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Rh(III)-catalyzed synthesis of unsymmetrical acridines from aldehydes and azides using transient directing strategy in biomass-derived γ-valerolactone

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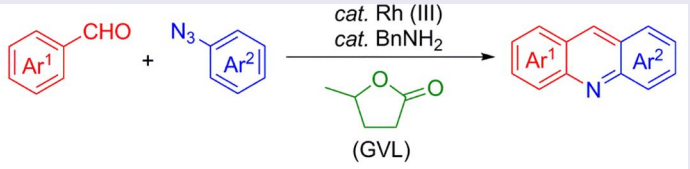
ABSTRACT

An Rh(III)-catalyzed synthesis of unsymmetrical acridines from aldehydes and azides through bilateral cyclization process in biomass-derived γ-valerolactone has been developed. The *in situ*-generated imino directing group (DG) from aldehyde and catalytic amount of $BnNH_2$ worked as a transient directing group, thereby no additional steps were required for installation and removal of the DG. A series of functional groups were well tolerated, affording the desired products in good to excellent yields. Gram-scale synthesis of the product was also achieved.

GRAPHICAL ABSTRACT



Rh(III)-catalyzed synthesis of unsymmetrical acridines using transient Directing strategy in γ-valerolactone has been developed.

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KEYWORDS
C–H Activation; green solvent; transient directing groups; unsymmetrical acridines

Introduction

Over the past decades, transition metal-catalyzed C–H functionalization has attracted much attention. It provides a powerful and atom-economic way to construct complex molecular scaffolds.[1] Particularly, with the assistance of suitable directing groups (DGs), good reactivity and regioselectivity can be achieved.[2] However, the traditional C–H activation processes still have some limitations: (i) additional steps are usually required for installation and removal of the DGs; (ii) the direct C–H functionalization of aldehydes or amines still remains a big challenge; and (iii) straightforward routes to highly functionalized molecules from simple starting materials through C–H activation are still less reported.

Recently, transient directing group (TDG)-assisted C–H functionalization has shown a promising way to overcome the aforementioned limitations.[3–17] In these reactions,

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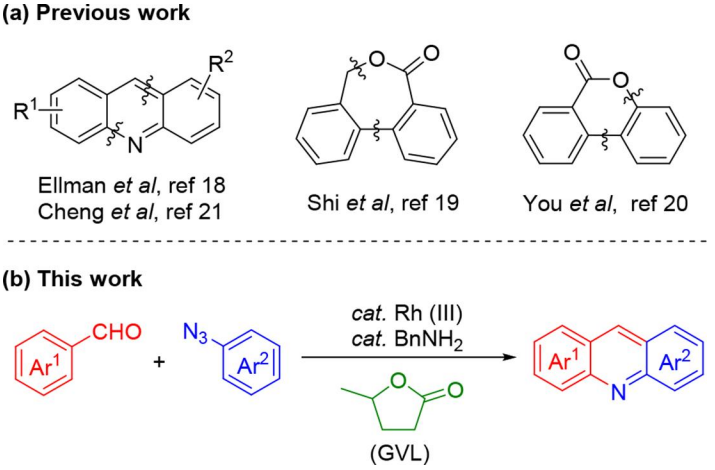
the TDG binds to the substrate *in situ* through an imine intermediate and dissociates from the product after reaction. Thus, extra prefunctionalization steps can be avoided. The synthetic values of these approaches would be further increased if the TDGs are readily available and cost effective. Although much effort has been devoted to exploring suitable TDGs and new C–H activation reactions in recent years, reports on bilateral cyclization between two aromatic substrates through intermolecular C–H functionalization are still rare.[18–20] It should be pointed out that the bilateral cyclization reactions featured a rapid construction of highly functionalized molecules from simple starting materials. For example, Ellman et al.[18] reported a formal [3 + 3] annulations of aromatic azides with aromatic imines through *in situ*-generated imines to construct acridines. Shi et al.[19] demonstrated an Rh(III)-catalyzed cross-coupling of aryl carboxylic acids and benzyl thioethers through double C–H activation. You et al.[20] reported an Rh(III)-catalyzed *ortho* C–H heteroarylation of aromatic carboxylic acids. Interestingly, this protocol provided a rapid and concise access to π-conjugated poly-heterocycles. Just recently, Cheng et al.[21] also developed an efficient Rh(III)-catalyzed bilateral cyclization process to access acridines from aldehydes and nitrosos (Scheme 1a).

