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Phosphine-mediated diverse reactivity of γ-substituted allenoates with aldehydes: syntheses of highly functionalized chromans and (*E*,*E*)-1,3-dienes

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This paper is dedicated to Professor Zhengming Li (Nankai University) on the occasion of his 80th birthday

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ABSTRACT

As an extension of our previous studies, the phosphine-mediated diverse reactivity of γ-substituted allenoates with aldehydes has been further investigated. Under the catalysis of tris(*p*-chlorophenyl) phosphine (20 mol %), ethyl 2,3-pentadienoate, namely ethyl γ-methyl allenoate, readily undergoes a formal [4+2] annulation with dual-functional salicylaldehydes, giving highly functionalized chromans in 47–97% yields. This transformation represents a novel reactivity pattern of electron-deficient allenes with aldehydes. Conversely, when the γ substituent in the allenoate changes from methyl to benzyl or the employed phosphine from weakly nucleophilic triarylphosphine to strongly trialkylphosphine, the phosphine-mediated reactivity of γ-substituted allenoates with aldehydes will be steered to a stoichiometric olefination reaction, leading to the highly stereoselective formation of (*E*,*E*)-1,3-dienes. Thus, under the mediation of equivalent PPh_3, ethyl γ-benzyl allenoate readily condenses with salicylaldehydes, affording (*E*,*E*)-1,3-dienes in 34–84% yields; with strongly nucleophilic 1,3,5-triaza-7-phosphaadamantane (PTA) used instead of PPh_3, ethyl γ-methyl allenoate also gives the corresponding olefination products in 32–73% yields with reactive aromatic aldehydes. On the basis of our previous studies and current work, these chemical transformations of γ-substituted allenoates with aldehydes, as well as their diverse reactivity, have been mechanistically rationalized.

1. Introduction

During the past decade, nucleophilic phosphine-mediated reactivity of electron-deficient allenes has been extensively explored, with a number of new allene-based reactions with enormous synthetic potential having emerged.[1] For example, an array of phosphine-catalyzed annulations of allenoates with various electrophiles like activated olefins, imines, and aldehydes provide attractive approaches for constructing carbocycles and heterocycles.[2] In those transformations, the phosphine acts as a nucleophilic organocatalyst. Apart from its pronounced nucleophilicity, the tertiary phosphine also possesses strong affinity for oxygen, which is believed to be the primary driving force for the famous Wittig and Mitsunobu reactions.[3] Recently, many interesting stoichiometric transformations involving allenoates and tertiary phosphines have been reported, in which both nucleophilicity and oxygen-affinity of the phosphine take effects.[4] All of those findings further strengthen the versatility of both allenoates and phosphines in organic synthesis.

In the phosphine-mediated reactions, allenoates exhibit rich and diverse reactivity. Generally, the new bond formation in the product occurs at α- or/and γ-olefinic carbons of allenoates.[1a,b] However, subtle structural changes, such as the introduction of a simple substituent like methyl at the α- or γ-carbon of allenoates, can significantly deflect the inherent reactivity pattern of non-substituted allenoates.[5] For example, under the catalysis of a nucleophilic phosphine, α-methyl allenoates undergo the [4+2] annulation with activated olefins or imines, rather than the normal [3+2] cycloadditions.[6] In another scenario, although they often retain similar reactivity to that of nonsubstituted allenoates when reacting with activated olefins or imines,[2e,7] γ-substituted allenoates exhibit some distinct reactivity with aldehydes from that of nonsubstituted allenoates. The early work by Kwon and co-workers has revealed that nonsubstituted allenoates readily undergo various annulations with aldehydes under the catalysis of tertiary phosphines, chemoselectively forming such oxygen heterocycles as 1,3-dioxanes,[8a] pyrones,[8b] or dihydropyrones.[8c] In our latest studies (Scheme 1),[2g,4d] we demonstrated that γ-methyl allenoate (**1a**) could undertake a novel phosphine-catalyzed [3+2] annulation with aromatic aldehydes to yield substituted tetrahydrofurans **2**[2g]; under the similar conditions, γ-benzyl or (methoxycarbonyl) methyl allenoates (**1b**, **1c**), however, underwent a stoichiometric phosphine-mediated olefination reaction with both aromatic and aliphatic aldehydes, affording polysubstituted (*E*,*E*)-1,3-dienes **3** with high stereoselectivity.[4d] These rich and diverse reactions of allenoates under the mediation of nucleophilic phosphines provide

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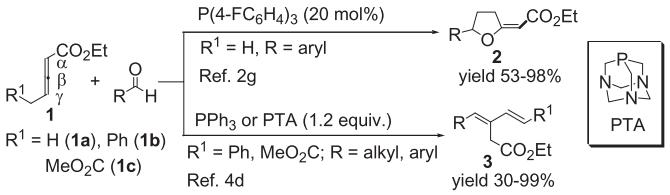


Scheme 1. Our previous studies on phosphine-mediated reactions of γ-substituted allenoates **1** with aldehydes.

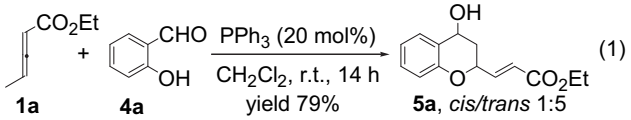
valuable synthetic tools for constructing molecular complexity in organic synthesis.

As an extension of our previous studies, herein the phosphine-mediated diverse reactivity of γ-substituted allenoates with aldehydes has been further investigated. A novel phosphine-catalyzed [4+2] annulation reaction of γ-methyl allenoate **1a** with dual-functional salicylaldehydes is described, in which the γ-methyl of the allenoate **1a** is involved in the new carbon–carbon bond formation. Additionally, it is also illustrated in this paper that the phosphine-mediated reactivity of γ-substituted allenoates **1** with aldehydes could be directed toward a stoichiometric olefination reaction, leading to the formation of 1,3-dienes **3** by varying the γ substituent in the allenoates **1** from methyl to benzyl or the employed phosphine from weakly nucleophilic triarylphosphine to strongly trialkylphosphine. On the basis of our preceding studies and current work, the distinct reactivity patterns of γ-substituted allenoates **1** with aldehydes are mechanistically rationalized.

2. Results and discussion

2.1. Phosphine-catalyzed [4+2] annulation of γ-methyl allenoate 1a with salicylaldehydes

Salicylaldehydes, possessing both nucleophilic phenolic hydroxyl and electrophilic formyl, have been often used as a class of versatile dual-functional synthons in the construction of a variety of oxygen heterocycle frameworks[9] including chromenes, chromans, and coumarins, which are widely present in the biologically important natural products and medicinal molecules.[10] Recently, a series of Lewis base-catalyzed annulations of salicylaldehydes or their corresponding imines with electron-deficient allenes have been elegantly developed by Shi[11a–c] and others.[11d–f] Tertiary amines and phosphines are most often used as effective catalysts in those reactions. In the course of our investigation on the phosphine-mediated reactions between allenoates and aldehydes,[1f] a formal Ph_3P-catalyzed [4+2] annulation of γ-methyl allenoate **1a** and salicylaldehyde **4a** was first observed, in which the γ-methyl of the allenoate was involved in the carbon–carbon bond formation [Eq. 1].[12] By comparison with other reported reactions of allenoates and aldehydes,[8,11] this [4+2] annulation does represent a novel reactivity pattern of allenoates with aldehydes, and also provides a facile synthesis of highly functionalized chromans **5**.



