An Unexpected Carbon Dioxide Insertion in the Reaction of Trans-2,4-Disubstituted Azetidine, Trans-2,5-Disubstituted Pyrrolidine, or Trans-2,6-Disubstituted Piperidine with Diphenylthiophosphinic Chloride and Diphenylselenophosphinic Chloride

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In the reaction of trans-2,4-disubstituted azetidine, trans-2,5-disubstituted pyrrolidine, or trans-2,6-disubstituted piperidine with diphenylthiophosphinic chloride or diphenylselenophosphinic chloride in acetonitrile in the presence of potassium carbonate at room temperature, an unexpected carbon dioxide insertion produced carbamic diphenylthiophosphinic or diphenylselenophosphinic anhydride in good yield. The same product could be also obtained when the reaction was carried out under carbon dioxide atmosphere using potassium hydroxide or triethylamine as a base. This is a very simple reaction process related to the fixation of carbon dioxide without a metal catalyst.

Introduction

Carbon dioxide, the earth's most abundant carbon resource, is remarkably little used as a chemical feedstock.[1] As the output of CO_2 from combustion into the environment continues to rise, threatening a global environmental crisis, the search for practical methods for regenerating organic compounds from CO_2 has assumed increased importance. The most active approach being examined toward this objective is the activation of carbon dioxide by transition-metal complexes.[2] However, recently another approach without using any metal catalyst for the fixation of CO_2 has attracted much attention. For example, the preparation of dialkyl carbonates from CO_2 and alcohols or alkoxides followed by alkylating agents[3] and the preparation of carbamate esters from the reaction of primary, secondary, and aromatic amines, CO_2, and a variety of electrophiles[4] have been reported. In the course of the syntheses of novel chiral C_2-symmetric chiral ligands, we incidentally found that in the reaction of trans-2,5-disubstituted pyrrolidine or trans-2,4-disubstituted azetidine with diphenylthiophosphinic chloride or diphenylselenophosphinic chloride in acetonitrile in the presence of potassium carbonate at room temperature, a carbon dioxide inserted carbamic diphenylthiophosphinic or diphenylselenophosphinic anhydride was obtained in good yield. In this paper, we wish to report the full details and the scope and limitation of this interesting CO_2 insertion reaction.

Results and Discussion

In our previous paper, we reported that the diphenylphosphoramide and the diphenylthiophosphoramide of (*R*,*R*)-(−)-1,2-diaminocyclohexane are very effective chiral ligands for titanium(IV) alkoxide-promoted addition reaction of diethylzinc to aldehydes.[5] This interesting result promoted us to synthesize chiral C_2-symmetric 2,5-disubstituted pyrrolidine derivatives **2** having a diphenylphosphinyl group or a diphenylthiophosphinyl group because we expect that these kinds of compounds can be used as chiral ligands for asymmetric reactions as well.[6] The starting materials **1a**−**c** were readily prepared according to the literature.[7] The preparation of **2** was first carried out from the reaction **1a**−**c** with diphenylphosphinic chloride and diphenylthiophosphinic chloride in acetonitrile in the presence of potassium carbonate or sodium carbonate at room temperature (Scheme 1). But surprisingly, we found that no reaction took place between **1a**−**c** and diphenylphosphinic chloride. Furthermore, in the reaction of **1a**−**c** with diphenylthiophosphinic chloride, the compounds **3a**−**c**, carbon dioxide inserted products were obtained in 60%, 40%, and 32% yields, respectively, with 20% of compound **4** rather than compound **2** being isolated. The structures of **3a**−**c** were established by spectral data and microanalysis.

In the ^{13}C NMR spectrum of **3a**, a doublet at 148.92 ppm (d, J_{C-O-P} 5.5 Hz) represented the N-carbonyl carbon, and two singlets at 171.54 and 172.14 ppm were assigned as the two carboxyl carbons, respectively.

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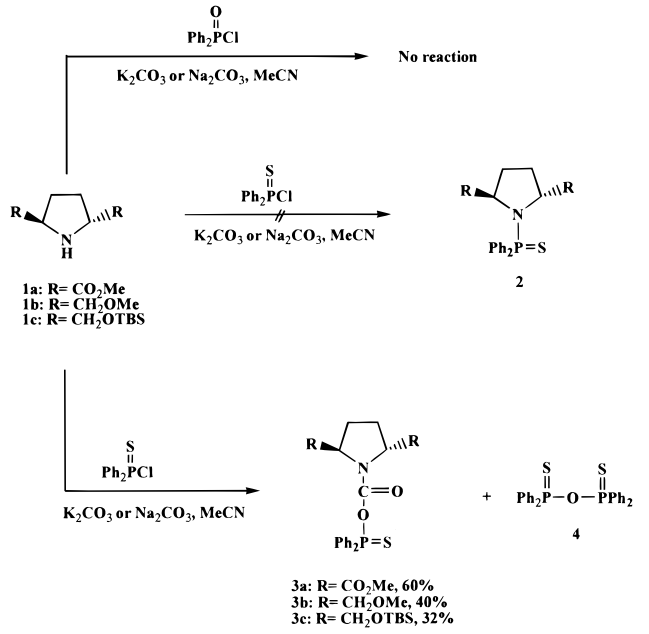
Scheme 1



