Efficient Synthesis of β-Oxoalkyl Carbamates from Carbon Dioxide, Internal Propargylic Alcohols, and Secondary Amines Catalyzed by Silver Salts and DBU

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Abstract: The three-component reaction of internal propargylic alcohols with secondary amines and carbon dioxide proceeded smoothly in the presence of a catalyst system comprising a silver salt and 1,8-diazabicyclo[5.4.0]undec-7-ene in 1,4-dioxane at 90 °C to give the corresponding β-oxoalkyl carbamates in good to high yields. The counterion of the silver salt had little effect on the reaction whereas the nature of the organic base had a marked influence.

Key words: amines, carbamates, carbon dioxide, catalysis, propargylic alcohols

Chemical fixation of carbon dioxide into valuable organic compounds is of great interest in connection with the protection of the environment and the utilization of carbon resources.[1] Carbon dioxide is abundant, nontoxic, nonflammable, and renewable. There are many possibilities for using carbon dioxide as a safe and cheap C_1 feedstock in organic synthesis. One of the most important methods in this field is the direct synthesis of carbamates, in which carbon dioxide is used as a clean and safe starting material to replace toxic phosgene or isocyanates.[2] Organic carbamates are very important precursors that are widely used in agriculture as pesticides, fungicides, and herbicides; in pharmacology as pharmaceuticals; and in the chemical industry as intermediates.[3] Carbamates are also useful as protective groups for amine functions in peptide synthesis.[4]

The one-pot, three-component, coupling reaction of propargylic alcohols, secondary amines, and carbon dioxide is a promising route to β-oxoalkyl carbamates. Although a number of catalysts have been developed for this reaction, including ruthenium complexes,[5] iron complexes,[6] and lanthanide chlorides,[7] their activity and/or selectivity is low, and only terminal propargylic alcohols have been investigated for use in these reactions. Copper complexes that are based on macrocycles containing a ferrocene group show a high activity for terminal propargylic alcohols, but when the internal propargylic alcohol 2-methyl-4-phenylbut-3-yn-2-ol was subjected to the reaction, the yield of carbamate fell sharply.[8]

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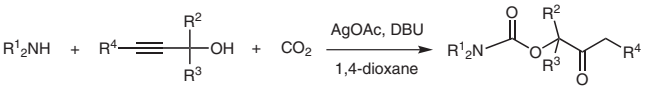
As part of our continuous efforts to fix carbon dioxide chemically,[9] we found that β-oxopropyl carbamates could be synthesized efficiently through coupling of propargylic alcohols, secondary amines, and carbon dioxide in the absence of any added catalyst or organic solvent under compressed carbon dioxide.[10] In our further explorations of the scope of this reaction, we also found that only terminal propargylic alcohols could be used and that internal propargylic alcohols showed almost no conversion into the desired products. This suggested that internal propargylic alcohols are less active than terminal ones and that they may need activating by an active catalyst.

With the goal of broadening the scope of the method, we examined the reactions of several inactive internal propargylic alcohols with secondary amines and carbon dioxide catalyzed by silver salts and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), in which various internal propargylic alcohols were activated and converted into the corresponding β-oxoalkyl carbamates in good to high yields (Scheme 1).



1a: diethylamine
1b: dipropylamine
1c: dibutylamine
1d: diallylamine
1e: pyrrolidine
1f: morpholine

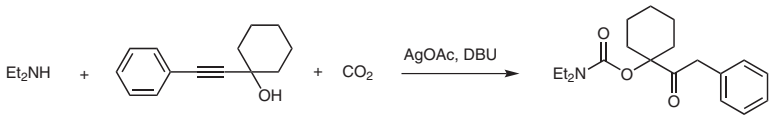
2a: R^2–R^3 = -$[CH_2]_5$-, R^4 = Ph
2b: R^2 = R^3 = Me, R^4 = Ph
2c: R^2 = Me, R^3 = H, R^4 = Ph
2d: R^2–R^3 = -$[CH_2]_5$-, R^4 = Me
2e: R^2 = R^3 = Me, R^4 = 4-$MeOC_6H_4$
2f: R^2 = R^3 = H, R^4 = Ph

Scheme 1 Synthesis of β-oxoalkyl carbamates from internal propargylic alcohols, secondary amines, and carbon dioxide

