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Rhodium(I)-Catalyzed Coupling−Cyclization of C═O Bonds with α-Diazoketones

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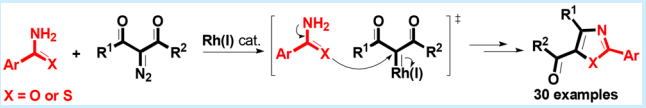
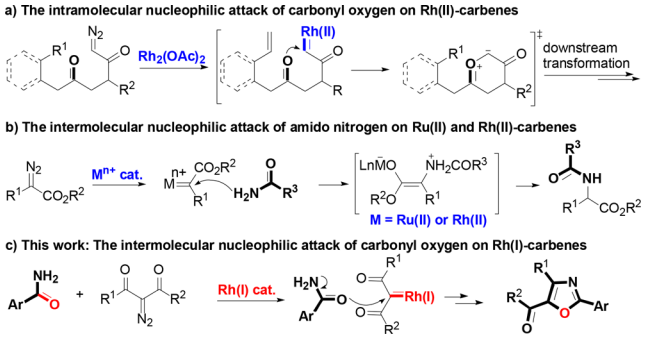
Supporting Information

ABSTRACT: An unprecedented intermolecular nucleophilic attack of C═X bonds (X = O and S) on the rhodium(I)-carbenes has been developed. This transformation allows for the coupling−cyclization of aroylamides with α-diazoketones and provides concise access to 2,4,5-trisubstituted 1,3-oxazoles and 1,3-thiazoles with a broad tolerance of functional groups.



Transition-metal-catalyzed cross-coupling between two fragments provides a powerful platform for chemistry transformations.[1] Among the different coupling partners, diazo-compound-derived metal carbenes have played important roles in modern organic chemistry because these active intermediates could couple with arenes,[2] alkanes,[3] olefins,[4] alcohols,[5] alkynes,[6] carboxylic acids,[7] amines[8] and others[9] to construct different C−X bonds (X = C, N, O, S, Si, etc.). In comparison, the coupling reactions involving metal carbenes and carbonyl (C═O) group are rarely explored. In this regard, Ibata and Padwa developed a Rh(II)-catalyzed intramolecular coupling reaction of carbonyl group (C═O) with diazo compounds, in which carbonyl oxygen attacks Rh(II) carbenes to generate carbonyl ylides (Scheme 1a).[10] For the intermolecular version, only Yoshikai recently employed ketimines to act as carbonyl group equivalents and couple with diazo compounds under a copper catalytic system, affording multisubstituted pyrroles through nucleophilic attack of ketimine nitrogen on copper carbenes.[11] To date, the intermolecular coupling reaction between carbonyl C═O bonds and diazo compounds has not yet been explored, although this type of transformation could provide an alternative approach for the assembly of structurally diverse molecules.

Scheme 1. Distinct Coupling Pathways between Diazo Compounds and Amides



It is well-known that amides belong to readily available carbonyl synthons, and these compounds have been widely utilized as "nitrogen" and carbonyl sources to make heterocycles, in which amidonitrogen generally acts as a "nucleophilic" monomer to trigger a reaction.[12] Although Che and Hu developed cross-couplings of amides with Ru(II) and Rh(II)-carbenes to furnish α-imino esters and prolines (Scheme 1b),[13] other transition-metal-carbene-involved coupling reactions with amides are extremely rare. However, considering that various metal carbenes, especially for the Rh(I)-carbene, possess particular and interesting reactivity in a few catalytic C−C bond-forming processes,[14] exploring a novel coupling model between Rh(I)-carbenes and amides is desirable and also will possibly provide a promising approach to construct nitrogen-containing heterocycles. Herein, we disclose a Rh(I)-catalyzed coupling−cyclization of amides with diazo compounds, in which an unusual nucleophilic attack of carbonyl oxygen on Rh(I)-carbenes led to the formation of 2,4,5-trisubstituted 1,3-oxazoles derivatives. These 1,3-oxazole skeletons are commonly encountered in bioactive natural products and pharmaceuticals.[15]

