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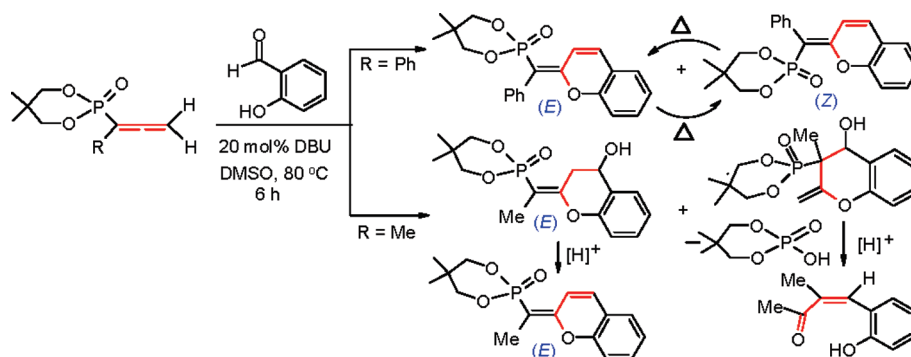
Reactivity of Allenylphosphonates toward Salicylaldehydes and Activated Phenols: Facile Synthesis of Chromenes and Substituted Butadienes

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The reaction of salicylaldehydes with allenylphosphonates in the presence of a base leads to a variety of phosphono-chromenes and allylic phosphonates. Optimization of reaction conditions reveals that DBU (base) in DMSO (solvent) is the best combination in most cases, with DBU acting as an organocatalyst. PEG-400 also gave good results, but the yields were slightly lower than that in DMSO. Several of the key products have been characterized by single-crystal X-ray crystallography. Interconversion of *E* and *Z* isomers of phosphono-chromenes is demonstrated by ^{31}P NMR spectroscopy. A novel P–C bond cleavage reaction of some of these chromenes leading to substituted enones is also reported. In a few cases, phenol addition products are also isolated. In order to probe the pathways in the latter reaction, allenylphosphonates have also been treated with activated phenols in the presence of base to selectively afford either allylic phosphonyl ethers or vinylic phosphonyl ethers depending on the substituents on the allenylphosphonate. Theoretical calculations were consistent with experimental results. Finally, utilization of allylic phosphonyl ether in the Horner–Wadsworth–Emmons reaction to afford substituted *trans*-1,3-butadiene in good yields is demonstrated.

Introduction

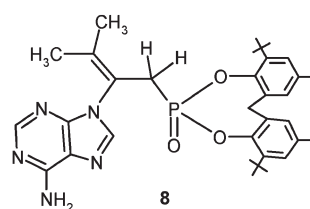
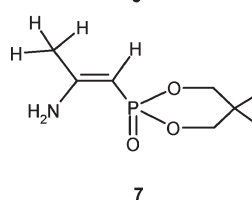
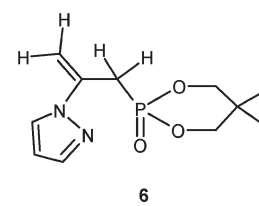
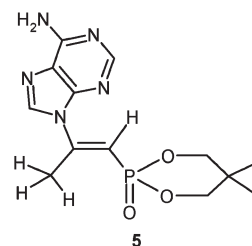
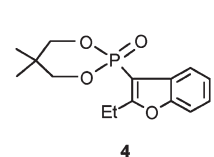
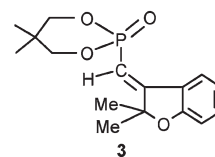
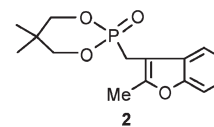
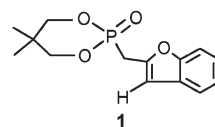
Allenenes with two cumulative double bonds are useful synthons for a variety of target molecules of industrial and biological significance.^{1–3} One of their interesting reactions is that with salicylaldehydes leading to chromenes (cf. Scheme 1), which has been elegantly developed by Shi and co-workers in recent years.^{4,5} Since chromenes are

widespread in natural products and are important precursors in medicinal chemistry, a lot of attention has been paid to their synthesis as well as biological activity.⁶ However, not much has been done with allenylphosphonates (phosphorylated allenenes) as precursors, although this class of readily accessible precursors can also be versatile building blocks in organic chemistry.⁷ We have previously shown that allenylphosphonates lead to a greater variety of benzofuran derivatives (e.g., **1–4**) compared to, say, allenyl esters or phenylallene in their reaction with 2-iodophenol using palladium(II) catalysts.^{7g} Even in simple nucleophilic additions of amines to allenylphosphonates, the structure of the products varies with the type of amine/allenylphosphonate used (e.g., **5–8**).^{7h} Furthermore, organophosphonates themselves are useful synthons in organic chemistry,^{7–9} have

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varied biological activity,¹⁰ and hence have been widely investigated. In this paper, we present our results on the facile base-catalyzed reaction of selected allenylphosphonates with salicylaldehydes that lead to diverse phosphono-chromenes. We also report a novel P–C bond cleavage reaction of the so obtained chromenes, as well as *cis*–*trans* (*Z/E*) interconversion on a set of phosphono-chromenes. For comparison, the reaction of allenylphosphonates with activated phenols and the utility of the products thus obtained are briefly described. Although we have tried to maximize the yields in many cases,

this work is mainly exploratory and is an effort to understand the nature and variety of products formed in such reactions. The presence of phosphorus in our system gives us a better diagnostic tool to check the formation of different products by means of ³¹P NMR, which is not possible in the case of nonphosphorylated allenes.



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Results and Discussion

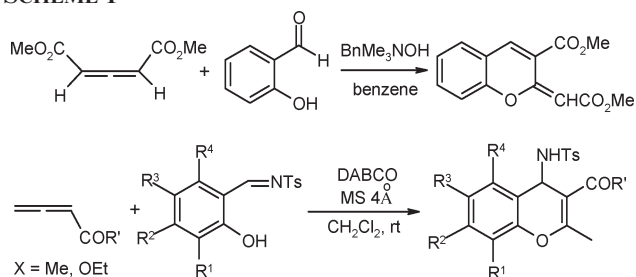
1. Reaction of Allenylphosphonate 9a with Salicylaldehydes and 2-Hydroxy Aceto-/Benzophenones. Details on the synthesis of the allenylphosphonate precursors **9a–e** used in this study have been reported recently.¹¹ As mentioned elsewhere, these are some of the most readily obtainable and inexpensive allenes.^{7g} In their reaction with salicylaldehydes, for standardization of conditions we have used allene **9a**, and hence we start with this. Thus, **9a** was treated with salicylaldehyde in the presence of various bases in different

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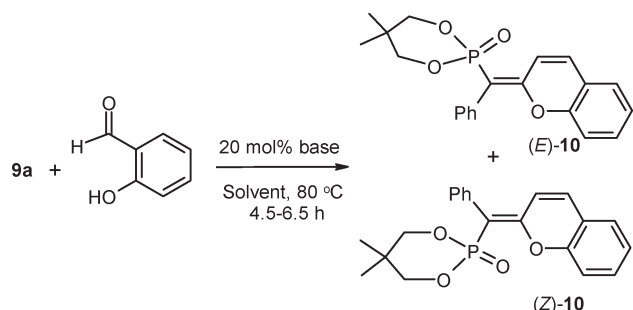
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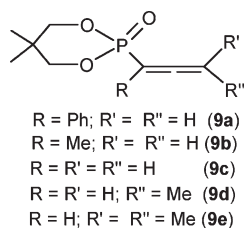
SCHEME 1



SCHEME 2



solvents (Scheme 2) to optimize the reaction conditions for the formation of the phosphono-chromenes (*E/Z*)-10. The results are summarized in Table 1. It was found that this reaction led exclusively [³¹P NMR evidence] to phosphono-chromene (*E/Z*)-10 using DBU as the base and dimethyl sulfoxide (DMSO) as the solvent. Use of K₂CO₃ also gave excellent yields based on the ³¹P NMR spectra of the reaction mixtures; however, we faced difficulties in extracting the product. Hence we used DBU as a base in all subsequent reactions. The greener solvent PEG-400 also gave good results, but the yields were marginally lower than that in DMSO.



Under optimized conditions, we have conducted the reactions of a variety of substituted salicylaldehydes and 2-hydroxy aceto-/benzophenone with **9a** for the synthesis of different phosphono-chromenes **10–16** and also for checking the scope and limitations of the reaction (Scheme 3; Table 2). We have also separated individual isomers in all cases except in **15** (only *E*-isomer isolated). Since the *R_f* values are too close, this separation of geometrical isomers was tedious and only small quantities of pure isomers were obtained, although the overall (combined) isolated yields of (*E*+*Z*) isomers are good to excellent. We have conducted the same reaction in PEG-400 also (Table 3). The yields were good but not better than that using DBU in DMSO.

