Deciphering composition and connectivity of a natural product with the assistance of MS and 2D NMR

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A complementary application of three analytical techniques, *viz.* multidimensional nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), and single-crystal X-ray diffractometry was required to identify and refine two natural products isolated from *Milletia versicolor* and solvent of crystallization. The two compounds, namely 3-(2*H*-1,3-benzodioxol-5-yl)-6-methoxy-8,8-dimethyl-4*H*,8*H*-pyrano[2,3-*h*]chromen-4-one, or durmillone, (I), and (2*E*)-1-(4-[[[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]oxy]-2-hydroxyphenyl]-3-(4-hydroxyphenyl)prop-2-en-1-one, (II), could not be separated by routine column chromatography and cocrystallized in a 2:1 ratio with 0.13 molecules of ethanol solvent. Compound (II) and ethanol could not be initially identified by single-crystal X-ray analysis due to complex disorder in the aliphatic chain region of (II). Mass spectrometry ensured that (II) represented only one species disordered over several positions in the solid state, rather than several species cohabitating on the same crystallographic site. The atomic identification and connectivity in (II) were established by several 2D (two-dimensional) NMR techniques, which in turn relied on a knowledge of its exact mass. The derived connectivity was then used in the single-crystal analysis to model the disorder of the aliphatic chain in (II) over three positions and allowed identification of a partially occupied ethanol solvent molecule that was disordered over an inversion center. The disordered moieties were refined with restraints and constraints.

1. Introduction

Flavonoids and isoflavonoids are recognized mostly as coming from the plant family Fabaceae (Veitch, 2007, 2009, 2013). Compounds isolated from the roots, leaves, and stem bark of *Milletia versicolor* (from the Fabaceae family) are of interest because the extracts from this plant have been shown to possess anti-inflammatory properties (Fotsing *et al.*, 2003).

The goals of the current study were to solvent extract different parts of the botanically isolated plants with organic solvents, and chromatographically isolate and characterize the secondary metabolites responsible for the observed bioactivity. Unequivocal identification of the constituents of the extract posed significant challenges due to the difficulty of separation of the components. In the present work, the two compounds in question could not be separated by the available laboratory methods, including column chromatography and preparative thin-layer chromatography (TLC). Frequently, we obtain novel compounds for which there may be

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no standards, thus the only way of elucidating structures is by using complementary spectroscopic and X-ray diffraction techniques.

This applies both to natural products and to their synthetically prepared congeners. In the fortunate instances when crystals of the product(s) are available, single-crystal X-ray diffraction (SCXRD) is used to authenticate the structures and possibly establish their absolute configuration. Recent examples of natural compounds whose structures were first elucidated by spectroscopic techniques and subsequently confirmed by SCXRD, include bioactive isoflavonoid phytochemicals extracted from *Garcinia nervosa* (Parveen *et al.*, 2017), novel isoflavonoids from *Cassia siamea* (Parveen *et al.*, 2016), 12 new flavan derivatives from *Populus balsamifera* (Simard *et al.*, 2014), a number of natural products with extensive antimicrobial properties (Saleem *et al.*, 2010), a novel iridoid compound from *Torricellia angulata* var. *intermedia* (Liang *et al.*, 2009), bioactive diterpenes from *Croton steenkampianus* (Adelekan *et al.*, 2008), extracts of diterpenoid glycosides from *Gleichenia quadripartite* (Socolsky *et al.*, 2007), flavonoids from the roots of *Dioclea grandiflora* (Lemos *et al.*, 2006), a novel diterpenoid from *Ballota limbata* (Riaz *et al.*, 2004), and novel isoflavones from *Ceiba pentandra* (Ngounou *et al.*, 2000).

Solution 1D and 2D (one- and two-dimensional) NMR techniques have become common for determining chemically specific detailed structural information about organic and organometallic compounds (Claridge, 2016; Friebolin, 2010; Berger & Braun, 2004). In our case, the interpretation of the NMR spectrum of the yet unknown (II) was somewhat complicated by the presence of a second species, *i.e.* (I), but it was possible to obtain local structural information about (II) and subsequently build a multiconformer crystallographic model.

We report herein structural studies of two natural products isolated from the stem bark of *Millettia versicolor*, namely durmillone, (I), and (2*E*)-1-(4-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]oxy)-2-hydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one, (II), with a detailed interpretation of the 2D NMR and MS spectra, and a description of the crystallographic

Table 1

Full assignment of unknown species (X) that was later established as (II) (see Fig. 1).

Label	¹ H (ppm)	¹³ C (ppm)	Predicted ¹³ C (ppm)
1	4.59	67.3	65.4
2	5.48	118.5	119.6
3	—	142.3	142.8
4	1.75	16.8	16.7
5	2.09	39.5	39.6
6	2.13	26.3	26.3
7	5.09	123.6	123.8
8	—	132.0	132.2
9	1.68	25.8	25.8
10	1.61	17.7	17.7
11	—	165.6	165.3
12	6.48	101.7	101.6
13	13.55 (OH)	166.6	166.6
14	—	114.0	114.0
15	7.82	131.1	131.1
16	6.49	108.2	111.0
17	—	191.8	191.7
18	7.45	117.8	117.5
19	7.84	144.2	145.9
20	—	127.4	127.6
21	7.55	130.5	130.5
22	6.88	116.0	116.1
23	—	158.4	158.4

refinement. These compounds form a 2(I):(II) cocrystal, with 0.13 molecules of solvent ethanol (see Scheme 1).

2. Experimental

2.1. Synthesis and crystallization

The *Millettia versicolor* stem bark was collected in Cameroon and the details recorded at Herbar National du Cameroun (HNC) under voucher specimen 45582 HNC. The stem bark was air dried, finely ground, and stored. About 500 g of the dried stem bark were weighed and soaked at room temperature and pressure in 1.6 l of a 1:1 (v/v) mixture of methylene dichloride (DCM) and MeOH in a closed vessel for 72 h. After 72 h, the plant material was filtered off using a normal Whatman filter paper under gravity. These extractions

Figure 1

The atom-labeling scheme for the NMR investigation of (II) (see Table 1).

Table 2

Ions in positive ion mode; $M = (I)$.

Ion	Calculated	Measured	Difference
$[M + H]^+$	379.1176	379.1170	0.0006
$[2M + Na]^+$	779.2099	779.2089	0.0010
$[3M + Na]^+$	1157.3202	1157.3207	0.0005

Table 3

Ions in negative ion mode; $M = (II)$.

Ion	Calculated	Measured	Difference
$[M - H]^-$	391.2279	391.1918	0.0361
$[M - C_{10}H_{17}]^-$	254.0948	254.0587	0.0361
$[M - C_9H_8O_2]^-$	148.0530	148.0168	0.0362

were repeated seven times and the combined solvents were removed using a rotary evaporator (Buchi, Switzerland) under reduced pressure. The resulting extract was then stored at 277 K until it was required for use.

The extract was chromatographed over silica gel using gradient solvent elution with hexane, DCM, and methanol. The compound, which was code-named MTF 20, crystallized out of the hexane/DCM eluent as pale-yellow crystals, which were filtered off and stored in an airtight container for structural characterization and biological evaluation.

2.2. NMR studies

All NMR spectra were collected on a Bruker 600 MHz AvanceHD spectrometer equipped with a TCI-F cryoprobe at 298 K with a 1H frequency of 599.77 MHz and a ^{13}C frequency of 150.83 MHz. The 2D COSYDQF (correlation spectroscopy double quantum filter) spectrum was acquired with a 8620.7 Hz spectral width in both dimensions using 2048×512 points and processed using 8192×1024 points, 2 scans per increment, and a relaxation delay of 2 s. Multiplicity-edited 1H - ^{13}C HSQC (heteronuclear single quantum coherence) spectra were acquired using a 9014.4 Hz spectral width in F2 and a 27174 Hz spectral width in F1, using 1024×512 points, and processed to 1024×1024 points, 2 scans per increment, a relaxation delay of 2 s, and 1-bond $J_{CH} = 145$ Hz. 1H - ^{13}C HMBC (heteronuclear multiple bond correlation) spectra were acquired using a 9014.4 Hz spectral width in F2 and a 31446.5 Hz spectral width in F1, using 2048×512 points, and processed to 2048×2048 points, 8 scans per increment, a relaxation delay of 2 s, and long-range $J_{CH} = 8$ Hz. 1D NOESY

Figure 2

Fragmentation pattern of (II) under negative ion electrospray ionization conditions.

Table 4

Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{18}O_6 \cdot C_{25}H_{28}O_4 \cdot 0.13C_2H_6O$
M_r	1155.42
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	12.519 (3), 12.594 (3), 19.975 (4)
α, β, γ (°)	80.12 (3), 89.69 (3), 68.02 (3)
V (Å ³)	2871.3 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.10
Crystal size (mm)	$0.11 \times 0.06 \times 0.02$
Data collection	
Diffractometer	Bruker APEXII Quazar
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
T_{min}, T_{max}	0.679, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42663, 11806, 7371
R_{int}	0.054
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.165, 1.03
No. of reflections	11806
No. of parameters	871
No. of restraints	193
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.47, -0.55

Computer programs: APEX3 (Bruker, 2016), SAINT-Plus (Bruker, 2016), SHELXT (Sheldrick, 2015a), SHELXL2016 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

(nuclear overhauser effect spectroscopy) spectra were collected with 500 ms of mixing time, 32 scans, and a relaxation delay of 3 s (Table 1 and Fig. 1).

2.3. Mass spectral analysis

A portion of 1 mg of the crystalline material was dissolved in 300 μ l of 10 mM NH_4OAc/CH_3CN and subjected to both positive ion (1 μ l) and negative ion (1 μ l) electrospray ionization on a Thermo Scientific Q Exactive PlusTM mass spectrometer. The positive ion spectrum was dominated by three related ions corresponding to compound (I) that could be assigned to $[M + H]^+$, $[2M + Na]^+$, and $[3M + Na]^+$ (Table 2). The distribution is typical for electrospray ionization from a concentrated solution of analyte. The presence of a phenol predicts an ion of (II) in a negative ion electrospray ionization. The negative ion mass spectrum had one intense ion at m/z 391.1918. Its MSMS (tandem) spectrum showed two major losses to give ions at m/z 254.0587 and 148.0168 (Table 3 and Fig. 2).

2.4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The single-crystal X-ray diffraction data were acquired in a routine fashion (Bruker, 2012, 2016). The structure was solved and refined by standard techniques (Dolomanov *et al.*, 2009; Krause *et al.*, 2015; Sheldrick, 2015a,b).

Figure 3
Molecular drawings of the two independent molecules of (I), showing (a) molecule (Ia) and (b) molecule (Ib), drawn with 50% probability displacement ellipsoids.

There are four symmetry-independent molecules in the asymmetric unit, *i.e.* two molecules of (I), one molecule of (II), and 0.13 molecules of ethanol solvent. Both molecules of compound (I) are ordered. Molecule (II) exhibited extensive positional disorder in the chain at atom C40. Atoms C42–C47 were modelled as disordered over three positions in a 49.7 (3):27.0 (2):23.3 (3) ratio. All 1–2 and 1···3 interatomic distances in all three of the disordered components were restrained to be the same. The following additional restraints and constraints were applied to the structure to achieve a computationally stable refinement. The C39–C40 and C44–C45 bond lengths were restrained to be similar, as were

Figure 4
A molecular drawing of (X), shown with the known labeled part of the molecule and the unknown portion of the structure represented by peaks of electron density. The color intensity of the golden spheres is proportional to the peak heights. The displacement ellipsoids are drawn at the 50% probability level.

C43–C44 and C42–C43. Atomic coordinates, as well as anisotropic displacement parameters, for atoms C42A and C42B were constrained to be identical. The anisotropic displacement parameters for atoms C44B, C45B, and C46B were constrained to be the same, as were those for atoms C39, C43A, and C43B.

The ethanol solvent molecule is disordered over a crystallographic inversion center with a partial occupancy of 13.5 (2)%. This molecule was refined with an idealized geometry (Guzei, 2014).

3. Results and discussion

The plant extract under investigation was isolated by thin-layer chromatography (TLC) and subsequent column chromatography (CC) in order to obtain a pure product. However, the product contained two components that could not be separated despite numerous CC runs executed under various conditions. Separatory CC was the only method utilized as a means of separating the two isolated flavonoids. Reversed phase chromatography (C18) has not been tried, as only normal phase (silica gel) was available. To separate the two compounds, a number of different HPLC (high performance liquid chromatography) or UHPLC (ultra-high performance liquid chromatography) column packings and gradients will need to be tried.

The typical FT–IR and ^1H and ^{13}C NMR experiments did not reveal the presence of a known compound; thus SCXRD was considered an ideal technique that could both identify the compound and possibly establish its absolute configuration.

A routine crystallographic characterization revealed that the extract crystallized in a centrosymmetric space group and therefore would be a racemic mixture if asymmetric C atoms were present. The asymmetric unit contained three symmetry-independent molecules with different compositions and possibly a solvent of crystallization. Thus, the components of the extract could not be resolved by crystallization. Two ordered molecules had identical compositions, hereafter (Ia) and (Ib) (Figs. 3a and 3b) [PubChem CID: 12309400; SMILES: CC1(C=CC2=CC(=CC(=C2O1)OC)C(=O)C(=CO3)C4=CC5=C(C(=C4)OCO5)C; InChIKeys: SQBVRNCD BATODN-UHFFFAOYSA-N].

