Carbanion-Accelerated Claisen Rearrangements. 8. Phosphonamide Anion-Stabilizing Groups

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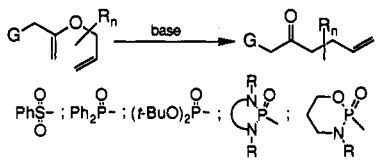
The utility of various phosphonamide groups has been examined in the context of the carbanion-accelerated Claisen rearrangement (CACR). An extensive survey has identified the *N,N'*-dibenzyl-1,3,2-diazaphospholidine group **11** to be optimal in the ease of construction of the CACR precursors and the facility and stereoselectivity of the rearrangement. Using *n*-butyllithium as the base, the phosphonamides rearranged readily at −20 °C with complete regioselectivity and in good yield (74–79%). The phosphonates also showed a high level of diastereoselectivity (>95% de) but the yield from the (*Z*)-2-butenyl precursor (anti product) was only 45%. A chiral *N,N'*-dibenzyl-1,3,2-diazaphospholidine **12** derived from *trans*-1,2-cyclohexanediamine was examined. Although the CACR proceeded very cleanly (71–85%) and with high internal selectivity (94% de), the relative asymmetric induction was poor (16–20% de). This was also the case for a chiral *N,N'*-dibenzyl-1,3,2-diazaphosphorinane **15** derived from (*R,R*)-1,3-diphenyl-1,3-propanediamine and *N,N'*-dibenzyl-1,3,2-diazaphosphepine **16** derived from 6,6'-dimethyl-2,2'-diaminobiphenyl. The characteristic features of the CACR were compared with the aryl sulfone and phosphonate versions.

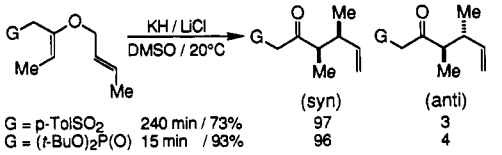
Introduction

The carbanion-accelerated Claisen rearrangement (CACR) of allyl vinyl ethers has proven to be a reaction of synthetic potential and mechanistic interest, Scheme I. Although the bulk of our original studies concentrated on the arylsulfonyl group to stabilize the carbanion,[1] we have recently reported in detail the incorporation of phosphine oxide and phosphonate groups into this methodology.[2] The premier advantage of the phosphorus-based anion stabilizing groups compared to the sulfone was found to be the enhanced rate of rearrangement. At similar levels of substitution, the phosphonate rearranged 10–20 times faster (with comparable diastereoselectivity) than the corresponding sulfone, Scheme II. The most serious drawback of the phosphonates, however, was the extensive optimization required for and variable yields obtained in the preparation of the precursor allyl vinyl ethers. Other disadvantages were seen in the failure of the (*Z*)-2-butenyl vinyl ethers to rearrange (to provide anti products) and the incorporation of effective chiral auxiliaries.[3] With these concerns in mind we pursued, in parallel, a systematic investigation of the viability and synthetic potential of cyclic phosphonamides as carbanion-stabilizing groups. Various features of this group appeared attractive, particularly with respect to the above-mentioned issues: (1) the anticipated higher thermodynamic basicity of the anion[4] promised still greater rearrangement rates, (2) the chemistry of the phosphonamide allyl anion was well-established,[5,6] (3) the reactivity of the precursor allenes and allyl vinyl ethers was readily tunable by choice of ring size and N-substituent, (4) the phosphonamide group is more stable toward attack at the phosphorus atom, and (5) the potential for chiral modification of the phosphorus is higher using readily available chiral diamines for auxiliary-based asymmetric induction.[7] This paper describes the full extent of our investigations of phosphonamides in the CACR including studies on the potential for asymmetric induction with chiral diamines. The intrinsically chiral

Scheme I



Scheme II



Scheme III

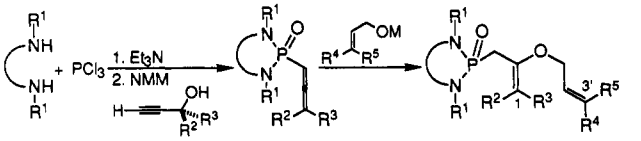
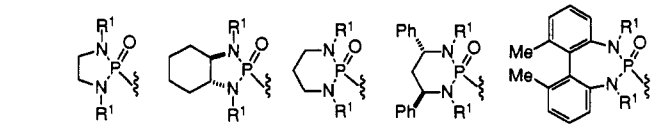


Chart I



(1) Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8878.

(2) Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1991**, *56*, 1003.

(3) Although no chiral phosphonates were investigated, our own structural studies and studies by Bartlett suggest that little asymmetric induction can be expected from phosphonates derived from chiral alcohols. Bartlett, P. A.; McLaren, K. *Phosphorus Sulfur Relat. Elem.* **1987**, *33*, 1.

(4) The pK_a of diethylbenzylphosphonate is 28 (DMSO). Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. The pK_a of phosphonamides has not been measured but we reason by analogy to the increase in pK_a of carboxylic amides compared to carboxylic esters and the higher pK_a of cyclic *P*-benzylphosphoramidates (30 in DMSO). We are grateful to Professor Frederick G. Bordwell and Dr. X. Zhang for these measurements.

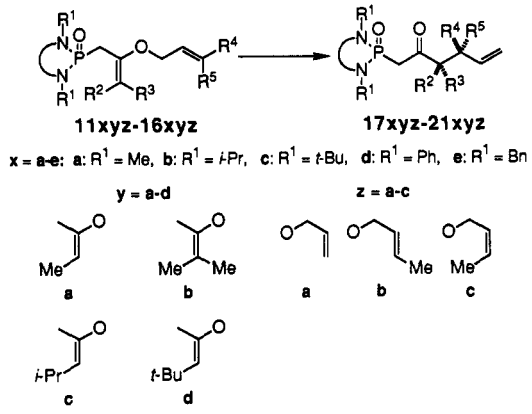
(5) (a) Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806. (b) Cramer, C. J. Ph.D. Thesis, University of Illinois, Urbana, IL, 1988.

(6) (a) Corey, E. J.; Cane, D. E. *J. Org. Chem.* **1969**, *34*, 3053. (b) Evans, D. A.; Takacs, J. M.; Hurst, K. M. *J. Am. Chem. Soc.* **1979**, *101*, 371. (c) Ahlbrecht, H.; Farnung, W. *Chem. Ber.* **1984**, *117*, 1.

(7) (a) Rachon, J.; Schöllkopf, U.; Wintel, T. *Liebigs Ann. Chem.* **1981**, 709. (b) Schöllkopf, U.; Schütze, R. *Ibid.* **1987**, 45. (c) Hua, D. H.; Chan-Yu-King, R.; McKie, J. A.; Myer, L. *J. Am. Chem. Soc.* **1987**, *109*, 5026. (d) Johnson, C. R.; Elliott, R. C.; Meanwell, N. A. *Tetrahedron Lett.* **1982**, *23*, 5005. (e) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754. (f) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *Chem. Scripta* **1985**, *25*, NS5. (h) Hanessian, S.; Bennani, Y.; Delorme, D. *Tetrahedron Lett.* **1990**, *31*, 6461. (i) Hanessian, S.; Bennani, Y. *Tetrahedron Lett.* **1990**, *31*, 6465.

0022-3263/91/1956-5063$02.50/0

Scheme IV



phosphoramidates shown in Scheme I have also been extensively examined for asymmetric induction in the CACR and will constitute the next paper in this series.[8]

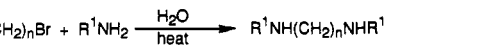
Results

1. Preparation of the Allyl Vinyl Ethers. The synthesis of the rearrangement substrates is identical with the method used in the phosphine and phosphonate series.[2,9] Thus, the allyl vinyl ethers arise from addition of an allyl oxide to the appropriate phosphorus allenes, themselves easily available from propargylic alcohols in a one-pot procedure from the appropriate diamine, Scheme III. As in the case of the phosphonates and phosphine oxides, all substrates bear at least one substituent at C(1). Although the present study only involved phosphonamides, there was a much greater substrate diversity than previously described. Furthermore, the nature of the phosphonamide group had a significant influence on the subsequent chemistry and serves as the primary rubric for categorization.

Five different classes of cyclic phosphonamides have been examined, two containing a five-membered heterocycle (1,3,2-diazaphospholidine), two containing a six-membered heterocycle (1,3,2-diazaphosphorinane), and one containing a seven-membered heterocycle (1,3,2-diazaphosphepine). These partial structures are collected in Chart I along with a listing of the numbers for the corresponding diamines, allenes, allyl vinyl ethers, and keto phosphonamides. Within each class there is considerable diversity of substitution pattern at three loci. Since most of the compounds studied herein arise from combination of similar subunits, a simplified numbering system is employed that allows recognition of families. Each structure is uniquely defined by the signature **N**xyz where **N** represents the five phosphonamide classes for the four kinds of compounds (**1**–**21**, Chart I). The substitution patterns are specified by x = a–e for the N-substituent (R^1), y = a–d for the C(1)-substituent (R^2 and R^3), and z = a–c for the C(3′)-substituents (R^4 and R^5) according to Scheme IV.

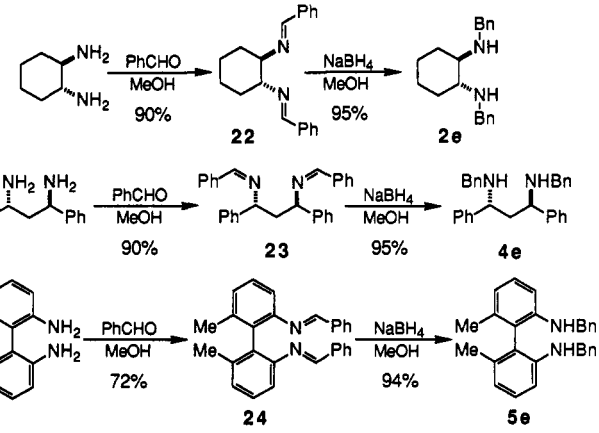
1.1. Synthesis of Diamines. The N,N′-disubstituted diamines **1a**, **1d**, and **1e** are commercially available. The other 1,2-ethane- and 1,3-propanediamines were prepared by a modification of the method of Boon[10] by refluxing the appropriate amine with the 1,*n*-dibromoalkane in the presence of water. The yields and conditions are summarized in Table I. The more complex diamines **2e**, **4e**, and **5e** were prepared by $NaBH_4$ reduction of the *bis*-benzylidene derivatives of the primary diamines, Scheme V.

Table I. Preparation of Diamines



entry	R^1	*n*	diamine	yield, %
1	*i*-Pr	2	**1b**	58
2	*t*-Bu	2	**1c**	70
3	*i*-Pr	3	**3b**	73
4	Bn	3	**3e**	58

Scheme V



1.2. Synthesis of Allenes. The basic approach for the preparation of the phosphonamide allenes was the same as used for the phosphonates, but the reaction protocol needed to be changed for best results. For all of the allenes in this study, the following procedure was found superior after some optimization. *Simultaneous addition* of a PCl_3 solution and the diamine/Et_3N solution to cold dichloromethane produced a chloro phosphorous amide that could be isolated in certain cases but was generally too labile to purify. In a one-pot procedure, this intermediate was then treated with *N*-methylmorpholine followed by the appropriate propargylic alcohol **25a–d**. This substitution produced an unstable phosphite that underwent a facile Horner–Mark [2,3]-rearrangement[11] at room temperature to produce the desired allenes as either crystalline solids (most of the benzyl series) or very high-boiling oils, Table II. The rearrangement products displayed the characteristic allene stretching band in the infrared spectrum (1945–1960 cm^{-1}) in addition to the strong P=O absorption for phosphonamides (1220–1250 cm^{-1}). Finally, the chiral allenes **7ea**, **7ec**, **7ed**, and **10ea** were produced as a mixture of diastereomers, which is of no consequence as the allenic stereogenic center is destroyed in the next step.

1.3. Optimization of Allyl Oxide Additions. One of the principle reasons for the broad survey in phosphonamide structural type was to address the problems encountered in capricious allyl oxide additions to phosphonates. The tendency of the allenes to tautomerize to acetylenes and suffer attack at the phosphorus atom were most troublesome. We have found that the size of the phosphonamide ring and nature of the N-substituent (R^1) are of primary importance in dictating the facility of isomerization and addition, respectively. We were pleased to find that nearly all of the allenes underwent addition and provided the expected allyl vinyl ether. Only the

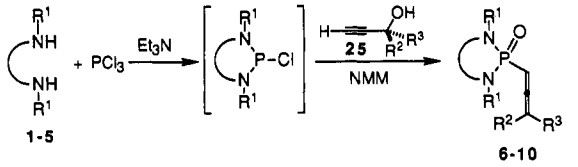
(8) Preliminary communications: Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1987**, *52*, 5742. (b) Denmark, S. E.; Rajendra, G.; Marlin, J. E. *Tetrahedron Lett.* **1989**, *30*, 2469.

(9) Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Org. Chem.* **1987**, *52*, 4031.

(10) Boon, W. R. *J. Chem. Soc.* **1947**, 307.

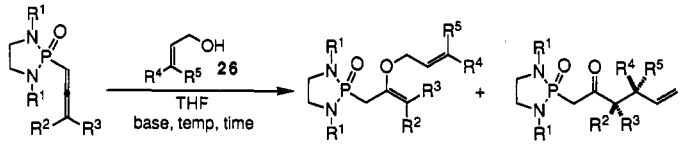
(11) Mark, V. In *Mechanism of Molecular Migrations*; Thyagajaran, B. S., Ed.; Wiley: New York, 1969; Vol. 3, pp 320–431.

Table II. Preparation of Phosphorus Allenes



entry	diamine	alcohol	R^1	R^2	R^3	allene	yield, %
1	**1a**	**25b**	Me	Me	Me	**6ab**	67
2	**1b**	**25b**	*i*-Pr	Me	Me	**6bb**	54
3	**1c**	**25b**	*t*-Bu	Me	Me	**6cb**	44
4	**1d**	**25b**	Ph	Me	Me	**6db**	55
5	**1e**	**25a**	Bn	Me	H	**6ea**	58
6	**1e**	**25b**	Bn	Me	Me	**6eb**	67
7	**2e**	**25a**	Bn	Me	H	**7ea**	61
8	**2e**	**25b**	Bn	Me	Me	**7eb**	74
9	**2e**	**25c**	Bn	*i*-Pr	H	**7ec**	75
10	**2e**	**25d**	Bn	*t*-Bu	H	**7ed**	71
11	**3b**	**25a**	*i*-Pr	Me	H	**8ba**	81
12	**3b**	**25b**	*i*-Pr	Me	Me	**8bb**	86
13	**3e**	**25a**	Bn	Me	H	**8ea**	63
14	**3e**	**25b**	Bn	Me	Me	**8eb**	69
15	**4e**	**25b**	Bn	Me	Me	**9eb**	81
16	**5e**	**25a**	Bn	Me	H	**10ea**	78

Table III. Allyl Oxide Additions to 6[a]



allene	ROH (equiv)	base (equiv)	time, h	temp, °C	product	R^1	R^2	R^3	R^4	R^5	yield, %
6ab	**26a** (1.0)	KH (1.0)	0.75	−20	*b*	Me	Me	Me	H	H	*c*
6bb	**26a** (1.0)	KH (1.0)	24	20	**11bba**[d]	*i*-Pr	Me	Me	H	H	53
6cb	**26a** (4.6)	KH (4.6)	48	20	**11cba**[e]	*t*-Bu	Me	Me	H	H	33
6db	**26a** (1.0)	KH (1.0)	1.0	−20	**11dba**	Ph	Me	Me	H	H	45
6ea	**26a** (1.1)	NaH (1.1)	1.5	−10	**11eaa**	Bn	Me	H	H	H	70
6ea	**26b** (1.1)	NaH (1.1)	1.5	−10	**11eab**	Bn	Me	H	Me	H	71
6ea	**26c** (1.1)	NaH (1.1)	0.25	−10	**11eac**	Bn	Me	H	H	Me	66
6eb	**26a** (1.2)	KH (1.0)	0.66	−20	**11eba**	Bn	Me	Me	H	H	70
6eb	**26b** (1.2)	KH (1.0)	1.0	−20	**11ebb**	Bn	Me	Me	Me	H	75

[a] All reactions run in THF. [b] A 1:1 mixture of **11aba** and **17aba**. [c] Not isolated. [d] Contained 5% of **17bba**. [e] Contained 33% of **17cba**.

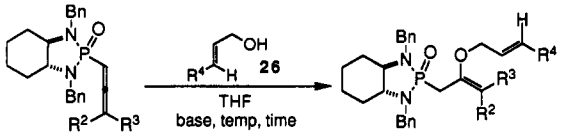
1,3,2-diazaphosphorinanes **8** were prone to extensive isomerization and will be discussed separately.

1.3.1. Addition to Diazaphospholidines 6. Within the diazaphospholidine class, we initially surveyed the importance of the N-substituent (R^1) in the selectivity of allyl oxide addition, Table III. The simplest member of this class, **6ab**, bearing *N*-methyl groups, underwent facile addition of potassium allyl oxide at −20 °C. Unfortunately, the in situ rearrangement of the adduct **11aba** (presumably as the anion) was competitive, affording an inseparable 1:1 mixture of the allyl vinyl ether (**11aba**) and the keto phosphonate (**17aba**) after 45 min. Shorter reaction times led to incomplete conversion. This problem was significantly diminished in the *N*-isopropyl case **6bb**, which provided a 95:5 mixture (again inseparable) of **11bba** and **17bba** in 53% yield. The addition was considerably slower in this case, requiring 24 h at room temperature to consume the allene. It is therefore not surprising that the *N*-*tert*-butyl substrate **6cd** reacted even more slowly. With an excess of potassium allyl oxide at room temperature after 2 days, the allene was still not consumed and an inseparable mixture of **11cba** and **17cba** was isolated in 33% yield. In an attempt to accelerate the addition and decelerate the rearrangement, we next examined the *N*-phenyl substrate **6db**. The mesomeric effect of the phenyl ring should make the allene more electrophilic and also stabilize the anion. In the event, these considerations proved correct as the addition occurred rapidly at −20 °C without competitive rearrangement affording the allyl vinyl ether **11dba** in 45% yield. Unfortunately, the increased electrophilicity of the phosphonamide unit also led to a competitive alcoholysis by allyl oxide opening of the ring. This side reaction could not be suppressed by changing the counterion to either lithium or sodium.

By far the substrate bearing an *N*-benzyl group was found to be superior. After a brief optimization it was discovered that the addition to the monomethylallene **6ea** goes to completion with minimal competitive rearrangement using 1.1 equiv of sodium allyl oxide in THF at −10 °C. The dimethylallene **6eb** is somewhat more prone to rearrangement and is best done with a slight excess of the allylic alcohol. The results in Table III show that this procedure is applicable to allyl-, (*E*)-, and (*Z*)-2-butenyl oxides (**26a**, **26b**, **26c**, respectively). An important advantage of the allyl vinyl ethers **11e** is their crystallinity allowing for the removal of traces of rearrangement products.

1.3.2. Addition to Diazaphospholidine 7e. On the basis of the experience with the allenes **6e** only the *N*-benzyl substrate **7e** was examined in a chiral series. By

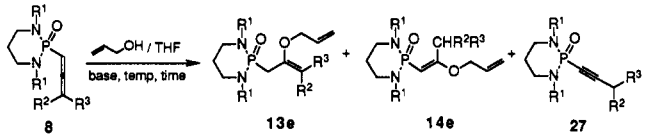
Table IV. Allyl Oxide Additions to 7e[a]



allene	ROH (equiv)	base (equiv)	time, h	temp, °C	product	R^2	R^3	R^4	yield, %
7ea	**26a** (1.2)	NaH (1.2)	1.0	−12	**12eaa**	Me	H	H	63
7ea	**26b** (1.2)	NaH (1.2)	1.5	−10	**12eab**	Me	H	Me	64
7eb	**26b** (1.2)	KH (1.2)	1.5	−20	**12ebb**	Me	Me	Me	64
7ec	**26a** (1.2)[b]	NaH (1.2)	1.5	−10	**12eca**	*i*-Pr	H	H	55

[a] All reactions run in THF. [b] 1.2 equiv of *tert*-butyl alcohol were added.

Table V. Allyl Oxide Additions to 8[a]



entry	allene	ROH (equiv)	base (equiv)	time, h	temp, °C	product	R^1	R^2	R^3	yield, %
1	**8ba**	**26a** (1.2)	KH (1.0)	0.5	−20	**27ba**	*i*-Pr	Me	H	88
2	**8ba**	**26a** (1.3)[b]	NaH (1.1)	15	20	**14bba**	*i*-Pr	Me	H	70
3	**8bb**	**26a** (1.2)	KH (1.0)	0.5	−20	**27bb**	*i*-Pr	Me	Me	54
4	**8bb**	**26a** (1.3)[b]	NaH (1.1)	15	20	**13bba**	*i*-Pr	Me	Me	57
5	**8ea**	**26a** (1.2)	KH (1.0)	0.5	−20	**27ea**	Bn	Me	H	87
6	**8ea**	**26a** (1.3)[b]	NaH (1.1)	15	20	**14eaa**	Bn	Me	H	76
7	**8eb**	**26a** (1.2)	KH (1.1)	0.5	−20	**27eb**	Bn	Me	Me	66
8	**8eb**	**26a** (1.3)[b]	NaH (1.1)	15	20	**13eba**	Bn	Me	Me	72

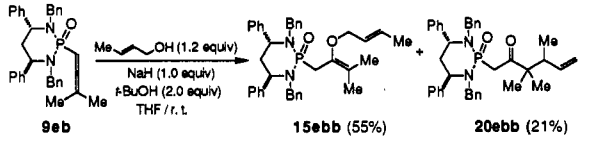
[a] All reactions done in THF. [b] 2.6 equiv of *tert*-butyl alcohol were added.

use of the analogous procedures, the allyl vinyl ethers **12ea/b** could be prepared on a 2–4 mmol scale from allyl- and (*E*)-2-butenyl oxides as outlined in Table IV. All of the products were nicely crystalline solids. In the addition of sodium allyl oxide to the isopropyl substrate **7ec**, 1.2 equiv of *tert*-butyl alcohol were needed to suppress the isomerization of the product to the undesired α,β-unsaturated isomer. Under no conditions was it possible to induce allyl oxide addition to the *tert*-butyl-substituted allene **7ed**.

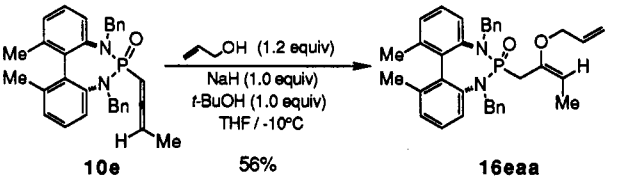
1.3.3. Addition to Diazaphosphorinane 8. For the allenes attached to a six-membered diazaphosphorinane, two N-substituents were examined, *N*-isopropyl **8b** and *N*-benzyl **8e**. However, in this series, the N-substituent had little effect on the course of the reaction. In all cases, under all conditions examined, the primary process was the isomerization to the acetylene **27**. For both mono- and dimethylated allenes the acetylene was produced as the kinetic product at low temperature and short reaction times and could be isolated and characterized as shown in entries 1, 3, 5, and 7, Table V. At higher temperatures and longer reaction times, allyl vinyl ethers were formed and their composition depended on the degree of allene substitution. Monomethylallenes gave the α,β-unsaturated isomers **14** (entries 2 and 6), while the dimethylallenes gave the desired β,γ-unsaturated isomers **13** (entries 4 and 8).

1.3.4. Addition to Diazaphosphorinane 9. Only one substrate was investigated for asymmetric rearrangements in this series due to the difficulties of allyl oxide addition described above. By use of allene **9eb** as the substrate, the addition of sodium (*E*)-2-butenyl oxide in the presence of *tert*-butyl alcohol gave the desired allyl vinyl ether **15ebb** in 55% yield along with 21% of the rearrangement product **20ebb**, Scheme VI. The allyl vinyl ether could not be obtained completely pure and was used in the rearrangements as a 92:8 mixture with **20ebb**.