We first examined the reaction of diethylamine (**1a**) with 1-(phenylethynyl)cyclohexanol (**2a**) and carbon dioxide under various conditions, and the results of these studies are presented in Table 1. We have previously shown that internal propargylic alcohols activated by silver salts can react with primary amines and carbon dioxide to afford 4-alkylidene-1,3-oxazolidin-2-ones.[9f] However, silver salts, such as silver acetate, alone did not catalyze the corresponding reaction of internal propargylic alcohols to give the corresponding carbamates under 2 MPa of CO_2 at 50 °C (Table 1, entry 1). To our delight however, when 30 mol% of DBU was added, the reaction took place and the

desired product, 1-(phenylacetyl)cyclohexyl diethylcarbamate (**3a**) was obtained in 28% yield (entry 2), along with (4*Z*)-4-benzylidene-1,3-dioxaspiro[4.5]decan-2-one, which was formed by incorporation of carbon dioxide into **2a** and obtained in 40% isolated yield.[11] A control experiment showed that DBU alone did not catalyze the reaction (entry 3). The presence of both the silver salt and DBU is therefore required for the reaction to occur. Raising the reaction temperature and prolonging the reaction time seem to favor the reaction. A yield of 89% was obtained when the reaction was performed at 90 °C for 15 h (entries 2, 4-6). However increasing the temperature from 90 °C to 110 °C led to a marked decrease in yield as a result of decomposition of product **2a** to give cyclohexanone and benzaldehyde as major byproducts (entry 7). The effect of the solvent was also evaluated (entries 6, 9–11). The use of 1,4-dioxane as the solvent gave a higher yield than was obtained in toluene, dichloromethane, or

Table 1 Optimization of the Synthesis of 1-(Phenylacetyl)cyclohexyl Diethylcarbamate (**3a**) by the Reaction of Diethylamine (**1a**), 1-(Phenylethynyl)cyclohexanol (**2a**) and Carbon Dioxide



Entry[a]	Catalyst	Base	Solvent	Temp(°C)	Time (h)	Yield (%)[b]
1	AgOAc	none	1,4-dioxane	50	10	0
2	AgOAc	DBU	1,4-dioxane	50	10	28
3	none	DBU	1,4-dioxane	50	10	0
4	AgOAc	DBU	1,4-dioxane	50	15	43
5	AgOAc	DBU	1,4-dioxane	70	15	73
6	AgOAc	DBU	1,4-dioxane	90	15	89
7	AgOAc	DBU	1,4-dioxane	110	15	76
8	AgOAc	none	1,4-dioxane	90	15	13
9	AgOAc	DBU	toluene	90	15	82
10	AgOAc	DBU	CH_2Cl_2	90	15	70
11	AgOAc	DBU	THF	90	15	86
12	AgOAc	DBU	none	90	15	62
13	AgOAc	DBU	none[c]	90	15	68
14	AgOAc	none	none[c]	120	24	41
15	$AgNO_3$	DBU	1,4-dioxane	90	15	85
16	$AgBF_4$	DBU	1,4-dioxane	90	15	84
17	Ag_2CO_3	DBU	1,4-dioxane	90	15	84
18	AgOAc	DABCO	1,4-dioxane	90	15	17
19	AgOAc	DMAP	1,4-dioxane	90	15	15
20	AgOAc	pyrridine	1,4-dioxane	90	15	21
21	AgOAc	Et_3N	1,4-dioxane	90	15	10
22	$FeCl_3$	DBU	1,4-dioxane	90	15	0
23	$PdCl_2$	DBU	1,4-dioxane	90	15	0
24	$SnCl_2$	DBU	1,4-dioxane	90	15	0
25	CuCl	DBU	1,4-dioxane	90	15	27

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), catalyst (0.075 mmol), base (0.15 mmol), solvent (1.5 mL), CO_2 (2 MPa).
[b] Isolated yield.
[c] The reaction was performed under 8 MPa of CO_2 without any additional organic solvent.

tetrahydrofuran. Moreover, a lower yield was also obtained when the reaction was carried out under neat or supercritical conditions (entries 12−13). Note that even at higher temperature or in supercritical carbon dioxide, the presence of DBU appears to be necessary to obtain satisfactory results (entries 8, 14). For example, in the absence of DBU at 90 °C in 1,4-dioxane, the reaction gave only a 13% yield of the carbamate, and most of the alcohol **2a** remained unreacted and could be recovered (entry 8).

