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[1–9-NαC]-Linusorb B3 (cyclolinopeptide A) acetonitrile disolvate

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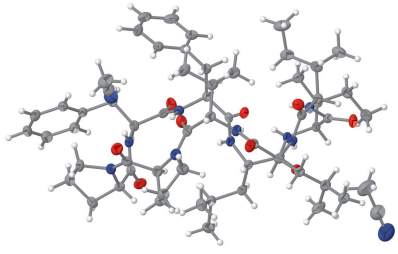
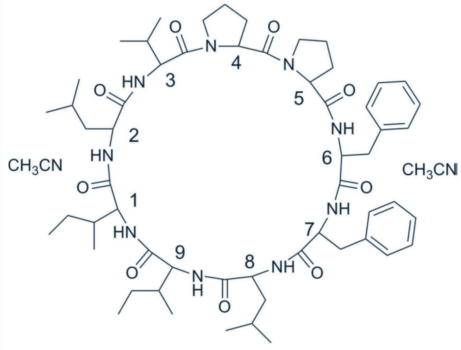
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{57}H_{85}N_9O_9\cdot 2C_2H_3N$ [systematic name: *cyclo*-(prolyl-prolyl-phenylalanyl-phenylalanyl-leucyl-isoleucyl-isoleucylleucyl-valyl) acetonitrile disolvate; synonym: cyclolinopeptide acetonitrile disolvate], is a polypeptide with nine amino acids, *viz*. NαC-(Pro^1–Pro^2–Phe^3–Phe^4–Leu^5–Ile^6–Ile^7–Leu^8–Val^9). It was extracted from flaxseed oil and crystallized from acetonitrile as a disolvate. In the title molecule, there are four intramolecular N—H···O hydrogen bonds. One of the two acetonitrile molecules is hydrogen bonded to Phe^3 *via* an N—H···N hydrogen bond, while the second acetonitrile molecule is located at the other side of the peptide ring and is linked to the title molecule by a C—H···N hydrogen bond. In the crystal, molecules are linked by N—H···O hydrogen bonds, forming chains along the *a*-axis direction. The chains are linked by C—H···O hydrogen bonds, forming undulating layers parallel to the *ac* plane.

3D view



Chemical scheme



Structure description

Several cyclic peptides have been isolated from flaxseed (*Linum usitatissimum* L). The isolation and purification procedures used have been reported (Kaufmann & Tobschirbel, 1959; Reaney *et al.*, 2013), as have the amino acid composition and sequencing methods (Prox & Weygand, 1966). Different solvents have been used to grow crystals of the title compound, and the crystal structures of a number of polymorphs have been reported. For example, different orthorhombic polymorphs have been obtained from chloroform (Huben *et al.*, 2014), methanol (Quail *et al.*, 2009), methanol/2-propanol

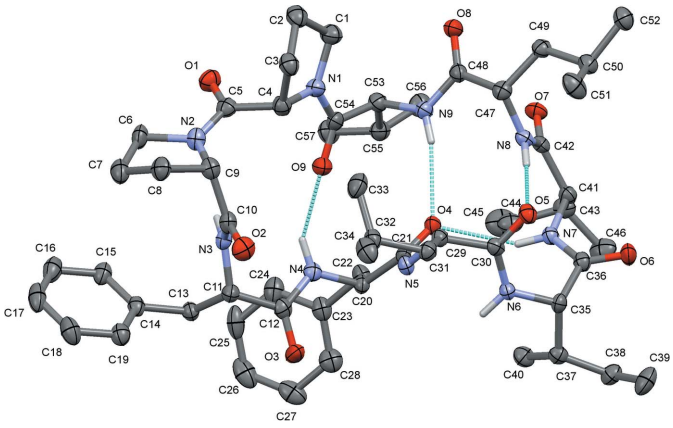


Figure 1
Crystal structure of the title [1–9-NαC]-linusorb B3 molecule, with atom labelling and 50% displacement ellipsoids. The intramolecular hydrogen bonds (see Table 1) are shown as dashed lines. For clarity, the solvent acteonitrile molecules and the C-bound H atoms have been omitted.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4*N*···O9	0.88	2.08	2.834 (5)	144
N7—H7···O4	0.88	2.30	3.112 (5)	153
N8—H8···O5	0.88	2.12	2.985 (5)	168
N9—H9*N*···O4	0.88	2.23	3.058 (5)	157
N3—H3···N1*S*	0.88	2.31	3.136 (7)	157
C13—H13*A*···N1*S*	0.99	2.67	3.451 (7)	136
N5—H5···O8^{i}	0.88	2.60	3.103 (5)	117
N6—H6···O8^{i}	0.88	2.42	3.153 (5)	141
C1—H1*A*···O3^{ii}	0.99	2.48	3.378 (7)	150
C31—H31*B*···O8^{i}	0.99	2.63	3.435 (6)	139
C37—H37···O7^{i}	1.00	2.17	3.041 (6)	145
C53—H53···O3^{ii}	1.00	2.35	3.187 (6)	140
C2*S*—H2*S*1···O6^{iii}	0.98	2.37	3.268 (7)	152
C4*S*—H4*S*1···O5	0.98	2.55	3.463 (9)	155
C4*S*—H4*S*2···O6	0.98	2.62	3.246 (9)	122

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

(Matsumoto *et al.*, 2002), water/2-2-propanol (Di Blasio *et al.*, 1987, 1989) and benzene/acetonitrile (Saviano *et al.*, 1995). The last polymorph crystallized as an acetonitrile monosolvate monohydrate. It has been shown that the title compound tends to self-assemble, under suitable conditions, from zero-dimensional objects to one-dimensional nanofibers and finally producing a three-dimensional supramolecular gel network (Rogers *et al.*, 2016).

A systematic naming system specifically for the Type VI cyclic peptides, such as the title compound, that 'reflects the taxonomic name of the species producing the orbitides and a numbering system that enables systematic representation of amino acid residues and modifications' has been proposed by our group (Shim *et al.*, 2015). Hence the name of the title compound [1–9-NαC]-linusorb B3 (cyclolinopeptide A). Herein, we report on the crystal structure of a new orthorhombic polymorph of the title compound that crystallized as an acteonitrile disolvate.

The molecular structure of the title [1–9-NαC]-linusorb B3 molecule is illustrated in Fig. 1. The peptide backbone ring is twisted to form four intramolecular hydrogen bonds between the amino acids (N4—H4*N*···O9, N9—H9*N*···O4, N8—H8···O5 and N7—H7···O5), as shown in Fig. 1 and Table 1.

In the crystal, one of the two acetonitrile molecules is hydrogen bonded to phe[3] *via* an N3—H3···N1*S* hydrogen bond (Table 1 and Fig. 2). The second acetonitrile molecule is located at the other side of the peptide ring and the C≡N bond is positioned proximate to a CH_x-rich environment, and is linked to the title molecule by a C—H···N hydrogen bond. The [1–9-NαC]-linusorb B3 molecules are linked in chains along the *a*-axis direction by two intermolecular hydrogen bonds, namely N5—H5···O8^{i} and N6—H6···O8^{i} (Table 1), as shown in Fig. 2. The chains are linked *via* C—H···O hydrogen bonds, forming undulating layers parallel to the *ac* plane (Fig. 3).

