

# Allyl 2-(2,2-dimethyl-3a,6a-dihydrofuro[3,2-d][1,3]dioxol-5-yl)-4-oxo-4H-chromene-3-carboxylate

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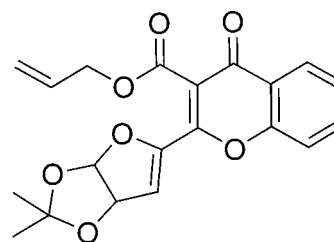
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å; disorder in main residue;  $R$  factor = 0.045;  $wR$  factor = 0.127; data-to-parameter ratio = 17.7.

In the title compound,  $\text{C}_{20}\text{H}_{18}\text{O}_7$ , the dioxolane ring adopts an envelope conformation with the dimethyl-substituted C atom as the flap, and its mean plane makes a dihedral angle of  $73.25(2)^\circ$  with the pyran ring mean plane. The furan ring makes dihedral angles of  $67.43(12)$  and  $6.20(11)^\circ$  with the mean plane of the dioxolane and pyran rings, respectively. The O atom attached to the pyran ring deviates by  $0.0219(2)$  Å from its mean plane. In the crystal, molecules are linked *via*  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming chains along  $[010]$  and enclosing  $R_2^2(9)$  loops. They stack along the  $a$  axis with  $\pi-\pi$  interactions involving the 4*H*-chromene units [centroid-centroid distances of  $3.6389(13)$  and  $3.6555(13)$  Å]. The terminal  $\text{CH}_2=\text{CH}-$  atoms of the allyl acetate group are disordered over two sets of sites with a refined occupancy ratio of  $0.717(6):0.283(6)$ .

## Related literature

For the biological importance of 4*H*-chromene derivatives, see: Cai (2007, 2008); Cai *et al.* (2006); Caine (1993); Gabor (1988); Brooks (1998); Valenti *et al.* (1993); Hyana & Saimoto (1987); Tang *et al.* (2007).



## Experimental

### Crystal data

|  |                                   |
|--|-----------------------------------|
| $\text{C}_{20}\text{H}_{18}\text{O}_7$ | $V = 1790.5(2)$ Å <sup>3</sup>    |
| $M_r = 370.34$                         | $Z = 4$                           |
| Orthorhombic, $P2_12_12_1$             | Mo $K\alpha$ radiation            |
| $a = 6.9461(6)$ Å                      | $\mu = 0.11$ mm <sup>-1</sup>     |
| $b = 15.5688(11)$ Å                    | $T = 293$ K                       |
| $c = 16.5572(11)$ Å                    | $0.30 \times 0.25 \times 0.20$ mm |

### Data collection

|  |  |
|--|--|
| Bruker SMART APEXII area-detector diffractometer         | 17828 measured reflections             |
| Absorption correction: multi-scan (SADABS; Bruker, 2008) | 4459 independent reflections           |
| $T_{\min} = 0.969$ , $T_{\max} = 0.979$                  | 2758 reflections with $I > 2\sigma(I)$ |
|  | $R_{\text{int}} = 0.072$               |

### Refinement

|                                 |   |
|---------------------------------|---|
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | 3 restraints  |
| $wR(F^2) = 0.127$               | H-atom parameters constrained                       |
| $S = 1.01$                      | $\Delta\rho_{\text{max}} = 0.16$ e Å <sup>-3</sup>  |
| 4459 reflections                | $\Delta\rho_{\text{min}} = -0.18$ e Å <sup>-3</sup> |
| 252 parameters                  |   |

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                     | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{C11}-\text{H11}\cdots\text{O3}^i$ | 0.93         | 2.47               | 3.190 (3)   | 134                  |
| $\text{C12}-\text{H12}\cdots\text{O2}^i$ | 0.98         | 2.54               | 3.477 (3)   | 160                  |

Symmetry code: (i)  $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$ .

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2620).

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## supporting information

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## Allyl 2-(2,2-dimethyl-3a,6a-dihydrofuro[3,2-d][1,3]dioxol-5-yl)-4-oxo-4H-chromene-3-carboxylate

Zeenat Fatima, Thothadri Srinivasan, Jonnalagadda Naga Siva Rao, Raghavachary Raghunathan and Devadasan Velmurugan

### S1. Comment

4H-Chromenes are biologically important compounds used as synthetic ligands in the design of drugs and discovery processes. They exhibit numerous biological and pharmacological properties, such as anti-viral, anti-fungal, anti-inflammatory, anti-diabetic, cardionthonic, anti-anaphylactic and anti-cancer activity (Cai, 2008, 2007; Cai *et al.*, 2006; Caine, 1993; Gabor, 1988; Brooks, 1998; Valenti *et al.*, 1993; Hyana & Saimoto, 1987; Tang *et al.*, 2007). In view of the different applications of this class of compounds, we have undertaken the synthesis and crystal structure analysis of the title compound.

