Synthesis of Phosphoramides for the Lewis Base-Catalyzed Allylation and Aldol Addition Reactions

Scott E. Denmark,* Xiping Su, Yutaka Nishigaichi, Diane M. Coe, Ken-Tsung Wong, Stephen B. D. Winter, and Jun Young Choi

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

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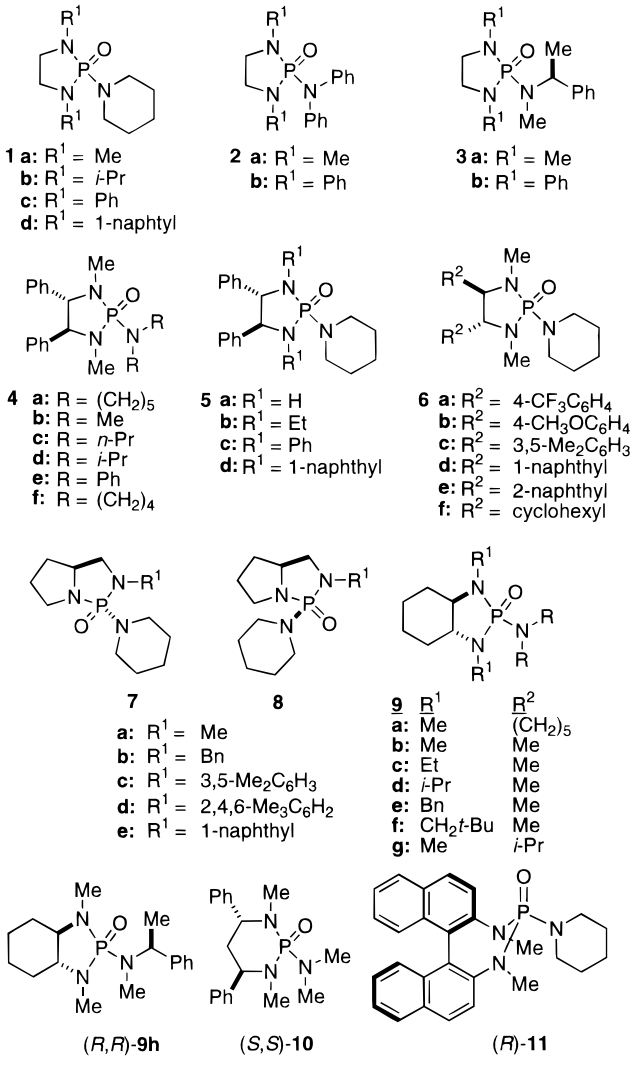
Both chiral and achiral phosphoramides of diverse structure were prepared from diamines by the coupling to phosphorus(V) or phosphorus(III) reagents. Several enantiopure 1,2-diphenyl-1,2-ethanediamine analogues have been prepared by the reductive coupling of the corresponding *N*-silylimine with $NbCl_4(THF)_2$ and subsequent resolution by the formation of diastereomeric menthyl carbamates. (*S*,*S*)-*N*,*N*′-Di-(1-naphthyl)-1,2-diphenyl-1,2-ethanediamine **15** was prepared by the arylation of (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine with naphthyl iodide.

Introduction

Phosphoramides, especially hexamethylphosphoric triamide (HMPA), have found extensive applications in organic chemistry.[1] The strong donor properties and Lewis basicity of the phosphoramides make them good ligands for metals and thus modulate the reactivity of the metal centers.[2] The three nitrogen subunits of a phosphoramide also provide the opportunity for a large number of structurally diverse analogues and hence a broad spectrum of properties and shapes can be customized.[3] It is therefore surprising that general methods for the synthesis of phosphoramides have not been systematically developed.[4,5]

In the course of our survey of Lewis-basic catalysts for allylation[6] and aldol reactions,[7] we required a variety of phosphoramides with broad structural diversity, especially containing a 1,3,2-diazaphospholidine 2-oxide skeleton derived from chiral and achiral 1,2-diamines. Herein we report on a number of general methods for the synthesis of such phosphoramides (Chart 1) as well as the preparation of their chiral 1,2-diamine precursors.

Chart 1. Phosphoramides Derived from Diamines



Results

The basic strategy for the synthesis of a phosphoramide is to couple a diamine to a phosphorus reagent. Three routes were explored within this construct: (1) a diamine was coupled to a dialkylaminophosphoric dichloride, (2)

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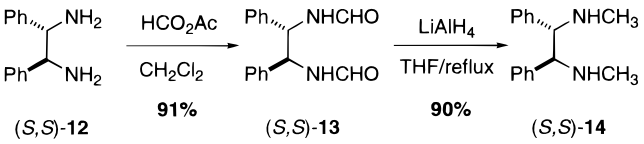
a diamine was coupled to a dialkylaminophosphorus dichloride to afford the corresponding phosphorus triamide followed by in-situ oxidation to give the desired phosphoramide, and (3) PCl_3 was combined first with a hindered diamine and then a secondary amine, followed by in-situ oxidation. Method 1 is applicable when both coupling partners are not sterically demanding. Methods 2 and 3 could be used for sterically hindered coupling partners where method 1 gave less than satisfactory results.

The diamines used in this study include achiral and chiral 1,2-diamines, (*R*,*R*)-*N*,*N*′-dimethyl-1,3-diphenylpropane-1,3-diamine and (*R*)-*N*,*N*′-dimethylbinaphthyl-1,1′-diamine. The preparation of some new, enantiomerically pure 1,2-diamines are also described herein.[8]

1. Preparation of Diamines. *N*,*N*′-Disubstituted-1,2-ethanediamines required for the synthesis of phosphoramide groups **1**−**3** were commercially available or made by the known procedures.[9] (*R*,*R*)/(*S*,*S*)-1,2-Diphenyl-1,2-ethanediamine (**12**) used for the preparation of phosphoramides **4** and **5** was synthesized and resolved by literature methods.[10,11] As has been reported in previous accounts, the phosphoramide **4a** has proven to be an effective catalyst for aldol reactions. Therefore, we have developed an improved procedure for the preparation of the diamine precursor (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine[12] (**14**) from the parent diamine (**12**), Scheme 1. We have found that the bis(formamide) **13** (easily prepared by formylation of **12** with acetic formic anhydride) is superior to the bis(ethyl carbamate)[12a] in yield, ease of purification and reproducibility of reduction.

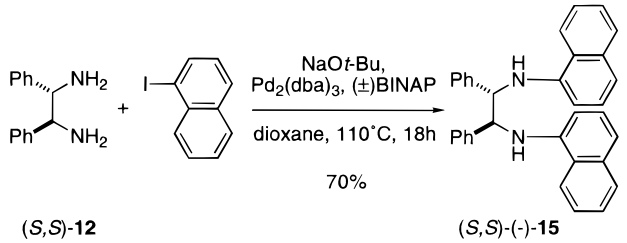
Scheme 1



(*S*,*S*)-**12** (*S*,*S*)-**13** (*S*,*S*)-**14**

1.1. Amine Arylation Reactions. *N*,*N*′-Disubstituted 1,2-diphenyl-1,2-ethanediamine used for the synthesis of phosphoramides **5a**−**e** were prepared either from diphenyl-1,2-ethanediamine itself (**5b** and **5d**) or by the coupling of benzylidene aniline.[12] (*S*,*S*)-*N*,*N*′-Diethyl-1,2-diphenyl-1,2-ethanediamine[13] was synthesized by the reduction of the bis(acetamide) of 1,2-diphenyl-1,2-ethanediamine. The unknown (*S*,*S*)-1,2-diphenyl-*N*,*N*′-dinaphthyl-1,2-ethanediamine (**15**) was synthesized from (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine (**12**) by the amine arylation method developed by Buckwald and Hartwig.[14] With judicious choice of reaction conditions, arylation of

Scheme 2



(*S*,*S*)-**12** (*S*,*S*)-(-)-**15**

(*S*,*S*)-(**12**) could be achieved in good yield without detectable racemization (Scheme 2).

In the presence of sodium *tert*-butoxide and catalytic amount of tris(dibenzylideneacetone)dipalladium, enantiomerically pure (*S*,*S*)-**12** was coupled with 1-naphthyl iodide to give the desired *N*,*N*′-dinaphthyldiamine **15** in 70% yield. Other combinations of catalysts and ligands gave either no reaction or low yield of the desired compound. This arylation method provides rapid access to the enantiopure diamine and should be useful for synthesis of other types of aryl substituted amines for asymmetric synthesis.

1.2. Reductive Coupling of Imines. Chiral, nonracemic 1,2-diamines have been used extensively in asymmetric synthesis.[8] Accordingly, the stereoselective synthesis of chiral 1,2-diamines has become an active area of research.[15−17] The reductive coupling of imines to give 1,2-diamines probably represents one of the most versatile methods for the synthesis of symmetrical 1,2-diamines because of the readily availability of imines from aldehydes. Many reducing agents have been employed in this transformation, including Ti,[18,19] Zr,[20] Sm,[16] Zn,[21] Al,[22] In,[23] and other metals.[24] However, usually a mixture of *d*,*l* and meso diastereomers is obtained.[25] The most *d*,*l*-selective imine coupling reactions to give 1,2-diphenyl-1,2-ethanediamine analogues is the coupling of *N*-silylimines by low valent niobium reagents reported by Pederson in 1987.[26] Thus, application of this method to imines of aromatic aldehydes with different substitution patterns provided the desired 1,2-diamines (Table 1).

N-Silylimines **17** were prepared in good yields according to literature procedures.[18,27] All of the imines **17** were coupled smoothly to give the desired *d*,*l*-1,2-diamines **18a**−**e** in good yields with high diastereoselectivity.

