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A general rhodium-catalyzed regioselective C–H functionalization: accessing heteroarylated and alkenylated arenes†

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Herein, an efficient and general rhodium-catalyzed C–H heteroarylation and alkenylation of pyridotriazoles and *ortho*-aryl heterocycles with iodonium ylides is reported. This strategy enables the synthesis of a wide array of heteroarylated and alkenylated heterocycles and arenes under mild reaction conditions. The triazole moiety in pyridotriazoles serves exclusively as an intrinsic directing group, showcasing distinct reactivity compared to previous reports. In addition, this transformation accommodates various N-containing heterocycles and oximes as directing groups, highlighting its versatility for heterocycles and arenes functionalization. This protocol exhibits broad substrate scope, good functional group tolerance, operational simplicity, air compatibility, and scalability with low catalyst loading. Moreover, a low kinetic isotope effect value indicates C–H bond cleavage is unlikely to be the rate-determining factor.

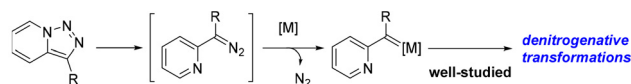
Introduction

Nitrogen-containing heterocycles frequently appear in bio-active compounds, natural products, and organic functional materials.¹ Thus, developing efficient methods for incorporating heterocyclic moieties would be beneficial and can rapidly increase molecular complexity. C–H functionalization remains a pivotal strategy in organic synthesis, offering a direct pathway to diverse chemical architectures.² In this context, rhodium-catalyzed C–H activation has attracted considerable interest for its capability to enable challenging transformations in recent years.^{2,3}

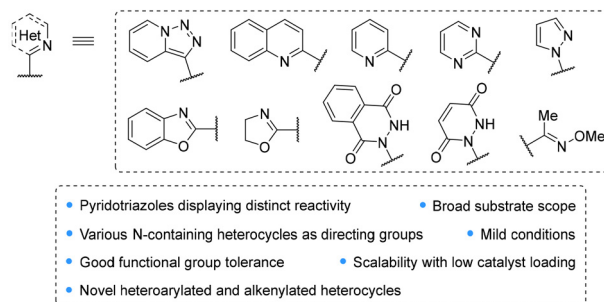
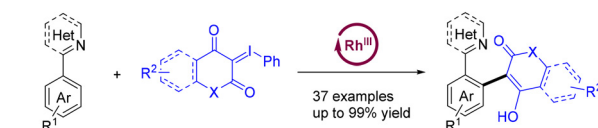
Over the past decade, pyridotriazoles have usually served as a source of metal carbenoids in transition metal-catalyzed denitrogenative transformations, facilitating the synthesis of

various molecules with *N*-heterocyclic moieties (Scheme 1a).^{4–7} Additionally, iodonium ylides, recognized for their stability and reactivity, frequently serve as versatile carbene precursors in C–H functionalization reactions.^{8,9} For instance, a Rh-catalyzed C–H activation/annulation involving pyridotriazoles and

a) TM-catalyzed denitrogenative transformations of pyridotriazoles (refs. 4–7, 10)



b) Rh-catalyzed C–H heteroarylation/alkenylation of heterocycles with iodonium ylides (this work)



Scheme 1 Rh-catalyzed C–H functionalization of pyridotriazoles and *ortho*-aryl heterocycles.

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iodonium ylides was developed recently, where the triazole component of pyridotriazoles serves both as a directing group and a carbene precursor.¹⁰

Inspired by previous studies^{4–10} and driven by our continuous pursuit of novel drug-like heterocyclic compounds,¹¹ we herein develop an efficient and mild rhodium-catalyzed C–H heteroarylation and alkenylation of pyridotriazoles and *ortho*-aryl heterocycles with iodonium ylides, accessing various heteroarylated and alkenylated arenes (Scheme 1b). Notably, the triazole moiety in pyridotriazoles acts exclusively as an intrinsic directing group, displaying a different chemical reactivity compared to previous reports.^{4–7,10} In addition, various N-containing heterocycles and oximes as directing groups are also compatible in this reaction, indicating the potential for general heteroarylation and alkenylation of arenes.

