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Synthesis, characterization, electrochemistry and optical properties of new 1,3,5-trisubstituted ferrocenyl pyrazolines and pyrazoles containing sulfonamide moiety

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ABSTRACT

This article describes the synthesis and characterization of a series of new 3-ferrocenyl-1-(4-sulphamylphenyl)-5-aryl-4,5-dihydro-1H-pyrazolines and the corresponding pyrazole derivatives derived from ferrocenyl chalcones and 4-hydrazino benzenesulfonamide hydrochloride. The compounds were characterized by spectroscopic means and the structure of the new ferrocenyl pyrazoline (**3a**) was determined by means of X-ray crystallography. The optical properties of these compounds were studied by means of UV/visible absorption spectroscopy and fluorescence spectroscopy (both steady state and time-resolved) in dichloromethane solvent. Electrochemical study revealed that all the compounds exhibited reversible oxidation behavior at 521–543 mV corresponding to ferrocene pyrazolines (**3a**–**l**) and 621–645 mV corresponding to ferrocene pyrazoles (**4a**–**j**) respectively, as confirmed by the $i_{pc}/i_{pa} = 0.92–1.00$.

1. Introduction

Ferrocene and its derivatives have displayed remarkable interdisciplinary activities ranging from their applications in material science, catalysis to biological assays [1,2]. Among these derivatives, ferrocene heterocycles containing moieties like condensed imidazoles [3,4], triazoles [5–8], guanidine [9], oxazoles [10,11], and pyrimidines [12–14] have predominantly attracted remarkable interest due to their widespread applications in various fields of chemistry including medicine [15], supramolecular chemistry [16,17], material science [18,19] and sensors [20]. Pyrazoles and pyrazolines, belonging to one such heterocyclic ring system, have propensity as blue light emitting fluorescent agents with high quantum yields [21–24] and hole transport tendency [25–28]. In recent times, Zhao *et al.* [29,30], and several others [31,32] have reported on the synthesis, characterization and optical properties of numerous ferrocenyl pyrazoline derivatives.

Further, it is well documented that sulfonamide hybrids, an important class of compounds, display a diverse range of biological and photophysical properties [33–37]. These properties are enhanced by attaching the sulfonamide groups within a central substituted planar ring system. Recently Supuran *et al.*, have reported on the biological properties of several metallocene based triazoles having sulfonamide derivatives [38], however, reports on ferrocenyl pyrazolines containing sulfonamide group are scarce in the literature. There is an increased interest in the design and synthesis of small molecules exhibiting fluorescent property. Hence, it would be of significant interest to explore a combined influence of the electrochemical property of ferrocene as well as the emission properties of the sulfonamide containing pyrazolines/pyrazoles in a single hybrid molecule.

Herein we report the synthesis, characterization and optical properties of 1,3,5-trisubstituted ferrocenyl pyrazolines and corresponding pyrazoles containing sulfonamide moiety. While UV–visible, fluorescence spectroscopies and electrochemical analysis were carried out on all these compounds, structure determination using single crystal X-ray crystallography was also done for the compound **3a**.

2. Results and discussion

2.1. Scheme of synthesis

The synthetic route for the target compounds is outlined in Scheme 1. The first step involves the base-catalyzed Claisen–

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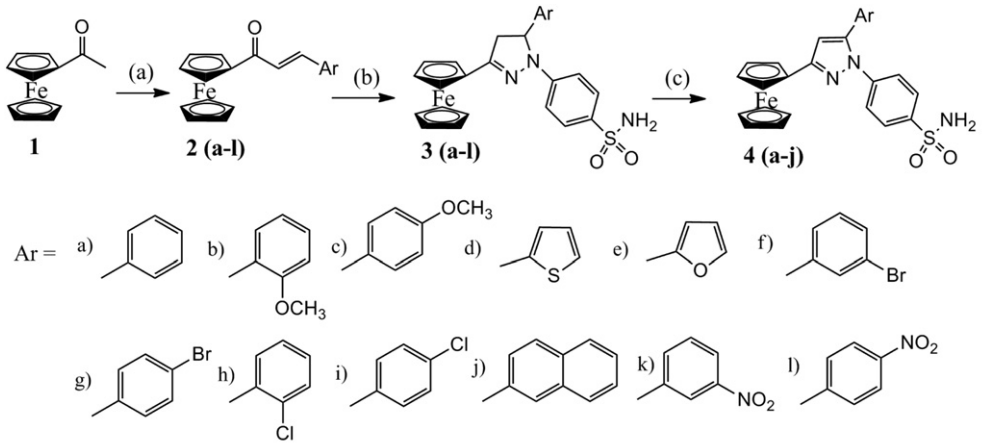

Reaction conditions: (a) Ar-CHO, 20% KOHaq, EtOH, RT (b) 4-Hydrazino benzenesulfonamide hydrochloride, EtOH: AcOH (1:2), 1000C (c) DDQ, DCM, RT

Scheme 1. Synthesis of 1,3,5-trisubstituted ferrocenyl pyrazolines (**3a**–**l**) and pyrazoles (**4a**–**j**) from acetylferrocene.

Schmidt condensation of acetylferrocene **1**, with the corresponding substituted benzaldehydes to prepare 3-ferrocenyl-1-aryl-2-propen-1-ones (**2a**–**l**) according to the literature procedures [39,40]. Reaction between the ferrocenyl chalcones (**2a**–**l**) and 4-hydrazino benzenesulfonamide hydrochloride in ethanol and acetic acid mixture (1:2, 12 ml/1 mmol) at 95–100 °C for 21–22 h gave the target compounds. The progress of the reaction was monitored by TLC (1:1, pet ether:chloroform), the reaction mixture was cooled, filtered, washed with water, dried and the products were purified by flash column chromatography on neutral alumina. The final step involves the oxidation of the pyrazoline compounds (**3a**–**j**) with DDQ (1.2 equiv) at room temperature in dichloromethane solvent [41]. After the completion of the reaction (8–9 h), the reaction mixture was passed through a small pad of neutral alumina using 2% methanol in chloroform to get the pyrazole derivatives. Crystallization from dichloromethane gave the analytically pure product (**4a**–**j**). Pyrazoline compounds with nitro substituents (**3k** and **3l**) did not give any products even at reflux temperatures for prolonged time.

2.2. Structural characterization

The structure of the new compounds was established on the basis of FT-IR, ^{1}H NMR, ^{13}C NMR, HR-MS and elemental analysis. The FT-IR spectrum of both pyrazoline (**3a**–**l**) and pyrazole compounds (**4a**–**j**) showed the presence of two weak bands in the region of 3580–3520 cm^{-1}, 3290–3200 cm^{-1} for typical hydrogen bonded –NH_2 stretching bands and two strong bands at 1345–1315 cm^{-1} and 1160–1150 cm^{-1} for the characteristic bands of SO_2 functional group. This clearly indicates the presence of the benzenesulfonamide group [42]. Apart from these, strong characteristic bands at 1610–1590 cm^{-1} and 1530–1510 cm^{-1} for the compounds (**4a**–**j**) confirm the presence of ν(C=C) and ν(C=N) respectively for the pyrazole moiety [40,41]. All the other additional bands observed in the IR spectra belonged to the aromatic substituents and the ferrocene ring.

The ^{1}H NMR spectra of pyrazoline compounds (**3a**–**l**) displayed three sets of signals with an ABX pattern at δ 2.90–3.10 ppm (4-H_{trans}), δ 3.85–4.05 ppm (4-H_{cis}) and δ 5.25–5.60 ppm (5-H) corresponding to the C4 and C5 hydrogens on the pyrazoline ring. This was further confirmed by the appearance of three signals at δ 150.5–151.6 ppm (C3), δ 43.0–44.6 ppm (C4) and δ 56.1–62.5 ppm (C5) in the ^{13}C NMR spectra. The presence of a singlet at δ 6.2–6.7 ppm in the ^{1}H spectrum and the absence of sp^3 carbons in ^{13}C spectrum of compounds (**4a**–**j**) indicated the formation of pyrazole ring. A broad signal at δ 6.60–6.95 ppm (**3a**–**l**) and δ 4.75–4.90 ppm (**4a**–**j**) for the –NH_2 protons indicated the presence of the sulfonamide group (for pyrazoline compounds more polar DMSO-d_6 was used as solvent whereas for pyrazole compounds less polar $CDCl_3$ was used as solvent for the NMR analysis). All the other additional peaks observed were in agreement with the respective aromatic substituents and ferrocene ring. The HR-MS spectral values and elemental analysis data were also in agreement with the proposed structure.

