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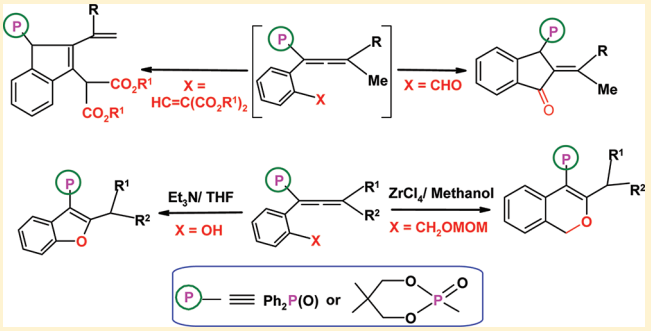
Allenylphosphonates/Allenylphosphine Oxides as Intermediates/Precursors for Intramolecular Cyclization Leading to Phosphorus-Based Indenes, Indenones, Benzofurans, and Isochromenes

K. V. Sajna and K. C. Kumara Swamy*

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

Supporting Information

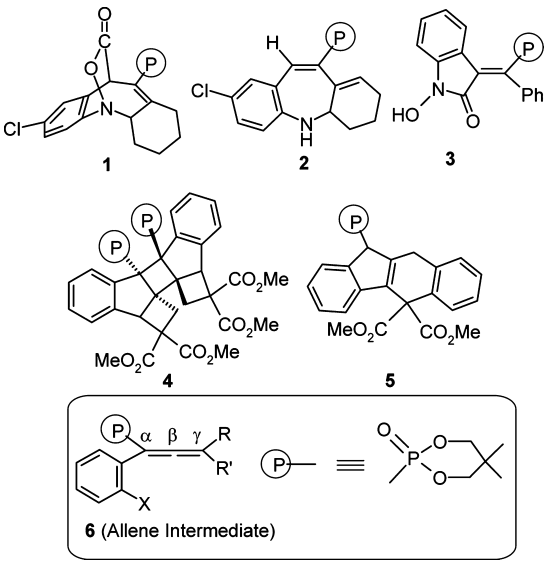
ABSTRACT: Utilizing internally available functional groups, a simple protocol for the efficient synthesis of phosphorus-based indenes, indenones, benzofurans, and isochromenes via intramolecular cyclization of allene intermediates/precursors is generated; the latter intermediates/precursors are conveniently obtained through aldehyde-, alkylidene-, and hydroxyl-functionalized propargyl alcohols and P^{III}−Cl precursors. The structures of key products have been unequivocally confirmed by X-ray crystallography.



INTRODUCTION

Allenes are useful precursors for the construction of key building blocks that are present in many natural products and pharmaceutically important molecules.[1,2] In the past decade, a vast number of polycycles and heterocycles have been synthesized via intramolecular or intermolecular cyclization/cycloaddition reactions by employing the functionalized allene derivatives.[3,4] For example, allenes can undergo cyclization reactions with nucleophiles having an additional functionality (e.g., −I, −Br, −CHO) to yield a diverse range of heterocycles.[4a−e] These reactions can be accomplished by transition-metal, Lewis acid, or Lewis base catalyzed conditions. Our research group has reported the synthesis of phosphono-benzofurans,[4a,c] -pyrazoles,[4b] -chromenes,[4d] -oxindoles,[4e] and multiply substituted furans[4f] from inexpensive allenes under Lewis acid, transition-metal, or base catalyzed conditions. In addition to these, very recently, we reported a novel synthesis of benzazipines, *N*-hydroxyindoles, and polycycles (compounds **1**−**5**; Chart 1) via allene intermediates;[5] the key to such an astounding variety of products is the functionalized allene intermediate (**6**). Encouraged by these results, and as a part of our studies focused toward the synthesis of novel functionalized allenylphosphonates/allenylphosphine oxides[6] for the development of cyclization reactions, we became interested in obtaining the propargyl alcohols **7**−**23** containing an alkylidene, a formyl, or a hydroxyphenyl group (Chart 2).[7] We also wish to point out that the amenability of ^{31}P NMR has significantly aided us in readily analyzing the course of such reactions and we believe that this knowledge can be gainfully employed in the case of non-phosphorylated allenes. In this context, we wish to disclose the formation/synthesis of different types of polycyclic and heterocyclic molecules by systematic alteration of inexpensive propargyl alcohols and P^{III}−Cl precursors. We should note that the normally expected products in such reactions are allenes.[6]

Chart 1. Heterocycles/Polycycles Prepared via Functionalized Propargyl Alcohols[5]



RESULTS AND DISCUSSION

We first focus on two new intramolecular ene reactions via allenic intermediates exhibited by the alkylidene-based propargyl alcohols **7**−**11** and the aldehyde-based propargyl

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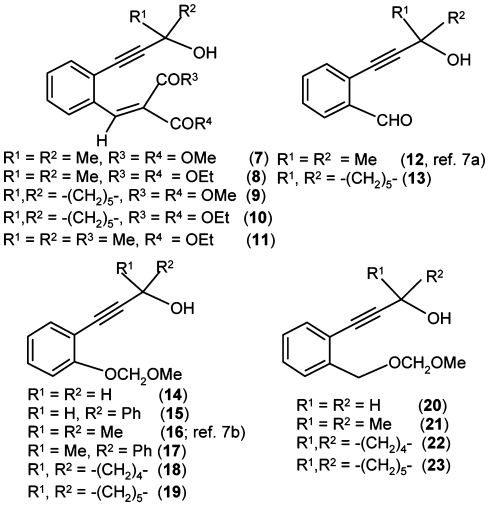
Chart 2. Functionalized Propargyl Alcohols 7−23 Used in the Present Study



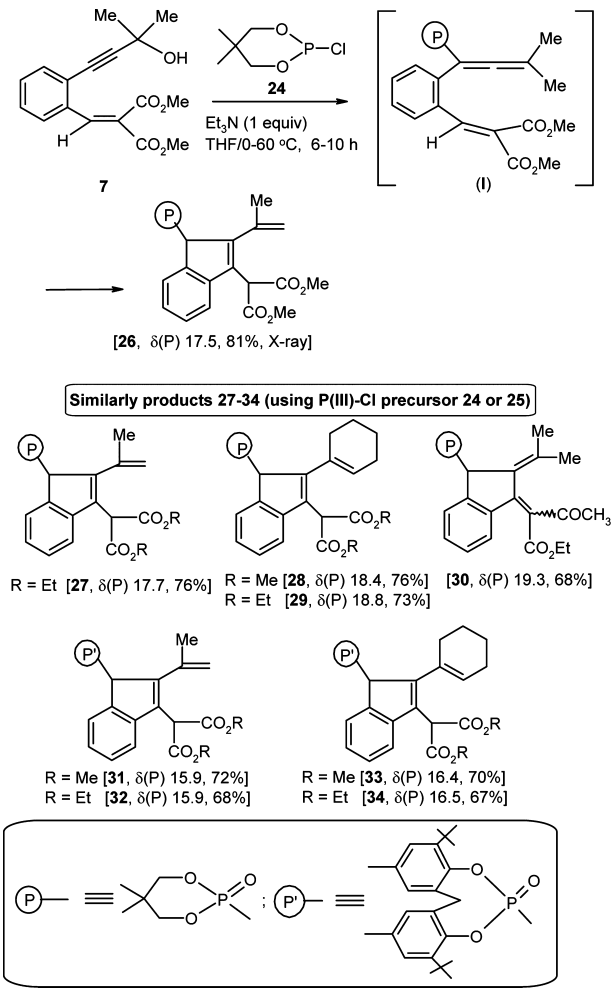
alcohols **12** and **13**, respectively. These will be followed by intramolecular cyclizations assisted by a base (Et_3N) or Lewis acid ($ZrCl_4$). We believe that these represent a class of reactions that have been previously unexplored.

(i). Reaction of Alkylidene-Based Propargyl Alcohols 7−11 with P^{III}−Cl Compounds 24 and 25: Synthesis of Phosphono-Indenes 26−34 via an Intramolecular Ene Reaction. Our initial aim was to synthesize the alkylidene-based allenylphosphonate **I** by using the propargyl alcohol **7** and P^{III}−Cl precursor **24** under the conditions mentioned in Scheme 1. To our surprise, however, we isolated the *indene derivative* **26** rather than the allene. The structure has been proven by single-crystal X-ray crystallographic studies (see the Supporting Information). We extended this work by using the propargyl alcohols **8**−**10** to obtain the products **27**−**29** in good yields (Scheme 1). By using the same method when propargyl alcohol **11** was treated with P^{III}−Cl precursor **24**, we obtained product **30**. Products **31**−**34**, similar to **26**−**29**, were formed when the P^{III}−Cl precursor **25** (containing an eight-membered ring; see Scheme1) was treated with the propargyl alcohols **7**−**10**.

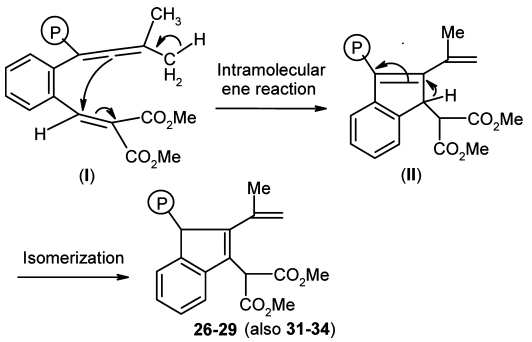
On the basis of previous studies,[6] it is reasonable to assume that the most viable primary intermediate in the above reaction is the allene **I** (Scheme 2). An intramolecular ene[8] reaction leads to species **II**, which on subsequent proton migration furnishes the final products **26**−**34**.

(ii). Reaction of Aldehyde Functionalized Propargyl Alcohols 12 and 13 with P^{III}−Cl Precursors 24/35: Formation of Phosphono-Indenone Derivatives 36−39. Encouraged by the above results, we thought that by employing the aldehyde-based propargyl alcohol **12** we could generate a new cyclic system. In order to explore this, we treated the propargyl alcohol **12** with the P^{III}−Cl precursor **24** (Scheme 3) by a procedure similar to what was described above. In the ^{31}P NMR spectrum, the reaction mixture showed only one peak at δ 19.8, which did not correspond to the allene (δ 6.5−8.0). After isolation, we surmised that this synthetic route afforded the *unexpected indenone derivative* **36** (on the basis of spectroscopic and analytical data) instead of the expected allene (vide infra). Thus, a simple and inexpensive route to indenones has been generated. The presence of the α-P−C*H* proton, as revealed by a doublet at δ 4.56 with a J(P−H) value

Scheme 1. Synthesis of Phosphono-Indenes 26−34



Scheme 2. Intramolecular Ene Pathway for the Formation of 26−30 (and 31−34)



of 23.2 Hz, indicates that the compound is allylphosphonate and not a vinylphosphonate. The scope of the reaction was then extended by using the P^{III}−Cl precursor **35**. In all the cases the final indenones **36**−**39** (Scheme 3) were obtained in good yields. The structure of product **38** was confirmed by X-ray crystallography (see the Supporting Information). The $Me_2C{=}C$ distance of 1.337(4) Å indicates a double bond between these two atoms, as depicted in the structural drawing (Scheme 3).

