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Rh(III)-Catalyzed Relay Double Carbenoid Insertion and Diannulation of Sulfoximine Benzamides with α-Diazo Carbonyl Compounds: Access to Furo[2,3-*c*]isochromenes

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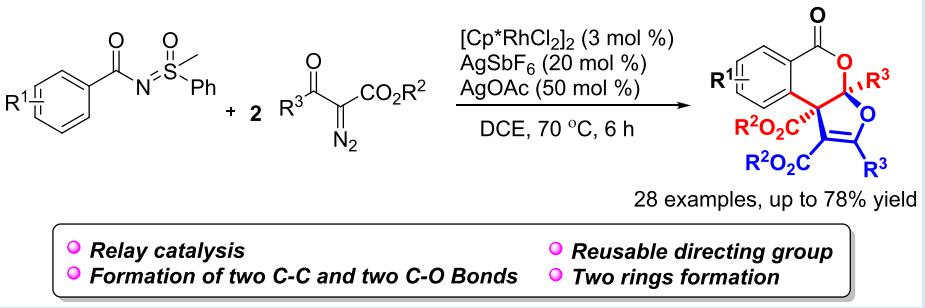

ABSTRACT: An efficient rhodium-catalyzed construction of furo[2,3-*c*]isochromene scaffolds through tandem double carbenoid insertion and diannulation of sulfoximine benzamides with α-diazo carbonyl compounds has been developed. Mechanistic studies revealed that the alkyl−rhodium intermediate generated by carbenoid insertion was directly trapped with another molecule of carbene species, followed by subsequent intramolecular cyclization reactions. Sulfoximine was released in situ, featuring a traceless directing fashion. The reactions proceeded smoothly under mild conditions with wide functional group tolerance.

Transition metal-catalyzed carbenoid insertion reactions have been extensively studied due to the unique and diverse reactivities of carbenes.[1] In particular, α-diazo carbonyl compounds were widely used as C2 building blocks in the construction of cyclic compounds based on its potency of coordinating to metal centers, migratory insertion, and subsequent condensation annulation of the carbonyl group with the directing groups (Scheme 1a).[2] A seminal work on the coupling of benzylmethylamines with diazomalonates was developed with isoquinolones being afforded efficiently by Yu and co-workers.[3] Later, continuous synthetic methods were reported under the catalysis of Rh,[4] Ir,[5] Ru,[6] Co,[7] etc.[8] For example, our group has developed efficient methods directed toward isocoumarins,[9] aminoisoquinolines,[10] and other N(O)-containing heterocycles[11] through Rh-catalyzed C−H bond activation and carbenoid insertion reactions. Very recently, an unexpected and interesting Rh-catalyzed cyclization of pyrazol-5-amine with 1,3-diketone-2-diazo compounds for the synthesis of pyrazolo[3,4-*b*]pyridines was disclosed using *N*,*N*-dimethylformamide as a carbon−hydrogen source.[12] However, compared with the transition metal-catalyzed monocyclization reactions mentioned above, relevant double carbenoid insertion and diannulations, which could facilitate the formation of complex fused heterocycles, have been studied far less. In 2016, Dong and co-workers developed an Ir-catalyzed synthesis of pentacyclic-fused carbazole derivatives via cascade cyclization of indoles with α-diazo carbonyl compounds (Scheme 1b).[13] In the same year, the Zeng group developed an elegant Rh-catalyzed relay cross-coupling/cyclization cascade between arylketoimines and diazoesters for the synthesis of π-conjugated 1-azaphenalenes via a double aryl C−H bond carbenoid functionalization process (Scheme 1c).[14] Later, the synthesis of naphthoquinolizinones through a Rh-catalyzed double C−H bond carbenoid insertion and annulation of 2-aryl-3-cyanopyridines with α-diazo carbonyl compounds was developed by Fan and co-workers (Scheme 1d).[15] Recently, the coupling of benzoylacetonitriles with α-diazo compounds through Rh-catalyzed double carbenoid insertion and diannulation to afford benzo[*de*]chromene derivatives was reported independently by Liu, Wang, and Fan (Scheme 1e).[16] To the best of our knowledge, Rh-catalyzed continuous double carbenoid insertion and tandem annulation for the synthesis of fused polyheterocyclic scaffolds have no precedent.