2.3. Single crystal X-ray structure of *3a*

The molecular structure of the 3-ferrocenyl pyrazoline **3a** was determined by means of X-ray diffraction studies and its crystallographic data and structural refinement parameters are given in Supplementary material. Red crystals of **3a** were obtained through slow evaporation of the chloroform solution. The compound crystallized in the triclinic space group $P\bar{1}$. The atom numbering scheme is given in Fig. 1, which shows a perspective view of compound **3a**. The pertinent bond length and bond angle data are listed in Supplementary material. The structure consists of a pyrazoline ring with the carbon atom C13 substituted by ferrocene and a benzene-sulfonamide group attached to the nitrogen atom N1. In the ORTEP diagram, the asymmetric unit of **3a** contains 3-ferrocenyl-pyrazoline ligand and two chloroform solvates. The pyrazoline ring (C11/C12/C13/N1/N2) adopts an envelope conformation with puckering parameter $Q = 0.250(3)$ Å and $\varphi = 316.7(8)°$. Atom C13 is displaced by 1.216(3) Å from the mean plane defined by the atoms N1/N2/C11/C12 (Supplementary material). The two cyclopentadienyl rings (C1–C5) and (C6–C10) of the ferrocenyl moiety are parallel with the dihedral angle of 0.66(14)° and the ferrocenyl moiety is in the eclipsed form. In addition to the regular features, it was observed that the sulfonamide group forms an eight member centrosymmetric dimer via N–H···O hydrogen bond interactions [N3–H1N···O1; 0.78(4), 2.24(4), 2.996(5) Å, 163(4)°; $-x-1, -y, -z+2$] (Fig. 2). Such eight member dimer via hydrogen bonds involving sulfonamide groups is prevalent in the literature [43,44]. Furthermore, Zhao and co-workers have reported significant inter and intramolecular hydrogen bonding within the crystal lattice of ferrocenyl pyrazoline compounds [29,30]. It was observed that only one chloroform solvate is involved in C–H···O

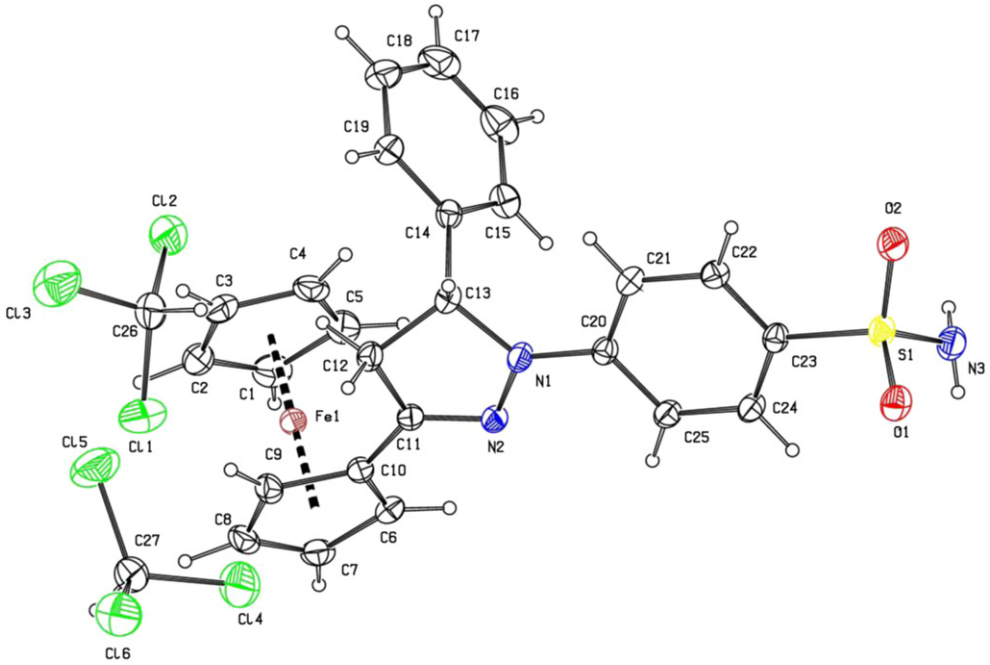

Fig. 1. ORTEP diagram of **3a** (showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.).

interaction with sulfonamide group [C26–H26···O2; 0.98, 2.40, 3.295(5) Å, 152°; $-x$, $-y$, $2-z$]. The other chloroform solvate is included in the crystal lattice by weak Vander walls interactions.

2.4. Absorption spectroscopy

Electronic absorption spectra of the ferrocenyl pyrazolines (**3a**–**l**) and ferrocenyl pyrazoles (**4a**–**j**) were recorded in dichloromethane solvent (Fig. S1, Supplementary material). Two distinct absorption bands, 275–285 nm and 345–360 nm were observed for all these compounds. These two bands were attributed to the $\pi \rightarrow \pi^*$ transition of pyrazole/pyrazoline moiety and the intramolecular charge transfer (ICT, from N1 to the benzenesulfonamide group) respectively. Ferrocene moiety also displayed MLCT band between 320 and 360 nm, hence the band at 345–360 nm may possess some ferrocene character [32]. As can be seen in Fig. 3, lower wavelength band (275–285 nm) of pyrazoles was found to be more intense than that of pyrazoline derivative due to the conjugation of C5-aromatic ring of pyrazole. On the other hand, the intensity of the longer wavelength band was almost identical for pyrazolines and pyrazoles (Fig. 3). No appreciable change in the absorption spectra was observed due to the substituent effect on C5-phenyl ring for both pyrazolines and pyrazole compounds.

2.5. Electrochemistry

The electrochemical characterization of the compounds **3a**–**l** and **4a**–**j**, was performed by means of cyclic voltammetry (CV) in DMSO as a solvent (Figs. 4 and S2), using a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode and standard calomel electrode (SCE) as the reference electrode with a scan rate of 100 mV s^{-1}. Tables 1 and 2

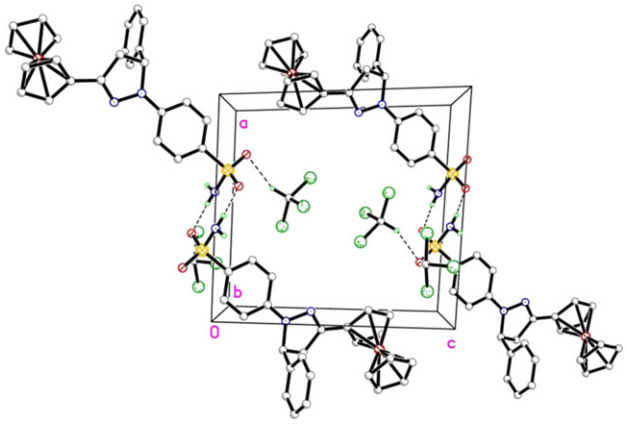

Fig. 2. Part of the crystal structure of **3a**, showing the centrosymmetric dimer between the sulfonamide groups through N–H···O hydrogen bonds. C–H···O bond interactions are also shown. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

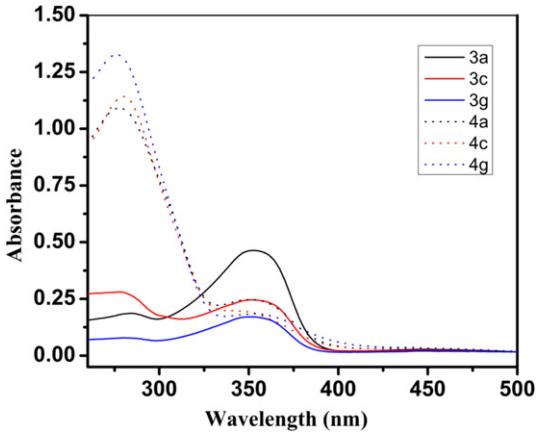

Fig. 3. Comparative UV–vis spectra of selected pyrazoline and pyrazole compounds in dichloromethane.

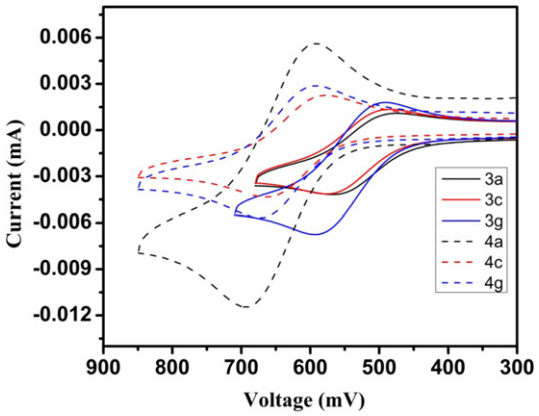

Fig. 4. Comparative electrochemical oxidative potential curves of selected compounds in dimethyl sulfoxide solvent vs. SCE at RT.

summarizes the redox potential data of all investigated compounds. Each compound undergoes one reversible oxidation. Wave analysis suggested that, in general, the oxidation was reversible ($i_{pc}/i_{pa} = 0.92–1.0$) and the diffusion-controlled ($i_{pc}/\nu^{1/2}$) constant in the scan rate (ν) range (50–500 mV/s) for one-electron transfer (ΔE_P) was 89–97 mV for the ferrocene/ferrocenium (FcH/FcH^+) couple. An anodic shift was observed in the oxidation of all compounds (521–543 mV for **3a**–**l** and 621–645 mV for **4a**–**j**) with respect to neat ferrocene (440 mV). The shift in the oxidation potential of compounds (**4a**–**j**) was due to extended conjugation in heterocyclic ring. The overall anodic shift of oxidation potential of ferrocene is due to the substituent effect of pyrazoline and pyrazoles subunits. Reduction potentials of pyrazolines (**3a**–**l**) are observed in the span range of −1.01 to −1.69 V and these may arise from the functionalized pyrazoline rather than from the ferrocene entity, whereas pyrazoles (**4a**–**j**) were observed in the span range of −622 to −646 mV as irreversible wave due to the ferrocenyl moiety.

2.6. Fluorescence

The fluorescence emission profile of ferrocenyl pyrazolines (**3a**–**l**) and ferrocenyl pyrazoles (**4a**–**j**) was recorded in dichloromethane solvent (Figs. 5 and S3). The emission maxima and quantum yields are collected in Tables 1 and 2. All the ferrocenyl pyrazoline compounds (**3a**–**l**) showed a single fluorescence emission band having maxima at 406 nm and shoulder at 430 nm. It was observed that the emission band of these compounds was red-shifted (50–60 nm) with respect to the absorption band maxima. The structured fluorescence emission spectra (Fig. 4) of these compounds suggested that the molecule emits from a locally excited (LE) state having identical geometry with that of ground state geometry [45]. On the other hand, a relatively less structured, single fluorescence emission band (Fig. S3) was observed for pyrazoles (**4a**–**j**) having the emission maxima between 425 and 460 nm. These fluorescence emission bands were more red-shifted with respect to the corresponding absorption spectra indicating the influence of extended conjugation on singlet state (S_1). From Tables 1 and 2 it was observed that, the fluorescence emission maxima of pyrazolines (**3a**–**l**) do not show any effect of the substituent at C5-aromatic ring (lack of conjugation with N1 atom), whereas the pyrazoles (**4a**–**j**) display some changes due to the conjugation of C5-aromatic ring with N1-aromatic ring. The non-emissive nature of pyrazolines was probably due to the lack of conjugation between the chromophore and the C5-aromatic ring.

