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Palladium-Catalyzed Coupling of Allenylphosphonates, Phenylallenes, and Allenyl Esters: Remarkable Salt Effect and Routes to Novel Benzofurans and Isocoumarins

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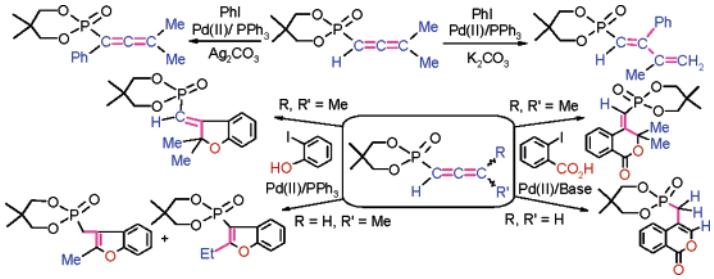

Coupling reactions of allenylphosphonates $(OCH_2CMe_2CH_2O)P(O)CH{=}C{=}CRR'$ [R, R′ = H (**1a**), R = H, R′ = Me (**1b**), R = R′ = Me (**1c**)] with aryl iodides, iodophenol, and iodobenzoic acid in the presence of palladium(II) acetate are investigated and compared with those of phenylallenes $PhCH{=}C{=}CR_2$ [R = H (**2a**), Me (**2b**)] and allenyl esters $EtO_2CCH{=}C{=}CR_2$ [R = H (**2c**), Me (**2d**)]. While **1b** and **1c** couple with different stereochemical outcomes using PhI in the presence of $Pd(OAc)_2/PPh_3/K_2CO_3$ to give phenyl-substituted 1,3-butadienes, **1a** does not undergo coupling but isomerizes to the acetylene $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CMe$ (**7**). In the reaction of **1c** with PhI, use of K_2CO_3 affords the butadiene (*Z*)-$(OCH_2CMe_2CH_2O)P(O)CH{=}C(Ph){-}C(Me){=}CH_2$ (**12**); in contrast, the use of Ag_2CO_3 leads to the allene $(OCH_2CMe_2CH_2O)P(O)C(Ph){=}C{=}CMe_2$ (**20**), showing that these bases differ very significantly in their roles. The reaction of **1a** with PhI or $PhB(OH)_2$ in the presence of $Pd(OAc)_2$/CsF/DMF leads mainly to (*E*)-$(OCH_2CMe_2CH_2O)P(O)CH{=}C(Me)Ph$ (**21**) and $(OCH_2CMe_2CH_2O)P(O)CH_2{-}C(Ph){=}CH_2$ (**22**) and is thus a net 1,2-addition of Ph−H. Compound **1b** reacts with iodophenol in the presence of $Pd(OAc)_2/PPh_3/K_2CO_3$ to give a benzofuran that has a structure different from that obtained by using **1c** under similar conditions. Treatment of **1a** with iodophenol/$Pd(OAc)_2$/CsF/DMF also gives a benzofuran whose structure is different from that obtained by using **2a** under similar conditions. In the reaction with 2-iodobenzoic acid, **1a** and **2c** afford one type of isocoumarin, while **1b**,**c** and **2a**,**b** give a second type of isocoumarin. The structures of key compounds are established by X-ray crystallography. Utility of the phosphonate products in the Horner−Wadsworth−Emmons reaction is demonstrated.

Introduction

Allenes or 1,2-dienes are versatile precursors for a variety of target molecules of industrial and biological significance.[1,2] Among their various reactions, transition-metal-catalyzed C−C or C−heteroatom bond formation has emerged as an important area in organic synthesis.[2] Allenylphosphonates (phosphorylated allenes) **1a**−**c** can also be used as versatile building blocks in organic chemistry.[3] Since phosphorus can impart a different electronic constraint relative to an aryl carbon of aryl-substituted allenes on the intermediates, the stereochemistry of the products in the palladium-catalyzed coupling using allenylphosphonates and phenyl-substituted allenes (e.g., **2a**,**b**) may be the result of different pathways. The allenyl esters (e.g., **2c**,**d**) may show an intermediate behavior. As an example, in the palladium-

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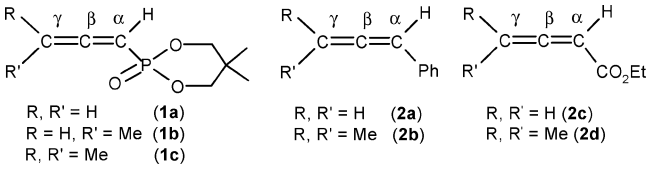
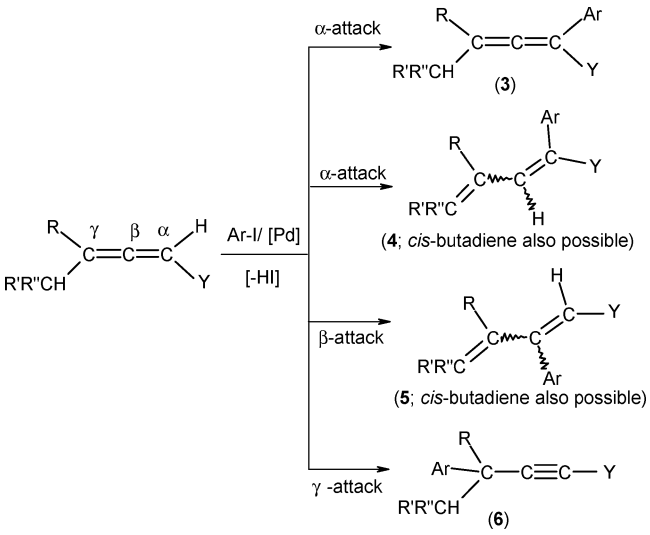


catalyzed reaction of an allene with aryl iodide shown in Scheme 1, the incoming aryl group can in principle attack any of the three carbon centers, α, *β*, or *γ*, depending upon the substituents present and the conditions used. The resulting products will be, respectively, (a) allene **3** or butadiene **4** (isomerism possible), (b) butadiene **5** (isomerism possible), or (c) acetylene **6**.[2a] If a terminal allene, such as (Y)-CH═C═CH_2, is used, the butadiene type of product **4** will not be possible. For any further application, it is important to know the stereospecificity of these reactions, and this is one aspect we are interested in.

SCHEME 1



When the iodoarene bears an additional functional group, such as that in 2-iodophenol or 2-iodobenzoic acid, cyclization could occur, but there are a large number of isomers possible. The resulting products are synthetically and biologically important heterocycles, such as benzofurans or isocoumarins.[4−7] In this area, some work on nonphosphorylated allenes is available.[8] With regard to allenylphosphonates, despite the fact that compounds **1a**−**c** constitute some of the most readily accessible and very inexpensive allenes,[9] investigations on the catalytic arylation (say, using Suzuki or Heck coupling) on this class of substrates are few in number.[3f−g] With this in mind and in continuation of our studies on organophosphorus chemistry,[10] we have begun investigating the palladium-catalyzed coupling reactions of allenylphosphonates. In this paper, we concentrate on the reactions of allenes **1a**−**c** with aryl iodides, 2-iodophenol, and 2-iodobenzoic acid. Where feasible, comparison is made to the corresponding phenylallenes PhCH═C═CR_2 [R = H (**2a**), Me (**2b**)] and allenyl esters EtO_2CCH═C═CR_2 [R = H (**2c**), Me (**2d**)]. Significant findings include the following: (i) stereospecific formation of different butadiene isomers in the reaction of ArI with **1b** and **1c**; (ii) a remarkable difference between the bases K_2CO_3 and Ag_2CO_3 in directing the product formation in the case of **1c**; (iii) isolation of proton-addition products in the reaction of **1a** with iodobenzene or phenylboronic acid in the presence of CsF; and (iv) first-time isolation and X-ray structural characterization of a variety of phosphono benzofurans and phosphono isocoumarins, many of which are of structural types different from those using nonphosphorylated allenes **2a**−**d**.

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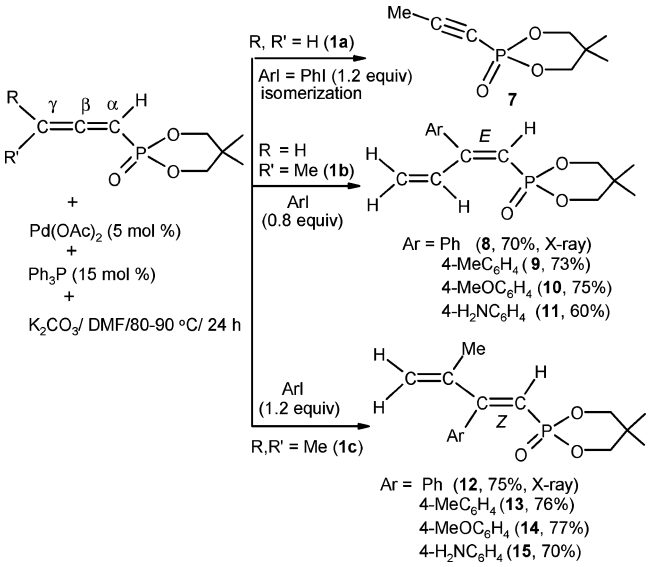
Possible mechanistic features as well as application in Horner−Wadsworth−Emmons (HWE) reaction are also discussed.

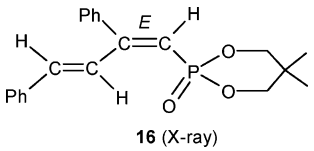
Results and Discussion

(i) Reaction of 1a−c and 2b−d with Aryl Iodides. (a) Formation of Aryl-Substituted 1,3-Butadienes and the Acetylene ($OCH_2CMe_2CH_2O$)P(O)C≡CMe (7): Scheme 2 depicts the products obtained in the reaction of **1a**−**c**[3c,9] with aryl iodides. The reaction of **1a** with iodobenzene using Pd(OAc)$_2$/PPh$_3$ in the presence of K_2CO_3 (or Et_3N) in DMF or acetonitrile led to the isomeric acetylene **7** as the predominant product.[9,11] Under the same conditions, the trisubstituted 1,3-*trans*-butadienes **8**−**15** are obtained by using **1b**,**c**. Optimization of reaction conditions was done using **1c** and iodobenzene. An assay varying the palladium catalyst/phosphine/base/solvent indicated that Pd(OAc)$_2$/Ph$_3$P/K_2CO_3/DMF gave the best results (Table 1).[12] The reaction mixture showed only one butadiene stereoisomer in >80% yield in each case.[13] A surprising result, however, was that **8** had *E* and **12** had *Z* configuration, as revealed by X-ray crystallography. We have confirmed this by checking cell dimensions of several crystals in both cases.

