

Electronic Supplementary Information

CH₃COONa As an Effective Catalyst for Methoxycarbonylation of 1,6-Hexanediamine by Dimethyl Carbonate to Dimethylhexane-1,6-dicarbamate

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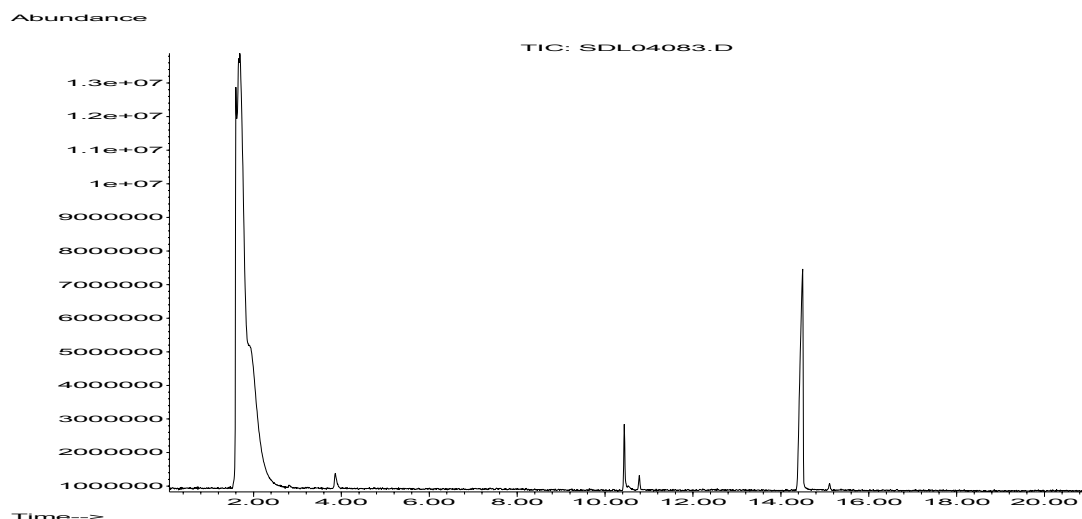
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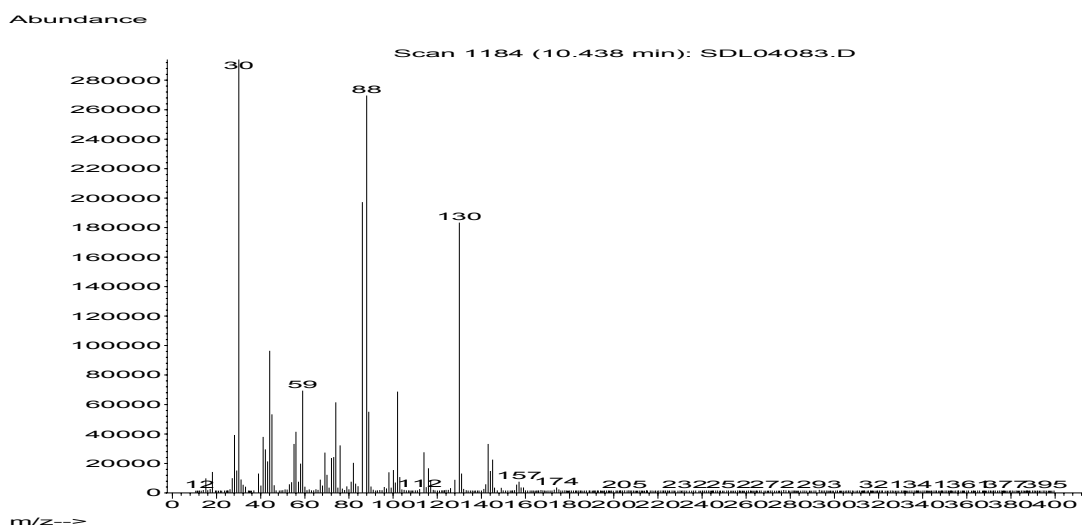
1. Identification of the by-products *1* and *7*

100 mmol HDA, 200 mmol (16.8 ml) DMC and 50 ml CH₃OH were employed in the methoxycarbonylation reaction and 14.7 mmol (1.2 g) CH₃COONa was used as catalyst. After the reaction was performed at 348 K for 9 h, the products mixture was cooled to room temperature and then subjected to GC/MS analysis.

