Light-Induced Metal-Free Transformations of Unactivated Pyridotriazoles

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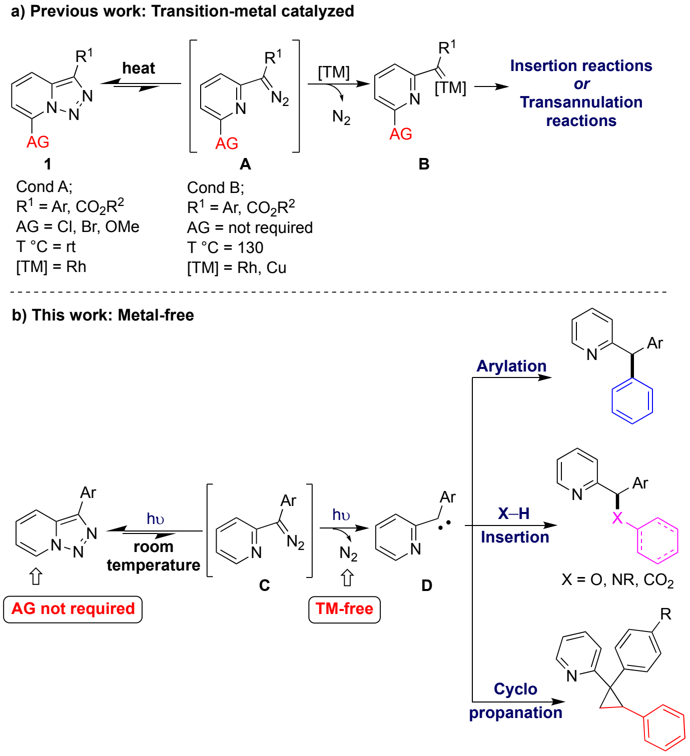
A highly efficient and practical method for incorporation of arylmethylpyridyl moiety into diverse molecules has been developed. This method features the transition metal-free light-induced room temperature transformation of pyridotriazoles into pyridyl carbenes, which are capable of smooth arylation, X–H insertion, and cyclopropanation reactions. The synthetic usefulness of the developed method was illustrated in a facile synthesis of biologically active molecules.

Transition metal-catalyzed denitrogenative transformations of pyridotriazoles have been recently evolving as a powerful tool for synthesis of diverse molecules possessing *N*-heterocyclic fragments.[1][2] These protocols take advantage of the well-known ring-chain tautomerism of the pyridotriazole core in solution into the corresponding diazo tautomer **A**, which then can be trapped by a transition metal catalyst to form the reactive pyridyl metal carbene intermediate **B** (Scheme 1 a). Since the first report on the transannulation reaction of pyridotriazoles in 2007,[3] numerous effective catalytic methods including transannulation,[4] X–H insertions,[5] and cyclopropanation[6] reactions have been developed.[7] However, all these methods are not without shortcomings. The reactions proceeding at room temperature require Cl, Br, or OMe activating groups (AG) at C7,[3a,b] otherwise high temperatures[3c,d,e] are necessary for achieving sufficient amounts of the open form of pyridotriazole A, which would lead to the reaction products. In either case, the employment of transition metal catalysts is required. Herein, we report room temperature efficient and operationally simple light-induced metal-free arylation, X–H insertion, and cyclopropanation reactions of pyridotriazoles giving access to various pyridyl-containing synthons, which can be used for convenient synthesis of bioactive molecules.



Scheme 1. Thermal and light-induced generation of carbenes from pyridotriazoles.

