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Indium-Catalyzed Denitrogenative Transannulation of Pyridotriazoles: Synthesis of Pyrido[1,2-*a*]indoles

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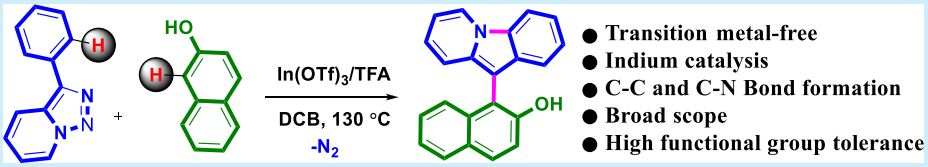
Supporting Information



ABSTRACT: Pyrido[1,2-*a*]indoles are known for medicinally and pharmaceutically important compounds; however, the efficient synthetic routes are scarce in the literature. We report herein a convenient and efficient route to synthesize these molecules through indium-catalyzed transannulation of pyridotriazoles with arenes. A library of compounds have been synthesized employing the method developed with various substituted pyrido[1,2-*a*]indole derivatives in moderate to good yields. The density functional theory study using SMD_{DCB}-M06/6-31++G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ method suggests that the reactions proceed via indium-carbenoid complex.

Nitrogen-fused heterocycles are the key structural motifs predominantly found in the field of medicinal chemistry and material chemistry.[1−3] Pyridine-fused heterocycles such as imidazo[1,2-*a*]pyridines, imidazo[1,5-*a*]pyridines, imidazo[1,2-*a*]pyrazines, indolizines, imidazo[2,1-*a*]isoquinolines, pyrazolo-[1,5-*a*]pyridines, and pyrido[1,2-*a*]indoles are important intermediates in both medicinal chemistry and drug development. Particularly, pyrido[1,2-*a*]indoles were known to exhibit a wide range of biological activities (Figure 1). Due to the importance of

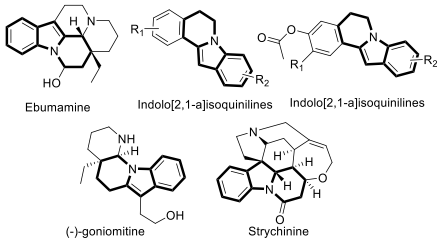


Figure 1.

these molecules in various fields, few elegant synthetic routes have been developed to access pyrido[1,2-*a*]indoles.[4−7] Despite the significance of these methods, it is highly desirable to develop an efficient approach utilizing easily available catalysts, with broad substrate scope, high atom economy, and an environment-friendly oxidants.

Alternately, transannulation methods are extraordinarily efficient and show excellent selectivity through in situ generation of metal-carbenoid species and their reactions with different coupling partners to transform into a desired products. Gevorgyan et al. reported the Rh(II)-catalyzed denitrogenative transannulations with desired substrates.[8]

Given the prevalence of denitrogenative transannulations to generate bioactive molecules, alternative synthetic routes are important to explore. In this regard, catalytic transformations are particularly promising. It has been recently reported that Cu and Rh catalysts can generate metal carbene intermediates to enhance the electrophilicity for the transannulations with other nucleophiles (Scheme 1).[9]

Based on the recent literature[10−15] for the generation of metal carbene intermediates through the ring opening of pyridotriazole **1a** (Scheme 2), we hypothesized to employ silver and indium as metal catalysts to generate electrophilic carbene intermediate **A**, and its subsequent reaction with 2-naphthol **2a** as nucleophile to generate tetracyclic heterocycle **3a′**(5-phenylnaphtho[2,1-*b*]-pyrido[1,2-*d*][1,4]oxazine) in line with our interest in the synthesis of fused heterocycles[16] and transannulation of pyridotriazoles.[17] Instead, we obtained an interesting product **3a** 1-(pyrido[1,2-*a*]indol-10-yl)naphthalen-2-ol in 20% isolated yield, when Ag(OTf) was used as catalyst (20 mol %) in dichlorobenzene (DCB) as solvent at 120 °C, after 5 h (Table 1, entry 1). With this reaction, we supposed to enhance the electrophilicity of metallocarbene by harnessing different metals and conditions. To this end, we screened different metal triflates and solvents, under these conditions either no reaction or low yield was observed (entries 2−6). With $In(OTf)_3$ as a catalyst, little improvement in yield of **3a** was observed (entry 7).