Table 1
Characterization data for 3-ferrocenyl-1-(4-sulphamylphenyl)-5-aryl-4,5-dihydro-1H-pyrazoline: cyclic voltammetry data obtained from voltammograms (vs. SCE) of compounds **3a**–**l** in DMSO/0.5–1.0 mM with TBAP (supporting electrolyte) at 25 °C at scan rate of 100 mV/s. $E^0_{ox}(= E_{pc} + E_{pa}/2)$, ΔE_p ($=E_{pc} - E_{pa}$), i_{pc}/i_{pa} (ratio between cathodic and anodic peak current), E^0_{red} (reduction potential), ε (extinction coefficient).

Comp. code	E^0_{ox} (mV)	ΔE_p (mV)	i_{pc}/i_{pa}	E^0_{red} (V)[a]	λ^{abs}_{max}, nm ($\varepsilon \times 10^4$)	λ^{em}_{max} (nm)	Stokes shift (nm)	Quantum yield[b]
3a	523	90.3	1.00	−1.26	352 (4.64)	406	54	0.021
3b	532	96.9	1.00	−1.65	356 (2.17)	406	50	0.012
3c	532	91.9	0.98	−1.69	351 (2.46)	406	54	0.014
3d	541	88.5	1.00	−1.55	348 (2.13)	406	58	0.012
3e	539	89.4	0.99	−1.52	349 (2.11)	406	60	0.013
3f	544	90.0	1.00	−1.55	351 (1.89)	406	55	0.009
3g	540	96.0	1.00	−1.51	351 (1.71)	406	55	0.009
3h	531	90.2	1.00	−1.29	352 (2.59)	406	54	0.014
3i	521	92.3	0.97	−1.23	352 (2.89)	406	54	0.021
3j	526	93.7	0.92	−1.25	351 (1.97)	406	55	0.010
3k	547	90.0	1.00	−1.01	348 (2.09)	406	58	0.004
3l	546	123.8	0.77	−1.03	345 (3.05)	406	61	0.003

[a] Irreversible.
[b] Quantum yield calculated by using quinine sulfate in 0.1 M H_2SO_4 as reference compound.

The change in the emission intensity as well as the quantum yields in pyrazoles may be due to the change in the electronic structure of the C5-aromatic group. For instance, the fluorescence emission of **4f** (4-bromo) was red-shifted by 38 nm compared to **4c** (4-methoxy). This behavior indicates that the molecule emits from a relatively more polar ICT state. Solvatochromism was observed on increasing the polarity of the medium leading to the red-shift of the fluorescence band (Figs. S4 and S5).

The fluorescence quantum yield of all these compounds (**3a**–**l**, **4a**–**j**) have been estimated using quinine sulfate as a standard (Experimental section) and are collected in Tables 1 and 2 The fluorescence quantum yields of pyrazolines were found to be smaller than those of pyrazoles. The quantum yields of **3a** and **3g** were found to be higher (~0.021) while the nitro-substituted compounds exhibited poor quantum yield (0.003 and 0.004). Similarly, **4g** and **4i** were more fluorescent (~0.050) in pyrazole series while **4c** and **4f** show poor quantum efficiency (~0.010). Better quantum efficiencies of the pyrazoles can be explained due

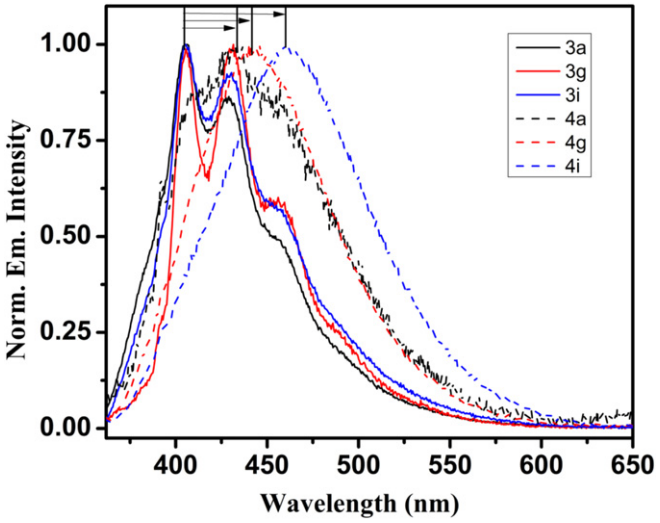

Fig. 5. Comparative fluorescence spectra of selected pyrazoline and pyrazole compounds in dichloromethane.

Table 2
Characterization data for 3-ferrocenyl-1-(4-sulphamylphenyl)-5-aryl-1H-pyrazoline: cyclic voltammetry data obtained from voltammograms (vs. SCE) of compounds **4a**–**j** in DMSO/0.5–1.0 mM with TBAP (supporting electrolyte) at 25 °C at scan rate of 100 mV/s. E^0_{ox}(= $E_{pc} + E_{pa}/2$), ΔE_p (=$E_{pc} - E_{pa}$), i_{pc}/i_{pa} (ratio between cathodic and anodic peak current), E^0_{red} (reduction potential), ε (extinction coefficient).

Comp. code	E^0_{ox} (mV)	ΔE_p (mV)	i_{pc}/i_{pa}	E^0_{red} (mV)[a]	λ^{abs}_{max}, nm ($\varepsilon \times 10^4$)	λ^{em}_{max} (nm)	Stokes shift (nm)	Quantum yield[b]
4a	645	100	0.94	−644	351 (2.52)	432	81	0.010
4b	640	101	1.00	−641	349 (2.30)	433	84	0.025
4c	621	89.0	0.98	−621	344 (2.01)	421	77	0.011
4d	633	84.2	1.00	−644	348 (1.79)	433	85	0.027
4e	638	80.0	1.00	−644	347 (2.17)	435	87	0.029
4f	643	91.0	1.01	−640	348 (1.39)	429	81	0.007
4g	634	83.0	1.00	−643	353 (1.84)	446	93	0.048
4h	636	84.2	0.98	−643	353 (1.67)	459	106	0.054
4i	636	85.3	0.98	−646	355 (1.14)	456	101	0.023
4j	634	94.8	1.02	−643	353 (1.16)	457	104	0.014

[a] Irreversible.
[b] Quantum yield calculated by using quinine sulfate in 0.1 M H_2SO_4 as reference compound.

to the reduced non-radiative decay path (planar pyrazole moiety and suppressed C5-aromatic ring rotation).

In order to understand the excited state properties, the fluorescence decay curves of few pyrazolines (**3a**, **3c**, **3g**) and pyrazoles (**4a**, **4c**, **4g**) were obtained on a time correlated single photon counting instrument (Experimental section). The decay parameters and average lifetimes are summarized in Table 3. As shown in Table 3, the pyrazoles have more average lifetime than that of pyrazolines. This observation clearly indicates that for the pyrazole compounds, the emitting state was an ICT. Usually, the ICT state has longer average lifetime (than LE state) due to the solvation (reorientation of solvent molecules around the probe molecule) in the excited state [45].

3. Conclusion

A series of new 3-ferroceny-1-(4-sulfamylphenyl)-5-aryl-4,5-dihydro-1H-pyrazoline (**3a**–**l**) and 3-ferroceny-1-(4-sulfamylphenyl)-5-aryl-1H-pyrazole (**4a**–**j**) derivatives were prepared and characterized by various spectroscopic techniques. Electrochemical studies of these compounds reveal reversible oxidation behavior. There was no significant effect of the substituents on the absorption spectra of pyrazolines and pyrazoles. The substituents and the solvent polarity influenced the fluorescence properties from pyrazolines to pyrazoles. From fluorescence spectra it was evident that the pyrazolines (**3a**–**l**) emitted from LE state while the pyrazoles (**4a**–**j**) emitted from ICT state. The fluorescence decay (lifetime) studies of these compounds further confirmed the nature of the emitting state of these compounds. It can be concluded that the photophysical properties of the pyrazoles were superior to the pyrazolines.

Table 3
Fluorescence decay parameters[a] of selected compounds in dichloromethane solvent.

Comp. name	τ_1	τ_2	τ_{avg}	χ^2
3a	1.56 (58.5)	2.95 (41.5)	2.47	1.34
3c	1.51 (68.5)	2.87 (31.5)	2.14	1.54
3g	1.41 (71.2)	2.89 (28.8)	2.11	1.66
4a	2.21 (72.5)	7.47 (27.2)	3.48	1.61
4c	1.92 (78.6)	5.07 (21.4)	3.23	1.60
4g	1.36 (66.9)	3.95 (33.1)	2.88	1.55

[a] The decay parameters are collected by using a laser excitation (λ_{ex} = 301 ns) source, lifetimes are expressed in nano-seconds (ns).

4. Experimental

4.1. General information

All reagent grade chemicals were purchased from Sigma–Aldrich; 4-hydrazino benzene-sulfonamide hydrochloride was purchased from Alfa Aesar and used as supplied. All the reactions were performed under argon using oven-dried glassware with magnetic stirring. TLC was performed on aluminum plates pre-coated with Silica Gel 60 F254 (E. Merck), the spots were detected visually and by UV light at 254 and 366 nm, respectively. Column chromatography was performed on neutral Alumina (Brockmann activity I). Melting points were determined using a Toshniwal apparatus and are uncorrected. FT-IR spectra were recorded on a Thermo Nicolet Nexus 670 spectrophotometer using KBr discs. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on Bruker Avance 300 or Varian Inova 500 spectrometer in $CDCl_3$ or DMSO-d_6 as solvent; chemical shifts (δ) were reported in parts per million downfield with TMS as an internal standard. Coupling constants (J) were given in hertz. Multiplicities were reported as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), and brs (broad singlet). For HR-MS, m/z values were expressed in atomic mass units.

