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Synthesis, structure and biological activity studies of 2-[(1*H*-1,2,4-triazol-1-yl)methyl]-1-aryl)-3-ferrocenyl prop-2-en-1-one derivatives

Jianbing Liu, Tao Liu, Hong Dai, Zhong Jin and Jianxin Fang*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Fifteen new ferrocene derivatives containing 1*H*-1,2,4-triazole moiety were synthesized in various yields by the condensation of ferrocenecarboxaldehyde with 1-aryl-3-(1*H*-1,2,4-triazo-1-yl)-propen-1-ones in toluene. Their structures have been confirmed by ^{1}H NMR, IR, MS and elemental analysis. In addition, the crystal structure of 4l was determined. The antifungal and plant growth regulatory activities of the title compounds are discussed. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: 1*H*-1,2,4-triazole; ferrocene; antifungal activity; plant growth regulatory activity

INTRODUCTION

It is well known that 1*H*-1,2,4-triazole compounds not only possesses broad-spectrum antifungal, anti-inflammatory, antiviral, antimicrobial, antitumorial, anticonvulsant, analgesic and antihypotensive activities,[1–7] but it also has been shown to have insecticidal, heribicidal and plant growth regulatory activities.[8–10] Many commercial 1*H*-1,2,4-triazole compounds had been used widely in plant protection and medicine, such as the agricultural fungicides Triadimefon, Triadimenol, Flusilazole, Bitertanol, and Cyproconazole, and clinical drugs such as Fluconazole and Itraconazole.[11,12]

Owing to its wide application in catalysis,[19] materials[20] and new biologically active compounds,[21,22] the chemistry of ferrocene has been attracting much attention from chemists for many years.[13–18] Recently, the biochemical study of ferrocenyl derivatives has received more interests from biochemists,[23–27] and many ferrocenyl derivatives have been reported to have antitumor,[23,24] antifungal,[16,25,26] insecticidal,[27] and plant growth regulatory activities.[16,25,26] Indeed, ferrocenyl moiety replacement of the phenyl group has already been shown to improve biologically activities of the molecules.[14,15,28,29] Encouraged by these and our previous reported results,[16,25,26] we designed and synthesized 15 new 1*H*-1,2,4-triazole derivatives containing ferrocenyl moiety (Scheme 1), which have been characterized by ^{1}H NMR, IR and MS spectra, together with elemental analysis and X-ray diffraction analysis. Preliminary bioassay showed *in vitro* biological activities and plant growth regulatory activities.

*Correspondence to: Jianxin Fang, State Key Laboratory and Insitute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P.R. China.
E-mail: liu_jianbing65@yahoo.com.cn
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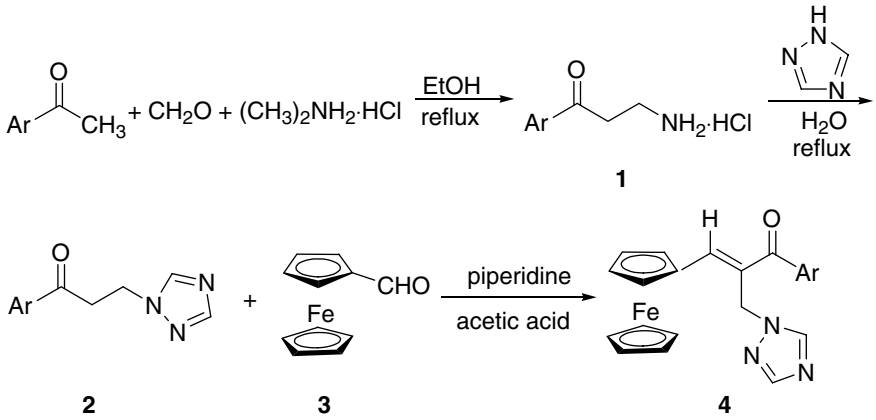
EXPERIMENTAL

Instruments

The title compound **4** was synthesized under nitrogen atmosphere and monitored using thin-layer chromatography. The ^{1}H NMR spectra were measured on a Bruker AC 300, using tetramethylsilane (TMS) as internal standard and deuterized chloroform as solvent. Chemical shift values (□) are given in ppm. IR spectra were recorded on a Bruker Equinox 55 spectrometer in KBr disks. MS spectra were undertaken using a VG ZAB-HS spectrometer using the EI method. Elemental analysis was determined with a Yanaco CHN Corder MT-3 elemental analyzer. Melting points were determined using X-4 digital melting point apparatus, and the thermometer was uncorrected.