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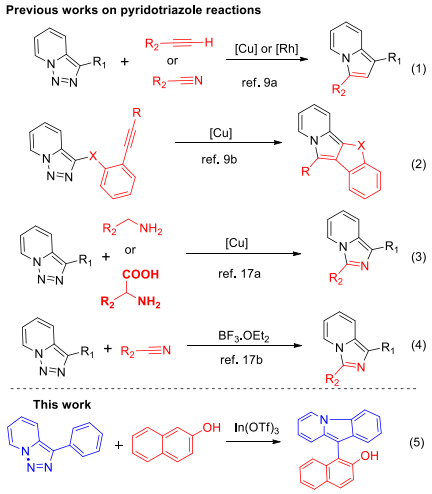
Scheme 1. Transannulation Reactions of Pyridotriazoles



Scheme 2. Transannulation of Pyridotriazole with 2-Naphthol

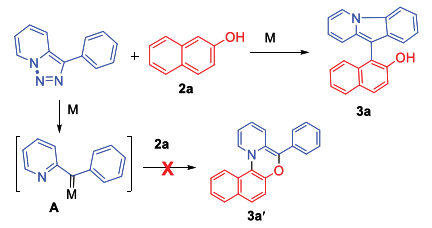
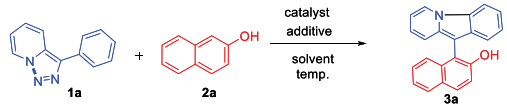


Table 1. Optimization of Reaction Conditions[a]



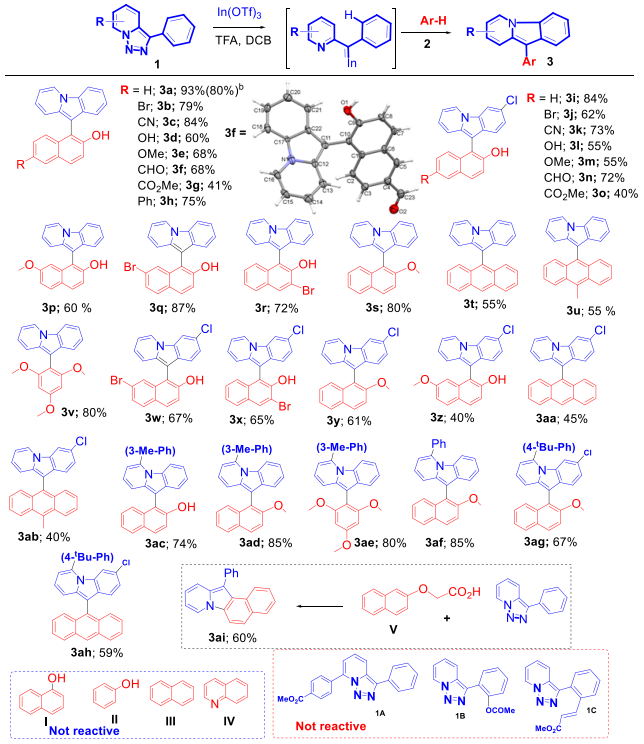
	2a (equiv)	catalyst (mol %)	additive (equiv)	solvent (1 mL)	temp (°C)	yield (%)
1	2	Ag(OTf)(20)		DCB	120	20
2	2	Ag(OTf)(20)		toluene	120	trace
3	2	Ag(OTf)(20)		DCE	120	nr
4	2	$Cu(OTf)_2$(20)		DCB	120	nr
5	2	$Ni(OTf)_2$ (20)		DCB	120	17
6	2	$Sc(OTf)_3$(20)		DCB	120	trace
7	2	$In(OTf)_3$(20)		DCB	120	24
8	2	$In(OTf)_3$(20)	TFA (1)	DCB	120	39
9	2	$In(OTf)_3$(20)	TFA (2)	DCB	120	42
10	2	$In(OTf)_3$(20)	TFA (2)	DCB	120	75
11	**1.5**	**$In(OTf)_3$(20)**	**TFA (2)**	**DCB**	**130**	**93**
12	1.5	$In(OTf)_3$(20)	TFA (2)	DCB	rt	nr
13	1.5	$In(OTf)_3$(20)	TFA (2)	DCB	100	50
14	1.5	$In(OTf)_3$(20)	TFA (2)	DCB	130	68
15	1.5	$In(OTf)_3$(20)	TFA (2)	DCB	130	35
16	1.5		TFA (2)	DCB	130	nr
17	1.5	$In(OTf)_3$(20)	TFA (2)	DCB +DCE	130	trace
18	1.5	$In(OTf)_3$(20)	TFA (2)	EtOH	130	nr
19	1.5	$In(OTf)_3$(20)	TFA (2)	MeOH	130	nr
20[b]	1.5	$In(OTf)_3$(20)	TFA (2)	DCB	130	16

