------------------------|
| C1  | 0.2090 (2) | 0.1750 (2)  | 0.91158 (15) | 0.0210 (5)                       |
| C2  | 0.3204 (2) | 0.0817 (2)  | 0.86310 (15) | 0.0198 (5)                       |
| H2  | 0.3938     | 0.1143      | 0.8498       | 0.024*                           |
| C3  | 0.2821 (2) | 0.0698 (2)  | 0.76154 (15) | 0.0184 (4)                       |
| H3  | 0.1858     | 0.1295      | 0.7447       | 0.022*                           |
| C4  | 0.2914 (2) | –0.0675 (2) | 0.76837 (15) | 0.0207 (5)                       |
| H4  | 0.3848     | –0.1344     | 0.7883       | 0.025*                           |
| C5  | 0.2414 (2) | –0.0651 (2) | 0.66551 (15) | 0.0225 (5)                       |
| H5B | 0.2627     | –0.1569     | 0.6672       | 0.027*                           |
| H5A | 0.1431     | –0.0182     | 0.6578       | 0.027*                           |
| C6  | 0.2999 (2) | 0.0002 (2)  | 0.57150 (15) | 0.0214 (5)                       |
| H6A | 0.3951     | –0.0565     | 0.5704       | 0.026*                           |
| H6B | 0.2523     | 0.0104      | 0.5082       | 0.026*                           |
| C7  | 0.2877 (2) | 0.1337 (2)  | 0.57361 (15) | 0.0191 (5)                       |
| H7  | 0.191      | 0.191       | 0.5717       | 0.023*                           |

|      |              |               |              |            |
|------|--------------|---------------|--------------|------------|
| C8   | 0.3583 (2)   | 0.1246 (2)    | 0.67110 (15) | 0.0183 (4) |
| C9   | 0.3595 (2)   | 0.2595 (2)    | 0.66630 (16) | 0.0199 (5) |
| H9B  | 0.4203       | 0.242         | 0.7246       | 0.024*     |
| H9A  | 0.4028       | 0.2871        | 0.6028       | 0.024*     |
| C10  | 0.2330 (2)   | 0.3811 (2)    | 0.66790 (16) | 0.0198 (5) |
| H10  | 0.1778       | 0.413         | 0.602        | 0.024*     |
| C11  | 0.1476 (2)   | 0.35654 (19)  | 0.75632 (16) | 0.0197 (5) |
| C12  | 0.0331 (2)   | 0.3454 (2)    | 0.73994 (15) | 0.0204 (5) |
| C13  | −0.0137 (2)  | 0.2618 (2)    | 0.82427 (16) | 0.0230 (5) |
| H13  | −0.1038      | 0.2705        | 0.8228       | 0.028*     |
| C14  | 0.0722 (2)   | 0.1738 (2)    | 0.90249 (16) | 0.0229 (5) |
| H14  | 0.0479       | 0.1105        | 0.9525       | 0.027*     |
| C15  | 0.1993 (2)   | 0.3171 (2)    | 0.86995 (15) | 0.0207 (5) |
| C16  | 0.3299 (2)   | 0.3293 (2)    | 0.88962 (16) | 0.0229 (5) |
| H16B | 0.3555       | 0.2938        | 0.9636       | 0.034*     |
| H16C | 0.317        | 0.4222        | 0.865        | 0.034*     |
| H16A | 0.4005       | 0.2795        | 0.8529       | 0.034*     |
| C17  | 0.0958 (2)   | 0.4076 (2)    | 0.92429 (16) | 0.0243 (5) |
| H17A | 0.0079       | 0.4077        | 0.9138       | 0.036*     |
| H17B | 0.092        | 0.4974        | 0.8955       | 0.036*     |
