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# Rhodium(III)-Catalyzed [4+1] Annulation of Aromatic and Vinylic Carboxylic Acids with Allenes: An Efficient Method Towards Vinyl-Substituted Phthalides and 2-Furanones

Parthasarathy Gandeepan, Pachaiyappan Rajamalli, and Chien-Hong Cheng*[a]

**Abstract:** A highly regio- and stereoselective synthesis of 3,3-disubstituted phthalides from aryl carboxylic acids and allenes using a rhodium(III) catalyst has been demonstrated. The reaction features broad functional group tolerance and provides a simple and straightforward route to the synthesis of various 3-vinyl-substituted phthalides. Furthermore, the catalytic reaction can also be applied to the synthesis of biologically active 5-vinyl-substituted 2-furanones from α,β-unsaturated carboxylic acids and allenes. The reactions proceed through a carboxylate-assisted *ortho*-C–H activation and [4+1] annulation. The preliminary mechanistic studies suggest that a C–H cleavage is the rate-determining step.

## Introduction

Transition-metal-catalyzed C–H activation has evolved as a promising strategy in organic synthesis and has been widely employed in the synthesis of natural and unnatural compounds.[1,2] In particular, directing-group (DG)-assisted *ortho*-C–H cleavage followed by coupling with π components is popular in the synthesis of hetero- and carbocyclic synthesis.[3] Among the π-coupling partners, alkyne and alkenes have been heavily tested, but allenes are less explored.[4] Our continuing interest in C–H activation reactions[5] and allene chemistry has prompted us to explore allenes as π components in C–H activation reactions.[6] Herein we report a practical method for the synthesis of 3,3-disubstituted phthalides from aryl carboxylic acids and allenes. It is worth mentioning that many C–H activation reactions are known involving carboxylic acids with different coupling partners, but allenes have never been studied.[7]

Phthalide (3*H*-isobenzofuran-1-one) is an important structural motif found in many natural and bioactive compounds (Figure 1).[8] They have also proven to be potential building blocks in organic synthesis.[9] Several strategies for their synthesis using transition-metal catalysts involving addition and coupling reactions have been developed.[8b,10] However, these reactions require functionalized starting compounds and are often limited by the availability of the starting compounds. Therefore the development of a new C–H activation route that employs less functionalized starting compounds for the synthesis of phthalide derivatives is highly sought after.[11]

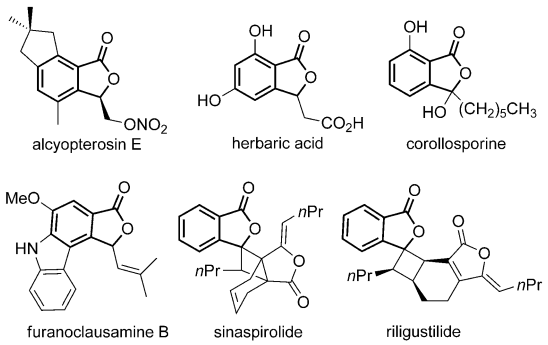


**Figure 1.** Phthalides containing natural and bioactive compounds.

## Results and Discussion

### Reaction optimization

The treatment of benzoic acid (**1a**; 0.60 mmol) and 2,3-butadienylbenzene (**2a**; 0.90 mmol) in the presence of 2 mol% $[RhCl_2Cp^*]_2$ and AgOAc (1.260 mmol) in $CH_3CN$ (3 mL) at 60 °C for 20 h gave (*E*)-3-methyl-3-styrylisobenzofuran-1(3*H*)-one (**3aa**) in an isolated yield of 88% (Table 1, entry 11). This compound was thoroughly characterized by $^1H$ and $^{13}C$ NMR spectroscopy and HRMS. The choice of solvent was crucial for the success of the reaction (Table 1, entries 1–9). Among the solvents tested, acetonitrile was the most suitable to give product **3aa** in high yield. Silver salts were found to be better oxidants than the other inorganic and organic oxidants tested for this reaction, with silver acetate being the most desirable for phthalide formation among the silver oxidants tested (Table 1, entries 11–16). Control experiments revealed that no product was obtained in the absence of either the rhodium catalyst or AgOAc (entries 20 and 21).

