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Methoxycarbonylation of Alkyl-, Cycloalkyl-, and Arylamines with Dimethyl Carbonate in the Presence of Binder-Free Zeolite

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Abstract—Methyl *N*-alkyl-, *N*-cycloalkyl-, and *N*-arylcarbamates were synthesized by reaction of the corresponding amines with dimethyl carbonate in the presence of binder-free FeHY zeolite. The optimal conditions (reactant ratio, amount of the catalyst, temperature, reaction time) were found to afford the target products with high yields.

Keywords: dimethyl carbonate, *N*-alkylcarbamates, *N*-cycloalkylcarbamates, *N*-arylcarbamates, zeolite catalyst

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N-Substituted carbamates are starting materials in phosgene-free syntheses of isocyanates that are widely used for the preparation of pesticides, fungicides, herbicides, medicines, cosmetics, as well as polyurethanes; they are also used as protecting groups in organic synthesis. Carbamates are of great interest as compounds exhibiting various biological activities, in particular anesthetics [1], anticholinesterase agents [2], preservatives [3], and insecticides [4]. Bi- and polyfunctional urethanes are widely used in the manufacture of construction materials, heat insulators, heavy duty revetments with specified properties, durable sealants, and adhesives [5].

Organic carbamates can be obtained by various methods. In particular, they are prepared by reaction of aliphatic or aromatic amines with dimethyl carbonate (40 equiv) in the presence of a base such as potassium *tert*-butoxide and sodium methoxide (1.2 equiv) [6]. Methoxycarbonylation of amines in solution can be catalyzed by transition metal compounds, e.g., $Mn(OAc)_2$, $Co(OAc)_2$, and $Cr(OAc)_3$. For example, the reaction of hexane-1,6-diamine with 4 equiv of dimethyl carbonate at 90°C (5 h) in the presence of $Mn(OAc)_2$ (7 wt %) afforded 98% of dimethyl *N*,*N*′-(hexane-1,6-diyl)dicarbamate [7]. However, the use of homogeneous catalysts has drawbacks related to the necessity of isolation of waste catalyst and impossibility of its repeated use. According to Baba et al. [8], $Pb(NO_3)_2$ catalyzed methoxycarbonylation of propyl-, butyl-, and hexylamines at 100°C (2 h). In a number of studies, primary amines were subjected to methoxycarbonylation with dimethyl carbonate in the presence of heterogeneous catalysts such as ZrO_2/SiO_2 (25 wt %) [9], La_2O_3/SiO_2 [10], and γ-Al_2O_3 [11]. These reactions required elevated temperature (150–170°C) and prolonged time (7–48 h). Sarmah and Srivastava [12] proposed a modified zeolite, meso-ZSM-5 containing 30% of MnO_2, to catalyze the reaction of benzylamine with dimethyl carbonate. The reaction was complete in 24 h at 80°C, and the yield of methyl benzylcarbamate was 64%. *N*-Benzylidenebenzylamine was also formed as by-product (yield 16%).

The goal of the present work was to develop a new general method for methoxycarbonylation of amines with dimethyl carbonate in the presence of micro-, macro-, and mesoporous zeolites. Preliminarily, the following zeolites were tested as catalysts in methoxycarbonylation of amines: NaX, Y, HY, and FeHY-mmm. No appreciable catalytic activity was demonstrated by NaX, Y, and HY zeolites. The iron-containing zeolite FeHY-mmm proved to be an efficient catalyst in the methoxycarbonylation of alkyl-, cycloalkyl-, and arylamines with dimethyl carbonate. It was prepared by impregnating binder-free micro-, macro-, and mesoporous HY-mmm zeolite with a solution of $Fe(NO_3)_3 \cdot 9H_2O$, followed by thermal treatment at

Table 1. Reaction of butan-1-amine (**1a**) with dimethyl carbonate

Temperature, °C	Reaction time, h	Yield, %	
		1b	**1c**
90	1	25	0
100	1	52	0
120	1	95	0
120	2	49	49

150°C for 4 h and at 450°C for 3 h. We thus obtained samples of FeHY-mmm containing 3–5 wt % of Fe_2O_3 [13, 14].