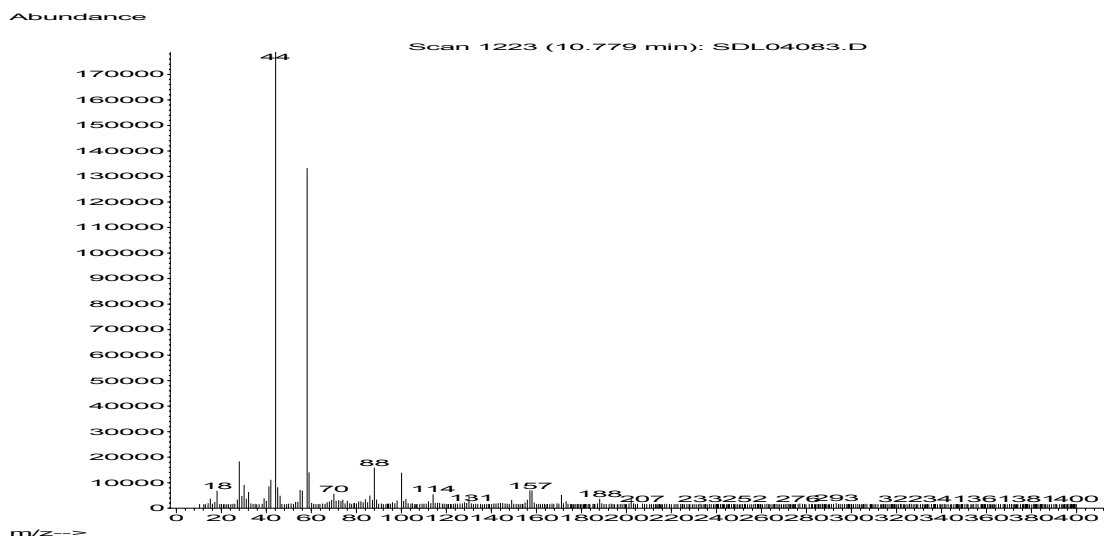
Fig. S1 shows the GC-MS chromatogram of the products mixture. In the total ion chromatogram (TIC), there are mainly five peaks at 2.5, 4.5, 14.46, 10.14 and 10.78. The peaks at ca. 2.5 and 4.5 min are respectively caused by the solvent and the impurity in the solvent. The MS spectra have been scanned for the peaks at 10.14, 10.78 and 14.46 min in the TIC, and the fragment ions detected and their assignments for the former two peaks are listed in Tables S1 and S2, respectively, which show clearly that the two peaks can be identified as the by-products *1* (NH₂(CH₂)₆NHCOOCH₃) and *7* (CH₃)₂N(CH₂)₆NHCH₃). The MS spectrum of the last peak (14.46 min) is the same as that of Fig. S3 (b) for purified *2*.



(a)



(b)



(c)

Fig. S1 GC/MS chromatogram of the products mixture

(a) TIC; (b) and (c), MS spectra of the peaks at 10.43 and 10.78 min in the TIC, respectively.

Table S1 GC/MS analysis of the by-product *1*

Ion	M/Z	fragment ion	Lost fragment ion
M ⁺	174	CH ₃ OONH(CH ₂) ₆ NH ₂	electron
M-16	158	(CH ₂) ₆ NHCOOCH ₃	NH ₂
M-31	143	NH ₂ (CH ₂) ₆ NHCO	CH ₃ O
M-59	115	NH ₂ (CH ₂) ₆ NH	COOCH ₃
M-74	100	NH ₂ (CH ₂) ₆	NHCOOCH ₃
M-88	86	NH ₂ (CH ₂) ₅	CH ₂ NHCOOCH ₃
M-102	72	NH ₂ (CH ₂) ₄	(CH ₂) ₂ NHCOOCH ₃
M-116	58	NH ₂ (CH ₂) ₃	(CH ₂) ₃ NHCOOCH ₃
M-130	44	NH ₂ (CH ₂) ₂	(CH ₂) ₄ NHCOOCH ₃
M-144	30	NH ₂ CH ₂	(CH ₂) ₅ NHCOOCH ₃
M-158	16	NH ₂	(CH ₂) ₆ NHCOOCH ₃
M-188	44	COO	CH ₃ , NH(CH ₂) ₆ NHCOOCH ₃

