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## **Crystal structure of Boc-(S)-ABOC-(S)-Ala-(S)ABOC-(S)-Phe-OBn chloroform monosolvate**

Emmanuel Wenger, Laure Moulat, Baptiste Legrand, Muriel Amblard, Monique Calmes, Claude Didierjean

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**Keywords:** crystal structure;  $\alpha,\beta$ -hybrid peptide; (*S*)-1-aminobicyclo[2.2.2]octane-2-carboxylic acid; (*S*)-ABOC; (*S*)-Ala; (*S*)-Phe; Boc; OBn; 11/9 helix; hydrogen bonding

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## Crystal structure of Boc-(*S*)-ABOC-(*S*)-Ala-(*S*)-ABOC-(*S*)-Phe-OBn chloroform monosolvate

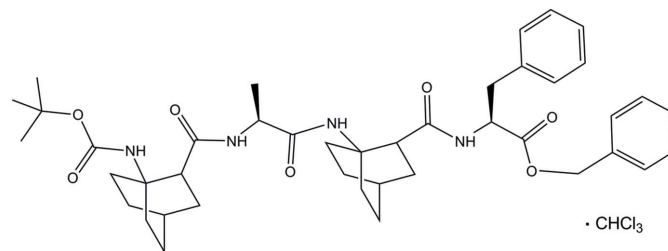
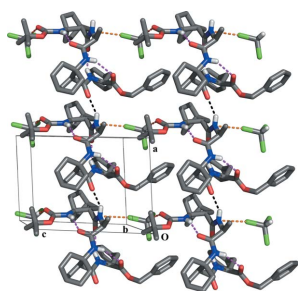
Emmanuel Wenger,<sup>a,b</sup> Laure Moulat,<sup>c</sup> Baptiste Legrand,<sup>c</sup> Muriel Amblard,<sup>c</sup> Monique Calmès<sup>c</sup> and Claude Didierjean<sup>a,b\*</sup>

<sup>a</sup>Université de Lorraine, UMR 7036 CRM2, Vandoeuvre-lès-Nancy, France, <sup>b</sup>CNRS, UMR 7036 CRM2, Vandoeuvre-lès-Nancy, France, and <sup>c</sup>IBMM, UMR 5247 CNRS-Université Montpellier-ENSCM, 15 avenue Charles Flahault, 34093 Montpellier Cedex 5, France

In the title compound, phenyl (*S*)-2-[(*S*)-(1-{2-[(*S*)-(1-[(*tert*-butoxy)carbonyl]amino)bicyclo[2.2.2]octan-2-yl]formamido]propanamido)bicyclo[2.2.2]octan-2-yl]formamido]-3-phenylpropanoate chloroform monosolvate, C<sub>42</sub>H<sub>56</sub>N<sub>4</sub>O<sub>7</sub>·CHCl<sub>3</sub>, the  $\alpha,\beta$ -hybrid peptide contains two non-proteinogenic amino acid residues of (*S*)-1-aminobicyclo[2.2.2]octane-2-carboxylic acid [(*S*)-ABOC], two amino acid residues of (*S*)-2-aminopropanoic acid [(*S*)-Ala] and (*S*)-2-amino-3-phenylpropanoic acid [(*S*)-Phe], and protecting groups of *tert*-butoxycarbonyl (Boc) and benzyl ester (OBn). The tetramer folds into a right-handed mixed 11/9 helix stabilized by intramolecular  $i,i+3$  and  $i,i-1$  C=O···H—N hydrogen bonds. In the crystal, the oligomers are linked by N—H···O=C hydrogen bonds into chains along the *a*-axis direction. The chloroform solvent molecules are intercalated between the folded chains *via* C—H···O=C interactions.

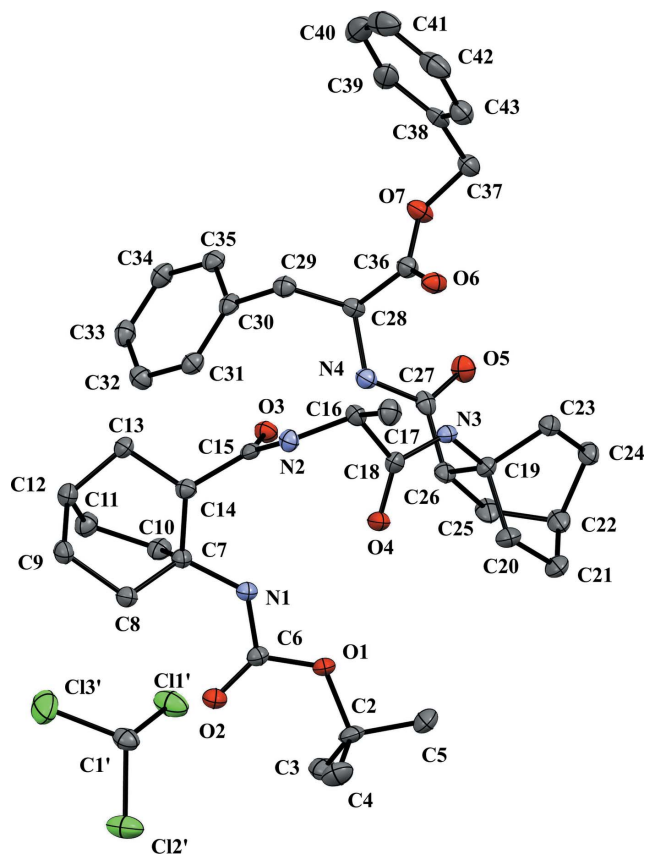
### 1. Chemical context

The title compound is an  $\alpha,\beta$ -hybrid tetrapeptide with alternating proteogenic  $\alpha$ -amino acid and ABOC residues. (*S*)-1-aminobicyclo[2.2.2]octane-2-carboxylic acid [(*S*)-ABOC] is a  $\beta^{2,3,3}$ -trisubstituted bicyclic amino acid which exhibits a high propensity to induce both a reverse turn into short peptides and helices in oligopeptides and in  $\alpha,\beta$ -hybrid peptides (Songis *et al.*, 2007; André *et al.*, 2012, 2013; Legrand *et al.*, 2012, 2014). In our last study we showed that short oligomers adopted an 11/9 helix, whereas an 18/16 helix was favored for longer oligomers in solution. NMR studies suggested a rapid interconversion between the 11/9 helix and the 18/16 helix for oligomers of intermediate length. In the solid state, only the 11/9 helix has been observed whatever the length of the oligomers capped by an *i*PrCO and an OBn group (Legrand *et al.*, 2014).



### 2. Structural commentary

For the title compound (Fig. 1), the triclinic unit cell consists of one molecule of  $\alpha,\beta$ -hybrid tetramer and one molecule of chloroform. The oligomer exhibits a right-handed mixed 11/9



**Figure 1**  
The molecular structure of the title compound showing the atom numbering scheme. All non-H atoms are represented by 25% probability displacement ellipsoids. H atoms are omitted for clarity.

helix stabilized by backbone  $\text{C}=\text{O}\cdots\text{HN}$  hydrogen bonds (Table 1), forming one C11 pseudocycle between the CO of the  $\beta$ -residue ( $i$ ) and the NH of the  $\alpha$ -residue ( $i + 3$ ) and two C9 pseudocycles between the CO of the  $\alpha$ -residue ( $i$ ) and the NH of the  $\beta$ -residue ( $i - 1$ ). The backbone torsion angles are quite similar to those of the characteristic 11/9 helix reported in the same  $\alpha,\beta$ -hybrid oligomers (Legrand *et al.*, 2014) and other  $\alpha/\beta$ -peptides (Lee *et al.*, 2013).