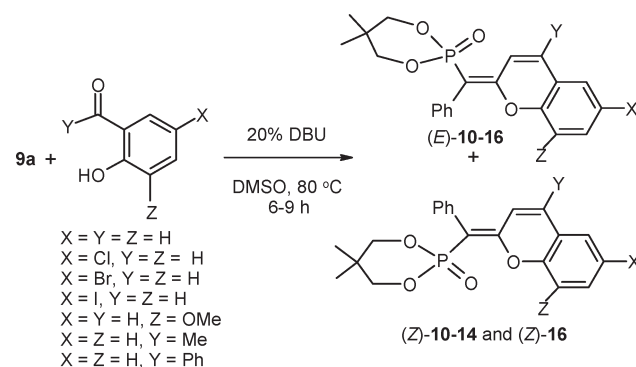
The structures of *E* and *Z* isomers of **12** were confirmed by X-ray crystallography (see Supporting Information, Figure S1). On the basis of these data, we could assign the ³¹P NMR chemical shifts for all of the other compounds. The signal for the

TABLE 1. Yields of (*E/Z*)-10 from **9a** in the Presence of Different Bases/Solvents

entry	base	temp (°C)/time (h)	solvent	yield (%) (<i>E/Z</i>) ^a
1	Na ₂ CO ₃	80/4.5	DMSO	90 (1.0:1.5)
2	NEt ₃	80/4	DMSO	24 (1.0:0.5)
3	PPh ₃	80/6	DMSO	20 (1.0:0.8)
4	CsF	80/6	DMSO	59 (1.0:0.8)
5	DABCO	80/6.5	DMSO	40 (1.0:0.6)
6	DMAP	80/6	DMSO	46 (1.0:1.5)
7	K ₂ CO ₃	80/4	DMSO	100 (1.0:1.2)
8	DBU	80/6	DMSO	100 (1.0:0.4)
9	DBU	80/6	DMF	95 (1.0:0.9)
10	DBU	80/6	acetonitrile	13 (1.0:0.8)
11	DBU	80/6	dichloroethane	23 (1.0:1.1)
12	DBU	80/6	ethanol	14 (1.0:2.4)
13	DBU	80/6	toluene	54 (1.0:0.7)
14	DBU	reflux/6	THF	41 (1.0:1.4)
15	DBU	reflux/6	chloroform	30 (1.0:1.1)
16	DBU	80/6	PEG-400	89 (1.0:1.1)
17	DBU	80/6	H ₂ O	> 24 (1.0:1.9)

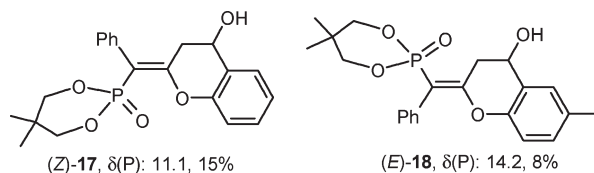
^aYields were based on ³¹P NMR spectra of the reaction mixtures.

SCHEME 3



E-isomer [$\delta(\text{P}) = 12.5$] appears downfield compared to that of the *Z*-isomer [$\delta(\text{P}) = 9.2$]. For the identification of *E*- and *Z*-isomers, ¹³C NMR and ¹H NMR spectra were also quite useful. In the ¹³C NMR, the ¹J(P–C) value for the *E*-isomer [~201.0 Hz] is larger than that for the *Z*-isomer [~180.7 Hz]. In the ¹H NMR, the (Ph)C=C–CH= proton signal appears as a doublet and is downfield [$\delta(\text{H}) \sim 7.96$] in the *E*-isomer when compared to the *Z*-isomer [$\delta(\text{H}) \sim 6.31$].

We have also isolated the phosphono-chromenol (*Z*)-17 from the PPh₃-catalyzed reaction of **9a** with salicylaldehyde. Compound (*E*)-18 was obtained along with **13** in the reaction of iodosalicylaldehyde, albeit in low yields. As can be easily seen, these chromenols are intermediates to the chromenes (*Z*)-10 and (*E*)-13, respectively. In both of these cases, the other stereoisomer could have been present in the reaction mixture, but because of ready dehydration leading to the corresponding chromene, it was not isolated. Also, after including the yield of isolated (*E*)-18 (cf. Table 2), it can be concluded that the above reactions generally work very well.



Interconversion of *E* and *Z* Isomers of 10. Normally, interconversion of *E* and *Z* isomers is not expected to take

TABLE 2. Yields of Compounds (*E/Z*)-**10**–(*E/Z*)-**16** Using DBU in DMSO

entry	compd	X	Y	Z	yield (%) (<i>E/Z</i>) ^a (isolated yield, %) ^b	δ(³¹ P) <i>E, Z</i>
1 ^c	(<i>E/Z</i>)- 10	H	H	H	100 (1.0:0.4) (91)	15.3, 12.2
2	(<i>E/Z</i>)- 11	Cl	H	H	77 (1.0:1.3) (70)	12.6, 10.8
3	(<i>E/Z</i>)- 12	Br	H	H	94 (1.0:1.6) (84)	12.5, 9.2
4	(<i>E/Z</i>)- 13	I	H	H	67 (1.0:1.3) (60)	14.8, 11.4
5	(<i>E/Z</i>)- 14	H	H	OMe	74 (1.0:0.7) (70)	15.5, 12.0
6	(<i>E</i>)- 15	H	Me	H	95 (1.0:0.6) (80)	16.4
7	(<i>E/Z</i>)- 16	H	Ph	H	65 (1.0:1.6) (59)	15.9, 12.5

^aYields are based on ³¹P NMR spectra of the reaction mixtures. The *E/Z* ratios of the compounds are given in the parentheses. ^bIsolated yields of the pure compounds = combined yield of *E* + *Z* isomers. ^cEntry 8 in Table 1.

place readily. However, in the chromenes synthesized as above, such interconversion takes place rather readily even at room temperature over a period of time. Figure S2 in Supporting Information depicts the ³¹P NMR spectra of isomer (*E*)-**10** at room temperature in CDCl₃ solution at different intervals of time. Initially, compound (*E*)-**10** showed a peak at δ 15.5. Slowly the peak due to (*Z*)-**10** [δ 12.2] started appearing. After four days, the ratio of the intensities of the signals for *E* and *Z* isomers was nearly 3:2. After 15 days, the corresponding ratio was nearly 8:7. We also heated the compound (*E*)-**10** at 80 °C in DMSO for one day; the conversion was faster as expected and the ratio of the signals was ~8:7. Similar *Z* to *E* conversion was also seen, but it was slower. In the case of (*Z*)-**14** also conversion to (*E*)-**14** took place, but the ratio of the intensities after 15 days was 2:1. In the case of **15**, however, the isomer conversion was not noticed. A possible pathway for the interconversion of these *E* and *Z* isomers via the oxonium form is shown in Scheme 4.

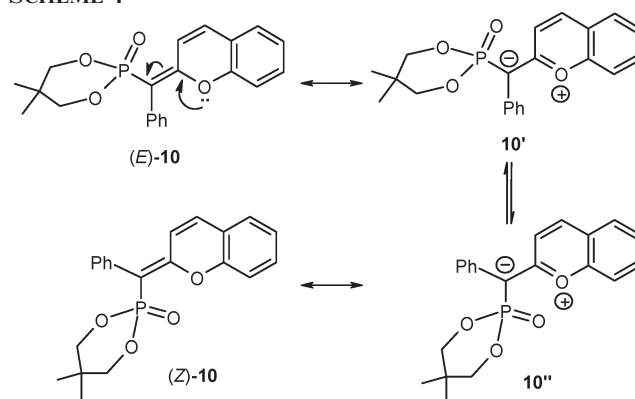
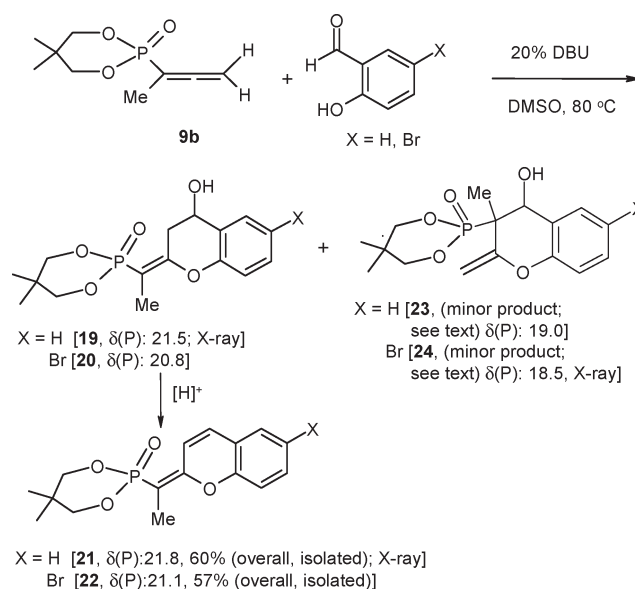
2. Reaction of Allenylphosphonate **9b with Salicylaldehydes.** Rather interestingly, use of the α-methyl allenylphosphonate **9b** led to different types of phosphono-chromenes (Scheme 5). We checked different reaction conditions using the bases DMAP, PPh₃, and DBU. Among these, DBU gave good results, and in the other cases the reaction was very sluggish. Phosphono-chromenols **19** and **20** were the major products. However, they were dehydrated to **21** and **22** in the presence of the base at high temperature (> 80 °C) or in the presence of 2 M HCl at room temperature.¹² Still the overall yields of phosphono-chromenes are good. Only *E*-isomers of **19**–**22** were isolated. This is in contrast to that of the reaction of phenyl-substituted allene **9a** discussed above and is probably a result of comparable bulkiness of phenyl and phosphono group in **9a**. The α-attack products **23** and **24** were minor (7–10%) but present (see below for more details).

To prove the identity and geometrical disposition of these compounds, we have determined the structures of **19**, **21**, and *trans*-**24** (P and -OH are *trans*) by X-ray crystallography (Figure S3, Supporting Information). The (P)(Me)C–C

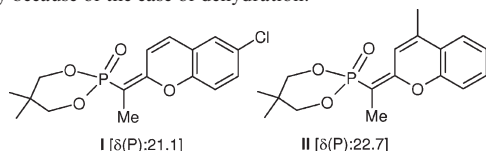
TABLE 3. Yields of Compounds (*E/Z*)-**10**–**16** using DBU in PEG-400 Medium^a

entry	compd	X	Y	Z	yield (%) (<i>E/Z</i>) ^b
1 ^c	(<i>E/Z</i>)- 10	H	H	H	89 (1.0:1.1)
2	(<i>E/Z</i>)- 11	Cl	H	H	60 (1.0:1.6)
3	(<i>E/Z</i>)- 12	Br	H	H	84 (1.0:1.1)
4	(<i>E/Z</i>)- 13	I	H	H	66 (1.0:0.7)
5	(<i>E/Z</i>)- 14	H	H	OMe	34 (1.0:0.8)
6	(<i>E</i>)- 15	H	Me	H	53 (1.0:1.4)
7	(<i>E/Z</i>)- 16	H	Ph	H	37 (1.0:0.7)

^aConditions: 20% DBU; 80 °C, 6–9 h. ^bYields are based on ³¹P NMR spectra of the reaction mixtures. ^cEntry 16 in Table 1.