| H17C | 0.1216       | 0.3753        | 0.9981       | 0.036*     |
| C18  | −0.0437 (2)  | 0.3934 (2)    | 0.63817 (16) | 0.0255 (5) |
| H18A | −0.0215      | 0.4638        | 0.5908       | 0.038*     |
| H18B | −0.1396      | 0.4273        | 0.648        | 0.038*     |
| H18C | −0.0202      | 0.3204        | 0.6094       | 0.038*     |
| C19  | 0.5062 (2)   | 0.0313 (2)    | 0.68131 (16) | 0.0211 (5) |
| H19B | 0.5135       | −0.0561       | 0.6827       | 0.032*     |
| H19C | 0.5482       | 0.0244        | 0.7452       | 0.032*     |
| H19A | 0.5512       | 0.0659        | 0.6225       | 0.032*     |
| O20  | 0.36857 (14) | −0.04110 (14) | 0.94740 (10) | 0.0226 (3) |
| C21  | 0.3358 (2)   | −0.0133 (2)   | 1.03550 (16) | 0.0229 (5) |
| O22  | 0.25645 (14) | 0.11453 (14)  | 1.01974 (10) | 0.0241 (3) |
| O23  | 0.37257 (15) | −0.09211 (15) | 1.11907 (11) | 0.0301 (4) |
| O24  | 0.34533 (13) | 0.19559 (14)  | 0.48470 (10) | 0.0200 (3) |
| C25  | 0.2682 (2)   | 0.2569 (2)    | 0.39610 (15) | 0.0204 (5) |
| O26  | 0.16003 (15) | 0.25445 (15)  | 0.38570 (11) | 0.0290 (4) |
| C27  | 0.3292 (2)   | 0.3303 (2)    | 0.31322 (15) | 0.0192 (4) |
| C28  | 0.2699 (2)   | 0.3799 (2)    | 0.21389 (16) | 0.0269 (5) |
| H28  | 0.1964       | 0.362         | 0.1999       | 0.032*     |
| C29  | 0.3180 (2)   | 0.4553 (2)    | 0.13538 (17) | 0.0300 (5) |
| H29  | 0.2785       | 0.4879        | 0.0673       | 0.036*     |
| C30  | 0.4233 (2)   | 0.4832 (2)    | 0.15603 (17) | 0.0299 (5) |
| H30  | 0.4553       | 0.5363        | 0.1023       | 0.036*     |
| C31  | 0.4824 (2)   | 0.4342 (2)    | 0.25464 (17) | 0.0279 (5) |
| H31  | 0.5552       | 0.4534        | 0.2684       | 0.033*     |
| C32  | 0.4363 (2)   | 0.3575 (2)    | 0.33317 (16) | 0.0218 (5) |
| H32  | 0.4776       | 0.3234        | 0.4008       | 0.026*     |
| O33  | 0.28434 (14) | 0.47725 (14)  | 0.66845 (11) | 0.0239 (3) |

|      |              |               |              |            |
|------|--------------|---------------|--------------|------------|
| C34  | 0.1863 (2)   | 0.6092 (2)    | 0.63828 (16) | 0.0246 (5) |
| H34A | 0.1914       | 0.653         | 0.6887       | 0.029*     |
| H34B | 0.0964       | 0.6075        | 0.6389       | 0.029*     |
| C35  | 0.2054 (2)   | 0.6865 (2)    | 0.53358 (16) | 0.0217 (5) |
| C36  | 0.1191 (2)   | 0.8177 (2)    | 0.49309 (17) | 0.0260 (5) |
| H36  | 0.0481       | 0.8562        | 0.5317       | 0.031*     |
| C37  | 0.1356 (2)   | 0.8926 (2)    | 0.39732 (17) | 0.0313 (5) |
| H37  | 0.0773       | 0.9827        | 0.3712       | 0.038*     |
| C38  | 0.2363 (2)   | 0.8373 (3)    | 0.33917 (18) | 0.0346 (6) |
| H38  | 0.2465       | 0.8885        | 0.2727       | 0.041*     |
