EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201403465

Silver-Mediated $C_\alpha(sp^3)$–H Functionalization of Primary Amines: An Oxidative C–N Coupling Strategy for the Synthesis of Two Different Types of 1,2,4,5-Tetrasubstituted Imidazoles

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Keywords: Nitrogen heterocycles / C–H activation / Cross-coupling / Cyclization / Silver / Amines

A new silver(I)-mediated $C_\alpha(sp^3)$–H bond functionalization of primary amines and subsequent oxidative C–N cross-coupling reaction has been demonstrated. This protocol provides a simple, highly efficient, and straightforward approach to form significantly diverse 1,2,4,5-tetrasubstituted imidazoles. In this course of the reaction, a stoichiometric amount of Ag_2CO_3 was employed. Upon completion of reaction, the silver species was successfully recycled and reused without any loss of activity. Good to excellent yields of the products were readily achieved by using this selective oxidative C–N coupling, which was promoted by a crucial silver(I) salt.

Introduction

A selective and efficient synthetic method for the preparation of the widely distributed and biologically significant molecule imidazole has been a continuous objective in the field of synthetic organic chemistry.[1] Imidazoles are an important class of nitrogen-containing five-membered heterocycles and are the core structures of many natural products and various biologically active molecules, such as histidine, histamine, and biotin.[2] Compounds that contain an imidazole moiety also have many pharmacological properties and play important roles in biochemical processes.[3] Although a number of synthetic methods have been reported in the literature,[4] straightforward and regioselective routes for the construction of this potent molecule are still highly attractive.

In the last few decades, the functionalization of carbon-hydrogen bonds by employing oxidative coupling transformations to form new carbon–carbon and carbon–heteroatom (N, O, and S) bonds has been thoroughly examined.[5] In this emerging field, a significant development was attained by using various transition-metal catalysts for the metalation of C–H bonds.[6] Compared to the traditional transition-metal-catalyzed coupling reactions, a silver(I)-mediated oxidative coupling between two different carbon-hydrogen or heteroatom-hydrogen bonds has the inherent advantage of avoiding the prefunctionalization of the substrates.[7] More interestingly, silver(I) species exhibit both carbophilic and oxophilic Lewis acid characteristics, with a slight preference for sigma over pi coordination.[8] These features distinguish silver(I) species as a good class of catalysts for the development of autotandem catalysis that involves the dual activation of C–H and unsaturated C–C bonds. Very recently, a number of silver-mediated oxidative coupling transformations to form C–C and C–N bonds were investigated by Lei et al., in which the efficiency of silver(I) towards the oxidative coupling transformation of terminal alkynes was remarkably notable.[7,9] However, these early studies revealed the relative ease of C(sp)–H bond functionalizations by using silver species to form direct C–C or C–N bonds (see Scheme 1). So, in the field of oxidative cross-coupling research, silver(I)-induced $C(sp^3)$–H bond functionalization to form a new C–C or C–N bond is still very challenging and not easily investigated.

On the basis of the known capabilities of silver(I), we designed the direct oxidative construction of 1,2,4,5-tetrasubstituted imidazoles by activating the $C_\alpha(sp^3)$–H of primary amines and subsequently carrying out an oxidative C–N cross-coupling reaction. However, the $C_\alpha(sp^3)$–H bond functionalization of primary amines is quite difficult and has many challenges. A few examples of $C_\alpha(sp^3)$–H bond functionalization of amines followed by an oxidative cyclization have been previously investigated by employing common transition-metal catalysts such as Cu^I or Ni^{II}.[10] However, in the first case, the Cu^I was utilized for the $C_\alpha(sp^3)$–H bond functionalization of benzylamines to form 2,4,5-trisubstituted oxazole derivatives only. In the later case, the formation of imidazoles required a high temperature for a long period of time. Furthermore, in both reactions, the activity of the catalyst was limited, as there was only one type of primary amine in the reaction, and the simultaneous use of two different types of primary amines in the reaction was not investigated. Thus, these reactions very much lack the versatility for the scope of this reaction.

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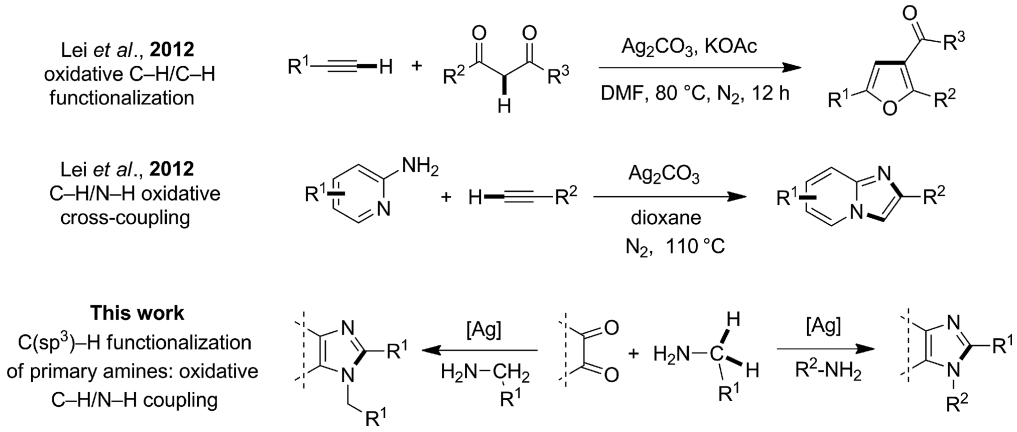
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201403465.



Scheme 1. Silver-mediated C–H bond functionalizations followed by oxidative cyclization (DMF = *N*,*N*-dimethylformamide).

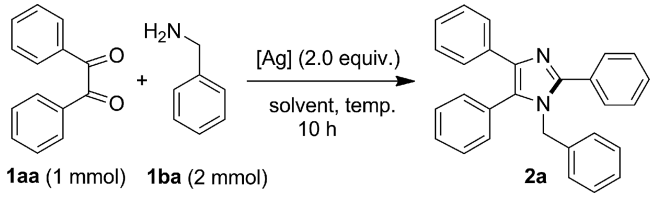
As part of our continuous efforts on silver-induced oxidative cross-coupling transformations, we herein present the silver(I)-mediated $C_\alpha(sp^3)$–H bond functionalization of primary amines and subsequent oxidative C–N coupling transformation to form two different types of highly diverse 1,2,4,5-tetrasubstituted imidazoles. These reactions are carried out at moderate temperatures as well as in a short period of time. Although a stoichiometric amount of Ag_2CO_3 was employed, the silver species was successfully recycled after the reaction for the next $C_\alpha(sp^3)$–H bond functionalization and oxidative cyclization.

Results and Discussion

To synthesize 1,2,4,5-tetrasubstituted imidazoles by oxidative cross-coupling transformations, we first chose the reaction between benzil (**1aa**, 1 mmol) and benzylamine (**1ba**, 2 mmol) to form 1-benzyl-2,4,5-triphenyl-1*H*-imidazole (**2a**). Initially, a number of probable transition-metal salts, including those with Fe^{III}, Au^{III}, or Pt^{II}, were investigated under different reaction conditions, but we did not reach our desired goal. On the basis of the known ability of silver carbonate towards oxidative coupling, we proposed that it might be the appropriate catalyst for this oxidative cross-coupling transformation. Interestingly, we found that the employment of silver carbonate (2.0 equiv.) in 1,4-dioxane (5 mL) at 80 °C effectively catalyzed the formation of 1-benzyl-2,4,5-triphenyl-1*H*-imidazole (**2a**) in excellent yield. We also observed that the use of any additives such as KOAc, NaOAc, K_2CO_3, Cs_2CO_3, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), or HOAc along with the silver carbonate did not increase the yield of the reaction, and 1.0 equiv. of Ag_2CO_3 only afforded a 40% yield of the isolated product (see Table 1, Entry 12). Further research was carried out in various solvents to determine how the catalytic activity of different silver salts compared to Ag_2CO_3 (see Table 1).

Hence, Ag_2CO_3 (2.0 equiv.) in 1,4-dioxane at 80 °C for 10 h was best in terms of both the $C_\alpha(sp^3)$–H functionalization of the primary amine and the oxidative cyclization to afford the desired compound **2a** in good yield within a short time (see Table 1, Entry 11). This unanticipated and highly

Table 1. Optimization of the reaction conditions for the formation of 1-benzyl-2,4,5-triphenyl-1*H*-imidazole (**2a**).



