



N-Tosylhydrazone as an oxidizing directing group for the redox-neutral access to isoquinolines via Cp*Co(III)-Catalyzed C–H/N–N activation

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ABSTRACT

Herein, an efficient and economic access has been revealed for the synthesis of isoquinolines via C–H bond activation strategy by using comparatively inexpensive and versatile cobalt catalyst. A hardly investigated directing group, *N*-tosylhydrazone has been effectively applied as an internal oxidant for an annulation reaction with internal alkynes via C–H/N–N bond functionalization. This catalytic protocol works for the extensive variety of substrates in moderate to excellent yields under external oxidant-free conditions. Additionally, the proposed protocol has advantages such as broad substrate coverage with significant product yields, readily synthesized substrates as well as scalability up to the gram quantity which further improves the competency of the methodology.

1. Introduction

Isoquinoline and its derivatives represents the important class of organic molecules which possess different biological activities such as anti-tumour, anti-malarial, cardiovascular, anti-inflammatory, anti-HIV, etc. [1] They are also utilized for the development of numerous inhibitors, alkaloids chiral ligands and organic light-emitting diodes [2]. Thus, this moiety has achieved a great deal of attention in the field of medicinal and pharmaceutical chemistry (see Schemes 1 and 2).

Straight C–H bond activation has appeared to be an influential tactic in synthetic chemistry by creating new opportunities in the retrosynthetic strategies as well as enhancing the entire capability of the anticipated conversions [3]. Being atom economic, transition-metal assisted coupling transformations by direct C–H bond activation would streamline the synthetic processes and reduce the formation of unwanted by products. Various prior approaches on C–H bond activations are mainly centered around complexes of transition-metals such as Pd, Rh, Ir and Ru for the efficient synthesis of important organic scaffolds [4]. Due to the shortcomings of cost efficiency, sustainability, plenitude and poisonous nature, the second-row transition-metals possess limitations for the wide application in drug discovery as well as large-scale manufacturing of active pharmaceutical ingredients (API) and natural products which would be the final aim of synthetic chemistry research.

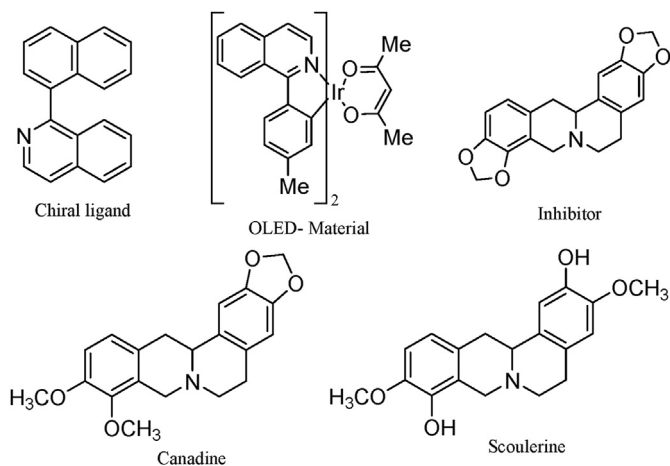
Therefore, taking into consideration the economic practicability of organic synthesis, there is a growing interest in developing catalysts in accordance with the economical first-row transition metals for C–H bond functionalization which represents an attractive alternative [5]. Among them, cobalt is having an extensive application of functionalizing the inactive C–H bonds [6]. Being fairly reactive, low-cost, abundant and comparatively less harmful by character in contrast to noble metals, it has turn into the centre of interest in the area of C–H activations. The initial Cp*Co(III)-catalyzed C–H activation reaction was reported by Matsunaga, Kanai, and co-workers in 2013 [7]. These Cp*Co(III) catalysts were proved to be suitable replacements to Cp*Rh(III) catalysts for C–H activations. A prevailing catalytic system utilizing Cp*Co(CO)I₂ [8] for C-2 selective C–H amidation of indoles with sulfonyl azides was testified by the same group [9]. Recently, new class of Cp*Co(III)-pNHC templates was utilized in catalytic annulation of azoles with internal alkynes [10].

