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Diversity-Oriented Synthesis through Rh-Catalyzed Selective Transformations of a Novel Multirole Directing Group

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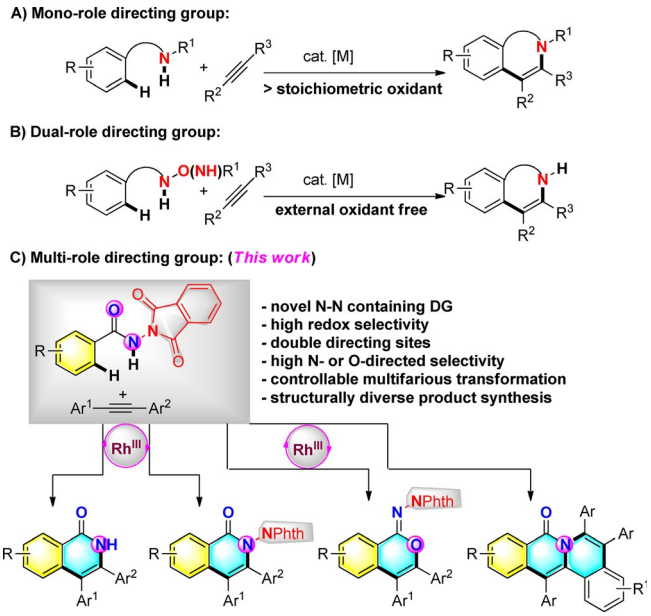
In the context of transition-metal-catalyzed C–H functionalization, directing-group strategy was developed for the improvement of chemical reactivity and selectivity. Recently, to avoid the inherent limitations of traditional mono-role directing groups, a dual-role oxidizing-directing-group strategy was developed, in which the directing group acts both as directing group and oxidant. Herein, we report a multirole directing group, which possesses multiple reactive sites, exhibits unique reactivity and selectivity, and leads to four different types of products from a single starting material through rhodium-catalyzed C–H activation/alkyne annulation reactions. The excellent product diversity and regio- and redox selectivity were well controlled by the tuning of solvents and oxidants.

Introduction

Diversity-oriented synthesis is an important access to the rapid build-up of molecular complexity and diverse synthesis, which, in turn, offers great opportunities for the discovery of new drugs and exploration of complex biological processes. General requirements for diversity-oriented synthesis include high functional-group tolerance, multiple reactive sites, and/or good controllability and selectivity. In the context of transition-metal-catalyzed C–H activation chemistry,[1] one important strategy to increase the selectivity and controllability is the introduction of a directing group (DG), which can direct the metal catalyst to one specific reactive site among many others and thus largely increase the selectivity.[2] However, the utilization of DGs also has some disadvantages,[3] including 1) the DG only plays a directing role at the C–H activation stage and always leaves a chemical trace in the product, 2) the introduction and removal of the DG increases the number of synthetic steps, and 3) further manipulation of the DG is always difficult and impractical, which largely limits the structure diversity of the product. To address these limitations, the development of multirole DGs has been paid more attention in the last several years. For example, although traditional oxidative cross-coupling/cyclization reactions have been widely applied in the construction of various heterocycles, such as indoles,[4] pyrroles,[4b,d,5] pyridones,[6] isoquinolines,[7] and isoquinolones,[6a,8] the DG plays solely a directing role, and a stoichiometric amount of external oxidants are indispensable for the regeneration of the catalysts (Scheme 1 A). To address these drawbacks, Fagnou and co-workers,[9] Tan and Hartwig,[10] Glorious and co-workers,[11] and other groups developed the dual-role oxidizing-directing-group (DG^{ox}) strategy (Scheme 1 B),[12] in which DG^{ox} acts both as directing group and oxidant. Among the pre-



Scheme 1. Evolution of the C–H activation strategy. Phth = phthaloyl.

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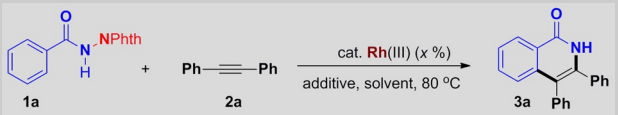
viously reported DG^{ox} variants, N–O bond containing functional groups have been well investigated because of their ready cleavability.[9–,12c–e,g–o,13] Relative to the N–O bond, the N–N counterpart was considered to be more difficult to cleave as a result of the elevated bond strength.[9b] However, some unique features make the N–N bond containing DG much more appealing as an alternative DG^{ox}: 1) The trivalent nitrogen atom can provide more chances to tune the properties (for example, reactivity, redox controllability of the DG^{ox}, regio- and chemoselectivity) by adjusting the substituents on it; 2) with well-controlled cleavage of the N–N bond, such a group may play multiple roles as a directing group, internal oxidant, and base; and, last but not least, 3) the intact N–N bond offers another access to diversify the reaction pathway to construct different scaffolds from the same starting materials. Although some attention has been paid to the development of novel N–N containing DG^{ox} compounds,[14] to the best of our knowledge, there is no such case in which the N–N bond containing DG^{ox} exhibited advantages over the previous N–O bond containing DG^{ox} counterparts. Herein, we first report a novel N–N bond containing DG^{ox} derived from benzohydrazine derivatives, which reacts with internal alkynes under Rh catalysis and results in some novel unparallel reactivities and unique site selectivity (Scheme 1 C).

