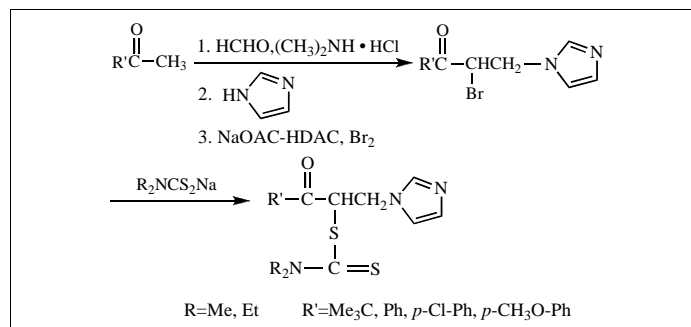


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Seven 1,2,4-triazole compounds containing the *N,N*-dialkyldithiocarbamate group were designed and synthesized. Their structures were identified using infrared spectroscopy, element analysis, ¹H NMR spectroscopy and mass spectrometry, and in two cases by single crystal X-ray diffraction. The result of the biological test showed that the seven compounds all have fungicidal and plant growth-regulating activities.

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Introduction.

1,2,4-Triazole and its derivative are one of the most widely used fungicides in modern society because of their highly efficient, low toxicity and absorbent properties [1-3]. At present, the studies on triazole derivatives are mainly concentrated on compounds with triazole as the only active group. The report has rarely been found about triazole compounds containing both triazole group and other active group in a single molecule. Dialkylsubstituted dithiocarbamate salts have also shown interesting biological effects [4]. *N,N*-Dialkyldithiocarbamate is also known as broad-range fungicides have a different fungicidal mechanism than that of triazole compounds [5]. Triazole compounds containing the *N,N*-dialkyl dithiocarbamate functional group have rarely been reported. In order to search for new triazole compounds with higher bioactivity, seven compounds were designed and synthesized and the biological activities of these compounds were tested. Also, their structures were determined by IR, elemental analysis, ¹H NMR spectra and single crystal X-ray diffraction.

Results and Discussion.

The molecular structures of compounds **1** (C₁₂H₂₀N₄O₂S₂) and **4** (C₁₅H₁₈N₄O₂S₂) are illustrated in Figure 1 and 2, respectively. Figure 3 shows a perspective view of the crystal packing in the unit cell for **4**. Selected bond distances and angles of **1** and **4** are listed in Table 1.

In both compounds **1** and **4**, the bond lengths and angles are generally normal in the triazole ring and *N,N*-dimethyldithiocarbamate group [6-8]. The triazole ring with the conjunction carbon atom are all fairly planar, and the largest deviation from the least squares plane through the ring atoms are 0.022 and 0.010 Å for **1** and **4**, respectively. All atoms in *N,N*-dimethyldithiocarbamate group in these two compounds are also quite planar, and the largest deviation from the least squares plane are 0.014 and 0.011 Å for **1** and **4**, respectively. The dihedral angle between the plane of *N,N*-dimethyldithiocarbamate group with the plane of triazole moiety are 9.96(2)° and 5.29(2)° for **1** and **4**, respectively.

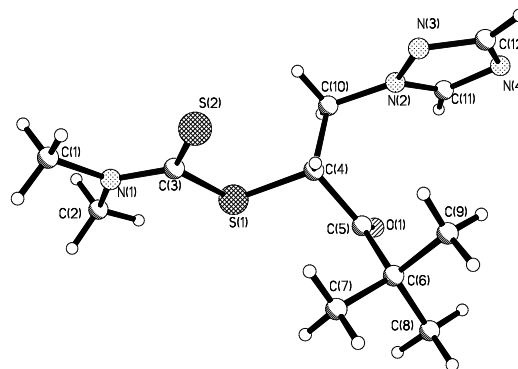


Figure 1 Molecular structure for **1** with the atomic numbering scheme.

