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Unexpected Insertion of CO_2 into the Pentacoordinate P−N Bond: Atherton−Todd-Type Reaction of Hydrospirophosphorane with Amines

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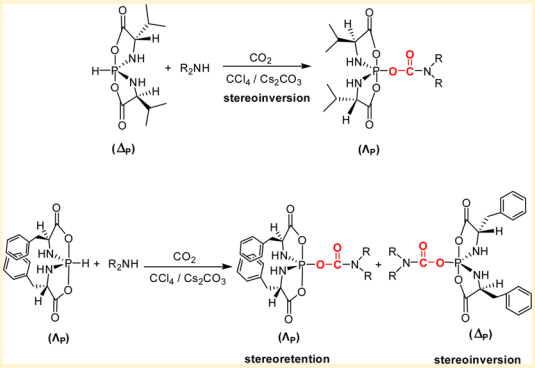
Supporting Information

ABSTRACT: The Atherton−Todd-type reaction of pentacoordinate hydrospirophosphoranes with amines was investigated, and a novel CO_2 insertion reaction into the pentacoordinate P−N bond under mild conditions was developed. The mechanism and stereochemistry of the CO_2 insertion reaction between hydrospirophosphoranes and secondary amines were proposed via a carbon-13 labeling experiment, a ^{31}P NMR tracing experiment, and X-ray diffraction analysis. The chlorinated spirophosphorane intermediate was first generated with stereoretention of the configuration at phosphorus and subsequently was attacked by a carbamate anion formed from CO_2 and a secondary amine. It was found that rear attack of nucleophilic substitution with stereoinversion at pentacoordinate phosphorus was the preferred route, although front attack happened for sterically hindered reactants. The configuration of the CO_2 insertion product depended mainly upon the original phosphorus configuration of the hydrospirophosphoranes.



INTRODUCTION

Pentacoordinate phosphorus compounds are essential in numerous biological processes such as hydrolyses of RNA or phosphoryl transfer reactions.[1] To elucidate the general principles related to pentacoordinate phosphorus compounds, many stable models have been designed. Hydrospirophosphorane (HSP) is one of the pentacoordinate spirophosphorane models involving a P−H bond which has enough chemical activity to be a precursor for organic synthesis. There are not enough reports on using pentacoordinate compounds as precursors for organic synthesis, although the direction is considered to be important to develop in the future.[2] The pentacoordinate bis(aminoacyl)spirophosphoranes with a P−H bond (AA-HSPs) are synthesized from amino acids, and they are rarely investigated. Furthermore, AA-HSP has three chiral centers; one is from phosphorus, and two come from the chiral carbon of amino acids. It appears as an ideal pentacoordinate phosphorane model with enough chemical stability to study the stereochemistry of pentacoordinate phosphorus compounds. Therefore, it is necessary to investigate the reaction activities and the stereochemistry of AA-HSPs as one of the pentacoordinate phosphorane models.

The classical Atherton−Todd reaction has been widely applied to the synthesis of tetracoordinated phosphorus compounds with different biological activities.[3] Considering the importance of the Atherton−Todd reaction and AA-HSP as a pentacoordinate phosphorane model, our group has previously synthesized different AA-HSPs and studied their stereochemical characteristics.[4] Recently, we reported the preliminary results of a stereochemical investigation of the Atherton−Todd-type reaction between an AA-HSP synthesized from L-valine and phenols.[5] It was found that the reaction produced phenoxyspirophosphoranes with stereoinversion of the phosphorus chiral center. The results are useful for further stereochemistry research of pentacoordinate phosphorus chemistry. As a continuing interest in investigating the reaction and stereochemical characteristics of pentacoordinate phosphorus compounds, we studied the Atherton−Todd-type reaction of AA-HSPs with amines. Unexpectedly, a novel CO_2 insertion reaction related to the pentacoordinate P−N bond was discovered.

It is well-known that CO_2 is an easily available renewable carbon resource, which has the advantages of being nontoxic, abundant, and economical. The development of new methodologies for chemical transformation of CO_2 into useful compounds is very important from the standpoint of C1 chemistry and green chemistry.[6] However, there have been only

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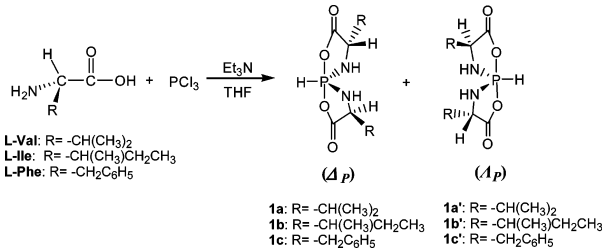
a few processes based on CO_2 as a raw material on a technical scale up to now, such as the production of urea, methanol, or salicylic acid.[7] While CO_2 insertion reactions of C−N bonds have been intensively investigated on the basis of CO_2 activation through molecular catalysis, a few examples of CO_2 insertion reactions of P−N bonds have been reported. There are several studies that have reported CO_2 insertion into tricoordinate P^{III}−N or tetracoordinate P^{IV}−N bonds,[8] and only Cavell's group observed the insertion of CO_2 into acyclic pentacoordinate P^{V}−N bonds about 30 years ago.[9] To the best of our knowledge, the insertion of CO_2 into the pentacoordinate P^{V}−N bond of spirophosphoranes has never been reported. Furthermore, most of the reactions involving CO_2 are commonly carried out with a transition-metal catalyst or at high pressure owing to its thermodynamic stability. The challenge is to develop a simple method to incorporate CO_2 into organic molecules under low pressure and without a transition-metal catalyst. We describe herein our efforts toward the investigation of the CO_2 insertion into the pentacoordinate P^{V}−N bond in mild conditions. Meanwhile, a series of new spirophosphoranes were produced. An insertion reaction mechanism between AA-HSPs and secondary amines was proposed, and the stereochemistry characteristic was revealed by a ^{31}P NMR tracing experiment, a carbon-13 labeling experiment, and X-ray diffraction analysis.

RESULTS AND DISCUSSION

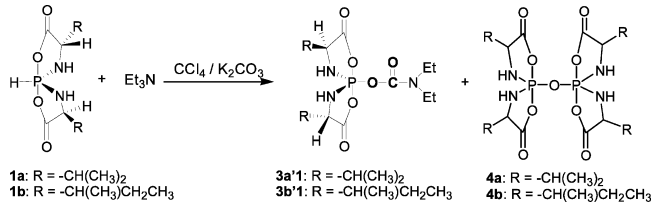
Discovery of a CO_2 Insertion Reaction. A pair of diastereoisomers of AA-HSPs were readily prepared from L-amino acids (Scheme 1),[4a] and they could be separated by column chromatography and recrystallization. The absolute configurations of the phosphorus chiral center of AA-HSPs are described by the nomenclature system for coordination compounds $[MX(AB)_2]$ (AB = heterobidentate ligand).[10] Further experiments found that a pair of diastereoisomers showed obviously different solubilities in organic solvents.[4e] Here the isomers with better solubility were selected to perform the reaction.

Scheme 1. Synthesis of AA-HSPs



A single crystal of **1a′**, one of the isomers synthesized from L-valine, was obtained, and its absolute configuration was defined as $[\Lambda_P, S_C, S_C]$.[4c] Another isomer, **1a**, with better solubility and absolute stereochemistry defined as $[\Delta_P, S_C, S_C]$ was first selected to perform the Atherton−Todd-type reaction. Initially, the Atherton−Todd-type reaction of reactant **1a** with alcohol was studied. After addition of carbon tetrachloride (CCl_4) and triethylamine (Et_3N) to the reaction solution of **1a** and alcohol, the corresponding alkoxyphosphoranes could not be produced as expected. The results showed that Et_3N participated in the reaction and CO_2 inserted into the pentacoordinate P^{V}−N bond unexpectedly. Two new types of pentacoordinate phosphorus compounds, CO_2 insertion product **3a′1** and dimeric spirophosphorane **4a**, were isolated with yields of 17% and 26%, respectively (Scheme 2). This new spirophosphorane **3** is here named a spirophosphorane carbamate, and product **4** is named a pyrospirophosphorane.

Scheme 2. Atherton−Todd-Type Reaction of AA-HSPs with a Tertiary Amine



In general, the CO_2 fixation is always achieved with a transition-metal catalyst and high pressure.[7] Because of the thermal stability and chemical inactivity of CO_2, there are only a few reports of the CO_2 fixation without a transition-metal catalyst. Moreover, organic carbamates hold unique applications in the field of pharmaceuticals and agriculture.[11] Accordingly, the new spirophosphorane carbamate **3** might be presumed to be a potential bioactive compound. In view of the importance of the CO_2 fixation and the possibility of spirophosphorane carbamates as potential bioactive compounds, the reaction conditions of the CO_2 insertion reaction between AA-HSPs and tertiary amines were further optimized. However, the results showed that, no matter how the conditions were optimized and no matter which kind of tertiary amines and AA-HSPs were used, the yield of the CO_2 insertion product **3** did not exceed 20% (Table 1, entries 1 and 14). It was presumed that the reason for the low yield might be the weak nucleophilicity of the tertiary amine and the existence of the byproduct **4**.