Despite these significant advances, current C–H activation reactions have largely been conducted in common organic solvents such as *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), or 1,2-dichloroethane (DCE), which present major issues due to their volatility and toxicity. Recently, the use of bio-based reaction medium such as γ-valerolactone (GVL) has become a hot field. This renewable chemical has been recognized as a sustainable solvent due to its high boiling and flash points, low toxicity, good chemical stability, and similar polarity compared with DMF and *N*-methylpyrrolidone.[22] To our best knowledge, although several reactions have been realized in GVL, reports on directing group-assisted C–H activation reactions are rare. Particularly, bilateral cyclization reaction between two aromatic substrates has never been reported. In this paper, we report an Rh(III)-catalyzed synthesis of unsymmetrical acridines using aromatic aldehydes and azides as the starting materials in GVL. The aromatic aldehydes survived well under the reaction conditions. Only catalytic amount of benzyl amine was required as the TDG to promote this transformation (Scheme 1b).



Scheme 1. C–H activation toward highly functionalized molecules.

Results and discussion

At the outset of our studies, we chose benzaldehyde **1a** and phenyl azide **2a** as substrates to screen the reaction conditions in the presence of $[RhCp^*Cl_2]_2$ (2.5 mol%) and $AgSbF_6$ (10 mol%) in GVL (1 mL) at 120 (C under N_2 for 16 h (Table 1).

No desired product **3aa** was observed under the above reaction conditions. Fortunately, **3aa** was detected in 23% yield in the presence of glycine (0.2 equiv.), indicating that a directing group was necessary for this transformation (entry 2). Switching glycine (**T1**) to amino acid **T2** still gave the desired product in poor yield (11%, entry 3). Different anilines were then tried and 42% yield of **3aa** was obtained when aniline (**T3**) was used as DG. Other anilines bearing electron-donating and electron-withdrawing groups such as **T4**–**T6** gave lower yields (37, 26, and 19%, respectively). Delightfully, benzyl amine turned out to be a good DG, affording the desired product in 63% yield (entry 8). Similarly, inferior yields were obtained when substituted benzyl amines were utilized (entries 9 and 10). *p*-Toluenesulfonamide ($TsNH_2$, **T10**) and acethydrazide (**T11**) were also tested, however, only trace amount of **3aa** was observed (entries 11 and 12). Different solvents were then evaluated. Reaction in conventional solvents such as DMF, DMSO, dioxane, and DCE provided poor yields of the desired product (entries 13–16), while the use of toluene and acetic acid led to the failure of the reaction (entries 17 and 18). Moreover, other catalysts such as $Rh(OOCCF_3)_2$ and $[RuCl_2(p\text{-cymene})]_2$ were ineffective for this reaction (entries 19 and 20). Meanwhile, no desired product was obtained in the absence of either $[RhCp^*Cl_2]_2$ or $AgSbF_6$ (entries 21 and 22). The survey of other parameters showed that $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), 120 (C, and 0.4 equiv. of **T7** were the optimized reaction conditions, providing **3aa** in 90% yield (entries 23 and 24).

