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Divergent Synthesis of Isoquinolone and Isocoumarin Derivatives by the Annulation of Benzoic Acid with *N*-Vinyl Amide

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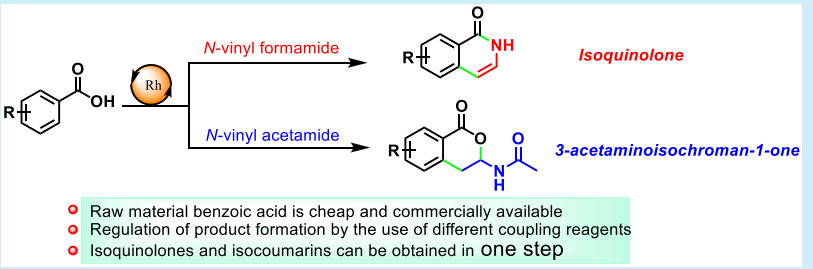
Supporting Information



ABSTRACT: A simple and efficient method for the synthesis of isoquinolone and isocoumarin derivatives is reported. The method for the first time provides a one-step divergent synthesis of important isoquinolone and isocoumarin skeletons from benzoic acid by switching the coupling partners. In addition, a reliable mechanism has been proposed on the basis of experimental investigations, including kinetic isotope effect experiments, ^{13}C labeling experiments, time-tracking experiments, and competitive experiments, as well as DFT calculation studies.

Isoquinolone and isocoumarin belong to six-membered heterocyclic compounds and are useful intermediates in organic synthesis.[1] Isoquinolone molecules have been extensively studied since their discovery in many natural products and biologically active molecules that act as antipsoriasis, antidiabetes, antiviral, hypotension, and anticancer drugs.[2] In addition, 3-acetaminoisochroman-1-one is the central core of many highly complex natural products such as Voacalgine (isolated from Voacanga grandifolia) and bipleiophylline (isolated from Alstonia angustifolia).[3] (Figure 1)

The transition-metal-catalyzed C−H activation of benzoic acid has attracted much attention in recent years because of the cheap and commercially available nature of the reacting materials.[4] Multistep syntheses of isoquinolone derivatives from benzoic acid catalyzed by Rh,[5] Ru,[6]o,[7] Ni,[8] Pd,[9] Fe,[10]nd Ir[11] has been extensively studied (Scheme 1a). The general methods require the installation of an amide directing group on benzoic acid and then preparation of isoquinolone derivatives by reaction with unsaturated compounds via transition metal catalysis. Additional steps are then needed

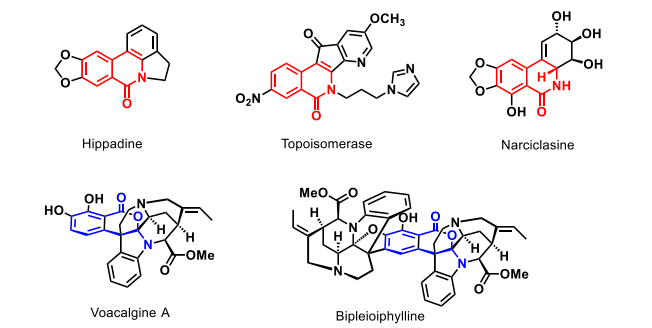
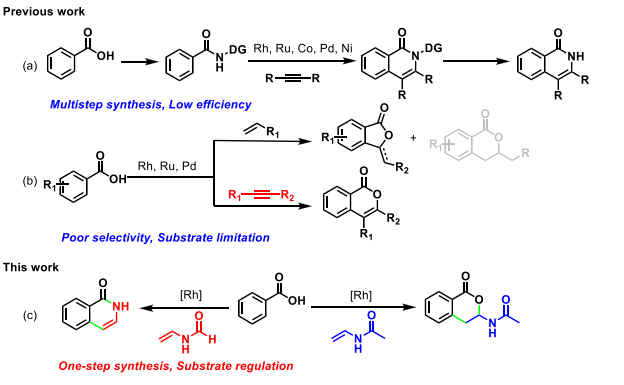


Figure 1. Representative natural and biological molecules containing the isoquinolone and isocoumarin skeleton.