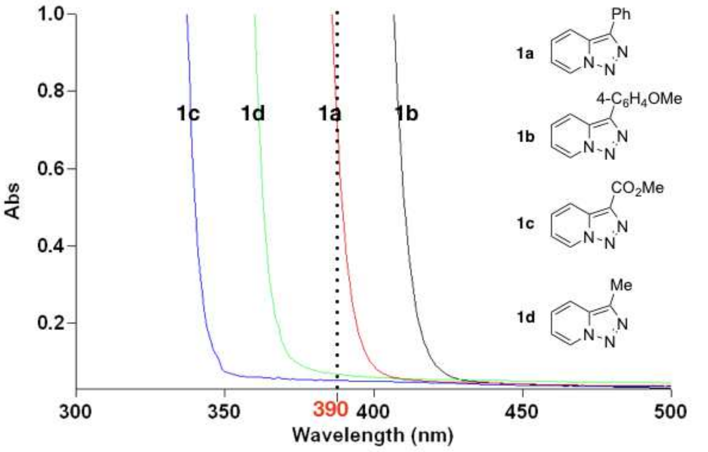


Figure 1. UV-vis absorption spectra of pyridotriazoles.

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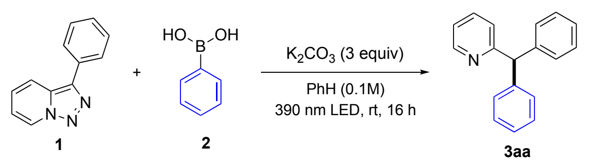
In continuation of our studies on application of pyridotriazoles in the synthesis of nitrogen-containing heterocycles,[3a-e] we hypothesized a metal-free strategy which can be accessed by utilizing light irradiation.[8] Compared with numerous methods reported for thermal processes, photochemical studies of pyridiotriazoles are relatively scarce.[9] Aiming at the development of milder reaction conditions, we started our investigation by analysing the UV-vis absorption spectra of pyridotriazoles **1a**-**d** (Figure 1, see SI for more details). Among them, only pyridotriazoles **1a** and **1b** bearing aryl substituents at the C3 position showed appreciable absorption around 390 nm region, which is attributed to the extended conjugation in these systems. Thus, we hypothesized that upon irradiation, the excited pyridotriazole **1a** could undergo a ring-chain tautomerism to deliver its diazo tautomer **C** (Scheme 1b), which upon denitrogenation[10] would deliver reactive carbene species **D**.

Table 1. Optimization of arylation reaction parameters.[a]



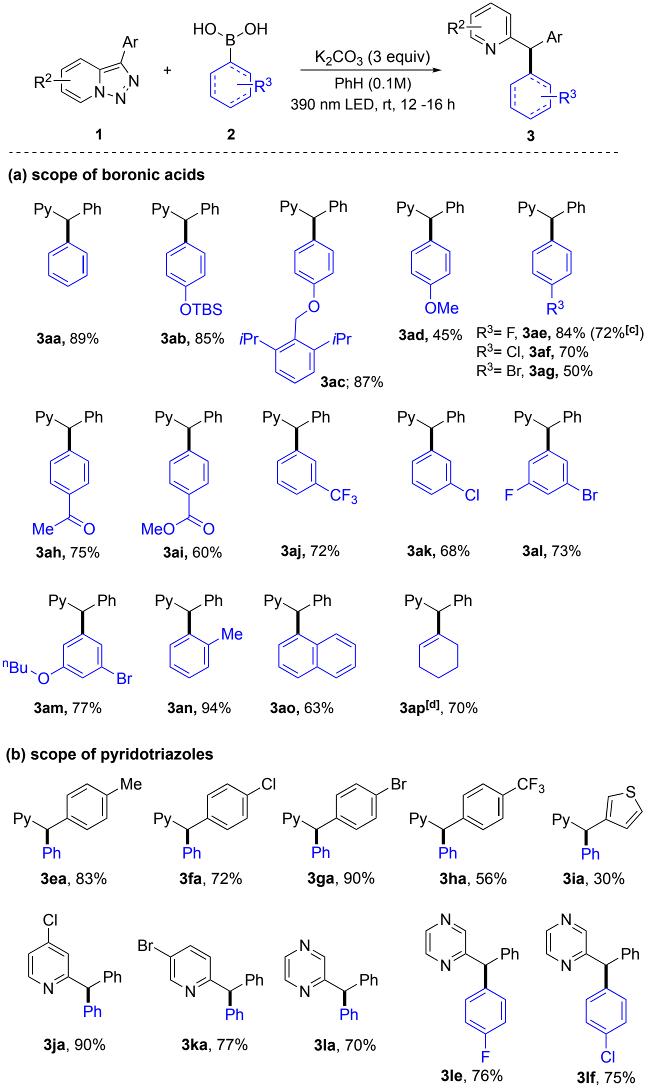
Entry	Deviation from standard conditions	Yield[b], %
1	None	89
2	Cs_2CO_3 instead of K_2CO_3	73
3	K_3PO_4 instead of K_2CO_3	44
4	NEt_3 instead of K_2CO_3	40
5	PhMe instead of PhH	84
6	THF instead of PhH	0
7	$CHCl_3$ instead of PhH	24
8	Without K_2CO_3	25
9	455 nm LED instead of 390 nm LED	0
10	427 nm LED instead of 390 nm LED	0
11	No light, dark, 50 to 120 °C	0