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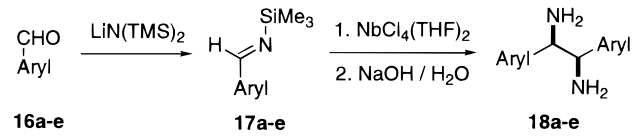
Table 1. Reductive Coupling of *N*-Silylimines

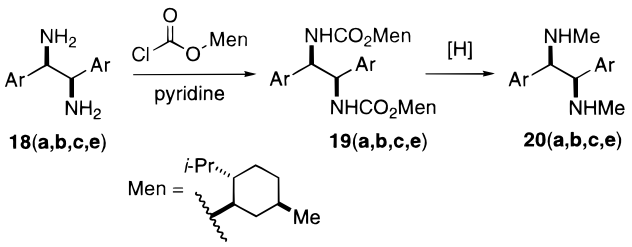


16a-e **17a-e** **18a-e**

entry	aryl	**17**, yield, %[a]	**18**, yield, %[b]	*dl*/meso[c]
1	4-$CF_3C_6H_4$ (**a**)	88	49	5/1
2	4-$MeOC_6H_4$ (**b**)	84	45	>10/1
3	3,5-$Me_2C_6H_3$ (**c**)	73	67	10/1
4	1-naphthyl (**d**)	76	52	>10/1
5	2-naphthyl (**e**)	62	48	>10/1

[a] Yield of isolated and distilled sample. [b] Yield after recrystallization. [c] Estimated by ^{1}H NMR analysis of the crude product.

Table 2. Resolution of Diamines 16 and Synthesis of 18



18(a,b,c,e) **19(a,b,c,e)** **20(a,b,c,e)**

entry	aryl	**19**, yield, %[a]	reductant	conditions	**20**, yield, %[b]
1	4-$CF_3C_6H_4$ (**a**)	92	BH_3•SMe_2	$PhCH_3$, 110 °C	51
2	4-$MeOC_6H_4$ (**b**)	69	$LiAlH_4$	DME, 85 °C	82
3	3,5-$Me_2C_6H_3$ (**c**)	86	$LiAlH_4$	DME, 85 °C	48
4	2-naphthyl (**e**)	75	BH_3•SMe_2	$PhCH_3$, 110 °C	69

[a] Chromatographically homogeneous material. [b] Yield after recrystallization.

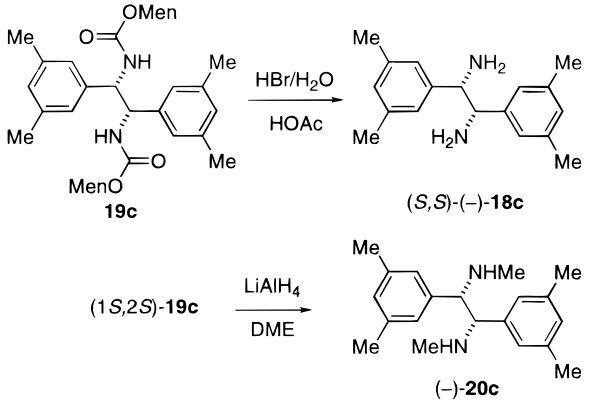
Fractional crystallization gave the pure diamines **18a**−**e** in 45−67% yields.

1.3. Resolution of 1,2-Diamines. Whereas 1,2-diphenyl-1,2-ethanediamine itself is readily resolved by fractional crystallization of the tartrate salt, initial experiments indicated that crystallization conditions for each diamine **18a**−**e** required extensive optimization.[10] To rapidly access the enantiomerically pure diamines **18a**−**e**, we employed the chromatographic separation of the corresponding menthyl carbamate diastereomers formed by the reaction of the diamine with (−)-menthyl chloroformate.[28] An additional advantage of the (−)-menthyl carbamate resolution is that direct reduction of **19** would provide the desired secondary diamine **20** and return the enantiopure menthol (Table 2).

Diamines **18a**−**c,e** reacted with (−)-menthyl chloroformate in the presence of pyridine to afford bis(carbamate) **19a**−**c,e** in good yields. Reduction of **19b** and **19c** with $LiAlH_4$ gave the corresponding secondary diamines **20b** and **20c** in good yields, but the reduction of **19a** and **19e** with $LiAlH_4$ met with difficulty, resulting in overreduction and other side reactions. A brief survey of reducing reagents revealed that borane−dimethyl sulfide was more suitable for these two substrates. Thus, with excess of borane−dimethyl sulfide the desired diamines **20a** and **20e** were obtained in 51 and 69% yields, respectively.

The absolute configuration of diamine **20c** was established by correlation to the known diamine (*S*,*S*)-(−)-**18c**

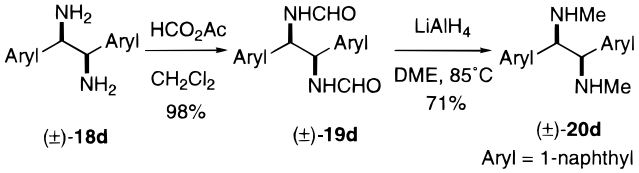
Scheme 3



(Scheme 3).[29] Thus, HBr hydrolysis of the more polar diastereomer of the bis(carbamate) **19c** led to the known diamine (*S*,*S*)-(−)-**18c** in 75% yield, while the reduction of the same carbamate **19c** led to the secondary diamine (−)-**20c** in 48% yield. The absolute configurations of other diamines **20a,b,e** was deduced by comparison of their ^{1}H NMR spectra and relative polarity on TLC of their corresponding bis(carbamate)s **19a,b,e** to those of **19c**. Thus, all the less polar diastereomers of **19** display a distinct doublet of triplets at around 4.5 ppm, which was assigned to the oxygen-bearing methine, and were assigned the (1*R*,2*R*) configuration at the nitrogen-bearing stereocenters. All the more polar diastereomers of **19** displayed a broad signal for the oxygen-bearing methine in their ^{1}H NMR spectra.

Diamine **18d** was not resolved because the corresponding phosphoramide **6d** was not a good catalyst for aldol reactions. The racemic diamine **18d** was converted to the racemic secondary diamine **20d** via its bis(formamide) **19d** (Scheme 4).

Scheme 4



(±)-**18d** (±)-**19d** (±)-**20d**

Aryl = 1-naphthyl

1,2-Dicyclohexyl-1,2-ethanediamine (**18f**) was prepared by the hydrogenation of (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine in 71% yield according to known procedures[30] and was then converted to the secondary diamine **20f** in moderate yields via the bis(carbamate) **19f** (Scheme 5).

1.4. Chiral Diamines from Amino Acids. Following a procedure developed by Mukaiyama and co-workers,[31] diamines **24** could be prepared in gram quantities from Cbz-L-proline **21** in good overall yields (Scheme 6).

2. Preparation of Phosphoramides. 2.1. Reaction of Diamines with Aminophosphoric Dichlorides. The most direct and commonly used way to prepare phosphoramides from diamines is to couple the diamines with a corresponding aminophosphoric dichloride (Table 3).[5,32] Although the protocol of fast addition of a diamine

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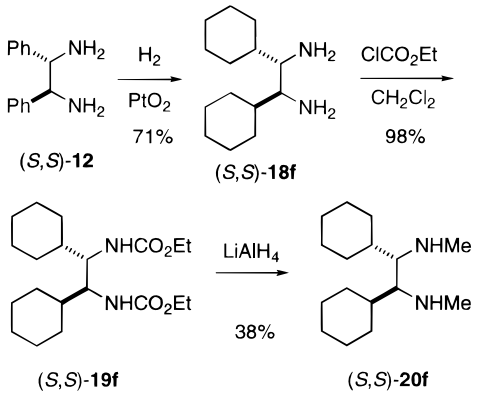
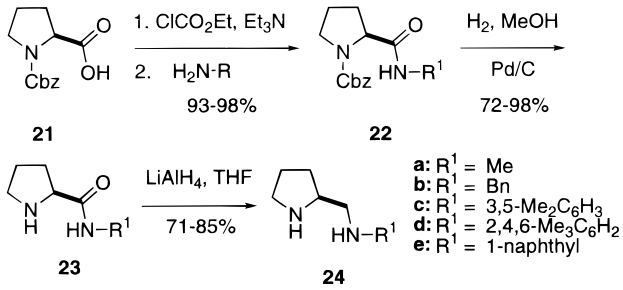
Scheme 5



Scheme 6



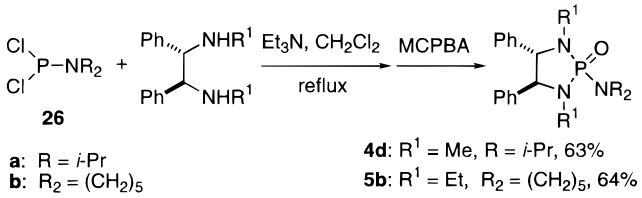
and an aminophosphoric dichloride to a solution of triethylamine worked well in a number of cases, the more reliable protocol is the simultaneous slow addition of a solution of the diamine and a solution of the corresponding phosphoric dichloride to a refluxing solution of triethylamine. This method worked well for most of the diamines in this study, but it failed for sterically more congested diamines.

With *N*,*N*′-dimethyl-1,2-ethanediamine, this method afforded high yields of the desired phosphoramides **1a**, **2a**, and **3a** with various aminophosphoric dichlorides **25** (entries 1, 4, and 5). It was also efficient in preparing most of the phosphoramides **4** and **6** (entries 6−11, 13−17), although slightly lower yields were observed. The reaction proceeded well at room temperature for sterically less-demanding diamines (entries 12, 18−20, 23, 24, 30), and elevated temperatures were required for sterically demanding coupling partners (entries 3, 21, 22). A bulky aminophosphoric dichloride gave a low yield (entry 29).

