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Trapping of carbamic acid species with (trimethylsilyl)diazomethane

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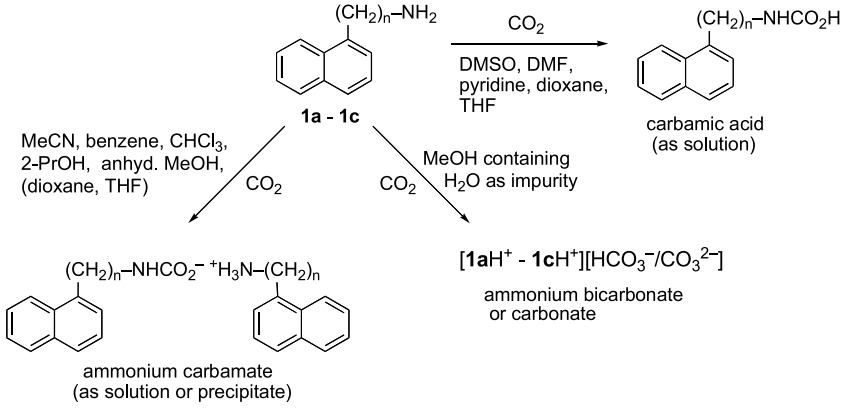
Abstract—Methoxycarbonylation of a variety of amines into the corresponding methyl carbamates was accomplished by allowing them to react with (trimethylsilyl)diazomethane $TMSCHN_2$ under bubbling of CO_2. The reaction was performed at room temperature for a period of ca. 2 h in benzene–MeOH (4/1 v/v), which was the solvent of choice. In this mixed solvent, undesirable bicarbonate is formed in equilibrium along with carbamate anion. Owing to the irreversibility in the esterification step by $TMSCHN_2$, however, the yield of methyl carbamate can reach very high.

1. Introduction

We and others have recently reported studies on the solvent dependence of the carbamic acid formation from ω-(1-naphthyl)alkylamines **1a–c** and carbon dioxide.[1,2] On the basis of NMR and IR analyses in situ after bubbling of CO_2 through solutions of these amines in DMSO, DMF or pyridine, it is concluded that they are completely converted to the corresponding carbamic acids in the protophilic, highly dipolar, aprotic solvents (see Scheme 1).[1] In dioxane (protophilic, dipolar, aprotic solvent), the carbamic acid and a small amount of the ammonium carbamate are formed. By contrast, in MeCN (protophobic, dipolar, aprotic solvent), in benzene or $CHCl_3$ (apolar, aprotic solvent), or in 2-PrOH or MeOH (dipolar, amphiprotic solvent), ammonium carbamates rather than carbamic acids are formed, although the ammonium bicarbonates/carbonates are competitively formed in hydrous MeOH. Not only solvent polarity and protic character but also its protophilicity was found to be a crucial factor. The selective generation of the undissociated carbamic acids in preference to the ammonium carbamates in protophilic, dipolar, aprotic solvent (DMSO, DMF, pyridine, or dioxane) was ascribed to the larger pK_a values[3] for the carbamic acids than for the amines **1a–c** in this class of solvent, that is, the equilibrium reaction 1 is shifted far to the left.



Scheme 1.

Keywords: Amine; Carbon dioxide; Carbamic acid; (Trimethylsilyl)diazomethane; Methyl carbamate.
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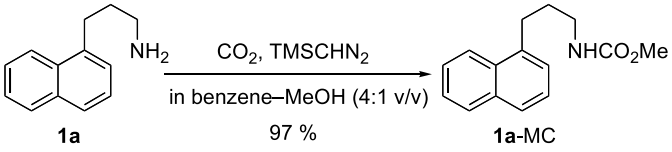
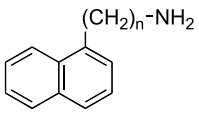
$$RNHCO_2H + RNH_2 \rightleftharpoons RNHCO_2^- + RNH_3^+ \quad \text{in protophilic, dipolar, aprotic solvent} \qquad (1)$$

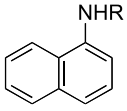
The ammonium carbamates often precipitated out from the solution and hence they could be separated. In order to trap unstable carbamic acids as the stable esters, we reacted 3-(1-naphthyl)propylamine (**1a**) in 4:1 v/v benzene/MeOH with (trimethylsilyl)diazomethane $TMSCHN_2$ under bubbling of CO_2.[1a] The corresponding methyl carbamate (**1a**-MC) was successfully obtained in essentially quantitative yield (Eq. 2). $TMSCHN_2$ is a well-known reagent for methylation of carboxylic acids.[4] In this paper, application of this *N*-methoxycarbonylation reaction to other amines such as **1**–**5** is investigated. Lately, amine has been utilized to fix carbon dioxide through various types of chemical reaction.[5] An example is the formation of carbamate ester (urethane) by using alkyl halide,[6] alcohol,[7] carbonate ester,[8] alkene,[9] alkyne,[9] or epoxide[9] as the alkylating agent, but $TMSCHN_2$ had not been employed to this aim before our previous report.[1a]



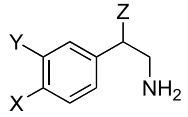
(2)



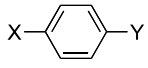
1a: n = 3
1b: n = 2
1c: n = 1



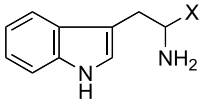
1d: R = H
1e: R = Me



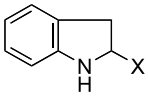
2a: X = Y = Z = H
2b: X = OH, Y = Z = H
2c: X = Y = OMe, Z = H
2d: X = Y = H, Z = OH (rac-)
2e: X = Y = OH, Z = H
2f: X = Y = Z = OH (rac-)



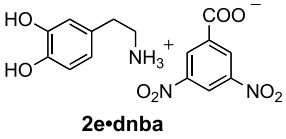
2g: X = H, Y = NH_2
2h: X = H, Y = NHMe
2i: X = H, Y = NMe_2
2j: X = OMe, Y = NH_2
2k: X = NMe_2, Y = NH_2



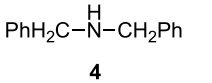
3a: X = H
3b: X = CO_2Me (L-)



5a: X = H
5b: X = Me



2e•dnba



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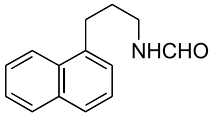

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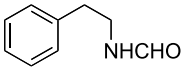