The rather unprecedented formation of phosphono-indenone derivatives **36**−**39** can be explained by the pathway shown

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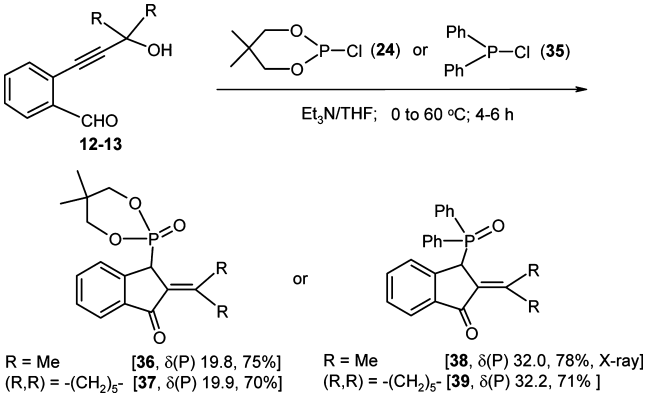
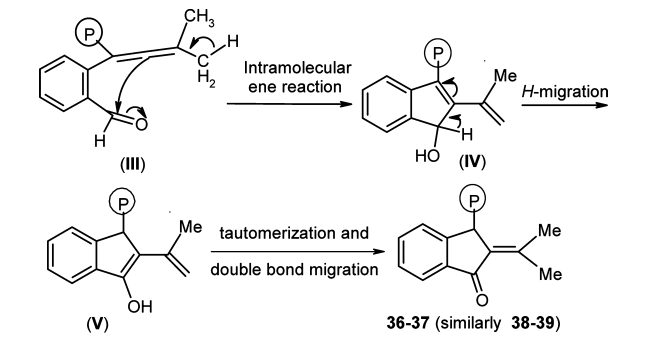
Scheme 3. Synthesis of Phosphono-Indenone Derivatives 36−39



Scheme 4. Intramolecular Ene Pathway for the Formation of 36−39

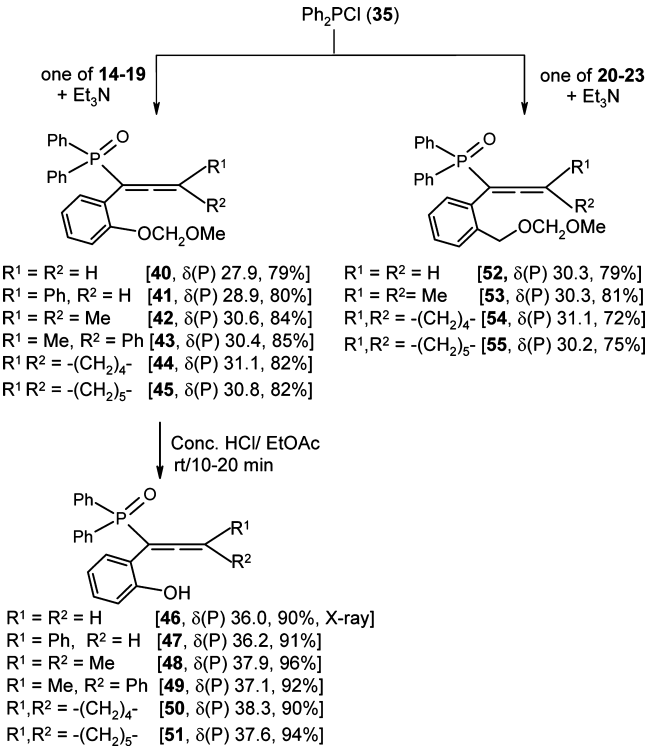


in Scheme 4. The initially formed allene intermediate **III** can undergo an intramolecular ene reaction leading to a cyclic intermediate (**IV**).[8] H migration in intermediate **IV** then afforded the enol intermediate **V**, which on subsequent tautomerization gave rise to the final product **36** (or **37**−**39**).

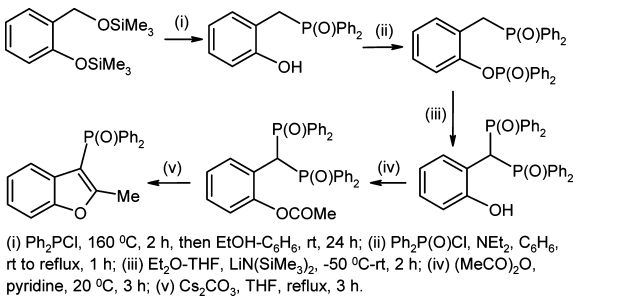
(iii). Cyclization Reaction of Allenes 46−51 Possessing a 2-Hydroxyphenol Side Group: Synthesis of 1,2-Disubstituted Benzofuran Derivatives 56−61. Intermolecular nucleophilic addition of amines, phenols, and thiols to allenylphosphonates has been fairly well explored.[3a,9,10] Also, having realized the potential of keeping an ortho functionality in aryl-substituted propargyl alcohols in the reactions discussed above, we turned our attention to the α-MOM-protected hydroxyphenyl allenylphosphine oxides **40**−**45**, which were synthesized readily by standard routes.[6] The hydroxyphenyl-substituted allenes **46**−**51** required for cyclization were then prepared from the hydrolysis of allenes **40**−**45** (Scheme 5; although the corresponding allenes with a benzylic alcohol residue from **52**−**55** may also be prepared in an analogous manner, this step was not required in the present study (vide infra)). In order to fully authenticate the multifunctional nature, one of these compounds (**46**) was characterized by single-crystal X-ray crystallography (see the Supporting Information). We then focused on the intramolecular nucleophilic-addition reactions of these functionalized allenes.

We first explored the intramolecular cyclization of **46** under basic (Et_3N) conditions. Although allene **46** did not cyclize in the presence of triethylamine (1 mol equiv) at room temperature, we succeeded in obtaining the expected benzofuran **56** when the mixture was heated under reflux for 2 h. This reaction was clean, and the product **56** was obtained

Scheme 5. Synthesis of Allenes 40−55



Scheme 6. Reported Method[11] for the Synthesis of Compound 56



(i) Ph_2PCl, 160 °C, 2 h, then EtOH-C_6H_6, rt, 24 h; (ii) $Ph_2P(O)Cl$, NEt_2, C_6H_6, rt to reflux, 1 h; (iii) Et_2O-THF, $LiN(SiMe_3)_2$, -50 °C-rt, 2 h; (iv) $(MeCO)_2O$, pyridine, 20 °C, 3 h; (v) Cs_2CO_3, THF, reflux, 3 h.

in excellent yield (95%; Table 1). The spectroscopic data are consistent with those reported in the literature; however, the literature route requires a large number of steps, as shown in Scheme 6.[11] Hence, we developed our simpler route by using various allenylphosphine oxides **47**−**51** that lead to various substituted benzofuran derivatives **57**−**61** (Table 1). The X-ray structure of the product **61** (see the Supporting Information) conclusively proved the formation of the benzofurans. It may be noted that the phenolic proton could have moved to the α-carbon (with respect to phosphorus) also, but formation of the benzofuran system is favored in the present case.

(iv). Formation of 3,4-Disubstituted Isochromenes 62−65 (via $ZrCl_4$ Catalysis) and Halobenzyl Products 66 and 67 from MOM-Protected Allenes 52−55. Inspired by the above results, and in order to extend the nucleophilic-addition reaction strategy, we chose the benzyloxy-MOM-protected allenes **52**−**55**. Since our strategy was to obtain the cyclized product, we made an attempt to deprotect allene **52** by employing the Lewis acid $ZrCl_4$.[12] Thus, we treated allene **52** with $ZrCl_4$ (0.5 mol equiv) in methanol under reflux over a period of 2 h. To our delight, this reaction straightaway ended

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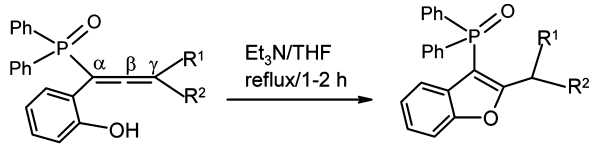
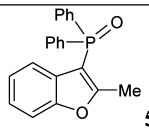
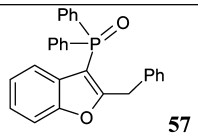
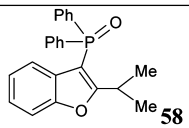
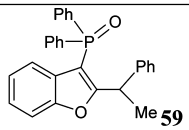
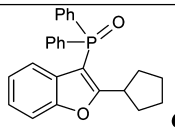
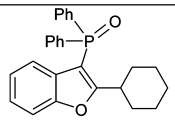
Table 1. Synthesis of 2,3-Disubstituted Benzofurans 56−61 via Allenes 46−51[a]



46-51 56-61

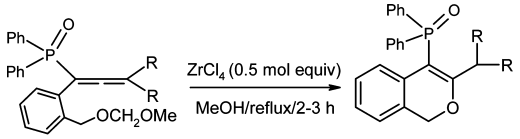
Entry	Allene	Product	Yield[b]	δ(P)
1	**46**	 **56**	95	21.3
2	**47**	 **57**	89	21.5
3	**48**	 **58**	90	21.5
4	**49**	 **59**	93	21.6
5	**50**	 **60**	88	21.7
6	**51**	 **61** (X-ray)	90	21.2

[a]Reaction conditions: allene (1.0 mol equiv), Et_3N (1.0 mol equiv), THF (2 mL), reflux for 1−2 h. [b]Yield of the isolated product.

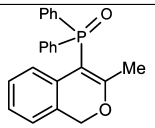
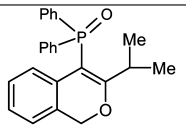
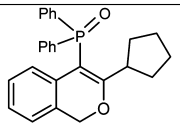
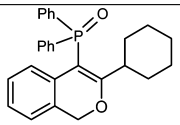
up with a nucleophilic addition−cyclization product, isochromene **62** (Table 2) *in one step* and there was no deprotected allene, thus alleviating the additional step. We explored this reaction further by employing various γ-dialkyl-substituted allenylphosphine oxides **53**−**55** to obtain 3,4-disubstituted isochromenes **63**−**65** in excellent yields (Table 2). For further structural confirmation, one of these compounds (**63**; Table 2, entry 2) was subjected to single-crystal X-ray crystallographic analysis (see the Supporting Information).

In place of $ZrCl_4$, when we used concentrated HX (X = Br, Cl) /EtOAc under reflux conditions, we obtained the noncyclized water-added benzylic halides **66** and **67** (Scheme 7; see the Supporting Information for the X-ray structure of **66**). Although this leads to synthetically useful allylic alcohols, since this was not the theme of the present work, we have not explored this reaction further.

Table 2. Synthesis of Isochromenes 62−65 via Allenes 52−55[a]

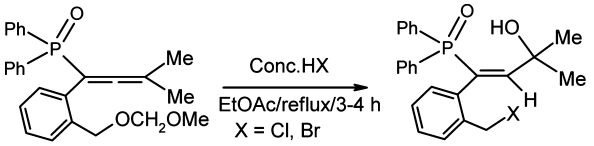


52-55 62-65

entry	allene	product	Yield[b]	δ(P)
1	**52**	 **62**	90	26.5
2	**53**	 **63** (X-ray)	92	26.7
3	**54**	 **64**	84	26.8
4	**55**	 **65**	87	25.8

[a]Reaction conditions: allene (1.0 mmol), $ZrCl_4$ (0.5 mol equiv), MeOH (2 mL), reflux for 2−3 h. [b]Yield of the isolated product.

Scheme 7. Formation of Allylic Alcohols 66 and 67



53

X = Cl [**66**, δ(P) 32.0, 88%, X-ray]
X = Br [**67**, δ(P) 32.3, 85%]

CONCLUSIONS

New cyclization reactions via an intramolecular ene-type or nucleophilic addition/cyclization pathway by employing functionalized propargyl alcohols and P^{III}−Cl precursors have been discovered. The α-(2-formyl/2-alkylidene)-phenyl-based allenes formed in situ gave indane-based compounds via an ene-type pathway, whereas the α-(2-hydroxyphenyl)- or α-((2-methylhydroxy)phenyl)-based allenes afforded the benzofurans or isochromenes via a nucleophilic addition/cyclization route. Thus, this chemistry provides a convenient access to a variety of indenes, indenones, benzofurans, and isochromenes from inexpensive functionalized propargyl alcohols and presents a

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substantial extension of the known synthetic routes to these types of derivatives.

EXPERIMENTAL SECTION

(i). General Comments. Solvents were dried according to known methods as appropriate.[13] ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H, 400 or 500 MHz; ^{13}C, 100 or 125 MHz; ^{31}P, 162 MHz) were recorded using a 400 or 500 MHz spectrometer in $CDCl_3$ with shifts referenced to $SiMe_4$ (δ 0) or 85% H_3PO_4 (δ 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 LC-MS and HRMS equipment.

(ii). Preparation of Propargylic Alcohol and P^{III}–Cl Precursors. The propargylic precursors **7**–**23** were synthesized by Sonogashira coupling reactions of the respective iodo/bromo substrates (2-(2-bromobenzylidene)malonic acid dimethyl (diethyl) esters were prepared according to the literature procedure[14] and 1-iodo-2-methoxymethoxybenzene[15a] and 1-iodo-2-methoxymethoxymethylbenzene[15b] were prepared by treating the corresponding alcohols with chloromethyl methyl ether in the presence of sodium hydride (NaH) in THF[15]) with propargyl alcohols.[7] Among these propargyl alcohols, **7**–**11**, **13**–**15**, and **17**–**23** are new. The general procedure for the synthesis of these compounds is given below.

The P^{III}–Cl precursor ($OCH_2CMe_2CH_2O$)PCl (**24**) was prepared by a well-known method involving the reaction of the corresponding diol with PCl_3 under neat conditions.[16a] CH_2[6-*t*-Bu-4-Me-C_6H_2O]$_2$PCl (**25**) is known,[16b] but in our work we have sublimed it (150 °C/0.1 mm). Chlorodiphenylphosphine Ph_2PCl (**35**) was distilled prior to use.

To a mixture of the bromo or iodo compound (1.0 mmol) and propargyl alcohol (1.2 mmol) in CH_3CN (20 mL) were added $PdCl_2(PPh_3)_2$ (0.02 mmol) and CuI (0.02 mmol) under a nitrogen atmosphere. After the reaction mixture was stirred for 5 min at room temperature, triethylamine (4.0 equiv) was added via a syringe. The reaction mixture was then heated to 70 °C. The solvent was removed under reduced pressure to give the crude product, which was purified by column chromatography on silica gel using an EtOAc–hexane mixture as eluent.