Optimization conditions for the coupling−cyclization of carbonyl C═O bonds with diazo compounds are summarized in Table 1. Initial efforts focused on screening various Mn(I), Co(III), Pd(II), Rh(III), Rh(II), and Rh(I) catalysts, which could possibly enable the cross-coupling of benzoylamide (**1a**) with α-diazo-β-ketoester (**2a**) in the presence of AgOAc (5 mol %) in EtOAc (2.0 mL) at 100 °C under an Ar atmosphere for 10 h (Table 1, entries 1−6). Gratifyingly, we did find that different types of metal carbenes showed different chemical selectivities, leading to the formation of 1,3-oxazole (**3-1a**) and

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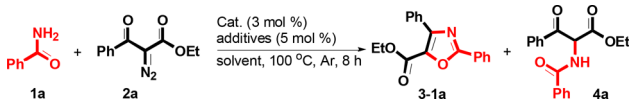
Table 1. Optimization of the Reaction Parameters[a]

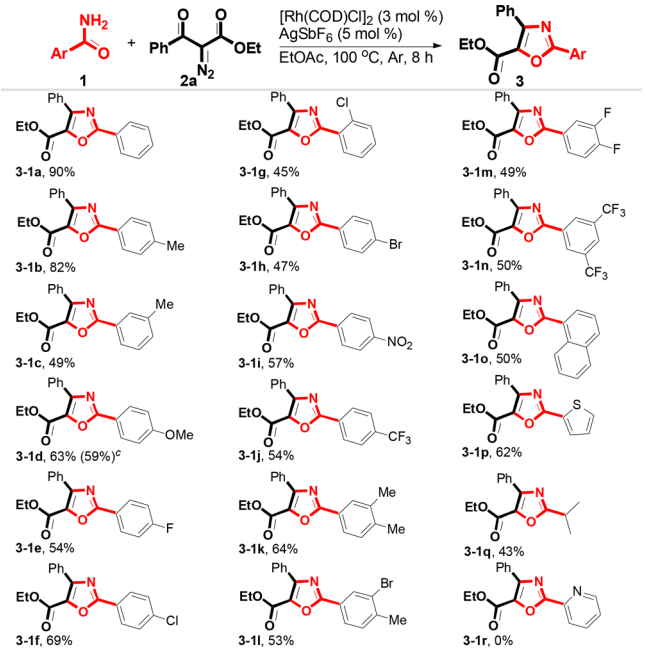


1a 2a 3-1a 4a

entry	catalyst	additive	solvent	yield (%) (3-1a/4a)[b]
1	$Mn(CO)_5Br$	AgOAc	EtOAc	0/0
2	$Cp^*Co(CO)I_2$	AgOAc	EtOAc	trace/0
3	$Pd(OAc)_2$	AgOAc	EtOAc	26/trace
4	$Rh_2(OAc)_4$	AgOAc	EtOAc	0/32
5	$RhCl_3$	AgOAc	EtOAc	22/18
6	$[Cp^*RhCl_2]_2$	AgOAc	EtOAc	<5/trace
7	$[Rh(COD)Cl]_2$	AgOAc	EtOAc	32/trace
8	$[Rh(COD)Cl]_2$	$AgClO_4$	EtOAc	12/21
9	$[Rh(COD)Cl]_2$	$AgNTf_2$	EtOAc	61/trace
10	$[Rh(COD)Cl]_2$	$AgBF_4$	EtOAc	66/trace
11	$[Rh(COD)Cl]_2$	$AgSbF_6$	EtOAc	90/trace[c]
12	$[Rh(COD)Cl]_2$	$AgSbF_6$	toluene	64/11
13	$[Rh(COD)Cl]_2$	$AgSbF_6$	CH_3CN	40/trace
14	$[Rh(COD)Cl]_2$	$AgSbF_6$	THF	80/trace
15	$[Rh(COD)Cl]_2$	$AgSbF_6$	DMF	<5/trace
16	$[Rh(COD)Cl]_2$	$AgSbF_6$	DCE	87/trace
17	$[Rh(COD)Cl]_2$	–	EtOAc	53/0
18	$[Rh(COD)Cl]_2$	$AgSbF_6$	EtOAc	56/0[d]