In the title molecule, Fig. 1, the dioxolane ring adopts an *envelope* conformation with atom C14 as the flap. The furan ring (O5/C10-C13) makes dihedral angles of 67.43 (12)° and 6.20 (11)° with the mean plane of the dioxolane ring (O6/O7/C12-C14) and the pyran ring (O1/C1/C6-C9), respectively. The dioxolane ring mean plane makes a dihedral angle of 73.25 (11)° with the pyran ring. The oxygen atom O2 attached with the pyran ring deviates by -0.0219 (2)Å. The methyl carbon atoms C15 and C16 attached with the mean plane of the dioxolane ring deviate by -0.7157 (3)Å and 1.6682 (3)Å, respectively.

In the crystal, molecules are linked via C-H...O hydrogen bonds into chains along [010], containing  $R_2^2(9)$  loops (Table 1 and Fig. 2). They stack along the *a* axis with  $\pi$ - $\pi$  interactions involving the 4H-chromene units, with centroid-to-centroid distances of 3.6389 (13) Å for Cg1-Cg2<sup>i</sup> and 3.6555 (13) Å for Cg1...Cg2<sup>ii</sup>, where Cg1 and Cg2 are the centroids of rings O1/C1/C6-C9 and C1-C6, respectively; symmetry codes: (i)  $x+1/2, -y+1/2, -z+1$ ; (ii)  $x-1/2, -y+1/2, -z+1$ .

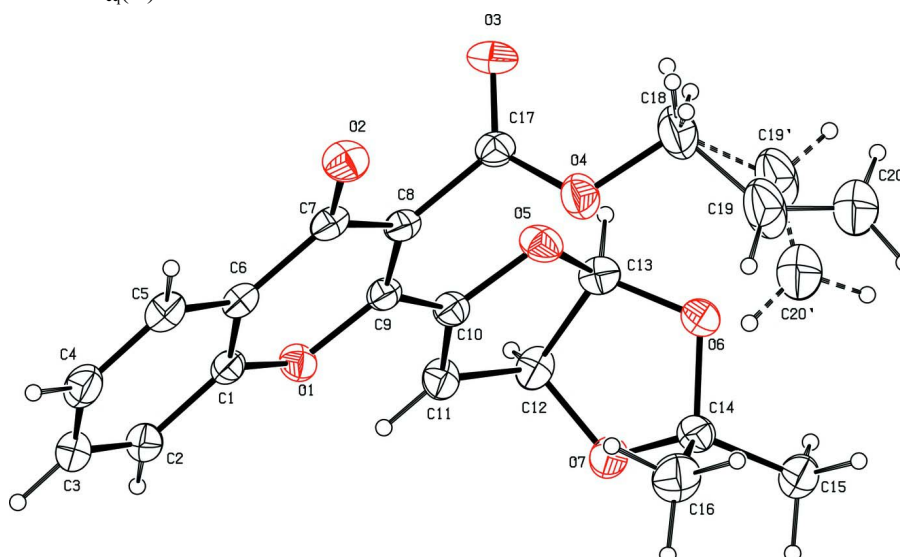
### S2. Experimental

Triethylamine (1.10 mL, 4 equiv) was added to a stirred solution of 4-hydroxycoumarin (0.32 g, 2 mmol) and (E)-6-(benzyloxy)-2,2-dimethyl-5-(2-nitrovinyl)tetrahydrofuro[3,2-d][1,3]dioxole (0.65 g, 4 mmol) in allyl alcohol (6 mL). The reaction mixture was heated at 343 - 353 K for 24h, and the progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated in vacuum. The resulting residue was further purified by flash column chromatography (ethyl acetate/hexane) on silica gel. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the title compound in ethyl acetate at room temperature.

