Vinylphosphonium Salts and Allenes from Carbonyl Compounds Using Titanium-Substituted Ylides

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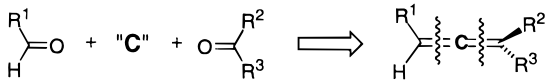
(*E*)-Vinylphosphonium salts are conveniently obtained from the reaction of carbonyl compounds with titanium-substituted ylide species $(Me_2N)_3P{=}CHTi(OiPr)Cl_2$ or $(Me_2N)_3P{=}CHTi(OiPr)_2Cl$. While a wide variety of nonenolizable aldehydes are tolerated, the steric bulk surrounding the ylide carbon limits the process to highly activated or unhindered ketones. The vinylphosphonium salts may be converted to allenes by deprotonation and condensation with a second aldehyde, thus accomplishing a two-step double olefination allene synthesis. This methodology, along with a previously reported one-pot reaction, comprises the most convenient route available for the synthesis of 1,3-disubstituted allenes. The metal-substituted ylide reagent may be generated *in situ* from commercially-available starting materials. Two representative vinylphosphonium salts were shown to undergo reversible isomerization to the (*Z*)-form upon irradiation.

We have previously reported the discovery of a one-pot procedure for the preparation of symmetric 1,3-diarylallenes by "double olefination" of aryl aldehydes using a metalated phosphorus methylide reagent prepared *in situ*.[1] The method is a simple and convenient realization of a modular strategy for allene synthesis from readily-available carbonyl and ylide starting materials (Scheme 1).[2,3] We now describe a modification of the original procedure and the first broad investigation of an allene-producing olefination process,[4] allowing for the straightforward preparation of a new class of vinylphosphonium compounds and for the coupling of two different carbonyl substrates to give mixed allenes.

Although not a common structural motif, allenes have attracted interest as intermediates in a variety of synthetic processes[5] and as components of various natural products.[5a,6] Most recently, allenes have emerged as

Scheme 1



reactive intermediates in the radical cyclization of the antitumor natural product neocarzinostatin and related compounds. Numerous syntheses of allenic neocarzinostatin analogues, and studies of their reactivity have appeared in the literature.[7,8] The majority of allene syntheses involve the rearrangement of bonds in an existing three-carbon skeleton, as in the dehydrohalogenation of vinylic halides, addition/elimination sequences with propargylic compounds, and reductive eliminations of halogenated cyclopropanes.[5a,b] The "triply-convergent" methodology described here offers the advantages of retrosynthetic simplicity and readily available starting materials.

A variety of methods are known for the synthesis of vinylphosphonium compounds, most of which also utilize an appropriately substituted carbon skeleton, such as an alkene or alkyne.[9] The most powerful of these is the efficient Pd-catalyzed preparation of Ph_3P-substituted vinylphosphonium compounds from vinyl triflates and PPh_3, developed by Stang and co-workers.[10] The olefi-

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(1) Reynolds, K. A.; Dopico, P. G.; Sundermann, M. J.; Hughes, K. A.; Finn, M. G. *J. Org. Chem.* **1993**, *58*, 1298−1299.

(2) Another "triply convergent" allene synthesis has been developed, comprising a three-step procedure involving thermal decarboxylation of α-alkylyidene-*β*-lactones: Danheiser, R. L.; Choi, Y. M.; Menichincheri, M.; Stoner, E. J. *J. Org. Chem.* **1993**, *58*, 322−327.

(3) The majority of allene syntheses involve the rearrangement of bonds in an existing three-carbon skeleton [see reference 5a,b]. Common examples include the dehydrohalogenation or reductive elimination of vinylic halides, and addition/elimination reactions of acetylenes (Pasto, D. J.; Shults, R. H.; McGrath, J. A.; Waterhouse, A. *J. Org. Chem.* **1978**, *43*, 1382−1384. Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shults, R. H.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1385−1388. Pasto, D. J.; Chou, S.-K.; Fritzer, E.; Shults, W.; Hennion, G. F. *J. Org. Chem.* **1978**, *43*, 1389−1394). Other methods include elimination of silyl groups (Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 171−174) and reductive eliminations of halogenated cyclopropanes (Binger, P. *Synthesis* **1974**, 190−192).

(4) Olefination syntheses of allenes not cited in reference 1: (a) Cumulenic phosphorane + aldehyde: Bestmann, H. J.; Schmid, G. *Tetrahedron Lett.* **1975**, 4025−4026. (b) Phosphorus methylide + 1,1-dibromoalkenes or 1-bromoalkynes: Bestmann, H. J.; Frey, H. *Synthesis* **1984**, 243. (c) Horner−Emmons-type olefination of aldehydes: Marszak, B.; Simalty, M.; Seuleiman, A. *Tetrahedron Lett.* **1974**, 1905−1908. (d) Diethylphosphonate anion alkylation of an acyl halide: Zimmerman, H. E.; Baker, M. R.; Bottner, R. C.; Morrissey, M. M.; Murphy, S. *J. Am. Chem. Soc.* **1993**, *115*, 459−466. (e) Double olefination of CO_2 with a tantalum alkylidene complex: Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399−5400. (f) Olefination of a ketene: Meyer, J.; Wittig, G.; Scholkopf, U. *Chem. Ber.* **1956**, *89*, 842. (g) Using an intermediate titanium vinylidene: Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490−5491. (h) The combination of Peterson- and Wittig-type olefination processes for the synthesis of allenes was suggested in: Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264−3268. (i) Matteson, D. S.; Majumdar, D. *Organometallics* **1983**, *2*, 230−236.

(5) (a) Schuster, H.; Coppola, G. *Allenes in Organic Synthesis;* John Wiley and Sons, Inc.: New York, 1984. (b) Patai, S., Ed. *The Chemistry of Ketenes, Allenes, and Related Compounds, Parts 1 and 2*; Wiley-Interscience: Chichester, 1980. (c) Pasto, J. D. *Tetrahedron* **1984**, *40*, 2805−2827. (d) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450−3451. (e) Okamura, W. H.; Aurrecechea, J. M.; Gibbs, R. A.; Norman, A. W. *J. Org. Chem.* **1989**, *54*, 4072−4083. (f) Corey, E. J.; De, B. *J. Am. Chem. Soc.* **1984**, *106*, 2735−2736. (g) Fox, D. N. A.; Lathbury, D.; Mahon, M. F.; Molloy, K. C.; Gallagher, T. *J. Am. Chem. Soc.* **1991**, *113*, 2652−2656.

(6) (a) Celmer, W. D.; Solomons, I. A. *J. Am. Chem. Soc.* **1952**, *74*, 2245−2248. (b) Bu'Lock, J. D.; Jones, E. R. H.; Leeming, P. R.; Thompson, J. M. *J. Chem. Soc.* **1956**, 3767−3771. (c) Landor, P. D.; Landor, S. R.; Mukasa, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1638−1639. (d) Meinwald, J.; Erikson, K. l.; Hartshorn, M.; Meinwald, Y. C.; Eisner, T. *Tetrahedron Lett.* **1968**, 2959−2962. (e) Meinwald, J.; Hendry, L. *Tetrahedron Lett.* **1969**, 1657−1660. (f) Bagby, M. O.; Smith, C. R., Jr.; Wolff, I. A. *J. Org. Chem.* **1965**, *30*, 4227−4229. (h) Landor, S. R.; Punja, N. *Tetrahedron Lett.* **1966**, 4905−4907.

(7) Nicolau, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387−1416 and references therein.

(8) (a) Myers, A. G.; Dragovich, P. S. *J. Am. Chem. Soc.* **1993**, *115*, 7021. (b) Myers, A. G.; Cohen, S. B.; Kwon, B.-M. *J. Am. Chem. Soc.* **1994**, *116*, 1670−1682. (c) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057−8059. (d) Myers, A. G.; Finney, N. S.; Kuo, E. Y. *Tetrahedron Lett.* **1989**, *30*, 5747−5750.

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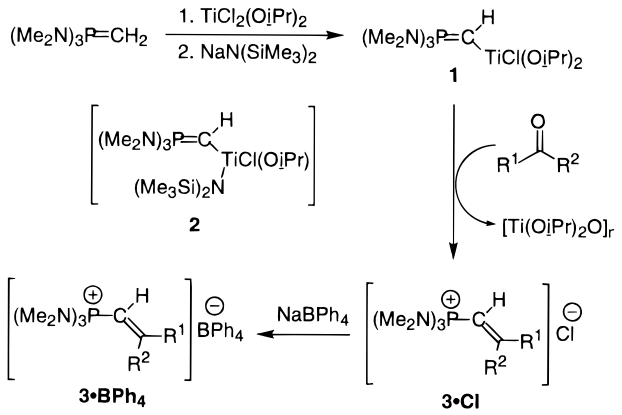
Scheme 2

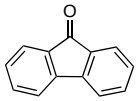


nation methodology presented here is notable for its convenience, *E*-stereoselectivity, and the variety of aldehydes for which it is applicable.

Results and Discussion

Synthesis of Vinylphosphonium Salts. Vinylphosphonium salts are produced as stable, isolable products of the reactions of titanium-substituted methylides with nonenolizable aldehydes. Thus, a 1:1 adduct of $(Me_2N)_3P{=}CH_2$[11] with either $TiCl_3O$*i*Pr or $TiCl_2(O$*i*$Pr)_2$ in THF[12] may be treated with with $NaN(SiMe_3)_2$ and aromatic aldehyde to afford (*E*)-vinylphosphonium salts **3** (Scheme 2). We have found that the reagent derived from $TiCl_2(O$*i*$Pr)_2$ is superior for both the direct synthesis of symmetric 1,3-diarylallenes by the original one-pot method[1] and for the synthesis of vinylphosphonium salts by the following procedure (method A, Experimental Section). A THF solution of $TiCl_2(O$*i*$Pr)_2$ is treated with 1.0 equiv of $(Me_2N)_3P{=}CH_2$, followed immediately by 1.0 equiv of $NaN(SiMe_3)_2$ to generate the Ti-substituted ylide species **1**.[13] Complex **1** is analogous to the previously-described[1] **2** prepared from $TiCl_3O$*i*Pr and shows similar multinuclear NMR resonances.[14] Addition of 1.0−1.5 equiv of aldehyde provides vinylphosphonium chlorides **3**•Cl, which usually precipitate from solution. Occasionally, products are contaminated with trace amounts (≤2%) of $[(Me_2N)_3PCH_3]I$, except as noted below. Filtration and reprecipitation from water as the BPh_4^- salts give spectroscopically—and often analytically—pure samples in nonoptimized yields shown in Table 1. Certain vinylphosphonium tetraphenylborates were further purified for microanalysis by column chromatography on silica gel. Vinylphosphonium compounds **3** are the first to be reported that bear a tris(dialkylamido)phosphorus substituent and are formed predominantly as the *E*-isomers; traces (≤5%) of what are tentatively identified as the the *Z*-isomers are occasionally observed. For a discussion of the mechanism of this process, see the accompanying paper.

Table 1. Isolated Yields of Vinylphosphonium Salts 3·BPh_4 (Scheme 2)

entry	compound	R^1	R^2	yield (%)	method
1	**3a**	4-Me-C_6H_4	H	68−78	A, B
2	**3b**	3-Me-C_6H_4	H	71	B
3	**3c**	2-Me-C_6H_4	H	66	B
4	**3d**	2,4,6-Me_3-C_6H_2	H	39	A
5	**3e**	4-OMe-C_6H_4	H	71	A
6	**3f**	3,4,5-$(OMe)_3$-C_6H_2	H	66	B
7	**3g**	2,3,4-$(OMe)_3$-C_6H_2	H	49	B
8	**3h**	2,4,6-$(OMe)_3$-C_6H_2	H	45	B
9	**3i**	4-NMe_2-C_6H_4	H	54	B
10	**3j**	4-Cl-C_6H_4	H	40	B
11	**3k**	3-F-C_6H_4	H	58	A
12	**3l**	4-NO_2-C_6H_4	H	36	B
13	**3m**	2-furyl	H	55	B
14	**3n**	1-naphthyl	H	66	A
15	**3o**	2-naphthyl	H	68	B
16	**3p**	9-phenanthryl	H	51	A
17	**3q**	*trans*-cinnamyl	H	46	B
18	**3r**	ferrocenyl	H	60	B
19	**3s**	3-pyridyl	H	45	B
20	**3t**	*tert*-butyl	H	43	B
21	**3u**	cyclohexyl	H	48	A
22	**3v**	cyclopropyl	H	22	A
23	**3w**	Ph	CF_3	43	B
24	**3x**			51	A

A wide variety of aromatic aldehydes may be converted to vinylphosphonium salts, including those bearing electron-donating (**3e**−**i**) and electron-withdrawing (**3j**−**l**) substituents, those with extended conjugation (**3m**−**q**), and ferrocenyl (**3r**) and pyridyl (**3s**) substrates. Some of these are not converted to allenes by the original one-pot double olefination procedure. Ketones are generally unreactive (*vide infra*), but examples in which the carbonyl is strongly activated (**3w**) or relatively unhindered (**3x**) are reported. Three nonaromatic cases are also included: vinylphosphonium salts derived from pivalaldehyde (**3t**), cyclohexanecarboxaldehyde (**3u**), and cyclopropanecarboxaldehyde (**3v**).[15] Compounds **3t** and **3x** were characterized by X-ray crystallography, as discussed in the Experimental Section.

