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A ruthenium-catalyzed free amine directed (5+1) annulation of anilines with olefins: diverse synthesis of phenanthridine derivatives†

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A ruthenium(II)-catalyzed cross-ring (5+1) annulation between 2-aminobiphenyls and activated olefins is disclosed for succinct synthesis of valuable phenanthridine scaffolds. The protocol avails a common organic functional group, free amine, as a directing group and represents a unique combination of C–H activation/annulation/C–C bond cleavage cascade that bodes well in the production of bioactive alkaloids including trisphaeridine and bicolorine.

Transition-metal-catalyzed annulation reactions exploiting ubiquitous and otherwise inactive C–H bonds represent an important synthetic strategy to fabricate polycyclic molecular frameworks.[1,2] Over the years, chemists have compiled a ruthenium-catalyzed reaction compendium that consists of a series of (4+2),[3a–e] (3+2),[3f–h] (2+2+2),[3i] and (4+1)[3j] annulations, forging diverse carbocycles and heterocycles. Despite these achievements, to date, ruthenium-catalyzed (5+1) annulation has remained largely underdeveloped.[4] In these annulation reactions, directing groups play fundamental roles in facilitating the C–H bond activation process and mitigate the problem of regioselectivity. Common organic functional groups like carboxylic acid, ester, amide, ketone, *etc.* are often employed as directing groups.[5] However, the free amine group (NH_2), one of the most valuable and widely abundant functionalities, has largely been ignored in ruthenium-catalyzed directed C–H bond activation reactions,[6] probably owing to the challenges associated with its strong coordinating ability with metal catalysts along with the superior nucleophilic reactivity that result in pivotal issues of catalyst deactivation and unwarranted side reactions.[6c,9b] Thus, there is ample scope in the free amine directed ruthenium(II)-catalyzed regioselective C–H bond activation/annulation manifold and importantly, it could potentially lead to high-value N-heterocycles when the amine directing group becomes the critical component of the ring structure.

Phenanthridine and benzophenanthridine alkaloids signify an important class of organic molecules with promising biological activities.[7,8] Some of the important natural products are presented in Fig. 1. The biological activities of such alkaloids range from anti-cancer to anti-fungal, and anti-bacterial, to name a few. Consequently, devising novel synthetic strategies towards such molecular frameworks is highly desirable.[8] Arguably, a C–H bond activation based (5+1) cross-ring-annulation (CRA) reaction of biaryl-2-amines would be a succinct route to access these scaffolds (Scheme 1).

Furthermore, the majority of the naturally occurring phenanthridine alkaloids do not possess any substitution at the C6-position and hence, challenges lie in the strategic design of a suitable one-carbon synthon for the CRA reaction. In 2012, the Li group reported an intriguing Pd-catalyzed (5+1) CRA reaction of biaryl-2-amines with activated alkenes (butyl acrylate) that features the pivotal C–C bond cleavage to offer C6-unsubstituted

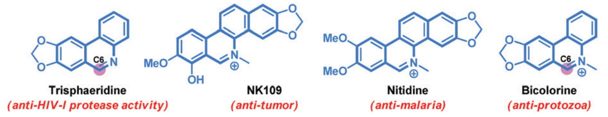
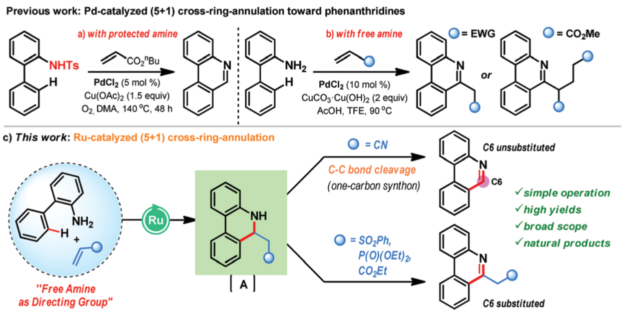


Fig. 1 Biologically important phenanthridine alkaloids.