SCHEME 2



Furthermore, when a 1:2 (or higher) mole ratio of **1b** to iodobenzene was used, the bisphenylated product **16** (X-ray) is obtained *quantitatively*.[14] The stereochemistry of the α,β C=C bonds in **16** and in **8** is the same.



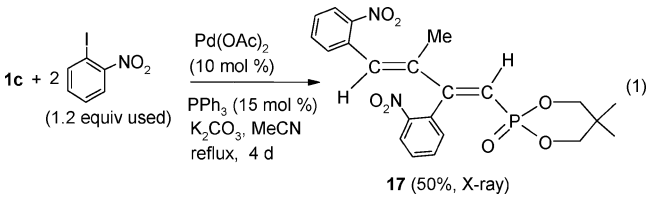
16 (X-ray)

In contrast to the above, from the reaction of **1c** with 1-iodo-2-nitrobenzene, the *bisarylated* product **17**, and not the *monoarylated* product, was isolated in fair yields (eq 1). Since the monoarylated butadiene could not be seen (NMR and TLC) during the progress of reaction,[15] it appears that once formed, monoarylated product is more reactive and leads to the bisproduct **17**. The *E* configuration at the β-carbon for **17** is similar to that for **12**, thus confirming that this is the preferred stereochemistry when **1c** is used. We are not aware of the any previous report of similar bisarylation in a two-component reaction using other allenes.

TABLE 1. Effect of Reaction Conditions on the Yield of 12 in the Coupling of 1c with Iodobenzene[a]

entry	palladium catalyst/ phosphine ligand	base/solvent	yield (%)[b]
1	Pd(OAc)$_2$/PPh$_3$	NEt$_3$, CH$_3$CN	60
2	Pd(OAc)$_2$/P(*o*-tolyl)$_3$	NEt$_3$, CH$_3$CN	58
3	Pd(OAc)$_2$/TDMPP[c]	NEt$_3$, CH$_3$CN	16
4	Pd(OAc)$_2$/PPh$_3$	NEt$_3$, 1,4-dioxane	50
5	Pd(OAc)$_2$/PPh$_3$	NEt$_3$, DMF	23
6	Pd(dba)$_2$/PPh$_3$	NEt$_3$, CH$_3$CN	50
7	Pd(dba)$_2$/PPh$_3$	NEt$_3$, DMF	30
8	Pd(CH$_3$CN)$_2$Cl$_2$/PPh$_3$	NEt$_3$, CH$_3$CN	60
9	Pd(PPh$_3$)$_4$	NEt$_3$, CH$_3$CN	52
10	Pd(OAc)$_2$/PPh$_3$	K_2CO_3, CH$_3$CN	80[d]
11	Pd(OAc)$_2$/PPh$_3$	K_2CO_3, DMF	80
12	Pd(OAc)$_2$/PPh$_3$	K_2CO_3, NMA	40
13	Pd(OAc)$_2$	K_2CO_3, CH$_3$CN	43

[a] All reactions were carried out at 90 °C for 24 h using **1c** (1.0 mmol), iodobenzene (1.2 mmol), Pd complex (0.05 mmol), base (2.0 mmol), and solvent (4 mL). [b] Yields were calculated by using integrated intensity ratios of the peaks in ^{1}H/^{31}P NMR. [c] TDMPP = Tris(2,6-dimethoxyphenyl)phosphine. [d] Isolated yield: 75%.



17 (50%, X-ray)

In the reaction of **2b** with iodobenzene, using the same conditions as that for the preparation of **12**, we obtained a single isomer of PhCH=C(Ph)−C(Me)=CH$_2$ (**18**, 70%) whose ^{1}H NMR spectrum matches with that of the *Z* isomer prepared by a different route.[16] This is consistent with the fact that in reactions of terminal methylallenes with aryl halides in the presence of Pd(dba)$_2$/PPh$_3$/K_2CO_3 using *N*,*N*-dimethylacetamide as the solvent, a *cis*-butadiene stereochemistry is assigned for the products.[2a] With regard to allenyl esters, we treated **2c** and **2d** with iodobenzene under conditions analogous to that for the preparation of **12**. Compound **2c** was not stable under these

(11) Compound **1a** (and likely **1b**) leads to the β-ketophosphonate (^{31}P NMR: δ 13.8) very readily in the presence of K_2CO_3, most likely by adventitious moisture. In reactions using **1b**,**c**, there was a minor product (5−10%; ^{1}H NMR: δ 2.86 (PC*H*$_2$, *J* = 27.0 Hz; ^{31}P NMR: δ 22−23), but it was not isolated. In some cases, there was unreacted allene (~5%).

(12) In the case of **1c**, CH$_3$CN also worked well, but for **1b**, this solvent gave poor results. This is probably due to the formation of (OCH_2CMe_2-CH_2O)P(O)CH_2C≡C(Me) [δ(P): 17.0] which could be isolated.

(13) The rest are unidentified products (presumably other isomers) + starting material. By contrast, the allene PhCH=C=CHMe (solvent: *N*,*N*-dimethylacetamide) reacts with 3-bromo-5,5-dimethyl-2-cyclohexen-1-one to give a mixture of *Z* and *E* isomers; see ref 2a.

(14) For this reason, in reactions using **1b**, a lower stoichiometry of aryl iodide (0.8 equiv, cf. Scheme 2) is utilized for optimum yields.

(15) The ^{1}H NMR spectrum of the reaction mixture suggests that a product (ca. 10%) containing a PC*H*$_2$ group [δ 2.99, *J* = 20.8 Hz] is present, but this compound could not be isolated.

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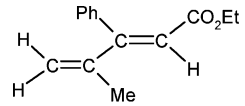
conditions, and we have not been successful in isolating a well-defined product using this allene. However, **2d** gave the product **19** cleanly. The stereochemistry for **19** is based on analogy to the phosphonate **12**, for which we have an X-ray structure.



19 (80%)

(b) Use of K_2CO_3 versus Ag_2CO_3—A Remarkable Salt Effect: While the use of Ag_2CO_3 as a base in the reaction of **1c** [^{31}P NMR: δ 8.8] with iodobenzene leads to the α-substituted product **20** [^{31}P NMR: δ 8.1] *quantitatively*, it is *essentially absent* when K_2CO_3 is used as a base under the same conditions (Figure 1) and only **12** [δ(P) 11.5] is isolated. The yield of **12** could be increased (≥80%) using longer reaction times (24 h). It has been noted recently by Fu and Ma that a combination of Ag_2CO_3 (5 mol %) and K_2CO_3 (2 equiv) drives the reaction of 1,2-allenyl sulfones with PhI to α-substituted products;[2l] under those conditions, our allene **1c** gives only the butadiene **12**. Chang and Cheng noted that, in the palladium-catalyzed reaction of $Me_2C{=}C{=}CH_2$ with 4-bromoacetophenone using Ag_2CO_3 as a base, 1,3-butadiene products were not formed.[2a] In the reaction of **2b** or **2d** with iodobenzene, however, we obtained the 1,3-butadienes **18** or **19**, respectively, irrespective of whether K_2CO_3 or Ag_2CO_3 was used. The rationale for the observed dramatic difference between Ag_2CO_3 and K_2CO_3 in the case of **1c** needs more detailed scrutiny.[17]

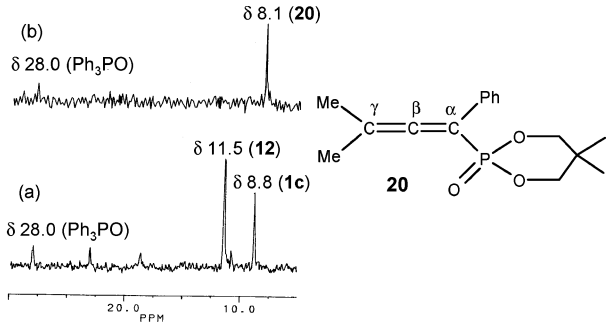


FIGURE 1. ^{31}P NMR spectra for the reaction mixture of **1c** with iodobenzene (1:1.2) using $Pd(OAc)_2/PPh_3$ (5 mol %/15 mol %) after 18 h reflux in CH_3CN with (a) K_2CO_3 (2 equiv) and (b) Ag_2CO_3 (2 equiv). Note the complete absence of a peak for **20** in (a) and the one for **12** in (b).

(c) Formation of Addition Products: The reaction of **1a** with iodobenzene or $PhB(OH)_2$ using $Pd(OAc)_2$/CsF/DMF afforded only one stereoisomer of the vinylphosphonate (*E*)-**21** (X-ray) along with the allylphosphonate **22** (Scheme 3 and Table 2). The yield of (*E*)-**21** was higher when $PhB(OH)_2$ was used. It may be noted that a proton is eliminated (as HI) in the formation of **8**−**15** while it is added in the formation of **21** and **22**. Thus formation of **8**−**15** and **21** and **22** follows different mechanistic pathways (vide infra).[2f] Addition of acetic acid improved the yield of the addition products. However, we obtained a fair yield of **21** and **22** *even without adding acetic acid* and by using Pd(II) acetate/CsF in the absence of Ph_3P. Reaction of **1c** with phenylboronic acid under the same conditions gave the butadiene **12** only and no addition product. It is pertinent here to note that the reaction of the allene **2c** using $Pd(PPh_3)_4/ArB(OH)_2$ in the presence of acetic acid led to the *E* isomer of $EtO_2CCH{=}C(Me)Ar$.[2f] Soon after the submission of our paper, addition of arylboronic acids to phosphorylated allenes using $Pd(PPh_3)_4$/acetic acid has been reported.[3h] Thus, using $H_2C{=}C{=}C(n\text{-Bu})P(O)(OEt)_2$ and $PhPB(OH)_2$/HOAc in THF, the authors have been able to obtain the vinylphosphonate $(H_3C)(Ph)C{=}C(n\text{-Bu})P(O)(OEt)_2$ in 81% yield. In our reactions (cf. Scheme 3), DMF was found to be a good solvent.