It is important to note that vinylphosphonium salts may also be obtained directly from $[(Me_2N)_3PCH_3]I$,

(9) (a) Phosphines and activated vinyl halides: Pattenden, G.; Walker, B. J. *J. Chem. Soc. (C)* **1969**, 531−535. (b) Base-catalyzed rearrangements of terminal allylphosphonium salts: McIntosh, J. M.; Goodbrand, H. B.; Masse, G. M. *J. Org. Chem.* **1974**, *39*, 202−206. (c) From alkenes via thioalkylphosphonium intermediates: Okuma, K.; Koike, T.; Yamamoto, S.; Takeuchi, H.; Yonekura, K.; Ono, M.; Ohta, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2375−2380. (d) Addition to alkynylphosphonium salts: Schweizer, E. E.; Goff, S. D.; Murray, W. P. *J. Org. Chem.* **1977**, *42*, 200−205. (e) Stoichiometric reaction of $ClRh(PPh_3)_3$ with α,β-unsaturated acid chlorides: Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478−1485. (f) Silyl-substituted ylide with cinnamaldehyde: Plénat, F. *Tetrahedron Lett.* **1981**, *22*, 4705−4708.

(10) Hinkle, R. J.; Stang, P. J.; Kowalski, M. H. *J. Org. Chem.* **1990**, *55*, 5033−5036.

(11) Issleib, V. K.; Lischewski, M. *J. Prakt. Chem.* **1970**, *312*, 135−144. See Experimental Section for a modified synthetic procedure.

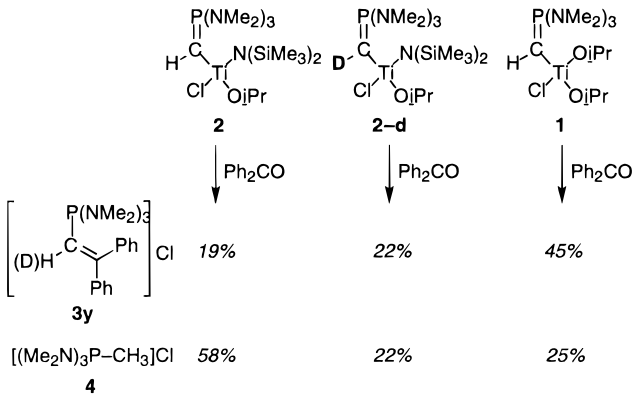
(12) The structure and properties of the adduct $(Me_2N)_3P{=}CH_2{\cdot}TiCl_3O_iPr$ are discussed in the accompanying paper.

(13) Titanium-substituted ylides: (a) (X-ray of $Cp_2Zr(C_l)(CHPPh_3)$, showing Zr−Cl and C−H in coplanar orientation): Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. Z. *Naturforsch. Teil B* **1980**, *35*, 1289−1297. (b) Schmidbaur, H.; Pichl, R.; Müller, G. *Chem. Ber.* **1987**, *120*, 39−44. (c) Schmidbaur, H.; Pichl, R.; Muller, G. *Chem. Ber.* **1987**, *120*, 789−794. (d) Schmidbaur, H.; Pichl, R. *Z. Naturforsch.* **1985**, *B40*, 352−356.

(14) Reynolds, K. A.; Finn, M. G., subsequent paper in this issue.

(15) Note that cyclohexanecarboxaldehyde is efficiently converted to a 1,3-diene in the one-pot procedure.[1]

Scheme 3



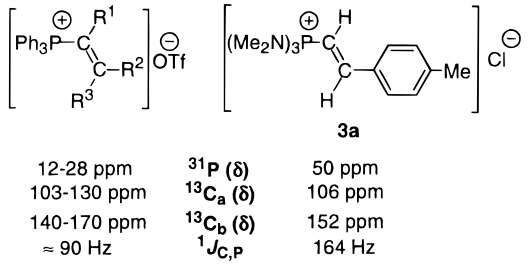
which is prepared in high yield from $P(NMe_2)_3$ and CH_3I and may be stored indefinitely. Thus, $(Me_2N)_3P{=}CH_2$ generated *in situ* from methylphosphonium salt and 1 equiv of $NaN(SiMe_3)_2$ may be used in exactly the same way as isolated methylide.[14] For added convenience in the performance of large numbers of reactions, we routinely prepare $(Me_2N)_3P{=}CH_2$ on a multigram scale, but the air-stable methylphosphonium compound has obvious advantages as an occasional starting material.

Ti-substituted ylide species **1** and **2** decompose at room temperature in the absence of carbonyl substrate to give substantial quantities of methylphosphonium compound $[(Me_2N)_3PCH_3]Cl$, **4**. Therefore, vinylphosphonium salts derived from carbonyl substrates that undergo slow reaction are usually contaminated with **4**. For example, **2** reacts slowly (24 h) with benzophenone to afford methylphosphonium salt **4** as the major product, as shown in Scheme 3.[16] The product ratio is the same in the presence of activated, powdered 3 Å molecular sieves, and thus the decomposition process appears unlikely to be due to water. The ratio of vinyl- to methylphosphonium salts is also the same when $TiCl_3(O\mathit{t}Bu)$ is substituted for $TiCl_3(O\mathit{i}Pr)$, indicating that the isopropyl group does not supply protons for the decomposition reaction. When $(Me_2N)_3P{=}CD_2$ is substituted for $(Me_2N)_3P{=}CH_2$, to give **2d** as an intermediate, the yield of methylphosphonium salt is diminished, but the production of vinylphosphonium product is unchanged. This suggests that decomposition involves self-consumption of ylide-bound protons, but the mechanism is unknown. Most importantly, the yield of vinylphosphonium **3y** from benzophenone is increased when $TiCl_2(O\mathit{i}Pr)_2$ is used, demonstrating the diminished steric demand of ylide **1** relative to **2**. This is also illustrated by the case of 2,4,6-trimethylbenzaldehyde, which gives a 1:2.5 ratio of methyl- to vinylphosphonium products from the reaction involving $TiCl_3O\mathit{i}Pr$, whereas the vinylphosphonium species **3d** is the sole identifiable product when $TiCl_2(O\mathit{i}Pr)_2$ is employed (Table 1, entry 4).

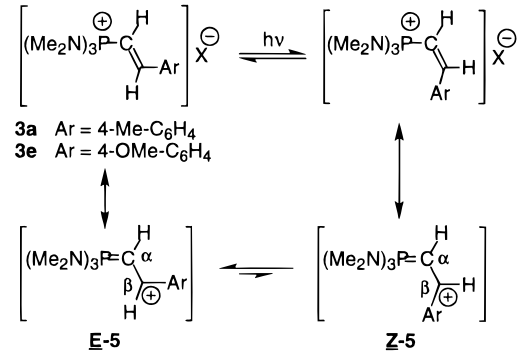
Spectroscopic Properties and Photoisomerization of Vinylphosphonium Salts. A comparison of NMR properties of a representative $(Me_2N)_3P$-bearing vinylphosphonium salt (**3a**·Cl) with a series of Ph_3P-bearing examples[10] is shown in Scheme 4. Of note are the differences in ^{31}P chemical shifts and $^1J_{CP}$ coupling constant.[17]

Irradiation of vinylphosphonium salts **3a**·BPh_4 in CD_3CN, **3a**·Cl in D_2O, or **3e**·Cl in D_2O results in the clean

Scheme 4



Scheme 5



appearance of a new set of NMR resonances in each case, which is assigned to the *Z*-vinylphosphonium isomer on the basis of coupling constants (Scheme 5). A ratio of approximately 2:1 *E*:*Z* is reached in each case at room temperature after 2−4 h; additional irradiation induces decomposition. To our knowledge, such a photoisomerization processes has not been previously reported for vinylphosphonium compounds. Interestingly, (*Z*)-**3a** converts completely back to the *E*-isomer upon standing in the dark at room temperature for 8−12 h, but only a small amount of isomerization is noted over a similar time at −10 °C. The contribution of resonance forms **5** would provide a means for such a rotation about the C_α−C_β bond.[18]

While the focus of our work has been on the synthesis of allenes (*vide infra*), vinylphosphonium compounds have been used in a variety of other transformations, including cycloadditions, the synthesis of functionalized alkenes, and the synthesis of various heterocyclic compounds.[19,9b] With the exception of one (undesired)

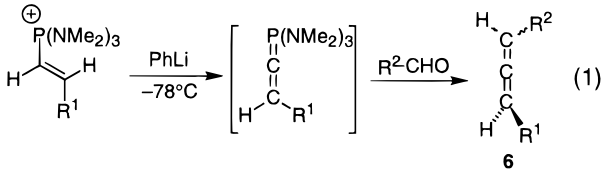
(16) Phosphonium compounds **4** and **3y** were separated on a short silica gel chromatography column.

(17) Both trends (downfield chemical shift and larger $^1J_{C,P}$) appear to be characteristic of the $(Me_2N)_3$ substituent: for example, $Ph_3P{=}CH_2$ shows ^{31}P NMR δ 19.6 (Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823−2831) and $^1J_{PC}$ 51.9 Hz (Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 940−942), whereas for $(Me_2N)_3P{=}CH_2$, ^{31}P NMR δ 70, and $^1J_{PC}$ 175 Hz. See also the subsequent paper in this issue.

(18) Similar resonance forms have been invoked to explain NMR chemical shifts in vinylphosphonium salts: reference 10, and Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 2946−2950.

(19) (a) See citations 1−14 in reference 10. (b) Zbiral, E. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: London, 1979; pp 250−266 and references therein. (c) Schweizer, E. E., Smucker, L. D.; Votral, R. J. *J. Org. Chem.* **1966**, *31*, 467−471. (d) Schweizer, E. E.; Light, K. *J. Org. Chem.* **1966**, *31*, 2912−2915. (e) Schweizer, E. E.; Smucker, L. D. *J. Org. Chem.* **1967**, *31*, 3146−3149. (f) Schweizer, E. E.; Liehr, J. G. *J. Org. Chem.* **1968**, *33*, 583−584. (g) Schweizer, E. E.; Kopay, C. M. *J. Org. Chem.* **1972**, *37*, 1561−1564. (h) Schweizer, E. E.; De Voe, S. V. *J. Org. Chem.* **1975**, *40*, 144−145. (i) Posner, G. H.; Lu, S.-B. *J. Am. Chem. Soc.* **1985**, *107*, 1424−1426. (j) Büchi, G.; Pawlak, M. *J. Org. Chem.* **1975**, *40*, 100−102. (k) Brückner, R.; Scheuplein, S. W. *Chem. Ber.* **1991**, *124*, 1871−1874. (l) White, J. D.; Jensen, M. S. *Tetrahedron Lett.* **1992**, *33*, 577−580. (m) White, J. D.; Kawasaki, M. *J. Am. Chem. Soc.* **1990**, *112*, 4991−4993.

Table 2. Isolated Yields of Allenes 6 from Vinylphosphonium Salts 3·BPh_4 and Aldehydes (eq 1)



entry	compound	R^1	R^2	yield (%)
1	**6a**	4-Me-C_6H_4	4-Me-C_6H_4	94
2	**6b**	4-Me-C_6H_4	2,4,6-Me_3-C_6H_2	89
3	**6c**	4-Me-C_6H_4	4-OMe-C_6H_4	80
4	**6d**	4-Me-C_6H_4	2,3,4-$(OMe)_3$-C_6H_2	64
5	**6e**	4-Me-C_6H_4	3,4,5-$(OMe)_3$-C_6H_2	39
6	**6f**	4-Me-C_6H_4	4-Cl-C_6H_4	62
7	**6g**	4-Me-C_6H_4	3-F-C_6H_4	78
8	**6h**	4-Me-C_6H_4	2-furyl	38
9	**6i**	4-Me-C_6H_4	ferrocenyl	25
10	**6j**	4-Me-C_6H_4	9-phenanthenryl	20
11	**6k**	4-Me-C_6H_4	0.5 equiv of 1,4-$(CHO)_2$-C_6H_4	37
12	**6l**	4-Me-C_6H_4	*tert*-Bu	18
13	**6m**	4-Me-C_6H_4	3-pyridyl	70
14	**6n**	4-Me-C_6H_4	cyclohexyl	21
15	**6o**	4-Me-C_6H_4	cyclopropyl	40
16	**6e**	3,4,5-$(OMe)_3$-C_6H_2	4-Me-C_6H_4	73
17	**6h**	2-furyl	4-Me-C_6H_4	30
18	**6j**	9-phenanthenryl	4-Me-C_6H_4	34
19	**6p**	2-naphthyl	4-Me-C_6H_4	63
20	**6o**	cyclopropyl	4-Me-C_6H_4	13
21	**6f**	4-Cl-C_6H_5	4-Me-C_6H_4	23
22	**6m**	3-pyridyl	4-Me-C_6H_4	52

nucleophilic addition to the β carbon described below, we have not yet explored the use of our dimethylamino-substituted phosphonium salts for similar transformations.

