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Pd-Catalyzed Reactions of Allenylphosphonates and Related Allenes with Functionalized 2-Iodophenols, 2-Iodobenzoic Acid, and 2-Iodobenzyl Alcohol Leading to Functionalized Benzofurans, Isocoumarins, and Benzopyrans

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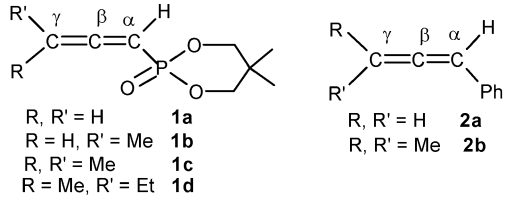
Regioselective, palladium-catalyzed coupling reactions of allenylphosphonates ($OCH_2CMe_2CH_2O$)P(O)CH=C=CRR′ [R, R′ = H (**1a**), R = H, R′ = Me (**1b**), R = R′ = Me (**1c**)] and phenyl allenes PhCH=C=CR_2 [R = H (**2a**), Me (**2b**)] with functionalized iodophenols (in PEG-400), 2-iodobenzoic acid, and 2-iodobenzyl alcohol are investigated. Benzofurans with free aldehyde functionalities are formed in high yields ($^1H/^{31}P$ NMR) in reactions by using functionalized iodophenols, essentially as single isomers. The synthetic potential of these products possessing an aldehyde functionality is demonstrated by isolating a compound with the skeleton of Obovaten and many other 2,3,5,7-tetrasubstituted benzofurans. From the reaction of 2-iodophenol and $Pd^{II}(OAc)_2/PAr_3$, isolation and structural characterization of the (hydroxy)aryl phosphane oxides $(Ar)_2P(O)(C_6H_4$-2-OH) (Ar = Ph, 4-MeO-C_6H_4) that suggests the *P–aryl* to *Pd–aryl* bond exchange, is described. An interesting structural problem related to the formation/crystallization of benzofurans is also highlighted. The reaction of allenes with iodobenzyl alcohol or iodobenzoic acid led to benzopyrans or isocoumarins (isochromanones), respectively, as single isomers in good to excellent yields. The reaction of 3-methylbuta-1,2-dienyl acetate with 2-iodobenzoic acid led to a novel acetic acid elimination product along with the expected isocoumarin. The structures of key compounds are confirmed by X-ray crystallography. These results establish that in the formation of benzofurans or benzopyrans, [β,γ] attack on the allene is preferred except in the case of PhC=C=CH_2, where [β,α] attack is observed.

Introduction

Availability of two reactive cumulative double bonds in allenes (or 1,2-dienes) makes this class of compounds valuable precursors for diverse synthetically and biologically useful applications.[1,2] Allenylphosphonates (e.g., **1a**–**d**), as a subset of this larger system, can also be used as important building blocks in organic chemistry.[3] In reactions using reagents such as 2-iodophenol or dialkylazodicarboxylates, the cyclization could occur through [α,β], [β,α], [β,γ], or [γ,β] attack on allenes **1** (or **2**), as shown by compounds **3**–**6**.[3m,4] An additional feature in such reactions is the formation of acyclic products of type **7** and **8**. An important question in such reactions is whether any of the products can be preferentially obtained or not. In this context, we wanted to employ aldehyde-functionalized iodophenols so that the resulting products could further be utilized. It is also relevant here to note that benzofurans so obtained are themselves synthetically and biologically important heterocycles.[5–7] We were also curious to see whether isomer maximization is possible in the formation of functionalized benzopyrans by using 2-iodobenzyl alcohol or 2-iodobenzoic acid in place of substituted 2-iodophenols. The present study is in continuation of our investigations on organophosphonates.[3h,3i,3m,4,8] We primarily utilized allenylphosphonates **1a**–**d** that are very readily accessible and relatively inexpensive.[9] For comparison, we have also used other non-phosphorus allenes including **2a**,**b**.



In the course of these investigations on palladium-catalyzed reaction of allenes, we also found (i) exchange of the aryl group of the triphenylphosphane (used as a ligand) with that of iodophenol residue, (ii) novel cocrystallization of isomeric phosphonobenzofurans [γ,β] and [β,γ] isomers, (iii) formation of elimination (acetic acid) products in addition to the expected isocoumarins in the reaction of allenyl acetate and 2-iodobenzoic acid, and (iv) whereas iodobenzyl alcohol leads to benzopyrans stereospecifically, 2-iodophenylacetic acid leads only to butadienes and no annulation takes place under the conditions employed. Be-

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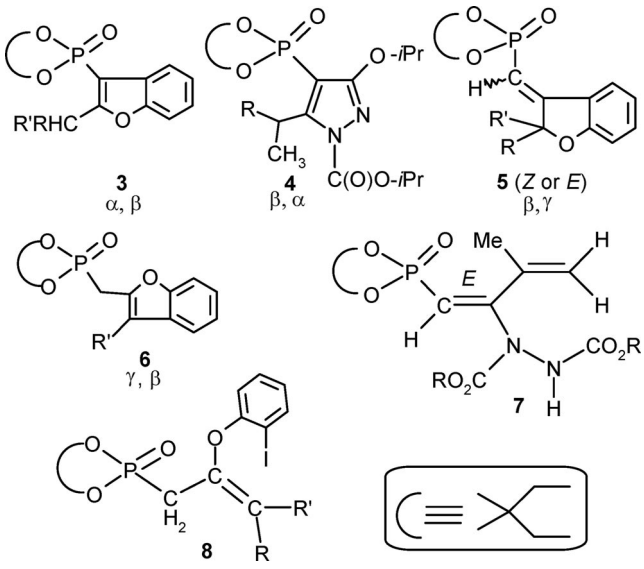
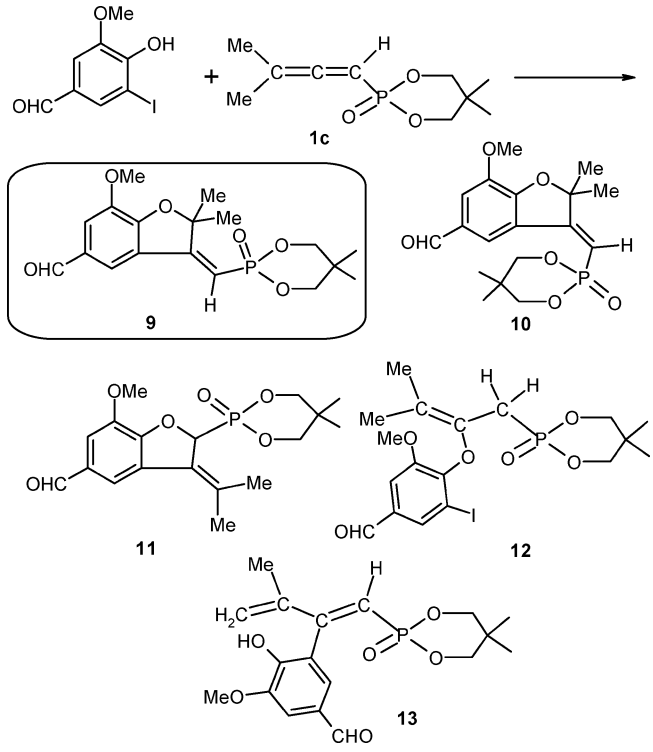


cause such reactions/behavior could have bearing on further studies in this area, we have included these results also in this paper.

Results and Discussion

Reaction of Allenes with Functionalized Iodophenols: Use of PEG-400 Medium

As mentioned above, we wanted to see if the yield of any specific benzofuran may be maximized or not by using **1c** and 5-iodovanillin (cf. compounds **9**–**13**; Scheme 1 and Table 1). The ^{31}P NMR spectra of the reaction mixtures for Entries 4 and 24 (Table 1) are shown in Figure 1; the former shows a larger number of products, and identification of all



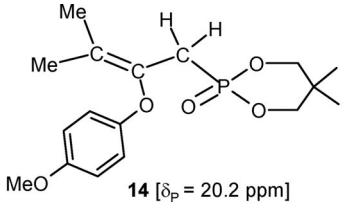
Scheme 1.

Table 1. Effect of reaction conditions on the yield of **9** in the coupling of **1c** with 5-iodovanillin.[a]

Entry	Palladium catalyst/phosphane	Base/solvent	Time [h]/Temp. [°C]	Yield [%][b]
1	$Pd(OAc)_2/PPh_3$	K_2CO_3, CH_3CN	24/90	no reaction
2	$Pd(OAc)_2/PPh_3$	K_2CO_3, THF	12/80	no reaction
3	$Pd(OAc)_2/PPh_3$	K_2CO_3, DMSO	24/80	7
4	$Pd(OAc)_2/PPh_3$	K_2CO_3, DMF	24/80	59[c,d]
5	$Pd(OAc)_2/PPh_3$	K_2CO_3, H_2O	48/r.t.	no reaction
6	$Pd(OAc)_2/PPh_3$	K_2CO_3, H_2O	4/80	61
7	$Pd(OAc)_2/PPh_3$	K_2CO_3, DMF + H_2O (9:1)	12/80	43[c]
8	$Pd(OAc)_2/PPh_3$	K_2CO_3, PEG-400 + H_2O (9:1)	4/80	34
9	$Pd(OAc)_2/PPh_3$	K_2CO_3, PEG-400 + H_2O (9:1)	12/80	50
10	$Pd(OAc)_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (9:1)	12/80	52
11	$Pd(OAc)_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (9:1)	24/80	36
12	$Pd(OAc)_2/PPh_3$	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	57
13	$Pd(OAc)_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	62
14	$Pd(OAc)_2$/dppe	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	no reaction
15	$Pd(OAc)_2$/TDMPP[c]	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	40
16	$Pd(OAc)_2/(o\text{-tolyl})_3P$	NaOAc, PEG-400 + H_2O (1:1)	12/90	54
17	$Pd(OAc)_2/(o\text{-tolyl})_3P$	K_3PO_4, PEG-400 + H_2O (1:1)	12/90	55
18	$Pd_2(dba)_3/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	48
19	$Pd(PPh_3)_2Cl_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	41
20	$PdCl_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400 + H_2O (1:1)	12/90	55[c]
21	$Pd(OAc)_2/Ph_3P$	nBu_4NBr, K_2CO_3, H_2O	4/90	58[c]
22	$Pd(OAc)_2/Ph_3P$	K_2CO_3, [bmim][BF_4]	48/90	no reaction
23	$Pd(OAc)_2$	CsF, PEG-400	12/90	79
24	$Pd(OAc)_2/(o\text{-tolyl})_3P$	K_2CO_3, PEG-400	12/90	81

[a] Use of microwave conditions (160 °C, 10 min, 160 W) with $Pd(OAc)_2/PPh_3/K_2CO_3$/PEG-400 or H_2O led only to <45% of the product. [b] Yields were calculated by using $^1H/^{31}P$ NMR spectroscopy. [c] Combined yield of (*E*/*Z*) forms. [d] In this case, a mixture of products was obtained, see Figure 1.

these was difficult. The major product shown in Figure 1b is compound **9**. The assignment of the *Z* stereochemistry for **9** is based on the X-ray structure of the product from the reaction of **1c** with 3-iodo-4-hydroxybenzaldehyde described below. Although *E*-isomer **10** and benzofuran **11** are also possible, they are not the major products here.[10] One of the minor peaks in the vicinity of δ_P = 20 ppm in Figure 1a may be ascribed to product **12**; this is consistent with the isolation of the analogous phenol addition product **14** (δ_P = 20.2 ppm) in high yields from the reaction of **1c** with 4-methoxy phenol/DBU.[11] We have not been able to identify a noncyclized product of type **13** in reactions of allenes with 2-iodophenols, but these may be present in trace quantities.



