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Triple bond Directed Csp^2-N Bond Formation through *N*-Fluorobenzenesulfonimide as Aminating Source: One-Step Transformation of Aldehyde into Amine

Sushmita,[†] Trapti Aggarwal,[†] Norio Shibata and Akhilesh K. Verma*

Dedication ((optional))

Abstract: A metal-free versatile triple bond directed approach for the decarbonylative C-H amination of *ortho*-alkynyl quinoline/pyridine aldehyde using *N*-Fluorobenzenesulfonimide as nitrogen source under mild reaction conditions has been described. The designed reaction strategy was triggered by trapping of fluorine through the base with subsequent attack of bis(phenylsulfonyl)-λ^2-azane on carbonyl carbon of heterocycle which gradually converted to amine via Curtius type rearrangement. This protocol provides one-step approach for the conversion of aldehyde to amine in good yields. The synthesized amines compounds were successfully transformed into biologically important pyrroloquinolines/pyridines.

Owing to the importance of amine molecules in natural products[1] and drug molecules,[2] numerous approaches have been developed for their synthesis.[3] The C-N bond forming reaction attracts the interest of synthetic chemist from the last century as the introduction of amino groups tune the physicochemical properties of the molecule and made them a biologically important structure.[4] Traditionally, metal-catalyzed C-N cross-coupling reactions such as Buchwald-Hartwig[5] and Ullmann-type coupling[6] have been exploited for the C-N bond formations. Previously, decarboxylative cross-coupling reactions such as Curtius, Schmidt, Hoffman and Lossen rearrangements using carboxylic acids and its derivatives have been reported for the synthesis of amines[7] (Figure 1). Curtius rearrangement was vitally used for the generation of amines from carboxylic acids, however; safety concern associated with azides restricts the use of Curtius rearrangement, leading to the pursuit of new strategies for this organic functional group transformation.[8] In 2012, Mainolfi group reported the synthesis of secondary anilines from substituted benzoic acid and amides through Cu-catalyst at high temperature (Scheme 1a).[9] Later, Ilangovan and co-workers synthesize primary anilines from substituted benzoic acid (scheme 1b).[10] However, to the best of our knowledge, metal-free synthesis of amines from aldehydes through *in situ* generated isocyanate intermediate has not been explored till date (Figure 1).

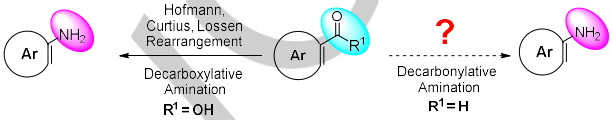
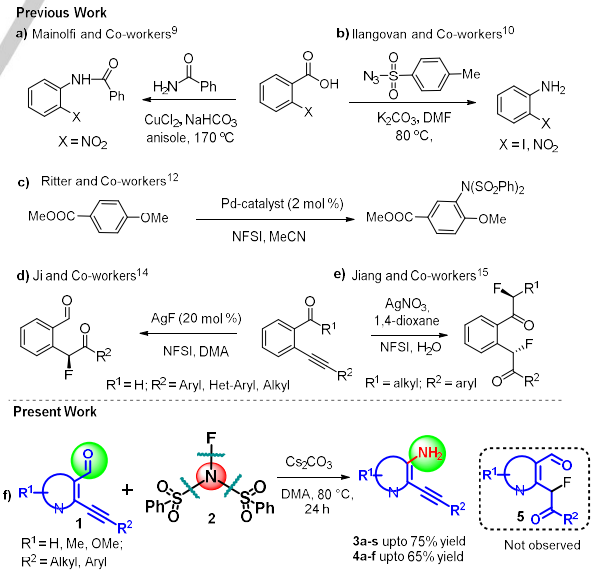


Figure 1. Organic functional group transformation

Interestingly, in 2012, Zhang and co-workers described a highly selective benzylic C-H amination reaction by copper catalysis.[11] Later in 2013, Ritter and co-workers disclosed the Pd-catalyzed amination of unactivated aryl ring using *N*-fluorobenzenesulfonimide as a nitrogen source (Scheme 1c).[12] Afterwards, various groups have reported amination using *N*-Fuorobenzenesulfonimide (NFSI) and it emerged as a powerful nitrogen source in C-H activation/amidation reactions.[13] In 2017, Ji[14] and Jiang[15] group reported the alkyne oxidation of *ortho*-alkynyl aldehydes in presence of a silver catalyst (Scheme 1d-e). However, decarbonylative amination using NFSI in presence of alkynes remains elusive.