Synthesis

1*H*-1,2,4-triazole was obtained from Nankai University Biochemical Science and Technology Development Company, Tianjin, People's Republic of China, and purified by recrystallizing with ethanol prior to use. Toluene were dried by standard methods and distilled prior to use. Ferrocenecarboxaldehyde was synthesized according to the literature method.[30] Intermediates **1** were prepared with a reported



Scheme 1.

procedure[31] in yields of 83.4–93.9%, and intermediates **2** were obtained by the reaction of intermediate **1** with 1*H*-1,2,4-triazole in water.[32]

Synthesis of the title compounds 4

To a stirred solution of ferrocenecarboxaldehyde (2.36 g, 0.011 mol), intermediates **2** (0.01 mol) and dry toluene (50 ml) were added five drops of piperidine and five drops of glacial acetic acid at room temperature under nitrogen atmosphere. The mixture was then heated to reflux and kept at this temperature for 4 h; meanwhile, the water generated in the reaction was evaporated. The toluene was evaporated under reduced pressure, then the residue was purified by column chromatography on silica gel with the solvent system of petroleum ether (60–90 °C)–ethyl acetate (v/v, 4 : 1), to give a purple solid in various yields.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-phenyl-3-ferrocenylprop-2-en-1-One (**4a**)*

Purple solid, m.p. 80–82 °C, yield 37.1%. ^{1}H NMR ($CDCl_3$): δ 4.15 (5H, s), 4.37 (2H, s), 4.53 (2H, s), 5.45 (2H, s), 7.37 (1H, s), 7.51–7.65 (5H, m), 8.10 (2H, s). Anal. found: C, 66.42; H, 4.75; N, 10.40. Calcd for $C_{22}H_{19}FeN_3O$: C, 66.52; H, 4.82; N, 10.58%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(4-fluorophenyl)-3-ferrocenylprop-2-en-1-one (**4b**)*

Purple solid, m.p. 123–125 °C, yield 45.6%. ^{1}H NMR ($CDCl_3$): δ 4.18 (5H, s), 4.57 (2H, s), 4.75 (2H, s), 5.39 (2H, s), 7.19–7.21 (2H, d), 7.34 (1H, s), 7.71–7.73 (2H, d), 8.03 (1H, s), 8.32 (1H, s). Anal. found: C, 63.54; H, 4.42; N, 10.17. Calcd for $C_{22}H_{18}FFeN_3O$: C, 63.64; H, 4.37; N, 10.12%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(2-chlorophenyl)-3-ferrocenylprop-2-en-1-one (**4c**)*

Purple solid, m.p. 149–150 °C, yield 46.7%. ^{1}H NMR ($CDCl_3$): δ 4.23 (5H, s), 4.61 (2H, s), 4.79 (2H, s), 5.36 (2H, s), 7.39 (1H, s), 7.41–7.66 (4H, m), 8.05 (1H, s). 8.29 (1H, s). Anal. found: C, 61.17; H, 4.23; N, 10.00. Calcd for $C_{22}H_{18}ClFeN_3O$: C, 61.22; H, 4.20; N, 9.73%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(3-chlorophenyl)-3-ferrocenylprop-2-en-1-One (**4d**)*

Purple solid, m.p. 158–160 °C, yield 41.2%. ^{1}H NMR ($CDCl_3$): δ 4.21 (5H, s), 4.60 (2H, s), 4.78 (2H, s), 5.38 (2H, s), 7.37 (1H, s), 7.42–7.65 (4H, m), 8.03 (1H, s). 8.28 (1H, s). Anal. found: C, 61.29; H, 4.23; N, 9.71. Calcd for $C_{22}H_{18}ClFeN_3O$: C, 61.22; H, 4.20; N, 9.73%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(4-chlorophenyl)-3-ferrocenylprop-2-en-1-one (**4e**)*