| C39  | 0.3217 (2)   | 0.7074 (3)    | 0.37825 (18) | 0.0334 (6) |
| H39  | 0.3909       | 0.6689        | 0.3383       | 0.04*      |
| C40  | 0.3080 (2)   | 0.6325 (2)    | 0.47451 (17) | 0.0269 (5) |
| H40  | 0.3688       | 0.5433        | 0.501        | 0.032*     |
| O41  | 0.20301 (14) | −0.09407 (14) | 0.84612 (10) | 0.0234 (3) |
| C42  | 0.2292 (2)   | −0.2270 (2)   | 0.89614 (17) | 0.0287 (5) |
| H42B | 0.194        | −0.2359       | 0.9653       | 0.034*     |
| H42A | 0.3269       | −0.2778       | 0.9054       | 0.034*     |
| O43  | 0.17233 (17) | −0.28080 (15) | 0.84205 (12) | 0.0328 (4) |
| C44  | 0.0307 (2)   | −0.2202 (2)   | 0.83398 (19) | 0.0352 (6) |
| H44C | −0.0029      | −0.2401       | 0.9026       | 0.053*     |
| H44A | −0.0046      | −0.254        | 0.7899       | 0.053*     |
| H44B | 0.0019       | −0.1246       | 0.8039       | 0.053*     |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1  | 0.0266 (11) | 0.0233 (12) | 0.0175 (11) | −0.0112 (9)  | 0.0021 (9)  | −0.0108 (9)  |
| C2  | 0.0242 (11) | 0.0197 (11) | 0.0184 (11) | −0.0102 (9)  | 0.0022 (9)  | −0.0081 (9)  |
| C3  | 0.0212 (10) | 0.0200 (11) | 0.0184 (10) | −0.0088 (9)  | 0.0023 (8)  | −0.0110 (9)  |
| C4  | 0.0234 (11) | 0.0212 (12) | 0.0221 (11) | −0.0102 (9)  | 0.0056 (9)  | −0.0118 (9)  |
| C5  | 0.0293 (12) | 0.0228 (12) | 0.0238 (11) | −0.0148 (10) | 0.0043 (9)  | −0.0129 (9)  |
| C6  | 0.0250 (11) | 0.0233 (12) | 0.0208 (11) | −0.0103 (9)  | 0.0021 (9)  | −0.0124 (9)  |
| C7  | 0.0210 (11) | 0.0224 (11) | 0.0182 (11) | −0.0104 (9)  | 0.0059 (9)  | −0.0102 (9)  |
| C8  | 0.0208 (11) | 0.0191 (11) | 0.0191 (10) | −0.0086 (9)  | 0.0026 (8)  | −0.0108 (9)  |
| C9  | 0.0224 (11) | 0.0222 (12) | 0.0201 (11) | −0.0115 (9)  | 0.0036 (9)  | −0.0102 (9)  |
| C10 | 0.0230 (11) | 0.0192 (11) | 0.0232 (11) | −0.0112 (9)  | 0.0006 (9)  | −0.0105 (9)  |
| C11 | 0.0204 (11) | 0.0151 (11) | 0.0264 (11) | −0.0057 (9)  | 0.0014 (9)  | −0.0118 (9)  |
| C12 | 0.0216 (11) | 0.0181 (11) | 0.0244 (11) | −0.0058 (9)  | 0.0037 (9)  | −0.0137 (9)  |
| C13 | 0.0203 (11) | 0.0268 (12) | 0.0281 (12) | −0.0094 (10) | 0.0054 (9)  | −0.0176 (10) |
| C14 | 0.0256 (12) | 0.0237 (12) | 0.0271 (12) | −0.0122 (10) | 0.0105 (10) | −0.0168 (10) |
| C15 | 0.0224 (11) | 0.0222 (12) | 0.0228 (11) | −0.0097 (9)  | 0.0032 (9)  | −0.0132 (9)  |
| C16 | 0.0272 (12) | 0.0264 (12) | 0.0225 (11) | −0.0127 (10) | 0.0007 (9)  | −0.0143 (9)  |
| C17 | 0.0287 (12) | 0.0237 (12) | 0.0256 (12) | −0.0107 (10) | 0.0043 (9)  | −0.0146 (10) |
| C18 | 0.0238 (11) | 0.0270 (13) | 0.0300 (12) | −0.0107 (10) | 0.0004 (10) | −0.0136 (10) |
| C19 | 0.0236 (11) | 0.0244 (12) | 0.0206 (11) | −0.0104 (9)  | 0.0040 (9)  | −0.0135 (9)  |
| O20 | 0.0280 (8)  | 0.0228 (8)  | 0.0176 (7)  | −0.0086 (7)  | 0.0013 (6)  | −0.0086 (6)  |