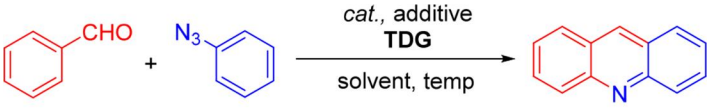
Next, we explored the scope and generality of the present protocol under the optimized reaction conditions. Initially, a series of aromatic aldehydes were evaluated (Fig. 1). In general, aromatic aldehydes containing both electron-withdrawing groups and electron-donating groups reacted with phenyl azide **2a** smoothly to give the desired products in good to excellent yields (**3aa**–**3ka**). For the *para*-substituted aldehydes, a series of functional groups including alkyl (^{i}Pr and ^{t}Bu), phenyl, methoxy, and chloro were well tolerated, among which the 4-chloro benzaldehyde afforded the highest yield (92%, **3fa**). Substrate **1g** also showed good activity to deliver the corresponding product **3ga** in 85% yield. Notably, for *meta*-substituted aldehydes **1h**–**1k**, the C–H activation occurred exclusively at the less hindered site, and no other isomers were detected.

Different aromatic azides were then checked. A series of azides bearing either electron-donating or electron-withdrawing groups showed good compatibilities toward this reaction. The alkyl, methoxy, halo, and ester groups were well tolerated, affording the corresponding products in good yields (**3ib**–**3ii**, 73–88%). Particularly, good tolerance of halogen atoms (Cl and Br) and ester group enabled the further manipulation of initial products. Notably, for *meta*-substituted azides **2h** and **2i**, good regioselectivity was observed, and the cyclization process took place at the least hindered site.

Furthermore, gram-scale synthesis was performed using the model reaction. Under the standard reaction conditions, product **3aa** was isolated in 76% yield at 10 mmol scale (Scheme 2), thereby providing a possibility for the practical scale-up synthesis of acridines.

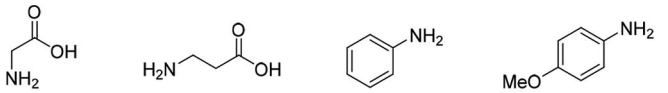
To gain some insight into the reaction, some control experiments were performed (Scheme 3). First, the intermolecular kinetic isotopic effect (KIE) experiment was studied

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3aa**

Entry	Catalyst	TDG	Solvent	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	–	GVL	0
2	$[RhCp^*Cl_2]_2$	**T1**	GVL	23
3	$[RhCp^*Cl_2]_2$	**T2**	GVL	11
4	$[RhCp^*Cl_2]_2$	**T3**	GVL	42
5	$[RhCp^*Cl_2]_2$	**T4**	GVL	37
6	$[RhCp^*Cl_2]_2$	**T5**	GVL	26
7	$[RhCp^*Cl_2]_2$	**T6**	GVL	19
8	$[RhCp^*Cl_2]_2$	**T7**	GVL	63
9	$[RhCp^*Cl_2]_2$	**T8**	GVL	44
10	$[RhCp^*Cl_2]_2$	**T9**	GVL	39
11	$[RhCp^*Cl_2]_2$	**T10**	GVL	trace
12	$[RhCp^*Cl_2]_2$	**T11**	GVL	trace
13	$[RhCp^*Cl_2]_2$	**T7**	DMF	12
14	$[RhCp^*Cl_2]_2$	**T7**	DMSO	10
15	$[RhCp^*Cl_2]_2$	**T7**	Dioxane	7
16	$[RhCp^*Cl_2]_2$	**T7**	DCE	32
17	$[RhCp^*Cl_2]_2$	**T7**	Toluene	0
18	$[RhCp^*Cl_2]_2$	**T7**	AcOH	0
19	$Rh(OOCCF_3)_2$	**T7**	GVL	trace
20	$[RuCl_2(p\text{-cymene})]_2$	**T7**	GVL	trace
21	–	**T7**	GVL	0
22	$[RhCp^*Cl_2]_2$	**T7**	GVL	0[c]
23	$[RhCp^*Cl_2]_2$	**T7**	GVL	72[d], 81[e], 82[f]
24	$[RhCp^*Cl_2]_2$	**T7**	GVL	70[g], 79[h], 90[i]

