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## Structure Reports

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# (S)-2-[(S,E)-4-(4-Chlorophenyl)-1-nitrobut-3-en-2-yl]cyclohexanone

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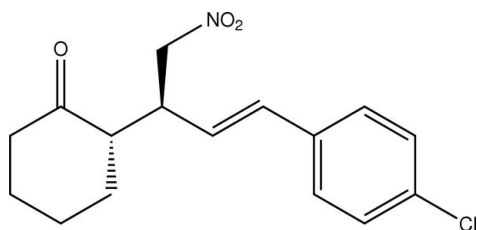
Received 11 July 2009; accepted 23 July 2009

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.124; data-to-parameter ratio = 11.2.

The title compound,  $\text{C}_{16}\text{H}_{18}\text{ClNO}_3$ , was obtained by the organocatalytic asymmetric Michael addition of cyclohexanone to 1-chloro-4-[(1*E*,3*E*)-4-nitrobuta-1,3-dienyl]benzene. The double bond has an *E* configuration. The cyclohexanone ring adopts a chair conformation. The conformation of the molecule is stabilized by a weak intramolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond.

## Related literature

For asymmetric Michael addition reactions employing chiral organocatalysts, see: Belot *et al.* (2008); Dalko & Moisan (2004); Yu *et al.* (2009). For details of the synthesis, see: Xu *et al.* (2008); For puckering parameters, see: Cremer & Pople (1975).



## Experimental

## Crystal data

 $\text{C}_{16}\text{H}_{18}\text{ClNO}_3$ 
 $M_r = 307.78$ 

 Orthorhombic,  $P2_12_12_1$ 
 $a = 5.5300$  (3) Å

 $b = 8.5175$  (6) Å

 $c = 34.0903$  (18) Å

 $V = 1605.71$  (17) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation  
 $\mu = 0.25$  mm<sup>-1</sup>
 $T = 296$  K  
 $0.48 \times 0.32 \times 0.28$  mm

## Data collection

 Rigaku R-Axis RAPID  
diffractometer  
Absorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
 $T_{\min} = 0.879$ ,  $T_{\max} = 0.933$ 

 15644 measured reflections  
2148 independent reflections  
1391 reflections with  $F^2 > 2\sigma(F^2)$   
 $R_{\text{int}} = 0.034$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.124$   
 $S = 1.00$   
2148 reflections  
192 parameters  
H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
1486 Friedel pairs  
Flack parameter: 0.27 (18)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C8}-\text{H81}\cdots\text{O1}$	0.97	2.37	3.020 (4)	124

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

We acknowledge the help of Professor Jianming Gu of Zhejiang University. We are also grateful for financial support by 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: BX2224).

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## supporting information

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**(S)-2-[(S,E)-4-(4-Chlorophenyl)-1-nitrobut-3-en-2-yl]cyclohexanone****Zhaobo Li, Yi Guo, Bailin Li and Shuping Luo****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 cyclohexanone ring adopts a chair conformation as shown by the Cremer & Pople (1975) puckering parameters [ $Q_T = 0.568$  (4) Å,  $\theta = 3.9$  (4)°,  $\varphi = 355$  (6)°]. The C1—C9—C10—C11 torsion angle of 175.2 (3) confirms the *E* configuration of the molecule with respect to the C9=C10 bond. The conformation of (I) is stabilized by one weak intramolecular C—H···O hydrogen bond, Table 1, Fig 1.