Scheme VI



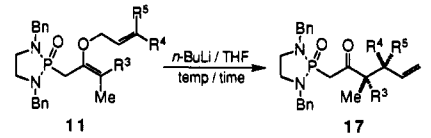
Scheme VII



1.3.5. Addition to Diazaphosphepine 10e. For the chiral diazaphosphepine **10e** derived from biphenyl-2,2′-diamine only one addition was performed using sodium allyl oxide **26a**, Scheme VII. In this case as well, 1.0 equiv of *tert*-butyl alcohol was necessary to obtain the desired β,γ-unsaturated isomer **16eaa**.

1.4. Structure of the Allyl Vinyl Ethers. The only structural ambiguity in the allyl vinyl ethers is the location and geometry of the vinyl ether double bond. The desired, β,γ-unsaturated isomers displayed a characteristic absorption (phosphorus coupled) for the α-methylene group. In the ^{1}H NMR spectra this resonance appeared at 2.8–3.1 ppm ($^2J_{PH}$ = 18–19 Hz) and was largely independent of ring size. In the chiral heterocycles, however, these protons are diastereotopic and show an eight-line pattern. Moreover, in **14** these protons are coincident with the ring fusion methine protons, making interpretation impossible. Fortunately, this methylene carbon is distinctive in all of the ^{13}C NMR spectra appearing as a strongly coupled doublet at 28–31 ppm ($^1J_{PC}$ = 111–115 Hz) supporting the

Table VI. Rearrangements of Diazaphospholidines 11[a]



11 17

educt	temp, °C	time, h	product	R^3	R^4	R^5	yield, %	syn:anti[b,c]
11eaa	0	1.0	**17eaa**	H	H	H	76	
11eba	-20	1.5	**17eba**	Me	H	H	79	
11ebb	0	0.75	**17ebb**	Me	Me	H	82	
11eab	0	1.0	**17eab**	H	Me	H	74	97:3
11eac	0	2.0[d]	**17eac**	H	H	Me	44	7:93

[a] All reactions run at ca. 0.1 M with 1.2 equiv of *n*-BuLi. [b] **17eab**:**17eac**. [c] Determined by ^{31}P NMR. [d] An additional 0.4 equiv of *n*-BuLi were added after 1.5 h.

β,γ-isomer structure. The infrared absorbance for the enol ether double bond was in the normal region (1660–1680 cm^{-1}). In all of these compounds only one isomer was ever detected. The vinyl ether double bonds in **11eaa–c**, **12eaa/b**, **12eca**, and **13eaa** were assigned the *E* configuration by analogy to the stereochemical course of addition to other phosphorus allenes.[2]

For the two α,β-unsaturated isomers the vinyl ether proton appeared as phosphorus-coupled doublet: **14bba**, 4.36 ppm ($^2J_{PH}$ = 7.0 Hz), and **14eba**, 4.42 ppm ($^2J_{PH}$ = 7.9 Hz). The ^{13}C NMR spectrum displayed a characteristic doublet for the C(1) carbon at 84–87 ppm ($^1J_{PC}$ = 170 Hz), which clearly indicates that an sp^2 carbon is attached to phosphorus. In these compounds the enol ether double bond resonance was shifted to lower energy by conjugation (1605–6 cm^{-1}).

Thus, a workable synthesis of the phosphorus-substituted allyl vinyl ethers was achieved. Importantly, the phosphonamides proved significantly superior to the phosphine oxides and phosphonates in their resistance to (1) nucleophilic attack at phosphorus and (2) tautomerization of the enol ether double bond. As in the phosphine oxides and phosphonates, the vinyl ether geometry is assured, which is critical for high internal and relative stereoselectivity in the subsequent rearrangement as described in the following section.

2. Anionic Rearrangements. From our previous experience with phosphonates and phosphine oxides and a simplisitic analysis of reactivity features, we expected the phosphonamides to rearrange qualitatively faster. Moreover, for preparative simplicity we wanted to move away from the base/solvent system (MH/DMSO, HMPA) used previously. The simple comparison of the pK_a values for carboxylic esters and amides and the expected resistance of the phosphonamides to attack at phosphorus suggested the use of soluble lithium bases in ethereal solvents. Orienting experiments with **11bba** showed that *both LDA and n-BuLi were effective at inducing the rearrangement at subambient temperatures (-10 to -20 °C) in THF solution.* Our expectations were thus realized; the phosphondiamides rearranged significantly faster than the phosphonates using a much simpler protocol. The following study examined the scope and stereoselectivity of the CACR with the diazaphospholidines (**11** and **12**), the diazaphosphorinanes (**13** and **15**), and the chiral diazaphosphepane **16**.

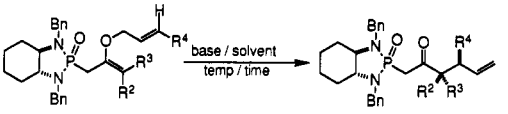
2.1. Achiral Diazaphospholidines 11. The initial results from **11dba** and **11bba** proved general in the rearrangement of the *N*-benzyl series **11e**. All of the substrates rearranged readily using *n*-BuLi in THF at -20 to 0 °C, Table VI. The keto phosphonamides were produced in good yield (74–82%) except for **11aec** derived from the *cis*-2-butenyl precursor (44%). The poor yield and slow reaction rate in this case find precedent in both the sulfone and phosphonate systems.[1,2] The suspected side reaction of E_2' elimination could not be suppressed by addition of LiCl.

The internal diastereoselectivity was tested in this system with substrates **11eab** and **11eac**. The level of diastereoselection was very high in both isomers and, as expected, complementary. The ratios of the two isomers were established by integration of the ^{31}P NMR spectra of the mixtures. The assignment of configuration was made by analogy to the rearrangement of the related phosphonates.

2.2. Chiral Diazaphospholidines 12. Up to this point our studies had clearly established the superiority of *N,N'*-dibenzyldiazaphospholidine as the anion-stabilizing group. We then chose to incorporate this into a chiral backbone and examine the potential asymmetric induction in the CACR. The diazaphospholidine series **12e** was chosen for accessibility and simplicity. All compounds were prepared and employed in racemic form. Thus, the extent of asymmetric induction from the chiral phosphonamide unit was measured as diastereomeric excess. The simple C(3') monomethyl substrate **12eaa** was chosen to survey reaction conditions for maximum relative diastereoselectivity without the additional complication of internal diastereoselection, Table VII. As expected Li^+-**12eaa**$^-$ rearranged rapidly (entries 1 and 2) in THF but with very disappointing diastereoselectivity (HPLC). The HPLC was calibrated with the authentic products from thermal rearrangement of **12eaa**, entry 5. No attempt was made to assign the relative configuration of the major diastereomer. Rearrangement using the KH/DMSO system proceeded cleanly, though more slowly, presumably due to the comparable pK_a's of **12eaa** and DMSO. The diastereoselectivity did indeed improve (entry 3) but, surprisingly, now in the opposite direction compared to Li^+**12eaa**$^-$. The importance of the counterion was demonstrated by the addition of LiCl (8 equiv) to the KH/DMSO mixture, entry 4. While the yield and rate of rearrangement were unaffected, the diastereoselectivity was shifted back toward the major isomer in entries 1 and 2. Remarkably, thermal rearrangement proceeded with modest selectivity, favoring the same product as Li^+**12eaa**$^-$.

The remaining substrates were deprotonated with *n*-BuLi in THF and rearranged smoothly, but again with poor diastereoselectivity. Disubstituted allyl vinyl ether **12eab** produced **18eab** with excellent internal diastereoselectivity (97:3) despite the meager relative asymmetric induction. Clearly these two features are not coupled. The rearrangements of **12eca** and **12ebb** with similar selectivity as **12eaa** were of mechanistic significance in focusing analysis of stereocontrol elements on the auxiliary (vide infra).

Table VII. Rearrangements of Chiral Diazaphospholidines 12[a]



12e 18e

entry	educt	base (equiv)	solvent	temp, °C	time, h	product	R^2	R^3	R^4	ds	syn:anti	yield, %
1	**12eaa**	*n*-BuLi (1.9)	THF	0	1.0	**18eaa**	Me	H	H	58:42		85
2	**12eaa**	LDA (1.9)	THF	0	0.75	**18eaa**	Me	H	H	58:42		64
3	**12eaa**	KH (2.3)	DMSO	20	2.0	**18eaa**	Me	H	H	31:69		79
4	**12eaa**	KH (2.1)[b]	DMSO	20	2.0	**18eaa**	Me	H	H	48:52		78
5	**12eaa**	none	toluene	110	2.0	**18eaa**	Me	H	H	63:38		81
6	**12eca**	*n*-BuLi (1.9)	THF	0	1.0	**18eca**	*i*-Pr	H	H	57:43		74
7	**12eab**	*n*-BuLi (1.9)	THF	0	1.0	**18eab**	Me	H	Me	57:43	97:3	74
8	**12ebb**	*n*-BuLi (1.9)	THF	−20	1.0	**18ebb**	Me	Me	Me	60:40		85

[a] All reactions run at ca. 0.1 M. [b] LiCl (8 equiv) was added.

Scheme VIII

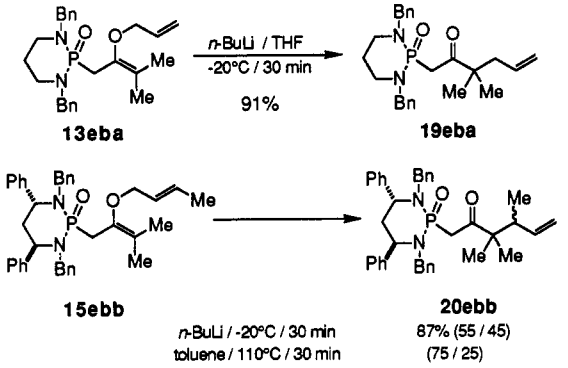
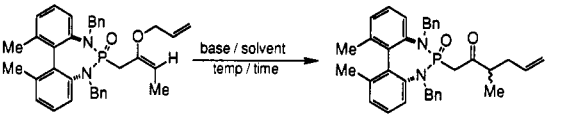


Table VIII. Rearrangements of Chiral Diazaphosphepine 16eaa[a]



16eaa 21eaa

entry	base	solvent	temp, °C	time, h	ds[b]	yield, %
1	none	toluene	110	4.0	30:70	75
2	*n*-BuLi	THF	0	1.0	75:25	39
3	KH	DMSO	20	1.0	40:60	60

[a] All reactions run at ca. 0.1 M. [b] Ratios determined by integration of ^{31}P NMR spectra.

2.3. Diazaphosphorinanes 13eba and 15ebb. Despite the problems associated with the preparation of these six-membered ring phosphonamides, we examined their CACR behavior for comparison purposes as well. The achiral allyl vinyl ether **13eba** underwent clean and facile CACR with *n*-BuLi at −20 °C, Scheme VIII. The keto phosphonamide was obtained as a single regioisomer. Similarly, the chiral diazaphosphorinane **15ebb** rearranged in high yield to the trisubstituted product **20ebb** under the same conditions. Unfortunately, the stereoselectivity in the creation of the stereocenter at C(4′) was meager as determined by both ^{31}P and ^{1}H NMR spectroscopy, Scheme VIII. Interestingly, the thermal rearrangement of **15ebb** was more selective! No attempt was made to assign the major product stereochemistry.

2.4. Chiral Diazaphosphepine 16eaa. The chiral phosphonamide **16eaa** was subjected to all three different rearrangement conditions, Table VIII. Thermal rearrangement proceeded in good yield to give a 7:3 ratio of keto phosphonamide products. Remarkably, rearrangement of Li^{+}**16eaa**$^{-}$ (entry 2) this time gave the opposite sense of diastereoselection, unfortunately in modest yield. As before, the rearrangement in the KH/DMSO system resulted in a switch of the major product diastereomer compared to *n*-BuLi, entry 3. Again, no attempt was made to assign the relative configuration of the major diastereomer.

Discussion

1. Preparation of Phosphonamide Allyl Vinyl Ethers. One of the major drawbacks of the phosphonate variant of the CACR is the difficulty of preparing the requisite β,γ-unsaturated allyl vinyl ethers.[2] These precursors are prone to tautomerization, and each substitution pattern requires independent optimization. Our expectation that the more basic phosphonamides would be less prone to isomerization was for the most part realized. The five- and seven-membered cyclic phosphonamides produced exclusively β,γ-unsaturated allyl vinyl ethers from additions to the allenes. However, the success of the addition also depends on the nature of the N-substituent to allow facile addition, suppress in situ rearrangement, and prevent nucleophilic attack at phosphorus. The *N*-benzyl and *N*-isopropyl groups were found to be satisfactory with the former enjoying the additional advantage of imparting crystallinity more often. Unfortunately, neither derivative of the six-membered phosphonamides was well-behaved. All five allenes examined suffered rapid tautomerization to the corresponding acetylenes in the presence of potassium allyl oxide. In the cases of dimethyl-substituted allenes **8bb**, **8eb**, and **9bb**, the desired β,γ-unsaturated allyl vinyl ethers were obtained by virtue of the thermodynamic stability of the tetrasubstituted enol ether. In the absence of accurate pK_a measurements, it is difficult to explain the anomalous behavior of these phosphonamides. We speculate that the kinetic preference for tautomization versus addition is a consequence of the different disposition of the N-substituents flanking the allenes. In the six-membered ring chain, the nitrogen atoms are planar[12] and the allene should take up an equatorial position. This conformation is suggested by extensive NMR analysis of 2-benzyl-1,3-dimethyl-1,3,2-diazaphosphorinane 2-oxide.[13] Thus, the *N*-isopropyl or *N*-benzyl groups directly eclipse

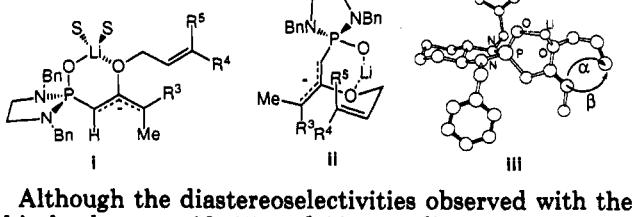
(12) (a) Garcia-Blanco, S.; Perales, A. *Acta Crystallogr., Sect. B* **1972**, *28*, 2647. (b) Brassfield, H. A.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4143. (c) Goodridge, R. J.; Hambley, T. W.; Ridley, D. D. *Aust. J. Chem.* **1986**, *39*, 591. (d) Perales, A.; Garcia-Blanco, S. *Acta Crystallogr., Sect. B* **1977**, *33*, 1935. (e) Bentrude, W. G.; Setzer, W. N.; Sopchik, A. E.; Chandrasekaran, S.; Ashby, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 7119.

(13) (a) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 865. (b) Dorow, R. L. Ph.D. Thesis, University of Illinois, Urbana, IL, 1990.

the allene and shield attack by the allyl oxide. In contrast, the nitrogen atoms are pyramidal in the five-membered ring,[14] and the substituents are also further removed from the allene. The large twist angle in the seven-membered ring due to the biphenyl unit moves the N-substituents in a staggered fashion about the allene exposing one face to addition.

2. Rearrangements of Phosphonamide Allyl Vinyl Ethers. The general features of the CACR previously established with sulfones and phosphonates (regioselectivity and internal diastereoselectivity) are well-reproduced here. The rate of rearrangement is markedly greater than any of the other derivatives, but direct comparisons cannot be made under identical conditions. The qualitative order of rate of rearrangement thus appears to be phosphonamide > phosphonate > phosphine oxide > sulfone. We suggest that the relative rate of rearrangement is a simple reflection of the electron density in the anion due to the different ability of phosphonamides versus phosphonates to stabilize negative charge. In an extensive study of stabilized benzyl carbanions, Pagani has examined the relationship between the change in the ^1H and ^{13}C NMR chemical shift and π-electron density at the benzylic (q_{CH}) and para (q_p) positions as a function of the stabilizing group electron demand (q_x).[15] On the basis of many criteria it is clear that the electron density of the carbanion is greater in phosphonyl compared to sulfonyl carbanions. Our own studies on the solution structure of phosphorus-stabilized benzyl anions show (by the same criteria) that the electron density is still greater in phosphonamide carbanions.[13] Moreover, our studies and those of Pagani show no major structural differences in the benzyl anions stabilized by phosphonates compared to phosphonamides.

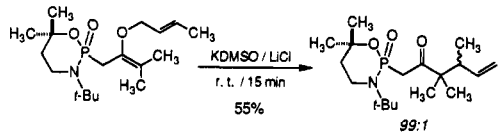
The behavior of *P*-allylphosphonamide anions has also been studied spectroscopically and computationally.[5] These species better reflect the reactive intermediates in the CACR's described here. The same qualitative picture emerges of a delocalized planar allyl anion with no carbon–lithium contacts, but strong oxygen–lithium bonds, even in THF solution. Integration of these features from NMR, X-ray, and computational studies produces the structure i for the ground state of the intermediate anion in the archiral diazaphospholidine series **11**. For this anion the chairlike transition state ii can be formulated. The excellent internal asymmetric induction observed for the phosphonamides is attributed to the strong preference for this chairlike transition state compared to the alternative boat due the nonbonding interactions with the *N*-benzyl groups. Furthermore, as in the case of phosphoryl-stabilized carbanions, the slower rate of rearrangement for **11eac** can also be understood in terms of the enhanced steric interactions between the *N*-benzyl groups and the pseudoaxial methyl group when R^5 = Me.



Although the diastereoselectivities observed with the chiral substrates **12**, **15**, and **16** were disappointing, it is nonetheless instructive to formulate a picture of the reactive conformation of the anion to identify potential stereocontrol features. Thus, annulation of a six-membered ring onto the structure i produces the chiral anion iii corresponding to Li^+**12eaa**$^-$. The basic attributes of the diazaphospholidine ring system are derived from an X-ray crystal structure analysis of a neutral phosphonamide by Hanessian.[14] The key structural features in this anion are as follows: (1) the sickle-shaped allyl anion, (2) the chelation of the lithium ion, (3) the pyramidality of the nitrogen atoms, and (4) the orientation of the benzyl groups. The anion configuration is firmly established by the high relative asymmetric induction in the sense **12eab** ((*E*)-2-butenyl ether) produced **18eab** (predominantly syn diastereomer). The chelation of the lithium cation is proposed to explain the change in sense of diastereoselection between Li^+ and K^+ (Table VII, entries 1–4). The pyramidality of the nitrogens and the disposition of the benzyl groups are suggested by the X-ray structure analysis of the neutral phosphonamide.[14] From this picture, it is seen that the origin of asymmetric induction derives from the preferred folding of the allyl ether appendage either to the frontside (β) or backside (α) of the allyl anion as indicated in iii. Thus, a critical stereocontrol feature is the nature and conformation of the N-substituents on the phosphonamide ligand since these groups can differentially shield the diastereotopic faces of the anion. The lack of appropriate parameters unfortunately precluded force field calculations. Inspection of molecular models reveals that the three limiting staggered conformations about each N–CH_2Ph bond may be unequally populated but no significant difference between the two sets of conformers (based on non-bonded interactions) could be discerned. Clearly, for the two faces of the allyl anion to be distinguishable, the conformational preferences for the two N-ligands must be different. It is therefore difficult to imagine how a phosphonamide derived from a chiral diamine of C_2 symmetry can lead to high diastereoselection.

With this picture in mind, it is perhaps not surprising that the most selective rearrangements observed thus far employ 1,3,2-oxazaphosphorinanes in which the two sides of the anion are highly differentiated, i.e., containing an oxygen lone pair and an *N*-*tert*-butyl group, Scheme IX. The details of internal and relative asymmetric induction in the CACR with scalemic oxazaphosphorinanes will be the subject of a future paper.

Scheme IX



Conclusions

The carbanion-accelerated Claisen rearrangement (CACR) has been further modified to include phosphonamides as anion-stabilizing groups. A wide variety of phosphonamide structural types (5-, 6-, and 7-membered rings) and N-substituents were examined. From the preparative perspective the *N*,*N*′-dibenzyl-1,3,2-diazaphospholidine group was found to be superior in the case of allene formation and efficiency of allyl oxide additions. All phosphonamides examined underwent extremely facile CACR using either *n*-BuLi or KH/DMSO as the base. All phosphonamide types (5-, 6-, and 7-membered rings) rearranged faster than the previously studied phosphonates as was expected based on the lower electron demand of phosphonamides. While internal asymmetric induction

(14) Belanger-Gariepy, F.; Delorme, D.; Hanessian, S.; Brisse, F. *Acta Crystallogr., Sect. C* **1986**, *42*, 856.
(15) (a) Bradamante, S.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1035. (b) Bradamante, S.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1047.

with (*E*)- and (*Z*)-2-butenyl ethers was high, the relative asymmetric induction with chiral versions of all three phosphonamide structural classes was poor. A model of the reactive anion conformation was formulated based on recent structural studies. This model features (1) a planar allyl anion in a parallel conformation and (2) chelation of lithium between phosphonyl and ether-type oxygens. In this model the N-ligands provided insufficient differentiation for asymmetric induction. The design of an appropriate auxiliary was seen to require either (1) a clear differentiation of the preferred orientation of N-groups on either side of the phosphonamide or (2) chemically distinct groups bearing substituents of highly disparate steric requirement (i.e, oxygen and *N*-alkyl). The development of such auxiliaries is under active study.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 300 MHz with tetramethylsilane (0.00 ppm) as an internal reference in $CDCl_3$ solutions. ^{13}C NMR spectra were recorded at 75.5 MHz with $CDCl_3$ (77.00 ppm) as internal reference in $CDCl_3$ solutions. ^{31}P NMR spectra were recorded at 121.5 MHz with 85% H_3PO_4 (0.0 ppm) as external reference in acetone-d_6/acetone solutions. *Chemical shifts are given in ppm (δ); coupling constants, J, are* reported in hertz. Infrared spectra (IR) were obtained on a IBM-32 FT infrared spectrometer in CCl_4 solutions unless otherwise specified. Peaks are reported in cm^{-1} with the following intensities: s (strong 67–100%), m (medium, 33–67%), w (weak, 0–33%). Mass spectra (EI) were obtained with a ionization voltage of 70 eV. Data are reported in the form *m/z* (intensity relative to base = 100). Elemental analysis were performed by the University of Illinois Microanalytical Service Laboratory. Analytical TLC was performed by using 0.25-mm silica gel plates (Merck) with F-254 indicator. Visualization was accomplished by UV light and iodine. Flash chromatography was performed by using 32–63-μm silica gel (Woelm) with technical-grade hexane (distilled from anhydrous $CaCl_2$) and reagent-grade acetone. Analytical HPLC was performed on a Perkin-Elmer Series 1 LC pump and LC-75 spectrophotometric detector or on a Hewlett-Packard HP 1099 liquid chromatograph. The column used was a Sperisorb S5W. Solvents for HPLC were distilled in glass and filtered immediately prior to use. All solvents used in reactions were distilled from appropriate drying agents before use: THF (sodium benzophenone ketyl), hexane (CaH_2), CH_2Cl_2 (CaH_2), DMSO (CaH_2). All reactions were performed in an atmosphere of dry nitrogen. *n*-Butyllithium was titrated by the double titration method.[16]

Starting Materials. The diamines **1a**, **1d**, **1e** and *trans*-1,2-cyclohexanediamine are commercially available. The following compounds were prepared by literature methods: (*Z*)-2-butenol **26c**,[9] (*E*)-2-butenol **26b**,[9] and 4-methyl-1-pentyn-3-ol **25c**[17] (for 4,4-dimethyl-1-pentyn-3-ol **25d**).

Preparation of Diamines 1 and 3. General Procedure. To a cold (0 °C) mixture of 1,2-dibromoethane or 1,3-dibromopropane (1.0 equiv) and water (3.0 equiv) was added alkylamine (5.0 equiv). The mixture was *slowly* allowed to warm to ambient temperature and then heated to reflux overnight. The resulting solution was cooled, diluted with a small portion of water, and then saturated with solid potassium hydroxide. The mixture was then extracted three times with three volumes of ethyl acetate, dried (Na_2SO_4), and concentrated and the residue purified by fractional distillation. While many of these amines have been prepared before by a similar method, the majority of the spectral data is not on record in the literature and is therefore presented here.

