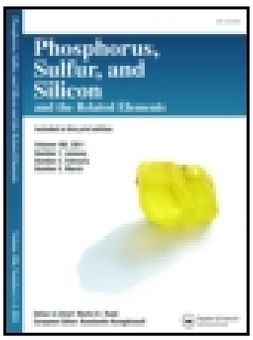

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Synthesis, Crystal Structure and Biological Activity of Some Novel Sulfoxide Compounds Containing 1,2,3-thiadiazole Moiety

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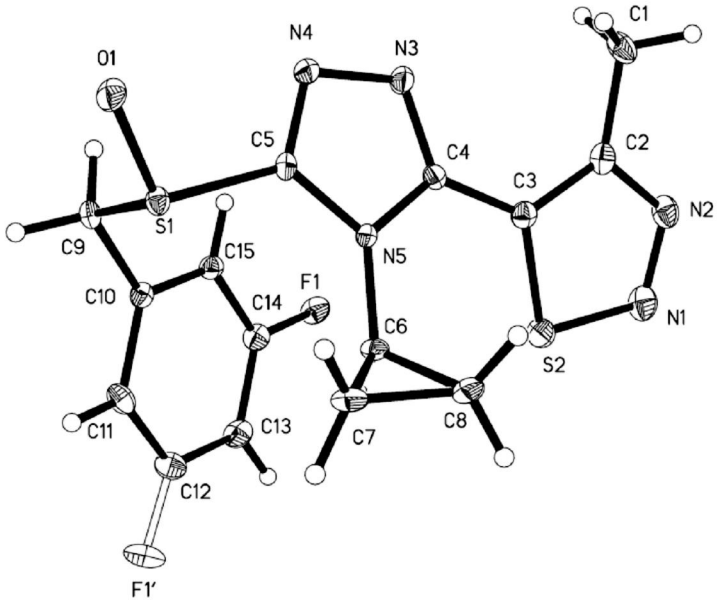
Abstract

Some new sulfoxide compounds containing 1,2,3-thiadiazole moiety were synthesized from diethyl carbonate and hydrazine hydrate by multi-step reactions. Their structures were confirmed by NMR, MS and elemental analysis. One of the title compounds,

5-(4-cyclopropyl-5-((3-fluorobenzyl)sulfinyl)-4H-1,2,4-triazol-3-yl)-4-methyl-1,2,3-thiadiazole ($C_{15}H_{14}FN_5OS_2$), was structurally determined by a single crystal X-ray diffraction study. The biological activity of the title compound was determined and the results showed that it displays moderate biological activities.



Keywords

crystal structure, synthesis, 1,2,3-thiadiazole, sulfoxide, herbicidal activity

INTRODUCTION

Research in heterocyclic compounds is an active area because of their medicinal and pesticidal importance [1-3], such as Keto-Acid Reducto-Isomerase activities [4], antifungal activities [5], anticancer activity[6], and antibacterial activity[7]. In recent years, 1,2,4-triazole compounds were shown to exhibit excellent activities[8]. For example, some of them have been developed as commercial drugs or pesticides (Figure 1). Due to their diverse properties, 1,2,4-triazole fungicides become one of the foci in drug research. As well as 1,2,4-triazole, 1,2,3-thiadiazole derivatives have also displayed a wide spectrum of remarkable biological activities (Figure 1), such as fungicidal activities [9-10], anti-HBV [11], and as neuroprotective agents [12]. Furthermore, the sulfoxide group is a key group in many biological molecules, perhaps the SO group is a hydrogen bond receptor. In the past years, many active compounds containing the sulfoxide group were discovered[13].

In view of these facts mentioned above, and also as a part of our work[14-20] on the synthesis of bioactive lead compounds, the title compounds were designed, synthesized and characterized by ^{1}H NMR, MS and elemental analysis. The crystal structure of title compound was determined. The biological activity of title compound was also tested.

RESULTS AND DISCUSSION

Chemistry and Activity

The presented research work illustrates the synthesis of new sulfoxides as outlined in

Scheme **1**. The parent molecule, the key intermediate 4-cyclopropyl-5-(4-methyl-1,2,3-thiadiazol-5-yl)-4*H*-1,2,4-triazole-3-thiol (**8)** was synthesized by the reaction of *N*-cyclopropyl-2-(4-methyl-1,2,3-thiadiazole-5-carbonyl) hydrazinecarbothioamide **(7)** under basic conditions. The product thioether **(9)** was obtained from 4-cyclopropyl-5-(4-methyl-1,2,3-thiadiazol-5-yl)-4*H*-1,2,4-triazole-3-thiol (**8)** with halides. The target compounds were obtained via oxidation. In the process of the oxidation, $KMnO_4$, $K_2S_2O_8$, *m*-CPBA or H_2O_2/HOAc were used as oxidizing agents. When we used $KMnO_4$, $K_2S_2O_8$, H_2O_2/HOAc as oxidation agents, the final product was a sulfone, indicating that the oxidation is too strong, while the use of *m*-CPBA as oxidation agent, afforded the sulfoxide, although the sulfone product was also found (Table 1).