SCHEME 3

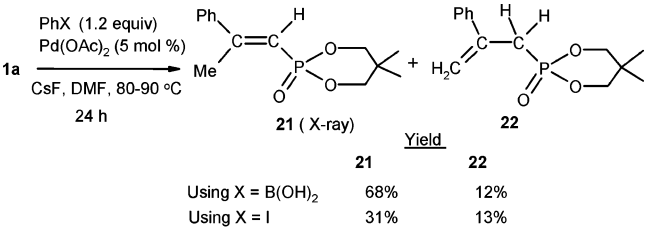


TABLE 2. Effect of Reaction Conditions on the Yield of 21 and 22 in the Coupling of 1a (1.0 mmol) with PhX [1.2 mmol; X = I or $B(OH)_2$]

entry	catalyst (0.05 mmol)	X	conditions	yield (%)[a]	**21**(*E*)/**22**
1	$Pd(OAc)_2$	$B(OH)_2$	CsF (2.0 mmol)/ DMF (4 mL)/ 90 °C/24 h	87	85/15
2	$Pd(OAc)_2$	I	CsF (2.0 mmol)/ DMF (4 mL)/ 90 °C/24 h	44	70/30[b]
3	$Pd(PPh_3)_4$	$B(OH)_2$	AcOH (10 mol %)/ 1,4-dioxane (4 mL)/ 60 °C/4 h	100	93/7
4	$Pd(PPh_3)_4$	I	AcOH (10 mol %)/ 1,4-dioxane (4 mL)/ 60 °C/4 h	47	95/5

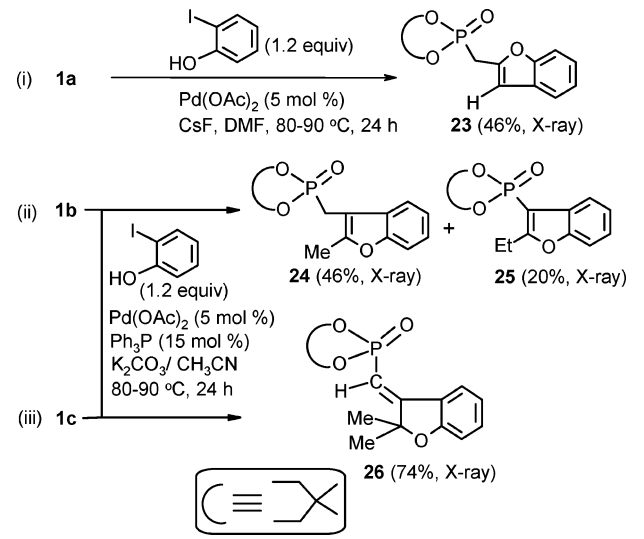
[a] Yields were calculated based on the integrated intensity ratios of the peaks in ^{1}H/^{31}P NMR. [b] There was an additional peak at δ 11.0 in the ^{31}P NMR spectrum, but the corresponding compound could not be isolated.

(ii) Reaction of 1a−c with 2-Iodophenol—Comparison to Phenylallenes 2a,b and Allenyl Esters 2c,d. These reactions lead to benzofurans **23**−**31** (Schemes 4 and 5). Because of the facile rearrangement of **1a** to acetylene **7** in the presence of K_2CO_3/CH_3CN, the reaction of this allene with iodophenol has been conducted using $Pd(OAc)_2$/CsF/DMF in the absence of Ph_3P. It gives mainly two compounds [ca 7:3 ratio; ^{31}P NMR δ(P): 17.5 and 22.3] from which the major product **23** [δ(P): 17.5] could be isolated. In contrast, **2a** affords the phenyl(methyl)benzo[*b*]furan **27** (50% yield). Although there are several methods for the synthesis of **27**,[18] this strategy offers the potential to prepare a range of analogues. For example, **30** is obtained when starting with **2c**, although the reaction also

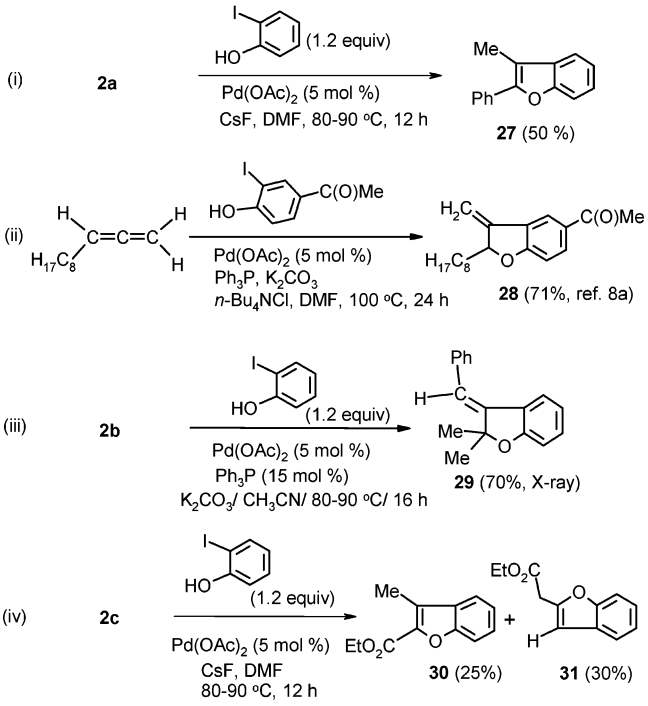
(17) One of the reviewers is of the opinion that the differences described here and the absence of such differences for other allenic substrates must be related to better coordinating properties of the P=O moiety, with a possibility of chelated intermediates with a Pd···O=P coordination.

(18) For other routes to compound **27**, see: (a) Koenigkramer, R. E.; Zimmer, H. *J. Org. Chem.* **1980**, *45*, 3994. (b) Brady, W. T.; Giang, Y. S. F.; Marchand, A. P.; Wu, A. H. *J. Org. Chem.* **1987**, *52*, 3457. (c) Furstner, A.; Jumbam, D. N. *Tetrahedron* **1992**, *48*, 5991. (d) Rele, S.; Talukdar, S.; Banerji, A.; Chattopadhyay, S. *J. Org. Chem.* **2001**, *66*, 2990. (e) Juhász, L.; Szilágyi, L.; Antus, S.; Visy, J.; Zsila, F.; Simonyi, M. *Tetrahedron* **2002**, *58*, 4261. (f) Willis, M. C.; Taylor, D.; Gillmore, A. T. *Org. Lett.* **2004**, *6*, 4755. (g) Xie, X.; Chen, B.; Lu, J.; Han, J.; She, X.; Pan, X. *Tetrahedron Lett.* **2004**, *45*, 6235. (h) Miyata, O.; Takeda, N.; Naito, T. *Org. Lett.* **2004**, *6*, 1761.

SCHEME 4



SCHEME 5

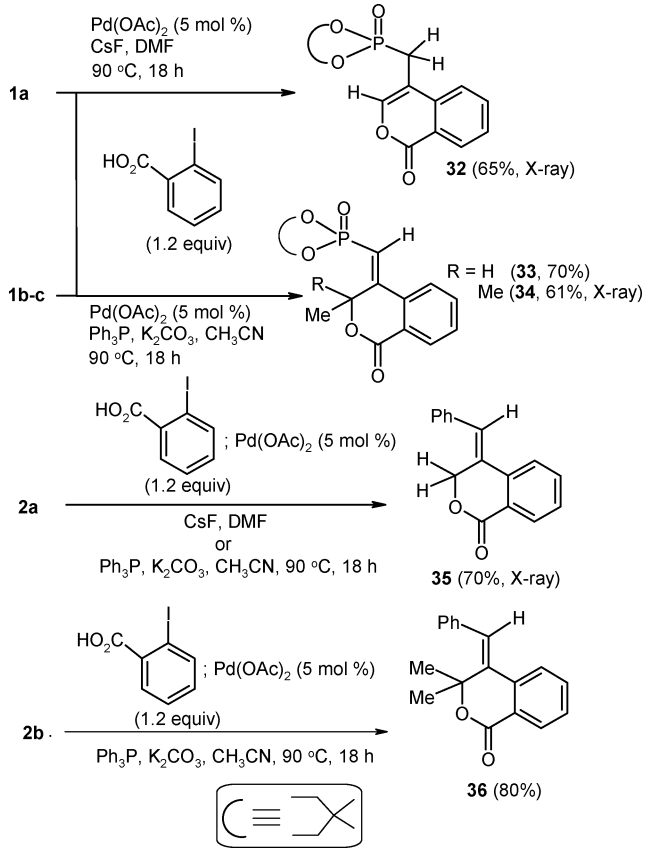


gives **31** that has a structure similar to **23**. This shows that the behavior of **2c** is intermediate to that of **1a** and **2a**. In earlier studies on annulation reactions of allenes,[8] from the reaction of n-$C_8H_{17}CH{=}C{=}CH_2$ with 2-iodo-4-acetophenol (5:1 molar stoichiometry), a nonrearranged benzofuran **28** with the terminal $=CH_2$ group still intact was obtained.[8a] A difference in the two types of products **27** and **28** arises probably because of the presence of the phenyl group in the former (that can lead to extended conjugation) and a n-C_8H_{17} group (that does not involve in extended conjugation) in the latter.

Compound **1b** gives the benzo[*b*]furans **24** and **25** in decent yields, while **1c** also affords dihydrobenzofuran (*E*)-**26** (stereoselective) that is of a *different type*. Hence, we believe the regiochemical and stereochemical outcomes of the reaction are new and not expected. In **25**, arylation has taken place at the carbon α to phosphorus. What is more interesting perhaps is that, although benzofurans are obtained even in the case of allenylphosphonates **1b**,**c**, none of these are alike, thus demonstrating a rich chemistry of these allenes. To our knowledge, such a structural diversity has not been reported before. Similar to **1c**, reaction of **2b** with 2-iodophenol gave dihydrobenzofuran (*E*)-**29**. On the other hand, **2d** gave a complicated mixture of at least three products (three OCH_2 multiplets in addition to the one due to the starting material were seen in the ^{1}H NMR spectrum). Although we have not isolated a pure product, this feature clearly suggests that **2d** behaves differently when compared to the allenylphosphonate **1c**.

(iii) Reactions of 1a−c and 2a−d with 2-Iodobenzoic acid. The reactions of **1a** and **1b**,**c** with 2-iodobenzoic acid are again qualitatively different, with the former affording isocoumarin (**32**) and the latter two giving isocoumarins (*Z*)-**33** and (*Z*)-**34** stereoselectively (Scheme 6). While compound **32** has an allylic double bond with respect to phosphorus, (*Z*)-**33** and (*Z*)-**34** have a vinylic double bond with respect to phosphorus. In contrast, phenylallenes **2a**,**b** afford products (*Z*)-**35** and (*Z*)-**36**, respectively, that are analogous to (*Z*)-**33** and (*Z*)-**34**, even under

SCHEME 6

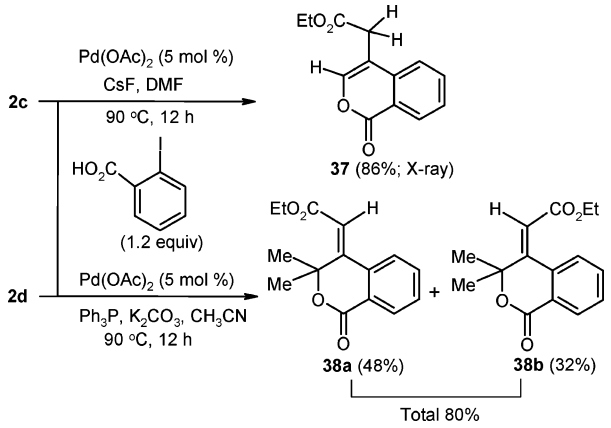


different conditions.[19] It is likely that conjugation involving the phenyl ring in the products may be responsible for the difference between the behavior of **1a** and **2a**. Compound **35** as a minor product (ca. 14%) has been reported earlier in a thallation−olefination reaction.[20] Compounds **2c** and **2d** gave **37** and a mixture of (*Z*)- and (*E*)-**38**, respectively. Although these products

(19) The allene PhCH=C=CH(Me) gave a mixture of *E*/*Z* isomers: Kato, F.; Hiroi, K. *Chem. Pharm. Bull.* **2004**, *52*, 95.