Table S2 GC/MS analysis of the by-product *7*

Ion	M/Z	fragment ion	Lost fragment ion
M ⁺	158	(CH ₃) ₂ N(CH ₂) ₆ NHCH ₃	electron
M-15	143	(CH ₃) ₂ N(CH ₂) ₆ NH or CH ₃ NH(CH ₂) ₆ NHCH ₃	CH ₃
M-30	128	N(CH ₂) ₆ NHCH ₃ or CH ₃ N(CH ₂) ₆ NH	2 × CH ₃
M-45	113	N(CH ₂) ₆ NH	3 × CH ₃
M-44	114	(CH ₃) ₂ N(CH ₂) ₅	CH ₂ NHCH ₃
M-58	100	(CH ₃) ₂ N(CH ₂) ₄	(CH ₂) ₂ NHCH ₃
M-72	86	(CH ₃) ₂ N(CH ₂) ₃	(CH ₂) ₃ NHCH ₃
M-86	72	(CH ₃) ₂ N(CH ₂) ₂	(CH ₂) ₄ NHCH ₃
M-100	58	(CH ₃) ₂ N(CH ₂)	(CH ₂) ₅ NHCH ₃
M-114	44	(CH ₃) ₂ N	(CH ₂) ₆ NHCH ₃
M-129	29	CH ₃ N	(CH ₂) ₆ NHCH ₃ , CH ₃

2. Analytical and calculation method

The concentration of component i in the product mixture, C_i , was calculated using the internal standard method, with propyl benzene as the internal standard using the expression

$$C_i \% = \frac{A_i \cdot f_{m,i}}{A_s \cdot f_{m,s}} \times \frac{m_s}{m} \times 100\%$$

, where A_i and $f_{m,i}$ are the chromatography peak area and the relative correction factor of the component i in the products mixture, respectively, and A_s and $f_{m,s}$ are those of the internal standard; m_s stands for the weight of the internal standard and m for that of the product mixture.

The conversion of HAD (χ_{HDA}), the selectivity to component i (S_i) and the yield of **2** (Y_2) were calculated using the expressions

$$\chi_{HDA} = \frac{C_{HDA} - C'_{HDA}}{C_{HDA}} \times 100\%$$

$$S_i = \frac{C_i}{\sum C_i} \times 100\%$$

$$Y_2 = (\chi_{HDA} \times S_2) / 100$$

, where C_{HDA} is the concentration of HDA before reaction and C'_{HDA} after reaction.

3. Identification of purified **2**

The crude **2** obtained via the methoxycarbonylation of HDA by DMC using sodium acetate as catalyst was subjected to re-crystallization, which involves the steps of dissolution in water at ca. 353 K, aging at room temperature for 2 h, filtration and washing with cold water. The re-crystallization procedure was repeated five times, and after drying in vacuo,

the purified **2** was finally obtained.

Fig. S2 shows the ^1H NMR spectrum of purified **2**. The chemical shifts observed and their assignments are as follows: $\delta = 1.33$ (*m*, 4H; -NHCH₂CH₂CH₂-), 1.48 (*m*, 4H; -NHCH₂CH₂CH₂-), 3.14 (*q*, 4H; -NHCH₂-), 3.66 (*s*, 6H; -OCH₃), 4.79 (broad, 2H; NHCO).

Fig. S3 presents the GC-MS chromatogram of purified **2**. While the large peak at ca. 2.5 min is due to the solvent (methanol) and the small peak at ca. 4.5 min to the impurity in the solvent, the peak at 14.46 min is caused by **2**. The fragment ions detected and their assignments are listed in Table S3.