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Scheme 1. Catalytic C−H Bond Carbenoid Insertion and Annulation Reactions

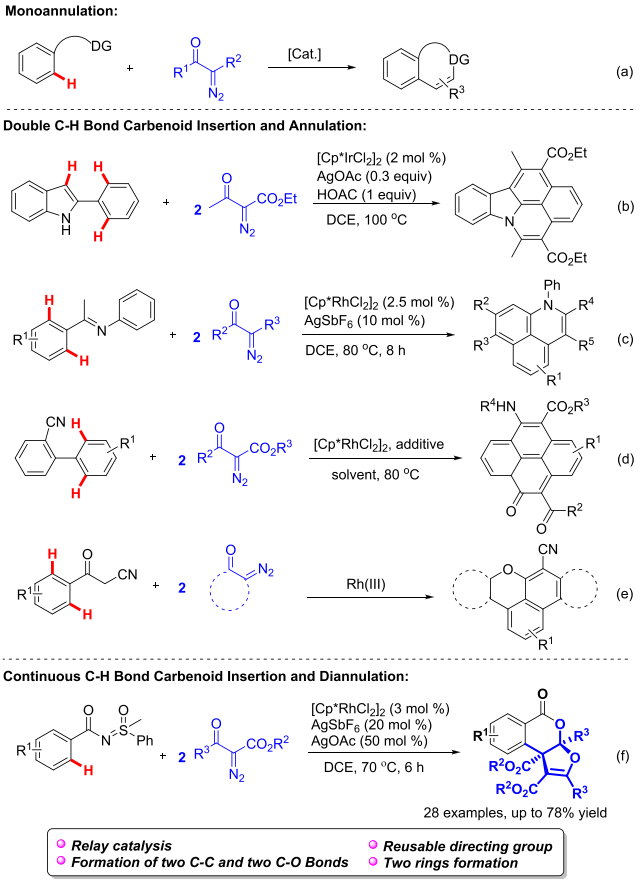
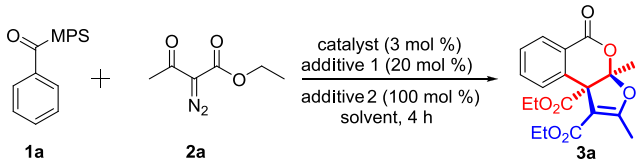


Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	additive 1	additive 2	solvent	yield[b] (%)
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	50
2	$[\{RuCl_2(p\text{-cymene})\}_2]$	$AgSbF_6$	AgOAc	DCE	42
3	$[Cp^*IrCl_2]_2$	$AgSbF_6$	AgOAc	DCE	0
4		$AgSbF_6$	AgOAc	DCE	0
5	$[Cp^*RhCl_2]_2$	$AgNTf_2$	AgOAc	DCE	37
6	$[Cp^*RhCl_2]_2$	$AgBF_4$	AgOAc	DCE	0
7	$[Cp^*RhCl_2]_2$		AgOAc	DCE	0
8	$[Cp^*RhCl_2]_2$	$AgSbF_6$	CsOAc	DCE	20
9	$[Cp^*RhCl_2]_2$	$AgSbF_6$	Ag_2CO_3	DCE	30
10	$[Cp^*RhCl_2]_2$	$AgSbF_6$	HOAc	DCE	0
11	$[Cp^*RhCl_2]_2$	$AgSbF_6$		DCE	0
12[c]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	45
13[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	54
14[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	MeOH	0
15[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	toluene	trace
16[d]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	acetone	26
17[d,e]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	68
18[d,f]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	46
19[d,e,g]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	75
20[d,e,h]	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	DCE	73

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (3 mol %), additive 1 (20 mol %), additive 2 (100 mol %), solvent (2.0 mL), 60 °C, 4 h. [b]Yield of isolated products. [c]With 25 mol % AgOAc. [d]With 50 mol % AgOAc. [e]At 70 °C. [f]At 80 °C. [g]For 6 h. [h]For 8 h.