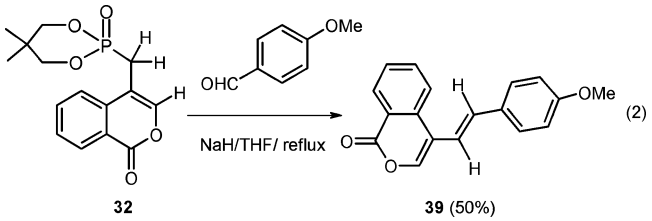
(20) Larock, R. C.; Varaprath, S.; Lau, H. H.; Fellows, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 5274.

SCHEME 7



have structures analogous to those of **32** and **34**, respectively, two geometrical isomers (**38a**,**b**) are isolated in the reaction using **2d** (Scheme 7).

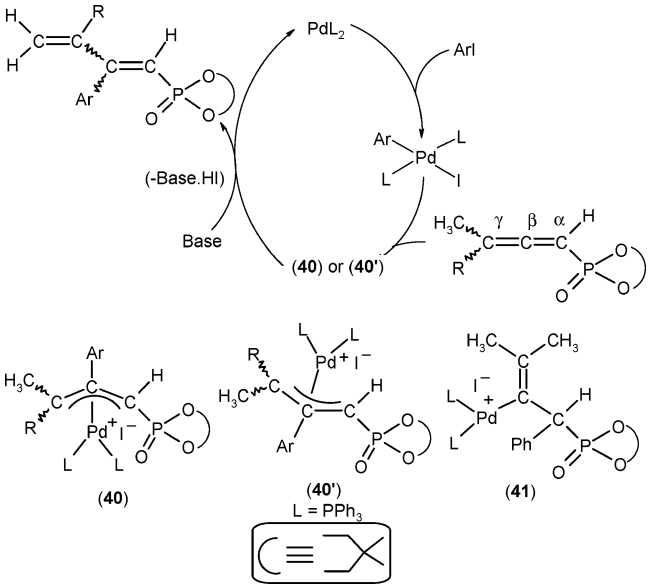
(iv) Horner−Wadsworth−Emmons (HWE) Reaction Using 32. We were interested to see if at least some of the phosphonate products synthesized in this work could be utilized further, and in this direction, we felt that the HWE reaction of phosphonate products from the above studies possessing a PCH_2 group should be straightforward. Thus we have been able to effect olefination of *p*-anisaldehyde using **32** to afford the isocoumarin **39** (eq 2). The yield is not optimized, but this reaction clearly shows one possible avenue for utilizing the products of allenylphosphonates with aryl iodides.



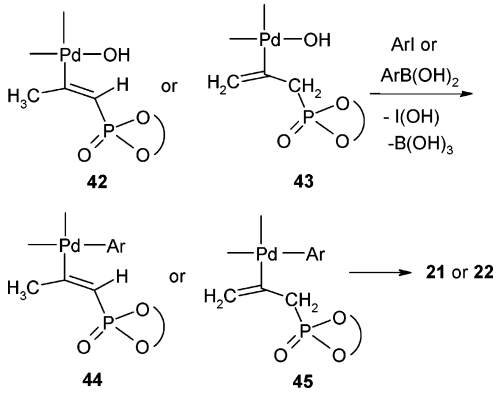
(v) Mechanistic Pathways. According to the known palladium chemistry, formation of the butadiene products **8**−**15** may be rationalized by invoking the allyl palladium complex **40** or **40′** shown in Scheme 8. The difference between **40** and **40′** lies in the orientation of the aryl group with respect to phosphorus. A proton is eliminated from the terminal CH_3 group as HI, along with PdL_2 in forming the products **8**−**15** from **40**/**40′**. It can be noted that, with a different orientation of the R and CH_3 groups, a *cis*-butadiene could have formed; this latter feature, however, is not observed for allenylphosphonates. The bisarylated products **16** and **17** are formed by subsequent Heck coupling at the least hindered site of the terminal $=CH_2$ group. Formation of α-phenylated allenylphosphonate **20** probably occurs through the complex **41** (cf. Scheme 8). Subsequent proton elimination occurs from the PC*H* end in order to get back to the allenic system present in **20**. The reaction using **1a** does not lead to a 1,3-butadiene because of the absence of a terminal CH_3 group.

In the formation of isomeric compounds **21** and **22**, in addition to the phenyl group, *one more proton* has been added to **1a**. We think that intermediates **42**/**43**, formed by addition of a [HPd(OH)] species to **1a**, and subsequently **44**/**45** are involved (Scheme 9). We have not used PPh_3 to generate a Pd(0) species, and hence the oxidation state of palladium is not

SCHEME 8



SCHEME 9

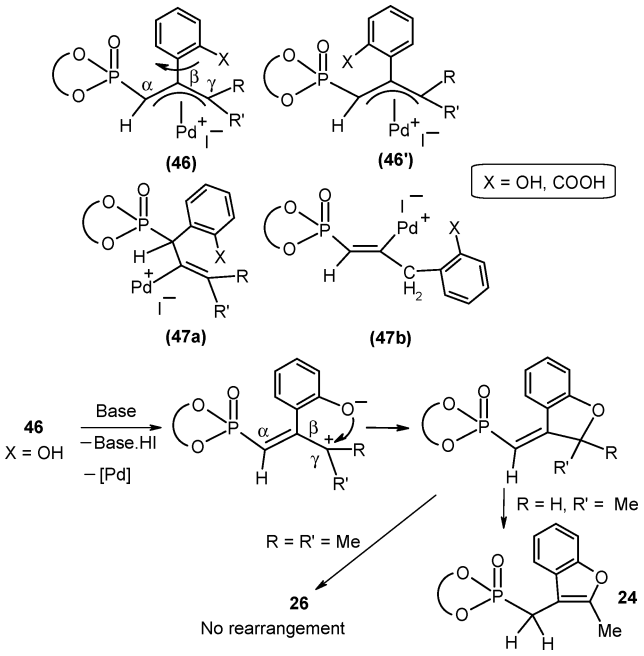


shown. A similar addition to the allenes $RR'C{=}C{=}CH_2$ leading to $RR'C{=}C(Ph)(CH_3)$ was reported recently, using $ArB(OH)_2$/acetic acid in the presence of $Pd(PPh_3)_4$ or $Pd(OAc)_2/PPh_3$.[2e,f] In this case, a [HPd(OAc)] species was invoked to explain the formation of the final products. This rationalization is logical for $ArB(OH)_2$, but for the reaction with ArI, there should be adventitious moisture present in the system for this mechanism to operate. This also may be the reason for the lower yields in the reaction using ArI. We have not probed this aspect further because of (a) isomerization **1a** to **7** in the presence of bases, such as Et_3N or even Ph_3P, and (b) competitive hydrolysis of **1a** to give the β-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)$-$CH_2C(O)CH_3$.[10]

For the formation of phosphono benzofurans **23**−**26** or phosphono isocoumarins **32**−**34**, we propose intermediates **46** and **47**. These are analogous to **40′** and **41**. Species **46′** is a rotamer of **46**. Since we did not use Ph_3P in reactions using **1a**, the oxidation state of palladium is uncertain and hence the other ligands on palladium are not shown. In the formation of furans **23**, **24**, and **26**, it is likely that a proton from the phenolic −OH group is removed from intermediate **46** by the base prior to cyclization (Scheme 10).[21] Subsequent to cyclization, a proton moves from the furan skeleton to the α-carbon in the case of

(21) Such a proton is not available in the reaction of **1a** with iodobenzene, and hence a simple substitution product is not obtained.

SCHEME 10



23 and **24**. This movement is not possible for **26** (R = R′ = Me). Compound **25** is formed by the attack of the aryl group on the α-carbon via intermediate **47**; the phenolic oxygen then attacks the *β*-carbon. A proton shift from the α- to *γ*-carbon is required in the final step to lead to **25**. In the case of **27**, species **46′** may be responsible for the cyclization by the attack of phenolic oxygen on the α-carbon. Formation of **29**, **30**, and **31** can be explained in a manner similar to those for **26**, **27**, and **23**, respectively.

The main differences in the formation of phosphono benzofurans **23**−**26** and phosphono isocoumarins **32**−**34** are that (i) derivative **33** does not undergo the proton shift (i.e., unlike compound **24**), and (ii) an isocoumarin product from the attack of aryl group on the α-carbon (analogous to **25**) is not observed. Formation of **32**−**34** can be explained in a manner similar to that for **24** and **26**. The product **35** using phenylallene **2a** did not undergo proton shift, but **37** obtained from 1,2-dialkadienoate **2c** did. Geometrical isomers are possible for **26** and **33**−**35** but not isolated. However, it can be noted that, in the benzofuran **26**, the aromatic ring is *cis* with respect to phosphorus, but in isocoumarin **34**, it is *trans*, although both are derived from the same allene **1c**. Only in the case of **38** are two geometrical isomers isolated.

Summary

The reactions of allenylphosphonates with a *γ*-methyl substituent provide 1,3-butadiene products. Doubly arylated butadienes (e.g., **16** and **17**) can be readily obtained by increasing the stoichiometry of the aryl iodide. In contrast, a similar reaction of terminal allene **1a** with iodobenzene using $Pd(OAc)_2$/Ph_3P/K_2CO_3 system does not take place. Instead, when $Pd(OAc)_2$/CsF combination is used, this allene (**1a**) undergoes a 1,2-addition of Ph−H with iodobenzene. A dramatic influence of the base (K_2CO_3 or Ag_2CO_3) on the course of arylation of allenylphosphonate **1c** is observed. Access to a new class of structurally diverse phosphono benzofurans and phosphono isocoumarins has been established. The stereochemical preference of the aromatic ring with respect to phosphorus [*cis* in **26** but *trans* in **34**] in harvesting new heterocycles needs further attention. It was shown that the Horner−Wadsworth−Emmons (HWE) reaction of PCH_2 products, such as **32**, with aldehydes leads to compounds such as **39**; this is a possible avenue for further exploration.

