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

Linden, Anthony; Mloston, Grzegorz; Grzelak, Paulina; Heimgartner, Heinz

Abstract: The title compounds, C_{19}H_{21}F_{3}O_{2}S and C_{24}H_{19}F_{3}O_{S}, were prepared via chemo- and regioselective [3 + 2]-cyclo-additions 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...Pi interactions link the molecules into sheets parallel to the (010) plane.

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Anthony Linden, Grzegorz Młożoń, Paulina Grzelak and Heinz Heimgartner

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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

Anthony Linden,a* Grzegorz Młośnić, Paulina Grzelakb and Heinz Heimgartnera

aDepartment of Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and
bDepartment of Organic and Applied Chemistry, University of Łódź, Tamka 12, PL-91-403 Łódź, Poland.
*Correspondence e-mail: anthony.linden@chem.uzh.ch

The title compounds, C_{19}H_{21}F_{3}O_{2}S and C_{24}H_{19}F_{3}OS, 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 are 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; Młośnić & 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.
1,4-Disubstituted α,β-unsaturated ketones are known as reactive dipolarophiles, and in the case of aryl trifluoromethyl-substituted representatives, the [3 + 2]-cycloadditions with electron-rich thiocarbonyl ylides occur chemoselectively either on the C=O bond, depending on the location of the CF$_3$ 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-tetramethylcyclobut-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.

1a

1b

1,4-Disubstituted α,β-unsaturated ketones are known as reactive dipolarophiles, and in the case of aryl trifluoromethyl-substituted representatives, the [3 + 2]-cycloadditions with electron-rich thiocarbonyl ylides occur chemoselectively either on the C=O bond, depending on the location of the CF$_3$ 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-tetramethylcyclobut-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, $\theta(2) = 359.73 (18)$° 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, $\theta(2) = 349.86 (19)$° 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
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-cyclohexyl-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) C2(8) (two different ones), C2(9) and C2(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 (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...
with the benzoyl ring of a neighbouring molecule related by a
slide 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⋯F3ii), albeit with a
rather sharp C—H⋯F angle of 121° [H15⋯F3ii = 2.53 Å,
C15⋯F3ii = 3.132 (2) Å; symmetry code as in Table 4].

4. Database survey
The CSD contains crystal structure data with atomic coordi-
mates 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 Mlostone et al. (2016). Thermal decom-
position 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 | C19H21F3O2S                                  | C24H19F3OS                                    |
| 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 (Å³)  | 1797.19 (3)                                    | 1911.22 (5)                                   |
| Z       | 4                                             | 4                                             |
| Radiation type | Mo Kα                                          | Mo Kα                                         |
| μ (mm⁻¹) | 0.22                                          | 0.21                                          |
| Crystal size (mm) | 0.30 × 0.27 × 0.25                           | 0.30 × 0.15 × 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 | 0.905, 0.949                                 | 0.904, 0.975                                  |
| No. of measured, independent and observed | 40775, 4120, 3322                          | 43080, 4376, 3216                            |
| R_int | 0.053                                         | 0.081                                         |
| (sin θ/λ)max (Å⁻¹) | 0.650                                        | 0.650                                         |
| Refinement |                                               |                                               |
| R[F² > 2σ(F²)], wR[F²], S | 0.043, 0.114, 1.06                          | 0.045, 0.118, 1.07                          |
| No. of reflections | 4119                                        | 4376                                          |
| No. of parameters | 231                                         | 263                                           |
| No. of H-atoms | H-atom parameters constrained                | H-atom parameters constrained                |
| Δρ_max, Δρ_min (e Å⁻³) | 0.32, -0.59                       | 0.30, -0.37                                  |

Computer programs: COLLECT (Nonius, 2000), DENZO-SMN and SCALEPACK (Ortwinski & Minor, 1997), SHELXS97 (Sheldrick, 2008), ORTEPH (Johnson, 1976), SHELXL2018 (Sheldrick, 2015) and PLATON (Spek, 2015).
tetramethylcyclobutanone, decomposes at 318 K, the less stable precursor 2b, derived from thiobenzophenone, already extrudes N₂ at 228 K. The ¹H 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 \( (C—H = 0.98 \text{ Å}) \) with \( U_{	ext{iso}}(H) = 1.5U_{\text{eq}}(C) \) 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 \( U_{	ext{iso}}(H) = 1.2U_{\text{eq}}(C) \). 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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Anthony Linden, Grzegorz Młośńo, Paulina Grzelak and Heinz Heimgartner

