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Synthesis, structure and antibacterial activities of novel ferrocenyl-containing 1-phenyl-3-ferrocenyl-4-triazolyl-5-aryl-dihydropyrazole derivatives

Jianxin Fang, Zhong Jin *, Zengming Li, Wei Liu

Institute and State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China

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Abstract

A series of substituted ferrocene-containing propenones have been prepared from acetylferrocene. Subsequently, condensation of these propenones with phenylhydrazine gave desired dihydropyrazole derivatives, which structures have been characterized by spectra data and crystal X-ray diffraction analysis. Their antibacterial activities were screened. The mechanism involving 1,4-addition of phenylhydrazine to these propenones by initial reaction at N-1 to give dihydropyrazole derives and by initial reaction at N-2 to give an intermediate has also been discussed.

Keywords: Dihydropyrazole; Ferrocene; 1,4-Addition; 1,2,4-Triazole; Biological activity

1. Introduction

For many years, much interest has focused on the use of the transition-metal complexes in medicine and other biological areas as well [1,2]. A successful example is the application of platinum complexes as anti-tumor agents [3]. Therefore, we have expected the potential of organometallic chemistry when directed at therapeutic uses.

Ferrocene and its derivatives, since the discovery of it, have been attracting much attention ranging from the viewpoint of catalysis, organic synthesis, new materials such as liquid crystals or polymers [4] and supramolecular chemistry [5]. Incorporation of a ferrocene fragment into a molecule of an organic compound often obtained unexpected biological activity, which is rationalized as being due to their different membrane-permeation properties and anomalous metabolism [6–9]. Moreover, the stability and nontoxicity of the ferrocenyl moiety is of particular interest rendering such drugs compatible with other treatment [10]. In this sense, the integration of one or more ferrocene units into a heterocyclic ring molecular has long been recognized as an attractive way to endow a novel molecule functionally [11].

It is well known that certain substituted dihydropyrazole derivatives have highly biological active as medicaments in human and/or veterinary therapy [12,13], insecticides [14,15], and herbicides [16] in the agriculture and horticulture, especially in the agricultural field as exemplified by RH 3421 [15a], PH 60-41 [17], PH 60-42 [18] (Fig. 1). Following our interest in the synthesis of new analogues of dihydropyrazole with potent biological activities, we have sought to develop approaches to such drugs involving ferrocenyl units.

In the present work, we describe the preparation, structures and biological activity of a series of highly substituted dihydropyrazole compounds, which have been characterized by spectra data and crystal X-ray diffraction analysis.

* Corresponding author. Tel.: +86-22-2350-4229; fax: +86-22-2350-4856.
E-mail address: jinzhong2000@263.net (Z. Jin).

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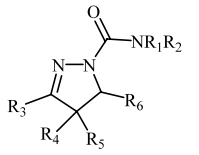


PH60-41 $R_1=R_4=R_5=R_6=H$, $R_2=R_3=p\text{-}ClC_6H_4$-
PH60-42 $R_1=R_4=R_6=H$, $R_2=R_3=p\text{-}ClC_6H_4$-, $R_5=Ph$
RH 3421 $R_1=R_6=H$, $R_2=p\text{-}CF_3C_6H_4$-, $R_3=p\text{-}C_6H_4$-, $R_4=CH_3$, $R_5=CO_2CH_3$

Fig. 1.

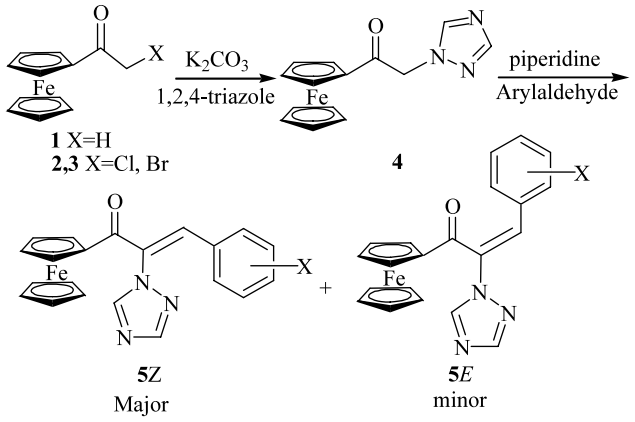
2. Result and discussion

2.1. Synthesis of 4,5-dihydropyrazole derivatives containing ferrocenyl unit

The α-chloroacetylferrocene (**2**) firstly had been prepared from ferrocene and α-haloacetyl chloride by the Friedel-Crafts acylation [19], which has recently been used as starting material for the preparation of chiral ferrocenyl-substituted β-aminocyclopentadienes [20]. Due to its low yield by this way [21], an alternative process was carried out as described by Tárraga et al. [22]. Therefore, metallation of acetylferrocene 1 with LDA at −78 °C followed by sequential treatment with trimethylchlorosilane and an excess of NBS provided the α-bromoacetylferrocene (**3**) in 80% yield, along with a small amount of the α,α-dibromoacetylferrocene.

Conversion of **2** and **3** into α-triazolylacetylferrocene (**4**) was achieved in perfect yield (95%) by using anhydrous potassium carbonate as a base. Sequentially, preparation of 2-(1,2,4-triazolyl)-3-aryl-1-ferrocenylpropenones (**5**) was achieved in good yield by condensation of **4** with substituted benzaldehydes under described conditions [23] (Scheme 1). After separation by silica gel column chromatography, the *Z*-isomers and *E*-isomers were obtained, respectively. In most cases of this reaction, the *Z*-isomers were obtained as the major products (yield: 45–75%) and the *E*-isomer as the minor ones (yield: below 15%).

Treatment of the propenones **5***Z* and **5***E*, respectively, with phenylhydrazine using glacial acetic acid as a catalyst afforded desired dihydropyrazoles **6** along with a small amount of by-products [14b] (Scheme 2).



Scheme 1.

The yields from *Z*-isomers are very close to the ones from *E*-isomers (Table 1). Moreover, it is interesting to note that, no matter from *Z*-isomer or *E*-isomer of **5**, the same conformational (**4***S*, **5***R*) dihydropyrazole product, which aryl group and triazole group are always in the *trans*-position of dihydropyrazole ring, was obtained by X-ray crystal structure analysis (Fig. 2). It is more likely that the same conformation has been caused as a result of the configuration inversion of the propenones **5** between *Z* and *E* taking place under acid catalysis.

