Organic LETTERS

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Access to Imidazo[1,2-*a*]pyridines via Annulation of *α*-Keto Vinyl Azides and 2-Aminopyridines

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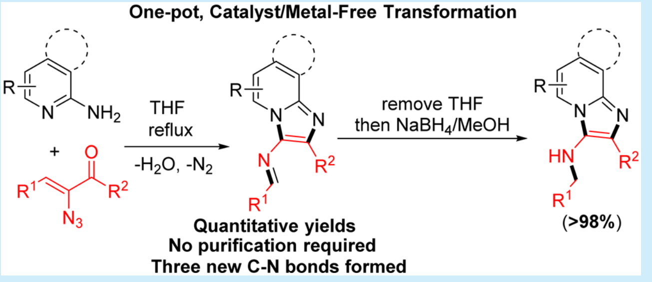
Supporting Information

ABSTRACT: A novel strategy for the synthesis of imidazo[1,2-*a*]pyridines via efficient catalyst/metal-free annulations of *α*-keto vinyl azides and 2-aminopyridines is described. Several imidazo[1,2-*a*]pyridines were synthesized from readily available vinyl azides and 2-aminopyridines and obtained in highly pure form by simply evaporating the reaction solvent. This remarkably high yielding and atom economical protocol allows the formation of three new C−N bonds through cascade reactions and rearrangements.

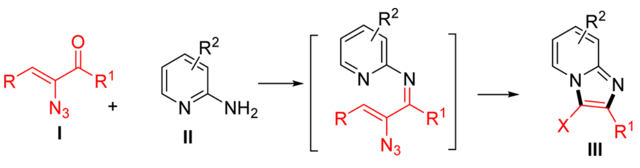


Developing efficient synthetic routes for biologically important heterocycles is a continuous enterprise in organic chemistry. Imidazo[1,2-*a*]pyridine lies among the most noteworthy pharmaceutically valuable heterocyclic motifs exhibiting a plethora of biological activities such as anticancer,[1] antimycobacterial,[2] antileishmanial,[3] anticonvulsant,[4] antiviral,[5] and others.[6] Many of the clinically used drugs for the treatment of insomnia (zolpidem),[7] anxiety (alpidem, necopidem and saripidem),[7,8] acute heart failure (olprinone),[9] peptic ulcer (zolimidine),[10] HIV infection (GSK812397),[11] and bacterial infections (rifaximin)[12] contain imidazo[1,2-*a*]pyridine as a key unit in their pharmacophores. Furthermore, imidazo[1,2-*a*]pyridine bearing molecules have been utilized as abnormal N-heterocyclic carbene ligands,[13] and as excited state intramolecular proton transfer (ESIPT) agents in optoelectronics.[14]

Owing to their importance and utility, considerable attention has been paid to construct imidazo[1,2-*a*]pyridine derivatives.[15,16] Among them, the three-component coupling of 2-aminopyridines, aldehydes, and isocyanides (Groebke reaction) is the most promising though the distressing odor of isocyanides and use of Bronsted or Lewis acid catalysts are the major concerns associated with it. Therefore, in recent years, synthetic approaches for imidazo[1,2-*a*]pyridines based on multicomponent reactions and tandem sequences are being keenly investigated.[16,17] The reported methods have their own drawbacks, including the necessity of expensive transition metal catalysts and special reagents, limited structural diversity of the product, harsh reaction conditions, and tedious workup/purification procedures. A synthetic route for imidazo[1,2-*a*]pyridines that uses simple and readily available starting materials and mild reaction conditions, gives high yields of products without formation of byproducts, and does not require any catalyst/additives and tedious workup/purification procedures may be considered an ideal synthesis. In this aspect, herein we report a novel synthetic strategy for imidazo[1,2-*a*]pyridines that fulfills the aforementioned criteria. Most of the organic syntheses require three basic operations (extraction, filtration, and evaporation) in their workup. However, the methodology described herein requires evaporation as the only purification step for getting final products. In addition, the initial condensation product [*N*-(imidazo[1,2-*a*]pyridin-3-yl)-1-arylmethanimine] of our synthetic strategy has a reactive imine functionality which can be utilized to yield various other derivatives of imidazo[1,2-*a*]pyridine in a one-pot operation.

Presented in this letter are the results of unprecedented annulations of vinyl azides **I** and 2-aminopyridines **II** (Scheme 1). Vinyl azides **I** can be obtained easily by a Knoevenagel type reaction of *α*-azido ketones with aldehydes.[18] We envisioned that the condensation of vinyl azides **I** with 2-aminopyridines **II** would lead to the formation of an imine which should undergo annulation to yield imidazo[1,2-*a*]pyridine **III**.