The other large molecule, (X), later identified as (II), contained an ordered portion and a disordered hydrocarbon chain. It was not clear whether the disordered portion of the structure contained a solvent of crystallization, was part of (X), or represented cohabitation of multiple species on the same crystallographic site (Fig. 4). In the absence of additional chemical information it was not possible to model the molecular disorder in (X) because the atomic identities and connectivity were unknown and multiple interpretations of residual electron-density peaks were possible.

The easiest and fastest available analysis that could shed light on the composition of the unknown was mass spectrometry. The positive ion spectrum was dominated by three related ions corresponding to $[(\text{I}) + \text{H}]^+$, $[(\text{I}) + \text{Na}]^+$, and $[(\text{I}) + \text{Na}]^+$. The negative ion mass spectrum had one intense ion at

Figure 5

The two portions of (II) identified by single-crystal X-ray analysis and NMR spectroscopy.

m/z 391.1918. Its MSMS spectrum showed two major losses to give ions at m/z 254.0587 and 148.0168. The results suggested that molecule (X) was a single disordered species. Unfortunately, the mass of 392 did not yield the possibility of an unambiguous assignment of the disordered atoms in (X); however, this mass information was critical to the success of the subsequent structure identification by NMR. When a structure is to be determined by NMR, two key pieces of information are essential, *i.e.* the exact mass and the nature of molecular fragments. In this case, both were available; the exact mass of (II) was known and a lion's share of the molecule was identified by X-ray diffractometry.

The crystals of the extract were dissolved in CDCl_3 and transferred to a Shigemi tube for NMR analysis. A unique feature of the unknown compound (X) was the allylic phenol ether revealed by partial X-ray structural analysis. This provided a handle that assisted the interpretation of a spectrum composed of the unknown. The CH_2 group of the phenol ether was readily identified as a doublet at 4.59 ppm by its chemical shift, multiplicity, and the unique long-range ^1H – ^{13}C coupling to the oxygen-bearing C atom on the aromatic ring at

Figure 6

The ^1H spectrum of the unassigned alkene and downfield aliphatic region. The chemical shift and multiplicities do not match any ^1H atoms expected from species (I) and thus are likely to be part of species (X).

Figure 7

COSYDQF spectrum of alkene and downfield aliphatic region.

165.6 ppm. From this point, the rest of the molecule was established using ^1H – ^1H coupling (COSY), ^1H – ^{13}C 1-bond and long-range coupling (HSQC and HMBC), and ^1H – ^1H through-space (NOESY) techniques (Fig. 5). The full structure of the unknown region after the allyl phenol ether functionality is an ethyl chain that terminates in a geminally dimethyl-substituted alkene. Additionally, the spectra match the ^1H and ^{13}C spectra reported in the isolation of 4'-*O*-geranylisoliquiritigenin (Deyou *et al.*, 2015).

In order to determine the unknown portion of species (X), the CH_2 and alkene groups of the phenol ether were selected as suitable handles as they were near the unknown portion and possessed a unique chemical shift and coupling pattern that could be easily distinguished from species (I) (Fig. 6).

By combining the partial information from the X-ray diffraction analysis with the exact mass of the compound, we could significantly limit the choices for potential functional groups attached to the allylic fragment. We utilized NMR

Figure 8

Selected HSQC and HMBC regions for identifying the boundary region between the X-ray-resolved and unknown regions. HSQC legend: red is CH_2 , blue CH/CH_3 , and grey HMBC cross-peaks.

Figure 9

Selected HSQCED and HMBC regions for the determination of the central functional group of the unknown segment. HSQCED legend: red is CH₂, blue CH/CH₃, and grey HMBC cross-peaks.

spectroscopy to find fingerprint chemical shifts and connectivity that would either support or eliminate certain options.

Analysis of the ¹H spectrum reveals two alkene resonances at 5.48 and 5.09 ppm, and a single downfield aliphatic doublet

at 4.59 ppm. The doublet at 4.59 ppm fits the expectation for H₁; however, either of the two alkene triplets could fit the description of the H₂. Therefore, a COSY experiment was performed to detect ¹H–¹H *J*-coupling interactions between the peaks from 4.5 to 5.6 ppm. Indeed, cross-peaks were observed between the alkene triplet at 5.48 ppm and the aliphatic doublet at 4.59 ppm, further supporting the theory that these are two sets of protons on the phenol ether of species (X) (Fig. 7).

¹H–¹³C-edited HSQC and HMBC experiments were then performed to determine the ¹³C atoms attached to the ¹H atoms, as well as neighboring ¹³C atoms multiple bonds away to confirm their identity (Fig. 8). In the HSQC spectrum, H₁ was observed to have a 1-bond correlation with a ¹³C at 67.3 ppm, consistent with an alcohol or ether. Furthermore, the multiplicity editing indicated that it was a CH₂ group. Additionally, H₂ correlated to a ¹³C at 118.5 ppm, indicative of an alkene or arene group. These 1-bond correlations provided further evidence of the identification of H₁ and H₂ as part of the allylic phenol ether, but the strongest evidence were the long-range correlation two quaternary centers of H₁, *i.e.* 142.3 and 165.6 ppm. The ¹³C at 142.3 ppm is C₃, confirmed by additional HMBC correlations (*vide infra*). The ¹³C signal at 165.6 ppm was a clear indicator that the phenol ether region had been correctly identified because arene C atoms bearing oxygen substituents uniquely/frequently appear in that region.

To determine the structure of the unknown region, ¹H–¹³C HMBC resonances were sought that correlated any additional ¹H atoms with C₂ or C₃. Three resonances (2.13, 2.09, and 1.75 ppm) were observed to couple to C₃, the quaternary alkene C atom (Fig. 9). The singlet at 1.75 ppm, which inte-

Figure 10

Selected HSQCED and HMBC regions for the determination of the terminal functional groups of the unknown segment. HSQCED legend: red is CH₂, blue CH/CH₃, and grey HMBC cross-peaks.

Figure 11

1D NOESY spectra, with the ¹H peaks at 1.68 and 1.61 ppm selected. Mix times of 0.5 s were used in both acquisitions. Artefacts appear as zero-integral (up/down in phase) peaks. A small impurity is found in the top spectrum, likely resulting from the selection of another impurity peak while selecting for 1.61 ppm.

Figure 12

A molecular drawing of the three conformations of disordered (II), shown with 50% probability displacement ellipsoids. All H atoms, except for hydroxy H atoms, have been omitted. Parts (a)–(c) correspond to the 49.7 (3):26.9 (2):23.4 (3) contributions of the three disorder components.

grates to three protons, couples *via* a 1-bond to a primary ^{13}C at 16.8 ppm and long range to both C_3 and C_2 , and therefore was assigned as H_4 . The ^1H multiplet at 2.09 ppm also showed long-range couplings with both C_2 and C_3 , indicating that it was next to the alkene group similar to H_4 . The edited HSQC spectrum revealed that these protons (H_5) were part of a CH_2 group at 39.5 ppm (C_5). The assignment of 2.09 ppm to H_5 was further supported by H_4 , showing a 3-bond coupling to C_5 . Next, the protons at 2.13 ppm (H_6) were assigned as a CH_2 group connected to H_5 from the coupling to C_3 (3-bonds) and C_5 (2-bonds).

The analysis continued from H_6 to determine the next functional group on the molecule. Two HMBC correlations to unassigned C atoms were observed at 123.6 and 132.0 ppm. The correlation at 123.6 ppm was also shared with H_5 , indi-

cating that the C atom (C_7) is likely immediately adjacent to H_6 . Analysis of the HSQCED spectrum revealed that the ^{13}C at 123.6 ppm is 1-bond coupled to the ^1H triplet at 5.09 ppm (H_7). The multiplicity and chemical shift of H_7 is indicative of not only an alkene functional group but also that the alkene is trisubstituted due to the lack of additional *cis* or *trans* couplings. This is additionally supported by the absence of HSQC correlations to the ^{13}C at 132.0 ppm, which was assigned to the quaternary ^{13}C , *i.e.* C_8 , of the alkene. To determine the two functional groups attached to other end of the alkene (C_8), HMBC correlations from ^1H atoms to C_7 and C_8 were explored. Only two sets of ^1H resonances, 1.68 and 1.61 ppm, aside from H_5 and H_6 , had HMBC correlations to C_7 and C_8 . Each of these ^1H resonances were strong singlets and integrated to three protons, which clearly indicated that the alkene was capped with two methyl groups (Fig. 10). The ^1H signals at 1.68 ppm were assigned to H_9 due to ^1H – ^1H NOEs between H_7 and H_9 from a selective 1D NOE experiment (Fig. 11). This assignment was confirmed by looking at NOE correlations from H_{10} , which revealed through-space correlations to H_5 and H_6 and not H_7 .

Armed with the exact knowledge of the composition and connectivity of (II) [PubChem CID: 10318361, SMILES: CC(=CCCC(=CCOC1=CC(=C(C=C1)C(=O)C=CC2=C(C=C(C=C2)O)O)C)C, InChIKeys: YGNHPWQWWZLUBY-UHGDPLQBSA-N], we modelled its positional disorder with confidence. The chain at atom C_{40} is disordered over three positions in a 49.7 (3):26.9 (2):23.4 (3) ratio (Figs. 12a–c), and was refined with restraints and constraints. The relative location of the remaining small residual peaks of electron density in the difference map were believed to belong to the solvent of crystallization. This molecule of solvent ethanol has a partial occupancy of 13.5 (2)% and is disordered over a crystallographic inversion center. This molecule was refined with an idealized geometry (Guzei, 2014) (Fig. 13) (PubChem CID: 702; SMILES: CCO; InChIKeys: LFGSCWFLJHTTHZ-UHFFFAOYSA-N).

The two symmetry-independent molecules of (I) can be overlaid without inversion, with an s.u. value of 0.260 Å for the non-H atoms. Molecules (*Ia*) and (*Ib*) both have very similar geometries with minor differences in the positions of

Figure 13

The contents of the asymmetric unit of the 2(I):(II):0.13EtOH cocrystal. All H atoms, except for hydroxy H atoms, have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

Figure 14
The packing diagram of the 2(I):(II):0.13EtOH cocrystal, viewed along [111]. All H atoms have been omitted.

the three methyl groups and the main difference being in the location of atoms C1/C1a that reside on opposite sides of their respective dioxole planes. The dioxole rings are characterized by the Cremer & Pople parameters (Cremer & Pople, 1975): $q_2 = 0.244(3) \text{ \AA}$ and $\varphi_2 = 32.9(6)^\circ$ for (Ia), and $q_2 = 0.137(2) \text{ \AA}$ and $\varphi_2 = 217.3(10)^\circ$ in (Ib). The puckering amplitude q_2 indicates a larger ring distortion in (Ia), whereas the phase angle φ_2 is indicative of distorted envelope conformation E_2 (ideal value = 36°) for (Ia) and 2E (ideal value = 214°) for (Ib). Atoms C1/C1a are the flap atoms in these envelopes. The dihedral angles between the envelope (O1/C2/C3/O2) and flap (O1/C1/C2) planes are $26.4(3)$ and $14.90(17)^\circ$ in molecules (Ia) and (Ib). The magnitude of this angle in 304 monosubstituted benzodioxole congeners reported to the Cambridge Structural Database (Groom *et al.*, 2016) ranges between 0 and 29.63° .

The dihedral angles between the arene plane of the benzodioxole and that of the 4*H*-chromene moiety of the fused three-ring portion in molecules (Ia) and (Ib) are $37.37(8)$ and $39.71(8)^\circ$, respectively. The pyran portions of the pyranochromenone ring systems in these molecules cannot be accurately described with one conformational type. Their shapes are closest to screw-boat 3S_4 and envelope 3E , with atoms C20/C20a serving as the flap atoms. The Cremer & Pople ring puckering coordinates are $Q = 0.286(3) \text{ \AA}$, $\theta = 113.8(6)^\circ$, and $\varphi = 138.5(6)^\circ$ for (Ia), and $Q = 0.341(2) \text{ \AA}$, $\theta = 112.2(5)^\circ$, and $\varphi = 138.0(5)^\circ$ for (Ib). The puckering amplitude Q suggests that the ring is more distorted in the latter, but the phase angles θ and φ attest that the overall conformations are essentially identical.

The molecule of (II) consists of an ordered near-planar portion and the disordered chain. In the ordered part, atoms O8–O10 and C29–C38 are coplanar within $0.045 \text{ \AA}$. This plane forms a dihedral angle of $7.85(10)^\circ$ with the phenol ring at atom C29.

All bond lengths and angles in the reported molecules fall in the usual ranges, as revealed by a *MOGUL* (Bruno *et al.*, 2004) molecular geometry check.

There are two types of hydrogen-bonding interactions in this structure. The strong interaction O7–H7...O4A($-x+1, -y+2, -z+1$) of type *D*(2) is observed between molecules (II) and (Ib) at ($-x+1, -y+2, -z+1$), described with $D\cdots A = 2.673(2) \text{ \AA}$ and $D-H\cdots A = 168.6^\circ$. The weak intramolecular *S*(6) interaction O9–H9...O8 in (II) is characterized with $D\cdots A = 2.527(2) \text{ \AA}$ and $D-H\cdots A = 147.1^\circ$.

