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Selective Synthesis of C4-Functionalized Benzofurans by Rhodium-Catalyzed Vinylene Transfer: Computational Study on the Cyclopentadienyl Ligand

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Supporting Information Placeholder
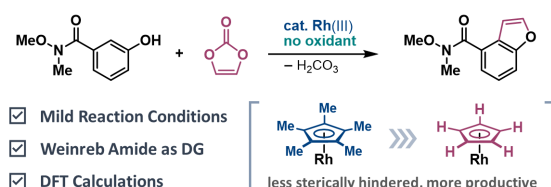
ABSTRACT: Benzofuran is a privileged structure in many bioactive compounds; however, the controlled synthesis of C2,C3-non-substituted benzofurans has been scares. In particular, cumbersome multistep processes are inevitable for the most inaccessible C4-substituted isomers. Herein, we report a Rh-catalyzed direct vinylene annulation of readily available *m*-salicylic acid derivatives with vinylene carbonate to achieve selective construction of C4-substituted benzofurans. The Weinreb amide directing group facilitated the following product derivatization. The reaction mechanism was investigated by DFT calculations.

Benzofuran derivatives have been among the most popular structural units in various natural products and biologically active compounds.[1] The furan fragment within the fused ring system is only weakly aromatic in nature and is significantly reactive than the benzenoid core. Consequently, it has been a tremendous challenge to achieve the selective and effective synthesis of functionalized benzofurans bearing substituents at only C4–C7 positions (Scheme 1a).

Scheme 1. Representative Synthetic Methods for the Functionalized Benzofuran Derivatives
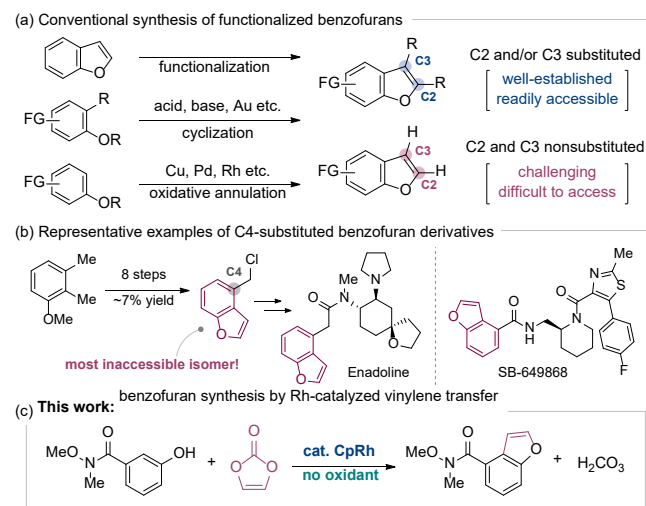

Benzofurans are generally synthesized by cyclization reactions of *ortho*-substituted phenol derivatives.[1,2] Acid-mediated dehydration of carbonyl compounds, base-mediated cyclization of active methylene compounds, cycloisomerization of *o*-alkynylphenols, and intramolecular Heck-type reaction are the most frequently used transformations in this category. Additionally, transition-metal-catalyzed (or mediated) direct oxidative annulation of phenolic substrates with alkynes through the C–H bond activation has emerged as a versatile tool over the past decade.[3,4] These methods are particularly effective for the synthesis of C2 and/or C3 substituted benzofurans, whereas little success has so far been achieved in constructing C2,C3-non-substituted benzofuran scaffolds (Scheme 1a).[5] A subclass of these, C4-substituted benzofurans, have remained the most inaccessible derivatives because the ring closure would not preferentially takes place at the sterically congested site.[6] Alternative synthetic processes are usually lengthy and low yielding,[7] but they are nevertheless important motifs widely occurring in potent drug candidates such as a κ-opioid agonist Enadoline[8] and an orexin receptor antagonist SB-649868[9] (Scheme 1b). Indeed, a key intermediate for the Enadoline synthesis, 4-benzofuranylmethyl chloride, was prepared from 2,3-dimethylanisole over 8 steps in less than 7% total yield.[10]

