

# Mechanistic Insights into an Unexpected Carbon Dioxide Insertion Reaction through the Crystal Structures of Carbamic Diphenylthiophosphinic Anhydride and 1-[(4-Nitrophenyl)sulfonyl]-*trans*-2,5-pyrrolidinedicarboxylic Acid Methyl Ester

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The crystal structures of an unexpected carbon dioxide inserted carbamic diphenylthiophosphinic anhydride and 1-[(4-nitrophenyl)sulfonyl]-*trans*-2,5-pyrrolidinedicarboxylic acid methyl ester were determined by X-ray analysis. They crystallized in the space group  $P2_1$  (# 4) with  $a = 0.9550(2)$ ,  $b = 0.9401(4)$ ,  $c = 1.2880(2)$  nm,  $\beta = 107.74^\circ$ ,  $V = 1.1013(5)$  nm<sup>3</sup>,  $D_{\text{calcd}} = 1.349$  g/cm<sup>3</sup>,  $Z = 2$  and  $P2_12_12_1$  (# 19) with  $a = 1.4666(2)$ ,  $b = 0.7195(2)$ ,  $c = 1.6339(2)$  nm,  $V = 1.7240(7)$  nm<sup>3</sup>,  $D_{\text{calcd}} = 1.434$  g/cm<sup>3</sup>,  $Z = 4$ , respectively. Through the investigation of these two crystal structures, the mechanistic insights into this unexpected carbon dioxide insertion in the reaction of *trans*-2,5-disubstituted pyrrolidine with diphenylthiophosphoryl chloride in the presence of potassium carbonate were disclosed.

**Keywords** *trans*-2,5-Disubstituted pyrrolidine, carbon dioxide insertion, carbamic diphenylthiophosphinic anhydride, 1-[(4-nitrophenyl)sulfonyl]-*trans*-2,5-pyrrolidinedicarboxylic acid methyl ester

## Introduction

In the course of synthesis of new chiral  $C_2$ -symmetric 2,5-disubstituted pyrrolidine derivatives having a diphenylphosphinyl or diphenylthiophosphinyl group as chiral ligands,<sup>1</sup> we incidentally found that in the reaction of  $C_2$ -symmetric 2,5-disubstituted pyrrolidine (**1a**) with diphenylthiophosphinic chloride, a carbon dioxide in-

serted product **2a** was formed as the only product (Scheme 1).<sup>2</sup> Moreover, its crystal structure has been unambiguously disclosed by X-ray analysis.<sup>2</sup> In order to clarify the scope and limitations of this interesting reaction, we carried out the reaction of 4-nitrobenzenesulfonyl chloride and benzoyl chloride with **1a** under the same reaction conditions (Scheme 2). As a result, we found that no carbon dioxide insertion occurred and the compounds **3a** and **3b** were obtained as the corresponding products, respectively. These results suggest that the structures of both cyclic amines and chlorides play very important roles in this unusual reaction.<sup>2</sup> In order to gain more mechanistic insights into this reaction, we decide to disclose the structure of **3a** or **3b** by X-ray analysis because we anticipate that, by comparing the structures of **2a** and **3a** or **3b**, the steric effect on this reaction could be unveiled. Thus, we wish herein to report the detailed X-ray crystal structures of **2a** and **3a** and the mechanistic information about the reaction shown in Scheme 1.