***N,N'*-Bis(1'-methylethyl)-1,2-ethanediamine (1b)**: yield 6.25 g (39%); bp 144 °C (400 Torr); ^{1}H NMR (200 MHz) 2.78 (septet, J = 6.1, 2 H, 2 × HC(1')), 2.72 (s, 4 H, H_2C), 1.08 (d, J = 6.1, 6 H, 2 × (H_3C)).

***N,N'*-Bis(1',1'-dimethylethyl)-1,2-ethanediamine (1c)**: yield 8.8 g (70%); bp 54–56 °C (0.20 Torr); ^{1}H NMR (200 MHz) 2.68 (s, 4 H, H_2C), 1.10 (s, 18 H, 6 × H_3C).

***N,N'*-Bis(1'-methylethyl)-1,3-propanediamine (3b)**: yield 35.5 g (75%); bp 85 °C (24 Torr); 56 °C (3.5 Torr); ^{1}H NMR (200 MHz) 2.40 (septet, J = 7.1, 2 H, 2 × HC(1')), 2.28 (t, J = 6.9, 4 H, H_2C(1), H_2C(3)), 1.27 (pentet, J = 6.9, 2 H, H_2C(2)), 0.66 (d, J = 7.1, 12 H, 4 × H_3C(2')); ^{13}C NMR (50.4 MHz) 48.10 (C(1')), 45.59 (C(1), C(3)), 30.46 (C(2)), 22.39 (C(2')).

***N,N'*-Dibenzyl-1,3-propanediamine (3e)**: yield 26.3 g (52%); bp 189 °C (0.6 Torr); ^{1}H NMR (200 MHz) 7.27 (m, 10 H, ArH), 3.72 (s, 4 H, 2 × H_2C(1')), 2.67 (t, J = 6.9, 4 H, H_2C(1), H_2C(3)), 1.69 (pentet, J = 6.9, 2 H, H_2C(2)), 1.41 (br s, 2 H, 2 × NH); ^{13}C NMR (50.4 MHz) 140.41 (Ar-ipso), 128.20, 127.92, 126.69 (Ar-para), 53.98 (C(1')), 47.85 (C(1), C(3)), 30.08 (C(2)).

Preparation of Diamines 2, 4, and 5. (*R,S*)-(1*l*,2*l*)-*N,N'*-Dibenzylidene-1,2-cyclohexanediamine (22). To a solution of 17.13 g (150 mmol) of *trans*-1,2-cyclohexanediamine in 90 mL of refluxing methanol was added 31.83 g (300 mmol) of benzaldehyde in small portions. After ca. 5 min a precipitate formed. The oil bath was removed after 30 min, and the solution was allowed to stand overnight. The precipitate was filtered off and dried to afford 39.22 g (90%) of diimine **22**: mp 134–135 °C (methanol); ^{1}H NMR (300 MHz) 8.19 (s, 2 H, N=CH), 7.59–7.55 (m, 4 H, Ar-ortho), 7.28–7.25 (m, 6 H, HAr), 3.43–3.99 (m, 2 H, HC(1), HC(2)), 1.95–1.70 (m, 6 H) and 1.60–1.40 (m, 2 H) (H_2C(3), H_2C(4), H_2C(5), H_2C(6)); ^{13}C NMR (75.5 MHz) 160.93 (*C*=N), 136.30, 130.13, 128.29, 127.83, 73.75 (C(1), C(2)), 32.91 (C(3), C(6)), 24.45 (C(5), C(6)); IR (CCl_4) 3068 m, 3065 m, 3028 m, 2934 s, 2858 s, 1645 s, 1581 m, 1455 m, 1450 s, 1379 m, 1344 m, 1307 m, 1219 m, 1170 m, 1138 m, 1091 m, 1068 m, 1028 m, 966 m, 935 m, 868 m; MS (70 eV) 290 (M^+, 3), 188 (38), 187 (100), 186 (100), 185 (32), 134 (38), 158 (12), 157 (12), 156 (26), 145 (13), 144 (27), 132 (14), 130 (28), 118 (21), 117 (49), 107 (40), 106 (100), 105 (27), 104 (92), 103 (13), 91 (77), 90 (35), 89 (25). Anal. Calcd for $C_{20}H_{22}N_2$ (290.41): C, 82.72; H, 7.64; N, 9.64. Found: C, 82.65; H, 7.76; N, 9.64.

(*R,S*)-(1*l*,2*l*)-*N,N'*-Dibenzyl-1,2-cyclohexanediamine (2e). Sodium borohydride (3.97 g, 105 mmol) was added in small portions to a solution of 14.54 g (50 mmol) of **22** in 120 mL of methanol over a period of 30 min. The solution was then heated to reflux for 15 min and then cooled. After addition of water the milky solution was extracted with CH_2Cl_2 (3×). The CH_2Cl_2 layer was dried (K_2CO_3), filtered, and concentrated. Kugelrohr distillation of the residue gave 13.96 g (95%) of diamine **2e** as a colorless oil that solidified upon standing: bp 180 °C (0.01 Torr); ^{1}H NMR (300 MHz) 7.50–7.20 (m, 10 H, HAr)), 3.89 (d, J = 13.2, 2 H, NC$H_a$$H_b$Ph), 3.65 (d, J = 13.2, 2 H, NC$H_a$$H_b$Ph), 2.40–2.05 (m, 4 H, HC(1), HC(2), H_aC(3), H_aC(6)), 2.05–1.80 (br s, 2 H, NH), 1.35–1.20 (m, 2 H) and 1.15–0.95 (m, 2 H) (H_2C(4), H_2C(5)); ^{13}C NMR (75.5 MHz) 141.12, 128.31, 128.06, 126.73, 60.93 (NCH_2Ph), 50.91 (C(1), C(2)), 31.60 (C(3), C(6)), 25.07 (C(4), C(5)); IR (CCl_4) 3304 w, 3088 w, 3065 m, 3028 m, 2932 s, 2856 s, 1605 w, 1495 m, 1454 s, 1356 m, 1242 w, 1203 m, 1116 m, 1053 m, 1028 m, 974 w, 858 m, 816 m; MS (70 eV) 294 (M^+, 5), 203 (14), 189 (16), 146 (9), 108 (15), 107 (19), 106 (34), 96 (18), 91 (100). Anal. Calcd for $C_{20}H_{26}N_2$ (294.44): C, 81.58; H, 8.90; N, 9.52. Found: C, 81.64; H, 9.09; N, 9.51.

(*R*)-(1*l*,3*l*)-*N,N'*-Dibenzyl-1,3-diphenyl-1,3-propanediamine (4e). To a cold (ice bath) suspension of 1.46 g (2.50 mmol) of (*R*)-(1*l*,3*l*)-1,3-diphenyl-1,3-propanediamine L-(−)-dibenzoyltartarate salt in 10 mL of water was slowly added 10 mL of 40% NaOH solution. The heterogeneous mixture was stirred for 30 min and extracted with $CHCl_3$ (3 × 20 mL). The extracts were combined, dried (K_2CO_3), concentrated, and vacuum dried to give 568 mg of colorless oil. The clear oil was dissolved in dry methanol (10 mL), and then 0.64 mL (6.30 mmol, 2.5 equiv) of benzaldehyde was added. The mixture was heated to reflux for 1 h. After the mixture was cooled to room temperature, $NaBH_4$ (463 mg, 12.5 mmol, 5.0 mol equiv) was added in small portions over 5 min. The mixture was stirred at ambient temperature for 1 h. After evaporation of methanol the residue was poured into brine (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extracts were combined, dried (Na_2SO_4, K_2CO_3), and concentrated to give a colorless oil that was purified by silica gel column chromatography eluting with hexane/acetone (4:1) to give 924 mg (91%) of (*R*)-(−)-**4e** as a colorless oil that slowly solidified upon standing. Analytical data for (±)-**4e**: mp 68–69 °C (pentane/ether); ^{1}H

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NMR (300 MHz) 7.37–7.18 (m, 10 H, ArH), 3.70 (t, J = 6.5, 2 H, HC(1), HC(3)), 3.52 (ABq, J = 12.9, 4 H, NCH_2Ph), 2.08 (t, J = 6.5, 2 H, $H_2C(2)$), 1.94 (br s, 2 H, NH); ^{13}C NMR (75.5 MHz) 143.79 and 140.42 (Ar-ipso), 128.46, 128.27, 128.14, 127.25, 127.04, 126.76, 59.91 (C(1), C(3)), 51.46 (NCH_2Ph), 46.20 (C(2)); IR (CCl_4) 3087 w, 3065 m, 3029 m, 2917 m, 2836 m, 1495 m, 1453 s, 1358 m, 1113 m, 1071 w, 1028 m, 851 m, 816 m; MS (70 eV) 299 (7), 208 (19), 197 (9), 196 (57), 194 (10), 106 (12), 104 (16), 92 (9), 91 (100), 65 (7). Anal. Calcd for $C_{29}H_{30}N_2$ (406.57): C, 85.67; H, 7.44; N, 6.89. Found: C, 85.66; H, 7.47; N, 6.84. Optical rotation for (*R*)-**4e** $[\alpha]^{24}_D$ −38.5 (*c* 1.09, $CHCl_3$).

***N*,*N*′-Dibenzylidene-6,6′-dimethyl-2,2′-biphenyldiamine (24).** To a solution of 6.37 g (30 mmol) of 6,6′-dimethyl-2,2′-biphenyldiamine in 50 mL of refluxing methanol was added benzaldehyde (6.37 g, 60 mmol) in small portions. The oil bath was removed after 30 min, and the solution was allowed to stand overnight. The precipitate was filtered off and dried to afford 8.46 g (72%) of the diimine **24** as light yellow needles: mp 98–99 °C (methanol); ^1H NMR (300 MHz) 8.15 (m, 2 H, N=CH), 7.52–7.49 (m) and 7.37–7.27 (m) (10 H, HAr), 7.21 (t, finely split, J = 8.3, 2 H, HC(4), HC(4′)), 7.08 (br d, J = 7.5) and 6.79 (br d, J = 7.7) (4 H, HC(2), HC(2′), HC(5), HC(5′)), 2.06 (d, J = 1.9, 6 H, $CH_3C(6)$, $CH_3C(6')$); ^{13}C NMR (75.5 MHz) 159.38 (*C*=N), 151.12, 136.92, 136.52, 131.97, 130.77, 128.45, 127.73, 126.68, 115.51, 19.99 ($CH_3C(6)$, $CH_3C(6')$); IR (CCl_4) 3063 m, 3028 w, 2920 w, 2864 w, 1632 s, 1576 m, 1493 w, 1454 m, 1309 m, 1250 w, 1209 m, 1170 m, 1103 w, 1072 w, 1026 w, 1005 w, 972 w, 941 w, 864 w, 817 m; MS (70 eV) 388 (M^+, 25), 373 (24), 285 (15), 284 (54), 283 (42), 282 (15), 270 (16), 268 (24), 209 (17), 208 (100), 165 (17). Anal. Calcd for $C_{28}H_{24}N_2$ (338.51): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.31; H, 6.31; N, 7.37.

***N*,*N*′-Dibenzyl-6,6′-dimethyl-2,2′-biphenyldiamine (5e).** Sodium borohydride (1.70 g, 45 mmol) was added in small portions to a solution of 7.85 g (20 mmol) of **24** in 35 mL of methanol over a period of 30 min. The solution was then heated under reflux for 15 min and then cooled. After addition of water the milky solution was extracted with CH_2Cl_2 (3×). The CH_2Cl_2 layer was dried (K_2CO_3), filtered, and concentrated to afford a light yellow solid. Recrystallization (diisopropyl ether) gave 7.43 g (94%) of **5e** as colorless plates: mp 118–119 °C; ^1H NMR (300 MHz) 7.29–7.16 (m, 10 H, HAr), 7.08 (dd, J = 7.8, 2.3, 2 H, HC(4), HC(4′)), 6.66 (d, J = 6.8, 2 H, HC(3), HC(3′)), 6.48 (d, J = 7.5, 2 H, HC(5), HC(5′)), 4.28 (br s, 4 H, NCH_2Ph), 4.03 (br s, 2 H, NH), 1.95 (d, J = 2.6, 6 H, $CH_3C(6)$, $CH_3C(6')$); ^{13}C NMR (75.5 MHz) 145.59, 139.95, 137.82, 128.61, 128.48, 126.82, 126.77, 121.42, 119.03, 108.31, 47.61 (NCH_2Ph), 19.70 ($CH_3C(6)$, $CH_3C(6')$); IR (CCl_4) 3428 m, 3067 w, 3032 w, 2920 w, 1583 s, 1510 m, 1495 s, 1470 s, 1454 m, 1360 w, 1323 m, 1296 m, 1277 m, 1230 w, 1172 w, 1028 w, 999 w; MS (70 eV) 392 (M^+, 15), 302 (30), 301 (91), 285 (14), 209 (18), 208 (24), 195 (10), 180 (10), 91 (27), 87 (24), 59 (11), 45 (100). Anal. Calcd for $C_{28}H_{28}N_2$ (392.55): C, 85.67; H, 7.19; N, 7.14. Found: C, 85.66; H, 7.20; N, 7.34.

Representative Procedure for the Preparation of Allenes. The detailed procedures for the preparation of **6ab** and **6ea** are given. The procedure has been optimized, and the unusual addition protocols are required for reproducibility. For all of the other allenes only the amounts of reagents and methods of purification are provided along with the analytical data.

1,3-Dimethyl-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphospholidine 2-Oxide (6ab). A solution of 1.3 mL (15 mmol) of PCl_3 in 5 mL of CH_2Cl_2 and a solution of 2.1 mL (15 mmol) of Et_3N and 1.9 mL (15 mmol) of *N*,*N*′-dimethylethylenediamine in 5 mL of CH_2Cl_2 were added simultaneously at a rate to keep the temperature below −30 °C to 5 mL of CH_2Cl_2 at −40 °C in a 100-mL three-necked round-bottom flask. After the addition was complete, the reaction mixture was warmed to −13 °C, and a solution of 2.1 mL (15 mmol) of triethylamine in 5 mL of CH_2Cl_2 was added dropwise. After addition the mixture was allowed to warm to room temperature and was then stirred for 15 min. The mixture then was cooled to −13 °C, and 1.6 mL (15 mmol) of *N*-methylmorpholine was added via syringe followed after 10 min by 1.45 mL (15 mmol) of 2-methyl-3-butyn-2-ol **25b**. The cold bath was removed and the mixture stirred at room temperature overnight. The reaction mixture then was filtered and concentrated. The residue was dissolved in diethyl ether, filtered again, and concentrated. This procedure was repeated two additional times. The resulting yellow oil was purified by Kugelrohr distillation to afford 2.0 g (67%) of the pale yellow allene **6ab**: bp 215–220 °C (0.05 Torr), ^1H NMR (200 MHz) 5.00 (m, 1 H, HC(1′)), 3.16 (m, 2 H, $H_aC(4)$, $H_aC(5)$), 2.88 (m, 2 H, $H_bC(4)$, $H_bC(5)$), 2.53 (d, J = 10.2, 6 H, NCH_3)), 1.66 (dd, J = 6.7, 3.2, 6 H, 2 × $CH_3C(3')$); ^{13}C NMR (50 MHz) 210.45 (C(2′)), 95.19 (J_{CP} = 14.7, C(3′)), 79.96 (J_{CP} = 160.5, C(1′)), 47.92 (J_{CP} = 9.1, C(4), C(5)), 31.57 (J_{CP} = 4.9, NCH_3), 19.71 (J_{CP} = 6.1, $CH_3C(3')$); IR (CCl_4) 2980 s, 2917 s, 1958 s, 1470 m, 1445 m, 1375 m, 1348 s, 1265 s, 1231 s, 1159 s, 1034 s, 941 s; MS (70 eV) 200 (M^+, 14), 133 (100), 90 (19), 44 (15), 42 (30), 41 (10); TLC R_f 0.30 (CH_2Cl_2/methanol (9:1)).

1,3-Bis(1-methylethyl)-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphospholidine 2-Oxide (6bb). From 20.3 mmol of PCl_3, 2 × 20.3 mmol of NEt_3, 20.3 mmol of **1b**, 20.3 mmol of *N*-methylmorpholine, and 20.3 mmol of 2-methyl-3-butyn-2-ol **25b**. Purification by column chromatography (hexane/acetone (7:3)) afforded 2.8 g (54%) of **6bb** as a pale yellow oil: ^1H NMR (200 MHz) 5.18 (sept, J = 3.2, 1 H, HC(1′)), 3.49 (dsept, J = 6.7, 6.1, 2 H, $NCH(CH_3)_2$), 3.20 (m, 2 H, $H_aC(4)$, $H_aC(5)$), 2.97 (m, 2 H, $H_bC(4)$, $H_bC(5)$), 1.73 (dd, J = 6.7, 3.2, 6 H, 2 × $CH_3C(3')$), 1.23 (d, J = 6.7, 6 H, $NCH(CH_3)_a(CH_3)_b$), 1.17 (d, J = 6.1, 6 H, $NCH(CH_3)_b(CH_3)_a$); ^{13}C NMR (50 MHz) 209.66 (C(2′)), 94.74 (J_{CP} = 15.1, C(3′)), 83.11 (J_{CP} = 163.0, C(1′)), 44.84 (J_{CP} = 4.5, $NCH(CH_3)_2$), 39.86 (J_{CP} = 9.0, C(4), C(5)), 21.59 ($NCH(CH_3)_a(CH_3)_b$), 21.10 (J_{CP} = 3.8, $NCH(CH_3)_b(CH_3)_a$), 19.74 (J_{CP} = 5.3, $CH_3C(3')$); IR (CCl_4) 2971 s, 2932 s, 2868 m, 1960 m, 1458 m, 1400 m, 1364 s, 1254 s, 1235 s, 1179 s; MS (70 eV) 256 (M^+, 18), 241 (11), 189 (100), 147 (51), 105 (59), 76 (12), 56 (10), 49 (16), 43 (12), 42 (13), 41 (23); TLC R_f 0.19 (hexane/acetone (2:1)).

1,3-Bis(1,1-dimethylethyl)-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphospholidine 2-Oxide (6cb). From 20.0 mmol of PCl_3, 2 × 20.0 mmol of NEt_3, 20.0 mmol of **1c**, 20.0 mmol of *N*-methylmorpholine, and 20.0 mmol of 2-methyl-3-butyn-2-ol **25b**. Purification by recrystallization from pentane afforded 2.5 g (44%) of the allene **6cb** as a white crystalline solid: mp 125–126 °C, ^1H NMR (200 MHz) 5.33 (dq, J = 6.4, 3.2, 1 H, HC(1′)), 3.23 (m, 2 H, $H_aC(4)$, $H_aC(5)$), 3.01 (m, 2 H, $H_bC(4)$, $H_bC(5)$), 1.73 (dd, J = 6.7, 3.2, 6 H, 2 × $CH_3C(3')$), 1.33 (s, 18 H, $N(CH_3)_3$); ^{13}C NMR (50 MHz) 208.67 (C(2′)), 95.06 (J_{CP} = 15.3, C(3′)), 88.70 (J_{CP} = 161.2, C(1′)), 52.93 (J_{CP} = 4.3, $NC(CH_3)_3$), 40.73 (J_{CP} = 9.2, C(4), C(5)), 28.74 (J_{CP} = 3.1, $(CH_3)_3CN$), 18.99 (J_{CP} = 6.1, $CH_3C(3')$); IR (CCl_4) 2976 s, 2868 m, 1962 m, 1539 m, 1362 s, 1273 s, 1221 s, 1105 s, 818 s; MS (70 eV) 284 (M^+, 11), 270 (20), 228 (25), 217 (26), 161 (49), 105 (100), 57 (13), 41 (22); TLC R_f 0.22 (hexane/acetone (3:1)). Anal. Calcd for $C_{15}H_{29}N_2OP$ (284.43): C, 63.34; H, 10.30; N, 9.85; P, 10.89. Found: C, 63.21; H, 10.29; N, 9.75; P, 10.75.

2-(3′-Methyl-1′,2′-butadienyl)-1,3-diphenyl-1,3,2-diazaphospholidine 2-Oxide (6db). From 10.0 mmol of PCl_3, 2 × 10.0 mmol of NEt_3, 20.0 mmol of **1d**, 10 mmol of *N*-methylmorpholine, and 20.0 mmol of 2-methyl-3-butyn-2-ol **25b**. Purification by column chromatography (hexane/EtOAc (3:2)) afforded 1.8 g (55%) of allene **6db** as a white crystalline solid: mp 150–150.5 °C, ^1H NMR (200 MHz) 7.24 (m, 8 H, HAr), 6.99 (m, 2 H, HAr), 5.29 (dq, J = 6.4, 3.2, 1 H, HC(1′)), 3.85 (m, 2 H, $H_aC(4)$, $H_aC(5)$), 3.69 (m, 2 H, $H_bC(4)$, $H_bC(5)$), 1.52 (dd, J = 7.6, 3.2, 6 H, 2 × $CH_3C(3')$); ^{13}C NMR (50 MHz) 211.44 (C(2′)), 141.72 (J_{CP} = 7.9, Ar-ipso), 129.24, 121.62, 116.36 (J_{CP} = 4.9, Ar-ortho), 97.38 (J_{CP} = 16.5, C(3′)), 81.33 (J_{CP} = 163.0, C(1′)), 43.02 (J_{CP} = 8.5, C(4), C(5)), 19.01 (J_{CP} = 6.7, $CH_3C(3')$); IR (CCl_4) 2940 m, 2868 m, 1960 m, 1599 s, 1501 s, 1356 m, 1273 s, 1250 s, 1127 m, 963 m, 822 m; MS (70 eV) 324 (M^+, 99), 323 (46), 258 (16), 257 (100), 172 (12), 152 (75), 106 (29), 105 (62), 104 (55), 77 (49), 51 (12), 41 (16); TLC R_f 0.29 (hexane/EtOAc (1:1)). Anal. Calcd for $C_{19}H_{21}N_2OP$ (324.39): C, 70.34; H, 6.54; N, 8.64; P, 9.55. Found: C, 70.41; H, 6.45, N, 8.78, P, 9.55.

1,3-Dibenzyl-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphospholidine 2-Oxide (6ea). A solution of 1.75 mL (20.0 mmol) of PCl_3 in 10 mL of CH_2Cl_2 and a solution of 2.8 mL (20 mmol) of NEt_3 and 4.80 g (20.0 mmol) of *N*,*N*′-dibenzylethylenediamine **1e** in 10 mL of CH_2Cl_2 were added simultaneously to 10 mL of CH_2Cl_2 at 0 °C in a 100-mL, three-necked round-bottom flask. After the addition was complete (ca. 20 min) a solution of 2.8 mL (20 mmol) of NEt_3 in 10 mL of CH_2Cl_2 was added dropwise. After addition the mixture was allowed to reach room temperature and was then stirred for 30 min. The mixture then was cooled to 0

°C, and 2.2 mL (20 mmol) of *N*-methylmorpholine was added via syringe followed after 15 min by 1.56 mL (20.0 mmol) of 3-butyn-2-ol **25a**. The cold bath was removed and the mixture stirred at room temperature overnight. The reaction mixture then was filtered and concentrated. The residue was dissolved in EtOAc, filtered again, and washed with saturated aqueous NH_4Cl (3×), H_2O, and brine and dried ($MgSO_4$). The organic layer was filtered and concentrated to a yellow oil, which was purified by column chromatography (hexane/acetone (1:1)) and afforded 4.55 g (67%) of **6ea** as a colorless oil: ^1H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.39–5.28 (m, 2 H, HC(1′), HC(3′)), 4.24–4.00 (m, 4 H, NCH_2Ph), 3.09–2.86 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 1.76–1.68 (m, 3 H, $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 212.26 (C(2′)), 137.33 (J_{CP} = 6.4, Ar-ipso)), 128.06, 127.79, 126.96, 85.56 (J_{CP} = 15.5, C(3′)), 82.76 (J_{CP} = 163.6, C(1′)), 48.67 (J_{CP} = 6.9), 48.58 (J_{CP} = 5.8, NCH_2Ph), 44.44 (J_{CP} = 8.4, C(4), C(5)), 12.95, 12.84 (C(4′)); IR (CCl_4) 3088 w, 3067 w, 3030 w, 2926 m, 2851 m, 1950 m, 1495 m, 1473 w, 1454 m, 1441 m, 1385 m, 1358 s, 1369 m, 1238 s, 1145 s, 1086 m, 1066 s, 1028 m, 929 m, 856 m; MS (70 eV) 338 (M^+, 12), 285 (21), 193 (6), 91 (100); high-resolution MS calcd for $C_{21}H_{25}N_2OP$ 338.1547, found 338.1549; TLC R_f 0.32 (hexane/acetone (1:1)).