To address this difficulty, we envisioned establishing a new synthetic approach based on the vinylene transfer strategy (Scheme 1c).[11] In 2019, we first reported a Rh-catalyzed direct annulation utilizing vinylene carbonate as an oxidizing acetylene surrogate.[11a] This reaction proceeds under neutral conditions without any external oxidant, giving carbonic acid as a

sole side product. Afterward, some research groups have contributed to design relevant reaction systems,[12] whereas only one example for the construction of oxygen heterocycles has been reported by our group.[11c] In this report, we developed a Rh-catalyzed direct annulation of readily available 3-hydroxybenzoic acid (*m*-salicylic acid) derivatives to achieve the selective synthesis of C4-substituted benzofurans (Scheme 1c). The use of Weinreb amide as a directing group would reinforce the synthetic utility of this protocol.[13] It is notable that a sterically less demanding Cp (cyclopentadienyl) ligand exhibited superior activity to the standard Cp* (Me5Cp) ligand. By virtue of pioneering contributors in this field, a number of sterically and electronically modified Cp ligands have been introduced into the direct C–H functionalization using group 9 metal complexes;[14,15] however, the simple unsubstituted Cp ligand has attracted considerable interest only in last several years.[16] We conducted DFT calculations to evaluate the ligand effect on the reaction efficiency.

To test the feasibility of the concept, we first conducted a model reaction of an *N,N*-diethylbenzamide **1a** with vinylene carbonate (VC) in the presence of $[Cp*Rh(MeCN)_3][SbF_6]_2$ catalyst in DCE solvent (Scheme 2). Although the desired C4-substituted benzofuran **2a** (48% yield) was obtained along with a lactone byproduct **3a** (24% yield),[17] the formation of **3a** could not be sufficiently suppressed after several attempts.

Scheme 2. An Initial Attempt
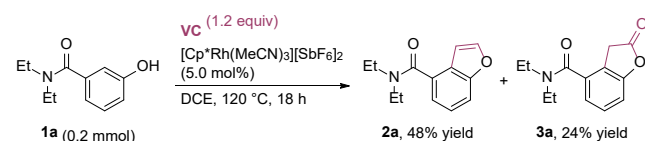
Scheme 3. Evaluation of the Ligand Effect [a]
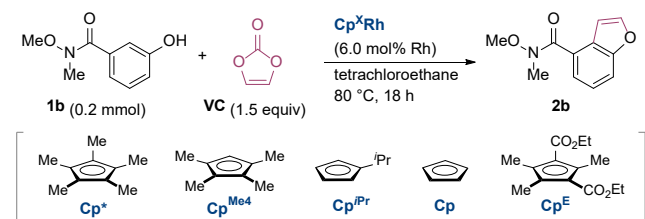
| entry	catalyst	**2b** yield [b]
1	$[Cp*Rh(MeCN)_3][SbF_6]_2$	30%
2	$[Cp^{Me4}RhCl_2]_2$ + AgSbF6 (15 mol%)	17%
3	$[Cp^{iPr}RhI_2]_2$ + AgSbF6 (15 mol%)	47%
4	$[CpRhI_2]_2$ + AgSbF6 (15 mol%)	55%
5	$[Cp^{E}RhCl_2]_2$ + AgSbF6 (15 mol%)	50%
6	$[CpRh(MeCN)_3][SbF_6]_2$	76%[c] (79%)
7 [d]	$[CpRh(MeCN)_3][SbF_6]_2$	(68%)

[a] Reaction conditions: **1b** (0.2 mmol), vinylene carbonate (0.3 mmol), and Rh catalyst (6.0 mol %) in tetrachloroethane (1.0 mL) at 80 °C for 18 h under N2. [b] Determined by NMR analysis. Isolated yield in parentheses. [c] Average of three runs. [d] 1.0 mmol scale.

Intriguingly, the use of Weinreb amide as the directing group was beneficial for solving this problem, and the target product **2b** was obtained in 30% yield (Scheme 3, entry 1). The corresponding lactone was not detected in this case. We thought further improvement of the yield was difficult with the standard

Cp* ligand (see the Supporting Information for additional data) and thus investigated the activity of several Rh complexes bearing sterically- and electronically-modified cyclopentadienyl ligand for the reaction of **1b** with vinylene carbonate. In combination with AgSbF6 as an anion donor, $[Cp^{Me4}RhCl_2]_2$ complex afforded **2b** in 17% yield (entry 2), whereas sterically less demanding Cp^{iPr} and Cp complexes gave the product in higher yields (entries 3 and 4). An electron deficient Cp^E ligand was moderately effective as well (entry 5). To our delight, further improvement of the productivity was achieved adopting a pre-activated cationic complex $[CpRh(MeCN)_3][SbF_6]_2$ (entry 6), whose structure was firstly characterized in this report (CCDC 2144305). This reaction was successfully performed in 1.0 mmol scale to deliver **2b** in 68% isolated yield (entry 7).

