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tert-Butyl (2*S*,3*R*,4*R*)-7′-bromo-4-methyl-2′,5-dioxo-4,5-dihydro-3*H*-spiro[furan-2,3′-indoline]-3-carboxylate

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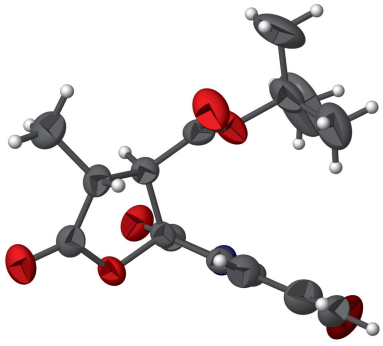
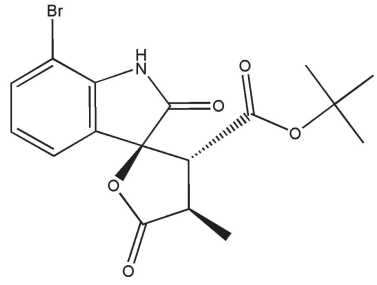
In the title compound, $C_{17}H_{18}BrNO_5$, the furan ring has an envelope conformation with the carboxylate substituted C atom as the flap. The planar indoline ring is inclined to the mean plane of the furan ring by 87.5 (2)°. In the crystal, molecules are linked by N—H···O and C—H···O hydrogen bonds forming chains propagating along the *a*-axis direction.

3D view



Chemical scheme



Structure description

Spirocyclic oxindoles are important structures in many biologically active molecules and natural products (Cui *et al.*, 1996). The key structural characteristic of these compounds is the spiro ring fused at the 3-position of the oxindole core (Cerisoli *et al.*, 2016) with varying degrees of substitution around it (Trost & Brennan, 2009; Wang *et al.*, 2013; Monari *et al.*, 2015). However, it is a challenge to synthesize chiral spirocyclic oxindoles with spiro quaternary centers and multiple chiral centers. Therefore, the development of simply and highly stereoselective methods to synthesize spirooxindoles remains an important research direction for chemists. The title compound was readily synthesized through organocatalytic Michael reaction of propionaldehyde and methyleneindolinones, with subsequent H_2O_2/K_2CO_3 system-mediated α-hydroxylation/hemiacetalization cascade reaction under oil/water two-phase conditions, and final oxidative γ-lactonization.

In the title compound, Fig. 1, the furan ring (O2/C7/C9–C11) has an envelope conformation with atom C9 as the flap. The indoline ring (N1/C1–C8) is inclined to the mean plane of the furan ring by 87.5 (2)°. In the crystal, molecules are linked by N—H···O and C—H···O hydrogen bonds forming chains propagating along the *a*-axis direction (Table 1 and Fig. 2).

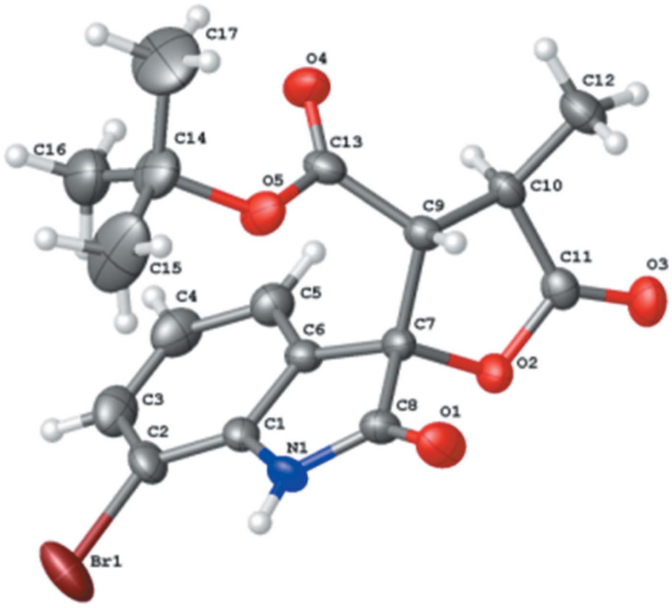


Figure 1
The structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Synthesis and crystallization