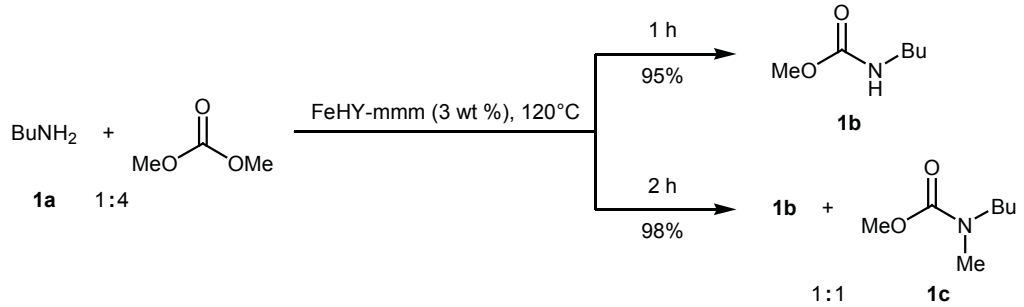
The yields of N-substituted carbamates in the reaction of amines with dimethyl carbonate catalyzed by FeHY-mmm depended on the initial amine, amount of the catalyst, and reaction conditions. The conditions were optimized (Table 1) using the reaction of butan-1-amine (**1a**) with dimethyl carbonate in the presence of 3 wt % of FeHY-mmm. It was found that the reaction at 120°C in 1 h produces 95% of methyl *N*-butylcarbamate **1b**. Prolonged reaction (2 h) led to the formation of 49% of methyl *N*-butyl-*N*-methylcarbamate (**1c**) as a result of methylation of **1b**. Dimethyl carbonate was taken in excess (4 equiv) since it acted simultaneously as reagent and solvent (Scheme 1).

Analogous reaction of heptan-1-amine (**2a**) with dimethyl carbonate in the presence of FeHY-mmm at 120°C (1 h) gave methyl *N*-heptylcarbamate (**2b**) in 93% yield, whereas after 2 h a mixture of compound **2b** and methyl *N*-heptyl-*N*-methylcarbamate (**2c**) at a ratio of 1:1 was formed (Scheme 2). Thus, the length of the alkyl chain in the initial amine almost does not affect the yield and selectivity.

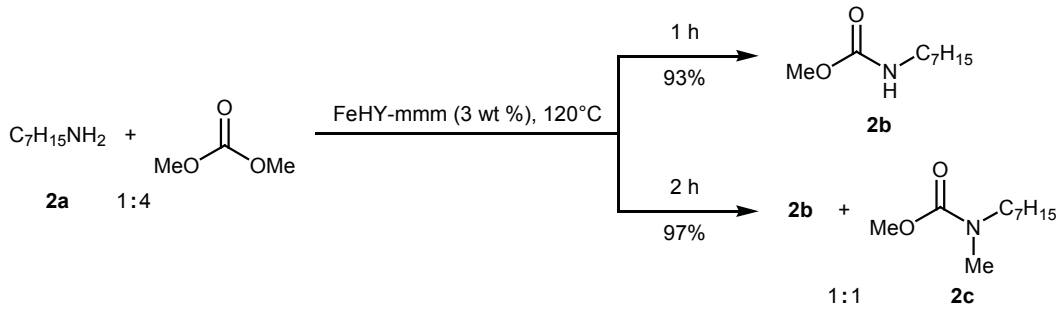
Cycloropanamine (**3a**) reacted with dimethyl carbonate under similar conditions (120°C, 30 min, 3 wt % FeHY-mmm) to produce a mixture of methyl *N*-cyclopropylcarbamate (**3b**) and methyl *N*-cyclopropyl-*N*-methylcarbamate (**3c**) at a ratio of 1:9, the conversion of **3a** being complete. Further increase of the reaction time was undesirable due to opening of the cyclopropane ring and formation of high-molecular-weight compounds (Scheme 3).

The reactions of cyclopentanamine (**4a**), cyclohexanamine (**5a**), cycloheptaneamine (**6a**), and cyclooctanamine (**7a**) with dimethyl carbonate at 120°C (1 h) gave 70–80% of the corresponding methyl *N*-cycloalkylcarbamates **4b**–**7b**, regardless of the ring size. When

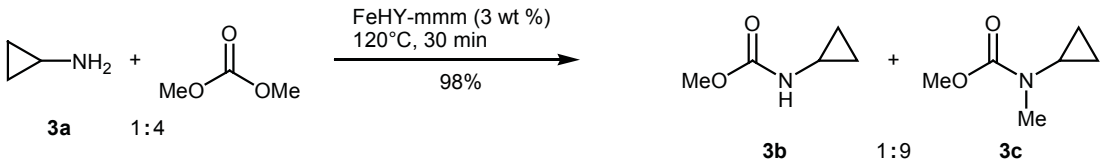
Scheme 1.



