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Reusable rhodium catalyst for the selective transvinylation of sp^2-C linked carboxylic acid

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ABSTRACT

The vinyl benzoate derivatives were successfully synthesized by the transvinylation reactions that vinyl group transferred from vinyl acetate to aromatic carboxylic acids with the recoverable catalyst $RhCl_3 \cdot 3H_2O$. This catalyst features air stable and tolerance of water, good reusable ability, meanwhile, shows high selectivity for aromatic carboxylic acid in the presence of phenolic hydroxyl. With this method, a variety of vinyl benzoate derivatives can be produced with up to 95% yield.

Introduction

Vinyl esters are widely used in polymer chemistry for their finely adjusted properties [1]. Particularly, as one of the most important vinyl esters, vinyl benzoates are widely used in practical chemicals such as degradable materials, coating materials, adhesive and printing ink [2]. They can also be used in organic synthetic chemistry like cycloadditions [3], hydroformylations [4], metathesis reactions [5], and Claisen rearrangements [6], enantioselective cyclopropanation reactions [7], as well as Heck reactions [8].

Vinyl benzoate was practically synthesized by esterification of carboxylic acids with terminal alkynes, nonetheless, the high cost of the raw materials decreased the synthetic value of the reaction (Fig. 1. Entry 1) [9–14]. Other methods for synthetizing vinyl benzoate compounds were also reported such as arylation of esters [15], thermal decomposition of carbonyl(1-oxoalkyl)metalate salts [16], decomposition of anhydrides [17], Baeyer-Villiger oxidation of α,β-unsaturated ketones [18] and so on [19]. However, these reactions require harsh reaction conditions, additional additives, and limited to narrow substrate scope. Consequently, reliable methods toward the facile generation of vinyl benzoates would be very desirable in both organic synthesis and material science research. Among all the synthetic methods, utilizing benzoate acid and vinyl acetate via transvinylation was an economic pathway and this research field had received an increasing attention in recent years. Several catalysts were reported such as $[IrCl(cod)]_2$ [13,20], $AuClPPh_3$ [21] and $PdX_2(CH_3CN)_2$ (X = Cl, Br) (Fig. 1. **Entry 2**) [22,23]. However, the $AuClPPh_3$ catalysts and $[IrCl(cod)]_2$ catalyst require harsh reaction conditions and are limited to a narrow substrate scope. In addition, the efficiency of $PdX_2(CH_3CN)_2$ catalysts was barely satisfactory, such as the transvinylation reactions with a catalytic amount of $PdCl_2(CH_3CN)_2$ resulted in only up to 51% yield. In a word, the above mentioned catalysts usually needed additional ligand and extra solvent (toluene or THF) to promote the reactivity and selectivity toward obtaining the corresponding products with good yields. Herein, as Fig. 1. **Entry 3** shown, we reported a ligand-free, air-stable and less toxic [24] Rh(III) catalyzed selective transvinylation reaction to synthesize the vinyl benzoates under the neat reaction conditions.

Results and discussion

Initially, we began our investigation with vinyl acetate and benzoic acid as the model substrates. Considering of developing a convenient method for scale-up reaction, the evaluating of several easy available and air & water stable inorganic compounds as the catalysts was firstly conducted. After screening an array of catalysts, including some copper, nickel, cobalt salts, and $RhCl_3 \cdot 3H_2O$ as well as Pd/C, only the last two catalysts could promote this

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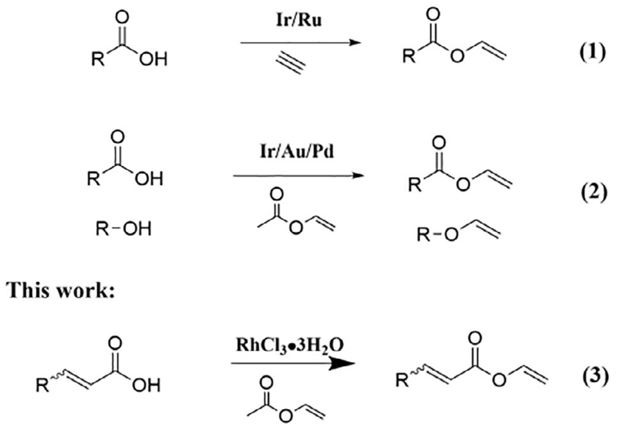


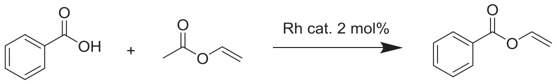
Fig. 1. Methods to synthesis of vinyl esters.