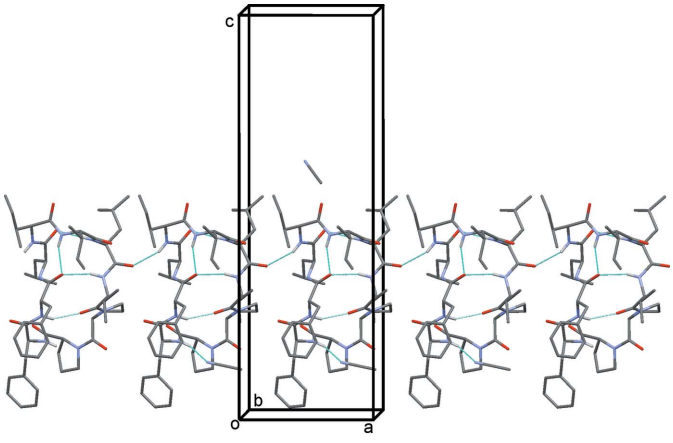


Figure 2
A partial view along the *b* axis of the crystal packing of the title compound. The hydrogen bonds (see Table 1) are shown as dashed lines, and, for clarity, the C-bound H atoms have been omitted.

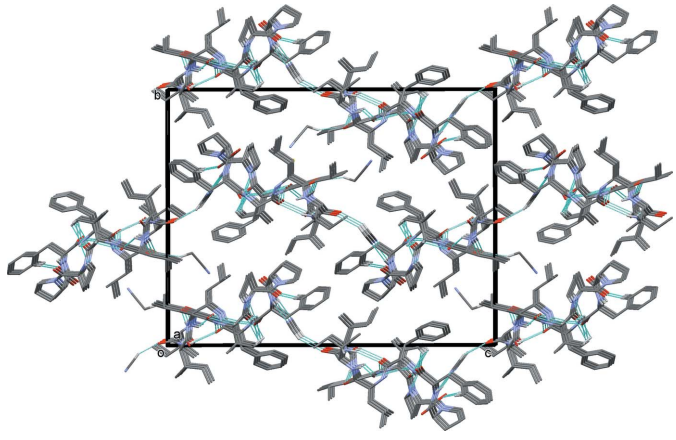


Figure 3
A view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds (see Table 1) are shown as dashed lines, and, for clarity, only the C-bound H atoms involved in hydrogen bonding have been included.

Synthesis and crystallization

Suitable crystals of the title compound were isolated from a solution of [1–9-NαC]-linusorb B3 in acetonitrile when the solvent was allowed to evaporate slowly at ambient temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflections 140, 038, 060, 119, 108, $\overline{1}$19, $\overline{1}$77 and 360 were affected by the beam-stop and were omitted from the final refinement.

Acknowledgements

The authors acknowledge the kind contribution of [1–9-NαC]-linusorb B3 from Prairie Tide Chemicals Inc. (Saskatchewan, Canada), and the assistance of Dr Youn Young Shim (University of Saskatchewan) with proof-reading this article. We are also grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Saskatchewan Ministry of Agriculture, through the Agricultural Development Fund (grant Nos. 20080205, 20120099 and 20120146), for financial support.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{57}H_{85}N_9O_9\cdot 2C_2H_3N$
M_r	1122.44
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	9.6524 (6), 22.6947 (13), 29.0945 (17)
V (Å^3)	6373.4 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.64
Crystal size (mm)	0.55 × 0.06 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.587, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47444, 11348, 9085
R_{int}	0.086
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.166, 1.05
No. of reflections	11348
No. of parameters	742
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.31
Absolute structure	Flack x determined using 3356 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.16 (11)

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXTL* (Sheldrick 2008) and *SHELXL2014* (Sheldrick, 2015).

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full crystallographic data

IUCrData (2016). **1**, x161706 [https://doi.org/10.1107/S2414314616017065]

[1–9-NαC]-Linusorb B3 (cyclolinopeptide A) acetonitrile disolvate

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Cyclo-(prolyl-prolyl-phenylalanyl-phenylalanyl-leucyl-isoleucyl-isoleucylleucyl-valyl) acetonitrile disolvate

Crystal data

$C_{57}H_{85}N_9O_9·2C_2H_3N$
M_r = 1122.44
Orthorhombic, $P2_12_12_1$
a = 9.6524 (6) Å
b = 22.6947 (13) Å
c = 29.0945 (17) Å
V = 6373.4 (7) Å^3
Z = 4
F(000) = 2424
D_x = 1.170 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9122 reflections
θ = 2.5–68.3°
μ = 0.64 mm^{-1}
T = 100 K
Rod, colourless
0.55 × 0.06 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
T_{min} = 0.587, T_{max} = 0.753
47444 measured reflections
11348 independent reflections
9085 reflections with $I > 2\sigma(I)$
R_{int} = 0.086
θ_{max} = 68.4°, θ_{min} = 2.5°
h = −11→6
k = −26→27
l = −33→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.166
S = 1.05
11348 reflections
742 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0949P)^2 + 1.8264P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack x determined using 3356 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: −0.16 (11)

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.9530 (4)	0.69914 (15)	0.15822 (12)	0.0353 (8)
O2	0.4072 (4)	0.75979 (15)	0.21331 (12)	0.0371 (8)
O3	0.2530 (4)	0.58487 (16)	0.22979 (12)	0.0350 (8)
O4	0.6377 (3)	0.55765 (14)	0.34502 (10)	0.0259 (7)
O5	0.5884 (3)	0.64306 (13)	0.45172 (11)	0.0270 (7)
O6	0.5764 (4)	0.51419 (15)	0.52030 (11)	0.0321 (8)
O7	1.0051 (3)	0.50867 (14)	0.42400 (11)	0.0297 (8)
O8	1.1564 (4)	0.61766 (15)	0.36511 (11)	0.0311 (8)
O9	0.7741 (4)	0.60902 (15)	0.24898 (12)	0.0329 (8)
N1	0.9425 (4)	0.67747 (17)	0.25304 (14)	0.0278 (9)
N2	0.7444 (4)	0.74399 (17)	0.15876 (14)	0.0290 (9)
N3	0.5053 (4)	0.68133 (16)	0.17730 (13)	0.0254 (9)
H3	0.5819	0.6658	0.1662	0.031*
N4	0.4845 (4)	0.59019 (15)	0.24245 (13)	0.0250 (9)
H4N	0.5634	0.6067	0.2345	0.030*
N5	0.4659 (4)	0.62382 (16)	0.33677 (13)	0.0241 (8)
H5	0.3893	0.6330	0.3220	0.029*
N6	0.4176 (4)	0.58452 (16)	0.42480 (12)	0.0229 (8)
H6	0.3603	0.5773	0.4019	0.028*
N7	0.6405 (4)	0.51027 (16)	0.44540 (13)	0.0235 (8)
H7	0.6144	0.5162	0.4168	0.028*
N8	0.8594 (4)	0.58549 (16)	0.43117 (12)	0.0231 (8)
H8	0.7744	0.5970	0.4374	0.028*
N9	0.9410 (4)	0.59572 (17)	0.33834 (13)	0.0263 (9)
H9N	0.8529	0.5930	0.3459	0.032*
C1	1.0742 (6)	0.7023 (2)	0.26951 (19)	0.0346 (12)
H1A	1.1540	0.6792	0.2579	0.042*
H1B	1.0773	0.7030	0.3035	0.042*
C2	1.0744 (6)	0.7641 (2)	0.24993 (19)	0.0371 (12)
H2A	1.1268	0.7915	0.2699	0.044*
H2B	1.1148	0.7648	0.2187	0.044*
C3	0.9219 (6)	0.7797 (2)	0.24890 (18)	0.0329 (11)
H3A	0.9037	0.8125	0.2273	0.039*
H3B	0.8882	0.7908	0.2799	0.039*
C4	0.8534 (5)	0.7222 (2)	0.23222 (17)	0.0287 (11)
H4	0.7565	0.7189	0.2441	0.034*
C5	0.8555 (5)	0.71933 (19)	0.17980 (17)	0.0280 (11)
C6	0.7463 (6)	0.7547 (2)	0.10845 (16)	0.0342 (12)
H6A	0.7449	0.7170	0.0913	0.041*
H6B	0.8296	0.7773	0.0994	0.041*
C7	0.6159 (6)	0.7898 (2)	0.09956 (18)	0.0382 (13)
H7A	0.5371	0.7635	0.0922	0.046*
H7B	0.6294	0.8179	0.0739	0.046*
C8	0.5911 (6)	0.8225 (2)	0.14493 (17)	0.0337 (12)
H8A	0.4931	0.8348	0.1480	0.040*

