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ARTICLE

Direct Synthesis of 2,4,5-Trisubstituted Imidazoles from Primary Alcohols by Diruthenium(II) Catalysts under Aerobic Conditions

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Herein we report a straightforward synthetic approach to 2,4,5-trisubstituted imidazoles from readily available primary alcohols using arene diruthenium(II) catalysts. Dinuclear arene ruthenium complexes have been synthesized and structurally characterized with the aid of analytical and spectral techniques. A library of 2,4,5-trisubstituted imidazoles was achieved with the yield up to 95% by loading 0.25 mol% of the catalyst. The present protocol is environmentally benign, which is performed under aerobic conditions and liberates water as the sole by-product.

Introduction

Nitrogen-containing heterocycles are ubiquitous in numerous biomolecules.[1] In particular, imidazole motifs are vital class of compounds due to their prevalence in several biomolecules such as biotin, purines, histidine, histamine[2a] and in natural products, primarily alkaloids.[2] They are considered as beneficial structural motifs because of their diverse range of applications in organic electroluminescent devices (OLED),[3a-c] as semiconductor devices,[4] as coordinating ligands,[5]as organocatalysts,[6] in metalloenzymes,[7] as fluorescent probes,[8] as ionic liquids,[9] as functional polymers,[10] etc.

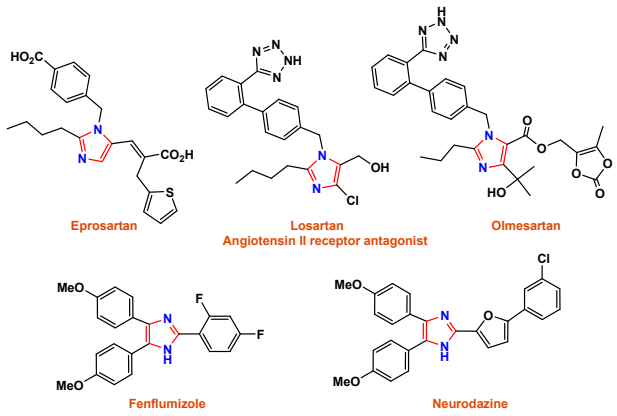

Figure 1 Selected examples of biologically active imidazoles.

Specifically, highly substituted imidazoles exhibit potent biological properties like antibacterial,[11a] anti-inflammatory,[11b,c] anticancer activities as well as inhibitors of angiotensin II or P38 MAP kinase. Especially, fenflumizole and neurodazine are potent anti-inflammatory and neurogenic agents[12]. Further, Eprosartan, Losarton, Olmesartan are some of the marketed drugs containing imidazoles ring(Figure 1).[13]

Generally, 2,4,5-trisubstituted imidazoles were synthesized by classical Radziszewski reaction which is of industrial significance involving the reaction of an diketones, an aldehyde, and dry ammonia.[14] Several developments have been made for the past few years towards the Radziszewski reaction but the reactions were limited to the use of aldehydes. Several groups have reported the use of keto-monoxime/R-hydroxy/ silyloxy/ acetoxy-ketone instead of 1, 2-diketone are some of the reactions performed with or without catalysts.[15]

Wang et al. reported a synthetic route to 2,4,5-trisubstitued imidazoles from internal alkynes and 1,2-diketone via pivalic acid.[16] Muthusubramanian's group demonstrated the use of α-azido chalcones in order to replace 1,2-diketones.[17] Highly substituted imidazoles have been prepared by Jiang[18a] and Ji[18b] independently by using aryl methyl ketones and benzylamines instead of 1,2-diketone. Wu et al reported the annulation of methyl ketones, anilines, and tosylmethylisocyanide (TosMIC) for the synthesis of highly substituted imidazoles.[19] However, there are no reports available on Radziszewski reactions with readily available alcohols replacing aldehydes.

Although there are several protocols available for the 2,4,5-trisubstituted imidazoles, they suffer from several drawbacks such as harsh conditions, low yields, prolonged reaction time, mixtures of products such as oxazole or reversed aldol condensations. These limitations make these strategies unsuited to employ under greener

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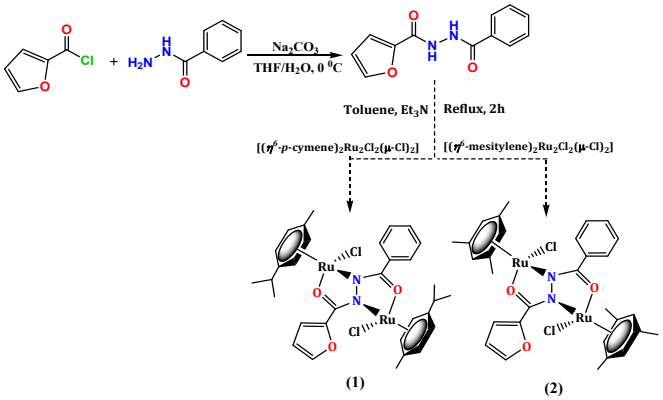
process. Therefore, development of environmentally benign methodology for the imidazoles synthesis is of great importance due to the significance of the target molecules.