(1)

An elaborate optimization of the reaction conditions including phosphine catalyst, solvent, and possible protic additive was recently carried out with the phosphine-catalyzed [4+2] annulation of **1a** and salicylaldehyde **4a** used as a model (Table 1). A series of common tertiary phosphines were examined (entries 1–8). Relatively more nucleophilic phosphines like PBu_3, $PhPMe_2$, and $P(4\text{-}CH_3OC_6H_4)_3$ all led to a complex mixture of products (entries 1, 2, and 5). Bisphosphine, such as 1,2-bis(diphenylphosphino)ethane (DPPE) proved ineffective in the model reaction (entry 8). Weakly nucleophilic phosphines like triarylphosphines emerged as effective catalysts with $P(4\text{-}ClC_6H_4)_3$ being the best among the screened phosphines in terms of the yield and diastereoselectivity of the product **5a** (entry 7).

With $P(4\text{-}ClC_6H_4)_3$ (20 mol %) chosen as the catalyst, common solvents other than CH_2Cl_2 were further examined (Table 1, entries 9–16). Arene solvents like benzene, toluene, and xylene all gave good yields of **5a** (entries 9–11); in polar solvents THF and acetonitrile, the annulation product **5a** was also obtained in fair to good yields (entries 12 and 14); strongly polar solvents 1,4-dioxane and DMSO and protic solvent ethanol were all detrimental to the reaction, resulting in low yields of **5a** (entries 13 and 15–16). Judged by the yield, diastereoselectivity (cis/trans ratio), and reaction time, CH_2Cl_2 remained the preferred solvent for the model reaction.

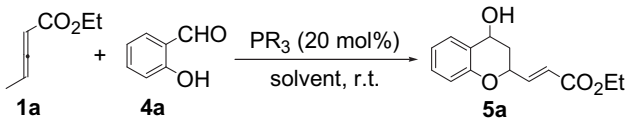
In the nucleophilic phosphine-catalyzed reactions, protic additives like water and alcohols often play significant roles in promoting the reaction rate and yield.[13] In this study, water and ethanol were also surveyed as protic additives in the model reaction. Under the catalysis of $P(4\text{-}ClC_6H_4)_3$ and in CH_2Cl_2 containing 20–200 mol % of the additive water or ethanol, the annulation product **5a** was readily obtained in 66–87% yields after 15 h (Table 1, entries 17–24). Addition of water up to 100 mol % (relative to the aldehyde) brought about the best yield of **5a** (entry 22), but in a lower cis/trans ratio (1:2.4) compared with that obtained under the standard conditions (entry 7).

With the optimized conditions in hand, a series of salicylaldehydes **4a**–**n** were explored in the $P(4\text{-}ClC_6H_4)_3$-catalyzed [4+2] annulations with γ-methyl allenoate **1a** (Table 2). With the water additive (100 mol %) used, the annulation reaction generally gave the chromans **5** in higher yields after shorter reaction times, but in inferior cis/trans ratios while compared with the corresponding reaction run without water additive (Table 2, entries 1–4, 8–10, and 13). Exceptional results were observed with salicylaldehydes **4e**–**g** (entries 5–7). For the salicylaldehydes bearing electron-donating groups, the chromans **5** were readily obtained in good to excellent yields under the optimized conditions with or without water additive (entries 1–7); for the salicylaldehydes with halogen or ester groups, the protic additive water significantly increased the reaction rate and yield (entries 8–10 and 13); the nitro-substituted salicylaldehyde **4n** failed to give the corresponding chroman product in appreciable yield after even elongated reaction time (entry 14).

In all cases of salicylaldehydes **4a**–**m**, the [4+2] annulation products **5** were obtained as a pair of cis- and trans-isomers with cis/trans ratios in the range of 1:1 to 1:17 (Table 2). In cases of salicylaldehydes **4i** and **4k**, their corresponding annulation products **5i** and **5k** were successfully isolated as pure cis- and trans-isomers by careful column chromatography on silica gel (entries 9 and 11); in other cases, the chromans **5** were only obtained as a mixture of cis- and trans-isomers, although **5b** and **5g** could be yielded with cis/trans ratios of 1:17 and 1:13, respectively (entries 2 and 7).

The structures of chromans **5** were identified by a combination of ^1H and ^{13}C NMR including NOESY analysis, elemental analysis, HRMS (ESI), IR spectroscopy, and X-ray crystallography. In the ^1H NMR spectra of chromans **5**, the coupling constant magnitude (ca. 15.6 Hz) for olefinic protons clearly confirms the *E*-configuration assignment for the alkene unit. The proton signals from the methylene group in the chroman backbone provide diagnostic information for the assignments of cis- and trans-configurations of chromans **5**. Furthermore, the NOESY analyses (for *cis*-**5i** and *trans*-**5k**) and X-ray crystal structure determination (for *trans*-**5j**, CCDC 790991)[14] provide unambiguous evidence for the structural determination of **5** (for the details, see Supplementary data).

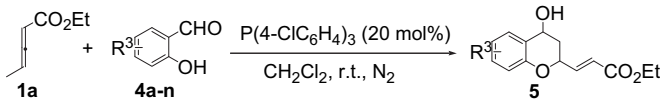
Table 1
Optimization on conditions of the model reaction between allenoate **1a** and salicylaldehyde **4a**[a]

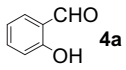
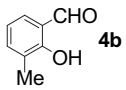
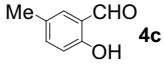
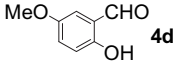
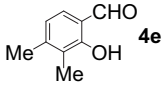
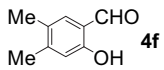


Entry	PR_3	Solvent	Time (h)	Yield of **5a**[b] (%)	*cis*-**5a**/*trans*-**5a**[c]
1	PBu_3	CH_2Cl_2	104	Complex	N/A
2	$PhPMe_2$	CH_2Cl_2	22	Complex	N/A
3	Ph_2PMe	CH_2Cl_2	39	75	1:4
4	PPh_3	CH_2Cl_2	14	79	1:5
5	$P(4\text{-}CH_3OC_6H_4)_3$	CH_2Cl_2	144	Complex	N/A
6	$P(4\text{-}FC_6H_4)_3$	CH_2Cl_2	17	83	1:2.5
7	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2	19	84	1:5
8	DPPE[d]	CH_2Cl_2	2	Complex	N/A
9	$P(4\text{-}ClC_6H_4)_3$	Benzene	38	77	1:2.3
10	$P(4\text{-}ClC_6H_4)_3$	Toluene	43	85	1:2.5
11	$P(4\text{-}ClC_6H_4)_3$	Xylene	38	81	1:2.2
12	$P(4\text{-}ClC_6H_4)_3$	THF	24	86	1:2.3
13	$P(4\text{-}ClC_6H_4)_3$	1,4-Dioxane	120	26	1:2.7
14	$P(4\text{-}ClC_6H_4)_3$	CH_3CN	43	69	1:2.8
15	$P(4\text{-}ClC_6H_4)_3$	DMSO	17	Trace	N/A
16	$P(4\text{-}ClC_6H_4)_3$	Ethanol	71	Trace	N/A
17	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+ethanol 200 mol %	15	66	1:2
18	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+ethanol 100 mol %	15	80	1:2
19	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+ethanol 50 mol %	15	75	1:2
20	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+ethanol 20 mol %	15	72	1:2
21	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+water 200 mol %	15	84	1:2.4
22	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+water 100 mol %	15	87	1:2.4
23	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+water 50 mol %	15	85	1:2.4
24	$P(4\text{-}ClC_6H_4)_3$	CH_2Cl_2+water 20 mol %	15	84	1:2.4