Scheme 1 Ru(II)-catalyzed free amine directed cross-ring (5+1) annulation towards phenanthridine alkaloids.

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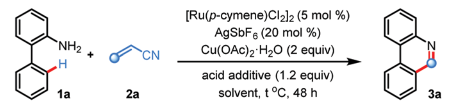
phenanthridines in high yields (Scheme 1a).[9a] In this case, the use of *N*-protected biaryl-2-amines was necessary as *N*-unprotected biaryl-2-amines gave poor yields. In parallel, the Zhang group also reported (5+1) CRA reaction of biaryl-2-amines with alkenes under Pd-catalysis in trifluoroethanol (Scheme 1b).[9b] This reaction is effective with unprotected amines, however, they did not observe any C–C bond cleavage phenomenon and, in the case of acrylate coupling partner, a second Michael addition was proposed for the aromatization step *en route* to C6-substituted phenanthridines. Currently, such a CRA reaction manifold for the production of phenanthridines is unknown with Ru-catalysis and herein, we disclose the first example of free amine directed (5+1) CRA reaction of biaryl-2-amines with activated alkenes under Ru-catalysis (Scheme 1c). When acrylonitrile is used as a coupling partner, it acts as a C1-synthone and delivers C6-unsubstituted phenanthridines after the C–C bond cleavage. In contrast, other activated olefins, such as vinyl sulfone, vinyl phosphate, and acrylate, furnished C6-substituted phenanthridines in very high yields.

We commenced our investigations following the model reaction of 2-aminobiphenyl **1a** with acrylonitrile **2a** (Table 1). The choice of acrylonitrile as an olefin coupling partner is intriguing as initially formed dihydrophenanthridine intermediate **A** bearing a cyanomethyl (–CH_2CN) functionality may experience a C–C bond cleavage phenomenon either through a radical pathway or a coordination assisted base promoted elimination mechanism to validate domino C–H activation based (5+1) annulation *en route* to the C6-unsubstituted phenanthridine scaffold (Scheme 1c). Accordingly, when we treated **1a** and **2a** in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.), $AgSbF_6$ (20 mol%), and CH_3CO_2H (1.2 equiv.) in THF solvent, we were delighted to find the desired 6-unsubstituted phenanthridine product **3a** in 52% yield (Table 1, entry 1). Switching the reaction solvent to DCE, dioxane, and DME furnished inferior results (entries 2–4). Screening of the acid additives revealed mesitoic acid as the best choice, delivering the desired product **3a** in 72% isolated yield (entry 5). Change of the reaction solvent from THF to higher boiling point 2-methyl tetrahydrofuran (2-Me-THF) gave only 37% yield of **3a** (entry 6). Further tuning of the reaction conditions, such as use of 1-$AdCO_2H$ acid (entry 7), increasing or decreasing of reaction temperature (entry 8), utilization of $AgBF_4$ additive and use of CuO oxidant (entry 9) had detrimental effects. Control experiments revealed that all the components were essential for the success of the reaction (entries 10 and 11). Yield also decreased in the presence of excess water in the reaction medium (entry 12). Other transition metals like Pd, Rh, and Ir based catalysts were ineffective under standard reaction conditions, highlighting the uniqueness of ruthenium in this protocol (entry 13).