Direct synthesis of target molecules with the aid of widely available reagents is a prominent strategy in organic synthesis. Further, the present methodology acceptorless dehydrogenation of alcohols is an atom-economical alternative.[20] In continuation of our growing quest towards the development of new ruthenium catalysts for the direct synthesis of amides and imines, [21] herein we describe an expedient direct synthetic approach for the synthesis of 2,4,5-trisubstituted imidazoles from alcohols and diketones/α-Hydroxyketone catalysed by diruthenium(II) catalysts under aerobic conditions. The feature of the present protocol merits attention as it is ecofriendly, due to the use of widely available less toxic alcohols and elimination of water as the only by-product. To the best of our knowledge, no reports available on the use of ruthenium(II) catalysts for the direct conversion of alcohols to 2,4,5-imidazoles.

Results and discussion



Scheme 1 Synthetic route to arenedinuclear ruthenium (II) complexes

The new arene dinuclear ruthenium(II) complexes of the molecular formula $[(\eta^6\text{-arene})_2Ru_2Cl_2(\mu\text{-L})]$ were synthesized by the reaction of equimolar quantity of a N'-benzoylfuran-2-carbohydrazide ligand (HL) and ruthenium arene starting precursors such as $[(\eta^6\text{-arene})_2Ru_2Cl_2(\mu\text{-Cl})_2]$, arene = *p*-cymene(1) and mesitylene(2), in the presence of Et_3N under reflux condition for 2h in toluene. All the synthesized complexes are air stable and highly soluble in polar organic solvents. The formation of the arene binuclear Ru(II) complexes were confirmed with the aid of elemental analysis, IR, UV/Vis, ^1H and ^{13}C NMR-spectroscopic techniques.

Single-crystal X-ray diffraction study of complex 2 revealed the exact mode of coordination of the ligand and geometry of the complex. Crystals of complex 2 grew from the slow diffusion of dichloromethane into ethanol solutions, and crystallised in a monoclinic form with the space group of $P2_1/c$. Each Ru(II) ion adopts a piano-stool pseudo octahedral geometry. The N'-benzoylfuran-2-carbohydrazide ligand coordinates to each ruthenium centre via carbonyl oxygens and hydrazinic nitrogens in a monoanionic bidentendate manner to form two five membered chelate rings. Rest of the sites of piano stool geometry were occupied by chlorine atoms and trimethylbenzene moieties. The bond lengths and bond angles of complex 2 are consistent with the reported data of similar Ru(II) complexes[21].

With the newly synthesized complexes 1 and 2 in hand, we began our investigation by employing benzyl alcohol and benzil as benchmark substrates and complex 1 as model catalyst to yield valuable Lophine (Table 1, 5a). In order to discover the effective reaction condition, base and solvent optimisation was carried out at different temperatures in the presence of NH_4OAc as N source. Firstly, the reaction performed in the absence of base was unsuccessful (Table 1, entry 1). Later, we carried out the reaction using several inorganic bases such as *t*-BuOK, $LiOH.H_2O$, KOH. Among the bases screened, KOH was found to be the best choice (Table 1, entry 4).

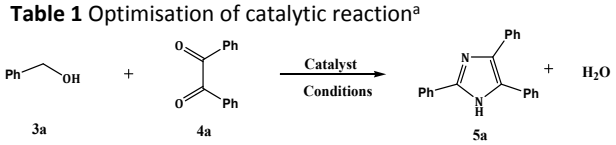
We further proceeded our investigation by testing the feasibility of the reaction using a range of polar and apolar solvents and the experimental results revealed that the reaction in toluene medium afforded the desired target molecule in excellent yield (Table 1, entry 4). The rest of the solvents gave poor yield or no product formation was observed. Further, the N source NH_4OAc was replaced with NH_4OH, but a decrease in the yield of the product 5a was observed (Table 1, entry 10). Furthermore, the reaction performed at room temperature had no impact on the formation of the desired product (Table 1, entry 11). Hence, we optimised the reaction using a range of temperatures (80-110 ºC) and 110 ºC was found to be the optimum temperature for imidazoles synthesis (Table 1, entry 4). The yield of 5a increased when complex 2 was used as catalyst(Table 1, entry 16). Subsequently, no products were obsevered when the reaction was performed in the absence of catalyst and ammonia source (Table 1, entries 15, 17). No appreciable yields were obtained on using ruthenium arene starting precursors. Thus, the above experimental results furnished the effective reaction conditions for the synthesis of 2,4,5-trisubstituted imidazoles.

