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Relay Rh(II)/Pd(0) Dual Catalysis: Selective Construction of Cyclic All-Quaternary Carbon Centers

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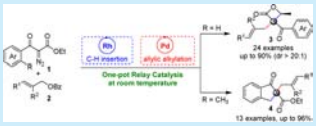
Supporting Information

ABSTRACT: A novel relay Rh(II)/Pd(0) dual catalysis strategy that promotes the divergent reaction of α-diazo-carbonyl compounds with allylic carboxylates for the selective construction of cyclic all-quaternary carbon centers has been developed. This binary catalyst system rendered domino C−H insertion/allylic alkylation process under mild conditions. Remarkably, the domino catalytic reaction shows good selectivity and excellent tolerance to various functionalities and is operationally simple.



A significant challenge in organic synthesis concerns the development of efficient catalytic reactions that furnish all-quaternary carbon centers.[1] All-quaternary carbon centers, especially cyclic all-quaternary carbon centers, are prevalent throughout most classes of naturally occurring biologically active compounds and pharmaceutical agents.[2] Although significant efforts have been devoted to the effective construction of all-quaternary centers in recent years.[1] New methodologies that could be advantageous in terms of functional-group tolerance, mild reaction conditions, and the use of readily available and stable starting materials are still highly desired.

Dual catalysis is an ideal strategy to synthesize heterocyclic scaffolds, as multiple bonds can be formed in one-pot.[3] Beyond the rapid construction of molecular complexity from stable and readily available starting materials, time and cost efficiencies resulting from the lack of purification of intermediates make such transformations attractive. Indeed, the combination of transition metal catalyst with organo-catalysts,[3b−f] such as amino-catalysts, phosphoric acids, and *N*-heterocyclic carbene catalysts, has emerged as a new and powerful strategy. However, dual catalysis with the right combination of transition metal catalysts is far less explored,[4,5] which is in part due to the difficulty in ensuring redox-compatibility between the catalysts, avoiding catalysts deactivation.[4i] Moreover, the mechanistic complexity of these dual catalytic systems has resulted in limited understanding and thus restricted development of effective dual transition-metal catalytic reactions. Recently, Liang demonstrated the palladium(0)-catalyzed coupling of allyl carboxylates with α-diazo carbonyl compounds to construct acyclic quaternary carbon centers.[6] Herein we report our discovery of a highly compatible Rh(II)/Pd(0) dual catalysis that promotes the reaction of α-diazo-β-ketoesters **1** with allyl carboxylates **2** for the selective construction of cyclic all-quaternary carbon centers (dr > 20:1) (Figure 1d). This binary catalyst system rendered domino Rh(II)-carbene-induced C−H insertion/Pd-catalyzed allylic alkylation process.

Diazo compounds have found wide applications in organic synthesis.[7] In particular, the Rh-catalyzed diverse transformations of diazo compounds involving the Rh-carbene species are

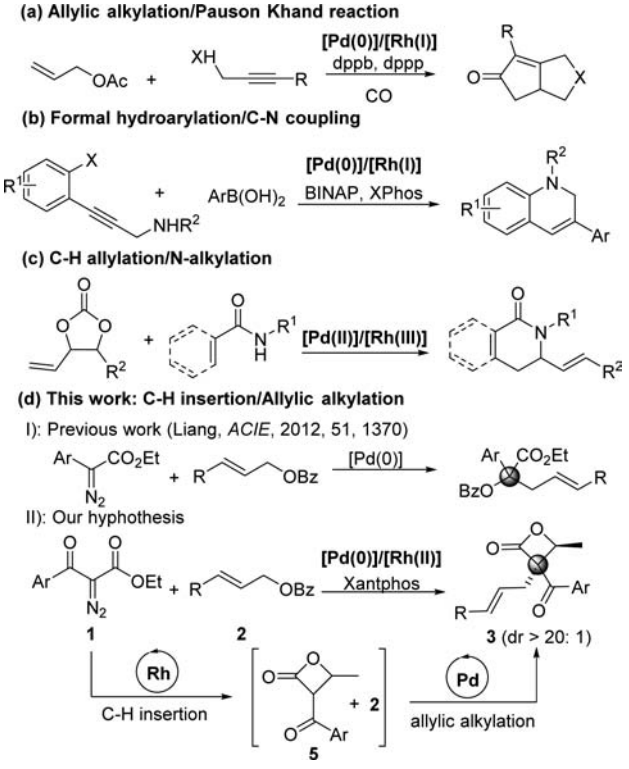


Figure 1. Developments in relay Pd/Rh dual catalysis.