### S3. Refinement

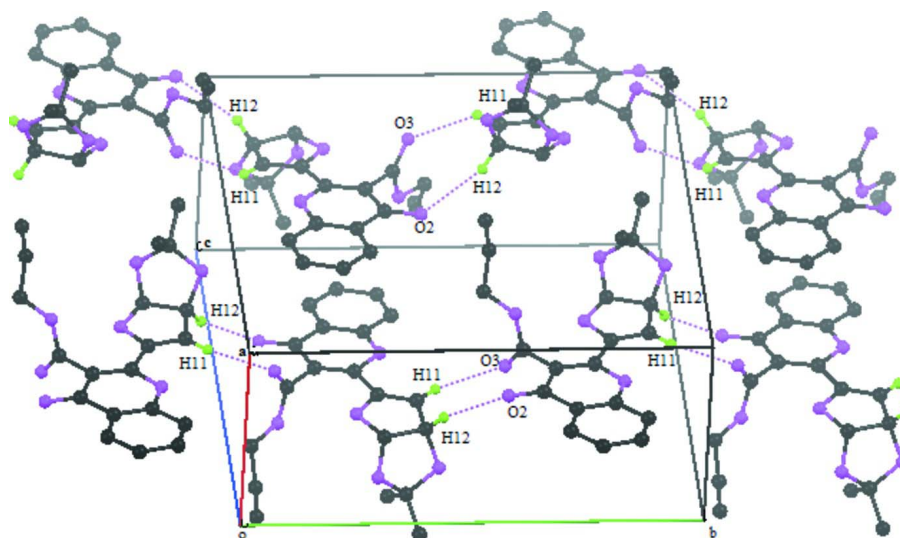
The terminal atoms, C19 and C20, of the allyl acetate group are disordered over two positions (C19/C19' & C20/C20') with a refined occupancy ratio of 0.717 (6):0.283 (6). The C-C distances of the disordered atoms were restrained to be equal. The displacement parameters of the disordered atoms were restrained to be equal for bonded atoms. The hydrogen atoms were placed in calculated positions and treated as riding atoms: C—H = 0.93 - 0.98 Å, with  $U_{iso}(H) = 1.5U_{eq}(C)$  for

methyl H atoms and  $= 1.2U_{\text{eq}}(\text{C})$  for other H atoms.



**Figure 1**

The molecular structure of the title molecule, with atom labelling. The displacement ellipsoids are drawn at the 30% probability level. The position of the disordered terminal atoms (C19' & C20') of the allyl acetate group are shown with dashed bonds.



**Figure 2**

The crystal packing of the title compound, viewed along the *a* axis. The hydrogen bonds (see Table 1 for details) are shown as dashed lines. H-atoms not involved in hydrogen bonding have been omitted for clarity.

### Allyl 2-(2,2-dimethyl-3a,6a-dihydrofuro[3,2-*d*][1,3]dioxol-5-yl)-4-oxo-4*H*-chromene-3-carboxylate

#### Crystal data

$\text{C}_{20}\text{H}_{18}\text{O}_7$   
 $M_r = 370.34$   
 Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab  
 $a = 6.9461 (6) \text{ \AA}$   
 $b = 15.5688 (11) \text{ \AA}$

$c = 16.5572 (11) \text{ \AA}$   
 $V = 1790.5 (2) \text{ \AA}^3$   
 $Z = 4$   
 $F(000) = 776$   
 $D_x = 1.374 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4459 reflections  
 $\theta = 1.8\text{--}28.4^\circ$   
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Block, colourless  
 $0.30 \times 0.25 \times 0.20 \text{ mm}$

*Data collection*

Bruker SMART APEXII area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2008)  
 $T_{\min} = 0.969, T_{\max} = 0.979$

17828 measured reflections  
 4459 independent reflections  
 2758 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.072$   
 $\theta_{\max} = 28.4^\circ, \theta_{\min} = 1.8^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -18 \rightarrow 20$   
 $l = -21 \rightarrow 22$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.127$   
 $S = 1.01$   
 4459 reflections  
 252 parameters  
 3 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1102P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

|    | <i>x</i>   | <i>y</i>     | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|----|------------|--------------|--------------|----------------------------------|-----------|
| C1 | 0.8806 (3) | 0.19806 (13) | 0.54128 (13) | 0.0478 (5)                       |           |
| C2 | 0.8795 (3) | 0.13352 (16) | 0.48303 (14) | 0.0610 (6)                       |           |
| H2 | 0.8815     | 0.0760       | 0.4981       | 0.073*                           |           |
| C3 | 0.8754 (4) | 0.15601 (18) | 0.40384 (16) | 0.0680 (7)                       |           |
| H3 | 0.8729     | 0.1135       | 0.3644       | 0.082*                           |           |
| C4 | 0.8749 (4) | 0.2410 (2)   | 0.38153 (14) | 0.0708 (7)                       |           |
| H4 | 0.8736     | 0.2554       | 0.3270       | 0.085*                           |           |
| C5 | 0.8762 (3) | 0.30481 (17) | 0.43860 (14) | 0.0601 (6)                       |           |
| H5 | 0.8751     | 0.3621       | 0.4226       | 0.072*                           |           |
| C6 | 0.8792 (3) | 0.28392 (13) | 0.52099 (12) | 0.0483 (5)                       |           |