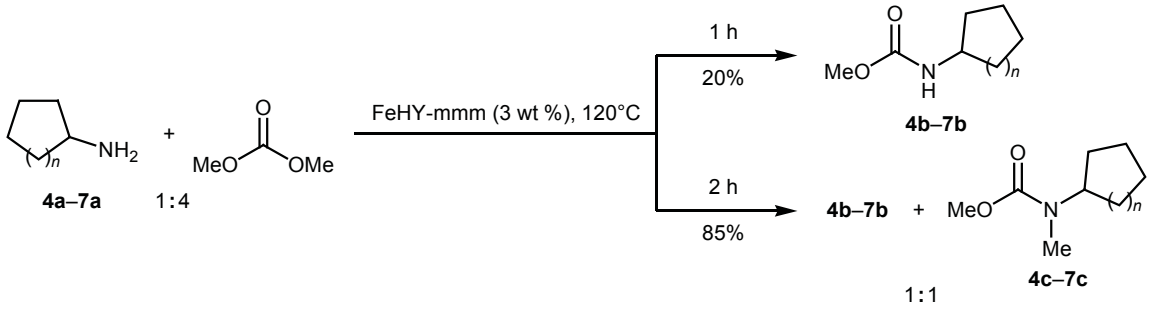
Scheme 2.



Scheme 3.

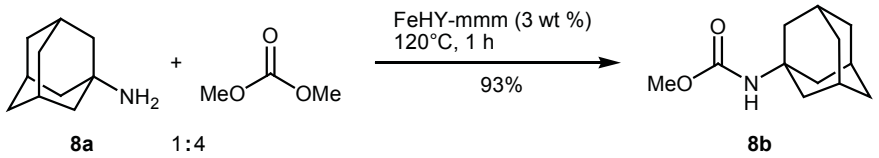


Scheme 4.

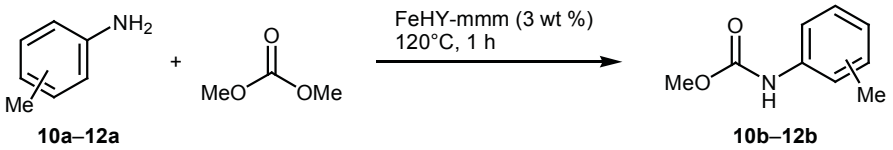


n = 1–4.

Scheme 5.



Scheme 6.



10, *o*-Me, 27%; **11**, *m*-Me, 45%; **12**, *p*-Me, 88%.

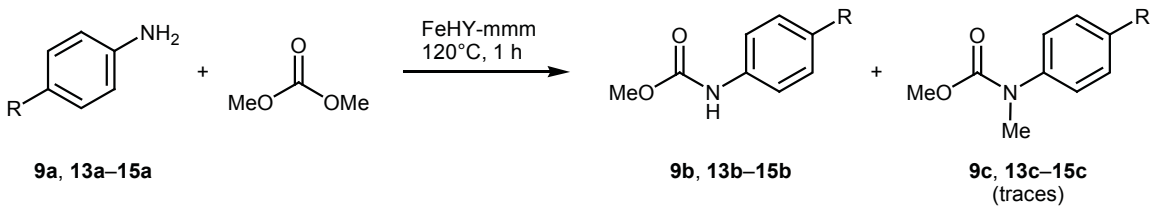
the reaction time was prolonged to 2 h, mixtures of approximately equal amounts of **4b**–**7b** and their *N*-methyl derivatives **4c**–**7c** were formed. Further increase of the reaction time to 5 h did not increase the yield of **4c**–**7c** but favored methylation of initial amines **4a**–**7a** (Scheme 4).

Despite the presence of a bulky substituent, adamantan-1-amine (**8a**) actively reacted with dimethyl carbonate under similar conditions, yielding methyl *N*-(adamantan-1-yl)carbamate (**8b**) as the only product (93%, Scheme 5). No further methylation of **8b** at the nitrogen atom was observed when the reaction time was prolonged or the amount of the catalyst was increased to 5 wt %, presumably due to steric effect of the bulky adamantane fragment.

Methoxycarbonylation of aniline (**9a**) with dimethyl carbonate in the presence of 5 wt % FeHY-mmm at 120°C (1 h) afforded 85% of methyl *N*-phenylcarbamate (**9b**). In the case of isomeric toluidines **10a**–**12a**, the position of the methyl group with respect to amino significantly influenced the yield of carbamates **10b**–**12b**. The highest yield was obtained for *p*-toluidine (**12a**). Raising the temperature or increasing the reaction time changed the reaction direction toward formation of the corresponding *N*-methylanilines (Scheme 6) [15].