Scheme 1. Previous reports v/s present work

Inspired from our ongoing research on *ortho*-alkynyl aldehydes,[16] herein we hypothesized the synthesis of fluorinated heterocycles through NFSI *via* metal-free strategy (Scheme 1f). Our preliminary studies revealed that the reaction failed to afford

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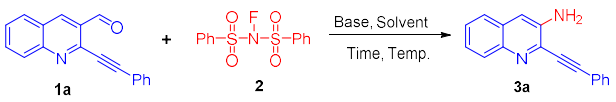
the proposed fluorinated product **5**, however, an aminated product **3** was isolated. The structure of **3b** was unambiguously established as 2-(*m*-tolylethynyl)quinolin-3-amine by X-ray crystallographic studies (see ESI, Figure S1). Importantly, the developed methodology provides 3-amino *N*-heterocycles which further cyclized to give the medicinally important pyrroloquinolines/ pyrrolopyridines.

To identify the optimal reaction conditions, we have screened various bases and solvents at different temperature.

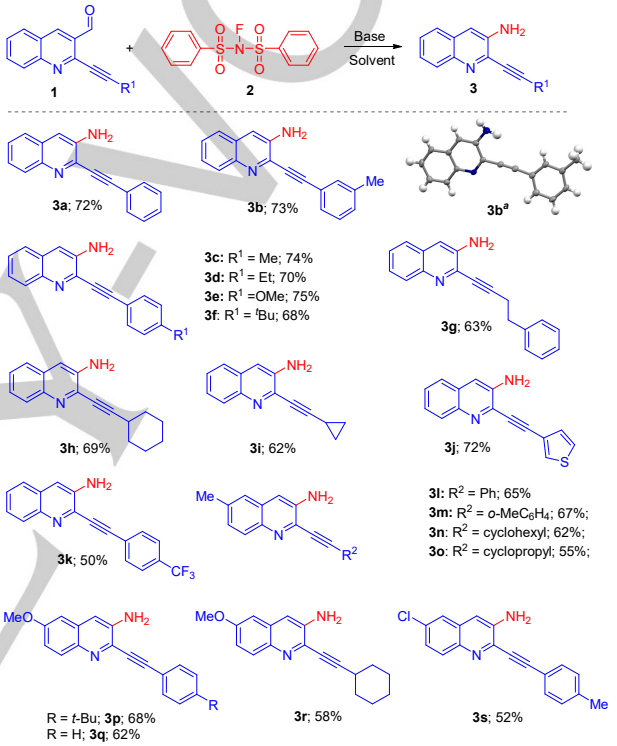
Table 1. Optimization of reaction conditions.[a]



entry	solvent	Base	temp (°C)	t (h)	yield[b] (%)
1	DMA	Cs_2CO_3	25	24	trace
2	DMA	Cs_2CO_3	50	24	50
3	DMA	Cs_2CO_3	80	24	72
4	DMA	Cs_2CO_3	100	24	-[c]
5	DMA	Cs_2CO_3	80	30	70
6	DMA	Cs_2CO_3	80	18	50
7	DMA	K_2CO_3	80	24	NR
8	DMA	*t*BuONa	80	24	50
9	DMA	KOH	80	24	45
10	DMA	-	80	24	NR
11	DMF	Cs_2CO_3	80	24	62
12	DMSO	Cs_2CO_3	80	24	55
13	Dioxane	Cs_2CO_3	80	24	NR
14	EtOH	Cs_2CO_3	80	24	00[d]
15	DMA	Cs_2CO_3	80	24	66[e]
16	DMA	Cs_2CO_3	80	24	NR[f]
17	DMA	Cs_2CO_3	80	24	NR[g]
18	DMA	Cs_2CO_3	80	24	NR[h]