Synthesis of Allenes. Deprotonation of vinylphosphonium salts with phenyllithium at low temperature gives intermediate allenic phosphoranes,[14] which afford allenes cleanly upon the addition of a variety of aromatic aldehydes (eq 1). Vinylphosphonium salt **3a** was used to explore the scope of the process; isolated yields of allenes are shown in Table 2.[20,21] While entries in Table 2 reflect a standard protocol involving the use of 2 equiv of PhLi and 3 equiv of aldehyde, lesser quantities of reagents may often be employed. For example, **3a** may be treated with 1.3 equiv of PhLi at −78 °C for 3 h followed by addition of 1.3 equiv of 4-Me-PhCHO to give a 75% yield of allene **6a**. Details of the optimization of the reaction of **3a**·BPh_4 with PhLi and *p*-tolualdehyde are provided as Supporting Information.[22] The competing reactions to be balanced are the deprotonation of vinylphosphonium salt and the decomposition of its conjugate base. For other, less reactive or more hindered bases, it appears that the deprotonation rate is unacceptably slow. For example, lithium diisopropylamide (LDA) at −78 °C and $NaN(SiMe_3)_2$ at −40 °C also give some allenic phosphorane, but yields of allenes are about half those obtained with PhLi. Interestingly, the use of DMPU (15% in THF) with LDA, a common modification of such processes, completely suppressed the desired allene formation. Sodium hydride, $NaNH_2$, *t*-BuLi, and $(Me_2N)_3P{=}CH_2$ all fail to provide significant quantities of allenes from vinylphosphonium salt **3a** and a large excess of trapping aldehyde. In contrast, the less-hindered *n*-butyllithium acts as a nucleophile instead of a base, attacking the β-carbon of vinylphosphonium **3a**, as described in the Experimental Section.

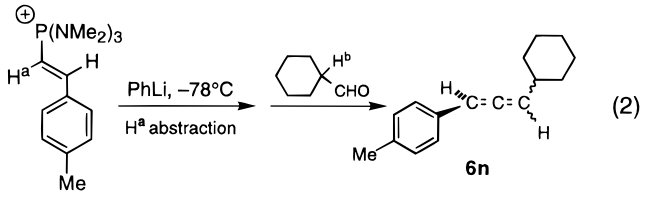
The absence of excess bis(trimethylsilyl)amide base in each of the two "separated" olefination steps eliminates the formation of α-amino alkoxides discussed in the subsequent paper in this issue and allows for the use of electron-deficient aldehydes. When these substrates are incorporated into vinylphosphonium species, the scope is still somewhat limited. For example, deprotonation of the vinylphosphonium salt derived from 4-chlorobenzaldehyde and addition of 4-methylbenzaldehyde provide the corresponding allene **6f** in only 23% yield, and the vinylphosphonium species derived from 4-nitrobenzaldehyde completely fails to produce allene upon analogous treatment. It is possible that the presence of strong electron-withdrawing groups renders the vinylphosphonium salt more prone to side reactions such as nucleophilic addition to the β-carbon and polymerization. More successful is the use of electron-deficient substrates (4-chlorobenzaldehyde, 3-fluorobenzaldehyde, and terephthalaldehyde) as the second, "trapping" carbonyl component.

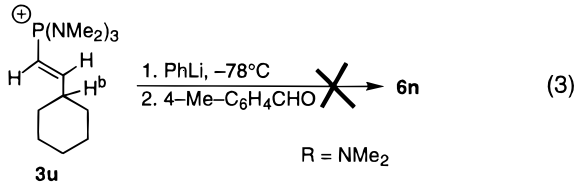
The ability to introduce an allene substituent from either the vinylphosphonium salt or the second, "trapping" aldehyde provides for some useful flexibility in the methodology. For example, the same mixed allene structure may be obtained from both possible routes in yields that are similar (entries 8 *vs* 17; 10 *vs* 18) or quite diverse (entries 13 *vs* 22; 5 *vs* 16; 15 *vs* 20), for reasons which are not entirely clear. Steric hindrance can play an important role, as in the case of vinylphosphonium **3u** derived from pivalaldehyde, which is too hindered to undergo deprotonation by PhLi. However, pivalaldehyde may be used in the second step to afford a modest yield of *t*-butyl-substituted allene (Table 2, entry 12). Acidity can also be an important contributing factor. For example, cyclohexanecarboxaldehyde is an effective trapping agent to produce allene **6n** (entry 14 and eq 2), whereas the converse approach from vinylphosphonium salt **3u** is not effective (eq 3). Under one-pot double-olefination reaction conditions, cyclohexanecarboxyaldehyde is converted to diene in high yield,[1] indicating that $NaN(SiMe_3)_2$ (and presumably PhLi in eq 3) deprotonates vinylphosphonium salt **3u** at H^b to give a vinyl-substituted ylide and thence diene. This suggests that the allenic phosphorane generated from **3a** is significantly less basic than phenyllithium, but it is not clear if this is for thermodynamic or kinetic (steric) reasons. Vinylphosphonium salt **3v**, derived from cyclopropanecarboxaldehyde, is successfully converted to allene **6o** under standard conditions (Table 2, entry 15, and eq 4). We assume this is due to the diminished acidity of H^b in structure **3v**, since the alkylidenecyclopropane moiety thus produced would suffer approximately 13 kcal of additional ring strain.[23] Allene **6o** is also obtained from **3a** and cyclopropanecarboxaldehyde (Table 2, entry 20).

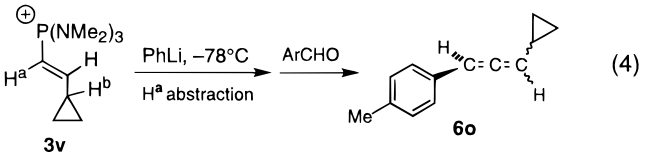
(20) For the production of allenes from allenic phosphoranes, see citations in reference 1 and Bestmann, H. J.; Saalfrank, R. W.; Snyder, J. P. *Chem. Ber.* **1973**, *106*, 2601−2607.

(21) Although the yields reported in Table 2 were obtained using solutions of PhLi obtained from commercial sources, we have subsequently found that yields may be significantly improved when pure PhLi, prepared from bromobenzene and *n*-butyllithium and isolated as a white solid,[26] is used. See Experimental Section.

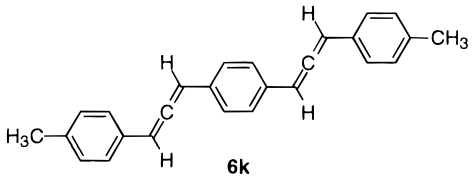
(22) Reactions performed with 1 equiv of PhLi show a marked increase in allene yield as the vinylphosphonium and PhLi are allowed to react for longer periods prior to addition of the trapping aldehyde, reaching a maximum of 70% upon addition of 1 equiv of PhLi at −78 °C for 3.5 h, or at −42 °C for 15 min. Only a trace of allene is formed from a reaction at 0 °C for 3 min.







The diallene **6k** was obtained as an equal mixture of diastereomers. Allene formation from vinylphosphonium salts or aldehydes bearing chiral centers closer to the reactive functionalities does proceed with some diastereoselectivity.[14]



It should be noted that diaryl allenes are not uniformly stable, particularly in ambient light. It appears that electron-donating groups often, but not always, render the compounds less robust, and that allene dimerization by [2 + 2] cycloaddition is at least partly responsible for decomposition. The photochemistry of allenes has been intensively studied.[24] While many of diaryl allene products are stable for long periods, we generally store these compounds in the dark at −20 °C in CH_2Cl_2 solution.

Conclusions

With the development of a stepwise coupling procedure, the double olefination methodology comprises a most convenient route to aromatic allenes. A single reaction using a boron-substituted phosphorus ylide in analogous fashion to our methodology was previously reported by Matteson and Majumdar.[4i] These authors chose not to develop the synthetic potential of the reaction, since at the time it apparently offered a route only to symmetrical products. The technology described here for the selective incorporation of different carbonyl compounds now offers significant opportunities for the development of both boron- and titanium-substituted phosphorus ylides as reagents for allene synthesis. The ready availability of suitable aldehydes plus the modular nature of the synthesis (for example, a variety of allenes is accessible from a single vinylphosphonium salt) makes it especially attractive when a series of compounds is desired for structure−activity correlations. We have taken advantage of this feature in the synthesis of aromatic allene−ynes for studies of the Myers cycloaromatization process, which will be described in due course.[25]

Experimental Section.

General Methods. ^1H,^{13}C, and ^{31}P NMR spectra were recorded at 300, 75.2, and 121.7 MHz, respectively. Melting points were measured on samples in unsealed capillary tubes and are uncorrected. Elemental analyses were performed in this department on a Perkin-Elmer Model 2400 CHN analyzer, using acetanilide as the calibration standard. We were unable to obtain satisfactory analyses on product oils; in these cases ≥95% purity is determined by ^1H and ^{13}C NMR spectroscopy. THF, hexane, and toluene were purified by distillation from Na benzophenone-ketyl; CH_2Cl_2 and $CDCl_3$ were purified by distillation from P_4O_{10}. $Ti(OiPr)_4$ was vacuum distilled and stored under nitrogen. All other reagents were purchased from commerical suppliers and used as recieved. $NaN(SiMe_3)_2$ was obtained either as a solid or in THF solution from Lancaster Chemical Co. or Aldrich Chemical Co. Use of recrystallized $NaN(SiMe_3)_2$ gave no improvement in yields; the lithium and potassium salts were somewhat less effective. All manipulations involving ylide species were conducted under dry nitrogen atmosphere, either in a glovebox or using standard Schlenk techniques.

Several batches of phenyllithium obtained from various commercial sources were contaminated with biphenyl, which is difficult to separate from hydrocarbon allenes. In addition, results were occasionally difficult to reproduce with the commercial material, whereas solid PhLi proved to be a very convenient and reliable base. The preparation of PhLi, adapted from that of McGrath and Grubbs,[26] is as follows. Under dry nitrogen atmosphere, a cooled solution (−20 °C) of bromobenzene (39.2 g, 250 mmol) in 350 mL of dry, degassed hexane is treated with *n*-BuLi (100 mL of a 2.5 M solution in hexane from Aldrich, 250 mmol) dropwise by addition funnel over 75 min with magnetic stirring. The reaction is stirred for 3 h, warming to room temperature, and is then allowed to stand at −78 °C overnight, inducing the formation of a precipitate. The reaction mixture is allowed to reach room temperature and is filtered through a medium frit in an inert-atmosphere glovebox. If a precipitate is not observed after cooling, the mixture should be stirred at room temperature until a substantial amount of the precipitate does form. The mixture is then cooled to −78 °C for 1 h to complete the precipitation process, followed by warming again to room temperature and filtration. *CAUTION! If precipitation of PhLi is still not observed, do not attempt to isolate the material by complete evaporation of the solvent. Reduce the volume by evaporation of a portion of the solvent and allow the solution to stand at room temperature until precipitation of PhLi occurs. Complete removal of solvent before precipitation produces PhLi as a yellow oil, which evolves heat and then explodes upon standing under inert atmosphere. We have observed this process to be coincident with crystallization of the oil, suggesting that PhLi releases a tremendous amount of energy of fusion in going from the pure liquid to the solid state. The solid PhLi produced by precipitation from hexane solution is safe in this regard.* The isolated solid is washed with hexane (100 mL) and dried under vacuum to obtain PhLi as a white powder

(23) Derived from Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1976; see tables on pp 273−4.

(24) (a) Johnson, R. P. *Org. Photochem.* **1985**, *7*, 75−147. (b) Lankin, D. C.; Chihal, D. M.; Bhacca, N. S.; Griffin, G. W. *J. Am. Chem. Soc.* **1975**, *97*, 7133−7141. (c) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107−1110. (d) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 2523−2526. (e) Steinmetz, M. G.; Mayes, R. T.; Yang, J.-C. *J. Am. Chem. Soc.* **1982**, *104*, 3518−3520. (f) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479−7483. (g) Zimmerman, H. E.; Baker, M. R.; Bottner, R. C.; Morrissey, M. M.; Murphy, S. *J. Am. Chem. Soc.* **1993**, *115*, 459−466.

