Chemo- and regioselective [3 + 2]-cycloadditions of thiocarbonyl ylides: crystal structures of *trans*-8-benzoyl-1,1,3,3-tetramethyl-7-trifluoromethyl-5-thiaspiro[3.4]octan-2-one and *trans*-3-benzoyl-2,2-diphenyl-4-(trifluoromethyl)tetrahydrothiophene
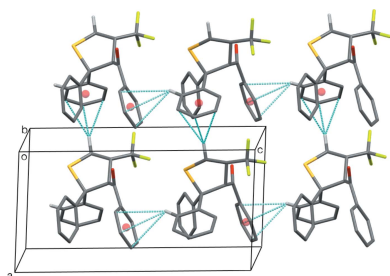
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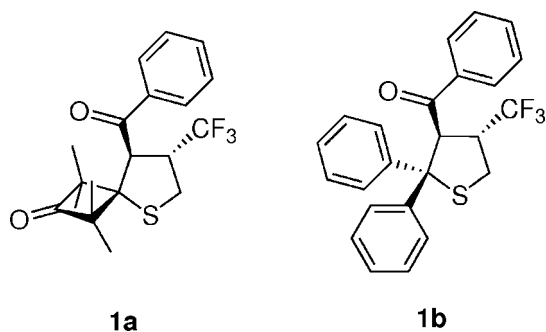
The title compounds, $C_{19}H_{21}F_3O_2S$ and $C_{24}H_{19}F_3OS$, were prepared *via* chemo- and regioselective [3 + 2]-cycloadditions of the respective thiocarbonyl ylides (thiocarbonyl *S*-methanides), generated *in situ*, with (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one. The thiophene ring in the crystal structure of each compound has an envelope conformation. The largest differences between the two molecular structures is in the bond lengths about the quaternary C atom of the thiophene ring; in the spirocyclic structure, the C—C bonds to the spiro C atom in the cyclobutane ring are around 1.60 Å, although this is also observed in related structures. In the same structure, weak intermolecular C—H···*X* (*X* = S, O) interactions link the molecules into extended ribbons running parallel to the [001] direction. In the other structure, weak C—H···π interactions link the molecules into sheets parallel to the (010) plane.

1. Chemical context

Tetrahydrothiophenes constitute a group of five-membered non-aromatic sulfur heterocycles and one of the most prominent representatives is biotin (Mistry & Dakshinamurti, 1964). In a series of our publications, we demonstrated that the [3 + 2]-cycloaddition of *in situ*-generated thiocarbonyl *S*-methanides with activated electron-deficient ethenes is the method of choice for the preparation of differently substituted tetrahydrothiophenes (Huisgen *et al.*, 1984; Mlostoń & Heimgartner, 2000). Recently, alternative methods have been published in a series of reports demonstrating the ongoing interest in their synthesis (Zamberlan *et al.*, 2018). For example, Lewis acid-catalysed reactions of thiocarbonyl compounds with 'donor–acceptor cyclopropanes' have been reported (Augustin *et al.*, 2017; Matsumoto *et al.*, 2018). In addition, radical cyclizations (Ram *et al.*, 2016) and 'sulfur Michael/Henry reactions' (Zhang *et al.*, 2018) were elaborated as new approaches to tetrahydrothiophenes. Furthermore, analogous domino reactions, *i.e.* 'sulfa-Michael/Aldol reactions' (Duan *et al.*, 2017) and 'double Michael reactions' (Meninno *et al.*, 2017) as well as 'Michael–Henry–Cascade–Rearrangement reactions' (Wang *et al.*, 2018) as asymmetric syntheses of highly substituted mono- and spirocyclic tetrahydrothiophene derivatives have been described.

1a　　　　　　　　**1b**

1,4-Disubstitued α,β-unsaturated ketones are known as reactive dipolarophiles, and in the case of aryl,trifluormethyl-substituted representatives, the [3 + 2]-cycloadditions with electron-rich thiocarbonyl ylides occur chemoselectively either on the C=C or C=O bond, depending on the location of the CF₃ group. In addition, the non-symmetrically substituted C=C bond can react with a thiocarbonyl S-methanide to give two different regioisomeric tetrahydrothiophenes. We recently reported that the addition of the 1,3-dipole onto the C=C bond occurs only in the case of (E)-1-aryl-4,4,4-trifluorobut-2-en-1-ones. On the other hand, the isomeric (E)-4-aryl-1,1,1-trifluorobut-3-en-2-ones undergo cycloaddition with the same thiocarbonyl S-methanide to afford 1,3-oxathiole derivatives exclusively (Mlostoń et al., 2016). In that work, the [3 + 2]-cycloadditions of (E)-4,4,4-trifluoro-1-phenylbut-2-en-

1-one with thiobenzophenone S-methanide as well as with 3-thioxo-2,2,4,4-tetramethylcyclobutan-3-one S-methanide led to the corresponding title tetrahydrothiophene derivatives, *trans*-8-benzoyl-1,1,3,3-tetramethyl-7-trifluoromethyl-5-thia-spiro[3.4]octan-2-one, **1a**, and *trans*-3-benzoyl-2,2-diphenyl-4-(trifluoromethyl)tetrahydrothiophene, **1b**, respectively, as crystalline products in high yields. Single crystals were grown from petroleum ether and used for single-crystal X-ray diffraction analyses, the results of which are reported here.

2. Structural commentary

Compounds **1a** and **1b** crystallized as racemates with the benzoyl and trifluoromethyl substituents on the thiophene ring in a *trans* configuration (Figs. 1 and 2). The thiophene ring in each case has an envelope conformation with the sulfur atom as the envelope flap. For **1a**, the ring puckering parameters (Cremer & Pople, 1975) for the atom sequence S1,C2–C5 are $Q(2) = 0.5164\,(14)$ Å, $\varphi(2) = 359.73\,(18)°$ and atom S1 is 0.853 (1) Å from the mean plane through the other four ring atoms. The corresponding puckering parameters for **1b** are $Q(2) = 0.5714\,(16)$ Å, $\varphi(2) = 349.86\,(19)°$ with atom S1 being 0.921 (1) Å from the mean plane through the other four ring atoms. These parameters show that the thiophene ring is slightly more distorted from an ideal envelope conformation in **1b** than in **1a**.

The most significant differences in the bond lengths within the two molecules appears at the spiro C atom, C2 (Table 1). The C2—C13 and C2—C14 bonds involving the cyclobutane ring in **1a**, at around 1.60 Å, are significantly longer than is usual for an alkyl C—C bond and 0.058 (3) and 0.072 (3) Å, respectively, longer than the corresponding bonds to the

