Synthetic Methods

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Rhodium(III)-Catalyzed Redox-Neutral Coupling of *N*-Phenoxyacetamides and Alkynes with Tunable Selectivity**

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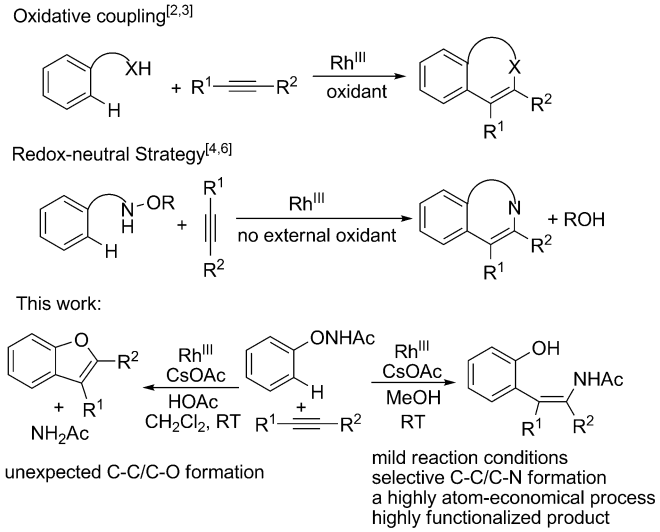
Transition-metal-catalyzed functionalization of arene C–H bonds has been developed as a powerful and straightforward synthetic approach for complex molecules from less-functionalized substrates.[1] Directing groups and stoichiometric amounst of oxidants are often required to achieve chemoselectivity and catalytic turnover. To meet the demand of green chemistry, a C–H functionalization should: 1) minimize the cost and waste associated with stoichiometric additives, and 2) avoid harsh reaction conditions which may be incompatible with sensitive functionalities. The development of innovative directing groups, which enable novel transformations to deliver valuable structures under mild and simple reaction conditions, are highly desirable.

Recently, rhodium(III) was used as an efficient catalyst for direct arene C–H functionalization under mild reaction conditions.[1c,d,i,2] In particular, rhodium(III)-catalyzed oxidative couplings of various aromatic substrates with alkynes by C–H and X–H (X = N or O) double activation has been widely investigated (Scheme 1).[2,3] This kind of reaction typically uses heteroatoms to direct cyclometalation at the *ortho* C–H bond. After alkyne insertion and subsequent C–X bond reductive elimination, the desired heterocycles are produced along with a rhodium(I) species. Thus stoichiometric amounts of external oxidants are necessary to regenerate the catalyst. To address this drawback, an attractive redox-neutral strategy employing an oxidizing directing group,[4–8] which acts as a directing group and internal oxidant, has been used in the elegant works from many groups.[6]

Oxidizing directing groups reported in the transition-metal-catalyzed C–H functionalization typically contain an N–O bond, such as an *N*-oxide, *N*-acyloxy, and *N*-methoxy group.[4–8] Normally, the oxidation of a low-valent metal by these internal oxidants will result in cleavage of an N–O bond accompanied by the departure of the oxygen-atom-containing unit. We envisioned that the rational design of an oxidizing directing group may enable all atoms in the starting material to be transformed into the product, and thus realize a highly atom-economical process. Herein, we disclose the development of a mild rhodium(III)-catalyzed redox-neutral C–H functionalization of *N*-phenoxyacetamides with alkynes for the synthesis of *ortho*-hydroxyphenyl-substituted enamides,[9] a highly atom-economical process (Scheme 1). Furthermore, an unexpected synthesis of valuable benzofuran derivatives through C-C/C–O bond formation was accomplished by simply switching the reaction conditions.



Scheme 1. The formation of C-C/C-X (X = N or O) bonds through rhodium(III)-catalyzed direct coupling of aromatic substrates with alkynes.

