Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 991–996
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and biological activity research of novel ferrocenyl-containing thiazole imine derivatives

Haibo Yu, Ling Shao, Jianxin Fang *

Institute and State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Weijin Road 94, Tianjin 300071, PR China

Received 18 July 2006; received in revised form 22 September 2006; accepted 27 October 2006
Available online 7 November 2006

Abstract

A series of novel N-substituted benzylidene-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine derivatives were synthesized by condensation of substituted-benzaldehydes with 2-amino-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazole and characterized by ^{1}H NMR, X-ray diffraction and elemental analysis. The results of bioassay showed that some title compounds exhibited some degree of plant growth regulatory and antifungal activities.

Keywords: Ferrocene; Triazole; Thiazole; Biological activity; Synthesis

1. Introduction

The thiazole ring is very important in nature. For example, it exists in thiamine, a coenzyme required for the oxidative decarboxylation of α-keto acids. A tetrahydrothiazole also appears in the skeleton of penicillin which is one of the first and still most important of the broad-spectrum antibiotics. Thiazolamines are key intermediates for synthesizing many pharmaceuticals [1]. Some thiazolidones are valuable medicines [2,3]. It is obvious that compounds with the thiazole ring have potential biological activity. We also know that some Schiff bases are effective antitumor and antibiotic drugs [4,5].

For many years, much interest has focused on ferrocenyl derivatives for their bioactivity [6,7]. Incorporation of ferrocene fragment into the molecule of an organic compound often leads to unexpected biological activity, which is due to their different membrane permeation properties and anomalous metabolism [8–12]. On the other hand, compounds containing the 1*H*-1,2,4-triazole ring system are highly active fungicides [13], especially on the *Basidiomycete* and *Ascomycete* groups of fungi. These compounds are known to inhibit the biosynthesis of ergosterol in fungi. In addition to their fungicidal activity, they also possess a very high level of plant growth regulatory activity on a wide variety of crops [14]. Recently, we reported some ferrocene-containing triazole compounds with biological activities, such as ferrocene-triadimefon analogues [15]; 1-ferrocenyl-3-aryl-2-(1*H*-1,2,4-triazol-1-yl)-prop-2-en-1-one derivatives [16]; 1-phenyl-3-ferrocenyl-4-triazolyl-5-aryl-dihydropyrazole [17]; 3-aryl-1-ferrocenylpropenone [18]. All the compounds show some degree of fungicidal activities and plant growth regulatory activities.

In order to search novel thiazole compounds with potent biological activities, our research group has synthesized some compounds which include aromatic group, thiazole and triazole fragment and obtained some biological compounds. For examples, *N*-(4-F-benzylidene)-4-phenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine exhibits 18.9% inhibitory ratio against *P. pircola*, 20.0% against *A. solani*, 22.2% against *C. ara*, 45.7 against *P. pircola* on the antifungal activities, respectively. It also was assayed for plant growth regulatory against Rape hypocotyls, the inhibitory ratio is −1.8%. The substitution of a phenyl group by a ferrocenyl group in a bioactive compound

* Corresponding author. Tel.: +86 22 2350 5330.
E-mail address: fjx@nankai.edu.cn (J. Fang).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.10.059

was expected to induce great changes in molecular properties, such as the solubility and hydrophobicity [19,20]. Following our interesting in synthesis of new thiazole and triazole compounds with potent biological activities, we engage in the incorporation of ferrocene fragment into thiazole compound. In the present work, we describe the synthesis, characterization and bioactivities of some N-substituted benzylidene-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine derivatives.

2. Results and discussion

2.1. Preparation

The compound **1** was prepared as described by Tárraga et al. [21]. Whereafter, metallation of acetylferrocene with LDA at −78 °C followed by sequential treatment with trimethylchlorosilane and an excess of NBS provided the α-bromoacetylferrocene (**1**) in 80% yield, along with small amount of α,α-dibromoacetylferrocene. Conversion of compound **1** into α-triazolylacetyl-ferrocene (**2**) was achieved in perfect yield (95%) by using anhydrous potassium carbonate as a base [17].

