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COMMUNICATION

Harnessing hypervalent iodonium ylide as carbene precursors; C-H activation of *N*-methoxybenzamides by Rh(III)-catalyst

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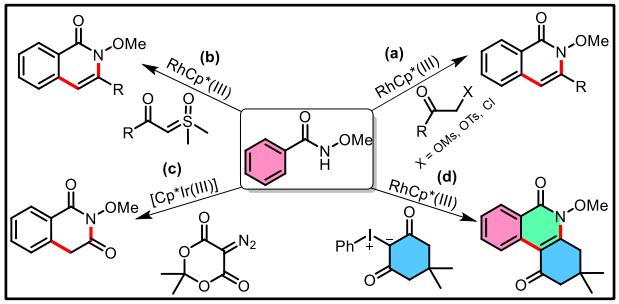
An expeditious generation of carbene from hypervalent iodonium ylide incorporating *N*-methoxybenzamide as a starting material upon Rh(III)-catalyst undergoes domino intermolecular C–H activation followed by intramolecular condensation to afford dihydrophenanthridines. KIE studies and DFT calculations were performed to substantiate the mechanistic pathway. To extend the synthetic utilisation, fluorescent pyranoisocoumarins were achived by using a Rh(III)-catalyzed peri-C-H/O-H activation/annulation reactions.

Hypervalent iodine-(III) ylides (HVI) have experienced a tremendous growth for its versatile synthetic applications.[1] Iodonium ylides exhibit their characteristic thermal stability and solubility in common organic solvents were being sought as precursors[2] for carbenes or metallocarbenoid intermediates for transformations in which they act as electrophiles or nucleophiles.[3] Among the deployed carbene precursors,[4] diazo surrogates are widely used.[5] HVI compounds have gained considerable attraction due to their reactivity is reminiscent of toxic and costly transition metals. Hence, these aryl iodides are environmentally benign and widely utilized.[6] Previously, sulfoxonium and sulfonium ylides[7] act as good carbene counterparts. The aryl iodonium ylides are well known surrogates utilized both in transition metal-catalyzed and a catalyst free reactions with alkenes, ketenes, alkynes, nitriles, isocyanates, thiols, and carbodiimides.[8] Owing to their affordability and ease of availability with special emphasis about its safety aspects compared to diazo surrogates, HVI has been deployed as the most preferred carbene counterpart and it provides access for a variety of polycyclic heteroarenes, carbocyclic and heterocyclic scaffolds.

The transition-metal-catalysed activation of C-H/C-C bonds,[9] with insertion of π-systems has become well-developed for the synthesis of carbocycles and heterocyclic compounds.[10] The discovery of transition-metal-catalysed C-H bond functionalization has been enormously implied in organic synthesis and revolutionized synthetic strategies.[11]



Scheme 1. C-H bond functionalization of different carbene precursor

Developing a protocol to validate a methodology for the selective functionalization of different C-H bonds in a given substrate has been a long-standing effort. In this context especially, the Rh(III)-catalysed transformation reactions were exploited predominantly with researcher's attention at large.[12] Meanwhile, Rh(III)-catalysed construction of nitrogen-containing heterocycles mediated by C–H activation explored extensively.[13] Previously, Glorius and co-workers have developed a C–H activation of *N*-methoxybenzamide and accomplished the synthesis of isoquinolones with α-MsO/TsO/Cl ketones as oxidized alkyne equivalents [Scheme 1, a].[14a] Li and co-workers utilized the sulfoxonium ylide as a carbene precursor for chemo divergent cyclization of N-methoxybenzamide that leads to *N*-methoxyisoquinolones [Scheme 1, b].[14b] Ramana and co-workers have developed the Ir(III)-catalyzed carbenoid functionalization of benzamides with diazo compounds towards the synthesis of *N*-Methoxyisoquinolinediones and *N*-Methoxyisoquinolinones [Scheme 1, c].[14c] However, to the best of our knowledge, Rh(III)-catalyzed oxidative C–H functionalization/intramolecular cyclisation with hypervalent iodonium ylide has not been reported in the literature ever before. To extrapolate our work in this context,[15] we have accomplished an efficient Rh(III)-catalyzed synthesis of 3,4-dihydrophenanthridins *via* cascade reaction of hypervalent iodonium ylides with N-methoxybenzamides under the mild reaction conditions [Scheme 1, d]. To investigate the present Rh(III)-catalyzed C-H