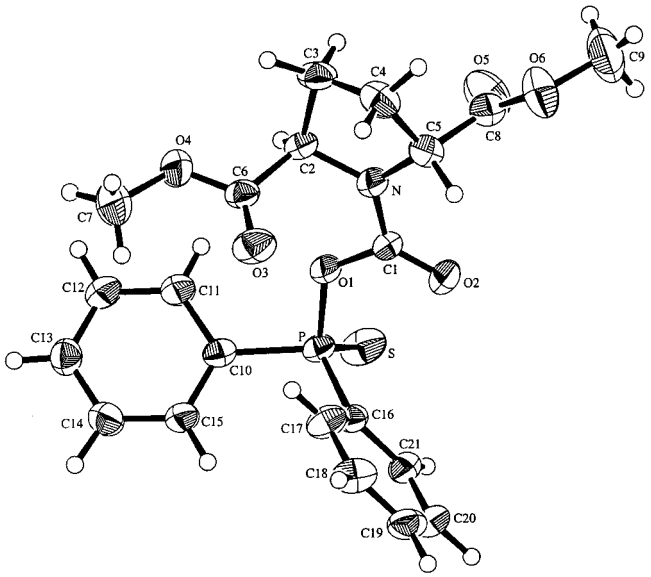
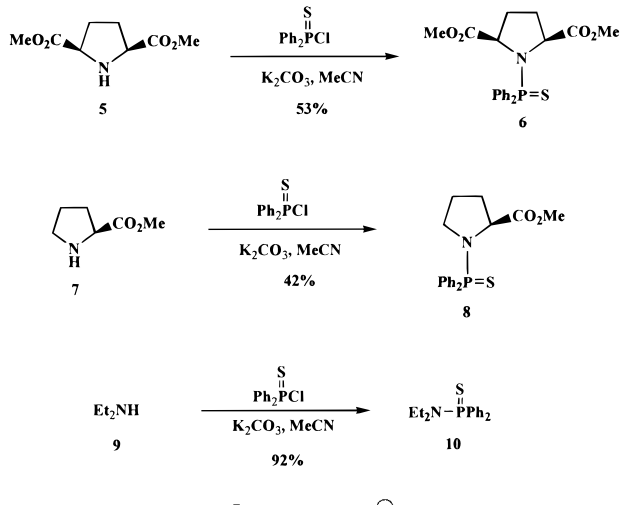


Figure 1. Crystal structure of **3a**.

Moreover, the crystal structure of **3a** was determined by X-ray analysis (Figure 1).[8] Thus, this is a general reaction for trans-2,5-disubstituted pyrrolidines. Increasing the reaction temperature to reflux did not improve the yields of **3a**−**c**. In all cases, the compounds **3a**−**c** were obtained combined with the formation of **4**, which was derived from the reaction of diphenylthiophosphinic chloride with water generated during the reaction. The racemates of **1a**−**c** also gave the corresponding same carbon dioxide inserted products. Thus, no matter if it is a chiral compound or racemate, for C_2-symmetric 2,5-disubstituted pyrrolidine this interesting reaction could take place. On the other hand, it should be noteworthy that cis-2,5-disubstituted pyrrolidine **5**,[7] L-proline methyl ester

Scheme 2



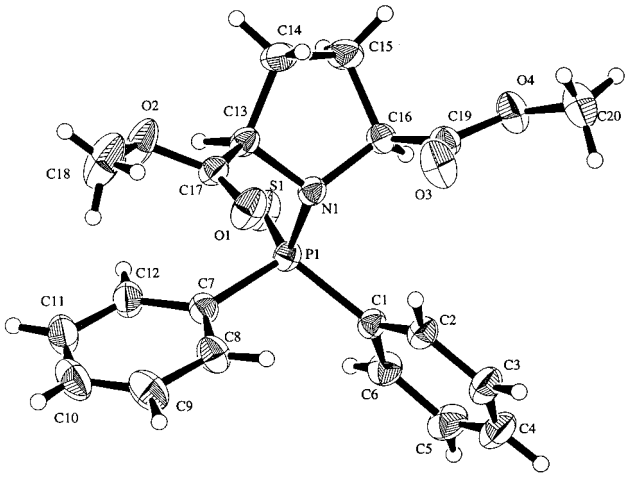


Figure 2. Crystal structure of **6**.

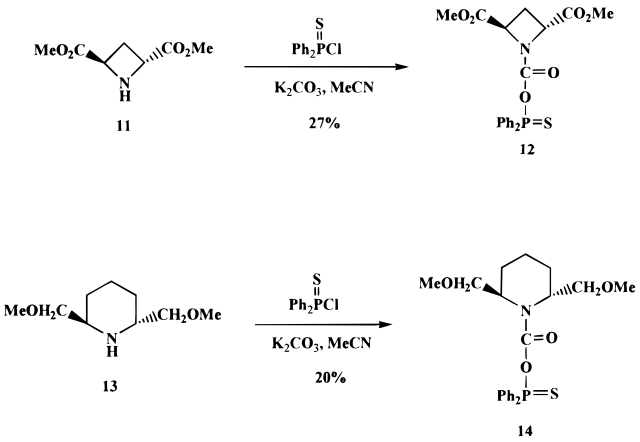
7, or diethylamine **9** reacted with diphenylthiophosphinic chloride under the same reaction conditions, giving the compounds **6**, **8**, and **10** without carbon dioxide insertion (Scheme 2). The structures of **6**, **8**, and **10** were confirmed by spectral data and high mass and microanalysis. In addition, the crystal structure of **6**, which was determined by X-ray analysis, is shown in Figure 2.[9] At the present stage, we do not understand why **1a**−**c** did not react with diphenylphosphinic chloride at all.

