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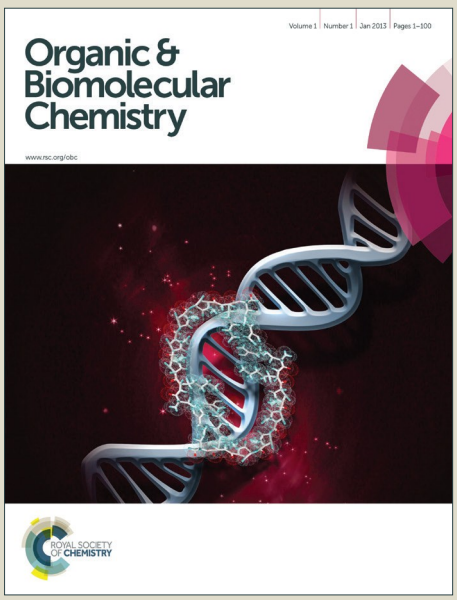

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ARTICLE

Switching the regioselectivity in the copper-catalyzed synthesis of iodoimidazo[1,2-*a*]pyridines

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Dedicated to Prof. Eiichi Nakamura on his occasion of 65th birthday

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A unique copper-catalyzed binucleophilic switching of 2-aminopyridine has been developed for the regioselective synthesis of 2- and 3-iodoimidazo[1,2-*a*]pyridines using alkene/alkyne as coupling partners in the presence of molecular iodine under aerobic reaction conditions. This method was also applied to the synthesis of 2-iodo-3-phenylbenzo[*d*]imidazo[2,1-*b*]thiazoles. This protocol offers an easy access towards the synthesis of 2,3-diarylimidazo[1,2-*a*]pyridines.

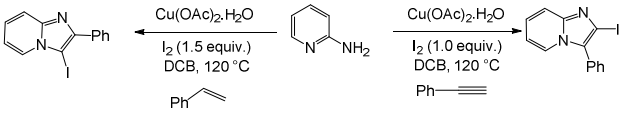
Introduction

Imidazo[1,2-*a*]pyridines are the prime target of the synthetic chemists over the years due to their immense biological and pharmaceutical activities.[1] They have also applications in material science.[2] In addition, a few of them exhibit excited-state intramolecular proton transfer (ESIPT).[2a] As a consequence a number of methodologies have been developed for the synthesis of functionalized imidazo[1,2-*a*]pyridines.[3] Among the functionalized imidazo[1,2-*a*]pyridines, halosubstituted imidazo[1,2-*a*]pyridines are one of the important derivatives as these can be further functionalized through a classical cross-coupling reaction. However, the synthetic strategies for these derivatives are very limited so far. These include the (a) oxidative coupling of haloalkynes with 2-aminopyridines,[4] (b) tandem cyclization/iodination between 2-aminopyridines and acetophenones,[5] (c) halogenation of imidazo[1,2-*a*]pyridines.[6] However, these methods afford either 2- or 3-haloimidazo[1,2-*a*]pyridines only. Very recently Zeng *et al*. reported a tandem chlorocyclization of 2-aminopyridines with carboxylic acids and ketones for the synthesis of chlorosubstitutedimidazo[1,2-*a*]pyridines.[7] Although this methodology provides regioselective synthesis of 2- or 3-chlorosubstituted imidazo[1,2-*a*]pyridines, but it involves the employment of hazardous reagent. Thus, a versatile and efficient methodology is in high demand for the regio-divergent synthesis of halosubstitutedimidazo[1,2-*a*]pyridines employing easily accessible starting materials under mild reaction conditions.

The majority of the reported methodologies for the synthesis of imidazo[1,2-*a*]pyridines have been developed employing binucleophilic 2-aminopyridine as the starting material. Due to the presence of two different nitrogen centers, 2-aminopyridine can react through either endocyclic or exocyclic nitrogen centre, as a consequence a regioselective product is obtained under the selective reaction conditions.[3e,f] It is worthy to mention that the synthesis of 2-functionalized imidazo[1,2-*a*]pyridines are limited so far.[3f,h] Therefore, we became interested for a protocol which can control the regioselectivity in the synthesis of functionalized imidazo[1,2-*a*]pyridine moiety under the same reaction conditions.