|      |             |              |              |             |           |
|------|-------------|--------------|--------------|-------------|-----------|
| C7   | 0.8791 (3)  | 0.34926 (13) | 0.58404 (14) | 0.0490 (5)  |           |
| C8   | 0.8760 (3)  | 0.31570 (12) | 0.66668 (12) | 0.0450 (4)  |           |
| C9   | 0.8759 (3)  | 0.23043 (12) | 0.68069 (12) | 0.0448 (4)  |           |
| C10  | 0.8641 (3)  | 0.18772 (13) | 0.75846 (12) | 0.0474 (5)  |           |
| C11  | 0.8519 (3)  | 0.10532 (14) | 0.77512 (13) | 0.0563 (6)  |           |
| H11  | 0.8573      | 0.0611       | 0.7374       | 0.068*      |           |
| C12  | 0.8280 (3)  | 0.09404 (15) | 0.86374 (14) | 0.0579 (6)  |           |
| H12  | 0.9320      | 0.0591       | 0.8866       | 0.069*      |           |
| C13  | 0.8357 (3)  | 0.18598 (15) | 0.89523 (13) | 0.0559 (5)  |           |
| H13  | 0.9438      | 0.1934       | 0.9326       | 0.067*      |           |
| C14  | 0.5271 (3)  | 0.13462 (15) | 0.91078 (15) | 0.0582 (6)  |           |
| C15  | 0.4091 (4)  | 0.10992 (19) | 0.98298 (17) | 0.0770 (8)  |           |
| H15A | 0.3295      | 0.1575       | 0.9987       | 0.116*      |           |
| H15B | 0.4930      | 0.0948       | 1.0268       | 0.116*      |           |
| H15C | 0.3292      | 0.0616       | 0.9696       | 0.116*      |           |
| C16  | 0.4054 (4)  | 0.1653 (2)   | 0.84136 (17) | 0.0866 (9)  |           |
| H16A | 0.3285      | 0.2132       | 0.8585       | 0.130*      |           |
| H16B | 0.3228      | 0.1196       | 0.8237       | 0.130*      |           |
| H16C | 0.4873      | 0.1828       | 0.7976       | 0.130*      |           |
| C17  | 0.8718 (3)  | 0.38088 (13) | 0.73205 (13) | 0.0521 (5)  |           |
| C18  | 0.6630 (5)  | 0.4621 (2)   | 0.81426 (19) | 0.0953 (10) |           |
| H18A | 0.6832      | 0.5197       | 0.7938       | 0.114*      | 0.717 (6) |
| H18B | 0.7520      | 0.4521       | 0.8584       | 0.114*      | 0.717 (6) |
| H18C | 0.7873      | 0.4735       | 0.8388       | 0.114*      | 0.283 (6) |
| H18D | 0.6207      | 0.5150       | 0.7891       | 0.114*      | 0.283 (6) |
| O1   | 0.8825 (2)  | 0.17128 (9)  | 0.62034 (8)  | 0.0526 (4)  |           |
| O2   | 0.8790 (2)  | 0.42692 (10) | 0.57063 (10) | 0.0661 (4)  |           |
| O3   | 1.0102 (3)  | 0.41371 (12) | 0.76106 (12) | 0.0808 (6)  |           |
| O4   | 0.6918 (2)  | 0.39953 (12) | 0.75106 (11) | 0.0700 (5)  |           |
| O5   | 0.8584 (2)  | 0.24039 (9)  | 0.82508 (9)  | 0.0600 (4)  |           |
| O6   | 0.6630 (2)  | 0.19952 (9)  | 0.93415 (9)  | 0.0576 (4)  |           |
| O7   | 0.6435 (2)  | 0.06344 (9)  | 0.88869 (10) | 0.0658 (5)  |           |
| C19  | 0.4667 (7)  | 0.4514 (4)   | 0.8412 (4)   | 0.113 (2)   | 0.717 (6) |
| H19  | 0.3771      | 0.4407       | 0.8007       | 0.135*      | 0.717 (6) |
| C20  | 0.4030 (9)  | 0.4545 (4)   | 0.9085 (4)   | 0.127 (2)   | 0.717 (6) |
| H20A | 0.4847      | 0.4649       | 0.9519       | 0.152*      | 0.717 (6) |
| H20B | 0.2720      | 0.4464       | 0.9172       | 0.152*      | 0.717 (6) |
| C19' | 0.5331 (18) | 0.4427 (12)  | 0.8768 (7)   | 0.113 (2)   | 0.283 (6) |
| H19' | 0.5573      | 0.4675       | 0.9269       | 0.135*      | 0.283 (6) |
| C20' | 0.395 (2)   | 0.3975 (11)  | 0.8720 (11)  | 0.127 (2)   | 0.283 (6) |
| H20C | 0.3645      | 0.3711       | 0.8232       | 0.152*      | 0.283 (6) |
| H20D | 0.3173      | 0.3886       | 0.9170       | 0.152*      | 0.283 (6) |