H8B	0.6514	0.8576	0.1475	0.040*
C9	0.6295 (5)	0.7757 (2)	0.18099 (16)	0.0277 (11)
H9	0.6636	0.7955	0.2095	0.033*
C10	0.5051 (5)	0.7374 (2)	0.19241 (16)	0.0272 (11)
C11	0.3796 (5)	0.6465 (2)	0.17925 (16)	0.0268 (10)
H11	0.2998	0.6746	0.1808	0.032*
C12	0.3674 (5)	0.6048 (2)	0.22016 (16)	0.0270 (11)
C13	0.3627 (5)	0.6099 (2)	0.13493 (16)	0.0261 (10)
H13A	0.4444	0.5840	0.1312	0.031*
H13B	0.2798	0.5845	0.1379	0.031*
C14	0.3478 (5)	0.6482 (2)	0.09237 (15)	0.0265 (10)
C15	0.4476 (6)	0.6463 (2)	0.05815 (16)	0.0313 (11)
H15	0.5263	0.6216	0.0616	0.038*
C16	0.4331 (7)	0.6806 (2)	0.01861 (18)	0.0403 (14)
H16	0.5010	0.6787	−0.0050	0.048*
C17	0.3207 (7)	0.7169 (2)	0.01388 (19)	0.0430 (15)
H17	0.3121	0.7412	−0.0126	0.052*
C18	0.2198 (7)	0.7183 (2)	0.04750 (19)	0.0423 (14)
H18	0.1401	0.7423	0.0436	0.051*
C19	0.2348 (6)	0.6847 (2)	0.08716 (17)	0.0325 (12)
H19	0.1668	0.6868	0.1107	0.039*
C20	0.4821 (5)	0.54731 (19)	0.27970 (15)	0.0236 (10)
H20	0.3830	0.5368	0.2854	0.028*
C21	0.5373 (5)	0.57641 (19)	0.32338 (15)	0.0221 (10)
C22	0.5582 (5)	0.4906 (2)	0.26685 (16)	0.0287 (11)
H22A	0.6562	0.4996	0.2597	0.034*
H22B	0.5562	0.4628	0.2931	0.034*
C23	0.4892 (6)	0.46284 (19)	0.22550 (17)	0.0294 (11)
C24	0.5391 (6)	0.4724 (2)	0.18170 (17)	0.0348 (12)
H24	0.6233	0.4934	0.1775	0.042*
C25	0.4671 (7)	0.4515 (2)	0.14341 (18)	0.0450 (15)
H25	0.5032	0.4578	0.1134	0.054*
C26	0.3453 (7)	0.4220 (2)	0.1488 (2)	0.0457 (15)
H26	0.2955	0.4090	0.1226	0.055*
C27	0.2942 (6)	0.4111 (2)	0.1919 (2)	0.0421 (14)
H27	0.2107	0.3894	0.1956	0.050*
C28	0.3660 (6)	0.4320 (2)	0.23042 (19)	0.0356 (12)
H28	0.3298	0.4251	0.2603	0.043*
C29	0.5101 (5)	0.66102 (19)	0.37490 (15)	0.0239 (10)
H29	0.6081	0.6730	0.3689	0.029*
C30	0.5073 (5)	0.62878 (19)	0.42061 (15)	0.0232 (10)
C31	0.4234 (5)	0.7166 (2)	0.37657 (16)	0.0266 (10)
H31A	0.4553	0.7409	0.4027	0.032*
H31B	0.3260	0.7054	0.3826	0.032*
C32	0.4282 (5)	0.7545 (2)	0.33260 (16)	0.0282 (11)
H32	0.3818	0.7319	0.3074	0.034*
C33	0.5744 (6)	0.7671 (2)	0.31781 (19)	0.0409 (13)
H33A	0.5734	0.7940	0.2915	0.061*

H33B	0.6199	0.7302	0.3090	0.061*
H33C	0.6252	0.7852	0.3433	0.061*
C34	0.3463 (6)	0.8111 (2)	0.3403 (2)	0.0401 (13)
H34A	0.3896	0.8340	0.3650	0.060*
H34B	0.2509	0.8013	0.3490	0.060*
H34C	0.3457	0.8344	0.3120	0.060*
C35	0.4103 (5)	0.54745 (19)	0.46583 (15)	0.0232 (10)
H35	0.3765	0.5726	0.4917	0.028*
C36	0.5510 (5)	0.52287 (19)	0.47959 (16)	0.0251 (10)
C37	0.3024 (5)	0.4991 (2)	0.45781 (16)	0.0249 (10)
H37	0.2137	0.5196	0.4501	0.030*
C38	0.2740 (6)	0.4624 (2)	0.50061 (17)	0.0327 (11)
H38A	0.2051	0.4316	0.4929	0.039*
H38B	0.3607	0.4423	0.5099	0.039*
C39	0.2204 (7)	0.4982 (2)	0.5410 (2)	0.0447 (15)
H39A	0.2927	0.5253	0.5515	0.067*
H39B	0.1952	0.4715	0.5662	0.067*
H39C	0.1387	0.5207	0.5315	0.067*
C40	0.3364 (6)	0.4590 (2)	0.41696 (17)	0.0317 (11)
H40A	0.4194	0.4358	0.4239	0.048*
H40B	0.3531	0.4831	0.3896	0.048*
H40C	0.2583	0.4323	0.4113	0.048*
C41	0.7780 (5)	0.4874 (2)	0.45410 (17)	0.0255 (10)
H41	0.7903	0.4870	0.4882	0.031*
C42	0.8912 (5)	0.5279 (2)	0.43471 (16)	0.0249 (10)
C43	0.7972 (5)	0.4237 (2)	0.43773 (18)	0.0321 (11)
H43	0.8966	0.4128	0.4424	0.039*
C44	0.7639 (6)	0.4165 (2)	0.38658 (19)	0.0361 (12)
H44A	0.6622	0.4185	0.3825	0.043*
H44B	0.8051	0.4499	0.3695	0.043*
C45	0.8158 (7)	0.3598 (3)	0.3658 (2)	0.0533 (16)
H45A	0.9169	0.3582	0.3684	0.080*
H45B	0.7892	0.3581	0.3333	0.080*
H45C	0.7749	0.3263	0.3822	0.080*
C46	0.7089 (6)	0.3826 (2)	0.4677 (2)	0.0411 (13)
H46A	0.6113	0.3940	0.4653	0.062*
H46B	0.7391	0.3857	0.4998	0.062*
H46C	0.7201	0.3419	0.4571	0.062*
C47	0.9618 (5)	0.62935 (19)	0.41727 (16)	0.0252 (10)
H47	0.9096	0.6667	0.4114	0.030*
C48	1.0320 (5)	0.6122 (2)	0.37119 (16)	0.0258 (10)
C49	1.0681 (5)	0.6434 (2)	0.45468 (16)	0.0263 (10)
H49A	1.1323	0.6096	0.4575	0.032*
H49B	1.1232	0.6779	0.4448	0.032*
C50	1.0069 (5)	0.6563 (2)	0.50175 (17)	0.0307 (11)
H50	0.9595	0.6198	0.5128	0.037*
C51	0.9008 (6)	0.7058 (3)	0.5012 (2)	0.0436 (14)
H51A	0.9432	0.7415	0.4884	0.065*