## Results and discussion

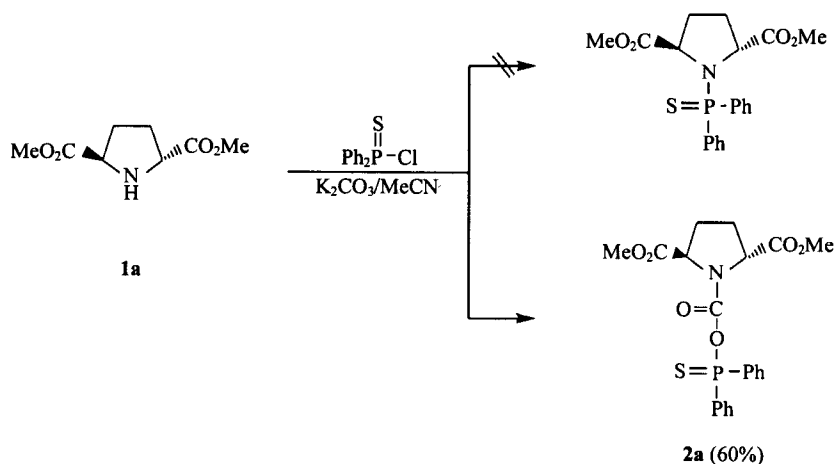
The compounds **2a**, **3a** and **3b** were readily synthesized by the reaction of *trans*-2,5-disubstituted pyrrolidine **1a** with diphenylthiophosphinic chloride and 4-nitrobenzenesulfonyl chloride in acetonitrile at room tempe-

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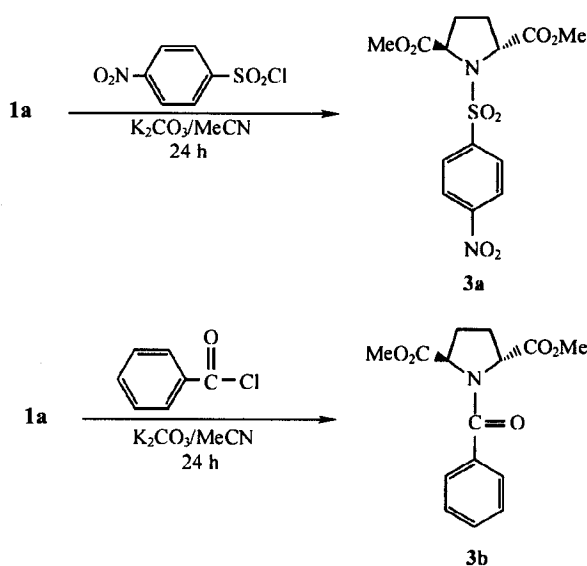
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Scheme 1



Scheme 2



rature in the presence of potassium carbonate, respectively.<sup>2</sup> Their structures were easily characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral data, mass spectroscopy, and microanalysis. **2a** and **3a** are white solids, but **3b** is an oily compound. The single crystal of **2a** was obtained by careful recrystallization from dichloromethane, while the single crystal of **3a** was obtained by careful recrystallization from ethyl acetate and petroleum ether (1/2). Their crystal data were summarized in Table 1 and their X-ray crystal structures were shown in Figs. 1 and 2, respectively. For **2a** (Fig. 1, Table 2, Table 3), the

pyrrolidine ring is obviously not a planar ring structure, but in an envelope conformation, and the C—C bond lengths are essentially equivalent (0.1537—0.1526 nm). The key structure is the carbamate group in which the bond lengths of N—C(1) and C(1)—O(1) are 0.1360 and 0.1363 nm, and the bond angle of N—C(1)—O(1) is 109.4° respectively (Table 4). Bond lengths and bond angles are normal. Diphenylthiophosphinyl group is tetrahedral with phosphorus atom at the center and the bond angle of C(10)—P—C(16) bearing two phenyl rings is 107.4°. This means that diphenylthiophosphinyl group is a bulky group. The direct attack of **1a** to diphenylthiophosphinyl chloride could be blocked out. The N—C(O)—O carbamate group plays an important role in the formation of **2a**. As can be seen from Fig. 1, it works like a joint by which the sterically bulky diphenylthiophosphinyl group can avoid direct contact with the two carboxyl groups on the two sides of *trans*-2,5-pyrrolidine ring, otherwise **1a** can not connect with the diphenylthiophosphoryl group due to the steric hindrance of the two molecules.