Table 1 Optimization of (5+1) annulation reaction[a]



Entry	Acid additive	Solvent	Temp (°C)	Yield[b] (%)
1	AcOH	THF	80	52
2	AcOH	DCE	80	32
3	AcOH	DME	80	38
4	AcOH	Dioxane	80	46
5	$MesCO_2H$	THF	80	72
6	$MesCO_2H$	2-Me-THF	80	37
7	1-$AdCO_2H$	THF	80	12
8	$MesCO_2H$	THF	100/60	62/0
9	$MesCO_2H$	THF	80	16[c]/11[d]
10[e]	$MesCO_2H$	THF	80	—
11[f]	—	THF	80	< 5
12[g]	$MesCO_2H$	THF	80	59
13	$MesCO_2H$	THF	80	16[h]/0[i]/0[j]

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), solvent (4.2 mL) for 48 h under an argon atmosphere. [b] Isolated yields. [c] $AgBF_4$ (20 mol%) was used as an additive. [d] CuO (2 equiv.) was used as an oxidant. [e] Reaction without $[Ru(p\text{-cymene})Cl_2]_2$ catalyst or $Cu(OAc)_2{\cdot}H_2O$ oxidant or $AgSbF_6$ additive. [f] Reaction without $MesCO_2H$ (mesitoic acid) additive. [g] 2 equiv. of water was added. [h] With $Pd(OAc)_2$. [i] With $(Cp^*RhCl_2)_2$ catalyst. [j] With $(Cp^*IrCl_2)_2$ catalyst.

Having acquired the optimal conditions, we sought to explore the scope of the (5+1) annulation reaction varying the electronic and steric nature in the arene ring (Table 2). The presence of electron-releasing groups such as alkyl (**3b–d**) and alkoxy (**3e–f**) at the *para*-position gave desired products in uniformly high yields (75–84%). Substrates bearing electron-withdrawing groups, for example halogens (**3g–i**), trifluoromethyl (**3j**), and ester (**3k**) were smoothly reacted to produce C6-unsubstituted phenanthridines in good yields.

Pleasingly, coordinating free-hydroxyl groups did not hamper the reaction, furnishing compound **3l** in 70% yield. When unsymmetrical *meta*-substitution was considered, annulations proceeded selectively at the sterically less hindered site to forge products **3n–p** in good yields. The protocol also worked efficiently with the 2-naphthyl derivative, generating important fused polyaromatic heterocycle benzo[*j*]phenanthridine (**3m**) in 72% yield. The effect of substituents in the aniline ring was also examined; a host of electron-rich and electron-deficient anilines were effective for this reaction, delivering **3q–t** in 62–75% isolated yields. Synthetically useful yield was also obtained with a sensitive ketone functionality (**3u**). Under the standard conditions, annulations

Table 2 Substrate scope of (5+1) annulation with respect to amines[a]

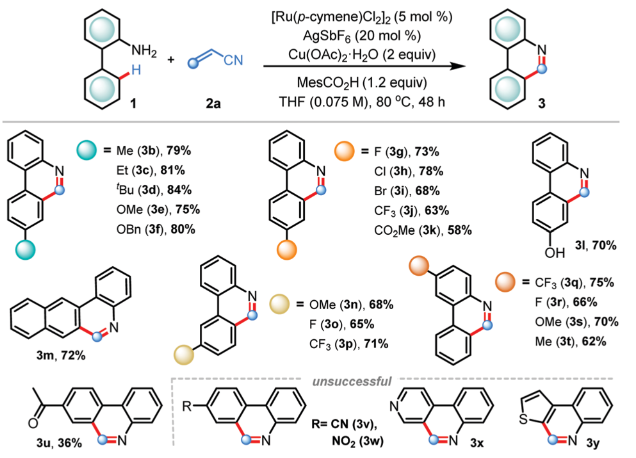
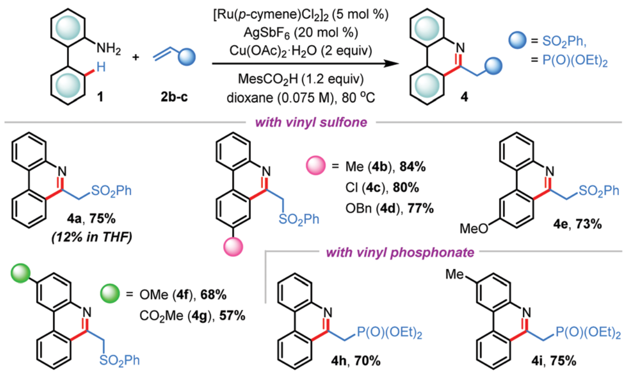
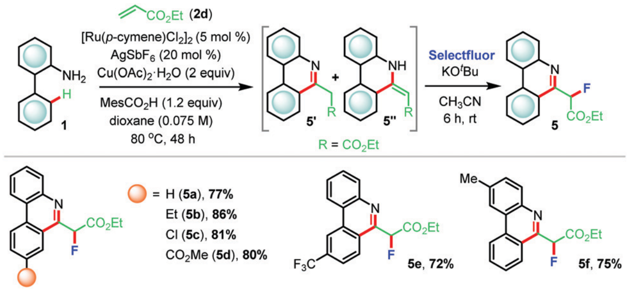