The use of versatile Weinreb amide as the directing group would highlight the significance of this reaction system. To demonstrate the synthetic utility, we examined some derivatization of the coupling product **2b** and **2c** (Scheme 4a). The controlled mono-addition of Grignard and organolithium reagents gave the corresponding ketone derivatives **4**, **5**, and **6** in high yields. A β-keto phosphonate **6** would be a useful reagent for the Horner-Wadsworth-Emmons condensation. Selective amide reduction to the aldehyde **7** was achieved upon treatment with LiAlH4. A base-mediated difluoromethylation using TMSCHF2 was effective to obtain the corresponding fluorinated ketone **8** in 90% yield.[18] The amide group was readily hydrolyzed to give benzofuran-4-carboxylic acid (**9**) in 83% yield. The directing group could be utilized for another direct C–H functionalization:[19] **2b** was coupled with butyl acrylate in the presence of Cp*Rh catalyst to give the C3-functionalized product **10** (Scheme 4b). The aldehyde **7** was successfully converted to the homologated acid **12** adopting Snowden's method (Scheme 4c),[20,21] and this compound would be a valuable synthetic intermediate for Enadoline and analogous drug candidates.

Scheme 4. Derivatization of the Coupling Products

(a) Derivatization of Weinreb amide directing group

(b) Additional C–H functionalization

(c) Aldehyde to homologated carboxylic acid
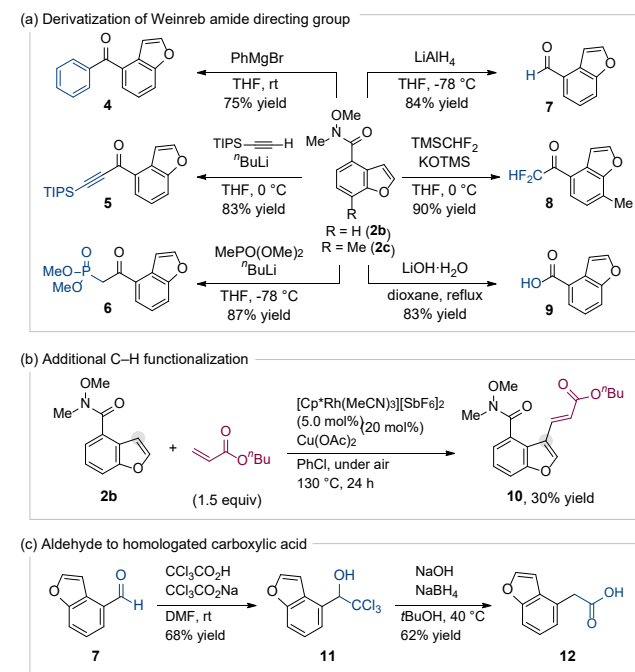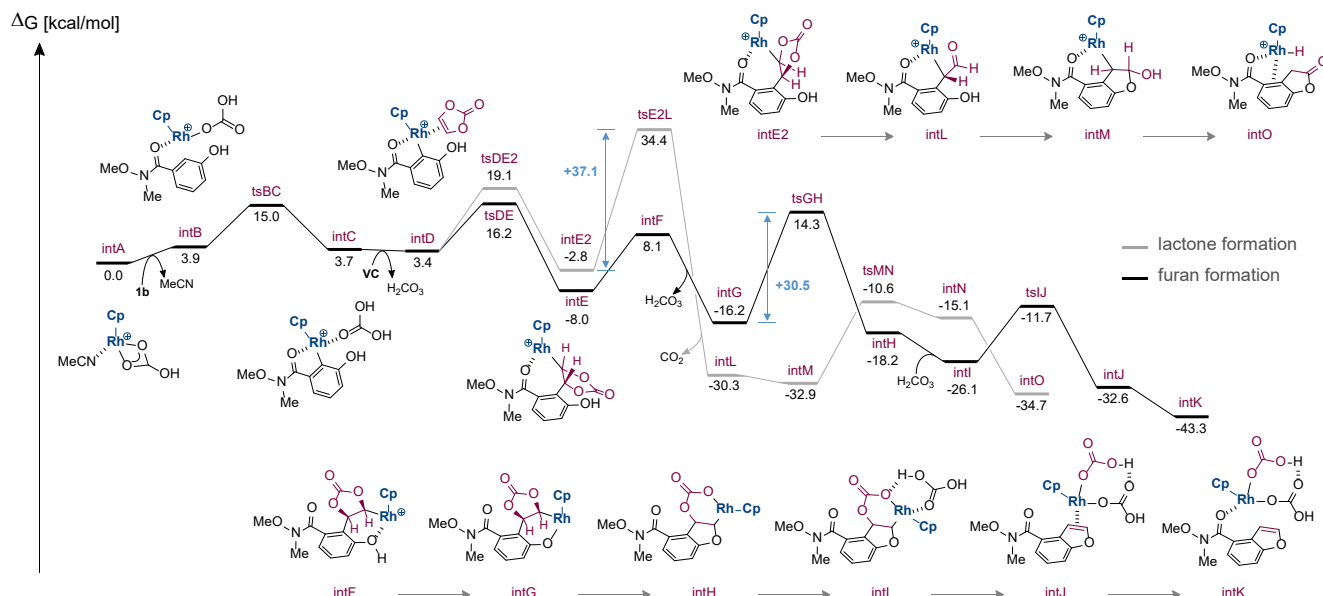
Figure 1. Gibbs free energy profile of the reaction. The calculations were conducted at the ωB97X-D/6-311+G(d,p)&SDD//ωB97X-D/6-31G+(d,p)&LanL2DZ level with IEF-PCM(DCE) solvation.