In light of exploring the generality and scope of the present protocol, we tested a wide range of substrates for the synthesis of imidazoles. Primary aromatic alcohols bearing electron-donating group (4-OMe, 4-Me) at *para*- position afforded the corresponding products in excellent yields (Table 2, entries 2 and 3). On the other hand, electron withdrawing group (4-Cl) yielded the desired product in good yield (Table 2, entry 4). hydroxy group at the *para*- position yielded 64% of the desired product (Table 2, entry 5). It is worthy to note that the electron releasing(3-Me) and electron withdrawing (3-F) groups at the meta position of the aromatic ring gave 86% and 83% respectively (Table 2, entries 6, 7).

Ortho-substituted benzyl alcohols participated well in the synthesis of the corresponding products in good to excellent yield inspite of the steric factor (Table 2, entries 8, 9). Interestingly, the

reaction of piperonyl alcohol with benzil proceeded smoothly and yielded 73% of the desired product (Table 2, entry 10).

Table 1 Optimisation of catalytic reaction[a]



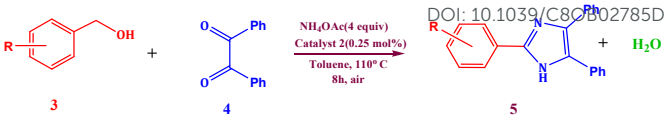
Entry	Complex	Solvent	Base	N source	T (°C)	Yield (%)[b]
1	1	Toluene	none	NH_4OAc	110	NR
2	1	Toluene	t-BuOK	NH_4OAc	110	83
3	1	Toluene	LiOH. H_2O	NH_4OAc	110	NR
4	1	Toluene	KOH	NH_4OAc	110	85
5	1	CH_2Cl_2	KOH	NH_4OAc	40	45
6	1	THF	KOH	NH_4OAc	66	68
7	1	MeOH	KOH	NH_4OAc	65	10
8	1	MeCN	KOH	NH_4OAc	82	NR
9	1	DMF	KOH	NH_4OAc	110	NR
10	1	Toluene	KOH	NH_4OH	110	56
11	1	Toluene	KOH	NH_4OAc	r.t.	NR
12	1	Toluene	KOH	NH_4OAc	80	62
13	1	Toluene	KOH	NH_4OAc	90	68
14	1	Toluene	KOH	NH_4OAc	100	76
15	1	Toluene	KOH	none	110	NR
16	2	Toluene	KOH	NH_4OAc	110	88
17	none	Toluene	KOH	NH_4OAc	110	NR

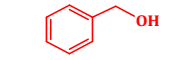
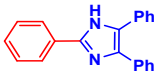
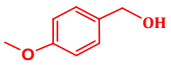
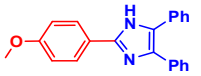
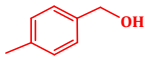
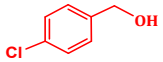
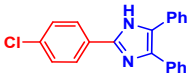
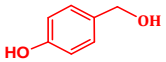
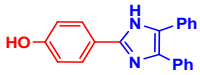
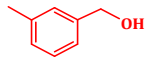
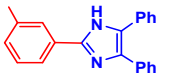
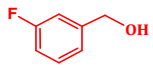
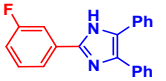
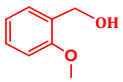
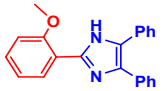
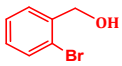
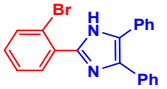
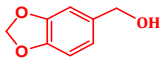
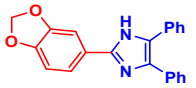
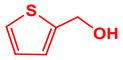
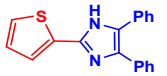
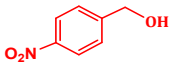
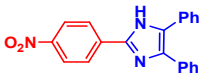
[a]Reaction conditions: Benzyl alcohol(1 mmol), Benzil(1 mmol) base (0.5 mol%), NH_4OAc(4 equiv) and catalyst (0.25 mol%) stirred for 8 h. [b] Isolated yields.

To our delight, heterocyclic alcohol was well tolerated to yield the desired compound in good yield (Table 2, entry 11). In addition, the reaction of *para*-nitro benzyl alcohol was performed and the yield of the corresponding imidazole was found to be excellent (Table 2, entry 12).