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2. Results and discussion

2.1. Methoxycarbonylation with $TMSCHN_2$

First, we looked for a suitable solvent for the *N*-methoxycarbonylation reaction. Since, according to Shioiri and co-workers,[4] methanol is indispensable for methylation of acids with $TMSCHN_2$, we carried out the reaction in benzene, dioxane, pyridine or DMF, each containing 20 (or 10) volume % of MeOH, or in pure MeOH.[†] Thus, to solutions of amines **1a**, **2a**, **2c**, **3a**, and **5a** in one of these solvents were added at room temperature 2–3equiv of $TMSCHN_2$ (an Aldrich 2.0 M solution in hexanes was used) with stirring under bubbling of CO_2. In less than half an hour, a yellow color of $TMSCHN_2$ disappeared and the corresponding methyl carbamates (MC's) resulted with excellent yields (83–100%) when benzene–MeOH (4/1) or dioxane–MeOH (4/1) was used (Table 1).[‡] However, the yields were much lower in the solvent like pyridine–MeOH (4/1 or 9/1), DMF–MeOH (4/1) or MeOH (22–61%). In the case of pyridine–MeOH, formation of a large amount of brown tar greatly impaired the reaction. When pure MeOH was used, $TMSCHN_2$ decomposed more rapidly as compared with the benzene–MeOH system. This is probably due to some side reactions. In DMF–MeOH, formamides **6** and **7** were obtained as additional products from **1a** and **2a**, respectively. From these results, benzene–MeOH (4/1) was employed as the solvent of choice for further experiments.

Solutions of amines **1**–**5** in 4:1 benzene–MeOH were treated with a $TMSCHN_2$ solution under bubbling of CO_2, as described above. As summarized in Table 2, primary alkyl amines **1a**–**c**, **2a**–**d**, **3a**, **3b** and secondary alkylamine **4** afforded their methyl carbamates (MC's) in excellent to good yields (76–100%). MC was obtained even from dopamine (**2e**), an important neurotransmitter in brain,[10] in a modest yield (17%) by using dopamine·3,5-dinitrobenzoic acid salt (**2e**·dnba)[11] as the starting amine. This methoxycarbonylation reaction is interesting, because **2e** itself is easily susceptible to oxidative polymerization to generate melanin, a structurally unelucidated black pigment.[11,12] Similar treatment of commercially available dopamine hydrochloride **2e**·HCl with $TMSCHN_2$ gave a very low yield of the crude MC (6%). MC was also obtained from DL-noradrenaline (**2f**) in 12% yield. One reason for the low yields of MC from catecholamines **2e** and **2f** is that their reactions had to be carried out in 4:1 pyridine/MeOH, since

[†] The possibility that the Me group comes from methanol in the methylation reaction was excluded by Shioiri by using methanol–^{13}C.[4]

[‡] The use of 1 equiv of $TMSCHN_2$ instead of 2 equiv decreased the yield of **2a**-MC from 97% (Table 1) to 78% in benzene–MeOH (4/1).

Table 1. Solvent effect on methoxycarbonylation of several amines with (trimethylsilyl)diazomethane under atmospheric pressure of CO_2 at room temperature

Amine	Solvent (v/v)	Product yield (%)[a]		Recovered amine (%)[b]
		Methyl carbamate	Others	
1a	Benzene–MeOH (4/1)	99[#]		Trace
1a	Dioxane–MeOH (4/1)	98[#]		0
1a	Pyridine–MeOH (9/1)	42[#]	[c]	51
1a	Pyridine–MeOH (4/1)	40	[c]	51
1a	DMF–MeOH (4/1)	22[#]	**6**, 52	0
1a	MeOH	38[#]		55
2a	Benzene–MeOH (4/1)	97[#]		0
2a	DMF–MeOH (4/1)	25	**7**, 7	0
2c	Benzene–MeOH (4/1)	100[#]		0
2c	MeOH	29		45
3a	Benzene–MeOH (4/1)	83[#]		10
3a	Pyridine–MeOH (4/1)	61	[c]	Trace
5a	Benzene–MeOH (4/1)	98 (97[#])		2
5a	Pyridine–MeOH (4/1)	32	[c]	50

[a] Isolation yield, unless marked with #, where it is the NMR yield. Values are based on the initial amount of amine.
[b] Estimated by NMR.
[c] A large amount of brown tar was formed.

2e·dnba, **2e**·HCl and **2f** are insoluble in 4:1 benzene/MeOH.

Other significant points found from inspection of Table 2 are that methoxycarbonylation reactions of arylamines **1d**, **2g**, **2h**, **2j**, **2k**, and **5b** are difficult (0–27% yields), although indoline (**5a**), which is an *N*-alkyl-substituted arylamine whose nitrogen atom is expected to be sterically less hindered than that of **5b** or **2h**, gave its methyl carbamate (**5a**-MC) in an excellent yield (98%). The MC yields from electron-rich *p*-anisidine (**2j**) and *N*,*N*-dimethyl-*p*-phenylenediamine (**2k**) (27 and 19%, respectively) were better than aniline (**2g**) (8%).

Alcohols react with CO_2 to form alkylcarbonic acids in the presence of tertiary amine bases under high-pressure or in the presence of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU).[13] Under our reaction conditions, however,

Table 2. Methoxycarbonylation of various amines with (trimethylsilyl)diazomethane under atmospheric pressure of CO_2 at room temperature

Amine	Product yield (%)[a]		Recovered amine (%)[b]
	Methyl carbamate	Others	
Primary alkylamine: $RNH_2 \rightarrow RNH–CO_2Me$			
1a	99[#]		Trace
1b	95		0
1c	95		0
2a	97[#]		0
2b	88		7
2c	100[#]		0
2d	82		0
2e[c]	17	[d]	[e,f]
2f[g]	12	[d]	15
3a	83[#]		10
3b	76		14[h]
Secondary alkylamine: $RR'NH \rightarrow RR'N–CO_2Me$			
4	78		3
Arylamine: $ArRNH \rightarrow ArRN–CO_2Me$			
1d	0	**1e**, 13	82
2g	8		[e,i]
2h	0	**2i**, 7	>75[i]
2j	27		52
2k	19		66
5a	98 (97[#])		2
5b	24 (40[#])		57

The solvent employed is benzene–MeOH (4/1 v/v) except for **2e** and **2f**.
[a] Isolation yield, unless marked with #, where it is the NMR yield. Values are based on the initial amount of amine.
[b] Estimated by NMR.
[c] Dopamine·3,5-dinitrobenzoic acid salt (**2e**·dnba)[11] dissolved in 4:1 pyridine/MeOH was reacted (**2e**·dnba is insoluble in 4:1 benzene/MeOH). The reaction of dopamine hydrochloride (**2e**·HCl) under the same conditions gave a lower yield of MC (6%).
[d] A large amount of brown tar was formed.
[e] Not estimated.
[f] Polymerized to melanin during the workup.
[g] The reaction was carried out in 4:1 pyridine/MeOH, since DL-noradrenaline (**2f**) is insoluble in 4:1 benzene/MeOH.
[h] Isolated.
[i] The recovered amine was partially lost on evaporation of the solvent.