1aa (1 mmol) **1ba** (2 mmol) **2a**

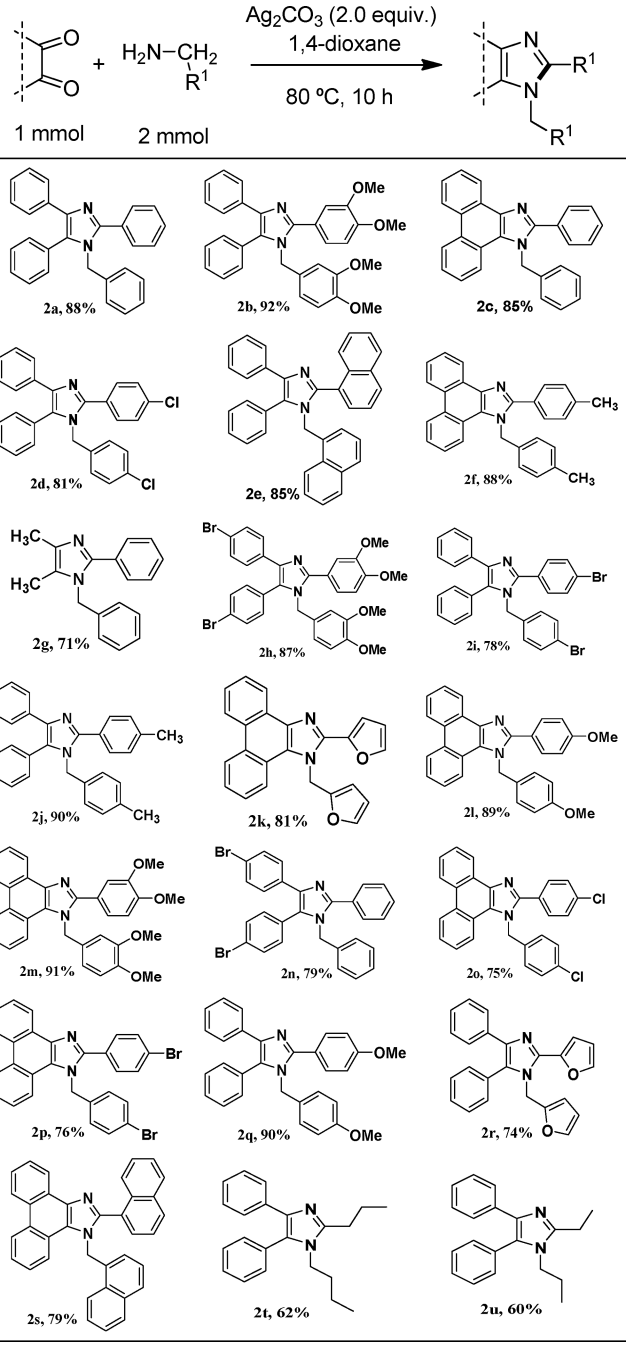
Entry	Temp. [°C]	[Ag] [equiv.]	Solvent	% Yield[a]
1	80	AgOAc (2)	1,4-dioxane	28
2	80	$AgNO_2$ (2)	1,4-dioxane	–
3	80	$AgNO_3$ (2)	1,4-dioxane	–
4	80	$AgClO_4$ (2)	1,4-dioxane	12
5	80	AgI (2)	1,4-dioxane	18
6	80	Ag_2O (2)	1,4-dioxane	35
7	80	Ag_2CO_3 (2)	DMF	45
8	80	Ag_2CO_3 (2)	DMSO[b]	32
9	80	Ag_2CO_3 (2)	toluene	53
10	80	Ag_2CO_3 (2)	DCE[b]	15
11	80	Ag_2CO_3 (2)	1,4-dioxane	88
12	80	Ag_2CO_3 (1)	1,4-dioxane	40
13	45	Ag_2CO_3 (2)	1,4-dioxane	55
14	25	Ag_2CO_3 (2)	1,4-dioxane	30

[a] Isolated yield. [b] DMSO = dimethyl sulfoxide, DCE = 1,2-dichloroethane.

efficient, straightforward approach to the 1,2,4,5-tetrasubstituted imidazoles encouraged us to further examine the feasibility of this oxidative protocol towards an efficient imidazole synthesis. We studied the scope of the reaction by using various electron-rich as well as electron-deficient benzylamines with different 1,2-diketones, and, as a result, we prepared a number of 1,2,4,5-tetrasubstituted imidazoles **2a**–**2u** (see Table 2). In all of the reactions, the product yields were quite satisfactory.

In continuation of our work, we performed two different crossover oxidative coupling reactions to study the electronic effects on the reaction course (see Schemes 2 and 3). First, we studied the reaction of benzil with the combination of an unsubstituted benzylamine and the activated 3,4-dimethoxybenzylamine, which afforded **2b** (28% yield) and **3b** (27% yield) as the major products, each with a 3,4-di-

Table 2. Library synthesis of of 1,2,4,5-tetrasubstituted imidazoles **2a**–**2u**.[a]



[a] Percentage yield provided for each structure.

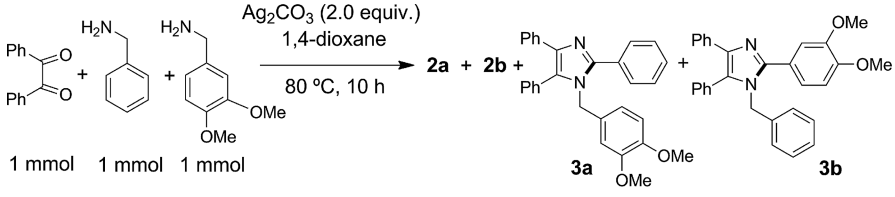
methoxybenzyl group at C-2 (see Scheme 2). On the other hand, the reaction of benzil with an unsubstituted benzylamine and the deactivated 4-bromobenzylamine afforded **2a** (25% yield) and **4a** (24% yield) as the major products, each with a phenyl group at C-2 (see Scheme 3).

We also investigated the scope of highly deactivated benzylamines, such as 2-nitrobenzylamine, but we did not find evidence of the corresponding 1,2,4,5-tetrasubstituted imidazole. The analysis of the results of the two crossover experiments (see Schemes 2 and 3) clearly indicates that electron-rich benzylamines are better suited for the formation of intermediates **II** and **III** than electron-deficient ones (see Scheme 4). After the successful study of the reaction between 1,2-diketones (1 mmol) and primary amines with the $–CH_2–NH_2$ group (2 mmol) to form 1,2,4,5-tetrasubstituted imidazoles, we investigated the reaction between a 1,2-diketone and a primary amine that contained a $–CH_2–NH_2$ group in the presence of a another primary amine that did not contain the $–CH_2–NH_2$ group to form other highly diverse 1,2,4,5-tetrasubstituted imidazoles. Interestingly, the reaction furnished the corresponding 1,2,4,5-tetrasubstituted imidazoles **5a**–**5p** (see Table 3) in good yields under the given optimized reaction conditions.

All of the synthesized 1,2,4,5-tetrasubstituted imidazoles were characterized by spectral and analytical methods. Finally, we confirmed the structures of the imidazole derivatives by using the single-crystal X-ray diffraction study of the two representative compounds **2j** and **5d** (see Figure 1).

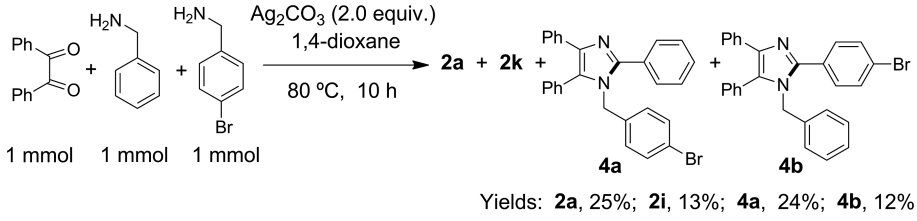
A plausible reaction mechanism was proposed for this silver-mediated $C_\alpha(sp^3)$–H functionalization of primary amines and the subsequent cyclization to form 1,2,4,5-tetrasubstituted imidazoles through an oxidative cross-coupling transformation (see Scheme 4).[7,11] First, the reaction between the 1,2-diketone and a primary amine gives addition product **I**. Next, the $C(sp^3)$–H functionalization by Ag_2CO_3 leads to the formation of intermediate **II**, and the subsequent addition of another primary amine converts **II** into intermediate **III**, which is possibly stabilized by the surrounding Ag^I species.[12] Finally, the silver-mediated oxidative cyclization of **III** furnishes the desired product **IV** (i.e., **2a**–**2u** and **5a**–**5p**) through two single-electron oxidations.

To realize the reaction mechanism of this silver-mediated $C_\alpha(sp^3)$–H functionalization of primary amines and subsequent cyclization to form 1,2,4,5-tetrasubstituted imidazoles, we performed one typical experiment with 9,10-phenanthraquinone (**1ab**) and 4-bromobenzylamine (**1bb**, see Scheme 5). Initially, we mixed 1 equiv. of 9,10-phen-

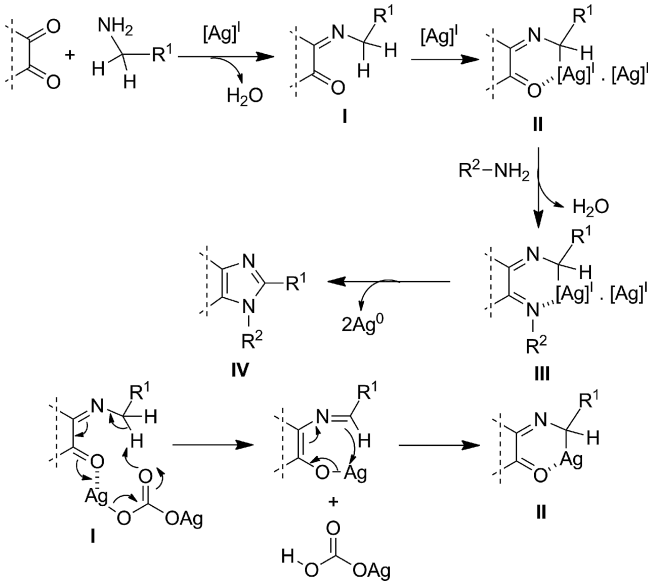


Yields: **2a**, 15%; **2b**, 28%; **3a**, 15%; **3b**, 27%

Scheme 2. Crossover experiment involving benzil, benzylamine, and 3,4-dimethoxybenzylamine.



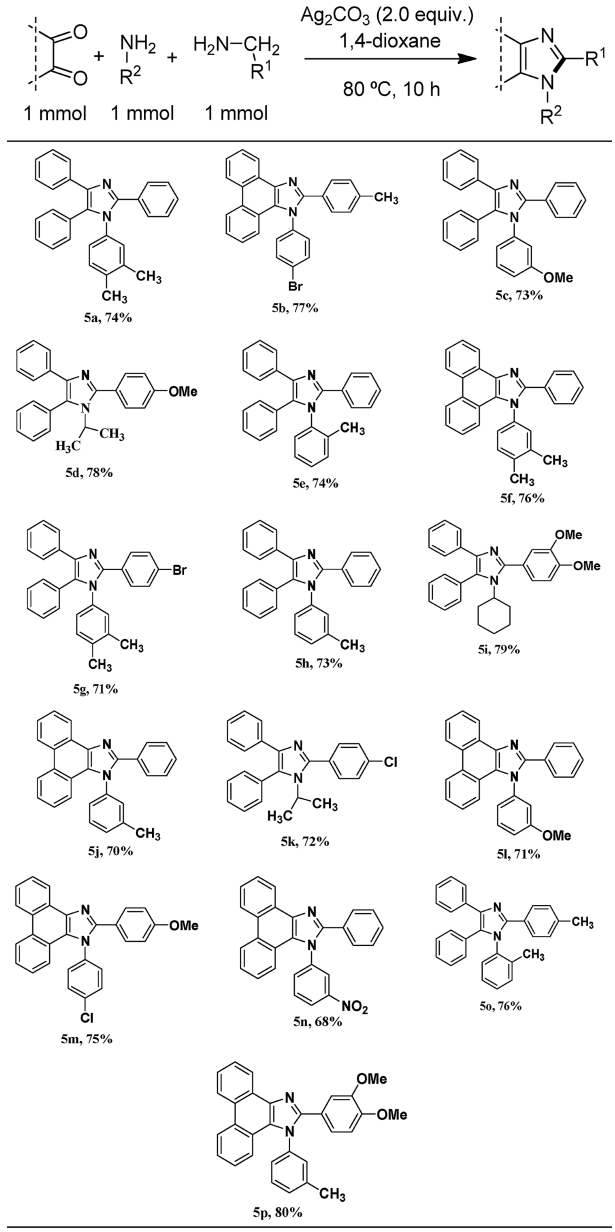
Scheme 3. Crossover experiment involving benzil, benzylamine, and 4-bromobenzylamine.



