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2,3,4,6-Tetra-*O*-benzoyl-4-nitrophenyl-1-thio-α-D-mannopyranoside–dichloromethane–diethyl ether mixed solvate (1/0.53/0.38)

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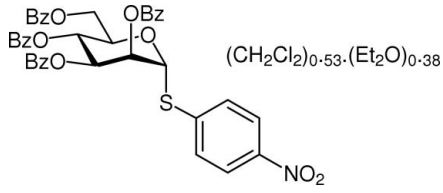
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.047; wR factor = 0.056; data-to-parameter ratio = 13.2.

The title compound, $C_{40}H_{31}NO_{11}S\cdot0.53CH_2Cl_2\cdot0.38C_4H_{10}O$, was synthesized in two steps from mannose pentaacetate and single crystals were grown by slow evaporation. The structure was determined by single-crystal X-ray diffraction, confirming the α-configuration of the anomeric thioaryl substituent. The asymmetric unit contains two crystallographically distinct molecules of the carbohydrate. The central pyranose rings of these are geometrically similar, but there are differences in the orientations of the benzoate substituents.

Related literature

For related literature, see: Cao *et al.* (1998); Shah & Bahl (1974); Cosier & Glazer (1986); France *et al.* (2004); Mootoo *et al.* (1988); Prince (1982); Roy *et al.* (1992); Watkin (1994).



Experimental

Crystal data

$C_{40}H_{31}NO_{11}S\cdot0.534CH_2Cl_2\cdot0.382C_4H_{10}O$
M_r = 770.56
Monoclinic, $P2_1$
a = 11.7508 (2) Å
b = 20.5564 (3) Å
c = 16.4633 (2) Å
β = 105.8699 (16)°
V = 3825.20 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 150 K
0.34 × 0.28 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.94, T_{max} = 0.96
35711 measured reflections
15110 independent reflections
13111 reflections with $I > 3\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.056
S = 1.09
13111 reflections
990 parameters
17 restraints
H-atom parameters not refined
$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$\Delta\rho_{min}$ = −0.92 e Å^{-3}
Absolute structure: Flack (1983), 6226 Friedel pairs
Flack parameter: 0.03 (5)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2055).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bruker (2000). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, S., Hernández-Matéo, F. & Roy, R. (1998). *J. Carbohydr. Chem.* **17**, 609–631.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
France, R. R., Compton, R. G., Davis, B. G., Fairbanks, A. J., Rees, N. V. & Wadhawan, J. D. (2004). *Org. Biomol. Chem.* **2**, 2195–2202.
Mootoo, D. R., Konradsson, P., Udodong, U. & Fraser-Reid, B. (1988). *J. Am. Chem. Soc.* **110**, 5583–5584.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*, pp. 104. New York: Springer-Verlag.
Roy, R., Andersson, F. O. & Letellier, M. (1992). *Tetrahedron Lett.* **33**, 6053–6056.
Shah, R. H. & Bahl, O. P. (1974). *Carbohydr. Res.* **32**, 15–23.
Watkin, D. (1994). *Acta Cryst.* A**50**, 411–437.

supplementary materials

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2,3,4,6-Tetra-*O*-benzoyl-4-nitrophenyl-1-thio-α-D-mannopyranoside-dichloromethane-diethyl ether mixed solvate (1/0.53/0.38)

L. Drouin, A. R. Cowley, A. J. Fairbanks and A. L. Thompson

Comment

Thioglycosides are extremely useful and versatile glycoside donors for the synthesis of oligosaccharides, which may be activated by a wide range of electrophiles and also by electrochemical methods (France *et al.*, 2004). The nature of an aromatic substituent of an aryl thioglycoside has a strongly modulating effect on the reactivity of such a thioglycoside; strongly electron withdrawing substituents greatly reduce their reactivity towards electrophiles (Roy *et al.*, 1992) and also increase their oxidation potentials. Such 'disarmed' (Mootoo *et al.*, 1988) thioglycosides may themselves therefore be used as acceptors for the glycosylation of more reactive 'armed' thioglycoside donors. The title compound was obtained by a *trans*-esterification sequence from the corresponding peracetylated thioglycoside, itself synthesized from mannose penta-acetate by treatment with 4-nitrothiophenol and boron trifluoride etherate in dichloromethane, by Zemplen deacetylation followed by reaction with benzoyl chloride in pyridine in the presence of *N*,*N*-dimethylaminopyridine (DMAP).

Experimental

1,2,3,4,6-Penta-*O*-acetyl-*D*-mannopyranoside (2.17 g, 3.55 mmol) and 4-nitrothiophenol (1.75 g, 11.26 mmol) were suspended in anhydrous dichloromethane (15 ml), under an atmosphere of argon, the mixture was cooled to 0°C, and boron trifluoride diethyl etherate (3.3 ml, 26 mmol) was added dropwise. The reaction mixture was then stirred at room temperature until after 66 h, t.l.c. (petroleum ether/ethyl acetate, 1:1) indicated complete consumption of the starting material, and the formation of a single product (Rf 1/2). The reaction was quenched by the addition of triethylamine (10 ml), and the mixture was then partitioned between water (200 ml) and dichloromethane (200 ml). The aqueous layer was re-extracted with dichloromethane (3 *x* 200 ml), and the combined organic layers were washed with a saturated aqueous solution of sodium hydrogencarbonate (200 ml), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 7:3) to afford 4-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-*D*-mannopyranoside (1.98 g, 74%) which recrystallized from petroleum ether/ethyl acetate as a yellow crystalline solid; m.p 134–136°C (petroleum ether/ethyl acetate); lit., 135–136°C (methanol, Shah & Bahl, 1974); $[\alpha]_D^{23}$ +158 (c, 0.9 $CHCl_3$); lit., $[\alpha]_D$ +142.6 (c, 0.93 $CHCl_3$, Shah & Bahl,(1974): ν_{max} (KBr) 1752 (νC=O ester), 1513, 1579, 1599 (νArC=C), 1233 (νCO ether), 1066 (νCO ether) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.03 (3*H*, s, CH_3CO), 2.04 (3, s, CH_3CO), 2.07 (3*H*, s, CH_3CO), 2.19 (3*H*, s, CH_3CO), 4.10 (1*H*, dd, $J_{5,6}$ 2.5 Hz, $J_{6,6'}$ 12.0 Hz, H-6), 4.31 (1*H*, dd, $J_{5,6'}$ 6.0 Hz, $J_{6,6'}$ 12.0 Hz, H-6'), 4.41 (1*H*, ddd, $J_{4,5}$ 9.5 Hz, $J_{5,6}$ 2.5 Hz, $J_{5,6'}$ 6.0 Hz, H-5), 5.28 (1*H*, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.37 (1*H*, at, $J_{3,4}$ 10.0 Hz, $J_{4,5}$ 10.0 Hz, H-4), 5.48 (1*H*, dd, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 3.5 Hz, H-2), 5.70 (1*H*, d, $J_{1,2}$ 2.0 Hz, H-1), 7.60 (2 *x* 1H, 2 *x* dd, J 7.0 Hz, J 2.0 Hz, 2 *x* ArH), 8.17 (2 *x* 1H, dd, J 7.0 Hz, J 2.0 Hz, 2 *x* ArH); δ_C (100 MHz, $CDCl_3$) 20.9 (2 *x* CH_3CO), 21.0 (CH_3CO), 21.1 (CH_3CO), 62.4 (C-6), 66.2 (C-4), 69.4 (C-3), 70.4 (C-5), 70.8 (C-2), 84.3 (C-1), 124.3 (2 *x* ArCH), 129.8 (2 *x* ArCH), 142.9 (ArC), 146.9 (ArC), 169.9 (C=O), 170.1 (C=O), 170.1 (C=O), 170.6 (C=O); (HMRS (ESI) Calcd. For $C_{20}H_{27}O_{11}N_2S$ $(M+NH_4)^+$ 503.1336. Found 503.1334). (Found: C, 49.49; H, 4.79; N, 2.88. $C_{20}H_{23}O_{11}SN$ requires: C, 49.48; H, 4.77; N, 2.88%).