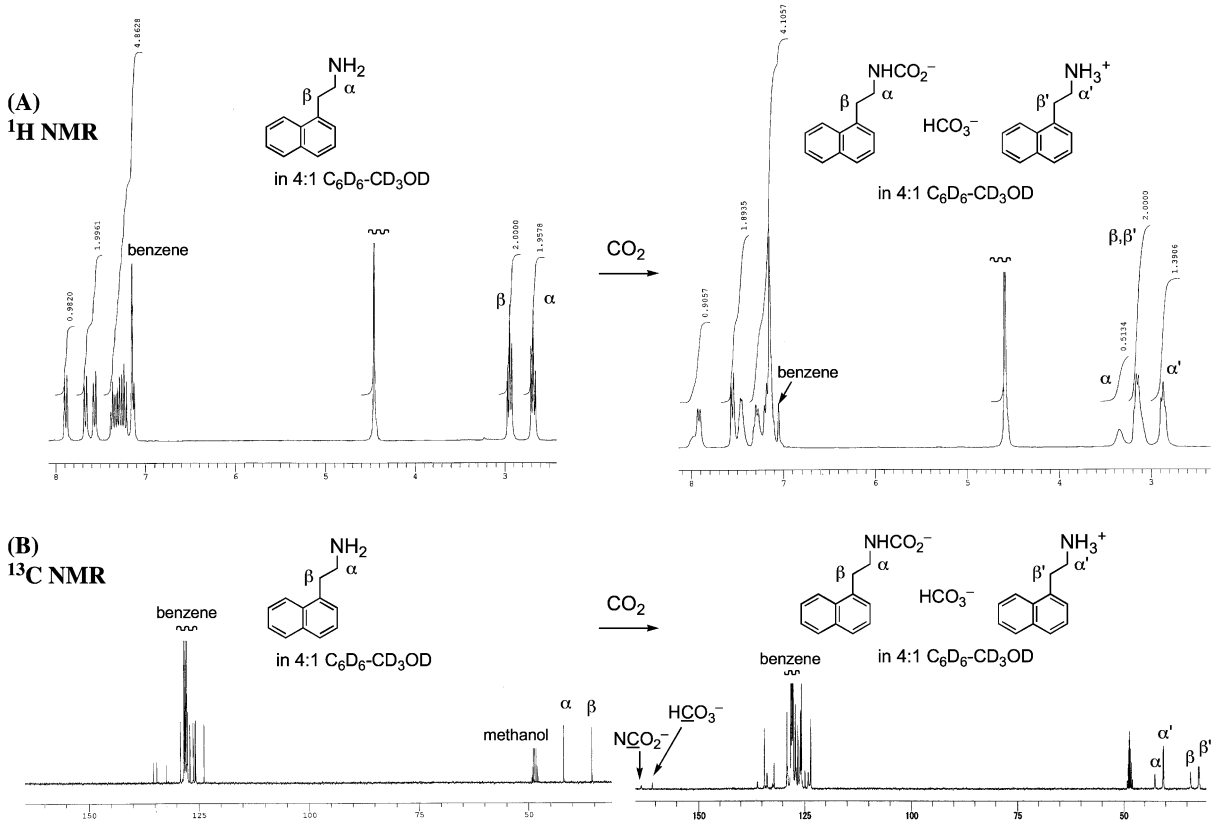

Figure 1. The ^{1}H and ^{13}C NMR spectra of **1b** in 4:1 C_6D_6/CD_3OD before and after CO_2 bubbling.

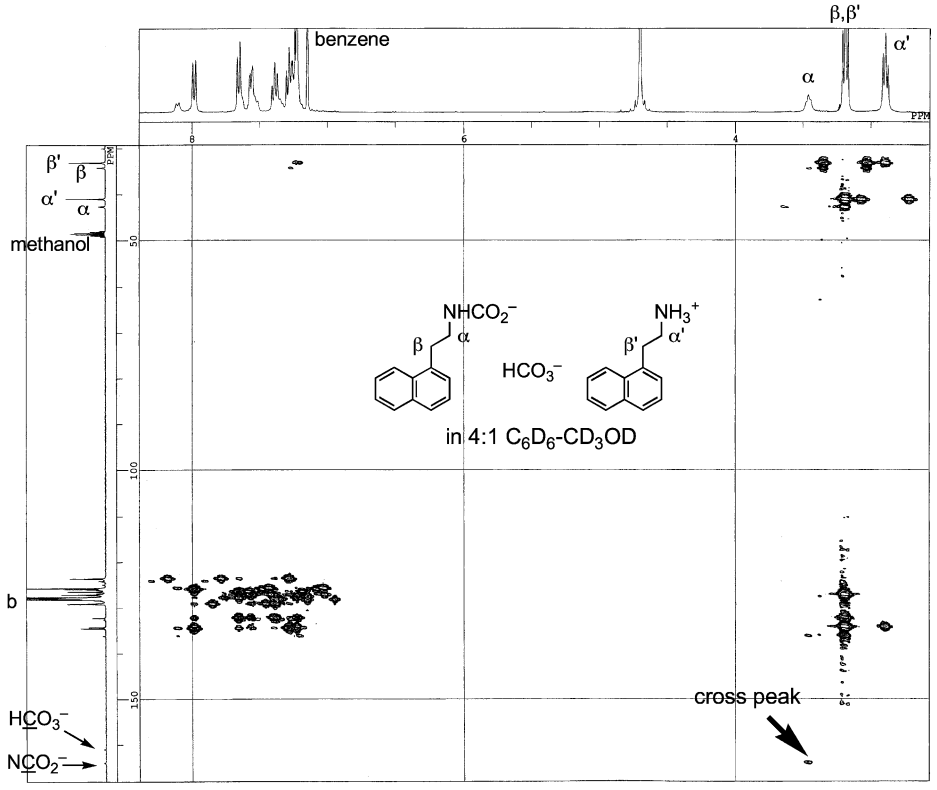

Figure 2. The HMBC spectrum of **1b** in 4:1 C_6D_6/CD_3OD after CO_2 bubbling.

