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Use of Allenylphosphonates as New Substrates for Phosphane-Catalyzed [3+2] and [4+2] Annulations

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The suitability of allenylphosphonates as substrates in phosphane-catalyzed annulation reactions has been investigated. Despite their lower reactivity relative to allenyl esters, allenylphosphonates overall display the anticipated behavior: pyrrolines, tetrahydropyridines, and cyclopentenes bearing phosphoryl functions were obtained from imines, α,β-unsaturated esters, and enones in Bu_3P- or iBu_3P-promoted reactions. Enantioselective variants of these cyclization reactions afforded enantiomeric excesses of up to 90 % when phosphepine $\mathbf{A_2}$ was used as the chiral catalyst.

Introduction

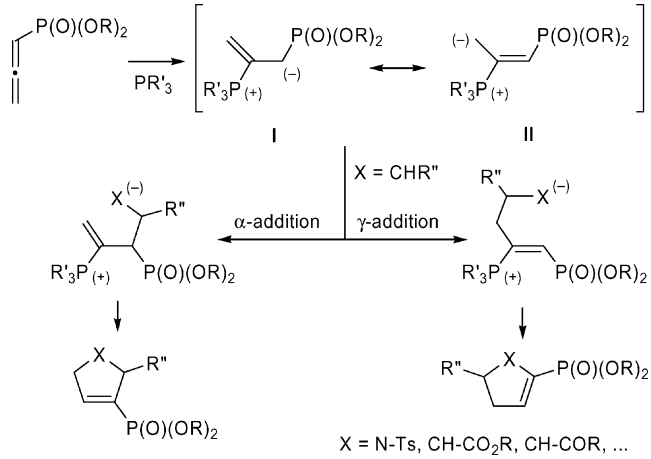
A number of literature reports show that electron-deficient allenes are suitable substrates for a range of phosphane-catalyzed transformations.[1] These involve the addition of a phosphorus nucleophile to the central carbon atom of the allene moiety as a key step, followed by reaction of the resulting dipole with electron-deficient substrates such as olefins (α,β-unsaturated esters, ketones, nitriles, sulfones, and nitroalkenes),[2] imines,[3] and aldehydes[4] in both inter- and intramolecular[2g] processes. In other instances, the zwitterionic phosphane–allene adduct causes deprotonation of weak acids and allows addition of the conjugated base to the allenic substrate in an "umpolung" approach.[5] The synthetic usefulness of these methods has been widely demonstrated[2g,6] and some enantioselective variants have been envisioned.[7]

So far, mainly buta-2,3-dienoates and, more recently, allenic ketones[7h,8] have been used as substrates in these phosphane-catalyzed processes. Thus, to extend the scope of the methodology, we have considered using allenylphosphonates as new substrates. Their transformations through phosphane-promoted reactions would give rise to versatile synthetic intermediates[9] as well as to a variety of unprecedented phosphoryl-functionalized compounds, including cyclic and heterocyclic frameworks, potentially relevant to agrochemical and medicinal chemistry.[10]

Herein, we report our investigations on the annulation reactions of allenylphosphonates with imines, α,β-unsaturated esters, and enones catalyzed by nucleophilic phosphanes and preliminary results on the use of enantiomerically pure promoters in the same reactions.

Results and Discussion

Dialkyl allenylphosphonates are readily available in multigram quantities from propargylic alcohols and dialkyl chlorophosphites[11] by thermally induced S_Ni'-type rearrangement of the intermediate 2-propynyl phosphites. Therefore they represent inexpensive and suitable starting materials in phosphonate chemistry.[12] The outcomes of their phosphane-promoted reactions with unsaturated electron-deficient substrates can be anticipated as a result of the possible activation of the allenic phosphonates by phosphane addition to the β-carbon atoms (Scheme 1).[1,3b] The resulting zwitterionic phosphonium salts are expected to re-



Scheme 1. Activation of allenylphosphonates by nucleophilic phosphanes.

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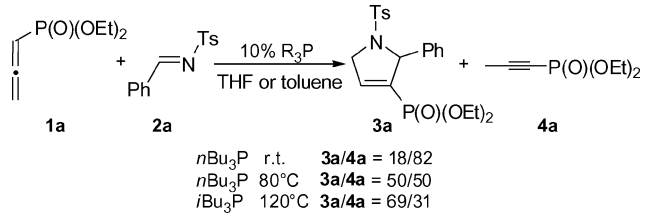
act then with electron-poor substrates (X=CHR′′ in Scheme 1, with X = NTs, $CHCO_2R$, CHCOR, etc.) via either their α- or γ-carbanionic forms **I** and **II**, respectively. Subsequent annulation would lead to the cyclic phosphonate derivatives.

In order to check the suitability of allenylphosphonates for such annulation processes, the reactivity of the allenylphosphonate **1a** was investigated first in the [3+2] cyclization reaction with *N*-tosylbenzaldimine (**2a**) (Scheme 2). With tributylphosphane as the catalyst, the reaction led to the anticipated pyrroline **3a** by formal addition of the α-carbanionic intermediate **I** to the imine, followed by cyclization, according to the reaction pathway postulated by Xu and Lu for allenic esters.[3b]



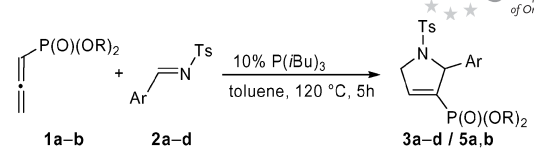
Scheme 2. [3+2] Annulation of diethyl allenylphosphonate (**1a**) with *N*-tosylbenzaldimine (**2a**).

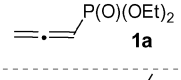
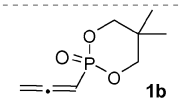
The allenylphosphonate displayed, however, much lower reactivity than the corresponding allenic ester: at room temperature, a reaction time of 4 d was required to afford total conversion of the starting allene. Moreover, the reaction led to an 18:82 mixture of the pyrroline **3a** and prop-1-ynylphosphonate **4a**, which shows that prototropic isomerization of the allenyl phosphonate, known to proceed in the presence of organic bases,[11c,13] may occur as a major competitive reaction. Changing the reaction conditions improved, however, the product distribution. Thus, for instance, running the reaction at 80 °C in THF improved the product distribution up to a 50:50 ratio of **3a**/**4a**. Finally, the highest conversion rate was attained when the reaction was run at high temperature (120 °C) in toluene in the presence of excess imine (allenylphosphonate/imine ratio = 1:2) with P(*i*Bu)$_3$ as the catalyst. Under these conditions, the amount of **3a** obtained increased to 69%. Total conversion was achieved after 5 h.

The optimized conditions above were then applied in further experiments in which the arylimine reactant and the phosphonate ester moiety were varied in order to evaluate the scope of the reaction (Scheme 3).

Starting from the *p*-nitrobenzaldimine **2b**, the desired pyrroline **3b** was predominantly formed (85:15 ratio of **3b**/**4a**), whereas with imines **2c** and **2d** the side-reaction that leads to the isomerization product predominates over the cyclization reaction. Therefore, only moderate conversion rates to **3c** and **3d** were observed. The cyclic phosphonate **1b**[14] displayed lower reactivity than **1a**.