### 3. Supramolecular features

The intermolecular interaction  $\text{N2}-\text{H2}\cdots\text{O5}^i$  (Table 1) connects the title  $\alpha,\beta$ -hybrid tetramer to form infinite chains along the  $a$ -axis direction (Fig. 2). In the  $ac$  plane the chloroform molecules link the chains *via* a  $\text{C}-\text{Cl}\cdots\text{N}$  interaction [ $\text{Cl}\cdots\text{N} = 3.281(3) \text{ \AA}$ ] and a  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond [ $\text{C}\cdots\text{O} = 3.071(4) \text{ \AA}$ ].

### 4. Comparison with related structures

The crystals of the title compound and those of the same tetramer with the N-terminal capping group *i*PrCO instead of Boc are not isomorphous. This latter crystallized in the space group  $P2_1$  with two independent molecules in the asymmetric unit. One independent molecule shows a single fully folded

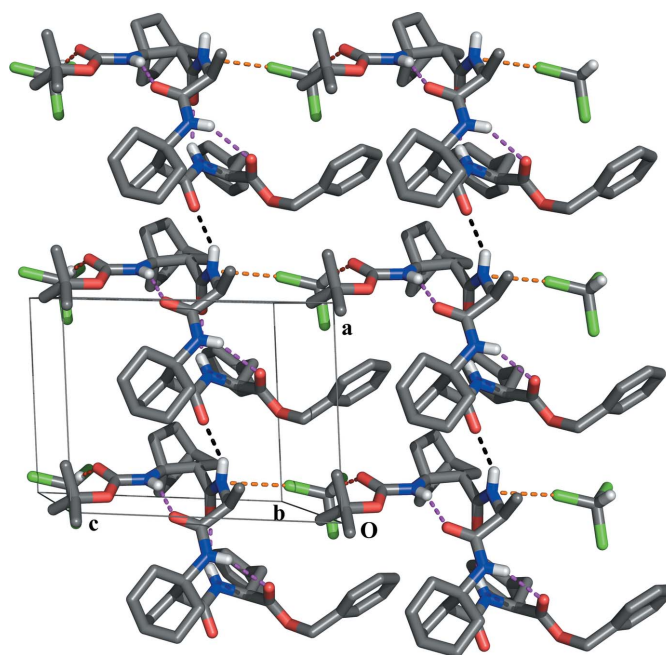
**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

| $D-\text{H}\cdots A$                   | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1}\cdots\text{O4}$   | 0.88         | 2.16               | 2.994 (4)   | 157                  |
| $\text{N2}-\text{H2}\cdots\text{O5}^i$ | 0.88         | 2.12               | 2.914 (3)   | 150                  |
| $\text{N3}-\text{H3N}\cdots\text{O6}$  | 0.88         | 2.51               | 3.159 (3)   | 131                  |
| $\text{N4}-\text{H4}\cdots\text{O3}$   | 0.88         | 2.20               | 3.009 (3)   | 153                  |
| $\text{Cl}'-\text{H1}'\cdots\text{O2}$ | 1.00         | 2.09               | 3.071 (4)   | 167                  |

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

11/9 helix as the title compound while the hydrogen-bond network is incomplete in the other molecule. The last C9 hydrogen bond between the carbonyl of the Phe residue and the  $\beta$ -residue amide proton was disrupted by the incorporation of a water molecule (Legrand *et al.*, 2014). This intercalation of water molecules has already been observed in oligoureas (Legrand *et al.*, 2012) and highlighted in an enzyme involved in the mitochondrial respiratory chain *i.e.* the mitochondrial bc1 complex. Its bovine crystal structure (Huang *et al.*, 2005) revealed that an intercalated water molecule in an  $\alpha$ -helix took part in the stabilization of the high potential cytochrome b heme. Usually,  $\alpha$ -helices interact laterally with their side chains. Water molecules adsorption on an  $\alpha$ -helice groove is an alternative tool available to the helical system to interact with partners.

For further related articles on hybrid peptides, see: Hayen *et al.* (2004); Sharma *et al.* (2009); Vasudev *et al.* (2011); Berlicki *et al.* (2012);



**Figure 2**  
Partial packing view of the title compound in the  $ac$  plane. Only selected H atoms are shown for clarity. Intramolecular hydrogen bonds are shown as magenta dashed lines. Intermolecular strong hydrogen bonds are shown as black dashed lines. Intermolecular weak hydrogen bonds are shown as red dashed lines. Intermolecular  $\text{C}-\text{Cl}\cdots\text{N}$  interactions are shown as orange dashed lines.

**Table 2**  
Experimental details.

|  |   |
|--|---|
| Crystal data   |   |
| Chemical formula   | C <sub>42</sub> H <sub>56</sub> N <sub>4</sub> O <sub>7</sub> ·CHCl <sub>3</sub>  |
| <i>M<sub>r</sub></i>   | 848.27  |
| Crystal system, space group  | Triclinic, <i>P</i> 1   |
| Temperature (K)  | 100   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 9.2194 (6), 10.8908 (6), 11.8698 (7)  |
| $\alpha$ , $\beta$ , $\gamma$ (°)  | 63.489 (2), 86.467 (2), 89.069 (2)  |
| <i>V</i> (Å <sup>3</sup> )   | 1064.38 (11)  |
| <i>Z</i>   | 1   |
| Radiation type   | Mo <i>K</i> α   |
| $\mu$ (mm <sup>-1</sup> )  | 0.27  |
| Crystal size (mm)  | 0.4 × 0.1 × 0.1   |
| Data collection  |   |
| Diffractometer   | D8 Venture Bruker   |
| Absorption correction  | Multi-scan ( <i>SADABS</i> ; Bruker, 2014)  |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>  | 0.908, 0.963  |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 42849, 8712, 8015   |
| <i>R<sub>int</sub></i>   | 0.037   |
| (sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.626   |
| Refinement   |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.038, 0.087, 1.08  |
| No. of reflections   | 8712  |
| No. of parameters  | 518   |
| No. of restraints  | 3   |
| H-atom treatment   | H-atom parameters constrained   |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )                                     | 0.30, -0.32   |
| Absolute structure   | Flack <i>x</i> determined using 3702 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013) |
| Absolute structure parameter   | 0.006 (18)  |

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SIR2008* (Burla *et al.*, 2007), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *pyMOL* (DeLano, 2002), *WinGX* (Farrugia, 2012) and *enCIFer* (Allen *et al.*, 2004).

## 5. Synthesis and crystallization

The synthesis of the title compound has recently been reported by Legrand *et al.* (2014). Single crystals were obtained by slow evaporation of a chloroform solution.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference Fourier map. The C/N-bonded H atoms were placed at calculated positions and refined using a riding model, with C—H = 0.95–1.00 Å and N—H = 0.88 Å. The *U*<sub>iso</sub>(H) parameters were fixed at 1.2*U*<sub>eq</sub>(C, N) for methine, methylene,

aromatic groups and NH groups, and at 1.5*U*<sub>eq</sub>(C) for methyl groups.

## Acknowledgements

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## supporting information

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## Crystal structure of Boc-(S)-ABOC-(S)-Ala-(S)-ABOC-(S)-Phe-OBn chloroform monosolvate

Emmanuel Wenger, Laure Moulat, Baptiste Legrand, Muriel Amblard, Monique Calmès and Claude Didierjean

### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SIR2008* (Burla *et al.*, 2007); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008) and *pyMOL* (DeLano, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *enCIFer* (Allen *et al.*, 2004).