To a solution of the chiral catalyst, (*S*)-2-{diphenyl[(trimethylsilyl)oxy]methyl}pyrrolidine (1.62 mg), carboxybenzene (1.22 mg) and *tert*-butyl (*E*)-2-(7-bromo-2-oxoindolin-3-ylidene)acetate (64.8 mg) in 0.5 ml acetonitrile and propionaldehyde (20.0 µl) were introduced *via* syringe. The mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum and K_2CO_3 (1 equiv.), [EtOAc (1 ml) and H_2O (0.1 ml)], H_2O_2 (4 equiv.) were added, and the reaction ran at room temperature for 4 h. After completion of the reaction, the mixture was extracted with EtOAc (3 × 5 ml), washed with water, dried and concentrated. The residue and PCC (pyridinium chlorochromate, 2.0 equiv.) in dry DCM (2 ml) was stirred at room temperature for 16 h, then diluted with EtOAc (10 ml). The mixture was filtered and the filtrate concentrated under vacuum and the residue purified by flash chromatography on silica gel eluting with petroleum ether/ethyl acetate 4:1 (*v*/*v*) to give a white solid. Single crystals were obtained by slow evaporation of a solution in petroleum ether/diethyl ether 5:1 (*v*/*v*).

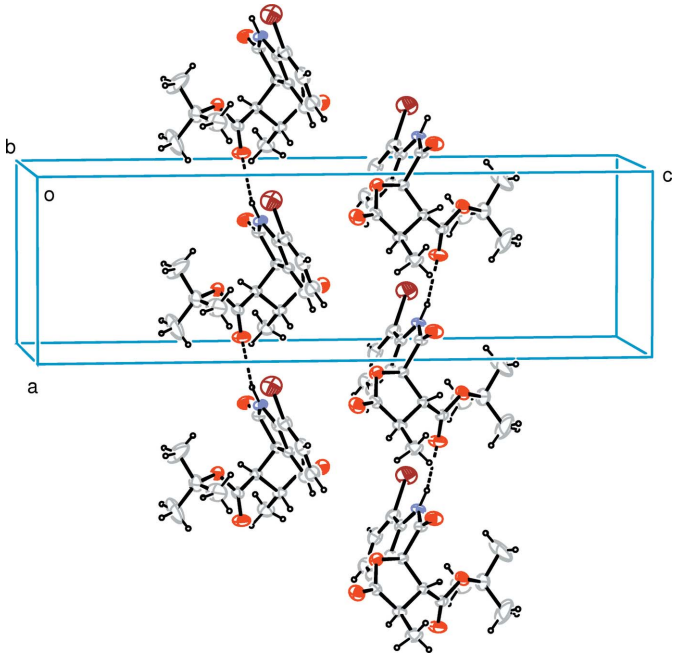


Figure 2
The crystal packing of the title compound showing the chain structure. Hydrogen bonds are drawn as dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.86	2.15	2.944 (4)	154
C12—H12*A*···O1^{ii}	0.96	2.59	3.415 (6)	144

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{18}BrNO_5$
M_r	396.23
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, *b*, *c* (Å)	7.7040 (18), 9.325 (2), 25.540 (6)
V (Å^3)	1834.8 (7)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	2.27
Crystal size (mm)	0.2 × 0.18 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.623, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15033, 4233, 2395
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.098, 1.00
No. of reflections	4233
No. of parameters	221
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.41
Absolute structure	Flack *x* determined using 776 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)
Absolute structure parameter	0.045 (8)

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

IUCrData (2017). **2**, x170412 [https://doi.org/10.1107/S2414314617004126]

