

Ethyl 3-[2-(3,4-dimethoxybenzyl)-1-phenylsulfonyl-1*H*-indol-3-yl]acrylate chloroform hemisolvate

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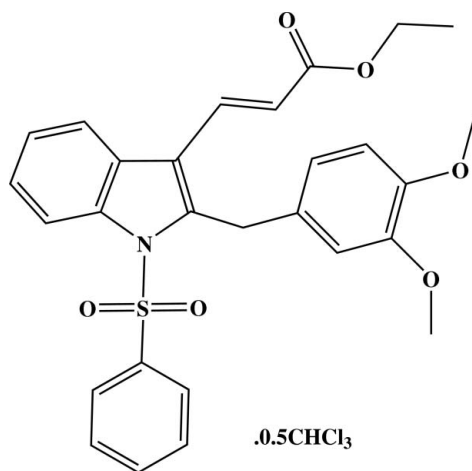
Received 4 April 2011; accepted 11 May 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in solvent or counterion; R factor = 0.056; wR factor = 0.189; data-to-parameter ratio = 29.2.

In the title compound, $\text{C}_{28}\text{H}_{27}\text{NO}_6\text{S}\cdot 0.5\text{CHCl}_3$, the ethyl acrylate substituent adopts an extended conformation with all torsion angles close to 180° . The chloroform solvent molecule is disordered across an inversion centre and is therefore half occupied. The molecular packing is controlled by intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For general background to indoles, see: Hu *et al.* (2005); Nieto *et al.* (2005); Mathiesen *et al.* (2005); Olgen & Nebioglu (2002). For the sulfonyl moiety, see: Bassindale (1984). For hybridization, see: Beddoes *et al.* (1986). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{28}\text{H}_{27}\text{NO}_6\text{S}\cdot 0.5\text{CHCl}_3$
 $M_r = 565.25$
Triclinic, $P\bar{1}$
 $a = 10.2154$ (3) Å
 $b = 12.0504$ (4) Å
 $c = 12.6310$ (4) Å
 $\alpha = 70.602$ (2)°
 $\beta = 69.613$ (1)°
 $\gamma = 77.056$ (2)°
 $V = 1364.39$ (7) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.913$, $T_{\max} = 0.941$
38797 measured reflections
10612 independent reflections
7709 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.189$
 $S = 1.04$
10612 reflections
364 parameters
27 restraints
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.73$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C15}-\text{H15}\cdots\text{O4}^i$	0.93	2.53	3.411 (3)	159
$\text{C24}-\text{H24B}\cdots\text{O7}^{ii}$	0.96	2.51	3.461 (2)	169
$\text{C24}-\text{H24A}\cdots\text{O7}^{iii}$	0.96	2.52	3.367 (3)	147
$\text{C30}-\text{H30A}\cdots\text{O3}^{iv}$	0.96	2.59	3.429 (7)	146
$\text{C30}-\text{H30A}\cdots\text{O4}^{iv}$	0.96	2.55	3.424 (7)	151

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXS97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

MT thanks the UGC for financial support in the form of a Research Fellowship in Science for Meritorious Students.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5508).

References

- Bassindale, A. (1984). *The Third Dimension in Organic Chemistry*, ch. 1, p. 11. New York: John Wiley and Sons.
Beddoes, R. L., Dalton, L., Joule, T. A., Mills, O. S., Street, J. D. & Watt, C. I. F. (1986). *J. Chem. Soc. Perkin Trans. 2*, pp. 787–797.
Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2004). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

- Hu, B., Jetter, J. W., Wrobel, J. E., Antrilli, T. M., Bauer, J. S., Di, L., Polakowski, S., Jain, U. & Crandall, D. L. (2005). *Bioorg. Med. Chem. Lett.* **15**, 3514–3518.
- Mathiesen, J. M., Ulven, T., Martini, L., Gerlach, L. O., Heinemann, A. & Kostenis, E. (2005). *Mol. Pharmacol.* **68**, 393–402.
- Nieto, M. J., Alovero, F. L., Manzo, R. H. & Mazzieri, M. R. (2005). *Eur. J. Med. Chem.* **40**, 361–369.
- Olgen, S. & Nebioglu, D. (2002). *Farmaco*, **57**, 677–683.
- Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.

supplementary materials

Acta Cryst. (2011). E67, o1460-o1461 [doi:10.1107/S1600536811017740]

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Comment

Carboxylic acid indoles act as inhibitors of plasminogen activator inhibitor-1 (Hu *et al.*, 2005). The benzenesulfonamide group attached to the indole ring exhibit significant biological activities, such as antibacterial *etc.*, (Nieto *et al.*, 2005). Also, the indole derivatives are identified as the molecules which interfere with a G protein-independent signaling pathway of the CRTH2 receptor (Mathiesen *et al.*, 2005). N-substituted indole carboxylic acid esters have been prepared as possible *cyclo*-oxygenase-2 (COX-2) enzyme inhibitors (Olgen & Nebioglu, 2002).

Fig.1 shows the *ORTEP* plot of the title compound. The indole moiety is planar with the maximum deviation of -0.033 (2)Å and 0.028 (2)Å for atoms C5 and C7, respectively. The indole ring system is oriented equatorially to the phenyl sulfonyl ring [dihedral angle = 78.18 (6)°]. The O—S—O and N—S—C angles [See Table1] deviate significantly from their ideal value due to the Thrope-Ingold effect (Bassindale, 1984). The dimethoxybenzyl group is also equatorially oriented to the planar indole ring, which can be observed from the dihedral angle [78.04 (4)°].