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**

C₁₉H₂₁F₃O₂S  
Mr = 370.42  
Monoclinic, P₂₁/n  
α = 10.4851 (1) Å  
b = 15.4106 (2) Å  
c = 11.4557 (1) Å  
β = 103.8526 (7)°  
V = 1797.19 (3) Å³  
Z = 4  
F(000) = 776

**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)

| Tmin | Tmax | 40775 measured reflections | 4120 independent reflections | 3322 reflections with I > 2σ(I) |
|------|------|-----------------------------|-------------------------------|-------------------------------|
| 0.895 | 0.949 | 4120 independent reflections |
| 0.30 < 0.27 < 0.25 mm |

**Supporting information**

*Acta Cryst.* (2018). *E74*, 1705-1709 [https://doi.org/10.1107/S2056989018015335]
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.114$
$S = 1.06$
4119 reflections
231 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2) + (0.0563P)^2 + 0.7139P$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta \sigma)_{\text{max}} = 0.001$
$\Delta \rho_{\text{max}} = 0.32 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.39 \text{ e Å}^{-3}$

Extinction correction: SHELXL2018 (Sheldrick, 2015),
$F_c^\text{e}=k F_c[1+0.001x F_c^2\lambda^3\sin(2\theta)/\lambda]^{-1/4}$
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 ($\text{Å}^2$)

|    | x      | y      | z      | $U_{iso}^\text{eq}/U_{eq}$ |
|----|--------|--------|--------|--------------------------|
| 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) | 0.88990(10) | 0.71659(12) | 0.0244(3) |
| H3 | 0.19918(18) | 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) |
|   |  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) | 0.0255 (8) | 0.0009 (6) | 0.0017 (6) | 0.0041 (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) |
### Geometric parameters (Å, °)

|     |         |         |         |         |         |         |         |         |         |         |         |
|-----|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 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) |

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

### Bond Torsion Angles

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

| D—H···A  | D—H  | H···A | D···A  | D—H···A |
|---------|------|------|-------|---------|
| C4—H4···S1i | 1.00 | 2.89 | 3.7370 (16) | 142 |
| C5—H51···O1i | 0.99 | 2.41 | 3.3417 (19) | 156 |
| C10—H10···S1ii | 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

$\beta = 92.6805$ (9)$^\circ$

$V = 1911.22$ (5) Å$^3$

$Z = 4$

$F(000) = 856$

Data collection

Nonius KappaCCD area-detector diffractometer

Radiation source: Nonius FR590 sealed tube generator

Horizontally mounted graphite crystal monochromator

Detector resolution: 9 pixels mm$^{-1}$

$\omega$ scans with $x$ offsets

Absorption correction: multi-scan (Blessing, 1995)

$T_{\text{min}} = 0.904, T_{\text{max}} = 0.975$

43080 measured reflections

4376 independent reflections

3216 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.081$

$\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.3^\circ$

$h = -9 \rightarrow 9$

$k = -22 \rightarrow 22$

$l = -18 \rightarrow 18$

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**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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.30 \text{ e Å}^{-3}$
$\Delta\rho_{\text{min}} = -0.37 \text{ e Å}^{-3}$

Extinction correction: SHELXL2018 (Sheldrick, 2015),

$F_c^e = k F_c [1 + 0.001 x F_c^2 / \lambda^2 \sin(2\theta)]^{-1/4}$
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 ($\AA^2$)**

|     | 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)   |
| 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*       |

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**supporting information**

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**electronic reprint**
### 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)     | -0.00228 (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)     | 0.0003 (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  |     C17  |     C18  |     C19  |     C20  |     C21  |     C22  |     C23  |     C24  |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|   | 0.0359 (11) | 0.0272 (10) | 0.0302 (11) | 0.0034 (8) | 0.0020 (8) | 0.0050 (8) |
|   | 0.0373 (11) | 0.0256 (10) | 0.0333 (11) | −0.0042 (8) | 0.0060 (8) | 0.0005 (8) |
|   | 0.0245 (9)  | 0.0306 (10) | 0.0387 (11) | −0.0020 (8) | 0.0021 (8) | −0.0066 (9) |
|   | 0.0260 (9)  | 0.0254 (9)  | 0.0310 (10) | 0.0030 (7)  | −0.0009 (8) | −0.0012 (8) |
|   | 0.0273 (9)  | 0.0311 (10) | 0.0276 (10) | 0.0019 (8)  | 0.0030 (8)  | 0.0009 (8)  |
|   | 0.0282 (10) | 0.0274 (10) | 0.0358 (11) | 0.0021 (8)  | 0.0001 (8)  | 0.0071 (8)  |
|   | 0.0270 (9)  | 0.0217 (9)  | 0.0397 (11) | 0.0019 (7)  | 0.0033 (8)  | 0.0004 (8)  |
|   | 0.0390 (11) | 0.0298 (11) | 0.0316 (11) | 0.0032 (8)  | 0.0034 (8)  | −0.0024 (8) |
|   | 0.0375 (11) | 0.0263 (10) | 0.0251 (10) | 0.0025 (8)  | 0.0007 (8)  | 0.0026 (8)  |