Figure 1
View of the molecule of **1a** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.
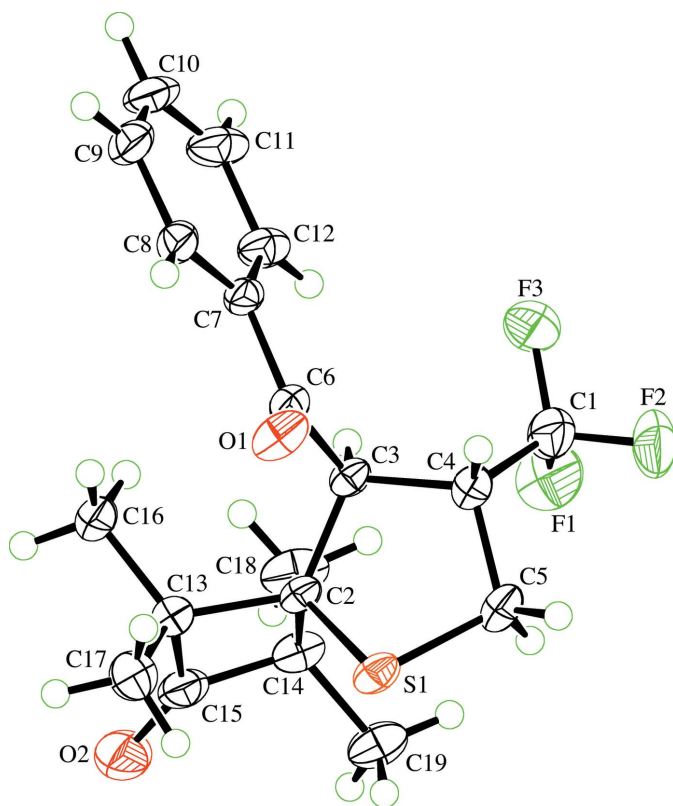

Figure 2
View of the molecule of **1b** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.
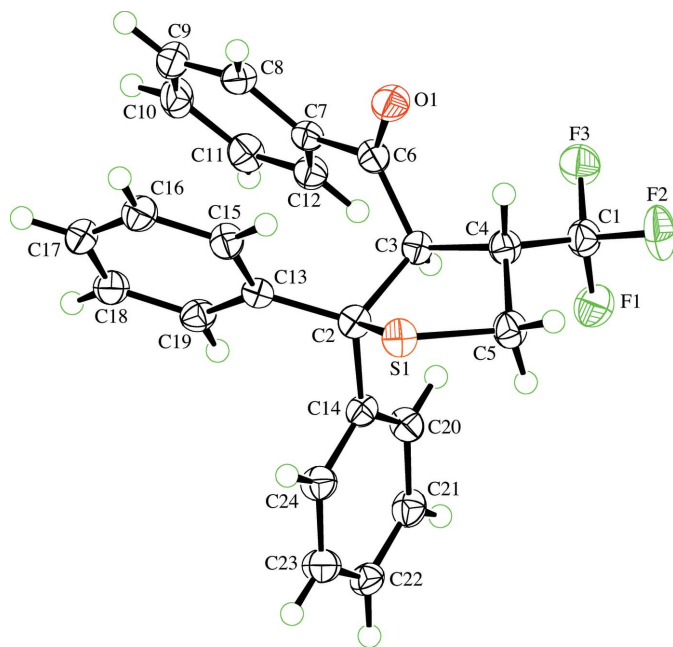
Table 1
Comparison of selected geometric parameters (Å, °) for compounds **1a** and **1b**.

Compound	**1a**	**1b**
S1—C2	1.8215 (14)	1.8567 (18)
S1—C5	1.7931 (17)	1.799 (2)
O1—C6	1.2187 (19)	1.215 (2)
C1—C4	1.493 (2)	1.503 (3)
C2—C3	1.556 (2)	1.590 (2)
C2—C13	1.592 (2)	1.534 (2)
C2—C14	1.609 (2)	1.537 (2)
C3—C4	1.562 (2)	1.544 (2)
C3—C6	1.529 (2)	1.532 (3)
C4—C5	1.537 (2)	1.533 (3)
C6—C7	1.495 (2)	1.495 (3)
C2—S1—C5	90.78 (7)	90.00 (8)
S1—C2—C3	104.75 (10)	103.16 (11)
S1—C2—C13	110.69 (10)	109.24 (12)
S1—C2—C14	112.84 (9)	107.10 (12)
C3—C2—C13	122.15 (12)	113.37 (14)
C3—C2—C14	116.78 (12)	113.04 (15)
C13—C2—C14	89.45 (12)	110.44 (14)
C2—C3—C4	108.37 (11)	108.88 (14)
C3—C4—C5	109.81 (13)	109.35 (15)
S1—C5—C4	105.22 (10)	102.77 (13)
C4—C3—C6—O1	−64.03 (18)	−23.0 (2)
O1—C6—C7—C8	−9.1 (2)	−29.5 (3)

Table 2
Hydrogen-bond geometry (Å, °) for **1a**.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯S1[i]	1.00	2.89	3.7370 (16)	142
C5—H51⋯O1[i]	0.99	2.41	3.3417 (19)	156
C10—H10⋯S1[ii]	0.95	2.86	3.7970 (17)	171

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

Table 3
Weak C—H⋯π interactions (Å, °) found in **1b**.

$Cg1$ and $Cg2$ are the centroids of the C14,C20–C24 and C7–C12 rings, respectively.

	H⋯Cg	C⋯Cg	C—H⋯Cg
C5—H51⋯$Cg1$[i]	2.84	3.810 (2)	165
C24—H24—$Cg2$[ii]	2.86	3.625 (2)	139

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

phenyl rings in **1b**. In concert, the S1—C2 and C2—C3 bonds are around 0.034 (2) Å shorter and the C3—C4 bond 0.018 (3) Å longer in **1a** than in **1b**; all other related bond lengths in the two molecules are comparable. Despite these variations and the acute 'bite angle' of the cyclobutane ring at C2 of the thiophene ring [89.45 (12)° compared with 110.44 (14)° for the diphenyl-substituted **1b**], the intra-ring bond angles in the thiophene rings of the two compounds are not very different. The above-mentioned differences in ring puckering presumably allow the bond-length variations not to impinge on the intra-ring angles. The Cambridge Structural Database (CSD, Version 5.39 with August 2018 updates; Groom *et al.*, 2016) contains one other example of a 2-cyclobutane-substituted thiophene ring (Seyfried *et al.*, 2006) and six examples of a 2,2-diphenyl-substituted thiophene ring (Huisgen *et al.*, 1986; Seyfried *et al.*, 2006; Augustin *et al.*, 2017). These seven structures display exactly the same relative patterns of bond lengths as that described above.

The carbonyl group in **1b** is significantly twisted out of the plane of the benzoyl ring, with the O1—C6—C7—C8 torsion angle being −9.1 (2) and −29.5 (3)° in **1a** and **1b**, respectively. The O1—C6—C3—C4 torsion angles also differ by about 41°, so that the carbonyl group is more slanted with respect to the mean plane of the thiophene ring in **1b** than in **1a**.

3. Supramolecular features

In **1a**, there are three unique potentially significant weak supramolecular contacts (Table 2). One of the methylene H atoms at C5 interacts with the carbonyl O atom of a neighbouring molecule related by a centre of inversion, while the

methine H atom at the CF₃-substituted C4 of this second molecule interacts with the S atom of the first molecule, thus forming centrosymmetric molecular pairs with a total of four interactions between them. Graph-set motifs (Bernstein *et al.*, 1995) $C_2^2(8)$ (two different ones), $C_2^2(9)$ and $C_2^2(12)$ can be discerned here. The third interaction is a C—H⋯S interaction between the *para*-H atom at C10 of the benzoyl ring and the S atom of a molecule related by one unit-cell translation parallel to the [001] direction. This forms a chain of molecules with a graph-set descriptor of $C(9)$. The combination of these interactions leads to double-stranded chains of molecules, or ribbons, running parallel to the [001] direction (Fig. 3). Within these ribbons, there is also a potential π–π interaction between adjacent parallel benzoyl rings, where the centroid–centroid distance is 3.8740 (10) Å and the perpendicular distance between the ring planes is 3.4342 (7) Å, although the offset of the rings is rather large at 1.79 Å, so that the separation may be a fortuitous consequence of the alignment resulting from the other interactions.