(25) Dopico, P. G. Ph.D. Thesis, University of Virginia, 1995.

(26) McGrath, D. Ph.D. Thesis, California Institute of Technology, 1992. We thank Prof. McGrath for bringing this method to our attention.

(11.5 g, 137 mmol, 55%), which is 92% pure by titration with standardized HCl. The mother liquor, of course, is highly reactive and should be quenched while taking suitable precautions.

Syntheses. $(Me_2N)_3P{=}CH_2$ (modified from reference 11). A toluene solution of $P(NMe_2)_3$ (50 g, 307 mmol, 0.4 M) was treated with a toluene solution of CH_3I (52.2 g, 368 mmol, in 50 mL solvent). The resulting precipitate was collected, washed sequentially with toluene and diethyl ether, and dried to afford $[(Me_2N)_3PCH_3]I$ (91.8 g, 301 mmol, 98%). ^1H NMR (D_2O, δ) 2.66 (d, $^3J_{PH} = 9.9$ Hz, 18H), 1.89 (d, $^2J_{PH} = 14.7$ Hz, 3H); ^{13}C NMR (D_2O, δ) 36.7 (d, $^2J_{PC} = 4.0$ Hz), 8.2 (d, $^1J_{PC} = 112.9$ Hz).

$[(Me_2N)_3PCH_3]I$ (27.9 g, 80 mmol) and $NaNH_2$ (4.68 g, 120 mmol, used as received from Aldrich Chemical Co.) were mixed, finely ground under a dry nitrogen atmosphere, and placed in a 2 L, two-necked, round-bottomed flask, equipped with a magnetic stir bar, a dry ice-cooled reflux condenser, and a nitrogen inlet. The flask was cooled to −78 °C, and 450 mL of liquid ammonia, previously condensed into a storage flask at −78 °C, was added by cannula. The resulting suspension was stirred at −78 °C for 2 h and then allowed to warm to room temperature overnight with nitrogen purge through an open needle vent. The residue was transferred to the drybox, stirred with dry Et_2O (100 mL), filtered, and washed with an additional 100 mL of Et_2O. The solution was evaporated under gentle vacuum to yield a yellow oil, taking care to avoid volatilizing the product. Vacuum distillation affords the pure ylide as a clear oil (12.2 g, 69 mmol, 86% yield), which may be stored in the absence of air at room temperature without decomposition. ^1H NMR (C_6D_6, δ) 2.39 (d, $^3J_{PH} = 9.6$ Hz, 18H), −0.042 (d, $^2J_{PH} = 12.6$ Hz, 2H); ^{13}C NMR (C_6D_6, δ) 37.7, −9.0 (d, $^1J_{PC} = 175$ Hz).

$(Me_2N)_3P{=}CD_2$. $[(Me_2N)_3PCD_3]I$ was prepared as above in 81% yield from CD_3I. ^1H NMR (D_2O, δ) 2.73 (d, $^3J_{PH} = 9.9$ Hz); ^{13}C NMR (D_2O, δ) 36.3 (d, $^2J_{PC} = 4.0$ Hz); ^2H NMR (H_2O, δ) 1.6 (d, $^2J_{PD} = 2.2$ Hz). Deprotonation of $[(Me_2N)_3PCD_3]I$ with $NaNH_2$ in NH_3 (l) as above yields $(Me_2N)_3{=}PCH_2$, not the desired compound. A THF suspension $[(Me_2N)_3PCD_3]I$ (3.0 g, 10 mmol, 0.1 M) was cooled to −78 °C and treated with solid PhLi (1.23 g, 15 mmol). The reaction mixture was stirred while warming to room temperature overnight. In the glovebox, the mixture was filtered and the solid washed with Et_2O. The solution was then evaporated and the product distilled as above to provide $(Me_2N)_3P{=}CD_2$ (141 mg, 0.8 mmol, 8% yield). ^1H NMR (C_6D_6, δ) 2.41 (d, $^3J_{PH} = 9.6$ Hz); ^{13}C NMR (C_6D_6, δ) 37.6 (d, $^2J_{PC} = 2.3$ Hz); ^2H NMR (C_6H_6, δ) 0.04.

Vinylphosphonium Method A. General Procedure. $TiCl_2(OiPr)_2$ is prepared by treating a hexane solution of $TiCl_4$ (stock solutions of 1−2 mmol/g were used) with an equimolar amount of neat $Ti(OiPr)_4$; the mixture can be used directly after addition of THF, or $TiCl_2(OiPr)_2$ can be stored for weeks in the absence of air as a white or pale yellow solid after evaporation of the solvent. Complex **1** is generated by treatment of a solution of $TiCl_2(OiPr)_2$ in THF (approximately 0.1 M) with a THF solution of 1 equiv of $(Me_2N)_3P{=}CH_2$ (giving a clear orange color), followed immediately by 1 equiv of $NaN(SiMe_3)_2$, causing an immediate color change to cloudy, dark brown (overall Ti-ylide concentration is approximately 0.05 M). Within a few minutes at room temperature, a THF solution of 1.1−1.5 equiv of aldehyde or ketone (as a 1−3 M solution in THF) is added rapidly, causing a color change to yellow and usually the formation of a precipitate. The reaction mixture is stirred for 1 h, except in the cases of hindered substrates, for which longer reaction periods are required. Most vinylphosphonium chlorides (**3**·Cl) may be isolated by filtration under nitrogen, since the chloride salts are extremely hygroscopic. They may be purified by dissolution in a minimum amount of water, filtration, and reprecipitation by addition of an equimolar aqueous solution of $NaBPh_4$. The addition of saturated aqueous NaCl to this mixture often gives tetraphenylborate salts that are less finely divided and easier to filter. Isolated vinylphosphonium tetraphenylborates are then washed well with water and dried in a vacuum desiccator. Small amounts (2−5%) of additional product may be recovered by evaporation of the THF filtrate, addition of water, filtration to remove insoluble metal byproducts, and addition of $NaBPh_4$. The addition of small amounts of hexane serves to precipitate **3**·Cl in the few cases that do not spontaneously precipitate from the THF reaction mixture. Alternatively, the THF solution may be evaporated to dryness, dissolved in water, and filtered and the aqueous-soluble **3**·Cl isolated by treatment with $NaBPh_4$.

Vinylphosphonium Method B. General Procedure. $TiCl_3(OiPr)$[27] is prepared by addition of 1 equiv of neat $Ti(OiPr)_4$ to 3 equiv of $TiCl_4$ in hexane (1−2 mmol/g), followed by dropwise addition of THF with vigorous stirring, or more conveniently by mixing equimolar hexane solutions of $TiCl_2(OiPr)_2$ and $TiCl_4$. We have found that $TiCl_3OiPr$ should not be stored as a solid or in solution for more than a few days; to insure reproducibility, we use freshly-prepared material. When evaporated under vacuum, a cream-colored crystalline solid is obtained, the NMR of which shows 2 equiv of coordinated THF: ^1H NMR (C_6D_6, δ) 5.42 (heptet, $J = 6.4$ Hz, 1H), 4.34 (br s, 8H, THF), 1.99 (br s, 8H, THF), 1.52 (d, $J = 6.2$ Hz, 6H). Usually, a $TiCl_3OiPr$ mixture is not evaporated, but rather is diluted with THF to approximately 0.1 M in Ti and is treated with a THF solution containing 1 equiv of ylide, followed immediately by a THF solution of 2 equiv of $NaN(SiMe_3)_2$, causing an immediate color change to orange-red (overall Ti-ylide concentration is approximately 0.05 M). After several minutes at room temperature, a THF solution of aldehyde or ketone (2−4 equiv) is added rapidly, causing an immediate color change to yellow and usually the formation of a precipitate. In many cases heat is evolved upon addition of the aldehyde. The reaction mixture is stirred for 1 h (longer for bulkier substrates), followed by workup as in method A.

Vinylphosphonium salts prepared by the above procedures are occasionally contaminated with small amounts of $[(Me_2N)_3PCH_3]^+$, **4** (NMR data below), especially if lower concentrations or hindered substrates are used. Filtration of the reaction mixture with a coarse-fritted funnel often provides separation by trapping the precipitated vinylphosphonium salt but not the more finely divided **4**. Samples may also be freed of **4** by chromatography on a short silica gel column, eluting with mixtures of dichloromethane and ethyl acetate. Typically, drying under vacuum in the presence of a desiccant for at least 24 h is required before these compounds can be used with stoichiometric quantities of phenyllithium. Upon extended storage (months), vinylphosphonium tetraphenylborate salts require recrystallization (acetone/water).

3a·Cl: ^1H NMR (D_2O, δ) 7.54 (d, $J = 7.8$ Hz, 2H), 7.34 (dd, $^3J_{HH} = 17.6$ Hz, $^2J_{PH} = 22.5$ Hz, H_α), 7.29 (d, $J = 7.8$ Hz, 2H), 6.52 (dd, $^3J_{HH} = 17.6$, $^3J_{PH} = 21.6$ Hz, 1H), 2.73 (d, $J_{PH} = 9.9$ Hz, 18H), 2.34 (s, 3H); ^{13}C NMR (D_2O, δ) 151.7 (d, $^2J_{PC} = 6.0$ Hz), 143.0, 131.8, 130.4, 128.9, 106.3 (d, $^1J_{PC} = 160.7$ Hz), 36.5 (d, $J_{PC} = 2.8$ Hz), 21.3; ^{31}P NMR (D_2O, δ) 48.3; UV-vis (D_2O) 204, 218, 280. **3a**·BPh_4 IR (KBr, cm^{-1}) 3220 (m), 2982 (m), 1602 (w), 1480 (m), 1300 (m), 1181 (m), 993 (s), 741 (s), 707 (s); UV-vis (CH_2Cl_2) 230, 278, 288; mp 168−170 °C. Anal. Calcd for $C_{39}H_{47}N_3BP{\cdot}{}^1/_2H_2O$: C, 76.97; H, 7.95; N, 6.90. Found: C, 76.84; H, 7.92; N, 6.92.

3b·Cl: ^1H NMR (D_2O, δ) 7.50−7.26 (m, 5H), 6.63 (dd, $J_{PH} = 21.6$ Hz, $J_{HH} = 17.7$ Hz, 1H), 2.74 (d, $^3J_{PH} = 9.9$Hz, 18H), 2.33 (s, 3H); ^{13}C NMR (D_2O, δ) 151.9 (d, $^2J_{PC} = 6.2$ Hz), 139.8, 134.4 (d, $^3J_{PC} = 22.3$ Hz), 132.7, 129.7, 129.3, 126.0, 107.5 (d, $^1J_{PC} = 162.6$ Hz), 36.6 (d, $^2J_{PC} = 4.0$ Hz), 21.0. **3b**·BPh_4: ^{31}P NMR (CH_3CN, δ) 51.9; IR (KBr, cm^{-1}) 3054, 2999, 2947, 1610, 1479, 1300, 1177, 993, 742, 708; UV-vis (CH_2Cl_2) 230, 278; mp 147−154 °C. Anal. Calcd for $C_{39}H_{47}N_3BP$: C, 78.12; H, 7.90; N, 7.01. Found: C, 77.75; H, 7.63; N, 7.33.

3c·Cl: ^1H NMR (D_2O, δ) 7.66 (d, $J = 7.5$ Hz, 1 H), 7.52 (dd, $J_{HH} = 17.4$ Hz, $J_{PH} = 22.8$ Hz, 1H), 7.39−7.24 (m, 3H), 6.52 (dd, $J_{HH} = 17.4$, $J_{PH} = 22.5$, 1H), 2.77 (d, $^3J_{PH} = 9.9$ Hz, 18 H), 2.35 (s, 3H); ^{13}C NMR (D_2O, δ) 149.4 (d, $^2J_{PC} = 6.6$ Hz), 138.4, 133.5 (d, $^3J_{PC} = 21.4$ Hz), 131.7, 131.5, 127.3, 127.1, 109.1 (d, $^1J_{PC} = 161.2$ Hz), 36.7 (d, $^2J_{PC} = 3.2$ Hz), 19.4. **3c**·BPh_4: ^{31}P NMR (CH_3CN, δ) 51.6; IR (KBr, cm^{-1}) 3217, 3053, 2999, 1479,

(27) (a) Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015−2025. (b) Bradley, D. C.; Hancock, D. C.; Wardlaw, W. *J. Chem. Soc.* **1952**, 2773−2778.