During last decade molecular iodine has received considerable attention due to its availability and immense reactivity to mediate various reactions such as coupling reaction, C-H amination, oxidative annulation,electrophilic cyclization etc.[8] Recently various heterocycles have also been synthesized using iodine as a catalyst.[9]

From the recent developments on the synthesis and functionalization of imidazoheterocycles, it is seen that a regio-divergent method is highly desirable that could provide both 2- and 3-iododerivatives. In continuation of our interest on imidazo[1,2-*a*]pyridines[10] herein we report a copper-catalyzed regioselective synthesis of 2- and 3-iodoimidazo[1,2-*a*]pyridines by the coupling between 2-aminopyridine and alkenes/alkynes in presence of iodine under ambient air (Scheme 1).



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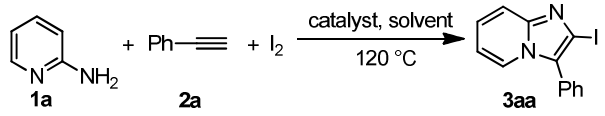
Scheme 1. Change of regioselectivity in the synthesis of imidazo[1,2-*a*]pyridines.

Results and discussion

We commenced our study by choosing the reaction between 2-aminopyridine (**1a**) and phenylacetylene (**2a**) as the model substrates. Based on our previous experiences,[10a,c,d] the reaction was carried out employing catalytic amount of $Cu(OAc)_2.H_2O$ (10 mol%) and 1 equiv. of I_2 in 1,2-dichlorobenzene (DCB) at 120 °C in air. Interestingly 2-iodo-3-phenylimidazo[1,2-*a*]pyridine (**3aa**) was obtained with high yield (82%) after 3 h (Table 1, entry 1). Formation of only one regioisomer was confirmed by the NMR spectra analysis of crude product. Inspired by this result we carried out the reaction under different conditions for the improvement of the yield and the results are summarized in the Table 1. The reaction was performed in other common solvents like DMF, DMSO, toluene, NMP and 1,2-DCE (Table 1, entries 2-6). No product was obtained in DMF, DMSO and NMP where as much lower yields were obtained in toluene and DCE. Bases like K_2CO_3, KOAc and Et_3N were not effective to improve the yield (Table 1, entries 7-9). Other copper salts like CuI, CuCl, $CuBr.Me_2S$ and $Cu(OTf)_2$ were also tested but these were not so effective like $Cu(OAc)_2.H_2O$ (Table 1, entries 10-13). No significant improvement of yield was observed by increasing the amount of I_2 to 1.5 equiv.; however using 0.5 equiv. of I_2 reduced the yield significantly (Table 1, entries 14 and 15). Much lower yield was obtained under the inert atmosphere (Table 1, entry 16). Thus optimum yield was obtained by carrying out the reaction employing 10 mol% $Cu(OAc)_2.H_2O$, 1 equiv. I_2 in DCB at 120 °C for 3 h under aerobic conditions (Table 1, entry 1).

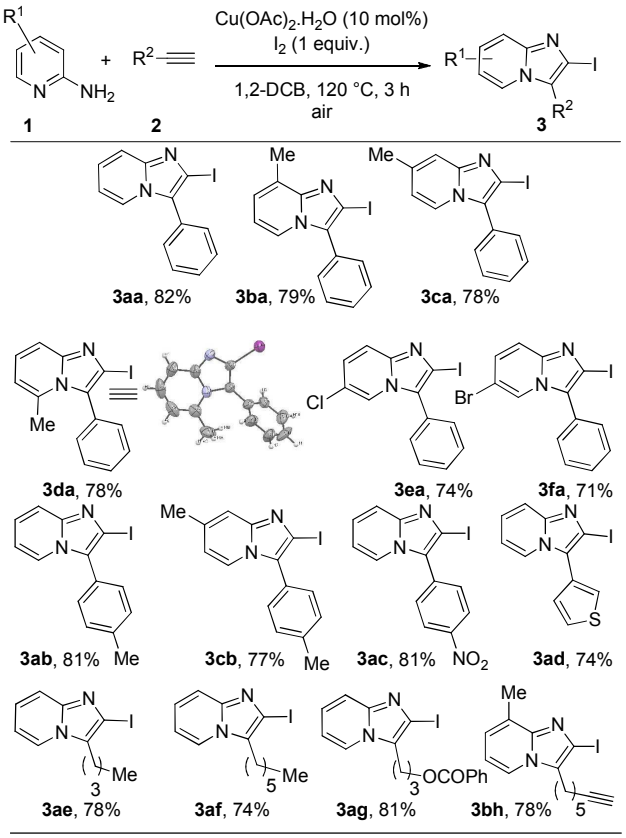
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (10 mol%)	Solvent	Additive	Yield (%)
1	$Cu(OAc)_2.H_2O$	1,2-DCB		82
2	$Cu(OAc)_2.H_2O$	DMF		nd
3	$Cu(OAc)_2.H_2O$	DMSO		nd
4	$Cu(OAc)_2.H_2O$	NMP		nd
5	$Cu(OAc)_2.H_2O$	Toluene		42
6	$Cu(OAc)_2.H_2O$	1,2-DCE		45
7	$Cu(OAc)_2.H_2O$	1,2-DCB	K_2CO_3	15
8	$Cu(OAc)_2.H_2O$	1,2-DCB	KOAc	18
9	$Cu(OAc)_2.H_2O$	1,2-DCB	Et_3N	24
10	CuI	1,2-DCB		70
11	CuCl	1,2-DCB		64
12	$CuBr.Me_2S$	1,2-DCB		<5
13	$Cu(OTf)_2$	1,2-DCB		<5
14	$Cu(OAc)_2.H_2O$	1,2-DCB		81[b]
15	$Cu(OAc)_2.H_2O$	1,2-DCB		55[c]
16	$Cu(OAc)_2.H_2O$	1,2-DCB		11[d]