well established.[7] However, Pd-catalyzed cross-couplings are nowadays recognized as one of the most powerful and reliable tools for the C−C bond formations.[8] Although rapid developments in these two important areas have been achieved, it is highly desirable to develop novel methodologies through combining these two areas together. In recent years, the combination of mechanistically distinct carbene transformation and

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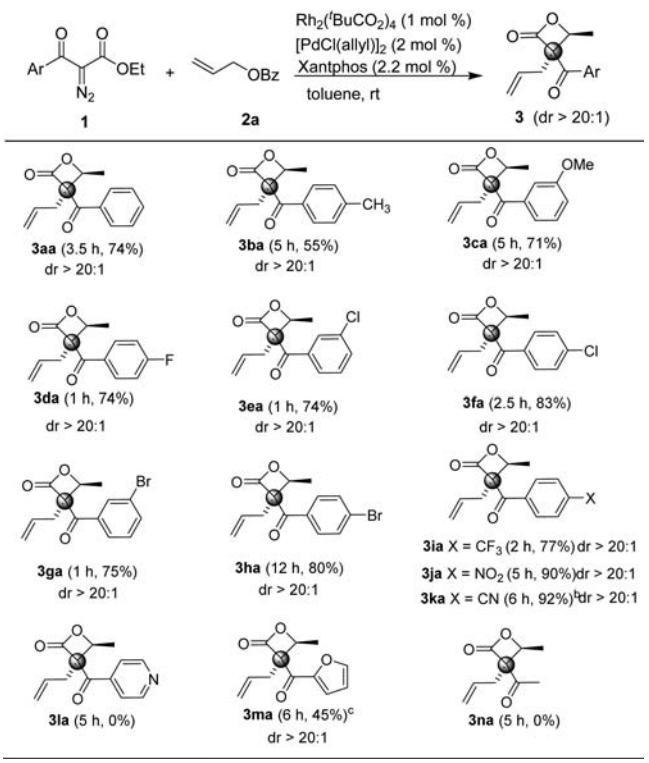
cross-coupling in a single catalytic cycle has been introduced as a new strategy for the formation of C−C bonds, which involved a single catalyst.[9] However, some transformations would be difficult or unattainable with monocatalysis. Thus, it may provide access to entirely new reactivity patterns by combining Pd and Rh catalysts in a single flask. The daunting challenge for this transformation resides in the compatibility between Rh and Pd catalysts. Jeong and coauthor demonstrated highly compatible Rh(I)/Pd(0) system for the allylic alkylation/Pauson Khand reaction (Figure 1a).[4a,5b] Lautens also developed Rh(I)/Pd(0) system for formal hydroarylation/C−N coupling (Figure 1b).[5f−k] Recently, the cross-compatible Pd(II)/Rh(III)[5l] system and Pd(0)/Rh(II) system[4n] were also reported. Our reaction design involves that the β-lactone **5** was generated first from the Rh(II)-carbene-induced intramolecular C−H insertion of α-diazo-β-ketoesters **1**.[10c,f] Subsequently, Pd(0)-catalyzed allylic alkylation[11] with allyl carboxylates **2** would access β-lactones **3** bearing an α-quaternary carbon center, which are often found in biologically active compounds (Figure 1d).[12]

