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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=CR₂ [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/PPh₃/K₂CO₃ 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 K₂CO₃ affords the butadiene (Z)- $(OCH_2CMe_2CH_2O)P(O)CH=C(Ph)-C(Me)=CH_2$ (12); in contrast, the use of Ag₂CO₃ leads to the allene (OCH₂CMe₂CH₂O)P(O)C(Ph)=C=CMe₂ (**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)-(OCH₂CMe₂CH₂O)P(O)CH=C(Me)Ph (21) and (OCH₂CMe₂CH₂O)P(O)CH₂-C(Ph)=CH₂ (22) and is thus a net 1,2-addition of Ph-H. Compound 1b reacts with iodophenol in the presence of Pd(OAc)₂/PPh₃/K₂CO₃ 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=CH₂, 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

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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=CR₂ [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 K₂CO₃ and Ag₂CO₃ 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 (OCH₂CMe₂CH₂O)P(O)C \equiv 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/PPh₃ in the presence of K₂CO₃ (or Et₃N) in DMF or acetonitrile led to the isomeric acetylene 7 as the predominant product.^{9,11} Under the same conditions, the trisubstituted 1,3trans-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/Ph₃P/K₂CO₃/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.



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)

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	K2CO3, CH3CN	80^d
11	Pd(OAc) ₂ /PPh ₃	K ₂ CO ₃ , DMF	80
12	Pd(OAc) ₂ /PPh ₃	K ₂ CO ₃ , NMA	40
13	Pd(OAc) ₂	K ₂ CO 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 ¹H/³¹P NMR. ^{*c*} TDMPP = Tris(2,6-dimethoxyphenyl)phosphine. ^{*d*} Isolated yield: 75%.

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.



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)=CH₂ (**18**, 70%) whose ¹H 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/PPh₃/K₂CO₃ 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

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⁽¹¹⁾ Compound **1a** (and likely **1b**) leads to the β -ketophosphonate (³¹P NMR: δ 13.8) very readily in the presence of K₂CO₃, most likely by adventitious moisture. In reactions using **1b**,c, there was a minor product (5–10%; ¹H NMR: δ 2.86 (PCH₂, J = 27.0 Hz; ³¹P NMR: δ 22–23), but it was not isolated. In some cases, there was unreacted allene (~5%).

⁽¹²⁾ In the case of **1c**, CH₃CN also worked well, but for **1b**, this solvent gave poor results. This is probably due to the formation of (OCH₂CM₂-CH₂O)P(O)CH₂C \equiv 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.

⁽¹⁵⁾ The ¹H NMR spectrum of the reaction mixture suggests that a product (ca. 10%) containing a PCH₂ group [δ 2.99, J = 20.8 Hz] is present, but this compound could not be isolated.

conditions, and we have not been successful in isolating a welldefined 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.



(b) Use of K₂CO₃ versus Ag₂CO₃-A Remarkable Salt Effect: While the use of Ag₂CO₃ as a base in the reaction of **1c** [³¹P NMR: δ 8.8] with iodobenzene leads to the α -substituted product **20** [³¹P 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 ($\geq 80\%$) using longer reaction times (24 h). It has been noted recently by Fu and Ma that a combination of Ag₂CO₃ (5 mol %) and K₂CO₃ (2 equiv) drives the reaction of 1,2-allenyl sulfones with PhI to α -substituted products;²¹ 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 K₂CO₃ or Ag₂CO₃ was used. The rationale for the observed dramatic difference between Ag₂CO₃ and K₂CO₃ in the case of 1c needs more detailed scrutiny.¹⁷



FIGURE 1. ³¹P 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 CH₃CN with (a) K₂CO₃ (2 equiv) and (b) Ag₂CO₃ (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 21 and 22 *even without adding acetic*



