

INTRODUCTION OF FUNCTIONAL GROUPS INTO THE  $\alpha$ -POSITION OF  
N-ALKOXYCARBONYLPYRROLIDINES<sup>1</sup>

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Abstract — The reactions for the introduction of O-, S-, N-, and C-  
 functional groups into the  $\alpha$ -position of N-alkoxycarbonylpyrrolidines  
 using N-alkoxycarbonyl- $\alpha$ -ethoxypyrrrolidines are described.

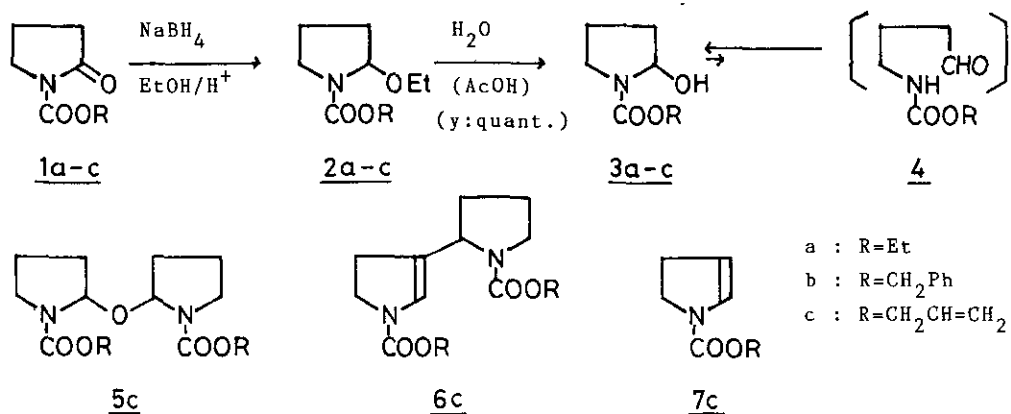
There are many well-known alkaloids, antibiotics and synthetic medicines with cyclic amine structures having various substituents (including fused rings) at the  $\alpha$ -position of nitrogen. Thus, reactions by which functional groups can be introduced into the  $\alpha$ -position of amines are presently of great interest.<sup>2</sup>

In the preceding paper,<sup>3</sup> we reported a convenient synthesis for  $\alpha$ -ethoxycarbamates (2) by the reduction of N-alkoxycarbonyllactams (1) with  $\text{NaBH}_4/\text{H}^+$  in ethanol. In the present research, the conversion of the ethoxy group of 2 into other functional groups is described.