In **1b**, the main supramolecular features are two C—H⋯π interactions (Table 3): C24—H24 of one phenyl ring interacts
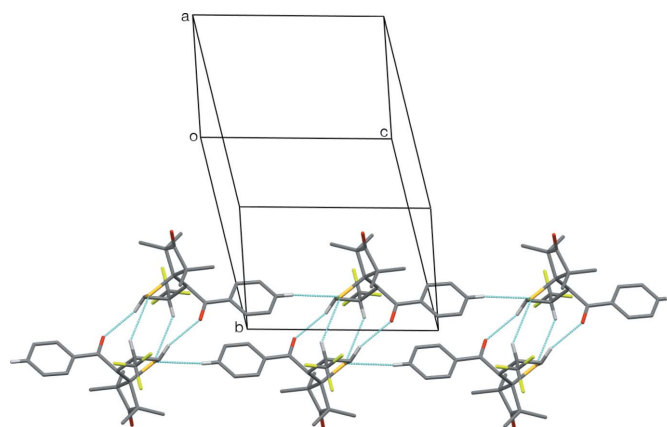

Figure 3
The ribbons formed by the weak intermolecular C—H⋯X (X = S, O) interactions in **1a**. Most H atoms have been omitted for clarity.
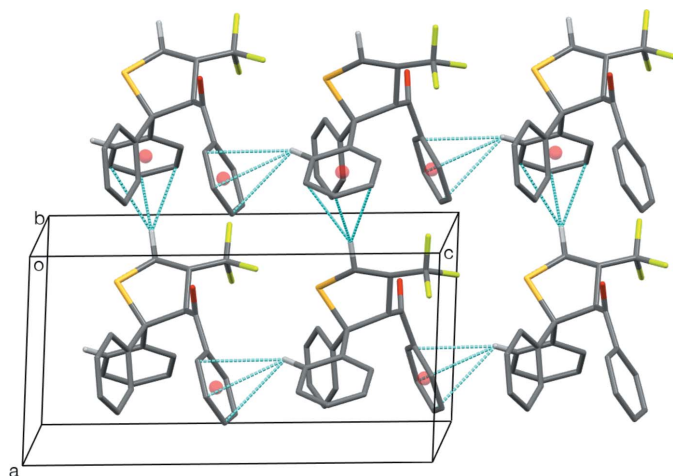
Figure 4
The sheets formed by the weak intermolecular C—H···π interactions in **1b**. The relevant centroids are shown as red spheres. Most H atoms have been omitted for clarity.

with the benzoyl ring of a neighbouring molecule related by a glide plane to give chains of molecules parallel to the [001] direction, while one of the methylene H atoms at C5 interacts with one of the phenyl rings in the molecule related by one unit cell translation parallel to the [100] direction. Together, these interactions link the molecules into sheets which lie parallel to the (010) plane (Fig. 4). Within these sheets, there is a potential intermolecular C—H···F interaction involving

another phenyl ring H atom (C15—H15···F3[ii]), albeit with a rather sharp C—H···F angle of 121° [H15···F3[ii] = 2.53 Å, C15···F3[ii] = 3.132 (2) Å; symmetry code as in Table 4].

4. Database survey

The CSD contains crystal structure data with atomic coordinates for 3225 monomeric organic compounds with the string *thiophene* in the compound name, of which 70 are named as *tetrahydrothiophenes* and 32 contain no substituents on the ring S atom. Recently published monocyclic crystal structures of tetrahydrothiophenes include those of Duan *et al.* (2017), Ram *et al.* (2016), Zamberlan *et al.* (2018) and Zhang *et al.* (2018). Spirocyclic examples involving two cojoined five-membered rings have been reported by Meninno *et al.* (2017) and Wang *et al.* (2018).

5. Synthesis and Crystallization

The title compounds were prepared according to the reaction sequence presented in Fig. 5 and fully described with full spectroscopic data by Mlostoń *et al.* (2016). Thermal decomposition of 1,3,4-thiadiazolines **2a** and **2b** in THF solution in the presence of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (**3**) leads to the tetrahydrothiophenes **1a** and **1b**, respectively, as the product of the [3 + 2]-cycloaddition of the intermediate thiocarbonyl *S*-methanides **4** with the activated C=C bond. Whereas the more stable **2a**, derived from 3-thioxo-2,2,4,4-

Table 4
Experimental details.

	1a	1b
Crystal data		
Chemical formula	$C_{19}H_{21}F_3O_2S$	$C_{24}H_{19}F_3OS$
M_r	370.42	412.45
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	160	160
a, b, c (Å)	10.4851 (1), 15.4106 (2), 11.4557 (1)	7.4578 (1), 17.6162 (3), 14.5634 (2)
β (°)	103.8526 (7)	92.6805 (9)
V (Å^3)	1797.19 (3)	1911.22 (5)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.22	0.21
Crystal size (mm)	$0.30 \times 0.27 \times 0.25$	$0.30 \times 0.15 \times 0.13$
Data collection		
Diffractometer	Nonius KappaCCD area-detector	Nonius KappaCCD area-detector
Absorption correction	Multi-scan (Blessing, 1995)	Multi-scan (Blessing, 1995)
T_{min}, T_{max}	0.895, 0.949	0.904, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40775, 4120, 3322	43080, 4376, 3216
R_{int}	0.053	0.081
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.114, 1.06	0.045, 0.118, 1.07
No. of reflections	4119	4376
No. of parameters	231	263
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.32, −0.39	0.30, −0.37

Computer programs: *COLLECT* (Nonius, 2000), *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997), *SHELXS97* (Sheldrick, 2008), *ORTEPII* (Johnson, 1976), *SHELXL2018* (Sheldrick, 2015) and *PLATON* (Spek, 2015).
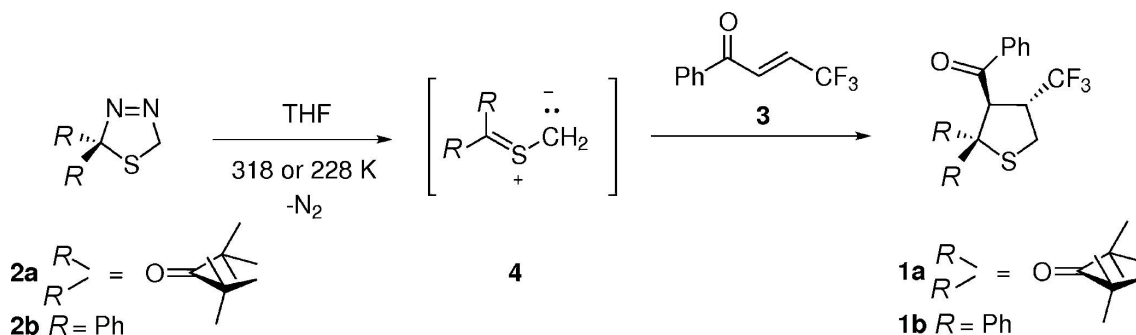
Figure 5
The reaction scheme leading to **1a** and **1b**.

tetramethylcyclobutanone, decomposes at 318 K, the less stable precursor **2b**, derived from thiobenzophenone, already extrudes N$_2$ at 228 K. The ^{1}H NMR analysis showed that only one product was formed in each case. After chromatographic purification, the isolated products were crystallized from petroleum ether by slow evaporation of the solvent.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with U_{iso}(H) = 1.5U_{eq}(C) while each group was allowed to rotate freely about its parent C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and U_{iso}(H) = 1.2U_{eq}(C). For **1a**, one low angle reflection was omitted from the final cycles of refinement because its observed intensity was much lower than the calculated value.