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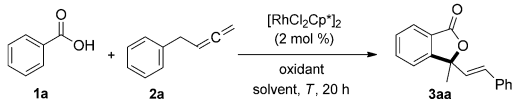
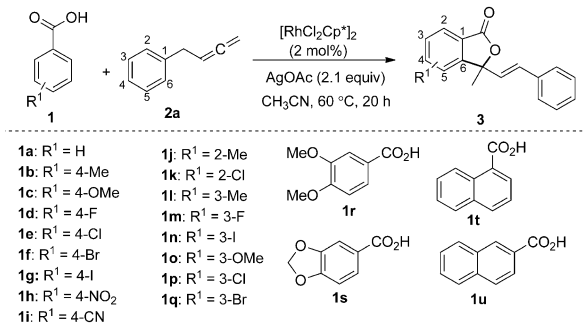
**Table 1.** Optimization of the reaction to give phthalide **3aa**.[a]




| Entry | Oxidant (amount [equiv]) | Solvent | $T$ [°C] | Yield [%][b] |
|---|---|---|---|---|
| 1 | $Cu(OAc)_2$ (2.1) | MeOH | 60 | 12 |
| 2 | $Cu(OAc)_2$ (2.1) | DCE | 60 | 16 |
| 3 | $Cu(OAc)_2$ (2.1) | 1,4-dioxane | 60 | 6 |
| 4 | $Cu(OAc)_2$ (2.1) | toluene | 60 | – |
| 5 | $Cu(OAc)_2$ (2.1) | DMF | 60 | – |
| 6 | $Cu(OAc)_2$ (2.1) | THF | 60 | – |
| 7 | $Cu(OAc)_2$ (2.1) | EtOAc | 60 | 15 |
| 8 | $Cu(OAc)_2$ (2.1) | $CH_3CN$ | 60 | 40 |
| 9 | $Cu(OAc)_2$ (2.1) | $CH_3NO_2$ | 60 | 31 |
| 10 | $Cu(OAc)_2$ (2.1) | $CH_3CN$ | 80 | 28 |
| 11 | AgOAc (2.1) | $CH_3CN$ | 60 | 91 (88)[c] |
| 12 | AgOAc (2.1) | $CH_3CN$ | 50 | 68 |
| 13 | AgOAc (2.1) | $CH_3NO_2$ | 60 | 62 |
| 14 | $Ag_2CO_3$ (1.1) | $CH_3CN$ | 60 | 75 |
| 15 | $Ag_2O$ (1.1) | $CH_3CN$ | 60 | 36 |
| 16 | $AgOCOCF_3$ (2.1) | $CH_3CN$ | 60 | 30 |
| 17 | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 60 | 11 |
| 18 | BQ[d] (2.1) | $CH_3CN$ | 60 | – |
| 19 | $O_2$ (1 atm) | $CH_3CN$ | 60 | – |
| 20 | AgOAc (2.1) | $CH_3CN$ | 60 | –[e] |
| 21 | – | $CH_3CN$ | 60 | – |

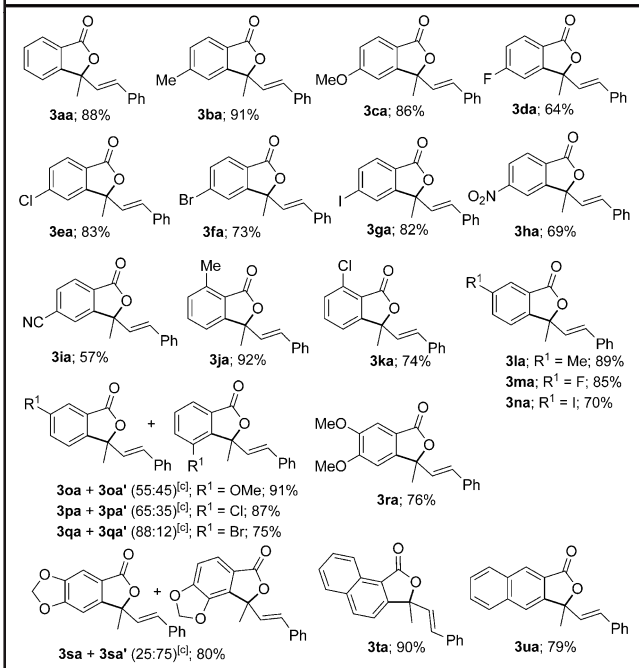
[a] All reactions were carried out by using benzoic acid **1a** (0.60 mmol), allene **2a** (0.90 mmol), $[RhCl_2Cp^*]_2$ (0.012 mmol), and oxidant in solvent (3 mL) at $T$ for 20 h. [b] Yields were determined by the $^1H$ NMR integration method using mesitylene as the internal standard. [c] The isolated yield is given in parentheses. [d] BQ = 1,4-benzoquinone. [e] No $[RhCl_2Cp^*]_2$ was used.