In preliminary experiments, *N*-phenoxyacetamide (**1a**)[10] was treated with [{Cp*RhCl$_2$}$_2$] (2.5 mol%), CsOAc (25 mol%), and diphenylacetylene (**2a**, 1.2 equiv) in MeOH (0.4 M) at room temperature for 16 hours, and the desired product **3a** was obtained in 82% yield (Table 1, entry 1). The structure of **3a** was confirmed by NMR spectroscopy, as well as IR, HRMS, and X-ray crystallography.[11] The reaction was not sensitive to air or moisture and the addition of water did not affect the yield (Table 1, entry 2). No product formation was observed in the absence of the rhodium catalyst or CsOAc additive (Table 1, entries 3 and 4). Some other acetate additives[1g] were tested. Slightly lower yields were obtained with AgOAc and NaOAc (Table 1, entries 5 and 6). Other alcoholic solvents such as EtOH were not as good as MeOH (Table 1, entry 7). Employing [Cp*Rh(OAc)$_2$] as the catalyst gave a result similar to that obtained with the [{Cp*RhCl$_2$}$_2$]/CsOAc system (Table 1, entry 8).

With the optimized reaction conditions in hand, we first explored the reaction scope for the synthesis of *ortho*-hydroxyphenyl-substituted enamides (**3**; Scheme 2). Several functional groups, such as hydroxy (**3f**), ester (**3g, 3h, 3i**), and

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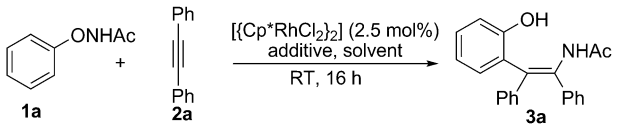
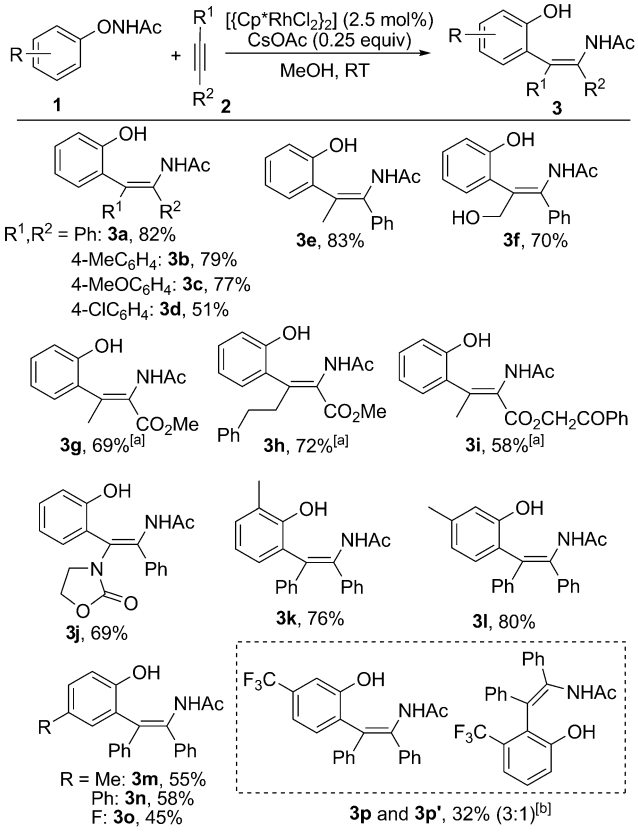
Table 1: Reaction optimizations for the synthesis of **3a**.[a]



1a 2a 3a

Entry	Additive (equiv)	Solvent	Yield [%][b]
1[c]	CsOAc (0.25)	MeOH	83
2	CsOAc (0.25), H_2O (10)	MeOH	82
3[d]	CsOAc (0.25)	MeOH	n.r.
4	none	MeOH	n.r.
5	AgOAc(0.25)	MeOH	80
6	NaOAc(0.25)	MeOH	75
7	CsOAc (0.25)	EtOH	53
8[e]	none	MeOH	82

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mol%), and additives in solvent (0.5 mL) at room temperature for 16 h under air. [b] Yields of isolated products. [c] Reaction was run under N_2. [d] Reaction was conducted in the absence of [{Cp*$RhCl_2$}$_2$]. [e] [Cp*$Rh(OAc)_2$] (2.5 mol%) was used as the catalyst. Cp* = C_5Me_5, n.r. = no reaction.