The molecules of (I) and (II) pack in layers (Fig. 14) with several π – π interactions between the conjugated systems in all three molecules. The benzopyranone rings in molecules (Ia) and (Ib) are nearly coplanar, with a separation of $3.36(4) \text{ \AA}$. The C30–C37/O8/O9 fragment of (II) forms a stacking interaction with its symmetry-related mate (II) at ($-x+1, -y+2, -z+1$), to which it is parallel, with an interplanar distance of $3.349(2) \text{ \AA}$ and with the benzopyranone portion of (Ib) at ($x, y+1, z$) at $3.3504(17) \text{ \AA}$.

4. Conclusion

The structural characterization of a natural product, a two-component extract of unknown composition, was conducted by standard crystallographic techniques, but would not have been possible without data obtained by 2D NMR spectroscopy and mass spectrometry. The cocrystal in question contained three components, namely two ordered molecules of (I), a disordered molecule of (II), and a partially occupied molecule of crystallization solvent, *i.e.* ethanol. The positional disorder in (II) required the use of a 2D NMR technique to establish the atomic identities and connectivity in the disordered hydrocarbon chain. The NMR results were confirmed by MS and literature data. A subsequent atomic disorder modelling allowed the crystallographic refinement of (II) to be completed. The remaining peaks of residual electron density were interpreted as a partially occupied solvent of crystallization.

We are currently developing a separation protocol for this compound mixture with the goal of testing the individual components for analgesic, antimalarial, and anti-inflammatory properties.

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Deciphering composition and connectivity of a natural product with the assistance of MS and 2D NMR

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT-Plus* (Bruker, 2016); data reduction: *SAINT-Plus* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

3-(2*H*-1,3-Benzodioxol-5-yl)-6-methoxy-8,8-dimethyl-4*H*,8*H*-pyrano[2,3-*h*]chromen-4-one–(2*E*)-1-(4-[(2*E*)-3,7-dimethylocta-2,6-dien-1-yl]oxy)-2-hydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one–ethanol (2/1/0.13)

Crystal data

$2\text{C}_{22}\text{H}_{18}\text{O}_6 \cdot \text{C}_{25}\text{H}_{28}\text{O}_4 \cdot 0.13\text{C}_2\text{H}_6\text{O}$

$M_r = 1155.42$

Triclinic, $P\bar{1}$

$a = 12.519$ (3) Å

$b = 12.594$ (3) Å

$c = 19.975$ (4) Å

$\alpha = 80.12$ (3)°

$\beta = 89.69$ (3)°

$\gamma = 68.02$ (3)°

$V = 2871.3$ (12) Å³

$Z = 2$

$F(000) = 1219$

$D_x = 1.336$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6163 reflections

$\theta = 2.5\text{--}25.2^\circ$

$\mu = 0.10$ mm⁻¹

$T = 100$ K

Block, yellow

$0.11 \times 0.06 \times 0.02$ mm

Data collection

Bruker APEX II Quazar

diffractometer

Radiation source: microfocus sealed X-ray tube,

Incoatec I μ s

Mirror optics monochromator

Detector resolution: 7.9 pixels mm⁻¹

0.5° ω and 0.5° φ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.679$, $T_{\max} = 0.745$

42663 measured reflections

11806 independent reflections

7371 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 1.0^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 15$

$l = -25 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.057$

$wR(F^2) = 0.165$

$S = 1.03$

11806 reflections

871 parameters

193 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0815P)^2 + 0.7244P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$$

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.

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)
O1	0.56890 (15)	−0.13223 (16)	0.00339 (10)	0.0432 (5)	
O2	0.70046 (14)	−0.24504 (15)	−0.06278 (9)	0.0368 (4)	
O3	1.00320 (13)	0.02748 (13)	0.14992 (9)	0.0293 (4)	
O4	0.66409 (14)	0.18670 (14)	0.07879 (9)	0.0353 (4)	
O5	0.75708 (13)	0.44891 (14)	0.22375 (9)	0.0337 (4)	
O6	0.97623 (13)	0.34022 (14)	0.26052 (9)	0.0341 (4)	
C1	0.6006 (2)	−0.2377 (2)	−0.02497 (15)	0.0434 (7)	
H1A	0.618844	−0.306631	0.011829	0.052*	
H1B	0.536444	−0.233931	−0.055303	0.052*	
C2	0.66991 (19)	−0.1149 (2)	0.00882 (12)	0.0285 (5)	
C3	0.7481 (2)	−0.1809 (2)	−0.03163 (12)	0.0307 (6)	
C4	0.8545 (2)	−0.1757 (2)	−0.03981 (13)	0.0354 (6)	
H4	0.906794	−0.218605	−0.069078	0.043*	
C5	0.8824 (2)	−0.1037 (2)	−0.00280 (13)	0.0332 (6)	
H5	0.955893	−0.098336	−0.006982	0.040*	
C6	0.8059 (2)	−0.0394 (2)	0.04013 (12)	0.0281 (5)	
C7	0.6956 (2)	−0.0442 (2)	0.04540 (12)	0.0286 (5)	
H7A	0.641183	−0.000145	0.073305	0.034*	
C8	0.8440 (2)	0.0263 (2)	0.08318 (12)	0.0276 (5)	
C9	0.9531 (2)	−0.0215 (2)	0.11070 (12)	0.0286 (5)	
H9A	0.999426	−0.096313	0.101903	0.034*	
C10	0.9372 (2)	0.1349 (2)	0.16427 (12)	0.0275 (5)	
C11	0.82200 (19)	0.1910 (2)	0.14116 (12)	0.0270 (5)	
C12	0.7671 (2)	0.1389 (2)	0.09904 (13)	0.0286 (5)	
C13	0.7590 (2)	0.2988 (2)	0.16075 (13)	0.0287 (5)	
H13	0.679674	0.338508	0.146223	0.034*	
C14	0.8110 (2)	0.3469 (2)	0.20055 (13)	0.0291 (5)	
C15	0.6354 (2)	0.5050 (2)	0.20840 (16)	0.0410 (7)	
H15A	0.619472	0.527343	0.158920	0.061*	
H15B	0.605461	0.574801	0.229127	0.061*	
H15C	0.597787	0.451518	0.226612	0.061*	
C16	0.9300 (2)	0.2893 (2)	0.22067 (12)	0.0284 (5)	
C17	0.99329 (19)	0.1816 (2)	0.20388 (12)	0.0273 (5)	
C18	1.1118 (2)	0.1207 (2)	0.23238 (13)	0.0334 (6)	

H18	1.153249	0.042039	0.228084	0.040*
C19	1.1612 (2)	0.1760 (2)	0.26440 (14)	0.0386 (7)
H19	1.236048	0.133875	0.286257	0.046*
C20	1.1028 (2)	0.3033 (2)	0.26724 (15)	0.0398 (7)
C21	1.1258 (2)	0.3311 (3)	0.33547 (17)	0.0508 (8)
H21A	1.079024	0.412859	0.336650	0.076*
H21B	1.207773	0.317551	0.341687	0.076*
H21C	1.105471	0.280869	0.372098	0.076*
C22	1.1381 (2)	0.3742 (2)	0.20857 (18)	0.0540 (9)
H22A	1.113083	0.361148	0.165364	0.081*
H22B	1.222209	0.350322	0.211383	0.081*
H22C	1.101768	0.457096	0.211032	0.081*
O1A	0.79383 (15)	0.55491 (14)	0.44566 (9)	0.0376 (4)
O2A	0.90429 (14)	0.47814 (14)	0.54799 (9)	0.0338 (4)
O3A	0.98022 (13)	−0.01385 (13)	0.34200 (8)	0.0299 (4)
O4A	0.68874 (14)	0.27032 (14)	0.35312 (9)	0.0353 (4)
O5A	0.58184 (13)	0.02020 (14)	0.20800 (9)	0.0324 (4)
O6A	0.77140 (13)	−0.16003 (13)	0.20853 (8)	0.0298 (4)
C1A	0.8164 (2)	0.5802 (2)	0.51056 (13)	0.0364 (6)
H1AA	0.842550	0.646219	0.503883	0.044*
H1AB	0.745350	0.601687	0.535757	0.044*
C2A	0.8450 (2)	0.4352 (2)	0.45289 (13)	0.0296 (6)
C3A	0.9101 (2)	0.3899 (2)	0.51380 (13)	0.0291 (5)
C4A	0.9707 (2)	0.2733 (2)	0.53390 (13)	0.0308 (6)
H4A	1.016927	0.242621	0.575523	0.037*
C5A	0.9614 (2)	0.2010 (2)	0.49004 (12)	0.0296 (6)
H5A	1.000597	0.119114	0.503025	0.035*
C6A	0.89666 (19)	0.2453 (2)	0.42816 (12)	0.0277 (5)
C7A	0.8371 (2)	0.3669 (2)	0.40805 (13)	0.0310 (6)
H7AA	0.793779	0.399680	0.365550	0.037*
C8A	0.8879 (2)	0.16453 (19)	0.38420 (12)	0.0278 (5)
C9A	0.9806 (2)	0.0690 (2)	0.37731 (12)	0.0292 (5)
H9AA	1.052004	0.058926	0.398962	0.035*
C10A	0.87817 (19)	−0.00108 (19)	0.30995 (12)	0.0262 (5)
C11A	0.77769 (19)	0.09522 (19)	0.31192 (12)	0.0260 (5)
C12A	0.7781 (2)	0.1837 (2)	0.34963 (13)	0.0290 (5)
C13A	0.6763 (2)	0.1053 (2)	0.27681 (12)	0.0279 (5)
H13A	0.607789	0.172158	0.276554	0.033*
C14A	0.67513 (19)	0.0199 (2)	0.24300 (12)	0.0270 (5)
C15A	0.4798 (2)	0.1244 (2)	0.20150 (14)	0.0372 (6)
H15D	0.418970	0.116261	0.174665	0.056*
H15E	0.497158	0.190853	0.178559	0.056*
H15F	0.453737	0.137283	0.246825	0.056*
C16A	0.7777 (2)	−0.07962 (19)	0.24395 (12)	0.0266 (5)
C17A	0.8803 (2)	−0.08961 (19)	0.27518 (12)	0.0267 (5)
C18A	0.9849 (2)	−0.1868 (2)	0.26507 (13)	0.0314 (6)
H18A	1.058771	−0.188249	0.277146	0.038*
C19A	0.9753 (2)	−0.2732 (2)	0.23875 (13)	0.0333 (6)

H19A	1.043151	−0.332796	0.228354	0.040*
C20A	0.8599 (2)	−0.2789 (2)	0.22507 (13)	0.0315 (6)
C21A	0.8545 (2)	−0.3305 (2)	0.16251 (13)	0.0364 (6)
H21D	0.775249	−0.323836	0.153119	0.055*
H21E	0.906153	−0.412820	0.170647	0.055*
H21F	0.878576	−0.288298	0.123353	0.055*
C22A	0.8254 (2)	−0.3424 (2)	0.28855 (14)	0.0382 (6)
H22D	0.825818	−0.303553	0.327017	0.057*
H22E	0.880521	−0.423302	0.299246	0.057*
H22F	0.747856	−0.341044	0.280085	0.057*
O7	0.53894 (15)	1.63181 (14)	0.67718 (10)	0.0380 (4)
H7	0.468312	1.671304	0.667639	0.057*
O8	0.78105 (14)	1.01492 (14)	0.51723 (9)	0.0370 (4)
O9	0.76654 (14)	0.86116 (14)	0.45556 (10)	0.0388 (5)
H9	0.797743	0.892645	0.478773	0.058*
C23	0.5718 (2)	1.53663 (19)	0.64682 (12)	0.0282 (5)
C24	0.6866 (2)	1.4602 (2)	0.65693 (13)	0.0314 (6)
H24	0.739534	1.475183	0.684138	0.038*
C25	0.7233 (2)	1.3625 (2)	0.62722 (12)	0.0293 (6)
H25	0.802016	1.311165	0.634110	0.035*
C26	0.64824 (19)	1.33647 (19)	0.58729 (12)	0.0272 (5)
C27	0.5329 (2)	1.4154 (2)	0.57716 (13)	0.0301 (6)
H27	0.479899	1.400792	0.549785	0.036*
C28	0.4954 (2)	1.5138 (2)	0.60640 (12)	0.0304 (6)
H28	0.417069	1.566226	0.598909	0.036*
C29	0.6899 (2)	1.2295 (2)	0.55953 (12)	0.0295 (6)
H29	0.768398	1.179834	0.570814	0.035*
C30	0.6292 (2)	1.1936 (2)	0.51978 (12)	0.0298 (6)
H30	0.551487	1.242765	0.505577	0.036*
C31	0.6789 (2)	1.0812 (2)	0.49754 (13)	0.0291 (5)
C32	0.61076 (19)	1.0458 (2)	0.45356 (12)	0.0269 (5)
C33	0.65832 (19)	0.9360 (2)	0.43389 (13)	0.0288 (5)
C34	0.5966 (2)	0.8986 (2)	0.39197 (12)	0.0284 (5)
H34	0.630598	0.824025	0.379703	0.034*
C35	0.4854 (2)	0.9712 (2)	0.36846 (12)	0.0291 (5)
C36	0.4349 (2)	1.0800 (2)	0.38788 (13)	0.0340 (6)
H36	0.357582	1.128881	0.372585	0.041*
O10	0.41744 (14)	0.94625 (14)	0.32554 (9)	0.0337 (4)
C37	0.4967 (2)	1.1160 (2)	0.42881 (13)	0.0314 (6)
H37	0.461489	1.190576	0.440911	0.038*
C38	0.4684 (2)	0.8399 (2)	0.29848 (13)	0.0325 (6)
H38A	0.497203	0.771654	0.335994	0.039*
H38B	0.533826	0.842004	0.270963	0.039*
C39	0.3756 (2)	0.8323 (2)	0.25516 (13)	0.0380 (6)
H39	0.311423	0.823963	0.277764	0.046*
C40	0.3734 (2)	0.8359 (2)	0.18817 (13)	0.0340 (6)
C41	0.4659 (3)	0.8484 (3)	0.14387 (15)	0.0494 (8)
H41A	0.524434	0.859567	0.171055	0.074*