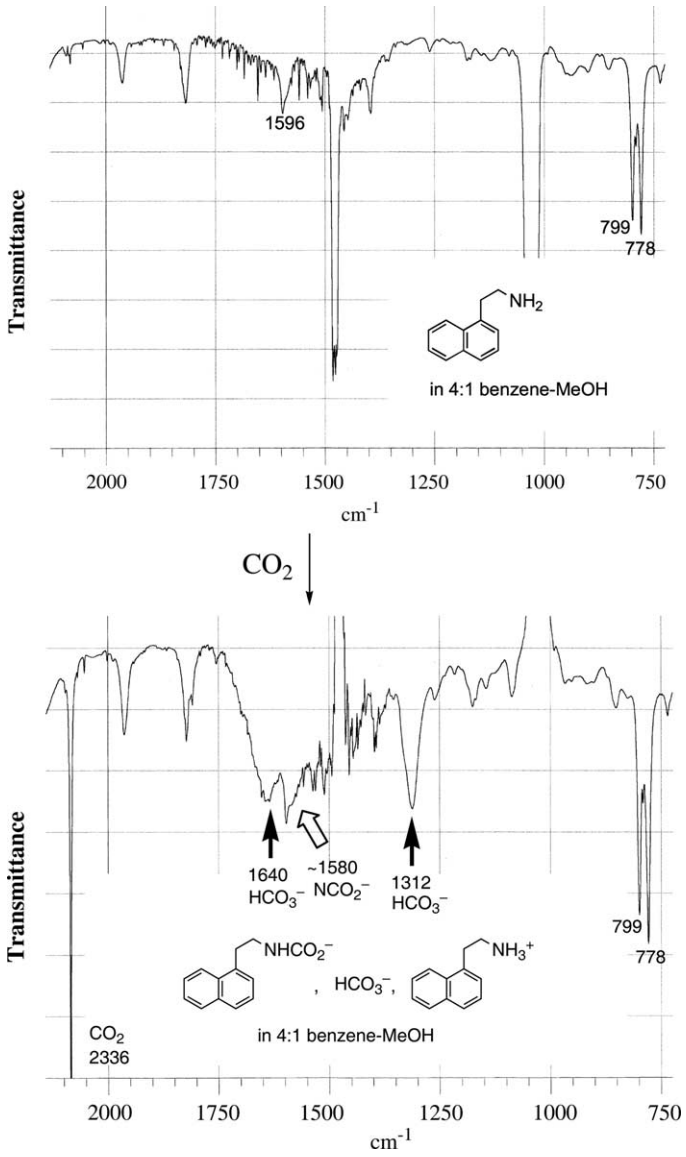

Figure 3. The IR spectra of **1b** in 4:1 benzene/MeOH before and after CO_2 bubbling.

methylcarbonic acid $CH_3OCO_2^-$ was probably not formed from the following reasons. Dimethyl carbonate, which is a possible product from the reaction of methylcarbonic acid with $TMSCHN_2$, was undetectable (NMR) in the reaction mixtures. Furthermore, the signals corresponding to $CD_3OCO_2^-$ were none by the in situ ^{13}C NMR experiments in C_6D_6–CD_3OD or in CD_3OD (Section 2.2 and Ref. 1a).

2.2. Carbamate anion formation in 4:1 benzene/MeOH

When we previously studied the solvent dependence of carbamic acid formation,[1] we did not investigate the benzene–MeOH mixed solvent. Therefore, by selecting 2-(1-naphthyl)ethylamine (**1b**) as a typical example, the ^1H and ^{13}C NMR, HMBC, and IR spectra in 4:1 benzene–MeOH before and after bubbling CO_2 were measured in situ (Figs. 1–3). It can be seen from these figures that a mixture of ammonium carbamate and bicarbonate was predominantly formed in this mixed solvent. From the ^1H NMR spectrum after CO_2 bubbling (Fig. 1A, right), the molar ratio between ammonium carbamate and ammonium bicarbonate is estimated as 54:46. The carbamyl carbon appeared at δ 163.5 and the bicarbonate carbon at δ 160.9 (Fig. 1B, right). In the HMBC spectrum (Fig. 2), there is an expected cross peak between the α-methylene proton and the carbamyl carbon, demonstrating the N– Cbond formation between the amine nitrogen and the CO_2 carbon. The IR spectrum (Fig. 3, bottom) showed a broad band at about 1580 cm^{-1}, which is assignable to the $NHCOO^-$ group of the carbamate anion.[14] The bands at 1640 and 1312 cm^{-1} should be attributed to bicarbonate.[1a] For comparison, the pertinent spectra in DMSO and DMF are displayed in Figures 4–6. As reported previously,[1] **1b** was quantitatively converted to the carbamic acid (1-Naph)$CH_2CH_2NHCO_2H$ in DMSO, DMF or pyridine (e.g., as can be seen from the NMR spectra in Figures 4 and 5).

2.3. Mechanistic consideration

Interconversion reactions among amine, carbamic acid, ammonium carbamate, and ammonium bicarbonate (formed

if H_2O is present as a contaminant in MeOH; see Scheme 1) are reversible processes,[5,15] whereas the formation of methyl carbamate (MC) is irreversible (Eqs. 3–6). It is assumed that $TMSCHN_2$ can esterify either undissociated or dissociated carbamic acid (Eq. 6). As aforementioned, upon CO_2 bubbling through the solution of **1b** in 4:1 benzene/MeOH, formation of both ammonium carbamate and bicarbonate (molar ratio 54:46) but no carbamic acid was observed (Figs. 1–3). Of course, there may exist a low concentration of the carbamic acid below the detection limit of the NMR and IR analysis. Apart from the ambiguity about the true species involved in the esterification, however, production of the methyl carbamate **1b**-MC in high yield (95%, Table 2) from the ammonium carbamate–bicarbonate mixture (carbamate content 54%) in 4:1 benzene/MeOH is feasible owing to the irreversibility of the reaction 6.

$$RR'NH + CO_2 \rightleftharpoons RR'NCO_2H \tag{3}$$

$$RR'NCO_2H + RR'NH \rightleftharpoons RR'NH_2^+ + RR'NCO_2^- \tag{4}$$

$$RR'NH + CO_2 + H_2O \rightleftharpoons RR'NH_2^+ + HCO_3^- \tag{5}$$

$$\left\{ \begin{array}{c} RR'NCO_2H \\ \rightleftharpoons \\ RR'NCO_2^- + H^+ \end{array} \right\} \xrightarrow[MeOH]{TMSCHN_2} RR'NCO_2Me \tag{6}$$

In the preceding paper[1] we have mentioned that the in situ yield of carbamic acid in CO_2-saturated DMSO-d_6 is generally much lower for arylamines than for alkylamines. More complete data supporting this statement are shown in Table 3. Many alkylamines underwent nearly complete conversion (~100%) into their respective carbamic acids. Among arylamines, those having an electron-donating group (**2j** and **2k**) and cyclic ones (**5a** and **5b**) exhibit relatively high carbamic acid yields (7–24%). It is interesting to note that the carbamic acid yields in DMSO-d_6 for alkyl- and arylamines (Table 3) are roughly correlated with their methoxycarbonylation yields (Table 2). On the assumption that the structural effect by different amines on the formation of either carbamic acid or carbamate anion is similar, it seems that $TMSCHN_2$ is a good reagent for trapping unstable carbamic acid species (carbamic acid or carbamate anion).