Scheme 1. Preparation of Isoquinolone and Isocoumarin from Benzoic Acid



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to remove the directing group. A one-step synthesis of isoquinolone from benzoic acid has not been reported.

There are many reports concerning the application of benzoic acid in the synthesis of isocoumarin derivatives (Scheme 1b). The Miura team reported the rhodium-catalyzed cyclization of benzoic acid with unsaturated hydrocarbons, in which isocoumarins were prepared from internal alkynes; reaction with olefins mainly resulted in pentacyclic products.[12] Subsequently, a series of reports by other groups concerning the reaction of benzoic acid with various olefins showed that the products were all five-membered cyclization products.[13] Only a few examples for the synthesis of isocoumarin from benzoic acid and olefins have been reported. Lee's group realized the synthesis of isocoumarins via the palladium-catalyzed reaction of various styrenes with benzoic acid which do not bear any *ortho* substituents.[14] Electron-rich geminal-substituted vinyl acetates as the coupling partner were applied to synthesize isocoumarins by Wen's research group.[15] Recently, the Daugulis team successfully synthesized isocoumarins and 3,4-dihydroisocoumarins from benzoic acid and various alkynes and olefins via an elegant cobalt catalyst system.[16] To date, there has been no reported case of the coupling of benzoic acid with *N*-vinyl amide which can provide 3-acetaminoisochroman-1-one as the sole product.

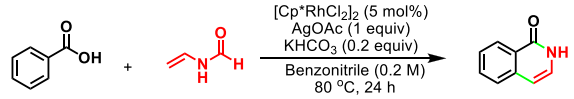
We describe, herein, the divergent synthesis of wide range of isoquinolone and 3-acetaminoisochroman-1-one derivatives from commercially available benzoic acids via rhodium catalyzed annulation reaction. To the best of our knowledge, *N*-vinyl amides have been, for the first time, explored as a coupling reagent to couple with benzoic acids. The two kinds of expected products can be readily obtained just by simply switching the coupling partner between the *N*-vinyl formamide and *N*-vinyl acetamide under similar conditions (Scheme 1c). This methodology provides a simple, efficient, and practical protocol for the synthesis of important drug molecules and natural product skeletons.

We started our studies using benzoic acid and *N*-vinyl formamide as model substrates (reaction A). The desired isoquinolone product was obtained in 79% yield with 0.25 mmol of benzoic acid, 6.0 equiv of *N*-vinyl formamide, 5 mol % $[Cp^*RhCl_2]_2$, 1 equiv of AgOAc, 20 mol % $KHCO_3$ in the 0.2 M of benzonitrile at 80 °C (Table 1, entry1). Due to the self-polymerization of *N*-vinyl formamide,[17] an excess amount was needed. When $Pd(OAc)_2$, $[Cp^*IrCl_2]_2$, $[F_3CSO_3]_3Ni$, $CoCl_2{\cdot}2TPPTs$, $Ru(cod)Cl_2$, and $[Rh(cod)Cl]_2$ were used instead of $[Cp^*RhCl_2]_2$ as catalysts, reaction A did not occur (Table 1, entry 2). The target product can also be obtained in high yield when the reaction is conducted at a temperature of 100 °C (Table 1, entry 3). The effect of other bases, oxidants, and solvents on the reaction was examined, with all of them being inferior to $KHCO_3$, AgOAc, and benzonitrile. No target product was obtained in the absence of oxidant, and the yield was greatly reduced in the absence of base (Table 1, entries 7–8). Reducing the amount of oxidant and increasing the amount of base had a negative influence on the reaction. Catalyst loading has a significant impact on the reaction with a reduction in catalyst loading leading to a large decrease in yield; unreacted benzoic acid was recovered (for details see the Supporting Information).

To our delight, 3-acetaminoisochroman-1-one derivatives are obtained when the coupling reagent is changed from *N*-vinyl formamide to *N*-vinyl acetamide (reaction B). The formation of a certain product can be controlled by careful substrate selection. The optimum conditions for reaction B were determined by adjusting the quantities and type of oxidant, base, solvent, and temperature (Table 2). The 3-acetaminoisochroman-1-one derivative was obtained in 76% yield in the presence of 0.25 mmol benzoic acid, 2.0 equiv of *N*-vinyl acetamide, 5 mol % $[Cp^*RhCl_2]_2$, 2 equiv of AgOAc, and 20 mol % $NaHSO_3$, in 0.25 M of acetonitrile at 60 °C.