1300, 1176, 993, 742, 708; UV-vis (CH_2Cl_2) 232, 276; mp 138−140 °C. Anal. Calcd for $C_{39}H_{47}N_3BP$: C, 78.12; H, 7.90; N, 7.01. Found: C, 77.85; H, 7.87; N, 7.42.

3d·Cl: ^{1}H NMR (D_2O, δ) 7.48 (dd, J_{PH} = 23.7 Hz, J_{HH} = 17.7 Hz, 1 H), 7.01 (s, 2H), 6.24 (dd, J_{PH} = 24.6 Hz, J_{HH} = 18.0 Hz, 1 H), 2.81 (d, J_{PH} = 9.9 Hz, 18 H), 2.29 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (D_2O, δ) 150.8 (d, $^2J_{PC}$ = 5.2 Hz), 140.2, 137.1, 131.7 (d, $^3J_{PC}$ = 21.0 Hz), 129.6, 113.9 (d, $^1J_{PC}$ = 156.1 Hz), 36.6 (d, $^2J_{PC}$ = 3.8 Hz), 20.7, 20.6; ^{31}P NMR (D_2O, δ) 50.0; UV-vis (H_2O) 200, 214, 274. **3d**·BPh_4: IR (KBr, cm^{-1}) 3055, 2970, 2860, 1612, 1482, 1303, 1202, 995, 700; mp 171−173 °C.

3e·Cl: ^{1}H NMR (D_2O, δ) 7.63 (d, J_{HH} = 8.7 Hz, 1H), 7.30 (dd, J_{PH} = 22.7 Hz, J_{HH} = 17.4 Hz, 1H), 7.02 (d, J_{HH} = 9.0 Hz, 1H), 6.46 (dd, J_{PH} = 21.5 Hz, J_{HH} = 17.4 Hz, 1H), 3.83 (s, 3H), 2.73 (d, $^3J_{PH}$ = 9.61 Hz, 18H); ^{13}C NMR (D_2O, δ) 161.9, 151.3 (d, $^2J_{PC}$ = 6.4 Hz), 130.7, 128.1, 115.0, 104.7 (d, $^1J_{PC}$ = 164.3 Hz), 56.0, 36.5 (d, $^2J_{PC}$ = 3.5 Hz). **3e**·BPh_4: ^{31}P NMR (CH_3CN, δ) 52.5; IR (KBr, cm^{-1}) 3054, 3005, 2944, 1601, 1512, 1479, 1302, 1261, 1177, 993, 735, 708; UV-vis (CH_2Cl_2) 234, 312; mp 206−221 °C.

3f·BPh_4: ^{1}H NMR ($CDCl_3$, δ) 7.43 (br s, 8H), 7.03 (t, J = 7.2 Hz, 8H), 6.94−6.86 (m, 5H), 6.69 (s, 2H), 5.97 (dd, $^3J_{PH}$ = 21.2 Hz, J_{HH} = 17.6 Hz, 1H), 4.16 (s, 3H), 3.82 (s, 6H), 2.46 (d, 3JPH = 9.9 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, $^1J_{BC}$ = 49.4 Hz), 154.1, 151.9 (d, $^2J_{PC}$ = 6.9 Hz), 136.19, 136.16, 130.0 (d, $^3J_{PC}$ = 23.0 Hz), 126.0, 122.2, 106.6, 106.4 (d, $^1J_{PC}$ = 162.9 Hz), 60.5, 56.4, 36.6 (d, $^2J_{PC}$ = 4.5 Hz); ^{31}P NMR (CD_3CN, δ) 52.6; IR (KBr, cm^{-1}) 3054, 2997, 2937, 1579, 1481, 1333, 1302, 1128, 991, 708; UV-vis (CH_2Cl_2) 232, 316; mp 190−192 °C.

3g·Cl: ^{1}H NMR (D_2O, δ) 7.34 (d, J = 8.7 Hz, 1H), 7.269 (dd, J_{PH} = 23.1 Hz, J_{HH} = 17.7 Hz, 1 H), 6.77 (d, J = 9.0 Hz, 1H), 6.44 (dd, J_{PH} = 22.4 Hz, J_{HH} = 17.7 Hz, 1 H), 3.72 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 2.61 (d, $^3J_{PH}$ = 9.6 Hz, 18 H); ^{13}C NMR (D_2O, δ) 156.1, 152.3, 145.4 (d, $^2J_{PC}$ = 7.3 Hz), 141.8, 124.26, 121.4 (d, $^3J_{PC}$ = 30.3 Hz), 109.3, 106.7 (d, $^1J_{PC}$ = 162.7 Hz), 62.4, 61.5, 56.5, 36.4 (d, $^2J_{PC}$ = 3.2 Hz). **3g**·BPh_4: ^{31}P NMR (CH_3CN, δ) 52.6; IR (KBr, cm^{-1}) 3055, 2999, 2937, 1618, 1491, 1300, 1176, 1096, 993, 735, 707; UV-vis (CH_2Cl_2) 234, 312; mp 178−180 °C. Anal. Calcd for $C_{41}H_{51}N_3BO_3P$: C, 72.88; H, 7.61; N, 6.22. Found: C, 72.45; H, 7.50; N, 6.32.

3h·Cl: ^{1}H NMR (D_2O, δ) 7.41 (dd, J_{PH} = 26.4 Hz, J_{HH} = 17.7 Hz, 1 H), 6.65 (dd, J_{PH} = 26.9 Hz, J_{HH} = 17.7 Hz, 1 H), 6.02 (s, 2H), 3.76 (s, 6H), 3.74 (s, 3H), 2.69 (d, $^3J_{PH}$ = 9.6 Hz, 18 H); ^{13}C NMR (D_2O, δ) 163.9, 161.4, 141.6 (d, $^2J_{PC}$ = 9.0 Hz), 105.2 (d, $^3J_{PC}$ = 21.5 Hz), 105.1 (d, $^1J_{PC}$ = 159.6 Hz), 91.1, 56.3, 55.9, 36.6 (d, $^2J_{PC}$ = 3.0 Hz). **3h**·BPh_4: ^{31}P NMR (CD_3CN, δ) 53.6; IR (KBr, cm^{-1}) 3054, 2999, 2940, 2858, 1505, 1488, 1298, 1207, 1159, 1120, 991, 734, 707; UV-vis (CH_2Cl_2) 234, 318; mp 160−163 °C. Anal. Calcd for $C_{41}H_{51}N_3BO_3P$: C, 72.88; H, 7.61; N, 6.22. Found: C, 73.03; H, 7.55; N, 6.00.

3i·Cl: ^{1}H NMR (D_2O, δ) 7. 56 (d, J = 8.7 Hz, 2H), 7.21 (dd, $^2J_{PH}$ = 22.5 Hz, J_{HH} = 17.4, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.26 (dd, $^3J_{PH}$ = 21.7 Hz, J_{HH} = 17.6 Hz, 1H), 2.95 (s, 6H), 2.72 (d, $^3J_{PH}$ = 10.2, 18H). **3i**·BPh_4: ^{1}H NMR ($CDCl_3$, d) 7.43 (br s, 8H), 7.35 (d, J = 9 Hz, 2H), 7.04 (t, J = 7.2 Hz, 8H), 6.96−6.86 (m, 3H), 5.66 (dd, $^3J_{PH}$ = 22.1, J_{HH} = 17.3, 1H), 3.05 (s, 6H), 2.49 (d, $^3J_{PH}$ = 9.6 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, 1J_{BC} = 49 Hz), 136.2, 126.1, 112.1, 39.8, 36.6; ^{31}P NMR (CH_3CN, δ) 53.6; IR (KBr, cm^{-1}) 3053, 2997, 2908, 1608, 1523, 1479, 1182, 993, 742, 706; UV-vis (CH_2Cl_2) 234, 322, 378; mp 193−195 °C. Anal. Calcd for $C_{38}H_{46}N_4BP$: C, 76.43; H, 8.02; N, 8.91. Found: C, 76.56; H, 7.90; N, 8.76.

3j·BPh_4: ^{1}H NMR ($CDCl_3$, δ) 7.67 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.74 (dd, J_{HH} = 17.7 Hz, J_{PH} = 19.5 Hz, 1H), 7.25 (br s, 8H), 6.97 (t, J = 7.2 Hz, 8H), 6.82, (t, J = 7.2 Hz, 4 H), 6.56 (dd, J_{HH} = 17.6 Hz, J_{PH} = 21.2 Hz, 1H), 2.73 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, $^1J_{BC}$ = 49.2 Hz), 150.4 (d, $^2J_{PC}$ = 6.6 Hz), 136.2, 130.4, 129.6, 126.0, 122.2, 108.6 (d, $^1J_{PC}$ = 162.3 Hz), 36.5 (d, $^2J_{PC}$ = 3.1 Hz); ^{31}P NMR (CH_3CN, δ) 51.6; IR (KBr, cm^{-1}) 3053, 2999, 2909, 1608, 1481, 1302, 1177, 995, 735, 708; UV-vis (CH_2Cl_2) 230, 276; mp 189−192 °C. Anal. Calcd for $C_{38}H_{44}N_3BClP$: C, 73.61; H, 7.15; N, 6.78. Found: C, 73.18; H, 7.04; N, 7.10.

3k·Cl: ^{1}H NMR (D_2O, δ) 7.52−7.23 (m, 5H), 6.70 (dd, J_{HH} = 17.7 Hz, J_{PH} = 21.0 Hz, 1H), 2.78 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (D_2O, δ) 163.2 (d, $^1J_{CF}$ = 244.1 Hz), 150.4 (d, $^2J_{PC}$ = 20.4 Hz), 136.7 (dd, $^3J_{CF}$ = 8.2 Hz, $^3J_{PC}$ = 23.3 Hz), 131.4 (d, $^3J_{CF}$ = 8.1 Hz), 125.0, 118.5 (d, $^2J_{CF}$ = 21.4 Hz), 114.8 (d, $^2J_{CF}$ = 22.3 Hz), 109.5 ($^1J_{PC}$ = 162.0 Hz), 36.5 (d, $^3J_{PC}$ = 3.8 Hz). **3k**·BPh_4: ^{1}H NMR (CD_3CN, δ) 7.50−7.47 (m, 3H), 7.36 (dd, J_{HH} = 17.7 Hz, J_{PH} = 22.5 Hz, 1H), 7.26 (br s, 9H), 6.98 (t, J = 7.5 Hz, 8H), 6.82 (t, J = 7.2 Hz, 4H), 6.61 (dd, J_{HH} = 17.7 Hz, J_{PH} = 21.3 Hz, 1H), 2.74 (d, $^3J_{PH}$ = 10.2 Hz); ^{31}P NMR (CH_3CN, δ) 51.4; IR (KBr, cm^{-1}) 3053, 3001, 2984, 2949, 2912, 1579, 1481, 1448, 1302, 1178, 995, 742, 708; UV-vis (CH_2Cl_2) 232, 268; mp 170−173 °C dec. Anal. Calcd for $C_{38}H_{44}N_3BFP$: C, 75.62; H, 7.35; N, 6.96. Found: C, 75.88; H, 7.23; N, 7.12.

3l·BPh_4: ^{1}H NMR (CD_3CN, δ) 8.28 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 9Hz, 2H), 7.45 (dd, J_{PH} = 22.5, J_{HH} = 17.9, 1 H), 7.25 (br s, 8H), 6.97 (t, J = 7.2 Hz, 8H), 6.84−6.69 (m, 5H), 2.74 (d, $^3J_{PH}$ = 10.2 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, $^1J_{BC}$ = 49.2 Hz), 149.5, 149.0 (d, $^2J_{PC}$ = 6.6 Hz), 140.5 (d, $^3J_{PC}$ = 22.9 Hz), 136.1, 129.8, 126.1, 124.5, 122.3, 112.9 (d, $^1J_{PC}$ = 160.7 Hz), 36.4 (d, $^2J_{PC}$ = 3.9 Hz); ^{31}P NMR (CD_3CN, δ) 50.7; IR (KBr, cm^{-1}) 3053, 2964, 2908, 1591, 1520, 1481, 1342, 1302, 1176, 995, 850, 708; UV-vis (CH_2Cl_2) 234, 276 (sh), 294; mp 202−203 °C. Anal. Calcd for $C_{38}H_{44}N_4BO_2P$: C, 72.38; H, 7.03; N, 8.89. Found: C, 71.90; H, 7.06; N, 8.85.