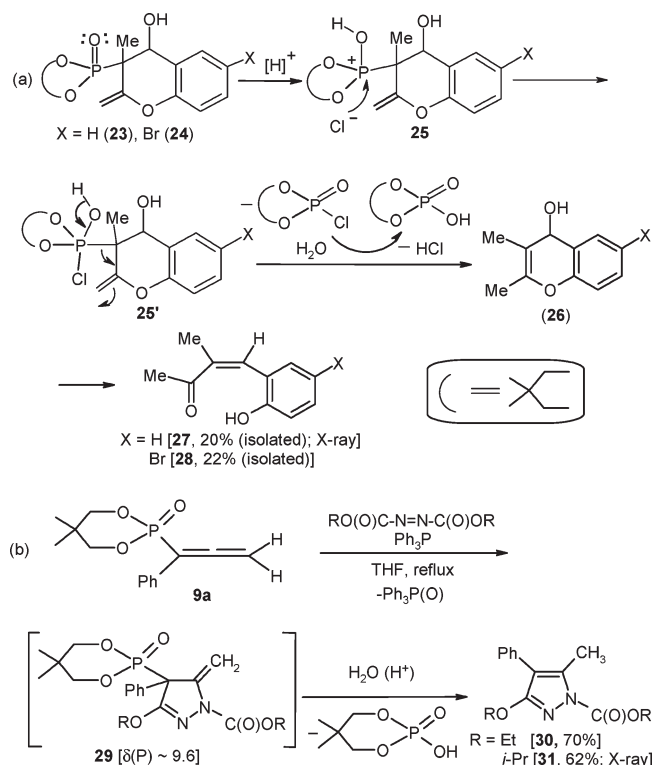
SCHEME 4**SCHEME 5**

(12) In the reactions using 5-chlorosalicylaldehyde and 2-hydroxy acetophenone, although reaction mixture showed products similar to **19** as the major components, we were able to isolate only the chromenes **I** and **II**, probably because of the ease of dehydration.



(ring) distances in **19** and **21** [1.335(3) and 1.353(4) Å, respectively] are clearly in the double bond range while the (P)(Me)C–C(ring)(OH) distance in *trans*-**24** [1.531(6) Å] shows that this is a single bond. The chromene ring oxygen atoms in **19** and **21** are clearly *trans* to phosphorus and hence prove the (*E*) stereochemistry in these two cases. The presence of hydrogen bonding involving the hydroxyl group in **19** and *trans*-**24** [Figures S4 and S5, Supporting Information] also confirms that in these two cases dehydration has not taken place. Whereas **19** forms a hydrogen-bonded dimer, **24**

SCHEME 6

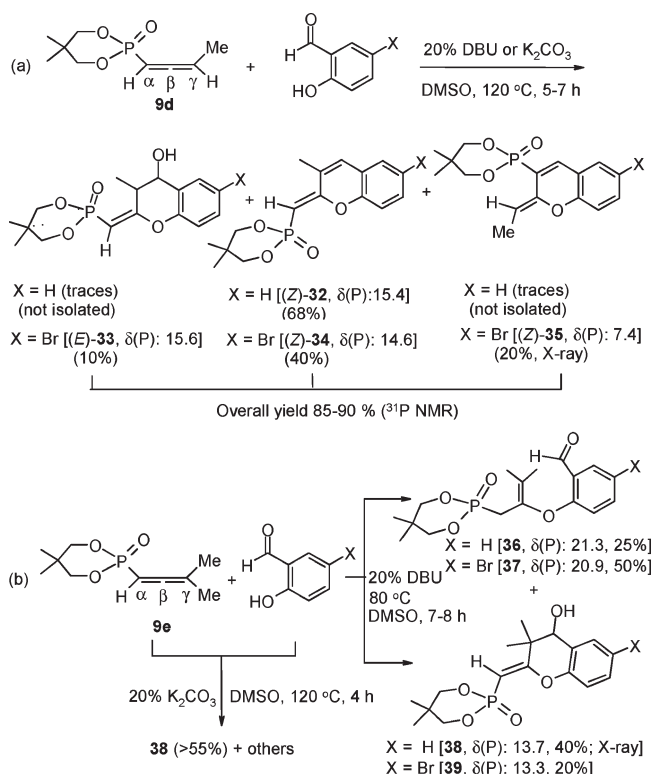


forms a tetramer, probably because of the intervening methyl group in the latter.

Novel P–C Bond Cleavage in Phosphono-chromenes **23 and **24**.** Compounds **23** and **24** were rather unstable toward moisture [^1H NMR evidence]. They underwent novel P–C bond cleavage to give the phosphate $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})(\text{OH})$ and 4-(2-hydroxy aryl)-3-methylbuten-2-ones **27** and **28** (Scheme 6a). The structure of compound **27** was confirmed by X-ray crystallography (Figure S6, Supporting Information). This reaction perhaps takes place with initial protonation and subsequent involvement of pentacoordinate phosphorus (cf. **25'**), but the details are not clear at the moment. The last step in the proposed mechanism for the formation of **27** and **28** is based on an earlier report on a species analogous to **26**, by McClelland and Gedge concerning the hydration of flavylum ion.¹³ P–C bond cleavage leading to phosphate and the pyrazoles **30** and **31** was also reported by us recently in the case of phosphono-pyrazoles **29** (Scheme 6b).^{7k} Thus the present reaction is quite interesting, but since there are other viable routes to compounds of type **27** and **28**, we have not investigated this aspect further.¹⁴

3. Reaction of Allenylphosphonates **9c–e with Salicylaldehydes.** The allene **9c** underwent only isomerization to the acetylene $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{O})\text{C}\equiv\text{CMe}$ under the above conditions as observed previously by us in other reactions.^{7g} In the reaction using **9d** and salicylaldehyde/5-bromosalicylaldehyde, we checked the bases DBU and K_2CO_3 in DMSO

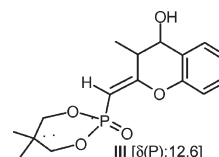
SCHEME 7



and found that both of these gave better results at 120 °C rather than at 80 °C. The chromenols (*Z*)-**32** and (*Z*)-**34** were readily isolated as major products in these cases. In addition, we could also isolate chromenol (*E*)-**33** and the chromene (*Z*)-**35** from the reaction using 5-bromosalicylaldehyde (Scheme 7a); analogous products were present in the reaction with salicylaldehyde also but could not be isolated. The overall yield of the products, based on ^{31}P NMR was 85–90%; isolated yields are given along with compound numbers in the scheme. We think that the *Z* forms of the chromenols corresponding **32** or **34** undergo dehydration more readily than the *E* forms and hence were not observed in these reaction mixtures.¹⁵ While (*Z*)-**32** and (*Z*)-**34** are the products of (β,γ) attack, (*Z*)-**35** is a (β,α) product. In the latter case, we have confirmed the structure by X-ray crystallography [Figure S7 (left drawing), Supporting Information]. The structure of (*Z*)-**32** is similar to (*Z*)-**12** for which solid-state X-ray structure is available. The main difference between this reaction and that of **9a** is that in this case we did not detect the *E* isomer of the chromene **32**.

In the case of **9e** though, the reaction stops at the chromenol stage, since dehydration cannot occur. The yields of the chromenols **38** and **39** are also lower, perhaps because of

(15) A small quantity of (*Z*)-chromenol (**III**) could also be isolated from the reaction performed at the lower temperature of 80 °C using **9d**, salicylaldehyde, and DBU as the base. At higher temperatures we could not detect this compound.



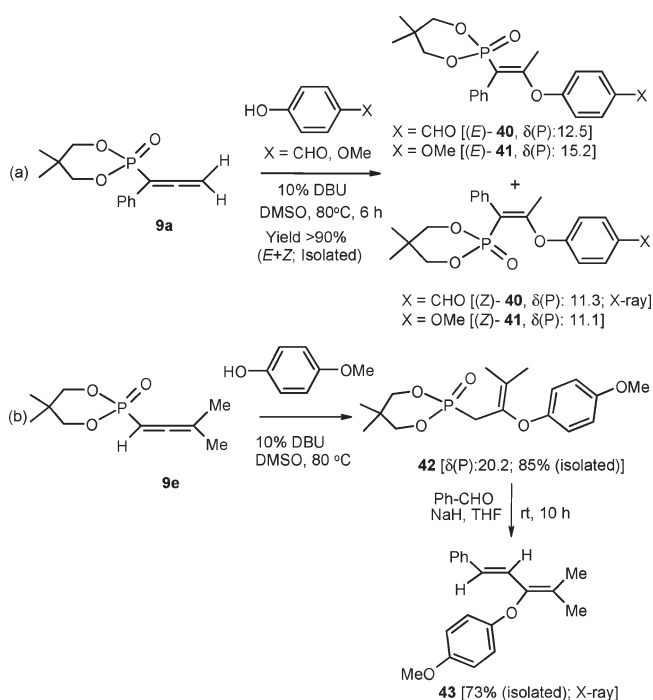
(13) McClelland, R. A.; Gedge, S. J. *Am. Chem. Soc.* **1980**, *102*, 5839.
 (14) (a) Finkelstein, B. L.; Benner, E. A.; Hendrixson, M. C.; Kranis, K. T.; Rauh, J. J.; Sethuraman, M. R.; McCann, S. F. *Bioorg. Med. Chem.* **2002**, *10*, 599. (b) Kawai, Y.; Hayashi, M.; Tokitoh, N. *Tetrahedron: Asymmetry* **2001**, *12*, 3007.

steric restraints. The allylic phosphonates **36** and **37** formed by phenol addition are found in significant quantities along with chromenols **38** and **39** (Scheme 7b).¹⁶ We have confirmed the structure of (*Z*)-**38** by X-ray crystallography [Figure S7 (right drawing), Supporting Information].