transvinylation reaction with 85% and 32% of yield, respectively (Table S1 in the supporting information). The assessment of other reaction parameters was summarized in Table 1. From **entry 1** to **entry 7**, we screened some other rhodium complex catalysts to facilitate this reaction. Compared to $Rh(acac)_3$, the $Rh(CO)_2acac$ catalyst showed the moderate catalytic activity with or without sodium formate (**entries 1,2** *vs* **entries 3,4**) which implied the necessity of carbonyl ligand. The CO-contained Rh catalyst such as $RhH(PPh_3)_3CO$ was also tested and shown the moderate yields (entry **5**). However, the $Rh(PPh_3)_3Cl$ and $RhCl_3{\cdot}3H_2O$ exhibited the highest conversion with HCOONa as the additive. It is notable that the basic additive is necessary in the reaction which is considered to promote the generating of CO ligand according to the Jennifer Ziriakus' report [25]. Considering the moderate price and without phosphorus ligand, we finally chose $RhCl_3{\cdot}3H_2O$ as the catalyst for further optimizing. From **entry 9** to **entry 13**, several bases were evaluated and only the sodium formate showed the best efficiency. The temperature was investigated in **entry 14** and **entry 15** and decreasing the reaction temperature was harmful to the reactivity. In addition, for the consideration of atomic economy, less amount of solvent and reactant was conducted but yielded less vinylation product as **entry 16** shown. Then, the condition listed in **entry 7** was employed as the optimum reaction condition.

With the optimum reaction conditions in hand, we then examined the substrate scope of this vinyl ester synthesis method (Table 2). The general yields of vinyl benzoate were moderate to excellent. Vinyl benzoates and p-substituted vinyl benzoates were obtained with excellent yields such as **2a**, **2b** and **2c**. The yields of m-substituted (**2d**) and o-substituted (**2e**) vinyl benzoates were lower than p-substituted vinyl benzoates, this may due to the steric effect hindered the transvinylation reaction. Similarly, the yields of **2h** and **2i** showed the same pattern. Othersubstrates with electron-withdrawing group, such as **2j** and **2k**, were well-tolerated and the 1-naphthoic acid substrate also shown the excellent yields (**2l**). It is worthy to point out that with both phenolic hydroxyl and carboxyl group, we could selectively obtain the carboxyl group vinylation products employing $RhCl_3{\cdot}3H_2O$ as the catalyst (**2f** and **2g**). Esterification of phenolic hydroxyl was observed when this reaction was catalyzed by Wilkinson catalyst, which gave low selectivity of this reaction. Subsequently, we used the model reaction condition to investigate the reuse ability of this catalyst. After completion of the transvinylation, the reaction mixture was evaporated to remove the organic compounds and thus remained the rhodium catalyst for further recycling properties investigation. The residual was then employed as the catalyst to promote the transvinylation of benzoate acid without addition of extra sodium formate. The results show that the catalyst is recyclable in 4 consecutive runs and the yields of vinyl benzoate, which was determined by GC with benzoate acid as external standard, were 85%, 71%, 74% and 58%, respectively.

The selectivity comparison of $RhCl_3{\cdot}3H_2O$ catalyst with Wilkinson catalyst was then investigated by utilizing the aromatic acid and aromatic alcohols as the substrates (Table 3). We obtained the selective vinylation product **a1** and **a2** without esterification by-products **b1** and **b2** with $RhCl_3{\cdot}3H_2O$ as the catalyst. What's more, only trace amount of vinylation side-product (4-(vinyloxy) benzoic acid) relative to **a1** was observed (entry 1) and no vinylation side-product was observed with 3-hydroxybenzoic acid as the substrate (entry 2). However, the Wilkinson catalyst showed lower selectivity of vinyl benzoates which preferred to esterification, yielded the side product **b1** and **b2** in good conversions. For the

Table 1
Optimization of reaction conditions with benzoic acid substrate.[a]



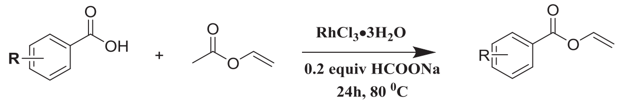
Entry	Rh catalyst	Additive	T (°C)	Yields[b]
1	$Rh(CO)_2acac$	–	80	27%
2	$Rh(CO)_2acac$	HCOONa	80	60%
3	$Rh(acac)_3$	–	80	0%
4	$Rh(acac)_3$	HCOONa	80	0%
5	$RhH(PPh_3)_3CO$	HCOONa	80	31%
6	$Rh(PPh_3)_3Cl$	HCOONa	80	86%
7	$RhCl_3{\cdot}3H_2O$	HCOONa	80	85%
8	$RhCl_3{\cdot}3H_2O$	–	80	0%
9	$RhCl_3{\cdot}3H_2O$	NaOAc	80	32%
10	$RhCl_3{\cdot}3H_2O$	$Cl_3CCOONa$	80	0%
11	$RhCl_3{\cdot}3H_2O$	$Na_2C_2O_4$	80	0%
12	$RhCl_3{\cdot}3H_2O$	Na_2HPO_4	80	0%
13	$RhCl_3{\cdot}3H_2O$	$HCOONH_4$	80	20%
14	$RhCl_3{\cdot}3H_2O$	HCOONa	71	25%
15	$RhCl_3{\cdot}3H_2O$	HCOONa	64	19%
16[c]	$RhCl_3{\cdot}3H_2O$	HCOONa	80	72%

[a] Conditions: 0.5 mmol benzoic acid, 2 mL vinyl acetate, 2 mmol% Rhodium catalyst, base (0.2 equiv), 24 h.