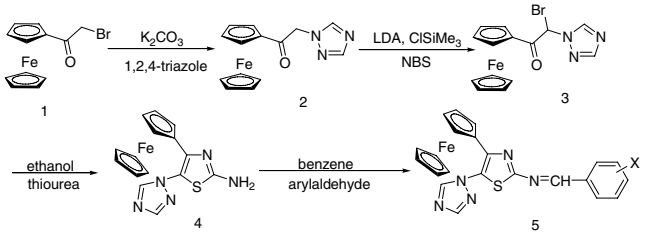
2-Bromo-2-(1*H*-1,2,4-triazol-1-yl)-acetylferrocene was prepared by the same methods described by Tárraga and co-workers [21], the yield of compound **3** is 83% and no by-products were found. Several methods for synthesis of 2-thiazolamine have been reported [22–26]. We prepared ferrocenyl-containing 2-thiazolamine with Hantzsch's method [27], the yield was 90%. When the amine condensed with aromatic aldehydes, the target N-substituted benzylidene-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine (**5a**–**q**) were readily obtained in good to excellent yields (Scheme 1).

2.2. ^1H NMR

All the compounds were completely characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR data of the title compounds are listed in Table 4.

The ^{1}H NMR chemical shifts of ferrocene are in character. The chemical shifts of the unsubstituted cyclopentadiene ring appear between 4.12 and 4.25 ppm as a single peak. The chemical shifts of the substituted cyclopentadiene ring appear as two peaks between 4.25 and 4.29 ppm. The protons of the imine display an acute single peak between 8.90 and 9.60 ppm. The protons of the triazole appear as two single peaks between 8.06 and 8.40 ppm.

All protons in the compounds have been identified and the total number of protons calculated from the integration curve tallies with what is expected from the molecular formula.



Scheme 1.

2.3. Crystal structure

An organe-plate crystal of compound **5a** was recrystallized from acetonitrile. Fig. 1 shows the molecular structure of compound **5a** and gives the atom numbering scheme. The selected bond distances and angels of the compound **5a** are listed in Table 1. Three planar rings in the compound **5a** are (i) the phenyl ring C17–C22; (ii) the thiazole ring C11/C12/S1/C15/N4; (iii) the triazole ring N1/C13/N3/N2/C14. The dihedral angles between planar i and ii and between planar ii and iii are 42.19 (13) and 81.15 (12), respectively [28].

2.4. Biological activities

The assessment of fungicidal activities in vitro for these 2-thiazoleimine compounds **5a**–**q** were examined against four selected fungi including *P. zeae*, *A. solani*, *P. pircola* and *C. ara* at the concentration of 50 mg/L. The screening

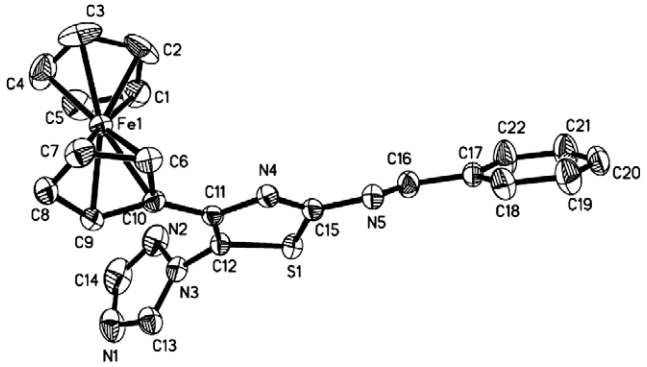


Fig. 1. The molecular structure of compound **5a**.