The ethyl acrylate group substituted at C3 position of the indole ring takes up an extended conformation which is evident from the torsion angle values [C25—C26—C27—O8 =] -179.10 (16)°; [C25—C26—C27- O7 =] 1.8 (3)°; [C26—C27—O8—C28 =] 179.8 (2)°; [C29—C28—O8—C27 =] 179.7 (2)°. The sum of the bond angles around N1[359.37°] shows that atom N1 exhibits *sp*² hybridization (Beddoes *et al.*, 1986). The chloroform solvent is disordered across inversion centre with the site occupancies of 0.5 for each.

The molecular packing is controlled by intra and intermolecular C—H···O interactions in addition to van der Waals forces (Table 2). Atom H15 of C15 form an intermolecular hydrogen bonding with atom O4, leading to a C11 linear chains (Bernstein *et al.*, 1995) with C—H···O type of interactions running along *a*-axis. The intermolecular interaction C24—H24A···O7 leads to *R*₂²(13) dimers, which are connected through C24—H24B···O7 interaction as closed loops running along *c*-axis. Intermolecular bifurcated C—H···O hydrogen bonds involving the two oxygen atoms of the dimethoxybenzyl group and the hydrogen atom of the chloroform, solvent generates *R*₁²(5) ring motif (Fig.2).

Experimental

To a solution of (*E*)-Ethyl 3-(2-(bromomethyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl) acrylate (0.3 g, 0.66 mmol) in dry DME (10 ml), ZnBr₂ (0.3 g, 1.3 mmol), K₂CO₃ (0.18 g, 1.33 mmol) and veratrole (0.11 g, 0.79 mmol) were added. The reaction mixture was then refluxed for 12hrs under N₂ atmosphere. The solvent was removed and the reaction mixture was quenched with ice-water (100 mL) containing 2 mL of conc.HCl. It was then extracted with chloroform (20 mL) and dried (Na₂SO₄). Removal of the solvent followed by crystallization from methanol afforded the product as pale yellow crystals.

Refinement

H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl and $1.2U_{\text{eq}}(\text{C})$ for other H atoms. The chloroform solvent is disordered across inversion centre with the site occupancies of 0.5 for each. The corresponding bond distances involving the disordered atoms C30, C11, C12 and C13 were restrained to 1.74 (1) Å and also their displacement parameters were restrained to an approximate isotropic behaviour.

Figures

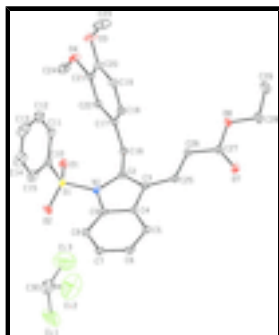


Fig. 1. The *ORTEP* plot of the title compound, showing 30% probability displacement ellipsoids. H atoms omitted for clarity.

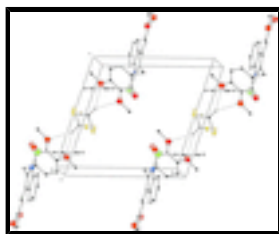


Fig. 2. The packing of the molecules showing intermolecular C—H...O hydrogen bonds (dashed lines).

Ethyl 3-[2-(3,4-dimethoxybenzyl)-1-phenylsulfonyl-1*H*-indol-3-yl]prop-2-enoate chloroform hemisolvate

Crystal data

$\text{C}_{28}\text{H}_{27}\text{NO}_6\text{S}\cdot 0.5\text{CHCl}_3$

$M_r = 565.25$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 10.2154\ (3)\ \text{\AA}$

$b = 12.0504\ (4)\ \text{\AA}$

$c = 12.6310\ (4)\ \text{\AA}$

$\alpha = 70.602\ (2)^\circ$

$\beta = 69.613\ (1)^\circ$

$\gamma = 77.056\ (2)^\circ$

$V = 1364.39\ (7)\ \text{\AA}^3$

$Z = 2$

$F(000) = 590$

$D_x = 1.376\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 10612 reflections

$\theta = 1.8\text{--}34.4^\circ$

$\mu = 0.31\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, yellow

$0.30 \times 0.25 \times 0.20\ \text{mm}$

Data collection

Bruker Kappa APEXII area-detector

10612 independent reflections

diffractometer	
Radiation source: fine-focus sealed tube	7709 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.026$
ω and φ scans	$\theta_{\text{max}} = 34.4^\circ$, $\theta_{\text{min}} = 1.8^\circ$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2001)	$h = -15 \rightarrow 16$
$T_{\text{min}} = 0.913$, $T_{\text{max}} = 0.941$	$k = -18 \rightarrow 18$
38797 measured reflections	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.056$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.189$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.1059P)^2 + 0.3616P]$
10612 reflections	where $P = (F_o^2 + 2F_c^2)/3$
364 parameters	$(\Delta/\sigma)_{\text{max}} = 0.005$
27 restraints	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

Special details

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

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C2	0.72857 (13)	0.61852 (12)	0.05863 (12)	0.0264 (2)	
C3	0.81718 (13)	0.63351 (12)	-0.05351 (12)	0.0274 (2)	
C4	0.95289 (13)	0.65050 (12)	-0.05427 (12)	0.0263 (2)	
C5	1.07996 (14)	0.66763 (13)	-0.14331 (13)	0.0315 (3)	
H5	1.0889	0.6670	-0.2189	0.038*	
C6	1.19275 (15)	0.68563 (15)	-0.11662 (15)	0.0364 (3)	
H6	1.2784	0.6974	-0.1750	0.044*	
C7	1.17913 (15)	0.68629 (15)	-0.00368 (16)	0.0379 (3)	
H7	1.2559	0.7000	0.0116	0.045*	
C8	1.05530 (15)	0.66722 (15)	0.08678 (14)	0.0356 (3)	

