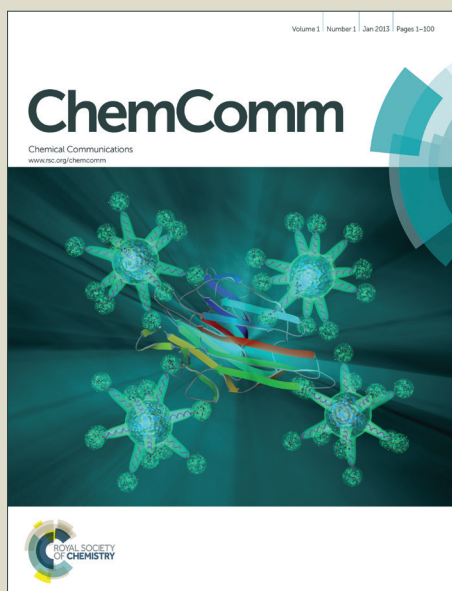


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Rhodium-Catalyzed C–H Activation of Hydrazines Leads to Isoquinolones with Tunable Aggregation-Induced Emission Property†

 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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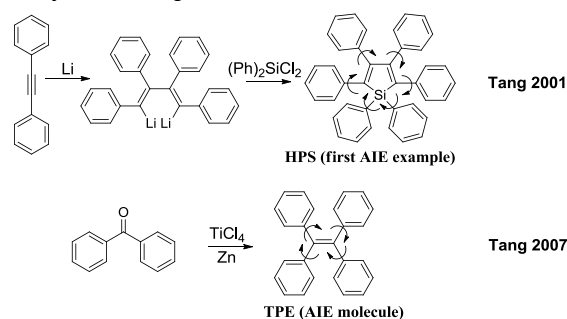
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Using an internally oxidizing directing group (DG) strategy, we report a Rh^{III}-catalyzed synthesis of isoquinolones via C–H activation/annulation of benzoylhydrazines and alkynes. Tunable double cascade cyclization of benzoylhydrazines with two equivalents of alkynes led to tetracyclic amides. These N-heterocycles demonstrated adjustable AIE properties.

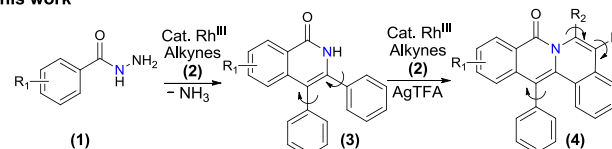
Aggregation-induced emission (AIE) refers to a photophysical phenomenon, in which the nonemissive molecules are induced to emit by aggregate formation.¹ The restriction of intramolecular rotation (RIR) in the aggregated state plays a key role in inducing luminescence. A number of luminogenic molecules with benzene rotors have been found to show pronounced AIE effect.² For example, Tang et al. first discovered hexaphenylsilole (HPS) and tetraphenylethene (TPE) (Scheme 1) as AIE molecules in which multiple phenyl groups rotated against the core stator in dilute solutions, non-radiatively dissipating the decay energy. Although AIE research has been rapidly developing in recent years, the stator rotors, core structures containing heteroatoms have also been investigated.³ However, the potential functionality of the stator cores are typically overlooked. New synthetic strategies for the incorporation of functionally tunable heteroatoms into the AIE molecular structure library are highly desirable.⁴

Metal-catalyzed C–H activation has been widely explored to convert cheap and abundant raw materials into complex structures with various functional groups.⁵ Utilizing C–H activation strategy,

Current synthetic strategies



This work



Scheme 1 N-heterocycles as new AIE molecules.

our group has synthesized several N-heterocyclic scaffolds with the aid of N-containing directing groups.⁶ Notably, the function availability of the N-heterocycles enabled proliferation control of reaction cascades, resulting in molecules with multiple phenyl groups. We hypothesized that these phenyl groups might serve as rotators for building AIE materials. To explore N-heterocycles as potential AIE molecules, we were attracted to recent examples of internal-oxidant directing, Rh^{III}-catalyzed C–H bond activation of arenes. In those cases, the oxidative cleavage of N–O and N–N bonds in the directing groups (DGs) have yielded diverse N-heterocycles such as indoles and isoquinolones.⁷ These N-heterocycles, as demonstrated in this study, are excellent AIE luminogens when properly substituted, whose photoluminescence properties have rarely been reported before (Scheme 1).

