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Synthesis and crystal structure analysis of substituted bicyclo[3.3.1]nonanones

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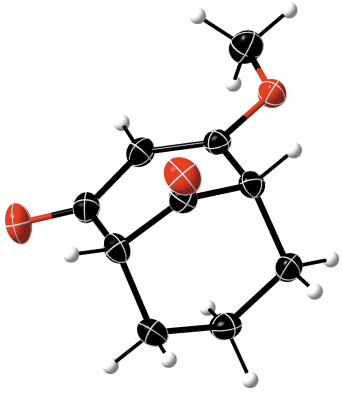
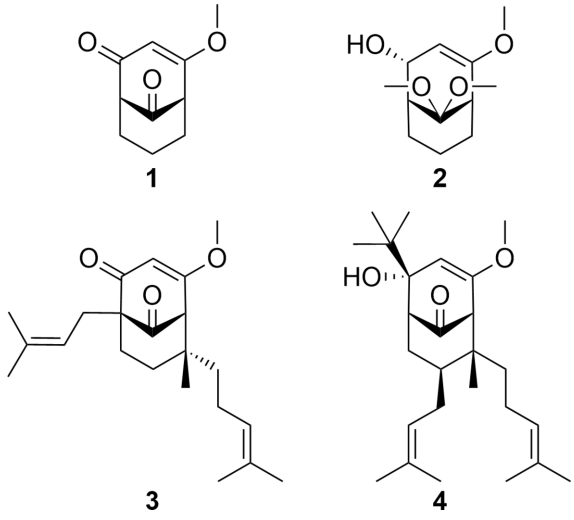
A set of novel bicyclo[3.3.1]nonanones, namely, 4-methoxybicyclo[3.3.1]non-3-ene-2,9-dione, $C_{10}H_{12}O_3$ (**1**), 4,9,9-trimethoxybicyclo[3.3.1]non-3-en-2-ol, $C_{12}H_{20}O_4$ (**2**), 4-methoxy-6-methyl-1-(3-methylbut-2-en-1-yl)-6-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]non-3-ene-2,9-dione, $C_{22}H_{32}O_3$ (**3**) and 4-(*tert*-butyl)-4-hydroxy-2-methoxy-8-methyl-7-(3-methylbut-2-en-1-yl)-8-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]non-2-en-9-one, $C_{26}H_{42}O_3$ (**4**), were synthesized and structurally elucidated by NMR, HRMS and X-ray crystallography.

1. Chemical context

Polycyclic polyprenylated acylphloroglucinols (PPAPs) are a class of structurally complex natural products predominantly isolated from plants of the *Hypericum* and *Garcinia* genera. Characterized by a highly oxygenated polycyclic core densely decorated with various substituents, these compounds exhibit remarkable chemical diversity and biological activity (Yang *et al.*, 2018). Notably, a single representative can already cover a wide range of different activities. The most important of these may include anti-inflammatory, antibacterial and antiviral activity, as well as cytotoxicity, antitumour properties and use as an antidepressant and neuroprotective agent. Hyperforin, the most prominent and best-studied PPAP to date, may serve as an example of the latter point in particular (Richard, 2014). The pronounced bicyclic framework, common to most PPAPs and many other natural compounds (Roy *et al.*, 2023), makes them particularly compelling for research in natural product chemistry and medicinal applications.





Several approaches have been explored to synthesize polycyclic polyprenylated acylphloroglucines (PPAPs), yet

achieving regioselective and diastereoselective control during modification of the core structure can be challenging due to the molecule's dense stereochemically rich framework. Consequently, precursors and intermediates often require rigorous confirmation of stereochemistry through advanced techniques, such as single-crystal X-ray diffraction, prior to further derivatization. Recent advancements in these stereochemical control strategies have opened new pathways not only to natural PPAPs but also to synthetic analogues with enhanced or modified bioactivity profiles.

In our approach to PPAP synthesis (König *et al.*, 2024, 2025), we focused on designing intermediate structures with a high degree of flexibility in substitution patterns, particularly at bridgehead positions. This flexibility is essential for achieving the precise stereochemical and functional complexity required for both natural and synthetic PPAPs, ultimately enhancing the efficiency and specificity of our synthetic route.

The title compounds **1**–**4** were synthesized as model structures to investigate the reductive and substitutional reactivity of the β-alkoxy enone system found in PPAP precursors.

2. Structural commentary

Crystals suitable for X-ray diffraction analysis were obtained for **1**–**4** and their molecular structures are illustrated in Fig. 1. Compound **1** crystallizes in the Sohnke space group $P2_1$ and was refined as an inversion twin. Compounds **2**, **3** and **4** crystallize in centrosymmetric space groups ($P\overline{1}$, $P2_1/n$ and $P2_1/c$, respectively) and thus occur as enantiomeric pairs in the crystal. Notably, although compound **2** crystallizes in $P\overline{1}$, the asymmetric unit contains two crystallographically distinct molecules ($Z' = 2$), **2a** and **2b**, which are chemically mirror images of each other [Fig. 1(*b*)]. Both compounds are related to their respective crystallographically enantiomeric partners through the inversion centre in the unit cell. The five mol-

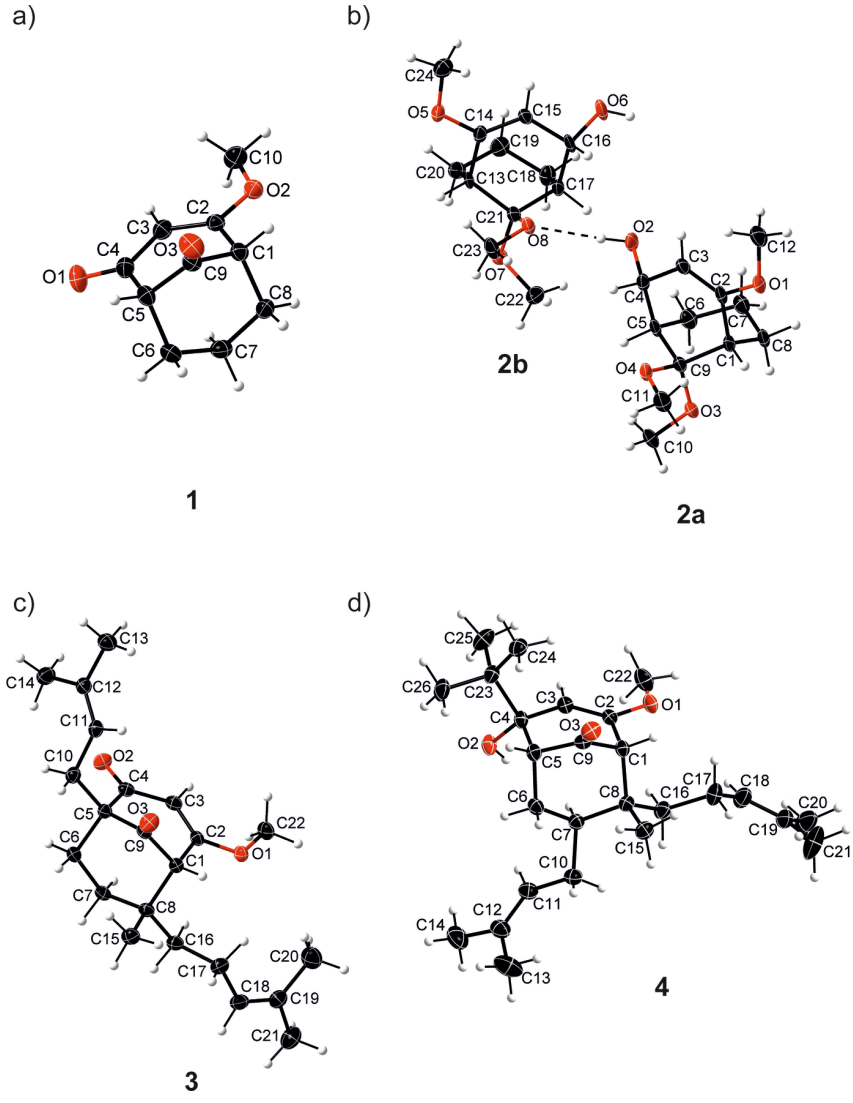
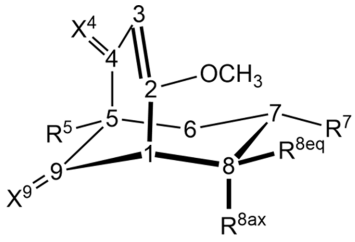


Figure 1
The molecular structures of compounds (*a*) **1**, (*b*) **2a** and **2b**, (*c*) **3** and (*d*) **4**, with the atom labelling and displacement ellipsoids drawn at the 50% probability level. The dashed line in part (*b*) indicates the intermolecular hydrogen bond between the enantiomeric compounds **2a** and **2 b**.



1: $X^4 = X^9 = O$, $R^5 = R^7 = R^{8ax} = R^{8eq} = H$

2: $X^4 = OH/H$, $X^9 = (OMe)_2$, $R^5 = R^7 = R^{8ax} = R^{8eq} = H$

3: $X^4 = X^9 = O$, $R^5 = CH_2CHC(CH_3)_2$, $R^7 = H$, $R^{8ax} = CH_3$, $R^{8eq} = CH_2CH_2CHC(CH_3)_2$

4: $X^4 = OH/C(CH_3)_3$, $X^9 = O$, $R^5 = H$, $R^7 = CH_2CHC(CH_3)_2$, $R^{8ax} = CH_3$, $R^{8eq} = CH_2CH_2CHC(CH_3)_2$

Figure 2
Numbering scheme for ring **I** (C1/C8/C7/C6/C5/C9) and ring **II** (C1–C5/C9) for the basic bicyclo[3.3.1]nonanone framework and its substituents X^4, X^9, R^5, R^7, R^{8ax} and R^{8eq} for the assignment of the molecular compounds **1**, **2**, **3** and **4**.

ecular compounds **1**, **2a**, **2b**, **3** and **4** share a bicyclo[3.3.1]-nonanone core structure but differ structurally at positions X^4, X^9, R^5, R^7, R^{8eq} and R^{8ax} (Fig. 2). In the crystal structures of compounds **2** and **4**, the OH groups form a hydrogen-bonded network.

To describe the structural characteristics of these molecules, puckering parameters (Cremer & Pople, 1975) were analyzed (Table 1). For consistent representation, all crystal structures were treated with a unified naming scheme for the bicyclo-[3.3.1]nonane core (Fig. 2). The starting atom for rings **I** and **II** is C1, with the rotation direction chosen as C1 toward C8 for ring **I** and C1 toward C2 for ring **II**. Focus was placed on the folding of the two six-membered rings C1/C8/C7/C6/C5/C9 (**I**) and C1–C5/C9 (**II**). The influence of substituents of ring **I** on its expected chair conformation [$^6C_1$; Fig. 3(*a*)] was determined using the puckering parameters. With regard to ring **II**, it is known that the introduction of three sp^2-hybridized atoms into the bicyclo[3.3.1]nonane skeleton (X^4 = O) leads to planarity of this part of the ring (Zefirov & Palyulin, 1991).

Table 1
Puckering parameters Q (Å), Θ (°) and Φ (°) of the cyclohexane rings **I** and **II** of **1**, **2a**, **2b**, **3** and **4**.

	Ring **I**			Ring **II**		
	Q (Å)	Θ (°)	Φ (°)	*Q* (Å)	Θ (°)	Φ (°)
1	0.590 (2)	172.2 (2)	104.4 (1)	0.505 (2)	56.7 (2)	306.0 (2)
2a	0.591 (3)	169.6 (3)	140.4 (2)	0.534 (3)	48.3 (3)	284.1 (4)
2b[a]	0.593 (3)	170.7 (3)	139.1 (2)	0.541 (3)	47.8 (3)	286.9 (4)
3	0.592 (2)	171.6 (2)	115.6 (1)	0.501 (2)	58.2 (2)	310.9 (2)
4	0.592 (1)	170.2 (1)	120.6 (7)	0.489 (1)	52.4 (1)	298.5 (2)

Note: (*a*) for **2b** (the enantiomer of **2a**), the tabulated values of Θ and Φ were calculated from the observed Θ′ and Φ′ using the equations Θ = 180° − Θ′ and Φ = 180° + Φ′.

Consequently one would expect a C_s-symmetric envelope conformation (E_9) for the six-membered ring in which there are five C atoms in the plane and C9 below [Fig. 3(*b*)]. However, replacing the sp^2-hybridized C atom at position 4 of ring **II** with an sp^3-hybridized C atom (X^4 = OH/H) alters the folding of the respective ring, leading to a C_2-symmetric half-chair conformation ($^5H_9$). In this conformation, four C atoms lie in the plane, with C5 positioned above and C9 below it [Fig. 3(*c*)].