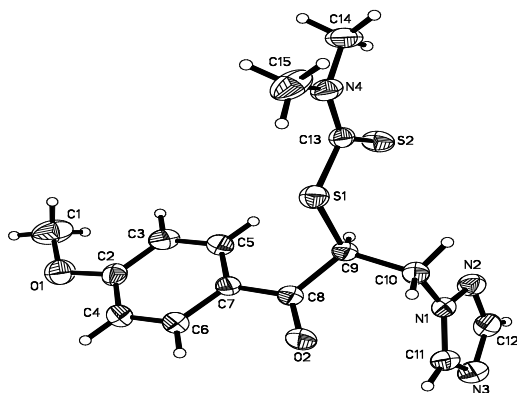


Figure 2 Molecular structure for **4** with the atomic numbering scheme.

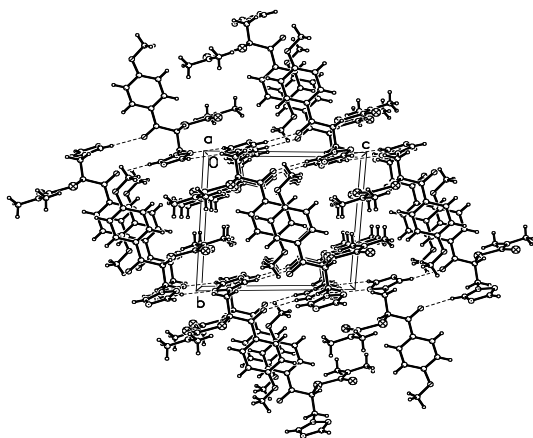


Figure 3 A view of the crystal packing down the *a* axis for the compound **4**

Table 1

Selected bond lengths [Å] and angles [°] for compounds **1** and **4**.

Compound 1		Compound 4	
S(1)-C(3)	1.780(2)	S(1)-C(13)	1.780(2)
S(1)-C(4)	1.810(2)	S(1)-C(9)	1.813(2)
S(2)-C(3)	1.651(2)	S(2)-C(13)	1.659(2)
N(1)-C(3)	1.333(3)	N(1)-C(11)	1.332(2)
C(3)-S(1)-C(4)	103.2(1)	C(13)-S(1)-C(9)	103.2(8)
S(2)-C(3)-S(1)	124.1(1)	C(11)-N(1)-N(2)	109.0(2)
N(1)-C(3)-S(1)	111.6(2)	C(11)-N(1)-(10)	131.2(2)
N(1)-C(3)-S(2)	124.4(2)	N(2)-N(1)-C(10)	119.8(1)
C(10)-C(4)-(1)	109.2(2)	C(12)-N(2)-N(1)	102.4(2)

In compound **1**, the bond lengths and angles in the tert-butyl group are in good agreement with the earlier report [9]. The C(4)-C(5) and C(4)-C(10) bond lengths of 1.535(3) Å and 1.525(3) Å are all similar to those of standard C-C single bond length 1.54 Å, while C(5)-O(1) bond length 1.205(4) Å is longer than that of standard

C=O double bond length 1.17 Å [10]. In compound **4**, bond lengths and angles are generally normal in the phenyl ring [11]. The C(4)-C(5) and C(4)-C(8) bond lengths of 1.527(4) Å and 1.540(4) Å are also similar to those of standard C-C single bond length, while C(8)-O(2) bond length 1.214(4) Å is much longer, which assign to the electron delocalization effect between phenyl ring and carbonyl group. The phenyl ring [C(2), C(3), C(4), C(5), C(6) and C(7)] with the conjunction carbon atom C(8) and methoxy group [C(1) and O(1)] are fairly planar, plane equation: $7.1646x - 0.5670y - 3.1279z = -0.0305$, and the largest deviation from the least squares plane is 0.042(3) Å. This plane is nearly perpendicular to the plane of *N,N*-dimethyldithiocarbamate group, with the dihedral angle of 89.26(2)°. The dihedral angle between the triazole ring moiety and the phenyl ring is 83.97(2)°.

