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Ayumu Kawase, Hirotaka Omura, Takayuki Doi, and Hirokazu Tsukamoto*

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Palladium(0)-Catalyzed [4+2] Annulation of Salicylaldehydes and Propargyl Carbonates to Produce 3,4-Dihydro-2-Methylene-2*H*-1-Benzopyran-4-Ols

Ayumu Kawase,[1] Hirotaka Omura,[1] Takayuki Doi,[1] and Hirokazu Tsukamoto*[1, 2]
[1]*Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3 Aza-aoba, Aramiki, Aoba-ku, Sendai 980-8578*
[2]*Department of Pharmaceutical Sciences, Yokohama University of Pharmacy, 601 Matano-cho, Totsuka-ku, Yokohama 245-0066*

E-mail: hirokazu.tsukamoto@hamayaku.ac.jp

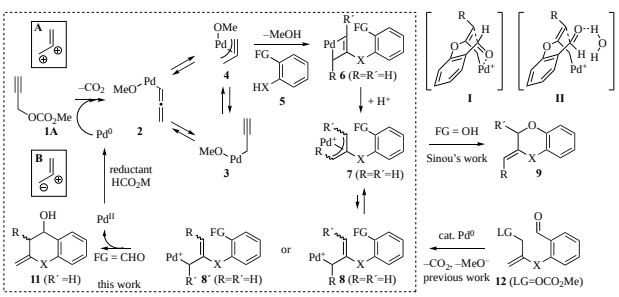
Palladium(0)-catalyzed synthesis of 3,4-dihydro-2-methylene-2*H*-1-benzopyran-4-ols via annulation between salicylaldehyde and propargyl carbonate using a formate reductant is reported herein. The annulation proceeds via common addition of the hydroxyl group in salicylaldehyde to the central carbon of η^3-allenyl-/propargylpalladium, wherein the latter is generated through the oxidative addition of propargyl carbonate to the catalyst and subsequent intramolecular umpolung allylation of the aldehyde.

Key words: Palladium catalyst | Salicylaldehyde | Propargyl carbonate | [4+2] Annulation | Umpolung Allylation

Transition metal-catalyzed annulation forming two or multiple bonds in a single step is one of the most useful methods to construct heterocycles and carbocycles, which are important in biology and material science fields.[1] Recently, a palladium-catalyzed annulation reaction using propargyl carbonate **1** as dicationic synthon **A** with various bifunctional pronucleophiles has been receiving increasing attention (Scheme 1).[2–14]

Propargyl carbonate **1A** undergoes oxidative addition to a palladium(0) complex and subsequent decarboxylation to afford η^1-allenylpalladium(II) **2**, which equilibrates with η^1-propargylpalladium(II) **3** and η^3-allenyl-/propargylpalladium(II) **4** (Scheme 1).[15–19] These (methoxo)palladium complexes **2–4** can deprotonate pronucleophiles, such as phenol **5** (X = O), generating an ion pair containing an anionic nucleophile and cationic palladium together with methanol. Then, a nucleophilic attack of the counter anion to the central carbon of η^3-allenyl/propargyl ligand in **4** occurs to form palladacyclobutene **6**, which is converted to η^3-allylpalladium(II) **7**, via protonation and subsequent isomerization of thermodynamically unfavorable η^1-allylpalladium(II) **8** or **8'**. The η^3-complex **7** can further react with another nucleophile. Therefore, a tethered bis(pronucleophile), such as catechol **5** (FG = OH, X = O), can undergo annulation with **1A** to afford 2,3-dihydro-1,4-benzodioxin **9**.[5] In contrast, the annulation of **1A** with substrate **5** bearing both pronucleophile and electrophilic moieties (FG = CHO), such as salicylaldehyde, can be developed because the intermediate **8** is rarely detected but it is sufficiently nucleophilic to attack the intramolecular carbonyl group.[20] However, to the best of our knowledge, the latter annulation process using **1A** as Zwitter ionic synthon **B** yielding functionalized 2*H*-1-benzopyran-4-ol **11** (X = O) has never been developed.[21, 22]

