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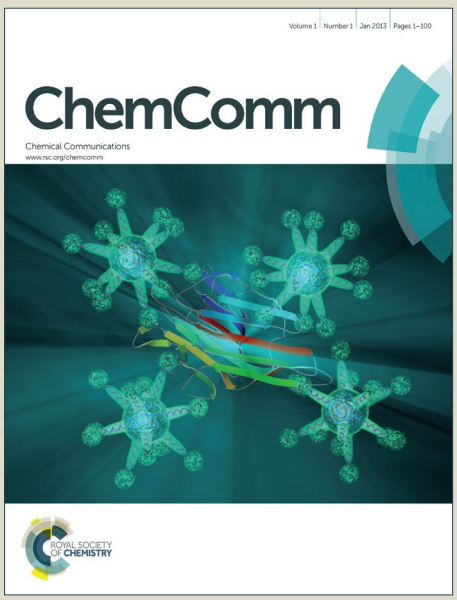

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Regioselective Synthesis of Multisubstituted Isoquinolones and Pyridones *via* Rh(III)-Catalyzed Annulation Reactions†

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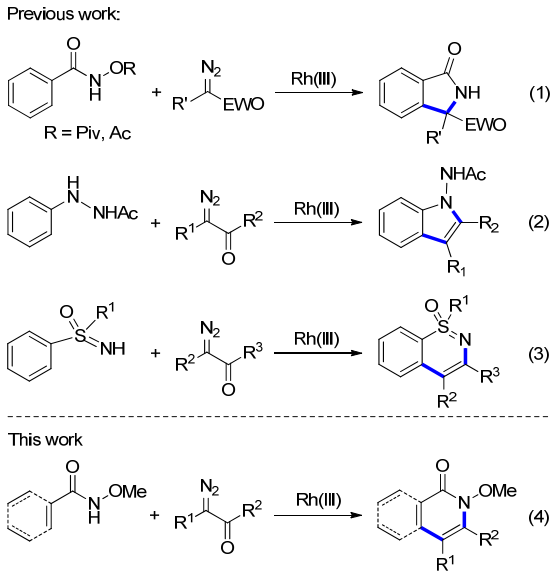
A mild and efficient Rh(III)-catalyzed regioselective synthesis of isoquinolones and pyridones has been developed. The protocol uses readily available *N*-methoxybenzamide or *N*-methoxymethacrylamide and diazo compounds as the starting materials. The process involving tandem C–H activation, cyclization, and condensation steps proceeds under mild conditions, and the corresponding isoquinolone and pyridone derivatives were obtained in good to excellent yields with excellent regioselectivities. The process provides a facile approach for the construction of isoquinolone and pyridone derivatives containing various functional groups.

Recently, great progress has been made in the Rh(III)-catalyzed C–H bond functionalization, which has become a useful tool for building various C–C, C–X bond, and afforded a streamlined and step-economical method for building desired valuable heterocycles without preactivtion of the coupling partner.[1] Over the past several years, Rh(III)-catalyzed C–H activation/annulation has focused on coupling amides, amines, oximes, and anilines with alkyne, alkene, and allene to obtain isoquinolones,[2] pyridones,[2d,3] isoquinolines,[4] pyridines,[4f,4p,5] indoles,[6] and pyrroles derivatives.[6d,7]

Rh-catalyzed C–H bond activation based on carbene migratory insertion has been developed as a fascinating strategy toward C–H functionalization.[8,9] In 2012, Yu and co-workers first reported Rh(III)-catalyzed carbene migratory insertion into arene C–H bonds with diazomalonates.[9a] Recently, Rovis, Yu, and Cramer groups developed the cyclization of benzamides and diazo compounds to access isoindolinones *via* Rh(III)-catalyzed C–C/C–N bond formation (Scheme 1, eq 1).[9b-d] Meanwhile, some interesting reactions of Rh(III)-catalyzed cyclization employ diazo compounds as coupling/cyclization partners have been reported by Cui, Glorius, Wan and Li, Wang, Xu and Yi, and other groups.[9] In 2014, our group reported Rh(III)-catalyzed cyclization of 2-acetyl-1-arylhydrazines with diazo compounds *via* tandem C-H activation, cyclization, and condension steps to synthesize 1-aminoindole derivatives (Scheme 1, eq 2).[9i] Very recently, Bolm's group described Rh(III)-catalyzed cyclization of S–aryl sulfoximines and diazo compounds to construct 1,2-benzothiazines through similar steps (Scheme 1, eq 3).[9t]

Isoquinolones and pyridinons are widely occurred in natural products and biologically active molecules. They are privileged scaffolds for the design and discovery of drugs and many of them exhibit potent biological activities.[10] Some approaches to isoquinolones and pyridinons have been developed,[2,3,11] however, these synthesis methods frequently require specific pre-activated C–X bond or restricted to regioselectivity.