In the crystal lattice of compounds **1** and **4**, there are some potentially weak (C-H...Y hydrogen bonds, Y = O, N and S) intermolecular interactions [12, 13]. In compound **1**, the N(4) atom with C(10) form weak C-H...N intermolecular interaction, the donor and acceptor distances are C(10)...N(4) 3.3635(1) Å. In compound **4**, the O(2) atom with C(6), and N(3) atom with C(7) form weak C-H...Y intermolecular interactions, the donor and acceptor distances are C(6)...O(2) of 3.2427 Å and C(7)...N(3) of 3.3627 Å. The other intermolecular interactions are due to the two different types of π bond interactions: C-H... π supramolecule interactions and π - π stacking interaction [14, 15]. There are two types of C-H... π supramolecule interactions between C-H and aromatic rings in compound **1**. The distances between C(9)-H(9A) and C(9)-H(9C) to triazole ring are all 3.667 Å, and bond angles are 114.41° and 103.31°, respectively. In compound **4**, there are two different types of π - π stacking interactions, the center-to-center distances between two adjacent phenyl rings are 3.963 Å and 3.902 Å, respectively. It is obvious that they form the stronger π - π stacking interaction [16]. In the solid state, all above extension hydrogen and intermolecular interactions stabilize the structure.

In the IR spectra, the absorption peaks at about 3100 cm^{-1} attribute to unsaturated =C-H bond stretching vibration, the absorption peak at 900~650 cm^{-1} is assigned to the =C-H outside-plane bending vibration. The C=N stretching vibrations are found for all compounds at about 1500 cm^{-1} [17]. The strong band in the range 1660-1700 cm^{-1} is attributed to the $\nu_{\text{C=O}}$ stretching vibration, the band in the range 1130-1200 cm^{-1} belonging to the $\nu_{\text{C=S}}$ stretching vibration [18, 19]. We found that the $\nu_{\text{C=O}}$ stretching vibration band peak for C = O connected to tertiary butyl group have shifted slightly to higher frequency by about 20-30 cm^{-1} compared with that of C = O groups connected with

aromatic rings. The IR data are in good agreement with the predicted structure of the target compounds.

The ^1H NMR data for seven compounds are as predicted except for two protons on triazole ring. The chemical shifts for triazole ring protons are affected by R' group. When R' is aromatic rings, the chemical shifts for two protons are at $\delta = 7.98$ - 8.22 . When R' is Me_3C , their chemical shifts are $\delta = 8.03$ and $\delta = 7.87$.

Compounds **1-7** were screened for their fungicidal activities against *P. Zeae*, *A. Solani*, *P. Asparagi*, *P. Piricola* and *C. Archidicala* at 50 $\mu\text{g/mL}$ concentrations following the agar plate diffusion method [20, 21] and compared with triazolone. Compounds **1**, **2**, **4** and **5** all exhibit some efficiency on *P. Zeae*, *A. Solani*, *P. Asparagi*, *P. Piricola* and *C. Archidicala*, but not significantly, the inhibiting rate of compounds **2** and **5** are

(4000-400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer. ^1H NMR spectra were measured with a JEOL FX-90Q nuclear magnetic resonance spectrometer (CDCl_3 as solvent, TMS as internal standard). The melting points were determined on a Yanaco MP-500 melting point apparatus.

The intermediates *N,N*-dialkyldithiocarbamate were prepared according to the literature report [22]. Alkyl *N*-imidazolepropyl ketone were prepared according to the literature [23] and [24]. The synthesis of the intermediate alkyl α -bromo- β -*N*-imidazole-propyl ketone and the seven target compounds are described below.

To a 100 mL flask 15 mmol of intermediate alkyl *N*-imidazole-propyl ketone, 25 mL acetic acid and 15 mmol sodium acetate were added. Then 15 mmol bromine was dropwise added with stirring at 15 ~ 25 $^\circ\text{C}$. The reaction was maintained until the mixture turned colorless or light yellow for about 2 ~ 3 h. Then 50 mL water and 40 mL chloroform were added. The organic layer was successively washed with saturated sodium bicarbonate solution and brine, then