We started our synthetic efforts from readily available benzoylhydrazines (1). Inspired by the landmark work by Glorius and Cheng groups,^{7d,7o} we hope to utilize the redox neutral N–N bond cleavage ability in the hydrazine acetyl DG to escort the Rh^{III}-catalyzed intermolecular coupling with alkynes (2) for generating isoquinolones (3). Compared to the several previously reported ingenious designs to access isoquinolones through N–O bond

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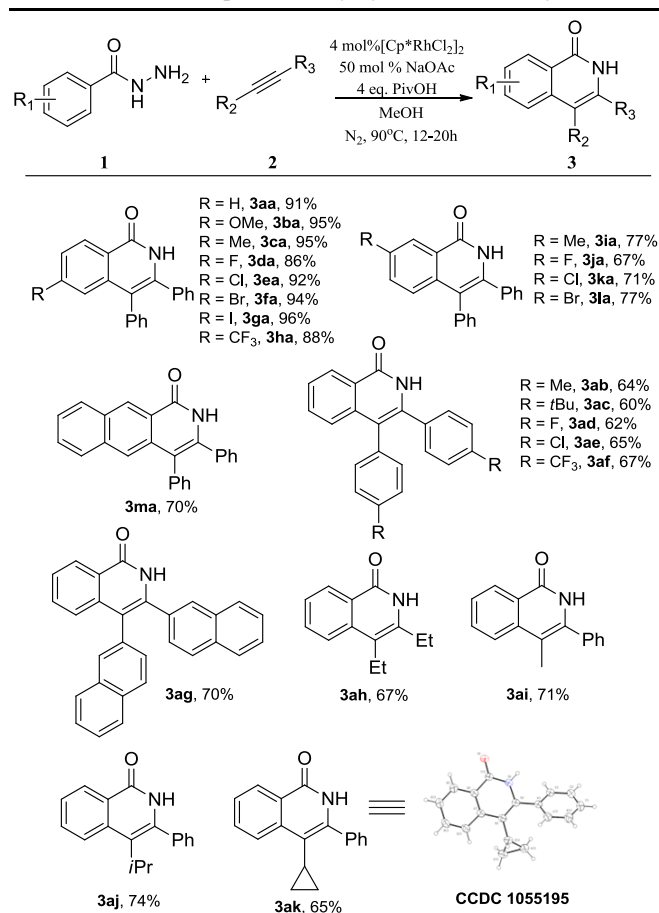
† Electronic supplementary information (ESI) available: Experimental procedures, characterization data for all new compounds. CCDC1055195 (3ak), CCDC1055196 (4ah), CCDC1055197 (4ai) and CCDC1055198 (4aj). For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/b000000x/

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cleavage, our approach is more cost-effective. This is, to the best of our knowledge, the first time that Rh^{III}-catalyzed redox-neutral C–H activation/cyclization strategy is used for AIE study.

In preliminary experiments, benzoylhydrazine (**1a**) was treated with [(Cp*RhCl₂)₂] (2.5 mol%), CsOAc (25 mol%), and diphenylacetylene (**2a**, 1.2 equiv) in MeOH under N₂ at 70 °C for 16 h, but no reaction occurred (Table S1, entry 1). When HOAc (1.2 equiv) was added, we could obtain product **3aa** in 38% yield without any external oxidants (Table S1, entry 2). A lower yield was isolated when a less polar solvent such as MeCN or DCE was used (Table S1, entry 3, 4). Adjusting the reaction temperature, as well as the catalyst and additive amount, improved the yield to 86% (Table S1, entry 5-9). Next, we examined different additives and found that when PivOH (4 equiv) and NaOAc (50 mol%) were used in place of HOAc and CsOAc, the yield further increased to 95% (Table S1, entry 10-12). Slightly lowering the catalyst loading from 5 mol% to 4 mol% and shortening the reaction time from 16 h to 12 h did not impact the reaction yield (Table S1, entry 13, 14). The yield obtained with [Cp*Rh(OAc)₂] as the catalyst was similar to those obtained with the [(Cp*RhCl₂)₂]/NaOAc system (Table S1, entry 15), thus indicating that [Cp*Rh(OAc)₂] might be the active catalyst. Eventually we set the standard reaction conditions to be [(Cp*RhCl₂)₂] (4 mol%), NaOAc (50 mol%), and PivOH (4 equiv) in MeOH under N₂.

