



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

Ruihang Jiang<sup>1</sup>, Zhangpei Chen<sup>\*,1</sup>, Kun Zhan, Lei Liu, Junjie Zhou, Yongjian Ai, Shuang Li, Hongjie Bao, Ze'nan Hu, Li Qi, Jingting Wang, Hong-bin Sun<sup>\*</sup>

Department of Chemistry, Northeastern University of China, Shenyang 110819, People's Republic of China



### ARTICLE INFO

#### Article history:

Received 30 May 2018

Revised 10 July 2018

Accepted 13 July 2018

Available online 18 July 2018

#### Keywords:

Rhodium chloride

Transvinylation

Vinyl benzoate

Vinyl ester

Transesterification

### 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.

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### 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 synthesizing 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  $\alpha,\beta$ -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],  $AuCIPPh_3$  [21] and  $PdX_2(CH_3CN)_2$  ( $X = Cl, Br$ ) (Fig. 1. Entry 2) [22,23]. However, the  $AuCIPPh_3$  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.

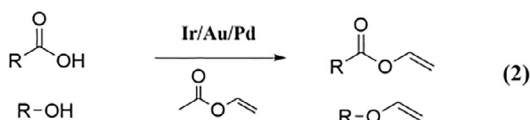
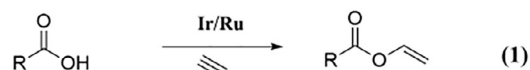
### Results and discussion

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

\* Corresponding authors.

E-mail addresses: [chenzhangpei@mail.neu.edu.cn](mailto:chenzhangpei@mail.neu.edu.cn) (Z. Chen), [sunhb@mail.neu.edu.cn](mailto:sunhb@mail.neu.edu.cn) (H.-b. Sun).

<sup>1</sup> These authors contributed equally.



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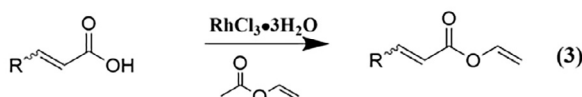


Fig. 1. Methods to synthesis of vinyl esters.

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)<sub>3</sub>, the Rh(CO)<sub>2</sub>acac 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<sub>3</sub>)<sub>3</sub>CO was also tested and shown the moderate yields (entry 5). However, the Rh(PPh<sub>3</sub>)<sub>3</sub>Cl and RhCl<sub>3</sub>·3H<sub>2</sub>O 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<sub>3</sub>·3H<sub>2</sub>O 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 econ-

omy, 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<sub>3</sub>·3H<sub>2</sub>O 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<sub>3</sub>·3H<sub>2</sub>O 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<sub>3</sub>·3H<sub>2</sub>O 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.<sup>a</sup>

Entry	Rh catalyst	Additive	T (°C)	Yields <sup>b</sup>
1	Rh(CO) <sub>2</sub> acac	–	80	27%
2	Rh(CO) <sub>2</sub> acac	HCOONa	80	60%
3	Rh(acac) <sub>3</sub>	–	80	0%
4	Rh(acac) <sub>3</sub>	HCOONa	80	0%
5	RhH(PPh <sub>3</sub> ) <sub>3</sub> CO	HCOONa	80	31%
6	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	HCOONa	80	86%
7	RhCl <sub>3</sub> ·3H <sub>2</sub> O	HCOONa	80	85%
8	RhCl <sub>3</sub> ·3H <sub>2</sub> O	–	80	0%
9	RhCl <sub>3</sub> ·3H <sub>2</sub> O	NaOAc	80	32%
10	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Cl <sub>3</sub> CCOONa	80	0%
11	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	80	0%
12	RhCl <sub>3</sub> ·3H <sub>2</sub> O	Na <sub>2</sub> HPO <sub>4</sub>	80	0%
13	RhCl <sub>3</sub> ·3H <sub>2</sub> O	HCOONH <sub>4</sub>	80	20%
14	RhCl <sub>3</sub> ·3H <sub>2</sub> O	HCOONa	71	25%
15	RhCl <sub>3</sub> ·3H <sub>2</sub> O	HCOONa	64	19%
16 <sup>c</sup>	RhCl <sub>3</sub> ·3H <sub>2</sub> O	HCOONa	80	72%

<sup>a</sup> Conditions: 0.5 mmol benzoic acid, 2 mL vinyl acetate, 2 mmol% Rhodium catalyst, base (0.2 equiv), 24 h.

<sup>b</sup> Yields determined by GC relative to benzoic acid external standard.

<sup>c</sup> 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<sub>3</sub>·3H<sub>2</sub>O.<sup>a</sup>

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 <sup>b</sup>	4-OH	2f	76
7 <sup>b</sup>	3-OH	2g	74
8 <sup>b</sup>	2-Cl	2h	56
9 <sup>b</sup>	4-Cl	2i	80
10 <sup>b</sup>	4-Br	2j	76
11 <sup>b,c</sup>	4-NO <sub>2</sub>	2k	84
12 <sup>b</sup>	1-naphthoic acid	2l	90

<sup>a</sup> Conditions: 0.5 mmol acid, 2 mL vinyl acetate, 2 mmol% RhCl<sub>3</sub>·3H<sub>2</sub>O catalyst, sodium formate (0.2 equiv), 24 h, yields determined by GC relative to acid external standard.

<sup>b</sup> Yields determined by HPLC relative to acid external standard.

<sup>c</sup> 4 mL vinyl acetate.

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