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(*S*)-3-[(*S*,*E*)-4-(4-Chlorophenyl)-1-nitrobut-3-en-2-yl]thian-4-one

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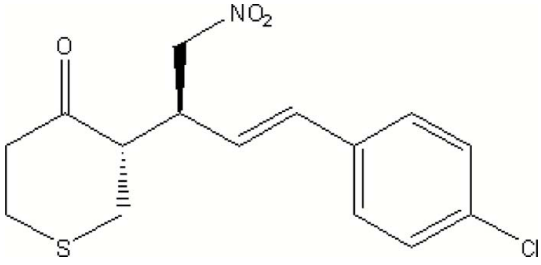
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.090; data-to-parameter ratio = 19.2.

The title compound, $C_{15}H_{16}ClNO_3S$, was obtained by the organocatalytic asymmetric Michael addition of thian-4-one to 1-chloro-4-[(1*E*,3*E*)-4-nitrobuta-1,3-dienyl]benzene. The double bond has an *E* configuration and the thian-4-one six-membered ring adopts a chair conformation. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonds.

Related literature

For asymmetric Michael addition employing chiral organocatalysts, see: Belot *et al.* (2008); Dalko & Moisan (2004); Xu *et al.* (2008); Yu *et al.* (2009).



Experimental

Crystal data

$C_{15}H_{16}ClNO_3S$
M_r = 325.80
Orthorhombic, $P2_12_12_1$
a = 5.5220 (2) Å
b = 8.3833 (3) Å
c = 34.7414 (12) Å
V = 1608.27 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 296 K
0.34 × 0.28 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.865, T_{max} = 0.932
15960 measured reflections
3666 independent reflections
2918 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.090
S = 1.00
3666 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Absolute structure: Flack (1983), 1501 Friedel pairs
Flack parameter: 0.03 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7B···O2^{i}	0.97	2.45	3.368 (4)	158
C2—H2B···O1^{i}	0.97	2.58	3.484 (3)	156

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

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We acknowledge the help of Professor Jianming Gu of Zhejiang University. We are also grateful for financial support from the Catalytic Hydrogenation Research Center of Zhejiang University of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2005).

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supporting information

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(*S*)-3-[(*S*,*E*)-4-(4-Chlorophenyl)-1-nitrobut-3-en-2-yl]thian-4-one

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S1. Comment

As one of the most important chiral carbon-carbon bond-forming processes in modern organic chemistry, the field of asymmetric Michael addition employing chiral organocatalysts has gained more and more attention and become the focus of intense research efforts (Dalko & Moisan, 2004; Belot *et al.*, 2008; Yu *et al.*, 2009). Consequently, we have synthesized a series of Michael adducts by employing *cyclo*-ketones to nitrodienes in our laboratory. We report here the crystal structure and the absolute configuration of the title compound, (I). The six-membered ring of thian-4-one adopts a chair conformation. The C8═C9 bond involves the *E* configuration with the C6—C8—C9—C10 torsion angle of 178.1 (17)°. The conformation of (I) is stabilized by weak intermolecular C7—H7B···O2 and C2—H2B···O1 interaction, Table 1, Fig 2.

S2. Experimental

A 1,2-dichloroethane (0.5 ml) solution of thian-4-one (0.25 mmol) and 1-chloro-4-((1*E*,3*E*)-4-nitrobuta-1,3-dienyl)benzene (0.25 mmol) in the presence of (*S*)-1-methyl-2-(pyrrolidin-2-ylmethylthio)-1*H*-imidazole (0.025 mmol) as amine catalyst and (*R*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-2-phenylacetic acid (0.025 mmol) as acid module at room tempreture was stirred vigorously (Xu *et al.*, 2008). After completion of the reaction, the resulted reaction mixture was purified directly by silica gel column chromatography (eluent: petroleum ether-EtOAc). Single crystals were obtained by slow evaporation of an ethanol-EtOAc solution.

S3. Refinement

All carbon-bonded H atoms were placed in calculated positions with C—H = 0.93 Å (aromatic), C—H = 0.98 Å (sp^2), C—H = 0.97 Å (sp^3) and refined using a riding model, with U_{iso}(H)=1.2$_{eq}$(C).

