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Rhodium-Catalyzed Annulations of 1,3-Dienes and Salicylaldehydes/2-Hydroxybenzyl Alcohols Promoted by 2-Ethylacrolein

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Abstract. A rhodium-catalyzed 2-ethylacrolein-promoted protocol enables the annulation reactions of 1,3-dienes with either salicylaldehydes or 2-hydroxybenzyl alcohols leading to 2-alkylchroman-4-ones with high regioselectivity. This research highlights the use of 2-ethylacrolein which probably serves as a tool of bidentate coordination to rhodium intermediates. Mechanistic studies reveal that the transformation proceeds through the 1,4-hydroacylation pathway to access unsaturated linear ketones with subsequent oxo-Michael addition.

Keywords: Rhodium catalysis; 2-Ethylacrolein promoted; 1,3-Dienes; 1,4-Hydroacylation; 2-Alkylchroman-4-ones

The last decade has seen a speedy expansion of using 1,3-dienes as important building blocks in the preparation of substantially more complex and value-added molecules.[1] In this regard, the intermolecular reductive couplings of 1,3-dienes to carbonyl compounds or alcohols catalyzed by transition metals, such as ruthenium,[2] nickel,[3] iridium,[4] and titanium,[5] have been demonstrated as attractive and powerful strategies with prominent regio-, diastereo- and enantioselectivities. It is noteworthy that only two examples of diene-carbonyl reductive couplings were achieved relying on the rhodium catalysis system.[6] In contrast with the extensively investigated intermolecular reductive couplings, illustrations on the 1,3-diene-participated hydroacylation remain limited. Since the pioneering work of Kondo and Mitsudo on the Ru-catalyzed intermolecular hydroacylation of 1,3-dienes with (hetero)aromatic aldehydes,[7] Krische[8] and Ryu[9] independently developed the Ru–H-catalyzed diene hydroacylation to deliver 1,2-addition products. In 2014, Dong and co-workers demonstrated an interesting Co-catalyzed regioselective hydroacylation of 1,3-dienes by oxidative cyclization, which could favor either 1,2- or 1,4-hydroacylation depending on the aldehyde component.[10] In view of the fact that only a few examples have been described for transition-metal-catalyzed C–C couplings of 1,3-dienes or their precursors with aldehydes or alcohols to access functionalized ketones,[7–10,11] it would be highly desirable to develop novel methodologies to achieve the conversion.

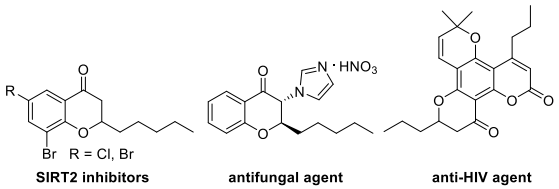

Figure 1. Representative Bioactive 2-Alkylchroman-4-ones

2-Alkylchroman-4-ones, as conspicuous privileged structures, have been found in numerous naturally occurring products and medicinally relevant compounds (Figure 1), possessing a broad range of pharmaceutical activities.[12] Consequently, extensive efforts have been devoted to the synthesis of this scaffold[13] from readily available materials. For example, the Glorius group[14] developed one example of the Rh(III)-catalyzed annulation reaction of salicylaldehyde with styrene to furnish a flavanone by use of stoichiometric silver salt. Meanwhile, the asymmetric hydrogenation using the chiral Ru–NHC complex with subsequent selective oxidation to access flavanones and chromanones was successively reported in the same group.[15] Miura[16] and Stanley[17] demonstrated the Rh(I)-catalyzed cyclization of

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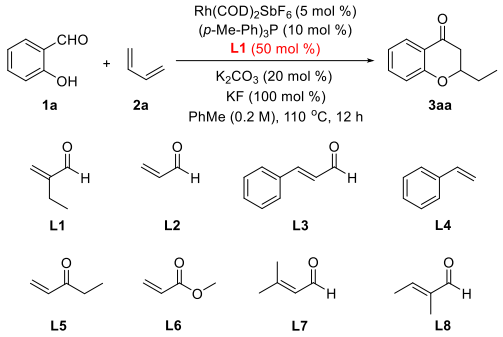
salicylaldehydes to internal alkynes via tandem alkyne hydroacylation and oxo-Michael addition. In 2016, Yoshikai realized the Co(I)-catalyzed reductive annulations using the same substrate partners in the presence of a superstoichiometric amount of Zn.[18]

