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Ir-Catalyzed Intramolecular Transannulation/C(sp^2)–H Amination of 1,2,3,4-Tetrazoles by Electrocyclization

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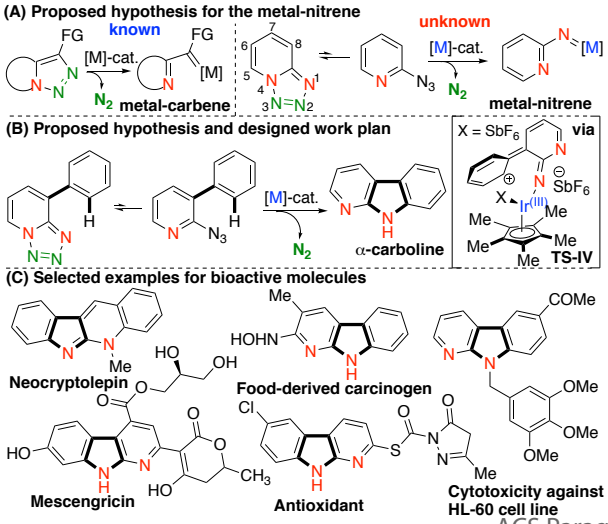
Supporting Information Placeholder

ABSTRACT: An efficient strategy for the intramolecular denitrogenative transannulation/C(sp^2)–H amination of 1,2,3,4-tetrazoles bearing C8-substituted arenes, heteroarenes and alkenes is described. The process involves the generation of the metal-nitrene intermediate from tetrazole by the combination of $[Cp^*IrCl_2]_2$ and $AgSbF_6$. It has been shown that the reaction proceeds via an unprecedented electrocyclization process. The method has been successfully applied for the synthesis of a diverse array of α-carbolines and 7-azaindoles.

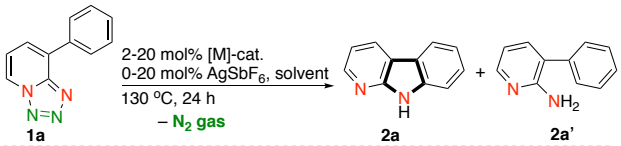
Transition metal-catalyzed denitrogenative transannulation[1] is one of the most efficient methods to construct nitrogen-containing heterocycles. It has been reported that while 1,2,3-triazoles readily undergo denitrogenative transannulation with transition metal catalysts via either an ionic[1,2] or a radical activation mechanism,[3] 1,2,3,4-tetrazoles remain completely inactive for the transannulation.[4] In this context, Wentrup's pioneering denitrogenative thermal and photochemical nitrene-nitrene rearrangement of tetrazoles is remarkable, which provide various nitrogen heterocycles.[5] Usually, 1,2,3,4-tetrazoles exist in equilibrium between closed and open form, the position of this equilibrium depends on (**Chart 1, A**) several parameters[6] (e.g. temperature, solvents and substituents). Although, Driver group[7] has studied well on metal-nitrene complexes derived from ortho-substituted aryl azides, however, the denitrogenative transannulation of 1,2,3,4-tetrazole via metal-nitrene is entirely underdeveloped to date. Thus, it would be highly intriguing to develop this transannulation/C–H amination[8] chemistry via metal-nitrene formation.

Chart 1. Concept for the Transannulation/C–H Amination



On the other hand, owing to the presence in molecules with a wide range of biological activity, α-carboline ring system has been branded as one of the privileged frameworks[9] for drug discovery (**Chart 1, C**). Numerous methods[10] exist for the assembly of various α-carboline, however, every method is associated with their own restrictions (e.g. selectivity issues, poor yield, requirement of particular classes of substrate etc.). Thus, it is highly desirable to develop new methods to overcome the existing shortcomings. Herein, we report a new concept[11] for the intramolecular denitrogenative transannulation/C(sp^2)–H amination of 1,2,3,4-tetrazoles by iridium catalysis, which undergo likely via the **TS-IV (Chart 1, B)** for the synthesis of diverse α-carbolines, 7-azaindoles and other important classes of heterocycles.