On the other hand, for **3a** (Fig. 2, Table 4, Table 5), the C—C bond lengths and the two N—C bond lengths of the five-membered ring are also essentially equivalent (0.1521—0.1536 nm and 0.1460—0.1467 nm, respectively). The pyrrolidine ring is in an envelope conformation as well. The bond lengths of N(1)—S(1) and S(1)—C(9) are 0.1621(3) nm and 0.1774(3) nm, respectively. They are the N—S and S—C single bonds. The phenyl ring is a planar structure with bond length (0.1377(4) nm). From Fig. 2, it is

very clear that, owing to the *p*-nitrophenylsulfonyl group being not a sterically bulky group, it can directly connect with the **1a** without any problem (Scheme 2).

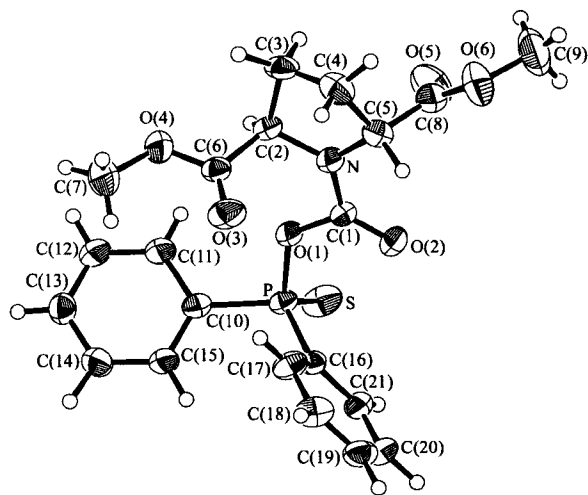


Fig. 1 Crystal structure of **2a**.

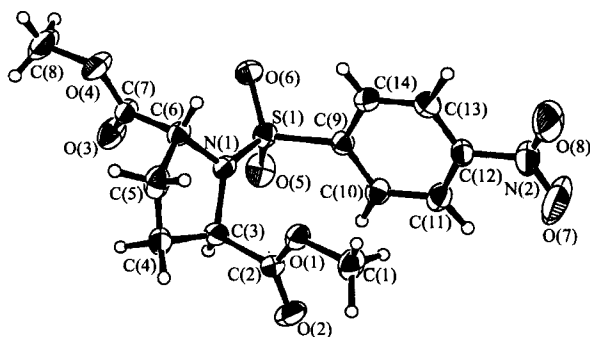


Fig. 2 Crystal structure of **3a**.

According to the two crystal structures and the previous results,<sup>2</sup> we can draw a mechanistic conclusion about this unusual carbon dioxide insertion reaction. The sterically hindered **1a** can not directly react with bulky diphenylthiophosphinic chloride. Thus it first reacted with carbon dioxide which was generated from the initial hydrochloric acid with potassium carbonate to give the intermediate **4** (Scheme 3), then because **4** can largely reduce the steric hindrance of **1a** by the N-C(O)-O carbamate group, it can further react with diphenylthiophosphinic chloride to produce the CO<sub>2</sub> inserted product and regenerate the hydrochloric acid. We believe the equilibrium largely leans to the left side. Namely, the concentration of the key intermediate **4** is low in the reaction system. Thus, for sterically small *p*-nitrophenyl-

sulfonyl chloride or benzoyl chloride, they readily react with **1a** to give directly the corresponding **3a** and **3b** without carbon dioxide insertion.

In conclusion, we have disclosed the mechanistic details of the novel CO<sub>2</sub> insertion reaction of **1a** with diphenylthiophosphinic chloride in the presence of potassium carbonate. This new reaction related with carbon dioxide certainly will open a new way to the fixation of carbon dioxide.<sup>3</sup> As a matter of fact, carbon dioxide, the earth's most abundant carbon resource, is remarkably little used as a chemical feedstock.<sup>3</sup> As the output of CO<sub>2</sub> from combustion into the environment continues to rise, threatening a global environmental crisis, the search for practical methods for regenerating organic compounds from CO<sub>2</sub> has assumed increased importance. Efforts are underway to identify systems enabling the carboxylation of other amines and phosphoryl group and subsequent transformation thereof.