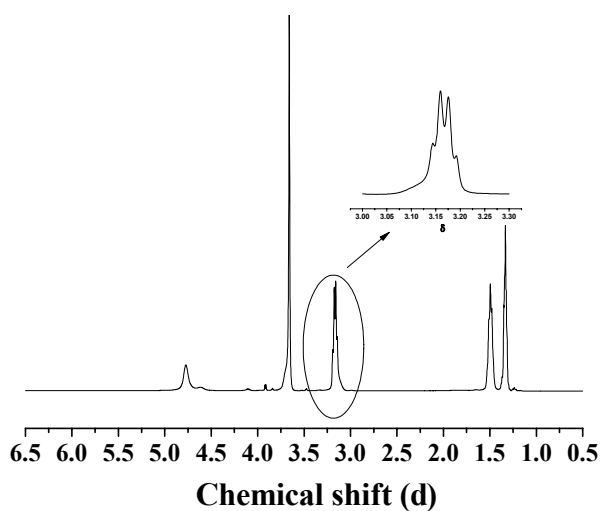
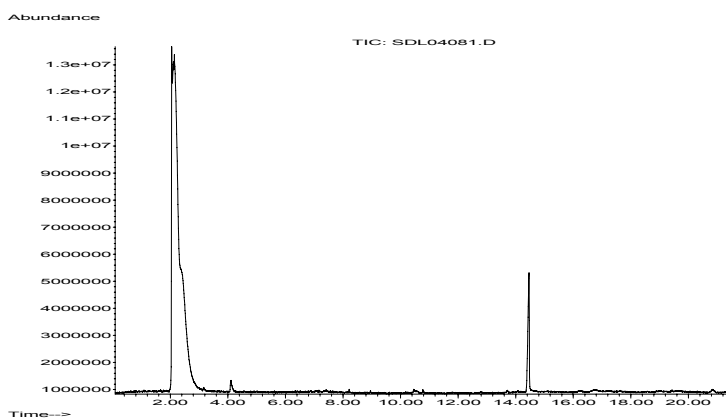


Fig. S2 ^1H NMR spectrum of purified **2**



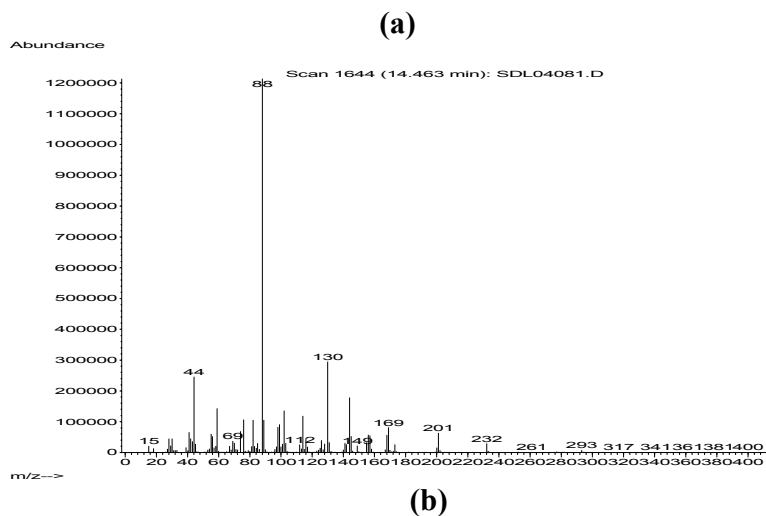


Fig. S3 GC-MS chromatogram of purified **2**

(a) Total ion chromatogram (TIC); (b) MS spectrum of the peak at 14.46 min in TIC)

Table S3 GC/MS analysis for **2**

Ion	M/Z	fragment ion	Lost fragment ion
M ⁺	232	CH ₃ OONH(CH ₂) ₆ NHCOOCH ₃	electron
M-31	201	CH ₃ COONH(CH ₂) ₆ NHCO	CH ₃ O
M-59	173	CH ₃ COONH(CH ₂) ₆ NH	COOCH ₃
M-74	158	CH ₃ COONH(CH ₂) ₆	NHCOOCH ₃
M-88	144	CH ₃ COONH(CH ₂) ₅	CH ₂ NHCOOCH ₃
M-102	130	CH ₃ COONH(CH ₂) ₄	(CH ₂) ₂ NHCOOCH ₃
M-116	116	CH ₃ COONH(CH ₂) ₃	(CH ₂) ₃ NHCOOCH ₃
M-118	114	NH(CH ₂) ₆ NH	2 × COOCH ₃
M-130	102	CH ₃ COONH(CH ₂) ₂	(CH ₂) ₄ NHCOOCH ₃
M-133	99	NH(CH ₂) ₆	COOCH ₃ , NHCOOCH ₃
M-144	88	CH ₃ COONHCH ₂	(CH ₂) ₅ NHCOOCH ₃
M-158	74	CH ₃ COONH	(CH ₂) ₆ NHCOOCH ₃
M-173	59	COOCH ₃	CH ₃ COONH(CH ₂) ₆ NH

