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# Efficient synthesis of 1-$R_1$-2-R-4,5-di(furan-2-yl)-1*H*-imidazoles and their luminescence properties

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ABSTRACT

In this study, a series of 1-$R_1$-2-R-4,5-di(furan-2-yl)-1*H*-imidazole derivatives were synthesized in better yield 59.0%∼89.8% by the treatment of purified imidazole compounds with benzyl chloride or allyl chloride in the presence of sodium hydride, and were characterized by FT–IR, HRMS, $^1$H NMR and $^{13}$C NMR spectroscopy. Furthermore, the luminescence properties of the synthesized products were investigated. It was found that N-substituted groups of imidazole have little influence on the absorption bands in a 0.1 N $H_2SO_4$ aqueous solution containing 0.5 mL of dissolved $CH_3OH$. However, the emission of some compounds in solution was sensitive to the polarity of the solvents.



## 1. Introduction

Imidazoles, because of the N-heterocycles [1], played a significant role in many application fields, such as drug cores [2], natural products [3], conjugated and functional polymers [4], coordination complexes [5], important ligands in metalloenzymes [6], precursors of stable carbene ligands [7], photosensitive material [8,9], nonlinear optical material [10], ionic liquids [11] and so on. Hence, 1,2,4,5-tetrasubstituted imidazoles were understandably suggested to hold an important position in imidazole derivatives. Tetrasubstituted imidazole compounds have been reported to possess good biological and pharmacological activities [12]. Especially, many of the substituted imidazoles were known as inhibitors of p38 MAP kinase, herbicides, fungicides, antibacterial, antitumor, therapeutic agents, pesticides and plant growth regulators [13,14]. Therefore, the synthesis and properties of these compounds have attracted much attention from the synthetic organic chemists and biologists.

Common methods for synthesizing 1,2,4,5-tetrasubstituted imidazoles included the cyclocondensation of the 1,2-dicarbonyl compound [15] or 2-hydroxy-1,2-diphenylethanone [16], aldehyde and ammonium acetate or amine, as well as between 1,2-dicarbonyl compounds, aromatic amine and aromatic cyanide [17], and the nucleophilic substitution reaction of a trisubstituted imidazole derivative and benzyl chloride [18]. However, the aromatic compounds mentioned here were correlated with benzene rings. The compounds bearing furan rings were rarely synthesized in the previous literature [15–18], because the furan ring possesses inherent chemical properties and disadvantages, such as electron richness, lower conjugation energy, easily ring-opening in Brønsted acid, the fact they easily become yellow in oxygen, and so on [19]. In addition, although the biological and pharmacological activity of tetrasubstituted imidazoles have been widely studied, their luminescence properties were seldom investigated, except for 1-$R_1$-2-R-4,5-dialkyl-1*H*-imidazoles [20]. Our work focused on the synthesis and luminescence properties of a series of novel

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tetrasubstituted imidazoles with furan rings. Herein, a series of novel tetrasubstituted imidazoles with furan rings were synthesized by the reaction of 2-R-4,5-di(furan-2-yl)imidazoles and benzyl chlorides or allyl chloride according to the reported procedure [18] (Scheme 1). Besides, the comparison of the fluorescence spectra of compounds 4,5-di(furan-2-yl)-1-(4-methylbenzyl)-2-phenyl-1H-imidazole (**3a**) and (*E*)-4,5-di(furan-2-yl)-1-(4-methylbenzyl)-2-styryl-1H-imidazole (**3h**) in different solutions suggested that long conjugated chain played a key role in the red shift of the fluorescence emission of compound **3h** in the same solution.

## 2. Experimental

2-R-4,5-di(furan-2-yl)imidazoles were synthesized according to the reported procedure [19]. All reagents were of analytical-reagent grade and used without further purification. All reported yields were isolated yields. All melting points were determined with a XT–4 melting point apparatus and were uncorrected. HRMS were an Agilent1290-micrOTOF Q II spectrometer. $^{1}H$ and $^{13}C$ NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer with TMS as an internal standard. FT-IR spectra were obtained as KBr pellets using an IRAffinity-1 instrument in the range between 500 and 3500 $cm^{-1}$. Fluorescence spectra were recorded with a Shimadzu RF-5301 spectrofluorimeter. The absorption spectra were recorded on an Australian GBC Cintra 10e UV–vis spectrometer within the wavelength range from 200 to 800 nm.

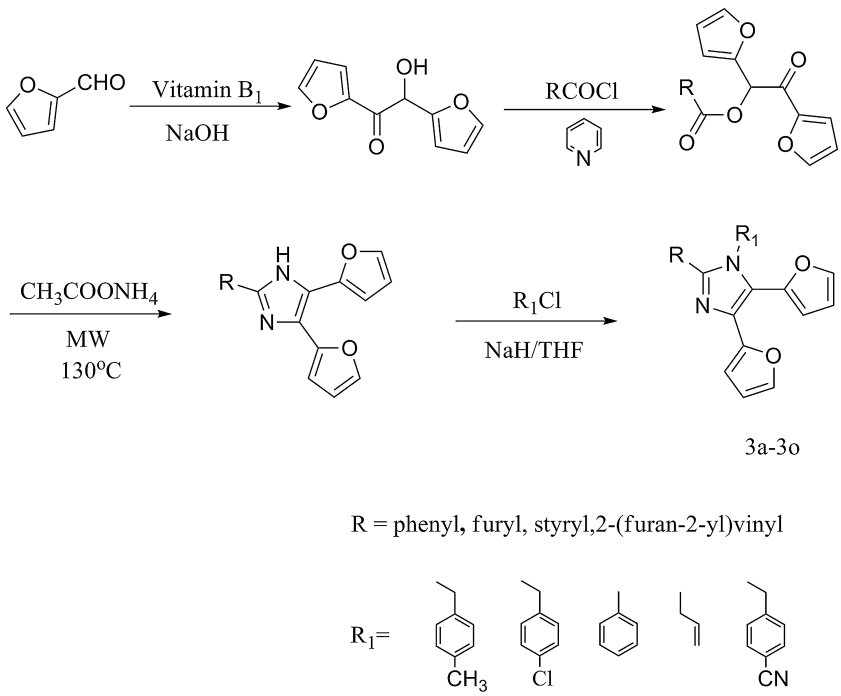
### 2.1. Experimental procedures for the synthesized compounds (3a–3o)