For trans-2,4-disubstituted azetidine **11** or trans-2,6-disubstituted piperidine **13**,[7] similarly the carbon dioxide inserted compound **12** or **14** was also obtained under the same reaction conditions, although the yield is lower than the corresponding **1a** (Scheme 3). But for trans-2,3-disubstituted aziridine **15**,[7] the direct connection of the amine with diphenylthiophosphinic chloride took place to afford the corresponding compound **16** without carbon dioxide insertion (Scheme 3). Comparing the space-filling models of **1a**−**c**, **11**, **13**, and **15**, we found that for trans-2,3-disubstituted aziridine **15** the two substituents are further away from the nitrogen atom than in **1a**−**c**, **11**, and **13**, namely the trans-2,5-disubstituted pyrrolidine, trans-2,6-disubstituted piperidine, or trans-2,4-disubsti-

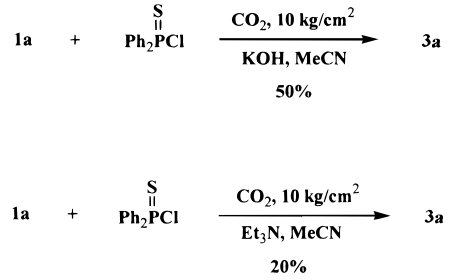
(8) Crystal data for **3a**: empirical formula, $C_{21}H_{22}NO_6PS$; formula weight, 447.44; crystal color, habit, colorless, prismatic; crystal dimensions, 0.20 × 0.20 × 0.30 mm; crystal system: monoclinic; lattice type, primitive; lattice parameters, a = 9.550(2) Å, b = 9.401(4) Å, c = 12.880(2) Å, β = 107.74(1)°, V = 1101.3(5) Å^3; space group: $P2_1$ (#4); Z_{value}= 2; D_{clalc}= 1.349 g/cm^3; F_{000} = 468.00; μ(Mo Kα) = 2.56 cm^{-1}.

(9) Crystal data for **5**: empirical formula, $C_{20}H_{22}NO_4PS$; formula weight, 403.43; crystal color, habit, colorless, column; crystal dimensions, 0.31 × 0.29 × 0.27 mm; crystal system, monoclinic; lattice type, C-centered; lattice parameters, a = 15.667(3)° A, b = 9.600(5) Å, c = 28.485(3) Å, β = 107.52(1)°, V = 4085(1) Å^3; space group, $C2/c$ (#15); Z_{value}= 8; D_{clalc}= 1.312 g/cm^3; F_{000} = 1696.00; μ(Mo Kα) = 2.61 cm^{-1}.

Scheme 3



Scheme 4



tuted azetidine are more sterically hindered than trans-2,3-disubstituted aziridine. This result strongly suggests that steric hindrance of cyclic amines **1a**−**c**, **11**, and **13** plays an important role for this novel carbon dioxide insertion reaction.

To get more mechanistic insights into this reaction, we carried out the reaction of **1a** with diphenylthiophosphinic chloride in acetonitrile under CO_2 atmosphere (10 kg/cm^2) (Scheme 4). We found that **3a** was also obtained in 50% yield using KOH as a base or in 20% yield using Et_3N as a base. This result suggests that the reaction shown in Schemes 1 and 3 would relate with the free carbon dioxide that was generated during the reaction process. The reaction between amine and carbon dioxide has been widely investigated for many years.[1] Recently, the world's dwindling petroleum reserves and increasing atmospheric concentrations of carbon dioxide have stimulated considerable interest in the capture and chemical conversion of carbon dioxide using amines.[10] In this paper, we disclosed the reaction of sterically hindered cyclic amine, CO_2, and diphenylthiophosphinic chloride

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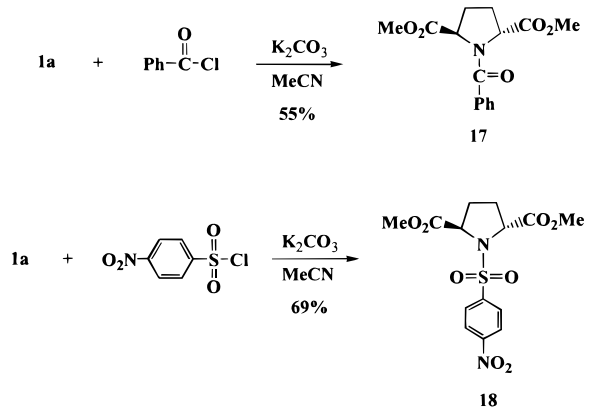
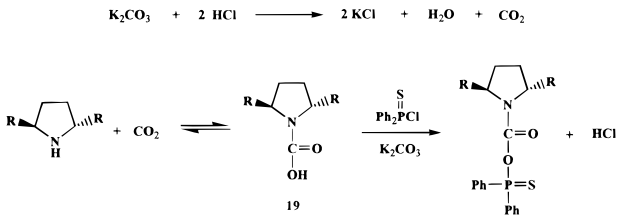
Scheme 5



Scheme 6



for the first time. This reaction highly depends on the structure of cyclic amines.