M-176	56	$\text{CH}_2(\text{CH}_2)_2\text{CH}_2$	$2 \times \text{CH}_2 \text{NHCOOCH}_3$
M-188	44	COO	$\text{CH}_3, \text{NH}(\text{CH}_2)_6\text{NHCOOCH}_3$

From Figs. S2 and S3 and Table S3, one can conclude that the purified **2** is consistent with $\text{CH}_3\text{O}(\text{O})\text{CNH}(\text{CH}_2)_6\text{NHC}(\text{O})\text{OCH}_3$, i.e., dimethyl hexane-1,6-dicarbamate.

4. Identification of reaction intermediates and products for the methoxycarbonylation of HAD by DMC

HDA (50 mmol), CH_3COONa (1.0 g / 12.2 mmol) and CH_3OH (20 ml) were mixed at room temperature with stirring, resulting in a solution with a small amount of white floccules, which are identified as NaOH in section 5. After heated up to 337 K, the white floccules disappeared within 10 minutes, turning to a clear solution. The solution was kept at 337 K for 1 h, cooled to room temperature, and then separated into two equal parts. One part of the above solution was vacuum-distilled, generating a white solid. The FT-IR characterization of the white solid indicated the presence of N-substituted acetamide, amine and acetate, as shown by Fig. S4 and Table S4.

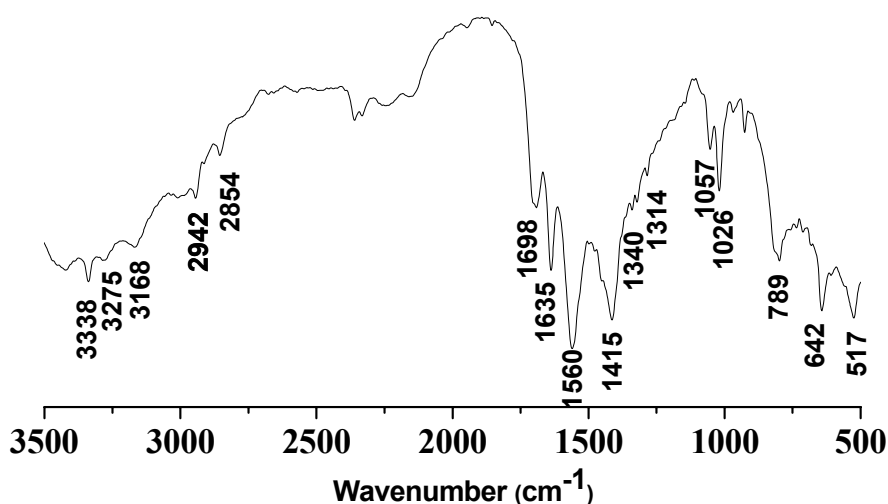


Fig. S4 FT-IR spectrum of the white solid obtained from the reaction of

HDA and CH₃COONa at 337 K for 1 h

Table S4 FT-IR bands observed in Fig.4 and their assignments

Bands (cm ⁻¹)	Assignments *
3338	ν (N-H in -C(=O)-NH-)
1635	ν (C=O in -C(=O)-NH-)
1560	δ (C-N-H in -C(=O)-NH-)
1340, 1314	ν (C-N in -C(=O)-NH-)
642	Δ (C-N in -C(=O)-NH-)
2942, 2854	ν (C-H in -CH ₃ - and -CH ₂ -)
3275, 3168	ν (N-H in -NH ₂)
1057, 1026	ν (C-N in -R-CH ₂ -NH ₂)
789	γ (-NH ₂) or ω (-NH ₂)
517	δ (C-C-N in R-CH ₂ -CH ₂ -NH ₂)
1415	ν (-CO ₂ -)
1698	ν (C=O in -C(=O)-O-)

* Analytical Chemistry Handbook, J. A. Dean (Ed.), McGraw-Hill, 1995.