Table 3. Carbamic acid formation from amines in DMSO-d_6 through bubbling of CO_2 at room temperature

Alkylamine	Carbamic acid yield (%)	Arylamine	Carbamic acid yield (%)
1a–c	~100	**1d**, **1e**, **2h**	0
2a–d, **2f**	~100	**2g**	1
2e·dnba	12 (31[a])	**2j**	11
3a	~100	**2k**	24
4	82	**5a**	22
		5b	7

The conversion or the carbamic acid yield was estimated in situ by ^1H NMR analysis. Some data are from Ref. 1a.
[a] In pyridine-d_5.

3. Conclusion

Methoxycarbonylation of a variety of amines into the corresponding methyl carbamates was accomplished by allowing them to react with (trimethylsilyl)diazomethane $TMSCHN_2$ under bubbling of CO_2 at room temperature. Benzene–MeOH (4/1 v/v) was the solvent of choice. Thus, primary alkyl amines **1a–c**, **2a–d**, **3a**, **3b** and secondary alkylamine **4** afforded their methyl carbamates in excellent to good yields (76–100%). On the other hand, methoxycarbonylation of arylamines (**1d**, **2g**, **2h**, **2j**, **2k** and **5b**) was difficult (0–27% yield), although indoline (**5a**), whose nitrogen atom is sterically less hindered, gave its methyl carbamate in an excellent yield (98%). Even oxidatively labile dopamine (**2e**) and DL-noradrenaline (**2f**) were successfully methoxycarbonylated, albeit a low yield (17 and 12%, respectively). By selecting 2-(1-naphthyl)ethylamine (**1b**) as a typical example, the ^1H and ^{13}C NMR, HMBC, and IR spectra in 4:1 benzene–MeOH were measured before and after CO_2 bubbling. These spectra have revealed that about an equimolar amount of the ammonium carbamate and the ammonium bicarbonate is formed in equilibrium in this mixed solvent. However, since the methyl esterification step by $TMSCHN_2$ is irreversible, the conversion of amine to methyl carbamate can be nearly quantitative.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL EX-270J, AL-300, or JUM-A400 spectrometer. Measurements of 2D NMR were carried out with JEOL JUM-A400. Mass and IR spectra were recorded on JEOL JMS-HX 110A and SHIMADZU FTIR-8400 spectrometers, respectively.

The in situ measurements of ^1H and ^{13}C NMR, HMBC, and IR spectra in benzene–MeOH (4/1 v/v) before and after bubbling CO_2 were carried out as described previously.[1a]

4.2. Methoxycarbonylation

4.2.1. A typical procedure: isolation of methyl *N*-[3-(1-naphthyl)propyl]carbamate (1a-MC). Through 5 mL of a 4:1 benzene/MeOH solution containing 73 mg (0.393 mmol) of amine **1a** was bubbled CO_2 gas for 15 min. Into this solution was added 0.5 mL (1.0 mmol) of (trimethylsilyl)diazomethane $TMSCHN_2$ (Aldrich 2.0 M solution in hexanes) in one portion at room temperature with both stirring and CO_2 bubbling. The yellow color of $TMSCHN_2$ disappeared in 20 min. The mixture was stirred for an additional 2 h under CO_2 bubbling. The resultant colorless solution was rotary-evaporated to afford 93 mg of a colorless viscous oil, which was almost pure **1a**-MC containing only a trace of **1a** on the basis of the NMR analysis. Further purification was carried out by preparative TLC on silica gel ($CHCl_3$/MeOH 20:1 v/v) to give 93 mg (97% yield) of **1a**-MC as a colorless viscous oil.

4.2.2. Isolation of methyl *N*-[2-(3,4-dihydroxyphenyl)-ethyl]carbamate (2e-MC). Through 12.5 mL of a 4:1

pyridine/MeOH solution containing 150 mg (0.411 mmol) of the salt **2e**·dnba[11] was bubbled CO_2 gas for 15 min. Into this solution was added 1.1 mL (2.2 mmol) of $TMSCHN_2$ in one portion at room temperature with both stirring and CO_2 bubbling. The mixture was stirred at room temperature for 2.5 h under CO_2 bubbling. Then the solvent was rotary-evaporated to leave 452 mg of a dark brown residue, which was dissolved in 10 mL of MeOH and was left overnight. An insoluble black solid (probably melanin) appeared and this was removed by filtration. The filtrate was subjected to repeated preparative TLC on silica gel ($CHCl_3$/MeOH 10:1 v/v) to afford 14 mg (17% yield) of **2e**-MC as a pale brown semisolid. Methyl 3,5-dinitrobenzoate was undetectable in the reaction mixture (NMR and TLC).

4.2.3. Spectral data for isolated products. Other amines were reacted in a manner similar to that described at Section 4.2.1. The products were separated by preparative TLC on silica gel ($CHCl_3$–MeOH) and were characterized by ^1H and ^{13}C NMR, IR, MS, and HRMS measurements. Further purification of the isolated products by recrystallization or distillation was usually not done. Spectral data for known compounds were well in agreement with the reported data.