Compound ***7***. This compound was prepared by using 2-(2-bromobenzylidene)malonic acid dimethyl ester (0.96 g, 3.2 mmol) and 2-methylbut-3-yn-2-ol (0.32 g, 3.8 mmol) and purified by column chromatography using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 0.73 g (72%, yellow oil); IR (neat, cm^{-1}) 3441, 2984, 1732, 1628, 1437, 1368, 1258, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 and 1.65 (2 s, 6H), 2.41 (br, 1H), 3.79 and 3.86 (2 s, 6H), 7.27–7.48 (m, 4H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 52.7, 52.8, 65.5, 79.3, 101.1, 124.2, 126.4, 127.4, 128.4, 130.1, 132.4, 134.7, 141.9, 164.5, 166.8; LC/MS *m*/*z* 303 [M + 1]$^+$. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.55; H, 6.08.

Compound ***8***. This compound was prepared by using 2-(2-bromobenzylidene)malonic acid diethyl ester (1.26 g, 4.0 mmol) and 2-methylbut-3-yn-2-ol (0.39 g, 4.6 mmol) and purified by column chromatography using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 0.71 g (70%, yellow oil); IR (neat, cm^{-1}) 3434, 2980, 1732, 1630, 1470, 1377, 1250, 1065; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 and 1.34 (2 t, *J* = 7.6 Hz, 6H), 1.65 (s, 6H), 2.45 (br, 1H), 4.26–4.34 (m, 4H), 7.26–7.34 (m, 2H), 7.45–7.47 (m, 2H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.2, 31.4, 61.7$_1$, 61.7$_4$, 65.6, 79.6, 100.8, 124.0, 127.4, 127.6, 128.3, 129.9, 132.4, 135.0, 140.9, 164.1, 166.4; LC/MS *m*/*z* 331 [M + 1]$^+$. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.21; H, 6.67.

Compound ***9***. This compound was prepared by using 2-(2-bromobenzylidene)malonic acid dimethyl ester (1.50 g, 5.0 mmol) and 1-ethynyl-1-cyclohexanol (0.75 g, 6.0 mmol) and purified by column chromatography using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 1.17 g (68%, yellow oil); IR (neat, cm^{-1}) 3470, 2938, 1732, 1628, 1437, 1373, 1256, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (br, 1H), 1.61–1.78 and 2.04–2.07 (2 m, 9H), 2.50 (br, 1H), 3.79 and 3.84 (2 s, 6H), 7.29–7.49 (m, 4H), 8.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 25.2, 39.9, 52.6, 52.9, 69.2, 81.6, 100.1, 124.4, 126.6, 127.4, 128.3, 130.1, 132.5, 134.7, 141.7, 164.4, 166.8; LC/MS *m*/*z* 342 [M]$^+$. Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.15; H, 6.58.

Compound ***10***. This compound was prepared by using 2-(2-bromobenzylidene)malonic acid diethyl ester (1.18 g, 3.6 mmol) and 1-ethynyl-1-cyclohexanol (0.54 g, 4.3 mmol) and purified by column chromatography using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 0.76 g (67%, yellow oil); IR (neat, cm^{-1}) 3461, 2936, 1730, 1632, 1449, 1379, 1254, 1065; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 and 1.34 (2 t, *J* = 7.0 Hz, 6H), 1.53–1.76 (m, 8H), 2.05 (br, 2H), 2.37 (br, 1H), 4.26–4.33 (m, 4H), 7.27–7.35 and 7.45–7.49 (2 m, 4H), 8.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.2, 23.4, 25.2, 39.9, 61.7, 69.2, 81.7, 99.8, 124.2, 127.5, 127.6, 128.3, 129.9, 132.5, 134.9, 140.9, 164.0, 166.4; LC/MS *m*/*z* 370 [M]$^+$. Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 71.25; H, 7.18.

Compound ***11***. This compound was prepared by using (*E* or *Z*)-ethyl 2-(2-bromobenzylidene)-3-oxobutanoate (0.50 g, 1.7 mmol) and 2-methylbut-3-yn-2-ol (0.17 g, 2.0 mmol) and purified by column chromatography using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 0.25 g (50%, yellow oil); IR (neat, cm^{-1}) 3449, 2982, 1703, 1620, 1368, 1248, 1059; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.3 Hz, 3H), 1.68 (s, 6H), 2.31 (s, 3H), 2.48 (br, 1H), 4.30–4.34 (m, 2H), 7.29–7.37 (m, 3H), 7.48–7.49 (m, 1H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 31.3, 31.4, 61.7, 65.7, 79.6, 101.0, 124.0, 128.3, 128.6, 129.9, 132.5, 134.8, 135.0, 139.0, 164.4, 203.0; LC/MS *m*/*z* 301 [M + 1]$^+$. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.83; H, 6.62.

Compound ***13***. This compound was prepared by using 2-bromobenzaldehyde (1.59 g, 8.6 mmol) and 1-ethynylcyclohexanol (1.28 g, 10.2 mmol). It was isolated by using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 1.29 g (66%, yellow oil); IR (neat, cm^{-1}) 3410, 2965, 1696, 1595, 1389, 1273, 1073; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–2.05 (m, 10H), 2.72 (br, 1H), 7.41–7.52 (m, 3H), 7.87–7.89 (m, 1H), 10.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 25.1, 39.9, 69.2, 79.9, 100.3, 126.5, 127.3, 128.6, 133.4, 133.8, 135.9, 191.8; LC/MS *m*/*z* 229 [M + 1]$^+$. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 7.12.

Compound ***14***. This compound was prepared by using 1-iodo-2-methoxymethoxybenzene (0.82 g, 3.1 mmol) and propargyl alcohol (0.21 g, 3.7 mmol). It was isolated by using an ethyl acetate/hexane (3/7) mixture as the eluent: yield 0.42 g (71%, brown oil); IR (neat, cm^{-1}) 3383, 2934, 1597, 1489, 1451, 1154; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (br, 1H), 3.52 (s, 3H), 4.54 (s, 2H), 5.25 (s, 2H), 6.94–6.98 (m, 1H), 7.11–7.13 (m, 1H), 7.25–7.29 (m, 1H), 7.40–7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 56.3, 81.9, 91.3, 95.0, 113.0, 115.1, 121.9, 129.9, 133.7, 157.8; LC/MS *m*/*z* 193 [M + 1]$^+$. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.85; H, 6.38.

Compound ***15***. This compound was prepared by using 1-iodo-2-methoxymethoxybenzene (0.73 g, 2.8 mmol) and 1-phenylprop-2-yn-1-ol (0.44 g, 3.3 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.48 g (65%, brown oil); IR (neat, cm^{-1}) 3400, 3065, 2928, 1597, 1489, 1447, 1154, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (br, 1H), 3.50 (s, 3H), 5.25 (s, 2H), 5.74 (s, 1H), 6.96–7.00 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.27–7.47 (m, 5H), 7.68–7.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 65.2, 83.1, 92.8, 94.9, 113.0, 115.1, 121.8, 126.9, 128.4, 128.6, 130.0, 133.6, 140.8, 158.0; LC/MS *m*/*z* 269 [M + 1]$^+$. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.21; H, 5.95.

Compound ***17***. This compound was prepared by using 1-iodo-2-methoxymethoxybenzene (0.80 g, 3.0 mmol) and 2-phenylbut-3-yn-2-ol (0.53 g, 3.6 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.58 g (68%, brown oil); IR (neat, cm^{-1}) 3428, 2928, 1597, 1489, 1451, 1154, 1080; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 2.70 (br, 1H), 3.53 (s, 3H), 5.27 (s, 2H), 6.99–7.03 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.29–7.49 (m, 5H), 7.82–7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 56.3, 70.6, 81.4, 94.9, 96.5, 113.2, 115.1, 121.8, 125.2, 127.7, 128.3, 129.8,

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133.4, 145.9, 157.9; LC/MS m/z 283 $[M + 1]^+$. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.68; H, 6.35.

Compound ***18***. This compound was prepared by using 1-iodo-2-methoxymethoxybenzene (0.92 g, 3.5 mmol) and 1-ethynylcyclopentanol (0.46 g, 4.2 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.53 g (62%, brown oil); IR (neat, cm^{-1}) 3418, 2959, 1491, 1198, 1154, 1078; ^1H NMR (400 MHz, $CDCl_3$) δ 1.75−2.09 (m, 8H), 2.43 (br, 1H), 3.53 (s, 3H), 5.24 (s, 2H), 6.93−6.97 (m, 1H), 7.08 (d, J = 8.4 Hz, 1H), 7.22−7.27 (m, 1H), 7.39 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 42.4, 42.5, 56.3, 75.0, 79.3, 95.1, 97.1, 113.7, 115.5, 121.9, 129.5, 133.5, 157.6, LC/MS m/z 245 $[M - 1]^+$. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.26; H, 7.29.

Compound ***19***. This compound was prepared by using 1-iodo-2-methoxymethoxybenzene (0.82 g, 6.1 mmol) and 1-ethynylcyclohexanol (0.91 g, 7.4 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 1.10 g (69%, brown oil); IR (neat, cm^{-1}) 3397, 2932, 1597, 1574, 1449, 1155; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26−1.74 (m, 8H), 2.01−2.03 (m, 2H), 2.65 (br, 1H), 3.51 (s, 3H), 5.24 (s, 2H), 6.93−6.97 (m, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.22−7.26 (m, 1H), 7.39 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 25.3, 40.1, 56.2, 69.3, 80.7, 94.9, 97.0, 113.6, 115.2, 121.8, 129.5, 133.4, 157.7; LC/MS m/z 261 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.69; H, 7.82.

Compound ***20***. This compound was prepared by using 1-iodo-2-methoxymethoxymethylbenzene (0.89 g, 3.1 mmol) and propargyl alcohol (0.21 g, 3.7 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.48 g (74%, brown oil); IR (neat, cm^{-1}) 3416, 2934, 1451, 1379, 1213, 1038; ^1H NMR (400 MHz, $CDCl_3$) δ 2.80 (br, 1H), 3.45 (s, 3H), 4.52 (s, 2H), 4.76 and 4.78 (2 s, 4H), 7.25−7.29 (m, 1H), 7.33−7.37 (m, 1H), 7.44−7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 55.4, 67.4, 83.2, 92.1, 95.7, 121.8, 127.6, 128.3, 128.7, 132.1, 139.6; LC/MS m/z 207 $[M + 1]^+$. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.75; H, 6.91.

Compound ***21***. This compound was prepared by using 1-iodo-2-methoxymethoxymethylbenzene (0.59 g, 2.1 mmol) and 2-methylbut-3-yn-2-ol (0.21 g, 2.5 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.38 g (76%, brown oil); IR (neat, cm^{-1}) 3414, 2982, 1601, 1377, 1150, 1049; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 2.89 (br, 1H), 3.44 (s, 3H), 4.74$_6$ and 4.74$_8$ (2 s, 4H), 7.23−7.27 (m, 1H), 7.31−7.35 (m, 1H), 7.41−7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 55.4, 65.5, 67.1, 79.9, 95.6, 98.6, 122.0, 127.6, 128.5, 128.6, 131.9, 139.5; LC/MS m/z 235 $[M + 1]^+$. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.62; H, 7.83.

Compound ***22***. This compound was prepared by using 1-iodo-2-methoxymethoxymethylbenzene (1.69 g, 6.1 mmol) and 1-ethynylcyclopentanol (0.80 g, 7.3 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 1.06 g (67%, brown oil); IR (neat, cm^{-1}) 3414, 2951, 1451, 1379, 1206, 1150, 1047; ^1H NMR (500 MHz, $CDCl_3$) δ 1.79−1.92 and 2.03−2.10 (2 m, 8H), 2.71 (br, 1H), 3.45 (s, 3H), 4.76 and 4.77 (2 s, 4H), 7.25−7.28 (m, 1H), 7.32−7.35 (m, 1H), 7.43−7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.5, 42.5, 55.4, 67.3, 74.8, 80.9, 95.7, 97.7, 122.2, 127.5, 128.3$_9$, 128.4$_3$, 131.9, 139.6; LC/MS m/z 261 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.69; H, 7.79.

Compound ***23***. This compound was prepared by using 1-iodo-2-methoxymethoxymethylbenzene (1.05 g, 3.8 mmol) and 1-ethynylcyclohexanol (0.56 g, 4.5 mmol). It was isolated by using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 1.75 g (72%, brown oil); IR (neat, cm^{-1}) 3412, 2934, 1601, 1449, 1150, 1049; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29−1.78 (m, 8H), 2.01−2.04 (m, 2H), 2.66 (br, 1H), 3.44 (s, 3H), 4.75 and 4.77 (2 s, 4H), 7.24−7.28 (m, 1H), 7.32−7.36 (m, 1H), 7.44−7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 25.3, 40.1, 55.4, 67.3, 69.1, 81.9, 95.7, 97.7, 122.1, 127.5, 128.3, 128.5, 132.1, 139.6; LC/MS m/z 275 $[M + 1]^+$. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.29; H, 8.12.