1,3-Dibenzyl-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphospholidine 2-Oxide (6eb). From 20 mmol of PCl_3, 2 × 20 mmol of NEt_3, 20 mmol of **1e**, 20 mmol of *N*-methylmorpholine, and 20 mmol of 2-methyl-3-butyn-2-ol **25b**. Recrystallization (diisopropyl ether) afforded 4.06 g (58%) of the allene **6eb**: mp 86.5–87.0 °C; ^1H NMR (300 MHz) 7.38–7.22 (m, 10 H, HAr), 5.28–5.34 (m, 1 H, HC(1′)), 4.21 (dd, J = 14.9, 6.8, 2 H, NCH_aH_bPh), 4.06 (dd, J = 14.9, 6.8, 2 H, NCH_aH_bPh), 3.11–3.00 (m, 2 H, $H_aC(4)$, $H_aC(5)$), 2.97–2.86 (m, 2 H, $H_bC(4)$, $H_bC(5)$), 1.76 (dd, J = 6.8, 3.2, 2 × $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 210.34 (C(2′)), 137.77 (J_{CP} = 6.6, Ar-ipso)) 128.40, 127.97, 127.17, 95.56 (J_{CP} = 15.3 C(3′)), 81.38 (J_{CP} = 163.9, C(1′)), 48.88 (J_{CP} = 5.4, NCH_2Ph), 44.68 (J_{CP} = 8.6, C(4), C(5)), 19.63 (J_{CP} = 7.4, $CH_3C(3')$); IR (CCl_4) 3088 w, 3067 w, 3030 w, 2982 w, 2920 w, 2851 m, 1958 m, 1356 s, 1269 m, 1228 s, 1145 s, 1066 m; MS (70 eV) 352 (M^+, 16), 285 (23), 193 (12), 92 (9), 91 (100), 65 (7); TLC R_f 0.39 (hexane/acetone (1:1)). Anal. Calcd for $C_{21}H_{25}N_2OP$ (352.45): C, 71.57; H, 7.15; N, 7.95; P, 8.79. Found: C, 71.57; H, 7.23; N, 7.81; P, 8.38.

(*R*,*S*)-(3a*l*,7a*l*,1′*lu*)-1,3-Dibenzyl-2-(1′,2′-butadienyl)-octahydro-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (7ea). From 20 mmol of PCl_3, 2 × 20 mmol of NEt_3, 20 mmol of **2e**, 20 mmol of *N*-methylmorpholine, and 20 mmol of 3-butyn-2-ol **25a**. Recrystallization (diisopropyl ether) afforded 4.82 g (61%) of **7ea** (2 diastereomers, 1:1) as a white crystalline solid: mp 118–120 °C; ^1H NMR (300 MHz) 7.50–7.20 (m, 10 H, HAr), 5.40–5.22 (m, 2 H, HC(1′) HC(3′)), 4.46–4.34 (m, 2 H, NCH_2Ph), 4.06 (dd, J = 8.1, 5.6, 0.5 H, NCH_2Ph), 4.01 (dd, J = 9.3, 6.7, 0.5 H, NCH_2Ph), 3.82 (dd, J = 15.0, 6.7, 0.5 H, NCH_2Ph), 3.78 (dd, J = 15.4, 6.5, 0.5 H, NCH_2Ph), 2.97–2.90 (m, 1 H) and 2.83–2.70 (m, 1 H) (HC(3a), HC(7a)), 1.75–1.58 (m, 7 H, $CH_3C(3')$, $H_2C(4)$, $H_2C(7)$), 1.13–0.94 (m, 4 H, $H_2C(5)$, $H_2C(6)$); ^{13}C NMR (75.5 MHz) 212.76, 212.25 (C(2′)), 139.64 (J_{CP} = 5.6), 139.02 (Ar-ipso), 128.08, 127.91, 127.57, 127.39, 126.79, 85.90 (J_{CP} = 14.6), 85.62 (J_{CP} = 15.2, C(3′)), 83.06 (J_{CP} = 161.9), 83.09 (J_{CP} = 157.7, C(1′)), 64.98 (J_{CP} = 7.2), 63.07 (J_{CP} = 5.5) and 63.01 (J_{CP} = 6.3) (C(3a), C(7a)), 47.22 (J_{CP} = 4.7), 47.06 (J_{CP} = 4.8), 46.79 (J_{CP} = 6.5), 46.71 (J_{CP} = 4.9, NCH_2Ph), 29.54 and 29.47 (C(4), C(7)), 24.16 and 24.01 (C(5), C(6)), 13.37 (J_{CP} = 7.3), 12.86 (J_{CP} = 7.1, $CH_3C(3')$); IR (CCl_4) 3065 m, 3030 m, 2941 s, 2862 m, 1948 m, 1495 m, 1454 m, 1367 m, 1325 m, 1271 m, 1236 s, 1172 s, 1151 m, 1111 m, 1066 m, 1051 m, 1028 m, 854 m, 802 m; MS (70 eV) 392 (M^+, 13), 340 (6), 339 (27), 301 (6), 247 (9), 152 (5), 106 (6), 92 (8), 91 (100), 65 (7); TLC R_f 0.43 (hexane/acetone (1:1)). Anal. Calcd for $C_{24}H_{29}N_2OP$ (392.48): C, 73.44; H, 7.45; N, 7.13; P, 7.89. Found: C, 73.33; H, 7.49; N, 7.07; P, 7.82.

(*R*,*S*)-(3a*l*,7a*l*)-1,3-Dibenzyloctahydro-2-(3′-methyl-1′,2′-butadienyl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (7eb). From 20 mmol of PCl_3, 2 × 20 mmol of NEt_3, 20 mmol of **2e**, 20 mmol of *N*-methylmorpholine, and 20 mmol of 2-methyl-3-butyn-2-ol **25b**. Recrystallization (diisopropyl ether) afforded 6.02 g (74%) of **7eb** as a white crystalline solid: mp 97–98 °C; ^1H NMR (300 MHz) 7.55–7.18 (m, 10 H, HAr), 5.26–5.19 (m, 1 H, HC(1′)), 4.46–4.31 (m, 2 H, NCH_2Ph), 4.06 (dd, J = 15.9, 8.4, 1 H, NCH_aH_bPh), 3.75 (dd, J = 15.9, 7.7, 1 H, NCH_aH_bPh), 2.92 and 2.71 (2 × ddd, J = 11.6, 11.6, 3.2, 2 H, HC(4a), HC(7a)), 1.76 (dd, J = 2.9, 1.2, 3 H, $CH_3C(3')$), 1.73 (dd, J = 2.5, 1.2, 3 H, $CH_3C(3')$), 1.75–1.50 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.20–0.88 (m, 4 H, $H_2C(5)$, $H_2C(6)$); ^{13}C NMR (75.5 MHz) 210.34 (C(2′)), 139.91 (J_{CP} = 7.2), 139.06 (Ar-ipso), 128.10, 127.94, 127.61, 127.41, 126.86, 95.45 (J_{CP} = 14.4, C(3′)), 81.65 (J_{CP} = 160.9, C(1′)), 65.16 (J_{CP} = 6.6) and 62.92 (J_{CP} = 5.8) (C(3a), C(7a)), 47.37 (J_{CP} = 4.2), 46.76 (J_{CP} = 4.1, NCH_2Ph), 29.69 (J_{CP} = 10.9) and 29.54 (C(4), C(7)), 24.22 and 24.06 (C(5), C(6)), 20.04 (J_{CP} = 7.3) and 19.72 (J_{CP} = 6.8) (2 × $CH_3C(3')$); IR (CCl_4) 3065 w, 3028 w, 2939 s, 2862 m, 1959 m, 1495 m, 1454 m, 1356 m, 1325 m, 1271 m, 1221 s, 1172 s, 1109 m, 1066 m, 1051 m, 1028 m, 879 w, 850 m, 821 m; MS (70 eV) 406 (M^+, 15), 339 (7), 315 (7), 247 (9), 106 (11), 96 (5), 92 (8), 91 (100), 71 (12), 65 (9); TLC R_f 0.31 (hexane/acetone (7:3)). Anal. Calcd for $C_{25}H_{31}N_2OP$ (406.51): C, 73.87; H, 7.87; N, 6.89; P, 7.63. Found: C, 73.58; H, 7.61; N, 6.92; P, 7.40.

(*R*,*S*)-(3a*l*,7a*l*,1′*lu*)-1,3-Dibenzyloctahydro-2-(4′-methyl-1′,2′-pentadienyl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (7ec). From 20 mmol of PCl_3, 2 × 20 mmol of NEt_3, 20 mmol of **2e**, 20 mmol of *N*-methylmorpholine, and 20 mmol of 4-methyl-1-pentyn-3-ol **25c**. Recrystallization (diisopropyl ether) afforded 6.34 g (75%) of **7ec** (2 diastereomers, 1:1) as a white crystalline solid: mp 118–122 °C; ^1H NMR (300 MHz) 7.53–7.15 (m, 10 H, HAr), 5.43–5.29 (m, 2 H, HC(1′), HC(3′)), 4.48–4.26 (m, 2 H), 4.16–3.99 (m, 1 H) and 3.81 (dd, J = 15.5, 6.5, 1 H) (NCH_2Ph), 2.97–2.74 (m, 2 H, HC(3a), HC(7a)), 2.46–2.32 (m, 1 H, HC(4′)), 1.78–1.57 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.21–0.85 (m, 10 H, 2 × $CH_3C(4')$, $H_2C(5)$, $H_2C(6)$); ^{13}C NMR (75.5 MHz) 210.40, 210.21 (C(2′)), 139.73, (J_{CP} = 5.2), 139.57 (J_{CP} = 4.9), 138.93 (J_{CP} = 5.5), 138.50 (J_{CP} = 4.8, Ar-ipso), 128.07, 128.00, 127.83, 127.50, 127.44, 127.28, 126.75, 98.56 (J_{CP} = 14.7), 98.07 (J_{CP} = 14.7, C(3′)), 84.86 (J_{CP} = 159.3), 84.69 (J_{CP} = 160.1, C(1′)), 65.13 (J_{CP} = 7.6), 64.73 (J_{CP} = 8.9), 62.89 (J_{CP} = 7.3) and 62.41 (J_{CP} = 6.7) (C(3a), C(7a)), 47.06, 47.02, 46.94, 46.71 (NCH_2Ph), 29.53, 29.42, 29.30, 29.14 (C(4), C(7)), 27.31, 27.23 (C(4′)), 24.14 and 23.92 (C(5), C(6)), 22.71, 22.51, 22.41, and 22.36 (2 × $CH_3C(4')$); IR (CCl_4) 3065 w, 3030 w, 2941 s, 2868 s, 1946 m, 1605 w, 1495 m, 1454 m, 1358 m, 1325 m, 1271 m, 1234 s, 1172 s, 1151 s, 1111 m, 1066 s, 1051 s, 1028 m, 968 m, 920 m, 879 m; MS (70 eV) 420 (M^+, 7), 339 (17), 247 (5), 189 (6), 108 (6), 107 (8), 106 (14), 96 (8), 92 (8), 91 (100); TLC R_f 0.39 (hexane/acetone (3:7)). Anal. Calcd for $C_{28}H_{37}N_2OP$ (420.53): C, 74.26; H, 7.91; N, 6.66; P, 7.36. Found: C, 74.12; H, 8.02; N, 6.61; P, 7.43.

(*R*,*S*)-(3a*l*,7a*l*,1′*lu*)-1,3-Dibenzyloctahydro-2-(4′,4′-dimethyl-1′,2′-pentadienyl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (7ed). From 15 mmol of PCl_3, 2 × 15 mmol of NEt_3 15 mmol of **2e**, 15 mmol of *N*-methylmorpholine, and 15 mmol of 4,4-dimethyl-1-pentyn-3-ol **25d**. Recrystallization (diisopropyl ether) gave 4.60 g (71%) of **7ed** (2 diastereomers, 1:1) as a white crystalline solid: mp 148–150 °C (diisopropyl ether); ^1H NMR (300 MHz) 7.51–7.18 (m, 10 H, HAr), 5.47–5.43 (m, 1 H) and 5.36–5.29 (m, 1 H) (HC(1′), HC(3′)), 4.49–4.16 (m, 1 H), 4.04 (dd, J = 16.0, 7.8, 1 H), 3.83 (dd, J = 12.2, 6.7, 1 H) and 3.78 (dd, J = 12.5, 6.6, 1 H) ((2 × NCH_2Ph), 2.96–2.77 (m, 2 H, HC(3a), HC(7a)), 1.81–1.58 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.18–0.84 (m, 13 H, 3 × $CH_3C(4')$, $H_2C(5)$, $H_2C(6)$); ^{13}C NMR (75.5 MHz) 209.34, 209.17 (C(2′)), 139.89 (J_{CP} = 5.0), 139.82 (J_{CP} = 5.7), 138.95 (J_{CP} = 4.3), 138.31 (J_{CP} = 4.3, Ar-ipso), 128.35, 128.14, 128.05, 127.92, 127.57, 127.50, 126.89, 126.79, 102.96 (J_{CP} = 14.8), 102.54 (J_{CP} = 14.3, C(3′)), 85.60 (J_{CP} = 158.27), 85.42 (J_{CP} = 161.0, C(1′)), 65.32 (J_{CP} = 7.6), 64.68 (J_{CP} = 6.9), 62.96 (J_{CP} = 6.6) and 62.06 (J_{CP} = 7.6) (C(3a), C(7a)), 47.09, 47.00, 46.89, 46.73 (NCH_2Ph), 32.18 (J_{CP} = 4.5), 31.57 (J_{CP} = 4.8, C(4′)), 30.22, 30.13, (3 × $CH_3C(4')$), 29.62, 29.49, 29.37, 29.17, 29.05 (C(4), C(7)), 24.28, 24.22, 24.00, 23.95 (C(5), C(6)); IR (CCl_4) 3067 w, 3030 w, 2943 s, 2864 m, 1948 m, 1605 w, 1495 m, 1475 w, 1554 m, 1360 m, 1325 m, 1271 m, 1238 s, 1209 s, 1172 m, 1151 m, 1111 m, 1066 m, 1051 m, 1028 m, 968 w, 920 w, 879 w, 864 m; MS (70 eV) 434 (M^+, 11), 418 (6), 343 (7), 340 (7), 338 (33), 247 (11), 234 (5), 231 (5), 152 (6), 92 (8), 91 (100), 63 (5); TLC R_f 0.41 (hexane/acetone (1:1)). Anal. Calcd for $C_{27}H_{35}N_2OP$ (434.56): C, 74.62; H, 8.12; N, 6.45; P, 7.13. Found: C, 74.59; H, 8.23; N, 6.50; P, 7.20.

1,3-Bis(1-methylethyl)-2-(1′,2′-butadienyl)-1,3,2-diazaphosphorinane 2-Oxide (8ba). From 20 mmol of PCl_3, 2 × 20 mmol of NEt_3, 20 mmol of **3b**, 20 mmol of *N*-methylmorpholine,

and 15 mmol of 3-butyn-2-ol **25a**. Purification by column chromatography (hexane/acetone (1:1)) and Kugelrohr distillation afforded 4.14 g (81%) of **8ba** as a clear colorless oil: bp 148–150 °C (0.2 Torr); ^{1}H NMR (300 MHz) 5.14 (m, 1 H, HC(1′)), 5.01 (m, 1 H, HC(3′)), 3.74 (m, 2 H, NC*H*(CH$_3$)$_2$), 2.87 (m, 2 H, H$_a$C(4), H$_a$C(6)), 2.76 (m, 2 H, H$_b$C(4), H$_b$C(6)), 1.63 (m, 1 H, H$_a$C(5)), 1.52 (m, 1 H, H$_b$C(5)), 1.51 (ddd, J = 7.0, 6.9, 3.6, 3 H, H$_3$C(4′)), 1.13 (d, J = 6.6, 6 H, 2 × NCH(C*H*$_3$)$_a$(CH$_3$)$_b$), 1.05 (d, J = 6.7, 6 H, 2 × NCH(CH$_3$)$_a$(C*H*$_3$)$_b$); ^{13}C NMR (75.5 MHz) 209.27 (C(2′)), 84.21 (J_{CP} = 14.7, C(3′)), 83.97 (J_{CP} = 153.80, C(1′)), 44.07 (C(1″)), 38.19, 38.05 (C(4), C(6)), 26.18 (C(5)), 20.82, 19.20 (4 × C(2″)), 12.71 (J_{CP} = 6.72, C(4′)); IR (CCl_4) 2853 m, 1948 m, 1454 m, 1365 m, 1273 m, 1240 s, 1203 m, 1136 m, 1086 m, 1059 s, 1028 m; MS (70 eV) 256 (M$^+$, 17), 204 (10), 203 (100), 161 (46), 119 (49), 76 (5), 56 (12), 53 (5), 42 (8); TLC R_f 0.24 (hexane/acetone (1:1)). Anal. Calcd for $C_{13}H_{25}N_2OP$ (256.33): C, 60.92; H, 9.83, N, 10.93; P, 12.08. Found: C, 60.71; H, 9.79; N, 10.84; P, 11.99.

1,3-Bis(1-methylethyl)-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphosphorinane 2-Oxide (8bb). From 50 mmol of PCl_3, 2 × 50 mmol of NEt_3, 50 mmol of **3b**, 50 mmol of *N*-methylmorpholine, and 50 mmol of 2-methyl-3-butyn-2-ol **25b**. Purification by column chromatography (hexane/acetone (1:1)) and Kugelrohr distillation afforded 11.61 g (86%) of **8bb** as a clear colorless oil: bp 156–158 °C (0.2 Torr); ^{1}H NMR (300 MHz) 5.22–5.19 (m, 1 H, HC(1′)), 3.91–3.83 (m, 2 H, NC*H*(CH$_3$)$_2$), 3.05–2.94 (m, 2 H, H$_a$C(4), H$_a$C(6)), 2.90–2.82 (m, 2 H, H$_b$C(4), H$_b$C(6)), 1.78–1.64 (m, 2 H, H$_2$C(5)), 1.66 (dd, J = 6.3, 3.4, 6 H, 2 × H$_3$CC(3′)), 1.13 (d, J = 6.6, 6 H, 2 × NCH(C*H*$_3$)$_a$(CH$_3$)$_b$), 1.04 (d, J = 6.7, 6 H, 2 × NCH(CH$_3$)$_a$(C*H*$_3$)$_b$); ^{13}C NMR (75.5 MHz) 205.27 (C(2′)), 91.78 (J_{CP} = 15.3 C(3′)), 81.43 (J_{CP} = 155.4, C(1′)), 42.62 (J_{CP} = 3.3, NC*H*(CH$_3$)$_2$), 36.78 (C(4), C(6)), 25.03 (C(5)), 19.53, 17.85 and 17.75 (C(4′), NCH(*C*H$_3$)$_2$); IR (CCl_4) 2970 s, 2932 m, 2868 m, 1948 m, 1464 m, 1460 m, 1365 s, 1250 s, 1171 s, 1122 m, 1032 m, 856 m; MS (70 eV) 270 (M$^+$, 19), 204 (11), 203 (100), 161 (48), 119 (47), 76 (5), 56 (13), 44 (6), 43 (9), 41 (9); TLC R_f 0.30 (hexane/acetone (1:1)). Anal. Calcd for $C_{14}H_{27}N_2OP$ (270.35): C, 62.20; H, 10.07; N, 10.36; P, 11.46. Found: C, 62.35; H, 10.05; N, 10.44; P, 11.36.

1,3-Dibenzyl-2-(1′,2′-butadienyl)-1,3,2-diazaphosphorinane 2-Oxide (8ea). From 30 mmol of PCl_3, 2 × 30 mmol of NEt_3, 30 mmol of **3e**, 30 mmol of *N*-methylmorpholine, and 30 mmol of 3-butyn-2-ol **25a**. Purification by column chromatography (hexane/acetone (2:1)) afforded 6.65 g (63%) of **8ea** as a clear colorless oil: ^{1}H NMR (300 MHz) 7.41–7.23 (m, 10 H, ArH), 5.48–5.43 (m, 1 H, HC(1′)), 5.33–5.24 (dq, J = 13.9, 7.0, 1 H, HC(3′)), 4.50 (dd, J = 14.4, 5.5, 1 H, NC*H*$_a$H$_b$Ph), 4.47 (dd, J = 14.4, 5.5, 1 H, NCH$_a$*H*$_b$Ph), 3.93 (dd, J = 14.4, 5.9, 1 H, NC*H*$_a$′H$_b$′Ph), 3.89 (dd, J = 14.4, 5.9, 1 H, NCH$_a$′*H*$_b$′Ph); ^{13}C NMR (75.5 MHz) 209.80 (C(2′)), 137.59 (J_{CP} = 3.0, Ar-ipso), 127.73, 126.61, 84.92 (J_{CP} = 14.5, C(3′)), 81.97 (J_{CP} = 151.4, C(1′)), 49.92 (N*C*H$_2$Ph), 46.26 (C(4), C(6)), 24.66 (J_{CP} = 2.7, C(5)), 12.97 (J_{CP} = 6.4, C(4′)); IR (CCl_4) 2973 s, 2934 m, 2868 m, 1960 m, 1462 m, 1399 m, 1364 s, 1264 s, 1246 s, 1171 s, 1125 m, 1032 s, 868 m, 853 m; MS (70 eV) 352 (M$^+$, 17), 300 (9), 299 (46), 207 (9), 92 (8), 91 (100), 86 (8), 84 (13), 65 (8), 47 (5); high-resolution MS calcd for $C_{21}H_{25}N_2OP$ 352.1705, found 352.1708; TLC R_f 0.38 (hexane/acetone (2:1)).

1,3-Dibenzyl-2-(3′-methyl-1′,2′-butadienyl)-1,3,2-diazaphosphorinane 2-Oxide (8eb). From 15 mmol of PCl_3, 2 × 15 mmol of NEt_3, 15 mmol of **3e**, 15 mmol of *N*-methylmorpholine, and 15 mmol of 2-methyl-3-butyn-2-ol **25b**. Purification by column chromatography (hexane/acetone (2:1)) afforded 3.78 g (69%) of **8eb** as a clear colorless oil: ^{1}H NMR (300 MHz) 7.42–7.23 (m, 10 H, ArH), 5.37–5.35 (m, 1 H, HC(1′)), 4.50 (dd, J = 14.8, 8.5, 2 H, 2 × NC*H*$_a$H$_b$Ph), 3.84 (dd, J = 14.8, 5.5, 2 H, 2 × NCH$_a$*H*$_b$Ph), 3.00–2.92 (m, 4 H, H$_2$C(4), H$_2$C(6)), 1.82–1.77 (m, 1 H, *H*$_a$H$_b$C(5)), 1.78 (dd, J = 6.5, 3.5, 6 H, 2 × H$_3$CC(4′)), 1.56–1.51 (m, 1 H, H$_a$*H*$_b$C(5)); ^{13}C NMR (75.5 MHz) 207.52 (C(2′)), 137.68 (J_{CP} = 6.0, Ar-ipso), 127.71, 126.58, 94.26 (J_{CP} = 14.0, C(3′)), 80.34 (J_{CP} = 151.9, C(1′)), 49.92 (J_{CP} = 3.9, N*C*H$_2$Ph), 46.22 (C(4), C(6)), 24.65 (C(5)), 19.38 (J_{CP} = 7.1, C(4′)); IR (CCl_4) 3030 m, 2938 m, 2851 m, 1960 m, 1495 m, 1454 m, 1358 s, 1265 m, 1233 s, 1134 m, 1057 s, 1028 s, 908 s, 870 m; MS (70 eV) 366 (M$^+$, 6), 299 (28), 106 (8), 105 (8), 91 (100), 77 (9), 65 (8); high-resolution MS calcd for $C_{22}H_{27}N_2OP$ 366.1861, found 366.1863; TLC R_f 0.47 (hexane/acetone (2:1)).