To put the above hypothesis to the test, our investigation began with α-diazo-β-ketoester **1a** and allyl benzoate **2a** at room temperature in the presence of 1.0 mol % $Rh_2(^tBuCO_2)_4$, 2.0 mol % $[PdCl(allyl)]_2$, and 2.2 mol % Xantphos. Under these conditions, the desired β-lactone **3aa** was obtained in 71% yield and with excellent diastereoselectivity (dr > 20:1) (entry 1, Table S1). The X-ray crystallography and 2D NMR analysis of the β-lactones **3** indicated that the methyl and allyl groups were in a *trans* position (see SI). Meanwhile, the product **7** was also detected, which was attributed to the Rh-catalyzed O−H insertion of benzoic acid with excessive α-diazo-β-ketoester **1a**. Encouraged by this initial result, we proceeded to optimize the reaction. After screening different Pd-catalysts (entries 2−5, Table S1), it was found that $Pd(PPh_3)_4$ did not deliver isolable coupling products (entry 5, Table S1). The efficiency of reaction was dramatically decreased by changing the Xantphos ligand to other phosphine ligands (entries 7−10, Table S1) or the Rh(II) catalysts (entries 11−12, Table S1). In addition, the yield could be further improved by changing the substrate ratio of **1a**/**2a** from 2.0:1.0 to 1.8:1.0 (entry 15, Table S1). Moreover, control experiments indicated that both palladium and rhodium are required for the reactivity. For example, when under the only Rh(II) catalyst, only the C−H inserted β-lactone **5a** was detected (entry 16, Table S1). However, when the reaction was carried out in the presence of only $[ClPd(allyl)]_2$/Xantphos, the Pd(0)-catalyzed cross-coupling of allylic carboxylates with α-diazo carbonyl compounds did not proceed at all (entry 17, Table S1).[6] Other allyl carboxylates such as allyl acetate did not improve the yield and resulted in a 62% yield of **3aa**.[13]

After having optimized the conditions, reaction of various α-diazo-β-ketoesters **1** and allyl benzoate **2a** afforded the corresponding β-lactones **3aa**−**3ma** in moderate to high yields (Scheme 1). The reaction was not significantly affected by electronic effect of the substituents on the aromatic ring of α-diazo-β-ketoesters **1**. Both electron-rich (**1b** and **1c**) and electron-poor (**1d**−**1k**) α-diazo-β-ketoesters can be readily employed. In particular, fluoro (**1d**), bromide (**1g** and **1h**), trifluoromethyl (**1i**), nitro (**1j**), and nitrile (**1k**) groups were well tolerated. Furthermore, by elevating the reaction temperature to 50 °C for 6 h, the furan-containing α-diazo-β-ketoesters **1m** could also be successfully incorporated into the product **3ma** in moderate yield. Unfortunately, the reaction did not give the corresponding product **3na** from alkyl substituted α-diazo-β-ketoester **1n**.[10c]

Scheme 1. Relay Rh(II)/Pd(0)-Catalyzed Reaction of α-Diazo-β-ketoesters 1 and Allyl Carboxylates 2a[a]



[a]Reaction conditions: **1** (0.36 mmol, 1.8 equiv), **2a** (0.20 mmol), in toluene (2.0 mL) at room temperature. Yields are isolated yield. [b]Compound **1k** (0.28 mmol, 1.4 equiv) was used. [c]Reaction carried out at 50 °C.

We next investigated the reactivity of α-diazo-β-ketoester **1a** and allyl carboxylate **2b** having 3-phenyl group. However, the corresponding product **3ab** could be obtained in low yield under the optimized reaction conditions.[13] To our delight, it was found that the addition of 2.0 equiv of K_2CO_3, which may help the Pd-catalyzed allylic alkylation, could significantly improve the yield affording **3ab** in 65% yield, while using only 1.4 equiv of α-diazo-β-ketoester **1a**. To further demonstrate the versatility of the reaction, a series of allyl carboxylates **2** were reacted with α-diazo-β-ketoesters **1a** (Scheme 2). Not surprisingly, the 3-phenyl substituted allyl carboxylates **2** having electron-donating methyl (**2c**) group and the electron-withdrawing fluoro (**2e**), chloro (**2f**), trifluoromethyl (**2j**), and nitro (**2k**) substituents at *para*-position of phenyl ring were well tolerated. The allyl carboxylates **2l** having naphthyl substituent could also effectively react to afford the desired product **3al** in 77% yield. Interestingly, only (*E*)-geometry **3ad** was also obtained from the reaction with sterically demanded *ortho*-methoxyphenyl substituted allyl carboxylate **2d** (*E*/*Z* = 5.9:1). In addition, it has been found that reaction with the *E*/*Z*-mixture of allyl carboxylates having bromide groups at the *o*-, *m*-, and *p*-positions (**2g**−**2i**) could give the corresponding (*E*)-geometry β-lactone products (**3ag**−**3ai**) without (*Z*)-geometry in good yields. These results clearly indicated that the geometry of olefin of allyl moiety is isomerized via η^1-η^3 π-allyl Pd complexes, and the Pd-catalyzed allylic alkylation occurred at the sterically less demanding terminal carbon.[14] The methallyl benzoate **2m** (R^1 = H, R^2 = Me) also afforded the corresponding **3am**.