H41B	0.432172	0.915845	0.107096	0.074*	
H41C	0.501715	0.777888	0.124338	0.074*	
C42	0.2788 (4)	0.8119 (7)	0.1549 (6)	0.043 (3)	0.497 (3)
H42A	0.254249	0.864854	0.110286	0.052*	0.497 (3)
H42B	0.211714	0.831318	0.183490	0.052*	0.497 (3)
C43	0.3112 (6)	0.6851 (5)	0.1436 (3)	0.0511 (18)	0.497 (3)
H43A	0.383065	0.663799	0.119040	0.061*	0.497 (3)
H43B	0.329353	0.633553	0.188787	0.061*	0.497 (3)
C44	0.2272 (5)	0.6590 (7)	0.1066 (4)	0.060 (2)	0.497 (3)
H44	0.150759	0.689519	0.120651	0.072*	0.497 (3)
C45	0.2398 (5)	0.5993 (6)	0.0561 (4)	0.047 (2)	0.497 (3)
C46	0.3505 (6)	0.5504 (6)	0.0255 (4)	0.066 (2)	0.497 (3)
H46A	0.375891	0.613372	0.006216	0.099*	0.497 (3)
H46B	0.341025	0.510431	−0.010698	0.099*	0.497 (3)
H46C	0.408322	0.494896	0.060435	0.099*	0.497 (3)
C47	0.1410 (8)	0.5804 (10)	0.0233 (7)	0.049 (3)	0.497 (3)
H47A	0.135190	0.508335	0.047440	0.073*	0.497 (3)
H47B	0.155258	0.574342	−0.024486	0.073*	0.497 (3)
H47C	0.068681	0.646227	0.025625	0.073*	0.497 (3)
C42A	0.2725 (4)	0.8328 (9)	0.1487 (6)	0.060 (4)	0.234 (3)
H42C	0.228484	0.909710	0.120188	0.072*	0.234 (3)
H42D	0.219934	0.809594	0.179676	0.072*	0.234 (3)
C43A	0.3301 (8)	0.7399 (9)	0.1038 (6)	0.0380 (6)	0.234 (3)
H43C	0.368236	0.774149	0.067567	0.046*	0.234 (3)
H43D	0.391691	0.673485	0.132496	0.046*	0.234 (3)
C44A	0.2578 (11)	0.6938 (8)	0.0713 (6)	0.049 (3)	0.234 (3)
H44A	0.204362	0.750683	0.037274	0.058*	0.234 (3)
C45A	0.2486 (12)	0.5905 (8)	0.0780 (10)	0.052 (5)	0.234 (3)
C46A	0.3343 (12)	0.4821 (9)	0.1161 (7)	0.057 (4)	0.234 (3)
H46D	0.411449	0.484605	0.112303	0.085*	0.234 (3)
H46E	0.332034	0.415911	0.097398	0.085*	0.234 (3)
H46F	0.316724	0.473326	0.164139	0.085*	0.234 (3)
C47A	0.156 (2)	0.5714 (18)	0.0387 (16)	0.054 (7)	0.234 (3)
H47D	0.086551	0.587604	0.064577	0.081*	0.234 (3)
H47E	0.184113	0.490441	0.031926	0.081*	0.234 (3)
H47F	0.137180	0.623773	−0.005588	0.081*	0.234 (3)
C42B	0.2725 (4)	0.8328 (9)	0.1487 (6)	0.060 (4)	0.269 (2)
H42E	0.225387	0.913821	0.126699	0.072*	0.269 (2)
H42F	0.224383	0.807046	0.182017	0.072*	0.269 (2)
C43B	0.2952 (9)	0.7563 (6)	0.0930 (4)	0.0380 (6)	0.269 (2)
H43E	0.224064	0.777242	0.063822	0.046*	0.269 (2)
H43F	0.356195	0.766740	0.063939	0.046*	0.269 (2)
C44B	0.3320 (9)	0.6372 (6)	0.1293 (5)	0.0467 (18)	0.269 (2)
H44B	0.316213	0.621655	0.175766	0.056*	0.269 (2)
C45B	0.3881 (8)	0.5498 (6)	0.0974 (5)	0.0467 (18)	0.269 (2)
C46B	0.4063 (9)	0.4373 (7)	0.1404 (6)	0.0467 (18)	0.269 (2)
H46G	0.394762	0.447379	0.187857	0.070*	0.269 (2)
H46H	0.485119	0.382611	0.136938	0.070*	0.269 (2)

H46I	0.351109	0.406539	0.125334	0.070*	0.269 (2)
C47B	0.4474 (11)	0.5457 (10)	0.0310 (5)	0.069 (3)	0.269 (2)
H47G	0.430097	0.625194	0.006434	0.104*	0.269 (2)
H47H	0.419473	0.503490	0.002970	0.104*	0.269 (2)
H47I	0.531009	0.505644	0.040563	0.104*	0.269 (2)
O11	−0.0152 (18)	0.5008 (18)	0.0211 (8)	0.079 (6)*	0.1346 (12)
H11	−0.014663	0.486948	0.063744	0.119*	0.1346
C48	0.079 (2)	0.541 (2)	0.0006 (10)	0.059 (6)*	0.1346 (12)
H48A	0.154264	0.480177	0.019082	0.071*	0.1346 (12)
H48B	0.068535	0.612548	0.018224	0.071*	0.1346 (12)
C49	0.074 (2)	0.564 (2)	−0.0753 (9)	0.070 (7)*	0.1346 (12)
H49A	0.136285	0.589958	−0.090649	0.105*	0.1346
H49B	−0.000611	0.625148	−0.092975	0.105*	0.1346
H49C	0.083207	0.492806	−0.092152	0.105*	0.1346

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0341 (10)	0.0472 (11)	0.0551 (13)	−0.0181 (8)	0.0028 (9)	−0.0208 (10)
O2	0.0325 (9)	0.0461 (11)	0.0394 (11)	−0.0188 (8)	0.0012 (8)	−0.0184 (9)
O3	0.0240 (8)	0.0278 (8)	0.0389 (10)	−0.0094 (7)	0.0020 (7)	−0.0143 (8)
O4	0.0263 (9)	0.0346 (9)	0.0462 (11)	−0.0121 (7)	−0.0046 (8)	−0.0095 (8)
O5	0.0254 (8)	0.0276 (9)	0.0470 (11)	−0.0061 (7)	−0.0005 (8)	−0.0134 (8)
O6	0.0249 (8)	0.0351 (9)	0.0448 (11)	−0.0098 (7)	−0.0006 (8)	−0.0180 (8)
C1	0.0394 (15)	0.0485 (17)	0.0477 (18)	−0.0208 (13)	0.0050 (13)	−0.0135 (14)
C2	0.0245 (12)	0.0306 (12)	0.0317 (14)	−0.0119 (10)	−0.0025 (10)	−0.0059 (11)
C3	0.0345 (13)	0.0315 (13)	0.0287 (14)	−0.0144 (11)	−0.0030 (11)	−0.0075 (11)
C4	0.0349 (14)	0.0421 (15)	0.0330 (15)	−0.0150 (11)	0.0054 (12)	−0.0156 (12)
C5	0.0312 (13)	0.0382 (14)	0.0353 (15)	−0.0175 (11)	0.0032 (11)	−0.0101 (12)
C6	0.0301 (12)	0.0295 (12)	0.0269 (13)	−0.0140 (10)	−0.0002 (10)	−0.0044 (10)
C7	0.0266 (12)	0.0290 (12)	0.0307 (14)	−0.0106 (10)	0.0016 (10)	−0.0064 (11)
C8	0.0278 (12)	0.0309 (12)	0.0281 (13)	−0.0151 (10)	0.0039 (10)	−0.0064 (10)
C9	0.0285 (12)	0.0288 (12)	0.0337 (14)	−0.0146 (10)	0.0043 (11)	−0.0106 (11)
C10	0.0274 (12)	0.0266 (12)	0.0304 (14)	−0.0112 (10)	0.0043 (10)	−0.0081 (10)
C11	0.0246 (12)	0.0290 (12)	0.0298 (14)	−0.0123 (10)	0.0034 (10)	−0.0067 (10)
C12	0.0278 (13)	0.0298 (12)	0.0316 (14)	−0.0149 (10)	0.0027 (11)	−0.0055 (11)
C13	0.0246 (12)	0.0267 (12)	0.0351 (14)	−0.0101 (10)	0.0012 (10)	−0.0054 (11)
C14	0.0290 (12)	0.0257 (12)	0.0325 (14)	−0.0094 (10)	0.0031 (11)	−0.0069 (11)
C15	0.0258 (13)	0.0349 (14)	0.0602 (19)	−0.0066 (11)	0.0000 (12)	−0.0146 (13)
C16	0.0264 (12)	0.0312 (13)	0.0323 (14)	−0.0143 (10)	0.0017 (10)	−0.0099 (11)
C17	0.0241 (11)	0.0290 (12)	0.0323 (14)	−0.0119 (10)	0.0038 (10)	−0.0108 (11)
C18	0.0242 (12)	0.0327 (13)	0.0438 (16)	−0.0076 (10)	0.0013 (11)	−0.0152 (12)
C19	0.0251 (12)	0.0384 (14)	0.0520 (18)	−0.0071 (11)	−0.0029 (12)	−0.0188 (13)
C20	0.0213 (12)	0.0396 (15)	0.0621 (19)	−0.0096 (11)	−0.0019 (12)	−0.0232 (14)
C21	0.0312 (14)	0.0486 (17)	0.074 (2)	−0.0063 (12)	−0.0108 (14)	−0.0347 (16)
C22	0.0338 (15)	0.0433 (16)	0.091 (3)	−0.0161 (13)	0.0123 (16)	−0.0250 (17)
O1A	0.0471 (11)	0.0268 (9)	0.0373 (11)	−0.0102 (8)	−0.0005 (8)	−0.0106 (8)
O2A	0.0363 (9)	0.0308 (9)	0.0354 (10)	−0.0109 (7)	−0.0004 (8)	−0.0133 (8)

