

# 1,3,5-Tris[[3-(1*H*-benzotriazol-1-yl-methyl)phenoxy]methyl]-2,4,6-trimethylbenzene

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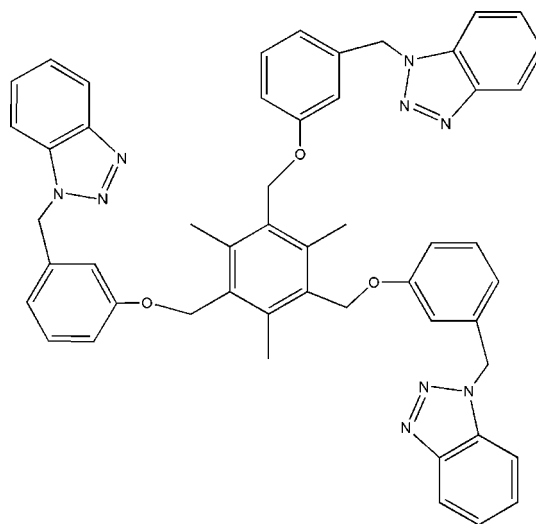
Received 16 July 2008; accepted 9 September 2008

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.058;  $wR$  factor = 0.187; data-to-parameter ratio = 14.4.

In the title compound,  $\text{C}_{51}\text{H}_{45}\text{N}_9\text{O}_3$ , three 1-(1*H*-benzotriazol-1-ylmethyl)-3-phenoxy (bmph) ligands are bonded to the central benzene ring in an asymmetric arrangement, two bmph located on one side of the central benzene ring and the other bmph located on the opposite side of the central benzene ring. The dihedral angles between the central benzene ring and the three pendant phenoxy rings are 76.71 (14), 67.81 (13) and 70.67 (16)°. In the crystal structure, one bmph is disordered over two sites in a 0.611 (5):0.389 (5) ratio. Some of the methyl H atoms are equally disordered over two sets of sites. Intermolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonding is present in the crystal structure.

## Related literature

For general background, see: Androsov & Neckers (2007); Blackman (2005); Fan *et al.* (2003); Fujita *et al.* (1995); Li *et al.* (2007); Zeng & Zimmerman (1997); Zhao *et al.* (2005). For related structures, see: Selvanayagam *et al.* (2004); Cai *et al.* (2004). For the synthesis, see: Gong *et al.* (2007); van der Made & van der Made (1993).



## Experimental

### Crystal data

$\text{C}_{51}\text{H}_{45}\text{N}_9\text{O}_3$

$M_r = 831.96$

Triclinic,  $P\bar{1}$

$a = 11.945$  (3) Å

$b = 13.524$  (3) Å

$c = 13.550$  (3) Å

$\alpha = 83.913$  (4)°

$\beta = 80.629$  (4)°

$\gamma = 84.766$  (4)°

$V = 2141.4$  (9) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 0.08$  mm<sup>-1</sup>

$T = 295$  (2) K

$0.23 \times 0.19 \times 0.18$  mm

### Data collection

Bruker SMART APEXII CCD

area-detector diffractometer

Absorption correction: none

16527 measured reflections

7926 independent reflections

3519 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

### Refinement

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

$wR(F^2) = 0.186$

$S = 1.01$

7926 reflections

552 parameters

60 restraints

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.15$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.28$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                        | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C2}-\text{H2}\cdots\text{N8}^i$      | 0.93         | 2.48               | 3.376 (7)   | 163                  |
| $\text{C27}-\text{H27}\cdots\text{N1}^{ii}$ | 0.93         | 2.54               | 3.453 (7)   | 166                  |

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2438).

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**supplementary materials**

*Acta Cryst.* (2008). E64, o1936-o1937 [ doi:10.1107/S1600536808028845 ]

## 1,3,5-Tris{[3-(1*H*-benzotriazol-1-ylmethyl)phenoxy]methyl}-2,4,6-trimethylbenzene

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### Comment

Tripodal ligands based on nitrogen heterocycles have been widely employed in many areas of inorganic chemistry (Blackman, 2005). For example, tripodal ligands with an arene core have been found to be one of the most useful organic building blocks in construction of metal-organic frameworks(MOFs) (Zeng & Zimmerman, 1997; Li *et al.*, 2007). Especially in the case of flexible tripodal ligands such as 1,3,5-tris(4-pyridylmethyl)benzene (Fujita *et al.*, 1995) and 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (Fan *et al.*, 2003), which have many more possible coordination modes due to their flexibility, and they can adopt different conformations according to geometric requirements of different metal ions (Zhao *et al.*, 2005). However, only a few examples of flexible tripodal benzotriazole ligands are reported (Androsov & Neckers, 2007). Herein we report the crystal structure of the title compound.

A view of the molecular structure of the title compound is given in Fig.1. IN the crystal structure the three 1-(1*H*-benzotriazol-1-ylmethyl)-3-phenyloxy (bmph) groups are bonded to the central benzene ring with an asymmetric arrangement, two bmph located on one side of the central benzene ring and the other bmph located on the opposite side of the central benzene ring. The dihedral angles between each benzotriazole moiety and the phenyloxy benzene rings are 86.1 (2), 91.8 (3) and 109.2 (2)°, respectively, and dihedral angles between mesitylene and phenyloxy benzene rings are 121.0 (2), 70.7 (3) and 112.2 (3)°. The N1-benzotriazole and N7-benzotriazole are approximately parallel to each other with a dihedral angle of 9.4 (2)°. All the bond distances and angles in the structure are within normal ranges, similar to those found in the related compound (Selvanayagam *et al.*, 2004; Cai *et al.*, 2004). Intermolecular C—H···N hydrogen bonding presents in the crystal structure (Table 1).

### Experimental

1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene and 1-(benzotriazol-1-ylmethyl)-3-hydroxybenzene were synthesized according to the reported procedure was (van der Made *et al.*, 1993; Gong *et al.*, 2007). 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (3 mmol), 1-(benzotriazol-1-ylmethyl)-3-hydroxybenzene (9 mmol) and NaH (27 mmol) were dissolved in dry dioxane (25 ml), then the resultant solution was refluxed for 6 h, removal of solvent resulted in a white powder that was recrystallized from dichloromethane-petroleum ether solution at room temperature to give the desired product as colorless crystals suitable for single-crystal X-ray diffraction (yield 55%; m.p > 573 K).

### Refinement

The N4-containing benzotriazole is disordered over two sites, occupancies were refined and converged to 0.611 (5):0.389 (5). The rigid-group mode was used in refinement for the disordered components, and atomic displacement parameters were constrained for disordered components. H atoms were placed in geometrically idealized positions and treated as riding with C—H = 0.93 (aromatic), 0.96 Å (methyl) and 0.97 Å (methylene), and constrained to ride on their parent atoms with  $U_{iso}(H) = 1.5U_{eq}(C)$  (for methyl) or  $1.2U_{eq}(C)$  for others.

## Figures

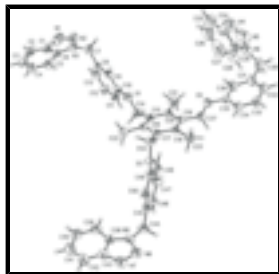


Fig. 1. The molecular structure of the title compound with 30% displacement probability ellipsoids.

