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Synthesis and Spectroscopic Properties of Novel Fluorescent Compounds Containing Bis-pyrazole Ring

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Abstract A series of pyrazoline derivatives containing pyrazole group were synthesized and characterized by means of ^{1}H NMR, FT-IR, MS and elemental analysis, and their UV–vis absorption behavior and fluorescent properties were also measured. Moreover, the influence of metal ions on spectral properties of synthetic products was examined with compound $\mathbf{A_5}$ as an example. It has been found that all synthetic pyrazoline derivatives show two remarkable absorption peaks at about 260 and 360 nm and the maximum emission peak at 445–467 nm. Especially, the joined of Co^{2+} can quench the fluorescence of compound $\mathbf{A_5}$ obviously.

Keywords Pyrazoline derivative · Pyrazole group · Synthesis · Ion recognition · Pectroscopic properties · Co^{2+}

Introduction

As a kind of important nitrogen heterocyclic compound, pyrazoline derivatives possess particular physicochemical property and biological activities. These compounds have been applied in biology [1], medicine [2], pesticide [3–5] and photoelectric material [6] area. Mnna F [7] have studied the inhibiting ability of 1-acetyl-3,5-diphenyl-4,5-dihydro-(1*H*)-pyrazole derivatives to amine oxidases activity; Ozdemir [8] have synthesized some 1-(4-phenyl-2-thiazolyl)-3-(2- thiophene)-5-aryl-2-pyrazoline derivatives and found that these compounds show strong antibacterial activity to escherichelloa, staphylococcus and salmonella. At the same time these compounds have been widely used as fluorescer [9], fluorescent probe [10], dyestuff [11] and electroluminescent materials [12, 13] etc.

The selective recognition of metal ion is of great significance in environment, chemistry, life science and medicine. As a kind of widely used organic fluorescent compounds, the excellent photoelectric properties and high fluorescence quantum yield of pyrazoline derivatives add to their wide use in the selective recognition of metal ion. Shi et al. [14] had found that the fluorescence recognition with 1 - (2 - benzothiazole) - 3 - (2 - thiophene) - 2 - pyrazoline to Zn^{2+} had good sensitivity and selectivity; Xu et al. [15] studied the selective recognition of 1,5-diaryl-3-(2- hydroxyl-4,6-dimethoxylphenyl)-2-pyrazolines to Cu^{2+}. Thus in the present research we adopt a simple procedure to synthesize bis-pyrazole ring compounds with chalcone and substituted phenylhydrazine hydrochloride as the starting materials, then their spectroscopic properties and fluorescence quenching behavior to different metal ions are researched.

Experiments

Physical Measurement and Materials

Mass spectra (MS) were measured in an Agilent 1100LC-MS mass spectrometer. Infrared (IR) spectra of target products within 400–4,000 cm^{-1} were determined with a AVATAR360 type Fourier transform infrared spectrometer (KBr). ^{1}H NMR spectra in $CDCl_3$ solvent were recorded with an AVANCE-400 type pulse Fourier transform nuclear

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magnetic resonance (NMR) spectrometer, and TMS as internal standard. A PE2400 elemental analysis apparatus have been used to elemental analysis. UV–vis absorption spectra of synthetic compounds were recorded with a Hitachi U-4,100 spectrophotometer in a wavelength range of 200–800 nm (to-be-tested compounds were separately dissolved in spectral grade dimethylfomamide (DMF) at a concentration of 5.0×10^{-5} mol/L). The fluorescence spectra of various synthetic compounds separately dissolved in spectral grade DMF at a concentration of 5.0×10^{-5} mol/L were recorded with a Hitachi F-7,000 spectrofluorometer in right angle detection mode (each solution was excited at λ_{max} and the corrected fluorescence emission spectrum was recorded also at a wavelength of 200–800 nm). Specifically, synthetic target compound **A_5** was dissolved in spectral grade DMF at a concentration of 5.0×10^{-5} mol/L while the twelve different kinds of metal ions (Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Ca^{2+}, Na^{+}, Pb^{2+}, Sn^{2+}, In^{3+}, Mn^{2+} ,Cd^{2+}, Mg^{2+}) were joined into **A_5** at molar ratio 2:1 (concentration of 2.5×10^{-5} mol/L for M^{+}), respectively, so as to explore the influence of metal ions on the spectroscopic properties of synthetic products.

All chemicals and solvents are of commercial reagent grade and used without further purification. A series of chalcone compounds were synthesized referencing to literature [16].

General Procedure for the Preparation of 4-(1-aryl-3-phenyl-4,5-dihydro- 1H-pyrazol-5- yl)-1-aryl-1H-pyrazole

1 mmol chalcone compound and 1.2 mmol phenylhydrazine (or 1 mmol substituted phenylhydrazine hydrochloride) were dissolved in 20 mL ethanol, 0.8 mL 0.8 mol/L HCl was added, stirred and heated refluxing 6 h. The mixture was cooled and left at room temperature overnight. 35 % K_2CO_3 solution was added and the mixture was adjusted to neutral, followed by filtered, dried, and the crude mixture was purified by column chromatography (silica gel, cyclohexane/ethyl acetate).

4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-phenyl-1*H*-pyrazole(**A_1**). Light yellow solid 0.12 g,yield 33 %.APCI-MS (m/z, M^{+}): 365.2. ^{1}H NMR($CDCl_3$) δ: 3.24(dd, 1H, *J*=16.8, 6.8Hz, pyrazoline-H), 3.82(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.37(dd, 1H, *J*=11.9, 6.7Hz, pyrazoline-H), 6.85(dd, 1H, *J*=14.3, 7.3Hz, Ar-H), 7.18–7.25(m, 5H, Ar-H), 7.30–7.42(m, 3H, Ar-H), 7.43–7.66(m, 5H, Ar-H), 7.68–7.79(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3054(Ar-H), 2924(CH_2), 1597(PyrazolineC=N), 1503,1477(C=C), 1243(C-N). Anal. Calc.: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.02; H, 5.61; N, 15.31.