The synthesis of the lead phosphoramide (*S*,*S*)-**4a** was further optimized by surveying solvents (CH_2Cl_2, $CHCl_3$, $(CH_2Cl)_2$), addition rates, and reaction times (2−4 d). Ultimately the yield of (*S*,*S*)-**4a** could be improved to 61% after chromatography and recrystallization (compare entries 6 and 7) by carrying out the preparation in chloroform at reflux for 48 h.

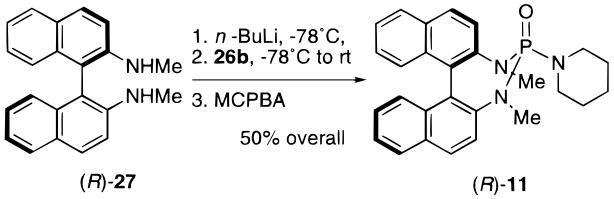
2.2. Reaction of Diamines with Aminophosphorus Dichloride. During the synthesis of **4d** and **5b**, the reaction of the diamines with the corresponding aminophosphoric dichloride resulted in the recovery of the starting diamines, presumably due to the low reactivity of the hindered substrates. To solve this problem, we took advantage of the fact that phosphorus(III) compounds are much more reactive than phosphorus(V) compounds toward nucleophilic displacement.[33] Phosphoramides **4d** and **5b** were prepared in overall yields of 63−64%, by the reaction of the corresponding diamines with the appropriate aminophosphorus dichloride **26**[34] followed by oxidation with MCPBA (Scheme 7).[35]

Scheme 7



Preparation of phosphoramide **11** required deprotonation with *n*-butyllithium (Scheme 8), because the diamine **27** is both sterically hindered and electronically deactivated. The desired phosphoramide was obtained in 50% overall yield after the three-step procedure.

Scheme 8



2.3. Reaction of Diamines with Phosphorus Trichloride. Hindered phosphoramides can also be prepared through the reaction of a diamine with phosphorus trichloride followed by reaction with a primary amine and oxidation with MCPBA.[36] Moderate yields of the desired phosphoramides were obtained over the three steps, Table 4. For the preparation of phosphoramides with bulky substituents R or R_1 on the nitrogens, this method gave the best results. For example, the coupling of *N*,*N*′-diphenylethylene-1,2-diamine with diphenylamine gave 72% of the phosphoramide **2b** with this method (entry 2).

Discussion

Preparation of Enantiomerically Pure Diamines. The synthesis of (*S*,*S*)-1,2-diphenyl-*N*,*N*′-dinaphthylethanediamine (**13**) provides an example for the rapid access of enantiomerically pure *N*-arylamines from readily available amines such as 1,2-diphenyl-1,2-ethanediamine or 1,2-cyclohexanediamine. Given the fact that good yields of the product were obtained in one chemical step without detectable racemization/epimerization, with the stringent requirements imposed by the reaction, i.e., diarylation with sterically hindered aryl halide, this method may find broad use in asymmetric synthesis.

The preparation of 1,2-diamines by reductive coupling of imines has some of the most appealing features of efficient synthesis; primary among them is that it creates

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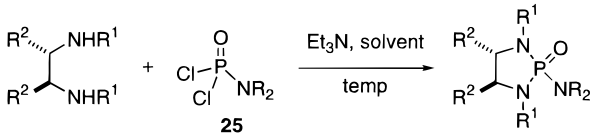
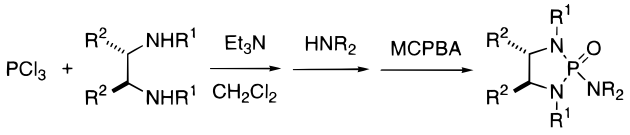
Table 3. Preparation of Phosphoramides from Diamines and Aminophosphoric Dichloride 25



entry[a]	diamine (R_1/R_2)	*T*, °C	time, h	product	R	R^1	R^2	yield, %[b]
1	Me/H	40	40	**1a**	$(CH_2)_5$	Me	H	99
2	*i*-Pr/H	40	36	**1b**	$(CH_2)_5$	*i*-Pr	H	50
3[c]	Ph/H	83	19	**1c**	$(CH_2)_5$	Ph	H	51
4	Me/H	40	15	**2a**	Ph	Me	H	87
5	Me/H	40	42	**3a**	see Chart 1	Me	H	80
6	Me/Ph	40	24	**4a**	$(CH_2)_5$	Me	Ph	50
7[d]	Me/Ph	61	48	**4a**	$(CH_2)_5$	Me	Ph	61
8	Me/Ph	40	6	**4b**	Me	Me	Ph	60
9	Me/Ph	40	96	**4c**	*n*-Pr	Me	Ph	46
10	Me/Ph	40	42	**4e**	*i*-Pr	Me	Ph	63
11	Me/Ph	40	16	**4f**	$(CH_2)_4$	Me	Ph	61
12	**12**	20	10	**5a**	$(CH_2)_5$	H	Ph	59
13	**20a**	40	96	**6a**	$(CH_2)_5$	Me	4-$CF_3C_6H_4$	41
14	**20b**	40	37	**6b**	$(CH_2)_5$	Me	4-$MeOC_6H_4$	75
15	**20c**	40	48	**6c**	$(CH_2)_5$	Me	3,5-$Me_2C_6H_3$	62
16	**20e**	40	48	**6e**	$(CH_2)_5$	Me	2-naphthyl	52
17	**20f**	40	66	**6f**	$(CH_2)_5$	Me	cyclohexyl	49
18[e]	**24a**	20	10	**7a/8a**	$(CH_2)_5$	see Chart 1		74
19[e]	**24b**	20	3	**7b/8b**	$(CH_2)_5$	see Chart 1		93
20[e]	**24c**	20	18	**7c/8c**	$(CH_2)_5$	see Chart 1		68
21[e]	**24d**	68	13	**7d/8d**	$(CH_2)_5$	see Chart 1		67
22[e]	**24e**	68	10	**7e/8e**	$(CH_2)_5$	see Chart 1		67
23[f]	Me/$(CH_2)_4$	20	10	**9a**	$(CH_2)_5$	Me	$(CH_2)_4$	58
24[f]	Me/$(CH_2)_4$	20	18	**9b**	Me	Me	$(CH_2)_4$	83
25	Et/$(CH_2)_4$	40	24	**9c**	Me	Et	$(CH_2)_4$	59
26	*i*-Pr/$(CH_2)_4$	40	20	**9d**	Me	*i*-Pr	$(CH_2)_4$	37
27	Bn/$(CH_2)_4$	40	14	**9e**	Me	Bn	$(CH_2)_4$	57
28	CH_2t-Bu/$(CH_2)_4$	40	21	**9f**	Me	CH_2t-Bu	$(CH_2)_4$	27
29	Me/$(CH_2)_4$	40	41	**9g**	*i*-Pr	Me	$(CH_2)_4$	7
30	Me/$(CH_2)_4$	20	11	**9h**	see Chart 1	Me	$(CH_2)_4$	63
31	DPPDA[g]	40	20	**10**	Me	Me	see Chart 1	51

[a] All reactions were carried out in CH_2Cl_2 unless otherwise noted. [b] Chromatographically homogeneous material. [c] $ClCH_2CH_2Cl$. [d] $CHCl_3$. [e] THF. [f] EtOAc. [g] *N,N′*-dimethyl-1,3-diphenylpropane-1,3-diamine.

Table 4. Phosphoramides from the Reactions of Diamines with PCl_3

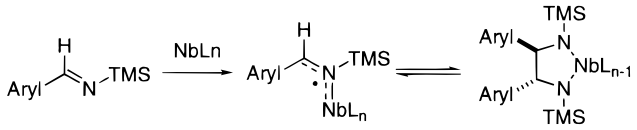


entry	R^2	R^1	R	product	yield, %[a]
1	H	1-naphthyl	$(CH_2)_5$	**1d**	46
2	H	Ph	Ph	**2b**	72
3	H	Ph	Me, PhCHMe	**3b**	50
4	Ph	Ph	$(CH_2)_5$	**5c**	42
5	Ph	1-naphthyl	$(CH_2)_5$	**5d**	55
6	1-naphthyl	Me	$(CH_2)_5$	**6d**	38[b]

[a] Analytically pure sample. [b] Chromatographically homogeneous sample.

two stereocenters while making a C−C bond. The origin of the high selectivity of the reductive coupling by niobium(IV) reagent is poorly understood. One plausible explanation is that the coupling step is reversible under the reaction conditions, and the thermodynamically more stable *d,l*-isomer would accumulate in the reaction mixture with time (Scheme 9). This hypothesis is consistent with the fact that the coupling of the electron-poor arylimine **17a** or aliphatic imines[26] was less selective than that of electron-rich arylimines. Because the radical intermediate **i** derived from imine **17a** or aliphatic imines is less stable than that derived from electron-rich aromatic imines, the degree of reversibility would be attenuated in the coupling of **17a** or aliphatic imines. Similar thermodynamic control has also been observed in other systems.[25,37]

Scheme 9



Synthesis of Phosphoramides. Nucleophilic substitution at phosphorus is much faster for P(III) compounds than P(V) compounds.[33] Electron-donating groups on phosphorus also greatly attenuate the ease of nucleophilic substitution, where the reactivity order for the phosphorus reagents is $PCl_3 > Cl_2PNR_2 > ClP(NR_2)_2 \geq Cl_2P(O)NR_2$. Several scenarios can be envisioned to formulate the synthesis of a phosphoramide from a diamine and a monoamine: (1) the diamine and the monoamine are both small, (2) a small diamine but a bulky monoamine, (3) a hindered diamine but a small monoamine, and (4) both the diamine and the monoamine are bulky. For the first scenario the use of less reactive reagents of the type, $Cl_2P(O)NR_2$, is desirable since the coupling reaction is facile and the less reactive reagents could prevent