## 1,3,5-Tris[[3-(1H-benzotriazol-1-ylmethyl)phenoxy]methyl]-2,4,6-trimethylbenzene

### Crystal data

$C_{51}H_{45}N_9O_3$

$M_r = 831.96$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 11.945\ (3)\ \text{\AA}$

$b = 13.524\ (3)\ \text{\AA}$

$c = 13.550\ (3)\ \text{\AA}$

$\alpha = 83.913\ (4)^\circ$

$\beta = 80.629\ (4)^\circ$

$\gamma = 84.766\ (4)^\circ$

$V = 2141.4\ (9)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 876$

$D_x = 1.290\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1969 reflections

$\theta = 2.5\text{--}20.4^\circ$

$\mu = 0.08\ \text{mm}^{-1}$

$T = 295\ (2)\ \text{K}$

Block, colourless

$0.23 \times 0.19 \times 0.18\ \text{mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 295\ (2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: none

16527 measured reflections

7926 independent reflections

3519 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\text{max}} = 25.5^\circ$

$\theta_{\text{min}} = 2.5^\circ$

$h = -14 \rightarrow 14$

$k = -16 \rightarrow 16$

$l = -16 \rightarrow 16$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.186$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 0.0204P]$

|  |  |
|--|--|
| $S = 1.01$   | where $P = (F_o^2 + 2F_c^2)/3$                         |
| 7926 reflections   | $(\Delta/\sigma)_{\max} < 0.001$                       |
| 552 parameters   | $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$  |
| 60 restraints  | $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none                            |

*Special details*

**Experimental.** Analysis found: C 73.85, H 5.29, N 15.37%; requires: C 73.63, H 5.45, N 15.15%. IR data ( $\nu_{\max}/\text{cm}^{-1}$ ): 3425, 2924, 1593, 1489, 1451, 1257, 1158, 1089, 1009, 781, 747. NMR  $\delta(\text{H})$  1.85(6H,brs), 2.32(9H,s), 4.99(6H,s), 5.84(6H,s), 6.90(6H,d), 6.95(3H,d), 7.26(3H,s), 7.35–7.43(9H,s), 8.08(3H,s). MS-ESI<sup>+</sup> [m/z]: 854.6(M+Na).

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes)

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

|      | $x$        | $y$        | $z$        | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|------------|------------|------------|----------------------------------|-----------|
| N6   | 0.8300 (6) | 1.4682 (5) | 0.5035 (4) | 0.0889 (13)                      | 0.611 (5) |
| N4   | 0.9689 (5) | 1.3866 (4) | 0.5597 (4) | 0.125 (2)                        | 0.611 (5) |
| N5   | 0.8893 (7) | 1.4545 (5) | 0.5804 (4) | 0.121 (2)                        | 0.611 (5) |
| C24  | 0.9686 (4) | 1.3515 (3) | 0.4672 (3) | 0.0935 (17)                      | 0.611 (5) |
| C25  | 1.0378 (4) | 1.2814 (4) | 0.4112 (4) | 0.114 (2)                        | 0.611 (5) |
| H25  | 1.1005     | 1.2456     | 0.4338     | 0.137*                           | 0.611 (5) |
| C26  | 1.0059 (5) | 1.2696 (4) | 0.3202 (4) | 0.125 (2)                        | 0.611 (5) |
| H26  | 1.0463     | 1.2209     | 0.2823     | 0.150*                           | 0.611 (5) |
| C27  | 0.9172 (5) | 1.3259 (5) | 0.2818 (4) | 0.112 (2)                        | 0.611 (5) |
| H27  | 0.9030     | 1.3169     | 0.2180     | 0.134*                           | 0.611 (5) |
| C28  | 0.8493 (5) | 1.3958 (5) | 0.3379 (4) | 0.0961 (15)                      | 0.611 (5) |
| H28  | 0.7888     | 1.4332     | 0.3133     | 0.115*                           | 0.611 (5) |
| C29  | 0.8757 (4) | 1.4072 (4) | 0.4326 (3) | 0.0780 (10)                      | 0.611 (5) |
| C30  | 0.7351 (8) | 1.5351 (7) | 0.5177 (6) | 0.1372 (18)                      | 0.611 (5) |
| H30A | 0.7104     | 1.5556     | 0.4534     | 0.165*                           | 0.611 (5) |
| H30B | 0.7558     | 1.5940     | 0.5436     | 0.165*                           | 0.611 (5) |

## supplementary materials

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|      |              |              |              |             |           |
|------|--------------|--------------|--------------|-------------|-----------|
| C1   | 0.8340 (3)   | 0.2950 (3)   | 0.9635 (4)   | 0.0977 (12) |           |
| N6'  | 0.8453 (10)  | 1.4436 (8)   | 0.5142 (7)   | 0.0889 (13) | 0.389 (5) |
| N4'  | 0.9868 (9)   | 1.3395 (7)   | 0.5248 (6)   | 0.125 (2)   | 0.389 (5) |
| N5'  | 0.9219 (11)  | 1.4049 (8)   | 0.5727 (6)   | 0.121 (2)   | 0.389 (5) |
| C24' | 0.9586 (6)   | 1.3312 (5)   | 0.4307 (6)   | 0.0935 (17) | 0.389 (5) |
| C25' | 1.0041 (7)   | 1.2740 (6)   | 0.3510 (6)   | 0.114 (2)   | 0.389 (5) |
| H25' | 1.0673       | 1.2288       | 0.3533       | 0.137*      | 0.389 (5) |
| C26' | 0.9478 (8)   | 1.2901 (6)   | 0.2689 (6)   | 0.125 (2)   | 0.389 (5) |
| H26' | 0.9718       | 1.2510       | 0.2159       | 0.150*      | 0.389 (5) |
| C27' | 0.8575 (9)   | 1.3611 (7)   | 0.2605 (6)   | 0.112 (2)   | 0.389 (5) |
| H27' | 0.8262       | 1.3709       | 0.2014       | 0.134*      | 0.389 (5) |
| C28' | 0.8132 (8)   | 1.4179 (7)   | 0.3401 (7)   | 0.0961 (15) | 0.389 (5) |
| H28' | 0.7520       | 1.4649       | 0.3357       | 0.115*      | 0.389 (5) |
| C29' | 0.8647 (7)   | 1.4011 (6)   | 0.4266 (6)   | 0.0780 (10) | 0.389 (5) |
| C30' | 0.7393 (14)  | 1.5328 (12)  | 0.5253 (10)  | 0.1372 (18) | 0.389 (5) |
| H30C | 0.7623       | 1.5882       | 0.5553       | 0.165*      | 0.389 (5) |
| H30D | 0.7209       | 1.5571       | 0.4594       | 0.165*      | 0.389 (5) |
| O1   | 0.52998 (17) | 0.80350 (16) | 0.79301 (16) | 0.0819 (7)  |           |
| O2   | 0.50213 (17) | 1.26023 (15) | 0.64934 (17) | 0.0810 (6)  |           |
| O3   | 0.22369 (16) | 0.99186 (17) | 0.46236 (15) | 0.0804 (7)  |           |
| N1   | 0.8768 (4)   | 0.3362 (4)   | 1.0342 (3)   | 0.1399 (15) |           |
| N2   | 0.8791 (3)   | 0.4321 (4)   | 1.0098 (3)   | 0.1267 (13) |           |
| N3   | 0.8385 (2)   | 0.4531 (2)   | 0.9210 (3)   | 0.0888 (9)  |           |
| N7   | -0.1788 (3)  | 0.9250 (3)   | 0.0660 (2)   | 0.0910 (9)  |           |
| N8   | -0.1573 (2)  | 0.9894 (2)   | 0.1239 (2)   | 0.0851 (8)  |           |
| N9   | -0.1164 (2)  | 0.9398 (2)   | 0.20454 (19) | 0.0675 (7)  |           |
| C2   | 0.8185 (5)   | 0.1936 (4)   | 0.9601 (5)   | 0.140 (2)   |           |
| H2   | 0.8392       | 0.1431       | 1.0073       | 0.168*      |           |
| C3   | 0.7706 (5)   | 0.1785 (5)   | 0.8811 (7)   | 0.172 (4)   |           |
| H3   | 0.7557       | 0.1133       | 0.8751       | 0.207*      |           |
| C4   | 0.7413 (4)   | 0.2490 (5)   | 0.8086 (5)   | 0.145 (2)   |           |
| H4   | 0.7080       | 0.2303       | 0.7566       | 0.174*      |           |
| C5   | 0.7601 (3)   | 0.3466 (3)   | 0.8110 (3)   | 0.1000 (12) |           |
| H5   | 0.7419       | 0.3956       | 0.7614       | 0.120*      |           |
| C6   | 0.8075 (3)   | 0.3680 (3)   | 0.8913 (3)   | 0.0755 (9)  |           |
| C7   | 0.8255 (3)   | 0.5545 (2)   | 0.8760 (3)   | 0.1036 (13) |           |
| H7A  | 0.8435       | 0.5545       | 0.8035       | 0.124*      |           |
| H7B  | 0.8799       | 0.5934       | 0.8976       | 0.124*      |           |
| C8   | 0.7072 (3)   | 0.6044 (2)   | 0.9025 (3)   | 0.0732 (9)  |           |
| C9   | 0.6679 (3)   | 0.6814 (2)   | 0.8388 (2)   | 0.0693 (8)  |           |
| H9   | 0.7135       | 0.7014       | 0.7789       | 0.083*      |           |
| C10  | 0.5610 (3)   | 0.7291 (2)   | 0.8634 (2)   | 0.0659 (8)  |           |
| C11  | 0.4925 (3)   | 0.7001 (2)   | 0.9517 (2)   | 0.0761 (9)  |           |
| H11  | 0.4200       | 0.7313       | 0.9677       | 0.091*      |           |
| C12  | 0.5323 (3)   | 0.6247 (3)   | 1.0157 (3)   | 0.0876 (11) |           |
| H12  | 0.4870       | 0.6057       | 1.0761       | 0.105*      |           |
| C13  | 0.6384 (3)   | 0.5767 (3)   | 0.9918 (3)   | 0.0880 (11) |           |
| H13  | 0.6640       | 0.5254       | 1.0359       | 0.106*      |           |
| C14  | 0.4173 (3)   | 0.8535 (2)   | 0.8129 (2)   | 0.0791 (10) |           |