With the optimal conditions for reactions A and B in hand, we next investigated the generality of the substrates for the two reactions. As can be seen in Scheme 2, the reaction conditions are amenable to a range of substrates. Various isoquinolone products were obtained in 16%–83% yields and 3-acetamino-isochroman-1-one derivatives in 10%–76% yields. 4-Alkyl benzoic acids can give their corresponding target products in good yield. Following an increase in chain length, the yield decreased slightly; however, branched chains had a positive effect on the two reactions (**2b–2g**, **3b–3g**). 4-Phenylbenzoic acid can also react smoothly giving the isoquinolone (**2h**) and 3-acetaminoisochroman-1-one derivatives (**3h**). The halogenated benzoic acids showed lower reactivity but still reacted to afford the expected products in reasonable to moderate yields (**2i–2l**, **3i–3l**), and the remaining halogen atoms provide the

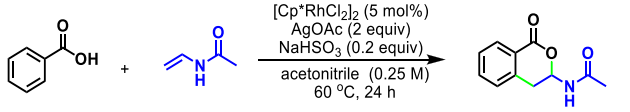
Table 1. Optimization of Reaction A Conditions[a]



entry	deviation from standard conditions	yield of **2a**[b] (%)
1	None	79 (82)[c]
2	Other catalyst instead of $[Cp^*RhCl_2]_2$	0
3	At 100 °C	69[d]
4	In acetonitrile	60[d,e]
5	K_2CO_3 instead of $KHCO_3$	48[d,e]
6	0.5 equiv of AgOAc	54[d,e]
7	In absence of oxidant	trace
8	In absence of base	47

[a]Reaction A standard conditions: benzoic acid (0.25 mmol), *N*-vinyl formamide (1.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOAc (0.25 mmol), $KHCO_3$ (0.05 mmol), benzonitrile (0.2 M), 80 °C, 24 h. [b]Isolated yield. [c]8 equiv of *N*-vinyl formamide. [d]4 equiv of *N*-vinyl formamide. [e]At 100 °C.

Table 2. Optimization of Reaction B Conditions[a]



entry	deviation from standard conditions	yield of **3a**[b] (%)
1	None	76
2	Ag_2CO_3 instead of AgOAc	64
3	At room temperature	NR
4	1 mol % $[Cp^*RhCl_2]_2$	25 (52)[c]
5	$KHCO_3$ instead of $NaHSO_3$	64
6	NaOH instead of $NaHSO_3$	70
7	1 equiv of AgOAc	54[d]

[a]Reaction B standard conditions: benzoic acid (0.25 mmol), *N*-vinyl acetamide (0.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOAc (0.5 mmol), $NaHSO_3$ (0.05 mmol), acetonitrile (0.25 M), 60 °C, 24 h. [b]Isolated yield. [c]2 mol % $[Cp^*RhCl_2]_2$. [d]$KHCO_3$ instead of $NaHSO_3$.