Directing group-assisted catalytic C−H bond functionalization and annulation has attracted much attention due to the feasibility and step economy for access to diverse cyclic heteroarenes, which are ubiquitous in many pharmaceuticals, natural products, and functional materials.[17] Due to our long-standing research interest in the construction of privileged heterocycles,[18] we envisioned that the transformable methyl-phenyl sulfoximine (MPS)[19] could promote transition metal-catalyzed carbenoid insertion and annulation reactions and open a novel avenue to challenging heterocycles. We herein developed the first Rh-catalyzed continuous double carbenoid insertion and diannulation reaction (Scheme 1f). The MPS-DG played a vital role in catalytic access to furo[2,3-*c*]isochromene derivatives. Closure of two oxygen-containing rings was realized in one pot accompanied by the formation of four new bonds (two C−C bonds and two C−O bonds). Mechanistic studies revealed that the alkyl−rhodium intermediate generated by carbenoid insertion was directly trapped with another molecule of carbene species, followed by tandem intramolecular cyclization reactions.

The study was initiated with *N*-benzoyl methyl phenyl sulfoximine (**1a**) and ethyl 2-diazo-3-oxobutanoate (**2a**) as the substrates using $[Cp^*RhCl_2]_2$ as the catalyst and $AgSbF_6$ and AgOAc as the additives in DCE at 60 °C (entry 1, Table 1). Surprisingly, an unexpected polycyclic product diethyl-2,3a-dimethyl-5-oxo-5*H*-furo[2,3-*c*]isochromene-1,9b(3*aH*)-dicarboxylate (**3a**) was generated in 50% yield, the structure of which has been characterized by X-ray crystallography analysis. We then moved onto the optimization of the reaction conditions. The reaction was less efficient or even suppressed when using $[\{RuCl_2(p\text{-cymene})\}_2]$ and $[Cp^*IrCl_2]_2$ as the catalyst (entries 2−4). No better results were obtained when the additives were changed to other silver salts (entries 5−11). $AgSbF_6$ and AgOAc proved to be essential in this transformation (entries 7 and 11). The reaction yield increased to 54% after the optimization of the equivalents of AgOAc (entry 13). Solvents were then screened using methanol, toluene, and acetone, and it was found that none of them was superior to DCE (entries 14−16). The desired product was obtained in 75% yield at an elevated temperature of 70 °C for 6 h (entries 17−20).

With the optimized conditions in hand, we then turned our attention to the substrate scope of *N*-aroyl methyl phenyl sulfoximine derivatives (**1**) with ethyl diazoacetoacetate (**2a**) as the reaction partner. Both electron-donating and -withdrawing groups on the phenyl ring could tolerate the reaction conditions, and the corresponding products were generated in moderate to good yields (Scheme 2, **3a**−**3q**). The efficiency of substrates bearing electron-withdrawing groups was lower than that of electron-donating ones, with isocoumarin scaffolds derived from monocarbenoid insertion and annulation reaction being generated as the main byproducts. For example, nitro-substituted product **3l** was obtained in only 38% yield. In addition, easily transformable bromide could survive the reaction conditions and the corresponding products **3j**, **3o**, and **3q** were generated in moderate yields. Dimethyl-substituted products **3r**−**3t** were afforded in 65%, 73%, and

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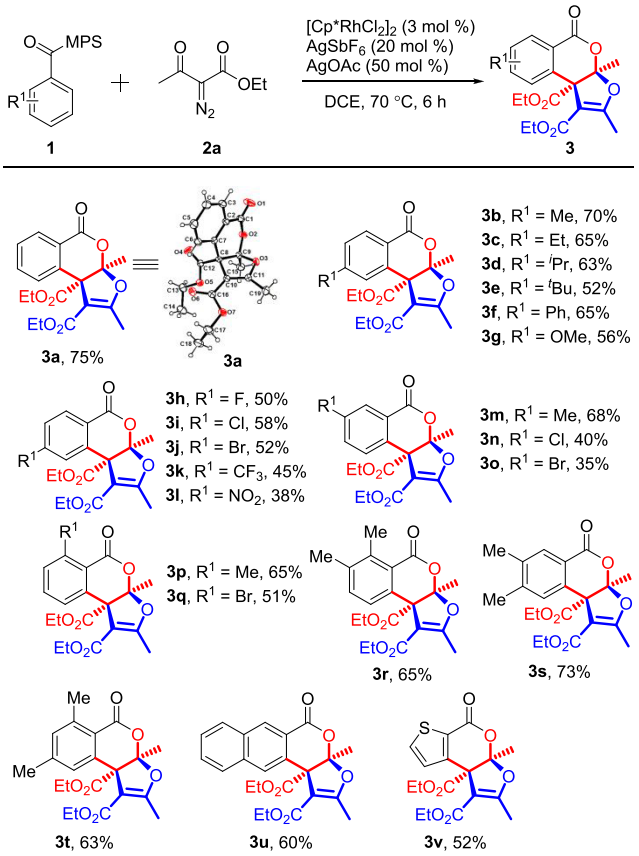
Scheme 2. Scope of *N*-Aroyl Methyl Phenyl Sulfoximine Derivatives[a]