Identification of the Structures of the CO_2 Insertion Products. The structures of the novel CO_2 insertion products **3** were identified by NMR, 2D NMR, IR, and ESI-MS/MS spectra. Compound **3a′1** was taken as an example for structural identification (Scheme 3). In the downfield region of the ^{13}C NMR spectrum of **3a′1**, in addition to a higher doublet at 169.4 ppm (d, $^2J_{C(O)-O-P}$ = 12.0 Hz) corresponding to the two intracyclic carboxyl carbons, another doublet at 150.0 ppm (d, $^2J_{C(O)-O-P}$ = 5.0 Hz) was observed, which was finally assigned to the *N*-carbonyl carbon. In the ^1H NMR spectrum of **3a′1**, additional signals at 3.21 ppm (m, 4H) and 1.15 ppm (dt, 6H), which were related to the protons of the *N*,*N*-diethylamino group, were observed in comparison with the spectrum of reactant **1a**. The correlation of the *N*-carbonyl carbon at 150.0 ppm and *N*-methylene protons at 3.21 ppm was observed in the HMBC spectrum, indicating that the *N*,*N*-diethylamino group was connected directly to the *N*-carbonyl carbon. Since the aminoacyl C(O)−N bond had a partial double bond property, the methylene and methyl protons of the *N*,*N*-diethylamino group showed chemical shift nonequivalence at room temperature. The methylene protons presented odd-shaped peaks as multiplets, while methyl protons appeared as two triplets. To further identify the presence of the aminoacyl C(O)−N moiety, the NMR sample was warmed from 293 to 318 K in $CDCl_3$. Then the C(O)−N bond rotated more quickly, and the protons of the *N*,*N*-diethylamino group could exchange their positions with higher frequency. Thus, the signals of the methyl protons

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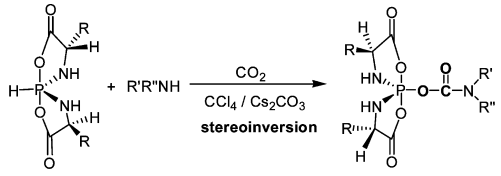
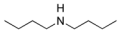
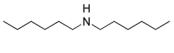
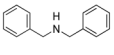
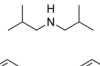
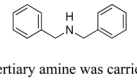
Table 1. Atherton–Todd-Type Reaction of AA-HSPs [Δ_P] with Amines



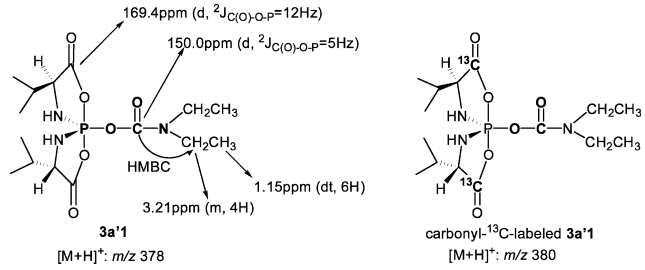
1a: R = -CH(CH$_3$)$_2$ (Δ_P) **3a'**: R = -CH(CH$_3$)$_2$ (Λ_P)
1b: R = -CH(CH$_3$)CH$_2$CH$_3$ (Δ_P) **3b'**: R = -CH(CH$_3$)CH$_2$CH$_3$ (Λ_P)

Entry	AA-HSP [Δ_P]	Amines	Base	Time(hr)	Yield of **3xn** [Λ_P] (%)
1	**1a**		K_2CO_3	11	**3a'1**: 17[a]
2	**1a**		K_2CO_3	48	**3a'1**: 52
3	**1a**		Cs_2CO_3	20	**3a'1**: 66
4	**1a**		Cs_2CO_3	20	**3a'2**: 58
5	**1a**		Cs_2CO_3	20	**3a'3**: 65
6	**1a**		Cs_2CO_3	20	**3a'4**: 46
7	**1a**		Cs_2CO_3	36	**3a'5**: 70
8	**1a**		Cs_2CO_3	20	**3a'6**: 69
9	**1a**		Cs_2CO_3	24	**3a'7**: 68
10	**1a**		Cs_2CO_3	28	**3a'8**: 48
11	**1a**		Cs_2CO_3	20	**3a'9**: 77[b]
12	**1a**		Cs_2CO_3	20	**3a'10**: 69[b]
13	**1a**		Cs_2CO_3	20	**3a'11**: 60[b]
14	**1b**		K_2CO_3	12	**3b'1**:16[a]
15	**1b**		Cs_2CO_3	20	**3b'1**: 68
16	**1b**		Cs_2CO_3	20	**3b'2**: 73
17	**1b**		Cs_2CO_3	20	**3b'3**: 59
18	**1b**		Cs_2CO_3	20	**3b'4**: 58
19	**1b**		Cs_2CO_3	20	**3b'5**: 63

[a] Reaction for AA-HSP and tertiary amine was carried out in air atmosphere (Scheme 2). [b] Presented two sets of signals in NMR since the cis-trans isomers of C(O)-N bond.

finally coalesced into a triplet. Although the signals of the methylene protons were also observed as a multiplet, the peak became narrower compared with that in the original spectrum. Thus, the temperature-dependent NMR dynamic experiment further confirmed the presence of the *N*,*N*-diethylcarbamic unit, $-O-C(O)-N(CH_2CH_3)_2$, in product **3a′1**.

Scheme 3. Structure and Identification of CO_2 Insertion Product 3a′1



Other structural features of product **3** were notable. The IR spectra also exhibited characteristic bands corresponding to two types of carbonyl groups. The stretching vibration peaks of two intracyclic carboxyl groups appeared in the 1740–1765 cm^{-1} region. Another absorption band observed in the 1700–1745 cm^{-1} region was attributed to the carbonyl of the amide group. Moreover, ESI-MS/MS spectra were used not only to confirm the molecular weight of compound **3**, but also to verify its partial structural moiety by the proposed fragmentation pathways of AA-HSPs.[12] The fragmentation pathways observed for products **3** were also in good agreement with those of homologous structures.

Atherton–Todd-Type Reaction of AA-HSPs with Secondary Amines. For a classical Atherton–Todd reaction, primary and secondary amines are most often used as nucleophilic reagents.[3] In general, tertiary amines cannot participate in the Atherton–Todd reaction, and they are always used as acid-binding agents. Therefore, after investigation of the reaction between AA-HSPs and tertiary amines, the reaction activities of primary and secondary amines were studied in detail. The reaction between AA-HSP **1a** and diethylamine was investigated to optimize the reaction conditions. The effects of different bases were explored first, and the results showed that K_2CO_3 and Cs_2CO_3 both presented good catalytic activity, but the reaction time could be apparently shortened with a better yield by using Cs_2CO_3 (Table 1, entries 2 and 3). Subsequently, a number of solvents, CH_3CN, THF, acetone, toluene, dioxane, NMP, CH_2Cl_2, DMF, and DMSO, were evaluated in the presence of Cs_2CO_3. It became evident that the reaction proceeded well in CH_3CN rather than in other solvents to some extent in terms of yield and reaction time. The effect of the reaction temperature was also examined. Higher temperatures were found to be more effective to shorten the reaction time, but they brought more byproducts and led to lower yields, while lower temperatures gave a longer reaction time. Only at room temperature, the reaction could give moderate or high yield for a reasonable time. Finally, air and CO_2 reaction atmospheres for the CO_2 insertion reaction were compared. To our delight, only CO_2 insertion product **3** was observed and no byproduct **4** was produced in a CO_2 atmosphere. Notably, a CO_2 atmosphere improved the yield of the reaction between **1a** and secondary amines, although it did not benefit the reaction between **1a** and tertiary amines. Therefore, the reaction conditions were determined to be use of Cs_2CO_3 as the base and CH_3CN as the solvent at room temperature in a CO_2 atmosphere. As shown in Table 1, the scope of both the AA-HSP and secondary amine for the CO_2 insertion reaction was then explored. At first, the reaction between **1a** and secondary amines was investigated in detail. Under optimized conditions, only CO_2 insertion product **3a′** was observed and isolated in

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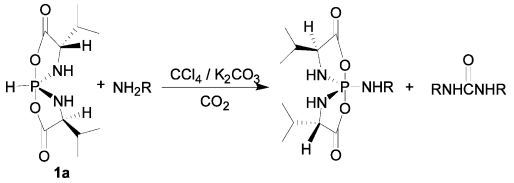
moderate to good yields (entries 3−13). The results showed that sterically hindered amines generally led to a lower yield or longer reaction time (entries 6, 7, and 10), while most secondary amines could complete the reaction in 20 h. It was noteworthy that a moderate yield was also achieved from **1a** and asymmetric secondary amines (entries 11−13). For the asymmetric secondary amines, the CO_2 insertion products **3a′** sometimes showed two sets of signals in NMR spectra due to the presence of cis−trans isomers coming from the restricted rotation of the C(O)−N bond and the asymmetrically substituted groups at the nitrogen atom. For the product **3a′9**, it was observed that the two signals in ^{31}P NMR finally coalesced into a singlet after the temperature was increased in the temperature-dependent NMR dynamic experiment.

Having discovered that a secondary amine and **1a** had efficient reactivity with CO_2 to give the corresponding CO_2 insertion product, we continued our study by examining other AA-HSPs to study the scope of this methodology. The isomer **1b** [Δ_P, S_C, S_C] with better solubility synthesized from L-isoleucine was then used to continue the reaction (Scheme 1). As expected, corresponding CO_2 insertion products **3b′** were isolated (Table 1, entries 15−19). The results also showed that the new CO_2 insertion reaction could be achieved between other AA-HSPs and secondary amines in moderate to good yields without any transition-metal catalyst at room temperatures and pressures.

For primary amines tested in the same reaction condition, no CO_2 insertion product was produced beyond our expectation. Corresponding amidophosphorane products and dialkylurea were formed and isolated. The Atherton−Todd-type reaction of AA-HSP **1a** with primary amines is shown in Scheme 4.

Scheme 4. Atherton−Todd-Type Reaction of AA-HSP 1a with Primary Amines

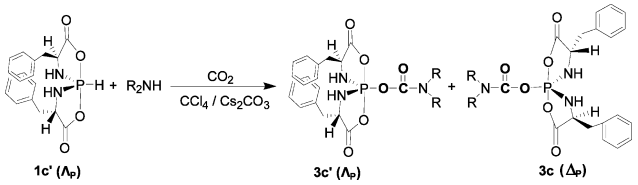


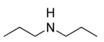
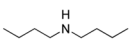
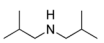
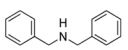
Because of the stronger nucleophilicity of the primary amine, the nitrogen atom could directly attack the phosphorus of the AA-HSP to produce the corresponding amidophosphorane as a typical product of the Atherton−Todd reaction. However, the yield of amidophosphorane products was low (10−20%) because of the production of dialkylurea. In the synthesis of urethane derivatives, CO_2 is known to readily react with nucleophiles, such as primary amines. Of course, various catalysts and/or high CO_2 pressures are always necessary to synthesize urethane derivatives.[7]

As above, the results showed that the yield of the CO_2 insertion product varied with the type of amine. Secondary amines could react with AA-HSPs to give CO_2 insertion products in moderate to good yields (Table 1, entries 2−13 and 15−17), while primary and tertiary amines showed no or relatively low activity. In the case of primary amines, amidophosphorane products and urethane derivatives were produced. For tertiary amines, because of their weak nucleophilicity and byproduct **4**, the yield of the CO_2 insertion product was considerably lowered (entries 1 and 14).