Scheme 4. Mechanism of the formation of 1,2,4,5-tetrasubstituted imidazoles **2a**–**2u** and **5a**–**5p**.

anthraquinone (**1ab**, 1 mmol) with 1 equiv. 4-bromobenzylamine (**1bb**, 1 mmol) in 1,4-dioxane (5 mL) at room temperature (25 °C) and monitored the reaction by ^{1}H NMR spectroscopic analysis. Primarily, the ^{1}H NMR spectrum (in [D$_6$]DMSO) of the reaction mixture showed only the presence of starting materials. Therefore, we added 2 equiv. of Ag_2CO_3 to the reaction and stirred the mixture for up to 3 h at room temperature. At this stage, we recorded another ^{1}H NMR spectrum (in [D$_6$]DMSO) of the reaction mixture, which showed the formation of intermediate **A**. Later, intermediate **A** was converted in situ into intermediate **B**. The reaction mixture was stirred for an additional 2 h at room temperature. When the ^{1}H NMR spectrum of the reaction mixture was finally recorded, no signal was observed. This result might indicate the formation of insoluble complex **B**. Thereafter, the reaction mixture was equally divided into three parts, and each part was studied differently under different reaction conditions (see Scheme S1). First a portion was heated at 80 °C for 8 h, which afforded only 2-(4-bromophenyl)phenanthro[9,10-*d*]oxazole (**6a**) as the product. The second portion was hydrolyzed with water, which mainly gave the two products 4-bromobenzaldehyde (**6b**)[13] and 9,10-phenanthraquinone (**1ab**).[14] Finally, 4-bromobenzylamine (**1bb**, 0.5 mmol) was added to the third portion, which was then heated at 80 °C for 8 h to give 1-(4-bromobenzyl)-2-(4-bromophenyl)-1*H*-phenanthro[9,10-*d*]-

Table 3. Library synthesis of 1,2,4,5-tetrasubstituted imidazoles **5a**–**5p**.[a]



[a] Percentage yield provided for each structure.

imidazole (**2p**) as the only product. The results of the ^{1}H NMR study as well as the formation of **2p**, **6a**, **6b**, and **1ab** supported the probable formation of complex **A** followed by the formation of complex **B** in the reaction medium.

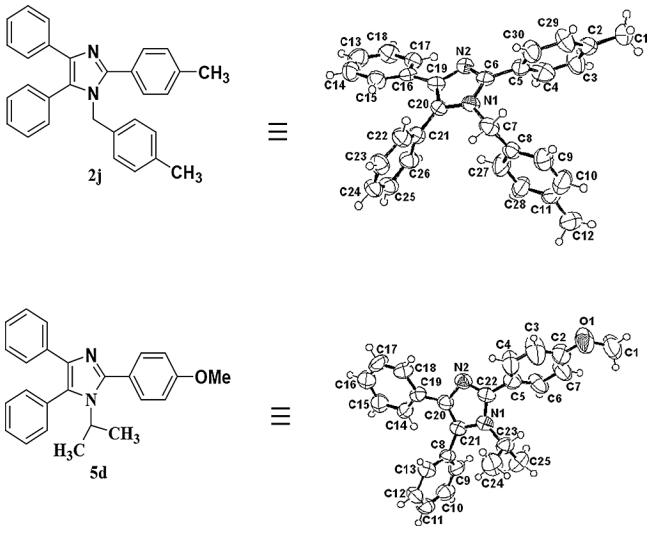
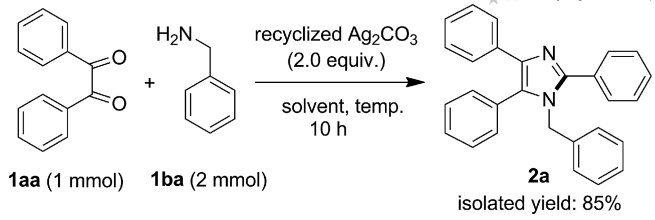


Figure 1. X-ray structures of **2j** and **5d**.

These studies definitely help to understand the reaction mechanism of this silver(I)-mediated oxidative C–N coupling/cyclization.

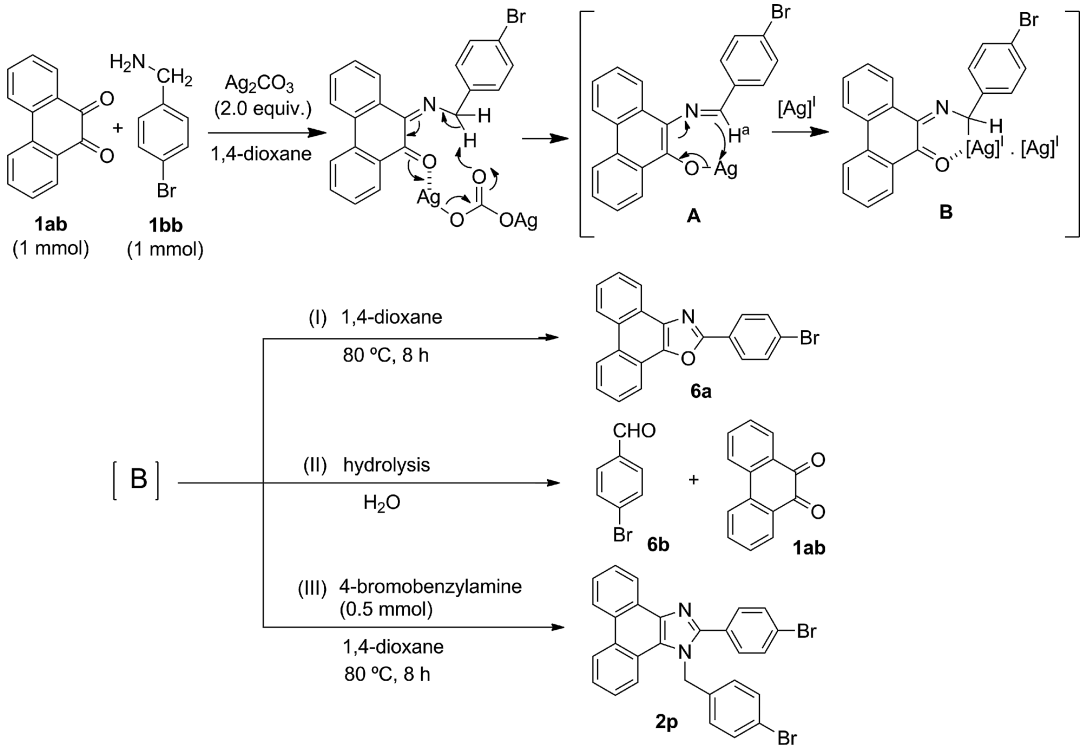
After the reaction, the silver species was successfully recycled[9a] and then reused in the reaction of benzil and benzylamine under the standard reaction conditions. The comparable yield of this reaction (85%) with that obtained by the same reaction with fresh Ag_2CO_3 demonstrates the retention of the activity of the silver species after being recycled (see Scheme 6).



Scheme 6. Reaction with recycled Ag_2CO_3.

Conclusions

In summary, this study led us to discover the ability of silver(I) species to mediate the $C_\alpha(sp^3)$-H functionalization of primary amines followed by an oxidative C–N coupling/cyclization to form two different types of highly diverse 1,2,4,5-tetrasubstituted imidazoles. Furthermore, Ag^I selectively formed one highly diverse 1,2,4,5-tetrasubstituted imidazole when a mixture of primary amines was used in the reaction course. In this oxidative coupling protocol, we have efficiently utilized aliphatic amines and both electron-rich as well as electron-deficient benzylamines, including heteroaromatic benzylamines, with various 1,2-diketones. Hence, the coupling reaction reported herein represents a highly efficient, straightforward approach that is promoted by a crucial silver(I) species for the formation of 1,2,4,5-tetrasubstituted imidazoles. Good to excellent yields of the products were achieved with this protocol.



Scheme 5. Extended experiments with 9,10-phenanthraquinone (**1ab**) and 4-bromobenzylamine (**1bb**).

Experimental Section

General Methods: The ^1H and ^{13}C spectroscopic data were recorded with a Bruker 300 MHz instrument at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million (ppm) downfield from TMS (tetramethylsilane) as the internal reference. Coupling constants (*J*) are reported in Hertz (Hz), and the spin multiplicities are reported as s (singlet), br. s (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). IR spectra were recorded on a Perkin–Elmer Spectrophotometer RX/FT-IR system. The positions of the bands are reported in reciprocal centimeters (cm^{-1}). The CHN analyses were carried out on a 2400 Series II CHNS Analyzer, Perkin–Elmer USA. X-ray diffraction was done on a Bruker SMART diffractometer that was equipped with a graphite monochromator and Mo-K_α (λ = 0.71073 Å) radiation. Melting points were measured by using an open capillary tube in an electric melting point apparatus. The progress of the reaction was monitored by TLC analysis using silica gel (300–400 mesh). Column chromatography was performed with silica gel (60–120 mesh). HRMS analysis of the compounds were performed by the electron spray ionization (ESI) technique at 25–70 eV in a Micromass Q-tof-Micro Quadruple mass spectrometer at The Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India. All the available reagents were purchased from commercial sources and used without purification. The solvents that were used for the reactions were distilled for purity.

General Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles 2a–2u: A mixture of the 1,2-diketone (1 mmol), the primary amine that contained a $–CH_2–NH_2$ group (2 mmol), and silver carbonate (2.0 equiv.) in 1,4-dioxane (5 mL) was stirred at 80 °C for 10 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the solid was removed by filtration and washed with dichloromethane. The solvent of the filtrate was then removed under vacuum, and the resulting crude product was purified by column chromatography over silica gel [60–120 mesh; ethyl acetate/petroleum ether (60–80 °C)]. No further purification was needed.

1-Benzyl-2,4,5-triphenyl-1*H*-imidazole (2a): (see Table 2, Entry 1). White solid (88% yield), m.p. 162–164 °C; ref.[10b] m.p. 160–164 °C). R_f = 0.48 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.50 (m, 4 H, ArH), 7.37–7.05 (m, 14 H, ArH), 6.74–6.72 (m, 2 H, ArH), 5.04 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.9, 137.9, 137.3, 134.3, 130.9, 130.8, 129.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.1, 126.6, 126.2, 125.8, 48.1 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 1603, 1498, 1445, 1027, 758 cm^{-1}. $C_{28}H_{22}N_2$ (386.50): calcd. C 87.01, H 5.74, N 7.25; found C 86.93, H 5.69, N 7.20.

1-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (2b): (see Table 2, Entry 2). Yellow solid (92% yield); m.p. 140–142 °C. R_f = 0.53 [40% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68 (br. s, 2 H, ArH), 7.60–7.15 (m, 10 H, ArH), 6.80–6.68 (m, 2 H, ArH), 6.35–6.27 (m, 2 H, ArH), 5.00 (s, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1, 148.5, 148.3, 147.7, 147.4, 137.2, 133.9, 130.5, 129.6, 129.3, 128.3, 128.1, 127.5, 126.3, 125.8, 122.9, 121.0, 118.1, 117.9, 111.9, 110.8, 109.0, 55.2, 55.1, 55.1, 47.2 ppm. IR (KBr): $\tilde{\nu}$ = 2371, 1608, 1508, 1498, 1495, 1252, 1233, 1025, 765, 699 cm^{-1}. $C_{32}H_{30}N_2O_4$ (506.60): calcd. C 75.87, H 5.97, N 5.53; found C 75.80, H 5.94, N 5.46.

1-Benzyl-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (2c): (see Table 2, Entry 3). White solid (85% yield), m.p. 240–242 °C; ref.[10b] m.p. 238–242 °C. R_f = 0.45 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 7.5 Hz, 1 H, ArH), 8.66 (d, *J* = 8.1 Hz, 1 H, ArH), 8.57 (d, *J* = 8.1 Hz, 1 H, ArH), 7.82 (d, *J* = 7.8 Hz, 1 H, ArH), 7.62–7.50 (m, 4 H, ArH), 7.42–7.07 (m, 10 H, ArH), 5.68 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 137.9, 137.0, 130.4, 129.6, 129.3, 129.2, 128.7, 128.2, 127.8, 127.3, 127.2, 127.0, 126.6, 125.6, 124.8, 124.2, 123.0, 122.9, 122.7, 121.0, 50.7 ppm. IR (KBr): $\tilde{\nu}$ = 1604, 1498, 1456, 1473, 1357, 773, 753, 736, 720, 696 cm^{-1}. $C_{28}H_{20}N_2$ (384.48): calcd. C 87.47, H 5.24, N 7.29; found C 87.39, H 5.20, N 7.25.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole (2d): (see Table 2, Entry 4). White solid (81% yield); m.p. 158–160 °C. R_f = 0.40 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.51 (m, 4 H, ArH), 7.37–7.24 (m, 5 H, ArH), 7.20–7.09 (m, 7 H, ArH), 6.67 (d, *J* = 8.4 Hz, 2 H, ArH), 5.00 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 138.4, 135.7, 135.1, 134.2, 133.4, 130.9, 130.6, 130.3, 130.1, 129.3, 129.0, 128.9, 128.1, 127.3, 126.8, 126.6, 47.7 ppm. IR (KBr): $\tilde{\nu}$ = 2362, 1482, 1093, 1013, 829, 764, 731, 696 cm^{-1}. $C_{28}H_{20}Cl_2N_2$ (455.39): calcd. C 73.85, H 4.43, N 6.15; found C 73.78, H 4.39, N 6.12.

2-(Naphthalen-1-yl)-1-[(naphthalen-1-yl)methyl]-4,5-diphenyl-1*H*-imidazole (2e): (see Table 2, Entry 5). White solid (85% yield); m.p. 218–222 °C. R_f = 0.43 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 7.2 Hz, 1 H, ArH), 7.82–7.74 (m, 5 H, ArH), 7.67–7.51 (m, 4 H, ArH), 7.44–7.21 (m, 13 H, ArH), 6.89 (d, *J* = 7.2 Hz, 1 H, ArH), 5.41 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 138.1, 134.6, 133.6, 133.1, 132.8, 132.7, 131.0, 130.8, 129.8, 129.7, 128.8, 128.5, 128.2, 128.1, 127.8, 126.8, 126.4, 126.0, 126.0, 125.5, 125.1, 124. 8, 123.8, 121.8, 46.1 ppm. IR (KBr): $\tilde{\nu}$ = 1599, 1500, 1442, 1401, 953, 780, 782, 699 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{36}H_{26}N_2$ [M + H]$^+$ 487.2174; found 487.2167. $C_{36}H_{26}N_2$ (486.61): calcd. C 88.86, H 5.39, N 5.76; found C 88.77, H 5.36, N 5.71.

1-(4-Methylbenzyl)-2-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole (2f): (see Table 2, Entry 6). White solid (88% yield), m.p. 226–228 °C; ref.[10b] m.p. 226–230 °C. R_f = 0.46 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 7.8 Hz, 1 H, ArH), 8.75 (d, *J* = 8.1 Hz, 1 H, ArH), 8.66 (d, *J* = 8.1 Hz, 1 H, ArH), 7.94 (d, *J* = 8.1 Hz, 1 H, ArH), 7.70 (t, *J* = 6.9 Hz, 1 H, ArH), 7.63–7.55 (m, 3 H, ArH), 7.49 (t, *J* = 7.8 Hz, 1 H, ArH), 7.36 (t, *J* = 7.5 Hz, 1 H, ArH), 7.21 (d, *J* = 8.1 Hz, 2 H, ArH), 7.13 (d, *J* = 7.5 Hz, 2 H, ArH), 7.05 (d, *J* = 7.5 Hz, 2 H, ArH), 5.74 (s, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.2, 139.6, 137.9, 137.4, 134.0, 130.0, 129.5, 129.4, 129.1, 128.2, 127.6, 127.4, 127.2, 127.0, 126.6, 125.6, 125.5, 124.6, 124.1, 123.0, 122.7, 121.1, 50.5, 21.4, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 2346, 1516, 1476, 824, 754, 720 cm^{-1}. $C_{30}H_{24}N_2$ (412.53): calcd. C 87.35, H 5.86, N 6.79; found C 87.27, H 5.80, N 6.72.

1-Benzyl-4,5-dimethyl-2-phenyl-1*H*-imidazole (2 g): (see Table 2, Entry 7). Light brown solid (71% yield); m.p. 148–150 °C. R_f = 0.58 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2 H, ArH), 7.27–7.21 (m, 6 H, ArH), 6.92 (d, *J* = 7.5 Hz, 2 H, ArH), 5.05 (s, 2 H, CH_2), 2.18 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4, 137.2, 133.7, 131.0, 128.8, 128.4, 128.3, 128.2, 127.4, 125.5, 123.8, 47.9, 12.7, 8.9 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 2882, 2438, 1502, 1471, 1344, 11215, 859, 672 cm^{-1}. $C_{18}H_{18}N_2$ (262.35): calcd. C 82.41, H 6.92, N 10.68; found C 82.34, H 6.85, N 10.65.

4,5-Bis(4-bromophenyl)-1-(3,4-dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-1*H*-imidazole (2h): (see Table 2, Entry 8). Yellow

gummy solid (87% yield). R_f = 0.55 [50% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2 H, ArH), 7.34–7.31 (m, 2 H, ArH), 7.26–7.23 (m, 2 H, ArH), 7.11–7.09 (m, 2 H, ArH), 7.02–6.99 (t, J = 6.9 Hz, 1 H, ArH), 7.63–7.55 (m, 3 H, ArH), 7.49 (t, J = 7.8 Hz, 1 H, ArH), 7.36 (m, 2 H, ArH), 6.80 (d, J = 8.7 Hz, 1 H, ArH), 6.66 (d, J = 8.4 Hz, 1 H, ArH), 6.31 (d, J = 8.4 Hz, 1 H, ArH), 6.21 (br. s, 1 H, ArH), 4.93 (s, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 149.1, 148.9, 148.4, 137.1, 133.1, 132.4, 132.1, 131.1, 129.7, 128.6, 128.3, 123.1, 121.4, 120.3, 118.3, 112.2, 111.2, 111.0, 109.2, 55.8, 55.7, 48.0 ppm. IR (KBr): $\tilde{\nu}$ = 2343, 1612, 1527, 1480, 1455, 1192, 1033, 825, 761 cm^{-1}. $C_{32}H_{28}Br_2N_2O_4$ (664.39): calcd. C 57.85, H 4.25, N 4.22; found C 57.79, H 4.18, N 4.20.

1-(4-Bromobenzyl)-2-(4-bromophenyl)-4,5-diphenyl-1*H*-imidazole (2i): (see Table 2, Entry 9). Off-white solid (78% yield); m.p. 128–130 °C. R_f = 0.45 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.5 Hz, 2 H, ArH), 7.47–7.37 (m, 5 H, ArH), 7.34–7.27 (m, 5 H, ArH), 7.22–7.08 (m, 4 H, ArH), 6.59 (d, J = 8.4 Hz, 2 H, ArH), 4.96 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.9, 136.3, 134.2, 131.9, 131.0, 130.6, 130.5, 130.4, 129.6, 129.1, 129.0, 128.4, 128.3, 128.1, 127.7, 126.9, 126.8, 123.5, 121.6, 47.8 ppm. IR (KBr): $\tilde{\nu}$ = 2359, 1508, 1248, 1066, 838, 773, 716 cm^{-1}. $C_{28}H_{20}Br_2N_2$ (544.29): calcd. C 61.79, H 3.70, N 5.15; found C 61.70, H 3.67, N 5.08.