Results and discussion

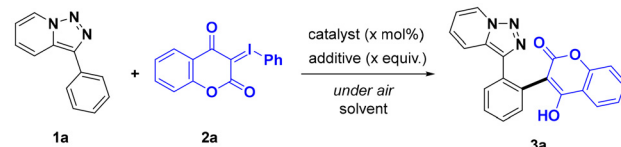
An optimization study was conducted using pyridotriazole **1a** and 3-(phenyl- λ^3 -iodanelylidene)chromane-2,4-dione **2a** as substrates. Initially, various metal catalysts were tested with NaOAc as an additive in TFE solvent (Table 1, entries 1–6). The results showed that $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$, $[\text{RuCl}_2(p\text{-cymene})]_2$, $\text{Pd}(\text{OAc})_2$, $\text{Rh}_2(\text{esp})_2$, and $\text{Rh}_2(\text{OAc})_4$ did not facilitate the reaction. In contrast, $[\text{Cp}^*\text{RhCl}_2]_2$ exhibited moderate catalytic activity, yielding the desired product **3a** in 39%. Next, a range of additives, including KOAc, CsOAc, $\text{Zn}(\text{OAc})_2$, and NaHCO_3 , were evaluated. $\text{Zn}(\text{OAc})_2$ proved to be the most effective, providing

the highest yield of **3a** (89%) in both HFIP (entry 9) and TFE (entry 13) when used with $[\text{Cp}^*\text{RhCl}_2]_2$. The solvent effect was also examined using 1,4-dioxane, MeOH, THF, and DCM (entries 11–15). These solvents delivered significantly lower yields, with some reactions resulting in no product or only trace amounts. In addition, when Na_2CO_3 and $\text{Zn}(\text{OTf})_2$ was used instead of $\text{Zn}(\text{OAc})_2$, only a trace amount of **3a** was obtained (entries 16 and 17). HFIP and TFE consistently outperformed other solvents, delivering the highest yields. The optimal reaction conditions were determined to be $[\text{Cp}^*\text{RhCl}_2]_2$ as the catalyst, $\text{Zn}(\text{OAc})_2$ as the additive, and either HFIP or TFE as the solvent, achieving an impressive yield of 89% under air at room temperature.

With optimal conditions established, the substrate scope of pyridotriazoles, *ortho*-aryl heterocycles, and iodonium ylides under rhodium catalysis was then investigated (Scheme 2). First, pyridotriazoles with methyl (**3b**) and methoxy (**3c**) on the phenyl ring delivered excellent yields, indicating enhanced reactivity. Additionally, electron-withdrawing groups, such as fluoro (**3d**, **3k**) and chloro (**3e**), produced slightly lower yields but demonstrated good compatibility. Electron-withdrawing groups at the phenyl ring like trifluoromethyl (**3h**) maintained high efficiency, whereas cyano (**3i**) slightly reduced the yield, likely due to its strong electron-withdrawing nature. Bulky substituent, *tert*-butyl (**3g**), showed minimal steric effect on the reaction outcome. Regarding heterocyclic directing groups, nitrogen-containing heterocycles, such as quinoline (**3l**), pyridine (**3m**), pyrimidine (**3n**), pyrazole (**3o**), benzoxazole (**3r**), and oxazoline (**3s**) exhibited good to excellent yields. Besides, 1-(2-*pyridine*-2-yl)-1*H*-indole and 1-(*pyrimidin*-2-yl)-1*H*-indole also performed well, affording the corresponding products **3p** and **3q** smoothly. In addition, replacing the directing group with a phthalazine-1,4-dione, pyridazine-3,6-dione, or *O*-methyl oxime moiety still enabled the reaction to proceed smoothly, affording the corresponding products **3t–3v**. The results demonstrate the broad applicability of the $\text{Rh}(\text{III})$ -catalyzed system across a wide range of functional groups and N-containing heterocyclic directing groups, underscoring the potential for diverse functionalization.

The substrate scope of iodonium ylides with pyridotriazole was subsequently explored. Halogen substituents on the coumarin ring, such as fluoro (**3w**), bromo (**3x**), and chloro (**3y**), exhibited a trend of increasing yields with larger halogens. Electron-donating groups, including methyl (**3z**, **3zb**) and methoxy (**3za**, **3zd**), produced excellent yields, underscoring their positive influence on reactivity. Similarly, the electron-withdrawing fluoro group (**3zc**) maintained high efficiency, demonstrating the reaction's broad tolerance to various functional groups. When the coumarin ring was replaced with other heteroaryl rings, such as 4-hydroxy-1-methylquinolinone, 4-hydroxy-thiochromenone, 4-hydroxy-6-methyl-pyranone, 6-hydroxy-2-phenylpyrimidinone, and 4-hydroxy-2*H*-pyrido[1,2-*a*]pyrimidinone, the desired products (**3ze–3zi**) were obtained smoothly, showcasing excellent compatibility with diverse heterocyclic frameworks. Additionally, aliphatic rings such as cyclohexane-1,3-dione and 5,5-dimethylcyclohexane-1,3-dione