[a]Reaction conditions: 0.2 mmol **1a** and 0.2 mmol **2a** in presence of catalyst (10 mol%), 0.2 mmol I_2 in solvent (2 mL) at 120 °C for 3 h. [b]0.3 mmol of I_2. [c]0.1 mmol of I_2. [d]Ar atmosphere.

After getting the optimized reaction conditions we became interested to explore the substrates scope of this methodology and the results are represented in the Scheme 2. 2-Aminopyridine with -Me group at different positions afforded the corresponding 2-iodo-imidazo[1,2-*a*]pyridines with almost equal ease (**3ba**, **3ca** and **3da**). 2-Aminopyridines substituted with halogens like –Cl and –Br also reacted efficiently (**3ea** and **3fa**). Phenylacetylene substituted with –Me and $–NO_2$ also gave the product with high yields (**3ab**, **3cb** and **3ac**). Heteroaryl alkyne like 3-ethynylthiophene reacted well under the optimized reaction conditions (**3ad**). Different aliphatic alkynes were also compatible under the reaction conditions (**3ae**, **3af** and **3ag**). Interestingly, 1,8-nonadiyne reacted with one terminal triple bond and produced 2-iodo-imidazo[1,2-*a*]pyridine moiety with a terminal alkyne functionality (**3bh**) which could be further functionalized. The structure of 2-Iodo-5-methyl-3-phenylimidazo[1,2-*a*]pyridine (**3da**) was confirmed by the X-ray crystallography.[11]



Scheme 2 Synthesis of 2-iodoimidazo[1,2-*a*]pyridines.

Next we extended our present methodology to 2-aminobenzothiazoles (Scheme 3). There is no reported method for the synthesis of 2-halobenzoimidazothiazole derivatives. To our delight 2-aminobenzothiazoles reacted well under the present reaction conditions to afford the corresponding 2-

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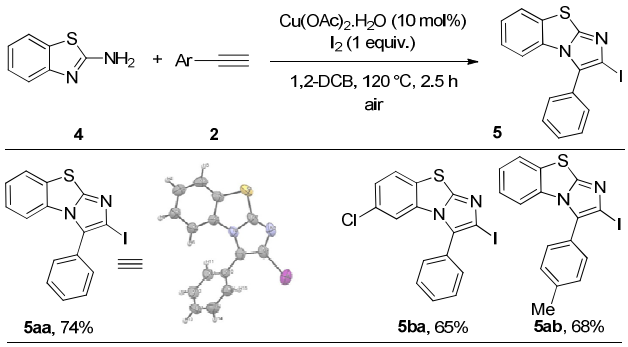
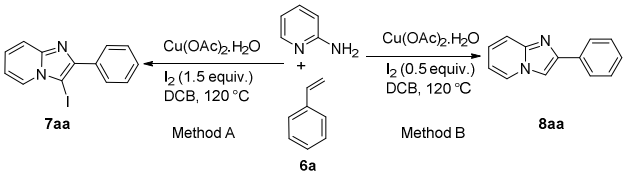
iodobenzo[*d*]imidazo[2,1-*b*]thiazoles with good yields after 2.5 h (**5aa**, **5ba** and **5ab**). The structure of 2-iodobenzo[*d*]imidazo[2,1-*b*]thiazole (**5aa**) was confirmed by the X-ray crystallography.[11]