1-(4-Methylbenzyl)-4,5-diphenyl-2-*p*-tolyl-1*H*-imidazole (2j): (see Table 2, Entry 10). White solid (90% yield), m.p. 132–134 °C; ref.[10b] m.p. 132–135 °C. R_f = 0.41 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.52 (m, 4 H, ArH), 7.28–7.26 (m, 3 H, ArH), 7.20–7.14 (m, 7 H, ArH), 6.97 (d, J = 7.8 Hz, 2 H, ArH), 6.67 (d, J = 7.5 Hz, 2 H, ArH), 5.02 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.0, 138.6, 137.9, 136.8, 134.6, 131.1, 131.0, 129.8, 129.2, 129.1, 128.8, 128.8, 128.6, 128.4, 128.1, 127.9, 126.7, 126.1, 125.8, 47.9, 21.2, 20.9 ppm. IR (KBr): $\tilde{\nu}$ = 3023, 2940, 2366, 1599, 1499, 1482, 1450, 1390, 1335, 822, 780, 703 cm^{-1}. $C_{30}H_{26}N_2$ (414.55): calcd. C 86.92, H 6.32, N 6.76; found C 86.83, H 6.25, N 6.73.

2-(Furan-2-yl)-1-[(furan-2-yl)methyl]-1*H*-phenanthro[9,10-*d*]imidazole (2k): (see Table 2, Entry 11). Brown solid (81% yield); m.p. 102–104 °C. R_f = 0.52 [15% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74–8.67 (m, 2 H, ArH), 8.57 (d, J = 8.1 Hz, 1 H, ArH), 8.08 (d, J = 6.9 Hz, 1 H, ArH), 7.64–7.37 (m, 6 H, ArH), 6.93–6.92 (m, 1 H, ArH), 6.50 (br. s, 1 H, ArH), 6.23 (br. s, 1 H, ArH), 6.06 (br. s, 1 H, ArH), 5.87 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 144.7, 143.9, 143.3, 142.6, 138.0, 129.4, 128.3, 127.2, 127.0, 126.7, 125.8, 125.1, 124.2, 123.0, 122.8, 120.9, 112.2, 111.7, 110.8, 108.1, 45.1 ppm. IR (KBr): $\tilde{\nu}$ = 2336, 1629, 1541, 1493, 1441, 1220, 1163, 782 cm^{-1}. $C_{24}H_{16}N_2O_2$ (364.40): calcd. C 79.11, H 4.43, N 7.69; found C 79.03, H 4.40, N 7.61.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1*H*-phenanthro[9,10-*d*]-imidazole (2l): (see Table 2, Entry 12). White solid (89% yield); m.p. 122–124 °C. R_f = 0.47 [30% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, J = 8.4 Hz, 1 H, ArH), 8.74 (d, J = 8.4 Hz, 1 H, ArH), 8.65 (d, J = 8.4 Hz, 1 H, ArH), 7.93 (d, J = 8.1 Hz, 1 H, ArH), 7.70 (t, J = 7.5 Hz, 1 H, ArH), 7.60 (d, J = 7.8 Hz, 3 H, ArH), 7.48 (t, J = 7.2 Hz, 1 H, ArH), 7.36 (t, J = 7.5 Hz, 1 H, ArH), 7.21 (d, J = 8.1 Hz, 2 H, ArH), 7.13 (d, J = 7.5 Hz, 2 H, ArH), 7.05 (d, J = 7.5 Hz, 1 H, ArH), 7.07 (d, J = 8.1 Hz, 2 H, ArH), 6.93 (d, J = 8.4 Hz, 2 H, ArH), 6.84 (d, J = 8.1 Hz, 2 H, ArH), 5.68 (s, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 159.1, 153.0, 137.8, 130.9, 129.0, 128.2, 127.4, 127.1, 126.9, 126.8, 126.6, 125.4, 124.6, 124.1, 123.0, 122.8, 122.6, 121.0, 114.7, 114.1, 55.3, 55.2, 50.2 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 2837, 2346, 1610, 1512, 1475, 1246, 1177, 1029, 754, 722 cm^{-1}. $C_{30}H_{24}N_2O_2$ (444.53): calcd. C 81.06, H 5.44, N 6.30; found C 81.01, H 5.43, N 6.25.

1-(3,4-Dimethoxybenzyl)-2-(3,4-dimethoxyphenyl)-1*H*-phenanthro-[9,10-*d*]imidazole (2m): (see Table 2, Entry 13). Light yellow solid (91% yield); m.p. 200–202 °C. R_f = 0.58 [50% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (d, J = 7.8 Hz, 1 H, ArH), 8.79 (d, J = 8.1 Hz, 1 H, ArH), 8.70 (d, J = 8.1 Hz, 1 H, ArH), 7.96 (d, J = 8.1 Hz, 1 H, ArH), 7.73 (t, J = 7.8 Hz, 1 H, ArH), 7.64 (t, J = 7.5 Hz, 1 H, ArH), 7.54 (t, J = 6.9 Hz, 1 H, ArH), 7.41 (t, J = 7.2 Hz, 1 H, ArH), 7.30–7.26 (m, 2 H, ArH), 6.91 (d, J = 8.1 Hz, 1 H, ArH), 6.84–6.74 (m, 3 H, ArH), 5.73 (s, 2 H, CH_2), 3.91 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0, 150.3, 149.8, 148.9, 148.6, 129.6, 129.1, 128.2, 127.2, 126.7, 125.5, 124.7, 124.2, 123.0, 122.9, 122.7, 122.2, 121.0, 118.0, 112.5, 111.8, 111.2, 108.6, 55.9, 55.9, 55.6, 50.6 ppm. IR (KBr): $\tilde{\nu}$ = 2934, 2341, 1607, 1509, 1491, 1459, 1251, 1136, 1023, 757, 723 cm^{-1}. $C_{32}H_{28}N_2O_4$ (504.58): calcd. C 76.17, H 5.59, N 5.55; found C 76.06, H 5.51, N 5.48.

1-Benzyl-4,5-bis(4-bromophenyl)-2-phenyl-1*H*-imidazole (2n): (see Table 2, Entry 14). White solid (79% yield), m.p. 128–130 °C; ref.[10b] m.p. 128–131 °C. R_f = 0.39 [10% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.58 (m, 2 H, ArH), 7.39–7.15 (m, 12 H, ArH), 6.99–6.96 (m, 2 H, ArH), 6.75–6.74 (m, 2 H, ArH), 5.02 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.7, 137.5, 137.1, 133.2, 132.5, 132.2, 131.3, 130.5, 129.7, 129.2, 129.0, 128.8, 128.7, 128.4, 127.6, 125.9, 123.3, 120.6, 48.5 ppm. IR (KBr): $\tilde{\nu}$ = 2353, 1588, 1338, 1136, 801, 754 cm^{-1}. $C_{28}H_{20}Br_2N_2$ (544.29): calcd. C 61.79, H 3.70, N 5.15; found C 61.76, H 3.61, N 5.04.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1*H*-phenanthro[9,10-*d*]imidazole (2o): (see Table 2, Entry 15). White solid (75% yield); m.p. 258–260 °C. R_f = 0.42 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86–8.68 (m, 3 H, ArH), 7.87 (d, J = 8.1 Hz, 1 H, ArH), 7.74–7.56 (m, 6 H, ArH), 7.45–7.34 (m, 4 H, ArH), 7.13 (d, J = 6.9 Hz, 2 H, ArH), 5.76 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.0, 129.8, 129.2, 127.6, 126.9, 123.0, 59.4, 53.4 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2342, 1607, 1490, 1474, 1408, 1350, 1094, 1014, 841, 759 cm^{-1}. $C_{28}H_{18}Cl_2N_2$ (453.37): calcd. C 74.18, H 4.00, N 6.18; found C 74.15, H 3.99, N 6.09.

1-(4-Bromobenzyl)-2-(4-bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole (2p): (see Table 2, Entry 16). White solid (76% yield); m.p. 230–232 °C. R_f = 0.49 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (d, J = 7.8 Hz, 2 H, ArH), 8.67–8.66 (m, 1 H, ArH), 7.93 (d, J = 8.4 Hz, 2 H, ArH), 7.58–7.39 (m, 9 H, ArH), 7.01 (d, J = 8.4 Hz, 2 H, ArH), 5.68 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.0, 132.7, 132.2, 131.0, 129.4, 129.1, 128.6, 128.4, 127.5, 127.3, 127.1, 126.9, 126.3, 125.9, 125.1, 124.4, 123.5, 122.6, 120.7, 50.3 ppm. IR (KBr): $\tilde{\nu}$ = 2338, 1601, 1505, 1451, 1421, 1377, 1035, 861, 772 cm^{-1}. $C_{28}H_{18}Br_2N_2$ (542.27): calcd. C 62.02, H 3.35, N 5.17; found C 61.96, H 3.32, N 5.11.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (2q): (see Table 2, Entry 17). Off-white solid (90% yield), m.p. 152–154 °C; ref.[10b] m.p. 152–154 °C. R_f = 0.44 [30% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 4 H, ArH), 7.29–7.27 (m, 3 H, ArH), 7.21–7.08 (m, 5 H, ArH), 6.90–6.87 (m, 2 H, ArH), 6.68 (br. s, 4 H, ArH), 4.98 (s, 2

H, CH_2), 3.73 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 158.6, 147.7, 137.6, 134.5, 131.1, 130.9, 130.2, 129.6, 129.5, 128.6, 128.3, 127.8, 127.0, 126.6, 126.0, 123.4, 113.8, 113.8, 55.1, 55.0, 47.5 ppm. IR (KBr): $\tilde{\nu}$ = 2380, 1700, 1611, 1437, 1242, 1178, 1032, 842, 698 cm^{-1}. $C_{30}H_{26}N_2O_2$ (446.55): calcd. C 80.69, H 5.87, N 6.27; found C 80.61, H 5.86, N 6.23.