Table 1. Optimization of the Rh^{III}-catalyzed redox-neutral C–H activation/annulation isoquinolinone synthesis.[a]



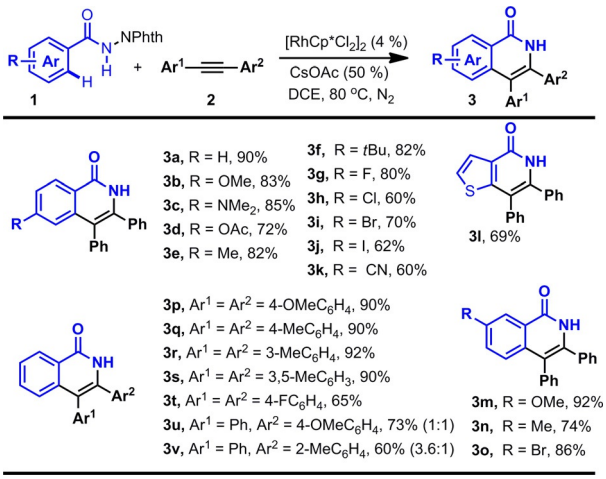
Entry	Catalyst ([mol%])	Additive ([mol%])	Solvent	Yield[b] [%]
1	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (25)	DCE	60
2	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	DCE	76
3	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (75)	DCE	75
4	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (100)	DCE	79
5	$[RhCp^*Cl_2]_2$ (3.0)	CsOAc (50)	DCE	88
6	$[RhCp^*Cl_2]_2$ (4.0)	CsOAc (50)	DCE	90
7	$[RhCp^*Cl_2]_2$ (5.0)	CsOAc (50)	DCE	90
8	$[RhCp^*(MeCN)_3](SbF_6)_2$ (5.0)	CsOAc (50)	DCE	61
9	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	DCE	0
10	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	DMF	trace
11	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	MeOH	0
12	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	*t*AmylOH	0
13[c]	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (50)	DCE	72
14[d]	$[RhCp^*Cl_2]_2$ (2.5)	–	DCE	76

[a] Reactions were carried out by using Rh^{III} catalyst, additive, **1a** (0.1 mmol), and **2a** (0.15 mmol) in solvent (1 mL) for 24 h at T = 80 °C under N_2. [b] Yield of isolated product. [c] **2a** (0.12 mmol) was used. [d] **2a** (0.20 mmol) was used.

Results and Discussion

We introduced a highly electron-withdrawing phthaloyl group at the distal nitrogen atom of benzohydrazine. In our design, the phthaloyl group not only increases the acidity of the proximal N–H group but also weakens the N–N bond. We initially investigated the reactivity of **1a** under external-oxidant-free conditions. Preliminary experimental results showed that compound **1a** and diphenylacetylene (**2a**) could be transformed into the desired C–H activation/annulation product **3a** in 60% yield if $[Cp^*RhCl_2]_2$ (2.5 mol%; Cp* = 1,2,3,4,5-cyclopentadienyl) and CsOAc (25 mol%) were employed in 1,2-dichloroethane (DCE) at T = 80 °C under N_2 (Table 1, entry 1). After extensive screening, the optimal reaction conditions were found to be $[Cp^*RhCl_2]_2$ (4.0 mol%) and CsOAc (50 mol%) in DCE at T = 80 °C under N_2 (Table 1, entry 6), which afforded **3a** in 90% yield.