(iii). Reaction of Alkylidene-Based Propargylic Alcohols 7−11 with P^{III}−Cl Precursors 24 and 25: Synthesis of Phosphono-Indenes 26−34. To a solution of substituted propargyl alcohol **7** (0.60 g, 2.00 mmol) in dry THF (30 mL) was added triethylamine (0.20 g, 0.28 mL, 2.00 mmol); the mixture was stirred for 5 min, and then $(OCH_2CMe_2CH_2O)PCl$ (**24**; 0.34 g, 2.00 mmol) was added dropwise at 0 °C. The contents were brought to room temperature and then heated under reflux for 6 h. The triethylamine hydrochloride that formed was filtered off and the solvent removed under vacuum from the filtrate. The product **26** was purified by column chromatography (silica gel; ethyl acetate/hexane 4/1). Compounds **27**−**34** were also prepared similarly.

Compound ***26***. Yield 0.70 g (81%); mp 98−100 °C (white solid); IR (KBr, cm^{-1}) 2928, 1732, 1435, 1256, 1057, 1008; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 and 1.01 (2 s, 6H), 2.10 (s, 3H), 3.61−3.77 (m, 8H), 4.02−4.07 (m, 2H), 4.51 (d, J = 32.8 Hz, 1H), 5.14 and 5.17 (2 s, 2H), 5.36 (s, 1H), 7.27−7.36 (m, 2H), 7.48−7.50 and 7.76−7.77 (2 m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.8, 23.7 (d, J = 6.0 Hz), 32.6 (d, J = 7.0 Hz), 50.4 (d, J = 131.0 Hz), 50.5, 52.6$_5$, 52.6$_8$, 76.0 (d, J = 7.0 Hz), 76.1 (d, J = 7.0 Hz), 117.5, 121.7, 125.2, 125.5, 127.6, 132.9 (d, J = 11.0 Hz), 137.3 (d, J = 5.0 Hz), 139.3, 143.5, 144.8, 167.9, 168.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.5; LC/MS m/z 435 $[M + 1]^+$; HRMS (ESI) calcd for $C_{22}H_{28}O_7P$ $[M + H]^+$ 435.1572, found 435.1572. Anal. Calcd for $C_{22}H_{27}O_7P$: C, 60.82; H, 6.26. Found: C, 60.91; H, 6.21. This compound was crystallized from a dichloromethane/hexane (3 + 1 mL) mixture. X-ray structural analysis was done for this sample.

Compound ***27***. This compound was obtained by using propargyl alcohol **8** (0.66 g, 2.0 mmol) and **24** (0.34 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (4/1) mixture as the eluent: yield 0.70 g (76%, gummy material); IR (KBr, cm^{-1}) 2978, 1732, 1638, 1472, 1372, 1008; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 and 0.98 (2 s, 6H), 1.17−1.22 (m, 6H), 2.08 (s, 3H), 3.58−3.71 (m, 2H), 3.99−4.04 (m, 2H), 4.15−4.23 (m, 4H), 4.48 (d, J = 32.8 Hz, 1H), 5.10 and 5.16 (2 s, 2H), 5.34 (s, 1H), 7.20−7.32 (m, 2H), 7.49−7.51 and 7.72−7.74 (2 m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.6, 21.8, 23.8, 32.6 (d, J = 7.1 Hz), 50.3 (d, J = 127.0 Hz), 61.7, 61.8, 76.0 (d, J = 6.9 Hz), 76.1 (d, J = 6.8 Hz), 117.5, 122.0, 125.1, 125.4, 127.5, 133.2 (d, J = 10.7 Hz), 137.3 (d, J = 4.9 Hz), 139.3, 143.5 (d, J = 4.8 Hz), 144.6 (d, J = 4.8 Hz), 167.5, 167.7 (d, J = 3.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.7; LC/MS m/z 463 $[M + 1]^+$; HRMS (ESI) calcd for $C_{24}H_{32}O_7P$ $[M + H]^+$ 463.1885, found 463.1885. Anal. Calcd for $C_{24}H_{31}O_7P$: C, 62.33; H, 6.76. Found: C, 62.21; H, 6.70.

Compound ***28***. This compound was obtained by using propargyl alcohol **9** (0.68 g, 2.0 mmol) and **24** (0.34 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (4/1) mixture as the eluent: yield 0.72 g (76%); mp 114−116 °C (white solid); IR (KBr, cm^{-1}) 2936, 1728, 1441, 1256, 1063, 1009; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 and 1.00 (2 s, 6H), 1.62−1.75 (m, 4H), 1.99−2.03 (m, 1H), 2.22 (br, 2H), 2.49−2.53 (m, 1H), 3.65−3.76 (m, 8H), 3.99−4.10 (m, 2H), 4.49 (d, J = 32.8 Hz, 1H), 5.10 (s, 1H), 5.90 (br, 1H), 7.21−7.34 (m, 2H), 7.42−7.44 and 7.74−7.76 (2 m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.9, 22.7, 25.5, 29.4, 32.6 (d, J = 7.1 Hz), 49.8 (d, J = 131.2 Hz), 50.6, 52.8, 75.8 (d, J = 6.7 Hz), 76.0 (d, J = 6.8 Hz), 121.2, 125.2 (d, J = 3.7 Hz), 127.6, 129.6, 131.7 (d, J = 10.9 Hz), 132.8, 137.1 (d, J = 4.7 Hz), 143.8 (d, J = 5.1 Hz), 145.7 (d, J = 6.6 Hz), 168.2, 168.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.4; LC/MS m/z 475 $[M + 1]^+$; HRMS (ESI) calcd for $C_{25}H_{32}O_7P$ $[M + H]^+$ 475.1885, found 475.1885. Anal. Calcd for $C_{25}H_{31}O_7P$: C, 63.28; H, 6.59. Found: C, 63.15; H, 6.68.

Compound ***29***. This compound was obtained by using propargyl alcohol **10** (0.74 g, 2.0 mmol) and **24** (0.34 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (4/1) mixture as the eluent: yield 0.74 g (73%, gummy material); IR (neat, cm^{-1}) 2924, 1728, 1665, 1368, 1223, 1017; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 and 1.01 (2 s, 6H), 1.21−1.28 (m, 6H), 1.62−1.77 (m, 4H), 2.06−2.08 (m, 1H), 2.25−2.26 (m, 2H), 2.49−2.53 (m, 1H), 3.65−3.73 (m, 2H), 4.03−4.27 (m, 6H), 4.51 (d, J = 32.0 Hz, 1H), 5.06 (s, 1H), 5.94 (br, 1H), 7.22−7.35 (m, 2H), 7.49 and 7.77 (2 d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.7, 21.9, 22.8, 25.5, 29.4, 32.6 (d, J = 7.1 Hz), 49.7 (d, J = 131.3 Hz), 51.0, 51.1,

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61.7, 61.8, 75.8 (d, J = 6.9 Hz), 75.9 (d, J = 7.0 Hz), 121.5, 125.1, 127.4, 129.5 (d, J = 1.3 Hz), 132.1 (d, J = 7.0 Hz), 132.9, 137.1 (d, J = 4.8 Hz), 143.9 (d, J = 5.1 Hz), 145.5 (d, J = 6.6 Hz), 167.8 (d, J = 2.1 Hz), 168.0 (d, J = 4.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.8; LC/MS m/z 503 $[M + 1]^+$; HRMS (ESI) calcd for $C_{27}H_{36}O_7P$ $[M + H]^+$ 503.2198, found 503.2199. Anal. Calcd for $C_{27}H_{35}O_7P$: C, 64.53; H, 7.02. Found: C, 64.38; H, 7.10.

Compound ***30***. This compound was obtained by using propargyl alcohol **11** (0.49 g, 1.6 mmol) and **24** (0.28 g, 1.6 mmol). It was purified by column chromatography using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.48 g (68%); mp 144−146 °C (white solid); IR (KBr, cm^{-1}) 2980, 1696, 1580, 1470, 1381, 1277, 1057; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 and 0.95 (2 s, 6H), 1.35 (t, J = 7.0 Hz, 3H), 1.64 and 1.82 (2 s, 6H), 2.33 (s, 3H), 3.35−3.42 (m, 1H), 3.84−4.05 (m, 2H), 4.16 (d, J = 32.8 Hz, 1H), 4.27−4.38 (m, 3H), 7.18−7.22 (m, 1H), 7.29−7.32 and 7.41−7.43 (2 m, 2H), 7.63−7.65 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 19.9, 21.6$_7$, 21.7$_3$, 24.5, 26.8, 32.7 (d, J = 6.3 Hz), 47.5 (d, J = 132.5 Hz), 60.2, 75.1 (d, J = 6.3 Hz), 76.4 (d, J = 7.5 Hz), 80.4, 104.0 (d, J = 2.5 Hz), 122.3, 124.7 (d, J = 1.3 Hz), 125.1 (d, J = 2.5 Hz), 127.4, 132.4 (d, J = 7.5 Hz), 134.7 (d, J = 11.3 Hz), 139.0 (d, J = 5.0 Hz), 142.3 (d, J = 3.8 Hz), 164.7, 166.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.3; LC/MS m/z 433 $[M + 1]^+$; HRMS (ESI) calcd for $C_{23}H_{29}O_6PNa$ $[M + Na]^+$ 455.1600, found 455.1605. Anal. Calcd for $C_{23}H_{29}O_6P$: C, 63.88; H, 6.76. Found: C, 63.72; H, 6.83.

Compound ***31***. This compound was obtained by using propargyl alcohol **7** (0.60 g, 2.0 mmol) and **25** (0.81 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.96 g (72%); mp 146−148 °C (white solid); IR (KBr, cm^{-1}) 2955, 1738, 1605, 1439, 1262, 1204, 1028, 922; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 and 1.53 (2 s, 18H), 2.18, 2.24, and 2.30 (3 s, 9H), 3.36 (d, $J \approx$ 13.4 Hz, 1H), 3.72 and 3.73 (2 s, 6H), 4.42 (d, $J \approx$ 13.4 Hz, 1H), 4.74 (d, J = 32.4 Hz, 1H), 5.18 (s, 1H), 5.25 and 5.46 (2 br, 2H), 6.91 and 7.02 (2 br, 2H), 7.08−7.10 (m, 2H), 7.27−7.31 (m, 1H), 7.40 (t, $J \approx$ 8.0 Hz, 1H), 7.64 and 8.00 (2 d, $J \sim\approx$8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.0, 23.7, 30.4, 31.8, 34.0, 34.3, 35.1, 50.7, 50.8 (d, J = 146.0 Hz), 52.7, 52.8, 119.0, 122.1, 125.7, 126.6, 127.4, 127.8, 128.1, 128.7 (d, J = 2.3 Hz), 133.0 (d, J = 11.0 Hz), 133.5 (d, J = 2.8 Hz), 134.7 (d, J = 1.3 Hz), 134.9, 136.7, 139.5, 141.2 (d, J = 4.4 Hz), 141.7 (d, J = 4.5 Hz), 143.3 (d, J = 7.1 Hz), 144.3 (d, J = 12.0 Hz), 144.8 (d, J = 12.2 Hz), 146.7 (d, J = 7.6 Hz), 167.8 (d, J = 4.2 Hz), 168.0 (d, J = 1.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.9; LC/MS m/z 672 $[M + 1]^+$; Anal. Calcd for $C_{40}H_{47}O_7P$: C, 71.62; H, 7.06. Found: C, 71.48; H, 7.15; HRMS (ESI) calcd for $C_{40}H_{48}O_7P$ $[M + H]^+$ 671.3137, found 671.3137.

Compound ***32***. This compound was obtained by using propargyl alcohol **8** (0.66 g, 2.0 mmol) and **25** (0.81 g, 2.0 mmol). It was purified by column chromatography using ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.95 g (68%); mp 112−114 °C (white solid); IR (KBr, cm^{-1}) 2959, 1736, 1466, 1368, 1273, 1209, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (s, 9H), 1.21−1.29 (m, 6H), 1.52 (s, 9H), 2.17, 2.23, and 2.29 (3 s, 9H), 3.35 (d, J = 13.6 Hz, 1H), 4.16−4.24 (m, 4H), 4.41 (d, J = 13.6 Hz, 1H), 4.73 (d, J = 32.0 Hz, 1H), 5.11 (s, 1H), 5.25 and 5.45 (2 br, 2H), 6.90 and 7.01 (2 br, 2H), 7.07−7.09 (m, 2H), 7.26−7.29 (m, 1H), 7.38 (t, $J \approx$ 8.0 Hz, 1H), 7.67 and 7.98 (2 d, $J \approx$ 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.9, 21.0, 23.8, 30.4, 31.8, 34.0, 34.3, 35.1, 50.8 (d, J = 146.1 Hz), 51.2, 61.7, 61.8, 118.9, 122.5, 125.6, 126.5, 127.4, 127.6, 128.1, 128.7 (d, J = 6.9 Hz), 133.4 (d, J = 12.0 Hz), 133.5 (d, J = 2.7 Hz), 133.8 (d, J = 2.9 Hz), 134.6, 134.9, 136.7, 139.4, 141.2 (d, J = 4.3 Hz), 141.7 (d, J = 4.5 Hz), 143.3 (d, J = 6.9 Hz), 141.7 (d, J = 4.5 Hz), 143.4 (d, J = 6.9 Hz), 144.3 (d, J = 12.8 Hz), 144.8 (d, J = 12.4 Hz), 146.6 (d, J = 7.3 Hz), 167.3 (d, J = 3.9 Hz), 167.6 (d, J = 2.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.9; LC/MS m/z 700 $[M + 1]^+$; HRMS (ESI) calcd for $C_{42}H_{51}O_7P$ $[M + H]^+$ 699.3451, found 699.3459. Anal. Calcd for $C_{42}H_{51}O_7P$: C, 72.19; H, 7.36. Found: C, 72.05; H, 7.41.