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $In(OTf)_3$ (20 mol %), TFA (0.4 mmol), DCB (1.0 mL), 130 °C, 5 h, isolated yield. [b]O_2 balloon; in this case, 2-benzoylpyridine was observed as major product. nr = no reaction

In addition to the $In(OTf)_3$, when trifluoroacetic acid (TFA) was used as additive up to two equivalents (w.r.t. **1a**), the yield of the desired product **3a** was increased to 75% (entries 8−10). When the reaction was performed by reducing the amount of **2a** (1.5 equiv w.r.t. **1a**) and increasing the temperature to 130 °C, the yield of the product was further increased to 93% (entry 11). Further, altering the catalyst load and temperature of the reaction, the yield was decreased (entries 12−15). Without indium catalyst (entry 16) and with the reaction in other solvents, no reactions were observed (entries 17−19). When the reaction was performed under oxygen atmosphere, the desired product was isolated only in 16% yield along with oxidized product 2-benzoylpyridine as the major product (entry 20).

With the optimized conditions (Table 1, entry 11) for the synthesis of 1-(pyrido[1,2-*a*]indol-10-yl)naphthalen-2-ol, the scope and limitations of the present transformation has been studied (Scheme 3). The results in Scheme 3 demonstrate that

Scheme 3. Scope of Indium-Catalyzed Transannulation of Pyridotriazoles[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), $In(OTf)_3$ (20 mol %), TFA (0.4 mmol), DCB (1.0 mL), 130 °C, 5 h, isolated yield. [b]Reaction yield at 1.0 mmol scale.

the reaction holds a high degree of functional group tolerance with broad substrate scope. Initially, the reaction of **1a** with 2-naphthols **2** bearing electron-donating and withdrawing substituents (H, OH, OMe, Br, CN, CHO, CO_2Me, and Ph) at C-6 position of **2**, gave the corresponding annulated products (**3a**−**3h**) in good yields (41−93%). One of the products **3f** was further confirmed by single crystal XRD. The reaction of 3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]pyridine **1b** was reacted with the above 2-naphthol derivatives and afforded the desired products (**3i**−**3o**) in good yields (40−84%). The methoxy and bromo substituents at C-7 of 2-naphthols were also reacted with **1a** under the optimized conditions to give the desired products (**3p**−**3r**) in 60−87% yields. We turned our attention to other