Investigation of the Stereochemistry of the CO_2 Insertion Reaction. To investigate the stereochemical characteristics of pentacoordinate phosphorus compounds, we tried to perform the CO_2 insertion reaction of AA-HSP with another configuration of phosphorus after assaying two AA-HSP isomers, **1a** and **1b**, with [Δ_P, S_C, S_C] configuration. However, the isomers with [Λ_P, S_C, S_C] configuration of AA-HSPs synthesized from L-valine (**1a′**) and L-isoleucine (**1b′**) have poor solubility in normal organic solvents. Therefore, the isomer **1c′** [Λ_P, S_C, S_C] (Scheme 1) with better solubility synthesized from L-phenylalanine was then used to continue the reaction to study the stereochemistry of AA-HSPs. It is known that the AA-HSP synthesized from L-amino acids with Λ_P configuration looks like a "resting moth", while the AA-HSP with Δ_P configuration looks like a "resting butterfly" with a bisipirocycle for the "body" and two R substituted groups of the amino acid for the "wings".[4e] This means different configurations of AA-HSPs have different steric hindrances when they are attacked at the phosphorus atom from the rear direction (Scheme 1). It was presumed that the configuration of phosphorus of AA-HSPs might influence the results of the Atherton−Todd-type reaction. Finally, the results of the reaction of compound **1c′** [Λ_P, S_C, S_C] with secondary amines showed that the CO_2 insertion products were a pair of P-diastereoisomers (Table 2). For example, the reaction of compound **1c′** and diethylamine produced a pair of P-diastereoisomers, **3c′1** and **3c1**, the ^{31}P NMR signals of which appeared at −58.8 and −60.0 ppm separately, and the ratio of the integration area of ^{31}P NMR was 1:6.8. In some cases, the isomers could be separated and purified by fractional crystallization and column chromatography, whereas some diastereoisomers were not easy to separate. No attempt was made to isolate all isomers, so the total yields of the diastereoisomers are given in Table 2. Although most of the diastereoisomers were purified and isolated, the absolute configuration of phosphorus of the CO_2 insertion products could not be confirmed without X-ray structure analysis.

Table 2. Atherton−Todd-Type Reaction of AA-HSP [Λ_P] with Secondary Amines



Entry	Secondary Amines	Ratio of ^{31}P NMR[a] [Λ_P] : [Δ_P]	Total yield of **3** (%)
1		**3c′1** : **3c1** = 1 : 6.8	65
2		**3c′2** : **3c2** = 1 : 2.5	66
3		**3c′3** : **3c3** = 1 : 1.8	61
4		**3c′4** : **3c4** = 1 : 3.0	68
5		**3c′5** : **3c5** = 1 : 2.1	69

[a] Reaction time: 20hr.

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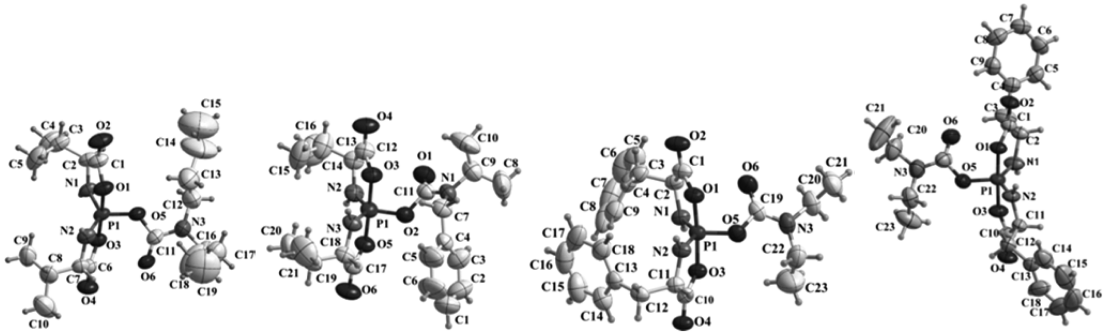


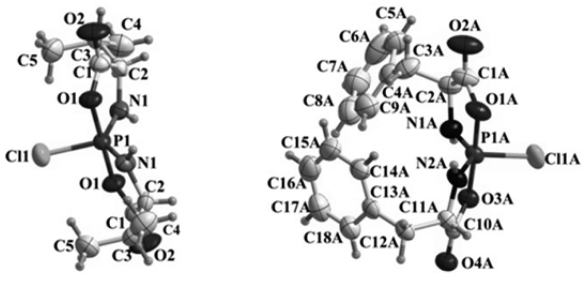
3a'3[Λ_P] **3a'9**[Λ_P] **3c'1**[Λ_P] **3c1**[Δ_P]

Figure 1. X-ray structures of **3a′3** [Λ_P], **3a′9** [Λ_P], **3c′1** [Λ_P], and **3c1** [Δ_P].

Fortunately, the single crystals of the CO_2 insertion products **3a′3**, **3a′9**, **3c′1**, and **3c1** were finally obtained. The absolute configurations of **3a′3**, **3a′9**, and **3c′1** were identified as [Λ_P, S_C, S_C], and that of **3c1** was identified as [Δ_P, S_C, S_C] as shown in Figure 1. The products **3c′1** and **3c1** were a pair of P-diastereoisomers. Therefore, it was proposed that the CO_2 insertion reaction of **1a** [Δ_P] led to the insertion product **3a′** [Λ_P] with stereoinversion of the phosphorus configuration, which is similar to the results of the Atherton–Todd-type reaction between AA-HSP and phenols.[5] In addition, the insertion products of **1c′** [Λ_P] were generated as a pair of P-diastereoisomers, **3c′** [Λ_P] and **3c** [Δ_P].

Proposed Mechanism of the CO_2 Insertion Reaction. To investigate the mechanism of the CO_2 insertion reaction, a ^{31}P NMR tracing experiment was used to detect the reaction of reactant **1a**. In the ^{31}P NMR tracing spectra, an intermediate singlet at δ −49 ppm was observed. For a classical Atherton–Todd reaction, dialkyl chlorophosphate has been reported to be the intermediate to give phosphates or phosphoramidates.[3b,c] As expected, the intermediate was isolated and identified to be the corresponding chlorinated spirophosphorane **2a**. Subsequently, the single crystal of intermediate **2a** was finally obtained, and it was testified to be produced from the reactant **1a** with stereoretention of the configuration at phosphorus.[5] Similarly, the single crystal of the intermediate **2c′** was also achieved from **1c′** and confirmed the stereoretention of the configuration at phosphorus again (Figure 2).

It is known that there is an equilibrium in solution between pentacoordinate HSP and a tricoordinated phosphate structure, which are a pair of P^{III}/P^{V} chain–ring tautomers.[13] Therefore, if AA-HSP reacts through its tricoordinated open-chain intermediate, the *N*-carbonyl group of insertion product **3** possibly comes from reactant **1**. To eliminate this possibility, carbonyl-^{13}C-labeled L-valine was used to synthesize carbonyl-^{13}C-labeled reactant **1a**. Then carbonyl-^{13}C-labeled **1a** reacted under the same condition to synthesize carbonyl-^{13}C-labeled **3a′1**. ESI-MS indicated that the molecular ion $[M + H]^+$ of carbonyl-^{13}C-labeled **3a′1** presented at *m*/*z* 380 (Scheme 3), just 2 mass units higher than that of non-^{13}C-labeled **3a′1** ($[M + H]^+$, *m*/*z* 378). This means that carbonyl-^{13}C-labeled **3a′1** included only two carbonyl ^{13}C atoms from the reactant. Therefore, the carbonyl-^{13}C-labeled experiment confirmed that the *N*-carbonyl group of **3a′1** was not from the reactant **1a**.



2a[Δ_P] **2c'**[Λ_P]

Figure 2. X-ray structures of intermediates **2a** [Δ_P][5] and **2c′** [Λ_P].

It has long been recognized that CO_2 readily adds to primary and secondary amines to afford the corresponding carbamic acids or carbonates, even at room temperature and under atmosphere pressure.[14] This step occurs almost spontaneously, but further transformation of carbamic acids into other organic compounds normally requires quite drastic conditions (>200 °C), higher CO_2 pressures (>100 atm), or quite expensive ionic liquids. In addition, sometimes CO_2 can be activated through the formation of carbamate/alkyl carbonate with Lewis basic nitrogen species. In basic medium, primary and secondary amines and CO_2 are commonly in equilibrium with a carbamate anion. If the equilibrium is sufficiently shifted toward the carbamate anion, it can be alkylated with several electrophiles in good yield. Up to now, there have been various methods reported to efficiently synthesize carbamates via a coupling of primary or secondary amines, CO_2, and alkyl halides.[15]

Therefore, a possible mechanism of the CO_2 insertion reaction between AA-HSPs and secondary amines as outlined in Scheme 5 was proposed considering that a carbamate anion was likely formed. As stated above, chlorinated spirophosphorane intermediate **2** was produced first with stereoretention of the configuration at phosphorus under the classical Atherton–Todd conditions. Then a carbamate anion formed from a secondary amine as a nucleophilic reagent attacked at the phosphorus of intermediate **2** to yield the CO_2 insertion product **3**.

