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Cycloaddition Reactions of Allenylphosphonates and Related Allenes with Dialkyl Acetylenedicarboxylates, 1,3-Diphenylisobenzofuran, and Anthracene

K. V. Sajna, Ramesh Kotikalapudi, Manab Chakravarty, N. N. Bhuvan Kumar, and K. C. Kumara Swamy*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, A. P., India

kckssc@yahoo.com; kckssc@uohyd.ernet.in

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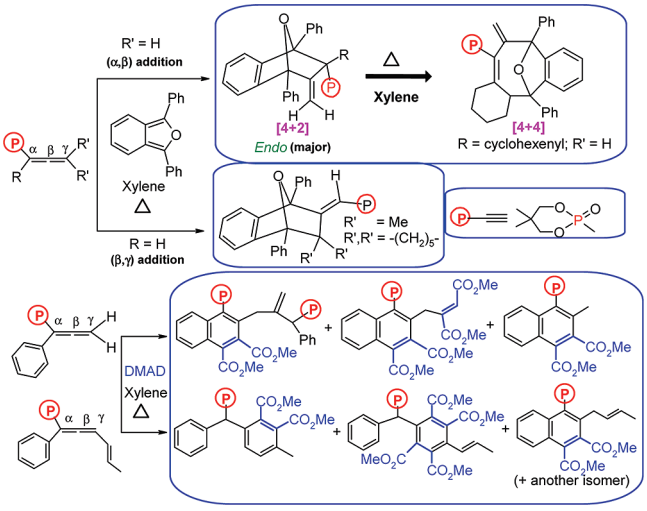

Cycloaddition reactions of allenylphosphonates $[(RO)_2P(O)[(R^1)C{=}C{=}CR^2{}_2]$ with dialkyl acetylenedicarboxylates, 1,3-diphenylisobenzofuran, and anthracene have been investigated and compared with those of allenoates $[(EtO_2C)RC{=}C{=}CH_2]$ and allenylphosphine oxides $[Ph_2P(O)(R^1)C{=}C{=}CR^2{}_2]$ in selected cases. Allenylphosphonates $(RO)_2P(O)(Ar)C{=}C{=}CH_2$ with an α-aryl group preferentially undergo [4 + 2] cycloaddition with DMAD/DEAD under thermal activation, but in addition to the expected 1:1 (allene: DMAD) product, the reaction also leads to 1:2 as well as 2:1 products that were not reported before. When an extra vinyl group is present at the γ-carbon of allenylphosphonate [e.g., $(OCH_2CMe_2CH_2O)P(O)(Ph)C{=}C{=}CH(C{=}CHMe)$], [4 + 2] cycloaddition takes place utilizing either the vinylic or the aryl end, but additionally a novel cyclization wherein complete opening of the [β,γ] carbon−carbon double bond of the allene is realized. In contrast to these, the reaction of allenylphosphonate $(OCH_2CMe_2CH_2O)P(O)(H)C{=}C{=}CMe_2$ possessing a terminal $=CMe_2$ group with DMAD occurs by both [2 + 2] cycloaddition and ene reaction. While the reaction of $=CH_2$ terminal allenylphosphonates as well as allenylphosphine oxides with 1,3-diphenylisobenzofuran afforded preferentially *endo*-[4 + 2] cycloaddition products via [α,β] attack, the analogous allenoates $[(EtO_2C)RC{=}C{=}CH_2]$ underwent *exo*-[4 + 2] cyclization. Under similar conditions, allenylphosphonates with a terminal $=CR_2$ group gave only [β,γ]-cycloaddition products. An unusual ring-opening of a [4 + 2] cycloaddition product followed by ring-closing via [4 + 4] cycloaddition, as revealed by ^{31}P NMR spectroscopy, is reported. Anthracene reacted in a manner similar to 1,3-diphenylisobenzofuran, albeit with lower reactivity. Key products, including a set of *exo*- and *endo*- [4 + 2] cycloaddition products, have been characterized by single crystal X-ray crystallography.

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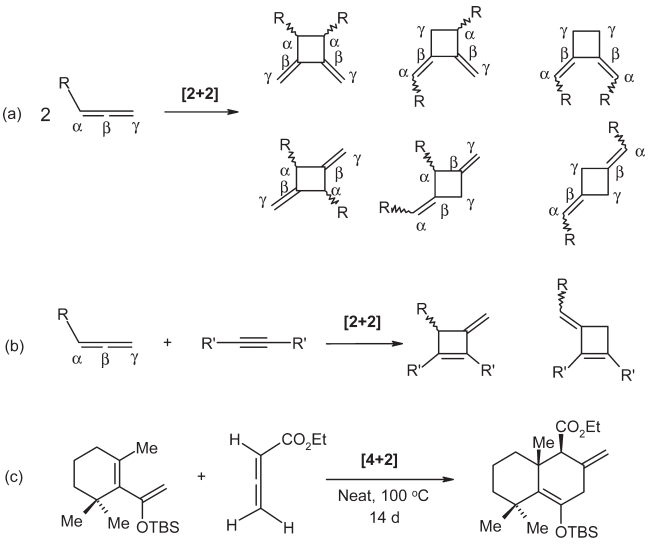
Introduction

Allenes, by virtue of their reactive and cumulative double bonds, are excellent partners for both [2 + 2] and [4 + 2] cycloaddition reactions.[1] These reactions provide an atom economical approach to a diverse range of products and hence are attractive from the synthetic chemist's point of view. As an example, the [2 + 2] cycloaddition of the monosubstituted allene $RCH{=}C{=}CH_2$ with itself or with another partner (e.g., $R'C{\equiv}CR'$) can lead to a range of cyclobutanes/cyclobutenes, with the nature of the product depending on the electronic and/or steric requirements (Scheme 1). While the intramolecular [2 + 2] version is a valuable synthetic route to bicyclic derivatives, the corresponding intermolecular [2 + 2] cycloaddition reactions serve as efficient methods for accessing strained cyclobutane/cyclobutene rings with an additional carbon−carbon

SCHEME 1



double bond for further elaboration. Allenes can also act as dienophiles in [4 + 2] cycloadditions (Scheme 1c).[2] Those precursors with an additional multiple bond [e.g., eneallenes] can themselves act as dienes[3] or take part in intramolecular [2 + 2] cycloadditions.[4] Variations like phosphine catalyzed [3 + 2] cycloadditions can pave the pathway to novel five-membered heterocycles also.[5] In addition to these, transition-metal catalyzed[6] or microwave mediated[7] cyclization offer opportunities for accelerating the sluggish reactions or for providing alternative pathways.

Allenylphosphonates (phosphorylated allenes) and allenylphosphine oxides constitute a class of compounds that are more readily accessible (and inexpensive) than most of the other allenes.[8,9] An added advantage of these precursors is the use of ^{31}P NMR spectroscopy in deciphering the reaction pathways; this aspect has been amply demonstrated on several occasions.[8a,c,e] There are only a few but important reports on cycloaddition reactions involving allenylphosphonates/allenylphosphine oxides.[10] In this paper, we primarily focus on the reaction of this class of compounds with DMAD [$MeO_2CC{\equiv}CCO_2Me$], anthracene or 1,3-diphenylisobenzofuran as the second component; it may be noted that the latter two reactants act as dienes in [4 + 2] cycloadditions,

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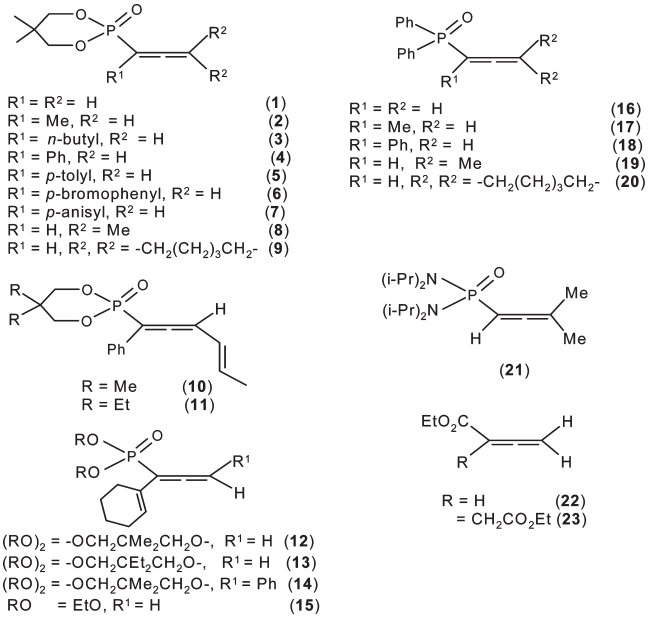
CHART 1



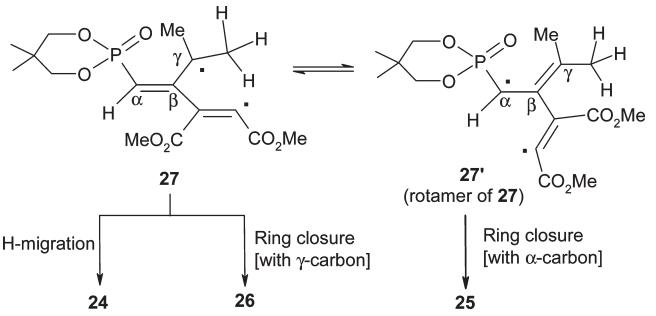
but very limited studies are reported using allenes.[10c,11] The current investigation is an effort to understand the nature and variety of products formed in these reactions. In addition to the [2 + 2] and [4 + 2] cycloadditions, we report a novel [4 + 4] cycloaddition as well as a new [2 + 2 + 2] cyclization reaction of an allene with DMAD (dimethyl acetylenedicarboxylate) /DEAD (diethyl acetylenedicarboxylate) wherein a C(β)═C(γ) allenic double bond is completely opened up.

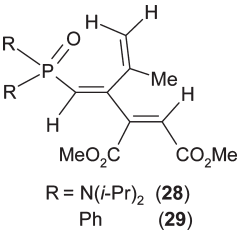
Results and Discussion

The phosphorus-based allenes **1**−**21**[8a,d,12a,b] and ester allenes **22**−**23**[8a,12c,d] used in the present study are shown in Chart 1; among these, compounds **3**, **6**, **9** and **11**−**15** are new.

(i) Reaction with Dialkyl Acetylenedicarboxylates RO$_2$CC≡CCO$_2$R [R = Me (DMAD), Et (DEAD)]. Our initial success involved the treatment of the allenylphosphonate (OCH$_2$CMe$_2$CH$_2$O)P(O)(H)C═C═CMe$_2$ (**8**) with DMAD under neat condition at 150 °C/24 h, since precursors (OCH$_2$CMe$_2$CH$_2$O)P(O)(R^1)C═C═CH$_2$ [R^1 = H (**1**), Me (**2**), (*n*-Bu (**3**)] did not undergo any perceptible reaction. The ^{31}P NMR spectrum of the reaction mixture showed several peaks, but compounds **24**−**26** were the major components [total ~85%] that could be readily isolated (Scheme 2). X-ray structures have been determined for **24** and **25** (see Supporting Information). The normal rationalization for the formation of alkylidenecyclobutenes **25**−**26** is a stepwise diradical or a concerted [2 + 2] cycloaddition.[1e,q,12b,13a,b] However, all three products **24**−**26** can also be formed via the common intermediate **27** (Scheme 3). Compound **24** can be formed[13a,c] by H-migration from **27**, and the ring closure involving γ-carbon leads to cyclobutene **26**. Similarly, the rotamer **27**′ (of **27**) affords product **25** by ring closure involving α-carbon.[14] The yield of **24** could be maximized by conducting the reaction in toluene under reflux conditions. Similar products (**28**−**29**) were also obtained upon treatment of the allenes **19** and **21** with DMAD.[15]

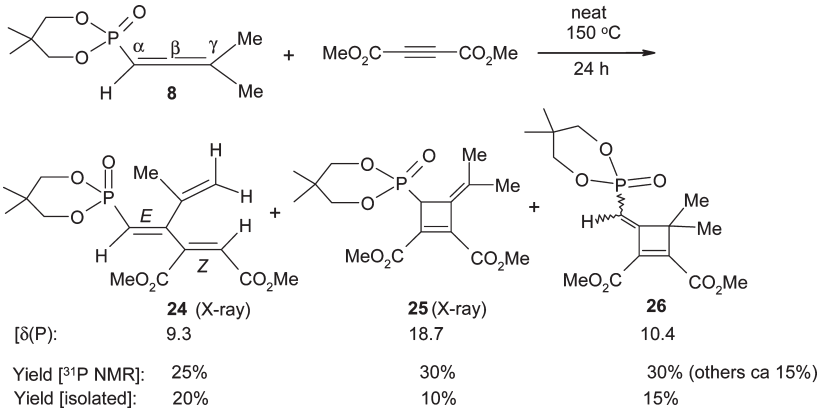
SCHEME 3



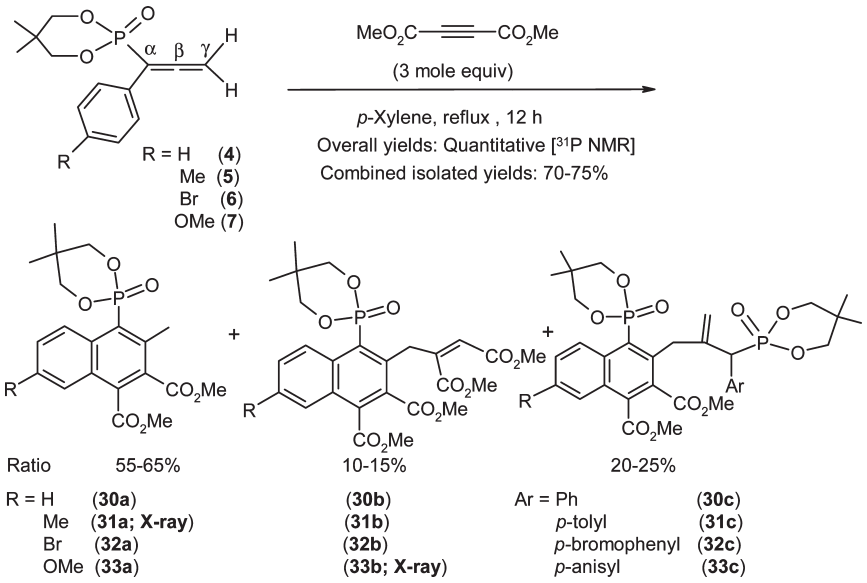


Allenes (OCH$_2$CMe$_2$CH$_2$O)P(O)(R^1)C═C═CH$_2$ [R^1 = Ph (**4**), *p*-tolyl (**5**), bromophenyl (**6**), *p*-anisyl (**7**)] with a terminal ═CH$_2$ group behaved in a manner entirely different from that of **8** (Scheme 4). The products are **30**(**a**−**c**)−**33**-(**a**−**c**). X-ray structures have been determined for **31a** and **33b** (see Supporting Information). Compound **33b** has

SCHEME 2



SCHEME 4



Z-stereochemistry at the terminal [-(MeO_2C)C=CH(CO_2Me)] moiety. Thus in each case, three distinct products are isolated. While formation of [4 + 2] cycloaddition compounds analogous to **30a-33a** has been reported recently by Ma and co-workers,[10g] the other two types of [4 + 2] cycloaddition products are new. It is clear that if an additional C=C bond is present next to the α-carbon of the allene, [4 + 2] cycloaddition is the preferred reaction. With regards to products **30b**−**33b** and **30c**−**33c**, despite relatively low yields, given the consistency with which they are formed in all the four reactions, a possible rationale is provided in Scheme 4. Although the [4 + 2] cycloaddition is expected to be concerted,[1a,b] the aromatization step is not and hence the DMAD or the allene could react further to lead to **30b**−**33b** and **30c**−**33c** (Scheme 5). A common intermediate in all these cases is **34**.

The observation made above that [4 + 2] cycloaddition is preferred over [2 + 2] under our experimental conditions is also shown in the 1:1 reaction of cyclohexenyl substituted allene **12** with DMAD wherein the product **35** is formed quantitatively (Scheme 6). However, unlike in the case of **30a**−**33a**, aromatization of the newly formed ring did not occur.[16]

Perhaps more interesting is the reaction of the vinyl allenes **10**−**11** with DMAD/DEAD using a higher molar stoichiometry of the latter reagents (Scheme 7); in 1:1 stoichiometric reaction, some unreacted allene remained. Four compounds [**36**−**39**] were formed in each case. X-ray structures for **36a**−**b** were determined (see Supporting Information). Clearly, there was competition between the vinylic end[10a,b,17] and aryl group with regards to [4 + 2] cycloaddition. The unique disubstituted products **36b**−**39b** resulted from complete opening up of the C(*β*)=C(*γ*) double bond. To our knowledge, there is no precedence for such a reaction in allene chemistry. Formation of **36a**−**39a**, **36c**−**39c** and **36d**−**39d** may be rationalized by using the pathways similar to that shown in Scheme 5. In the case of **36b**−**39b**, we believe that [2 + 2] cycloaddition happens first [cf. structure **40** in Scheme 8] followed by cyclobutene ring cleavage and subsequent addition of a second molecule o DMAD/DEAD. It may be noted that unlike compounds **25**−**26**, wherein the cyclization site on the allene is either the C(α)=C(*β*) or C(*β*)=C(*γ*) double bond, the formation of

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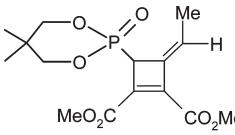
(14) Only the cyclized product was isolated in ca. 25% yield (rest: other products) from the reaction of allene ($OCH_2CMe_2CH_2O$)P−CH=C=CH-(Me) with DMAD [mp: 176−178 °C; IR: 1726 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.74 and 0.86 (2 s, 6H), 2.35 (d, *J*(H−H) ~2.0 Hz, 3H), 3.59−3.66 (m, 2H), 3.88 and 3.90 (2 s, 6H), 4.12−4.16 (m, 2H), 4.13 (d, *J*(P−H) = 22.9 Hz, 1H), 4.16 (br, 1H). ^{13}C NMR ($CDCl_3$): δ 17.4, 21.2, 25.5 (d, *J*(P-C) = 134.1 Hz, PCH), 32.3 (d, *J*(P−C) = 5.8 Hz), 52.7 and 52.8 (2 s), 74.9 (d, *J*(P−C) = 6.3 Hz), 127.9, 133.4, 133.9, 136.6, 166.8 and 167.5. ^{31}P NMR: δ 20.8.].



[δ(P): 20.8]

(15) This result may be contrasted with that of tetramethylallene Me_2C=C=CMe_2 with DMAD wherein a mixture of *Z* and *E* isomers of Me_2C=C(C(Me)=CH_2)-C(CO_2Me)=CH(CO_2Me) was obtained. See: Chia, H.-A.; Kirk, B. E.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. I* **1974**, *11*, 1209.

(16) Huisgen and coworkers have reported [4 + 2] cycloaddition using styrene as the diene and 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF) as the dienophile wherein aromaticity is lost in the final compound. This paper also deals with the competition between [4 + 2] and [2 + 2] cycloadditions. See: Brückner, R.; Huisgen, R.; Schmid, J. *Tetrahedron Lett.* **1990**, *31*, 7129.

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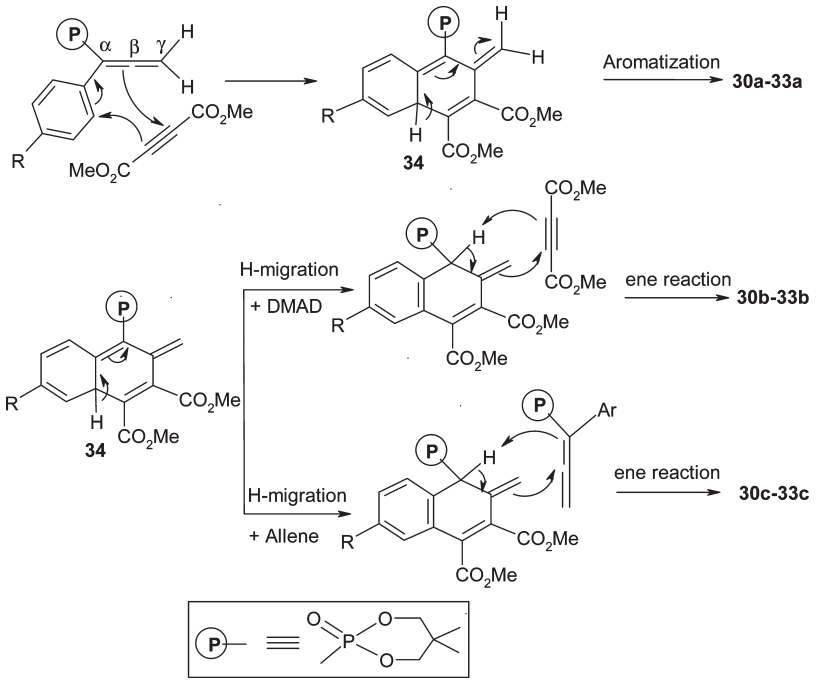
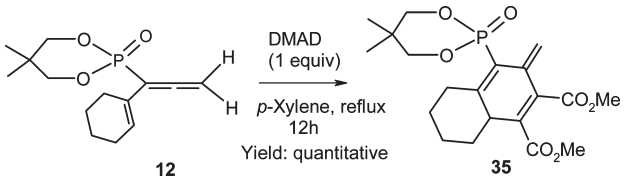
SCHEME 5



SCHEME 6



36b−**39b** involves only the C(β)═C(γ) double bond. Use of ^{31}P NMR spectroscopy in conjunction with chromatography during the course of this reaction was essential to identify and separate the products.