The puckering parameters *Q*, Θ and Φ allow a complete description of the conformations of **I** and **II** in polar coordinates, with every possible conformation represented as a point on a sphere of radius *Q*, the polar angle Θ [angle with respect to the positive polar axis (the north pole) with $0 \le \Theta \le 180°$], and the azimuthal angle Φ (rotation around the equator with $0 \le \Phi \le 360°$) (Cremer & Pople, 1975; Giacovazzo *et al.*, 2011). On this sphere, the ideal chair conformation (C) (D_{3d}) is located at the poles with Θ = 0° and Θ = 180° (Φ undefined). The two higher-energy states, half-chair (H) (C_2) and envelope (E) (C_s), are situated towards the equator at $\tan\Theta = \pm\sqrt{3}/2$ (Θ = 50.8°) and $\tan\Theta = \pm\sqrt{2}$ (Θ = 54.7°), and interconvert *via* pseudorotation [$\Phi = n \times 60° + 30°$ for (H) and $\Phi = n \times 60°$ for (E)]. Table 1 summarizes the puckering parameters for rings **I** and **II**. In the five investigated structures **1**, **2a**, **2b**, **3** and **4** of the bicyclo[3.3.1]nonane core, all conformations of the six-membered rings **I** are very close to the ideal chair conformation ($^6C_1$), with very tightly grouped Θ values ($169.6 < \Theta < 172.2°$). In accordance with a previous report (Zefirov & Palyulin, 1991), the influence of substituents R^5, R^7, R^{8eq} and

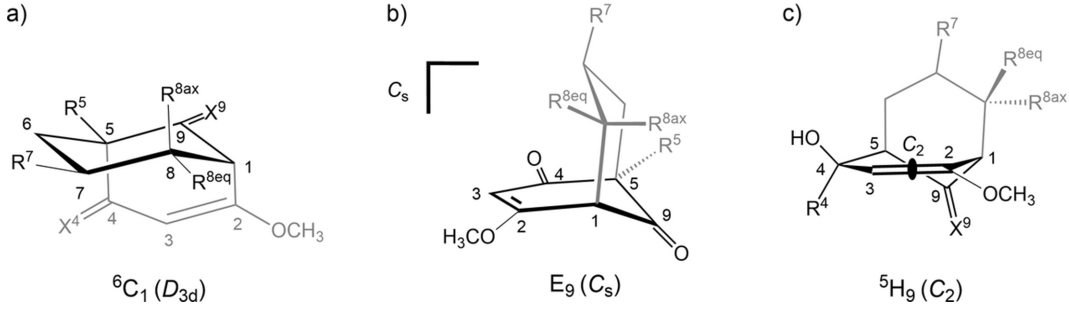


Figure 3
Overview of the cyclohexane conformations (bold black bonds) and their symmetries as described in the text: (*a*) chair conformation (D_{3d}), with four atoms in the plane and atom C6 above and C1 below ($^6C_1$); (*b*) envelope conformation (C_s) with atoms C1–C5 in the plane and C9 below (E_9); (*c*) half-chair conformation (C_2) with atoms C1–C4 in the plane and atom C5 above and C9 below (looking towards the twofold axis in the middle of bond C2—C3 and bond C5—C9).

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6O···O4^{i}	0.84 (1)	2.03 (1)	2.863 (3)	172 (3)
O2—H2O···O8	0.84 (1)	2.02 (1)	2.858 (3)	176 (3)

Symmetry code: (i) $x+1, y, z$.

R^{8ax}, as well as the difference between the keto group at C9 in compounds **1**, **3** and **4** compared to the dimethoxy group in **2**, appears to have no significant impact on the $^{6}C_{1}$ conformation of ring **I**. Even bulky substituents in the axial position at C7, for example, OCH_2Ph [Inouye *et al.*, 1987; Q = 0.561 (3) Å, Θ = 165.0 (3) and Φ = 118.1 (13)°] or $CH_2CHC(CH_3)_2$ [Biber *et al.*, 2011; Q = 0.560 Å, Θ = 170.8 (5) and Φ = 128 (3)°] leave the six-membered ring **I** in a nearly ideal chair conformation with a small distortion towards ^{7}E.

A closer examination of the puckering parameters for ring **II** reveals a slightly different picture. Compounds **1** and **3** with X^4 = O adopt a nearly ideal envelope conformation (E_9) (**1**: Θ = 56.7° and Φ = 306.0°; **3**: Θ = 58.2° and Φ = 310.9°), with C9 lying out of the plane of the ring and a mirror plane passing through atoms C3 and C9 [Fig. 3(*b*)]. When the C4 keto group is reduced to an alcohol ($sp^2 \rightarrow sp^3$), the ring exhibits greater flexibility. In this case, compound **2** adopts a conformation close to the half-chair form ($^{5}H_9$) (**2a**: Θ = 48.3° and Φ = 284.1°; **2b**: Θ = 47.8° and Φ = 286.9°), with a twofold axis passing through the bonds C2—C3 and C5—C9 [Fig. 3(*c*)]. In contrast, compound **4** is better described as a linear combination of E_9 and $^{5}H_9$ (Θ = 52.4° and Φ = 298.5°).

3. Supramolecular features

Compounds **2** and **4** feature an OH group at C4, with the H atom capable of acting as a donor in C—H···O hydrogen bonding (Tables 2 and 3). In the crystal structure of **2**, there are two crystallographically independent molecules in the asymmetric unit, which are chemically enantiomers of each other. **2a** and **2b** are interconnected *via* hydrogen bonds [Fig. 4(*a*)]. **2a** forms a hydrogen bond perpendicular to the *a* axis and directed along the *b* axis, with H2O as the donor and O8 in **2b** as the acceptor [O2—H2O···O8 = 2.858 (3) Å and 176 (3)°]. Respectively, **2b** forms another hydrogen bond nearly parallel to the first (angle between lines O2···O8 and O6···O4^{i}; symmetry code: (i) $x+1, y, z$: 13.67 (8)°], with H6O as the donor and O4 in **2a** as the acceptor [O6—H6O···O4^{i}; 2.863 (3)Å and 171 (3)°]. The distances between the strands are approximately equidistant [H6O···H2O = 3.82 (4) Å and H2O^{i}···H6O = 3.92 (4) Å]. In both **2a** and **2b**, six atoms are involved in the bonding resulting in an infinite $C(6)$ chain of hydrogen-bonded molecules along the *a* direction (Bernstein *et al.*, 1995). The crystal structure of **4** possesses a crystallographic glide mirror plane, which transforms the hydrogen bonds between **4** with H2 as donor and its enantiomer with O3^{ii} as acceptor [symmetry code: (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$] into one another [Fig. 4(*b*)]. In this case, the hydrogen bonds are slightly tilted from the glide-plane in the *c* direction [angle between the line O3^{ii}···O2 and the *c*-glide plane = 12.40 (4)°].

Table 3
Hydrogen-bond geometry (Å, °) for **4**.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3^{i}	0.85 (1)	2.06 (1)	2.8736 (11)	162 (2)

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

Here too an infinite $C(6)$ chain forms. The symmetry class of this Frieze group is *p*11g (No. 5 in International Tables for Crystallography, 2010).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.45, November 2024; Groom *et al.*, 2016) indicated 441, 165 and 15 compounds incorporating a bicyclo[3.3.1]non-2-ene, bicyclo[3.3.1]non-2-en-9-one and 4-methoxybicyclo-[3.3.1]non-3-ene-2,9-dione motif, respectively.

5. Synthesis and crystallization

5.1. 4-Methoxybicyclo[3.3.1]non-3-ene-2,9-dione (1)

The reaction was carried out in a round-bottomed flask under ambient conditions. To a solution of 4-hydroxybicyclo-[3.3.1]non-3-ene-2,9-dione (97.9 mg, 0.59 mmol; Shishido *et al.*, 1986; Schönwälder *et al.*, 1984) in 6 ml of acetone was added K_2CO_3 (333 mg, 2.41 mmol) and dimethyl sulfate

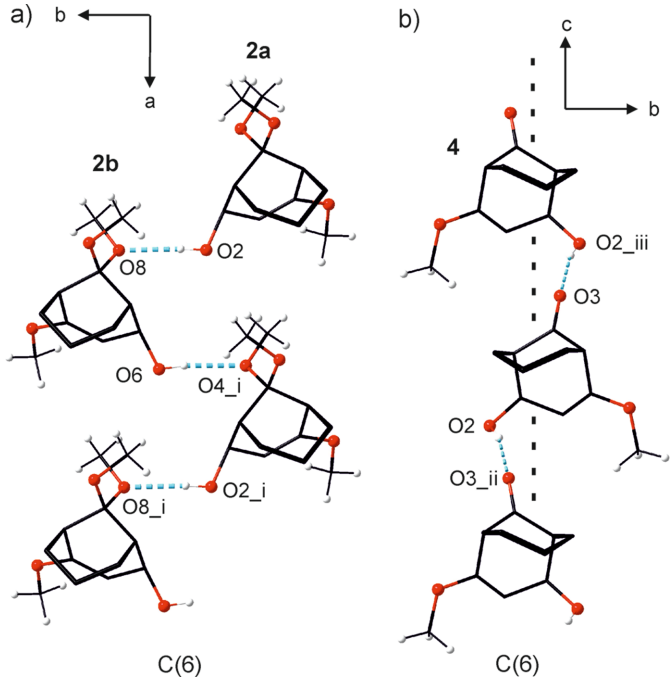


Figure 4
Hydrogen-bonding network of **2** and **4**. (*a*) Hydrogen bonds (blue dashed lines) perpendicular to the *a* direction between **2a** and **2b** *via* O2—H20 and O8, and O6—H6O and O4^{i} [symmetry code: (i) $x+1, y, z$]. The formed $C(6)$ chain is aligned in *a* direction. (*b*) The hydrogen bonds (blue dashed lines) in the *c* direction *via* O2—H2 and O3^{ii} [symmetry code: (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$ and *via* O2^{iii}—H2^{iii} and O3 [symmetry code: (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$], are deflected by 12.40 (4)° against the *c*-glide plane (black dashed line). The formed $C(6)$ chain has the symmetry of the Frieze group *p*11g.

(70 µl, 0.74 mmol). The suspension was refluxed for 2 h. The reaction mixture was allowed to reach room temperature and treated with H_2O. The layers were separated and the aqueous layer was extracted thrice with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash column chromatography (^{n}Pen/Et_2O = 1:2) afforded **1** (yield: 84.2 mg, 0.47 mmol, 79%; m.p. 365.1–366.4 K) as a colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.79 (*s*, 1H), 3.79 (*s*, 3H), 3.21–3.19 (*m*, 2H), 2.22–2.16 (*m*, 1H), 2.14–2.07 (*m*, 1H), 2.00–1.86 (*m*, 2H), 1.79–1.60 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.4, 195.6, 175.6, 105.9, 61.3, 56.9, 53.3, 32.6, 30.5, 17.5.

HRMS (ESI) *m*/*z* calculated for $C_{10}H_{12}O_3^+$ $[M + H]^+$: 181.08592, found: 181.08547.

5.2. 4,9,9-Trimethoxybicyclo[3.3.1]non-3-en-2-ol (2)

This compound was synthesized over two steps.

The reaction was carried out in a flame-dried round-bottomed flask under inert conditions. To a solution of 4-hydroxybicyclo[3.3.1]non-3-ene-2,9-dione (504 mg, 3.02 mmol; Shishido *et al.*, 1986; Schönwälder *et al.*, 1984) in 30 ml of dry methanol was added PTSA (117 mg, 0.62 mmol). The reaction mixture was refluxed overnight. The reaction mixture was allowed to reach room temperature and concentrated *in vacuo*. Purification of the residue by flash column chromatography (^{n}Pen/Et_2O = 1:1) afforded 4,9,9-trimethoxybicyclo-[3.3.1]non-3-en-2-one (yield: 593 mg, 2.62 mmol, 87%) as a colourless oil that solidifies in the cold.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.47 (*s*, 1H), 3.64 (*s*, 3H), 3.12 (*s*, 3H), 3.05 (*s*, 3H), 2.74 (*q*, *J* = 3.2 Hz, 1H), 2.68–2.66 (*m*, 1H), 1.76 (*tdd*, *J* = 13.3, 5.1, 3.9 Hz, 1H), 1.66 (*tdd*, *J* = 13.6, 5.4, 4.4 Hz, 1H), 1.55 (*dddt*, *J* = 15.0, 4.7, 3.1, 1.6 Hz, 1H), 1.49 (*dddt*, *J* = 13.5, 5.0, 3.2, 1.6 Hz, 1H), 1.42–1.24 (*m*, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 199.7, 176.6, 103.7, 100.7, 56.1, 48.8, 47.7, 46.8, 42.1, 24.1, 22.7, 16.4.

HRMS (ESI) *m*/*z* calculated for $C_{12}H_{19}O_4^+$ $[M + H]^+$: 227.12779, found: 227.12863.