[a] Conditions: under N_2 atmosphere, a mixture of allenoate **1a** (0.75 mmol), salicylaldehyde **4a** (0.5 mmol), and catalyst phosphine (0.1 mmol, 20 mol %) in solvent (5 mL) was stirred at room temperature.
[b] Isolated yield based on **4a**.
[c] Determined by ^1H NMR of **5a** as a mixture of cis/trans-isomers.
[d] 1,2-Bis(diphenylphosphino)ethane.

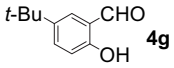
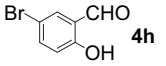
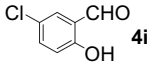
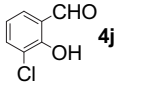
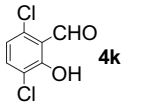
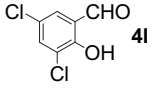
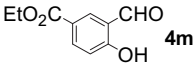
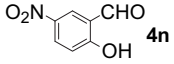
Table 2
Phosphine-catalyzed [4+2] annulation of γ-methyl allenoate **1a** and salicylaldehydes[a]



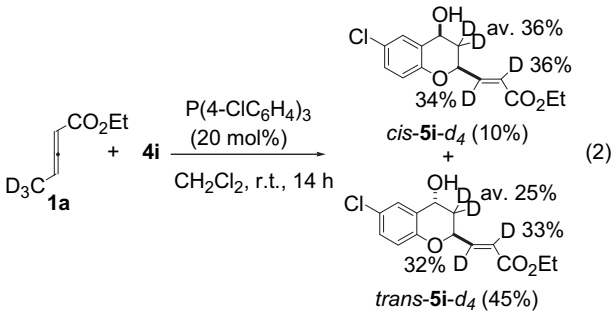
Entry	Salicylaldehydes	Time (h)[b]	Yield of **5**[b,c] (%)	cis/trans[b,d]
1	 **4a**	19 (15)	**5a**, 84 (87)	1:5 (1:2.4)
2	 **4b**	26 (24)	**5b**, 92 (92)	1:17 (1:4.3)
3	 **4c**	18 (16)	**5c**, 91 (92)	1:3.7 (1:2.2)
4	 **4d**	15 (13)	**5d**, 85 (97)	1:2.4 (1:1.9)
5	 **4e**	148 (124)	**5e**, 82 (81)	1:2.2 (1:1.4)
6	 **4f**	19 (48)	**5f**, 88 (85)	1:2.7 (1:2)

(*continued on next page*)

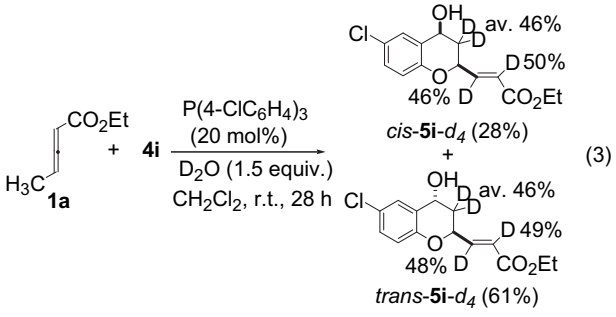
Table 2 (*continued*)

Entry	Salicylaldehydes	Time (h)[b]	Yield of **5**[b,c] (%)	cis/trans[b,d]
7	 **4g**	19 (20)	**5g**, 79 (72)	1:13 (1:2)
8	 **4h**	27 (21)	**5h**, 66 (90)	1:2.1 (1:1.5)
9	 **4i**	44 (19)	**5i**, 62 (90)	1:1.8 (1:2)
10	 **4j**	41 (35)	**5j**, 61 (85)	1:1.7 (1:1)
11	 **4k**	43	**5k**, 61	1:2.9
12	 **4l**	61	**5l**, 47	1:5.3
13	 **4m**	91 (81)	**5m**, 60 (72)	1:3 (1:1)
14	 **4n**	148	Trace	N/A

[a] Typical procedure: a mixture of allenoate **1a** (0.75 mmol), salicylaldehydes (0.5 mmol), and phosphine (0.1 mmol) in CH_2Cl_2 (5 mL) with or without water (0.5 mmol) was stirred at room temperature.
[b] Data in parentheses obtained from reactions with water additive.
[c] Isolated yield based on salicylaldehyde **4**.
[d] Determined by ^1H NMR of isomeric mixture **5** or by yields of separated isomers *cis*-/*trans*-**5**.



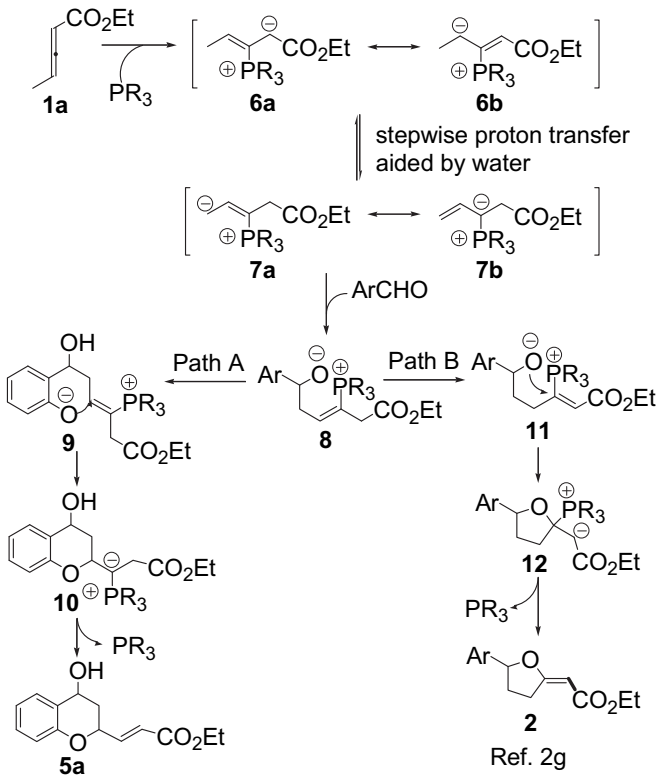
(2)



(3)

To better understand the mechanism of the phosphine-catalyzed [4+2] annulation reaction between γ-methyl allenoate **1a** and salicylaldehydes, deuterium-labeling experiments were conducted [Eqs. 2 and 3]. Under the optimal conditions without water additive, γ-methyl-deuterated allenoate **1a**-d_3 (purity>99%) was employed in the P(4-ClC_6H_4)$_3$-mediated [4+2] annulation with 5-chloro salicylaldehyde **4i**, leading to the formation of partially deuterated annulation products *cis*-**5i**-d_4 and *trans*-**5i**-d_4 in 55% combined yield and cis/trans ratio of 1:4.5 [Eq. 2]; however, under similar conditions except that D_2O (1.5 equiv) was added as an additive, the non-deuterated allenoate **1a** and salicylaldehyde **4i** also afforded the deuterated products *cis*-**5i**-d_4 and *trans*-**5i**-d_4 in 89% combined yield with slightly higher deuterium incorporations after routine chromatographic isolation on silica gel [Eq. 3]. Furthermore, the isolated annulation product *trans*-**5i** was quantitatively recovered without detectable deuterium incorporation after treatment with D_2O under the same conditions as listed in Eq. 3, followed by column chromatographic isolation. These results clearly imply that a water-involved proton transfer process is likely to occur at α-, β-, and δ-carbons of the allenoate **1a** in the annulation reaction.