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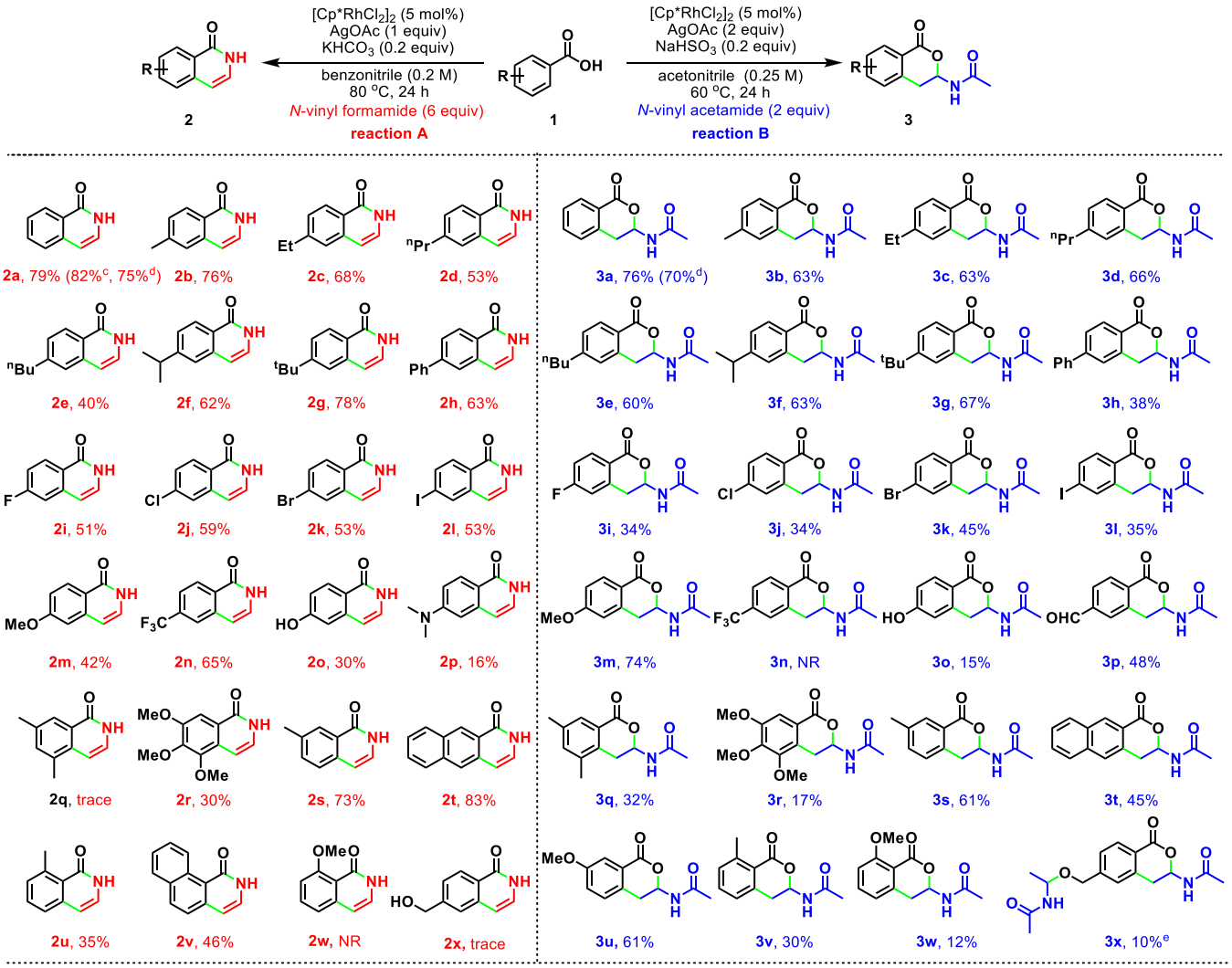
Scheme 2. Scope of Benzoic Acids to Synthesize Isoquinolone and Isocoumarin Derivatives[a,b]



[a]Reaction A conditions: benzoic acid (0.25 mmol), *N*-vinyl formamide (1.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOAc (0.25 mmol), $KHCO_3$ (0.05 mmol), benzonitrile (0.2 M), 80 °C, 24 h. Reaction B conditions: benzoic acid (0.25 mmol), *N*-vinyl acetamide (0.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AgOAc (0.5 mmol), $NaHSO_3$ (0.05 mmol), acetonitrile (0.25 M), 60 °C, 24 h. [b]Isolated yield. [c]8 equiv of *N*-vinyl formamide was used. [d]1.0 mmol of benzoic acid was used. [e]4-Hydroxymethyl benzoic acid as substrate.