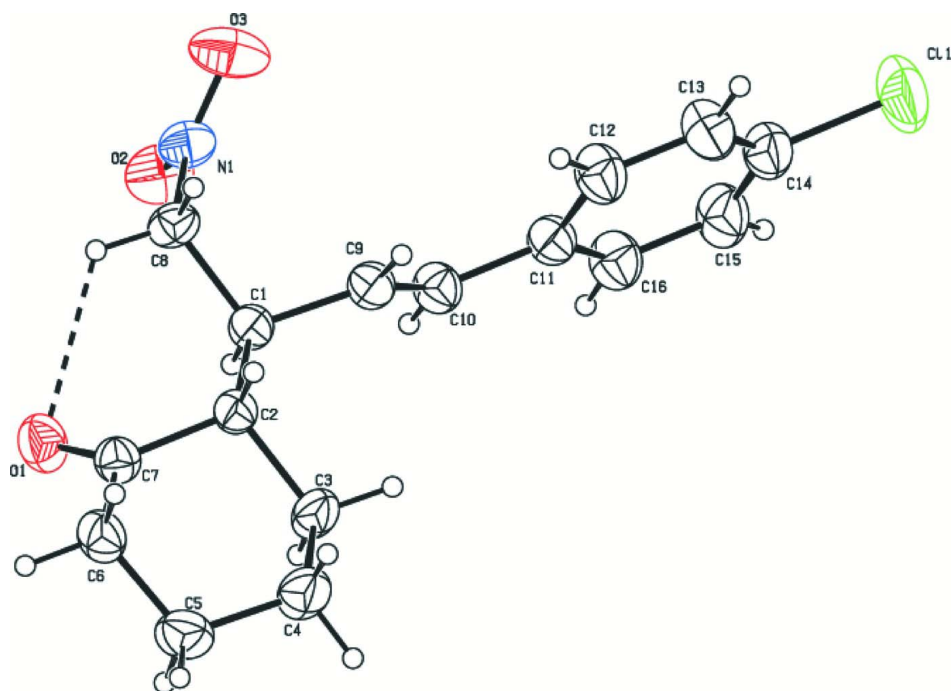
**S2. Experimental**

A 1,2-dichloroethane (0.5 ml) solution of cyclohexanone (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 temperature 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-dichloromethane 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*<sup>2</sup>), C—H = 0.97 Å (*sp*<sup>3</sup>) and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2_{\text{eq}}(\text{C})$ .

The absolute configuration of this compound is established from both the diffraction data and the absolute configuration of a similar compound reported in Xu *et al.* (2008), therein the organocatalyst has the same structure as in the title compound.

**Figure 1**

The asymmetric unit of the title compound with the atomic labeling scheme; displacement ellipsoids are drawn at the 30% probability level. Dotted lines show hydrogen bonding.

**(I)***Crystal data*

$C_{16}H_{18}ClNO_3$

$M_r = 307.78$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.5300$  (3) Å

$b = 8.5175$  (6) Å

$c = 34.0903$  (18) Å

$V = 1605.71$  (17) Å<sup>3</sup>

$Z = 4$

$F(000) = 648.00$

$D_x = 1.273$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 9533 reflections

$\theta = 3.0\text{--}27.4^\circ$

$\mu = 0.25$  mm<sup>-1</sup>

$T = 296$  K

Chunk, colourless

$0.48 \times 0.32 \times 0.28$  mm

*Data collection*

Rigaku R-Axis RAPID

diffractometer

Detector resolution: 10.00 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.879$ ,  $T_{\max} = 0.933$

15644 measured reflections

2148 independent reflections

1391 reflections with  $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 27.4^\circ$

$h = -7 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -43 \rightarrow 44$

*Refinement*

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.124$

$S = 1.00$

2148 reflections

192 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 1.2P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 2008)  
 Extinction coefficient: 0.027 (2)  
 Absolute structure: Flack (1983), 1486 Friedel pairs  
 Absolute structure parameter: 0.27 (18)