Table 1
Selected bond lengths and angels of compound **5a**

Bond lengths (Å)		Bond angles (°)	
S (1)–C (12)	1.729 (3)	C (13)–N (1)–C (14)	102.3 (3)
S (1)–C (15)	1.743 (3)	C (14)–N (2)–N (3)	100.1 (3)
N (1)–C (13)	1.310 (4)	C (13)–N (3)–N (2)	110.4 (3)
N (1)–C (14)	1.343 (6)	C (15)–N (4)–C (11)	111.3 (2)
N (2)–C (14)	1.317 (5)	C (16)–N (5)–C (15)	121.4 (3)
N (2)–N (3)	1.368 (4)	C (11)–C (12)–S (1)	111.8 (2)
N (3)–C (13)	1.337 (4)	N (3)–C (12)–S (1)	121.2 (2)
N (4)–C (15)	1.299 (4)	N (1)–C (13)–N (3)	110.2 (3)
N (4)–C (11)	1.379 (3)	N (2)–C (14)–N (1)	116.9 (4)
N (5)–C (16)	1.249 (4)	N (4)–C (15)–S (1)	115.4 (2)
N (5)–C (15)	1.386 (4)	N (5)–C (15)–S (1)	123.2 (2)
		N (5)–C (16)–C (17)	122.5 (3)

Table 2
Biological activities of the title compound **5**

Entry	X	Relative inhibitory ratio (%)				
		P. zeae	*A. solani*	*P. pircola*	*C. ara*	Plant growth regulatory activity
5a	H	22.6	0	45.9	10.0	59.3
5b	4-F	19.4	16.7	55.4	10.0	61.4
5c	3-F	19.4	16.7	50.0	5.0	54.4
5d	2-Cl	19.4	16.7	47.3	10.0	52.3
5e	2-F	25.8	16.7	58.1	15.0	60.7
5f	4-Cl	43.4	22.4	50.0	23.5	49.0
5g	2,4-Cl_2	18.9	20.0	36.8	11.8	51.6
5h	2,4-Me_2	9.7	8.3	47.3	0	50.9
5i	2-MeO	9.7	0	44.6	5.0	56.5
5j	2,4-MeO_2	6.5	8.3	52.7	10.0	55.1
5k	4-Me	19.4	12.5	58.1	10.0	46.7
5l	2-OH	29.0	0	56.8	15.0	55.8
5m	2-NO_2	45.2	29.2	62.2	35.0	40.3
5n	3-OH	22.6	12.5	45.9	10.0	50.9
5o	4-Br	9.7	8.3	45.9	0	53.7
5p	4-OH	0	8.3	56.8	10.0	41.7
5q	4-MeO	9.7	0	54.1	10.0	58.6

data revealed that all the title compounds **5** showed some antifungal activities, among which **5m** showed 62.2% inhibitory ratio against *P. pircola*. The plant growth regulatory activities of the title compounds were tested by Rape hypocotyls test at the concentration of 10 mg/L. All the compounds exhibited some inhibitory activities on the growth of Rape hypocotyls, and the inhibitory ratio is 40.3–61.4%. The data of biological activities of the title compounds **5** were outlined in Table 2.

To our disappointment, the results of the screening of antifungal and plant growth regulatory activities are not exciting, but compared to the phenyl substituted thiazole imine compound, the biological activities are increased. It is interesting to note that the fungicidal activities in vitro of the title compounds appeared to be weakly associated with the substituent group on the benzene cycle. The fungicidal activities of the derivatives with electron-withdrawing groups on phenyl fragments are superior to those with electron-donating groups, but the effect is not obviously. The X-ray structure of **5a** shows that, because of the bulkiness of ferrocene, the ferrocene group was spatially repulsed and swerved to nearby triazole group (Fig. 1), and most of this series of compounds display low fungicidal activity. This may imply that a bulky group close to the triazole cycle is not a wise choice for the generation of compounds with fungicidal activities. In addition, it is well known that the antifungal activities of the triazole derivatives are related to their interference with steroid biosynthesis and fungal cell-wall formation mediated by ferrous cytochrome-P450 enzymes [29]. It was also hypothesized that binding of the triazole to ferrous atom of cytochrome-P450 enzymes was replaced with binding of the triazole to ferrous atom of ferrocene group by intramolecular or intermolecular interaction, as a result, the antifungal activities of title compounds **5a**–**q** was depressed.