Recently, Rh-catalyzed intermolecular hydroacylation of alkenes[19] with salicylaldehydes has been exquisitely investigated to afford linear or branched carbonyl products. Inspired by Tanaka's work on strong coordination of various acrylamides to the rhodium intermediates,[20] we hypothesized that the presence of an appropriate *α,β*-unsaturated compound could promote the intermolecular couplings of conjugated dienes to salicylaldehydes. To continue our efforts in the difunctionalization of 1,3-dienes,[21] herein we describe the successful rhodium-catalyzed 2-ethylacrolein-assisted couplings of 1,3-dienes with either salicylaldehydes or 2-hydroxybenzyl alcohols resulting in 2-alkylchroman-4-ones in a highly regioselective manner.

Table 1. Optimization of the Reaction Conditions.[a]



entry	deviation from the standard conditions	yield[b] (%)
1	None	77(74)[c]
2	PPh_3 instead of (*p*-Me-Ph)$_3$P	71
3	Without **L1**	13
4	**L2** instead of **L1**	14
5	**L3** instead of **L1**	62
6	**L4** instead of **L1**	61
7	**L5** instead of **L1**	7
8	**L6** instead of **L1**	66
9	**L7** instead of **L1**	7
10	**L8** instead of **L1**	73
11[d]	None	73
12[d]	Without **L1**	58

[a] Unless otherwise noted, all reactions were carried out in N_2 atmosphere using **1a** (0.3 mmol, 1 equiv) and **2a** (2.5 equiv) in 1.5 mL of toluene.
[b] Determined by ^{1}H NMR analysis using diethyl phthalate as the internal standard.
[c] Isolated yield in parentheses.
[d] 2-Hydroxybenzyl alcohol (**1a′**) was used as the substrate.

Reaction optimization (Table 1) was initially carried out by coupling salicylaldehyde (**1a**) with 1,3-butadiene (**2a**). With the previous reported acylrhodium intermediates stabilized by the bidentate chelation of acrylamides in mind,[20] we tested various *α,β*-unsaturated compounds to promote the model reaction. Indeed, the best results were obtained when the reaction was performed under the Rh(COD)$_2$SbF$_6$/(*p*-Me-Ph)$_3$P catalytic system using 2-ethylacrolein (**L1**) as the ligand and KF as the additive, providing the desired 2-ethylchroman-4-one **3aa** in 77% yield (Table 1, entry 1). Replacing (*p*-Me-Ph)$_3$P with PPh_3 delivered a slightly lower yield (Table 1, entry 2). The reaction turnover is extremely dependent on the ligand, and the yield of the product dropped significantly to 13% without **L1** (Table 1, entry 3). The specific nature of the ligand was proved to be very important, as the simpler acrolein (**L2**) could not promote the annulation reaction at all (Table 1, entry 4). Cinnamaldehyde (**L3**) produced a yield similar to that achieved with styrene (**L4**) (Table 1, entry 5–6). It is noteworthy that the reaction assisted by 1-penten-3-one (**L5**) was far less effective than that by methyl acrylate (**L6**) (Table 1, entry 7–8). Additionally, 3-methylcrotonaldehyde (**L7**) and (*E*)-2-methylcrotonaldehyde (**L8**) as structural analogues showed totally different results from each other (Table 1, entry 9–10), and **L8** gave a yield comparable to **L1**. To our delight, when 2-hydroxybenzyl alcohol (**1a′**) was exposed to the reaction conditions, the corresponding product was afforded in 73% yield (Table 1, entry 11), and as expected, the control experiment revealed that the absence of **L1** had a detrimental impact on the reaction conversion (Table 1, entry 12).

Subsequently, the optimal reaction conditions were utilized to investigate the scope of a variety of commercially available salicylaldehydes for the annulation reactions with **2a** (Scheme 1). Initially, salicylaldehyde derivatives substituted with electron-donating groups such as alkoxy and alkyl on the benzene ring proved to be good substrates with the Rh(COD)$_2$SbF$_6$/(*p*-Me-Ph)$_3$P catalytic couple to give rise to the expected compounds (**3ba**–**3fa**) in moderate to good yields; but unfortunately, the substrate with the dimethylamino group at the *meta* position of the hydroxyl group was not amenable to this transformation. Actually, exposure of electron-neutral 2-hydroxy-1-naphthaldehyde to the reaction conditions revealed that a good yield of **3ga** was obtained. Good compatibility with a host of functional groups for the one-pot synthesis of 2-ethylchroman-4-ones was observed, with trifluoromethoxy (**3ha**), fluoro (**3ia**–**3ja**), chloro (**3qa**–**3ra**) and trifluoromethyl groups (**3ma**) all being well-tolerated. However, the substrates bearing bromo substituents (**3ka**–**3la**, **3sa**) were found to be subjected to debromination. It is worth mentioning that a chromanone **3na** derived from methyl 3-formyl-4-