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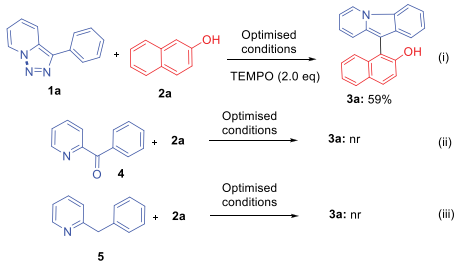
arenes such as 2-methoxy naphthalene, anthracene, 9-methylanthracene, and 1,3,5-trimethoxybenzene as nucleophiles to the present conditions. Delightfully, these substrates reacted smoothly with **1a** under the optimized conditions and delivered the corresponding annulated products (**3s**−**3v**) in 55−80% yields. As evident from the yields of products (**3b**−**3v**), the steric and electronic effects do not affect the efficiency of the present reaction.

We then focused on the reaction of 3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]pyridine **1b**, with different naphthols and anthracene derivatives, and obtained the corresponding products (**3w**−**3ab**) in moderate yields. Further, to enhance the substrate scope, substituted pyridotriazoles such as 3-phenyl-7-(*m*-tolyl)-[1,2,3]triazolo[1,5-*a*]pyridines, 3,7-diphenyl-[1,2,3]triazolo-[1,5-*a*]pyridine, and 7-(4-(*tert*-butyl)phenyl)-3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]pyridines were reacted with different arenes (2-methoxy naphthalene, 1,3,5-trimethoxybenzene, and anthracene) under the optimized conditions. These substrates afford the corresponding annulated products (**3ad**−**3ah**) in 59% to 85% yields, respectively. Unfortunately, the arene substrates (**I**−**IV**) and ester substituted pyridotriazoles (**1A**−**1C**) were not reactive under the present conditions, whereas the reaction of 2-(naphthalen-2-yloxy)aceticacid (**v**) with **1a** under the same conditions gave the unexpected transannulated product 12-phenylbenzo[e]pyrido[1,2-*a*]indole **3ai** in 60% isolated yield.

To establish the reaction mechanism, some selective and control experiments were performed (Scheme 4). Under the

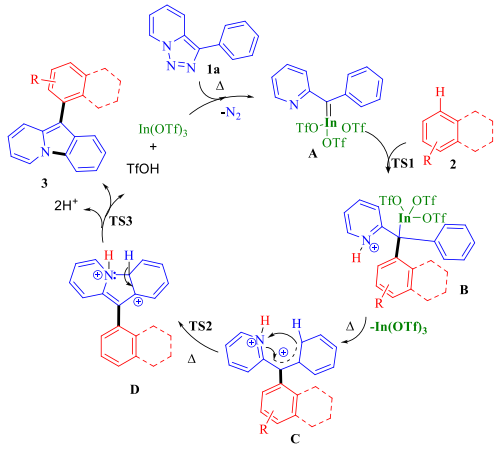
Scheme 4. Control Experiments



optimized conditions, the reaction of **1a** and **2a** was subjected to two equivalent of TEMPO as a radical scavenger; under these conditions, the desired product **3a** was obtained in 59% yield (Scheme 4, eq i). This reaction indicates that the present transformation does not proceed through radical path. Further, the reaction of 2-benzoylpyridine **4** and 2-benzylpyridine **5** were subjected with **2a** under the present conditions instead of **1a**, to know the possible intermediate in the present transformation, but these reactions failed to afford the desired product **3a** (eqs ii and iii). These reactions designate that substrates **4** and **5** are not intermediates in the present transformation (Scheme 4).

Based on the literature reports[6,7,9−15] and with the above observations, a plausible reaction mechanism has been proposed (Scheme 5). Denitrogenation of **1** with indiumtriflate (In(OTf)$_3$) may generate the indium carbenoid **A**. The insertion of **2** to the intermediate **A** may generate metalated pyridinium Aza-Nazarov type intermediate **B**,[6b,c] which upon elimination of In(OTf)$_3$ under acidic conditions give the biscationic pyridinium tertiary carbocation **C**.[6b,d] High temperature and steric hindrance of two bulky aryl groups of **C** may drive the phenyl group close to the pyridine nitrogen and lead to the formation of another intermediate **D** via intramolecular C−H amination. The subsequent oxidation of **D** will deliver the desired product **3**.