We also investigated the catalytic activities of several other silver salts such as silver nitrate, silver tetrafluoroborate, and silver carbonate (entries 15-17) and we found that the counterion of the silver salt had little effect on the reaction. On the other hand, the nature of the organic base had a marked effect on the reaction. Replacement of DBU with other organic bases such as 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-(*N*,*N*-dimethylamino)pyridine (DMAP), pyridine, or triethylamine led to marked reductions in the yield, and large amounts of unreacted alcohol were recovered (entries 18−21). With other metal salts such as iron(III) chloride, palladium(II) chloride, tin(II) chloride, or copper(I) chloride as catalysts, trace or low yields of the product were obtained and most of the alcohol remained unreacted (entries 22-25). Therefore, the optimum reaction conditions are as follows: diethylamine (**1a**, 0.5 mmol), 1-(phenylethynyl)cyclohexanol (**2a**, 0.5 mmol), 1,4-dioxane (1.5 mL), AgOAc (0.075 mmol), DBU (0.15 mmol), a temperature of 90 °C, a CO_2 pressure of 2 MPa, and a reaction time of 15 hours.

A single crystal of product **3a** was obtained by slow crystallization from a mixture of petroleum ether and ethyl acetate, and its structure was established by single-crystal X-ray analysis (Figure 1).

With the optimized reaction conditions in hand, we extended the process to a variety of internal propargylic alcohols and secondary amines. Some representative examples are listed in Table 2. The reaction between 1-(phenylethynyl)cyclohexanol (**2a**) and various secondary amines[12] **1a–f** occurred smoothly to give desired β-oxoalkylcarbamate in yields of 80–93% (Table 2, entries 1−6). However, when bulky diisopropylamine (**1g**) was subjected to the reaction, none of the desired carbamate was detected and the cyclic carbonate (4*Z*)-4-benzylidene-1,3-dioxaspiro[4.5]decan-2-one was obtained in 18% yield (entry 7). Other internal tertiary propargylic alcohols (**2b**, **2d**, and **2e**), a secondary propargylic alcohol (**2c**), and a primary propargylic alcohol (**2f**) also underwent reaction with various secondary amines to give the corresponding products in good-to-high yields (entries 8−19). Note that the less-hindered alkyne **2f** did not react with **1g** to afford the desired product under the optimized conditions but instead gave the cyclic carbonate 4-benzylidene-1,3-dioxolan-2-one in 8% yield (entry 20).

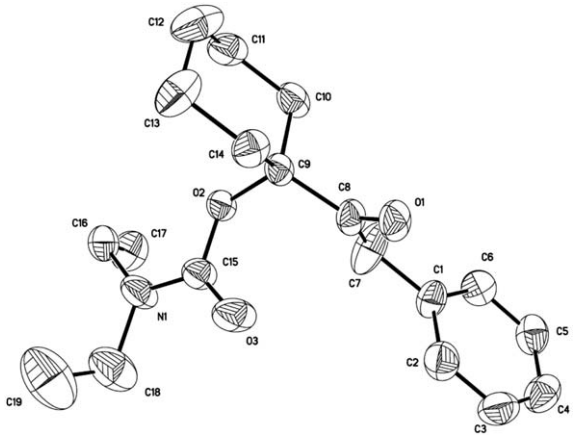
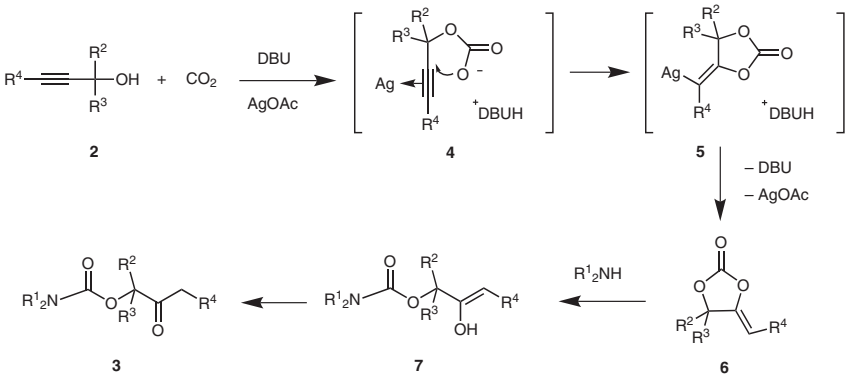


Figure 1 X-ray crystal structure of **3a**; ellipses are shown at the 30% probability level

On the basis of previous reports[5a,b,9e,f,10,13] and our experimental results, a plausible mechanism for the reaction is postulated in Scheme 2. Firstly, the *Z*-alkylidene cyclic carbonate **6** is formed through incorporation of carbon dioxide into the internal propargylic alcohol in the presence of silver acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene via **4** and **5**. The carbonate **6** then undergoes nucleophilic addition with the secondary amine to give the intermediate **7**, which tautomerizes to give the corresponding carbamate **3**.