### Phenyl (S)-2-[(S)-(1-[2-[(S)-(1-[(*tert*-butoxy)carbonyl]amino)bicyclo[2.2.2]octan-2-yl]formamido]propanamido)bicyclo[2.2.2]octan-2-yl]formamido]-3-phenylpropanoate chloroform monosolvate

#### Crystal data

C<sub>42</sub>H<sub>56</sub>N<sub>4</sub>O<sub>7</sub>·CHCl<sub>3</sub>  
*M<sub>r</sub>* = 848.27  
 Triclinic, *P*1  
 Hall symbol: P 1  
*a* = 9.2194 (6) Å  
*b* = 10.8908 (6) Å  
*c* = 11.8698 (7) Å  
 $\alpha$  = 63.489 (2)°  
 $\beta$  = 86.467 (2)°  
 $\gamma$  = 89.069 (2)°  
*V* = 1064.38 (11) Å<sup>3</sup>

*Z* = 1  
*F*(000) = 450  
*D<sub>x</sub>* = 1.323 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 9972 reflections  
 $\theta$  = 5.7–52.9°  
 $\mu$  = 0.27 mm<sup>-1</sup>  
*T* = 100 K  
 Needle, colourless  
 0.4 × 0.1 × 0.1 mm

#### Data collection

D8 Venture Bruker  
 diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2014)  
*T<sub>min</sub>* = 0.908, *T<sub>max</sub>* = 0.963  
 42849 measured reflections

8712 independent reflections  
 8015 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.037  
 $\theta_{\max}$  = 26.4°,  $\theta_{\min}$  = 2.8°  
*h* = -11→11  
*k* = -13→13  
*l* = -14→14

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.087  
*S* = 1.08  
 8712 reflections

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

$$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.6225P]$$

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

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

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack  $x$  determined using  
3702 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter: 0.006 (18)

### Special details

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

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

|     | $x$        | $y$         | $z$        | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|-------------|------------|----------------------------------|
| O1  | 1.0678 (2) | 0.1293 (2)  | 0.8411 (2) | 0.0231 (5)                       |
| O2  | 1.1876 (3) | 0.3080 (2)  | 0.8461 (2) | 0.0250 (5)                       |
| O3  | 0.9584 (2) | 0.4011 (2)  | 0.4043 (2) | 0.0217 (5)                       |
| O4  | 0.9878 (3) | 0.1030 (2)  | 0.5964 (2) | 0.0291 (6)                       |
| O6  | 0.6629 (2) | 0.2149 (2)  | 0.2316 (2) | 0.0227 (5)                       |
| O5  | 0.4408 (2) | 0.2042 (2)  | 0.4540 (2) | 0.0255 (5)                       |
| O7  | 0.4784 (3) | 0.3516 (2)  | 0.1340 (2) | 0.0258 (5)                       |
| N1  | 1.1424 (3) | 0.3010 (3)  | 0.6606 (2) | 0.0193 (5)                       |
| H1  | 1.1204     | 0.2444      | 0.6294     | 0.023*                           |
| N2  | 1.1419 (3) | 0.2721 (3)  | 0.3845 (2) | 0.0184 (5)                       |
| H2  | 1.2365     | 0.2643      | 0.375      | 0.022*                           |
| N3  | 0.8189 (3) | 0.0590 (3)  | 0.4865 (2) | 0.0182 (5)                       |
| H3N | 0.8047     | 0.0582      | 0.4143     | 0.022*                           |
| N4  | 0.6448 (3) | 0.3312 (3)  | 0.4007 (2) | 0.0201 (6)                       |
| H4  | 0.7247     | 0.354       | 0.4241     | 0.024*                           |
| C2  | 1.0641 (4) | 0.0413 (3)  | 0.9781 (3) | 0.0247 (7)                       |
| C3  | 0.9992 (4) | 0.1148 (4)  | 1.0520 (3) | 0.0320 (8)                       |
| H3A | 1.0722     | 0.1771      | 1.0557     | 0.048*                           |
| H3B | 0.9688     | 0.0472      | 1.1378     | 0.048*                           |
| H3C | 0.9148     | 0.1676      | 1.0101     | 0.048*                           |
| C4  | 1.2169 (4) | -0.0068 (4) | 1.0145 (3) | 0.0340 (8)                       |
| H4A | 1.2551     | -0.0538     | 0.9655     | 0.051*                           |
| H4B | 1.2152     | -0.0701     | 1.1046     | 0.051*                           |
| H4C | 1.2793     | 0.0726      | 0.9968     | 0.051*                           |
| C5  | 0.9658 (5) | -0.0760 (4) | 0.9937 (3) | 0.0337 (8)                       |
| H5A | 0.8681     | -0.0413     | 0.9694     | 0.051*                           |
| H5B | 0.9609     | -0.1455     | 1.082      | 0.051*                           |
| H5C | 1.0048     | -0.1171     | 0.9398     | 0.051*                           |
| C6  | 1.1374 (3) | 0.2516 (3)  | 0.7879 (3) | 0.0188 (6)                       |
| C7  | 1.1821 (3) | 0.4427 (3)  | 0.5718 (3) | 0.0184 (6)                       |
| C8  | 1.3291 (3) | 0.4874 (3)  | 0.5974 (3) | 0.0209 (6)                       |
| H8A | 1.4024     | 0.416       | 0.6087     | 0.025*                           |
| H8B | 1.3192     | 0.4987      | 0.6757     | 0.025*                           |
| C9  | 1.3792 (4) | 0.6251 (3)  | 0.4845 (3) | 0.0228 (7)                       |