Compound ***33***. This compound was obtained by using propargyl alcohol **9** (0.68 g, 2.0 mmol) and **25** (0.81 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.99 g (70%); mp 184−186 °C (white solid); IR (KBr, cm^{-1}) 2947, 1736, 1439, 1265, 1209, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 and 1.53 (2 s, 18H), 1.57−1.63 (m, 3H), 2.06−2.29 (m, 10H), 2.60−2.64 (m, 1H), 3.38 (d, $J \approx$ 12.7 Hz, 1H), 3.69 and 3.71 (2 s, 6H), 4.41 (dd, $J \approx$ 12.7 Hz, 3.0 Hz, 1H), 4.71 (d, J = 33.2 Hz, 1H), 5.09 (s, 1H), 5.93 (br, 1H), 6.88 and 7.00 (2 br, 2H), 7.06−7.09 (m, 2H), 7.23−7.27 (m, 1H), 7.36 (t, $J \approx$ 8.0 Hz, 1H), 7.58 and 7.98 (2 d, $J \approx$ 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.0, 22.0, 22.7, 25.7, 29.6, 30.4, 31.8, 33.5, 34.3, 35.1, 50.5 (d, J = 147.1 Hz), 50.8, 52.7, 52.8, 121.8, 125.4, 126.8, 127.4, 127.7, 128.1, 128.6, 130.6, 132.2 (d, J = 10.6 Hz), 133.0, 133.6, 134.8, 136.5, 141.3 (d, J = 6.5 Hz), 141.7 (d, J = 3.7 Hz), 143.6, 144.9 (d, J = 11.0 Hz), 147.7 (d, J = 6.0 Hz), 168.1 (d, J = 4.0 Hz), 168.3 (d, J = 3.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.4; LC/MS m/z 710 $[M]^+$; HRMS (ESI) calcd for $C_{43}H_{52}O_7P$ $[M + H]^+$ 711.3450, found 711.3450. Anal. Calcd for $C_{43}H_{51}O_7P$: C, 72.66; H, 7.23. Found: C, 72.85; H, 7.16.

Compound ***34***. This compound was obtained by using propargyl alcohol **10** (0.74 g, 2.0 mmol) and **25** (0.81 g, 2.0 mmol). It was purified by column chromatography using an ethyl acetate/hexane (1/4) mixture as the eluent: yield 0.99 g (67%); mp 126−128 °C (white solid); IR (KBr, cm^{-1}) 2924, 1732, 1603, 1454, 1155, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (s, 9H), 1.22−1.31 (m, 6H), 1.55 (s, 9H), 1.61 (br, 2H), 2.20, 2.24, and 2.31 (3 s, 11H), 2.63−2.67 (m, 1H), 3.40 (d, J = 12.8 Hz, 1H), 4.16−4.25 (m, 4H), 4.43 (dd, J = 12.8 Hz, 2.4 Hz, 1H), 4.73 (d, J = 32.8 Hz, 1H), 5.06 (s, 1H), 5.93 (br, 1H), 6.90 (s, 1H), 7.02−7.03 (m, 1H), 7.09−7.11 (m, 2H), 7.24−7.28 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.64 and 7.98 (2 d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.9, 21.0, 22.0, 22.7, 25.7, 29.6, 30.4, 30.9, 31.7, 33.5, 34.3, 35.1, 50.4 (d, J = 146.2 Hz), 51.3, 61.6, 61.7, 122.2, 125.3, 126.6, 127.4, 127.5, 128.1, 128.6, 128.7, 130.5, 132.6 (d, J = 11.1 Hz), 133.0, 133.5 (d, J = 2.7 Hz), 133.6 (d, J = 2.9 Hz), 134.6, 134.8, 136.5, 141.3 (d, J = 4.3 Hz), 141.8 (d, J = 4.6 Hz), 143.7 (d, J = 7.0 Hz), 144.3 (d, J = 12.0 Hz), 144.9 (d, J = 12.3 Hz), 147.6 (d, J = 7.1 Hz), 167.5 (d, J = 3.8 Hz), 167.8 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.5; LC/MS m/z 738 $[M]^+$; HRMS (ESI) calcd for $C_{45}H_{56}O_7P$ $[M + H]^+$ 739.3763, found 739.3763. Anal. Calcd for $C_{45}H_{55}O_7P$: C, 73.15; H, 7.50. Found: C, 73.31; H, 7.42.

(iv). Reaction of Aldehyde-Functionalized Propargyl Alcohols 12 and 13 with P^{III}−Cl Precursors 24/35: Synthesis of Phosphono-Indenone Derivatives 36−39. The phosphono-indenones **36−39** were obtained by following the procedure mentioned in section iii.

Compound ***36***. This compound was obtained by using propargyl alcohol **12** (0.55 g, 2.90 mmol) and **24** (0.50 g, 2.90 mmol). It was purified by column chromatography using an ethyl acetate/hexane (4/1) mixture as the eluent: yield 0.71 g (75%); mp 170−172 °C (white solid); IR (KBr, cm^{-1}) 2932, 1696, 1638, 1466, 1252, 1059, 1015; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 and 0.85 (2 s, 6H), 2.17 and 2.45 (2 s, 6H), 3.51−3.63 and 4.09−4.18 (2 m, 4H), 4.56 (d, J = 23.2 Hz, 1H), 7.43−7.47 and 7.58−7.62 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.2, 21.3, 25.8, 32.6 (d, J = 6.2 Hz), 42.8 (d, J = 136.9 Hz), 75.1, 75.3, 124.0, 127.2, 127.9, 128.5, 133.8, 139.7, 143.4, 153.0, 192.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8; LC/MS m/z 319 $[M - 1]^+$; HRMS (ESI) calcd for $C_{17}H_{21}O_4PNa$ $[M + Na]^+$ 343.1075, found 343.1075. Anal. Calcd for $C_{17}H_{21}O_4P$: C, 63.74; H, 6.61. Found: C, 63.58; H, 6.71.

Compound ***37***. This compound was prepared by using propargyl alcohol **13** (0.74 g, 3.3 mmol) and **24** (0.55 g, 3.3 mmol): yield 0.82 g (70%); mp 162−164 °C (white solid); IR (KBr, cm^{-1}) 2930, 1711, 1599, 1462, 1235, 1053, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 and 0.86 (2 s, 6H), 1.66−1.91 (m, 6H), 2.46−2.58 and 3.07−3.32 (m, 4H), 3.55−3.62 and 4.10−4.21 (2 m, 4H), 4.61 (d, J = 23.2 Hz, 1H), 7.44−7.48 and 7.59−7.63 (m, 2H), 7.75−7.77 (m, 1H), 7.83 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.5, 26.2, 27.9, 28.1, 29.2 (d, J = 1.8 Hz), 32.6 (d, J = 6.0 Hz), 35.2 (d, J = 1.3 Hz), 42.3 (d, J = 136.8 Hz), 75.1 (d, J = 6.5 Hz), 75.2 (d, J = 6.6 Hz), 124.0 (d, J = 2.4 Hz), 125.2 (d, J = 7.3 Hz), 127.1 (d, J = 4.0 Hz), 128.4 (d, J = 2.9 Hz), 133.8 (d, J = 3.1 Hz), 140.0 (d, J = 5.8 Hz), 143.2 (d, J = 9.5 Hz), 160.2 (d, J = 5.9 Hz), 192.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.9; LC/MS m/z 361 $[M + 1]^+$; HRMS (ESI) calcd for

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$C_{20}H_{25}O_4PNa$ $[M + Na]^+$ 383.1388, found 383.1388. Anal. Calcd for $C_{20}H_{25}O_4P$: C, 66.66; H, 6.99. Found: C, 66.82; H, 6.91.

Compound ***38***. This compound was prepared by using propargyl alcohol **12** (0.55 g, 2.9 mmol) and **35** (0.64 g, 2.9 mmol): yield 0.84 g (78%); mp 212−214 °C (white solid); IR (KBr, cm^{-1}) 2934, 1684, 1620, 1435, 1292, 1194, 1111; ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H), 2.35 (d, J = 2.8 Hz, 3H), 5.01 (d, J = 17.2 Hz, 1H), 7.01 (d, J = 7.2 Hz, 1H), 7.28−7.51 (m, 10H), 7.59 (d, J = 7.2 Hz, 1H), 7.69−7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 25.8, 47.7 (d, J = 62.7 Hz), 123.9 (d, J = 15.5 Hz), 127.8, 128.1, 128.2, 128.6, 130.8, 131.5, 131.7, 132.2, 132.3, 133.4, 140.1, 143.9, 153.6, 192.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; LC/MS m/z 373 $[M + 1]^+$; HRMS (ESI) calcd for $C_{24}H_{21}O_2PNa$ $[M + Na]^+$ 395.1177, found 395.1177. Anal. Calcd for $C_{24}H_{21}O_2P$: C, 77.41; H, 5.68. Found: C, 77.35; H, 5.61. This compound was crystallized from tetrahydrofuran (2 mL) at 30 °C. An X-ray structure was determined for this sample.

Compound ***39***. This compound was prepared by using propargyl alcohol **13** (0.74 g, 3.3 mmol) and **35** (0.73 g, 3.3 mmol): yield 0.97 g (71%); mp 174−176 °C (white solid); IR (KBr, cm^{-1}) 2928, 1705, 1603, 1439, 1186, 1119; ^1H NMR (400 MHz, $CDCl_3$) δ 1.56−2.35 (m, 8H), 2.82−2.85 and 3.33−3.35 (m, 2H), 5.06 (d, J = 17.2 Hz, 1H), 6.95−6.97 (m, 1H), 7.27−7.60 (m, 11H), 7.71−7.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2, 28.2, 28.3, 29.3, 35.3, 47.1 (d, J = 62.5 Hz), 123.9 (d, J = 2.4 Hz), 125.8 (d, J = 4.5 Hz), 126.5 (d, J = 3.4 Hz), 128.0, 128.1, 128.4, 128.5, 131.5, 131.6, 132.0 (d, J = 3.3 Hz), 132.1 (d, J = 2.6 Hz), 132.4, 132.5, 133.2 (d, J = 2.6 Hz), 140.5 (d, J = 4.6 Hz), 143.8 (d, J = 5.1 Hz), 161.2 (d, J = 4.9 Hz), 192.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2; LC/MS m/z 411 $[M - 1]^+$; HRMS (ESI) calcd for $C_{27}H_{26}O_2P$ $[M + H]^+$ 413.1670, found 413.1670. Anal. Calcd for $C_{27}H_{25}O_2P$: C, 78.62; H, 6.11. Found: C, 78.51; H, 6.02.

(v). Synthesis of Functionalized Allenes 40−55. *(a). Synthesis of Allenes* ***40−45***. The phosphorus-based allenes **40−45** were synthesized according to literature procedures.[6]

Compound ***40***. This compound was prepared from propargyl alcohol **14** (0.92 g, 4.8 mmol) and **35** (1.06 g, 4.8 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 1.42 g (79%, gummy material); IR (neat, cm^{-1}) 2982, 1925, 1597, 1491, 1364, 1155; ^1H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 3H), 4.79 and 4.82 (2 s, 2H), 4.92 (s, 2H), 6.91−6.95 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.16−7.20 (m, 1H), 7.39−7.49 (m, 7H), 7.75−7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.0, 76.5 (d, J = 12.5 Hz), 94.5, 96.7 (d, J = 101.2 Hz), 114.5, 121.7 (d, J = 4.8 Hz), 121.9, 128.0, 128.1, 129.4, 130.8 (d, J = 3.7 Hz), 131.5 (d, J = 2.8 Hz), 131.7, 131.8, 133.0 (d, J = 106.4 Hz), 154.7 (d, J = 3.9 Hz), 214.1 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9; LC/MS m/z 377 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{21}O_3P$: C, 73.39; H, 5.62. Found: C, 73.29; H, 5.68.