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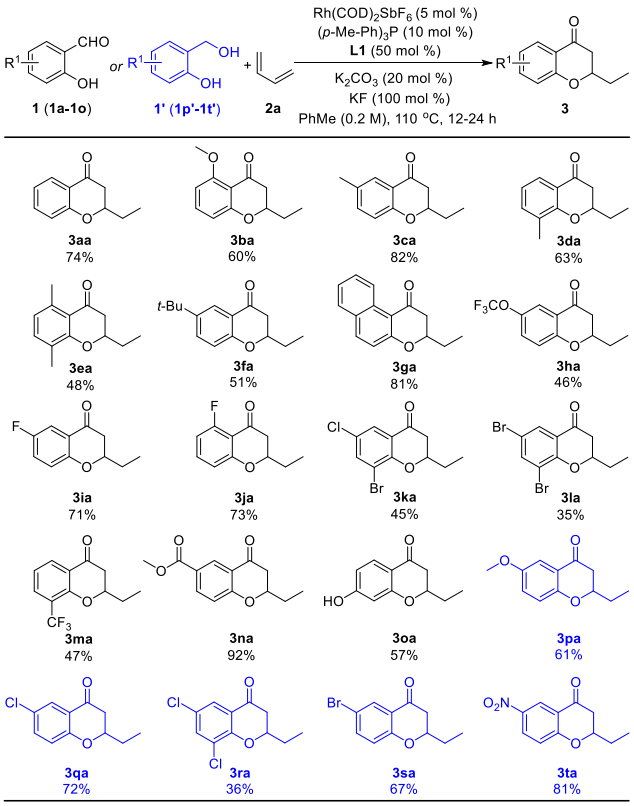
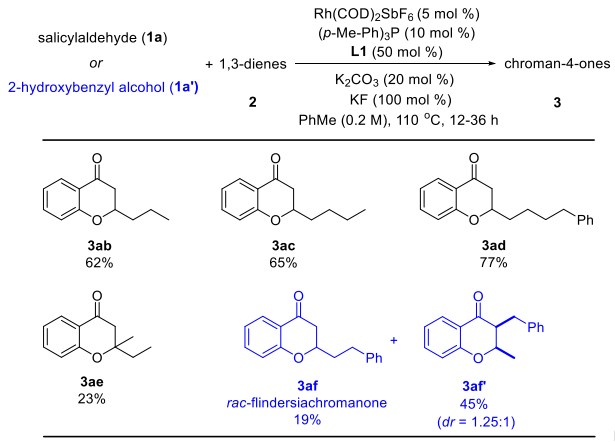
hydroxybenzoate was provided in an excellent yield, thus demonstrating the applicability of our technique. Strikingly, 2,4-dihydroxybenzaldehyde was successfully coupled with 1,3-butadiene to deliver a modest yield of the target product **3oa** with a free phenolic hydroxyl group. In general, the electronic factor had no prominent effect on the transformation of the salicylaldehydes. On the other hand, 2-hydroxybenzyl alcohols (**1p′**–**1t′**), which were readily prepared by reduction of the corresponding salicylaldehydes by $NaBH_4$/EtOH, were also tolerable under the standard reaction conditions, regardless of either electron-donating group (**3pa**) or electron-withdrawing groups (**3qa**–**3ta**) on the benzene ring.