Earlier, almost transition-metal-catalyzed C–H activation strategies required stoichiometric or super-stoichiometric amount of oxidizing agent in order to maintain the catalytic cycle. These are mostly toxic metal salts, which certainly gives rise to reduced atom-economy by generating off-cycle lateral transformations and unwanted waste. The constraint of the necessity of an oxidizing agent has been resolved by fixing a multifunctional group in substrate which plays the role of directing group and oxidizing agent both [11]. In this strategy, the

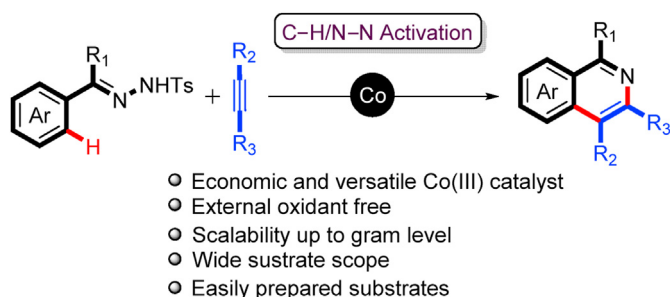
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Scheme 1. Demonstrative biologically active and other vital molecules containing isoquinoline skeleton.



Scheme 2. *N*-Tosylhydrazone directed redox-neutral synthesis of isoquinolines via Cp*Co(III)-catalyzed C–H activation.

cleavage of N–N, N–O or O–O bonds for the redox-neutral methods were employed as an essential tool. The technique has potential for the enhanced reactivity as well as has obvious merits of selectivity, better

yields and substrate coverage.

Due to the wealth of isoquinoline skeletons, many synthetic routes have been given for their synthesis that are established by Pomeranz–Fritsch, Pictet–Spengler, and Bischler–Napieralski reactions [12]. However, such approaches are suffered by some drawbacks like poor yield, low regioselectivity, limited substrate scope, longer reaction duration and tedious as well as harsh reaction conditions in some cases. To overcome these shortcomings, potent alternate routes were given by cyclization kind of transformations with alkynes through C–H bond activation [13]. Further, the ‘external-oxidant-free’ ideal strategy which is modest, secured, and ecologically benign also contributed in the rationalized access of isoquinolines via transition-metal-catalyzed C–H bond activations. Transition metals such as Pd [14], Ru [15] and Rh [13, 16] were employed significantly for the streamlined synthesis of isoquinolines using “external-oxidant-free” approach. These catalysts showed effective catalytic activity, a wide substrate scope, and high functional group compatibility. However, comparatively low cost and abundant cobalt catalyst attracted scientists to give alternate inexpensive and efficient external oxidant free methodologies for the synthesis of isoquinolines. In these strategies, the N–O and N–N bonds have been employed as a significant handle for both C–N cyclization and catalyst turnover. Considering the N–O bond as an internal oxidant, in 2015, Ackermann [17], Sundararaju [18] and Matsunaga [19] groups, independently reported cobalt-catalyzed C–H/N–O activations for the synthesis of isoquinolines using different oxidizing directing groups. Subsequently, in 2016, Cheng [20] and Jeganmohan [21] research groups reported Co catalyzed annulation reactions for the access of isoquinolines using similar strategy. Recently, in 2019, Song and co-workers mentioned Cp*-free cobalt-catalyzed C–H activation using N,O-bidentate directing group in order to synthesize isoquinolines [22]. On the other hand, N–N bond was also recruited as an internal oxidant for the redox-neutral synthesis of isoquinolines. Zhu group [23] and Lade group [24], in 2016, reported C–H/N–N functionalization reactions for the synthesis of isoquinolines under external oxidant free conditions.

Our research group has also paid substantial attention for various protocols in order to access isoquinolines using different directing groups and transition-metals as catalysts [25]. In 2019, *N*-Cbz hydrazone was utilized as a directing group for the synthesis of isoquinolines using Cp*Co(III)-catalyst through C–H and N–N bond functionalization [25e].