[a] Reaction conditions: pyridotriazole **1** (0.05 mmol), boronic acids **2** (1.5 equiv), K_2CO_3 (3 equiv), benzene (0.1 M), and a 40 W 390 nm LED at room temperature. [b] GC/MS yields.

To test this hypothesis, we examined a metal-free arylation reaction of 3-phenyl[1,2,3]triazolo[1,5-a]pyridine **1a** with boronic acid **2** (Table 1). The optimization studies indicated that performing this reaction under 390 nm irradiation in 0.1 M benzene solution with 1.5 equiv. of boronic acid in the presence of 3 equiv. K_2CO_3 at room temperature allows to produce diphenyl-2-pyridylmethane **3aa** in 89% yield (entry 1). Employment of other additives (entries 2-4) or solvents (entries 5-7) led to diminished yields. Only 25% of the product was formed without K_2CO_3 (entry 8), which points on the importance of the base for formation of the reactive triphenylboronxine arylating reagent[7a]. The control experiments indicated no reaction under 455 nm or 427 nm LED irradiating (entries 9 and 10) or under thermal conditions in the absence of light (entry 11).[11] Expectedly, the attempts on employment of pyridotriazoles **1c** and **1d**, which are transparent in 390 nm region under these reaction conditions failed. Although the pyridotriazole **1d** showed notable absorbtion in 370 nm region, the attempts of its arylation under irradiation with 370 nm LED lamp failed probably due to competing side reactions of the formed unstable carbene.