4.2.3.1. Methyl *N*-[3-(1-naphthyl)propyl]carbamate (1a-MC). Obtained as a colorless thick oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, d, J=8.2 Hz), 7.85 (1H, dd, J=8, 1.7 Hz), 7.71 (1H, d, J=8.1 Hz), 7.53–7.44 (2H, m), 7.38 (1H, t, J=7.6 Hz), 7.31 (1H, d, J=7 Hz), 4.74 (1H, br s), 3.67 (3H, s), 3.28 (2H, quar, J=6.5 Hz), 3.10 (2H, t, J=7.6 Hz), 1.96 (2H, quin, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.13, 137.44, 133.91, 131.72, 128.84, 126.83, 125.97, 125.88, 125.53, 125.52, 123.58, 52.06, 40.95, 30.88, 30.11; IR (neat) 3336 (m), 1705 (br s), 1538 (br s), 1258 (s), 778 (s) cm^{-1}; MS (FAB$^+$) *m/z* 244 (MH^+, 100), 243 (M^+, 58), 212 (13), 168 (21); HRMS (FAB$^+$) calcd for $C_{15}H_{17}NO_2$ 243.1259, found 243.1259.

4.2.3.2. *N*-[3-(1-Naphthyl)propyl]formamide (6). Obtained as a colorless thick oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (0.84H, s), 8.05 (0.16H, d, J=12.3 Hz), 8.01–7.95 (1H, m), 7.87–7.83 (1H, m), 7.76–7.70 (1H, m), 7.54–7.28 (4H, m), 5.8 and 5.59 (ca. 0.15 and 0.85H, two br s), 3.41 (1.66H, quar, J=6.8 Hz), 3.28 (0.34H, quar, J=6.7 Hz), 3.12 (2H, t, J=7.8 Hz), 1.99 (2H, quin, J=7.4 Hz); ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 164.55,[§] 161.09, 137.06, 136.49,[§] 133.84,[§] 133.78, 131.54, 131.47,[§] 129.42,[§] 128.84,[§] 128.77, 127.03,[§] 126.83, 126.00,[§] 125.94, 125.85, 125.57,[§] 125.47, 125.44, 125.40,[§] 123.41, 123.28,[§] 41.41,[§] 38.07, 31.92,[§] 30.40, 30.31, 29.73[§]; IR (neat) 3287 (m), 1666 (s), 1537 (m), 1386 (m), 779 (s) cm^{-1}; MS (EI$^+$) *m/z* 213 (M^+, 89), 168 (100), 153 (71), 141 (95), 115 (48); HRMS (EI$^+$) calcd for $C_{14}H_{15}NO$ 213.1154, found 213.1155.

4.2.3.3. Methyl *N*-[2-(1-naphthyl)ethyl]carbamate (1b-MC). Obtained as a pale yellow thick oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (1H, d, J=7.8 Hz), 7.85 (1H, d, J=7.5 Hz), 7.79 (1H, d, J=7.8 Hz), 7.55–7.45 (2H, m), 7.39 (1H, t, J=7.7 Hz), 7.31 (1H, d, J=6.6 Hz), 4.78 (1H, br s), 3.67 (3H, s), 3.54 (2H, quar, J=6.6 Hz), 3.28 (2H, t, J=7.1 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.05, 134.77, 133.90, 131.87, 128.79, 127.31, 126.77, 126.14, 125.66, 125.45, 123.55, 52.04, 41.65, 33.37; IR (neat) 3337 (m), 1705 (s), 1530 (s), 1254 (s), 777 (s) cm^{-1}; MS (EI$^+$) *m/z* 229 (M^+, 31), 154 (83), 141 (100), 115 (58), 88 (52); HRMS (EI$^+$) calcd for $C_{14}H_{15}NO_2$ 229.1103, found 229.1105.

4.2.3.4. Methyl *N*-[(1-naphthyl)methyl]carbamate (1c-MC). Obtained as a pale yellow solid, mp 84–88 °C (lit.[16] mp 66–69 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (1H, d, J=7.8 Hz), 7.86 (1H, d,[¶] J=8.1 Hz), 7.79 (1H, dd, J=6.5, 2.8 Hz), 7.56–7.47 (2H, m), 7.42–7.37 (2H, m), 5.00 (1H, br s), 4.81 (2H, d, J=5.4 Hz), 3.69 (3H, s);[8b] ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.82, 133.82, 133.62, 131.23, 128.77, 128.49, 126.52, 126.13, 125.91, 125.36, 123.29, 52.24, 43.19; IR (neat) 3298 (m), 1695 (s), 1550 (m), 1296 (m), 1259 (m), 799 (m) cm^{-1}; MS (EI$^+$) *m/z* 215 (M^+, 100), 200 (72), 156 (61), 141 (77), 129 (85); [8b] HRMS (EI$^+$) calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0944.

4.2.3.5. Methyl *N*-(2-phenylethyl)carbamate (2a-MC). Obtained as a colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.38–7.21 (5H, m), 4.75 (1H, br s), 3.70 (3H, s), 3.48 (2H, quar, J=6.5 Hz), 2.85 (2H, t, J=6.9 Hz);[6c] ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 156.84, 138.64, 128.68, 128.53, 126.41, 52.07, 42.22, 36.19;[6c] IR (neat) 3335 (m), 1705 (s), 1532 (s), 1258 (s), 700 (m) cm^{-1}; MS (EI$^+$) *m/z* 179 (M^+, 32), 104 (60), 91 (59), 88 (100); HRMS (EI$^+$) calcd for $C_{10}H_{13}NO_2$ 179.0946, found 179.0944.

4.2.3.6. *N*-(2-Phenylethyl)formamide (7). Obtained as a colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ 8.07 (0.85H, s), 7.85 (0.15H, d, J=11.9 Hz), 7.28–7.09 (5H, m), 5.7 and 5.56 (1H, two br s), 3.52 (1.7H, quar, J=6.7 Hz), 3.42 (0.3H, quar, J=6.7 Hz), 2.78 (2H, t, J=6.9 Hz);[17] ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 164.33,[§] 161.07, 138.31, 137.41,[§] 128.78,[§] 128.75,[§] 128.65 (two peaks), 126.86,[§] 126.60, 43.20,[§] 39.25, 37.73,[§] 35.50;[17] IR (neat) 3283 (m), 1667 (s), 1534 (m), 1384 (m), 1239 (m), 699 (m) cm^{-1};[17] MS (EI$^+$) *m/z* 149 (M^+, 13), 104 (100), 91 (44); HRMS (EI$^+$) calcd for $C_9H_{11}NO$ 149.0841, found 149.0842.