14 [δ_P = 20.2 ppm]

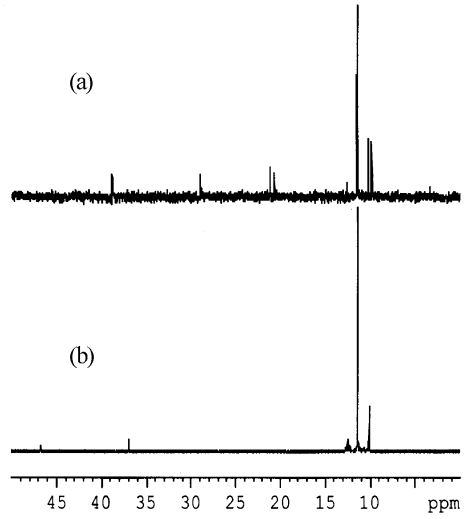
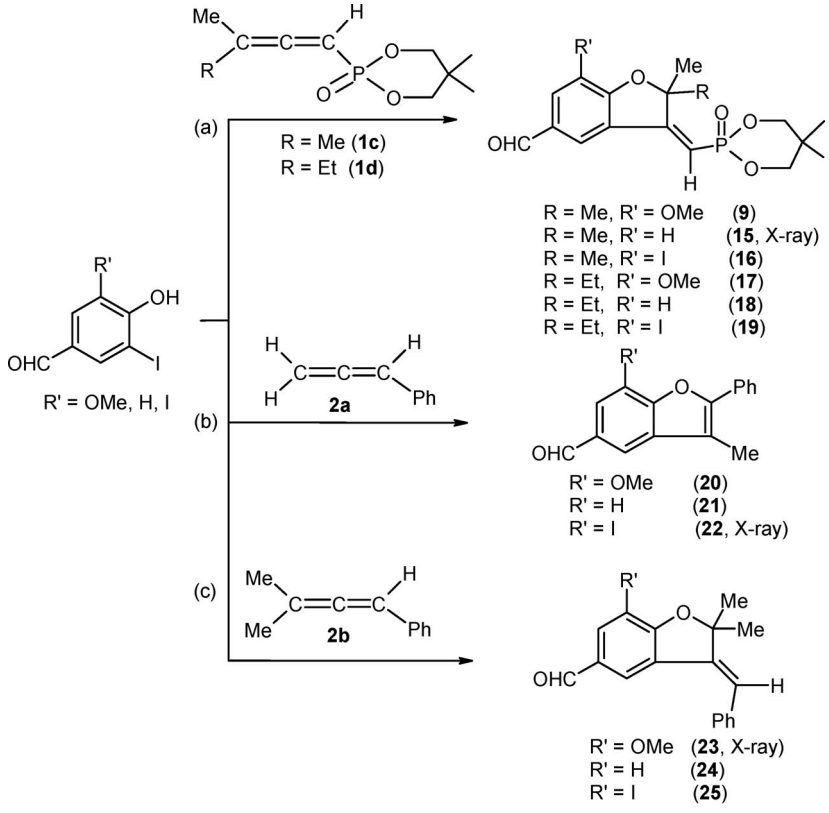


Figure 1. ^{31}P NMR spectra for the reaction mixture of **1c** with 5-iodovanillin in (a) DMF at 80 °C for 24 h, (b) PEG-400 at 90 °C for 12 h.

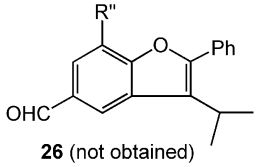
As can be seen from Table 1, the conditions previously used in reactions using iodophenol[4] were *ineffective* (Table 1, Entry 1) *or led to a mixture* (Table 1, Entry 4; Figure 1) wherein the yield of **9** was only moderate. In some cases, a mixture of isomers [Table 1, Entries 4, 7, 18, 19; δ_P = 11.6 (for **9**), 11.4 ppm (for **10**), assignment of configuration tentative] was obtained. Also, the use of (*o*-tolyl)$_3$P in place of Ph_3P improved the yield (Table 1, Entries 12 and 13), and the best combination was Pd(OAc)$_2$/(*o*-tolyl)$_3$P/K_2CO_3/PEG-400 (Table 1, Entry 24).

Employing the above conditions, we were able to generate functionalized benzofurans **9** and **15**–**25** in yields of 65–70% rather easily (Scheme 2, Table 2). The highlighting feature of this work is that only one product is formed pre-



Scheme 2.

dominantly, but the structure varies with the type of precursor allene used. We have confirmed the structure of each type (i.e., **15**, **22**, **23**) by X-ray crystallography (Figure 2). Thus, $=CH_2$ terminal allene **2a** gives [β,α] products **20**–**22**, but $=CMe_2$ terminal allene **2b** gives [β,γ] product **23**–**25**; in the latter case, [β,α] product **26** was not obtained.



26 (not obtained)

Table 2. Details on the yields of benzofurans **9** and **15**–**25** in PEG medium.

Entry	Allene	R′ in iodophenol	Product	Yield [%] ^{31}P NMR; isolated	^{31}P NMR δ [ppm]
1	**1a**	OMe	**9**	81; 70	11.8
2	**1a**	H	**15**	76; 65	11.4
3	**1a**	I	**16**	65; 59	10.6
4	**1d**	OMe	**17**	64; 55	11.8
5	**1d**	H	**18**	63; 57	11.5
6	**1d**	I	**19**	63; 57	10.6
7	**2a**	OMe	**20**	68[a]	–
8	**2a**	H	**21**	69[a]	–
9	**2a**	I	**22**	51[a]	–
10	**2b**	OMe	**23**	66[a]	–
11	**2b**	H	**24**	62[a]	–
13	**2b**	I	**25**	52[a]	–

[a] These are isolated yields; reaction mixture suggested yields in the range 65–75% (^{1}H NMR).

In contrast to the above results, when the allenylphosphonate has a γ-hydrogen as in **1b** or **27**, use of triarylphosphane does not give clean products. A probable reason for this observation is the isomerization of allenylphosphonate into the corresponding alkyne. Here, the use CsF as a base worked well in obtaining the optimum yields of benzofurans **28**–**31** (Scheme 3, bottom; Figure S1 in the Supporting Information for X-ray structure of **30**). It is important to note that with CsF as a base, the use of the phosphane ligand is avoided.

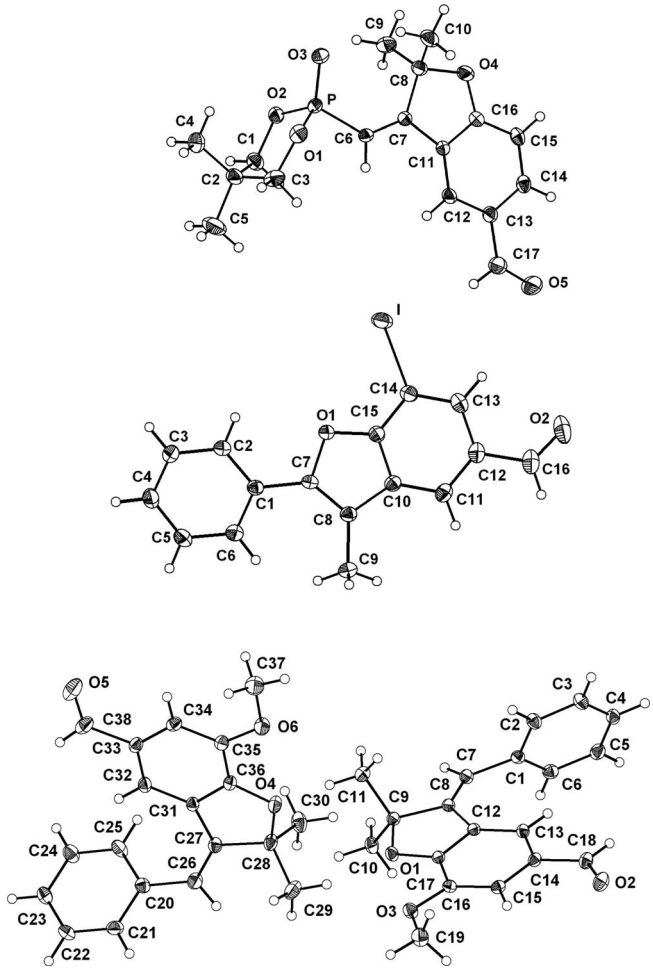
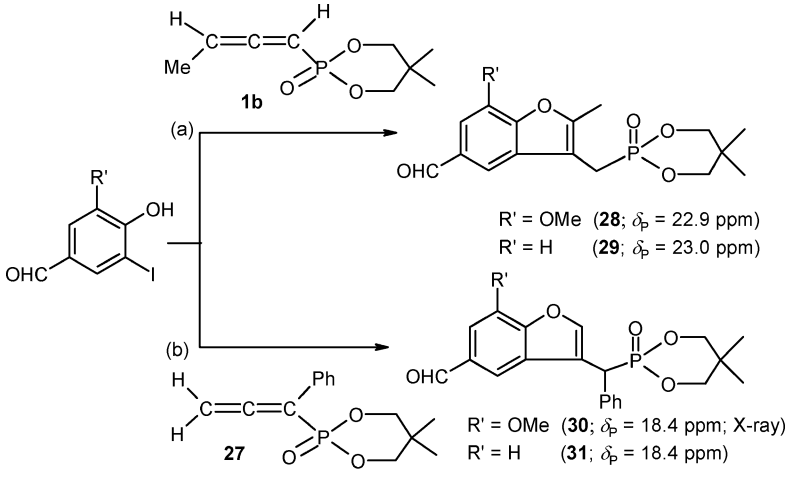
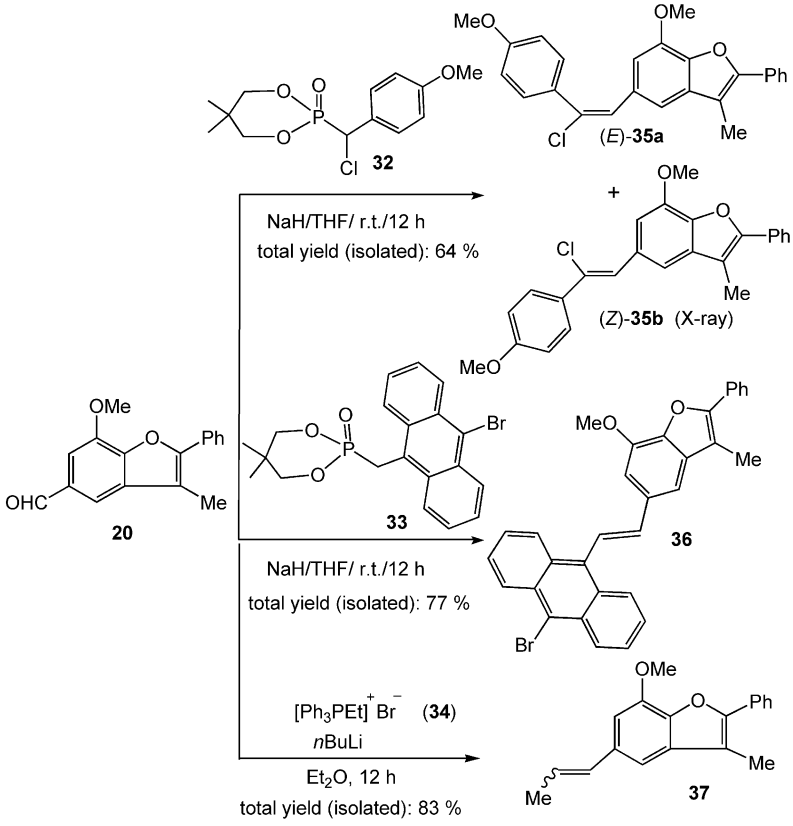


Figure 2. ORTEP diagrams of compounds **15** (top), **22** (middle), and **23** (bottom).