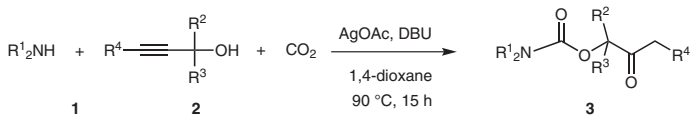
In conclusion, we have developed a convenient and efficient one-pot synthesis of β-oxoalkyl carbamates from carbon dioxide as a starting material. Cooperation between the silver salt and 1,8-diazabicyclo[5.4.0]undec-7-ene is a key factor in activating the transformation. This study extends the range of substrates that can be used in



Scheme 2 Proposed mechanism for the formation of carbamates

the three-component reaction of propargylic alcohols, secondary amines, and carbon dioxide. Further studies on efficient chemical transformations of carbon dioxide into valuable fine chemicals are ongoing in our laboratory.

Table 2 Reactions of Various Propargylic Alcohols, Secondary Amines, and Carbon Dioxide in the Presence of Silver Acetate and 1,8-Diazabicyclo[5.4.0]undec-7-ene



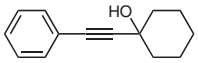
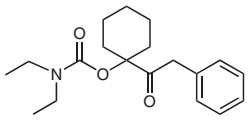
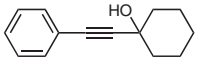
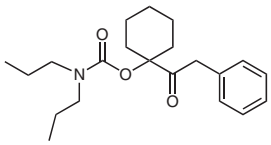
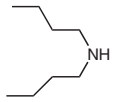
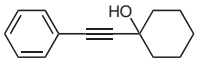
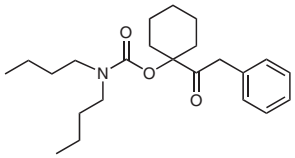
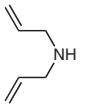
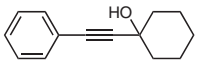
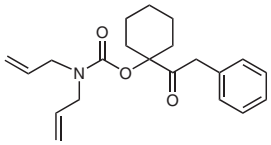
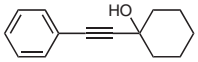
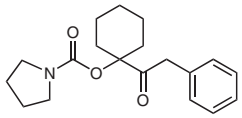
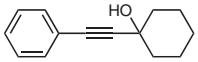
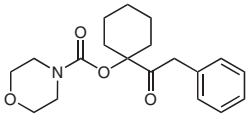
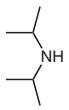
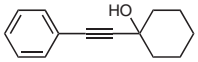
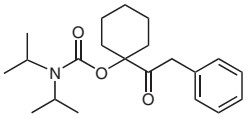
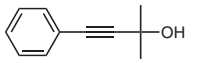
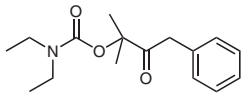
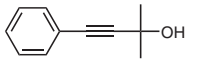
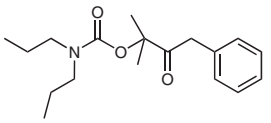
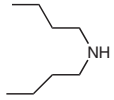
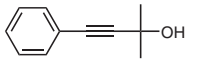
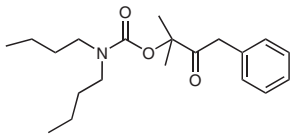
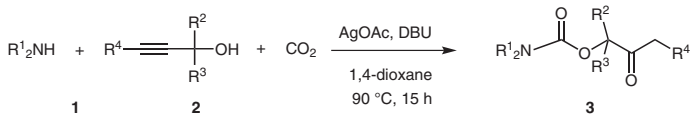
Entry[a]	Amine		Propargylic alcohol		Conversion[b] (%)	Product		Yield[c] (%)
1	**1a**		**2a**		quant	**3a**		89
2	**1b**		**2a**		99	**3b**		88
3	**1c**		**2a**		98	**3c**		85
4	**1d**		**2a**		quant	**3d**		93
5	**1e**		**2a**		98	**3e**		80
6	**1f**		**2a**		97	**3f**		74
7	**1g**		**2a**		98	**3g**		0
8	**1a**		**2b**		97	**3h**		87
9	**1b**		**2b**		98	**3i**		88
10	**1c**		**2b**		97	**3j**		85

Table 2 Reactions of Various Propargylic Alcohols, Secondary Amines, and Carbon Dioxide in the Presence of Silver Acetate and 1,8-Diazabicyclo[5.4.0]undec-7-ene (continued)