Scheme 5. Plausible Reaction Pathway for the Formation of Pyrido[1,2-*a*]indoles



We have examined this mechanistic pathway computationally at SMD$_{DCB}$-M06/6-31++G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ level of theory in *o*-dichlorobenzene phase (ε = 10.0) (Scheme 5 and Figure 2).[18] The computational results

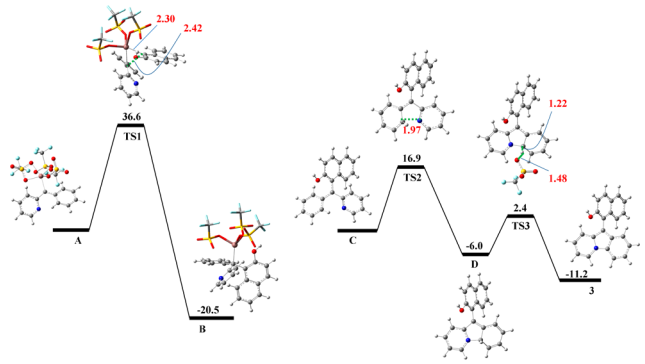


Figure 2. SMD$_{DCB}$-M06/6-31++G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ level of theory DFT calculated free energy profile of the formation of **3**. The free energies are given in kcal/mol and distances (red color) are given in Å.

suggest that In(OTf)$_3$ can form stable intermediate, **A**, with **1a**, and the intermediate **A** is stable by 10.3 kcal/mol; however, the intermediate **A′** formed by AgOTf and **1a** is unstable by 13.1 kcal/mol (Figure 2).[19] We have further examined the formation of pyrido[1,2-*a*]indole at the SMD$_{DCB}$-M06/6-31++G(d,p)/LANL2DZ level of theory in *o*-dichlorobenzene. The naphthol anion attacks the indium-carbenoid carbon and forms the intermediate **B**. The activation free energy barrier is 36.6 kcal/mol, and the intermediate **B** is energetically stable by 20.5 kcal/mol (Figure 2). The carbocation **C** is generated via a barrier less process of the elimination of In(OTf)$_3$ at higher temperature (130 °C). The carbocation **C** promotes stepwise cyclization followed by oxidation leads the desired product **3**. The pyridine nitrogen attacks the ortho position of the phenyl ring and form the cyclic intermediate **D**. The activation free energy barrier in this step is 16.9 kcal/mol, and the intermediate **D** is stable by 6.0 kcal/mol at the SMD$_{DCB}$-M06/6-31++G(d,p)/LANL2DZ level of theory. Furthermore, the aromatization of intermediate **D** is assisted by the triflate anion via an 8.4 kcal/mol activation free energy barrier compared to the preceding intermediate. The desired product **3** is stable by 11.2 kcal/mol compared to **C**. The

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DFT results further suggest that the formation of the intermediate **A′** from AgOTf and is thermodynamically less preferred compared to that of $In(OTf)_3$ and is corroborated by the experimentally observed product of 20% yield.

To conclude, we have revealed an expeditious indium-catalyzed denitrogenative transannulation of pyridotriazoles with *β*-naphthols to obtain pyrido[1,2-*a*]indole derivatives. The methodology also works very well with a variety of other substrates such as methoxy naphthalenes, trimethoxybenzenes, and anthracene derivatives. The method shows very good functional group tolerance with broad substrate scope and with good yields. The DFT studies indicates that the reaction proceeds through an indium-carbenoid intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00180.

Copies of NMR spectra for all compounds and HRMS spectra for new compounds; computational details and the B3LYP/6-31G(d)/LANL2DZ level of theory optimized Cartesian coordinates (PDF)

Accession Codes

CCDC 1842992 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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