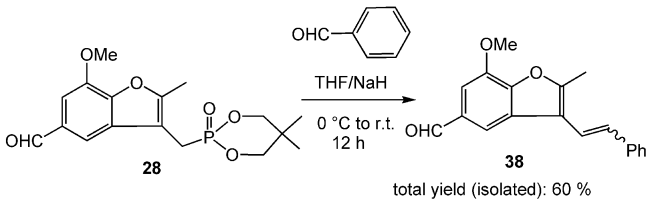
Conditions: CsF/$Pd(OAc)_2$/PEG-400, 90 °C, 12 h
Yields (^{31}P NMR, isolated): 63–70 %; 55–63 %

Scheme 3.

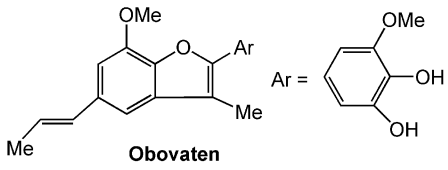


Scheme 4.

With several aldehyde appended benzofurans prepared as above, we thought that it should be possible to synthesize a variety of 3,5-disubstituted benzofurans. This idea is exemplified by using **20** in the Horner–Wadsworth–Emmons and Wittig reactions to lead to, say **35**–**37**, as shown in Scheme 4 (see Figure S2 in the Supporting Information for the X-ray structure of **35b**). It may be noted that Wittig product **37** is similar to Obovaten, which is a natural product and a known antitumor agent.[12] Even phosphonobenzofurans of type **28** are of synthetic value as shown by the synthesis of **38** (Scheme 5). Interestingly, in this case, we were able to retain the less reactive aldehyde moiety present in phosphonobenzofuran **28**; this aldehyde group has marginally more steric hindrance.



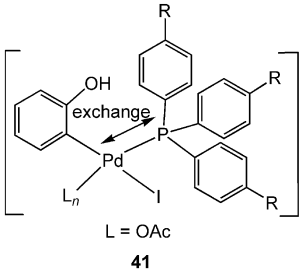
Scheme 5.



Isolation of a Hydroxyphenylphosphane Oxide in the 2-Iodophenol-Exchange of Aryl Groups on the Phosphane with Phenol Residue?

In the reaction of allenes **1b**,**c** with 2-iodophenol/$Pd(OAc)_2/PPh_3$, in addition to the expected benzofurans, the reaction mixture after workup showed a minor peak in the region δ_P = 33–39 ppm that did not contain the allenic residue. We were able to characterize this compound as (hydroxyphenyl)diphenylphosphane oxide (**39**).[13] Compound **39** is an oxidized derivative of triphenylphosphane where one phenyl ring is substituted with phenol moiety. Single-crystal X-ray data shows the presence of the expected groups (Figure 3); the presence of hydrogen bonding also confirms that there is a phenolic OH group. The straightforward treatment of 2-iodophenol with triphenylphosphane in the presence of $Pd(OAc)_2/K_2CO_3/CH_3CN$ under reflux conditions also afforded compound **39** in 15% yield. The ^{31}P NMR spectrum of the reaction mixture showed two other major peaks at δ = 21.2 (not assigned, ca. 34%) and 29.9 ppm (triphenylphosphane oxide, ca. 50%) along with that for compound **39**. Though the yield was lower, compound **39** was isolated easily by using column chromatography. In a similar fashion, using $(4\text{-}MeOC_6H_4)_3P$ in place of triphenylphosphane we could obtain **40**. This result suggests that in addition to the expected reaction, P–C bond exchange also occurs in palladium-catalyzed transformations. It may be noted that the palladium-catalyzed reactions of PPh_3 with aryl halides are reported,[14] but for-

mation of products such as **39** is not elaborated in the literature. It can also be noted that in the ^{31}P NMR spectra shown in Figure 1a, there is a minor peak at 37 ± 2 ppm [with slight variability in the chemical shift]. Although we could not isolate the compound corresponding to this, we believe that this is the phosphane oxide with exchange of aryl groups. Formation of **39** and **40** could have occurred via the intermediate such as could occur in an intermediate of type **41**. These observations, we believe, should act as a caveat while using the Pd^{II}/Ar_3P catalytic system.



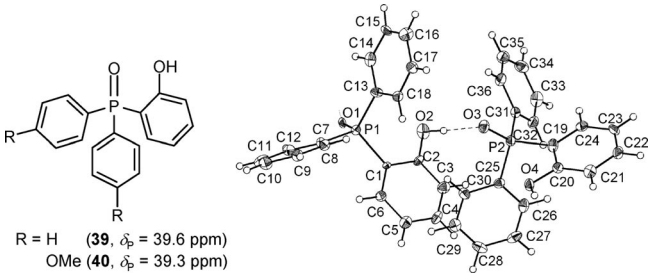
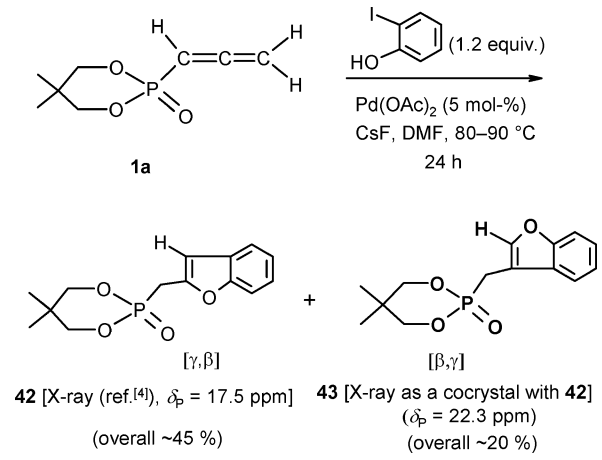


Figure 3. Chemical drawing of **39** and **40** as well as an ORTEP picture of compound **39**. The molecule has some disorder (see Supporting Information). H-bond parameters {[Å, Å, Å, °]: O(4)–H(4O)···O(1′) 0.84, 1.75, 2.582(4), 171.4 ($x - 1/2$, $1/2 - y$, z); O(2)–H(2O)···O(3) 0.84, 1.76, 2.591(4), 172.3} also show the presence of an O–H group.

Formation of [γ,β] and [β,γ] Products

In the reaction of **1a** with 2-iodophenol, two types of phosphonobenzofurans **42** and **43** (δ_P = 22.3 and 17.5 ppm, respectively) are obtained; whereas the former is a [γ,β] product, the latter is a [β,γ] product. Although compound **42** can be isolated readily,[4] compound **43** is obtained only as a cocrystal of **42** and **43**. By looking at the two structures, we may assume that the packing motifs can be similar (Scheme 6). An ORTEP view of the structure is shown in Figure 4, which gives better visualization. A situation like this could complicate the analysis of the results. The situation presented here gives an idea of the difficulty in analyzing reactions of non-phosphorylated allenes wherein the ^{31}P NMR as a tool is lacking.



Scheme 6.

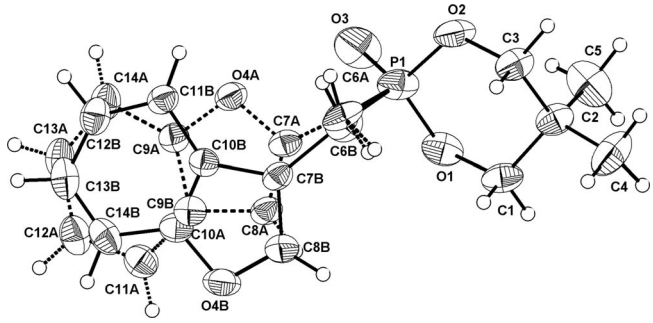
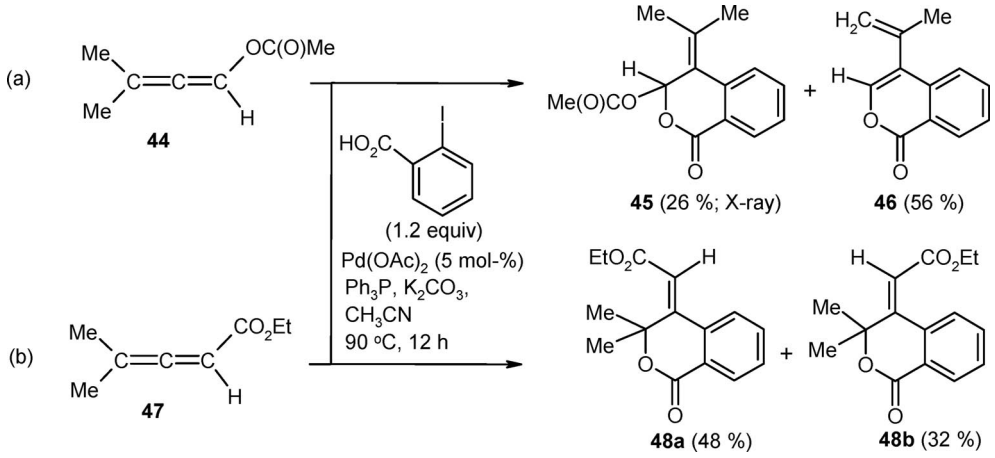


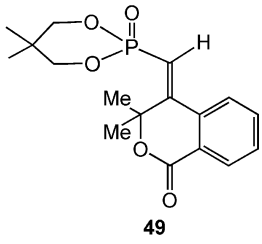
Figure 4. An ORTEP drawing of the [**42** + **43**] cocrystal. The carbon atoms C6A–C14A correspond to [γ,β] product **42**, whereas the carbon atoms C6B–C14B correspond to [β,γ] product **43**. Both fit into the same unit cell nicely, and it is important to note that there is no disorder at the 1,3,2-dioxaphosphorinane ring.