(ii) Reaction with 1,3-Diphenylisobenzofuran. Due to the aromatization of the six-membered ring during cycloadditions, 1,3-diphenylisobenzofuran is a very reactive diene that readily undergoes [4 + 2] cycloaddition (Diels−Alder) reaction with a wide range of dienophiles.[18] However, this feature has been utilized only to a very limited extent in allene chemistry.[11b,d] Hence we explored the reaction of allenes **1**−**5**, **7**−**9**, **19**−**20** and **22**−**23** with 1,3-diphenylisobenzofuran (Schemes 9−10) that led to the products **41**−**52**. Except in the cases of **8**−**9** and **19**−**20**, all the allenes investigated underwent Diels−Alder reaction almost exclusively at the (α,β) carbon−carbon double bond. In the cases of **8**−**9** and **19**−**20** that have terminal alkyl groups, the cycloaddition occurred only at the (β,γ) carbon−carbon double bond.

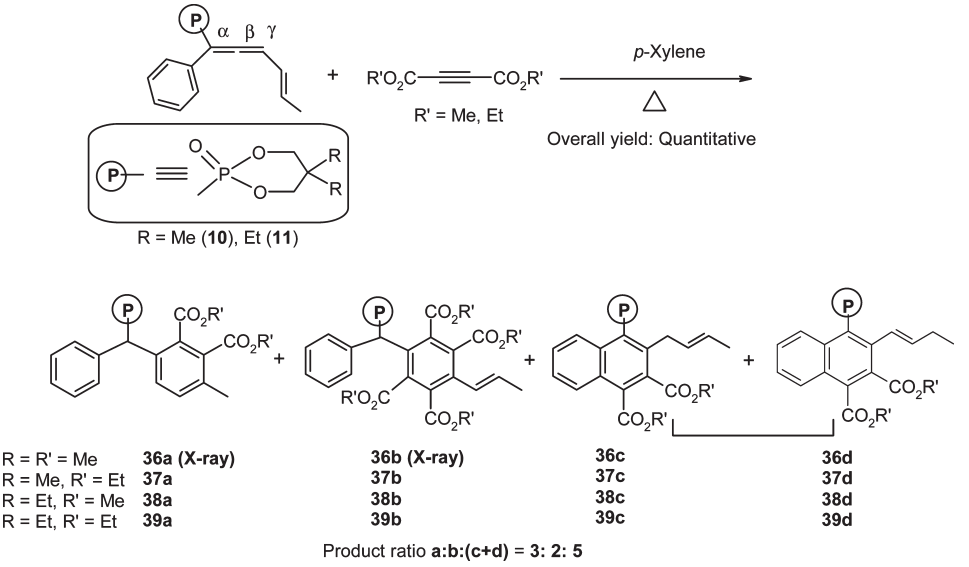
It can be readily recognized that two configurational isomers are possible for each of **41**−**48** (i.e., excluding diastereomers due to chiral centers). If we consider the phosphorus substituent, these isomers can be termed as *endo* and *exo*. In the case of phosphorus compounds the presence of isomers is readily ascertained by ^{31}P NMR spectroscopy [$\Delta\delta \approx +3$ ppm]. In four cases [**43a**−**b, 45a**−**b, 46a**−**b** and **47a**−**b**], we have been successful in isolating both these isomers. Delightedly, X-ray structures were obtained for both *endo* and *exo* *p*-anisyl substituted isomers **46a** and **46b** [see Supporting Information]. Structures of **44a**, **47a** and **52** were also determined to further confirm their identities. Although the *endo* isomer was the major product in the case of **41**−**46**, there appeared to be a reversal in the reactions using allenoates **22**−**23** that lead to the products **47**−**48** in which the *exo*-(with respect to CO_2Et group) isomer [**47b** or **48b**] was the major product. The *endo* preference had been rationalized earlier by invoking secondary orbital interactions (SOIs) but a recent paper suggests that closed shell interactions are involved.[19] This could explain the formation of *endo*-phosphonate products **41**−**46**. An *endo*-selective Diels−Alder reaction of diphenyl(1,2-propadienyl)phosphine oxide with cyclopentadiene has been reported by Scheufler and Maier.[10d] In the case of allenoate products **47a**−**b** the ratio was ~2:3 in favor of *exo*, while for **48** the preferred product was again *exo* (i.e., **48b**). The latter feature is understandable since there is a slightly bulkier germinal $-CH_2CO_2Et$ group that could tilt the balance in favor of *exo*. *Exo*-selective [4 + 2] cycloaddition of allenoate **22** with other dienes has also been noted by Jung and co-workers recently.[2f−i]

With respect to the X-ray structures [see Supporting Information], the nonbonded P1···O4 distance between the bridgehead oxygen and the phosphorus in the *endo* [**46a**] and *exo* [**46b**] isomers are, respectively, 3.981(3) Å and 3.328(1) Å and hence these isomers are easily distinguishable. Another

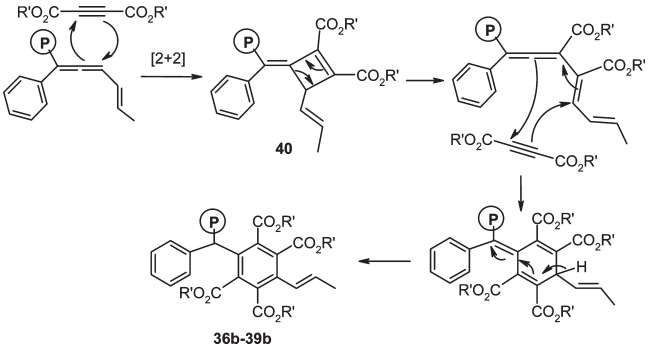
(18) (a) Back, T. G.; Parvez, M.; Zhai, H. *J. Org. Chem.* **2006**, *71*, 5254. (b) Dyke, A. M.; Gill, D. M.; Harvey, J. N.; Hester, A. J.; Lloyd-Jones, G. C.; Muñoz, M. P.; Shepperson, I. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5067. (c) Shastin, A. V.; Nenajdenko, V. G.; Muzalevskiy, V. M.; Balenkova, E. S.; Fröhlich, R.; Haufe, G. *Tetrahedron* **2008**, *64*, 9725. (d) Quintana, I.; Peña, D.; Pérez, D.; Guitián, E. *Eur. J. Org. Chem.* **2009**, 5519. (e) Patrick, T. B.; Li, H. *J. Flourine Chem.* **2009**, *130*, 544.

(19) García, J. I.; Mayoral, J. A.; Salvatella, L. *Eur. J. Org. Chem.* **2005**, 85.

SCHEME 7



SCHEME 8



interesting feature in these compounds is the unusually long C6−C7 *single* bond distances of 1.635(5) and 1.623(2) Å [see Supporting Information]. This may be because of steric repulsions involving two moderately bulky groups at C6.

It may be expected that an electron withdrawing group [e.g., phosphonyl] on the dienophile will activate this center for [4 + 2] cycloaddition, but in the reactions of allenes **8**−**9** and **19**−**20** that have a terminal $=CR_2$ group, the cycloaddition occurs at the (β,γ) position, away from the phosphonyl group [cf. Scheme 10]. We do not have a ready explanation for this result, but it does not appear to be a steric effect. The electronegativity of the −Me group is slightly higher than that of hydrogen according to some calculations,[20] but to know whether this factor tilts the reaction in favor of (β,γ)-cycloaddition or not needs further investigations.

A rather unusual [4 + 4] cycloaddition was observed in the reaction using the cyclohexenyl substituted allenes **12**−**15** leading to **53**−**56** (Scheme 11). To our knowledge, such [4 + 4] cycloadditions involving allenes are rather rare.[3a] It is very likely that this reaction occurs via *retro* Diels−Alder reaction followed by [4 + 4] cycloaddition. Indeed, from the reaction performed at lower temperature (80 °C), [4 + 2] cycloaddition was observed, but only in the reaction using **12**, we succeeded in isolating such a product (**57**). A pure sample of **57** upon heating at ca. 140 °C/8 h, led cleanly to the cyclooctene derivative **53** [Scheme 12] as shown by ^{31}P NMR spectroscopy [Figure 1]. X-ray structure of **53** was determined [see Supporting Information]. During the course of heating compound **57**, the characteristic yellow color of the isobenzofuran was also observed.

(iii) Reaction with Anthracene. It is known that anthracene as a diene has low reactivity in [4 + 2] cycloaddition and to our knowledge, this diene has not been explored much in allene chemistry.[10c,11a,c] The reaction using allenes **1**−**5** and **7** led to isolatable products **58**-**63** (Scheme 13) although it took a longer time and higher temperature than that required in the case of 1,3-diphenylisobenzofuran. The X-ray structures of **61**, **64** and **66** have been determined for confirmation (see Supporting Information for details). In all these products, again the (α,β) carbon−carbon double bond preferentially acted as the dienophile. Only in the case of unsubstituted allene **1**, the (β,γ) product **64** was isolated as a minor product. Allenylphosphine oxides **16**−**18** also afforded (α,β) cycloaddition products (**65**−**68**). In the reaction with **16**, the expected product **65** was obtained along with the rearranged product **66** (ratio 1:3). Overall, these results were consistent with those obtained with 1,3-diphenylisobenzofuran discussed above.

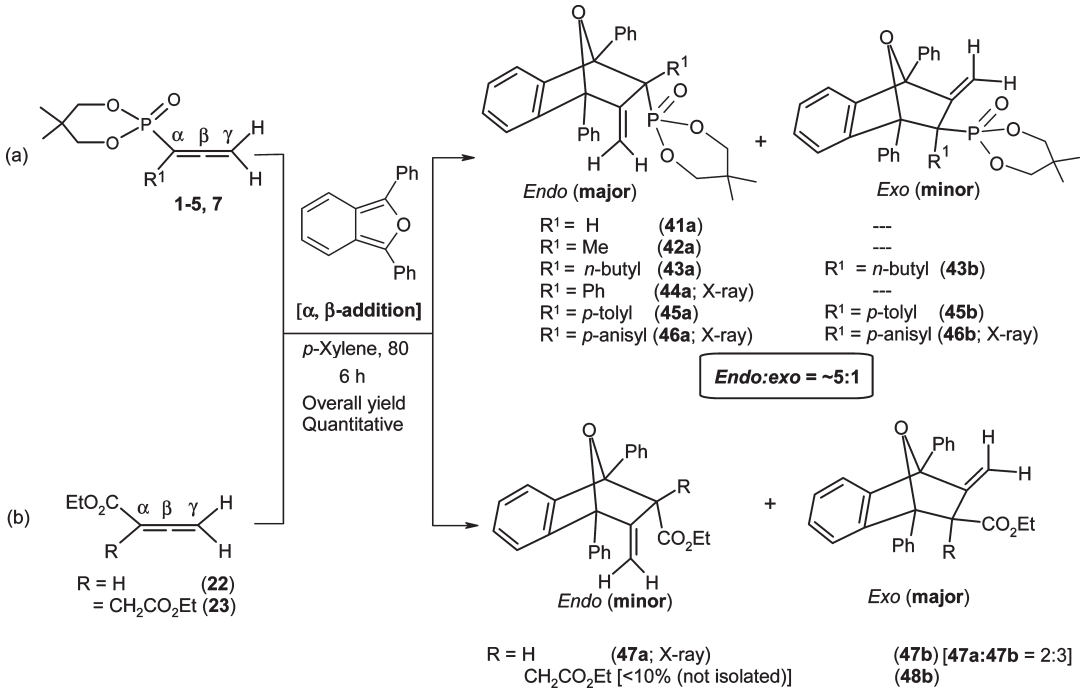
Our initial attempt using the $=CMe_2$ terminal allene **8** and anthracene led only to the self-dimerized [2 + 2] cycloaddition product **69**.[12b] Compound **2**, in addition to the Diels−Alder product **59**, also afforded **70** (Scheme 14; see Supporting Information for X-ray structure). It may be noted that this [2 + 2] addition takes place at the (β,γ)-position while the Diels−Alder cycloaddition leading to **59** preferentially takes place at (α,β)-position of the allene, clearly reflecting the different electronic requirement in the two types of cycloaddition reactions.

Summary

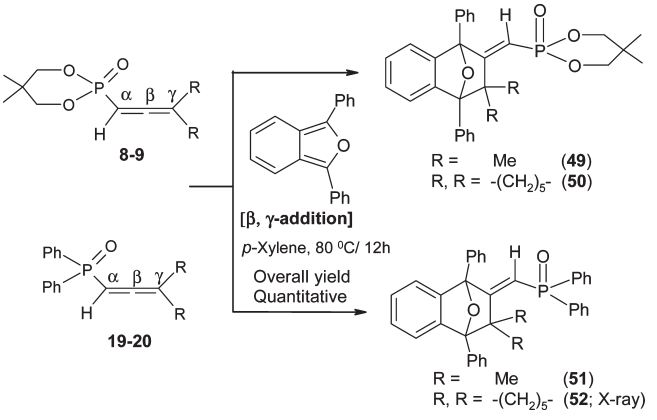
Allenylphosphonates with an α-aryl group preferentially undergo [4 + 2] cycloaddition with DMAD/DEAD under

(20) Huheey, J. E.; Keiter, E. A.; Keiter, R. L.; Medhi, O. K. *Inorganic Chemistry: Principles of Structure and Reactivity*; Pearson Education: Boston, 2007; pp 155−170.

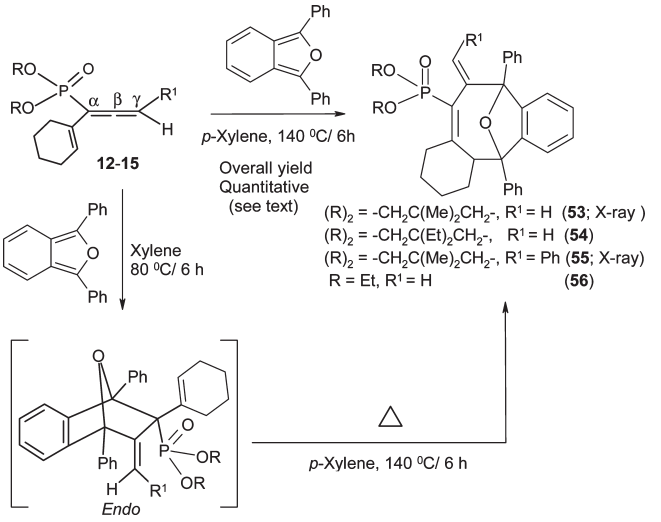
SCHEME 9



SCHEME 10

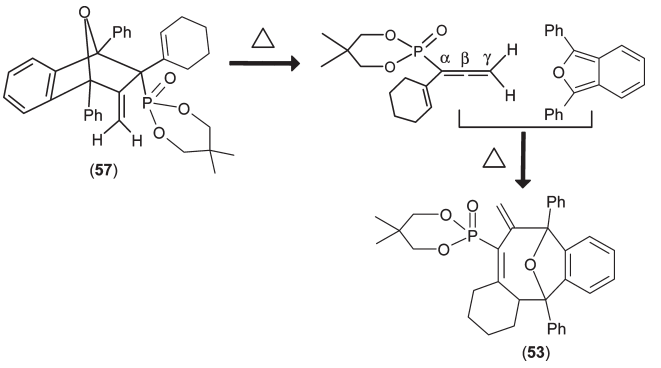


SCHEME 11

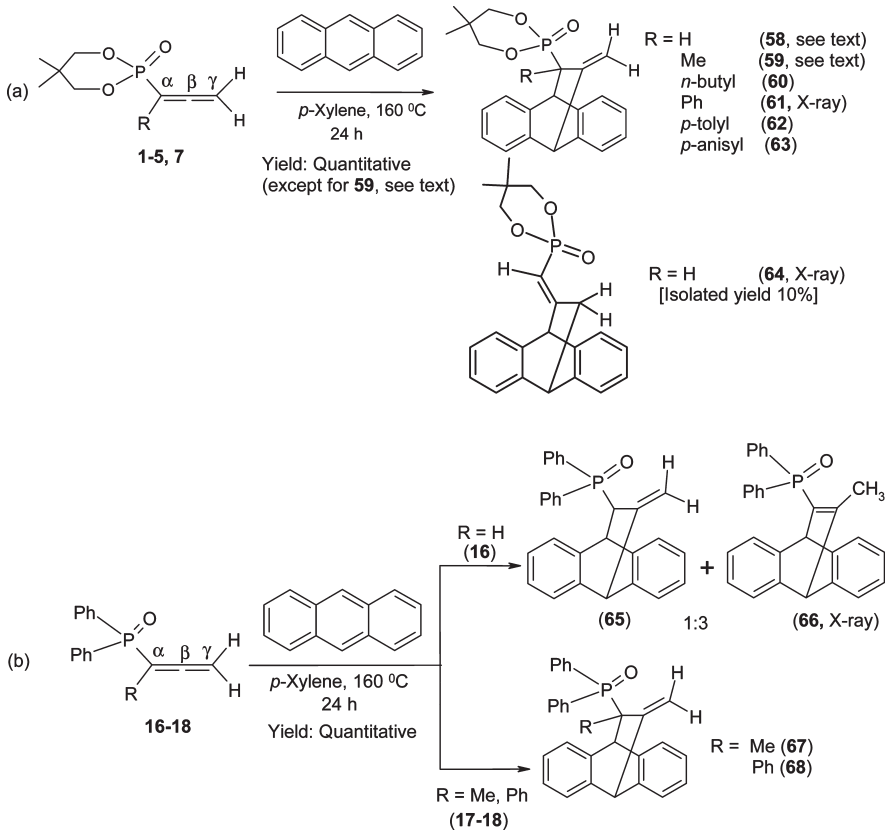


thermal activation, but in addition to the expected 1:1 product, the reaction leads to 1:2 as well as 2:1 products [e.g., **30**−**33**] that were not described before. When an additional vinyl group is present in the allenylphosphonate [4 + 2] cycloaddition takes place utilizing either the vinylic [e.g., **36a**−**39a**] or the aryl end [e.g., **36c-39c, 36d-39d**], but additionally a novel cyclization product [e.g., **36b**−**39b**], wherein complete opening up of [β,γ] carbon−carbon double bond of the allene is realized. In contrast to these results, the reaction of allenylphosphonate **8** possessing a terminal $=CMe_2$ group with DMAD occurs by both [2 + 2] cycloaddition and ene reaction. While the reaction of $=CH_2$ terminal allenylphosphonates as well as allenylphosphine oxides with 1,3-diphenylisobenzofuran afforded preferentially *endo*-[4 + 2] cycloaddition products [e.g., **41a**−**46a**] via [α,β] attack, the analogous allenoates led to *exo*-[4 + 2] cyclization [e.g., **47b**−**48b**]. In contrast to both of these, under similar conditions, allenylphosphonates with a terminal $=CR_2$ group

SCHEME 12



SCHEME 13



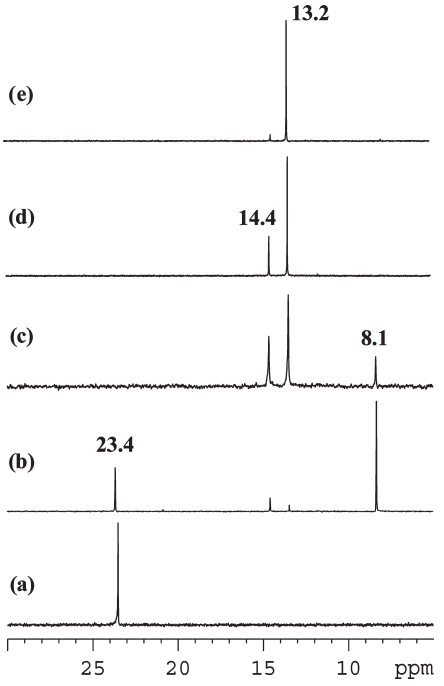
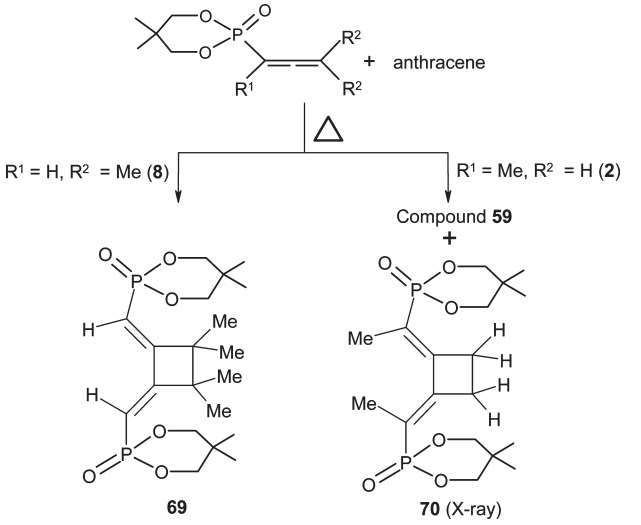


FIGURE 1. ^{31}P NMR spectra showing the conversion of [4 + 2] cycloaddition compound **57** [δ(P): 23.4] to [4 + 4] cycloaddition compound **53** [δ(P): 13.2] *via* allene precursor **12** [δ(P): 8.1] at 140 °C in *p*-xylene: (a) after 10 min, (b) after 3 h, (c) after 5 h, (d) after 6 h, and (e) after 8 h.

gave only [β,γ]-cycloaddition products [e.g., **49**−**52**]. A new ring-opening followed by ring-closing reaction entailing

SCHEME 14



conversion of a [4 + 2] cycloaddition product to [4 + 4] cycloaddition derivative [i.e., **57**→**53**] was discovered. Anthracene reacted in a manner similar to 1,3-diphenylisobenzofuran, although reactivity was lower in this case. Wherever possible, rationale for the observed reactions is provided. All the key compounds were characterized by single crystal X-ray crystallography. The ready recognition of diverse products by ^{31}P NMR spectra as an additional tool, that could help when analyzing reactions of nonphosphorylated allenes, is also highlighted.

Experimental Section

General Comments. Solvents were dried according to known methods as appropriate.[21] ^{1}H, ^{13}C and ^{31}P NMR spectra (^{1}H-400 MHz, ^{13}C-100 MHz and ^{31}P-162 MHz) were recorded using a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using GCMS or LCMS instruments.