Entry[a]	Amine	Propargylic alcohol	Conversion[b] (%)	Product	Yield[c] (%)
11	**1d**	**2b**	99	**3k**	86
12	**1e**	**2b**	91	**3l**	82
13	**1a**	**2c**	90	**3m**	87
14	**1b**	**2c**	92	**3n**	82
15	**1d**	**2c**	97	**3o**	90
16	**1a**	**2d**	93	**3p**	89
17	**1c**	**2d**	quant	**3q**	84
18	**1a**	**2e**	quant	**3r**	70
19	**1d**	**2f**	74	**3s**	73
20	**1g**	**2f**	12	**3t**	0

[a] Reaction conditions: secondary amine (0.5 mmol), alcohol (0.5 mmol), AgOAc (0.075 mmol), DBU (0.15 mmol), 1,4-dioxane (1.5 mL), CO_2 (2 MPa), 90 °C, 15 h.
[b] Determined by GC analysis.
[c] Isolated yield.

^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. GC analyses were performed on a GC-7900 chromatograph with a flame-ionization detector and equipped with an AT.SE-30 capillary column (internal diameter = 0.32 mm, length = 30 m). Mass spectra were recorded on a Shimadzu GCMS–QP5050A mass spectrometer operating at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30

m). IR spectra were recorded on a Bruker Tensor 27 spectrometer. Melt points were recorded on a Büchi B-545 instrument. All starting materials and catalysts were commercially purchased and used without further purification. Crystallographic data for compound 3a have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 764657; copies can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033 or email: deposit@ccdc.cam.ac. uk].

Carbamates 3; General Procedure

A 15 mL poly(tetrafluoroethylene) reaction vessel was charged with secondary amine **1** (0.5 mmol), propargylic alcohol **2** (0.5 mmol), AgOAc (0.075 mmol), and DBU (0.015 mmol). The vessel was loaded into a stainless-steel autoclave with a pressure-regulating system, and the autoclave was sealed. CO_2 was introduced from a cylinder and the reaction was carried out at the selected temperature under magnetic stirring for the required reaction time. A constant pressure of CO_2 was maintained during the reaction. When the reaction was complete, the vessel was cooled in an ice bath and the pressure was slowly released to atmospheric pressure. The residual material was extracted with Et_2O. The products were purified by column chromatography [silica gel, petroleum–EtOAc (10:1)], and identified by MS and ^1H and ^{13}C NMR spectrometry.

1-(Phenylacetyl)cyclohexyl Diethylcarbamate (3a)

White solid; mp 74–75 °C.

IR (KBr): 2935, 2863, 1695, 1427, 1274, 1132, 987, 772, 702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 7.2 Hz, 3 H), 1.22–1.28 (m, 4 H), 1.50–1.55 (m, 2 H), 1.63–1.71 (m, 5 H), 2.11–2.14 (m, 2 H), 3.32 (q, *J* = 7.2 Hz, 2 H), 3.41 (q, *J* = 7.2 Hz, 2 H), 3.77 (s, 2 H), 7.20–7.30 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.2, 21.3, 24.9, 31.1, 41.5, 41.7, 41.9, 84.4, 126.3, 128.1, 129.6, 134.8, 154.2, 207.1.

MS (70 eV): *m/z* (%) = 317 [M^+], 226, 100 (100), 72, 44, 28.

Anal. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57; N, 4.41. Found: C, 71.78; H, 8.64; N, 4.52.

1-(Phenylacetyl)cyclohexyl Dipropylcarbamate (3b)

Orange oil.

IR (KBr): 2935, 2867, 1791, 1432, 1245, 1170, 766 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H), 1.22–1.28 (m, 1 H), 1.56–1.73 (m, 11 H), 2.13–2.16 (m, 2 H), 3.26 (q, *J* = 7.2 Hz, 2 H), 3.33 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 2 H), 7.22–7.33 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 21.2, 21.3, 21.6, 25.0, 31.2, 41.9, 48.8, 49.3, 84.4, 126.3, 128.1, 129.6, 134.9, 154.2, 207.2.

MS (70 eV): *m/z* (%) = 345 [M^+], 254, 128 (100), 109, 91, 43.

Anal. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.04; N, 4.05. Found: C, 73.28; H, 8.91; N, 4.13.

1-(Phenylacetyl)cyclohexyl Dibutylcarbamate (3c)

Orange oil.

IR (KBr): 2938, 2870, 1684, 1427, 1260, 1107, 766, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H), 1.20–1.48 (m, 5 H), 1.50–1.75 (m, 11 H), 2.10–2.14 (m, 2 H), 3.27 (q, *J* = 7.6 Hz, 2 H), 3.35 (q, *J* = 7.6 Hz, 2 H), 3.78 (s, 2 H), 7.22–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.9, 20.1, 21.5, 25.1, 30.2, 31.0, 31.3, 42.0, 47.1, 47.2, 84.6, 126.5, 128.2, 129.8, 135.0, 154.7, 207.2.