Compound ***41***. This compound was prepared from propargyl alcohol **15** (0.57 g, 2.2 mmol) and **35** (0.47 g, 2.2 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.77 g (80%, gummy material); IR (neat, cm^{-1}) 3057, 1933, 1595, 1489, 1439, 1242, 1194, 1117; ^1H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 4.93 (s, 2H), 6.17 (d, J = 10.8 Hz, 1H), 6.91−6.95 (m, 1H), 7.09−7.43 (m, 13H), 7.66−7.85 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 94.3, 96.0 (d, J = 13.5 Hz), 100.5 (d, J = 99.7 Hz), 114.2, 121.7 (d, J = 5.4 Hz), 121.9, 127.2 (d, J = 2.0 Hz), 127.5, 128.0 (d, J = 1.2 Hz), 128.1 (d, J = 1.2 Hz), 128.5, 129.4, 130.6 (d, J = 3.4 Hz), 131.5, 131.6$_1$, 131.6$_4$, 131.7, 132.7 (d, J = 106.1 Hz), 132.8 (d, J = 105.2 Hz), 154.7 (d, J = 4.6 Hz), 213.8 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; LC-MS m/z 452 $[M]^+$. Anal. Calcd for $C_{29}H_{25}O_3P$: C, 76.98; H, 5.57. Found: C, 76.85; H, 5.67.

Compound ***42***. This compound was prepared from propargyl alcohol **16** (0.48 g, 2.2 mmol) and **35** (0.48 g, 2.2 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.74 g (84%, gummy material); IR (neat, cm^{-1}) 2907, 1954, 1738, 1593, 1489, 1439, 1366, 1236; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 and 1.47 (2 s, 6H), 3.32 (s, 3H), 4.95 (s, 2H), 6.90−6.94 (m, 1H), 7.05−7.18 (m, 2H), 7.40−7.55 (m, 8H), 7.74−7.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 18.9, 55.8, 94.5, 94.6 (d, J = 104.5 Hz), 97.4 (d, J = 13.8 Hz), 114.4, 121.8, 123.0 (d, J = 7.0 Hz), 127.9, 128.0, 128.6 (d, J = 4.1 Hz), 128.7, 128.9, 130.9 (d, J = 3.7 Hz), 131.2 (d, J = 2.6 Hz), 131.5, 131.6, 131.8, 133.8 (d, J = 105.1 Hz), 154.7 (d, J = 4.3 Hz), 211.4 (d, J = 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; LC/MS m/z 405 $[M + 1]^+$. Anal. Calcd for $C_{25}H_{25}O_3P$: C, 74.24; H, 6.23. Found: C, 74.12; H, 6.35.

Compound ***43***. This compound was prepared from propargyl alcohol **17** (0.76 g, 2.7 mmol) and **35** (0.59 g, 2.7 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 1.06 g (85%, gummy material); IR (neat, cm^{-1}) 2955, 1931, 1730, 1595, 1491, 1439; ^1H NMR (500 MHz, $CDCl_3$) δ 1.87 (s, 3H), 3.27 (s, 3H), 4.93 (s, 2H), 6.94−6.97 (m, 1H), 7.10−7.46 (m, 13H), 7.71−7.80 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.7 (d, J = 5.9 Hz), 55.8, 94.4, 98.4 (d, J = 100.9 Hz), 102.7 (d, J = 14.1 Hz), 114.3, 121.9, 125.9 (d, J = 1.5 Hz), 127.2, 127.9, 128.0, 128.1, 128.2, 129.1, 130.8$_0$, 130.8$_2$, 131.4, 131.4$_9$, 131.5$_2$, 131.5$_7$, 131.6$_0$, 132.6, 132.8, 133.0 (d, J = 105.8 Hz), 133.7, 134.9 (d, J = 6.6 Hz), 154.8 (d, J = 4.9 Hz), 213.8 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4; LC/MS m/z 467 $[M + 1]^+$. Anal. Calcd for $C_{30}H_{27}O_3P$: C, 77.24; H, 5.83. Found: C, 77.45; H, 5.76.

Compound ***44***. This compound was prepared from propargyl alcohol **18** (0.62 g, 2.5 mmol) and **35** (0.56 g, 2.5 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.89 g (82%, gummy material); IR (neat, cm^{-1}) 2955, 1946, 1593, 1489, 1437, 1236, 1117; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32−1.34 (m, 2H), 1.50−1.51 (m, 2H), 1.90−1.95 (m, 2H), 2.33−2.38 (m, 2H), 3.30 (s, 3H), 4.93 (s, 2H), 6.90−6.93 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.13−7.17 (m, 1H), 7.40−7.56 (m, 7H), 7.74−7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 30.5$_9$, 30.6$_4$, 55.9, 94.6, 96.8 (d, J = 105.1 Hz), 105.7 (d, J = 14.5 Hz), 114.4, 121.8, 123.3 (d, J = 6.9 Hz), 127.9, 128.0, 128.6, 128.8, 130.9, 131.1, 131.5, 131.6, 131.8, 132.5, 134.1 (d, J = 105.3 Hz), 154.6 (d, J = 4.1 Hz), 207.1 (d, J = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1; LC/MS m/z 432 $[M + 1]^+$. Anal. Calcd for $C_{27}H_{27}O_3P$: C, 75.33; H, 6.32. Found: C, 75.51; H, 6.18.

Compound ***45***. This compound was prepared from propargyl alcohol **19** (0.79 g, 3.0 mmol) and **35** (0.67 g, 3.0 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 1.10 g (82%, gummy material); IR (neat, cm^{-1}) 2930, 1950, 1738, 1591, 1439, 1117; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98−1.07 (m, 2H), 1.30−1.51 (m, 4H), 1.89−2.06 (m, 4H), 3.34 (s, 3H), 4.96 (s, 2H), 6.92−6.96 (m, 1H), 7.08−7.24 (m, 3H), 7.41−7.81 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 26.0, 26.1, 29.6, 29.7, 55.8, 94.5$_2$, 94.5$_4$ (d, J = 106.3 Hz), 103.4 (d, J = 13.8 Hz), 114.4, 121.8, 123.3 (d, J = 7.1 Hz), 128.0, 128.1, 128.8, 130.9 (d, J = 3.6 Hz), 131.1, 131.2 (d, J = 2.6 Hz), 131.4, 131.6, 131.7, 133.9 (d, J = 105.3 Hz), 154.7 (d, J = 4.0 Hz), 208.1 (d, J = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; LC/MS m/z 445 $[M + 1]^+$. Anal. Calcd for $C_{28}H_{29}O_3P$: C, 75.66; H, 6.58. Found: C, 75.48; H, 6.63.

(b). Synthesis of Phenol-Based Allenes ***46−51***. To a homogeneous solution of allene **40** (0.20 g, 0.50 mmol) in ethyl acetate (2 mL) was added hydrochloric acid (35%, 1.0 mL), and the contents were stirred for 5 min. To this stirred solution was added water (10 mL) after completion of the reaction (TLC or ^{31}P NMR). The organic layer was separated, and the aqueous layer was washed with EtOAc (10 mL). The combined organic layer was washed with brine solution and dried (Na_2SO_4), the solvent removed by a rotary evaporator, and the product **46** thus obtained was used as such for the next step. Compounds **47−51** were also prepared similarly.

Compound ***46***. Yield 0.16 g (90%); mp 124−126 °C (white solid); IR (KBr, cm^{-1}) 3059, 1925, 1715, 1485, 1437, 1246, 1154, 1121; ^1H NMR (400 MHz, $CDCl_3$) δ 4.80 and 4.82 (2 s, 2H), 6.78−6.81 (m, 1H), 6.94 (d, J = 8.0 Hz, 1H), 7.12−7.17 (m, 2H), 7.47−7.57 (m, 6H), 7.74−7.79 (m, 4H), 10.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.4 (d, J = 12.1 Hz), 99.5 (d, J = 99.5 Hz), 119.4, 120.1, 128.5, 128.6, 129.3, 130.3, 131.9, 132.0, 132.6, 155.7, 214.3 (d, J = 8.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.0; LC/MS m/z 333 $[M + 1]^+$. Anal. Calcd for $C_{21}H_{17}O_2P$: C, 75.90; H, 5.16. Found: C, 75.81; H, 5.23. This compound was crystallized from an ethyl acetate/hexane (9/1) mixture at 25 °C. An X-ray structure was determined for this sample.

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Compound 47. This product was synthesized from compound **41** (0.20 g, 0.4 mmol): yield 0.16 g (91%); mp 134−136 °C (white solid); IR (KBr, cm^{-1}) 3061, 1931, 1736, 1439, 1244, 1161, 1119; ^1H NMR (500 MHz, $CDCl_3$) δ 6.23 (d, J = 10.8 Hz, 1H), 6.77−6.81 (m, 1H), 6.96−7.52 (m, 14H), 7.74−7.81 (m, 4H), 10.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 96.5 (d, J = 12.8 Hz), 104.3 (d, J = 97.5 Hz), 119.4, 119.7 (d, J = 4.8 Hz), 120.2, 127.0 (d, J = 1.6 Hz), 128.1, 128.4, 128.5, 128.6, 128.8, 130.5, 131.6$_7$, 131.7$_2$, 131.7$_5$, 131.9, 132.5 (d, J = 2.6 Hz), 132.6 (d, J = 2.6 Hz), 155.7, 213.8 (d, J = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.2; LC/MS m/z 407 $[M - 1]^+$. Anal. Calcd for $C_{27}H_{21}O_2P$: C, 79.40; H, 5.18. Found: C, 79.26; H, 5.22.

Compound 48. This product was synthesized from compound **42** (0.20 g, 0.5 mmol): yield 0.17 g (96%); mp 142−144 °C (white solid); IR (KBr, cm^{-1}) 3057, 2924, 1956, 1524, 1437, 1254, 1148; ^1H NMR NMR (400 MHz, $CDCl_3$) δ 1.47 and 1.48 (2 s, 6H), 6.76−6.80 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 7.09−7.15 (m, 2H), 7.44−7.55 (m, 6H), 7.72−7.76 (m, 4H), 10.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0$_8$, 19.1$_3$, 97.9 (d, J = 100.9 Hz), 98.3 (d, J = 13.4 Hz), 119.2, 119.9, 120.9 (d, J = 6.0 Hz), 128.4, 128.5, 129.9, 130.7 (d, J = 106.2 Hz), 131.7, 131.8, 132.3, 155.7, 211.8 (d, J = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.9; LC/MS m/z 361 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87. Found: C, 76.75; H, 5.82.

Compound 49. This product was synthesized from compound **43** (0.28 g, 0.6 mmol): yield 0.23 g (92%); mp 170−172 °C (white solid); IR (KBr, cm^{-1}) 3059, 1931, 1738, 1439, 1244, 1159, 1121; ^1H NMR (400 MHz, $CDCl_3$) δ 1.88 (d, J = 5.6 Hz, 3H), 6.79−6.82 (m, 1H), 6.97 (d, J = 8.0 Hz, 1H), 7.16−7.53 (m, 13H), 7.71−7.77 (m, 4H), 10.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2 (d, J = 5.5 Hz), 102.0 (d, J = 98.6 Hz), 103.7 (d, J = 13.2 Hz), 116.1, 119.4, 120.1, 125.7, 127.8, 128.3, 128.4, 128.5, 130.2 (d, J = 106.7 Hz), 130.3, 131.6, 131.7, 131.8, 132.4, 134.2 (d, J = 6.2 Hz), 155.7, 214.0 (d, J = 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.1; LC/MS m/z 423 $[M + 1]^+$. Anal. Calcd for $C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.55; H, 5.52.

Compound 50. This product was synthesized from compound **44** (0.20 g, 0.5 mmol): yield 0.16 g (90%); mp 148−150 °C (white solid); IR (KBr, cm^{-1}) 3057, 1944, 1595, 1453, 1281, 1152, 1096; ^1H NMR NMR (400 MHz, $CDCl_3$) δ 1.28 (br, 2H), 1.54 (br, 2H), 1.95 (br, 2H), 2.41−2.42 (m, 2H), 6.77−6.80 (m, 1H), 6.91−6.95 (m, 1H), 7.13 (br, 2H), 7.46−7.53 (m, 6H), 7.72−7.76 (m, 4H), 10.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.9, 31.0 (d, J = 4.4 Hz), 100.1 (d, J = 102.5 Hz), 106.3 (d, J = 13.8 Hz), 119.2, 119.9, 121.2, 128.3, 128.4, 129.9, 131.0 (d, J = 106.0 Hz), 131.7, 131.8, 132.2, 155.7, 207.3 (d, J = 8.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.3; LC/MS m/z 387 $[M + 1]^+$. Anal. Calcd for $C_{25}H_{23}O_2P$: C, 77.70; H, 6.00. Found: C, 77.56; H, 6.12.

Compound 51. This product was synthesized from compound **45** (0.20 g, 0.4 mmol): yield 0.15 g (94%); mp 162−164 °C (white solid); IR (KBr, cm^{-1}) 3057, 2928, 1941, 1572, 1483, 1439, 1404, 1294, 1244, 1148; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97−1.48 (m, 6H), 1.81−2.06 (m, 4H), 6.77−6.81 (m, 1H), 6.93 (d, J = 8.0 Hz, 1H), 7.09−7.16 (m, 2H), 7.48−7.55 (m, 6H), 7.74−7.89 (m, 4H), 10.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 26.1, 29.8$_7$, 29.9$_1$, 97.8 (d, J = 105.9 Hz), 104.0 (d, J = 13.1 Hz), 119.1, 119.9, 121.3 (d, J = 7.8 Hz), 128.4, 128.6, 129.8, 130.8 (d, J = 106.7 Hz), 131.8, 131.9, 132.2, 155.7, 208.4 (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.6; LC/MS m/z 401 $[M + 1]^+$. Anal. Calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 77.81; H, 6.37.

