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Rhodium(III)-catalyzed chemoselective C–H functionalization of benzamides with methyleneoxetanones controlled by the solvent†

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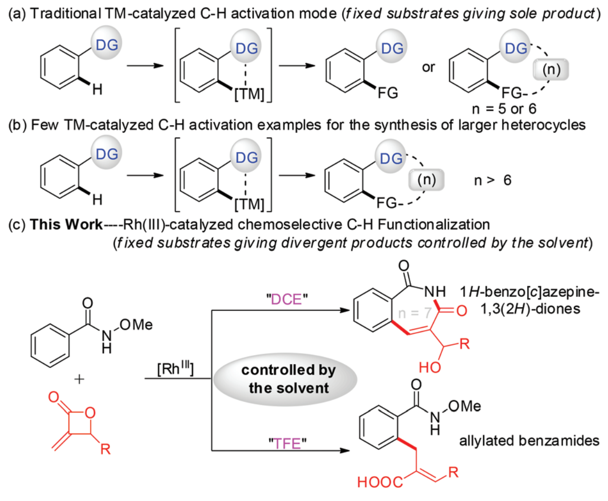
Described herein is a Rh(III)-catalyzed and solvent-controlled double C–H functionalization of common benzamides *via* selective acyl C–O cleavage (β-H elimination) or alkyl C–O cleavage (β-O elimination) of the methyleneoxetanone substrate, which provides a straightforward way for the divergent synthesis of chain alkylated benzamides and seven-membered 1*H*-benzo[*c*]azepine-1,3(2*H*)-diones in a highly chemoselective manner. Through a series of experimental investigations together with theoretical studies, the effect of the solvent has been systematically elucidated.

Since the end of the twentieth century, the progressive developments in transition-metal (TM)-catalyzed C–H activation have established a solid basis for current organic chemistry.[1,2] Undeniably, compared with the classical organic synthetic methodology, the direct functionalization of ubiquitous C–H bonds provides more straightforward and atom/step-economical shortcuts toward the preparation of various kinds of highly valuable organic compounds, ranging from relatively small molecules like drug candidates to complex polydisperse scaffolds such as polymers.[2]

Driven by the pioneering work from the research groups of Lewis,[3] Murai[4] and Fujiwara,[5] indeed, significant progress has been made in this topic, making C–H bond activation one of the most exciting and rapidly developing fields of modern organic chemistry over the past 20 years or so. Accordingly, a vast number of elegant and versatile examples have stood out.[6] Despite these relevant advances, there is room for innovation and breakthrough, especially for the reasons below: (1) each reaction almost only led to a specific main product when a fixed catalyst/substrate was used, which to some extent casts a shadow on subsequent synthetic applications, and (2) compared with the synthesis of five or six-membered heterocycles, the C–H activation methods to allow the construction of larger heterocyclic ring frameworks[7] are still underexplored despite the widespread existence and the potential utility of such products in nature (Scheme 1).

To simultaneously address the aforementioned limitations and on the basis of literature precedents involving a privileged benzamide core bearing a NH-OR substituent as the fashionable oxidizing-directing group (ODG),[8,9] we reasoned that the nature of the solvent[10] should have a direct impact on the reaction outcome. By rationally adjusting the solvent to affect the coordination environment and/or binding mode of the TM catalyst, the regio- and/or chemo-selectivity of the reaction might be switched from one type to another type, thus giving



Scheme 1 TM-catalyzed C–H activation mode.

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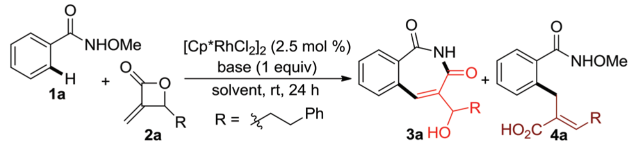
the divergent reaction outcome in a controllable way when an appropriate coupling partner was introduced.

To confirm our above hypothesis and in combination with our continuing efforts to develop Rh(III)-catalyzed C–H functionalization,[11] we here would like to report a divergent and diversity-oriented unified strategy to construct both acyclic (allylated benzamides) and seven-membered heterocyclic frameworks (1*H*-benzo[*c*]azepine-1,3(2*H*)-diones) in one pot at room temperature using classical benzamides and recently prevalent methyleneoxetanones[10b,12] as the model substrates *via* Rh(III)-catalyzed redox-neutral C–H activation, where the double divergence is enabled by judicious choice of the solvent. A mechanistic rationale based on experimental and computational studies for clarifying such chemoselectivity is also discussed.