|      |             |            |            |             |      |
|------|-------------|------------|------------|-------------|------|
| H14A | 0.4053      | 0.8782     | 0.8787     | 0.095*      |      |
| H14B | 0.3602      | 0.8072     | 0.8117     | 0.095*      |      |
| C15  | 0.4073 (2)  | 0.9381 (2) | 0.7340 (2) | 0.0626 (8)  |      |
| C16  | 0.3786 (2)  | 0.9206 (2) | 0.6416 (3) | 0.0638 (8)  |      |
| C17  | 0.3626 (2)  | 1.0009 (2) | 0.5703 (2) | 0.0610 (8)  |      |
| C18  | 0.3663 (2)  | 1.0990 (2) | 0.5952 (2) | 0.0627 (8)  |      |
| C19  | 0.3975 (2)  | 1.1159 (2) | 0.6862 (2) | 0.0602 (8)  |      |
| C20  | 0.4227 (2)  | 1.0347 (2) | 0.7532 (2) | 0.0618 (8)  |      |
| C21  | 0.4674 (3)  | 1.0522 (3) | 0.8487 (3) | 0.0912 (11) |      |
| H21A | 0.4045      | 1.0677     | 0.8999     | 0.137*      |      |
| H21B | 0.5154      | 1.1067     | 0.8349     | 0.137*      |      |
| H21C | 0.5103      | 0.9930     | 0.8714     | 0.137*      |      |
| C22  | 0.3609 (3)  | 0.8167 (2) | 0.6193 (3) | 0.0963 (11) |      |
| H22A | 0.3750      | 0.7702     | 0.6753     | 0.145*      | 0.50 |
| H22B | 0.4125      | 0.7998     | 0.5604     | 0.145*      | 0.50 |
| H22C | 0.2840      | 0.8141     | 0.6079     | 0.145*      | 0.50 |
| H22D | 0.3394      | 0.8192     | 0.5538     | 0.145*      | 0.50 |
| H22E | 0.3019      | 0.7896     | 0.6687     | 0.145*      | 0.50 |
| H22F | 0.4303      | 0.7752     | 0.6211     | 0.145*      | 0.50 |
| C23  | 0.3347 (3)  | 1.1869 (3) | 0.5227 (3) | 0.0932 (11) |      |
| H23A | 0.3152      | 1.1628     | 0.4640     | 0.140*      | 0.50 |
| H23B | 0.3981      | 1.2274     | 0.5035     | 0.140*      | 0.50 |
| H23C | 0.2706      | 1.2262     | 0.5548     | 0.140*      | 0.50 |
| H23D | 0.3407      | 1.2481     | 0.5509     | 0.140*      | 0.50 |
| H23E | 0.2579      | 1.1835     | 0.5113     | 0.140*      | 0.50 |
| H23F | 0.3853      | 1.1847     | 0.4601     | 0.140*      | 0.50 |
| C31  | 0.6374 (3)  | 1.4917 (3) | 0.5896 (3) | 0.0865 (10) |      |
| C32  | 0.5693 (4)  | 1.5536 (3) | 0.6508 (3) | 0.0880 (11) |      |
| H32  | 0.5862      | 1.6194     | 0.6505     | 0.106*      |      |
| C33  | 0.4763 (3)  | 1.5194 (3) | 0.7124 (3) | 0.0913 (11) |      |
| H33  | 0.4304      | 1.5621     | 0.7541     | 0.110*      |      |
| C34  | 0.4491 (3)  | 1.4217 (3) | 0.7139 (3) | 0.0795 (9)  |      |
| H34  | 0.3852      | 1.3991     | 0.7560     | 0.095*      |      |
| C35  | 0.5171 (3)  | 1.3589 (2) | 0.6528 (2) | 0.0692 (8)  |      |
| C36  | 0.6102 (3)  | 1.3938 (3) | 0.5901 (3) | 0.0850 (10) |      |
| H36  | 0.6555      | 1.3516     | 0.5475     | 0.102*      |      |
| C37  | 0.4026 (3)  | 1.2207 (2) | 0.7102 (3) | 0.0768 (9)  |      |
| H37A | 0.3347      | 1.2608     | 0.6958     | 0.092*      |      |
| H37B | 0.4074      | 1.2217     | 0.7809     | 0.092*      |      |
| C38  | -0.1114 (2) | 0.8400 (3) | 0.1982 (2) | 0.0667 (8)  |      |
| C39  | -0.0778 (3) | 0.7585 (3) | 0.2608 (3) | 0.0853 (10) |      |
| H39  | -0.0506     | 0.7654     | 0.3200     | 0.102*      |      |
| C40  | -0.0876 (3) | 0.6666 (3) | 0.2290 (4) | 0.1050 (13) |      |
| H40  | -0.0656     | 0.6092     | 0.2675     | 0.126*      |      |
| C41  | -0.1294 (4) | 0.6577 (4) | 0.1413 (4) | 0.1147 (15) |      |
| H41  | -0.1352     | 0.5942     | 0.1232     | 0.138*      |      |
| C42  | -0.1626 (4) | 0.7386 (4) | 0.0797 (3) | 0.1080 (13) |      |
| H42  | -0.1908     | 0.7312     | 0.0211     | 0.130*      |      |
| C43  | -0.1521 (3) | 0.8316 (3) | 0.1091 (3) | 0.0754 (9)  |      |

## supplementary materials

|      |             |            |            |             |
|------|-------------|------------|------------|-------------|
| C44  | -0.0932 (2) | 0.9947 (3) | 0.2840 (2) | 0.0778 (9)  |
| H44A | -0.1220     | 0.9599     | 0.3482     | 0.093*      |
| H44B | -0.1345     | 1.0598     | 0.2797     | 0.093*      |
| C45  | 0.0306 (2)  | 1.0086 (2) | 0.2814 (2) | 0.0619 (8)  |
| C46  | 0.0954 (3)  | 1.0492 (2) | 0.1951 (2) | 0.0717 (9)  |
| H46  | 0.0644      | 1.0635     | 0.1361     | 0.086*      |
| C47  | 0.2056 (3)  | 1.0681 (2) | 0.1973 (2) | 0.0779 (9)  |
| H47  | 0.2492      | 1.0947     | 0.1390     | 0.094*      |
| C48  | 0.2531 (3)  | 1.0488 (2) | 0.2836 (2) | 0.0716 (9)  |
| H48  | 0.3280      | 1.0626     | 0.2839     | 0.086*      |
| C49  | 0.1888 (2)  | 1.0089 (2) | 0.3698 (2) | 0.0618 (8)  |
| C50  | 0.0784 (2)  | 0.9872 (2) | 0.3678 (2) | 0.0641 (8)  |
| H50  | 0.0360      | 0.9578     | 0.4253     | 0.077*      |
| C54  | 0.3440 (2)  | 0.9854 (3) | 0.4660 (2) | 0.0791 (10) |
| H54A | 0.3801      | 1.0357     | 0.4181     | 0.095*      |
| H54B | 0.3779      | 0.9204     | 0.4484     | 0.095*      |