[b] Yields determined by GC relative to benzoic acid external standard.

[c] 0.5 mmol benzoic acid, 1 mL vinyl acetate, 2 mmol% Rhodium catalyst, base (0.2 equiv), 24 h.

Table 2
Synthesis vinyl esters catalyzed by $RhCl_3{\cdot}3H_2O$.[a]



Entry	R	Product	Yield/%
1	H	**2a**	85
2	4-tBu	**2b**	95
3	4-Me	**2c**	82
4	3-Me	**2d**	61
5	2-Me	**2e**	30
6[b]	4-OH	**2f**	76
7[b]	3-OH	**2g**	74
8[b]	2-Cl	**2h**	56
9[b]	4-Cl	**2i**	80
10[b]	4-Br	**2j**	76
11[b,c]	$4\text{-}NO_2$	**2k**	84
12[b]	1-naphthoic acid	**2l**	90

[a] Conditions: 0.5 mmol acid, 2 mL vinyl acetate, 2 mmol% $RhCl_3{\cdot}3H_2O$ catalyst, sodium formate (0.2 equiv), 24 h, yields determined by GC relative to acid external standard.

[b] Yields determined by HPLC relative to acid external standard.

[c] 4 mL vinyl acetate.

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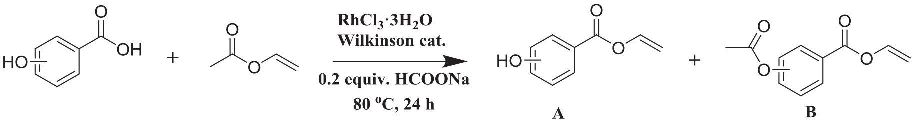
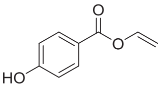
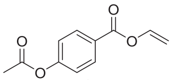
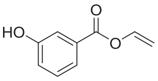
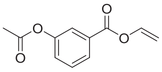
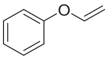
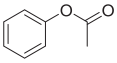
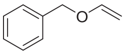
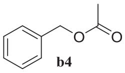
Table 3
Selectivity of $RhCl_3{\cdot}3H_2O$ compared with Wilkinson catalyst.[a]



Entry	Product A	Product B	Ratio of A:B	$RhCl_3{\cdot}3H_2O$	Wilkinson cat.
1	 **a1**	 **b1**	100:0[b]	37:63[e]	
2	 **a2**	 **b2**	100:0[b]	52:48[e]	
3	 **a3**	 **b3**	100:0[b]	5:95[e]	
4	 **a4**	 **b4**	0:0[c]	0:100[d]	

[a] Reaction conditions, 0.5 mmol substrates, 2 mol% rhodium catalyst, HCOONa 0.2 equiv, 80 °C for 24 h.

[b] Only transvinylation product was found (**a1**–**a3**), and the yields of vinyl esters were 76%, 74% and 33% determined by GC–MS, respectively.

[c] None of transvinylation or esterification product were found.

[d] Only esterification product (**b4**) was found, and the yields were 86% determined by GC–MS.

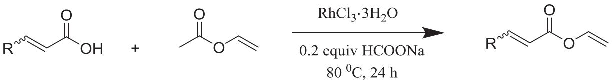
[e] The conversion of substrates in entries 1–3 were 89%, 73% and 37% respectively.

phenol substrate, only transvinylation of phenol (**a3**) was observed catalyzed by $RhCl_3{\cdot}3H_2O$ while phenol had been mostly esterificated (**b3**) catalyzed by Wilkinson catalyst. The $RhCl_3{\cdot}3H_2O$ also showed catalytic activity for phenol substrate albeit with moderate efficiency (33% yields). In addition, no transvinylation product (**a4**) of benzyl alcohol catalyzed by $RhCl_3{\cdot}3H_2O$ was observed and all these means that $RhCl_3{\cdot}3H_2O$ shows higher selectivity of carboxyl than that of phenolic hydroxyl.