The reaction was carried out in a flame-dried round-bottomed flask under inert conditions. To a solution of 4,9,9-trimethoxybicyclo[3.3.1]non-3-en-2-one (704 mg, 3.11 mmol) in 60 ml of dry THF was added dropwise DIBAL-H (6.2 ml, 6.20 mmol, 1.0 *M* in hexane) at 195 K. After stirring for 2 h, the reaction mixture was warmed to 233 K and then to 273 K. The reaction mixture was treated with an aqueous solution of potassium sodium tartrate. The layers were separated, and the aqueous layer was extracted thrice with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash column chromatography (^{n}Pen/Et_2O = 1:1) afforded **2** (yield: 485 mg, 2.12 mmol, 69%; m.p. 336.8–337.4 K) as a colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.81 (*d*, *J* = 2.8 Hz, 1H), 4.57–4.52 (*m*, 1H), 3.54 (*s*, 3H), 3.19 (*s*, 3H), 3.16 (*s*, 3H), 2.52 (*q*, *J* = 3.0 Hz, 1H), 2.34–2.30 (*m*, 1H), 1.92–1.85 (*m*, 1H), 1.73 (*ttd*, *J* = 12.6, 4.4, 1.1 Hz, 1H), 1.61–1.31 (*m*, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.5, 101.7, 98.7, 68.6, 54.7, 47.6, 46.8, 40.5, 38.4, 24.7, 21.8, 15.75.

HRMS (ESI) *m*/*z* calculated for $C_{12}H_{19}O_4^-$ $[M - H]^-$: 227.12888,found: 227.12864.

5.3. 4-Methoxy-6-methyl-1-(3-methylbut-2-en-1-yl)-6-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]non-3-ene-2,9-dione (3)

The reaction was carried out in a flame-dried round-bottomed flask under inert conditions. To a solution of 4-methoxy-6-methyl-6-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]-non-3-ene-2,9-dione (55.4 mg, 0.20 mmol; König *et al.*, 2024) and prenyl bromide (1.1 ml, 9.52 mmol) in 2.2 ml dry THF was added over 3 min a freshly prepared solution of LDA (1.6 ml, 0.40 mmol) at 173 K. The now yellow solution was allowed to reach 195 K over 30 min and then treated with H_2O. The layers were separated, and the aqueous layer was extracted thrice with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash column chromatography (^{n}Pen/Et_2O = 3:1→1:1) afforded **3** (yield: 9.6 mg, 27.9 µmol, 14%; m.p. 341.9–342.2 K) as a colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.71 (*s*, 1H), 5.01 (tsept, *J* = 7.0, 1.2 Hz, 1H), 4.97 (tsept, *J* = 7.0, 1.2 Hz, 1H), 3.74 (*s*, 3H), 2.99 (*s*, 1H), 2.42 (*d*, *J* = 6.8 Hz, 2H), 2.08 (*tt*, *J* = 12.5, 6.1 Hz, 1H), 1.90 (*tt*, *J* = 12.7, 6.6 Hz, 1H), 1.82–1.78 (*m*, 2H), 1.76–1.69 (*m*, 1H), 1.68 (*s*, 3H), 1.66 (*s*, 3H), 1.63 (*s*, 3H), 1.60 (*s*, 3H), 1.38–1.32 (*m*, 1H), 1.22 (*td*, *J* = 11.3, 5.1 Hz, 2H), 1.00 (*s*, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.9, 197.8, 174.9, 133.8, 131.6, 124.0, 119.6, 106.0, 63.1, 62.6, 56.4, 42.4, 41.7, 34.5, 31.2, 29.3, 25.9, 25.7, 21.9, 21.3, 18.0, 17.5.

HRMS (ESI) *m*/*z* calculated for $C_{22}H_{33}O_3^+$ $[M + H]^+$: 345.24242, found: 345.24241.

5.4. 4-*tert*-Butyl-4-hydroxy-2-methoxy-8-methyl-7-(3-methylbut-2-en-1-yl)-8-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]-non-2-en-9-one (4)

The reaction was carried out in a flame-dried round-bottomed flask under inert conditions. To a solution of 4-methoxy-6-methyl-7-(3-methylbut-2-en-1-yl)-6-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]-non-3-ene-2,9-dione (17.4 mg, 50.5 µmol; König *et al.*, 2025) in 5 ml of dry THF was added dropwise *t*-BuLi (53 µl, 101 µmol) at 168 K. The reaction mixture was stirred for 90 min and then treated with a saturated aqueous solution of NH_4Cl. The layers were separated, and the aqueous layer was extracted thrice with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash column chromatography (^{n}Pen/Et_2O = 10:1) afforded **4** (yield: 19.0 mg, 47.3 µmol, 94%; m.p. 382.7.1–384.3 K) as a colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.07–5.01 (*m*, 3H), 3.56 (*s*, 3H), 2.83 (*bs*, 1H), 2.70 (*s*, 1H), 2.29 (*ddd*, *J* = 14.3, 3.9 Hz, 2.7 Hz, 1H), 2.23–2.16 (*m*, 1H), 2.10 (*dd*, *J* = 13.7, 4.9 Hz, 1H), 1.85–1.77 (*m*, 1H), 1.68 (*s*, 6H), 1.65–1.62 (*m*, 1H), 1.61 (*s*, 3H), 1.57 (*s*, 3H), 1.54–1.39 (*m*, 3H), 1.22–1.15 (*m*, 1H), 0.92 (*s*, 9H), 0.84 (*s*, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.0, 155.4,

Table 4
Experimental details.

Experiments were carried out with Mo $K\alpha$ radiation using a Bruker D8 VENTURE PHOTON II. Absorption was corrected for by multi-scan methods (*SADABS*; Krause *et al.*, 2015).

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	$C_{10}H_{12}O_3$	$C_{12}H_{20}O_4$	$C_{22}H_{32}O_3$	$C_{26}H_{42}O_3$
M_r	180.20	228.28	344.47	402.59
Crystal system, space group	Monoclinic, $P2_1$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	153	152	133	143
a, b, c (Å)	6.4819 (4), 7.4766 (5), 9.0627 (5)	7.7330 (15), 10.976 (2), 13.874 (3)	14.1871 (6), 6.3306 (2), 22.4159 (8)	15.1165 (5), 13.9068 (4), 12.8150 (4)
α, β, γ (°)	90, 99.546 (2), 90	101.984 (5), 92.032 (5), 90.293 (5)	90, 101.702 (1), 90	90, 113.218 (1), 90
V (Å^3)	433.12 (5)	1151.2 (4)	1971.39 (13)	2475.81 (13)
Z	2	4	4	4
μ (mm^{-1})	0.10	0.10	0.08	0.07
Crystal size (mm)	0.38 × 0.08 × 0.06	0.28 × 0.24 × 0.04	0.18 × 0.14 × 0.04	0.26 × 0.16 × 0.08
Data collection				
T_{min}, T_{max}	0.699, 0.746	0.578, 0.746	0.687, 0.746	0.704, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8258, 2031, 1948	8885, 4662, 2677	28995, 4348, 3271	87917, 5484, 4697
R_{int}	0.028	0.055	0.067	0.048
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658	0.625	0.642	0.642
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.074, 1.08	0.057, 0.139, 0.98	0.046, 0.116, 1.05	0.040, 0.108, 1.05
No. of reflections	2031	4662	4348	5484
No. of parameters	119	301	232	274
No. of restraints	1	2	0	1
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.15	0.24, −0.24	0.28, −0.22	0.29, −0.20
Absolute structure	Refined as an inversion twin	–	–	–
Absolute structure parameter	0.5	–	–	–

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2019* (Sheldrick, 2015*b*), *ShelXle* (Hübschle *et al.*, 2011), *DIAMOND* (Brandenburg, 2020) and *publCIF* (Westrip, 2010).

132.7, 131.0, 124.9, 123.1, 101.6, 77.5, 58.6, 54.6, 52.2, 46.2, 41.2, 39.8, 38.5, 32.5, 28.2, 25.8, 25.7, 25.3, 21.7, 17.9, 17.5, 17.3.

HRMS (ESI) m/z calculated for $C_{26}H_{41}O_3^-$ $[M - H]^-$: 401.30612, found: 401.30503.

All compounds were crystallized after flash chromatography by dissolving 10 mg to 30 mg of the respective purified compound in a 10 ml round-bottomed flask with 1–2 ml DCM. The flasks were topped with a septum and a cannula to allow slow solvent evaporation. All solutions were left undisturbed at room temperature for two to four weeks to yield colourless to pale yellow crystals.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were treated as recommended by Müller *et al.* (2006). A riding model was used for the C-bonded H atoms, with $U_{iso}(H) = 1.5U_{eq}$(methyl C) and $1.2U_{eq}(C)$ for other C-bound H atoms. The positional parameters of the O-bonded H atoms of **2a**, **2b** and **4** were refined using isotropic displacement parameters which were set at 1.5 times the U_{eq} value of the parent atom. In addition, restraints of 0.84 (1) Å were used for the O—H bond lengths. The crystal structure of compound **1** was refined as an inversion twin (BASF = 0.5).

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Synthesis and crystal structure analysis of substituted bicyclo[3.3.1]nonanones

Julien A. König, Bernd Morgenstern and Johann Jauch

Computing details

4-Methoxybicyclo[3.3.1]non-3-ene-2,9-dione (1)

Crystal data

$C_{10}H_{12}O_3$
M_r = 180.20
Monoclinic, $P2_1$
a = 6.4819 (4) Å
b = 7.4766 (5) Å
c = 9.0627 (5) Å
β = 99.546 (2)°
V = 433.12 (5) Å^3
Z = 2
$F(000)$ = 192
D_x = 1.382 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6064 reflections
θ = 2.3–27.9°
μ = 0.10 mm^{-1}
T = 153 K
Rod, colourless
0.38 × 0.08 × 0.06 mm

Data collection

Bruker D8 VENTURE PHOTON II diffractometer
Radiation source: INCOATEC IÂμS microfocus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.699, T_{max} = 0.746
8258 measured reflections
2031 independent reflections
1948 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 27.9°, θ_{min} = 2.3°
h = −8→7
k = −9→9
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.074
S = 1.08
2031 reflections
119 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.0624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.5

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. Refined as a 2-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.6356 (2)	0.20219 (18)	0.73144 (16)	0.0358 (3)
O2	0.80123 (19)	0.73388 (16)	0.49209 (12)	0.0255 (3)
O3	0.2740 (2)	0.7098 (2)	0.73484 (15)	0.0345 (3)
C1	0.6305 (3)	0.7548 (2)	0.70026 (17)	0.0214 (3)
H1	0.578127	0.868685	0.649526	0.026*
C2	0.7203 (2)	0.6369 (2)	0.59258 (16)	0.0207 (3)
C10	0.8884 (3)	0.6368 (3)	0.3793 (2)	0.0318 (4)
H10A	0.930016	0.721305	0.306964	0.048*
H10B	0.783321	0.554093	0.327603	0.048*
H10C	1.011125	0.569139	0.426813	0.048*
C3	0.7170 (3)	0.4564 (2)	0.59890 (18)	0.0241 (3)
H3	0.773987	0.388629	0.526623	0.029*
C4	0.6278 (3)	0.3647 (2)	0.71463 (18)	0.0242 (3)
C5	0.5211 (3)	0.4780 (2)	0.82067 (18)	0.0240 (3)
H5	0.397653	0.412087	0.846504	0.029*
C6	0.6779 (3)	0.5196 (2)	0.96573 (19)	0.0285 (4)
H6A	0.604837	0.586413	1.036072	0.034*
H6B	0.729428	0.405919	1.014438	0.034*
C7	0.8636 (3)	0.6296 (2)	0.93294 (18)	0.0277 (4)
H7A	0.951032	0.665124	1.028598	0.033*
H7B	0.950543	0.554829	0.877127	0.033*
C8	0.7938 (3)	0.7970 (2)	0.84179 (19)	0.0252 (4)
H8A	0.917481	0.854469	0.810933	0.030*
H8B	0.732289	0.882757	0.905492	0.030*
C9	0.4511 (3)	0.6540 (2)	0.74873 (17)	0.0224 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0417 (8)	0.0189 (6)	0.0482 (8)	0.0001 (6)	0.0112 (6)	0.0026 (5)
O2	0.0288 (7)	0.0263 (6)	0.0225 (5)	−0.0041 (5)	0.0078 (4)	−0.0002 (4)
O3	0.0259 (7)	0.0372 (7)	0.0423 (7)	0.0078 (6)	0.0109 (5)	0.0059 (6)
C1	0.0235 (8)	0.0187 (8)	0.0219 (7)	0.0019 (6)	0.0033 (6)	0.0010 (6)
C2	0.0190 (7)	0.0237 (7)	0.0189 (6)	−0.0012 (6)	0.0015 (6)	0.0008 (6)
C10	0.0338 (10)	0.0371 (9)	0.0274 (8)	−0.0049 (8)	0.0139 (7)	−0.0061 (8)
C3	0.0247 (8)	0.0227 (8)	0.0250 (8)	0.0005 (6)	0.0041 (6)	−0.0039 (6)
C4	0.0222 (9)	0.0205 (8)	0.0291 (8)	−0.0004 (6)	0.0020 (6)	0.0003 (6)
C5	0.0236 (9)	0.0231 (8)	0.0264 (8)	−0.0017 (6)	0.0070 (6)	0.0041 (6)

C6	0.0348 (10)	0.0282 (9)	0.0227 (7)	−0.0008 (7)	0.0050 (6)	0.0056 (6)
C7	0.0270 (9)	0.0315 (9)	0.0230 (7)	−0.0001 (7)	−0.0007 (6)	0.0008 (7)
C8	0.0283 (9)	0.0235 (8)	0.0237 (8)	−0.0037 (7)	0.0042 (6)	−0.0030 (6)
C9	0.0236 (8)	0.0225 (7)	0.0219 (7)	0.0021 (6)	0.0057 (6)	−0.0012 (6)