(*R*)-(4*l*,6*l*)-1,3-Dibenzyl-2-(3′-methyl-1′,2′-butadienyl)-4,6-diphenyl-1,3,2-diazaphosphorinane 2-Oxide (9eb). To a solution of 0.16 mL (1.84 mmol) of PCl_3 and 2 × 0.25 mL (1.79 mmol) of NEt_3 in 10 mL of CH_2Cl_2 was added 686 mg (1.68 mmol) of **4e** in 5 mL of CH_2Cl_2 at room temperature in a 50 mL, three-necked round-bottom flask. After the addition (ca. 10 min) the mixture was then stirred for 30 min. *N*-Methylmorpholine (0.19 mL, 1.73 mmol) was added via syringe followed by 0.17 mL (1.76 mmol) of 3-butyn-2-ol **25b**. The mixture was stirred at room temperature overnight. After removal of CH_2Cl_2 the residue was diluted with dry ether (50 mL) then filtered and concentrated to afford a colorless oil, which was purified by column chromatography (hexane/acetone (2:1)) to afford 712 mg (81%) of **9eb** as a gummy oil: $[\alpha]^{24}_D$ +64.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR (300 MHz) 7.40–7.15 (m, 10 H, HAr), 5.75 (m, 1 H, HC(1′)), 4.80 (dd, J = 14.4, 9.2, 1 H, NC*H*$_a$H$_b$Ph), 4.60 (dd, J = 15.5, 9.1, 1 H, NC*H*$_a$′H$_b$′Ph), 4.20 (dt, J = 14.0, 4.3, 1 H, HC(6)), 3.95 (dd, J = 15.5, 6.5, 1 H, NCH$_a$′*H*$_b$′Ph), 3.79 (dt, J = 11.4, 4.2, 1 H, HC(4)), 3.53 (dd, J = 14.4, 11.8, 1 H, NCH$_a$*H*$_b$Ph), 2.39 (ddd, J = 15.0, 11.4, 4.5, 1 H, H$_{ax}$C(5)), 2.00 (dt, J = 14.4, 4.0, H$_{eq}$C(5)), 1.83 (dd, J = 7.1, 3.2, 3 H, CH$_3$C(3′)), 1.80 (dd, J = 8.6, 3.2, 3 H, CH$_3$C(3′)); ^{13}C NMR (75.5 MHz) 207.35 (C(2′)), 141.36 (J_{CP} = 3.0), 139.51, 137.23 (J_{CP} = 4.0) and 136.88 (Ar-ipso), 129.78, 128.66, 128.49, 128.37, 128.23, 128.17, 128.07, 128.01, 127.78, 127.69, 127.39, 127.25, 127.04, 126.97, 126.79, 95.99 (J_{CP} = 16.1, C(3′)), 87.24 (J_{CP} = 173.9, C(1′)), 58.62 and 55.86 (C(4), C(6)), 49.27 (J_{CP} = 5.4) and 47.54 (J_{CP} = 4.6) (NCH$_2$Ph), 42.00 (J_{CP} = 6.8, C(5)), 19.70 (J_{CP} = 6.5) and 19.36 (J_{CP} = 6.6) (2 × *C*H$_3$C(3′)); IR (CCl_4) 3067 w, 3031 w, 2921 w, 1958 m, 1495 m, 1455 m, 1360 m, 1281 w, 1221 s, 1138 m, 1090 m, 1053 s, 1028 m, 916 m, 863 m; MS (70 eV) 518 (M$^+$, 5), 452 (9), 451 (30), 242 (12), 193 (10), 133 (10), 122 (47), 121 (19), 115 (10), 91 (100), 43 (27), 41 (13); high-resolution MS calcd for $C_{34}H_{35}N_2OP$ 518.2487, found 518.2488; TLC R_f = 0.30 (hexane/acetone (3:1)).

(*R*,*S*)-(1′*lu*)-1,3-Dibenzyl-2-(1′,2′-butadienyl)dihydro-7,8-dimethyl-3*H*-1,3,2-dibenzo[*d*,*f*]diazaphosphepine 2-Oxide (10ea). From 10 mmol of PCl_3, 2 × 10 mmol of NEt_3, 10 mmol of **5e**, 10 mmol of *N*-methylmorpholine, and 10 mmol of 3-butyn-2-ol **25a**. Purification by column chromatography (hexane/acetone (7:3)) afforded 3.68 g (78%) of **10ea** as a white foam: ^{1}H NMR (300 MHz) 7.41–6.66 (m, 16 H, HAr), 5.34–5.08 (m, 2 H, HC(1′), HC(3′)), 4.98–4.65 (m) and 4.36–4.28 (m) (4 H, NCH$_2$Ph), 1.82 (s, 1.5 H), 1.79 (s, 1.5 H), 1.53 (s, 1.5 H), and 1.51 (s, 1.5 H) (CH$_3$C(7), CH$_3$C(8)), 1.63–1.49 (m, 3 H, CH$_3$C(3′); ^{13}C NMR (75.5 MHz) 212.61 (C(2′)), 141.04, 139.11, 137.98, 137.91, 137.86, 137.52, 137.39, 136.52, 136.40, 134.99, 128.34, 127.73, 127.19, 126.73, 126.59, 123.09, 122.22, 122.06, 121.99, 86.67 (J_{CP} = 14.4), 86.13 (J_{CP} = 15.7, C(3′)), 80.67 (J_{CP} = 163.8), 80.45 (J_{CP} = 163.4, C(1′)), 51.38 (J_{CP} = 5.5), 51.23 (J_{CP} = 6.5), 50.33 (J_{CP} = 8.3), 49.98 (J_{CP} = 9.4, NCH$_2$Ph), 19.59 and 19.34 (*C*H$_3$C(7), *C*H$_3$C(8)), 12.94 (J_{CP} = 5.2), 12.72 (J_{CP} = 4.7, *C*H$_3$C(3′)); IR (CCl_4) 3065 m, 3030 m, 2924 m, 2866 m, 1950 m, 1570 w, 1495 m, 1454 s, 1365 m, 1321 m, 1234 s, 1203 m, 1101 s, 1074 m, 1039 m, 1028 m, 931 m, 900 w, 856 m, 835 m; MS (70 eV) 491 (M$^+$ + 1, 36), 490 (M$^+$, 100), 489 (5), 438 (18), 437 (55), 399 (10), 301 (22), 106 (10), 91 (24); high-resolution MS calcd for $C_{32}H_{31}N_2O_2P$ 490.2174, found 490.2177; TLC R_f 0.35 (hexane/acetone (1:1)).

Representative Procedure for the Preparation of the Allyl Vinyl Ethers. The detailed procedure for the preparation of **11eaa** is given. For all of the other allyl vinyl ethers only the amounts of reagents and methods of purification are provided along with the analytical data. See Table III for times and temperatures.

(2′*E*)-1,3-Dibenzyl-2-[2-(2″-propenyloxy)-2′-butenyl]-1,3,2-diazaphospholidine 2-Oxide (11eaa). Sodium hydride suspension (107 mg of 50%, 2.20 mmol) was placed in a 25 mL three-necked, round-bottom flask equipped with septa, N_2 inlet, and thermometer. The NaH suspension was washed with hexane (3 × 1 mL) and then dried. After flushing the flask with nitrogen, 15 mL of THF was added and the mixture was cooled to −10 °C. Allyl alcohol **26a** (150 μL, 2.20 mmol) was added and after 15 min a solution of dimethylallene **6aa** (677 mg, 2.00 mmol) in 5 mL of THF was added dropwise via syringe. The reaction was quenched after 90 min (TLC) by addition of water. The mixture was extracted with EtOAc (3 × 25 mL) after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated

to afford a light yellow oil that was purified by column chromatography (EtOAc/hexane (1:1)) to afford 556 mg (70%) of a mixture of allyl vinyl ether **11eaa** as a colorless oil: ^{1}H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.97 (ddd, J = 17.5, 10.3, 5.6, 1 H, HC(2″)), 5.32 (d, finely split, J = 17.5, 1 H, HC(3″)), 5.22 (d, finely split, J = 10.3, 1 H, HC(3″)), 4.62–4.54 (m, 1 H, HC(3′)), 4.32 (dd, J = 14.9, 5.6, 2 H, NCH_aH$_b$Ph), 4.21 (d, J = 5.6, 2 H, H$_2$C(1″)), 4.07 (dd, J = 14.9, 6.9, 2 H, NCH$_a$$H_b$Ph), 3.04 (d, J = 18.9, 2 H, H$_2$C(1′)), 2.99–2.85 (m, 4 H, H$_2$C(4), H$_2$C(5)), 1.65 (dd, J = 6.8, 3.9, 3 H, CH$_3$C(3′)); ^{13}C NMR (75.5 MHz) 149.11 (J_{CP} = 10.1, C(2′)), 137.68 (J_{CP} = 6.1, Ar-ipso)), 133.46 (C(2″)), 128.22, 128.00, 127.09, 117.44 (C(3″)), 93.81 (J_{CP} = 11.1, C(3′)), 67.76 (C(1″)), 48.84 (J_{CP} = 5.3, NCH$_2$Ph), 44.19 (J_{CP} = 9.4, C(4), C(5)), 30.23 (J_{CP} = 113.3, C(1′)), 12.24 (CH$_3$C(3′); IR (CCl$_4$) 3088 w, 3065 w, 3028 w, 2980 m, 2922 m, 2856 m, 1666 s, 1605 w, 1495 m, 1454 m, 1402 m, 1387 m, 1356 s, 1240 s, 1149 s, 1099 s, 1070 s, 1028 m, 929 s, 837 m, 816 s; MS (70 eV) 396 (M$^+$, 4), 355 (29), 285 (24), 193 (7), 92 (8), 91 (100); high-resolution MS calcd for C$_{23}$H$_{29}$N$_2$O$_2$P 396.1966, found 396.1972; TLC R_f 0.39 (hexane/acetone (1:1)).

(2′*E*,2″*E*)-1,3-Dibenzyl-2-[2′-(2″-butenyloxy)-2′-butenyl]-1,3,2-diazaphospholidine 2-Oxide (11eab). From 2.2 mmol of NaH suspension, 2.2 mmol of **26b** and 2.0 mmol **6ea**. Purification by column chromatography (hexane/acetone (1:1)) gave 617 mg (71%) of **11eab**: ^{1}H NMR (300 MHz) 7.46–7.22 (m, 10 H, HAr), 5.80–5.58 (m, 2 H, HC(2″)), HC(3″)), 4.61–4.53 (m, 1 H, HC(3′)), 4.31 (dd, J = 14.9, 6.1, 2 H, NCH_aH$_b$Ph), 4.13 (d, J = 7.2, 2 H, H$_2$C(1″), 4.08 (dd, J = 14.9, 6.7, 2 H, NCH$_a$$H_b$Ph), 3.03 (d, J = 18.9, 2 H, H$_2$C(1′)), 2.96–2.84 (m, 4 H, H$_2$C(4), H$_2$C(5)), 1.71 (d, J = 6.7, 3 H, CH$_3$C(3″), 1.65 (dd, J = 6.7, 3.9, 3 H, CH$_3$C(3′)); ^{13}C NMR (75.5 MHz) 149.19 (J_{CP} = 11.3, C(2′)), 137.74 (J_{CP} = 6.7, Ar-ipso)), 129.82 (C(2″)), 128.20, 128.00, 127.05, 126.35 (C(4″)), 93.45 (J_{CP} = 9.1, C(3′)), 67.47 (C(1″)), 48.88 (J_{CP} = 5.4, NCH$_2$Ph), 44.18 (J_{CP} = 8.8, C(4), C(5)), 30.26 (J_{CP} = 113.0, C(1′)), 17.64, 12.24 (CH$_3$C(3′), CH$_3$C(3″)); IR (CCl$_4$) 3065 w, 3028 w, 2920 m, 2856 m, 1664 s, 1605 w, 1495 m, 1464 m, 1402 m, 1385 m, 1356 m, 1242 s, 1149 s, 1099 s, 1072 s, 1028 w, 1012 w, 966 w, 929 m, 908 m, 837 m; MS (70 eV) 410 (M$^+$, 10), 286 (5), 285 (20), 134 (15), 91 (100); high-resolution MS calcd for C$_{24}$H$_{31}$N$_2$O$_2$P 410.2123, found 410.2127; TLC R_f 0.40 (hexane/acetone (1:1)).

(1′*E*,2″*Z*)-1,3-Dibenzyl-2-[2′-(2″-butenyloxy)-2′-butenyl]-1,3,2-diazaphospholidine 2-Oxide (11eac). From 2.2 mmol of NaH suspension, 2.2 mmol of **26c**, and 2.0 mmol of **6ea**. Purification by column chromatography (hexane/acetone (1:1)) gave 535 mg (66%) of **11eac**: ^{1}H NMR (300 MHz) 7.44–7.20 (m, 10 H, HAr), 5.70–5.60 (m, 2 H, HC(2″)), HC(3″)), 4.60 (qd, J = 6.7, 3.9, 1 H, HC(3′)), 4.32 (dd, J = 14.9, 6.2, 2 H, NCH_aH$_b$Ph), 4.28 (d, J = 5.6, 2 H, H$_2$C(1″)), 4.08 (dd, J = 14.9, 6.8, 2 H, NCH$_a$$H_b$Ph), 3.04 (d, J = 18.9, 2 H, H$_2$C(1′)), 2.99–2.84 (m, 4 H, H$_2$C(4), H$_2$C(5)), 1.67–1.53 (m, 6 H, CH$_3$C(3″); CH$_3$C(3′)); ^{13}C NMR (75.5 MHz) 149.49 (J_{CP} = 11.2, C(2′)), 137.89 (J_{CP} = 5.6, Ar-ipso)), 128.33, 128.13, 127.18, 127.63, 125.92 (C(2′), C(3′)), 93.64 (J_{CP} = 9.8, C(3′)), 62.51 (C(1″)), 48.98 (J_{CP} = 6.9, NCH$_2$Ph), 44.35 (J_{CP} = 9.3, C(4), C(5)), 30.32 (J_{CP} = 113.9, C(1′)), 13.19, 12.35 (CH$_3$C(3′), CH$_3$(C-(3″)); IR (CCl$_4$) 3030 w, 2922 m, 2856 m, 1666 s, 1495 w, 1454 m, 1387 w, 1356 m, 1269 m, 1242 s, 1197 s, 1149 s, 1099 m, 1070 s, 1028 w, 1008 w, 929 m, 908 m, 817 m; MS (70 eV) 410 (M$^+$, 5), 355 (12), 286 (5), 285 (17), 134 (10), 92 (8), 91 (100); high-resolution MS calcd for C$_{24}$H$_{31}$N$_2$O$_2$P 410.2123, found 410.2115; TLC R_f 0.40 (hexane/acetone (1:1)).

1,3-Dibenzyl-2-[3′-methyl-2′-(2″-propenyloxy)-2′-butenyl]-1,3,2-diazaphospholidine 2-Oxide (11eba). From 0.99 mmol of KH suspension, 1.18 mmol of **26a**, and 0.99 mmol of **6eb**. Purification by recrystallization (EtOAc/hexane at −20 °C) afforded 286 mg (70%) of a mixture of allyl vinyl ether **11eaa** and CACR product **17eaa** (96:4): mp 87–88 °C; ^{1}H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.99 (ddd, J = 17.2, 10.3, 5.6, 1 H, HC(2″)), 5.34 (finely split, J = 17.2, 1 H, HC(3″)), 5.21 (d, finely split, J = 10.3, 1 H, HC(3″)), 4.29 (dd, J = 14.8, 6.4, 2 H, NCH_aCH$_b$Ph), 4.17 (d, J = 5.6, 2 H, H$_2$C(1″)), 4.01 (dd, J = 14.8, 6.4, 2 H, NCH$_a$$H_b$Ph), 3.01 (d, J = 18.9, 2 H, H$_2$C(1′)), 2.93 (d, J = 8.6, 4 H, H$_2$C(4), H$_2$C(5)), 1.71 (d, J = 5.8, 3 H) and 1.64 (d, J = 4.2, 3 H) (2 × CH$_3$C(3′)); ^{13}C NMR (75.5 MHz) 141.72 (J_{CP} = 12.2, C(2′)), 137.80 (J_{CP} = 6.9, Ar-ipso)), 134.41 (C(2″)), 128.33, 128.14, 127.15, 118.49 (J_{CP} = 12.2, C(3″)), 116.83 (C(3′)), 70.53 (C(1″)), 48.86 (J_{CP} = 6.1, NCH$_2$Ph), 44.22 (J_{CP} = 8.5, C(4), C(5)), 28.41 (J_{CP} = 114.5, C(1′)), 19.40, 17.37 (2 × CH$_3$C(3′)); IR (CCl$_4$) 3067 w, 3030 w, 2928 m, 2916 m, 2856 m, 1678 s, 1605 w, 1495 m, 1454 m, 1423 m, 1387 m, 1356 m, 1267 m, 1238 s, 1199 s, 1147 s, 1084 s, 1028 m, 995 m, 927 m, 858 w, 837 w; MS (70 eV) 410 (M$^+$, 6), 369 (5), 327 (6), 286 (5), 285 (23), 195 (6), 193 (6), 179 (10), 134 (20), 120 (7), 106 (6), 92 (8), 91 (100); TLC R_f 0.43 (hexane/acetone (1:1)). Anal. Calcd for C$_{24}$H$_{31}$N$_2$O$_2$P (410.54): C, 70.21; H, 7.63; N, 6.83; P, 7.54. Found: C, 70.47; H, 7.42; N, 6.89; P, 7.76.

(2″*E*)-1,3-Dibenzyl-2-[3′-methyl-2′-(2″-butenyloxy)-2′-butenyl]-1,3,2-diazaphospholidine 2-Oxide (11ebb). From 1.42 mmol of KH, 1.70 mmol of **26b**, and 1.42 mmol of **6eb**. Recrystallization (diisopropyl ether) afforded 453 mg (75%) of **11ebb**: mp 77–79 °C; ^{1}H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.74–5.65 (m, 2 H, HC(2″), HC(3″)), 4.33 (dd, J = 14.9, 6.4, 2 H, NCH_aH$_b$Ph), 4.10 (d, J = 5.8, 2 H, H$_2$C(1″)), 4.04 (dd, J = 14.9, 7.2, 2 H, NCH$_a$$H_b$Ph), 3.01 (d, J = 19.0, 2 H, H$_2$C(1′)), 2.92 (d, J = 8.6, 4 H, H$_2$C(4), H$_2$C(5)), 1.73 (d, J = 6.4, 3 H), 1.71 (d, J = 6.3, 3 H) and 1.63 (d, J = 4.2, 3 H) (2 × CH$_3$C(3′) and CH$_3$C(4″)); ^{13}C NMR (75.5 MHz) 141.64 (J_{CP} = 13.2, C(2′)), 137.69 (J_{CP} = 4.0, Ar-ipso)), 129.19 (C(2″)), 128.18, 127.99, 127.01, 127.15 (C(3″)), 118.24 (J_{CP} = 12.2, C(3′)), 70.32 (C(1″)), 48.73 (J_{CP} = 6.1, NCH$_2$Ph)), 44.05 (J_{CP} = 8.7, C(4), C(5)), 28.27 (J_{CP} = 112.9, C(1′)), 19.24, 17.67 (CH$_3$C(3′), CH$_3$C(4″)), 17.34 (J_{CP} = 4.8, CH$_3$C(3′)); IR (CCl$_4$) 3088 w, 3067 w, 3030 w, 2920 m, 2856 m, 1676 s, 1605 w, 1495 m, 1454 m, 1385 m, 1356 s, 1265 m, 1238 s, 1199 s, 1147 s, 1088 s, 1072 s, 1028 m, 999 m, 996 s, 929 m, 858 w, 835 w; MS (70 eV) 424 (M$^+$, 8), 369 (5), 301 (6), 286 (6), 285 (29), 195 (6), 193 (6), 179 (6), 134 (20), 120 (7), 106 (7), 92 (9), 91 (100); TLC R_f 0.41 (hexane/acetone (1:1)). Anal. Calcd for C$_{25}$H$_{33}$N$_2$O$_2$P (424.52): C, 70.72; H, 7.85; N, 6.60; P, 7.28. Found: C, 71.02; H, 7.80; N, 6.76; P, 7.49.

2-[3′-Methyl-2′-(2″-propenyloxy)-2′-butenyl]-1,3-diphenyl-1,3,2-diazaphospholidine 2-Oxide (11dba). From 0.95 mmol of KH suspension, 0.95 mmol of **26a**, and 0.95 mmol of **6db**. Purification by column chromatography (hexane/EtOAc (7:3)) afforded 165 mg (45%) of **11dba** as a white crystalline solid: mp 112.5–113 °C; ^{1}H NMR (200 MHz) 7.30 (m, 8 H, HAr), 7.00 (m, 2 H, HAr), 5.46 (m, 1 H, HC(2″)), 4.88 (m, 2 H, H$_2$C(3″)), 3.71 (m, 4 H, H$_a$C(4), H$_a$C(5), H$_2$C(1″)), 3.55 (m, 2 H, H$_b$C(4), H$_b$C(5)), 3.20 (d, J = 18.7, 2 H, H$_2$C(1′)), 1.46 (d, J = 6.4, 3 H, CH$_3$C(3′)), 0.91 (d, J = 4.8, 3 H, CH$_3$C(3′)); ^{13}C NMR (50 MHz) 142.14 (J_{CP} = 8.6, Ar-ipso)), 139.98 (J_{CP} = 13.5, C(2′)), 134.02 (C(2″)), 129.29, 121.37, 120.16 (J_{CP} = 2.2, C(3′)), 117.05 (C(3″)), 115.99 (J_{CP} = 4.9, Ar-ortho)), 70.48 (J_{CP} = 2.5, C(1″)), 42.52 (J_{CP} = 8.5, C(4), C(5)), 26.16 (J_{CP} = 108.1, C(1′)), 18.31 (CH$_3$C(3′)), 17.12 (J_{CP} = 3.0, CH$_3$C(3′)); IR (CDCl$_3$) 2953 m, 1700 w, 1600 s, 1501 s, 1472 s, 1273 s, 1202 s, 1142 m, 1088 m, 1036 m, 998 s, 963 s, 934 s, 916 s, 888 s; MS (70 eV) 382 (M$^+$, 37), 341 (14), 299 (28), 272 (23), 258 (19), 257 (100), 152 (38), 119 (24), 118 (12), 106 (31), 105 (44), 104 (32), 91 (11), 77 (27), 55 (19), 41 (27); TLC R_f 0.19 (hexane/EtOAc (7:3)). Anal. Calcd for C$_{22}$H$_{27}$N$_2$O$_2$P (382.48): C, 69.08; H, 7.13; N, 7.32. Found: C, 68.81; H, 7.00; N, 7.23.