Other *para*-substituted anilines, 4-chloroaniline (**13a**), 4-bromoaniline (**14a**), and 4-nitroaniline (**15a**), also smoothly reacted with dimethyl carbonate under the given conditions to produce methyl *N*-(4-chlorophenyl)carbamate (**13b**), methyl *N*-(4-bromophenyl)-carbamate (**14b**), and methyl *N*-(4-nitrophenyl)carbamate (**15b**), respectively, in 85–88% yields (Scheme 7). No further methylation of **13b**–**15b** was

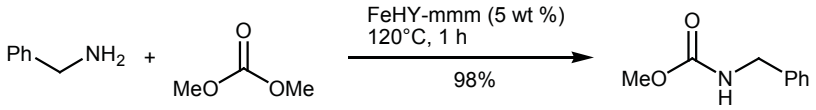
Scheme 7.



9a, **13a–15a** **9b**, **13b–15b** **9c**, **13c–15c** (traces)

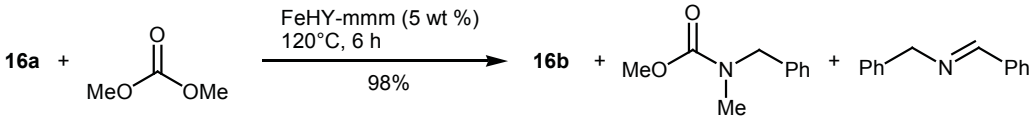
9, R = H; **13**, R = Cl; **14**, R = Br; **15**, R = NO_2.

Scheme 8.



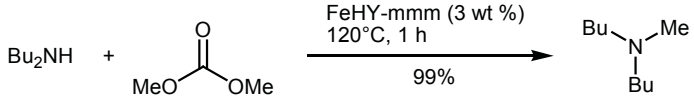
16a **16b**

Scheme 9.



25% **16c**, 51% **16d**, 24%

Scheme 10.



17a 1:4 **17b**

observed when the reaction time was prolonged, but the corresponding *N*-methylanilines RC_6H_4NHMe were formed.

Methoxycarbonylation of benzylamine (**16a**) with dimethylcarbonate in the presence of 5 wt % FeHY-mmm at 120°C (1 h) quantitatively afforded methyl *N*-benzylcarbamate (**16b**) (Scheme 8). After 6 h, a mixture of **16b**, methyl *N*-benzyl-*N*-methylcarbamate (**16c**), and *N*-benzylidenebenzylamine (**16d**) at a ratio of 1:2:1 was obtained (Scheme 9).

Secondary amines, in particular dibutylamine (**17a**), reacted with dimethyl carbonate in the presence of FeHY-mmm to give only the corresponding tertiary amine, *N*-butyl-*N*-methylbutan-1-amine (**17b**) (Scheme 10).

Thus, we have developed a method for the synthesis of methyl *N*-alkyl-, *N*-cycloalkyl-, and *N*-arylcarbamates in high yields by methoxycarbonylation of the corresponding primary amines with dimethyl carbonate in the presence of binder-free FeHY-mmm zeolite catalyst.

EXPERIMENTAL

Initial reactants of pure and chemically pure grades were commercial products (Sigma–Aldrich). The ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (Germany) at 100.62 MHz using $CDCl_3$ as solvent (unless otherwise stated). The mass spectra (electron impact, 70 eV) were obtained with a Shimadzu GCMS-QP2010Plus instrument (Japan) equipped with an SPB-5 capillary column, 30 m× 0.25 mm; carrier gas helium; oven temperature programming from 40 to 300°C at a rate of 8 deg/min, injector temperature 280°C. The IR spectra were recorded in KBr or mineral oil on a Bruker-Vertex 79V spectrometer (Germany). The elemental compositions were determined using a Carlo Erba 1106 elemental analyzer (Italy).

The progress of reactions and the purity of the isolated compounds were monitored by GLC with a Shimadzu GC-9A or GC-2014 chromatograph (Japan) using a 2-m×3-mm column packed with SE-30 (5%) on Chromaton N-AW-HMDS; oven temperature

programming from 50 to 270°C at a rate of 8 deg/min; carrier gas helium, flow rate 47 mL/min.

The binder-free zeolite catalyst (FeHY-mmm) was prepared as described in [13, 14].

General procedure for the methoxycarbonylation of alkyl-, cycloalkyl-, and arylamines with dimethyl carbonate. The reactions were carried out in a 17-mL stainless steel high-pressure micro reactor or a 20-mL glass ampule. The results of parallel runs were almost the same. The reactor (ampule) was charged with 3–5 wt % of FeHY-mmm, 10 mmol of the corresponding amine, and 40 mmol of dimethyl carbonate. The reactor was hermetically closed (the ampule was sealed) and heated at 120°C for 0.5–2 h. When the reaction was complete, the reactor (ampule) was cooled to room temperature and opened, the mixture was filtered through a layer of alumina, excess dimethyl carbonate was distilled off, and the residue was distilled under atmospheric or reduced pressure or crystallized from ethanol.