H51B	0.8691	0.7136	0.5326	0.065*
H51C	0.8216	0.6942	0.4821	0.065*
C52	1.1236 (6)	0.6707 (2)	0.53541 (18)	0.0351 (12)
H52A	1.1963	0.6407	0.5330	0.053*
H52B	1.0869	0.6712	0.5668	0.053*
H52C	1.1625	0.7095	0.5280	0.053*
C53	0.9795 (5)	0.5821 (2)	0.29114 (16)	0.0285 (11)
H53	1.0796	0.5917	0.2865	0.034*
C54	0.8905 (5)	0.6238 (2)	0.26157 (16)	0.0273 (11)
C55	0.9558 (5)	0.5164 (2)	0.28067 (17)	0.0303 (11)
H55	0.8601	0.5058	0.2909	0.036*
C56	1.0589 (6)	0.4799 (2)	0.30845 (18)	0.0357 (12)
H56A	1.0401	0.4379	0.3037	0.054*
H56B	1.0494	0.4895	0.3412	0.054*
H56C	1.1533	0.4890	0.2983	0.054*
C57	0.9683 (6)	0.5025 (2)	0.22992 (18)	0.0388 (13)
H57A	0.8995	0.5253	0.2127	0.058*
H57B	0.9520	0.4603	0.2250	0.058*
H57C	1.0614	0.5128	0.2192	0.058*
C1S	0.8290 (6)	0.5854 (2)	0.12039 (18)	0.0355 (12)
C2S	0.9706 (6)	0.5686 (3)	0.1108 (2)	0.0489 (15)
H2S1	0.9714	0.5339	0.0908	0.073*
H2S2	1.0179	0.5593	0.1397	0.073*
H2S3	1.0183	0.6013	0.0955	0.073*
C3S	0.4920 (9)	0.6854 (3)	0.5991 (3)	0.068 (2)
C4S	0.5619 (11)	0.6418 (4)	0.5704 (3)	0.088 (3)
H4S1	0.5633	0.6555	0.5385	0.131*
H4S2	0.5121	0.6042	0.5722	0.131*
H4S3	0.6571	0.6364	0.5813	0.131*
N1S	0.7185 (5)	0.5986 (2)	0.12775 (17)	0.0437 (12)
N2S	0.4386 (8)	0.7210 (3)	0.6218 (2)	0.086 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.034 (2)	0.0395 (19)	0.032 (2)	0.0004 (16)	0.0068 (16)	−0.0039 (15)
O2	0.041 (2)	0.0338 (18)	0.036 (2)	0.0014 (16)	0.0054 (16)	−0.0083 (16)
O3	0.024 (2)	0.048 (2)	0.033 (2)	−0.0012 (16)	0.0033 (15)	0.0133 (16)
O4	0.0266 (18)	0.0322 (16)	0.0188 (17)	0.0017 (14)	−0.0005 (14)	−0.0004 (13)
O5	0.0324 (19)	0.0253 (15)	0.0234 (18)	−0.0024 (14)	−0.0041 (14)	−0.0028 (13)
O6	0.033 (2)	0.0434 (19)	0.0199 (19)	0.0029 (16)	−0.0015 (14)	0.0056 (14)
O7	0.0212 (19)	0.0322 (17)	0.036 (2)	0.0024 (15)	−0.0032 (14)	−0.0001 (14)
O8	0.024 (2)	0.0426 (19)	0.0262 (18)	−0.0033 (15)	−0.0004 (14)	−0.0019 (15)
O9	0.029 (2)	0.0381 (18)	0.0311 (19)	−0.0088 (15)	−0.0047 (15)	0.0056 (15)
N1	0.024 (2)	0.033 (2)	0.027 (2)	−0.0026 (17)	−0.0006 (17)	−0.0008 (17)
N2	0.035 (2)	0.028 (2)	0.025 (2)	0.0025 (18)	0.0012 (17)	0.0008 (17)
N3	0.029 (2)	0.0278 (19)	0.019 (2)	0.0003 (17)	0.0026 (16)	0.0006 (15)
N4	0.028 (2)	0.0234 (18)	0.024 (2)	−0.0012 (16)	−0.0006 (16)	−0.0006 (15)

N5	0.026 (2)	0.0272 (19)	0.019 (2)	0.0025 (17)	−0.0039 (16)	0.0006 (15)
N6	0.025 (2)	0.0258 (19)	0.0182 (19)	−0.0008 (17)	−0.0027 (15)	0.0013 (15)
N7	0.024 (2)	0.0261 (19)	0.020 (2)	−0.0001 (17)	−0.0013 (16)	−0.0015 (15)
N8	0.020 (2)	0.0252 (19)	0.024 (2)	0.0009 (16)	−0.0025 (16)	−0.0019 (15)
N9	0.023 (2)	0.033 (2)	0.022 (2)	−0.0006 (17)	0.0016 (16)	−0.0022 (16)
C1	0.031 (3)	0.035 (3)	0.038 (3)	−0.004 (2)	−0.003 (2)	0.000 (2)
C2	0.043 (3)	0.034 (3)	0.034 (3)	−0.006 (2)	−0.007 (2)	−0.001 (2)
C3	0.039 (3)	0.030 (2)	0.029 (3)	0.000 (2)	−0.004 (2)	−0.002 (2)
C4	0.028 (3)	0.031 (2)	0.027 (3)	0.003 (2)	−0.001 (2)	0.0010 (19)
C5	0.031 (3)	0.024 (2)	0.030 (3)	−0.003 (2)	0.001 (2)	0.000 (2)
C6	0.047 (3)	0.037 (3)	0.018 (3)	−0.003 (2)	0.002 (2)	0.003 (2)
C7	0.053 (4)	0.034 (3)	0.027 (3)	−0.007 (2)	−0.005 (2)	0.004 (2)
C8	0.041 (3)	0.027 (2)	0.033 (3)	0.002 (2)	−0.001 (2)	0.007 (2)
C9	0.033 (3)	0.023 (2)	0.026 (3)	0.004 (2)	−0.002 (2)	−0.0024 (19)
C10	0.034 (3)	0.027 (2)	0.021 (2)	0.002 (2)	−0.001 (2)	0.0018 (19)
C11	0.028 (3)	0.029 (2)	0.023 (2)	−0.004 (2)	−0.0011 (19)	0.0024 (19)
C12	0.031 (3)	0.028 (2)	0.022 (2)	0.003 (2)	0.001 (2)	−0.0060 (19)
C13	0.029 (3)	0.027 (2)	0.023 (2)	−0.002 (2)	−0.003 (2)	0.0017 (19)
C14	0.036 (3)	0.023 (2)	0.021 (2)	−0.005 (2)	−0.003 (2)	−0.0002 (18)
C15	0.044 (3)	0.026 (2)	0.024 (3)	−0.005 (2)	0.003 (2)	0.000 (2)
C16	0.060 (4)	0.036 (3)	0.024 (3)	−0.013 (3)	0.004 (3)	−0.003 (2)
C17	0.076 (5)	0.028 (3)	0.025 (3)	−0.009 (3)	−0.007 (3)	0.005 (2)
C18	0.059 (4)	0.034 (3)	0.034 (3)	0.006 (3)	−0.013 (3)	0.002 (2)
C19	0.039 (3)	0.030 (3)	0.028 (3)	−0.001 (2)	−0.003 (2)	0.000 (2)
C20	0.028 (3)	0.023 (2)	0.019 (2)	−0.0024 (19)	−0.0014 (19)	0.0022 (17)
C21	0.024 (3)	0.024 (2)	0.019 (2)	−0.0009 (19)	0.0017 (19)	0.0051 (18)
C22	0.034 (3)	0.027 (2)	0.025 (3)	0.003 (2)	−0.006 (2)	−0.0001 (19)
C23	0.040 (3)	0.021 (2)	0.027 (3)	0.006 (2)	−0.003 (2)	−0.0034 (18)
C24	0.052 (4)	0.024 (2)	0.028 (3)	0.003 (2)	0.002 (2)	−0.001 (2)
C25	0.076 (5)	0.036 (3)	0.022 (3)	0.019 (3)	−0.002 (3)	−0.002 (2)
C26	0.067 (4)	0.029 (3)	0.042 (3)	0.009 (3)	−0.019 (3)	−0.011 (2)
C27	0.044 (4)	0.028 (3)	0.055 (4)	0.004 (2)	−0.014 (3)	−0.013 (2)
C28	0.043 (3)	0.025 (2)	0.038 (3)	0.002 (2)	−0.001 (2)	−0.005 (2)
C29	0.027 (3)	0.025 (2)	0.019 (2)	−0.0042 (19)	0.0006 (19)	−0.0019 (17)
C30	0.022 (3)	0.026 (2)	0.022 (2)	0.0018 (19)	0.0002 (19)	−0.0060 (17)
C31	0.030 (3)	0.026 (2)	0.023 (3)	−0.001 (2)	0.002 (2)	−0.0017 (18)
C32	0.036 (3)	0.026 (2)	0.022 (2)	−0.002 (2)	−0.004 (2)	−0.0005 (19)
C33	0.054 (4)	0.037 (3)	0.032 (3)	−0.007 (3)	0.006 (3)	0.006 (2)
C34	0.054 (4)	0.026 (2)	0.040 (3)	0.000 (2)	−0.012 (3)	0.002 (2)
C35	0.026 (3)	0.025 (2)	0.018 (2)	0.001 (2)	0.0031 (19)	0.0001 (18)
C36	0.029 (3)	0.023 (2)	0.023 (3)	−0.0001 (19)	−0.002 (2)	−0.0004 (18)
C37	0.023 (3)	0.025 (2)	0.027 (3)	0.0028 (19)	0.0005 (19)	−0.0011 (19)
C38	0.035 (3)	0.030 (2)	0.033 (3)	−0.002 (2)	0.005 (2)	0.006 (2)
C39	0.062 (4)	0.036 (3)	0.037 (3)	−0.005 (3)	0.017 (3)	0.007 (2)
C40	0.034 (3)	0.030 (2)	0.032 (3)	−0.001 (2)	−0.003 (2)	−0.005 (2)
C41	0.023 (3)	0.029 (2)	0.024 (3)	0.002 (2)	−0.0027 (19)	0.0009 (19)
C42	0.022 (3)	0.030 (2)	0.022 (2)	−0.003 (2)	−0.0058 (19)	−0.0002 (19)
C43	0.029 (3)	0.027 (2)	0.041 (3)	0.003 (2)	−0.001 (2)	0.003 (2)