1-phenyl-4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole(**A_2**). Light yellow solid 0.29 g,yield 77 %.APCI-MS (m/z, M^{+}): 379.6. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 3H, CH_3), 3.21(dd, 1H, *J*=16.7, 7.1Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.9, 7.1Hz, pyrazoline-H), 7.02–7.10(m, 3H, Ar-H), 7.27–7.35(m, 2H, Ar-H), 7.38–7.48(m, 5H, Ar-H), 7.58–7.61(m, 2H, Ar-H), 7.68–7.75(m, 3H, Ar-H), 7.80(s, 1H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2920(CH_2), 1602(PyrazolineC=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.39; H, 5.81; N, 14.83.

4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-phenyl-1*H*-pyrazole (**A_3**). Light yellow solid 0.20 g,yield 51 %.APCI-MS (m/z, M^{+}): 393.6. ^{1}H NMR($CDCl_3$) δ: 2.16(s, 3H, CH_3), 2.22(s, 3H, CH_3), 3.20(dd, 1H, *J*=16.7, 7.1Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.9Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.7, 7.0Hz, pyrazoline-H), 6.82–6.86(m, 1H, Ar-H), 6.95–7.00(m, 1H, Ar-H), 7.27–7.36(m, 2H, Ar-H), 7.39(d, 3H, *J*=7.4Hz, Ar-H), 7.41–7.47(m, 2H, Ar-H), 7.60(m, 2H, Ar-H), 7.70–7.76(m, 3H, Ar-H), 7.80(s, 1H, Ar-H). IR(KBr, cm^{-1}) ν: 3025(Ar-H), 2921(CH_2), 1601(PyrazolineC=N), 1507, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.52; H, 6.11; N, 14.31.

4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-phenyl-1*H*-pyrazole (**A_4**). Yellow solid 0.21 g,yield 55 %.APCI-MS (m/z, M^{+}): 383.6. ^{1}H NMR($CDCl_3$) δ: 3.23(dd, 1H, *J*=16.7, 7.2Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.8, 11.8Hz, pyrazoline-H), 5.29(dd, 1H, *J* =11.7, 7.2Hz, pyrazoline-H), 6.91–6.96(m, 2H, Ar-H), 7.09–7.13(m, 2H, Ar-H), 7.28–7.37(m, 2H, Ar-H), 7.39–7.49(m, 4H, Ar-H), 7.59–7.62(m, 2H, Ar-H), 7.69–7.75(m, 3H, Ar-H), 7.80(s, 1H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2919(CH_2), 1608(PyrazolineC=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 75.37; H, 5.01; N, 14.65. Found: C, 75.32; H, 5.04; N, 14.61.

4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-1-phenyl-1H-pyrazole (**A_5**). Yellow solid 0.25 g,yield 56 %.APCI-MS (m/z, M^{+}): 444.3. ^{1}H NMR($CDCl_3$) δ: 3.24(dd, 1H, *J*=16.7, 6.4Hz, pyrazoline-H), 3.82(dd, 1H, *J* =16.8, 12.0Hz, pyrazoline-H), 5.34(dd, 1H, *J*=11.7, 6.7Hz, pyrazoline-H), 7.04(d, 2H, *J*=9.0Hz, Ar-H), 7.30(t, 3H, *J*=6.3Hz, Ar-H), 7.39–7.51(m, 5H, Ar-H), 7.59–7.63 (m, 2H, Ar-H), 7.68–7.75(m, 3H, Ar-H), 7.77(s, 1H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2922(CH_2), 1608(Pyrazoline C=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 65.02; H, 4.32; N, 12.64. Found: C, 65.05; H, 4.36; N, 12.60.

4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-*p*-tolyl-1*H*-pyrazole (**B_1**). Light yellow solid 0.11 g,yield 29 %.APCI-MS (m/z, M^{+}): 379.2. ^{1}H NMR($CDCl_3$) δ: 1.95(s, 3H, CH_3), 3.24(dd, 1H, *J*=16.7, 6.8Hz, pyrazoline-H), 3.82(dd, 1H, *J*=17.0, 11.8Hz, pyrazoline-H), 5.37(dd, 1H, *J*=11.8, 6.4Hz, pyrazoline-H), 6.81–6.89(m, 1H, Ar-H), 7.17–7.25(m, 3H, Ar-H), 7.31–7.46(m, 5H, Ar-H), 7.52–

7.66(m, 4H, Ar-H), 7.71–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3056(Ar-H), 2920(CH_2), 1596(PyrazolineC=N), 1503, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.30; H, 5.89; N, 14.75.

4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-*p*-tolyl-1*H*-pyrazole (**B_2**). Yellow solid 0.11 g,yield 28 %.APCI-MS (m/z, M^+):393.2. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 3H, CH_3), 2.35(s, 3H, CH_3), 3.21(dd, 1H, *J*=16.7, 7.0Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.30(dd, 1H, *J*=11.8, 7.2Hz, pyrazoline-H), 7.06(dd, 3H, *J*=22.5, 8.7Hz, Ar-H), 7.20(t, 2H, *J*=9.5Hz, Ar-H), 7.28–7.43(m, 5H, Ar-H), 7.47(t, 2H, *J*=6.8Hz, Ar-H), 7.67(s, 1H, Ar-H), 7.73–7.75(m, 2H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2919(CH_2), 1600(PyrazolineC=N), 1517, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.52; H, 6.11; N, 14.21.

4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-*p*-tolyl-1*H*-pyrazole (**B_3**). Light yellow solid 0.15 g,yield 37 %.APCI-MS (m/z, M^++Na):429.5. ^{1}H NMR($CDCl_3$) δ: 2.17(s, 3H, CH_3), 2.23(s, 3H, CH_3), 2.35(s, 3H, CH_3), 3.20(dd, 1H, *J*=16.7, 7.0Hz, pyrazoline-H), 3.78(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.30(dd, 1H, *J*=11.8, 7.0Hz, pyrazoline-H), 6.84(dd, 1H, *J*=8.2, 2.4Hz, Ar-H), 6.97(d, 1H, *J*=8.2Hz, Ar-H), 7.09(d, 1H, *J*=2.1Hz, Ar-H), 7.19(d, 2H, *J*=8.1Hz, Ar-H), 7.31–7.44(m, 3H, Ar-H), 7.46–7.49(m, 2H, Ar-H), 7.68(s, 1H, Ar-H), 7.74–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3025(Ar-H), 2918(CH_2), 1612(PyrazolineC=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.77; H, 6.45; N, 13.78. Found: C, 79.72; H, 6.48; N, 13.72.