Table 1 Substrate Scope of Benzoylhydrazines and Alkynes^{a,b}

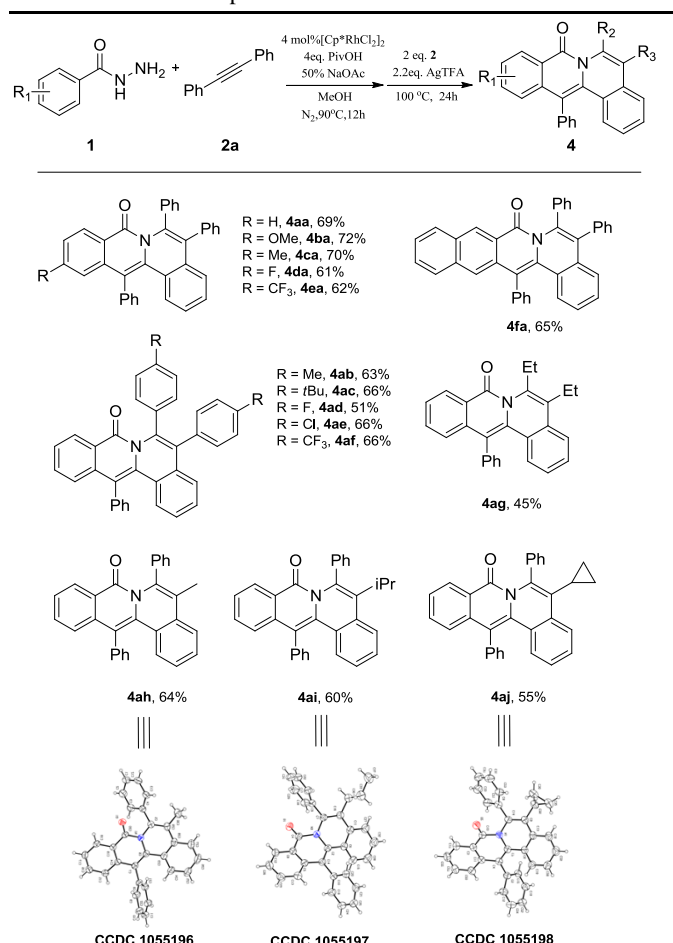


^aReaction conditions: **1** (0.2 mmol), **2** (0.24 mmol) in MeOH (1 mL),
^bisolated yields.

Generally, the C–H activation synthetic methodology with internal oxidant features improved reactivity and selectivity, as well as a broader scope, compared to that with an external oxidant. Taking this advantage, we prepared a series of isoquinolones which allowed us to further explore their structure-property relationship. As shown in Table 1, benzoylhydrazine derivatives bearing electron-donating substitution groups such as methoxy (**1b**), methyl (**1c**, **1i**) or electron-withdrawing substitution groups such as trifluoromethyl (**1h**) participated well in this reaction and gave desired products in good to excellent yields ranging from 77% to 95%. The reaction of **2a** with halo-substituted benzoylhydrazines (**1d-g**, **1j-l**) also afforded the corresponding isoquinolones in yields ranging from 67% to 96%. With the same substitution group, the yield was much higher for the *para*-substituted benzoylhydrazines than those with the *ortho*-positions occupied (**3ca** > **3ia**, **3da** > **3ja**, **3ea** > **3ka**, **3fa** > **3la**). Fused benzene rings were also tolerated, and the reaction of **2a** with 2-naphthoic hydrazide (**1m**) resulted in moderate yield of 70%. As for the coupling partner, both symmetrical and unsymmetrical alkynes were tolerated. Besides symmetrical diphenylacetylenes with *p*-Me, *p*-*t*Bu, *p*-F, *p*-Cl and *p*-CF₃ substitution groups (**2b-f**), as well as di(β -naphthyl)acetylene (**2g**) and 3-hexyne (**2h**) reacted well with **1a** under the standard reaction conditions to afford isoquinolones (**3ab-h**) in yields ranging from 60% to 70%. For unsymmetrical alkynes, the present reaction showed excellent regioselectivity. Thus, the reaction of alkyl-(phenyl)alkynes (**2i-k**) with **1a** gave single regioisomeric products (**3ai-k**) in yields ranging from 65% to 74%. The structures of the regioisomers were confirmed by 1D-NOESY study or X-ray crystallography.