Scheme 5. Proposed Reaction Mechanism
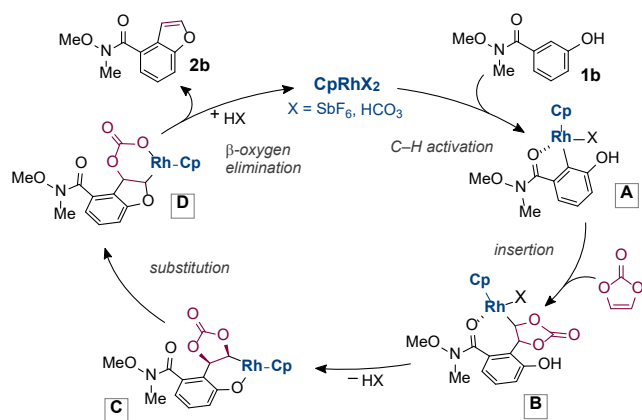
Based on previous reports,[11,22] we would like to propose a catalytic cycle as shown in Scheme 5. The reaction initiates with the coordination-assisted C–H bond activation at the proximal position to form an intermediate **A**. Coordination and migratory insertion of vinylene carbonate into the Rh–C bond afford a seven-membered complex **B**, where the β-hydrogen elimination is configurationally restricted. Thereafter, this is converted to the corresponding phenoxy complex **C** with the liberation of an acid molecule. Intramolecular nucleophilic substitution at the carbon atom adjacent to the Rh takes place, and the subsequent β-oxygen elimination from an intermediate **D** produces the benzofuran **2b**.

We conducted DFT calculations on the proposed reaction pathway to shed light on the mechanism. Figure 1 displays an energy profile relative to a cationic Rh complex **intA**. After the coordination of **1b**, the proximal C–H bond is activated adopting the bicarbonate anion as an internal base with an activation barrier $\Delta G^{\ddagger} = +11.1$ kcal/mol (**intB**→**intC**), whereas a comparable value $\Delta G^{\ddagger} = +12.3$ kcal/mol was obtained for the C–H activation at the other side, i.e., para to the hydroxyl group (**intB2**→**intC2**, see the Supporting Information). These processes are suggested to be reversible under the catalytic conditions. For

the insertion of vinylene carbonate to the Rh–C bond, two possible configurations were considered from **intD**. A transition state in which the carbonate moiety is located distant from the Cp ligand requires lower energy (**tsDE**, $\Delta G^{\ddagger} = +12.9$ kcal/mol) than that of the other (**tsDE2**, $\Delta G^{\ddagger} = +15.7$ kcal/mol). The amide directing group dissociates from the metal, and the corresponding six-membered phenoxy complex forms (**intE**→**intG**). The direct reductive elimination from **intG** or its H_2CO_3 adduct was not feasible, whereas a concerted intramolecular S_N2-type reaction was calculated to have an acceptable energy barrier (**tsGH**, $\Delta G^{\ddagger} = +30.5$ kcal/mol). This step would be rate-limiting for the benzofuran production, and the energy value is reasonable for the reaction temperature. After the coordination of an H_2CO_3 molecule (**intI**), another transition state for the β-oxygen elimination (**tsIJ**, $\Delta G^{\ddagger} = +14.4$ kcal/mol) is traversed to eventually give the coupling product **2b**. On the other hand, **intE2** does not lead to the benzofuran formation because the leaving carbonate oxygen atom cannot occupy the opposite side to the attacking phenolic hydroxyl group. Alternatively, 1,2-rhodium shift occurs through a transition state **tsE2L** with an energy barrier $\Delta G^{\ddagger} = +37.1$ kcal/mol. According to the IRC calculation, this directly undergoes decarboxylation to afford an enolate complex **intL** (for details, see the Supporting Information). The following hemiacetal formation (**intM**), β-hydrogen elimination (**tsMN**, $\Delta G^{\ddagger} = +22.3$ kcal/mol), and tautomerization (**intN**→**intO**) would afford a lactone product, which was not detected under the optimized reaction conditions. Protonation and dehydration of **intM** might afford **2b**; however, we assume this is not a main productive pathway.