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|      |            |             |            |            |
|------|------------|-------------|------------|------------|
| H9A  | 1.4202     | 0.6865      | 0.5161     | 0.027*     |
| H9B  | 1.4557     | 0.6079      | 0.4312     | 0.027*     |
| C10  | 1.0661 (4) | 0.5433 (3)  | 0.5752 (3) | 0.0212 (7) |
| H10A | 1.0424     | 0.5261      | 0.6636     | 0.025*     |
| H10B | 0.9763     | 0.5293      | 0.5405     | 0.025*     |
| C11  | 1.1215 (4) | 0.6921 (3)  | 0.4972 (3) | 0.0250 (7) |
| H11A | 1.1538     | 0.7293      | 0.554      | 0.03*      |
| H11B | 1.0423     | 0.7503      | 0.4483     | 0.03*      |
| C12  | 1.2495 (4) | 0.6932 (3)  | 0.4068 (3) | 0.0229 (7) |
| H12  | 1.2749     | 0.7893      | 0.3434     | 0.027*     |
| C13  | 1.2037 (4) | 0.6084 (3)  | 0.3410 (3) | 0.0209 (6) |
| H13A | 1.273      | 0.6244      | 0.2685     | 0.025*     |
| H13B | 1.1059     | 0.6362      | 0.3088     | 0.025*     |
| C14  | 1.2014 (3) | 0.4545 (3)  | 0.4365 (3) | 0.0180 (6) |
| H14  | 1.2989     | 0.4167      | 0.4283     | 0.022*     |
| C15  | 1.0890 (3) | 0.3744 (3)  | 0.4071 (3) | 0.0168 (6) |
| C16  | 1.0454 (3) | 0.1744 (3)  | 0.3755 (3) | 0.0196 (6) |
| H16  | 0.9842     | 0.2224      | 0.3018     | 0.024*     |
| C17  | 1.1352 (4) | 0.0646 (3)  | 0.3577 (3) | 0.0259 (7) |
| H17A | 1.0701     | -0.002      | 0.3515     | 0.039*     |
| H17B | 1.1951     | 0.0176      | 0.4301     | 0.039*     |
| H17C | 1.1982     | 0.1078      | 0.2803     | 0.039*     |
| C18  | 0.9468 (3) | 0.1090 (3)  | 0.4981 (3) | 0.0197 (6) |
| C19  | 0.7011 (3) | 0.0056 (3)  | 0.5867 (3) | 0.0201 (6) |
| C20  | 0.7585 (4) | -0.0962 (4) | 0.7133 (3) | 0.0283 (8) |
| H20A | 0.8161     | -0.1678     | 0.7019     | 0.034*     |
| H20B | 0.8229     | -0.0474     | 0.7443     | 0.034*     |
| C21  | 0.6307 (4) | -0.1633 (4) | 0.8104 (3) | 0.0329 (8) |
| H21A | 0.6228     | -0.2616     | 0.8305     | 0.04*      |
| H21B | 0.6476     | -0.157      | 0.8892     | 0.04*      |
| C22  | 0.4899 (4) | -0.0907 (4) | 0.7570 (3) | 0.0291 (8) |
| H22  | 0.4081     | -0.1283     | 0.8229     | 0.035*     |
| C23  | 0.5919 (3) | -0.0714 (3) | 0.5489 (3) | 0.0215 (7) |
| H23A | 0.6379     | -0.1539     | 0.5483     | 0.026*     |
| H23B | 0.5616     | -0.0117     | 0.4629     | 0.026*     |
| C24  | 0.4578 (4) | -0.1144 (4) | 0.6431 (3) | 0.0251 (7) |
| H24A | 0.3729     | -0.0596     | 0.6017     | 0.03*      |
| H24B | 0.4344     | -0.2125     | 0.6711     | 0.03*      |
| C25  | 0.5078 (4) | 0.0630 (4)  | 0.7147 (3) | 0.0293 (8) |
| H25A | 0.5363     | 0.0786      | 0.7864     | 0.035*     |
| H25B | 0.4141     | 0.1091      | 0.6871     | 0.035*     |
| C26  | 0.6258 (4) | 0.1254 (3)  | 0.6041 (3) | 0.0208 (7) |
| H26  | 0.6998     | 0.1757      | 0.6264     | 0.025*     |
| C27  | 0.5618 (3) | 0.2238 (3)  | 0.4817 (3) | 0.0199 (7) |
| C28  | 0.5981 (3) | 0.4082 (3)  | 0.2734 (3) | 0.0184 (6) |
| H28  | 0.4997     | 0.4461      | 0.2785     | 0.022*     |
| C29  | 0.7008 (3) | 0.5276 (3)  | 0.1918 (3) | 0.0201 (6) |
| H29A | 0.8023     | 0.4964      | 0.2074     | 0.024*     |

|      |              |              |              |             |
|------|--------------|--------------|--------------|-------------|
| H29B | 0.6859       | 0.5548       | 0.1019       | 0.024*      |
| C30  | 0.6795 (3)   | 0.6509 (3)   | 0.2164 (3)   | 0.0184 (6)  |
| C31  | 0.7622 (3)   | 0.6728 (3)   | 0.3003 (3)   | 0.0215 (7)  |
| H31  | 0.8332       | 0.6077       | 0.3449       | 0.026*      |
| C32  | 0.7416 (4)   | 0.7892 (3)   | 0.3191 (3)   | 0.0234 (7)  |
| H32  | 0.7984       | 0.8032       | 0.3766       | 0.028*      |
| C33  | 0.6387 (4)   | 0.8849 (3)   | 0.2545 (3)   | 0.0241 (7)  |
| H33  | 0.6258       | 0.9652       | 0.2663       | 0.029*      |
| C34  | 0.5550 (4)   | 0.8624 (3)   | 0.1729 (3)   | 0.0232 (7)  |
| H34  | 0.4832       | 0.927        | 0.1293       | 0.028*      |
| C35  | 0.5748 (4)   | 0.7466 (3)   | 0.1541 (3)   | 0.0215 (7)  |
| H35  | 0.5161       | 0.7323       | 0.0978       | 0.026*      |
| C36  | 0.5859 (3)   | 0.3116 (3)   | 0.2127 (3)   | 0.0210 (7)  |
| C37  | 0.4548 (4)   | 0.2729 (3)   | 0.0647 (3)   | 0.0239 (7)  |
| H37A | 0.3512       | 0.2783       | 0.0456       | 0.029*      |
| H37B | 0.4769       | 0.1753       | 0.1182       | 0.029*      |
| C38  | 0.5472 (4)   | 0.3240 (4)   | -0.0556 (3)  | 0.0245 (7)  |
| C39  | 0.5375 (4)   | 0.4594 (4)   | -0.1454 (4)  | 0.0319 (8)  |
| H39  | 0.4758       | 0.5207       | -0.1284      | 0.038*      |
| C40  | 0.6175 (5)   | 0.5056 (5)   | -0.2598 (4)  | 0.0459 (11) |
| H40  | 0.6111       | 0.5985       | -0.3209      | 0.055*      |
| C41  | 0.7064 (4)   | 0.4168 (5)   | -0.2849 (4)  | 0.0455 (12) |
| H41  | 0.7596       | 0.4482       | -0.3641      | 0.055*      |
| C42  | 0.7187 (4)   | 0.2817 (5)   | -0.1953 (4)  | 0.0383 (9)  |
| H42  | 0.781        | 0.2209       | -0.2123      | 0.046*      |
| C43  | 0.6393 (4)   | 0.2362 (4)   | -0.0806 (3)  | 0.0284 (8)  |
| H43  | 0.6482       | 0.144        | -0.0186      | 0.034*      |
| C1'  | 1.0834 (4)   | 0.5291 (4)   | 0.9249 (3)   | 0.0258 (7)  |
| H1'  | 1.132        | 0.4645       | 0.8961       | 0.031*      |
| C11' | 0.89599 (9)  | 0.52131 (11) | 0.91218 (9)  | 0.0383 (2)  |
| C12' | 1.12316 (10) | 0.47771 (11) | 1.08293 (9)  | 0.0413 (2)  |
| C13' | 1.15106 (13) | 0.69484 (11) | 0.82768 (10) | 0.0495 (3)  |

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

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0315 (13) | 0.0226 (12) | 0.0123 (11) | -0.0053 (10) | -0.0028 (9)  | -0.0049 (9)  |
| O2 | 0.0315 (13) | 0.0266 (12) | 0.0178 (11) | -0.0034 (10) | -0.0019 (9)  | -0.0107 (10) |
| O3 | 0.0192 (12) | 0.0247 (12) | 0.0221 (12) | 0.0005 (9)   | -0.0045 (9)  | -0.0107 (10) |
| O4 | 0.0364 (14) | 0.0320 (13) | 0.0152 (11) | -0.0141 (11) | -0.0039 (10) | -0.0065 (10) |
| O6 | 0.0273 (12) | 0.0230 (12) | 0.0203 (11) | 0.0059 (10)  | -0.0049 (9)  | -0.0117 (9)  |
| O5 | 0.0175 (11) | 0.0283 (12) | 0.0307 (13) | -0.0003 (9)  | -0.0002 (9)  | -0.0134 (10) |
| O7 | 0.0270 (12) | 0.0291 (13) | 0.0284 (13) | 0.0060 (10)  | -0.0111 (10) | -0.0183 (11) |
| N1 | 0.0228 (14) | 0.0205 (13) | 0.0144 (13) | -0.0030 (11) | -0.0014 (10) | -0.0076 (11) |
| N2 | 0.0145 (12) | 0.0208 (13) | 0.0193 (13) | -0.0031 (10) | 0.0017 (10)  | -0.0085 (11) |
| N3 | 0.0204 (13) | 0.0207 (13) | 0.0124 (12) | -0.0024 (11) | -0.0011 (10) | -0.0064 (11) |
| N4 | 0.0206 (14) | 0.0229 (14) | 0.0185 (13) | -0.0018 (11) | -0.0017 (10) | -0.0105 (11) |
| C2 | 0.0307 (18) | 0.0261 (18) | 0.0108 (15) | -0.0006 (14) | -0.0026 (13) | -0.0022 (13) |