A mixture of compounds 2-R-4,5-di(furan-2-yl) imidazoles (1 mmol) and NaH (36 mg, 1.5 mmol) in 20 mL of anhydrous THF was heated until the reaction temperature was about 60 °C. An amount of 1.5 mmol of benzyl chloride or allyl chloride dissolved in 3 mL of anhydrous THF was dropped into the mixture, and the resulting mixture was refluxed for 13–37.5 h. The reaction progress was monitored by TLC on Silufol-254 plates. After the reaction was over, the reaction mixture was filtered while cooled to room temperature, and washed with anhydrous THF ($2 \times 5$ mL). The combined filtration was poured into 20 mL of water ice water. The organic phase dried by anhydrous $Na_2SO_4$ was concentrated. The residue was purified by column chromatography on Chemapol (200–300 mesh) silica gel using petroleum ether/ethyl acetate (3:1) as an eluent to afford the compound.

### 2.2. Physical and spectroscopic data

#### 2.2.1. 4,5-Di(furan-2-yl)-1-(4-methylbenzyl)-2-phenyl-1H-imidazole (3a)

Mp: 127–129 °C. Yield: 69.7%. IR (KBr) $\nu$ ($cm^{-1}$): 3090, 3020, 2920, 1600, 1520, 1470, 1440, 1400, 1360, 1310, 1210, 1170, 1070, 1020, 968, 887, 773, 733, 592. $^{1}H$ NMR (500 MHz, DMSO): $^{1}H$ NMR (500 MHz, DMSO) $\delta$ (ppm): 7.80 (dd, $J$ = 1.7, 0.9 Hz, 1H), 7.64–7.58 (m, 3H), 7.50–7.44 (m, 3H), 7.05 (d, $J$ = 7.8 Hz, 2H), 6.71 (d, $J$ = 8.1 Hz, 2H), 6.61–6.55 (m, 2H), 6.51 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.47 (dd, $J$ = 3.3, 0.8 Hz, 1H), 5.22 (s, 2H), 2.21 (s, 3H). $^{13}C$ NMR




**Scheme 1.**

(125 MHz, DMSO): δ (ppm) 149.3, 149.1, 144.6, 142.7, 142.6, 136.9, 134.5, 133.1, 130.5, 129.8, 129.7, 129.1, 126.0, 120.3, 113.0, 111.9, 111.7, 107.04, 48.6, 21.0. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{25}H_{21}N_2O_2$ 381.1603, found 381.1605.

*2.2.2. 1-(4-Chlorobenzyl)-4,5-di(furan-2-yl)-2-phenyl-1*H-*imidazole (**3b**)*

Mp: 144–145 °C. Yield: 89.8%. IR (KBr) ν ($cm^{-1}$): 3090, 2930, 1890, 1600, 1490, 1440, 1400, 1350, 1320, 1210, 1160, 1090, 1020, 968, 887, 773, 733, 700, 592. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.79 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.63–7.59 (m, 3H), 7.50–7.46 (m, 3H), 7.32–7.29 (m, 2H), 6.87–6.83 (m, 2H), 6.60 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.58 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.51 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.49 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.25 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 149.2, 149.2, 144.7 142.7, 142.4, 136.5, 133.2, 132.4, 130.3, 129.9, 129.2, 128.1, 120.2, 113.3, 111.9, 111.8, 107.1, 48.3. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{24}H_{18}ClN_2O_2$ 401.1057, found 401.1067.

*2.2.3. 1-Benzyl-4,5-di(furan-2-yl)-2-phenyl-1*H-*imidazole (**3c**)*

Mp: 68–70 °C. Yield: 78.6%. (KBr) ν ($cm^{-1}$): 3100, 3060, 3020, 2370, 1970, 1600, 1500, 1470, 1440, 1400, 1360, 1320, 1210, 1160, 1070, 1020, 964, 887, 777, 733, 698, 592, 503. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.79 (t, *J* = 1.3 Hz, 1H), 7.63–7.59 (m, 3H), 7.49–7.45 (m, 3H), 7.26–7.18 (m, 3H), 6.82 (d, *J* = 7.1 Hz, 2H), 6.59–6.54 (m, 2H), 6.51 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.48 (dd, *J* = 3.4, 0.6 Hz, 1H), 5.27 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 149.3, 149.2, 142.6, 137.5, 133.1, 130.5, 129.8, 129.2, 129.0, 127.8, 126.2, 120.3, 113.1, 111.9, 111.8, 107.1, 48.8. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{24}H_{19}N_2O_2$ 367.1447, found 367.1444.