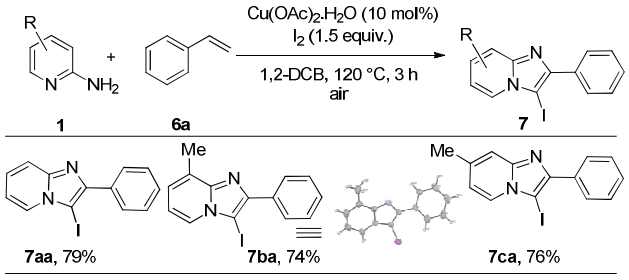
Scheme 3 Synthesis of 2-iodobenzo[*d*]imidazo[2,1-*b*]thiazoles.

Next we investigated the coupling of 2-aminopyridine with styrene under the optimized reaction conditions. Interestingly, 3-iodoimidazo[1,2-*a*]pyridine derivative (**7aa**) was obtained as the major product along with the 2-phenylimidazo[1,2-*a*]pyridine (**8aa**) after 3 h at 120 °C. After a careful optimization of the reaction conditions, it was found that the amount of I_2 plays an important role in this conversion. When the reaction was carried out in the presence of the 1.5 equiv. of I_2, 3-iodoimidazo[1,2-*a*]pyridine was obtained as the sole product (Scheme 4, Method A). Whereas the use of 0.5 equiv. of I_2 produced 2-phenylimidazo[1,2-*a*]pyridine as the single product (Scheme 4, Method B). This is the beauty of the current methodology that we could synthesize either 3-iodoimidazo[1,2-*a*]pyridines or 2-phenylimidazo[1,2-*a*]pyridines according to our choice only by varying the amount of I_2.



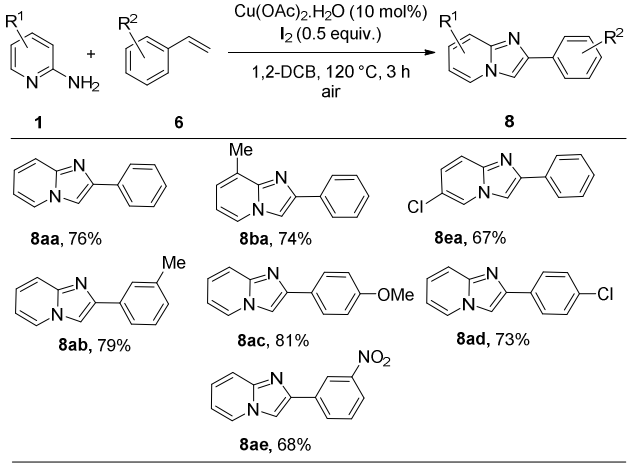
Scheme 4 Synthesis of 3-iodoimidazo[1,2-*a*]pyridine and 2-phenylimidazo[1,2-*a*]pyridine.

Next we explored the scope of reaction employing various 2-aminopyridines with styrene using 1.5 equiv. of I_2 (Scheme 5). To our delight the corresponding 3-iodoimidazo[1,2-*a*]pyridines were obtained with high yields in all cases (**7aa**, **7ba** and **7ca**). The structure of 3-Iodo-8-methyl-2-phenylimidazo[1,2-*a*]pyridine(**7ba**) was confirmed by the X-ray crystallography.[11]



Scheme 5 Synthesis of 3-iodoimidazo[1,2-*a*]pyridines.

Moreover, various 2-phenylimidazo[1,2-*a*]pyridines were synthesized using 0.5 equiv. of I_2 (Scheme 6). 2-Aminopyridines with substituents like –Me and –Cl reacted well to give the corresponding imidazo[1,2-*a*]pyridines (**8ba** and **8ea**) with good to high yields. Styrene with different functionalities like –Me, –OMe, –Cl and $–NO_2$ were well tolerated under the optimized reaction conditions to produce the respective derivatives (**8ab**, **8ac**, **8ad** and **8ae**).



Scheme 6 Synthesis of 2-arylimidazo[1,2-*a*]pyridines.

The current protocol was also tested for different internal alkynes (Scheme 7). Gratifyingly diarylacetylenes reacted well with 2-aminopyridines under the present reaction conditions to afford the 2,3-diarylimidazo[1,2-*a*]pyridines with high yields (**10aa, 10ab** and **10ba**). The reported methods for the one-step construction of 2,3-diarylimidazo[1,2-*a*]pyridines are very limited so far.[3k] However, unsymmetric diarylacetylenes produced a mixture of inseparable regioisomers. Internal alkynes like 4-octyne and 1-phenyl-1-propyne were unreacted under the present reaction conditions.