(**A**) **Synthesis of Allenes 1−23.** The phosphorus-based allenes **1**−**21**[8a,d,12a,b] and ester allenes **22**−**23**[8a,12c,d] were synthesized according to literature procedures. Compounds **3**, **6**, **9**, and **11**−**15** are new.

Compound 3. This compound was prepared by following a literature procedure[12b] using hept-2-yn-1-ol (1.09 g, 9.7 mmol) and $(OCH_2CMe_2CH_2O)PCl$[22] (1.63 g, 9.7 mmol). It was purified by using silica gel column chromatography [ethyl acetate/hexane (1:1)]. Isolated yield 1.80 g (76%); white solid; mp 58−60 °C; IR (KBr, cm^{-1}) 2965, 2928, 1942, 1472, 1258, 1047, 997; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, ^3J(H−H) ≈ 6.2 Hz, 3H), 0.95 and 1.17 (2 s, 6H), 1.32−1.37 and 1.48−1.51 (m, 4H), 2.16 (br, 2H), 3.90−4.05 (m, 4H), 4.99 and 5.02 (2 s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.0, 21.7, 22.1, 27.5 (d, ^3J(P−C) = 6.0 Hz), 30.0 (d, ^2J(P−C) = 6.4 Hz), 32.5 (d, ^3J(P−C) = 6.0 Hz), 76.7 (d, ^3J(P−C) = 6.5 Hz), 77.2 and 77.3 (2 d, ^2J(P−C) ≈ 5.5 Hz), 91.9 (d, ^1J(P−C) = 182.3 Hz), 211.5 (d, ^2J(P−C) = 6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.9; LC/MS m/z 245 $[M + 1]^+$. Anal. calcd for $C_{12}H_{21}O_3P$: C, 59.00; H, 8.67. Found: C, 59.15; H, 8.59.

Compound 6. This compound was prepared by following a procedure similar to that for compound **3** using 3-(4-bromophenyl)-prop-2-yn-1-ol[23] (1.00 g, 4.7 mmol) and $(OCH_2CMe_2CH_2O)PCl$ (1.04 g, 4.7 mmol). It was purified by column chromatography [ethyl acetate/hexane (1:1)]. Isolated yield 1.54 g (95%); white solid; mp 78−80 °C; IR (KBr, cm^{-1}) 2984, 2961, 1964, 1931, 1485, 1264, 1154, 1053, 1003, 843, 787; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 and 1.26 (2 s, 6H), 3.88−3.95 (m, 4H), 5.34 and 5.37 (2 s, 2H), 7.43 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.8, 32.6 (d, ^3J(P−C) = 6.8 Hz), 77.4, 77.5, 79.4 (d, ^3J(P−C) = 14.2 Hz), 94.6 (d, ^1J(P−C) = 181.3 Hz), 122.0, 129.2 (d, ^3J(P−C) = 6.0 Hz), 129.6 (d, ^2J(P−C) = 7.3 Hz), 131.8, 212.6 (d, ^2J(P−C) = 3.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 6.5; LC/MS m/z 342 $[M]^+$ and 344 $[M + 2]^+$. Anal. calcd for $C_{14}H_{16}BrO_3P$: C, 49.00; H, 4.70. Found: C, 49.12; H, 4.65.

Compound 9. The procedure was similar to that for **3** by using 1-ethynyl-1-cyclohexanol (2.71 g, 21.8 mmol) and $(OCH_2CMe_2CH_2O)PCl$ (3.68 g, 21.8 mmol). Purification was done by column chromatography [ethyl acetate/hexane (2:3)]. Isolated yield 4.71 g (85%); white solid; mp 108−112 °C; IR (KBr, cm^{-1}) 2976, 2932, 2843, 1962, 1483, 1447, 1267, 1055, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 and 1.19 (2 s, 6H), 1.51−1.56 (m, 2H), 1.60−1.66 (m, 4H), 2.19−2.22 (m, 4H), 3.93−4.05 (m, 4H), 5.18−5.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 25.6, 26.6, 26.7, 30.0, 30.1, 32.6 (d, ^3J(P−C) = 6.5 Hz), 76.0 (d, ^1J(P−C) = 193.7 Hz), 76.6$_6$, 76.7$_1$, 103.7 (d, ^3J(P−C) = 16.5 Hz), 207.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.0; LC/MS m/z 257 $[M + 1]^+$. Anal. calcd for $C_{13}H_{21}O_3P$: C, 60.93; H, 8.26. Found: C, 60.85; H, 8.30.

Compound 11. The procedure was similar to that for **3** by using 1-phenyl-4-hexen-1-yn-3-ol[24] (0.70 g, 4.0 mmol) and $(OCH_2CEt_2CH_2O)PCl$ (1.00 g, 4.0 mmol). It was purified by column chromatography [ethyl acetate/hexane (1:2)]. Isolated yield 1.06 g (80%); gummy; IR (neat, cm^{-1}) 2971, 1923, 1717, 1462, 1385, 1252, 1075, 1030, 845; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 0.91 (2 t, ^3J(H−H) = 7.6 and 7.4 Hz respectively, 6H), 1.12−1.28 (m, 2H), 1.76−1.84 (m, 5H), 3.97−4.13 (m, 4H), 5.88 and 6.00 (m, 2H), 6.42 (dd, ^4J(P−H) = 2.4 Hz, ^3J(H−H) ∼ 9.9 Hz each, 1H), 7.29−7.61 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.7, 6.9, 18.1, 22.0, 22.8, 37.1 (d, ^3J(P−C) = 6.0 Hz), 74.4 and 74.7 (2 d, ^3J(P−C) = 7.0 Hz each), 96.8 (d, ^1J(P−C) = 181.0 Hz), 97.4 (d, ^3J(P−C) = 14.0 Hz), 122.4 (d, ^2J(P−C) = 10.0 Hz), 127.4 (d, ^3J(P−C) = 6.0 Hz), 127.7, 128.4, 130.9 (d, ^3J(P−C) = 8.0 Hz), 131.9 (d, ^3J(P−C) = 5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.5; LC/MS m/z 334 $[M + 2]^+$. Anal. calcd for $C_{19}H_{25}O_3P$: C, 68.66; H, 7.58 Found: C, 68.51; H, 7.62.

Compound 12. The procedure was similar to that for compound **3** by using 3-cyclohex-1-enyl-prop-2-yn-1-ol[25] (3.00 g, 22.0 mmol) and $(OCH_2CMe_2CH_2O)PCl$ (3.71 g, 22.0 mmol). It was purified by column chromatography [ethyl acetate/hexane (1:1)]. Isolated yield 3.80 g (64%); white solid; mp 78−80 °C; IR (KBr, cm^{-1}) 2961, 2934, 1921, 1474, 1262, 1059, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 and 1.28 (2 s, 6H), 1.54−1.70 (m, 4H), 2.08 and 2.14 (2 br s, 4H), 3.99−4.01 (m, 4H), 5.18 and 5.21 (2 s, 2H), 6.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.7, 21.9, 22.6, 25.9, 27.1 (d, ^3J(P−C) = 8.1 Hz), 32.6 (d, ^3J(P−C) = 7.1 Hz), 77.2, 77.3, 79.0 (d, ^2J(P−C) = 14.9 Hz), 97.2 (d, ^1J(P−C) = 177.8 Hz), 126.7 (d, ^2J(P−C) = 6.2 Hz), 128.9 (d, ^3J(P−C) = 4.5 Hz), 212.1 (d, ^2J(P−C) = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.1; LC/MS m/z 269 $[M + 1]^+$. Anal. calcd for $C_{14}H_{21}O_3P$: C, 62.67; H, 7.89. Found: C, 62.85; H, 7.82.

Compound 13. The procedure was similar to that for compound **3** by using 3-cyclohex-1-enyl-prop-2-yn-1-ol[25] (1.68 g, 12.3 mmol) and $(OCH_2CEt_2CH_2O)PCl$ (2.43 g, 12.3 mmol). Purification was done by column chromatography [ethyl acetate/hexane (2:3)]. Isolated yield 2.19 g (60%); white solid; mp 80−82 °C; IR (KBr, cm^{-1}) 2940, 1929, 1464, 1260, 1080, 1034; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76−0.80 and 0.83−0.88 (2 m, 6H), 1.18−1.22 and 1.51−1.75 (2 m, 8H), 2.04 and 2.09 (br, 4H), 3.92−4.07 (m, 4H), 5.15 and 5.18 (2 s, 2H), 6.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9, 7.2, 21.7, 22.0, 22.6, 23.1, 25.9, 27.0 (d, ^3J(P−C) = 8.2 Hz), 37.4 (d, ^3J(P−C) = 6.0 Hz), 74.6, 74.7, 78.8 (d, ^2J(P−C) = 14.9 Hz), 97.2 (d, ^1J(P−C) = 175 . 1 Hz), 126.7 (d, ^2J(P−C) = 6.1 Hz), 128.8, 212.0 (d, ^2J(P−C) = 4.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.1; LC/MS m/z 297 $[M + 1]^+$. Anal. calcd for $C_{16}H_{25}O_3P$: C, 64.85; H, 8.50. Found: C, 64.72; H, 8.56.

Compound 14. The procedure was similar to that for compound **3** by using 3-cyclohexenyl-1-(phenyl)prop-2-yn-1-ol[26] (0.90 g, 3.5 mmol) and $(OCH_2CMe_2CH_2O)PCl$ (0.59 g, 3.5 mmol). It was purified by column chromatography [ethyl acetate/hexane (1:1)]. Isolated yield 0.90 g (74%); white solid; mp 108−110 °C; IR (KBr, cm^{-1}) 2948, 2917, 2830, 1919, 1599, 1456, 1260, 1061, 1013; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 and 1.27 (2 s, 6H), 1.59−1.67 (m, 4H), 2.04 and 2.19 (m, 4H), 3.80−4.09 (m, 4H), 6.47−6.48 (m, 1H), 6.65 (d, ^4J(P−H) = 3.1 Hz, 1H), 7.25−7.28 (m, 2H), 7.32−7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.8, 22.0, 22.6, 26.1, 27.3 (d, ^3J(P−C) = 8.0 Hz), 32.5 (d, ^3J(P−C) = 7.0 Hz), 76.9 (d, ^2J(P−C) = 6.7 Hz), 77.5 (d, ^2J(P−C) = 7.0 Hz), 98.2 (d, ^3J(P−C) = 15.0 Hz), 101.9 (d, ^1J(P−C) = 174.0 Hz), 127.0$_9$, 127.1$_1$, 127.5 (d, ^4J(P−C) = 6.8 Hz), 128.0 (d, ^3J(P−C) = 1.5 Hz), 129.0$_2$, 129.0$_3$, 130.1, 132.4

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(d, ^2J(P−C) = 8.2 Hz), 210.4 (d, ^2J(P−C) = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 6.8; LC/MS m/z 345 $[M + 1]^+$. Anal. calcd for $C_{20}H_{25}O_3P$: C, 69.75; H, 7.32. Found: C, 69.85; H, 7.23.

Compound 15. The procedure was similar to that for compound **3** by using 3-cyclohex-1-enyl-prop-2-yn-1-ol[25] (0.64 g, 4.7 mmol) and $(EtO)_2PCl$ (0.74 g, 4.7 mmol). It was purified by column chromatography [ethyl acetate/hexane (1:2)]. Isolated yield 0.79 g (65%); brown oil; IR (Neat, cm^{-1}) 2976, 2936, 1923, 1713, 1445, 1248, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32−1.35 (m, 6H), 1.58−1.69 (m, 4H), 2.09 and 2.15 (2 br, 4H), 4.10−4.18 (m, 4H), 5.14 and 5.17 (2 s, 2H), 6.27 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1_7, 16.2_4, 21.8, 22.7, 26.0, 27.3 (d, ^3J(P−C) = 8.2 Hz), 62.5_5, 62.6_1, 78.4 (d, ^2J(P−C) = 14.7 Hz), 98.8 (d, ^1J(P−C) = 182.9 Hz), 127.2 (d, ^2J(P−C) = 6.0 Hz), 128.2 (d, ^3J(P−C) = 3.8 Hz), 213.0 (d, ^2J(P−C) = 4.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.3; LC/MS m/z 257 $[M + 1]^+$. Anal. calcd for $C_{13}H_{21}O_3P$: C, 60.93; H, 8.26. Found: C, 60.85; H, 8.21.

(B) Reaction of Allenylphosphophonates with DMAD/DEAD. (i) Synthesis of Compounds 24−26 and 28−29. Compounds 24−26. A mixture of allenylphosphonate **8** (0.40 g, 1.80 mmol) and DMAD (0.27 g, 1.80 mmol) was heated under neat condition at 150 °C for 12 h. After this, the products **24**−**26** were separated by silica gel column chromatography (vide infra). **Compound 24:** This compound was eluted by using ethyl acetate/hexane (2:3) mixture. Yield 85% [combined, **24**+**25**+**26**, ratio 5:6:6, by ^{31}P NMR], 0.14 g (isolated, 20%, **24**); mp 114−116 °C; IR (KBr, cm^{-1}) 1736, 1620, 1574, 1377, 1334, 1277, 1057, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 and 1.15, (2 s, 6H), 1.98 (s, 3H), 3.77 (s, 3H), 3.82−3.87 (m, 2H), 3.91 (s, 3H), 4.02−4.08 (m, 2H), 5.11 and 5.37 (2 s, 2H), 5.83 (d, J(P−H) = 15.6 Hz, 1H), 6.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.6, 22.2, 32.4 (d, J(P−C) = 6.0 Hz), 52.2, 52.9, 76.0 (d, J(P−C) = 6.0 Hz), 119.1 (d, J(P−C) = 185.3 Hz), 119.8, 123.2, 139.5 (d, J(P−C) = 7.2 Hz), 147.5 (d, J(PC) = 21.3 Hz), 156.6 (d, J(P−C) = 7.8 Hz), 164.9, 167.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.3; GC-MS m/z 358 $[M]^+$. Anal. calcd for $C_{16}H_{23}O_7P$: C, 53.63; H, 6.47. Found: C, 53.72; H, 6.47. It was crystallized from ethyl acetate at 25 °C. **Compound 25:** This compound was eluted by using ethyl acetate/hexane (3:2) mixture. Yield 85% [combined, **24**+**25**+**26**, by ^{31}P NMR], 0.07 g (isolated, 10%, **25**); mp 180−182 °C; IR (KBr, cm^{-1}) 2953, 1732, 1698, 1595, 1435, 1265, 1061, 1009, 830, 735, 617; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 and 1.06 (2 s, 6H), 1.90 and 1.92 (2 s, 6H), 3.78 and 3.91 (2 s, 6H), 3.94−4.24 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.3, 21.6_0, 21.6_3, 32.7 (d, ^3J(P−C) = 5.9 Hz), 43.3 (d, ^1J(P−C) = 145.1 Hz), 52.1, 52.4, 75.5, and 75.6 (2 d, ^3J(P−C) ≈ 6.5 each), 123.7 (d, ^3J(P−C) = 8.7 Hz), 130.5 (d, ^2J(P−C) = 11.4 Hz), 134.7, 145.8 (d, ^2J(P−C) = 15.9 Hz), 161.4, 162.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.7; LC/MS m/z 359 $[M + 1]^+$. Anal. calcd for $C_{16}H_{23}O_7P$: C, 53.63; H, 6.47. Found: C, 53.25; H, 6.91. This compound was crystallized from ethyl acetate at 25 °C. The sample was not particularly stable in solution for more than a day. **Compound 26:** This compound was eluted by using ethyl acetate/hexane (1:2) mixture. Yield 85% [combined, **24**+**25**+**26**, by ^{31}P NMR], 0.11 g (isolated, 15%, **26**); mp 166−168 °C; IR (KBr, cm^{-1}) 2961, 2930, 1742, 1723, 1669, 1437, 1260, 1059, 1009, 824; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 and 1.12 (2 s, 6H), 1.60 (s, 6H), 3.85 and 3.87 (2 s, 6H), 3.91 (t buried in the signals due to $COOCH_3$ protons, 2H), 4.19 (dd→t, $^{2,3}J \sim 12.0$ Hz each, 2H), 6.01 (d, ^2J(P−H) = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 21.9, 32.5 (d, ^3J(P−C) = 6.0 Hz), 52.1, 52.3, 53.4 (d, ^3J(P−C) = 10.0 Hz), 75.4_0, 75.4_4, 103.5 (d, ^1J(P−C) = 191.0 Hz), 136.0 (d, ^2J(P−C) = 27.0 Hz), 159.0, 159.9, 161.5, 164.3 (d, ^3J(P−C) = 9.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.4; LC-MS m/z 359 $[M + 1]^+$. Anal. calcd for $C_{16}H_{23}O_7P$: C, 53.63; H, 6.47. Found: C, 53.21; H, 6.12.

Compound 28. This compound was prepared by the above procedure from phosphorylated allene **21** (0.50 g, 1.60 mmol) and DMAD (0.23 g, 1.60 mmol); it was isolated by column chromatography using ethyl acetate/hexane (2:3) mixture as the eluent. Although the starting material was completely consumed, there were at least three other products [δ(P) 19.0, 21.6 26.1; total ∼45%] in the reaction mixture. Yield 53% by ^{31}P NMR, 0.33 g (isolated, 45%); mp 128−130 °C; IR (KBr, cm^{-1}) 2970, 1744, 1719, 1613, 1370, 1335, 1264, 1020, 986, 882, 789; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 and 1.26 (2 d, $J \approx 6.7$ Hz for each, (12H + 12H = 24H)), 2.05 (s, 3H), 3.51−3.59 (m, 4H), 3.74 and 3.89 (2s, 6H), 4.82 (s, 1H), 5.30 (m, $J \approx 1.6$ Hz, 1H), 5.88 (d, ^2J(P−H) = 12.4 Hz, 1H), 6.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 23.4, 45.7 (d, ^2J(P−C) = 4.8 Hz), 52.1, 52.6, 117.2, 120.6, 128.6 (d, ^1J(P−C) = 144.3 Hz), 140.0 (d, ^3J(P−C) = 5.2 Hz), 148.0 (d, ^3J(P−C) = 7.3 Hz), 149.8 (d, ^2J(P−C) = 21.6 Hz), 165.7, 168.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.9; LC/MS m/z 456 $[M]^+$. Anal. calcd for $C_{23}H_{41}N_2O_5P$: C 60.51; H 9.05; N 6.14. Found: C 60.25; H 8.89; N 6.12.

Compound 29. This compound was prepared by the above procedure from allenylphosphine oxide **19** (0.50 g, 1.87 mmol) and DMAD (0.26 g, 1.87 mmol). The ^{31}P NMR spectrum of the reaction mixture at this stage showed compound **29** (ca. 60%) along with other minor products [δ(P) 7.8, 26.2, 28.1, 45.2]. The reaction mixture was chromatographed by using ethyl acetate/hexane (2:3) mixture as the eluent to obtain compound **29** in a pure state. Yield ∼60% by ^{31}P NMR, 0.34 g (isolated, 44%); mp 110−112 °C; IR (KBr, cm^{-1}) 3058, 2961, 1730, 1617, 1435, 1262, 1102, 1017, 797, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (s, 3H), 3.76 and 3.88 (2 s, 6H), 4.86 and 5.11 (2 s, 2H), 6.10 (s, 1H), 6.43 (d, ^2J(P−H) = 19.2 Hz, 1H), 7.44−7.73 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 52.3, 52.9, 120.5, 122.4, 126.6 (d, J(P−C) = 100.0 Hz), 128.4 (d, ^2J(P−C) = 16.0 Hz), 131.1 (d, ^3J(P−C) = 10.0 Hz), 131.8, 133.8 (d, ^1J(P−C) = 106.0 Hz), 139.0 (d, ^3J(P−C) = 6.3 Hz), 147.3 (d, ^2J(P−C) = 18.1 Hz), 156.3, 165.1, 167.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.9; LC/MS m/z 411 $[M + 1]^+$. Anal. calcd for $C_{23}H_{23}O_5P$: C 67.31; H 5.65. Found: C 66.85; H 5.63.