Purple solid, m.p. 113–115 °C, yield 42.8%. ^{1}H NMR ($CDCl_3$): δ 4.15 (5H, s), 4.55 (2H, s), 4.73 (2H, s), 5.48 (2H, s), 7.24 (1H, s), 7.46–7.59 (4H, m), 8.32 (2H, s). Anal. found: C, 61.21; H, 4.40; N, 9.60. Calcd for $C_{22}H_{18}ClFeN_3O$: C, 61.22; H, 4.20; N, 9.73%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(2,4-dichlorophenyl)-3-ferrocenylprop-2-en-1-ton (**4f**)*

Purple solid, m.p. 137–139 °C, yield 47.1%. ^{1}H NMR ($CDCl_3$): δ 4.18 (5H, s), 4.69(2H, s), 4.83 (2H, s), 5.41 (2H, s), 7.29–7.48 (3H, m), 7.75 (1H, s), 8.12 (1H, s) 8.48 (1H, s). Anal. found: C, 56.78; H, 3.69; N, 8.96. Calcd for $C_{22}H_{17}Cl_2FeN_3O$: C, 56.69; H, 3.68; N, 9.01%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(2, 5-dichlorophenyl)-3-ferrocenylprop-2-en-1-one (**4g**)*

Purple solid, m.p. 135–136 °C, yield 46.2%. ^{1}H NMR ($CDCl_3$): δ 4.14 (5H, s), 4.63 (2H, s), 4.77 (2H, s), 5.39 (2H, s), 7.24–7.43 (3H, m), 7.69 (1H, s), 8.06 (1H, s) 8.42 (1H, s). Anal. found: C, 56.60; H, 3.68; N, 9.18. Calcd for $C_{22}H_{17}Cl_2FeN_3O$: C, 56.69; H, 3.68; N, 9.01%.

*2-[(1H-1,2,4-triazol-1-yl)methyl)-1-(2-bromophenyl)-3-ferrocenylprop-2-en-1-one (**4h**)*

Purple solid, m.p. 135–136 °C, yield 46.2%. ^{1}H NMR ($CDCl_3$): δ 4.13 (5H, s), 4.60 (2H, s), 4.74 (2H, s), 5.36 (2H, s), 7.16–7.47 (4H, m), 7.66 (1H, s), 8.03 (1H, s) 8.39 (1H, s). Anal. found: C, 55.65; H, 3.90; N, 8.95. Calcd for $C_{22}H_{18}BrFeN_3O$: C, 55.49; H, 3.81; N, 8.82%.

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*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(3-bromophenyl)-3-ferrocenylprop-2-en-1-one (**4i**)*

Purple solid, m.p. 166–167 °C, yield 32.2%. ^{1}H NMR ($CDCl_3$): δ 4.11 (5H, s), 4.57 (2H, s), 4.68 (2H, s), 5.33 (2H, s), 7.12–7.42 (4H, m), 7.65 (1H, s), 8.00 (1H, s) 8.32 (1H, s). Anal. found: C, 55.59; H, 3.97; N, 8.90. Calcd for $C_{22}H_{18}BrFeN_3O$: C, 55.49; H, 3.81; N, 8.82%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(4-bromophenyl)-3-ferrocenylprop-2-en-1-one (**4j**)*

Purple solid, m.p. 114–116 °C, yield 47.3%. ^{1}H NMR ($CDCl_3$): δ 4.15 (5H, s), 4.55 (2H, s), 4.72 (2H, s), 5.32 (2H, s), 7.31 (1H, s), 7.54 (2H, d), 7.60 (2H, d) 7.79 (1H, s) 8.26 (1H, s). Anal. found: C, 55.36; H, 3.87; N, 8.65. Calcd for $C_{22}H_{18}BrFeN_3O$: C, 55.49; H, 3.81; N, 8.82%. IR (KBr): 3403, 1608, 1560, 1501, 1479, 1381, 1352, 1272, 1190, 1171, 1113, 1064, 1010, 980, 938, 887, 839, 816, 759, 636, 484.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(4-methoxyphenyl)-3-ferrocenylprop-2-en-1-one (**4k**)*