4. Comparison of the Reactivity of Allenylphosphonates with Nonphosphorylated Allenes. Under base-catalyzed reactions, the reactivity of allenylphosphonates with salicylaldehyde is lower (and different) when compared to those with ester or keto allenenes⁵ but higher when compared with phenyl allene $\text{PhCH}=\text{C}=\text{CH}_2$, which did not react under these conditions. For comparable yields, the reaction of allenylphosphonates with salicylaldehyde in the presence 10 mol % DBU took a longer time (more than 24 h), whereas it is reported that ester allenenes took 6–15 h under similar conditions. In the case of α -substituted allenylphosphonates (**9a**, **b**), (β,γ) attack is favored, whereas in the case of ester or keto allenenes (β,α) attack is favored.^{5b,5c} The allenylphosphonate **9c** isomerized to acetylene ($\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$) $\text{P}(\text{O})\text{C}\equiv\text{CMe}$ (i.e., it did not react with salicylaldehyde) in the presence of a base, but ester or keto allenenes gave chromenes.^{7g} The allenylphosphonate (**9e**) gave phenol-addition product allylic phosphonates (**36** and **37**) and (β,γ)-attack afforded the phosphono-chromenols (**38** and **39**).

5. Reaction of Allenylphosphonates **9a and **9e** with Activated Phenols: Clues to Reaction Pathway.** It may be noted that when steric factors are present, just phenol addition products **36** and **37** can be obtained in good yields. This also gives an idea about the first step in the formation of chromene products. To probe this further, we have checked the reactivity of the phenols with allenylphosphonates in the presence of a base. Surprisingly, we observed very good selectivity here. Thus the allenyl phosphonate **9a** reacted with 4-hydroxy benzaldehyde or anisole in the presence of DBU to lead to the isomeric vinylic phosphonates (*E/Z*)-**40** and **-41** (Scheme 8a) in yields of >95% based on ³¹P NMR spectra of the reaction mixtures. The structure of (*Z*)-**40** is confirmed by X-ray crystallography (Figure S8, Supporting Information). The *E/Z* isomeric ratio was ~1:1; this was the case even in the presence of 10 mol % PPh_3 as a base. This reaction proceeded through the phenoxide attack at the β -position with the proton addition taking place at the γ -position. The phenol attacked at the γ -position [generally termed as umpolung addition] in the case of ester allene $\text{H}_2\text{C}=\text{C}=\text{CH}(\text{CO}_2\text{Me})$,¹⁷ whereas in the case of **9a**, the phenol attacked at the β -position and gave vinylic phosphonate ethers (**40** and **41**). Thus the reactivity of phenols with ester allene and allenylphosphonate **9a** in the presence of PPh_3 are entirely different. The reaction between **9e** with 4-hydroxy anisole in the presence of 10 mol % of DBU gave only allylic phosphono ether **42** (Scheme 8b) that could be readily converted to the substituted butadiene **43** via Horner–Wadsworth–Emmons (HWE) reaction. The latter compound was characterized by X-ray crystallography (Figure S9, Supporting Information). Thus, the product **42**

SCHEME 8



is also formed by phenoxide attack at β -position, but proton addition took place at the α -carbon.

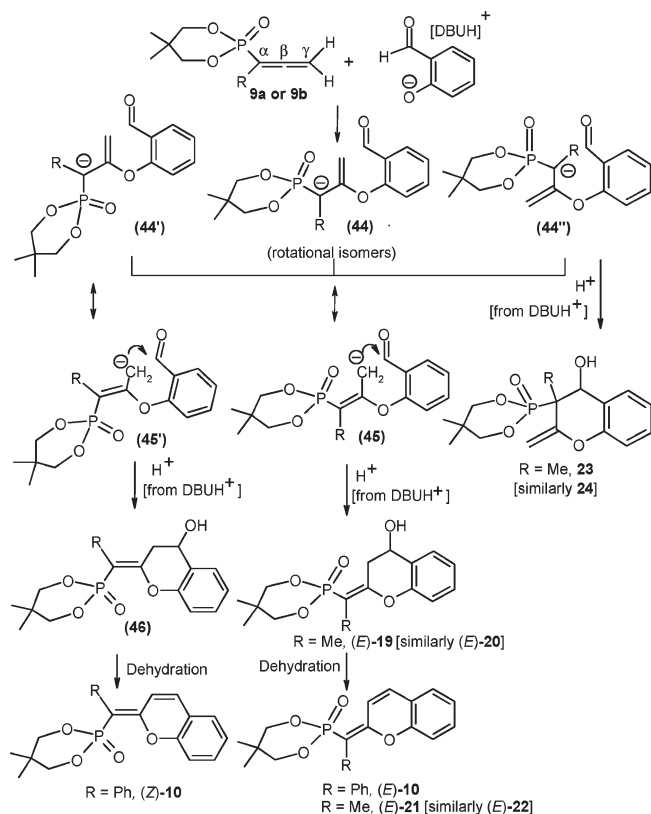
6. Mechanistic Pathways. A plausible mechanism for the reaction based on the available literature^{5c} is shown in Scheme 9. First, the phenoxide reacts with allenylphosphonate at the β -position to give **44** or one of its rotamers **44'**–**44''**. This is consistent with the isolation of phenol addition products **36** and **37** and amine/nucleobase addition products (cf. **5**–**8**) reported by us before.^{7h} It is also consistent with the ¹⁸O label experiments reported by Shi and co-workers.^{5d} An NMR tube experiment on DBU + **9a** revealed four peaks at $\delta(\text{P})$ 22.2, 21.7, 18.6, and 17.3 (not isolated), but these peaks were absent in the mixture when salicylaldehyde was present. This observation also suggests only phenoxide attack on allenylphosphonate. In the following step, species **44''** can directly undergo cyclization to give the chromenol **23** (or **24**). Species **44** and **44'** are in resonance with the anions **45** and **45'** that undergo cyclization to give the respective chromenols. Theoretical calculations (Table S1, Supporting Information) at the B3LYP/6-311++G* level suggested that when R = Ph, the (*E*)-**45** and (*Z*)-**45'** forms were close in energy (difference 3.3 kJ mol⁻¹). However, when R = Me, the *E* form **45** is significantly more stable (by 23.6 kJ mol⁻¹) than the *Z* form. The isolation of mixture of isomers for R = Ph [(*Z*)-**10** and (*E*)-**10**] but only the *E* isomer for R = Me [(*E*)-**21** and (*E*)-**22**] is consistent with these calculations.

Dehydration of chromenols leads to the phosphono-chromenes [(*Z*)-**10**, (*E*)-**10**, (*E*)-**21**, or (*E*)-**22**]. In the cyclization process leading to the minor products **23** (or **24**), the α -carbon of the allene attacks the aldehydic carbon while in the formation of (*E*)-**10**, (*Z*)-**10**, (*E*)-**19**, (*E*)-**20**, (*E*)-**21**, or (*E*)-**22**, the γ -carbon of the allene attacks the aldehydic carbon. Thus these results are consistent with the available literature.^{5c} Formation of (*Z*)-**32**, (*Z*)-**34**, **38**, and **39** also occurs by (β,γ) attack. Finally, although intermediate **44** can in principle undergo internal

(16) Compound **36** did undergo self-HWE reaction in the presence of NaH/THF at rt; however, intermolecular reaction is also possible and hence purification was difficult, although a fraction after column chromatography contained this product as a major component [¹H NMR δ 1.71 (s, 3H), 1.79 (s, 3H), 6.19 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 6.75–7.06 (m, 4H)].

(17) (a) Zhang, C.; Lu, X. *Synlett* **1995**, 645. (b) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535.

SCHEME 9

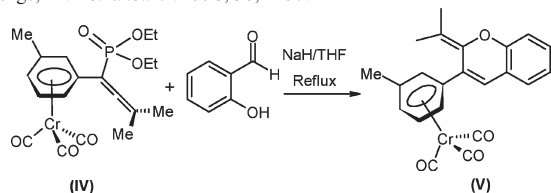


HWE reaction,^{16,18} we did not find evidence for such products in the present study involving the base DBU or K₂CO₃.

Summary

Allenylphosphonates react with salicylaldehydes under organocatalytic conditions to lead to phosphono-chromenols that undergo dehydration to phosphono-chromenes. Both (β,α) and (β,γ) products are observed. An unusual room temperature isomerization of (*Z*)- and (*E*)-phosphono-chromenes is demonstrated by ³¹P NMR spectroscopy. A novel P–C bond cleavage reaction of some of these chromenes leading to substituted enones is also reported. Possible mechanistic pathways are discussed. When steric factors dominate, only phenol addition products are obtained at room temperatures, whereas the phosphono-chromenes are obtained at elevated temperatures; similar allylic phosphonyl ether products obtained by straightforward routes are shown to be good candidates as HWE precursors. Key compounds are characterized by X-ray crystallography. The ready recognition of diverse products by ³¹P NMR

(18) The allenylphosphonate complex **IV** reacts smoothly with salicylaldehyde in the presence of sodium hydride to give chromene (**V**) by internal HWE reaction in good yield as a crystalline solid. See: Müller, T. J. J.; Ansorge, M. *Tetrahedron* **1998**, *54*, 1457.



spectra as an additional tool that could help when analyzing reactions of nonphosphorylated allenes is also highlighted.

Experimental Section

General experimental conditions are given in Supporting Information. Precursors **9a–e** were prepared using literature procedures.¹¹ Experimental details pertaining to allyl/vinyl phosphonyl ethers **40–42** and the HWE product **43** are given in Supporting Information.

1. Reaction of Allenylphosphonate 9a with Salicylaldehydes and 2-Hydroxy Aceto-/Benzophenone. Synthesis of Phosphono-chromenes 10–16 and Chromenols 17 and 18. To a solution of allenylphosphonate **9a** (0.422 g, 1.67 mmol) and salicylaldehyde (2.51 mmol) in DMSO (4 mL) was added a 10% solution of DBU in DMSO (0.5 mL, corresponds to 0.05 g of DBU, 0.33 mmol), and the mixture was heated at 80 °C for 6–9 h. The contents were washed with water (2 × 10 mL) and extracted with DCM (dichloromethane) (2 × 25 mL). The solvent was removed, and the products were isolated by column chromatography using ethyl acetate and hexane mixture (2:3). In all cases except **15**, we separated the *E* and *Z* isomers. Use of K₂CO₃ also gave excellent yields based on the ³¹P NMR of reaction mixture; however, we faced difficulties in extracting the compound, and hence DBU was used in subsequent reactions.