Recently, we reported palladium(0)-catalyzed umpolung cyclizations of allylic carbonate-aldehydes in the presence of formate reductant.[23, 24] The type II cyclization of **12** is supposed to proceed through η^1-allylpalladium(II) intermediate **8** (Scheme 1). The formate can selectively reduce the alkoxopalladium(II) species (generated at the end of the catalytic cycle) over η^3-allylpalladium(II) **7**. Unfortunately, the preparation of substrate **12** requires multiple laborious steps. Subsequently, we anticipated that the palladium-catalyzed *in situ* preparation of **8** from propargyl carbonate **1A** and salicylaldehyde **5** (FG = CHO, X = O) followed by umpolung allylation, which affords **11**, could solve the problem. To achieve the annulation reaction, it is essential to seek reaction conditions that do not reduce palladium(II) intermediates **2–4**[25] as well as **7** and **8**.[26]



Scheme 1. Palladium-catalyzed annulation of **1** and **5** and type II umpolung cyclization of **12** leading to **11**.

First, reductants (HCO_2H, HCO_2H-Bu_3N, HCO_2NH_4, HCO_2Na, HCO_2K, and HCO_2Cs, 1.5 equiv) and phosphine ligands (dppe [1,2-bis(diphenylphosphino)ethane], dppp [1,3-bis(diphenylphosphino)propane], dppb [1,4-bis(diphenylphosphino)butane], dppf [1,1'-bis(diphenylphosphino)ferrocene], DPEphos [2,2'-bis(diphenylphosphino)-dipheyl ether, 40 mol%] were examined for the coupling reaction of salicylaldehyde (**5a**) with 2 equiv of methyl propargyl carbonate (**1A**) under catalysis of $Pd_2(dba)_3{\cdot}CHCl_3$ in 1,4-dioxane at 50 °C (See Supporting Information, Tables S1 and S2). A combination of potassium formate[27] and dppp as the reductant and ligand, respectively provided the best result, affording 2-methylenechroman-4-ol (**11aA**) in 38% yield, although it was still necessary to improve the yield. Interestingly, the use of dppf or DPEphos[10a–c] afforded 2,2'-(prop-2-ene-1,2-diylbis(oxy))-dibenzaldehyde (**13aA**), rather than **11aA**, in high yield, whereas dppb afforded an equal amount of **11aA**

and **13aA** in low yields (See Supporting Information, Table S2, Entries 2–4).

Considering the inevitable reduction of propargyl carbonate **1A**, 5 equiv of **1A** and potassium formate was utilized to screen a solvent for the annulation of salicylaldehyde (**5a**) under 10 mol% $Pd_2dba_3{\cdot}CHCl_3$-dppp catalysis while heating at 50 °C (Table 1). Remarkably, the yield of **11aA** increased to 76% when 20 vol% of water was added to 1,4-dioxane (Entries 1–4).[28] The concentration of **5a** also affected the yield of **11aA**, with 0.10 M concentration offering the best result (Entry 5). Use of 2 equiv of **1A** and potassium formate instead of 5 equiv lowered the yield of **11aA** (Entry 6). Notably, the annulation proceeded even in the absence of formate; however, it accompanied the formation of diyne derived from oxidative dimerization of **1A** (Entry 7). Reducing the catalyst loading to 5 mol% lowered the yield of **11aA** (Entry 8). Other palladium sources such as $Pd(OAc)_2$ and (allyl)CpPd instead of $Pd_2dba_3{\cdot}CHCl_3$ required longer reaction time for the complete consumption of **5a** (Entries 9 and 10). Fortunately, the reaction at 65 °C with *tert*-butyl carbonate **1B** instead of **1A** recovered the yield of **11aA** to 78% (Entry 12). The consumption of **1B** via its oxidative dimerization is suppressed by its steric bulkiness, as observed in Entry 7.