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H8	1.0476	0.6666	0.1625	0.043*
C9	0.94241 (13)	0.64898 (12)	0.05935 (12)	0.0279 (2)
C10	0.70544 (17)	0.78432 (16)	0.26272 (14)	0.0377 (3)
C11	0.5742 (2)	0.84292 (17)	0.25639 (15)	0.0432 (4)
H11	0.5084	0.8035	0.2523	0.052*
C12	0.5421 (3)	0.9606 (2)	0.2561 (2)	0.0574 (5)
H12	0.4541	1.0006	0.2523	0.069*
C13	0.6404 (3)	1.0186 (2)	0.2616 (3)	0.0744 (8)
H13	0.6187	1.0980	0.2609	0.089*
C14	0.7695 (3)	0.9599 (3)	0.2680 (3)	0.0806 (9)
H14	0.8348	0.9999	0.2720	0.097*
C15	0.8049 (2)	0.8418 (2)	0.2685 (2)	0.0587 (6)
H15	0.8931	0.8022	0.2727	0.070*
C16	0.58220 (13)	0.58587 (12)	0.10469 (13)	0.0292 (3)
H16A	0.5727	0.5253	0.1792	0.035*
H16B	0.5688	0.5514	0.0504	0.035*
C17	0.46644 (13)	0.68702 (12)	0.12265 (12)	0.0269 (2)
C18	0.47327 (14)	0.79830 (13)	0.04363 (13)	0.0312 (3)
H18	0.5530	0.8133	-0.0208	0.037*
C19	0.36222 (16)	0.88845 (13)	0.05909 (14)	0.0347 (3)
H19	0.3682	0.9628	0.0047	0.042*
C20	0.24365 (15)	0.86818 (14)	0.15431 (15)	0.0350 (3)
C21	0.23710 (14)	0.75648 (14)	0.23783 (13)	0.0326 (3)
C22	0.34699 (14)	0.66710 (13)	0.22105 (12)	0.0296 (3)
H22	0.3417	0.5928	0.2756	0.036*
C23	0.1240 (3)	1.0559 (2)	0.0848 (3)	0.0857 (10)
H23A	0.1932	1.1019	0.0787	0.129*
H23B	0.0323	1.1002	0.1029	0.129*
H23C	0.1440	1.0385	0.0115	0.129*
C24	0.1089 (2)	0.6366 (2)	0.42176 (19)	0.0577 (5)
H24A	0.1140	0.5729	0.3903	0.087*
H24B	0.0213	0.6415	0.4826	0.087*
H24C	0.1855	0.6224	0.4539	0.087*
C25	0.79102 (15)	0.63214 (13)	-0.15877 (13)	0.0311 (3)
H25	0.8700	0.6102	-0.2158	0.037*
C26	0.67095 (15)	0.65761 (15)	-0.18607 (13)	0.0342 (3)
H26	0.5864	0.6751	-0.1316	0.041*
C27	0.67332 (16)	0.65776 (16)	-0.30294 (13)	0.0358 (3)
C28	0.5395 (2)	0.6890 (3)	-0.43115 (17)	0.0634 (6)
H28A	0.5753	0.6117	-0.4448	0.076*
H28B	0.5976	0.7465	-0.4927	0.076*
C29	0.3931 (3)	0.7211 (3)	-0.4337 (2)	0.0673 (7)
H29A	0.3356	0.6655	-0.3710	0.101*
H29B	0.3881	0.7196	-0.5077	0.101*
H29C	0.3599	0.7993	-0.4242	0.101*
N1	0.80387 (12)	0.62707 (11)	0.13020 (10)	0.0292 (2)
O1	0.61261 (13)	0.58330 (11)	0.31986 (10)	0.0420 (3)
O2	0.85541 (15)	0.58180 (14)	0.31850 (11)	0.0509 (3)
O3	0.12766 (14)	0.94873 (12)	0.17533 (14)	0.0550 (4)

O4	0.11775 (12)	0.74569 (12)	0.33019 (12)	0.0468 (3)	
O7	0.77576 (14)	0.63380 (17)	-0.37800 (13)	0.0608 (4)	
O8	0.54527 (12)	0.68657 (14)	-0.31723 (10)	0.0482 (3)	
S1	0.74189 (4)	0.63276 (4)	0.26998 (3)	0.03379 (10)	
C30	1.0269 (8)	-0.0254 (6)	0.4558 (6)	0.113 (3)	0.50
H30A	1.0428	-0.0660	0.3979	0.136*	0.50
Cl1	0.9317 (6)	0.1115 (4)	0.4302 (5)	0.199 (2)	0.50
Cl2	0.9683 (8)	-0.1068 (4)	0.5950 (4)	0.223 (3)	0.50
Cl3	1.1858 (5)	0.0222 (6)	0.4566 (6)	0.241 (2)	0.50