C44	0.033 (3)	0.030 (2)	0.046 (3)	−0.005 (2)	0.001 (2)	−0.006 (2)
C45	0.057 (4)	0.037 (3)	0.066 (4)	0.002 (3)	0.004 (3)	−0.017 (3)
C46	0.041 (3)	0.028 (3)	0.055 (4)	−0.002 (2)	0.002 (3)	0.005 (2)
C47	0.029 (3)	0.021 (2)	0.027 (3)	0.0000 (19)	0.001 (2)	−0.0010 (18)
C48	0.029 (3)	0.026 (2)	0.023 (2)	−0.002 (2)	−0.003 (2)	0.0026 (18)
C49	0.027 (3)	0.026 (2)	0.027 (3)	−0.003 (2)	0.000 (2)	−0.0027 (19)
C50	0.032 (3)	0.033 (2)	0.027 (3)	−0.003 (2)	−0.003 (2)	−0.002 (2)
C51	0.046 (4)	0.047 (3)	0.037 (3)	0.009 (3)	−0.009 (3)	−0.017 (3)
C52	0.040 (3)	0.035 (3)	0.030 (3)	0.001 (2)	−0.005 (2)	−0.004 (2)
C53	0.028 (3)	0.031 (2)	0.026 (3)	−0.003 (2)	−0.001 (2)	−0.003 (2)
C54	0.026 (3)	0.035 (3)	0.021 (2)	−0.001 (2)	0.0046 (19)	−0.0010 (19)
C55	0.030 (3)	0.032 (2)	0.029 (3)	−0.001 (2)	0.002 (2)	−0.004 (2)
C56	0.037 (3)	0.035 (3)	0.035 (3)	0.003 (2)	0.004 (2)	−0.005 (2)
C57	0.042 (3)	0.045 (3)	0.030 (3)	−0.001 (2)	0.000 (2)	−0.009 (2)
C1S	0.037 (4)	0.040 (3)	0.029 (3)	−0.005 (3)	−0.003 (2)	−0.002 (2)
C2S	0.038 (4)	0.060 (4)	0.049 (4)	0.003 (3)	0.006 (3)	−0.015 (3)
C3S	0.090 (6)	0.062 (4)	0.052 (4)	0.002 (4)	−0.004 (4)	−0.006 (4)
C4S	0.117 (7)	0.080 (5)	0.066 (5)	0.007 (5)	−0.016 (5)	−0.029 (4)
N1S	0.036 (3)	0.045 (3)	0.049 (3)	0.000 (2)	0.001 (2)	0.001 (2)
N2S	0.109 (6)	0.086 (5)	0.062 (4)	0.022 (4)	−0.001 (4)	−0.008 (4)

Geometric parameters (Å, º)

O1—C5	1.221 (6)	C26—C27	1.369 (9)
O2—C10	1.233 (6)	C26—H26	0.9500
O3—C12	1.226 (6)	C27—C28	1.402 (8)
O4—C21	1.232 (5)	C27—H27	0.9500
O5—C30	1.240 (5)	C28—H28	0.9500
O6—C36	1.226 (6)	C29—C31	1.514 (7)
O7—C42	1.223 (6)	C29—C30	1.518 (6)
O8—C48	1.220 (6)	C29—H29	1.0000
O9—C54	1.229 (6)	C31—C32	1.542 (6)
N1—C54	1.340 (6)	C31—H31A	0.9900
N1—C4	1.462 (6)	C31—H31B	0.9900
N1—C1	1.470 (7)	C32—C33	1.503 (8)
N2—C5	1.355 (6)	C32—C34	1.525 (7)
N2—C9	1.472 (6)	C32—H32	1.0000
N2—C6	1.484 (6)	C33—H33A	0.9800
N3—C10	1.347 (6)	C33—H33B	0.9800
N3—C11	1.449 (6)	C33—H33C	0.9800
N3—H3	0.8800	C34—H34A	0.9800
N4—C12	1.345 (6)	C34—H34B	0.9800
N4—C20	1.457 (6)	C34—H34C	0.9800
N4—H4N	0.8800	C35—C36	1.522 (7)
N5—C21	1.336 (6)	C35—C37	1.530 (6)
N5—C29	1.458 (6)	C35—H35	1.0000
N5—H5	0.8800	C37—C38	1.523 (7)
N6—C30	1.332 (6)	C37—C40	1.533 (7)