Based on the experimental results from both current and previous studies,[2g] a plausible mechanism for phosphine-catalyzed [4+2] annulation between γ-methyl allenoate **1a** and salicylaldehydes is depicted in Scheme 2. As generally accepted in the nucleophilic phosphine catalysis,[1a,b] the nucleophilic attack of the tertiary phosphine at the β-carbon of the allenoate **1a** initially generates the



Scheme 2. A plausible mechanism for the phosphine-catalyzed [4+2] annulation between γ-methyl allenoate **1a** and salicylaldehyde.

resonance-stabilized zwitterionic intermediate **6**. Through stepwise, water-aided proton transfers,[15] **6** reversibly converts to an allylic phosphorus ylide **7**, which also presumably exists in two resonance forms **7a** and **7b**. The ylide **7** preferentially undergoes an addition to aromatic aldehydes including salicylaldehydes in its allylic carbanion form **7a**, leading to the formation of the phosphonium alkoxide zwitterions **8**. When the aryl group in **8** comes from a dual-functional salicylaldehyde, a proton transfer process accordingly occurs between the alkoxide anion and phenolic hydroxyl leading to the formation of the intermediate **9** (Scheme 2, path A), which is subjected to a Michael addition to form the phosphorus ylide intermediate **10**. The ylide **10** subsequently undergoes a set of proton transfers, followed by the elimination of the phosphine to furnish the [4+2] annulation product **5a**.[16] For the purpose of comparison, the proposed mechanism for the [3+2] annulation of **1a** with aromatic aldehydes is also depicted in Scheme 2.[2g] When the aryl group in **8** does not bear any nucleophilic group, namely hydroxyl, then **8** is prone to a double-bond migration, giving rise to the intermediate **11** (Scheme 2, path B). Subsequently, **11** undergoes a ring closure through an intramolecular Michael addition followed by elimination of the catalyst phosphine to afford the [3+2] annulation product **2**. Thus, in the phosphine-catalyzed [3+2] and [4+2] annulations of γ-methyl allenoate **1a** with aromatic aldehydes, the reaction steps leading to the formation of the intermediate **8** are very likely common.

2.2. Stoichiometric olefination between γ-substituted allenoate 1, aldehyde, and phosphine

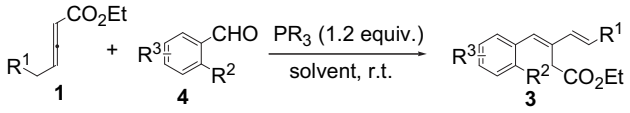
In our preceding studies,[4d] it has been found that under the mediation of equivalent PPh_3 or PTA, γ-benzyl allenoate **1b** (R^1=Ph) or γ-(methoxycarbonyl)methyl allenoate **1c** (R^1=CO_2Me) readily underwent a stoichiometric olefination with both aromatic and aliphatic aldehydes, giving trisubstituted 1,3-dienes **3** in satisfactory yields and high *E*-selectivity (Scheme 1). Following the optimized reaction conditions set in the previous studies[4d] except the solvent 1,4-dioxane used instead, the olefination of the allenoate **1b** was investigated with a series of representative salicylaldehydes. Under the mediation of PPh_3 (1.2 equiv), salicylaldehydes bearing electron-donating or -withdrawing groups readily underwent an olefination with γ-benzyl allenoate **1b**, giving the corresponding trisubstituted (*E*,*E*)-1,3-dienes **3** in modest to good yields (Table 3, entries 1–6). For γ-(methoxycarbonyl)methyl allenoate **1c**, its olefination with salicylaldehyde **4a** was best mediated by the more nucleophilic phosphine PTA, affording a mixture of (*E*,*E*)- and (*E*,*Z*)-1,3-dienes **3g** with a ratio of 8:1 (entry 7). Therefore, for the γ-substituted allenoates **1b** and **1c**, their phosphine-mediated reactions with the dual-functional salicylaldehydes still tended to the highly stereoselective stoichiometric olefination.

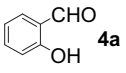
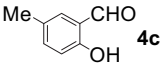
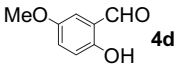
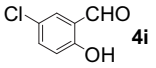
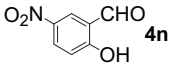
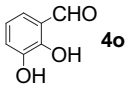
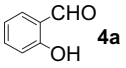
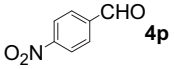
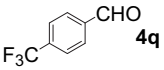
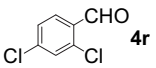
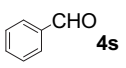
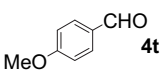
As illustrated in our previous report[2g] and current work, under the catalysis of weakly nucleophilic triarylphosphine, γ-methyl allenoate **1a** chemoselectively underwent the [3+2] and [4+2] annulations with aromatic aldehydes and dual-functional salicylaldehydes, respectively. Our further investigations, however, indicated that, under the mediation of a more nucleophilic phosphine, such as PTA, a stoichiometric olefination between the allenoate **1a** and electron-poor aromatic aldehydes could be chemoselectively realized (Table 3). For selected benzaldehydes **4p**–**r** bearing electron-withdrawing groups, their PTA-mediated olefination with the allenoate **1a** readily afforded the corresponding 1,3-dienes **3** in modest yields (Table 3, entries 8–10). Relatively more electron-rich benzaldehyde **4s** also brought about the olefination product **3k**, but in a lower yield (entry 11). *p*-Methoxybenzaldehyde **4t**, however, failed in giving the corresponding olefination product in appreciable yield (entry 12). The electron-rich benzaldehydes were apparently less reactive in the PTA-mediated olefination with the allenoate **1a**.