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0239 (5)	0.0266 (6)	0.0284 (6)	-0.0029 (4)	-0.0068 (4)	-0.0083 (5)
C3	0.0237 (5)	0.0287 (6)	0.0294 (6)	-0.0024 (4)	-0.0067 (4)	-0.0093 (5)
C4	0.0233 (5)	0.0246 (6)	0.0297 (6)	-0.0015 (4)	-0.0063 (4)	-0.0084 (5)
C5	0.0256 (6)	0.0342 (7)	0.0311 (6)	-0.0035 (5)	-0.0032 (5)	-0.0102 (5)
C6	0.0237 (6)	0.0394 (8)	0.0433 (8)	-0.0042 (5)	-0.0032 (5)	-0.0149 (6)
C7	0.0250 (6)	0.0452 (8)	0.0483 (9)	-0.0049 (5)	-0.0097 (6)	-0.0199 (7)
C8	0.0286 (6)	0.0450 (8)	0.0383 (8)	-0.0033 (5)	-0.0102 (5)	-0.0186 (6)
C9	0.0242 (5)	0.0283 (6)	0.0311 (6)	-0.0017 (4)	-0.0072 (4)	-0.0102 (5)
C10	0.0395 (7)	0.0459 (8)	0.0285 (7)	-0.0127 (6)	-0.0010 (5)	-0.0162 (6)
C11	0.0526 (9)	0.0454 (9)	0.0356 (8)	-0.0058 (7)	-0.0139 (7)	-0.0158 (7)
C12	0.0707 (13)	0.0472 (11)	0.0538 (12)	-0.0002 (9)	-0.0168 (10)	-0.0197 (9)
C13	0.0876 (18)	0.0528 (13)	0.0797 (18)	-0.0212 (12)	0.0009 (14)	-0.0335 (12)
C14	0.0689 (15)	0.0828 (18)	0.102 (2)	-0.0386 (14)	0.0080 (14)	-0.0570 (17)
C15	0.0406 (9)	0.0773 (15)	0.0694 (14)	-0.0203 (9)	0.0008 (8)	-0.0441 (12)
C16	0.0246 (5)	0.0294 (6)	0.0327 (6)	-0.0057 (4)	-0.0051 (5)	-0.0095 (5)
C17	0.0223 (5)	0.0303 (6)	0.0278 (6)	-0.0055 (4)	-0.0055 (4)	-0.0081 (5)
C18	0.0268 (6)	0.0339 (7)	0.0293 (6)	-0.0069 (5)	-0.0041 (5)	-0.0066 (5)
C19	0.0325 (6)	0.0293 (7)	0.0364 (7)	-0.0056 (5)	-0.0072 (5)	-0.0038 (5)
C20	0.0287 (6)	0.0310 (7)	0.0409 (8)	-0.0015 (5)	-0.0059 (5)	-0.0104 (6)
C21	0.0250 (6)	0.0362 (7)	0.0332 (7)	-0.0061 (5)	-0.0021 (5)	-0.0104 (6)
C22	0.0260 (5)	0.0300 (6)	0.0296 (6)	-0.0064 (4)	-0.0052 (5)	-0.0055 (5)
C23	0.0520 (12)	0.0391 (11)	0.113 (2)	0.0090 (9)	0.0024 (13)	0.0079 (12)
C24	0.0444 (9)	0.0549 (11)	0.0452 (10)	-0.0098 (8)	0.0117 (8)	-0.0017 (8)
C25	0.0298 (6)	0.0364 (7)	0.0278 (6)	-0.0047 (5)	-0.0068 (5)	-0.0110 (5)
C26	0.0302 (6)	0.0446 (8)	0.0295 (6)	-0.0017 (5)	-0.0078 (5)	-0.0156 (6)
C27	0.0322 (6)	0.0477 (8)	0.0293 (7)	-0.0073 (6)	-0.0066 (5)	-0.0141 (6)
C28	0.0493 (10)	0.116 (2)	0.0294 (8)	-0.0157 (11)	-0.0110 (7)	-0.0228 (10)
C29	0.0630 (13)	0.103 (2)	0.0438 (11)	-0.0165 (13)	-0.0262 (10)	-0.0151 (12)
N1	0.0253 (5)	0.0349 (6)	0.0271 (5)	-0.0041 (4)	-0.0054 (4)	-0.0106 (4)
O1	0.0429 (6)	0.0477 (7)	0.0297 (5)	-0.0165 (5)	-0.0017 (4)	-0.0060 (5)
O2	0.0485 (7)	0.0687 (9)	0.0352 (6)	-0.0030 (6)	-0.0203 (5)	-0.0084 (6)
O3	0.0369 (6)	0.0367 (6)	0.0681 (9)	0.0056 (5)	0.0009 (6)	-0.0092 (6)
O4	0.0319 (5)	0.0444 (7)	0.0440 (7)	-0.0035 (5)	0.0078 (5)	-0.0077 (5)
O7	0.0395 (7)	0.1053 (13)	0.0413 (7)	-0.0004 (7)	-0.0046 (5)	-0.0383 (8)
O8	0.0346 (6)	0.0831 (10)	0.0283 (5)	-0.0080 (6)	-0.0089 (4)	-0.0174 (6)

supplementary materials

S1	0.03402 (18)	0.0409 (2)	0.02481 (17)	-0.00679 (14)	-0.00670 (12)	-0.00787 (14)
C30	0.145 (6)	0.099 (5)	0.098 (5)	0.038 (4)	-0.053 (4)	-0.047 (4)
C11	0.273 (5)	0.147 (3)	0.235 (5)	0.091 (3)	-0.201 (5)	-0.071 (3)
C12	0.327 (6)	0.129 (3)	0.147 (3)	-0.070 (4)	0.001 (4)	-0.003 (2)
C13	0.162 (3)	0.292 (6)	0.246 (5)	0.010 (4)	-0.066 (3)	-0.065 (4)

Geometric parameters (Å, °)