The formation of the alkyne byproduct **4** thus represents a major drawback of the above reactions, all the more so because the mixture of **3** and **4** is difficult to separate by

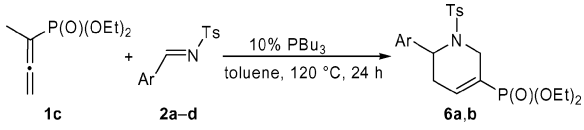


	Phosphonate	Ar (imine)	Product	Conv.
1		Ph (**2a**)	**3a**	69[a]
2		*p*-$NO_2C_6H_4$ (**2b**)	**3b**	71[b]
3		*p*-$MeOC_6H_4$ (**2c**)	**3c**	44[b]
4		*o*-Me C_6H_4 (**2d**)	**3d**	33[b]
5		Ph (**2a**)	**5a**	66[b]
6		*p*-$NO_2C_6H_4$ (**2b**)	**5b**	35[c]

Scheme 3. Triisobutylphosphane-catalyzed [3+2] annulations of allenylphosphonates with imines. Conditions: 1:2 phosphonate/imine ratio. Conversion rates refer to the amount of pyrroline in the crude reaction mixture (^{1}H NMR) with respect to the total amount of phosphonate derivatives. Total conversion of the starting phosphonate was mainly observed. Isolated yields: [a] 40%; [b] 20–30%; [c] not determined.

chromatography and, consequently, only moderate-to-low yields (20–40%) of the pure pyrrolines **3** could be obtained. The alkyne byproduct **4** could not be further converted into the desired pyrroline, even after prolonged heating at 120 °C in the presence of *N*-tosylbenzaldimine and PBu_3, at variance with the known behavior of but-2-ynoates, which usually undergo phosphane-promoted cyclizations.[3b]

Better results were obtained in a second series of experiments (Scheme 4) in which the α-substituted diethyl buta-2,3-dienylphosphonate (**1c**)[15] was treated with various imines with the aim of accessing functionalized tetrahydropyridines.[3c] The anticipated formal [4+2] cyclization reactions are supposed to involve addition of the γ-carbanion **II** (Scheme 1) to the imine and subsequent cyclization.



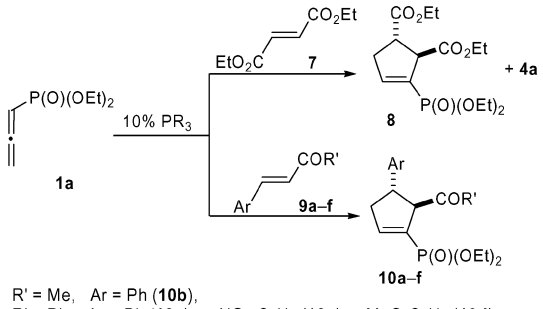
Entry	Ar (imine)	Prod.	Yield (%)
1	C_6H_5 (**2a**)	**6a**	70
2	*p*-$NO_2C_6H_4$ (**2b**)	–	0
3	*p*-$MeOC_6H_4$ (**2c**)	**6c**	74
4	*o*-Me C_6H_4 (**2d**)	**6d**	75

Scheme 4. [4+2] Annulation reactions of allenylphosphonate **1c** with imines.

As shown in Scheme 4, the expected 3-phosphoryl-tetrahydropyridines **6a**,**c**,**d** were obtained in good yields. PBu_3 is a suitable catalyst leading to total conversion of **1c** after 24 h at 120 °C, whereas P(*i*Bu$_3$) displayed rather moderate catalytic activity (60% conversion of **1c** into **6a** under the same conditions). Of the four imines tested so far, only the *p*-nitrophenyl-substituted imine **2b** failed to react in the [4+2] cyclization reaction, although its electron-poor character would be expected to favor nucleophilic additions. In-

hibition of the reaction might result from extra stabilization of a zwitterionic intermediate by the electron-withdrawing *p*-NO_2-phenyl moiety.

The phosphane-promoted annulations of allenylphosphonates were then extended to electrophilic alkenes as cyclization partners. Since the pioneering work of Zhang and Lu,[2a] alkenes bearing electron-withdrawing substituents are known to react with electron-deficient allenes under phosphane catalysis to give cyclopentenes through formal [3+2] cycloaddition reactions.[2d,2e,7d] Analogous reactions were performed therefore starting from the allenylphosphonate **1a** (Scheme 5).



R' = Me, Ar = Ph (**10b**),
R' = Ph, Ar = Ph (**10a**), *p*-NO_2-C_6H_4 (**10c**), *p*-MeO-C_6H_4 (**10d**), 2-furyl (**10e**), 1-naphthyl (**10f**)

Entry	Catalyst	Olefin	Product	Conv. (yield)
1	PPh_3	**7**	**8**	0
2	PBu_3	**7**	**8**	61
3	P(*i*Bu)$_3$	**7**	**8**	90(80)
4	P(*i*Bu)$_3$	**9a**	**10a**	72 (50)
5		**9b**	**10b**	78 (34)
6		**9c**	**10c**	83(35)
7		**9d**	**10d**	70(40)
8		**9e**	**10e**	69(25)
9		**9f**	**10f**	81(42)

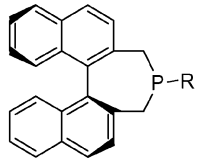
Scheme 5. [3+2] Annulations of allenylphosphonate **1a** with electron-poor alkenes. Reaction conditions: experiments were performed in toluene at 120 °C for 24 h with an allenylphosphonate/olefin ratio of 1:2 at a phosphonate concentration of 0.1 M. Conversion rates refer to the amount of **8** or **10** in the crude reaction mixture.

In the reaction of the allenylphosphonate **1a** with diethyl fumarate, a mixture of the desired cyclopentenylphosphonate **8** and the alkyne **4a** were obtained, the relative amounts of which were highly dependent on the reaction conditions (catalyst, temperature, solvent, and dilution). Optimized conditions involve a high temperature (120 °C), the use of toluene as solvent,[16] a 0.1 M concentration of substrates, and 10 mol-% of P(*i*Bu)$_3$ as the catalyst. Total conversion of the starting allene was achieved after 5 h and an **8**/**4a** ratio of 90:10 was observed in the crude reaction mixture (entry 3). The higher efficiency of P(*i*Bu)$_3$ (entry 3 vs. 2) might be assigned to its lower basicity [pK_a($MeNO_2$) = 7.97][17] with respect to PBu_3 [pK_a ($MeNO_2$) = 8.43], as more basic phosphanes are expected to favor the competitive isomerization of the allenylphosphonate to diethyl propynylphosphonate.[18] The amount of phosphane catalyst could be reduced to 5% without a significant decrease in the conversion rate or the **8**/**4a** ratio.