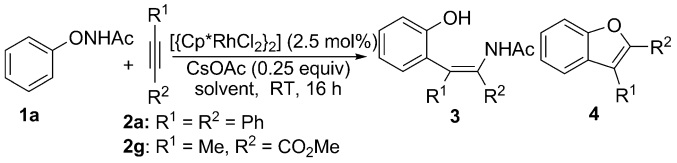


Scheme 2. Reaction scope for the synthesis of the *ortho*-hydroxyphenyl-substituted enamides **3** under reaction conditions A: **1** (0.2 mmol), **2** (0.24 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mol%), and CsOAc (0.25 equiv) in MeOH (0.5 mL) at room temperature for 16 h under air. Yields for isolated products are given. [a] Amberlite IRA-400 (OH) (40 mg) was added. [b] Contained an inseparable mixture of isomers; the ratio was determined by ^{1}H NMR spectroscopy.

ketone (**3i**) groups, were well tolerated in this reaction. As shown in Scheme 2, a range of internal alkynes are viable in this reaction. Symmetrical diaryl acetylenes bearing various substituents reacted smoothly, thus affording the corresponding product **3** in moderate to good yields (**3a**–**3d**). Insertion of aryl-alkyl disubstituted alkynes resulted in high regioselectivity with the aryl-substituted carbon center being installed on the acetamido group (**3e**, **3f**). It is worth mentioning that both electron-deficient alkynes and ynamides participated well in this reaction yielding single regioisomers (**3g**–**3j**). When electron-deficient alkynes were employed, an anion-exchange resin (Amberlite IRA-400) was added to obtain a decent yield of the enamides (**3g**–**3i**). Of note, dialkyl alkynes provided low yields of the desired product and no reaction occurred using terminal alkynes. Different substituted *N*-phenoxyacetamides were also tested and the reaction provided the desired product regardless of the electronic properties of the substituents (**3k**–**3o**). When *N*-(*m*-tolyloxy)acetamide was used, the arene rhodation occurred at the less-hindered site (**3l**). In contrast, 3-trifluoromethyl-substituted *N*-phenoxyacetamide gave a mixture of two regioisomers.

During the scope studies for the synthesis of *ortho*-hydroxyphenyl-substituted enamides, we found that additives were vital to the reaction outcome when using the ester-substituted alkynes **2g**–**2i** as substrates. For example, when **2g** was subjected to reaction conditions A, only a low yield of **3g** was detected and the predominant product was the benzofuran **4g** (Table 2, entry 1). While addition of base such as

Table 2: Reaction optimization for benzofuran synthesis.[a]



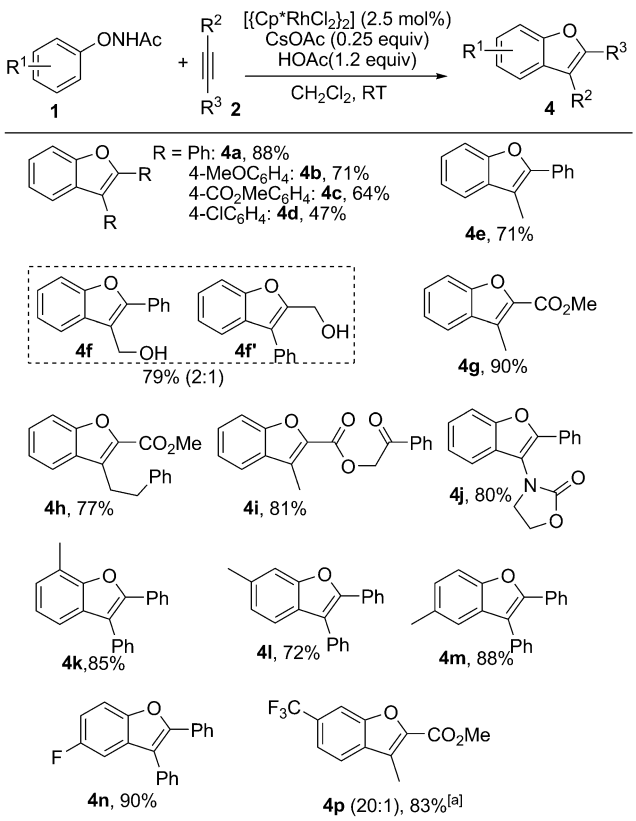
Entry	2	Solvent	Additives (equiv)[b]	Yield [%][c]	
				3	4
1	**2g**	MeOH	–	6	84
2	**2g**	MeOH	Amberlite IRA-400 (OH)[d]	69	11
3	**2g**	CH_2Cl_2	–	trace	94
4	**2a**	CH_2Cl_2	–	trace	79
5[e]	**2a**	CH_2Cl_2	HOAc (1.2)	trace	88
6[e]	**2g**	CH_2Cl_2	HOAc (1.2)	trace	90

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mol%), CsOAc (0.25 equiv), and other additives in solvent (0.5 mL) at room temperature for 16 h under air. [b] Additives besides CsOAc. [c] Yields of isolated products. [d] Amberlite IRA-400 (OH) (40 mg) were added. [e] **1a**/**2** = 1.2:1.