MS (70 eV): *m/z* (%) = 373 [M^+], 282, 156 (100), 109, 91, 58.

Anal. Calcd for $C_{23}H_{35}NO_3$: C, 73.96; H, 9.44; N, 3.75. Found: C, 73.83; H, 9.60; N, 3.82.

1-(Phenylacetyl)cyclohexyl Diallylcarbamate (3d)

Orange oil.

IR (KBr): 3077, 3027, 2936, 2860, 1695, 1457, 1413, 1295, 929, 770, 704 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.28 (m, 1 H), 1.48–1.57 (m, 2 H), 1.62–1.70 (m, 5 H), 2.11–2.15 (m, 2 H), 3.76 (s, 2 H), 3.91 (d, *J* = 5.6 Hz, 2 H), 3.97 (d, *J* = 5.6 Hz, 2 H), 5.16–5.23 (m, 4 H), 5.78–5.86 (m, 2 H), 7.19–7.28 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 25.1, 31.3, 42.1, 49.0, 49.1, 85.2, 116.9, 117.2, 126.6, 128.2, 129.9, 133.2, 133.4, 134.9, 154.6, 206.9.

MS (70 eV): *m/z* (%) = 341 [M^+], 250, 124 (100), 91, 41.

Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.87; H, 7.97; N, 4.10. Found: C, 73.75; H, 8.11; N, 4.23.

1-(2-Phenylacetyl)cyclohexyl Pyrrolidine-1-carboxylate (3e)

White solid; mp 116–117 °C.

IR (KBr): 2937, 2869, 1691, 1417, 1333, 1253, 1093, 718 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.27 (m, 1 H), 1.52–1.58 (m, 2 H), 1.64–1.71 (m, 5 H), 1.89–1.98 (m, 4 H), 2.14–2.17 (m, 2 H), 3.43 (t, *J* = 6.8 Hz, 2 H), 3.51 (q, *J* = 6.8 Hz, 2 H), 3.85 (s, 2 H), 7.21–7.32 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 24.9, 25.2, 25.8, 31.4, 42.3, 46.1, 46.2, 84.5, 126.5, 128.2, 129.9, 135.0, 153.6, 207.5.

MS (70 eV): *m/z* (%) = 315 [M^+], 224, 98 (100), 70, 55, 28.

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.22; H, 8.08; N, 4.31.

1-(Phenylacetyl)cyclohexyl Morpholine-4-carboxylate (3f)

White solid; mp 102–103 °C.

IR (KBr): 2932, 2857, 1694, 1426, 1234, 1119, 765, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.19–1.26 (m, 1 H), 1.47–1.53 (m, 2 H), 1.64–1.71 (m, 5 H), 2.11–2.14 (m, 2 H), 3.47−3.61 (m, 4 H), 3.69–3.72 (m, 4 H), 3.79 (s, 2 H), 7.20–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 25.1, 31.3, 42.3, 43.9, 44.8, 66.7, 85.1, 126.6, 128.3, 129.8, 134.7, 153.9, 206.8.

MS (70 eV): *m/z* (%) = 331 [M^+], 240, 114 (100), 91, 70, 42, 28.

Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.98; H, 7.42; N, 4.32.

1,1-Dimethyl-2-oxo-3-phenylpropyl Diethylcarbamate (3h)

Orange oil.

IR (KBr): 2980, 1699, 1430, 1284, 1154, 1060, 775, 722 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.15–1.20 (m, 6 H), 1.48 (s, 6 H), 3.25–3.48 (m, 4 H), 3.79 (s, 2 H), 7.20–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.2, 24.0, 41.7, 41.9, 42.1, 83.2, 126.6, 128.3, 129.8, 134.8, 154.7, 206.9.

MS (70 eV): *m/z* (%) = 277 [M^+], 186, 100 (100), 72, 28.

Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.01; H, 8.55; N, 5.12.

1,1-Dimethyl-2-oxo-3-phenylpropyl Dipropylcarbamate (3i)

Orange oil.

IR (KBr): 2966, 2875, 1694, 1466, 1423, 1250, 1148, 727 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H), 1.48 (s, 6 H), 1.55–1.65 (m, 4 H), 3.20–3.26 (m, 4 H), 3.79 (s, 2 H), 7.21–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 21.2, 21.8, 23.9, 42.0, 48.8, 49.3, 83.2, 126.6, 128.2, 129.8, 134.9, 155.1, 206.8.