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supporting information

Chemo- and regioselective [3 + 2]-cycloadditions of thiocarbonyl ylides: crystal structures of *trans*-8-benzoyl-1,1,3,3-tetramethyl-7-trifluoromethyl-5-thiaspiro-[3.4]octan-2-one and *trans*-3-benzoyl-2,2-diphenyl-4-(trifluoromethyl)tetra-hydrothiophene

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Computing details

For both structures, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015) and *PLATON* (Spek, 2015).

***trans*-8-Benzoyl-1,1,3,3-tetramethyl-7-trifluoromethyl-5-thiaspiro[3.4]octan-2-one (1a)**

Crystal data

$C_{19}H_{21}F_3O_2S$	$D_x = 1.369$ Mg m^{-3}
$M_r = 370.42$	Melting point: 387.3 K
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.4851$ (1) Å	Cell parameters from 41828 reflections
$b = 15.4106$ (2) Å	$\theta = 2.0$–27.5°
$c = 11.4557$ (1) Å	$\mu = 0.22$ mm^{-1}
$\beta = 103.8526$ (7)°	$T = 160$ K
$V = 1797.19$ (3) Å^3	Prism, colourless
$Z = 4$	$0.30 \times 0.27 \times 0.25$ mm
$F(000) = 776$	

Data collection

Nonius KappaCCD area-detector diffractometer	$T_{min} = 0.895$, $T_{max} = 0.949$
Radiation source: Nonius FR590 sealed tube generator	40775 measured reflections
	4120 independent reflections
Horizontally mounted graphite crystal monochromator	3322 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.053$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
ω scans with κ offsets	$h = -13 \rightarrow 13$
Absorption correction: multi-scan (Blessing, 1995)	$k = -19 \rightarrow 20$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.7139P]$
$wR(F^2) = 0.114$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
4119 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
231 parameters	$\Delta\rho_{min} = -0.39$ e Å^{-3}
0 restraints	Extinction correction: SHELXL2018 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0172 (19)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch
Solvent used: petroleum ether Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: on a glass fibre
Client: Grzegorz Mloston Sample code: MG-1226 (HG1701)
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 (Å^2)

	x	y	z	U_{iso}^*/U_{eq}
S1	0.20161 (4)	0.95486 (3)	0.50667 (3)	0.02982 (13)
F1	0.05271 (15)	0.72049 (7)	0.62746 (12)	0.0645 (4)
F2	−0.13401 (13)	0.78097 (10)	0.55354 (12)	0.0703 (4)
F3	−0.04964 (13)	0.78355 (9)	0.74481 (11)	0.0620 (4)
O2	0.60425 (13)	0.88052 (12)	0.65763 (13)	0.0581 (4)
O1	0.13585 (13)	1.03713 (7)	0.75063 (10)	0.0382 (3)
C1	−0.0212 (2)	0.79034 (13)	0.63701 (17)	0.0456 (5)
C2	0.28653 (15)	0.90617 (10)	0.64896 (12)	0.0250 (3)
C3	0.17678 (14)	0.88890 (10)	0.71659 (12)	0.0244 (3)
H3	0.199188	0.835746	0.767439	0.029*
C4	0.04466 (15)	0.87394 (10)	0.62132 (13)	0.0298 (3)
H4	−0.016358	0.921985	0.630370	0.036*
C5	0.06769 (17)	0.88032 (11)	0.49408 (13)	0.0330 (4)
H51	−0.011859	0.902266	0.436656	0.040*
H52	0.090577	0.822850	0.466259	0.040*
C6	0.15834 (14)	0.96546 (10)	0.79587 (13)	0.0258 (3)
C7	0.16542 (14)	0.95313 (10)	0.92674 (13)	0.0268 (3)
C8	0.16453 (15)	1.02830 (12)	0.99516 (15)	0.0340 (4)
H8	0.158220	1.083677	0.957765	0.041*
C9	0.17284 (17)	1.02194 (15)	1.11734 (16)	0.0453 (5)
H9	0.173785	1.073012	1.163988	0.054*
C10	0.17976 (17)	0.94132 (16)	1.17150 (15)	0.0492 (5)
H10	0.185190	0.937279	1.255300	0.059*
C11	0.17884 (18)	0.86679 (15)	1.10481 (15)	0.0450 (5)

H11	0.182779	0.811594	1.142426	0.054*
C12	0.17211 (16)	0.87256 (12)	0.98213 (14)	0.0344 (4)
H12	0.172109	0.821221	0.936230	0.041*
C13	0.41591 (16)	0.95942 (11)	0.70821 (14)	0.0325 (4)
C14	0.37631 (16)	0.82468 (11)	0.63197 (14)	0.0326 (4)
C15	0.49199 (17)	0.88639 (13)	0.66570 (14)	0.0378 (4)
C16	0.45250 (17)	0.96613 (14)	0.84639 (15)	0.0414 (4)
H161	0.402906	1.013595	0.871564	0.062*
H162	0.546810	0.977600	0.874510	0.062*
H163	0.431050	0.911455	0.881007	0.062*
C17	0.4327 (2)	1.04824 (13)	0.65521 (17)	0.0457 (5)
H171	0.420606	1.043024	0.567987	0.069*
H172	0.521016	1.070364	0.690990	0.069*
H173	0.367175	1.088436	0.672592	0.069*
C18	0.3887 (2)	0.75333 (12)	0.72822 (17)	0.0448 (5)
H181	0.403045	0.780143	0.807879	0.067*
H182	0.463169	0.715555	0.725600	0.067*
H183	0.307813	0.718887	0.712424	0.067*
C19	0.3591 (2)	0.78204 (12)	0.50888 (16)	0.0420 (4)
H191	0.438204	0.748806	0.506841	0.063*
H192	0.344879	0.826937	0.446508	0.063*
H193	0.283109	0.743019	0.494278	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0407 (2)	0.0293 (2)	0.01836 (19)	0.00149 (16)	0.00501 (15)	0.00383 (14)
F1	0.0989 (10)	0.0296 (6)	0.0672 (8)	−0.0136 (6)	0.0241 (7)	−0.0031 (5)
F2	0.0639 (8)	0.0832 (10)	0.0567 (8)	−0.0422 (7)	0.0005 (6)	−0.0081 (7)
F3	0.0719 (8)	0.0713 (9)	0.0476 (7)	−0.0330 (7)	0.0235 (6)	0.0000 (6)
O2	0.0366 (7)	0.0939 (12)	0.0461 (8)	0.0053 (7)	0.0149 (6)	−0.0121 (8)
O1	0.0596 (8)	0.0268 (6)	0.0266 (6)	0.0075 (5)	0.0073 (5)	0.0008 (4)
C1	0.0551 (11)	0.0441 (11)	0.0375 (9)	−0.0184 (9)	0.0108 (8)	−0.0058 (8)
C2	0.0313 (8)	0.0263 (7)	0.0170 (6)	0.0009 (6)	0.0050 (5)	0.0010 (5)
C3	0.0309 (7)	0.0230 (7)	0.0186 (6)	0.0017 (6)	0.0041 (5)	0.0013 (5)
C4	0.0319 (8)	0.0308 (8)	0.0250 (7)	−0.0016 (6)	0.0031 (6)	−0.0023 (6)
C5	0.0395 (9)	0.0340 (9)	0.0216 (7)	−0.0005 (7)	−0.0003 (6)	−0.0022 (6)
C6	0.0268 (7)	0.0282 (8)	0.0212 (7)	0.0016 (6)	0.0038 (5)	−0.0009 (6)
C7	0.0214 (7)	0.0384 (9)	0.0199 (7)	0.0036 (6)	0.0037 (5)	−0.0013 (6)
C8	0.0271 (8)	0.0463 (10)	0.0284 (8)	−0.0008 (7)	0.0063 (6)	−0.0106 (7)
C9	0.0316 (9)	0.0751 (14)	0.0290 (9)	0.0006 (9)	0.0067 (7)	−0.0190 (9)
C10	0.0338 (9)	0.0956 (17)	0.0191 (7)	0.0113 (10)	0.0083 (6)	−0.0009 (9)
C11	0.0405 (10)	0.0701 (13)	0.0267 (8)	0.0167 (9)	0.0124 (7)	0.0158 (8)
C12	0.0340 (8)	0.0447 (10)	0.0254 (8)	0.0099 (7)	0.0091 (6)	0.0063 (7)
C13	0.0313 (8)	0.0420 (10)	0.0244 (7)	−0.0051 (7)	0.0074 (6)	−0.0031 (6)
C14	0.0401 (9)	0.0343 (9)	0.0245 (7)	0.0102 (7)	0.0101 (6)	0.0021 (6)
C15	0.0357 (9)	0.0567 (11)	0.0217 (7)	0.0056 (8)	0.0081 (6)	0.0007 (7)
C16	0.0309 (8)	0.0657 (13)	0.0260 (8)	−0.0057 (8)	0.0040 (6)	−0.0093 (8)