NaOH, Cs_2CO_3, pyridine, or DMAP suppressed the reaction, anion-exchange resin (Amberlite IRA-400) was effective for improving the yield of **3g** (Table 1, entry 2). To our delight, simply changing the solvent from methanol to CH_2Cl_2 significantly increased the yield of **4g** (Table 1, entry 3). Since the benzofuran moiety is abundant in biologically active molecules, these results prompted us to reinvestigate the reaction conditions for other internal alkynes to produce the benzofuran selectively. Finally, reaction conditions B,

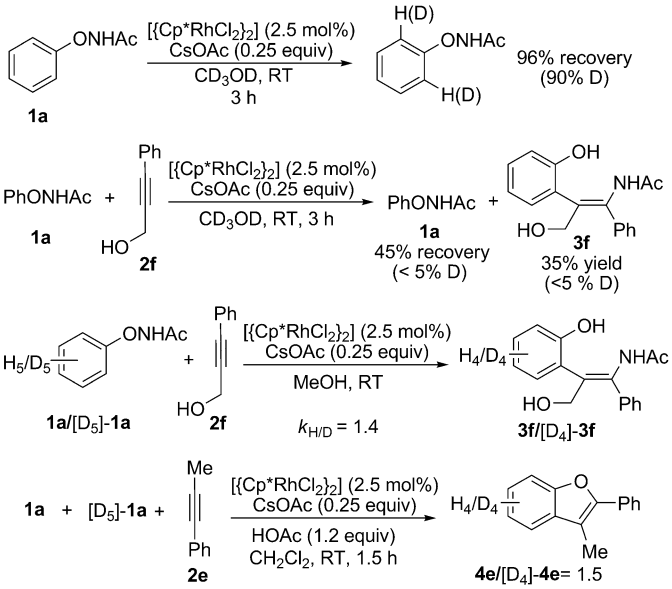
employing CH_2Cl_2 as solvent and acetic acid (1.2 equiv) as an additive, were found to be general for benzofuran synthesis, thus affording **4a** and **4g** in good yields (Table 1, entries 5 and 6).

The scope for the synthesis of benzofurans was next assessed with various internal alkynes and different substituted *N*-phenoxyacetamides (Scheme 3). The reaction proceeded smoothly under reaction conditions B, thus leading to the corresponding benzofurans in moderate to good yields from symmetrical diaryl acetylenes, aryl–alkyl disubstituted alkynes, electron-deficient alkynes and ynamide reacting with *N*-phenoxyacetamide. In the case of 3-phenyl-2-propyn-1-ol, a mixture of regioisomers (**4f** and **4f′**) was observed. In contrast, a single product (**3f**) was formed with the same substrates under reaction conditions A. The difference in regioselectivity might be explained by a more pronounced coordinating effect of the hydroxy group with rhodium in CH_2Cl_2 compared to that in MeOH. Substituted *N*-phenoxyacetamides such as methyl-, 4-fluoro-, and 3-trifluoromethyl-substituted *N*-phenoxyacetamide, can also be efficiently converted into the corresponding benzofurans.



Scheme 3. Reaction scope for the synthesis of the benzofurans **4** under reaction conditions B: **1** (0.24 mmol), **2** (0.2 mmol), $[\{Cp^*RhCl_2\}_2]$ (2.5 mol%), CsOAc (0.25 equiv), and HOAc(1.2 equiv) in CH_2Cl_2 (0.5 mL) at room temperature for 12–48 h, under air. Yields of isolated products are given. [a] Contained an inseparable mixture of isomers; the ratio was determined by ^{1}H NMR spectroscopy.