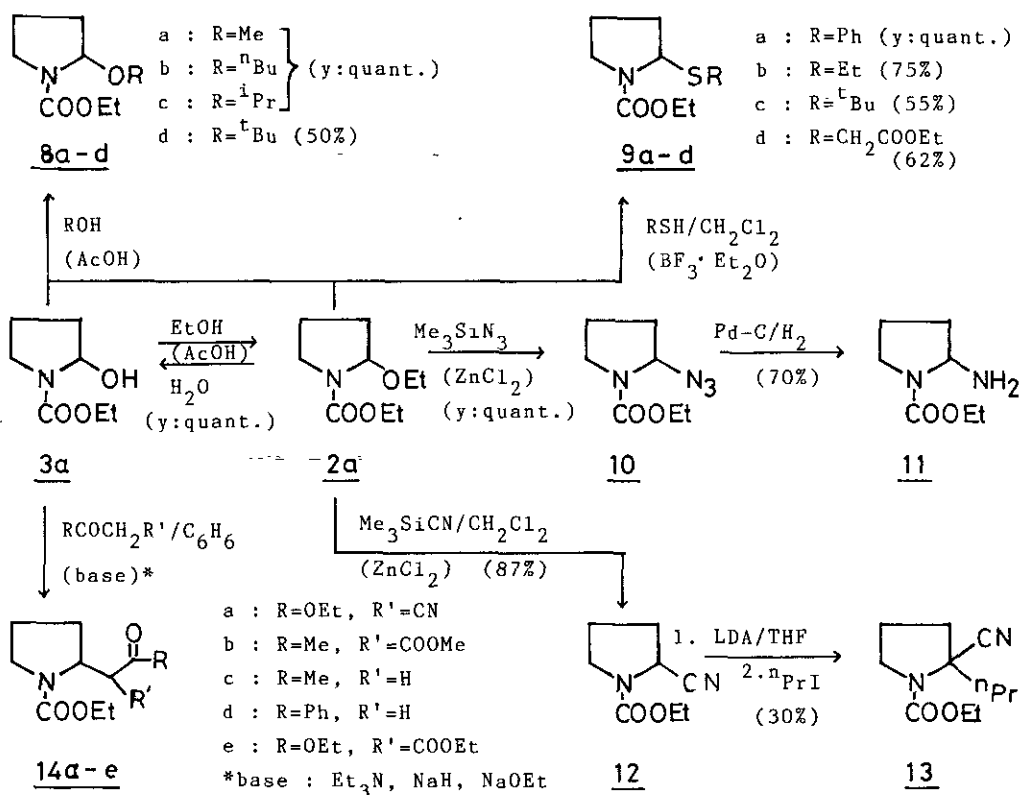
An investigation was first made of the synthesis of 2-hydroxycarbamate (3), which appears more reactive toward nucleophiles than 2-ethoxycarbamate (2), on the basis of a general idea of its equivalent isomer (4). Although the direct reduction of 1 to 3 could not be carried out successfully,<sup>4</sup> Hydrolysis of 2 in aqueous acetic acid gave 3 in nearly a quantitative yield. Other conditions (5% $\text{HCl}$ ,  $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ ,  $\text{ZnCl}_2/\text{CH}_2\text{Cl}_2$ ) for the hydrolysis of 2 caused contamination of 3 with the production of dimers 5 and 6 and enamine 7.<sup>5</sup>

Oxygen-functional Group: The refluxing of 2a or 3a in alcohols such as  $\text{MeOH}$ , n- $\text{BuOH}$ , and iso- $\text{PrOH}$  in the presence of a small amount of acetic acid gave the expected 2-alkoxycarbamates (8a-c) in quantitative yield. But the yield of 2-

Scheme 1



Scheme 2



tert-butoxy-carbamate (8d) using tert-butanol did not exceed 50%.

Sulfur-functional Group: The substitution of 2-ethoxy and 2-hydroxy groups with sulfur groups was carried out by stirring 2a or 3a at room temperature with mercaptanes in dichloromethane in the presence of a catalytic amount of trifluoroborane-etherate. The reaction proceeded very quickly with good yield. Without the catalyst, the starting materials could be recovered even though they melted at 100°C.

Nitrogen-functional Group: We have already reported the reaction for introducing amines, amides and carbamates into the  $\alpha$ -position of the pyrrolidine ring using 5-ethoxy- and 5-acetoxy-2-pyrrolidinones.<sup>6</sup> However, these conditions were not found adequate in the case of 2a in spite of much effort. Finally, the reaction of 2a with trimethylsilyl azide in the presence of a catalytic amount of zinc chloride in dichloromethane gave azidocarbamate (10) in quantitative yield. The catalytic hydrogenation of 10 with 5% palladium-carbon gave rather unstable aminocarbamate (11).