(ii) Synthesis of Compounds 30(a−c)−33(a−c), 35, and 36-(a−d)−39(a−d). Compounds 30(a−c). A mixture of allenylphosphonate **4** (0.80 g, 3.03 mmol) and DMAD (1.29 g, 9.08 mmol) [1:3 ratio] in *p*-xylene (6 mL) was heated under reflux for 12 h. The solvent was removed in vacuo using a rotary evaporator. After this, the products **30a**−**c** were separated by using silica gel column chromatography (vide infra). Compound **30a** eluted first followed by **30b** and then **30c**. **Compound 30a:** It was separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield 80% [combined, **30a**+**30b**+**30c**, ratio 4:1:3, by ^{31}P NMR], 0.43 g (isolated, 35%, **30a**); white solid; mp 120−122 °C; IR (KBr, cm^{-1}) 2955, 2886, 1736, 1439, 1343, 1252, 1202, 1156, 1059, 1009, 830, 816, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 and 1.37 (2 s, 6H), 2.78 (d, ^4J(P−H) = 2.0 Hz, 3H), 3.61−3.58 (m, 2H), 3.91−4.01 (m, 2H), 3.96 and 4.03 (2 s, 6H), 7.59−8.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.6 (d, ^3J(P−C) = 5.1 Hz), 22.1, 32.1 (d, ^3J(P−C) = 5.7 Hz), 52.9, 53.1, 76.6_0, 76.6_3, 125.3, 126.2, 126.3 (d, ^3J(P−C) = 4.3 Hz), 127.5, 127.8 (d, ^2J(P−C) = 12.7 Hz), 128.9, 132.5 (d, ^2J(P−C) = 17.2 Hz), 133.9 (d, ^3J(P−C) = 5.4 Hz), 134.0 (d, ^4J(P−C) = 2.8 Hz), 138.9 (d, ^3J(P−C) = 11.0 Hz), 167.7, 168.2; ^{31}P NMR (162 MHz, $CDCl_3$) 10.8; LC/MS m/z 407 $[M + 1]^+$. Anal. calcd for $C_{20}H_{23}O_7P$: C 59.11; H 5.70. Found: C 58.91, H 5.75. **Compound 30b:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent Yield [**30a**+**30b**+**30c**] 80% by ^{31}P NMR, 0.12 g (isolated, 7%, **30b**); white solid; mp 124−126 °C; IR (KBr, cm^{-1}) 2955, 1744, 1732, 1651, 1435, 1373, 1150, 1059, 918, 828, 783; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 and 1.20 (2 s, 6H), 3.67 (s, 3H), 3.75 (t, 2H, ^3J(H−H) = 10.4 Hz), 3.85, 3.90, and 4.02 (3 s, 9H), 4.20 (t, 2H, ^3J(H−H) = 10.2 Hz), 4.48 (s, 2H), 5.41 (s, 1H),

7.66−8.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.7, 32.4 (d, ^3J(P−C) = 5.0 Hz), 36.4, 51.9, 52.7, 53.2, 76.8, 122.4, 126.4, 127.1, 128.3, 128.7 (d, ^2J(P−C) = 13.0 Hz), 129.3, 130.0, 131.4 (d, ^2J(P−C) = 17.0 Hz), 134.0 (d, ^3J(P−C) = 18.5 Hz), 135.4, 135.6, 135.7, 146.8, 165.6, 167.6, 167.7, 167.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.8; LC/MS m/z 549 $[M + 1]^+$. Anal. calcd for $C_{26}H_{29}O_{11}P$: C 56.94; H 5.33. Found: C 57.21; H 5.35. **Compound 30c:** It was separated by using ethyl acetate/hexane (4:1) mixture as the eluent. Yield [**30a**+**30b**+**30c**] 80% by ^{31}P NMR, 0.47 g (isolated, 23%, **30c**); white solid; mp 160−162 °C; IR (KBr, cm^{-1}) 2955, 1734, 1644, 1543, 1456, 1260, 1059, 1009, 828, 781, 519; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67, 0.82, 1.10, and 1.28 (4 s, 12H), 3.50−4.07 (m, 15H), 4.27 (s, 2H), 4.89 and 5.92 (2 s, 2H), 5.92 (s, 1H), 7.12−8.74 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.8, 21.9, 22.0, 32.2, and 32.5 (2 d, ^3J(P−C) = 5.0 and 7.0 Hz respectively), 40.9 (d, ^3J(P−C) = 11.0 Hz), 47.2 (d, ^1J(P−C) = 125.0 Hz), 52.7, 53.0, 76.3, and 76.4 (2 d, ^3J(P−C) = 7.0 Hz each, OCH_2), 117.2, 126.3, 126.6, 126.9, 127.4, 127.8, 128.2, 128.4, 128.6, 129.0, 129.5 (d, ^3J(P−C) = 7.0 Hz), 131.6 (d, ^2J(P−C) = 17.0 Hz), 133.9, 134.0, 135.1, 139.6 (d, ^2J(P−C) = 11.0 Hz), 142.0, 167.6, 167.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.8 and 17.8; LC/MS m/z 670 $[M]^+$. Anal. calcd for $C_{34}H_{40}O_{10}P_2$: C 60.89; H 6.01. Found: C 60.75; H 6.11.

Compounds 31(a−c). These compounds were prepared by a procedure similar to that for **30a−c** using allenylphosphonate **5** (1.00 g, 3.6 mmol) and DMAD (1.60 g, 10.8 mmol). **Compound 31a:** This compound was separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield 97% [combined, **31a**+**31b**+**31c**, ratio 15:2:3, by ^{31}P NMR], 1.02 g (isolated, 67%, **31a**); white solid; mp 122−124 °C; IR (KBr, cm^{-1}) 2957, 2919, 1732, 1568, 1505, 1441, 1061, 1009, 945, 916, 835, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 and 1.37 (2 s, 6H), 2.52 (s, 3H), 2.75 (d, ^4J(P−H) = 2.0 Hz, 3H), 3.58−3.60 (m, 2H), 3.89−3.98 (m, 2H), 3.96 and 4.03 (2 s, 6H), 7.46−8.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 20.3 (d, ^3J(P−C) = 4.8 Hz), 21.5, 22.0, 31.9 (d, ^3J(P−C) = 5.5 Hz), 52.7, 52.9, 76.5$_0$, 76.5$_3$, 124.9, 125.7 (d, ^1J(P−C) = 171.0 Hz), 125.9 (d, ^3J(P−C) = 4.0 Hz), 128.0 (d, ^2J(P−C) = 12.7 Hz), 131.1, 132.2, 132.3 (d, ^2J(P−C) = 28.7 Hz), 133.3, 137.5, 137.7 (d, ^2J(P−C) = 11.0 Hz), 167.7, 168.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.4; LC/MS m/z 421 $[M + 1]^+$. Anal. calcd for $C_{21}H_{25}O_7P$: C 60.00; H 5.99. Found: C 60.21; H 5.88. This compound was crystallized from toluene/ethyl acetate (1:4) mixture at 25 °C. **Compound 31b:** This compound was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield [**31a**+**31b**+**31c**] 97% by ^{31}P NMR, 0.12 g (isolated, 6%, **31b**); white solid; mp 132−134 °C; IR (KBr, cm^{-1}) 2953, 1741, 1437, 1362, 1267, 1055, 1007, 831, 785, 529; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 1.20 (2 s, 6H), 2.54 (s, 3H), 3.66 (s, 3H), 3.73 (dd→t, $^{2,3}J \sim$ 11.0 Hz each, 2H), 3.84, 3.89, and 4.00 (3 s, 9 H), 4.18 (dd→t, $^{2,3}J \sim$ 11.0 Hz each, 2H), 4.46 (s, 2H), 5.41 (s, 1H), 7.52−8.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.8, 32.4, 36.4, 51.9, 52.7, 53.2, 76.8, 122.3, 125.2, 126.9, 128.8 (d, ^1J(P−C) = 174.8 Hz), 129.0 (d, ^2J(P−C) = 13.8 Hz), 131.3, 131.6, 132.4 (d, ^2J(P−C) = 10.3 Hz), 134.6 (d, ^3J(P−C) = 8.5 Hz), 134.9, 138.6, 147.0, 165.7 167.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.1; LC/MS m/z 563 $[M + 1]^+$. Anal. calcd for $C_{27}H_{31}O_{11}P$: C 57.65; H 5.55. Found: C 57.48; H 5.65. **Compound 31c:** This compound was separated by using ethyl acetate/hexane (4:1) mixture as the eluent. Yield [**31a**+**31b**+**31c**] 97% by ^{31}P NMR, 0.25 g (isolated, 10%, **31c**); white solid; mp 164−166 °C; IR (KBr, cm^{-1}) 2957, 2892, 1732, 1724, 1644, 1437, 1256, 1059, 1009, 828, 783, 530; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65, 0.84, 1.10, and 1.28 (4 s, 12H), 2.23 and 2.25 (2 s, 6H), 3.49−4.03 (m, 15H), 4.24 (s, 2H), 4.87 and 5.89 (2 s, 2H), 6.89−8.62 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.7, 20.9, 21.5, 21.8, 21.9, 32.0, and 32.4 (2 d, ^3J(P−C) = 6.0 Hz each), 40.7 (d, ^3J(P−C) = 9.0 Hz), 46.4 (d, ^1J(P−C) = 129.0 Hz), 52.5, 52.8, 76.2, and 76.3 (2 d, ^3J(P−C) = 7.0 and 6.0 Hz respectively), 116.9, 124.9, 126.2, 126.3, 128.0, 128.4, 128.5, 128.7, 129.1 (d, ^3J(P−C) = 6.0 Hz), 130.6 (d, ^3J(P−C) = 7.0 Hz), 131.2, 131.4 (d, ^2J(P−C) = 18.0 Hz), 132.2 (d, ^2J(P−C) = 12.0 Hz), 134.4, 136.8, 137.8, 138.5 (d, ^2J(P−C) = 11.0 Hz), 142.1, 167.6, 167.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.8 and 17.8; LC/MS m/z 700 $[M + 2]^+$; Anal. calcd for $C_{36}H_{44}O_{10}P_2$: C 61.89; H 6.35. Found: C 61.75; H 6.41.

Compounds 32(a−c). These compounds were prepared by a procedure similar to that for **30a−c** using allenylphosphonate **6** (0.50 g, 1.46 mmol) and DMAD (0.62 g, 4.38 mmol). **Compound 32a:** It was separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield 95% [combined, **32a**+**32b**+**32c**, ratio 12:2:5, by ^{31}P NMR], 0.39 g (isolated, 55%, **32a**); white solid; mp 136−138 °C; IR (KBr, cm^{-1}) 2959, 2878, 1732, 1435, 1273, 1055, 1011, 821, 523; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 and 1.36 (2 s, 6H), 2.75 (s, 3H), 3.59−3.90 (m, 4H), 3.96 and 4.03 (2 s, 6H), 7.69−8.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.6 (d, ^3J(P−C) = 4.6 Hz), 22.0, 32.1 (d, ^3J(P−C) = 5.5 Hz), 53.0, 53.3, 76.7, 122.2, 126.8 (d, ^1J(P−C) = 172.1 Hz), 128.0 (d, ^3J(P−C) = 3.8 Hz), 128.3, 129.2 (d, ^2J(P−C) = 12.6 Hz), 132.2, 132.3, 132.5, 133.9 (d, ^2J(P−C) = 16.8 Hz), 139.2 (d, ^3J(P−C) = 10.8 Hz), 167.0, 168.0; ^{31}P NMR (162 MHz, $CDCl_3$) 10.1; LC/MS m/z 485 $[M + 1]^+$, 487 $[M + 3]^+$. Anal. calcd for $C_{20}H_{22}BrO_7P$: C 49.50; H 4.57. Found: C 49.61; H 4.48. **Compound 32b:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield [**32a**+**32b**+**32c**] 95% by ^{31}P NMR, 0.06 g (isolated, 6%, **32b**); white solid; mp 144−146 °C; IR (KBr, cm^{-1}) 2955, 1732, 1651, 1437, 1256, 1057, 1013, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 and 1.17 (2 s, 6H), 3.65 (s, 3H), 3.72−3.78 (m, 2H), 3.83, 3.88, and 4.00 (3 s, 9H), 4.18 (dd→t, 2H, $^{2,3}J$ = 12.0 Hz), 4.43 (s, 2H), 5.37 (s, H), 7.73−8.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.6, 32.5 (d, ^3J(P−C) = 6.0 Hz), 36.4 (d, ^3J(P−C) = 3.7 Hz), 52.0, 52.7, 53.3, 53.4, 76.8, and 76.9 (2s, OCH_2), 122.6, 123.2, 128.4, 128.9 (d, ^3J(P−C) = 3.5 Hz), 129.9 (d, ^2J(P−C) = 12.5 Hz), 132.4, 132.5, 132.8 (d, ^2J(P−C) = 16.9 Hz), 134.0, 135.9 (d, ^3J(P−C) = 10.9 Hz), 146.4, 165.5, 166.9, 167.3, 167.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.1; LC/MS m/z 627 $[M + 1]^+$, 629 $[M + 3]^+$. Anal. calcd for $C_{26}H_{28}BrO_{11}P$: C 49.78; H 4.50. Found: C 49.62; H 4.58. **Compound 32c:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield [**32a**+**32b**+**32c**] 95% by ^{31}P NMR, 0.22 g (isolated, 18%, **32c**); pale yellow solid; mp 168−170 °C; IR (KBr, cm^{-1}) 2957, 2888, 1736, 1721, 1641, 1576, 1476, 1256, 1067, 828, 785, 741, 687; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70, 0.88, 1.12, and 1.33 (4 s, 12H), 3.46−4.15 (m, 15H), 4.31 (s, 2H), 5.06 and 5.91 (2 s, 2H), 6.97−8.59 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.7, 21.9, 22.0, 32.1, and 32.5 (2 d ^3J(P−C) = 5.4 and 6.3 Hz respectively), 41.4 (d, ^3J(P−C) = 8.3 Hz), 45.2 (d, ^1J(P−C) = 113.0 Hz), 52.8, 53.2, 76.3, and 76.5 (2 d, ^3J(P−C) = 6.5 and 5.8 Hz), 118.6, 121.2, 122.7, 126.8, 127.9 (d, ^3J(P−C) = 2.7 Hz), 128.4, 129.4 (d, ^2J(P−C) = 13.0 Hz), 130.7, 132.3, 132.4, 132.6, 132.8, 134.1, 140.1 (d, ^2J(P−C) = 11.5 Hz), 141.0, 167.0, 167.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.2 and 17.3; LC/MS m/z 827 $[M + 1]^+$, 829 $[M + 3]^+$, 831 $[M + 5]^+$. Anal. calcd for $C_{34}H_{38}Br_2O_{10}P_2$: C 49.29; H 4.62. Found: 49.38; H 4.56.

Compounds 33(a−c). These compounds were prepared by a procedure similar to that for **30a−c** using allenylphosphonate **7** (0.40 g, 1.36 mmol) and DMAD (0.58 g, 4.08 mmol). **Compound 33a:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 98% [combined, **33a**+**33b**+**33c**, ratio 12:3:5, by ^{31}P NMR], 0.30 g (isolated, 50%, **33a**); white solid; mp 148−150 °C; IR (KBr, cm^{-1}) 2955, 2882, 1732, 1624, 1507, 1435, 1227, 1150, 1059, 1005, 912, 830, 783, 527; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 and 1.36 (2 s, 6H), 2.72 (d, ^4J(P−H) = 2.0 Hz, 3H), 3.58−3.61 (m, 2H), 3.90−4.01 (m, 11H), 7.27−8.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2 (d, ^3J(P−C) = 5.0 Hz), 20.3, 22.1, 32.0 (d, ^3J(P−C) = 5.0 Hz), 52.8, 53.0, 55.3, 76.6$_0$, 76.6$_1$, 104.4, 121.3, 126.2 (d, ^1J(P−C) = 170.6 Hz), 127.8 (d, ^3J(P−C) = 4.1 Hz), 129.4, 129.6, 129.7, 129.8, 131.9, 133.5

(d, ^2J(P−C) = 17.1 Hz), 135.8 (d, ^2J(P−C) = 10.8 Hz), 158.4, 167.7, 168.5; ^{31}P NMR (162 MHz, $CDCl_3$) 11.3; LC/MS m/z 437 $[M + 1]^+$. Anal. calcd for $C_{21}H_{25}O_8P$: C 57.80; H 5.77. Found: C 57.68; H 5.86. **Compound 33b:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield [**33a**+**33b**+**33c**] 98% by ^{31}P NMR, 0.06 g (isolated, 8%, **33b**); white solid; mp 158−160 °C; IR (KBr, cm^{-1}) 2957, 1740, 1622, 1507, 1437, 1377, 1264, 1169, 1057, 1009, 830, 511; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 and 1.20 (2 s, 6H), 3.67 (s, 3H), 3.74 (dd→t, $^{2,3}J$ = 12.0 Hz, 2H), 3.85, 3.89, 3.94, and 4.00 (4 s, 12H), 4.16 (dd→t, $^{2,3}J$ = 12.0 Hz, 2H), 4.42 (s, 2H), 5.40 (s, 1H), 7.32−8.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 and 21.7, 32.4 (d, ^3J(P−C) = 5.6 Hz), 36.2, 51.9, 52.6, 53.1, 55.5, 76.8, 104.4, 121.7, 122.2, 128.7, 129.6 (d, ^2J(P−C) = 11.9 Hz), 129.9, 130.7 (d, ^2J(P−C) = 14.7 Hz), 132.4, 132.5, 132.6, 133.5, 147.1, 159.0, 165.6, 167.7, 167.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.3; LC/MS m/z 578 $[M]^+$. Anal. calcd for $C_{27}H_{31}O_{12}P$: C 56.06; H 5.40 Found: C 56.18; H 5.35. This compound was crystallized from ethyl acetate/dichloromethane (1:2) mixture at 25 °C. **Compound 33c:** It was separated by using ethyl acetate/hexane (4:1) mixture as the eluent. Yield [**33a**+**33b**+**33c**] 98% by ^{31}P NMR, 0.23 g (isolated, 23%, **33c**); white solid; mp 170−172 °C; IR (KBr, cm^{-1}) 2968, 1740, 1620, 1510, 1264, 1009, 828; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67, 0.85, 1.11, and 1.31 (4 s, 12H), 3.49−4.05 (m, 21H), 4.23 (s, 2H), 4.91 and 5.87 (2 s, 2H), 6.59−8.65 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.7, 21.8, 22.0, 32.0, and 32.4 (2 d ^{3}J(P−C) = 5.0 and 6.4 Hz respectively), 40.7, 45.5 (d, ^1J(P−C) = 123.2 Hz), 52.6, 53.8, 55.0, 55.3, 76.2, and 76.3 (2 d, ^3J(P−C) = 6.9 and 6.4 Hz respectively), 104.2, 113.3, 117.0 (d, ^3J(P−C) = 4.0 Hz), 121.3, 125.2, 125.5 (d, ^3J(P−C) = 5.2 Hz), 127.9, 128.1, 129.0, 129.4 (d, ^2J(P−C) = 11.6 Hz), 130.0, 130.1, 130.2 (d, ^3J(P−C) = 4.6 Hz), 132.4 (d, ^2J(P−C) = 16.7 Hz), 133.2, 136.7 (d, ^2J(P−C) = 10.4 Hz), 142.1, 158.5, 158.7, 167.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.7 and 17.9; LC/MS m/z 731 $[M + 1]^+$. Anal. calcd for $C_{36}H_{44}O_{12}P_2$: C 59.18; H 6.07. Found: C 59.32; H 5.95.

Compound 35. This compound was prepared by using above procedure, but the molar ratio of allene:DMAD was 1:1. Treatment of allenylphosphonate **12** (0.30 g, 1.11 mmol) and DMAD (0.16 g, 1.11 mmol) resulted in compound **35**. It was purified by using silica gel column chromatography [ethyl acetate/hexane (2:3)]. Yield quantitative by ^{31}P NMR, 0.39 g (isolated, 85%); gummy solid; IR (neat, cm^{-1}) 2953, 1734, 1640, 1437, 1269, 1059, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 and 1.32 (2 s, 6H), 1.58−1.66 and 1.84−1.87 (2 m, 3H), 2.07−2.28 (m, 3H), 3.33−3.47 (m, 2H), 3.72−3.78 (m, 2H), 3.81−3.93 (m, 9H), 5.36 and 5.90 (2 br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 22.2, 26.2, 29.9, 32.2 (d, ^3J(P−C) = 5.7 Hz), 34.2 (d, J(P−C) = 6.5 Hz), 36.6, 44.1 (d, J(P−C) = 14.7 Hz), 52.5, 52.7, 76.4 (d, ^2J(P−C) = 6.3 Hz), 76.6 (d, ^2J(P−C) = 6.5 Hz), 116.9 (d, ^1J(P−C) = 172.6 Hz), 119.2, 128.5, 133.1 (d, J(P−C) = 15.9 Hz), 140.5 (d, J(P−C) = 10.8 Hz), 160.6 (d, J = 8.6 Hz), 165.5, 168.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.0; LC/MS m/z 411 $[M + 1]^+$. Anal. calcd for $C_{20}H_{27}O_7P$: C, 58.53; H, 6.63. Found: C, 58.45; H, 6.69.