[a]Unless otherwise noted, all the reactions were performed using amide **1a** (0.40 mmol) and diazo compound **2a** (0.40 mmol) in the presence of catalysts (3 mol %) with an additive (5 mol %) in solvent (2.0 mL) at 100 °C for 8 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2. [b]Isolated yield. [c]Employing 2 mol % of $[Rh(COD)Cl]_2$ produced a 68% yield of **3-1a**. [d]The reaction was carried out at 80 °C.

Scheme 2. Scope of Aroylamides[a,b]



[a]All the reactions were performed using amide **1** (0.4 mmol) and diazo compound **2a** (0.40 mmol) with $[Rh(COD)Cl]_2$ catalysts (3 mol %) in the presence of $AgSbF_6$ (5 mol %) in EtOAc (2.0 mL) at 100 °C for 8 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2. [b]Isolated yield. [c]59% yield on 1.0 mmol scale.

α-amido-*β*-ketoester (**4a**), respectively. Among them, $Mn(CO)_5Br$, $Cp^*Co(CO)I_2$, and $[Cp^*RhCl_2]_2$ catalysts did not efficiently enhance the coupling reaction at all (entries 1, 2 and 6), and Rh(II)-carbene was easily attacked by the amidonitrogen of **1a** to afford a 32% yield of *α*-amido-*β*-ketoester **4a** (entry 4). On the contrary, $Pd(OAc)_2$ and $[Rh(COD)Cl]_2$ could successfully allow the coupling−cyclization of amide **1a** with diazo compound **2a** to produce 1,3-oxazole **3-1a** through the nucleophilic attack of the C═O group of **1a** on the metal carbenes, and $[Rh(COD)Cl]_2$ was proven to be the most efficient catalyst (compare entry 3 with 7). However, $RhCl_3$ did not show good chemical selectivity (compare entries 3 and 7 with 5), affording 1,3-oxazole (**3-1a**) and **4a** in a ratio of almost 1:1 (entry 5). Subsequently, various silver salts including $AgClO_4$, $AgNTf_2$, $AgBF_4$, and $AgSbF_6$ were further evaluated in the presence of $[Rh(COD)Cl]_2$ catalysts in order to increase the reaction conversion, and $AgSbF_6$ could signficantly improve the yield of **3-1a** from 32% to 90% (compare entries 7−10 with 11). Finally, the additional solvent screening revealed that toluene, 1,2-dichloroethane (DCE), DMF, etc. gave inferior results (compare entries 12−16 with 11). It should still be noted that the reaction yield would be decreased to 53% in the absence of $AgSbF_6$ (compare entry 17 with 11), and also running the reaction at lower temperature (80 °C) led to poorer reaction conversion (compare entry 11 with 18).

With the optimized reaction conditions known, we then investigated the scope of aroylamides using 2-diazo-3-oxo-3-phenyl-propionic acid ethyl ester (**2a**) as the coupling reagent. As shown in Scheme 2, the electron-rich amides, such as 4-methyl-benzamide and 4-methoxy-benzamide, could produce the corresponding 1,3-oxazoles (**3-1b** and **3-1d**) in good to excellent yields (82% and 63%).[16] In comparison, electron-withdrawing group (4-F, 4-Cl, 4-Br, 4-NO_3, and 4-CF_3)-substituted benzamides led to poorer substrate conversion, affording moderate to good yields of the products **3-1e**−**3-1j** (47% − 69%).[17] Meanwhile, the steric hindrance of the *meta*- or *ortho*-substituent on benzamides inhibited the reaction conversion to some degree (49% for **3-1c** and 45% for **3-1g**). Moreover, the 3,4- or 3,5-disubstituted benzamides also tolerate the assembly of the cyclized products, and different types of substituents and substitution at various positions of phenyl ring did not significantly affect the reactivity (**3-1k**−**3-1n**, 49−64% yields). It should be noted that 1-naphthoylamide, 2-furoylamide, and isobutyramide[18] are still amenable under our reaction conditions with moderate yields (50% for **3-1o**, 62% for **3-1p**, and 43% for **3-1q**), but pyridine-2-carboxylic acid amide did not produce the target products **3-1q**.[19]