Formation of Six- and Higher-Membered Rings: Synthesis of Isocoumarins (Isochromanones), and Benzopyrans

2-Iodobenzoic acid reacts with allenes to afford isocoumarins. However, it has been inferred previously that carboxylate displacement occurs at the more highly substituted terminus of π-allylpalladium compounds.[15] We believe, however, that the displacement of the carboxylic group depends on the reaction conditions and the allenic substrates. Thus, the reaction of 3-methylbuta-1,2-dienyl acetate (**44**) with 2-iodobenzoic acid in the presence of $Pd(OAc)_2/PPh_3/K_2CO_3/CH_3CN$ affords isocoumarins **45** (X-ray structure in Figure S3, Supporting Information) and **46** (Scheme 7). In this case, carboxylate displacement occurs at the less-substituted carbon atom. Product **46** is likely to be formed by the elimination of acetic acid from **45**. Such a situation is different from that observed by us before in the reaction of ester allene **47**, leading to isocoumarins **48a**,**b** or that of allenylphosphonate **1c** giving **49**, wherein [β,γ] products were favored. It is also different from the $Pd_2(dba)_3$-catalyzed reaction of $EtO(O)CCH{=}C{=}CH_2$ with ethyl(2-iodophenoxy)acetate, wherein the [β,γ] product was obtained.[16]



Scheme 7.



The reaction of 2-iodobenzylalcohol with allenes works smoothly, but as the PEG-400 medium was ineffective, we used DMF as the solvent. The cyclization process in the reaction using **1c**, **1d**, **2b**, or **27** is similar to that observed in the reactions with 2-iodobenzoic acid, leading to [β,γ] cyclized products **50**–**52** (X-ray structure of **51**; Figure 5) and **54**. However, reaction using **2a** led to [β,α] product **53**, which shows three separate signals for the olefinic and the C(Ph)*H* protons. It may be noted that a similar type of reactivity was observed in the formation of benzofurans **20**–**22** (vide supra). Use of CsF in place of Ph_3P/K_2CO_3 in the case of **1a** or **1c** led to a mixture of products (Scheme 8).

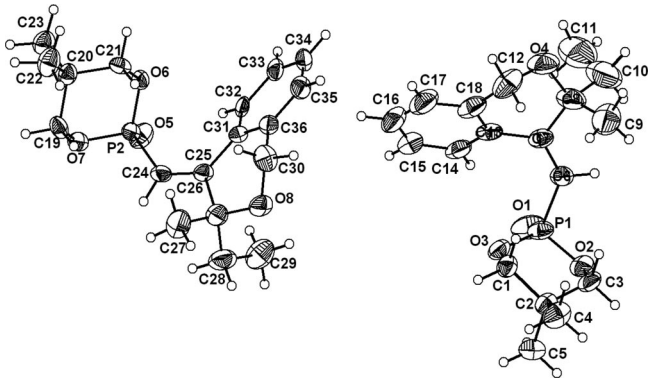


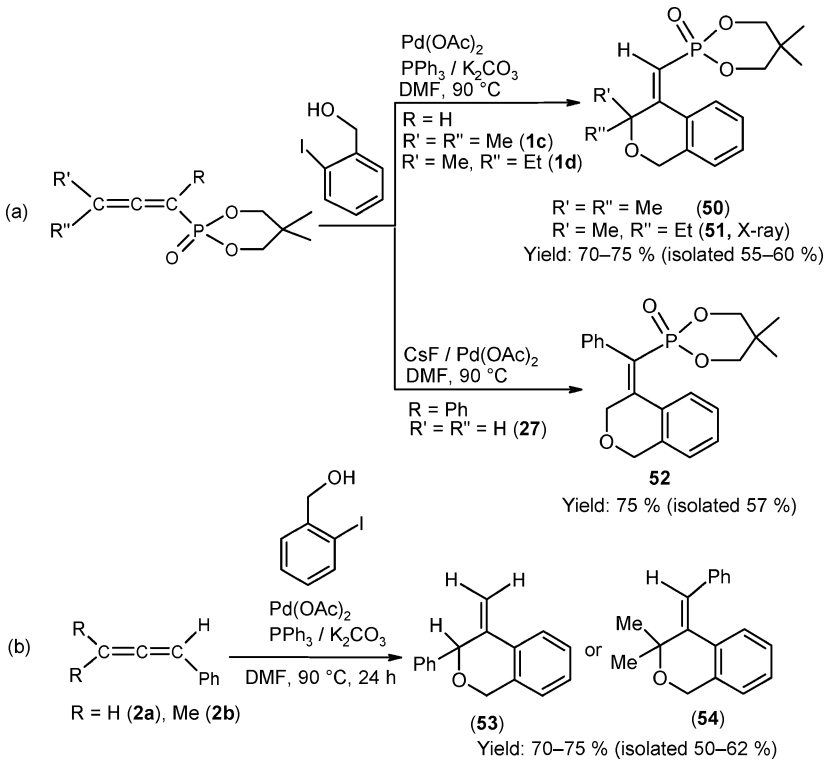
Figure 5. ORTEP diagram of compound **51**.

In an attempt to check the feasibility of forming seven-membered rings, we treated **1c** and **2b** with 2-iodophenylacetic acid in the presence of $Pd(OAc)_2/PPh_3/NEt_3/CH_3CN$. These reactions afforded only butadienes **55** and **56** in good yields (Scheme 9). The same reaction in the presence of K_2CO_3 (in place of NEt_3) did not work well, most likely due to the formation of the insoluble potassium salt of the acid. An X-ray structure was determined for **55** (Figure S4, Supporting Information).[17] Here, no cyclization product was obtained, probably due to the nonproximity of the –OH residue to the α or γ carbon center or due to geometrical restriction.

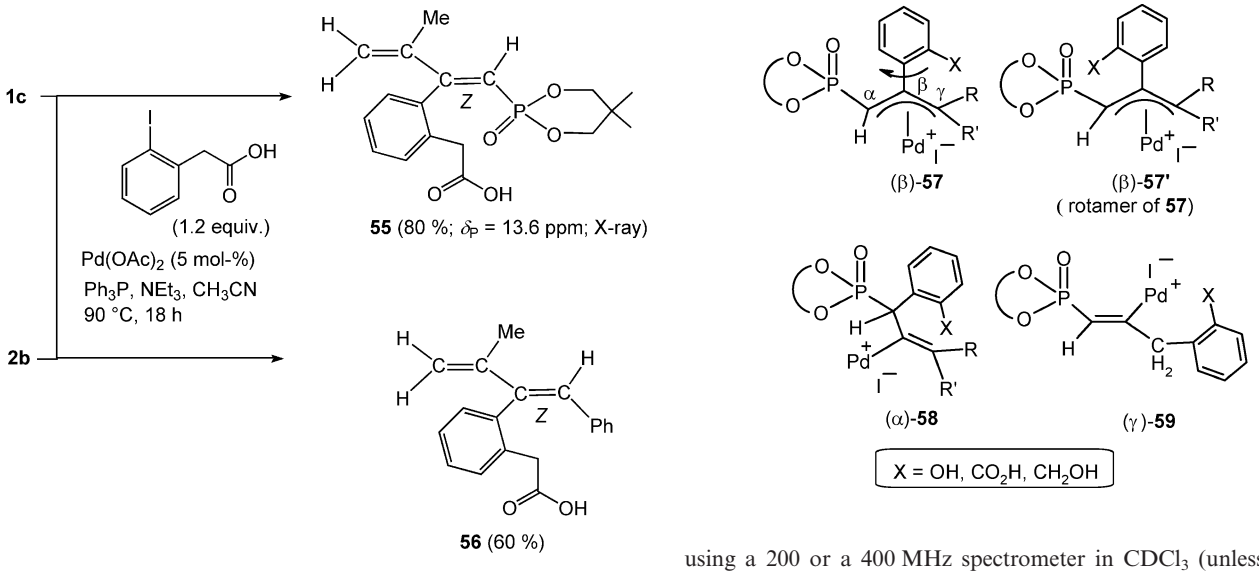
Species **57**–**59** are probable intermediates prior to cyclization in the above reactions. The initial β-attack (cf. **57** and **57′**) is expectedly the most common, with α or γ carbon atoms involved in subsequent cyclization. Substituents on the allene have a major role in the cyclization step (e.g., **45** and **46** vs. **48**). The reaction of $=CH_2$ terminal allenylphosphonate works better with CsF as a base in place of Ph_3P, but the cyclization in general could involve a [β,α] or [β,γ] process (cf. **53** and **54**).

Conclusions

Pd-catalyzed regioselective formation of aldehyde-functionalized benzofurans from allenylphosphonates was achieved by using PEG-400 mediated coupling reactions. In the reactions of =CHR terminal allenylphosphonates, CsF as a base avoided the requirement of a phosphane ligand. The synthetic utility of several of these as Horner–Wadsworth–Emmons reagents was demonstrated. Regiospecific synthesis of isocoumarins and isochromans was achieved from the reactions of allenes with 2-iodobenzyl alcohol and 2-iodobenzoic acid; here, the PEG-400 medium was not effective. The cyclization generally takes place through [β,γ] attack. This may be due to the lower steric congestion at the γ-position. In the reaction of **2a**, however, [β,α] attack is favored, perhaps due to the ease of aromatization. A novel exchange of a *hydroxyphenyl* group of the iodophenol with an *aryl* group of the triarylphosphane in these palladium-catalyzed reactions is highlighted. This observation adds an interesting facet to our understanding of Pd-catalyzed reactions. The use of allenylphosphonates has allowed the analysis of different products more readily by ^{31}P NMR spectroscopy. An interesting structural problem relating to the formation/crystallization of benzofurans was also brought to light in the present investigation.



Scheme 8.



Scheme 9.

Experimental Section

General: Allene precursors **1a**–**d**,[9] **2a**,**b**,[18] **27**,[9,19] and **44**[18] were prepared by literature procedures. 4-Hydroxy-3-iodo-benzaldehyde and 4-hydroxy-3-iodo-5-methoxy-benzaldehyde (5-iodovanillin) were prepared by using reported procedures.[20] 4-Hydroxy-3,5-diiodo-benzaldehyde was prepared by a procedure analogous to that for 4-hydroxy-3,5-diiodo-benzoic acid.[21] The Horner–Wadsworth–Emmons/Wittig reagents **32**–**34** were also prepared by known routes.[22] Compounds **42** and **43** were isolated as described before.[4] General experimental conditions are given in the Supporting Information ^{1}H, ^{13}C{^{1}H}, and ^{31}P{H} NMR spectra were recorded using a 200 or a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ (δ = 0 ppm) or 85% H_3PO_4 (δ = 0 ppm). Infrared spectra were recorded neat or by using KBr pellets with an FTIR spectrometer. Microanalyses were performed by using a CHNS analyzer.

