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Re/Mg Bimetallic Tandem Catalysis for [4+2] Annulation of Benzamides and Alkynes via C-H/N-H Functionalization

Qiuzheng Tang,[‡] Dexin Xia,[†] Xiqing Jin,[†] Qing Zhang,[†] Xiao-Qiang Sun,*[,‡] and Congyang Wang*[,†]

[†]Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

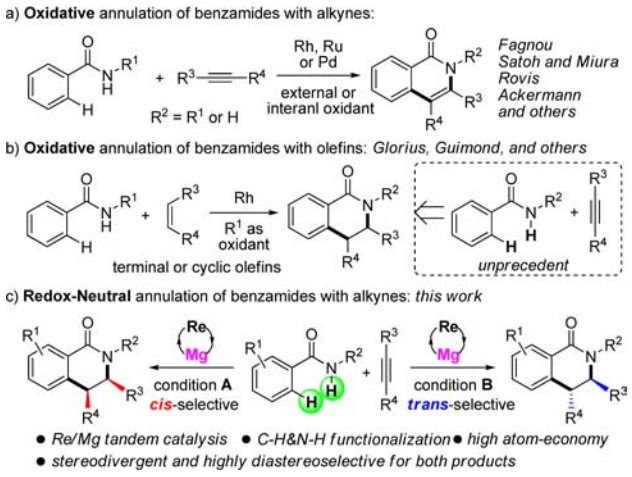
Supporting Information

ABSTRACT: A rhenium-magnesium cocatalyzed [4+2] annulation of benzamides and alkynes via C-H/N-H functionalization is described. The reaction features a divergent and high level of diastereoselectivities, which are readily switchable by subtle tuning of reaction conditions. Thus, a wide range of both *cis*- and *trans*-3,4-dihydroisoquinolinones is expediently synthesized in a highly atom-economical manner. Moreover, mechanistic studies unraveled a tandem mode of action between rhenium and magnesium in the catalytic cycles.

In the past few decades, C-H activation has attracted immense interest since it might significantly streamline the organic synthesis.[1] In principle, the direct transformations of C-H bonds widely occurring in organic molecules can obviate the preactivation of reaction substrates, diminish the generation of undesired waste, and allow for late-stage C-H elaborations, thus ultimately improving the atom and step economy of the whole event.[2] As a consequence, the application of C-H activation in the synthesis of heterocyclic compounds, commonly found as key structural motifs in a vast majority of natural products, pharmaceuticals, and biologically active molecules,[3] has emerged as an important alternative to the traditional approaches.

The construction of isoquinolinone derivatives is illustrative, where both the condensation/cyclization routes[4a−c] and the transition-metal-catalyzed coupling annulations,[4d−f] aza-Wacker-type reactions,[4g−i] denitrogenative[4j,k] and decarbonylative[4l,m] cycloadditions, etc.,[4n,o] requires the prefunctionalization of starting materials. Recently, by using the C-H activation strategy, the groups of Fagnou, Satoh and Miura, Rovis, and others have disclosed the synthesis of isoquinolinones via Rh-,[5a,j] Ru-,[5k−m] Pd-,[5n,o] or Ni-catalyzed[5p] oxidative annulations of benzamides with alkynes (Scheme 1a). From the mechanistic point of view, it should be pointed out that either external or internal oxidants are intrinsically required to reoxidize low oxidation-state metal species to high oxidation-state ones (e.g., Rh^{I}/Rh^{III}, Ru^{0}/Ru^{II}, Pd^{0}/Pd^{II}, etc.) in the final step of these catalytic cycles thus achieving the key catalytic turnovers. Meanwhile, Glorius, Guimond, and others elegantly described Rh-catalyzed oxidative annulations of benzamide derivatives with olefins leading to 3,4-dihydrioisoquinolinones, though the scope of olefins is limited to terminal and cyclic ones, thus no issue of diastereoselectivity being involved (Scheme 1b, left).[6,5e] Again, internal oxidants are the prerequisites to gain the closed catalytic cycles of rhodium

Scheme 1. [4+2] Annulation of Benzamide via C-H Activation



(Rh^{I}/Rh^{III}). So far, to the best of our knowledge, the redox-neutral annulation of benzamides with alkynes, one of the most straightforward routes to 3,4-dihydroisoquinolinones, remains an unmet challenge (Scheme 1b, right). We surmise that accomplishment of a nonredox catalytic cycle of active metal species might be the major obstacle for harnessing such a process. With this regard, we herein disclose the first redox-neutral [4+2] annulation of benzamides with alkynes via C-H/N-H functionalization by means of Re/Mg tandem catalysis (Scheme 1c). Remarkably, both the *cis*- and *trans*-3,4-dihydroiso-quinolinones are readily accessed in a highly diastereoselective fashion simply by subtle tuning of reaction conditions, which adds further values to this bimetallic catalyst system.