However, there remains a problem with tertiary amines. The product from CO_2 and a tertiary amine is mostly reported to be an alkylammonium hydrogen carbonate rather than the alkylammonium carbamate formed with a secondary amine.[16,14a] At the present stage, it is difficult to explain how a tertiary amine reacts with CO_2 and how an alkyl group is lost in the reaction. Thus, the mechanism of the CO_2 insertion

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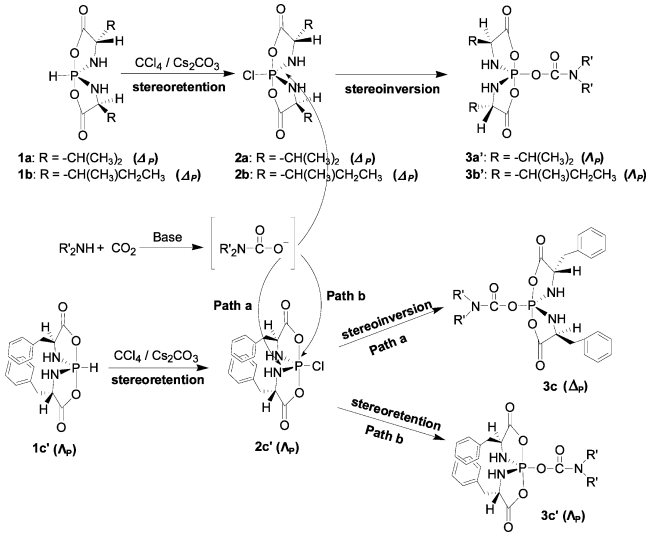
Scheme 5. Proposed Mechanism of the CO_2 Insertion Reaction between AA-HSPs and Secondary Amines



reaction between AA-HSPs and tertiary amines is still in question. The investigation of the mechanism related to a tertiary amine is under way in our group.

As shown in Scheme 5, the last step is a kind of nucleophilic substitution reaction at pentacoordinate phosphorus. The nucleophilic substitution reaction at carbon is ubiquitous in chemistry and has been well studied for a long time. Even for nucleophilic substitution at tetracoordinate phosphorus, its flexibility and stereochemistry have been the subject of systematic investigations. Most studies have concluded that substitution at tetracoordinate phosphorus occurs by inversion in most cases, and it is commonly depicted as a direct S_N2 displacment.[17] For example, Han's group has reported the reaction of H-phosphinates or secondary phosphine oxides with amines and alcohols proceeds highly stereospecifically with inversion of configuration at the phosphorus center under the Atherton–Todd reaction conditions.[17c,d] However, the nucleophilic substitution reaction at pentacoordinate phosphorus is more complicated than that at carbon or tetracoordinate phosphorus, especially for studying its stereochemistry. A definitive study of the stereochemical consequences of nucleophilic substitution at pentacoordinate phosphorus has been hindered by the lack of a suitable substrate. Now, AA-HSP appears as an ideal pentacoordinate phosphorane model to study its stereochemistry, so it is necessary to further investigate the stereochemistry of the CO_2 insertion reaction in detail.

Pentacoordinate phosphorus compounds always present a trigonal bipyramind structure with phosphorus as the central atom. There are two apical bonds that are collinear with the phosphorus atom and three equatorial bonds in a plane passing through the phosphorus atom and perpendicular to the direction of the apical bonds. Because of the existence of two spirocycles in a spirophosphorane molecule and because each spirocycle definitely occupies one apical bond and one equatorial bond, it is rational to assume that the attack of the nucleophile takes place within the equatorial plane. Therefore, nucleophiles are assumed to enter and leaving groups depart from the equatorial position through a hexacoordinate intermediate. Thus, the mechanism at pentacoordinate phosphorus is different from S_N2 displacement at carbon. It is conceivable that the nucleophilic substitution at phosphorus of spirophosphorane occurs by two separate mechanisms: rear attack of the leaving group and front attack of the leaving group, one for inversion and one for retention of the phosphorus configuration. Because the nucleophile tends to be in line with the leaving group and the leaving group can readily be eliminated from the hexacoordinate intermediate, rear attack is always presumed to be the electronically preferred route, although front attack on the equatorial leaving group is possible in some cases. Therefore, the nucleophilic substitution reaction at pentacoordinate phosphorus is normally considered to take place within the equatorial plane, with the nucleophile attacking one of the equatorial bonds from the rear side.[18]

As shown in Scheme 5, from the reactants **1a** and **1b** with Δ_P configuration that look like a resting butterfly, the wings of the two R substituted groups of the amino acid are opened, so there is hardly any steric hindrance at the rear side of the phosphorus of AA-HSPs. After the formation of the chlorinated spirophosphorane intermediate **2** with retention of the configuration at phosphorus, the carbamate anion formed under basic conditions attacked phosphorus from the rear direction of the P–Cl bond to form the CO_2 insertion product with inversion of the configuration at phosphorus. Thus, the AA-HSPs **1a** and **1b** with Δ_P configuration converted to the CO_2 insertion products with Λ_P configuration. However, the reactant **1c′** with Λ_P configuration looks like a resting moth, and its wings of two benzyl groups are closed to a certain degree. Accordingly, bigger steric hindrance exists at the rear side of the phosphorus of intermediate **2c′**. When the carbamate anion as the nucleophile attacked the phosphorus of **2c′** from the rear direction of teh P–Cl bond, two benzyl groups hindered the reaction to some extent. Consequently, the attack from the front direction of teh P–Cl bond happened simultaneously, and a pair of P-diastereoisomers of the CO_2 insertion product were produced. The isomer ratios were determined upon integration of the peaks in the ^{31}P NMR spectra of the isomer mixtures, and the results showed that the main product was still the isomer with inversion of the configuration at phosphorus in most cases (Table 2).

The results showed that the stereochemical outcome of the CO_2 insertion reaction mainly depended upon the steric hindrance at the rear side of the phosphorus of the reactants. The mechanism at pentacoordinate phosphorus was presumed to be a kind of S_N2 displacement. The nucleophilic substitution at the phosphorus of spirophosphorane preferred rear attack of the leaving group, and the product was mainly formed with stereoinversion of the phosphorus configuration. Retention of the configuration increased when the steric hindrance at the rear side of the phosphorus of AA-HSP increased obviously. We believe that our results, which correlate with those obtained previously from the reaction between AA-HSP and phenols,[5] strengthen our assumption that the nucleophilic substitution at pentacoordinate phosphorus mainly occurs with stereoinversion of the phosphorus configuration. The suggested mechanism is admittedly tentative but does explain our observations in the Atherton–Todd-type reaction.

■ CONCLUSIONS

In summary, we have investigated the Atherton–Todd-type reaction of AA-HSPs and amines. A novel CO_2 insertion reaction into the pentacoordinate P^V–N bond was developed without a transition-metal catalyst. A new type of spirophosphorane carbamate, **3**, was synthesized in moderate to good yields. Moreover, a preliminary mechanism and the stereo-

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chemistry of the CO_2 insertion reaction between AA-HSPs and secondary amines were proposed via a ^{31}P NMR tracing experiment, a carbon-13 labeling experiment, and X-ray diffraction analysis. The CO_2 insertion products were formed via the initial generation of chlorinated spirophosphorane intermediate **2** with stereoretention of the configuration at phosphorus, followed by the nucleophilic attack of a carbamate anion. It was found that rear attack of nucleophilic substitution with stereoinversion at phosphorus was the preferred route, although front attack happened for sterically hindered reactants. For the reactant with Δ_P configuration of AA-HSPs, the CO_2 insertion product was obtained with stereoinversion by the rear attack of phosphorus. However, for the reactant with Λ_P configuration, which had bigger steric hindrance at the rear side of phosphorus, rear attack and front attack happened simultaneously to produce a pair of P-diastereoisomers. The investigations of the CO_2 insertion reaction stepped forward in the stereochemistry research of pentacoordinate phosphorus compounds and might provide a new transition-metal-free methodology for the fixation of CO_2. Efforts are presently under way to enlarge the reaction scope and further elucidate the proposed mechanism of the CO_2 insertion reaction.

EXPERIMENTAL SECTION

General Information. All commercial reagents and solvents were used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard, and ^{31}P NMR spectra were obtained in $CDCl_3$ with H_3PO_4 as the internal standard. ESI-MS and ESI-MS/MS were acquired on an ion trap mass spectrometer, and ESI-HRMS was performed on a Q-TOF mass spectrometer. Column chromatography was carried out on columns of silica gel (200−300 mesh).

Preparation of Intermediates 2a, 2b, and 2c′. Compounds **1a**, **1b**, and **1c′** were prepared according to literature procedures.[4a] To a stirred solution of compound **1** (131 mg for **1a**, 146 mg for **1b**, and 179 mg for **1c′**, 0.5 mmol) in CH_3CN (3 mL) were added CCl_4 (1.0 mmol) and K_2CO_3 (208 mg, 1.5 mmol). The reaction mixture was stirred at room temperature until the ^{31}P NMR signal of reactant **1** disappeared. Then the mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography to give **2** as a white solid.

*Data for Compound **2a**.* ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −50.4 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.03 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.06 (d, 6H, J = 6.8 Hz, 2 × CH_3), 2.21−2.27 (m, 2H, 2 × CH), 3.82−3.88 (m, 2H, 2 × CH), 4.24 (d, 2H, $^2J_{HNP}$ = 18.0 Hz, 2 × NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.2, 19.1, 30.1 (d, $^3J_{CCNP}$ = 22.0 Hz), 60.4 (d, $^2J_{CNP}$ = 4.0 Hz), 168.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3366 (N−H), 2966 (C−H), 1760 (C═O), 1233 (br, P−O−CO), 1071, 906, 834 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 297; $[M + Na]^+$, 319.

*Data for Compound **2b**.* Mp: 203−205 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −50.8 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.94 (t, 6H, J = 8.0 Hz, 2 × CH_3), 1.06 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.34−1.45 (m, 2H, CH_2), 1.50−1.56 (m, 2H, CH_2), 1.93 (s, 2H, 2 × CH), 3.91 (dd, 2H, J = 2.8 Hz, $^3J_{HCNP}$ = 19.6 Hz, 2 × CH), 4.22 (d, 2H, $^2J_{HNP}$ = 18.0 Hz, 2 × NH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.7, 15.6, 24.6, 38.1 (d, $^3J_{CCNP}$ = 3.0 Hz), 59.9 (d, $^2J_{CNP}$ = 3.0 Hz), 168.4 (d, $^2J_{C(O)OP}$ = 11.0 Hz) ppm. FTIR (KBr): ν_{max} 3397 (N−H), 2967 (C−H), 2922 (C−H), 2851 (C−H), 1736 (C═O), 1518, 1464, 1256 (P−O−CO), 1045, 914 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 325.