| C21 | 0.0209 (11) | 0.0281 (13) | 0.0234 (12) | −0.0109 (10) | 0.0025 (9)  | −0.0115 (10) |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O22 | 0.0316 (8)  | 0.0251 (9)  | 0.0187 (8)  | −0.0111 (7)  | 0.0022 (6)   | −0.0112 (6)  |
| O23 | 0.0337 (9)  | 0.0333 (9)  | 0.0214 (9)  | −0.0122 (7)  | −0.0010 (7)  | −0.0064 (7)  |
| O24 | 0.0216 (7)  | 0.0235 (8)  | 0.0181 (7)  | −0.0104 (6)  | 0.0018 (6)   | −0.0088 (6)  |
| C25 | 0.0211 (11) | 0.0186 (11) | 0.0229 (11) | −0.0053 (9)  | −0.0003 (9)  | −0.0112 (9)  |
| O26 | 0.0252 (9)  | 0.0362 (10) | 0.0278 (8)  | −0.0154 (7)  | −0.0016 (7)  | −0.0080 (7)  |
| C27 | 0.0208 (11) | 0.0173 (11) | 0.0211 (11) | −0.0066 (9)  | 0.0018 (9)   | −0.0095 (9)  |
| C28 | 0.0292 (12) | 0.0304 (13) | 0.0271 (12) | −0.0163 (11) | −0.0025 (10) | −0.0098 (10) |
| C29 | 0.0380 (14) | 0.0318 (14) | 0.0219 (12) | −0.0148 (11) | −0.0017 (10) | −0.0084 (10) |
| C30 | 0.0365 (13) | 0.0330 (13) | 0.0246 (12) | −0.0198 (11) | 0.0044 (10)  | −0.0073 (10) |
| C31 | 0.0286 (12) | 0.0316 (13) | 0.0308 (13) | −0.0171 (11) | 0.0036 (10)  | −0.0130 (10) |
| C32 | 0.0218 (11) | 0.0227 (12) | 0.0209 (11) | −0.0065 (9)  | −0.0013 (9)  | −0.0092 (9)  |
| O33 | 0.0247 (8)  | 0.0195 (8)  | 0.0317 (8)  | −0.0110 (7)  | −0.0002 (6)  | −0.0101 (7)  |
| C34 | 0.0248 (11) | 0.0210 (12) | 0.0322 (12) | −0.0088 (10) | 0.0035 (10)  | −0.0146 (10) |
| C35 | 0.0232 (11) | 0.0249 (12) | 0.0252 (11) | −0.0134 (9)  | −0.0005 (9)  | −0.0131 (9)  |
| C36 | 0.0247 (12) | 0.0270 (13) | 0.0317 (13) | −0.0109 (10) | 0.0004 (10)  | −0.0153 (10) |
| C37 | 0.0319 (13) | 0.0323 (14) | 0.0318 (13) | −0.0165 (11) | −0.0032 (11) | −0.0065 (11) |
| C38 | 0.0395 (14) | 0.0462 (16) | 0.0291 (13) | −0.0300 (13) | 0.0020 (11)  | −0.0090 (12) |
| C39 | 0.0321 (13) | 0.0495 (17) | 0.0345 (14) | −0.0269 (13) | 0.0136 (11)  | −0.0221 (12) |
| C40 | 0.0232 (12) | 0.0292 (13) | 0.0371 (13) | −0.0128 (10) | 0.0031 (10)  | −0.0191 (11) |
| O41 | 0.0320 (8)  | 0.0214 (8)  | 0.0227 (8)  | −0.0143 (7)  | 0.0076 (6)   | −0.0108 (6)  |
| C42 | 0.0376 (13) | 0.0233 (13) | 0.0267 (12) | −0.0149 (11) | 0.0049 (10)  | −0.0063 (10) |
| O43 | 0.0443 (10) | 0.0288 (9)  | 0.0386 (9)  | −0.0219 (8)  | 0.0153 (8)   | −0.0207 (7)  |
| C44 | 0.0416 (15) | 0.0379 (15) | 0.0379 (14) | −0.0252 (12) | 0.0096 (11)  | −0.0164 (12) |

*Geometric parameters (Å, °)*

|        |           |          |           |
|--------|-----------|----------|-----------|
| C1—O22 | 1.457 (2) | C18—H18B | 0.98      |
| C1—C14 | 1.514 (3) | C18—H18C | 0.98      |
| C1—C15 | 1.533 (3) | C19—H19B | 0.98      |
| C1—C2  | 1.548 (3) | C19—H19C | 0.98      |
| C2—O20 | 1.454 (2) | C19—H19A | 0.98      |
| C2—C3  | 1.537 (3) | O20—C21  | 1.334 (2) |
| C2—H2  | 1.0       | C21—O23  | 1.196 (3) |