As our continuous interest in rhenium catalysis,[7,8] we first examined the reaction of benzamide **1a** and diphenylacetylene **2a** with rhenium catalysts. After an extensive survey of reaction parameters,[9] we delightedly found that, with a catalytic amount of $ReBr(CO)_5$ and PhMgBr, the annulation proceeded smoothly with an excellent diastereoselectivity providing *cis*-3,4-dihydroisoquinolinone **4aa** in 85% isolated yield (Scheme 2). Importantly, no products were observed in the absence of either $ReBr(CO)_5$ or PhMgBr. With the optimized conditions in hand, we set out to investigate the substrate scope. Both aliphatic and aromatic substituents on the N-atom of benzamides are well

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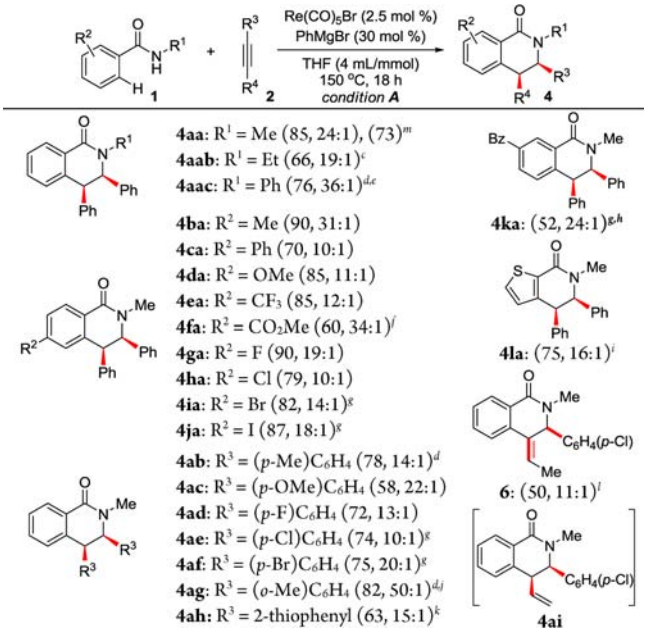
Scheme 2. Substrate Scope for the Formation of 4[a,b]

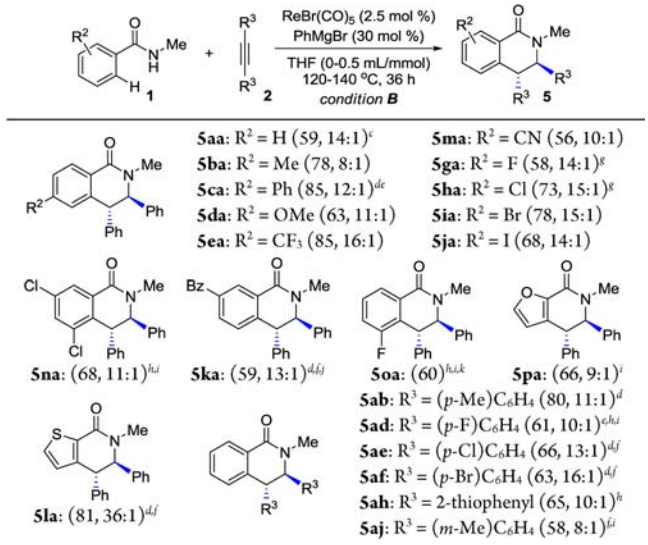


[a]Reaction conditions: **1** and **2** (1.0 mmol), $ReBr(CO)_5$ (2.5 mol %, 0.025 mmol), PhMgBr (30 mol %, 1.0 M in THF, 0.3 mmol), THF (4.0 mL), 150 °C, 18 h. [b]Listed in brackets are isolated yields of pure **4** and the ratios of **4**/**5** (0.2 mmol scale). [c]48 h. [d]36 h. [e]THF (0.5 mL). [f]THF (4.5 mL). [g]THF (5.0 mL). [h]Regioisomer **4ka**′ was also detected, **4ka**/**4ka**′ = 9:1. [i]THF (6.0 mL). [j]THF (0.25 mL), 130 °C. [k]THF (8.0 mL), [l]Ratio of **6**/**6**′ (*E*-isomer) is listed. [m]10 mmol scale with 1 mol % $ReBr(CO)_5$ for 36 h.