## Experimental

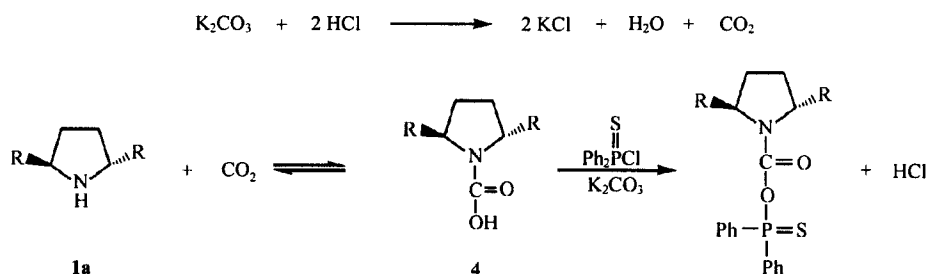
### General

Melting points (Mps) were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were determined for solutions in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal standard on a Bruker AMX-300 spectrometer; *J*-values are in Hz. IR spectra were determined by a Perkin-Elmer 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument. High Mass spectra were recorded on a Finnigan MA+ instrument. All solid compounds reported in this paper gave satisfactory CHN microanalyses with a Italian Carlo-Erba 1106 analyzer. The single crystal of **2a** was obtained by careful recrystallization from dichloromethane and the single crystal of **3a** was obtained from ethyl acetate and petroleum ether (1/2). Their X-ray data were summarized in Table 1, respectively. Atomic coordinates are given in Table 2 and Table 3.

### Crystallography

A suitable crystal was mounted on the top of a glass capillary. Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo K<sub>α</sub> radiation λ = 0.071069 nm using the ω-2θ technique at

Scheme 3

**Table 1** Crystal data and summary of intensity data collection and structure refinement of **2a** and **3a**

Empirical formula	C <sub>21</sub> H <sub>22</sub> NO <sub>6</sub> PS	C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> S
Formular weight	447.44	372.35
Crystal color, habit	colorless, prismatic	colorless, column
Crystal dimensions (mm)	0.20 × 0.20 × 0.30	0.38 × 0.38 × 0.28
Crystal system	monoclinic	orthorhombic
Lattice type	primitive	primitive
Lattice parameters		
<i>a</i> (nm)	0.9550(2)	1.4666(2)
<i>b</i> (nm)	0.9401(2)	0.7195(2)
<i>c</i> (nm)	1.2880(2)	1.6339(3)
β (°)	10.774(1)	
<i>V</i> (nm <sup>3</sup> )	1.1013(5)	1.7240(7)
Space group	<i>P</i> 2 <sub>1</sub> (# 4)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> (# 19)
<i>Z</i> value	2	4
<i>D</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.349	1.434
<i>F</i> <sub>(000)</sub>	468.00	776.00
μ (Mo <i>K</i> <sub>α</sub> ) (cm <sup>-1</sup> )	2.56	2.32
Diffractometer/scan	Rigaku AFC7R	Rigaku AFC7R
Radiation graphite monochromator	Mo <i>K</i> <sub>α</sub> (λ = 0.71069 nm)	Mo <i>K</i> <sub>α</sub> (λ = 0.71069 nm)
Crystal to detector distane (mm)	235	235
Temperature (°C)	24.0	24.0
Scan type	ω-2θ	ω-2θ
Scan rate (°/min) (in ω)	16.0 up to 4 scans	4.0 up to 3 scans
2θ <sub>max</sub> (°)	55.0	55.0
Scan width (°)	1.63 + 0.30 tan θ	1.73 + 0.30 tan θ
Structure solution	Direct methods (TEXSAN)	Direct Methods (TEXSAN)
Refinement	Full-matrix least-squares	Full-matrix teast-squares
ρ-factor	0.030	0.069
Reflection/parameter ratio	7.97	7.92
Residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.036; 0.044	0.053; 0.060
Max shift/error in final cycle	0.030	0.006
Maximum peak in final diff. map	0.37 × 10 <sup>-3</sup> e <sup>-</sup> /nm <sup>3</sup>	0.26 × 10 <sup>-3</sup> e <sup>-</sup> /nm <sup>3</sup>
Minimum peak in final diff. map	-0.21 × 10 <sup>-3</sup> e <sup>-</sup> /nm <sup>3</sup>	-0.26 × 10 <sup>-3</sup> e <sup>-</sup> /nm <sup>3</sup>