Table 2

The fungicidal and plant grown regulator activities of compounds **1-7**

Compound No	Fungicidal activities(c=0.005%,inhibition)					Plant growth regulator activities		
	P.zeae	A.solani	P.asparagi	P.piricola	C.arachidicala	Wheat coleoptile elongation	Rooting of cucumber cotyledon	Rape hypocotyls inhibition
1	20.0	35.5	28.6	20.0	23.5	-7.8	+39.3	-5.9
2	45.0	35.5	28.6	24.4	35.3	-3.9	+33.8	-9.1
3	30.8	0	0	24.6	0	-17.1	+1.0	-7.7
4	15.5	22.6	28.6	20.0	23.5	-22.1	+25.6	-12.3
5	45.0	35.5	28.6	24.4	35.3	-28.7	+83.0	11.9
6	10.0	12.9	0	33.3	11.8	-3.9	+14.7	-5.0
7	11.5	0	33.3	26.2	0	-7.0	+77.5	-9.1
triazolone	46.2	0	22.5	64.6	0	-24.0	+50.2	-64.2

the highest in these compounds and only reach to 24.4 ~ 45.0%. The plant growth regulator activities of compounds **1-7** have also been tested towards *wheat coleoptile elongation*, *rooting of cucumber cotyledon* and *rape hypocotyls inhibition* at 10 $\mu\text{g/mL}$ and compared with triazolone. Compounds **5** and **7** show remarkable growth-promoting activity of 83.0% and 77.5% on *rooting of cucumber cotyledon*. As far as the relation of structure and activity is concerned, when R' group is Me_3C , the compounds **1** and **5** have better comprehensive inhibiting rates than when the R' is an aryl group. As far as R is concerned, inhibiting activities of the compounds (R = Et) are higher than the compounds (R = Me). Meanwhile, it can be seen from Table 2 that the relationship changes between structure and activity are not regular.

EXPERIMENTAL

All chemical reagents were obtained from a commercial source and used without further purification. Elemental analyses were measured with a Perkin-Elmer 1400C analyzer. IR spectra

dried over sodium sulfate and the chloroform solution containing about 15 mmol of intermediate alkyl α -bromo- β -*N*-imidazole-propyl ketone was filtrated into a 100 mL flask. Cooled with ice-water and 30 mL acetone solution of intermediate *N,N*-dialkyldithiocarbamate (R = Me, Et) was added under stirring and the mixture was stirred at around 0 $^\circ\text{C}$ for about 1 h. The solution was filtered, concentrated and purified by flash chromatography (silica gel, $V_{\text{ethyl ethanoate}}: V_{\text{cyclohexane}} = 5:1$) to afford the seven target compounds. Single crystals suitable for X-ray measurements of compounds **1** and **4** were obtained by recrystallization from ethyl ethanoate at room temperature.

tert-Butyl α -*S*-dimethyldithiocarbamate- β -imidazole-propyl ketone (**1**).

Colorless crystal, yield 39.4%, mp 110-112 $^\circ\text{C}$; ir (KBr), 3123m (CH), 1696 (CO), 1504 (CN), 1141 (CS). ^1H nmr (300 MHz; CD_3Cl ; Me_4Si): 8.03 (s, 1H, Tr-H), 7.87 (s, 1H, Tr-H), 5.57~5.75 (dd, 1H, SCH, J=4.38 Hz, J=10.12 Hz), 4.59~4.88 (dd, H, CH_2 , J=10.12Hz, J=13.18 Hz), 4.26~ 4.48 (dd, H, CH_2 , J=4.38Hz, J=13.18Hz), 3.59 (s, 3H, N- CH_3), 3.34 (s, 3H, N- CH_3), 0.99 (s, 9H, Me_3C).

Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}_2$: C, 47.97% H, 6.71% N, 18.65%; Found: C, 48.06% H, 6.65% N, 18.61%.

Phenyl α -S-dimethyldithiocarbamate- β -imidazole-propyl ketone (2).

Colorless crystal, yield 42.9%, mp 99-101°C; ir (KBr), 3116m (CH), 1676 (CO), 1596 and 1580 (C=C), 1503 (CN), 1135 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.22 (s, 1H, Tr-H), 8.02 (s, 1H, Tr-H), 3.59 (s, 3H, N-CH₃), 3.34 (s, 3H, N-CH₃), 4.44~4.67 (dd, H, CH₂, J=4.38Hz, J=13.5Hz), 4.86~5.18 (dd, H, CH₂, J=9.48Hz, J=13.5Hz), 6.30~6.48 (dd, 1H, SCH, J=4.38Hz, J=9.18Hz), 7.27~8.03 (m, 5H, Ph). Ms: m/z 321 (MH⁺), 251 [(PhCO(CH₂)CH₂⁺S₂N(CH₃)₂)], 200 (PhCOCH₂⁺CH₂Im), 131 (PhCOCH₂⁺CH₂), 105 (PhCOH⁺), 77 (PhH⁺).