Compounds 36(a−d). These compounds were prepared by a procedure similar to that for **30a−c** using allenylphosphonate **10** (0.7 g, 2.3 mmol) and DMAD (0.81 g, 6.9 mmol). Isomers **36(c,d)** eluted first followed by **36a** and then **36b**. **Compound 36a:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield quantitative [**36a**+**36b**+**36(c,d)**, ratio 3:2:5 by ^{31}P NMR], 0.24 g (isolated, 28%, **36a**); mp 134−136 °C; IR (KBr, cm^{-1}) 2953, 2882, 1732, 1715, 1601, 1435, 1406, 1373, 1161, 1109, 1057, 833, 787, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 and 1.06 (2 s, 6H), 2.38 (s, 3H), 3.79 and 3.85 (2 s, 6H), 3.88−4.13 (m, 4H), 5.44 (d, ^2J(P−H) = 24.0 Hz, 1H), 7.22−8.00 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.6, 32.5 (d, ^3J(P−C) = 6.0 Hz), 43.1 (d, ^1J(P−C) = 134.0 Hz), 52.4, 52.6, 76.0 (d, ^2J(P−C) = 7.0 Hz), 76.2 (d, ^2J(P−C) = 6.0 Hz), 127.5, 128.7, 129.6 (d, ^2J(P−C) = 8.0 Hz), 131.9 (d, ^2J(P−C) = 11.0 Hz), 132.3 (d, ^3J(P−C) = 5.0 Hz), 132.5, 133.0 (d, ^3J(P−C) = 3.0 Hz), 133.1, 135.7 (d, ^3J(P−C) = 6.0 Hz), 136.1, 168.5, 168.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.0; LC/MS m/z 447 $[M + 1]^+$. Anal. calcd for $C_{23}H_{27}O_7P$: C 61.88; H 6.10. Found: C 61.68; H 6.02. This compound was crystallized from ethyl acetate/hexane (4:1) mixture at 25 °C. **Compound 36b:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative [**36a**+**36b**+**36(c,d)**] by ^{31}P NMR, 0.19 g (isolated, 14%, **36b**); mp 126−128 °C; IR (KBr, cm^{-1}) 2953, 1732, 1439, 1314, 1254, 1204, 1059, 1007, 824, 696, 534; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 and 0.99 (2 s, 6H), 1.83 (d, ^3J(H−H) = 6.4 Hz, 3H), 3.64 (s, 6H), 3.67−3.88 (m, 2H), 3.80 (s, 3H), 4.13−4.21 (m, 2H), 5.78−5.85 (m, 2H), 6.43 (d, ^2J(P−H) = 16.0 Hz, 1H), 7.22−7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.4, 21.6, 32.6 (d, ^3J(P−C) = 7.0 Hz), 44.6 (d, ^1J(P−C) = 139.0 Hz), 52.7, 52.8, 75.7 (d, ^2J(P−C) = 4.0 Hz), 125.3, 127.0, 128.1, 129.9 (d, ^2J(P−C) = 10.0 Hz), 131.6 (d, ^2J(P−C) = 7.0 Hz), 134.0, 134.8, 135.2, 135.4, 135.5, 135.6, 166.7, 167.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6; LC/MS m/z 589 $[M + 1]^+$. Anal. calcd for $C_{29}H_{33}O_{11}P$: C 59.18; H 5.65. Found: C 59.15; H 5.58. This compound was crystallized from ethyl acetate at 25 °C. **Isomeric compounds 36(c,d):** These compounds were separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield quantitative [**36a**+**36b**+**36(c,d)**] by ^{31}P NMR, 0.44 g (isolated, 43%, **36(c,d)** ∼ 1:1); gummy; IR (neat, cm^{-1}) 2963, 2928, 1734, 1447, 1416, 1261, 1094, 1019, 801; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 and 0.67 (2 s, 6H), 0.81 (t, ^3J(H−H) = 7.0 Hz, 3H, isomer **36d**), 1.27 and 1.29 (2 s, 6H), 1.57 (d, ^3J(H−H) = 4.4 Hz, 3H, isomer **36c**), 3.54−3.77 (m, 4H), 3.82−3.83 (2 s, 6H), 3.86−3.94 (m, 4H), 3.96−3.97 (2 s, 6H), 4.06 (s, 2H, isomer **36c**), 5.38−5.46 (m, 2H), 5.75−5.81 (m, 1H), 6.67 (d, J(H−H) = 11.2 Hz, isomer **36d**), 7.52−8.70 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.5_2, 22.0, 22.1, 32.1_0, 32.1_1, 32.2, 35.7 (d, ^3J(P−C) = 5.0 Hz), 52.7, 53.1, 76.9, 77.0, 125.2, 125.3, 125.4, 125.9, 126.1, 126.2, 126.6 (d, ^3J(P−C) = 4.0 Hz), 126.9, 127.1 (d, ^3J(P−C) = 4.0 Hz), 127.6, 127.9, 128.0, 128.5 (d, ^2J(P−C) = 12.0 Hz), 128.9, 129.0, 131.5, 131.7, 133.6, 133.7, 133.9 (d, ^2J(P−C) = 12.0 Hz), 135.0 (d, ^3J(P−C) = 4.0 Hz), 138.5, 138.8 (d, ^2J(P−C) = 11.0 Hz), 142.2 (d, ^2J(P−C) = 12.0 Hz) 167.5, 168.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.7 and 11.1; LC/MS m/z 447 $[M + 1]^+$. Anal. calcd for $C_{23}H_{27}O_7P$: C 61.88; H 6.10. Found: C 61.75; H 6.22.

Compounds 37(a−d). These compounds were prepared by a procedure similar to that for **30a−c** by using allenylphosphonate **10** (0.80 g, 2.63 mmol) and DMAD (1.34 g, 7.89 mmol). **Compound 37a:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield quantitative [**37a**+**37b**+**37(c,d)**, ratio 3:2:5 by ^{31}P NMR], 0.25 g (isolated, 25%, **37a**); mp 128−130 °C; IR (KBr, cm^{-1}) 2973, 2926, 1728, 1472, 1370, 1285, 1059, 826, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 and 1.07 (2 s, 6H), 1.26 and 1.36 (2 t, ^3J(H−H) = 6.0 Hz each, 6H), 2.39 (s, 3H), 3.86−4.13 (m, 4H), 4.25 and 4.32 (2 qrt, 4H), 5.46 (d, ^2J(P−H) = 24.0 Hz, 1H), 7.22−8.02 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.0, 19.8, 21.0, 21.5, 32.4 (d, ^3J(P−C) = 6.0 Hz), 43.0 (d, ^1J(P−C) = 134.0 Hz), 61.4, 61.7, 75.9, and 76.1 (2 d, ^2J(P−C) = 6.0 Hz each), 127.3, 128.6, 129.5 (d, ^2J(P−C) = 8.0 Hz), 132.0 (d, ^3J(P−C) = 5.0 Hz), 132.1 (d, ^2J(P−C) = 11.0 Hz), 132.7, 132.8, 135.6 (d, ^3J(P−C) = 6.0 Hz), 135.7, 168.0_0, 168.0_2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.1; LC/MS m/z 475 $[M + 1]^+$. Anal. calcd for $C_{25}H_{31}O_7P$: C 63.28; H 6.59. Found: C 63.41; H 6.52. **Compound 37b:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative [**37a**+**37b**+**37(c,d)**] by ^{31}P NMR, 0.25 g (isolated, 15%, **37b**); mp 124−126 °C; IR (KBr, cm^{-1}) 2975, 2926, 1728, 1727, 1470, 1414, 1370, 1198, 1061, 1013, 824, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 1.00 (2 s, 6H), 1.10 and 1.29 (2 t, 12H, ^3J(H−H) = 6.6 and 6.8 Hz respectively), 1.81 (d, ^3J(H−H) = 6.0 Hz, 3H), 3.67 (dd→t, $^{2,3}J \approx$ 12.0 Hz each, 2H), 3.84 (dd→t, $^{2,3}J \approx$ 12.0 Hz each, 2H), 4.12 and 4.26 (2 qrt, 8H), 5.74−5.86 (m, 2H),

6.43 (d, ^2J(P−H) = 15.6 Hz, 1H), 7.19−7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.0, 18.7, 21.3, 21.7, 32.5 (d, ^3J(P−C) = 6.9 Hz), 44.9 (d, ^1J(P−C) = 138.5 Hz), 61.8, 62.1, 75.9, 76.0, 125.6, 126.9, 128.0, 130.1 (d, ^2J(P−C) = 8.9 Hz), 131.1 (d, ^2J(P−C) = 7.4 Hz), 133.5, 134.8, 135.2 (d, ^3J(P−C) = 5.4 Hz), 135.7 (d, ^3J(P−C) = 6.4 Hz), 166.2, 167.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.2; LC/MS m/z 645 $[M + 1]^+$. Anal. calcd for $C_{33}H_{41}O_{11}P$: C 61.48; H 6.41. Found: C 61.32; H 6.45. **Isomeric compounds 37(c,d):** These compounds were separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield quantitative [**37a**+**37b**+**37(c,d)**] by ^{31}P NMR, 0.41 g (isolated, 42%, **37(c,d)** ≈ 1:1); gummy; IR (neat, cm^{-1}) 2978, 2942, 1730, 1470, 1372, 1258, 1059, 828, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 and 0.73 (2 s, 6H), 0.87 (t, ^3J(H−H) = 8.0 Hz, 3H, isomer **37d**), 1.29−1.47 (m, 18H), 1.62 and 1.64 (2 br s, 5H), 3.58−3.97 (m, 8H), 4.12 (s, 2H, isomer **37c**), 4.29−4.50 (m, 8H), 5.45−5.85 (m, 3H), 6.71 (d, ^3J(H−H) = 12.0 Hz, 1H, isomer **37d**), 7.59−8.74 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 13.8, 14.0$_0$, 14.0$_3$, 14.1, 17.9, 20.4, 20.5, 21.9$_5$, 22.0$_3$, 22.1, 32.0, and 32.1 (2 d, ^3J(P−C) = 5.0 and 7.0 Hz respectively), 35.5 (d, ^3J(P−C) = 5.0 Hz, isomer **37c**), 61.8, 61.9, 62.3, 63.3, 76.3, and 76.5 (2 d, ^3J(P−C) = 7.0 and 5.0 Hz respectively), 76.9$_0$, 76.9$_2$, 125.4, 125.6, 126.0, 126.1, 126.5 (d, ^3J(P−C) = 4.0 Hz), 127.0 (d, ^3J(P−C) = 4.0 Hz), 127.3, 127.5, 127.7, 127.9, 128.1, 128.5, 128.6, 128.7, 128.8, 131.6 (d, ^2J(P−C) = 18.0 Hz), 132.1 (d, ^2J(P−C) = 17.0 Hz), 133.5, 133.6, 133.7, 133.8, 133.9, 135.1 (d, ^3J(P−C) = 4.0 Hz), 138.4, 138.8 (d, ^2J(P−C) = 11.0 Hz), 142.3 (d, ^2J(P−C) = 9.0 Hz), 167.0, 167.5, 167.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.9 and 11.3; LC/MS m/z 475 $[M + 1]^+$. Anal. calcd for $C_{25}H_{31}O_7P$: C 63.28; H 6.59. Found: C 63.15; H 6.62.

Compounds 38(a−d). These compounds were prepared by a procedure similar to that for **30a−c** using allenylphosphonate **11** (0.35 g, 1.1 mmol) and DMAD (0.45 g, 3.2 mmol). **Compound 38a:** It was separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield quantitative [**38a**+**38b**+**38(c,d)**, ratio 3:2:5 by ^{31}P NMR], 0.13 g (isolated, 24%, **38a**); mp 132−134 °C; IR (KBr, cm^{-1}) 2963, 1742, 1721, 1601, 1433, 1281, 1196, 1076, 1032, 835, 787, 696, 517; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 and 0.82 (2 t, ^3J(H−H) = 6.0 and 8.0 Hz respectively, 6H), 1.19 and 1.49 (2 qrt, 4H), 2.38 (s, 3H), 3.80 and 3.85 (2 s, 6H), 3.87−4.16 (m, 4H), 5.45 (d, ^2J(P−H) = 24.0 Hz, 1H), 7.23−7.99 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.0, 7.1, 19.9, 22.5, 22.8, 37.4 (d, ^3J(P−C) = 5.7 Hz), 43.1 (d, ^1J(P−C) = 133.4 Hz), 52.4, 52.6, 73.4, and 73.6 (2 d, ^3J(P−C) = 6.5 and 6.3 Hz respectively), 127.5, 128.7, 129.6, 129.7, 131.9, 132.3 (d, ^3J(P−C) = 5.1 Hz), 132.6, 133.1, 135.8 (d, ^3J(P−C) = 5.0 Hz), 136.1, 168.5$_1$, 168.5$_4$; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.9; LC/MS m/z 475$[M + 1]^+$. Anal. calcd for $C_{25}H_{31}O_7P$: C 63.28; H 6.59. Found: C 63.22; H 6.65. **Compound 38b:** It was separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield quantitative [**38a**+**38b**+**38(c,d)**] by ^{31}P NMR, 0.10 g (isolated, 14%, **38b**); mp 124−126 °C; IR (KBr, cm^{-1}) 2965, 1732, 1636, 1439, 1395, 1256, 1075, 941, 831, 733, 704; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 and 0.79 (2 t, ^3J(H−H) = 8.0 Hz each, 6H), 1.13 and 1.37 (2 qrt, 4H), 1.83 (d, ^3J(H−H) = 4.0 Hz, 3H), 3.62 and 3.79 (2 s, 12H), 3.93 (dd→t, $^{2,3}J \sim$ 12.0 Hz, 2H), 4.18 (dd→t, $^{2,3}J \sim$ 10.0 Hz, 2H), 5.74−5.86 (m, 2H), 6.42 (d, ^2J(P−H) = 16.0 Hz, 1H), 7.21−7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.0, 19.0, 22.3, 23.3, 37.4 (d, ^3J(P−C) = 5.0 Hz), 44.8 (d, ^1J(P−C) = 138.0 Hz), 52.7, 52.9, 73.0, and 73.4 (2 d, ^3J(P−C) = 6.0 Hz each), 125.3, 127.1, 128.2, 130.1, 130.2, 131.8 (d, ^3J(P−C) = 7.0 Hz), 134.0, 134.8, 135.4 (d, ^2J(P−C) = 22.0 Hz), 135.6 (d, ^3J(P−C) = 6.0 Hz), 166.7, 167.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.3; LC/MS m/z 618 $[M + 1]^+$. Anal. calcd for $C_{31}H_{37}O_{11}P$: C 60.39; H 6.05. Found: C 60.29; H 6.12. **Isomeric compounds 38(c,d):** These compounds were separated by using ethyl acetate/hexane (1:2) mixture as the eluent. Yield quantitative [**38a**+**38b**+**38(c,d)**] by ^{31}P NMR, 0.22 g (isolated, 42%, **38(c,d),** ratio ≈ 1:1); gummy; IR (neat, cm^{-1}) 2967, 2888, 1734, 1647, 1445, 1254, 1075, 833, 783; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67−1.10 (m, 23H), 1.63 (d, ^3J(H−H) = 4.0 Hz, 3H, isomer **38c**), 1.77−1.86 (m, 2H, isomer **38d**), 3.57−3.61 (m, 4H), 3.87, 3.88, 4.02, and 4.03 (4 s, 12H), 4.05−4.13 (m, 6H), 5.44−5.86 (m, 3H), 6.72 (dd, ^3J(H−H) = 11.8 Hz, ^4J(P−H) ≈ 1.8 Hz, 1H, isomer **38d**), 7.57−8.75 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8, 7.3, 13.4, 18.0, 22.0, 22.1$_0$, 22.1$_4$, 22.9, 35.6 (d, ^3J(P−C) = 4.7 Hz), 37.1 and 37.2 (2 d, ^3J(P−C) = 5.7 and 5.0 Hz respectively), 52.7, 53.1$_0$, 53.1$_3$, 73.8, 74.0, 74.4 (d, ^3J(P−C) = 6.3 Hz), 125.4, 125.5 (d, ^3J(P−C) = 4.0 Hz), 126.1, 126.2, 126.8 (d, ^3J(P−C) = 3.7 Hz), 127.1, 127.2, 127.6, 128.0$_0$, 128.0$_2$, 128.1, 128.2, 128.5, 128.8, 129.0, 131.6 (d, ^2J(P−C) = 16.8 Hz), 132.1 (d, ^2J(P−C) = 16.8 Hz), 133.6, 133.7, 133.8, 133.9, 134.0, 134.1, 134.9, 138.4, 138.8 (d, ^2J(P−C) = 11.0 Hz), 142.1 (d, ^2J(P−C) = 12.6 Hz), 167.6, 168.0$_0$, 168.0$_2$, 168.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ11.0 and 12.5; LC/MS m/z 474 $[M]^+$. Anal. calcd for $C_{25}H_{31}O_7P$: C 63.28; H 6.59. Found: C 63.45; H 6.51.

Compounds 39(a−d). These compounds were prepared by a procedure similar to that for **30a−c** by using allenylphosphonate **11** (0.40 g, 1.20 mmol) and DMAD (0.62 g, 3.60 mmol). **Compound 39a:** It was separated by using ethyl acetate/hexane (1:1) mixture as the eluent. Yield quantitative [**39a**+**39b**+**39(c,d)**, ratio 3:2:5 by ^{31}P NMR] 0.13 g (isolated, 22%, **39a**); gummy; IR (neat, cm^{-1}) 2980, 2938, 1728, 1468, 1075, 1024, 835, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 and 0.82 (2 t, ^3J(H−H) = 7.6 Hz each, 6H), 1.14 (m, 8H), 1.49 (qrt, 2H), 2.39 (s, 3H), 3.91 and 4.19 (m, 4H), 4.24 and 4.32 (2 qrt, 4H), 5.47 (d, ^2J(P−H) = 23.6 Hz, 1H), 7.22−8.00 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.0, 7.1, 13.9, 14.1, 19.9, 22.5, 22.8, 37.3 (d, ^3J(P−C) = 5.0 Hz), 43.0 (d, ^1J(P−C) = 134.0 Hz), 61.4, 61.7, 73.4, and 73.5 (2 d, ^3J(P−C) = 8.0 and 7.0 Hz respectively), 127.4, 128.6, 129.6 (d, ^2J(P−C) = 8.0 Hz), 132.1 (d, ^3J(P−C) = 5.0 Hz), 132.3, 132.8, 135.8, 168.0, 168.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; LC/MS m/z 502 $[M]^+$. Anal. calcd for $C_{27}H_{35}O_7P$: C 64.53; H 7.02. Found: C 64.59; H 6.93. **Compound 39b:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative [**39a**+**39b**+**39(c,d)**] by ^{31}P NMR 0.11 g (isolated, 13%, **39b**); gummy; IR (neat, cm^{-1}) 2975, 2938, 1732, 1603, 1470, 1416, 1287, 1192, 1076, 1032, 938, 843, 787, 700, 623; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 and 0.79 (2 t, ^3J(H−H) = 7.4 Hz and 7.6 respectively, 6H), 1.05−1.44 (m, 16H), 1.82 (d, ^3J(H−H) = 6.4 Hz, 3H), 3.92−4.32 (m, 12H), 5.79−5.87 (m, 2H), 6.43 (d, ^2J(P−H) = 16.0 Hz, 1H), 7.20−7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.0$_0$, 7.0$_3$, 13.5, 14.0, 18.8, 22.3, 23.4, 37.3 (d, ^3J(P−C) = 5.7 Hz), 45.0 (d, ^1J(P−C) = 137.7 Hz), 61.8, 62.1, 73.1, and 73.4 (2d, ^3J(P−C) = 6.4 and 6.8 Hz), 125.5, 126.9, 128.0, 130.4 (d, ^2J(P−C) = 9.9 Hz), 131.5 (d, ^3J(P−C) = 6.3 Hz), 133.5, 134.7, 135.0, 135.2, 135.6 (d, ^3J(P−C) = 7.7 Hz), 166.2, 167.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.8; LC/MS m/z 672 $[M]^+$. Anal. calcd for $C_{35}H_{45}O_{11}P$: C 62.49; H 6.74. Found: C 62.31; H 6.82. **Isomeric compounds 39(c,d):** These compounds were separated by using ethyl acetate/hexane (2:3) mixture as the eluent. Yield quantitative [**39a**+**39b**+**39(c,d)**] by ^{31}P NMR, 0.24 g (isolated, 40%, **39(c,d)** ratio ~1:1); gummy; IR (neat, cm^{-1}) 2976, 2936, 1732, 1719, 1555, 1464, 1372, 1262, 1154, 1075, 1034, 938; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70−1.07 (m, 23H), 1.35−1.46 (m, 12H), 1.62 (d, ^3J(H−H) = 4.4 Hz, 3H, isomer **39c**), 1.77−1.86 (m, 2H, isomer **39d**), 3.57 and 3.60 (m each, 4H), 4.04−4.12 (m, 6H), 4.32 and 4.49 (2 qrt, 8H), 5.45−5.85 (m, 3H), 6.72 (d, ^3J(H−H) = 11.2 Hz, 1H, isomer **39d**), 7.57−8.74 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8, 7.3, 13.4, 13.9, 14.0, 14.1$_0$, 14.1$_3$, 18.0, 21.9, 22.1, 22.8, 35.5 (d, ^3J(P−C) = 3.6 Hz), 37.0 and 37.1 (2 d, ^3J(P−C) = 4.9 and 5.4 Hz respectively), 61.8, 61.9, 62.3$_0$, 62.3$_4$, 74.3, 74.4, 125.1, 125.5 (d, ^3J(P−C) = 4.0 Hz), 125.7 (d, ^2J(P−C) = 9.4 Hz), 125.9, 126.0, 126.1, 126.6, 126.7 (d, ^3J(P−C) = 4.1 Hz), 126.9, 127.1 (d, ^3J(P−C) = 4.5 Hz), 127.5, 127.7, 127.9, 128.0$_0$, 128.0$_4$, 128.1, 128.3, 128.7, 128.8, 129.7, 129.8 (d, ^3J(P−C) = 5.3 Hz),

131.3, 131.5, 131.7, 132.1, (d, ^3J(P−C) = 5.6 Hz), 133.5, 133.7, 133.8, 133.9, 135.1, 135.2, 138.4, 138.8, 142.0 (d, ^2J(P−C) = 11.8 Hz), 146.2, 147.5, 167.5, 167.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.1 and 12.6; LC/MS m/z 503 $[M + 1]^+$. Anal. calcd for $C_{27}H_{35}O_7P$: C 64.53; H 7.02. Found: C 64.42; H 7.11.

(C) Reaction of Allenylphosphonates with 1,3-Diphenylisobenzofuran. (i) Synthesis of Compounds 41−52. Compound 41a. A mixture of allenylphosphonate **1** (0.30 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol) in *p*-xylene (3 mL) was heated at 80 °C for 6−12 h. The solvent was removed under reduced pressure and the product **41a** was isolated by using silica gel column chromatography [ethyl acetate/hexane (3:2)]. Yield quantitative by ^{31}P NMR, 0.40 g (isolated, 55%); mp 144−146 °C; IR (KBr, cm^{-1}) 2965, 1499, 1460, 1350, 1260, 1059, 993; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 and 1.04 (2 s, 6H), 3.46 and 3.61 (2 dd, ^3J(P−H) ≈ 16.4 Hz, ^2J(H−H) ≈ 11.6 Hz, 2H), 4.00 (dd, ^3J(P−H) ≈ 11.2 Hz, ^2J(H−H) ≈ 6.0 Hz, 1H), 4.08 (d, ^2J(P−H) = 18.0 Hz, 1H), 4.15 (dd, ^3J(P−H) ≈ 11.2 Hz, ^2J(H−H) ≈ 6.0 Hz, 1H), 5.34 and 5.41 (br, 2H), 7.25−7.34 (m, 3H), 7.43−7.54 (m, 7H), 7.81 (d, ^3J(H−H) = 8.2 Hz, 2H), 7.97 (d, ^3J(H−H) = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.3, 32.8 (d, ^3J(P−C) = 6.7 Hz), 47.9 (d, ^1J(P−C) = 144.3 Hz), 74.3 (d, ^2J(P−C) = 6.3 Hz), 74.8 (d, ^2J(P−C) = 5.5 Hz), 89.2 (d, J(P−C) = 3.1 Hz), 90.2 (d, J(P−C) = 6.7 Hz), 109.1 (d, J(P−C) = 4.3 Hz), 119.7, 122.5, 126.7, 127.0, 127.6, 128.1, 128.2, 128.5 (d, J(P−C) = 8.3 Hz), 128.8, 135.0, 135.9, 144.7, 145.4, 146.1 (d, J(P−C) = 3.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.8; LC/MS m/z 459 $[M + 1]^+$. Anal. calcd for $C_{28}H_{27}O_4P$: C, 73.35; H, 5.94. Found: C, 73.41; H, 5.86.