When allyl carboxylates **2a** were treated with α-diazo-β-ketoesters **1o** under the above conditions, the corresponding

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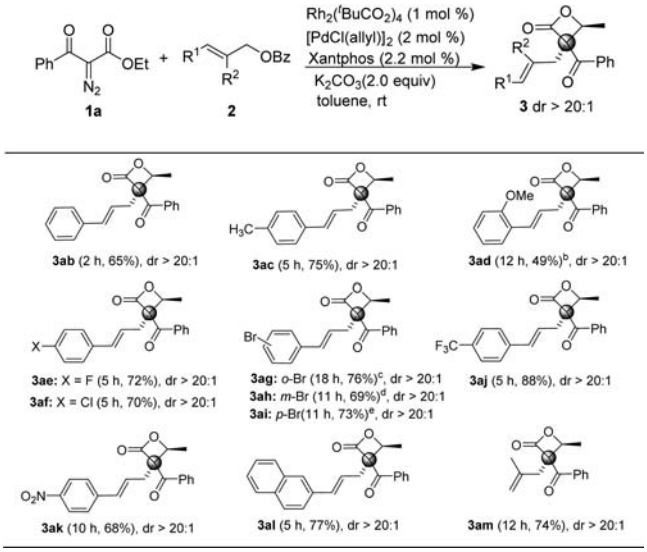
Scheme 2. Relay Rh(II)/Pd(0)-Catalyzed Reaction of α-Diazo-β-ketoesters 1a and Allyl Carboxylates 2[a]

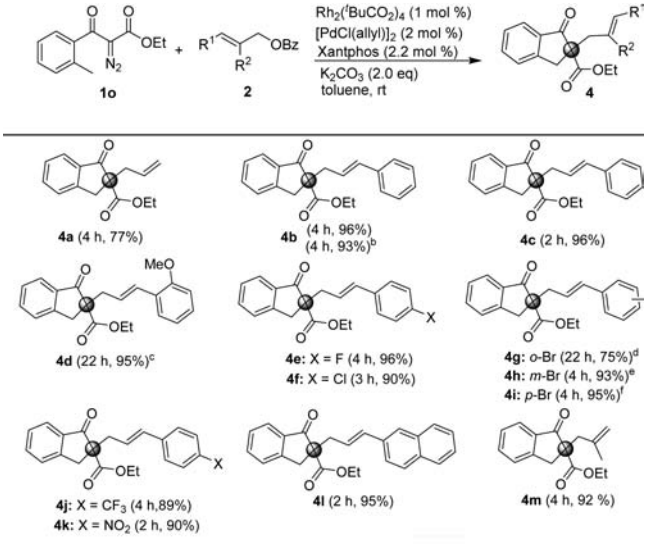


[a]Reaction conditions: **1a** (0.28 mmol, 1.4 equiv), **2** (0.20 mmol), in toluene (2.0 mL) at room temperature. Yields are isolated yield. [b]Compound **2d** (*E*/*Z* = 5.9:1) was used. [c]Compound **2g** (*E*/*Z* = 3:1) was used. [d]Compound **2h** (*E*/*Z* = 50:1) was used. [e]Compound **2i** (*E*/*Z* = 33:1) was used.