4-Nitrophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-*D*-mannopyranoside, as prepared above, (1.66 g, 3.43 mmol) was dissolved in methanol (26 ml) and sodium methoxide (0.20 g, 3.80 mmol) was added. The reaction mixture was then stirred at 22°C and, after 45 min, t.l.c. (petroleum ether/ethyl acetate, 1:1) indicated complete consumption of the starting material (Rf 0.6) and the formation of a single product (Rf 0.1). Cation exchange resin IR-120 was then added until neutral pH was attained, and then the mixture was filtered and the solvent was removed under reduced pressure. Azeotropic evaporation with toluene (15 ml) furnished the crude product, which was used in the next step without further purification. The residue was dissolved in pyridine (10 ml) and the mixture was cooled to 0°C. Benzoyl chloride (2.5 ml, 21.52 mmol), and *N*,*N*-dimethylaminopyridine (97 mg, 0.79 mmol) were added and the reaction mixture was stirred at room temperature for 24 h after which time, t.l.c.(petroleum ether/ethyl acetate, 7:3) indicated complete consumption of the starting material (Rf 0.0) and the formation of three major products (Rf 0.2 identified as 4-nitrothiophenyl 2,3,6-tri-*O*-benzoyl-α,*D*-mannopyranoside; Rf 0.3, Rf 0.4 identified as 1,2,3,4,6-penta-*O*-benzoyl-*D*-mannopyranoside; Rf 0.5 identified as the desired 4-nitrothiophenyl 2,3,4,6-tetra-*O*-benzoyl-α,*D*-mannopyranoside). The mixture was partitioned between water (40 ml) and dichloromethane (70 ml), and the aqueous layer was re-extracted with dichloromethane (3 *x* 70 ml). The combined organic extracts were washed with aqueous hydrochloric acid (1*M*, 3 *x* 70 ml), a saturated aqueous solution of sodium hydrogen carbonate (140 ml), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) and then re-crystallized from petroleum ether/ethyl acetate to afford 4-nitrothiophenyl 2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranoside (934 mg, 37%) as yellow crystals; m.p 119–120°C (from petroleum ether/ethyl acetate); a sample suitable for X-ray analysis was then re-crystallized by slow evaporation of a solution in dichloromethane/diethyl ether; $[\alpha]_D^{23}$ +77 (c, 1.0 in $CHCl_3$); ν_{max} (KBr) 1728 (νC=O ester), 1452, 1518, 1581, 1600 (νArC=C), 1265 (νCO ester), 1093 (νCO ester), 709 (νArCH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.61 (1*H*, dd, $J_{5,6}$ 6.0 Hz, $J_{6,6'}$ 12.5 Hz, H-6), 4.66 (1*H*, dd, $J_{5,6'}$ 3.0 Hz, $J_{6,6'}$ 12.5 Hz, H-6'), 4.93 (1*H*, dd, $J_{4,5}$ 10.0 Hz, $J_{5,6}$ 6.0 Hz, $J_{5,6'}$ 3.0 Hz, H-5), 5.88 (1*H*, dd, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 10.0 Hz, H-3), 5.96 (1*H*, dd, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.0 Hz, H-2), 6.04 (1*H*, d, $J_{1,2}$ 1.5 Hz, H-1), 6.14 (1*H*, at, $J_{3,4}$ 10.0 Hz, $J_{4,5}$ 10.0 Hz, H– 4), 7.20–8.20 (24 *x* 1H, m, 24 *x* ArH); δ_C (100 MHz, $CDCl_3$) 60.6 (C-6), 63.0 (C-4), 67.0 (C-3), 70.4 (C-5), 71.6 (C-2), 84.0 (C-1), 124.3 (2 *x* ArCH), 128.6 (2 *x* ArCH), 128.8 (2 *x* ArCH), 128.9 (2 *x* ArCH), 129.1 (2 *x* ArC), 129.5 (2 *x* ArCH), 129.6 (2 *x* ArC), 129.8 (2 *x* ArCH), 130.0 (2 *x* ArCH), 130.1 (2 *x* ArCH), 130.1 (2 *x* ArCH), 130.2 (2 *x* ArCH), 133.6 (ArCH), 133.7 (ArCH), 133.9 (ArCH), 134.0 (ArCH), 142.6 (ArC), 146.7 (ArC), 165.5 (C=O), 165.7 (2 *x* C=O), 166.1 (C=O); m/*z* (ESI) 792.12 ($[M+NH_4+CH_3CN]^+$, 100%). (Found: C, 65.40; H, 4.78; N, 1.98; S, 4.27. $C_{40}H_{31}O_{11}SN$ requires: C, 65.48; H, 4.26; N, 1.91; S, 4.37%).

Refinement

A single-crystal (approximately 0.24 *x* 0.28 *x* 0.34 mm) was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit (Cosier and Glazer, 1986). Diffraction data were measured using an Enraf–Nonius KappaCCD diffractometer (graphite-monochromated Mo *K*α radiation, λ = 0.71073 Å). Intensity data were processed using the *DENZO-SMN* package (Otwinowski and Minor, 1997).

The structure was solved in the space group P 2_1 using the direct-methods program *SIR92* (Altomare *et al.*, 1994), which located all ordered non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the *CRYSTALS* program suite (Betteridge *et al.*, 2003). Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined.

A difference Fourier map showed the presence of several peaks of electron density located within a small cavity within the lattice. These were identified as the non-hydrogen atoms of a disordered mixture of CH_2Cl_2 and Et_2O. The coordinates, isotropic thermal parameters and site occupancies of these were refined. The C—Cl distances were restrained to 1.77 (2) Å, the C—O distances to 1.44 (2) Å and the C—C distances to 1.50 (2) Å. Bond angles were restrained to 112 (2)° and similarity restraints applied to the thermal parameters of directly-bonded atoms.

All hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied $w = [1-(||F_o|-F_c||/6\sigma(F_o))^2]^2 / [1.64T_0(x)+0.395T_1(x) + 1.16]*T_{n-1}(x)]$ (Watkin, 1994, Prince, 1982).

Figures

Fig. 1. Synthesis of (I).

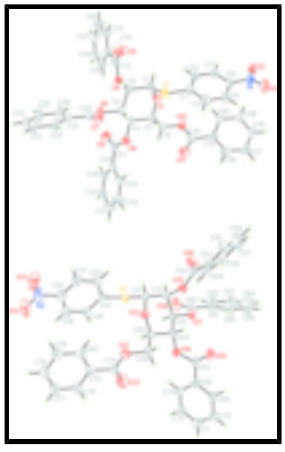


Fig. 2. The molecular structure of 4-Nitrophenyl-2,3,4,6,-tetra-*O*-benzoyl-1-thio-α-*D*-mannopyranoside (I) drawn with probability ellipsoids drawn at 50%.

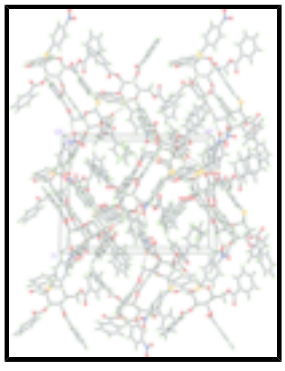


Fig. 3. The crystal structure of (I) viewed down the *c* axis. The diethylether (the minor component of the disordered solvent) is omitted for clarity and intermolecular contacts are shown with a broken bond.

2,3,4,6-Tetra-*O*-benzoyl-4-nitrophenyl-1-thio-α-*D*-mannopyranoside– dichloromethane–diethyl ether (1/0.53/0.38)

Crystal data

$C_{40}H_{31}NO_{11}S·0.534CH_2Cl_2·0.382C_4H_{10}O$	F_{000} = 1604.9
M_r = 770.56	D_x = 1.338 Mg m^{-3}
Monoclinic, $P2_1$	Melting point = 392–393 K

Hall symbol: P 2yb	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 11.7508 (2) Å	Cell parameters from 35711 reflections
b = 20.5564 (3) Å	θ = 5–28º
c = 16.4633 (2) Å	μ = 0.19 mm^{-1}
β = 105.8699 (16)º	T = 150 K
V = 3825.20 (10) Å^3	Block, colourless
Z = 4	0.34 × 0.28 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer	13111 reflections with $I > 3\sigma(I)$
Monochromator: graphite	R_{int} = 0.033
T = 150 K	θ_{max} = 27.5º
ω scans	θ_{min} = 5.2º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −15→15
T_{min} = 0.94, T_{max} = 0.96	k = −22→26
35711 measured reflections	l = −21→20
15110 independent reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.047	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = F /Fmax Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta$F$/6*sigma$F$)^2]^2 A_i are: 1.64 0.395 1.16
$wR(F^2)$ = 0.056	$(\Delta/\sigma)_{max}$ = 0.022
S = 1.09	$\Delta\rho_{max}$ = 1.02 e Å^{-3}
13111 reflections	$\Delta\rho_{min}$ = −0.92 e Å^{-3}
990 parameters	Extinction correction: None
17 restraints	Absolute structure: Flack (1983), 6226 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.03 (5)