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Crystal data

$C_{17}H_{18}BrNO_5$
M_r = 396.23
Orthorhombic, $P2_12_12_1$
a = 7.7040 (18) Å
b = 9.325 (2) Å
c = 25.540 (6) Å
V = 1834.8 (7) Å^3
Z = 4
$F(000)$ = 808
D_x = 1.434 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2454 reflections
θ = 2.7–21.2°
μ = 2.27 mm^{-1}
T = 296 K
Block, colourless
0.2 × 0.18 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.623, T_{max} = 0.746
15033 measured reflections
4233 independent reflections
2395 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.6°, θ_{min} = 2.3°
h = −8→10
k = −12→12
l = −30→33

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.098
S = 1.00
4233 reflections
221 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 0.3907P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Absolute structure: Flack x determined using 776 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)
Absolute structure parameter: 0.045 (8)

Special details

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

Refinement. H atoms were placed in calculated positions and refined in riding mode with C—H distances 0.93, 0.97 and 0.98 Å, for aryl, methylene and methine H atoms; U_{iso}(H) = 1.2U_{eq} of the carrier atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.15873 (10)	0.22044 (8)	0.38775 (3)	0.1040 (3)
O1	0.3158 (4)	0.7880 (4)	0.37124 (14)	0.0668 (10)
O2	0.5385 (4)	0.7426 (3)	0.46266 (11)	0.0491 (8)
O3	0.6907 (5)	0.9121 (4)	0.50236 (13)	0.0632 (9)
O4	0.9313 (4)	0.5704 (4)	0.35412 (15)	0.0710 (11)
O5	0.6721 (4)	0.5706 (4)	0.31393 (12)	0.0589 (9)
N1	0.2987 (4)	0.5445 (4)	0.38441 (15)	0.0456 (9)
H1	0.200354	0.527700	0.369701	0.055*
C1	0.3996 (5)	0.4405 (5)	0.40811 (16)	0.0403 (11)
C2	0.3682 (7)	0.2968 (5)	0.41343 (19)	0.0555 (13)
C3	0.4891 (8)	0.2103 (6)	0.4385 (2)	0.0669 (15)
H3	0.467995	0.112717	0.442548	0.080*
C4	0.6398 (8)	0.2692 (6)	0.4573 (2)	0.0665 (14)
H4	0.721780	0.210557	0.473309	0.080*
C5	0.6716 (7)	0.4152 (5)	0.45275 (18)	0.0541 (12)
H5	0.773123	0.454872	0.466110	0.065*
C6	0.5513 (5)	0.4998 (5)	0.42830 (17)	0.0393 (10)
C7	0.5467 (5)	0.6563 (5)	0.41609 (17)	0.0390 (10)
C8	0.3726 (5)	0.6752 (5)	0.38708 (19)	0.0438 (10)
C9	0.7002 (5)	0.7210 (4)	0.38479 (17)	0.0404 (9)
H9	0.654755	0.798353	0.362711	0.049*
C10	0.8135 (5)	0.7878 (5)	0.42684 (17)	0.0445 (10)
H10	0.891596	0.714153	0.440759	0.053*
C11	0.6835 (6)	0.8254 (5)	0.46789 (18)	0.0448 (11)