*Special details*

**Geometry.** ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

**Refinement.** Refinement using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on *F*<sup>2</sup>. *R*-factor (*gt*) are based on *F*. The threshold expression of *F*<sup>2</sup> > 2.0  $\sigma(F^2)$  is used only for calculating *R*-factor (*gt*).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
Cl1	0.6163 (3)	0.6280 (2)	1.07164 (3)	0.1211 (6)
O1	0.9458 (5)	0.1436 (3)	0.77121 (8)	0.0735 (8)
O2	1.2699 (5)	0.5169 (4)	0.83637 (10)	0.0841 (9)
O3	0.9882 (6)	0.6855 (3)	0.84395 (12)	0.1019 (12)
N1	1.0607 (6)	0.5581 (4)	0.83299 (10)	0.0633 (8)
C1	0.8554 (6)	0.3047 (4)	0.84336 (9)	0.0497 (8)
C2	0.6749 (6)	0.1873 (4)	0.82559 (9)	0.0486 (7)
C3	0.6291 (9)	0.0456 (4)	0.85244 (10)	0.0705 (12)
C4	0.4412 (9)	-0.0647 (5)	0.83580 (12)	0.0801 (13)
C5	0.5077 (9)	-0.1218 (5)	0.79532 (12)	0.0764 (12)
C6	0.5632 (7)	0.0143 (4)	0.76796 (10)	0.0643 (10)
C7	0.7474 (7)	0.1200 (4)	0.78612 (10)	0.0532 (8)
C8	0.8838 (7)	0.4463 (4)	0.81622 (10)	0.0562 (9)
C9	0.7707 (7)	0.3624 (4)	0.88279 (9)	0.0552 (8)
C10	0.8919 (7)	0.3590 (4)	0.91561 (10)	0.0601 (9)
C11	0.8194 (7)	0.4250 (4)	0.95375 (10)	0.0596 (9)
C12	0.6144 (9)	0.5173 (5)	0.95838 (12)	0.0754 (12)
C13	0.5508 (9)	0.5783 (5)	0.99460 (12)	0.0809 (13)
C14	0.6932 (9)	0.5491 (5)	1.02636 (12)	0.0754 (12)
C15	0.8973 (10)	0.4591 (6)	1.02286 (12)	0.0837 (14)
C16	0.9577 (8)	0.3972 (5)	0.98675 (11)	0.0726 (12)
H1	1.0127	0.2531	0.8464	0.060*
H2	0.5206	0.2421	0.8221	0.058*
H9	0.6159	0.4048	0.8839	0.066*
H10	1.0415	0.3092	0.9148	0.072*
H12	0.5177	0.5386	0.9367	0.090*
H13	0.4118	0.6389	0.9972	0.097*
H15	0.9943	0.4398	1.0446	0.100*
H16	1.0952	0.3350	0.9846	0.087*
H31	0.7795	-0.0114	0.8558	0.085*
H32	0.5737	0.0833	0.8777	0.085*
H41	0.4259	-0.1546	0.8531	0.096*
H42	0.2875	-0.0101	0.8344	0.096*
H51	0.3737	-0.1816	0.7847	0.092*