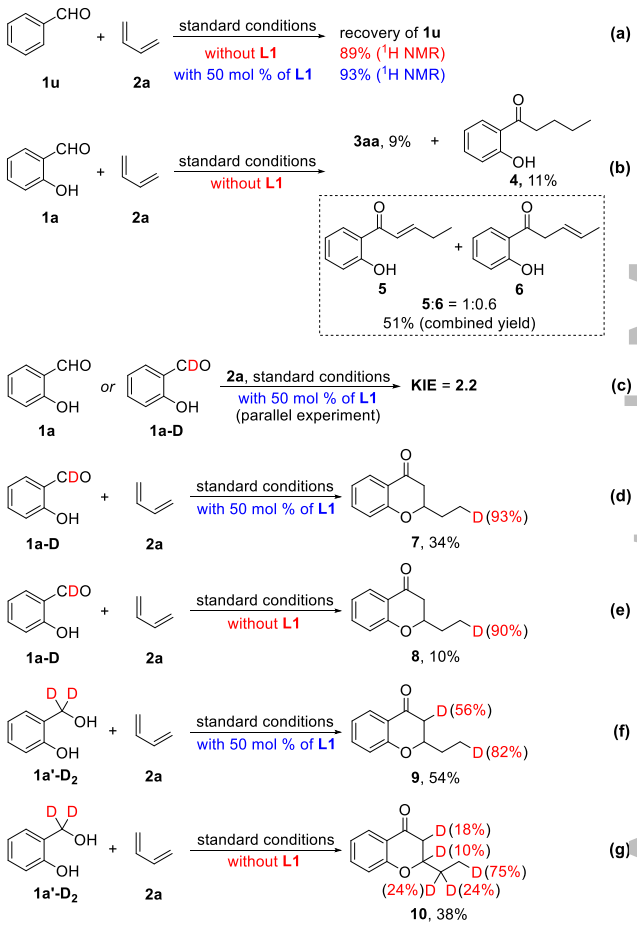


Scheme 1. Reaction Scope with Respect to Salicylaldehydes.

During exploration of the scope of 1,3-dienes in the annulation reactions, it was found that our protocol could also be suitable for the functionalization of other representative conjugated dienes (Scheme 2). For example, alkyl-substituted 1,3-butadienes were reacted with salicylaldehyde (**1a**) smoothly under the optimized conditions to afford the exclusively regioselective products (**3ab**–**3ad**) in moderate to good yields. However, isoprene proceeded sluggishly with a low yield of 2,2-dialkyl-substituted compound (**3ae**) obtained. Likewise, this strategy could be extended to the coupling reaction of terminal aryl-substituted dienes with 2-hydroxybenzyl alcohol (**1a′**) rather than salicylaldehyde (**1a**), furnishing a natural product—*rac*-flindersiachromanone (**3af**) and its regioisomer (**3af′**) in a combined yield of 64%.



Scheme 2. Reaction Scope with Respect to 1,3-Dienes.

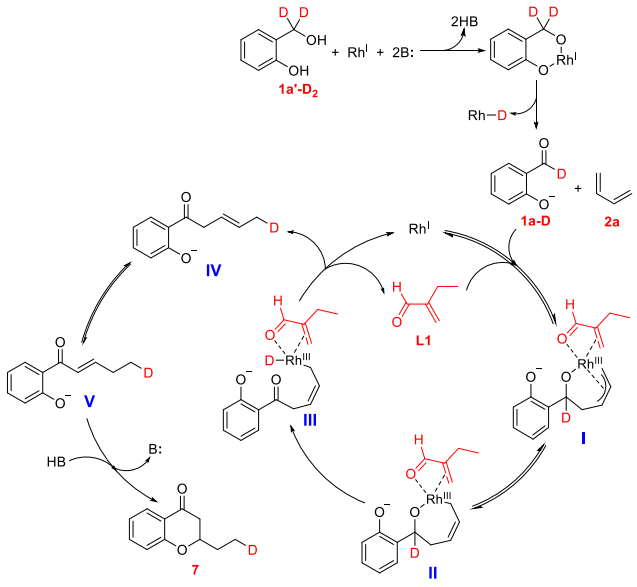


Scheme 3. Investigation of Mechanism.