Carbon-functional Group: Asher<sup>7</sup> and Shono<sup>8</sup> reported the reaction of  $\alpha$ -methoxyamide or  $\alpha$ -methoxycarbamate with trimethylsilyl cyanide in the presence of a Lewis acid to give  $\alpha$ -cyanoamide or  $\alpha$ -cyanocarbamate, respectively, in high yield.  $\alpha$ -Cyanocarbamate (12), obtained from 2a in 87% yield by this method, was lithiated with lithium diisopropylamide in tetrahydrofuran and alkylated to give 2-cyano-2-n-propylcarbamate (13) in 30% yield. This reaction holds promise as a general method for introducing various carbon functional groups into the  $\alpha$ -position of cyclic amines.<sup>9</sup>

The reaction of 2-hydroxycarbamates (3) with several carbonyl compounds including a simple ketone such as acetone in the presence of a base was examined<sup>10</sup> and the results are shown in Table I. Although the reaction of 3 with cyanoacetate or acetoacetate proceeded in the presence of triethylamine, its reaction with acetone, acetophenone, and malonate required sodium ethoxide or sodium hydride. Sodium hydride in benzene was a suitable condition for this reaction to proceed. The infrared and proton nuclear magnetic resonance spectra of the 2-substituted N-alkoxycarbonylpyrrolidine derivatives<sup>11</sup> described in the present paper are listed in Table II.

The synthesis of alkaloids from these  $\alpha$ -ethoxycarbamates is presently being investigated and the results will be published in the near future.

Table I. Reactions of  $\alpha$ -Hydroxycarbamates (3) with Active Methylene Compounds

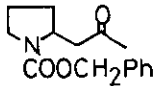
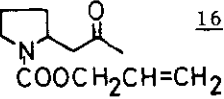
Run	Carbamate	Active Methylene Compound	Base/Solvent	Reflux Time (h)	Product	Yield (%)
1	<u>3a</u>	NCCH <sub>2</sub> CO <sub>2</sub> Et	Et <sub>3</sub> N/EtOH	42	<u>14a</u>	80
2	<u>3a</u>	NCCH <sub>2</sub> CO <sub>2</sub> Et	Et <sub>3</sub> N/C <sub>6</sub> H <sub>6</sub>	19	<u>14a</u>	88
3	<u>3a</u>	MeCOCH <sub>2</sub> CO <sub>2</sub> Me	Et <sub>3</sub> N/C <sub>6</sub> H <sub>6</sub>	22	<u>14b</u>	73
4	<u>3a</u>	MeCOMe	NaOEt/EtOH	44	<u>14c</u>	31
5	<u>3a</u>	MeCOMe	NaH/C <sub>6</sub> H <sub>6</sub>	44	<u>14c</u>	71
6	<u>3a</u>	PhCOMe	NaOEt/EtOH	16	<u>14d</u>	33
7	<u>3a</u>	PhCOMe	NaH/C <sub>6</sub> H <sub>6</sub>	16	<u>14d</u>	60
8	<u>3a</u>	CH <sub>2</sub> (CO <sub>2</sub> Et) <sub>2</sub>	NaH/C <sub>6</sub> H <sub>6</sub>	17	<u>14e</u>	40
9	<u>3b</u>	MeCOMe	NaH/C <sub>6</sub> H <sub>6</sub>	12		<u>15</u> 40
10	<u>3c</u>	MeCOMe	NaH/C <sub>6</sub> H <sub>6</sub>	9		<u>16</u> 70

Table II. IR and  $^1\text{H-NMR}$  Spectra of 2-Substituted  $\underline{\text{N}}$ -Alkoxy carbonylpyrrolidine Derivatives