For the unusual reactivity of 2,5-disubstituted pyrrolidine **1a**, Kemp reported in 1988 that, in the protection of **1a** using Boc_2O in acetonitrile, an attempt to accelerate the reaction of **1a** by addition of a trace of potent acylation catalyst 4-(dimethylamino)pyridine (DMAP) resulted in the formation of high yield of the novel, unstable carbamic carbonic anhydride.[11] It decomposed relatively rapidly at 23 °C. But in our case, the products **3a**−**c**, **12**, and **14** are very stable and can be stored at room temperature for a quite long time without decomposition.

The sterically hindered diphenylthiophosphoryl group also plays an important role in this reaction because no CO_2 insertion reaction took place from the reaction of **1a** with benzoyl chloride or 4-nitrobenzenesulfonyl chloride and only the amide products **17** and **18** were obtained, respectively (Scheme 5). These observed structure/reactivity features in combination with the reactivity with CO_2 led us to propose Scheme 6 as a tentative mechanism. The steric hindrance of cyclic amines and a little hydrochloric acid existed in diphenylthiophosphinic chloride would play important roles in this interesting reaction. Namely, the sterically hindered trans-2,4-disubstituted azetidine, trans-2,5-disubstituted pyrrolidine, or trans-2,6-disubstituted piperidine cannot directly react with diphenylthiophosphinic chloride. Thus, they first reacted with carbon dioxide, which was generated from the initial hydrochloric acid with potassium carbonate to give the intermediate **19**, then it further reacted with diphenylthiophosphinic chloride to produce the CO_2-inserted products and regenerate the hydrochloric acid. When the reaction was carried out under CO_2 atmosphere, the amine directly reacted with CO_2 to give the intermediate **19** and then produced the final product. As a result, the highest yield of **3a** is 60% using sodium carbonate or potassium carbonate. To enhance the chemi-

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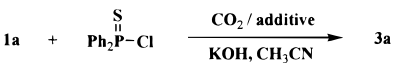
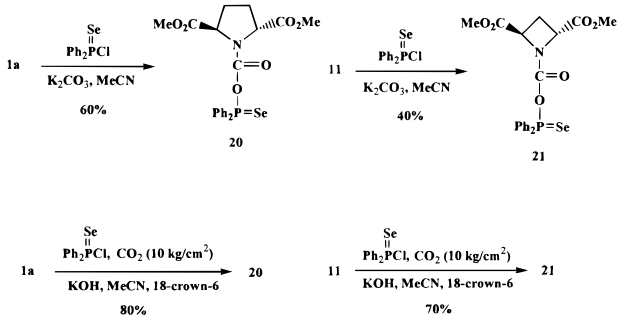
Table 1. Reaction of 1a with Diphenylthiophosphinic Chloride under Carbon Dioxide Atmosphere in Acetonitrile under Different Reaction Conditions



	reaction conditions			
entry	pressure of CO_2 (kg/cm^2)	time/h	additive	yield[b]/%
1	10	48	none	50
2	10	48	18-crown-6[a]	85
3	10	24	18-crown-6[a]	50
4	30	24	18-crown-6[a]	48
5	60	24	18-crown-6[a]	52
6	60	48	18-crown-6[a]	85

[a] 0.1 equiv of additive. [b] Isolated yield.

Scheme 7



cal yield of product and optimize the reaction conditions, we carried out the reaction under different pressure of carbon dioxide using potassium hydroxide as a base in acetonitrile under different pressures of CO_2 and reaction conditions (Table 1). We found that the yield of **3a** can be enhanced up to 85% with the addition of 0.1 equiv of 18-crown-6 ether and the reaction needs about 48 h for completion. Increasing the pressure of CO_2 did not improve the reaction efficiency.

Furthermore, we also found that trans-2,5-disubstituted pyrrolidine or trans-2,4-disubstituted azetidine reacts with diphenylselenophosphinic chloride in acetonitrile in the presence of potassium carbonate at room temperature to give the corresponding carbon dioxide inserted compound **20** and **21** in moderate yield (Scheme 7). When the reaction was carried out under CO_2 atmosphere using potassium hydroxide as a base with the addition of 0.1 equiv of 18-crown-6 ether, the same product could be obtained in 80% and 70% yield, respectively, as well.

In conclusion, we have discovered a new reaction of trans-2,4-disubstituted azetidine, trans-2,5-disubstituted pyrrolidine, and trans-2,6-disubstituted piperidine with CO_2 with diphenylthiophosphinic chloride or diphenylselenophosphinic chloride. This new reaction using carbon dioxide certainly will open a new way to fixation of carbon dioxide.[1] Efforts are underway to elucidate the more mechanistic details of this reaction and to identify systems enabling the carboxylation of other amines and phosphoryl groups and subsequent transformations thereof.