Methyl *N*-butylcarbamate (1b). Yield 1.246 g (95%), bp 82–83°C (9 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 13.68 (CH_3), 20.01 (C^3), 31.93 (C^2), 40.65 (C^1), 51.70 (OCH_3), 157.67 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 131 (3) $[M]^+$, 117 (1), 103 (15), 90 (5), 77 (56), 70 (100), 55 (85), 41 (57), 29 (35). Found, %: C 54.37; H 9.49; N 10.22. $C_6H_{13}NO_2$. Calculated, %: C 54.94; H 9.99; N 10.68. *M* 131.172.

Methyl *N*-butyl-*N*-methylcarbamate (1c). Yield 0.711 g (49%), bp 70–71°C (20 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 13.57 (CH_3), 19.81 (C^3), 30.47 (C^2), 49.65 (C^1), 52.17 (OCH_3), 157.17 (C=O). Found, %: C 56.95; H 10.17; N 9.12. $C_7H_{15}NO_2$. Calculated, %: C 57.90; H 10.41; N 9.65. *M* 145.199.

Methyl *N*-heptylcarbamate (2b). Yield 1.611 g (93%), mp 31–32°C (from CH_2Cl_2–hexane). ^{13}C NMR spectrum, δ_C, ppm: 14.10 (CH_3), 22.61 (C^6), 26.89 (C^3), 28.90 (C^4), 30.63 (C^2), 31.69 (C^5), 41.20 (C^1), 51.70 (OCH_3), 157.87 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 174 (3) $[M]^+$, 158 (3), 144 (2), 130 (3), 103 (5), 88 (100), 76 (16), 59 (15), 44 (37), 29 (10). Found, %: C 62.97; H 10.99; N 7.82. $C_9H_{19}NO_2$. Calculated, %: C 62.39; H 11.05; N 8.08. *M* 173.252.

Methyl *N*-heptyl-*N*-methylcarbamate (2c). Yield 0.898 g (48%), bp 94–95°C (5 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 14.10 (CH_3), 22.68 (C^6), 27.89 (C^3), 29.25 (C^2), 29.89 (C^4), 32.29 (C^5), 33.65 (NCH_3), 50.60 (C^1), 52.17 (OCH_3), 156.87 (C=O). Found, %: C 63.85; H 10.97; N 6.92. $C_{10}H_{21}NO_2$. Calculated, %: C 64.13; H 11.30; N 7.48. *M* 187.279.

Methyl *N*-cyclopropylcarbamate (3b). Yield 1.036 g (90%), colorless oil, bp 84–85°C (11 mm Hg); published data [16]: bp 95–96°C (12 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 6.68 (C^1), 22.89 (C^2), 51.95 (C^4), 158.47 (C^3). Found, %: C 51.85; H 7.45; N 11.92. $C_5H_9NO_2$. Calculated, %: C 52.116; H 7.88; N 12.17. *M* 115.130.

Methyl *N*-cyclopropyl-*N*-methylcarbamate (3c). Yield 0.129 g (10%), colorless oil, bp 84–85°C (11 mm Hg). IR spectrum, ν, cm^{-1}: 1028 m, 1040 m, 1159 s, 1287 s, 1363 m, 1375 m, 1695 s, 2984 s, br. ^{13}C NMR spectrum, δ_C, ppm: 7.68 (C^2, C^3), 30.52 (C^1), 34.80 (CH_3), 52.07 (OCH_3), 158.47 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 129 (60) $[M]^+$, 115 (80), 100 (100), 84 (40), 70 (90), 59 (92), 40 (95). Found, %: C 54.97; H 7.99; N 8.22. $C_6H_{11}NO_2$. Calculated, %: C 55.80; H 8.58; N 10.84. *M* 129.157.

Methyl *N*-cyclopentylcarbamate (4b). Yield 1.39 g (97%), bp 72–73°C (2 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 23.52 d (C^3, C^4), 33.39 d (C^2, C^5), 51.80 (C^1), 52.75 (OCH_3), 156.60 (C=O), 42.32. Found, %: C 57.95; H 8.29; N 9.66. $C_7H_{13}NO_2$. Calculated, %: C 58.72; H 9.15; N 9.78. *M* 143.183.

Methyl *N*-cyclopentyl-*N*-methylcarbamate (4c). Yield 0.628 g (40%), bp 80–81°C (8 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 23.58 d (C^3, C^4), 28.59 (CH_3), 33.18 d (C^2, C^5), 56.65 (C^1), 51.96 (OCH_3), 156.46 (C=O). Found, %: C 59.95; H 9.29; N 8.66. $C_8H_{15}NO_2$. Calculated, %: C 61.12; H 9.62; N 8.91. *M* 157.210.