N6—C35	1.462 (6)	C37—H37	1.0000
N6—H6	0.8800	C38—C39	1.520 (8)
N7—C36	1.348 (6)	C38—H38A	0.9900
N7—C41	1.448 (6)	C38—H38B	0.9900
N7—H7	0.8800	C39—H39A	0.9800
N8—C42	1.346 (6)	C39—H39B	0.9800
N8—C47	1.460 (6)	C39—H39C	0.9800
N8—H8	0.8800	C40—H40A	0.9800
N9—C48	1.351 (6)	C40—H40B	0.9800
N9—C53	1.456 (6)	C40—H40C	0.9800
N9—H9N	0.8800	C41—C43	1.533 (7)
C1—C2	1.515 (7)	C41—C42	1.536 (7)
C1—H1A	0.9900	C41—H41	1.0000
C1—H1B	0.9900	C43—C44	1.531 (8)
C2—C3	1.514 (8)	C43—C46	1.535 (7)
C2—H2A	0.9900	C43—H43	1.0000
C2—H2B	0.9900	C44—C45	1.506 (7)
C3—C4	1.541 (7)	C44—H44A	0.9900
C3—H3A	0.9900	C44—H44B	0.9900
C3—H3B	0.9900	C45—H45A	0.9800
C4—C5	1.527 (7)	C45—H45B	0.9800
C4—H4	1.0000	C45—H45C	0.9800
C6—C7	1.512 (8)	C46—H46A	0.9800
C6—H6A	0.9900	C46—H46B	0.9800
C6—H6B	0.9900	C46—H46C	0.9800
C7—C8	1.533 (7)	C47—C49	1.529 (7)
C7—H7A	0.9900	C47—C48	1.552 (7)
C7—H7B	0.9900	C47—H47	1.0000
C8—C9	1.538 (7)	C49—C50	1.520 (7)
C8—H8A	0.9900	C49—H49A	0.9900
C8—H8B	0.9900	C49—H49B	0.9900
C9—C10	1.519 (7)	C50—C51	1.520 (8)
C9—H9	1.0000	C50—C52	1.528 (7)
C11—C12	1.526 (7)	C50—H50	1.0000
C11—C13	1.542 (7)	C51—H51A	0.9800
C11—H11	1.0000	C51—H51B	0.9800
C13—C14	1.519 (6)	C51—H51C	0.9800
C13—H13A	0.9900	C52—H52A	0.9800
C13—H13B	0.9900	C52—H52B	0.9800
C14—C19	1.378 (7)	C52—H52C	0.9800
C14—C15	1.386 (7)	C53—C55	1.538 (7)
C15—C16	1.396 (7)	C53—C54	1.541 (7)
C15—H15	0.9500	C53—H53	1.0000
C16—C17	1.370 (9)	C55—C57	1.515 (7)
C16—H16	0.9500	C55—C56	1.526 (7)
C17—C18	1.380 (9)	C55—H55	1.0000
C17—H17	0.9500	C56—H56A	0.9800
C18—C19	1.391 (7)	C56—H56B	0.9800

C18—H18	0.9500	C56—H56C	0.9800
C19—H19	0.9500	C57—H57A	0.9800
C20—C22	1.528 (6)	C57—H57B	0.9800
C20—C21	1.528 (6)	C57—H57C	0.9800
C20—H20	1.0000	C1S—N1S	1.128 (7)
C22—C23	1.513 (7)	C1S—C2S	1.445 (9)
C22—H22A	0.9900	C2S—H2S1	0.9800
C22—H22B	0.9900	C2S—H2S2	0.9800
C23—C24	1.380 (7)	C2S—H2S3	0.9800
C23—C28	1.387 (8)	C3S—N2S	1.164 (10)
C24—C25	1.397 (8)	C3S—C4S	1.458 (11)
C24—H24	0.9500	C4S—H4S1	0.9800
C25—C26	1.361 (9)	C4S—H4S2	0.9800
C25—H25	0.9500	C4S—H4S3	0.9800

C54—N1—C4	119.1 (4)	C32—C31—H31B	108.5
C54—N1—C1	127.7 (4)	H31A—C31—H31B	107.5
C4—N1—C1	112.2 (4)	C33—C32—C34	111.7 (4)
C5—N2—C9	126.8 (4)	C33—C32—C31	111.8 (4)
C5—N2—C6	120.2 (4)	C34—C32—C31	109.4 (4)
C9—N2—C6	111.3 (4)	C33—C32—H32	108.0
C10—N3—C11	120.1 (4)	C34—C32—H32	108.0
C10—N3—H3	120.0	C31—C32—H32	108.0
C11—N3—H3	120.0	C32—C33—H33A	109.5
C12—N4—C20	120.6 (4)	C32—C33—H33B	109.5
C12—N4—H4N	119.7	H33A—C33—H33B	109.5
C20—N4—H4N	119.7	C32—C33—H33C	109.5
C21—N5—C29	122.5 (4)	H33A—C33—H33C	109.5
C21—N5—H5	118.7	H33B—C33—H33C	109.5
C29—N5—H5	118.7	C32—C34—H34A	109.5
C30—N6—C35	122.7 (4)	C32—C34—H34B	109.5
C30—N6—H6	118.7	H34A—C34—H34B	109.5
C35—N6—H6	118.7	C32—C34—H34C	109.5
C36—N7—C41	122.3 (4)	H34A—C34—H34C	109.5
C36—N7—H7	118.8	H34B—C34—H34C	109.5
C41—N7—H7	118.8	N6—C35—C36	112.5 (4)
C42—N8—C47	121.9 (4)	N6—C35—C37	108.7 (4)
C42—N8—H8	119.0	C36—C35—C37	112.6 (4)
C47—N8—H8	119.0	N6—C35—H35	107.6
C48—N9—C53	124.0 (4)	C36—C35—H35	107.6
C48—N9—H9N	118.0	C37—C35—H35	107.6
C53—N9—H9N	118.0	O6—C36—N7	123.4 (5)
N1—C1—C2	103.5 (4)	O6—C36—C35	119.5 (4)
N1—C1—H1A	111.1	N7—C36—C35	117.1 (4)
C2—C1—H1A	111.1	C38—C37—C35	113.0 (4)
N1—C1—H1B	111.1	C38—C37—C40	110.3 (4)
C2—C1—H1B	111.1	C35—C37—C40	113.5 (4)
H1A—C1—H1B	109.0	C38—C37—H37	106.5

C3—C2—C1	102.8 (4)	C35—C37—H37	106.5
C3—C2—H2A	111.2	C40—C37—H37	106.5
C1—C2—H2A	111.2	C39—C38—C37	113.7 (4)
C3—C2—H2B	111.2	C39—C38—H38A	108.8
C1—C2—H2B	111.2	C37—C38—H38A	108.8
H2A—C2—H2B	109.1	C39—C38—H38B	108.8
C2—C3—C4	103.1 (4)	C37—C38—H38B	108.8
C2—C3—H3A	111.2	H38A—C38—H38B	107.7
C4—C3—H3A	111.2	C38—C39—H39A	109.5
C2—C3—H3B	111.2	C38—C39—H39B	109.5
C4—C3—H3B	111.2	H39A—C39—H39B	109.5
H3A—C3—H3B	109.1	C38—C39—H39C	109.5
N1—C4—C5	112.1 (4)	H39A—C39—H39C	109.5
N1—C4—C3	101.8 (4)	H39B—C39—H39C	109.5
C5—C4—C3	110.2 (4)	C37—C40—H40A	109.5
N1—C4—H4	110.8	C37—C40—H40B	109.5
C5—C4—H4	110.8	H40A—C40—H40B	109.5
C3—C4—H4	110.8	C37—C40—H40C	109.5
O1—C5—N2	122.2 (5)	H40A—C40—H40C	109.5
O1—C5—C4	122.6 (5)	H40B—C40—H40C	109.5
N2—C5—C4	115.1 (4)	N7—C41—C43	113.2 (4)
N2—C6—C7	104.2 (4)	N7—C41—C42	111.9 (4)
N2—C6—H6A	110.9	C43—C41—C42	111.4 (4)
C7—C6—H6A	110.9	N7—C41—H41	106.6
N2—C6—H6B	110.9	C43—C41—H41	106.6
C7—C6—H6B	110.9	C42—C41—H41	106.6
H6A—C6—H6B	108.9	O7—C42—N8	122.1 (4)
C6—C7—C8	103.8 (4)	O7—C42—C41	121.3 (4)
C6—C7—H7A	111.0	N8—C42—C41	116.6 (4)
C8—C7—H7A	111.0	C44—C43—C41	112.2 (4)
C6—C7—H7B	111.0	C44—C43—C46	111.8 (4)
C8—C7—H7B	111.0	C41—C43—C46	109.2 (4)
H7A—C7—H7B	109.0	C44—C43—H43	107.8
C7—C8—C9	102.5 (4)	C41—C43—H43	107.8
C7—C8—H8A	111.3	C46—C43—H43	107.8
C9—C8—H8A	111.3	C45—C44—C43	114.3 (5)
C7—C8—H8B	111.3	C45—C44—H44A	108.7
C9—C8—H8B	111.3	C43—C44—H44A	108.7
H8A—C8—H8B	109.2	C45—C44—H44B	108.7
N2—C9—C10	114.3 (4)	C43—C44—H44B	108.7
N2—C9—C8	102.7 (4)	H44A—C44—H44B	107.6
C10—C9—C8	110.7 (4)	C44—C45—H45A	109.5
N2—C9—H9	109.6	C44—C45—H45B	109.5
C10—C9—H9	109.6	H45A—C45—H45B	109.5
C8—C9—H9	109.6	C44—C45—H45C	109.5
O2—C10—N3	123.5 (5)	H45A—C45—H45C	109.5
O2—C10—C9	118.5 (4)	H45B—C45—H45C	109.5
N3—C10—C9	117.9 (4)	C43—C46—H46A	109.5