24°C. The data were collected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.<sup>4</sup> The non-hydrogen atoms were refined anisotropically by full-matrix least squares. All hydrogen atoms were included in calculated position. All calculations were performed using the TEXSAN crystallographic software package. For **2a**, final  $R$  and  $R_w$  values were 0.036 and 0.044 for 2161 observed reflection. For **3a**, final  $R$  and  $R_w$  values were 0.053 and 0.060 for 2304 observed reflection. These crystal structures of **2a** and **3a** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 149750 for **2a** and CCDC 149831 for **3a**.

Table 2 Atomic coordinates for **2a**

Atom	$x$	$y$	$z$	$B_{eq}$
S	0.8828(1)	-0.1591	0.73807(9)	5.23(2)
P	0.89383(8)	0.0283(1)	0.68080(6)	3.09(2)
O(1)	0.9020(2)	0.1590(3)	0.7677(2)	3.41(5)
O(2)	0.6625(3)	0.1661(4)	0.7611(2)	5.17(6)
O(3)	0.9380(3)	0.4703(3)	0.7117(2)	5.25(6)
O(4)	1.1637(3)	0.4578(4)	0.8310(2)	5.32(7)
O(5)	0.7167(4)	0.2432(4)	1.0260(3)	7.03(10)
O(6)	0.5494(3)	0.4160(4)	0.9851(3)	6.85(9)
N	0.8257(3)	0.3272(4)	0.8592(2)	3.43(5)
C(1)	0.7837(3)	0.2118(4)	0.7933(2)	3.45(7)
C(2)	0.9729(3)	0.3866(4)	0.8944(2)	3.30(6)
C(3)	0.9587(4)	0.5080(4)	0.9706(3)	4.46(8)
C(4)	0.7982(5)	0.5535(4)	0.9247(3)	4.70(9)
C(5)	0.7165(4)	0.4138(4)	0.8867(3)	3.86(7)
C(6)	1.0199(4)	0.4424(4)	0.8001(3)	3.51(7)
C(7)	1.2266(6)	0.5246(8)	0.7534(4)	7.6(1)
C(8)	0.6628(4)	0.3460(5)	0.9742(3)	4.37(8)
C(9)	0.4802(7)	0.3652(8)	1.0617(6)	9.2(2)
C(10)	1.0633(3)	0.0694(4)	0.6551(2)	3.24(6)
C(11)	1.1844(4)	0.1008(6)	0.7412(3)	4.87(9)
C(12)	1.3183(4)	0.1310(6)	0.7241(3)	5.04(9)
C(13)	1.3288(4)	0.1359(5)	0.6197(3)	4.26(8)
C(14)	1.2075(4)	0.1055(5)	0.5340(3)	4.67(9)
C(15)	1.0752(4)	0.0729(5)	0.5504(3)	4.13(7)
C(16)	0.7462(3)	0.0755(4)	0.5600(2)	3.15(6)
C(17)	0.7403(4)	0.2110(4)	0.5152(3)	4.24(8)
C(18)	0.6243(5)	0.2454(5)	0.4232(3)	4.86(9)
C(19)	0.5168(4)	0.1473(6)	0.3779(3)	4.84(9)
C(20)	0.5228(4)	0.0128(5)	0.4215(3)	4.70(9)
C(21)	0.6390(3)	-0.0230(4)	0.5136(3)	3.83(7)