As shown in Scheme 3, indirect evidence was assembled to elucidate the role of 2-ethylacrolein (**L1**) in company with the catalytic mechanism. The incompetent reaction of benzaldehyde (**1u**) with 1,3-butadiene (**2a**) either in the presence or the absence of 2-ethylacrolein (**L1**) by ^{1}H NMR analysis of the crude

mixture distinctly revealed the significance of a hydroxy group[14,19e] in initiating the annulation reaction (Scheme 3a). The cyclization of **1a** to **2a** without **L1** was discreetly studied (Scheme 3b), isolating the product **3aa** (9% yield), a saturated ketone **4** (11% yield) and a pair of inseparable unsaturated regioisomers **5** and **6** (51% combined yield). These results indicated that the two isomers were more likely to be the intermediates in the present catalytic system and that the reactions proceeded in an excellent linear selectivity. Moreover, employing 50 mol % of **L1** in the transformation of salicylaldehyde (**1a**) as well as 2-hydroxybenzyl alcohol (**1a′**) increased the yield of **3aa** to 77% and 73% (Table 1, entry 1 *vs* entry 3, entry 11 *vs* entry 12), respectively, which could highlight the bidentate chelation assistance of **L1**.[20]

Finally, mechanistic studies on the kinetic isotope effect (KIE) and the deuterium labeling experiments are reported. The value of k_H/k_D = 2.2 from two parallel reactions reveals that *β*-hydride or reductive elimination might be involved in the turnover-limiting step (Scheme 3c).[10] When the annulation is carried out using deuterated salicylaldehyde (**1a-D**) as the substrate with and without **L1**, about 90% deuterium is incorporated at the terminal methyl group (Scheme 3d–e). In addition, detectable deuterium at other aliphatic carbon atoms is also observed while performing the reactions of deuterated 2-hydroxybenzyl alcohol (**1a′-D₂**), which might be attributed to the Rh−D species generated *in situ* (Scheme 3f–g).



Scheme 4. Plausible Reaction Mechanism.

On the basis of the above observations and the previous reports on the coupling reactions of 1,3-dienes,[2g,3d,10,22] a tentative mechanism is proposed in Scheme 4. First, the rhodium catalyst would trigger oxidative cyclization between the aldehyde (**1a-D**) and 1,3-butadiene (**2a**) to form intermediate **I**, which undergoes transformation to obtain the seven-membered rhodiumacycle **II**[10] with the chelation assistance of **L1**.[20] The subsequent *β*-H elimination delivers intermediate **III**, which upon reductive elimination produces the linear unsaturated ketone **IV** (1,4-hydroacylation pathway) and regenerates the Rh(I) catalyst. Isomerization of **IV** under high temperature gives rise to the more stable *α*,*β*-unsaturated ketone **V** which is converted into the target product **7** through the final intramolecular oxo-Michael addition. In the case of deuterated 2-hydroxybenzyl alcohol (**1a′-D₂**), alkyloxyrhodium intermediate[9,11a,23] initially forms with subsequent *β*-H elimination, leading to the Rh–D species and the aldehyde (**1a-D**). Note that the Rh–D species exert double bond isomerization through iterative hydrorhodation/*β*-H elimination[9,11a,23b,23c] that accounts for the complex deuterium distribution on the product.

In conclusion, efficient construction of 2-alkylchroman-4-ones through rhodium-catalyzed 2-ethylacrolein-promoted cyclization of 1,3-dienes to either salicylaldehydes or 2-hydroxybenzyl alcohols has been developed. The participation of 2-ethylacrolein in the reaction might stabilize different kinds of rhodium intermediates. An oxidative cyclization mechanism is proposed to afford the 1,4-hydroacylation product as the key intermediate. This methodology features readily available materials, good functional group tolerance, and high regioselectivity. More insights into the catalytic mechanism and the synthetic applications in the bioactive pharmaceuticals are underway in our laboratory.

Experimental Section

To an oven-dried sealed tube equipped with a stirrer bar was added $Rh(COD)_2SbF_6$ (8.3 mg, 0.015 mmol, 5 mol %), tri(*p*-tolyl)phosphine (9.1 mg, 0.03 mmol, 10 mol %), K_2CO_3 (8.3 mg, 0.06 mmol, 20 mol %), KF (17.4 mg, 0.3 mmol, 1.0 equiv), salicylaldehyde **1a** (36.6 mg, 0.3 mmol, 1.0 equiv), 1,3-butadiene **2a** (500 μL, 0.75 mmol, 2.5 equiv, ca. 1.5 mol/L in THF), and 2-ethylacrolein **L1** (12.6 mg, 0.15 mmol, 50 mol %). Then dry toluene (1.5 mL, 0.2 M) was added. After the mixture was stirred at room temperature for 15 min, the resulting mixture was removed from the glove box, and then stirred at 110 ℃ for 12 h. Upon completion of the reaction, the mixture was concentrated and the residue was purified by silica gel flash chromatography (hexane/EtOAc) to afford the desired product **3aa**.

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