4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-*p*-tolyl-1*H*-pyrazole (**B_4**). Light yellow solid 0.19 g,yield 48 %.APCI-MS (m/z, M^+): 397.4. ^{1}H NMR($CDCl_3$) δ: 2.35(s, 3H, CH_3), 3.23(dd, 1H, *J*=16.8, 7.2Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.8, 11.8Hz, pyrazoline-H), 5.28(dd, 1H, *J*=11.8, 7.2Hz, pyrazoline-H), 6.81–6.95(m, 2H, Ar-H), 7.10–7.13(m, 1H, Ar-H), 7.17–7.25(m, 3H, Ar-H), 7.33–7.44(m, 3H, Ar-H), 7.46–7.55(m, 2H, Ar-H), 7.67(s, 1H, Ar-H), 7.72–7.75(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2920(CH_2), 1617(PyrazolineC=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 75.74; H, 5.34; N, 14.13. Found: C, 75.70; H, 5.39; N, 14.11.

4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-*p*-tolyl-1*H*-pyrazole (**B_5**). Light yellow solid 0.19 g,yield 42 %.APCI-MS (m/z, M^+): 458.9. ^{1}H NMR($CDCl_3$) δ: 2.35(s, 3H, CH_3), 3.24(m, 1H, *J*=16.9, 6.4Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.9, 11.8Hz, pyrazoline-H), 5.33(dd, 1H, *J*=11.8, 6.4Hz, pyrazoline-H), 7.02–7.06(m, 2H, Ar-H), 7.20(d, 2H, *J*=8.2Hz, Ar-H), 7.27–7.44(m, 5H, Ar-H), 7.46–7.54(m, 2H, Ar-H), 7.65(s, 1H, Ar-H), 7.72–7.75(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2922(CH_2), 1613(PyrazolineC=N), 1519, 1477(C=C), 1243(C-N). Anal. Calc.: C, 65.65; H, 4.63; N, 12.25. Found: C, 65.60; H, 4.67; N, 12.21.

1-(3,4-dimethylphenyl)-4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**C_1**). Light yellow solid 0.14 g,yield 36 %.APCI-MS (m/z, M^+): 393.2. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 3H, CH_3), 2.28(s, 3H, CH_3), 3.23(dd, 1H, *J*=16.8, 6.7Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.35(dd, 1H, *J*=11.9, 6.7Hz, pyrazoline-H), 6.81–6.83(m, 1H, Ar-H), 7.13–7.25(m, 5H, Ar-H), 7.28–7.36(m, 2H, Ar-H), 7.38–7.53(m, 4H, Ar-H), 7.68(s, 1H, Ar-H), 7.74–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3051(Ar-H), 2918(CH_2), 1595(PyrazolineC=N), 1505, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.59; H, 6.18; N, 14.25.

1-(3,4-dimethylphenyl)-4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**C_2**). Light yellow solid 0.17 g,yield 42 %.APCI-MS (m/z, M^+):407.6. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 6H, CH_3), 2.28(s, 3H, CH_3), 3.21(dd, 1H, *J*=16.7, 7.2Hz, pyrazoline-H), 3.79(dd, 1H, *J* =16.7, 11.9Hz, pyrazoline-H), 5.30(dd, 1H, *J*=11.8, 7.2Hz, pyrazoline-H), 7.02–7.19(m, 5H, Ar-H), 7.28–7.35(m, 2H, Ar-H), 7.38–7.43(m, 3H, Ar-H), 7.67(s, 1H, Ar-H), 7.73–7.75(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3025(Ar-H), 2919(CH_2), 1613(PyrazolineC=N), 1515, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.77; H, 6.45; N, 13.78. Found: C, 79.78; H, 6.43; N, 13.76.

1-(3,4-dimethylphenyl)-4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**C_3**).Light yellow solid 0.17 g,yield 40 %.APCI-MS (m/z, M^+):421.5. ^{1}H NMR($CDCl_3$) δ: 2.17(s, 3H, CH_3), 2.23(s, 3H, CH_3), 2.26(s, 3H, CH_3), 2.29(s, 3H, CH_3), 3.21(dd, 1H, *J*=16.7, 7.1Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.9, 7.0Hz, pyrazoline-H), 6.83–6.86(m, 1H, Ar-H), 6.97(d, 1H, *J*=8.3Hz, Ar-H), 7.09–7.20(m, 2H, Ar-H), 7.29–7.35(m, 2H, Ar-H), 7.39–7.45(m, 3H, Ar-H), 7.68(s, 1H, Ar-H), 7.74–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2919(CH_2), 1612(PyrazolineC=N), 1506, 1477(C=C), 1243(C-N). Anal. Calc.: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.92; H, 6.74; N, 13.27.

1-(3,4-dimethylphenyl)-4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*- pyrazole (**C_4**). Yellow solid 0.15 g,yield 37 %.APCI-MS (m/z, M)$^+$:411.5. ^{1}H NMR($CDCl_3$) δ: 2.26(s, 3H, CH_3), 2.28(s, 3H, CH_3), 3.23(dd, 1H, *J*=16.8, 7.3Hz, pyrazoline-H), 3.80(dd, 1H, *J*=16.8, 11.7Hz, pyrazoline-H), 5.27(dd, 1H, *J*=11.7, 7.2Hz, pyrazoline-H), 6.90–6.95(m, 2H, Ar-H), 7.10–7.16(m, 2H, Ar-H), 7.28–7.36(m, 2H, Ar-H), 7.39–7.44(m, 3H, Ar-H), 7.49–7.53(m, 1H,Ar-H), 7.66(s, 1H, Ar-H), 7.73–7.75(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2924(CH_2), 1613(PyrazolineC=N), 1509, 1477(C=C), 1243(C-N). Anal. Calc.: C, 76.08; H, 5.65; N, 13.65. Found: C, 76.02; H, 5.68; N, 13.70.