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

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| N6   | 0.098 (3)   | 0.083 (4)   | 0.089 (3)   | -0.033 (2)   | -0.024 (2)   | 0.011 (2)    |
| N4   | 0.123 (4)   | 0.130 (5)   | 0.124 (5)   | -0.022 (4)   | -0.034 (4)   | 0.015 (4)    |
| N5   | 0.128 (5)   | 0.137 (6)   | 0.102 (3)   | -0.037 (4)   | -0.031 (3)   | 0.009 (3)    |
| C24  | 0.089 (3)   | 0.086 (3)   | 0.102 (4)   | -0.014 (3)   | -0.011 (3)   | 0.007 (3)    |
| C25  | 0.103 (4)   | 0.089 (3)   | 0.140 (6)   | 0.004 (3)    | 0.002 (4)    | -0.002 (4)   |
| C26  | 0.121 (5)   | 0.087 (4)   | 0.159 (6)   | -0.015 (4)   | 0.003 (4)    | -0.012 (4)   |
| C27  | 0.121 (6)   | 0.100 (5)   | 0.115 (4)   | -0.034 (4)   | -0.003 (4)   | -0.015 (3)   |
| C28  | 0.094 (5)   | 0.086 (4)   | 0.111 (3)   | -0.019 (3)   | -0.018 (3)   | -0.006 (3)   |
| C29  | 0.084 (2)   | 0.070 (2)   | 0.084 (2)   | -0.0271 (19) | -0.020 (2)   | 0.0054 (19)  |
| C30  | 0.142 (4)   | 0.069 (3)   | 0.184 (5)   | -0.019 (3)   | 0.037 (4)    | -0.024 (3)   |
| C1   | 0.088 (3)   | 0.082 (3)   | 0.111 (3)   | 0.019 (2)    | -0.007 (2)   | 0.011 (3)    |
| N6'  | 0.098 (3)   | 0.083 (4)   | 0.089 (3)   | -0.033 (2)   | -0.024 (2)   | 0.011 (2)    |
| N4'  | 0.123 (4)   | 0.130 (5)   | 0.124 (5)   | -0.022 (4)   | -0.034 (4)   | 0.015 (4)    |
| N5'  | 0.128 (5)   | 0.137 (6)   | 0.102 (3)   | -0.037 (4)   | -0.031 (3)   | 0.009 (3)    |
| C24' | 0.089 (3)   | 0.086 (3)   | 0.102 (4)   | -0.014 (3)   | -0.011 (3)   | 0.007 (3)    |
| C25' | 0.103 (4)   | 0.089 (3)   | 0.140 (6)   | 0.004 (3)    | 0.002 (4)    | -0.002 (4)   |
| C26' | 0.121 (5)   | 0.087 (4)   | 0.159 (6)   | -0.015 (4)   | 0.003 (4)    | -0.012 (4)   |
| C27' | 0.121 (6)   | 0.100 (5)   | 0.115 (4)   | -0.034 (4)   | -0.003 (4)   | -0.015 (3)   |
| C28' | 0.094 (5)   | 0.086 (4)   | 0.111 (3)   | -0.019 (3)   | -0.018 (3)   | -0.006 (3)   |
| C29' | 0.084 (2)   | 0.070 (2)   | 0.084 (2)   | -0.0271 (19) | -0.020 (2)   | 0.0054 (19)  |
| C30' | 0.142 (4)   | 0.069 (3)   | 0.184 (5)   | -0.019 (3)   | 0.037 (4)    | -0.024 (3)   |
| O1   | 0.0603 (14) | 0.0778 (15) | 0.0961 (16) | 0.0050 (11)  | 0.0009 (12)  | 0.0168 (13)  |
| O2   | 0.0683 (14) | 0.0627 (15) | 0.1113 (17) | -0.0157 (11) | 0.0020 (13)  | -0.0201 (12) |
| O3   | 0.0506 (13) | 0.1262 (19) | 0.0672 (14) | -0.0247 (12) | -0.0066 (11) | -0.0100 (12) |
| N1   | 0.151 (4)   | 0.135 (4)   | 0.128 (3)   | 0.040 (3)    | -0.043 (3)   | 0.005 (3)    |
| N2   | 0.128 (3)   | 0.123 (3)   | 0.140 (3)   | 0.017 (3)    | -0.058 (3)   | -0.030 (3)   |
| N3   | 0.083 (2)   | 0.067 (2)   | 0.116 (3)   | 0.0078 (15)  | -0.0247 (19) | -0.0026 (18) |
| N7   | 0.096 (2)   | 0.106 (3)   | 0.075 (2)   | -0.0250 (19) | -0.0233 (17) | 0.0031 (19)  |