Compound 42a. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphonate **2** (0.32 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.57 g (81%); mp 231−232 °C; IR (KBr, cm^{-1}) 3063, 1659, 1603, 1451, 1300, 1236, 1051, 997; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 and 1.03 (2 s, 6H), 1.43 (d, ^3J(P−H) = 16.0 Hz, 3H), 3.24 and 3.72 (2 dd, ^3J(P−H) ≈ 17.8 Hz, ^2J(H−H) ≈ 11.2 Hz, 2H), 3.91 and 4.26 (2 dd, ^3J(P−H) ∼ 10.6 Hz, ^2J(H−H) ≈ 4.0 Hz, 2H), 5.33 (br s, 2H), 7.17−7.19 (m, 2H), 7.37−7.58 (m, 8H), 7.85 (d, ^3J(H−H) = 7.6 Hz, 2H), 8.28 (d, ^3J(H−H) = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.1, 22.4, 33.0 (d, ^3J(P−C) = 6.0 Hz), 52.6 (d, ^1J(P−C) = 142.0 Hz), 74.3 (d, ^2J(P−C) = 7.0 Hz), 74.7 (d, ^2J(P−C) = 6.0 Hz), 89.8 (d, ^3J(P−C) = 6.0 Hz), 91.3 (d, ^2J(P−C) = 7.0 Hz), 108.5 (d, J(P−C) = 4.0 Hz), 119.7, 121.8, 126.3, 127.0, 127.3, 127.4, 127.8, 127.9, 128.1, 128.5, 135.6 (d, J(P−C) = 6.0 Hz), 144.7, 145.8, 152.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.2, LC/MS m/z 474 $[M + 1]^+$. Anal. calcd for $C_{29}H_{29}O_4P$: C, 73.71; H, 6.19. Found: C, 73.61; H, 6.28.

Compounds 43a−b. These compounds were prepared by a procedure similar to that for **41a** by using allenylphosphonate **3** (0.39 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). **Compound 43a:** It was eluted by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield [**43a**+**43b**] quantitative by ^{31}P NMR; 0.44 g (isolated, 70%, **43a**); mp 240−242 °C; IR (KBr, cm^{-1}) 2963, 1651, 1601, 1497, 1456, 1345, 1258, 1073, 997; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (t, ^3J(H−H) = 7.2 Hz, 3H), 0.80 (s, 3H), 0.90−0.98 (m, 5H), 1.17−1.33 (m, 2H), 1.92−2.13 (m, 2H), 3.11 and 3.71 (2 dd, ^3J(P−H) ∼17.8 Hz, ^2J(H−H) ∼ 11.4 Hz, 2H), 3.81 and 4.23 (2 dd, ^3J(P−H) ∼ 11.0 Hz, ^2J(H−H) ≈ 4.4 Hz, 2H), 5.26 and 5.37 (2 d, ^2J(H−H) = 4.4 Hz, 2H), 7.13−7.59 (m, 10H), 7.86 (d, ^3J(H−H) = 7.6 Hz, 2H), 8.36 (d, ^3J(H−H) = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 21.7, 22.4, 23.0, 25.8, 25.9, 32.7, 32.9 (d, ^3J(P−C) = 5.9 Hz), 56.5 (d, ^1J(P−C) = 138.3 Hz), 74.5 (d, ^2J(P−C) = 6.6 Hz), 74.8 (d, ^2J(P−C) = 6.3 Hz), 89.3 (d, ^3J(P−C) = 5.3 Hz), 91.6 (d, ^2J(P−C) = 7.3 Hz), 108.9 (d, J(P−C) = 5.1 Hz), 119.5, 121.8, 126.4, 126.9, 127.1, 127.4, 127.6, 127.9, 128.0, 128.5, 135.8, 145.4, 146.9, 149.2 (d, J(P−C) = 3.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.7; LC/MS m/z 515 $[M + 1]^+$. Anal. calcd for $C_{32}H_{35}O_4P$: C, 74.69; H, 6.86. Found: C, 74.62; H, 6.99. **Compound 43b:** It was isolated by using ethyl acetate/hexane (7:3) mixture as the eluent. Yield [**43a**+**43b**] quantitative by ^{31}P NMR; 0.12 g (isolated, 19%, **43b**); gummy; IR (neat, cm^{-1}) 2961, 1649, 1458, 1343, 1256, 1074, 1003, 909; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63−0.76 (m, 7H), 0.98 (s, 3H), 1.07−1.63 (m, 4H), 2.28−2.37 (m, 1H), 3.34 and 3.77 (dd→t, ^3J(P−H) ≈ ^2J(H−H) ≈ 10.7 Hz, 2H), 3.89 and 3.99 (dd→t, ^3J(P−H) ≈ ^2J(H−H) ∼ 10.0 Hz, 2H), 5.41 and 5.42 (2 s, 2H), 7.15−7.56 (m, 10H), 7.88 (d, ^3J(H−H) = 7.6 Hz, 2H), 7.94 (d, ^3J(H−H) = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.9, 22.4, 23.5, 27.3, 27.4, 32.8 (d, ^3J(P−C) = 8.0 Hz), 34.9, 57.4 (d, ^1J(P−C) = 135.0 Hz), 75.3 (d, ^2J(P−C) = 6.0 Hz), 75.9 (d, ^2J(P−C) = 7.0 Hz), 89.8, 91.0, 112.0 (d, J(P−C) = 6.0 Hz), 119.7, 122.1, 126.6, 127.5, 127.9, 128.3, 128.5, 135.5, 136.5, 145.3, 146.9 (d, J(P−C) = 12.0 Hz), 149.5 (d, J(P−C) = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.1; LC/MS m/z 515 $[M + 1]^+$. Anal. calcd for $C_{32}H_{35}O_4P$: C, 74.69; H, 6.86. Found: C, 74.62; H, 6.95.

Compound 44a. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphonate **4** (0.42 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.51 g (84%); mp 221−223 °C; IR (KBr, cm^{-1}) 2975, 1651, 1601, 1499, 1451, 1256, 1074, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 and 0.94 (2 s, 6H), 3.21 and 3.64 (dd, ^3J(P−H) ≈ 17.0 Hz, ^2J(H−H) ≈ 11.2 Hz, 2H), 3.85 and 4.21 (dd, ^3J(P−H) ≈ 10.8 Hz, ^2J(H−H) ≈ 5.4 Hz, 2H), 5.33 and 5.64 (d, ^2J(H−H) ≈ 4.6 Hz, 2H), 7.00−7.01 (m, 3H), 7.16−7.27 (m, 5H), 7.48−7.56 (m, 4H), 7.62−7.65 (m, 2H), 7.78 (d, ^3J(H−H) = 6.8 Hz, 1H), 7.96−8.01 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.7, 33.1 (d, ^3J(P−C) = 6.6 Hz), 64.3 (d, ^1J(P−C) = 145.0 Hz), 75.1 (d, ^2J(P−C) = 6.1 Hz), 75.3 (d, ^2J(P−C) = 6.1 Hz), 89.5, 93.4 (d, ^2J(P−C) = 6.6 Hz), 111.6, 119.4, 122.6, 126.3, 126.8, 126.9, 127.1, 127.3, 127.5, 128.0, 128.4, 128.7, 129.7, 129.8, 130.4 (d, J(P−C) = 7.6 Hz), 133.0, 135.6 (d, J(P−C) = 10.5 Hz), 137.0, 137.2, 140.0, 145.2, 145.8, 151.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.1; LC/MS m/z 535 $[M+1]^+$. Anal. calcd for $C_{34}H_{31}O_4P$: C, 76.39; H, 5.84. Found: C, 76.32; H, 5.87. It was crystallized from dichloromethane/hexane (4:1) mixture at 25 °C.

Compounds 45a−b. These compounds were prepared by a procedure similar to that for **41a** by using allenylphosphonate **5** (0.44 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). **Compounds 45a:** It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield [**45a**+**45b**] quantitative by ^{31}P NMR, 0.39 g (isolated, 66%, **45a**); mp 212−214 °C; IR (KBr, cm^{-1}) 2959, 1653, 1603, 1512, 1458, 1300, 1236, 1078, 1051, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 and 0.93 (2 s, 6H), 2.16 (s, 3H), 3.16−3.23 and 3.62−3.67 (2 m, 2H), 3.83−3.87 and 4.19−4.22 (2 m, 2H), 5.33 and 5.63 (d, ^2J(H−H) ∼ 4.6 Hz, 2H), 6.81 (d, ^3J(H−H) = 8.4 Hz, 2H), 7.17−7.27 (m, 5H), 7.41−7.77 (m, 7H), 7.95−8.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.9, 22.7, 33.0 (d, ^3J(P−C) = 6.6 Hz), 63.9 (d, ^1J(P−C) = 144.9 Hz), 74.9 (d, ^2J(P−C) = 6.5 Hz), 75.2 (d, ^2J(P−C) = 6.3 Hz), 89.5 (d, ^3J(P−C) = 5.1 Hz), 93.4 (d, ^2J(P−C) = 7.3 Hz), 111.6 (d, J(P−C) = 4.7 Hz), 119.3, 122.6, 126.3, 127.1, 127.2, 127.3, 127.4, 127.7, 128.0, 128.6, 130.3 (d, J(P−C) = 7.2 Hz), 133.8, 135.7 (d, J(P−C) = 8.5 Hz), 145.4, 145.8, 151.2 (d, J(P−C) = 4.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; LC/MS m/z 549 $[M + 1]^+$. Anal. calcd for $C_{35}H_{33}O_4P$: C, 76.63; H, 6.06. Found: C, 76.81; H, 6.21. **Compound 45b:** It was isolated by using ethyl acetate/hexane (7:3) mixture as the eluent. Yield [**45a**+**45b**] quantitative by ^{31}P NMR, 0.16 g (isolated, 27%, **45b**); mp 194−196 °C; IR (KBr, cm^{-1}) 2963, 1655, 1460, 1370, 1300, 1246, 1049, 990; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 and 1.08 (2 s, 6H), 2.29 (s, 3H), 2.93−2.99 and 3.90−4.09 (2 m, 4H), 5.40 and 5.48 (2 d, ^2J(H−H) ∼ 4.8 Hz, 2H), 6.65 (d, ^3J(H−H) = 7.6 Hz, 1H), 6.87−7.02 (m, 5H), 7.27−7.62 (m, 10H), 8.09 (d, ^3J(H−H) = 6.8 Hz, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 21.0, 22.0, 22.7, 32.9 (d, ^3J(P−C) = 8.4 Hz), 65.3 (d, ^1J(P−C) = 137.9 Hz), 74.7 (d, ^2J(P−C) = 6.3 Hz), 75.9 (d, ^2J(P−C) = 7.7 Hz), 91.1 (d, ^3J(P−C) = 1.3 Hz), 91.8 (d, ^2J(P−C) = 2.1 Hz), 113.3 (d, J = 7.1 Hz), 120.0, 123.0, 126.3, 127.7, 127.9 (d, J = 7.4 Hz), 128.6, 128.9, 130.2 (d, J = 7.5 Hz), 134.4 (d, J = 10.1 Hz), 137.1 (d, J = 10.3 Hz), 144.2, 146.4 (d, J = 11.5 Hz), 152.2 (d, J = 8.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1; LC/MS m/z 549 $[M + 1]^+$. Anal. calcd for $C_{35}H_{33}O_4P$: C, 76.63; H, 6.06. Found: C, 76.58; H, 6.15.

Compounds 46a−b. These compounds were prepared by a procedure similar to that for **41a** by using allenylphosphonate **7** (0.47 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). **Compounds 46a:** It was separated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield [**46a**+**46b**] quantitative by ^{31}P NMR, 0.40 g (isolated, 69%, **46a**); mp 199−201 °C; IR (KBr, cm^{-1}) 2963, 1607, 1512, 1462, 1372, 1296, 1248, 1086, 939; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 and 0.94 (2 s, 6H), 3.16−3.23 (m, 1H), 3.61−3.66 (m, 4H), 3.83−3.87 and 4.20−4.23 (2 m, 2H), 5.34 (s, 1H), 5.63 (d, ^2J(H−H) = 4.0 Hz, 1H), 6.54 (d, ^3J(P−H) = 8.8 Hz, 2H), 7.17−7.26 (m, 5H), 7.45−7.77 (m, 7H), 7.96 (d, J(H−H) = 7.2 Hz, 2H), 8.01 (d, J(H−H) = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.7, 33.0 (d, ^3J(P−C) = 6.5 Hz), 55.0, 63.5 (d, ^1J(P−C) = 145.0 Hz), 74.9 (d, ^2J(P−C) = 6.4 Hz), 75.2 (d, ^2J(P−C) = 6.3 Hz), 89.5 (d, ^3J(P−C) = 5.3 Hz), 93.5 (d, ^2J(P−C) = 7.5 Hz), 111.6 (d, J(P−C) = 4.7 Hz), 112.3, 119.3, 122.5, 126.3, 127.1, 127.2 (d, J(P−C) = 3.9 Hz), 127.4, 128.0, 128.7, 128.9, 131.6 (d, J(P−C) = 7.3 Hz), 135.7 (d, J(P−C) = 6.0 Hz), 145.3, 145.7, 151.3 (d, J(P−C) = 4.4 Hz), 158.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; LC/MS m/z 563 $[M - 1]^+$. Anal. calcd for $C_{35}H_{33}O_5P$: C, 74.45; H, 5.89. Found: C, 74.42; H, 5.85. It was crystallized from dichloromethane/hexane (4:1) mixture at 25 °C. **Compound 46b:** It was separated by using ethyl acetate/hexane (7:3) mixture as the eluent. Yield [**46a**+**46b**] quantitative by ^{31}P NMR, 0.11 g (isolated, 19%, **46b**); mp 209−210 °C; IR (KBr, cm^{-1}) 2965, 1607, 1512, 1460, 1341, 1256, 1188, 1074, 1007, 912; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 and 1.08 (2 s, 6H), 2.94 (dd→t, ^3J(P−H) ≈ ^2J(H−H) ≈ 11.4 Hz, 1H), 3.77 (s, 3H), 3.89−4.09 (m, 3H), 5.40 and 5.48 (2 br s, 2H), 6.61−6.67 (m, 3H), 6.89−7.61 (m, 13H), 8.08 (d, ^3J(H−H) = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.7, 32.9 (d, ^3J(P−C) = 8.1 Hz), 55.1, 65.0 (d, ^1J(P−C) = 138.0 Hz), 74.8 (d, ^2J(P−C) = 5.8 Hz), 76.0 (d, ^2J(P−C) = 7.4 Hz), 91.1, 91.8, 112.4, 113.3 (d, J = 6.5 Hz), 120.0, 123.0, 126.3, 126.4, 127.8, 128.0, 128.6, 128.9, 129.1, 129.5, 131.6 (d, J = 7.2 Hz), 134.4, 137.0, 144.1, 146.4 (d, J = 11.4 Hz), 152.4 (d, J = 8.3 Hz), 158.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1; LC/MS m/z 565 $[M + 1]^+$. Anal. calcd for $C_{35}H_{33}O_5P$: C, 74.45; H, 5.89. Found: C, 74.39; H, 5.86. This compound was crystallized from dichloromethane/hexane (4:1) mixture at 25 °C.

Compounds 47a−b. These compounds were prepared by a procedure similar to that for **41a** by using allene **22** (0.18 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). **Compound 47a:** It was separated by using ethyl acetate/hexane (1:4) mixture as the eluent. Yield 0.32 g (isolated, 31%); mp 90−92 °C; IR (KBr, cm^{-1}) 2975, 2926, 1736, 1661, 1449, 1300, 1179, 997; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, ^3J(H−H) = 7.2 Hz, 3H), 4.04−4.08 (m, 2H), 4.32 (s, 1H), 5.22 and 5.25 (2 s, 2H), 7.16−7.25 (m, 4H), 7.43−7.55 (m, 6H), 7.73 (d, ^3J(H−H) = 6.8 Hz, 2H), 7.84 (d, ^3J(H−H) = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 55.1, 60.9, 89.1, 90.4, 107.8, 119.1, 123.0, 126.6, 127.2, 127.4$_0$, 127.4$_2$, 128.3, 128.4, 128.5, 128.6, 134.9, 136.8, 145.1, 146.1, 149.1, 170.3; LC/MS m/z 383 $[M + 1]^+$. Anal. calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.62, H; 5.75. It was crystallized from dichloromethane/hexane (4:1) mixture at 25 °C. **Compound 47b:** It was separated by using ethyl acetate/hexane (1:2) as the eluent. Yield 0.60 g (isolated, 59%); gummy; IR (neat, cm^{-1}) 2978, 1746, 1719, 1499, 1449, 1310, 1254, 1148, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, ^3J(H−H) = 7.2 Hz, 3H), 3.85−4.08 (m, 3H), 5.19 and 5.23 (2 m, 2H), 7.11−7.27 (m, 3H), 7.37−7.68 (m, 9H), 7.95−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 56.3, 60.7, 89.2, 90.2, 108.5, 119.5, 119.9, 125.2, 127.2, 127.5, 127.6, 127.8, 128.3, 128.4, 128.6, 134.6, 136.2, 145.2, 148.1, 149.6, 170.7; LC/MS m/z 381 $[M - 1]^+$. Anal. calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.65; H, 5.82.

Compound 48b. This compound was prepared by a procedure similar to that for **41a** by using allene **23** (0.32 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (1:2) mixture as the eluent. Yield 0.55 g (isolated, 78%); gummy; IR (neat, cm^{-1}) 2982, 1740, 1499, 1449, 1346, 1304, 1182, 1065, 1024, 993; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, ^3J(H−H) = 7.2 Hz, 3H), 1.21 (t, ^3J(H−H) = 7.2 Hz, 3H), 1.83 (d, ^2J(H−H) = 16.8 Hz, 1H), 3.52 (d, ^2J(H−H) = 16.8 Hz, 1H), 3.65−3.69 and 3.82−3.86 (2 m, 2H), 4.07 (q, ^3J(H−H) = 7.2 Hz, 2H), 5.22 and 5.60 (2 s, 2H), 7.25−7.61 (m, 10H), 7.79 (d, ^3J(H−H) = 7.6 Hz, 2H), 8.03−8.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.1, 41.6, 60.5, 60.7, 60.8, 90.6, 91.2, 110.8, 120.3, 121.5, 125.8, 126.7, 128.1, 128.2, 128.5, 128.6, 128.7, 134.9, 135.6, 144.6, 146.0, 152.8, 170.7, 170.8; LC/MS m/z 469 $[M + 1]^+$. Anal. calcd for $C_{30}H_{28}O_5$: C, 76.90; H, 6.02. Found: C, 76.85; H, 6.10.

Compound 49. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphonate **8** (0.35 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was purified by column chromatography using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.58 g (isolated, 86%); mp 182−184 °C; IR (KBr, cm^{-1}) 2969, 1636, 1458, 1368, 1248, 1061, 1005, 874; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (br s, 6H), 1.35 and 1.43 (2 s, 6H), 3.57−3.73 (m, 2H), 4.03−4.12 (m, 2H), 5.62 (d, ^2J(P−H) = 12.8 Hz, 1H), 7.21−7.59 (m, 10H), 7.76 (d, ^3J(H−H) = 7.2 Hz, 2H), 7.88 (d, ^3J(H−H) = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.6, 24.1, 24.3, 32.5 (d, ^3J(P−C) = 5.7 Hz), 50.6 (d, ^3J(P−C) = 3.6 Hz), 75.0 (d, ^2J(P−C) = 3.2 Hz), 75.1 (d, ^2J(P−C) = 3.5 Hz), 91.6 (d, ^3J(P−C) = 23.4 Hz), 92.2, 105.6 (d, ^1J(P−C) = 190.8 Hz), 120.6, 121.6, 125.7, 127.1, 127.5 (d, J(P−C) = 7.8 Hz), 128.1, 128.3, 128.7, 128.8, 134.9, 136.4, 142.7 (d, J(P−C) = 1.3 Hz), 147.2, 176.2 (d, ^2J(P−C) = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.8; LC/MS m/z 486 $[M]^+$. Anal. calcd for $C_{30}H_{31}O_4P$: C, 74.06; H, 6.42. Found: C, 74.25; H, 6.45.

Compound 50. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphonate **9** (0.41 g, 0.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.51 g (isolated, 83%); mp 228−230 °C; IR (KBr, cm^{-1}): 2930, 1634, 1447, 1265, 1063, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 and 1.04 (2 s, 6H), 1.17−1.77 (m, 7H), 2.23−2.29 and 2.52−2.61 (m, 3H), 3.60−3.74 and 4.11−4.19 (2 m, 4H), 5.54 (d, ^2J(P−H) = 10.5 Hz, 1H), 7.30−7.58 (m, 9H), 7.85−7.93 (m, 3H), 8.01−8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.7, 21.9, 22.7, 23.4, 32.3, 32.5 (d, ^3J(P−C) = 5.6 Hz), 32.8, 54.5 (d, ^3J(P−C) = 2.7 Hz), 74.8 (d, ^2J(P−C) = 6.1 Hz), 74.9 (d, ^2J(P−C) = 5.9 Hz), 90.5 (d, ^3J(P−C) = 23.9 Hz), 92.6, 104.4 (d, ^1J(P−C) = 192.7 Hz), 120.9, 122.4, 127.0, 127.5, 127.6, 127.9, 128.2, 128.6, 128.7, 135.0, 138.0, 143.0, 147.4, 179.1 (d, ^2J(P−C) = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.3; LC/MS m/z 528 $[M + 1]^+$. Anal. calcd for $C_{33}H_{35}O_4P$: C, 75.27; H, 6.70. Found: C, 75.12; H, 6.81.