4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-(3,4-dimethylphenyl)-1*H*-pyrazole (**C_5**). Yellow solid 0.12 g,yield 25 %.APCI-MS (m/z, M^+):472.4. ^{1}H NMR($CDCl_3$) δ: 2.27(s, 3H, CH_3), 2.29(s, 3H, CH_3), 3.25(dd, 1H, *J*=16.8, 6.4Hz, pyrazoline-H), 3.82(dd, 1H, *J*=16.8, 11.8Hz, pyrazoline-H), 5.34(dd, 1H, *J*=11.7, 6.5Hz, pyrazoline-H), 7.03–7.07(m, 2H, Ar-H), 7.16(d, 1H, *J*=8.2Hz, Ar-H), 7.29–7.32(m, 3H, Ar-H), 7.35–7.43(m, 4H, Ar-H), 7.66(s, 1H, Ar-H), 7.73–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2919(CH_2), 1613(PyrazolineC=N), 1503,1477(C=C), 1243(C-N). Anal. Calc.: C, 66.25; H, 4.92; N, 11.89. Found: C, 66.22; H, 4.95; N, 11.90.

4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-(4-fluorophenyl)-1*H*-pyrazole (**D_1**). Light yellow solid 0.18 g,yield 47 %.APCI-MS (m/z,M^++Na):405.2. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.8, 6.5Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.36(dd, 1H, *J*=11.8, 6.6Hz, pyrazoline-H), 6.82–6.86(m, 1H, Ar-H), 7.06–7.12(m, 2H, Ar-H), 7.17–7.24(m, 3H, Ar-H), 7.33–7.42(m, 3H, Ar-H), 7.45–7.59(m, 3H, Ar-H), 7.69(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3056(Ar-H), 2929(CH_2), 1597(PyrazolineC=N), 1503, 1477(C=C), 1243(C-N). Anal. Calc.: C, 75.37; H, 5.01; N, 14.65. Found: C, 75.35; H, 5.05; N, 14.62.

1-(4-fluorophenyl)-4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**D_2**). Light yellow solid 0.17 g,yield 43 %.APCI-MS (m/z,M^+): 397.3. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 3H, CH_3), 3.20(dd, 1H, *J*=16.7, 7.0Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.8, 7.0Hz, pyrazoline-H), 7.05–7.09(m, 4H, Ar-H), 7.27–7.36(m, 2H, Ar-H), 7.36–7.47(m, 3H, Ar-H), 7.51–7.58(m, 3H, Ar-H), 7.68(s, 1H, Ar-H), 7.71–7.75(m, 2H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2921(CH_2), 1616(PyrazolineC=N), 1516,1477(C=C), 1243(C-N). Anal. Calc.: C, 75.74; H, 5.34; N, 14.13. Found: C, 75.76; H, 5.38; N, 14.10.

4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-(4-fluorophenyl)-1*H*-pyrazole (**D_3**). Yellow solid 0.14 g,yield 34 %.APCI-MS (m/z, M^+):411.4. ^{1}H NMR($CDCl_3$) δ: 2.17(s, 3H, CH_3), 2.22(s, 3H, CH_3), 3.19(dd, 1H, *J*=16.7, 6.9Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.9Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.9, 6.9Hz, pyrazoline-H), 6.81–6.84(m, 1H, Ar-H), 7.07–7.11(m, 2H, Ar-H), 7.31–7.45(m, 4H, Ar-H), 7.52–7.57(m, 3H, Ar-H), 7.69(s, 1H, Ar-H), 7.73–7.75(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3028(Ar-H), 2920(CH_2), 1611(PyrazolineC=N), 1514, 1477(C=C), 1243(C-N). Anal. Calc.: C, 76.08; H, 5.65; N, 13.65. Found: C, 76.06; H, 5.61; N, 13.61.

1-(4-fluorophenyl)-4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**D_4**). Light yellow solid 0.19 g,yield 48 %.APCI-MS (m/z, M^+): 401.2. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.8, 7.1Hz, pyrazoline-H), 3.81(dd, 1H, J=16.7, 11.8Hz, pyrazoline-H), 5.29(dd, 1H, *J*=11.6, 7.2Hz, pyrazoline-H), 6.93(d, 2H, *J*=8.7Hz, Ar-H), 7.10(t, 4H, *J*=7.6Hz, Ar-H), 7.33–7.46(m, 3H, Ar-H), 7.50–7.58(m, 2H, Ar-H), 7.68(s, 1H, Ar-H), 7.72–7.77(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3055(Ar-H), 2928(CH_2), 1611(Pyrazoline C=N), 1512, 1477(C=C), 1243(C-N). Anal. Calc.: C, 71.99; H, 4.53; N, 13.99. Found: C, 72.02; H, 4.58; N, 13.97.

4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-(4-fluorophenyl)-1*H*-pyrazole (**D_5**). Yellow solid 0.12 g,yield 26 %.APCI-MS (m/z,M^+): 462.7. ^{1}H NMR($CDCl_3$) δ: 3.23(dd, 1H, *J* =16.9, 6.3Hz, pyrazoline-H), 3.82(dd, 1H, *J*=16.8, 11.8Hz, pyrazoline-H), 5.34(dd, 1H, *J*=11.8, 6.1Hz, pyrazoline-H), 7.03(d, 2H, *J*=9.0Hz, Ar-H), 7.10(t, 2H, *J*=8.6Hz, Ar-H), 7.30(d, 2H, *J*=9.0Hz, Ar-H), 7.34–7.423(m, 3H, Ar-H), 7.51–7.61(m, 2H, Ar-H), 7.66(s, 1H, Ar-H), 7.69–7.77(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3056(Ar-H), 2929(CH_2), 1597(PyrazolineC=N), 1515, 1477(C=C), 1243(C-N). Anal. Calc.: C, 62.48; H, 3.93; N, 12.14. Found: C, 62.45; H, 3.96; N, 12.12.

1-(4-chlorophenyl)-4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**E_1**). Light yellow solid 0.16 g,yield 40 %.APCI-MS (m/z,M^++Na): 421.1. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.8, 6.5Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.36(dd, 1H, *J*=11.9, 6.6Hz, pyrazoline-H), 6.82–6.87(m, 1H, Ar-H), 7.16–7.23(m, 3H, Ar-H), 7.33–7.42(m, 5H, Ar-H), 7.43–7.56(m, 3H, Ar-H), 7.70(s, 1H, Ar-H), 7.76–7.79(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3054(Ar-H), 2921(CH_2), 1596(PyrazolineC=N), 1502, 1477(C=C), 1243(C-N). Anal. Calc.: C, 72.27; H, 4.80; N, 14.05. Found: C, 72.25; H, 4.86; N, 1402.