The cyclopentenylphosphonate **8** was isolated as a single diastereomer. The *trans* stereochemistry was assigned to this compound on the basis of the coupling constants of the ring hydrogen atoms and by analogy to literature data.[2a,19]

The α,β-unsaturated enones **9a**–**f** also underwent formal [3+2] cycloaddition reactions with **1a** to afford the corresponding cyclopentenones **10** with excellent regio- and stereoselectivity. The geometry of the starting olefins is retained in the cyclization reactions, which thus give the *trans* isomers of **10**.[20] If we assume that a stepwise mechanism is taking place here,[21] it appears that **10** results from attack of the γ-carbanionic form **II** of the dipole intermediate (Scheme 1) on the enone substrate. Potentially competitive α-addition processes were not unambiguously noticed in these experiments: small amounts of side-products were observed in the crude reaction mixtures, but they were not isolated in pure form. In the analogous cyclization reactions of allenic esters with electron-poor olefins both α and γ additions were reported, with products ratios ranging from 1 to 30. As a general trend, α addition took place preferentially when terminal olefins were used as cyclization partners,[2a,2d,7a] whereas chalcone and other substituted olefins mainly afforded the γ-addition products.[7d,7i]

Having determined that the behavior of allenylphosphonates in phosphane-promoted reactions with both imines and electron-poor olefins parallels that of the corresponding allenic esters, we next envisioned an enantioselective version of the same cyclization reactions. As a preliminary investigation, we explored the use of phosphepines **A**[22] as chiral catalysts for the same transformations.



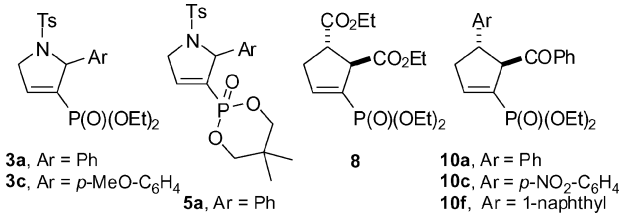
(*S*)-$\mathbf{A_1}$ R = Ph
(*S*)-$\mathbf{A_2}$ R = *t*Bu

Phosphepines **A** have previously been used in enantioselective [3+2] cyclization reactions between buta-2,3-dienoates and both imines[7g] and chalcones[7d] as well as in [4+2] annulations.[7c] In this work, the potential of phosphepines (*S*)-$\mathbf{A_1}$ and (*S*)-$\mathbf{A_2}$ as chiral catalysts was evaluated in the cyclization reactions that lead to phosphonates **3**, **5**, **8**, and **10** (Table 1).

Phosphepines **A** displayed moderate-to-low conversion rates because of the above-mentioned isomerization of the allenylphosphonates to the corresponding alkynes, which here becomes highly competitive. A high reaction temperature was required to ensure total conversion of the starting material as well as to reduce the amount of alkyne side-product. Nevertheless, despite the harsh reaction conditions, high enantioselectivities could be attained, in some instances at least, when using the *tert*-butyl-substituted phosphepine $\mathbf{A_2}$ as the catalyst (Table 1).

When the reactions between **1a** and imines **2a** and **2c** were performed at 120 °C with phosphepine $\mathbf{A_2}$ as the catalyst, pyrrolines **3a** and **3c** were obtained in moderate enan-

Table 1. Asymmetric [3+2] cyclization reactions of allenylphosphonates **1a** and **1b** promoted by phosphepines (*S*)-$\mathbf{A_2}$.



3a, Ar = Ph
3c, Ar = *p*-MeO-C_6H_4
5a, Ar = Ph
8
10a, Ar = Ph
10c, Ar = *p*-NO_2-C_6H_4
10f, Ar = 1-naphthyl

Entry	Product	Reaction conditions[a]	Conv. (% yield)	% *ee*
1	**3a**	dioxane, 80 °C	25	68
2	**3a**	dioxane, 120 °C	45	57
3	**3c**	dioxane, 120 °C	25	58
4	**5a**	dioxane, 120 °C	30	65
5	**8**	toluene, 120 °C	70 (55)	91
6	**10a**	toluene, 120 °C[b]	35	89
7	**10c**	toluene, 120 °C	61 (35)	85
8	**10f**	toluene, 120 °C	9	81

[a] Reaction time: 24 h, 10 mol-% catalyst, 1:2 reactant ratio. Enantiomeric excesses (*ee*) were determined by chiral HPLC. [b] Reaction time: 48 h.

tiomeric excesses (57 and 58%, respectively, entries 2 and 3). The *ee* was slightly higher at a lower temperature (**3a**: *ee* 68% at 80 °C, entry 1). The *P*-phenyl-substituted phosphepine $\mathbf{A_1}$ afforded very low enantioselectivities. As an example, when the cyclization leading to **3a** was performed with $\mathbf{A_1}$ as the catalyst at 80 °C in THF, an *ee* of <10% was obtained.

In the [3+2] cyclization between **1a** and diethyl fumarate, cyclopentenylphosphonate **8** was obtained in up to 91% *ee* (entry 5). For comparison purposes it is worth noting that the analogous reaction of ethyl buta-2,3-dienoate with diethyl fumarate, promoted by phosphepine (*S*)-$\mathbf{A_2}$, afforded triethyl cyclopent-3-ene-1,2,3-tricarboxylate[2a,7a] in comparable *ee* (93% *ee*).[23]

The annulations between phosphonate **1a** and the enones (entries 6–8) led to enantiomeric excesses of up to 89%, which are fully comparable to those obtained by Wilson and Fu[7d] in the reactions between ethyl buta-2,3-dienoate and enones with phosphepine (*S*)-$\mathbf{A_2}$ as the catalyst. Enones **9d** and **9e** failed to react under the above conditions.

From these preliminary experiments it appears that phosphepine (*S*)-$\mathbf{A_2}$ is a suitable catalyst for enantioselective annulations of allenylphosphonate **1a** with electron-poor olefins, as far as enantioselectivity levels are concerned. These reactions are hampered, however, by rather moderate conversion rates.

Conclusions

We have shown that allenic phosphonates can be used as substrates in some phosphane-catalyzed [3+2] and [4+2] annulation reactions leading to new phosphonate derivatives. The scope and limitations of these reactions have been investigated. The use of the binaphthyl-derived phosphepine (*S*)-$\mathbf{A_2}$ allowed asymmetric versions of the [3+2] annulations to be performed with moderate-to-high enantioselectivity levels.

Experimental Section

Diethyl (propa-1,2-dienyl)phosphonate (**1a**),[11a] (5,5-dimethyl-2-oxo-2-propa-1,2-dienyl)-1,3,2-dioxaphosphinane (**1b**)[14] and diethyl (buta-2,3-dien-2-yl)phosphonate (**1c**)[15] were prepared by thermal rearrangement of the corresponding 2-propynyl phosphites as described in the literature.

[3+2] Cyclization Reactions between Allenylphosphonates and Imines. Typical Procedure: The allenylphosphonate (0.3 mmol, 53 mg of **1a** or 56 mg of **1b**) and the imine (0.3 mmol, e.g., 78 mg of *N*-tosylbenzaldimine) were dissolved in anhydrous solvent (1 mL) under argon in an oven-dried 5 mL vial. A 1 M solution of the phosphane catalyst in toluene (30 μL, 0.03 mmol) was added. The vial was capped and the reaction mixture was heated at the given temperature for 24 h. The solvent was removed and the conversion rate and product ratio were determined by ^{1}H NMR analysis. The final pyrroline was purified by column chromatography. Enantiomeric excesses were determined by chiral HPLC.