H52	0.6493	-0.1886	0.7972	0.092*
H61	0.6255	-0.0263	0.7434	0.077*
H62	0.4162	0.0732	0.7631	0.077*
H81	0.9403	0.4111	0.7908	0.067*
H82	0.7287	0.4981	0.8133	0.067*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.1546 (14)	0.1453 (13)	0.0635 (6)	-0.0040 (13)	0.0179 (8)	-0.0299 (7)
O1	0.0658 (17)	0.0833 (19)	0.0716 (16)	-0.0074 (17)	0.0162 (14)	-0.0129 (15)
O2	0.0494 (16)	0.086 (2)	0.117 (2)	-0.0064 (16)	-0.0101 (17)	0.006 (2)
O3	0.087 (2)	0.0605 (17)	0.158 (3)	-0.005 (2)	-0.018 (2)	-0.023 (2)
N1	0.0585 (19)	0.0535 (18)	0.078 (2)	-0.0089 (18)	-0.0045 (18)	0.0029 (17)
C1	0.0521 (19)	0.0498 (18)	0.0472 (16)	-0.0037 (18)	-0.0020 (16)	-0.0009 (15)
C2	0.0516 (18)	0.0480 (18)	0.0462 (15)	-0.0035 (17)	0.0013 (15)	-0.0015 (14)
C3	0.101 (3)	0.061 (2)	0.0486 (18)	-0.032 (2)	0.001 (2)	0.0005 (17)
C4	0.109 (3)	0.067 (2)	0.064 (2)	-0.037 (2)	-0.000 (2)	-0.003 (2)
C5	0.095 (3)	0.058 (2)	0.076 (2)	-0.010 (2)	-0.009 (2)	-0.009 (2)
C6	0.072 (2)	0.068 (2)	0.0534 (19)	-0.009 (2)	-0.0023 (19)	-0.0126 (18)
C7	0.057 (2)	0.053 (2)	0.0501 (17)	0.0003 (19)	-0.0022 (17)	-0.0014 (16)
C8	0.060 (2)	0.050 (2)	0.0583 (19)	-0.014 (2)	-0.0097 (18)	0.0038 (16)
C9	0.058 (2)	0.055 (2)	0.0526 (17)	-0.0046 (19)	-0.0029 (17)	-0.0023 (17)
C10	0.063 (2)	0.064 (2)	0.0537 (18)	0.005 (2)	-0.0053 (18)	-0.0025 (17)
C11	0.064 (2)	0.060 (2)	0.0547 (19)	-0.005 (2)	-0.0032 (18)	-0.0040 (17)
C12	0.079 (2)	0.089 (3)	0.058 (2)	0.010 (2)	-0.006 (2)	-0.006 (2)
C13	0.085 (3)	0.089 (3)	0.069 (2)	0.014 (3)	0.002 (2)	-0.012 (2)
C14	0.090 (3)	0.079 (2)	0.058 (2)	-0.012 (3)	0.006 (2)	-0.007 (2)
C15	0.097 (3)	0.101 (3)	0.053 (2)	-0.006 (3)	-0.011 (2)	-0.005 (2)
C16	0.075 (2)	0.085 (3)	0.059 (2)	0.004 (2)	-0.011 (2)	-0.003 (2)

*Geometric parameters (Å, °)*

C11—C14	1.736 (4)	C14—C15	1.370 (7)
O1—C7	1.226 (4)	C15—C16	1.380 (5)
O2—N1	1.214 (4)	C1—H1	0.980
O3—N1	1.216 (4)	C2—H2	0.980
N1—C8	1.480 (5)	C3—H31	0.970
C1—C2	1.537 (4)	C3—H32	0.970
C1—C8	1.528 (4)	C4—H41	0.970
C1—C9	1.506 (4)	C4—H42	0.970
C2—C3	1.536 (5)	C5—H51	0.970
C2—C7	1.516 (4)	C5—H52	0.970
C3—C4	1.512 (6)	C6—H61	0.970
C4—C5	1.509 (5)	C6—H62	0.970
C5—C6	1.519 (5)	C8—H81	0.970
C6—C7	1.494 (5)	C8—H82	0.970
C9—C10	1.305 (4)	C9—H9	0.930