Experimental Section

Precursors **1a**−**c**[9], **2a**,[22] and **2c**,**d**[23] were prepared using literature procedures; a procedure analogous to that for **2a** was adapted for **2b**. Pure acetylene **7** [δ(P) −12.9] was prepared by treating **1a** with triethylamine;[9] it was formed normally under basic conditions, even in the presence of Ph_3P as mentioned above. General experimental conditions are given in the Supporting Information.

General Procedure for Preparation of 8−**11:** A 25 mL round-bottomed flask containing allenylphosphonate **1b** (0.30 g, 1.48 mmol), $Pd(OAc)_2$ (0.017 g, 0.074 mmol), PPh_3 (0.059 g, 0.222 mmol), iodobenzene (0.242 g, 1.18 mmol), and K_2CO_3 (0.414 g, 2.96 mmol) was purged with nitrogen gas several times. To the flask was then added dry DMF (5 mL). The contents were heated at 80−90 °C for 18−24 h [on TLC, the products were easily visualized under UV light or iodine, whereas allenylphosphonates were active in iodine but not under UV light]. The reaction mixture was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc, 55/45) to afford the desired product **8**. For the synthesis of compounds **9**−**11**, similar molar quantities of the respective allenes were used. The yields ($^{31}P/^1H$ NMR) using the combinations K_2CO_3/CH_3CN, Et_3N/1,4-dioxane, and Et_3N/CH_3CN were 26, 50, and 55%, respectively.

Compound 8: Yield 0.23 g (70%); mp 88−90 °C; IR (KBr, cm^{-1}) ν 1551, 1483, 1260, 1057, 1005; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01, 1.13 (2s, 6H), 3.88 (dd → t, $J \sim 10.7$ Hz each, 2H), 4.12 (dd → t, $J \sim 10.7$ Hz each, 2H), 5.33 (d, $J = 17.2$ Hz, 1H), 5.59 (br, $J = 11.2$ Hz, $=CH_{cis}H_{trans}$, 1H), 5.64 (d, 1H, $J = 18.2$ Hz, $=CH_{cis}H_{trans}$, 1H), 7.29−7.36 (m, 5H), 7.52 (dd, $J \sim 10.7$, 17.0 Hz, 1H, $CH=CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.6, 32.5 (d, $J = 5.9$ Hz), 75.7 (d, $J = 5.9$ Hz), 113.7 (d, $J = 180.1$ Hz), 125.5, 128.3, 128.5, 128.8, 134.1 (d, $J = 8.8$ Hz), 139.5 (d, $J = 21.6$ Hz), 160.5 (d, $J = 6.0$ Hz); ^{31}P NMR (50 MHz, $CDCl_3$) δ 11.0; LC/MS (R_t 0.82 min) m/z 279 $[M + 1]^+$. X-ray structure was done on this sample.

Compound 9: Yield 73%; mp 130−132 °C; IR (KBr, cm^{-1}) ν 1616, 1555, 1470, 1262, 1059, 1005; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 and 1.15 (2s, 6H), 2.38 (s, 3H), 3.89 (dd → t, $J \sim 10.8$ Hz each, 2H), 4.14 (dd → t, $J \sim 10.8$ Hz each, 2H), 5.38 (d, $J = 17.6$ Hz, 1H), 5.61 (br, $J = 10.4$ Hz, $=CH_{cis}H_{trans}$, 1H), 5.63 (d, $J = 18.4$ Hz, $=CH_{cis}H_{trans}$, 1H), 7.12−7.24 (m, 4H), 7.47 (not resolved, m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 21.7, 32.5 (d, $J = 6.0$ Hz), 75.6 (d, $J = 6.0$ Hz), 113.0 (d, $J = 180.0$ Hz), 125.4, 128.5, 129.0, 134.1 (d, $J = 6$ Hz), 136.6 (d, $J = 22.0$ Hz), 138.9, 160.5 (d, $J = 5.0$ Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.3; LC/MS (R_t 0.74 min) m/z 293 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{21}O_3P$: C, 65.75; H, 7.19. Found: C, 65.81; H, 7.18.

Compound 10: Yield 75%; mp 96−98 °C; IR (KBr, cm^{-1}) ν 1613, 1580, 1466, 1265, 1175, 1061, 1007; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04, 1.15 (2s, 6H), 3.84 (s, 3H), 3.87 (dd → t, $J \sim 10.8$ Hz each, 2H), 4.15 (dd → t, $J \sim 10.8$ Hz each, 2H), 5.40 (d, $J = 17.6$ Hz, 1H), 5.62 (d, $J = 9.2$ Hz, $=CH_{cis}H_{trans}$, 1H), 5.63 (d, $J = 18.4$ Hz, $=CH_{cis}H_{trans}$, 1H), 6.89 and 7.27 (AA′MM′ set, $J \sim 8.4$ Hz, 4H), 7.30 (not resolved, m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.6, 32.5 (d, $J = 6.0$ Hz), 55.3, 75.5 (d, $J = 6.0$ Hz),

(22) Brandsma, L. *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*; Elsevier: Kidlington, Oxford, U.K., 2004; p 243.

(23) (a) Lang, R. W.; Hansen, H. -J. *Organic Synthesis*; Wiley & Sons: New York, 1990; Collect. Vol. 7, p 232. (b) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem.* **2002**, *67*, 2837.

112.4 (d, J = 181.0 Hz), 113.7, 125.3, 129.9, 131.8 (d, J = 22.6 Hz), 134.3 (d, J = 8.3 Hz), 160.1 (d, J = 15.3 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.6; LC/MS (R_t 0.96 min) m/z 309 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{21}O_4P$: C, 62.33; H, 6.86. Found: C, 62.28; H, 6.86.

Compound 11: Yield 60% (purity ~97%) gummy solid; IR (KBr, cm^{-1}) ν 3468, 3345, 3227, 1609, 1514, 1265, 1182, 1059, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01, 1.13 (2s, 6H), 3.87 (dd → t, J ~ 10.2 Hz each, 2H), 4.13 (dd, J ~ 10.2, 13.3 Hz, 2H), 5.44 (d, J = 17.2 Hz, 1H), 5.58 (br, J = 9.2 Hz, =CH_{cis}H$_{trans}$, 1H), 5.59 (d, J = 17.2 Hz, =CH$_{cis}$H$_{trans}$, 1H), 6.64 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.40 (not resolved, m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 21.7, 32.5 (d, J = 6.0 Hz), 75.6 (d, J = 6.0 Hz), 110.7 (d, J = 181.9 Hz), 114.5, 125.0, 128.7, 129.9, 132.0, 132.2, 134.4 (d, J = 9.7 Hz) 147.6, 160.5 (d, J = 7.2 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 13.4; LC/MS (R_t 0.71 min) m/z 294 $[M + 1]^+$.

General Procedure for Preparation of 12−15: A 25 mL round-bottomed flask containing allenylphosphonate **1c** (0.300 g, 1.38 mmol), $Pd(OAc)_2$ (0.015 g, 0.069 mmol), PPh_3 (0.054 g, 0.207 mmol), iodobenzene (0.339 g, 1.66 mmol), and K_2CO_3 (0.381 g, 2.76 mmol) was purged with nitrogen gas several times. To the flask was then added dry DMF (5 mL). The contents were heated at 80−90 °C for 18−24 h. The reaction mixture was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc, 55/45) to afford the desired product **12**. For the preparation of compounds **13−15**, similar molar quantities of the respective allenes were used. Conditions used for optimization are given in Table 1.

Compound 12: Yield 0.31 g (75%); mp 136−138 °C; IR (KBr, cm^{-1}) ν 1586, 1476, 1267, 1061, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82, 1.08 (2s, 6H), 2.04 (s, 3H), 3.60−3.76 (m, 4H), 4.92, 5.36 (2s, 2H), 5.84 (d, J = 16.0 Hz, 1H), 7.26−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.0, 21.7, 32.2 (d, J = 6.2 Hz), 75.9 (d, J = 6.0 Hz), 112.0 (d, J = 183.1 Hz), 123.3, 127.7, 127.9, 128.4 129.0, 137.4 (d, J = 8.0 Hz), 144.0 (d, J = 21.9 Hz), 161.8 (d, J = 5.6 Hz); ^{31}P NMR (80 MHz, $CDCl_3$) δ 11.5; LC/MS (R_t 0.72 min) m/z 293 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{21}O_3P$: C, 65.75; H, 7.19. Found: C, 65.58; H, 7.13. An X-ray structure was performed on this sample.

Compound 13: Yield 76%; mp 158−159 °C; IR (KBr, cm^{-1}) ν 1582, 1462, 1265, 1111, 1057, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82, 1.10 (2s, 6H), 2.03 (s, 3H), 2.36 (s, 3H), 3.62−3.76 (m, 4H), 4.95 (s, 1H), 5.34 (s, 1H), 5.81 (d, J = 16.8 Hz, 1H), 7.15−7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 21.0, 21.4, 21.8, 32.2 (d, J = 7.0 Hz), 75.8 (d, J = 6.0 Hz), 111.5 (d, J = 183.0 Hz), 123.0, 128.4, 128.9, 134.4, 138.3, 144.1 (d, J = 22.0 Hz), 162.3; ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.8. LC/MS (R_t 0.71 min) m/z 307 $[M + 1]^+$. Anal. Calcd for $C_{17}H_{23}O_3P$: C, 66.66; H, 7.52. Found: C, 66.67; H, 7.54.

Compound 14: Yield 77%; mp 128−130 °C; IR (KBr, cm^{-1}) ν 1613, 1580, 1466, 1265, 1175, 1061, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82, 1.10 (2s, 6H), 2.02 (s, 3H), 3.62−3.76 (m, 4H), 3.82 (s, 3H), 4.97 (s, 1H), 5.34 (s, 1H), 5.78 (d, J = 16.6 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.8, 21.0, 21.8, 32.2 (d, J = 7.3 Hz), 55.1, 75.8 (d, J = 5.8 Hz), 111.4 (d, J = 180.7 Hz), 113.2, 122.4, 130.5, 143.5, 144.0, 159.9, 162.0; ^{31}P NMR (160 MHz, $CDCl_3$) δ 13.0. LC/MS (R_t 0.69 min) m/z 323 $[M + 1]^+$. Anal. Calcd for $C_{17}H_{23}O_4P$: C, 63.35; H, 7.14. Found: C, 63.42; H, 7.15.