3. Summary

A series of ferrocene-containing N-substituted benzylidene-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine derivatives were synthesized and their structures were verified by elemental analysis, ^{1}H NMR and X-ray diffraction analysis. These novel 2-thiazoleimine derivatives were screened for their biological activities. The screening data revealed that compounds **5** show some antifungal activities and plant growth regulatory activity. Further structure modification and optimization of these ferrocene-containing thiazole derivatives are necessary.

4. Experimental

All reactions were carried out under nitrogen atmosphere and monitored by TLC. All solvents were pre-dried and distilled prior to use. All melting points were determined on a Yanaco-241 apparatus and thermometer was uncorrected. The ^{1}H NMR spectra were measured on a Brucker AC-300 spectrometer in $CDCl_3$ or d_6-DMSO solution with TMS as internal standard. Elemental analyses were determined on a Yanaco CHN Corder elemental analyzer.

*4.1. Synthesis of 2-bromo-2-(1H-1,2,4-triazol-1-yl)-acetylferrocene (**3**)*

n-Butyllithium 1.6 M in hexane (45.2 mL, 72.3 mmol) was dropped to a solution of diisopropylamine (7.32 g, 72.3 mmol) in dry THF (20 mL), at −78 °C under nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h. Then, a solution of α-(1*H*-1,2,4-triazol-1-yl)-acetyl-ferrocene (12.93 g, 43.8 mmol) in 100 mL dry THF was dropped. The mixture was stirred for 2 h, and chlorotrimethylsilane

(6.30 g, 57 mmol) was added in dropwise. After 4 h under these reaction conditions, NBS (10.14 g, 57 mmol) was added in a single addition, and the mixture was stirred until the reaction reached room temperature (6–8 h). The reaction mixture was filtered through a silica gel layer, the resulting solution was evaporated to dryness and chromato-

Table 3
Physical properties and elemental analysis data for compound **5**

Entry	X	Yield (%)	M.p. (°C)	Elemental analysis data (Calc. %)		
				C	H	N
5a	H	88	165–166	60.27 (60.15)	4.04 (3.90)	16.03 (15.94)
5b	4-F	85	171–172	57.75 (57.78)	3.57 (3.53)	15.12 (15.31)
5c	3-F	64	152–153	57.83 (57.78)	3.65 (3.53)	15.31 (15.31)
5d	2-Cl	84	157–158	55.79 (55.77)	3.47 (3.40)	14.55 (14.78)
5e	2-F	80	152–153	58.01 (57.78)	3.75 (3.53)	15.25 (15.31)
5f	4-Cl	62	199–200	55.71 (55.77)	3.45 (3.40)	14.66 (14.78)
5g	2,4-Cl_2	80	169–170	51.89 (51.99)	3.08 (2.98)	13.85 (13.78)
5h	2,4-Me_2	82	151–152	61.64 (61.68)	4.75 (4.53)	14.95 (14.98)
5i	2-MeO	79	160–161	58.76 (58.86)	4.08 (4.29)	14.83 (14.92)
5j	2,4-MeO_2	82	156–157	58.01 (57.72)	4.12 (4.24)	13.92 (14.02)
5k	4-Me	82	161–162	61.20 (60.94)	4.12 (4.22)	15.40 (15.45)
5l	2-OH	69	167–168	58.08 (58.03)	3.87 (3.76)	15.36 (15.38)
5m	2-NO_2	70	69–70	54.31 (54.56)	3.52 (3.33)	17.30 (17.35)
5n	3-OH	68	159–160	57.92 (58.03)	3.96 (3.76)	15.22 (15.38)
5o	4-Br	91	198–199	50.95 (50.99)	3.17 (3.11)	13.57 (13.51)
5p	4-OH	65	156–157	58.34 (58.03)	4.01 (3.76)	15.36 (15.38)
5q	4-MeO	89	159–160	58.73 (58.86)	3.95 (4.08)	14.70 (14.92)