C2—C3	1.3669 (19)	C23—O3	1.416 (3)
C2—N1	1.4146 (17)	C23—H23A	0.9600
C2—C16	1.4948 (17)	C23—H23B	0.9600
C3—C4	1.4424 (17)	C23—H23C	0.9600
C3—C25	1.4503 (19)	C24—O4	1.430 (2)
C4—C5	1.3932 (18)	C24—H24A	0.9600
C4—C9	1.3956 (19)	C24—H24B	0.9600
C5—C6	1.385 (2)	C24—H24C	0.9600
C5—H5	0.9300	C25—C26	1.332 (2)
C6—C7	1.387 (2)	C25—H25	0.9300
C6—H6	0.9300	C26—C27	1.467 (2)
C7—C8	1.381 (2)	C26—H26	0.9300
C7—H7	0.9300	C27—O7	1.1969 (19)
C8—C9	1.3931 (19)	C27—O8	1.3355 (19)
C8—H8	0.9300	C28—O8	1.451 (2)
C9—N1	1.4148 (17)	C28—C29	1.467 (3)
C10—C11	1.384 (3)	C28—H28A	0.9700
C10—C15	1.385 (2)	C28—H28B	0.9700
C10—S1	1.7581 (18)	C29—H29A	0.9600
C11—C12	1.381 (3)	C29—H29B	0.9600
C11—H11	0.9300	C29—H29C	0.9600
C12—C13	1.377 (4)	N1—S1	1.6749 (12)
C12—H12	0.9300	O1—S1	1.4211 (12)
C13—C14	1.366 (4)	O2—S1	1.4225 (13)
C13—H13	0.9300	C30—C30 ⁱ	1.341 (14)
C14—C15	1.387 (4)	C30—C12 ⁱ	1.512 (8)
C14—H14	0.9300	C30—C11 ⁱ	1.601 (8)
C15—H15	0.9300	C30—C12	1.673 (7)
C16—C17	1.5121 (19)	C30—C11	1.708 (6)
C16—H16A	0.9700	C30—C13	1.842 (8)
C16—H16B	0.9700	C30—C13 ⁱ	2.065 (10)
C17—C18	1.380 (2)	C30—H30A	0.9600
C17—C22	1.4028 (18)	C11—C12 ⁱ	0.952 (7)
C18—C19	1.393 (2)	C11—C30 ⁱ	1.601 (8)
C18—H18	0.9300	C11—C13 ⁱ	2.054 (8)
C19—C20	1.377 (2)	C12—C11 ⁱ	0.952 (7)
C19—H19	0.9300	C12—C30 ⁱ	1.512 (8)
C20—O3	1.3613 (19)	C12—C13 ⁱ	1.871 (8)
C20—C21	1.406 (2)	C13—C12 ⁱ	1.871 (8)

C21—O4	1.3577 (17)	C13—C11 ⁱ	2.054 (8)
C21—C22	1.382 (2)	C13—C30 ⁱ	2.065 (10)
C22—H22	0.9300		
C3—C2—N1	108.14 (11)	C26—C25—H25	115.1
C3—C2—C16	127.64 (12)	C3—C25—H25	115.1
N1—C2—C16	123.93 (12)	C25—C26—C27	119.37 (13)
C2—C3—C4	108.30 (12)	C25—C26—H26	120.3
C2—C3—C25	129.64 (12)	C27—C26—H26	120.3
C4—C3—C25	122.05 (12)	O7—C27—O8	122.46 (15)
C5—C4—C9	119.96 (12)	O7—C27—C26	125.42 (15)
C5—C4—C3	132.26 (13)	O8—C27—C26	112.11 (13)
C9—C4—C3	107.78 (11)	O8—C28—C29	109.08 (17)
C6—C5—C4	118.49 (14)	O8—C28—H28A	109.9
C6—C5—H5	120.8	C29—C28—H28A	109.9
C4—C5—H5	120.8	O8—C28—H28B	109.9
C5—C6—C7	120.58 (13)	C29—C28—H28B	109.9
C5—C6—H6	119.7	H28A—C28—H28B	108.3
C7—C6—H6	119.7	C28—C29—H29A	109.5
C8—C7—C6	122.15 (14)	C28—C29—H29B	109.5
C8—C7—H7	118.9	H29A—C29—H29B	109.5
C6—C7—H7	118.9	C28—C29—H29C	109.5
C7—C8—C9	116.95 (14)	H29A—C29—H29C	109.5
C7—C8—H8	121.5	H29B—C29—H29C	109.5
C9—C8—H8	121.5	C2—N1—C9	108.64 (11)
C8—C9—C4	121.85 (13)	C2—N1—S1	128.29 (9)
C8—C9—N1	131.06 (13)	C9—N1—S1	122.44 (10)
C4—C9—N1	107.10 (11)	C20—O3—C23	116.43 (16)
C11—C10—C15	121.11 (18)	C21—O4—C24	117.78 (14)
C11—C10—S1	118.80 (13)	C27—O8—C28	115.21 (14)
C15—C10—S1	120.02 (16)	O1—S1—O2	120.63 (8)
C12—C11—C10	119.32 (19)	O1—S1—N1	106.73 (7)
C12—C11—H11	120.3	O2—S1—N1	105.65 (7)
C10—C11—H11	120.3	O1—S1—C10	108.29 (8)
C13—C12—C11	120.1 (2)	O2—S1—C10	108.90 (9)
C13—C12—H12	120.0	N1—S1—C10	105.65 (7)
C11—C12—H12	120.0	C30 ⁱ —C30—C12 ⁱ	71.5 (6)
C14—C13—C12	120.2 (2)	C30 ⁱ —C30—C11 ⁱ	70.3 (6)
C14—C13—H13	119.9	C12 ⁱ —C30—C11 ⁱ	128.4 (6)
C12—C13—H13	119.9	C30 ⁱ —C30—C12	59.0 (5)
C13—C14—C15	121.2 (2)	C12 ⁱ —C30—C12	130.5 (5)
C13—C14—H14	119.4	C11 ⁱ —C30—C12	33.7 (3)
C15—C14—H14	119.4	C30 ⁱ —C30—C11	62.0 (5)
C10—C15—C14	118.2 (2)	C12 ⁱ —C30—C11	33.7 (3)
C10—C15—H15	120.9	C11 ⁱ —C30—C11	132.3 (4)
C14—C15—H15	120.9	C12—C30—C11	112.0 (4)
C2—C16—C17	115.26 (11)	C30 ⁱ —C30—C13	79.2 (7)