Table 1
Optimization of reaction parameters.^a

Entry	Co Catalyst	Additive 1	Additive 2	Solvent	Temp (°C)	Time (h)	Yield ^b (%)
1	Co(OAc) ₂ ·4H ₂ O	AgSbF ₆	NaOAc	TFE	110 °C	24	–
2	[Cp*Co(II)] ₂	AgSbF ₆	NaOAc	TFE	110 °C	24	18
3	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	TFE	110 °C	24	34
4 ^c	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	TFE	110 °C	24	35
5 ^d	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	TFE	110 °C	24	21
6	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	1,2-DCE	110 °C	24	Trace
7	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	MeOH	110 °C	24	–
8	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	TAA	110 °C	24	–
9	[Cp*Co(CO)I ₂]	AgSbF ₆	NaOAc	HFIP	110 °C	24	54
10	[Cp*Co(CO)I ₂]	AgSbF ₆	KOAc	HFIP	110 °C	24	59
11	[Cp*Co(CO)I ₂]	AgSbF ₆	CsOAc	HFIP	110 °C	24	66
12	[Cp*Co(CO)I ₂]	AgSbF ₆	AcOH	HFIP	110 °C	24	84
13	[Cp*Co(CO)I ₂]	KPF ₆	AcOH	HFIP	110 °C	24	49
14	[Cp*Co(CO)I ₂]	AgSbF ₆	AcOH	HFIP	100 °C	24	83
15	[Cp*Co(CO)I ₂]	AgSbF ₆	AcOH	HFIP	90 °C	24	63
16	[Cp*Co(CO)I ₂]	AgSbF ₆	AcOH	HFIP	100 °C	12	81
17	[Cp*Co(CO)I ₂]	AgSbF ₆	AcOH	HFIP	100 °C	10	69

^a reaction conditions: ketazine **1a** (0.2 mmol), diphenylacetylene **2a** (0.4 mmol), Co catalyst 10 mol%, Additive 1 (20 mol %), Additive 2 (20 mol%), Solvent 2 mL.

^b GC yield.

^c 15 mol% Co catalyst was used.

^d 5 mol% Co catalyst was used. TFE: 2,2,2-Trifluoroethanol; 1,2-DCE: 1,2-Dichloroethane; MeOH: Methanol; TAA: *tert*-Amyl alcohol; HFIP: Hexafluoro-2-propanol.

In 2018, we reported *N*-tosylhydrazone directing group in order to generate isoquinoline derivatives utilizing ruthenium as a catalyst [25a]. Although, the protocol is highly efficient, it required external oxidant and comparatively expensive ruthenium catalyst. On the other hand, to the best of our knowledge, a directing group, *N*-tosylhydrazone was not reported for C–H functionalization reactions under external oxidant free conditions and using comparatively economic first row transition-metal catalyst. In this context, it is highly desired to develop a protocol for the activation of C–H/N–N bonds of *N*-tosylhydrazones which fulfils these shortcomings. With the concern for the effective synthesis of heterocyclic moieties, here, we provide a potential method for the access of isoquinoline derivatives by C–H/N–N bond activation policy employing *N*-tosylhydrazone directing group and $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ as a catalyst using external oxidant free circumstances.

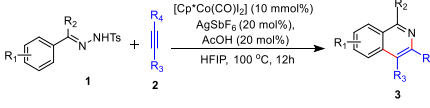
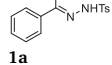
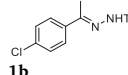
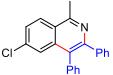
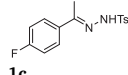
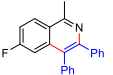
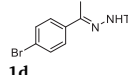
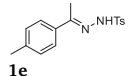
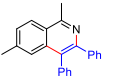
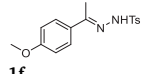
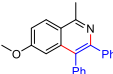
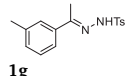
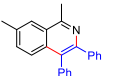
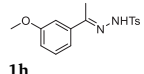
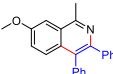
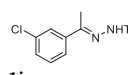
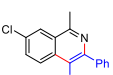
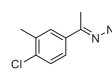
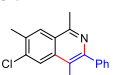
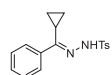
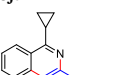
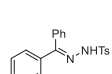
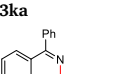
2. Results and discussion