C17	0.0521 (11)	0.0458 (11)	0.0413 (10)	−0.0192 (9)	0.0151 (8)	−0.0049 (8)
C18	0.0599 (12)	0.0410 (10)	0.0369 (9)	0.0233 (9)	0.0183 (8)	0.0120 (8)
C19	0.0563 (11)	0.0392 (10)	0.0328 (9)	0.0122 (8)	0.0154 (8)	−0.0046 (7)

Geometric parameters (Å, º)

S1—C2	1.8215 (14)	C9—H9	0.9500
S1—C5	1.7931 (17)	C10—C11	1.378 (3)
F1—C1	1.346 (3)	C10—H10	0.9500
F2—C1	1.339 (2)	C11—C12	1.393 (2)
F3—C1	1.342 (2)	C11—H11	0.9500
O2—C15	1.206 (2)	C12—H12	0.9500
O1—C6	1.2187 (19)	C13—C17	1.525 (2)
C1—C4	1.493 (2)	C13—C15	1.525 (2)
C2—C3	1.556 (2)	C13—C16	1.540 (2)
C2—C13	1.592 (2)	C14—C15	1.517 (3)
C2—C14	1.609 (2)	C14—C19	1.527 (2)
C3—C4	1.562 (2)	C14—C18	1.541 (2)
C3—C6	1.529 (2)	C16—H161	0.9800
C3—H3	1.0000	C16—H162	0.9800
C4—C5	1.537 (2)	C16—H163	0.9800
C4—H4	1.0000	C17—H171	0.9800
C5—H51	0.9900	C17—H172	0.9800
C5—H52	0.9900	C17—H173	0.9800
C6—C7	1.495 (2)	C18—H181	0.9800
C7—C12	1.388 (2)	C18—H182	0.9800
C7—C8	1.400 (2)	C18—H183	0.9800
C8—C9	1.385 (2)	C19—H191	0.9800
C8—H8	0.9500	C19—H192	0.9800
C9—C10	1.383 (3)	C19—H193	0.9800
C2—S1—C5	90.78 (7)	C10—C11—C12	119.87 (19)
F2—C1—F3	107.18 (16)	C10—C11—H11	120.1
F2—C1—F1	106.45 (16)	C12—C11—H11	120.1
F3—C1—F1	105.77 (16)	C7—C12—C11	120.20 (17)
F2—C1—C4	111.22 (17)	C7—C12—H12	119.9
F3—C1—C4	112.90 (15)	C11—C12—H12	119.9
F1—C1—C4	112.88 (16)	C17—C13—C15	114.60 (14)
S1—C2—C3	104.75 (10)	C17—C13—C16	108.96 (15)
S1—C2—C13	110.69 (10)	C15—C13—C16	110.92 (14)
S1—C2—C14	112.84 (9)	C17—C13—C2	117.44 (14)
C3—C2—C13	122.15 (12)	C15—C13—C2	86.61 (12)
C3—C2—C14	116.78 (12)	C16—C13—C2	116.74 (13)
C13—C2—C14	89.45 (12)	C15—C14—C19	114.56 (14)
C6—C3—C2	112.18 (12)	C15—C14—C18	109.87 (15)
C6—C3—C4	108.16 (12)	C19—C14—C18	108.97 (15)
C2—C3—C4	108.37 (11)	C15—C14—C2	86.28 (12)
C6—C3—H3	109.4	C19—C14—C2	120.29 (13)

C2—C3—H3	109.4	C18—C14—C2	114.97 (13)
C4—C3—H3	109.4	O2—C15—C14	132.00 (18)
C1—C4—C5	110.59 (13)	O2—C15—C13	132.42 (18)
C1—C4—C3	113.68 (14)	C14—C15—C13	95.54 (13)
C3—C4—C5	109.81 (13)	C13—C16—H161	109.5
C1—C4—H4	107.5	C13—C16—H162	109.5
C5—C4—H4	107.5	H161—C16—H162	109.5
C3—C4—H4	107.5	C13—C16—H163	109.5
S1—C5—C4	105.22 (10)	H161—C16—H163	109.5
C4—C5—H51	110.7	H162—C16—H163	109.5
S1—C5—H51	110.7	C13—C17—H171	109.5
C4—C5—H52	110.7	C13—C17—H172	109.5
S1—C5—H52	110.7	H171—C17—H172	109.5
H51—C5—H52	108.8	C13—C17—H173	109.5
O1—C6—C7	119.97 (13)	H171—C17—H173	109.5
O1—C6—C3	119.06 (13)	H172—C17—H173	109.5
C7—C6—C3	120.96 (13)	C14—C18—H181	109.5
C12—C7—C8	119.37 (14)	C14—C18—H182	109.5
C12—C7—C6	123.84 (14)	H181—C18—H182	109.5
C8—C7—C6	116.79 (14)	C14—C18—H183	109.5
C9—C8—C7	120.00 (18)	H181—C18—H183	109.5
C9—C8—H8	120.0	H182—C18—H183	109.5
C7—C8—H8	120.0	C14—C19—H191	109.5
C10—C9—C8	120.06 (18)	C14—C19—H192	109.5
C10—C9—H9	120.0	H191—C19—H192	109.5
C8—C9—H9	120.0	C14—C19—H193	109.5
C11—C10—C9	120.49 (16)	H191—C19—H193	109.5
C11—C10—H10	119.8	H192—C19—H193	109.5
C9—C10—H10	119.8		