Geometric parameters (Å, º)

O1—C4	1.225 (2)	C3—H3	0.9500
O2—C2	1.3377 (19)	C4—C5	1.529 (2)
O2—C10	1.443 (2)	C5—C9	1.505 (2)
O3—C9	1.208 (2)	C5—C6	1.554 (2)
C1—C2	1.502 (2)	C5—H5	1.0000
C1—C9	1.510 (2)	C6—C7	1.527 (3)
C1—C8	1.554 (2)	C6—H6A	0.9900
C1—H1	1.0000	C6—H6B	0.9900
C2—C3	1.351 (2)	C7—C8	1.526 (2)
C10—H10A	0.9800	C7—H7A	0.9900
C10—H10B	0.9800	C7—H7B	0.9900
C10—H10C	0.9800	C8—H8A	0.9900
C3—C4	1.451 (2)	C8—H8B	0.9900
C2—O2—C10	116.97 (14)	C9—C5—H5	109.7
C2—C1—C9	107.21 (13)	C4—C5—H5	109.7
C2—C1—C8	111.78 (13)	C6—C5—H5	109.7
C9—C1—C8	108.24 (12)	C7—C6—C5	111.67 (13)
C2—C1—H1	109.8	C7—C6—H6A	109.3
C9—C1—H1	109.8	C5—C6—H6A	109.3
C8—C1—H1	109.8	C7—C6—H6B	109.3
O2—C2—C3	125.52 (15)	C5—C6—H6B	109.3
O2—C2—C1	111.23 (14)	H6A—C6—H6B	107.9
C3—C2—C1	123.25 (14)	C8—C7—C6	111.97 (15)
O2—C10—H10A	109.5	C8—C7—H7A	109.2
O2—C10—H10B	109.5	C6—C7—H7A	109.2
H10A—C10—H10B	109.5	C8—C7—H7B	109.2
O2—C10—H10C	109.5	C6—C7—H7B	109.2
H10A—C10—H10C	109.5	H7A—C7—H7B	107.9
H10B—C10—H10C	109.5	C7—C8—C1	112.38 (14)
C2—C3—C4	120.89 (15)	C7—C8—H8A	109.1
C2—C3—H3	119.6	C1—C8—H8A	109.1
C4—C3—H3	119.6	C7—C8—H8B	109.1
O1—C4—C3	123.06 (16)	C1—C8—H8B	109.1
O1—C4—C5	119.00 (15)	H8A—C8—H8B	107.9
C3—C4—C5	117.94 (14)	O3—C9—C5	124.04 (16)
C9—C5—C4	110.31 (13)	O3—C9—C1	124.16 (15)
C9—C5—C6	107.41 (13)	C5—C9—C1	111.78 (14)
C4—C5—C6	110.00 (14)		
C10—O2—C2—C3	1.4 (2)	C9—C5—C6—C7	−57.61 (19)

C10—O2—C2—C1	−178.52 (14)	C4—C5—C6—C7	62.47 (18)
C9—C1—C2—O2	149.74 (13)	C5—C6—C7—C8	52.43 (19)
C8—C1—C2—O2	−91.79 (15)	C6—C7—C8—C1	−50.79 (18)
C9—C1—C2—C3	−30.1 (2)	C2—C1—C8—C7	−63.52 (18)
C8—C1—C2—C3	88.33 (19)	C9—C1—C8—C7	54.34 (18)
O2—C2—C3—C4	179.00 (15)	C4—C5—C9—O3	125.58 (18)
C1—C2—C3—C4	−1.1 (3)	C6—C5—C9—O3	−114.54 (18)
C2—C3—C4—O1	−174.35 (17)	C4—C5—C9—C1	−56.12 (18)
C2—C3—C4—C5	5.1 (2)	C6—C5—C9—C1	63.76 (17)
O1—C4—C5—C9	−157.28 (16)	C2—C1—C9—O3	−123.17 (17)
C3—C4—C5—C9	23.2 (2)	C8—C1—C9—O3	116.10 (18)
O1—C4—C5—C6	84.41 (19)	C2—C1—C9—C5	58.54 (16)
C3—C4—C5—C6	−95.07 (17)	C8—C1—C9—C5	−62.20 (17)

4,9,9-Trimethoxybicyclo[3.3.1]non-3-en-2-ol (2)

Crystal data

$C_{12}H_{20}O_4$
$M_r = 228.28$
Triclinic, $P\overline{1}$
$a = 7.7330$ (15) Å
$b = 10.976$ (2) Å
$c = 13.874$ (3) Å
$\alpha = 101.984$ (5)°
$\beta = 92.032$ (5)°
$\gamma = 90.293$ (5)°
$V = 1151.2$ (4) Å^3
$Z = 4$
$F(000) = 496$
$D_x = 1.317$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1376 reflections
$\theta = 3.0$–$25.0°$
$\mu = 0.10$ mm^{-1}
$T = 152$ K
Plate, colourless
0.28 × 0.24 × 0.04 mm

Data collection

Bruker D8 VENTURE PHOTON II diffractometer
Radiation source: INCOATEC IÂμS microfocus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.578$, $T_{max} = 0.746$
8885 measured reflections
4662 independent reflections
2677 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 26.4°$, $\theta_{min} = 1.5°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.139$
$S = 0.98$
4662 reflections
301 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.2250 (2)	0.37070 (16)	0.13978 (14)	0.0244 (5)
O2	0.7476 (2)	0.61301 (17)	0.27191 (16)	0.0288 (5)
H2O	0.741 (4)	0.6909 (10)	0.278 (2)	0.043*
O1	0.5543 (2)	0.27872 (16)	0.40336 (14)	0.0248 (5)
O4	0.2372 (2)	0.50789 (16)	0.29210 (14)	0.0219 (4)
O5	1.0600 (2)	1.16441 (16)	0.39368 (14)	0.0252 (5)
O6	1.2486 (2)	0.75906 (17)	0.26446 (16)	0.0311 (5)
H6O	1.234 (4)	0.6854 (14)	0.271 (2)	0.047*
O7	0.7194 (2)	0.92784 (17)	0.13891 (14)	0.0252 (5)
O8	0.7424 (2)	0.87754 (16)	0.29317 (13)	0.0208 (4)
C1	0.4127 (3)	0.3167 (2)	0.2597 (2)	0.0207 (6)
H1	0.317759	0.267373	0.281279	0.025*
C2	0.5345 (3)	0.3652 (2)	0.3458 (2)	0.0206 (6)
C3	0.6152 (3)	0.4749 (2)	0.3592 (2)	0.0211 (6)
H3	0.695548	0.498054	0.413456	0.025*
C4	0.5835 (3)	0.5635 (2)	0.2916 (2)	0.0210 (6)
H4	0.514429	0.634247	0.327706	0.025*
C5	0.4824 (3)	0.5061 (2)	0.1964 (2)	0.0213 (6)
H5	0.430621	0.575362	0.168691	0.026*
C6	0.5910 (3)	0.4263 (3)	0.1161 (2)	0.0263 (7)
H6A	0.520091	0.406174	0.053892	0.032*
H6B	0.692026	0.476413	0.104437	0.032*
C7	0.6560 (3)	0.3048 (3)	0.1411 (2)	0.0276 (7)
H7A	0.749392	0.323841	0.192827	0.033*
H7B	0.705050	0.252400	0.081777	0.033*
C8	0.5107 (3)	0.2326 (2)	0.1773 (2)	0.0244 (7)
H8A	0.560293	0.161608	0.202263	0.029*
H8B	0.428924	0.198770	0.121522	0.029*
C9	0.3347 (3)	0.4262 (2)	0.2210 (2)	0.0200 (6)
C10	0.1260 (4)	0.4544 (3)	0.0941 (2)	0.0324 (7)
H10A	0.054707	0.406678	0.039144	0.049*
H10B	0.204374	0.510236	0.069224	0.049*
H10C	0.051003	0.503695	0.142526	0.049*
C11	0.0995 (3)	0.4525 (3)	0.3350 (2)	0.0306 (7)
H11A	0.019317	0.517320	0.364698	0.046*
H11B	0.147237	0.411031	0.385985	0.046*
H11C	0.037487	0.391278	0.283835	0.046*
C12	0.6804 (4)	0.3079 (3)	0.4830 (2)	0.0311 (7)
H12A	0.682747	0.240840	0.519879	0.047*

H12B	0.650051	0.386227	0.526962	0.047*
H12C	0.794670	0.316700	0.456675	0.047*
C13	0.9185 (3)	1.0473 (2)	0.2509 (2)	0.0212 (6)
H13	0.826248	1.109938	0.271311	0.025*
C14	1.0410 (3)	1.0473 (2)	0.3369 (2)	0.0203 (6)
C15	1.1210 (3)	0.9454 (2)	0.3512 (2)	0.0200 (6)
H15	1.203910	0.952686	0.404336	0.024*
C16	1.0862 (3)	0.8197 (2)	0.2871 (2)	0.0225 (6)
H16	1.019848	0.769528	0.326094	0.027*
C17	0.9785 (3)	0.8221 (2)	0.1917 (2)	0.0214 (6)
H17	0.923065	0.738204	0.168204	0.026*
C18	1.0814 (3)	0.8527 (2)	0.1075 (2)	0.0268 (7)
H18A	1.005550	0.839472	0.047137	0.032*
H18B	1.178675	0.793939	0.094485	0.032*
C19	1.1541 (3)	0.9861 (3)	0.1278 (2)	0.0281 (7)
H19A	1.249799	0.994633	0.178169	0.034*
H19B	1.201510	1.003598	0.066630	0.034*
C20	1.0141 (3)	1.0806 (3)	0.1641 (2)	0.0264 (7)
H20A	0.929714	1.083264	0.109210	0.032*
H20B	1.067692	1.164458	0.185194	0.032*
C21	0.8344 (3)	0.9177 (2)	0.2176 (2)	0.0198 (6)
C22	0.6196 (4)	0.8179 (3)	0.0962 (2)	0.0347 (8)
H22A	0.531624	0.838293	0.049607	0.052*
H22B	0.563015	0.786549	0.148393	0.052*
H22C	0.696186	0.754021	0.061296	0.052*
C23	0.6060 (3)	0.9566 (3)	0.3360 (2)	0.0288 (7)
H23A	0.535246	0.912043	0.375069	0.043*
H23B	0.533485	0.979948	0.283521	0.043*
H23C	0.656028	1.031866	0.378740	0.043*
C24	1.1744 (4)	1.1781 (3)	0.4781 (2)	0.0305 (7)
H24A	1.172238	1.264278	0.515319	0.046*
H24B	1.292245	1.157427	0.457040	0.046*
H24C	1.137482	1.121833	0.520074	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0254 (10)	0.0188 (10)	0.0306 (12)	0.0042 (7)	−0.0063 (9)	0.0099 (9)
O2	0.0218 (10)	0.0161 (10)	0.0522 (15)	−0.0008 (8)	0.0037 (9)	0.0149 (10)
O1	0.0323 (10)	0.0170 (10)	0.0288 (12)	0.0030 (8)	−0.0047 (9)	0.0141 (9)
O4	0.0210 (9)	0.0145 (10)	0.0318 (12)	0.0038 (7)	0.0054 (8)	0.0081 (8)
O5	0.0311 (10)	0.0146 (10)	0.0297 (12)	0.0001 (8)	−0.0046 (9)	0.0052 (9)
O6	0.0242 (10)	0.0181 (11)	0.0546 (15)	0.0102 (8)	0.0080 (10)	0.0145 (10)
O7	0.0263 (10)	0.0212 (11)	0.0296 (12)	−0.0021 (8)	−0.0062 (9)	0.0102 (9)
O8	0.0200 (9)	0.0168 (10)	0.0278 (12)	0.0046 (7)	0.0033 (8)	0.0091 (8)
C1	0.0223 (13)	0.0135 (14)	0.0289 (17)	0.0014 (10)	−0.0007 (12)	0.0106 (12)
C2	0.0225 (13)	0.0151 (14)	0.0271 (17)	0.0069 (10)	0.0043 (12)	0.0105 (12)
C3	0.0203 (13)	0.0194 (15)	0.0260 (17)	0.0031 (11)	−0.0013 (12)	0.0102 (12)