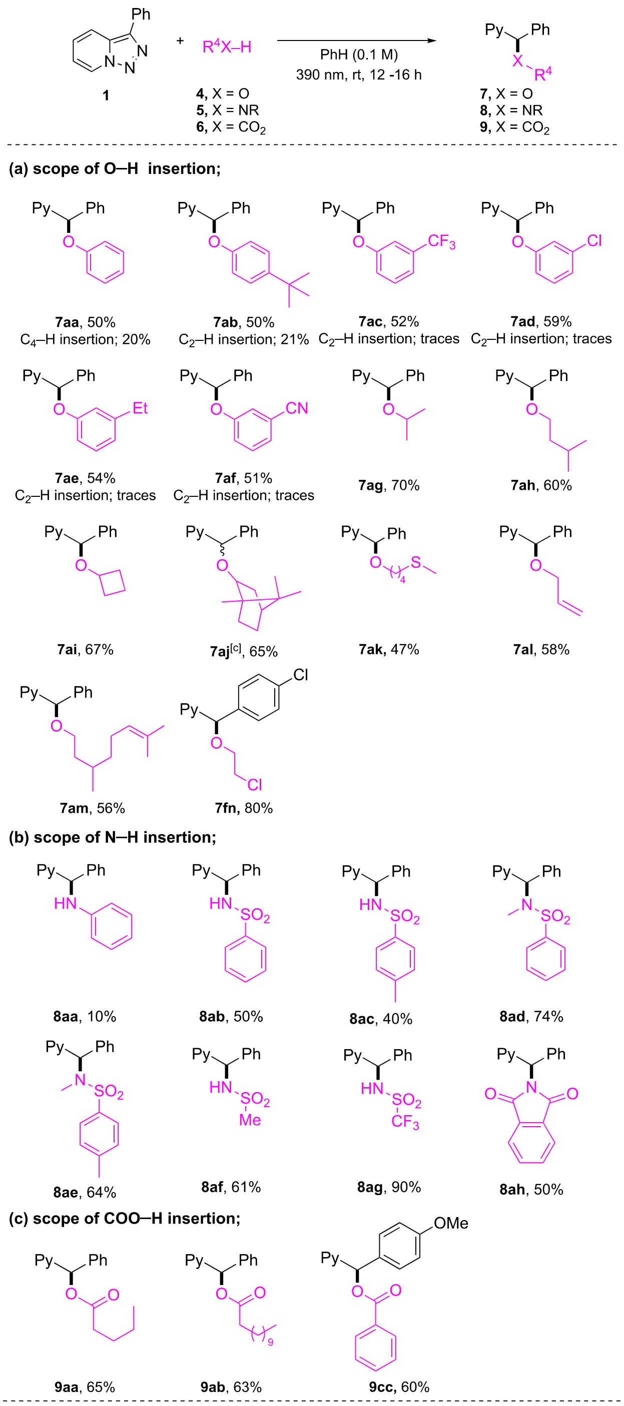
Intrigued by the uncovered novel reactivity of pyridotriazoles under photo-induced conditions and inspired by the importance of triarylmethanes,[12] we further explored the scope of this arylation reaction. Markedly, this C–C coupling reaction showed wide scope and high functional-group tolerance on both reaction partners (Table 2 a). Thus, diversely

Table 2. Arylation reactions of pyridotriazoles.[a,b]



[a] Reaction conditions: pyridotriazole **1** (0.2 mmol), boronic acids **2** (1.5 equiv), K_2CO_3 (3 equiv), benzene (0.1 M), 40 W 390 nm LED at room temperature. [b] Yield of isolated product. [c] Reaction was performed in 1 mmol scale. [d] Toluene (0.1 M) used as a solvent.

Table 3. X–H insertion reactions.[a,b]