[a] Reactions were performed using 0.50 mmol of **1a**, 0.60 mmol of NFSI **2** , 3.0 equiv of base in 2.0 mL solvent unless otherwise noted. [b] Isolated yield.[c] Complex mixture. [d] Ethyl 2-(phenylethynyl)quinoline-3-carboxylate was formed[16e] [e] Using 1.0 mmol of NFSI and 4.0 equiv of Cs_2CO_3.[f] Without using NFSI. [g] Using Selectfluor (0.6 mmol) instead of NFSI. [h] Using KF (0.6 mml) instead of NFSI. N.R.= No reaction, DMA = Dimethylacetamide

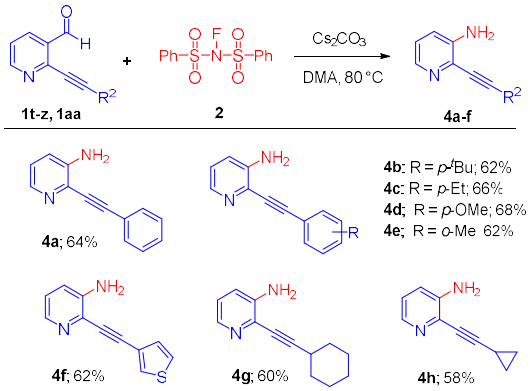
We began our study with 0.50 mmol of substrate **1a**, 0.60 mmol of **2**, 3.0 equiv of Cs_2CO_3 in DMA at 25 °C, resulted in the formation of trace amount of product **3a** after 24h (Table 1, entry 1). On increasing the reaction temperature to 50 °C and then to 80 °C provided the desired product **3a** in 50 and 72% yield, respectively (entries 2 and 3). Further elevating the temperature to 100 °C leads to the decomposition of the reaction (entry 4). No significant effect was observed when the reaction was stirred for longer time (entry 5). While monitoring the reaction for a short interval of time at 80 °C, the product **3a** was obtained in 50% yield along with starting material (entry 6). After obtaining successful results with Cs_2CO_3, various other bases were investigated. K_2CO_3 was proved to be ineffective for the reaction, while lower yield was obtained with *t*-BuONa and KOH (entries 7-9). However in the absence of base no reaction was observed (entry 10). Next, we screened the different solvents for the designed reaction and interestingly the reaction proceeds in DMF and DMSO while Dioxane was failed to give the desired product (entries 11-13). When EtOH was employed as a solvent, Ethyl 2-(phenylethynyl)quinoline-3-carboxylate was formed[16e] instead of designed product **3a** (entry 14). Increasing the amount of NFSI and Cs_2CO_3 made no improvement in the yield of product **3a** (entry 15). The substrate remains unreacted in the absence of NFSI (entry 16). While other fluorinating agents like selectfluor and KF were failed to give the desired product (entry 17-18).



Scheme 2. Scope of *ortho*-alkynylaldehyde. Reaction condition: alkynyl quinoline aldehydes **1** (0.50 mmol), NFSI **2** (0.60 mmol), 3.0 equiv Cs_2CO_3 in 2.0 mL DMA at 80 °C for 24 h. [a] The CCDC no. of compound **3b** is 1814897.