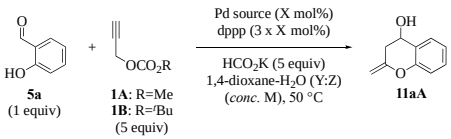


Table 1. Effects of solvent and concentration

Entry	**1**	Pd source (X mol%)	Y:Z	*conc.* (M)	Time (h)	Yield[a] (%)
1	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	1:0	0.25	6	52
2	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	9:1	0.25	10	69
3	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	4:1	0.25	6	76
4	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	1:1	0.25	6	44
5	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	4:1	0.10	6	87
6[b]	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	4:1	0.10	3	69
7[c]	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (10 mol%)	4:1	0.10	6	52
8	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (5 mol%)	4:1	0.10	6	65
9[d]	**1A**	$Pd(OAc)_2$ 10 mol%	4:1	0.10	18	62
10[d]	**1A**	(allyl)CpPd 10 mol%	4:1	0.10	18	56
11[e]	**1A**	$Pd_2dba_3{\cdot}CHCl_3$ (5 mol%)	4:1	0.10	2	65
12[e]	**1B**	$Pd_2dba_3{\cdot}CHCl_3$ (5 mol%)	4:1	0.10	9	78 (74)[f]

[a] NMR yield of **11aA**. [b] Reaction with 2 equiv of **1A** and HCO_2K. [c] Reaction without HCO_2K. [d] 15 mol% of dppp was used. [e] Reaction at 65 °C. [f] Isolated yield of **11aA** is shown in parenthesis.

With the optimized reaction conditions (Table 1, Entry 12), the reactions of commercially available salicylaldehydes **5b–l** having various substituents at the 3-, 4-, or 5-positions were tested (Table 2, Entries 1–11). Results showed that electron-donating methyl, methoxy, and diethylamino groups were compatible, and the position of the methoxy group affected the product yields to some extent (Entries 1–5). Salicylaldehydes **5g–j** with an electron-withdrawing halogen or nitro group at the 3-position also participated in the annulation to afford **11(g–j)A** in moderate yield (Entries 6–9). Notably, the bromo substituent in **5i** remained intact without suffering reduction under the palladium catalysis (Entry 8). Both 2-hydroxy-1-naphthaldehyde **5k** and its isomer **5l** equally underwent annulation to afford tricyclic products **11kA** and **11lA**, respectively in good yields (Entries 10 and 11). The annulation of *o*-nitrobenzenesulfonyl-protected 2-aminobenzaldehyde **5m**, instead of salicylaldehyde, also occurred, affording 2-methylene-1,2,3,4-tetrahydroquinoline **11mA** in 57% yield (Table 2, Entry 12).

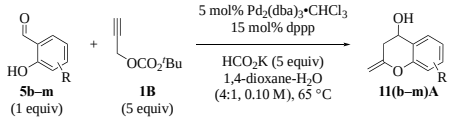
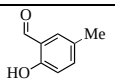
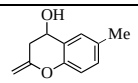
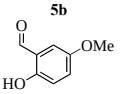
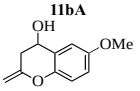
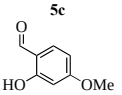
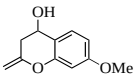
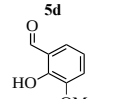
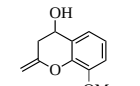
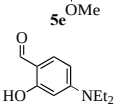
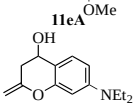
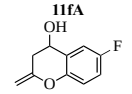
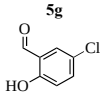
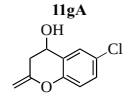
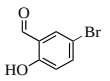
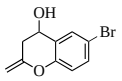
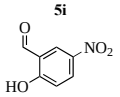
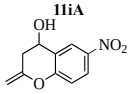
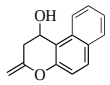
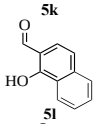
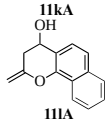
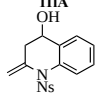


Table 2. Scope of salicylaldehydes **5**

Entry	**5**	Product	Time (h)	Yield[a] (%)
1	 **5b**	 **11bA**	16	64
2	 **5c**	 **11cA**	17	52
3	 **5d**	 **11dA**	7	72
4	 **5e**	 **11eA**	10	71
5	 **5f**	 **11fA**	19	36[b]
6	 **5g**	 **11gA**	25	43
7	 **5h**	 **11hA**	9	46

8	 **5i**	 **11iA**	9	47
9	 **5j**	 **11jA**	4	36
10	 **5k**	 **11kA**	4	60
11	 **5l**	 **11lA**	10	65
12	 **5m**	 **11mA**	10	57

[a] Isolated yield of **11aA**. [b] Substrate **5f** was recovered in 36% yield.