The final product was collected by the addition of cold water and filtration/solvent extraction depending upon the conditions of the products. The structures of the new compounds were verified by ^{1}H-NMR and mass spectral data, elemental analysis data and the X-ray data as illustrated above in the experimental section.

Compound **10a** was obtained as a white power having the molecular formula $C_{15}H_{14}FN_5OS_2$. In its ESI-MS spectrum, molecule **10a** showed a 2M+Na peak(*m/z* 748.78) and M+Na peak(*m/z* 386.10) respectively. In the ^{1}H-NMR spectrum, the signals of CH_2 nearby sulfonyl group resonated at 4.77 ppm and 5.10 ppm as two doublets with *J* coupling of 12.96 and 12.93 Hz. The signals of cyclopropane group appeared at 0.93-1.16 and 1.25-1.37 as two multi-peaks

respectively. The signal of CH_3 of 1,2,3-thaidiazole appeared at 3.03 ppm. The elemental analysis results are in accord with the theoretical value.

To investigate the KARI inhibitory activity and herbicidal activity of these synthesized title compounds, cyclopropane-1,1-dicarboxylic acid (CPD), a potent inhibitor of KARI *in vitro*, was used as the control. We found that title compound **10a** showed moderate inhibition abilities on rape root than the control CPD at 100 ε g/mL (41.7%). It displayed only weak activity against *Echinochloa crusgalli* (31.7%) and KARI (18.76%) at 100 ε g/mL.

Crystal Structure

Selected bond lengths, bond angles and torsion angles are shown in Table **2**. The molecular structure of the title compound is shown in Figure **2**. The molecular packing of the molecule is shown in Figure S 1 (Supplemental Materials).

Generally, the average bond lengths and bond angles of ring system (phenyl, cyclopropane, triazole and 1,2,3-thiadiazole) are in the observed normal ranges [20-26]. However, the C2=N2 bond [1.357(3) Å] and C3=N4 [1.326(3) Å] are longer than the general C=N double bond length of 1.27 Å [27]. As shown in Figure 2, the 1,2,3-thiadiazole ring is nearly planar with 1,2,4-triazole ring with a small dihedral angle (d) of 24.9º. The triazole ring (N3, N4, C5, N5, C4) and thiadiazole ring (N1, N2, S1, C3, C2) is essentially planar, with plane equation -1.264x + 1.117y + 11.170z = 8.2129 and -0.332x + 6.591y + 9.665z = 7.8466 respectively, and the largest deviation from the least squares plane is 0.00066 Å and 0.00020 Å. Meanwhile, the phenyl ring

is parallel with both the 1,2,3-thiadiazole ring and the 1,2,4-triazole ring with the respective dihedral angles of 25.6 º and 26.5 º. The cyclopropane ring is nearly vertical with 1,2,3-thiadiazole ring(123.7º), 1,2,4-triazole ring(99.2º) and phenyl ring(104.9º) respectively. The S1=O1 bond length is 1.4822(17) Å. It is larger than that bond of SO_2. The torsion angle of thioether group C5ï S1ï C9ï C10 is 60.48(19)°.

In the intermolecular edge-to-face ´-´ stacking pattern of the title compound, it is worth mentioning that the two molecules of each stacking unit are centrosymmetric, which can be proven by the relative position of the CH_3 of H and thiadiazole rings of the two molecules: the centroid separation of them is 3.411 Å, and their dihedral angle is 76.35º. Another intramolecular edge-to-face ´-´ stacking pattern of the title compound can be proved by the relative position of the H of cyclopropane and phenyl ring of the title molecule: the centroid separation of them is 2.759 Å, and their dihedral angle is 92.33º.

The title compound has an extensive network of hydrogen bonding. In the *ab* plane, they are linked together by C-H···O hydrogen bonds to form a one-dimensional chain. The slight discrepancy of crystal structures is probably the consequence of the weakness of this hydrogen bond and van der Waals interactions in the solid-state structure.