*Data for Compound **2c′**.* Mp: 221−223 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −52.6 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.76−2.82 (dd, 2H, J = 8.4 Hz, J = 14.0 Hz, 2 × CH_2), 3.21−3.25 (dd, 2H, J = 6.0 Hz, J = 13.6 Hz, 2 × CH_2), 3.91 (d, 2H, $^2J_{HNP}$ = 16.8 Hz, 2 × NH), 4.14−4.19 (m, 2H, 2 × CH), 7.13 (d, J = 6.4 Hz, 4H, Ar−H), 7.33−7.40 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 38.8 (d, $^3J_{CCNP}$ = 8.0 Hz), 55.6 (d, $^2J_{CNP}$ = 5.0 Hz), 127.6, 129.0, 129.5, 135.4, 167.8 (d, $^2J_{C(O)OP}$ = 11.0 Hz) ppm. FTIR (KBr): ν_{max} 3279 (N−H), 2922 (C−H), 1758 (C═O), 1454, 1250 (P−O−CO), 1243, 1132, 900, 864, 756, 698 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 393.

Preparation of Carbonyl-^{13}C-Labeled 3a′1. Carbonyl-^{13}C-labeled compound **1a** was prepared from carbonyl-^{13}C-labeled L-valine according to the same procedures used to synthesize compound **1a**. To a stirred solution of carbonyl-^{13}C-labeled compound **1a** (132 mg, 0.5 mmol) in CH_3CN (3 mL) were added CCl_4 (1.0 mmol), Et_3N (1.0 mmol), and K_2CO_3 (208 mg, 1.5 mmol). The reaction mixture was stirred at room temperature until the ^{31}P NMR signal of intermediate **2a** disappeared. Then the mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/AcOEt, 3:1) and gave carbonyl-^{13}C-labeled compound **3a′1** (32 mg, 17%) as a white solid.

*Data for Carbonyl-^{13}C-Labeled Compound **3a′1**.* ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.00 (d, 6H, J = 7.2 Hz, 2 × CH_3), 1.10−1.15 (m, 6H, 2 × CH_3), 2.16−2.22 (m, 2H, 2 × CH), 3.16−3.35 (m, 4H, 2 × CH_2), 3.74 (dd, 2H, $^2J_{HNP}$ = 16.0 Hz, $^3J_{HNC^{13}C}$ = 10.0 Hz, 2 × NH), 3.92−3.94 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.0, 14.1, 16.5, 18.9 (d, $^3J_{CCC^{13}C}$ = 3.0 Hz), 30.7 (d, $^3J_{CCNP}$ = 8.0 Hz), 42.3, 42.5, 60.2 (dd, $^2J_{CNP}$ = 3.5 Hz, $^1J_{C^{13}C}$ = 52.0 Hz), 150.0 (d, $^2J_{NC(O)OP}$ = 4.0 Hz,), 169.6 (d, $^2J_{^{13}C(O)OP}$ = 13.0 Hz) ppm. ESI-MS: m/z $[M + H]^+$, 380; $[M + Na]^+$, 402.

Typical Experimental Procedure for the Preparation of 3. To a stirred solution of compound **1** (131 mg for **1a**, 146 mg for **1b**, and 179 mg for **1c′**, 0.5 mmol) in 3 mL of CH_3CN were successively added CCl_4 (1.0 mmol), amine (1.0 mmol), and Cs_2CO_3 (488 mg, 1.5 mmol) at room temperature in a CO_2 atmosphere. The reaction mixture was stirred at room temperature in a CO_2 atmosphere until the ^{31}P NMR signal of reactant **1** disappeared. Then the mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography to afford the product **3** as a white solid.

*Data for Compound **3a′1**.* Petroleum ether/AcOEt, 3:1. Yield: 124 mg, 66%. Mp 180−182 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −56.9 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.97 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.03 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.15 (t, 3H, J = 7.2 Hz, CH_3), 2.20−2.27 (m, 2H, 2 × CH), 3.17−3.37 (m, 4H, 2 × CH_2), 3.57 (d, 2H, $^2J_{HNP}$ = 15.8 Hz, 2 × NH), 3.96−3.99 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.0, 14.1, 16.5, 19.1, 30.6 (d, $^3J_{CCNP}$ = 7.2 Hz), 42.4, 42.5, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 150.0 (d, $^2J_{NC(O)OP}$ = 5.0 Hz,), 169.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3320 (N−H), 3295 (N−H), 2970 (C−H), 1748 (C═O), 1722 (O═C—N), 1268 (P−O−CO), 1152, 961, 835 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 378; $[M + Na]^+$, 400. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{15}H_{28}NaN_3O_6P$ 400.1613, found 400.1611.

*Data for Compound **3a′2**.* CH_2Cl_2/CH_3COCH_3, 90:1. Yield: 117 mg, 58%. Mp: 167−169 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.0 ppm. ^1H NMR (400 MHz,$CDCl_3$, TMS): δ 0.87 (t, 6H, J = 7.6 Hz, 2 × CH_3), 0.97 (d, 6H, J = 6.4 Hz, 2 × CH_3), 1.03 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.52−1.61 (m, 4H, 2 × CH_2), 2.18−2.26 (m, 2H, 2 × CH), 3.07−3.27 (m, 4H, 2 × CH_2), 3.57 (d, 2H, $^2J_{HNP}$ = 15.6 Hz, 2 × NH), 3.94−3.98 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 11.3, 16.5, 19.0, 20.9, 21.9, 30.6 (d, $^3J_{CCNP}$ = 7.0 Hz), 49.6, 49.8, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 150.4 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.4 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3313 (N−H), 2966 (C−H), 2934 (C−H), 2875 (C−H), 1765 (C═O), 1723 (O═C—N), 1464, 1422, 1269 (P−O−CO), 1238, 1153, 1061, 910, 836 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 406; $[M + Na]^+$, 428. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{17}H_{32}NaN_3O_6P$ 428.1926, found 428.1924.

*Data for Compound **3a′3**.* Petroleum ether/AcOEt, 3:1. Yield: 141 mg, 65%. Mp: 146−148 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.0 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.91 (t, 6H, J = 6.4 Hz, 2 × CH_3), 0.96 (d, 6H, J = 6.4 Hz, 2 × CH_3), 1.02 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.27−1.32 (m, 4H, 2 × CH_2), 1.50−1.54 (m, 4H, 2 × CH_2), 2.17−2.25 (m, 2H, 2 × CH), 3.13−3.29 (m, 4H, 2 × CH_2), 3.62 (d, 2H, $^2J_{HNP}$ = 15.6 Hz, 2 × NH), 3.93−3.96 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.2, 13.8, 16.5, 19.0,

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19.9, 20.0, 29.8, 30.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 30.8, 47.7, 47.8, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 150.3 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3370 (N−H), 3315 (N−H), 2962 (C−H), 2933 (C−H), 2874 (C−H), 1757 (C═O), 1702 (O═C—N), 1466, 1424, 1228 (P−O−CO), 1155, 1072, 905, 836 cm^{-1}. ESI-MS: m/z [M + H]$^+$, 434; [M + Na]$^+$, 456. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{19}H_{36}NaN_3O_6P$ 456.2239, found 456.2238.

Data for Compound ***3a′4***. CH_2Cl_2/CH_3COCH_3, 30:1. Yield: 93 mg, 46%. Mp: 184−186 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.2 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.01 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.19 (d, 12H, J = 6.4 Hz, 4 × CH_3), 2.14−2.19 (m, 2H, 2 × CH), 3.69−3.73 (m, 3H, CH, 2 × NH), 3.94−4.01 (m, 3H, 3 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.5, 19.0, 20.1, 21.6, 30.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 46.5, 47.2, 60.2 (d, $^2J_{CNP}$ = 3.0 Hz), 149.4 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.6 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3297 (N−H), 2966 (C−H), 2934 (C−H), 2875 (C−H), 1748 (C═O), 1703 (O═C—N), 1440, 1273 (P−O−CO), 1033, 908, 836 cm^{-1}. ESI-MS: m/z [M + H]$^+$, 406; [M + Na]$^+$, 428. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{17}H_{32}NaN_3O_6P$ 428.1926, found 428.1922.

Data for Compound ***3a′5***. Petroleum ether/AcOEt, 6:1. Yield: 152 mg, 70%. Mp: 173−175 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.1 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88−0.90 (m, 12H, 4 × CH_3), 0.96 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.02 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.86−2.23 (m, 2H, 2 × CH), 2.18−2.25 (m, 2H, 2 × CH), 2.95−3.15 (m, 4H, 2 × CH_2), 3.60 (d, 2H, $^2J_{HNP}$ = 16.0 Hz, 2 × NH), 3.93−3.96 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.5, 19.0, 19.9, 20.0, 26.7, 27.7, 30.6 (d, $^3J_{CCNP}$ = 7.0 Hz), 55.4, 55.9, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 150.8 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3302 (N−H), 2962 (C−H), 2933 (C−H), 2874 (C−H), 1750 (C═O), 1721 (O═C—N), 1466, 1420, 1252 (br, P−O−CO),1156, 1065, 908, 837 cm^{-1}. ESI-MS: m/z [M + H]$^+$, 434; [M + Na]$^+$, 456. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{19}H_{36}NaN_3O_6P$ 456.2239, found 456.2236.

Data for Compound ***3a′6***. Petroleum ether/AcOEt, 3:1. Yield: 169 mg, 69%. Mp: 113−114 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −56.8 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (d, 3H, J = 6.4 Hz, CH_3), 0.90 (d, 3H, J = 6.4 Hz, CH_3), 0.96 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.01 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.27 (s, 12H, 6 × CH_2), 1.52 (s, 4H, 2 × CH_2), 2.20−2.23 (m, 2H, 2 × CH), 3.06−3.29 (m, 4H, 2 × CH_2), 3.57 (d, 2H, $^2J_{HNP}$ = 14.6 Hz, 2 × NH), 3.93−3.95 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.0, 16.5, 19.0, 22.5, 22.6, 26.4, 27.7, 28.6, 30.6 (d, $^3J_{CCNP}$ = 8.0 Hz), 31.4, 31.5, 48.0, 48.1, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 150.2 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.3 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3303 (N−H), 2961 (C−H), 2928 (C−H), 2858 (C−H), 1750 (C═O), 1728 (O═C—N), 1466, 1421, 1270 (P−O−CO), 1196, 1064, 999, 907, 637 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{23}H_{44}NaN_3O_6P$ 512.2860, found 512.2861.