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)	Х	conditions	yield (%) ^a	21 (<i>E</i>)/ 22
1	Pd(OAc) ₂	B(OH) ₂	CsF (2.0 mmol)/ DMF (4 mL)/	87	85/15
2	Pd(OAc) ₂	Ι	90°C/24 h CsF (2.0 mmol)/ DMF (4 mL)/	44	70/30 ^b
3	$Pd(PPh_3)_4$	B(OH) ₂	90 °C/24 h AcOH (10 mol %)/ 1,4-dioxane (4 mL)/	100	93/7
4	Pd(PPh ₃) ₄	Ι	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 ¹H/³¹P NMR. ^{*b*} There was an additional peak at δ 11.0 in the ³¹P NMR spectrum, but the corresponding compound could not be isolated.

acid and by using Pd(II) acetate/CsF in the absence of Ph₃P. 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(PPh₃)₄/ArB(OH)₂ in the presence of acetic acid led to the *E* isomer of EtO₂CCH=C(Me)Ar.^{2f} Soon after the submission of our paper, addition of arylboronic acids to phosphorylated allenes using Pd(PPh₃)₄/acetic acid has been reported.^{3h} Thus, using H₂C=C=C(*n*-Bu)P(O)(OEt)₂ and PhPB(OH)₂/ HOAc in THF, the authors have been able to obtain the vinylphosphonate (H₃C)(Ph)C=C(*n*-Bu)P(O)(OEt)₂ in 81% yield. In our reactions (cf. Scheme 3), DMF was found to be a good solvent.

(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 Ph₃P. It gives mainly two compounds [ca 7:3 ratio; ³¹P 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

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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 OCH₂ multiplets in addition to the one due to the starting material were seen in the ¹H 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.



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 PCH₂ 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 CH₃ group as HI, along with PdL₂ in forming the products 8-15 from 40/40'. It can be noted that, with a different orientation of the R and CH₃ 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 =CH₂ group. Formation of α -phenylated allenylphosphonate 20 probably occurs through the complex 41 (cf. Scheme 8). Subsequent proton elimination occurs from the PCH 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 CH₃ 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 PPh₃ to generate a Pd-(0) species, and hence the oxidation state of palladium is not





shown. A similar addition to the allenes RR'C=C=CH₂ leading to RR'C=C(Ph)(CH₃) was reported recently, using ArB(OH)₂/ acetic acid in the presence of Pd(PPh₃)₄ or Pd(OAc)₂/PPh₃.^{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 Et₃N or even Ph₃P, and (b) competitive hydrolysis of **1a** to give the β -ketophosphonate (OCH₂CMe₂CH₂O)P(O)-CH₂C(O)CH₃.¹⁰

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 Ph₃P 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/ Ph₃P/K₂CO₃ 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 (K₂CO₃ or Ag₂CO₃) 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 PCH₂ 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 Ph₃P as mentioned above. General experimental conditions are given in the Supporting Information.

General Procedure for Preparation of 8-11: A 25 mL roundbottomed flask containing allenylphosphonate 1b (0.30 g, 1.48 mmol), Pd(OAc)₂ (0.017 g, 0.074 mmol), PPh₃ (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 \times 20 mL), dried (Na₂SO₄), 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 (${}^{31}P/{}^{1}H$ NMR) using the combinations K₂CO₃/CH₃CN, Et₃N/1,4-dioxane, and Et₃N/CH₃CN 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, CDCl₃) δ 1.01, 1.13 (2s, 6H), 3.88 (dd \rightarrow t, $J \sim$ 10.7 Hz each, 2H), 4.12 (dd \rightarrow 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=CH₂); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (50 MHz, CDCl₃) 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, CDCl₃) δ 1.03 and 1.15 (2s, 6H), 2.38 (s, 3H), 3.89 (dd \rightarrow t, $J \sim$ 10.8 Hz each, 2H), 4.14 (dd \rightarrow t, $J \sim$ 10.8 Hz each, 2H), 5.38 (d, J = 17.6 Hz, 1H), 5.61 (br, J = 10.4 Hz, =C $H_{cis}H_{trans}$, 1H), 5.63 (d, J = 18.4 Hz, =C $H_{cis}H_{trans}$, 1H), 7.12–7.24 (m, 4H), 7.47 (not resolved, m, 1H); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (160 MHz, CDCl₃) δ 12.3; LC/MS (R_t 0.74 min) m/z 293 [M + 1]⁺. Anal. Calcd for C₁₆H₂₁O₃P: 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, CDCl₃) δ 1.04, 1.15 (2s, 6H), 3.84 (s, 3H), 3.87 (dd \rightarrow t, $J \sim$ 10.8 Hz each, 2H), 4.15 (dd \rightarrow t, $J \sim$ 10.8 Hz each, 2H), 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); ¹³C NMR (100 MHz, CDCl₃) δ 21.4, 21.6, 32.5 (d, J = 6.0 Hz), 55.3, 75.5 (d, J = 6.0 Hz),