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

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| C1 | 0.0385 (10) | 0.0503 (12) | 0.0547 (11) | -0.0032 (10) | 0.0064 (10) | 0.0001 (10)  |
| C2 | 0.0558 (13) | 0.0592 (14) | 0.0681 (14) | -0.0029 (12) | 0.0104 (12) | -0.0096 (11) |

|      |             |             |             |              |              |              |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C3   | 0.0587 (14) | 0.0806 (18) | 0.0649 (15) | -0.0089 (14) | 0.0150 (13)  | -0.0147 (13) |
| C4   | 0.0567 (14) | 0.101 (2)   | 0.0543 (13) | -0.0098 (16) | 0.0078 (12)  | 0.0022 (14)  |
| C5   | 0.0498 (12) | 0.0694 (16) | 0.0613 (14) | -0.0040 (12) | 0.0034 (11)  | 0.0117 (12)  |
| C6   | 0.0363 (10) | 0.0534 (12) | 0.0552 (12) | -0.0036 (9)  | 0.0037 (10)  | 0.0065 (9)   |
| C7   | 0.0378 (10) | 0.0440 (12) | 0.0652 (13) | -0.0029 (9)  | 0.0030 (10)  | 0.0102 (10)  |
| C8   | 0.0368 (10) | 0.0390 (11) | 0.0591 (11) | -0.0031 (9)  | 0.0010 (9)   | 0.0031 (9)   |
| C9   | 0.0391 (10) | 0.0402 (11) | 0.0551 (11) | -0.0023 (9)  | 0.0046 (10)  | 0.0014 (9)   |
| C10  | 0.0457 (11) | 0.0405 (11) | 0.0559 (11) | 0.0014 (9)   | 0.0013 (10)  | 0.0009 (9)   |
| C11  | 0.0634 (14) | 0.0384 (11) | 0.0670 (13) | 0.0082 (11)  | 0.0120 (11)  | 0.0043 (10)  |
| C12  | 0.0576 (13) | 0.0470 (13) | 0.0691 (14) | 0.0098 (10)  | 0.0112 (11)  | 0.0136 (11)  |
| C13  | 0.0568 (13) | 0.0558 (13) | 0.0552 (12) | -0.0033 (11) | -0.0054 (10) | 0.0083 (11)  |
| C14  | 0.0545 (12) | 0.0504 (13) | 0.0697 (14) | 0.0003 (11)  | 0.0034 (12)  | -0.0100 (11) |
| C15  | 0.0736 (16) | 0.0735 (17) | 0.0841 (17) | -0.0069 (14) | 0.0211 (14)  | -0.0063 (15) |
| C16  | 0.0611 (16) | 0.113 (2)   | 0.0854 (19) | 0.0091 (15)  | -0.0148 (14) | -0.0031 (17) |
| C17  | 0.0566 (13) | 0.0391 (11) | 0.0607 (13) | -0.0057 (10) | 0.0023 (11)  | 0.0062 (9)   |
| C18  | 0.119 (3)   | 0.081 (2)   | 0.0861 (19) | 0.0074 (19)  | 0.027 (2)    | -0.0218 (17) |
| O1   | 0.0619 (9)  | 0.0387 (7)  | 0.0572 (8)  | 0.0002 (7)   | 0.0054 (7)   | -0.0002 (7)  |
| O2   | 0.0776 (10) | 0.0426 (9)  | 0.0781 (10) | -0.0026 (8)  | 0.0005 (9)   | 0.0134 (7)   |
| O3   | 0.0786 (12) | 0.0649 (11) | 0.0988 (14) | -0.0292 (10) | -0.0059 (10) | -0.0146 (10) |
| O4   | 0.0706 (11) | 0.0701 (11) | 0.0694 (10) | 0.0107 (9)   | 0.0055 (9)   | -0.0126 (9)  |
| O5   | 0.0813 (10) | 0.0417 (8)  | 0.0568 (8)  | -0.0106 (8)  | -0.0030 (9)  | 0.0032 (7)   |
| O6   | 0.0622 (9)  | 0.0487 (9)  | 0.0618 (9)  | -0.0015 (7)  | 0.0016 (8)   | -0.0060 (7)  |
| O7   | 0.0734 (11) | 0.0411 (8)  | 0.0830 (11) | -0.0022 (8)  | 0.0250 (9)   | 0.0000 (8)   |
| C19  | 0.085 (4)   | 0.147 (5)   | 0.106 (5)   | 0.043 (4)    | -0.007 (3)   | -0.051 (4)   |
| C20  | 0.102 (3)   | 0.155 (6)   | 0.124 (4)   | -0.006 (4)   | 0.028 (3)    | -0.045 (4)   |
| C19' | 0.085 (4)   | 0.147 (5)   | 0.106 (5)   | 0.043 (4)    | -0.007 (3)   | -0.051 (4)   |
| C20' | 0.102 (3)   | 0.155 (6)   | 0.124 (4)   | -0.006 (4)   | 0.028 (3)    | -0.045 (4)   |