tolerant (**4aab-c**). Benzamides bearing either electron-donating or -withdrawing groups on the benzene moiety reacted smoothly with **2a** affording the expected products in good to excellent yields (**4ba-fa**). Of particular note, halogen functionalities, including the Br and I groups often fragile under other transition-metal catalysis, remain intact after reaction, which provides easy handling for further synthetic elaborations (**4ga-ja**). A *meta*-benzoyl substituent led to the regioselective cleavage of the less sterically congested C-H bond (**4ka**). Thiophene-2-carboxamide was also amenable to the reaction conditions (**4la**). Aromatic alkynes containing an array of functionalities with varied electronic and steric properties are easily compatible in the reactions (**4ab-g**). Product **4ah** derived from a heteroaromatic alkyne was also accessed without difficulty. Remarkably, good to excellent diastereoselectivities (up to 50:1) were generally observed in this reaction, which shows the high fidelity of the rhenium-magnesium bimetallic system. The double-bond migrated product **6** rather than the expected **4ai** was obtained when 1-vinylphenylacetylene was used. Of note, only C-H alkenylated product **3ak** was formed when 4-octyne was subjected to the reaction (Scheme 4), which gave a clue to the possible reaction mechanism. Lastly, a gram-scale synthesis of **4aa** was demonstrated (2.3 g, 73% isolated yield) with 1 mol % of $ReBr(CO)_5$.

In the course of screening reaction parameters, we found that the reaction concentration had a profound influence on the diastereoselectivities of the annulation.[9] Interestingly, the formation of *trans*-3,4-dihydroisoquinolinone **5** was favored when the reactions were conducted at high concentration (Scheme 3). Moreover, the reaction temperature can be further reduced while maintaining the reaction outcome. This proved to

Scheme 3. Substrate Scope for the Formation of 5[a,b]

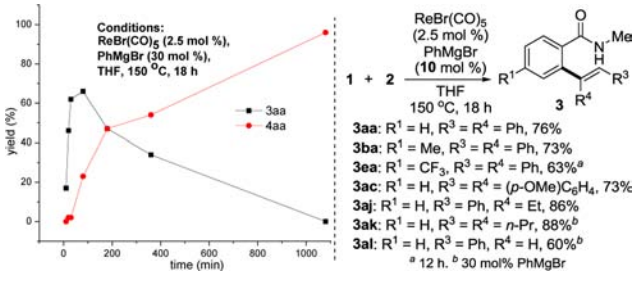


[a]Reaction conditions: **1** and **2** (1.0 mmol), $ReBr(CO)_5$ (2.5 mol %, 0.025 mmol), PhMgBr (30 mol %, 1.0 M, 0.3 mmol), 120 °C, 36 h. [b]Listed in brackets are the isolated yields of pure **5** and the ratios of **5**/**4** determined by ^1H NMR analysis of the reaction mixture on 0.2 mmol scale. [c]130 °C. [d]140 °C. [e]48 h. [f]THF (0.5 mL). [g]24 h. [h]THF (0.25 mL). [i]150 °C. [j]Regioisomer **5ka**′ was also detected, **5ka**/**5ka**′ = 11:1. [k]Single regioisomer.

be quite general to a variety of benzamides and alkynes. Specifically, despite their disparate properties, a multitude of functional groups (Ph, OMe, CF_3, CN, F, Cl, Br, I, etc.) were well tolerant (**5aa-ja**). Benzamide with enhanced steric repulsion on both *meta* positions gave smoothly the expected product **5na**. Notably, highly regio- and diastereoselective formation of **5ka** was found when *m*-benzoylbenzamide was examined. We proposed the steric hindrance of benzoyl group governed predominantly the observed regioselectivity. In contrast, the annulation of *m*-fluorobenzamide with **2a** took place solely at the 2-position, giving rise to **5oa** as a single product. The observed site selectivity is possibly attributed to the C-H bond acidity or the Re-C bond stability in the cyclorhenation step.[5k,10] Also, furan- and thiophene-2-carboxamides are amenable to the reaction conditions leading to **5pa** and **5la**, respectively. Finally, an array of (hetero)aromatic alkynes was shown to be applicable to this protocol giving the expected products **5ab-j** successfully.