2.3. Rationale for the diverse reactivity of γ-substituted allenoates 1 and aldehydes under the mediation of phosphines

Based on the experimental results from both current and previous studies, the diverse phosphine-mediated reactivity of γ-substituted allenoates **1** with aldehydes could be rationalized with regard to the in situ formed phosphorus ylide intermediate **14**, which may be expressed in two resonance forms **14a** and **14b** (Scheme 3). The phosphorus ylide **14** is presumably generated from the nucleophilic attack of the phosphine PR_3 at the allenoate **1** followed by a stepwise, water-aided proton transfer.[15] The ylide is believed to be the common intermediate, which is responsible for chemical transformations, such as the [3+2]/[4+2] annulations and Wittig olefination between γ-substituted allenoates **1** and aldehydes. The steric and electronic properties of both the γ substituent of **1** and the phosphine PR_3 impose major influence on the reactivity of the phosphorus ylide intermediate **14**, and consequently on the reaction patterns of γ-substituted allenoates with aldehydes, although the reaction conditions also have considerable effects as observed in our studies. When R^1 is hydrogen and PR_3 is a weakly nucleophilic triarylphosphine, the formed there-of phosphorus ylide **14** (from γ-methyl allenoate **1a**) tends to undergo an addition to aromatic aldehydes in its resonance form allylic carbanion **14a** (R^1=H), leading to the [3+2] and [4+2] annulations as shown in Scheme 2. The addition of the allylic carbanion **14a** to aldehydes is kinetically preferred over that of the allylic phosphorus ylide **14b** (R^1=H) with respect to the steric hindrance. On the other hand, as the substituent R^1 in **14** changes from hydrogen to a more conjugative phenyl or methoxycarbonyl, the more stable resonance form **14b** (R^1=Ph, CO_2Me) represents the major contributor to the intermediate **14**. As a consequence, the reactivity pattern of the γ-substituted allenoates **1** with aldehydes accordingly shifts from the catalytic [3+2] or [4+2]

Table 3
Phosphine-mediated olefination of γ-substituted allenoates **1** and aldehydes **4**[a]



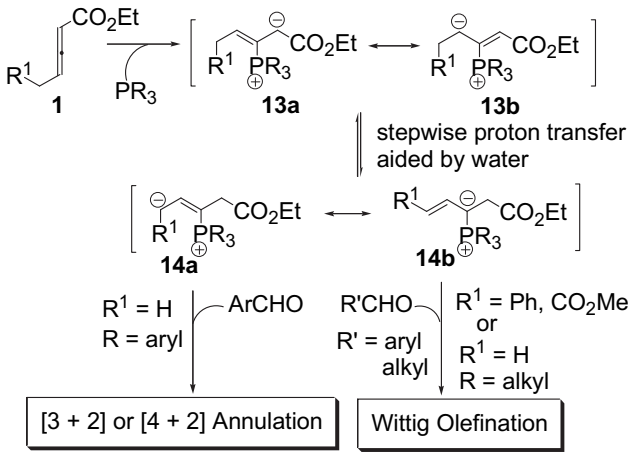
Entry	R^1 in **1**	Aldehydes **4**	Conditions	Yield of **3**[b] (%)
1	Ph (**1b**)	 **4a**	PPh_3, 1,4-dioxane, 12 h	**3a**, 73
2	Ph (**1b**)	 **4c**	PPh_3, 1,4-dioxane, 27 h	**3b**, 84
3	Ph (**1b**)	 **4d**	PPh_3, 1,4-dioxane, 22 h	**3c**, 70
4	Ph (**1b**)	 **4i**	PPh_3, 1,4-dioxane, 22 h	**3d**, 74
5	Ph (**1b**)	 **4n**	PPh_3, 1,4-dioxane, 18 h	**3e**, 62
6	Ph (**1b**)	 **4o**	PPh_3, 1,4-dioxane, 22 h	**3f**, 34
7[c]	MeO_2C (**1c**)	 **4a**	PTA, CH_2Cl_2, 48 h	**3g**, 71[d]
8	H (**1a**)	 **4p**	PTA, CH_2Cl_2, 12 h	**3h**, 73
9	H (**1a**)	 **4q**	PTA, CH_2Cl_2, 48 h	**3i**, 66
10	H (**1a**)	 **4r**	PTA, CH_2Cl_2, 46 h	**3j**, 53
11	H (**1a**)	 **4s**	PTA, CH_2Cl_2, 48 h	**3k**, 32
12	H (**1a**)	 **4t**	PTA, CH_2Cl_2, 48 h	Trace

[a] Typical procedure: a mixture of allenoate **1** (0.6 mmol), aldehyde **4** (0.5 mmol), and phosphine (0.6 mmol) in the specified solvent (2 mL) was stirred at room temperature.
[b] Isolated yield based on **4**.
[c] Cited from Ref. 4d.
[d] As a mixture of (*E*,*E*)- and (*E*,*Z*)-isomers with a ratio of 8:1.

annulation to the stoichiometric Wittig olefination. In another scenario, when R^1 is hydrogen but PR_3 is a strongly nucleophilic trialkylphosphine, the reactivity of the allylic phosphorus ylide **14b** for the Wittig olefination is promoted with the electron-rich trialkylphosphine PR_3, such as PTA,[17] and therefore the PTA-mediated olefination could be realized between γ-methyl allenoate **1a** (R^1=H) and reactive aromatic aldehydes (Table 3, entries 8–11). Thus, the diverse reactivity patterns between γ-substituted allenoates **1** and aldehydes are predominantly controlled by the nature of the γ substituent in **1** and the employed phosphine.

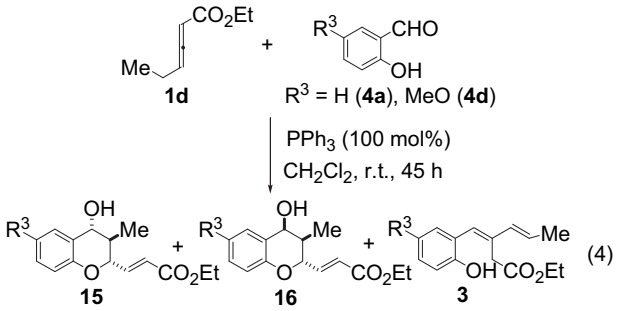
Results from PPh_3-mediated competitive reactions between γ-ethyl allenoate **1d** (R^1=Me) and salicylaldehydes (**4a**, **4d**) could corroborate the above rationale about the diverse reactivity of γ-substituted allenoates **1** [Eq. 4]. Regarding the steric and electronic properties, methyl group is in a transitional place between hydrogen and conjugative phenyl. Accordingly, the phosphorus ylide intermediate **14** (R^1=Me) from the allenoate **1d** and PPh_3 presumptively possesses both reactivity patterns of the annulation and olefination with aldehyde (Scheme 3). As assumed, under the mediation of equivalent PPh_3, the [4+2] annulation[18] and olefination reactions between **1d** and salicylaldehydes competitively occurred, affording substituted chromans (**15** and **16**, major) and the corresponding 1,3-dienes **3** (minor) [Eq. 4]. The chromans **15** and **16** were only isolated as an isomeric mixture by column chromatography on silica gel.