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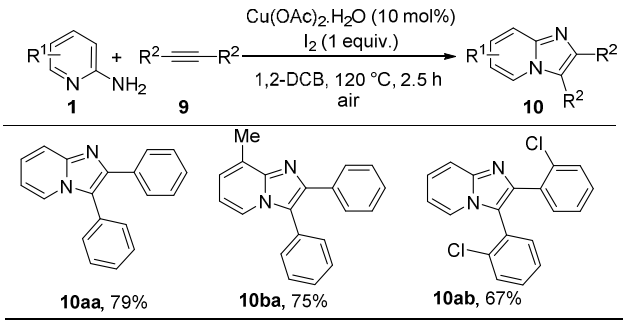
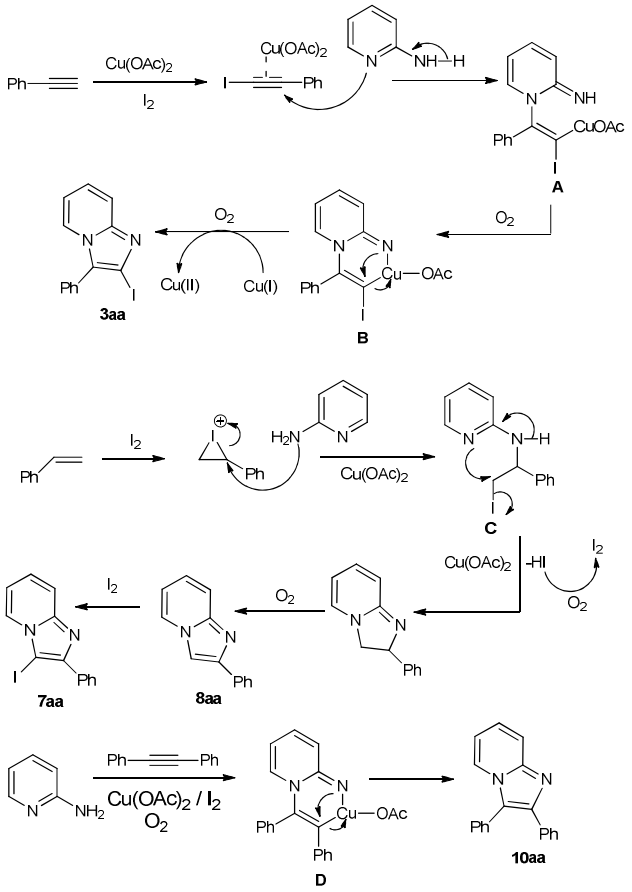


Scheme 7 Synthesis of 2,3-diarylimidazo[1,2-*a*]pyridines.

On the basis of the experimental results and literature reports,[4] we propose a mechanism for this reaction (Scheme 8). First, the alkyne reacts with molecular iodine to produce iodoalkyne. When the reaction was carried out without adding 2-aminopyridine into the reaction mixture, iodoalkyne is formed under the reaction conditions. Then 2-aminopyridine reacts with iodoalkyne in presence of $Cu(OAc)_2$ through endocyclic pyridine nitrogen[3f] to form the intermediate **A** which is subsequently converted into the Cu(III) complex **B** in presence of O_2.[10c,12] Upon reductive elimination the desired product **3aa** is formed**.** The catalyst Cu(II) is regenerated on aerial oxidation. The reaction between 1-iodoalkyne and 2-aminopyridine also afforded the desired product in presence of $Cu(OAc)_2$ without I_2 under the present reaction conditions. In case of alkene, the reaction probably proceeds through the formation of iodonium ion intermediate followed by coupling with 2-aminopyridine through exocyclic amino group to afford 2-phenylimidazo[1,2-*a*]pyridine. Finally 3-iodoimidazo[1,2-*a*]pyridine was obtained through the iodination of 2-phenylimidazo[1,2-*a*]pyridine. The formation of two regioisomers is possibly due to hard and soft nature of two different nucleophilic centres of 2-aminopyridine.[4f] Although the precise role of I_2 is unknown for the coupling between 2-aminopyridine and diarylalkyne, it is necessary for this reaction. Probably the reaction proceeds through the Cu(III) intermediate D.