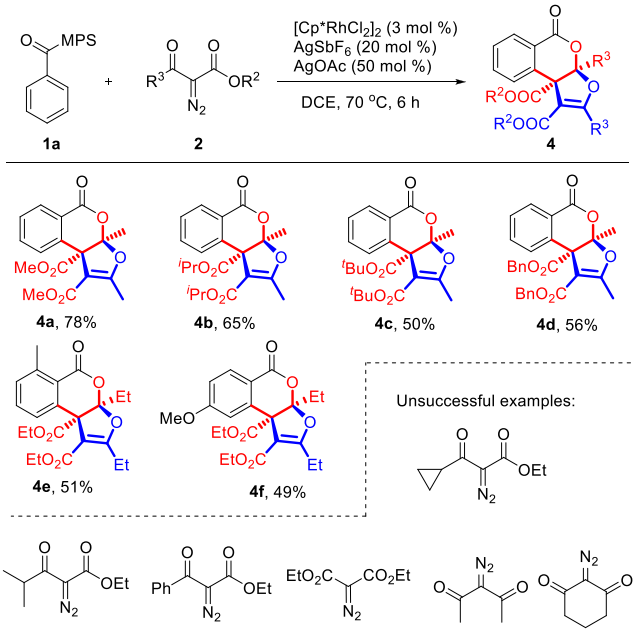
[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), $AgSbF_6$ (20 mol %), and AgOAc (50 mol %) in DCE (2.0 mL) at 70 °C for 6 h. Yield of isolated products.

63% yields, respectively. The 2-naphthoic acid-derived substrate underwent catalytic carbenoid insertion and annulation smoothly, delivering **3u** in 60% yield. Fortunately, thiophenyl C−H bond double carbenoid insertion was carried out smoothly to give **3v** in 52% yield.

Next, the scope of diazo compounds **2** was investigated with *N*-benzoyl methyl phenyl sulfoximine (**1a**) (Scheme 3). When R^2 was Me, ^{i}Pr, ^{t}Bu, and Bn, **4a**−**4d** were produced in moderate to good yields. Ethyl-substituted products **4e** and **4f** were obtained in 51% and 49% yields, respectively. However, large steric propyl- and cyclopropyl-substituted diazo compounds could not undergo the reaction to give the desired products. Efforts to broaden the utility of the reaction to other types of diazo compounds were not successful either.

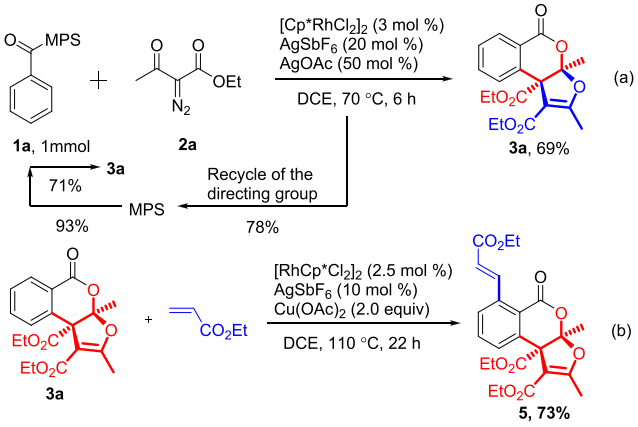
A 1 mmol scale preparation of **3a** was conducted, and the product was obtained in 69% yield with 78% of MPS being recovered, which could be used for the synthesis of starting material **1a** in 93% yield. The catalytic annulation could be repeated without a loss of efficiency using the recovered substrate (71% yield), thus demonstrating the reusability of the directing group (Scheme 4a). Further derivatization of product **3a** was carried out to demonstrate the potential synthetic applications of this reaction (Scheme 4b). The cyclic carbonyl group of **3a** could act as an effective directing group that assisted the oxidative C−H bond olefination under Rh catalysis, affording the corresponding product **5** in 73% yield.[20]