1-(4-chlorophenyl)-4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**E_2**). Light yellow solid 0.14 g,yield 34 %.APCI-MS (m/z,M^+): 413.2. ^{1}H NMR($CDCl_3$) δ: 2.26(s, 3H, CH_3), 3.20(dd, 1H, *J*=16.7, 7.0Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.9Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.9, 7.0Hz, pyrazoline-H), 7.02–7.09(m, 3H, Ar-H), 7.28–7.38(m, 3H, Ar-H), 7.39–7.47(m, 2H, Ar-H), 7.50–7.60(m, 3H, Ar-H), 7.69(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3066(Ar-H), 2929(CH_2), 1613(PyrazolineC=N), 1500, 1477(C=C), 1243(C-N). Anal. Calc.: C, 72.72; H, 5.13; N, 13.57. Found: C, 72.70; H, 5.16; N, 13.52.

1-(4-chlorophenyl)-4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**E_3**). Yellow solid 0.15 g,yield 35 %.APCI-MS (m/z,M^+): 427.2. ^{1}H NMR($CDCl_3$) δ: 2.17(s, 3H, CH_3), 2.23(s, 3H, CH_3), 3.19(dd, 1H, *J*=16.7, 6.9Hz, pyrazoline-H), 3.78(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.30(dd, 1H, *J*=11.8, 6.8Hz, pyrazoline-H), 6.82(dd, 1H, *J* =8.1, 2.4Hz, Ar-H), 6.93–7.03(m, 1H, Ar-H), 7.08(d, 1H, *J*=2.3Hz, Ar-H), 7.31–7.36(m, 2H, Ar-H), 7.37–7.45(m, 3H, Ar-H), 7.52–7.56(m,

2H, Ar-H), 7.70(s, 1H, Ar-H), 7.73–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3065(Ar-H), 2919(CH_2), 1613(PyrazolineC=N), 1502, 1477(C=C), 1243(C-N). Anal. Calc.: C, 73.14; H, 5.43; N, 13.12. Found: C, 73.15; H, 5.46; N, 13.10.

1-(4-chlorophenyl)-4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**E_4**).Light yellow solid 0.15 g,yield 35 %.APCI-MS (m/z,M^+): 417.4. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.7, 7.2Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.28(dd, 1H, *J*=11.7, 7.2Hz, pyrazoline-H), 6.94(dd, 1H, *J*=11.9, 5.7Hz, Ar-H), 7.08–7.18(m, 2H, Ar-H), 7.33–7.47(m, 5H, Ar-H), 7.50–7.60(m, 3H, Ar-H), 7.69(s, 1H, Ar-H), 7.72–7.80(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3054(Ar-H), 2924(CH_2), 1600(PyrazolineC=N), 1509, 1477(C=C), 1243(C-N). Anal. Calc.: C, 69.15; H, 4.35; N, 13.44. Found: C, 69.11; H, 4.38; N, 13.42.

4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1-(4-chlorophenyl)-1*H*-pyrazole (**E_5**). Light yellow solid 0.19 g,yield 40 %.APCI-MS (m/z,M^++Na): 500.8. ^{1}H NMR($CDCl_3$) δ: 3.23(dd, 1H, *J*=16.8, 6.3Hz, pyrazoline-H), 3.82(dd, 1H, *J*=16.8, 11.8Hz, pyrazoline-H), 5.33(dd, 1H, *J*=11.9, 6.2Hz, pyrazoline-H), 7.01–7.05(m, 2H, Ar-H), 7.28–7.32(m, 2H, Ar-H), 7.34–7.47(m, 5H, Ar-H), 7.49–7.56(m, 2H, Ar-H), 7.67(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3059(Ar-H), 2929(CH_2), 1591(PyrazolineC=N), 1500, 1477(C=C), 1243(C-N). Anal. Calc.: C, 60.33; H, 3.80; N, 11.73. Found: C, 60.35; H, 3.76; N, 11.72.

1-(4-bromophenyl)-4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**F_1**). Light yellow solid 0.16 g,yield 36 %.APCI-MS (m/z,M^+): 444.6. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.8, 6.5Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.8, 11.9Hz, pyrazoline-H), 5.35(dd, 1H, *J*=11.9, 6.5Hz, pyrazoline-H), 6.82–6.85(m, 1H, Ar-H), 7.16–7.23(m, 3H, Ar-H), 7.33–7.36(m, 3H, Ar-H), 7.39–7.62(m, 5H, Ar-H), 7.70(s, 1H, Ar-H), 7.69–7.77(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3052(Ar-H), 2920(CH_2), 1595(PyrazolineC=N), 1498, 1477(C=C), 1243(C-N). Anal. Calc.: C, 65.02; H, 4.32; N, 12.64. Found: C, 65.05; H, 4.36; N, 12.62.

1-(4-bromophenyl)-4-(3-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**F_2**). Light yellow solid 0.16 g,yield 35 %.APCI-MS (m/z,M^+): 458.4. ^{1}H NMR($CDCl_3$) δ: 2.25(s, 3H, CH_3), 3.20(dd, 1H, *J*=16.8, 7.0Hz, pyrazoline-H), 3.79(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.31(dd, 1H, *J*=11.8, 7.0Hz, pyrazoline-H), 7.02–7.08(m, 3H, Ar-H), 7.32–7.41(m, 3H, Ar-H), 7.47–7.53(m, 5H, Ar-H), 7.70(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3025(Ar-H), 2920(CH_2), 1614(PyrazolineC=N), 1513, 1477(C=C), 1243(C-N). Anal. Calc.: C, 65.65; H, 4.63; N, 12.25. Found: C, 65.62; H, 4.66; N, 12.22.