3m·BPh_4: ^{1}H NMR (CD_3CN, δ) 7.67 (s, 1H), 7.21−7.12 (br s and partial dd from vinyl H, 9H), 6.98 (t, J = 7.5 Hz, 8H), 6.88−6.81 (m, 5H), 6.60 (br s, 1H), 6.27 (J_{HH} = 17.2 Hz, $^3J_{PH}$ = 21.6 Hz, 1H), 2.71 (d, $^3J_{PH}$ = 9.9 Hz, 18H); ^{13}C NMR (CD_3CN, δ) 164.3 (q, $^1J_{BC}$ = 49.3 Hz), 150.8 (d, $^3J_{PC}$ = 25.4 Hz), 146.9, 137.9 (d, $^2J_{PC}$ = 7.9 Hz), 136.2, 126.0, 122.2, 117.5, 113.4, 103.7 (d, $^1J_{PC}$ = 167.2), 36.5 (d, $^2J_{PC}$ = 3.9 Hz); ^{31}P NMR (CH_3CN, δ) 51.9; IR (KBr, cm^{-1}) 3051, 2999, 2906, 1616, 1479, 1302, 1167, 991, 860, 741, 706; UV-vis (CH_2Cl_2) 234, 304; mp decomposed to brown solid at 120 °C. Anal. Calcd for $C_{36}H_{43}N_3BOP$: C, 75.13; H, 7.53; N, 7.30. Found: C, 74.96; H, 7.72; N, 7.15.

3n·Cl: ^{1}H NMR (D_2O, δ) 7.68−7.21 (m, 8H), 6.18 (dd, J_{PH} = 22.5 Hz, J_{HH} = 17.7 Hz, 1H), 2.55 (d, J_{PH} = 10.2 Hz, 18 H); ^{13}C NMR (D_2O, δ) 147.8 (d, $^2J_{PC}$ = 5.4 Hz), 133.6, 131.8, 131.1 (d, $^3J_{PC}$ = 21.9 Hz), 130.8, 129.2, 129.0, 128.0, 127.1, 126.2, 122.9, 110.6 (d, $^1J_{PC}$ = 161.2 Hz), 36.5 (d, $^2J_{PC}$ = 2.5 Hz); ^{31}P NMR (CH_3CN, δ) 51.1. **3n**·BPh_4: IR (KBr, cm^{-1}) 3051, 2999, 2947, 2908, 1579, 1479, 1300, 1174, 1064, 993, 743, 708; UV-vis (CH_2Cl_2) 230, 244, 328; mp 160−162 °C. Anal. Calcd for $C_{42}H_{47}N_3BP$: C, 79.36; H, 7.45; N, 6.61. Found: C, 79.12; H, 7.24; N, 6.99.

3o·BPh_4: ^{1}H NMR (CD_3CN, δ) 8.16 (s, 1H), 7.97−7.82 (m, 4H), 7.60−7.47 (m, 3H, naphthalene aromatics and one vinyl proton), 7.25 (br s, 8H), 6.97 (t, J = 7.2 Hz, 8H), 6.82 (t, J = 7.2 Hz, 4H), 6.68 (dd, J_{HH} = 17.7 Hz, J_{PH} = 21.6, 1H), 2.77 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, $^1J_{BC}$ = 49.6 Hz), 151.9 (d, $^2J_{PC}$ = 6.5 Hz), 136.1, 134.9, 133.5, 132.3, 131.2, 129.3, 129.2, 128.4, 128.2, 127.6, 126.0, 123.9, 122.2, 107.7 (d, $^1J_{PC}$ = 162.4 Hz), 36.5 (d, $^2J_{PC}$ = 4.1 Hz); ^{31}P NMR (CH_3CN, δ) 51.9; IR (KBr, cm^{-1}) 3053, 2999, 2949, 1608, 1481, 1481, 1300, 1177, 993, 735, 708; UV-vis (CH_2Cl_2) 234, 270, 310, 354 (sh); mp 222−227 °C. Anal. Calcd for $C_{42}H_{47}N_3BP$: C, 79.36; H, 7.45; N, 6.61. Found: C, 79.64; H, 7.28; N, 6.49.

3p·Cl: ^{1}H NMR (D_2O, δ) 7.71−7.19 (m, 7H), 7.01−6.93 (m, 3H), 5.82 (dd, J_{PH} = 22.2 Hz, J_{HH} = 17.4 Hz, 1 H), 2.48 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (D_2O, δ) 148.1 (d, $^2J_{PC}$ = 6.0 Hz), 130.8, 130.7, 130.2 (d, $^3J_{PC}$ = 22.0 Hz), 130.0, 129.7, 129.1, 128.3, 127.9, 127.6, 127.4, 127.2, 124.0, 123.0, 122.4, 111.1 (d, $^1J_{PC}$ = 161.3 Hz), 36.3 (d, $^2J_{PC}$ = 3.6 Hz). **3p**·BPh_4: ^{31}P NMR (CD_3CN, δ) 49.9; IR (KBr, cm^{-1}) 3053, 2999, 2906, 1601, 1579, 1479, 1302, 1174, 991, 744, 708; UV-vis (CH_2Cl_2) 248, 334; mp 204−208 °C. Anal. Calcd for $C_{46}H_{49}N_3BP$: C, 80.58; H, 7.20; N, 6.13. Found: C, 80.06; H, 7.19; N, 6.46.

3q·BPh_4: ^{1}H NMR (CD_3CN, δ) 7.56 (d, J = 7.5 Hz, 2H), 7.41−6.82 (aromatics and vinyls; overlapping peaks, 28 H), 6.12−5.99 (m, 1H), 2.70 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.2 (q, $^1J_{BC}$ = 49.4 Hz), 152.0 (d, $^2J_{PC}$ = 5.9 Hz), 142.9, 136.2, 130.2, 129.5, 128.3, 127.9, 127.0 (d, $^2J_{PC}$ = 13.1 Hz), 126.0, 122.2, 109.8 (d, $^1J_{PC}$ = 162.8 Hz); ^{31}P NMR (CH_3CN, δ) 51.2; IR (KBr, cm^{-1}) 3055, 2999, 2951−2822, 1622, 1597, 1479, 1300, 1176, 993, 747, 708; UV-vis (CH_2Cl_2) 232, 316; mp 229−232 °C. Anal. Calcd for $C_{40}H_{47}N_3BP\cdot{}^1/_2H_2O$: C, 78.55; H, 7.75; N, 6.87. Found: C, 78.61; H, 7.67; N, 7.10.

3r·Cl: ^{1}H NMR (D_2O, δ) 7.30 (dd, J_{HH} = 17.4 Hz, $^2J_{PH}$ = 21.6 Hz, 1H), 6.19 (dd, J_{HH} = 17.4, $^3J_{PH}$ = 22.5 Hz, 1H), 4.68 (br s, 2H), 4.55 (br s, 2H), 4.2 (s, 5H), 2.72 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (D_2O, δ) 156.1 (d, $^2J_{PC}$ = 6.3 Hz), 104.9 (d, $^1J_{PC}$ = 164.5 Hz), 81.6 (d, $^3J_{PC}$ = 24.8 Hz), 75.0, 72.9, 72.2, 39.1. **3r**·BPh_4: ^{1}H NMR ($CDCl_3$, δ) 7.45 (br s, 8H), 7.06 (t, J = 6.6 Hz, 9H), 6.94−6.90 (m, 5H), 5.56 (dd, J_{HH} = 17.1 Hz, $^3J_{PH}$ = 22.8 Hz, 1H), 4.55 (s, 2H), 4.5 (s, 2H), 4.16 (s, 5H), 2.42 (d, $^3J_{PH}$ = 9.9 Hz, 18H); ^{31}P NMR (CH_3CN, δ) 51.8; IR (KBr, cm^{-1}) 3052, 2999, 2904, 1602, 1479, 1300, 1177, 991, 743, 708; UV-vis (CH_2Cl_2) 234, 296, 364 (br), 484 (br), 580; mp 177−178 °C. Anal. Calcd for $C_{42}H_{49}N_3BPFe$: C, 72.74; H, 7.12; N, 6.06. Found: C, 72.38; H, 7.54; N, 6.06.

3s·Cl: ^{1}H NMR (D_2O, δ) 8.71 (s, 1H), 8.55 (d, J = 4.5 Hz, 1H), 8.14 (d, J = 7.8 Hz), 7.54−7.50 (m, 1H), 7.44 (dd, J_{PH} = 22.5 Hz, J_{HH} = 17.7 Hz, 1H), 6.84 (dd, J_{HH} = 17.8 Hz, J_{PH} = 20.4 Hz, 1H), 2.78 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (D_2O, δ) 151.0, 149.2, 148.1 (d, $^2J_{PC}$ = 6.6 Hz), 136.3, 131.0 (d, $^3J_{PC}$ = 23.1 Hz), 125.0, 111.1 (d, $^1J_{PC}$ = 161.8 Hz), 36.4 (d, $^3J_{PC}$ = 12.9 Hz). **3s**·BPh_4: ^{31}P NMR (CH_3CN, δ) 51.2; IR (KBr, cm^{-1}) 3053, 2984, 1637, 1479, 1300, 1172, 993, 734, 705; UV-vis (CH_2Cl_2) 232, 274 (sh); mp decomposed 150 °C. Anal. Calcd for $C_{37}H_{44}N_4BP$: C, 75.76; H, 7.56; N, 9.55. Found: C, 75.42; H, 7.78; N, 9.49.

3t·Cl: ^{1}H NMR (D_2O, δ) 6.74 (dd, J_{PH} = 23.1 Hz, J_{HH} = 17.7 Hz, 1 H), 5.92 (dd, J_{PH} = 24.3 Hz, J_{HH} = 17.4 Hz, 1 H), 2.70 (d, $^3J_{PH}$ = 9.6 Hz, 18H), 1.10 (s, 9H); ^{13}C NMR (D_2O, δ) 168.2 (d, $^2J_{PC}$ = 2.3 Hz), 105.7 (d, $^1J_{PC}$ = 157.8 Hz), 36.4 (d, $^3J_{PC}$ = 3.8 Hz), 35.8 (d, $^2J_{PC}$ = 18.3 Hz), 27.9; UV-vis (H_2O) 202. **3t**·BPh_4: ^{1}H NMR ($CDCl_3$, δ) 7.42 (br s, 8H), 7.05 (t, J = 7.2 Hz, 8 H), 6.89 (t, J = 6.9 Hz, 4 H), 6.47 (dd, J_{PH} = 22.6 Hz, J_{HH} = 17.5 Hz, 1 H), 5.49 (dd, J_{PH} = 24.3 Hz, J_{HH} = 17.4 Hz, 1 H), 2.4 (d, $^3J_{PH}$ = 9.9 Hz, 18H), 1.13 (s, 9H); ^{1}H NMR (CD_3CN, δ) 8.69 (d, J = 5.7 Hz, 2H), 7.55 (d, J = 5.7 Hz, 2H) 7.41−7.28 (m, 9H), 7.06 (t, J = 7.2 Hz, 8 H), 6.90 (t, J = 7.2 Hz, 4H), 6.78 (dd, J_{HH} = 17.7 Hz, J_{PH} = 21.0 Hz, 1H), 2.70 (d, $^3J_{PH}$ = 9.9 Hz, 18 H); ^{13}C NMR (CD_3CN, δ) 164.3 (q, $^1J_{BC}$ = 49.5 Hz), 151.1, 149.3 (d, $^3J_{PC}$ = 6.0 Hz), 136.3, 134.9, 126.1, 122.5, 122.3, 113.4 (d, $^1J_{PC}$ = 160.2 Hz), 36.6 (d, $^3J_{PC}$ = 3.3 Hz); ^{31}P NMR (CD_3CN, δ) 51.7; IR (KBr, cm^{-1}) 3051, 2997, 1479, 1427, 1302, 1179, 993, 745, 707.

3u·Cl: ^{1}H NMR (D_2O, δ) 7.77 (ddd, $^2J_{PH}$ = 23.1 Hz, J_{HH} = 17.1, J_{HH} = 6 Hz, 1H), 6.02 (dd, $^1J_{PH}$ = 25.2 Hz, J_{HH} = 17.7 Hz, 1H), 2.74 (d, $^3J_{PH}$ = 9.9 Hz, 18H), 2.36 (br m, 1H), 1.84−1.65 (m, 5 H), 1.4−1.17 (m, 5H); ^{13}C NMR (D_2O, δ) 163.7, 107.9 (d, $^1J_{PC}$ = 157.3 Hz), 42.5 (d, $^3J_{PC}$ = 19.2 Hz), 36.4 (d, $^2J_{PC}$ = 3.9 Hz), 31.3, 26.0, 25.7. **3u**·BPh_4: ^{31}P NMR (CH_3CN, δ) 51.1; IR (KBr, cm^{-1}) 3053, 2999, 2949, 2908, 1608, 1481, 1302, 1177, 995, 735, 708; UV-vis (CH_2Cl_2) 232; mp 149−153 °C. Anal. Calcd for $C_{38}H_{51}N_3BP$: C, 77.15; H, 8.69; N, 7.10. Found: C, 77.04; H, 8.35; N, 6.71.