Diethyl (2-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)phosphonate (3a): Purification was performed by silica gel column chromatography with heptane/ethyl acetate (2:8) as the eluent (R_f = 0.3). Pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 13 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, ^3J = 7.0 Hz, 3 H, Me), 1.18 (t, ^3J = 7.0 Hz, 3 H, Me), 2.39 (s, 3 H, Me), 3.44–3.52 (m, 1 H, OCH_2), 3.7–3.8 (m, 2 H, OCH_2), 3.8–3.9 (m, 1 H, OCH_2), 4.40 (m, $^2J_{AB}$ = 12 Hz, 1 H, NCH_2), 4.51 (m, $^2J_{AB}$ = 12 Hz, 1 H, NCH_2), 5.67 (1 H, NCHPh), 6.68 (d, $^3J_{H,P}$ = 11.8 Hz, 1 H, C=CH), 7.17 (d, ^3J = 8.0 Hz, 2 H, Ts), 7.2–7.4 (5 H, Ph), 7.46 (d, ^3J = 8.0 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.7 (d, $^3J_{C,P}$ = 7.1 Hz, Me), 16.1 (d, $^3J_{C,P}$ = 6.6 Hz, Me), 21.4 (Me), 55.8 (d, $^3J_{C,P}$ = 22.9 Hz, NCH_2), 61.8 (d, $^2J_{C,P}$ = 8.5 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 8.8 Hz, OCH_2), 71.1 (d, $^2J_{C,P}$ = 19.7 Hz, N*C*HPh), 127.1, 127.7, 128.1, 128.3, 129.4, 134.1 (d, $^1J_{C,P}$ = 196 Hz, =C,P), 135.4 (C), 139.1 (C), 140.1 (d, $^2J_{C,P}$ = 11.8 Hz, *C*H=C), 143.4 (*C*-Me) ppm. HRMS: calcd. for $C_{21}H_{26}NNaO_5PS$ 458.1167; found 458.1201. HPLC: Kromasil column, *n*-heptane/*i*PrOH (8:2), 1 mL/min, 14 and 16 min (major).

Diethyl [2-(*p*-Nitrophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl]phosphonate (3b): Purification was performed by silica gel column chromatography with heptane/ethyl acetate (2:8) as the eluent (R_f = 0.3). Pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 9 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, ^3J = 7.0 Hz, 3 H, Me), 1.16 (t, ^3J = 7.0 Hz, 3 H, Me), 2.41 (s, 3 H, Me), 3.6–3.7 (m, 1 H, OCH_2), 3.8–4.0 (m, 2 H, OCH_2), 4.0–4.1 (m, 1 H, OCH_2), 4.50 (2 H, NCH_2), 5.71 (1 H, NCHPh), 6.72 (d, $^3J_{H,P}$ = 10.9 Hz, 1 H, C=CH), 7.25 (d, ^3J = 8.1 Hz, 2 H, Ts), 7.46 (d, ^3J = 8.6 Hz, 2 H), 7.54 (d, ^3J = 8.1 Hz, 2 H, Ts), 8.16 (d, ^3J = 8.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.9 (d, $^3J_{C,P}$ = 6.7 Hz, Me), 16.2 (d, $^3J_{C,P}$ = 6.3 Hz, Me), 21.5 (Me), 56.1 (d, $^3J_{C,P}$ = 17.2 Hz, NCH_2), 62.1 (d, $^2J_{C,P}$ = 5 Hz, OCH_2), 62.2 (d, $^2J_{C,P}$ = 5 Hz, OCH_2), 70.3 (d, $^2J_{C,P}$ = 19.5 Hz, N*C*HPh), 123.5, 127.2, 128.7, 129.8, 133.2 (d, $^1J_{C,P}$ = 197 Hz, =C,P), 134.7 (C), 140.7 (d, $^2J_{C,P}$ = 11.5 Hz, *C*H=C), 144.2 (C-Me), 146.7 (C), 148.1 (C) ppm. HRMS: calcd. for $C_{21}H_{25}N_2NaO_7PS$ 503.1018; found 503.1006.

Diethyl [2-(*p*-Methoxyphenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl]-phosphonate (3c): Purification was performed by silica gel column

chromatography with heptane/ethyl acetate (2:8) as the eluent (R_f = 0.3). Pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 10 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.0 Hz, 3 H, Me), 1.17 (t, ^3J = 7.0 Hz, 3 H, Me), 2.38 (s, 3 H, Me), 3.5–3.6 (m, 1 H, OCH_2), 3.7–3.9 (m, 3 H, OCH_2), 3.78 (s, 3 H, OMe), 4.34 (m, 1 H, NCH_2), 4.48 (m, 1 H, NCH_2), 5.62 (1 H, NCHPh), 6.62 (d, $^3J_{H,P}$ = 12.0 Hz, 1 H, C=CH), 6.78 (d, ^3J = 8.7 Hz, 2 H), 7.13 (d, ^3J = 8.7 Hz, 2 H), 7.17 (d, ^3J = 8.2 Hz, 2 H, Ts), 7.46 (d, ^3J = 8.2 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.8 (d, $^3J_{C,P}$ = 7.0 Hz, Me), 16.2 (d, $^3J_{C,P}$ = 6.6 Hz, Me), 21.5 (Me), 55.3 (OMe), 55.6 (d, $^3J_{C,P}$ = 17.4 Hz, NCH_2), 61.9 (d, $^2J_{C,P}$ = 6 Hz, OCH_2), 62.0 (d, $^2J_{C,P}$ = 6 Hz, OCH_2), 70.6 (d, $^2J_{C,P}$ = 19.8 Hz, N*C*HPh), 113.6, 127.1, 128.9, 129.4, 131.3 (C), 134.0 (d, $^1J_{C,P}$ = 196 Hz, =C,P), 135.5 (C), 139.8 (d, $^2J_{C,P}$ = 11.8 Hz, *C*H=C), 143.3 (*C*-Me), 159.5 (C-OMe) ppm. HRMS: calcd. for $C_{22}H_{28}NNaO_6PS$ 488.1273; found 488.1272. HPLC: Chiracel AD, heptanes/*i*PrOH (80:20), 1 mL/min, 15.0 (major) and 17.2 min.