Table 1. Evaluation and Reaction Optimizations[a]



#	cat.	additive	solvent	2a/2a'
1	Cu-cat.	–	PhMe	0
2	Zn-cat.	–	DCE	0
3	Co-cat.	–	PhH	0
4	Fe-cat.	–	PhH	0
5	Mn-cat.	–	PhH	0
6	Ru-cat.	–	dioxane	0
7	Rh-cat.	–	DCE	0
8	$[Ir(cod)(Cl)]_2$	$AgSbF_6$	PhH	0/40
9	**$[Cp^*IrCl_2]_2$**	**$AgSbF_6$**	**PhH**	**100 (96)**
10	$[Cp^*IrCl_2]_2$	–	PhH	0

Cu-cat. = $Cu(MeCN)_4{\cdot}PF_6$, CuI, CuBr, $CuBr{\cdot}Me_2S$, $Cu(acac)_2$, $Cu(OTf){\cdot}C_6H_6$; **Zn-cat.** = ZnI_2; **Co-cat.** = Co(TPP), **Fe-cat.** = $FeBr_2$, Fe(TPP)Cl; **Mn-cat.** = Mn(TPP)Cl, **Ru-cat.** = [Ru(*p*-cymene)Cl]$_2$; **Rh-cat.** = $Rh_2(OAc)_4$, $Rh_2(oct)_4$, $Rh_2(O_2CC_3F_7)_4$, $Rh_2(esp)_4$, Rh_2(s-dosp)$_4$

[a]Reactions were conducted with 0.25 mmol scale and NMR conversions were determined using 1,3,5-trimethoxybenzene as internal standard; in parenthesis, isolated yield is given.

Thus, we started our initial investigations with substrate **1a** using a variety of transition metal catalysts (**Table 1**, entries 1-7, see: SI, for detail optimization) based on the proposed hypothesis that in presence of metal catalysts tetrazole would first generate the metal-nitrene intermediate and subsequently undergo intramolecular transannulation/C(sp^2)–H amination.[12] To our surprise, none of the metal catalysts afforded desired product and the tetrazole remain completely unreacted under the employed reaction conditions. For this extreme inertness[13] of the tetrazole, we reasoned that metal catalysts such as Cu, Zn, Co, Fe, Mn, Ru and Rh might be strongly coordinating

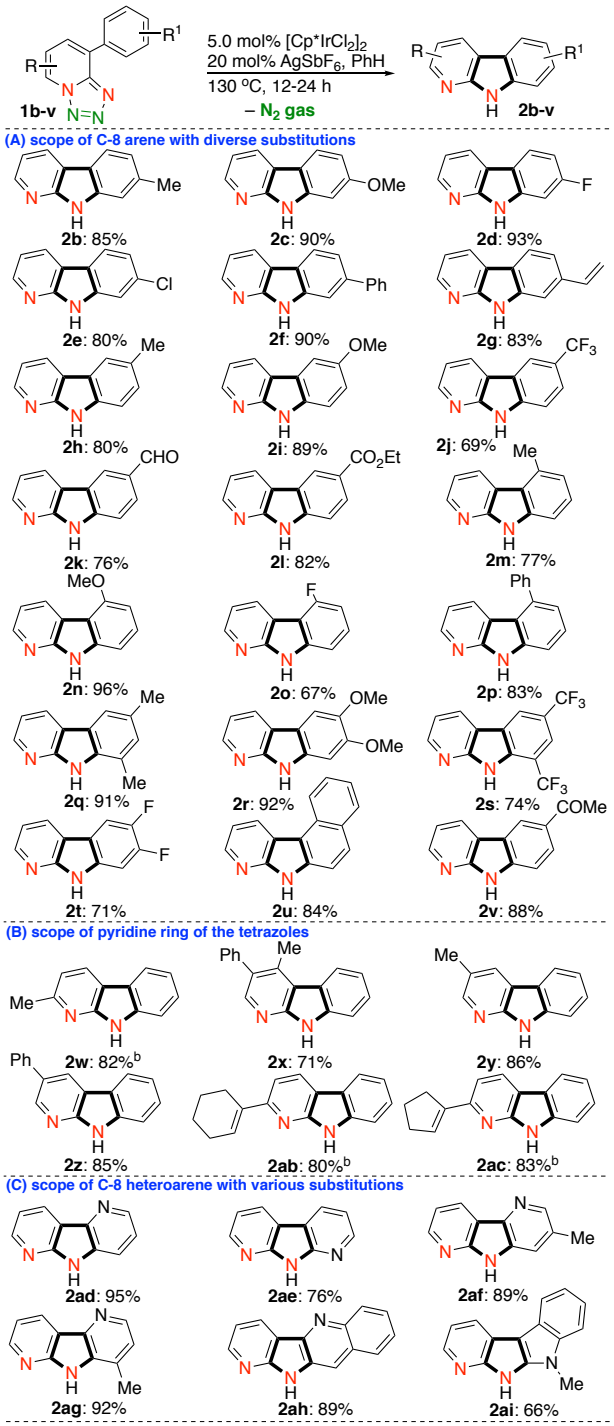
with both the nitrogen atoms of the tetrazole (i.e. pyridine and azide nitrogen) and inhibiting the catalytic process for the generation of the metal-nitrene intermediate.[14] Next, considering the unique reactivity of Chang's amidation,[15] we turned our attention towards iridium-based catalytic systems. Thus, transannulation was carried out by the combination of $[Ir(cod)Cl]_2$ and $AgSbF_6$, which gave 40% reduced product (**2a′**, entry 8). Remarkably, when the same reaction was performed in presence of $[Cp^*IrCl_2]_2$ and $AgSbF_6$ in benzene solution, we observed quantitative conversion of the starting tetrazole into the desired transannulation product (**2a**) in 96% isolated yield (entry 9). In order to verify the role of the $AgSbF_6$, same reaction was carried out without $AgSbF_6$, which resulted in no reaction (entry 10). Moreover, conducting the reaction with only $AgSbF_6$, no product formation observed.