*2.2.4. 2,4,5-Tri(furan-2-yl)-1-(4-methylbenzyl)-1*H-*imidazole (**3d**)*

Mp: 114–116 °C. Yield: 82.4%. IR (KBr) ν ($cm^{-1}$): 3100, 3020, 2920, 2860, 1600, 1520, 1460, 1400, 1360, 1320, 1220, 1170, 1120, 1070, 1020, 916, 885, 812, 735, 660, 592, 523. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.83 (d, *J* = 9.0 Hz, 2H), 7.63 (s, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.84 (dd, *J* = 14.7, 5.4 Hz, 3H), 6.63 (dd, *J* = 6.0, 4.4 Hz, 3H), 6.50 (dd, *J* = 13.7, 2.0 Hz, 2H), 5.36 (s, 2H), 2.22 (s, 3H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 148.9, 144.9, 144.6, 142.7, 142.0, 140.2, 137.1, 134.4, 133.4, 129.7, 126.2, 120.3, 113.6, 112.3, 112.0, 111.8, 111.3, 107.3, 48.4, 21.0. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{23}H_{19}N_2O_3$ 371.1396, found 371.1395.

*2.2.5. 1-(4-Chlorobenzyl)-2,4,5-tri(furan-2-yl)-1*H-*imidazole (**3e**)*

Mp: 90–92 °C. Yield: 85.1%. IR (KBr) ν ($cm^{-1)}$: 3110, 2920, 1600, 1490, 1410, 1370, 1220, 1170, 1090, 1010, 885, 816, 739, 644, 594. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.82 (d, *J* = 6.3 Hz, 2H), 7.64 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 3.1 Hz, 1H), 6.64 (ddd, *J* = 10.6, 4.9, 2.4 Hz, 3H), 6.51 (dd, *J* = 11.0, 2.2 Hz, 2H), 5.40 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 148.8, 144.5, 142.8, 141.8, 140.2, 136.5, 133.5, 132.5, 129.1, 128.2, 120.1, 113.8, 112.3, 112.0, 111.8, 111.4, 107.4, 48.2. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{22}H_{16}ClN_2O_3$ 391.0850, found 391.0849.

*2.2.6. 1-Benzyl-2,4,5-tri(furan-2-yl)-1*H-*imidazole (**3f**)*

Mp: 58–60 °C. Yield: 76.1%. IR (KBr) ν ($cm^{-1}$): 3120, 3030, 2930, 1600, 1500, 1450, 1400, 1360, 1320, 1220, 1170, 1080, 1010, 920, 887, 822, 735, 594. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.83 (dd, *J* = 5.8, 1.2 Hz, 2H), 7.63 (d, *J* = 0.8 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 3.4 Hz, 1H), 6.68–6.60 (m, 3H), 6.52 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 5.41 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 148.9, 144.9, 144.6, 144.6, 142.8, 142.0, 140.3, 137.4, 133.4, 132.5, 129.1, 127.9, 126.3, 120.3, 113.6, 112.3, 112.0, 111.8, 111.34, 107.3, 48.7. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{22}H_{17}N_2O_3$ 357.1239, found 357.1241.

*2.2.7. 1-Allyl-2,4,5-tri(furan-2-yl)-1*H-*imidazole (**3g**)*

Mp: 86–88 °C. Yield: 59.0%. IR (KBr) ν ($cm^{-1}$): 3120, 2920, 2350, 1650, 1560, 1460, 1400, 1360 1320, 1220, 1170, 1080, 1010, 920, 887, 812, 739, 594. $^1$H NMR (500 MHz, DMSO) δ (ppm): 7.88 (m, 2H), 7.62 (s, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 6.77 (d, *J* = 2.7 Hz, 1H), 6.68 (m, 2H), 6.49 (m, 2H), 5.94 (m, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 4.77 (dd, *J* = 23.0, 9.5 Hz, 3H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 149.0, 144.6, 142.0, 140.0, 134.0, 133.1, 120.0, 116.8, 113.5, 112.3, 112.0, 111.8, 111.2, 107.1, 47.7. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{18}H_{15}N_2O_3$ 307.1083, found 307.1084.

*2.2.8. (*E*)-4,5-Di(furan-2-yl)-1-(4-methylbenzyl)-2-styryl-1*H-*imidazole (**3h**)*

Mp: 112–114 °C. Yield: 71.6%. IR (KBr) ν ($cm^{-1}$): 3120, 3030, 2920, 2850, 1600, 1520, 1460, 1420, 1350, 1320, 1210, 1010, 891, 800, 742, 688, 594. $^1$H NMR (500 MHz, $CDCl_3$) δ (ppm): $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 11.5 Hz, 1H), 7.54 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.48–7.41 (m, 3H), 7.34–7.30 (m, 2H), 7.29–7.26 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.56–6.43 (m, 3H), 6.40 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.19 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 148.9, 146.8, 142.8, 141.7, 137.6, 136.4, 134.5, 133.6, 129.6, 128.7, 128.4, 126.9, 126.0, 119.7, 113.0, 112.6, 111.3, 111.1, 106.7, 47.4, 21.1. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{27}H_{23}N_2O_2$ 407.1760, found 407.1736.

*2.2.9. (*E*)-1-(4-Chlorobenzyl)-4,5-di(furan-2-yl)-2-styryl-1*H-*imidazole (**3i**)*

Mp: 74–76 °C. Yield: 77.5%. IR (KBr) ν ($cm^{-1}$): 3110, 3050, 1630, 1600, 1490, 1410, 1370, 1270, 1210, 1010, 891, 804, 742, 680, 594. $^1$H NMR (500 MHz, DMSO): δ (ppm): 7.82 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.70–7.67 (m, 2H), 7.64–7.58 (m, 2H), 7.39–7.36 (m, 4H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.65 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.62 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.51 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.47 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.42 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) δ (ppm): 148.7, 146.3, 142.2, 141.9, 136.4, 136.0, 133.3, 133.1, 132.0, 128.7, 128.7, 128.5, 128.0, 127.1, 119.2, 113.8, 112.7, 111.5, 111.3, 106.7, 45.9. HRMS, *m*/*z*: $(M+H)^+$ calcd for $C_{26}H_{20}ClN_2O_2$ 427.1213, found 427.1204.