Compound 15: Yield 70%; mp 158−160 °C; IR (KBr, cm^{-1}) ν 3453, 3360, 3242, 1611, 1574, 1248, 1173, 1057, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82, 1.14 (2s, 6H), 2.01 (s, 3H), 3.63−3.75 (m, 4H), 5.05 (s, 1H), 5.32 (s, 1H), 5.72 (d, J = 16.7 Hz, 1H), 6.66 and 7.16 (2d, J = 7.9 Hz each, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.0, 21.8 (2s, CH_3 and another CH_3, merged with δ 20.9), 32.2 (br), 75.8 (d, J = 5.8 Hz), 110.3 (d, J = 181.8 Hz), 114.2, 121.8, 130.5, 144.9 (d, J = 22.3 Hz), 147.1, 162.4; ^{31}P NMR (80 MHz, $CDCl_3$) δ 12.4; LC/MS (R_t 0.70 min): 308 $[M]^+$. Anal. Calcd for $C_{16}H_{22}NO_3P$: C, 62.54; H, 7.16; N, 4.56. Found: C, 62.59; H, 7.17; N, 4.52.

Compound 16: This compound was prepared by reacting **1b** (0.30 g, 1.48 mmol) with an excess (3 molar equiv) of iodobenzene by using a procedure similar to that for **8**: Yield quantitative; mp 126−128 °C; IR (KBr, cm^{-1}) ν 1615, 1560, 1491, 1343, 1310, 1242, 1059, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05, 1.16 (2s, 6H), 3.92 (dd → t, J ~ 10.8 Hz each, 2H), 4.18 (dd → t, J ~ 12.2 Hz each, 2H), 5.62 (d, J = 17.8 Hz, 1H), 6.60 (d, J = 16.0 Hz, 1H), 7.26−7.47 (m, 10H), 8.02 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.7, 32.6 (d, J = 5.9 Hz), 75.7 (d, J = 5.9 Hz), 112.8 (d, J = 180.5 Hz), 126.0, 126.1, 127.6, 128.4, 128.6, 128.7, 128.8, 129.0, 136.1, 139.7, 140.1, 140.3, 160.7 (d, J = 6.1 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 11.6. X-ray structure was determined for this compound.

Preparation of 17: A 25 mL round-bottomed flask containing allenylphosphonate **1c** (0.45 g, 2.08 mmol), $Pd(OAc)_2$ (0.023 g, 0.104 mmol), PPh_3 (0.082 g, 0.312 mmol), 2-nitroiodobenzene (0.662 g, 2.49 mmol), and K_2CO_3 (0.575 g, 4.16 mmol) was purged with nitrogen gas several times. Dry acetonitrile (10 mL) was then added, and the contents were heated under reflux for 48 h. TLC [R_f = 0.19 (hexane/EtOAc, 50/50)] and ^{31}P NMR showed only 10% product formation. More $Pd(OAc)_2$ (0.022 g, 0.09 mmol) was added, and the reaction continued for 48 h more. Then the reaction mixture was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc, 50/50) to afford product **17**: Yield 0.47 g (50%) (remaining was unreacted allene); mp 190−192 °C; IR (KBr, cm^{-1}) ν 1520, 1474, 1343, 1263, 1059, 1006, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89, 1.06 (2s, 6H), 2.06 (s, 3H), 3.67−3.99 (m, 4H), 6.12 (d, J = 15.3 Hz, 1H), 6.37 (s, 1H), 7.26 (d, J = 6.0 Hz, 1H), 7.43 (t, J = 7.3 Hz, 1H), 7.60−7.65 (m, 3H), 7.74 (t, J = 7.3 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.0, 21.1, 21.6, 32.4 (d, J = 6.6 Hz), 75.8 (br), 112.9 (d, J = 185.6 Hz), 124.9, 128.6, 130.0, 131.5, 131.8, 132.7, 133.2, 133.7, 137.5, 147.5 (d, J = 15.7 Hz), 159.7; ^{31}P NMR (160 MHz, $CDCl_3$) δ 11.0. Anal. Calcd for $C_{22}H_{23}O_7N_2P$: C, 57.64; H, 5.05; N, 6.11. Found: C, 57.78; H, 5.05; N, 6.11. X-ray structure was determined for this compound.

Preparation of 18: A 25 mL round-bottomed flask containing allene **2b** (0.279 g, 1.94 mmol), $Pd(OAc)_2$ (0.021 g, 0.09 mmol), PPh_3 (0.074 g, 0.29 mmol), iodobenzene (0.475 g, 2.33 mmol), and K_2CO_3 (0.525 g, 3.88 mmol) was purged with nitrogen gas several times. Dry acetonitrile (4 mL) was then added. The contents were refluxed for 12 h. The reaction mixture was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane) to afford the desired product **18**. It was finally purified (~95% purity) by vacuum distillation (oil bath temperature ~80 °C/0.5 mm): Yield 0.298 g (70%); IR (neat, cm^{-1}) ν 1672, 1602, 1491, 1445, 1367, 1074, 897, 756, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (s, 3H), 4.72 (s, 1H), 5.14 (s, 1H), 6.74 (s, 1H), 6.90−7.37 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 117.5, 126.6, 127.0, 127.1, 127.9, 128.5, 129.6, 130.0, 137.2, 139.9, 143.6, 145.4 [lit[16]: ^{1}H NMR ($CDC1_3$) δ 2.16 (s, 3H), 4.80 (s, 1H), 5.21 (s, 1H), 6.87 (s, 1H), 6.90−7.20 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 21.08, 117.44, 126.57, 126.99, 127.09, 127.83, 128.24, 128.47, 129.01, 129.52, 129.96, 131.61]; GC-MS (R_t 4.09 min; column temperature 200 °C) m/z 220 $[M]^+$.

Preparation of 19: This compound was prepared by using a procedure similar to that for **18** by the use of **2d** (0.108 g, 0.77 mmol). The compound was purified by column chromatography (hexane) to afford **19**: Yield 0.132 g (80%) (oil); IR (KBr, cm^{-1}) ν 1726, 1711, 1597, 1445, 1370, 1262, 1161, 1038; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 7.1 Hz, 3H), 2.06 (s, 3H), 4.00 (q, J = 7.1 Hz, 2H), 4.87 (s, 1H), 5.36 (s, 1H), 6.08 (s, 1H), 7.11−7.37 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 20.6, 59.9, 117.2,

123.3, 127.4, 127.6, 128.6, 138.5, 144.0, 156.3, 166.4; LC/MS (R_t 0.69 min) m/z 217 $[M + 1]^+$. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.87; H, 7.48. Assignment of stereochemistry is tentative but based on the available X-ray structure of **12**. The same compound was obtained by using either K_2CO_3 or Ag_2CO_3 (^{1}H NMR evidence).

Preparation of 20: A 25 mL round-bottomed flask containing **1c** (0.10 g, 0.46 mmol), $Pd(OAc)_2$ (0.005 g, 0.023 mmol), PPh_3 (0.018 g, 0.069 mmol), iodobenzene (0.113 g, 0.55 mmol), and Ag_2CO_3 (0.255 g, 0.92 mmol) was purged with nitrogen gas several times. Dry acetonitrile (4 mL) was then added. The contents were heated under reflux for 18 h. The reaction mixture was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc, 50/50) to afford the desired product **20**: Yield quantitative; mp 120−122 °C; IR (KBr, cm^{-1}) ν 1954, 1491, 1368, 1262, 1057, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87, 1.29 (2s, 6H), 1.92 (d, J = 6.36 Hz, 6H), 3.95 (d, J = 12.0 Hz, 4H), 7.25−7.57 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.7, 19.8, 20.9, 22.0, 32.5 (d, J = 6.8 Hz), 77.0 (d, J = 6.2 Hz), 93.6 (d, J = 180.0 Hz), 99.9 (d, J = 15.6 Hz), 127.6, 127.7, 128.6, 132.6 (d, J = 10.5 Hz), 208.7; ^{31}P NMR (80 MHz, $CDCl_3$) δ 8.1; GC-MS (R_t 4.72 min; column temperature 240 °C) m/z 292 $[M]^+$. Anal. Calcd for $C_{16}H_{21}O_3P$: C, 65.74; H, 7.24. Found: C, 65.76; H, 7.29.

A similar reaction with **2b** gave **18** (see above) and an additional product that could not be satisfactorily characterized.

Preparation of 21 and 22: A 25 mL round-bottomed flask was charged with $Pd(OAc)_2$ (0.006 g, 0.026 mmol), allenylphosphonate **1a** (0.10 g, 0.53 mmol), cesium fluoride (0.16 g, 1.06 mmol), phenylboronic acid (0.08 g, 0.63 mmol) or iodobenzene (0.13 g, 0.63 mmol), and dry DMF (5 mL). Then the system was evacuated for 0.5 h and purged with dry nitrogen. This mixture was heated at 90 °C for 18−24 h, quenched with water, extracted with ether (3 × 10 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by column chromatography (hexane/EtOAc, 60/40) to afford the addition products **21** and **22**. Total isolated yield was 0.113 g (80% using boronic acid). The yields obtained under different conditions are given in Table 2.

Compound 21: Yield 0.096 g (68%); mp 140−142 °C; IR (KBr, cm^{-1}) ν 1605, 1472, 1256, 1055, 999; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06, 1.16 (2s, 6H), 2.56 (d, J = 3.0 Hz, 3H), 3.90 (dd → t, J ∼ 11.8 Hz each, 2H), 4.18 (dd → t, J ∼ 11.8 Hz each, 2H), 5.95 (d, J = 18.5 Hz, 1H), 7.39−7.50 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8 (d, J = 7.2 Hz), 21.3, 21.6, 32.5 (d, J = 6.0 Hz), 75.6, 111.3 (d, J = 185.4 Hz), 126.0, 128.6, 129.5, 141.5 (d, J = 23.3 Hz), 160.1 (d, J = 7.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 14.1. X-ray structure was determined for this sample.

Compound 22: Yield 0.017 g (12%); mp 82−84 °C; IR (KBr, cm^{-1}) ν 1622, 1476, 1262, 1057, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97, 1.02 (2s, 6H), 3.20 (d, J = 23.2 Hz, 2H), 3.70 (dd → t, J ∼ 10.9 Hz each, 2H), 4.17 (dd → t, J ∼ 8.2 Hz each, 2H), 5.41 (d, J = 5.4 Hz, 1H) and 5.59 (d, J = 5.4 Hz, 1H), 7.28−7.50 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 21.6, 31.9 (d, J = 134.6 Hz, CH_2), 32.5, 75.0 (d, J = 6.0 Hz), 117.5 (d, J = 10.9 Hz), 126.2, 127.9, 128.4, 138.5; ^{31}P NMR (80 MHz, $CDCl_3$) δ 21.9; LC/MS (R_t 0.71 min) m/z 267 $[M + 1]^+$. Anal. Calcd for $C_{14}H_{19}O_3P$: C, 63.15; H, 7.14. Found: C, 63.11; H, 7.19.