In order to explore the versatility and generality of the present protocol, varieties of substituted aromatic alcohols and 1,2-diketons were taken as substrates towards the synthesis of 2,4,5-trisubstituted imidazoles. In particular, reaction of 4,4'-dimethylbenzil with benzyl alcohol afforded the corresponding product in 76% yield (Table 3, entry 1).

Table 2 One-Pot Synthesis of 2,4,5-Trisubstituted Imidazoles[a]



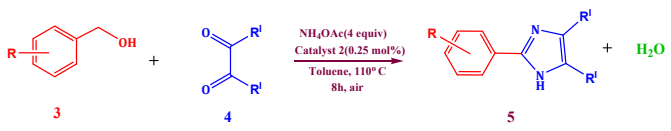
Entry	3	5	Yield(%)[b]
1			5a, 88%
2			5b, 95%
3			5c, 92%
4			5d, 72%
5			5e, 64%
6			5f, 86%
7			5g, 83%
8			5h, 81%
9			5i, 65%
10			5j, 73%
11			5k, 68%
12			5l, 82%

[a]Reaction conditions: Primary alcohols(1 mmol), Benzil(1 mmol) base (0.5 mol%), NH_4OAc(4 equiv) and catalyst 2(0.25 mol%) stirred for 8 h in open air. [b]Isolated yields.

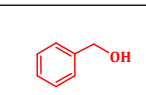
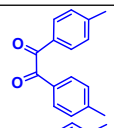
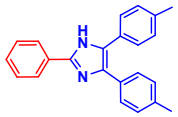
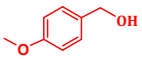
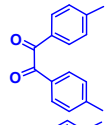
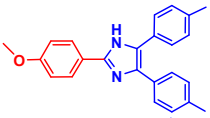
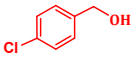
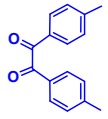
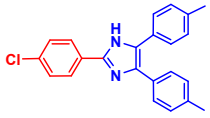
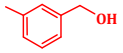
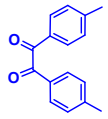
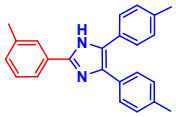
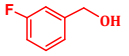
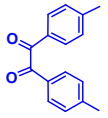
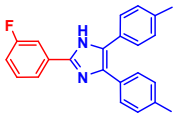
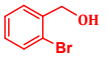
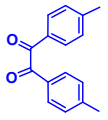
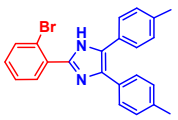
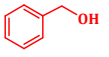
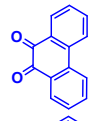
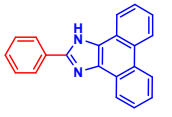
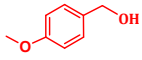
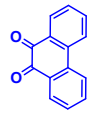
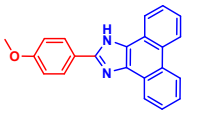
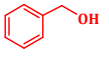
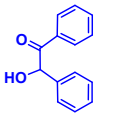
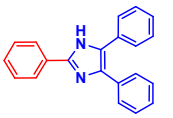
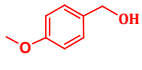
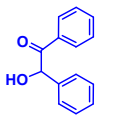
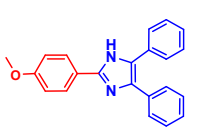
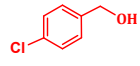
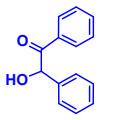
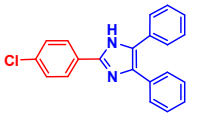
Furthermore, electron donating and electron withdrawing groups at *ortho-*,*para-* and *meta-* position of aromatic benzyl alcohols afforded the desired products in good to excellent yields(Table 3, entries 2-6). Notably, fluorescent phenanthroimidazoles products were synthesized smoothly by the reaction of substituted benzyl alcohols and 9, 10-phenanthrenedione to yield the target compounds in moderate to excellent yields (Table 3, entry 7). Especially, 4-methoxy benzyl alcohol and 9, 10-phenanthrenedione afforded 85% of the corresponding product (Table 3, entry 8). Noteworthy, the reactions of alpha-hydroxy ketone, benzoin with substituted benzyl alcohols were performed and the reactions proceeds well with medium to good yields (Table 3, entries 9-11). Further, we have also carried out the reaction with 1,2-diol, hydrobenzoinand 4-methoxy benzyl

alcohol. It has been observed that no appreciable yields were obtained even after prolonged reaction time.