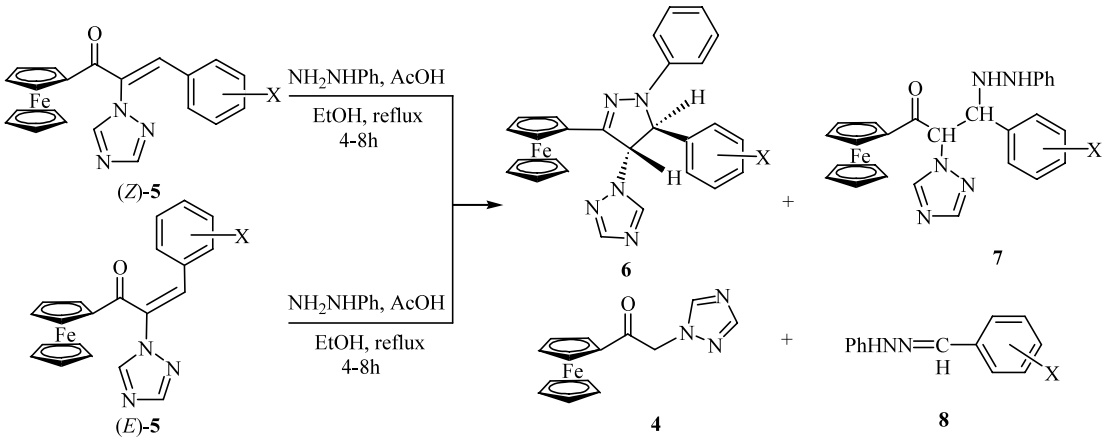
As above-mentioned, except for target compounds, a small amount of α-triazolylacetylferrocene (**4**), substituted benzaldehyde phenylhydrazones (**8**), and the intermediates **7** were also obtained as accompaniments. The reaction of the propenones **5** with phenylhydrazine involves competitive 1,2-addition and 1,4-addition reactions of the two nitrogen atoms in the phenylhydrazine. It has generally been accepted that the reaction does not proceed via 1,2-addition but 1,4-addition procedure [24]. In our present work, 1,4-addition of N-1 in the phenylhydrazine to the propenones **5** afforded the designed dihydropyrazole derivatives **6**. In contrast, 1,4-addition of N-2 in the phenylhydrazine caused to yield the intermediates **7** (Scheme 3). Base catalysis was observed for reaction at N-2 but not for reaction at N-1 [25]. However, the intermediate 7 isolated explicitly presented evidence for a mechanism involving 1,4-addition reaction at N-2 in the phenylhydrazine under acid catalysis.

With monitoring by GC-MS, equal quantitative α-triazolylacetylferrocene (**4**) and substituted benzaldehyde phenylhydrazones (**8**) were also observed and isolated. In addition, the yields of them varied regularly with the change of X group in the aryl (Table 2). We inferred that they are possibly from the cleavage of intermediates **7** under severe conditions. Because of massive special resistance of phenyl and ferrocenyl in compounds **7**, the cyclization of the intermediates **7** to dihydropyrazole was unable to proceed. Alternatively, they cleaved to the α-triazolylacetylferrocene (**4**) and phenylhydrazones (**8**) at the reacting conditions via a rearrangement (Scheme 4). As a result, equal quantitative **4** and phenylhydrazone (**8**) were detected.

2.2. Biological evaluation

Some selected dihydropyrazole derivatives containing ferrocenyl unit **6a**–**g** were screened for their antibacterial activity in vitro against *Isariopsis clavispora*, *Bremia lactucae*, *Cladosporium fulvum*, *Erysiphe graminis*, *Alternaria mali*, and their relative inhibitory ratio (%) were determined. The results of such studies are reported in Table 3.

The screening data indicate that compounds **6c**, **6g** carrying 3-chloro and 4-methoxy, respectively, show a



Scheme 2.

Table 1
The yields of compounds **6** from *Z*-isomers and *E*-isomers of **5**

Entry	Compounds **5**		X	Yields[a] (%) of compounds **6**
1	**5a**	*Z*	H	69.0
		E		68.1
2	**5c**	*Z*	3-Cl	82.9
		E		83.3
3	**5d**	*Z*	4-Cl	54.3
		E		68.5
4	**5f**	*Z*	4-CH_3	58.6
		E		62.0

[a] Isolated yields and 0.5 mol.% AcOH as catalyst.

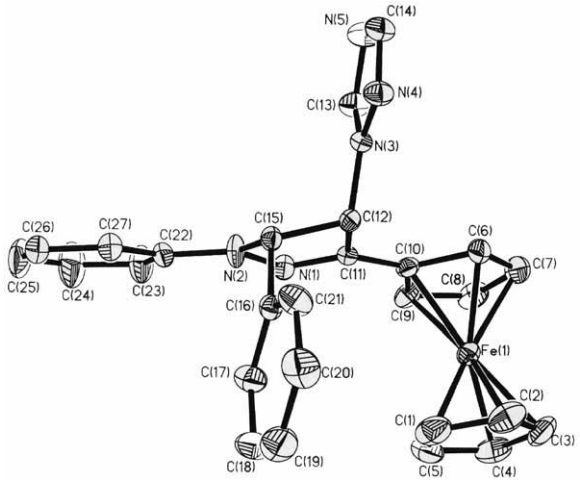


Fig. 2. Molecular structure and crystallographic numbering scheme for compound **6a**. Selected bond lengths (Å): Fe(1)–C(6) 2.022(4); Fe(1)–C(7) 2.025(5); N(1)–C(11) 1.291(4); N(1)–N(2) 1.375(4); N(2)–C(22) 1.378(4); N(2)–C(15) 1.456(4); N(3)–C(13) 1.317(4); N(3)–N(4) 1.354(4); N(3)–C(12) 1.454(4); C(13)–N(5) 1.307(4); C(1)–C(5) 1.385(6); C(6)–C(10) 1.421(4); C(10)–C(11) 1.428(5); C(12)–C(15) 1.528(4); C(16)–C(17) 1.375(5). Selected bond angels (°): C(11)–N(1)–N(2) 108.6(3); N(1)–N(2)–C(22) 121.0(3); C(22)–N(2)–C(5) 126.7(3); C(6)–C(10)–C(11) 125.2(3); N(1)–C(11)–C(10) 123.8(3); N(3)–C(12)–C(11) 108.5(2); N(3)–C(12)–C(15) 112.4(2); N(2)–C(15)–C(16) 114.4(3); N(2)–C(15)–C(12) 100.7(2); C(16)–C(15)–C(12) 111.3(2).