C4	0.0192 (13)	0.0148 (14)	0.0310 (17)	0.0022 (10)	0.0051 (12)	0.0086 (12)
C5	0.0210 (13)	0.0144 (14)	0.0320 (17)	0.0066 (10)	0.0036 (12)	0.0119 (12)
C6	0.0291 (15)	0.0262 (16)	0.0268 (17)	0.0032 (12)	0.0048 (13)	0.0120 (14)
C7	0.0271 (15)	0.0246 (16)	0.0310 (18)	0.0077 (12)	0.0030 (13)	0.0047 (14)
C8	0.0290 (15)	0.0155 (14)	0.0289 (18)	0.0075 (11)	−0.0036 (13)	0.0058 (13)
C9	0.0182 (13)	0.0169 (14)	0.0259 (16)	0.0028 (10)	0.0005 (12)	0.0071 (12)
C10	0.0336 (16)	0.0265 (17)	0.040 (2)	0.0082 (13)	−0.0095 (14)	0.0160 (15)
C11	0.0243 (14)	0.0288 (17)	0.043 (2)	0.0037 (12)	0.0103 (14)	0.0154 (15)
C12	0.0379 (17)	0.0286 (17)	0.0294 (18)	0.0076 (13)	−0.0025 (14)	0.0126 (14)
C13	0.0237 (13)	0.0108 (13)	0.0313 (17)	0.0035 (10)	−0.0031 (12)	0.0100 (12)
C14	0.0224 (13)	0.0147 (14)	0.0248 (16)	−0.0008 (10)	0.0024 (12)	0.0062 (12)
C15	0.0194 (13)	0.0186 (14)	0.0236 (16)	0.0027 (10)	−0.0010 (11)	0.0083 (12)
C16	0.0179 (13)	0.0152 (14)	0.0380 (18)	0.0080 (10)	0.0057 (12)	0.0127 (13)
C17	0.0213 (13)	0.0129 (13)	0.0310 (17)	0.0015 (10)	0.0012 (12)	0.0071 (12)
C18	0.0304 (15)	0.0226 (16)	0.0283 (18)	0.0014 (12)	0.0082 (13)	0.0063 (13)
C19	0.0311 (15)	0.0286 (17)	0.0273 (18)	−0.0036 (12)	0.0046 (13)	0.0118 (14)
C20	0.0258 (14)	0.0260 (16)	0.0309 (18)	−0.0042 (12)	−0.0027 (13)	0.0150 (14)
C21	0.0201 (13)	0.0166 (14)	0.0242 (16)	0.0006 (10)	−0.0015 (12)	0.0084 (12)
C22	0.0385 (17)	0.0254 (17)	0.039 (2)	−0.0050 (13)	−0.0139 (15)	0.0060 (15)
C23	0.0255 (15)	0.0244 (16)	0.040 (2)	0.0108 (11)	0.0106 (13)	0.0121 (14)
C24	0.0343 (16)	0.0291 (17)	0.0285 (18)	−0.0054 (13)	−0.0017 (14)	0.0079 (14)

Geometric parameters (Å, º)

O3—C9	1.415 (3)	C10—H10B	0.9800
O3—C10	1.431 (3)	C10—H10C	0.9800
O2—C4	1.435 (3)	C11—H11A	0.9800
O2—H2O	0.843 (10)	C11—H11B	0.9800
O1—C2	1.367 (3)	C11—H11C	0.9800
O1—C12	1.431 (3)	C12—H12A	0.9800
O4—C9	1.427 (3)	C12—H12B	0.9800
O4—C11	1.431 (3)	C12—H12C	0.9800
O5—C14	1.365 (3)	C13—C14	1.497 (4)
O5—C24	1.425 (3)	C13—C21	1.536 (3)
O6—C16	1.438 (3)	C13—C20	1.541 (4)
O6—H6O	0.842 (10)	C13—H13	1.0000
O7—C21	1.406 (3)	C14—C15	1.328 (3)
O7—C22	1.436 (3)	C15—C16	1.496 (4)
O8—C21	1.429 (3)	C15—H15	0.9500
O8—C23	1.435 (3)	C16—C17	1.543 (4)
C1—C2	1.499 (4)	C16—H16	1.0000
C1—C9	1.533 (3)	C17—C18	1.529 (3)
C1—C8	1.538 (4)	C17—C21	1.534 (3)
C1—H1	1.0000	C17—H17	1.0000
C2—C3	1.329 (3)	C18—C19	1.533 (4)
C3—C4	1.500 (3)	C18—H18A	0.9900
C3—H3	0.9500	C18—H18B	0.9900
C4—C5	1.526 (4)	C19—C20	1.528 (4)

C4—H4	1.0000	C19—H19A	0.9900
C5—C9	1.528 (3)	C19—H19B	0.9900
C5—C6	1.543 (4)	C20—H20A	0.9900
C5—H5	1.0000	C20—H20B	0.9900
C6—C7	1.529 (4)	C22—H22A	0.9800
C6—H6A	0.9900	C22—H22B	0.9800
C6—H6B	0.9900	C22—H22C	0.9800
C7—C8	1.529 (4)	C23—H23A	0.9800
C7—H7A	0.9900	C23—H23B	0.9800
C7—H7B	0.9900	C23—H23C	0.9800
C8—H8A	0.9900	C24—H24A	0.9800
C8—H8B	0.9900	C24—H24B	0.9800
C10—H10A	0.9800	C24—H24C	0.9800

C9—O3—C10	116.1 (2)	H12A—C12—H12B	109.5
C4—O2—H2O	110 (2)	O1—C12—H12C	109.5
C2—O1—C12	116.2 (2)	H12A—C12—H12C	109.5
C9—O4—C11	116.6 (2)	H12B—C12—H12C	109.5
C14—O5—C24	116.6 (2)	C14—C13—C21	109.5 (2)
C16—O6—H6O	106 (2)	C14—C13—C20	110.8 (2)
C21—O7—C22	116.0 (2)	C21—C13—C20	109.1 (2)
C21—O8—C23	116.4 (2)	C14—C13—H13	109.1
C2—C1—C9	109.6 (2)	C21—C13—H13	109.1
C2—C1—C8	109.8 (2)	C20—C13—H13	109.1
C9—C1—C8	109.5 (2)	C15—C14—O5	126.7 (2)
C2—C1—H1	109.3	C15—C14—C13	122.6 (2)
C9—C1—H1	109.3	O5—C14—C13	110.7 (2)
C8—C1—H1	109.3	C14—C15—C16	122.8 (2)
C3—C2—O1	126.4 (2)	C14—C15—H15	118.6
C3—C2—C1	123.2 (2)	C16—C15—H15	118.6
O1—C2—C1	110.3 (2)	O6—C16—C15	108.7 (2)
C2—C3—C4	122.2 (2)	O6—C16—C17	110.7 (2)
C2—C3—H3	118.9	C15—C16—C17	114.2 (2)
C4—C3—H3	118.9	O6—C16—H16	107.7
O2—C4—C3	108.1 (2)	C15—C16—H16	107.7
O2—C4—C5	111.5 (2)	C17—C16—H16	107.7
C3—C4—C5	113.9 (2)	C18—C17—C21	109.5 (2)
O2—C4—H4	107.7	C18—C17—C16	114.9 (2)
C3—C4—H4	107.7	C21—C17—C16	108.0 (2)
C5—C4—H4	107.7	C18—C17—H17	108.1
C4—C5—C9	108.7 (2)	C21—C17—H17	108.1
C4—C5—C6	114.8 (2)	C16—C17—H17	108.1
C9—C5—C6	109.0 (2)	C17—C18—C19	114.0 (2)
C4—C5—H5	108.0	C17—C18—H18A	108.8
C9—C5—H5	108.0	C19—C18—H18A	108.8
C6—C5—H5	108.0	C17—C18—H18B	108.8
C7—C6—C5	114.4 (2)	C19—C18—H18B	108.8
C7—C6—H6A	108.7	H18A—C18—H18B	107.6

C5—C6—H6A	108.7	C20—C19—C18	111.1 (2)
C7—C6—H6B	108.7	C20—C19—H19A	109.4
C5—C6—H6B	108.7	C18—C19—H19A	109.4
H6A—C6—H6B	107.6	C20—C19—H19B	109.4
C6—C7—C8	111.6 (2)	C18—C19—H19B	109.4
C6—C7—H7A	109.3	H19A—C19—H19B	108.0
C8—C7—H7A	109.3	C19—C20—C13	111.6 (2)
C6—C7—H7B	109.3	C19—C20—H20A	109.3
C8—C7—H7B	109.3	C13—C20—H20A	109.3
H7A—C7—H7B	108.0	C19—C20—H20B	109.3
C7—C8—C1	111.1 (2)	C13—C20—H20B	109.3
C7—C8—H8A	109.4	H20A—C20—H20B	108.0
C1—C8—H8A	109.4	O7—C21—O8	109.84 (19)
C7—C8—H8B	109.4	O7—C21—C17	115.2 (2)
C1—C8—H8B	109.4	O8—C21—C17	104.9 (2)
H8A—C8—H8B	108.0	O7—C21—C13	105.2 (2)
O3—C9—O4	109.76 (19)	O8—C21—C13	113.6 (2)
O3—C9—C5	115.0 (2)	C17—C21—C13	108.3 (2)
O4—C9—C5	105.4 (2)	O7—C22—H22A	109.5
O3—C9—C1	105.0 (2)	O7—C22—H22B	109.5
O4—C9—C1	113.5 (2)	H22A—C22—H22B	109.5
C5—C9—C1	108.5 (2)	O7—C22—H22C	109.5
O3—C10—H10A	109.5	H22A—C22—H22C	109.5
O3—C10—H10B	109.5	H22B—C22—H22C	109.5
H10A—C10—H10B	109.5	O8—C23—H23A	109.5
O3—C10—H10C	109.5	O8—C23—H23B	109.5
H10A—C10—H10C	109.5	H23A—C23—H23B	109.5
H10B—C10—H10C	109.5	O8—C23—H23C	109.5
O4—C11—H11A	109.5	H23A—C23—H23C	109.5
O4—C11—H11B	109.5	H23B—C23—H23C	109.5
H11A—C11—H11B	109.5	O5—C24—H24A	109.5
O4—C11—H11C	109.5	O5—C24—H24B	109.5
H11A—C11—H11C	109.5	H24A—C24—H24B	109.5
H11B—C11—H11C	109.5	O5—C24—H24C	109.5
O1—C12—H12A	109.5	H24A—C24—H24C	109.5
O1—C12—H12B	109.5	H24B—C24—H24C	109.5

C12—O1—C2—C3	−3.0 (4)	C24—O5—C14—C15	−1.5 (4)
C12—O1—C2—C1	174.1 (2)	C24—O5—C14—C13	−179.6 (2)
C9—C1—C2—C3	−25.6 (4)	C21—C13—C14—C15	27.9 (4)
C8—C1—C2—C3	94.7 (3)	C20—C13—C14—C15	−92.4 (3)
C9—C1—C2—O1	157.2 (2)	C21—C13—C14—O5	−153.9 (2)
C8—C1—C2—O1	−82.5 (3)	C20—C13—C14—O5	85.8 (3)
O1—C2—C3—C4	−179.8 (2)	O5—C14—C15—C16	177.4 (2)
C1—C2—C3—C4	3.4 (4)	C13—C14—C15—C16	−4.7 (4)
C2—C3—C4—O2	−136.6 (3)	C14—C15—C16—O6	135.7 (3)
C2—C3—C4—C5	−12.2 (4)	C14—C15—C16—C17	11.7 (4)
O2—C4—C5—C9	165.22 (19)	O6—C16—C17—C18	−41.7 (3)

C3—C4—C5—C9	42.6 (3)	C15—C16—C17—C18	81.3 (3)
O2—C4—C5—C6	42.8 (3)	O6—C16—C17—C21	−164.30 (19)
C3—C4—C5—C6	−79.8 (3)	C15—C16—C17—C21	−41.3 (3)
C4—C5—C6—C7	68.5 (3)	C21—C17—C18—C19	54.7 (3)
C9—C5—C6—C7	−53.7 (3)	C16—C17—C18—C19	−67.0 (3)
C5—C6—C7—C8	48.6 (3)	C17—C18—C19—C20	−49.6 (3)
C6—C7—C8—C1	−50.6 (3)	C18—C19—C20—C13	51.3 (3)
C2—C1—C8—C7	−60.8 (3)	C14—C13—C20—C19	61.2 (3)
C9—C1—C8—C7	59.5 (3)	C21—C13—C20—C19	−59.4 (3)
C10—O3—C9—O4	53.5 (3)	C22—O7—C21—O8	−55.6 (3)
C10—O3—C9—C5	−65.1 (3)	C22—O7—C21—C17	62.5 (3)
C10—O3—C9—C1	175.8 (2)	C22—O7—C21—C13	−178.3 (2)
C11—O4—C9—O3	61.6 (3)	C23—O8—C21—O7	−59.8 (3)
C11—O4—C9—C5	−174.1 (2)	C23—O8—C21—C17	175.9 (2)
C11—O4—C9—C1	−55.6 (3)	C23—O8—C21—C13	57.7 (3)
C4—C5—C9—O3	177.56 (19)	C18—C17—C21—O7	56.6 (3)
C6—C5—C9—O3	−56.6 (3)	C16—C17—C21—O7	−177.58 (19)
C4—C5—C9—O4	56.6 (2)	C18—C17—C21—O8	177.5 (2)
C6—C5—C9—O4	−177.5 (2)	C16—C17—C21—O8	−56.7 (2)
C4—C5—C9—C1	−65.2 (3)	C18—C17—C21—C13	−60.9 (3)
C6—C5—C9—C1	60.6 (3)	C16—C17—C21—C13	64.9 (3)
C2—C1—C9—O3	179.1 (2)	C14—C13—C21—O7	178.6 (2)
C8—C1—C9—O3	58.6 (2)	C20—C13—C21—O7	−60.0 (3)
C2—C1—C9—O4	−61.0 (3)	C14—C13—C21—O8	58.4 (3)
C8—C1—C9—O4	178.5 (2)	C20—C13—C21—O8	179.81 (19)
C2—C1—C9—C5	55.7 (3)	C14—C13—C21—C17	−57.7 (3)
C8—C1—C9—C5	−64.8 (3)	C20—C13—C21—C17	63.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···O4^{i}	0.84 (1)	2.03 (1)	2.863 (3)	172 (3)
O2—H2*O*···O8	0.84 (1)	2.02 (1)	2.858 (3)	176 (3)

Symmetry code: (i) *x*+1, *y*, *z*.