Diethyl [2-(*o*-Tolyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl]phosphonate (3d): Purification was performed by silica gel column chromatography with heptane/ethyl acetate (2:8) as the eluent (R_f = 0.3). Pale-yellow solid, m.p. 90 °C. ^{31}P NMR ($CDCl_3$): δ = 10 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.0 Hz, 3 H, Me), 1.18 (t, ^3J = 7.1 Hz, 3 H, Me), 2.38 (s, 3 H, Me), 2.49 (s, 3 H, Me), 3.4 (m, 1 H, OCH_2), 3.7–3.9 (m, 3 H, OCH_2), 4.42 (m, $^2J_{AB}$ = 16 Hz, 1 H, NCH_2), 4.54 (m, $^2J_{AB}$ = 16 Hz, 1 H, NCH_2), 6.02 (1 H, NCHPh), 6.69 (d, $^3J_{H,P}$ = 11.6 Hz, 1 H, C=CH), 6.9–7.1 (4 H, CH_{Tol}), 7.14 (d, ^3J = 8.4 Hz, 2 H, Ts), 7.40 (d, ^3J = 8.4 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.7 (d, $^3J_{C,P}$ = 6.9 Hz, Me), 16.1 (d, $^3J_{C,P}$ = 6.3 Hz, Me), 19.0 (Me), 21.4 (Me), 55.8 (d, $^3J_{C,P}$ = 22.9 Hz, NCH_2), 61.8 (d, $^2J_{C,P}$ = 5 Hz, OCH_2), 61.9 (d, $^2J_{C,P}$ = 5 Hz, OCH_2), 67.1 (d, $^2J_{C,P}$ = 20 Hz, N*C*HPh), 126.0, 127.0, 127.8, 128.0, 129.4, 130.5, 134.0 (d, $^1J_{C,P}$ = 199 Hz, =C,P), 135.7 (C), 136.2 (C), 137.3 (C), 140.0 (d, $^2J_{C,P}$ = 12.2 Hz, *C*H=C), 143.2 (C-Me) ppm. HRMS: calcd. for $C_{22}H_{28}NNaO_5PS$ 472.1324; found 472.1313.

5,5-Dimethyl-2-oxo-2-(2-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)-1,3,2-dioxaphosphinane (5a): Purification was performed by silica gel column chromatography with heptane/ethyl acetate (3:7) as the eluent (R_f = 0.2). Colorless solid, m.p. 186 °C. ^{31}P NMR ($CDCl_3$): δ = 5 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.70 (s, 3 H, Me), 0.98 (s, 3 H, Me), 2.37 (s, 3 H, Me), 3.40 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 3.43 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 3.76 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 3.92 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 4.39 (m, $^2J_{AB}$ = 16.5 Hz, 1 H, NCH_2), 4.89 (m, $^2J_{AB}$ = 16.5 Hz, 1 H, NCH_2), 5.75 (1 H, NCHPh), 6.73 (d, $^3J_{H,P}$ = 12.5 Hz, 1 H, C=CH), 7.16 (d, ^3J = 8.0 Hz, 2 H, Ts), 7.3–7.4 (5 H, Ph), 7.43 (d, ^3J = 8.0 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.1 (Me), 21.5 (Me), 21.6 (Me), 32.2 (d, $^3J_{C,P}$ = 6.7 Hz, *C*Me$_2$), 55.7 (d, $^3J_{C,P}$ = 17.2 Hz, NCH_2), 70.9 (d, $^2J_{C,P}$ = 20.6 Hz, N*C*HPh), 75.8 (d, $^2J_{C,P}$ = 85.0 Hz, OCH_2), 75.9 (d, $^2J_{C,P}$ = 85.1 Hz, OCH_2), 127.1, 128.1, 128.4, 129.6, 132.6 (d, $^1J_{C,P}$ = 194 Hz, =C,P), 135.2 (C), 138.7 (C), 141.4 (d, $^2J_{C,P}$ = 11.3 Hz, *C*H=C), 143.5 (*C*-Me) ppm. HRMS: calcd. for $C_{22}H_{26}NNaO_5PS$ 470.1167; found 470.1187. HPLC: Chiralpak AD column, heptane/2-propanol (80:20), 1 mL/min, 18.9 (major) and 24.9 min.

5,5-Dimethyl-2-oxo-2-[2-(*p*-nitrophenyl)-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl]-1,3,2-dioxaphosphinane (5b): Purification was performed by silica gel column chromatography with heptane/ethyl acetate (3:7) as the eluent (R_f = 0.2). Pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 4 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.82 (s, 3 H, Me), 0.97 (s, 3 H, Me), 2.40 (s, 3 H, Me), 3.48 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 3.63 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 3.86 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 4.06 (t, $J_{H,H}$ = $J_{H,P}$ = 11 Hz, 1 H, OCH_2), 4.48 (m, 2 H, NCH_2), 5.79 (1 H, NCHPh), 6.73 (d, $^3J_{H,P}$ = 11.9 Hz, 1 H, C=CH), 7.23 (d, ^3J = 8.0 Hz, 2 H, Ts), 7.48 (d, ^3J = 8.5 Hz, 2 H), 7.52 (d, ^3J = 8.0 Hz, 2 H, Ts), 8.14 (d, ^3J = 8.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.3 (Me), 21.5 (Me), 32.3 (d, $^3J_{C,P}$ = 6.4 Hz, *C*Me$_2$), 56.1 (d, $^3J_{C,P}$ = 16.9 Hz, NCH_2), 70.0 (d, $^2J_{C,P}$ = 20.5 Hz, N*C*HPh), 75.9 (d, $^2J_{C,P}$ = 108.8 Hz, OCH_2), 75.9 (d, $^2J_{C,P}$ = 109.1 Hz, OCH_2), 123.6, 127.2, 128.8, 129.9, 131.6 (d, $^1J_{C,P}$ = 196 Hz, =C,P), 134.5 (C), 141.6 (d, $^2J_{C,P}$ = 11.1 Hz, *C*H=C), 144.2 (C-Me), 146.0 (C), 147.8 (C) ppm. HRMS: calcd. for $C_{22}H_{26}N_2NaO_7PS$ 515.1018; found 515.1003.

[4+2] Cyclization Reactions Between Diethyl (Buta-2,3-dien-2-yl)-phosphonate (1c) and Imines. Typical Procedure: Diethyl (buta-2,3-dien-2-yl)phosphonate (**1c**) (0.3 mmol, 60 mg) and the imine (0.3 mmol) were dissolved in anhydrous toluene (1 mL) under Ar in an oven-dried 5 mL vial. A 1 M solution of the phosphane catalyst in toluene (30 μL, 0.03 mmol) was then added. The vial was capped and the reaction mixture heated at 120 °C for 24 h. The solvent was removed and the final product was purified by column chromatography.

Diethyl (6-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)phosphonate (6a): Column chromatography on silica gel with heptane/ethyl acetate (2:8) as the eluent afforded 94 mg (70% yield) of **6a** (R_f = 0.3) as a colorless solid, m.p. 81 °C. ^{31}P NMR ($CDCl_3$): δ = 15.6 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.11 (t, ^3J = 7.2 Hz, 3 H, Me), 1.31 (t, ^3J = 7.0 Hz, 3 H, Me), 2.43 (4 H, Me, CH_2), 2.63 (d, J = 18 Hz, 1 H, CH_2), 3.34 (d, $^2J_{AB}$ = 19 Hz, 1 H, NCH_2), 3.8 (m, 1 H, OCH_2), 3.9 (m, 1 H, OCH_2), 4.0 (m, 2 H, OCH_2), 4.29 (dd, $^2J_{AB}$ = 19, J = 5.2 Hz, 1 H, NCH_2), 5.34 (d, ^3J = 6.4 Hz, 1 H, NCHPh), 6.81 (d, $^3J_{H,P}$ = 21 Hz, 1 H, C=CH), 7.2–7.3 (7 H), 7.70 (d, ^3J = 8.0 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 6.1 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6.5 Hz, Me), 21.5 (Me), 26.5 (d, $^3J_{C,P}$ = 15.5 Hz, CH_2), 39.8 (d, $^2J_{C,P}$ = 17.4 Hz, NCH_2), 52.0 (N*C*HPh), 61.8 (d, $^2J_{C,P}$ = 5.1 Hz, OCH_2), 61.9 (d, $^2J_{C,P}$ = 5.4 Hz, OCH_2), 125.9 (d, $^1J_{C,P}$ = 184 Hz, =C,P), 127.0, 127.1, 127.2, 127.9, 128.5, 129.7, 137.5 (C), 137.9 (C), 139.8 (d, $^2J_{C,P}$ = 7.9 Hz, *C*H=C), 143.5 (C-Me) ppm. HRMS: calcd. for $C_{22}H_{28}NNaO_5PS$ 472.1324; found 472.1313.

