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Synthesis and fluorescence of pyrazolines substituted with pyrimidine and ferrocene subunits

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Abstract: 1,3,5-Trisubstituted 2-pyrazolines were synthesized by the reaction of chalcones with hydrazine in hot ethanol. Their structures were elucidated by ^{1}H NMR, ^{13}C NMR, IR, MS and elemental analysis. The fluorescence spectra were measured in different organic solvents. The emission wavelength is blue shifted with the increase in solvent polarity.

Keywords: ferrocene; fluorescence; pyrazoline; pyrimidine; synthesis.

Introduction

Pyrazoline derivatives have attracted increasing attention due to their pharmaceutical properties such as antimicrobial [1–3], antiamoebic [4, 5], antinociceptive [6], anticancer [7] and antidepressant [8] activities. In addition, because of their excellent fluorescence [9, 10], they have been widely used as fluorescent brightening agents, fluorescence chemosensors, hole-transport materials in electrophotography, as components of OLEDs and as novel fluorescent materials [11–21].

Substituted pyrimidines [22–26] are central subunits of interesting pharmacological agents, such as calcium channel modulators, α1 a-adrenergic receptor antagonists, mitotic kinesin inhibitors and hepatitis B virus replication inhibitors [27–31]. Ferrocene has been used for the preparation of small bioactive molecules due to its good biocompatibility [32–34]. Recently, ferrocene containing multichannel chemosensors with electrochemical properties have received considerable attention. In light of these data, we would like to report the synthesis, characterization and fluorescence of novel ethyl 2-(3-ferrocenyl)-5-aryl-4,5-dihydropyrazol-1-yl)-6-methyl-5-phenylpyrimidine-4-carboxylates **6a-h** (Scheme 1).

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Results and discussion

Starting compounds **1-5** were prepared by using literature procedures [35]. The desired pyrazoline derivatives **6a-h** were obtained by the reaction of ferrocenyl chalcones **5** with pyrimidin-2-ylhydrazine **4** under reflux conditions in 51–82% yields. The structures of products **6a-h** were characterized by spectroscopic methods and elemental analysis.

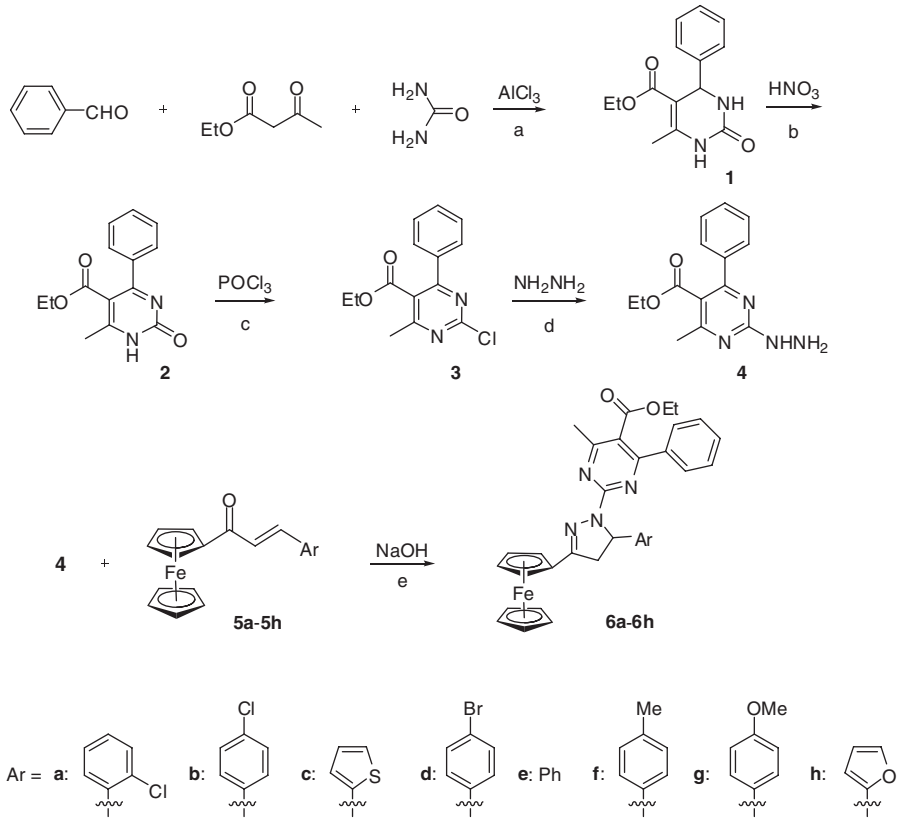
The fluorescence spectra of compounds **6a-h** were recorded in chloroform, tetrahydrofuran and dichloromethane (1×10^{-5} M) at room temperature at the excitation wavelength of 371 nm. The emission wavelengths are from 422 nm to 434 nm. The spectra are shown in Figures 1–3. It can be concluded that different aromatic groups at C5 of the central 4,5-dihydropyrazole moiety have little influence on the emission wavelengths.