| C3—C4  | 1.530 (3) | C21—O22  | 1.347 (3) |
| C3—C8  | 1.561 (3) | O24—C25  | 1.346 (2) |
| C3—H3  | 1.0       | C25—O26  | 1.213 (2) |
| C4—O41 | 1.438 (2) | C25—C27  | 1.490 (3) |
| C4—C5  | 1.530 (3) | C27—C32  | 1.389 (3) |
| C4—H4  | 1.0       | C27—C28  | 1.391 (3) |
| C5—C6  | 1.524 (3) | C28—C29  | 1.383 (3) |
| C5—H5B | 0.99      | C28—H28  | 0.95      |
| C5—H5A | 0.99      | C29—C30  | 1.379 (3) |
| C6—C7  | 1.512 (3) | C29—H29  | 0.95      |
| C6—H6A | 0.99      | C30—C31  | 1.382 (3) |
| C6—H6B | 0.99      | C30—H30  | 0.95      |
| C7—O24 | 1.456 (2) | C31—C32  | 1.379 (3) |
| C7—C8  | 1.537 (3) | C31—H31  | 0.95      |
| C7—H7  | 1.0       | C32—H32  | 0.95      |

|            |             |               |             |
|------------|-------------|---------------|-------------|
| C8—C19     | 1.537 (3)   | O33—C34       | 1.428 (2)   |
| C8—C9      | 1.553 (3)   | C34—C35       | 1.491 (3)   |
| C9—C10     | 1.543 (3)   | C34—H34A      | 0.99        |
| C9—H9B     | 0.99        | C34—H34B      | 0.99        |
| C9—H9A     | 0.99        | C35—C36       | 1.390 (3)   |
| C10—O33    | 1.436 (2)   | C35—C40       | 1.396 (3)   |
| C10—C11    | 1.508 (3)   | C36—C37       | 1.379 (3)   |
| C10—H10    | 1.0         | C36—H36       | 0.95        |
| C11—C12    | 1.348 (3)   | C37—C38       | 1.380 (3)   |
| C11—C15    | 1.554 (3)   | C37—H37       | 0.95        |
| C12—C13    | 1.473 (3)   | C38—C39       | 1.374 (4)   |
| C12—C18    | 1.502 (3)   | C38—H38       | 0.95        |
| C13—C14    | 1.330 (3)   | C39—C40       | 1.375 (3)   |
| C13—H13    | 0.95        | C39—H39       | 0.95        |
| C14—H14    | 0.95        | C40—H40       | 0.95        |
| C15—C16    | 1.537 (3)   | O41—C42       | 1.400 (3)   |
| C15—C17    | 1.541 (3)   | C42—O43       | 1.405 (3)   |
| C16—H16B   | 0.98        | C42—H42B      | 0.99        |
| C16—H16C   | 0.98        | C42—H42A      | 0.99        |
| C16—H16A   | 0.98        | O43—C44       | 1.421 (3)   |
| C17—H17A   | 0.98        | C44—H44C      | 0.98        |
| C17—H17B   | 0.98        | C44—H44A      | 0.98        |
| C17—H17C   | 0.98        | C44—H44B      | 0.98        |
| C18—H18A   | 0.98        |               |             |
| O22—C1—C14 | 107.39 (16) | C15—C17—H17A  | 109.5       |
| O22—C1—C15 | 112.26 (16) | C15—C17—H17B  | 109.5       |
| C14—C1—C15 | 109.44 (17) | H17A—C17—H17B | 109.5       |
| O22—C1—C2  | 100.39 (15) | C15—C17—H17C  | 109.5       |
| C14—C1—C2  | 115.12 (16) | H17A—C17—H17C | 109.5       |
| C15—C1—C2  | 111.91 (17) | H17B—C17—H17C | 109.5       |
| O20—C2—C3  | 114.77 (16) | C12—C18—H18A  | 109.5       |
| O20—C2—C1  | 102.39 (15) | C12—C18—H18B  | 109.5       |
| C3—C2—C1   | 116.91 (17) | H18A—C18—H18B | 109.5       |