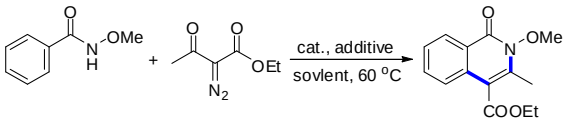


Scheme 1. Rh(III)-catalyzed C–H activation/annulations using diazo compounds as cyclization partners.

Continuing interest in heterocycle building,[9i,12] herein, we report an efficient Rh(III)-catalyzed approach to multisubstituted isoquinolones and pyridinons *via* cascade reactions of *N*-methoxybenzamides and *N*-methoxymethacrylamides with diazo compounds under mild conditions (Scheme 1, eq (4)).

As shown in Table 1, reaction of *N*-methoxybenzamide (**1a**) with ethyl diazoacetoacetate (**2a**) was used as the model to optimize reaction conditions including the solvents, additives, and catalysts system. The initial experiments were performed with *N*-methoxybenzamide (**1a**) (0.2 mmol) and ethyl diazoacetoacetate (**2a**) (0.24 mmol) in the presence of $[Cp^*RhCl_2]_2$ (5 mol%), and $AgSbF_6$ (20 mol%) as catalyst system at 60 °C under Ar atmosphere in MeCN (2 mL) for 12 h as given in Table 1. This condition indeed accessed desired target

Table 1 Rh(III)-catalyzed C–H activation/annulation of *N*-methoxybenzamide **1a** and ethyl diazoacetoacetate **2a**[a]



1a **2a** **3aa**

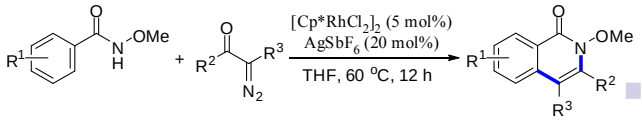
Entry	Catalyst System	Solvent	Additive	Yields [%][b]
1	$[Cp^*RhCl_2]_2/AgSbF_6$	MeCN		65
2	$[Cp^*RhCl_2]_2/AgSbF_6$	CH_2Cl_2		77
3	$[Cp^*RhCl_2]_2/AgSbF_6$	DCE		75
4	**$[Cp^*RhCl_2]_2/AgSbF_6$**	**THF**		**92**
5	$[Cp^*RhCl_2]_2/AgSbF_6$	dioxane		86
6	$[Cp^*RhCl_2]_2/AgSbF_6$	MeOH		79
7	$[Cp^*RhCl_2]_2/AgSbF_6$	H_2O		59
8	$AgSbF_6$	THF		0
9	$[Cp^*RhCl_2]_2$	THF		0
10	$[Cp^*RhCl_2]_2/AgSbF_6$	THF	AgOAc	92
11	$[Cp^*RhCl_2]_2/AgSbF_6$	THF	NaOAc	91
12	$[Cp^*RhCl_2]_2/AgSbF_6$	THF	CsOAc	90
13	$[Cp^*RhCl_2]_2/AgSbF_6$	THF	HOAc	89
14	$[Cp^*Rh(MeCN)_3][(SbF_6)_2]$	THF		87
15	$[(p\text{-cymene})RuCl_2]_2/AgSbF_6$	THF		Trace
16	$[Cp^*IrCl_2]_2/AgNTf_2$	THF		41

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), additive (0.06 mmol), solvent (2 mL), 60 °C, 12 h, under Ar atmosphere. [b]Isolated yield.