$$B_{eq} = 8/3\pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

### Preparation of mixed carbamic anhydride (**2a**)

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  $\times$  2) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatograph (eluent: petroleum ether/EtOAc = 1/4) to give **2a** as a white solid. This solid was further recrystallized from dichloromethane/petroleum ether = 1/4 to afford a monoclinic crystal: 86 mg, 60%, m. p. 108–110°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, TMS)  $\delta$ : 2.0–2.30 (m, 2H,  $\text{CH}_2$ ), 2.30–2.60 (m, 2H,  $\text{CH}_2$ ), 3.65 (s, 3H,  $\text{CH}_3$ ), 3.69 (s, 3H,  $\text{CH}_3$ ), 4.55 (dd,  $J = 7.5$ , 1.4 Hz, 1H, CH), 4.68 (dd,  $J = 7.5$ , 1.4 Hz, 1H, CH), 7.30–7.60 (m, 6H, Ar), 7.70–8.0 (m, 4H, Ar);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz, TMS)  $\delta$ : 28.15, 29.08, 52.51, 59.93, 60.09, 128.40 (d,  $J_{\text{C-P}} = 13.7$  Hz), 128.45 (d,  $J_{\text{C-P}} = 13.7$  Hz), 130.99 (d,  $J_{\text{C-P}} = 12.0$  Hz), 131.51 (d,  $J_{\text{C-P}} = 12.0$  Hz), 132.04 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.14 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.40 (d,  $J_{\text{C-P}} = 110.3$  Hz), 133.92 (d,  $J_{\text{C-P}} = 110.3$  Hz), 148.92 (d,  $J_{\text{C-O-P}} = 5.5$  Hz), 171.54, 172.14; IR (neat)  $\nu$ : 1720 (C=O)  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 448 (44) ( $\text{MH}^+$ ), 213 (100) ( $\text{M}^+ - 234$ ), 186 (72) ( $\text{M}^+ - 261$ ); found: C 56.43, H 4.92, N 3.07. HRMS (EI)  $m/z$  447.0913.  $\text{C}_{21}\text{-H}_{22}\text{NO}_6\text{PS}$  447.0905 requires C 56.37, H 4.96, N 3.13.

### Preparation of 1-[(4-nitrophenyl)sulfonyl]-2,5-pyrrolidinedicarboxylic acid methyl ester (**3a**)

Compound **3a** was obtained from the reaction of **1a** (70 mg, 0.37 mmol) with 4-nitrobenzenesulfonyl chloride (80 mg, 0.39 mmol) in acetonitrile at room temperature for 24 h. After the acetonitrile was removed under reduced pressure, the residue was purified by silica gel column chromatograph (eluent: petroleum ether/EtOAc = 1/4) to give **3a** as a white solid: m. p. 122–124°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, TMS)  $\delta$ : 2.03–

2.10 (m, 2H, CH<sub>2</sub>), 2.41—2.47 (m, 2H, CH<sub>2</sub>), 3.73 (s, 6H, OCH<sub>3</sub>), 4.56 (t, *J* = 7.9 Hz, 2H, CH), 8.03 (d, *J* = 8.7 Hz, 2H, Ar), 8.36 (d, *J* = 8.7 Hz, 2H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS) δ: 45.20, 59.90, 66.90, 127.54, 128.15, 128.54, 128.70, 136.51, 138.39, 202.71; MS (EI) *m/z* (%): 342 (M<sup>+</sup> + 1). Anal. calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S: C 45.16, H 4.33, N 7.52; found: C 44.89, H 4.27, N 7.43.

*Preparation of N-benzoyl-2,5-pyrrolidinedicarboxylic acid methyl ester (3b)*

Compound **3b** was obtained in the same manner as

that described above as a colorless oil: 52 mg, 55%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS) δ: 2.0—2.15 (m, 2H), 2.25—2.60 (m, 2H), 3.53 (s, 3H, OMe), 3.80 (s, 3H, OMe), 4.52 (dd, *J* = 6.8, 0.2 Hz, 1H), 4.89 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.30—7.46 (m, 5H, Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 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; IR (neat) ν: 1720 (C = O) cm<sup>-1</sup>; MS (EI) *m/z* (%): 292 (17) (MH<sup>+</sup>), 260 (4) (M<sup>+</sup> - 31), 232 (24) (M<sup>+</sup> - 59), 105 (100) (M<sup>+</sup> - 186); Anal calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>5</sub>: C 61.85, H 5.88, N 4.81; found: C 62.14, H 6.05, N 4.54.