N3—C11—C12	115.7 (4)	C43—C46—H46B	109.5
N3—C11—C13	110.4 (4)	H46A—C46—H46B	109.5
C12—C11—C13	108.1 (4)	C43—C46—H46C	109.5
N3—C11—H11	107.4	H46A—C46—H46C	109.5
C12—C11—H11	107.4	H46B—C46—H46C	109.5
C13—C11—H11	107.4	N8—C47—C49	113.5 (4)
O3—C12—N4	123.8 (4)	N8—C47—C48	111.4 (4)
O3—C12—C11	118.5 (4)	C49—C47—C48	112.0 (4)
N4—C12—C11	117.7 (4)	N8—C47—H47	106.5
C14—C13—C11	112.6 (4)	C49—C47—H47	106.5
C14—C13—H13A	109.1	C48—C47—H47	106.5
C11—C13—H13A	109.1	O8—C48—N9	124.4 (4)
C14—C13—H13B	109.1	O8—C48—C47	122.0 (4)
C11—C13—H13B	109.1	N9—C48—C47	113.4 (4)
H13A—C13—H13B	107.8	C50—C49—C47	114.9 (4)
C19—C14—C15	119.3 (4)	C50—C49—H49A	108.5
C19—C14—C13	120.5 (5)	C47—C49—H49A	108.5
C15—C14—C13	120.1 (4)	C50—C49—H49B	108.5
C14—C15—C16	120.3 (5)	C47—C49—H49B	108.5
C14—C15—H15	119.8	H49A—C49—H49B	107.5
C16—C15—H15	119.8	C51—C50—C49	113.2 (4)
C17—C16—C15	119.8 (5)	C51—C50—C52	110.2 (4)
C17—C16—H16	120.1	C49—C50—C52	109.4 (4)
C15—C16—H16	120.1	C51—C50—H50	107.9
C16—C17—C18	120.1 (5)	C49—C50—H50	107.9
C16—C17—H17	119.9	C52—C50—H50	107.9
C18—C17—H17	119.9	C50—C51—H51A	109.5
C17—C18—C19	120.1 (6)	C50—C51—H51B	109.5
C17—C18—H18	119.9	H51A—C51—H51B	109.5
C19—C18—H18	119.9	C50—C51—H51C	109.5
C14—C19—C18	120.2 (5)	H51A—C51—H51C	109.5
C14—C19—H19	119.9	H51B—C51—H51C	109.5
C18—C19—H19	119.9	C50—C52—H52A	109.5
N4—C20—C22	111.9 (4)	C50—C52—H52B	109.5
N4—C20—C21	108.9 (3)	H52A—C52—H52B	109.5
C22—C20—C21	113.6 (4)	C50—C52—H52C	109.5
N4—C20—H20	107.4	H52A—C52—H52C	109.5
C22—C20—H20	107.4	H52B—C52—H52C	109.5
C21—C20—H20	107.4	N9—C53—C55	110.8 (4)
O4—C21—N5	122.3 (4)	N9—C53—C54	104.7 (4)
O4—C21—C20	123.4 (4)	C55—C53—C54	113.7 (4)
N5—C21—C20	114.3 (4)	N9—C53—H53	109.2
C23—C22—C20	109.5 (4)	C55—C53—H53	109.2
C23—C22—H22A	109.8	C54—C53—H53	109.2
C20—C22—H22A	109.8	O9—C54—N1	122.4 (5)
C23—C22—H22B	109.8	O9—C54—C53	120.5 (4)
C20—C22—H22B	109.8	N1—C54—C53	116.9 (4)
H22A—C22—H22B	108.2	C57—C55—C56	110.5 (4)

C24—C23—C28	118.3 (5)	C57—C55—C53	112.6 (4)
C24—C23—C22	121.0 (5)	C56—C55—C53	108.9 (4)
C28—C23—C22	120.4 (5)	C57—C55—H55	108.2
C23—C24—C25	120.7 (5)	C56—C55—H55	108.2
C23—C24—H24	119.7	C53—C55—H55	108.2
C25—C24—H24	119.7	C55—C56—H56A	109.5
C26—C25—C24	120.3 (5)	C55—C56—H56B	109.5
C26—C25—H25	119.9	H56A—C56—H56B	109.5
C24—C25—H25	119.9	C55—C56—H56C	109.5
C25—C26—C27	120.5 (5)	H56A—C56—H56C	109.5
C25—C26—H26	119.8	H56B—C56—H56C	109.5
C27—C26—H26	119.8	C55—C57—H57A	109.5
C26—C27—C28	119.5 (6)	C55—C57—H57B	109.5
C26—C27—H27	120.3	H57A—C57—H57B	109.5
C28—C27—H27	120.3	C55—C57—H57C	109.5
C23—C28—C27	120.8 (5)	H57A—C57—H57C	109.5
C23—C28—H28	119.6	H57B—C57—H57C	109.5
C27—C28—H28	119.6	N1S—C1S—C2S	179.8 (8)
N5—C29—C31	110.2 (4)	C1S—C2S—H2S1	109.5
N5—C29—C30	112.5 (4)	C1S—C2S—H2S2	109.5
C31—C29—C30	111.3 (4)	H2S1—C2S—H2S2	109.5
N5—C29—H29	107.5	C1S—C2S—H2S3	109.5
C31—C29—H29	107.5	H2S1—C2S—H2S3	109.5
C30—C29—H29	107.5	H2S2—C2S—H2S3	109.5
O5—C30—N6	122.7 (4)	N2S—C3S—C4S	178.5 (10)
O5—C30—C29	120.2 (4)	C3S—C4S—H4S1	109.5
N6—C30—C29	117.1 (4)	C3S—C4S—H4S2	109.5
C29—C31—C32	114.9 (4)	H4S1—C4S—H4S2	109.5
C29—C31—H31A	108.5	C3S—C4S—H4S3	109.5
C32—C31—H31A	108.5	H4S1—C4S—H4S3	109.5
C29—C31—H31B	108.5	H4S2—C4S—H4S3	109.5