Anal. Calcd. for C₁₄H₁₆N₄O₂S₂: C, 52.48% H, 5.03% N, 17.40%; Found: C, 52.70% H, 4.99% N, 17.29%.

ρ -Chlorophenyl α -S-dimethyldithiocarbamate- β -imidazole-propyl ketone (3).

Colorless crystal, yield 53.5%, mp 92-93°C; ir (KBr), 3129m (CH), 1681 (CO), 1590 (C=C), 1504 (CN), 1141 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.18 (s, 1H, Tr-H), 7.94 (s, 1H, Tr-H), 3.56 (s, 3H, N-CH₃), 3.32 (s, 3H, N-CH₃), 4.57~4.78 (dd, H, CH₂, J=4.40Hz, J=13.46Hz), 4.82~4.93 (dd, H, CH₂, J=9.30Hz, J=13.46Hz), 6.26~6.38 (dd, 1H, SCH, J=4.14Hz, J=9.25Hz), 7.26~7.97 (m, 4H, Ph)

Anal. Calcd. for C₁₄H₁₅ClN₄O₂S₂: C, 47.38% H, 4.26% N, 15.79%; Found: C, 47.51% H, 4.21% N, 15.80%.

ρ -Methoxyphenyl α -S-dimethyldithiocarbamate- β -imidazole-propyl ketone (4).

Colorless crystal, yield 73.3%, mp 120-122°C; ir (KBr), 3138m (CH), 1666 (CO), 1302 (C=C), 1505 (CN), 1138 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.15 (s, 1H, Tr-H), 7.98 (s, 1H, Tr-H), 3.55 (s, 3H, N-CH₃), 3.32 (s, 3H, N-CH₃), 4.56~4.79 (dd, H, CH₂, J=4.36Hz, J=12.92Hz), 4.82~4.93 (dd, H, CH₂, J=9.30Hz, J=12.92Hz), 6.21~6.33 (dd, 1H, SCH, J=4.36Hz, J=9.23Hz), 6.81~8.00 (m, 4H, Ph), 3.82 (s, 3H, MeO)

Anal. Calcd. for C₁₅H₁₈N₄O₂S₂: C, 51.41% H, 5.18% N, 15.99%; Found: C, 51.17% H, 5.16% N, 16.30%.

tert-Butyl α -S-diethyldithiocarbamate- β -imidazole-propyl ketone (5).

Colorless crystal, yield 23.1%, mp 65-66°C; ir (KBr), 3124m (CH), 1700 (CO), 1502 (CN), 1205 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.05 (s, 1H, Tr-H), 7.88 (s, 1H, Tr-H), 1.18~1.36 (t, 6H, 2CH₃), 0.97 (s, 9H, Me₃), 3.67~4.00 (m, 4H, 2N-CH₂), 4.34~4.51 (dd, H, CH₂, J=4.33Hz, J=12.98Hz), 4.60~5.01 (dd, H, CH₂, J=10.02Hz, J=12.98Hz), 5.62~5.75 (dd, 1H, SCH, J=4.33Hz, J=10.02Hz)

Anal. Calcd. for C₁₄H₂₄N₄O₂S₂: C, 50.19% H, 7.36% N, 17.06%; Found: C, 50.13% H, 7.32% N, 17.01%.

Phenyl α -S-diethyldithiocarbamate- β -imidazole-propyl ketone (6).

Colorless crystal, yield 29.6%, mp 102-103°C; ir (KBr), 3118m (CH), 1678 (CO), 1594 and 1580 (C=C), 1497 (CN), 1203 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.17 (s, 1H, Tr-H), 8.01 (s, 1H, Tr-H), 1.26~1.80 (t, 6H, 2CH₃), 7.24~8.02 (m, 5H, Ph), 3.62~4.05 (m, 4H, 2N-CH₂), 4.50~4.66 (dd, H, CH₂, J=4.43Hz, J=13.10Hz), 4.82~5.10 (dd, H, CH₂, J=9.28Hz, J=13.10Hz), 6.31~6.48 (dd, 1H, SCH, J=4.43Hz, J=9.12Hz).