**Table 2.** Scope of arenecarboxylic acids in the reactions leading to phthalide formation.[a,b]




**1a**: $R^1$ = H
**1b**: $R^1$ = 4-Me
**1c**: $R^1$ = 4-OMe
**1d**: $R^1$ = 4-F
**1e**: $R^1$ = 4-Cl
**1f**: $R^1$ = 4-Br
**1g**: $R^1$ = 4-I
**1h**: $R^1$ = 4-$NO_2$
**1i**: $R^1$ = 4-CN
**1j**: $R^1$ = 2-Me
**1k**: $R^1$ = 2-Cl
**1l**: $R^1$ = 3-Me
**1m**: $R^1$ = 3-F
**1n**: $R^1$ = 3-I
**1o**: $R^1$ = 3-OMe
**1p**: $R^1$ = 3-Cl
**1q**: $R^1$ = 3-Br




[a] All reactions were performed by using arenecarboxylic acid **1** (0.80 mmol), allene **2a** (1.20 mmol), $[Cp^*RhCl_2]_2$ (0.016 mmol), and AgOAc (1.680 mmol) in $CH_3CN$ (4.0 mL) at 60 °C for 20 h. [b] Isolated yields. [c] The ratios of regioisomers are given in parentheses and were determined by $^1H$ NMR analysis.

### Scope of aryl carboxylic acids in the synthesis of phthalides

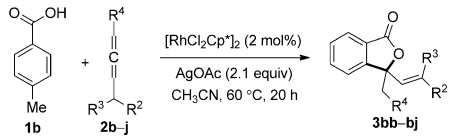
To realize the scope of the reaction, we examined the performance of various substituted benzoic acids with **2a** under the optimized reaction conditions and the results are shown in Table 2. The reaction of *p*-toluic acid (**1b**) and *p*-anisic acid (**1c**) gave the desired products **3ba** and **3ca** in yields of 91 and 86%, respectively. Halo-substituted benzoic acids were well tolerated under the reaction conditions, giving the expected phthalide products. Thus, *p*-fluoro-, *p*-chloro, *p*-bromo, and *p*-iodo-substituted benzoic acids (**1d–g**) gave the corresponding desired products **3da–3ga** in high yields. The bromo- and iodo-substituted products **3fa** and **3ga** are appropriate for further functionalization through cross coupling. The reaction also worked well with benzoic acids bearing electron-withdrawing groups; *p*-nitro- and *p*-cyano-substituted benzoic acids (**1h** and **1i**) gave the expected [4+1] cycloaddition products **3ha** and **3ia** in good yields. Sterically hindered *ortho*-substituted benzoic acids were also compatible under the reaction conditions and yielded the expected phthalides. Thus, the reactions of 2-methyl- and 2-chloro-substituted benzoic acids (**1j** and **1k**) with **2a** afforded the products **3ja** and **3ka** in yields of 92 and 74%, respectively.

Next, we examined the reactions of a variety of *meta*-substituted benzoic acids (**1l–q**) with **2a**. 3-Methyl-, 3-fluoro-, and 3-iodo-substituted benzoic acids (**1l–n**), selectively functionalized at the less hindered *ortho* position, gave the desired phthalides **3la–na** in yields of 70–89%. However, 3-methoxy-, 3-chloro-, and 3-bromo-substituted benzoic acids gave mixtures of regioisomeric products in high yields. A single regioisomeric product **3ra** was obtained from the reaction of **1r** with **2a**, but piperonylic acid (**1s**) delivered two regioisomeric products **3sa** and **3sa′** in a ratio of 3:1. The results obtained suggest that the regioselectivity of the C–H cleavage in *meta*-substituted benzoic acids is controlled by both electronic and steric effects.[12] Under the optimized reaction conditions, 1- and 2-naphthoic acid (**1t** and **1u**) also yielded the expected phthalides **3ta** and **3ua** in yields of 90 and 79%, respectively.