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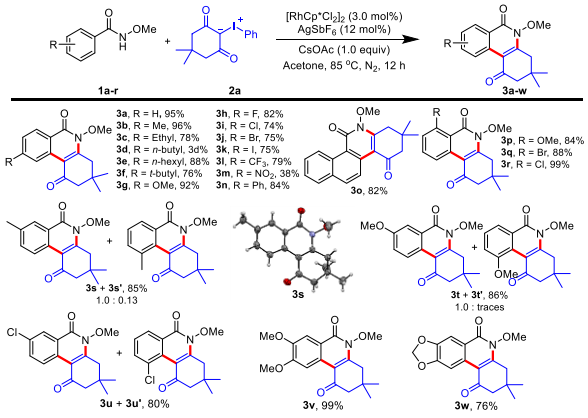
activation/annulation reaction, *N*-methoxybenzamide **1a** and 5,5-dimethyl-2-(phenyl-l3-iodanylidene)cyclohexane-1,3-dione **2a** were used as a trail substrates under different reaction conditions (for details see supporting information (ESI)).

Table 1. Substrate scope of **1a-w** with **2a**[a]



Reaction conditions: **1a** (0.6 mmol), **2b-k** (0.6 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.0 mol%), CsOAc (1.0 equiv.) and $AgSbF_6$ (12 mol%) in Acetone (5.0 mL) at 85 °C for 12 h. [a] Isolated yields.

With the optimized reaction conditions in hand, the generality of this procedure was first investigated by testing the catalytic reaction with various electronically substituted *N*-methoxybenzamides **1b-1w** with **2a** as shown in (**Table 1**). The para alkyl substituted *N*-methoxy benzamide **1b-f** underwent cyclization with **2a**, afforded the titled dihydrophenanthridines (**3b-3f**) in excellent yield. Next, we treated electron donating group (methoxy) substitution at 4th position with **2a** which provided the corresponding dihydrophenanthridine **3g** in 92% of yield. It was found that halogen substituted benzamides F, Cl, Br and I at the p-position could be coupled smoothly with **2a** in **3h**, **3i**, **3j** and **3k** afforded in excellent yield. Substitution of the strong electron withdrawing groups at the *p*-position of phenyl ring CF_3 and NO_2 of the benzamide provided **3l** and **3m** in 79% and 38% of the yield. In addition, the reaction was extended to biphenyl and naphthyl fused *N*-methoxybenzamide which also coupled with **2a** gives 84% and 82% of **3n** and **3o** of yields. The cyclization of *o*-substituted *N*-methoxybenzamides **2p-r** with 2a provided **3p-r** in 84%, 88% and 99% yields, respectively. The structure of compound **3s** unambiguously confirmed by using XRD analysis (See ESI table 3). Subsequently, the reaction was tested with *m*-methyl, methoxy and chlorine substituted *N*-methoxybenzamides treated with **2a** afforded **3s-u** in 85%, 86% and 80% of yield, respectively. Further, 3,4-dimethoxy benzamide **1u**, *N*-methoxybenzo[d][1,3]dioxole-5-carboxamide **1v** with **2a** afforded **3v** and **3w** in 99% and 76% of yields.

The scope of annulation reaction was examined with various substituted hypervalent iodonium ylides **2b–k** (**Table 2**). The reaction was compatible with R^1, R^2 = H substituted ylide **2b** with **1a** provided annulated **3x** in 48% yield. In the reaction, 3-arylated hypervalent iodonium ylides **2c** were treated with **1a** provided good yield 75% of **3y**. A hypervalent iodonium ylide bearing an aryl at 4th substitution such as 4-Me, 4-OMe, 3,4-dimethoxy and 3,4,5-trimethoxy on the aromatic group reacted smoothly to give **3z**, **3aa**, **3ab** and **3ac** in 65%, 70%, 72% and 55% of yields, respectively. While 3-aryl halide substituents with hypervalent iodonium ylides (**2h-k**) had significant effect on the outcome of reaction producing **3ad-3ag** with moderate yields.