(c). Synthesis of Allenes 52−55. The phosphorus-based allenes **52−55** were synthesized according to literature procedures.[6]

Compound 52. This compound was prepared from propargyl alcohol **20** (0.44 g, 2.1 mmol) and **35** (0.47 g, 2.1 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.66 g (79%, gummy material); IR (neat, cm^{-1}) 3059, 1933, 1591, 1439, 1262, 1044; ^1H NMR (400 MHz, $CDCl_3$) δ 3.39 (s, 3H), 4.64 and 4.66 (2 s, 4H), 4.85 and 4.87 (2 s, 2H), 7.13−7.27 (m, 2H), 7.35−7.53 (m, 8H), 7.76−7.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 66.7, 95.8, 98.3 (d, J = 97.6 Hz), 127.6, 128.1, 128.2, 128.3, 128.7, 129.7 (d, J = 2.9 Hz), 130.5 (d, J = 4.9 Hz), 131.6 (d, J = 105.2 Hz), 131.9, 132.0, 136.9 (d, J = 4.9 Hz), 212.2 (d, J = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3; LC/MS m/z 391 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{23}O_3P$: C, 73.83; H, 5.94. Found: C, 73.91; H, 5.85.

Compound 53. This compound was prepared from propargyl alcohol **21** (0.44 g, 1.9 mmol) and **35** (0.42 g, 1.9 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 0.64 g (81%, gummy material); IR (neat, cm^{-1}) 2924, 1948, 1439, 1186, 1117, 1042; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 and 1.49 (2 s, 6H), 3.39 (s, 3H), 4.67 and 4.71 (2 s, 4H), 7.12−7.23 (m, 2H), 7.40−7.53 (m, 8H), 7.73−7.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8$_6$, 18.9$_0$, 55.3, 66.7, 95.7, 96.8 (d, J = 100.1 Hz), 97.8 (d, J = 13.6 Hz), 127.3, 127.6, 128.1, 128.1$_8$, 128.2$_0$, 129.8 (d, J = 2.6 Hz), 131.6 (d, J = 2.3 Hz), 131.6$_8$, 131.7$_2$, 132.7 (d, J = 103.9 Hz), 136.6 (d, J = 5.5 Hz), 209.8 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3; LC/MS m/z 419 $[M + 1]^+$. Anal. Calcd for $C_{26}H_{27}O_3P$: C, 74.62; H, 6.50. Found: C, 74.53; H, 6.58.

Compound 54. This compound was prepared from propargyl alcohol **22** (1.23 g, 4.7 mmol) and **35** (1.04 g, 4.7 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 1.51 g (72%, gummy material); IR (neat, cm^{-1}) 2953, 1942, 1437, 1379, 1283, 1188, 1044; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30−1.32 (m, 2H), 1.48−1.50 (m, 2H), 1.94−1.99 (m, 2H), 2.32−2.37 (m, 2H), 3.39 (s, 3H), 4.68 and 4.70 (2 s, 4H), 7.11−7.22 (m, 2H), 7.38−7.60 (m, 8H), 7.73−7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 30.5$_7$, 30.6$_2$, 55.3, 66.8, 95.8, 98.4 (d, J = 100.8 Hz), 106.1 (d, J = 14.1 Hz), 127.3, 127.6, 128.0, 128.1, 128.2, 129.5, 131.5$_6$, 131.6$_3$, 131.7, 132.9 (d, J = 104.1 Hz), 136.5 (d, J = 5.5 Hz), 205.9 (d, J = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1; LC/MS m/z 445 $[M + 1]^+$. Anal. Calcd for $C_{28}H_{29}O_3P$: C, 75.66; H, 6.58. Found: C, 75.48; H, 6.64.

Compound 55. This compound was prepared from propargyl alcohol **23** (2.11 g, 7.7 mmol) and **35** (1.70 g, 7.7 mmol). It was isolated by using an ethyl acetate/hexane (3/2) mixture as the eluent: yield 2.65 g (75%, gummy material); IR (neat, cm^{-1}) 2932, 1944, 1591, 1437, 1190, 1117, 1044; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01−1.04 (m, 2H), 1.30−1.48 (m, 4H), 1.92−2.04 (m, 4H), 3.41 (s, 3H), 4.69 and 4.74 (2 s, 4H), 7.13−7.25 (m, 2H), 7.41−7.57 (m, 8H), 7.75−7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.3, 25.9, 26.0, 29.6, 29.7, 55.3, 66.6, 95.7, 96.6 (d, J = 100.3 Hz), 103.7 (d, J = 13.9 Hz), 127.3, 127.5, 127.9, 128.2, 128.3, 129.8 (d, J = 2.9 Hz), 131.5 (d, J = 3.0 Hz), 131.7$_7$, 131.8$_4$, 132.0, 132.9 (d, J = 102.9 Hz), 136.6 (d, J = 6.4 Hz), 206.5 (d, J = 6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2; LC/MS m/z 457 $[M - 1]^+$. Anal. Calcd for $C_{29}H_{31}O_3P$: C, 75.96; H, 6.81. Found: C, 75.85; H, 6.72.

(vi). Cyclization Reactions of Allenes 46−51 Possessing a 2-Hydroxyphenol Side Group: Synthesis of 1,2-Disubstituted Benzofuran Derivatives 56−61. To a solution of allene **46** (0.10 g, 0.30 mmol) in THF (2 mL) was added triethylamine (0.04 mL, 0.30 mmol), and the mixture was stirred at 70 °C for 1 h. The solvent was removed by rotary evaporation, and the crude product thus obtained was purified by column chromatography (silica gel; 4/1 ethyl acetate/hexane) to yield the colorless solid product **56**. Compounds **57−61** were also prepared by following the same method.

Compound 56. This compound is known but was prepared by an entirely different (multistep) route:[11] yield 0.10 g (95%); mp 142−144 °C (white solid); IR (KBr, cm^{-1}) 2851, 1925, 1485, 1437, 1246, 1154, 1119; the ^1H NMR spectrum was identical with that reported before;[11] ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 105.9 (d, J = 119.0 Hz), 110.9, 120.8, 123.3, 124.1, 128.7, 128.8, 131.7, 131.8, 132.2 (d, J = 3.0 Hz), 133.1 (d, J = 109.0 Hz), 154.1 (d, J = 11.0 Hz), 164.7 (d, J = 18.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3; LC/MS m/z 333 $[M + 1]^+$. Anal. Calcd for $C_{21}H_{17}O_2P$: C, 75.90; H, 5.16. Found: C, 75.86; H, 5.09.

Compound 57. This product was synthesized from the allene **47** (0.10 g, 0.2 mmol). It was isolated by using an ethyl acetate/hexane (7/3) mixture as the eluent: yield 0.09 g (89%); mp 140−142 °C (white solid); IR (KBr, cm^{-1}) 3057, 1555, 1453, 1435, 1306, 1254, 1190, 1121; ^1H NMR (400 MHz, $CDCl_3$) δ 4.49 (s, 2H), 6.69 (d, J = 7.2 Hz, 1H), 6.99−7.03 (m, 1H), 7.18−7.31 (m, 6H), 7.44−7.58 (m, 7H), 7.73−7.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2, 106.4

(d, J = 117.9 Hz), 111.3, 121.1, 123.4, 124.4, 126.6, 128.5, 128.7, 128.8, 129.2, 131.7, 131.8, 132.3, 133.2 (d, J = 108.4 Hz), 137.0, 154.5 (d, J = 11.5 Hz), 166.3 (d, J = 17.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.5; LC/MS m/z 409 $[M + 1]^+$; HRMS (ESI) calcd for $C_{27}H_{21}O_2PNa$ $[M + Na]^+$ 431.1177, found 431.1177. Anal. Calcd for $C_{27}H_{21}O_2P$: C, 79.40; H, 5.18. Found: C, 79.55; H, 5.12.

Compound ***58***. This product was synthesized from the allene **48** (0.10 g, 0.3 mmol). It was isolated by using an ethyl acetate/hexane (7:3) mixture as the eluent: yield 0.09 g (90%); mp 128−130 °C (white solid); IR (KBr, cm^{-1}) 2868, 1559, 1437, 1250, 1194, 1119; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.8 Hz, 6H), 3.65−3.72 (m, 1H), 6.61 (d, J = 7.6 Hz, 1H), 6.97−7.01 (m, 1H), 7.20−7.23 (m, 1H), 7.47−7.59 (m, 7H), 7.72−7.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 27.8, 103.9 (d, J = 119.6 Hz), 111.1, 121.0, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1 (d, J = 2.6 Hz), 133.4 (d, J = 108.3 Hz), 154.1 (d, J = 11.7 Hz), 172.7 (d, J = 18.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.5; LC/MS m/z 361 $[M + 1]^+$; HRMS (ESI) calcd for $C_{23}H_{22}O_2P$ $[M + H]^+$ 361.1357, found 361.1357. Anal. Calcd for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87. Found: C, 76.52; H, 5.93.

Compound ***59***. This product was synthesized from the allene **49** (0.21 g, 0.5 mmol). It was isolated by using an ethyl acetate/hexane (4/1) mixture as the eluent: yield 0.20 g (93%); mp 160−162 °C (white solid); IR (KBr, cm^{-1}) 2975, 1555, 1453, 1437, 1250, 1188, 1121, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (d, J = 6.8 Hz, 3H), 5.14−5.20 (m, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.97−7.01 (m, 1H), 7.16−7.26 (m, 4H), 7.38−7.80 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 37.9, 105.0 (d, J = 118.4 Hz), 111.3, 121.1, 123.4, 124.3, 126.2, 127.9, 128.4, 128.6, 128.7, 128.8, 131.7, 131.8, 131.9, 132.2 (d, J = 13.5 Hz), 133.2 (d, J = 108.5 Hz), 133.3 (d, J = 108.3 Hz), 142.3, 154.4 (d, J = 11.5 Hz), 169.8 (d, J = 18.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.6; LC/MS m/z 423 $[M + 1]^+$; HRMS (ESI) calcd for $C_{28}H_{24}O_2P$ $[M + H]^+$ 423.1514, found 423.1514. Anal. Calcd for $C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.48; H, 5.57.

Compound ***60***. This product was synthesized from the allene **50** (0.10 g, 0.3 mmol). It was isolated by using an ethyl acetate/hexane (7/3) mixture: yield 0.09 g (88%); mp 102−104 °C (white solid); IR (KBr, cm^{-1}) 2957, 1555, 1454, 1437, 1312, 1254, 1182, 1121; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (br, 2H), 1.81−1.86 (m, 6H), 3.62−3.67 (m, 1H), 6.62−6.64 (m, 1H), 6.97−7.00 (m, 1H), 7.18−7.21 (m, 1H), 7.45−7.58 (m, 7H), 7.72−7.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 32.2, 38.2, 104.9 (d, J = 120.1 Hz), 111.0, 120.9, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1, 133.4 (d, J = 108.2 Hz), 154.1 (d, J = 11.7 Hz), 171.2 (d, J = 18.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.7; LC/MS m/z 387 $[M + 1]^+$; HRMS (ESI) calcd for $C_{25}H_{24}O_2P$ $[M + H]^+$ 387.1514, found 387.1514. Anal. Calcd for $C_{25}H_{23}O_2P$: C, 77.70; H, 6.00. Found: C, 77.85; H, 5.93.

Compound ***61***. This product was synthesized from the allene **51** (0.10 g, 0.2 mmol). It was isolated by using an ethyl acetate/hexane (7/3) mixture as the eluent: yield 0.09 g (90%); mp 150−152 °C (white solid); IR (KBr, cm^{-1}) 2926, 1551, 1454, 1314, 1256, 1179, 1119, 1042; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10−1.26 (m, 3H), 1.65−1.74 (m, 7H), 2.92−2.98 (m, 1H), 6.84 (d, J = 7.6 Hz, 1H), 7.00−7.03 (m, 1H), 7.20−7.23 (m, 1H), 7.46−7.59 (m, 7H), 7.73−7.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 25.9, 31.2, 37.2, 104.2 (d, J = 119.9 Hz), 110.9, 121.3, 123.2, 124.0, 128.6, 128.7, 131.7, 131.8, 132.1 (d, J = 2.6 Hz), 133.4 (d, J = 108.1 Hz), 154.0 (d, J = 11.5 Hz), 171.4 (d, J = 19.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.2; LC/MS m/z 401 $[M + 1]^+$; HRMS (ESI) calcd for $C_{26}H_{26}O_2P$ $[M + H]^+$ 401.1670, found 401.1670. Anal. Calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 78.12; H, 6.21. This compound was crystallized from dichloromethane/hexane (9/1) at 25 °C. An X-ray structure was determined for this sample.