Special details

Refinement. Geometric restraints were applied to the disordered solvent. The C—Cl bond lengths of the dichloromethane were restrained to 1.77 (2) Å and the Cl—C—Cl angle t0 112 (2) °. The C—O bond lengths of the diethyl ether were restrained to 1.44 (2) Å, the C—C bond lengths to 1.50 (2) Å and athe C—O—C and C—C—O angles to 112 (2) °. Similarity restraints were applied to the displacement parameters of directly-bonded atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.3485 (2)	0.20275 (12)	0.75601 (14)	0.0334	
C2	0.4009 (2)	0.24747 (12)	0.83156 (14)	0.0327	
C3	0.5206 (2)	0.22266 (14)	0.88413 (14)	0.0351	
C4	0.5142 (2)	0.15140 (13)	0.90501 (15)	0.0347	
C5	0.4704 (2)	0.11426 (13)	0.82197 (14)	0.0333	
C6	0.4623 (2)	0.04204 (14)	0.83407 (16)	0.0419	
O1	0.35374 (13)	0.13699 (9)	0.78018 (10)	0.0333	
S1	0.42285 (5)	0.21933 (4)	0.67336 (4)	0.0367	
C7	0.3479 (2)	0.16471 (13)	0.59285 (14)	0.0350	
C8	0.4099 (2)	0.14367 (18)	0.53705 (19)	0.0517	
C9	0.3541 (3)	0.10490 (19)	0.46936 (19)	0.0558	
C10	0.2387 (2)	0.08738 (14)	0.45869 (15)	0.0387	
C11	0.1773 (2)	0.10510 (14)	0.51562 (15)	0.0377	
C12	0.2327 (2)	0.14418 (15)	0.58333 (16)	0.0412	
N1	0.17696 (19)	0.04720 (13)	0.38677 (14)	0.0445	
O2	0.08023 (17)	0.02439 (11)	0.38503 (13)	0.0502	
O3	0.2256 (2)	0.03731 (16)	0.33113 (15)	0.0737	
O4	0.32209 (14)	0.24493 (9)	0.88592 (10)	0.0341	
C13	0.2288 (2)	0.28532 (14)	0.86521 (16)	0.0401	
O5	0.2118 (2)	0.32160 (13)	0.80651 (15)	0.0661	
C14	0.1482 (2)	0.27773 (14)	0.92039 (15)	0.0397	
C15	0.0434 (3)	0.3124 (2)	0.89847 (18)	0.0582	
C16	−0.0371 (3)	0.3063 (2)	0.9459 (2)	0.0672	
C17	−0.0103 (3)	0.2666 (2)	1.0161 (2)	0.0643	
C18	0.0939 (3)	0.23243 (18)	1.03802 (19)	0.0543	
C19	0.1729 (2)	0.23770 (14)	0.98923 (16)	0.0430	
O6	0.55718 (16)	0.25928 (10)	0.96153 (10)	0.0401	
C20	0.63117 (19)	0.31012 (15)	0.96216 (16)	0.0405	
O7	0.6610 (2)	0.32637 (12)	0.90037 (15)	0.0612	
C21	0.6683 (2)	0.34271 (15)	1.04521 (18)	0.0455	
C22	0.7575 (3)	0.3887 (2)	1.0578 (3)	0.0674	
C23	0.7963 (3)	0.4197 (2)	1.1352 (3)	0.0811	
C24	0.7428 (4)	0.4052 (2)	1.1990 (3)	0.0810	
C25	0.6532 (5)	0.3621 (2)	1.1864 (2)	0.0847	
C26	0.6147 (4)	0.3292 (2)	1.1087 (2)	0.0655	
O8	0.63060 (15)	0.12817 (10)	0.94727 (10)	0.0376	
C27	0.6491 (2)	0.10785 (14)	1.02859 (15)	0.0397	
O9	0.5775 (2)	0.11496 (13)	1.06783 (12)	0.0579	
C28	0.7662 (2)	0.07626 (14)	1.06209 (16)	0.0404	
C29	0.7884 (3)	0.04481 (15)	1.13976 (17)	0.0458	
C30	0.8962 (3)	0.01456 (17)	1.17299 (19)	0.0538	
C31	0.9806 (3)	0.0155 (2)	1.1289 (2)	0.0646	
C32	0.9594 (3)	0.0466 (2)	1.0523 (2)	0.0704	
C33	0.8506 (3)	0.0774 (2)	1.0176 (2)	0.0569	
O10	0.42552 (16)	0.00992 (9)	0.75326 (12)	0.0423	

C34	0.5109 (2)	−0.00435 (14)	0.71473 (18)	0.0434
O11	0.61203 (18)	0.01133 (13)	0.74273 (16)	0.0635
C35	0.4616 (2)	−0.04244 (13)	0.63676 (16)	0.0381
C36	0.5396 (2)	−0.07579 (16)	0.6013 (2)	0.0494
C37	0.4961 (3)	−0.11516 (18)	0.5318 (2)	0.0562
C38	0.3762 (3)	−0.12077 (18)	0.49602 (18)	0.0552
C39	0.2977 (3)	−0.08711 (18)	0.53029 (19)	0.0544
C40	0.3405 (2)	−0.04780 (16)	0.60101 (18)	0.0450
C41	0.26154 (19)	0.41580 (12)	0.67278 (14)	0.0315
C42	0.18643 (19)	0.37068 (12)	0.60558 (15)	0.0328
C43	0.17341 (18)	0.39855 (12)	0.51761 (14)	0.0309
C44	0.12700 (18)	0.46724 (12)	0.51285 (14)	0.0304
C45	0.21561 (19)	0.50790 (12)	0.57930 (14)	0.0314
C46	0.1785 (2)	0.57783 (13)	0.58226 (16)	0.0373
O12	0.22502 (14)	0.48116 (9)	0.66179 (9)	0.0321
S2	0.41553 (5)	0.40293 (4)	0.67172 (4)	0.0381
C47	0.49023 (19)	0.45247 (12)	0.75730 (14)	0.0324
C48	0.5753 (2)	0.49391 (15)	0.74431 (16)	0.0413
C49	0.6451 (2)	0.52957 (16)	0.81047 (19)	0.0472
C50	0.6256 (2)	0.52333 (15)	0.88889 (17)	0.0417
C51	0.5401 (3)	0.48353 (18)	0.90353 (17)	0.0504
C52	0.4707 (3)	0.44757 (16)	0.83690 (17)	0.0464
N2	0.6997 (2)	0.56152 (14)	0.95943 (17)	0.0532
O13	0.6792 (2)	0.55904 (17)	1.02758 (15)	0.0808
O14	0.7772 (2)	0.59475 (16)	0.94602 (18)	0.0797
O15	0.07157 (13)	0.36799 (9)	0.62155 (10)	0.0331
C53	0.0279 (2)	0.30843 (14)	0.62848 (16)	0.0395
O16	0.0725 (2)	0.25897 (11)	0.6129 (2)	0.0670
C54	−0.0811 (2)	0.31107 (15)	0.65817 (15)	0.0381
C55	−0.1444 (3)	0.25400 (17)	0.6570 (3)	0.0622
C56	−0.2436 (3)	0.25451 (19)	0.6878 (3)	0.0680
C57	−0.2768 (2)	0.3098 (2)	0.72114 (19)	0.0549
C58	−0.2135 (2)	0.36720 (18)	0.72253 (18)	0.0500
C59	−0.1163 (2)	0.36789 (14)	0.68942 (16)	0.0397
O17	0.09266 (14)	0.35917 (9)	0.45580 (10)	0.0355
C60	0.1424 (2)	0.30785 (15)	0.42710 (16)	0.0412
O18	0.24693 (18)	0.29581 (12)	0.44975 (15)	0.0578
C61	0.0530 (3)	0.26855 (15)	0.36537 (18)	0.0485
C62	0.0943 (4)	0.21823 (19)	0.3241 (2)	0.0659
C63	0.0116 (6)	0.1813 (2)	0.2643 (3)	0.0904
C64	−0.1078 (6)	0.1937 (2)	0.2493 (3)	0.1019
C65	−0.1476 (4)	0.2425 (2)	0.2901 (3)	0.0978
C66	−0.0677 (3)	0.28158 (19)	0.3485 (3)	0.0688
O19	0.12558 (13)	0.49534 (9)	0.43191 (9)	0.0333
C67	0.0178 (2)	0.50624 (13)	0.37719 (15)	0.0341
O20	−0.07288 (14)	0.48790 (12)	0.38980 (12)	0.0470
C68	0.0252 (2)	0.54598 (12)	0.30379 (14)	0.0322
C69	−0.0793 (2)	0.57149 (14)	0.25221 (15)	0.0381
C70	−0.0772 (2)	0.61037 (15)	0.18393 (16)	0.0439