Experimental

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Melting points were recorded on electrothermal digital melting point apparatus and were uncorrected. Aromatic aldehydes, ethyl acetoacetate, phosphorus oxychloride and hydrazine were purchased from the Alladin Chemical Company and were used without further purification. All solvents were dried using standard methods before use. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ on a Bruker AVANCE III 400 instrument. IR spectra were recorded with an FTIR 1730 spectrometer. Fluorescence spectra were obtained on a Sanyo 970CRT spectrofluorometer with the excitation wavelength of 371 nm. Starting materials **1-5** were prepared by using literature procedures [36–39].

Synthesis of compounds 6a-h

To a mixture of ferrocenyl chalcone **5a-h** (0.01 mol) and pyrimidine hydrazine **4** (0.012 mol) in ethanol (30 mL) was added sodium



Scheme 1 Reagents, conditions and yields: (a) $AlCl_3$, EtOH, reflux 3 h, 78–83%; (b) HNO_3(50–60%), ice-bath 1 h, 68–79%; (c) $POCl_3$, EtOH, reflux, 3 h, 69–85%; (d) NH_2NH_2, EtOH, reflux 4 h, 77–85%; (e) acetic acid, Ar-CHO, EtOH, reflux 8–12 h, 75–80%.

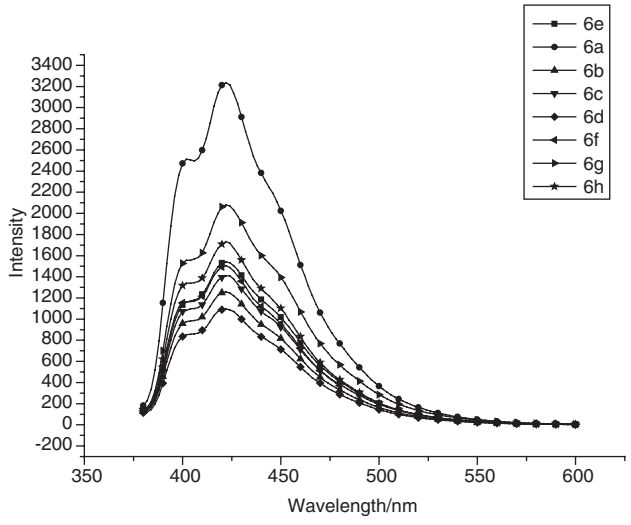


Figure 1 Fluorescence emission spectra of compounds **6a-h** in $CHCl_3$.

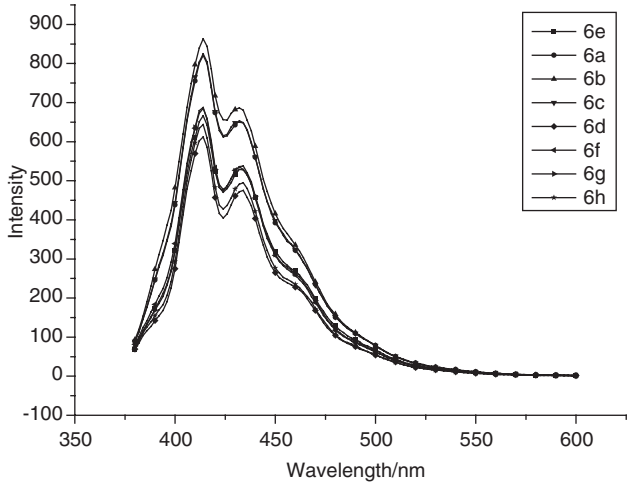


Figure 2 Fluorescence emission spectra of **6a-h** in THF.