*2.2.10. (*E*)-4-((4,5-Di(furan-2-yl)-2-styryl-1*H-*imidazol-1-yl)methyl)benzonitrile (**3j**)*

Mp: 148–150 °C. Yield: 86.5%. IR (KBr) ν ($cm^{-1}$): 3090, 3020, 2240, 1600, 1500, 1460, 1410, 1360, 1250, 1220,

1010, 891, 831, 741, 688, 592. $^1$H NMR (500 MHz, DMSO) $\delta$ (ppm): 7.81–7.76 (m, 3H), 7.68 (d, $J$ = 7.4 Hz, 2H), 7.65–7.60 (m, 2H), 7.38 (t, $J$ = 7.5 Hz, 2H), 7.34–7.29 (m, 2H), 7.17 (d, $J$ = 8.4 Hz, 2H), 6.63 (d, $J$ = 3.4 Hz, 1H), 6.60 (dd, $J$ = 3.4, 1.9 Hz, 1H), 6.52 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.49 (dd, $J$ = 3.3, 0.6 Hz, 1H), 5.54 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm): 146.4, 143.1, 142.2, 141.4, 136.2, 133.5, 133.2, 132.6, 128.7, 128.5, 127.1, 126.9, 119.2, 118.5, 113.6, 112.8, 111.5, 111.3, 110.2, 106.8, 46.4. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{27}H_{20}N_3O_2$ 418.1556, found 418.1558.

*2.2.11. (E)-1-Benzyl-4,5-di(furan-2-yl)-2-styryl-1H-imidazole (**3k**)*

Mp: 117–118 °C. Yield: 74.2%. IR (KBr) $\nu$ (cm$^{-1}$): 3110, 3010, 1600, 1500, 1450, 1410, 1350, 1310, 1210, 1010, 887, 808, 735, 588. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm): $^1$H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, $J$ = 15.8 Hz, 1H), 7.53 (dd, $J$ = 1.6, 1.0 Hz, 1H), 7.46–7.42 (m, 3H), 7.32 (ddd, $J$ = 7.7, 4.9, 1.8 Hz, 4H), 7.28–7.26 (m, 2H), 7.10–7.05 (m, 2H), 6.82 (d, $J$ = 15.8 Hz, 1H), 6.53–6.45 (m, 3H), 6.40 (dd, $J$ = 3.4, 1.8 Hz, 1H), 5.23 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm): 148.8, 146.8, 142.8, 136.6, 136.3, 134.6, 133.7, 128.9, 128.7, 128.5, 127.8, 126.9, 126.1, 119.7, 112.9, 112.7, 111.3, 111.1, 106.8, 47.6. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{26}H_{21}N_2O_2$ 393.1603, found 393.1575.

*2.2.12. (E)-4,5-Di(furan-2-yl)-2-(2-(furan-2-yl)vinyl)-1-(4-methylbenzyl)-1H-imidazole (**3l**)*

Mp: 94–95 °C. Yield: 79.7%. IR (KBr) $\nu$ (cm$^{-1}$): 3110, 3020, 2920, 1740, 1640, 1520, 1460, 1350, 1320, 1260, 1210, 1150, 1070, 1010, 960, 883, 802, 737, 594, 538. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ (ppm):7.58 (d, $J$ = 15.6 Hz, 1H), 7.52 (dd, $J$ = 1.6, 1.0 Hz, 1H), 7.43 (dd, $J$ = 1.7, 0.8 Hz, 1H), 7.36 (s, 1H), 7.10 (d, $J$ = 7.9 Hz, 2H), 6.93 (d, $J$ = 8.1 Hz, 2H), 6.75 (d, $J$ = 15.6 Hz, 1H), 6.46 (m, 3H), 6.40 (d, $J$ = 1.3 Hz, 2H), 6.38 (m, 1H), 5.17 (s, 2H), 2.30 (s, 3H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm): 152.3, 149.3, 146.4, 144.3, 142.6, 142.5, 137.2, 134.7, 133.4, 129.8, 126.4, 121.1, 112.0, 113.2, 112.9, 112.3, 112.0, 111.8, 111.8, 107.1, 46.8, 21.1. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{25}H_{21}N_2O_3$ 397.1552, found 397.1534.

*2.2.13. (E)-1-(4-Chlorobenzyl)-4,5-di(furan-2-yl)-2-(2-(furan-2-yl)vinyl)-1H-imidazole (**3m**)*

Mp: 87–89 °C. Yield: 84.1%. IR (KBr) $\nu$ (cm$^{-1}$): 3110, 2950, 1640, 1490, 1410, 1370, 1220, 1160, 1090, 1010, 955, 885, 804, 739, 669, 594. $^1$H NMR (500 MHz, DMSO) $\delta$ (ppm): 7.82 (d, $J$ = 1.1 Hz, 1H), 7.72 (d, $J$ = 1.2 Hz, 1H), 7.63 (d, $J$ = 0.9 Hz, 1H), 7.44 (d, $J$ = 15.6 Hz, 1H), 7.39 (d, $J$ = 8.5 Hz, 2H), 7.01 (d, $J$ = 8.5 Hz, 2H), 6.90 (d, $J$ = 15.6 Hz, 1H), 6.74 (d, $J$ = 3.3 Hz, 1H), 6.65 (d, $J$ = 3.3 Hz, 1H), 6.62 (dd, $J$ = 3.3, 1.9 Hz, 1H), 6.57 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.51 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.48 (d, $J$ = 2.7 Hz, 1H), 5.34 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm): 152.3, 149.2, 146.5, 144.8, 144.4, 142.7, 142.3, 136.7, 133.5, 132.6, 129.2, 128.3, 121.3, 119.8, 113.3, 112.9, 112.4, 112.0, 111.8, 111.6, 107.2, 46.5. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{24}H_{18}ClN_2O_3$ 417.1006, found 417.0999.