supplementary materials

C2—C16—H16A	108.5	Cl2 ⁱ —C30—Cl3	67.0 (4)
C17—C16—H16A	108.5	Cl1 ⁱ —C30—Cl3	72.9 (4)
C2—C16—H16B	108.5	Cl2—C30—Cl3	101.7 (5)
C17—C16—H16B	108.5	Cl1—C30—Cl3	97.4 (4)
H16A—C16—H16B	107.5	C30 ⁱ —C30—Cl3 ⁱ	61.2 (6)
C18—C17—C22	118.73 (13)	Cl2 ⁱ —C30—Cl3 ⁱ	98.2 (4)
C18—C17—C16	121.92 (12)	Cl1 ⁱ —C30—Cl3 ⁱ	92.5 (4)
C22—C17—C16	119.34 (12)	Cl2—C30—Cl3 ⁱ	59.0 (4)
C17—C18—C19	120.84 (13)	Cl1—C30—Cl3 ⁱ	65.2 (3)
C17—C18—H18	119.6	Cl3—C30—Cl3 ⁱ	140.4 (4)
C19—C18—H18	119.6	C30 ⁱ —C30—H30A	166.2
C20—C19—C18	120.44 (14)	Cl2 ⁱ —C30—H30A	113.6
C20—C19—H19	119.8	Cl1 ⁱ —C30—H30A	111.7
C18—C19—H19	119.8	Cl2—C30—H30A	114.6
O3—C20—C19	125.06 (15)	Cl1—C30—H30A	114.5
O3—C20—C21	115.52 (13)	Cl3—C30—H30A	114.6
C19—C20—C21	119.42 (13)	Cl3 ⁱ —C30—H30A	105.0
O4—C21—C22	125.01 (14)	Cl2 ⁱ —Cl1—C30 ⁱ	77.3 (4)
O4—C21—C20	115.26 (13)	Cl2 ⁱ —Cl1—C30	61.8 (5)
C22—C21—C20	119.73 (13)	C30 ⁱ —Cl1—C30	47.7 (4)
C21—C22—C17	120.79 (13)	Cl2 ⁱ —Cl1—Cl3 ⁱ	126.3 (5)
C21—C22—H22	119.6	C30 ⁱ —Cl1—Cl3 ⁱ	59.0 (4)
C17—C22—H22	119.6	C30—Cl1—Cl3 ⁱ	65.8 (3)
O3—C23—H23A	109.5	Cl1 ⁱ —Cl2—C30 ⁱ	84.5 (6)
O3—C23—H23B	109.5	Cl1 ⁱ —Cl2—C30	69.0 (5)
H23A—C23—H23B	109.5	C30 ⁱ —Cl2—C30	49.5 (5)
O3—C23—H23C	109.5	Cl1 ⁱ —Cl2—Cl3 ⁱ	139.6 (5)
H23A—C23—H23C	109.5	C30 ⁱ —Cl2—Cl3 ⁱ	65.0 (4)
H23B—C23—H23C	109.5	C30—Cl2—Cl3 ⁱ	71.0 (4)
O4—C24—H24A	109.5	C30—Cl3—Cl2 ⁱ	48.0 (3)
O4—C24—H24B	109.5	C30—Cl3—Cl1 ⁱ	48.2 (3)
H24A—C24—H24B	109.5	Cl2 ⁱ —Cl3—Cl1 ⁱ	91.0 (3)
O4—C24—H24C	109.5	C30—Cl3—C30 ⁱ	39.6 (4)
H24A—C24—H24C	109.5	Cl2 ⁱ —Cl3—C30 ⁱ	50.0 (2)
H24B—C24—H24C	109.5	Cl1 ⁱ —Cl3—C30 ⁱ	49.0 (2)
C26—C25—C3	129.71 (14)		
N1—C2—C3—C4	0.77 (15)	O7—C27—O8—C28	-1.2 (3)
C16—C2—C3—C4	-173.17 (13)	C26—C27—O8—C28	179.76 (18)
N1—C2—C3—C25	179.76 (14)	C29—C28—O8—C27	179.7 (2)
C16—C2—C3—C25	5.8 (2)	C2—N1—S1—O1	21.70 (15)
C2—C3—C4—C5	178.86 (15)	C9—N1—S1—O1	-168.44 (11)
C25—C3—C4—C5	-0.2 (2)	C2—N1—S1—O2	151.24 (13)
C2—C3—C4—C9	-1.78 (15)	C9—N1—S1—O2	-38.90 (14)