| O20—C2—H2  | 107.4       | C12—C18—H18C  | 109.5       |
| C3—C2—H2   | 107.4       | H18A—C18—H18C | 109.5       |
| C1—C2—H2   | 107.4       | H18B—C18—H18C | 109.5       |
| C4—C3—C2   | 114.36 (16) | C8—C19—H19B   | 109.5       |
| C4—C3—C8   | 112.76 (16) | C8—C19—H19C   | 109.5       |
| C2—C3—C8   | 111.37 (16) | H19B—C19—H19C | 109.5       |
| C4—C3—H3   | 105.9       | C8—C19—H19A   | 109.5       |
| C2—C3—H3   | 105.9       | H19B—C19—H19A | 109.5       |
| C8—C3—H3   | 105.9       | H19C—C19—H19A | 109.5       |
| O41—C4—C3  | 104.79 (15) | C21—O20—C2    | 108.37 (16) |
| O41—C4—C5  | 109.40 (16) | O23—C21—O20   | 124.3 (2)   |
| C3—C4—C5   | 109.75 (17) | O23—C21—O22   | 123.56 (19) |
| O41—C4—H4  | 110.9       | O20—C21—O22   | 112.13 (18) |
| C3—C4—H4   | 110.9       | C21—O22—C1    | 108.85 (15) |

|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C5—C4—H4    | 110.9       | C25—O24—C7    | 116.56 (15) |
| C6—C5—C4    | 114.71 (17) | O26—C25—O24   | 123.60 (19) |
| C6—C5—H5B   | 108.6       | O26—C25—C27   | 123.88 (19) |
| C4—C5—H5B   | 108.6       | O24—C25—C27   | 112.51 (17) |
| C6—C5—H5A   | 108.6       | C32—C27—C28   | 119.65 (19) |
| C4—C5—H5A   | 108.6       | C32—C27—C25   | 122.37 (18) |
| H5B—C5—H5A  | 107.6       | C28—C27—C25   | 117.85 (19) |
| C7—C6—C5    | 110.62 (16) | C29—C28—C27   | 120.1 (2)   |
| C7—C6—H6A   | 109.5       | C29—C28—H28   | 120.0       |
| C5—C6—H6A   | 109.5       | C27—C28—H28   | 120.0       |
| C7—C6—H6B   | 109.5       | C30—C29—C28   | 120.0 (2)   |
| C5—C6—H6B   | 109.5       | C30—C29—H29   | 120.0       |
| H6A—C6—H6B  | 108.1       | C28—C29—H29   | 120.0       |
| O24—C7—C6   | 110.82 (15) | C29—C30—C31   | 120.2 (2)   |
| O24—C7—C8   | 108.01 (15) | C29—C30—H30   | 119.9       |
| C6—C7—C8    | 112.06 (17) | C31—C30—H30   | 119.9       |
| O24—C7—H7   | 108.6       | C32—C31—C30   | 120.3 (2)   |
| C6—C7—H7    | 108.6       | C32—C31—H31   | 119.8       |
| C8—C7—H7    | 108.6       | C30—C31—H31   | 119.8       |
| C19—C8—C7   | 110.94 (16) | C31—C32—C27   | 119.86 (19) |
| C19—C8—C9   | 104.78 (16) | C31—C32—H32   | 120.1       |
| C7—C8—C9    | 111.49 (16) | C27—C32—H32   | 120.1       |
| C19—C8—C3   | 110.89 (16) | C34—O33—C10   | 113.59 (15) |
| C7—C8—C3    | 104.62 (15) | O33—C34—C35   | 111.86 (17) |
| C9—C8—C3    | 114.26 (16) | O33—C34—H34A  | 109.2       |
| C10—C9—C8   | 123.76 (17) | C35—C34—H34A  | 109.2       |
| C10—C9—H9B  | 106.4       | O33—C34—H34B  | 109.2       |
| C8—C9—H9B   | 106.4       | C35—C34—H34B  | 109.2       |
| C10—C9—H9A  | 106.4       | H34A—C34—H34B | 107.9       |
| C8—C9—H9A   | 106.4       | C36—C35—C40   | 118.3 (2)   |
| H9B—C9—H9A  | 106.5       | C36—C35—C34   | 119.20 (19) |
| O33—C10—C11 | 113.16 (16) | C40—C35—C34   | 122.5 (2)   |