Our initial study was performed with the annulation reaction of *N*-tosylhydrazone **1a** (0.2 mmol) with diphenylacetylene **2a** (0.4 mmol) in presence of Co catalyst and AgSbF_6 & NaOAc as additives in order to generate isoquinolines **3aa** as model reaction (Table 1). The introduction of AgSbF_6 and acetate source was determined by previous studies which are required for the generation of active cationic $\text{Cp}^*\text{Co}(\text{III})$ species in order to complete the desired transformation [17,19,23]. To examine the catalytic efficiency, three cobalt catalysts i.e. $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $[\text{Cp}^*\text{CoI}_2]$ and $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ were screened for a standard transformation at 110°C for 24 h in 2,2,2-trifluoroethanol as solvent (Table 1, entries 1–3). Out of these catalysts, $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ exhibited the highest catalytic activity with 34% yield (Table 1, entry 3), whereas $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was inefficient for the proposed transformation (Table 1, entry 1). Further, optimization studies to determine the exact requirement of amount of catalyst were performed. With 15 mol% $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$, no significant impact on the yield of product was detected, whereas on lowering the catalyst concentration to 5 mol%, the yield of the desired product was decreased to 21%. (Table 1, entries 4 and 5). Screening various solvents for the proposed methodology, trace amount of isoquinoline **3aa** was obtained when 1,2-dichloroethane was used (Table 1, entry 6). While, two other solvents such as methanol and *tert*-amyl alcohol were non-efficient for the suggested transformation (Table 1, entry 7 and 8). On the other hand, attempting the reaction in HFIP, we found that the reaction worked efficiently to produce 54% product yield (Table 1, entry 9). This indicates that HFIP found to be the most suitable among various solvents for the stated methodology. Next, different additives like KOAc, CsOAc and HOAc were also screened for the given reaction. Out of those, HOAc proved to be superior in order to produce the anticipated product with 84% yield (Table 1, entries 10–12). Consequently, an attempt was made to replace AgSbF_6 with KPF_6 as an additive, however, unfortunately, the reaction efficiency deteriorated giving product **3aa** with 49% yield (Table 1, entry 13). Next, to visualize the effect of temperature on the reaction efficiency, the reactions were attempted at different temperatures. Performing the reaction at 100°C , no considerable consequence on the yield of product **3aa** was detected, although further decrease in temperature results in lowering of the product yield (Table 1, entries 14 and 15). At the end, optimum time study was performed. By reducing the reaction time to 12 h, the reaction worked with similar efficiency, while further decrease in time to 10 h lowered the product yield (Table 1, entries 16 and 17). So, the optimum reaction parameters are *N*-tosylhydrazone **1a** (0.2 mmol), diphenylacetylene **2a** (0.4 mmol), $[\text{Cp}^*\text{Co}(\text{CO})\text{I}_2]$ (10 mol%), AgSbF_6 (20 mol %), AcOH (20 mol%), HFIP (2 mL), 100°C , 12 h.

With the optimum reaction parameters, the extent of the annulation reaction of substituted *N*-tosylhydrazones (**1a–p**) with diphenylacetylene (**2a**) was analysed. A wide range of *N*-tosylhydrazones (**1a–p**) bearing various electron withdrawing and donating groups (e.g. Me, OMe, Ph, F, Cl, Br, I) were employed for annulation reaction with diphenylacetylene (**2a**) which could lead to successful formation of anticipated products. *N*-

Table 2

$\text{Co}(\text{III})$ catalyzed annulation of *N*-tosylhydrazones for the synthesis of isoquinolines.^a

				
Entry	Azine (1)	Alkyne (2)	Product (3)	Yield ^b (%)
1	 1a	 2a	 3aa	81
2	 1b	2a	 3ba	76
3	 1c	2a	 3ca	73
4	 1d	2a	 3da	78
5	 1e	2a	 3ea	83
6	 1f	2a	 3fa	87
7	 1g	2a	 3ga	80
8	 1h	2a	 3ha	49 33
9	 1i	2a	 3ia	71
10	 1j	2a	 3ja	74
11	 1k	2a	 3ka	78
12	 1l	2a	 3la	89
13	 1m	2a	 3ma	84