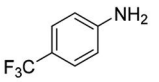


T1

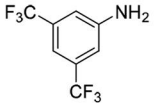
T2

T3

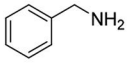
T4



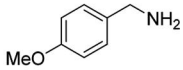
T5



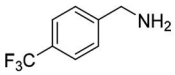
T6



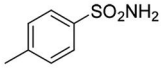
T7



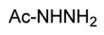
T8



T9



T10



T11

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), catalyst (2.5 mol%), $AgSbF_6$ (10 mol%), TDG (0.2 equiv.), solvent (1 mL), 120 (C under N_2 for 16 h in a sealed tube.
[b]NMR yields using 1,1,2,2-tetrachloroethane as internal standard.
[c]Without $AgSbF_6$.
[d]TDG (0.3 equiv.).
[e]TDG (0.4 equiv.).
[f]TDG (0.5 equiv.).
[g]At 110 °C.
[h]At 130 °C.
[i]5 mol% catalyst and $AgSbF_6$ (20 mol%) were used.

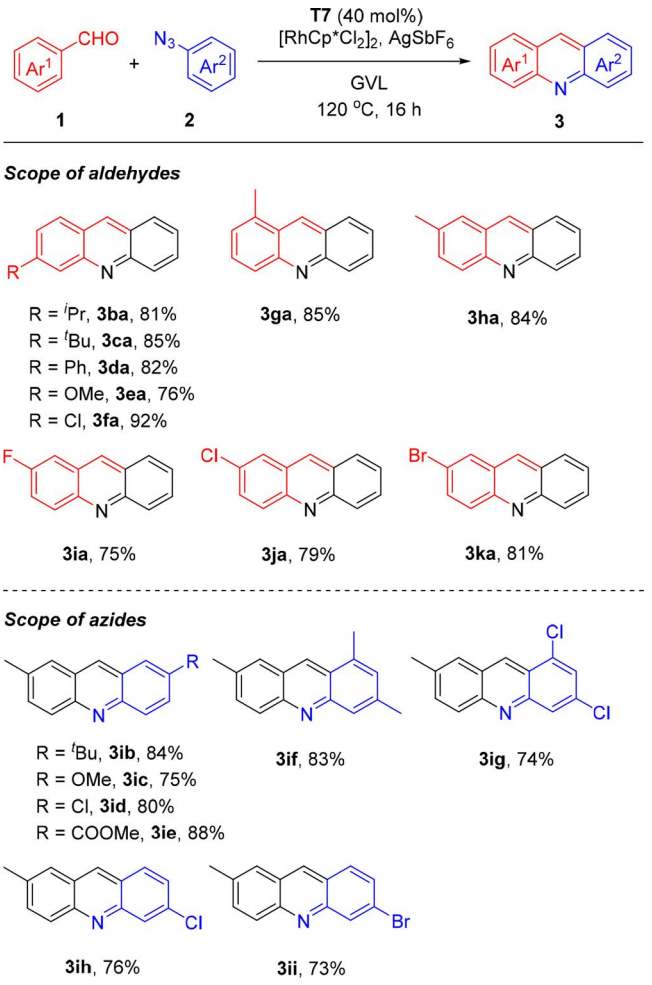
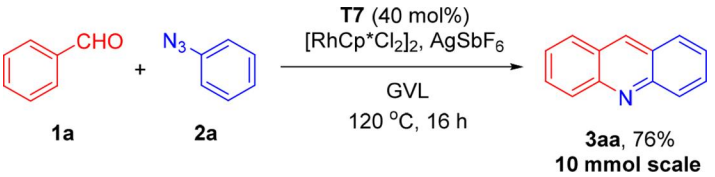
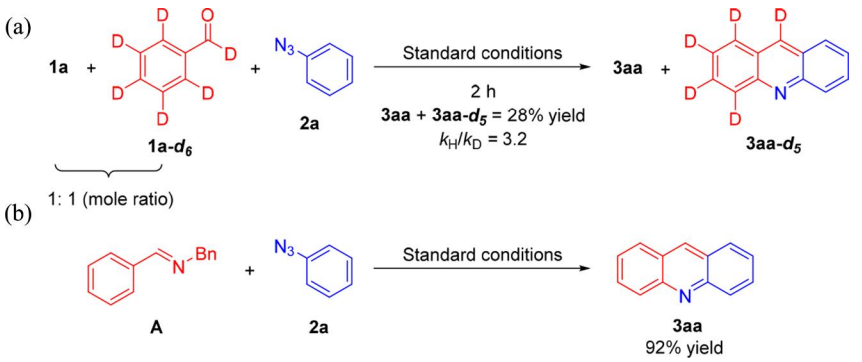