Purple solid, m.p. 97–99 °C, yield 30.5%. ^{1}H NMR ($CDCl_3$): δ 3.88 (3H, s), 4.17 (5H, s), 4.53 (2H, s), 4.70 (2H, s), 5.40 (2H, s), 6.97 (1H, s), 7.36–8.017.71 (4H, m), 8.10 (2H, s). Anal. found: C, 64.53; H, 5.00; N, 9.60. Calcd for $C_{23}H_{21}FeN_3O_2$: C, 64.65; H, 4.95; N, 9.83%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(2,5-dimethoxyphenyl)-3-ferrocenylprop-2-en-1-one (**4l**)*

Purple solid, m.p. 132–133 °C, yield 37.9%. ^{1}H NMR ($CDCl_3$): δ 3.79–3.83 (6H, d), 4.08 (5H, s), 4.52 (2H, s), 4.60 (2H, s), 5.34 (2H, s), 6.81–7.04 (3H, m), 7.34 (1H, s), 8.05 (1H, s), 8.32 (1H, s). Anal. found: C, 62.98; H, 4.98; N, 9.26. Calcd for $C_{24}H_{23}N_3O_3$: C, 63.03; H, 5.07; N, 9.19%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(3-nitrophenyl)-3-ferrocenylprop-2-en-1-one (**4m**)*

Purple solid, m.p. 172–174 °C, yield 54.6%. ^{1}H NMR ($CDCl_3$): δ 4.21 (5H, s), 4.60 (2H, s), 4.76 (2H, s), 5.52 (2H, s), 7.43 (1H, s), 7.78–8.01 (4H, m), 8.10 (2H, s). Anal. found: C, 59.25; H, 4.25; N, 12.65. Calcd for $C_{22}H_{18}FeN_4O_3$: C, 59.74; H, 4.10; N, 12.67%.

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(4-nitrophenyl)-3-ferrocenylprop-2-en-1-one (**4n**)*

Purple solid, m.p. 174–176 °C, yield 57.4%. ^{1}H NMR ($CDCl_3$): δ 4.17 (5H, s), 4.62 (2H, s), 4.77 (2H, s), 5.44 (2H, s), 7.31 (1H, s), 7.77 (4H, m), 8.34 (2H, s). Anal. found: C, 59.78; H, 4.13; N, 12.62. Calcd for $C_{22}H_{18}FeN_4O_3$: C, 59.74; H, 4.10; N, 12.67%. IR (KBr): 3411, 1608, 1513, 1345, 1269, 1199, 1134, 1101, 1008, 966, 849, 803, 716, 677, 495. EI MS (%): m/z 442.0 (M^+, 100), 377.0 (12), 308 (10), 121 (82), 104 (54), 76 (36), 56 (38).

*2-[(1H-1,2,4-triazol-1-yl)methyl]-1-(naphthalene-2-yl)-3-ferrocenylprop-2-en-1-one (**4o**)*

Purple solid, m.p. 66–68 °C, yield 39.4%. ^{1}H NMR ($CDCl_3$): δ 4.03 (5H, s), 4.52 (5H, s), 4.69 (5H, s), 5.43 (2H, s), 7.27 (1H, s), 7.47–7.95 (7H, m), 8.06 (1H, s) 8.41 (1H, s). Anal. found: C, 69.60; H, 4.85; N, 9.19. Calcd for $C_{26}H_{21}FeN_3O$: C, 69.81; H, 4.73; N, 9.39%.

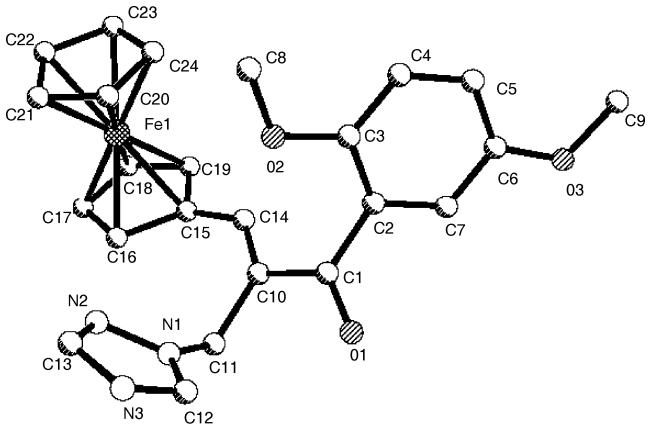

Figure 1. Molecular structure of compound **4l**.