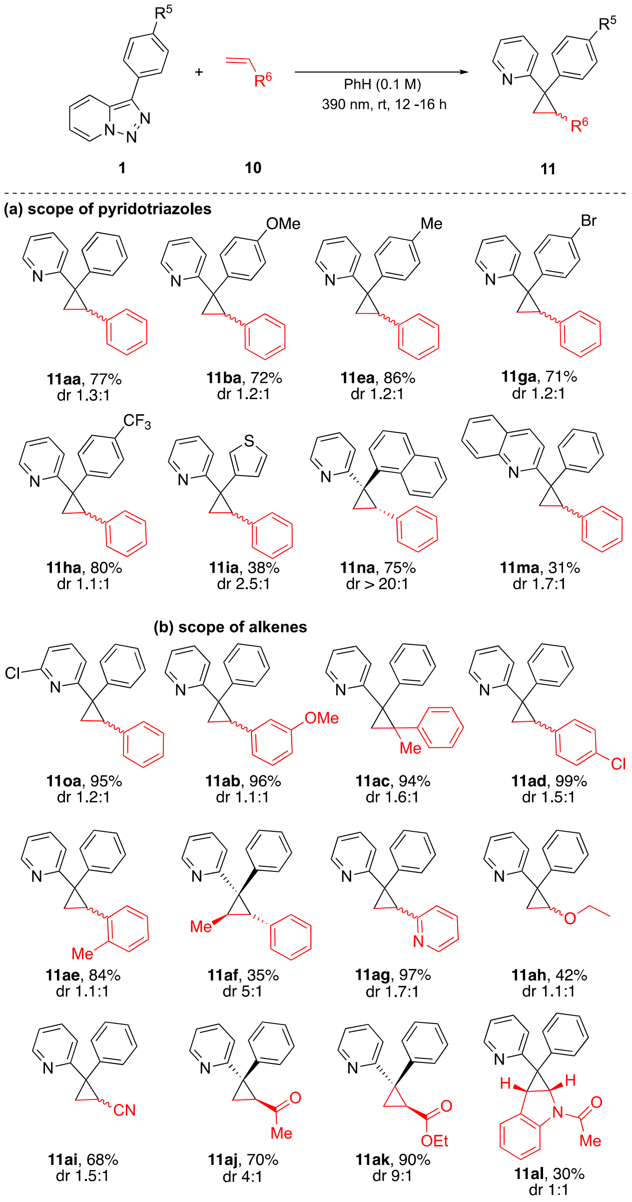


[a] Reaction conditions: pyridotriazole **1** (0.2 mmol), X–H insertion partners **4**, **5** or **6** (4 equiv), benzene (0.1 M), 40 W 390 nm LED at room temperature. [b] Yield of isolated product. [c] dr 1:1.

functionalized boronic acids **2** bearing electron-rich (**2b**-**2d**), electron-deficient (**2h**-**2j**), electron-neutral (**2n**), halogen-containing (**2e**-**2g** and **2k**-**2m**), and sterically encumbered (**2o**) substituents at the *ortho*-, *meta*- and *para*-positions smoothly reacted with 3-phenyl[1,2,3]triazolo[1,5-a]pyridine **1a** to produce diphenyl-2-pyridylmethanes **3aa**-**3an** in good to excellent yields. In addition, the reaction of phenylboronic acid with the *para*-siloxy substituent worked well to give **3ab** in good yield, which upon desilylation offered access to the phenol product. Notably, the reaction also efficiently proceeded with the alkenyl boronic acid **2p** providing cyclohexen-1-yl product **3ap** in 70% yield. Studies on the scope of pyridotriazoles showed that pyridotriazoles **1** bearing different 4-substitued phenyl or heteroaryl groups at C3 position furnished the corresponding triarylmethane products **3ea**-**3ia** in moderate to high yields. In addition, 5-chloro pyridotriazole, 6-bromo pyridotriazole and *N*-fused heterocyclic pyrazinotriazole successfully underwent arylation with different arylboronic acids to give **3ja**, **3ka**, 2-(diphenylmethyl) pyrazine (**3la**, **3le** and **3lf**) in good yields.

Next, we turned our attention to carbene X–H insertion reactions[10a] (Table 3). To this end, pyridotriazoles **1**, under standard reaction conditions, were examined in reactions with phenols, alcohols, sulfonamides, and carboxylic acids (Table 3 a). All

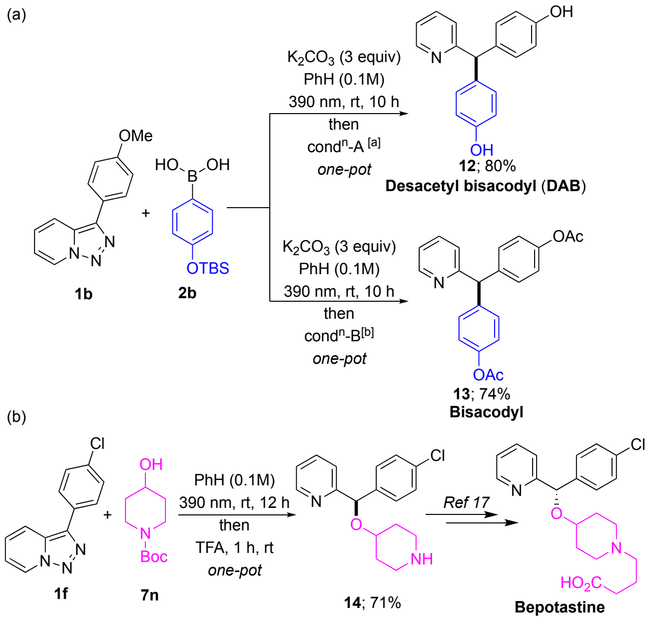
Table 4. Cyclopropanation reactions.[a]