C5—S1—C2—C3	−40.88 (11)	C9—C10—C11—C12	0.6 (3)
C5—S1—C2—C13	−174.32 (11)	C8—C7—C12—C11	−0.5 (2)
C5—S1—C2—C14	87.17 (12)	C6—C7—C12—C11	179.82 (15)
C13—C2—C3—C6	35.81 (18)	C10—C11—C12—C7	−0.4 (3)
C14—C2—C3—C6	143.53 (13)	C3—C2—C13—C17	−111.55 (16)
S1—C2—C3—C6	−90.84 (12)	C14—C2—C13—C17	126.71 (15)
C13—C2—C3—C4	155.15 (13)	S1—C2—C13—C17	12.42 (18)
C14—C2—C3—C4	−97.12 (14)	C3—C2—C13—C15	132.39 (14)
S1—C2—C3—C4	28.50 (13)	C14—C2—C13—C15	10.65 (11)
F2—C1—C4—C5	−56.2 (2)	S1—C2—C13—C15	−103.63 (11)
F3—C1—C4—C5	−176.76 (15)	C3—C2—C13—C16	20.6 (2)
F1—C1—C4—C5	63.34 (19)	C14—C2—C13—C16	−101.10 (15)
F2—C1—C4—C3	179.72 (15)	S1—C2—C13—C16	144.61 (13)
F3—C1—C4—C3	59.2 (2)	C3—C2—C14—C15	−136.96 (12)
F1—C1—C4—C3	−60.71 (19)	C13—C2—C14—C15	−10.72 (11)
C6—C3—C4—C1	−113.10 (15)	S1—C2—C14—C15	101.58 (11)
C2—C3—C4—C1	125.06 (15)	C3—C2—C14—C19	106.66 (17)
C6—C3—C4—C5	122.43 (14)	C13—C2—C14—C19	−127.10 (16)

C2—C3—C4—C5	0.59 (17)	S1—C2—C14—C19	−14.8 (2)
C1—C4—C5—S1	−156.24 (13)	C3—C2—C14—C18	−26.7 (2)
C3—C4—C5—S1	−30.00 (15)	C13—C2—C14—C18	99.49 (16)
C2—S1—C5—C4	41.32 (11)	S1—C2—C14—C18	−148.21 (14)
C2—C3—C6—O1	55.44 (18)	C19—C14—C15—O2	−44.8 (3)
C4—C3—C6—O1	−64.03 (18)	C18—C14—C15—O2	78.2 (2)
C2—C3—C6—C7	−125.53 (14)	C2—C14—C15—O2	−166.6 (2)
C4—C3—C6—C7	115.00 (14)	C19—C14—C15—C13	132.98 (14)
O1—C6—C7—C12	170.63 (16)	C18—C14—C15—C13	−103.99 (14)
C3—C6—C7—C12	−8.4 (2)	C2—C14—C15—C13	11.24 (12)
O1—C6—C7—C8	−9.1 (2)	C17—C13—C15—O2	47.7 (3)
C3—C6—C7—C8	171.89 (14)	C16—C13—C15—O2	−76.2 (2)
C12—C7—C8—C9	1.2 (2)	C2—C13—C15—O2	166.4 (2)
C6—C7—C8—C9	−179.03 (14)	C17—C13—C15—C14	−130.09 (15)
C7—C8—C9—C10	−1.1 (3)	C16—C13—C15—C14	106.02 (14)
C8—C9—C10—C11	0.2 (3)	C2—C13—C15—C14	−11.36 (12)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯S1[i]	1.00	2.89	3.7370 (16)	142
C5—H51⋯O1[i]	0.99	2.41	3.3417 (19)	156
C10—H10⋯S1[ii]	0.95	2.86	3.7970 (17)	171

Symmetry codes: (i) −x, −y+2, −z+1; (ii) x, y, z+1.

trans-3-Benzoyl-2,2-diphenyl-4-(trifluoromethyl)tetrahydrothiophene (1b)

Crystal data

$C_{24}H_{19}F_3OS$
$M_r = 412.45$
Monoclinic, $P2_1/c$
$a = 7.4578$ (1) Å
$b = 17.6162$ (3) Å
$c = 14.5634$ (2) Å
$β = 92.6805$ (9)°
$V = 1911.22$ (5) Å^3
$Z = 4$
$F(000) = 856$

$D_x = 1.433$ Mg m$^{−3}$
Melting point: 401.4 K
Mo $Kα$ radiation, $λ = 0.71073$ Å
Cell parameters from 36099 reflections
$θ = 2.0–27.5°$
$μ = 0.21$ mm$^{−1}$
$T = 160$ K
Prism, colourless
$0.30 × 0.15 × 0.13$ mm

Data collection

Nonius KappaCCD area-detector
    diffractometer
Radiation source: Nonius FR590 sealed tube
    generator
Horizontally mounted graphite crystal
    monochromator
Detector resolution: 9 pixels mm^{-1}
$ω$ scans with $κ$ offsets
Absorption correction: multi-scan
    (Blessing, 1995)

$T_{min} = 0.904$, $T_{max} = 0.975$
43080 measured reflections
4376 independent reflections
3216 reflections with $I > 2σ(I)$
$R_{int} = 0.081$
$θ_{max} = 27.5°$, $θ_{min} = 2.3°$
$h = −9→9$
$k = −22→22$
$l = −18→18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.118$

$S = 1.07$

4376 reflections

263 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.850P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.30$ e Å^{-3}

$\Delta\rho_{min} = -0.37$ e Å^{-3}

Extinction correction: SHELXL2018 (Sheldrick, 2015), $Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0046 (10)

Special details

Experimental. Data collection and full structure determination done by Prof. Anthony Linden: anthony.linden@chem.uzh.ch

Solvent used: petroleum ether Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: on a glass fibre

Client: Grzegorz Mloston Sample code: MG-1225 (HG1704)

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*	$U_{iso}*/U_{eq}$
S1	0.28849 (6)	0.65984 (3)	0.67818 (3)	0.02909 (15)
F1	0.31015 (18)	0.55032 (7)	0.95378 (9)	0.0437 (3)
F2	0.03380 (16)	0.58579 (8)	0.94518 (9)	0.0483 (4)
F3	0.23272 (16)	0.65536 (7)	1.01552 (8)	0.0389 (3)
O1	0.29001 (18)	0.80937 (8)	0.86995 (11)	0.0357 (3)
C1	0.2026 (3)	0.61134 (12)	0.94108 (14)	0.0313 (4)
C2	0.4966 (2)	0.67383 (10)	0.75124 (12)	0.0240 (4)
C3	0.4232 (2)	0.68733 (10)	0.85069 (12)	0.0237 (4)
H3	0.502705	0.659132	0.896173	0.028*
C4	0.2324 (2)	0.65367 (11)	0.85349 (13)	0.0261 (4)
H4	0.145855	0.697070	0.850258	0.031*
C5	0.1943 (3)	0.60455 (11)	0.76790 (13)	0.0298 (4)
H51	0.063735	0.596885	0.756069	0.036*
H52	0.253808	0.554471	0.774256	0.036*
C6	0.4260 (2)	0.77143 (10)	0.87760 (13)	0.0261 (4)
C7	0.6005 (2)	0.80580 (10)	0.91069 (12)	0.0256 (4)
C8	0.6280 (3)	0.88269 (11)	0.89188 (13)	0.0304 (4)
H8	0.534813	0.911678	0.862177	0.036*
C9	0.7914 (3)	0.91680 (12)	0.91654 (14)	0.0349 (5)
H9	0.811317	0.968572	0.901888	0.042*
C10	0.9249 (3)	0.87515 (12)	0.96249 (14)	0.0351 (5)
H10	1.036380	0.898546	0.979438	0.042*
C11	0.8971 (3)	0.79961 (12)	0.98390 (14)	0.0327 (4)
H11	0.988277	0.771614	1.016652	0.039*