Table 4
^{1}H NMR date for compound **5**

Entry	X	^{1}H NMR spectra data (δ, $CDCl_3$)
5a	H	9.02 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.63–7.51 (m, 5H, ArH), 4.27 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5b	4-F	8.98 (s, 1H, N=CH), 8.08 (s, 1H, TrH), 8.06 (s, 1H, TrH), 8.06–7.20 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5c	3-F	9.03 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.81–7.29 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5d	2-Cl	9.50 (s, 1H, N=CH), 8.40 (s, 1H, TrH), 8.27 (s, 1H, TrH), 8.31–7.42 (m, 4H, ArH), 4.28 (s, 4H, C_5H_4), 4.14 (s, 5H, C_5H_5)
5e	2-F	9.35 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.62–7.17 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5f	4-Cl	9.01 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 8.01–7.50 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5g	2,4-Cl_2	9.45 (s, 1H, N=CH), 8.35 (s, 1H, TrH), 8.31 (s, 1H, TrH), 8.25–7.39 (m, 3H, ArH), 4.28 (s, 2H, C_5H_4), 4.27 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5h	2,4-Me_2	9.27 (s, 1H, N=CH), 8.30 (s, 1H, TrH), 8.24 (s, 1H, TrH), 8.16–7.11 (m, 3H, ArH), 4.27 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 2.64 (s, 3H, CH_3), 2.40 (s, 3H, CH_3)
5i	2-MeO	9.40 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.58–6.98 (m, 4H, ArH), 4.27 (s, 2H, C_5H_4), 4.27 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 3.96 (s, 3H, OCH_3)
5j	2,4-MeO_2	9.24 (s, 1H, N=CH), 8.30 (s, 1H, TrH), 8.24 (s, 1H, TrH), 8.26–6.41 (m, 3H, ArH), 4.27 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 3.93 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3)
5k	4-Me	8.96 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.96–7.23 (m, 4H, ArH), 4.27 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 2.47 (s, 3H, CH_3)
5l	2-OH	12.11 (s, 1H, OH), 9.27 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.58–7.01 (m, 4H, ArH), 4.29 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5m	2-NO_2	9.60 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.24 (s, 1H, TrH), 8.46–7.73 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5n	3-OH	11.99 (s, 1H, OH), 8.95 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.25 (s, 1H, TrH), 7.57–7.10 (m, 4H, ArH), 4.27 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.12 (s, 5H, C_5H_5)
5o	4-Br	8.99 (s, 1H, N=CH), 8.30 (s, 1H, TrH), 8.25 (s, 1H, TrH),7.92–7.66 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.24 (s, 2H, C_5H_4), 4.12 (s, 5H, C_5H_5)
5p	4-OH	9.88 (s, 1H, OH), 8.87 (s, 1H, N=CH), 8.31 (s, 1H, TrH), 8.30 (s, 1H, TrH), 7.96–6.97 (m, 4H, ArH), 4.28 (s, 2H, C_5H_4), 4.25 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5)
5q	4-MeO	8.90 (s, 1H, N=CH), 8.30 (s, 1H, TrH), 8.25 (s, 1H, TrH), 8.02–7.02 (m, 4H, ArH), 4.26 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5), 3.92 (s, 3H, OCH_3)

graph on a silica gel column using ethyl acetate/petroleum ether (1:3) as eluent, 2-bromo-2-(1*H*-1,2,4-triazol-1-yl)-acetylferrocene (**3**) was obtained as an organic crystal in 83% yield; m.p. 114–116 °C; ^{1}H NMR (d_6-DMSO, δ ppm): 9.08 (s, 1H, TrH), 8.23 (s, 1H, TrH), 5.08 (s, 1H, CHBr), 4.80 (s, 2H, C_5H_4), 4.30 (s, 5H, C_5H_5), 3.41 (s, 2H, C_5H_4).