In conclusion, as the continuation of our efforts on the phosphine-mediated reactivity of electron-deficient allenoates with



Scheme 3. Rationale for the diverse reactivity of γ-substituted allenoates **1**.

aldehydes,[2g,4d] the diverse reactivity patterns between γ-substituted allenoates **1** (R^1=H, Ph, CO_2Me, and Me) and aldehydes including dual-functional salicylaldehydes have been further investigated in this work. An unprecedented [4+2] annulation reaction between γ-methyl allenoate **1a** and salicylaldehydes has been successfully realized under the catalysis of P(4-ClC_6H_4)$_3$ (20 mol %) and very mild conditions, giving a series of highly functionalized chromans **5** in modest to excellent yields. In contrast with this annulation, under the mediation of equivalent PPh_3 or PTA, γ-benzyl allenoate **1b** or γ-(methoxycarbonyl)methyl allenoate **1c** readily undergoes a stoichiometric olefination with salicylaldehydes, leading to a highly stereoselective synthesis of trisubstituted 1,3-dienes **3** in medium yields. For γ-methyl allenoate **1a**, a stoichiometric olefination, rather than a catalytic [3+2] annulation,[2g] with reactive aromatic aldehydes proceeds following treatment with an equivalent of strongly nucleophilic trialkylphosphine PTA, affording the corresponding 1,3-dienes **3** in modest yields. For γ-ethyl allenoate **1d**, however, both [4+2] annulation and olefination between **1d** and salicylaldehydes could competitively occur under the influence of equivalent PPh_3.



R^3	yield of (**15** + **16**)	ratio of **15**/**16**	yield of **3**
H	**15a** + **16a**, 46%	1:2.4	**3l**, 9%
MeO	**15b** + **16b**, 60%	1:1.2	**3m**, 16%

Based on the experimental results including deuterium-labeling, a plausible mechanism for the phosphine-catalyzed [4+2] annulation between γ-methyl allenoate **1a** and salicylaldehydes is proposed. Furthermore, the diverse reactivity patterns between γ-substituted allenoates **1** and aldehydes are mechanistically rationalized with regard to the in situ formed allylic phosphorus ylide **14** being the key intermediate. The diverse reaction patterns of the allenoates **1** and aldehydes are predominantly controlled by the nature of the γ substituent in **1** and the nucleophile phosphine. As demonstrated in this study, while the new chemistry of the electron-deficient allenes under the influence of nucleophilic tertiary phosphines is extensively explored, new reactions with highly synthetic potential keeps emerging. Future significant achievements in this area will further strengthen the versatility of both the allenes and phosphines in organic synthesis.

3. Experimental section

3.1. General

General experimental conditions are given in Supplementary data. γ-Substituted allenoates **1a**–**d** and **1a**-d_3 were prepared according to the previous procedures.[2g,4d] 1,3,5-Triaza-7-phosphaadamantane (PTA) was prepared from tetris(hydroxymethyl) phosphonium sulfate and hexamethylenetetramine by the reported method.[19]

*3.1.1. Phosphine-catalyzed [4+2] annulation of γ-methyl allenoate **1a** with salicylaldehydes (typical procedure).* (A) *Without water additive*. At room temperature, to a stirred solution of 5-chloro salicylaldehydes **4i** (78 mg, 0.5 mmol) and tris(*p*-chlorophenyl) phosphine (37 mg, 0.1 mmol) in dichloromethane (5 mL) was added γ-methyl allenoate **1a** (95 mg, 0.75 mmol) by the means of a microsyringe over 5 min. The resulting reaction mixture was stirred until the salicylaldehyde was completely consumed (44 h), as monitored by TLC. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1 to 10:1) to afford chromans *trans*-**5i** (yellowish oil, the earlier fraction, 56 mg, yield 40%) and *cis*-**5i** (white solid, mp 83–84 °C, the later fraction, 31 mg, yield 22%).

(B) *With water additive*. At room temperature, to a stirred solution of 5-chloro salicylaldehydes **4i** (78 mg, 0.5 mmol), tris (*p*-chlorophenyl)phosphine (37 mg, 0.1 mmol), and water (9 μL, 0.5 mmol) in dichloromethane (5 mL) was added the allenoate **1a** (95 mg, 0.75 mmol) by the means of a microsyringe over 5 min. The resulting reaction mixture was stirred until the salicylaldehyde was completely consumed (19 h), as monitored by TLC. After the same work-up and isolation as in above procedure A, the pure chromans *trans*-**5i** and *cis*-**5i** were obtained in combined 90% yield (127 mg, cis/trans 1:2) (Table 2, entry 9). For *trans*-**5i**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.27 (d, *J*=2.4 Hz, 1H), 7.18 (dd, *J*=8.8, 2.4 Hz, 1H), 7.01 (dd, *J*=15.6, 4.4 Hz, 1H), 6.85 (d, *J*=8.8 Hz, 1H), 6.22 (dd, *J*=15.6, 2.0 Hz, 1H), 4.90 (m, 1H), 4.74 (t, *J*=3.0 Hz, 1H), 4.21 (q, *J*=7.2 Hz, 2H), 2.66 (br s, 1H), 2.16 (dt, *J*=14.0, 2.8 Hz, 1H), 1.84 (ddd, *J*=14.0, 11.6, 3.2 Hz, 1H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.3, 152.4, 145.4, 129.9, 129.4, 125.6, 124.7, 121.6, 118.7, 69.9, 62.8, 60.7, 35.3, 14.1 ppm; HRMS (ESI) calcd for $C_{14}H_{15}ClO_4Na^+$ requires 305.0551, found 305.0546; IR (neat, cm^{-1}): 3434, 1720, 1662, 1482, 1307, 1072. For *cis*-**5i**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (d, *J*=2.0 Hz, 1H), 7.15 (dd, *J*=8.8, 2.4 Hz, 1H), 6.99 (dd, *J*=15.6, 4.4 Hz, 1H), 6.80 (d, *J*=8.8 Hz, 1H), 6.18 (dd, *J*=15.6, 2.0 Hz, 1H), 4.94 (dd, *J*=9.6, 6.0 Hz, 1H), 4.82 (m, 1H), 4.22 (q, *J*=7.2 Hz, 2H), 2.42 (ddd, *J*=13.6, 6.0, 2.8 Hz, 1H), 2.08 (br s, 1H), 1.88 (pseudo dt, *J*=13.6, 10.2 Hz, 1H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.2, 151.9, 145.0, 129.2, 127.2, 126.8, 126.0, 121.5, 118.0, 73.2, 64.6, 60.7, 36.6, 14.2 ppm; HRMS (ESI) calcd for $C_{14}H_{15}ClO_4Na^+$ requires 305.0551, found 305.0547; IR (KBr, cm^{-1}): 3438, 1722, 1595, 1420, 1306, 1068, 1031.

Following the above typical procedures, other chromans **5a**–**m** listed in Table 2 were prepared from the allenoate **1a** and

corresponding salicylaldehydes **4**. Their spectroscopic and analytical data are given in Supplementary data.