*2.2.14. (E)-4-((4,5-Di(furan-2-yl)-2-(2-(furan-2-yl)vinyl)-1H-imidazol-1-yl)methyl)benzonitrile (**3n**)*

Mp: 99–101 °C. Yield: 88.9%. IR (KBr) $\nu$ (cm$^{-1}$): 3120, 2930, 2230, 1740, 1610, 1510, 1470, 1410, 1370, 1260, 1220, 1160, 1070, 1020, 953, 885, 816, 741, 594, 548. $^1$H NMR (500 MHz, DMSO) $\delta$ (ppm): 7.80 (d, $J$ = 8.0 Hz, 3H), 7.71 (s, 1H), 7.63 (s, 1H), 7.45 (d, $J$ = 15.5 Hz, 1H), 7.17 (d, $J$ = 7.6 Hz, 2H), 6.89 (d, $J$ = 15.5 Hz, 1H), 6.74 (s, 1H), 6.64 (s, 1H), 6.62–6.58 (m, 1H), 6.57 (d, $J$ = 1.5 Hz, 1H), 6.51 (d, $J$ = 4.5 Hz, 2H), 5.46 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm):152.2, 149.1, 146.6, 144.4, 143.4, 142.8, 142.2, 133.6, 133.2, 127.4, 121.6, 119.8, 119.0, 113.3, 112.9, 112.5, 112.0, 111.8, 111.4, 110.8, 107.3, 46.9. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{25}H_{18}N_3O_3$ 408.1348, found 408.1345.

*2.2.15. (E)-1-Benzyl-4,5-di(furan-2-yl)-2-(2-(furan-2-yl)vinyl)-1H-imidazole (**3o**)*

Mp: 62–64 °C. Yield: 81.6%. IR (KBr) $\nu$ (cm$^{-1}$): 3120, 3030, 2930, 1740, 1640, 1500, 1450, 1360, 1260, 1220, 1160, 1070, 1010, 955, 885, 808, 735, 594. $^1$H NMR (500 MHz, DMSO) $\delta$ (ppm): 7.83 (d, $J$ = 1.2 Hz, 1H), 7.71 (d, $J$ = 1.4 Hz, 1H), 7.63 (d, $J$ = 1.0 Hz, 1H), 7.43 (d, $J$ = 15.6 Hz, 1H), 7.32 (t, $J$ = 7.5 Hz, 2H), 7.25 (t, $J$ = 7.3 Hz, 1H), 7.00 (d, $J$ = 7.4 Hz, 2H), 6.91 (d, $J$ = 15.6 Hz, 1H), 6.73 (d, $J$ = 3.3 Hz, 1H), 6.64 (d, $J$ = 3.3 Hz, 1H), 6.62 (dd, $J$ = 3.3, 1.9 Hz, 1H), 6.57 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.52 (dd, $J$ = 3.3, 1.8 Hz, 1H), 6.50–6.46 (m, 1H), 5.35 (s, 2H). $^{13}$C NMR (125 MHz, DMSO) $\delta$ (ppm): 152.3, 149.2, 146.5, 144.7, 144.3, 142.6, 142.5, 137.7, 133.5, 129.2, 128.0, 126.4, 121.2, 112.0, 113.2, 112.9, 112.3, 112.0, 111.8, 107.2, 47.1. HRMS, $m/z$: $(M+H)^+$ calcd for $C_{24}H_{19}N_2O_3$ 383.1396, found 383.1380.

### 2.3. Determination of the fluorescence quantum yield

The fluorescent quantum yields were measured against quinine sulfate ($\phi_s$ = 0.55 in 0.1 N sulfuric acid, 200 nm ≤ λ ≤ 400 nm) as a standard [21,22] and were calculated following Eq. (1) improved according to the literature [23]. The crossing wavelength of UV–vis absorption (λ ≥ 300 nm) was chosen to excite the sample and the standard. If not, 320 nm was confirmed as the excitation wavelength.

$$\phi_u = \phi_s \cdot (F_u/F_s) \cdot (A_s/A_u) = \phi_s \cdot (F_u/F_s) \quad (1)$$

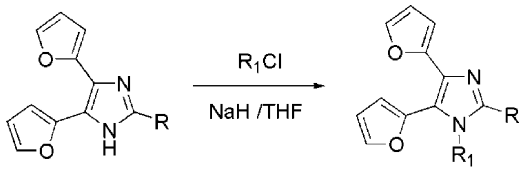
where $A_u$ and $A_s$ are the absorbance of the sample and the standard ($A \leq 0.05$), respectively. $F_u$ and $F_s$ are the integrated emission intensities of the sample and the standard, respectively. $\phi_u$ and $\phi_s$ are the fluorescence quantum yields of the sample and the standard, respectively.

## 3. Results and discussion

### 3.1. Synthesis of the compounds

In the present work, a wide range of benzyl chloride and allyl chloride were employed and fifteen new 1-$R_1$-2-R-4,5-di(furan-2-yl)-1*H*-imidazoles were obtained in better yield from 59.0% to 89.8%. Herein, the nucleophilic substitution reaction of 2-R-4,5-(di-furan-yl)-1*H*-imidazole with 1.5 equiv of benzyl chloride or allyl chloride was readily carried out using NaH as a base under mild reaction conditions referring to the reported method [18] (Table 1). The structures of 1,2,4,5-tetrasubstituted imidazoles

**Table 1**
Synthesis of 1,2,4,5-tetrasubstituted imidazoles containing furan rings under anhydrous THF[a] and their luminescence properties in a 0.1 N $H_2SO_4$ aqueous solution with 0.5 mL of dissolved $CH_3OH$.