Table 3 One-Pot Synthesis of 2,4,5-Trisubstituted Imidazoles[a]

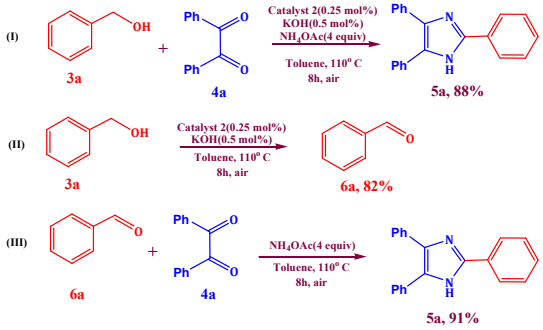


3 4 5

Entry	3	4	5	Yield(%)[b]
1				5m, 76%
2				5n, 81%
3				5o, 75%
4				5p, 78%
5				5q,71%
6				5r, 68%
7				5s, 66%
8				5t, 85%
9				5a, 58%
10				5b, 76%
11				5d, 71%

[a]Reaction conditions: Primary alcohols(1 mmol), Benzil(1 mmol) base (0.5 mol%), NH_4OAc(4 equiv) and catalyst 2 (0.25 mol%) stirred for 8 h in open air. [b]Isolated yields.

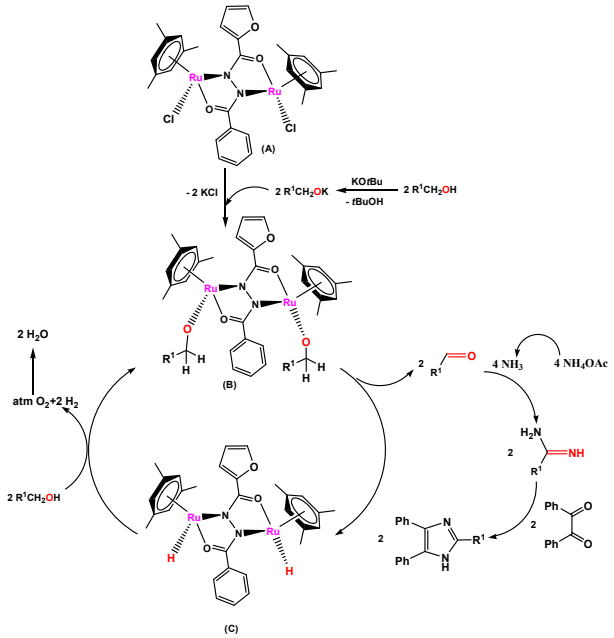
In order to gain insights about the formation of 2,4,5-trisubstituted imidazoles, control experiments were carried out (Scheme 2). Firstly, we performed the reaction in the absence of benzil and ammonium acetate and observed the formation of **6a**.



Scheme 2 Control Experiments for Mechanistic Investigation

Thus the formation of **6a** confirms that initially an alcohol is converted to an aldehyde. Later, the reaction of benzaldehyde **6a** and benzil in the presence of ammonium acetate yielded the corresponding products.

Based on the results obtained from the control experiments and literature reports, we herein propose a mechanism for the synthesis of trisubstituted imidazoles (Scheme 3). The first step is believed to proceed via the formation of ruthenium alkoxide species(B). In the next step the (B) is converted to ruthenium hydride species (C) with the release of an aldehyde intermediate.



Scheme 3 Proposed mechanism

Further, (C) enters into the next catalytic cycle with the elimination of water as the only by-product. Meanwhile, the aldehyde intermediate will react with ammonium acetate to produce an amidine which upon cyclocondensation with benzil generates the desired 2,4,5-trisubstituted imidazoles.

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Lophine synthesized using current methodology was extracted after the completion of the reaction by the addition of ethyl acetate and washed with water. The catalyst was then dried and reused for the next catalytic cycle. From the experiments, we found that the catalyst was active upto four runs with a gradual fall in the yields of the product.

Conclusions

In summary, we have synthesized and characterized new arene diruthenium(II) complexes and successfully employed them as efficient catalysts for the direct synthesis of 2,4,5-trisubstituted imidazoles from primary alcohols and diketones/α-Hydroxyketone. The reaction proceeds efficiently using 0.25 mol% of catalyst loading and water as the only by-product. We believe that the present protocol is simple, atom economic and easy to handle methodology for the synthesis of 2,4,5-trisubstituted imidazoles.

Experimental section

General experimental details

(a) General method for the synthesis of diruthenium(II) complexes(catalyst):N'-benzoylfuran-2-carbohydrazide ligand (HL) and $[(\eta^6\text{-arene})_2Ru_2Cl_2(\mu\text{-L})]$ arene = *p*-cymene/mesitylene in the presence of few drops of Et_3N were refluxed in toluene for 2h. The solution was concentrated under reduced pressure. Upon addition of petroleum ether (60−80 °C), a clear orange solid precipitated. The product was filtered, washed with pet.ether, and dried in vaccuo.