(continued on next page)

Table 2 (continued)

Entry	Azine (1)	Alkyne (2)	Product (3)	Yield ^b (%)
14		2a		76
15		2a		nd
16		2a		73
17	1a			71
18	1a			74
19	1a			83
20	1a			nd

^a reaction conditions: azine **1** (0.2 mmol), alkyne **2** (0.4 mmol), [Cp*Co(CO)I₂] catalyst (10 mol%), AgSbF₆ (20 mol %), HOAc (20 mol%), HFIP (2 mL), 100 °C, 12 h.

^b isolated yields.

tosylhydrazone with no substitution on the phenyl ring could generate corresponding product **3aa** with 81% yield (Table 2, entry 1). Electron-withdrawing substituents like Cl, F and Br at *para*-position of the aromatic ring of hydrazones afforded the respective target molecules **3ba**, **3ca** and **3da** in 76%, 73% and 78% yields respectively (Table 2, entries 2–4). The presence of electron-donating substituents such as –Me and –OMe at the *para* position of the benzene ring of the *N*-tosylhydrazone improved the yields of respective target moieties to 83% and 87% respectively (Table 2, entries 5 and 6). Substituents such as –Me and –Cl at the *meta* position of the benzene of *N*-tosylhydrazone provided anticipated moieties **3ga** and **3ia** solely with 80% and 71% yields correspondingly, whereas, –OMe at the *meta* position of the hydrazone produced moieties **3ha** and **3ha'** with 49% and 33% yields correspondingly (Table 2, entries 7–9). Furthermore, the proposed methodology is appropriate for various disubstituted *N*-tosylhydrazones also and the desired product **3ja** was detected in good yields and particular regioselectivity (Table 2, entry 10). Consequently, cyclopropyl phenyl ketone, benzophenone and propiophenone was also utilized as substrates for *N*-tosylhydrazones preparation which could generate the desired substituted isoquinolines **3ka**, **3la** and **3ma** with 78%, 89% and 84% product yields correspondingly (Table 2, entries 11–13). Satisfyingly, even hydrazone derived from 1-acetylnaphthalene functioned for the projected transformation, generating anticipated molecule **3na** with 76% yield (Table 2, entry 14). In addition, the ability of *N*-tosylhydrazone prepared from heterocyclic ketones (e.g. 4-acetylpyridine and 2-acetylthiophene) was also evaluated for the proposed protocol. Out of those, hydrazones derived from 4-acetylpyridine couldn't produce an

anticipated product, while, hydrazone from 2-acetylthiophene gave desired isoquinoline product **3pa** with 73% yield (Table 2, entries 15–16).

Finally, we briefly investigated the scope of the symmetrical, unsymmetrical as well as substituted internal alkynes for the proposed transformation. To the gratification, 3-hexyne and 1-phenyl-1-propyne worked effectively for the annulation with hydrazone **1a** to generate corresponding isoquinolines **3ab** and **3ac** with 71% and 74% yields respectively (Table 2, entries 17–18). Also, diphenylacetylene with methyl substituents at *para* position provided desired product **3ad** with 83% yield (Table 2, entry 19). However, terminal alkyne was ineffective under a projected methodology (Table 2, entry 20).

3. Conclusion

In summary, Cp*Co(III) catalyzed annulation reaction of *N*-tosylhydrazones with alkynes has been established via C–H/N–N bond activation in order to synthesize isoquinoline derivatives. In the proposed protocol, *N*-tosylhydrazone played a dual role, i.e. directing group as well as internal oxidant efficiently. This protocol is applicable to an extensive series of *N*-tosylhydrazones possessing electron withdrawing and donating groups without using any external oxidizing agent. The developed methodology proved to be efficient as an air stable catalytic system Cp*Co(III) worked effectively for this transformation and the reported methodology could also work for the gram level synthesis with slight reduction in the yield of product. Furthermore, a wide range of isoquinoline derivatives could be fruitfully obtained with moderate to excellent yields under a proposed protocol.

Declaration of competing interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jics.2021.100001>.

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