Compound 51. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphine oxide **19** (0.43 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.49 g (isolated, 80%); mp 200−202 °C; IR (KBr, cm^{-1}) 2969, 1624, 1435, 1348, 1302, 1204, 1115, 995; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 1.38 (s, 6H), 5.99 (d, ^2J(P−H) = 20.8 Hz, 1H), 7.25−7.57 (m, 20H), 7.74 (d, ^3J(H−H) = 7.6 Hz, 2H), 7.86 (d, J(H−H) = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 24.9, 50.7 (d, ^3J(P−C) = 3.0 Hz), 91.9 (d, ^3J(P−C) = 17.0 Hz), 92.3, 112.1 (d, ^1J(P−C) = 102.0 Hz), 120.4, 121.8, 125.7, 127.0, 127.3, 127.5, 128.2, 128.3_6, 128.4 (d, J(P−C) = 5.0 Hz), 128.5, 128.7, 128.8, 130.7, 130.7_5 (d, J(P−C) = 2.0 Hz), 130.8, 131.3 (d, J(P−C) = 2.0 Hz), 134.5, 134.8, 135.0, 135.5, 135.8, 136.5, 142.9, 147.5, 174.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7; LC/MS m/z 539 $[M + 1]^+$. Anal. calcd for $C_{37}H_{31}O_2P$: C, 82.51; H, 5.80. Found: C, 82.39; H, 5.87.

Compound 52. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphine oxide **20** (0.49 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.48 g (isolated, 85%); mp 208−210 °C; IR (KBr, cm^{-1}) 2922, 1618, 1435, 1345, 1198, 1101, 993; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11−1.73 (m, 7H), 2.20−2.76 (m, 3H), 5.86 (d, ^2J(P−H) = 20.0 Hz), 7.27−7.56 (m, 19H), 7.82 (d, ^3J(H−H) = 8.0 Hz, 2H), 7.93−7.95 (m, 1H), 8.01 (d, ^3J(H−H) = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.8, 23.5, 33.1, 33.5, 54.4 (d, ^3J(P−C) = 2.0 Hz), 90.8 (d, ^3J(P−C) = 16.6 Hz), 92.6, 110.8 (d, ^1J(P−C) = 102.6 Hz), 120.6, 122.6, 126.9, 127.4, 127.6, 127.9, 128.4 (d, J = 3.2 Hz), 128.4_6, 128.4_9, 128.6, 128.7, 130.8 (d, J = 3.0 Hz), 130.9 (d, J = 3.6 Hz), 131.2_6, 131.3_0, 131.3_3, 134.5, 134.8, 135.2, 135.6, 135.9, 138.3, 143.4, 147.7, 176.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6; LC/MS m/z 580 $[M + 1]^+$. Anal. calcd for $C_{40}H_{35}O_2P$: C, 83.02, H; 6.10. Found: C, 83.21; H, 6.03.

(ii) Synthesis of Compounds 53−56. Compound 53. A mixture of allenylphosphonate **12** (0.30 g, 1.1 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol) in *p*-xylene (3 mL) was heated at 140 °C for 6 h. The solvent was removed in vacuo using a rotary evaporator. It was isolated by using silica gel column chromatography [ethyl acetate/hexane (4:1)]. Yield quantitative by ^{31}P NMR, 0.50 g (isolated, 83%, **53**); mp 268−270 °C; IR (KBr, cm^{-1}) 2936, 1730, 1605, 1447, 1262, 1061, 1013; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 and 1.24 (2 s, 6H), 1.51−2.11 (m, 7H), 2.83−2.87 and 3.15−3.18 (m, 2H), 3.37−3.54 (m, 2H), 3.82−3.91 (m, 2H), 5.24 (d, ^2J(H−H) = 2.4 Hz, 1H), 5.57 (br s, 1H), 7.11−7.52 (m, 10H), 7.80 (d, ^3J(H−H) = 8.0 Hz, 2H), 7.94 (d, ^3J(H−H) = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 22.2, 26.8, 29.7, 31.4, 32.2 (d, ^3J(P−C) = 5.6 Hz), 40.0 (d, J(P−C) = 9.2 Hz), 61.5 (d, J(P−C) = 20.9 Hz), 75.2 (d, ^2J(P−C) = 6.8 Hz), 75.5 (d, ^2J(P−C) = 6.9 Hz), 88.3, 90.2 (d, ^3J(P−C) = 10.6 Hz), 119.2 (d, J(P−C) = 4.9 Hz), 120.7 (d, ^1J(P−C) = 166.6 Hz), 121.3, 122.0, 125.4, 126.9, 127.3, 127.4 (d, J(P−C) = 6.3 Hz), 128.0, 128.4, 128.6, 141.1, 142.9 (d, J(P−C) = 10.5 Hz), 146.0, 147.2 (d, J(P−C) = 12.4 Hz), 161.6 (d, J(P−C) = 8.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.4; LC/MS m/z 539 $[M + 1]^+$. Anal. calcd for $C_{34}H_{35}O_4P$: C, 75.82; H, 6.55. Found: C, 75.91; H, 6.71.It was crystallized from dichloromethane/hexane (10:1) mixture at 25 °C.

Compound 54. This compound was prepared by a procedure similar to that for **53** by using allenylphosphonate (**13**) (0.33 g, 1.1 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.46 g (isolated, 80%); mp 140−142 °C; IR (KBr, cm^{-1}) 2938, 1601, 1448, 1265, 1076, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 and 0.87 (2 t, ^3J(H−H) ∼ 7.5 Hz, 6H), 1.06−1.17 (m, 2H), 1.26−1.30 (m, 1H), 1.67−1.81 and 1.88−1.93 (m, 6H), 2.07−2.10 (m, 2H), 2.85−2.89 and 3.15−3.19 (m, 2H), 3.38−3.41 (m, 1H), 3.67−3.85 (m, 2H), 4.01−4.15 (m, 1H), 5.25 (d, ^2J(H−H) = 2.8 Hz, 1H), 5.59 (d, ^2J(H−H) = 2.4 Hz, 1H), 7.14−7.23 (m, 3H), 7.33−7.54 (m, 7H), 7.81−7.83 (m, 2H), 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9, 7.2, 21.4, 22.4, 26.9, 29.7, 31.4, 32.2, 37.1 (d, ^3J(P−C) = 4.6 Hz), 40.0 (d, J(P−C) = 9.3 Hz), 61.4 (d, J(P−C) = 21.1 Hz), 72.7 (d, ^2J(P−C) = 7.1 Hz), 73.1 (d, ^2J(P−C) = 6.6 Hz), 88.3, 90.2 (d, ^3J(P−C) = 10.8 Hz), 119.1 (d, J(P−C) = 6.1 Hz), 121.3, 122.0, 125.4, 126.9, 127.3, 127.4, 127.5, 128.0, 128.4, 128.6, 141.1, 142.9 (d, J(P−C) = 10.3 Hz), 145.9, 147.2 (d, J(P−C) = 12.2 Hz), 161.4 (d, J(P−C) = 8.6 Hz), [the doublet due to ^1J(P−C) was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.8; LC/MS m/z 567 $[M + 1]^+$. Anal. calcd for $C_{36}H_{39}O_4P$: C, 76.30; H, 6.94. Found: C, 76.41; H, 6.88.

Compound 55. This compound was prepared by a procedure similar to that for **53** by using allenylphosphonate **14** (0.38 g, 1.1 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol) It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.45 g (isolated, 82%); mp 108−110 °C; IR (KBr, cm^{-1}) 2924, 1599, 1460, 1269, 1067, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 and 1.01 (2 s, 6H), 1.27 (br, 1H), 1.63−1.69 (br, 1H), 1.98 (br, 3H), 2.13−2.16 (br, 2H), 2.93−2.98 and 3.21−3.24 (2 m, 2H), 3.49−3.55 and 3.87−3.95 (m, 4H), 6.65 (br, 1H), 7.11−7.26 (m, 7H), 7.33−7.42 (m, 5H), 7.48−7.56 (m, 4H), 7.85−8.03 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 22.2, 27.1, 31.0, 31.1, 32.5 (d, ^3J(P−C) = 6.0 Hz), 40.6 (d, J(P−C) = 8.0 Hz), 62.1 (d, J(P−C) = 21.0 Hz), 74.1 (d, ^2J(P−C) = 5.0 Hz), 75.2 (d, ^2J(P−C) = 6.0 Hz), 88.1, 92.3 (d, J(P−C) = 9.0 Hz), 120.2 (d, ^1J(P−C) = 174.0 Hz), 120.9, 122.7, 125.5, 126.9, 127.3, 127.5, 127.6, 127.7, 128.2, 128.4, 128.7, 130.4, 132.3, 136.3, 139.7 (d, J(P−C) = 10.0 Hz), 142.2, 142.4, 142.6, 146.3, 164.1 (d, J(P−C) = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.3; LC/MS m/z 615 $[M + 1]^+$. Anal. calcd for $C_{40}H_{39}O_4P$: C, 78.16; H, 6.39. Found: C, 78.23; H, 6.31.

Compound 56. This compound was prepared by a procedure similar to that for **53** by using allenylphosphonate **15** (0.28 g, 1.11 mmol) and 1,3-diphenylisobenzofuran (0.41 g, 1.52 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.49 g (isolated, 80%); gummy; IR (neat, cm^{-1}) 2932, 1599, 1447, 1240, 1022, 961; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28−1.31 (m, 6H), 1.34−1.38 (m, 1H), 1.59−1.66 (m, 2H), 1.71−1.75 (m, 2H), 2.41−2.49 (m, 1H), 2.68−2.74 (m, 1H), 3.58−3.63 (m, 1H), 3.77−4.04 (m, 4H), 5.29 (d, ^2J(H−H) ∼ 3.4 Hz, 1H), 5.43 (d, ^2J(H−H) ∼ 3.4 Hz, 1H), 7.22−7.43 (m, 10H), 7.68−7.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3 (d, ^3J(P−C) = 3.0 Hz), 16.4 (d, ^3J(P−C) = 2.9 Hz), 22.0, 23.2, 27.5, 31.8 (d, J(P−C) = 8.1 Hz), 56.4 (d, J(P−C) = 21.2 Hz), 61.3 (d, ^2J(P−C) = 6.1 Hz), 61.5 (d, ^2J(P−C) = 5.9 Hz), 89.6 (d, ^3J(P−C) = 7.5 Hz), 89.8 (d, ^4J(P−C) = 1.8 Hz), 117.7 (d, J(P−C) = 5.3 Hz), 122.5, 123.1, 124.7 (d, ^1J(P−C) = 180.7 Hz), 126.0, 127.1, 127.4 (d, J(P−C) = 7.4 Hz), 127.5, 127.7_9, 127.8_4, 128.3, 141.5, 143.6, 147.5, 150.1 (d, J(P−C) = 10.2 Hz), 160.7 (d, J(P−C) = 9.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.9; LC/MS m/z 527 $[M + 1]^+$. Anal. calcd for $C_{33}H_{35}O_4P$: C, 75.27; H, 6.70. Found: C, 75.15; H, 6.81.

Compound 57. This compound was prepared by a procedure similar to that for **41a** by using allenylphosphonate **12** (0.30 g, 1.60 mmol) and 1,3-diphenylisobenzofuran (0.65 g, 2.39 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. In this reaction, compound **53** (20%, ^{31}P NMR) was also formed. Yield [**53** + **57**] quantitative by ^{31}P NMR, 0.41 g (isolated, 68%, **57**); mp 202−204 °C; IR (KBr, cm^{-1}) 2926, 1827, 1655, 1601, 1451, 1343, 1298, 1256, 1076, 1005, 912; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (s, 3H), 0.95 (br s, 4H), 1.15−1.26 (m, 3H), 1.71−2.05 (m, 4H), 3.06−3.13 (m, 1H), 3.65−3.77 (m, 2H), 4.18−4.22 (m, 1H), 5.25 and 5.46 (2 d, ^2J(H−H) ∼ 4.0 Hz, 2H), 6.03 (br s, 1H), 7.15−7.67 (m, 10H), 7.87 (d, ^3J(H−H) = 8.0 Hz, 2H), 8.25 (d, ^3J(H−H) = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.9, 22.7, 22.9, 26.0, 28.3 (d, J(P−C) = 5.9 Hz), 33.0 (d, ^3J(P−C) = 6.4 Hz), 65.1 (d, ^1J(P−C) = 142.5 Hz), 74.7 (d, ^2J(P−C) = 6.5 Hz), 75.0 (d, ^2J(P−C) = 6.5 Hz), 89.2 (d, ^3J(P−C) = 5.1 Hz), 93.1 (d, ^2J(P−C) = 7.3 Hz), 110.8 (d, J(P−C) = 5.1 Hz), 119.3, 122.3, 126.3, 127.1 (d, J(P−C) = 13.8 Hz), 127.3_7, 127.4_2, 127.7, 127.9, 128.5, 130.6 (d, J(P−C) = 8.9 Hz), 132.8, 135.8, 136.0, 145.7, 146.0, 149.6 (d, J(P−C) = 4.3 Hz); ^{31}P NMR

(162 MHz, $CDCl_3$) δ 23.4; LC-MS m/z 537 $[M - 1]^+$. Anal. calcd for $C_{34}H_{35}O_4P$: C, 75.82; H, 6.55. Found: C, 75.65; H, 6.71.

(D) Reaction of Allenylphosphonates with Anthracene. Synthesis of [4 + 2] Cycloaddition Compounds 58−68 and the [2 + 2] Dimerized Product 70. Compounds 58 and 64. A mixture of allenylphosphonate **1** (0.30 g, 1.60 mmol) and anthracene (1.00 g, 5.58 mmol) in *p*-xylene (3 mL) was heated under reflux for 24 h. The solvent was removed under reduced pressure. Excess anthracene was removed by using a short column (neutral alumina, ethyl acetate/hexane: 1:4) and the crude products **58** and **64** (same R_f values) were eluted by using ethyl acetate/hexane (3:2) mixture. Pure compounds **58** (powdery) and **64** (crystals) were separated by hand−picking after crystallization from dichloromethane/hexane (4:1). **Compound 58:** Yield [**58** + **64**] quantitative by ^{31}P NMR, 0.41 g (isolated, 70%, **58**); mp 176−178 °C; IR (KBr, cm^{-1}) 3010, 2885, 2298, 1467, 1270, 1056, 1003, 911; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 and 1.03 (2 s, 6H), 3.15 (d, ^2J(P−H) = 23.2 Hz, 1H), 3.42−3.45 and 3.72−3.76 (2 m, 2H), 3.94 and 4.15 (2 dd, ^3J(P−H) = 10.8 Hz, ^2J(H−H) ≈ 6.4 Hz, 2H), 4.80−4.82 (m, 2H), 5.18 and 5.36 (2 d, ^2J(H−H) = 4.8 Hz, 2H), 7.11−7.42 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.3, 32.8 (d, ^3J(P−C) = 6.2 Hz), 43.0 (d, ^1J(P−C) = 138.3 Hz), 45.2, 55.4 (d, ^3J(P−C) = 4.0 Hz), 74.5 and 75.3 (2 d, ^2J(P−C) = 6.3 Hz), 111.3 (d, ^2J(P−C) = 6.7 Hz), 123.4, 123.5, 123.6, 123.7, 125.4, 126.2, 126.3, 126.6, 140.1, 141.3, 142.0, 142.1, 143.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.8; LC/MS m/z 367 $[M+1]^+$; Anal. Calcd. for $C_{22}H_{23}O_3P$: C, 72.12; H, 6.33. Found: C, 72.35; H, 6.26. **Compound 64:** Yield [**58** + **64**] quantitative by ^{31}P NMR, 0.06 g (isolated, 10%, **24**); mp 168−172 °C; IR (KBr, cm^{-1}) 2922, 2852, 2301, 1627, 1463, 1264, 1060, 1007, 909; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 and 1.05 (2 s, 6H), 2.83−2.85 (m, 2H), 3.67−4.12 (m, 4H), 4.49 (br s, 1H), 4.84 (s, 1H), 5.78 (d, ^2J(P−H) = 19.6 Hz, 1H) 7.11−7.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.3, 32.8 (d, ^3J(P−C) ≈ 6.2 Hz), 36.0, 44.6, 58.1 (d, ^3J(P−C) = 23.3 Hz), 74.9, 75.0, 106.4 (d, ^1J(P−C) = 187.3 Hz), 123.7, 124.0, 126.3, 126.7, 139.8, 143.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.6; LC/MS m/z 367 $[M + 1]^+$. Anal. calcd for $C_{22}H_{23}O_3P$: C, 72.12; H, 6.33. Found: C, 72.05; H, 6.38. It was crystallized from dichloromethane/hexane (4:1) mixture at 25 °C.

Compound 59. This compound was prepared by a procedure similar to that for **58** and **64** by using compound **2** (0.32 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was formed along with self-dimerized product **70** (yield: 15%) The eluent used for compound **59** was ethyl acetate/hexane (3:2) mixture. Yield [**59** + **70**] quantitative by ^{31}P NMR, 0.38 g (isolated, 67%, **59**); mp 208−210 °C; IR (KBr, cm^{-1}) 2967, 1470, 1372, 1277, 1059, 1003, 831; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 and 1.00 (2 s, 6H), 1.25 (d, ^3J(P−H) = 16.0 Hz, 3H), 3.24−3.31 (m, 1H), 3.68−3.84 (m, 2H), 4.18−4.22 (m, 1H), 4.55 (br, 1H), 4.75 (s, 1H), 5.09 and 5.37 (2 d, 2H, ^2J(H−H) ≈ 4.8 Hz), 7.10−7.44 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 22.2, 24.8 (d, ^2J(P−C) = 1.8 Hz), 32.8 (d, ^3J(P−C) = 6.3 Hz), 46.0 (d, ^1J(P−C) = 139.4 Hz), 51.8, 55.8 (d, ^3J(P−C) = 3.0 Hz), 74.6 and 75.4 (2 d, ^2J(P−C) ≈ 6.8 Hz), 111.0 (d, ^2J(P−C) = 6.8 Hz), 123.0, 123.2, 125.6, 125.9, 126.1, 126.3, 126.6, 140.0, 140.1, 141.0, 141.1 (d, J(P−C) = 3.1 Hz), 142.6 (d, J(P−C) = 2.9 Hz), 148.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9; LC/MS m/z 381 $[M + 1]^+$. Anal. calcd for $C_{23}H_{25}O_3P$: C, 72.62; H, 6.62. Found: C, 72.65; H, 6.56.

Compound 60. This compound was prepared by a procedure similar to that for **58** and **64** by using allenylphosphonate **3** (0.39 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.35 g (isolated, 68%); mp 82−84 °C; IR (KBr, cm^{-1}) 3042, 2957, 1640, 1464, 1370, 1227, 1053; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81−0.96 (m, 11H), 1.08−1.22 (m, 2H), 1.18−1.93 (m, 2H), 3.27 and 3.60 (2 dd, ^3J(P−H) ≈ 15.5 Hz, ^2J(H−H) ≈ 11.0 Hz, 2H), 3.81 and 4.15 (2 dd, ^3J(P−H) ≈ 10.8 Hz, ^2J(H−H) ≈ 6.0 Hz, 2H), 4.74 (s, 1H), 4.84 and 5.06 (2 d, ^2J(H−H) ≈ 4.0 Hz, 1H), 5.33 (d, ^3J(P−H) = 5.2 Hz, 1H), 7.07−7.12 (m, 4H), 7.24−7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.0, 22.5, 23.2, 26.8, 32.8 (d, ^3J(P−C) = 6.6 Hz), 39.1, 48.2, 50.1 (d, ^1J(P−C) = 136.9 Hz), 56.0 (d, ^3J(P−C) = 3.2 Hz), 74.5 and 75.2 (2 d, ^2J(P−C) ≈ 6.5 Hz), 110.3 (d, J(P−C) = 6.7 Hz), 123.0 (d, J(P−C) = 6.8 Hz), 125.2, 125.8 (d, ^3J(P−C) = 3.5 Hz), 126.0, 126.2, 126.5, 139.8, 140.0, 140.6 (d, J(P−C) = 2.8 Hz), 142.3, 142.4, 149.6 (d, J(P−C) = 5.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.1; LC/MS m/z 424 $[M + 1]^+$. Anal. calcd for $C_{26}H_{31}O_3P$: C, 73.91; H, 7.40. Found: C, 74.12; H, 7.48.

Compound 61. This compound was prepared by a procedure similar to that for **58** and **64** by using allenylphosphonate **4** (0.42 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was isolated by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.35 g (isolated, 70%); mp 176−178 °C; IR (KBr, cm^{-1}) 3065, 2965, 1638, 1495, 1399, 1370, 1233, 1049; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 and 0.87 (2 s, 6H), 3.25−3.31 and 3.57−3.64 (2 m, 2H), 3.82−3.86 and 4.13−4.16 (2 m, 2H), 4.91 (s, 1H), 4.98 (d, ^3J(P−C) = 4.0 Hz, 1H), 5.25 and 5.78 (2 d, ^2J(H−H) ∼ 4.2 Hz, 2H), 6.61 (d, ^3J(H−H) = 7.2 Hz, 1H), 6.77 (∼t, ^3J(H−H) ∼ 7.4 Hz, 1H), 6.98 (∼t, ^3J(H−H) = 7.2 Hz, 1H), 7.10−7.55 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.5, 33.0 (d, ^3J(P−C) = 6.3 Hz), 55.6, 56.7, 56.9 (d, ^1J(P−C) = 139.4 Hz), 75.1 and 75.8 (2 d, ^2J(P−C) ∼ 6.3 Hz), 114.9 (d, ^2J(P−C) = 6.0 Hz), 122.9, 123.3, 125.5, 125.8, 126.1, 126.2, 126.3, 126.6, 126.9, 127.8, 128.2 (d, J(P−C) = 4.7 Hz), 139.1, 139.8, 140.1, 140.2, 141.3, 142.5, 144.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.5; LC/MS m/z 443 $[M + 1]^+$. Anal. calcd for $C_{28}H_{27}O_3P$: C, 76.00; H, 6.15. Found: C, 76.15; H, 6.14.