To gain a better mechanistic understanding (Scheme 4),[3g,6b–d] **1a** was treated with a catalytic amount of $[\{Cp^*RhCl_2\}_2]$ and CsOAc in deuterated methanol. After stirring at room temperature for 3 hours, deuterium was incorporated exclusively at the *ortho* position to the directing group. In contrast, no deuterium incorporation was found in the absence of CsOAc. These experiments indicated that the first step of the reaction may be a facile cyclometalation, and the acetate anion is crucial to this step.[1g] When the reaction was conducted in deuterated methanol for **1a** and **2f** under reaction conditions A for 3 hours, deuterium incorporation was not observed in the unreacted **1a** and product **3f**. The KIE was determined to be 1.4 and 1.5 under the reactions conditions A and B, respectively, thus indicating that the C–H bond-cleavage process is not involved in the rate-determining step.

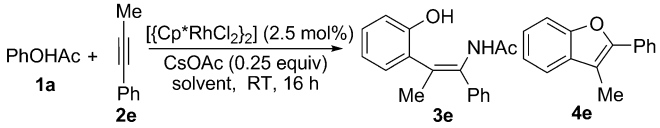


Scheme 4. Deuteration experiments and the study of the kinetic isotope effects.

Experiments were conducted to test whether the benzofuran product **4** could be obtained from the enamide product **3**. Under the reaction conditions A and B, neither **3a** nor **3g** could be converted into benzofuran products. Furthermore, no trace of **4a** was observed when **3a** was treated with 2 equivalents of triflic acid, acetic acid, or TFA in CH_2Cl_2.[12] From these experiments, we believe that the products **3** and **4** are produced through different pathways, the selectivities of which are influenced by the solvents and additives.

The unexpected selectivity prompted us to further investigate the solvent and additive effects. Experiments (Table 3) showed that the selectivity was controlled mainly by the solvent. No reaction occurred in strongly coordinating solvents, such as DMSO and DMF. While methanol and ethylene glycol gave the enamide **3e** in high yield, sterically hindered alcohols (*i*PrOH, *t*BuOH, *t*AmOH) and noncoordinating solvents (CH_2Cl_2, toluene) gave the benzofuran **4e** as the major product. A mixed solvent ($MeOH/CH_2Cl_2 = 1:1$) afforded **3e** in good selectivity (Table 3, entry 8), thus suggesting that the presence of a weakly coordinating solvent favored the formation of the enamide product. Acetic acid

Table 3: Examination of solvent and additive effects.[a]

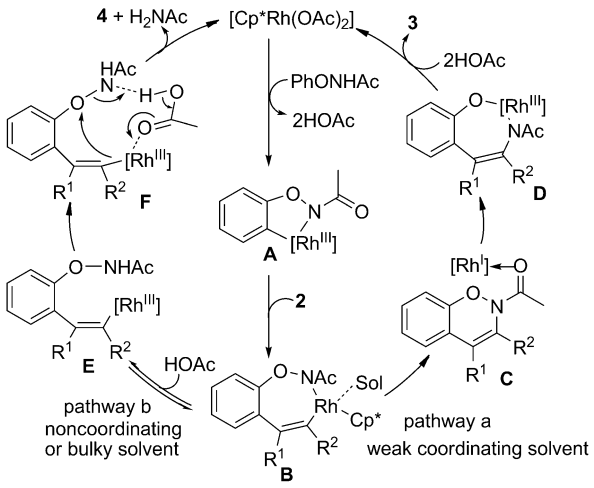


Entry	Solvent	Additives (equiv)[b]	Yield [%][b]	
			3e	**4e**
1	MeOH	–	84	7
2	ethylene glycol	–	72	25
3	*i*PrOH	–	31	53
4	*t*BuOH	–	10	79
5	*t*AmOH	–	10	76
6	CH_2Cl_2	–	11	67
7	toluene	–	12	65
8	MeOH/CH_2Cl_2(1:1)	–	75	14
9	MeOH	HOAc (1.2)	84	16
10	CH_2Cl_2	HOAc (1.2)	trace	83[c]

[a] Reaction conditions: **1a** (0.2 mmol), **2e** (0.24 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mol%), CsOAc (0.25 equiv), in solvent (0.5 mL) at room temperature for 16 h under air. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture using trimethoxybenzene as the internal standard. [c] Yields of the isolated products.

can enhance the yield of **4e** in CH_2Cl_2 but is not crucial for the selectivity (Table 3, entries 9 and 10).