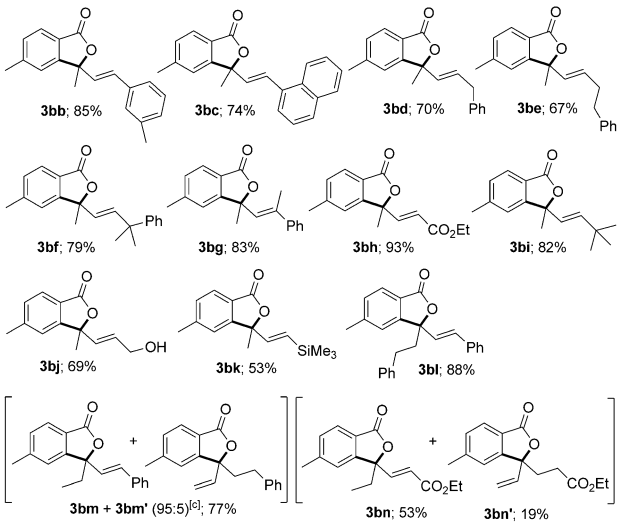
### Scope of allenes in the synthesis of phthalides

Next, we investigated the scope of allenes in this $Rh^{III}$-catalyzed *ortho*-C–H activation of aryl carboxylic acids. The reactions of a variety of allenes were examined with **1b** and their results are shown in Table 3. 3-Methylbenzylallene (**2b**) gave phthalide

**Table 3.** Scope of allenes in the reactions leading to phthalide formation.[a,b]




**2b**; $R^2$ = 3-Me-Ph, $R^3$ = $R^4$ = H
**2c**; $R^2$ = 1-naphthyl, $R^3$ = $R^4$ = H
**2d**; $R^2$ = $CH_2Ph$, $R^3$ = $R^4$ = H
**2e**; $R^2$ = $CH_2CH_2Ph$, $R^3$ = $R^4$ = H
**2f**; $R^2$ = $C(CH_3)_2Ph$, $R^3$ = $R^4$ = H
**2g**; $R^2$ = Ph, $R^3$ = Me, $R^4$ = H
**2h**; $R^2$ = $CO_2Et$, $R^3$ = $R^4$ = H
**2i**; $R^2$ = $C(CH_3)_3$, $R^3$ = $R^4$ = H
**2j**; $R^2$ = $CH_2OH$, $R^3$ = $R^4$ = H
**2k**; $R^2$ = $SiMe_3$, $R^3$ = $R^4$ = H
**2l**; $R^2$ = Ph, $R^3$ = H, $R^4$ = $CH_2Ph$
**2m**; $R^2$ = Ph, $R^3$ = H, $R^4$ = Me
**2n**; $R^2$ = $CO_2Et$, $R^3$ = H, $R^4$ = Me




[a] All reactions were performed by using *p*-toluic acid (**1b**; 0.80 mmol), allene **2** (1.20 mmol), $[Cp^*RhCl_2]_2$ (0.016 mmol), and AgOAc (1.68 mmol) in $CH_3CN$ (4.0 mL) at 60 °C for 20 h. [b] Isolated yields. [c] The ratios of regioisomers are given in parentheses and were determined by $^1H$ NMR analysis.

**3bb** in a yield of 85%. Similarly, 1-(buta-2,3-dien-1-yl)naphthalene (**2c**) reacted readily with **1b** to give **3bc** in a yield of 74%. In addition to benzyl-substituted allenes, alkyl-containing allenes (**2d–f**) also underwent the catalytic reaction to afford the desired [4+1] annulation products in good-to-excellent yields (Table 3, products **3bd–bf**). Penta-3,4-dien-2-ylbenzene (**2g**) containing a methyl group at the benzylic position also afforded the corresponding phthalide **3bg** in a yield of 83% under similar reaction conditions. The reaction of ester-substituted allene **2h** with **1b** provided the expected product **3bh** in a yield of 93%. *tert*-Butyl-substituted allene **2i** effectively underwent reaction with **1b** to afford the product **3bi** in a yield of 82%. Similarly, hydroxy- and trimethylsilyl-substituted allenes **2j–2k** also reacted with **1b** to furnish the expected products **3bj** and **3bk**, respectively, in moderate yields. Internal allenes were also reactive under the reaction conditions, giving the desired phthalides in good yields. The reaction of 1,3-dibenzyl-substituted symmetrical allene **2l** with **1b** produced the phthalide product **3bl** in a yield of 88%. However, unsymmetrical internal allenes penta-2,3-dien-1-ylbenzene (**2m**) and ethyl hexa-3,4-dienoate (**2n**) reacted with **1b** to give the regioisomeric products **3bm**+**3bm′** and **3bn**+**3bn′**, respectively, in good yields with high regioselectivity.