Synthesis of dinuclear $[(\eta^6\text{-}p\text{-Cymene})_2Ru_2Cl_2(\mu\text{-L})]$ (1): Orange Solid. Yield:86%; Found: C, 49.86; H, 4.79; N, 3.61%. Calc. for $C_{32}H_{36}Cl_2N_2O_3Ru_2$: (769.69 g mol^{-1}): C, 49.93; H, 4.71; N, 3.64%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm), 7.98 (m, 2 H, ArH), 7.57(m, 1 H, ArH), 7.45 (m, 3 H, ArH&FurH), 7.36 (d, $^3J_{H-H}$ = 3.6 Hz, 1H, FurH), 6.69 (t, $^3J_{H-H}$ = 1.6 Hz, 1 H, FurH), 5.19 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 5.13 (d, $^3J_{H-H}$ = 6 Hz, 1H, CH *p*-cym), 5.09 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 5.01 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym),4.82 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 4.44 (m, 2H, CH *p*-cym), 3.78 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 2.72 (sept, 1H, $CH(CH_3)_2$), 2.53 (sept, 1H, $CH(CH_3)_2$), 2.48 (s, 3H, CH_3 *p*-cym), 2.46 (s, 3H, CH_3 *p*-cym), 1.15 (m, 6H, $CH(CH_3)_2$ *p*-cym), 1.06 (m, 6H, $CH(CH_3)_2$ *p*-cym). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm), 173.38, 164.10, 147.36, 143.26, 136.41, 129.50, 127.77, 114.44, 110.73, 110.14, 100.23, 100.15, 99.89, 83.40, 82.54, 81.52, 81.15, 80.33, 80.04, 79.87, 79.56, 30.42, 30.38, 22.80, 22.33, 22.26, 22.13, 18.74, 18.72. FT-IR (cm^{-1}): 1525, 1480, 1382, 1035. UV-vis (CH_2Cl_2, λ_{max} nm; ε dm^3 mol^{-1} cm^{-1}): 450 (1,200), 325 (6,800), 256 (11,000).

Synthesis of dinuclear $[(\eta^6\text{-Mesitylene})_2Ru_2Cl_2(\mu\text{-L})]$ (2): Reddish brown Solid. Yield: 84%; Found: C, 48.62; H, 4.30; N, 3.72%. Calc. for $C_{30}H_{32}Cl_2N_2O_3Ru_2$: (741.63 g mol^{-1}): C, 48.58; H, 4.35; N, 3.78%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm), 8.19 (m, 2 H, ArH), 7.68 (d, $^3J_{H-H}$ = 2.8 Hz, 1H, ArH), 7.57(m, 1H, ArH), 7.46 (m, 3 H, ArH&FurH), 6.48 (m, 1H, FurH), 4.46 (s, 3H, ArH mes), 4.24(s, 3H, ArH mes), 2.00 (s, 9H, CH_3 mes), 1.96 (s, 9H, CH_3 mes). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm), 173.36, 168.98, 147.43, 143.18, 136.63, 130.85, 129.51, 127.38, 115.56, 110.63, 101.86, 99.43, 78.91, 18.24, 18.19. FT-IR (cm^{-1}). 1522, 1483, 1374, 1030. UV-vis (CH_2Cl_2, λ_{max} nm; ε dm^3 mol^{-1} cm^{-1}): 445 (1,500), 328 (6,100), 257 (10,000).

(b)General procedure for the synthesis of tri-substituted imidazoles (5a-5s):

The mixture of alcohol (1 mmol), KOH (10 mol%), catalyst (0.25 mol%), was stirred in toluene under reflux condition. After 3 hours benzil/benzoin (1 mmol), NH_4OAc (4 equiv.) and few drops of glac. AcOH were added and stirred for 5 hours. The reaction was monitored by TLC until completion. After completion of the reaction, the solvent was evaporated under reduced pressure. Then the resulting residue was purified by silica gel column chromatography using EtOAc: hexane to afford imidazoles.

(c) Procedure for recycling of 5a:

After completion of the reaction, the product mixture was cooled to room temperature and concentrated under reduced pressure. Precipitation occurs on addition of diethyl ether and the catalyst was recovered by centrifugation, then washed thoroughly with diethyl ether and finally with hexane. The recovered catalyst was dried under vacuum at 100−120 °C overnight. The catalyst was re-used in four successive cycles under identical conditions. The combined organic layers were concentrated in vaccuo, and the remaining residue was purified by column chromatography using EtOAc : hexane to yield imidazole products.