MS (70 eV): *m/z* (%) = 305 [M$^+$], 214, 128 (100), 86, 43.

Anal. Calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59. Found: C, 71.01; H, 8.88; N, 4.51.

1,1-Dimethyl-2-oxo-3-phenylpropyl Dibutylcarbamate (3j)
Orange oil.

IR (KBr): 2965, 2868, 1696, 1465, 1252, 1152, 1150, 772, 727 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 1.30–1.37 (m, 4 H), 1.48 (s, 6 H), 1.51–1.58 (m, 4 H), 3.22–3.29 (m, 4 H), 3.79 (s, 2 H), 7.22–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.9, 23.9, 30.2, 30.9, 42.0, 46.8, 47.1, 83.2, 126.6, 128.2, 129.8, 134.9, 155.1, 206.8.

MS (70 eV): *m/z* (%) = 333 [M$^+$], 242, 156 (100), 91, 57, 29.

Anal. Calcd for $C_{20}H_{31}NO_3$: C, 72.04; H, 9.37; N, 4.20. Found: C, 71.84; H, 9.48; N, 4.25.

1,1-Dimethyl-2-oxo-3-phenylpropyl Diallylcarbamate (3k)
Orange oil.

IR (KBr): 3076, 3026, 2973, 2866, 1698, 1465, 1250, 1151, 1150, 772, 726 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 6 H), 3.78 (s, 2 H), 3.94 (d, *J* = 4.8 Hz, 4 H), 5.15–5.19 (m, 4 H), 5.75–5.83 (m, 2 H), 7.20–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 42.1, 49.0, 49.2, 83.7, 116.8, 117.3, 126.6, 128.3, 129.8, 133.2, 133.4, 134.9, 154.9, 206.7.

MS (70 eV): *m/z* (%) = 301 [M$^+$], 210, 124 (100), 91, 65, 41, 28.

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.42; H, 7.78; N, 4.66.

1,1-Dimethyl-2-oxo-3-phenylpropyl Pyrrolidine-1-carboxylate (3l)
White solid; mp 74–75 °C

IR (KBr): 2975, 2876, 1688, 1405, 1153, 1056, 769, 729 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 6 H), 1.85–1.93 (m, 4 H), 3.37–3.44 (m, 4 H), 3.83 (s, 2 H), 7.21–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 24.9, 25.7, 42.3, 46.1, 83.1, 126.6, 128.2, 129.8, 134.8, 153.8, 207.1.

MS (70 eV): *m/z* (%) = 275 [M$^+$], 184, 98 (100), 55, 41.

Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.97; H, 7.59; N, 5.12.

1-Methyl-2-oxo-3-phenylpropyl Diethylcarbamate (3m)
Orange oil.

IR (KBr): 2980, 1700, 1433, 1274, 1171, 1087, 773, 707 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14–1.18 (m, 6 H), 1.35 (d, *J* = 7.2 Hz, 3 H), 3.32–3.34 (m, 4 H), 3.81 (s, 2 H), 5.14 (q, *J* = 7.2 Hz, 1 H), 7.19–7.33 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 14.0, 16.5, 41.4, 42.0, 45.3, 74.8, 126.9, 128.5, 129.6, 133.5, 155.0, 206.2.

MS (70 eV): *m/z* (%) = 263 [M$^+$], 172, 100 (100), 72, 44, 28.

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.69; H, 7.93; N, 5.41.

1-Methyl-2-oxo-3-phenylpropyl Dipropylcarbamate (3n)
Orange oil.

IR (KBr): 2964, 1701, 1428, 1245, 1167, 1095, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 8.0 Hz, 6 H), 1.35 (d, *J* = 8.0 Hz, 3 H), 1.55–1.65 (m, 4 H), 3.15–3.27 (m, 4 H), 3.81 (s, 2 H), 5.13 (q, *J* = 8.0 Hz, 1 H), 7.21–7.31 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 16.5, 21.2, 21.8, 45.2, 48.8, 49.3, 74.9, 126.9, 128.5, 129.6, 133.5, 155.5, 206.2.

MS (70 eV): *m/z* (%) = 291 [M$^+$], 200, 128 (100), 91, 43, 28.

Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.76; H, 8.78; N, 4.92.

1-Methyl-2-oxo-3-phenylpropyl Diallylcarbamate (3o)
Orange oil.