1-(4-bromophenyl)-4-(1-(3,4-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**F_3**).Light yellow solid 0.18 g,yield 38 %.APCI-MS (m/z, M^+): 472.1. ^{1}H NMR($CDCl_3$) δ: 2.16(s, 3H, CH_3), 2.22(s, 3H, CH_3), 3.19(dd, 1H, *J*=16.7, 6.9Hz, pyrazoline-H), 3.78(dd, 1H, *J*=16.7, 11.9Hz, pyrazoline-H), 5.30(dd, 1H, *J*=11.9, 6.9Hz, pyrazoline-H), 6.80–6.84(m, 1H, Ar-H), 6.97(d, 1H, *J*=8.2Hz, Ar-H), 7.07(d, 1H, *J*=2.1Hz, Ar-H), 7.31–7.38(m, 2H, Ar-H), 7.40–7.43(m, 2H, Ar-H), 7.49–7.51(m, 3H, Ar-H), 7.70(s, 1H, Ar-H), 7.73–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3025(Ar-H), 2921(CH_2), 1614(PyrazolineC=N), 1497, 1477(C=C), 1243(C-N). Anal. Calc.: C, 66.25; H, 4.92; N, 11.89. Found: C, 66.27; H, 4.90; N, 11.84.

1-(4-bromophenyl)-4-(1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**F_4**).Light yellow solid 0.12 g,yield 26 %.APCI-MS (m/z,M^++K): ,500.8. ^{1}H NMR($CDCl_3$) δ: 3.22(dd, 1H, *J*=16.8, 7.1Hz, pyrazoline-H), 3.81(dd, 1H, *J*=16.7, 11.8Hz, pyrazoline-H), 5.28(dd, 1H, *J*=11.7, 7.1Hz, pyrazoline-H), 6.93(t, 2H, *J*=8.8Hz, Ar-H), 7.08–7.12(m, 2H, Ar-H), 7.35–7.44(m, 3H, Ar-H), 7.48–7.54(m, 4H, Ar-H), 7.69(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3031(Ar-H), 2920(CH_2), 1618(PyrazolineC=N), 1502,1477(C=C), 1243(C-N).

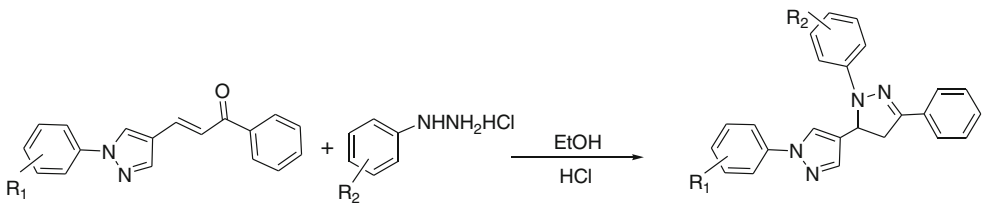

Fig. 1 The synthesis routes of 4-(1- aryl −3-phenyl-4, 5-dihydro- 1*H*-pyrazol-5-yl)-1-aryl-1*H*-pyrazole

R_1=H;R_2=H(A_1);4-CH_3(A_2);3,4-di-CH_3(A_3);4-F(A_4);4-Br(A_5)
R_1=4-CH_3;R_2=H(B_1);4-CH_3(B_2);3,4-di-CH_3(B_3);4-F(B_4);4-Br(B_5)
R_1=3,4-di-CH_3;R_2=H(C_1);4-CH_3(C_2);3,4-di-CH_3(C_3);4-F(C_4);4-Br(C_5)
R_1=4-F;R_2=H(D_1);4-CH_3(D_2);3,4-di-CH_3(D_3);4-F(D_4);4-Br(D_5)
R_1=4-Cl;R_2=H(E_1);4-CH_3(E_2);3,4-di-CH_3(E_3);4-F(E_4);4-Br(E_5)
R_1=4-Br;R_2=H(F_1);4-CH_3(F_2);3,4-di-CH_3(F_3);4-F(F_4);4-Br(F_5)

Anal. Calc.: C, 62.48; H, 3.93; N, 12.14. Found: C, 62.47; H, 3.95; N, 12.11.

1-(4-bromophenyl)-4-(1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-1*H*-pyrazole (**F_5**). Light yellow solid 0.12 g,yield 23 %.APCI-MS (m/z,M^+): 523.0. ^{1}H NMR($CDCl_3$) δ: 3.23(dd, 1H, J=16.8, 6.2Hz, pyrazoline-H), 3.82(dd, 1H, J=16.7, 11.8Hz, pyrazoline-H), 5.30(dd, 1H, J=11.8, 6.2Hz, pyrazoline-H), 7.03(d, 2H, J=8.8Hz, Ar-H), 7.32(t, 2H, J=9.1Hz, Ar-H), 7.35–7.43(m, 3H, Ar-H), 7.47–7.53(m, 4H, Ar-H), 7.67(s, 1H, Ar-H), 7.72–7.76(m, 3H, Ar-H). IR(KBr, cm^{-1}) ν: 3053(Ar-H), 2923(CH_2), 1601(PyrazolineC=N), 1490, 1477(C=C), 1243(C-N). Anal. Calc.: C, 55.20; H, 3.47; N, 10.73. Found: C, 55.17; H, 3.46; N, 10.72.