4.2. General procedure for the preparation of 1,3,5-trisubstituted pyrazoline (*3a*–*k*)

Appropriate 3-ferrocenyl-1-aryl-2-propen-1-ones (0.5 mmol) and 4-hydrazino benzene-sulfonamide hydrochloride (0.55 mmol, 1.1 equiv) were taken in a 6 ml ethanol:acetic acid mixture (1:2) under argon and the contents were heated at 95–100 °C. The progress of the reaction was monitored by TLC (1:1, pet ether:-chloroform). After completion of reaction (22 h), the reaction mixture was cooled and the solvent was evaporated by co-distilled using ethyl acetate to give a brown solid which was washed several times with chilled water and dried. Purification was done by repeated column chromatography on neutral alumina using chloroform to separate any unreacted chalcone compounds and then with 2% methanol in chloroform to give a yellow color band of product. Crystallization from chloroform and methanol gave the analytically pure product in 49–74% yield.

4.2.1. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-phenyl-4,5-dihydro-1H-pyrazoline (*3a*)

According to the general procedure, the reaction of 158 mg of chalcone **2a** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 121 mg (50%) of **3a** as red solid. M.p. 196–197 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 3.01 (1H, dd, ^3J = 12.2 Hz, ^2J = 4.8 Hz, 4-H_{trans}, pyrazoline), 3.84 (1H, dd, ^3J = 12.2 Hz, ^2J = 4.8 Hz, 4-H_{cis}, pyrazoline), 4.04 (5H, s, C_5H_5), 4.36 (2H, br s, meta-C_5H_4), 4.53 (1H, s, ortho-C_5H_4), 4.67 (1H, s, ortho-C_5H_4), 5.34–5.40 (1H, br s, pyrazoline), 6.67–6.75 (2H, br s, NH_2), 6.94 (2H, d, J = 8.5 Hz, sulfonamide), 7.25–7.30 (3H, m, C_6H_5), 7.33–7.37 (2H, m, C_6H_5), 7.57 (2H, d, J = 8.5 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 44.4, 61.4, 151.4 (pyrazoline), 69.0, 69.3 (C_5H_5), 66.6, 67.2 (ortho-C_5H_4), 69.8, 69.9 (meta-C_5H_4), 76.2 (ipso-C_5H_4), 111.3, 125.6, 127.1, 127.5, 129.0, 132.0, 141.6, 145.9 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3355 and 3251 $\nu(NH_2)$, 3081 ν(C–H)$_{Ar}$, 2927 ν(C–H)$_{Al}$, 1590 ν(C=C)$_{Ar}$, 1506 ν(C=N)$_{Ar}$, 1392 ν_b(C–H), 1319 $\nu_{as}(SO_2)$, 1152 $\nu_s(SO_2)$, 1093 ν_s(C–N), 861 ν(C–H)$_{Ar}$, 734 ν(C=C)$_{oop}$, 700 ν(C=C)$_{oop}$, 539 and 477 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 486.0943 $[M + H]^+$, calculated for $C_{25}H_{24}O_2N_3FeS$: 486.0933. Anal. Calculated for $C_{25}H_{23}O_2N_3FeS$: C, 61.86; H, 4.78; N, 8.66; S, 6.61. Found: C, 61.12; H, 4.56; N, 8.52; S, 6.60.

*4.2.2. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-methoxyphenyl)-4,5-dihydro-1H-pyrazoline (**3b**)*

According to the general procedure, the reaction of 173 mg of chalcone **2b** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 147 mg (57%) of **3b** as brown solid. M.p. 169–170 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): δ 2.88 (1H, dd, ^3J = 12.0 Hz, ^2J = 4.9 Hz, 4-H$_{trans}$, pyrazoline), 3.80 (1H, dd, ^3J = 12.0 Hz, ^2J = 4.9 Hz, 4-H$_{cis}$, pyrazoline), 3.99 (3H, s, –OCH$_3$), 4.03 (5H, s, C$_5$H$_5$), 4.34 (2H, br s, meta-C$_5$H$_4$), 4.52 (1H, s, ortho-C$_5$H$_4$), 4.66 (1H, s, ortho-C$_5$H$_4$), 5.88 (1H, dd, ^3J = 11.0 Hz, ^2J = 4.9 Hz, pyrazoline), 6.63–6.69 (2H, br s, NH$_2$), 6.82 (1H, t, J = 7.3 Hz, aromatic), 6.93 (1H, d, J = 7.3 Hz, aromatic), 7.01 (1H, d, J = 7.3 Hz, aromatic), 6.88 (2H, d, J = 8.5 Hz, sulfonamide), 7.58 (2H, d, J = 8.5 Hz, sulfonamide) 7.23 (1H, t, J = 7.3 Hz, aromatic). ^{13}C NMR (75 MHz, DMSO-d$_6$, ppm): δ 43.0, 56.1, 151.0 (pyrazoline), 55.0 (–OCH$_3$), 68.3 (C$_5$H$_5$), 66.0, 66.6 (ortho-C$_5$H$_4$), 69.3, 69.4 (meta-C$_5$H$_4$), 75.9 (ipso-C$_5$H$_4$), 110.4, 110.8, 120.0, 125.1, 126.9, 127.8, 131.1, 145.7, 155.5 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3366 and 3245 ν(NH$_2$), 3084 ν(C–H)$_{Ar}$, 2947 ν(C–H)$_{Al}$, 1590 ν(C=C)$_{Ar}$, 1508 ν(C=N)$_{Ar}$, 1395 ν_b(C–H), 1318 ν_{as}(SO$_2$), 1241 ν_s(C–O), 1154 ν(SO$_2$)$_s$,1097 ν_s(C–N), 866 ν(C–H)$_{Ar}$, 751 ν(C–H)$_{Ar}$, 481 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 516.1047 [M + H]$^+$, calculated for C$_{26}$H$_{26}$O$_3$N$_3$FeS: 516.1038. Anal. Calculated for C$_{26}$H$_{25}$O$_3$N$_3$FeS: C, 60.59; H, 4.89; N, 8.15; S, 6.22. Found: C, 60.92; H, 4.75; N, 8.13; S, 6.19.

*4.2.3. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazoline (**3c**)*

According to the general procedure, the reaction of 173 mg of chalcone **2c** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 137 mg (53%) of **3c** as pale brown solid. M.p. 153–154 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): δ 3.80 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{cis}$, pyrazoline), 3.78 (3H, s, –OCH$_3$), 4.11 (5H, s, C$_5$H$_5$), 4.39 (2H, d, J = 7.0 Hz, meta-C$_5$H$_4$), 4.56 (1H, s, ortho-C$_5$H$_4$), 4.70 (1H, s, ortho-C$_5$H$_4$), 5.28 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, pyrazoline), 6.38–6.50 (2H, br s, NH$_2$), 6.88 (2H, d, J = 9.0 Hz, sulfonamide), 7.63 (2H, d, J = 9.0 Hz, sulfonamide), 6.97 (2H, d, J = 8.0 Hz, aromatic), 7.19 (2H, d, J = 8.0 Hz, aromatic). ^{13}C NMR (75 MHz, DMSO-d$_6$, ppm): δ 44.0, 60.9, 151.3 (pyrazoline) 54.9 (–OCH$_3$), 68.3 (C$_5$H$_5$), 66.5, 67.1 (ortho-C$_5$H$_4$), 69.7, 69.8 (meta-C$_5$H$_4$), 76.3 (ipso-C$_5$H$_4$), 111.3, 114.2, 126.8, 127.0, 131.9, 133.5, 145.8, 158.4 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3364 and 3287 ν(NH$_2$), 3013 ν(C–H)$_{Ar}$, 2922 ν(C–H)$_{Al}$, 1592 ν(C=C)$_{Ar}$, 1512 ν(C=N)$_{Ar}$, 1401 ν_b(C–H), 1331 ν_{as}(SO$_2$), 1245 ν_s(C–O), 1152 ν_s(SO$_2$), 1094 ν_s(C–N), 820 ν(C–H)$_{Ar}$, 748 ν(C–H)$_{Ar}$, 538 and 489 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 516.1053 [M + H]$^+$, calculated for C$_{26}$H$_{26}$O$_3$N$_3$FeS: 516.1038. Anal. Calculated for C$_{26}$H$_{25}$O$_3$N$_3$FeS: C, 60.59; H, 4.89; N, 8.15; S, 6.22. Found: C, 60.65; H, 4.82; N, 8.23; S, 6.35.

*4.2.4. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-thiophene)-4,5-dihydro-1H-pyrazoline (**3d**)*

According to the general procedure, the reaction of 161 mg of chalcone **2d** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 126 mg (51%) of **3d** as brown powder. M.p. 222–223 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): δ 3.15 (1H, d, J = 16.0 Hz, 4-H$_{trans}$, pyrazoline), 3.85 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{cis}$, pyrazoline), 4.16 (5H, s, C$_5$H$_5$), 4.43 (2H, s, meta-C$_5$H$_4$), 4.65 (1H, s, ortho-C$_5$H$_4$), 4.74 (1H, s, ortho-C$_5$H$_4$), 5.80–5.89 (1H, dd, J = 8.0 Hz, pyrazoline), 6.96 (1H, s, aromatic), 6.98–7.01 (2H, br s, NH$_2$), 7.05 (2H, d, J = 8.0 Hz, sulfonamide), 7.11 (1H, s, aromatic), 7.39 (1H, s, aromatic), 7.57 (2H, d, J = 8.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d$_6$, ppm): δ 44.5, 57.5, 151.4 (pyrazoline), 68.9 (C$_5$H$_5$), 66.4, 67.0 (ortho-C$_5$H$_4$), 69.6, 69.7 (meta-C$_5$H$_4$), 75.9 (ipso-C$_5$H$_4$), 111.6, 124.9, 125.2, 126.2, 126.8, 132.4, 145.0, 145.9 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3355 and 3257 ν(NH$_2$), 3102 ν(C–H)$_{Ar}$, 2926 ν(C–H)$_{Al}$, 1592 ν(C=C)$_{Ar}$, 1507 ν(C=N)$_{Ar}$, 1390 ν_b(C–H), 1323 ν_{as}(SO$_2$), 1233 ν(C$_5$H$_4$), 1154 ν(C=C)$_{Ar}$, 1092 ν(C–H)$_{Ar}$, 834 ν(C–H)$_{Ar}$, 547 and 479 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 492.0509 [M + H]$^+$, calculated for C$_{23}$H$_{22}$O$_2$N$_3$FeS$_2$: 492.0497. Anal. Calculated for C$_{23}$H$_{21}$O$_2$N$_3$FeS$_2$: C, 56.22; H, 4.31; N, 8.55; S, 13.05. Found: C, 56.38; H, 4.26; N, 8.41; S, 13.1.