*Geometric parameters (Å, °)*

|        |           |          |            |
|--------|-----------|----------|------------|
| C1—O1  | 1.374 (2) | C14—O7   | 1.420 (3)  |
| C1—C6  | 1.378 (3) | C14—O6   | 1.436 (3)  |
| C1—C2  | 1.393 (3) | C14—C15  | 1.500 (3)  |
| C2—C3  | 1.357 (4) | C14—C16  | 1.505 (4)  |
| C2—H2  | 0.9300    | C15—H15A | 0.9600     |
| C3—C4  | 1.373 (4) | C15—H15B | 0.9600     |
| C3—H3  | 0.9300    | C15—H15C | 0.9600     |
| C4—C5  | 1.371 (4) | C16—H16A | 0.9600     |
| C4—H4  | 0.9300    | C16—H16B | 0.9600     |
| C5—C6  | 1.403 (3) | C16—H16C | 0.9600     |
| C5—H5  | 0.9300    | C17—O3   | 1.190 (3)  |
| C6—C7  | 1.458 (3) | C17—O4   | 1.322 (3)  |
| C7—O2  | 1.229 (2) | C18—C19' | 1.407 (10) |
| C7—C8  | 1.465 (3) | C18—O4   | 1.443 (3)  |
| C8—C9  | 1.348 (3) | C18—C19  | 1.444 (6)  |
| C8—C17 | 1.484 (3) | C18—H18A | 0.9700     |
| C9—O1  | 1.360 (2) | C18—H18B | 0.9700     |
| C9—C10 | 1.452 (3) | C18—H18C | 0.9700     |