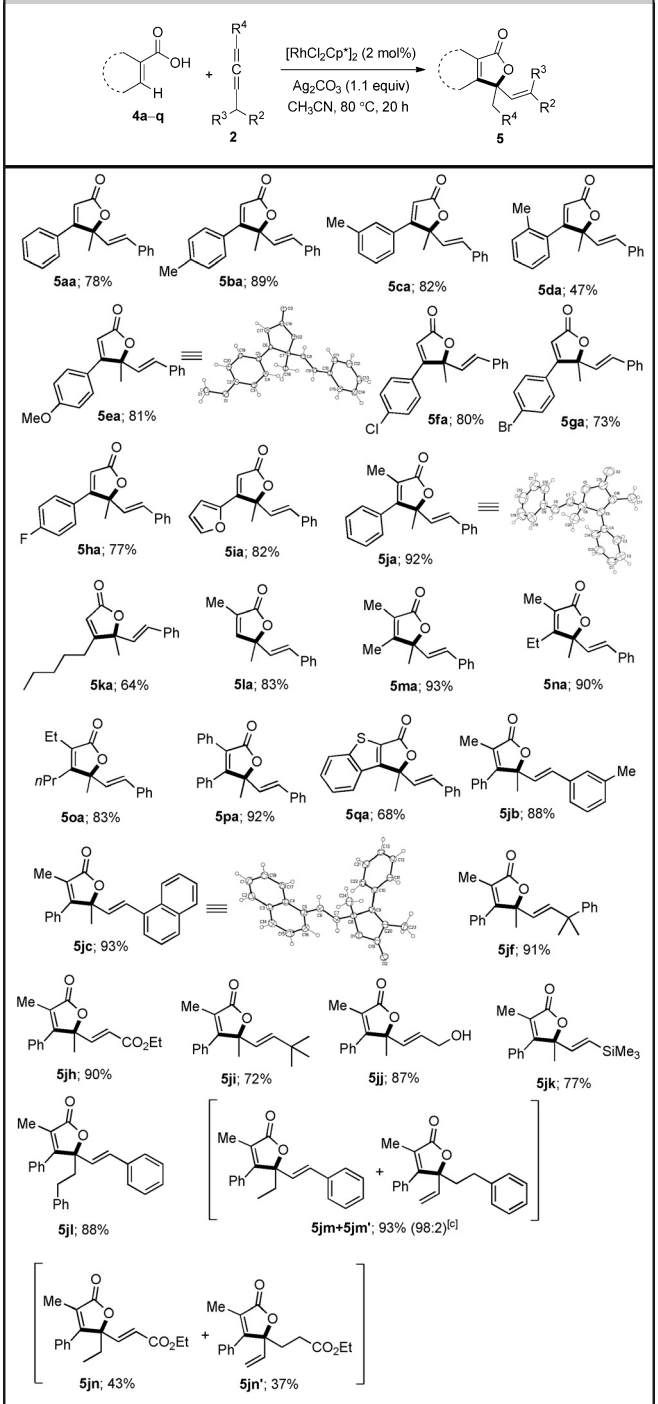
### $Rh^{III}$-catalyzed [4+1] annulation of vinylic carboxylic acids and allenes