X-ray crystallography

A crystal of compound **4l** (Fig. 1) was obtained from a solvent system of petroleum ether (60–90 °C)–ethyl acetate (v/v, 3 : 1). Diffraction measurements of compound **4l** were carried out on a Bruker SMART 1000CCD diffractiometer operating at 50 kV and 20 mA using Mo K_α radiation ($\lambda = 0.71073$ Å). Data collection at 294 K and reduction were performed using the SMART and SAINT software.[33] A multiscan method was applied to the raw intensities.[34] The crystal structure was determined by direct methods and refined by full-matrix least squares using the SHELXTL-PC program package.[35] Non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically, 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 1.

Biological activities

The title compounds **4** were screened for their biological activities *in vitro* against *G. zeae*, *A. solani*, *C. arachidicola*, *P. piricola*, *P. asparagi* and *C. cucumerinum*, at the concentration of 50 mg/l, and the relative inhibition ratios (%) against these fungi are listed in Table 3. The plant growth regulatory activities were tested by wheat coleoptile and cucumber cotyledon test at the concentration of 10 mg/l (Table 4). The biological activity was assayed at the Biological Assay Centre, Nankai University according to procedures described previously.[25]

RESULTS AND DISCUSSION

Preparations

Ferrocenecarboxaldehyde was prepared according to the literature procedure,[30] and the reaction mixture was poured

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Table 1. Crystallographic data for compound **4l**

Empirical	$C_{24}H_{23}N_3O_3$
Crystal system	Triclinic, P-1
Space group	
Unit cell dimensions	
a (Å)	8.4129(16)
b (Å)	11.352(2)
c (Å)	11.972(2)
α (deg)	95.763(3)
β (deg)	101.223(3)
γ (deg)	106.415(3)
V (Å^3)	1061.0(3)
Z	2
D_{cacl} (mg mm^{-3})	1.431
Absorption coefficient (mm^{-3})	0.742
F (0 0 0)	476
Crystal size (mm^3)	0.24 × 0.20 × 0.12 mm
θ range for data collection (deg)	1.76–25.01
Limiting indices	$-8 \le h \le 10$, $-9 \le k \le 13$, $-12 \le l \le 14$
Reflections collected	5425
Independent reflections	3709 ($R_{int} = 0.0203$)
Completeness to $\theta = 25.01$	99.3%
GOF	1.067
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0378$, $wR_2 = 0.0820$
R indices (all data)	$R_1 = 0.0572$, $wR_2 = 0.0917$

into ice water to remove the inorganic salts. Ice water containing rongalite described in the literature was not necessary. Intermediates **1** were obtained in high yields using the literature method,[31] and can be converted to intermediates **2** in yields of 82.6–91.3% without purification. Intermediates **1** and **2** were colorless solids.

Title compounds **4** were prepared by the condensation of ferrocenecarboxaldehyde with intermediates **2** using piperidine and acetic acid as catalyst, under nitrogen atmosphere in toluene. Benzene was also used as a solution in the reaction, but the yields were lower. Piperidine was also investigated as a catalyst, but the yields were lower than that for piperidine and acetic acid.

Table 2. Selected bond lengths and angles of compound **4l**

Bond lengths(Å)		Bond angles (deg)	
O(1)–C(1)	1.219(3)	C(10)–C(14)–C(15)	130.5(2)
O(2)–C(8)	1.432(3)	C(10)–C(11)–N(1)	113.06(19)
N(1)–C(11)	1.460(3)	**C(11)–C(10)–C(14)**	**124.9(2)**
N(1)–N(2)	1.362(3)	C(24)–Fe(1)–C(17)	179.41(14)
N(3)–C(13)	1.340(4)	C(1)–C(10)–C(14)	120.7(2)
N(3)–C(12)	1.322(3)	C(1)–C(10)–C(11)	114.1(2)
C(10)–C(11)	1.510(3)	C(8)–O(2)–C(3)	116.5(2)
C(14)–C(15)	1.450(3)	C(2)–C(1)–O(1)	117.9(2)
C(1)–C(2)	1.503(3)	C(10)–C(1)–O(1)	120.0(2)
C(15)–C(19)	1.443(3)	**C(10)–C(1)–C(2)**	**122.1(2)**
C(23)–C(24)	1.383(5)	C(3)–C(2)–C(7)	118.6(2)
Fe(1)–C(15)	2.037(2)	C(19) C(18) Fe(1)	68.71(15)