*3.1.2. Phosphine-catalyzed [4+2] annulation of γ-methyl-deuterated allenoate **1a**-d_3 with 5-chloro salicylaldehyde **4i** [Eq. 2].* Following the typical procedure A for the P(4-ClC_6H_4)$_3$-catalyzed [4+2] annulation of the allenoate **1a** with salicylaldehydes, deuterated allenoate **1a**-d_3 (99% D, 39 mg, 0.31 mmol) was added into a stirred solution of 5-chloro salicylaldehyde **4i** (73 mg, 0.46 mmol) and tris (*p*-chlorophenyl)phosphine (37 mg, 0.1 mmol) in dichloromethane (5 mL) and the resulting mixture was stirred for 14 h. After work-up and subsequent isolation by column chromatography on silica gel, two fractions were collected: pure partially deuterated chroman *trans*-**5i**-d_4 (30 mg, 35% yield) and a mixture of *cis*-**5i**-d_4 and *trans*-**5i**-d_4 with cis/trans ratio of ca. 1:1 (17 mg, 20% yield). For the fraction of *trans*-**5i**-d_4: colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.28 (d, *J*=2.4 Hz, 1H), 7.20 (dd, *J*=8.8, 2.4 Hz, 1H), 7.03 (m, 0.68H), 6.87 (d, *J*=8.8 Hz, 1H), 6.24 (m, 0.67H), 4.92 (m, 1H), 4.77 (t, *J*=3.0 Hz, 1H), 4.23 (q, *J*=7.2 Hz, 2H), 2.24 (br s, 1H), 2.18 (m, 0.79H), 1.84 (m, 0.70H), 1.31 (t, *J*=7.2 Hz, 3H) ppm. For the fraction of *cis*-**5i**-d_4 and *trans*-**5i**-d_4 mixture: colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (dd *J*=2.4 Hz, 0.5H), 7.28 (d, *J*=2.4 Hz, 0.5H), 7.18 (m, 1H), 6.97 (m, 0.66H), 6.87 (d, *J*=8.8 Hz, 0.5H), 6.80 (d, *J*=8.8 Hz, 0.5H), 6.19 (m, 0.64H), 4.91 (m, 1H), 4.83 (m, 1H), 4.22 (m, 2H), 2.41 (m, 0.34H), 2.26 (br s, 0.4H), 2.19 (m, 0.6H), 1.85 (m, 0.64H), 1.31 (m, 3H) ppm.

*3.1.3. Phosphine-catalyzed [4+2] annulation of γ-methyl allenoate **1a** with 5-chloro salicylaldehyde **4i** in the presence of D_2O additive [Eq. 3].* Following the procedure for the P(4-ClC_6H_4)$_3$-catalyzed [4+2] annulation of the allenoate **1a** with 5-chloro salicylaldehyde **4i** in the presence of water additive (typical procedure B), a reaction mixture comprising of γ-methyl allenoate **1a** (95 mg, 0.75 mmol), 5-chloro salicylaldehyde **4i** (78 mg, 0.5 mmol), tris(*p*-chlorophenyl) phosphine (37 mg, 0.1 mmol), and D_2O (15 μL, 0.75 mmol) in dichloromethane (5 mL) was stirred at room temperature for 28 h. After work-up and subsequent isolation by column chromatography on silica gel, pure partially deuterated chromans *trans*-**5i**-d_4 and *cis*-**5i**-d_4 were obtained in 89% combined yield. For the fraction *trans*-**5i**-d_4: colorless oil, 87 mg, 61% yield; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.26 (d, *J*=2.4 Hz, 1H), 7.18 (dd, *J*=8.8, 2.4 Hz, 1H), 7.00 (m, 0.51H), 6.85 (d, *J*=8.8 Hz, 1H), 6.21 (m, 0.52H), 4.89 (m, 1H), 4.73 (t, *J*=2.8 Hz, 1H), 4.21 (q, *J*=7.2 Hz, 2H), 2.88 (br s, 1H), 2.16 (m, 0.53H), 1.86 (m, 0.55H), 1.30 (t, *J*=7.2 Hz, 3H) ppm. For the fraction *cis*-**5i**-d_4: colorless oil, 40 mg, 28% yield; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (dd, *J*=2.4, 0.6 Hz, 1H), 7.15 (dd, *J*=8.8, 2.4 Hz, 1H), 6.99 (m, 0.54H), 6.80 (d, *J*=8.8 Hz, 1H), 6.19 (m, 0.50H), 4.93 (d, *J*=5.6 Hz, 1H), 4.82 (m, 1H), 4.22 (q, *J*=7.2 Hz, 2H), 2.42 (m, 0.54H), 2.16 (br s, 1H), 1.88 (m, 0.55H), 1.31 (t, *J*=7.2 Hz, 3H) ppm.

*3.1.4. PPh_3-mediated olefination of γ-benzyl allenoate **1b** with salicylaldehydes (typical procedure).* At room temperature, to a stirred solution of salicylaldehyde **4a** (61 mg, 0.5 mmol) and PPh_3 (157 mg, 0.6 mmol) in 1,4-dioxane (2 mL) was added γ-benzyl allenoate **1b** (121 mg, 0.6 mmol) by the means of a microsyringe over 5 min. The resulting reaction mixture was further stirred for 12 h. At that time the salicylaldehyde **4a** disappeared, as monitored by TLC. After removal of the solvent on a rotary evaporator under reduced pressure, the residue was subjected to column chromatography isolation on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1 to 5:1), giving the olefination product diene **3a** (112 mg, yield 73%) as colorless oil (Table 3, entry 1). For **3a**, ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ 7.43 (d, *J*=7.2 Hz, 2H), 7.36–7.31 (m, 2H), 7.27–7.22 (m, 1H), 7.19–7.14 (m, 2H), 6.98 (d, *J*=16.3 Hz, 1H), 6.88–6.95 (m, 2H), 6.79 (s, 1H), 6.60 (d, *J*=16.3 Hz, 1H), 6.24 (br s, 1H), 4.22 (q, *J*=7.2 Hz, 2H), 3.40 (s, 2H), 1.28 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 172.4, 153.6, 136.9, 135.4, 131.1, 129.9, 129.7, 129.7, 128.8, 128.6, 127.7, 126.5, 123.4, 120.2, 116.2, 61.4, 34.3, 14.0 ppm. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54; found: C, 77.61; H, 6.22.

Following the above typical procedure, other dienes **3b**–**f** listed in Table 3 were prepared from the allenoate **1b** and corresponding salicylaldehydes **4**. Their spectroscopic and analytical data are given in Supplementary data.

*3.1.5. PTA-mediated olefination of γ-methyl allenoate **1a** with aromatic aldehydes (typical procedure).* At room temperature, to a stirred solution of *p*-nitro benzaldehyde **4p** (76 mg, 0.5 mmol) and PTA (94 mg, 0.6 mmol) in dichloromethane (2 mL) was added γ-methyl allenoate **1a** (76 mg, 0.6 mmol) by the means of a microsyringe over 5 min. The reaction mixture was further stirred for 12 h. At that time the aldehyde was consumed, as monitored by TLC. Then water (15 mL) was added to dissolve the PTA oxide. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3×10 mL). The combined extracting was dried over sodium sulfate. After filtration and concentration, the residue was subjected to column chromatography isolation on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1 to 5:1) to afford the product diene **3h** (98 mg, yield 73%) as colorless oil (Table 3, entry 8). For **3h**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.21 (d, *J*=8.4 Hz, 2H), 7.56 (d, *J*=8.4 Hz, 2H), 6.78 (s, 1H), 6.55 (dd, *J*=17.4, 10.7 Hz, 1H), 5.44 (d, *J*=17.4 Hz, 1H), 5.29 (d, *J*=10.7 Hz, 1H), 4.22 (q, *J*=7.2 Hz, 2H), 3.43 (s, 2H), 1.30 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 170.7, 146.7, 143.4, 139.3, 135.9, 132.0, 129.4, 123.5, 115.8, 61.1, 33.5, 14.0 ppm; HRMS (ESI) calcd for $C_{14}H_{15}NO_4Na^+$ requires 284.0893, found 284.0892.