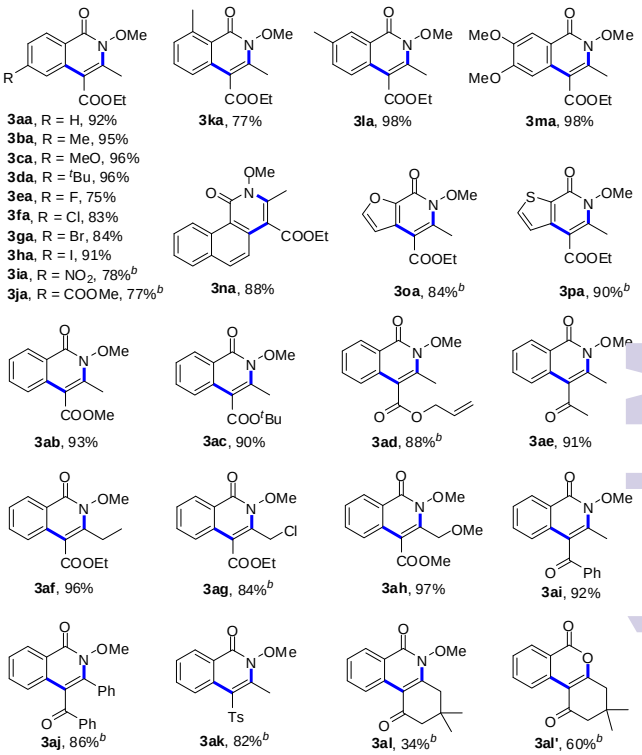
product **3aa** in 65% yield. The structure of **3aa** was confirmed by ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS). Encouraged by this result, first, effect of solvents was investigated (compare entries 1–7), and THF gave the best result, as the yield of **3aa** increased to 92% yield (Table 1, entry 4). Control experiment uncovered that no target product was accessed in the absence of $[Cp^*RhCl_2]_2$ or $AgSbF_6$ (entries 8–9). Several additives were screened (Table 1, entries 10–13), but the yields were slightly reduced than the yield in the absence of an additive (Table 1, entry 4). The use of $[Cp^*Rh(MeCN)_3][(SbF_6)_2]$ as the catalyst afforded a slightly lower yield to those obtained using the $[Cp^*RhCl_2]_2/AgSbF_6$ catalyst system (Table 1, compare entry 4, 14). The transformation did not occur by using $[(p\text{-cymene})RuCl_2]_2/AgSbF_6$ as a catalyst system (Table 1, entry 15). When $[Cp^*IrCl_2]_2/AgNTf_2$ were employed instead of $[Cp^*RhCl_2]_2/AgSbF_6$, the yield of **3aa** declined to 41% yield (Table 1, entry 16).

Under the obtained optimum reaction conditions above, we explored the applicability of a scope of diversely substituted *N*-methoxybenzamide. Ethyl diazoacetoacetate (**2a**) was kept as a representative reaction partner (Table 2). The tested isoquinolones provided good to excellent yields. Various *N*-methoxybenzamide having substituents at the *para*- position with electron-donating substituents (e.g. Me, OMe, and ^{t}Bu) reacted to access the desired products **3ba**–**da** in 95–96% yields. Probably because of the electrophilic C–H activation process,[12] substrates with strong electron-withdrawing groups (e.g. NO_2, and CO_2Me) at the same position inhibited the reaction, affording products **3ia** and **3ja** in slight lower respective yields of 78% and 77%. It is noteworthy that the halo-substituted (e.g. F, Cl, Br, and I)

Table 2 Rh(III)-catalyzed C–H activation/annulations of *N*-methoxybenzamides **1** and diazo compounds **2**[a]



1 **2** **3**

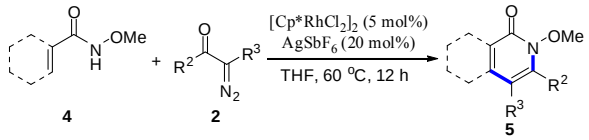


[a]Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), THF (2 mL), 60 °C, 12 h, under Ar atmosphere, isolated yields are shown. [b]Using AgOAc (0.06 mmol) as additive.

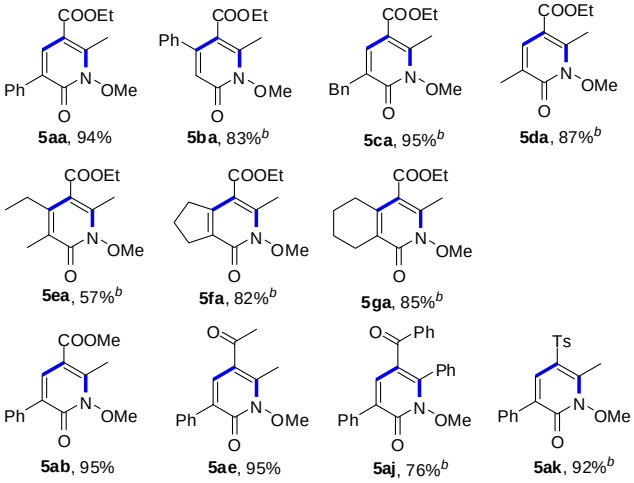
substrates performed well to afford the corresponding products in good yields. *Ortho*-methyl-substituted benzamide als participated in the reaction, providing the product **3ka** in 77% yield. Unexpected, the completely regioselective coupling occurred at the less hindered position for the *meta*-substituted substrate (**3la**). C–H cyclization referring to 3,4-dimethoxy-substituted benzamide reacted at the less hindered position, gave **3ma** as the single isomer in 98% yield. Naphthalene and heterocyclic derivatives were also tested in this annulation reations, and moderate to good yields of the corresponding products **3na**, **3oa**, and **3pa** were obtained.