With these encouraging results, transannulations/C(sp^2)–H aminations were performed for a series of 1,2,3,4-tetrazoles (**Table 2**). Irrespective of the substituents present in the C8 arene, for example, alkyl, alkoxy, phenyl, vinyl, ester, trifluoromethyl, and ketone were well tolerated under the reaction conditions (**Table 2, A**). Remarkably, in case of the meta-substituted C8-arene, the reaction produced exclusively one regioisomer out of the possible two regioisomers (entries **2h-2l**, **2v**). Moreover, various disubstituted arenes at C8 position (**2q-2t**) including a bulky naphthyl group (**2u**) led to the α-carbolines in good yield. For further elaboration, we examined various substitutions at the pyridine moiety of the 1,2,3,4-tetrazoles (**Table 2**, **B**). Thus, 1,2,3,4-tetrazoles with different substituents at pyridine such as, 5-methyl (**2w**), 6-phenyl-7-methyl (**2x**), 6-methyl (**2y**) and 6-phenyl (**2z**) were found to be compatible. Moreover, 5-hexenyl (**2ab**) and 5-pentenyl (**2ac**) also tolerated in the reaction conditions delivering α-carbolines in excellent yield.[16]

Next, we explored the substrate scope with respect to the different types of heteroaromatic systems for C8 substituted 1,2,3,4-tetrazoles (**Table 2**, **C**). A range of heterocyclic systems smoothly underwent transannulation/amination to afford the desired multiple-nitrogen-containing molecules in excellent yields. For example, variously substituted pyridines (**2ad-2ag**), quinoline (**2ah**) and *N*-methylindole (**2ai**) gave the corresponding products in excellent yields. In this context, it deserves mentioning that in case of C8-substituted heterocycle (**2ae**), out of two possible regioisomers, we observed only the aforementioned isomer as the sole products. For further application of this newly developed strategy, we have demonstrated that the alkaloid Neocryptolepin (**4**) and an important molecule, which exhibits cytotoxicity against HL-60 cell line (**5**) can be synthesized efficiently with excellent yields from the corresponding tetrazoles (**Chart 2**).

Towards this end, we were interested in the further development of this method with respect to the C8-substituted alkenes. Pleasingly, the developed method was found to be equally efficient with numerous alkenes and the results are summarized in **Table 3**. Performing the reactions with electronically neutral alkene (**6a**), electron-deficient alkenes (**6b-c**) and electron-rich alkenes (**6d-e**) provided the corresponding 7-azaindoles (**7a-e**) with excellent yields. Moreover, transannulations of cyclic alkenes-bearing 1,2,3,4-tetrazoles were also found to be compatible delivering consistently in good yields (**7f-g**). Furthermore, substitution at the pyridine ring of the tetrazole-bearing styrene type of alkenes smoothly underwent denitrogenative transannulation/C(sp^2)–H amination to give the substituted 7-azaindole derivatives.

Table 2. Scope of Reaction with Diverse Substrates



[a]Reactions were conducted with 0.5 mmol scale; isolated yields were reported after purification. [b]Reaction completed within 12 h.