hydroxide (0.005 mol) at room temperature, and the resulting mixture was stirred at reflux for 10 h. Then the mixture was cooled to room temperature, poured into ice water and neutralized with hydrochloric acid. The resultant precipitate was filtrated, washed with water and crystallized from ethanol to afford compound **6a-h**.

Ethyl 2-(3-ferrocenyl-5-(2-chlorophenyl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6a) This compound was obtained as pale yellow powder in 81% yield; mp 250–251°C; ^{1}H NMR: δ 7.48 (d, J = 6.8 Hz, 1H, aromatic), 7.35 (d, J = 7.4 Hz, 4H, aromatic), 7.25 (d, J = 11.2 Hz, 3H, aromatic), 6.16 (dd, J = 11.9, 4.5 Hz, 1H, pyrazoline), 4.91 (s, 1H, ortho-C_5H_4), 4.61 (s, 1H, ortho-C_5H_4), 4.42 (d, J = 9.7 Hz, 2H, meta-C_5H_4), 4.13 (s, 5H, C_5H_5), 4.08

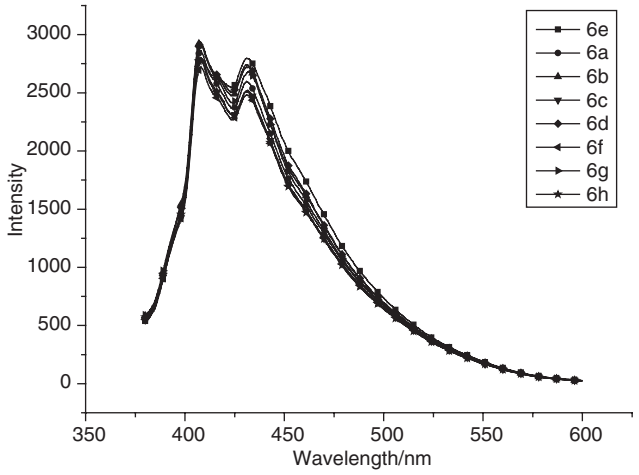


Figure 3 Fluorescence emission spectra of compounds **6a-h** in CH_2Cl_2.

(m, 2H, methylene), 3.83 (dd, *J* = 16.9, 11.4 Hz, 1H, pyrazoline), 3.05 (dd, *J* = 17.9, 4.2 Hz, 1H, pyrazoline), 2.59 (s, 3H, methyl), 1.01 (t, *J* = 7.1 Hz, 3H, methyl); ^{13}C NMR: δ 168.8, 167.7, 165.27, 156.7, 155.4, 155.3, 142.4, 138.8, 131.8, 129.6, 128.3, 127.7, 121.1, 116.2, 75.8, 75.8, 70.4, 70.2, 69.3, 68.0, 67.6, 61.1, 43.7, 23.4, 13.6; IR: 2982(CH, aliphatic), 1704(C=O), 1544(C=N), 1510(C=N), 1466(C=N) cm^{-1}; MS: *m/z* 605.1(M^++1). Anal. Calcd for $C_{33}H_{29}ClFeN_4O_2$: C, 65.52; H, 4.83; N, 9.26. Found: C, 65.37; H, 4.64; N, 9.06.