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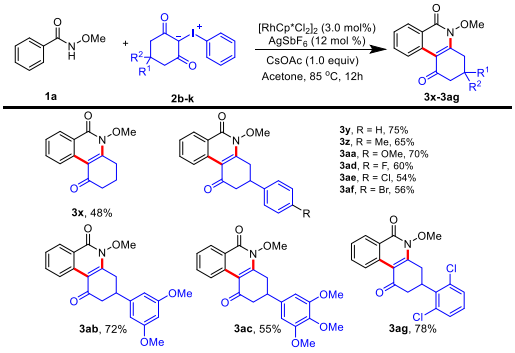
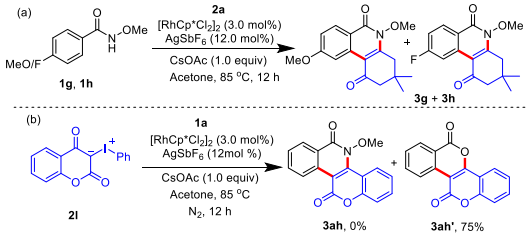
Table 2. Substrate scope of **2b-k** with **1a**[a]



Reaction conditions: **1a** (0.6 mmol), **2b-k** (0.6 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (3.0 mol%), CsOAc (1.0 equiv.) and $AgSbF_6$ (12 mol%) in Acetone (5.0 mL) at 85 °C for 12 h. [a] Isolated yields.

The competitive experiment was performed between *N*,4-dimethoxybenzamide having an electron-donating **1g** and 4-fluoro-*N*-methoxybenzamide an electron withdrawing **1h** with **2a** enabled preferential formation of **3g** (3g:3h = 1.0 :0.33, **Scheme 2, a**). We envisaged the reaction efficiency of **1a** with **2l** under the chosen reaction conditions (**Scheme 2, b**). The reaction led to the formation of isochromenone derivative **3ah'** in 75% of yield instead of above-mentioned product isoquinolinone derivative **3ah**. When the reaction was carried out using *N*-methyl benzamide **1x** or *N*-phenyl benzamide **1y** instead of *N*-methoxybenzamide **1a** with **2a** under the optimized reaction condition, resulted in no formation of the product **3ai** and **3aj** (See ESI, Scheme 9). Similarly, the control reaction between **1a** with 1,3-diketone **2m** instead of **2a** did not provide the desired product **3a** (See ESI, Scheme 10). Also, the addition of (diacetoxyiodo)benzene (PIDA) to the reaction between **1a** with 1,3-diketone **2m** under optimized reaction condition resulted in traces of **3a** only (See ESI, Scheme 11). Meanwhile, the five membered HVI **2m** was tested with **1a** with the same reaction condition has led to no formation of desired product **3ak** (See ESI, **Scheme 12**)

Scheme 2. Competitive experiments and reaction with **2l**



To gain a preliminary mechanistic insight, the deuterium labelling experiment was performed. A 49% deuterium incorporation at ortho-C-H bonds of **1b** was observed in the presence of D_2O (2.5 equiv.), which indicates that the C-H bond cleavage step is reversible (**Scheme 3, a**). Further, in the reaction of **1a-*d*$_5$** with **2a** under the same reaction condition, the expected cyclized products **3a-*d*$_4$** were observed in the yield of 72% (**Scheme 3, b**). The competitive parallel kinetic isotopic experiments (KIE) were performed using substrates **1a** and **1a-*d*$_5$** with **2a** that provided k_H/k_D = 1.28. These results indicate that

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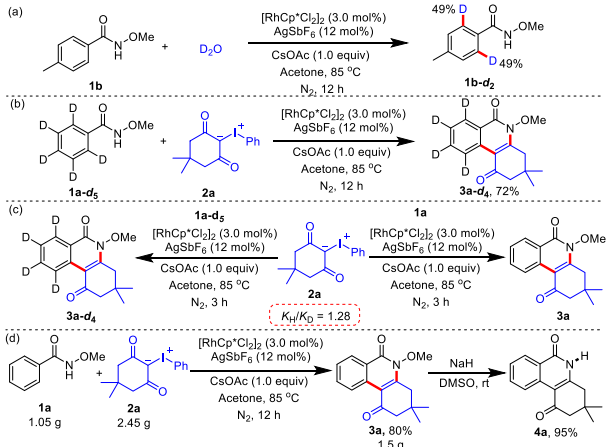
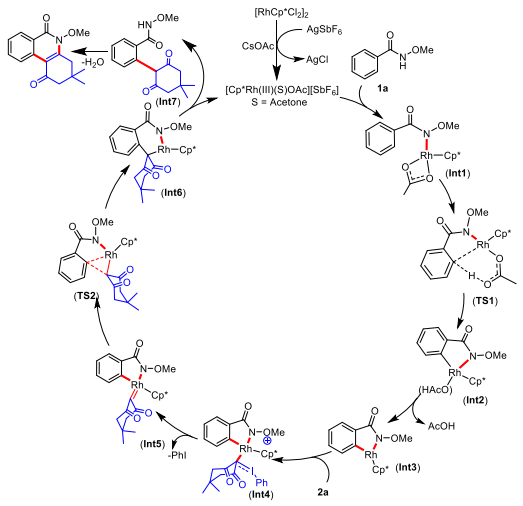
the C-H bond activation process is not the rate-determining step of this reaction (**Scheme 3, c**). We carried out a scale-up synthesis of **3a** using **1a** (1.05 g, 7.0 mmol) and **2a** (2.45 g, 7.0 mmol). The desired product **3a** (1.5 g) was isolated in 80% of yield. Also, N-deprotection reaction was performed as a representative for **3a** (**Scheme 3, d**). The transformation of **3a** was accomplished using NaH in DMSO at room temperature for 30 minutes. The corresponding free N-H product **4a** was obtained in excellent yield (95%).