(*R*,*S*)-(2″*E*)-(3a*I*,7a*I*)-1,3-Dibenzyl-2-[2′-(2″-butenyloxy)-3′-methyl-2′-butenyl]octahydro-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (12ebb). From 3.96 mmol of 35% KH suspension, 3.96 mmol of **26b**, and 3.3 mmol of dimethylallene **7eb**. Recrystallization (EtOAc/hexane at −20 °C) afforded 1.021 g (64%) of **12ebb** as a white crystalline solid: mp 109–111 °C; ^{1}H NMR (300 MHz) 7.55–7.17 (m, 10 H, HAr), 5.79–5.61 (m, 2 H, HC(2″), HC(3″)), 4.45 (dd, J = 16.1, 11.4, 1 H, NCH$_2$Ph), 4.35–4.02 (m, 4 H, NCH$_2$Ph, H$_2$C(1″)), 3.83 (dd, J = 16.1, 5.9, 1 H, NCH$_2$Ph), 3.01–2.67 (m, 4 H, H$_2$C(1′), HC(3a), HC(7a)), 1.82–1.46 (m, 4 H, H$_2$C(4), H$_2$C(7)), 1.73 (d, J = 5.8, 3 H) and 1.69 (d, J = 5.8, 3 H) (2 × CH$_3$C(3′)), 1.61 (d, J = 4.3, 3 H, CH$_3$C(3″)), 1.20–0.76 (m, 4 H, H$_2$C(5), H$_2$C(6)); ^{13}C NMR (75.5 MHz) 141.23 (J_{CP} = 12.9), 140.96 (J_{CP} = 4.7), 137.84 (Ar-ipso), 129.35, 128.75, 128.21, 127.36, 126.95, 126.63, 118.49 (J_{CP} = 12.2 C(3″)), 70.25 (C(1″)), 64.09 (J_{CP} = 7.8) and 62.09 (J_{CP} = 5.2) (C(3a), C(7a)), 47.09 (J_{CP} = 2.9), 46.72 (J_{CP} = 6.4, NCH$_2$Ph), 29.87 (J_{CP} = 7.3) and 29.21 (J_{CP} = 8.6) (C(4), C(7)), 28.42 (J_{CP} = 93.5, C(1′)), 24.29 and 24.00 (C(5), C(6)), 19.60, 17.79, 17.47 (2 × CH$_3$C(3′), CH$_3$C-(3″)); IR (CCl$_4$) 3065 w, 3028 w, 2939 s, 2860 m, 1676 w, 1551 w, 1495 m, 1454 m, 1404 w, 1358 m, 1342 m, 1325 m, 1232 s, 1132 m, 1111 m, 1066 m, 1051 m, 1028 m, 1001 m, 968 m, 906 w, 881 w; MS (70 eV) 478 (M$^+$, 5), 388 (5), 387 (20), 381 (5), 340 (5), 339 (17), 188 (11), 187 (6), 186 (7), 152 (6), 106 (13), 92 (8), 91 (100);

TLC R_f 0.38 (hexane/acetone (7:3)). Anal. Calcd for $C_{29}H_{39}N_2O_2P$ (478.26): C, 72.77; H, 8.21; N, 5.85; P, 6.47. Found: C, 72.59; H, 8.19; N, 5.80; P, 6.62.

(*R*,*S*)-(2′*E*)-(3a*l*,7a*l*)-1,3-Dibenzyloctahydro-2-[2′-(2″-propenyloxy)-2′-butenyl]-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (12eaa). From 4.8 mmol of 50% NaH suspension, 4.8 mmol of **26a**, and 4.0 mmol of **7ea**. Purification by column chromatography (hexane/acetone (2:3)) afforded a colorless oil, which slowly crystallized. Recrystallization (diisopropyl ether) gave 1.146 g (63%) of **12eaa** as a white crystalline solid: mp 95–96 °C; ^{1}H NMR (300 MHz) 7.54–7.15 (m, 10 H, HAr), 5.60 (ddd, J = 16.1, 11.0, 5.7, 1 H, HC(2″)), 5.37 (dd, J = 16.1, 1.1, 1 H, HC(3″)), 5.24 (d, J = 11.0, 1 H, HC(3″)), 4.62–4.45 (m, 2 H, NCH_aH$_b$Ph, HC(3′)), 4.35–4.13 (m, 4 H, NCH$_2$Ph, H$_2$C(1″)), 3.87 (dd, J = 16.1, 6.3, 1 H, NCH$_a$$H_b$Ph), 3.07–2.74 (m, 4 H, H$_2$C(1′), HC(3a), HC(7a)), 1.80–1.40 (m, 7 H, H$_2$C(4), HC (7), CH$_3$C(3′)), 1.14–0.81 (m, 4 H, H$_2$C(5), H$_2$C(6)); ^{13}C NMR (75.5 MHz) 149.01 (J_{CP} = 9.6, C(2′)), 140.68 (J_{CP} = 7.3), 140.64 (Ar-ipso), 133.58 (C(2″)), 128.28, 128.12, 128.02, 127.37, 126.86, 126.64, 117.55 (C(3″)), 94.06 (J_{CP} = 9.7, C(3′)), 67.80 (C(1″)), 64.10 (J_{CP} = 7.9) and 62.67 (J_{CP} = 5.1) (C(3a), C(7a)), 47.24, 46.80 (J_{CP} = 4.9, NCH$_2$Ph), 30.52 (J_{CP} = 112.51, C(1′)), 29.73 (J_{CP} = 7.9) and 29.27 (J_{CP} = 9.3) (C(4), C(7)), 24.36 and 23.99 (C(5), C(6)), 12.34 (*C*H$_3$C(3′)); IR (CCl$_4$) 3065 w, 3028 w, 2939 m, 2862 m, 1666 m, 1605 w, 1495 w, 1454 m, 1402 w, 1356 m, 1344 m, 1325 m, 1271 m, 1242 s, 1226 s, 1207 s, 1174 w, 1155 m, 1101 m, 1066 m, 1063 m, 1028 m, 968 w, 922 m; MS (70 eV) 450 (M$^+$ 5), 409 (8), 359 (20), 340 (5), 339 (17), 247 (10), 188 (9), 187 (6), 186 (6), 152 (6), 106 (13), 92 (8), 91 (100); TLC R_f 0.36 (hexane/acetone (3:2)). Anal. Calcd for $C_{27}H_{35}N_2O_2P$ (450.56): C, 71.98; H, 7.83; N, 6.22; P, 6.87. Found: C, 71.98; H, 8.09; N, 6.05; P, 7.26.

(*R*,*S*)-(2′*E*,2″*E*)-(3a*l*,7a*l*)-1,3-Dibenzyl-2-[2′-(2″-butenyloxy)-2′-butenyl]octahydro-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (12eab). From 2.4 mmol of 50% NaH suspension, 2.4 mmol of **26b**, and 2.0 mmol of **7ea**. Purification by column chromatography (hexane/acetone (1:1)) afforded a colorless oil that slowly crystallized. Recrystallization (diisopropyl ether) gave 0.602 g (64%) of **12eab** as white crystalline solid: mp 98–99 °C; ^{1}H NMR (300 MHz) 7.53–7.16 (m, 10 H, HAr), 5.80–5.63 (m, 2 H, HC(2″), HC(3″)), 4.58–4.07 (m, 6 H, NCH$_2$Ph, NCH_aH$_b$Ph, HC(3′), H$_2$C(1″)), 3.87 (dd, J = 16.1, 6.4, 1 H, NCH$_a$$H_b$Ph), 3.05–2.74 (m, 4 H, H$_2$C(1′), HC(3a), HC(7a)), 1.80–1.65 (m, 4 H, H$_2$C(4), H$_2$C(7)), 1.73 (d, J = 5.8, 3 H, CH$_3$C(3″)), 1.56 (dd, J = 6.8, 3.9, 3 H, CH$_3$C(3′)), 1.20–0.82 (m, 4 H, H$_2$C(5), H$_2$C(6)); ^{13}C NMR (75.5 MHz) 149.19 (J_{CP} = 12.2, C(2′)), 140.82 (J_{CP} = 4.4), 138.60 (J_{CP} = 4.8, Ar-ipso), 130.03 (C(2″)), 128.29, 128.15, 128.06, 127.86, 127.74, 127.44, 126.88, 126.66, 126.53, 93.75 (J_{CP} = 10.3, C(3′)), 67.57 (C(1″)), 64.06 (J_{CP} = 8.0) and 62.89 (J_{CP} = 6.2) (C(3a), C(7a)), 47.37, 46.92 (J_{CP} = 5.8, NCH$_2$Ph), 30.61 (J_{CP} = 112.55, C(1′)), 29.81 (J_{CP} = 8.3) and 29.27 (J_{CP} = 10.1) (C(4), C(7)), 24.42 and 24.06 (C(5), C(6)), 17.76 and 12.36 (*C*H$_3$C(3′), *C*H$_3$C(3″); IR (CCl$_4$) 3065 w, 3028 w, 2939 m, 2862 m, 1664 m, 1551 s, 1495 m, 1454 m, 1356 m, 1344 m, 1325 m, 1242 s, 1155 m, 1101 m, 1066 m, 1053 m, 1028 m, 1007 m, 968 m, 908 w, 881 w; MS (70 eV) 464 (M$^+$, 3), 372 (14), 339 (12), 247 (9), 188 (8), 187 (6), 186 (6), 152 (6), 106 (12), 92 (7), 91 (100); TLC R_f 0.46 (hexane/acetone (1:1)). Anal. Calcd for $C_{28}H_{37}N_2O_2P$ (464.59): C, 72.39; H, 8.02; N, 6.03; P, 6.67. Found: C, 72.45; H, 8.05; N, 6.02; P, 6.70.

(*R*,*S*)-(2′*E*)-(3a*l*,7a*l*)-1,3-Dibenzyl-2-[4′-methyl-2′-(2″-propenyloxy)-2′-pentenyl]octahydro-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (12eca). From 2.4 mmol of 50% NaH suspension, 2.4 mmol of **26a**, 2.4 mmol of *tert*-butyl alcohol, and 2.0 mmol of **7ec**. Purification by column chromatography (hexane/acetone (1:1)) afforded a colorless oil, which slowly crystallized. Recrystallization (diisopropyl ether) gave 0.536 g (55%) of **12eca** as a white crystalline solid: mp 115–117 °C; ^{1}H NMR (300 MHz) 7.54–7.17 (m, 10 H, HAr), 6.00 (dd, J = 16.3, 11.0, 5.7, 1 H, HC(2″), 5.33 (dd, J = 16.3, 1.3, 1 H, HC(3″)), 5.23 (d, J = 11.0, 1 H, HC(3″)), 4.49 (dd, J = 16.1, 11.1, 1 H, NCH_aH$_b$Ph)), 4.35–4.10 (m, 5 H, NCH$_2$Ph, HC(3′), H$_2$C(1′)), 3.86 (dd, J = 16.1, 6.5, 1 H, NCH$_a$$H_b$Ph)), 3.04–2.72 (m, 4 H, H$_2$C(1′), HC(3a), HC(7a)), 2.36–2.26 (m, 1 H, HC(4′)), 1.80–1.62 (m, 1 H) and 1.62–1.45 (m, 3 H) (H$_2$C(4), H$_2$C(7)), 1.13–0.81 (m, 4 H, H$_2$C(5), H$_2$C(6)), 0.97 (d, J = 6.5, 3 H) and 0.96 (d, J = 6.5, 3 H) (2 × CH$_3$C(4′)); ^{13}C NMR (75.5 MHz) 146.92 (J_{CP} = 11.6, C(2′)), 140.77 (J_{CP} = 3.9), 138.34 (Ar-ipso), 133.60 (C(2″)), 128.54, 128.19, 128.08, 127.43, 126.95, 126.68, 117.61 (C(3″)), 108.44 (J_{CP} = 10.7, C(3′)), 67.04 (C(1″)), 63.98 (J_{CP} = 8.2) and 62.68 (J_{CP} = 4.6) (C(3a), C(7a)), 47.27, 46.77 (J_{CP} = 4.7, NCH$_2$Ph), 31.17 (J_{CP} = 111.29, C(1′)), 29.74 (J_{CP} = 7.6) and 29.23 (J_{CP} = 8.9) (C(4), C(7)), 26.85 (C(4′)), 24.43, 24.26, 24.14, 24.06 (C(5), C(6), 2 × *C*H$_3$C(4′)); IR (CCl$_4$) 3088 w, 3065 w, 3028 w, 2943 s, 2864 m, 1660 m, 1549 m, 1495 m, 1554 m, 1402 m, 1381 w, 1358 m, 1325 m, 1306 m, 1271 m, 1213 s, 1155 m, 1113 s, 1066 s, 1053 m, 1028 m, 983 m, 922 m, 883 m, 850 m; MS (70 eV) 478 (M$^+$, 2), 437 (15), 387 (13), 340 (5), 339 (17), 247 (9), 188 (8), 187 (5), 186 (6), 151 (5), 106 (10), 92 (8), 91 (100); TLC R_f 0.46 (hexane/acetone (1:1)). Anal. Calcd for $C_{29}H_{39}N_2O_2P$ (478.61): C, 72.77; H, 8.21; N, 5.85; P, 6.47. Found: C, 72.85; H, 8.34; N, 5.86; P, 6.43.

1,3-Bis(1-methylethyl)-2-[3′-methyl-2′-(2″-propenyloxy)-2′-butenyl]-1,3,2-diazaphosphorinane 2-Oxide (13bba). From 1.5 mmol of 60% NaH suspension, 1.76 mmol of **26a**, 3.7 mmol of *tert*-butyl alcohol, and 1.4 mmol of **8bb**. Purification by column chromatography (hexane/acetone (3:1)) afforded 0.263 g (57%) of **13bba** as a colorless oil: ^{1}H NMR (300 MHz) 6.02–5.89 (m, 1 H, HC(2″)), 5.34–5.09 (m, 2 H, H$_2$C(3″)), 4.18 (ddd, J = 5.9, 1.7, 1.1, 2 H, H$_2$C(1″)), 3.97–3.82 (m, 2 H, NC*H*(CH$_3$)$_2$), 3.10–2.90 (m, 4 H, H$_2$C(4), H$_2$C(6)), 2.75 (d, J = 18.1, 2 H, H$_2$C(1′)), 1.78–1.63 (m, 2 H, H$_2$C(5)), 1.67 (s, 3 H, H$_3$CC(3′)), 1.64 (d, J = 2.5, 3 H, H$_3$CC(3′)), 1.12 (d, J = 6.7, 6 H, NCH(*C*H$_3$)$_a$(CH$_3$)$_b$), 1.03 (d, J = 6.7, 6 H, NCH(CH$_3$)$_a$(*C*H$_3$)$_b$); ^{13}C NMR (75.5 MHz) 142.36 (J_{CP} = 12.5, C(2′)), 134.59 (C(2″)), 116.78 (J_{CP} = 10.8, C(3′)), 115.87 (C(3″)), 69.91 (C(1″), 44.60 (N*C*H(CH$_3$)$_2$), 38.35 (C(4), C(6)), 29.79 (J_{CP} = 114.9, C(1′)), 26.83 (C(5)), 21.45, 19.90, 19.85, 17.27 (6× *C*H$_3$); TLC R_f 0.30 (hexane/acetone (3:1)). Anal. Calcd for $C_{17}H_{33}N_2O_2P$ (328.43): C, 62.17; H, 10.13; N, 8.53; P, 9.43. Found: C, 62.15; H, 10.08; N, 8.56; P, 9.40.

1,3-Dibenzyl-2-[3′-methyl-2′-(2″-propenyloxy)-2′-butenyl]-1,3,2-diazaphosphorinane 2-Oxide (13eba). From 1.5 mmol of 60% NaH suspension, 1.76 mmol of **26a**, 3.7 mmol of *tert*-butyl alcohol, and 1.4 mmol of **8eb**. Purification by column chromatography (hexane/acetone (3:1)) afforded 0.458 g (72%) of **13eba** as a colorless oil: ^{1}H NMR (300 MHz) 7.44–7.22 (m, 10 H, ArH), 6.02 (m, 1 H, HC(2″)), 5.39 (dd, J = 17.4, 1.3, H$_{cis}$C(3″)), 5.22 (d, J = 10.8, 1 H, H$_{trans}$C(3″)), 4.59 (dd, J = 14.7, 8.5, 2 H, NCH_aH$_b$Ph), 4.20 (d, J = 5.4, 2 H, H$_3$C(1″)), 3.78 (dd, J = 14.7, 5.9, 2 H, NCH$_a$$H_b$Ph), 3.07–2.81 (m, 4 H, H$_2$C(4), H$_2$C(6)), 2.93 (d, J = 18.2, 2 H, H$_2$C(1′)), 1.73 (d, J = 4.3, 3 H, H$_3$CC(3′)), 1.71 (d, J = 6.1, 3 H, H$_3$CC(3′)), 1.72–1.60 (m, 1 H, H$_a$C(5)), 1.57–1.45 (m, 1 H, H$_b$C(5)); ^{13}C NMR (75.5 MHz) 141.50 (J_{CP} = 12.2, C(2′)), 138.39 (J_{CP} = 4.9, Ar-ipso), 134.30 (C(2″)), 128.17, 127.98, 126.80, 118.28 (J_{CP} = 10.8, C(3′)), 116.51 (C(3″)), 70.19 (J_{CP} = 2.1, C(1″)), 50.18 (J_{CP} = 3.9, NCH$_2$Ph), 46.22 (C(4)), 27.96 (J_{CP} = 108.3, C((1′)), 24.93 (J_{CP} = 3.5, C(5)), 19.29 (J_{CP} = 2.9, *C*H$_3$C(3′)), 17.19 (J_{CP} = 2.9, *C*H$_3$C(3′)); IR (neat) 3061 w, 3027 w, 2915 m, 2853 m, 1648 w, 1605 w, 1495 m, 1454 m, 1364 m, 1321 m, 1271 m, 1233 s, 1194 s, 1130 m, 1088 s, 1063 s, 1026 m, 974 w, 918 m, 868 m; MS (70 eV) 424 (M$^+$, 3), 300 (8), 299 (31), 148 (13), 92 (9), 91 (100), 41 (8); high-resolution MS calcd for $C_{25}H_{33}N_2O_2P$ 424.2280, found 424.2285; TLC R_f 0.26 (hexane/acetone (3:1)).

1,3-Bis(1-methylethyl)-2-[2′-(2″-propenyloxy)-1′-butenyl]-1,3,2-diazaphosphorinane 2-Oxide (14baa). From 1.8 mmol of 60% NaH suspension, 2.2 mmol of **26a**, 4.6 mmol of *tert*-butyl alcohol, and 1.8 mmol of **8ba**. Purification by column chromatography (hexane/acetone (3:1)) afforded a white solid that was recrystallized from hexane to afford 0.400 g (70%) of **14baa**: mp 56–67 °C; ^{1}H NMR (300 MHz) 5.96–5.90 (m, 1 H, HC(2″)), 5.34 (dd, J = 17.0, 1.4, 1 H, HC(3″)), 5.24 (dd, J = 12.3, 1.4, 1 H, HC(3″)), 4.36 (d, J = 7.0, 1 H, HC(1′)), 4.26 (d, J = 5.1, 2 H, H$_2$C(1″)), 3.81–3.73 (m, 2 H, NC*H*(CH$_3$)$_2$), 3.12–2.96 (m, 2 H, H$_a$C(4), H$_a$C(6)), 2.95–2.84 (m, 2 H, H$_b$C(4), H$_b$C(6)), 2.70 (q, J = 7.2, 2 H, H$_2$C(3′)), 1.90–1.72 (m, 2 H, H$_2$C(5)), 1.16 (d, J = 6.7, 6 H, NCH(*C*H$_3$)$_a$(CH$_3$)$_b$), 1.09 (t, J = 7.2, 3 H, H$_3$C(4′)), 1.00 (d, J = 6.7, 6 H, NCH(CH$_3$)$_a$(*C*H$_3$)$_b$); ^{13}C NMR (75.5 MHz) 171.55 (J_{CP} = 18.0, C(2′)), 132.27 (C(2″)), 116.72 (C(3″)), 87.24 (J_{CP} = 170.2, C(1′)), 67.37 (C(1″)), 44.75 (J_{CP} = 3.6, NCH(CH$_3$)$_2$), 37.93 (C(4), C(6)), 26.48 (C(3′)), 24.84 (C(5)), 19.72, 19.68 (NCH(*C*H$_3$)$_2$), 11.49 (C(4′)); IR (CCl$_4$) 2936 s, 2864 m, 1709 m, 1605 m, 1456 m, 1386 m, 1345 m, 1297 s, 1156 s, 1027 s, 907 m; MS (70 eV) 314 (M$^+$, 30), 300 (15), 299 (80), 245 (17), 205 (22), 203 (100), 202 (33), 187 (78), 163 (30), 161 (42), 155 (32), 145 (30), 119 (55), 100 (21),

98 (53), 86 (30), 84 (65), 72 (44), 70 (38), 58 (50), 57 (49), 56 (82), 44 (36), 43 (55), 42 (51); TLC R_f 0.32 (hexane/acetone (3:1)). Anal. Calcd for $C_{16}H_{31}N_2O_2P$ (314.41): C, 61.12; H, 9.94; N, 8.91; P, 9.85. Found: C, 61.08; H, 9.96; N, 8.83; P, 9.81.

1,3-Dibenzyl-2-[2′-(2″-propenyloxy)-1′-butenyl]-1,3,2-diazaphosphorinane 2-Oxide (14eaa). From 2.0 mmol of 60% NaH suspension, 2.4 mmol of **26a**, 5.0 mmol of *tert*-butyl alcohol, and 1.9 mmol of **8ba**. Purification by column chromatography (hexane/acetone (3:1)) afforded 0.593 g (76%) of **14eaa** as a clear colorless oil: ^{1}H NMR (300 MHz) 7.43–7.23 (m, 10 H, ArH), 5.94–5.88 (m, 1 H, HC(2″)), 5.32 (dd, J = 17.6, 1.2, 1 H, HC(3′)), 5.23 (dd, J = 10.4, 1.2, 1 H, HC(3′)), 4.42 (d, J = 7.9, 1 H, HC(1′)), 4.25 (d, J = 5.2, 2 H, HC(1″)), 4.13 (d, J = 7.1, 4 H, NCH_2Ph), 3.09–2.83 (m, 4 H, $H_2C(4)$, $H_2C(6)$), 2.80 (q, J = 7.3, $H_2C(3')$), 1.79–1.62 (m, 2 H, $H_2C(5)$), 1.13 (t, J = 7.3, 3 H, $H_3C(4')$); ^{13}C NMR (75.5 MHz) 174.19 (J_{CP} = 19.5, C(2′)), 137.89 (J_{CP} = 6.8, Ar-ipso), 131.75, 127.73, 126.68 (C(2″)), 116.94 (C(3″)), 84.41 (J_{CP} = 169.9, C(1′)), 67.49 (C(1″)), 50.30 (NCH_2Ph), 45.44 (C(4), C(6)), 25.31 (C(5)), 24.56 (C(3′)), 11.76 (C(4′)); IR (CCl_4) 2934 m, 1606 s, 1495 m, 1454 m, 1344 m, 1306 m, 1192 m, 1132 m, 1093 m, 1055 m, 1028 m, 929 m, 864 m; MS (70 eV) 410 (M^+, 15), 299 (22), 279 (9), 207 (10), 167 (20), 149 (47), 71 (14), 70 (14), 57 (23), 43 (18); TLC R_f 0.16 (hexane/acetone, 3/1). Anal. Calcd for $C_{24}H_{31}N_2O_2P$ (410.50): C, 70.22; H, 7.61; N, 6.82; P, 7.55. Found: C, 70.34; H, 7.58; N, 6.72; P, 7.42.