C71	0.0292 (3)	0.62314 (16)	0.16675 (17)	0.0474	
C72	0.1334 (3)	0.59729 (16)	0.21751 (18)	0.0485	
C73	0.1322 (2)	0.55882 (14)	0.28612 (15)	0.0395	
O21	0.27237 (16)	0.61394 (9)	0.63867 (11)	0.0395	
C74	0.3472 (2)	0.64617 (15)	0.60414 (17)	0.0423	
O22	0.3395 (2)	0.64607 (15)	0.52988 (14)	0.0735	
C75	0.4403 (2)	0.68082 (14)	0.66897 (17)	0.0400	
C76	0.5086 (3)	0.72712 (18)	0.64269 (18)	0.0537	
C77	0.5959 (3)	0.76050 (19)	0.7011 (2)	0.0598	
C78	0.6167 (3)	0.74684 (17)	0.7860 (2)	0.0536	
C79	0.5496 (3)	0.70121 (16)	0.81305 (18)	0.0491	
C80	0.4611 (2)	0.66776 (14)	0.75483 (17)	0.0424	
C81	0.1792 (8)	0.4317 (5)	0.1287 (6)	0.0898 (14)*	0.534 (4)
Cl1	0.1465 (2)	0.37865 (12)	0.20622 (15)	0.0858 (8)*	0.534 (4)
Cl2	0.2986 (3)	0.40333 (15)	0.09106 (18)	0.0981 (9)*	0.534 (4)
O23	0.2198 (6)	0.3899 (4)	0.1234 (5)	0.079 (2)*	0.382 (9)
C82	0.1264 (9)	0.4009 (6)	0.1491 (7)	0.074 (2)*	0.382 (9)
C83	0.0459 (9)	0.4470 (5)	0.1026 (7)	0.072 (2)*	0.382 (9)
C84	0.2408 (9)	0.4219 (5)	0.0637 (7)	0.069 (2)*	0.382 (9)
C85	0.3509 (8)	0.4000 (5)	0.0541 (7)	0.068 (2)*	0.382 (9)
H11	0.2623	0.2122	0.7323	0.0403*	
H21	0.4102	0.2921	0.8101	0.0400*	
H31	0.5791	0.2282	0.8505	0.0420*	
H41	0.4603	0.1451	0.9420	0.0414*	
H51	0.5286	0.1221	0.7887	0.0400*	
H61	0.5415	0.0251	0.8663	0.0489*	
H62	0.4032	0.0331	0.8664	0.0489*	
H81	0.4945	0.1565	0.5458	0.0644*	
H91	0.3977	0.0898	0.4285	0.0702*	
H111	0.0941	0.0900	0.5081	0.0455*	
H121	0.1896	0.1576	0.6253	0.0501*	
H151	0.0256	0.3419	0.8483	0.0703*	
H161	−0.1139	0.3304	0.9293	0.0822*	
H171	−0.0672	0.2627	1.0512	0.0805*	
H181	0.1128	0.2038	1.0890	0.0678*	
H191	0.2481	0.2121	1.0045	0.0521*	
H221	0.7939	0.3994	1.0112	0.0794*	
H231	0.8620	0.4522	1.1452	0.0910*	
H241	0.7714	0.4273	1.2550	0.0875*	
H251	0.6142	0.3535	1.2322	0.0994*	
H261	0.5494	0.2964	1.0994	0.0783*	
H291	0.7267	0.0441	1.1713	0.0533*	
H301	0.9129	−0.0080	1.2289	0.0609*	
H311	1.0583	−0.0067	1.1531	0.0724*	
H321	1.0216	0.0471	1.0212	0.0834*	
H331	0.8342	0.0999	0.9617	0.0668*	
H361	0.6269	−0.0712	0.6263	0.0606*	
H371	0.5523	−0.1398	0.5073	0.0701*	
H381	0.3454	−0.1491	0.4453	0.0650*	

H391	0.2105	−0.0911	0.5042	0.0628*	
H401	0.2842	−0.0236	0.6259	0.0529*	
H411	0.2520	0.4051	0.7298	0.0381*	
H421	0.2236	0.3267	0.6080	0.0390*	
H431	0.2526	0.3987	0.5060	0.0373*	
H441	0.0461	0.4669	0.5216	0.0371*	
H451	0.2918	0.5065	0.5633	0.0380*	
H461	0.1060	0.5799	0.6029	0.0440*	
H462	0.1609	0.5971	0.5244	0.0440*	
H481	0.5868	0.4983	0.6866	0.0503*	
H491	0.7083	0.5592	0.8017	0.0576*	
H511	0.5278	0.4804	0.9612	0.0601*	
H521	0.4072	0.4184	0.8459	0.0556*	
H551	−0.1192	0.2130	0.6343	0.0784*	
H561	−0.2910	0.2138	0.6855	0.0850*	
H571	−0.3469	0.3091	0.7446	0.0680*	
H581	−0.2375	0.4077	0.7471	0.0605*	
H591	−0.0721	0.4093	0.6882	0.0480*	
H621	0.1808	0.2087	0.3368	0.0799*	
H631	0.0391	0.1460	0.2325	0.1099*	
H641	−0.1661	0.1663	0.2077	0.1106*	
H651	−0.2345	0.2505	0.2783	0.1058*	
H661	−0.0966	0.3182	0.3776	0.0773*	
H691	−0.1563	0.5617	0.2645	0.0443*	
H701	−0.1524	0.6291	0.1473	0.0502*	
H711	0.0311	0.6512	0.1175	0.0566*	
H721	0.2101	0.6065	0.2044	0.0593*	
H731	0.2076	0.5404	0.3227	0.0467*	
H761	0.4945	0.7364	0.5811	0.0656*	
H771	0.6438	0.7944	0.6820	0.0720*	
H781	0.6811	0.7703	0.8282	0.0629*	
H791	0.5645	0.6921	0.8748	0.0579*	
H801	0.4126	0.6344	0.7744	0.0507*	
H811	0.2002	0.4756	0.1547	0.1077*	0.534
H812	0.1071	0.4353	0.0798	0.1077*	0.534
H821	0.1536	0.4164	0.2089	0.0892*	0.382
H822	0.0832	0.3587	0.1470	0.0892*	0.382
H831	0.0809	0.4687	0.0607	0.0858*	0.382
H832	0.0289	0.4803	0.1420	0.0858*	0.382
H833	−0.0293	0.4246	0.0722	0.0858*	0.382
H841	0.2451	0.4694	0.0773	0.0833*	0.382
H842	0.1768	0.4141	0.0103	0.0833*	0.382
H851	0.3701	0.4244	0.0071	0.0812*	0.382
H852	0.4142	0.4077	0.1078	0.0812*	0.382
H853	0.3459	0.3525	0.0408	0.0812*	0.382