Experimental Section

General Methods. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai 60F_{254} silica gel coated plates. Flash column chromatography was carried out using 300−400 mesh silica gel at increased pressure.

A General Procedure for the Formation of Mixed Carbamic Anhydride 3a. To a suspension of **1a** (60 mg, 0.32 mmol) and potassium carbonate (52 mg, 0.38 mmol) in anhydrous acetonitrile (5 mL) was added diphenylthiophosphinic chloride (89 mg, 0.35 mmol), and the reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure. Dichloromethane (30 mL) and water (20 mL) were added into the residue. The organic layer was further washed with water (20 mL × 2) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give **3a** as a white solid. This solid was further recrystallized from dichloromethane/petroleum ether = 1/4 to afford a monoclinic crystal: 86 mg, 60%; mp 108−110 °C; IR (neat) ν 1720 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.0−2.30 (2H, m, CH_2), 2.30−2.60 (2H, m, CH_2), 3.65 (3H, s, CH_3), 3.69 (3H, s, CH_3), 4.55 (1H, dd, J = 7.5, 1.4 Hz, CH), 4.68 (1H, dd, J = 7.5, 1.4 Hz, CH), 7.30−7.60 (6H, m, Ar), 7.70−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 28.15, 29.08, 52.51, 59.93, 60.09, 128.40 (d, J_{C-P} = 13.7 Hz), 128.45 (d, J_{C-P} = 13.7 Hz), 130.99 (d, J_{C-P} = 12.0 Hz), 131.51 (d, J_{C-P} = 12.0 Hz), 132.04 (d, J_{C-P} = 2.7 Hz), 132.14 (d, J_{C-P} = 2.7 Hz), 132.40 (d, J_{C-O-P} = 110.3 Hz), 133.92 (d, J_{C-O-P} = 110.3 Hz), 148.92 (d, J_{C-O-P} = 5.5 Hz), 171.54, 172.14; MS (EI) m/z 448 (44) (MH^+), 213 (100) (M^+ − 234), 186 (72) (M^+ − 261); HRMS (EI) m/z 447.0905, found 447.0913. Anal. Calcd for $C_{21}H_{22}NO_6PS$: C, 56.37; H, 4.96; N, 3.13. Found: C, 56.43; H, 4.92; N, 3.07.

The Formation of 3b. This compound was produced in the same manner as that described above as a colorless oil: 53 mg, 40%; IR (neat) ν 1720 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.80−2.30 (4H, m, CH_2), 3.23 (3H, s, CH_3), 3.29 (3H, s, CH_3), 3.33 (1H, dd, J = 9.3, 8.2 Hz), 3.42 (1H, dd, J = 9.3, 6.7 Hz), 3.49 (1H, dd, J = 9.3, 3.1 Hz), 3.55 (1H, dd, J = 9.3, 3.3 Hz), 3.90−4.03 (1H, m), 4.11−4.18 (1H, m), 7.40−7.60 (6H, m, Ar), 7.80−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 25.96, 26.84, 57.88, 58.32, 58.99, 59.02, 71.14, 73.28, 128.46 (d, J_{C-P} = 13.8 Hz), 128.49 (d, J_{C-P} = 13.8 Hz), 131.08 (d, J_{C-P} = 11.9 Hz), 131.12 (d, J_{C-P} = 11.9 Hz), 132.02, 132.04, 133.80 (d, J_{C-P} = 110.5 Hz), 133.94 (d, J_{C-P} = 110.5 Hz), 147.70 (d, J_{C-O-P} = 5.5 Hz); MS (EI) m/z 420 (2) (MH^+), 235 (41) (M^+ − 184), 217 (47) (M^+ − 202), 186 (100) (M^+ − 233); HRMS (EI) m/z 420.1393, $C_{21}H_{27}NO_4PS$ requires MH 420.1398.

The Formation of 3c. This compound was produced in the same manner as that described above as a colorless solid that was further recrystallized from dichloromethane/petroleum ether 1/4: 64 mg, 32%; mp 106−108 °C; IR (KBr) ν 1720 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.068 (6H, s, Me), 0.1 (6H, s, Me), 0.92 (9H, s, CMe_3), 0.93 (9H, s, CMe_3), 1.80−2.30 (4H, m, CH_2), 3.53 (1H, dd, J = 9.5, 7.5 Hz), 3.67 (1H, dd, J = 10.1, 3.0 Hz), 3.79 (1H, dd, J = 9.5, 7.5 Hz), 3.87 (1H, dd, J = 10.1, 3.0 Hz), 4.07 (1H, td, J = 7.5, 3.0 Hz), 7.40−7.60 (6H, m, Ar), 7.80−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ −5.41, −5.37, 18.17, 18.20, 25.73, 25.86, 25.89, 26.56, 60.06, 60.60, 62.03, 63.58, 128.41 (d, J_{C-P} = 13.9 Hz), 128.58 (d, J_{C-P} = 13.8 Hz), 131.15 (d, J_{C-P} = 11.9 Hz), 131.18 (d, J_{C-P} = 11.9 Hz), 131.90, 131.94, 133.90 (d, J_{C-P} = 111.8 Hz), 134.01 (d, J_{C-P} = 111.8 Hz), 147.95 (d, J_{C-O-P} = 5.5 Hz); MS (EI) m/z 604 (0.6) (M^+ − 15), 562 (20) (M^+ − 57), 430 (8) (M^+ − 189), 386 (100) (M^+ − 233); HRMS (EI) m/z 620.2787, $C_{31}H_{51}NO_4PSSi_2$ requires MH 620.2815.