Anal. Calcd. for C₁₆H₂₀N₄O₂S₂: C, 55.14% H, 5.78% N, 16.08%; Found: C, 55.09% H, 5.74% N, 16.20%.

ρ -Methoxyphenyl α -S-diethyldithiocarbamate- β -imidazole-propyl ketone (7).

Colorless crystal, yield 36.4%, mp 99-100°C; ir (KBr), 3124m (CH), 1673 (CO), 1597 (C=C), 1490 (CN), 1205 (CS). ¹H nmr (300 MHz; CD₃Cl; Me₄Si): 8.14 (s, 1H, Tr-H), 7.98 (s, 1H, Tr-H), 1.17~1.31 (t, 6H, 2CH₃), 6.24~8.00 (m, 4H, Ph), 3.62~4.15 (m, 4H, 2N-CH₂), 4.44~4.63 (dd, H, CH₂, J=4.50Hz, J=13.76Hz), 4.80~5.08 (dd, H, CH₂, J=9.23Hz, J=13.76Hz), 6.24~6.41 (dd, 1H, SCH, J=4.50Hz, J=9.20Hz). Ms: m/z 379 (MH⁺), 309 [(CH₃OPhCO(CH₂)CH₂⁺S₂N(CH₃CH₂)₂)], 230 (CH₃OPhCOCH₂⁺CH₂Im), 162 (CH₃OPhCOCH₂⁺CH₂).

Anal. Calcd. for C₁₇H₂₂N₄O₂S₂: C, 53.94% H, 5.86% N, 14.08%; Found: C, 54.01% H, 5.83% N, 14.01%.

X-ray Structure Determination.

In the determination of the structure of the single crystal, X-ray intensities were recorded by Rigaku Raxis-IV diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) graphite monochromator. The structure was solved by direct methods using SHELXS-97 program [25]. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations, but their positions were not refined. The contributions of these hydrogen atoms were included in structure-factor calculations. The summaries of the key crystallographic information for compounds **1** and **4** are given in Table 3.

Table 3
Crystallographic details for compounds **1** and **4**

Empirical formula	C ₁₂ H ₂₀ N ₄ O ₂ S ₂ 1	C ₁₅ H ₁₈ N ₄ O ₂ S ₂ 4
Formula weight	300.44	350.45
Crystal system,		
space group	Monoclinic, P2 ₁ /c	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 12.315(3) \AA $\alpha = 90^\circ$ b = 12.057(2) \AA $\beta = 118.55(3)^\circ$ c = 12.532(3) \AA $\gamma = 90^\circ$	a = 7.348(2) \AA $\alpha = 90.32(3)^\circ$ b = 11.051(2) \AA $\beta = 101.97(3)^\circ$ c = 11.209(2) \AA $\gamma = 105.13(3)^\circ$
Volume	1634.5(6) \AA^3	857.8(3) \AA^3
Z, D _c (Mg/m ³)	4, 1.221	2, 1.357
F(000)	640	368
θ range	1.88 to 27.53°	1.86 to 27.53°
Limiting indices	-15 $\leq h \leq 15$, -5 $\leq k \leq 15$, -13 $\leq l \leq 16$	-9 $\leq h \leq 9$, 0 $\leq k \leq 14$, -14 $\leq l \leq 14$
Reflections collected / unique	5132 / 3130 [R _{int} = 0.0248]	2877 / 2877 [R _{int} = 0.0000]
$\theta_{max} = 27.51^\circ$	82.8 %	72.7 %
GOF	1.017	1.031
Final R indices	R1 = 0.0449, [I > 2 σ (I)] wR2 = 0.1043	R1 = 0.0552, wR2 = 0.1384
Largest diff. peak and hole	0.235 and -0.191 e. \AA^{-3}	0.319 and -0.334 e. \AA^{-3}

Acknowledgments

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