(E)-10. Yield (*E*+*Z*) 0.56 g (91%); mp 160–161 °C; IR (KBr, cm⁻¹) 2967, 2888, 1630, 1568, 1545, 1453, 1406, 1264, 1229, 1055, 1003; ¹H NMR (400 MHz, CDCl₃) δ 0.64 and 0.93 (2 s, 6H), 3.55–3.62 (m, 2H), 4.08–4.13 (m, 2H), 6.74 (d, ³*J* = 7.8 Hz, 1H), 6.94 (d, ³*J* = 9.8 Hz, 1H), 7.03–7.38 (m, 8H), 7.90 (d, ³*J* = 9.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 21.7, 32.3 (d, ³*J* = 6.0 Hz), 75.1₆, 75.2₂, 100.4 (d, ¹*J*(P–C) = 202.0 Hz), 115.8, 119.8, 120.4, 123.6, 126.9, 127.1, 128.1, 130.3, 130.4, 131.0₈, 131.1₃, 134.3, 134.4, 152.9, 159.7 (d, ²*J* = 34.0 Hz); ³¹P NMR (160 MHz, CDCl₃) δ 15.3; LC-MS *m/z* 369 [M+1]⁺. Anal. Calcd for C₂₁H₂₁O₄P: C, 68.47; H, 5.75. Found: C, 68.45; H, 5.74.

(Z)-10. Mp 155–157 °C; IR (KBr, cm⁻¹) 3058, 2963, 1719, 1628, 1572, 1549, 1453, 1402, 1244, 1059, 1007; ¹H NMR (400 MHz, CDCl₃) δ 0.76 and 1.16 (2 s, 6H), 3.68–3.86 (m, 4H), 6.25 (dd, ³*J* = 9.9 Hz, ⁴*J* = 1.2 Hz, 1H), 6.72 (dd, ³*J* = 9.9 Hz, ⁵*J* = 3.2 Hz, 1H), 7.00–7.35 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 21.0, 22.0, 32.2 (d, ³*J* = 6.0 Hz), 75.8, 75.9, 100.7 (d, ¹*J*(P–C) = 180.0 Hz), 116.1, 118.4, 118.6, 120.0, 123.5, 127.0, 127.5, 128.7, 130.6, 130.8, 131.0, 131.1, 134.2₅, 134.2₉, 152.9, 158.7; ³¹P NMR (160 MHz, CDCl₃) δ 12.2; LC-MS *m/z* 369 [M+1]⁺. Anal. Calcd for C₂₁H₂₁O₄P: C, 68.47; H, 5.75. Found: C, 68.48; H, 5.67.

(E)-11. Yield (*E*+*Z*) 0.47 g (70%); mp 201–203 °C; IR (KBr, cm⁻¹) 3108, 2965, 2886, 1782, 1634, 1570, 1476, 1428, 1285, 1223, 1049, 997; ¹H NMR (400 MHz, CDCl₃) δ 0.63 and 0.92 (2 s, 6H), 3.55–3.61 and 4.01–4.14 (2 m, 4H), 6.67 (d, ³*J* = 8.7 Hz, 1H), 6.85 (d, ³*J* = 10.2 Hz, 1H), 7.10–7.40 (m, 7H), 7.97 (d, ³*J* = 10.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.1, 21.6, 32.2 (d, ³*J* = 6.0 Hz), 75.1₆, 75.2₂, 101.9 (d, ¹*J*(P–C) = 201.5 Hz), 117.1, 120.9₇, 121.0, 121.6, 126.2, 127.1₉, 127.2, 128.1, 128.5, 128.8, 129.0, 129.3, 129.9, 130.8₇, 130.9, 151.3, 159.0 (d, ²*J* = 34.8 Hz); ³¹P NMR (160 MHz, CDCl₃) δ 12.6; LC-MS *m/z* 403 [M]⁺, 405 [M+2]⁺. Anal. Calcd for C₂₁H₂₀O₄PCl: C, 62.62; H, 5.00. Found: C, 62.59; H, 5.08.

(Z)-11. Mp 172–174 °C; IR (KBr, cm⁻¹) 3057, 2957, 2888, 1626, 1572, 1480, 1426, 1244, 1213, 1057, 1009; ¹H NMR (400 MHz, CDCl₃) δ 0.79 and 1.18 (2 s, 6H), 3.68–3.92 (m, 4H), 6.32 (dd, ³*J* = 9.9 Hz, ⁴*J* = 1.7 Hz, 1H), 6.66 (dd, ³*J* = 9.9 Hz, ⁵*J* = 3.5 Hz, 1H), 7.11–7.38 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 21.1, 22.0, 32.4 (d, ³*J* = 6.0 Hz), 75.9, 76.0, 102.3 (d, ¹*J*(P–C) = 181.0 Hz), 117.6, 119.9, 120.0, 121.3, 126.5, 127.0, 127.8, 128.2, 128.6, 128.9, 129.4, 130.7, 131.0₈, 131.1₃, 134.0₆, 134.1₁, 151.5, 158.3; ³¹P NMR (160 MHz, CDCl₃) δ 10.8; LC-MS *m/z* 403 [M]⁺, 405 [M+2]⁺. Anal. Calcd for C₂₁H₂₀O₄PCl: C, 62.62; H, 5.00. Found: C, 62.59; H, 5.03.

(E)-12. Yield (*E* + *Z*) 0.63 g (84%); mp 192–194 °C; IR (KBr, cm^{-1}) 3108, 2965, 2886, 1781, 1632, 1566, 1476, 1426, 1285, 1221, 1049, 995; ^1H NMR (400 MHz, CDCl_3) δ 0.63 and 0.92 (2 s, 6H), 3.55–3.61 and 4.09–4.14 (2 m, 4H), 6.61 (d, $^3J = 8.7$ Hz, 1H), 6.84 (d, $^3J = 10.1$ Hz, 1H), 7.25–7.40 (m, 7H), 7.96 (d, $^3J = 10.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.6, 32.3 (d, $^3J = 6.0$ Hz), 75.2, 75.3, 101.9 (d, $^1J(\text{P}-\text{C}) = 201.0$ Hz), 115.9, 117.5, 121.0, 121.1, 122.1, 127.3, 128.1, 128.9, 129.3, 130.9, 131.0, 132.8, 133.9₆, 134.0, 151.8, 159.0 (d, $^2J = 35.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 12.5; LC-MS m/z 447 $[\text{M}]^+$, 449 $[\text{M} + 2]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{PBr}$: C, 56.39; H, 4.51. Found: C, 56.33; H, 4.52. X-ray structure was determined for this compound.

(Z)-12. Mp 182–185 °C; IR (KBr, cm^{-1}) 2967, 2924, 1883, 1748, 1628, 1570, 1476, 1422, 1254, 1213, 1057, 1005; ^1H NMR (400 MHz, CDCl_3) δ 0.79, 1.18 (2 s, 6H), 3.68–3.92 (m, 4H), 6.31 (d, $^3J = 10.0$ Hz, 1H), 6.65 (dd, $^3J = 10.0$ Hz, $^5J = 3.1$ Hz, 1H), 7.07–7.41 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 22.0, 32.3 (d, $^3J = 6.0$ Hz), 75.8₇, 75.9₄, 101.9 (d, $^1J(\text{P}-\text{C}) = 180.7$ Hz), 115.8, 117.9, 119.8, 119.9, 121.8, 127.7₂, 127.7₄, 128.8, 129.1, 129.3, 130.9₈, 131.0, 133.5, 133.9₇, 134.0, 151.9, 158.1; ^{31}P NMR (160 MHz, CDCl_3) δ 9.2; LC-MS m/z 447 $[\text{M}]^+$, 449 $[\text{M} + 2]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{PBr}$: C, 56.39; H, 4.51. Found: C, 56.44; H, 4.52. X-ray structure was determined for this compound.

(E)-13 (Isomer Purity ~95%). Yield (*E* + *Z*) 0.50 g (60%); mp 172–174 °C; IR (KBr, cm^{-1}) 3104, 2959, 2884, 1773, 1632, 1563, 1474, 1422, 1285, 1221, 1049, 995; ^1H NMR (400 MHz, CDCl_3) δ 0.63 and 0.92 (2 s, 6H), 3.55–4.14 (m, 4H), 6.50 (d, $^3J = 8.7$ Hz, 1H), 6.82 (d, $^3J \approx 10.2$ Hz, 1H), 7.26–7.49 (m, 7H), 7.94 (d, $^3J \approx 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.6, 32.2 (d, $^3J = 6.0$ Hz), 75.1₅, 75.2₁, 101.8 (d, $^1J(\text{P}-\text{C}) = 201.0$ Hz), 117.8, 120.8, 122.6, 127.2, 128.1, 128.7, 130.9, 133.9, 135.2, 138.7, 152.6, 159.0 (d, $^2J = 34.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 14.8; LC-MS m/z 495 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{PI}$: C, 51.03; H, 4.08. Found: C, 51.08; H, 4.01.

(Z)-13 (Isomeric Purity ~95%). Mp 177–179 °C; IR (KBr, cm^{-1}) 3057, 2967, 1624, 1593, 1566, 1476, 1420, 1244, 1211, 1057, 1005; ^1H NMR (400 MHz, CDCl_3) δ 0.80 and 1.19 (2 s, 6H), 3.69–3.93 (m, 4H), 6.30 (d, $^3J = 8.0$ Hz, 1H), 6.65 (dd, $^3J = 8.0$ Hz, $^5J = 4.0$ Hz, 1H), 6.95–7.60 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 21.6, 32.3 (d, $^3J = 6.0$ Hz), 75.8, 75.9, 102.3 (d, $^1J(\text{P}-\text{C}) = 180.0$ Hz), 118.2, 119.6, 122.3, 126.4, 128.9, 129.3, 131.0, 134.0, 135.3, 139.4, 152.7, 158.0; ^{31}P NMR (160 MHz, CDCl_3) δ 11.4; LC-MS m/z 495 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{PI}$: C, 51.03; H, 4.08. Found: C, 51.08; H, 4.01.