Methyl *N*-cyclohexylcarbamate (5b). Yield 1.446 g (92%), mp 74–75.0°C (from cyclohexane); published data [17]: mp 74–74.5°C. IR spectrum (KBr), ν, cm^{-1}: 778 m, 894 m, 1052 s, br, 1238 s, 1250 s, 1284 s, 1350 s, 1451 s, 1533 s, 1695 s, 3320 m, 3350 s. ^{13}C NMR spectrum, δ_C, ppm: 24.85 (C^3, C^5), 25.48 (C^4), 33.59 (C^2, C^6), 49.82 (C^1), 51.82 (OCH_3), 156.56 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 156 (5) $[M]^+$, 140 (1), 128 (100), 115 (6), 102 (9), 90 (14), 83 (5), 67 (3), 55 (10), 28 (2). Found, %: C 60.97; H 9.29; N 8.22. $C_8H_{15}NO_2$. Calculated, %: C 61.12; H 9.62; N 8.91. *M* 157.210.

Methyl *N*-cyclohexyl-*N*-methylcarbamate (5c). Yield 0.77 g (45%), bp 85–86°C (1 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 26.15 (C^3, C^5), 26.48 (C^4), 31.29 (C^2, C^6), 41.28 (CH_3), 56.42 (C^1), 51.22 (OCH_3), 158.06 (C=O). Found, %: C 62.97; H 9.51; N 8.42. $C_9H_{17}NO_2$. Calculated, %: C 63.13; H 10.01; N 8.18. *M* 171.236.

Methyl *N*-cycloheptylcarbamate (6b). Yield 1.54 g (90%), bp 89–90°C (1 mm Hg). ^{13}C NMR

spectrum, δ_C, ppm: 22.64 (C^3, C^6), 31.57 (C^4, C^5), 36.33 (C^2, C^7), 51.12 (C^1), 51.79 (OCH_3), 156.26 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 171 (10) $[M]^+$, 156 (15), 142 (15), 128 (60), 114 (100), 101 (40), 96 (60), 88 (55), 82 (56), 76 (100), 59 (50), 41 (72), 40 (100). Found, %: C 62.97; H 9.69; N 7.82. $C_9H_{17}NO_2$. Calculated, %: C 63.13; H 10.01; N 8.18. *M* 171.236.

Methyl *N*-cycloheptyl-*N*-methylcarbamate (6c). Yield 0.833 g (45%), bp 95–96°C (3 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 23.86 (C^3, C^6), 28.02 (C^4, C^5), 30.21 (CH_3), 35.33 (C^2, C^7), 51.79 (OCH_3), 57.72 (C^1), 156.26 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 185 (10) $[M]^+$, 170 (1), 156 (1), 142 (2), 128 (100), 114 (45), 102 (20), 96 (20), 90 (20), 76 (10), 71 (10), 59 (10), 41 (25), 42 (30), 40 (90). Found, %: C 63.87; H 9.89; N 7.28. $C_{10}H_{19}NO_2$. Calculated, %: C 64.83; H 10.34; N 7.56. *M* 185.263.

Methyl *N*-cyclooctylcarbamate (7b). Yield 1.684 g (91%), bp 115–115.5°C (2 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 23.50 (C^3, C^7), 26.44 (C^5), 27.22 (C^4, C^6), 31.56 (C^2, C^8), 50.91 (C^1), 51.57 (OCH_3), 156.40 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 185 (45) $[M]^+$, 170 (48), 156 (49), 142 (100), 128 (99), 114 (97), 101 (95), 76 (96), 56 (88), 40 (91). Found, %: C 63.97; H 9.99; N 7.22. $C_{10}H_{19}NO_2$. Calculated, %: C 64.83; H 10.34; N 7.56. *M* 185.263.

Methyl *N*-cyclooctyl-*N*-methylcarbamate (7c). Yield 0.916 g (46%), bp 100–101°C (2 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 24.96 (C^3, C^7), 25.38 (C^4, C^6), 26.06 (C^5), 27.22 (CH_3), 32.34 (C^2, C^8), 51.91 (OCH_3), 57.79 (C^1), 156.48 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 199 (5) $[M]^+$, 184 (0.5), 170 (1), 156 (1), 142 (2), 128 (100), 114 (30), 102 (15), 90 (30), 76 (10), 71 (15), 56 (20), 42 (40), 41 (38), 40 (40). Found, %: C 65.97; H 9.99; N 6.82. $C_{11}H_{21}NO_2$. Calculated, %: C 66.29; H 10.62; N 7.03. *M* 199.289.