Data for Compound ***3a′7***. Petroleum ether/AcOEt, 3:1. Yield: 170 mg, 68%. Mp: 133−136 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.2 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.94 (d, 6H, J = 6.8 Hz, 2 × CH_3), 0.98 (d, 6H, J = 6.8 Hz, 2 × CH_3), 2.17−2.21 (m, 2H, 2 × CH), 3.53 (d, 2H, $^2J_{HNP}$ = 14.8 Hz, 2 × NH), 3.84−3.87 (m. 2H, 2 × CH), 4.29−4.60 (m, 4H, 2 × CH_2), 7.18−7.20 (d, 2H, Ar−H), 7.24−7.37 (m, 8H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.4, 19.1, 30.6 (d, $^3J_{CCNP}$ = 5.0 Hz), 50.3, 50.4, 60.2 (d, $^2J_{CNP}$ = 3.0 Hz),127.1, 127.2, 127.7, 127.9, 128.1, 128.3, 128.5, 128.8, 136.1, 136.6, 151.1 (d, $^2J_{NC(O)OP}$ = 4.0 Hz), 169.3 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3322 (N−H), 2962 (C−H), 2929 (C−H), 2874 (C−H), 1759 (C═O), 1724 (O═C—N), 1455 (Ar), 1410, 1266 (br, P−O−CO), 1215, 1059, 897, 839 cm^{-1}. ESI-MS: m/z [M + H]$^+$, 501; [M + Na]$^+$, 524. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{25}H_{32}NaN_3O_6P$ 524.1921, found 524.1927.

Data for Compound ***3a′8***. Petroleum ether/AcOEt, 3:1. Yield: 116 mg, 48%. Mp: 251 °C, sublimation. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.4 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 0.98 (t, 6H, J = 6.8 Hz, 2 × CH_3), 1.03 (t, 6H, J = 6.8 Hz, 2 × CH_3), 1.20−1.40 (m, 5H, CH_2), 1.57−1.75 (m, 10H, CH_2), 1.75−1.88 (m, 5H, CH_2), 2.22−2.25 (m, 2H, 2 × CH), 3.18 (br, 1H, N−CH), 3.60 (d, 2H, $^2J_{HNP}$ = 15.6 Hz, 2 × NH), 3.67 (br, 1H, N−CH), 3.95−3.98 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.5, 19.1, 24.8, 24.9, 25.3, 25.9, 26.3, 29.3, 30.2, 30.3, 30.6 (d, $^3J_{CCNP}$ = 8.0 Hz), 31.8, 31.9, 53.7, 56.0, 56.3, 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 149.7, 169.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3312 (N−H), 2962 (C−H), 2932 (C−H), 2855 (C−H), 1755 (C═O), 1708 (O═C—N), 1452, 1439, 1238 (br, P−O−CO), 1183, 1072, 999, 911, 837 cm^{-1}. ESI-MS: m/z [M + H]$^+$, 485; [M + Na]$^+$, 508. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{23}H_{40}NaN_3O_6P$ 508.2547, found 508.2555.

Data for Compound ***3a′9***. CH_2Cl_2/CH_3COCH_3, 30:1. Yield: 174 mg, 77%. Mp: 188−190 °C. Appeared as two cis−trans isomers. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.7/-57.0 (2.4:1) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87/1.17 (d, 6H, J = 6.8 Hz, 2 × CH_3), 0.92/1.19 (d, 6H, J = 7.2 Hz, 2 × CH_3), 0.98/1.11 (d, 3H, J = 6.8 Hz, CH_3), 1.03/1.12 (d, 3H, J = 7.2 Hz, CH_3), 2.11−2.15/2.18−2.25 (m, 2H, 2 × CH), 3.29/3.71 (d, 2H, $^2J_{HNP}$ = 15.2 Hz, 2 × NH), 3.62−3.64/3.99−4.03 (m, 2H, 2 × CH), 4.35−4.45/4.26−4.31 (m, 2H, CH_2), 7.24−7.30/7.31−7.37 (m, 5H, 5 × Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.2, 16.5, 19.0, 20.2, 30.4 (d, $^3J_{CCNP}$ = 7.0 Hz), 46.8/47.8, 48.8/49.6, 60.0/60.3 (d, $^2J_{CNP}$ = 4.0 Hz), 126.3, 127.1, 128.6, 139.0/138.0, 150.4/151.2 (d, $^2J_{NC(O)OP}$ = 5.0 Hz,), 169.4/169.5 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3300 (N−H), 2967 (C−H), 2934 (C−H), 2876 (C−H), 1749 (C═O), 1722 (O═C—N), 1497 (Ar), 1455 (Ar), 1432, 1371, 1266 (P−O−CO), 1207, 1049, 910, 836 cm^{-1} . HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{21}H_{32}NaN_3O_6P$ 476.1921, found 476.1921.

Data for Compound ***3a′10***. CH_2Cl_2/CH_3COCH_3, 30:1. Yield: 146 mg, 69%. Mp: 190−191 °C. Appeared as two cis−trans isomers. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.3 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.94−1.04 (m, 12H, 4 × CH_3), 2.18−2.22 (m, 2H, 2 × CH), 2.85/2.91 (s, 3H, CH_3), 3.68/3.79 (d, 2H, $^2J_{HNP}$ = 16.0 Hz, 2 × NH), 3.88/4.00 (dd, 2H, J = 2.0 Hz, J = 0.4 Hz, 2 × CH), 4.36−4.52 (m, 2H, CH_2), 7.23−7.39 (m, 5H, 5 × Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.5, 19.0, 30.5/30.6 (d, $^3J_{CCNP}$ = 7.0 Hz), 34.5/34.9, 52.6/53.5, 60.2/60.3 (d, $^2J_{CNP}$ = 3.0 Hz), 127.2, 127.7/127.8, 128.8/128.9, 136.1/136.5, 150.6/151.2 (d, $^2J_{NC(O)OP}$ = 5.0 Hz,), 169.5/169.6 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3297 (N−H), 2967 (C−H), 2934 (C−H), 2876 (C−H), 1749 (C═O), 1722 (O═C—N), 1498 (Ar), 1469 (Ar), 1455, 1413, 1391, 1266 (P−O−CO), 1207, 1049, 911, 836 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{19}H_{28}NaN_3O_6P$ 448.1608, found 448.1615.

Data for Compound ***3a′11***. Petroleum ether/AcOEt, 2:1. Yield: 113 mg, 60%. Mp: 168−170 °C. Appeared as two cis−trans isomers. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −56.7/-56.9 (1:1) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.90 (t, 3H, J = 7.2 Hz, CH_3), 0.96 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.02 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.52−1.61 (m, 2H, CH_2), 2.12−2.27 (m, 2H, 2 × CH), 2.89 (s, 3H, CH_3), 3.13−3.30 (m, 2H, CH_2), 3.63 (d, 2H, $^2J_{HNP}$ = 15.2 Hz, 2 × NH), 3.64−3.97 (m, 2H, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.0/11.1, 16.6, 18.9, 20.3/21.1, 30.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 34.7/34.9, 50.9/51.4, 60.2 (d, $^2J_{CNP}$ = 3.0 Hz), 150.5, 169.6 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3290 (N−H), 2966 (C−H), 2934 (C−H), 2876 (C−H), 1750 (C═O), 1720 (O═C—N), 1462, 1434, 1405, 1273 (P−O−CO), 1228, 1074, 910, 837 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{15}H_{28}NaN_3O_6P$ 400.1608, found 400.1611.

Data for Compound ***3b′1***. CH_2Cl_2/CH_3COCH_3, 60:1. Yield: 137 mg, 68%. Mp: 156−158 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.3 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.93 (t, 6H, J = 7.2 Hz, 2 × CH_3), 1.01 (d, 6H, J = 7.2 Hz, 2 × CH_3), 1.13 (d, 3H, J = 7.2 Hz, CH_3), 1.14 (d, 3H, J = 7.2 Hz, CH_3), 1.26−1.39 (m, 2H, CH_2), 1.42−1.52 (m, 2H, CH_2), 1.88−1.89 (m, 2H, 2 × CH), 3.15−3.37 (m, 4H, 2 × CH_2), 3.61 (d, 2H, $^2J_{HNP}$ = 12.0 Hz, 2 × NH), 3.99 (dd. 2H, J = 8.0, 2.0 Hz, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS):δ11.8, 13.0, 14.1, 15.7, 24.4, 37.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 42.3, 42.5, 59.8 (d, $^2J_{CNP}$ = 4.0 Hz), 150.0 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.5 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3311 (N−H), 3249 (N−H), 2965 (C−H), 2935 (C−H), 2877 (C−H), 1755 (C═O), 1722 (O═C—N), 1462, 1424, 1266 (P−O−CO), 1230, 1155, 961, 837

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cm^{-1}. ESI-MS: m/z $[M + H]^+$, 406; $[M + Na]^+$, 428. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{17}H_{32}NaN_3O_6P$ 428.1926, found 428.1923.