*4.2.5. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-furan)-4,5-dihydro-1H-pyrazoline (**3e**)*

According to the general procedure, the reaction of 153 mg of chalcone **2e** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 122 mg (52%) of **3e** as brown powder. M.p. 188–189 °C. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 3.30 (1H, dd, ^3J = 11.8 Hz, ^2J = 4.8 Hz, 4-H$_{trans}$, pyrazoline), 3.80 (1H, dd, ^3J = 11.8 Hz, ^2J = 4.8 Hz, 4-H$_{cis}$, pyrazoline), 4.17 (5H, s, C$_5$H$_5$), 4.40 (2H, d, J = 11.8 Hz, meta-C$_5$H$_4$), 4.55 (1H, s, ortho-C$_5$H$_4$), 4.75 (1H, s, ortho-C$_5$H$_4$), 4.58 (2H, br s, NH$_2$), 5.36 (1H, dd, ^3J = 7.8 Hz, ^2J = 4.2 Hz, pyrazoline), 6.23 (1H, s, aromatic), 6.30 (1H, s, aromatic), 7.10 (2H, d, J = 9.0 Hz, sulfonamide), 7.39 (1H, s, aromatic), 7.73 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d$_6$, ppm): δ 44.4, 57.4, 151.5 (pyrazoline), 68.7 (C$_5$H$_5$), 66.6, 67.2 (ortho-C$_5$H$_4$), 69.9, 70.1 (meta-C$_5$H$_4$), 76.1 (ipso-C$_5$H$_4$), 111.9, 124.4, 126.1, 126.9, 127.4, 132.8, 145.2, 145.9 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3349 and 3268 ν(NH$_2$), 3112 ν(C–H)$_{Ar}$, 2932 ν(C–H)$_{Al}$, 1598 ν(C=C)$_{Ar}$, 1517 ν(C=N)$_{Ar}$, 1398 ν_b(C–H), 1329 ν_{as}(SO$_2$), 1159 ν(C=C)$_{Ar}$, 1099 ν(C–H)$_{Ar}$, 844 ν(C–H)$_{Ar}$, 475 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 476.0809 [M + H]$^+$, calculated for C$_{23}$H$_{22}$O$_3$N$_3$FeS: 476.0847. Anal. Calculated for C$_{23}$H$_{21}$O$_3$N$_3$FeS: C, 58.12; H, 4.45; N, 8.84; S, 6.75. Found: C, 58.38; H, 4.36; N, 8.91; S, 6.83.

*4.2.6. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(3-bromophenyl)-4,5-dihydro-1H-pyrazoline (**3f**)*

According to the general procedure, the reaction of 197 mg of chalcone **2f** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride to furnishes 154 mg (55%) **3f** as orange powder. M.p. 137–138 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): δ 3.04 (1H, dd, ^3J = 18.0 Hz, ^2J = 5.0 Hz, 4-H$_{trans}$, pyrazoline), 3.85 (1H, dd, ^3J = 18.0 Hz, ^2J = 5.0 Hz, 4-H$_{cis}$, pyrazoline), 4.11 (5H, s, C$_5$H$_5$), 4.41 (2H, d, J = 7.0 Hz, meta-C$_5$H$_4$), 4.56 (1H, s, ortho-C$_5$H$_4$), 4.72 (1H, s, ortho-C$_5$H$_4$), 5.32–5.38 (1H, m, pyrazoline), 6.60–6.67 (2H, br s, NH$_2$), 6.97 (2H, d, J = 8.5 Hz, sulfonamide), 7.66 (2H, d, J = 8.5 Hz, sulfonamide), 7.25–7.31 (2H, m, aromatic), 7.40–7.44 (2H, m, aromatic). ^{13}C NMR (75 MHz, DMSO-d$_6$, ppm): δ 44.2, 60.7, 151.5 (pyrazoline), 66.9 (C$_5$H$_5$), 66.5, 67.2 (ortho-C$_5$H$_4$), 69.0, 69.7 (meta-C$_5$H$_4$), 75.9 (ipso-C$_5$H$_4$), 111.3, 122.0, 124.6, 127.1, 128.3, 130.4, 131.2, 132.3, 144.3, 145.6 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3356 and 3254 ν(NH$_2$), 3034 ν(C–H)$_{Ar}$, 2947 ν(C–H)$_{Al}$, 1591 ν(C=C)$_{Ar}$, 1510 ν(C=N)$_{Ar}$, 1397 ν_b(C–H), 1316 ν_{as}(SO$_2$), 1229 ν(C$_5$H$_4$), 1154 ν_s(SO$_2$), 1096 ν(C-Br), 1000 ν(C–Br), 826 ν(C–H)$_{Ar}$, 742 ν(C–H)$_{Ar}$, 539 and 483 ν_{as}(Cp-Fe-Cp). HR-MS: found, m/z 564.0057 [M + H]$^+$, calculated for C$_{25}$H$_{23}$O$_2$N$_3$BrFeS: 564.0038. Anal. Calculated for C$_{25}$H$_{22}$O$_2$N$_3$BrFeS: C, 61.99; H, 4.58; N, 8.68; S, 6.62. Found: C, 62.11; H, 4.49; N, 8.76; S, 6.72.

*4.2.7. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-bromophenyl)-4,5-dihydro-1H-pyrazoline (**3g**)*

According to the general procedure, the reaction of 197 mg of chalcone **2g** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 138 mg (49%) of **3g** as orange powder. M.p. 141–142 °C. ^{1}H NMR (500 MHz, DMSO-d$_6$, ppm): δ 2.98 (1H, dd, ^3J = 12.8 Hz, ^2J = 9.0 Hz, 4-H$_{trans}$, pyrazoline), 3.77–3.90 (1H, dd, ^3J = 12.8 Hz, ^2J = 9.0 Hz, 4-H$_{cis}$, pyrazoline), 4.09 (5H, s, C$_5$H$_5$), 4.36 (2H, s, meta-C$_5$H$_4$), 4.54 (1H, s, ortho-C$_5$H$_4$), 4.65 (1H, s, ortho-C$_5$H$_4$), 5.31–5.40 (1H, m, pyrazoline), 6.61–6.70 (2H, br s, NH$_2$), 6.93 (2H, d, J = 8.3 Hz, sulfonamide), 7.60 (2H, d, J = 8.3 Hz, sulfonamide), 7.21 (2H, d, J = 8.2 Hz, aromatic), 7.49 (2H, d, J = 8.2 Hz,

aromatic). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 44.1, 60.8, 151.4 (pyrazoline), 68.9 (C_5H_5), 66.5, 67.0 (ortho-C_5H_4), 69.7, 69.8 (meta-C_5H_4), 75.9 (ipso-C_5H_4), 111.3, 120.4, 127.0, 127.8, 131.8, 132.1, 140.9, 145.7 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3362 and 3258 $\nu(NH_2)$, 3021 ν(C–H)$_{Ar}$, 2920 ν(C–H)$_{Al}$, 1590 ν(C=C)$_{Ar}$, 1508 ν(C=N)$_{Ar}$, 1400 ν_b(C–H), 1314 $\nu_{as}(SO_2)$, 1231 $\nu(C_5H_4)$, 1156 $\nu_s(SO_2)$, 822 ν(C–H)$_{Ar}$, 541 and 492 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 564.0034 $[M + H]^+$, calculated for $C_{25}H_{23}O_2N_3BrFeS$: 564.0038. Anal. Calculated for $C_{25}H_{22}O_2N_3BrFeS$: C, 61.99; H, 4.58; N, 8.68; S, 6.62. Found: C, 61.99; H, 4.62; N, 8.72; S, 6.52.

4.2.8. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-chlorophenyl)-4,5-dihydro-1H-pyrazoline (**3h**)

According to the general procedure, the reaction of 175 mg of chalcone **2h** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 146 mg (56%) of **3h** as orange solid. M.p. 216–217 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 2.98 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{trans}$, pyrazoline), 3.91 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{cis}$, pyrazoline), 4.08 (5H, s, C_5H_5), 4.38–4.42 (2H, br s, meta-C_5H_4), 4.57 (1H, s, ortho-C_5H_4), 4.70 (1H, s, ortho-C_5H_4), 5.66 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, pyrazoline), 6.55–6.67 (2H, br s, NH_2), 6.90 (2H, d, J = 9.0 Hz, sulfonamide), 7.66 (2H,d, J = 9.0 Hz, sulfonamide), 7.08 (1H, d, J = 7.0 Hz, aromatic), 7.21 (1H, t, J = 7.0 Hz, aromatic), 7.28 (1H, t, J = 7.0 Hz, aromatic), 7.50 (1H, d, J = 7.0 Hz, aromatic). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 43.0, 59.1, 151.7 (pyrazoline), 69.0 (C_5H_5), 66.6, 67.2 (ortho-C_5H_4), 69.8, 69.9 (meta-C_5H_4), 75.8 (ipso-C_5H_4), 111.1, 126.6, 127.2, 127.2, 127.7, 129.7, 129.4, 130.1, 131.1, 132.3, 145.5 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3356 and 3262 $\nu(NH_2)$, 3054 ν(C–H)$_{Ar}$, 2930 ν(C–H)$_{Al}$, 1592 ν(C=C)$_{Ar}$, 1513 ν(C=N)$_{Ar}$, 1400 ν_b(C–H), 1338 $\nu_{as}(SO_2)$, 1154 $\nu_s(SO_2)$, 1094 ν_s(C–N), 821 ν(C–H)$_{Ar}$, 751 ν(C–H)$_{Ar}$, 542 and 492 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 520.0540 $[M + H]^+$, calculated for $C_{25}H_{23}O_2N_3ClFeS$: 520.0543. Anal. Calculated for $C_{25}H_{22}O_2N_3ClFeS$: C, 57.76; H, 4.27; N, 8.08; S, 6.17. Found: C, 58.09; H, 4.15; N, 8.13; S, 6.25.