4.2. Synthesis of 2-amino-4-ferrocenyl-5-(1H-1,2,4-triazol-1-yl)-1,3-thiazole (4)

2-Bromo-2-(1*H*-1,2,4-triazol-1-yl)-acetylferrocene (**3**) 1.39 g (3.7 mmol) and thiourea 0.40 g (5.3 mmol) were dissolved in 10 mL of warm ethanol. The mixture was refluxed for 3 h and then poured into 80 mL of ammonia spirit. The yellow solids that formed were filtered and dried. After recrystallization from the solvent of methanol, 1.30 g of amine **4** was obtained. ^{1}H NMR (d_6-DMSO, δ ppm): 8.82 (s, 1H, TrH), 8.27 (s, 1H, TrH), 7.44 (s, 2H, NH_2), 4.42 (s, 2H, C_5H_4), 4.00 (s, 5H, C_5H_5), 3.84 (s, 2H, C_5H_4). Yield 90%; m.p. 248–250 °C.

4.3. General procedure for synthesis of N-substituted benzylidene-4-ferrocenyl-5-(1H-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine (5a–q)

2-Amino-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazole (0.35 g, 1 mmol) and substituted benzaldehyde (1 mmol) were dissolved in 10 mL of benzene. One drop of piperidine was added to the mixture solution. The solution was heated and refluxed in a 50 mL flask equipped with a Dean-Stark trap condenser until no water appeared (ca. 2 h). After the reaction solution was concentrated and purified by silica column chromatography using ethyl acetate/petroleum ether (1:3) as eluent, an organic crystal was obtained. The physical properties, elemental analysis data and ^{1}H NMR spectra of compounds **5a–q** are given in Tables 3 and 4, respectively.

4.4. X-ray crystallography

A crystal of compound **5a** was obtained from acetonitrile. Diffraction measurements of compound **5a** was carried out on a Bruker SMART 1000CCD diffractometer operating at 50 kV and 20 mA using Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection at 293 K and reduction was performed using the SMART and SAINT software [30]. An empirical absorption correction (SADABS) was applied to the raw intensities [31]. The crystal structure was determined by direct methods and refined by full-matrix least-squares using the SHELXTL-PC program package [32]. Non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically (C–H lengths fixed at 0.93 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement. A summary of the crystal data is given in Table 5.

Table 5
Crystallographic data for compound **5a**

Empirical formula	$C_{22}H_{17}FeN_5S$
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	8.826 (4)
b (Å)	10.608 (5)
c (Å)	11.619 (5)
α (°)	64.982 (7)
β (°)	83.064 (8)
γ (°)	83.064 (8)
V (Å^3)	976.0 (8)
Z	2
D_{calc} (mg mm^{-3})	1.495
Absorption coefficient (mm^{-1})	0.898
F (000)	452
Crystal size (mm^{-3})	$0.22 \times 0.20 \times 0.18$
θ Range for data collection (°)	1.94–25.01
Limiting indices	$-10 \leqslant h \leqslant 8$, $-12 \leqslant k \leqslant 12$, $-11 \leqslant l \leqslant 13$
Reflections collected	4998
Independent reflections	3425 ($R_{int} = 0.0245$)
Completeness to $\theta = 25.01$	99.3%
Goodness-of-fit	1.038
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0381$, $wR_2 = 0.0904$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.1029$
Large difference peak and hole (e Å^{-3})	0.266 and −0.257

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (NNSFC) (No. 20172030) and the Key Project of Chinese Ministry of Education (No. 105046) for financial support.