Subsequently, we evaluated the scope of *α*-diazo-*β*-ketoesters (Scheme 3) and found electron-rich phenyl-substituted diazo compounds could be efficiently transferred into 1,3-oxazoles in 81−94% yields (**3-2a**, **3-2b**, and **3-2d**).[20] On the contrary, electron-deficient phenyl-substituted diazo compounds resulted in lower yields of the products **3-2e**−**3-2h** (57−77% yields). Besides the *α*-diazo-*β*-phenyl-substituted ketoesters, the *α*-diazo-*β*-(2-naphthyl)-substituted ketoester and *α*-diazo-*β*-(2-furyl)-substituted ketoester also gave good yields of 1,3-oxazoles **3-2i** (68%) and **3-2j** (65%). Moreover, further evaluation revealed that *α*-diazo-*β*-alkyl-substituted ketoesters and *α*-diazo-*β*-diketone could proceed smoothly to access 4-alkyl-5-acyl-substituted 1,3-oxazoles in moderate yields (**3-2k**−**3-2m**, 48−53% yields). It is gratifying that the

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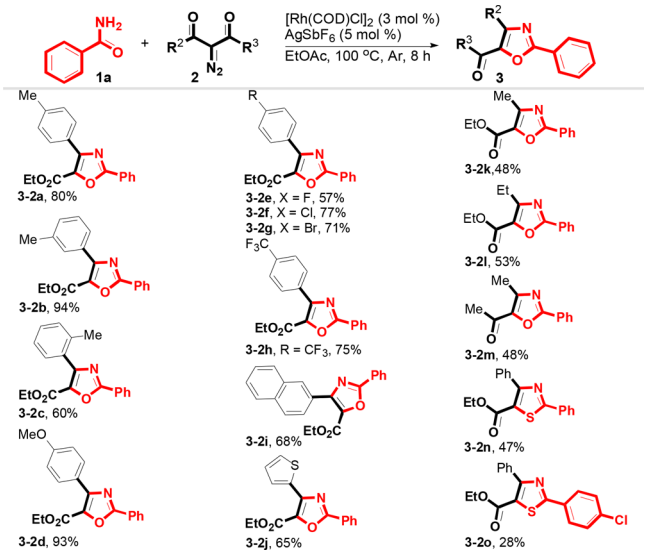
Scheme 3. Scope of α-Diazo-β-Ketoesters[a,b]

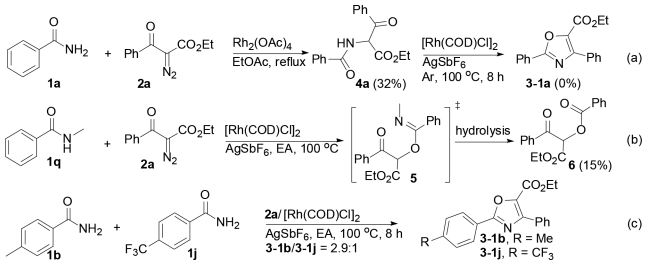


[a]All the reactions were performed using benzamide **1a** (0.4 mmol) and diazo compound **2** (0.40 mmol) with $[Rh(COD)Cl]_2$ catalysts (3 mol %) in the presence of $AgSbF_6$ (5 mol %) in EtOAc (2.0 mL) at 100 °C for 8 h under Ar in a sealed reaction tube. Followed by flash chromatography on SiO_2. [b]Isolated yield.

reaction system could be further extended to thiobenzamides, furnishing 2,4,5-substituted 1,3-thiazoles (**3-2n** and **3-2o**) in acceptable yields using **1a** as coupling partners.