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0348 (11)	0.0378 (14)	0.0282 (10)	−0.0020 (9)	0.0098 (8)	0.0008 (9)
C2	0.0385 (11)	0.0328 (13)	0.0287 (10)	−0.0015 (9)	0.0124 (9)	−0.0002 (9)
C3	0.0375 (11)	0.0385 (13)	0.0290 (10)	−0.0065 (10)	0.0083 (8)	−0.0071 (10)
C4	0.0321 (11)	0.0400 (14)	0.0315 (11)	−0.0002 (9)	0.0078 (9)	0.0015 (10)
C5	0.0341 (11)	0.0338 (13)	0.0322 (11)	−0.0005 (9)	0.0094 (9)	−0.0026 (9)
C6	0.0522 (14)	0.0359 (14)	0.0343 (12)	−0.0005 (11)	0.0063 (10)	−0.0055 (10)
O1	0.0317 (7)	0.0353 (9)	0.0312 (8)	−0.0043 (6)	0.0057 (6)	0.0000 (7)
S1	0.0418 (3)	0.0403 (3)	0.0303 (3)	−0.0084 (3)	0.0137 (2)	−0.0034 (2)
C7	0.0388 (12)	0.0403 (15)	0.0275 (11)	0.0008 (10)	0.0115 (9)	0.0017 (9)
C8	0.0393 (13)	0.071 (2)	0.0507 (15)	−0.0119 (13)	0.0225 (12)	−0.0155 (15)
C9	0.0456 (14)	0.081 (2)	0.0491 (15)	−0.0076 (14)	0.0265 (12)	−0.0249 (15)
C10	0.0376 (12)	0.0467 (16)	0.0317 (11)	0.0001 (10)	0.0092 (9)	−0.0071 (10)
C11	0.0333 (11)	0.0467 (15)	0.0338 (11)	0.0008 (10)	0.0105 (9)	−0.0049 (11)
C12	0.0380 (12)	0.0505 (17)	0.0367 (12)	−0.0010 (11)	0.0132 (10)	−0.0075 (11)
N1	0.0401 (11)	0.0582 (16)	0.0367 (11)	0.0032 (10)	0.0130 (9)	−0.0124 (10)
O2	0.0414 (10)	0.0613 (14)	0.0462 (10)	−0.0042 (9)	0.0090 (8)	−0.0164 (9)
O3	0.0587 (13)	0.111 (2)	0.0564 (13)	−0.0140 (13)	0.0236 (11)	−0.0436 (14)
O4	0.0394 (8)	0.036 (1)	0.0287 (7)	0.0014 (7)	0.0128 (6)	0.0003 (7)
C13	0.0420 (13)	0.0426 (15)	0.0370 (12)	0.0054 (10)	0.0132 (10)	0.0061 (11)
O5	0.0702 (14)	0.0738 (18)	0.0638 (13)	0.0298 (12)	0.0342 (11)	0.0348 (13)
C14	0.0408 (12)	0.0464 (16)	0.0315 (11)	0.0013 (10)	0.0090 (10)	−0.0033 (10)
C15	0.0546 (15)	0.077 (2)	0.0441 (14)	0.0182 (17)	0.0154 (12)	0.0118 (16)
C16	0.0498 (16)	0.099 (3)	0.0562 (17)	0.0191 (18)	0.0213 (13)	0.008 (2)
C17	0.0559 (17)	0.090 (3)	0.0554 (18)	0.0011 (17)	0.0294 (15)	0.0001 (17)
C18	0.0590 (17)	0.067 (2)	0.0435 (14)	0.0053 (14)	0.0248 (13)	0.0080 (14)
C19	0.0428 (13)	0.0506 (18)	0.0370 (12)	0.0042 (11)	0.0133 (10)	0.0052 (11)
O6	0.0450 (9)	0.0457 (11)	0.0298 (8)	−0.0091 (8)	0.0104 (7)	−0.0112 (7)
C20	0.0289 (10)	0.0447 (14)	0.0472 (13)	−0.0025 (10)	0.0093 (9)	−0.0125 (13)
O7	0.0669 (13)	0.0626 (16)	0.0641 (13)	−0.0295 (11)	0.0348 (11)	−0.0241 (11)
C21	0.0392 (12)	0.0455 (16)	0.0470 (14)	0.0074 (11)	0.0033 (11)	−0.0163 (12)
C22	0.0427 (15)	0.073 (3)	0.083 (2)	−0.0063 (14)	0.0111 (15)	−0.042 (2)
C23	0.0489 (17)	0.077 (3)	0.102 (3)	0.0016 (16)	−0.0062 (18)	−0.060 (2)
C24	0.079 (2)	0.075 (3)	0.065 (2)	0.024 (2)	−0.0213 (19)	−0.043 (2)
C25	0.117 (3)	0.081 (3)	0.0506 (19)	−0.002 (3)	0.013 (2)	−0.027 (2)
C26	0.080 (2)	0.069 (3)	0.0467 (16)	−0.0095 (17)	0.0162 (15)	−0.0203 (15)
O8	0.0356 (8)	0.0465 (11)	0.0291 (8)	0.0001 (7)	0.0061 (6)	0.0000 (7)
C27	0.0449 (13)	0.0434 (15)	0.0284 (11)	−0.0005 (11)	0.0062 (9)	−0.0050 (10)
O9	0.0641 (13)	0.0794 (17)	0.0353 (9)	0.0232 (11)	0.0221 (9)	0.0074 (10)
C28	0.0417 (12)	0.0421 (15)	0.0332 (11)	−0.0026 (10)	0.0030 (9)	−0.0059 (10)
C29	0.0504 (14)	0.0447 (16)	0.0383 (13)	−0.0001 (12)	0.0050 (11)	0.0005 (12)
C30	0.0545 (16)	0.0551 (19)	0.0427 (15)	0.0018 (13)	−0.0018 (12)	0.0049 (13)
C31	0.0415 (15)	0.076 (2)	0.064 (2)	0.0066 (14)	−0.0073 (13)	0.0021 (17)
C32	0.0377 (15)	0.106 (3)	0.065 (2)	0.0067 (16)	0.0099 (13)	0.010 (2)
C33	0.0417 (14)	0.079 (2)	0.0461 (15)	0.0024 (14)	0.0059 (12)	0.0082 (15)

O10	0.0431 (9)	0.0378 (10)	0.0442 (10)	−0.0035 (7)	0.0091 (8)	−0.0095 (8)
C34	0.0360 (12)	0.0407 (15)	0.0532 (15)	0.0025 (10)	0.0119 (11)	−0.0020 (12)
O11	0.0382 (10)	0.0710 (16)	0.0776 (15)	−0.0068 (10)	0.0096 (10)	−0.0244 (12)
C35	0.0379 (12)	0.0363 (14)	0.0389 (12)	0.0011 (10)	0.0085 (10)	0.0018 (10)
C36	0.0377 (13)	0.0578 (19)	0.0560 (16)	0.0009 (11)	0.0184 (12)	−0.0018 (13)
C37	0.0618 (17)	0.066 (2)	0.0477 (15)	0.0091 (15)	0.0261 (14)	−0.0027 (14)
C38	0.0607 (17)	0.063 (2)	0.0384 (13)	0.0064 (14)	0.0086 (12)	−0.0089 (13)
C39	0.0449 (14)	0.066 (2)	0.0466 (15)	0.0032 (13)	0.0018 (12)	−0.0070 (14)
C40	0.0390 (13)	0.0512 (17)	0.0421 (13)	0.0089 (11)	0.0068 (10)	−0.0029 (12)
C41	0.0289 (10)	0.0355 (13)	0.0308 (10)	0.0007 (8)	0.0092 (8)	0.0026 (9)
C42	0.0278 (10)	0.0337 (13)	0.0359 (11)	−0.0021 (9)	0.0072 (8)	0.0020 (10)
C43	0.0269 (9)	0.0357 (13)	0.0307 (10)	−0.0055 (9)	0.0089 (8)	−0.0033 (9)
C44	0.0274 (10)	0.0372 (13)	0.0282 (10)	−0.0028 (8)	0.0102 (8)	0.0007 (9)
C45	0.0311 (10)	0.0375 (14)	0.0264 (10)	−0.0049 (9)	0.0095 (8)	0.0031 (9)
C46	0.0391 (12)	0.0337 (14)	0.0373 (12)	−0.0062 (10)	0.0076 (9)	0.0015 (10)
O12	0.0361 (8)	0.0348 (9)	0.0263 (7)	−0.0016 (6)	0.0099 (6)	−0.0002 (6)
S2	0.0288 (2)	0.0468 (4)	0.0366 (3)	−0.0002 (2)	0.0056 (2)	−0.0082 (3)
C47	0.0290 (10)	0.0332 (13)	0.0323 (11)	0.0030 (9)	0.0039 (8)	−0.0038 (9)
C48	0.0359 (12)	0.0532 (17)	0.0367 (12)	−0.0047 (11)	0.0131 (10)	−0.0059 (11)
C49	0.0375 (12)	0.0537 (18)	0.0528 (15)	−0.0090 (11)	0.0161 (11)	−0.0118 (13)
C50	0.0340 (11)	0.0481 (17)	0.0408 (13)	0.0033 (10)	0.0063 (10)	−0.0121 (11)
C51	0.0491 (15)	0.066 (2)	0.0356 (13)	−0.0083 (14)	0.0097 (11)	−0.0070 (13)
C52	0.0507 (15)	0.0531 (18)	0.0352 (12)	−0.0147 (12)	0.0115 (11)	−0.0008 (12)
N2	0.0364 (11)	0.0617 (17)	0.0580 (15)	0.0009 (11)	0.0070 (10)	−0.0244 (13)
O13	0.0728 (15)	0.123 (3)	0.0431 (12)	−0.0163 (16)	0.0106 (11)	−0.0338 (14)
O14	0.0610 (14)	0.096 (2)	0.0817 (17)	−0.0294 (14)	0.0179 (12)	−0.0446 (16)
O15	0.0312 (7)	0.0325 (9)	0.0385 (8)	−0.0003 (6)	0.0144 (7)	0.0050 (7)
C53	0.0371 (11)	0.0329 (13)	0.0507 (13)	0.0009 (10)	0.0156 (10)	0.0012 (12)
O16	0.0563 (12)	0.0360 (12)	0.124 (2)	−0.0050 (9)	0.0505 (14)	−0.0074 (13)
C54	0.0324 (10)	0.0403 (13)	0.0432 (12)	−0.0030 (10)	0.0134 (9)	0.0073 (12)
C55	0.0524 (16)	0.0423 (18)	0.101 (3)	−0.0005 (13)	0.0370 (17)	0.0115 (18)
C56	0.0467 (16)	0.056 (2)	0.110 (3)	−0.0028 (14)	0.0359 (18)	0.027 (2)
C57	0.0376 (12)	0.079 (2)	0.0534 (15)	0.0057 (15)	0.0211 (11)	0.0234 (17)
C58	0.0387 (13)	0.071 (2)	0.0421 (14)	0.0058 (13)	0.0131 (11)	−0.0019 (13)
C59	0.0346 (11)	0.0471 (16)	0.0382 (12)	0.0011 (10)	0.0114 (10)	0.0033 (11)
O17	0.0313 (7)	0.0393 (10)	0.0341 (8)	−0.0049 (6)	0.0059 (6)	−0.0060 (7)
C60	0.0444 (12)	0.0416 (15)	0.0388 (12)	−0.0091 (11)	0.0135 (10)	−0.0047 (12)
O18	0.0448 (10)	0.0617 (15)	0.0696 (13)	0.0009 (9)	0.0203 (10)	−0.0206 (11)
C61	0.0607 (17)	0.0391 (16)	0.0437 (14)	−0.0129 (12)	0.0111 (12)	−0.0047 (12)
C62	0.096 (3)	0.0479 (19)	0.0562 (18)	−0.0132 (18)	0.0243 (17)	−0.0141 (16)
C63	0.158 (5)	0.053 (2)	0.064 (2)	−0.030 (3)	0.036 (3)	−0.0232 (19)
C64	0.145 (5)	0.062 (3)	0.069 (3)	−0.038 (3)	−0.020 (3)	−0.011 (2)
C65	0.090 (3)	0.069 (3)	0.106 (3)	−0.033 (2)	−0.022 (3)	−0.010 (3)
C66	0.063 (2)	0.055 (2)	0.075 (2)	−0.0173 (16)	−0.0038 (17)	−0.0102 (17)
O19	0.0279 (7)	0.0441 (10)	0.0269 (7)	−0.0040 (6)	0.0058 (6)	0.0040 (7)
C67	0.0313 (11)	0.0352 (13)	0.0323 (11)	0.0000 (9)	0.0026 (8)	−0.0042 (9)
O20	0.0285 (8)	0.0665 (14)	0.0439 (10)	−0.0055 (8)	0.0062 (7)	0.0091 (9)
C68	0.0328 (11)	0.0338 (13)	0.0275 (10)	0.0003 (9)	0.0040 (8)	−0.0011 (9)
C69	0.0381 (12)	0.0389 (14)	0.0339 (11)	0.0029 (10)	0.0040 (9)	−0.0020 (10)