2-(Furan-2-yl)-1-[(furan-2-yl)methyl]-4,5-diphenyl-1*H*-imidazole (2r): (see Table 2, Entry 18). Brown gummy solid (74% yield); R_f = 0.40 [20% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.02 (m, 12 H, ArH), 6.84–6.82 (m, 1 H, ArH), 6.44–6.42 (m, 1 H, ArH), 6.12–6.11 (m, 1 H, ArH), 5.75–5.74 (m, 1 H, ArH), 5.12 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 145.1, 142.8, 142.2, 138.8, 138.0, 133.9, 131.2, 130.1, 130.0, 128.9, 128.0, 126.9, 126.5, 111.5, 110.4, 107.8, 41.9 ppm. IR (KBr): $\tilde{\nu}$ = 2353, 1613, 1588, 1511, 1446, 1383, 1074, 767 cm^{-1}. $C_{24}H_{18}N_2O_2$ (366.42): calcd. C 78.67, H 4.95, N 7.65; found C 78.63, H 4.90, N 7.62.

2-(Naphthalen-1-yl)-1-(naphthalen-1-ylmethyl)-1*H*-phenanthro[9,10-*d*]-imidazole (2s): (see Table 2, Entry 19). Light brown solid (79% yield); m.p. 244–246 °C. R_f = 0.36 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.87 (d, J = 7.8 Hz, 1 H, ArH), 8.76 (d, J = 8.4 Hz, 1 H, ArH), 8.70 (d, J = 8.1 Hz, 1 H, ArH), 7.92–7.85 (m, 3 H, ArH), 7.78–7.60 (m, 6 H, ArH), 7.56–7.41 (m, 6 H, ArH), 7.29 (t, J = 7.5 Hz, 1 H, ArH), 7.21–7.13 (m, 2 H, ArH), 6.92 (d, J = 6.9 Hz, 1 H, ArH), 6.02 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.4, 138.1, 133.8, 133.7, 133.0, 131.8, 130.3, 129.7, 129.2, 129.1, 128.6, 128.4, 128.3, 127.6, 127.5, 127.4, 127.2, 126.8, 126.7, 126.4, 126.1, 125.8, 125.7, 125.0, 124.8, 124.2, 123.8, 123.2, 123.1, 123.0, 122.8, 121.8, 121.0, 48.8 ppm. IR (KBr): $\tilde{\nu}$ = 1612, 1523, 1458, 1411, 1053, 791, 708 cm^{-1}. $C_{36}H_{24}N_2$ (484.60): calcd. C 89.23, H 4.99, N 5.78; found C 89.22, H 4.92, N 5.75.

1-Butyl-4,5-diphenyl-2-propyl-1*H*-imidazole (2t): (see Table 2, Entry 20).[10b] Yellow gummy solid (62% yield); R_f = 0.65 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.32 (m, 5 H, ArH), 7.26–7.24 (m, 2 H, ArH), 7.10–6.99 (m, 3 H, ArH), 3.64 (t, J = 7.8 Hz, 2 H, NCH_2), 2.67 (t, J = 8.1 Hz, 2 H, CH_2), 1.88–1.80 (m, 2 H, CH_2), 1.41–1.36 (m, 2 H, CH_2), 1.11–0.99 (m, 5 H, 1 CH_2, 1 CH_3), 0.68 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.6, 136.2, 134.8, 131.6, 130.8, 128.6, 128.1, 127.8, 127.7, 126.4, 125.6, 43.2, 32.6, 29.2, 21.7, 19.5, 13.9, 13.2 ppm. IR (KBr): $\tilde{\nu}$ = 2912, 2845, 1606, 1464, 1072, 766, 692 cm^{-1}. $C_{22}H_{26}N_2$ (318.46): calcd. C 82.97, H 8.23, N 8.80; found C 82.90, H 8.21, N 8.72.

2-Ethyl-4,5-diphenyl-1-propyl-1*H*-imidazole (2u): (see Table 2, Entry 21). White solid (60% yield); m.p. 78–80 °C. R_f = 0.65 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5 H, ArH), 7.23–7.20 (m, 2 H, ArH), 7.08–6.95 (m, 3 H, ArH), 3.57 (t, J = 6.3 Hz, 2 H, NCH_2), 2.70 (q, J = 7.5 Hz, 2 H, CH_2), 1.46–1.31 (m, 5 H, CH_2, CH_3), 0.64 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 136.3, 134.8, 131.7, 130.9, 128.8, 128.2, 128.0, 127.8, 126.5, 125.7, 45.1, 23.9, 20.6, 12.6, 10.9 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2838, 1592, 1458, 1070, 783, 703 cm^{-1}. $C_{20}H_{22}N_2$ (290.41): calcd. C 82.72, H 7.64, N 9.65; found C 82.68, H 7.61, N 9.61.

1-(3,4-Dimethoxybenzyl)-2,4,5-triphenyl-1*H*-imidazole (3a): Yellow gummy solid (15% yield); R_f = 0.41 [40% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.63 (m, 2 H, ArH), 7.57–7.54 (m, 2 H, ArH), 7.40–7.32 (m, 7 H, ArH), 7.26–7.11 (m, 4 H, ArH), 6.65 (d, J = 8.1 Hz, 1 H, ArH), 6.28 (d, J = 8.1 Hz, 1 H, ArH), 6.20 (s, 1 H, ArH), 5.03 (s, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 148.1, 147.8, 137.9, 134.2, 131.0, 130.8, 129.9, 129.7, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 127.9, 126.7, 126.3, 118.5, 111.0, 109.5, 55.7, 55.6, 47.8 ppm. IR (KBr): $\tilde{\nu}$ = 2933, 2834, 2369, 1603, 1509, 1459, 1237, 1139, 1026, 774, 696 cm^{-1}. $C_{30}H_{26}N_2O_2$ (446.55): calcd. C 80.69, H 5.87, N 6.27; found C 80.65, H 5.81, N 6.22.

1-Benzyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (3b): Light yellow solid (27% yield); m.p. 158–160 °C. R_f = 0.39 [40% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H, ArH), 7.23–7.04 (m, 13 H, ArH), 6.81–6.75 (m, 3 H, ArH), 5.00 (s, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.6, 148.7, 147.9, 137.8, 137.8, 134.4, 130.9, 129.8, 128.7, 128.5, 128.0, 127.2, 126.7, 126.2, 125.8, 123.5, 121.5, 112.2, 111.0, 55.8, 55.5, 48.1 ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2361, 1714, 1630, 1442, 1249, 1185, 1058, 764 cm^{-1}. $C_{30}H_{26}N_2O_2$ (446.55): calcd. C 80.69, H 5.87, N 6.27; found C 80.61, H 5.84, N 6.22.

1-(4-Bromobenzyl)-2,4,5-triphenyl-1*H*-imidazole (4a): White solid (24% yield); m.p. 172–174 °C. R_f = 0.45 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 4 H, ArH), 7.29–7.01 (m, 13 H, ArH), 6.53 (d, J = 8.4 Hz, 2 H, ArH), 4.93 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.7, 138.0, 136.2, 134.0, 131.4, 130.8, 130.6, 129.6, 128.7, 128.5, 128.3, 127.8, 127.4, 126.5, 126.2, 125.7, 121.0, 47.4 ppm. IR (KBr): $\tilde{\nu}$ = 2343, 1498, 1261, 1109, 867, 779 cm^{-1}. $C_{28}H_{21}BrN_2$ (465.39): calcd. C 72.26, H 4.55, N 6.02; found C 72.20, H 4.49, N 5.99.

1-Benzyl-2-(4-bromophenyl)-4,5-diphenyl-1*H*-imidazole (4b): White solid (12% yield); m.p. 146–148 °C. R_f = 0.46 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.42 (m, 2 H, ArH), 7.36 (br. s, 4 H, ArH), 7.27–7.01 (m, 11 H, ArH), 6.69–6.67 (m, 2 H, ArH), 4.95 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 137.1, 134.2, 131.6, 130.9, 130.6, 130.3, 129.6, 128.8, 128.6, 128.0, 127.4, 126.7, 126.4, 125.7, 123.2, 48.2 ppm. IR (KBr): $\tilde{\nu}$ = 2353, 1511, 1263, 1082, 847, 763 cm^{-1}. $C_{28}H_{21}BrN_2$ (465.39): calcd. C 72.26, H 4.55, N 6.02; found C 72.19, H 4.51, N 5.93.

General Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles 5a–5r: A mixture of the 1,2-diketone (1 mmol), the primary amine with a $–CH_2–NH_2$ group (1 mmol), another primary amine without any $–CH_2–NH_2$ group (1 mmol), and silver carbonate (2.0 equiv.) in 1,4-dioxane (5 mL) was stirred at 80 °C for 10 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the solid was removed by filtration and washed with dichloromethane. The solvent of the filtrate was then removed under vacuum, and the resulting crude product was purified by column chromatography over 60–120 mesh silica gel [ethyl acetate/petroleum ether (60–80 °C)]. No further purification was needed.

1-(3,4-Dimethylphenyl)-2,4,5-triphenyl-1*H*-imidazole (5a): (see Table 3, Entry 1). White solid (74% yield); m.p. 164–166 °C. R_f = 0.39 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.8 Hz, 2 H, ArH), 7.53–7.51 (m, 2 H, ArH), 7.30–7.18 (m, 11 H, ArH), 7.01 (d, J = 7.8 Hz, 1 H, ArH), 6.84–6.80 (m, 2 H, ArH), 2.22 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 138.2, 137.5, 136.8, 134.7, 134.6, 131.2, 131.1, 130.9, 130.8, 130.1, 129.3, 128.9, 128.3, 128.2, 127.9, 127.5, 126.6, 125.7, 19.7, 19.5 ppm. IR (KBr): $\tilde{\nu}$ = 3025, 1601, 1499, 1478, 1445, 959, 768, 704, 692 cm^{-1}. $C_{29}H_{24}N_2$ (400.52): calcd. C 86.97, H 6.04, N 6.99; found C 86.88, H 6.01, N 6.97.