**Table 3** Bond lengths (10<sup>-1</sup> nm) and bond angle (°) of **2a**

S—P	1.925(1)	P—O(1)	1.648(2)
P—C(10)	1.790(3)	P—C(6)	1.808(3)
O(1)—C(1)	1.363(4)	O(2)—C(1)	1.185(4)
O(3)—C(6)	1.198(4)	O(4)—C(6)	1.315(4)
O(4)—C(7)	1.457(5)	O(5)—C(8)	1.198(5)
O(6)—C(8)	1.311(5)	O(6)—C(9)	1.427(6)
N—C(1)	1.360(4)	N—C(2)	1.451(4)
N—C(5)	1.450(4)	C(2)—C(3)	1.537(4)
C(2)—C(6)	1.512(4)	C(3)—C(4)	1.526(6)
C(4)—C(5)	1.530(5)	C(5)—C(8)	1.514(5)
S-P-O(1)	114.8(1)	S-P-C(10)	115.3(1)
S-P-C(16)	115.8(1)	O(1)-P-C(10)	96.1(1)
O(1)-P-C(16)	105.4(1)	C(10)-P-C(16)	107.4(1)
P-O(1)-C(1)	124.4(2)	C(6)-O(4)-C(7)	116.7(3)
C(8)-O(6)-C(9)	118.5(5)	C(1)-N-C(2)	125.1(3)
C(1)-N-C(5)	120.2(3)	C(2)-N-C(5)	114.1(3)
O(1)-C(1)-O(2)	125.2(3)	O(1)-C(1)-N	109.4(3)
O(2)-C(1)-N	125.4(3)	N-C(2)-C(3)	102.7(3)
N-C(2)-C(6)	112.3(2)	C(3)-C(2)-C(6)	111.2(3)
C(2)-C(3)-C(4)	103.6(3)	C(3)-C(4)-C(5)	103.7(3)
N-C(5)-C(4)	103.0(3)	N-C(5)-C(8)	112.2(3)
C(4)-C(5)-C(8)	112.2(3)	O(3)-C(6)-O(4)	125.7(3)
O(3)-C(6)-C(2)	124.9(3)	O(4)-C(6)-O(2)	109.4(3)
O(5)-C(8)-O(6)	125.1(4)	O(5)-C(8)-C(5)	124.7(4)
O(6)-C(8)-C(5)	110.2(4)	P-C(10)-C(11)	120.3(2)
P-C(10)-C(15)	122.1(2)	P-C(16)-C(17)	120.2(2)
P-C(16)-C(21)	119.4(3)		