EXPERIMENTAL

Materials and Methods

Melting points were determined using an X-4 apparatus and uncorrected. ^{1}H NMR spectra were

measured on a Bruker AV-400 instrument using TMS as an internal standard and $CDCl_3$ as the solvent. Elemental analyses were performed on a Vario EL elemental analyzer. Crystallographic data of the compound were collected on a Rigaku Saturn Diffractometer. All the reagents are of analytical grade or freshly prepared before use.

Synthesis

The title compounds were synthesized according to the route shown in Scheme **1**, and the yields were not optimized.

Intermediate 4-methyl-1,2,3-thiadiazole-5-carboxylic acid hydrazide (**5~9)** was synthesized according to the literature [4]. A mixture of acylhydrazine (**5**) with isothiocyanatocyclopropane (**6)** (1.5 g) was refluxed for 3 h in ethanol. After cooling down to room temperature, the products were obtained and recrystallized from methanol to give **7,** yellow crystals, yield 88.5%, m.p. 117-118 ^oC, ^1H NMR (400 MHz, $CDCl_3$): 0.40-0.79(m, 4H, CH_2), 2.78(m, 1H, CH), 3.31(s, 3H, Me). A mixture of compound (**7**) (10 mmol) in aqueous NaOH solution (5 mL, 2N) was refluxed for 4 h. After cooling down to room temperature, HCl aqueous solution (4N) was added to afford a large amount of precipitate. The solid was filtered, dried and recrystallized from methanol to give intermediate **(8)**, yellow crystal, yield 85.6%, m.p. 205-209 ^oC, ^1H NMR (400 MHz, $CDCl_3$): 1.13-1.25(m, 4H, CH_2), 2.42(s, 3H, CH_3), 2.91-2.97(m, 1H, CH), 10.86(br, 1H, SH). To a stirred solution of **8** (5.1 mmol) and K_2CO_3 (0.2 g, 5.6 mmol) in DMF (15 mL), a mixture of a substituted benzyl chloride or alkyl halide (5.6 mmol) was added dropwise. The resulting

mixture was stirred at room temperature for overnight. The mixture was poured into water, The precipitate formed was filtered off and recrystallized from petroleum ether/acetone to give (**9)** in good yields. To a stirred solution of compound **9** (2 mmol) in CH_2Cl_2 (8 mL) was added *m*-CPBA (1.1 mmol). The reaction was monitored by TLC. When the reaction was complete, the solvent was removed under reduced pressure vacuum. The crude product was purified by chromatography over silica gel to give **10**. (PE : EA = 5 : 1). The Supplemental Materials contains representative ^{1}H NMR spectra for 10a-10d (Figures S 2 ï S 5).

5-(4-cyclopropyl-5-((3-fluorobenzyl)sulfinyl)-4*H*-1,2,4-triazol-3-yl)-4-methyl-1,2,3-thiadiazole (10a) white crystal, yield, 37.0%; m.p., 117-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$), 0.93-1.16(m, 2H, CH_2), 1.25-1.37(m, 2H, CH_2), 3.03(s, 3H, Het-CH_3), 3.21-3.27(m, 1H, cyclopropane-CH), 4.77(d, *J* = 12.96 Hz, 1H, CH_2), 5.10(d, *J* = 12.93 Hz, 1H, CH_2), 7.06-7.59(m, 4H, Ph-H); ESI-MS: 748.78$[2M+Na]^+$, 386.10$[M+Na]^+$; Anal. Calcd for $C_{15}H_{14}FN_5OS_2$ (%): C, 49.57; H, 3.88; N, 19.27. Found: C, 49.40; H, 4.17; N, 18.82.

4-(((4-cyclopropyl-5-(4-methyl-1,2,3-thiadiazol-5-yl)-4*H*-1,2,4-triazol-3-yl)sulfinyl)methyl)benzonitrile (10b) white yellow crystal, yield 36%, m.p.152-155ŭC; ^{1}H NMR ($CDCl_3$, 500 MHz), δ:1.06(m, 2H, CH_2), 1.32(m, 2H, CH_2), 3.04(s, 3H, CH_3), 3.36(m, 1H, CH), 4.90(d, *J*=13.05Hz, 1H, SCH_2), 5.12(d, *J*=13.05Hz, 1H, SCH_2), 7.62(d, *J*=8.25Hz, 2H, ArH), 7.70(d, *J*=8.25Hz, 2H, ArH). MS (ESI), m/z: 371.07 $(M+1)^+$. Elemental anal. (%), calculated: C, 51.87; H, 3.81; N, 22.69; found: C, 51.65; H, 3.76; N, 22.71.