4.2.9. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-chlorophenyl)-4,5-dihydro-1H-pyrazoline (**3i**)

According to the general procedure, the reaction of 175 mg of chalcone **2i** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 135 mg (52%) of **3i** as brown solid. M.p. 111–112 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.99 (1H, dd, ^3J = 12.0 Hz, ^2J = 7.0 Hz, 4-H$_{trans}$, pyrazoline), 4.07 (1H, dd, ^3J = 12.0 Hz, ^2J = 4.0 Hz, 4-H$_{cis}$, pyrazoline), 4.07 (5H, s, C_5H_5), 4.35 (2H, d, J = 8.0 Hz, meta-C_5H_4), 4.50 (1H, s, ortho-C_5H_4), 4.63 (1H, s, ortho-C_5H_4), 5.21 (1H, dd, ^3J = 12.0 Hz, ^2J = 7.0 Hz, pyrazoline), 6.93 (2H, d, J = 9.0 Hz, sulfonamide), 7.33 (2H, d, J = 9.0 Hz, sulfonamide), 7.19 (2H, d, J = 8.0 Hz, aromatic), 7.65 (2H, d, J = 8.0 Hz, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6, ppm): δ 44.3, 61.3, 150.3 (pyrazoline), 68.6, 68.9 (C_5H_5), 66.0, 66.6 (ortho-C_5H_4), 69.3, 69.4 (meta-C_5H_4), 75.9 (ipso-C_5H_4), 111.1, 113.9, 126.2, 126.7, 131.3, 132.9, 145.5, 158.3 (aromatic). FT-IR{ KBr, ν (cm^{-1})}: 3354 and 3249 $\nu(NH_2)$, 3069 ν(C–H)$_{Ar}$, 2919 ν(C–H)$_{Al}$, 1592 ν(C=C)$_{Ar}$, 1521 ν(C=N)$_{Ar}$, 1397 ν_b(C–H), 1349 $\nu_{as}(SO_2)$, 1239 $\nu(C_5H_4)$, 1158 $\nu_s(SO_2)$, 858 ν(C–H)$_{Ar}$, 839 ν(C–H)$_{Ar}$, 542 and 485 ν_{as}(Cp-Fe-Cp). HR-MS: found, m/z 520.0548 $[M + H]^+$, calculated for $C_{25}H_{23}O_2N_3ClFeS$: 520.0543. Anal. Calculated for $C_{25}H_{22}O_2N_3ClFeS$: C, 57.76; H, 4.27; N, 8.08; S, 6.17. Found: C, 57.53; H, 4.35; N, 8.19; S, 6.29.

4.2.10. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-napthyl)-4,5-dihydro-1H-pyrazoline (**3j**)

According to the general procedure, the reaction of 183 mg of chalcone **2j** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 198 mg (74%) of **3j** as brown solid. M.p. 124–125 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 3.10 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{trans}$, pyrazoline), 3.90 (1H, dd, ^3J = 12.0 Hz, ^2J = 5.0 Hz, 4-H$_{cis}$, pyrazoline), 4.04 (5H, s, C_5H_5), 4.36 (2H, d, J = 9.0 Hz, meta-C_5H_4), 4.54 (1H, s, ortho-C_5H_4), 4.69 (1H, s, ortho-C_5H_4), 5.52 (1H, dd, ^3J = 12.0 Hz, ^2J = 5 Hz, pyrazoline), 6.56 (2H, s, NH_2), 7.00 (2H, d, J = 9.0 Hz, sulfonamide), 7.57 (2H, d, J = 9.0 Hz, sulfonamide), 7.39 (1H, d, J = 8.0 Hz, aromatic), 7.43–7.48 (2H, m, aromatic), 7.74 (1H, s, aromatic), 7.78–7.82 (2H, br s, aromatic), 7.86 (1H, d, J = 8.0 Hz, aromatic). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 44.3, 61.7, 151.4 (pyrazoline) 69.0 (C_5H_5), 66.6, 67.2 (ortho-C_5H_4), 69.8, 69.9 (meta-C_5H_4), 76.2 (ipso-C_5H_4), 111.3, 123.6, 124.1, 126.0, 126.4, 127.1, 127.5, 217.6, 129.0, 132.0, 132.3, 139.2, 145.9 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3338 and 3245 $\nu(NH_2)$, 3056 ν(C–H)$_{Ar}$, 2923 ν(C–H)$_{Al}$, 1664 ν(C=C)$_{Ar}$, 1591 ν(C=C)$_{Ar}$, 1510 ν(C=N)$_{Ar}$, 1398 ν_b(C–H), 1317 $\nu_{as}(SO_2)$, 1153 $\nu_s(SO_2)$, 1097 ν(C–H)$_{Ar}$, 820 ν(C–H)$_{Ar}$, 743 ν(C–H)$_{Ar}$, 537 and 473 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 536.1099 $[M + H]^+$, calculated for $C_{29}H_{26}O_2N_3FeS$: 536.1089. Anal. Calculated for $C_{29}H_{25}O_2N_3FeS$: C, 65.05; H, 4.71; N, 7.85; S, 5.99. Found: C, 65.12; H, 4.86; N, 7.94; S, 6.09.

4.2.11. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazoline (**3k**)

According to the general procedure, the reaction of 181 mg of chalcone **2k** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 129 mg (49%) of **3k** as pale brown solid. M.p. 181–182 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 3.0 (1H, d, J = 6.0 Hz, 4-H$_{trans}$, pyrazoline), 3.92 (1H, dd, ^3J = 12.0 Hz, ^2J = 6.0 Hz, 4-H$_{cis}$, pyrazoline), 4.08 (5H, s, C_5H_5), 4.36–4.39 (2H, br s, meta-C_5H_4), 4.56 (1H, s, ortho-C_5H_4), 4.67 (1H, s, ortho-C_5H_4), 5.56–5.63 (1H, m, pyrazoline), 6.69–6.74 (2H, br s, NH_2), 6.96 (2H, d, J = 8.0 Hz, sulfonamide), 7.60–7.65 (3H, m, aromatic), 7.69 (1H, d, J = 7.0 Hz, aromatic), 8.14 (1H, d, J = 8.0 Hz, aromatic), 8.18 (1H, s, aromatic). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 44.2, 60.8, 151.5 (pyrazoline), 69.0 (C_5H_5), 66.5, 67.2 (ortho-C_5H_4), 69.7, 69.9 (meta-C_5H_4), 76.0 (ipso-C_5H_4), 111.3, 122.0, 124.7, 128.3, 130.4, 131.2, 132.3, 144.4, 145.6 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3362 and 3253 $\nu(NH_2)$, 3071 ν(C–H)$_{Ar}$, 3053 ν(C–H)$_{Ar}$, 2919 ν(C–H)$_{Al}$, 1590 ν(C=C)$_{Ar}$, 1524 $\nu_{as}(NO_2)$, 1509 ν(C=N)$_{Ar}$, 1401 ν_b(C–H), 1357 $\nu_s(NO_2)$, 1328 $\nu_{as}(SO_2)$, 1239 $\nu(C_5H_4)$, 1156 $\nu_s(SO_2)$, 839 ν(C–H)$_{Ar}$, 741 ν(C–H)$_{Ar}$, 542 and 485 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 531.0793 $[M + H]^+$, calculated for $C_{25}H_{23}O_4N_4FeS$: 531.0783. Anal. Calculated for $C_{25}H_{22}O_4N_4FeS$: C, 56.61; H, 4.18; N, 10.56; S, 6.05. Found: C, 56.82; H, 4.21; N, 10.79; S, 5.99.

4.2.12. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-nitrophenyl)-4,5-dihydro-1H-pyrazoline (**3l**)

According to the general procedure, the reaction of 181 mg of chalcone **2l** and 123 mg of 4-hydrazino benzenesulfonamide hydrochloride furnishes 133 mg (50%) of **3l** as orange red solid. M.p. 134–135 °C. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 3.91 (1H, dd, ^3J = 11.8 Hz, ^2J = 4.5 Hz, 4-H$_{cis}$, pyrazoline), 4.08 (5H, s, C_5H_5), 4.37 (2H, s, meta-C_5H_4), 4.56 (1H, s, ortho-C_5H_4), 4.63 (1H, s, ortho-C_5H_4), 5.44–5.54 (1H, m, pyrazoline), 6.52–6.66 (2H, br s, NH_2), 6.92 (2H, d, J = 8.2 Hz, sulfonamide), 7.62 (2H, d, J = 8.0 Hz, sulfonamide), 7.53 (2H, d, J = 9.1 Hz, aromatic), 8.22 (2H, d, J = 9.1 Hz, aromatic). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 44.0, 60.8, 151.5 (pyrazoline) 69.0 (C_5H_5), 66.7, 67.1 (ortho-C_5H_4), 69.9, 75.7 (meta-C_5H_4), 79.0 (ipso-C_5H_4), 111.4, 124.3, 127.2, 132.5, 145.6, 146.8, 149.1 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3358 and 3249 $\nu(NH_2)$, 3053 ν(C–H)$_{Ar}$, 2919 ν(C–H)$_{Al}$, 1592 ν(C=C)$_{Ar}$, 1512 $\nu_{as}(NO_2)$, 1397 ν_b(C–H), 1349 $\nu_s(NO_2)$, 1328 $\nu_{as}(SO_2)$, 1241 $\nu(C_5H_4)$, 1158 $\nu_s(SO_2)$, 858 ν(C–H)$_{Ar}$, 839 ν(C–H)$_{Ar}$, 542 and 485 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 531.0797 $[M + H]^+$, calculated for $C_{25}H_{23}O_4N_4FeS$: 531.0783. Anal. Calculated for $C_{25}H_{22}O_4N_4FeS$: C, 56.61; H, 4.18; N, 10.56; S, 6.05. Found: C, 56.55; H, 4.16; N, 10.70; S, 6.12.