3a-3o

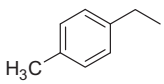
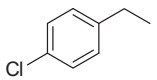
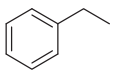
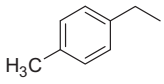
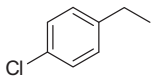
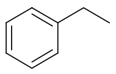
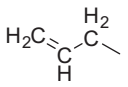
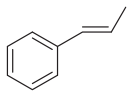
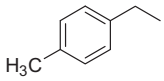
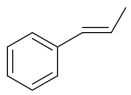
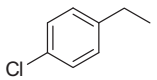
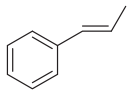
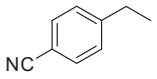
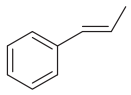
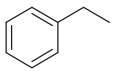
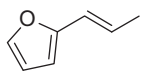
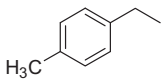
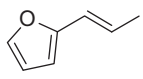
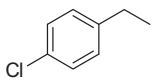
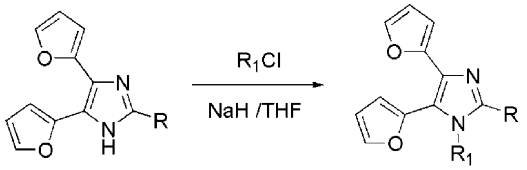
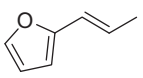
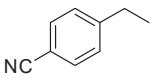
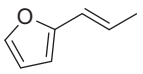
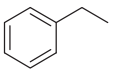
| Entry | R | $R_1$ | Product | Reaction time (h) | Yield (%)[b] | $\lambda_{max}$(nm) | PL/$\lambda$ (nm) | $\phi_u$[c] |
|---|---|---|---|---|---|---|---|---|
| 1 |  |  | **3a** | 37.5 | 69.7 | 285 | 473 | 0.151 |
| 2 |  |  | **3b** | 18 | 89.8 | 287 | 471 | 0.118 |
| 3 |  |  | **3c** | 29 | 78.6 | 287 | 467 | 0.101 |
| 4 |  |  | **3d** | 35 | 82.4 | 312 | 466 | 0.069 |
| 5 |  |  | **3e** | 19 | 85.1 | 307 | 464 | 0.056 |
| 6 |  |  | **3f** | 25 | 76.1 | 306 | 467 | 0.070 |
| 7 |  |  | **3g** | 29.5 | 59.0 | 311 | 448 | 0.084 |
| 8 |  |  | **3h** | 37 | 71.6 | 350 | 506 | 0.132 |
| 9 |  |  | **3i** | 20 | 77.5 | 347 | 505 | 0.078 |
| 10 |  |  | **3j** | 14 | 86.5 | 351 | 506 | 0.112 |
| 11 |  |  | **3k** | 25 | 74.2 | 345 | 507 | 0.161 |
| 12 |  |  | **3l** | 36 | 79.7 | 342 | 501 | 0.010 |
| 13 |  |  | **3m** | 19 | 84.1 | 351 | 502 | 0.009 |

**Table 1** (*Continued*)




3a-3o

| Entry | R | $R_1$ | Product | Reaction time (h) | Yield (%)[b] | $\lambda_{max}$(nm) | PL/$\lambda$ (nm) | $\phi_u$[c] |
|---|---|---|---|---|---|---|---|---|
| 14 |  |  | **3n** | 13 | 88.9 | 346 | 503 | 0.004 |
| 15 |  |  | **3o** | 27 | 81.6 | 346 | 506 | 0.008 |

[a] Reaction condition: 1 mmol 2-R-4,5-di(furan-2-yl) imidazoles, 1.5 mmol NaH, and 1.5 mmol benzyl chloride or allyl chloride dropped in 20 mL anhydrous THF were refluxed.
[b] Isolated product yield
[c] Quinine sulfate as standards, calculated by means of Eq. (1).

including furan rings were confirmed by FT-IR, $^1H$ and $^{13}C$ NMR and HRMS analysis. The aryl–$CH_2$–N–RC = N–protons of the compounds exhibited resonances at 5.17–5.55 ppm when using DMSO as the solvent, while the resonances for the corresponding aryl–$CH_2$–N–RC=N–carbon atom were observed between 45.9 and 48.8 ppm. The resonances for the – N–RC=N – carbon atom on the imidazole ring were observed at 141.4–144.7 ppm.

As shown in Table 1, for clarity, the results indicated that good yields were obtained when 4-substituted benzyl chlorides containing electron–withdrawing groups (–CN,–Cl) were used as starting materials (entries **2**, **5**, **9**, **10**, **13** and **14**), whereas the better yields were obtained when benzyl chloride and 4-substituted benzyl chlorides containing electron-donating groups were employed (entries **1**, **3**, **6**, **8**, **11**, **12** and **15**). Moreover, the yields of the synthesized compounds were enhanced and the reaction time was shortened with increasing electron-withdrawing effects. For example, the reaction time was 13 h and 36 h, respectively when 4-cyanobenzyl chloride (entry **14)** and 4-methyl benzyl chloride (entry **12**) were employed in the reaction. Besides, the desired compound was not obtained when 4-methoxy benzyl chloride was employed. The reason might be that the interactions between the conjugation of the benzene ring and the inductive effect of electron-withdrawing–CN or–Cl made the electron atmosphere of cyanobenzyl and chlorobenzyl reduce and be facilely attacked by nucleophilic C–$N^-$–C of the imidazole ring. Conversely, the electron-donating inductive effect was contrary to the benzene ring conjugation when the 4-substituent on benzyl chloride is –$CH_3$. Therefore, the yield was low, the reaction time was long, and even the desired product could not be obtained.