|     |             |             |             |              |              |              |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N8  | 0.078 (2)   | 0.091 (2)   | 0.087 (2)   | -0.0187 (16) | -0.0211 (17) | 0.0105 (18)  |
| N9  | 0.0588 (16) | 0.079 (2)   | 0.0680 (17) | -0.0132 (13) | -0.0170 (13) | -0.0058 (15) |
| C2  | 0.091 (4)   | 0.085 (4)   | 0.208 (6)   | 0.023 (3)    | 0.026 (4)    | 0.052 (4)    |
| C3  | 0.087 (4)   | 0.075 (4)   | 0.334 (12)  | 0.017 (3)    | 0.019 (5)    | -0.021 (6)   |
| C4  | 0.096 (4)   | 0.127 (5)   | 0.224 (7)   | -0.001 (3)   | -0.015 (4)   | -0.098 (5)   |
| C5  | 0.083 (3)   | 0.104 (3)   | 0.116 (3)   | 0.000 (2)    | -0.016 (2)   | -0.028 (3)   |
| C6  | 0.066 (2)   | 0.058 (2)   | 0.096 (3)   | 0.0031 (17)  | -0.004 (2)   | 0.002 (2)    |
| C7  | 0.077 (3)   | 0.060 (2)   | 0.166 (4)   | -0.0003 (18) | -0.009 (2)   | 0.003 (2)    |
| C8  | 0.063 (2)   | 0.0493 (19) | 0.106 (3)   | -0.0070 (16) | -0.011 (2)   | -0.0034 (18) |
| C9  | 0.060 (2)   | 0.0561 (19) | 0.089 (2)   | -0.0108 (16) | -0.0023 (17) | -0.0028 (17) |
| C10 | 0.061 (2)   | 0.0575 (19) | 0.077 (2)   | -0.0105 (16) | -0.0081 (18) | 0.0016 (17)  |
| C11 | 0.061 (2)   | 0.073 (2)   | 0.086 (2)   | 0.0013 (17)  | 0.0001 (19)  | 0.0042 (19)  |
| C12 | 0.074 (2)   | 0.088 (3)   | 0.091 (3)   | -0.003 (2)   | 0.000 (2)    | 0.018 (2)    |
| C13 | 0.081 (3)   | 0.079 (2)   | 0.099 (3)   | -0.007 (2)   | -0.017 (2)   | 0.018 (2)    |
| C14 | 0.059 (2)   | 0.079 (2)   | 0.089 (2)   | 0.0016 (17)  | 0.0027 (17)  | 0.0127 (19)  |
| C15 | 0.0456 (17) | 0.065 (2)   | 0.073 (2)   | -0.0032 (14) | -0.0016 (15) | 0.0032 (17)  |
| C16 | 0.0449 (17) | 0.063 (2)   | 0.083 (2)   | -0.0096 (14) | -0.0028 (16) | -0.0085 (18) |
| C17 | 0.0380 (16) | 0.080 (2)   | 0.066 (2)   | -0.0111 (14) | -0.0068 (14) | -0.0110 (18) |
| C18 | 0.0421 (17) | 0.068 (2)   | 0.075 (2)   | -0.0090 (14) | -0.0055 (15) | 0.0083 (17)  |
| C19 | 0.0480 (17) | 0.060 (2)   | 0.073 (2)   | -0.0074 (14) | -0.0072 (15) | -0.0085 (17) |
| C20 | 0.0448 (17) | 0.077 (2)   | 0.063 (2)   | -0.0041 (15) | -0.0049 (14) | -0.0082 (17) |
| C21 | 0.073 (2)   | 0.117 (3)   | 0.088 (3)   | -0.002 (2)   | -0.021 (2)   | -0.019 (2)   |
| C22 | 0.087 (3)   | 0.073 (2)   | 0.131 (3)   | -0.0124 (19) | -0.011 (2)   | -0.026 (2)   |
| C23 | 0.075 (2)   | 0.093 (3)   | 0.108 (3)   | -0.0092 (19) | -0.024 (2)   | 0.023 (2)    |
| C31 | 0.102 (3)   | 0.062 (2)   | 0.095 (3)   | -0.021 (2)   | -0.001 (2)   | -0.009 (2)   |
| C32 | 0.106 (3)   | 0.063 (2)   | 0.098 (3)   | -0.006 (2)   | -0.021 (2)   | -0.012 (2)   |
| C33 | 0.101 (3)   | 0.072 (3)   | 0.102 (3)   | 0.003 (2)    | -0.015 (2)   | -0.020 (2)   |
| C34 | 0.079 (2)   | 0.068 (2)   | 0.092 (2)   | -0.0046 (19) | -0.012 (2)   | -0.0094 (19) |
| C35 | 0.070 (2)   | 0.058 (2)   | 0.084 (2)   | -0.0053 (17) | -0.0175 (18) | -0.0135 (18) |
| C36 | 0.083 (3)   | 0.074 (2)   | 0.096 (3)   | -0.0157 (19) | 0.006 (2)    | -0.0192 (19) |
| C37 | 0.061 (2)   | 0.068 (2)   | 0.099 (2)   | -0.0078 (16) | -0.0021 (18) | -0.0105 (18) |
| C38 | 0.0533 (19) | 0.073 (2)   | 0.074 (2)   | -0.0151 (16) | -0.0047 (16) | -0.0031 (18) |
| C39 | 0.064 (2)   | 0.098 (3)   | 0.092 (3)   | -0.005 (2)   | -0.0127 (19) | 0.004 (2)    |
| C40 | 0.081 (3)   | 0.084 (3)   | 0.146 (4)   | -0.002 (2)   | -0.012 (3)   | -0.005 (3)   |
| C41 | 0.096 (3)   | 0.094 (4)   | 0.156 (5)   | -0.021 (3)   | 0.000 (3)    | -0.042 (3)   |
| C42 | 0.105 (3)   | 0.120 (4)   | 0.109 (3)   | -0.030 (3)   | -0.012 (3)   | -0.042 (3)   |
| C43 | 0.071 (2)   | 0.090 (3)   | 0.068 (2)   | -0.0172 (19) | -0.0101 (18) | -0.012 (2)   |
| C44 | 0.053 (2)   | 0.101 (3)   | 0.085 (2)   | -0.0101 (17) | -0.0092 (17) | -0.032 (2)   |
| C45 | 0.0502 (18) | 0.069 (2)   | 0.069 (2)   | -0.0087 (15) | -0.0041 (16) | -0.0224 (16) |
| C46 | 0.061 (2)   | 0.085 (2)   | 0.070 (2)   | -0.0075 (17) | -0.0101 (17) | -0.0101 (17) |
| C47 | 0.064 (2)   | 0.100 (3)   | 0.069 (2)   | -0.0247 (18) | -0.0005 (18) | -0.0050 (18) |
| C48 | 0.0545 (19) | 0.094 (2)   | 0.068 (2)   | -0.0223 (17) | -0.0070 (17) | -0.0080 (18) |
| C49 | 0.0497 (18) | 0.077 (2)   | 0.060 (2)   | -0.0137 (15) | -0.0023 (15) | -0.0155 (16) |
| C50 | 0.0510 (18) | 0.078 (2)   | 0.064 (2)   | -0.0156 (15) | 0.0026 (15)  | -0.0175 (16) |
| C54 | 0.049 (2)   | 0.114 (3)   | 0.076 (2)   | -0.0111 (17) | -0.0075 (16) | -0.0170 (19) |

Geometric parameters (Å, °)

N6—N5

1.3401

C11—H11

0.9300

## supplementary materials

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|           |            |          |           |
|-----------|------------|----------|-----------|
| N6—C29    | 1.3481     | C12—C13  | 1.376 (4) |
| N6—C30    | 1.3851     | C12—H12  | 0.9300    |
| N4—N5     | 1.2782     | C13—H13  | 0.9300    |
| N4—C24    | 1.3871     | C14—C15  | 1.492 (4) |
| C24—C29   | 1.4007     | C14—H14A | 0.9700    |
| C24—C25   | 1.4014     | C14—H14B | 0.9700    |
| C25—C26   | 1.3775     | C15—C20  | 1.392 (4) |
| C25—H25   | 0.9300     | C15—C16  | 1.399 (4) |
| C26—C27   | 1.3855     | C16—C17  | 1.396 (4) |
| C26—H26   | 0.9300     | C16—C22  | 1.508 (4) |
| C27—C28   | 1.3936     | C17—C18  | 1.410 (4) |
| C27—H27   | 0.9300     | C17—C54  | 1.505 (4) |
| C28—C29   | 1.3972     | C18—C19  | 1.391 (4) |
| C28—H28   | 0.9300     | C18—C23  | 1.521 (4) |
| C30—C31   | 1.513 (13) | C19—C20  | 1.392 (4) |
| C30—H30A  | 0.9700     | C19—C37  | 1.497 (4) |
| C30—H30B  | 0.9700     | C20—C21  | 1.526 (4) |
| C1—N1     | 1.347 (5)  | C21—H21A | 0.9600    |
| C1—C6     | 1.367 (5)  | C21—H21B | 0.9600    |
| C1—C2     | 1.407 (7)  | C21—H21C | 0.9600    |
| N6'—N5'   | 1.3420     | C22—H22A | 0.9600    |
| N6'—C29'  | 1.3500     | C22—H22B | 0.9600    |
| N6'—C30'  | 1.6672     | C22—H22C | 0.9600    |
| N4'—N5'   | 1.2800     | C22—H22D | 0.9600    |
| N4'—C24'  | 1.3891     | C22—H22E | 0.9600    |
| C24'—C29' | 1.4027     | C22—H22F | 0.9600    |
| C24'—C25' | 1.4034     | C23—H23A | 0.9600    |
| C25'—C26' | 1.3795     | C23—H23B | 0.9600    |
| C25'—H25' | 0.9300     | C23—H23C | 0.9600    |
| C26'—C27' | 1.3875     | C23—H23D | 0.9600    |
| C26'—H26' | 0.9300     | C23—H23E | 0.9600    |
| C27'—C28' | 1.3956     | C23—H23F | 0.9600    |
| C27'—H27' | 0.9300     | C31—C32  | 1.362 (5) |
| C28'—C29' | 1.3992     | C31—C36  | 1.390 (4) |
| C28'—H28' | 0.9300     | C32—C33  | 1.363 (5) |
| C30'—C31  | 1.49 (2)   | C32—H32  | 0.9300    |
| C30'—H30C | 0.9700     | C33—C34  | 1.386 (4) |
| C30'—H30D | 0.9700     | C33—H33  | 0.9300    |
| O1—C10    | 1.380 (3)  | C34—C35  | 1.368 (4) |
| O1—C14    | 1.447 (3)  | C34—H34  | 0.9300    |
| O2—C35    | 1.369 (3)  | C35—C36  | 1.373 (4) |
| O2—C37    | 1.443 (3)  | C36—H36  | 0.9300    |
| O3—C49    | 1.375 (3)  | C37—H37A | 0.9700    |
| O3—C54    | 1.441 (3)  | C37—H37B | 0.9700    |
| N1—N2     | 1.306 (5)  | C38—C39  | 1.389 (4) |
| N2—N3     | 1.363 (4)  | C38—C43  | 1.392 (4) |
| N3—C6     | 1.360 (4)  | C39—C40  | 1.379 (5) |
| N3—C7     | 1.446 (4)  | C39—H39  | 0.9300    |
| N7—N8     | 1.301 (4)  | C40—C41  | 1.382 (6) |