Figure 1. Reaction scope. Reaction conditions: **1** (0.2 mmol), **2** (1.5 equiv.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), **T7** (0.4 equiv.), GVL (1 mL), 120 °C under N_2 for 16 h in a sealed tube, isolated yields.

(Scheme 3a). The result showed $k_H/k_D = 3.2$, indicating that the C–H bond cleavage of benzaldehyde may be the rate-determining step. Second, to determine the role of benzyl amine, imine **A** was prepared and reacted with azide **2a** under the standard reaction conditions. The product **3aa** was isolated in 92% yield, indicating that the imine **A** was the key intermediate (Scheme 3b).

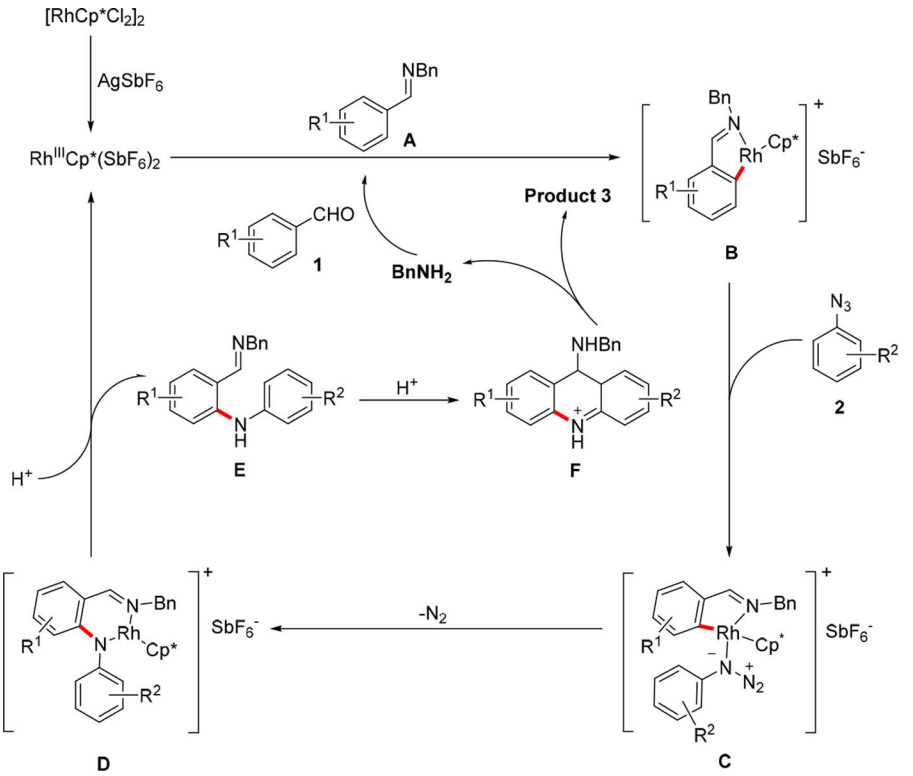


Scheme 2. Gram-scale synthesis of **3aa**.