(37) Smith, J. G.; Ho, I. *J. Org. Chem.* **1972**, *37*, 653.

complications arising from polymerization. For the type 2 coupling, it is best to use reagents of type Cl_2PNR_2 as exemplified by the synthesis of **4d** and **5b** in this study. The logic is to use the most reactive phosphorus reagent, PCl_3, to react with the least reactive amine, in this case, the monoamine. This reasoning also applies to type 3 coupling; thus a hindered diamine is reacted with PCl_3 to give intermediates of the type $ClP(NR_2)_2$, which was then reacted with a monoamine. A typical example of this type is the synthesis of **5d**, where an extremely hindered diamine (*S*,*S*)-**15** was used and yet a good yield of the desired phosphoramide was obtained. The most challenging coupling reaction is the type 4 where both partners are hindered or difficulty for coupling arises from other reasons such as the coupling of electronically deactivated amines. In this case, the coupling of a diamine with PCl_3 and then with a monoamine worked well in some instances, such as the synthesis of **2b** and **3b** in this study. Occasionally, the activation of one of the reaction partners may be needed, such as in the synthesis of phosphoramide **11** from *N*,*N*′-dimethylbinaphthyl-1,1′-diamine (**27**) wherein the deprotonation of the diamine **27** with *n*-BuLi and the use of reactive phosphorus reagent **26b** were required. Other conditions failed to give any detectable product.

Conclusion

In summary, we have described in detail the preparation of cyclic phosphoramides of broad structural diversity. Three methods have been examined for the synthesis of these phosphoramides starting with both P(III) and P(V) reagents. The steric bulk of the coupling amines is the key factor which affects the choice of coupling methods. Arylation of readily available enantiomerically pure primary amines provided a novel route for the synthesis of enantiomerically pure *N*-arylamines. Reductive coupling of *N*-silylimines and the following resolution via (−)-menthyl carbamate provided rapid access to enantiomerically pure symmetrical 1,2-diamines.

Experimental Section

General Methods. See Supporting Information. **Representative Procedure 1. Synthesis of Phosphoramides from Dialkylaminophosphoric Dichloride. 1,3-Dimethyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (1a).** To a refluxing solution of triethylamine (2.3 mL, 17 mmol, 2.5 equiv) in 150 mL of CH_2Cl_2 were simultaneously added solutions of *N*,*N*′-dimethyl-1,2-ethanediamine (0.71 mL, 6.7 mmol) in 30 mL of CH_2Cl_2 and piperidinylphosphoric dichloride[34] (1.02 mL, 6.7 mmol, 1.0 equiv) in 30 mL of CH_2Cl_2 over 2 h under nitrogen using a syringe pump. The solution was heated to reflux for 40 h and then was evaporated under reduced pressure to provide a colorless residue. The crude product was purified by column chromatography (SiO_2, EtOAc, EtOAc/*i*-PrOH, 9/1, and then EtOAc/*i*-PrOH, 7/3 as eluents) and Kugelrohr distillation (bp 120−125 °C/(air-bath temperature (ABT))/0.05 mmHg) to give 1.45 g (99%) of **1a** as colorless, hygroscopic crystals. An analytical sample was prepared by further recrystallization from hexane, mp 55−56 °C (hexane); TLC R_f = 0.20 (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.44. Anal. Calcd for $C_9H_{20}N_3OP$ (217.25): C, 49.76; H, 9.28; N, 19.34; P, 14.26. Found: C, 49.56; H, 9.22; N, 19.46; P, 14.34.

A slightly modified procedure (Representative Procedure 1a) is identical to Representative Procedure 1 except that the reagents and substrates were mixed together at room temperature and then were heated to reflux for the indicated time.

1,3-Di-(1-methylethyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (1b). Following Representative Procedure 1, from triethylamine (2.4 mL, 17.5 mmol, 2.5 equiv), *N*,*N*′-di-(1-methylethyl)-1,2-ethanediamine (1.27 mL, 7.0 mmol), and piperidinylphosphoric dichloride (1.07 mL, 7.0 mmol, 1.0 equiv) in CH_2Cl_2 (150+30+30 mL) was obtained 0.949 g (50%) of **1b** as colorless crystals after chromatography (SiO_2, EtOAc, EtOAc/*i*-PrOH, 19/1, and then EtOAc/*i*-PrOH, 9/1 as eluents). mp 52−53 °C (hexane); bp 145 °C (0.05 mmHg); TLC R_f = 0.71 (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.44. Anal. Calcd for $C_{13}H_{28}N_3OP$ (273.36): C, 57.12; H, 10.32; N, 15.37; P, 11.33. Found: C, 56.82; H, 10.46; N, 15.56; P, 11.21.

1,3-Diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (1c). Following Representative Procedure 1a, from triethylamine (3.5 mL, 25 mmol, 2.5 equiv) *N*,*N*′-diphenyl-1,2-ethanediamine (2.12 g, 10 mmol), and piperidinylphosphoric dichloride (1.53 mL, 10 mmol, 1.0 equiv) in dichloroethane (20 mL) was obtained 1.74 g (51%) of **1c** as colorless needles after chromatography (SiO_2, CH_2Cl_2 then CH_2Cl_2/*i*-PrOH, 20/1 as eluents) and recrystallization from benzene/hexane, mp: 169−171 °C (benzene/hexane); TLC R_f = 0.83 (EtOAc). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.32. Anal. Calcd for $C_{19}H_{24}N_3OP$ (341.39): C, 66.85; H, 7.09; N, 12.31; P, 9.07. Found: C, 66.66; H, 7.04; N, 12.19; P, 8.88.

1,3-Dimethyl-2-(diphenylamino)-1,3,2-diazaphospholidine 2-Oxide (2a). Following Representative Procedure 1, from triethylamine (1.74 mL; 12.5 mmol), *N*,*N*′-dimethyl-1,2-ethanediamine (0.53 mL, 5.0 mmol) and diphenylaminophosphoric dichloride[38] (1.43 g, 5.0 mmol) in CH_2Cl_2 (150+15+15 mL), was obtained 1.32 g (87%) of **2a** as colorless needles after column chromatography (SiO_2, EtOAc, then EtOAc/*i*-PrOH, 10/1 as eluents) and recrystallization (CH_2Cl_2/hexane); mp: 115−116 °C (CH_2Cl_2-hexane); TLC R_f = 0.61 (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.39. Anal. Calcd for $C_{16}H_{20}N_3OP$ (301.33): C, 63.78; H, 6.69; N, 13.95; P, 10.28. Found: C, 63.73; H, 6.79; N, 14.21; P, 9.97.

(*S*)-1,3-Dimethyl-2-[methyl(1′-phenylethyl)amino]-1,3,2-diazaphospholidine 2-Oxide (3a). Following Representative Procedure 1, from triethylamine (3.5 mL; 25 mmol, 2.5 equiv), *N*,*N*′-dimethyl-1,2-ethanediamine (1.06 mL; 10 mmol), and (*S*)-*N*-methyl-*N*-(1-phenylethyl)aminophosphoric dichloride (2.52 g, 10 mmol, 1.0 equiv) in CH_2Cl_2 (200+25+25 mL) was obtained 2.14 g (80%) of **3a** as colorless crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH, 10/1, 10/2, then 10/3 as eluents) and distillation (bp 160−165 °C/0.1 mmHg; Kugelrohr). An analytical sample was obtained recrystallization from hexane, mp: 51−52 °C (hexane). $[\alpha]^{22}_D$ = −1.6° (*c* = 1.1, $CHCl_3$); TLC R_f = 0.58 (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.93. Anal. Calcd for $C_{13}H_{22}N_3OP$: C, 58.41; H, 8.30; N, 15.72; P, 11.59. Found: C, 58.39; H, 8.38; N, 15.77; P, 11.37.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-1-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (4a). Following Representative Procedure 1, from triethylamine (2.34 mL, 16.8 mmol, 2.5 equiv), (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (**12**), (1.6 g, 6.66 mmol), and piperidinylphosphoric dichloride (1.04 mL, 6.69 mmol, 1.0 equiv) in CH_2Cl_2 (100+50+50 mL) was obtained 1.228 g (50%) of **4a** as white needles after chromatography (SiO_2, EtOAc/*i*-PrOH, 9/1) and recrystallization from hexane, mp: 110−111 °C (hexane). $[\alpha]^{22}_D$ = +18.2° (*c* = 1.3, $CHCl_3$); TLC R_f = 0.42 (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (122 MHz, $CDCl_3$) δ 27.35. Anal. Calcd for $C_{21}H_{28}N_3OP$ (369.45): C, 68.27; H, 7.64; N, 11.37; P, 8.38. Found: C, 68.00; H, 7.68; N, 11.31; P, 8.23.

Following Representative Procedure 1a, from triethylamine (1.45 mL, 10.4 mmol, 2.5 equiv), diamine **12** (1.0 g, 4.16 mmol, 1.0 equiv), and piperidinephosphoric dichloride (0.70 mL, 4.58 mmol, 1.1 equiv) in $CHCl_3$ (83 mL) was obtained 0.934 g (61%) of **4a** as white needles after chromatography (SiO_2, EtOAc/*i*-PrOH, 9/1) and recrystallization from hexane. mp 111−112 °C (hexane).