4-Methoxy-6-methyl-1-(3-methylbut-2-en-1-yl)-6-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]non-3-ene-2,9-dione (3)

Crystal data

$C_{22}H_{32}O_3$
M_r = 344.47
Monoclinic, $P2_1/n$
a = 14.1871 (6) Å
b = 6.3306 (2) Å
c = 22.4159 (8) Å
β = 101.702 (1)°
V = 1971.39 (13) Å^3
Z = 4
$F(000)$ = 752
D_x = 1.161 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5403 reflections
θ = 2.9–27.0°
μ = 0.08 mm^{-1}
T = 133 K
Plate, colourless
0.18 × 0.14 × 0.04 mm

Data collection

Bruker D8 VENTURE PHOTON II diffractometer
Radiation source: INCOATEC IÂμS microfocus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.687, T_{max} = 0.746
28995 measured reflections
4348 independent reflections
3271 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 27.1°, θ_{min} = 2.9°
h = −18→18
k = −8→7
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.116
S = 1.05
4348 reflections
232 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.8443P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.39938 (7)	0.15883 (17)	0.60348 (5)	0.0219 (2)
O2	0.65032 (8)	0.42454 (18)	0.51454 (5)	0.0248 (3)
O3	0.69009 (8)	0.20509 (19)	0.71052 (5)	0.0270 (3)
C1	0.53136 (10)	0.3264 (2)	0.66586 (7)	0.0180 (3)
H1	0.511136	0.232666	0.696903	0.022*
C2	0.48471 (10)	0.2511 (2)	0.60337 (7)	0.0177 (3)
C11	0.81757 (10)	0.2004 (3)	0.60868 (7)	0.0212 (3)
H11	0.807199	0.084368	0.633448	0.025*
C12	0.85993 (11)	0.1573 (3)	0.56230 (7)	0.0223 (3)
C13	0.89729 (12)	−0.0610 (3)	0.55400 (8)	0.0299 (4)
H13A	0.865158	−0.116923	0.514308	0.045*
H13B	0.884177	−0.153610	0.586396	0.045*
H13C	0.966851	−0.054570	0.555907	0.045*
C14	0.87732 (13)	0.3143 (3)	0.51526 (8)	0.0310 (4)
H14A	0.848722	0.261744	0.474485	0.047*
H14B	0.946743	0.333557	0.518615	0.047*
H14C	0.847832	0.449848	0.522063	0.047*
C15	0.55095 (12)	0.6122 (3)	0.74496 (7)	0.0265 (4)
H15A	0.532511	0.755107	0.754900	0.040*
H15B	0.621187	0.603420	0.750744	0.040*

H15C	0.528252	0.510118	0.771758	0.040*
C16	0.39580 (11)	0.5993 (3)	0.66583 (7)	0.0218 (3)
H16A	0.384466	0.751796	0.671266	0.026*
H16B	0.369708	0.565027	0.622540	0.026*
C17	0.33786 (11)	0.4754 (3)	0.70482 (7)	0.0257 (4)
H17A	0.339038	0.323133	0.694948	0.031*
H17B	0.367411	0.493600	0.748477	0.031*
C18	0.23549 (11)	0.5523 (3)	0.69309 (8)	0.0279 (4)
H18	0.225678	0.687173	0.709382	0.033*
C19	0.15695 (12)	0.4559 (3)	0.66287 (8)	0.0268 (4)
C20	0.15578 (14)	0.2407 (3)	0.63505 (9)	0.0399 (5)
H20A	0.104596	0.155924	0.646702	0.060*
H20B	0.218028	0.171697	0.649642	0.060*
H20C	0.143955	0.253524	0.590581	0.060*
C21	0.06030 (12)	0.5629 (3)	0.65247 (9)	0.0378 (5)
H21A	0.015217	0.476108	0.669694	0.057*
H21B	0.035856	0.580812	0.608633	0.057*
H21C	0.066863	0.701625	0.672309	0.057*
C22	0.34621 (11)	0.0763 (3)	0.54652 (8)	0.0271 (4)
H22A	0.288167	0.004550	0.553438	0.041*
H22B	0.386501	−0.024249	0.529772	0.041*
H22C	0.327832	0.192700	0.517674	0.041*
C3	0.52562 (10)	0.2750 (2)	0.55459 (7)	0.0202 (3)
H3	0.493355	0.222681	0.516124	0.024*
C4	0.61796 (11)	0.3789 (2)	0.55963 (7)	0.0190 (3)
C5	0.67586 (10)	0.4359 (2)	0.62303 (7)	0.0180 (3)
C6	0.65342 (11)	0.6707 (2)	0.63564 (7)	0.0218 (3)
H6A	0.692482	0.713146	0.675594	0.026*
H6B	0.672651	0.761032	0.604069	0.026*
C7	0.54739 (11)	0.7092 (2)	0.63586 (7)	0.0220 (3)
H7A	0.509788	0.691352	0.593857	0.026*
H7B	0.539427	0.857263	0.648144	0.026*
C8	0.50547 (10)	0.5620 (2)	0.67851 (7)	0.0191 (3)
C9	0.63940 (10)	0.3078 (2)	0.67122 (7)	0.0182 (3)
C10	0.78446 (11)	0.4122 (3)	0.62607 (7)	0.0222 (3)
H10A	0.804318	0.519739	0.599017	0.027*
H10B	0.818498	0.444174	0.668169	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0186 (5)	0.0217 (6)	0.0243 (6)	−0.0033 (4)	0.0018 (4)	−0.0049 (5)
O2	0.0266 (6)	0.0293 (6)	0.0191 (6)	0.0028 (5)	0.0061 (5)	0.0040 (5)
O3	0.0232 (6)	0.0330 (7)	0.0229 (6)	0.0051 (5)	0.0002 (5)	0.0084 (5)
C1	0.0191 (7)	0.0180 (7)	0.0164 (7)	0.0000 (6)	0.0026 (6)	0.0009 (6)
C2	0.0160 (7)	0.0134 (7)	0.0221 (7)	0.0018 (5)	0.0000 (6)	0.0001 (6)
C11	0.0162 (7)	0.0226 (8)	0.0235 (8)	−0.0006 (6)	0.0007 (6)	0.0025 (6)
C12	0.0171 (7)	0.0229 (8)	0.0253 (8)	0.0003 (6)	0.0007 (6)	−0.0007 (6)

C13	0.0256 (8)	0.0272 (9)	0.0359 (10)	0.0047 (7)	0.0039 (7)	−0.0028 (8)
C14	0.0327 (9)	0.0318 (10)	0.0308 (9)	0.0006 (7)	0.0119 (7)	0.0016 (8)
C15	0.0246 (8)	0.0327 (9)	0.0213 (8)	−0.0013 (7)	0.0022 (6)	−0.0069 (7)
C16	0.0208 (8)	0.0222 (8)	0.0219 (8)	0.0032 (6)	0.0031 (6)	−0.0022 (6)
C17	0.0224 (8)	0.0319 (9)	0.0231 (8)	0.0017 (7)	0.0050 (6)	−0.0011 (7)
C18	0.0246 (8)	0.0313 (9)	0.0291 (9)	0.0026 (7)	0.0087 (7)	−0.0041 (7)
C19	0.0254 (8)	0.0319 (10)	0.0235 (8)	0.0005 (7)	0.0060 (7)	0.0035 (7)
C20	0.0359 (10)	0.0408 (12)	0.0402 (11)	−0.0035 (9)	0.0009 (8)	−0.0066 (9)
C21	0.0230 (9)	0.0478 (12)	0.0417 (11)	0.0009 (8)	0.0048 (8)	0.0060 (9)
C22	0.0212 (8)	0.0291 (9)	0.0281 (9)	−0.0046 (7)	−0.0017 (7)	−0.0087 (7)
C3	0.0205 (7)	0.0212 (8)	0.0170 (7)	0.0018 (6)	−0.0008 (6)	−0.0037 (6)
C4	0.0203 (7)	0.0165 (7)	0.0194 (8)	0.0054 (6)	0.0022 (6)	0.0013 (6)
C5	0.0172 (7)	0.0185 (8)	0.0180 (7)	−0.0003 (6)	0.0025 (6)	−0.0006 (6)
C6	0.0241 (8)	0.0176 (8)	0.0245 (8)	−0.0014 (6)	0.0065 (6)	−0.0012 (6)
C7	0.0242 (8)	0.0159 (7)	0.0262 (8)	0.0026 (6)	0.0058 (6)	−0.0014 (6)
C8	0.0198 (7)	0.0201 (8)	0.0170 (7)	0.0013 (6)	0.0025 (6)	−0.0025 (6)
C9	0.0207 (7)	0.0163 (7)	0.0161 (7)	0.0005 (6)	0.0003 (6)	−0.0018 (6)
C10	0.0183 (7)	0.0236 (8)	0.0242 (8)	−0.0015 (6)	0.0035 (6)	−0.0002 (6)

Geometric parameters (Å, º)

O1—C2	1.3445 (17)	C17—H17A	0.9900
O1—C22	1.4425 (19)	C17—H17B	0.9900
O2—C4	1.2263 (18)	C18—C19	1.329 (2)
O3—C9	1.2078 (18)	C18—H18	0.9500
C1—C2	1.501 (2)	C19—C20	1.497 (3)
C1—C9	1.518 (2)	C19—C21	1.505 (2)
C1—C8	1.575 (2)	C20—H20A	0.9800
C1—H1	1.0000	C20—H20B	0.9800
C2—C3	1.346 (2)	C20—H20C	0.9800
C11—C12	1.331 (2)	C21—H21A	0.9800
C11—C10	1.498 (2)	C21—H21B	0.9800
C11—H11	0.9500	C21—H21C	0.9800
C12—C13	1.505 (2)	C22—H22A	0.9800
C12—C14	1.505 (2)	C22—H22B	0.9800
C13—H13A	0.9800	C22—H22C	0.9800
C13—H13B	0.9800	C3—C4	1.450 (2)
C13—H13C	0.9800	C3—H3	0.9500
C14—H14A	0.9800	C4—C5	1.533 (2)
C14—H14B	0.9800	C5—C9	1.523 (2)
C14—H14C	0.9800	C5—C10	1.536 (2)
C15—C8	1.532 (2)	C5—C6	1.558 (2)
C15—H15A	0.9800	C6—C7	1.525 (2)
C15—H15B	0.9800	C6—H6A	0.9900
C15—H15C	0.9800	C6—H6B	0.9900
C16—C17	1.532 (2)	C7—C8	1.538 (2)
C16—C8	1.542 (2)	C7—H7A	0.9900
C16—H16A	0.9900	C7—H7B	0.9900

C16—H16B	0.9900	C10—H10A	0.9900
C17—C18	1.503 (2)	C10—H10B	0.9900
C2—O1—C22	117.71 (12)	C19—C20—H20C	109.5
C2—C1—C9	107.24 (12)	H20A—C20—H20C	109.5
C2—C1—C8	113.22 (12)	H20B—C20—H20C	109.5
C9—C1—C8	109.15 (12)	C19—C21—H21A	109.5
C2—C1—H1	109.1	C19—C21—H21B	109.5
C9—C1—H1	109.1	H21A—C21—H21B	109.5
C8—C1—H1	109.1	C19—C21—H21C	109.5
O1—C2—C3	125.94 (14)	H21A—C21—H21C	109.5
O1—C2—C1	111.29 (12)	H21B—C21—H21C	109.5
C3—C2—C1	122.77 (13)	O1—C22—H22A	109.5
C12—C11—C10	127.01 (15)	O1—C22—H22B	109.5
C12—C11—H11	116.5	H22A—C22—H22B	109.5
C10—C11—H11	116.5	O1—C22—H22C	109.5
C11—C12—C13	120.73 (15)	H22A—C22—H22C	109.5
C11—C12—C14	125.18 (15)	H22B—C22—H22C	109.5
C13—C12—C14	114.07 (14)	C2—C3—C4	121.28 (14)
C12—C13—H13A	109.5	C2—C3—H3	119.4
C12—C13—H13B	109.5	C4—C3—H3	119.4
H13A—C13—H13B	109.5	O2—C4—C3	121.74 (14)
C12—C13—H13C	109.5	O2—C4—C5	119.27 (14)
H13A—C13—H13C	109.5	C3—C4—C5	118.99 (13)
H13B—C13—H13C	109.5	C9—C5—C4	109.70 (12)
C12—C14—H14A	109.5	C9—C5—C10	113.49 (12)
C12—C14—H14B	109.5	C4—C5—C10	111.23 (12)
H14A—C14—H14B	109.5	C9—C5—C6	105.56 (12)
C12—C14—H14C	109.5	C4—C5—C6	107.55 (12)
H14A—C14—H14C	109.5	C10—C5—C6	108.98 (12)
H14B—C14—H14C	109.5	C7—C6—C5	113.00 (12)
C8—C15—H15A	109.5	C7—C6—H6A	109.0
C8—C15—H15B	109.5	C5—C6—H6A	109.0
H15A—C15—H15B	109.5	C7—C6—H6B	109.0
C8—C15—H15C	109.5	C5—C6—H6B	109.0
H15A—C15—H15C	109.5	H6A—C6—H6B	107.8
H15B—C15—H15C	109.5	C6—C7—C8	114.29 (13)
C17—C16—C8	117.03 (13)	C6—C7—H7A	108.7
C17—C16—H16A	108.0	C8—C7—H7A	108.7
C8—C16—H16A	108.0	C6—C7—H7B	108.7
C17—C16—H16B	108.0	C8—C7—H7B	108.7
C8—C16—H16B	108.0	H7A—C7—H7B	107.6
H16A—C16—H16B	107.3	C15—C8—C7	109.82 (13)
C18—C17—C16	110.21 (14)	C15—C8—C16	110.96 (12)
C18—C17—H17A	109.6	C7—C8—C16	107.18 (12)
C16—C17—H17A	109.6	C15—C8—C1	107.69 (13)
C18—C17—H17B	109.6	C7—C8—C1	109.14 (12)
C16—C17—H17B	109.6	C16—C8—C1	112.04 (12)