Compound*	$^1\text{H-NMR}$	
	IR $\nu$ ( $\text{cm}^{-1}$ )	$\delta$ (ppm) ( $\text{CDCl}_3$ )
<u>3a</u>	( $\text{CHCl}_3$ ) 3575, 3425, 1690	1.27 (3H, t, $\underline{\text{J}}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 1.67-2.17 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.13-3.67 (3H, m, $\text{CH}_2\text{N}$ , OH), 4.17 (2H, q, $\underline{\text{J}}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 5.50 (1H, m, OCHN)
<u>3b</u>	( $\text{CHCl}_3$ ) 3575, 3430, 1680	1.80-2.12 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.31-3.80 (3H, m, $\text{CH}_2\text{N}$ , OH), 5.18 (2H, s, $\text{OCH}_2\text{Ph}$ ), 5.55 (1H, m, OCHN), 7.42 (5H, s, Ph)
<u>3c</u>	( $\text{CHCl}_3$ ) 3575, 3450 1690	1.70-2.31 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.20-3.78 (2H, m, $\text{CH}_2\text{N}$ ), 4.03 (1H, br, OH), 4.67 (2H, m, $\text{OCH}_2$ ), 5.16-5.47 (2H, m, $\text{CH}=\text{CH}_2$ ), 5.47-5.70 (1H, m, OCHN), 5.79-6.22 (1H, m, $\text{CH}=\text{CH}_2$ )
<u>5c</u>	(neat) 1700, 1100	1.70-2.29 (8H, m, $\text{CH}_2\text{CH}_2$ x 2), 3.21-3.70 (4H, m, $\text{CH}_2\text{N}$ x 2), 4.65 (4H, m, $\text{OCH}_2$ x 2), 5.15-5.46 (4H, m, $\text{CH}=\text{CH}_2$ x 2), 5.46-5.70 (2H, m, CHN x 2), 5.78-6.20 (2H, m, $\text{CH}=\text{CH}_2$ x 2)
<u>6c</u>	( $\text{CHCl}_3$ ) 1680, 1650	1.58-2.19 (4H, m, $\text{CH}_2\text{CH}_2$ ), 2.37-2.76 (2H, m, $\text{CH}_2\text{CH}_2\text{C}=\text{CH}$ ), 3.20-3.65 (2H, m, $\text{CH}_2\text{N}$ ), 3.72 (2H, t, $\underline{\text{J}}=9\text{Hz}$ , $\text{CH}_2\text{N}$ ), 4.57 (5H, m, $\text{OCH}_2$ x 2, $\text{C}=\text{CCHN}$ ), 5.07-5.50 (4H, m, $\text{CH}=\text{CH}_2$ x 2), 5.72-6.20 (2H, m, $\text{CH}=\text{CH}_2$ x 2), 6.42 (1H, m, $\text{NCH}=\text{C}$ )
<u>7c</u>	(neat) 1710, 1620	2.46-2.83 (2H, m, $\text{CH}_2\text{CH}_2\text{N}$ ), 3.77 (3H, t, $\underline{\text{J}}=9\text{Hz}$ , $\text{CH}_2\text{N}$ ), 4.60 (2H, m, $\text{OCH}_2$ ), 5.20 (1H, m, $\text{NCH}=\text{CH}$ ), 5.0-5.48 (2H, m, $\text{CH}=\text{CH}_2$ ), 5.72-6.30 (1H, m, $\text{CH}=\text{CH}_2$ ), 6.60 (1H, br s, $\text{NCH}=\text{CH}$ )
<u>8a</u>	(neat) 1700, 1080	1.25 (3H, t, $\underline{\text{J}}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.50-2.30 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.22-3.64 (2H, m, $\text{CH}_2\text{N}$ ), 3.33 (3H, s, $\text{OCH}_3$ ), 4.18 (2H, q, $\underline{\text{J}}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 5.20 (1H, m, OCHN)
<u>8b</u>	(neat) 1700, 1090	0.89 (3H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.00-2.10 (8H, m, $\text{CH}_2\text{CH}_2$ x 2), 1.24 (3H, t, $\underline{\text{J}}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 3.12-3.63 (4H, m, $\text{CH}_2\text{N}$ , $\text{OCH}_2\text{CH}_2$ ), 4.17 (2H, q, $\underline{\text{J}}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 5.26 (1H, m, OCHN)