C10—C11	1.472 (5)	C10—H10	0.930
C11—C12	1.389 (6)	C12—H12	0.930
C11—C16	1.381 (5)	C13—H13	0.930
C12—C13	1.385 (6)	C15—H15	0.930
C13—C14	1.362 (6)	C16—H16	0.930
O2—N1—O3	122.9 (3)	C2—C3—H32	108.8
O2—N1—C8	118.7 (3)	C4—C3—H31	108.8
O3—N1—C8	118.4 (3)	C4—C3—H32	108.8
C2—C1—C8	110.0 (2)	H31—C3—H32	109.5
C2—C1—C9	111.2 (2)	C3—C4—H41	108.8
C8—C1—C9	108.3 (2)	C3—C4—H42	108.8
C1—C2—C3	112.5 (2)	C5—C4—H41	108.8
C1—C2—C7	115.1 (2)	C5—C4—H42	108.8
C3—C2—C7	106.0 (2)	H41—C4—H42	109.5
C2—C3—C4	112.2 (3)	C4—C5—H51	109.0
C3—C4—C5	112.1 (3)	C4—C5—H52	109.0
C4—C5—C6	111.4 (3)	C6—C5—H51	109.0
C5—C6—C7	110.1 (3)	C6—C5—H52	109.0
O1—C7—C2	122.9 (3)	H51—C5—H52	109.5
O1—C7—C6	122.5 (3)	C5—C6—H61	109.3
C2—C7—C6	114.5 (3)	C5—C6—H62	109.3
N1—C8—C1	110.0 (2)	C7—C6—H61	109.3
C1—C9—C10	126.8 (3)	C7—C6—H62	109.3
C9—C10—C11	127.5 (3)	H61—C6—H62	109.5
C10—C11—C12	122.6 (3)	N1—C8—H81	109.3
C10—C11—C16	120.2 (3)	N1—C8—H82	109.3
C12—C11—C16	117.2 (3)	C1—C8—H81	109.3
C11—C12—C13	121.4 (4)	C1—C8—H82	109.3
C12—C13—C14	119.6 (4)	H81—C8—H82	109.5
C11—C14—C13	119.6 (3)	C1—C9—H9	116.6
C11—C14—C15	119.7 (3)	C10—C9—H9	116.6
C13—C14—C15	120.6 (4)	C9—C10—H10	116.2
C14—C15—C16	119.4 (4)	C11—C10—H10	116.2
C11—C16—C15	121.8 (4)	C11—C12—H12	119.3
C2—C1—H1	109.1	C13—C12—H12	119.3
C8—C1—H1	109.1	C12—C13—H13	120.2
C9—C1—H1	109.1	C14—C13—H13	120.2
C1—C2—H2	107.6	C14—C15—H15	120.3
C3—C2—H2	107.6	C16—C15—H15	120.3
C7—C2—H2	107.6	C11—C16—H16	119.1
C2—C3—H31	108.8	C15—C16—H16	119.1
O2—N1—C8—C1	64.7 (4)	C3—C4—C5—C6	-52.9 (5)
O3—N1—C8—C1	-112.9 (3)	C4—C5—C6—C7	52.5 (5)
C2—C1—C8—N1	-179.0 (2)	C5—C6—C7—O1	118.3 (4)
C8—C1—C2—C3	-177.3 (3)	C5—C6—C7—C2	-58.0 (4)
C8—C1—C2—C7	61.1 (3)	C1—C9—C10—C11	175.2 (3)

C2—C1—C9—C10	126.2 (4)	C9—C10—C11—C12	-7.3 (6)
C9—C1—C2—C3	-57.3 (4)	C9—C10—C11—C16	173.2 (4)
C9—C1—C2—C7	-178.8 (2)	C10—C11—C12—C13	-179.8 (4)
C8—C1—C9—C10	-112.8 (4)	C10—C11—C16—C15	179.0 (4)
C9—C1—C8—N1	59.2 (3)	C12—C11—C16—C15	-0.6 (6)
C1—C2—C3—C4	176.8 (3)	C16—C11—C12—C13	-0.2 (6)
C1—C2—C7—O1	7.5 (5)	C11—C12—C13—C14	0.8 (7)
C1—C2—C7—C6	-176.2 (3)	C12—C13—C14—C11	179.0 (3)
C3—C2—C7—O1	-117.6 (4)	C12—C13—C14—C15	-0.5 (7)
C3—C2—C7—C6	58.7 (4)	C11—C14—C15—C16	-179.8 (3)
C7—C2—C3—C4	-56.6 (4)	C13—C14—C15—C16	-0.3 (6)
C2—C3—C4—C5	56.4 (4)	C14—C15—C16—C11	0.8 (7)

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C8—H81...O1	0.97	2.37	3.020 (4)	124