Table 3. Fungicidal activities of compounds **4** (50 mg/l)

	Relative inhibitory ratio (%)					
Entry	*G. zeae*	*A. solani*	*P. asparagi*	*P. piricola*	*C. achidicola*	*C. cucumerinum*
4a	29.3	19.9	13.6	0	27.6	18.0
4b	37.1	48.1	38.8	44.9	6.80	16.0
4c	36.5	39.8	36.4	36.7	25.1	28.7
4d	23.9	35.1	31.8	25.6	29.8	18.1
4e	38.7	48.6	45.6	29.3	33.4	29.9
4f	26.9	46.5	34.2	16.8	8.90	28.0
4g	37.1	45.8	46.1	19.5	21.9	35.7
4h	39.5	48.7	46.1	39.1	38.6	30.0
4i	19.5	37.7	35.9	42.2	35.9	29.7
4j	28.9	33.3	26.6	36.1	36.8	31.5
4k	25.1	30.1	25.9	29.7	27.4	28.7
4l	26.9	29.9	46.8	35.8	29.6	29.7
4m	18.5	31.7	40.1	29.5	28.7	33.4
4n	12.0	28.8	19.9	29.1	30.1	0
4o	25.8	39.4	35.4	35.6	28.8	35.1

^{1}H NMR, IR and mass spectra

The title compounds **4** were characterized by ^{1}H NMR and elemental analysis. Compounds **4j** and **4n** were characterized by IR spectra, and **4n** was also characterized by electron-impact mass spectrometry (EI MS). Their ^{1}H NMR are

Table 4. Plant growth regulatory activities of compounds **4** (10 mg/l)

Entry ratio[a]	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**	**4i**	**4j**	**4k**	**4l**	**4m**	**4n**	**4o**
Wheat coleoptile	−3.2	−5.6	−4.5	−3.9	−3.1	−6.9	−8.7	−9.4	−3.7	−5.6	−8.1	−3.9	−10.6	−11.5	−14.8
Cucumber cotyledon	−6.8	−10.6	−5.9	−6.8	−7.7	−15.3	−10.0	−8.9	−4.6	−5.5	−7.9	−4.0	−8.2	−10.1	−13.1

[a] Ratio: relative inhibitory ratio (%).

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characteristic: the ferrocenyl substitute gave rise to a five-proton singlet for the non-substituted cyclopentadienyl ring and a double peak for the monosubstituted ring. The IR spectra of compounds **4j** and **4n** have been recorded in the range of 400–4000 cm^{-1}. The characteristic bands of the ferrocenyl group in the IR spectra of compound **4j** and **4n** appear at 1113, 1010, 1101 and 1008 cm^{-1}, respectively. The strong absorptions of **4j** and **4n** at 1608 cm^{-1} are the asymmetric vibration of C═O. The MS spectra show that the molecular ion peak of compound **4n** is $m/z = 442$ and the base peak is $m/z = 442$.

Crystal structure

X-ray diffraction analysis of compound **4l** showed that the configuration of this compound **4** was *E* configuration. Figure 1 shows the molecular structures, and selected bond distances and angles of the compound are listed in Table 2.

Biological activities

The screening data revealed that all compounds **4** showed some degree of antifungal activity. Compound **4** exhibited low inhibitory activities on the growth of wheat coleoptile and cucumber cotyledon, and the inhibitory ratio was −3.2 to −15.3%.

Compared with a commercial antifungal analog (Triadimenfon), the antibacterial activities of most title compounds were not encouraging, although some compounds manifested some antibacterial activity. To the best of our knowledge, a linkage between the triazole ring and the aryl group via a carbon–carbon single or double bond is essential for fungicidal activities. In addition, it has been proved that an extended carbon backbone linking the triazole cycle and the aryl group in an almost linear fashion possesses higher activity than a distorted backbone. The X-ray structure of **4l** shows that, because of the bulkiness of ferrocene, the triazole cycle and the aryl group are not connected in such a way, but via a bent linkage [bond angle: C(10)–C(11)–N(1), 113.06°; C(11)–C(10)–C(14), 124.9°; C(1)–C(10)–C(11), 114.1°; C(10)–C(1)–C(2), 122.1°; 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.

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