Methyl *N*-(adamantan-1-yl)carbamate (8b). Yield 2.05 g (98%), mp 117–119°C (from CH_2Cl_2–hexane) {118–120°C [18]}. IR spectrum (KBr), ν, cm^{-1}: 1722 (C=O), 3271 (NH). ^{13}C NMR spectrum, δ_C, ppm: 29.95 (C^3, C^5, C^7), 36.38 (C^4, C^6, C^{10}), 41.29 (C^2, C^8, C^9), 51.02 (C^1), 51.22 (OCH_3), 154.98 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 209 (35) $[M]^+$, 152 (100), 120 (68). Found, %: C 67.97; H 9.89; N 6.22. $C_{12}H_{19}NO_2$. Calculated, %: C 68.87; H 9.15; N 6.69. *M* 209.284.

Methyl *N*-phenylcarbamate (9b). Yield 1.299 g (86%), mp 45–46.5°C (from cyclohexane); published data [18]: mp 47–48°C. IR spectrum (KBr), ν, cm^{-1}: 710 m, 730 m, 905 m, 1032 m, 1072 s, 1247 s, 1324 s, 1453 s, 1505 m, 1546 s, 1605 s, 1615 m, 1709 s, 3322 m. ^{13}C NMR spectrum, δ_C, ppm: 52.35 (OCH_3), 118.81 (C^2, C^6), 123.48 (C^4), 128.89 (C^3, C^5), 138.61 (C^1), 154.72 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 151 (100) $[M]^+$, 135 (4), 119 (75), 106 (97), 92 (48), 77 (30), 65 (80), 51 (20), 39 (40), 28 (10). Found, %: C 62.97; H 5.89; N 8.92. $C_8H_9NO_2$. Calculated, %: C 63.56; H 6.00; N 9.27. *M* 151.162.

Methyl *N*-(2-methylphenyl)carbamate (10b). Yield 0.743 g (45%), mp 67–68°C (from CH_2Cl_2–hexane); published data [19]: mp 69–69.3°C. ^{13}C NMR spectrum, δ_C, ppm: 15.57 (CH_3), 52.52 (OCH_3), 121.75 (C^6), 124.79 (C^4), 127.45 (C^5), 128.88 (C^1), 130.87 (C^3), 138.95 (C^1), 154.73 (C=O). Found, %: C 64.87; H 5.99; N 8.12. $C_9H_{11}NO_2$. Calculated, %: C 65.44; H 6.71; N 8.48. *M* 165.189.

Methyl *N*-(3-methylphenyl)carbamate (11b). Yield 0.743 g (45%), mp 69–70°C (from CH_2Cl_2–hexane); published data [19]: mp 69–69.3°C. ^{13}C NMR spectrum, δ_C, ppm: 21.27 (CH_3), 52.65 (OCH_3), 115.92 (C^6), 118.86 (C^2), 123.29 (C^4), 130.55 (C^5), 138.08 (C^3), 138.95 (C^1), 154.83 (C=O). Found, %: C 64.99; H 6.19; N 8.32. $C_9H_{11}NO_2$. Calculated, %: C 65.44; H 6.71; N 8.48. *M* 165.189.

Methyl *N*-(4-methylphenyl)carbamate (12b). Yield 1.452 g (88%), mp 97.5–98.5°C (from cyclohexane); published data [18]: mp 98.3–99°C. IR spectrum (KBr), ν, cm^{-1}: 816 m, 1073 m, 1236 s, 1317 m, 1512 m, 1538 m, 1599 m, 1704 s, 3328 m. ^{13}C NMR spectrum, δ_C, ppm: 20.65 (CH_3), 52.35 (OCH_3), 118.84 (C^2, C^6), 129.48 (C^3, C^5), 132.84 (C^4), 136.65 (C^1), 154.73 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 165 (100) $[M]^+$, 150 (6), 133 (78), 120 (15), 106 (41), 91 (14), 77 (36), 51 (95), 29 (2). Found, %: C 64.97; H 6.09; N 8.12. $C_9H_{11}NO_2$. Calculated, %: C 65.44; H 6.71; N 8.48. *M* 165.189.

Methyl *N*-(4-chlorophenyl)carbamate (13b). Yield 1.58 g (85%), mp 115–116.5°C (from CH_2Cl_2–hexane); published data [18]: mp 115.6–116.1°C. IR spectrum (KBr), ν, cm^{-1}: 1092, 1238, 1546, 1606, 1704, 3345. ^{13}C NMR spectrum, δ_C, ppm: 52.65 (OCH_3), 120.18 (C^2, C^6), 128.34 (C^4), 129.08 (C^3, C^5), 137.05 (C^1), 154.43 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 185 (44) $[M]^+$, 153 (46), 140 (39), 128 (11), 112 (8), 99 (29), 90 (17), 73 (20), 62 (25), 49 (18), 32 (100). Found, %: C 50.97; H 4.09; Cl 18.85; N 7.22. $C_8H_8ClNO_2$. Calculated, %: C 51.77; H 4.34; Cl 19.10; N 7.55. *M* 185.607.