1-(4-Bromophenyl)-2-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole (5b): (see Table 3, Entry 2). Orange solid (77% yield); m.p. 196–198 °C.

R_f = 0.41 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (d, J = 7.8 Hz, 1 H, ArH), 8.61 (d, J = 8.4 Hz, 1 H, ArH), 8.55 (d, J = 8.1 Hz, 1 H, ArH), 7.64–7.49 (m, 4 H, ArH), 7.38 (t, J = 7.2 Hz, 1 H, ArH), 7.30 (d, J = 7.2 Hz, 2 H, ArH), 7.22–7.15 (m, 3 H, ArH), 7.06 (d, J = 8.1 Hz, 1 H, ArH), 7.00 (d, J = 7.2 Hz, 2 H, ArH), 2.22 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 139.0, 137.9, 137.4, 133.2, 130.7, 129.3, 129.2, 129.0, 128.2, 127.7, 127.3, 127.2, 127.1, 126.3, 125.6, 124.8, 124.1, 123.6, 123.0, 122.8, 120.5, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 1605, 1499, 1457, 1023, 785, 712 cm^{-1}. $C_{28}H_{19}BrN_2$ (463.38): calcd. C 72.58, H 4.13, N 6.05; found C 72.54, H 4.08, N 5.99.

1-(3-Methoxyphenyl)-2,4,5-triphenyl-1*H*-imidazole (5c): (see Table 3, Entry 3). White solid (73% yield); m.p. 146–148 °C. R_f = 0.34 [20% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.53 (m, 2 H, ArH), 7.52–7.49 (m, 2 H, ArH), 7.30–7.17 (m, 12 H, ArH), 6.86–6.72 (m, 1 H, ArH), 6.68–6.66 (m, 1 H, ArH), 6.58–6.57 (m, 1 H, ArH), 3.61 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 146.8, 138.2, 138.1, 134.5, 131.0, 130.7, 130.6, 129.6, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 126.5, 120.7, 114.3, 113.9, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 3055.4, 1602.5, 1488.2, 1463.8, 761.7, 710.1, 690.6 cm^{-1}. $C_{28}H_{22}N_2O$ (402.49): calcd. C 83.56, H 5.51, N 6.96; found C 83.48, H 5.43, N 6.91.

1-Isopropyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5d): (see Table 3, Entry 4). White solid (78% yield); m.p. 166–168 °C. R_f = 0.51 [30% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.4 Hz, 2 H, ArH), 7.54–7.43 (m, 7 H, ArH), 7.16–7.07 (m, 3 H, ArH), 6.99 (d, J = 8.7 Hz, 2 H, ArH), 4.46–4.41 (m, 1 H, NCH), 3.84 (s, 3 H, OCH_3), 1.24 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 147.2, 137.4, 134.5, 132.4, 132.0, 131.2, 128.6, 128.5, 127.7, 126.5, 125.8, 124.5, 113.6, 55.1, 49.1, 23.0 ppm. IR (KBr): $\tilde{\nu}$ = 3036, 1612, 1491, 1433, 1002, 751 cm^{-1}. $C_{25}H_{24}N_2O$ (368.48): calcd. C 81.49, H 6.57, N 7.60; found C 81.48, H 6.53, N 7.55.

2,4,5-Triphenyl-1-*o*-tolyl-1*H*-imidazole (5e): (see Table 3, Entry 5). White solid (74% yield); m.p. 162–164 °C. R_f = 0.41 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.54 (m, 2 H, ArH), 7.39–7.36 (m, 2 H, ArH), 7.20–7.02 (m, 15 H, ArH), 1.80 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7, 138.4, 136.3, 136.1, 134.5, 130.9, 130.7, 130.6, 129.4, 129.0, 128.2, 128.1, 127.9, 127.3, 126.6, 126.5, 17.6 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 1602, 1495, 1441, 960, 764, 696 cm^{-1}. $C_{28}H_{22}N_2$ (386.50): calcd. C 87.01, H 5.74, N 7.25; found C 86.95, H 5.68, N 7.18.

1-(3,4-Dimethylphenyl)-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (5f): (see Table 3, Entry 6). White solid (76% yield); m.p. 222–224 °C. R_f = 0.45 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (d, J = 8.1 Hz, 1 H, ArH), 8.70–8.62 (m, 2 H, ArH), 7.71 (t, J = 7.8 Hz, 1 H, ArH), 7.63–7.55 (m, 3 H, ArH), 7.46–7.40 (m, 1 H, ArH), 7.27–7.20 (m, 8 H, ArH), 2.36 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.9, 138.6, 138.3, 137.2, 136.2, 131.0, 130.7, 129.6, 129.3, 129.1, 128.6, 128.2, 128.0, 127.3, 127.1, 126.1, 125.4, 124.6, 123.9, 123.1, 123.0, 122.7, 120.9, 19.7, 19.6 ppm. IR (KBr): $\tilde{\nu}$ = 3044, 1613, 1499, 1452, 1379, 826, 759, 727, 696 cm^{-1}. $C_{29}H_{22}N_2$ (398.51): calcd. C 87.41, H 5.56, N 7.03; found C 87.38, H 5.50, N 6.95.

2-(4-Bromophenyl)-1-(3,4-dimethylphenyl)-4,5-diphenyl-1*H*-imidazole (5g): (see Table 3, Entry 7). White solid (71% yield); m.p. 144–146 °C. R_f = 0.47 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.4 Hz, 1 H, ArH), 7.53 (d, J = 7.8 Hz, 2 H, ArH), 7.41–7.39 (m, 1 H, ArH), 7.33–7.00 (m, 10 H, ArH), 6.99 (d, J = 7.8 Hz, 1 H, ArH), 6.76–6.72 (m, 2 H, ArH), 2.20 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.7, 138.2, 137.7, 137.1, 134.3, 131.3, 131.0, 130.5, 130.2, 129.4, 129.0, 128.3, 128.1, 127.4, 126.6, 125.5, 122.5, 19.6, 19.4 ppm. IR (KBr): $\tilde{\nu}$ = 3048, 1604, 1505, 1431, 988, 194, 719 cm^{-1}. $C_{29}H_{23}BrN_2$ (479.42): calcd. C 72.65, H 4.84, N 5.84; found C 72.58, H 4.80, N 5.77.

2,4,5-Triphenyl-1-*m*-tolyl-1*H*-imidazole (5h): (see Table 3, Entry 8). White solid (73% yield); m.p. 182–184 °C. R_f = 0.43 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.4 Hz, 2 H, ArH), 7.38–7.35 (m, 2 H, ArH), 7.14–6.97 (m, 13 H, ArH), 6.75 (br. s, 2 H, ArH), 2.09 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.5, 139.7, 138.9, 137.7, 135.2, 131.8, 131.6, 131.4, 131.3, 129.6, 129.5, 129.4, 128.9, 128.7, 128.5, 128.0, 127.1, 126.1, 21.7 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 1601, 1490, 1444, 962, 776, 696 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{28}H_{22}N_2$ [M + H]$^+$ 387.1861; found 387.1859. $C_{28}H_{22}N_2$ (386.50): calcd. C 87.01, H 5.74, N 7.25; found C 86.96, H 5.73, N 7.21.

1-Cyclohexyl-2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazole (5i): (see Table 3, Entry 9). Yellow solid (79% yield); m.p. 124–126 °C. R_f = 0.54 [50% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (br. s, 7 H, ArH), 7.18–7.01 (m, 5 H, ArH), 6.93 (d, J = 8.1 Hz, 1 H, ArH), 4.03–3.87 (m, 7 H, NCH, 2 OCH_3), 1.85–1.82 (m, 2 H, 2 CH), 1.64–1.42 (m, 5 H, 5 CH), 1.10–0.98 (m, 2 H, CH_2), 0.80–0.76 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.5, 148.6, 147.4, 137.4, 134.5, 132.4, 132.0, 128.8, 128.6, 128.5, 128.0, 127.9, 127.7, 126.5, 125.8, 124.7, 122.4, 113.2, 110.7, 58.2, 55.8, 33.4, 26.0, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 3036, 1596, 1483, 1421, 1038, 788, 704 cm^{-1}. $C_{29}H_{30}N_2O_2$ (438.57): calcd. C 79.42, H 6.89, N 6.39; found C 79.38, H 6.85, N 6.32.

2-Phenyl-1-*m*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole (5j): (see Table 3, Entry 10). White solid (70% yield); m.p. 168–170 °C. R_f = 0.46 [20% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (d, J = 8.1 Hz, 1 H, ArH), 8.59–8.50 (m, 2 H, ArH), 7.55–7.40 (m, 4 H, ArH), 7.32–7.23 (m, 2 H, ArH), 7.14–7.04 (m, 8 H, ArH), 2.23 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.7, 140.2, 138.5, 137.1, 131.2, 130.4, 130.3, 130.0, 129.7, 129.4, 129.3, 129.2, 128.7, 128.2, 128.0, 127.1, 126.1, 126.0, 125.4, 127.7, 124.0, 123.0, 122.8, 122.7, 120.8, 116.5, 21.2 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 1603, 1471, 1456, 1378, 989, 758, 728, 703 cm^{-1}. $C_{28}H_{20}N_2$ (384.48): calcd. C 87.47, H 5.24, N 7.29; found C 87.43, H 5.18, N 7.25.

2-(4-Chlorophenyl)-1-isopropyl-4,5-diphenyl-1*H*-imidazole (5k): (see Table 3, Entry 11). White solid (72% yield); m.p. 152–154 °C. R_f = 0.43 [12% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.29 (m, 11 H, ArH), 7.16–7.05 (m, 3 H, ArH), 4.45–4.36 (m, 1 H, NCH), 1.23 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.1, 138.0, 135.0, 134.3, 132.0, 131.2, 130.6, 129.1, 128.8, 128.6, 128.5, 128.1, 128.0, 127.8, 126.6, 126.1, 49.3, 23.1 ppm. IR (KBr): $\tilde{\nu}$ = 3049, 1596, 1484, 1429, 1242, 789, 698 cm^{-1}. $C_{24}H_{21}ClN_2$ (372.90): calcd. C 77.30, H 5.68, N 7.51; found C 77.27, H 5.65, N 7.44.