Diethyl [6-(*p*-Methoxyphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]phosphonate (6c): Purification by column chromatography on silica gel with heptane/ethyl acetate (2:8) as the eluent afforded 107 mg (74% yield) of **6c** (R_f = 0.3) as a colorless solid, m.p. 92 °C. ^{31}P NMR ($CDCl_3$): δ = 15.7 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, ^3J = 7.0 Hz, 3 H, Me), 1.33 (t, ^3J = 7.0 Hz, 3 H, Me), 2.43 (4 H, Me, CH_2), 2.58 (br. d, 1 H, CH_2), 3.34 (d, $^2J_{AB}$ = 19 Hz, 1 H, NCH_2), 3.79 (s, 3 H, OMe), 3.8 (m, 1 H, OCH_2), 3.9 (m, 1 H, OCH_2), 4.0 (m, 2 H, OCH_2), 4.28 (dd, $^2J_{AB}$ = 19, J = 6.0 Hz, 1 H, NCH_2), 5.30 (d, ^3J = 7.0 Hz, 1 H, NCH), 6.8 (3 H, C=CH, $CH_{o\text{-}Me}$), 7.20 (d, ^3J = 8.5 Hz, 2 H, Ar), 7.27 (d, ^3J = 8.0 Hz, 2 H, Ar), 7.71 (d, ^3J = 8.5 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 5.5 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 5.9 Hz, Me), 21.5 (Me), 26.8 (d, $^3J_{C,P}$ = 15.3 Hz, CH_2), 39.7 (d, $^2J_{C,P}$ = 17.3 Hz, NCH_2), 51.6 (NCH), 55.3 (OMe), 61.8 (d, $^2J_{C,P}$ = 4.8 Hz, OCH_2), 61.9 (d, $^2J_{C,P}$ = 5.2 Hz, OCH_2), 113.8 ($CH_{o\text{-}MeO}$), 126.0 (d, $^1J_{C,P}$ = 184 Hz, =C,P), 127.0, 128.5, 129.7, 129.9 (C), 137.6 (C), 139.9 (d, $^2J_{C,P}$ = 7.7 Hz, *C*H=C), 143.5 (C-Me), 159.2 (*C*-OMe) ppm. HRMS: calcd. for $C_{23}H_{30}NNaO_6PS$ 502.1429; found 502.1397.

Diethyl [6-(*o*-Tolyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]phosphonate (6d): Purification by column chromatography on silica gel with heptane/ethyl acetate (2:8) as the eluent afforded 103 mg (75% yield) of **6d** (R_f = 0.25) as a colorless oil. ^{31}P NMR ($CDCl_3$): δ = 15.7 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.13 (t, ^3J = 7.0 Hz, 3 H, Me), 1.31 (t, ^3J = 7.0 Hz, 3 H, Me), 2.33 (s, 3 H, Me), 2.45 (s, 3 H, Me),

2.3–2.5 (2 H, CH_2), 3.24 (d, $^2J_{AB}$ = 19.0 Hz, 1 H, NCH_2), 3.8 (m, 1 H, OCH_2), 3.9 (m, 1 H, OCH_2), 4.0 (m, 2 H, OCH_2), 4.17 (dd, $^2J_{AB}$ = 19, J = 6.0 Hz, 1 H, NCH_2), 5.43 (d, ^3J = 6.5 Hz, 1 H, NCHPh), 6.71 (d, $^3J_{H,P}$ = 20.5 Hz, 1 H, C=CH), 6.9–7.0 (2 H), 7.1–7.2 (4 H), 7.65 (d, ^3J = 8.0 Hz, 2 H, Ts) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2 (d, $^3J_{C,P}$ = 6.2 Hz, Me), 16.4 (d, $^3J_{C,P}$ = 6.5 Hz, Me), 19.9 (Me), 21.5 (Me), 27.2 (d, $^3J_{C,P}$ = 15.3 Hz, CH_2), 40.1 (d, $^2J_{C,P}$ = 16.8 Hz, NCH_2), 50.0 (NCH), 61.9 (OCH_2), 125.5, 125.9, 126.1 (d, $^1J_{C,P}$ = 138 Hz, =C,P), 127.5, 128.3, 129.5, 131.4, 136.0 (C), 136.9 (C), 138.0 (C), 140.6 (d, $^2J_{C,P}$ = 8.2 Hz, *C*H=C), 143.6 (C-Me) ppm. HRMS: calcd. for $C_{23}H_{30}NNaO_5PS$ 486.1480; found 486.1462.

Synthesis of Diethyl 3-(Diethoxyphosphoryl)cyclopent-3-ene-1,2-dicarboxylate (8): The allenylphosphonate **1a** (0.5 mmol, 88 mg), diethyl fumarate (0.17 g, 1.0 mmol), and degassed toluene (5 mL) were introduced into a Schlenk tube under argon. The mixture was purged with argon and the phosphane catalyst [P(*i*Bu)$_3$, 0.05 mmol, 1 M solution in toluene] was added. The reaction mixture was heated at 120 °C for 24 h. After evaporation of the solvent, the conversion rate and the **8/4a** ratio was evaluated by ^{1}H NMR of the crude material. The final product was purified by column chromatography on silica gel with heptanes/AcOEt (2:8) as the eluent. R_f = 0.2. Yield 0.14 g (80%). Pale-yellow oil. ^{31}P NMR (300 MHz, $CDCl_3$): δ = 16 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.22–1.32 (12 H, Me), 2.83 (dddt, $^2J_{AB}$ = 18.3, ^3J = 6.3, J = 3.6, J = 2.4 Hz, 1 H, CH_2), 2.99 (dddt, $^2J_{AB}$ = 18.3, ^3J = 9.3, J = 3.6, J = 2.7 Hz, 1 H, CH_2), 3.54 (dt, ^3J = 9.3, ^3J = 6.3 Hz, 1 H, 1-H), 3.9–4.3 (9 H, OCH_2, 2-H), 6.75 (dq, $^3J_{H-P}$ = 11.1, J = 2.2 Hz, 1 H, =CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.1 (Me), 14.2 (Me), 16.3 (d, $^3J_{C,P}$ = 6 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6 Hz, Me), 37.0 (d, $^3J_{C,P}$ = 19.6 Hz, CH_2), 47.3 (d, $^3J_{C,P}$ = 10.6 Hz, C-1), 54.8 (d, $^2J_{C,P}$ = 14.1 Hz, C-2), 61.3 (OCH_2), 61.4 (OCH_2), 62.0 (d, $^2J_{C,P}$ = 5.7 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.4 Hz, OCH_2), 131.0 (d, $^1J_{C,P}$ = 192.8 Hz, CH=*C*,P), 149.5 (d, $^2J_{C,P}$ = 13.6 Hz, *C*H=C,P), 172.6 (CO_2), 173.2 (CO_2) ppm. HRMS: calcd. for $C_{15}H_{25}NaO_7P$ 371.1236; found 371.1228. HPLC: Chiracel OD-H, heptane/*i*PrOH (90:10), 1 mL/min, 7.2 (major) and 8.5 min.