The initial experiments were performed by treating *N*-methoxybenzamide (**1a**) with 3-methylene-4-phenethyloxetan-2-one (**2a**) under a Cp*Rh(III)-catalyzed system to deliver the corresponding [4 + 3] annulated product 1*H*-benzo[*c*]azepine-1,3(2*H*)-dione **3a** *via* the tandem C–H activation/β-H elimination/cyclization process (Table 1). After systematic screening of several parameters such as the catalyst, the solvent (Table 1, entries 1–5), the base (entries 6 and 7) and the proportion of substrates (entry 8, see Table S1 in the ESI† for details), we were pleased to determine the optimal conditions for the construction of the 1*H*-benzo[*c*]azepine-1,3(2*H*)-dione framework in 88% isolated yield (**1a** (0.2 mmol), **2a** (1.2 equiv.), [Cp*RhCl$_2$]$_2$ (2.5 mol%) and CsOAc (1 equiv.) in DCE (0.1 M) at room temperature for 24 h under an atmosphere of air). Control experiments confirmed that no reaction occurred in the absence of either the TM catalyst or the base additive. Interestingly, an alternative reaction mode involving the C–H activation/β-O elimination cascade could be achieved by accurately tuning the reaction solvent, delivering the *ortho*-allylation product **4a** in an atom-economical manner. Further examination indicated that TFE was the key factor in tuning the chemoselectivity, since other selected solvents all failed to give the carboxylic acid derivative **4a**. Through an intensive investigation (entries 9–11 and see Table S2 in the ESI† for details), we ultimately obtained the best reagent blend consisting of [Cp*RhCl$_2$]$_2$ (5 mol%), **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), and KOPiv (1 equiv.) in TFE (0.1 M), which operated at room temperature for 16 h under air to give the desired product **4a** in 67% isolated yield.

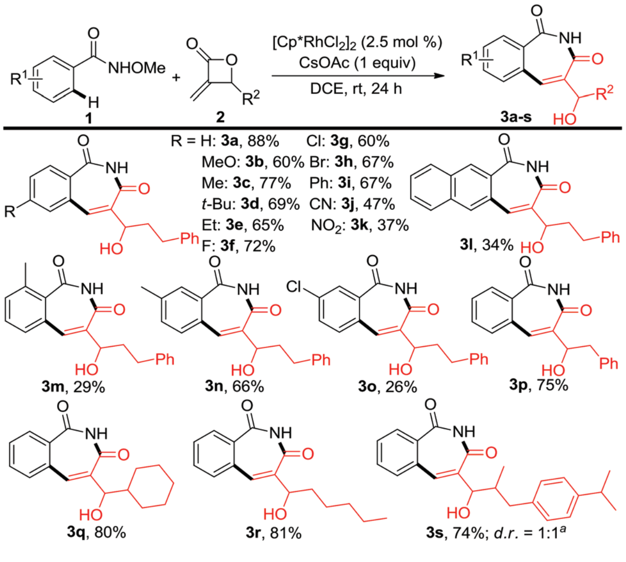
With the establishment of the optimal reaction conditions, we next examined the scope and generality of this methodology for the efficient synthesis of 1*H*-benzo[*c*]azepine-1,3(2*H*)-diones (Scheme 2). Delightfully, a variety of substituted *N*-methoxybenzamides bearing various commonly encountered functional groups including alkyl (**3c–e**, **3m** and **3n**), methoxy (**3b**), halogens (**3f–h** and **3o**), phenyl (**3i**), nitrile (**3j**) and nitro (**3k**) were well tolerated for this transformation, furnishing the corresponding 1*H*-benzo[*c*]azepine-1,3(2*H*)-dione derivatives in moderate to good yields. Moreover, the naphthalene substrate was also compatible with the reaction conditions, furnishing the desired product **3l** in 34% yield. Of note is that when *meta*-substituted *N*-methoxybenzamides were employed, the reaction proceeded smoothly at the less hindered position to give the specific regioselective product (**3n** and **3o**). Subsequently, several methyleneoxetanones were assessed to further demonstrate the versatility of this transformation. The results revealed that the developed Rh(III)-catalyzed [4 + 3] annulation was broadly applicable with these

Table 1 Optimization of reaction conditions[a]



Entry	Base	Solvent	Yield[b] (%) 3a	Yield[b] (%) 4a
1	CsOAc	Dioxane	68	n.d.
2	CsOAc	MeOH	53	n.d.
3	CsOAc	DCE	70	n.d.
4	CsOAc	TFE	11	36
5	CsOAc	HFIP	39	<5
6	NaOAc	DCE	43	n.d.
7	K_2CO_3	DCE	21	n.d.
8[c]	CsOAc	DCE	88	n.d.
9[d]	NaOAc	TFE	11	26
10[d]	KOPiv	TFE	<5	56
11[d,e]	KOPiv	TFE	<5	67