Scheme 3. Primary mechanistic investigation and gram scale synthesis



To understand the mechanism (**Scheme 4**), DFT calculations were performed with the SDD and M06 hybrid functional to get a Gibbs free energy profile diagram at 273.15 K. The intermediate **Int1** undergoes C-H bond activation *via* transition state **TS-1**, in which the acetate ligand deprotonates an ortho C-H to afford the intermediate **Int2** at relative energy of 6.8 kcal/mol (**Figure 1**).[16]

Scheme 4. Proposed catalytic pathway for the reaction of **1a** with **2a** using Rh(III)-catalyst



These concerted metalation-deprotonation (CMD) step is not as much of energy demanding process (11.3 kcal/mol), which suggests that the C-H activation is not the rate-determining step. Consecutively, the five-membered rhodacycle intermediate **Int2** loses -AcOH, which providing a vacant binding site on Rh(III) for the iodosocarbene coordination. The resulting intermediate **Int3** is located at -4.5 kcal/mol. The coordination of the iodosocarbene **2a** to **Int3** forms intermediate **Int4** with exothermicity (-10.7 kcal/mol). The subsequent de-iodination of intermediate **Int4** readily provides Rh-carbene intermediate **Int5** that located at -139.6 kcal/mol. The transition state **TS2** for the migratory insertion step is located at -132.8 kcal/mol with a barrier of 6.8 kcal/mol, which forming six-membered Rh(III) complex **Int6** (-164.2 kcal/mol). Subsequently, the intermediate **Int7** is formed by the protonation of C–Rh bond of **Int6** with acetic acid, and regenerates the active catalyst. Further, the enamine type reaction of **Int6** takes place to provide the product **3a**. Our DFT studies revealed that the C-H activation process is not the rate-determining step, which was in good agreement with our small experimental KIE results (k_H/k_D = 1.28).[17]

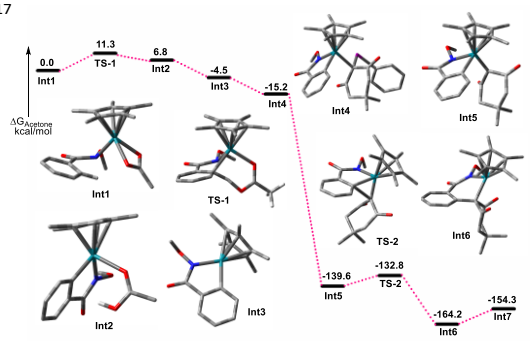
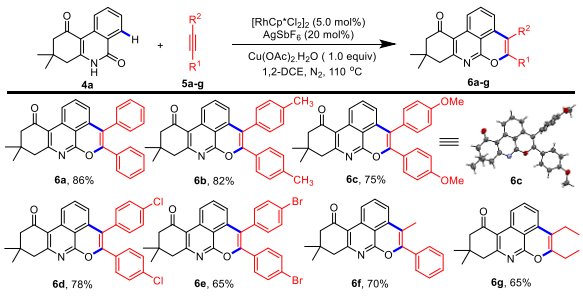


Figure 1. Gibbs free energy profile (kcal/mol) obtained at the SMD/M06/6-311++G(d,p), SDD(Rh) level of theory in acetone solvent.