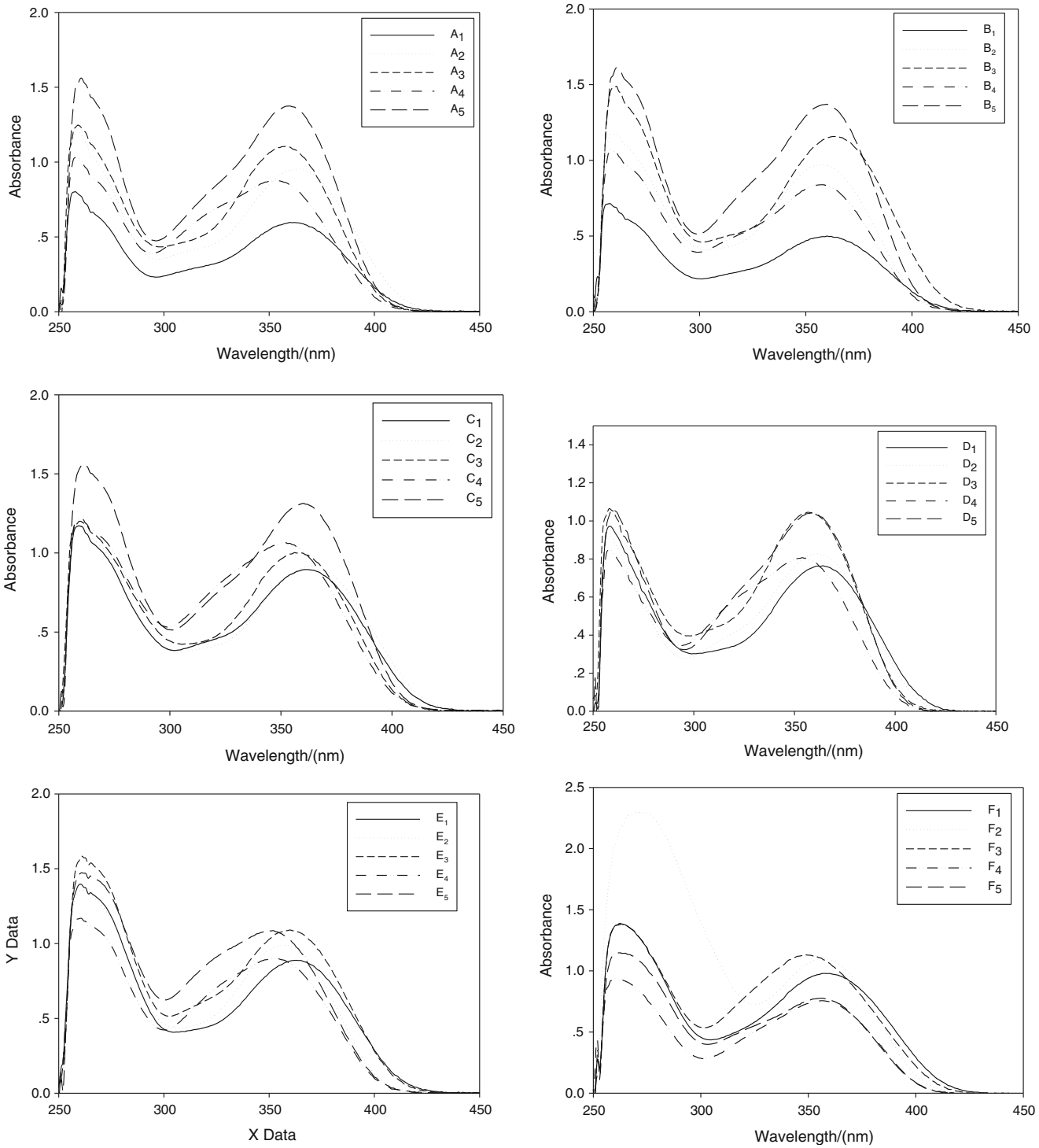

Fig. 2 The UV–vis spectra of target compounds

Results and Discussion

Synthesis

The synthetic route of 4-(1-aryl-3-phenyl-4, 5-dihydro-1*H*-pyrazol-5-yl)-1-aryl-1*H*-pyrazole is shown in Fig. 1.

Under normal circumstances, the pyrazoline derivatives are synthesized in solvent of acetic acid or propionic acid for the excellent solubility property and catalytic performance. But in our research, we found that the yield of this reaction was low and the purification of product was difficult when acetic acid or propionic acid was used as solvent, and the results were improved when ethanol was used as solvent and diluted HCl (0.8 $mol \cdot L^{-1}$) was used as catalyst. Maybe the lower boiling point of ethanol and stronger acidity of HCl compared with acetic acid were advantageous for this reaction. On the one hand, we found that the proper ratio to chalcone was 1.2:1 for phenylhydrazine and 1:1 for substituted phenylhydrazine hydrochloride in this reaction respectively. That is to say, the appropriate excessive of phenylhydrazine is advantageous to the reaction, but for substituted phenylhydrazine hydrochloride this is not necessary.