possibility for further functionalization. Interestingly, benzoic acids bearing the strong electron-donating MeO group gave 3-acetaminoisochroman-1-one with better yields than the isoquinolones (**3m**, **3u**, **3w** vs **2m**, **2w**). In contrast, the *para*-CF_3 substituted benzoic acid reacted smoothly under condition A to deliver the isoquinolone with good yield, whereas no reaction was observed under condition B (**2n** vs **3n**). Nevertheless, reaction B is compatible with 4-formylbenzoic acid, which could provide 3-acetamino-isochroman-1-one derivative **3p** in a moderate yield of 48%. Moreover, the *meta* substituted benzoic acids could also react with the *N*-vinyl amides under both conditions with good selectivity at the less hindered site; for example, 3-methylbenzoic acid produced the corresponding isoquinolones **2s** and 3-acetaminoisochroman-1-one derivatives **3s** in good yields. Two *meta*-substitutions resulted in low reactivity in both reactions (**2q**, **2r**, **3q**, and **3r**). *Ortho*-methylated benzoic acids can also participate in reactions A and B with reasonable yields (**2u**, **2v**, **3v**); however, the presence of an *ortho*-MeO substituent retarded the reactions greatly (**2w**, **3w**). Finally, the naphthalene-based carboxylic acids are also suitable substrates and gave their products in moderate to good yields (**2t**, **2v**, **3t**). It is worth mentioning that both reactions displayed a moderate functional group tolerance, but the hydroxyl and amino groups are not compatible (**2o**, **2x**, **3o**, **3x**).

To gain insight into the two reactions, a series of experiments were conducted. First, the benzoic acid was treated with the standard conditions A and B in the presence of D_2O (20 equiv) and absence of vinyl amide; [D]-**1a** was obtained in 87% and 75% yield, respectively, indicating that the C−H bond activation is reversible in nature. Then, the deuterium kinetic isotope effects (KIEs) were determined by two independent parallel reactions; the observed k_H/k_D = 2.4 (A) and 1.5 (B) suggested that C−H bond cleavage might not be the rate-determining step in both reactions. Furthermore, the competition reactions by reacting 1:1 mixture of 1a and d_5-1a with vinyl amide under the standard conditions A and B were also investigated, and the k_H/k_D value revealing the product ratio were observed to be 4.5 and 3.8, respectively. (Scheme 3a). Determination of the origin of the carbonyl

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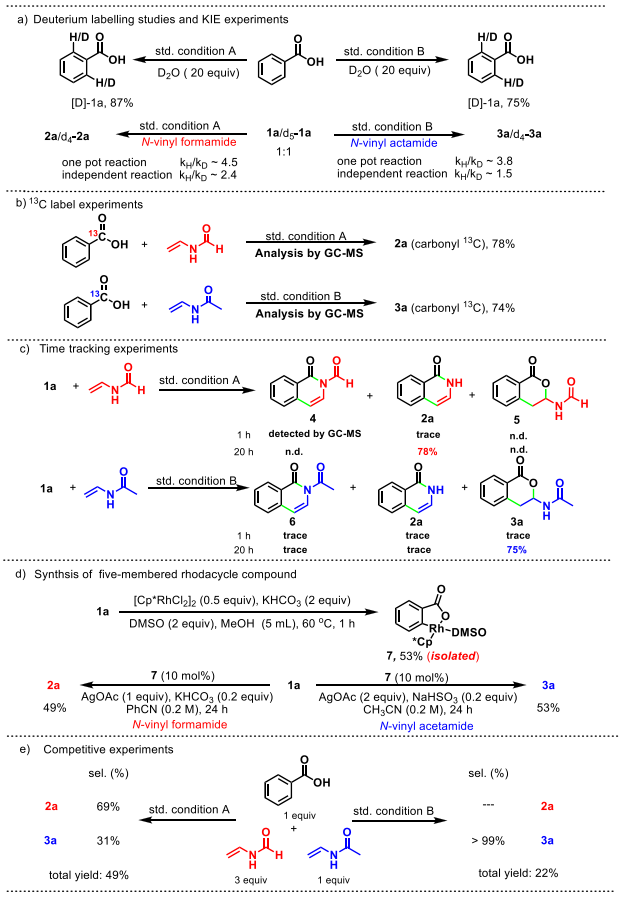
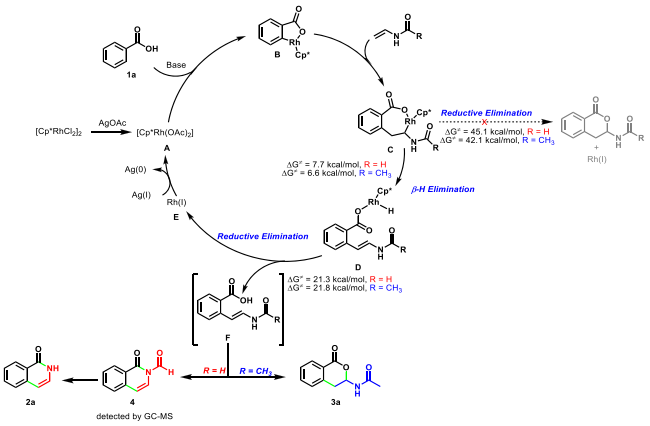
Scheme 3. Mechanistic Studies