O3A	0.0265 (8)	0.0270 (8)	0.0351 (10)	−0.0071 (7)	−0.0033 (7)	−0.0095 (7)
O4A	0.0286 (9)	0.0283 (9)	0.0459 (11)	−0.0040 (7)	−0.0004 (8)	−0.0142 (8)
O5A	0.0254 (8)	0.0349 (9)	0.0363 (10)	−0.0097 (7)	−0.0029 (7)	−0.0084 (8)
O6A	0.0314 (9)	0.0247 (8)	0.0335 (10)	−0.0097 (7)	−0.0021 (7)	−0.0077 (7)
C1A	0.0416 (15)	0.0288 (13)	0.0365 (15)	−0.0093 (11)	0.0007 (12)	−0.0094 (11)
C2A	0.0292 (12)	0.0237 (12)	0.0367 (15)	−0.0104 (10)	0.0038 (11)	−0.0070 (11)
C3A	0.0275 (12)	0.0318 (13)	0.0333 (14)	−0.0139 (10)	0.0063 (11)	−0.0142 (11)
C4A	0.0270 (12)	0.0337 (13)	0.0315 (14)	−0.0098 (10)	−0.0004 (11)	−0.0092 (11)
C5A	0.0273 (12)	0.0278 (12)	0.0327 (14)	−0.0081 (10)	0.0038 (11)	−0.0086 (11)
C6A	0.0264 (12)	0.0271 (12)	0.0301 (14)	−0.0086 (10)	0.0014 (10)	−0.0099 (10)
C7A	0.0309 (13)	0.0308 (13)	0.0311 (14)	−0.0115 (10)	−0.0006 (11)	−0.0052 (11)
C8A	0.0309 (12)	0.0247 (12)	0.0275 (13)	−0.0097 (10)	0.0010 (10)	−0.0058 (10)
C9A	0.0300 (12)	0.0282 (12)	0.0307 (14)	−0.0114 (10)	−0.0028 (11)	−0.0073 (11)
C10A	0.0255 (12)	0.0244 (12)	0.0270 (13)	−0.0086 (9)	−0.0006 (10)	−0.0020 (10)
C11A	0.0267 (12)	0.0228 (11)	0.0285 (13)	−0.0091 (9)	0.0037 (10)	−0.0055 (10)
C12A	0.0293 (12)	0.0245 (12)	0.0312 (14)	−0.0082 (10)	0.0039 (11)	−0.0043 (10)
C13A	0.0262 (12)	0.0261 (12)	0.0303 (14)	−0.0088 (10)	0.0032 (10)	−0.0051 (10)
C14A	0.0239 (12)	0.0301 (12)	0.0266 (13)	−0.0105 (10)	0.0011 (10)	−0.0039 (10)
C15A	0.0268 (13)	0.0385 (14)	0.0405 (16)	−0.0070 (11)	−0.0039 (11)	−0.0038 (12)
C16A	0.0305 (12)	0.0254 (12)	0.0255 (13)	−0.0122 (10)	0.0016 (10)	−0.0055 (10)
C17A	0.0299 (12)	0.0229 (11)	0.0266 (13)	−0.0095 (9)	0.0018 (10)	−0.0041 (10)
C18A	0.0269 (12)	0.0293 (13)	0.0356 (15)	−0.0078 (10)	−0.0020 (11)	−0.0064 (11)
C19A	0.0327 (13)	0.0270 (12)	0.0358 (15)	−0.0057 (10)	−0.0006 (11)	−0.0073 (11)
C20A	0.0348 (13)	0.0229 (12)	0.0346 (15)	−0.0078 (10)	−0.0008 (11)	−0.0067 (11)
C21A	0.0414 (15)	0.0296 (13)	0.0390 (16)	−0.0119 (11)	−0.0005 (12)	−0.0121 (12)
C22A	0.0438 (15)	0.0297 (13)	0.0397 (16)	−0.0127 (11)	0.0025 (13)	−0.0055 (12)
O7	0.0334 (9)	0.0304 (9)	0.0498 (12)	−0.0076 (7)	−0.0023 (9)	−0.0167 (9)
O8	0.0269 (9)	0.0322 (9)	0.0495 (12)	−0.0053 (7)	−0.0022 (8)	−0.0146 (8)
O9	0.0280 (9)	0.0296 (9)	0.0547 (13)	−0.0036 (7)	−0.0087 (8)	−0.0140 (8)
C23	0.0323 (13)	0.0231 (12)	0.0297 (14)	−0.0103 (10)	0.0031 (11)	−0.0065 (10)
C24	0.0278 (12)	0.0315 (13)	0.0377 (15)	−0.0140 (10)	0.0014 (11)	−0.0072 (11)
C25	0.0242 (12)	0.0277 (12)	0.0348 (14)	−0.0091 (10)	0.0035 (11)	−0.0044 (11)
C26	0.0256 (12)	0.0259 (12)	0.0287 (13)	−0.0086 (9)	0.0049 (10)	−0.0040 (10)
C27	0.0271 (12)	0.0287 (12)	0.0329 (14)	−0.0080 (10)	−0.0020 (11)	−0.0070 (11)
C28	0.0274 (12)	0.0290 (12)	0.0313 (14)	−0.0066 (10)	−0.0015 (11)	−0.0061 (11)
C29	0.0244 (12)	0.0274 (12)	0.0349 (14)	−0.0073 (10)	0.0053 (11)	−0.0071 (11)
C30	0.0264 (12)	0.0269 (12)	0.0323 (14)	−0.0059 (10)	0.0010 (11)	−0.0053 (11)
C31	0.0260 (12)	0.0291 (12)	0.0311 (14)	−0.0089 (10)	0.0039 (10)	−0.0064 (11)
C32	0.0254 (12)	0.0276 (12)	0.0281 (13)	−0.0100 (10)	0.0050 (10)	−0.0066 (10)
C33	0.0247 (12)	0.0276 (12)	0.0324 (14)	−0.0082 (10)	0.0015 (10)	−0.0050 (11)
C34	0.0316 (13)	0.0251 (12)	0.0286 (14)	−0.0098 (10)	0.0030 (11)	−0.0076 (10)
C35	0.0315 (13)	0.0334 (13)	0.0233 (13)	−0.0139 (10)	0.0029 (10)	−0.0042 (11)
C36	0.0308 (13)	0.0343 (13)	0.0304 (14)	−0.0047 (11)	−0.0015 (11)	−0.0064 (11)
O10	0.0333 (9)	0.0350 (9)	0.0331 (10)	−0.0112 (7)	−0.0020 (8)	−0.0110 (8)
C37	0.0316 (13)	0.0294 (13)	0.0309 (14)	−0.0078 (10)	0.0028 (11)	−0.0082 (11)
C38	0.0362 (13)	0.0317 (13)	0.0311 (14)	−0.0138 (11)	0.0026 (11)	−0.0077 (11)
C39	0.0389 (14)	0.0459 (14)	0.0363 (14)	−0.0236 (12)	0.0034 (11)	−0.0089 (12)
C40	0.0326 (13)	0.0280 (13)	0.0374 (15)	−0.0060 (10)	−0.0002 (11)	−0.0081 (11)

C41	0.0530 (18)	0.0602 (19)	0.0348 (16)	−0.0204 (15)	0.0053 (14)	−0.0107 (14)
C42	0.038 (5)	0.049 (4)	0.038 (5)	−0.009 (3)	−0.005 (4)	−0.013 (4)
C43	0.057 (4)	0.032 (3)	0.068 (5)	−0.020 (3)	−0.020 (3)	−0.009 (3)
C44	0.037 (3)	0.067 (5)	0.086 (6)	−0.021 (3)	0.003 (3)	−0.036 (4)
C45	0.038 (4)	0.046 (4)	0.055 (6)	−0.012 (3)	−0.003 (3)	−0.013 (3)
C46	0.070 (4)	0.071 (5)	0.065 (5)	−0.028 (4)	0.018 (4)	−0.034 (4)
C47	0.037 (4)	0.053 (6)	0.061 (8)	−0.018 (4)	−0.011 (4)	−0.019 (5)
C42A	0.039 (5)	0.091 (7)	0.055 (7)	−0.019 (4)	0.003 (4)	−0.041 (6)
C43A	0.0389 (14)	0.0459 (14)	0.0363 (14)	−0.0236 (12)	0.0034 (11)	−0.0089 (12)
C44A	0.083 (10)	0.047 (6)	0.038 (7)	−0.048 (7)	0.016 (6)	−0.011 (6)
C45A	0.086 (12)	0.045 (7)	0.041 (11)	−0.043 (7)	−0.006 (7)	−0.008 (7)
C46A	0.071 (9)	0.058 (7)	0.055 (9)	−0.042 (7)	−0.011 (7)	0.000 (6)
C47A	0.085 (15)	0.031 (9)	0.045 (12)	−0.027 (9)	−0.032 (9)	0.006 (7)
C42B	0.039 (5)	0.091 (7)	0.055 (7)	−0.019 (4)	0.003 (4)	−0.041 (6)
C43B	0.0389 (14)	0.0459 (14)	0.0363 (14)	−0.0236 (12)	0.0034 (11)	−0.0089 (12)
C44B	0.036 (3)	0.029 (3)	0.073 (5)	−0.013 (3)	−0.019 (3)	−0.003 (3)
C45B	0.036 (3)	0.029 (3)	0.073 (5)	−0.013 (3)	−0.019 (3)	−0.003 (3)
C46B	0.036 (3)	0.029 (3)	0.073 (5)	−0.013 (3)	−0.019 (3)	−0.003 (3)
C47B	0.074 (9)	0.059 (8)	0.078 (8)	−0.043 (7)	−0.017 (6)	0.019 (6)

Geometric parameters (Å, °)

O1—C1	1.451 (3)	C23—C28	1.394 (3)
O1—C2	1.369 (3)	C24—H24	0.9500
O2—C1	1.439 (3)	C24—C25	1.379 (3)
O2—C3	1.390 (3)	C25—H25	0.9500
O3—C9	1.359 (3)	C25—C26	1.397 (3)
O3—C10	1.374 (3)	C26—C27	1.405 (3)
O4—C12	1.237 (3)	C26—C29	1.457 (3)
O5—C14	1.369 (3)	C27—H27	0.9500
O5—C15	1.428 (3)	C27—C28	1.381 (3)
O6—C16	1.356 (3)	C28—H28	0.9500
O6—C20	1.475 (3)	C29—H29	0.9500
C1—H1A	0.9900	C29—C30	1.341 (3)
C1—H1B	0.9900	C30—H30	0.9500
C2—C3	1.384 (3)	C30—C31	1.463 (3)
C2—C7	1.367 (3)	C31—C32	1.459 (3)
C3—C4	1.365 (3)	C32—C33	1.409 (3)
C4—H4	0.9500	C32—C37	1.407 (3)
C4—C5	1.400 (4)	C33—C34	1.391 (3)
C5—H5	0.9500	C34—H34	0.9500
C5—C6	1.399 (3)	C34—C35	1.379 (3)
C6—C7	1.407 (3)	C35—C36	1.399 (3)
C6—C8	1.481 (3)	C35—O10	1.363 (3)
C7—H7A	0.9500	C36—H36	0.9500
C8—C9	1.345 (3)	C36—C37	1.367 (3)
C8—C12	1.472 (3)	O10—C38	1.449 (3)
C9—H9A	0.9500	C37—H37	0.9500

C10—C11	1.388 (3)	C38—H38A	0.9900
C10—C17	1.393 (3)	C38—H38B	0.9900
C11—C12	1.464 (3)	C38—C39	1.494 (4)
C11—C13	1.412 (3)	C39—H39	0.9500
C13—H13	0.9500	C39—C40	1.331 (3)
C13—C14	1.374 (3)	C40—C41	1.491 (4)
C14—C16	1.416 (3)	C40—C42	1.510 (4)
C15—H15A	0.9800	C40—C42A	1.510 (4)
C15—H15B	0.9800	C40—C42B	1.510 (4)
C15—H15C	0.9800	C41—H41A	0.9800
C16—C17	1.389 (3)	C41—H41B	0.9800
C17—C18	1.456 (3)	C41—H41C	0.9800
C18—H18	0.9500	C42—H42A	0.9900
C18—C19	1.326 (4)	C42—H42B	0.9900
C19—H19	0.9500	C42—C43	1.551 (6)
C19—C20	1.504 (3)	C42—C43B	1.500 (10)
C20—C21	1.518 (4)	C43—H43A	0.9900
C20—C22	1.515 (4)	C43—H43B	0.9900
C21—H21A	0.9800	C43—C44	1.453 (6)
C21—H21B	0.9800	C43—C42B	1.759 (11)
C21—H21C	0.9800	C43—C43B	1.192 (11)
C22—H22A	0.9800	C43—C44B	0.673 (8)
C22—H22B	0.9800	C43—C45B	1.996 (9)
C22—H22C	0.9800	C44—H44	0.9500
O1A—C1A	1.441 (3)	C44—C45	1.332 (4)
O1A—C2A	1.382 (3)	C44—C43B	1.722 (12)
O2A—C1A	1.429 (3)	C44—C44B	1.303 (13)
O2A—C3A	1.380 (3)	C44—C45B	1.997 (10)
O3A—C9A	1.357 (3)	C45—C46	1.468 (8)
O3A—C10A	1.374 (3)	C45—C47	1.518 (7)
O4A—C12A	1.248 (3)	C45—C45B	1.867 (11)
O5A—C14A	1.363 (3)	C46—H46A	0.9800
O5A—C15A	1.435 (3)	C46—H46B	0.9800
O6A—C16A	1.356 (3)	C46—H46C	0.9800
O6A—C20A	1.473 (3)	C46—C45B	1.511 (12)
C1A—H1AA	0.9900	C46—C47B	1.197 (13)
C1A—H1AB	0.9900	C47—H47A	0.9800
C2A—C3A	1.377 (3)	C47—H47B	0.9800
C2A—C7A	1.371 (3)	C47—H47C	0.9800
C3A—C4A	1.364 (3)	C47—C48	1.20 (3)
C4A—H4A	0.9500	C42A—H42C	0.9900
C4A—C5A	1.402 (3)	C42A—H42D	0.9900
C5A—H5A	0.9500	C42A—C43A	1.554 (6)
C5A—C6A	1.390 (3)	C43A—H43C	0.9900
C6A—C7A	1.414 (3)	C43A—H43D	0.9900
C6A—C8A	1.486 (3)	C43A—C44A	1.452 (6)
C7A—H7AA	0.9500	C44A—H44A	0.9500
C8A—C9A	1.351 (3)	C44A—C45A	1.332 (4)