To the second part of the above solution, 100 mmol (8.4 ml) of DMC was added at room temperature with stirring. Then the temperature was raised to 348 K and kept at that temperature for 5 h. The white viscous gel obtained was vacuum-distilled until a white powder was generated. The FT-IR characterization of the white powder indicated the presence of mainly **2**, much less **1** and very little **3** ~ **7**, as shown by Fig. S5 and Table S5.

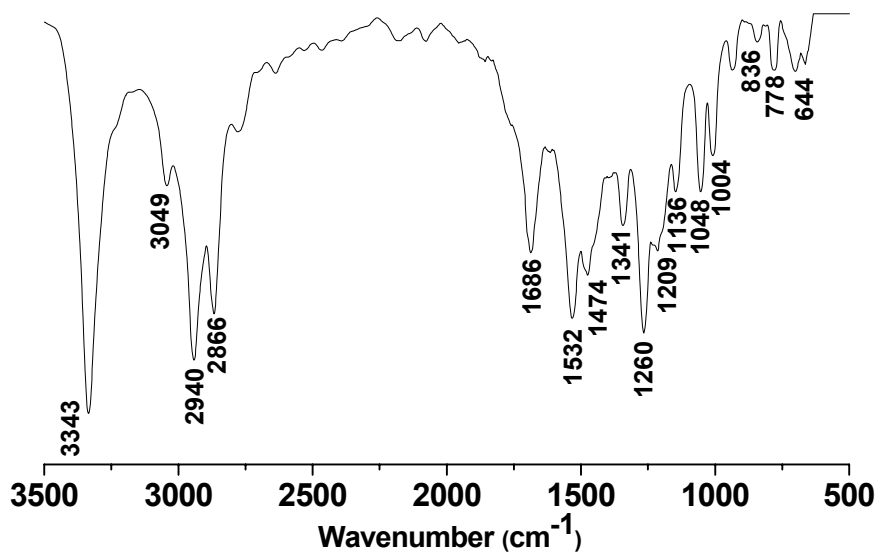


Fig. S5 FT-IR spectrum of the white powder obtained by reacting HDA with CH_3COONa at 373 K for 1 h and then by reacting the resulted products mixture with DMC at 348 K for 5 h

Table S5 FT-IR bands observed in Fig. 5 and their assignments

Bands (cm^{-1})	Assignments *
3343, 3049	$\nu(\text{N-H in } -\text{C}(=\text{O})-\text{NH}-)$
2940, 2866	$\nu(\text{C-H in } -\text{CH}_3\text{- and } -\text{CH}_2\text{-})$
1686	$\text{CH}_3\text{-O-C}(=\text{O})\text{-NH-}$ or $\nu(\text{C=O in } -\text{C}(=\text{O})-\text{NH}-)$
1532, 1474	δ_{as} or δ_{s} ($\text{C-N-H in } -\text{C}(=\text{O})-\text{NH}-$)
1341, 1260	$\nu(\text{C-N in } -\text{C}(=\text{O})-\text{NH}-)$
1136, 1048, 1004	$\nu(\text{C-O and/or C-O-C in } -\text{C}(=\text{O})-\text{O-C})$
836, 778	$\gamma(\text{NH}_2 \text{ in } -\text{CH}_2\text{NH}_2)$, $\omega(\text{NH}_2 \text{ in } -\text{CH}_2\text{NH}_2)$ or $\delta_{\text{s}}(\text{C-N in } -\text{NR}_2)$
644	$\Delta(\text{C-N in } -\text{C}(=\text{O})-\text{NH}-)$ or $\omega(\text{NH}_2 \text{ in } -\text{C}(=\text{O})-\text{NH}_2)$

* Analytical Chemistry Handbook, J. A. Dean (Ed.), McGraw-Hill, 1995.