Standardization of Reaction Conditions Leading to Benzofuran 9 from Allene 1c and Iodovanillin: To a 25-mL, round-bottomed flask containing allene **1c** (0.300 g, 1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), triphenyl or tri(*o*-tolyl)phosphane (0.21 mmol), 5-iodovanillin (0.466 g, 1.67 mmol), and the base [K_2CO_3, K_3PO_4, or NaOAc; 2.78 mmol] was added the solvent [THF, DMF, DMSO, H_2O, CH_3CN, [bmim][BF_4], PEG-400 or PEG-400 + H_2O (1:1); 5 mL] under a N_2 atmosphere. The contents were evacuated in vacuo for 15 min and then heated at 90–100 °C (reflux for THF/CH_3CN) for 4–48 h under a N_2 atmosphere. The reaction mixture

was quenched with water (5 mL), extracted with diethyl ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The reaction mixture was checked by $^{31}P/^{1}H$ NMR spectroscopy at this stage. Other details are presented in Table 1.

Synthesis of Benzofurans 9 and 15–25

Representative Procedure for 9: The residue, after removing the solvents from the above reaction mixture, using allene **1c** (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), (*o*-tolyl)$_3$P (0.095 g, 0.21 mmol), 5-iodovanillin (1.67 mmol), and K_2CO_3 (0.384 g, 2.78 mmol) in PEG-400 (5 mL), was subjected to column chromatography (hexane/EtOAc) to afford desired product **9**. Yield (NMR; isolated): 81%; 0.28 g (70%). Gummy solid. IR (KBr): $\tilde{\nu}$ = 2973, 1688, 1595, 1495, 1323, 1271, 1121, 1059, 1007 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.69 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.93 (s, 6 H, 2 CH_3), 3.87–3.94 (m, 2 H, OCH_2), 4.00 (s, 3 H, OCH_3), 4.26–4.31 (m, 2 H, OCH_2), 5.95 [d, J = 9.8 Hz, 1 H, =(CH)P], 7.47 (s, 1 H, Ar), 7.62 (s, 1 H, Ar), 9.89 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.4, 21.7, 26.1, 26.1, 32.6 (d, J = 5.0 Hz), 56.3, 75.3 (d, J = 6.0 Hz), 94.8 (d, J = 6.0 Hz), 98.4 (d, J = 199.0 Hz), 113.1, 118.9, 125.7 (d, J = 23.0 Hz), 131.2, 146.3, 156.4, 165.0 (d, J = 9.0 Hz), 190.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.8 ppm. LC–MS: m/z = 367 [M + H]$^+$. $C_{18}H_{23}O_6P$ (366.4): calcd. C 59.01, H 6.33; found C 59.15, H 6.32.

15: Yield (NMR; isolated): 76%; 0.27 g (65%). M.p. 142–146 °C. IR (KBr): $\tilde{\nu}$ = 2975, 2812, 1688, 1605, 1487, 1294, 1260 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.09 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.86 (s, 6 H, 2 CH_3), 3.90–3.96 (m, 2 H, OCH_2), 4.21–4.26 (m, 2 H, OCH_2) 6.04 [d, J = 10.0 Hz, 1 H, =(CH)P] 7.00–8.03 (m, 3 H, Ar) 9.91 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.4, 21.6, 26.1, 26.1, 32.5 (d, J = 5.0 Hz), 75.4 (d, J = 6.0 Hz), 93.7 (d, J = 5.0 Hz), 98.7 (d, J = 198.0 Hz), 111.9, 124.1, 125.7 (d, J = 23.0 Hz), 130.3, 136.2, 164.2 (d, J = 9.0 Hz), 166.3, 190.1 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.4 ppm. LC–MS: m/z = 337 [M + H]$^+$. $C_{17}H_{21}O_5P$ (336.3): calcd. C 60.71, H 6.29; found C 60.75, H 6.28. X-ray structure was done on this sample.

16: Yield (NMR; isolated): 65%; 0.16 g (59%). M.p. 162–166 °C. IR (KBr): $\tilde{\nu}$ = 2932, 2884, 1692, 1595, 1273, 1053, 997, 831 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.08 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.92 (s, 6 H, 2 CH_3), 3.88–3.95 (m, 2 H, OCH_2), 4.25–4.30 (m, 2 H, OCH_2), 6.00 [d, J = 9.6 Hz, 1 H, =(CH)P], 7.97 (s, 1 H, Ar), 8.27 (s, 1 H, Ar), 9.85 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.4, 20.7, 25.2, 31.6 (d, J = 6.0 Hz), 77.4 (d, J = 6.0 Hz), 93.5, 99.5 (d, J = 198.0 Hz), 122.4, 124.2 (d, J = 23.0 Hz), 130.9, 143.5, 163.3, 163.4, 165.2, 187.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.6 ppm. LC–MS: m/z = 463 [M + H]$^+$. $C_{17}H_{20}IO_5P$ (462.2): calcd. C 44.18, H 4.36; found C 44.12, H 4.38.

17: Yield (NMR; isolated): 64%; 0.25 g (55%). M.p. 118–122 °C. IR (KBr): $\tilde{\nu}$ = 2963, 1682, 1593, 1495, 1462, 1318, 1254, 1146, 1125, 1057, 1011 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.83–0.87 (m, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3), 2.19–2.25 (m, 1 H, CH_AH$_B$), 2.56–2.60 (m, 1 H, CH$_A$$H_B$), 3.87–3.93 (m, 2 H, OCH_2), 4.00 (s, 3 H, OCH_3), 4.25–4.30 (m, 2 H, OCH_2), 6.01 [d, J = 9.8 Hz, 1 H, =(CH)P], 7.46 (s, 1 H, Ar), 7.61 (s, 1 H, Ar), 9.88 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.9, 21.4, 21.8, 25.2, 32.0, 32.6 (d, J = 5.0 Hz), 56.3, 75.3 (d, J = 2.0 Hz), 75.3$_1$ (d, J = 2.0 Hz), 97.8 (d, J = 5.0 Hz), 98.5 (d, J = 199.0 Hz), 113.2, 118.6, 126.6 (d, J = 23.0 Hz), 131.0, 146.0, 157.1, 163.8 (d, J = 9.0 Hz), 190.1 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.8 ppm. LC–MS: m/z = 379 [M – H]$^+$. $C_{19}H_{25}O_6P$ (380.4): calcd. C 60.00, H 6.62; found C 59.97, H 6.70.

18: Yield (NMR; isolated): 63%; 0.26 g (57%). M.p. 126–130 °C. IR (KBr): $\tilde{\nu}$ = 2973, 2880, 1807, 1690, 1605, 1487, 1329, 1256 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.81–0.86 (m, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3), 2.15–2.20 (m, 1 H, CH_AH$_B$), 2.49–2.54 (m, 1 H, CH$_A$$H_B$) 3.90–3.94 (m, 2 H, OCH_2), 4.22–4.27 (m, 2 H, OCH_2), 6.07 [d, J = 10.1 Hz, 1 H, =(CH)P], 7.00–8.02 (m, 3 H, Ar), 9.90 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.9, 21.4, 21.6, 24.9, 32.0, 32.6 (d, J = 6.0 Hz), 75.3 (d, J = 3.0 Hz), 75.4 (d, J = 3.0 Hz), 96.7, 98.9 (d, J = 198.0 Hz), 111.6, 123.8, 126.4 (d, J = 23.0 Hz), 130.2, 136.3, 163.2 (d, J = 9.0 Hz), 167.1, 190.2 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.5 ppm. LC–MS: m/z = 351 [M + H]$^+$. $C_{18}H_{23}O_5P$ (350.4): calcd. C 61.71, H 6.62; found C 61.69, H 6.58.

19: Yield (NMR; isolated): 63%; 0.25 g (57%). M.p. 136–140 °C. IR (KBr): $\tilde{\nu}$ = 2971, 1688, 1591, 1464, 1323, 1275, 1059, 1007, 828 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84–0.89 (m, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3), 2.21–2.27 (m, 1 H, CH_AH$_B$), 2.50–2.56 (m, 1 H, CH$_A$$H_B$), 3.88–3.95 (m, 2 H, OCH_2), 4.24–4.29 (m, 2 H, OCH_2), 6.05 [d, J = 9.6 Hz, 1 H, =(CH)P], 7.97–8.27 (m, 2 H, Ar), 9.8 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.4, 21.9, 22.2, 25.5, 32.6, 33.1 (d, J = 5.0 Hz), 75.9 (d, J = 4.0 Hz), 97.9 (d, J = 5.0 Hz), 101.2 (d, J = 198.0 Hz), 123.6, 126.4 (d, J = 23.0 Hz), 132.3, 144.9, 163.8, 163.9, 167.4, 189.4 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.6 ppm. LC–MS: m/z = 477 [M + H]$^+$. $C_{18}H_{22}IO_5P$ (476.3): calcd. C 45.40, H 4.66; found C 45.42, H 4.67.

20: Yield: 0.29 g (68%). M.p. 102–104 °C. IR (KBr): $\tilde{\nu}$ = 2820, 1682, 1593, 1233, 1140, 1051 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.54 (s, 3 H, CH_3), 4.12 (s, 3 H, OCH_3), 7.41–7.87 (m, 7 H, Ar), 10.06 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.6, 56.3, 105.1, 112.1, 117.6, 126.9, 128.5, 128.7, 130.5, 132.9, 133.0, 146.0, 146.7, 152.7, 191.8 ppm. LC–MS: m/z = 267 [M + H]$^+$. $C_{17}H_{14}O_3$ (266.3): calcd. C 76.68, H 5.30; found C 76.60, H 5.31.

21: Yield: 0.38 g (69%). Gummy solid. IR (KBr): $\tilde{\nu}$ = 2832, 1688, 1593, 1454, 1263, 1173 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.53 (s, 3 H, CH_3), 7.41–8.10 (m, 8 H, Ar), 10.10 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.4, 111.6, 111.7, 122.2, 126.4, 126.8, 128.5, 128.8, 130.6, 131.9, 152.7, 157.3, 191.8 ppm. LC–MS: m/z = 237 [M + H]$^+$. $C_{16}H_{12}O_2$ (236.3): Calcd. C. 81.34, H 5.12; found C 81.32, H 5.11.

22: Yield: 0.15 g (51%). M.p. 80–84 °C. IR (KBr): $\tilde{\nu}$ = 1690, 1566, 1445, 1422, 1262, 1165, 1071, 801 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.54 (s, 3 H, CH_3), 7.28–8.23 (m, 7 H, Ar), 10.03 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.7, 75.6, 112.7, 122.0, 127.0, 128.5, 128.9, 128.9, 130.1, 131.5, 133.5, 134.7, 190.4 ppm. LC–MS: m/z = 363 [M + H]$^+$. $C_{16}H_{11}IO_2$ (362.2): calcd. C 53.06, H 3.06; found C 53.08, H 3.03. X-ray structure was done on this sample.

23: Yield: 0.28 g (66%). M.p 128–132 °C. IR (KBr): $\tilde{\nu}$ = 2714, 1688, 1584, 1485, 1356, 1298 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.68 (s, 6 H, 2 CH_3), 3.97 (s, 3 H, OCH_3), 6.43 [s, 1 H, =(CH)Ph], 7.28–7.44 (m, 7 H, Ar), 9.56 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.8, 56.1, 92.4, 110.3, 120.5, 122.5, 124.9, 127.8, 128.5, 128.7, 130.4, 136.3, 144.1, 146.0, 155.8, 190.7 ppm. LC–MS: m/z = 295 [M + H]$^+$. $C_{19}H_{18}O_3$ (294.4): calcd. C 77.53, H 6.16; found C 77.52, H 6.14. X-ray structure was done on this sample.