Table 3 Substrate scope of (5+1) annulation with vinyl sulfone and vinyl phosphonate[a]



[a] Reaction conditions: **1** (0.3 mmol), **2b** or **2c** (0.36 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2 equiv.), $MesCO_2H$ (1.2 equiv.), $AgSbF_6$ (20 mol%), dioxane (4.2 mL) at 80 °C for 48 h under argon.

Table 4 Substrate scope with acrylate followed by fluorination[a]



[a] Reaction conditions: **1** (0.3 mmol), **2d** (0.36 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (2 equiv.), $MesCO_2H$ (1.2 equiv.), $AgSbF_6$ (20 mol%), dioxane (4.2 mL) at 80 °C for 48 h under argon. Then, KO^tBu (1.2 equiv.) and Selectfluor (1.2 equiv.) were used in dry acetonitrile at room temperature for 6 h.

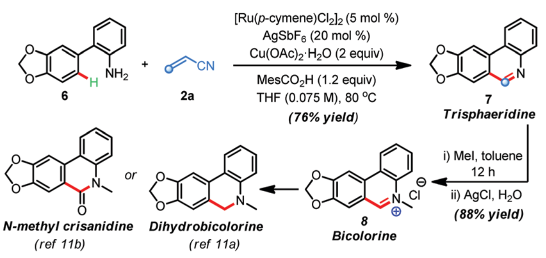
did not take place with substrates having strongly electron withdrawing cyano (**3v**) and nitro (**3w**) groups as well as with anilines derived from heterocycles (**3x–y**).

After successful implementation of our hypothesis, we questioned whether other activated olefinic coupling partners would participate in this ruthenium(II)-catalyzed CRA reaction (Table 3).[10] When phenyl vinyl sulfone **2b** was reacted with 2-aminobiphenyl **1a** under the conditions established with acrylonitrile **2a**, the desired (5+1) annulation reaction did not take place effectively with the recovery of the starting materials, indicating that a revision of the reaction conditions was necessary. Delightfully, the same reaction proceeded smoothly when the reaction solvent was changed to dioxane; however, we did not observe the concomitant C–C bond cleavage in this case and 6-substituted phenanthridine derivative **4a** was isolated in 75% yield. Other substituted 2-arylanilines also rendered products **4b–g** in good to high yields (57–84%). Similarly, reactions with diethyl vinylphosphonate **2c** were fruitful to offer alkyl phosphonate hinged phenanthridines **4h** and **4i** in 70% and 75% yields, respectively (Table 3). These findings reinforce the uniqueness of acrylonitrile in (5+1) cross-ring-annulation (CRA) for exclusive access of 6-unsubstituted phenanthridines.