(E)-14. Yield (*E* + *Z*) 0.47 g (70%); mp 132–134 °C; IR (KBr, cm^{-1}) 3042, 2961, 1632, 1578, 1553, 1474, 1412, 1260, 1231, 1096, 1061, 1003; ^1H NMR (400 MHz, CDCl_3) δ 0.65 and 0.94 (2 s, 6H), 3.48 (s, 3H), 3.58–3.64 and 4.08–4.13 (2 m, 4H), 6.81 (d, $^3J = 7.6$ Hz, 1H), 6.92 (m, $^3J \sim 10.0$ Hz, 1H), 7.26–7.45 (m, 7H), 7.88 (d, $^3J = 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.7, 32.3 (d, $^3J = 6.0$ Hz), 57.4, 75.2, 75.3, 100.4 (d, $^1J(\text{P}-\text{C}) = 202.0$ Hz), 116.2, 119.6, 119.8, 119.9, 121.2, 123.4, 127.1, 128.1, 130.6, 131.0₆, 131.1₂, 134.3, 143.3, 147.1, 159.5 (d, $^2J = 35.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 15.5; LC-MS m/z 399 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_5\text{P}$: C, 66.33; H, 5.82. Found: C, 66.39; H, 5.82.

(Z)-14. Mp 151–154 °C; IR (KBr, cm^{-1}) 3067, 2961, 1630, 1580, 1476, 1441, 1402, 1248, 1092, 1059, 1009, 986; ^1H NMR (400 MHz, CDCl_3) δ 0.78 and 1.21 (2 s, 6H), 3.79–3.94 (m, 4H), 3.95 (s, 3H), 6.26 (d, $^3J = 9.6$ Hz, 1H), 6.70–6.77 (m, 2H), 6.93–7.39 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 22.2, 32.2 (d, $^3J = 6.0$ Hz), 57.4, 75.9, 76.0, 100.8 (d, $^1J(\text{P}-\text{C}) = 181.0$ Hz), 115.6, 118.9, 119.1, 119.4, 120.9, 123.3, 127.5, 128.0, 128.8, 130.5, 131.1₆, 131.2₁, 134.5₅, 134.6₁, 143.0, 147.6, 158.1; ^{31}P NMR (160 MHz, CDCl_3) δ 12.0; LC-MS m/z 399 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_5\text{P}$: C, 66.33; H, 5.82. Found: C, 66.42; H, 5.75.

(E)-15. Yield 0.51 g (80%); mp 165–167 °C; IR (KBr, cm^{-1}) 3077, 2961, 2882, 1634, 1597, 1557, 1476, 1447, 1383, 1289, 1221, 1051, 997; ^1H NMR (400 MHz, CDCl_3) δ 0.66 and 0.94 (2 s, 6H), 2.29 (s, 3H), 3.60 (dd, $^3J = 16.0$ Hz, $^2J \sim 11.1$ Hz, 2H), 4.08–4.13 (dd–t, $^3J = ^2J \sim 11.1$ Hz, 2H), 6.75–7.39 (m, 9H), 7.77 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.5, 21.2, 21.7, 32.3 (d, $^3J = 5.9$ Hz), 75.1, 75.2, 98.1 (d, $^1J(\text{P}-\text{C}) = 202.7$ Hz), 115.9, 117.8, 117.8₃, 121.6, 123.4, 123.7, 126.9, 128.0, 131.2₇, 131.3₂, 134.4, 134.5, 138.3, 152.6, 159.9 (d, $^2J = 34.5$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 16.4; LC-MS m/z 383 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_4\text{P}$: C, 69.10; H, 6.06. Found: C, 69.18; H, 6.10. The other isomer [$\delta(\text{P})$ 13.0] was present in the reaction mixture, but we did not succeed in isolating it in a pure state.

(E)-16. Yield (*E* + *Z*) 0.44 g (59%); mp 201–203 °C; IR (KBr, cm^{-1}) 3077, 2963, 1626, 1595, 1572, 1555, 1445, 1370, 1285, 1221, 1055, 1005; ^1H NMR (400 MHz, CDCl_3) δ 0.66 and 0.92 (2 s, 6H), 3.57–3.63 and 4.06–4.11 (2 m, 4H), 6.82–7.46 (m, 14H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.6, 32.3 (d, $^3J = 5.0$ Hz), 75.1, 75.2, 100.4 (d, $^1J(\text{P}-\text{C}) = 202.0$ Hz), 116.2, 118.8, 120.4, 123.3, 125.9, 127.0, 128.0, 128.5, 128.6, 128.7, 128.8, 131.0, 134.3, 136.6, 142.5, 153.1, 159.6 (d, $^2J = 35.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 15.9; LC-MS m/z 445 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{P}$: C, 72.96; H, 5.67. Found: C, 72.87; H, 5.68.

(Z)-16. Mp 167–169 °C; IR (KBr, cm^{-1}) 3057, 2975, 2878, 1620, 1595, 1566, 1441, 1364, 1265, 1057, 1005, 988, 945; ^1H NMR (400 MHz, CDCl_3) δ 0.80 and 1.21 (2 s, 6H), 3.73–3.91 (m, 4H), 6.26 (s, 1H), 6.99–7.42 (m, 14H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 22.1, 32.4 (d, $^3J \sim 6.0$ Hz), 75.9₅, 76.0₁, 100.7 (d, $^1J(\text{P}-\text{C}) = 181.1$ Hz), 116.6, 117.4, 117.5, 120.3, 123.3, 126.0, 127.5, 128.5, 128.7, 128.8, 131.0, 131.1, 131.2, 134.4, 134.5, 136.4, 142.8, 153.3, 158.7; ^{31}P NMR (160 MHz, CDCl_3) δ 12.5; LC-MS m/z 445 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{P}$: C, 72.96; H, 5.67. Found: C, 72.87; H, 5.69.

(Z)-17. The procedure was similar to that for **10**, but here we used 20 mol % of PPh_3 as a catalyst. Yield 0.10 g (15%); mp 201–203 °C; IR (KBr, cm^{-1}) 3351, 3059, 2949, 1642, 1607, 1485, 1352, 1225, 1059, 1005, 945; ^1H NMR (400 MHz, CDCl_3) δ 0.77 and 1.19 (2 s, 6H), 2.57 (br d, $^2J = 14.8$ Hz, $^3J < 2.0$ Hz, 1H), 2.84 (dd, $^2J = 14.8$ Hz, $^3J = 5.6$ Hz, 1H), 3.70–3.84 (m, 5H), 4.70 (br, 1H), 6.99–7.35 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 22.1, 32.3 (d, $^3J = 6.0$ Hz), 33.2 (d, $^3J = 10.0$ Hz), 63.3, 76.1, and 76.2 (2 d, $^2J \sim 7.0$ Hz), 108.8 (d, $^1J(\text{P}-\text{C}) = 172.0$ Hz), 116.9, 123.1, 124.9, 127.7, 128.1, 128.7, 130.1, 130.8, 130.9, 133.9, 134.0, 151.3, 160.5; ^{31}P NMR (160 MHz, CDCl_3) δ 11.1; LC-MS m/z 387 $[\text{M} + 1]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{O}_5\text{P}$: C, 65.28; H, 6.00. Found: C, 65.30; H, 5.99.

(E)-18. This compound isolated along with **13** from the reaction of allene **9a** with 5-iodo salicylaldehyde. Yield 0.07 g (8%); mp 214–216 °C; IR (KBr, cm^{-1}) 3279, 3059, 2920, 1640, 1595, 1472, 1406, 1225, 1053, 1003; ^1H NMR (400 MHz, CDCl_3) δ 0.62 and 0.96 (2 s, 6H), 2.85 (br, 1H), 3.29–3.33 (m, 1H), 3.56–3.66 (m, 2H), 3.78–3.83 (m, 1H), 4.05 (m, 2H), 4.90–4.93 (m, 1H), 6.48–7.69 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 21.8, 32.5 (d, $^3J = 6.3$ Hz), 33.5, 62.9, 75.6, 75.7, 118.9, 127.4, 128.0, 128.1, 130.7, 130.8, 133.5, 133.9, 134.0, 151.3, 160.1 (d, $^2J = 33.8$ Hz). The spectrum was very noisy, probably because of dehydration during recording. Hence the position of P–C carbon was not identified. ^{31}P NMR (160 MHz, CDCl_3) δ 14.2; LC-MS: m/z 512 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5\text{PI}$: C, 49.24; H, 4.33. Found: C, 49.21; H, 4.25.

2. Reaction of Allene 9b with Salicylaldehydes and 2-Hydroxyacetophenone. Synthesis of Phosphono-chromenols (19, 20, 23, 24) and Phosphono-chromenes (21, 22). General Procedure. To a solution of allene **9b** (0.420 g, 2.08 mmol) and salicylaldehyde (3.12 mmol) in DMSO (4 mL) was added a 10% solution of DBU in DMSO (0.6 mL, corresponds to 0.06 g of DBU, 0.42 mmol), and the mixture was heated at 80 °C for 10–12 h. The contents were washed with water (2 \times 10 mL) and extracted with

DCM (2×25 mL). The solvent was removed, and the products **19–24** were isolated by column chromatography using ethyl acetate and hexane (3:7). Compounds **19** and **20** could be converted quantitatively to **21** and **22**, respectively, in the presence of 2 M HCl at room temperature.