In order to further estimate the application possibility, we applied this attractive protocol to the transvinylation of other carboxylic acids. To our delight, the $RhCl_3{\cdot}3H_2O$ catalyst exhibited good efficiency for the vinylation of sp^2-C linked carboxylic acid towards alkyl carboxylic acid. The yields of **3a** and **3b** were good (Table 4). What's more, the cinnamic acid was applied to this reaction and the yield of **3c** was also good.

The reaction mechanism was then investigated. From the results of optimum reaction conditions, catalysts without CO ligand couldn't promote this reaction unless with NaOAc or HCOONa as the additive. According to the Jennifer Ziriakus' research, CO ligand could derive from the substrates and solvent with the assistance of base NaOH, we supposed that the formate sodium was indispensable to provide CO ligand through dehydration in our reaction [26]. The vinyl esters would further to hydrogenate and convert to esters in our reaction conditions if the formate sodium undergoes the dehydrogenation according to Blum Jochanan's reported [27]. However, no esters could be detected from the GC–MS analysis, this phenomenon confirmed our above hypothesis. Then we investigated the influence of chloride ions in the model reaction by changing the ratio of $RhCl_3{\cdot}3H_2O$ to $AgBF_4$ (Table S2 listed in Supporting information) and the results showed that the chloride ions were necessary to high conversion. What's more, we also observed the side production acetic acid in the reaction system, implied that the reaction pathway was transvinylation rather than transesterification. In order to further understanding the reaction mechanism, we conducted the XPS experiments to

Table 4
Transvinylation of α-olefin carboxylic acid.[a]



Entry	R	Product	Yield (%)
1	(*E*)-Me	**3a**	71
2	H	**3b**	67
3	(*E*)-phenyl	**3c**	59

[a] Conditions: 0.5 mmol acid, 2 mL vinyl acetate, 2 mmol% $RhCl_3{\cdot}3H_2O$, sodium formate (0.2 equiv), 24 h, yields determined by GC relative to acid external standard.

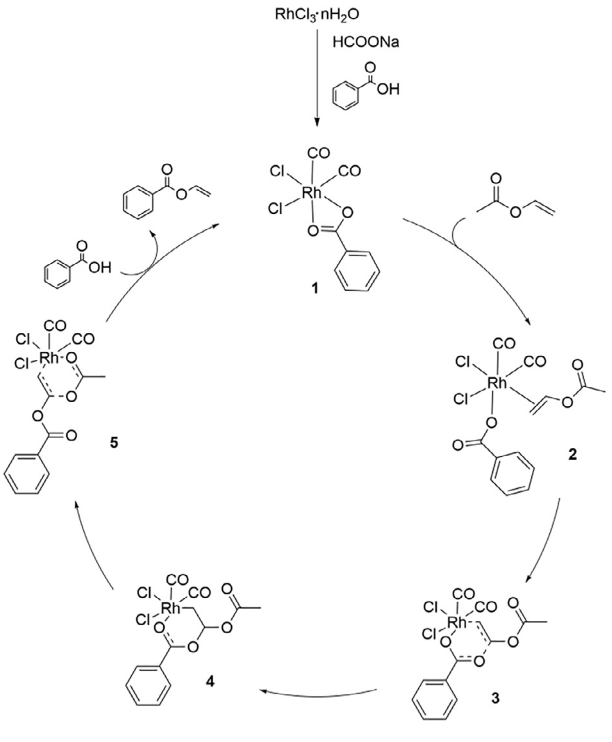


Fig. 2. Proposed reaction mechanism for transvinylation catalyzed by $RhCl_3{\cdot}3H_2O$.

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analysis the structure of Rh species. As Fig. S1 shown (in Supporting information), two peaks of Rh were observed at 314.1 eV and 309.4 eV which corresponded to Rh $3d_{3/2}$ level and $3d_{5/2}$ level, assigned to Rh(III) species [28]. These results demonstrated that the valence state of the Rh species maintained in trivalence.

Based on these facts, we proposed the mechanism for the $RhCl_3 \cdot 3H_2O$ catalyzed transvinylation reactions that depicted in Fig. 2. The intermediate **1** was generated from $RhCl_3 \cdot 3H_2O$ with sodium formate [29], which underwent coordination with benzoic acid to form the intermediate **2**. Then the intermediate **3** was formed via addition of the Rh center and the carboxylate ligand to the vinyl double bond [25]. Sequent, such intermediate transformed to intermediate **5** through transient intermediate **4**. After the β-elimination of acetyl, the vinyl benzoate was generated and the Rh species coordinated with benzoic acid to regenerate intermediate **1** to further facilitate the reaction.

Conclusions

In conclusion, we reported a rhodium catalyst for selective transvinylation of aromatic carboxylic acids. The catalyst system is ligand-free and air & water stable, does not generate esters byproduct while the substrates contain hydroxyl. The reusability of the rhodium catalyst shows its high practical application value.

Acknowledgments

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.tetlet.2018.07.039.

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