3v·Cl: ^{1}H NMR (D_2O, δ) 6.31−6.02 (m, 2H), 2.73 (d, $^3J_{PNCH}$ = 9.9 Hz, 18 H), 1.28−1.76 (m, 1H), 1.18 (d, J = 6.3, 1H), 1.05 (d, J = 6.3, 1H) 0.77 (br s, 2H); ^{13}C NMR (D_2O, δ) 163.1 (d, $^2J_{PC}$ = 5.59 Hz), 106.0 (d, $^1J_{PC}$ = 162.6 Hz), 36.4 (d, $^2J_{PNC}$ = 3.4 Hz), 16.8 (d, $^3J_{PC}$ = 27.3 Hz) 9.1; ^{31}P NMR (D_2O, δ) 51.6. **3v**·BPh_4: IR (KBr, cm^{-1}) 3051, 2997, 2908, 1620, 1479, 1302, 1172, 993, 734, 707; UV-vis (CH_2Cl_2) 234; decomposes to brown solid at 150 °C. Anal. Calcd for $C_{35}H_{45}N_3BP$: C, 76.50; H, 8.25; N, 7.65. Found: C, 76.40; H, 8.16; N, 7.83.

3w·Cl: ^{1}H NMR (D_2O, δ) 7.53 (m, 3 H), 7.41 (m, 2 H), 7.09 (d, J_{PH} = 14.1 Hz, 1H), 2.48 (d, $^3J_{PH}$ = 10.2 Hz, 18H); ^{13}C NMR (D_2O, δ) 149.4 (dq, $^2J_{CF}$ = 31.3 Hz, $^2J_{PC}$ = 7.0 Hz), 131.1, 130.5 (d, $^3J_{PC}$ = 6.6 Hz) 129.5, 129.1, 122.2 (dq, $^1J_{CF}$ = 276.1 Hz, $^3J_{PC}$ = 27.7 Hz), 118.9 (dd, $^1J_{PC}$ = 153.3 Hz, $^3J_{CF}$ = 4.1 Hz), 36.6 (d, $^2J_{PC}$ = 3.9 Hz); ^{31}P NMR (D_2O, δ) 36.4. **3w**·BPh_4: IR (KBr, cm^{-1}) 3054, 2999, 2912, 1481, 1303, 1258, 1186, 997, 706; UV-vis (CH_2Cl_2) 234, 266 (sh), 332 (br); mp 209−212 °C. Anal. Calcd for $C_{39}H_{44}N_3BF_3P$: C, 71.67; H, 6.79; N, 6.43. Found: C, 71.75; H, 6.97; N, 6.31. Upon irradiation of the ^{1}H NMR resonance due to the NMe_2 groups in a standard NOE experiment on a deoxygenated sample of **3w**·Cl in D_2O, the vinylic signal at 7.12 ppm (d, J_{PH} = 13.8 Hz) was enhanced by 17.5%, and the *ortho* hydrogens of the phenyl ring displayed an enhancement of 11.8%. The strong NOE enhancement in the latter case suggests that the trifluoromethyl group is found *trans* to the phosphorus moiety. However, since both isomers are not available, the structure cannot be conclusively identified.

3x·Cl: ^{1}H NMR (D_2O, δ) 7.66 (d, J = 7.5 Hz, 1H), 7.57−7.26 (m, 7 H), 6.22 (d, J_{PH} = 11.4 Hz, 1H), 2.72 (d, $^3J_{PH}$ = 9.6 Hz, 18 H); ^{13}C NMR (D_2O, δ) 156.3, 143.4, 140.5, 134.1, 134.0, 132.9, 132.6, 128.9, 127.3, 122.8, 121.2, 120.7, 101.6 (d, $^1J_{PC}$ = 164.4 Hz), 36.2 (d, $^2J_{PC}$ = 3.2 Hz). **3x**·BPh_4: ^{31}P NMR (CH_3CN, δ) 46.9; IR (KBr, cm^{-1}) 3051, 2997, 2947, 1561, 1479, 1302, 1172, 993, 734, 707; UV-vis (CH_2Cl_2) 230, 258 (sh), 266, 286, 326; mp 243−246 °C. Anal. Calcd for $C_{44}H_{47}N_3BP$: C, 80.12; H, 7.18; N, 6.37. Found: C, 80.26; H, 7.51; N, 6.25.

3y·Cl: ^{1}H NMR (D_2O, δ) 7.3−7.6 (m, 10H), 6.51 (d, $^2J_{PH}$ = 17.1 Hz), 2.53 (d, $^3J_{PH}$ = 10.2 Hz); ^{13}C NMR (D_2O, δ) 164.1 (d, $^2J_{PC}$ = 5.6 Hz), 141.5 (d, $^3J_{PC}$ = 20.5 Hz), 138.2 (d, $^3J_{PC}$ = 6.9 Hz), 131.1, 129.9, 129.2, 129.1, 128.9, 108.6 (d, $^1J_{PC}$ = 161.3 Hz), 36.8 (d, $^2J_{PC}$ = 4.1 Hz); ^{31}P NMR (CH_3CN, δ) 46.3; IR (KBr, cm^{-1}) 3051, 2997, 1602, 1479, 1302, 1180, 991, 744, 708; UV-vis (CH_2Cl_2) 232, 268 (sh), 276 (sh), 292 (sh); mp 215−217 °C.

4·Cl: ^{1}H NMR (D_2O, δ) 2.70 (d, $^3J_{PH}$ = 9.9 Hz, 18H), 1.93 (d, $^2J_{PH}$ = 14.7 Hz, 3H); ^{13}C NMR (D_2O, δ) 36.1 (d, $^2J_{PC}$ = 3.7 Hz), 7.2 (d, $^1J_{PC}$ = 113.3 Hz); ^{31} P NMR (D_2O, δ) 59.2; IR (KBr, cm^{-1}) 3069, 2997, 2914, 1479, 1425, 1313, 1180, 991, 732, 708.

X-ray Crystallography. Crystals of **3t**·Cl were obtained directly from the reaction mixture as needles, and crystals of **3x**·BPh_4 were obtained from CH_2Cl_2−hexane solution. ORTEP structures are shown in Figure 1; tables of crystallographic parameters, atomic coordinates, and bond distances and angles are available from the authors, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Photoisomerization of Vinylphosphonium Salts. A solution of **3a**·BPh_4 in CD_3CN (approximately 20 mg/mL) is irradiated with a 450 W mercury lamp (Hanovia) at room temperature in a standard glass NMR tube under nitrogen. After 2 h, a new set of resonances is observed, in a ratio of original to new peaks of 2:1. Irradiation for a further 3 h results in the complete disappearance of the new signals with concomitant partial decomposition of the original compound, as evidenced by the appearance of many new resonances in aliphatic and aromatic regions of the spectrum which were not assigned. ^{1}H NMR data after 2 h irradiation: original resonances, assigned as (*E*)-**3a**·BPh_4, δ BPh_4 resonances (7.6 (d), 7.32, 7.03 (t), 6.85 (t)), ca. 7.35 (q, partially obstructed by BPh_4 peak, H_α), 6.49 (dd, $^3J_{HH}$ = 17.6 Hz, $^3J_{PH}$ = 21.9 Hz, H_β), 2.73 (d, J = 9.9 Hz, 18H), 2.40, (s, 3H); new resonances, assigned as (*Z*)-**3a**·BPh_4, δ BPh_4 resonances as above, 5.77 (dd, $^3J_{HH}$ = 14.5 Hz, $^3J_{PH}$ = 17.3 Hz, H_β), 2.56 (d, J = 9.9 Hz), 2.40 (s). When allowed to stand overnight in the dark, the original spectrum is completely restored.

Irradiation of **3a**·Cl in D_2O in a similar fashion provides a 1:1.5 ratio of new:old resonances after 4 h. NMR data for the (*E*)-isomer is given above; for (*Z*)-**3a**·Cl δ 7.69 (dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{PH}$ = 49.8 Hz, H_α), 5.76 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{PH}$ = 17.1 Hz, H_β), 2.43 (d, J_{PH} = 9.8 Hz, NMe_2); no changes observed in aromatic or tolyl CH_3 resonances. Upon standing at −10 °C overnight, the (*Z*):(*E*) ratio was 1:2, indicating slow reversion to the thermodynamically stable structure. Complete conversion to the (*E*) structure was observed upon storage in the dark at room temperature.

Irradiation of **3e**·Cl in D_2O for 2 h produces a 1:1.6 ratio of new:old resonances. NMR data for the (*E*)-isomer is given above; for (*Z*)-**3e**·Cl, ^{1}H NMR δ 7.49 (dd, $^3J_{HH}$ = 14.4 Hz, $^2J_{PH}$ = 49.8 Hz (downfield doublet partially obscured by aromatic resonance), H_α), 7.23 (d, aromatic 2H), 5.65 (dd, $^3J_{HH}$ = 14.4 Hz, $^3J_{PH}$ = 16.2 Hz, H_β), 3.88 (s, OMe), 2.47 (d, J = 9.4 Hz, NMe_2); no change observed in one of the aromatic doublets. For (*Z*)-**3e**·Cl, ^{13}C NMR δ 161.2, 152.8, 131.9, 114.5, 107.0, 104.9, 36.2; no change observed in methoxy resonance.

Nucleophilic Addition to a Vinylphosphonium Salt. Reaction of **3a**·BPh_4 with *n*-BuLi (eq 5)

A solution of **3a**·BPh_4 (0.088 g, 0.147 mmol) in 50 mL of THF was treated at −40 °C with 2 equiv of *n*-BuLi. After stirring 30 min, excess *p*-tolualdehyde (0.3 mL, 2.6 mmol) was added rapidly by syringe. The reaction mixture was allowed to warm to room temperature and then stirred an additional

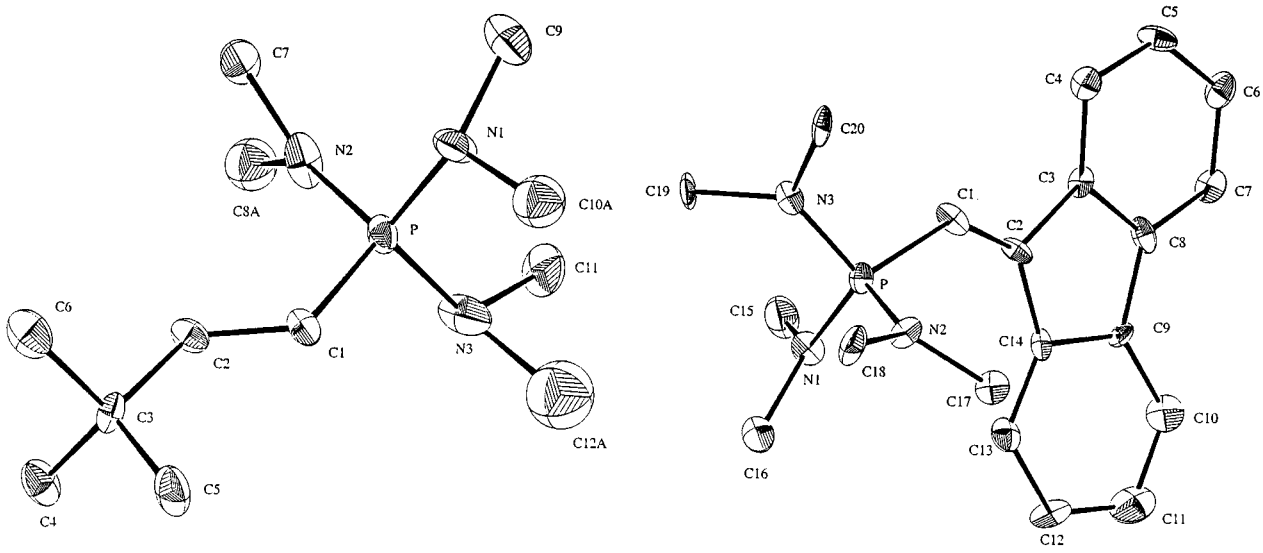
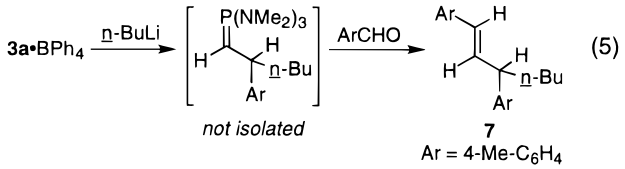


Figure 1. ORTEP diagrams showing 30% probablility thermal ellipsoids of the cations of compounds **3t**·Cl (left) and **3x**·BPh_4 (right).