The substrate scope was then surveyed (Scheme 2). Various substituted benzohydrazines **1** reacted smoothly with diphenylacetylene (**2a**), and those bearing electron-donating groups gave relatively higher yields. Notably, different substituents (for example, free amine in **3c**, acetyl in **3d**, various halogens (including iodine) in **3g**–**3j**, and cyan in **3k**) and a thiophene (in **3l**) were well tolerated. As a result of the bulkiness of the directing group, the reaction was sensitive to steric effects. If *meta*-substituted (**3m**–**3o**) benzoyl hydrazines were employed, single regioisomers were isolated. Unfortunately, *ortho*-substituted (Me and MeO) substrates did not react. The scope of the accepted diarylacetylenes was also examined. Both electron-rich and electron-poor aryl-substituted alkynes gave good yields, and electron-rich substrates showed higher reactivities. Unsymmetrical alkynes gave a mixture of regioisomers (**3u**). If

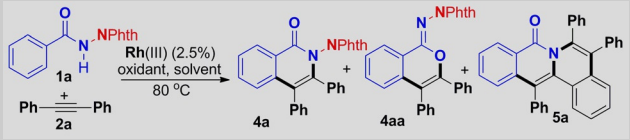


Scheme 2. Reaction scope for the formation of N–N cleaved product **3**. Reactions were carried out by using **1** (0.1 mmol), **2** (0.15 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), and CsOAc (50 mol%) in DCE (1 mL) for 24 h at T = 80 °C under N_2. Yields refer to isolated products.

a methyl group was introduced at the 2-position of the aryl group, the regioselectivity increased (**3v**).

To test the redox versatility of the newly developed oxidizing directing group and with the aim of keeping the valuable N–N bond intact, we next introduced an external oxidant to the reaction system. It was found that, if $Cu(OAc)_2$ (2.0 equiv.) was employed in DCE, the desired product **4a** was obtained in 69% yield (Table 2, entry 5). Interestingly, besides compound **4a**, the oxygen-directed product **4aa** and cascade cyclization product **5a** were also detected. To our satisfaction, these trans-

Table 2. Optimization of the oxidizing controllable directing group directedRh^{III}-catalyzed diversified products syntheses.[a]

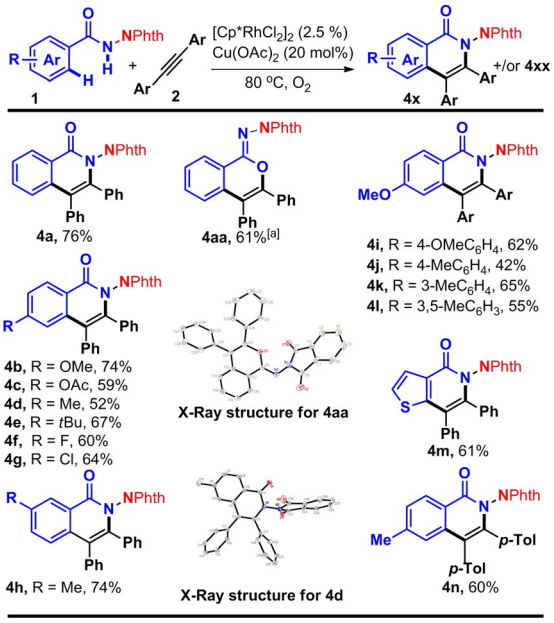


Entry	Oxidant ([equiv.])	Solvent	Yield of **4a**+**4aa**[b] [%]	Yield of **5a**[b] [%]
1	$Cu(OAc)_2$ (2.0)	THF	trace	trace
2	$Cu(OAc)_2$ (2.0)	MeOH	trace	trace
3	$Cu(OAc)_2$ (2.0)	MeCN	9+28	32
4	$Cu(OAc)_2$ (2.0)	DMF	18+35	25
5	$Cu(OAc)_2$ (2.0)	DCE	69+14	12
6	$Cu(OAc)_2$ (2.0)	toluene	66+18	10
7[c]	$Cu(OAc)_2$ (2.0)	toluene	78+8	trace
8[c]	$Cu(OAc)_2$ (0.2)	toluene	(76+7)[d]	–
9	AgOAc (2.2)	MeCN	(7+61)[d]	29
10	AgOAc (2.2)	PhCN	6+58	41
11[e]	AgOAc (2.2)	MeCN	–	63[d]
12[e]	AgOAc (4.4)	MeCN	–	58[d]
13[e]	AgOTs (2.2)	MeCN	trace	trace
14[e]	AgF (2.2)	MeCN	trace	trace
15[e]	$AgNO_3$ (2.2)	MeCN	trace	trace
16[e]	AgOTFA (2.2)	MeCN	trace	trace
17[e]	AgOTf (2.2)	MeCN	trace	trace