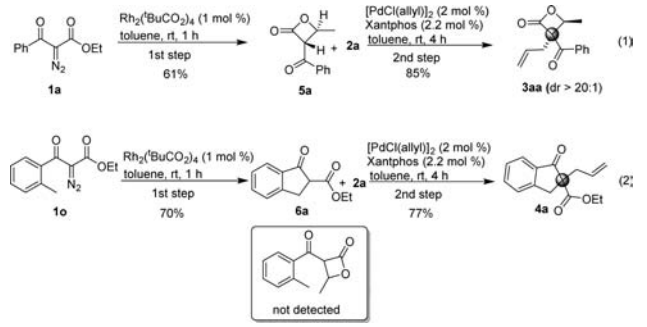
β-lactones **3oa** could not be obtained. Surprisingly, a 2,3-dihydro-1*H*-inden-1-one **4a** was obtained in 77% yield, a result that we attribute to Rh-catalyzed 1,5-C−H insertion instead of 1,4-C−H insertion. Next, to demonstrate the generality of this reaction, various allyl carboxylates **2** were reacted with α-diazo-β-ketoesters **1o**. As shown in Scheme 3, this reaction afforded the corresponding products **4** in high to excellent yields. Allyl carboxylates **2** bearing electron-donating (**2c** and **2d**) and electron-withdrawing groups (**2e**−**2k**) can be used. Functional groups including fluoro, trifluoromethyl, nitro, and 2-naphthyl groups were well tolerated in this reaction. Notably, the halogen substituents on the aromatic ring, especially bromide (**2g**−**2i**), remained inert in the reaction, allowing further transformations through cross-coupling reactions. Also, the reaction was not noticeably affected by the position of substituents on the aromatic ring of allyl carboxylates, although the reaction rate decreased in the case of the substituents on *ortho*-positions of the aromatic ring of allyl carboxylates (**2d** and **2g**). Finally, the molecular structures of **3ha** and **4k** were unambiguously confirmed through X-ray crystallography.[15]

In order to shed light on the mechanism, several experiments were performed. First, α-diazo-β-ketoesters **1a** and **1o** were subjected to the intramolecular C−H insertion using only Rh(II) carboxylates as the catalyst, respectively. The desired β-lactone **5a**[10a−d,f] was obtained in 61% yield by Rh-catalyzed 1, 4−C-H insertion of the **1a** (eq 1). However, reaction with the α-diazo-β-ketoesters **1o** afforded the 1,5-C−H insertion product **6a** in 70% yield, while the 1,4-C−H insertion product was not detected at all. This result clearly suggested that 1,5-C−H insertion is preferable to 1,4-C−H insertion (eq 2). We next focused our attention on Pd-catalyzed allylic alkylation[11] of **5a** and **6a** with allyl benzoate **2a**, which were readily achieved by employing [PdCl(allyl)]$_2$/Xantphos in toluene. These results clearly imply that this catalytic system was a relay Rh(II)/Pd(0) dual catalysis, and the relay catalytic system could provide superior efficiency compared to its stepwise counterpart.

Scheme 3. Relay Rh(II)/Pd(0)-Catalyzed Reaction of α-Diazo-β-ketoesters 1o and Allyl Carboxylates 2[a]



[a]Reaction conditions: **1o** (0.24 mmol, 1.2 equiv), **2** (0.20 mmol), in toluene (2.0 mL) at room temperature. Yields are isolated yield. [b]Compound **1o** (1.2 mmol, 1.2 equiv) and **2b** (1.0 mmol) were used in toluene (10.0 mL). [c]Compound **2d** (*E*/*Z* = 5.9:1) was used. [d]Compound **2g** (*E*/*Z* = 3:1) was used. [e]Compound **2h** (*E*/*Z* = 50:1) was used. [f]Compound **2i** (*E*/*Z* = 33:1) was used.



In summary, we have developed a novel method for the formation of two different C−C bonds on the same carbon atom in one-pot by relay Rh(II)/Pd(0) dual catalysis. This binary catalyst system rendered domino C−H insertion/allylic alkylation process under mild conditions. Notably, this reaction provides a new strategy for the construction of cyclic all-quaternary carbon centers. The corresponding β-lactones **3** and 2,3-dihydro-1*H*-inden-1-one **4** can also be selectively obtained, depending on the choice of α-diazo-carbonyl compounds. Furthermore, the relay catalytic process shows good selectivity and excellent tolerance to various functionalities, which is operationally simple.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02958.

Detailed experimental procedures and characterization data for **3** and **4** (PDF)
X-ray crystallographic data for **4k** (CIF)
X-ray crystallographic data for **3ha** (CIF)

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Notes

The authors declare no competing financial interest.

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(13) When allyl carbonate **2b′** was chosen as the substrate, the main product (**3ab**) and byproduct (**8**) gave the same spot on TLC, which they cannot be separated by silica-gel column chromatography.

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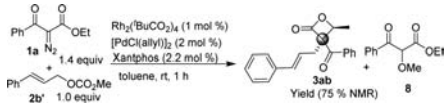
(15) For X-ray structure data for **3ha** (CCDC 1511263) and **4k** (CCDC 1495029), see the Supporting Information.



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