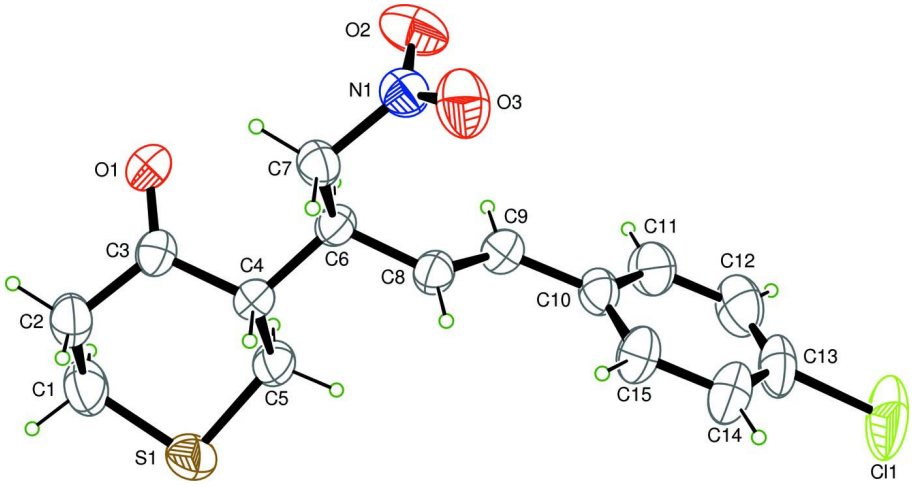

Figure 1

The asymmetric unit of the title compound with the atomic labeling scheme; displacement ellipsoids are drawn at the 50% probability level.

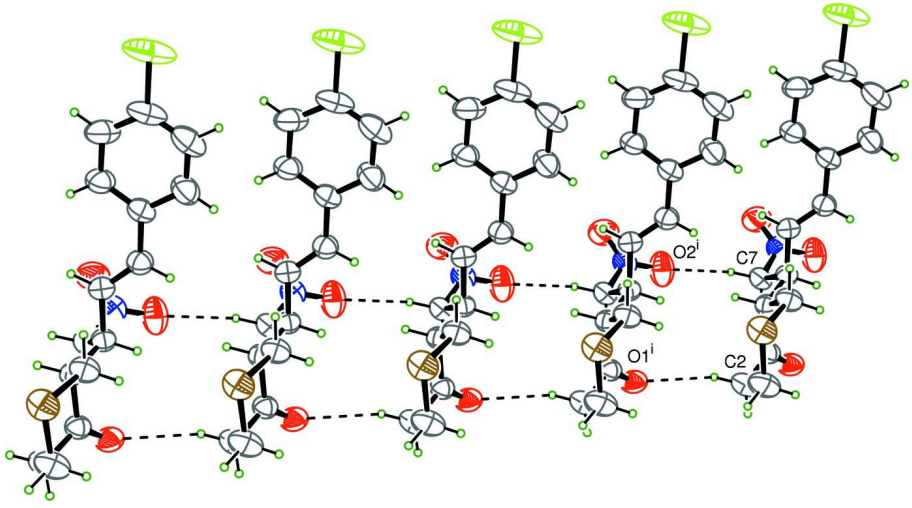

Figure 2

The view of intermolecular interaction illustrated as dash lines.

(*S*)-3-[(*S*,*E*)-4-(4-Chlorophenyl)-1-nitrobut-3-en- 2-yl]thian-4-one

Crystal data

$C_{15}H_{16}ClNO_3S$
M_r = 325.80
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 5.5220 (2) Å
b = 8.3833 (3) Å
c = 34.7414 (12) Å
V = 1608.27 (10) Å^3
Z = 4
F(000) = 680
D_x = 1.346 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 12670 reflections
θ = 3.0–27.5°
μ = 0.38 mm^{-1}
T = 296 K
Block, colorless
0.34 × 0.28 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: rotating anode
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.865, T_{max} = 0.932