C8A—C12A	1.458 (3)	C45A—C46A	1.467 (8)
C9A—H9AA	0.9500	C45A—C47A	1.518 (7)
C10A—C11A	1.389 (3)	C46A—H46D	0.9800
C10A—C17A	1.403 (3)	C46A—H46E	0.9800
C11A—C12A	1.450 (3)	C46A—H46F	0.9800
C11A—C13A	1.406 (3)	C47A—H47D	0.9800
C13A—H13A	0.9500	C47A—H47E	0.9800
C13A—C14A	1.369 (3)	C47A—H47F	0.9800
C14A—C16A	1.417 (3)	C42B—H42E	0.9900
C15A—H15D	0.9800	C42B—H42F	0.9900
C15A—H15E	0.9800	C42B—C43B	1.551 (6)
C15A—H15F	0.9800	C43B—H43E	0.9900
C16A—C17A	1.384 (3)	C43B—H43F	0.9900
C17A—C18A	1.461 (3)	C43B—C44B	1.450 (6)
C18A—H18A	0.9500	C44B—H44B	0.9500
C18A—C19A	1.330 (3)	C44B—C45B	1.330 (4)
C19A—H19A	0.9500	C45B—C46B	1.464 (8)
C19A—C20A	1.502 (4)	C45B—C47B	1.516 (7)
C20A—C21A	1.517 (3)	C46B—H46G	0.9800
C20A—C22A	1.529 (4)	C46B—H46H	0.9800
C21A—H21D	0.9800	C46B—H46I	0.9800
C21A—H21E	0.9800	C47B—H47G	0.9800
C21A—H21F	0.9800	C47B—H47H	0.9800
C22A—H22D	0.9800	C47B—H47I	0.9800
C22A—H22E	0.9800	O11—H11	0.8400
C22A—H22F	0.9800	O11—C48	1.47 (3)
O7—H7	0.8400	C48—H48A	0.9900
O7—C23	1.361 (3)	C48—H48B	0.9900
O8—C31	1.257 (3)	C48—C49	1.491 (17)
O9—H9	0.8400	C49—H49A	0.9800
O9—C33	1.350 (3)	C49—H49B	0.9800
C23—C24	1.391 (3)	C49—H49C	0.9800
C2—O1—C1	104.48 (18)	C38—C39—H39	116.6
C3—O2—C1	102.90 (19)	C40—C39—C38	126.7 (3)
C9—O3—C10	118.00 (18)	C40—C39—H39	116.6
C14—O5—C15	116.40 (19)	C39—C40—C41	124.6 (3)
C16—O6—C20	118.84 (18)	C39—C40—C42	118.6 (5)
O1—C1—H1A	110.5	C39—C40—C42A	122.5 (5)
O1—C1—H1B	110.5	C39—C40—C42B	122.5 (5)
O2—C1—O1	106.3 (2)	C41—C40—C42	116.4 (5)
O2—C1—H1A	110.5	C41—C40—C42A	112.9 (5)
O2—C1—H1B	110.5	C41—C40—C42B	112.9 (5)
H1A—C1—H1B	108.7	C42B—C40—C42	9.6 (7)
O1—C2—C3	108.6 (2)	C40—C41—H41A	109.5
C7—C2—O1	129.0 (2)	C40—C41—H41B	109.5
C7—C2—C3	122.4 (2)	C40—C41—H41C	109.5
C2—C3—O2	110.7 (2)	H41A—C41—H41B	109.5

C4—C3—O2	127.3 (2)	H41A—C41—H41C	109.5
C4—C3—C2	121.9 (2)	H41B—C41—H41C	109.5
C3—C4—H4	121.8	C40—C42—H42A	108.4
C3—C4—C5	116.5 (2)	C40—C42—H42B	108.4
C5—C4—H4	121.8	C40—C42—C43	115.5 (4)
C4—C5—H5	118.8	H42A—C42—H42B	107.5
C6—C5—C4	122.4 (2)	C43—C42—H42A	108.4
C6—C5—H5	118.8	C43—C42—H42B	108.4
C5—C6—C7	119.3 (2)	C43B—C42—C40	122.8 (7)
C5—C6—C8	120.0 (2)	C43B—C42—H42A	63.1
C7—C6—C8	120.5 (2)	C43B—C42—H42B	128.5
C2—C7—C6	117.4 (2)	C43B—C42—C43	46.0 (5)
C2—C7—H7A	121.3	C42—C43—H43A	107.8
C6—C7—H7A	121.3	C42—C43—H43B	107.8
C9—C8—C6	118.2 (2)	C42—C43—C42B	5.0 (7)
C9—C8—C12	118.7 (2)	C42—C43—C45B	154.9 (7)
C12—C8—C6	123.1 (2)	H43A—C43—H43B	107.1
O3—C9—H9A	117.0	C44—C43—C42	118.1 (5)
C8—C9—O3	126.1 (2)	C44—C43—H43A	107.8
C8—C9—H9A	117.0	C44—C43—H43B	107.8
O3—C10—C11	121.4 (2)	C44—C43—C42B	115.2 (5)
O3—C10—C17	115.6 (2)	C44—C43—C45B	68.7 (4)
C11—C10—C17	123.0 (2)	C42B—C43—H43A	105.7
C10—C11—C12	121.0 (2)	C42B—C43—H43B	112.8
C10—C11—C13	117.8 (2)	C42B—C43—C45B	151.0 (7)
C13—C11—C12	121.2 (2)	C43B—C43—C42	64.8 (6)
O4—C12—C8	123.3 (2)	C43B—C43—H43A	72.1
O4—C12—C11	122.0 (2)	C43B—C43—H43B	171.1
C11—C12—C8	114.7 (2)	C43B—C43—C44	80.6 (6)
C11—C13—H13	119.6	C43B—C43—C42B	59.8 (5)
C14—C13—C11	120.9 (2)	C43B—C43—C45B	94.5 (5)
C14—C13—H13	119.6	C44B—C43—C42	161.0 (15)
O5—C14—C13	125.4 (2)	C44B—C43—H43A	56.5
O5—C14—C16	115.0 (2)	C44B—C43—H43B	88.4
C13—C14—C16	119.6 (2)	C44B—C43—C44	63.7 (11)
O5—C15—H15A	109.5	C44B—C43—C42B	156.7 (14)
O5—C15—H15B	109.5	C44B—C43—C43B	98.2 (12)
O5—C15—H15C	109.5	C44B—C43—C45B	7.0 (12)
H15A—C15—H15B	109.5	C45B—C43—H43A	49.5
H15A—C15—H15C	109.5	C45B—C43—H43B	91.3
H15B—C15—H15C	109.5	C43—C44—H44	114.7
O6—C16—C14	117.0 (2)	C43—C44—C43B	43.1 (4)
O6—C16—C17	122.1 (2)	C43—C44—C45B	68.6 (4)
C17—C16—C14	120.7 (2)	C45—C44—C43	130.6 (6)
C10—C17—C18	123.8 (2)	C45—C44—H44	114.7
C16—C17—C10	117.9 (2)	C45—C44—C43B	112.1 (7)
C16—C17—C18	118.2 (2)	C45—C44—C45B	64.7 (4)
C17—C18—H18	120.3	C43B—C44—H44	115.1

C19—C18—C17	119.4 (2)	C43B—C44—C45B	80.2 (4)
C19—C18—H18	120.3	C44B—C44—C43	27.6 (4)
C18—C19—H19	118.9	C44B—C44—H44	138.7
C18—C19—C20	122.2 (2)	C44B—C44—C45	105.0 (6)
C20—C19—H19	118.9	C44B—C44—C43B	55.2 (4)
O6—C20—C19	110.8 (2)	C44B—C44—C45B	41.2 (3)
O6—C20—C21	104.1 (2)	C45B—C44—H44	161.6
O6—C20—C22	107.8 (2)	C44—C45—C46	122.5 (6)
C19—C20—C21	112.6 (2)	C44—C45—C47	123.4 (7)
C19—C20—C22	109.3 (2)	C44—C45—C45B	75.2 (4)
C22—C20—C21	112.0 (2)	C46—C45—C47	114.1 (6)
C20—C21—H21A	109.5	C46—C45—C45B	52.2 (5)
C20—C21—H21B	109.5	C47—C45—C45B	153.8 (6)
C20—C21—H21C	109.5	C45—C46—H46A	109.5
H21A—C21—H21B	109.5	C45—C46—H46B	109.5
H21A—C21—H21C	109.5	C45—C46—H46C	109.5
H21B—C21—H21C	109.5	C45—C46—C45B	77.6 (5)
C20—C22—H22A	109.5	H46A—C46—H46B	109.5
C20—C22—H22B	109.5	H46A—C46—H46C	109.5
C20—C22—H22C	109.5	H46B—C46—H46C	109.5
H22A—C22—H22B	109.5	C45B—C46—H46A	92.8
H22A—C22—H22C	109.5	C45B—C46—H46B	151.7
H22B—C22—H22C	109.5	C45B—C46—H46C	44.4
C2A—O1A—C1A	105.10 (19)	C47B—C46—C45	139.3 (7)
C3A—O2A—C1A	105.00 (18)	C47B—C46—H46A	55.4
C9A—O3A—C10A	118.46 (17)	C47B—C46—H46B	111.3
C14A—O5A—C15A	116.10 (19)	C47B—C46—H46C	56.5
C16A—O6A—C20A	118.02 (18)	C47B—C46—C45B	66.9 (6)
O1A—C1A—H1AA	110.1	C45—C47—H47A	109.5
O1A—C1A—H1AB	110.1	C45—C47—H47B	109.5
O2A—C1A—O1A	107.79 (18)	C45—C47—H47C	109.5
O2A—C1A—H1AA	110.1	H47A—C47—H47B	109.5
O2A—C1A—H1AB	110.1	H47A—C47—H47C	109.5
H1AA—C1A—H1AB	108.5	H47B—C47—H47C	109.5
C3A—C2A—O1A	109.5 (2)	C48—C47—C45	165.9 (15)
C7A—C2A—O1A	127.8 (2)	C48—C47—H47A	59.5
C7A—C2A—C3A	122.7 (2)	C48—C47—H47B	69.5
C2A—C3A—O2A	110.4 (2)	C48—C47—H47C	83.6
C4A—C3A—O2A	127.7 (2)	C40—C42A—H42C	111.0
C4A—C3A—C2A	122.0 (2)	C40—C42A—H42D	111.0
C3A—C4A—H4A	121.7	C40—C42A—C43A	103.6 (5)
C3A—C4A—C5A	116.6 (2)	H42C—C42A—H42D	109.0
C5A—C4A—H4A	121.7	C43A—C42A—H42C	111.0
C4A—C5A—H5A	118.9	C43A—C42A—H42D	111.0
C6A—C5A—C4A	122.1 (2)	C42A—C43A—H43C	107.7
C6A—C5A—H5A	118.9	C42A—C43A—H43D	107.7
C5A—C6A—C7A	119.8 (2)	H43C—C43A—H43D	107.1
C5A—C6A—C8A	119.9 (2)	C44A—C43A—C42A	118.3 (7)

C7A—C6A—C8A	120.3 (2)	C44A—C43A—H43C	107.7
C2A—C7A—C6A	116.7 (2)	C44A—C43A—H43D	107.7
C2A—C7A—H7AA	121.6	C43A—C44A—H44A	112.4
C6A—C7A—H7AA	121.6	C45A—C44A—C43A	135.1 (9)
C9A—C8A—C6A	120.7 (2)	C45A—C44A—H44A	112.4
C9A—C8A—C12A	118.3 (2)	C44A—C45A—C46A	123.9 (9)
C12A—C8A—C6A	121.0 (2)	C44A—C45A—C47A	122.5 (10)
O3A—C9A—H9AA	117.3	C46A—C45A—C47A	113.1 (9)
C8A—C9A—O3A	125.4 (2)	C45A—C46A—H46D	109.5
C8A—C9A—H9AA	117.3	C45A—C46A—H46E	109.5
O3A—C10A—C11A	121.4 (2)	C45A—C46A—H46F	109.5
O3A—C10A—C17A	116.95 (19)	H46D—C46A—H46E	109.5
C11A—C10A—C17A	121.7 (2)	H46D—C46A—H46F	109.5
C10A—C11A—C12A	120.1 (2)	H46E—C46A—H46F	109.5
C10A—C11A—C13A	119.0 (2)	C45A—C47A—H47D	109.5
C13A—C11A—C12A	120.9 (2)	C45A—C47A—H47E	109.5
O4A—C12A—C8A	122.1 (2)	C45A—C47A—H47F	109.5
O4A—C12A—C11A	121.5 (2)	H47D—C47A—H47E	109.5
C11A—C12A—C8A	116.31 (19)	H47D—C47A—H47F	109.5
C11A—C13A—H13A	119.6	H47E—C47A—H47F	109.5
C14A—C13A—C11A	120.8 (2)	C40—C42B—C43	104.5 (5)
C14A—C13A—H13A	119.6	C40—C42B—H42E	107.5
O5A—C14A—C13A	125.7 (2)	C40—C42B—H42F	107.5
O5A—C14A—C16A	115.2 (2)	C40—C42B—C43B	119.5 (6)
C13A—C14A—C16A	119.1 (2)	C43—C42B—H42E	144.7
O5A—C15A—H15D	109.5	C43—C42B—H42F	76.7
O5A—C15A—H15E	109.5	H42E—C42B—H42F	107.0
O5A—C15A—H15F	109.5	C43B—C42B—C43	41.6 (4)
H15D—C15A—H15E	109.5	C43B—C42B—H42E	107.5
H15D—C15A—H15F	109.5	C43B—C42B—H42F	107.5
H15E—C15A—H15F	109.5	C42—C43B—C44	106.0 (7)
O6A—C16A—C14A	116.2 (2)	C42—C43B—C42B	9.4 (8)
O6A—C16A—C17A	122.1 (2)	C42—C43B—H43E	115.0
C17A—C16A—C14A	121.6 (2)	C42—C43B—H43F	115.1
C10A—C17A—C18A	124.5 (2)	C43—C43B—C42	69.3 (6)
C16A—C17A—C10A	117.8 (2)	C43—C43B—C44	56.3 (5)
C16A—C17A—C18A	117.6 (2)	C43—C43B—C42B	78.6 (7)
C17A—C18A—H18A	120.4	C43—C43B—H43E	118.0
C19A—C18A—C17A	119.2 (2)	C43—C43B—H43F	125.3
C19A—C18A—H18A	120.4	C43—C43B—C44B	27.3 (4)
C18A—C19A—H19A	119.2	C44—C43B—H43E	64.3
C18A—C19A—C20A	121.6 (2)	C44—C43B—H43F	136.1
C20A—C19A—H19A	119.2	C42B—C43B—C44	112.2 (7)
O6A—C20A—C19A	109.59 (19)	C42B—C43B—H43E	110.6
O6A—C20A—C21A	103.73 (19)	C42B—C43B—H43F	110.6
O6A—C20A—C22A	107.68 (19)	H43E—C43B—H43F	108.7
C19A—C20A—C21A	113.1 (2)	C44B—C43B—C42	96.3 (6)
C19A—C20A—C22A	110.1 (2)	C44B—C43B—C44	47.6 (6)