C70	0.0469 (14)	0.0426 (16)	0.0360 (12)	0.0074 (11)	0.0011 (10)	0.0008 (11)
C71	0.0589 (16)	0.0488 (18)	0.0337 (12)	0.0084 (13)	0.0116 (11)	0.0098 (11)
C72	0.0467 (14)	0.0575 (19)	0.0441 (14)	0.0024 (12)	0.0172 (11)	0.0094 (13)
C73	0.0378 (12)	0.0454 (16)	0.0337 (11)	0.0056 (10)	0.0072 (9)	0.0034 (10)
O21	0.0462 (9)	0.0371 (10)	0.0351 (8)	−0.0083 (7)	0.0108 (7)	0.0003 (7)
C74	0.0482 (14)	0.0419 (16)	0.0384 (13)	−0.0109 (11)	0.0145 (11)	−0.0019 (11)
O22	0.0796 (16)	0.105 (2)	0.0397 (11)	−0.0443 (15)	0.0233 (11)	−0.0079 (12)
C75	0.0410 (13)	0.0375 (15)	0.0419 (13)	−0.0053 (10)	0.0118 (10)	−0.0026 (11)
C76	0.0556 (16)	0.063 (2)	0.0456 (14)	−0.0186 (14)	0.0186 (12)	0.0017 (14)
C77	0.0572 (17)	0.063 (2)	0.0600 (18)	−0.0248 (15)	0.0172 (14)	−0.0008 (15)
C78	0.0449 (14)	0.0547 (19)	0.0578 (17)	−0.0136 (13)	0.0080 (12)	−0.0062 (14)
C79	0.0478 (14)	0.0525 (19)	0.0446 (14)	−0.0049 (12)	0.0086 (11)	0.0021 (12)
C80	0.0425 (13)	0.0420 (15)	0.0424 (13)	−0.0035 (11)	0.0108 (10)	0.0044 (11)

Geometric parameters (Å, °)

C1—H11	1.000	C43—C44	1.508 (4)
C1—S1	1.839 (2)	C44—H441	1.000
C1—O1	1.406 (3)	C44—O19	1.448 (3)
C1—C2	1.534 (3)	C44—C45	1.535 (3)
C2—H21	1.000	C45—H451	1.000
C2—O4	1.454 (3)	C45—O12	1.441 (3)
C2—C3	1.524 (3)	C45—C46	1.507 (4)
C3—H31	1.000	C46—H462	1.000
C3—O6	1.441 (3)	C46—H461	1.000
C3—C4	1.511 (4)	C46—O21	1.439 (3)
C4—H41	1.000	S2—C47	1.765 (2)
C4—O8	1.436 (3)	C47—C52	1.395 (4)
C4—C5	1.527 (3)	C47—C48	1.374 (4)
C5—H51	1.000	C48—H481	1.000
C5—O1	1.434 (3)	C48—C49	1.381 (4)
C5—C6	1.504 (4)	C49—H491	1.000
C6—H62	1.000	C49—C50	1.378 (4)
C6—H61	1.000	C50—N2	1.473 (3)
C6—O10	1.442 (3)	C50—C51	1.367 (4)
S1—C7	1.776 (3)	C51—H511	1.000
C7—C12	1.386 (4)	C51—C52	1.388 (4)
C7—C8	1.389 (4)	C52—H521	1.000
C8—H81	1.000	N2—O14	1.207 (4)
C8—C9	1.381 (4)	N2—O13	1.211 (4)
C9—H91	1.000	O15—C53	1.344 (3)
C9—C10	1.368 (4)	C53—C54	1.492 (3)
C10—N1	1.463 (3)	C53—O16	1.203 (4)
C10—C11	1.379 (3)	C54—C59	1.384 (4)
C11—H111	1.000	C54—C55	1.387 (4)
C11—C12	1.384 (4)	C55—H551	1.000
C12—H121	1.000	C55—C56	1.392 (5)
N1—O3	1.222 (3)	C56—H561	1.000
N1—O2	1.223 (3)	C56—C57	1.365 (6)

O4—C13	1.343 (3)	C57—H571	1.000
C13—C14	1.488 (4)	C57—C58	1.392 (5)
C13—O5	1.193 (3)	C58—H581	1.000
C14—C19	1.366 (4)	C58—C59	1.394 (4)
C14—C15	1.382 (4)	C59—H591	1.000
C15—H151	1.000	O17—C60	1.352 (4)
C15—C16	1.387 (4)	C60—C61	1.485 (4)
C16—H161	1.000	C60—O18	1.208 (3)
C16—C17	1.379 (5)	C61—C66	1.395 (5)
C17—H171	1.000	C61—C62	1.395 (5)
C17—C18	1.371 (5)	C62—H621	1.000
C18—H181	1.000	C62—C63	1.402 (6)
C18—C19	1.388 (4)	C63—H631	1.000
C19—H191	1.000	C63—C64	1.380 (8)
O6—C20	1.358 (3)	C64—H641	1.000
C20—C21	1.477 (4)	C64—C65	1.359 (9)
C20—O7	1.210 (3)	C65—H651	1.000
C21—C26	1.389 (5)	C65—C66	1.399 (5)
C21—C22	1.384 (5)	C66—H661	1.000
C22—H221	1.000	O19—C67	1.357 (3)
C22—C23	1.386 (5)	C67—C68	1.481 (3)
C23—H231	1.000	C67—O20	1.201 (3)
C23—C24	1.396 (7)	C68—C73	1.392 (3)
C24—H241	1.000	C68—C69	1.390 (3)
C24—C25	1.348 (7)	C69—H691	1.000
C25—H251	1.000	C69—C70	1.385 (4)
C25—C26	1.408 (5)	C70—H701	1.000
C26—H261	1.000	C70—C71	1.381 (4)
O8—C27	1.362 (3)	C71—H711	1.000
C27—C28	1.485 (4)	C71—C72	1.386 (4)
C27—O9	1.201 (3)	C72—H721	1.000
C28—C33	1.385 (4)	C72—C73	1.382 (4)
C28—C29	1.392 (4)	C73—H731	1.000
C29—H291	1.000	O21—C74	1.345 (3)
C29—C30	1.383 (4)	C74—C75	1.485 (4)
C30—H301	1.000	C74—O22	1.201 (3)
C30—C31	1.380 (5)	C75—C80	1.393 (4)
C31—H311	1.000	C75—C76	1.388 (4)
C31—C32	1.375 (5)	C76—H761	1.000
C32—H321	1.000	C76—C77	1.382 (4)
C32—C33	1.401 (5)	C77—H771	1.000
C33—H331	1.000	C77—C78	1.381 (5)
O10—C34	1.357 (3)	C78—H781	1.000
C34—C35	1.480 (4)	C78—C79	1.376 (4)
C34—O11	1.195 (3)	C79—H791	1.000
C35—C40	1.388 (4)	C79—C80	1.388 (4)
C35—C36	1.393 (4)	C80—H801	1.000
C36—H361	1.000	C81—H812	1.000
C36—C37	1.381 (5)	C81—H811	1.000