To gain insights into the reaction mechanism, a series of experiments were conducted. First, the generation of olefin **3aa** was detected as the reaction (**1a** and **2a**) plot showed in Scheme 4 (left).[9] Specifically, olefin **3aa** was initially formed in the early stage and subsequently transformed into the cyclized product

Scheme 4. Probing Intermediacy and Selective Formation of 3



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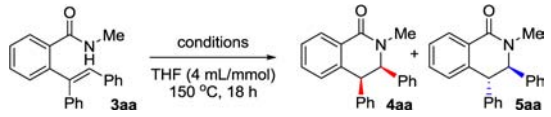
4aa with the elongation of reaction time. Interestingly, chemoselective formation of **3aa** can be obtained simply by decreasing the amount of PhMgBr to 10 mol %, and **3aa** was isolated in 76% yield. Remarkably, only *E*-olefin **3aa** was observed after reaction, which showed a perfect stereocontrol in the alkenylation process. This protocol proved quite general for an array of benzamides and alkynes (Scheme 4, right).[9] Of note, this reaction also represents the first example of rhenium-catalyzed C-H alkenylation of benzamide derivatives.[11]

Second, the isolated olefin **3aa** was then subjected to the catalytic reaction conditions leading smoothly to **4aa** and **5aa** (Table 1, entry 1), which is in contrast to the previous

Table 1. Cyclization of Olefin 3aa[a]



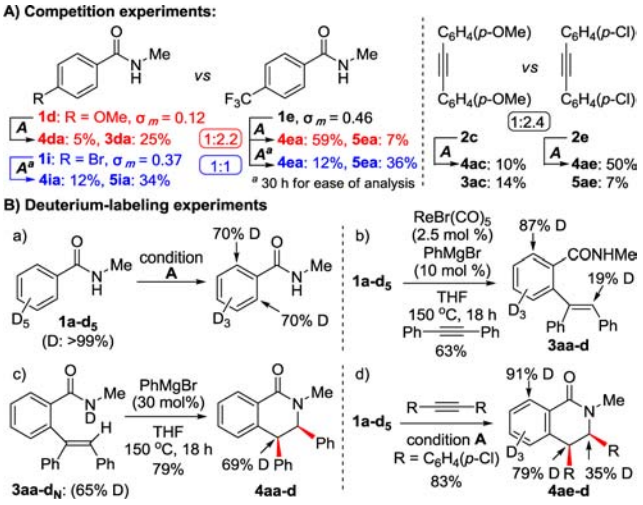
entry	conditions	combined yield (%)[b]	4aa/5aa[b]
1	$Re(CO)_5Br$ (2.5 mol %), PhMgBr (30 mol %)	79	1:6
2	$ReBr(CO)_5$ (2.5 mol %)	0	–[c]
3	PhMgBr (1.0 equiv), $Re(CO)_5Br$ (1.0 equiv)	trace	–[c]
4	PhMgBr (1.0 equiv)	47	1:6
5	PhMgBr (30 mol %)	73	1:23

[a]Reaction conditions: **3aa** (0.1 mmol), THF (0.4 mL), 150 °C, 18 h, others as indicated. [b]Determined by ^{1}H NMR analysis of the reaction mixture with mesitylene as an internal standard. [c]**5aa** was not detected.

isoquinolinone synthesis.[5] To verify which metal, rhenium or magnesium, plays a key role in the cyclization of **3aa**, a set of experiments were examined. No cyclized products were formed with mere use of catalytic $ReBr(CO)_5$ (entry 2). Similar results were obtained when stoichmetric amounts of PhMgBr and $ReBr(CO)_5$ were added into the reaction in either one-portion or stepwise manner (entry 3).[9] However, the cyclized products were formed in moderate yield in the sole presence of PhMgBr (entry 4). Interestingly, the yield increased remarkably with using just catalytic amount of PhMgBr (entry 5). We speculated that **3aa** served also as a proton source thus rendering the cyclization catalytic in magnesium. Thus, it is the metal of magnesium rather than rhenium that catalyzes the cyclization of olefin **3aa** affording 3,4-dihydroisoquinolinones eventually.