Ethyl 2-(3-ferrocenyl-5-(4-chlorophenyl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6b) This compound was obtained as pale yellow powder in 75% yield; mp 218–219°C; ^{1}H NMR: δ 7.42 (s, 2H, aromatic), 7.38–7.32 (m, 6H, aromatic), 7.31 (s, 1H, aromatic), 5.73 (dd, *J* = 12.6, 4.4 Hz, 1H, pyrazoline), 4.90 (s, 1H, ortho-C_5H_4), 4.63 (s, 1H, ortho-C_5H_4), 4.44 (d, *J* = 10.1 Hz, 2H, meta-C_5H_4), 4.15 (s, 5H, C_5H_5), 4.12 – 4.05 (m, 2H, methylene), 3.77 (dd, *J* = 17.9, 11.9 Hz, 1H, pyrazoline), 3.11 (dd, *J* = 17.5, 3.7 Hz, 1H, pyrazoline), 2.58 (s, 3H, methyl), 0.99 (t, *J* = 7.1 Hz, 3H, methyl); ^{13}C NMR: δ 168.8, 167.5, 165.3, 156.8, 155.4, 142.1, 138.6, 130.3, 129.6, 128.9, 128.3, 128.1, 127.4, 121.3, 75.9, 70.3, 70.2, 69.3, 68.0, 67.7, 61.2, 57.2, 43.9, 23.4, 13.6; IR: 2977(CH, aliphatic), 1708(C=O), 1547(C=N), 1511(C=N), 1465(C=N) cm^{-1}; MS: *m/z* 605.1(M+1). Anal. Calcd for $C_{33}H_{29}ClFeN_4O_2$: C, 65.52; H, 4.83; N, 9.26. Found: C, 65.45; H, 4.76; N, 9.13.

Ethyl 2-(3-ferrocenyl-5-(thiophene-2-yl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6c) This compound was obtained as pale yellow powder in 71% yield; mp199–200°C. ^{1}H NMR: δ 7.49 (d, *J* = 6.9 Hz, 5H, aromatic), 7.29–7.18 (m, 1H, aromatic), 7.10 (d, *J* = 2.9 Hz,1H, aromatic), 7.08 – 6.91 (m, 1H, aromatic), 6.10 (dd, *J* = 11.4, 3.9 Hz, 1H, pyrazoline), 4.96 (s, 1H, ortho-C_5H_4), 4.59 (s, 1H, ortho-C_5H_4), 4.45 (t, *J* = 18.4 Hz, 2H, meta-C_5H_4), 4.12 (s, 5H, C_5H_5), 4.10 (m, 2H, methylene), 3.74 (dd, *J* = 17.1, 11.6 Hz, 1H, pyrazoline), 3.32 (dd, *J* = 17.1, 4.0 Hz, 1H, pyrazoline), 2.61 (s, 3H, methyl), 1.00 (t, *J* = 7.1 Hz, 3H, methyl); ^{13}C NMR: δ 168.9, 167.7, 165.3, 156.9, 155.6, 146.0, 138.7, 129.6, 128.4, 128.1, 126.6, 124.5, 124.4, 116.2, 75.7, 70.4, 70.1, 69.4, 68.1, 67.5, 61.2, 57.1, 43.9, 23.4, 13.6; IR: 2987(CH, aliphatic), 1702(C=O), 1580(C=N), 1503(C=N), 1469(C=N) cm^{-1}; MS: *m/z* 577.1(M^++1). Anal. Calcd for $C_{31}H_{28}FeN_4O_2S$: C, 64.59; H, 4.90; N, 9.72. Found: C, 65.32; H, 4.72; N, 9.54.

Ethyl 2-(3-ferrocenyl-5-(4-bromophenyl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6d) This compound was obtained as pale yellow powder in 86% yield; mp 198–199°C; ^{1}H NMR: δ 7.48 (d, *J* = 8.2 Hz, 2H, aromatic), 7.39 (d, *J* = 4.9 Hz, 1H, aromatic), 7.33 (d, *J* = 5.8 Hz, 3H, aromatic), 7.24 (d, *J* = 9.5 Hz, 3H, aromatic), 5.69 (dd, *J* = 12.5, 2.9 Hz, 1H, pyrazoline), 4.87 (s, 1H, ortho-C_5H_4), 4.59 (s, 1H, ortho-C_5H_4), 4.41 (d, *J* = 10.1 Hz, 2H, meta-C_5H_4), 4.12 (s, 5H, C_5H_5), 4.06 (m, 2H, methylene), 3.75 (dd, *J* = 16.9, 12.1 Hz, 1H, pyrazoline), 3.09 (dd, *J* = 17.4, 4.4 Hz, 1H, pyrazoline), 2.56 (s, 3H, methyl), 0.96 (t, *J* = 7.2 Hz, 3H, methyl); ^{13}C NMR: δ 168.8, 167.6, 165.4, 156.9, 155.4, 146.1, 138.9, 129.5, 128.4, 128.1, 126.6, 124.4, 124.3, 116.4, 76.0, 70.3, 70.0, 69.4, 68.1, 67.5, 61.1, 57.1, 43.8, 23.3, 13.1; IR: 2926(CH, aliphatic), 1712(C=O), 1545(C=N), 1513(C=N), 1466(C=N) cm^{-1}; MS: *m/z* 649.1(M^++1). Anal. Calcd for $C_{33}H_{29}BrFeN_4O_2$: C, 61.04; H, 4.50; N, 8.63. Found: C, C, 60.91; H, 4.35; N, 8.41.