The Physical Data of 4. This compound was obtained in the same manner as that described above as a colorless solid that was further recrystallized from dichloromethane: 15 mg, 20%; mp 204−206 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.35−7.60 (6H, m, Ar), 7.78−7.98 (4H, m, Ar); ^{13}C NMR (75

MHz, $CDCl_3$, TMS) δ 128.28 (d, J_{C-P} = 7.1 Hz), 128.37 (d, J_{C-P} = 7.1 Hz), 131.42 (d, J_{C-P} = 6.2 Hz), 131.48 (d, J_{C-P} = 6.2 Hz), 132.12, 132.13, 133.9 (d, J_{C-P} = 124.4 Hz), 134.16 (d, J_{C-P} = 124.4 Hz); MS (EI) *m/z* 450 (2) (M^+), 344 (4) ($M^+ - 106$), 217 (35) ($M^+ - 228$), 186 (100) ($M^+ - 264$). Anal. Calcd for $C_{24}H_{20}OP_2S_2$: C, 63.99; H, 4.47. Found: C, 63.95; H, 4.36.

The Formation of 6. This compound was obtained in the same manner as that described above as a colorless solid that was further recrystallized from diethyl ether/petroleum ether 1/14: 69 mg, 53%; mp 115−117 °C; IR (KBr) ν 1269 cm^{-1} (P═S); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.10−2.35 (4H, m, CH_2), 3.50 (6H, s, CH_3), 4.20−4.40 (2H, m, CH_2), 7.30−7.60 (6H, m, Ar), 8.10−8.20 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 30.65, 30.70, 51.77, 61.45 (d, J_{C-N-P} = 3.0 Hz), 128.16 (d, J_{C-P} = 13.7 Hz), 128.65 (d, J_{C-P} = 13.7 Hz), 130.96 (d, J_{C-P} = 12.0 Hz), 131.52 (d, J_{C-P} = 12.0 Hz), 132.04 (d, J_{C-P} = 2.7 Hz), 132.53 (d, J_{C-P} = 2.7 Hz), 132.47 (d, J_{C-P} = 110.3 Hz), 133.95 (d, J_{C-P} = 110.3 Hz), 172.96, 173.05; MS (EI) *m/z* 404 (2) (MH^+), 344 (4) ($M^+ - 59$), 217 (35) ($M^+ - 186$), 186 (100) ($M^+ - 217$). Anal. Calcd for $C_{20}H_{22}NO_4PS$: C, 59.58; H, 5.27; N, 3.49. Found: C, 59.55; H, 5.46; N, 3.47.

The Formation of 8. This compound was obtained in the same manner as that described above as a colorless oil: 47 mg, 42%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.90−2.10 (3H, m, CH_2), 2.10−2.30 (1H, m, CH_2), 3.15−3.23 (1H, m), 3.24−3.40 (1H, m), 3.50 (3H, s, OMe), 4.05−4.16 (1H, m), 7.35−7.60 (6H, m, Ar), 7.90−8.05 (2H, m, Ar), 8.07−8.20 (2H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 25.79 (d, J_{C-N-P} = 4.8 Hz), 32.15 (d, J_{C-N-P} = 3.8 Hz), 48.42, 51.79, 60.87 (d, J_{C-N-P} = 4.2 Hz), 128.15 (d, J_{C-P} = 12.8 Hz), 128.50 (d, J_{C-P} = 12.8 Hz), 131.46 (d, J_{C-P} = 12.2 Hz), 131.64 (d, J_{C-P} = 12.2 Hz), 132.64 (d, J_{C-P} = 2.0 Hz), 132.71 (d, J_{C-P} = 2.0 Hz), 133.28 (d, J_{C-P} = 110.2 Hz), 133.48 (d, J_{C-P} = 110.2 Hz); MS (EI) *m/z* 346 (3) (MH^+), 286 (6) ($M^+ - 59$), 217 (33) ($M^+ - 128$), 128 (100) ($M^+ - 217$); HRMS (EI) *m/z* 345.0952, $C_{18}H_{20}NO_2PS$ requires M 345.0952.

The Formation of 10. This compound was obtained in the same manner as that described above as a colorless solid that was further recrystallized from diethyl ether/petroleum ether 1/20: 86 mg, 92%; mp 72−76 °C; IR (KBr) ν 1290 cm^{-1} (P═S); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.02 (6H, t, J = 7.0 Hz, CH_3), 3.02 (2H, q, J = 7.0 Hz, CH_2), 3.07 (2H, q, J = 7.0 Hz, CH_2), 7.40−7.60 (6H, m, Ar), 7.95−8.05 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 13.61, 13.68, 40.41, 40.45, 128.28 (d, J_{C-P} = 12.7 Hz), 131.36 (d, J_{C-P} = 2.9 Hz), 132.0 (d, J_{C-P} = 10.6 Hz), 133.82 (d, J_{C-P} = 102.6 Hz); MS (EI) *m/z* 290 (0.8) (MH^+), 248 (3) ($M^+ - 41$), 218 (12) ($M^+ - 71$), 72 (100) ($M^+ - 217$); HRMS (EI) *m/z* 289.1052, $C_{16}H_{20}NPS$ requires M 289.1054.