Compound 62. This compound was prepared by a procedure similar to that for **58** and **64** by using allenylphosphonate **5** (0.44 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.33 g (isolated, 67%); mp 144−146 °C; IR (KBr, cm^{-1}) 2967, 1640, 1512, 1460, 1368, 1233, 1051, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 0.88 (2 s, 6H), 2.22 (s, 3H), 3.23−3.30 and 3.57−3.63 (2 m, 2H), 3.82−3.85 and 4.13−4.16 (2 m, 2H), 4.89 (s, 1H), 4.96 (s, 1H), 5.23 (s, 1H), 5.75 (s, 1H), 6.64−7.00 (m, 6H), 7.13−7.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 22.1, 22.5, 32.9 (d, ^3J(P−C) = 3.8 Hz), 55.6, 56.7 (d, ^1J(P−C) = 138.8 Hz), 56.8, 75.0, 75.7, 114.7, 122.9, 123.2, 125.6, 125.8, 126.1, 126.3, 126.5, 128.1, 128.6, 136.0, 136.4, 140.0, 140.2 140.3, 141.4, 142.6, 145.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8; LC/MS m/z 457 $[M + 1]^+$. Anal. Calcd for $C_{29}H_{29}O_3P$: C, 76.30; H, 6.40. Found: C, 76.55; H, 6.48.

Compound 63. This compound was prepared by a procedure similar to that for **58** and **64** by using allenylphosphonate **7** (0.47 g, 1.60 mmol) and anthracene (0 99 g, 5.58 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.33 g (69%); mp 152−154 °C; IR (KBr, cm^{-1}) 2957, 1607, 1510, 1464, 1252, 1051, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 0.88 (2 s, 6H), 3.27 (dd, ^3J(P−H) ≈ 16.0 Hz, ^2J(H−H) ≈ 10.9 Hz, 1H), 3.61 (dd, ^3J(P−H) ≈ 16.0 Hz, ^2J(H−H) ≈ 10.9 Hz, 1H), 3.71(s, 3H), 3.83 (dd, ^3J(P−H) ≈ 10.7 Hz, ^2J(H−H) ≈ 5.7 Hz, 1H), 4.14 (dd, ^3J(P−H) ≈ 10.7 Hz, ^2J(H−H) ≈ 5.7 Hz, 1H), 4.90 (s, 1H), 4.95 (d, ^3J(P−H) = 4.4 Hz, 1H), 5.24 and 5.76 (2 d, ^2J(H−H) ≈ 4.8 Hz, 2H), 6.63−6.66 (m, 3H), 6.80 (∼t, ^3J(H−H) ≈ 7.4 Hz, 1H), 6.99 (∼t, ^3J(H−H) = 7.2 Hz, 1H), 7.11−7.55 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.4, 32.9 (d, ^3J(P−C) = 6.7 Hz), 55.0, 55.5, 56.1 (d, ^1J(P−C) = 139.3 Hz), 56.6, 75.0, and 75.7 (2 d, ^2J(P−C) ≈ 6.7 Hz), 113.0, 114.6 (d, J(P−C) = 7.3 Hz), 122.8, 123.1, 125.6, 125.9, 126.0, 126.1, 126.2, 126.5, 129.3 (d, J(P−C) = 5.3 Hz), 131.0 (d, J(P−C) = 3.4 Hz), 139.8 (d, J(P−C) = 2.2 Hz), 140.1, 140.3, 141.2 (d, J(P−C) = 3.2 Hz), 142.4, 145.0

(d, J(P−C) = 5.4 Hz), 158.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.0; LC/MS m/z 473 $[M + 1]^+$. Anal. calcd for $C_{29}H_{29}O_4P$: C, 73.71; H, 6.19. Found: C, 73.85; H, 6.26.

Compounds 65 and 66. These compounds were prepared by a procedure similar to that for **58** and **64** by using allenylphosphine oxide **16** (0.38 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). The crude containing products **65-66** were isolated by using ethyl acetate/hexane (3:2) mixture. Pure compounds **65** and **66** were separated by hand−picking after crystallization from dichloromethane-hexane (4:1). Compound **66** appeared as block type of crystals while compound **65** was powdery. **Compound 65:** Yield [**65** + **66**] quantitative by ^{31}P NMR; 0.12 g (isolated, 23%, **65**); mp 180−182 °C; IR (KBr, cm^{-1}) 2930, 1624, 1468, 1435, 1177; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (dd, ^2J(P−H) = 16.8 Hz, ^3J(H−H) ≈ 2.4 Hz, 1H), 4.21−4.23 (m, 1H), 4.73 (s, 1H), 4.98−5.00 and 5.13−5.15 (2 m, 2H), 6.73 (∼t, ^3J(H−H) ≈ 7.2 Hz, 1H), 6.87 (∼t, ^3J(H−H) ≈ 7.4 Hz, 1H), 7.00 (d, ^3J(H−H) = 8.0 Hz, 1H), 7.09−7.19 (m, 5H), 7.26−7.61 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 46.2 (d, ^1J(P−C) = 67.9 Hz), 56.4, 111.2 (d, ^2J(P−C) = 3.6 Hz), 123.2, 123.3, 123.5, 125.6, 126.0, 126.2, 126.3, 126.5, 127.7, 127.8, 128.5, 128.7, 131.2, 131.4, 131.5, 131.8, 132.0, 132.1, 139.6, 140.5, 142.6, 143.3, (^1J(PC) due to PPh_2 group was difficult to assign); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0; LC/MS m/z 419 $[M + 1]^+$. Anal. calcd for $C_{29}H_{23}OP$: C, 83.24; H, 5.54. Found: C, 83.10; H, 5.48. **Compound 66:** Yield [**65** + **66**] quantitative by ^{31}P NMR, 0.34 g (isolated, 65%, **66**); mp 190−192 °C; IR (KBr, cm^{-1}) 2957, 2201, 1607, 1462, 1437, 1273, 1202, 1051, 999; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (d, 3H, ^4J(P−H) = 2.8 Hz), 4.80 (d, ^3J(P−H) = 8.8 Hz, 1H), 4.97 (d, ^4J(P−H) = 3.2 Hz, 1H), 6.89−7.00 (m, 6H), 7.30−7.46 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6 (d, ^3J(P−C) = 4.8 Hz), 53.6 (d, ^2J(P−C) = 12.2 Hz), 60.5 (d, ^3J(P−C) = 10.7 Hz), 123.0, 123.3, 124.9, 125.1, 128.6, 128.7, 131.0, 131.8, 131.9, 132.3, 132.7, 132.9 (d, ^1J(P−C) = 105.1 Hz), 133.7, 144.2 (d, J(P−C) = 2.7 Hz), 144.4 (d, J(P−C) = 2.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6; LC/MS m/z 419 $[M + 1]^+$. Anal. calcd for $C_{29}H_{23}OP$: C, 83.24; H, 5.54. Found: C, 83.30; H, 5.59.

Compound 67. These compounds were prepared by a procedure similar to that for **58** and **64** by using allenylphosphine oxide **17** (0.41 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.33 g (65%); mp 210−212 °C; IR (KBr, cm^{-1}) 3056, 2924, 1638, 1437, 1310, 1184, 1119, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, ^3J(P−H) = 14.0 Hz, 3H), 4.77−4.80 (m, 2H), 4.89 and 5.41 (d, ^2J(H−H) ≈ 4.0 Hz, 2H), 6.55 (∼t, ^3J(H−H) ≈ 7.2 Hz, 1H), 6.64 (∼t, ^3J(H−H) ≈ 7.0 Hz, 1H), 7.01 (d, ^3J(H−H) = 7.2 Hz, 1H), 7.07−7.12 (m, 5H), 7.18−7.39 (m, 6H), 7.65 (∼t, ^3J(H−H) ≈ 8.8 Hz, 2H), 7.74 (∼t, ^3J(H−H) ≈ 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 48.1 (d, ^1J(P−C) = 69.3 Hz), 51.5, 56.7, 112.0 (d, ^2J(P−C) = 5.4 Hz), 122.8, 123.7, 125.8, 125.9, 126.1, 126.4, 126.6, 126.8, 127.5 (d, J(P−C) = 11.3 Hz), 127.9 (d, J(P−C) = 11.0 Hz), 130.3, 131.2, 131.6, 131.8 (d, J(P−C) = 7.5 Hz), 132.8 (d, J(P−C) = 8.2 Hz), 140.5, 141.3 (d, J(P−C) = 10.2 Hz), 143.3, 150.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5; LC/MS m/z 432 $[M]^+$. Anal. calcd for $C_{30}H_{25}OP$: C, 83.31; H, 5.83. Found: C, 83.45; H, 5.72.

Compound 68. These compounds were prepared by a procedure similar to that for **58** and **64** by using allenylphosphine oxide **18** (0.51 g, 1.60 mmol) and anthracene (0.99 g, 5.58 mmol). It was purified by using ethyl acetate/hexane (3:2) mixture as the eluent. Yield quantitative by ^{31}P NMR, 0.30 g (64%); mp 212−214 °C; IR (KBr, cm^{-1}) 3052, 2944, 1634, 1433, 1263, 1181, 1092, 945; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.86 (s, 1H), 5.60 and 5.83 (2 s, 2H), 6.66−7.60 (m, 23H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.9, 57.7, 59.0 (d, ^1J(P−C) = 65.1 Hz), 116.9 (d, ^2J(P−C) = 5.5 Hz), 122.9, 123.2, 125.6 (d, J(P−C) = 7.3 Hz), 126.1, 126.9 (d, J(P−C) = 8.0 Hz), 127.2, 127.3, 127.4 (d, J(P−C) = 4.1 Hz), 127.5, 130.4, 130.6, 130.9, 131.5, 132.6, 132.7, 132.8, 132.9, 133.9, 139.3, 139.6, 141.4, 141.5, 141.7, 144.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8; LC/MS m/z 496 $[M + 1]^+$. Anal. calcd for $C_{35}H_{27}OP$: C, 85.00; H, 5.50. Found: C, 85.12; H, 5.48.

Compound 70. In the reaction of allenylphosphonate **2** (0.32 g, 1.60 mmol) with anthracene (0.99 g, 5.58 mmol), self-dimerized product **70** (yield: 15%) was formed along with product **59**. The eluent used for compound **70** was ethyl acetate/hexane (4:1) mixture. Yield [**59** + **70**] quantitative by ^{31}P NMR, 0.09 g (isolated, 15%, **70**); mp 258−260 °C; IR (KBr, cm^{-1}) 2969, 2930, 2886, 1632, 1468, 1372, 1262, 1057, 1005, 984; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 and 1.08 (2 s, 12H), 1.97 (d, ^3J(P−H) = 14.4 Hz, 6H), 2.89 (s, 4H), 3.78 (dd→t, ^3J(P−H) = ^2J(H−H) ≈ 11.4 Hz, 4H), 4.16 (dd→t, ^3J(P−H) = ^2J(H−H) = 11.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 18.1, 21.6, 30.5 (d, ^3J(P−C) = 5.0 Hz), 32.5 (d, ^3J(P−C) = 5.8 Hz), 75.3_0, 75.3_3, 116.8 (d, ^1J(P−C) = 174.0 Hz), 155.2 (d, ^2J(P−C) = 38.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.2; LC/MS m/z 405 $[M + 1]^+$. Anal. calcd for $C_{18}H_{30}O_6P_2$: C, 53.46, H; 7.48. Found: C, 53.51; H, 7.40.

X-Ray Data. X-ray data for compounds **24**, **25**.CH_2Cl_2, **31a**, **33b**.$CHCl_3$, **36a**, **36b**.H_2O, **44a**, **46a**.CH_2Cl_2, **46b**, **47a**, **52**, **53**, **55**, **61**, **64**, **66** and **70** were collected on Bruker AXS SMART or OXFORD diffractometer using Mo−K_α (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[27] CCDC numbers are CCDC 800084 - 800100.

Crystal Data. 24: $C_{16}H_{23}O_7P$, M = 358.31, Monoclinic, Space group $P2(1)/c$, a = 15.4896(13), b = 6.3827(5), c = 22.4035(15) Å, β = 121.467(4)°, V = 1889.2(3) Å^3, Z = 4, μ = 0.177 mm^{-1}, data/restraints/parameters: 4444/0/222, R indices ($I > 2\sigma(I)$): $R1$ = 0.0678, $wR2$ (all data) = 0.1473. CCDC no. 800084.

25: CH_2Cl_2: $C_{17}H_{25}Cl_2O_7P$, M = 443.24, Monoclinic, Space group $P2(1)/c$, a = 13.9539(13), b = 9.8610(9), c = 16.9007(16) Å, β = 111.638(2)°, V = 2161.7(3) Å^3, Z = 4, μ = 0.408 mm^{-1}, data/restraints/parameters: 3801/0/250, R indices ($I > 2\sigma(I)$): $R1$ = 0.0853, $wR2$ (all data) = 0.1886. CCDC no. 800085.

31a: $C_{21}H_{25}O_7P$, M = 420.38, Monoclinic, Space group $P2/c$, a = 16.4839(11), b = 6.6740(4), c = 22.516(2) Å, β = 120.625(6)°, V = 2131.6(3) Å^3, Z = 4, μ = 0.168 mm^{-1}, data/restraints/parameters: 3068/0/268, R indices ($I > 2\sigma(I)$): $R1$ = 0.0447, $wR2$ (all data) = 0.0991. CCDC no. 800086.

33b: $CHCl_3$: $C_{109}H_{125}Cl_3O_{48}P_4$, M = 2433.32, Monoclinic, Space group $C2/c$, a = 17.863(3), b = 24.4265(19), c = 16.784(2) Å, β = 118.377(18)°, V = 6443.4(14) Å^3, Z = 2, μ = 0.204 mm^{-1}, data/restraints/parameters: 5613/0/376, R indices ($I > 2\sigma(I)$): $R1$ = 0.0807, $wR2$ (all data) = 0.2176. CCDC no. 800087.

36a: $C_{23}H_{27}O_7P$, M = 446.42, Monoclinic, Space group $P2(1)/c$, a = 9.7156(4), b = 12.7031(6), c = 20.6130(10) Å, β = 112.620(4)°, V = 2348.32(19) Å^3, Z = 4, μ = 0.157 mm^{-1}, data/restraints/parameters: 4117/0/284, R indices ($I > 2\sigma(I)$): $R1$ = 0.0595, $wR2$ (all data) = 0.1789. CCDC no. 800088.

36b: H_2O: $C_{29}H_{35}O_{12}P$, M = 606.54, Monoclinic, Space group $P2(1)/c$, a = 14.9743(8), b = 10.9942(6), c = 18.6852(10) Å, β = 91.7590(10)°, V = 3074.7(3) Å^3, Z = 4, μ = 0.150 mm^{-1}, data/restraints/parameters: 5398/0/392, R indices ($I > 2\sigma(I)$): $R1$ = 0.0470, $wR2$ (all data) = 0.1235. CCDC no. 800089.

44a: $C_{34}H_{31}O_4P$, M = 534.56, Monoclinic, Space group $P2(1)/c$, a = 11.7888(17), b = 14.997(2), c = 16.960(4) Å, β = 112.545(16)°, V = 2769.3(8) Å^3, Z = 4, μ = 0.137 mm^{-1}, data/restraints/parameters: 4861/0/354, R indices ($I > 2\sigma(I)$): $R1$ = 0.0350, $wR2$ (all data) = 0.0857. CCDC no. 800090.

(27) (a) Sheldrick, G. M., *SADABS, Siemens Area Detector Absorption Correction*; University of Göttingen: Germany, 1996. (b) Sheldrick, G. M., *SHELX-97- A program for crystal structure solution and refinement*; University of Göttingen: Germany, 1997. (c) Sheldrick, G. M., *SHELXTL NT Crystal Structure Analysis Package*, version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999.

46a: CH_2Cl_2: $C_{36}H_{35}Cl_2O_5P$, $M = 649.51$, Monoclinic, Space group $P2(1)/c$, $a = 9.9415(2)$, $b = 27.0182(6)$, $c = 14.0924(4)$ Å, $\beta = 124.847(2)^o$, $V = 3106.47(13)$ Å^3, $Z = 4$, $\mu = 0.304$ mm^{-1}, data/restraints/parameters: 5461/0/400, R indices ($I > 2\sigma(I)$): $R1 = 0.0684$, $wR2$ (all data) = 0.1751. CCDC no. 800091.

46b: $C_{35}H_{33}O_5P$, $M = 564.58$, Monoclinic, Space group $P2(1)/c$, $a = 10.3316(7)$, $b = 16.5344(11)$, $c = 17.8866(16)$ Å, $\beta = 108.912(7)^o$, $V = 2890.6(4)$ Å^3, $Z = 4$, $\mu = 0.138$ mm^{-1}, data/restraints/parameters: 5083/0/373, R indices ($I > 2\sigma(I)$): $R1 = 0.0383$, $wR2$ (all data) = 0.0906. CCDC no. 800092.

47a: $C_{26}H_{22}O_3$, $M = 382.44$, Triclinic, Space group $P\bar{1}$, $a = 9.315(5)$, $b = 10.467(6)$, $c = 11.211(6)$ Å, $\alpha = 76.848(9)^o$, $\beta = 76.187(10)^o$, $\gamma = 75.850(10)^o$, $V = 1012.5(10)$ Å^3, $Z = 2$, $\mu = 0.081$ mm^{-1}, data/restraints/parameters: 3561/0/263, R indices ($I > 2\sigma(I)$): $R1 = 0.0785$, $wR2$ (all data) = 0.1640. CCDC no. 800093.

52: $C_{40}H_{35}O_2P$, $M = 578.65$, Triclinic, Space group $P\bar{1}$, $a = 9.8726(6)$, $b = 11.7485(7)$, $c = 14.2263(9)$ Å, $\alpha = 94.0200(10)^o$, $\beta = 91.4210(10)^o$, $\gamma = 111.2630(10)^o$, $V = 1531.73(16)$ Å^3, $Z = 2$, $\mu = 0.125$ mm^{-1}, data/restraints/parameters: 5395/0/388, R indices ($I > 2\sigma(I)$): $R1 = 0.0457$, $wR2$ (all data) = 0.1100. CCDC no. 800094.

53: $C_{34}H_{35}O_4P$, $M = 538.59$, Monoclinic, Space group $P2(1)/c$, $a = 13.2152(16)$, $b = 14.2689(15)$, $c = 17.500(3)$ Å, $\beta = 121.267(10)^o$, $V = 2820.6(7)$ Å^3, $Z = 4$, $\mu = 0.135$ mm^{-1}, data/restraints/parameters: 4948/0/354, R indices ($I > 2\sigma(I)$): $R1 = 0.0446$, $wR2$ (all data) = 0.1052. CCDC no. 800095.

55: $C_{40}H_{39}O_4P$, $M = 614.68$, Monoclinic, Space group $P2(1)/c$, $a = 15.8406(19)$, $b = 14.0154(11)$, $c = 19.0996(19)$ Å, $\beta = 108.257(12)^o$, $V = 4026.9(7)$ Å^3, $Z = 4$, $\mu = 0.102$ mm^{-1}, data/restraints/parameters: 6919/0/408, R indices ($I > 2\sigma(I)$): $R1 = 0.0807$, $wR2$ (all data) = 0.2574. CCDC no. 800096.

61: $C_{28}H_{27}O_3P$, $M = 442.47$, Monoclinic, Space group $P2(1)c$, $a = 9.9536(8)$, $b = 16.2868(13)$, $c = 15.5212(10)$ Å, $\beta = 112.478(4)^o$, $V = 2325.0(3)$ Å^3, $Z = 4$, $\mu = 0.146$ mm^{-1}, data/restraints/parameters: 4097/0/291, R indices ($I > 2\sigma(I)$): R1 = 0.0528, $wR2$ (all data) = 0.1219. CCDC no. 800097.

64: $C_{22}H_{23}O_3P$, $M = 366.37$, Orthorhombic, Space group $Pnma$, $a = 23.597(9)$, $b = 13.366(5)$, $c = 6.132(3)$ Å, $V = 1934.0(14)$ Å^3, $Z = 4$, $\mu = 0.160$ mm^{-1}, data/restraints/parameters: 1782/0/133, R indices ($I > 2\sigma(I)$): $R1 = 0.0679$, $wR2$ (all data) = 0.1397. CCDC no. 800098.

66: $C_{29}H_{23}OP$, $M = 418.44$, Monoclinic, Space group Cc, $a = 15.8800(15)$, $b = 9.9538(9)$, $c = 15.1330(14)$ Å, $\beta = 107.2870(10)^o$, $V = 2284.0(4)$ Å^3, $Z = 4$, $\mu = 0.138$ mm^{-1}, data/restraints/parameters: 4351/0/281, R indices ($I > 2\sigma(I)$): $R1 = 0.0381$, $wR2$ (all data) = 0.0926. CCDC no. 800099.

70: $C_{18}H_{30}O_6P_2$, $M = 404.36$, Orthorhombic, Space group $Pbcn$, $a = 16.291(6)$, $b = 12.324(4)$, $c = 10.331(4)$ Å, $V = 2074.1(13)$ Å^3, $Z = 4$, $\mu = 0.239$ mm^{-1}, data/restraints/parameters: 2536/0/121, R indices ($I > 2\sigma(I)$): $R1 = 0.0463$, $wR2$ (all data) = 0.1234. CCDC no. 800100.

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Supporting Information Available: ORTEP drawings, CIF files, copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.