1-(3-Methoxyphenyl)-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (5l): (see Table 3, Entry 12). White solid (71% yield); m.p. 172–174 °C. R_f = 0.38 [20% EtOAc/petroleum ether (60–80 °C)]. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (d, J = 7.8 Hz, 1 H, ArH), 8.70–8.62 (m, 2 H, ArH), 7.70 (t, J = 7.2 Hz, 1 H, ArH), 7.62–7.59 (m, 3 H, ArH), 7.46–7.38 (m, 2 H, ArH), 7.28–7.23 (m, 5 H, ArH), 7.09–7.05 (m, 2 H, ArH), 6.96 (br. s, 1 H, ArH), 3.70 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 150.8, 139.6, 137.3, 130.6, 130.5, 129.2, 129.1, 128.8, 128.2, 128.1, 128.0, 127.2,

126.2, 125.5, 124.8, 124.0, 123.0, 122.9, 122.7, 121.2, 120.9, 115.6, 114.4, 55.5 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 1601, 1589, 1495, 1471, 1453, 840, 773, 759, 696 cm^{-1}. $C_{28}H_{20}N_2O$ (400.48): calcd. C 83.98, H 5.03, N 7.00; found C 83.93, H 4.98, N 6.95.

1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1*H*-phenanthro[9,10-*d*]-imidazole (5m): (see Table 3, Entry 13). Off-white solid (75% yield); m.p. 232–234 °C. R_f = 0.39 [30% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.85 (d, J = 8.1 Hz, 1 H, ArH), 8.71 (d, J = 8.4 Hz, 1 H, ArH), 8.65 (d, J = 8.1 Hz, 1 H, ArH), 7.71 (t, J = 7.5 Hz, 1 H, ArH), 7.61 (t, J = 8.4 Hz, 1 H, ArH), 7.54–7.36 (m, 7 H, ArH), 7.26 (t, J = 7.5 Hz, 1 H, ArH), 7.15 (d, J = 8.4 Hz, 1 H, ArH), 6.80 (d, J = 8.7 Hz, 2 H, ArH), 3.76 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 150.9, 137.3, 137.2, 135.6, 130.8, 130.4, 130.3, 129.1, 128.2, 127.6, 127.2, 126.9, 126.3, 125.4, 124.8, 124.1, 123.0, 122.7, 122.4, 120.4, 113.7, 55.2 ppm. IR (KBr): $\tilde{\nu}$ = 3043, 1609, 1504, 1459, 947, 782, 719 cm^{-1}. $C_{28}H_{19}ClN_2O$ (434.92): calcd. C 77.33, H 4.40, N 6.44; found C 77.29, H 4.39, N 6.42.

1-(3-Nitrophenyl)-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (5n): (see Table 3, Entry 14). Yellow solid (68% yield); m.p. 228–230 °C. R_f = 0.40 [20% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.89 (d, J = 7.8 Hz, 1 H, ArH), 8.72–8.63 (m, 2 H, ArH), 8.43 (d, J = 8.1 Hz, 1 H, ArH), 8.35–8.34 (m, 1 H, ArH), 7.78–7.62 (m, 4 H, ArH), 7.50–7.45 (m, 3 H, ArH), 7.32–7.22 (m, 4 H, ArH), 7.04 (d, J = 8.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 148.9, 139.9, 137.7, 135.2, 130.9, 129.8, 129.6, 129.3, 129.2, 128.4, 128.3, 127.7, 127.4, 127.0, 126.4, 125.9, 125.1, 124.5, 124.3, 124.2, 123.1, 122.8, 122.4, 120.2 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 1602, 1524, 1474, 1450, 1377, 777, 753, 721, 695 cm^{-1}. $C_{27}H_{17}N_3O_2$ (415.45): calcd. C 78.06, H 4.12, N 10.11; found C 77.95, H 4.09, N 10.04.

4,5-Diphenyl-1-*o*-tolyl-2-*p*-tolyl-1*H*-imidazole (5o): (see Table 3, Entry 15). White solid (76% yield); m.p. 126–128 °C. R_f = 0.45 [12% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.5 Hz, 2 H, ArH), 7.33 (d, J = 8.1 Hz, 2 H, ArH), 7.24–7.06 (m, 12 H, ArH), 6.99 (d, J = 8.1 Hz, 2 H, ArH), 2.24 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 138.2, 138.0, 136.3, 136.0, 134.5, 130.9, 130.6, 130.5, 129.3, 128.9, 128.8, 128.2, 128.0, 127.9, 127.8, 127.3, 126.5, 126.4, 21.1, 17.6 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 1612, 1501, 1481, 1074, 775 cm^{-1}. $C_{29}H_{24}N_2$ (400.52): calcd. C 86.97, H 6.04, N 6.99; found C 86.89, H 5.98, N 6.93.

2-(3,4-Dimethoxyphenyl)-1-*m*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole (5p): (see Table 3, Entry 16). Light brown solid (80% yield); m.p. 174–176 °C. R_f = 0.52 [40% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.92 (d, J = 7.8 Hz, 1 H, ArH), 8.74 (d, J = 8.1 Hz, 1 H, ArH), 8.68 (d, J = 8.4 Hz, 1 H, ArH), 7.74 (t, J = 7.2 Hz, 1 H, ArH), 7.63 (t, J = 8.1 Hz, 1 H, ArH), 7.51–7.41 (m, 3 H, ArH), 7.35–7.16 (m, 6 H, ArH), 6.77 (d, J = 8.4 Hz, 1 H, ArH), 3.85 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 2.43 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4, 149.4, 148.2, 140.2, 138.8, 136.9, 130.3, 129.7, 129.4, 128.9, 128.0, 127.8, 127.0, 126.0, 125.3, 124.5, 123.8, 122.9, 122.8, 122.6, 120.6, 112.2, 110.6, 55.6, 55.4, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 1612, 1509, 1470, 993, 755, 709 cm^{-1}. $C_{30}H_{24}N_2O_2$ (444.53): calcd. C 81.06, H 5.44, N 6.30; found C 80.99, H 5.35, N 6.28.

2-(4-Bromophenyl)phenanthro[9,10-*d*]oxazole (6a): Yellow solid (77% yield); m.p. 248–250 °C. R_f = 0.36 [8% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.79–8.74 (m, 2 H, ArH), 8.63 (d, J = 7.2 Hz, 1 H, ArH), 8.35 (d, J = 8.1 Hz, 1 H, ArH), 8.26 (d, J = 8.4 Hz, 2 H, ArH), 7.78–7.74 (m, 6 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3, 135.6, 132.2, 129.5, 129.0, 128.6, 127.5, 127.3, 126.6, 126.3, 126.1, 125.5, 123.8, 123.5, 122.9, 121.0, 120.9 ppm. IR (KBr): $\tilde{\nu}$ = 2365.0, 2341.9, 1477.7, 1070.0, 1008.3, 827.3, 759.6, 724.7, 670.4 cm^{-1}. $C_{21}H_{12}BrNO$ (374.24): calcd. C 67.40, H 3.23, N 3.74; found C 67.34, H 3.16, N 3.78.

4-Bromobenzaldehyde (6b): White solid (24% yield), m.p. 56–58 °C; ref.[13] m.p. 55–58 °C. R_f = 0.59 [3% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 9.95 (s, 1 H, CHO), 7.78 (br. s, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 192.3, 135.2, 132.3, 131.2, 128.7 ppm. IR (KBr): $\tilde{\nu}$ = 2858.2, 2757.9, 1710.7, 1690.0, 1665.1, 1588.3, 1573.5, 1479.0, 1384.5, 1289.0, 1204.8, 1154.0, 1065.7, 1008.7, 834.8, 810.6 cm^{-1}. C_7H_5BrO (185.02): calcd. C 45.44, H 2.72; found C 45.40, H 2.71.

Phenanthrene-9,10-dione (1ab): Orange solid (21% yield), m.p. 208–210 °C; ref.[14] m.p. 208–210 °C. R_f = 0.53 [10% EtOAc/petroleum ether (60–80 °C)]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 8.23 (d, J = 8.1 Hz, 2 H, ArH), 7.99 (dd, J = 7.8 Hz, J = 1.2 Hz, 2 H, ArH), 7.77–7.72 (m, 2 H, ArH), 7.50 (t, J = 7.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 173.8, 130.3, 130.1, 126.0, 124.2, 124.0, 119.3 ppm. IR (KBr): $\tilde{\nu}$ = 1673.8, 1650.9, 1591.5, 1450.7, 1293.8, 1281.8, 1228.8, 924.8, 763.2, 715.5 cm^{-1}. $C_{14}H_8O_2$ (208.22): calcd. C 80.76, H 3.87; found C 80.75, H 3.85.

CCDC-1006486 (for **2j**) and -1006487 (for **5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copies of ^1H and ^{13}C NMR spectra of products **2a**–**2u**, **3a**, **3b**, **4a**, **4b**, **5a**–**5p**, **6a**, **6b**, and **1ab**.

Acknowledgments

One of the authors (R. S.) thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, for his fellowship (SRF). We also thank the CAS Instrumentation Facility, University of Calcutta for the spectroscopic data.

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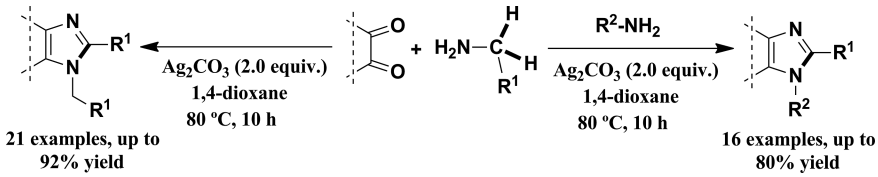
Received: November 12, 2014
Published Online: ■



A new silver(I)-mediated $C_\alpha(sp^3)$–H bond functionalization of primary amines followed by an oxidative C–N cross-coupling reaction to form highly diverse 1,2,4,5-tetrasubstituted imidazoles has been demonstrated. This protocol provides a simple, highly efficient, and straightforward approach, which is promoted by a silver species, to give the products in good to excellent yields.

Nitrogen Heterocycles

Keywords: Nitrogen heterocycles / C–H activation / Cross-coupling / Cyclization / Silver / Amines