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|      |             |             |             |              |              |              |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C3   | 0.033 (2)   | 0.043 (2)   | 0.0204 (17) | -0.0050 (17) | 0.0013 (15)  | -0.0156 (16) |
| C4   | 0.036 (2)   | 0.034 (2)   | 0.0256 (19) | 0.0067 (16)  | -0.0073 (15) | -0.0063 (16) |
| C5   | 0.045 (2)   | 0.0283 (19) | 0.0205 (18) | -0.0120 (16) | 0.0028 (16)  | -0.0042 (15) |
| C6   | 0.0206 (15) | 0.0198 (15) | 0.0149 (14) | -0.0002 (12) | -0.0006 (12) | -0.0069 (12) |
| C7   | 0.0208 (16) | 0.0194 (15) | 0.0153 (15) | -0.0035 (12) | 0.0003 (12)  | -0.0081 (12) |
| C8   | 0.0216 (16) | 0.0232 (17) | 0.0173 (15) | -0.0031 (13) | -0.0017 (12) | -0.0083 (13) |
| C9   | 0.0219 (16) | 0.0243 (17) | 0.0225 (17) | -0.0079 (13) | 0.0009 (13)  | -0.0107 (14) |
| C10  | 0.0216 (16) | 0.0236 (17) | 0.0188 (16) | 0.0002 (13)  | 0.0024 (13)  | -0.0103 (14) |
| C11  | 0.0296 (18) | 0.0217 (17) | 0.0235 (17) | -0.0009 (14) | 0.0018 (14)  | -0.0103 (14) |
| C12  | 0.0258 (17) | 0.0193 (16) | 0.0216 (16) | -0.0055 (13) | 0.0003 (13)  | -0.0075 (13) |
| C13  | 0.0227 (16) | 0.0205 (16) | 0.0159 (15) | -0.0059 (13) | 0.0009 (12)  | -0.0049 (13) |
| C14  | 0.0161 (15) | 0.0211 (15) | 0.0161 (15) | -0.0010 (12) | 0.0002 (12)  | -0.0078 (13) |
| C15  | 0.0185 (15) | 0.0184 (15) | 0.0096 (13) | -0.0018 (12) | -0.0005 (11) | -0.0028 (12) |
| C16  | 0.0183 (15) | 0.0200 (16) | 0.0213 (16) | -0.0020 (12) | -0.0027 (12) | -0.0097 (13) |
| C17  | 0.0273 (18) | 0.0232 (17) | 0.0287 (18) | 0.0008 (14)  | 0.0001 (14)  | -0.0132 (15) |
| C18  | 0.0242 (16) | 0.0149 (15) | 0.0183 (15) | -0.0009 (12) | -0.0027 (13) | -0.0057 (12) |
| C19  | 0.0224 (16) | 0.0203 (16) | 0.0153 (15) | -0.0048 (12) | 0.0004 (12)  | -0.0060 (13) |
| C20  | 0.036 (2)   | 0.0286 (18) | 0.0153 (16) | -0.0058 (15) | -0.0033 (14) | -0.0054 (14) |
| C21  | 0.044 (2)   | 0.033 (2)   | 0.0163 (17) | -0.0165 (17) | 0.0027 (15)  | -0.0052 (15) |
| C22  | 0.0334 (19) | 0.035 (2)   | 0.0195 (17) | -0.0143 (16) | 0.0082 (14)  | -0.0134 (15) |
| C23  | 0.0250 (17) | 0.0222 (16) | 0.0181 (16) | -0.0039 (13) | -0.0003 (13) | -0.0095 (13) |
| C24  | 0.0272 (17) | 0.0287 (18) | 0.0207 (16) | -0.0105 (14) | 0.0048 (14)  | -0.0126 (14) |
| C25  | 0.037 (2)   | 0.036 (2)   | 0.0196 (17) | -0.0117 (16) | 0.0106 (14)  | -0.0177 (15) |
| C26  | 0.0248 (16) | 0.0233 (16) | 0.0167 (15) | -0.0053 (13) | 0.0028 (12)  | -0.0116 (13) |
| C27  | 0.0179 (16) | 0.0224 (16) | 0.0244 (16) | -0.0025 (13) | 0.0035 (13)  | -0.0155 (14) |
| C28  | 0.0189 (15) | 0.0212 (16) | 0.0179 (15) | 0.0026 (12)  | -0.0040 (12) | -0.0110 (13) |
| C29  | 0.0196 (16) | 0.0223 (16) | 0.0186 (15) | 0.0004 (13)  | 0.0003 (12)  | -0.0095 (13) |
| C30  | 0.0200 (15) | 0.0181 (15) | 0.0150 (14) | -0.0017 (12) | 0.0050 (12)  | -0.0060 (12) |
| C31  | 0.0211 (16) | 0.0214 (16) | 0.0193 (16) | 0.0001 (13)  | 0.0015 (12)  | -0.0072 (13) |
| C32  | 0.0238 (17) | 0.0259 (17) | 0.0237 (17) | -0.0005 (13) | -0.0011 (13) | -0.0139 (14) |
| C33  | 0.0279 (17) | 0.0187 (16) | 0.0265 (17) | -0.0018 (13) | 0.0046 (14)  | -0.0116 (14) |
| C34  | 0.0229 (16) | 0.0182 (16) | 0.0238 (17) | 0.0028 (13)  | 0.0011 (13)  | -0.0054 (13) |
| C35  | 0.0221 (16) | 0.0233 (16) | 0.0168 (15) | -0.0017 (13) | 0.0016 (13)  | -0.0073 (13) |
| C36  | 0.0208 (16) | 0.0229 (17) | 0.0197 (16) | -0.0012 (13) | -0.0019 (13) | -0.0097 (13) |
| C37  | 0.0280 (18) | 0.0236 (17) | 0.0233 (17) | -0.0008 (14) | -0.0059 (14) | -0.0126 (14) |
| C38  | 0.0238 (17) | 0.0284 (17) | 0.0238 (17) | -0.0042 (14) | -0.0102 (14) | -0.0128 (15) |
| C39  | 0.0273 (19) | 0.0280 (19) | 0.034 (2)   | -0.0013 (15) | -0.0129 (15) | -0.0069 (16) |
| C40  | 0.036 (2)   | 0.045 (2)   | 0.035 (2)   | -0.0161 (19) | -0.0136 (18) | 0.0036 (19)  |
| C41  | 0.027 (2)   | 0.075 (3)   | 0.027 (2)   | -0.023 (2)   | -0.0011 (16) | -0.015 (2)   |
| C42  | 0.028 (2)   | 0.061 (3)   | 0.037 (2)   | -0.0103 (18) | -0.0017 (16) | -0.031 (2)   |
| C43  | 0.0280 (18) | 0.0317 (19) | 0.0279 (18) | -0.0047 (15) | -0.0034 (14) | -0.0150 (15) |
| C1'  | 0.0252 (17) | 0.0344 (19) | 0.0222 (16) | -0.0014 (14) | 0.0004 (13)  | -0.0165 (15) |
| C11' | 0.0243 (4)  | 0.0616 (6)  | 0.0342 (5)  | -0.0032 (4)  | -0.0015 (4)  | -0.0259 (5)  |
| C12' | 0.0409 (5)  | 0.0598 (6)  | 0.0259 (5)  | 0.0046 (5)   | -0.0090 (4)  | -0.0208 (5)  |
| C13' | 0.0607 (7)  | 0.0457 (6)  | 0.0387 (6)  | -0.0254 (5)  | 0.0144 (5)   | -0.0172 (5)  |