Ethyl 2-(3-ferrocenyl-5-phenyl-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6e) This compound was obtained as pale yellow powder in 83% yield; mp 195–196°C; ^{1}H NMR: δ 7.38 (d, *J* = 4.3 Hz, 5H, aromatic), 7.36–7.29 (m, 5H, aromatic), 5.77 (dd, *J* = 11.9, 4.8 Hz, 1H, pyrazoline), 4.92 (s, 1H, ortho-C_5H_4), 4.60 (s, 1H, ortho-C_5H_4), 4.42 (d, *J* = 11.2 Hz, 2H, meta-C_5H_4), 4.14 (s, 5H, C_5H_5), 4.12–4.03 (m, 2H, methylene), 3.77 (dd, *J* = 17.1, 11.9 Hz, 1H, pyrazoline), 3.16 (dd, *J* = 17.0, 4.3 Hz, 1H, pyrazoline), 2.59 (s, 3H, methyl), 0.98 (t, *J* = 7.2 Hz, 3H, methyl); ^{13}C NMR: δ 168.9, 167.7, 165.6, 156.8, 155.5, 143.3, 138.8, 129.5, 128.7, 128.3, 128.0, 127.4, 125.9, 115.9, 76.1, 70.3, 70.0, 69.3, 68.1, 67.6, 61.6, 61.1, 43.9, 23.4, 13.6; IR: 2975(CH, aliphatic), 1700(C=O), 1545(C=N), 1515(C=N), 1466(C=N) cm^{-1}; MS: *m/z* 571.1(M^++1). Anal. Calcd for $C_{33}H_{30}FeN_4O_2$: C, 69.48; H, 5.30; N, 9.82. Found: C, 69.22; H, 5.15; N, 9.64.

Ethyl 2-(3-ferrocenyl-5-(4-methylphenyl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6f) This compound was obtained as pale yellow powder in 81% yield; mp 195–196°C; ^{1}H NMR: δ 7.37 (s, 3H, aromatic), 7.28 (d, *J* = 5.4 Hz, 2H, aromatic), 7.18 (d, *J* = 8.1 Hz, 2H, aromatic), 5.74 (dd, *J* = 12.4, 4.6 Hz, 1H, pyrazoline), 4.91 (s, 1H, ortho-C_5H_4), 4.60 (s, 1H, ortho-C_5H_4), 4.42 (d, *J* = 11.2 Hz, 2H, meta-C_5H_4), 4.15 (s, 5H, C_5H_5), 4.11–4.04 (m, 2H, methylene), 3.75 (dd, *J* = 17.2, 12.2 Hz, 1H, pyrazoline), 3.14 (dd, *J* = 17.2, 3.8 Hz, 1H, pyrazoline), 2.59 (s, 3H, methyl), 2.36 (s, 3H, methyl), 0.99 (t, *J* = 7.0 Hz, 3H, methyl); ^{13}C NMR: δ 169.9, 167.6, 165.2, 156.8, 155.5, 140.3, 138.9, 137.0, 129.4, 129.3, 128.4, 128.0, 125.9, 115.8, 76.2, 70.3, 70.00, 69.3, 68.0, 67.6, 61.4, 61.1, 43.9, 23.4, 21.1, 13.6; IR: 1703(C=O), 1583(C=N), 1512(C=N), 1469(C=N) cm^{-1}; MS: *m/z* 585.1(M+1). Anal. Calcd for $C_{34}H_{32}FeN_4O_2$: C, 69.87; H, 5.52; N, 9.59. Found: C, 69.65; H, 5.31; N, 9.37.