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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); ³¹P NMR (160 MHz, CDCl₃) δ 12.6; LC/MS (R_t 0.96 min) m/z 309 [M + 1]⁺. Anal. Calcd for C₁₆H₂₁O₄P: 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; ¹H NMR (400 MHz, CDCl₃) δ 1.01, 1.13 (2s, 6H), 3.87 (dd \rightarrow t, $J \sim 10.2$ Hz each, 2H), 4.13 (dd, $J \sim 10.2$, 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); ¹³C NMR (50 MHz, CDCl₃) 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); ³¹P NMR (160 MHz, CDCl₃) 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 roundbottomed flask containing allenylphosphonate 1c (0.300 g, 1.38 mmol), Pd(OAc)₂ (0.015 g, 0.069 mmol), PPh₃ (0.054 g, 0.207 mmol), iodobenzene (0.339 g, 1.66 mmol), and K₂CO₃ (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 (Na₂SO₄), 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (80 MHz, CDCl₃) δ 11.5; LC/MS (R_t 0.72 min) m/z 293 [M + 1]⁺. Anal. Calcd for C₁₆H₂₁O₃P: 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (160 MHz, CDCl₃) δ 12.8. LC/MS (R_t 0.71 min) m/z 307 [M + 1]⁺. Anal. Calcd for C₁₇H₂₃O₃P: 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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; ³¹P NMR (160 MHz, CDCl₃) δ 13.0. LC/MS (R_t 0.69 min) m/z 323 [M + 1]⁺. Anal. Calcd for C₁₇H₂₃O₄P: 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) δ 21.0, 21.8 (2s, CH₃ and another CH₃, 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; ³¹P NMR