C12	0.7359 (2)	0.76487 (11)	0.95745 (13)	0.0284 (4)
H12	0.717806	0.712819	0.971322	0.034*
C13	0.6006 (2)	0.74187 (10)	0.71509 (12)	0.0236 (4)
C14	0.6081 (2)	0.60080 (10)	0.74477 (13)	0.0245 (4)
C15	0.5139 (3)	0.80438 (11)	0.67449 (13)	0.0288 (4)
H15	0.386722	0.804491	0.666591	0.035*
C16	0.6108 (3)	0.86634 (11)	0.64552 (13)	0.0311 (4)
H16	0.549354	0.908407	0.617999	0.037*
C17	0.7956 (3)	0.86759 (11)	0.65621 (14)	0.0319 (4)
H17	0.861442	0.909989	0.635663	0.038*
C18	0.8842 (3)	0.80624 (11)	0.69729 (14)	0.0313 (4)
H18	1.011281	0.806856	0.705772	0.038*
C19	0.7879 (2)	0.74429 (11)	0.72587 (13)	0.0276 (4)
H19	0.850178	0.702451	0.753418	0.033*
C20	0.6661 (2)	0.55616 (11)	0.81886 (13)	0.0286 (4)
H20	0.635747	0.570169	0.879184	0.034*
C21	0.7683 (2)	0.49105 (11)	0.80606 (14)	0.0305 (4)
H21	0.806329	0.461316	0.857799	0.037*
C22	0.8150 (2)	0.46917 (11)	0.71956 (14)	0.0294 (4)
H22	0.883792	0.424547	0.711065	0.035*
C23	0.7591 (3)	0.51386 (11)	0.64507 (14)	0.0334 (5)
H23	0.790809	0.499834	0.584969	0.040*
C24	0.6579 (3)	0.57844 (11)	0.65723 (13)	0.0296 (4)
H24	0.621489	0.608249	0.605295	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0258 (2)	0.0342 (3)	0.0268 (3)	−0.00113 (19)	−0.00414 (18)	0.00193 (19)
F1	0.0556 (8)	0.0331 (7)	0.0430 (7)	0.0025 (6)	0.0071 (6)	0.0098 (5)
F2	0.0357 (7)	0.0685 (9)	0.0408 (7)	−0.0228 (6)	0.0049 (5)	0.0058 (6)
F3	0.0442 (7)	0.0441 (7)	0.0283 (6)	−0.0049 (5)	0.0006 (5)	−0.0035 (5)
O1	0.0272 (7)	0.0284 (7)	0.0516 (9)	0.0052 (6)	0.0038 (6)	0.0013 (6)
C1	0.0280 (10)	0.0341 (11)	0.0318 (11)	−0.0058 (8)	0.0026 (8)	−0.0014 (8)
C2	0.0227 (9)	0.0257 (9)	0.0233 (9)	0.0004 (7)	−0.0027 (7)	0.0010 (7)
C3	0.0215 (9)	0.0245 (9)	0.0248 (9)	−0.0005 (7)	−0.0009 (7)	0.0021 (7)
C4	0.0232 (9)	0.0285 (10)	0.0264 (10)	−0.0015 (7)	−0.0004 (7)	0.0001 (8)
C5	0.0251 (9)	0.0343 (11)	0.0297 (10)	−0.0051 (8)	−0.0011 (8)	−0.0014 (8)
C6	0.0254 (9)	0.0279 (10)	0.0253 (10)	0.0013 (8)	0.0032 (7)	0.0019 (8)
C7	0.0279 (9)	0.0261 (10)	0.0230 (9)	−0.0014 (7)	0.0046 (7)	−0.0037 (7)
C8	0.0345 (10)	0.0259 (10)	0.0311 (10)	0.0018 (8)	0.0047 (8)	−0.0016 (8)
C9	0.0429 (12)	0.0298 (10)	0.0326 (11)	−0.0095 (9)	0.0079 (9)	−0.0016 (8)
C10	0.0308 (10)	0.0416 (12)	0.0330 (11)	−0.0120 (9)	0.0038 (8)	−0.0045 (9)
C11	0.0284 (10)	0.0391 (11)	0.0305 (11)	−0.0017 (8)	−0.0007 (8)	−0.0016 (9)
C12	0.0295 (10)	0.0289 (10)	0.0269 (10)	−0.0012 (8)	0.0020 (8)	−0.0008 (8)
C13	0.0236 (9)	0.0238 (9)	0.0234 (9)	0.0015 (7)	0.0022 (7)	−0.0014 (7)
C14	0.0233 (9)	0.0221 (9)	0.0278 (10)	−0.0008 (7)	−0.0011 (7)	0.0005 (7)
C15	0.0272 (9)	0.0294 (10)	0.0297 (10)	0.0020 (8)	0.0012 (8)	0.0044 (8)

C16	0.0359 (11)	0.0272 (10)	0.0302 (11)	0.0034 (8)	0.0020 (8)	0.0050 (8)
C17	0.0373 (11)	0.0256 (10)	0.0333 (11)	−0.0042 (8)	0.0060 (8)	0.0005 (8)
C18	0.0245 (9)	0.0306 (10)	0.0387 (11)	−0.0020 (8)	0.0021 (8)	−0.0066 (9)
C19	0.0260 (9)	0.0254 (9)	0.0310 (10)	0.0030 (7)	−0.0009 (8)	−0.0012 (8)
C20	0.0273 (9)	0.0311 (10)	0.0276 (10)	0.0019 (8)	0.0030 (8)	0.0009 (8)
C21	0.0282 (10)	0.0274 (10)	0.0358 (11)	0.0021 (8)	0.0001 (8)	0.0071 (8)
C22	0.0270 (9)	0.0217 (9)	0.0397 (11)	0.0019 (7)	0.0033 (8)	0.0004 (8)
C23	0.0390 (11)	0.0298 (11)	0.0316 (11)	0.0032 (8)	0.0034 (8)	−0.0024 (8)
C24	0.0375 (11)	0.0263 (10)	0.0251 (10)	0.0025 (8)	0.0007 (8)	0.0026 (8)

Geometric parameters (Å, º)