(Continued)  
8c

(neat) 1700, 1090	1.15 (3H, d, $\underline{J}$ =7Hz, $\text{CHCH}_3$ ), 1.17 (3H, d, $\underline{J}$ =7Hz, $\text{CHCH}_3$ ), 1.29 (3H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3$ ), 1.51-2.19 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.49 (2H, m, $\text{CH}_2\text{N}$ ), 4.18 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 5.32 (1H, m, $\text{OCHN}$ )
(neat) 1700, 1100	1.20 (3H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3$ ), 1.23 (9H, s, $^t\text{Bu}$ ), 1.55-2.20 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.09-3.58 (2H, m, $\text{CH}_2\text{N}$ ), 4.12 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 5.32 (1H, m, $\text{OCHN}$ )
(neat) 1700	1.18 (3H, m, $\text{CH}_2\text{CH}_3$ ), 1.66-2.42 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.42 (2H, m, $\text{CH}_2\text{N}$ ), 4.10 (2H, m, $\text{OCH}_2\text{CH}_3$ ), 5.42 (1H, m, $\text{SCHN}$ ), 7.30-7.83 (5H, m, Ph)
(neat) 1700	1.25 (6H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3 \times 2$ ), 1.8-2.3 (4H, m, $\text{CH}_2\text{CH}_2$ ), 2.5-2.9 (2H, m, $\text{SCH}_2\text{CH}_3$ ), 3.3-3.6 (2H, m, $\text{CH}_2\text{N}$ ), 4.15 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 5.25 (1H, m, $\text{NCHS}$ )
(neat) 1700	1.25 (3H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3$ ), 1.36 (9H, s, $^t\text{Bu}$ ), 1.60-2.41 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.21-3.36 (2H, m, $\text{CH}_2\text{N}$ ), 4.18 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 5.20 (1H, m, $\text{SCHN}$ )
(neat) 1730, 1690	1.20 (3H, t, $\underline{J}$ =7.5Hz, $\text{OCH}_2\text{CH}_3$ ), 1.22 (3H, t, $\underline{J}$ =7.5Hz, $\text{OCH}_2\text{CH}_3$ ), 1.7-2.3 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.2-3.7 (4H, m, $\text{CH}_2\text{N}$ , $\text{SCH}_2$ ), 3.95-4.30 (4H, m, $\text{OCH}_2\text{CH}_3 \times 2$ ), 5.40 (1H, d, $\underline{J}$ =6Hz, $\text{NCHS}$ )
(neat) 2110, 1710	1.30 (3H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3$ ), 1.90 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.10-3.75 (2H, m, $\text{CH}_2\text{N}$ ), 4.23 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 5.61 (1H, m, $\text{NCHN}$ )
(neat) 3400, 3300, 1700	1.28 (3H, t, $\underline{J}$ =7.5Hz, $\text{CH}_2\text{CH}_3$ ), 1.5-2.5 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.42 (2H, t, $\underline{J}$ =6Hz, $\text{CH}_2\text{N}$ ), 4.15 (2H, q, $\underline{J}$ =7.5Hz, $\text{CH}_2\text{CH}_3$ ), 4.78 (1H, m, $\text{NCHN}$ )
(neat) 2240, 1700	1.30 (3H, t, $\underline{J}$ =7Hz, $\text{CH}_2\text{CH}_3$ ), 1.98-2.41 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.22-3.64 (2H, m, $\text{CH}_2\text{N}$ ), 4.23 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 4.59 (1H, m, $\text{NCHCN}$ )
(neat) 2240, 1700	0.95 (3H, t, $\underline{J}$ =6Hz, $\text{CH}_2\text{CH}_3$ ), 1.25 (3H, t, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ ), 1.3-2.6 (8H, m, $\text{CH}_2\text{CH}_2 \times 2$ ), 3.2-3.8 (2H, m, $\text{CH}_2\text{N}$ ), 4.17 (2H, q, $\underline{J}$ =7Hz, $\text{OCH}_2\text{CH}_3$ )