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-(dimethylamino)-1,3,2-diazaphospholidine 2-Oxide (4b). Following Representative Procedure 1, from triethylamine (0.21 mL, 0.154 g,

(38) Otto, P. *Ber*. **1895**, *28*, 613.

1.53 mmol), (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (0.146 g, 0.61 mmol), and *N*,*N*-dimethylphosphoramic dichloride (0.073 mL, 0.099 g, 0.61 mmol) in CH_2Cl_2 (5+1+1 mL), was obtained 0.121 g (60%) of **4b** as a white solid after chromatography (SiO_2, EtOAc/*i*-PrOH 10/1). An analytical sample was obtained by recrystallization from hexane, mp: 161−163 °C (hexane); $[\alpha]^{22}_D = -5.10°$ ($c = 1.02$, $CHCl_3$); TLC $R_f = 0.23$ (EtOAc/*i*-PrOH, 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.61. Anal. Calcd for $C_{18}H_{24}N_3OP$ (329.381): C, 65.64; H, 7.34; N, 12.76; P, 9.40. Found: C, 65.68; H, 7.30; N, 12.65; P, 9.34.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-(dipropylamino)-1,3,2-diazaphospholidine 2-Oxide (4c). Following Representative Procedure 1a, from triethylamine (0.42 mL, 3.0 mmol, 3.0 equiv), (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (0.248 g, 1.0 mmol), and *N*,*N*-dipropylphosphoramic dichloride (0.218 mL, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was obtained 0.179 g (46%) of **4c** as a thick oil after column chromatography (SiO_2, EtOAc/*i*-PrOH 10/1). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.74. Anal. Calcd for $C_{22}H_{32}N_3OP$ (385.49): C, 68.55; H, 8.37; N, 10.90. Found: C, 68.52; H, 8.07; N, 10.98.

(4*R*,5*R*)-1,3-Dimethyl-4,5-diphenyl-2-(diphenylamino)-1,3,2-diazaphospholidine 2-Oxide (4e). Following Representative Procedure 1, from triethylamine (0.42 mL; 3.0 mmol, 2.3 equiv), (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (314 mg, 1.31 mmol), and diphenylaminophosphoric dichloride (450 mg, 1.57 mmol, 1.2 equiv) in CH_2Cl_2 (30+15+15 mL) was obtained 372 mg (63%) of **4e** as an amorphous solid after chromatography (SiO_2, CH_2Cl_2, CH_2Cl_2/*i*-PrOH, 50/1 then 25/1), $[\alpha]^{22}_D = +25.7°$ ($c = 0.65$, $CHCl_3$); TLC $R_f = 0.73$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.76.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-(1-pyrrolidinyl)-1,3,2-diazaphospholidine 2-Oxide (4f). Following Representative Procedure 1, from triethylamine (0.55 mL, 3.93 mmol, 2.5 equiv), (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (0.377 g, 1.57 mmol), and 1-pyrrolidinylphosphoramic dichloride (0.295 g, 1.57 mmol, 1.0 equiv) in CH_2Cl_2 (20+8+8 mL) was obtained 0.34 g (61%) of **4f** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH 9/1) and recrystallization (hexane), mp: 105−106 °C (hexane); TLC $R_f = 0.32$ (EtOAc/*i*-PrOH, 10/1). Anal. Calcd for $C_{20}H_{26}N_3OP$ (355.42): C, 67.5; H, 7.37; N, 11.82. Found: C, 67.36; H, 7.13; N, 11.78.

(4*S*,5*S*)-4,5-Diphenyl-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (5a). Following Representative Procedure 1, from triethylamine (0.63 mL, 4.5 mmol, 3.0 equiv), (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine (0.318 g, 1.5 mmol), and 1-piperidinylphosphoric dichloride (0.23 mL, 1.5 mmol, 1.0 equiv) in CH_2Cl_2 (14+8+8 mL) was obtained 0.301 g (59%) of **5a** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH 10/1) and recrystallization ($CHCl_3$/hexane). Anal. Calcd for $C_{19}H_{24}N_3OP$ (341,37): C, 66.85; H, 7.09; N, 12.31. Found: C, 66.52; H, 6.90; N, 12.13.

(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(4-(trifluoromethyl)phenyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (6a). Following Representative Procedure 1a, from triethylamine (230 μL, 1.64 mmol, 4.5 equiv), **20a** (137 mg, 0.364 mmol), and piperidinylphosphoric dichloride (61 μL, 0.4 mmol, 1.1 equiv) in 70 mL of CH_2Cl_2 was obtained 75 mg (41%) of **6a** as white needles after column chromatography (SiO_2, TBME/MeOH, 19/1) and recrystallization, mp: 138−139 °C (hexane). $[\alpha]^{22}_D = +0.6°$ ($c = 2.10$, $CHCl_3$ (+24.2° at 405 nm)); TLC $R_f = 0.38$ (TBME/MeOH, 20/1); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.54; ^{19}F NMR (470 MHz, $CDCl_3$) δ −64.18, −64.22; HRMS (CI) for $C_{23}H_{27}F_6N_3OP$ Calcd: 506.1796, Found: 506.1790. Anal. Calcd for $C_{23}H_{26}F_6N_3OP$ (505.45): C, 54.66; H, 5.18; N, 8.31. Found: C, 54.75; H, 5.22; N, 7.84. HPLC t_R (+)-(*R*,*R*)-6a, 20.73 min (Daicel ChiralCel AD, hexane/EtOH, 97/3, 0.5 mL/min).

(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(4-methoxyphenyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (6b). Following Representative Procedure 1a, from triethylamine (610 μL, 4.35 mmol, 2.5 equiv), the diamine **20b** (523 mg, 1.74 mmol), and piperidinylphosphoric dichloride (280 μL, 1.83 mmol, 1.05 equiv) in 160 mL of CH_2Cl_2 was obtained 560 mg (75%) of **6b** as white foam after column chromatography (SiO_2, EtOAc/*i*-PrOH, 9/1), which was recrystallized (hexane) to give white needles (251 mg, 34%), mp: 115−117 °C (hexane). $[\alpha]^{22}_D = +49.9°$ ($c = 1.12$, $CHCl_3$); TLC $R_f = 0.32$ (TBME/MeOH, 20/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.11. Anal. Calcd for $C_{23}H_{32}N_3O_3P$ (429.50): C, 64.32; H, 7.51; N, 9.78; P, 7.21. Found: C, 64.18; H, 7.68; N, 9.66; P, 6.96.

(4*S*,5*S*)-1,3-Dimethyl-4,5-bis(3,5-dimethylphenyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (6c). Following Representative Procedure 1a, from triethylamine (185 μL; 1.33 mmol, 2.4 equiv), the diamine **20c** (164 mg, 0.55 mmol), and piperidinylphosphoric dichloride (86 μL, 0.56 mmol, 1.02 equiv) in 65 mL of CH_2Cl_2 was obtained 145 mg (62%) of **6c** as a white foam after column chromatography (SiO_2, TBME/MeOH, 19/1). An analytical sample was obtained by recrystallization from hexane, mp: 149−150 °C (hexane); $[\alpha]^{22}_D = +7.2°$ ($c = 1.00$, $CHCl_3$); TLC $R_f = 0.47$ (TBME/MeOH, 20/1), ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.48. Anal. Calcd for $C_{25}H_{36}N_3OP$ (425.56): C, 70.56; H, 8.53; N, 9.87. Found: C, 70.74; H, 8.63; N, 9.82. HPLC t_R (+)-(*S*,*S*)-**6a**, 9.93 min (Daicel ChiralCel AD, hexane/EtOH, 97/3, 0.5 mL/min.).

(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(2-naphthyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (6e). Following Representative Procedure 1a, from triethylamine (185 μL, 1.32 mmol, 3.5 equiv), the diamine **20e** (180 mg, 0.529 mmol), and piperidinylphosphoramic dichloride (89 μL, 0.582 mmol, 1.1 equiv) in 50 mL of CH_2Cl_2 was obtained 75 mg (30%) of **6e** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH, 9/1) and recrystallization (hexane), mp: 205−206 °C (hexane); $[\alpha]^{22}_D = +80.7°$ ($c = 1.38$, $CHCl_3$); TLC $R_f = 0.39$ (TBME/MeOH 20/1); ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.38. Anal. Calcd for $C_{29}H_{32}N_3OP$ (469.59): C, 74.18; H, 6.87; N, 8.95; P, 6.60. Found: C, 74.12; H, 6.75; N, 8.68; P, 6.72.

(4*S*,5*S*)-1,3-Dimethyl-4,5-dicyclohexyl-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (6f). Following Representative Procedure 1a, from triethylamine (305 μL, 2.19 mmol, 2.4 equiv), the diamine **20f** (230 mg, 0.911 mmol), and piperidinylphosphoric dichloride (153 μL, 0.929 mmol, 1.02 equiv) in 100 mL of CH_2Cl_2 was obtained 172 mg (49%) of **6f** as a white foam after column chromatography (SiO_2, EtOAc/*i*-PrOH, 19/1), $[\alpha]^{22}_D = +1.5°$ ($c = 2.31$, $CHCl_3$); TLC $R_f = 0.52$ (EtOAc/*i*-PrOH 19/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.48. HRMS (CI) for $C_{21}H_{41}N_3OP$ Calcd: 382.2987, Found: 382.2991.