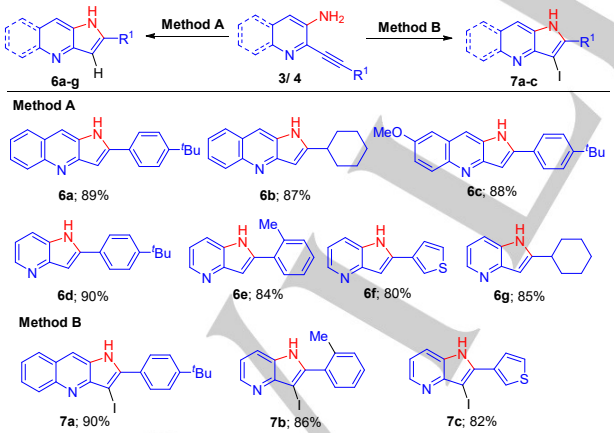
With the optimized reaction conditions, we explored the viability of differently substituted *ortho*-alkynyl quinoline carbaldehyde **1a**–**s** (Scheme 2). The substrates having an electron-donating group at the phenyl ring on distal end of the triple bond reacted smoothly to give the desired aminated products **3b**–**f** in 68-75% yields. Interestingly, the substrates bearing aliphatic and cyclic alkynes were also compatible to afford the designed products **3g**–**i** in good yields. The reaction with 2-(thiophen-2-ylethynyl)quinoline-3-carbaldehyde **1j** gave the desired product **3j** in 72% yield. The electron-deficient -CF_3 embedded alkyne **1k** provided the desired product **3k** in 50% yield. The above results encouraged us to explore substituted quinoline aldehydes as substrate. Therefore, next we investigated 6-methyl, 6-methoxy and 6-chloro substituted alkynyl quinoline-3-

carbaldehydes **1l–s** having cyclohexyl and variety of electron-rich alkynes. The substitution on quinoline ring made no considerable effect on the progress of reaction and the corresponding products **3l–r** was obtained in 55-68% yields. While moderate yield of product **3s** was obtained when chloro substituted quinolin-aldehyde **2s** was used as substrate.



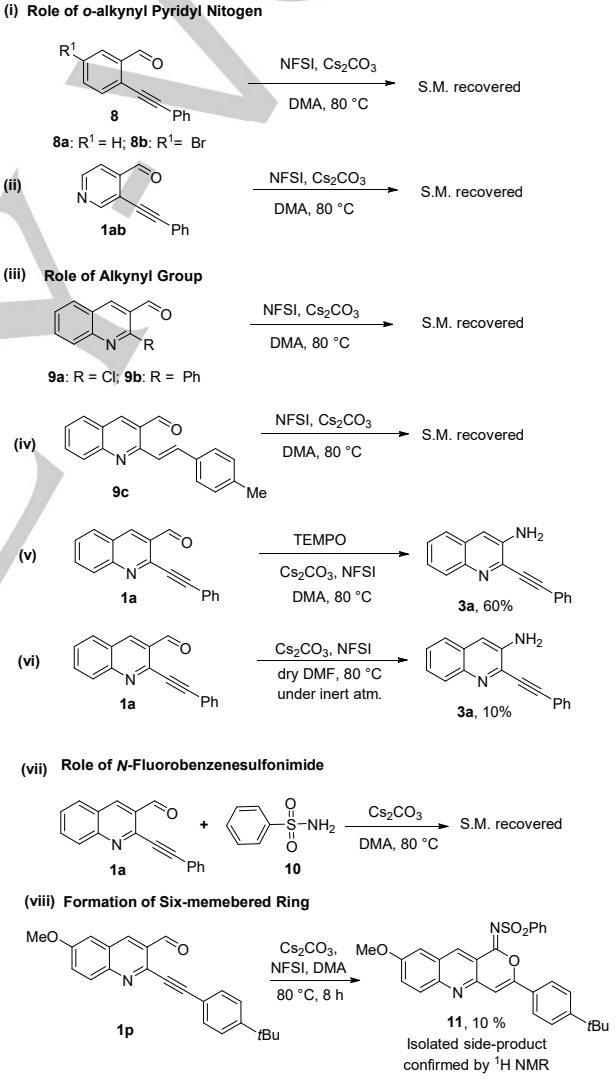
Scheme 3. Synthesis of 2-alkynyl-pyridin-3-amine. Reaction condition: Alkynyl pyridine aldehydes **1** (0.50 mmol), NFSI **2** (0.60 mmol), Cs_2CO_3 (3.0 equiv) in 2.0 mL DMA at 80 °C for 24 h.