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*Geometric parameters (Å, °)*

|          |           |          |           |
|----------|-----------|----------|-----------|
| O1—C6    | 1.346 (4) | C17—H17B | 0.98      |
| O1—C2    | 1.472 (4) | C17—H17C | 0.98      |
| O2—C6    | 1.222 (4) | C19—C23  | 1.529 (4) |
| O3—C15   | 1.233 (4) | C19—C20  | 1.536 (4) |
| O4—C18   | 1.221 (4) | C19—C26  | 1.556 (4) |
| O6—C36   | 1.203 (4) | C20—C21  | 1.536 (5) |
| O5—C27   | 1.231 (4) | C20—H20A | 0.99      |
| O7—C36   | 1.334 (4) | C20—H20B | 0.99      |
| O7—C37   | 1.454 (4) | C21—C22  | 1.527 (6) |
| N1—C6    | 1.357 (4) | C21—H21A | 0.99      |
| N1—C7    | 1.465 (4) | C21—H21B | 0.99      |
| N1—H1    | 0.88      | C22—C25  | 1.527 (5) |
| N2—C15   | 1.336 (4) | C22—C24  | 1.531 (5) |
| N2—C16   | 1.442 (4) | C22—H22  | 1         |
| N2—H2    | 0.88      | C23—C24  | 1.542 (4) |
| N3—C18   | 1.346 (4) | C23—H23A | 0.99      |
| N3—C19   | 1.475 (4) | C23—H23B | 0.99      |
| N3—H3N   | 0.88      | C24—H24A | 0.99      |
| N4—C27   | 1.347 (4) | C24—H24B | 0.99      |
| N4—C28   | 1.452 (4) | C25—C26  | 1.556 (4) |
| N4—H4    | 0.88      | C25—H25A | 0.99      |
| C2—C5    | 1.514 (5) | C25—H25B | 0.99      |
| C2—C4    | 1.515 (5) | C26—C27  | 1.517 (5) |
| C2—C3    | 1.521 (5) | C26—H26  | 1         |
| C3—H3A   | 0.98      | C28—C29  | 1.526 (4) |
| C3—H3B   | 0.98      | C28—C36  | 1.527 (4) |
| C3—H3C   | 0.98      | C28—H28  | 1         |
| C4—H4A   | 0.98      | C29—C30  | 1.503 (4) |
| C4—H4B   | 0.98      | C29—H29A | 0.99      |
| C4—H4C   | 0.98      | C29—H29B | 0.99      |
| C5—H5A   | 0.98      | C30—C35  | 1.391 (5) |
| C5—H5B   | 0.98      | C30—C31  | 1.393 (5) |
| C5—H5C   | 0.98      | C31—C32  | 1.391 (5) |
| C7—C10   | 1.530 (4) | C31—H31  | 0.95      |
| C7—C8    | 1.539 (4) | C32—C33  | 1.385 (5) |
| C7—C14   | 1.552 (4) | C32—H32  | 0.95      |
| C8—C9    | 1.553 (4) | C33—C34  | 1.380 (5) |
| C8—H8A   | 0.99      | C33—H33  | 0.95      |
| C8—H8B   | 0.99      | C34—C35  | 1.383 (5) |
| C9—C12   | 1.525 (5) | C34—H34  | 0.95      |
| C9—H9A   | 0.99      | C35—H35  | 0.95      |
| C9—H9B   | 0.99      | C37—C38  | 1.494 (5) |
| C10—C11  | 1.540 (4) | C37—H37A | 0.99      |
| C10—H10A | 0.99      | C37—H37B | 0.99      |
| C10—H10B | 0.99      | C38—C43  | 1.385 (5) |
| C11—C12  | 1.542 (5) | C38—C39  | 1.387 (5) |

|            |           |               |           |
|------------|-----------|---------------|-----------|
| C11—H11A   | 0.99      | C39—C40       | 1.386 (6) |
| C11—H11B   | 0.99      | C39—H39       | 0.95      |
| C12—C13    | 1.529 (5) | C40—C41       | 1.378 (7) |
| C12—H12    | 1         | C40—H40       | 0.95      |
| C13—C14    | 1.548 (4) | C41—C42       | 1.386 (6) |
| C13—H13A   | 0.99      | C41—H41       | 0.95      |
| C13—H13B   | 0.99      | C42—C43       | 1.385 (5) |
| C14—C15    | 1.518 (4) | C42—H42       | 0.95      |
| C14—H14    | 1         | C43—H43       | 0.95      |
| C16—C17    | 1.526 (4) | C1'—C13'      | 1.751 (4) |
| C16—C18    | 1.545 (4) | C1'—C11'      | 1.751 (3) |
| C16—H16    | 1         | C1'—C12'      | 1.762 (3) |
| C17—H17A   | 0.98      | C1'—H1'       | 1         |
|            |           |               |           |
| C6—O1—C2   | 121.4 (2) | C23—C19—C26   | 110.5 (3) |
| C36—O7—C37 | 117.1 (3) | C20—C19—C26   | 108.6 (3) |
| C6—N1—C7   | 124.1 (3) | C21—C20—C19   | 109.8 (3) |
| C6—N1—H1   | 118       | C21—C20—H20A  | 109.7     |
| C7—N1—H1   | 118       | C19—C20—H20A  | 109.7     |
| C15—N2—C16 | 120.6 (3) | C21—C20—H20B  | 109.7     |
| C15—N2—H2  | 119.7     | C19—C20—H20B  | 109.7     |
| C16—N2—H2  | 119.7     | H20A—C20—H20B | 108.2     |
| C18—N3—C19 | 124.5 (3) | C22—C21—C20   | 109.6 (3) |
| C18—N3—H3N | 117.8     | C22—C21—H21A  | 109.7     |
| C19—N3—H3N | 117.8     | C20—C21—H21A  | 109.7     |
| C27—N4—C28 | 117.8 (3) | C22—C21—H21B  | 109.7     |
| C27—N4—H4  | 121.1     | C20—C21—H21B  | 109.7     |
| C28—N4—H4  | 121.1     | H21A—C21—H21B | 108.2     |
| O1—C2—C5   | 102.2 (3) | C25—C22—C21   | 109.5 (3) |
| O1—C2—C4   | 108.5 (3) | C25—C22—C24   | 109.2 (3) |
| C5—C2—C4   | 111.6 (3) | C21—C22—C24   | 108.9 (3) |
| O1—C2—C3   | 111.8 (3) | C25—C22—H22   | 109.8     |
| C5—C2—C3   | 110.5 (3) | C21—C22—H22   | 109.8     |
| C4—C2—C3   | 111.7 (3) | C24—C22—H22   | 109.8     |
| C2—C3—H3A  | 109.5     | C19—C23—C24   | 109.9 (3) |
| C2—C3—H3B  | 109.5     | C19—C23—H23A  | 109.7     |
| H3A—C3—H3B | 109.5     | C24—C23—H23A  | 109.7     |
| C2—C3—H3C  | 109.5     | C19—C23—H23B  | 109.7     |
| H3A—C3—H3C | 109.5     | C24—C23—H23B  | 109.7     |
| H3B—C3—H3C | 109.5     | H23A—C23—H23B | 108.2     |
| C2—C4—H4A  | 109.5     | C22—C24—C23   | 109.3 (3) |
| C2—C4—H4B  | 109.5     | C22—C24—H24A  | 109.8     |
| H4A—C4—H4B | 109.5     | C23—C24—H24A  | 109.8     |
| C2—C4—H4C  | 109.5     | C22—C24—H24B  | 109.8     |
| H4A—C4—H4C | 109.5     | C23—C24—H24B  | 109.8     |
| H4B—C4—H4C | 109.5     | H24A—C24—H24B | 108.3     |
| C2—C5—H5A  | 109.5     | C22—C25—C26   | 110.4 (3) |
| C2—C5—H5B  | 109.5     | C22—C25—H25A  | 109.6     |