C21A—C20A—C22A	112.2 (2)	C44B—C43B—C42B	105.7 (7)
C20A—C21A—H21D	109.5	C44B—C43B—H43E	110.6
C20A—C21A—H21E	109.5	C44B—C43B—H43F	110.6
C20A—C21A—H21F	109.5	C43—C44B—C44	88.7 (12)
H21D—C21A—H21E	109.5	C43—C44B—C43B	54.5 (10)
H21D—C21A—H21F	109.5	C43—C44B—H44B	66.4
H21E—C21A—H21F	109.5	C43—C44B—C45B	169.5 (18)
C20A—C22A—H22D	109.5	C44—C44B—C43B	77.2 (7)
C20A—C22A—H22E	109.5	C44—C44B—H44B	94.0
C20A—C22A—H22F	109.5	C44—C44B—C45B	98.7 (8)
H22D—C22A—H22E	109.5	C43B—C44B—H44B	120.2
H22D—C22A—H22F	109.5	C45B—C44B—C43B	119.7 (7)
H22E—C22A—H22F	109.5	C45B—C44B—H44B	120.2
C23—O7—H7	109.5	C43—C45B—C44	42.7 (2)
C33—O9—H9	109.5	C45—C45B—C43	81.8 (3)
O7—C23—C24	117.8 (2)	C45—C45B—C44	40.1 (2)
O7—C23—C28	122.7 (2)	C46—C45B—C43	121.5 (6)
C24—C23—C28	119.5 (2)	C46—C45B—C44	87.7 (5)
C23—C24—H24	120.2	C46—C45B—C45	50.1 (4)
C25—C24—C23	119.6 (2)	C46—C45B—C47B	46.6 (6)
C25—C24—H24	120.2	C44B—C45B—C43	3.5 (6)
C24—C25—H25	118.9	C44B—C45B—C44	40.2 (6)
C24—C25—C26	122.1 (2)	C44B—C45B—C45	79.7 (7)
C26—C25—H25	118.9	C44B—C45B—C46	121.2 (8)
C25—C26—C27	117.4 (2)	C44B—C45B—C46B	111.0 (7)
C25—C26—C29	120.1 (2)	C44B—C45B—C47B	132.2 (8)
C27—C26—C29	122.5 (2)	C46B—C45B—C43	113.4 (7)
C26—C27—H27	119.5	C46B—C45B—C44	108.2 (7)
C28—C27—C26	121.0 (2)	C46B—C45B—C45	104.7 (7)
C28—C27—H27	119.5	C46B—C45B—C46	110.0 (7)
C23—C28—H28	119.8	C46B—C45B—C47B	116.2 (7)
C27—C28—C23	120.4 (2)	C47B—C45B—C43	129.4 (7)
C27—C28—H28	119.8	C47B—C45B—C44	123.9 (8)
C26—C29—H29	116.5	C47B—C45B—C45	94.7 (8)
C30—C29—C26	127.0 (2)	C45B—C46B—H46G	109.5
C30—C29—H29	116.5	C45B—C46B—H46H	109.5
C29—C30—H30	118.9	C45B—C46B—H46I	109.5
C29—C30—C31	122.1 (2)	H46G—C46B—H46H	109.5
C31—C30—H30	118.9	H46G—C46B—H46I	109.5
O8—C31—C30	119.2 (2)	H46H—C46B—H46I	109.5
O8—C31—C32	120.2 (2)	C46—C47B—C45B	66.5 (7)
C32—C31—C30	120.6 (2)	C46—C47B—H47G	95.1
C33—C32—C31	120.2 (2)	C46—C47B—H47H	53.6
C37—C32—C31	123.4 (2)	C46—C47B—H47I	154.6
C37—C32—C33	116.5 (2)	C45B—C47B—H47G	109.5
O9—C33—C32	121.3 (2)	C45B—C47B—H47H	109.5
O9—C33—C34	116.5 (2)	C45B—C47B—H47I	109.5
C34—C33—C32	122.2 (2)	H47G—C47B—H47H	109.5

C33—C34—H34	120.4	H47G—C47B—H47I	109.5
C35—C34—C33	119.1 (2)	H47H—C47B—H47I	109.5
C35—C34—H34	120.4	C48—O11—H11	109.5
C34—C35—C36	120.1 (2)	C47—C48—O11	140.1 (19)
O10—C35—C34	124.7 (2)	C47—C48—H48A	67.5
O10—C35—C36	115.1 (2)	C47—C48—H48B	44.0
C35—C36—H36	119.9	C47—C48—C49	110 (2)
C37—C36—C35	120.1 (2)	O11—C48—H48A	110.2
C37—C36—H36	119.9	O11—C48—H48B	110.2
C35—O10—C38	117.74 (18)	O11—C48—C49	107.4 (19)
C32—C37—H37	119.0	H48A—C48—H48B	108.5
C36—C37—C32	121.9 (2)	C49—C48—H48A	110.2
C36—C37—H37	119.0	C49—C48—H48B	110.2
O10—C38—H38A	110.4	C48—C49—H49A	109.5
O10—C38—H38B	110.4	C48—C49—H49B	109.5
O10—C38—C39	106.7 (2)	C48—C49—H49C	109.5
H38A—C38—H38B	108.6	H49A—C49—H49B	109.5
C39—C38—H38A	110.4	H49A—C49—H49C	109.5
C39—C38—H38B	110.4	H49B—C49—H49C	109.5
O1—C2—C3—O2	−1.6 (3)	C40—C42—C43B—C43	95.1 (9)
O1—C2—C3—C4	175.8 (2)	C40—C42—C43B—C44	138.7 (8)
O1—C2—C7—C6	−177.7 (2)	C40—C42—C43B—C42B	−89 (3)
O2—C3—C4—C5	179.7 (2)	C40—C42—C43B—C44B	91.1 (10)
O3—C10—C11—C12	−1.6 (4)	C40—C42A—C43A—C44A	165.2 (9)
O3—C10—C11—C13	177.2 (2)	C40—C42B—C43B—C42	74.8 (16)
O3—C10—C17—C16	−179.1 (2)	C40—C42B—C43B—C43	78.3 (10)
O3—C10—C17—C18	−3.4 (4)	C40—C42B—C43B—C44	124.4 (9)
O5—C14—C16—O6	0.6 (3)	C40—C42B—C43B—C44B	74.4 (12)
O5—C14—C16—C17	176.2 (2)	C41—C40—C42—C43	76.7 (9)
O6—C16—C17—C10	178.2 (2)	C41—C40—C42—C43B	24.2 (10)
O6—C16—C17—C18	2.2 (4)	C41—C40—C42A—C43A	49.9 (9)
C1—O1—C2—C3	17.1 (3)	C41—C40—C42B—C43	87.2 (7)
C1—O1—C2—C7	−164.2 (3)	C41—C40—C42B—C43B	45.0 (10)
C1—O2—C3—C2	−14.7 (3)	C42—C40—C42B—C43	−26 (3)
C1—O2—C3—C4	168.0 (3)	C42—C40—C42B—C43B	−68 (3)
C2—O1—C1—O2	−26.3 (3)	C42—C43—C44—C45	133.7 (10)
C2—C3—C4—C5	2.7 (4)	C42—C43—C44—C43B	54.7 (8)
C3—O2—C1—O1	24.8 (3)	C42—C43—C44—C44B	158.7 (16)
C3—C2—C7—C6	0.7 (4)	C42—C43—C44—C45B	153.4 (8)
C3—C4—C5—C6	−0.4 (4)	C42—C43—C42B—C40	55 (4)
C4—C5—C6—C7	−1.6 (4)	C42—C43—C42B—C43B	174 (4)
C4—C5—C6—C8	174.0 (2)	C42—C43—C43B—C44	−127.3 (5)
C5—C6—C7—C2	1.5 (3)	C42—C43—C43B—C42B	−0.6 (3)
C5—C6—C8—C9	−37.0 (3)	C42—C43—C43B—C44B	171.2 (14)
C5—C6—C8—C12	145.1 (2)	C42—C43—C44B—C44	−100 (4)
C6—C8—C9—O3	178.3 (2)	C42—C43—C44B—C43B	−25 (4)
C6—C8—C12—O4	1.4 (4)	C42—C43—C44B—C45B	34 (11)

C6—C8—C12—C11	−178.7 (2)	C42—C43B—C44B—C43	8.2 (13)
C7—C2—C3—O2	179.7 (2)	C42—C43B—C44B—C44	105.9 (7)
C7—C2—C3—C4	−2.9 (4)	C42—C43B—C44B—C45B	−161.3 (10)
C7—C6—C8—C9	138.6 (2)	C43—C42—C43B—C44	43.6 (4)
C7—C6—C8—C12	−39.3 (3)	C43—C42—C43B—C42B	176 (2)
C8—C6—C7—C2	−174.2 (2)	C43—C42—C43B—C44B	−4.0 (7)
C9—O3—C10—C11	1.7 (3)	C43—C44—C45—C46	−2.9 (15)
C9—O3—C10—C17	−179.2 (2)	C43—C44—C45—C47	179.8 (9)
C9—C8—C12—O4	−176.4 (2)	C43—C44—C45—C45B	20.3 (10)
C9—C8—C12—C11	3.5 (3)	C43—C44—C43B—C42	−50.7 (5)
C10—O3—C9—C8	1.1 (4)	C43—C44—C43B—C42B	−58.1 (7)
C10—C11—C12—O4	178.9 (2)	C43—C44—C43B—C44B	33.2 (7)
C10—C11—C12—C8	−1.0 (3)	C43—C44—C44B—C43B	−53.8 (11)
C10—C11—C13—C14	0.9 (4)	C43—C44—C44B—C45B	−172.4 (15)
C10—C17—C18—C19	174.1 (3)	C43—C42B—C43B—C42	−4 (2)
C11—C10—C17—C16	0.0 (4)	C43—C42B—C43B—C44	46.1 (5)
C11—C10—C17—C18	175.7 (2)	C43—C42B—C43B—C44B	−3.9 (7)
C11—C13—C14—O5	−178.1 (2)	C43—C43B—C44B—C44	97.6 (14)
C11—C13—C14—C16	1.7 (4)	C43—C43B—C44B—C45B	−170 (2)
C12—C8—C9—O3	−3.7 (4)	C43—C44B—C45B—C44	−134 (8)
C12—C11—C13—C14	179.7 (2)	C43—C44B—C45B—C45	−126 (8)
C13—C11—C12—O4	0.1 (4)	C43—C44B—C45B—C46	−96 (8)
C13—C11—C12—C8	−179.7 (2)	C43—C44B—C45B—C46B	133 (8)
C13—C14—C16—O6	−179.3 (2)	C43—C44B—C45B—C47B	−38 (8)
C13—C14—C16—C17	−3.7 (4)	C43—C45B—C47B—C46	−98.8 (10)
C14—C16—C17—C10	2.8 (4)	C44—C43—C42B—C40	−179.3 (6)
C14—C16—C17—C18	−173.2 (2)	C44—C43—C42B—C43B	−61.0 (8)
C15—O5—C14—C13	4.1 (4)	C44—C43—C43B—C42	127.3 (5)
C15—O5—C14—C16	−175.8 (2)	C44—C43—C43B—C42B	126.7 (5)
C16—O6—C20—C19	−33.5 (3)	C44—C43—C43B—C44B	−61.5 (12)
C16—O6—C20—C21	−154.8 (2)	C44—C43—C44B—C43B	75.2 (10)
C16—O6—C20—C22	86.1 (3)	C44—C43—C44B—C45B	134 (8)
C16—C17—C18—C19	−10.2 (4)	C44—C45—C46—C45B	28.9 (9)
C17—C10—C11—C12	179.4 (2)	C44—C45—C46—C47B	−0.5 (19)
C17—C10—C11—C13	−1.9 (4)	C44—C45—C47—C48	−127 (6)
C17—C18—C19—C20	−5.4 (4)	C44—C45—C45B—C43	−11.2 (6)
C18—C19—C20—O6	26.2 (4)	C44—C45—C45B—C46	−155.1 (8)
C18—C19—C20—C21	142.3 (3)	C44—C45—C45B—C44B	−8.3 (7)
C18—C19—C20—C22	−92.5 (3)	C44—C45—C45B—C46B	101.0 (8)
C20—O6—C16—C14	−163.3 (2)	C44—C45—C45B—C47B	−140.4 (7)
C20—O6—C16—C17	21.1 (4)	C44—C43B—C44B—C43	−97.6 (14)
O1A—C2A—C3A—O2A	−0.3 (3)	C44—C43B—C44B—C45B	92.8 (11)
O1A—C2A—C3A—C4A	−179.7 (2)	C44—C44B—C45B—C43	134 (8)
O1A—C2A—C7A—C6A	−178.9 (2)	C44—C44B—C45B—C45	8.3 (7)
O2A—C3A—C4A—C5A	179.3 (2)	C44—C44B—C45B—C46	37.7 (10)
O3A—C10A—C11A—C12A	−1.4 (4)	C44—C44B—C45B—C46B	−93.7 (9)
O3A—C10A—C11A—C13A	178.4 (2)	C44—C44B—C45B—C47B	95.3 (14)
O3A—C10A—C17A—C16A	178.5 (2)	C44—C45B—C47B—C46	−45.3 (9)