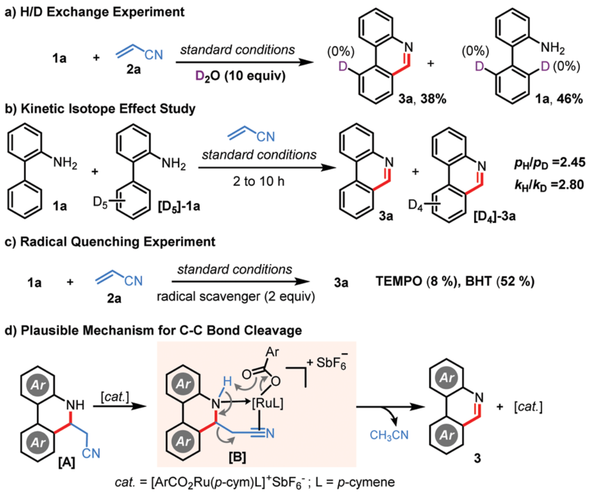
Furthermore, reaction of 2-aminobiphenyl **1a** with ethyl acrylate **2d** afforded a mixture of two products which were inseparable by column chromatography (Table 4). ^{1}H-NMR analysis implied the presence of desired (5+1) annulated product **5a′** along with its tautomer **5a″**. At this juncture, we posited to use a suitable electrophile to functionalize the acidic C–H bond adjacent to the carboxylate group (R = CO_2Et) that might compel the formation of a phenanthridine moiety. We focused on electrophilic fluorination since fluorinated analogues of phenanthridine might exert interesting pharmaceutical properties. Consequently, the crude reaction mixture thus obtained from the (5+1) annulation step was exposed to Selectfluor in the presence of KO^tBu in anhydrous acetonitrile at room temperature and, to our satisfaction, the desired product **5a** was formed in 77% yield (Table 4). Following the same sequence, fluorinated analogues **5b–f** were prepared in very high yields (72–86%).

The synthetic utility of this protocol was highlighted in the preparation of phenanthridine-based natural products. For example, trisphaeridine that displays excellent antiproliferative effects on both human and mouse cells was rapidly prepared from the reaction of 2-phenylaniline[11] **6** with acrylonitrile **2a** under the standard conditions in 76% yield (Scheme 2). Subsequent methylation gave the natural product bicolorine **8** in 88% yield and synthesis of dihydrobicolorine and *N*-methyl crisanidine from bicolorine is a known process (Scheme 2).[12a,b]

To gain mechanistic insights, we performed a few control experiments. No significant deuterium incorporation was observed when bench-mark reaction of **1a** and **2a** was performed in the presence of excess D_2O, approving an irreversible C–H metalation step (Scheme 3a). Kinetic isotope effect (KIE) studies through independent parallel (k_H/k_D = 2.80) and competitive (p_H/p_D = 2.45) experiments suggested that the C–H metalation could be the rate-determining step (Scheme 3b). Furthermore, the reaction was ineffective in the presence of TEMPO, but **3a** was isolated in 52% yield in the presence of BHT, implying that TEMPO might hamper the Ru-catalysis and the involvement of a radical pathway is rather unlikely (Scheme 3c). While the exact reaction mechanism must await further investigations, we believe, in contrast to other alkenes, that the unique C–C bond cleavage in the case of acrylonitrile is facilitated through the coordination of the cationic Ru-catalyst followed by carboxylate assisted deprotonation as shown in Scheme 3d.[9c,d,13]



Scheme 2 Synthesis of bioactive alkaloids trisphaeridine and bicolorine.



Scheme 3 Control experiments.

In conclusion, an efficient (5+1) cross-ring-annulation (CRA) reaction using readily available 2-aminobiphenyls and activated olefins under common functional group free amine assisted ruthenium(II) catalysis has been accomplished to prepare a library of high-value functionalized phenanthridines in very high yields. Identification of acrylonitrile as a one-carbon synthon was a critical parameter for achieving the concomitant C–C bond cleavage, furnishing 6-unsubstituted phenanthridines in a succinct manner. Also, the applications of this methodology in syntheses of bioactive alkaloids like trisphaeridine and bicolorine add to the fruitfulness of the protocol. Further applications of Ru(II)-catalyzed annulation are currently ongoing in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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