References

[1] J.V. Metzger, The chemistry of heterocyclic compounds, in: Thiazole and Its DerivativesA Series of Monographs, vol. 34, Wiley, Chichester, 1979.
[2] B. Dash, S. Praharaj, P.K. Mohapatra, J. Indian Chem. Soc. LVIII (1981) 1184.
[3] H.D. Troutman, L.M. Long, J. Am. Chem. Soc. 70 (1948) 3436.
[4] B. Dash, M. Patra, S. Praharaj, Indian J. Chem. 19B (1980) 894.
[5] B. Dash, P.K. Mahapatra, D. Panda, J.M. Pattnaik, J. Indian Chem. Soc. LXI (1984) 1061.
[6] N. Motohashi, R. Meyer, S.R. Gollapudi, J. Organometal. Chem. 205 (1990) 398.
[7] E.L. Michelotti, D.P. Le, G.R. Carlson, A.R. Egan, US Patent 5 075471, 1991.
[8] L. Chen, Q.M. Wang, R.Q. Huang, C.H. Mao, J. Shang, H.B. Song, Appl. Organometal. Chem. 19 (2005) 45.
[9] L. Chen, Q.L. Xie, L.J. Sun, H.L. Wang, J. Organometal. Chem. 678 (2003) 90.
[10] L . Chen, J.X. Chen, L.J. Sun, Q.L. Xie, Appl. Organometal. Chem. 19 (2005) 1038.
[11] X.Q. Song, Z.Q. Yang, Q.L. Xie, J. Organometal. Chem. 103 (1998) 566.

[12] H.K. Sun, Q.M. Wang, R.Q. Huang, J. Organometal. Chem. 182 (2002) 655.
[13] H. Buchenauer, Proc. Br. Crop. Protect. Conf. 2 (1977) 699.
[14] H. Buchenauer, J. Plant. Dis. Protect. (Z. Pflanzenkr. Pflanzenschutz) 10 (1979) 341.
[15] Z. Jin, Y. Hu, A.H. Huo, W.F. Tao, L. Shao, J.B. Liu, J.X. Fang, J. Organomet. Chem. 691 (2006) 2340.
[16] J.B. Liu, L.C. Li, H. Dai, Z. Liu, J.X. Fang, J. Organomet. Chem. 691 (2006) 2686.
[17] J.X. Fang, Z. Jin, Z.M. Li, W. Liu, J. Organomet. Chem. 674 (2003) 1.
[18] J.X. Fang, Z. Jin, Z.M. Li, W. Liu, Appl. Organometal. Chem. 17 (2003) 145.
[19] C. Biot, L. Delhaes, H. Abessolo, J. Organomet. Chem. 59 (1999) 589.
[20] C. Biot, J. Med. Chem. 35 (2000) 707.
[21] A. Tárraga, P. Molina, D. Curiel, J.L. Lo'pez, M.D. Velasco, Tetrahedron 55 (1999) 14701.
[22] L.C. King, R.J. Hlavacek, J. Am. Chem. Soc. 72 (1950) 3722.
[23] A.A. Monton, H.P. Penner, J. Am. Chem. Soc. 73 (1951) 3300.
[24] V.K. Gewald, H. Bottcher, R. Mayer, J. Prakt. Chem. 23 (1964) 298.
[25] R. Dahiya, H.K. Pujari, Indian J. Chem. Sect. B 25 (1986) 966.
[26] R.M. Moriarty, B.K. Vaid, M.P. Duncan, S.G. Levy, O. Prakash, S. Goyal, Synthesis (1992) 845.
[27] E.B. Knot, J. Chem. Soc. (1947) 1656.
[28] H.B. Yu, L. Shao, Z. Jin, J.B. Liu, J.X. Fang, Acta Crystallogr., Sect. E 61 (2005) m2031.
[29] J.C. Kapteyn, J.B. Pillmoor, M.A. De Waard, Pest. Sci. 34 (1992) 37.
[30] SMART 5.0 and Saint 4.0 for windows NT: Area Detector Control and Integration Software, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1998.
[31] G.M. Sheldrick, SADABS: program for empirical absorption correction of area detector data, University of Göttingen, Germany, 1996.
[32] G.M. Sheldrick, SHELXTL 5.10 for Windows NT: structure determination software programs, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.