carbon of the product is helpful for mechanistic studies. ^{13}C=O labeled benzoic acid was reacted under the standard conditions. Through GS-MS analysis, it can be determined that both the carbonyl carbons of the isoquinolone and 3-acetaminoisochroman-1-one products originate from the benzoic acid substrate (Scheme 3b). We also conducted time tracking experiments. Using GC-MS analysis, compound **4** could be clearly detected in system A after 1 h of reaction, which then disappeared after 20 h. This phenomenon indicates that **4** is an intermediate of reaction A. It is also worth noting that no 3-acetaminoisochroman-1-one product **5** was detected throughout reaction A. On the other hand, 3-acetaminoisochroman-1-one product **3a** was predominant in the reaction B system after 20 h with only a trace amount of isoquinolone **2a** and its precursor **6** being detected (Scheme 3c). To capture the metal intermediate of the reaction, benzoic acid was treated with a stoichiometric amount of $[Cp^*RhCl_2]_2$ at 60 °C in CH_3CN; however, the desired complex could not be isolated. Therefore, we prepared DMSO-stabilized rhodacycle **7**.[18] Compound **7** can be successfully applied in both catalytic reactions A and B to provide isoquinolone and isocoumarin derivatives in 49% and 53% yields, respectively (Scheme 3d). This indicates that the carboxylic moiety acts as a directing group and the *in situ* formed five-membered rhodacycle complex is the possible catalyst resting state. Additionally, we carried two intermolecular competitive experiments between *N*-vinyl formamide and *N*-vinyl acetamide with benzoic acid under conditions A and B, respectively, and the result revealed that both two reactions exhibited good chemoselectivity, especially reaction B, where nearly complete selectivity (>99%) was observed (Scheme 3e).

According to the mechanistic studies and related literature reports,[18] we have proposed a possible reaction mechanism (Scheme 4). First, the catalyst precursor $[Cp^*RhCl_2]_2$ is

Scheme 4. Proposed Mechanism



activated to species **A** in the presence of AgOAc. Species **A** breaks the *ortho* C−H bond of the benzoic acid **1a** with the assistance of base and gives a five-membered rhodacycle intermediate **B**. Subsequently, the C=C bond of the *N*-vinyl amide coordinates with the rhodium center of species **B** and selectively inserts into the C−Rh bond to give the seven-membered ring rhodium intermediate **C**. The intermediate **C** undergoes β-H elimination to Rh−H species **D** with an activation free energy of 7.7 kcal·mol^{-1} (R = H) or 6.6 kcal·mol^{-1} (R = CH_3), whereby a reductive elimination occurs with a free energy barrier of 21.3 kcal·mol^{-1} (R = H) or 21.8 kcal·mol^{-1} (R = CH_3) to form Rh(I) and release the alkenylated product **F**. An intramolecular amide formation takes place (R = H), followed by decarbonylation, to give the product **2a**, or an intramolecular lactonization occurs (R = CH_3) to generate **3a**. Finally, oxidation of Rh(I) with AgOAc regenerates Rh(III) to complete the catalytic cycle. Alternatively, the intermediate **C** may undergo reductive elimination to give the 3-acetaminoisochroman-1-one product directly, but this pathway seems unlikely since the relative free energy required for this step is calculated to be much higher than that for the above-mentioned sequential β-H elimination and reductive elimination pathway by 16.1 (R = H) and 13.7 kcal mol^{-1} (R = CH_3), respectively.

In summary, a novel and efficient Rh-catalyzed annulation of benzoic acids with *N*-vinyl amides has been deveolped, which allows us rapid access to a wide range of important isoquinolone and 3-acetaminoisochroman-1-one skeletons from commercially available benzoic acids by simply switching coupling partners between the *N*-vinyl formamide and *N*-vinyl acetamide. Moreover, a plausible mechanism has been proposed based on a series of mechanistic studies. DFT calculations further support our proposed mechanism.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental details and full spectroscopic data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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