O3A—C10A—C17A—C18A	−6.6 (3)	C45—C44—C43B—C42	−177.2 (6)
O5A—C14A—C16A—O6A	1.8 (3)	C45—C44—C43B—C43	−126.5 (7)
O5A—C14A—C16A—C17A	177.3 (2)	C45—C44—C43B—C42B	175.4 (7)
O6A—C16A—C17A—C10A	179.3 (2)	C45—C44—C43B—C44B	−93.3 (7)
O6A—C16A—C17A—C18A	4.0 (4)	C45—C44—C44B—C43	160.6 (13)
C1A—O1A—C2A—C3A	−8.7 (3)	C45—C44—C44B—C43B	106.8 (8)
C1A—O1A—C2A—C7A	172.2 (3)	C45—C44—C44B—C45B	−11.9 (9)
C1A—O2A—C3A—C2A	9.3 (3)	C45—C46—C45B—C43	−43.2 (7)
C1A—O2A—C3A—C4A	−171.3 (3)	C45—C46—C45B—C44	−15.8 (5)
C2A—O1A—C1A—O2A	14.4 (3)	C45—C46—C45B—C44B	−39.0 (9)
C2A—C3A—C4A—C5A	−1.4 (4)	C45—C46—C45B—C46B	92.8 (8)
C3A—O2A—C1A—O1A	−14.6 (3)	C45—C46—C45B—C47B	−159.6 (9)
C3A—C2A—C7A—C6A	2.1 (4)	C45—C46—C47B—C45B	31.4 (13)
C3A—C4A—C5A—C6A	1.8 (4)	C45—C47—C48—O11	94 (7)
C4A—C5A—C6A—C7A	−0.4 (4)	C45—C47—C48—C49	−106 (6)
C4A—C5A—C6A—C8A	−178.8 (2)	C45—C45B—C47B—C46	−15.6 (7)
C5A—C6A—C7A—C2A	−1.6 (4)	C46—C45—C47—C48	55 (7)
C5A—C6A—C8A—C9A	−39.7 (4)	C46—C45—C45B—C43	143.9 (6)
C5A—C6A—C8A—C12A	137.8 (2)	C46—C45—C45B—C44	155.1 (8)
C6A—C8A—C9A—O3A	175.7 (2)	C46—C45—C45B—C44B	146.8 (7)
C6A—C8A—C12A—O4A	2.9 (4)	C46—C45—C45B—C46B	−104.0 (8)
C6A—C8A—C12A—C11A	−175.8 (2)	C46—C45—C45B—C47B	14.7 (6)
C7A—C2A—C3A—O2A	178.8 (2)	C47—C45—C46—C45B	−153.7 (9)
C7A—C2A—C3A—C4A	−0.6 (4)	C47—C45—C46—C47B	176.9 (13)
C7A—C6A—C8A—C9A	141.9 (3)	C47—C45—C45B—C43	−149.8 (18)
C7A—C6A—C8A—C12A	−40.6 (3)	C47—C45—C45B—C44	−139 (2)
C8A—C6A—C7A—C2A	176.9 (2)	C47—C45—C45B—C46	66.3 (19)
C9A—O3A—C10A—C11A	1.4 (3)	C47—C45—C45B—C44B	−146.9 (19)
C9A—O3A—C10A—C17A	−178.6 (2)	C47—C45—C45B—C46B	−38 (2)
C9A—C8A—C12A—O4A	−179.5 (2)	C47—C45—C45B—C47B	81 (2)
C9A—C8A—C12A—C11A	1.8 (3)	C42A—C43A—C44A—C45A	−113 (2)
C10A—O3A—C9A—C8A	0.3 (4)	C43A—C44A—C45A—C46A	−13 (3)
C10A—C11A—C12A—O4A	−178.9 (2)	C43A—C44A—C45A—C47A	175 (2)
C10A—C11A—C12A—C8A	−0.2 (3)	C42B—C40—C42—C43	147 (4)
C10A—C11A—C13A—C14A	2.2 (4)	C42B—C40—C42—C43B	95 (4)
C10A—C17A—C18A—C19A	171.8 (2)	C42B—C43—C44—C45	129.0 (10)
C11A—C10A—C17A—C16A	−1.6 (4)	C42B—C43—C44—C43B	50.0 (6)
C11A—C10A—C17A—C18A	173.4 (2)	C42B—C43—C44—C44B	154.1 (16)
C11A—C13A—C14A—O5A	179.4 (2)	C42B—C43—C44—C45B	148.7 (7)
C11A—C13A—C14A—C16A	0.2 (4)	C42B—C43—C43B—C42	0.6 (3)
C12A—C8A—C9A—O3A	−1.9 (4)	C42B—C43—C43B—C44	−126.7 (5)
C12A—C11A—C13A—C14A	−178.0 (2)	C42B—C43—C43B—C44B	171.9 (14)
C13A—C11A—C12A—O4A	1.2 (4)	C42B—C43—C44B—C44	−93 (3)
C13A—C11A—C12A—C8A	179.9 (2)	C42B—C43—C44B—C43B	−18 (3)
C13A—C14A—C16A—O6A	−178.9 (2)	C42B—C43—C44B—C45B	41 (10)
C13A—C14A—C16A—C17A	−3.4 (4)	C42B—C43B—C44B—C43	8.3 (14)
C14A—C16A—C17A—C10A	4.0 (4)	C42B—C43B—C44B—C44	105.9 (8)
C14A—C16A—C17A—C18A	−171.2 (2)	C42B—C43B—C44B—C45B	−161.3 (9)

C15A—O5A—C14A—C13A	5.9 (3)	C43B—C42—C43—C44	−62.8 (8)
C15A—O5A—C14A—C16A	−174.9 (2)	C43B—C42—C43—C42B	−6 (4)
C16A—O6A—C20A—C19A	−39.2 (3)	C43B—C42—C43—C44B	28 (4)
C16A—O6A—C20A—C21A	−160.2 (2)	C43B—C42—C43—C45B	36.9 (12)
C16A—O6A—C20A—C22A	80.6 (2)	C43B—C43—C44—C45	79.0 (10)
C16A—C17A—C18A—C19A	−13.3 (4)	C43B—C43—C44—C44B	104.0 (14)
C17A—C10A—C11A—C12A	178.6 (2)	C43B—C43—C44—C45B	98.7 (6)
C17A—C10A—C11A—C13A	−1.5 (4)	C43B—C43—C42B—C40	−118.3 (9)
C17A—C18A—C19A—C20A	−5.6 (4)	C43B—C43—C44B—C44	−75.2 (10)
C18A—C19A—C20A—O6A	30.6 (3)	C43B—C43—C44B—C45B	59 (8)
C18A—C19A—C20A—C21A	145.8 (2)	C43B—C44—C45—C46	43.4 (11)
C18A—C19A—C20A—C22A	−87.7 (3)	C43B—C44—C45—C47	−133.8 (9)
C20A—O6A—C16A—C14A	−160.6 (2)	C43B—C44—C45—C45B	66.7 (6)
C20A—O6A—C16A—C17A	24.0 (3)	C43B—C44—C44B—C43	53.8 (11)
O7—C23—C24—C25	179.8 (2)	C43B—C44—C44B—C45B	−118.6 (7)
O7—C23—C28—C27	−179.5 (2)	C43B—C44B—C45B—C43	54 (7)
O8—C31—C32—C33	1.1 (4)	C43B—C44B—C45B—C44	−80.2 (10)
O8—C31—C32—C37	−179.1 (2)	C43B—C44B—C45B—C45	−71.9 (10)
O9—C33—C34—C35	179.7 (2)	C43B—C44B—C45B—C46	−42.5 (15)
C23—C24—C25—C26	−0.5 (4)	C43B—C44B—C45B—C46B	−173.8 (9)
C24—C23—C28—C27	0.7 (4)	C43B—C44B—C45B—C47B	15.2 (19)
C24—C25—C26—C27	1.1 (4)	C44B—C43—C44—C45	−25.1 (16)
C24—C25—C26—C29	−177.2 (2)	C44B—C43—C44—C43B	−104.0 (14)
C25—C26—C27—C28	−0.8 (4)	C44B—C43—C44—C45B	−5.4 (11)
C25—C26—C29—C30	−178.9 (2)	C44B—C43—C42B—C40	−98 (3)
C26—C27—C28—C23	−0.1 (4)	C44B—C43—C42B—C43B	21 (3)
C26—C29—C30—C31	−176.9 (2)	C44B—C43—C43B—C42	−171.2 (14)
C27—C26—C29—C30	2.8 (4)	C44B—C43—C43B—C44	61.5 (12)
C28—C23—C24—C25	−0.4 (4)	C44B—C43—C43B—C42B	−171.9 (14)
C29—C26—C27—C28	177.5 (2)	C44B—C44—C45—C46	−14.6 (12)
C29—C30—C31—O8	1.4 (4)	C44B—C44—C45—C47	168.1 (9)
C29—C30—C31—C32	−179.2 (2)	C44B—C44—C45—C45B	8.6 (7)
C30—C31—C32—C33	−178.3 (2)	C44B—C44—C43B—C42	−83.9 (6)
C30—C31—C32—C37	1.5 (4)	C44B—C44—C43B—C43	−33.2 (7)
C31—C32—C33—O9	0.7 (4)	C44B—C44—C43B—C42B	−91.3 (7)
C31—C32—C33—C34	−179.9 (2)	C44B—C45B—C47B—C46	−96.0 (13)
C31—C32—C37—C36	−179.7 (2)	C45B—C43—C44—C45	−19.7 (9)
C32—C33—C34—C35	0.4 (4)	C45B—C43—C44—C43B	−98.7 (6)
C33—C32—C37—C36	0.0 (4)	C45B—C43—C44—C44B	5.4 (11)
C33—C34—C35—C36	−1.4 (4)	C45B—C43—C42B—C40	−88.0 (11)
C33—C34—C35—O10	177.9 (2)	C45B—C43—C42B—C43B	30.3 (10)
C34—C35—C36—C37	1.7 (4)	C45B—C43—C43B—C42	−165.2 (5)
C34—C35—O10—C38	−4.9 (3)	C45B—C43—C43B—C44	67.5 (4)
C35—C36—C37—C32	−1.0 (4)	C45B—C43—C43B—C42B	−165.8 (5)
C35—O10—C38—C39	178.4 (2)	C45B—C43—C43B—C44B	6.0 (12)
C36—C35—O10—C38	174.3 (2)	C45B—C43—C44B—C44	−134 (8)
O10—C35—C36—C37	−177.6 (2)	C45B—C43—C44B—C43B	−59 (8)
O10—C38—C39—C40	115.4 (3)	C45B—C44—C45—C46	−23.3 (7)

C37—C32—C33—O9	−179.0 (2)	C45B—C44—C45—C47	159.5 (11)
C37—C32—C33—C34	0.3 (4)	C45B—C44—C43B—C42	−119.8 (6)
C38—C39—C40—C41	0.1 (4)	C45B—C44—C43B—C43	−69.1 (6)
C38—C39—C40—C42	172.5 (4)	C45B—C44—C43B—C42B	−127.2 (6)
C38—C39—C40—C42A	−177.2 (5)	C45B—C44—C43B—C44B	−35.9 (4)
C38—C39—C40—C42B	−177.2 (5)	C45B—C44—C44B—C43	172.4 (15)
C39—C40—C42—C43	−96.3 (8)	C45B—C44—C44B—C43B	118.6 (7)
C39—C40—C42—C43B	−148.8 (8)	C45B—C45—C46—C47B	−29.4 (12)
C39—C40—C42A—C43A	−132.5 (7)	C45B—C45—C47—C48	3 (8)
C39—C40—C42B—C43	−95.2 (5)	C46B—C45B—C47B—C46	93.4 (10)
C39—C40—C42B—C43B	−137.4 (7)	C47B—C46—C45B—C43	116.5 (9)
C40—C42—C43—C44	−174.8 (7)	C47B—C46—C45B—C44	143.8 (8)
C40—C42—C43—C42B	−118 (5)	C47B—C46—C45B—C45	159.6 (9)
C40—C42—C43—C43B	−112.0 (10)	C47B—C46—C45B—C44B	120.6 (10)
C40—C42—C43—C44B	−84 (4)	C47B—C46—C45B—C46B	−107.6 (9)
C40—C42—C43—C45B	−75.1 (15)		