To investigate the ligand effect on the reaction efficiency, we also calculated an energy profile from **intA** to **intH** adopting Cp* as the supporting ligand (Figure 2, top). In path B, considerably higher energy values were obtained for **intC**, **intD**, and **tsDE** probably due to the sterically demanding nature of the Cp* ligand. Indeed, dihedral angels between the benzene ring and the carbonyl group are significantly larger for the path B (23.2 ° for **intC**, 19.9 ° for **intD**) as compared to those of path A (17.4 ° for **intC**, 12.1 ° for **intD**). Additionally, bond lengths within the four-membered transition state **tsDE** are relatively

shorter for the path A to construct a "compact TS".[16d] As a result, the Cp ligand would significantly accelerate the C–H activation and the migratory insertion steps. The C–H activation step computed for Cp* requires 16.4 kcal/mol and it is endothermic by 9.1 kcal/mol, which facilitates the reversible process and would invalidate the reaction to proceed. We also examine the electronic effect of Cp and Cp* ligands by Natural bond orbital (NBO) analysis; however no significant difference in total interaction energies was observed (for details, see the supporting information).
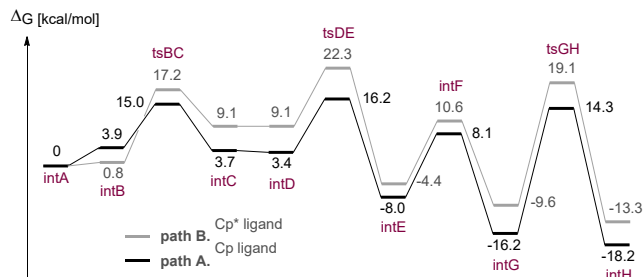
Figure 2. Partial Gibbs free energy profile of the reaction with Cp (path A) and Cp* (path B) as the ligand calculated at the ωB97X-D/6-311+G(d,p)&SDD//ωB97X-D/6-31G+(d,p)&LanL2DZ level with IEF-PCM(DCE) solvation.

Finally, we utilized the developed protocol to the synthesis of substituted benzofurans (Scheme 6). Ortho-substituted phenols (**1c, 1d**) and meta-substituted phenols (**1e–1i**) were successfully converted to the corresponding benzofurans in moderate to high yields, whereas para-substituted phenols were not applicable (not shown). It is notable that the chloro (**1e**), bromo (**1f**), and alkynyl (**1i**) functionalities were tolerated under the catalytic conditions, which would be beneficial for further decollation of the benzofuran scaffold.

Scheme 6. Scope of Substrate and Post-Functionalization [a]
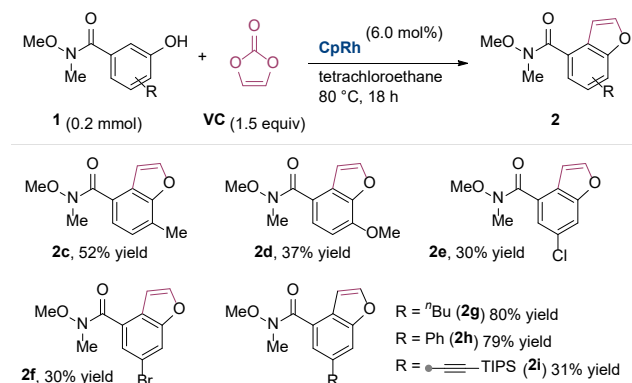
[a] Reaction conditions: **1b** (0.2 mmol), vinylene carbonate (0.3 mmol), and Rh catalyst (6.0 mol %) in tetrachloroethane (1.0 mL) at 80 °C for 18 h under N_2.

In summary, we have established a new entry of Rh-catalyzed vinylene transfer strategy for the synthesis of C2,C3-nonsubstituted benzofurans. The synthetic utility of this reaction system would be highlighted by the following features: (1) direct vinylene annulation under neutral and oxidant-free conditions, (2) selective and effective construction of commonly less accessible C4-substituted benzofurans from readily available *m*-salicylic acid derivatives, and (3) varied possible derivatization of the Weinreb amide directing group to versatile functionalities.

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Author Contributions

J.K. and Y.N. conducted the experiments and corrected the product identification data. M.M. organized the project. The manuscript was written by Y.N. and M.M.

Notes

The authors declare no competing financial interest.

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