Following the above typical procedure, other dienes **3i**–**k** listed in Table 3 were prepared from the allenoate **1a** and corresponding aromatic aldehydes **4**. Their spectroscopic and analytical data are given in Supplementary data.

*3.1.6. PPh_3-mediated competitive reactions between γ-ethyl allenoate **1d** and salicylaldehydes (general procedure).* At room temperature, to a stirred solution of salicylaldehyde **4a** or **4d** (0.5 mmol) and PPh_3 (131 mg, 0.5 mmol) in dichloromethane (5 mL) was added γ-ethyl allenoate **1d** (105 mg, 0.75 mmol) by the means of a microsyringe over 5 min. The resulting reaction mixture was continuously stirred for 45 h. After removal of the solvent and volatile components on a rotary evaporator under reduced pressure, the residue was subjected to column chromatography isolation on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1 to 10:1), affording the corresponding olefination product **3** (the earlier fraction, minor) and the [4+2] annulation products **15** and **16** as a stereoisomeric mixture (the later fraction, major).

Following the above general procedure, salicylaldehyde **4a** (61 mg, 0.5 mmol) afforded the olefination product diene **3l** (pale yellow oil, 11 mg, yield 9%) and the annulation products **15a** and **16a** as an isomeric mixture (yellowish oil, 62 mg, yield 47%, ratio **15a**/**16a** 1:2.4). For **3l**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.18 (t, *J*=8.0 Hz, 1H), 7.06 (d, *J*=8.0 Hz, 1H), 6.92 (d, *J*=8.0 Hz, 1H), 6.88 (t, *J*=8.0 Hz, 1H), 6.51 (s, 1H), 6.28 (d, *J*=15.6 Hz, 1H), 6.11 (br s, 1H), 5.77 (dq, *J*=15.6, 6.8 Hz, 1H), 4.19 (q, *J*=7.2 Hz, 2H), 3.22 (s, 2H), 1.83 (d, *J*=6.8 Hz, 3H), 1.27 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 172.6, 153.5, 136.5, 133.3, 129.8, 129.0, 126.7, 126.4, 123.3, 120.2, 116.3, 61.4, 34.4, 18.4, 14.1 ppm; HRMS (ESI) calcd for $C_{15}H_{18}O_3Na^+$ requires 269.1148, found 269.1150. Selected data for the isomer **15a**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.45 (d, *J*=8.0 Hz, 1H), 7.28–6.86 (m, 4H), 6.18 (dd, *J*=15.6, 1.6 Hz, 1H), 4.50–4.38 (m, 2H), 4.22 (q, *J*=7.2 Hz, 2H), 1.88 (m, 1H), 1.78 (br s, 1H), 1.30 (t, *J*=7.2 Hz, 3H), 1.16 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.1, 153.0, 144.6, 129.6, 127.8, 124.7, 122.7, 121.2, 116.5, 78.3, 70.7, 60.6, 40.2, 14.4, 12.6 ppm. Selected data for **16a**, ^{1}H NMR

($CDCl_3$, 400 MHz, TMS): δ 7.28–6.86 (m, 5H), 6.24 (dd, J=15.6, 1.6 Hz, 1H), 4.68 (dd, J=10.0, 5.6 Hz, 1H), 4.58 (d, J=3.2 Hz, 1H), 4.23 (q, J=7.2 Hz, 2H), 1.98 (m, 1H), 1.78 (br s, 1H), 1.32 (t, J=7.2 Hz, 3H), 1.15 (d, J=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.1, 153.3, 144.8, 130.1, 129.4, 123.9, 123.1, 120.9, 116.9, 74.7, 67.4, 60.6, 37.3, 14.2, 12.6 ppm. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; found: C, 68.61; H, 6.72; HRMS (ESI) calcd for $C_{15}H_{18}O_4Na^+$ requires 285.1097, found 285.1101.

Following the general procedure, PPh_3-mediated reactions of γ-ethyl allenoate **1d** with 5-methoxy salicylaldehyde **4d** (76 mg, 0.5 mmol) brought about the corresponding olefination product **3m** (yellowish oil, 22 mg, yield 16%) and the annulation products **15b** and **16b** as an isomeric mixture (yellowish oil, 88 mg, yield 60%, **15b**/**16b** ratio 1:1.2). For **3m**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 6.85 (d, J=8.8 Hz, 1H), 6.75 (dd, J=8.8, 2.8 Hz, 1H), 6.64 (d, J=2.8 Hz, 1H), 6.49 (s, 1H), 6.27 (d, J=15.6 Hz, 1H), 5.82 (br s, 1H), 5.79 (dq, J=15.6, 6.8 Hz, 1H), 4.19 (q, J=7.2 Hz, 2H), 3.74 (s, 3H), 3.24 (s, 2H), 1.83 (dd, J=6.8, 1.0 Hz, 3H), 1.27 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 172.6, 153.1, 147.6, 136.4, 133.3, 126.8, 126.5, 123.9, 117.1, 114.8, 114.3, 61.4, 55.7, 34.5, 18.4, 14.1 ppm; HRMS (ESI) calcd for $C_{16}H_{20}O_4Na^+$ requires 299.1254, found 299.1254. Selected data for **15b**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.00, 6.78 (m, 4H), 6.15 (dd, J=15.6, 1.6 Hz, 1H), 4.35 (m, 2H), 4.20 (q, J=7.2 Hz, 2H), 3.74 (s, 3H), 2.41 (br s, 1H), 1.83 (m, 1H), 1.30 (t, J=7.2 Hz, 3H), 1.16 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.1, 153.9, 147.0, 144.7, 125.3, 122.6, 117.1, 115.6, 111.7, 78.2, 70.8, 60.6, 55.6, 40.2, 14.2, 12.4 ppm. Selected data for **16b**, ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.00, 6.78 (m, 4H), 6.19 (dd, J=15.6, 1.6 Hz, 1H), 4.58 (dd, J=10.0, 5.6 Hz, 1H), 4.49 (d, J=3.2 Hz, 1H), 4.21 (q, J=7.2 Hz, 2H), 3.74 (s, 3H), 2.41 (br s, 1H), 1.95 (m, 1H), 1.31 (t, J=7.2 Hz, 3H), 1.15 (d, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 166.1, 153.5, 147.1, 145.1, 124.1, 122.8, 117.5, 116.4, 113.5, 74.7, 67.4, 60.5, 55.6, 37.3, 14.1, 12.4 ppm. Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90; found: C, 65.57; H, 7.12; HRMS (ESI) calcd for $C_{16}H_{20}O_5Na^+$ requires 315.1203, found 315.1208.

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Supplementary data

General experiment conditions; spectroscopic and analytical data for compounds **3** and **5**; more details in structure determination of chromans **5** by ^{1}H NMR data; ORTEP drawing of *trans*-**5j**; NOESY spectra for *cis*-**5i** and *trans*-**5k**; ^{1}H and ^{13}C NMR spectroscopic copies for all new compounds in this study. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.12.051. These data include MOL files and InChIKeys of the most important compounds described in this article.

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