|              |           |               |           |
|--------------|-----------|---------------|-----------|
| N7—C43       | 1.367 (4) | C40—H40       | 0.9300    |
| N8—N9        | 1.358 (3) | C41—C42       | 1.374 (6) |
| N9—C38       | 1.356 (4) | C41—H41       | 0.9300    |
| N9—C44       | 1.447 (4) | C42—C43       | 1.381 (5) |
| C2—C3        | 1.335 (8) | C42—H42       | 0.9300    |
| C2—H2        | 0.9300    | C44—C45       | 1.502 (4) |
| C3—C4        | 1.360 (8) | C44—H44A      | 0.9700    |
| C3—H3        | 0.9300    | C44—H44B      | 0.9700    |
| C4—C5        | 1.364 (6) | C45—C50       | 1.377 (4) |
| C4—H4        | 0.9300    | C45—C46       | 1.384 (4) |
| C5—C6        | 1.373 (5) | C46—C47       | 1.369 (4) |
| C5—H5        | 0.9300    | C46—H46       | 0.9300    |
| C7—C8        | 1.514 (4) | C47—C48       | 1.372 (4) |
| C7—H7A       | 0.9700    | C47—H47       | 0.9300    |
| C7—H7B       | 0.9700    | C48—C49       | 1.377 (4) |
| C8—C9        | 1.379 (4) | C48—H48       | 0.9300    |
| C8—C13       | 1.385 (4) | C49—C50       | 1.381 (4) |
| C9—C10       | 1.383 (4) | C50—H50       | 0.9300    |
| C9—H9        | 0.9300    | C54—H54A      | 0.9700    |
| C10—C11      | 1.377 (4) | C54—H54B      | 0.9700    |
| C11—C12      | 1.369 (4) |               |           |
| N5—N6—C29    | 109.9     | C17—C18—C23   | 119.8 (3) |
| N5—N6—C30    | 114.4     | C18—C19—C20   | 119.2 (3) |
| C29—N6—C30   | 135.5     | C18—C19—C37   | 119.4 (3) |
| N5—N4—C24    | 112.7     | C20—C19—C37   | 121.4 (3) |
| N4—N5—N6     | 107.3     | C19—C20—C15   | 120.7 (3) |
| N4—C24—C29   | 102.9     | C19—C20—C21   | 119.4 (3) |
| N4—C24—C25   | 134.3     | C15—C20—C21   | 119.9 (3) |
| C29—C24—C25  | 122.8     | C20—C21—H21A  | 109.5     |
| C26—C25—C24  | 114.8     | C20—C21—H21B  | 109.5     |
| C26—C25—H25  | 122.6     | H21A—C21—H21B | 109.5     |
| C24—C25—H25  | 122.6     | C20—C21—H21C  | 109.5     |
| C25—C26—C27  | 124.1     | H21A—C21—H21C | 109.5     |
| C25—C26—H26  | 118.0     | H21B—C21—H21C | 109.5     |
| C27—C26—H26  | 118.0     | C16—C22—H22A  | 109.5     |
| C26—C27—C28  | 120.5     | C16—C22—H22B  | 109.5     |
| C26—C27—H27  | 119.7     | H22A—C22—H22B | 109.5     |
| C28—C27—H27  | 119.7     | C16—C22—H22C  | 109.5     |
| C27—C28—C29  | 117.3     | H22A—C22—H22C | 109.5     |
| C27—C28—H28  | 121.4     | H22B—C22—H22C | 109.5     |
| C29—C28—H28  | 121.4     | C16—C22—H22D  | 109.5     |
| N6—C29—C28   | 132.4     | H22A—C22—H22D | 141.1     |
| N6—C29—C24   | 107.2     | H22B—C22—H22D | 56.3      |
| C28—C29—C24  | 120.4     | H22C—C22—H22D | 56.3      |
| N6—C30—C31   | 112.7 (4) | C16—C22—H22E  | 109.5     |
| N6—C30—H30A  | 109.0     | H22A—C22—H22E | 56.3      |
| C31—C30—H30A | 109.0     | H22B—C22—H22E | 141.1     |
| N6—C30—H30B  | 109.0     | H22C—C22—H22E | 56.3      |
| C31—C30—H30B | 109.0     | H22D—C22—H22E | 109.5     |

## supplementary materials

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| H30A—C30—H30B  | 107.8     | C16—C22—H22F  | 109.5     |
| N1—C1—C6       | 109.3 (4) | H22A—C22—H22F | 56.3      |
| N1—C1—C2       | 127.4 (5) | H22B—C22—H22F | 56.3      |
| C6—C1—C2       | 123.4 (5) | H22C—C22—H22F | 141.1     |
| N5'—N6'—C29'   | 109.9     | H22D—C22—H22F | 109.5     |
| N5'—N6'—C30'   | 134.1     | H22E—C22—H22F | 109.5     |
| C29'—N6'—C30'  | 115.9     | C18—C23—H23A  | 109.5     |
| N5'—N4'—C24'   | 112.7     | C18—C23—H23B  | 109.5     |
| N4'—N5'—N6'    | 107.3     | H23A—C23—H23B | 109.5     |
| N4'—C24'—C29'  | 102.9     | C18—C23—H23C  | 109.5     |
| N4'—C24'—C25'  | 134.3     | H23A—C23—H23C | 109.5     |
| C29'—C24'—C25' | 122.8     | H23B—C23—H23C | 109.5     |
| C26'—C25'—C24' | 114.8     | C18—C23—H23D  | 109.5     |
| C26'—C25'—H25' | 122.6     | H23A—C23—H23D | 141.1     |
| C24'—C25'—H25' | 122.6     | H23B—C23—H23D | 56.3      |
| C25'—C26'—C27' | 124.1     | H23C—C23—H23D | 56.3      |
| C25'—C26'—H26' | 118.0     | C18—C23—H23E  | 109.5     |
| C27'—C26'—H26' | 118.0     | H23A—C23—H23E | 56.3      |
| C26'—C27'—C28' | 120.5     | H23B—C23—H23E | 141.1     |
| C26'—C27'—H27' | 119.7     | H23C—C23—H23E | 56.3      |
| C28'—C27'—H27' | 119.7     | H23D—C23—H23E | 109.5     |
| C27'—C28'—C29' | 117.3     | C18—C23—H23F  | 109.5     |
| C27'—C28'—H28' | 121.3     | H23A—C23—H23F | 56.3      |
| C29'—C28'—H28' | 121.3     | H23B—C23—H23F | 56.3      |
| N6'—C29'—C28'  | 132.4     | H23C—C23—H23F | 141.1     |
| N6'—C29'—C24'  | 107.2     | H23D—C23—H23F | 109.5     |
| C28'—C29'—C24' | 120.4     | H23E—C23—H23F | 109.5     |
| C31—C30'—N6'   | 109.4 (7) | C32—C31—C36   | 119.3 (3) |
| C31—C30'—H30C  | 109.8     | C32—C31—C30'  | 117.7 (5) |
| N6'—C30'—H30C  | 109.8     | C36—C31—C30'  | 123.0 (5) |
| C31—C30'—H30D  | 109.8     | C32—C31—C30   | 118.0 (4) |
| N6'—C30'—H30D  | 109.8     | C36—C31—C30   | 122.5 (4) |
| H30C—C30'—H30D | 108.2     | C31—C32—C33   | 120.1 (4) |
| C10—O1—C14     | 117.7 (2) | C31—C32—H32   | 120.0     |
| C35—O2—C37     | 117.5 (2) | C33—C32—H32   | 120.0     |
| C49—O3—C54     | 118.1 (2) | C32—C33—C34   | 121.0 (4) |
| N2—N1—C1       | 108.9 (4) | C32—C33—H33   | 119.5     |
| N1—N2—N3       | 107.8 (4) | C34—C33—H33   | 119.5     |
| C6—N3—N2       | 109.4 (3) | C35—C34—C33   | 119.4 (3) |
| C6—N3—C7       | 129.3 (4) | C35—C34—H34   | 120.3     |
| N2—N3—C7       | 121.2 (4) | C33—C34—H34   | 120.3     |
| N8—N7—C43      | 108.0 (3) | C34—C35—O2    | 125.3 (3) |
| N7—N8—N9       | 109.0 (3) | C34—C35—C36   | 119.6 (3) |
| C38—N9—N8      | 110.1 (3) | O2—C35—C36    | 115.1 (3) |
| C38—N9—C44     | 130.1 (3) | C35—C36—C31   | 120.7 (3) |
| N8—N9—C44      | 119.7 (3) | C35—C36—H36   | 119.6     |
| C3—C2—C1       | 111.9 (6) | C31—C36—H36   | 119.6     |
| C3—C2—H2       | 124.0     | O2—C37—C19    | 108.0 (2) |
| C1—C2—H2       | 124.0     | O2—C37—H37A   | 110.1     |