|               |           |               |           |
|---------------|-----------|---------------|-----------|
| H5A—C5—H5B    | 109.5     | C26—C25—H25A  | 109.6     |
| C2—C5—H5C     | 109.5     | C22—C25—H25B  | 109.6     |
| H5A—C5—H5C    | 109.5     | C26—C25—H25B  | 109.6     |
| H5B—C5—H5C    | 109.5     | H25A—C25—H25B | 108.1     |
| O2—C6—O1      | 125.0 (3) | C27—C26—C25   | 112.1 (3) |
| O2—C6—N1      | 126.0 (3) | C27—C26—C19   | 109.6 (2) |
| O1—C6—N1      | 109.0 (3) | C25—C26—C19   | 108.2 (3) |
| N1—C7—C10     | 111.5 (2) | C27—C26—H26   | 109       |
| N1—C7—C8      | 112.5 (2) | C25—C26—H26   | 109       |
| C10—C7—C8     | 108.5 (3) | C19—C26—H26   | 109       |
| N1—C7—C14     | 109.2 (2) | O5—C27—N4     | 120.5 (3) |
| C10—C7—C14    | 109.5 (2) | O5—C27—C26    | 121.8 (3) |
| C8—C7—C14     | 105.5 (2) | N4—C27—C26    | 117.7 (3) |
| C7—C8—C9      | 109.4 (3) | N4—C28—C29    | 112.5 (2) |
| C7—C8—H8A     | 109.8     | N4—C28—C36    | 109.2 (2) |
| C9—C8—H8A     | 109.8     | C29—C28—C36   | 109.9 (3) |
| C7—C8—H8B     | 109.8     | N4—C28—H28    | 108.4     |
| C9—C8—H8B     | 109.8     | C29—C28—H28   | 108.4     |
| H8A—C8—H8B    | 108.2     | C36—C28—H28   | 108.4     |
| C12—C9—C8     | 109.3 (3) | C30—C29—C28   | 113.4 (3) |
| C12—C9—H9A    | 109.8     | C30—C29—H29A  | 108.9     |
| C8—C9—H9A     | 109.8     | C28—C29—H29A  | 108.9     |
| C12—C9—H9B    | 109.8     | C30—C29—H29B  | 108.9     |
| C8—C9—H9B     | 109.8     | C28—C29—H29B  | 108.9     |
| H9A—C9—H9B    | 108.3     | H29A—C29—H29B | 107.7     |
| C7—C10—C11    | 110.1 (3) | C35—C30—C31   | 118.5 (3) |
| C7—C10—H10A   | 109.6     | C35—C30—C29   | 119.6 (3) |
| C11—C10—H10A  | 109.6     | C31—C30—C29   | 121.9 (3) |
| C7—C10—H10B   | 109.6     | C32—C31—C30   | 120.4 (3) |
| C11—C10—H10B  | 109.6     | C32—C31—H31   | 119.8     |
| H10A—C10—H10B | 108.2     | C30—C31—H31   | 119.8     |
| C10—C11—C12   | 108.8 (3) | C33—C32—C31   | 120.4 (3) |
| C10—C11—H11A  | 109.9     | C33—C32—H32   | 119.8     |
| C12—C11—H11A  | 109.9     | C31—C32—H32   | 119.8     |
| C10—C11—H11B  | 109.9     | C34—C33—C32   | 119.4 (3) |
| C12—C11—H11B  | 109.9     | C34—C33—H33   | 120.3     |
| H11A—C11—H11B | 108.3     | C32—C33—H33   | 120.3     |
| C9—C12—C13    | 108.9 (3) | C33—C34—C35   | 120.5 (3) |
| C9—C12—C11    | 108.5 (3) | C33—C34—H34   | 119.7     |
| C13—C12—C11   | 107.8 (3) | C35—C34—H34   | 119.7     |
| C9—C12—H12    | 110.5     | C34—C35—C30   | 120.8 (3) |
| C13—C12—H12   | 110.5     | C34—C35—H35   | 119.6     |
| C11—C12—H12   | 110.5     | C30—C35—H35   | 119.6     |
| C12—C13—C14   | 109.0 (3) | O6—C36—O7     | 125.0 (3) |
| C12—C13—H13A  | 109.9     | O6—C36—C28    | 125.1 (3) |
| C14—C13—H13A  | 109.9     | O7—C36—C28    | 109.9 (3) |
| C12—C13—H13B  | 109.9     | O7—C37—C38    | 112.1 (3) |
| C14—C13—H13B  | 109.9     | O7—C37—H37A   | 109.2     |