S1—C2	1.8567 (18)	C11—C12	1.387 (3)
S1—C5	1.799 (2)	C11—H11	0.9500
F1—C1	1.349 (2)	C12—H12	0.9500
F2—C1	1.341 (2)	C13—C15	1.394 (3)
F3—C1	1.343 (2)	C13—C19	1.399 (2)
O1—C6	1.215 (2)	C14—C20	1.388 (3)
C1—C4	1.503 (3)	C14—C24	1.401 (3)
C2—C3	1.590 (2)	C15—C16	1.386 (3)
C2—C13	1.534 (2)	C15—H15	0.9500
C2—C14	1.537 (2)	C16—C17	1.380 (3)
C3—C4	1.544 (2)	C16—H16	0.9500
C3—C6	1.532 (3)	C17—C18	1.388 (3)
C3—H3	1.0000	C17—H17	0.9500
C4—C5	1.533 (3)	C18—C19	1.381 (3)
C4—H4	1.0000	C18—H18	0.9500
C5—H51	0.9900	C19—H19	0.9500
C5—H52	0.9900	C20—C21	1.394 (3)
C6—C7	1.495 (3)	C20—H20	0.9500
C7—C12	1.393 (3)	C21—C22	1.378 (3)
C7—C8	1.399 (3)	C21—H21	0.9500
C8—C9	1.391 (3)	C22—C23	1.389 (3)
C8—H8	0.9500	C22—H22	0.9500
C9—C10	1.384 (3)	C23—C24	1.381 (3)
C9—H9	0.9500	C23—H23	0.9500
C10—C11	1.385 (3)	C24—H24	0.9500
C10—H10	0.9500		
C2—S1—C5	90.00 (8)	C9—C10—H10	119.8
F2—C1—F3	106.23 (15)	C11—C10—H10	119.8
F2—C1—F1	106.26 (16)	C10—C11—C12	119.89 (19)
F3—C1—F1	105.88 (16)	C10—C11—H11	120.1
F2—C1—C4	112.36 (16)	C12—C11—H11	120.1
F3—C1—C4	111.89 (16)	C11—C12—C7	120.45 (18)
F1—C1—C4	113.67 (16)	C11—C12—H12	119.8
S1—C2—C3	103.16 (11)	C7—C12—H12	119.8
S1—C2—C13	109.24 (12)	C15—C13—C19	117.66 (17)

S1—C2—C14	107.10 (12)	C15—C13—C2	122.06 (16)
C3—C2—C13	113.37 (14)	C19—C13—C2	120.22 (16)
C3—C2—C14	113.04 (15)	C20—C14—C24	117.52 (17)
C13—C2—C14	110.44 (14)	C20—C14—C2	125.20 (17)
C6—C3—C4	111.45 (15)	C24—C14—C2	117.28 (16)
C6—C3—C2	112.12 (14)	C16—C15—C13	120.87 (18)
C2—C3—C4	108.88 (14)	C16—C15—H15	119.6
C6—C3—H3	108.1	C13—C15—H15	119.6
C4—C3—H3	108.1	C17—C16—C15	120.70 (18)
C2—C3—H3	108.1	C17—C16—H16	119.7
C1—C4—C5	112.39 (16)	C15—C16—H16	119.7
C1—C4—C3	112.68 (15)	C16—C17—C18	119.30 (18)
C3—C4—C5	109.35 (15)	C16—C17—H17	120.4
C1—C4—H4	107.4	C18—C17—H17	120.4
C5—C4—H4	107.4	C19—C18—C17	120.09 (18)
C3—C4—H4	107.4	C19—C18—H18	120.0
S1—C5—C4	102.77 (13)	C17—C18—H18	120.0
C4—C5—H51	111.2	C18—C19—C13	121.38 (18)
S1—C5—H51	111.2	C18—C19—H19	119.3
C4—C5—H52	111.2	C13—C19—H19	119.3
S1—C5—H52	111.2	C14—C20—C21	120.96 (18)
H51—C5—H52	109.1	C14—C20—H20	119.5
O1—C6—C7	121.13 (17)	C21—C20—H20	119.5
O1—C6—C3	120.47 (16)	C22—C21—C20	121.03 (18)
C7—C6—C3	118.37 (15)	C22—C21—H21	119.5
C12—C7—C8	119.17 (17)	C20—C21—H21	119.5
C12—C7—C6	123.27 (17)	C21—C22—C23	118.44 (18)
C8—C7—C6	117.56 (16)	C21—C22—H22	120.8
C9—C8—C7	120.16 (18)	C23—C22—H22	120.8
C9—C8—H8	119.9	C24—C23—C22	120.84 (19)
C7—C8—H8	119.9	C24—C23—H23	119.6
C10—C9—C8	119.86 (19)	C22—C23—H23	119.6
C10—C9—H9	120.1	C23—C24—C14	121.20 (18)
C8—C9—H9	120.1	C23—C24—H24	119.4
C9—C10—C11	120.43 (18)	C14—C24—H24	119.4
C5—S1—C2—C13	−161.09 (13)	C8—C9—C10—C11	0.2 (3)
C5—S1—C2—C14	79.28 (13)	C9—C10—C11—C12	1.4 (3)
C5—S1—C2—C3	−40.22 (12)	C10—C11—C12—C7	−1.0 (3)
C13—C2—C3—C6	15.9 (2)	C8—C7—C12—C11	−0.9 (3)
C14—C2—C3—C6	142.53 (15)	C6—C7—C12—C11	178.02 (17)
S1—C2—C3—C6	−102.15 (14)	C14—C2—C13—C15	150.47 (17)
C13—C2—C3—C4	139.65 (15)	C3—C2—C13—C15	−81.5 (2)
C14—C2—C3—C4	−93.67 (17)	S1—C2—C13—C15	32.9 (2)
S1—C2—C3—C4	21.64 (16)	C14—C2—C13—C19	−32.4 (2)
F2—C1—C4—C5	−59.3 (2)	C3—C2—C13—C19	95.64 (19)
F3—C1—C4—C5	−178.69 (15)	S1—C2—C13—C19	−149.93 (15)
F1—C1—C4—C5	61.4 (2)	C13—C2—C14—C20	118.39 (19)

F2—C1—C4—C3	176.63 (15)	C3—C2—C14—C20	−9.8 (3)
F3—C1—C4—C3	57.2 (2)	S1—C2—C14—C20	−122.75 (17)
F1—C1—C4—C3	−62.7 (2)	C13—C2—C14—C24	−60.3 (2)
C6—C3—C4—C1	−98.19 (18)	C3—C2—C14—C24	171.47 (15)
C2—C3—C4—C1	137.62 (16)	S1—C2—C14—C24	58.53 (19)
C6—C3—C4—C5	136.06 (16)	C19—C13—C15—C16	0.4 (3)
C2—C3—C4—C5	11.9 (2)	C2—C13—C15—C16	177.58 (17)
C1—C4—C5—S1	−167.14 (13)	C13—C15—C16—C17	0.0 (3)
C3—C4—C5—S1	−41.22 (17)	C15—C16—C17—C18	−0.6 (3)
C2—S1—C5—C4	47.49 (13)	C16—C17—C18—C19	0.9 (3)
C4—C3—C6—O1	−23.0 (2)	C17—C18—C19—C13	−0.5 (3)
C2—C3—C6—O1	99.3 (2)	C15—C13—C19—C18	−0.1 (3)
C4—C3—C6—C7	158.71 (16)	C2—C13—C19—C18	−177.36 (17)
C2—C3—C6—C7	−78.9 (2)	C24—C14—C20—C21	−0.7 (3)
O1—C6—C7—C12	151.51 (19)	C2—C14—C20—C21	−179.45 (17)
C3—C6—C7—C12	−30.3 (3)	C14—C20—C21—C22	0.1 (3)
O1—C6—C7—C8	−29.5 (3)	C20—C21—C22—C23	0.5 (3)
C3—C6—C7—C8	148.70 (17)	C21—C22—C23—C24	−0.5 (3)
C12—C7—C8—C9	2.5 (3)	C22—C23—C24—C14	−0.2 (3)
C6—C7—C8—C9	−176.52 (17)	C20—C14—C24—C23	0.8 (3)
C7—C8—C9—C10	−2.1 (3)	C2—C14—C24—C23	179.60 (18)