4.3. General procedure for the preparation of 1,3,5-trisubstituted pyrazoles (**4a–j**)

DDQ (0.3 mmol, 1.2 equiv) in 10 ml of dry dichloromethane is added drop wise to a solution of appropriate pyrazoline compounds (**3a–j**, 0.25 mmol) dissolved in 20 ml of dry dichloromethane and stirred at room temperature. The progress of the reaction was monitored by TLC (1:1, pet ether:chloroform). After the completion of reaction (8–9 h), the reaction mixture was passed through a pad of neutral alumina using 2% methanol in chloroform as eluent to give a yellow color band of product. Crystallization from dichloromethane gave the analytically pure product in 49–69% yield.

4.3.1. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-phenyl-1H-pyrazoline (**4a**)

According to the general procedure, the reaction of 122 mg of pyrazoline (**3a**) and 68 mg of DDQ furnishes 73 mg (61%) of **4a** as red solid. M.p. decomposes at 181–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.16 (5H, s, C_5H_5), 4.36 (2H, s, meta-C_5H_4), 4.78 (2H, s, ortho-C_5H_4), 4.92 (2H, br s, NH_2), 6.57 (1H, s, pyrazole), 7.29 (2H, m, C_6H_5), 7.39 (3H, m, C_6H_5), 7.47 (2H, d, J = 8.5 Hz, sulfonamide), 7.85 (2H, d, J = 8.5 Hz, sulfonamide). ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6, ppm): δ 66.2 (ortho-C_5H_4), 68.1 (meta-C_5H_4), 68.9 (C_5H_5), 106.4, 123.8, 126.9, 128.1, 129.6, 141.5, 141.9, 143.2, 151.6 (Aromatic). FT-IR {KBr, ν (cm^{-1})}: 3359 and 3242 ν(NH_2), 1590 ν(C=C)$_{Ar}$, 1506 ν(C=N)$_{Ar}$, 1319 ν_{as}(SO_2), 1152 ν_s(SO_2), 485 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 484.0756 $[M + H]^+$, calculated for $C_{25}H_{22}O_2N_3FeS$: 484.0776. Anal. Calculated for $C_{25}H_{21}O_2N_3FeS$: C, 62.12; H, 4.38; N, 8.69; S, 6.63. Found: C, 62.40; H, 4.31; N, 8.71; S, 6.72.

4.3.2. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-methoxyphenyl)-1H-pyrazoline (**4b**)

According to the general procedure, the reaction of 129 mg of pyrazoline (**3b**) and 68 mg of DDQ furnishes 72 mg (56%) of **4b** as brown solid. M.p. 162–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.40 (3H, s, –OCH_3), 4.20 (5H, s, C_5H_5), 4.39 (2H, s, meta-C_5H_4), 4.79–4.91 (4H, br s, ortho-C_5H_4 and NH_2), 6.50 (1H, s, pyrazole), 6.85 (1H, d, J = 8.3 Hz, aromatic), 7.05 (1H, d, J = 7.6 Hz, aromatic), 7.36 (2H, d, J = 7.6 Hz, aromatic), 7.42 (2H, d, J = 9.0 Hz, sulfonamide), 7.80 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 54.4 (–OCH_3), 66.2 (ortho-C_5H_4), 68.1 (meta-C_5H_4), 68.9 (C_5H_5), 107.1, 110.9, 119.0, 120.3, 122.0, 125.9, 130.2, 130.4, 140.1, 140.8, 142.9, 151.2, 155.6 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3358 and 3239 ν(NH_2), 1590 ν(C=C)$_{Ar}$, 1508 ν(C=N)$_{Ar}$, 1328 ν_{as}(SO_2), 1251 ν_s(C–O), 1159 ν(SO_2)$_s$,1099 ν_s(C–N), 871 ν(C–H)$_{Ar}$, 488 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 514.0876 $[M + H]^+$, calculated for $C_{26}H_{24}O_3N_3FeS$: 514.0882. Anal. Calculated for $C_{26}H_{23}O_3N_3FeS$: C, 60.83; H, 4.52; N, 8.18; S, 6.25. Found: C, 60.79; H, 4.58; N, 8.12; S, 6.19.

4.3.3. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-methoxyphenyl)-1H-pyrazoline (**4c**)

According to the general procedure, the reaction of 129 mg of pyrazoline **3c** and 68 mg of DDQ furnishes 89 mg (69%) of **4c** as pale brown solid. M.p. 100–101 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.85 (3H, s, –OCH_3), 4.14 (5H, s, C_5H_5), 4.33 (2H, t, J = 2.3 Hz, meta-C_5H_4), 4.74 (2H, t, J = 2.3 Hz, ortho-C_5H_4), 4.82 (2H, br s, NH_2), 6.52 (1H, s, pyrazole), 6.90 (2H, d, J = 8.3 Hz, aromatic), 7.20 (2H, d, J = 8.3 Hz, aromatic), 7.50 (2H, d, J = 9.0 Hz, sulfonamide), 7.87 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d_6 + $CDCl_3$, ppm): δ 55.3 (–OCH_3), 66.9 (ortho-C_5H_4), 68.9 (meta-C_5H_4), 69.5 (C_5H_5), 106.8, 114.2, 122.3, 124.7, 127.2, 130.6, 139.7, 143.3, 144.0, 152.8, 159.9 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3359 and 3292 ν(NH_2), 1592 ν(C=C)$_{Ar}$, 1515 ν(C=N)$_{Ar}$, 1411 ν_b(C-H), 1336 ν_{as}(SO_2), 1249 ν_s(C–O), 1154 ν_s(SO_2), 1099 ν_s(C–N), 538 and 489 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 514.0873 $[M + H]^+$, calculated for $C_{26}H_{24}O_3N_3FeS$: 514.0888. Anal. Calculated for $C_{26}H_{23}O_3N_3FeS$: C, 60.83; H, 4.52; N, 8.18; S, 6.25. Found: C, 60.91; H, 4.49; N, 8.23; S, 6.21.

4.3.4. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-thiophene)-1H-pyrazoline (**4d**)

According to the general procedure, the reaction of 122 mg of pyrazoline **3d** and 68 mg of DDQ furnishes 71 mg (59%) of **4d** as yellow powder. M.p. decomposes at 220–221 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.16 (5H, s, C_5H_5), 4.34 (2H, s, meta-C_5H_4), 4.74 (2H, s, ortho-C_5H_4), 4.88 (2H, br s, NH_2), 6.61 (1H, s, pyrazole), 6.96 (1H, s, aromatic), 7.45 (2H, d, J = 8.0 Hz, sulfonamide), 7.11 (1H, s, aromatic), 7.39 (1H, s, aromatic), 7.87 (2H, d, J = 8.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d_6, ppm): δ 66.3 (ortho-C_5H_4), 68.4 (meta-C_5H_4), 68.5 (C_5H_5), 76.8 (ipso-C_5H_4), 105.7, 109.4, 111.3, 124.2, 126.5, 133.7, 141.7, 142.8, 151.5 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3349 and 3262 ν(NH_2), 1592 ν(C=C)$_{Ar}$, 1507 ν(C=N)$_{Ar}$, 1323 ν_{as}(SO_2), 1153 ν_s(SO_2), 479 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 490.0262 $[M + H]^+$, calculated for $C_{23}H_{20}O_2N_3FeS_2$: 490.0277. Anal. Calculated for $C_{23}H_{19}O_2N_3FeS_2$: C, 56.45; H, 3.91; N, 8.59; S, 13.10. Found: C, 56.50; H, 3.87; N, 8.62; S, 13.03.

4.3.5. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-furan)-1H-pyrazoline (**4e**)

According to the general procedure, the reaction of 120 mg of pyrazoline **3e** and 68 mg of DDQ furnishes 76 mg (63%) of **4e** as yellow solid. M.p. decomposes at 197–198 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.12 (5H, s, C_5H_5), 4.32 (2H, br s, meta-C_5H_4), 4.74 (2H, br s, ortho-C_5H_4), 6.72 (1H, s, pyrazole), 6.31 (1H, s, aromatic), 6.45 (1H, s, aromatic), 6.65 (1H, s, aromatic), 6.85 (2H, s, NH_2), 7.56 (2H, d, J = 8.5 Hz, sulfonamide), 7.98 (2H, d, J = 8.5 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d_6 + $CDCl_3$, ppm): δ 66.1 (ortho-C_5H_4), 68.2 (meta-C_5H_4), 68.9 (C_5H_5), 76.7 (ipso-C_5H_4), 105.3, 109.5, 111.0, 124.0, 126.3, 133.9, 141.9, 142.9, 151.6 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3355 and 3248 ν(NH_2), 1598 ν(C=C)$_{Ar}$, 1517 ν(C=N)$_{Ar}$, 1319 ν_{as}(SO_2), 1149 ν_s(SO_2), 485 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 474.0496 $[M + H]^+$, calculated for $C_{23}H_{20}O_3N_3FeS$: 474.0502. Anal. Calculated for $C_{23}H_{19}O_3N_3FeS$: C, 58.36; H, 4.05; N, 8.88; S, 6.77. Found: C, 58.50; H, 4.17; N, 8.82; S, 6.79.