The reactions of substituted acrylic acids with allenes catalyzed by the $Rh^{III}$ complex were also investigated.[13] Thus, cinnamic acid (**4a**) was treated with **2a** under reaction conditions similar to those shown in Tables 2 and 3 to give 2-furanone derivative (*E*)-5-methyl-4-phenyl-5-styrylfuran-2(5*H*)-one (**5aa**) in a yield of 28%. Fortunately, the use of $Ag_2CO_3$ instead of AgOAc improved the yield of **5aa** to 61%. Finally, raising the temperature to 80 °C gave **5aa** in an isolated yield of 78%. It is worth mentioning that 2-furanone is an important heterocyclic moiety found in many natural and biologically active molecules and an intermediate in natural product synthesis.[14] Several reports for the synthesis of this type of compounds by cross-coupling and intramolecular cyclization are known,[15] but the synthetic method described herein to obtain 5-vinyl-substituted 2-furanones in a single step from readily available simple starting compounds is unique.

To probe the scope of the formation of 2-furanone derivatives, we investigated the reactions of different cinnamic acids with allenes (Table 4). Thus, the treatment of *o*-, *m*-, and *p*-methylcinnamic acids with **2a** afforded the corresponding [4+1] annulation products **5ba–da** in good yields. Owing to the steric hindrance of the *o*-methyl substituent, the product **5da** was obtained in only a moderate yield. In addition, 4-methoxycinnamic acid (**5e**) smoothly reacted with **2a** to give **5ea** in a yield of 81%. Halogen-substituted cinnamic acids **4f–h** provided the expected products **5fa–ha**, respectively, in yields of 73–80%. Furan-substituted acrylic acid **4i** was also effectively transformed into lactone **5ia** in a yield of 82%. Next, we treated α-methylcinnamic acid (**4j**) with **2a** under the reaction conditions, and the expected product **5ja** was obtained in a yield of 92%. Both α- and β-alkyl-substituted acrylic acids were compatible under the reaction conditions, yielding the desired products **3ka** and **3la** in yields of 64 and 83%, respectively. Similarly, α,β-dialkyl-substituted acrylic acids **5m–o** underwent [4+1] annulation with **2a** to give the corresponding products **5ma–oa** in yields of 83–93%. In a similar manner, 2,3-diphenylacrylic acid (**4p**) also effectively coupled with **2a** to furnish product **5pa** in a yield of 92%. Furthermore, benzothiophene-2-carboxylic acid (**4q**) underwent the $Rh^{III}$-catalyzed [4+1] annulation reaction to give the expected product **5qa** in a yield of 68%.

Next we investigated the scope of allenes in the $Rh^{III}$-catalyzed vinylic C–H activation and [4+1] annulation reactions. Different aryl- and alkyl-substituted terminal allenes efficiently

**Table 4.** Scope of the $Rh^{III}$-catalyzed [4+1] annulation of vinylic carboxylic acids and allenes.[a,b]

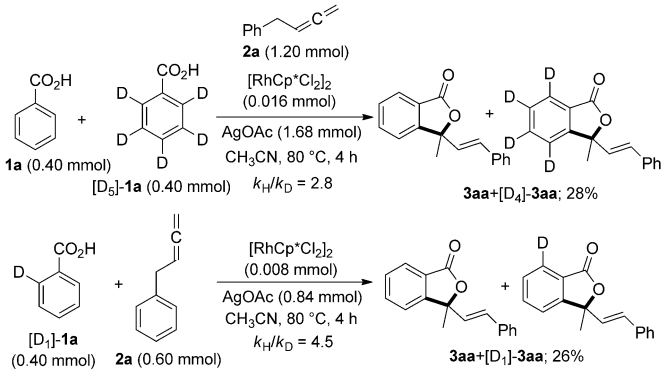



[a] All reactions were performed by using vinyl carboxylic acid **4** (0.80 mmol), allene **2** (1.20 mmol), $[Cp^*RhCl_2]_2$ (0.016 mmol), and $Ag_2CO_3$ (0.88 mmol) in $CH_3CN$ (4.0 mL) at 80 °C for 20 h. [b] Isolated yields. [c] The ratios of regioisomers are given in parentheses and were determined by $^1H$ NMR analysis.

participated in the reaction with α-methylcinnamic acid (**4j**) to afford the corresponding 2-furanone derivatives in excellent yields. Both symmetrical and unsymmetrical internal allenes were compatible under the reaction conditions, affording the corresponding [4+1] annulation products; mixtures of regioisomeric products were obtained with the unsymmetrical internal allenes (Table 4, products **5jm** and **5jn**). The identities of compounds **5ea**, **5ja**, and **5jc** were further confirmed by single-crystal X-ray structure analysis.[16]