(7a*S*,3*S*)- and (7a*S*,3*R*)-3-Piperidino-1,2,5,6,7,7a-hexahydro-2-methylpyrrolo[1,2-*c*][1,3,2]diazaphosphole 3-Oxide (7a and 8a). Following Representative Procedure 1a, from triethylamine (7.08 mL, 50.8 mmol, 2.1 equiv), the diamine **24a**[30] (2.75 g, 24.1 mmol), and piperidinylphosphoric dichloride (4.0 mL, 25.4 mmol, 1.05 equiv) in 125 mL of THF were obtained 1.587 g (27%) of **7a** and 1.891 g (32%) of **8a** as colorless oils after column chromatography (SiO_2, TBME/MeOH, 9/1) and Kugelrohr distillation.[31] Data for 7a: bp: 160−161 °C (ABT, 0.01 mmHg); $[\alpha]^{22}_D = +2.7°$ ($c = 1.43$, $CHCl_3$); TLC $R_f = 0.29$ (TBME/MeOH, 19/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.22. Anal. Calcd for $C_{11}H_{22}N_3OP$ (243.29): C, 54.31; H, 9.11; N, 17.27. Found: C, 54.49; H, 9.23; N, 17.24. Data for **8a**: bp: 195−196 °C (ABT, 0.01 mmHg); $[\alpha]^{22}_D = -14.2°$ ($c = 1.28$, $CHCl_3$); TLC $R_f = 0.18$ (TBME/MeOH, 19/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.12.

(7a*S*,3*S*)- and (7a*S*,3*R*)-3-Piperidino-1,2,5,6,7,7a-hexahydro-2-(phenylmethyl)pyrrolo[1,2-c][1,3,2]diazaphosphole 3-Oxide (7b and 8b). Following Representative Procedure 1a, from triethylamine (4.24 mL, 30.5 mmol, 2.1 equiv), the diamine **24b**[31] (2.74 g, 14.5 mmol), and piperidinylphosphoric dichloride (2.32 mL, 15.2 mmol, 1.05 equiv) in 80 mL of THF were obtained **7b** (1.79 g, 45%) and **8b** (1.95 g, 49%) after column chromatography (SiO_2, TBME/MeOH, 19/1, and then 4/1) and Kugelrohr distillation. Data for **7b**: bp: 231 °C (ABT, 0.01 mmHg); $[\alpha]^{22}_D = -28.6°$ ($c = 2.40$, $CHCl_3$); TLC $R_f = 0.36$ (EtOAc/*i*-PrOH, 19/1). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.36. Anal. Calcd for $C_{17}H_{26}N_3OP$ (319.39): C, 63.93; H, 8.21; N, 13.16, P, 9.70. Found: C, 64.08; H, 8.23; N, 13.18, P, 9.73. **8b**: TLC $R_f = 0.19$ (EtOAc/*i*-PrOH 19/1). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.62.

Preparation of (−)-(7a*S*,3*S*)- and (+)-(7a*S*,3*R*)-3-Piperidino-1,2,5,6,7,7a-hexahydro-2-(3,5-dimethylphenyl)-pyrrolo[1,2-*c*][1,3,2]-diazaphosphole 3-Oxide (7c and 8c).

Following Representative Procedure 1a, from triethylamine (0.94 mL, 6.73 mmol 2.1 equiv), the diamine **24c**[31] (655 mg, 3.21 mmol), and piperidinylphosphoric dichloride (0.52 mL, 3.37 mmol, 1.05 equiv) in 80 mL of THF were obtained **7c** (270 mg, 25%) and **8c** (278 mg, 26%) after column chromatography (SiO_2, TBME/MeOH, 19/1) and recrystallization (EtOAc/hexane). Data for **7c**: mp: 136−137 °C (EtOAc/hexane); $[\alpha]^{22}_D = -29.6°$ ($c = 1.38$, $CHCl_3$); TLC $R_f = 0.43$ (TBME/MeOH 20/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.51. Anal. Calcd for $C_{18}H_{28}N_3OP$ (333.42): C, 64.84; H, 8.46; N, 12.60; P, 9.29. Found: C, 64.73; H, 8.50; N, 12.56; P, 8.89. Data for **8c**: mp: 148−149 °C (EtOAc/hexane); $[\alpha]^{22}_D = +68.1°$ ($c = 1.14$, $CHCl_3$); TLC $R_f = 0.28$ (TBME/MeOH, 20/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.11. Anal. Calcd for $C_{18}H_{28}N_3OP$ (333.42): C, 64.84; H, 8.46; N, 12.60; P, 9.29. Found: C, 64.85; H, 8.36; N, 12.61; P, 9.27.

Preparation of (−)-(7a*S*,3*S*)- and (+)-(7a*S*,3*R*)-3-Piperidino-1,2,5,6,7,7a-hexahydro-2-(2,4,6-trimethylphenyl)-pyrrolo[1,2-*c*][1,3,2]-diazaphosphole 3-Oxide (7d and 8d). Following Representative Procedure 1, from triethylamine (1.18 mL, 8.45 mmol 2.1 equiv), the diamine **24d**[31] (879 mg, 4.03 mmol), and piperidinylphosphoric dichloride (0.65 mL, 4.23 mmol, 1.05 equiv) in 100 mL of THF were obtained **7d** (463 mg, 33%) and **8d** (371 mg, 26%) as thick oils after column chromatography (SiO_2, TBME/MeOH, 32/1) and Kugelrohr distillation. Data for **7d**: bp: 175 °C (ABT, 3.8×10^{-5} mmHg); TLC $R_f = 0.58$ (TBME/MeOH 19/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.20. Data for **8d**: bp: 185 °C (ABT, 3.8×10^{-5} mmHg); TLC $R_f = 0.41$ (TBME/MeOH, 19/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.27.

Preparation of (+)-(7a*S*,3*S*)- and (+)-(7a*S*,3*R*)-3-Piperidinyl-1,2,5,6,7,7a-hexahydro-2-(1-naphthyl)pyrrolo-[1,2-*c*][1,3,2]-diazaphosphole 3-Oxide (7e and 8e). Following Representative Procedure 1a, from triethylamine (3.26 mL, 23.4 mmol 2.1 equiv), the diamine **24e**[31] (2.56 g, 11.3 mmol), and piperidinylphosphoric dichloride (1.82 mL, 11.9 mmol, 1.05 equiv) in THF (150 mL) were obtained **7e** (1.36 g, 34%) and **8e** (1.36 g, 34%) after column chromatography (SiO_2, TBME/MeOH, 19/1) and recrystallization (EtOAc/hexane).[5] Data for **7e**: mp: 129−131 °C (EtOAc/hexane); $[\alpha]^{22}_D = +42.3$ ($c = 1.90$, $CHCl_3$); TLC $R_f = 0.39$ (TBME/MeOH, 20/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.88. Anal. Calcd for $C_{20}H_{26}N_3OP$ (355.42): C, 67.59; H, 7.37; N, 11.82; P, 8.71. Found: C, 67.37; H, 7.15; N, 11.57; P, 8.68.

(3a*R*,7a*R*)-1,3-Dimethyloctahydro-2-piperidinyl-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9a). Following Representative Procedure 1a, from triethylamine (0.50 mL, 3.60 mmol, 2.0 equiv), (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine (0.253 g, 1.80 mmol), and piperidinylphosphoric dichloride (0.364 g, 1.80 mmol, 1.0 equiv) in EtOAc (18 mL) was obtained 0.282 g (58%) of **9a** as white needles after chromatography (SiO_2, EtOAc/*i*-PrOH, 10/1) and recrystallization (hexane), mp: 111−112 °C (hexane). $[\alpha]^{22}_D = -90.8°$ ($c = 1.15$, $CHCl_3$); TLC $R_f = 0.20$ (EtOAc/*i*-PrOH, 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.50. Anal. Calcd for $C_{13}H_{26}N_3OP$ (271.34): C, 57.54; H, 9.66; N, 15.49; P, 11.41. Found: C, 57.49; H, 9.62; N, 15.40; P, 11.36.

(3a*R*,7a*R*)-1,3-Dimethyloctahydro-2-(dimethylamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9b). Following Representative Procedure 1a, from triethylamine (0.84 mL, 0.61 g, 6.04 mmol, 2.01 equiv), (1*R*,2*R*)-*N*,*N*-dimethyl-1,2-cyclohexanediamine (0.424 g, 3.00 mmol), and dimethylaminophosphoric dichloride (0.36 mL, 3.00 mmol, 1.0 equiv) in 30 mL of EtOAc was obtained 0.578 g (83%) of **9b** as a white solid after chromatography (SiO_2, EtOAc/*i*-PrOH, 10/1) and Kugelrohr distillation, bp: 170−175 °C (ABT, 0.3 mmHg); mp: 57−60 °C (melt). $[\alpha]^{22}_D = -88.70$ ($c = 1.0$, $CHCl_3$); TLC $R_f = 0.22$ (SiO_2, EtOAc/*i*-PrOH, 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.77. Anal. Calcd for $C_{10}H_{22}N_3OP$ (231.28): C, 51.93; H, 9.59; N, 18.17; P, 13.39. Found: C, 51.94; H, 9.62; N, 18.17; P, 13.32.

(3a*R*,7a*R*)-1,3-Diethyloctahydro-2-(dimethylamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9c). Following Representative Procedure 1a, from triethylamine (0.29 mL, 2.08 mmol, 2.5 equiv), (1*R*,2*R*)-*N*,*N*′-diethyl-1,2-cyclohexanediamine (0.140 g, 0.83 mmol), and dimethylaminophosphoric dichloride (0.099 mL, 0.83 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was obtained 0.126 g (59%) of **9c** as a colorless oil after chromatography (SiO_2, EtOAc/*i*-PrOH, 10/1) and Kugelrohr distillation, bp: 185−190 °C (0.5 mmHg); $[\alpha]^{22}_D = -94.58$ ($c = 1.13$, $CHCl_3$); TLC $R_f = 0.22$ (SiO_2, EtOAc/*i*-PrOH, 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.80. Anal. Calcd for $C_{12}H_{26}N_3OP$ (259.33): C, 55.58; H, 10.11; N, 16.20; P, 11.94. Found: C, 55.50; H, 10.16; N, 16.15; P, 11.79.