Although numerous approaches in formulating isoquinoline derivatives have been developed,[18] owing to their importance, the development of novel and expeditious methods for the divergent construction of polycyclic isoquinolines from readily available starting materials are still highly desirable. When **4a** was treated with **5a** in the presence of $[RhCp^*Cl_2]_2$ (5.0 mol%), $AgSbF_6$ (20 mol%) and $Cu(OAc)_2.H_2O$ (1.0 equiv) in 1,2-DCE heated at 110 °C under nitrogen for 12 hours (See, the detailed optimization study ESI), the annulated product **6a** was isolated as yellow solid with 85% yield. The substrate scope (**Scheme 5**) of the annulation reaction was examined with differently substituted alkyne **5b-e** smoothly coupled with **4a** to give corresponding **6b-e** in 65-78% of yield, respectively.

Scheme 5. Rh(III)-catalyzed synthesis of pyranoisocoumarins by using **4a** with alkynes



Additionally, the structure of compound **6c** unambiguously confirmed by X-ray diffraction analysis (for details see ESI table 4). The unsymmetrical alkyne (**5f**) underwent smoothly with **6f** (70%) yield and exhibits an excellent regioselectivity. Likewise, symmetrical aliphatic alkyne was annulated thus resulted the product **6g** with 65% of yield. We surprisingly found that pyranoisocoumarins could exhibit bright fluorescence, which can be utilized to measure photoluminescence properties,

excited states for **6a-e** in solution and solid state. Our studies can further be applied in developing new organic fluorophores,[15] by investigating their photophysical properties and potential applications of organic fluorescent molecules in smart materials, optoelectronic devices, fluorescent sensors, and biomedical imaging.[19] We have measured the absorption and emission spectra in DCM solution and thin-film are listed in (Figure 2). The fluorescence of compound **6a–6e** shows emission maxima at 456–472 nm in DCM solution and 492-529 nm in thin-film (for details of PL study see ESI).

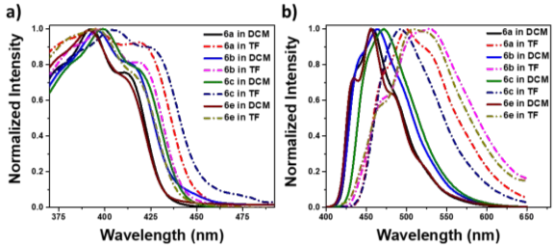


Figure 2. (a) Normalized absorption of **6a**, **6b**, **6c**, and **6e** in DCM solution (solid line), and thin film (dotted line); (b) Normalized fluorescence **6a**, 6b, 6c, and 6e in DCM solution (solid line), and thin film (dotted line); Con 5.0 μM; Excitation wavelength is 380 nm.

In summary, the first example of Rh(III)-catalysed C-H bond activation of *N*-methoxybenzamide with HVI deployed as a carbene precursor has been reported. The cyclisation reaction is compatible with various electronically substituted functional groups, substituted benzamides and HVI's. The detailed mechanistic investigation was demonstrated by deuterium labelling studies, competitive experiments and DFT calculations. Furthermore, DFT calculations revealed that the C–H activation process is the rate-limiting step, which is in good agreement with experimental KIE results. Besides, the N-deprotected dihydrophenanthridines were subjected to peri C-H/O-H bond activation/annulation with alkyne upon Rh(III)-catalyst and the resulted pyranoisocoumarins and their photophysical properties were investigated.

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Conflicts of interest

There are no conflicts to declare

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Harnessing hypervalent iodonium ylide as carbene precursors; C-H activation of *N*-methoxybenzamides by Rh(III)-catalyst

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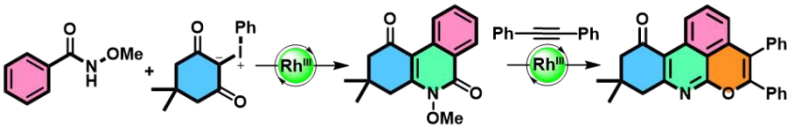

- ✓ Iodonium ylide as a carbene precursor
- ✓ Good functional group tolerance
- ✓ Broad substrate scope (33 examples)
- ✓ Scale up experiment
- ✓ Extended synthesis of pyranoisoquinolines
- ✓ Promising photoluminescence properties
- ✓ Deuterium labelling experiments
- ✓ DFT calculations including transition state

The first ever attempt of Hypervalent Iodonium ylides with readily available N-methoxybenzamides by using Rh(III)-catalyst has been well exploited