C54—N1—C1—C2	−178.5 (5)	C25—C26—C27—C28	2.1 (8)
C4—N1—C1—C2	−10.0 (5)	C24—C23—C28—C27	0.1 (7)
N1—C1—C2—C3	31.4 (5)	C22—C23—C28—C27	173.7 (5)
C1—C2—C3—C4	−41.0 (5)	C26—C27—C28—C23	−1.1 (7)
C54—N1—C4—C5	−87.7 (5)	C21—N5—C29—C31	170.1 (4)
C1—N1—C4—C5	102.7 (5)	C21—N5—C29—C30	−65.0 (5)
C54—N1—C4—C3	154.5 (4)	C35—N6—C30—O5	−2.3 (7)
C1—N1—C4—C3	−15.1 (5)	C35—N6—C30—C29	176.0 (4)
C2—C3—C4—N1	34.2 (5)	N5—C29—C30—O5	151.1 (4)
C2—C3—C4—C5	−84.9 (5)	C31—C29—C30—O5	−84.7 (5)
C9—N2—C5—O1	−172.3 (4)	N5—C29—C30—N6	−27.2 (6)
C6—N2—C5—O1	−8.4 (7)	C31—C29—C30—N6	96.9 (5)
C9—N2—C5—C4	4.1 (6)	N5—C29—C31—C32	−58.5 (5)
C6—N2—C5—C4	168.0 (4)	C30—C29—C31—C32	176.0 (4)
N1—C4—C5—O1	−25.4 (6)	C29—C31—C32—C33	−51.3 (6)
C3—C4—C5—O1	87.3 (5)	C29—C31—C32—C34	−175.5 (4)

N1—C4—C5—N2	158.3 (4)	C30—N6—C35—C36	−51.3 (5)
C3—C4—C5—N2	−89.1 (5)	C30—N6—C35—C37	−176.7 (4)
C5—N2—C6—C7	−172.2 (4)	C41—N7—C36—O6	−2.6 (7)
C9—N2—C6—C7	−6.0 (5)	C41—N7—C36—C35	179.2 (4)
N2—C6—C7—C8	28.2 (5)	N6—C35—C36—O6	148.2 (4)
C6—C7—C8—C9	−39.5 (5)	C37—C35—C36—O6	−88.5 (5)
C5—N2—C9—C10	−93.4 (5)	N6—C35—C36—N7	−33.5 (5)
C6—N2—C9—C10	101.5 (5)	C37—C35—C36—N7	89.7 (5)
C5—N2—C9—C8	146.6 (5)	N6—C35—C37—C38	−173.1 (4)
C6—N2—C9—C8	−18.5 (5)	C36—C35—C37—C38	61.5 (5)
C7—C8—C9—N2	35.1 (5)	N6—C35—C37—C40	60.4 (5)
C7—C8—C9—C10	−87.4 (5)	C36—C35—C37—C40	−65.0 (5)
C11—N3—C10—O2	9.1 (7)	C35—C37—C38—C39	59.7 (6)
C11—N3—C10—C9	−167.9 (4)	C40—C37—C38—C39	−172.1 (5)
N2—C9—C10—O2	176.2 (4)	C36—N7—C41—C43	112.4 (5)
C8—C9—C10—O2	−68.5 (6)	C36—N7—C41—C42	−120.7 (4)
N2—C9—C10—N3	−6.7 (6)	C47—N8—C42—O7	−4.2 (7)
C8—C9—C10—N3	108.7 (5)	C47—N8—C42—C41	174.3 (4)
C10—N3—C11—C12	−98.5 (5)	N7—C41—C42—O7	−154.2 (4)
C10—N3—C11—C13	138.4 (4)	C43—C41—C42—O7	−26.3 (6)
C20—N4—C12—O3	1.7 (7)	N7—C41—C42—N8	27.3 (6)
C20—N4—C12—C11	−175.6 (4)	C43—C41—C42—N8	155.2 (4)
N3—C11—C12—O3	163.1 (4)	N7—C41—C43—C44	56.3 (6)
C13—C11—C12—O3	−72.6 (5)	C42—C41—C43—C44	−70.9 (5)
N3—C11—C12—N4	−19.5 (6)	N7—C41—C43—C46	−68.2 (5)
C13—C11—C12—N4	104.8 (5)	C42—C41—C43—C46	164.6 (4)
N3—C11—C13—C14	−62.6 (5)	C41—C43—C44—C45	164.7 (5)
C12—C11—C13—C14	170.0 (4)	C46—C43—C44—C45	−72.2 (6)
C11—C13—C14—C19	−64.5 (6)	C42—N8—C47—C49	−73.9 (5)
C11—C13—C14—C15	116.0 (5)	C42—N8—C47—C48	53.6 (5)
C19—C14—C15—C16	−0.7 (7)	C53—N9—C48—O8	0.1 (7)
C13—C14—C15—C16	178.9 (4)	C53—N9—C48—C47	174.9 (4)
C14—C15—C16—C17	1.0 (7)	N8—C47—C48—O8	−137.5 (5)
C15—C16—C17—C18	−1.9 (8)	C49—C47—C48—O8	−9.2 (6)
C16—C17—C18—C19	2.6 (8)	N8—C47—C48—N9	47.5 (5)
C15—C14—C19—C18	1.3 (7)	C49—C47—C48—N9	175.8 (4)
C13—C14—C19—C18	−178.2 (4)	N8—C47—C49—C50	−48.7 (5)
C17—C18—C19—C14	−2.3 (8)	C48—C47—C49—C50	−175.9 (4)
C12—N4—C20—C22	112.4 (5)	C47—C49—C50—C51	−55.5 (6)
C12—N4—C20—C21	−121.3 (4)	C47—C49—C50—C52	−178.9 (4)
C29—N5—C21—O4	7.2 (7)	C48—N9—C53—C55	113.3 (5)
C29—N5—C21—C20	−173.8 (4)	C48—N9—C53—C54	−123.7 (5)
N4—C20—C21—O4	−122.1 (5)	C4—N1—C54—O9	6.4 (7)
C22—C20—C21—O4	3.3 (6)	C1—N1—C54—O9	174.2 (5)
N4—C20—C21—N5	58.9 (5)	C4—N1—C54—C53	−169.4 (4)
C22—C20—C21—N5	−175.8 (4)	C1—N1—C54—C53	−1.6 (7)
N4—C20—C22—C23	−60.5 (5)	N9—C53—C54—O9	−88.4 (5)
C21—C20—C22—C23	175.7 (4)	C55—C53—C54—O9	32.6 (6)

C20—C22—C23—C24	96.4 (5)	N9—C53—C54—N1	87.5 (5)
C20—C22—C23—C28	−77.0 (5)	C55—C53—C54—N1	−151.5 (4)
C28—C23—C24—C25	0.0 (7)	N9—C53—C55—C57	169.1 (4)
C22—C23—C24—C25	−173.6 (4)	C54—C53—C55—C57	51.6 (6)
C23—C24—C25—C26	0.9 (8)	N9—C53—C55—C56	−67.9 (5)
C24—C25—C26—C27	−2.0 (8)	C54—C53—C55—C56	174.5 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*N*···O9	0.88	2.08	2.834 (5)	144
N7—H7···O4	0.88	2.30	3.112 (5)	153
N8—H8···O5	0.88	2.12	2.985 (5)	168
N9—H9*N*···O4	0.88	2.23	3.058 (5)	157
N3—H3···N1*S*	0.88	2.31	3.136 (7)	157
C13—H13*A*···N1*S*	0.99	2.67	3.451 (7)	136
N5—H5···O8^{i}	0.88	2.60	3.103 (5)	117
N6—H6···O8^{i}	0.88	2.42	3.153 (5)	141
C1—H1*A*···O3^{ii}	0.99	2.48	3.378 (7)	150
C31—H31*B*···O8^{i}	0.99	2.63	3.435 (6)	139
C37—H37···O7^{i}	1.00	2.17	3.041 (6)	145
C53—H53···O3^{ii}	1.00	2.35	3.187 (6)	140
C2*S*—H2*S*1···O6^{iii}	0.98	2.37	3.268 (7)	152
C4*S*—H4*S*1···O5	0.98	2.55	3.463 (9)	155
C4*S*—H4*S*2···O6	0.98	2.62	3.246 (9)	122

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+3/2, -y+1, z-1/2$.