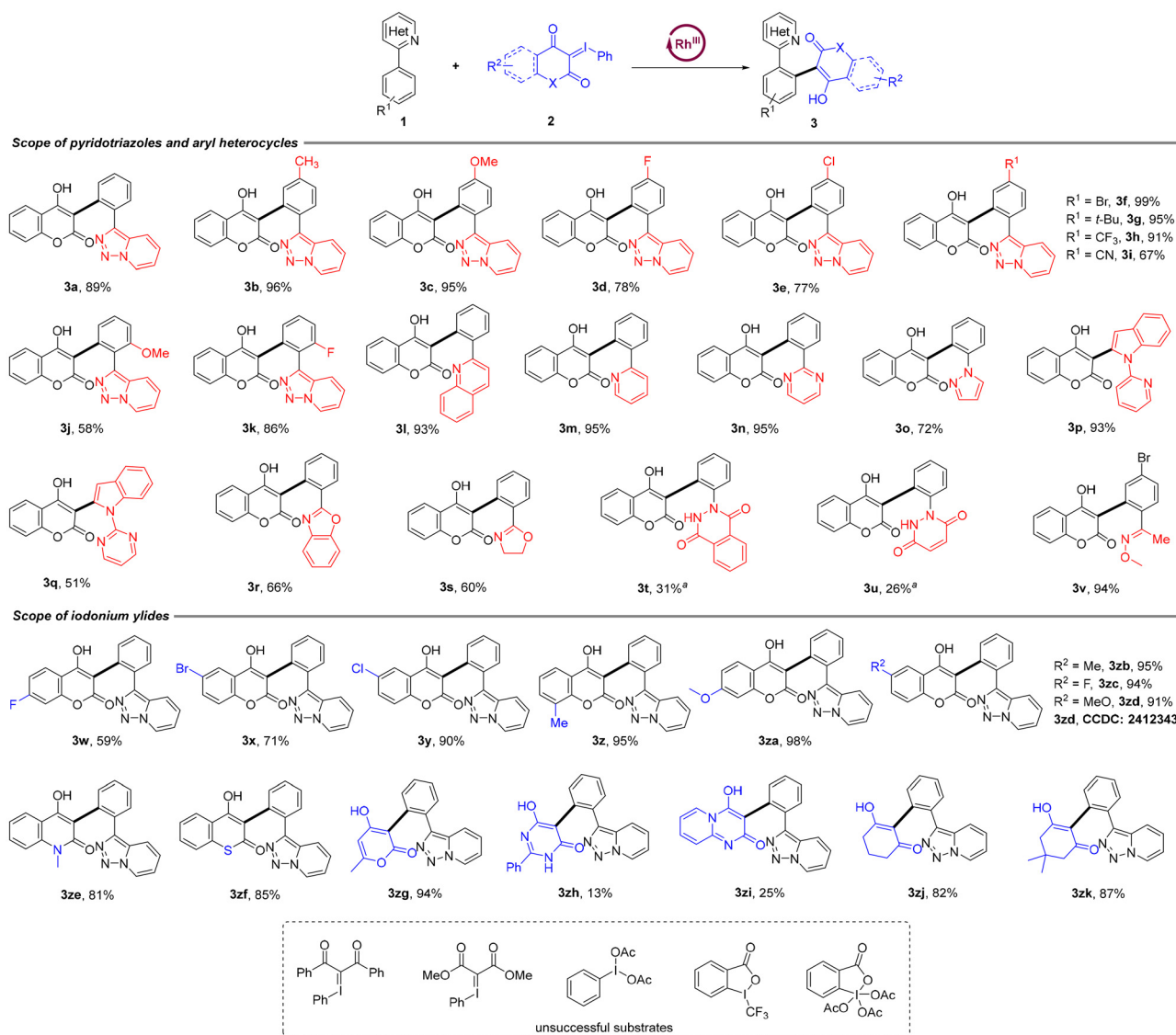
Table 1 Optimization of reaction conditions^a