Data for Compound ***3b′2***. CH_2Cl_2/CH_3COCH_3, 80:1. Yield: 158 mg, 73%. Mp: 120−122 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.4 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (t, 6H, J = 7.6 Hz, 2 × CH_3), 0.94 (t, 6H, J = 7.6 Hz, 2 × CH_3), 1.01 (d, 6H, J = 6.8 Hz, 2 × CH_3), 1.30−1.37 (m, 2H, CH_2), 1.42−1.50 (m, 2H, CH_2), 1.52−1.62 (m, 4H, 2 × CH_2), 1.86−1.94 (m, 2H, 2 × CH), 3.10−3.28 (m, 4H, 2 × CH_2), 3.64 (d, 2H, $^2J_{HNP}$ = 15.6 Hz, 2 × NH), 3.99 (d. 2H, J = 6.0 Hz, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 11.4, 11.8, 15.7, 20.9, 21.9, 24.4, 37.7 (d, $^3J_{CCNP}$ = 8.0 Hz), 49.6, 49.8, 59.8 (d, $^2J_{CNP}$ = 4.0 Hz), 150.4 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.5 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3303 (N−H), 2965 (C−H), 2935 (C−H), 2876 (C−H), 1743 (C═O), 1725 (O═C—N), 1465, 1422, 1258 (br, P−O−CO), 1154, 1066, 1026, 917, 838 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 434; $[M + Na]^+$, 456. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{19}H_{36}NaN_3O_6P$ 456.2239, found 456.2237.

Data for Compound ***3b′3***. CH_2Cl_2/CH_3COCH_3, 100:1. Yield: 136 mg, 59%. Mp: 111−113 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.5 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.90−0.96 (m, 12H, 4 × CH_3), 1.01 (d, 6H, J = 7.2 Hz, 2 × CH_3), 1.26−1.39 (m, 6H, 3 × CH_2), 1.42−1.56 (m, 6H, 3 × CH_2), 1.88−1.91 (m, 2H, 2 × CH), 3.09−3.31 (m, 4H, 2 × CH_2), 3.61 (d, 2H, $^2J_{HNP}$ = 16.0 Hz, 2 × NH), 3.98 (dd. 2H, J = 6.0, 2.0 Hz, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.8, 13.79, 13.84, 15.7, 19.9, 20.0, 24.4, 29.8, 30.7, 37.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 47.66, 47.72, 59.8 (d, $^2J_{CNP}$ = 3.0 Hz), 150.3 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.5 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3380 (N−H), 3321 (N−H), 2962 (C−H), 2932 (C−H), 2875 (C−H), 1756 (C═O), 1702 (O═C—N), 1464, 1425, 1228 (br, P−O−CO), 1150, 1045, 896, 834 cm^{-1}. ESI-MS: m/z $[M + H]^+$, 462; $[M + Na]^+$, 484. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{21}H_{40}NaN_3O_6P$ 484.2552, found 484.2550.

Data for Compound ***3b′4***. CH_2Cl_2/CH_3COCH_3, 50:1. Yield: 133 mg, 58%. Mp: 163−165 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.5 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88−0.95 (m, 18H, 6 × CH_3), 1.01−1.06 (m, 6H, 2 × CH_3), 1.27−1.49 (m, 4H, 2 × CH_2), 1.89−1.99 (m, 4H, 2 × CH_2), 2.96−3.14 (m, 4H, 4 × CH), 3.65 (d, 2H, $^2J_{HNP}$ = 15.6 Hz, 2 × NH), 3.97 (dd, 2H, J = 2.0 Hz, J = 0.4 Hz, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.8, 15.6, 19.9, 20.2, 24.4, 26.7, 27.7, 37.7 (d, $^3J_{CCNP}$ = 7.0 Hz), 55.4, 55.9, 59.8 (d, $^2J_{CNP}$ = 3.0 Hz), 150.8 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.4 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3280 (N−H), 2961 (C−H), 2935 (C−H), 2875 (C−H), 1751 (C═O), 1729 (O═C—N), 1470, 1422, 1269 (P−O−CO), 1247 (br, P−O−CO), 1158, 1062, 914, 839 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{21}H_{40}NaN_3O_6P$ 484.2547, found 484.2545.

Data for Compound ***3b′5***. Petroleum ether/AcOEt, 3:1. Yield: 166 mg, 63%. Mp: 134−135 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −57.6 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (t, 6H, J = 7.2 Hz, 2 × CH_3), 0.97 (d, 6H, J = 7.2 Hz, 2 × CH_3), 1.29−1.34 (m, 2H, CH_2), 1.42−1.46 (m, 2H, CH_2), 1.80−1.90 (m, 2H, 2 × CH), 3.52 (d, 2H, $^2J_{HNP}$ = 16.0 Hz, 2 × NH), 3.88 (dd, 2H, J = 2.0 Hz, J = 0.6 Hz, 2 × CH), 4.26−4.59 (m, 4H, 2 × CH_2), 7.18−7.26 (m, 4H, Ar−H), 7.28−7.31 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.8, 15.7, 24.4, 37.6 (d, $^3J_{CCNP}$ = 7.0 Hz), 50.3, 50.4, 59.7 (d, $^2J_{CNP}$ = 3.0 Hz), 127.2, 127.7, 127.9, 128.1, 128.8, 136.1, 136.6, 151.1 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.3 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3331 (N−H), 3260 (N−H), 2963 (C−H), 2934 (C−H), 2877 (C−H), 1752 (C═O), 1721 (O═C—N), 1496 (Ar), 1464 (Ar), 1420, 1266 (br, P−O−CO), 1090, 1063, 1026, 891, 839 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{27}H_{36}NaN_3O_6P$ 552.2234, found 552.2238.

Data for Compound ***3c′1***. CH_2Cl_2/CH_3COCH_3, 30:1. Mp: 190−191 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −58.8 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08−1.13 (m, 6H, 2 × CH_3), 2.76 (dd, 2H, J = 8.4 Hz, J = 13.6 Hz, 2 × CH), 3.16−3.30 (m, 6H, 2 × CH_2, 2 × CH), 3.65 (d, 2H, $^2J_{HNP}$ = 17.2 Hz, 2 × NH), 4.18−4.22 (m, 2H, 2 × CH), 7.13 (d, 4H, J = 7.2 Hz, Ar−H), 7.31−7.37 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.0, 14.1, 39.0 (d, $^3J_{CCNP}$ = 7.0 Hz), 42.3, 42.5, 56.2 (d, $^2J_{CNP}$ = 5.0 Hz), 127.4, 128.8, 129.6, 136.1, 149.8 (d, $^2J_{NC(O)OP}$ = 4.0 Hz), 169.4 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3288 (N−H), 2974 (C−H), 2929 (C−H), 1750 (C═O), 1717 (O═C—N), 1604 (Ar), 1497 (Ar), 1455 (Ar), 1425, 1262 (P−O−CO), 1152, 1053, 968, 875, 860 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{23}H_{28}NaN_3O_6P$ 496.1608, found 496.1611.

Data for Compound ***3c1***. CH_2Cl_2/CH_3COCH_3, 30:1. Mp: 152−154 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −60.0 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18−1.26 (m, 6H, 2 × CH_3), 2.98 (dd, 2H, J = 10.8 Hz, J = 13.2 Hz, 2 × CH), 3.22−3.39 (m, 6H, 2 × CH_2, 2 × CH), 3.59 (d, 2H, $^2J_{HNP}$ = 18.0 Hz, 2 × NH), 3.98−4.06 (m, 2H, 2 × CH), 7.22−7.29 (m, 6H, Ar−H), 7.33−7.36 (m, 4H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.1, 14.3, 39.1 (d, $^3J_{CCNP}$ = 3.0 Hz), 42.4, 42.6, 56.5 (d, $^2J_{CNP}$ = 6.0 Hz), 127.3, 129.0, 129.2, 136.8, 149.1 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.0 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3368 (N−H), 2927 (C−H), 2853 (C−H), 1753 (C═O), 1717 (O═C—N), 1604 (Ar), 1497 (Ar), 1456 (Ar), 1425, 1249 (P−O−CO), 1151, 1055, 968, 892 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{23}H_{28}NaN_3O_6P$ 496.1608, found 496.1612.

Data for Compound ***3c′2***. Petroleum ether/AcOEt, 3:1. Mp: 170−171 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −59.0 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.83−0.89 (m, 6H, 2 × CH_3), 1.49−1.57 (m, 4H, 2 × CH_2), 2.75 (dd, 2H, J = 8.4 Hz, J = 13.6 Hz, 2 × CH), 3.06−3.21 (m, 6H, 2 × CH_2, 1 × CH), 3.52 (d, 2H, $^2J_{HNP}$ = 16.8 Hz, 2 × NH), 4.17−4.22 (m, 2H, 2 × CH), 7.12 (d, 4H, J = 6.8 Hz, Ar−H), 7.30−7.38 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.1, 11.3, 20.9, 21.9, 39.1 (d, $^3J_{CCNP}$ = 7.0 Hz), 49.5, 49.7, 56.1 (d, $^2J_{CNP}$ = 5.0 Hz), 127.4, 128.9, 129.5, 136.1, 150.2 (d, $^2J_{NC(O)OP}$ = 4.0 Hz), 169.2 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3396 (N−H), 3028 (N−H), 2962 (C−H), 2926 (C−H), 2874 (C−H), 2854 (C−H), 1755 (C═O), 1720 (O═C—N), 1603 (Ar), 1496 (Ar), 1454 (Ar), 1422, 1259 (P−O−CO), 1146, 1066, 1023, 916, 854, 702 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{25}H_{32}NaN_3O_6P$ 524.1921, found 524.1924.

Data for Compound ***3c2***. Petroleum ether/AcOEt, 3:1. Mp: 127−130 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −60.0 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95−1.00 (m, 6H, 2 × CH_3), 1.61−1.75 (m, 4H, 2 × CH_2), 2.97 (dd, 2H, J = 11.2 Hz, J = 13.6 Hz, 2 × CH), 3.17−3.37 (m, 6H, 2 × CH_2, 1 × CH), 3.56 (d, 2H, $^2J_{HNP}$ = 18.0 Hz, 2 × NH), 3.99−4.06 (m, 2H, 2 × CH), 7.24−7.28 (d, 4H, Ar−H), 7.30−7.39 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.2, 11.4, 21.0, 22.1, 39.1 (d, $^3J_{CCNP}$ = 3.0 Hz), 49.7, 50.0, 56.5 (d, $^2J_{CNP}$ = 6.0 Hz), 127.4, 129.0, 129.2, 136.9, 149.5 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.0 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3310 (N−H), 3029 (N−H), 2963 (C−H), 2929 (C−H), 2856 (C−H), 1752 (C═O), 1724 (O═C—N), 1712 (O═C—N), 1604 (Ar), 1496 (Ar), 1456 (Ar), 1423, 1307, 1259 (P−O−CO), 1146, 1017, 885 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{25}H_{32}NaN_3O_6P$ 524.1921, found 524.1921.