Scheme 3. Control experiments.

Based on these results, we proposed a mechanism for this transformation. As shown from Scheme 4, initially, aldehyde **1** condensed with $BnNH_2$ to form intermediate **A**. Then **A** underwent *ortho* C–H activation in the presence of Rh(III) catalyst to give metallacycle **B**. Afterward, coordination of azide **2** to intermediate **B** provided intermediate **C**, which released rhodacycle **D** and nitrogen by migratory insertion.[23] Then protonation of **D** released the Rh(III) catalyst and intermediate **E**, which underwent intramolecular aromatic electrophilic substitution to give intermediate **F**. Finally, aromatization of **F** delivered the product **3** and $BnNH_2$.



Scheme 4. Plausible mechanism.

Conclusion

In summary, we have developed an Rh(III)-catalyzed synthesis of unsymmetrical acridines from aldehydes and azides utilizing inexpensive $BnNH_2$ as a TDG and GVL as the green reaction medium. The present C–H amination/cyclization/aromatization cascade featured a rapid construction of highly functionalized acridines from simple starting materials. The aldehydes could be directly used, and no additional steps were required for installation and removal of DGs. A series of functional groups were well tolerated, affording the desired products in good to excellent yields. KIE experiment showed that the aromatic C–H bond cleavage of the aldehyde was the rate-determining step. Gram-scale synthesis of the product was also achieved. Importantly, GVL could be used as a practical and efficient alternative to the conventional organic solvents, thereby significantly reducing the environmental impact and energy cost.

Experimental

General remarks

All reagents were obtained from local commercial suppliers and used without further purification. The progress of the reaction was monitored by TLC using analytical grade silica gel plates (GF254) under UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). Chemical shifts are given in parts per million (δ, ppm) and were referenced to $CDCl_3$ (7.26 or 77.0 ppm). The coupling constants *J* are given in Hz. Mass spectrometry was performed on an LCMS-2010 EV (Shimadzu) instrument with an ESI source.

General procedure for synthesis of acridines

In an N_2-filled glovebox, a 10-mL Schlenk tube equipped with a stir bar was charged with aromatic aldehyde **1** (0.2 mmol, 1.0 equiv.), aryl azide **2** (0.30 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), benzyl amine (**T7**, 0.4 equiv.) in GVL (1 mL). The tube was sealed, and the reaction mixture was stirred at 120 (C for 16 h in oil bath. After completion of the reaction, the mixture was extracted by EtOAc and washed with water for several times. The organic layer was then dried over anhydrous Na_2SO_4, concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether and EtOAc as the eluent to give the pure acridine products.

Selected data: acridine (**3aa**).[18] Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.26 (dd, *J* = 8.8, 0.8 Hz, 2H), 8.01 (dd, *J* = 8.5, 0.6 Hz, 2H), 7.82–7.77 (m, 2H), 7.57–7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 136.1, 130.3, 129.4, 128.2, 126.6, 125.7; MS (ESI) *m*/*z* 180 $[M+H]^+$.

KIE experiment

The **1a**-d_6 was prepared according to the previous literature.[24] In an N_2-filled glovebox, a 10-mL Schlenk tube equipped with a stir bar was charged with aromatic aldehyde **1a** (0.1 mmol), **1a**-d_6 (0.1 mmol), phenyl azide **2a** (0.30 mmol, 1.5 equiv.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), benzyl amine (**T7**, 0.4 equiv.) in GVL (1 mL). The tube was sealed, and the reaction mixture was stirred at 120 (C for 2 h in oil bath. After that,

the mixture was extracted by EtOAc and washed with water for several times. The organic layer was then dried over anhydrous Na_2SO_4, concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel with petroleum ether and EtOAc as the eluent to give the products **3aa** and **3aa-d_5** in 28% yield. The mixture was analyzed using ^{1}H NMR spectrometer to calculate the k_H/k_D value.

Funding

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