|               |           |               |           |
|---------------|-----------|---------------|-----------|
| C2—C3—C4      | 126.6 (7) | C19—C37—H37A  | 110.1     |
| C2—C3—H3      | 116.7     | O2—C37—H37B   | 110.1     |
| C4—C3—H3      | 116.7     | C19—C37—H37B  | 110.1     |
| C3—C4—C5      | 120.8 (6) | H37A—C37—H37B | 108.4     |
| C3—C4—H4      | 119.6     | N9—C38—C39    | 132.6 (3) |
| C5—C4—H4      | 119.6     | N9—C38—C43    | 104.0 (3) |
| C4—C5—C6      | 115.8 (5) | C39—C38—C43   | 123.4 (4) |
| C4—C5—H5      | 122.1     | C40—C39—C38   | 115.3 (4) |
| C6—C5—H5      | 122.1     | C40—C39—H39   | 122.3     |
| N3—C6—C1      | 104.6 (4) | C38—C39—H39   | 122.3     |
| N3—C6—C5      | 134.0 (4) | C39—C40—C41   | 121.5 (4) |
| C1—C6—C5      | 121.4 (4) | C39—C40—H40   | 119.2     |
| N3—C7—C8      | 113.7 (3) | C41—C40—H40   | 119.2     |
| N3—C7—H7A     | 108.8     | C42—C41—C40   | 122.9 (4) |
| C8—C7—H7A     | 108.8     | C42—C41—H41   | 118.6     |
| N3—C7—H7B     | 108.8     | C40—C41—H41   | 118.6     |
| C8—C7—H7B     | 108.8     | C41—C42—C43   | 116.7 (4) |
| H7A—C7—H7B    | 107.7     | C41—C42—H42   | 121.6     |
| C9—C8—C13     | 118.8 (3) | C43—C42—H42   | 121.6     |
| C9—C8—C7      | 119.9 (3) | N7—C43—C42    | 130.9 (4) |
| C13—C8—C7     | 121.2 (3) | N7—C43—C38    | 109.0 (3) |
| C8—C9—C10     | 120.4 (3) | C42—C43—C38   | 120.1 (4) |
| C8—C9—H9      | 119.8     | N9—C44—C45    | 114.2 (2) |
| C10—C9—H9     | 119.8     | N9—C44—H44A   | 108.7     |
| C11—C10—O1    | 124.3 (3) | C45—C44—H44A  | 108.7     |
| C11—C10—C9    | 120.5 (3) | N9—C44—H44B   | 108.7     |
| O1—C10—C9     | 115.2 (3) | C45—C44—H44B  | 108.7     |
| C12—C11—C10   | 119.1 (3) | H44A—C44—H44B | 107.6     |
| C12—C11—H11   | 120.4     | C50—C45—C46   | 119.3 (3) |
| C10—C11—H11   | 120.4     | C50—C45—C44   | 119.6 (3) |
| C11—C12—C13   | 120.9 (3) | C46—C45—C44   | 120.9 (3) |
| C11—C12—H12   | 119.6     | C47—C46—C45   | 119.5 (3) |
| C13—C12—H12   | 119.6     | C47—C46—H46   | 120.3     |
| C12—C13—C8    | 120.3 (3) | C45—C46—H46   | 120.3     |
| C12—C13—H13   | 119.8     | C46—C47—C48   | 121.5 (3) |
| C8—C13—H13    | 119.8     | C46—C47—H47   | 119.2     |
| O1—C14—C15    | 108.5 (2) | C48—C47—H47   | 119.2     |
| O1—C14—H14A   | 110.0     | C47—C48—C49   | 119.2 (3) |
| C15—C14—H14A  | 110.0     | C47—C48—H48   | 120.4     |
| O1—C14—H14B   | 110.0     | C49—C48—H48   | 120.4     |
| C15—C14—H14B  | 110.0     | O3—C49—C48    | 125.0 (3) |
| H14A—C14—H14B | 108.4     | O3—C49—C50    | 115.2 (3) |
| C20—C15—C16   | 120.1 (3) | C48—C49—C50   | 119.7 (3) |
| C20—C15—C14   | 120.2 (3) | C45—C50—C49   | 120.7 (3) |
| C16—C15—C14   | 119.7 (3) | C45—C50—H50   | 119.7     |
| C17—C16—C15   | 119.4 (3) | C49—C50—H50   | 119.7     |
| C17—C16—C22   | 119.5 (3) | O3—C54—C17    | 109.3 (2) |
| C15—C16—C22   | 121.0 (3) | O3—C54—H54A   | 109.8     |
| C16—C17—C18   | 119.7 (3) | C17—C54—H54A  | 109.8     |