Further, we investigated the scope of diazo compounds with *N*-methoxybenzamide (**1a**) as the reaction partner. Diazo substrates contain substituents such as alkyl, ether, ketone, phenyl chloromethyl, and phenylsulfone accessed the desired product **3ab**–**ak** in 82–97% yields, except the low yield of 34% for **3al**. Among them, unsymmetrical diketone (**2i**) reacted under the optimal conditions to give only one regioisomer of **3ai** in 92% yield. Similarly, 1-diazo-1-tosylpropan-2-one (**2k**) underwent the desired reaction to give product **3ak** in 82% yield. Interestingly, 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**2l**) reacted with **1a** to give the corresponding product **3al** in 34% yield. Unexpectedly,

Table 3 Rh(III)-catalyzed C–H activation/annulations of *N*-methoxymethacrylamides **4** and diazo compounds **2**[a]



4 2 5



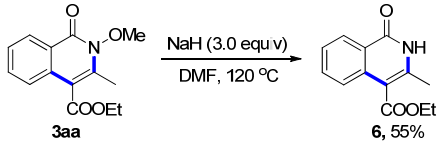
[a]Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), THF (2 mL), 60 °C, 12 h, under Ar atmosphere, isolated yields are shown. [b]Using AgOAc (0.06 mmol) as additive.

the reaction provided **3al'** as the major product under the standard conditions.

This cyclization was also extended to pyridones synthesis by using *N*-methoxymethacrylamide and diazo compounds as starting materials. We were delighted to find that reaction of *N*-methoxy-2-phenylacrylamide (**4a**) and ethyl diazoacetoacetate (**2a**) afforded the target product **5aa** in 94% yield under the standard conditions. Varieties of alkenyl amides **4b–g** also accessed corresponding products **5ba–ga** in 57–95%. Other diazo compounds such as methyl 2-diazo-3-oxobutanoate (**2b**), 3-diazopentane-2,4-dione (**2e**), 2-diazo-1,3-diphenylpropane-1,3-dione (**2j**), and 2-diazo-1-tosylbutane-1,3-dione (**2k**) reacted smoothly with the *N*-methoxy-2-phenylacrylamide to afford the corresponding cyclization products in 76–95% yields.

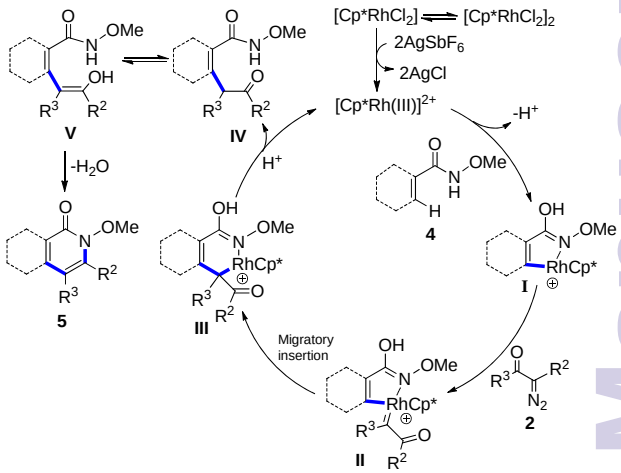
In order to further confirm the structure of the product **3aa**, the methoxy group of **3aa** was removed by treating with 3 equiv of sodium hydride in DMF at 120 °C for 2 h, and isoquinolin-1(2*H*)-one **6** was obtained in 55% yield (Scheme 2).[13] The ^1H and ^{13}C NMR spectra and HRMS of **6** were consistent with literature.[11]

On the basis of literature reports,[9f,i,u] a plausible mechanism was proposed (Scheme 3). First, *N*-methoxybenzamide or *N*-methoxymethacrylamide reacts with Cp*Rh(III) through directed C–H cleavage to form intermediate **I**, which is followed by generation of Rh(III)-carbene **II**. Subsequently, migratory insertion of the carbene into the Rh–C bond accesses rhodacycle intermediate **III**. Protonolysis of **III** leads to the intermediate **IV**, and releases the Rh(III) catalyst, which starts a new catalytic cycle. Then tautomerization of intermediate **IV** generates in situ enol intermediate **V**, which undergoes ring-closing elimination of water to give the final product.



3aa 6, 55%

Scheme 2. Deprotection of *N*-methoxyisoquinolinone **3aa**.



Scheme 3. Possible mechanism for Rh(III)-catalyzed C–H activation/annulations of *N*-methoxybenzamides or *N*-methoxymethacrylamides and diazo compounds.

In summary, we have developed a mild and efficient Rh(III)-catalyzed synthesis of multisubstituted isoquinolones and pyridones. The protocol uses readily available *N*-methoxybenzamide or *N*-methoxymethacrylamide and diazo compounds as the starting materials, $[Cp^*RhCl_2]_2/AgSbF_6$ as catalyst system, thus providing target products in high yields with excellent regioselectivities. This intermolecular annulation procedure undergoes domino C–H activation, cyclization, and condensation steps, releases H_2O and N_2 as byproducts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details, characterization and NMR spectra of the target products are provided. See DOI: 10.1039/b000000x/

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