Scheme 1. Proposed Annulations of Vinyl Azides I with 2-Aminopyridines II To Yield Imidazo[1,2-*a*]pyridine Scaffold III



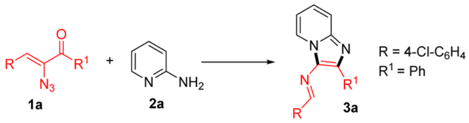
At the onset, we started investigating the feasibility of the annulation of vinyl azide **1a** with 2-aminopyridine **2a**.

Received: July 23, 2015

DOI: 10.1021/acs.orglett.5b02124
Org. Lett. XXXX, XXX, XXX−XXX

Annulations of **1a** and **2a** did not proceed in toluene at ambient temperature; however, heating the reaction mixture to a higher temperature guided the formation of **3a** in good yields (Table 1, entries 1−3). The structure of **3a** was assigned by analyzing its MS/HRMS, IR, and ^{1}H and ^{13}C NMR spectra. In order to find the best solvent for the annulations, several solvents such as toluene, EtOH, CH_3CN, $CHCl_3$, THF, 1,2-DCE, and 1,4-dioxane were screened (Table 1). The reaction proceeded smoothly in most of the solvents, and it gave a quantitative yield of imidazo[1,2-*a*]pyridine in THF (Table 1, entry 7).

Table 1. Annulations of Vinyl Azide 1a and 2-Aminopyridine 2a To Yield Imidazo[1,2-*a*]pyridine 3a[a]



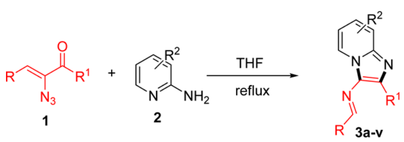
entry	solvent	*T* (°C)	time (h)	yield,[b] %
1	toluene	30	48	0
2	toluene	70	12	78
3	toluene	110	12	70
4	EtOH	80	12	81
5	CH_3CN	85	6	91
6	$CHCl_3$	70	6	97
7	THF	70	6	>99[c]
8	1,2-DCE	80	12	87
9	1,4-dioxane	100	12	65

[a]Reaction conditions: vinyl azide **1a** (0.5 mmol), 2-aminopyridine **2a** (0.5 mmol), solvent (5 mL), stir. [b]Isolated yields. [c]The crude reaction product obtained after evaporating the solvent was very pure under ^{1}H NMR analysis.

Encouraged by the successful efficient annulations of vinyl azide **1a** with 2-aminopyridine **2a**, we started exploring the scope of the reaction. A number of vinyl azides derived from aromatic aldehydes bearing halogen, electron-withdrawing, and electron-donating functional groups yielded a quantitative amount of the desired imidazo[1,2-*a*]pyridine derivatives (Table 2).

Vinyl azides derived from heteroaromatic aldehydes quantitatively yielded imidazo[1,2-*a*]pyridine derivatives (Table 2, entry 9). The reaction was not successful with vinyl azides derived from the condensation of ketones (cyclohexanone) or aliphatic aldehydes (*n*-butanal) with α-azido ketones. These ketones and aldehydes contain α-hydrogen atoms which probably lead to the formation of reactive imine/enamines that further reacted with themselves or other substrates present in the reaction system to give a complex mixture. Furthermore, vinyl azides derived from aromatic α-azido ketones bearing halogen and electron withdrawing/releasing functional groups gave quantitative yields of the products. Vinyl azides derived from aliphatic α-azido ketones could not be prepared using our standard protocol; therefore, they could not be attempted for our study. The reaction was successful with 2-aminopyridines containing several functional groups such as halogen and esters (Table 2, entries 21−22). The reaction was also successful with 1-aminoisoquinoline **2b**

Table 2. Scope of the Annulations of Vinyl Azide 1 and 2-Aminopyridine 2 To Yield Imidazo[1,2-*a*]pyridine 3[a]