## supplementary materials

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| C16—C17—C54         | 121.5 (3) | O3—C54—H54B      | 109.8      |
| C18—C17—C54         | 118.8 (3) | C17—C54—H54B     | 109.8      |
| C19—C18—C17         | 120.4 (3) | H54A—C54—H54B    | 108.3      |
| C19—C18—C23         | 119.8 (3) |                  |            |
| C24—N4—N5—N6        | 0.8       | O1—C14—C15—C16   | 83.8 (3)   |
| C29—N6—N5—N4        | -0.7      | C20—C15—C16—C17  | -1.6 (4)   |
| C30—N6—N5—N4        | 175.6     | C14—C15—C16—C17  | 176.2 (2)  |
| N5—N4—C24—C29       | -0.5      | C20—C15—C16—C22  | -179.7 (3) |
| N5—N4—C24—C25       | 178.1     | C14—C15—C16—C22  | -1.9 (4)   |
| N4—C24—C25—C26      | -179.8    | C15—C16—C17—C18  | -5.3 (4)   |
| C29—C24—C25—C26     | -1.4      | C22—C16—C17—C18  | 172.8 (3)  |
| C24—C25—C26—C27     | 3.9       | C15—C16—C17—C54  | 173.4 (2)  |
| C25—C26—C27—C28     | -3.9      | C22—C16—C17—C54  | -8.5 (4)   |
| C26—C27—C28—C29     | 1.0       | C16—C17—C18—C19  | 6.8 (4)    |
| N5—N6—C29—C28       | -176.8    | C54—C17—C18—C19  | -171.9 (2) |
| C30—N6—C29—C28      | 7.9       | C16—C17—C18—C23  | -172.5 (3) |
| N5—N6—C29—C24       | 0.4       | C54—C17—C18—C23  | 8.9 (4)    |
| C30—N6—C29—C24      | -174.8    | C17—C18—C19—C20  | -1.3 (4)   |
| C27—C28—C29—N6      | 178.3     | C23—C18—C19—C20  | 177.9 (3)  |
| C27—C28—C29—C24     | 1.4       | C17—C18—C19—C37  | 179.0 (2)  |
| N4—C24—C29—N6       | 0.1       | C23—C18—C19—C37  | -1.7 (4)   |
| C25—C24—C29—N6      | -178.8    | C18—C19—C20—C15  | -5.7 (4)   |
| N4—C24—C29—C28      | 177.7     | C37—C19—C20—C15  | 174.0 (3)  |
| C25—C24—C29—C28     | -1.2      | C18—C19—C20—C21  | 174.4 (3)  |
| N5—N6—C30—C31       | -75.3 (4) | C37—C19—C20—C21  | -5.9 (4)   |
| C29—N6—C30—C31      | 99.7 (4)  | C16—C15—C20—C19  | 7.2 (4)    |
| C24'—N4'—N5'—N6'    | 0.8       | C14—C15—C20—C19  | -170.6 (3) |
| C29'—N6'—N5'—N4'    | -0.7      | C16—C15—C20—C21  | -172.9 (3) |
| C30'—N6'—N5'—N4'    | -177.7    | C14—C15—C20—C21  | 9.3 (4)    |
| N5'—N4'—C24'—C29'   | -0.5      | N6'—C30'—C31—C32 | 145.2 (3)  |
| N5'—N4'—C24'—C25'   | 178.1     | N6'—C30'—C31—C36 | -34.2 (7)  |
| N4'—C24'—C25'—C26'  | -179.8    | N6'—C30'—C31—C30 | -120 (8)   |
| C29'—C24'—C25'—C26' | -1.4      | N6—C30—C31—C32   | 145.2 (3)  |
| C24'—C25'—C26'—C27' | 4.0       | N6—C30—C31—C36   | -39.5 (5)  |
| C25'—C26'—C27'—C28' | -3.9      | N6—C30—C31—C30'  | 58 (7)     |
| C26'—C27'—C28'—C29' | 1.0       | C36—C31—C32—C33  | 0.7 (6)    |
| N5'—N6'—C29'—C28'   | -176.8    | C30'—C31—C32—C33 | -178.8 (6) |
| C30'—N6'—C29'—C28'  | 0.8       | C30—C31—C32—C33  | 176.1 (4)  |
| N5'—N6'—C29'—C24'   | 0.4       | C31—C32—C33—C34  | -0.2 (6)   |
| C30'—N6'—C29'—C24'  | 178.0     | C32—C33—C34—C35  | 0.3 (5)    |
| C27'—C28'—C29'—N6'  | 178.3     | C33—C34—C35—O2   | 177.7 (3)  |
| C27'—C28'—C29'—C24' | 1.4       | C33—C34—C35—C36  | -0.9 (5)   |
| N4'—C24'—C29'—N6'   | 0.1       | C37—O2—C35—C34   | 4.1 (4)    |
| C25'—C24'—C29'—N6'  | -178.8    | C37—O2—C35—C36   | -177.1 (3) |
| N4'—C24'—C29'—C28'  | 177.7     | C34—C35—C36—C31  | 1.4 (5)    |
| C25'—C24'—C29'—C28' | -1.2      | O2—C35—C36—C31   | -177.4 (3) |
| N5'—N6'—C30'—C31    | -80.7 (7) | C32—C31—C36—C35  | -1.3 (5)   |
| C29'—N6'—C30'—C31   | 102.5 (7) | C30'—C31—C36—C35 | 178.1 (6)  |
| C6—C1—N1—N2         | -0.3 (5)  | C30—C31—C36—C35  | -176.5 (4) |

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| C2—C1—N1—N2     | 179.0 (4)  | C35—O2—C37—C19  | 174.0 (3)  |
| C1—N1—N2—N3     | -0.8 (5)   | C18—C19—C37—O2  | -73.4 (3)  |
| N1—N2—N3—C6     | 1.6 (4)    | C20—C19—C37—O2  | 107.0 (3)  |
| N1—N2—N3—C7     | 177.2 (3)  | N8—N9—C38—C39   | -179.1 (3) |
| C43—N7—N8—N9    | 0.1 (4)    | C44—N9—C38—C39  | -3.9 (5)   |
| N7—N8—N9—C38    | 0.1 (3)    | N8—N9—C38—C43   | -0.3 (3)   |
| N7—N8—N9—C44    | -175.7 (3) | C44—N9—C38—C43  | 175.0 (3)  |
| N1—C1—C2—C3     | 178.0 (5)  | N9—C38—C39—C40  | 178.5 (3)  |
| C6—C1—C2—C3     | -2.8 (7)   | C43—C38—C39—C40 | -0.2 (5)   |
| C1—C2—C3—C4     | 1.8 (9)    | C38—C39—C40—C41 | -0.7 (5)   |
| C2—C3—C4—C5     | 0.1 (10)   | C39—C40—C41—C42 | 0.7 (6)    |
| C3—C4—C5—C6     | -1.2 (7)   | C40—C41—C42—C43 | 0.3 (6)    |
| N2—N3—C6—C1     | -1.7 (4)   | N8—N7—C43—C42   | 177.7 (4)  |
| C7—N3—C6—C1     | -176.8 (3) | N8—N7—C43—C38   | -0.3 (4)   |
| N2—N3—C6—C5     | 178.2 (4)  | C41—C42—C43—N7  | -178.9 (4) |
| C7—N3—C6—C5     | 3.1 (6)    | C41—C42—C43—C38 | -1.1 (5)   |
| N1—C1—C6—N3     | 1.2 (4)    | N9—C38—C43—N7   | 0.4 (3)    |
| C2—C1—C6—N3     | -178.0 (4) | C39—C38—C43—N7  | 179.3 (3)  |
| N1—C1—C6—C5     | -178.7 (3) | N9—C38—C43—C42  | -177.9 (3) |
| C2—C1—C6—C5     | 2.0 (6)    | C39—C38—C43—C42 | 1.1 (5)    |
| C4—C5—C6—N3     | -179.8 (4) | C38—N9—C44—C45  | 82.8 (4)   |
| C4—C5—C6—C1     | 0.1 (5)    | N8—N9—C44—C45   | -102.3 (3) |
| C6—N3—C7—C8     | 80.2 (5)   | N9—C44—C45—C50  | -131.3 (3) |
| N2—N3—C7—C8     | -94.4 (4)  | N9—C44—C45—C46  | 53.2 (4)   |
| N3—C7—C8—C9     | -154.6 (3) | C50—C45—C46—C47 | -0.5 (5)   |
| N3—C7—C8—C13    | 27.8 (5)   | C44—C45—C46—C47 | 174.9 (3)  |
| C13—C8—C9—C10   | -0.7 (5)   | C45—C46—C47—C48 | -0.8 (5)   |
| C7—C8—C9—C10    | -178.4 (3) | C46—C47—C48—C49 | 0.5 (5)    |
| C14—O1—C10—C11  | -0.8 (4)   | C54—O3—C49—C48  | -20.2 (4)  |
| C14—O1—C10—C9   | 177.7 (3)  | C54—O3—C49—C50  | 162.8 (3)  |
| C8—C9—C10—C11   | -0.2 (5)   | C47—C48—C49—O3  | -175.7 (3) |
| C8—C9—C10—O1    | -178.7 (3) | C47—C48—C49—C50 | 1.1 (5)    |
| O1—C10—C11—C12  | 179.6 (3)  | C46—C45—C50—C49 | 2.1 (4)    |
| C9—C10—C11—C12  | 1.2 (5)    | C44—C45—C50—C49 | -173.4 (3) |
| C10—C11—C12—C13 | -1.3 (5)   | O3—C49—C50—C45  | 174.7 (2)  |
| C11—C12—C13—C8  | 0.4 (6)    | C48—C49—C50—C45 | -2.4 (4)   |
| C9—C8—C13—C12   | 0.6 (5)    | C49—O3—C54—C17  | 161.4 (3)  |
| C7—C8—C13—C12   | 178.3 (3)  | C16—C17—C54—O3  | 94.9 (3)   |
| C10—O1—C14—C15  | 173.4 (3)  | C18—C17—C54—O3  | -86.4 (3)  |
| O1—C14—C15—C20  | -98.4 (3)  |                 |            |

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D-H\cdots A$                     | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| C2—H2 $\cdots$ N8 <sup>i</sup>    | 0.93  | 2.48        | 3.376 (7)   | 163           |
| C27—H27 $\cdots$ N1 <sup>ii</sup> | 0.93  | 2.54        | 3.453 (7)   | 166           |

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

Fig. 1