Preparation of 23: A mixture of **1a** (0.300 g, 1.6 mmol), 2-iodophenol (0.42 g, 1.9 mmol), $Pd(OAc)_2$ (0.028 g, 0.08 mmol), and CsF (0.486 g, 3.2 mmol) in a 25 mL round-bottomed flask was evacuated under vacuum for 0.5 h. The mixture was heated for 18−24 h at 90 °C in dry DMF (7 mL) under nitrogen atmosphere, then quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue [^{31}P NMR: δ 22.3 (20%), 17.5 (45%), 14.5 (5%, β-ketophosphonate $(OCH_2CMe_2CH_2O)P(O)CH_2C(O)CH_3$), 12.4 (30%)] was purified by column chromatography (hexane/EtOAc, 60/40) to obtain a solid (0.205 g; 46% isolated yield). This was crystallized to obtain fractions **I** and **II**. The yield of the products was affected significantly by the quality of DMF used in the reaction.

Fraction I (major component **23** ∼90%; minor component (unassigned) ∼10%; see ^{1}H NMR): Yield 0.205 g (46% isolated yield); mp 128−130 °C; IR (KBr, cm^{-1}) ν 1605, 1455, 1265, 1055, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91, 1.03 (2s, 6H), 3.50 (d, J = 23.0 Hz, 2H), 3.60 (dd, 2H), 4.12 (dd, 2H), 6.69 (d, J ∼ 3.8 Hz), 7.20−7.53 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 21.6, 26.4 (d, J = 139.5 Hz), 32.6 (d, J = 6.0 Hz), 75.9 (d, J = 6.0 Hz), 105.8, 111.0, 111.8, 120.8, 122.9, 124.1, 124.6; ^{31}P NMR (80 MHz, $CDCl_3$) δ 17.5; LC/MS (R_t 0.70 min) m/z 281 $[M + 1]^+$. The minor component showed peaks at δ 0.85, 0.93, 3.30 (J ∼ 21.0 Hz), 3.55−3.65 (m), 4.10−4.30 (m), and 7.10−7.70 (m) in the ^{1}H NMR and at δ 22.3 in the ^{31}P NMR. An X-ray structure was performed on the major component in fraction **I**. **Fraction II:** This was a crystalline sample probably containing **23** and another compound (likely to be a co-crystal). Repeated checking by ^{31}P NMR showed peaks at δ 22.3 and 17.5 in the ratio 1:1 (^{1}H NMR showed two PCH_2 groups in a 1:1 ratio). Although we collected the X-ray data on this crystal also, the structure could not be solved satisfactorily. LC/MS (R_t 0.72 min) m/z 281 $[M + 1]^+$.

Preparation of 24 and 25: A mixture of **1b** (0.50 g, 2.47 mmol), 2-iodophenol (0.65 g, 2.97 mmol), $Pd(OAc)_2$ (0.027 g, 0.12 mmol), PPh_3 (0.097 g, 0.37 mmol), and K_2CO_3 (0.68 g, 4.94 mmol) was taken in a 25 mL round-bottomed flask and evacuated under vacuum for 0.5 h. The mixture was heated in dry acetonitrile (10 mL) under reflux for 24 h in nitrogen atmosphere. The mixture was then quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by column chromatography (hexane/EtOAc, 60/40) to obtain **24** followed by **25**.

Compound 24: Yield 0.334 g (46%); mp 148−150 °C; IR (KBr, cm^{-1}) ν 1630, 1456, 1271, 1202, 1057, 1005, 918; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72, 0.88 (2s, 6H), 2.44 (d, J = 4.4 Hz, 3H), 3.25 (d, J = 20.8 Hz, 2H), 3.60 (dd, J ∼ 5.0, 11.2 Hz, 2H), 4.12 (dd, J ∼ 5.0, 11.2 Hz, 2H), 7.20−7.50 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.1, 20.1, 21.3, 21.5 (d, J = 141.9 Hz), 32.4 (d, J = 6.0 Hz), 75.0 (d, J = 6.0 Hz), 104.9 (d, J = 12.1 Hz), 110.6, 119.1, 122.5, 123.6, 129.0, 152.8, 153.8, 203.8; ^{31}P NMR (80 MHz, $CDCl_3$) δ 22.2; GC-MS (R_t 4.5 min, column temperature 250 °C) m/z 294 $[M]^+$. Anal. Calcd for $C_{15}H_{19}O_4P$: C, 61.22; H, 6.51. Found: C, 61.21; H, 6.51. X-ray structure was done on this sample.

Compound 25: Yield 0.145 g (20%); mp 112−114 °C; IR (KBr, cm^{-1}) ν 1574, 1456, 1279, 1262, 1063, 1007; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09, 1.18 (2s, 6H), 1.37 (t, J = 7.8 Hz, 3H), 3.09 (q, J = 1.9 Hz, 2H), 3.89 (dd → t, J ∼ 11.7 Hz each, 2H), 4.28 (dd → t, J ∼ 11.7 Hz each, 2H), 7.26−7.77 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.6, 21.8, 32.6 (d, J = 5.6 Hz), 75.6 (d, J = 6.0 Hz), 100.6 (d, J ∼ 205.0 Hz), 111.1, 120.9, 123.8, 124.6, 127.5 (d, J = 12.0 Hz), 154.2 (d, J = 15.0 Hz), 169.0 (d, J = 29.0 Hz); ^{31}P NMR (80 MHz, $CDCl_3$) δ 10.9; GC-MS (R_t 4.4 min, column temperature 250 °C) m/z 294 $[M]^+$. Anal. Calcd for $C_{15}H_{19}O_4P$: C, 61.22; H, 6.51. Found: C, 61.22; H, 6.54. X-ray structure was determined for this compound.

Preparation of 26: Compound **26** was prepared by using **1c** following a procedure analogous to that for **24/25** using similar molar quantities: Yield 74%; mp 148−150 °C; IR (KBr, cm^{-1}) ν 1611, 1466, 1262, 1140, 1061, 1005, 951; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03, 1.22 (2s, 6H), 1.55, 1.61 (2s, 6H), 3.87 (dd → t, 2H), 4.12 (dd, 2H), 5.31 (d, J = 13.6 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.97 and 7.37 (t each, J = 3.0 Hz, 2H), 8.39 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.6, 28.0, 28.1, 32.6 (d, J = 6.0 Hz), 76.0 (d, J = 6.0 Hz), 90.0 (d, J = 22.5 Hz), 98.0 (d, J = 192.2 Hz), 111.1, 121.2 (J = 6.1 Hz), 127.9, 134.0, 163.4, 166.9 (J = 5.0 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.8; LC/MS (R_t 0.74 min) m/z 309 $[M + 1]^+$; Anal. Calcd for $C_{16}H_{21}O_4P$: C, 62.33; H, 6.87. Found: C, 62.42; H, 6.86. X-ray structure was determined for this compound.

Preparation of 27: A mixture of **2a** (0.500 g, 4.3 mmol), 2-iodophenol (1.13 g, 5.2 mmol), $Pd(OAc)_2$ (0.048 g, 0.215 mmol), and CsF (1.306 g, 8.6 mmol) in a 25 mL round-bottomed flask was evacuated under vacuum for 0.5 h. It was heated for 12 h at 90 °C in dry DMF (7 mL) under nitrogen atmosphere, then quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by column chromatography (hexane) to obtain **27** as colorless oil. Yield 0.448 g (50%). This is a known compound; the ^{1}H and ^{13}C NMR spectra are similar to those reported in the literature, but there is a shift of ca. 0.09 ppm of the methyl signals in the ^{1}H NMR:[17e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.35−7.95 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.57, 111.1, 111.4, 119.4, 122.5, 124.5, 126.8, 127.3, 127.9, 128.7, 128.9, 131.3, 131.6, 150.8, 153.9 [lit.[17e] ^{1}H NMR ($CDC1_3$) δ 2.48 (s, 3H), 7.15−8.45 (m, 9H); ^{13}C NMR δ 9.2 (CH_3), 150.7, 153.9].

Preparation of 29: A mixture of **2b** (0.20 g, 1.40 mmol), 2-iodophenol (0.365 g, 1.60 mmol), $Pd(OAc)_2$ (0.016 g, 0.07 mmol), PPh_3 (0.055 g, 0.21 mmol), and K_2CO_3 (0.387 g, 2.80 mmol) in a 25 mL round-bottomed flask was evacuated under vacuum for 0.5 h. This mixture was heated under reflux in dry acetonitrile (4 mL) for 16 h under nitrogen atmosphere. Then it was quenched with water, extracted with ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was purified by column chromatography (hexane) to obtain **29**: Yield 0.228 g (70%); mp 54−56 °C; IR (KBr, cm^{-1}) ν 1458, 1362, 1271, 1125, 1092, 1024, 930; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 6H), 6.31 (s, 1H), 6.66 (br, 1H), 6.83 (d, J = 8.0 Hz, 1H), 7.17−7.44 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.9, 89.1, 110.8, 118.8, 119.9, 124.3, 127.3, 128.6, 128.7, 130.7, 137.3, 145.9, 161.6. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.48; H, 6.81. X-ray structure was also determined for this compound.

Reaction of 2-Iodophenol with 2c: Synthesis of 30 and 31: Compounds **30** and **31** were prepared by using a procedure similar to that for **27** using **2c** (0.100 g, 0.90 mmol). The mixture was subjected to column chromatography (hexane) to obtain compounds **30** and **31** with a total yield of 55%.

Compound 30 (R_f = 0.48; hexane/EtOAc, 95/5). It was eluted along with hexane and could be obtained only in a purity of ∼95%: Yield (after chromatography) 0.045 g (25%) (oil); IR (KBr, cm^{-1}) ν 1713, 1599, 1454, 1236, 1179, 1085; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (t, J ∼ 7.0 Hz, 3H), 2.80 (s, 3H), 4.44 (q, J ∼ 7.0 Hz, 2H), 7.28−8.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 29.7, 60.3, 110.7, 121.7, 123.7, 124.3, 126.3, 153.6, 163.6, 164.5; LC/MS (R_t 0.72 min) m/z 205 $[M + 1]^+$.

Compound 31: (R_f = 0.42; hexane/EtOAc, 95/5): Yield (after chromatography) 0.055 g (30%) (oil); IR (KBr, cm^{-1}) ν 1740, 1607, 1454, 1370, 1252, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J ∼ 7.0 Hz, 3H), 3.85 (s, 2H), 4.24 (q, J ∼ 7.0 Hz, 2H), 6.66 (s, 1H), 7.22−7.55 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 34.8, 61.4, 105.0, 111.1, 120.7, 122.7, 123.9, 129.0 164.0 (weak); LC/MS (R_t 0.73 min) m/z 205 $[M + 1]^+$. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.55; H, 5.94.