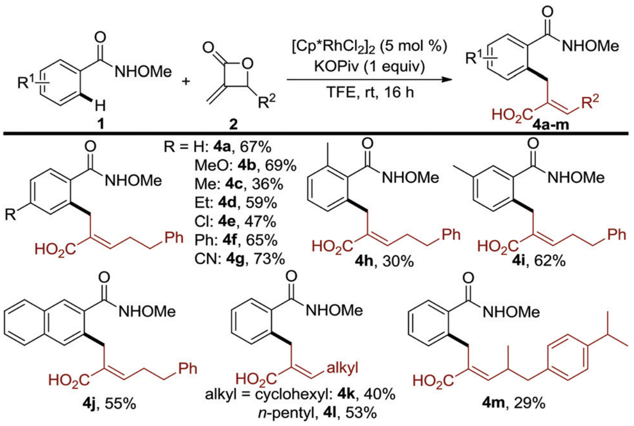
[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.15 mmol), [Cp*RhCl$_2$]$_2$ (2.5 mol%) and base (1 equiv.) in solvent (0.1 M) at rt for 24 h without exclusion of air or moisture. [b] Isolated yields. [c] **2a** (1.2 equiv.). [d] The reaction was conducted on a 0.2 mmol scale with 5 mol% of [Cp*RhCl$_2$]$_2$ for 16 h. [e] **2a** (1.5 equiv.).



Scheme 2 Scope of substrates for the synthesis of 1*H*-benzo[*c*]azepine-1,3(2*H*)-diones. Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), [Cp*RhCl$_2$]$_2$ (2.5 mol%) and CsOAc (1 equiv.) in DCE (0.1 M) at room temperature for 24 h under air; isolated yields were reported. [a] The ratio was determined by ^{1}H-NMR analysis.

enumerated methyleneoxetanones to produce the desired 1*H*-benzo[*c*]azepine-1,3(2*H*)-dione products bearing different substituents including benzyl (**3p**), cyclohexyl (**3q**) and *n*-pentyl (**3r**), as well as the derivatives of readily accessible natural products such as cyclamen aldehyde (**3s**).

Considering the potential reaction diversity of methyleneoxetanones and the eagerness to develop a divergent synthetic strategy, we were next intrigued to explore the feasibility of the developed C–H allylation for the construction of diverse carboxylic acids. On the basis of the established optimal conditions, a variety of substituted *N*-methoxybenzamides and methyleneoxetanones were tested. As shown in Scheme 3, various *N*-methoxybenzamides bearing different substituents at either the *para*-, *ortho*- or *meta*-position were fully tolerated regardless of the electrical properties of the substituent, yielding the desired carboxylic acids in moderate to good yields (**4a–i**). In addition, the derivatives of 3-methylene-4-oxetan-2-one bearing various substituents including cyclohexyl, long-chain alkyl and cyclamen aldehyde groups at the 4-position were also compatible with this TFE-controlled C–H allylation, leading to the efficient synthesis of the corresponding carboxylic acid products (**4k–m**).



Scheme 3 Substrate scope for C–H allylation. Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), [Cp*RhCl$_2$]$_2$ (5 mol%) and KOPiv (1 equiv.) in TFE (0.1 M) at room temperature for 16 h under air; isolated yields were reported.

Given the distinctive reaction modes for the divergent synthesis of both acyclic and annulate skeletons, we next conducted a set of density functional theory (DFT) studies to clarify the origin of the multifarious chemoselectivities controlled by the solvent. Briefly, all the structures were optimized at the M06-2X level in experimental solvents (DCE and TFE, respectively) to figure out how the solvent uniquely switches different pathways to give the diverse products from the same substrates (Fig. 1).