| O33—C10—C9  | 103.42 (15) | C37—C36—C35   | 120.6 (2)   |
| C11—C10—C9  | 114.58 (17) | C37—C36—H36   | 119.7       |
| O33—C10—H10 | 108.5       | C35—C36—H36   | 119.7       |
| C11—C10—H10 | 108.5       | C36—C37—C38   | 120.4 (2)   |
| C9—C10—H10  | 108.5       | C36—C37—H37   | 119.8       |
| C12—C11—C10 | 119.94 (18) | C38—C37—H37   | 119.8       |
| C12—C11—C15 | 117.22 (18) | C39—C38—C37   | 119.4 (2)   |
| C10—C11—C15 | 121.82 (17) | C39—C38—H38   | 120.3       |
| C11—C12—C13 | 118.68 (19) | C37—C38—H38   | 120.3       |
| C11—C12—C18 | 126.2 (2)   | C38—C39—C40   | 120.7 (2)   |
| C13—C12—C18 | 114.38 (18) | C38—C39—H39   | 119.6       |
| C14—C13—C12 | 118.85 (19) | C40—C39—H39   | 119.6       |
| C14—C13—H13 | 120.6       | C39—C40—C35   | 120.5 (2)   |
| C12—C13—H13 | 120.6       | C39—C40—H40   | 119.8       |
| C13—C14—C1  | 119.8 (2)   | C35—C40—H40   | 119.8       |
| C13—C14—H14 | 120.1       | C42—O41—C4    | 116.28 (16) |

|               |              |                 |              |
|---------------|--------------|-----------------|--------------|
| C1—C14—H14    | 120.1        | O41—C42—O43     | 112.97 (18)  |
| C1—C15—C16    | 112.74 (17)  | O41—C42—H42B    | 109.0        |
| C1—C15—C17    | 111.81 (17)  | O43—C42—H42B    | 109.0        |
| C16—C15—C17   | 104.00 (16)  | O41—C42—H42A    | 109.0        |
| C1—C15—C11    | 101.58 (15)  | O43—C42—H42A    | 109.0        |
| C16—C15—C11   | 117.71 (17)  | H42B—C42—H42A   | 107.8        |
| C17—C15—C11   | 109.19 (17)  | C42—O43—C44     | 112.09 (17)  |
| C15—C16—H16B  | 109.5        | O43—C44—H44C    | 109.5        |
| C15—C16—H16C  | 109.5        | O43—C44—H44A    | 109.5        |
| H16B—C16—H16C | 109.5        | H44C—C44—H44A   | 109.5        |
| C15—C16—H16A  | 109.5        | O43—C44—H44B    | 109.5        |
| H16B—C16—H16A | 109.5        | H44C—C44—H44B   | 109.5        |
| H16C—C16—H16A | 109.5        | H44A—C44—H44B   | 109.5        |
| O22—C1—C2—O20 | 26.87 (18)   | C3—C8—C9—C10    | −51.5 (3)    |
| C14—C1—C2—O20 | −88.07 (19)  | C8—C9—C10—O33   | 176.60 (17)  |
| C15—C1—C2—O20 | 146.14 (16)  | C8—C9—C10—C11   | 53.0 (3)     |
| O22—C1—C2—C3  | 153.21 (16)  | O33—C10—C11—C12 | 137.37 (19)  |
| C14—C1—C2—C3  | 38.3 (3)     | C9—C10—C11—C12  | −104.4 (2)   |
| C15—C1—C2—C3  | −87.5 (2)    | O33—C10—C11—C15 | −54.5 (2)    |
| O20—C2—C3—C4  | 4.3 (2)      | C9—C10—C11—C15  | 63.8 (2)     |
| C1—C2—C3—C4   | −115.6 (2)   | C10—C11—C12—C13 | 150.34 (18)  |
| O20—C2—C3—C8  | −124.98 (18) | C15—C11—C12—C13 | −18.4 (3)    |
| C1—C2—C3—C8   | 115.07 (19)  | C10—C11—C12—C18 | −19.5 (3)    |
| C2—C3—C4—O41  | 58.5 (2)     | C15—C11—C12—C18 | 171.80 (18)  |
| C8—C3—C4—O41  | −172.95 (15) | C11—C12—C13—C14 | −17.7 (3)    |