Scheme 3. Scope of Diazo Compounds[a]



[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), $AgSbF_6$ (20 mol %), and AgOAc (50 mol %) in DCE (2.0 mL) at 70 °C for 6 h. Yield of isolated products.

Scheme 4. Derivatization of Product 3a[a]



[a]Reaction conditions: (a) **1a** (1 mmol), **2a** (3 mmol), $[Cp^*RhCl_2]_2$ (3 mol %), $AgSbF_6$ (20 mol %), and AgOAc (50 mol %) in DCE (20 mL) at 70 °C for 6 h; (b) **3a** (0.2 mmol), ethyl acrylate (0.4 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and $Cu(OAc)_2$ (2.0 equiv) in DCE (2.0 mL) at 110 °C for 22 h.

To gain further insights into the mechanism of this novel transformation, a control experiment using benzoic acid in place of N-benzoylated sulfoximine was carried out first (Scheme 5, eq 1). No desired product was detected, revealing the essential role of the MPS-DG. The isocoumarin remained unreacted when it was subjected to the reaction with **2a**, indicating that the possibility of isocoumarin acting as an intermediate for the formation of **3a** could be ruled out (eq 2). The intermolecular competitive reactions between equimolar mixtures of **1a** and *para*-substituted N-benzoylated sulfoximines **1b** (*p*-Me), **1g** (*p*-OMe), **1i** (*p*-Cl), and **1l** (*p*-NO_2) under standard conditions were carried out in 10 min, to test the electronic preference of the reaction (eq 3). The ratios of

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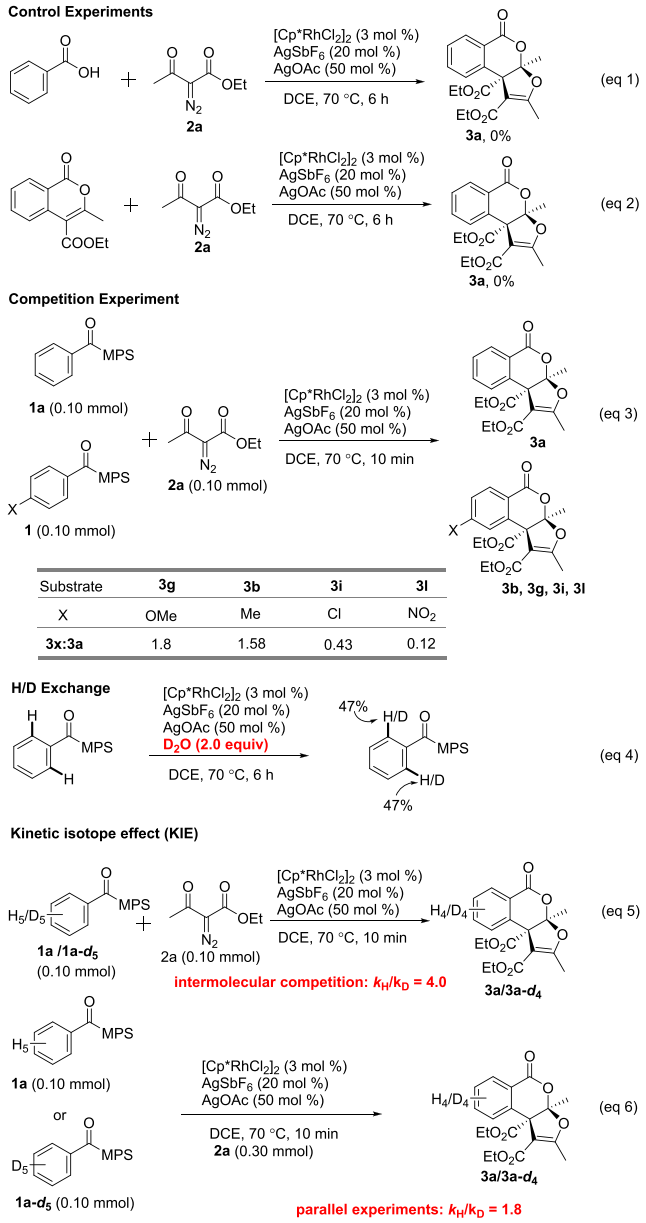
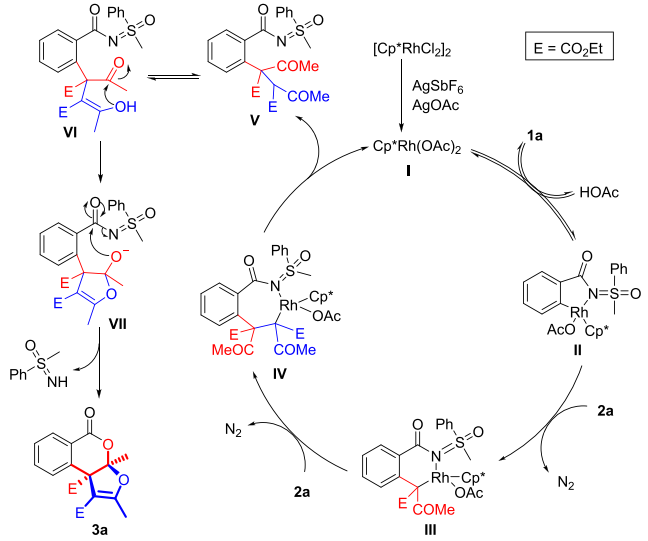
Scheme 5. Mechanistic Studies