24: Yield: 0.26 g (62%). Gummy solid. IR (KBr): $\tilde{\nu}$ = 2978, 2818, 1692, 1599, 1480, 1445, 1285, 1198 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.54 (s, 6 H, 2 CH_3), 6.35 [s, 1 H, =(CH)-Ph], 6.83–7.70 (m, 8 H, Ar), 9.55 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.7, 91.4, 111.3, 121.0, 124.7, 127.0, 128.2, 128.3, 128.8, 129.0, 129.8, 136.3, 143.8, 166.3, 190.5 ppm. LC–MS: *m*/*z* = 265 $[M + H]^+$. $C_{18}H_{16}O_2$ (264.3): calcd. C 81.79, H 6.10; found C 81.85, H 6.19.

25: Yield: 0.09 g (52%). M.p. 122–126 °C. IR (KBr): $\tilde{\nu}$ = 2851, 1682, 1586, 1416, 1262, 1094, 801 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.58 (s, 6 H, 2 CH_3), 6.47 [s, 1 H, =(CH)-Ph], 7.39–7.48 (m, 5 H, Ar), 7.66 (s, 1 H, Ar), 8.13 (s, 1 H, Ar), 9.56 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.8, 75.9, 92.0, 122.5, 124.6, 126.2, 128.1, 128.2, 128.9, 131.4, 135.8, 141.1, 143.9, 165.9, 189.1 ppm. LC–MS: *m*/*z* = 391 $[M + H]^+$. $C_{18}H_{15}IO_2$ (390.2): calcd. C 55.40, H 3.87; found C 55.44, H 3.88.

General Procedure for the Preparation of Compounds 28–31: To a 25-mL, round-bottomed flask containing allene **1b** or **27** (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), substituted iodophenol (1.67 mmol), and CsF (0.420 g, 2.78 mmol), was added PEG-400 (5 mL) under a N_2 atmosphere. The contents were heated at 90–100 °C for 12 h, quenched with water (5 mL), extracted with diethyl ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (hexane/EtOAc) to afford desired products **28**–**31**.

28: Yield (NMR; isolated): 64%; 0.31 g (60%). M.p. 150–154 °C. IR (KBr): $\tilde{\nu}$ = 2973, 1694, 1595, 1485, 1368, 1265, 1134 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.81 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 2.50 (d, 3 H, CH_3), 3.26 (d, *J* = 20.6 Hz, 2 H, PCH_2), 3.63–3.70 (m, 2 H, OCH_2), 4.10 (s, 3 H, OCH_3), 4.22–4.26 (m, 2 H, OCH_2), 7.35 (s, 1 H, Ar), 7.68 (s, 1 H, Ar), 10.02 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 12.2 (d, *J* = 3.0 Hz), 21.0 (d, *J* = 143.0 Hz), 21.1, 21.3, 32.5 (d, *J* = 6.0 Hz), 56.2, 74.8 (d, *J* = 7.0 Hz), 103.9, 106.2, (d, *J* = 11.0 Hz), 118.0, 130.7, 133.2, 145.6, 146.6, 154.8 (d, *J* = 11.0 Hz), 191.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.9 ppm. LC–MS: *m*/*z* = 353 $[M + H]^+$. $C_{17}H_{21}O_6P$ (352.3): calcd. C 57.95, H 6.01; found C 58.07, H 6.00.

29: Yield (NMR; isolated): 66%; 0.28 g (58%). M.p. 168–172 °C. IR (KBr): $\tilde{\nu}$ = 2965, 2903, 1684, 1628, 1586, 1476, 1346, 1254, 1055, 1005 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.82 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 2.49–2.50 (d, 3 H, CH_3), 3.26 (d, *J* = 20.1 Hz, 2 H, PCH_2), 3.64–3.71 (m, 2 H, OCH_2), 4.22–4.26 (m, 2 H, OCH_2), 7.49–8.07 (m, 3 H, Ar), 10.06 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 12.2 (d, *J* = 3.0 Hz), 20.5 (d, *J* = 142.0 Hz), 21.1, 21.2, 32.5 (d, *J* = 5.0 Hz), 74.7 (d, *J* = 7.0 Hz), 105.6 (d, *J* = 11.0 Hz), 111.4, 122.5, 125.1, 129.6 (d, *J* = 2.0 Hz), 132.0, 155.1 (d, *J* = 11.0 Hz), 157.3, 191.9 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 23.0 ppm. LC–MS: *m*/*z* = 323 $[M + H]^+$. $C_{16}H_{19}O_5P$ (322.3): calcd. C 59.63, H 5.94; found C 59.61, H 5.91.

30: Yield (NMR; isolated): 70%; 0.25 g (63%). M.p. 198–200 °C. IR (KBr): $\tilde{\nu}$ = 2892, 1688, 1618, 1595, 1481, 1404, 1366, 1258, 1142, 1011, 988 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 3.65–3.82 (m, 2 H, OCH_2), 4.07 (s, 3 H, OCH_3), 4.19–4.25 (m, 2 H, OCH_2), 4.73 [d, *J* = 24.8 Hz, 1 H, P(CH)], 7.28–7.48 (m, 7 H, Ar), 8.18 (s, 1 H, Ar), 9.90 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.3, 21.5, 32.6 (d, *J* = 7.0 Hz), 39.6 (d, *J* = 137.3 Hz), 56.3, 76.0 (d, *J* = 6.9 Hz), 104.9, 116.3 (d, *J* = 4.6 Hz), 118.1, 128.0 (d, *J* = 2.9 Hz), 128.9 (d, *J* = 2.3 Hz), 129.0, 129.4 (d, *J* = 6.1 Hz), 133.2, 134.1 (d, *J* = 7.6 Hz), 145.6 (d, *J* = 6.2 Hz), 146.3, 148.1, 191.6 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.4 ppm. LC–MS: *m*/*z* = 415 $[M + H]^+$. $C_{22}H_{23}O_6P$ (414.4): calcd. C 63.77, H 5.59; found C 63.58, H 5.62. X-ray structure was done on this sample.

31: Yield (NMR; isolated): 63%; 0.25 g (55%). M.p. 198–200 °C. IR (KBr): $\tilde{\nu}$ = 2803, 1682, 1586, 1476, 1061, 1013 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.85 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3), 3.66–3.83 (m, 2 H, OCH_2), 4.18–4.24 (m, 2 H, OCH_2), 4.74 [d, *J* = 24.4 Hz, 1 H, P(CH)], 7.28–7.86 (m, 8 H, Ar), 8.20 (s, 1 H, Ar), 9.97 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ = 21.3, 21.5, 32.6 (d, *J* = 6.6 Hz), 39.3 (d, *J* = 137.0 Hz), 75.9_8 (d, *J* = 5.8 Hz), 76.0 (d, *J* = 6.4 Hz), 112.4, 115.9 (d, *J* = 4.5 Hz), 123.0, 126.4, 127.9, 128.1, 128.9 (d, *J* = 2.5 Hz), 129.4, 132.0, 134.0 (d, *J* = 7.5 Hz), 145.8 (d, *J* = 6.7 Hz), 158.5, 191.7 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.4 ppm. LC–MS: *m*/*z* = 384 $[M]^+$. $C_{21}H_{21}O_5P$ (384.4): calcd. C 65.62, H 5.51; found C 65.55, H 5.58.

General Procedure for the Synthesis of 35a,b and 36: To NaH (0.026 g, 1.12 mmol) and the appropriate phosphonate (**32** or **33**; 0.75 mmol) in dry THF (10 mL) at 0 °C was added aldehyde (0.200 g, 0.75 mmol). The contents were stirred at room temperature for 12 h. Water (20 mL) was added, and the aqueous layer thoroughly extracted with diethyl ether (3 × 20 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated to give crude product, which was subjected to column chromatography (hexane/EtOAc) to afford desired products **35a**,**b** and **36**.

35a: Yield (combined with **35b**; isolated): >64%; 0.07 g (32%). M.p. 98–102 °C. IR (KBr): $\tilde{\nu}$ = 2963, 2922, 1603, 1508, 1460, 1250, 1171, 1144 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.35 (s, 3 H, CH_3), 3.68 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.44 [s, 1 H, =(CH)Ph], 6.83–7.79 (m, 11 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.7, 55.4, 55.7, 107.6, 108.7, 111.6, 112.6, 113.2, 113.8, 114.0, 125.1, 126.8, 128.0, 128.6, 128.7, 130.3, 130.9, 131.1, 131.8, 132.7, 142.6, 144.5, 151.5, 160.0 ppm. LC–MS: *m*/*z* = 405 $[M]^+$, 407 $[M + 2H]^+$. $C_{25}H_{21}ClO_3$ (404.9): calcd. C 74.16, H 5.23; found C 74.15, H 5.21.

35b: Yield (combined with **35a**; isolated): >64%; 0.07 g (32%). M.p. 146–150 °C. IR (KBr): $\tilde{\nu}$ = 2959, 1613, 1591, 1505, 1458, 1240, 1173, 1146, 1034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.47 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 4.07 (s, 3 H, OCH_3), 6.92–7.50 [m, 12 H, =(CH)Ph and Ar] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.7, 55.4, 56.3, 108.6, 111.7, 113.2, 113.8, 125.1, 126.9, 128.0, 128.6, 130.7, 130.9, 131.1, 132.1, 132.8, 142.6, 144.6, 151.5, 160.0 ppm. LC–MS: *m*/*z* = 405 $[M]^+$, 407 $[M + 2H]^+$. $C_{25}H_{21}ClO_3$ (404.9): calcd. C 74.16, H 5.23; found C 74.19, H 5.25. X-ray structure was done on this sample.

36: Yield: 0.30 g (77%). M.p. 204–206 °C. IR (KBr): $\tilde{\nu}$ = 3015, 2930, 1613, 1601, 1318, 1227, 1142 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.55 (s, 3 H, CH_3), 4.18 (s, 3 H, OCH_3), 7.00–8.64 [m, 17 H, =(CH) Ph and Ar] ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.71, 56.4, 105.4, 110.6, 111.7, 122.5, 123.2, 125.2, 125.4, 125.6, 126.1, 126.7, 126.9, 127.0, 128.1, 128.2, 128.6, 128.7, 130.4, 130.6, 131.1, 132.8, 133.3, 133.9, 138.6, 143.3, 145.4 ppm. LC–MS: *m*/*z* = 519 $[M]^+$, 521 $[M + 2H]^+$. $C_{32}H_{23}BrO_2$ (519.4): calcd. C 73.99, H 4.46; found C 74.06, H 4.47.