Scheme 8 Proposed mechanism.

Conclusions

In summary, we have developed a regio-divergent method for the synthesis of 2- and 3-iodoimidazo[1,2-*a*]pyridines through a copper-catalyzed oxidative coupling between 2-aminopyridine and alkynes/alkenes in the presence of I_2. This versatile methodology is useful to attain the unsubstituted imidazo[1,2-*a*]pyridines and 2,3-diphenylimidazo[1,2-*a*]pyridine. The current methodology is also applicable for the synthesis of a new class of functionalized heterocycles, 2-iodo-3-phenylbenzo[*d*]imidazo[2,1-*b*]thiazoles by the coupling of 2-aminobenzothiazoles with alkynes. We believe the present protocol would provide useful applications in organic, medicinal and material chemistry.

Experimental Section

^{1}H NMR spectra were determined on a 400 MHz and 300 MHz spectrometers as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and are referenced to tetramethylsilane (TMS) as internal standard and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants *J* were given in Hz. ^{13}C NMR spectra were recorded at 100 MHz and 75 MHz in $CDCl_3$ solution. HRMS analysis was performed on a Q-TOF mass

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analyzer using the ESI ionization method. TLC was done on silica gel coated glass slide. Silica gel (60-120 mesh) was used for column chromatography. Petroleum ether refers to the fraction boiling in the range of 60-80 °C unless otherwise mentioned. All solvents were dried and distilled before use. Commercially available substrates were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware.

Typical experimental procedure for 3: A mixture of 2-aminopyridine (**1**, 0.2 mmol), alkyne (**2**, 0.2 mmol) and molecular iodine (0.2 mmol) was taken in an oven dried 10 mL round bottom flask in presence of $Cu(OAc)_2.H_2O$ (10 mol%) in 1,2-DCB (2 mL) and was stirred at 120 °C for 3 h under open atmosphere. After completion of the reaction (TLC) the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture petroleum ether and ethyl acetate (15:1) as an eluting solvent to afford the pure product. 2-Iodo-3-phenylimidazo[1,2-*a*]pyridine[4] (**3aa**): White solid (52 mg, 82%), mp: 139-141 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 6.8 Hz, 1H), 7.51-7.37 (m, 6H), 7.10-7.06 (m, 1H), 6.66-6.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.7, 129.9, 129.1, 129.0, 128.2, 126.8, 124.8, 123.0, 117.0, 112.7, 93.6; HRMS calcd for $C_{13}H_{10}IN_2$ $[M+H]^+$: 320.9889; found $[M+H]^+$: 320.9897.

Typical Experimental Procedure for 5: A mixture of 2-aminobenzothiozole (4, 0.2 mmol), alkyne (2, 0.2 mmol) and molecular iodine (0.2 mmol) was taken in an oven dried 10 mL round bottom flask in presence of $Cu(OAc)_2.H_2O$ (10 mol%) in 1,2-DCB (2 mL) and was stirred at 120 °C for 2.5 h under open atmosphere. After completion of the reaction (TLC) the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture petroleum ether and ethyl acetate (10:1) as an eluting solvent to afford the pure product.

Typical Experimental Procedure for 7: A mixture of 2-aminopyridine (**1**, 0.2 mmol), styrene (**6**, 0.2 mmol) and molecular iodine (0.3 mmol) was taken in an oven dried 10 mL round bottom flask in presence of $Cu(OAc)_2.H_2O$ (10 mol%) in 1,2-DCB (2 mL) and was stirred at 120 °C for 3 hours under open atmosphere. After completion of the reaction (TLC) the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture petroleum ether and ethyl acetate (4:1) as an eluting solvent to afford the pure product.

Typical Experimental Procedure for 8: Solvent in vacuum and was purified by column chromatography on silica gel using a mixture petroleum ether and ethyl acetate (6:1) as an eluting solvent to afford the pure product.

Typical Experimental Procedure for 10: A mixture of 2-aminopyridine (**1**, 0.2 mmol) diarylacetylene (**9**, 0.2 mmol), and molecular iodine (0.2 mmol) was taken in oven dried 10 mL round bottom flask in presence of $Cu(OAc)_2.H_2O$ (10 mol%) in 1,2-DCB (2 mL) and was stirred at 120 °C for 2.5 h under open atmosphere. After completion of the reaction (TLC) the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture petroleum ether and ethyl acetate (16:1) as an eluting solvent to afford the pure product.

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