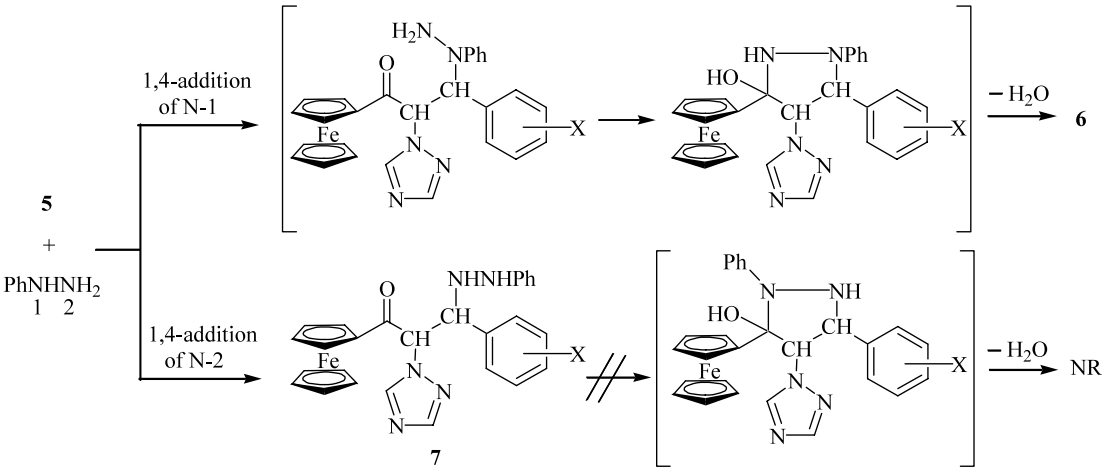
similar degree of antibacterial activity. Compared with known commercial agents, the antibacterial activities of this type of compounds were not encouraging, although some compounds manifested certain antibacterial activity. The other biological activities such as insecticide were tested at the moment and the results will be presented in the future.

3. Conclusion

A series of highly substituted dihydropyrazole derivatives have been synthesized and their structures have been verified by ^{1}H-NMR, IR, MS spectra data and crystal X-ray diffractions analysis. The mechanism involving 1,4-addition of phenylhydrazine to the ferrocenyl-substituted propenones by initial reaction at N-1 to give dihydropyrazole derives and by initial reaction at N-2 to give an intermediate has been discussed, and these new dihydropyrazole derivatives were also tested for their antibacterial activities.

4. Experimental

All reactions were carried out under nitrogen and monitored by TLC. All solvents were distilled prior to use. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. The ^{1}H-NMR spectra were measured on a JEOL-FX-90Q spectrometer or a Bruker Ac-200 Spectrometer in $CDCl_3$ and d_6-DMSO solution with TMS as internal standard. Elemental analyses were determined on an MT-3 elemental analyzer. IR spectra were recorded on a



Scheme 3.

Table 2
The varied yields of **3** in the syntheses of compounds **6**

Entry	Compound **6**	X	Yields (%) of compound **4**
1	**6d**	4-Cl	2.5
2	**6a**	H	11.0
3	**6f**	4-CH_3	11.4
4	**6g**	4-OCH_3	18.3
5	**6i**	4-OH	32.6

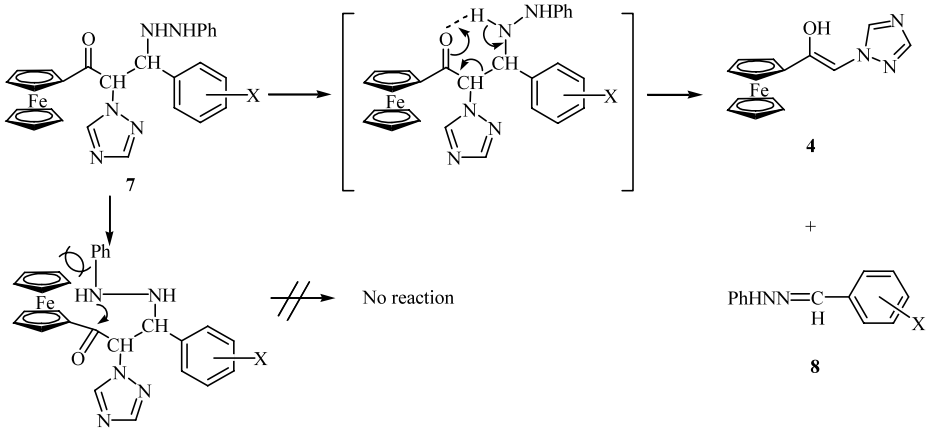
Bruker Equinox 55 spectrometer with KBr discs. Mass spectra were recorded on an HP-5988A at 70 eV; the temperature of ionization was 200 °C. α-Chloroacetylferrocene (**2**) and α-bromoacetylferrocene (**3**) were prepared according to the reported methods [19,22], respectively.

4.1. Synthesis of α-triazolylacetylferrocene (*4*)

To a suspension of α-chloroacetylferrocene (5.6 g, 21 mmol) and anhydrous potassium carbonate (3.0 g, 22 mmol) in dry acetone (100 ml), 1H-1,2,4-triazole (1.52 g, 22 mmol) was added under stirring. After refluxed for 8 h, the reacting mixture was filtered and washed with acetone (30 ml). Evaporation of combined solvent mixture gave a brown solid, and the residue was isolated by column chromatography on a silica gel column, to give a yellow crystal, α-triazolylacetylferrocene (**4**) (5.6 g) in 95% yield, which was crystallized from ethyl acetate/petroleum ether. M.p. 116–118 °C. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.46(s, 1H, triazole), 8.16(s, 1H, triazole), 5.38(s, 2H, CH_2), 4.86(s, 2H, C_5H_4), 4.56(s, 2H, C_5H_4), 4.30(s, 5H, C_5H_5). M/S (70 eV): $m/z = 295$ [M^+], Anal. Calc. for $C_{14}H_{13}FeN_3O$ (295.1) C 56.98; H 4.44; N 14.24. Found: C 56.96; H 4.40; N 14.09.

4.2. General procedure for syntheses of 2-(1,2,4-triazolyl)-3-aryl-1-ferrocenylpropenones (*5*)

To a stirred solution of the α-triazolylacetylferrocene (**4**) (2.95 g, 10 mmol), piperidine (0.1 ml), glacial acetic acid (0.5 mol.%) in dry toluene (30 ml) was added substituted benzaldehyde (10 mmol) at room tempera-



Scheme 4.