2.5 h before it was exposed to air. Diethyl ether was added and the organic mixture washed with aqueous 10% tartaric acid. The organic layer was dried over Na_2SO_4, and solvents were removed by rotary evaporation. TLC analysis (petroleum ether) revealed the presence of a major nonpolar compound, which was isolated by flash chromatography and shown to be olefin **7** (20 mg, 0.072 mmol, 49% yield). A single compound was detected, assigned as the *E*-isomer by virtue of the $^3J_{HH}$ olefinic coupling constant of 15.9 Hz. ^{1}H NMR ($CDCl_3$, δ) 7.26 (d, J = 7.8 Hz, 2H), 7.11 (m, 6H), 6.37 (d, J = 15.9 Hz, 1H), 6.28 (dd, J = 15.8, 7.0 Hz, 1H), 3.44 (apparent q, J = 7.5 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 1.79 (m, 2H), 1.3 (m, 4H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, δ) 141.4, 136.1, 135.1, 134.5, 133.2, 128.7 (coincident resonances of two aromatic CH sites), 128.4, 127.0, 125.6, 48.3, 35.3, 29.4, 22.2, 20.7, 20.6, 13.6; GC-MS (DB5 capillary column) shows one major elution peak displaying 278 (M^+), 221 (base peak, [M − butyl]$^+$), 161 (allylic cleavage).

Synthesis of Mixed Allenes. Representative Procedure for the Conversion of Vinylphosphonium Salts to Unsymmetrical Allenes. Under inert atmosphere, the vinylphosphonium salt is vigorously stirred in THF to create a solution or a suspension of fine white powder (0.17 mmol per 50 mL of THF, 3.3 mM.) The mixture is chilled to −78 °C and treated with a solution of 2.0 equiv of PhLi in THF via cannula or syringe, resulting in the appearance of a slightly cloudy, yellow-orange solution. After stirring at −78 °C for approximately 30 min, 3 equiv of the desired trapping aldehyde, in 5 mL of THF and under inert atmosphere, is added via cannula or syringe. The cooling bath is removed immediately and the solution allowed to warm to room temperature and stirred for at least 4 h. The reaction mixture is partitioned between ether and water and the ether layer dried over Na_2SO_4 before rotary evaporation. Most allenes may be obtained by filtration of the crude product through a short column of silica gel, eluting with a nonpolar solvent (NMR spectra of the resulting products are supplied in the Supporting Information). Occasionally, flash chromatography on silica gel is required for additional purification.

6a:[1] ^{1}H NMR ($CDCl_3$, δ) 7.28 (d, J = 8.1 Hz, 4H), 7.15 (d, J = 8.1 Hz, 4H), 6.59 (s, 2H), 2.37 (s, 6H); ^{13}C NMR ($CDCl_3$, δ) 207.9, 137.6, 131.4, 130.0, 127.5, 98.8 (allene C1 and C3), 21.8; IR ($CDCl_3$, cm^{-1}) 2925, 2863, 1935, 1702, 1605, 1510, 1178, 883. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: 92.31; H, 7.43.

6b: ^{1}H NMR ($CDCl_3$, δ) 7.29 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.91 (s, 2H), 6.76 (d, J = 6.6 Hz, 1H), 6.37 (d, 6.9 Hz, 1H), 2.40 (s, 6H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 208.3, 137.1, 135.9, 131.9, 131.1, 129.8, 129.6, 128.6, 127.9, 127.4, 95.7, 94.1, 21.8, 21.7, 21.4; IR (CH_2Cl_2, cm^{-1}) 3023 (w), 2974, 2922 (s), 2862, 1932 (m), 1512 (s), 1479 (s), 1458 (m, br), 883 (s), 856 (s), 827 (s); UV-vis (CH_2Cl_2) 228, 264.

6c: ^{1}H NMR ($CDCl_3$, δ) 7.29 (t, J = 8.7 Hz, 4 H), 7.15 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 8.4 Hz), 6.57 (s, 2H), 3.82 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 206.8, 158.9, 136.9, 129.3, 127.9, 126.7, 114.1, 98.0, 97.6, 55.2, 21.1; IR (CH_2Cl_2, cm^{-1}) 3009, 2958, 2935, 2839, 1934 (w), 1606, 1512 (s), 1483, 1300, 1238, 1172, 1033, 839; UV-vis (CH_2Cl_2) 232, 268.

6d: ^{1}H NMR ($CDCl_3$, δ) 7.24 (d, J = 9.6 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.7 Hz, 1H), 6.82 (d, J = 6.6 Hz, 1H), 6.63 (d, J = 8.7 Hz, 1H), 6.53 (d, J = 6.6 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 2.33 (s, 3H).

6e: ^{1}H NMR ($CDCl_3$, δ) 7.28 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 6.61 (d, J = 6.6 Hz, 1H), 6.60 (s, 2H), 6.53 (d, J = 6.6 Hz, 1H), 3.86 (s, 9H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 207.7, 154.0, 137.9, 137.7, 131.0, 129.9, 129.8, 127.4, 104.3, 99.0, 61.4, 56.5, 21.7; IR (CH_2Cl_2, cm^{-1}) 3009, 2963, 2942, 2253, 1588, 1507, 1466, 1330, 1234, 1130; UV-vis (CH_2Cl_2) 248, 268.

6f: ^{1}H NMR ($CDCl_3$, δ) 7.27−7.22 (m, 6H), 7.13 (d, J = 7.8 Hz, 2H), 6.58 (d, J = 6.6 Hz, 1H), 6.53 (d, J = 6.6 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 208.1, 137.8, 133.3, 132.8, 130.6, 129.9, 129.3, 128.6, 127.4, 99.1, 97.9, 21.7; IR (CH_2Cl_2, cm^{-1}) 3025, 2918, 2856, 1938 (w), 1512, 1091, 879, 841 (s), 823; UV-vis (CH_2Cl_2) 244 (sh), 264.

6g: ^{1}H NMR ($CDCl_3$, δ) 7.62−6.90 (m, 8H), 6.62 (d, J = 6.3 Hz, 1H), 6.56 (d, J = 6.3 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 208.3, 163.9 (d, $^1J_{CF}$ = 257.5 Hz)137.9, 136.8 (d, $^3J_{CF}$ = 7.9 Hz), 130.5 (d, $^3J_{CF}$ = 8.3 Hz), 130.0, 123.1, 114.5 (d, $^2J_{CF}$ = 21.5 Hz), 113.9 (d, $^2J_{CF}$ = 22.0), 99.1, 98.1, 21.7; IR (CH_2Cl_2, cm^{-1}) 3026 (m), 2926 (s), 2856, 1938 (w), 1726 (w), 1612 (s), 1587 (s), 1512 (s), 1487 (s), 1448, 1238 (w), 1140, 883, 825, 790; UV-vis (CH_2Cl_2) 230 (sh), 260.

6h: ^{1}H NMR ($CDCl_3$, δ) 7.38 (br s, 1H), 7.27 (d, J = 6.9 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.61 (d, J = 6.6 Hz, 1H), 6.55 (d, J = 6.6 Hz, 1H), 6.41−6.39 (m, 1H), 6.29 (d, J = 3.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 207.3, 142.7, 138.7, 129.9, 127.6, 111.9, 108.1, 99.2, 89.4, 21.7; IR (CH_2Cl_2, cm^{-1}) 3024, 2924, 2864, 1936 (w), 1512 (s), 1263 (m, br), 1012, 883, 827, 740 (s, br); UV-vis (CH_2Cl_2) 232 (sh), 244 (sh), 268, 356 (br).

6i: ^{1}H NMR ($CDCl_3$, δ) 7.29 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.32 (s, 2H), 4.36 (br s, 1H), 4.33 (br s, 1H), 4.23 (br s, 7H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 206.3, 137.3,

131.7, 129.9, 127.2, 97.3, 95.2, 69.7, 69.0, 68.9, 67.9, 67.4, 21.7; IR (CH_2Cl_2, cm^{-1}) 3097, 3024, 2924, 2862, 1934 (w), 1512 (s), 1105 (m), 1031 (m), 1001 (m), 861, 823 (s); UV-vis (CH_2Cl_2) 232 (sh), 256, 344 (br), 454 (v br).

6j: ^{1}H NMR ($CDCl_3$, δ) 8.76 (d, J = 7.8 Hz, 1H), 8.67 (d, J = 8.1 Hz, 1H), 8.41 (d, J = 7.8 Hz, 1H), 7.87 (s, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.72−7.54 (m, 4H), 7.36 (d, J = 6.6 Hz, 2H), 7.29 (d, J = 6.6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H), 7.17 (d, 7.5 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 209.3, 137.6, 132.2, 131.25, 131.18, 130.6, 130.5, 130.0, 128.9, 127.7, 127.4, 127.2, 127.0, 126.9, 124.9, 123.6, 122.9, 97.6, 95.9, 21.7; IR (KBr, cm^{-1}) 3083, 2995, 1938, 1596, 1512, 1449, 1246, 896, 825, 744; UV-vis (CH_2Cl_2) 232 (sh), 260, 304, 318.

6k: ^{1}H NMR ($CDCl_3$, δ) 7.30 (s, 4H), 7.25 (d, J = 7.5 Hz, 4H), 7.13 (d, J = 7.5 Hz, 4H), 6.58 (s, 4H), 2.35 (s, 4H); ^{13}C NMR ($CDCl_3$, δ) 208.3, 137.6, 133.2, 130.9, 129.9, 127.8, 127.4, 98.8, 98.6, 21.7; IR (CH_2Cl_2, cm^{-1}) 3026, 2924, 2866, 1934 (m), 1510 (s), 885 (s), 850 (s) 825 (s); UV-vis (CH_2Cl_2) 230, 242 (sh), 254, 282, 292, 376 (br).

6l: ^{1}H NMR ($CDCl_3$, δ) 7.19 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.68 (d, J = 6.3 Hz, 1H), 5.56 (d, J = 6.3 Hz, 1H), 2.33 (s, 3H), 1.125 (s, 9H); ^{13}C NMR ($CDCl_3$, δ) 202.5, 136.8, 132.7, 129.7, 126.7, 107.2, 96.4, 33.2, 30.7, 21.6; IR ($CDCl_3$, cm^{-1}) 3024, 2963, 2866, 1948, 1512, 1462, 1363, 1190, 826; UV-vis (CH_2Cl_2) 230, 255.

6m: ^{1}H NMR ($CDCl_3$, δ) 8.80−8.49 (br m, 3H), 7.66 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 6.65 (d, J = 6.3 Hz, 1H), 6.58 (d, J = 6.3 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 208.4, 153.8, 151.3, 148.8, 138.0, 137.4, 134.1, 130.0, 127.4, 124.0, 99.3, 95.6, 21.7; UV-vis (CH_2Cl_2) 230 (sh), 258, 284 (w sh), 354 (w), 372.

6n: ^{1}H NMR ($CDCl_3$, δ) 7.19 (d, J = 7.5 Hz, 2H), 7.1 (d, J = 7.5 Hz, 2H), 6.14−6.11 (m, 1H), 5.54 (t, J = 6.3 Hz, 1H), 2.32 (s, 3H), 1.85−1.35 (m, 11 H); ^{13}C NMR ($CDCl_3$, δ) 204.2, 136.7, 132.6, 129.7, 126.8, 101.4, 95.6, 38.1, 33.6, 33.5, 32.8, 26.6, 26.5, 21.6; IR (CH_2Cl_2, cm^{-1}) 3026 (w), 2926 (s), 2854 (s) 1946 (w), 1512, 1448, 873 (w), 825, 700 (br, m); UV-vis (CH_2Cl_2) 256.

6o: ^{1}H NMR ($CDCl_3$, δ) 7.21 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.21 (d, J = 6.3 Hz, 1H), 5.46 (d, J = 6.9 Hz, 1H), 2.35 (s, 3H), 1.39−1.29 (m, 1H), 0.78−0.68 (m, 2H), 0.49−0.45 (1H); ^{13}C NMR ($CDCl_3$, δ) 204.9, 137.0, 132.4, 129.7, 127.0, 99.7, 96.5, 21.6, 10.0, 7.3, 7.5; UV-vis (CH_2Cl_2) 232 (sh), 254.

6p: ^{1}H NMR ($CDCl_3$, δ) 7.81−7.74 (m, 4H), 7.54−7.43 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.77 (d, J = 6.6 Hz, 1H), 6.66 (d, J = 6.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 208.6, 137.7, 134.2, 133.2, 131.8, 131.0, 129.9, 128.8, 128.2, 127.4, 126.7, 126.3, 126.2, 125.2, 99.2, 98.9; IR ($CDCl_3$, cm^{-1}) 3057, 3026, 2926, 2864, 1936, 1512, 1163, 922, 825, 756, 718; UV-vis (CH_2Cl_2) 238, 262, 288, 300; mp 99−102 °C.

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Supporting Information Available: NMR spectra of allenes **6** and vinylphosphonium salt **3t**; summary of base screening and reaction optimization studies for the conversion of **3a** to allene **6a** (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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