Several control experiments were performed to elucidate the plausible mechanism. First, the coupling−cyclization of benzamide (**1a**) with α-diazo ester (**2a**) in the presence of $Rh_2(OAc)_4$ catalysts produced α-amido-β-ketoester **4a** (32% yield) through a nucleophilic attack of carboxamido nitrogen on the Rh(II)-carbenes, but **4a** could not further produce 1,3-oxazole (**3-1a**) under our standard conditions, implying that α-amido-β-ketoester (**4a**) was not the possible intermediate of this transformation (Scheme 4a). Then, the Rh(I)-catalyzed

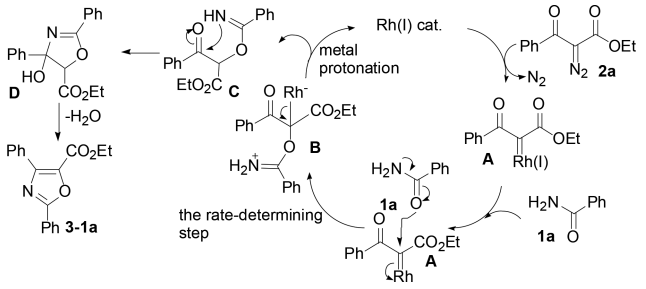
Scheme 4. Preliminary Mechanistic Studies



coupling reaction of *N*-methyl-benzamide (**1q**) with diazo compound **2a** afforded the α-acyoxy-β-ketoester **6**, which is derived from the hydrolysis of ketoimine **5**. This result demonstrated that a nucleophilic attack of carbonyl oxygen on the Rh(I)-carbenes was involved in this reaction (Scheme 4b). Moreover, the competive coupling−cyclization between diazo compound **2a** and aroylamides (**1b** and **1c**) differing in electronic effects implied that nucleophilic attack on Rh(I)-carbenes possibly belongs to the rate-determining step in the cyclization process (Scheme 4c).

Based on the above experiments, we have proposed a plausible mechanism in Scheme 5. The initial reaction of α-

Scheme 5. Possible Reaction Mechanism



diazo-β-ketoester (**2a**) with Rh(I) catalysts affords rhodium(I) carbene complex **A** with the extrusion of a N_2 molecule. Subsequently, nucleophilic attack of carbonyl oxygen of amide **2a** on Rh(I) carbene **A** generates intermadiate **B**, which further produces β-ketoester **C** via metal protonation with concomitant regeneration of Rh(I) catalysts. Finally, **C** undergoes an intramolecular cyclization/dehydration cascade to yield 2,4,5-trisubstituted 1,3-oxazole **3a**.

In conclusion, we have developed a novel Rh(I)-catalyzed coupling−cyclization of carbonyl C═O bonds with α-diazo-β-ketoesters. This transformation proceeds through a rare intermolecular nucleophilic attack of carbonyl oxygen on Rh(I)-carbenes and provides efficient access to versatile 2,4,5-trisubstituted 1,3-oxazole skeletons. Wide functional group tolerance from aroylamides and diazo compounds is observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01541.

Detailed experimental procedures, characterization data, copies of ^{1}H NMR and ^{13}C NMR spectra for all isolated compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(16) The strong electron-donating group possibly cause the amide nitrogen to possess stronger nucleophilicity and led to the formation of complex byproducts. For the 4-methoxy-benzamide, a 7% yield of α-amido-β-ketoester (**4b**) was obtained (see SI)

(17) Compared with benzamide **1a**, these electron-withdrawing groups on the benzene ring decreased the nucleophilicity of carbonyl oxygen and resulted in lower yields.

(18) Employing acetamide as a substrate did not give the corresponding 1,3-oxazole.

(19) Pyridine-2-carboxylic acid amide possibly poisoned the Rh(I)-catalysts by the pyridine−amide coordination.

(20) For the α-diazo-β-(2-methylphenyl)-substituted ketoester, a lower yield of **3-2c** (60%) was obtained possibly due to the steric hindrance of the *ortho*-methyl substitution.

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