The Formation of 12. This compound was obtained in the same manner as that described above as a colorless oil: 38 mg, 27%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.56 (2H, t, J = 7.3 Hz, CH_2), 3.73 (3H, s, Me), 3.74 (3H, s, Me), 4.78 (1H, t, J = 7.3 Hz, CH), 4.96 (1H, t, J = 7.3 Hz, CH), 7.40−7.60 (6H, m, Ar), 7.80−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 24.87, 52.67, 58.68, 59.87, 128.37 (d, J_{C-P} = 13.9 Hz), 128.41 (d, J_{C-P} = 13.9 Hz), 130.98 (d, J_{C-P} = 11.9 Hz), 131.23 (d, J_{C-P} = 11.9 Hz), 132.14, 132.16, 132.90 (d, J_{C-P} = 111.8 Hz), 133.40 (d, J_{C-P} = 111.8 Hz), 148.07 (d, J_{C-O-P} = 5.6 Hz), 169.99, 170.43; MS (EI) *m/z* 433 (10) (M^+), 217 (100) ($M^+ - 216$), 201 (30) ($M^+ - 232$), 172 (57) ($M^+ - 261$); HRMS (EI) *m/z* 433.0747 (M^+), $C_{20}H_{20}NO_6PS$ requires M 433.0749.

The Formation of 14. This compound was obtained in the same manner as that described above as a colorless oil: 28 mg, 20%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.22−1.42 (2H, m, CH_2), 1.50−1.72 (4H, m, CH_2), 3.36 (2H, dd, J = 11.1, 4.6 Hz), 3.43 (3H, s, CH_3), 3.49 (3H, s, CH_3), 3.56 (2H, dd, J = 4.6, 0.2 Hz), 3.90−4.03 (1H, m), 4.20−4.38 (1H, m), 7.40−7.60 (6H, m, Ar), 7.80−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 22.26, 28.95, 29.12, 52.86, 59.98, 60.09, 128.46 (d, J_{C-P} = 13.7 Hz), 128.55 (d, J_{C-P} = 13.7 Hz), 131.08 (d, J_{C-P} = 12.0 Hz), 131.55 (d, J_{C-P} = 12.0 Hz), 132.14 (d, J_{C-P} = 2.7 Hz), 132.28 (d, J_{C-P} = 2.7 Hz), 132.70 (d, J_{C-P} = 110.3 Hz), 133.88 (d, J_{C-P} = 110.3 Hz), 148.92 (d, J_{C-O-P} = 5.5 Hz), 171.54, 172.14; MS (EI) *m/z* 434 (2) (MH^+), 402 (4) ($M^+ - 31$), 247 (35) ($M^+ - 186$), 216 (100) ($M^+ - 217$). Anal. Calcd for $C_{22}H_{28}NO_4PS$: C, 60.95; H, 6.51; N, 3.23. Found: C, 61.15; H, 6.46; N, 3.21.

The Formation of 16. This compound was obtained in the same manner as that described above as a colorless oil: 69 mg, 62%; IR (neat) ν 1269 cm^{-1} (P═S); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.98 (1H, tdd, J = 4.4, 4.4 Hz, J_{P-N-CH} = 4.4 Hz, CH), 3.01 (1H, tdd, J = 4.4, 4.4 Hz, J_{P-N-CH} = 4.4 Hz, CH), 3.20 (6H, s, OMe), 3.60−3.75 (4H, m, CH_2), 7.40−7.60 (6H, m, Ar), 7.90−8.10 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 41.55 (d, J_{C-N-P} = 7.1 Hz), 58.61, 70.51, 70.59, 128.16 (d, J_{C-P} = 13.7 Hz), 128.45 (d, J_{C-P} = 13.7 Hz), 131.13 (d, J_{C-P} = 12.0 Hz), 131.65 (d, J_{C-P} = 12.0 Hz), 132.14 (d, J_{C-P} = 2.7 Hz), 132.28 (d, J_{C-P} = 2.7 Hz), 132.70 (d, J_{C-P} = 110.3 Hz), 133.12 (d, J_{C-P} = 110.3 Hz); MS (EI) *m/z* 348 (4) (MH^+), 316 (13) ($M^+ - 31$), 302 (66) ($M^+ - 45$), 217 (100) ($M^+ - 130$); HRMS (EI) *m/z* 348.1183 (MH^+), $C_{18}H_{23}NO_2PS$ requires MH 348.1187.