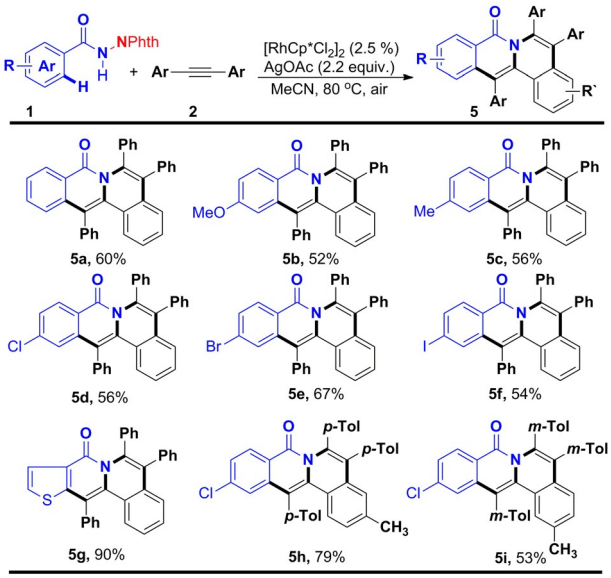
[a] Reactions were carried out by using Rh^{III} catalyst (2.5%), oxidant, **1a** (0.1 mmol), and **2a** (0.15 mmol) in solvent (1 mL) for 12 h at T=80 °C under air. [b] NMR spectroscopy yield with 1,3,5-trimethoxybenzene as an internal standard. [c] The reaction was conducted under O_2. [d] Yield of isolated product. [e] **2a** (0.30 mmol) was used. OTs=toluene-4-sulfonate; TFA=trifluoroacetic acid; OTf=trifluoromethanesulfonate.

formations can be well controlled by slightly changing the reaction conditions. The formation of nitrogen-directed product **4a** was favored in nonpolar solvents (Table 2, entries 5 and 6), whereas compounds **4aa** and **5a** were preferentially formed in polar solvents (Table 2, entries 3 and 4). If the reaction was carried out in toluene under O_2, both the oxygen-directed product **4aa** and the cascade cyclization product **5a** were largely suppressed (Table 2, entry 7). Importantly, if the loading of $Cu(OAc)_2$ was reduced to catalytic amounts (Table 2, entry 8), comparable results were achieved. Interestingly, if $Cu(OAc)_2$ was replaced with AgOAc (Table 2, entry 9), compound **4aa** became the major product. With an increase in the amount of **2a** to 3.0 equivalents, cascade cyclization product **5a** was obtained as the major product in synthetically useful yields (Table 2, entry 11), and it could be easily separated from compounds **4a** and **4aa**. Other silver salts gave inferior results (Table 2, entries 13–17).

Various benzoylhydrazines **1** and diarylacetylenes **2** were tested for the synthesis of **4** (Scheme 3). Similar reactivity was observed to that in previous studies. Differently substituted benzoylhydrazine derivatives **1** reacted with various alkynes **2** smoothly, to give the N-directed products **4** with an intact N–N bond in moderate to good yields. The structures of compounds **4aa** and **4d** were unambiguously confirmed by X-ray analysis.[15] Through treatment with hydrazine hydrate in ethanol, the phthaloyl group in **4a** could be easily be removed in



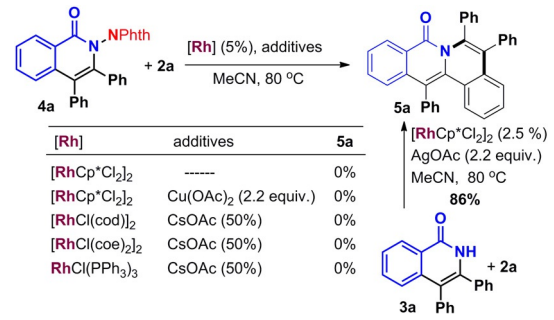
Scheme 3. Reaction scope for the formation of N–N intact product **4**. Reactions were carried out by using **1** (0.1 mmol), **2** (0.15 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol%), and $Cu(OAc)_2$ (20 mol%) in toluene (1 mL) for 12 h at T=80 °C under O_2. Yields refer to isolated products. [a] AgOAc (2.0 equiv) was used in MeCN (1 mL) for 12 h at T=80 °C under air.



Scheme 4. Reaction scope for the formation of cascade cyclization product **5**. Reactions were carried out by using **1** (0.1 mmol), **2** (0.30 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol%), and AgOAc (2.2 equiv) in MeCN (1 mL) for 12 h at T=80 °C under air. Yields refer to isolated products. *p*-Tol=*p*-tolyl; *m*-Tol=*m*-tolyl.

good yield (for a detailed procedure, see the Supporting Information).