C12	0.9204 (7)	0.9154 (6)	0.4098 (2)	0.0705 (16)
H12A	1.003919	0.885478	0.384145	0.106*
H12B	0.979583	0.954926	0.439560	0.106*
H12C	0.845509	0.986824	0.394879	0.106*
C13	0.7859 (6)	0.6122 (5)	0.34975 (19)	0.0468 (12)
C14	0.7091 (8)	0.4580 (7)	0.2748 (2)	0.0746 (17)
C15	0.5424 (9)	0.4487 (10)	0.2447 (3)	0.148 (4)
H15A	0.447612	0.435786	0.268690	0.223*
H15B	0.547288	0.368761	0.221100	0.223*
H15C	0.525443	0.535527	0.225212	0.223*
C16	0.7422 (9)	0.3181 (8)	0.3026 (3)	0.101 (2)
H16A	0.844640	0.326657	0.323833	0.151*
H16B	0.758473	0.243214	0.277316	0.151*
H16C	0.644720	0.295365	0.324514	0.151*
C17	0.8646 (12)	0.5021 (10)	0.2419 (3)	0.150 (4)
H17A	0.838599	0.589484	0.223605	0.225*
H17B	0.890277	0.427893	0.216985	0.225*
H17C	0.963218	0.516752	0.264217	0.225*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0990 (5)	0.0819 (4)	0.1311 (6)	−0.0540 (4)	−0.0142 (5)	−0.0005 (5)
O1	0.0514 (19)	0.056 (2)	0.093 (3)	0.0064 (18)	−0.0066 (19)	0.011 (2)
O2	0.0485 (17)	0.052 (2)	0.0472 (18)	−0.0080 (16)	0.0063 (15)	−0.0150 (16)
O3	0.067 (2)	0.060 (2)	0.063 (2)	−0.0021 (19)	−0.0095 (19)	−0.0219 (19)
O4	0.037 (2)	0.086 (3)	0.090 (3)	−0.0005 (19)	−0.0036 (18)	−0.031 (2)
O5	0.0500 (18)	0.081 (2)	0.0455 (19)	0.004 (2)	−0.0080 (17)	−0.0234 (17)
N1	0.0298 (18)	0.051 (2)	0.056 (2)	−0.0074 (16)	−0.0081 (19)	−0.005 (2)
C1	0.040 (2)	0.040 (2)	0.041 (3)	−0.004 (2)	0.008 (2)	0.000 (2)
C2	0.062 (3)	0.045 (3)	0.060 (3)	−0.017 (3)	0.012 (3)	−0.001 (2)
C3	0.088 (4)	0.046 (3)	0.067 (4)	0.001 (3)	0.017 (3)	0.011 (3)
C4	0.072 (4)	0.063 (4)	0.065 (3)	0.016 (3)	0.006 (3)	0.015 (3)
C5	0.052 (3)	0.055 (3)	0.055 (3)	0.005 (3)	0.000 (3)	0.002 (2)
C6	0.033 (2)	0.044 (3)	0.040 (3)	−0.002 (2)	0.003 (2)	−0.002 (2)
C7	0.034 (2)	0.044 (3)	0.039 (3)	−0.0039 (19)	0.002 (2)	−0.010 (2)
C8	0.033 (2)	0.049 (2)	0.050 (3)	−0.0010 (19)	0.000 (2)	0.000 (3)
C9	0.035 (2)	0.045 (2)	0.041 (2)	−0.0041 (19)	−0.001 (2)	−0.002 (2)
C10	0.036 (2)	0.043 (2)	0.055 (3)	−0.007 (2)	−0.005 (2)	−0.005 (2)
C11	0.046 (3)	0.045 (3)	0.043 (3)	−0.003 (2)	−0.010 (2)	−0.001 (2)
C12	0.058 (3)	0.068 (4)	0.085 (4)	−0.024 (3)	0.003 (3)	−0.007 (3)
C13	0.037 (3)	0.059 (3)	0.044 (3)	−0.012 (2)	0.004 (2)	−0.001 (2)
C14	0.082 (4)	0.091 (5)	0.051 (3)	0.000 (4)	0.006 (3)	−0.029 (3)
C15	0.127 (6)	0.192 (9)	0.125 (7)	0.047 (7)	−0.081 (6)	−0.092 (7)
C16	0.090 (5)	0.096 (6)	0.116 (5)	−0.007 (4)	0.003 (4)	−0.046 (5)
C17	0.182 (8)	0.187 (9)	0.081 (5)	−0.037 (8)	0.068 (6)	−0.049 (6)