entry	R	R^1	R^2	product	purity,[b] %
1	4-Cl-C_6H_4	C_6H_5	H	**3a**	98.3
2	4-Br-C_6H_4	C_6H_5	H	**3b**	87.4
3	2-naphthyl	C_6H_5	H	**3c**	98.7
4	4-NO_2-C_6H_4	C_6H_5	H	**3d**	98.5
5	3-NO_2-C_6H_4	C_6H_5	H	**3e**	98.3
6	4-CN-C_6H_4	C_6H_5	H	**3f**	98.1
7	3-C_6H_5O-C_6H_4	C_6H_5	H	**3g**	98.7
8	3,5-$(OCH_3)_2$-C_6H_3	C_6H_5	H	**3h**	99.8
9	2-furyl	4-F-C_6H_4	H	**3i**	98.4
10	3,5-$(OCH_3)_2$-C_6H_3	4-Cl-C_6H_4	H	**3j**	99.3 (99.5)[c]
11	4-Br-C_6H_4	4-Cl-C_6H_4	H	**3k**	99.9
12	4-CH_3-C_6H_4	4-Cl-C_6H_4	H	**3l**	98.9
13	4-NO_2-C_6H_4	4-Cl-C_6H_4	H	**3m**	99.2
14	3,4,5-$(OCH_3)_3$-C_6H_2	4-Cl-C_6H_4	H	**3n**	98.0
15	C_6H_5	4-Cl-C_6H_4	H	**3o**	99.3
16	4-Cl-C_6H_4	3-CH_3O-C_6H_4	H	**3p**	98.4
17	4-NO_2-C_6H_4	3-CH_3O-C_6H_4	H	**3q**	99.5
18	4-NO_2-C_6H_4	4-CH_3O-C_6H_4	H	**3r**	98.2
19	4-Cl-C_6H_4	4-CH_3O-C_6H_4	H	**3s**	98.6
20	3,5-$(OCH_3)_2$-C_6H_3	4-CN-C_6H_4	H	**3t**	95.0
21	3,5-$(OCH_3)_2$-C_6H_3	4-Cl-C_6H_4	4-Cl	**3u**	93.9
22	3,5-$(OCH_3)_2$-C_6H_3	4-Cl-C_6H_4	4-COOMe	**3v**	99.6

[a]Reaction conditions: vinyl azide **1** (0.5 mmol), 2-aminopyridine **2** (0.5 mmol), dry THF (5 mL), reflux. [b]Determined by HPLC analysis of the crude product which was obtained in quantitative yields after evaporating the reaction solvent. [c]Values in the parentheses represent purity of a sample which was obtained quantitatively in a gram scale (10 mmol scale) reaction.

DOI: 10.1021/acs.orglett.5b02124
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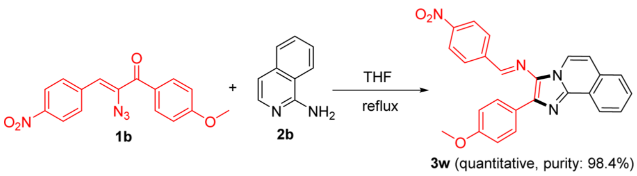
and yielded imidazo[2,1-*a*]isoquinoline **3w** in quantitative yield (Scheme 2). Unambiguous proof for the structure of

Scheme 2. Annulation of Vinyl Azide 1b and 1-Aminoisoquinoline 2b To Yield Imidazo[2,1-*a*]isoquinoline 3w

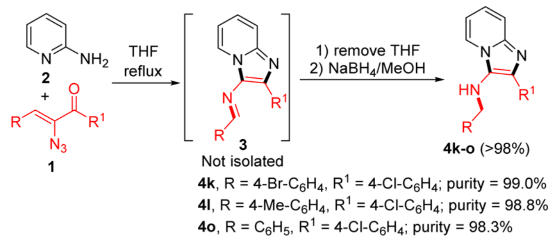


imidazo[1,2-*a*]pyridine was obtained by single crystal X-ray analysis of the compound **3d** (the details of the X-ray analysis can be found in the Supporting Information).

It is noteworthy that the imidazo[1,2-*a*]pyridines **3a−w** were obtained simply by removing THF from the reaction mixture under a reduced pressure and were very pure. HPLC analysis of the crude mass obtained after evaporating the reaction solvent (THF) was carried out which showed high purity (87.4−99.9%) of the imidazo[1,2-*a*]pyridines **3a−w** (Table 2). It is also notable that, in contrast to earlier reports, our methodology gives quantitative yields of the products and allows unsymmetrical substitution (R and R^1) in the imidazo[1,2-*a*]pyridine unit. Next, in order to demonstrate the synthetic competence of our strategy, a gram scale reaction (10 mmol scale) was performed (Table 2, entry 10). The quantitative yield (purity: 99.5%) of the imidazo[1,2-*a*]pyridine in the gram scale synthesis showed that the strategy has the potential for industrial scale up production.