After obtaining successful results with alkynyl quinoline-3-carbaldehydes, we were intrigued to extend the scope of reaction on *ortho*-alkynyl nicotinaldehyde **1t–z** and **1aa** (Scheme 3). The optimized reaction conditions were compatible with pyridine substrates and afforded the targeted product **4a–h** in 58–68% yield. The phenyl and electron-rich substituted alkynes provided the corresponding product **4a–e**, in good yields. The reaction also tolerates the heteroaromatic substituted alkynes and afforded the desired product **4f** in 62% yield. While, moderate yield of products **4g–h** was obtained when cyclic alkyne was employed as substrate.



Scheme 4. Structural elaboration for the synthesis of pyrrolo quinolines Reaction conditions: Method **A**: **3/4** (0.5 mmol), *t*-BuOK (3.0 equiv) in 2.0 mL NMP at 40 °C for 8 h. Method **B**: **3/4** (0.5 mmol), I_2 (1.0 equiv) in 2.0 mL DCE at 70 °C for 3 h.

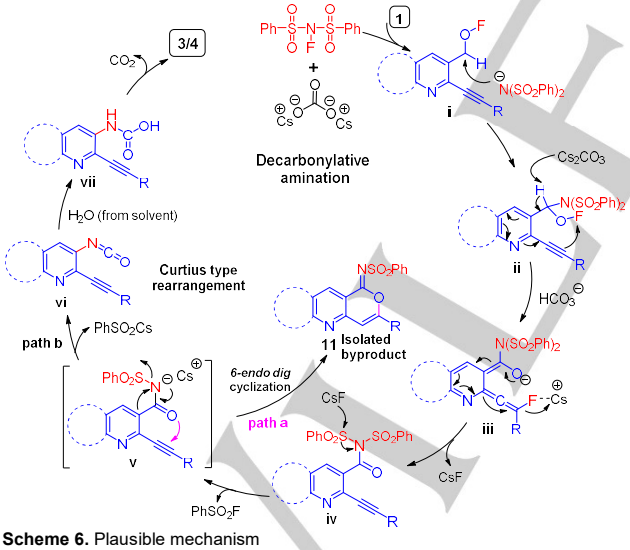
To illustrate the synthetic utility of the synthesized amines, we have designed the synthesis of biologically important pyrroloquinolines/pyridines. Pyrroloquinolines are present in many drugs like molecules, camptothecin,[17a] Lutonin A,[17] Crytolepine[18]. The potential biological activity of pyrroloquinolines captivates the organic chemist to design a facile route for their synthesis. The unsubstituted and OMe-substituted quinoline amines **3f, 3h** and **3p** were cyclized in the *t*-BuOK in NMP at 40 °C[19] and gave the corresponding pyrroloquinolines **6a–c** in 87–89% yield (Scheme 4). Next, pyrrolopyridines **6d–g** were obtained in good yields from aminopyridines under base-mediated conditions. The viability of aminoquinolines was further extended through the synthesis of iodo-substituted pyrroloquinoline/ pyridines **7a–c** using molecular iodine in DCE (Scheme 4). The iodo compounds were obtained through iodocyclization[20] in good to excellent yield. Iodo-substituted quinolines and pyridines are noteworthy as halogen atoms play an important role in a compound's bioactivity and provide handle for further structural elaboration.



Scheme 5. Control experiments

To study the mechanistic pathway for the synthesis of aminoquinolines various preliminary experiments have been

performed (Scheme 5). We began our study with the importance on the role of *ortho*-alkynyl heteroatom. When 2-(phenylethynyl) benzaldehydes **8a**–**b** were treated with NFSI, no desired product was observed after 24 h, only starting material was recovered (Scheme 5(i)). Similarly, no progress in the reaction was observed when 3-((4-methoxyphenyl)ethynyl) isonicotinaldehyde (**1ab**) was employed as the substrate, only starting material was recovered in 70% yield (Scheme 5 (ii)). The result of above experiments validates the presence of nitrogen adjacent to the alkyne group was essential. The role of the alkynyl group was justified, when the reaction of chloro and phenyl substituted quinolin-3-aldehyde **9a–b** under-designed reaction condition was failed to give the aminated product (Scheme 5iii). Next, we employed alkenyl substituted quinolin-aldehyde **9c** under the optimized reaction condition, but we failed to obtain the desired product (Scheme 5iv). This result supported the importance of alkynyl group in the substrate. We also perform the reaction using TEMPO along with NFSI, 60% yield of product **3a** cancels the probability of radical formation in this reaction (Scheme 5v). Furthermore, when substrate **1a** was subjected for the reaction using dry DMF under inert atmosphere, the reaction was significantly inhibited and afforded the desired product only in 10% yield. This experiment suggests that H_2O present in DMA is involved in the conversion of isocyanate into the product **3a** (Scheme 5vi). The role of *N*-fluorinating reagent was supported by the failure of reaction between benzenesulfonamide **10** and **1a** (Scheme 5vii). Further to support the formation of six-membered intermediate, we have stirred the reaction for 8 h and isolated the side-product **11** in 10% yield, which later gets degraded during the course of reaction (Scheme 5viii).