Table 3
Antibacterial activity of ferrocenyl-substituted dihydropyrazole derivatives

Entry	Substituent X	Relative inhibitory ratio (%)				
		I. clavispora	*B. lactucae*	*C. fulvum*	*E. graminis*	*A. mali*
6a	H	6.7	22.2	4.5	7.7	0
6b	2-Cl	0	0	13.6	0	6.5
6c	3-Cl	13.3	22.2	9.1	11.5	0
6d	4-Cl	0	0	13.6	3.8	3.2
6e	2,4-Cl_2	6.7	0	0	7.7	0
6f	4-CH_3	13.3	0	4.5	11.5	0
6g	4-OCH_3	6.7	11.1	9.1	11.5	0

ture under nitrogen. The mixture was then heated to reflux and kept at this temperature until completion of the reaction, while the water generated was evaporated off. The solvent was evaporated off in vacuum and the residue was purified by chromatography on silica gel with the solvent system of ethyl acetate/petroleum ether. The *Z*-ketone analogs **5** were obtained as the first elute and the *E*-ketone analogs **5** were obtained as the second elute of the chromatography.

*4.2.1. 2-(1,2,4-Triazolyl)-3-phenyl-1-ferrocenylpropenone (**5a**)*

(*Z*)-**5a**: yield: 57.2%; purple solid; m.p. 128–130 °C. IR (KBr): $v = 1629.2$, 1096.7, 1001.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.04(m, 2H), 7.84(s, 1H), 7.48–7.36(m, 5H), 4.66(m, 4H), 4.34(s, 5H). MS (EI): *m*/*z* (%): 383 [M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O$ C 65.82; H 4.47; N 10.96. Found: C 65.70; H 4.47; N 10.86.

(*E*)-**5a**: yield: 10.1%; deep red solid; m.p. 140–141 °C. IR (KBr): $v = 1625.2$, 1102.7, 1008.3 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.77(s, 1H), 8.39(s, 1H), 7.53(s, 1H), 6.61–6.59(m, 5H), 4.58(s, 2H), 4.33(s, 2H), 4.26(s, 5H). MS (EI): *m*/*z* (%): 383 [M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O$ C 65.82; H 4.47; N 10.96. Found: C 65.60; H 4.71; N 10.79.

*4.2.2. 2-(1,2,4-Triazolyl)-3-(2′-chlorophenyl)-1-ferrocenylpropenone (**5b**)*

(*Z*)-**5b**: yield: 47.6%; purple solid; m.p. 127–129 °C. IR (KBr): $v = 1627.0$, 1099.9, 1001.1 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 7.96(m, 2H), 7.64(s, 1H), 7.44–7.00(m, 4H), 4.68(s, 2H), 4.58(s, 2H), 4.26(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.30; H 3.70; N 9.95.

(*E*)-**5b**: yield: 7.2%; deep red solid; m.p. 138–139 °C. IR (KBr): $v = 1619.2$, 1092.7, 1003.9 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.32(s, 1H), 8.09(s, 1H), 7.23(s, 1H), 6.66–6.50(m, 4H), 4.49(s, 2H), 4.36(s, 2H), 4.20(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.32; H 3.90; N 10.09.

*4.2.3. 2-(1,2,4-Triazolyl)-3-(3′-chlorophenyl)-1-ferrocenylpropenone (**5c**)*

(*Z*)-**5c**: yield: 50.3%; deep red solid; m.p. 123–124 °C. IR (KBr): $v = 1630.5$, 1010.2, 1005.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.77(s, 1H), 8.40(s, 1H), 7.93(s, 1H), 7.64–6.90(m, 4H), 4.70(s, 2H), 4.53(s, 2H), 4.31(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.35; H 4.00; N 9.95.

(*E*)-**5c**: yield: 11.7%; red solid; m.p. 122–123 °C. IR (KBr): $v = 1619.2$, 1092.7, 1003.9 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 9.09(s, 1H), 8.24(s, 1H), 7.51(s, 1H), 7.50–7.35(m, 4H), 4.56(m, 4H), 4.14(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.40; H 3.76; N 9.85.

*4.2.4. 2-(1,2,4-Triazolyl)-3-(4′-chlorophenyl)-1-ferrocenylpropenone (**5d**)*

(*Z*)-**5d**: yield: 65.2%; purple solid; m.p. 149–151 °C. IR (KBr): $v = 1624.5$, 1103.2, 998.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.76(s, 1H), 8.37(s, 1H), 7.95(s, 1H), 7.42(d, $J = 5$ Hz, 2H), 6.96(d, $J = 5$ Hz, 2H), 4.69(s, 2H), 4.51(s, 2H), 4.31(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.14; H 3.52; N 9.97.

(*E*)-**5d**: yield: 12.5%; deep red solid; m.p. 133–134 °C. IR (KBr): $v = 1623.6$, 1099.5, 1001.9 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 9.08(s, 1H), 8.24(s, 1H), 7.51(s, 1H), 7.40(m, 4H), 4.56(s, 2H), 4.53(s, 2H), 4.16(s, 5H). MS (EI): *m*/*z* (%): 417 [100, M^+], 419 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}ClFeN_3O$ C 60.39; H 3.86; N 10.06. Found: C 60.15; H 3.71; N 9.94.

*4.2.5. 2-(1,2,4-Triazolyl)-3-(2′,4′-dichlorophenyl)-1-ferrocenylpropenone (**5e**)*

(*Z*)-**5e**: yield: 62.3%; purple solid; m.p. 195–196 °C. IR (KBr): $v = 1630.5$, 1109.2, 996.8 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.36–8.16(m, 2H), 8.00(s, 1H), 7.58(s, 1H), 7.18(d, $J = 5$ Hz, 1H), 6.67(d, $J = 5$ Hz, 1H), 4.73(m, 4H), 4.44(s, 5H). MS (EI): *m*/*z* (%): 452 [100,

M^+]. Anal. Calc. for $C_{21}H_{15}Cl_2FeN_3O$ C 55.79; H 3.34; N 9.29. Found: C 55.66; H 3.35; N 8.89.