### 3.2. UV-vis and photoluminescence spectra analysis

The UV-vis absorption spectra of compounds **3a**–**3o** ($4.0 \times 10^{-6}$ mol/L) in a 0.1 N $H_2SO_4$ aqueous solution in which 0.5 mL of $CH_3OH$ has been dissolved are shown in Fig. 1. Two main absorption peaks of **3a**–**3c** were around 220–231 nm and 281–293 nm, respectively. Two main absorption peaks of **3d**–**3g** were around 217–236 nm and 302–318 nm, respectively. Such a red-shift at 280–320 nm compared with that of 2-phenyl (entries **1**, **2**, and **3**) was attributed to the new n–$\pi$ conjugated structure of 2-furyl (entries **4**, **5**, and **6**). Three absorption peaks of **3h**–**3k** were around 220–234 nm, 278–289 nm and 337–371 nm, respectively. Three absorption peaks of **3l**–**3o** were around 220–238 nm, 284–295 nm and 340–380 nm, respectively. Such a red-shift compared with 2-phenyl (entries **1**, **2** and **3**) or 2-furyl (entries **4**, **5** and **6**) substituted group on imidazole was attributed to 2-styryl (entries **8**, **9** and **11**) or (2-furan-2-yl)vinyl (entries **12**, **13** and **15**). The substituted groups on imidazole possess a long conjugated chain lead to the $\pi \rightarrow \pi^*$ transition energy decrease [24]. However, we can see that the different N-substituted groups slightly affected the absorption of the synthesized compound.

In general, the emission spectra of the compounds did not change in a given solvent with varying the excitation