4.2.3.7. Methyl *N*-[2-(4-hydroxyphenyl)ethyl]carbamate or *N*-(methoxycarbonyl)tyramine (2b-MC). Obtained as a colorless thick oil; ^1H NMR (270 MHz, $CDCl_3$) δ 6.99 (2H, d,[¶] J=8.5 Hz), 6.76 (2H, d,[¶] J=8.5 Hz), 4.80 and 4.69 (1H, two br s), 3.64 (3H, s), 3.37 (2H, quar, J=6.7 Hz), 2.69 (2H, t, J=7.0 Hz); ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 157.23, 154.64, 130.03, 129.70, 115.45, 52.27, 42.47, 35.21; IR (neat) 3335 (s), 1700 (s), 1515 (s), 1260 (s), 827 (m) cm^{-1}; MS (EI$^+$) *m/z* 195 (M^+, 14), 120 (100), 107 (95); HRMS (EI$^+$) calcd for $C_{10}H_{13}NO_3$ 195.0895, found 195.0896.

4.2.3.8. Methyl *N*-[2-(3,4-dimethoxyphenyl)ethyl]carbamate (2c-MC). Obtained as a colorless thick oil; ^1H NMR (270 MHz, $CDCl_3$) δ 6.81 (1H, d, J=7.9 Hz), 6.74–6.70 (2H, m), 4.69 (1H, br s), 3.87 (3H, s), 3.86 (3H, s), 3.66 (3H, s), 3.42 (2H, quar, J=6.6 Hz), 2.76 (2H, t, J=6.9 Hz);[18] ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.95, 148.99,

[§] The peaks probably belonging to the minor isomer.

[¶] Each peak is finely split (J=1–2 Hz).

147.66, 131.21, 120.64, 111.87, 111.32, 55.89, 55.84, 52.03, 42.28, 35.69;[18] IR (neat) 3365 (m), 1710 (s), 1516 (s), 1260 (s), 1236 (s), 1142 (s), 1028 (s) cm^{-1};[18] MS (FAB^+) *m/z* 240 (MH^+, 87), 239 (M^+, 100), 165 (59); HRMS (FAB^+) calcd for $C_{12}H_{17}NO_4$ 239.1158, found 239.1164.

4.2.3.9. Methyl *N*-(2-hydroxy-2-phenylethyl)carbamate (2d-MC). Obtained as a colorless solid, mp 85–89 °C (lit.[8a] mp 88–90 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29–7.19 (5H, m), 5.11 (1H, br s), 4.74 (1H, dd, $J=8$, 3 Hz), 3.60 (3H, s), 3.44 (1H, br d, $J=14$ Hz), 3.21 (1H, br dd, $J=14$, 8 Hz), 2.56 (1H, br s);[8a] ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.81, 141.52, 128.54, 127.93, 125.84, 73.58, 52.33, 48.53;[8a] IR (nujol) 3374 (m), 3272 (m), 1689 (s), 1551 (m), 1285 (m), 1277 (m), 704 (m) cm^{-1};[8a] MS (EI^+) *m/z* 195 (M^+, 11), 177 (20), 120 (29), 107 (58), 89 (100); HRMS (EI^+) calcd for $C_{10}H_{13}NO_3$ 195.0895, found 195.0895.

4.2.3.10. Methyl *N*-[2-(3,4-dihydroxyphenyl)ethyl]-carbamate or *N*-(methoxycarbonyl)dopamine (2e-MC). Obtained as a pale brown semisolid; ^1H NMR (400 MHz, CD_3OD) δ 6.66 (1H, d, $J=8.1$ Hz), 6.62 (1H, d, $J=2.0$ Hz), 6.50 (1H, dd, $J=8.0$, 2.0 Hz), 3.60 (3H, s), 3.23 (2H, t, $J=$ 7.5 Hz), 2.60 (2H, t, $J=7.5$ Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 159.54, 146.23, 144.74, 132.04, 121.02, 116.85, 116.33, 52.36, 43.76, 36.57; IR (neat) 3335 (s), 1700 (s), 1525 (s), 1283 (s) cm^{-1}; MS (EI^+) *m/z* 211 (M^+, 21), 136 (100), 123 (92); HRMS (EI^+) calcd for $C_{10}H_{13}NO_4$ 211.0845, found 211.0842.

4.2.3.11. Methyl *N*-[2-hydroxy-2-(3,4-dihydroxy-phenyl)ethyl]carbamate or *N*-(methoxycarbonyl)nor-adrenaline (2f-MC). Obtained as a pale brown semisolid; ^1H NMR (400 MHz, CD_3OD) δ 6.80 (1H, d, $J=1.8$ Hz), 6.72 (1H, d, $J=8.1$ Hz), 6.66 (1H, dd, $J=8.1$, 1.8 Hz), 4.55 (1H, dd, $J=7.9$, 4.9 Hz), 3.61 (3H, s), 3.29–3.17 (2H, m); ^{13}C NMR (100 MHz, CD_3OD) δ 159.70, 146.25, 145.89, 135.39, 118.73, 116.12, 114.39, 73.71, 52.49, 49.47; IR (KBr) 3335 (s), 1700 (s), 1535 (m), 1290 (s) cm^{-1}; MS (EI^+) *m/z* 227 (M^+, 9), 209 (82), 177 (23), 152 (21), 139 (100), 93 (45); HRMS (EI^+) calcd for $C_{10}H_{13}NO_5$ 227.0794, found 227.0793.

4.2.3.12. Methyl *N*-phenylcarbamate (2g-MC). Obtained as a colorless thick oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.33–7.19 (4H, m), 7.00 (1H, t,¶ $J=7.2$ Hz), 6.54 (1H, br s), 3.71 (3H, s);[19] ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 153.91, 137.70, 128.98, 123.41, 118.62, 52.37;[19] IR (neat) 3318 (m), 1713 (s), 1602 (m), 1544 (s), 1448 (s), 1235 (s), 1070 (m), 755 (m), 691 (m) cm^{-1};[19] MS (EI^+) *m/z* 151 (M^+, 100), 119 (47), 106 (60); HRMS (EI^+) calcd for $C_8H_9NO_2$ 151.0633, found 151.0636.

4.2.3.13. Methyl *N*-(4-methoxyphenyl)carbamate (2j-MC). Obtained as a pale brown semisolid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (2H, d, $J=8.2$ Hz), 6.82 (2H, d, $J=8.2$ Hz), 6.58 (1H, br s), 3.76 (3H, s), 3.74 (3H, s);[20] ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.04, 154.49, 130.87, 120.83, 114.23, 55.47, 52.25; [20] IR (neat) 3319 (m), 1710 (s), 1602 (m), 1514 (s), 1298 (m), 1231 (s), 1180 (m), 1073 (m), 1034 (m), 829 (m) cm^{-1};[20] MS (EI^+) *m/z* 181 (M^+, 100), 149 (96), 122 (85); HRMS (EI^+) calcd for $C_9H_{11}NO_3$ 181.0739, found 181.0740.