Compounds 19, 21, and 23. Compound 19. Yield 0.30 g (45%); mp 139–141 °C; IR (KBr, cm^{-1}) 3262, 2959, 1645, 1607, 1470, 1370, 1254, 1196, 1057, 1003, 911; ^1H NMR (200 MHz, CDCl_3) δ 1.00 and 1.22 (2 s, 6H), 2.03 (d, $^3J = 13.7$ Hz, 3H), 3.15–3.19 (m, 1H), 3.39 (br, 1H), 3.67–3.77 (m, 1H), 3.77–3.88 (m, 2H), 4.27–4.32 (m, 2H), 4.88 (br, 1H), 7.03–7.41 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.9 (d, $^2J = 5.3$ Hz), 21.6, 22.1, 32.6 (d, $^3J = 5.3$ Hz), 33.6, 63.4, 74.67 and 74.72 (2 merged d, $^3J(\text{P}-\text{C}) \sim 5.3$ Hz), 100.4 (d, $^1J(\text{P}-\text{C}) = 198.3$ Hz), 116.5, 122.9, 125.4, 128.0, 129.8, 151.4, 160.4 ($^2J = 35.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 21.5; LC-MS m/z 307 $[\text{M}-18]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_5\text{P}$: C, 59.26; H, 6.53. Found: C, 59.38; H, 6.54. X-ray structure was determined for this compound.

Compound 21. Yield: 0.10 g (15%); mp 155–157 °C; IR (KBr, cm^{-1}) 2930, 2886, 1634, 1578, 1454, 1285, 1231, 1206, 1051, 993; ^1H NMR (200 MHz, CDCl_3) δ 0.97 and 1.26 (2 s, 6H), 2.01 (d, $^3J = 14.1$ Hz, 3H), 3.75–4.38 (m, 4H), 6.77 (d, $^3J = 10.0$ Hz, 1H), 7.04–7.38 (m, 4H), 7.76 (d, $^3J = 10.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 12.0 (d, $^2J = 3.6$ Hz), 21.5, 22.2, 32.5 (d, $^3J = 6.1$ Hz), 74.4, 74.5, 92.7 (d, $^1J(\text{P}-\text{C}) = 203.8$ Hz), 115.4, 119.9, 120.5, 123.5, 126.9, 128.2, 130.0, 153.1, 159.6 (d, $^2J = 36.4$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 21.8; LC-MS m/z 307 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{P}$: C, 62.74; H, 6.25. Found: C, 62.87; H, 6.24. X-ray structure was determined for this compound.

Compound trans-23. This compound was hydrolytically unstable, ^{31}P NMR spectrum showed a yield of 8%. ^1H NMR (400 MHz, CDCl_3) δ 0.98 and 1.03 (2 s, 6H), 1.72 (d, $^3J = 15.6$ Hz, 3H), 3.81–4.15 (m, 4H), 4.73 (d, $^3J = 3.4$ Hz, 1H), 4.95 (s, 1H), 5.09 (m, 1H), 6.92–7.35 (m, 4H); ^{31}P NMR (80 MHz, CDCl_3) δ 18.5. Because of the moisture sensitivity of this compound, other data were not recorded.

Compounds 20, 22, and trans-24. Compound 20. Yield 0.34 g (40%); mp 178–182 °C; IR (KBr, cm^{-1}) 3252, 2957, 1644, 1601, 1472, 1370, 1256, 1188, 1051, 910; ^1H NMR (400 MHz, CDCl_3) δ 0.97 and 1.21 (2 s, 6H), 1.99 (d, $^3J = 13.6$ Hz, 3H), 3.37–3.43 (br m, 3H), 3.78–4.30 (m, 4H), 4.81–4.84 (m, 1H), 6.88–7.55 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.9 (d, $^2J = 5.3$ Hz), 21.6, 22.2, 32.6 (d, $^3J = 5.3$ Hz), 33.5, 62.9, 74.7, and 74.8 (2 d, $^3J = 5.3$ Hz), 100.5 (d, $^1J(\text{P}-\text{C}) = 198.8$ Hz), 115.3, 118.1, 128.2, 130.5, 132.3, 150.4, 160.4 (d, $^2J = 35.3$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 20.8; LC-MS m/z 385 $[\text{M}-18]^+$, 387 $[\text{M}-16]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{PBr}$: C, 47.66; H, 5.00. Found: C, 47.67; H, 4.94.

Compound 22. Yield 0.14 g (17%); mp 172–174 °C; IR (KBr, cm^{-1}) 3100, 2874, 1630, 1574, 1474, 1422, 1283, 1231, 1055, 1001; ^1H NMR (400 MHz, CDCl_3) δ 0.96 and 1.27 (2 s, 6H), 2.00 (d, $^3J = 14.2$ Hz, 3H), 3.78 (dd, $^2J = 10.8$ Hz, $^3J = 17.8$ Hz, 2H), 4.36 (dd, $^2J = 10.8$ Hz, $^3J = 5.5$ Hz, 2H), 6.67 (d, $^3J = 10.2$ Hz, 1H), 6.93–7.37 (m, 3H), 7.81 (d, $^3J = 10.2$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 12.0 (d, $^2J = 4.9$ Hz), 21.5, 22.3, 32.5 (d, $^3J = 4.9$ Hz), 74.4, 74.5, 94.4 (d, $^1J(\text{P}-\text{C}) = 202.6$ Hz), 115.7, 117.2, 121.2, 122.3, 126.8, 129.3, 132.6, 152.1, 159.6 (d, $^2J = 36.4$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 21.1; LC-MS m/z 385 $[\text{M}]^+$, 387 $[\text{M}+2]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{PBr}$: C, 49.89; H, 4.71. Found: C, 49.87; H, 4.71.

Compound trans-24. This compound was hydrolytically unstable, ^{31}P NMR spectrum showed a yield of 8%. Mp 160–164 °C; IR (KBr, cm^{-1}) 3376, 2963, 1655, 1601, 1480, 1423, 1248, 1190, 1055, 1011, 872; ^1H NMR (200 MHz, CDCl_3) δ 1.02 (s, 6H), 1.70 (d, $^3J = 15.0$ Hz, 3H), 2.35 (s, 1H), 3.81–4.15 (m, 4H), 4.74–4.76 (m, 1H), 4.91 (br s, 1H), 5.07–5.08 (br m, 1H), 6.81 (d, $^3J = 8.7$ Hz, 1H), 7.28–7.46 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 16.6, 21.5, 21.7, 32.7 (d, $^3J = 6.0$ Hz), 44.5 (d, $^1J(\text{P}-\text{C}) =$

125.0 Hz), 63.4, ~ 76.6 (OCH_2 , merged with signals due to CDCl_3), 96.7 (d, $^3J = 8.5$ Hz), 114.1, 117.4, 124.9, 132.0, 133.3, 151.5, 160.1 (d, $^2J = 9.7$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 19.0; LC-MS m/z 403 $[\text{M}]^+$, 405 $[\text{M}+2]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{PBr}$: C, 47.66; H, 5.00. Found: C, 47.62; H, 5.03. X-ray structure was determined for this compound.

3. Synthesis of 4-(2-Hydroxyphenyl)-3-methyl Buten-2-ones 27 and 28. Compounds **23** and **24** were moisture-sensitive and eliminated phosphate to give the products **27** and **28**; the conversion was faster in the presence of 2 M HCl (5 mL per 0.5 g of the material).

Compound 27. Yield: 0.10 g (20%); mp 120–122 °C [lit. 124.6–126.0 °C¹⁴]; IR (KBr, cm^{-1}) 3337, 1638, 1603, 1456, 1364, 1306, 1258, 1107, 1003, 893; ^1H NMR (400 MHz, CDCl_3) δ 1.99 (s, 3H), 2.50 (s, 3H), 5.87 (s, 1H), 6.90–7.30 (m, 4H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.2, 26.0, 115.9, 120.5, 123.0, 130.25, 130.34, 135.7, 138.5, 154.0, 201.5. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 74.98; H, 6.86. Found: C, 74.81; H, 6.78. X-ray structure was determined for this compound.

Compound 28. Yield: 0.12 g (22%); mp 116–118 °C; IR (KBr, cm^{-1}) 3341, 2924, 1651, 1628, 1595, 1491, 1410, 1271, 1177, 1115, 1007, 907; ^1H NMR (400 MHz, CDCl_3) δ 1.96 (s, 3H), 2.47 (s, 3H), 5.31 (s, 1H), 6.78–7.36 (m, 3H), 7.51 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.2, 26.0, 112.6, 117.5, 124.9, 132.4, 132.7, 132.9, 140.1, 152.5, 200.1; LC-MS m/z 253 $[\text{M}-2]^+$, 255 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{Br}$: C, 51.79; H, 4.35. Found: C, 51.74; H, 4.33.

4. Reaction of Allene 9d with Salicylaldehydes. Synthesis of Phosphono-chromenes (Z)-32, (Z)-34, (Z)-35, and Phosphono-chromenol (E)-33. A mixture of allene **9d** (0.53 g, 2.48 mmol), salicylaldehyde/5-bromosalicylaldehyde (3.73 mmol), and DBU or K_2CO_3 (20 mol %) was heated in DMSO (5 mL) at 120 °C for 5 h. The contents were washed with water (2×10 mL), extracted with dichloromethane (2×25 mL), and dried (anhydrous Na_2SO_4). The ^{31}P NMR spectra of these reaction mixtures were similar to that done using DBU at 120 °C. There was no starting material left (^{31}P NMR). [When the reaction was done at 80 °C, more peaks were observed in the ^{31}P NMR spectrum.] After removal of solvent, compounds **32–35** were purified by column chromatography using ethyl acetate and hexane (1:3 v/v). The elution order for **33–35** was **35** (first), **34**, and **33** (last to elute).

(Z)-32. Yield 0.51 g (68%); mp 153–155 °C; IR (KBr, cm^{-1}) 2928, 1825, 1636, 1568, 1462, 1256, 1055, 1007, 872; ^1H NMR (400 MHz, CDCl_3) δ 1.13 and 1.17 (2 s, 6H), 2.03 (s, 3H), 3.92–4.20 (m, 4H), 4.63 (d, $^2J = 8.8$ Hz, 1H), 6.83 (s, 1H), 7.06–7.31 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 21.7, 21.84, 32.7 (d, $^3J = 6.0$ Hz), 75.6, 75.7, 81.3 (d, $^1J(\text{P}-\text{C}) = 195.0$ Hz), 115.7, 120.2, 123.4, 123.7, 126.6, 127.0, 127.1 (d, $^3J = 16.0$ Hz), 129.5, 130.0, 152.2, 163.5; ^{31}P NMR (160 MHz, CDCl_3) δ 15.4; LC-MS m/z 307 $[\text{M}+1]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_4\text{P}$: C, 62.74; H, 6.25. Found: C, 62.64; H, 6.25.