^1H NMR and ^{13}C NMR data of tri-substituted imidazoles (5a-5t)

2,4,5-triphenyl-1*H*-imidazole(5a)[22]: Colourless Solid. ^1H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.73 (br s, 1H,), 8.10 (d, *J* = 7.2 Hz, 2H), 7.54-7.24 (m, 13H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 145.49, 137.08, 135.15, 131.06, 130.30, 128.66, 128.43, 128.21, 127.75, 127.04, 126.49, 125.15.

2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole(5b)[23]: Colourless Solid. ^1H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.52 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 6.4 Hz, 1H), 7.53 (m, 2H), 7.49 (m, 2H), 7.43-7.30(m, 5H), 7.23 (d, J = 6.0 Hz, 1H), 7.05 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 159.38, 145.60, 135.33, 131.30, 128.29, 127.58, 127.04, 126.67, 123.10, 114.05, 55.15.

4,5-diphenyl-2-p-tolyl-1H-imidazole(5c)[24]: Colourless Solid. ^1H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.63 (s, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.53-7.48 (m, 4H), 7.37-7.27(m, 7H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 145.66, 142.73, 137.66, 129.28, 129.22, 129.01, 128.65, 128.40, 127.63, 125.15, 20.85.

2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole(5d)[24]: Colourless Solid. ^1H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.80 (br s, 1H,), 8.12 (d, *J* = 8.4 Hz, 2H), 7.55-7.22 (m, 12H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 144.40, 137.27, 134.98, 129.17, 128.73, 128.63, 128.39, 128.17, 127.83, 127.05, 126.81, 126.57.

4-(4,5-diphenyl-1H-imidazol-2-yl)phenol(5e)[24]: Colourless Solid. ^1H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.41 (br s, 1H), 9.73 (br s, 1H) 7.91 (d, *J* = 8.4 Hz, 2H), 7.54-7.20 (m, 10H), 6.86 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 157.73, 146.02, 136.57, 135.38, 131.28, 128.58, 128.26, 128.10, 127.00, 126.80, 121.58, 115.36.

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4,5-diphenyl-2-m-tolyl-1H-imidazole(5f)[25]: Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.65 (s, 1H), 7.93 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.56–7.18 (m, 12H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 145.59, 137.80, 137.01, 130.17, 128.92, 128.61, 128.35, 128.16, 127.72, 127.06, 126.50, 125.70, 122.34, 21.06.

2-(3-fluorophenyl)-4,5-diphenyl-1H-imidazole(5g): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: *δ* 12.85 (s, 1H), 8.10-7.19 (m, 14H). ^{13}C NMR (100 MHz, DMSO-*d6*): 166.31, 163.14, 160.70, 144.25, 144.22, 132.50, 130.72, 128.41, 125.38, 121.16, 119.54, 115.79, 114.75, 111.72. HRMS (ESI) Calcd for $C_{21}H_{15}FN_2$ $[M+H]^+$ 315.1297; found, 315.1300.

2-(2-methoxyphenyl)-4,5-diphenyl-1H-imidazole(5h)[26]: Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 11.90 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.54–7.05 (m, 13H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 115.96, 143.12, 136.37, 135.23, 131.21, 129.74, 128.53, 128.11, 127.04, 120.55, 118.86, 111.55, 55.5.

2-(2-bromophenyl)-4,5-diphenyl-1H-imidazole(5i): Pale white solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.65 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.56-7.21(m, 11H). ^{13}C NMR (100 MHz, DMSO-*d6*): 144.61, 136.63, 135.10, 133.33, 131.78, 128.67, 128.18, 128.07, 127.62, 127.13, 126.53, 121.61. HRMS (ESI) Calcd for $C_{21}H_{15}BrN_2$ $[M+H]^+$ 375.0496; found, 375.0494.

2-(benzo[d][1,3]dioxol-5-yl)-4,5-diphenyl-1H-imidazole(5j)[27]: Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.51 (s, 1H), 7.63-7.01 (m, 13H), 6.08 (s, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): 147.59, 147.37, 145.37, 128.26, 127.60, 127.02, 126.47, 124.61, 119.27, 108.52, 105.51, 101.67, 101.23.

4,5-diphenyl-2-(thiophen-2-yl)-1H-imidazole(5k): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.80 (s, 1H), 7.69-7.14 (m, 13H). ^{13}C NMR (100 MHz, DMSO-*d6*):141.58, 133.86, 128.22, 127.91, 127.08, 126.60, 126.23, 124.25. HRMS (ESI) Calcd for $C_{19}H_{14}N_2S$ $[M+H]^+$ 303.0955; found, 303.0949.