15960 measured reflections
3666 independent reflections
2918 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −7→6
k = −10→10
l = −45→45

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.090
S = 1.00
3666 reflections
191 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.182P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0061 (13)
Absolute structure: Flack (1983), 1501 Friedel pairs
Absolute structure parameter: 0.03 (7)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C13	−0.1203 (6)	0.9836 (3)	0.01706 (6)	0.0747 (7)
S1	0.55221 (10)	0.17716 (7)	0.117335 (15)	0.06690 (17)
Cl1	−0.1215 (2)	1.11399 (9)	−0.022097 (18)	0.1245 (4)
C6	0.0659 (3)	0.5010 (2)	0.16547 (4)	0.0447 (4)
H6	−0.0877	0.4429	0.1634	0.054*
O1	0.0671 (3)	0.22754 (16)	0.21132 (4)	0.0613 (3)
C4	0.2745 (3)	0.3803 (2)	0.16338 (4)	0.0444 (4)
H4	0.4264	0.4371	0.1684	0.053*
N1	−0.1196 (3)	0.7113 (2)	0.20576 (4)	0.0555 (4)
C5	0.2912 (4)	0.3026 (2)	0.12328 (5)	0.0555 (4)
H5A	0.2954	0.3859	0.1039	0.067*
H5B	0.1466	0.2394	0.1189	0.067*

C8	0.0775 (3)	0.6222 (2)	0.13348 (5)	0.0476 (4)
H8	0.2189	0.6816	0.1310	0.057*
C7	0.0736 (3)	0.5865 (2)	0.20462 (5)	0.0496 (4)
H7A	0.0481	0.5101	0.2252	0.059*
H7B	0.2309	0.6356	0.2083	0.059*
C3	0.2507 (3)	0.2460 (2)	0.19269 (5)	0.0492 (4)
C9	−0.0980 (3)	0.6500 (2)	0.10879 (5)	0.0522 (4)
H9	−0.2357	0.5869	0.1113	0.063*
O3	−0.0587 (3)	0.84976 (18)	0.20651 (5)	0.0819 (5)
C2	0.4615 (4)	0.1319 (3)	0.19524 (6)	0.0669 (5)
H2A	0.4315	0.0550	0.2155	0.080*
H2B	0.6073	0.1906	0.2017	0.080*
C15	0.0781 (4)	0.8818 (2)	0.07241 (5)	0.0631 (5)
H15	0.2076	0.8847	0.0895	0.076*
O2	−0.3289 (3)	0.6674 (2)	0.20483 (5)	0.0838 (5)
C10	−0.1020 (3)	0.7694 (2)	0.07758 (5)	0.0519 (4)
C1	0.4989 (5)	0.0446 (3)	0.15734 (6)	0.0757 (6)
H1A	0.3568	−0.0196	0.1519	0.091*
H1B	0.6359	−0.0270	0.1599	0.091*
C11	−0.2923 (4)	0.7687 (3)	0.05161 (6)	0.0691 (6)
H11	−0.4169	0.6951	0.0547	0.083*
C12	−0.3010 (5)	0.8756 (3)	0.02114 (6)	0.0819 (7)
H12	−0.4291	0.8732	0.0038	0.098*
C14	0.0704 (5)	0.9901 (3)	0.04238 (6)	0.0745 (6)
H14	0.1920	1.0658	0.0394	0.089*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C13	0.122 (2)	0.0560 (12)	0.0463 (9)	0.0278 (14)	−0.0102 (12)	0.0075 (8)
S1	0.0674 (3)	0.0707 (3)	0.0626 (3)	0.0147 (3)	0.0095 (2)	−0.0069 (2)
Cl1	0.2253 (11)	0.0834 (4)	0.0646 (3)	0.0384 (6)	−0.0194 (5)	0.0284 (3)
C6	0.0489 (8)	0.0463 (8)	0.0387 (7)	−0.0005 (8)	0.0019 (8)	0.0031 (6)
O1	0.0645 (8)	0.0616 (8)	0.0578 (7)	−0.0018 (7)	0.0091 (7)	0.0157 (6)
C4	0.0466 (8)	0.0457 (9)	0.0410 (8)	−0.0008 (7)	0.0026 (7)	0.0035 (7)
N1	0.0581 (9)	0.0606 (10)	0.0478 (8)	0.0061 (8)	−0.0027 (7)	−0.0059 (7)
C5	0.0667 (10)	0.0568 (11)	0.0428 (8)	0.0090 (9)	0.0022 (8)	0.0012 (8)
C8	0.0539 (10)	0.0429 (8)	0.0460 (8)	0.0007 (8)	0.0025 (8)	0.0031 (7)
C7	0.0516 (9)	0.0514 (10)	0.0457 (8)	0.0085 (8)	−0.0046 (8)	−0.0011 (7)
C3	0.0569 (10)	0.0486 (10)	0.0420 (8)	0.0003 (8)	−0.0041 (8)	0.0029 (7)
C9	0.0555 (10)	0.0536 (10)	0.0475 (9)	−0.0008 (9)	0.0003 (8)	0.0036 (7)
O3	0.1031 (12)	0.0509 (9)	0.0918 (11)	0.0066 (9)	−0.0103 (10)	−0.0046 (8)
C2	0.0719 (12)	0.0675 (13)	0.0615 (11)	0.0137 (11)	−0.0082 (10)	0.0124 (9)
C15	0.0780 (13)	0.0597 (11)	0.0516 (10)	−0.0048 (11)	−0.0136 (10)	0.0107 (8)
O2	0.0491 (8)	0.1071 (13)	0.0954 (11)	0.0053 (9)	0.0029 (7)	−0.0237 (11)
C10	0.0614 (10)	0.0519 (10)	0.0423 (8)	0.0094 (9)	−0.0049 (8)	0.0009 (7)
C1	0.0906 (16)	0.0619 (13)	0.0746 (13)	0.0252 (12)	−0.0040 (12)	0.0032 (10)
C11	0.0678 (12)	0.0778 (15)	0.0618 (11)	0.0038 (11)	−0.0150 (10)	0.0045 (10)