The structures of **3** include an unprotected amide which, according to the previous reports,⁸ might undergo additional C–H functionalization cascades that would allow direct access to structurally more complex polycyclic heterocycles in one pot. Therefore, we investigated the one-pot double cascade reaction of **1a** with the same or different alkynes. Encouragingly, 5,6,13-triphenyl-8*H*-dibenzo[*a,g*]quinolizin-8-one derivatives **4** were produced in moderate to high yields ranging from 45% to 72%, (Table 2). As a confirmation of our previous observation, the progress of the current reaction cascades were also fully controlled by oxidants and temperature. After careful screening of the reaction conditions for the subsequent ring closing metathesis, we chose to use 2.2 equiv. of the second alkyne **2**, 2.2 equiv. AgTFE and reaction temperature of 100 °C. Both aryl,aryl- and alkyl,alkyl-disubstituted alkynes were tolerated. X-ray crystallography data proved the assembly of tetracyclic amides **4**, as well as the configurations of single regioisomers obtained with unsymmetrical internal acetylenes.

Isotope experiments were carried out for probing the catalytic reaction mechanism. First, the substrate **1a** was subjected into deuterated PivOH and CH₃OH, affording the corresponding product with 92% deuterium incorporation. This suggested that C–H bond activation was reversible [Fig. S1a, Eq. (1)]. When the standard reaction was carried out in the deuterated conditions, we obtained the desired product without any D-substitution at C-8 position [Fig. S1a, Eq. (2)]. This result showed that the alkyne insertion was irreversible. The parallel experiments gave the ratio of *K*_H/*K*_D=3.1, indicating that C–H bond cleavage was involved in the

Table 2 Substrate Scope in One-Pot Double Cascade^{a,b}

^aReaction conditions: **1** (0.2 mmol), **2a** (0.21 mmol), **2** (0.40 mmol) in MeOH (1 mL). ^bisolated yields.

rate-determining step[Fig. S1a, Eq. (3)].⁹

A plausible mechanism was proposed (Fig. S1b). First, the active catalyst Cp*Rh(OAc)₂ was generated via anion exchange. Then C–H activation of benzoylhydrazine with Cp*Rh(OAc)₂ afforded a five-membered cyclorhodium intermediate **A**, which was followed by alkyne insertion, thus affording the seven-membered species **B**. Then, reductive elimination allowed the C–N bond formation of intermediate **C**. Subsequently, a fast oxidative addition of CpRh(I) to N–N bond produced intermediate **D**, which was finally protonated by acid to yield the desired product **3** and regenerated the catalyst.^{7d,7o} The mechanism of Rh^{III}-catalyzed oxidative annulation of **3** with alkynes has been investigated,⁸ and a Rh^{III}/Rh^I/Rh^{III} catalytic cycle has been proposed for the reaction.¹⁰

Gratifyingly, the obtained 3,4-diphenyl isoquinolone **3aa** exhibits AIE behaviors. Adding anti-solvent of water into the THF solution of **3aa** induced solute aggregation, and at the same time, increased the photoluminescence of **3aa** at an emission wavelength of 394 nm. Compared to THF solution of **3aa**, the emission increased 12 fold for the suspension of **3aa** in a mixed solvent of 95% water and 5% THF. The solids of **3aa** emitted blue light and were of rectangle prism shape with size of 300–500 nm as revealed by SEM images (Fig. 1).

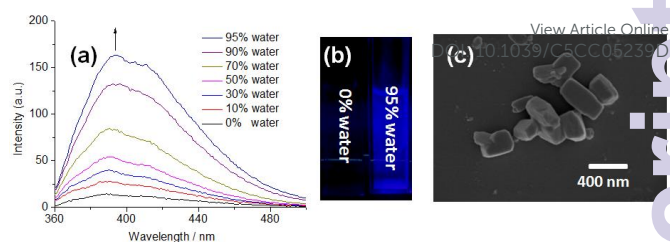


Fig. 1 (a) Emission spectra of **3aa** in THF/water mixtures with different water fractions with an excitation wavelength of 310 nm (concentration: 10 μM); (b) Fluorescent photographs of **3aa** with (0% and 95% water) under a hand-held UV lamp with an excitation wavelength of 365 nm; (c) SEM image of the nanoaggregates formed with 95% water.