**Geometric parameters (Å, °)**

|   | 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 | 1.393 (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) |
| Bond                  | Angle (°)     | Bond                  | Angle (°)     |
|----------------------|---------------|----------------------|---------------|
| 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—C2          | 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         |
| S1—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)   |
supporting information

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\begin{align*}
F_2-C_1-C_4-C_3 & \quad 176.63 \pm (15) \quad C_3-C_2-C_14-C_20 & \quad -9.8 \pm (3) \\
F_3-C_1-C_4-C_3 & \quad 57.2 \pm (2) \quad S_1-C_2-C_14-C_20 & \quad -122.75 \pm (17) \\
F_1-C_1-C_4-C_3 & \quad -62.7 \pm (2) \quad C_13-C_2-C_14-C_24 & \quad -60.3 \pm (2) \\
C_6-C_3-C_4-C_1 & \quad -98.19 \pm (18) \quad C_3-C_2-C_14-C_24 & \quad 171.47 \pm (15) \\
C_2-C_3-C_4-C_1 & \quad 137.62 \pm (16) \quad S_1-C_2-C_14-C_24 & \quad 58.53 \pm (19) \\
C_6-C_3-C_4-C_5 & \quad 136.06 \pm (16) \quad C_19-C_13-C_15-C_16 & \quad 0.4 \pm (3) \\
C_2-C_3-C_4-C_5 & \quad 11.9 \pm (2) \quad C_2-C_13-C_15-C_16 & \quad 177.58 \pm (17) \\
C_1-C_4-C_5-S_1 & \quad -167.14 \pm (13) \quad C_13-C_15-C_16-C_17 & \quad 0.0 \pm (3) \\
C_3-C_4-C_5-S_1 & \quad -41.22 \pm (17) \quad C_15-C_16-C_17-C_18 & \quad -0.6 \pm (3) \\
C_2-S_1-C_5-C_4 & \quad 47.49 \pm (13) \quad C_16-C_17-C_18-C_19 & \quad 0.9 \pm (3) \\
C_4-C_3-C_6-O_1 & \quad -23.0 \pm (2) \quad C_17-C_18-C_19-C_13 & \quad -0.5 \pm (3) \\
C_2-C_3-C_6-O_1 & \quad 99.3 \pm (2) \quad C_15-C_13-C_19-C_18 & \quad -0.1 \pm (3) \\
C_4-C_3-C_6-C_7 & \quad 158.71 \pm (16) \quad C_2-C_13-C_19-C_18 & \quad -177.36 \pm (17) \\
C_2-C_3-C_6-C_7 & \quad -78.9 \pm (2) \quad C_24-C_14-C_20-C_21 & \quad -0.7 \pm (3) \\
O_1-C_6-C_7-C_12 & \quad 151.51 \pm (19) \quad C_2-C_14-C_20-C_21 & \quad -179.45 \pm (17) \\
C_3-C_6-C_7-C_12 & \quad -30.3 \pm (3) \quad C_14-C_20-C_21-C_22 & \quad 0.1 \pm (3) \\
O_1-C_6-C_7-C_8 & \quad -29.5 \pm (3) \quad C_20-C_21-C_22-C_23 & \quad 0.5 \pm (3) \\
C_3-C_6-C_7-C_8 & \quad 148.70 \pm (17) \quad C_21-C_22-C_23-C_24 & \quad -0.5 \pm (3) \\
C_12-C_7-C_8-C_9 & \quad 2.5 \pm (3) \quad C_22-C_23-C_24-C_14 & \quad -0.2 \pm (3) \\
C_6-C_7-C_8-C_9 & \quad -176.52 \pm (17) \quad C_20-C_14-C_24-C_23 & \quad 0.8 \pm (3) \\
C_7-C_8-C_9-C_10 & \quad -2.1 \pm (3) \quad C_2-C_14-C_24-C_23 & \quad 179.60 \pm (18)
\end{align*}
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