### Mechanistic studies

To understand the inherent nature of the present C–H activation reaction, we determined the inter- and intramolecular kinetic isotope effects (KIEs) of the reaction of **1a** and **2a**. An intermolecular KIE ($k_H/k_D$) of 2.8 was determined for the reaction of benzoic acid (**1a**) and [$D_5$]benzoic acid ([$D_5$]-**1a**) with **2a** (Scheme 1). Furthermore, an intramolecular competition reaction between [$D_1$]benzoic acid ([$D_1$]-**1a**) and **2a** showed a $k_H/k_D$ of 4.5. The large KIEs values observed suggest that the C–H cleavage step is the rate-determining step.[17]

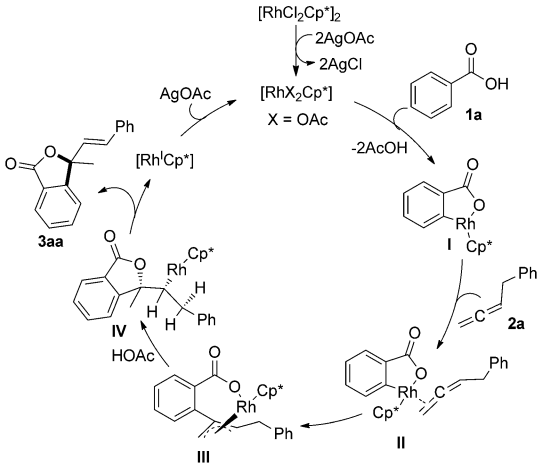



**Scheme 1.** Kinetic isotope experiments.

Based on the experimental results reported herein and existing literature data,[4,13] a plausible catalytic cycle that describes the mechanism of this reaction is presented in Scheme 2 with **1a** and **2a** as the reaction substrates. The catalytic cycle is likely initiated by the removal of chloride from the $Rh^{III}$ dimer to form an unsaturated $Rh^{III}$ complex. Next, the coordination of the carboxylic acid group of **1a** to the $Rh^{III}$ center followed by cyclometalation through *ortho*-C–H cleavage leads to five-membered rhodacycle **I**. The coordination of allene **2a** to **I** to give intermediate **II** and subsequent insertion of the C–Rh bond into an allene double bond of **II** provides π-allylic rhodacycle **III**. Intramolecular nucleophilic addition of the coordinated carboxylate oxygen to the π-allyl of **III** followed by protonation gives intermediate **IV**. β-Hydride elimination of **IV** leaves the final product **3aa** and $Rh^I$. The $Rh^{III}$-active catalyst is regenerated from $Rh^I$ by AgOAc oxidation.

## Conclusion

We have developed a novel and efficient method for the synthesis of 3,3-disubstituted phthalides from aryl carboxylic acids and allenes. The reaction proceeds under mild reaction conditions and has a broad substrate scope. The catalytic reaction




**Scheme 2.** Proposed reaction mechanism.

occurs through $Rh^{III}$-catalyzed carboxylic acid assisted *ortho*-C–H bond activation and annulation reactions. Kinetic isotope experiments revealed that the rate-limiting step involves C–H cleavage. This $Rh^{III}$-catalyzed C–H activation and [4+1] annulation reaction has been successfully extended to $\alpha,\beta$-unsaturated carboxylic acids to give highly substituted 2-furanone. Further extension of this reaction to asymmetric systems and detailed mechanistic studies are now in progress.

## Experimental Section

### General information

Unless otherwise stated, all catalytic reactions were performed under a nitrogen atmosphere on a dual-manifold Schlenk line and in oven-dried glassware. All reagents were purchased commercially and used without further purification. Reagent grade acetonitrile (J. T. Baker) was distilled and dried over $CaH_2$ prior to use. NMR spectra ($^1H$ and $^{13}C$) were measured on a Varian MERCURY 400 MHz spectrometer. High resolution (HR) mass data were measured with a Thermo Finnigan MAT 95XL spectrometer. Infrared spectra were recorded on a HORIBA FT-IR 720 using KBr plates.