(3a*R*,7a*R*)-1,3-Bis(1′-methylethyl)octahydro-2-(dimethylamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9d). Following Representative Procedure 1a, from (1*R*,2*R*)-*N*,*N*′-bis(1′-methylethyl)-1,2-cyclohexanediamine (0.162 g, 0.82 mmol), triethylamine (0.285 mL, 2.04 mmol, 2.5 equiv), and dimethylaminophosphoric dichloride (0.097 mL, 0.82 mmol, 1.0 equiv) in 10 mL of CH_2Cl_2 was obtained 0.087 g (37%) of **9d** as a white solid after chromtography (SiO_2, EtOAc/*i*-PrOH, 10/1). Data for **9d**: TLC $R_f = 0.36$ (SiO_2, EtOAc/*i*-PrOH, 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.42.

(3a*R*,7a*R*)-1,3-Bis(phenylmethyl)octahydro-2-(dimethylamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9e). Following Representative Procedure 1a, from triethylamine (0.29 mL, 2.08 mmol, 3.7 equiv), (1*R*,2*R*)-*N*,*N*′-bis(phenylmethyl)-1,2-cyclohexanediamine (0.164 g, 0.56 mmol), and dimethylaminophosphoric dichloride (0.066 mL, 0.56 mmol, 1.0 equiv) in CH_2Cl_2 (6 mL) was obtained 0.123 g (57%) of **9e** as a white solid after chromatography (SiO_2, EtOAc/hexane, 2/1) and recrystallization (hexane), mp: 135−136 °C (hexane); $[\alpha]^{22}_D = -94.19$ ($c = 1.05$, $CHCl_3$); TLC $R_f = 0.14$ (EtOAc/hexane, 2/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.25. Anal. Calcd for $C_{22}H_{30}N_3OP$ (383.230): C, 68.91; H, 7.89; N, 10.96; P, 8.08. Found: C, 68.88; H, 7.88; N, 10.95; P, 8.05.

(3a*R*,7a*R*)-1,3-Bis(2′,2′-dimethylpropyl)octahydro-2-(dimethylamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9f). Following Representative Procedure 1, from triethylamine (0.17 mL, 1.20 mmol, 2.5 equiv), (1*R*,2*R*)-*N*,*N*′-bis(2′,2′-dimethylpropyl)-1,2-cyclohexanediamine (0.123 g, 0.48 mmol), and dimethylaminophosphoric dichloride (0.057 mL, 0.48 mmol, 1.0 equiv) in CH_2Cl_2 (14+1+1 mL) was obtained 45 mg (27%) of **9f** as a white solid after chromatography (SiO_2, EtOAc/hexane, 1/1). Data for **9f**: TLC $R_f = 0.36$ (EtOAc/hexane, 1/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.64.

(3a*R*,7a*R*)-1,3-Dimethyl-2-(bis(1-methylethyl)amino-2*H*-1,3,2-octahydrobenzodiazaphosphole 2-Oxide (9g). Following Representative Procedure 1a, from triethylamine (0.35 mL, 2.50 mmol, 2.5 equiv), (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine (0.143 g, 1.02 mmol), and bis(1-methylethyl)aminophosphoric dichloride (0.216 g, 1.00 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) was obtained 0.019 g (7%) of **9g** as a white solid after chromatography (SiO_2, EtOAc). Data for **9g**: TLC $R_f = 0.17$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.81.

(3a*R*,7a*R*,1′*S*)-1,3-Dimethyloctahydro-2-[methyl(1′-phenylethyl)amino]-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9h). Following Representative Procedure 1a, from triethylamine (0.20 mL, 1.43 mmol, 2.5 equiv), (1*R*,2*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine (0.80 g, 1.80 mmol, 3.2 equiv), and *N*-methyl-(1′-phenylethyl)aminophosphoric dichloride (0.143 g, 0.57 mmol, 1.0 equiv) in 6 mL of CH_2Cl_2 was obtained 0.115 g (63%) of **9h** as a white solid after chromatography (SiO_2, EtOAc/*i*-PrOH, 15/1) and recrystallization (hexane), mp: 107−108 °C (hexane); $[\alpha]^{22}_D = -52.96$ ($c = 1.06$, $CHCl_3$); TLC $R_f = 0.16$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.11. Anal. Calcd for $C_{17}H_{28}N_3OP$ (321.40): C, 63.53; H, 8.78; N, 13.07; P, 9.64. Found: C, 63.57; H, 8.82; N, 13.04; P, 9.56.

(*R*,*R*)-1,3-Dimethyl-2-(dimethylamino)-4,6-diphenyl-1,3,2-diazaphosphorinane 2-Oxide (10). Following Representative Procedure 1, from triethylamine (0.13 mL, 0.93 mmol, 2.5 equiv), (*R*,*R*)-*N*,*N*′-dimethyl-1,3-diphenyl-1,3-propanediamine (0.094 g, 0.37 mmol), and dimethylaminophosphoric dichloride (0.044 mL, 0.37 mmol, 1.0 equiv) in CH_2Cl_2 (3+1+1 mL) was obtained 0.066 g (51%) of **10** as a white solid after chromatography (SiO_2, EtOAc/*i*-PrOH, 50/1). An analytical sample was obtained by recrystallization from hexane, mp: 122−123 °C (hexane); $[\alpha]^{22}_D = +16.87$ ($c = 1.12$, $CHCl_3$); TLC $R_f = 0.16$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.00.

Anal. Calcd for $C_{19}H_{26}N_3OP$ (343.41): C, 66.45; H, 7.63; N, 12.24; P, 9.02. Found: C, 66.46; H, 7.66; N, 12.23; P, 8.98.

Representative Procedure 2 for the Synthesis of Phosphoramides from Aminophosphorus Dichloride. (4*S*,5*S*)-(+)-1,3-Diethyl-4,5-diphenyl-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide ((*S*,*S*)-5b). To a solution of triethylamine (0.66 mL, 4.73 mmol, 2.2 equiv) in 80 mL of CH_2Cl_2 at reflux was added a solution of (1*S*,2*S*)-*N*,*N*′-diethyl-1,2-diphenyl-1,2-ethanediamine (578 mg, 2.15 mmol) in 5 mL of CH_2Cl_2 and a solution of piperidinylphosphorus dichloride (0.33 mL, 2.15 mmol, 1.0 equiv)[34] in 5 mL of CH_2Cl_2 simultaneously via a syringe pump in 2 h. After addition the solution was heated to reflux for an additional 30 min and then was cooled back to 0 °C. A solution of MCPBA in 10 mL of CH_2Cl_2 was then added via a syringe, and the solution was stirred at room temperature overnight. The slightly yellow solution was poured into a separatory funnel and washed with water (20 mL), saturated aqueous $NaHCO_3$ (2 × 20 mL), and brine (20 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo to afford a crude product that was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 19/1) to give 549 mg (64%) of (*S*,*S*)-**5b** as a white solid. Recrystallization from hexane gave 255 mg (30%) of white prisms, mp: 150−152 °C (hexane); $[\alpha]^{22}_D = +6.2°$ ($c = 1.20$, $CHCl_3$); TLC $R_f = 0.33$ (CH_2Cl_2/MeOH, 19/1); ^{31}P NMR: δ 28.12. Anal. Calcd for $C_{23}H_{32}N_3OP$ (397.50): C, 69.50%; H, 8.11%; N, 10.57%; P, 7.79%. Found: C, 69.48%; H, 8.08%; N, 10.55%; P, 8.04%.

(4*S*,5*S*)-(+)-1,3-Dimethyl-4,5-diphenyl-2-(bis(1-methylethyl)amino)-1,3,2-diazaphospholidine 2-Oxide ((*S*,*S*)-4d). Following Representative Procedure 2, from (*S*,*S*)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (483 mg, 2.01 mmol), triethylamine (0.62 mL, 4.42 mmol, 2.2 equiv), and bis(1-methylethyl)aminophosphoric dichloride[39] (0.414 mL, 2.01 mmol, 1.0 equiv) in CH_2Cl_2 (80+10+10 mL) was obtained 0.549 g (71%) of **4d** as a white foam after chromatography (SiO_2, TBME/MeOH, 49/1). TLC $R_f = 0.35$ (TBME/MeOH, 19/1). ^{31}P NMR (202 MHz, $CDCl_3$): δ 28.12. HRMS (CI) for $C_{22}H_{32}N_3OP$ Calcd: 385.2283, Found: 385.2284.