[a] Reaction conditions: pyridotriazole **1** (0.2 mmol), styrene **10** (3 equiv), benzene (0.1 M), 40 W 390 nm LED at room temperature.

substituted phenols tested provided the O–H insertion products **7aa**-**7af** in moderate yields, albeit with trace to substantial amounts of the C–H insertion regioisomers.[13] These reaction conditions appeared to be very general for reactions with alcohols **4g**-**4n**. Thus, alcohols possessing various alkyl, alkenyl, thiomethyl, and even sterically hindered bicyclo groups all reacted well, providing ethers **7ag**-**7fm** in good to high yields. Moreover, this reaction chemoselectively gave O–H insertion products with alkenols (**7al** and **7am**), double bond moiety of which was not compromised. Likewise, aliphatic chlorine substituent was tolerated in **4n**, which constitutes an additional handle for further derivatizations. In contrast to a facile O–H insertion reaction with phenols, the insertion into the N–H bond of aniline **5a** was sluggish (Table 3 b), which can probably be attributed to its higher pKa value.[5d] However, more acidic primary and secondary sulfonamides **5b**-**g** reacted smoothly to produce the N–H insertions products **8ab**-**8ag** in reasonable to high yields. Phthalimide **5h** provided the insertion product **8ah** in reasonable yield. Furthermore, both aliphatic and aromatic carboxylic acids **6a**-**6c** were also found to be the competent substrates for the COO–H insertion reactions producing the corresponding esters **9aa**-**9cc** in good yields (Table 3 c).

In addition, it was also found that upon photoirradtion, the pyridotriazoles underwent efficient cyclopropanation with alkenes **10** (Table 4). The scope of pyridotriazoles was studied first. Pyridotriazoles **1** bearing different 4-substitued phenyl or heteroaryl groups at C3 position gave the corresponding cyclopropanes **11aa**-**11ia** in moderate to high yields.[14] 3-Naphthalenyl pyridotriazole furnished product **11na** in high yield. Furthermore, *N*-fused heterocyclic quinolinotriazole and 7-chloro pyridotriazole successfully underwent cyclopropanation with styrene to give **11ma**, **11oa**. The scope of the process with respect to the alkene components was examined next. Cyclopropanes **11ab**-**11ae** were obtained from a diverse array of *ortho*-, *meta*-, *para*- and disubstituted styrenes in high yields. 2-Vinylpyridine, vinyl ether, acrylonitrile, vinyl ketone and ethyl acrylate efficiently participated in the reaction to give the products **11ag**-**11ak**. Notably, a double bond of indole also participated in this reaction, providing fused product **11al** in moderate yield.



Scheme 2. Synthesis of biologically active molecules. [a] Conditions A: HBr/AcOH = 1:1, reflux, overnight. [b] Conditions B: HBr/AcOH = 1:1, reflux, overnight. Then Et_3N (3 equiv), Ac_2O (4 equiv), DCM (0.1 M), rt, overnight.

Synthetic usefulness of this methodology was illustrated on the facile syntheses of selected bioactive molecules. Thus, desacetyl bisacodyl (DAB) **12**[15] and Bisacodyl **13**,[16] which are used as stimulant laxative drugs, were efficiently obtained via the one-pot procedures from the pyridotriazole **1b** with arylboronic acid **2b** (Scheme 2 a). Furthermore, piperidine derivative **14**, [17] the synthetic precursor of antihistamine agent Bepotastine, was easily accessed by the O–H insertion reaction of **7n** with pyridotriazole **1f** (Scheme 2 b).

Conclusions

We developed general and efficient arylation, X– H insertions, and cyclopropanation reactions of pyridotriazoles. This transition metal-free light-induced[18] protocol, operating under mild conditions, exhibits wide functional-group tolerance efficiently producing valuable triarylmethanes and heteroatom- substituted benzylpyridine derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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