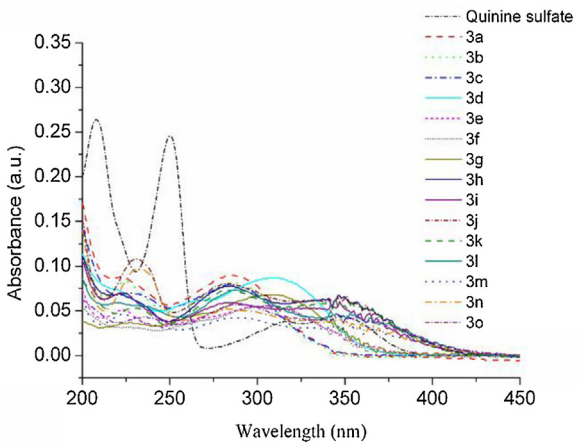



**Fig. 1.** UV-vis spectra of **3a**–**3o**.

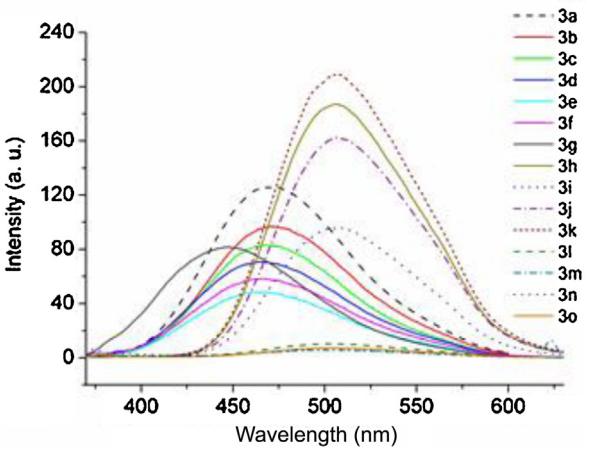



**Fig. 2.** Fluorescence emission spectra of **3a**–**3o**.

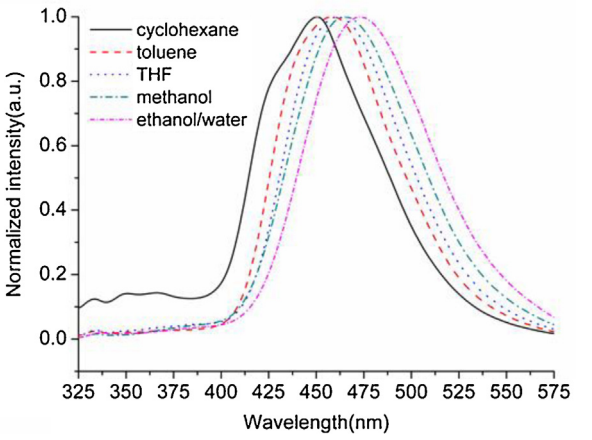



**Fig. 4.** Normalized emission spectra of **3h** in the solvents with different polarities ($\lambda_{ex}$ = 300 nm).

wavelengths in the lower wavelength range. However, the intensity of the emission spectra changed as the excitation wavelength [25]. The fluorescence emission spectra of **3a**–**3o** ($4.0 \times 10^{-6}$ mol/L) in the 0.1 N $H_2SO_4$ aqueous solution containing 0.5 mL of dissolved $CH_3OH$ are shown in Fig. 2. The emission spectra of **3a**–**3o** were in the blue and green regions, around 450–550 nm. The fluorescence quantum yields ($\phi_u$) of products **3a**–**3o** were calculated according to Eq. (1). The calculated fluorescence quantum yield of each compound is summarized in Table 1. In general, the fluorescence quantum yields of the imidazole derivatives bearing the conjugated units furan rings and substituted furan rings on the 2-position of imidazole (entries **4**, **5**, **6**, **7**, **12**, **13**, **14** and **15**) were lower than that of bearing the conjugated units of the benzene ring and the substituted benzene ring on the 2-position of imidazole (entries **1**, **2**, **3**, **8**, **9**, **10** and **11**) against quinine sulfate as a standard [21–23,26,27]. The reason for the higher fluorescence quantum yields of the synthesized compounds (entries **1**, **2**, **3**, **8**, **9**, **10** and **11**) might be that the conjugated effect of the benzene ring made the plane of the trisubstituted imidazole twist a less angle [20,28]. Besides, benzyl groups or allyl group introduced to the 1-position of trisubstituted imidazole increase the chance of a rotational degree of freedom and result in a non-planar conformation. Therefore, the fluorescence quantum yields of the synthesized tetrasubstituted imidazole derivatives were generally lower (Table 1). The reason for the fluorescence quenching of the synthesized compounds (entries **12**, **13**, **14** and **15**) might be the interaction of ground-state molecules and excimers of (2-furan-2-yl)vinyl to form a dimer under light irradiation.

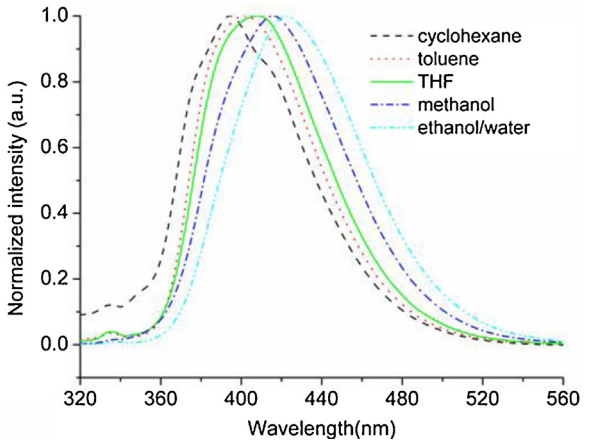



**Fig. 3.** Normalized emission spectra of **3a** in the solvents with different polarities ($\lambda_{ex}$ = 300 nm).

In addition, the fluorescence emission spectra of **3a** and **3h** ($4.0 \times 10^{-6}$ mol/L) in solvents with different polarity (cyclohexane, toluene, THF, methanol and ethanol/water v/v = 1/1) are shown in Figs. 3 and 4, respectively. The corresponding data are summarized in Table 2.

Notably, the emission bands of compounds **3a** and **3h** were significantly red-shifted with an increase of the solvent polarity. In cyclohexane, the emissions of **3a** and **3h** were at 394 nm (Fig. 3) and 450 nm (Fig. 4), respectively. However, in ethanol/water (ethanol/water, v/v = 1/1), they were red-shifted to 423 nm (**3a**) and 473 nm (**3h**), respectively. The red-shift of the emission band might be due to the stronger interaction between the solvent and the excited state molecules. The excited state of **3a** was more stabilized in polar solvents than in non-polar solvents. This led to a red shift of the emission with increasing solvent polarity [10,29]. Therefore, both compounds **3a** and **3h** exhibited a broad shape of the emission spectra and a solvent dependence of the emission [30,31]. The emission of **3a** was blue-shifted to 394 nm compared with the emission at 423 nm in the solution, so that the

**Table 2**
The emission wavelength of **3a** and **3h** in the solvents with different polarities ($\lambda_{ex}$ = 300 nm).

| Solvent | Emission wavelength (nm) | | Shift (nm) |
|---|---|---|---|
| | **3a** | **3h** | |
| Cyclohexane | 394 | 450 | 56 |
| Toluene | 402 | 459 | 57 |
| THF | 409 | 461 | 52 |
| Methanol | 416 | 465 | 49 |
| Ethanol/water | 423 | 473 | 50 |

emitting color was purple (Fig. 3 and Table 2). However, the emission of **3h**, blue-shifted to 450 nm, can be compared to the emission at 473 nm in the solution, which was nicely in the range of blue light when excited at 300 nm (Fig. 4 and Table 2). Moreover, in the solvents with different polarities, the red-shift was about 49–57 nm when comparing the emission of **3h** with that of **3a** (Figs. 3 and 4, Table 2). The reason was that **3h** with styryl exhibited a longer conjugated chain than **3a** with the benzene ring. However, **3a** and **3h** were respectively red-shifted to 473 nm and 506 nm in the 0.1 N $H_2SO_4$ aqueous solution containing 0.5 mL of dissolved $CH_3OH$ (Table 1). The reason might be that the 0.1 N $H_2SO_4$ aqueous solution with 0.5 mL of dissolved $CH_3OH$ exhibited higher polarity and lower pH than the ethanol/water solvent (v/v = 1/1).

## 4. Conclusion

A series of novel 1,2,4,5-tetrasubstituted imidazoles containing furan rings were successfully synthesized using 2-R-4,5-di(furan-2-yl)imidazoles and a series of benzyl chloride and allyl chloride. The luminescent properties of the synthesized compounds were studied. In the 0.1 N $H_2SO_4$ aqueous solution with 0.5 mL of dissolved $CH_3OH$, the absorption bands exhibited a red shift with increasing the long conjugation or introducing a n-electron on the 2-position of imidazole. Their maximum emission was 440–510 nm, which basically emits blue or green light with fluorescence quantum yields of 0.004–0.161 against quinine sulfate as a standard. Meanwhile, the emission of compounds **3a** and **3h** in solution could be tuned by varying the polarity of the solvents. Such functional compounds might possess potential applications in the detection of environments and the material science fields.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.crci.2013.05.014.

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