|                |            |                 |             |
|----------------|------------|-----------------|-------------|
| H13A—C13—H13B  | 108.3      | C38—C37—H37A    | 109.2       |
| C15—C14—C13    | 111.6 (3)  | O7—C37—H37B     | 109.2       |
| C15—C14—C7     | 114.1 (2)  | C38—C37—H37B    | 109.2       |
| C13—C14—C7     | 108.5 (2)  | H37A—C37—H37B   | 107.9       |
| C15—C14—H14    | 107.4      | C43—C38—C39     | 119.4 (3)   |
| C13—C14—H14    | 107.4      | C43—C38—C37     | 120.7 (3)   |
| C7—C14—H14     | 107.4      | C39—C38—C37     | 119.9 (3)   |
| O3—C15—N2      | 122.2 (3)  | C40—C39—C38     | 120.1 (4)   |
| O3—C15—C14     | 122.8 (3)  | C40—C39—H39     | 119.9       |
| N2—C15—C14     | 115.0 (3)  | C38—C39—H39     | 119.9       |
| N2—C16—C17     | 109.2 (3)  | C41—C40—C39     | 120.0 (4)   |
| N2—C16—C18     | 108.5 (2)  | C41—C40—H40     | 120         |
| C17—C16—C18    | 110.5 (3)  | C39—C40—H40     | 120         |
| N2—C16—H16     | 109.6      | C40—C41—C42     | 120.3 (4)   |
| C17—C16—H16    | 109.6      | C40—C41—H41     | 119.8       |
| C18—C16—H16    | 109.6      | C42—C41—H41     | 119.8       |
| C16—C17—H17A   | 109.5      | C43—C42—C41     | 119.4 (4)   |
| C16—C17—H17B   | 109.5      | C43—C42—H42     | 120.3       |
| H17A—C17—H17B  | 109.5      | C41—C42—H42     | 120.3       |
| C16—C17—H17C   | 109.5      | C42—C43—C38     | 120.6 (4)   |
| H17A—C17—H17C  | 109.5      | C42—C43—H43     | 119.7       |
| H17B—C17—H17C  | 109.5      | C38—C43—H43     | 119.7       |
| O4—C18—N3      | 124.9 (3)  | C13'—C1'—C11'   | 110.4 (2)   |
| O4—C18—C16     | 120.3 (3)  | C13'—C1'—C12'   | 110.83 (19) |
| N3—C18—C16     | 114.8 (3)  | C11'—C1'—C12'   | 110.70 (19) |
| N3—C19—C23     | 108.1 (2)  | C13'—C1'—H1'    | 108.3       |
| N3—C19—C20     | 111.5 (3)  | C11'—C1'—H1'    | 108.3       |
| C23—C19—C20    | 107.7 (3)  | C12'—C1'—H1'    | 108.3       |
| N3—C19—C26     | 110.3 (2)  |                 |             |
|                |            |                 |             |
| C2—O1—C6—N1    | 171.0 (3)  | N3—C19—C20—C21  | -172.7 (3)  |
| C6—N1—C7—C14   | 170.3 (3)  | C23—C19—C20—C21 | -54.2 (4)   |
| N1—C7—C14—C15  | 40.5 (3)   | C26—C19—C20—C21 | 65.5 (3)    |
| C7—C14—C15—N2  | -115.8 (3) | C19—C20—C21—C22 | -9.3 (4)    |
| C14—C15—N2—C16 | 169.9 (3)  | C20—C21—C22—C25 | -54.1 (4)   |
| C15—N2—C16—C18 | -56.0 (4)  | C20—C21—C22—C24 | 65.1 (4)    |
| N2—C16—C18—N3  | 155.4 (3)  | N3—C19—C23—C24  | -173.3 (3)  |
| C16—C18—N3—C19 | -173.2 (3) | C20—C19—C23—C24 | 66.0 (3)    |
| C18—N3—C19—C26 | 72.4 (4)   | C26—C19—C23—C24 | -52.5 (3)   |
| N3—C19—C26—C27 | 60.2 (3)   | C25—C22—C24—C23 | 66.2 (4)    |
| C19—C26—C27—N4 | -92.4 (3)  | C21—C22—C24—C23 | -53.3 (4)   |
| C26—C27—N4—C28 | 167.0 (3)  | C19—C23—C24—C22 | -10.8 (4)   |
| C27—N4—C28—C36 | -58.1 (4)  | C21—C22—C25—C26 | 64.3 (4)    |
| N4—C28—C36—O7  | 147.0 (3)  | C24—C22—C25—C26 | -54.8 (4)   |
| C6—O1—C2—C5    | 175.6 (3)  | C22—C25—C26—C27 | 113.0 (3)   |
| C6—O1—C2—C4    | -66.3 (4)  | C22—C25—C26—C19 | -7.9 (4)    |
| C6—O1—C2—C3    | 57.3 (4)   | C23—C19—C26—C27 | -59.3 (3)   |
| C2—O1—C6—O2    | -9.0 (5)   | C20—C19—C26—C27 | -177.3 (3)  |

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| C7—N1—C6—O2     | -13.3 (5)  | N3—C19—C26—C25  | -177.4 (3) |
| C7—N1—C6—O1     | 166.7 (3)  | C23—C19—C26—C25 | 63.2 (3)   |
| C6—N1—C7—C10    | -68.6 (4)  | C20—C19—C26—C25 | -54.8 (3)  |
| C6—N1—C7—C8     | 53.5 (4)   | C28—N4—C27—O5   | -10.1 (4)  |
| N1—C7—C8—C9     | 168.0 (2)  | C25—C26—C27—O5  | -35.5 (4)  |
| C10—C7—C8—C9    | -68.2 (3)  | C19—C26—C27—O5  | 84.6 (4)   |
| C14—C7—C8—C9    | 49.1 (3)   | C25—C26—C27—N4  | 147.5 (3)  |
| C7—C8—C9—C12    | 17.7 (4)   | C27—N4—C28—C29  | 179.6 (3)  |
| N1—C7—C10—C11   | 171.1 (3)  | N4—C28—C29—C30  | -78.8 (3)  |
| C8—C7—C10—C11   | 46.7 (3)   | C36—C28—C29—C30 | 159.3 (3)  |
| C14—C7—C10—C11  | -68.0 (3)  | C28—C29—C30—C35 | -85.7 (4)  |
| C7—C10—C11—C12  | 18.9 (4)   | C28—C29—C30—C31 | 94.4 (3)   |
| C8—C9—C12—C13   | -68.8 (3)  | C35—C30—C31—C32 | -1.1 (5)   |
| C8—C9—C12—C11   | 48.2 (3)   | C29—C30—C31—C32 | 178.8 (3)  |
| C10—C11—C12—C9  | -69.9 (3)  | C30—C31—C32—C33 | -0.1 (5)   |
| C10—C11—C12—C13 | 47.9 (4)   | C31—C32—C33—C34 | 1.1 (5)    |
| C9—C12—C13—C14  | 44.8 (3)   | C32—C33—C34—C35 | -0.9 (5)   |
| C11—C12—C13—C14 | -72.7 (3)  | C33—C34—C35—C30 | -0.3 (5)   |
| C12—C13—C14—C15 | 150.0 (3)  | C31—C30—C35—C34 | 1.3 (5)    |
| C12—C13—C14—C7  | 23.4 (3)   | C29—C30—C35—C34 | -178.6 (3) |
| C10—C7—C14—C15  | -81.8 (3)  | C37—O7—C36—O6   | -1.0 (5)   |
| C8—C7—C14—C15   | 161.6 (3)  | C37—O7—C36—C28  | 178.1 (3)  |
| N1—C7—C14—C13   | 165.6 (2)  | N4—C28—C36—O6   | -33.9 (4)  |
| C10—C7—C14—C13  | 43.3 (3)   | C29—C28—C36—O6  | 90.0 (4)   |
| C8—C7—C14—C13   | -73.3 (3)  | C29—C28—C36—O7  | -89.1 (3)  |
| C16—N2—C15—O3   | -10.0 (4)  | C36—O7—C37—C38  | -87.1 (3)  |
| C13—C14—C15—O3  | -59.4 (4)  | O7—C37—C38—C43  | 124.5 (3)  |
| C7—C14—C15—O3   | 64.1 (4)   | O7—C37—C38—C39  | -57.7 (4)  |
| C13—C14—C15—N2  | 120.7 (3)  | C43—C38—C39—C40 | 1.1 (5)    |
| C15—N2—C16—C17  | -176.4 (3) | C37—C38—C39—C40 | -176.7 (3) |
| C19—N3—C18—O4   | 8.4 (5)    | C38—C39—C40—C41 | 0.3 (6)    |
| N2—C16—C18—O4   | -26.1 (4)  | C39—C40—C41—C42 | -1.3 (6)   |
| C17—C16—C18—O4  | 93.5 (4)   | C40—C41—C42—C43 | 0.8 (6)    |
| C17—C16—C18—N3  | -85.0 (3)  | C41—C42—C43—C38 | 0.6 (5)    |
| C18—N3—C19—C23  | -166.8 (3) | C39—C38—C43—C42 | -1.6 (5)   |
| C18—N3—C19—C20  | -48.5 (4)  | C37—C38—C43—C42 | 176.2 (3)  |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| N1—H1...O4              | 0.88        | 2.16          | 2.994 (4)             | 157                     |
| N2—H2...O5 <sup>i</sup> | 0.88        | 2.12          | 2.914 (3)             | 150                     |
| N3—H3N...O6             | 0.88        | 2.51          | 3.159 (3)             | 131                     |
| N4—H4...O3              | 0.88        | 2.20          | 3.009 (3)             | 153                     |
| C1'—H1'...O2            | 1.00        | 2.09          | 3.071 (4)             | 167                     |

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