C12	0.0969 (18)	0.0897 (18)	0.0590 (11)	0.0216 (16)	−0.0267 (12)	0.0023 (12)
C14	0.1063 (17)	0.0566 (11)	0.0606 (11)	−0.0037 (14)	−0.0062 (13)	0.0150 (9)

Geometric parameters (Å, º)

C13—C12	1.355 (4)	C8—H8	0.9300
C13—C14	1.373 (4)	C7—H7A	0.9700
C13—Cl1	1.745 (2)	C7—H7B	0.9700
S1—C5	1.7959 (19)	C3—C2	1.509 (3)
S1—C1	1.804 (2)	C9—C10	1.476 (2)
C6—C8	1.507 (2)	C9—H9	0.9300
C6—C4	1.534 (2)	C2—C1	1.520 (3)
C6—C7	1.539 (2)	C2—H2A	0.9700
C6—H6	0.9800	C2—H2B	0.9700
O1—C3	1.213 (2)	C15—C10	1.382 (3)
C4—C3	1.524 (2)	C15—C14	1.383 (3)
C4—C5	1.541 (2)	C15—H15	0.9300
C4—H4	0.9800	C10—C11	1.385 (3)
N1—O3	1.209 (2)	C1—H1A	0.9700
N1—O2	1.213 (2)	C1—H1B	0.9700
N1—C7	1.494 (2)	C11—C12	1.388 (3)
C5—H5A	0.9700	C11—H11	0.9300
C5—H5B	0.9700	C12—H12	0.9300
C8—C9	1.315 (3)	C14—H14	0.9300
C12—C13—C14	121.62 (19)	O1—C3—C2	122.19 (16)
C12—C13—Cl1	119.81 (19)	O1—C3—C4	121.53 (16)
C14—C13—Cl1	118.5 (2)	C2—C3—C4	116.17 (15)
C5—S1—C1	98.11 (10)	C8—C9—C10	127.61 (17)
C8—C6—C4	112.19 (13)	C8—C9—H9	116.2
C8—C6—C7	109.65 (14)	C10—C9—H9	116.2
C4—C6—C7	109.17 (13)	C3—C2—C1	111.04 (16)
C8—C6—H6	108.6	C3—C2—H2A	109.4
C4—C6—H6	108.6	C1—C2—H2A	109.4
C7—C6—H6	108.6	C3—C2—H2B	109.4
C3—C4—C6	113.01 (13)	C1—C2—H2B	109.4
C3—C4—C5	107.25 (14)	H2A—C2—H2B	108.0
C6—C4—C5	111.50 (13)	C10—C15—C14	121.53 (19)
C3—C4—H4	108.3	C10—C15—H15	119.2
C6—C4—H4	108.3	C14—C15—H15	119.2
C5—C4—H4	108.3	C11—C10—C15	117.69 (18)
O3—N1—O2	123.82 (19)	C11—C10—C9	119.13 (18)
O3—N1—C7	118.28 (17)	C15—C10—C9	123.17 (16)
O2—N1—C7	117.86 (18)	C2—C1—S1	113.15 (17)
C4—C5—S1	113.56 (12)	C2—C1—H1A	108.9
C4—C5—H5A	108.9	S1—C1—H1A	108.9
S1—C5—H5A	108.9	C2—C1—H1B	108.9
C4—C5—H5B	108.9	S1—C1—H1B	108.9