Since imidazo[1,2-*a*]pyridine **3** was obtained in pure form simply by evaporating the reaction solvent, the reactive imine group of **3** could be utilized to yield numerous derivatives in a one-pot operation. In order to demonstrate it, after the formation of **3** was complete, the solvent (THF) was removed under reduced pressure and the reaction mixtures were directly treated with $NaBH_4$/MeOH to give amines **4** (Scheme 3). It is

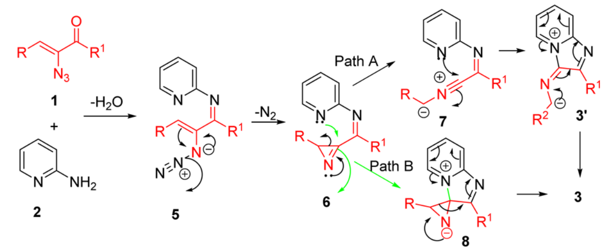
Scheme 3. One-Pot Synthesis of Groebke Imidazo[1,2-*a*]pyridines



worth noting that highly pure (98.3−99.0%) amines **4** were obtained after removing methanol and extracting the crude product by EtOAc/water in excellent yields (>98%). Since imidazo[1,2-*a*]pyridines **4** can be synthesized by Groebke reaction, prior to synthesizing them one can compare both strategies based on their pros and cons. In general, our methodology is superior to other reported syntheses in terms of reaction simplicity, purity, workup/purifications, yields, and more importantly offering reactive imines **3** for further derivatization.

Annulations of vinyl azides **1** with 2-aminopyridines **2** can be explained by a plausible mechanism depicted in Scheme 4.

Scheme 4. Mechanistic Rationalization for the Annulations of Vinyl Azides and 2-Aminopyridines To Yield Imidazo[1,2-*a*]pyridine Derivatives



Under heating the imine **5** generated from the condensation of vinyl azide **1** and 2-aminopyridine **2** loses nitrogen to yield a 2*H*-azirine intermediate **6**. Formation of the imidazo[1,2-*a*]pyridine **3** from the intermediate **6** can be explained in two ways (Scheme 4, path A and B). Path A: The 2*H*-azirine is opened up by the lone pair of the nitrogen forming a C−N triple bond, and the C−C bond of the 2*H*-azirine is cleaved. This leads to the formation of a zwitterion **7** which is attacked by the lone pair of pyridine yielding a different zwitterion **3′** which is actually a resonance form of the product. Path B: The lone pair of the pyridine attacks the 2*H*-azirine intramolecularly to yield a zwitterion intermediate **8** which rearranges to final product **3**.

An alternative mechanism based on generation of a 2*H*-azirine from **1** at the very first step and its subsequent annulation with **2** seems also possible. However, a significant amount of byproducts can be expected if the reaction followed this pathway, since thermal conversion of vinyl azides bearing an α-keto carbonyl group (vinyl azides of type **1**) to 2*H*-azirines is a poor yielding process due to competing nitrile and indole forming reactions.[19,20] We did not observe the formation of noticeable byproducts in our annulations study even when a control reaction was performed in an NMR tube (for details of the control experiment, see Supporting Information). This evidence indicates that the nitrogen of pyridine is the key which drives the annulation forward right after the formation of imine **5** probably through 2*H*-azirine type intermediates.

In conclusion, we have developed a novel and efficient methodology for the synthesis of diverse and functionalized imidazo[1,2-*a*]pyridines through an unprecedented annulation of readily available vinyl azides and 2-aminopyridines. To the best of our knowledge, it is the first report of any heterocycle synthesis which gives quantitative yields of products and requires evaporation of the solvent as the only purification step. This operationally simple strategy allows the formation of three new C−N bonds, with the release of H_2O and N_2 as the sole byproduct, through a condensation, cyclization, and ring opening reaction cascade, in a process that is highly atom economical, convenient, and scalable to fulfill the demands of academia and industry. A series of 23 different imidazo[1,2-*a*]pyridine derivatives were synthesized in high yields by reacting vinyl azides and 2-aminopyridines. In addition, this catalyst/metal-free synthetic route allows the formation of *N*-(imidazo[1,2-*a*]pyridin-3-yl)-1-arylmethanimines that contain a reactive imine functionality which can be utilized in multiple ways to generate numerous imidazo[1,2-*a*]pyridines in a one-pot protocol.

DOI: 10.1021/acs.orglett.5b02124
Org. Lett. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02124.

Full experimental details, characterization data for all products, copies of ^{1}H and ^{13}C spectra, X-ray analysis, and HPLC chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.A.M. is thankful to the Department of Science & Technology, India for financial support (GAP 0378 and GAP 0470). Financial support in part from 12th Five Year Plan Project "Affordable Cancer Therapeutics (ACT-CSC-0301)" is also acknowledged. P.R.A. acknowledges CSIR New Delhi, and G.S.M. acknowledges NIPER Hyderabad for financial support.

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DOI: 10.1021/acs.orglett.5b02124
Org. Lett. XXXX, XXX, XXX−XXX