C37—H371	1.000	C81—Cl2	1.780 (9)
C37—C38	1.376 (5)	C81—Cl1	1.798 (10)
C38—H381	1.000	O23—C84	1.262 (11)
C38—C39	1.390 (5)	O23—C82	1.298 (11)
C39—H391	1.000	C82—H822	1.000
C39—C40	1.393 (4)	C82—H821	1.000
C40—H401	1.000	C82—C83	1.408 (12)
C41—H411	1.000	C83—H833	1.000
C41—S2	1.833 (2)	C83—H832	1.000
C41—O12	1.407 (3)	C83—H831	1.000
C41—C42	1.526 (3)	C84—H842	1.000
C42—H421	1.000	C84—H841	1.000
C42—O15	1.445 (3)	C84—C85	1.418 (12)
C42—C43	1.526 (3)	C85—H853	1.000
C43—H431	1.000	C85—H852	1.000
C43—O17	1.436 (3)	C85—H851	1.000
H11—C1—S1	108.133	O17—C43—C42	109.64 (19)
H11—C1—O1	105.002	C44—C43—C42	110.00 (19)
S1—C1—O1	113.25 (16)	H441—C44—O19	111.263
H11—C1—C2	109.784	H441—C44—C45	112.798
S1—C1—C2	108.81 (16)	O19—C44—C45	105.87 (17)
O1—C1—C2	111.72 (18)	H441—C44—C43	109.343
H21—C2—O4	113.523	O19—C44—C43	109.53 (18)
H21—C2—C3	109.556	C45—C44—C43	107.91 (18)
O4—C2—C3	106.43 (18)	H451—C45—O12	113.187
H21—C2—C1	108.826	H451—C45—C46	108.868
O4—C2—C1	107.19 (18)	O12—C45—C46	106.36 (19)
C3—C2—C1	111.3 (2)	H451—C45—C44	106.177
H31—C3—O6	110.270	O12—C45—C44	109.04 (18)
H31—C3—C4	108.728	C46—C45—C44	113.35 (19)
O6—C3—C4	109.06 (19)	H462—C46—H461	109.467
H31—C3—C2	108.323	H462—C46—O21	109.445
O6—C3—C2	109.5 (2)	H461—C46—O21	109.445
C4—C3—C2	110.98 (19)	H462—C46—C45	109.446
H41—C4—O8	109.877	H461—C46—C45	109.446
H41—C4—C5	111.404	O21—C46—C45	109.6 (2)
O8—C4—C5	108.1 (2)	C41—O12—C45	115.32 (17)
H41—C4—C3	110.112	C47—S2—C41	100.71 (11)
O8—C4—C3	109.44 (19)	C52—C47—C48	120.3 (2)
C5—C4—C3	107.86 (19)	C52—C47—S2	122.3 (2)
H51—C5—O1	113.085	C48—C47—S2	117.24 (18)
H51—C5—C6	108.034	H481—C48—C49	119.770
O1—C5—C6	107.33 (19)	H481—C48—C47	119.770
H51—C5—C4	107.263	C49—C48—C47	120.5 (2)
O1—C5—C4	108.10 (19)	H491—C49—C50	120.842
C6—C5—C4	113.1 (2)	H491—C49—C48	120.842
H62—C6—H61	109.467	C50—C49—C48	118.3 (3)
H62—C6—O10	109.313	N2—C50—C51	119.0 (3)
H61—C6—O10	109.314	N2—C50—C49	118.4 (3)

H62—C6—C5	109.313	C51—C50—C49	122.7 (2)
H61—C6—C5	109.314	H511—C51—C52	120.629
O10—C6—C5	110.1 (2)	H511—C51—C50	120.629
C1—O1—C5	114.29 (17)	C52—C51—C50	118.7 (3)
C7—S1—C1	101.30 (11)	H521—C52—C51	120.258
C12—C7—C8	120.3 (2)	H521—C52—C47	120.258
C12—C7—S1	123.15 (19)	C51—C52—C47	119.5 (3)
C8—C7—S1	116.6 (2)	O14—N2—O13	123.0 (3)
H81—C8—C9	120.193	O14—N2—C50	118.1 (3)
H81—C8—C7	120.193	O13—N2—C50	118.9 (3)
C9—C8—C7	119.6 (2)	C53—O15—C42	116.57 (19)
H91—C9—C10	120.297	C54—C53—O16	124.3 (3)
H91—C9—C8	120.298	C54—C53—O15	112.1 (2)
C10—C9—C8	119.4 (2)	O16—C53—O15	123.6 (2)
N1—C10—C11	117.6 (2)	C59—C54—C55	120.3 (2)
N1—C10—C9	120.5 (2)	C59—C54—C53	121.5 (2)
C11—C10—C9	121.9 (2)	C55—C54—C53	118.1 (3)
H111—C11—C12	120.571	H551—C55—C56	120.389
H111—C11—C10	120.571	H551—C55—C54	120.387
C12—C11—C10	118.9 (2)	C56—C55—C54	119.2 (3)
H121—C12—C11	120.076	H561—C56—C57	119.561
H121—C12—C7	120.074	H561—C56—C55	119.561
C11—C12—C7	119.8 (2)	C57—C56—C55	120.9 (3)
O3—N1—O2	122.7 (2)	H571—C57—C58	119.952
O3—N1—C10	118.1 (2)	H571—C57—C56	119.952
O2—N1—C10	119.2 (2)	C58—C57—C56	120.1 (2)
C13—O4—C2	115.77 (19)	H581—C58—C59	120.198
C14—C13—O5	124.5 (2)	H581—C58—C57	120.198
C14—C13—O4	113.0 (2)	C59—C58—C57	119.6 (3)
O5—C13—O4	122.4 (2)	H591—C59—C54	120.102
C19—C14—C15	119.9 (3)	H591—C59—C58	120.102
C19—C14—C13	122.9 (2)	C54—C59—C58	119.8 (3)
C15—C14—C13	117.2 (2)	C60—O17—C43	114.99 (18)
H151—C15—C16	119.913	C61—C60—O18	124.7 (3)
H151—C15—C14	119.914	C61—C60—O17	111.8 (2)
C16—C15—C14	120.2 (3)	O18—C60—O17	123.5 (2)
H161—C16—C17	120.318	C66—C61—C62	121.0 (3)
H161—C16—C15	120.318	C66—C61—C60	121.5 (3)
C17—C16—C15	119.4 (3)	C62—C61—C60	117.5 (3)
H171—C17—C18	119.771	H621—C62—C63	120.781
H171—C17—C16	119.769	H621—C62—C61	120.782
C18—C17—C16	120.5 (3)	C63—C62—C61	118.4 (4)
H181—C18—C19	120.080	H631—C63—C64	119.944
H181—C18—C17	120.080	H631—C63—C62	119.949
C19—C18—C17	119.8 (3)	C64—C63—C62	120.1 (4)
H191—C19—C14	119.879	H641—C64—C65	119.396
H191—C19—C18	119.879	H641—C64—C63	119.408
C14—C19—C18	120.2 (3)	C65—C64—C63	121.2 (4)
C20—O6—C3	116.38 (19)	H651—C65—C66	119.789

C21—C20—O7	124.9 (3)	H651—C65—C64	119.793
C21—C20—O6	112.5 (2)	C66—C65—C64	120.4 (5)
O7—C20—O6	122.6 (2)	H661—C66—C61	120.608
C26—C21—C22	120.3 (3)	H661—C66—C65	120.608
C26—C21—C20	121.7 (3)	C61—C66—C65	118.8 (4)
C22—C21—C20	117.9 (3)	C67—O19—C44	116.78 (17)
H221—C22—C23	120.084	C68—C67—O20	124.5 (2)
H221—C22—C21	120.083	C68—C67—O19	112.38 (19)
C23—C22—C21	119.8 (4)	O20—C67—O19	123.0 (2)
H231—C23—C24	120.295	C73—C68—C69	119.9 (2)
H231—C23—C22	120.295	C73—C68—C67	122.2 (2)
C24—C23—C22	119.4 (4)	C69—C68—C67	117.9 (2)
H241—C24—C25	119.413	H691—C69—C70	119.845
H241—C24—C23	119.413	H691—C69—C68	119.845
C25—C24—C23	121.2 (3)	C70—C69—C68	120.3 (2)
H251—C25—C26	119.999	H701—C70—C71	120.193
H251—C25—C24	119.999	H701—C70—C69	120.194
C26—C25—C24	120.0 (4)	C71—C70—C69	119.6 (2)
H261—C26—C21	120.406	H711—C71—C72	119.868
H261—C26—C25	120.407	H711—C71—C70	119.868
C21—C26—C25	119.2 (4)	C72—C71—C70	120.3 (3)
C27—O8—C4	116.93 (19)	H721—C72—C73	119.754
C28—C27—O9	124.6 (2)	H721—C72—C71	119.754
C28—C27—O8	112.4 (2)	C73—C72—C71	120.5 (3)
O9—C27—O8	123.0 (2)	H731—C73—C72	120.291
C33—C28—C29	120.8 (3)	H731—C73—C68	120.291
C33—C28—C27	121.4 (2)	C72—C73—C68	119.4 (2)
C29—C28—C27	117.8 (2)	C74—O21—C46	117.13 (19)
H291—C29—C30	120.205	C75—C74—O22	124.6 (2)
H291—C29—C28	120.206	C75—C74—O21	111.8 (2)
C30—C29—C28	119.6 (3)	O22—C74—O21	123.6 (2)
H301—C30—C31	120.055	C80—C75—C76	119.5 (2)
H301—C30—C29	120.055	C80—C75—C74	121.8 (2)
C31—C30—C29	119.9 (3)	C76—C75—C74	118.7 (2)
H311—C31—C32	119.579	H761—C76—C77	119.801
H311—C31—C30	119.580	H761—C76—C75	119.801
C32—C31—C30	120.8 (3)	C77—C76—C75	120.4 (3)
H321—C32—C33	119.989	H771—C77—C78	120.126
H321—C32—C31	119.989	H771—C77—C76	120.127
C33—C32—C31	120.0 (3)	C78—C77—C76	119.7 (3)
H331—C33—C28	120.556	H781—C78—C79	119.742
H331—C33—C32	120.556	H781—C78—C77	119.742
C28—C33—C32	118.9 (3)	C79—C78—C77	120.5 (3)
C34—O10—C6	117.2 (2)	H791—C79—C80	119.948
C35—C34—O11	126.1 (3)	H791—C79—C78	119.948
C35—C34—O10	110.9 (2)	C80—C79—C78	120.1 (3)
O11—C34—O10	123.0 (3)	H801—C80—C79	120.136
C40—C35—C36	119.9 (2)	H801—C80—C75	120.136
C40—C35—C34	121.5 (2)	C79—C80—C75	119.7 (3)