(80 MHz, CDCl₃) δ 12.4; LC/MS (R_t 0.70 min): 308 [M]⁺. Anal. Calcd for C₁₆H₂₂NO₃P: 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; ¹H NMR (400 MHz, CDCl₃) δ 1.05, 1.16 (2s, 6H), 3.92 (dd \rightarrow t, $J \sim 10.8$ Hz each, 2H), 4.18 (dd \rightarrow t, $J \sim 12.2$ 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); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (160 MHz, CDCl₃) 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), PPh₃ (0.082 g, 0.312 mmol), 2-nitroiodobenzene (0.662 g, 2.49 mmol), and K₂CO₃ (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 $[R_{\rm f} = 0.19$ (hexane/EtOAc, 50/50)] and ³¹P 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 $(3 \times 20 \text{ mL})$, dried (Na₂SO₄), 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) v 1520, 1474, 1343, 1263, 1059, 1006, 820; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) δ 16.0, 21.1, 21.6, 32.4 (d, J = 6.6 Hz), 75.8 (br), 112.9 (d, J = 185.6Hz), 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; ³¹P NMR (160 MHz, CDCl₃) δ 11.0. Anal. Calcd for C₂₂H₂₃O₇N₂P: 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), PPh₃ (0.074 g, 0.29 mmol), iodobenzene (0.475 g, 2.33 mmol), and K₂CO₃ (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 $(3 \times 20 \text{ mL})$, dried (Na₂SO₄), 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) v 1672, 1602, 1491, 1445, 1367, 1074, 897, 756, 696; ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 4.72 (s, 1H), 5.14 (s, 1H), 6.74 (s, 1H), 6.90-7.37 (m, 10H); ¹³C NMR (50 MHz, CDCl₃) 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 [lit¹⁶: ¹H NMR (CDC1₃) δ 2.16 (s, 3H), 4.80 (s, 1H), 5.21 (s, 1H), 6.87 (s, 1H), 6.90-7.20 (m, 10H); ¹³C 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 (Rt 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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 C₁₄H₁₆O₂: 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 K₂CO₃ or Ag₂CO₃ (¹H 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), PPh₃ (0.018 g, 0.069 mmol), iodobenzene (0.113 g, 0.55 mmol), and Ag₂CO₃ (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 \times 20 mL), dried (Na₂SO₄), 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) v 1954, 1491, 1368, 1262, 1057, 1005; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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; ³¹P NMR (80 MHz, CDCl₃) δ 8.1; GC-MS (R_t 4.72 min; column temperature 240 °C) m/z 292 [M]⁺. Anal. Calcd for C₁₆H₂₁O₃P: 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 (Na₂SO₄), 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; ¹H NMR (400 MHz, CDCl₃) δ 1.06, 1.16 (2s, 6H), 2.56 (d, J = 3.0 Hz, 3H), 3.90 (dd \rightarrow t, $J \sim$ 11.8 Hz each, 2H), 4.18 (dd \rightarrow t, $J \sim$ 11.8 Hz each, 2H), 5.95 (d, J = 18.5 Hz, 1H), 7.39–7.50 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (160 MHz, CDCl₃) 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; ¹H NMR (400 MHz, CDCl₃) δ 0.97, 1.02 (2s, 6H), 3.20 (d, J = 23.2 Hz, 2H), 3.70 (dd \rightarrow t, $J \sim$ 10.9 Hz each, 2H), 4.17 (dd \rightarrow t, $J \sim$ 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); ¹³C NMR (50 MHz, CDCl₃) δ 21.4, 21.6, 31.9 (d, J = 134.6 Hz, *C*H₂), 32.5, 75.0 (d, J = 6.0 Hz), 117.5 (d, J = 10.9 Hz), 126.2, 127.9, 128.4, 138.5; ³¹P NMR (80 MHz, CDCl₃) δ 21.9; LC/MS (R_1 0.71 min) m/z 267 [M + 1]⁺. Anal. Calcd for C₁₄H₁₉O₃P: 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 (Na₂SO₄), filtered, and concentrated under vacuum. The residue [³¹P NMR: δ 22.3 (20%), 17.5 (45%), 14.5 (5%, β-ketophosphonate (OCH₂CMe₂CH₂O)P(O)CH₂C(O)CH₃), 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) $\sim 10\%$; see ¹H NMR): Yield 0.205 g (46% isolated yield); mp 128–130 °C; IR (KBr, cm⁻¹) v 1605, 1455, 1265, 1055, 1011; ¹H NMR (400 MHz, CDCl₃) 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, $J \sim 3.8$ Hz), 7.20–7.53 (m, 4H); $^{13}\mathrm{C}$ NMR (50 MHz, CDCl₃) 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; ³¹P NMR (80 MHz, CDCl₃) 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 ¹H NMR and at δ 22.3 in the ³¹P 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 ³¹P NMR showed peaks at δ 22.3 and 17.5 in the ratio 1:1 (¹H 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), PPh₃ (0.097 g, 0.37 mmol), and K₂CO₃ (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 (Na₂-SO₄), 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; ¹H NMR (400 MHz, CDCl₃) 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, $J \sim 5.0$, 11.2 Hz, 2H), 4.12 (dd, $J \sim 5.0$, 11.2 Hz, 2H), 7.20–7.50 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) 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; ³¹P NMR (80 MHz, CDCl₃) δ 22.2; GC-MS (R_t 4.5 min, column temperature 250 °C) m/z 294 [M]⁺. Anal. Calcd