Third, the competition experiment between equimolar amount of benzamide **1d** and **1e**, bearing a *para* methoxyl and trifluoromethyl group, respectively, was examined (Scheme 5A, left, red color). The total C-H transformation from the more electron-deficient benzamide **1e** was favored, which suggests an electrophilic C-H activation is less likely operative in this reaction. Furthermore, when equimolar amount of **1i** and **1e**, with Br and CF_3 substituents of similar σ_m values, respectively,[5c] were examined, nearly equal amounts of C-H transformation from **1i** and **1e** were observed (blue color). These results imply that the rhenium-catalyzed C-H activation here might take place through a deprotonative cyclometalation mechanism. In addition, competition experiments between two electro-biased alkynes, **2c** and **2e**, showed that the transformation of electron-deficient **2e** was preferred (Scheme 5A, right). Lastly, deuterium-labeling experiments (Scheme 5B) were conducted to probe the detailed nature of C-H bond cleavage: (a) When pentadeuterated benzamide **1a-d$_5$** was solely subjected to the reaction

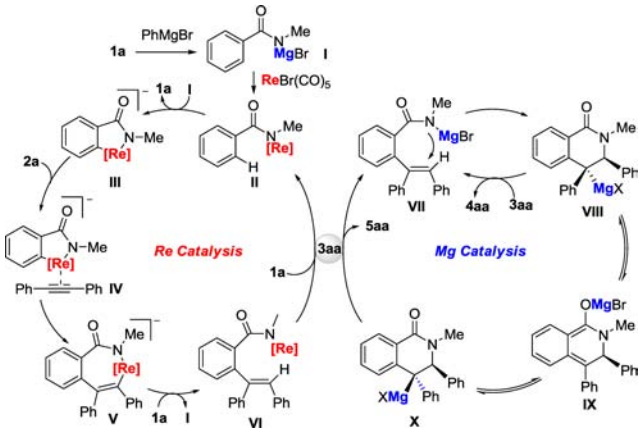
Scheme 5. Competition and Deuterium-Labeling Studies



conditions, partial loss of deuterium (30%) on both *ortho* positions of **1a-d$_5$** was found, which suggests a deprotonation/protonation equilibrium might exist in the reaction. (b) It was observed that only 19% of deuterium was incorporated on the olefinic position along with 13% deuterium loss on the *ortho* position of **3aa-d** in the first alkenylation step of **1a-d$_5$** with alkyne **2a**.[9] (c) The cyclization of N-deuterated **3aa-d$_N$** with catalytic PhMgBr resulted in the regiospecific D-incorporation on the 4-position of **4aa-d**. (d) When **1a-d$_5$** was treated with alkyne **2e**, the slight loss of deuterium on the *ortho* position and the scrambling of D/H on both 3- and 4-positions of **4ae-d** were observed, which again confirm the occurrence of D/H crossover in the reaction cascade.[9]

From these results, a plausible reaction mechanism is shown in Scheme 6. With the aid of PhMgBr, amido-rhenium **II** is initially

Scheme 6. Plausible Bimetallic Catalytic Cycles



formed via amido-magnesium **I**, which then undergoes a deprotonative cyclorhenation affording rhenacycle **III**.[12] The ensuing coordination and insertion of an alkyne gives rise to seven-membered rhenacycle **V**, which further leads to intermediate **VI** upon protonation. Transmetalation between intermediate **VI** and substrate **1a** results in the regeneration of amido-rhenium **II** and formation of **3aa**, which, after deprotonation, suffers an intramolecular nucleophilic addition/cyclization generating species **VIII** or further leading to **X** via intermediate **IX**. Protonation of these species by **3aa** would

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afford the final products and regenerate amido-magnesium **VII**, thus closing the entire Re/Mg bimetallic tandem catalytic cycles.

In summary, we developed the first redox-neutral [4+2] annulation of benzamides and alkynes via C-H/N-H functionalization. The valuable assets of this reaction are further represented by its high atom economy, stereodivergency, and high diastereoselectivities. Thus, it allows for a rapid access to a variety of *cis*- and *trans*-3,4-dihydroisoquinolinones and also *ortho*-alkenylated benzamides, if needed. Mechanistic studies reveal a rhenium-magnesium bimetallic tandem catalysis operating in this reaction, which showcases a superb example of the cooperation and compatibility between transition-metal and main-group metal catalysts. Further studies to explore novel transformations based on this concept are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wangcy@iccas.ac.cn; xqsun@cczu.edu.cn

Notes

The authors declare no competing financial interest.

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