(vii). Formation of 3,4-Disubstituted Isochromenes 62−65 and Halobenzyl Products 66 and 67 from MOM-Protected Allenes 52−55. *(a). Synthesis of 3,4-Disubstituted Isochromenes* ***62−65***. To a solution of allene **52** (0.30 g, 0.77 mmol) in MeOH (2 mL) was added $ZrCl_4$ (0.09 g, 0.38 mmol), and the contents were heated under reflux for 6 h. Water (10 mL) was added after completion of the reaction. Then EtOAc (10 mL) was added, the phases were separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with saturated aqueous NaCl. After drying over Na_2SO_4, the solvent was removed in vacuo. The product **62** was purified by column chromatography (silica gel; ethyl acetate/hexane 4/1). Compounds **63−65** were also prepared similarly.

Compound ***62***. Yield 0.24 g (90%, gummy solid); IR (neat, cm^{-1}) 2926, 1588, 1561, 1487, 1437, 1265, 1159, 1049; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (d, J = 1.2 Hz, 3H), 5.08 (s, 2H), 6.96−6.97 (m, 2H), 7.07−7.09 (m, 2H), 7.41−7.52 (m, 6H), 7.78−7.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 69.3, 104.9 (d, J = 113.9 Hz), 123.9, 124.4 (d, J = 3.5 Hz), 125.9, 127.0 (d, J = 7.3 Hz), 127.9, 128.6, 128.8, 130.7 (d, J = 7.6 Hz), 131.5, 131.6, 134.6 (d, J = 105.7 Hz), 168.8 (d, J = 17.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.5; LC/MS m/z 347 $[M + 1]^+$; HRMS (ESI) calcd for $C_{22}H_{20}O_2P$ $[M + H]^+$ 347.1201, found 347.1201. Anal. Calcd for $C_{22}H_{19}O_2P$: C, 76.29; H, 5.53. Found: C, 76.41; H, 5.58.

Compound ***63***. This product was synthesized from the allene **53** (0.25 g, 0.6 mmol): yield 0.21 g (92%); mp 162−164 °C (white solid); IR (KBr, cm^{-1}) 2971, 1588, 1483, 1437, 1223, 1161, 1117; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, J = 6.4 Hz, 6H), 3.05−3.12 (m, 1H), 5.03 (s, 2H), 6.91−6.96 (m, 2H), 7.06−7.07 (m, 2H), 7.41−7.49 (m, 6H), 7.77−7.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 32.8 (d, J = 2.9 Hz), 69.5, 103.6 (d, J = 114.3 Hz), 123.8, 124.9 (d, J = 3.8 Hz), 125.7, 127.6 (d, J = 7.3 Hz), 127.7, 128.5, 128.6, 131.2 (d, J = 8.0 Hz), 131.4 (d, J = 2.5 Hz), 131.6, 131.7, 135.1 (d, J = 105.3 Hz), 176.5 (d, J = 17.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.7; LC/MS m/z 375 $[M + 1]^+$; HRMS (ESI) calcd for $C_{24}H_{23}O_2PNa$ $[M + Na]^+$ 397.1333, found 397.1334. Anal. Calcd for $C_{24}H_{23}O_2P$: C, 76.99; H, 6.19. Found: C, 76.85; H, 6.23. This compound was crystallized from dichloromethane/hexane (9/1) at 25 °C. An X-ray structure was determined for this sample.

Compound ***64***. This product was synthesized from the allene **54** (0.57 g, 1.3 mmol): yield 0.43 g (84%); mp 152−154 °C (white solid); IR (KBr, cm^{-1}) 2951, 1582, 1553, 1437, 1267, 1175, 1047; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30−1.31 and 1.53−1.58 (2 m, 8H), 3.02−3.09 (m, 1H), 5.03 (s, 2H), 6.95−7.01 (m, 2H), 7.07−7.08 (m, 2H), 7.40−7.49 (m, 6H), 7.77−7.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 31.2, 43.8 (d, J = 3.3 Hz), 69.6, 104.4 (d, J = 114.8 Hz), 123.8, 124.8 (d, J = 3.9 Hz), 125.7, 127.5 (d, J = 7.2 Hz), 127.8, 128.5, 128.6, 131.3 (d, J = 7.8 Hz), 131.4 (d, J = 2.6 Hz), 131.6, 131.7, 135.2 (d, J = 105.3 Hz), 175.0 (d, J = 17.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.8; LC/MS m/z 401 $[M + 1]^+$; HRMS (ESI) calcd for $C_{26}H_{26}O_2P$ $[M + H]^+$ 401.1670, found 401.1670.Anal. Calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 77.85; H, 6.22.

Compound ***65***. This product was synthesized from the allene **55** (0.26 g, 0.6 mmol): yield 0.21 g (87%); mp 164−166 °C (white solid); IR (KBr, cm^{-1}) 2928, 1547, 1437, 1273, 1175, 1049; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71−0.76 and 1.01−1.04 (2 m, 3H), 1.31−1.53 (m, 7H), 2.49−2.55 (m, 1H), 5.00 (s, 2H), 6.97−7.14 (m, 4H), 7.41−7.50 (m, 6H), 7.79−7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 25.7, 29.8, 42.7, 69.3, 103.8 (d, J = 114.7 Hz), 123.8, 125.1, 125.7, 127.6 (d, J = 7.1 Hz), 127.8, 128.5, 128.6, 131.1 (d, J = 7.4 Hz), 131.4, 131.6, 131.7, 135.3 (d, J = 105.0 Hz), 174.9 (d, J = 18.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8; LC/MS m/z 415 $[M + 1]^+$; HRMS (ESI) calcd for $C_{27}H_{28}O_2P$ $[M + H]^+$ 415.1827, found 415.1827. Anal. Calcd for $C_{27}H_{27}O_2P$: C, 78.24; H, 6.57. Found: C, 78.15; H, 6.63.

(b). Synthesis of Halobenzyl Products ***66*** *and* ***67*** *from MOM-Protected Allene* ***53***. To a solution of allene **53** (0.20 g, 0.48 mmol) in EtOAc (2 mL) was added 35% hydrochloric acid (1 mL), and the contents were heated under reflux for 6 h. Water (10 mL) was added after completion of the reaction (TLC). Then EtOAc (10 mL) was added, the phases were separated, and the aqueous layer was extracted with EtOAc. The organic layers were combined and washed with saturated aqueous NaCl. After drying over Na_2SO_4, the solvent was removed by using a rotary evaporator. The product **66** was purified by column chromatography (silica gel; ethyl acetate/hexane 2/3). Compound **67** was also prepared similarly.

Compound ***66***. Yield 0.17 g (88%); mp 148−150 °C (white solid); IR (KBr, cm^{-1}) 3241, 2976, 1609, 1439, 1225, 1161, 1117; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 and 1.70 (2 s, 6H), 3.70 and 4.07 (2 d, J =

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11.5 Hz, 2H), 6.82−6.91 (m, 2H), 7.07−7.26 (m, 7H), 7.39−7.43 (m, 1H), 7.51−7.62 (m, 3H), 7.86−7.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 31.2, 43.6, 71.0, 127.3 (d, J = 89.6 Hz), 127.6, 127.7, 128.0, 128.3 (d, J = 1.5 Hz), 128.5 (d, J = 106.5 Hz), 128.6, 128.7, 130.1 (d, J = 2.5 Hz), 130.4, 131.9, 132.3, 132.4, 132.5, 132.8, 132.9, 136.7$_9$, 136.8$_2$, 138.7 (d, J = 11.8 Hz), 163.2 (d, J = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; LC/MS m/z 411 $[M + 1]^+$, 413 $[M + 3]^+$; HRMS (ESI) calcd for $C_{24}H_{24}ClO_2PNa$ $[M + Na]^+$ 433.1100, found 433.1100. Anal. Calcd for $C_{24}H_{24}ClO_2P$: C, 70.16; H, 5.89. Found: C, 70.25; H, 5.81. This compound was crystallized from dichloromethane/hexane (9/1) at 25 °C. An X-ray structure was determined for this sample.

Compound **67**. This product was synthesized from the allene **53** (0.20 g, 0.48 mmol) and concentrated HBr (1 mL): yield 0.19 g (85%); mp 170−172 °C (white solid); IR (KBr, cm^{-1}) 3262, 2926, 1605, 1437, 1225, 1163, 1117; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 and 1.71 (2 s, 6H), 3.63 and 3.91 (2 d, $J \approx$ 9.8 Hz, 2H), 6.79−6.81 (m, 1H), 6.88−7.24 (m, 9H), 7.37−7.60 (m, 4H), 7.84−7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 31.2, 31.3, 71.1 (d, J = 4.5 Hz), 127.3 (d, J = 89.7 Hz), 127.5, 127.7, 128.1, 128.4, 128.6, 128.7, 129.1, 130.3, 130.8, 131.7, 131.9, 132.4 (d, J = 7.8 Hz), 132.5, 132.8 (d, J = 8.5 Hz), 137.0, 138.6 (d, J = 11.6 Hz), 162.7 (d, J = 5.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3; LC/MS m/z 455 $[M + 1]^+$, 457 $[M + 3]^+$; HRMS (ESI) calcd for $C_{24}H_{25}BrO_2P$ $[M + H]^+$ 455.0775, found 455.0778. Anal. Calcd for $C_{24}H_{24}BrO_2P$: C, 63.31; H, 5.31. Found: C, 63.21; H, 5.39.

X-ray Data. X-ray data for compounds **26**, **38**, **46**, **61**, **63**, and **66** were collected using Mo Kα (λ = 0.710 73 Å) radiation. The structures were solved and refined by standard methods.[17] The CCDC numbers are CCDC 871308−871313.

Crystal Data. **26**: $C_{22}H_{27}O_7P$, M = 434.41, monoclinic, space group $P2_1/c$, a = 13.0951(10) Å, b = 9.4194(7) Å, c = 20.0552(12) Å, β = 117.713(4)°, V = 2190.0(3) Å^3, Z = 4, μ = 0.166 mm^{-1}, 3836/0/276 data/restraints/parameters, R indices ($I > 2\sigma(I)$) R1 = 0.0498 and wR2 (all data) = 0.1268, CCDC No. 871308.

38: $C_{24}H_{21}O_2P$, M = 372.38, monoclinic, space group $P2_1/c$, a = 6.6332(6) Å, b = 19.8814(18) Å, c = 15.5910(14) Å, β = 105.794(8)°, V = 1978.5(3) Å^3, Z = 4, μ = 0.154 mm^{-1}, 3465/0/246 data/restraints/parameters, R indices ($I > 2\sigma(I)$) R1 = 0.0518 and wR2 (all data) = 0.1307, CCDC No. 871309.

46: $C_{21}H_{17}O_2P$, M = 332.32, monoclinic, space group $P2_1/c$, a = 12.678(2) Å, b = 17.397(3) Å, c = 17.716(5) Å, β = 114.278(18)°, V = 3561.9(13) Å^3, Z = 8, μ = 0.163 mm^{-1}, 5114/0/439 data/restraints/parameters, R indices ($I > 2\sigma(I)$) R1 = 0.0426 and wR2 (all data) = 0.0916, CCDC No. 871310.

61: $C_{26}H_{25}O_2P$, M = 400.43, triclinic, space group $P\bar{1}$, a = 9.892(3) Å, b = 11.884(4) Å, c = 18.630(6) Å, α = 97.442(5)°, β = 98.266(6)°, γ = 90.151(5)°, V = 2148.6(12) Å^3, Z = 4, μ = 0.147 mm^{-1}, 7550/0/523 data/restraints/parameters, R indices ($I > 2\sigma(I)$): R1 = 0.0674, $wR2$ (all data) = 0.1789. CCDC no. 871311.

63: $C_{24}H_{23}O_2P$, M = 374.39, Monoclinic, Space group $P2(1)/c$, a = 11.4961(7), b = 14.8975(11), c = 16.1208(12) Å, β = 132.778(4)°, V = 2026.5(2) Å^3, Z = 4, μ = 0.151 mm^{-1}, data/restraints/parameters: 3525/0/246, R indices ($I > 2\sigma(I)$) R1 = 0.0584 and wR2 (all data) = 0.1145, CCDC No. 871312.

66: $C_{24}H_{24}ClO_2P$, M = 410.85, orthorhombic, space group $Pna2_1$, a = 17.5578(8) Å, b = 8.6412(4) Å, c = 28.8289(17) Å, V = 4373.9(4) Å^3, Z = 8, μ = 0.264 mm^{-1}, 4599/0/509 data/restraints/parameters, R indices ($I > 2\sigma(I)$) R1 = 0.0397 and wR2 (all data) = 0.0893, CCDC No. 871313.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and CIF files giving ORTEP drawings, copies of ^{1}H/^{13}C NMR spectra of all new products, and crystal data for **26**, **38**, **46**, **61**, **63**, and **66**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+91)-40-23012460. E-mail: kckssc@yahoo.com; kckssc@uohyd.ernet.in.

Notes

The authors declare no competing financial interest.

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