(*E*)-**5e**: yield: 10.3%; deep red solid; m.p. 173–174 °C. IR (KBr): $\nu = 1626.7$, 1092.1, 1004.2 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.92(s, 1H) 8.30(s, 1H), 7.70(s, 1H), 7.60–7.40(m, 3H), 4.52(s, 2H), 4.49(s, 2H), 4.20(s, 5H). MS (EI): *m*/*z* (%): 452 [100, M^+]. Anal. Calc. for $C_{21}H_{15}Cl_2FeN_3O$ C 55.79; H 3.34; N 9.29. Found: C 55.76; H 3.62; N 9.21.

*4.2.6. 2-(1,2,4-Triazolyl)-3-(4′-methylphenyl)-1-ferrocenylpropenone (**5f**)*

(*Z*)-**5f**: yield: 61.5%; purple solid; m.p. 156–157 °C. IR (KBr): $\nu = 1615.5$, 1098.0, 1009.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.38–8.22(m, 2H), 7.96(s, 1H), 7.20(d, $J = 5$ Hz, 2H), 6.90(d, $J = 5$ Hz, 2H), 4.66(m, 4H), 4.34(s, 5H). MS (EI): *m*/*z* (%): 397 [100, M^+]. Anal. Calc. for $C_{22}H_{19}FeN_3O$ C 66.52; H 4.82; N 10.58. Found: C 66.47; H 4.79; N 10.59.

(*E*)-**5f**: yield: 11.7%; deep red solid; m.p. 131–132 °C. IR (KBr): $\nu = 1645.6$, 1109.6, 994.5 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.28(s, 1H) 8.02(s, 1H), 7.38(s, 1H), 7.60–7.40(m, 4H), 4.50(m, 4H), 4.18(s, 5H). MS (EI): *m*/*z* (%): 397 [100, M^+]. Anal. Calc. for $C_{22}H_{19}FeN_3O$ C 66.52; H 4.82; N 10.58. Found: C 66.49; H 4.83; N 10.39.

*4.2.7. 2-(1,2,4-Triazolyl)-3-(4′-methoxyphenyl)-1-ferrocenylpropenone (**5g**)*

(*Z*)-**5g**: yield: 63.2%; purple solid; m.p. 159–161 °C. IR (KBr): $\nu = 1620.6$, 1109.0, 1001.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.60–8.30(m, 2H), 7.87(s, 1H), 6.80(s, 4H), 4.54(s, 4H), 4.24(s, 5H), 3.78(s, 3H). MS (EI): *m*/*z* (%): 413 [100, M^+]. Anal. Calc. for $C_{22}H_{19}FeN_3O_2$ C 63.94; H 4.63; N 10.17. Found: C 63.85; H 4.62; N 10.10.

(*E*)-**5g**: yield: 8.1%; deep red solid; m.p. 134–136 °C. IR (KBr): $\nu = 1638.0$, 1099.6, 998.5 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.75(s, 1H), 8.15(s, 1H), 7.37(s, 1H), 7.25(d, $J = 5$ Hz, 2H), 6.74(d, $J = 5$ Hz, 2H), 4.63(s, 2H), 4.45(s, 2H), 4.06(s, 5H), 3.74(s, 3H). MS (EI): *m*/*z* (%): 413 [100, M^+].

Anal. Calc. for $C_{22}H_{19}FeN_3O_2$ C 63.94; H 4.63; N 10.17. Found: C 63.90; H 4.62; N 10.14.

*4.2.8. 2-(1,2,4-Triazolyl)-3-(2′-hydroxyphenyl)-1-ferrocenylpropenone (**5h**)*

(*Z*)-**5h**: yield: 54.8%; deep red solid; m.p. 166–167 °C. IR (KBr): $\nu = 1643.9$, 1102.4, 997.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.70(s, 1H), 8.37(s, 1H), 8.30(s, 1H), 7.24(t, $J = 4$ Hz, 1H), 6.96(d, $J = 4$ Hz, 1H), 6.61(t, $J = 4$ Hz, 1H), 6.13(d, $J = 4$ Hz, 1H), 4.69(s, 2H), 4.56(s, 2H), 4.35(s, 5H), 2.30–2.20(m, 1H). MS (EI): *m*/*z* (%): 399 [100, M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O_2$ C 63.18; H 4.29; N 10.53. Found: C 63.15; H 4.32; N 10.35.

(*E*)-**5h**: yield: 8.2%; red solid; m.p. 161–163 °C. IR (KBr): $\nu = 1628.0$, 1093.6, 1002.0 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.50–8.20(m, 2H), 7.95(s, 1H), 6.80–6.40(m, 4H), 4.33(m, 4H), 4.15(s, 5H), 2.60–2.40(m, 1H). MS (EI): *m*/*z* (%): 399 [100, M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O_2$ C 63.18; H 4.29; N 10.53. Found: C 63.21; H 4.20; N 10.61.

*4.2.9. 2-(1,2,4-Triazolyl)-3-(4′-hydroxyphenyl)-1-ferrocenylpropenone (**5i**)*

(*Z*)-**5i**: yield: 45.1%; purple solid; m.p. 190–192 °C. IR (KBr): $\nu = 1640.1$, 1092.1, 989.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.76(s, 1H), 8.37(s, 1H), 7.92(s, 1H), 6.80–6.60(m, 4H), 4.66(s, 2H), 4.42(s, 2H), 4.27(s, 5H), 1.80–1.70(m, 1H). MS (EI): *m*/*z* (%): 399 [100, M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O_2$ C 63.18; H 4.29; N 10.53. Found: C 63.15; H 4.35; N 10.59.

(*E*)-**5i**: yield: 8.9%; red solid; m.p. 178–180 °C. IR (KBr): $\nu = 1622.6$, 1088.2, 981.3 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.42(s, 1H), 8.12(s, 1H), 7.56(s, 1H), 6.60–6.00(m, 4H), 4.13(m, 4H), 4.05(s, 5H), 2.60–2.40(m, 1H). MS (EI): *m*/*z* (%): 399 [100, M^+]. Anal. Calc. for $C_{21}H_{17}FeN_3O_2$ C 63.18; H 4.29; N 10.53. Found: C 63.13; H 4.26; N 10.32.

*4.2.10. 2-(1,2,4-Triazolyl)-3-(4′-N,N-dimethylaminophenyl)-1-ferrocenylpropenone (**5j**)*

(*Z*)-**5j**: yield: 59.2%; deep red solid; m.p. 153–154 °C. IR (KBr): $\nu = 1635.7$, 1090.5, 994.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.20–7.90(m, 2H), 7.35(s, 1H), 7.00–6.50(m, 4H), 4.56(m, 4H), 4.30(s, 5H), 3.06(s, 6H). MS (EI): *m*/*z* (%): 426 [100, M^+]. Anal. Calc. for $C_{23}H_{22}FeN_4O$ C 64.80; H 5.20; N 13.14. Found: C 64.75; H 5.30; N 13.10.