IR (KBr): 3076, 2986, 2931, 1707, 1420, 1244, 1098, 928, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 7.2 Hz, 3 H), 3.80 (s, 2 H), 3.89 (d, *J* = 5.6 Hz, 4 H), 5.13–5.18 (m, 5 H), 5.77–5.81 (m, 2 H), 7.18–7.33 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5, 45.2, 48.7, 49.2, 75.3, 116.9, 117.3, 127.0, 128.5, 129.6, 133.1, 133.3, 133.4, 155.3, 205.9.

MS (70 eV): *m/z* (%) = 287 [M$^+$], 196, 124 (100), 91, 41.

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.17; H, 7.32; N, 4.78.

1-Propionylcyclohexyl Diethylcarbamate (3p)
Orange oil.

IR (KBr): 2937, 2868, 1700, 1431, 1272, 1070, 778 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 4.0 Hz, 3 H), 1.01–1.18 (m, 6 H), 1.38–1.50 (m, 2 H), 1.56–1.62 (m, 6 H), 2.02–2.10 (m, 2 H), 2.39 (q, *J* = 4.0 Hz, 2 H), 3.21–3.31 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.0, 13.4, 14.2, 21.2, 25.1, 28.4, 31.4, 41.6, 41.7, 84.2, 154.3, 210.7.

MS (70 eV): *m/z* (%) = 255 [M$^+$], 226, 198, 100 (100), 72, 57, 28.

Anal. Calcd for $C_{14}H_{25}NO_3$: C, 65.85; H, 9.87; N, 5.49. Found: C, 65.54; H, 9.99; N, 5.62.

1-Propionylcyclohexyl Dibutylcarbamate (3q)
Orange oil.

IR (KBr): 2938, 2866, 1699, 1461, 1226, 1134, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.91 (t, *J* = 8.0 Hz, 3 H), 0.96 (t, *J* = 8.0 Hz, 3 H), 1.05 (s, 3 H), 1.20–1.42 (m, 8 H), 1.44–1.67 (m, 8 H), 2.02–2.10 (m, 2 H), 2.43 (q, *J* = 8.0 Hz, 2 H), 3.20 (t, *J* = 8.0 Hz, 2 H), 3.28 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.1, 13.8, 19.9, 20.1, 21.5, 25.2, 28.4, 30.1, 30.9, 31.4, 47.0, 47.1, 84.3, 154.7, 210.8.

MS (70 eV): *m/z* (%) = 311 (M+), 282, 254, 156 (100), 100, 57, 29.

Anal. Calcd for $C_{18}H_{33}NO_3$: C, 69.41; H, 10.68; N, 4.50. Found: C, 69.13; H, 10.81; N, 4.55.

3-(4-Methoxyphenyl)-1,1-dimethyl-2-oxo-propyl Diethylcarbamate (3r)
Orange oil.

IR (KBr): 2980, 1698, 1430, 1250, 1157, 782 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13–1.22 (m, 6 H), 1.48 (s, 6 H), 3.32 (t, *J* = 6.8 Hz, 4 H), 3.73 (s, 3 H), 3.77 (s, 2 H), 6.83–6.85 (m, 2 H), 7.13–7.15 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 24.0, 41.2, 41.7, 41.9, 55.2, 83.1, 113.8, 126.9, 128.1, 130.7, 154.7, 158.4, 207.3.

MS (70 eV): *m/z* (%) = 307 [M^+], 186, 162, 121, 100 (100), 72, 44, 29.

Anal. Calcd for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56. Found: C, 66.29; H, 7.95; N, 4.62.

2-Oxo-3-phenylpropyl Diallylcarbamate (3s)
Orange oil.

IR (KBr): 3076, 2928, 1708, 1460, 1417, 1244, 1097, 929, 761, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 2 H), 3.90 (d, *J* = 5.6 Hz, 4 H), 4.71 (s, 2 H), 5.15–5.18 (m, 4 H), 5.74–5.79 (m, 2 H), 7.20–7.35 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.1, 48.7, 49.2, 68.5, 116.9, 117.3, 127.0, 128.7, 129.4, 132.9, 133.0, 133.2, 155.3, 202.3.

MS (70 eV): *m/z* (%) = 273 [M^+] 182, 124 (100), 91, 41, 27.

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 69.94; H, 7.23; N, 5.31.

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(11) (4*Z*)-4-Benzylidene-1,3-dioxaspiro[4.5]decan-2-one could be quantitatively transformed into **3a** by treatment with Et_2NH (1 equiv) in 1,4-dioxane at 90 °C for 15 h.

(12) When a primary amine(butylamine) was used under the same conditions, 4-benzylidene-3-butyl-1-oxa-3-azaspiro[4.4]nonan-2-one was obtained in 81% yield (*E*/*Z* = 52:48).

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