C25—C3—C4—C9	179.13 (13)	C2—N1—S1—C10	-93.43 (13)
C9—C4—C5—C6	-1.5 (2)	C9—N1—S1—C10	76.43 (13)
C3—C4—C5—C6	177.80 (15)	C11—C10—S1—O1	-25.83 (15)
C4—C5—C6—C7	0.1 (2)	C15—C10—S1—O1	151.37 (15)
C5—C6—C7—C8	1.2 (3)	C11—C10—S1—O2	-158.70 (13)
C6—C7—C8—C9	-1.0 (2)	C15—C10—S1—O2	18.50 (18)
C7—C8—C9—C4	-0.4 (2)	C11—C10—S1—N1	88.22 (14)
C7—C8—C9—N1	179.80 (15)	C15—C10—S1—N1	-94.58 (16)
C5—C4—C9—C8	1.7 (2)	C30 ⁱ —C30—C11—C12 ⁱ	98.6 (8)
C3—C4—C9—C8	-177.79 (13)	C11 ⁱ —C30—C11—C12 ⁱ	98.6 (8)
C5—C4—C9—N1	-178.49 (12)	C12—C30—C11—C12 ⁱ	131.0 (6)
C3—C4—C9—N1	2.06 (15)	C13—C30—C11—C12 ⁱ	25.1 (6)
C15—C10—C11—C12	-0.1 (3)	C13 ⁱ —C30—C11—C12 ⁱ	167.8 (7)
S1—C10—C11—C12	177.03 (15)	C12 ⁱ —C30—C11—C30 ⁱ	-98.6 (8)
C10—C11—C12—C13	0.3 (3)	C11 ⁱ —C30—C11—C30 ⁱ	0.0
C11—C12—C13—C14	-0.4 (4)	C12—C30—C11—C30 ⁱ	32.3 (5)
C12—C13—C14—C15	0.3 (5)	C13—C30—C11—C30 ⁱ	-73.5 (6)
C11—C10—C15—C14	0.1 (3)	C13 ⁱ —C30—C11—C30 ⁱ	69.2 (6)
S1—C10—C15—C14	-177.1 (2)	C30 ⁱ —C30—C11—C13 ⁱ	-69.2 (6)
C13—C14—C15—C10	-0.2 (4)	C12 ⁱ —C30—C11—C13 ⁱ	-167.8 (7)
C3—C2—C16—C17	-103.22 (16)	C11 ⁱ —C30—C11—C13 ⁱ	-69.2 (6)
N1—C2—C16—C17	83.73 (16)	C12—C30—C11—C13 ⁱ	-36.8 (5)
C2—C16—C17—C18	40.18 (19)	C13—C30—C11—C13 ⁱ	-142.7 (4)
C2—C16—C17—C22	-141.19 (13)	C30 ⁱ —C30—C12—C11 ⁱ	-101.1 (8)
C22—C17—C18—C19	-1.8 (2)	C12 ⁱ —C30—C12—C11 ⁱ	-101.1 (8)
C16—C17—C18—C19	176.82 (13)	C11—C30—C12—C11 ⁱ	-134.6 (6)
C17—C18—C19—C20	0.4 (2)	C13—C30—C12—C11 ⁱ	-31.5 (6)
C18—C19—C20—O3	-177.63 (16)	C13 ⁱ —C30—C12—C11 ⁱ	-174.0 (7)
C18—C19—C20—C21	1.8 (2)	C12 ⁱ —C30—C12—C30 ⁱ	0.0
O3—C20—C21—O4	-2.2 (2)	C11 ⁱ —C30—C12—C30 ⁱ	101.1 (8)
C19—C20—C21—O4	178.36 (15)	C11—C30—C12—C30 ⁱ	-33.4 (4)
O3—C20—C21—C22	176.88 (15)	C13—C30—C12—C30 ⁱ	69.6 (6)
C19—C20—C21—C22	-2.6 (2)	C13 ⁱ —C30—C12—C30 ⁱ	-72.9 (6)
O4—C21—C22—C17	-179.85 (14)	C30 ⁱ —C30—C12—C13 ⁱ	72.9 (6)
C20—C21—C22—C17	1.2 (2)	C12 ⁱ —C30—C12—C13 ⁱ	72.9 (6)
C18—C17—C22—C21	1.0 (2)	C11 ⁱ —C30—C12—C13 ⁱ	174.0 (7)
C16—C17—C22—C21	-177.68 (13)	C11—C30—C12—C13 ⁱ	39.4 (5)
C2—C3—C25—C26	26.6 (3)	C13—C30—C12—C13 ⁱ	142.5 (4)
C4—C3—C25—C26	-154.55 (16)	C30 ⁱ —C30—C13—C12 ⁱ	-74.4 (5)
C3—C25—C26—C27	175.66 (15)	C11 ⁱ —C30—C13—C12 ⁱ	-146.9 (5)
C25—C26—C27—O7	1.8 (3)	C12—C30—C13—C12 ⁱ	-129.3 (5)
C25—C26—C27—O8	-179.10 (16)	C11—C30—C13—C12 ⁱ	-14.8 (3)