4.3.6. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(3-bromophenyl)-1H-pyrazoline (**4f**)

According to the general procedure, the reaction of 141 mg of pyrazoline **3f** and 68 mg of DDQ furnishes 83 mg (59%) of **4f** as brown solid. M.p. 97–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.14 (5H, s, C_5H_5), 4.35 (2H, s, meta-C_5H_4), 4.75 (2H, s, ortho-C_5H_4), 4.8 (2H, br s, NH_2), 6.57 (1H, s, pyrazole), 7.10–7.24 (2H, m, aromatic), 7.48 (2H, d, J = 9.0 Hz, sulfonamide), 7.50–7.56 (2H, m, aromatic), 7.90 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, DMSO-d_6 + $CDCl_3$, ppm): δ 66.2 (ortho-C_5H_4), 68.2 (meta-C_5H_4), 68.9 (C_5H_5), 106.8, 121.9, 123.8, 126.4, 126.9, 129.7, 130.7, 130.9, 131.2, 141.5, 141.6, 142.0, 151.8 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3349 and 3242 ν(NH_2), 1591 ν(C=C)$_{Ar}$, 1510 ν(C=N)$_{Ar}$, 1316 ν_{as}(SO_2), 1154 ν_s(SO_2), 1101 ν(C-Br), 487 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 561.9866 $[M + H]^+$, calculated for $C_{25}H_{21}O_2N_3BrFeS$: 561.9881. Anal. Calculated for $C_{25}H_{20}O_2N_3BrFeS$: C, 53.40; H, 3.59; N, 7.47; S, 5.70. Found: C, 53.49; H, 3.64; N, 7.39; S, 5.62.

4.3.7. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-bromophenyl)-1H-pyrazoline (**4g**)

According to the general procedure, the reaction of 120 mg of pyrazoline **3g** and 68 mg of DDQ furnishes 82 mg (58%) of **4g** as

brown solid. M.p. 108–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 4.17 (5H, s, C_5H_5), 4.32 (2H, s, meta-C_5H_4), 4.74 (2H, br s, ortho-C_5H_4), 6.75 (2H, s, NH_2), 6.59 (1H, s, pyrazole), 7.18 (2H, d, J = 8.0 Hz, aromatic), 7.43 (2H, d, J = 8.0 Hz, aromatic), 7.51 (2H, d, J = 9.0 Hz, sulfonamide), 7.90 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 66.2 (ortho-C_5H_4), 68.2 (meta-C_5H_4), 68.9 (C_5H_5), 106.5, 122.0, 123.9, 126.3, 126.9, 128.6, 131.3, 141.5, 141.9, 142.0, 151.7 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3358 and 3262 $\nu(NH_2)$, 1590 $\nu(C{=}C)_{Ar}$, 1508 $\nu(C{=}N)_{Ar}$, 1316 $\nu_{as}(SO_2)$, 1161 $\nu_s(SO_2)$, 498 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 561.9871 $[M + H]^+$, calculated for $C_{25}H_{21}O_2N_3BrFeS$: 561.9881. Anal. Calculated for $C_{25}H_{20}O_2N_3BrFeS$: C, 53.40; H, 3.59; N, 7.47; S, 5.70. Found: C, 53.36; H, 3.57; N, 7.51; S, 5.72.

4.3.8. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-chlorophenyl)-1H-pyrazoline (**4h**)

According to the general procedure, the reaction of 129 mg of pyrazoline **3h** and 68 mg of DDQ furnishes 85 mg (66%) of **4h** as brown solid. M.p. 161–162 °C. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 4.16 (5H, s, C_5H_5), 4.36 (2H, s, meta-C_5H_4), 4.75 (2H, s, ortho-C_5H_4), 4.81 (2H, s, NH_2), 6.58 (1H, s, pyrazole), 7.45 (1H, d, J = 8.0 Hz, aromatic), 7.31–7.43 (3H, m, aromatic), 7.43 (2H, d, J = 9.0 Hz, sulfonamide), 7.82 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 66.3 (ortho-C_5H_4), 68.3 (meta-C_5H_4), 69.0 (C_5H_5), 107.9, 122.4, 126.4, 126.6, 129.4, 130.1, 131.3, 133.2, 140.0, 140.6, 151.6 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3362 and 3253 $\nu(NH_2)$, 1597 $\nu(C{=}C)_{Ar}$, 1517 $\nu(C{=}N)_{Ar}$, 1341 $\nu_{as}(SO_2)$, 1158 $\nu_s(SO_2)$, 539 and 497 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 518.0543 $[M + H]^+$, calculated for $C_{25}H_{21}O_2N_3ClFeS$: 518.0539. Anal. Calculated for $C_{25}H_{20}O_2N_3ClFeS$: C, 57.99; H, 3.89; N, 8.11; S, 6.19. Found: C, 58.06; H, 3.92; N, 8.08; S, 6.17.

4.3.9. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(4-chlorophenyl)-1H-pyrazoline (**4i**)

According to the general procedure, the reaction of 129 mg of pyrazoline **3i** and 68 mg of DDQ furnishes 85 mg (66%) of **4i** as brown solid. M.p. 127–128 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.16 (5H, s, C_5H_5), 4.36 (2H, s, meta-C_5H_4), 4.77 (2H, s, ortho-C_5H_4), 4.83 (2H, s, NH_2), 6.56 (1H, s, pyrazole), 7.23 (2H, d, J = 8.3 Hz, aromatic), 7.37 (2H, d, J = 8.3 Hz, aromatic), 7.47 (2H, d, J = 9.0 Hz, sulfonamide), 7.89 (2H, d, J = 9.0 Hz, sulfonamide). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 66.17 (ortho-C_5H_4), 68.22 (meta-C_5H_4), 68.90 (C_5H_5), 106.43, 123.89, 126.38, 128.11, 128.32, 129.43, 133.87, 141.39, 141.68, 142.01, 151.85 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3349 and 3256 $\nu(NH_2)$, 1601 $\nu(C{=}C)_{Ar}$, 1531 $\nu(C{=}N)_{Ar}$, 1353 $\nu_{as}(SO_2)$, 1163 $\nu_s(SO_2)$, 489 ν_{as}(Cp–Fe–Cp). HR-MS: found, m/z 518.0543 $[M + H]^+$, calculated for $C_{25}H_{21}O_2N_3ClFeS$: 518.0548. Anal. Calculated for $C_{25}H_{20}O_2N_3ClFeS$: C, 57.99; H, 3.89; N, 8.11; S, 6.19. Found: C, 58.02; H, 3.92; N, 8.17; S, 6.25.

4.3.10. 3-Ferrocenyl-1-(4-sulphamylphenyl)-5-(2-napthyl)-1H-pyrazoline (**4j**)

According to the general procedure, the reaction of 134 mg of pyrazoline **3j** and 68 mg of DDQ furnishes 91 mg (68%) of **4j** as brown solid. M.p. 126–127 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.17 (5H, s, C_5H_5), 4.35 (2H, s, meta-C_5H_4), 4.79 (2H, s, ortho-C_5H_4), 4.88 (2H, s, NH_2), 6.69 (1H, s, pyrazole), 7.53 (2H, d, J = 8.8 Hz, sulfonamide), 7.29 (1H, s, aromatic), 7.56 (2H, t, J = 4.4 Hz, aromatic), 7.80–7.86 (5H, m, aromatic), 7.88 (1H, t, J = 4.4 Hz, aromatic), 7.90 (1H, s, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ 65.53 (ortho-C_5H_4), 67.54 (meta-C_5H_4), 68.87 (C_5H_5), 106.06, 123.05, 124.95, 125.64, 126.40, 126.46, 126.65, 126.90, 127.06, 131.53, 131.71, 140.83, 141.19, 142.51, 151.04 (aromatic). FT-IR {KBr, ν (cm^{-1})}: 3349 and 3233 $\nu(NH_2)$, 1638 $\nu(C{=}C)_{Ar}$, 1510 $\nu(C{=}N)_{Ar}$, 1329 $\nu_{as}(SO_2)$, 1164 $\nu_s(SO_2)$, 531 and 487 ν_{as}(Cp-Fe-Cp). HR-MS: found, m/z 534.0916 $[M + H]^+$, calculated for $C_{29}H_{24}O_2N_3FeS$: 534.0933. Anal. Calculated for $C_{29}H_{23}O_2N_3FeS$: C, 65.30; H, 4.35; N, 7.88; S, 6.01. Found: C, 65.33; H, 4.38; N, 7.86; S, 5.17.

4.4. Single crystal X-ray diffraction studies

X-ray data for the compound was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) with ω-scan method [46]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 9132 reflections in the range of $2.37 < \theta < 27.92°$ for **3a**. Integration and scaling of intensity data were accomplished using SAINT program. The structure was solved by direct methods using SHELXS97 [47] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [47].

Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atoms attached to nitrogen atom were located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C–H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(c)$ for H atoms].

4.5. Electrochemistry

Cyclic voltammetric measurements of compounds **3a**–**k** were performed using CH instruments model 620C series, version 5.01 interfaced with computer. The electrochemical cell consists of a three-electrode cell, which involved a glassy carbon as a working electrode, saturated calomel as a reference electrode, and platinum wire as the counter electrode. The measurement was performed using concentrations of samples were 0.5–1.0 mM, in the presence of 0.1 M tetra-butyl ammonium perchlorate, TBAP (supporting electrolyte) in dry DMSO under N_2 atmosphere at RT.

4.6. Fluorescence and lifetime instrumentation

Steady state fluorescence spectra were recorded on a spectrofluorimeter (FluoroLog-3, Horiba Jobin Yvon). For fluorescence quantum yield measurements, the solutions of compounds **3a**–**k** in dichloromethane were optically matched at the excitation wavelength (350 nm) and then the quantum yield was calculated by comparing the integrated areas under the emission curves. Quinine sulfate in 0.1 M H_2SO_4 (Φ_f = 0.57, at 22 °C) was used as reference [45]. The measured Φ_f values are accurate within ±10%.

Lifetime measurements were made on a picosecond time-correlated single photon counting (TCSPC) setup (FluoroLog-3 Triple Illuminator, IBH) employing a picosecond NanoLED laser as excitation source (λ_{ex} = 301 nm) and photomultiplier tube (Hamamatsu) having a response time of 500 ps as the detector. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The width of the instrument function, which was limited by the full width at half maxima (FWHM) of the excitation source, was 1.07 ns at 301 nm. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (version 2.3) decay analysis software. The quality of the fits was measured by the χ^2 values and distribution of the residuals.

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Appendix A. Supplementary material

CCDC 868950 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.08.011.

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