Chart 2. Short Synthesis of Important Molecules

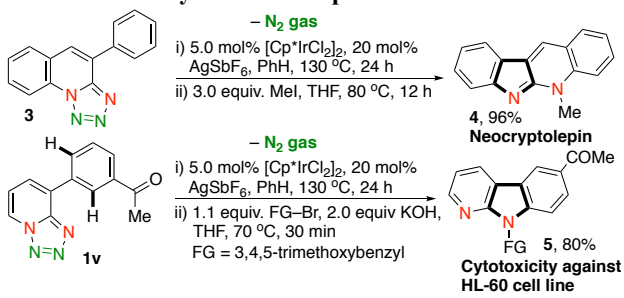
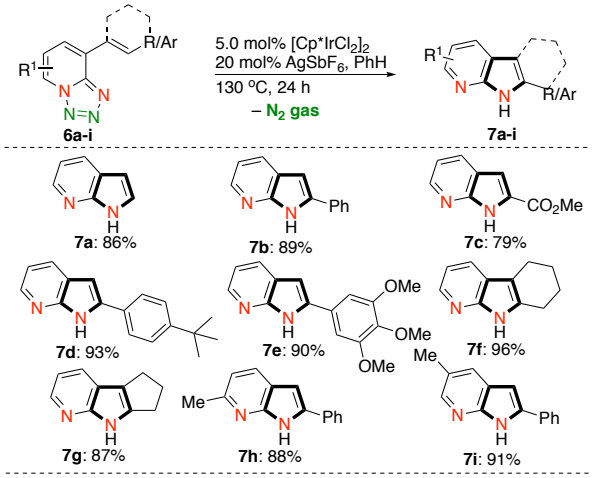


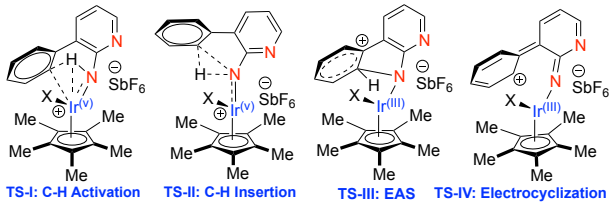
Table 3. Scope of Transannulation with Alkenes[a]



[a]Reactions were conducted with 0.5 mmol scale; isolated yields were reported after purification.

Next, we studied the mechanism and the product formation might be explained by the following four mechanisms, which are depicted in **Chart 3**, such as: i) C–H activation[15] via **TS-I**, ii) C–H insertion via **TS-II**, iii) electrophilic aromatic substitution (EAS) via **TS-III** and iv) electrocyclization via **TS-IV**.[17]

Chart 3. Possible Four Mechanistic Pathways



Thus, to shed light on the mechanistic aspects of the proposed pathways, we executed several control experiments (**Chart 4**). According to the literature report, since the $[Cp^*IrCl_2]_2$ is known[15] to catalyze the reaction via direct C-H activation mechanism, we thus decided to verify whether our transannulation/C(sp^2)–H amination would follow the same C-H activation or π-electron participation. For that reason, we conducted a control experiment with substrate **8**, where conjugation was disturbed by one methylene group. We observed that substrate **8** does not give even a trace amount of the desired product, which indicates that the present transannulation/amination strategy might not follow neither C–H activation mechanism (**TS-I**) nor C–H insertion mechanism (**TS-II**). For further studies, we performed another control experiment with substrate **10** (*Z*-isomer),[18] where C-H bond is away from the reaction center. We anticipated that due to the geometric constrain, transannulation should not occur with the *Z*-isomer (**10**). But, to our surprise, substrate **10** smoothly underwent the transannulation affording 69% product conversion, which also oppose the C-H activation and C–H insertion mechanism (**TS-I** & **TS-II**). Finally, determining the KIE value (intermolecular and intramolecular), we observed a secondary kinetic isotope effect (~1.0), which is again ruling out the possibility of **TS-I** and **TS-II**.

Next, we hypothesized that if the reaction goes via electrophilic aromatic substitution (EAS, **TS-III**), then substrate **11** should furnish the corresponding transannulation product **12**, because continuous conjugation is not essential for the EAS process. Following this hypothesis, reaction was performed with substrate **11** and observed no reaction, which clearly indicates that conjugation is essential for the reaction.