for C₁₅H₁₉O₄P: 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; ¹H NMR (200 MHz, CDCl₃) 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 \rightarrow t, $J \sim 11.7$ Hz each, 2H), 4.28 (dd \rightarrow t, $J \sim 11.7$ Hz each, 2H), 7.26–7.77 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 12.6, 21.8, 32.6 (d, J = 5.6 Hz), 75.6 (d, J = 6.0 Hz), 100.6 (d, $J \sim 205.0$ 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); ³¹P NMR (80 MHz, CDCl₃) δ 10.9; GC-MS (R_t 4.4 min, column temperature 250 °C) m/z 294 [M]⁺. Anal. Calcd for C₁₅H₁₉O₄P: 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (160 MHz, CDCl₃) δ 12.8; LC/MS (*R*_t 0.74 min) *m*/z 309 [M + 1]⁺; Anal. Calcd for C₁₆H₂₁O₄P: 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 \times 20 mL), dried (Na₂-SO₄), 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 ¹H and ¹³C 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 ¹H NMR:^{17e} ¹H NMR (400 MHz, CDCl₃) δ 2.57 (s, 3H), 7.35-7.95 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) 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} ¹H NMR (CDC1₃) δ 2.48 (s, 3H), 7.15-8.45 (m, 9H); ¹³C NMR δ 9.2 (CH₃), 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), PPh₃ (0.055 g, 0.21 mmol), and K₂CO₃ (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 \times 20 mL), dried (Na₂SO₄), 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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 C₁₇H₁₆O: 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; ¹H NMR (400 MHz, CDCl₃) δ 1.47 (t, $J \sim 7.0$ Hz, 3H), 2.80 (s, 3H), 4.44 (q, $J \sim 7.0$ Hz, 2H), 7.28–8.00 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) 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; ¹H NMR (400 MHz, CDCl₃) δ 1.31 (t, $J \sim 7.0$ Hz, 3H), 3.85 (s, 2H), 4.24 (q, $J \sim 7.0$ Hz, 2H), 6.66 (s, 1H), 7.22–7.55 (m, 4H); ¹³C NMR (50 MHz, CDCl₃) 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 C₁₂H₁₂O₃: 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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; ³¹P NMR (80 MHz, CDCl₃) δ 21.0; LC/MS (R_t 0.74 min) m/z 309 [M + 1]⁺. Anal. Calcd for C₁₅H₁₇O₅P: 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 K₂CO₃ (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 (Na₂SO₄), 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; ¹H NMR (200 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) δ 21.5 (two CH₃ 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; ³¹P NMR (80 MHz, CDCl₃) 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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (50 MHz, CDCl₃) 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; ³¹P NMR (80 MHz, CDCl₃) δ 9.0; LC/ MS (R_t 0.69 min) m/z 337 [M + 1]⁺. Anal. Calcd for C₁₇H₂₁O₅P: C, 60.71; H, 6.29. Found: C, 60.70; H, 6.28. Another isomer as a minor product (<10%) was also seen (¹H 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), PPh₃ (0.06 g, 0.232 mmol), and 2-iodobenzoic acid (0.462 g, 1.86 mmol) in dry acetonitrile (5 mL) was added K₂CO₃ (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 (Na₂SO₄), 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) v 1719, 1597, 1458, 1263, 1231, 1117, 1090, 995; ¹H NMR (400 MHz, CDCl₃) δ 5.32 (s, 2H), 7.23–7.67 (m, 9H), 8.16 (d, J = 7.6 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) 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 (Rt 5.2 min, column temperature 250 °C) m/z 236 [M]⁺. Anal. Calcd for C₁₆H₁₂O₂: 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 \sim 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; ¹H NMR (200 MHz, CDCl₃) δ 1.65 (s, 6H), 6.89 (s, 1H), 7.13–7.26 (m, 8H), 8.07 (d, J = 7.8 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) 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; ¹H NMR (400 MHz, CDCl₃) 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 CDCl₃ peak), 7.50–7.59 (m, 2H), 7.80 (t, J = 7.5 Hz, 1H), 8.37 (d, J = 7.7 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) 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 \sim 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) v 1721, 1642, 1603, 1460, 1302, 1260, 1202, 1109, 1038; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 ($R_t 0.74 \text{ min}$) $m/z 261 [M + 1]^+$. 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) v 1725, 1636, 1599, 1460, 1302, 1263, 1194, 1090, 1032; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 (Na₂SO₄), 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; ¹H NMR (200 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₈H₁₄O₃: 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 K α ($\lambda = 0.71073$ 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, ¹H and ¹³C 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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