Preparation of 32: A procedure similar to that for **23** was followed by using **1a** (0.300 g, 1.60 mmol) and 2-iodobenzoic acid (0.470 g, 1.92 mmol): Yield 0.320 g (65%); mp 184−186 °C; IR (KBr, cm^{-1}) ν 2969, 1717, 1603, 1487, 1273, 1055, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89, 0.96 (2s, 6H), 3.19 (d, J = 20.8 Hz, 2H), 3.67−4.27 (br m, 4H), 7.27−7.82 (m, 4H), 8.34 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.2, 21.6, 24.3 (d, J= 140.7 Hz), 32.6 (d, J = 4.8 Hz), 75.1 (d, J = 6.0 Hz), 108.5 (d, J = 9.7 Hz), 121.5, 123.6, 128.8, 130.2, 134.8, 135.9, 143.9 (d, J = 10.9 Hz), 161.7; ^{31}P NMR (80 MHz, $CDCl_3$) δ 21.0; LC/MS (R_t 0.74 min) m/z 309 $[M + 1]^+$. Anal. Calcd for $C_{15}H_{17}O_5P$: C, 58.44; H, 5.51. Found: C, 58.49; H, 5.50. X-ray structure was determined for this compound.

Preparation of 33 and 34: To a solution of allenylphosphonate **1b** (0.10 g, 0.495 mmol), $Pd(OAc)_2$ (0.006 g, 0.024 mmol), PPh_3 (0.019 g, 0.074 mmol), and 2-iodobenzoic acid (0.147 g, 0.593 mmol) in dry acetonitrile (5 mL) was added K_2CO_3 (0.136 g, 0.99 mmol) under nitrogen atmosphere. The mixture was heated under reflux for 16−18 h, quenched with water, extracted with ether, dried (Na_2SO_4), filtered, and concentrated under vacuum. Compound **33** was isolated through column chromatography (hexane/EtOAc, 60/40): Yield 0.11 g (70%); low melting solid; IR (KBr, cm^{-1}) ν 2973, 1721, 1620, 1597, 1476, 1375, 1273, 1119, 1096, 1057, 1009; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08, 1.11 (2s, 6H), 1.52 (d, J = 6.8 Hz, 3H), 3.86−4.20 (m, 5H), 6.22 (d, J = 13.6 Hz, 1H), 7.30−7.65 (m, 3H), 8.15 (d, J = 6.84 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5 (two CH_3 carbon signals have merged), 22.2, 32.6, 75.3 (d, J = 7.3 Hz), 75.9, 111.4 (d, J = 187.9 Hz), 124.3, 124.7, 128.4, 128.6, 130.4, 131.5, 132.0, 132.2, 134.3, 153.7 (br), 162.8; ^{31}P NMR (80 MHz, $CDCl_3$) δ 8.0. LC/MS (R_t 0.72 min) m/z 323 $[M + 1]^+$.

Compound 34: This compound was prepared by starting with **1c** using a procedure similar to that for **33**: Yield 0.095 g (61%); mp 146−148 °C; IR (KBr, cm^{-1}) ν 2969, 1723, 1593, 1481, 1302, 1262, 1117, 1061, 1013; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07, 1.15 (2s, 6H), 1.88 (s, 6H), 3.91−4.23 (br m, 4H), 6.30 (d, J = 8.3 Hz, 1H), 7.59−7.69 (br m, 3H), 8.18 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.4, 21.5, 28.1, 32.6 (d, J = 6.0 Hz), 75.8 (d, J = 6.0 Hz), 84.4 (br), 112.9 (d, J = 189.9 Hz), 124.4, 125.3, 130.0, 131.0, 134.3, 164.2; ^{31}P NMR (80 MHz, $CDCl_3$) δ 9.0; LC/MS (R_t 0.69 min) m/z 337 $[M + 1]^+$. Anal. Calcd for $C_{17}H_{21}O_5P$: C, 60.71; H, 6.29. Found: C, 60.70; H, 6.28. Another isomer as a minor product (<10%) was also seen (^{1}H NMR) but could not be isolated. X-ray structure was determined for **34**.

Preparation of 35: To a solution of **2a** (0.18 g, 1.55 mmol), $Pd(OAc)_2$ (0.017 g, 0.078 mmol), PPh_3 (0.06 g, 0.232 mmol), and 2-iodobenzoic acid (0.462 g, 1.86 mmol) in dry acetonitrile (5 mL) was added K_2CO_3 (0.428 g, 3.10 mmol) under nitrogen atmosphere. The mixture was heated under reflux for 16−18 h, quenched with water, extracted with ether, dried (Na_2SO_4), filtered, and concentrated under vacuum. Compound **35** was isolated as the major product using column chromatography (hexane/EtOAc): Yield 0.256 g (70%); mp 122−124 °C; IR (KBr, cm^{-1}) ν 1719, 1597, 1458, 1263, 1231, 1117, 1090, 995; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 2H), 7.23−7.67 (m, 9H), 8.16 (d, J = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 67.0, 123.5, 128.3, 128.6, 128.8, 129.2, 129.8, 130.3, 134.0, 135.1, 138.3, 164.2; GC-MS (R_t 5.2 min, column temperature 250 °C) m/z 236 $[M]^+$. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.11. Found: C, 81.34; H, 5.14. A GC of the reaction mixture showed the yield of **35** to be ∼75%. X-ray structure was determined for this sample.

Compound 36: This was prepared in a manner similar to **35** by using **2b**:Yield 0.263 g (80%); mp 110−112 °C; IR (KBr, cm^{-1}) ν 2978, 1709, 1601, 1460, 1300, 1252, 1107, 1038, 937; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 6H), 6.89 (s, 1H), 7.13−7.26 (m, 8H), 8.07 (d, J = 7.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.1, 84.1, 125.9, 127.8, 127.9, 128.6, 128.9, 129.2, 129.7, 132.6, 136.0, 164.9; LC/MS (R_t 0.77 min) m/z 265 $[M + 1]^+$.

Reaction of 2-Iodobenzoic acid with 2c—Synthesis of 37: Compound **37** was prepared following a procedure analogous to that for **32** using **2c** (0.100 g, 0.90 mmol), but the reaction was complete in 12 h: Yield 0.178 g (86%); mp 82−84 °C; IR (KBr, cm^{-1}) ν 1721, 1647, 1603, 1487, 1296, 1152, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 3H), 3.57 (s, 2H), 4.20 (q, J = 7.1 Hz, 2H), 7.28 (s, 1H, merged with $CDCl_3$ peak), 7.50−7.59 (m, 2H), 7.80 (t, J = 7.5 Hz, 1H), 8.37 (d, J = 7.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 33.6, 61.4, 111.2, 121.6, 123.0, 128.7, 130.3, 134.8, 136.4, 143.7, 170.3. X-ray structure was determined for this compound.

Reaction of 2-Iodobenzoic acid with 2d—Isolation of Isomeric Compounds 38a and 38b: Compounds **38a**,**b** were prepared by using **2d** following a procedure analogous to that for **34** using similar molar quantities; the reaction was complete in 12 h. It gave isomeric products in the ratio ∼3:2. We have isolated both; the assignment of stereochemistry is tentative, but the major isomer is

assigned *Z* configuration based on the structure of **34**. **Major Isomer (38a):** Yield 0.089 g (48%) (oil); IR (KBr, cm^{-1}) ν 1721, 1642, 1603, 1460, 1302, 1260, 1202, 1109, 1038; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, $J \sim 7.0$ Hz, 3H), 1.58 (s, 6H), 4.20 (q, $J \sim 7.0$ Hz, 2H), 6.17 (s, 1H), 7.53−7.60 (m, 3H), 8.09−8.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 27.0, 61.1, 83.1, 117.7, 125.2, 128.7, 129.6, 130.4, 132.9, 133.8, 147.1, 163.8, 166.3; LC/MS (R_t 0.74 min) *m*/*z* 261 $[M + 1]^+$. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 69.32; H, 6.16. **Minor Isomer (38b):** Yield 0.060 g (32%) (oil); IR (KBr, cm^{-1}) ν 1725, 1636, 1599, 1460, 1302, 1263, 1194, 1090, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, $J = 6.8$ Hz, 3H), 1.74 (s, 6H), 4.30 (q, $J = 6.8$ Hz, 2H), 6.46 (s, 1H), 7.55−8.19 (d, $J = 7.6$ Hz, 1H), 7.62−7.66 (m, 2H), 8.17 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 27.6, 61.4, 83.7, 118.3, 124.1, 124.9, 129.9, 130.2, 134.3, 136.0, 143.0, 163.5, 166.9; LC/MS (R_t 0.74 min) *m*/*z* 261 $[M + 1]^+$.

Synthesis of 39 Using the HWE Reaction of 32 with 4-Methoxybenzaldehyde: The phosphonate **32** (0.10 g, 0.33 mmol) was dissolved in dry THF (5 mL) and slowly added to a suspension of NaH (0.016 g, 0.65 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred at this temperature for 0.5 h. Then, 4-methoxybenzaldehyde (0.053 g, 0.39 mmol) in THF (10 mL) was added and the mixture heated under reflux for 48 h. Water (20 mL) was added, and the aqueous layer was thoroughly extracted with ether (3 × 20 mL). The organic layer was collected, dried (Na_2SO_4), filtered, and the solvent removed from the filtrate to give a residue that was purified by column chromatography to obtain **39** as yellow−green solid: Yield 0.05 g (50%); mp 138−140 °C; IR (KBr, cm^{-1}) ν 1732, 1601, 1510, 1269, 1061, 1022; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.41 (s, 1H), 6.57 (d, $J = 15.9$ Hz, 1H), 6.91 (d, $J = 8.7$ Hz, 2H), 7.38−7.49 (m, 4H), 7.64−7.71 (m, 2H), 8.28 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 104.9, 113.7, 114.3, 117.3, 125.6, 127.8, 128.6, 129.8, 132.6, 134.8, 153.0, 160.3 (the assignment of *trans*-butadiene structure as shown is tentative); LC/MS (R_t 0.69 min) *m*/*z* 279 $[M + 1]^+$. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.84; H, 5.08.

X-ray Crystallography: Single-crystal X-ray data were collected on an Enraf-Nonius MACH3 or on a Bruker AXS-SMART diffractometer using Mo Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined by full-matrix least-squares method using standard procedures.[24] Absorption corrections were done using SADABS program, where applicable. In general, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry or located by a difference Fourier map and refined isotropically. Details of the crystallographic data are available as Supporting Information.

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Supporting Information Available: PLATON drawings, ^{1}H and ^{13}C NMR spectra, crystal data and CIF files of **8**, **12**, **16**, **17**, **21**, **23**−**26**, **29**, **32**, **34**, **35**, and **37**. This material is available free of charge via the Internet at http://pubs.acs.org.

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