On the basis of our previous work and precedent literature,[8,10b,12,13,14] the facile C–H bond cleavage followed by migratory insertion of the alkene process was involved to give a seven-membered rhodacycle intermediate, which was rationally selected as the starting point (**INT-1**). The distinguished β-H and β-O elimination pathways were computed under both DCE and TFE conditions to reveal the solvent effect in determining the chemoselectivity between products **3** (**PC1**) and **4** (**PC2**). Firstly, β-H elimination and subsequent hydrogen transfer occurred *via* **TS-2** with an energy barrier of 23.7 kcal mol^{-1} in DCE. A further oxidative addition process occurred with an energy barrier of 26.4 kcal mol^{-1} (from **INT-4** to **TS-3**), resulting in the cleavage of the N–O bond together with the regeneration of Rh(III) species (**INT-6**). The following intramolecular nucleophilic substitution/ring-opening process led to the facile construction of the 1*H*-benzo[*c*]azepine-1,3(2*H*)-dione framework. By contrast, a higher energy barrier of 30.1 kcal mol^{-1}

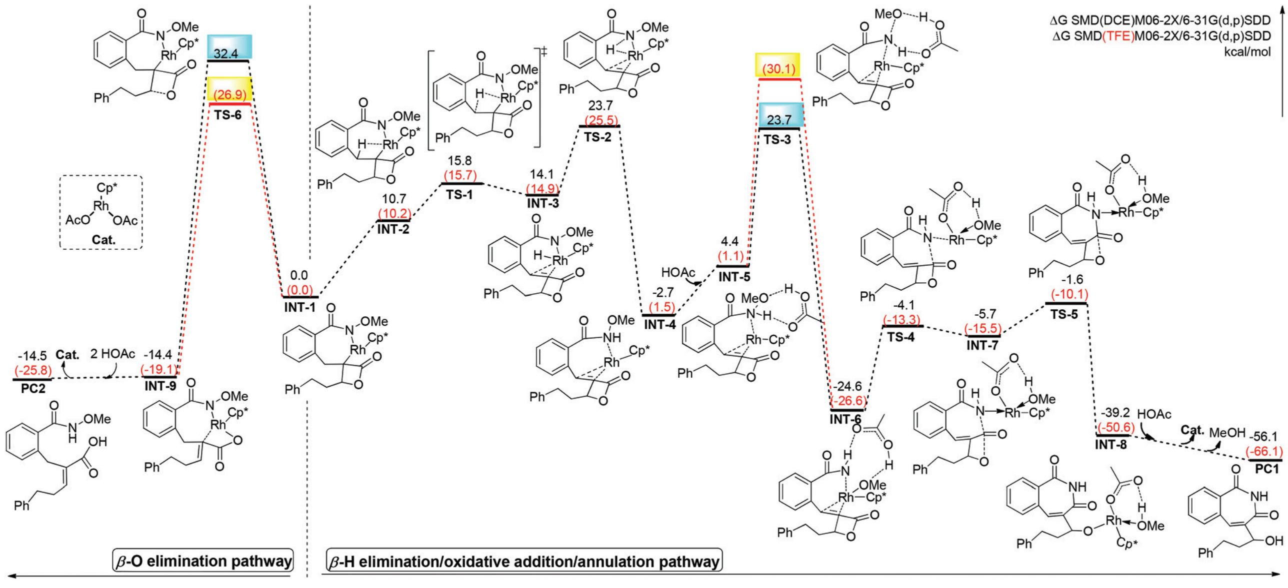


Fig. 1 Computed Gibbs free energy changes of the reaction pathways in both DCE and TFE.

(from **INT-1** to **TS-3**) was involved in TFE for such a β-H elimination/oxidative addition/annulation process, suggesting that a more reasonable β-O elimination process might be preferred in TFE since the energy barrier of 26.9 kcal mol^{-1} (from **INT-1** to **TS-6**) is lower than 30.1 kcal mol^{-1}. In contrast, the β-O elimination process could be obviously excluded under DCE conditions due to the high energy barrier up to 32.4 kcal mol^{-1}.[15] Summarizing these results, we can draw the conclusion that the β-H elimination process is more likely involved in DCE while alternative β-O elimination proceeds in TFE, thus leading to the observed chemoselectivity controlled by the solvent.

In summary, by rationally tuning the fine structure of the substrates and the reaction conditions, double chemoselective C–H functionalization has been achieved for the divergent synthesis of two intriguing frameworks including allylated benzamides and 1*H*-benzo[*c*]azepine-1,3(2*H*)-diones with good functional group compatibility. Considering the diversity-oriented and controllable C–H activation reaction modes with simple and fixed substrates for one-pot construction of chain and large heterocyclic ring frameworks, this strategy not only has the potential for a wide synthetic utility, but also opens up a window for the development of current organic chemistry, especially in the field of TM-catalyzed C–H activation. In combination with DFT studies, two distinguished solvent-controlled reaction pathways were rationally clarified. Further investigations on the detailed mechanism and the expansion of such a C–H activation strategy for more diverse transformations are in progress.

Conflicts of interest

There are no conflicts to declare.

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