S1—C5—H5B	108.9	H1A—C1—H1B	107.8
H5A—C5—H5B	107.7	C10—C11—C12	121.3 (2)
C9—C8—C6	124.67 (17)	C10—C11—H11	119.3
C9—C8—H8	117.7	C12—C11—H11	119.3
C6—C8—H8	117.7	C13—C12—C11	119.1 (2)
N1—C7—C6	109.27 (13)	C13—C12—H12	120.5
N1—C7—H7A	109.8	C11—C12—H12	120.5
C6—C7—H7A	109.8	C13—C14—C15	118.7 (2)
N1—C7—H7B	109.8	C13—C14—H14	120.6
C6—C7—H7B	109.8	C15—C14—H14	120.6
H7A—C7—H7B	108.3		

C8—C6—C4—C3	−173.58 (14)	C6—C8—C9—C10	178.10 (17)
C7—C6—C4—C3	64.67 (18)	O1—C3—C2—C1	114.2 (2)
C8—C6—C4—C5	−52.68 (19)	C4—C3—C2—C1	−62.0 (2)
C7—C6—C4—C5	−174.43 (14)	C14—C15—C10—C11	−0.1 (3)
C3—C4—C5—S1	−62.42 (17)	C14—C15—C10—C9	178.8 (2)
C6—C4—C5—S1	173.37 (12)	C8—C9—C10—C11	172.61 (19)
C1—S1—C5—C4	56.38 (16)	C8—C9—C10—C15	−6.3 (3)
C4—C6—C8—C9	123.85 (19)	C3—C2—C1—S1	58.3 (2)
C7—C6—C8—C9	−114.67 (19)	C5—S1—C1—C2	−53.16 (18)
O3—N1—C7—C6	−112.49 (18)	C15—C10—C11—C12	0.8 (3)
O2—N1—C7—C6	65.5 (2)	C9—C10—C11—C12	−178.2 (2)
C8—C6—C7—N1	53.18 (19)	C14—C13—C12—C11	−0.2 (4)
C4—C6—C7—N1	176.45 (14)	Cl1—C13—C12—C11	177.53 (19)
C6—C4—C3—O1	9.8 (2)	C10—C11—C12—C13	−0.6 (4)
C5—C4—C3—O1	−113.44 (18)	C12—C13—C14—C15	0.9 (4)
C6—C4—C3—C2	−173.94 (15)	Cl1—C13—C14—C15	−176.91 (18)
C5—C4—C3—C2	62.78 (19)	C10—C15—C14—C13	−0.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*B*···O2^{i}	0.97	2.45	3.368 (4)	158
C2—H2*B*···O1^{i}	0.97	2.58	3.484 (3)	156

Symmetry code: (i) *x*+1, *y*, *z*.