substituted products to **3a** were 1.8, 1.58, 0.43, and 0.12 for OMe, Me, Cl, and NO_2, respectively, indicating that an electrophilic C−H bond activation was probably involved in the reaction mechanism.[21] Then the H/D exchange experiment with N-benzoylated sulfoximines **1a** with D_2O was carried out, and 47% of **1a** was deuterated, revealing a reversible C−H bond activation process (eq 4). Finally, a set of KIE experiments were performed to understand the rate-determining step of this annulation reaction. The intermolecular competition experiment between **1a** and **1a**-d_5 (1:1) with **2a** was carried out for 10 min and exhibited a k_H/k_D of 4.0 (eq 5). Parallel reactions of **2a** with **1a** and **1a**-d_5 were conducted under the standard conditions for 10 min. Products **3a** and **3a**-d_4 were generated with a ratio of 1.8:1 (eq 6). These results indicated that the electrophilic metalation rather than C−H bond activation was probably involved in the rate-limiting step.

On the basis of the experimental results and literature reports, a possible reaction mechanism is depicted in Scheme 6. After the in situ generation of active catalytic species **I**, MSP-

Scheme 6. Proposed Mechanism



DG coordinated to the metal center and assisted C−H bond cleavage for the formation of five-membered rhodium cyclic intermediate **II**. Carbene coordination and migratory insertion generated intermediate **III**, which was trapped by another molecule of a carbene species immediately. Intermediate **IV** was generated, followed by protonation to give **V**, with catalyst **I** being released to complete the catalytic cycle. Subsequent intramolecular tandem cyclization afforded the title product **3a**, and MPS-DG was released.

In conclusion, we have developed efficient access to furo[2,3-*c*]isochromenes through rhodium-catalyzed relay double carbenoid insertion and diannulation of sulfoximine benzamides with α-diazo carbonyl compounds. The reactions proceed smoothly under mild conditions with wide functional group tolerance. Mechanistic studies revealed that the alkyl−rhodium intermediate generated by carbenoid insertion was directly trapped with another molecule of a carbene species, followed by tandem intramolecular cyclization reactions. Sulfoximine was released in situ, featuring a traceless directing strategy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b04659.

General experimental procedure and characterization data of the compounds (PDF)

Accession Codes

CCDC 1970166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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