Finally, the scope of propargyl carbonates was briefly investigated (Table 3). Both isomeric methyl-substituted carbonates **1C** and **1C´** were converted to *cis*- and *trans*-**11aC** in a ca. 4:1 ratio (Entries 1 and 2), which implies that these reactions proceeded through a common η^3-allylpalladium(II). Similarly, phenyl-substituted **1D** and **1D´** yielded *cis*- and *trans*-**11aD** with poor diastereoselectivity (Entries 3 and 4). Notably, the annulations with internal alkynes (**1C´** and **1D´**) were less efficient than those with terminal alkynes (**1C** and **1D**) because of the formation of byproducts derived from the reduction of η^3-allylpalladium(II) intermediates (Entries 1, 3 vs. 2, 4). Although each pair of the isomers should behave similarly, the differences in the product yields are ascribed to the initially formed η^1-allylpalladium(II) **8** and **8'** (R = Me or Ph, R´ = H) (Scheme 1).[29] Interestingly, the use of non-aqueous solvent in the annulation between **5a** and **1C** resulted in the reversal of diastereoselectivity (Entries 1 vs. 5). The diastereoselectivity was determined via the Zimmerman–Traxler transition state **I** in non-aqueous solvents or the antiperiplanar transition state **II** in aqueous solvents; both states are derived from thermodynamically favored *syn*-η^3-allylpalladium(II) intermediates (Scheme 1).

In conclusion, we have developed a palladium(0)-catalyzed annulation of salicylaldehydes with propargyl carbonate that affords 3,4-dihydro-2-methylene-2*H*-1-benzopyran-4-ols in good to moderate yields. Various substituents, including bromide on the salicylaldehydes, were tolerated under mild reaction conditions. It was demonstrated that the allylpalladium intermediate, generated by the addition of the hydroxy group in the salicylaldehyde to η^3-allenyl-/propargylpalladium(II), could undergo nucleophilic addition to intramolecular aldehyde using a formate reductant.

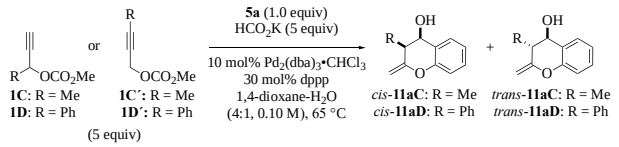
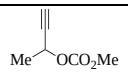
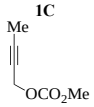
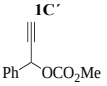
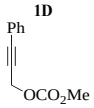
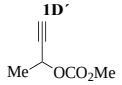


Table 3. Scope of propargyl carbonates **1**

Entry	**1**	Product	Time (h)	Yield (*cis*:*trans*)[a]
1	 **1C**	**11aC**	5	54% (4.2:1)[b]
2	 **1C´**	**11aC**	5	39% (4.4:1)[c]
3	 **1D**	**11aD**	1.5	58% (1.1:1)
4	 **1D´**	**11aD**	1.5	39% (1.1:1)[d]
5[e]	 **1C**	**11aC**	1.5	60% (1:3.3)

[a] The *dr* was determined by ^{1}H-NMR analysis of the diastereomeric mixture. [b] 2-(But-1-en-2-yloxy)benzaldehyde (**14**) was also observed in 4% NMR yield. [c] **14** and (*Z*)-2-(but-2-en-2-yloxy)benzaldehyde (**15**) were also observed in 33% and 7% NMR yields, respectively. [d] 2-((3-phenylprop-1-en-2-yl)oxy)benzaldehyde (**16**) and (*Z*)-2-((1-phenylprop-1-en-2-yl)oxy)benzaldehyde (**17**) were also observed in 33% and 22% NMR yields, respectively. [e] Reaction in 1,4-dioxane.

Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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29 The annulation between **5a** and deuterated propargyl carbonate **1B** afforded deuterated **11aA**, in which deuteriums are incorporated at allylic and vinylic positions equally (see

Supporting Information). This result indicates that initially formed η^1-allylpalladium(II) should undergo isomerization into η^3-complex prior to umpolung carbonyl allylation. However, it might be possible that a substituent on the vinyl group in η^1-allylpalladium **8'** retards the isomerization to some extent due to steric repulsion with a dppp ligand.