4.2.3.14. Methyl *N*-[4-(dimethylamino)phenyl]carbamate (2k-MC). Obtained as a dark plates (from benzene–hexane), mp 87–99 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (2H, br d, $J=7.8$ Hz), 6.68 (2H, d,¶ $J=8$ Hz), 6.52 (1H, br s), 3.73 (3H, s), 2.88 (6H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.76, 147.71, 127.67, 121.00, 113.28, 52.11, 40.97; IR (KBr) 3331 (m), 1700 (s), 1536 (s), 1323 (m), 1244 (s), 1074 (m), 811 (m) cm^{-1}; MS (EI^+) *m/z* 194 (M^+, 100), 162 (89), 135 (66); HRMS (EI^+) calcd for $C_{10}H_{14}N_2O_2$ 194.1055, found 194.1055.

4.2.3.15. Methyl *N*-[2-(3-indolyl)ethyl]carbamate or *N*-(methoxycarbonyl)tryptamine (3a-MC). Obtained as a colorless semisolid; ^1H NMR (270 MHz, $CDCl_3$) δ 8.11 (1H, br s), 7.62 (1H, d, $J=7.6$ Hz), 7.38 (1H, d,¶ $J=7.9$ Hz), 7.22 (1H, t,¶ $J=7.5$ Hz), 7.14 (1H, t,¶ $J=7.5$ Hz), 7.04 (1H, s¶), 4.78 (1H, br s), 3.67 (3H, s), 3.53 (2H, quar, $J=6.8$ Hz), 2.98 (2H, t, $J=6.8$ Hz);[21] ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 156.89, 136.21, 127.08, 122.03, 121.91, 119.32, 118.57, 112.74, 111.08, 51.97, 41.20, 25.75; IR (neat) 3412 (s), 3334 (s), 1700 (s), 1530 (m), 1454 (m), 1260 (m), 744 (m) cm^{-1}; MS (FAB^+) *m/z* 219 (MH^+, 73), 218 (M^+, 100), 144 (69), 130 (72);[21] HRMS (FAB^+) calcd for $C_{12}H_{14}N_2O_2$ 218.1055, found 218.1055.

4.2.3.16. *N*α-Methoxycarbonyl-L-tryptophan methyl ester (3b-MC). Obtained as a colorless semisolid; ^1H NMR (270 MHz, CD_3OD) δ 7.56 (1H, d, $J=7.9$ Hz), 7.38 (1H, d, $J=7.9$ Hz), 7.14 (1H, t, $J=7.1$ Hz), 7.11 (1H, s), 7.05 (1H, t, $J=7.0$ Hz), 4.54 (1H, t, $J=6.7$ Hz), 3.69 (3H, s), 3.64 (3H, s), 3.32 (1H, dd, $J=14.6$, 6 Hz), 3.18 (1H, dd, $J=14.6$, 7.7 Hz);[22] ^{13}C NMR (67.7 MHz, CD_3OD) δ 174.28, 158.87, 137.90, 128.53, 124.33, 122.33, 119.71, 118.96, 112.22, 110.60, 56.44, 52.63, 28.71;[22] IR (neat) 3400 (m), 1733 (s), 1700 (s), 1454 (m), 1356 (m), 1221 (m), 745 (m) cm^{-1}; MS (EI^+) *m/z* 276 (M^+, 26), 130 (100); HRMS (EI^+) calcd for $C_{14}H_{16}N_2O_4$ 276.1110, found 276.1116.

4.2.3.17. Methyl *N*,*N*-dibenzylcarbamate (4-MC). Obtained as a colorless oil; ^1H NMR (270 MHz, $CDCl_3$) δ 7.33–7.15 (10H, m), 4.43 (2H, s), 4.38 (2H, s), 3.79 (3H, s);[23] ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 157.29, 137.26, 128.50, 128.03, 127.31, 52.98, 49.43, 48.90; IR (neat) 1700 (s), 1471 (m), 1454 (m), 1407 (m), 1238 (s), 1119 (m), 699 (m) cm^{-1};[23] MS (EI^+) *m/z* 255 (M^+, 21), 164 (93), 121 (25), 91 (100); HRMS (EI^+) calcd for $C_{16}H_{17}NO_2$ 255.1259, found 255.1257.

4.2.3.18. 1-(Methoxycarbonyl)indoline (5a-MC). Obtained as a pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.9–7.15 (1H, br), 7.07–7.00 (2H, m), 6.81 (1H, t, $J=7.5$ Hz), 3.86 (2H, t, $J=8.3$ Hz), 3.69 (3H, s), 2.97 (2H, t, $J=8.7$ Hz);[24] ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.68, 142.47, 130.82, 127.41, 124.65, 122.48, 114.66, 52.45, 47.36, 27.46; IR (neat) 1710 (s), 1488 (s), 1444 (s), 1395 (s), 1337 (m), 1317 (m), 1137 (m), 1058 (m), 752 (m) cm^{-1};[24] MS (EI^+) *m/z* 177 (M^+, 100), 162 (19), 132 (30), 118 (48), 91 (38); HRMS (EI^+) calcd for $C_{10}H_{11}NO_2$ 177.0790, found 177.0787.

4.2.3.19. 1-Methoxycarbonyl-2-methylindoline (5b-MC). Obtained as a pale brown thick oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 (1H, very br), 7.07–7.00 (2H, m), 6.82 (1H, t, J=7.3 Hz), 4.41 (1H, br quin, J=7 Hz), 3.70 (3H, s), 3.22 (1H, dd, J=15.9, 9.6 Hz), 2.49 (1H, dd, J=15.9, 2.4 Hz), 1.15 (3H, d, J=6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.62, 130.03, 127.42, 125.01, 122.67, 115.32, 55.33, 52.40, 35.83, 21.06; IR (neat) 1708 (s), 1485 (s), 1441 (s), 1390 (s), 1285 (m), 1060 (m), 751 (m) cm^{-1}; MS (EI$^+$) *m/z* 191 (M$^+$, 83), 176 (100), 132 (40), 117 (76); HRMS (EI$^+$) calcd for $C_{11}H_{13}NO_2$ 191.0946, found 191.0942.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.09.116. The ^{1}H and ^{13}C NMR spectra of **1b** in DMF-d_7 before and after CO_2 bubbling (Fig. 4). The HMBC spectrum of **1b** in DMSO-d_6 after CO_2 bubbling (Fig. 5). The IR spectra of **1b** in DMSO before and after CO_2 bubbling (Fig. 6).

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