| Entry | Catalyst | Additive | Solvent | Yield ^b |
|-------|---|---------------------------|---------|--------------------|
| 1 | $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ | NaOAc | TFE | NR |
| 2 | $[\text{RuCl}_2(p\text{-cymene})]_2$ | NaOAc | TFE | NR |
| 3 | $\text{Pd}(\text{OAc})_2$ | NaOAc | TFE | NR |
| 4 | $[\text{Cp}^*\text{RhCl}_2]_2$ | NaOAc | TFE | 39% |
| 5 | $\text{Rh}_2(\text{OAc})_4$ | NaOAc | TFE | NR |
| 6 | $\text{Rh}_2(\text{esp})_2$ | NaOAc | TFE | NR |
| 7 | $[\text{Cp}^*\text{RhCl}_2]_2$ | KOAc | HFIP | 31% |
| 8 | $[\text{Cp}^*\text{RhCl}_2]_2$ | CsOAc | HFIP | 31% |
| 9 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | HFIP | 89% |
| 10 | $[\text{Cp}^*\text{RhCl}_2]_2$ | NaHCO_3 | HFIP | NR |
| 11 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | Dioxane | NR |
| 12 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | MeOH | 19% |
| 13 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | TFE | 89% |
| 14 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | THF | Trace |
| 15 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OAc})_2$ | DCM | 33% |
| 16 | $[\text{Cp}^*\text{RhCl}_2]_2$ | Na_2CO_3 | HFIP | Trace |
| 17 | $[\text{Cp}^*\text{RhCl}_2]_2$ | $\text{Zn}(\text{OTf})_2$ | HFIP | Trace |

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (5 mol%), additive (0.2 mmol), under air, room temperature, solvent (2.0 mL), 12 h. ^b Isolated yield. NR = no reaction.





Scheme 2 Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (5.0 mol%), $\text{Zn}(\text{OAc})_2$ (0.2 mmol), under air, HFIP (2.0 mL), rt, 12 h; isolated yields are reported. ^a $[\text{Cp}^*\text{RhCl}_2]_2$ (3.0 mol%), AgSbF_6 (0.3 equiv.), under air, TFE (2.0 mL), rt, 12 h.

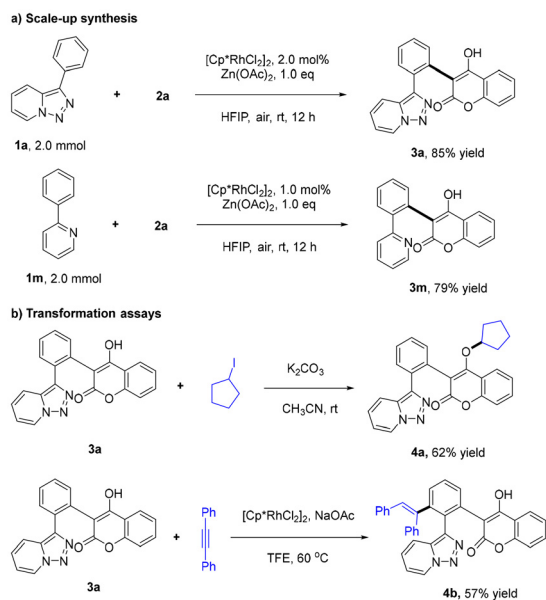
(**3zj**, **3zk**) also worked. Moreover, the reaction does not tolerate non-cyclic iodonium ylides, Dess–Martin periodinane, Togni Reagent II, or (diacetoxyiodo)benzene. Overall, this methodology demonstrates good functional group tolerance, compatibility with diverse heterocyclic moieties and high efficiency. It efficiently delivers structurally complex products across diverse frameworks, including phenyl, heteroaryl, and aliphatic rings, emphasizing its potential for versatile functionalization.

In addition, scale-up synthesis and subsequent transformation experiments were carried out to demonstrate the practicality and versatility of the developed methodology (Scheme 3). For the scale-up synthesis, pyridotriazole **1a** was treated with **2a** in HFIP at room temperature for 12 hours, affording compound **3a** in 85% yield when 2.0 mol% $[\text{Cp}^*\text{RhCl}_2]_2$ was used. Furthermore, when the reaction was conducted with 1.0 mol% $[\text{Cp}^*\text{RhCl}_2]_2$, compound **3m** was obtained in 79% yield, high-