5. Identification of the NaOH formed via the reaction between HDA and CH₃COONa

HDA (10 mmol) was first mixed with a solution of CH₃COONa (0.8 g / 9.8 mmol) in CH₃OH (20.0 ml) with stirring at room temperature, resulting in an appreciable amount of white floccules in the solution. When the temperature was raised to 337 K, the white floccules disappeared within 10 minutes, resulting in a clear solution. After 4 h of reaction at 337 K, the solution was cooled to room temperature until a large amount of white floccules re-appeared. The floccules were recovered by centrifugal separation. The solid obtained was found to be very soluble in water, with liberation of heat, and its 5 wt% solution had a pH of ca. 13. When this solution was added to a CaCl₂ solution, a white precipitate was formed, which was re-dissolved by adding a HCl solution. One can conclude that the solid contained mainly NaOH, since HDA is only slightly and Ca(OOCCH₃)₂ is highly soluble in water and the sodium acetate aqueous solution has a pH < 9.

6. Identification of the products mixture of the methoxycarbonylation of acetamide by DMC in the absence of any catalyst

Acetamide (50 mmol) was mixed with DMC (200 mmol / 16.8 ml) and methanol (20 ml) at room temperature with stirring, and then the temperature was raised to 348 K and kept at that temperature for reacting for 6 h. After that, the reaction mixture was vacuum-distilled, resulting in a white powder. The FT-IR analysis of the white powder indicated the presence of methyl carbamate (CH₃OCONH₂) and of unconverted acetamide, as shown by Fig. S6 and Table 6.

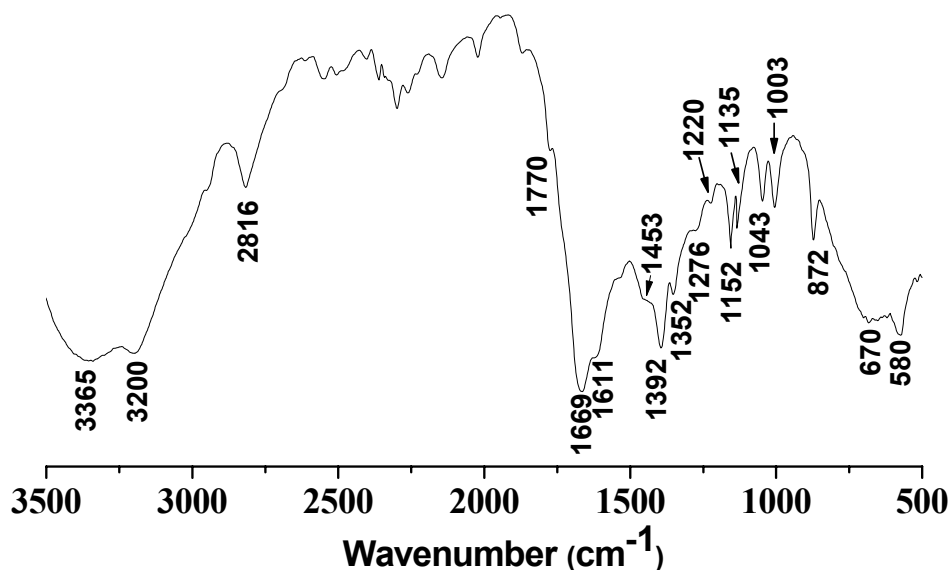


Fig. S6 FT-IR spectrum of the white powder obtained from the reaction of acetamide and DMC at 348 K for 6 h

Table S6 FT-IR bands observed in Fig.6 and their assignments

Bands (cm ⁻¹)	Assignments *
3365, 3200, 1611	ν (NH ₂ in -C(=O)-NH ₂)
2816, 1453, 1352	ν (C-H in -CH ₃)
1770	ν (C=O in -C(=O)-O-C C=O in -C(=O)-O-C and/or N-C(=O)-O-C)
1669	ν (C=O in -C(=O)-NH ₂)
1392	ν (C-N in -C(=O)-NH ₂)
1276, 1220, 1152, 1135, 1043, 1003	ν (C-O and/or C-O-C in -C(=O)-O-C)
872, 670	γ ((-NH ₂) and ω (-NH ₂))
580	O=C-N in -C(=O)-NH ₂

* Analytical Chemistry Handbook, J. A. Dean (Ed.), McGraw-Hill, 1995.