(*E*)-**5j**: yield: 11.2%; red solid; m.p. 144–145 °C. IR (KBr): $\nu = 1620.6$, 1080.0, 993.3 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.02(s, 1H), 7.60(s, 1H), 6.96(s, 1H), 6.60–6.40(m, 4H), 4.35(m, 4H), 4.13(s, 5H), 2.96(s, 6H). MS (EI): *m*/*z* (%): 426 [100, M^+]. Anal. Calc. for $C_{23}H_{22}FeN_4O$ C 64.80; H 5.20; N 13.14. Found: C 64.78; H 5.25; N 13.06.

*4.2.11. 2-(1,2,4-Triazolyl)-3-(4′-N,N-diethylaminophenyl)-1-ferrocenylpropenone (**5k**)*

(*Z*)-**5k**: yield: 72.6%; purple solid; m.p. 162–163 °C. IR (KBr): $\nu = 1633.8$, 1091.3, 994.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.77(s, 1H), 8.39(s, 1H), 7.92(s, 1H), 7.59(d, $J = 5$ Hz, 2H), 7.52(d, $J = 5$ Hz, 2H), 4.58(s, 2H), 4.32(s, 2H), 4.26(s, 5H), 3.36(m, 4H), 1.06(t, $J = 6$ Hz, 6H). MS (EI): *m*/*z* (%): 454 [100, M^+]. Anal. Calc. for $C_{25}H_{26}FeN_4O$ C 66.09; H 5.77; N 12.33. Found: C 66.10; H 5.80; N 12.20.

(*E*)-**5k**: yield: 7.4%; red solid; m.p. 149–150 °C. IR (KBr): $\nu = 1628.4$, 1082.7, 999.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.20–7.92(m, 2H), 7.46(s, 1H), 7.00–6.80(m, 4H), 4.32(s, 2H), 4.17(s, 2H), 4.03(s, 5H),

3.08(m, 4H), 1.10(m, 6H). MS (EI): *m/z* (%): 454 [100, M^+]. Anal. Calc. for $C_{25}H_{26}FeN_4O$ C 66.09; H 5.77; N 12.33. Found: C 66.01; H 5.66; N 12.13.

4.2.12. 2-(1,2,4-Triazolyl)-3-(3′-bromophenyl)-1-ferrocenylpropenone (*5l*)

(*Z*)-**5l**: yield: 57.6%; deep red solid; m.p. 131–133 °C. IR (KBr): $\nu = 1633.2$, 1115.9, 1006.0 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 7.90–7.80(m, 2H), 7.60(s, 1H), 7.50–7.10(m, 3H), 7.10–6.70(m, 1H), 4.65(m, 4H), 4.35(s, 5H). MS (EI): *m/z* (%): 462 [100, M^+], 464 [33.3, M+2]. Anal. Calc. for $C_{21}H_{16}BrFeN_3O$ C 54.58; H 3.49; N 9.09. Found: C 54.58; H 3.49; N 8.89.

(*E*)-**5l**: yield: 8.8%; light red solid; m.p. 129–130 °C. IR (KBr): $\nu = 1618.4$, 1112.2, 991.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 7.74(s, 1H), 7.60(s, 1H), 7.28(s, 1H), 7.16–6.80(m, 4H), 4.56(m, 2H), 4.32(m, 2H), 4.22(s, 5H). MS (EI): *m/z* (%): 462 [100, M^+], 464(33.3, M+2). Anal. Calc. for $C_{21}H_{16}BrFeN_3O$ C 54.58; H 3.49; N 9.09. Found: C 54.36; H 3.46; N 8.93.

4.2.13. 2-(1,2,4-Triazolyl)-3-(3′-nitrophenyl)-1-ferrocenylpropenone (*5m*)

(*Z*)-**5m**: yield: 59.8%; purple solid; m.p. 156–157 °C. IR (KBr): $\nu = 1649.7$, 1125.0, 1016.3 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.90(s, 1H), 8.40(s, 1H), 8.10(d, $J = 4$ Hz, 1H), 8.02(s, 1H), 7.80(s, 1H), 7.70(t, $J = 4$ Hz, 1H), 7.40(d, $J = 4$ Hz, 1H), 4.72(s, 2H), 4.58(s, 2H), 4.33(s, 5H). MS (EI): *m/z* (%): 429 [100, M^+]. Anal. Calc. for $C_{21}H_{16}FeN_4O_3$ C 58.79; H 3.76; N 13.05. Found: C 58.62; H 3.82; N 13.12.

(*E*)-**5m**: yield: 16.7%; red solid; m.p. 144–146 °C. IR (KBr): $\nu = 1638.4$, 1122.2, 1008.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 9.10(s, 1H), 8.30(s, 1H), 8.27(s, 1H), 8.08(d, $J = 4$ Hz, 1H), 7.84(d, $J = 4$ Hz, 1H), 7.68(s, 1H), 7.60(t, $J = 4$ Hz, 1H), 4.56(m, 4H), 4.14(s, 5H). MS (EI): *m/z* (%): 429 [100, M^+]. Anal. Calc. for $C_{21}H_{16}FeN_4O_3$ C 58.79; H 3.76; N 13.05. Found: C 58.79; H 3.85; N 13.12.

4.2.14. 2-(1,2,4-Triazolyl)-3-(4′-nitrophenyl)-1-ferrocenylpropenone (*5n*)

(*Z*)-**5n**: yield: 18.5%; purple solid; m.p. 191 °C. IR (KBr): $\nu = 1654.9$, 1128.0, 1012.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.22(s, 1H), 8.14(s, 1H), 8.10(d, $J =$ 5 Hz, 1H), 7.71(s, 1H), 7.09(d, $J = 5$ Hz, 1H), 4.62(s, 2H), 4.57(s, 2H), 4.25(s, 5H). MS (EI): *m/z* (%): 429 [100, M^+]. Anal. Calc. for $C_{21}H_{16}FeN_4O_3$ C 58.79; H 3.76; N 13.05. Found: C 58.69; H 3.86; N 12.98.