Scheme 6. Plausible mechanism

On the basis of preliminary results, we have proposed a plausible mechanism for the decarbonylative amination (Scheme 6). Accordingly, the reaction was initiated through the complex formation between NFSI and Cs_2CO_3 which generates F^+ that was immediately trapped by oxygen of carbonyl group present in the substrate **1** and subsequently attack of $N(SO_2Ph)_2$ anion on the carbonyl carbon generates reactive species **ii**, that immediately rearrange to give allene intermediate **iii**. Due to the instability of allene fluoride species **iii**, it will reorganize to attain aromaticity and alkynyl group by removal of CsF. Further the CsF triggers the exclusion of $PhSO_2F$[21] (confirmed by ^{19}F NMR, See ESI) and gave intermediate **v**. Now, two pathways are possible; path **a** leads to the formation of side-product by releasing through *6-endo dig* cyclization. In Path **b,** reaction proceeds through Curtius type rearrangement to generate isocyanate species **vi**. Then in the presence of H_2O present in DMA[22] generates carbamic acid intermediate **vii** which on removal of CO_2 generated the targeted aminated compound **3/4**.

In conclusions, we have demonstrated a novel triple bond directed approach for the direct conversion of *ortho*- alkynyl quinoline/pyridyl-3-aldehydes into ortho-alkynyl quinoline/pyridyl-3-amine using *N*-fluorobenzenesulfonamide as nitrogen source under basic condition. The designed transition-metal-free strategy was directed through triple bond and well-tolerated by a variety of electron-rich and electron-deficient alkynes. The preliminary studies suggested the importance of pyridyl nitrogen and alkyne in this reaction. Further, the synthesized amino-quinolines/pyridines were elaborated to give biologically important pyrrolquinolines and iodo-pyrroloquinolines. The iodo-substituted compounds will provide a handle for structural elaboration.

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Keywords: Curtius Rearrangement • Pyrroloquinoline • *N*-fluorobenzenesulfonamide • *ortho*-alkynyl aldehyde • CH-Amination

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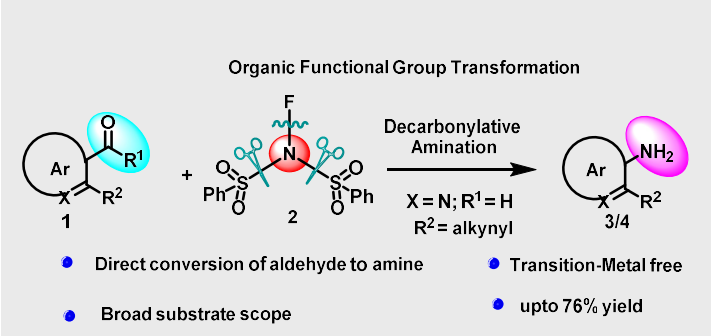
COMMUNICATION



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Triple bond Directed Csp^2-N Bond Formation through *N*-Fluorobenzenesulfonimide as Aminating Source: One-Step Transformation of Aldehyde into Amine

Transition metal-free decarbonylative C-H amination of *ortho*-alkynyl quinoline/pyridine aldehyde using *N*-Fluorobenzenesulfonimide as nitrogen source under basic medium.