(E)-33. Yield 0.10 g (10%); mp 174–176 °C; IR (KBr, cm^{-1}) 3299, 2971, 1645, 1599, 1478, 1246, 1188, 1053, 995; ^1H NMR (400 MHz, CDCl_3) δ 0.98 (d, $^3J = 8.0$ Hz, 3H), 1.03 and 1.11 (2 s, 6H), 3.86–4.13 (m, 5H), 4.47 (br s, 1H), 5.36 (d, $^2J(\text{P}-\text{H}) = 8.0$ Hz, 1H), 6.86–7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.0, 21.2, 21.7, 32.5 (d, $^3J = 7.0$ Hz), 36.7, 68.1, 75.8, 75.9, 91.3 (d, $^1J(\text{P}-\text{C}) = 202.0$ Hz), 115.2, 118.0, 124.4, 132.9, 133.1, 149.9, 170.5 (d, $^2J = 27.0$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 15.6. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{PBr}$: C, 47.66; H, 5.00. Found: C, 47.76; H, 5.08.

(Z)-34. Yield 0.41 g (40%); mp 190–193 °C; IR (KBr, cm^{-1}) 2930, 2880, 1634, 1568, 1476, 1402, 1362, 1242, 1057, 1007, 858; ^1H NMR (400 MHz, CDCl_3) δ 1.12 and 1.15 (2 s, 6H), 2.01 (s, 3H), 3.88–4.17 (m, 4H), 4.67 (d, $^2J = 8.8$ Hz, 1H), 6.70 (s, 1H), 7.02–7.36 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 21.6, 21.8, 32.7 (d, $^3J = 6.0$ Hz), 75.67, 75.73, 82.8 (d, $^1J(\text{P}-\text{C}) = 193.0$ Hz), 115.9, 117.4, 121.9, 128.0, 128.4 (d, $^3J = 16.0$ Hz), 128.8, 132.6,

151.1, 162.8; ^{31}P NMR (160 MHz, CDCl_3) δ 14.6. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{PBr}$: C, 49.89; H, 4.71. Found: C, 49.82; H, 4.76.

(Z)-35. Yield 0.21 g (20%); mp 178–180 °C; IR (KBr, cm^{-1}) 2971, 1642, 1599, 1476, 1269, 1248, 1186, 1055, 1003, 984; ^1H NMR (400 MHz, CDCl_3) δ 0.99 and 1.23 (2 s, 6H), 1.73 (d, $^3J = 7.2$ Hz, 3H), 3.93–4.16 (m, 4H), 5.29 (q, $^3J = 7.2$ Hz, 1H), 6.71–7.31 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 10.3, 21.2, 21.8, 32.7 (d, $^3J = 7.0$ Hz), 76.8, 76.9, 105.3, 114.3, 116.8, 121.2, 121.4, 122.5 (d, $^1J(\text{P}-\text{C}) = 184.0$ Hz), 130.2, 131.8₆, 131.9₁, 134.5, 144.7 (d, $^2J(\text{P}-\text{C}) = 22.0$ Hz), 153.7; ^{31}P NMR (160 MHz, CDCl_3) δ 7.4. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{PBr}$: C, 49.89; H, 4.71. Found: C, 49.96; H, 4.68. X-ray structure was determined for this compound.

5. Reaction of Allene 9e with Salicylaldehydes. Synthesis of Allylic Phosphonates 36 and 37 and Phosphono-chromenes 38 and 39. The procedure was similar to that described for **10**, using allene **9e** (0.463 g, 2.14 mmol) and 3.21 mmol of salicylaldehydes. In these cases, the phenol addition products (**36** and **37**) and the aldehyde addition products (**38** and **39**) were obtained.

Compounds 36 and (Z)-38. Compound 36. Yield 0.18 g (25%); mp 106–108 °C; IR (KBr, cm^{-1}) 2975, 2915, 1690, 1599, 1478, 1458, 1400, 1273, 1225, 1059, 1013; ^1H NMR (400 MHz, CDCl_3) δ 0.97 and 1.08 (2 s, 6H), 1.72 (d, $^5J = 6.2$ Hz, 3H, $\text{C}=\text{C}(\text{CH}_3)_2(\text{A})$), 1.87 (d, $^5J = 4.8$ Hz, 3H, $\text{C}=\text{C}(\text{CH}_3)_2(\text{B})$), 2.90 (d, $^2J = 21.4$ Hz, 2H), 3.74–4.26 (m, 4H), 6.84–7.89 (m, 4H), 10.52 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7 (d, $^4J = 4.0$ Hz, $\text{C}=\text{C}(\text{CH}_3)_2(\text{A})$), 19.2 (d, $^4J = 3.0$ Hz, $\text{C}=\text{C}(\text{CH}_3)_2(\text{B})$), 21.2, 21.3, 26.4 (d, $^1J(\text{P}-\text{C}) = 139.0$ Hz), 32.5 (d, $^3J = 6.0$ Hz), 75.1, 75.2, 125.1 (d, $^3J = 11.0$ Hz), 134.2 (d, $^2J = 15.0$ Hz), 114.5, 122.0, 125.6, 128.5, 135.7, 158.5 (d, $^4J = 3.0$ Hz), 189.7; ^{31}P NMR (160 MHz, CDCl_3) δ 21.3; LC-MS m/z 339 [$\text{M} + 1$] $^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_5\text{P}$: C, 60.35; H, 6.85. Found: C, 60.44; H, 6.89.

Compound (Z)-38. Yield: 0.29 g (40%); mp 167–169 °C; IR (KBr, cm^{-1}) 3343, 2971, 2880, 1638, 1605, 1456, 1385, 1235, 1094, 1057, 1005, 818; ^1H NMR (400 MHz, CDCl_3) δ 0.84 and 0.94 (2 s, 6H), 1.03 and 1.06 (2 s, 6H), 3.74–3.92 (m, 4H), 4.12 (s, 1H), 4.75 (d, $^2J = 8.0$ Hz, 1H), 6.83–7.13 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.2, 21.3, 21.9, 24.1, 32.5 (d, $^3J = 6.1$ Hz), 39.9 (d, $^3J = 12.1$), 71.7, 75.9, 76.0, 87.9 (d, $^1J(\text{P}-\text{C}) = 184.3$ Hz), 115.7, 123.2, 124.3, 128.6, 129.6, 150.1, 173.4 (d, $^2J = 3.9$ Hz); ^{31}P NMR (160 MHz, CDCl_3) δ 13.7; LC-MS m/z 339 [$\text{M} + 1$] $^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{O}_5\text{P}$: C, 60.35; H, 6.85. Found: C,

60.59; H, 6.82. X-ray structure was determined for this compound.

Compounds 37 and (Z)-39. Compound 37. Yield 0.45 g (50%). Semisolid. After several washings with ether also, we could not get this as a well-defined solid. IR (KBr, cm^{-1}) 2968, 2886, 1715, 1684, 1591, 1470, 1393, 1223, 1142, 1061; ^1H NMR (400 MHz, CDCl_3) δ 0.97 and 1.09 (2 s, 6H), 1.71 (d, $^5J = 6.0$ Hz, 3H, $\text{C}=\text{C}(\text{CH}_3)_2(\text{A})$), 1.87 (d, $^5J = 4.8$ Hz, 3H, $\text{C}=\text{C}(\text{CH}_3)_2(\text{B})$), 2.89 (d, $^2J = 21.2$ Hz, 2H), 3.73–4.23 (m, 4H), 6.78–7.97 (m, 3H), 10.43 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.8 (d, $^4J = 3.2$ Hz), 19.3 (d, $^4J = 2.9$ Hz), 21.2, 21.4, 26.4 (d, $^1J(\text{P}-\text{C}) = 139.1$ Hz), 32.6 (d, $^3J = 6.0$ Hz), 75.0, 75.1, 125.7 (d, $^3J = 11.5$ Hz), 134.2 (d, $^2J = 14.7$ Hz), 114.9, 116.6, 126.8, 131.1, 138.2, 157.5 (d, $^4J = 2.4$ Hz), 188.3; ^{31}P NMR (160 MHz, CDCl_3) δ 20.9; LC-MS m/z 417 [M] $^+$, 419 [$\text{M} + 2$] $^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{P}$: C, 48.94; H, 5.31. Found: C, 49.05; H, 5.28.

Compound (Z)-39. Yield 0.18 g (20%); mp 167–169 °C; IR (KBr, cm^{-1}) 3364, 2973, 2880, 1638, 1601, 1476, 1238, 1059, 1007, 870; ^1H NMR (400 MHz, CDCl_3) δ 1.01, 1.12, 1.18, and 1.20 (4 s, 12H), 3.87–4.12 (m, 4H), 4.25 (s, 1H), 4.95 (d, $^2J = 12.0$ Hz, 1H), 6.86–7.43 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.9, 21.3, 21.8, 23.8, 32.6 (d, $^3J = 6.0$ Hz), 39.7 (d, $^3J = 12.0$ Hz), 70.8, 76.0, and 76.1 (2 d, $^2J = 7.0$ Hz), 88.4 (d, $^1J(\text{P}-\text{C}) = 184.0$ Hz), 115.5, 117.5, 126.7, 131.1, 132.3, 149.1, 173.5; ^{31}P NMR (160 MHz, CDCl_3) δ 13.3; LC-MS m/z 417 [M] $^+$, 419 [$\text{M} + 2$] $^+$. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{P}$: C, 48.94; H, 5.31. Found: C, 48.91; H, 5.26.

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Supporting Information Available: Additional experimental data, ORTEP drawings, table pertaining to theoretical calculations, ^{31}P NMR spectra illustrating *E/Z* isomer conversion in **10**, copies of ^1H and ^{13}C NMR spectra, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.