Geometric parameters (Å, º)

Br1—C2	1.882 (5)	C7—C9	1.550 (6)
O1—C8	1.209 (5)	C9—H9	0.9800
O2—C7	1.438 (5)	C9—C10	1.518 (6)
O2—C11	1.364 (5)	C9—C13	1.506 (6)
O3—C11	1.196 (5)	C10—H10	0.9800
O4—C13	1.191 (5)	C10—C11	1.492 (7)
O5—C13	1.325 (5)	C10—C12	1.511 (6)
O5—C14	1.478 (6)	C12—H12A	0.9600
N1—H1	0.8600	C12—H12B	0.9600
N1—C1	1.382 (5)	C12—H12C	0.9600
N1—C8	1.347 (5)	C14—C15	1.498 (8)
C1—C2	1.369 (6)	C14—C16	1.508 (10)
C1—C6	1.392 (6)	C14—C17	1.520 (9)
C2—C3	1.389 (7)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C3—C4	1.371 (7)	C15—H15C	0.9600
C4—H4	0.9300	C16—H16A	0.9600
C4—C5	1.388 (7)	C16—H16B	0.9600

C5—H5	0.9300	C16—H16C	0.9600
C5—C6	1.368 (6)	C17—H17A	0.9600
C6—C7	1.493 (6)	C17—H17B	0.9600
C7—C8	1.543 (6)	C17—H17C	0.9600
C11—O2—C7	111.2 (3)	C11—C10—H10	108.8
C13—O5—C14	123.2 (4)	C11—C10—C12	112.6 (4)
C1—N1—H1	124.0	C12—C10—C9	115.6 (4)
C8—N1—H1	124.0	C12—C10—H10	108.8
C8—N1—C1	112.0 (3)	O2—C11—C10	110.4 (4)
N1—C1—C6	110.9 (4)	O3—C11—O2	119.5 (4)
C2—C1—N1	129.1 (4)	O3—C11—C10	130.2 (4)
C2—C1—C6	120.0 (4)	C10—C12—H12A	109.5
C1—C2—Br1	119.2 (4)	C10—C12—H12B	109.5
C1—C2—C3	119.7 (5)	C10—C12—H12C	109.5
C3—C2—Br1	121.1 (4)	H12A—C12—H12B	109.5
C2—C3—H3	120.1	H12A—C12—H12C	109.5
C4—C3—C2	119.8 (5)	H12B—C12—H12C	109.5
C4—C3—H3	120.1	O4—C13—O5	126.2 (5)
C3—C4—H4	119.6	O4—C13—C9	125.2 (4)
C3—C4—C5	120.9 (5)	O5—C13—C9	108.5 (4)
C5—C4—H4	119.6	O5—C14—C15	102.9 (5)
C4—C5—H5	120.5	O5—C14—C16	109.1 (5)
C6—C5—C4	119.0 (5)	O5—C14—C17	109.5 (5)
C6—C5—H5	120.5	C15—C14—C16	109.6 (7)
C1—C6—C7	106.9 (4)	C15—C14—C17	114.1 (6)
C5—C6—C1	120.6 (4)	C16—C14—C17	111.2 (6)
C5—C6—C7	132.5 (4)	C14—C15—H15A	109.5
O2—C7—C6	112.1 (4)	C14—C15—H15B	109.5
O2—C7—C8	107.2 (3)	C14—C15—H15C	109.5
O2—C7—C9	104.0 (3)	H15A—C15—H15B	109.5
C6—C7—C8	103.5 (3)	H15A—C15—H15C	109.5
C6—C7—C9	118.1 (4)	H15B—C15—H15C	109.5
C8—C7—C9	111.8 (3)	C14—C16—H16A	109.5
O1—C8—N1	128.2 (4)	C14—C16—H16B	109.5
O1—C8—C7	125.1 (4)	C14—C16—H16C	109.5
N1—C8—C7	106.8 (4)	H16A—C16—H16B	109.5
C7—C9—H9	108.1	H16A—C16—H16C	109.5
C10—C9—C7	103.5 (3)	H16B—C16—H16C	109.5
C10—C9—H9	108.1	C14—C17—H17A	109.5
C13—C9—C7	112.2 (3)	C14—C17—H17B	109.5
C13—C9—H9	108.1	C14—C17—H17C	109.5
C13—C9—C10	116.4 (4)	H17A—C17—H17B	109.5
C9—C10—H10	108.8	H17A—C17—H17C	109.5
C11—C10—C9	102.0 (3)	H17B—C17—H17C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.86	2.15	2.944 (4)	154

Symmetry code: (i) $x-1, y, z$.