Compared with the [{Cp*$RhCl_2$}$_2$]/CsOAc system, similar results were gained with [Cp*Rh(OAc)$_2$] as the catalyst, thus indicating that [Cp*Rh(OAc)$_2$] might be the active catalyst. On the basis of deuteration experiments, we proposed[13] the first step to be facile arene rhodation (**A**), which is followed by alkyne insertion, thus affording the seven-membered rhodacycle intermediate **B** (Scheme 5).[3n,14] The structure of the products **3g–3i**, **4g–4i** demonstrated that the alkyne was inserted into the Rh–C bond rather than the Rh–N bond of **A**. The dramatic solvent effect on the selectivity can be explained by the coordinating ability of the solvent. Weakly coordinating solvents, such as methanol, might stabilize **B** by forming an 18-electron species, which could undergo reductive elimination/oxidative addition (pathway a) to deliver the enamide product **3**.[15] Since d^6 rhodium(III) species can undergo reductive elimination readily[3n,16] and the N–O bond could be reduced by rhodium(I),[17] we envisioned the $Rh^{III}/Rh^{I}/Rh^{III}$ cycle to be feasible. Otherwise, in noncoordinating or bulky solvents, the N–Rh bond in **B** might be protonated more easily, thus affording the intermediate **E**. Since *N*-phenoxyacetamide is a known precursor of the phenoxemium ion in the presence of acid,[18] an intramolecular substitution[6i] might occur to form the C–O bond and break the N–O bond with the aid of acetic acid.[19]



Scheme 5. Proposed mechanism.

In contrast with diaryl acetylenes and aryl-alkyl alkynes, ester-substituted alkynes afforded benzofurans predominantly, even in methanol (Table 2, entry 1). We reasoned that the vinyl–rhodium bond in **B** (Scheme 5), starting from ester-substituted alkynes, is more nucleophilic and is beneficial for the substitution pathway b. For the reaction of ester-substituted alkynes, an anion-exchange resin was necessary to get high selectivity of enamide product (Table 2, entry 2). These results indicated that neutralizing the acetic acid produced in the reaction disfavored the formation of the benzofuran, and is in accord with our proposed mechanism.

In conclusion, employment of a novel oxidizing directing group, a mild rhodium(III)catalyzed C–H functionalization for the synthesis of *ortho*-hydroxyphenyl-substituted enamides or benzofurans with high selectivity was developed. Considering the valuable structure of the products and good functionality tolerance, these reactions should have potential synthetic utility. Additional mechanism studies on the unexpected chemoselectivity and more transformations starting from *N*-phenoxyacetamides are being carried out in our laboratory.

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[10] Substrates with some other protecting groups (PhONHBz, PhONHTs, and PhONHPiv) did not give any desired product under the optimized reaction conditions.

[11] CCDC 917130 (**3a**), 917131 (**3g**), and 917132 (**3j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] N. Takeda, O. Miyata, T. Naito, *Eur. J. Org. Chem.* **2007**, 1491. In this paper, there was one example demonstrating that *ortho*-hydroxyphenyl-substituted *N*-cyclopentenyl trifluoroacetamide could be readily converted into dihydrobenzofuran upon treatment with trifluoroacetic acid. Normally, benzofuran could be generated from dihydrobenzofurans in the presence of acid.

[13] Radical mechanism was not proposed because the presence of 1 equivalent of the radical trap (TEMPO) or a catalytic amount of BHT did not affect reaction under conditions A and B.

[14] a) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 12414; b) L. Li, Y. Jiao, W. W. Brennessel, W. D. Jones, *Organometallics* **2010**, *29*, 4593.

[15] The possibility of oxidative addition before reductive elimination involving a rhpdium(V) species cannot be ruled out at present.

[16] R. H. Crabtree, *the Organometallic Chemistry of the Transition Metals*, Wiley-Interscience, New Jersey, **2005**, p. 159.

[17] Stoichiometric experiments (see the Supporting Information) demonstrated that *N*-phenoxyacetamide could be reduced to phenol by a rhodium(I) complex.

[18] For some examples, see: a) R. A. Abramovitch, M. Inbasekaran, S. Kato, *J. Am. Chem. Soc.* **1973**, *95*, 5428; b) Y. Endo, K. Shudo, T. Okamoto, *J. Am. Chem. Soc.* **1982**, *104*, 6393.

[19] For the reaction of **1a** with **2g** under reactions conditions B to furnish the benzofuran, acetamide was detected in the reaction mixture by ^{1}H NMR spectroscopy and then isolated by flash chromatography after the reaction completed.