5-(4-cyclopropyl-5-((2-methylbenzyl)sulfinyl)-4*H*-1,2,4-triazol-3-yl)-4-methyl-1,2,3-thiadiazole (10c) white yellow crystal, yield 28%, m.p.176-179℃; ^{1}H NMR ($CDCl_3$, 500 MHz), δ:1.00(m, 2H, CH_2), 1.24(m, 2H, CH_2), 2.48(s, 3H, CH_3), 2.96(m, 1H, CH), 3.03(s, 3H, CH_3), 4.86(d, *J*=12.85Hz, 1H, SCH_2), 5.13(d, *J*=12.85Hz, 1H, SCH_2), 7.16-7.31(m, 4H, ArH). MS (ESI), m/z: 360.09 $(M+1)^+$. Elemental anal. (%), calculated: C, 53.46; H, 4.77; N, 19.48; found: C, 53.44; H, 4.81; N, 19.69.

2-((4-cyclopropyl-5-(4-methyl-1,2,3-thiadiazol-5-yl)-4*H*-1,2,4-triazol-3-yl)sulfinyl)acetonitrile (10d)

white yellow crystal, yield 33%, m.p.152-154℃; ^{1}H NMR ($CDCl_3$, 500 MHz), δ:1.10-1.18(m, 2H, CH_2), 1.41-1.53(m, 2H, CH_2), 3.07(s, 3H, CH_3), 3.51-3.53(m, 1H, CH), 4.43 (d, *J*=15.55Hz, 1H, SCH_2), 4.90(d, *J*=15.55Hz, 1H, SCH_2). MS (ESI), m/z: 295.04 $(M+1)^+$. Elemental anal. (%), calculated: C, 40.80; H, 3.42; N, 28.55; found: C, 41.23; H, 3.81; N, 28.71.

Bioassay

The herbicidal activity and KARI activity are determined according the references[27-29].

Crystal Structure Determination

The cube-shaped single crystal of the title compound was obtained by recrystallization from EtOH. The crystal with dimensions of 0.20mm ×0.16mm × 0.10mm was mounted on a Rigaku Saturn Diffractometer with a graphite-monochromated MoKα radiation (λ = 0.71073Å) by using a Phi scan modes at 113(2) K in the range of 3.02°≤θ≤25.02°. A total of 10549 reflections were

collected, of which 2766 were independent (R_{int} = 0.0728) and 2155 were observed with I > 2σ(I). The calculations were performed with SHELXS-97 program[30] and the empirical absorption corrections were applied to all intensity data. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were determined with theoretical calculations and refined isotropically. The final full-matrix least squares refinement gave R = 0.0428 and wR = 0.1017 ($w = 1/[\sigma^2(F_o^2) + (0.0519P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$), S = 1.04, $(\Delta/\sigma)_{max} < 0.0001$, $\Delta\rho_{max}$ = 0.31 and $\Delta\rho_{min}$ = -0.31 e Å^{-3}. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography[31]. A summary of the key crystallographic information were given in Table 3. CCDC 1051855 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. The Effects of Oxidant and Temperature on the Oxidation of Thioether

condition	sulfoxide
H_2O_2/HOAc/r.t.	no.
H_2O_2/HOAc/reflux	no.
$KMnO_4$/ r.t.	no.
m-CPBA/ r.t.	yes/ 1 h
$K_2S_2O_4$/ r.t.	no.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Angle	(°)
S(1)-O(1)	1.4822(17)	O(1)-S(1)-C(5)	106.34(11)
S(1)-C(5)	1.798(3)	C(5)-S(1)-C(9)	94.51(11)
S(1)-C(9)	1.831(2)	N(1)-S(2)-C(3)	93.35(13)
S(2)-N(1)	1.671(2)	N(2)-N(1)-S(2)	111.12(18)
S(2)-C(3)	1.701(2)	C(4)-N(3)-N(4)	106.9(2)
F(1)-C(14)	1.309(3)	C(5)-N(5)-C(4)	104.14(19)
N(1)-N(2)	1.310(3)	C(5)-N(5)-C(6)	129.0(2)
N(2)-C(2)	1.357(3)	N(2)-C(2)-C(1)	118.5(2)
N(3)-C(4)	1.326(3)	C(3)-C(2)-C(1)	128.0(2)
N(3)-N(4)	1.391(3)	N(4)-C(5)-N(5)	111.6(2)
N(4)-C(5)	1.315(3)	N(3)-C(4)-C(3)	123.7(2)
N(5)-C(5)	1.361(3)	C(6)-C(7)-C(8)	60.35(16)
N(5)-C(6)	1.449(3)	C(15)-C(10)-C(9)	120.6(2)
C(1)-C(2)	1.503(3)	F(1)-C(14)-C(13)	119.7(2)
C(2)-C(3)	1.383(4)	N(4)-C(5)-S(1)	123.34(19)
C(3)-C(4)	1.454(3)	N(5)-C(5)-S(1)	125.03(18)
C(6)-C(7)	1.494(3)	N(5)-C(6)-C(7)	120.08(19)
C(9)-C(10)	1.501(3)	N(5)-C(6)-C(8)	117.23(19)
C(10)-C(15)	1.400(3)	C(7)-C(6)-C(8)	59.96(16)
C(10)-C(11)	1.401(3)	N(3)-C(4)-N(5)	110.6(2)