(Continued)**				
<u>14a</u>	(neat)	2250, 1750, 1690	1.21 (3H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.25 (3H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.73-2.33 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.47 (1H, m, $\text{CHCN}$ ), 3.50 (2H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{N}$ ), 4.07-4.43 (4H, m, $\text{OCH}_2\text{CH}_3 \times 2$ ), 4.70-4.80 (1H, m, $\text{CHN}$ )	
<u>14b</u> **	( $\text{CHCl}_3$ )	1740, 1710, 1690	1.23 (3H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.67-2.03 (4H, m, $\text{CH}_2\text{CH}_2$ ), 2.13 (3H, s, $\text{COCH}_3$ ), 3.13-3.57 (2H, m, $\text{CH}_2\text{N}$ ), 3.73 (3H, s, $\text{OCH}_3$ ), 4.11 (2H, q, $\underline{J}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 4.15 (1H, m, $\text{COCHCO}$ ), 4.33-4.47 (1H, m, $\text{CHN}$ )	
<u>14c</u>	( $\text{CHCl}_3$ )	1710, 1680	1.27 (3H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.57-2.60 (6H, m, $\text{CH}_2\text{CH}_2$ , $\text{CH}_2\text{CO}$ ), 2.17 (3H, s, $\text{COCH}_3$ ), 3.40 (2H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{N}$ ), 4.13 (2H, q, $\underline{J}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 4.15 (1H, m, $\text{CHN}$ )	
<u>14d</u>	( $\text{CHCl}_3$ )	1690, 1670	1.27 (3H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3$ ), 1.73-2.00 (5H, m, $\text{CH}_2\text{CH}_2$ , $\text{HCHCO}$ ), 2.53-2.97 (1H, m, $\text{HCHCO}$ ), 3.33-3.50 (2H, m, $\text{CH}_2\text{N}$ ), 4.13 (2H, q, $\underline{J}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 4.30-4.43 (1H, m, $\text{CHN}$ ), 7.43-7.60, 7.97-8.07 (5H, m, Ph)	
<u>14e</u>	(neat)	1740, 1700	1.25 (9H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{CH}_3 \times 3$ ), 1.60-2.30 (4H, m, $\text{CH}_2\text{CH}_2$ ), 3.30 (2H, m, $\text{CH}_2\text{N}$ ), 3.60 (1H, m, $\text{CH}(\text{COOEt})_2$ ), 4.15 (2H, q, $\underline{J}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3$ ), 4.20 (4H, q, $\underline{J}=7\text{Hz}$ , $\text{OCH}_2\text{CH}_3 \times 2$ ), 4.38 (1H, m, $\text{CHN}$ )	
<u>15</u>	(neat)	1740, 1700	1.40-2.17 (4H, m, $\text{CH}_2\text{CH}_2$ ), 2.12 (3H, br s, $\text{COCH}_3$ ), 2.22-3.20 (2H, m, $\text{CH}_2\text{CO}$ ), 3.30-3.54 (2H, m, $\text{CH}_2\text{N}$ ), 4.07-4.38 (1H, m, $\text{CHN}$ ), 5.20 (2H, s, $\text{PhCH}_2$ ), 7.41 (5H, s, Ph)	
<u>16</u>	(neat)	1740, 1700	1.60-2.09 (4H, m, $\text{CH}_2\text{CH}_2$ ), 2.17 (3H, s, $\text{COCH}_3$ ), 2.29-3.28 (2H, m, $\text{CH}_2\text{CO}$ ), 3.42 (2H, t, $\underline{J}=7\text{Hz}$ , $\text{CH}_2\text{N}$ ), 4.09-4.39 (1H, m, $\text{CHN}$ ), 4.60 (2H, m, $\text{OCH}_2\text{CH}=\text{C}$ ), 5.12-5.45 (2H, m, $\text{CH}=\text{CH}_2$ ), 5.77-6.21 (1H, m, $\text{CH}=\text{CH}_2$ )	

\* All synthesized compounds were oils, which gave satisfactory elemental analyses and/or mass spectra.

\*\* This compound appears a single product judging from its NMR spectrum and TLC spot.

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