Table 4 Atomic coordinates for 3a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
S(1)	0.38824(5)	0.7173(1)	0.39228(5)	3.80(1)
O(1)	0.2929(1)	0.2491(3)	0.3996(1)	4.44(5)
O(2)	0.2586(2)	0.3030(5)	0.5302(2)	6.55(7)
O(3)	0.5999(2)	0.6377(5)	0.4531(2)	5.71(6)
O(4)	0.6591(2)	0.5351(5)	0.3364(2)	5.91(6)
O(5)	0.3742(2)	0.8084(4)	0.4688(2)	5.50(6)
O(6)	0.4443(2)	0.7992(4)	0.3305(2)	5.18(5)
O(7)	-0.0451(2)	0.598(1)	0.2914(3)	13.7(2)
O(8)	0.0105(3)	0.583(1)	0.1771(3)	12.8(2)
N(1)	0.4284(2)	0.5103(3)	0.4076(1)	3.55(4)
N(2)	0.0176(2)	0.6045(7)	0.2486(3)	6.72(10)
C(1)	0.2045(3)	0.1647(6)	0.3876(4)	5.88(9)
C(2)	0.3097(2)	0.3127(5)	0.4735(2)	4.12(6)
C(3)	0.4042(2)	0.4010(5)	0.4802(2)	3.98(6)
C(4)	0.4787(2)	0.2511(6)	0.4831(3)	5.37(9)
C(5)	0.5159(3)	0.2416(5)	0.3963(3)	5.31(8)
C(6)	0.5097(2)	0.4422(5)	0.3656(2)	3.65(6)
C(7)	0.5934(2)	0.5526(5)	0.3909(2)	3.87(5)
C(8)	0.7443(3)	0.627(1)	0.3580(4)	7.8(1)
C(9)	0.2781(2)	0.6807(4)	0.3503(2)	3.63(6)
C(10)	0.2030(2)	0.6810(5)	0.4009(2)	4.12(6)
C(11)	0.1166(2)	0.6551(5)	0.3679(2)	4.72(7)
C(12)	0.1099(2)	0.6303(5)	0.2846(2)	4.56(7)
C(13)	0.1839(3)	0.6300(7)	0.2334(2)	5.25(8)
C(14)	0.2693(2)	0.6563(6)	0.2670(2)	4.69(7)

$$B_{eq} = 8/3\pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 5 Bond lengths (10<sup>-1</sup> nm) and bond angle (°) of 3a

S(1)—O(5)	1.427(2)	S(1)—O(6)	1.429(3)
S(1)—N(1)	1.621(3)	S(1)—C(9)	1.774(3)
O(1)—C(1)	1.445(4)	O(1)—C(2)	1.315(4)
O(2)—C(2)	1.194(4)	O(3)—C(7)	1.315(4)
O(4)—C(7)	1.318(4)	O(4)—C(8)	1.191(4)
O(7)—N(2)	1.156(6)	O(8)—N(2)	1.457(5)
N(1)—C(3)	1.467(4)	N(1)—C(6)	1.184(6)
N(2)—C(12)	1.487(4)	C(3)—C(4)	1.460(4)
C(2)—C(3)	1.528(4)	C(4)—C(5)	1.536(5)
C(5)—C(6)	1.531(5)	C(6)—C(7)	1.520(4)
O(5)-S(1)-O(6)	120.9(2)	O(5)-S(1)-N(1)	109.8(2)
O(5)-S(1)-C(9)	106.0(2)	O(6)-S(1)-N(1)	106.2(1)
O(6)-S(1)-C(9)	108.2(2)	N(1)-S(1)-C(9)	104.7(1)
C(1)-O(1)-C(2)	116.1(3)	C(7)-O(4)-C(8)	114.8(3)
S(1)-N(1)-C(3)	122.0(2)	S(1)-N(1)-C(6)	122.2(2)
C(3)-N(1)-C(6)	113.4(3)	O(7)-N(2)-O(8)	121.5(4)
O(7)-N(2)-C(12)	119.4(4)	O(8)-N(2)-C(12)	119.1(4)
O(1)-C(2)-O(2)	125.1(3)	O(1)-C(2)-C(3)	112.4(3)
O(2)-C(2)-C(3)	122.6(3)	N(1)-C(3)-C(2)	112.6(2)
N(1)-C(3)-C(4)	103.3(3)	C(2)-C(3)-C(4)	110.8(3)
C(3)-C(4)-C(5)	105.0(3)	C(4)-C(5)-C(6)	104.0(3)
N(1)-C(6)-C(7)	110.9(2)	N(1)-C(6)-C(5)	102.2(3)
C(5)-C(6)-C(7)	110.8(3)	O(3)-C(7)-O(4)	124.6(3)
O(3)-C(7)-O(6)	124.4(3)	O(4)-C(7)-C(6)	110.9(2)
S(1)-C(9)-C(10)	119.8(2)	S(1)-C(9)-C(14)	119.0(2)
N(2)-C(12)-C(13)	118.7(3)	N(2)-C(12)-C(11)	118.1(3)

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