| C2—C3—C4—C5   | 175.84 (17)  | C18—C12—C13—C14 | 153.33 (19)  |
| C8—C3—C4—C5   | −55.6 (2)    | C12—C13—C14—C1  | 9.1 (3)      |
| O41—C4—C5—C6  | 163.01 (17)  | O22—C1—C14—C13  | 155.28 (18)  |
| C3—C4—C5—C6   | 48.5 (2)     | C15—C1—C14—C13  | 33.2 (2)     |
| C4—C5—C6—C7   | −50.2 (2)    | C2—C1—C14—C13   | −93.9 (2)    |
| C5—C6—C7—O24  | 179.13 (16)  | O22—C1—C15—C16  | 53.1 (2)     |
| C5—C6—C7—C8   | 58.4 (2)     | C14—C1—C15—C16  | 172.27 (16)  |
| O24—C7—C8—C19 | −65.5 (2)    | C2—C1—C15—C16   | −58.9 (2)    |
| C6—C7—C8—C19  | 56.9 (2)     | O22—C1—C15—C17  | −63.6 (2)    |
| O24—C7—C8—C9  | 50.9 (2)     | C14—C1—C15—C17  | 55.5 (2)     |
| C6—C7—C8—C9   | 173.24 (16)  | C2—C1—C15—C17   | −175.65 (16) |
| O24—C7—C8—C3  | 174.89 (15)  | O22—C1—C15—C11  | −179.97 (16) |
| C6—C7—C8—C3   | −62.8 (2)    | C14—C1—C15—C11  | −60.82 (19)  |
| C4—C3—C8—C19  | −57.8 (2)    | C2—C1—C15—C11   | 68.0 (2)     |
| C2—C3—C8—C19  | 72.3 (2)     | C12—C11—C15—C1  | 56.4 (2)     |
| C4—C3—C8—C7   | 61.8 (2)     | C10—C11—C15—C1  | −112.1 (2)   |
| C2—C3—C8—C7   | −168.02 (16) | C12—C11—C15—C16 | 179.97 (18)  |
| C4—C3—C8—C9   | −175.95 (16) | C10—C11—C15—C16 | 11.5 (3)     |
| C2—C3—C8—C9   | −45.8 (2)    | C12—C11—C15—C17 | −61.8 (2)    |
| C19—C8—C9—C10 | −173.02 (18) | C10—C11—C15—C17 | 129.69 (19)  |
| C7—C8—C9—C10  | 66.9 (2)     | C3—C2—O20—C21   | −149.52 (17) |

*Hydrogen-bond geometry (Å, °)*

Cg is the centroid of the C35–C40 benzene ring.

| <i>D</i> —H $\cdots$ <i>A</i>               | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|---------------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C34—H34 <i>A</i> $\cdots$ O43 <sup>i</sup>  | 0.99        | 2.42                | 3.377 (3)                  | 163                           |
| C38—H38 $\cdots$ O23 <sup>ii</sup>          | 0.95        | 2.44                | 3.295 (3)                  | 149                           |
| C31—H31 $\cdots$ O33 <sup>iii</sup>         | 0.95        | 2.49                | 3.426 (3)                  | 168                           |
| C2—H2 $\cdots$ O23 <sup>iv</sup>            | 1.00        | 2.51                | 3.433 (3)                  | 153                           |
| C16—H16 <i>A</i> $\cdots$ O23 <sup>iv</sup> | 0.98        | 2.53                | 3.357 (3)                  | 142                           |
| C19—H19C $\cdots$ O23 <sup>iv</sup>         | 0.98        | 2.54                | 3.477 (3)                  | 160                           |
| C18—H18C $\cdots$ Cg <sup>v</sup>           | 0.98        | 2.89                | 3.492 (3)                  | 121                           |

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*+1, *z*−1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*, −*z*+2; (v) −*x*, −*y*+1, −*z*+1.