|             |             |               |             |
|-------------|-------------|---------------|-------------|
| C10—C11     | 1.315 (3)   | C18—H18D      | 0.9700      |
| C10—O5      | 1.375 (2)   | C19—C20       | 1.200 (7)   |
| C11—C12     | 1.487 (3)   | C19—H19       | 0.9300      |
| C11—H11     | 0.9300      | C20—H20A      | 0.9300      |
| C12—O7      | 1.429 (3)   | C20—H20B      | 0.9300      |
| C12—C13     | 1.524 (3)   | C19'—C20'     | 1.194 (10)  |
| C12—H12     | 0.9800      | C19'—H19'     | 0.9300      |
| C13—O6      | 1.378 (3)   | C20'—H20C     | 0.9300      |
| C13—O5      | 1.446 (3)   | C20'—H20D     | 0.9300      |
| C13—H13     | 0.9800      |               |             |
| O1—C1—C6    | 121.77 (19) | C14—C15—H15A  | 109.5       |
| O1—C1—C2    | 116.2 (2)   | C14—C15—H15B  | 109.5       |
| C6—C1—C2    | 122.1 (2)   | H15A—C15—H15B | 109.5       |
| C3—C2—C1    | 118.9 (2)   | C14—C15—H15C  | 109.5       |
| C3—C2—H2    | 120.6       | H15A—C15—H15C | 109.5       |
| C1—C2—H2    | 120.6       | H15B—C15—H15C | 109.5       |
| C2—C3—C4    | 120.5 (2)   | C14—C16—H16A  | 109.5       |
| C2—C3—H3    | 119.7       | C14—C16—H16B  | 109.5       |
| C4—C3—H3    | 119.7       | H16A—C16—H16B | 109.5       |
| C5—C4—C3    | 120.8 (2)   | C14—C16—H16C  | 109.5       |
| C5—C4—H4    | 119.6       | H16A—C16—H16C | 109.5       |
| C3—C4—H4    | 119.6       | H16B—C16—H16C | 109.5       |
| C4—C5—C6    | 120.2 (2)   | O3—C17—O4     | 125.0 (2)   |
| C4—C5—H5    | 119.9       | O3—C17—C8     | 124.9 (2)   |
| C6—C5—H5    | 119.9       | O4—C17—C8     | 110.01 (18) |
| C1—C6—C5    | 117.5 (2)   | C19'—C18—O4   | 118.5 (8)   |
| C1—C6—C7    | 120.15 (18) | O4—C18—C19    | 106.1 (3)   |
| C5—C6—C7    | 122.3 (2)   | C19'—C18—H18A | 123.3       |
| O2—C7—C6    | 123.8 (2)   | O4—C18—H18A   | 110.5       |
| O2—C7—C8    | 121.3 (2)   | C19—C18—H18A  | 110.5       |
| C6—C7—C8    | 114.84 (17) | C19'—C18—H18B | 79.6        |
| C9—C8—C7    | 120.80 (19) | O4—C18—H18B   | 110.5       |
| C9—C8—C17   | 123.24 (18) | C19—C18—H18B  | 110.5       |
| C7—C8—C17   | 115.96 (17) | H18A—C18—H18B | 108.7       |
| C8—C9—O1    | 122.74 (18) | C19'—C18—H18C | 107.6       |
| C8—C9—C10   | 127.15 (18) | O4—C18—H18C   | 107.7       |
| O1—C9—C10   | 110.10 (16) | C19—C18—H18C  | 137.1       |
| C11—C10—O5  | 114.30 (18) | H18A—C18—H18C | 81.3        |
| C11—C10—C9  | 129.54 (19) | C19'—C18—H18D | 107.7       |
| O5—C10—C9   | 116.12 (16) | O4—C18—H18D   | 107.7       |
| C10—C11—C12 | 109.2 (2)   | C19—C18—H18D  | 86.8        |
| C10—C11—H11 | 125.4       | H18B—C18—H18D | 130.8       |
| C12—C11—H11 | 125.4       | H18C—C18—H18D | 107.1       |
| O7—C12—C11  | 115.1 (2)   | C9—O1—C1      | 119.63 (16) |
| O7—C12—C13  | 104.20 (17) | C17—O4—C18    | 116.9 (2)   |
| C11—C12—C13 | 102.87 (17) | C10—O5—C13    | 107.35 (15) |
| O7—C12—H12  | 111.4       | C13—O6—C14    | 109.78 (16) |