With a wealth of structures at hand, we then measured their photophysical spectra to systematically investigate their AIE behaviors. The absorption spectra of the compounds **3** and **4** in THF solutions (10 μM) are given in Fig. S2 and S3. Most compounds showed absorption maxima at ~310 nm except for **3ma** (338 nm), **3ag** (321 nm) and **3ah** (339 nm). The absorption maxima of compounds **4** are located at ~395 nm, being red-shifted in comparison with those of compounds **3**. The photoluminescence (PL) spectra and fluorescence quantum yields (ϕ) in THF (10 μM) and in powders are given in Fig. S4, S5 and Table S2. Most compounds show weak emission in THF solutions but enhanced emission in powders, indicating they are AIE-active. The powders of **3** and **4** show blue and green emissions, respectively. The emission wavelengths of these powdery products could be further tuned by different substituents, which, in our case, were 389–467 nm for **3** and 500–550 nm for **4**. The emission enhancements (Table S2) calculated as the fluorescence quantum yield of the powders over that of the THF solutions (10 μM), are as high as 21.8 and 36.3, for **3** and **4**, respectively.

The impact of substitution groups on the AIE activity is further studied taking compounds **3** as models. As a basis, the ϕ value of **3aa** in powders was 4.4 times higher than that in THF solution. Different substituents on the isoquinolone skeleton of the 3,4-diphenyl isoquinolones (**3ba–3ma**) greatly affected the values of emission enhancement. In general, the *para*-positioned substituents such as methoxy as in **3ba** and fluoro in **3da** contributed to a marked AIE activity, showing more than 20 times emission enhancement. The electron-withdrawing substitution groups, however, exhibited no obvious contributions to the AIE activity. For instance, **3ha** bearing trifluoromethyl barely gave a 1.1-fold enhancement. With the same substitution group, when the *para*-positions of the isoquinolone moiety was occupied, their emission enhancements were higher than the corresponding *ortho*-substituted products (**3ca** > **3ia**, **3da** > **3ja**, **3ea** > **3ka**). With halo-substituted group as Br or I, the emission of products (**3fa**, **3ga** and **3ia**) was weak both in solution and in powders, due to the heavy atom effect.

Altering the substitution groups in the rotors (**3ab–3ak**) also showed significant impact on their AIE property. Isoquinolones **3aa–3af** with two benzene rotors gave obviously higher emission enhancements than **3ai** or **3aj** with one benzene rotor. **3ag** with two naphthyl rotors shows a low emission enhancement because of a higher ϕ value in THF solution and a lower one in the powders, caused by

lowered rotational motions of naphthyl rings and increased intermolecular interactions between larger naphthyl rings in the aggregated state, respectively. When the aromatic rotors are replaced by the alky chains, such as ethyl chains in **3ah**, the non-radiative decay channel of the excited state is blocked to a larger extent, resulting in a higher ϕ value in solutions. Meanwhile, owing to the planar conformation of **3ah**, intermolecular interactions are promoted, leading to a decreased ϕ value in aggregated state. Both effects work collectively, making **3ah** exhibit aggregation-caused quenching effect (ACQ). **3ma** also shows ACQ effect because fusing a phenyl ring to isoquinolone can effectively elongate the conjugation of the stator, resulting in red-shifted absorption and emission, and improved ϕ value in solution. The large planar core is prone to form intermolecular interaction, rendering a decreased ϕ value in the aggregated state. Such ACQ effect, however, is alleviated in compounds **4** because of the twisted conformation of the stator as disclosed by their crystal structures (Fig. S6–S8).

Taken together, we have developed a novel rhodium(III)-catalyzed redox-neutral C–H activation/cyclization strategy to prepare isoquinolones by coupling readily available benzoylhydrazines with alkynes. The N–N bond acted as an oxidizing DG to facilitate *ortho* C–H activation. With this powerful synthetic strategy, we successfully assembled new AIE molecules **3** with isoquinolone skeleton and **4** containing tetracyclic amides. The broad substrate scope and the high reaction efficiency allowed us to freely adjust the substitutions on the stator as well as the chemical structures of the rotors. Our preliminary results on the structure–property relationships suggested the following trends:

- (1) molecules with two benzene rotors showed more pronounced AIE effect than those with one benzene rotor or two naphthyl rotors or two ethyl rotors;
- (2) with same benzene rotors, molecules with larger aromatic stator as the naphthyl ring showed ACQ behavior;
- (3) decreasing the planarity of large aromatic stator is helpful to suppress the ACQ effect and improve AIE property.

We expect that this work will help researchers to identify and synthesize AIE molecules with diverse molecular designs and with more functions.

This work is financially supported by the Doctoral Fund of Ministry of Education of China, the Shenzhen Government (CXZZ20140419131807788 and JCYJ20140627145302109), the Guangdong Government (S20120011226), the National Science Foundation of China (21332005) and the MOST of China (2014AA020512).

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