H17A—C17—H17B	108.1	O3—C9—C1	122.82 (14)
C19—C18—C17	128.37 (16)	O3—C9—C5	124.51 (14)
C19—C18—H18	115.8	C1—C9—C5	112.66 (12)
C17—C18—H18	115.8	C11—C10—C5	116.15 (13)
C18—C19—C20	124.57 (16)	C11—C10—H10A	108.2
C18—C19—C21	121.04 (17)	C5—C10—H10A	108.2
C20—C19—C21	114.36 (16)	C11—C10—H10B	108.2
C19—C20—H20A	109.5	C5—C10—H10B	108.2
C19—C20—H20B	109.5	H10A—C10—H10B	107.4
H20A—C20—H20B	109.5		

C22—O1—C2—C3	0.3 (2)	C6—C7—C8—C15	67.77 (17)
C22—O1—C2—C1	−179.43 (13)	C6—C7—C8—C16	−171.61 (13)
C9—C1—C2—O1	147.89 (12)	C6—C7—C8—C1	−50.07 (17)
C8—C1—C2—O1	−91.66 (15)	C17—C16—C8—C15	−57.88 (18)
C9—C1—C2—C3	−31.9 (2)	C17—C16—C8—C7	−177.78 (13)
C8—C1—C2—C3	88.60 (17)	C17—C16—C8—C1	62.53 (17)
C10—C11—C12—C13	174.40 (15)	C2—C1—C8—C15	175.62 (12)
C10—C11—C12—C14	−4.1 (3)	C9—C1—C8—C15	−65.02 (15)
C8—C16—C17—C18	171.90 (13)	C2—C1—C8—C7	−65.22 (16)
C16—C17—C18—C19	107.5 (2)	C9—C1—C8—C7	54.14 (16)
C17—C18—C19—C20	1.7 (3)	C2—C1—C8—C16	53.33 (16)
C17—C18—C19—C21	−176.41 (16)	C9—C1—C8—C16	172.69 (12)
O1—C2—C3—C4	179.48 (14)	C2—C1—C9—O3	−122.71 (16)
C1—C2—C3—C4	−0.8 (2)	C8—C1—C9—O3	114.28 (16)
C2—C3—C4—O2	−170.94 (15)	C2—C1—C9—C5	58.69 (16)
C2—C3—C4—C5	8.2 (2)	C8—C1—C9—C5	−64.32 (15)
O2—C4—C5—C9	−162.44 (13)	C4—C5—C9—O3	128.82 (16)
C3—C4—C5—C9	18.39 (18)	C10—C5—C9—O3	3.7 (2)
O2—C4—C5—C10	−36.05 (19)	C6—C5—C9—O3	−115.57 (16)
C3—C4—C5—C10	144.78 (14)	C4—C5—C9—C1	−52.61 (16)
O2—C4—C5—C6	83.22 (16)	C10—C5—C9—C1	−177.70 (12)
C3—C4—C5—C6	−95.96 (15)	C6—C5—C9—C1	63.01 (15)
C9—C5—C6—C7	−55.72 (16)	C12—C11—C10—C5	117.26 (17)
C4—C5—C6—C7	61.36 (16)	C9—C5—C10—C11	68.76 (17)
C10—C5—C6—C7	−177.95 (13)	C4—C5—C10—C11	−55.51 (18)
C5—C6—C7—C8	52.82 (18)	C6—C5—C10—C11	−173.92 (13)

4-*tert*-Butyl-4-hydroxy-2-methoxy-8-methyl-7-(3-methylbut-2-en-1-yl)-8-(4-methylpent-3-en-1-yl)bicyclo[3.3.1]non-2-en-9-one (4)

Crystal data

$C_{26}H_{42}O_3$
M_r = 402.59
Monoclinic, $P2_1/c$
a = 15.1165 (5) Å
b = 13.9068 (4) Å
c = 12.8150 (4) Å
β = 113.218 (1)°
V = 2475.81 (13) Å^3
Z = 4
$F(000)$ = 888
D_x = 1.080 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9769 reflections
θ = 2.9–27.1°

μ = 0.07 mm^{-1}
T = 143 K

Prism, colourless
0.26 × 0.16 × 0.08 mm

Data collection

Bruker D8 VENTURE PHOTON II diffractometer
Radiation source: INCOATEC IÂμS microfocus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.704, T_{max} = 0.746

87917 measured reflections
5484 independent reflections
4697 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.1°, θ_{min} = 2.1°
h = −19→19
k = −16→17
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.108
S = 1.05
5484 reflections
274 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.8245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.58921 (6)	0.47108 (5)	0.43047 (6)	0.02376 (18)
O2	0.51178 (6)	0.14696 (6)	0.37950 (7)	0.02551 (18)
H2	0.5478 (10)	0.1689 (11)	0.3487 (12)	0.038*
O3	0.61221 (6)	0.30868 (6)	0.73617 (6)	0.02674 (19)
C1	0.65561 (7)	0.36534 (7)	0.58638 (9)	0.0191 (2)
H1	0.668130	0.427362	0.629287	0.023*
C2	0.58011 (7)	0.38158 (7)	0.46865 (9)	0.0187 (2)
C3	0.51410 (8)	0.31676 (8)	0.41130 (9)	0.0202 (2)
H3	0.470212	0.333360	0.336969	0.024*
C4	0.50402 (8)	0.21886 (7)	0.45585 (9)	0.0198 (2)
C5	0.58310 (8)	0.20205 (7)	0.57770 (9)	0.0202 (2)
H5	0.556494	0.158196	0.620023	0.024*
C6	0.67741 (8)	0.15818 (8)	0.57903 (10)	0.0229 (2)
H6A	0.718889	0.140699	0.658210	0.028*
H6B	0.661579	0.098106	0.533934	0.028*
C7	0.73503 (8)	0.22364 (8)	0.53245 (9)	0.0210 (2)
H7	0.695333	0.232637	0.449626	0.025*
C8	0.75364 (7)	0.32539 (8)	0.58735 (9)	0.0205 (2)

C9	0.61403 (7)	0.29414 (8)	0.64324 (9)	0.0197 (2)
C10	0.82710 (8)	0.16941 (9)	0.54227 (10)	0.0276 (2)
H10A	0.869428	0.213478	0.522244	0.033*
H10B	0.862400	0.148432	0.621810	0.033*
C11	0.80410 (8)	0.08302 (9)	0.46537 (10)	0.0274 (2)
H11	0.752582	0.090867	0.393411	0.033*
C12	0.84620 (9)	−0.00269 (9)	0.48468 (11)	0.0318 (3)
C13	0.92703 (13)	−0.03188 (12)	0.59291 (14)	0.0542 (4)
H13A	0.982739	−0.051060	0.576768	0.081*
H13B	0.906467	−0.086094	0.626814	0.081*
H13C	0.944762	0.022430	0.645939	0.081*
C14	0.81468 (12)	−0.07908 (11)	0.39421 (15)	0.0473 (4)
H14A	0.758079	−0.056563	0.329342	0.071*
H14B	0.798374	−0.137879	0.424891	0.071*
H14C	0.867064	−0.092552	0.369481	0.071*
C15	0.82707 (8)	0.32225 (9)	0.71095 (10)	0.0272 (2)
H15A	0.890430	0.304716	0.712693	0.041*
H15B	0.806850	0.274391	0.753214	0.041*
H15C	0.830812	0.385648	0.745833	0.041*
C16	0.78978 (8)	0.39199 (8)	0.51636 (10)	0.0255 (2)
H16A	0.848819	0.363159	0.513943	0.031*
H16B	0.740565	0.392664	0.437600	0.031*
C17	0.81238 (9)	0.49662 (9)	0.55609 (11)	0.0331 (3)
H17A	0.756181	0.525580	0.565571	0.040*
H17B	0.867730	0.498447	0.630446	0.040*
C18	0.83575 (9)	0.55326 (9)	0.47056 (12)	0.0347 (3)
H18	0.790871	0.547761	0.394072	0.042*
C19	0.91070 (9)	0.60995 (9)	0.48753 (12)	0.0336 (3)
C20	0.92557 (11)	0.65611 (12)	0.38952 (14)	0.0478 (4)
H20A	0.870648	0.641423	0.318709	0.072*
H20B	0.984685	0.631054	0.385359	0.072*
H20C	0.931060	0.725920	0.400634	0.072*
C21	0.98769 (13)	0.63083 (14)	0.60163 (15)	0.0597 (5)
H21A	1.048455	0.602150	0.606663	0.090*
H21B	0.969451	0.603470	0.660797	0.090*
H21C	0.995622	0.700564	0.612238	0.090*
C22	0.53199 (10)	0.49151 (9)	0.31424 (10)	0.0335 (3)
H22A	0.549538	0.554761	0.294582	0.050*
H22B	0.463789	0.491517	0.302071	0.050*
H22C	0.543299	0.442285	0.266167	0.050*
C23	0.40054 (8)	0.20444 (8)	0.45525 (10)	0.0244 (2)
C24	0.38671 (9)	0.26723 (9)	0.54585 (11)	0.0298 (3)
H24A	0.402128	0.334181	0.535978	0.045*
H24B	0.429455	0.244724	0.621440	0.045*
H24C	0.319688	0.262973	0.538096	0.045*
C25	0.32344 (9)	0.23243 (11)	0.33952 (11)	0.0378 (3)
H25A	0.335664	0.198822	0.279316	0.057*
H25B	0.325506	0.302032	0.328713	0.057*