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|-----------------|--------------|-------------------|--------------|
| C11—C12—H12     | 111.4        | C14—O7—C12        | 108.99 (16)  |
| C13—C12—H12     | 111.4        | C20—C19—C18       | 129.0 (6)    |
| O6—C13—O5       | 112.41 (18)  | C20—C19—H19       | 115.5        |
| O6—C13—C12      | 105.87 (18)  | C18—C19—H19       | 115.5        |
| O5—C13—C12      | 106.21 (17)  | C19—C20—H20A      | 120.0        |
| O6—C13—H13      | 110.7        | C19—C20—H20B      | 120.0        |
| O5—C13—H13      | 110.7        | H20A—C20—H20B     | 120.0        |
| C12—C13—H13     | 110.7        | C20'—C19'—C18     | 126.4 (14)   |
| O7—C14—O6       | 104.14 (16)  | C20'—C19'—H19'    | 116.8        |
| O7—C14—C15      | 108.5 (2)    | C18—C19'—H19'     | 116.8        |
| O6—C14—C15      | 108.96 (19)  | C19'—C20'—H20C    | 120.0        |
| O7—C14—C16      | 111.8 (2)    | C19'—C20'—H20D    | 120.0        |
| O6—C14—C16      | 110.6 (2)    | H20C—C20'—H20D    | 120.0        |
| C15—C14—C16     | 112.5 (2)    |                   |              |
| O1—C1—C2—C3     | 179.2 (2)    | O7—C12—C13—O5     | -119.41 (19) |
| C6—C1—C2—C3     | -0.5 (3)     | C11—C12—C13—O5    | 1.1 (2)      |
| C1—C2—C3—C4     | 0.8 (4)      | C9—C8—C17—O3      | 93.4 (3)     |
| C2—C3—C4—C5     | -0.8 (4)     | C7—C8—C17—O3      | -87.0 (3)    |
| C3—C4—C5—C6     | 0.3 (4)      | C9—C8—C17—O4      | -89.1 (2)    |
| O1—C1—C6—C5     | -179.62 (18) | C7—C8—C17—O4      | 90.6 (2)     |
| C2—C1—C6—C5     | 0.1 (3)      | C8—C9—O1—C1       | -3.0 (3)     |
| O1—C1—C6—C7     | -0.2 (3)     | C10—C9—O1—C1      | 175.57 (17)  |
| C2—C1—C6—C7     | 179.58 (19)  | C6—C1—O1—C9       | 2.4 (3)      |
| C4—C5—C6—C1     | 0.0 (3)      | C2—C1—O1—C9       | -177.38 (16) |
| C4—C5—C6—C7     | -179.5 (2)   | O3—C17—O4—C18     | -2.7 (3)     |
| C1—C6—C7—O2     | 179.6 (2)    | C8—C17—O4—C18     | 179.8 (2)    |
| C5—C6—C7—O2     | -1.0 (3)     | C19'—C18—O4—C17   | -131.5 (8)   |
| C1—C6—C7—C8     | -1.4 (3)     | C19—C18—O4—C17    | -162.3 (3)   |
| C5—C6—C7—C8     | 178.04 (18)  | C11—C10—O5—C13    | -1.2 (3)     |
| O2—C7—C8—C9     | 179.9 (2)    | C9—C10—O5—C13     | 176.71 (18)  |
| C6—C7—C8—C9     | 0.8 (3)      | O6—C13—O5—C10     | -115.4 (2)   |
| O2—C7—C8—C17    | 0.3 (3)      | C12—C13—O5—C10    | 0.0 (2)      |
| C6—C7—C8—C17    | -178.81 (17) | O5—C13—O6—C14     | 99.2 (2)     |
| C7—C8—C9—O1     | 1.4 (3)      | C12—C13—O6—C14    | -16.4 (2)    |
| C17—C8—C9—O1    | -179.03 (18) | O7—C14—O6—C13     | 26.2 (2)     |
| C7—C8—C9—C10    | -176.96 (18) | C15—C14—O6—C13    | 141.8 (2)    |
| C17—C8—C9—C10   | 2.7 (3)      | C16—C14—O6—C13    | -94.0 (2)    |
| C8—C9—C10—C11   | 175.5 (2)    | O6—C14—O7—C12     | -25.7 (2)    |
| O1—C9—C10—C11   | -3.0 (3)     | C15—C14—O7—C12    | -141.66 (19) |
| C8—C9—C10—O5    | -2.1 (3)     | C16—C14—O7—C12    | 93.7 (2)     |
| O1—C9—C10—O5    | 179.38 (16)  | C11—C12—O7—C14    | -95.8 (2)    |
| O5—C10—C11—C12  | 2.0 (3)      | C13—C12—O7—C14    | 16.0 (2)     |
| C9—C10—C11—C12  | -175.6 (2)   | C19'—C18—C19—C20  | 21.5 (15)    |
| C10—C11—C12—O7  | 110.8 (2)    | O4—C18—C19—C20    | 140.6 (7)    |
| C10—C11—C12—C13 | -1.8 (3)     | O4—C18—C19'—C20'  | -29 (2)      |
| O7—C12—C13—O6   | 0.3 (2)      | C19—C18—C19'—C20' | 44.0 (15)    |
| C11—C12—C13—O6  | 120.75 (19)  |                   |              |

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*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H··· <i>A</i>   | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| C11—H11···O3 <sup>i</sup> | 0.93        | 2.47          | 3.190 (3)             | 134                     |
| C12—H12···O2 <sup>i</sup> | 0.98        | 2.54          | 3.477 (3)             | 160                     |

Symmetry code: (i)  $-x+2, y-1/2, -z+3/2$ .