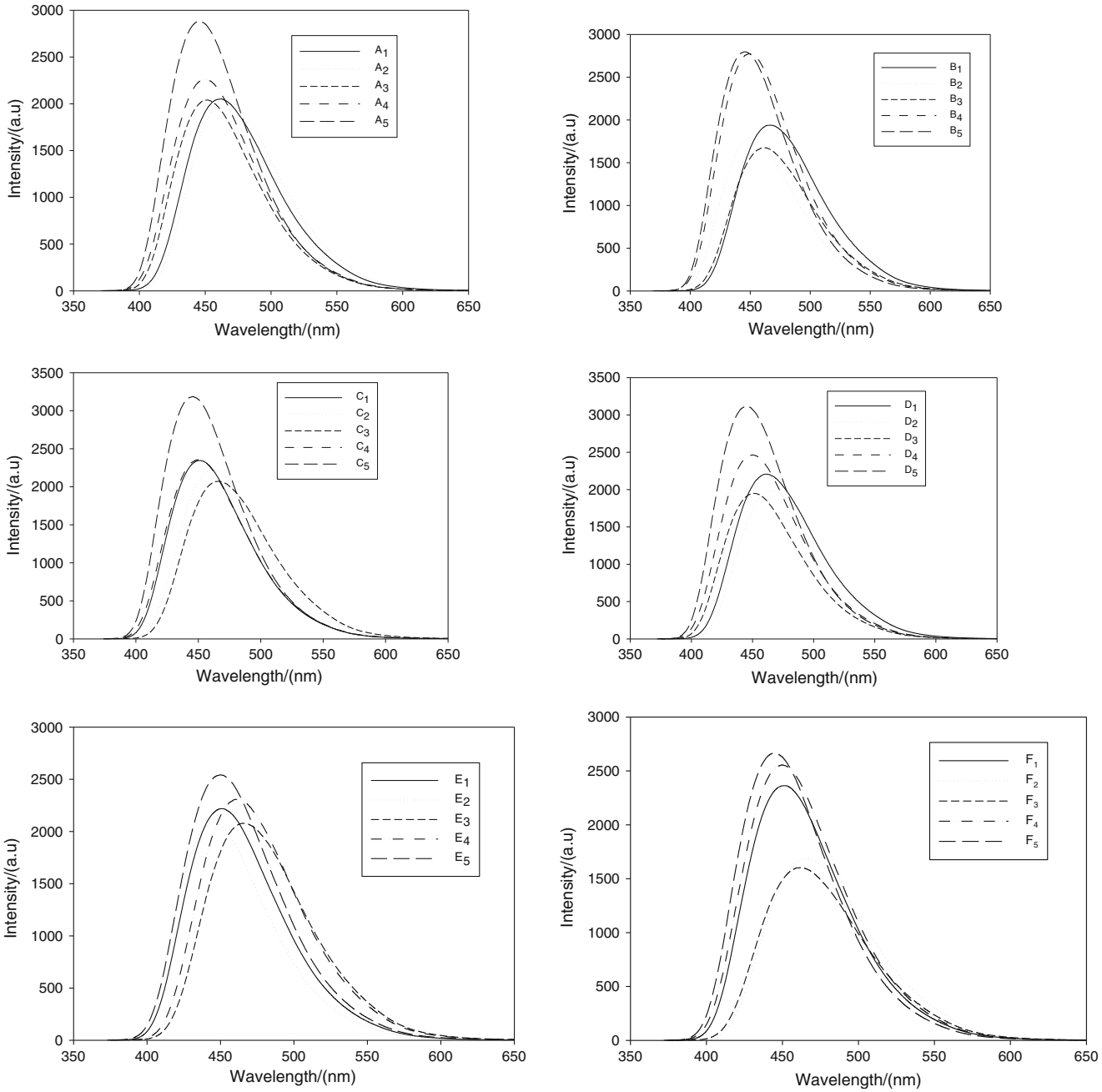

Fig. 3 The fluorescence spectra of target compounds

The structure of synthetic compounds has been characterized by mass spectrometry(MS), nuclear magnetic resonance (NMR), infrared spectra (IR) and elemental analysis. Because of different chemical environment of the 4-H in pyrazoline ring, 5-H is splitted into quartet instead of the usual triplet in the range of 5.27 to 5.37.

UV–vis Spectrum

The UV–vis spectra of the six series of target compounds measured in DMF are shown in Fig. 2, and their maximum absorption wavelengths data are listed in Table s1. Within the exploited wavelength range of 200–800 nm, there are two remarkable absorption peaks at about 260 and 360 nm (Fig. 2), which are attributed to the n- π* and π–π* transitions, respectively. In the meantime, substituent R_1 and R_2 of the phenyl group has influence on the absorption wavelength and absorbance. On the one hand, the introduction of auxochrome group such as -F, −Cl, −Br to the phenyl group leads to p–π conjugation formed by nonbonding electron with π electron and shift of absorption peak towards longer wavelength. On the other hand, the introduction of alkyl group to the conjugated systems allows the electron of C-H bond of the alkyl group to overlap with the π electron of the conjugated system (the so-called hyperconjugation), also leading to shift of the absorption peak towards longer wavelength.

Fluorescence Spectrum

The fluorescence spectra of the target compounds are shown in Fig. 3, and their maximum emission wavelengths data are listed in Table s2. The target compounds show the maximum emission peak at 445-467 nm (Table s2). The experimental results show that R_2 has major impact on the fluorescence spectra of the target compounds while this influence caused by R_1 is negligible. Compared with R_2 is H, electron withdrawing substituents such as *p*-Br and *p*-F cause a slight blue-shift (0-5 nm) of the fluorescent spectra and an increase of the fluorescence intensity, while electron donating substituent like *p*-CH_3 and 3,4-di-CH_3 can cause 5-17 nm red-shift (5-11 nm for A series, 13-17 nm for B series, 10-15 nm for C series, 11-15 nm for D series, 12-15 nm for E series and 10-14 nm for F series) of the fluorescent spectra and reduce the fluorescence intensity. The substitution effects on the fluorescence spectrum display some abnormal situation (for example, the effect of heavy atoms has not arised when R_1 or R_2 is *p*-Br) and the same results have obtained after the tests were repeated. So,we suppose that the combined action of the nonradiative attenuation, p–π conjugation effect and the solvent effect leads to the results.

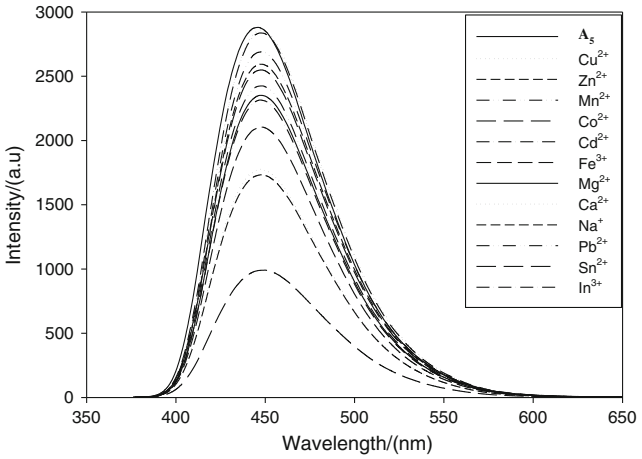

Fig. 4 Influence of metal ions on spectral properties of compounds $\mathbf{A_5}$

Influence of Metal Ions on Spectral Properties of Compounds A_5

The influence of metal ions on the fluorescence spectrum of compound $\mathbf{A_5}$ is shown in Fig. 4 and the spectrum data are listed in Table s3. It can be seen that the addition of metal ions has a weak impact on the maximum emission peak of compound $\mathbf{A_5}$ (red-shift 1-3 nm). But the fluorescence intensity of compound $\mathbf{A_5}$ reduced to different degree after the addition of different metal ions. Especially, the fluorescence of compound $\mathbf{A_5}$ is quenched over 2/3 when Co^{2+} is added. The experimental results imply that synthetic products maybe have the function of selective recognition to Co^{2+}.

Conclusion

Six series of pyrazoline derivatives containing pyrazole group were synthesized and characterized by means of ^{1}H NMR, FT-IR, MS and elemental analysis, and their UV–vis absorption behavior and fluorescent properties were also measured. Moreover, the influence of metal ions on spectral properties of synthetic products was examined with compound $\mathbf{A_5}$ as an example. The experimental results show that synthetic products have the function of selective recognition to Co^{2+}.

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