[3+2] Cyclization Reactions between 1a and α,β-Unsaturated Ketones. Typical Procedure: The allenylphosphonate **1a** (0.5 mmol, 88 mg), the enone (1 mmol), and degassed toluene (2.5 mL) were introduced into a Schlenk tube under argon. The mixture was purged with argon and the phosphane catalyst [P(*i*Bu)$_3$, 0.05 mmol, 1 M solution in toluene] was added. The flask was dipped in an oil bath at 120 °C and the mixture was stirred for 24 h. After evaporation of the solvent, the conversion rate and the **10/4a** ratios were evaluated by ^{1}H NMR of the crude material. When significant amounts of residual allenylphosphonate **1a** or alkyne **4a** were observed in the final mixture, they were removed by Kugelrohr distillation (ca. 90 °C/6 × 10^{-5} bar). The final product was purified by column chromatography on silica gel. The same procedure was applied to the reactions of **1a** (0.3 mmol) with enones **9a**, **9c**, and **9f** (1.2 mmol) in the presence of phosphepine (*S*)-**A$_2$** (11 mg, 0.03 mmol).

Diethyl (5-Benzoyl-4-phenylcyclopenten-1-yl)phosphonate (10a): Purification by column chromatography with heptane/ethyl acetate (3:7) as the eluent afforded 95 mg (50% yield) of **10a** (R_f = 0.3) as a pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 14 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, ^3J = 6.9 Hz, 6 H, Me), 2.72 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.26 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.75 (m, 1 H, 4-H), 3.9–4.0 (4 H, OCH_2), 4.86 (1 H, 5-H), 7.03 (d, $^2J_{H,P}$ = 11.1 Hz, 1 H, CH=C,P), 7.2–7.3 (5 H, Ph), 7.4 (2 H, Ph), 7.55 (1 H, Ph), 7.88 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 6.9 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6.6 Hz, Me), 42.9 (d, $^3J_{C,P}$ = 19.9 Hz, CH_2), 49.6 (d, $^3J_{C,P}$ = 10.3 Hz, *C*HPh), 61.4 (d, $^2J_{C,P}$ = 12.8 Hz, *C*HCOPh), 61.7 (d, $^2J_{C,P}$ = 5.7 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.3 Hz, OCH_2), 126.8, 127.1, 128.6, 128.9, 129.0, 132.1 (d, $^1J_{C,P}$ = 189.4 Hz, CH=*C*,P), 133.3, 136.8 (C), 145.0 (C), 150.7 (d, $^2J_{C,P}$ = 14.0 Hz, *C*H=C,P), 200.0 (COPh) ppm. HRMS: calcd. for $C_{22}H_{25}NaO_4P$ 407.1388; found 407.1390. HPLC: Kromasil 3-cellucoat column, heptane/2-propanol (97:3), 1 mL/min, 12.7 and 14.4 min (major).

Diethyl (5-Acetyl-4-phenylcyclopenten-1-yl)phosphonate (10b): Purification by column chromatography with heptane/ethyl acetate (2:8) as the eluent (R_f = 0.2) afforded 55 mg of **10b** as a pale-yellow oil (34% yield; contains 8% of the minor isomer). ^{31}P NMR ($CDCl_3$): δ = 14 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7.0 Hz, 3 H, Me), 1.33 (t, ^3J = 7.0 Hz, 3 H, Me), 2.25 (s, Me), 2.69 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.16 (dddt, $^2J_{AB}$ = 18.3, ^3J = 9.0, J = 4.2, J = 2.4 Hz, 1 H, CH_2), 3.70 (dt, ^3J = 9.0, J = 5.4 Hz, 1 H, CH,Ph), 3.95–4.0 (1 H, CHCOMe), 4.0–4.2 (4 H, OCH_2), 6.91 (dq, $^2J_{H,P}$ = 11.1, J = 2.1 Hz, 1 H, CH=C,P), 7.2–7.35 (Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.3 (d, $^3J_{C,P}$ = 6.8 Hz, Me), 16.4 (d, $^3J_{C,P}$ = 6.6 Hz, Me), 30.6 (COMe), 42.7 (d, $^3J_{C,P}$ = 19.7 Hz, CH_2), 48.5 (d, $^3J_{C,P}$ = 10.6 Hz, CH,Ph), 61.9 (d, $^2J_{C,P}$ = 5.7 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.4 Hz, OCH_2), 67.4 (d, $^2J_{C,P}$ = 13.1 Hz, *C*HCOMe), 126.7, 127.0, 129.0, 131.7 (d, $^1J_{C,P}$ = 190.4 Hz, CH=*C*,P), 144.5 (C), 150.3 (d, $^2J_{C,P}$ = 13.6 Hz, *C*H=C,P), 208.4 (COMe) ppm. HRMS: calcd. for $C_{17}H_{23}NaO_4P$, 345.1232; found 345.1241.

Diethyl [5-Benzoyl-4-(*p*-nitrophenyl)cyclopenten-1-yl]phosphonate (10c): Purification by column chromatography with diethyl ether/ethanol (80:1) as the eluent afforded 75 mg (35% yield) of **10c** (R_f = 0.25) as a pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 13 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.0 Hz, 6 H, Me), 2.7 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.3 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.8–4.0 (m, 5 H, 4-H, OCH_2), 4.83 (1 H, CHCO), 6.99 (m, $^2J_{H,P}$ = 11.1 Hz, 1 H, CH=C,P), 7.35 (d, ^3J = 8.4 Hz, 2 H, Ar), 7.4 (2 H), 7.56 (1 H, Ph), 7.87 (d, ^3J = 8.4 Hz, 2 H, Ar), 8.15 (d, ^3J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 6.9 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6.5 Hz, Me), 42.6 (d, $^3J_{C,P}$ = 19.9 Hz, CH_2), 49.1 (d, $^3J_{C,P}$ = 10.5 Hz, CHAr), 60.8 (d, $^2J_{C,P}$ = 13.1 Hz, CHCOPh), 61.8 (d, $^2J_{C,P}$ = 5.9 Hz, OCH_2), 62.2 (d, $^2J_{C,P}$ = 5.5 Hz, OCH_2), 124.3, 127.7, 128.7, 128.8, 132.5 (d, $^1J_{C,P}$ = 190.5 Hz, CH=*C*,P), 133.7, 136.5 (C), 147.1 (C), 149.9 (d, $^2J_{C,P}$ = 13.8 Hz, *C*H=C,P), 152.3 (C), 199.3 (COPh) ppm. HRMS: calcd. for $C_{22}H_{24}NNaO_6P$ 452.1239; found 452.1246. HPLC: Chiracel OD-H, heptane/2-propanol (93:7), 1 mL/min, retention times 24.1 (major) and 28.1 min.