Synthesis of 37: To a solution of *n*BuLi (1.6 M in hexane, 0.42 mL) in dry ether (15 mL) was cautiously added the ylide (0.254 g, 0.68 mmol; obtained from PPh_3 and EtBr in toluene), and the mixture was stirred at room temperature. After 4 h, aldehyde (0.200 g,

0.68 mmol) was added and stirring was continued. After 12 h, the mixture was filtered, and the precipitate was washed with diethyl ether (2 × 10 mL). The combined organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/EtOAc) to afford desired product **37**. Yield: 0.13 g (83%; *E*/*Z* = 2:1). M.p. 72–76 °C. IR (KBr): $\tilde{\nu}$ = 2961, 1597, 1460, 1223, 1144 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.90–1.92 and 1.95–1.97 (m, 3 H for two isomers, CH_3), 2.44 and 2.45 (s, 3 H for two isomers, CH_3), 4.03_6 and 4.03_9 (s, 3 H for two isomers, OCH_3), 5.70–5.85 (m, 2 H, 2 =CH for minor isomer), 6.19–6.24 (m, 2 H, 2 =CH for major isomer), 6.47–7.83 (m, 8 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.6, 13.7, 17.4, 55.1, 55.2 103.9, 107.4, 108.3, 110.6, 110.9, 123.4, 124.8, 125.7_6, 125.7_9, 126.8, 127.2, 127.5, 129.4, 130.2, 130.5, 131.7, 131.9, 132.0, 132.7, 140.9, 141.4, 143.6, 144.0, 150.2 ppm. LC–MS: *m*/*z* = 279 $[M + H]^+$. $C_{19}H_{18}O_2$ (278.4): calcd. C 81.99, H 6.52; found C 82.02, H 6.52.

38: Yield: 0.05 g (60%; *E*/*Z* = 3:1). M.p. 108–112 °C. IR (KBr): $\tilde{\nu}$ = 3472, 1682, 1595, 1462, 1400, 1370, 1290, 1142 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.62 (s, 3 H, CH_3), 4.09 (s, 3 H, OCH_3), 7.08–7.98 (m, 9 H, Ar), 10.07 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 12.8, 56.2, 104.6, 114.9, 118.3, 118.5, 126.2, 126.7, 127.8, 128.8, 130.0, 133.4, 137.4, 145.7, 147.1, 155.3, 191.8 ppm. LC–MS: *m*/*z* = 293 $[M + H]^+$. $C_{19}H_{16}O_3$ (292.3): calcd. C 78.06, H 5.52; found C 78.21, H 5.58.

Preparation of Phosphane Oxides [$(C_6H_5)_2P(O)(2\text{-}OH\text{-}C_6H_4)$] (39) and [$(4\text{-}MeO\text{-}C_6H_4)_2P(O)(2\text{-}(OH)\text{-}C_6H_4)$] (40): Compound **39** was obtained originally as a first fraction while performing the column chromatography of the reaction mixture from allenylphosphonates **1b**,**c** with 2-iodophenol in the molar ratio 1:1.2 [conditions: $Pd(OAc)_2/Ph_3P/CH_3CN$/80–90 °C/24 h]. Yield: 0.03 g [30% while using 0.097 g (0.37 mmol) of Ph_3P]. This compound was also prepared by straightforward reaction of Ph_3P with 2-iodophenol. Thus, to a solution of PPh_3 (0.2 g, 0.763 mmol), $Pd(OAc)_2$ (0.009 g, 0.04 mmol), and 2-iodophenol (0.2 g, 0.916 mmol) in dry acetonitrile (8 mL) was added K_2CO_3 (0.211 g, 1.5 mmol). The mixture was heated under reflux for 18–20 h, quenched with water, extracted with diethyl ether, dried (Na_2SO_4), and filtered, and the filtrate was concentrated under vacuum. Compound **39** was isolated by using column chromatography (EtOAc/hexane, 15:85). Yield: 0.023 g (10% based on triphenylphosphane). M.p. 226–228 °C. IR (KBr): $\tilde{\nu}$ = 3100 (br.), 1591, 1439, 1375, 1302, 1173, 1098, 1071 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.85–7.70 (m, 14 H, Ar), 11.2 (s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C, TMS): δ = 117.0, 119.7, 128.8, 128.9, 131.7, 131.8, 132.2, 133.1, 133.8, 133.9, 134.1, 134.7, 161.0 ppm (Due to the low solubility in $CDCl_3$, the ^{13}C NMR data was recorded in [D_6]DMSO solution). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 39.6 ppm. LC–MS: *m*/*z* = 295 $[M + H]^+$. X-ray structure was determined for this sample.

Compound **40** was synthesized in a manner similar to compound **39** in the absence of allene by using $P(4\text{-}MeOC_6H_4)_3$ (0.10 g). Yield: 0.020 g (20% based on phosphane). M.p. 158–160 °C. IR (KBr): $\tilde{\nu}$ = 3400 (br.), 1593, 1441, 1385, 1304, 1154, 1099, 1019 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.87 (s, 6 H, 2 OCH_3), 6.83–7.65 (m, 12 H, Ar), 11.3 (s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 55.4, 112.2 (d, *J* = 104.5 Hz), 114.2 (d, *J* = 13.4 Hz), 118.4 (d, *J* = 7.4 Hz), 118.9 (d, *J* = 12.3 Hz), 123.2 (d, *J* = 111.1 Hz), 131.9 (d, *J* = 9.9 Hz), 134.0 (d, *J* = 11.9 Hz), 134.1, 162.9, 163.8 (2 d, *J* ≈ 2.6 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 39.3 ppm. LC–MS: *m*/*z* = 355 $[M + H]^+$. $C_{20}H_{19}O_4P$ (354.34): calcd. C 67.79, H 5.40; found C 67.91, H 5.45.

Preparation of 45 and 46 by Reaction of 44 with 2-Iodobenzoic Acid: To allene **44** (0.20 g, 1.6 mmol), $Pd(OAc)_2$ (0.018 g, 0.08 mmol), PPh_3 (0.063 g, 0.24 mmol), 2-iodobenzoic acid (0.476 g, 1.92 mmol), and K_2CO_3 (0.442 g, 3.2 mmol) was added dry CH_3CN (5 mL), and the contents were heated under reflux for 6 h. The reaction mixture was quenched with water, extracted with diethyl ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated under vacuum. The residue was subjected to column chromatography (silica gel, hexane) to afford product **46** followed by **45**.

45: Yield: 0.10 g (26%). M.p. 120–122 °C. IR (KBr): $\tilde{\nu}$ = 1736, 1647, 1601, 1373, 1211, 1076 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.98 [s, 3 H, $C(O)CH_3$], 2.12 and 2.13 (2 s, 6 H, 2 CH_3), 7.44–8.14 (m, 5 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.9, 21.4, 22.8, 91.4, 121.2, 124.1, 127.7, 128.4, 130.0, 133.3, 135.7, 140.5, 169.0 ppm. X-ray structural analysis was done for this compound.

46: Yield: 0.162 g (56%). Viscous liquid. IR (KBr): $\tilde{\nu}$ = 1730, 1628, 1603, 1483, 1238, 1105, 1009 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.09 (s, 3 H, CH_3), 5.14 and 5.35 (2 s, 2 H, $=CH_2$), 7.17 (s, 1 H, Ar), 7.49–8.36 (m, 4 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 23.8, 118.5, 121.5, 122.1, 124.4, 128.4, 130.1, 134.7, 136.2, 137.7, 140.8, 162.2 ppm. GC–MS: *m*/*z* = 186 $[M]^+$.

Synthesis of Benzopyrans (Isochromans) 50–54: To allene **1c**,**d** or **2b** (1.39 mmol), $Pd(OAc)_2$ (0.016 g, 0.074 mmol), (o-tolyl)$_3$P (0.094 g, 0.21 mmol), 2-iodobenzyl alcohol (1.67 mmol), and K_2CO_3 (0.384 g, 2.78 mmol) was added DMF (5 mL) under a N_2 atmosphere. The contents were heated at 90–100 °C for 24 h. The mixture was then quenched with water (5 mL), extracted with diethyl ether (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/EtOAc) to afford products **50**–**54**.

50: Yield (NMR; isolated): 73%; 0.40 g (55%). M.p. 148–150 °C. IR (KBr): $\tilde{\nu}$ = 1597, 1458, 1368, 1258, 1163, 1057, 1001 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.83 and 1.20 (2s, 6 H, 2 CH_3), 1.47 (s, 6 H, 2 CH_3), 3.65–3.83 (m, 4 H, 2 OCH_2), 4.80 (s, 2 H, OCH_2), 5.65 [d, *J* = 12.7 Hz, 1 H, =(CH)P], 7.08 (d, *J* = 8.0 Hz, 1 H, Ar), 7.32–7.38 (m, 2 H, Ar), 8.14 (d, *J* = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.8, 21.8, 26.3, 32.4 (d, *J* = 6.1 Hz), 63.5, 76.0 (d, *J* = 6.1 Hz), 76.3 (d, *J* = 6.0 Hz), 106.1 (d, *J* = 179.6 Hz), 123.5, 126.7, 129.3 (d, *J* = 7.9 Hz), 130.1, 130.5, 136.5, 160.9 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.5 ppm. LC–MS: *m*/*z* = 322 $[M]^+$. $C_{17}H_{23}O_4P$ (322.3): calcd. C 63.35, H 7.19; found C 63.40, H 7.17.

51: Yield (NMR; isolated): 75%; 0.26 g (60%). M.p. 178–180 °C. IR (KBr): $\tilde{\nu}$ = 2975, 1597, 1458, 1258, 1053, 999 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84 (s, 3 H, CH_3), 0.88–0.92 (t, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.66–1.80 (m, 2 H, CH_2), 3.51–3.92 (m, 4 H, OCH_2), 4.74–4.79 (m, 2 H, OCH_2), 5.59 [d, *J* = 12.8 Hz, 1 H, =(CH)P], 7.09–7.40 (m, 3 H, Ar), 8.12–8.14 (d, 1 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.4, 20.9, 21.8, 24.1, 31.9, 32.3, 63.4, 76.0 (d, *J* = 5.9 Hz), 76.4 (d, *J* = 6.0 Hz), 78.9, 106.4 (d, *J* = 179.8 Hz), 123.5, 126.9, 130.1, 130.3, 137.0, 160.8 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.3 ppm. LC–MS: *m*/*z* = 337 $[M + H]^+$. $C_{18}H_{25}O_4P$ (336.4): calcd. C 64.27, H 7.49; found C 64.37, H 7.48.

52: Yield (NMR; isolated): 76%; 0.21 g (57%). M.p. 158–162 °C. IR (KBr): $\tilde{\nu}$ = 2957, 1605, 1476, 1256, 1111, 1057, 1007 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.66 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 3.53–3.58 (m, 2 H, OCH_2), 3.94–4.00 (m, 2 H, OCH_2), 4.84 (s, 2 H, OCH_2), 5.03–5.04 (d, 2 H, OCH_2), 6.60–7.31

(m, 9 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 21.0, 21.8, 32.3 (d, J = 6.1 Hz), 68.3 (d, J = 7.6 Hz), 68.6, 75.9, 124.4, 124.8 (d, J = 175.5 Hz), 125.6, 127.8, 128.8, 129.9, 130.5, 131.3 (d, J = 21.9 Hz), 137.4 (d, J = 8.2 Hz), 137.8, 147.7 (d, J = 13.7 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.7 ppm. LC–MS: m/z = 371 $[M + H]^+$. $C_{21}H_{23}O_4P$ (370.4): calcd. C 68.10, H 6.26; found C 68.12, H 6.25.