(*E*)-**5n**: yield: 3.6%; purple solid; m.p. 191–193 °C. IR (KBr): $\nu = 1639.2$, 1120.2, 1010.7 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.70(s, 1H), 8.10(s, 1H), 8.07(d, $J =$ 5 Hz, 1H), 7.55(s, 1H), 7.45(d, $J = 5$ Hz, 1H), 4.61(s, 2H), 4.50(s, 1H), 4.04(s, 5H). MS (EI): *m/z* (%): 429 [100, M^+]. Anal. Calc. for $C_{21}H_{16}FeN_4O_3$ C 58.79; H 3.76; N 13.05. Found: C 58.65; H 3.85; N 13.08.

4.3. General procedure for syntheses of 1-phenyl-3-ferrocenyl-4-triazolyl-5-aryl-dihydropyrazole derivatives *6*

To a Schlenk reaction flask were added 2-(1,2,4-triazolyl)-3-aryl-1-ferrocenylpropenone (**5**) (4 mmol), phenylhydrazine (5 mmol), ethanol (10 ml), and glacial acetic acid (0.5 mol.%). The reaction mixture was heated to refluxing. After stirred at the temperature for 4 h, the mixture was cooled and the solvent was removed in vacuum. Chromatography on a silica gel column afforded the 2-pyrazolin derivatives **6** in modest to good yields. Only the intermediate **7f** was isolated and characterized, and the others were detected with GC-MS and HPLC-MS chromatography.

4.3.1. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-phenyl-dihydropyrazole (*6a*)

Yield: 69%; red solid; m.p. 197–199 °C (ethanol) IR (KBr): $\nu = 1599.2$, 1501.3 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.99(s, 1H), 8.07(s, 1H), 7.42–7.30(m, 5H), 7.15(t, $J = 5$ Hz, 2H), 6.98(d, $J = 5$ Hz, 2H), 6.82(t, $J = 5$ Hz, 1H), 6.06(d, $J = 5$ Hz, 1H), 5.53(d, $J = 5$ Hz, 1H), 4.75(s, 1H), 4.39(s, 1H), 4.30(s, 1H), 4.12(s, 1H), 4.02(s, 5H). MS (EI): *m/z* (%): 473 [100, M^+]. Anal. Calc. for $C_{27}H_{23}FeN_5$ C 68.50; H 4.90; N 14.80. Found: C 68.74; H 4.68; N 14.69.

4.3.2. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(2′-chlorophenyl)-dihydropyrazole (*6b*)

Yield: 35.2%; orange solid; m.p. 213–215 °C (ethanol) IR (KBr): $\nu = 1595.9$, 1497.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.10–8.00(m, 2H), 7.61(d, $J = 6$ Hz, 1H), 7.35–7.15(m, 5H), 6.98(d, $J = 6$ Hz, 2H), 6.85(t, $J = 6$ Hz, 1H), 5.80–5.60(m, 2H), 4.77(s, 1H), 4.35(s, 1H), 4.24(s, 1H), 3.92(s, 6H). MS (EI): *m/z* (%): 508 [100, M^+]. Anal. Calc. for $C_{27}H_{22}ClFeN_5$ C 63.86; H 4.37; N 13.79. Found: C 63.80; H 4.40; N 13.87.

4.3.3. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(3′-chlorophenyl)-dihydropyrazole (*6c*)

Yield: 83.0%; orange solid; m.p. 149–150 °C (acetone) IR (KBr): $\nu = 1597.3$, 1496.9 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.06(s, 1H), 8.03(s, 1H), 7.40–7.30(m, 4H), 7.20(t, $J = 5$ Hz, 2H), 7.00(d, $J = 5$ Hz, 2H), 6.84(t, $J = 5$ Hz, 1H), 5.64(s, 1H), 5.22(s, 1H), 4.85(s, 1H), 4.40(s, 1H), 4.25(s, 1H), 4.01(s, 1H), 3.98(s, 5H). MS (EI): *m/z* (%): 508 [100, M^+]. Anal. Calc. for $C_{27}H_{22}ClFeN_5$ C 63.86; H 4.37; N 13.79. Found: C 63.42; H 4.40; N 14.10.

4.3.4. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-chlorophenyl)-dihydropyrazole (*6d*)

Yield: 59.4%; orange solid; m.p. 167–168 °C (ethanol) IR (KBr): $\nu = 1596.2$, 1497.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.10–8.00(m, 2H), 7.40–7.30(m, 4H),

7.18(d, $J = 5$ Hz, 2H), 7.00(d, $J = 5$ Hz, 2H), 6.84(t, $J = 5$ Hz, 1H), 5.70(s, 1H), 5.20(s, 1H), 4.83(s, 1H), 4.39(s, 1H), 4.25(s, 1H), 3.97(s, 6H). MS (EI): *m/z* (%): 508 [100, M^+]. Anal. Calc. for $C_{27}H_{22}ClFeN_5$ C 63.86; H 4.37; N 13.79. Found: C 63.85; H 4.60; N 13.97.

*4.3.5. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(2′,4′-dichlorophenyl)-dihydropyrazole (**6e**)*

Yield: 53.0%; orange solid; m.p. 200–201 °C (ethanol) IR (KBr): $\nu = 1596.4$, 1498.7 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.10(s, 1H), 8.02(s, 1H), 7.53(s, 1H), 7.24–6.90(m, 7H), 5.61(m, 2H), 4.82(s, 1H), 4.38(s, 1H), 4.32(s, 1H), 4.26(s, 1H), 3.94(s, 5H). MS (EI): *m/z* (%): 542 [100, M^+]. Anal. Calc. for $C_{27}H_{21}Cl_2FeN_5$ C 59.81; H 3.90; N 12.92. Found: C 59.42; H 4.26; N 12.87.

*4.3.6. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-methylphenyl)-dihydropyrazole (**6f**)*

Yield: 59.2%; orange solid; m.p. 173–175 °C (acetone) IR (KBr): $\nu = 1604.5$, 1506.1 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.10–8.00(m, 2H), 7.30–7.15(m, 6H), 7.00(d, $J = 5$ Hz, 2H), 6.82(t, $J = 5$ Hz, 1H), 5.64(s, 1H), 5.21(s, 1H), 4.84(s, 1H), 4.37(s, 1H), 4.22(s, 1H), 3.98(s, 1H), 3.96(s, 5H), 2.32(s, 3H). MS (EI): *m/z* (%): 487 [100, M^+]. Anal. Calc. for $C_{28}H_{25}FeN_5$ C 69.00; H 5.30; N 13.37. Found: C 68.90; H 5.17; N 13.36.