C36—C35—C34	118.5 (2)	H812—C81—H811	109.469
H361—C36—C37	120.040	H812—C81—Cl2	108.589
H361—C36—C35	120.040	H811—C81—Cl2	108.588
C37—C36—C35	119.9 (3)	H812—C81—Cl1	108.585
H371—C37—C38	119.747	H811—C81—Cl1	108.585
H371—C37—C36	119.747	Cl2—C81—Cl1	113.0 (5)
C38—C37—C36	120.5 (3)	C84—O23—C82	121.8 (8)
H381—C38—C39	119.995	H822—C82—H821	109.462
H381—C38—C37	119.995	H822—C82—C83	107.770
C39—C38—C37	120.0 (3)	H821—C82—C83	107.769
H391—C39—C40	120.001	H822—C82—O23	107.761
H391—C39—C38	120.002	H821—C82—O23	107.762
C40—C39—C38	120.0 (3)	C83—C82—O23	116.2 (9)
H401—C40—C35	120.188	H833—C83—H832	109.477
H401—C40—C39	120.188	H833—C83—H831	109.473
C35—C40—C39	119.6 (3)	H832—C83—H831	109.479
H411—C41—S2	109.987	H833—C83—C82	109.465
H411—C41—O12	102.869	H832—C83—C82	109.468
S2—C41—O12	113.81 (16)	H831—C83—C82	109.466
H411—C41—C42	110.796	H842—C84—H841	109.457
S2—C41—C42	106.38 (16)	H842—C84—C85	109.960
O12—C41—C42	113.05 (18)	H841—C84—C85	110.000
H421—C42—O15	112.140	H842—C84—O23	109.950
H421—C42—C43	107.906	H841—C84—O23	109.980
O15—C42—C43	109.32 (17)	C85—C84—O23	107.5 (9)
H421—C42—C41	111.144	H853—C85—H852	109.475
O15—C42—C41	105.98 (19)	H853—C85—H851	109.494
C43—C42—C41	110.35 (19)	H852—C85—H851	109.469
H431—C43—O17	109.614	H853—C85—C84	109.480
H431—C43—C44	109.257	H852—C85—C84	109.443
O17—C43—C44	109.35 (17)	H851—C85—C84	109.467
H431—C43—C42	108.964		

Fig. 1

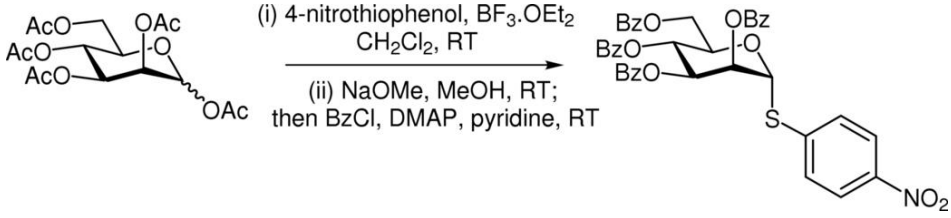
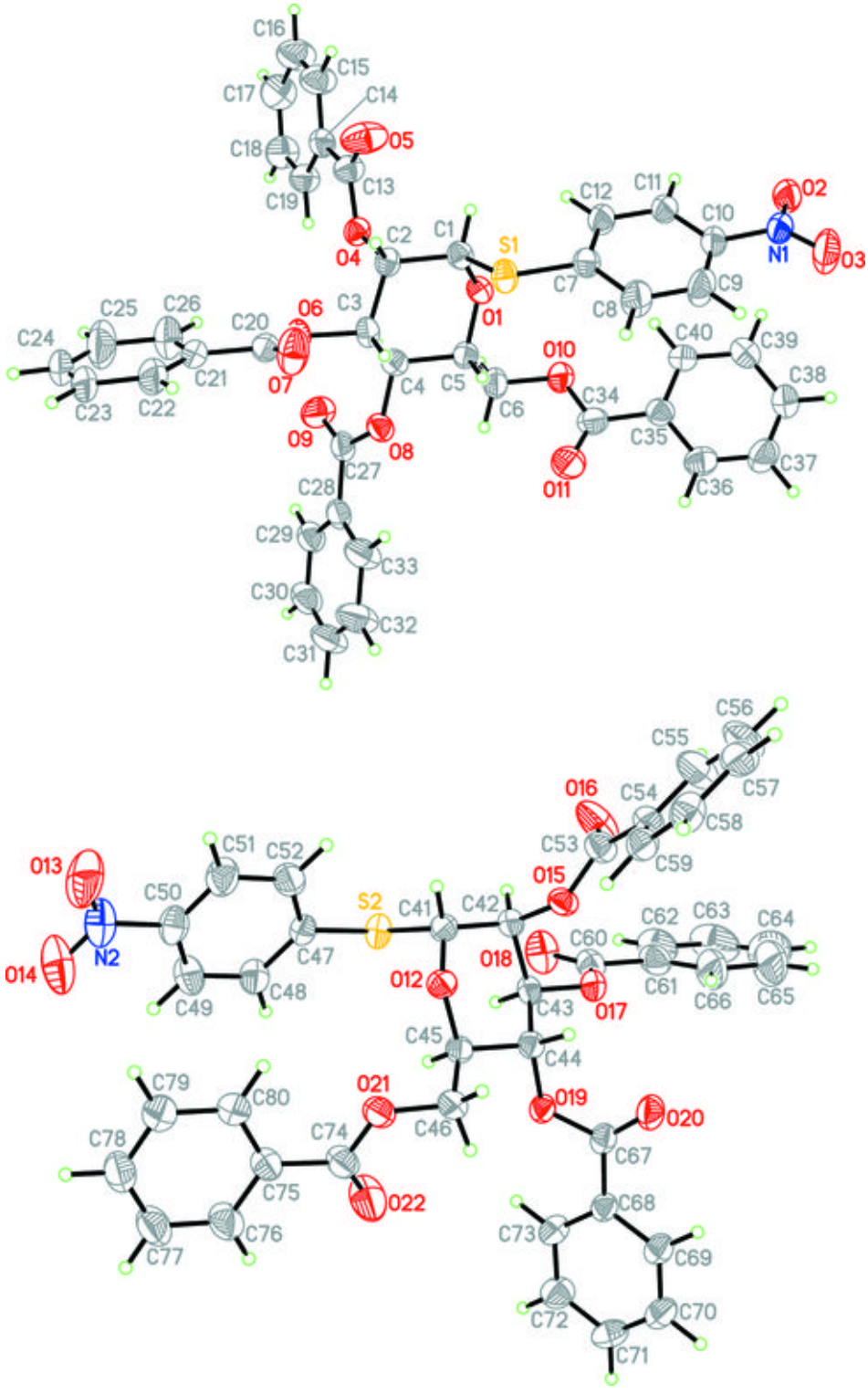

AcO
OAc
AcO
AcO
OAc
(i) 4-nitrothiophenol, BF3.OEt2
CH2Cl2, RT
(ii) NaOMe, MeOH, RT;
then BzCl, DMAP, pyridine, RT
BzO
OBz
BzO
BzO
S
NO2

Fig. 2


C16
C15
C17
C14
C18
O5
C19
C13
O4
C2
C1
S1
C12
C11
C10
O2
N1
O3
C7
C9
C8
C25
C26
C24
C20
O6
C3
O1
C40
C39
C21
O7
C4
C5
O10
C38
C23
C22
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O12
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O20
C78
C74
C46
C67
C75
O22
C68
C73
C69
C77
C76
C72
C70
C71

Fig. 3