Several different compounds **1** and **2** were also examined for the corresponding cascade cyclization to produce **5**. Most of them worked well to produce **5** in moderate to good yields (Scheme 4). Notably, if the thiophene-2-carbohydrazide deriva-



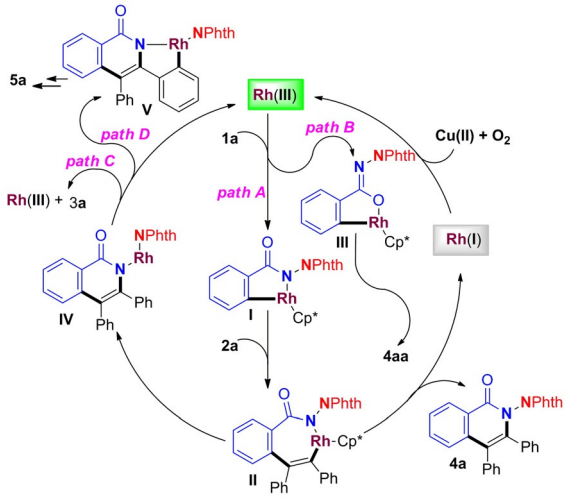
[Rh]	additives	5a
$[RhCp^*Cl_2]_2$	------	0%
$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$ (2.2 equiv.)	0%
$[RhCl(cod)]_2$	CsOAc (50%)	0%
$[RhCl(coe)_2]_2$	CsOAc (50%)	0%
$RhCl(PPh_3)_3$	CsOAc (50%)	0%

Scheme 5. Control experiments. cod = cycloocta-1,5-diene; coe = cyclooctene.

tive was used, compound **5g** was isolated in 90% yield, with only a trace amount of other byproducts.

To probe the process of the formation of **5a**, some control experiments were done (Scheme 5). If **4a** was subjected to the standard reaction conditions to form **5a** in the presence of either Rh^{III} or Rh^{I} catalysts, no **5a** was detected. If **3a** was treated with the Rh^{III} catalyst in the presence of **2a**, **5a** was obtained in 86% yield. These results implied that **3** might be a specific intermediate for the formation of **5**.

Based on the observations and previous studies, an illustrative mechanism was proposed to explain the product diversity (Scheme 6). All product formation was initiated by the directed



Scheme 6. Proposed mechanism for the formation of diversified products.

C–H activation of substrate **1**. In the nonpolar solvent, N-directed aza-cyclorhodium species **I** was formed preferentially (path A) and then coordinated with alkyne **2a**; this was followed by migratory insertion to afford the seven-membered rhodium intermediate **II**. After reductive elimination, product **4a** with the N–N bond intact was formed, and the resulting Rh^{I} species was reoxidized to the Rh^{III} catalytic species by copper(II) under O_2. In polar solvents, O-directed C–H activation was favored to give intermediate **III** (path B), and the isomer **4aa** was produced through a similar process to that for **4a**. Under external-oxidant-free conditions, intermediate **II** might have undergone migratory insertion to give intermediate **IV**,[9,12a,14a] which then afforded product **3a** after protonation in the nonpolar solvent (path C). However, in the presence of an Ag^{I} species, sequential C–H activation occurred (path D) to furnish intermediate **V**, which gave product **5a** after the second alkyne insertion and protonation processes.

Conclusions

We have developed a novel N–N bond containing oxidizing directing group. To the best of our knowledge, this is a unique directing group, which displays a range of advantages, including readily availability, multiple reactive sites, high redox selectivity and controllability, and multifarious transformations toward important scaffolds and structural diversification. This directing group enables N–N bond cleavage, N–N intact N-directed and O-directed annulations, and cascade cyclizations highly selectively from the same single starting material through Rh^{III} catalysis. The features of redox controllability of the directing group and great product diversity were accessed by tuning of the oxidants and solvents. We hope that this chemistry can inspire more structure-diversity-oriented synthesis with new developments of directing groups in the field of C–H activation.

Experimental Section

Compounds **1** (0.1 mmol), **2** (0.15 mmol), $[RhCp^*Cl_2]_2$ (4.0%, 2.5 mg), and CsOAc (50%, 9.6 mg) were added to a 50 mL dry schlenk tube with a stirring bar under N_2. The tube was degassed and refilled with N_2. DCE (1.0 mL) was injected and the mixture was stirred at $T = 80\,^{\circ}C$ for 24 h. After the reaction mixture had cooled to room temperature, the solvent was removed and compound **3** was obtained by column chromatography purification (silica gel, CH_2Cl_2/EtOAc).

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Keywords: alkynes · C–H activation · directing groups · redox chemistry · rhodium

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[15] CCDC 1031437 (**4aa**) and 1031438 (**4d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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