2-(4-nitrophenyl)-4,5-diphenyl-1H-imidazole(5l): Yellow Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 13.16 (s, 1H), 8.37 (m, 4H), 7.62 (m, 4H), 7.49 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.35(m, 2H), 7.27 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 147.02, 143.86, 138.93, 136.58, 135.07, 130.97, 130.55, 129.22, 129.01, 128.77, 127.61, 127.38, 126.22, 124.76. HRMS (ESI) Calcd for $C_{21}H_{15}N_3O_2$ $[M+H]^+$ 342.1242; found, 342.1236.

2-phenyl-4,5-dip-tolyl-1H-imidazole(5m): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.49 (s, 1H), 7.99 (m, 2H), 7.39–7.22 (m, 8H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 145.14, 136.96, 136.85, 135.48, 132.39, 130.39, 129.15, 128.72, 128.61, 128.20, 128.07, 127.84, 126.96, 125.08. HRMS (ESI) Calcd for $C_{23}H_{20}N_2$ $[M+H]^+$ 325.1704; found, 325.1700.

2-(4-methoxyphenyl)-4,5-dip-tolyl-1H-imidazole(5n): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.41 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 159.27, 145.26, 136.77, 136.48, 135.34, 132.54, 129.12, 128.69, 128.35, 128.10, 127.22, 126.94, 126.59, 123.20, 114.01, 55.15, 20.81, 20.74. HRMS (ESI) Calcd for $C_{24}H_{22}N_2O$ $[M+H]^+$ 355.1810; found, 355.1806.

2-(4-chlorophenyl)-4,5-dip-tolyl-1H-imidazole(5o): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.67 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H),), 7.12 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 144.06, 137.09, 135.61, 132.55, 132.20, 129.23, 129.17, 128.75, 128.71, 128.16, 128.01, 126.96, 126.73, 20.82, 20.74. HRMS (ESI) Calcd for $C_{23}H_{20}N_2$ $[M+H]^+$ 359.1315; found, 359.1276.

2-m-tolyl-4,5-dip-tolyl-1H-imidazole(5p): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.58 (s, 1H), 7.92 (m, 2H), 7.44-7.32 (m, 5H), 7.23-7.10 (m, 5H), 2.38 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 145.24, 137.72, 129.12, 128.74, 128.51, 128.15, 126.97, 125.63, 122.28, 21.07. HRMS (ESI) Calcd for $C_{24}H_{22}N_2$ $[M+H]^+$ 339.1861; found, 339.1857.

2-(3-fluorophenyl)-4,5-dip-tolyl-1H-imidazole(5q): Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.72 (s, 1H), 7.94-7.85 (m, 2H), 7.54-7.40 (m, 6H), 7.25-7.12 (m, 5H), 2.35 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 163.65, 161.23, 143.92, 137.13, 135.69, 132.70, 132.62, 130.80, 130.71, 129.14, 128.77, 128.18, 127.02, 121.12, 114.80, 114.60, 111.63, 111.40, 79.15, 20.78. HRMS (ESI) Calcd for $C_{23}H_{19}FN_2$ $[M+H]^+$ 343.1610; found, 343.1619.

2-(2-bromophenyl)-4,5-dip-tolyl-1H-imidazole(5r): Pale white solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 12.53 (s, 1H), 7.78-7-70 (m, 2H), 7.52-7.37 (m, 6H), 7.23 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d6*): 144.27, 136.89, 136.40, 135.50, 133.30, 132.38, 132.27, 131.76, 130.35, 129.19, 128.73, 128.08, 127.88, 127.57, 127.41, 127.05, 121.59, 79.15, 20.80, 20.75. HRMS (ESI) Calcd for $C_{23}H_{19}BrN_2$ $[M+H]^+$ 403.0809; found, 403.0846.

2-phenyl-1H-phenanthro[9,10-d]imidazoles(5s)[28]: Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 13.54 (s, 1H), 8.90-8.64 (m, 4H), 8.39-8.36 (m, 2H), 7.80-7.70 (m, 2H), 7.68-7.56 (m, 4H), 7.55(m, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): 149.08, 136.91, 132.82, 130.30, 129.23, 128.93, 128.54, 127.63, 127.50, 127.12, 126.12, 125.36, 125.16, 124.06, 123.72, 122.36, 121.96.

2-(4-methoxyphenyl)-1H-phenanthro[9,10-d]imidazoles(5t)[29]: Colourless Solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ, ppm: 13.33 (s, 1H), 8.83 (m, 2H), 8.57 (m, 2H), 8.28 (m, 2H), 7.91-7. 61 (m, 4H), 7.02(m, 2H). 3.86(s, 3H) ^{13}C NMR (100 MHz, DMSO-*d6*): 160.15, 149.26, 131.32, 127.69, 127.42, 127.00, 125.01, 123.79, 122.99, 121.84, 114.32, 113.75, 55.28.

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