(*R*)-(4*l*,6*l*)-(2″*E*)-1,3-Dibenzyl-2-[2′-(2″-butenyloxy)-3′-methyl-2′-butenyl]-4,6-diphenyl-1,3,2-diazaphosphorinane 2-Oxide (15ebb). From 0.424 mmol of **9eb**, 0.424 mmol of 60% NaH suspension, 1.06 mmol of *tert*-butyl alcohol, and 0.509 mmol of **26b**. Purification by column chromatography (hexane/acetone (3:1)) afforded 138 mg (55%) of **15ebb** as a colorless oil that is contaminated with 8% of rearranged product **20ebb** and 52 mg (21%) of **20ebb** (2 diastereomers, 75:25, ^{31}P NMR). Data for **15ebb**: ^{1}H NMR (300 MHz) 7.38–7.09 (m, 20 H, ArH), 5.83–5.66 (m, 2 H, HC(2″), HC(3″)), 4.83 (dd, J = 14.6, 8.7, 1 H, NCH_aH_bPh), 4.69 (dd, J = 15.7, 8.3, 1 H, $NCH_a'H_b'Ph$), 4.35–4.14 (m, 3 H, HC(4), HC(6), $H_aC(1'')$), 3.95 (dd, J = 15.7, 6.4, 1 H, $NCH_a'H_b'Ph$), 3.69 (br d, J = 12.4, 1 H, $H_bC(1'')$), 3.45 (dd, J = 14.6, 13.4, 1 H, NCH_aH_bPh), 3.39 (dd, J = 19.1, 15.1, 1 H, $H_aC(1')$), 2.99 (dd, J = 17.5, 15.1, 1 H, $H_bC(1')$), 2.43 (ddd, J = 14.4, 12.6, 4.4, 1 H, $H_aC(5)$), 1.89 (dt, J = 14.4, 3.0, 1 H, $H_bC(5)$), 1.78 (d, J = 4.2, 3 H, $CH_3C(3')$), 1.77 (d, J = 3.8, 3 H, $CH_3C(3')$), 1.74 (d, J = 5.2, 3 H, $H_3C(4')$); ^{13}C NMR 142.40 (J_{CP} = 13.2, C(2′)), 141.52 (J_{CP} = 4.3), 139.48, 137.62 (J_{CP} = 3.9) and 137.06 (Ar-ipso), 130.22, 128.80, 128.49, 128.36, 128.23, 128.17, 127.71, 127.60, 127.44, 127.05, 126.94, 126.84, 118.89 (J_{CP} = 11.4, C(3′)), 70.71 (J_{CP} = 2.7, C(1″)), 58.96 and 55.56 (C(4), C(6)), 49.15 (J_{CP} = 4.6) and 47.67 (J_{CP} = 3.8) (NCH_2Ph), 42.01 (J_{CP} = 5.8, C(5)), 36.04 (J_{CP} = 123.7, C(1′)), 19.62 (J_{CP} = 2.6), 17.83 and 17.79 (CH_3 × 3); ^{31}P NMR (121.6 MHz) 24.20; IR (CCl_4) 3065 m, 3031 m, 2921 m, 2874 m, 1495 m, 1455 m, 1374 m, 1227 s, 1204 m, 1188 m, 1138 m, 1090 s, 1051 s, 1028 m, 909 m; MS (70 eV) 590 (M^+, 1), 451 (9), 395 (25), 341 (14), 236 (11), 196 (10), 193 (10), 152 (9), 106 (18), 91 (100); high-resolution MS calcd for $C_{38}H_{46}N_2O_2P$ 590.3062, found 590.3068; TLC R_f 0.26 (hexane/acetone (4:1)).

(*R*,*S*)-(2′*E*)-1,3-Dibenzyldihydro-7,8-dimethyl-2-[2′-(2″-propenyloxy)-2′-butenyl]-3*H*-1,3,2-dibenzo[*d*,*f*]diazaphosphepine 2-Oxide (16eaa). From 3.0 mmol of 50% NaH suspension, 3.6 mmol of **26a**, 3.0 mmol of *tert*-butyl alcohol, and 3.0 mmol of **10e**. Purification by column chromatography (hexane/acetone (7:3)) afforded a colorless oil that slowly crystallized. Recrystallization (diisopropyl ether) gave 0.919 g (56%) of **16eaa** as a white crystalline solid: mp 102–103 °C; ^{1}H NMR (300 MHz) 7.49–6.62 (m, 16 H, HAr), 6.13 (ddd, J = 15.9, 10.5, 5.4, 1 H, HC(2″)), 5.42 (d, finely split, J = 15.9, 1 H, HC(3″)), 5.31 (d, finely split, J = 10.5, 1 H, HC(3″)), 4.85–4.65 (m, 3 H, NCH_2Ph, NCH_aH_bPh), 4.33–4.29 (m, 2 H, HC(1″)), 4.20 (dd, J = 14.4, 5.5, 1 H, NCH_aH_bPh)), 3.03 (dd, J = 15.1, 15.1, 1 H, $H_aC(1')$), 2.57 (dd, J = 15.1, 15.1, 1 H, $H_bC(1')$), 1.81 (s, 3 H) and 1.14 (s, 3 H) ($CH_3C(7)$, $CH_3C(8)$), 1.69 (dd, J = 6.9, 3.9, 3 H, $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 148.59 (J_{CP} = 9.4, C(2′)), 141.48, 140.38, 137.94, 137.85, 137.63, 137.25, 136.79, 135.30, 133.66, 128.43, 128.10, 127.75, 127.68, 127.57, 127.14, 126.84, 126.41, 123.90, 122.67, 118.00, 95.20 (J_{CP} = 9.6, C(3′)), 86.25 (C(1″)), 52.23 (J_{CP} = 6.8), 51.16 (J_{CP} = 7.1, NCH_2Ph), 27.91 (J_{CP} = 111.6, C(1′)), 19.67 (J_{CP} = 4.1) and 19.28 (J_{CP} = 4.0) ($CH_3C(7)$, $CH_3C(8)$), 12.39 ($CH_3C(3')$); IR (CCl_4) 3065 w, 3030 w, 2922 w, 2866 w, 1668 m, 1576 w, 1495 w, 1454 s, 1402 w, 1360 w, 1342 w, 1223 s, 1101 s, 1076 m, 1039 m, 1028 m, 929 m, 856 w, 816 m; MS (70 eV) 549 (M^+ + 1, 13), 548 (M^+, 32), 438 (39), 437 (100), 392 (12), 391 (40), 390 (15), 389 (44), 91 (8); TLC R_f 0.41 (hexane/acetone (7:3)). Anal. Calcd for $C_{35}H_{37}N_2O_2P$ (548.66): C, 76.62; H, 6.79; N, 5.10; P, 5.64. Found: C, 76.67; H, 6.81; N, 5.09; P, 5.74.

General Procedure for the Carbanionic Claisen Rearrangement with *n*-BuLi in THF. The detailed procedure for the preparation of **17eaa** is given. For all of the other CACR's with *n*-BuLi only the amounts of reagents and methods of purification are provided along with the analytical data. CACR's under different conditions are specifically described.

1,3-Dibenzyl-2-(3′-methyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphospholidine 2-Oxide (17eaa). *n*-BuLi (0.61 mL, 0.90 mmol, 1.47 M in hexane) was added dropwise to a solution of **11eaa** (297 mg, 0.75 mmol) in 7.5 mL of THF at 0 °C. The yellow solution was stirred for 60 min at 0 °C and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (1:1)) afforded 227 mg (76%) of **17eaa** as a colorless oil: ^{1}H NMR (300 MHz) 7.44–7.24 (m, 10 H, HAr), 5.76–5.62 (m, 1 H, HC(5′)), 5.07–5.00 (m, 2 H, $H_2C(6')$), 4.26 (dd, J = 14.7, 7.3, 2 H, NCH_aH_bPh), 4.12 (dd, J = 14.7, 7.4, 2 H, NCH_aH_bPh), 3.28 (d, J_{CP} = 19.7, 2 H, $H_2C(1')$), 3.05–2.92 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 2.74 (sextet, J = 6.8, 1 H, HC(3′)), 2.41–2.32 (m, 1 H, $H_aC(4')$), 2.12–2.02 (m, 1 H, $H_bC(4')$), 1.06 (d, J = 7.5, 3 H, $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 207.32 (J_{CP} = 8.1, C(2′)), 137.15 (Ar-ipso), 135.24 (C(5′)), 128.45, 128.21, 127.42, 117.06 (C(6′)), 49.01 (J_{CP} = 4.6, NCH_2Ph), 46.87 (C(3′)), 44.51 (J_{CP} = 9.5, C(4), C(5)), 42.89 (J_{CP} = 101.8, C(1′)), 36.61 (C(4′)), 15.50 ($CH_3C(3')$); IR (CCl_4) 3067 w, 3030 w, 2978 w, 2932 m, 2855 m, 1707 s, 1641 w, 1606 w, 1495 m, 1454 m, 1387 m, 1358 m, 1271 m, 1234 s, 1145 s, 1070 m, 1028 m, 916 m, 856 w; MS (70 eV) 396 (M^+, 15), 285 (27), 179 (11), 134 (25), 91 (100), 86 (50), 84 (78); high-resolution MS calcd for $C_{23}H_{29}N_2O_2P$ 396.1966, found 396.1968; TLC R_f 0.43 (hexane/acetone (1:1)).

1,3-Dibenzyl-2-(3′,3′-dimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphospholidine 2-Oxide (17eba). From 1.0 mmol of **11eba**, 1.2 mmol of *n*-BuLi (1.5 M in hexane) for 90 min at −20 °C. Purification by column chromatography (hexane/acetone (1:1)) afforded 224 mg (79%) of **17eba** as a colorless oil: ^{1}H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.76–5.62 (m, 1 H, HC(5′)), 5.08–5.02 (m, 2 H, $H_2C(6')$), 4.28 (dd, J = 14.9, 7.1, 2 H, NCH_aH_bPh)), 4.10 (dd, J = 14.9, 7.4, 2 H, NCH_aH_bPh), 3.33 (d, J_{CP} = 18.2, 2 H, $H_2C(1')$), 3.11–2.95 (m, 4 H, $H_2C(4)$, $H_2(5)$), 2.25 (d, J = 7.3, 2 H, $H_2C(4')$), 1.14 (s, 6 H, 2 × $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 208.84 (J_{CP} = 7.8, C(2′)), 137.27 (J_{CP} = 4.9, Ar-ipso), 133.49 (C(5′)), 128.29, 127.98, 127.19, 118.12 (C(6′)), 48.85 (J_{CP} = 5.1, NCH_2Ph), 48.29 (J_{CP} = 2.7, C(3′)), 44.28 (J_{CP} = 9.8, C(4), C(5)), 43.48 (C(4′)), 36.94 (J_{CP} = 111.1, C(1′)), 23.74 (2 × $CH_3C(3')$); IR (CCl_4) 3067 w, 3030 w, 2972 m, 2855 m, 1703 s, 1639 m, 1601 m, 1495 m, 1468 w, 1454 m, 1387 m, 1360 s, 1230 s, 1147 s, 1072 m, 1030 m, 1001 w, 920 m, 844 m; MS (70 eV) 410 (M^+, 3), 285 (12), 134 (14), 106 (6), 91 (100); high-resolution MS calcd for $C_{24}H_{31}N_2O_2P$ 410.2123, found 410.2131; TLC R_f 0.43 (hexane/acetone (1:1)).

1,3-Dibenzyl-2-(3′,3′,4′-trimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphospholidine 2-Oxide (17ebb). From 0.54 mmol of **11ebb** and 0.64 mmol of *n*-BuLi (1.47 M, in hexane) for 45 min at 0 °C. Purification by column chromatography (hexane/acetone (1:1)) afforded 188 mg (82%) of **17ebb** as a colorless oil: ^{1}H NMR (300 MHz) 7.40–7.20 (m, 10 H, HAr), 5.73–5.61 (m, 1 H, HC(5′)), 5.10–5.00 (m, 2 H, $H_2C(6)$), 4.28 (dd, J = 14.8, 7.2, 2 H, NCH_aH_bPh)), 4.09 (ddd, J = 14.7, 7.6, 3.4, 2 H, NCH_aH_bPh), 3.30 (d, J_{CP} = 18.0, 2 H, $H_2C(1')$), 3.12–2.95 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 2.47 (quint, J = 7.5, 1 H, HC(4′)), 1.08 (s, 6 H, 2 × $CH_3C(3')$), 0.94 (d, J = 6.8, 3 H, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 209.25 (J_{CP} = 6.3, C(2′)), 139.08 (C(5′)), 137.33 (J_{CP} = 5.4, Ar-ipso), 128.31, 128.04, 127.21, 115.96 (C(6′)), 51.23 (J_{CP} = 4.9, NCH_2Ph), 48.91 (J_{CP} = 5.4, C(4), C(5)), 44.30 (J_{CP} = 9.6, C(3′)), 43.96 (C(4′)), 37.33 (J_{CP} = 110.0, C(1′)), 21.77, 20.02, 15.00 (2 × $CH_3C(3')$, $CH_3C(4')$); IR (CCl_4) 3067 m, 3030 m, 2974 m, 2878 m, 1703 s, 1637 w, 1599 m, 1495 m, 1445 m, 1387 m, 1360 m, 1221 s, 1228 s, 1147 s, 1072 m, 1028 m, 997 m, 908 w, 843 m, 817 m; MS (70 eV) 424 (M^+, 10),

326 (5), 285 (29), 134 (19), 91 (100); high-resolution MS calcd for $C_{25}H_{33}N_2O_2P$ 424.2277, found 424.2274; TLC R_f 0.47 (hexane/acetone (1:1)).

(*R*,*S*)-(3*l*,4*u*)-1,3-Dibenzyl-2-(3′,4′-dimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphospholidine 2-Oxide (*syn*-17eab). From 0.75 mmol of **11eab** and 0.90 mmol of *n*-BuLi (1.47 M in hexane) for 60 min at 0 °C. Purification by chromatography (hexane/acetone (1:1)) afforded 225 mg (74%) of a mixture of *syn*-**17eab** and *anti*-**17eab** (97:3, ^{31}P NMR) as a colorless oil: ^{1}H NMR (300 MHz) 7.41–7.24 (m, 10 H, HAr), 5.72 (ddd, J = 17.4, 10.3, 7.4, 1 H, HC(5′)), 5.00 (d, J = 17.4, 1 H, HC(6′)), 4.98 (d, J = 10.3, 1 H, HC(6′)), 4.32–4.00 (m, 4 H, NCH_2Ph)), 3.34 (dd, J = 19.6, 14.2, 1 H, $H_aC(1')$, 3.17 (dd, J = 19.6, 14.2, 1 H, $H_bC(1')$), 3.03–2.91 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 2.66 (quint, J = 6.7, 1 H, HC(3′)), 2.46 (sextet, J = 6.7, 1 H, HC(4′)), 1.00 (d, J = 6.7, 3 H) and 0.95 (d, J = 6.7, 3 H) ($CH_3C(3')$, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 207.38 (J_{CP} = 7.1, C(2′)), 141.54 (C(5′)), 137.17 (J_{CP} = 5.1, Ar-ipso), 128.40, 128.24, 128.15, 127.36, 114.33 (C(6′)), 51.91 (C(3′)), 49.14 (J_{CP} = 4.9), 48.85 (J_{CP} = 5.5, NCH_2Ph)), 44.61 (J_{CP} = 9.3), 44.38 (J_{CP} = 9.7, C(4), C(5)), 43.11 (J_{CP} = 103.1, C(1′)), 39.23 (C(4′)), 15.46, 12.13 ($CH_3C(3')$, $CH_3C(4')$); ^{31}P NMR (121.5 MHz, acetone-d_6/acetone) 30.37; IR (CCl_4) 3067 w, 3030 w, 2974 m, 2930 m, 2874 m, 1705 s, 1639 w, 1606 w, 1495 w, 1454 m, 1385 m, 1358 m, 1269 m, 1232 s, 1145 s, 1068 m, 1028 m, 910 m, 858 w; MS (70 eV) 396 (M^+, 8), 286 (5), 285 (24), 237 (5), 193 (5), 179 (6), 152 (5), 134 (20), 91 (100), 83 (14); high-resolution MS calcd for $C_{23}H_{29}N_2O_2P$ 410.2123, found 410.2127; TLC R_f 0.43 (hexane/acetone (1:1)).

(*R*,*S*)-(3*l*,4*l*)-1,3-Dibenzyl-2-(3′,4′-dimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphospholidine 2-Oxide (*anti*-17eac). From 0.75 mmol **11eac** and 0.90 mmol of *n*-BuLi (1.57 M in hexane) for 90 min followed by the addition of 0.2 mL of *n*-BuLi (1.57 N, 0.31 mmol in hexane) and stirred for another 30 min. Purification by column chromatography (hexane/acetone (1:1)) afforded 136 mg (44%) of a mixture of *anti*-**17eac** and *syn*-**17eac** (93:7, ^{31}P NMR) as a colorless oil: ^{1}H NMR (300 MHz) 7.40–7.25 (m, 10 H, HAr), 5.68–5.56 (m, 1 H, HC(5′)), 5.01 (d, J = 10.8, 1 H, HC(6′)), 5.00 (d, J = 16.7, 1 H, HC(6′)), 4.31–4.07 (m, 4 H, NCH_2Ph), 3.39 (dd, J = 19.2, 14.1, 1 H, $H_aC(1')$), 3.17 (dd, J = 19.8, 14.1, 1 H, $H_bC(1')$), 3.04–2.93 (m, 4 H, $H_2C(4)$, $H_2C(5)$), 2.60 (quint, J = 6.8, 1 H, HC(3′)), 2,46 (sextet, J = 6.8, 1 H, HC(4′)), 1.00 (d, J = 6.8, 6 H, $CH_3C(3')$, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 207.62 (C(2′)), 140.41 (C(5′)), 137.30 (J_{CP} = 5.3, Ar-ipso), 128.54, 128.35, 127.53, 105.77 (C(6′)), 52.32 (C(3′)), 49.26 (J_{CP} = 4.6), 49.06 (J_{CP} = 6.6, NCH_2Ph), 44.77 (J_{CP} = 9.7), 44.55 (J_{CP} = 9.7, C(4), C(5)), 43.18 (J_{CP} = 102.6, C(1′)), 39.88 (C(4′)), 18.18, 13.33 ($CH_3C(3')$, $CH_3C(4')$); ^{31}P NMR (121.5 MHz, acetone-d_6/acetone) 30.43; IR (CCl_4) 3067 w, 3030 w, 2974 m, 2952 m, 2855 m, 1705 s, 1606 w, 1496 w, 1454 m, 1358 m, 1271 m, 1232 s, 1145 s, 1068 m, 1028 m, 910 m, 858 w; MS (70 eV) 410 (M^+, 7), 285 (18), 179 (8), 134 (21), 120 (9), 118 (10), 91 (95), 87 (39), 83 (100); high-resolution MS calcd for $C_{23}H_{29}N_2O_2P$ 410.2123, found 410.2115; TLC R_f 0.42 (hexane/acetone (1:1)).

(*R*,*S*)-(3a*l*,7a*l*,3′*lu*)-1,3-Dibenzyloctahydro-2-(3′-methyl-2′-oxo-5′-hexen-1′-yl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (18eaa). From 0.5 mmol of **12eaa** and 0.6 mmol of *n*-BuLi (1.57 M in hexane) for 50 min at 0 °C. Purification by column chromatography (hexane/acetone (7:3)) afforded 160 mg (85%) of **18eaa** (2 diastereomers, ratio 42:58, HPLC) as a colorless solid: mp 100–102 °C; ^{1}H NMR (300 MHz) 7.49–7.18 (m, 10 H, HAr), 5.72–5.54 (m, 1 H, HC(5′)), 5.06–4.95 (m, 2 H, $H_2C(6')$), 4.49–4.26 (m, 2 H, NCH_2Ph), 4.10–3.96 (m, 2 H, NCH_2Ph), 3.19–2.94 (m, 2 H, $H_2C(1')$), 2.94–2.79 (m, 2 H, HC(3a), HC(7a)), 2.51–2.44 (m), 2.34–2.17 (m) and 2.03–1.89 (m) (3 H, HC(3′), $H_2C(4')$), 1.75–1.50 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.25–0.80 (m, 4 H, $H_2C(5)$, $H_2C(6)$), 0.96 (d, J = 6.8) and 0.93 (d, J = 7.1) (3 H, $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 207.62, 207.53 (C(2′)), 139.94, 139.90, 137.87, 135.65 and 134.92 (Ar-ipso, C(5′)), 128.96, 128.43, 128.14, 127.49, 127.36, 126.89, 117.13 and 116.85 (C(6′)), 64.25 (J_{CP} = 7.4), 64.16 (J_{CP} = 7.2), 63.51 (J_{CP} = 6.1) and 63.44 (J_{CP} = 5.5) (C(3a), C(7a)), 47.32, 46.70 and 46.58 (C(3′), NCH_2Ph)), 42.49 (J_{CP} = 99.3) and 41.98 (J_{CP} = 99.3) (C(1′)), 36.97 and 36.13 (C(4′)), 29.28, 29.71, 29.49 and 29.39 (C(4), C(7)), 24.14 and 24.04 (C(5), C(6)), 15.75 and 14.95, ($CH_3C(3')$); IR (CCl_4) 3067 w, 3030 w, 2939 s, 2864 m, 1705 s, 1641 w, 1606 w, 1495 m, 1454 m, 1358 m, 1325 m, 1271 m, 1223 s, 1174 s, 1111 m, 1066 m, 1028 m, 993 m, 966 m, 918 m, 881 m, 854 m; MS (70 eV) 450 (M^+, 5), 359 (20), 339 (12), 247 (10), 188 (10), 187 (7), 186 (7), 106 (16), 92 (8), 91 (100); TLC R_f 0.36 (hexane/acetone (3:2)); HPLC t_R 12.27 min (42%); 13.06 min (58%) (SiO_2, hexane/isopropyl alcohol (95:5)). Anal. Calcd for $C_{27}H_{35}N_2O_2P$ (450.56): C, 71.97; H, 7.83; N, 6.21; P, 6.87. Found: C, 72.02; H, 7.87; N, 6.12; P, 6.80.

(*R*,*S*)-(3a*l*,7a*l*,3′*lu*)-1,3-Dibenzyloctahydro-2-(3′-isopropyl-2′-oxo-5′-hexen-1′-yl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (18eca). From 0.5 mmol of **12eca** and 0.6 mmol of *n*-BuLi (1.57 M in hexane) for 50 min at 0 °C. Purification by column chromatography (hexane/acetone (7:3)) afforded 178 mg (74%) of **18eca** (2 diastereomers, ratio 43:57, HPLC) as a colorless oil, which slowly crystallized: mp 97–100 °C; ^{1}H NMR (300 MHz) 7.50–7.18 (m, 10 H, HAr), 5.74–5.59 (m, 1 H, HC(5′)), 5.09–4.90 (m, 2 H, $H_2C(6')$), 4.51–4.24 (m, 2 H, NCH_2Ph), 4.07–3.87 (m, 2 H, NCH_2Ph), 3.17–2.78 (m, 4 H, $H_2C(1')$, HC(3a), HC(7a)), 2.37–2.02 (m) and 1.92–1.80 (m) (4 H, HC(3′), $H_2C(4')$, $CH(CH_3)_2$), 1.66–1.48 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.13–0.80 (m, 4 H, $H_2C(5)$, $H_2C(6)$), 0.91 (d, J = 6.7), 0.83 (d, J = 7.1), 0.87 (d, J = 6.8) and 0.74 (d, J = 6.9) (6 H, $CH(CH_3)_2$); ^{13}C NMR (75.5 MHz) 206.84 and 206.60 (J_{CP} = 6.9, C(2′)), 140.15, 140.09, 138.10, 137.89, 136.73, 135.76 ((Ar-ipso), C(5′)), 129.34, 128.95, 128.43, 128.15, 127.32, 127.41, 127.30, 127.15 (C(Ar)), 116.60 and 116.40 (C(6′)), 64.13, 64.05, 63.94 and 63.67 (C(3a), C(7a)), 58.74 and 58.54 (C(3′)), 47.57, 47.39 (J_{CP} = 7.9), 46.92 (J_{CP} = 5.4), 46.80 (J_{CP} = 6.9, NCH_2Ph), 43.84 (J_{CP} = 101.9), 42.92 (J_{CP} = 100.5, C(1′)), 31.47, 30.28, 28.54, 28.04 (C(4′), $CH(CH_3)_2$)), 29.29 (J_{CP} = 7.8), 29.81 (J_{CP} = 7.9), 29.27 (J_{CP} = 4.5), 29.21 (J_{CP} = 4.4, C(4), C(7)), 24.13 (C(5), C(6)), 21.25, 20.47, 18.98, 18.67 ($CH(CH_3)_2$); IR (CCl_4) 3067 w, 3030 w, 2941 s, 2870 m, 1701 s, 1495 w, 1454 m, 1358 m, 1325 m, 1271 m, 1221 s, 1174 s, 1111 m, 1068 m, 1045 m, 1028 m, 914 m, 854 w; MS (70 eV) 478 (M^+, 5), 386 (25), 338 (18), 247 (9), 188 (13), 187 (9), 186 (8), 106 (16), 92 (9), 91 (100); TLC R_f 0.46 (hexane/acetone (3:2)); HPLC t_R 17.20 min (43%), 18.00 min (57%) (SiO_2, hexane/isopropyl alcohol (96:4)). Anal. Calcd for $C_{29}H_{39}N_2O_2P$ (468.61): C, 72.77; H, 8.21; N, 5.85; P, 6.47. Found: C, 72.70; H, 8.31; N, 5.77; P, 6.39.