Diethyl [5-Benzoyl-4-(*p*-methoxyphenyl)cyclopenten-1-yl]phosphonate (10d): Purification by column chromatography with diethyl ether/ethanol (100:1) as the eluent afforded 82 mg (40% yield) of **10d** (R_f = 0.2) as a pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 14 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.0 Hz, 6 H, Me), 2.65 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.20 (m, $^2J_{AB}$ = 18.3 Hz, 1 H, CH_2), 3.67 (dt, ^3J = 8.7, J = 4.2 Hz, 1 H, 4-H), 3.77 (s, 3 H, OMe), 3.9–4.0 (4 H, OCH_2), 4.8 (m, 1 H, CHCO), 6.81 (d, ^3J = 8.7 Hz, 2 H, Ar), 6.99 (m, $^2J_{H,P}$ = 11.1 Hz, 1 H, CH=C,P), 7.09 (d, ^3J = 8.7 Hz, 2 H, Ar), 7.3–7.55 (3 H), 7.9 (2 H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2 (d, $^3J_{C,P}$ = 6.9 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6.7 Hz, Me), 43.1 (d, $^3J_{C,P}$ = 19.9 Hz, CH_2), 49.0 (d, $^3J_{C,P}$ = 10.2 Hz, CHAr), 55.4 (OMe), 61.7 (d, $^2J_{C,P}$ = 12 Hz, CHCOPh), 61.7 (d, $^2J_{C,P}$ = 6 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.2 Hz, OCH_2), 114.3, 127.8, 128.6, 128.9, 132.0 (d, $^1J_{C,P}$ = 193.4 Hz, CH=*C*,P), 133.3, 136.9 (C), 137.2 (C), 150.7 (d, $^2J_{C,P}$ = 13.8 Hz, *C*H=C,P), 158.6 (COMe), 200.1 (COPh) ppm. HRMS: calcd. for $C_{23}H_{27}NNaO_6P$ 437.1494; found 437.1492.

Diethyl [5-Benzoyl-4-(2-furyl)cyclopenten-1-yl]phosphonate (10e): Purification by column chromatography with diethyl ether/ethanol (100:1) as the eluent afforded 47 mg (25% yield) of **10e** (R_f = 0.3) as a yellow oil. ^{31}P NMR ($CDCl_3$): δ = 14 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.0 Hz, 3 H, Me), 1.14 (t, ^3J = 7.0 Hz, 3 H, Me), 2.80 (m, $^2J_{AB}$ = 18.0 Hz, 1 H, CH_2), 3.10 (dddt, $^2J_{AB}$ = 18.0, ^3J = 8.4, J = 4.2, J = 2.1 Hz, 1 H, CH_2), 3.9–4.0 (5 H, OCH_2, 4-H), 4.9 (m, 1 H, CHCO), 6.03 (d, ^3J = 3.0 Hz, 1 H, CH_{furyl}), 6.26 (dd, ^3J = 3.0, ^3J = 1.8 Hz 1 H, CH_{furyl}), 6.95 (m, $^2J_{H,P}$ = 11.1 Hz, 1 H, CH=C,P), 7.31 (1 H), 7.4–7.6 (3 H), 7.98 (2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1 (d, $^3J_{C,P}$ = 7.3 Hz, Me), 16.2 (d, $^3J_{C,P}$ = 7.1 Hz, Me), 39.4 (d, $^3J_{C,P}$ = 19.8 Hz, CH_2), 43.1 (d, $^3J_{C,P}$ = 10.8 Hz, CHAr), 58.3 (d, $^2J_{C,P}$ = 13.2 Hz, CHCOPh), 61.7 (d, $^2J_{C,P}$ = 5.6 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.2 Hz, OCH_2), 105.2 (C=CH_{furyl}), 110.3 (C=CH=CH_{furyl}), 128.6, 128.9, 131.9 (d, $^1J_{C,P}$ = 191.8 Hz, CH=C,P), 133.4, 136.9 (C), 141.9 (OCH=CH_{furyl}), 150.2 (d, $^2J_{C,P}$ = 13.7 Hz, CH=C,P), 156.5 (O-C_{furyl}), 200.0 (COPh) ppm. HRMS: calcd. for $C_{20}H_{23}NaO_5P$, 397.1181; found 397.1176.

Diethyl [5-Benzoyl-4-(1-naphthyl)cyclopenten-1-yl]phosphonate (10f): Purification by column chromatography with heptane/ethyl acetate (2:8) as the eluent afforded 91 mg (42% yield) of **10f** (R_f = 0.4) as a pale-yellow oil. ^{31}P NMR ($CDCl_3$): δ = 14 ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 6.9 Hz, 3 H, Me), 1.18 (t, ^3J = 6.9 Hz, 3 H, Me), 2.81 (m, $^2J_{AB}$ = 18.6 Hz, 1 H, CH_2), 3.4–3.6 (m, $^2J_{AB}$ = 18.6 Hz, 1 H, CH_2), 4.0 (m, 4 H, OCH_2), 4.55 (m, 1 H, 4-H), 5.1 (m, 1 H, CHCO), 7.07 (m, $^2J_{H,P}$ = 10.1 Hz, 1 H, CH=C,P), 7.3–7.5 (7 H), 7.8 (1 H), 7.9 (4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.2 (d, $^3J_{C,P}$ = 6.9 Hz, Me), 16.3 (d, $^3J_{C,P}$ = 6.6 Hz, Me), 42.8 (d, $^3J_{C,P}$ = 20.2 Hz, CH_2), 45.3 (d, $^3J_{C,P}$ = 7.1 Hz, CHAr), 60.2 (d, $^2J_{C,P}$ = 13 Hz, CHCOPh), 61.8 (d, $^2J_{C,P}$ = 5.8 Hz, OCH_2), 62.1 (d, $^2J_{C,P}$ = 5.3 Hz, OCH_2), 123.3, 123.6, 125.6, 125.7, 126.2, 127.6, 128.5, 128.8, 129.1, 130.9 (C), 132.4 (d, $^1J_{C,P}$ = 191.4 Hz, CH=C,P), 133.4, 134.2, 136.8, 140.4 (C), 150.7 (d, $^2J_{C,P}$ = 13.9 Hz, CH=C,P), 200.5 (COPh) ppm. HRMS: calcd. for $C_{26}H_{27}NaO_4P$ 457.1545; found 457.1540. HPLC: Kromasil 3-cellucoat heptane/2-propanol (97:3), 1 mL/min, retention times 18.1 (major) and 23.7 min.

Supporting Information (see also the footnote on the first page of this article): ^{13}C NMR spectra for compounds **3a**–**d**, **5a**,**b**, **6a**,**c**,**d**, **8**, **10a**–**f**.

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[19] The coupling constants for vicinal hydrogen atoms in the cyclopentene ring of compound **8** are J_{cis} = 9.3 Hz and J_{trans} = 6.3 Hz. The observed coupling constant for CH(1) to CH(2) is 6.3 Hz.

[20] Assignment based on the coupling constants of ring hydrogen atoms in the ^{1}H NMR spectra, $^3J_{cis}$ being usually larger than $^3J_{trans}$.

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