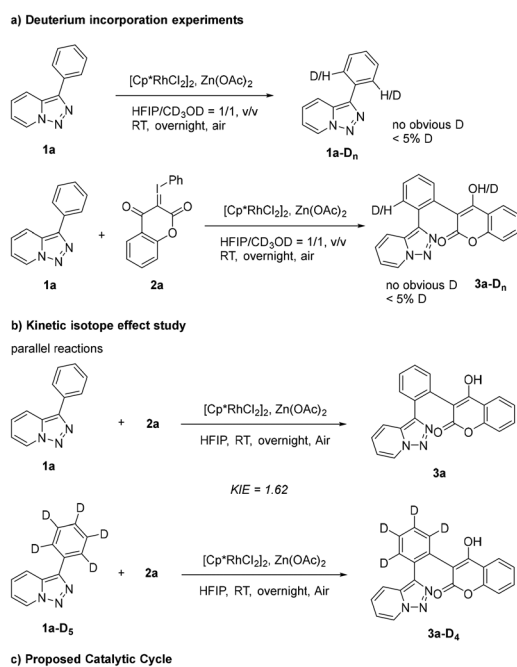
lighting the scalability and efficiency of the reaction. In the transformation assays, **3a** underwent etherification with iodo-cyclopentane in the presence of K_2CO_3 in CH_3CN to afford **4a** (62%). Additionally, further functionalization of **3a** was achieved *via* C–H activation using $[\text{Cp}^*\text{RhCl}_2]_2$ and NaOAc with diphenylacetylene in TFE at 60 °C, providing **4b** in good yield. These results underscore the synthetic utility of these reactions, enabling the efficient generation of structurally diverse compounds and expanding its applicability for further functionalization.

In the deuterium incorporation experiments (Scheme 4a), reactions were conducted in a mixture of HFIP and CD_3OD (1 : 1) with $[\text{Cp}^*\text{RhCl}_2]_2$. The resulting products, **1a-D_n** and **3a-D_n**, showed negligible deuterium incorporation (<5% D). In the KIE study (Scheme 4b), parallel reactions of **1a** and fully deuterated **1a-D₅** with **2a** under standard conditions yielded **3a**





Scheme 3 Scale-up synthesis and transformation.



Scheme 4 Mechanism study.

and 3a-D₄, respectively. The calculated KIE value of 1.62, derived from the relative reaction rates ($k_{\text{H}}/k_{\text{D}}$), suggests a moderate isotopic influence on the reaction mechanism.

Based on preliminary mechanistic studies and existing literatures,^{8,10} the proposed catalytic cycle illustrates the transformation of substrate 1a into product 3a using the rhodium catalyst $[\text{Cp}^*\text{RhCl}_2]_2$ in the presence of iodonium ylide 2a and $\text{Zn}(\text{OAc})_2$ (Scheme 4c). The cycle begins with the activation of the rhodium catalyst to generate the active catalytic species $\text{Cp}^*\text{Rh}(\text{OAc})_2$. This species undergoes C–H bond activation with 1a, forming the rhodium–arene complex A while releasing acetic acid. Subsequently, compound 2a reacts with intermediate A to generate the rhodium-carbenoid intermediate B. This intermediate then undergoes migratory insertion, forming intermediate C. Finally, protonolysis of C with acetic acid releases the desired product 3a, while regenerating the active rhodium catalyst to close the cycle. This process elegantly integrates C–H activation and carbene transfer, enabling efficient and selective product formation.

Conclusions

In summary, we present an efficient and general rhodium-catalyzed methodology for the C–H heteroarylation and alkenylation of pyridotriazoles and *ortho*-aryl heterocycles using iodonium ylides as coupling partners. This approach unlocks access to a broad range of heteroarylated and alkenylated heterocycles and arenes under mild conditions. Notably, the triazole moiety in pyridotriazoles functions exclusively as an intrinsic directing group, exhibiting distinct chemical reactivity compared to prior studies. The scope of this transformation is further demonstrated by its compatibility with diverse N-containing heterocycles, including quinoline, pyridine, pyrimidine, pyrazole, benzoxazole, oxazoline, phthalazine-1,4-dione, pyridazine-3,6-dione, and *O*-methyl oxime moiety, highlighting the methodology's adaptability for *ortho*-aryl heterocycle functionalization. Good functional group tolerance, operational simplicity, air compatibility, and scalability with low catalyst loading are also demonstrated. In addition, the low KIE value indicates the C–H bond cleavage is unlikely to be the rate-determining step.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†



Acknowledgements

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