H25C	0.259812	0.214354	0.336505	0.057*
C26	0.38494 (9)	0.09832 (9)	0.47587 (12)	0.0345 (3)
H26A	0.320208	0.089861	0.474739	0.052*
H26B	0.432888	0.078417	0.549936	0.052*
H26C	0.391761	0.058869	0.416106	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0315 (4)	0.0169 (4)	0.0221 (4)	−0.0007 (3)	0.0097 (3)	0.0035 (3)
O2	0.0346 (4)	0.0228 (4)	0.0247 (4)	−0.0073 (3)	0.0177 (3)	−0.0078 (3)
O3	0.0294 (4)	0.0363 (5)	0.0168 (4)	−0.0006 (3)	0.0115 (3)	−0.0018 (3)
C1	0.0230 (5)	0.0177 (5)	0.0171 (5)	−0.0021 (4)	0.0086 (4)	−0.0023 (4)
C2	0.0236 (5)	0.0171 (5)	0.0183 (5)	0.0011 (4)	0.0112 (4)	0.0010 (4)
C3	0.0239 (5)	0.0213 (5)	0.0155 (5)	−0.0003 (4)	0.0079 (4)	0.0008 (4)
C4	0.0247 (5)	0.0186 (5)	0.0181 (5)	−0.0039 (4)	0.0107 (4)	−0.0032 (4)
C5	0.0246 (5)	0.0191 (5)	0.0196 (5)	−0.0018 (4)	0.0117 (4)	0.0021 (4)
C6	0.0268 (5)	0.0188 (5)	0.0250 (5)	0.0012 (4)	0.0121 (4)	0.0027 (4)
C7	0.0218 (5)	0.0210 (5)	0.0213 (5)	0.0004 (4)	0.0096 (4)	−0.0002 (4)
C8	0.0204 (5)	0.0219 (5)	0.0196 (5)	−0.0016 (4)	0.0084 (4)	−0.0009 (4)
C9	0.0193 (5)	0.0237 (5)	0.0160 (5)	0.0018 (4)	0.0068 (4)	0.0013 (4)
C10	0.0239 (5)	0.0282 (6)	0.0318 (6)	0.0026 (4)	0.0120 (5)	−0.0021 (5)
C11	0.0279 (6)	0.0303 (6)	0.0269 (6)	0.0033 (5)	0.0140 (5)	−0.0008 (5)
C12	0.0348 (6)	0.0296 (6)	0.0382 (7)	0.0040 (5)	0.0222 (6)	0.0022 (5)
C13	0.0608 (10)	0.0476 (9)	0.0506 (9)	0.0248 (8)	0.0181 (8)	0.0114 (7)
C14	0.0577 (9)	0.0333 (7)	0.0629 (10)	0.0009 (6)	0.0364 (8)	−0.0108 (7)
C15	0.0239 (5)	0.0318 (6)	0.0230 (5)	−0.0012 (4)	0.0062 (4)	−0.0010 (5)
C16	0.0237 (5)	0.0267 (6)	0.0287 (6)	−0.0035 (4)	0.0131 (5)	0.0012 (4)
C17	0.0332 (6)	0.0293 (6)	0.0369 (7)	−0.0111 (5)	0.0140 (5)	−0.0011 (5)
C18	0.0268 (6)	0.0327 (6)	0.0399 (7)	−0.0055 (5)	0.0082 (5)	0.0079 (5)
C19	0.0278 (6)	0.0265 (6)	0.0461 (8)	−0.0023 (5)	0.0141 (5)	0.0053 (5)
C20	0.0330 (7)	0.0471 (8)	0.0615 (10)	−0.0042 (6)	0.0167 (7)	0.0222 (7)
C21	0.0559 (10)	0.0690 (12)	0.0518 (10)	−0.0365 (9)	0.0186 (8)	−0.0119 (8)
C22	0.0497 (8)	0.0228 (6)	0.0247 (6)	0.0035 (5)	0.0109 (5)	0.0072 (5)
C23	0.0237 (5)	0.0264 (6)	0.0250 (5)	−0.0062 (4)	0.0115 (4)	−0.0040 (4)
C24	0.0262 (6)	0.0340 (6)	0.0332 (6)	−0.0033 (5)	0.0160 (5)	−0.0062 (5)
C25	0.0253 (6)	0.0515 (8)	0.0318 (7)	−0.0085 (5)	0.0062 (5)	−0.0019 (6)
C26	0.0366 (7)	0.0293 (6)	0.0444 (7)	−0.0127 (5)	0.0232 (6)	−0.0050 (5)

Geometric parameters (Å, º)

O1—C2	1.3640 (12)	C14—H14B	0.9800
O1—C22	1.4254 (14)	C14—H14C	0.9800
O2—C4	1.4357 (12)	C15—H15A	0.9800
O2—H2	0.846 (9)	C15—H15B	0.9800
O3—C9	1.2189 (13)	C15—H15C	0.9800
C1—C9	1.5058 (14)	C16—C17	1.5350 (17)
C1—C2	1.5073 (14)	C16—H16A	0.9900

C1—C8	1.5781 (14)	C16—H16B	0.9900
C1—H1	1.0000	C17—C18	1.5005 (18)
C2—C3	1.3305 (15)	C17—H17A	0.9900
C3—C4	1.5071 (14)	C17—H17B	0.9900
C3—H3	0.9500	C18—C19	1.3261 (17)
C4—C5	1.5652 (14)	C18—H18	0.9500
C4—C23	1.5741 (15)	C19—C21	1.495 (2)
C5—C9	1.5016 (15)	C19—C20	1.5042 (19)
C5—C6	1.5446 (15)	C20—H20A	0.9800
C5—H5	1.0000	C20—H20B	0.9800
C6—C7	1.5342 (15)	C20—H20C	0.9800
C6—H6A	0.9900	C21—H21A	0.9800
C6—H6B	0.9900	C21—H21B	0.9800
C7—C10	1.5439 (15)	C21—H21C	0.9800
C7—C8	1.5558 (15)	C22—H22A	0.9800
C7—H7	1.0000	C22—H22B	0.9800
C8—C15	1.5350 (15)	C22—H22C	0.9800
C8—C16	1.5414 (15)	C23—C24	1.5315 (16)
C10—C11	1.5051 (16)	C23—C25	1.5319 (17)
C10—H10A	0.9900	C23—C26	1.5338 (16)
C10—H10B	0.9900	C24—H24A	0.9800
C11—C12	1.3277 (17)	C24—H24B	0.9800
C11—H11	0.9500	C24—H24C	0.9800
C12—C13	1.498 (2)	C25—H25A	0.9800
C12—C14	1.5047 (19)	C25—H25B	0.9800
C13—H13A	0.9800	C25—H25C	0.9800
C13—H13B	0.9800	C26—H26A	0.9800
C13—H13C	0.9800	C26—H26B	0.9800
C14—H14A	0.9800	C26—H26C	0.9800

C2—O1—C22	116.82 (9)	H14A—C14—H14C	109.5
C4—O2—H2	107.9 (11)	H14B—C14—H14C	109.5
C9—C1—C2	106.68 (8)	C8—C15—H15A	109.5
C9—C1—C8	109.54 (8)	C8—C15—H15B	109.5
C2—C1—C8	113.50 (8)	H15A—C15—H15B	109.5
C9—C1—H1	109.0	C8—C15—H15C	109.5
C2—C1—H1	109.0	H15A—C15—H15C	109.5
C8—C1—H1	109.0	H15B—C15—H15C	109.5
C3—C2—O1	125.44 (10)	C17—C16—C8	117.27 (10)
C3—C2—C1	123.95 (9)	C17—C16—H16A	108.0
O1—C2—C1	110.61 (9)	C8—C16—H16A	108.0
C2—C3—C4	124.65 (9)	C17—C16—H16B	108.0
C2—C3—H3	117.7	C8—C16—H16B	108.0
C4—C3—H3	117.7	H16A—C16—H16B	107.2
O2—C4—C3	108.86 (8)	C18—C17—C16	109.94 (11)
O2—C4—C5	109.90 (8)	C18—C17—H17A	109.7
C3—C4—C5	111.18 (8)	C16—C17—H17A	109.7
O2—C4—C23	104.83 (8)	C18—C17—H17B	109.7

C3—C4—C23	111.22 (9)	C16—C17—H17B	109.7
C5—C4—C23	110.64 (8)	H17A—C17—H17B	108.2
C9—C5—C6	104.37 (8)	C19—C18—C17	128.62 (13)
C9—C5—C4	112.18 (8)	C19—C18—H18	115.7
C6—C5—C4	114.12 (9)	C17—C18—H18	115.7
C9—C5—H5	108.7	C18—C19—C21	124.14 (13)
C6—C5—H5	108.7	C18—C19—C20	121.07 (13)
C4—C5—H5	108.7	C21—C19—C20	114.76 (12)
C7—C6—C5	115.11 (9)	C19—C20—H20A	109.5
C7—C6—H6A	108.5	C19—C20—H20B	109.5
C5—C6—H6A	108.5	H20A—C20—H20B	109.5
C7—C6—H6B	108.5	C19—C20—H20C	109.5
C5—C6—H6B	108.5	H20A—C20—H20C	109.5
H6A—C6—H6B	107.5	H20B—C20—H20C	109.5
C6—C7—C10	108.08 (9)	C19—C21—H21A	109.5
C6—C7—C8	113.13 (9)	C19—C21—H21B	109.5
C10—C7—C8	114.26 (9)	H21A—C21—H21B	109.5
C6—C7—H7	107.0	C19—C21—H21C	109.5
C10—C7—H7	107.0	H21A—C21—H21C	109.5
C8—C7—H7	107.0	H21B—C21—H21C	109.5
C15—C8—C16	110.22 (9)	O1—C22—H22A	109.5
C15—C8—C7	111.66 (9)	O1—C22—H22B	109.5
C16—C8—C7	108.81 (9)	H22A—C22—H22B	109.5
C15—C8—C1	108.24 (8)	O1—C22—H22C	109.5
C16—C8—C1	109.51 (9)	H22A—C22—H22C	109.5
C7—C8—C1	108.35 (8)	H22B—C22—H22C	109.5
O3—C9—C5	124.47 (10)	C24—C23—C25	108.05 (10)
O3—C9—C1	122.56 (10)	C24—C23—C26	109.99 (10)
C5—C9—C1	112.80 (8)	C25—C23—C26	107.54 (10)
C11—C10—C7	111.61 (9)	C24—C23—C4	110.86 (9)
C11—C10—H10A	109.3	C25—C23—C4	110.35 (9)
C7—C10—H10A	109.3	C26—C23—C4	109.98 (9)
C11—C10—H10B	109.3	C23—C24—H24A	109.5
C7—C10—H10B	109.3	C23—C24—H24B	109.5
H10A—C10—H10B	108.0	H24A—C24—H24B	109.5
C12—C11—C10	128.65 (12)	C23—C24—H24C	109.5
C12—C11—H11	115.7	H24A—C24—H24C	109.5
C10—C11—H11	115.7	H24B—C24—H24C	109.5
C11—C12—C13	124.87 (13)	C23—C25—H25A	109.5
C11—C12—C14	120.48 (13)	C23—C25—H25B	109.5
C13—C12—C14	114.64 (12)	H25A—C25—H25B	109.5
C12—C13—H13A	109.5	C23—C25—H25C	109.5
C12—C13—H13B	109.5	H25A—C25—H25C	109.5
H13A—C13—H13B	109.5	H25B—C25—H25C	109.5
C12—C13—H13C	109.5	C23—C26—H26A	109.5
H13A—C13—H13C	109.5	C23—C26—H26B	109.5
H13B—C13—H13C	109.5	H26A—C26—H26B	109.5
C12—C14—H14A	109.5	C23—C26—H26C	109.5

C12—C14—H14B	109.5	H26A—C26—H26C	109.5
H14A—C14—H14B	109.5	H26B—C26—H26C	109.5
C12—C14—H14C	109.5		

C22—O1—C2—C3	−9.12 (16)	C9—C1—C8—C7	54.45 (10)
C22—O1—C2—C1	171.02 (9)	C2—C1—C8—C7	−64.65 (11)
C9—C1—C2—C3	−27.68 (14)	C6—C5—C9—O3	−111.33 (11)
C8—C1—C2—C3	93.05 (12)	C4—C5—C9—O3	124.61 (11)
C9—C1—C2—O1	152.17 (8)	C6—C5—C9—C1	64.07 (11)
C8—C1—C2—O1	−87.10 (10)	C4—C5—C9—C1	−59.99 (11)
O1—C2—C3—C4	−178.78 (9)	C2—C1—C9—O3	−128.15 (10)
C1—C2—C3—C4	1.06 (17)	C8—C1—C9—O3	108.61 (11)
C2—C3—C4—O2	−122.62 (11)	C2—C1—C9—C5	56.35 (11)
C2—C3—C4—C5	−1.41 (14)	C8—C1—C9—C5	−66.88 (11)
C2—C3—C4—C23	122.37 (11)	C6—C7—C10—C11	66.44 (12)
O2—C4—C5—C9	150.21 (8)	C8—C7—C10—C11	−166.66 (9)
C3—C4—C5—C9	29.61 (12)	C7—C10—C11—C12	−142.25 (12)
C23—C4—C5—C9	−94.50 (10)	C10—C11—C12—C13	1.6 (2)
O2—C4—C5—C6	31.76 (11)	C10—C11—C12—C14	−177.64 (12)
C3—C4—C5—C6	−88.83 (10)	C15—C8—C16—C17	−57.38 (13)
C23—C4—C5—C6	147.06 (9)	C7—C8—C16—C17	179.86 (10)
C9—C5—C6—C7	−55.79 (11)	C1—C8—C16—C17	61.59 (12)
C4—C5—C6—C7	67.01 (12)	C8—C16—C17—C18	−173.70 (10)
C5—C6—C7—C10	178.96 (9)	C16—C17—C18—C19	−129.72 (15)
C5—C6—C7—C8	51.40 (12)	C17—C18—C19—C21	−2.1 (2)
C6—C7—C8—C15	71.38 (11)	C17—C18—C19—C20	175.86 (14)
C10—C7—C8—C15	−52.86 (12)	O2—C4—C23—C24	172.12 (9)
C6—C7—C8—C16	−166.73 (9)	C3—C4—C23—C24	−70.39 (12)
C10—C7—C8—C16	69.03 (11)	C5—C4—C23—C24	53.69 (12)
C6—C7—C8—C1	−47.73 (11)	O2—C4—C23—C25	−68.21 (11)
C10—C7—C8—C1	−171.97 (9)	C3—C4—C23—C25	49.28 (12)
C9—C1—C8—C15	−66.80 (11)	C5—C4—C23—C25	173.36 (9)
C2—C1—C8—C15	174.10 (9)	O2—C4—C23—C26	50.27 (11)
C9—C1—C8—C16	173.01 (8)	C3—C4—C23—C26	167.75 (9)
C2—C1—C8—C16	53.90 (11)	C5—C4—C23—C26	−68.16 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.85 (1)	2.06 (1)	2.8736 (11)	162 (2)

Symmetry code: (i) *x*, −*y*+1/2, *z*−1/2.