Methyl *N*-(4-bromophenyl)carbamate (14b). Yield 2 g (87%), mp 125–126°C (from CH_2Cl_2–hexane); published data [18]: mp 125.1–125.7°C.

^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 52.65 (OCH_3), 116.34 (C^4), 120.15 (C^2, C^6), 131.58 (C^3, C^5), 136.15 (C^1), 153.73 (C=O). Found, %: C 40.97; H 3.09; Br 33.85; N 5.82. $C_8H_8BrNO_2$. Calculated, %: C 41.77; H 3.50; Br 34.73; N 6.09. *M* 230.058.

Methyl *N*-(4-nitrophenyl)carbamate (15b). Yield 1.686 g (86%), mp 176.5–178°C (from CH_2Cl_2–hexane); published data [18]: mp 177.2–178°C. IR spectrum (KBr), ν, cm^{-1}: 1220, 1326, 1506, 1596, 1740, 3394. ^{13}C NMR spectrum, δ_C, ppm: 52.65 (OCH_3), 117.38 (C^2, C^6), 125.08 (C^3, C^5), 143.05 (C^1), 146.04 (C^4), 154.83 (C=O). Found, %: C 47.97; H 3.89; N 13.42. $C_8H_8N_2O_4$. Calculated, %: C 48.98; H 4.11; N 14.28. *M* 196.160.

Methyl *N*-benzylcarbamate (16b). Yield 1.6 g (97%), mp 64–65°C (from CH_2Cl_2–hexane; published data [20]: mp 62.2–62.9°C. IR spectrum (KBr), ν, cm^{-1}: 704, 739, 999, 1144, 1273 s, 1495 m, 1536 s, 1692 s, 3344 m. ^{13}C NMR spectrum, δ_C, ppm: 45.07 (CH_2), 52.25 (OCH_3), 127.29 (C^4), 127.55 (C^2, C^6), 128.08 (C^3, C^5), 137.65 (C^1), 156.83 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 165 (40) $[M]^+$, 150 (78), 133 (32), 121 (9), 106 (12), 91 (100), 79 (66), 77 (10), 65 (29), 59 (12), 29 (9). Found, %: C 64.87; H 6.19; N 7.82. $C_9H_{11}NO_2$. Calculated, %: C 65.44; H 6.71; N 8.48. *M* 165.189.

Methyl *N*-benzyl-*N*-methylcarbamate (16c). Yield 1.003 g (56%), colorless oil, R_f 0.44 (hexane–EtOAc, 2:1). IR spectrum (KBr), ν, cm^{-1}: 701, 771, 1144, 1146 s, 1454 m, 1484, 1536 s, 1705 s, 2955, 3030 m. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 35.7 (CH_3), 52.29 (OCH_3), 53.74 (CH_2), 126.97 (C^2, C^6), 127.56 (C^4), 128.02 (C^3, C^5), 137.68 (C^1), 156.45 (C=O). Found, %: C 66.87; H 6.99; N 7.72. $C_{10}H_{13}NO_2$. Calculated, %: C 67.02; H 7.31; N 7.82. *M* 179.215.

***N*-Benzylidenebenzylamine (16d).** Yield 0.488 g (25%), bp 124–125°C (2 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 65.05 (Ph**C**H_2), 127.98 (C^2, C^6), 128.49 (C^3, C^5), 128.60 ($C^{3'}$, $C^{5'}$), 128.63 (C^4), 130.76 ($C^{4'}$), 136.17 ($C^{1'}$), 139 (C^1), 162.00 (N=CH). Mass spectrum, *m*/*z* (I_{rel}, %): 195.25 (35) $[M]^+$, 194 (33), 165 (5), 152 (3), 117 (15), 91 (100), 65 (20), 51 (5). Found, %: C 85.87; H 6.19; N 6.92. $C_{10}H_{21}N$. Calculated, %: C 86.12; H 6.71; N 7.17. *M* 195.2597.

***N*-Butyl-*N*-methylbutan-1-amine (17b).** Yield 1.418 g (99%), bp 85–86°C (50 mm Hg). ^{13}C NMR spectrum, δ_C, ppm: 14.60 (C^4, $C^{4'}$), 21.10 (C^3, $C^{3'}$), 29.31 (C^2, $C^{2'}$), 42.18 (NCH_3), 58.21 (C^1, $C^{1'}$). Found, %: C 76.87; H 13.99; N 9.12. $C_9H_{21}N$. Calculated, %: C 75.45; H 14.77; N 9.78. *M* 143.269.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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