The Formation of 17. This compound was obtained in the same manner as that described above as a colorless oil: 52 mg, 55%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.0−2.15 (2H, m), 2.25−2.60 (2H, m), 3.53 (3H, s, OMe), 3.80 (3H, s, OMe), 4.52 (1H, dd, J = 6.8, 0.2 Hz), 4.89 (1H, dd, J = 6.8, 2.3 Hz), 7.30−7.46 (5H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 27.58, 30.03, 52.32, 52.40, 59.43, 61.54, 126.51, 128.38, 129.94, 136.20, 170.55, 172.33, 172.38; MS (EI) *m/z* 292 (17) (MH^+), 260 (4) ($M^+ - 31$), 232 (24) ($M^+ - 59$), 105 (100) ($M^+ - 186$). Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 62.14; H, 6.05; N, 4.54.

The Formation of 18. This compound was obtained in the same manner as that described above as a slight yellow solid that was further recrystallized from dichloromethane: 82 mg, 69%; mp 122−123 °C; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.0−2.15 (2H, m), 2.40−2.60 (2H, m), 3.68 (6H, s, OMe), 4.56 (2H, dd, J = 7.9, 0.2 Hz), 8.13 (2H, d, J = 8.8 Hz, Ar), 8.38 (2H, d, J = 8.8 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 27.30, 45.20, 66.90, 127.45, 128.15, 128.54, 128.70, 136.51, 138.39, 181.40; MS (EI) *m/z* 372 (0.3) ($M^+ - 30$), 313 (3) ($M^+ - 59$), 283 (24) ($M^+ - 89$), 128 (100) ($M^+ - 244$). Anal. Calcd for $C_{14}H_{16}N_2O_8S$: C, 45.16; H, 4.33; N, 7.52. Found: C, 44.99; H, 4.22; N, 7.44.

The Formation of 20. This compound was obtained in the same manner as that described above as a colorless oil: 95 mg, 60%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.0−2.30 (2H, m, CH_2), 2.30−2.60 (2H, m, CH_2), 3.67 (3H, s, CH_3), 3.71 (3H, s, CH_3), 4.57 (1H, dd, J = 7.5, 1.4 Hz, CH), 4.70 (1H, dd, J = 7.5, 1.4 Hz, CH), 7.30−7.60 (6H, m, Ar), 7.70−8.0 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 28.21, 30.06, 52.69, 59.87, 60.12, 128.33 (d, J_{C-P} = 13.5 Hz), 128.47 (d, J_{C-P} = 13.5 Hz), 131.08 (d, J_{C-P} = 11.8 Hz), 131.65 (d, J_{C-P} = 11.8 Hz), 132.04 (d, J_{C-P} = 2.8 Hz), 132.14 (d, J_{C-P} = 2.8 Hz), 132.35 (d, J_{C-P} = 111.2 Hz), 133.92 (d, J_{C-P} = 111.2 Hz), 148.92 (d, J_{C-O-P} = 5.5 Hz), 171.64, 172.54; MS (EI) *m/z* 495 (11) (MH^+), 282 (14) ($M^+ - 212$), 265 (21) ($M^+ - 229$), 186 (100) ($M^+ - 308$); HRMS (EI) *m/z* 495.0356 (M^+), $C_{21}H_{22}NO_6PSe$ requires M 495.0350.

The Formation of 21. This compound was obtained in the same manner as that described above as a colorless oil: 62 mg, 40%; IR (neat) ν 1720 cm^{-1} (C═O); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 2.74 (2H, t, J = 6.4 Hz, CH_2), 3.77 (3H, s, OMe), 3.80 (3H, s, OMe), 4.25 (1H, t, J = 6.4 Hz, CH), 4.40 (1H, t, J = 6.4 Hz), 7.40−7.60 (6H, m, Ar), 7.90−8.10 (4H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 25.66, 52.89, 58.64, 59.90, 128.33 (d, J_{C-P} = 13.9 Hz), 128.47 (d, J_{C-P} = 13.9 Hz), 131.14 (d, J_{C-P} = 11.9 Hz), 131.42 (d, J_{C-P} = 11.9 Hz), 132.14, 132.16, 132.90 (d, J_{C-P} = 110.9 Hz), 133.40 (d, J_{C-P} = 110.9 Hz), 148.13 (d, J_{C-O-P} = 5.6 Hz), 170.12, 170.87; MS (EI) *m/z* 482 (10) (MH^+), 265 (90) ($M^+ - 215$), 201 (55) ($M^+ - 279$), 183 (100) ($M^+ - 297$); HRMS (EI) *m/z* 481.0197 (M^+), $C_{20}H_{20}NO_6PSe$ requires M 481.0193.

A General Procedure for the Formation of Mixed Carbamic Anhydride 3a under CO_2 Atmosphere. 1a (60 mg, 0.32 mmol), diphenylthiophosphinic chloride (89 mg, 0.35 mmol), potassium hydroxide (22 mg, 0.38 mmol), 18-crown-6

ether (8.5 mg, 0.032 mmol), anhydrous acetonitrile (10 mL), and a magnetic stir bar were placed in the 50 mL glass liner of a stainless steel autoclave under a nitrogen purge. After the autoclave was purged several times with CO_2, it was pressurized with CO_2 (10 atm), sealed, and stirred at room temperature for 24 h. After release of the pressure, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatograph (eluent: petroleumether/EtOAc= 1/4) to give **3a** as a white solid.

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Supporting Information Available: The X-ray data of ORTEP diagrams and tables for **3a** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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