Ethyl 2-(3-ferrocenyl-5-(4-methoxyphenyl)-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6g) This compound was obtained as pale yellow powder in 79% yield; mp 185–186°C; ^{1}H NMR: δ 7.38 (s, 4H, aromatic), 7.28 (s, 4H, aromatic), 5.73 (dd, *J* = 10.4, 4.3 Hz, 1H, pyrazoline), 4.91 (s, 1H, ortho-C_5H_4), 4.61 (s, 1H, ortho-C_5H_4), 4.42 (d, *J* = 10.2 Hz, 2H, meta-C_5H_4), 4.15 (s, 5H, C_5H_5), 4.12–4.02 (m, 2H, methylene), 3.82 (s, 3H, methoxy), 3.73 (dd, *J* = 12.0, 3.4 Hz, 1H, pyrazoline), 3.14 (dd, *J* = 16.0, 4.2 Hz, 1H, pyrazoline), 2.59 (s, 3H, methyl), 0.98 (t, *J* = 5.8 Hz, 3H, methyl); ^{13}C NMR: δ 168.9, 167.3, 166.4, 156.7, 154.8, 141.4, 140.0, 138.0, 128.3, 128.4, 128.2, 127.9, 125.0, 116.9, 76.3, 70.6, 70.0, 69.4, 68.3, 67.4, 62.1, 61.1, 55.8, 43.0, 23.4, 13.6; IR: 1713(C=O), 1584(C=N), 1512(C=N), 1467(C=N) cm^{-1}; MS: *m/z* 601.1(M+1). Anal. Calcd for $C_{34}H_{32}FeN_4O_3$: C, 68.01; H, 5.37; N, 9.33. Found: C, 67.88; H, 5.16; N, 9.14.

Ehyl 2-(3-ferrocenyl-5-furan-2-yl-4,5-dihydropyrazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (6h) This compound was obtained as pale yellow powder in 79% yield; mp 105–106°C; ^{1}H NMR: δ 7.54 (s, 2H, aromatic), 7.41 (d, *J* = 19.1 Hz, 3H, aromatic), 7.28 (s, 1H, aromatic), 5.91 (dd, *J* = 11.2, 3.4 Hz, 1H, pyrazoline), 5.01 (s, 1H, ortho-C_5H_4), 4.55 (s, 1H, ortho-C_5H_4), 4.43 (d, *J* = 13.1 Hz, 2H, meta-C_5H_4), 4.23 (s, 5H, C_5H_5), 4.15–4.01 (m, 2H, methylene), 3.60 (dd, *J* = 17.4, 11.3 Hz, 1H, pyrazoline), 3.42 (dd, *J* = 17.9, 5.1 Hz, 1H, pyrazoline), 2.61 (s, 3H, methyl), 0.99 (t, *J* = 4.7 Hz, 3H, methyl); ^{13}C NMR: δ 168.7, 167.0, 165.4, 157.9, 156.1, 146.2, 139.1, 129.6, 128.5, 128.0, 126.2, 125.3, 124.4, 117.1, 76.2, 70.7, 70.2, 69.6, 68.9, 67.6, 62.1, 56.9, 44.1, 23.6, 13.7;IR: 1715(C=O), 1630(C=N), 1511(C=N), 1468(C=N) cm^{-1}; MS: *m/z* 561.1(M+1). Anal. Calcd for $C_{31}H_{28}FeN_4O_3$: C, 66.44; H, 5.04; N, 10.00. Found: C, 66.21; H, 4.87; N, 9.86.

Conclusions

We have designed and synthesized a series of novel pyrazoline chromophores containing pyrimidine and ferrocene moieties which show a blue emission. This fluorescence is blue shifted with the increase of solvent polarity. The synthetic strategy is straightforward, benefits from high yield and facile purification without tedious silica gel chromatography.

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