### Representative procedure for $Rh^{III}$-catalyzed phthalide formation from aromatic carboxylic acids and allenes

A sealed tube containing benzoic acid **1a** (100 mg, 0.80 mmol), $[Cp^*RhCl_2]_2$ (10 mg, 0.016 mmol), and AgOAc (279 mg, 1.680 mmol) was evacuated and purged with nitrogen gas three times. Then a solution of allene **2a** (156 mg, 1.20 mmol) in $CH_3CN$ (4.0 mL) was added to the system by syringe under a nitrogen atmosphere and the mixture was stirred at 60 °C for 20 h. At the end of the reaction, the mixture was diluted with $CH_2Cl_2$ (10 mL) and filtered through a short pad of Celite, which was washed with $CH_2Cl_2$ (3×20 mL). The combined filtrates were concentrated under reduced pressure and the crude mixture purified by silica gel column chromatography using *n*-hexane/EtOAc (80:20) as eluent to afford the desired pure product **3aa** in a yield of 88% (176 mg).

**(*E*)-3-Methyl-3-styrylisobenzofuran-1(3*H*)-one (3aa)**: Pale-yellow oily liquid (176 mg, 88%); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.90 (d, $J$ = 8.0 Hz, 1H), 7.69 (t, $J$ = 7.6 Hz, 1H), 7.53 (t, $J$ = 8.4 Hz, 1H), 7.46 (d, $J$ = 7.6 Hz, 1H), 7.36–7.26 (m, 5H), 6.70 (d, $J$ = 16.0 Hz, 1H), 6.37 (d, $J$ = 16.0 Hz, 1H), 1.85 ppm (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 169.6 (ester carbonyl), 152.9 (C), 135.5 (C), 134.2 (CH), 130.2 (CH), 129.1 (CH), 128.6 (3 CH), 128.2 (CH), 126.6 (2 CH), 125.8 (CH), 125.1 (C), 121.6 (CH), 86.5 (C), 25.8 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 2923, 1758, 1280, 1126, 1033 and 694 $cm^{-1}$; HRMS ($EI^+$): *m/z* calcd for $C_{17}H_{14}O_2$: 250.0994; found: 250.1001.

### Representative procedure for $Rh^{III}$-catalyzed 2-furanone formation from vinyl carboxylic acids and allenes

A sealed tube containing cinnamic acid **4a** (118 mg, 0.80 mmol), $[Cp^*RhCl_2]_2$ (10 mg, 0.016 mmol), and $Ag_2CO_3$ (243 mg, 0.880 mmol) was evacuated and purged with nitrogen gas three times. Then a solution of allene **2a** (156 mg, 1.20 mmol) in $CH_3CN$ (4.0 mL) was added to the system by syringe under a nitrogen atmosphere and the mixture was stirred at 80 °C for 20 h. At the end of the reaction, the mixture was diluted with $CH_2Cl_2$ (10 mL) and filtered through a short pad of Celite, which was washed with $CH_2Cl_2$ (3×20 mL). The combined filtrates were concentrated under reduced pressure and the crude mixture purified by silica gel column chromatography using *n*-hexane/EtOAc (80:20) as eluent to afford the desired pure product **5aa** in a yield of 78% (172 mg).

**(*E*)-5-Methyl-4-phenyl-5-styrylfuran-2(5*H*)-one (5aa)**: Pale-yellow oily liquid (172 mg, 78%); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60 (d, $J$ = 6.4 Hz, 2H), 7.46–7.29 (m, 8H), 6.80 (d, $J$ = 16.0 Hz, 1H), 6.35 (s, 1H), 6.34 (d, $J$ = 16.0 Hz, 1H), 1.85 ppm (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 171.5 (ester carbonyl), 170.1 (C), 135.5 (C), 132.9 (CH), 131.0 (CH), 129.9 (C), 129.0 (2 CH), 128.7 (2 CH), 128.6 (CH), 127.8 (2 CH), 127.5 (CH), 126.8 (2 CH), 114.5 (CH), 87.9 (C), 23.7 ppm ($CH_3$); IR (KBr): $\tilde{\nu}$ = 2923, 1751, 1612, 1450, 1241, 964, 771, 694 $cm^{-1}$; HRMS ($EI^+$): *m/z* calcd for $C_{19}H_{16}O_2$: 276.1150; found: 276.1152.

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