53: Yield: 0.43 g (62%). M.p. 36–38 °C. IR (KBr): $\tilde{\nu}$ = 3038, 2832, 1817, 1626, 1483, 1451, 1368, 1024 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.76 [d, J = 1.2 Hz, 1 H, (CH)Ph], 4.77 (AB q, $J \approx$ 12.2 Hz, 2 H, OCH_2), 5.41 (s, 1 H, $=CH_AH_B$), 5.79 (s, 1 H, $=CH_AH_B$), 7.05–7.42 (m, 11 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 66.5, 80.3, 110.2, 123.8, 124.5, 127.0, 127.9$_6$, 128.0$_2$, 128.1, 128.4, 131.7, 134.5, 139.4, 141.3 ppm. GC–MS: m/z = 222 $[M]^+$. $C_{16}H_{14}O$ (222.3): calcd. C 86.45, H 6.35; found C 86.56, H 6.28.

54: Yield: 0.24 g (50%). Viscous liquid. IR (KBr): $\tilde{\nu}$ = 1722, 1597, 1485, 1447, 1364, 1144, 1088 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.50 (s, 6 H, 2 CH_3), 4.81 (s, 2 H, OCH_2), 6.66 [s, 1 H, =(CH)Ph], 6.93–7.29 (m, 9 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 26.9, 63.9, 75.6, 123.3, 124.1, 125.8, 126.8, 127.4, 128.3, 129.2, 129.8, 137.3, 138.1 ppm. $C_{18}H_{18}O$ (250.3): calcd. C 86.36, H 7.25; found C 86.32, H 7.22.

Synthesis of 1,3-Butadienes 55 and 56: To a solution of allene **1c** or **2b** (1.38 mmol), $Pd(OAc)_2$ (0.016 g, 0.069 mmol), PPh_3 (0.046 g, 0.207 mmol), and 2-iodophenylacetic acid (0.434 g, 1.660 mmol) in acetonitrile (10 mL) was added Et_3N (0.280 g, 2.760 mmol) under a N_2 atmosphere. Use of K_2CO_3 was not possible because of the formation of an insoluble salt. The mixture was heated under reflux for 16–18 h, quenched with water, extracted with diethyl ether (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was subjected to column chromatography (hexane/EtOAc) to afford products **55** or **56**.

55: Yield: 0.375 g (80%). M.p. 158–160 °C. IR (KBr): $\tilde{\nu}$ = 3422, 1721, 1588, 1231, 1159, 1063, 986 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.00 and 1.07 (2 s, 6 H, 2 CH_3), 2.08 (s, 3 H, CH_3), 3.55 (dd→q, J = 15.1 Hz, 2 H, OCH_2), 3.76 (t, $J \approx$ 11.6 Hz, 1 H, CH_AH_BPh), 3.92 (dd→q, $J \approx$ 11.6 Hz, 2 H, OCH_2), 4.11 (t, $J \approx$ 11.5 Hz, 1 H, CH_AH_BPh), 4.73 and 5.40 (2 s, 2 H, $=CH_AH_B$), 6.04 [d, J = 18.9 Hz, 1 H, =(CH)P], 7.02–7.41 (m, 4 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.7, 21.3, 21.4, 32.5 (d, J = 6.0 Hz), 39.9, 75.9, 75.6 (2 d, J = 6.0 Hz each), 112.1 (d, J = 187.9 Hz), 125.3, 126.7, 128.5, 129.2, 132.2, 136.9, 142.5, 142.9, 162.6, 172.3 ppm. ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.6 ppm. X-ray structural analysis was done for this compound.

56: Yield: 0.347 g (60%). M.p. 198–200 °C. IR (KBr): $\tilde{\nu}$ = 3414, 1709, 1491, 1451, 1233, 1159, 926 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.15 (s, 3 H, CH_3), 3.43 (dd→q, J = 16.4, 18.4 Hz, 2 H, $PhCH_2$), 4.53 and 5.05 (2 s, 2 H, $=CH_2$), 6.77 [s, 1 H, =(CH)Ph], 6.80–7.36 (m, 9 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.8, 38.0, 117.8, 127.0, 128.0, 128.3, 128.5, 128.6, 129.1, 129.3, 130.2, 130.4, 130.8, 132.1, 136.6, 139.6, 141.2, 144.3, 177.8 ppm. $C_{19}H_{18}O_2$ (278.4): calcd. C 81.98, H 6.52; found C 81.97, H 6.53.

X-ray Crystallography: Single-crystal X-ray data were collected with a Bruker AXS-SMART diffractometer by using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by the full-matrix least-squares method by using standard procedures.[23] Absorption corrections were done with the 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. CCDC-738742 (for **15**), -738743 (for **22**), -738744 (for **23**), -738745 (for **30**), -738746 (for **35b**), -738747 (for **39**), -738748 (for **42+43**), -738749 (for **45**), -738750 (for **51**), and -738751 (for **55**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 15: $C_{17}H_{21}O_5P$, M = 336.31, orthorhombic, space group $Pbca$, a = 15.453(3) Å, b = 11.092(2) Å, c = 20.668(4) Å, V = 3542.9(12) Å^3, Z = 8, μ = 0.176 mm^{-1}, data/restraints/parameters: 3122/0/212, R indices [$I > 2\sigma(I)$]: R_1 = 0.0547, wR_2 (all data) = 0.1269.

Crystal Data for 22: $C_{16}H_{11}IO_2$, M = 362.15, monoclinic, space group $P2_1/c$, a = 7.5106(17) Å, b = 10.308(2) Å, c = 17.818(4) Å, β = 93.047(4)° V = 1377.5(5) Å^3, Z = 4, μ = 2.319 mm^{-1}, data/restraints/parameters: 2430/0/174, R indices [$I > 2\sigma(I)$]: R_1 = 0.0239, wR_2 (all data) = 0.0611.

Crystal Data for 23: $C_{19}H_{18}O_3$, M = 294.33, triclinic, space group $P\bar{1}$, a = 9.1407(6) Å, b = 9.4304(6) Å, c = 18.9283(13) Å, α = 83.9640(10)°, β = 80.3730(10)°, γ = 88.3500(10)°, V = 1599.63(18) Å^3, Z = 4, μ = 0.082 mm^{-1}, data/restraints/parameters: 5619/0/403, R indices [$I > 2\sigma(I)$]: R_1 = 0.0453, wR_2 (all data) = 0.1247.

Crystal Data for 30: $C_{22}H_{23}O_6P$, M = 414.37, triclinic, space group $P\bar{1}$, a = 12.457(3) Å, b = 13.536(3) Å, c = 13.599(3) Å, α = 94.92(3)°, β = 107.88(3)°, γ = 100.94(3)°, V = 2117.0(7) Å^3, Z = 4, μ = 0.165 mm^{-1}, data/restraints/parameters: 7435/0/529, R indices [$I > 2\sigma(I)$]: R_1 = 0.0599, wR_2 (all data) = 0.1036.

Crystal Data for 35b: $C_{25}H_{21}ClO_3$, M = 404.87, monoclinic, space group $P2_1/n$, a = 9.5190(19) Å, b = 16.437(3) Å, c = 13.107(3) Å, β = 106.83(3)°, V = 1962.9(7) Å^3, Z = 4, μ = 0.219 mm^{-1}, data/restraints/parameters: 3461/0/265, R indices [$I > 2\sigma(I)$]: R_1 = 0.0750, wR_2 (all data) = 0.1267.

Crystal Data for 39: $C_{18}H_{15}O_2P$, M = 294.27, orthorhombic, space group $Pna2_1$, a = 18.0934(11) Å, b = 8.2115(5) Å, c = 19.4692(12) Å, V = 2892.6(3) Å^3, Z = 8, μ = 0.191 mm^{-1}, data/restraints/parameters: 5090/402/376, R indices [$I > 2\sigma(I)$]: R_1 = 0.0622, wR_2 (all data) = 0.1500. The data for this compound was collected both at room temperature and at low temperature (100 K), as there was some disorder in the molecule. Even from the low-temperature data, there was a residual density of ca 1.8 Å^3 in the vicinity of phosphorus. For the room-temperature data refinement was done by using another model in which the residuals were taken care of; however, complete anisotropic refinement was not possible, and hence, only the low-temperature data is presented here.

Crystal Data for 42+43: $C_{14}H_{17}O_4P$, M = 280.25, orthorhombic, space group $Pbca$, a = 10.6917(9) Å, b = 12.5616(11) Å, c = 21.2188(18) Å, V = 2849.8(4) Å^3, Z = 8, μ = 0.200 mm^{-1}, data/restraints/parameters: 2503/354/265, R indices [$I > 2\sigma(I)$]: R_1 = 0.0413, wR_2 (all data) = 0.1050.

Crystal Data for 45: $C_{14}H_{14}O_4$, M = 246.25, triclinic, space group $P\bar{1}$, a = 8.1278(10) Å, b = 8.9358(11) Å, c = 10.2925(13) Å, α = 111.636(2)°, β = 110.865(2)°, γ = 93.407(2)°, V = 633.44(14) Å^3, Z = 2, μ = 0.095 mm^{-1}, data/restraints/parameters: 2226/0/166, R indices [$I > 2\sigma(I)$]: R_1 = 0.0560, wR_2 (all data) = 0.1609.

Crystal Data for 51: $C_{18}H_{25}O_4P$, M = 336.35, monoclinic, space group $P2_1$, a = 13.557(3) Å, b = 6.4360(13) Å, c = 19.936(4) Å, β = 90.00(3)° V = 1739.5(6) Å^3, Z = 4, μ = 0.175 mm^{-1}, data/restraints/parameters: 6208/1/423, R indices [$I > 2\sigma(I)$]: R_1 = 0.0879, wR_2 (all data) = 0.1789. Although the data suggested orthorhombic space group ($P222_1$), it was not possible in our hands to solve the structure in this space group. WINGX suggested only the monoclinic space group as given here.

Crystal Data for 55: $C_{18}H_{23}O_5P$, M = 350.33, monoclinic, space group $P2_1/c$, a = 10.2373(7) Å, b = 9.1781(6) Å, c = 19.7894(13) Å, β = 101.8320(10)°, V = 1819.9(2) Å^3, Z = 4, μ = 0.174 mm^{-1}, data/restraints/parameters: 4361/0/224, R indices [$I > 2\sigma(I)$]: R_1 = 0.0533, wR_2 (all data) = 0.1431.

Supporting Information (see footnote on the first page of this article): General experimental section, additional ORTEP drawings, and copies of the ^{1}H and ^{13}C NMR spectra.

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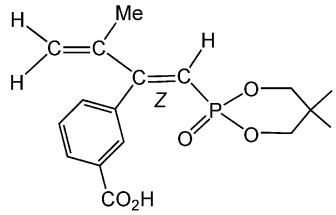

I (50 %; δ_P = 12.5 ppm)

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