*4.3.7. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-methoxyphenyl)-dihydropyrazole (**6g**)*

Yield: 52.8%; orange solid; m.p. 162–164 °C (acetone) IR (KBr): $\nu = 1608.7$, 1509.0 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.10–8.00(m, 2H), 7.30–7.15(m, 4H), 7.02(d, $J = 5$ Hz, 2H), 6.90(d, $J = 5$ Hz, 2H), 6.62(t, $J = 5$ Hz, 1H), 5.64(s, 1H), 5.21(s, 1H), 4.84(s, 1H), 4.37(s, 1H), 4.23(s, 1H), 4.00(s, 1H), 3.97(s, 5H), 3.77(s, 3H). MS (EI): *m/z* (%): 503 [100, M^+]. Anal. Calc. for $C_{28}H_{25}FeN_5O$ C 66.81; H 5.01; N 13.91. Found: C 66.69; H 4.99; N 14.08.

*4.3.8. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(2′-hydroxyphenyl)-dihydropyrazole (**6h**)*

Yield: 33.9%; red solid; m.p. 195–196 °C (acetone) IR (KBr): $\nu = 1610.2$, 1513.7 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.85(s, 1H), 7.90(s, 1H), 7.10–6.70(m, 9H), 5.43(s, 1H), 5.38(s, 1H), 4.96(s, 1H), 4.88(s, 2H), 4.75(s, 1H), 4.30(m, 1H), 4.20(s, 5H). MS (EI): *m/z* (%): 489 [100, M^+]. Anal. Calc. for $C_{27}H_{23}FeN_5O$ C 66.27; H 4.74; N 14.31. Found: C 66.21; H 4.73; N 14.33.

*4.3.9. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-hydroxyphenyl)-dihydropyrazole (**6i**)*

Yield: 71.2%; orange solid; m.p. 224–226 °C (acetone) IR (KBr): $\nu = 1613.5$, 1515.8 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 9.50(m, 1H), 8.96(s, 1H), 8.06(s, 1H), 7.20–6.70(m, 9H), 5.97(d, $J = 4$ Hz, 1H), 5.36(d, $J = 4$ Hz, 1H), 4.74(s, 1H), 4.38(s, 1H), 4.29(s, 1H), 4.09(s, 1H), 4.03(s, 5H). MS (EI): *m/z* (%): 489 [100, M^+]. Anal. Calc. for $C_{27}H_{23}FeN_5O$ C 66.27; H 4.74; N 14.31. Found: C 66.20; H 4.75; N 14.34.

*4.3.10. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-N,N-dimethylaminophenyl)-dihydropyrazole (**6j**)*

Yield: 63.3%; orange solid; m.p. 166–168 °C (ethanol) IR (KBr): $\nu = 1611.0$, 1512.6 cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.03(m, 2H), 7.30–6.75(m, 9H), 5.77(s, 1H), 5.30(s, 1H), 4.82(s, 1H), 4.36(s, 1H), 4.22(s, 1H), 3.97(m, 6H), 2.95(s, 6H). MS (EI): *m/z* (%): 516 [100, M^+]. Anal. Calc. for $C_{29}H_{28}FeN_6$ C 67.45; H 5.42; N 16.27. Found: C 67.28; H 5.40; N 16.35.

*4.3.11. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(4′-N,N-diethylaminophenyl)-dihydropyrazole (**6k**)*

Yield: 30.6%; orange solid; m.p. 181–183 °C (ethanol) IR (KBr): $\nu = 1610.9$, 1511.4 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.95(s, 1H), 8.05(s, 1H), 7.20–6.60(m, 9H), 5.96(d, $J = 4$ Hz, 1H), 5.29(d, $J = 4$ Hz, 1H), 4.74(s, 1H), 4.38(s, 1H), 4.29(s, 1H), 4.09(s, 1H), 4.05(s, 5H), 3.28(q, $J = 4$ Hz, 4H), 1.03(t, $J = 4$ Hz, 6H). MS (EI): *m/z* (%): 545 [100, M^+]. Anal. Calc. for $C_{31}H_{32}FeN_6$ C 68.38; H 5.92; N 15.43. Found: C 68.36; H 6.01; N 15.35.

*4.3.12. 1-Phenyl-3-ferrocenyl-4-triazolyl-5-(3′-bromophenyl)-dihydropyrazole (**6l**)*

Yield: 74.7%; orange solid; m.p. 154–155 °C (ethanol) IR (KBr): $\nu = 1596.5$, 1495.8 cm^{-1}. ^{1}H-NMR δ (200 MHz, d_6-DMSO): 8.96(s, 1H), 8.06(s, 1H), 7.55–7.30(m, 5H), 7.20(t, $J = 5$ Hz, 2H), 6.99(d, $J = 5$ Hz, 2H), 6.86(t, $J = 5$ Hz, 1H), 6.08(d, $J = 5$ Hz, 1H), 5.60(d, $J = 5$ Hz, 1H), 4.78(s, 1H), 4.40(s, 1H), 4.31(s, 1H), 4.13(s, 1H), 4.04(s, 5H). MS (EI): *m/z* (%): 552 [100, M^+]. Anal. Calc. for $C_{27}H_{22}BrFeN_5$ C 58.72; H 4.02; N 12.68. Found: C 58.60; H 4.04; N 12.70.

*4.4. 2-(1,2,4-Triazolyl)-3-(4′-methylphenyl)-3-(N′-phenylhydrazinyl)-1-ferrocenyl-one (**7f**)*

Yield: 17.8%; orange solid; m.p. 138–139 °C (ethanol) IR (KBr): $\nu = 1655.7$ cm^{-1}. ^{1}H-NMR δ (200 MHz, $CDCl_3$): 8.85(s, 1H), 8.01(s, 1H), 7.20–7.05(m, 6H), 6.88(t, $J = 5$ Hz, 1H), 6.60(d, $J = 5$ Hz, 2H), 5.92(d, $J = 5$ Hz, 1H), 4.75–4.50(m, 7H), 3.93(s, 5H), 2.27(s, 3H). MS (EI): *m/z* (%): 505 [100, M^+]. Anal. Calc. for $C_{27}H_{22}BrFeN_5$ C 58.72; H 4.02; N 12.68. Found: C 58.60; H 4.04; N 12.70.

5. Supplementary material

Crystallographic data for the structures **6a**, (*E*)-**5d**, and (*Z*)-**5d** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 190 329-

190 331. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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