Data for Compound ***3c′3***. Petroleum ether/AcOEt, 2:1. Mp: 163−164 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −59.0 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.89−0.93 (m, 6H, 2 × CH_3), 1.22−1.31 (m, 4H, 2 × CH_2), 1.45−1.51 (m, 4H, 2 × CH_2), 2.76 (dd, 2H, J = 8.4 Hz, J = 13.6 Hz, 2 × CH), 3.08−3.22 (m, 6H, 2 × CH_2, 1 × CH), 3.55 (d, 2H, $^2J_{HNP}$ = 17.2 Hz, 2 × NH), 4.17−4.21 (m, 2H, 2 × CH), 7.12−7.14 (d, 4H, Ar−H), 7.31−7.38 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 13.7, 13.8, 19.8, 19.9, 29.7, 30.7, 39.1 (d, $^3J_{CCNP}$ = 8.0 Hz), 47.6, 47.7, 56.1 (d, $^2J_{CNP}$ = 6.0 Hz), 127.4, 128.9, 129.5, 136.1, 150.1 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.2 (d, $^2J_{C(O)OP}$ = 13.0 Hz) ppm. FTIR (KBr): ν_{max} 3320 (N−H), 3029 (N−H), 2959 (C−H), 2931 (C−H), 2873 (C−H), 1756 (C═O), 1721 (O═C—N), 1604 (Ar), 1496 (Ar), 1454 (Ar), 1421, 1261 (P−O−CO), 1147, 1049, 859, 701 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$, calcd for $C_{27}H_{36}NaN_3O_6P$ 552.2234, found 552.2236.

Data for Compound ***3c3***. Petroleum ether/AcOEt, 2:1. Mp: 109−111 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −59.9 ppm. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.97−1.01 (m, 6H, 2 × CH_3), 1.31−1.43 (m, 4H, 2 × CH_2), 1.59−1.67 (m, 4H, 2 × CH_2), 2.97 (dd,

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2H, J = 11.6 Hz, J = 13.6 Hz, 2 × CH), 3.23−3.37 (m, 6H, 2 × CH_2, 1 × CH), 3.57 (d, 2H, $^2J_{HNP}$ = 18.0 Hz, 2 × NH), 3.98−4.06 (m, 2H, 2 × CH), 7.24−7.28 (d, 4H, Ar−H), 7.29−7.39 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.1, 19.0, 20.3, 29.4, 31.0, 39.1 (d, $^3J_{CCNP}$ = 3.0 Hz), 47.7, 48.0, 56.5 (d, $^2J_{CNP}$ = 6.0 Hz), 127.4, 128.8, 129.0, 136.9, 149.4 (d, $^2J_{NC(O)OP}$ = 6.0 Hz), 169.0 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3361 (N−H), 3302 (N−H), 3030 (N−H), 2958 (C−H), 2921 (C−H), 2851 (C−H), 1771 (C═O), 1702 (O═C—N), 1604 (Ar), 1497 (Ar), 1455 (Ar), 1425, 1252 (P−O−CO), 1157, 1080, 868, 749, 700 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{27}H_{36}NaN_3O_6P$ 552.2234, found 552.2238.

Data for Compound ***3c′4***. Petroleum ether/AcOEt, 3:1. Mp: 162−164 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −59.2 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.84 (t, 12H, J = 6.8 Hz, 4 × CH_3), 1.81−1.96 (m, 2H, 2 × CH), 2.73 (dd, 2H, J = 14.0 Hz, J = 12.4 Hz, 2 × CH), 2.89−3.08 (m, 4H, 2 × CH_2), 3.16 (dd, 4H, J = 13.6 Hz, J = 7.2 Hz, 2 × CH), 3.53 (d, 2H, $^2J_{HNP}$ = 16.8 Hz, 2 × NH), 4.15−4.20 (m, 2H, 2 × CH), 7.09−7.11 (d, 4H, Ar−H), 7.26−7.35 (m, 6H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.87, 19.94, 20.17, 20.19, 26.7, 27.6, 39.1 (d, $^3J_{CCNP}$ = 8.0 Hz), 55.4, 55.8, 56.1 (d, $^2J_{CNP}$ = 6.0 Hz), 127.4, 128.9, 129.5, 136.1, 150.6 (d, $^2J_{NC(O)OP}$ = 5.0 Hz), 169.2 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3324 (N−H), 3029 (N−H), 2958 (C−H), 2922 (C−H), 2851 (C−H), 1750 (C═O), 1721 (O═C—N), 1604 (Ar), 1496 (Ar), 1455 (Ar), 1421, 1260 (P−O−CO), 1152, 1061, 950, 859, 701 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{27}H_{36}NaN_3O_6P$ 552.2234, found 552.2236.

Data for Compound ***3c′5***. CH_2Cl_2/CH_3COCH_3, 50:1. Mp: 170−172 °C. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −59.2 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.70 (dd, 2H, J = 8.4 Hz, J = 13.6 Hz, 2 × CH), 3.13 (dd, 2H, J = 3.2 Hz, J = 13.2 Hz, 2 × CH), 3.42 (d, 2H, $^2J_{HNP}$ = 16.8 Hz, 2 × NH), 4.05−4.10 (dt, 2H, J = 3.6 Hz, J = 7.6 Hz, 2 × CH), 4.23 (d, 1H, J = 16.0 Hz, CH), 4.31−4.36 (m, 2H, 2 × CH), 4.50 (d, 1H, J = 15.2 Hz, CH), 7.07−7.29 (m, 20H, Ar−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 39.0 (d, $^3J_{CCNP}$ = 7.0 Hz), 50.4 (d, $^4J_{CCNP}$ = 2.0 Hz), 56.1 (d, $^2J_{CNP}$ = 5.0 Hz), 127.1, 127.4, 127.7, 127.9, 128.1, 128.7, 128.8, 128.9, 129.5, 136.0, 136.5, 150.5 (d, $^2J_{NC(O)OP}$ = 4.0 Hz), 169.0 (d, $^2J_{C(O)OP}$ = 12.0 Hz) ppm. FTIR (KBr): ν_{max} 3323 (N−H), 3062 (N−H), 3029 (N−H), 2926 (C−H), 1759 (C═O), 1716 (O═C—N), 1603 (Ar), 1496 (Ar), 1454 (Ar), 1419, 1259 (br, P−O−CO), 1089, 1062, 960, 860, 700 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{33}H_{32}NaN_3O_6P$ 620.1921, found 620.1924.

Preparation of Pyrospirophosphoranes 4. To a stirred solution of compound **1** (131 mg for **1a** and 146 mg for **1b**, 0.5 mmol) in 3 mL of CH_3CN were successively added CCl_4 (1.0 mmol), Et_3N (1.0 mmol), and K_2CO_3 (208 mg, 1.5 mmol). The reaction mixture was stirred at room temperature for several hours until the ^{31}P NMR signal of intermediate **2** disappeared. Then the mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography to give **4** as a white solid.

Data for Compound ***4a***. Petroleum ether/AcOEt, 3:1. Mp: 272 °C, sublimation. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −62.0 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95 (d, 12H, J = 6.8 Hz, 4 × CH_3), 1.02 (d, 12H, J = 6.8 Hz, 4 × CH_3), 2.19−2.22 (m, 4H, 4 × CH), 3.69−3.73 (m, 4H, 4 × NH), 3.91 (m, 4H, 4 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.2, 19.1, 30.2 (d, $^3J_{CCNP}$ = 3.0 Hz), 60.2 (d, $^2J_{CNP}$ = 4.0 Hz), 168.5 (d, $^2J_{C(O)OP}$ = 11.0 Hz) ppm. FTIR (KBr): ν_{max} 3404 (N−H), 3287 (N−H), 2966 (C−H), 2935 (C−H), 2877 (C−H), 1749 (C═O), 1465, 1465, 1247 (br, P−O−CO), 1002 (P−O−P), 909, 839 cm^{-1}. ESI-MS: m/z [M + Na]$^+$, 561. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{20}H_{36}NaN_4O_9P_2$ 561.1856, found 561.1858.

Data for Compound ***4b***. Petroleum ether/AcOEt, 3:1. Mp: 228 °C, sublimation. ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4): δ −62.2 ppm. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (t, 12H, J = 7.2 Hz, 4 × CH_3), 0.99 (d, 12H, J = 6.4 Hz, 4 × CH_3), 1.26−1.37 (m, 4H, 2 × CH_2), 1.39−1.47 (m, 4H, 2 × CH_2), 1.84−1.90 (m, 4H, 4 × CH), 3.82−3.86 (m, 4H, 4 × NH), 3.92 (d, 4H, J = 3.2 Hz, 2 × CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 11.8, 15.5, 24.5, 37.7 (d, $^3J_{CCNP}$ = 4.0 Hz), 59.3, 168.9 (d, $^2J_{C(O)OP}$ = 6.0 Hz) ppm. FTIR (KBr): ν_{max} 3262 (N−H), 2964 (C−H), 2936 (C−H), 2877 (C−H), 1745 (C═O), 1463, 1274 (br, P−O−CO), 1020 (P−O−P), 957, 838 cm^{-1}. ESI-MS: m/z [M + Na]$^+$, 617. HRMS (ESI): m/z [M + Na]$^+$, calcd for $C_{24}H_{44}NaN_4O_9P_2$ 617.2481, found 617.2478.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectra from the ^{31}P NMR tracing experiment, spectra from the temperature-dependent NMR dynamic experiment of compounds **3a′1** and **3a′9**, NMR and IR spectra for all new compounds, and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for structures **2a**, **2c′**, **3a′3**, **3a′9**, **3c′1**, and **3c1** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC 893144 (**2a**), CCDC 949556 (**2c′**), CCDC 937366 (**3a′3**), CCDC 951765 (**3a′9**), CCDC 949558 (**3c′1**), and CCDC 949557 (**3c1**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax +44 (0) 1223 336033 or e-mail deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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