Chart 4. Mechanistic Studies/Control Experiments

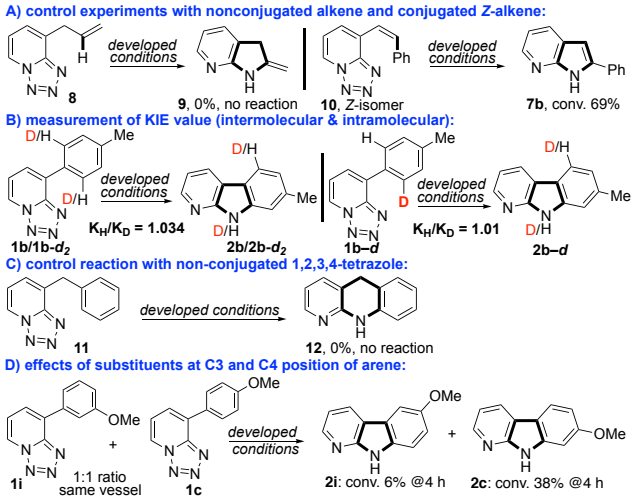
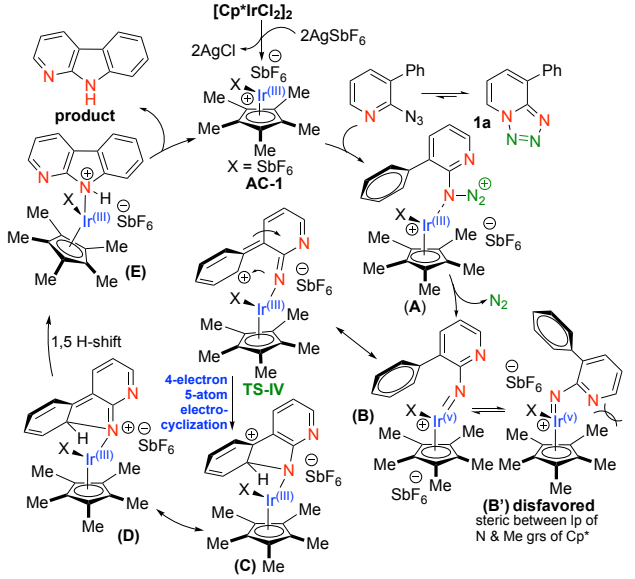


Chart 5. Proposed Electrocyclization Mechanism



To gain more insight, we conducted another competitive experiment using a 1/1 mixture of 3-OMe and 4-OMe-substituted substrates (**1i/1c**), hypothesizing that the EAS (**TS-III**) and electrocyclization process (**TS-IV**) would be more favored with **1i** and **1c** respectively, producing more product conversion due to the electronic effects (**Chart 4, D**).[19] However, we virtually observed that whereas, substrate **1i** gave only 6% conversion, substrate **1c** afforded 38% conversion, which is evidencing the proof-of-concept for the electrocyclization process (**TS-IV**).

Thus, based on the experimental evidences, we proposed the following electrocyclization mechanism (**Chart 5**). Treating with $AgSbF_6$, dimeric $[Cp^*IrCl_2]_2$ generates the active catalytic species (**AC-1**),[15a,20] which coordinates with the N1 atom of the tetrazole (**1a**) to form the species (**A**). Then, the species (**A**), might produce the sterically favored **(B)**[21] by the loss of dinitrogen. Next, the metal-nitrene (**B**) upon rearrangement of its π-electron generates the **TS-IV**, which undergoes 4-electron-5-atom electrocyclization to form the C–N bond in species (**C**). Subsequently, by a routine 1,5-H shift from the

resonating structure (**D**) of (**C**) led to the product formation with the regeneration of the active catalytic species (**AC-1**).

In conclusion, we have developed an efficient intramolecular denitrogenative transannulation/C(sp^2)–H amination method for the synthesis of a wide number of carbolines and 7-azaindoles by Ir(III)-catalyzed electrocyclization process. The essential requirement of this approach is the employment of $[Cp^*IrCl_2]_2$ and $AgSbF_6$ to generate the active catalytic species that help to form the metal-nitrene intermediate for the transannulation/amination. This is the first report for the denitrogenative transannulation/amination via metal-nitrene formation, which undergoes via an unprecedented electrocyclization process. The developed method shows very broad substrate scope and functional group tolerance. The synthetic benefits of the developed approach are showcased with a short synthesis of important bioactive molecules. More efforts are underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information Available: Full characterization, copies of all spectral data, experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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SKD and SR contributed equally.

Notes

The authors declare no competing financial interest.

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(11) This is the first report for the intramolecular denitrogenative transannulation/C(sp^2)–H amination of fused 1,2,3,4-tetrazoles via metal-nitrene. Attempted transannulation of 1,2,3,4-tetrazoles with alkynes and nitriles failed under the developed reaction conditions.

(12) Extensive screenings were carried out by the different combinations of solvents, catalysts and additives, for details, see: SI.

(13) Based on the NMR studies at room temperature, we observed that 1,2,3,4-tetrazole always exits in closed form, there is no effect of substituent at C8 position. However, halogen substituent at C5 position gives appreciable amount of open form. For details, see ref. 6.

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