(*R*)-1,3-Dimethyl-2,3-dihydro-2-piperidinyl-dinaphtho-[2,1-*c*:1′2′-*e*]-1H-[1,3,2]diazaphosphepine 2-Oxide ((*R*)-11). A solution of (*R*)-*N*,*N*′-Dimethyl-1,1′-binaphthyl-2,2′-diamine[40] ((*R*)-27) (780 mg, 2.5 mmol) in THF (25 mL) was cooled to −72 °C in a dry ice/acetone bath. *n*-Butyllithium (1.44 M, 3.82 mL, 5.5 mmol) was added dropwise. The resulting orange solution was allowed to warm to −30 °C before it was cooled back to −75 °C. 1-Piperidinylphosphoric dichloride (512 mg, 2.75 mmol) in THF (25 mL) was added dropwise over 30 min and the solution was allowed to slowly warm to room temperature and stirred overnight. A solution of MCPBA (559 mg, 2.75 mmol) THF (12 mL) was then added dropwise at 0 °C, and the mixture was stirred at room temperature overnight before it was transferred to a separatory funnel containing saturated aqueous $NaHCO_3$ (150 mL) solution. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (5 × 35 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The yellow residue was purified by column chromatography (SiO_2, EtOAc/*i*-PrOH, 32/1 then 19/1) to give 742 mg (67%) of (*R*)-**11** as a slightly yellow solid. An analytical sample was obtained by chromatotron separation (SiO_2, EtOAc/*i*-PrOH, 49/1, 32/1 then 19/1) and crystallization from toluene/hexane to give white crystals (593 mg, 54%), mp: 276−277 °C (toluene/hexane); $[\alpha]^{22}_D = -472°$ ($c = 1.18$, $CHCl_3$); TLC $R_f = 0.34$ (EtOAc/*i*-PrOH, 19/1); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.38. Anal. Calcd for $C_{27}H_{28}N_3OP$ (441.52): C, 73.45; H, 6.39; N, 9.52; P, 7.02. Found: C, 73.71; H, 6.42; N, 9.44; P, 6.81. HPLC: t_R (*R*)-**11**, 21.21 min (99.76%), t_R (S)-**11**, 14.85 min (0.24%) (β-GEM-1, hexane/*i*-PrOH, 65/35, 0.6 mL/min).

Representative Procedure 3 for the Synthesis of Phosphoramides from PCl_3. 1,3-Di(1-naphthyl)-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (1d). To a stirred, cold (−78 °C) solution of PCl_3 (0.61 mL, 7.0 mmol, 1.1 equiv) in 10 mL of CH_2Cl_2 was added a solution of 1,2-bis(1-naphthylamino)ethane[12] (2.0 g, 6.4 mmol) in 10 mL of CH_2Cl_2 under nitrogen through a dropping funnel. Triethylamine (2.2 mL, 16 mmol, 2.5 equiv) was then added at the same temperature. The mixture was warmed to room temperature and stirred for an additional 24 h. After filtration of the precipitates, the filtrate was condensed under reduced pressure to remove the excess reagents.

The residue was suspended in 13 mL of CH_2Cl_2, and piperidine (2.3 mL, 23 mmol, 3.6 equiv) was added with stirring at room temperature. The mixture was stirred for 20 h and filtered to remove the precipitates, and the filtrate was concentrated under reduced pressure to remove excess piperidine.

To a solution of the residue in CH_2Cl_2 (10 mL) was added a solution of MCPBA (50%, 2.21 g; 6.4 mmol) in CH_2Cl_2 (10 mL) dropwise at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 24 h. Then, saturated aqueous $NaHCO_3$ was added with stirring. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, benzene then benzene/EtOAc, 4/1 as eluents) and recrystallization (Et_2O/hexane) to give slightly tan crystals (1.29 g; 46%), mp: 170−171 °C (CH_2Cl_2/hexane); TLC $R_f = 0.83$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.56. Anal. Calcd for $C_{27}H_{28}N_3OP$ (441.51): C, 73.45; H, 6.39; N, 9.52; P, 7.02. Found: C, 73.32; H, 6.42; N, 9.61; P, 6.74.

1,3-Diphenyl-2-(diphenylamino)-1,3,2-diazaphospholidine 2-Oxide (2b). Following Representative Procedure 3, from PCl_3 (0.5 mL, 5.73 mmol, 1.0 equiv), *N*,*N*′-diphenyl-1,2-ethanediamine (1.10 g, 5.17 mmol), triethylamine (1.8 mL, 13 mmol, 2.5 equiv), diphenylamine (0.875 g, 5.17 mmol, 1.0 equiv), and MCPBA (50%, 1.78 g, 5.17 mmol, 1.0 equiv) was obtained 1.59 g (72%) of **2b** as colorless needles after chromatography (SiO_2, hexane/CH_2Cl_2, 2/1 then hexane/CH_2Cl_2/*i*-PrOH, 2/1/0.03 as eluents) and recrystallization (benzene/hexane), mp: 210−211 °C (hexane); TLC $R_f = 0.16$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 7.43. Anal. Calcd for $C_{26}H_{24}N_3OP$ (425.47): C, 73.40; H, 5.69; N, 9.88; P, 7.28. Found: C, 73.48; H, 5.63; N, 9.92; P, 6.98.

(*S*)-1,3-Diphenyl-2-[methyl(1-phenylethyl)amino]-1,3,2-diazaphospholidine 2-Oxide (3b). Following Representative Procedure 3, from PCl_3 (0.95 mL; 11 mmol, 1.1 equiv), *N*,*N*′-1,2-diphenyl-1,2-ethanediamine (2.12 g, 10 mmol), triethylamine (3.5 mL; 25 mmol, 2.5 equiv), (*S*)-*N*-methyl-*N*-(1-phenylethyl)amine (1.45 mL, 10 mmol, 1.0 equiv), and MCPBA (50%, 3.45 g; 10 mmol, 1.0 equiv) was obtained 1.96 g (50%) of **3b** as colorless fine needles after chromatography (SiO_2, benzene/CH_2Cl_2/*i*-PrOH, 30/20/1) and recrystallization (CH_2Cl_2/hexane). An analytical sample was given by sublimation at 0.05 mmHg: mp: 204−205 °C (0.05 mmHg). $[\alpha]^{22}_D = +1.7°$ ($c = 1.10$, $CHCl_3$); TLC $R_f = 0.87$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.31. Anal. Calcd for $C_{23}H_{26}N_3OP$ (391.45): C, 70.57; H, 6.69; N, 10.73; P, 7.91. Found: C, 70.35; H, 6.56; N, 10.79; P, 7.86.

(−)-(4*S*,5*S*)-1,3,4,5-Tetraphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (5c). Following Representative Procedure 3, from PCl_3 (69 μL, 0.79 mmol, 1.1 equiv), (*S*,*S*)-*N*,*N*′,1,2-tetraphenyl-1,2-ethanediamine (261 mg, 0.716 mmol), triethylamine (0.22 mL, 1.57 mmol, 2.2 equiv), piperidine (0.21 mL, 2.15 mmol, 3.0 equiv), and MCPBA (50%, 250 mg; 0.72 mmol, 1.0 equiv) was obtained 196 mg (55%) of **5c** as an amorphous solid after chromatography (SiO_2, CH_2Cl_2/*i*-PrOH, 20/1), mp: 195−197 °C (hexane); $[\alpha]^{22}_D = -194°$ ($c = 1.01$, $CHCl_3$); TLC $R_f = 0.49$ (EtOAc); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.30. Anal. Calcd for $C_{31}H_{32}N_3OP$ (493.59): C, 75.44; H, 6.53; N, 8.51; P, 6.28. Found: C, 75.31; H, 6.30; N, 8.46; P, 6.09.

(−)-(4*S*,5*S*)-1,3-Di-(1-naphthyl)-4,5-diphenyl-2-piperidino-2H-1,3,2-diazaphospholidine 2-Oxide (5d). Following Representative Procedure 3, from PCl_3 (100 μL, 1.14 mmol,

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1.1 equiv), (*S*,*S*)-*N*,*N*′-di-(1-naphthyl)-1,2-diphenyl-1,2-ethanediamine (482 mg, 1.04 mmol), triethylamine (363 μL, 3.12 mmol, 3.0 equiv), piperidine (310 μL, 3.12 mmol, 3.0 equiv), and MCPBA (50%, 431 mg, 1.25 mmol, 1.2 equiv) was obtained 309 mg (50%) of **5d** as an off-white foam after column chromatography (hexane/EtOAc, 3/1 to 1/1), which was recrystallized from toluene/hexane to give white amorphous powder, mp: 188−190 °C (toluene/hexane); $[\alpha]^{22}_D = -356°$ (*c* = 1.01, $CHCl_3$); TLC $R_f = 0.33$ (hexane/EtOAc, 1/1); ^{31}P NMR (202 MHz, $CDCl_3$) mixture of rotamers: δ 21.29 (br), 20.25 (br), 14.02 (minor). Anal. Calcd for $C_{39}H_{36}N_3OP$ (593.72): C, 78.90; H, 6.11; N, 7.08; P, 5.22. Found: C, 78.86; H, 6.26; N, 6.91; P, 5.18.

(±)-1,3-Dimethyl-4,5-di-(1-naphthyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (6d). Following Representative Procedure 3, from PCl_3 (97 μL, 1.11 mmol, 1.02 equiv), (±)-*N*,*N*′-dimethyl-1,2-di-(1-naphthyl)-1,2-ethanediamine (370 mg, 1.09 mmol), triethylamine (318 μL, 2.28 mmol, 2.1 equiv), piperidine (269 μL, 2.72 mmol, 2.5 equiv), and MCPBA (70%, 563 mg, 2.28 mmol, 2.1 equiv) was obtained 196 mg (38%) of **6d** as a white solid after column chromatography (EtOAc/*i*-PrOH, 19/1 to 9/1) and recrystallization (hexane), mp: 183−186 °C (hexane); $R_f = 0.38$ (EtOAc/*i*-PrOH, 9/1); ^{31}P NMR (202 MHz, $CDCl_3$): mixture of rotamers: δ 28.4 (br), 26.4 (br), 25.8 (br). Anal. Calcd for $C_{29}H_{32}N_3OP$ (469.57): C, 74.18; H, 6.87; N, 8.95. Found: C, 74.10; H, 6.75; N, 8.88.

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Supporting Information Available: Characterizations of the phosphoramides in Chart 1 and the synthesis and characterizations of their amine precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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