(*R*,*S*)-(3a*l*,7a*l*,3′*lu*,4′*lu*)-1,3-Dibenzyl-2-(3′,4′-dimethyl-2′-oxo-5′-hexen-1′-yl)octahydro-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (18eab). From 0.5 mmol of **12eab** and 0.6 mmol of *n*-BuLi (1.57 M in hexane) for 60 min at 0 °C. Purification by column chromatography (hexane/acetone (7:3)) afforded 172 mg (74%) of **18eab** (2 diastereomers, ratio 43:57, HPLC) as a colorless oil, which slowly crystallized: mp 105–110 °C; ^{1}H NMR (300 MHz) 7.49–7.18 (m, 10 H, HAr), 5.74–5.53 (m, 1 H, HC(5′)), 5.00–4.89 (m, 2 H, $H_2C(6')$), 4.51–4.26 (m, 2 H, NCH_2Ph)), 4.11–3.87 (m, 2 H, NCH_2Ph)), 3.21–2.80 (m, 4 H, $H_2C(1')$, HC(3a), HC(7a)), 2.49–2.21 (m, 2 H, HC(3′), HC(4′)), 1.94–1.86 (m) and 1.66–1.57 (m) (4 H, $H_2C(4)$, $H_2C(7)$), 1.21–1.02 (m) and 0.97–0.83 (m) (4 H, $H_2C(5)$, $H_2C(6)$), 0.91 (d, J = 6.8) and 0.84 (d, J = 6.4) (6 H, $CH_3C(3')$, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 207.91, 207.51 (J_{CP} = 7.4, C(2′)), 141.93, 141.35, 139.99 (J_{CP} = 4.5), 137.91 ((Ar-ipso), C(5′)), 129.13, 128.85, 128.42, 128.13, 127.47, 127.30, 126.87 (C(Ar)), 114.37, 114.17 (C(6′)), 64.35 (J_{CP} = 7.4), 64.03 (J_{CP} = 7.8), 63.52 (J_{CP} = 4.1), 63.49 (C(3a), C(7a)), 51.55, 51.62 (C(3′)), 47.41, 47.20, 46.88 (J_{CP} = 5.3), 46.66 (NCH_2Ph), 43.43 (J_{CP} = 98.6), 42.93 (J_{CP} = 98.8, C(1′)), 39.43, 38.75 (C(4′)), 29.87 (J_{CP} = 7.9), 29.71 (J_{CP} = 7.4), 29.43 (J_{CP} = 10.7), 29.25 (J_{CP} = 9.8, C(4), C(7)), 24.16, 24.09, 24.04 (C(5), C(6)), 15.46, 15.20, 12.26, 11.68 ($CH_3C(3')$, $CH_3C(4')$); IR (CCl_4) 3067 w, 3030 w, 2941 s, 2866 m, 1703 s, 1637 w, 1605 w, 1495 m, 1454 s, 1358 m, 1325 m, 1271 m, 1223 s, 1174 s, 1111 m, 1068 m, 1028 m, 966 m, 916 m, 881 m; MS (70 eV) 464 (M^+, 3), 373 (18), 339 (13), 247 (10), 188 (10), 187 (7), 185 (7), 106 (14), 92 (8), 91 (100); TLC R_f 0.46 (hexane/acetone (1:1)); HPLC t_R 17.87 min (43%), 18.67 min (57%) (SiO_2, hexane/isopropyl alcohol (95:5)). Anal. Calcd for $C_{28}H_{37}N_2O_2P$ (464.59): C, 72.39; H, 8.02; N, 6.03; P, 6.66. Found: C, 72.36; H, 7.97; N, 6.07; P, 6.85.

(*R*,*S*)-(3a*l*,7a*l*,4′*lu*)-1,3-Dibenzyloctahydro-2-(3′,3′,4′-trimethyl-2′-oxo-5′-hexen-1′-yl)-1*H*-1,3,2-benzodiazaphosphole 2-Oxide (18ebb). From 0.5 mmol of **12ebb** and 0.6 mmol of *n*-BuLi (1.57 M in hexane) for 45 min at −20 °C. Purification by column chromatography (hexane/acetone (7:3)) afforded 203 mg (85%) of **18ebb** (2 diastereomers, ratio 40:60, ^{1}H NMR) as a colorless oil, which slowly crystallized: mp 110–113 °C; ^{1}H NMR (300 MHz) 7.49–7.18 (m, 10 H, HAr), 5.63 (dd, J = 18.9, 10.4)

and 5.99 (dd, J = 18.9, 10.4) (1 H, HC(5′)), 5.03–4.97 (m, 2 H, $H_2C(6')$), 4.50–3.91 (m, 4 H, NCH_2Ph)), 3.28 (dd, J = 16.6, 16.6, 1 H, $H_aC(1')$), 3.02 (dd, J_{CP} = 19.2, 16.6, 1 H, $H_bC(1')$), 3.18–3.04 (m, 1 H) and 2.88–2.74 (m, 1 H) (HC(3a), HC(7a)), 2.34–2.29 (m, 1 H, HC(4′)), 1.82–1.54 (m, 4 H, $H_2C(4)$, $H_2C(7)$), 1.21–0.81 (m, 4 H, $H_2C(5)$, $H_2C(6)$), 0.99 (s) and 0.98 (s) (6 H, 2 × $CH_3C(3')$), 0.89 (d, J = 6.8, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 209.23 and 209.13 (C(2′)), 140.18, 140.12, 139.21, 139.11, 137.90 (Ar-ipso, C(5′)), 128.56, 128.29, 128.09, 127.80, 127.63, 127.43, 127.11, 126.88, 126.79 (C(Ar)), 115.97 and 115.93 (C(6′)), 63.85, 63.73, 63.06, 62.98 (C(3a), C(7a)), 51.27, 51.21 (C(3′)), 47.14, 46.70 (J_{CP} = 4.2, NCH_2Ph)), 36.93 (C(4′)), 29.77, 29.66, 29.21, 29.08 (C(4), C(7)), 24.15, 24.00 (C(5), C(6)), 22.22, 21.54, 20.18, 19.65, 15.04 (2 × $CH_3C(3')$, $CH_3C(4')$); IR (CCl_4) 3065 w, 3028 w, 2939 s, 2866 m, 1701 s, 1603 m, 1495 m 1454 m, 1358 m, 1325 m, 1271 m, 1221 s, 1172 m, 1111 m, 1066 m, 1028 m, 997 m, 966 m, 920 m, 881 m; MS (70 eV) 478 (M^+, 3), 387 (17), 339 (15), 247 (7), 188 (10), 106 (13), 92 (9), 91 (100); TLC R_f 0.38 (hexane/acetone (7:3)). Anal. Calcd for $C_{29}H_{39}N_2O_2P$ (478.26): C, 72.77; H, 8.21; N, 5.85; P, 6.47. Found: C, 72.70; H, 8.16; N, 5.93; P, 6.45.

Variation of Conditions in the CACR with 12eaa. (a) LDA. A solution of **12eaa** (225 mg, 0.5 mmol) in 1 mL of THF was added to a solution of 0.6 mmol of LDA in 4 mL of THF at 0 °C. The yellow solution was stirred for 45 min at 0 °C and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 146 mg (64%) of **18eaa** (2 diastereomers, ratio 42:58, HPLC). **(b) KDMSO.** Potassium hydride (20.2 mg of 35% dispersion, 7.1 mg KH, 0.176 mmol) was placed in a 5-mL two-necked round-bottom flask with septa and N_2-inlet. The KH suspension was washed with hexane (3 × 1 mL) and then dried by evacuating the flask. After the flask was flushed with N_2, 1 mL of DMSO was added. After 15 min, a solution of **12eaa** (56.3 mg, 0.125 mmol) in 1 mL of DMSO was added at room temperature. The yellow solution was stirred for 2 h at room temperature and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 45.5 mg (79%) of **18eaa** (2 diastereomers, ratio 69:31, HPLC). **(c) KDMSO/LiCl.** Potassium hydride (20.2 mg of 35% dispersion, 7.1 mg KH, 0.176 mmol) was placed in a 5-mL two-necked round-bottom flask with septa and N_2-inlet. The KH suspension was washed with hexane (3 × 1 mL) and then dried by evacuating the flask. After the flask was flushed with N_2, 42.4 mg (1 mmol) of LiCl and 1 mL of DMSO were added (H_2 evolution). After 15 min a solution of **12eaa** (56.3 mg, 0.125 mmol) in 1 mL of DMSO was added at room temperature. The yellow solution was stirred for 2 h at room temperature and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 44.6 mg (78%) of **18eaa** (2 diastereomers, ratio 52:48, HPLC). **(d) Thermal.** A solution of **12eaa** (36 mg, 0.08 mmol) in 2 mL of toluene was refluxed for 2 h. The solution was evaporated to afford a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 29 mg (81%) of **18eaa** (2 diastereomers, ratio 38:62, HPLC).

1,3-Dibenzyl-2-(3′,3′-dimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphosphorinane 2-Oxide (19eba). From 0.254 mmol of **13eba** and 0.30 mmol of n-BuLi (1.51 M in hexane) for 30 min at −20 °C. Purification by column chromatography (hexane/acetone (2:1)) afforded 98 mg (91%) of **19eba** as a colorless oil: ^1H NMR (300 MHz) 7.43–7.24 (m, 10 H, ArH), 5.74 (m, 1 H, HC(5′)), 5.08 (d, J = 12.1, 1 H, HC(6′)), 5.07 (d, J = 15.1, 1 H, HC(6′)), 4.53 (dd, J = 14.7, 9.1, 2 H, NCH_aH_bPh), 3.79 (dd, J = 14.7, 5.8, 2 H, NCH_aH_bPh), 3.26 (d, J = 17.9, 2 H, $H_2C(1')$), 3.17–2.89 (m, 4 H, $H_2C(4)$, $H_2C(6)$), 2.32 (d, J = 7.4, 2 H, $H_2C(4')$), 1.80–1.52 (m, 2 H, $H_2C(5)$), 1.23 (s, 6 H, $(H_3C)_2C(3')$); ^{13}C NMR (75.5 MHz) 210.01 (J_{CP} = 6.6, C(2′)), 138.11 (J_{CP} = 5.1, Ar-ipso), 133.82 (C(5′)), 128.26, 128.24, 127.13, 118.05 (C(6′)), 50.43 (J_{CP} = 3.5, NCH_2Ph), 48.46 (C(3′)), 46.48 (C(4), C(6)), 43.77 (C(4′)), 37.01 (J_{CP} = 96.3, C(1′)), 25.18 (J_{CP} = 3.8 (C(5)), 23.92 ($(CH_3)_2C(3')$); IR (CCl_4) 3065 w, 3030 m, 2963 m, 2926 m, 2855 m, 1694 s, 1605 w, 1495 m, 1455 m, 1364 m, 1273 m, 1240 s, 1132 m, 1086 m, 1061 s, 1028 m, 974 w, 918 m, 870 m; MS (70 eV) 424 (M^+, 3), 341 (7), 333 (7), 300 (8), 299 (30), 207 (6), 148 (18), 146 (7), 92 (8), 91 (100), 55 (7), 41 (7); TLC R_f 0.34 (hexane/acetone (2:1)). Anal. Calcd for $C_{25}H_{33}N_2O_2P$ (424.52): C, 70.73; H, 7.83; N, 6.60; P, 7.30. Found: C, 70.40; H, 8.12; N, 6.32; P, 6.89.

(*R*)-(4*l*,6*l*,4′*lu*)-1,3-Dibenzyl-4,6-diphenyl-2-(3′,3′,4′-trimethyl-2′-oxo-5′-hexen-1′-yl)-1,3,2-diazaphosphorinane 2-Oxide (20ebb). (a) *n*-BuLi. From 0.317 mmol of **15ebb** and 0.380 mmol of n-BuLi (1.47 M in hexane) for 30 min at −20 °C. Purification by column chromatography (hexane/acetone (9:1)) afforded 162 mg (87%) of **20ebb** (2 diastereomers, 55:45, ^{31}P NMR) as a colorless oil. **(b) Thermal.** A solution of 27 mg (0.048 mmol) of **15ebb** in 1 mL of toluene was heated to reflux for 2 h. The solution was evaporated to afforded a light yellow oil. Assay by ^{31}P NMR (121.6 MHz) showed **20ebb** as a mixture of two diastereomers (75:25, ^{31}P NMR): ^1H NMR (300 MHz) 7.37–7.12 (m, 20 H, ArH), 5.83–5.68 (m, 1 H, HC(5′)), 5.09–5.00 (m, 2 H, $H_2C(6')$), 4.80 (dd, J = 15.4, 8.7, 1 H, NCH_aH_bPh), 4.83–4.75 (m, 1 H, HC(6)), 4.41 (dt, J = 14.3, 3.5, 1 H, HC(4)), 3.90–3.69 (m, 3 H, NCH_aH_bPh, $NCH_a'H_b'Ph$, $H_aC(1')$), 3.54 (t, J = 14.4, 0.55 H, $NCH_a'H_b'Ph$), 3.53 (t, J = 14.4, 0.45 H, $NCH_a'H_b'Ph$), 3.03 (dd, J = 20.6, 14.1, 1 H, $H_bC(1')$), 2.56–2.41 (m, 2 H, $H_aC(5)$, HC(4′)), 2.08–1.98 (m, 1 H, $H_bC(5)$), 1.25 (s, 1.65 H, $CH_3C(3')$), 1.23 (s, 1.35 H, $CH_3C(3')$), 1.19 (s, 1.35 H, $CH_3C(3')$), 1.16 (s, 1.65 H, $CH_3C(3')$), 1.02 (d, J = 6.8, 1.65 H, $H_3CC(4')$), 0.98 (d, J = 6.9, 1.35 H, $CH_3C(4')$); ^{13}C NMR (75.5 MHz) 209.91 (J_{CP} = 6.9) and 209.88 (J_{CP} = 7.3) (C(2′)), 141.23 (J_{CP} = 3.2, Ar-ipso), 139.70 and 139.47 (C(5′)), 137.56, 137.52, 137.46 and 136.61 (J_{CP} = 2.4) (Ar-ipso), 128.63, 128.51, 128.27, 128.07, 127.88, 127.66, 127.32, 127.29, 127.05, 127.01, 126.99, 126.86, 126.60, 115.81 and 115.58 (C(6′)), 59.29 and 55.85 (C(4), C(6)), 51.36 (J_{CP} = 4.5) and 48.71 (J_{CP} = 4.9) (NCH_2Ph), 47.69 (J_{CP} = 3.7, C(3′)), 45.86 (J_{CP} = 113.2) and 45.56 (J_{CP} = 112.6) (C(1′)), 44.40 and 44.06 (C(4′)), 41.80 (J_{CP} = 6.9, C(5)), 22.57, 21.93, 20.34 and 19.71 ($CH_3C(3')$), 15.16 and 15.13 ($CH_3C(4')$); ^{31}P NMR (121.6 MHz) 19.47 (minor-**20ebb**), 19.41 (major-**20ebb**); IR (CCl_4) 3065 m, 3031 m, 2974 m, 2932 m, 1742 s, 1696 m, 1603 m, 1495 m, 1455 m, 1374 m, 1335 m, 1240 s, 1203 m, 1140 m, 1090 m, 1051 s, 1028 s, 916 m, 868 m; MS (70 eV) 590 (M^+, 1), 396 (11), 395 (41), 236 (13), 196 (10), 193 (11), 152 (9), 106 (19), 92 (9), 91 (100), 55 (11); high-resolution MS calcd for $C_{38}H_{43}N_2O_2P$ 590.3062, found 590.3062; TLC R_f 0.34 (hexane/acetone (4:1)).

(*R,S*)-(3′*lu*)-1,3-Dibenzyldihydro-2-(3′-methyl-2′-oxo-5′-hexen-1′-yl)-3*H*-1,3,2-dibenzo[*d,f*]diazaphosphepine 2-Oxide (21eaa). (a) *n*-BuLi. n-BuLi (0.23 mL, 0.36 mmol, 1.57 M in hexane) was added dropwise to a solution of **16eaa** (165 mg, 0.3 mmol) in 3 mL of THF at 0 °C. The yellow solution was stirred for 50 min at 0 °C and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 64.2 mg (39%) of **21eaa** as a colorless oil (2 diastereomers, ratio 75:25, ^1H NMR). **(b) KDMSO.** KH suspension (30.2 mg of 35% in oil, 10.5 mg KH, 0.25 mmol) was placed in a 10-mL three-necked round-bottom flask with septa and N_2-inlet and was washed with 1 mL of hexane (3×) and dried. DMSO (1 mL) was added, and the solution was stirred for 15 min. A solution of **16eaa** (49 mg, 0.1 mmol) in 0.5 mL of THF was added. The yellow solution was stirred for 60 min at room temperature and then quenched with water. The mixture was extracted with EtOAc after addition of brine. The EtOAc layer was dried ($MgSO_4$), filtered, and concentrated to give a light yellow oil. Purification by column chromatography (hexane/acetone (7:3)) afforded 29.5 mg (60%) of **21eaa** as a colorless oil (2 diastereomers, ratio 40:60, ^1H NMR). **(c) Thermal.** A solution of 110 mg (0.22 mmol) of **16eaa** in 2 mL of toluene was heated to reflux for 4 h. The solution was evaporated to afford a light yellow oil. Purification by column chromatography (hexane/acetone (1:1)) afforded 82 mg (75%) of **21eaa** as a colorless oil (2 diastereomers, ratio 30:70, ^1H NMR) (from thermal reaction): ^1H NMR (300 MHz) 7.65–6.58 (m, 16 H, HAr), 5.88–5.69 (m, 1 H, HC(5′)), 5.13–5.00 (m, 2 H, $H_2C(6')$), 4.81–4.58 (m, 3 H, NCH_2Ph, NCH_aH_bPh), 4.26 (dd, J = 14.6, 8.8, 1 H, NCH_aH_bPh)), 3.48 (dd, J = 16.5, 12.6) and 3.47 (dd, J = 18.4, 12.9) (1 H, $H_aC(1')$), 3.14–3.01 (m, 1 H, $HC_a(4')$), 2.77 (dd, J = 18.4, 12.9) and 2.76 (dd,

J = 18.1, 12.6) (1 H, $H_bC(1')$), 2.61–2.51 (m) and 2.45–2.33 (m) (1 H, $H_bC(4')$), 2.15 (quint, J = 7.4, 1 H, HC(3')), 1.80 (s, 3 H) and 1.37 (s, 3 H) ($CH_3C(7)$, $CH_3C(8)$), 1.18 (d, J = 6.8) and 1.13 (d, J = 7.1) (3 H, $CH_3C(3')$); ^{13}C NMR (75.5 MHz) 207.78 (J_{CP} = 4.9), 207.46 (J_{CP} = 4.7, C(2')), 140.39, 139.68, 137.94, 137.37, 137.23, 137.14, 136.59, 135.81, 135.15, 128.35, 128.19, 128.03, 127.81, 127.60, 127.52, 127.02, 126.77, 126.53, 123.81, 122.60 (C(Ar), C(5')), 117.18, 116.80 (C(6')), 52.55, 52.50, 51.13, 51.05 (NCH_2Ph), 47.20 (C(3')), 40.23 (J_{CP} = 99.9), 39.36 (J_{CP} = 100.3, C(1')), 37.33, 36.19 (C(4')), 19.63, 19.58, 19.25, 19.19 ($CH_3C(1')$, $CH_3C(1'')$), 16.05, 15.25 ($CH_3C(3')$); IR (CCl_4) 3065 m, 3030 m, 2978 m, 2928 m, 2874 w, 1707 s, 1595 w, 1495 m, 1454 s, 1360 m, 1317 m, 1223 s, 1170 m, 1101 s, 1076 m, 1028 s, 993 m, 929 s, 868 m, 829 m; MS (70 eV) 549 (M^+ + 1, 19), 548 (M^+, 43), 438 (37), 437 (100), 392 (11), 391 (36), 390 (13), 389 (42), 105 (11); high-resolution MS calcd for $C_{35}H_{37}N_2O_2P$ 548.2593, found 548.2589; TLC R_f 0.48 (hexane/acetone (7:3)).

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The Reaction of Thioimides with Phosphorus Ylides

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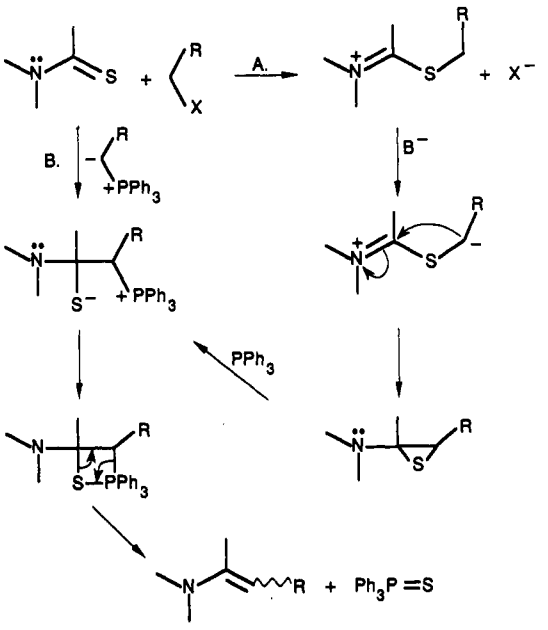
The reaction of a series of thioimides with phosphorus ylides, in a manner analogous to the Wittig reaction, has been examined. The resulting reaction products represent potentially valuable intermediates in tetrapyrrole pigment synthesis. In addition to the desired thio-Wittig-type coupling reaction, the presence of two competing reaction pathways, S-alkylation and oxidation/reduction, has been observed with certain substrates. These empirical observations have been correlated to theoretical data, derived from MNDO and ab initio calculations, which delineate the structure–reactivity relationships governing product distribution from the various reaction pathways. A detailed analysis is presented of the mechanisms of the thio-Wittig coupling reaction and the competitive S-alkylation reaction.

Introduction

The Wittig reaction has a place of obvious importance in synthetic organic chemistry. A wide array of carbonyl and phosphorus ylide components react under relatively mild conditions to form carbon–carbon double bonds, often as a crucial step in convergent syntheses. A limitation of the reaction is the low degree of reactivity of carboxylic acid derivatives, e.g., amides, with ylides.[1] From the standpoint of electrostatic interactions, this can be ascribed to the decreased carbon electrophilicity of these carbonyl groups when compared with ketones and aldehydes. If this decreased reactivity could be overcome, such an extension of the Wittig reaction would often be convenient for carbon–carbon bond formation at an amide functionality, under conditions compatible with the presence of other functional groups, while leaving the carbon–nitrogen bond intact.

Two methods involving the activation of amides as thioamides have been devised to achieve this type of transformation. The first method involves successive S-alkylation and sulfide contraction and has been well documented.[2-4] The second involves reaction of a phosphorus ylide with a thioamide. This sulfur analogue of the Wittig reaction, also called a thio-Wittig reaction, has received less attention.[5-13]

Scheme I. Postulated Sulfur Contraction and Thio-Wittig Mechanisms



A. S-alkylation/sulfur contraction path.
B. Thio-Wittig path

Although the mechanistic details of these reactions are not entirely clear, both routes are thought to proceed through betaine and/or thiaphosphetane intermediates, leading to the observed enamine-type products and tri-

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