Table 3 Crystal Structure and Data Refinement Parameters

Compound	
Empirical Formula	$C_{15}H_{14}FN_5OS_2$
Formula Weight	379.43
Crystal System / Space Group	Monoclinic, P2(1)/n
a / Å	10.597(2)
b / Å	13.487(3)
c / Å	11.261(2)
α / °	90
ϐ / °	102.41(3)
ɔ / °	90
V / $Å^3$	1572.0(5)
Z	4
D_{calc} (g/cm^3)	1.536
ε (mm^{-1})	0.36
Crystal size (mm)	0.20 x 0.16 x 0.10
Color / Shape	Colorless/Cube
Temp (K)	113(2)
Theta range for collection	3.02 to 25.02
Reflections collected	10549
Independent reflections	2766
Data/restraints/parameters	2766 / 0 / 228
Goodness of fit on F^2	1.045
Final R indices [I > 2ů(I)]	R1 = 0.0428, wR2 = 0.1017
R indices (all data)	R1 = 0.0580, wR2 = 0.1075
Largest difference peak/hole	0.309 and -0.315 e.A^-3

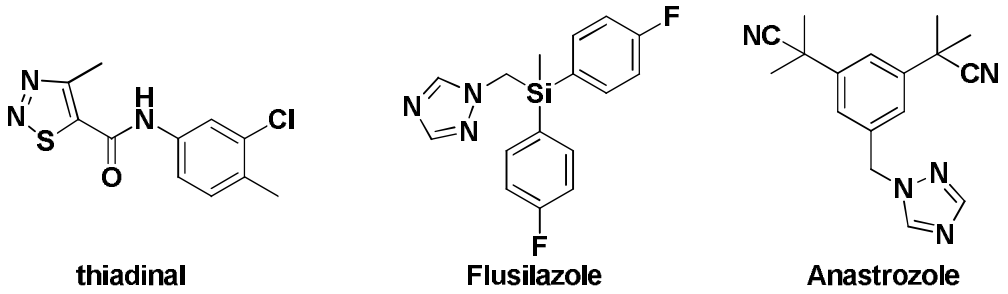


Figure 1. The commercial pesticides contain 1,2,3-thiadiazole or 1,2,4-triazole group