supplementary materials

C3—C2—N1—C9	0.52 (15)	Cl3 ⁱ —C30—Cl3—Cl2 ⁱ	-74.4 (5)
C16—C2—N1—C9	174.73 (12)	C30 ⁱ —C30—Cl3—Cl1 ⁱ	72.6 (5)
C3—C2—N1—S1	171.49 (10)	Cl2 ⁱ —C30—Cl3—Cl1 ⁱ	146.9 (5)
C16—C2—N1—S1	-14.3 (2)	Cl2—C30—Cl3—Cl1 ⁱ	17.7 (3)
C8—C9—N1—C2	178.21 (15)	Cl1—C30—Cl3—Cl1 ⁱ	132.1 (4)
C4—C9—N1—C2	-1.62 (15)	Cl3 ⁱ —C30—Cl3—Cl1 ⁱ	72.6 (5)
C8—C9—N1—S1	6.6 (2)	Cl2 ⁱ —C30—Cl3—C30 ⁱ	74.4 (5)
C4—C9—N1—S1	-173.23 (10)	Cl1 ⁱ —C30—Cl3—C30 ⁱ	-72.6 (5)
C19—C20—O3—C23	7.7 (3)	Cl2—C30—Cl3—C30 ⁱ	-54.9 (5)
C21—C20—O3—C23	-171.8 (2)	Cl1—C30—Cl3—C30 ⁱ	59.5 (5)
C22—C21—O4—C24	4.9 (3)	Cl3 ⁱ —C30—Cl3—C30 ⁱ	0.000 (1)
C20—C21—O4—C24	-176.06 (18)		

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C8—H8 \cdots O2	0.93	2.38	2.928 (2)	118
C15—H15 \cdots O4 ⁱⁱ	0.93	2.53	3.411 (3)	159
C16—H16A \cdots O1	0.97	2.30	2.831 (2)	114
C24—H24B \cdots O7 ⁱⁱⁱ	0.96	2.51	3.461 (2)	169
C24—H24A \cdots O7 ^{iv}	0.96	2.52	3.367 (3)	147
C25—H25 \cdots O7	0.93	2.46	2.821 (2)	103
C30—H30A \cdots O3 ^v	0.96	2.59	3.429 (7)	146
C30—H30A \cdots O4 ^v	0.96	2.55	3.424 (7)	151

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

Fig. 1

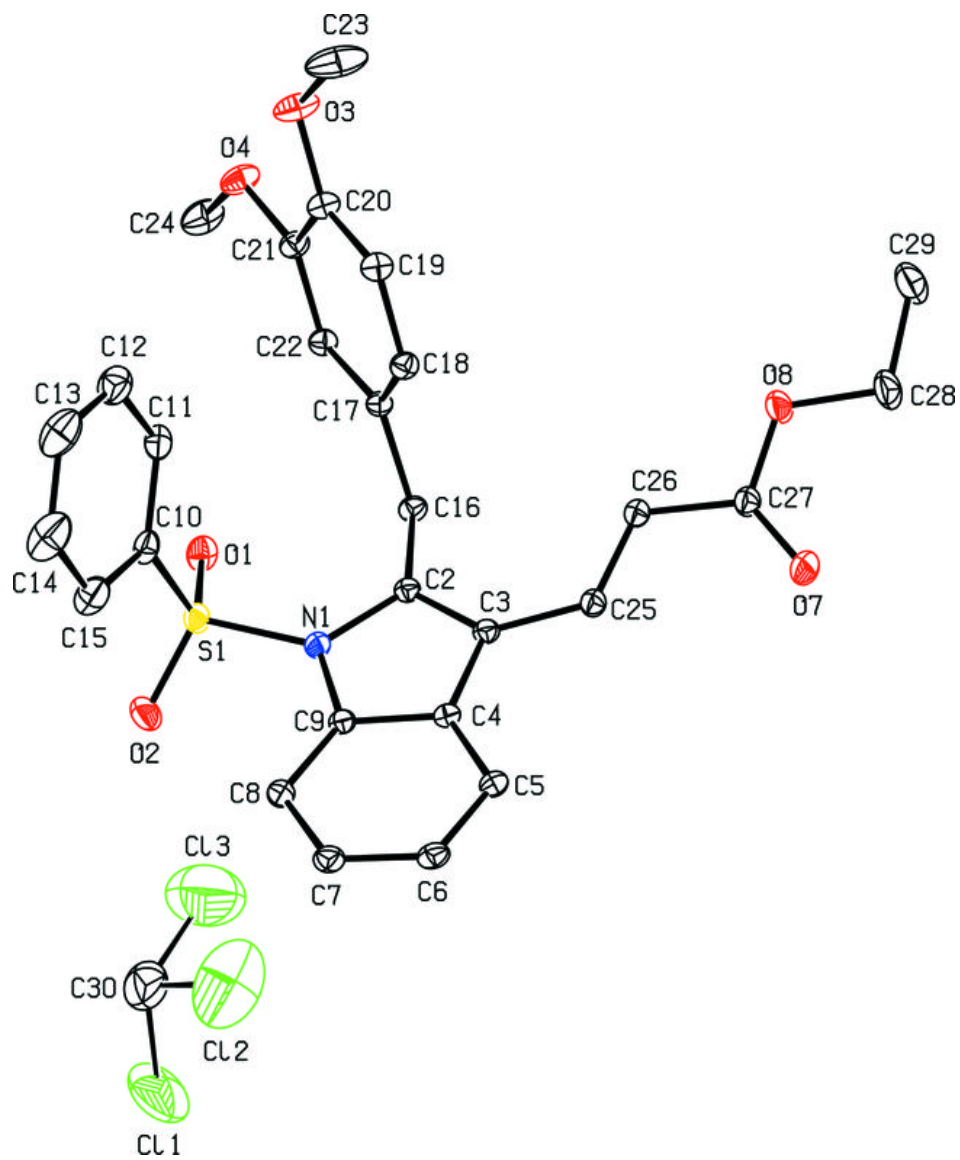


Fig. 2