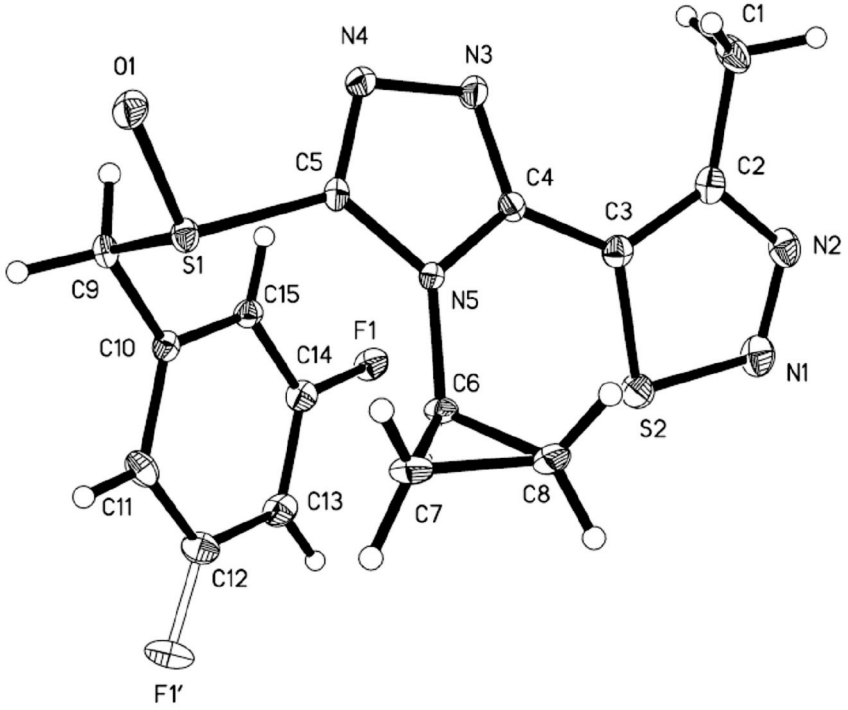
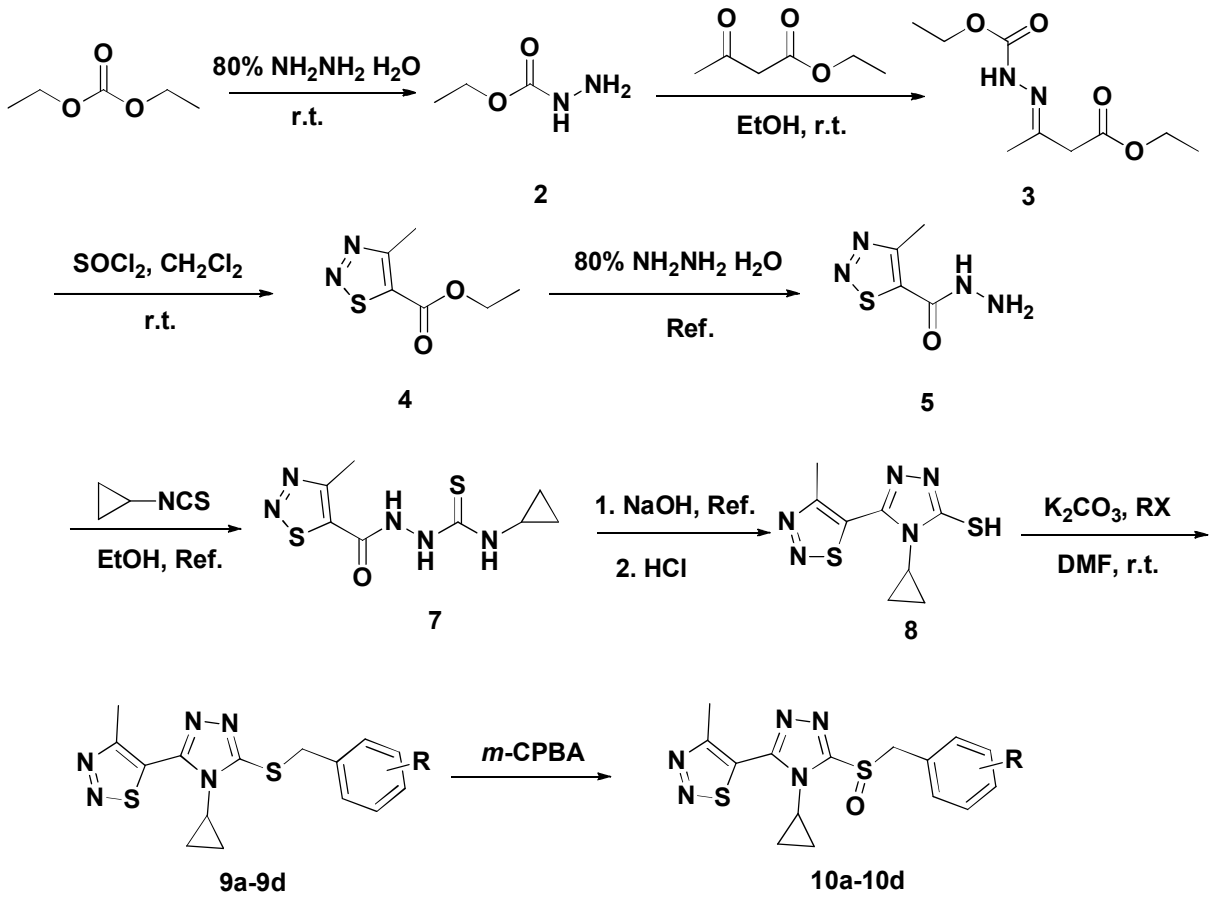


Figure **2** The molecular structure of the title compound



Scheme **1** The synthetic route of title compound