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Electronic Supplementary Information (ESI)

Acid catalyzed reactions of amines with dimethyl carbonate.

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Contents

1. Control experiments for all the substrates investigated in this research

Table S1. Reaction of amines with DMC in the absence of acid catalyst at 90 C°

Amines	%Conv(x)±SD	Selectivity±SD[a,b]		
		Product 1	**Product 2**	**Product 3**
Aniline	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Benzylamine	35.96±5.67	6.81± 1.21	20.47±0.65	44.17±0.98
Hexylamine	39.72±0.67	15.16±0.61	11.34±0.32	73.50±1.12
Octylamine	44.30±3.51	16.49 ±4.2	17.07±0.12	66.34±2.19
Dibuthylamine	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00

Reaction conditions: Amine/DMC = 1.00 mmol : 20 mmol; T = 90 °C; Reaction time 24 h.
[a]Conversions and selectivity were determined by GC analysis.
[b]Products were confirmed by GC-MS and ^{1}H-NMR.

Table S2. Reaction of amines with DMC in the absence of acid catalyst at 150 C°

Amines	%Conv(x)±SD	Selectivity±SD[a,b]		
		Product 1	**Product 2**	**Product 3**
Aniline	22.51±2.03	-	69.41±1.65	30.59±1.89
Benzylamine	90.84±0.20	-	-	56.79±0.63
Hexylamine	95.69±0.11	-	15.34±0.94	84.66±0.95
Octylamine	93.12±1.24	-	26.37±2.45	73.62±2.12
Dibuthylamine	68.34±2.03	-	-	99.00±0.00

Reaction conditions: Amine/DMC = 1.00 mmol : 20 mmol; T = 150 °C; Reaction time 24 h.
[a]Conversions and selectivity were determined by GC analysis.
[b]Products were confirmed by GC-MS and ^{1}H-NMR.

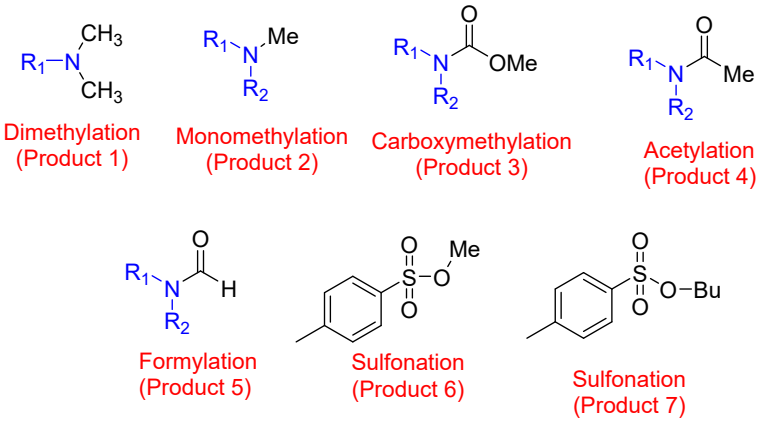
2. Experimental results for the reactions between amines and DMC in the presence of various Brønsted acid catalysts

Table S3. Reaction of amines with DMC Experimental results for the reactions between amines and DMC in the presence of various Bronsted acid catalysts.

Amine	**Stoichiometric loading (0.5 or 1.0 equivalent)**							
	H_3PO_4		**Citric**		**Succinic**		**Oxalic**	
	%Conv.[a]	%Selec.[a]	%Conv.[a]	%Selec.[a]	%Conv.[a]	%Selec.[a]	%Conv.[a]	%Selec.[a]
Aniline	0	0	0	0	0	0	0	0
Benzylamine	0	0	0	0	0	0	0	0
Hexylamine	0	0	0	0	0	0	0	0
Octylamine	0	0	0	0	0	0	0	0
Dibuthylamine	0	0	0	0	0	0	0	0

[a]Conversions and selectivity were determined by GC analysis.

3. Characterization of structures of products



R_1= Phenyl, Benzyl, Hexyl, Octyl; R2 = H
**except for dibutylamine R_1, R_2 = Butyl

The products of reaction of amines with DMC in the acid catalyzed.

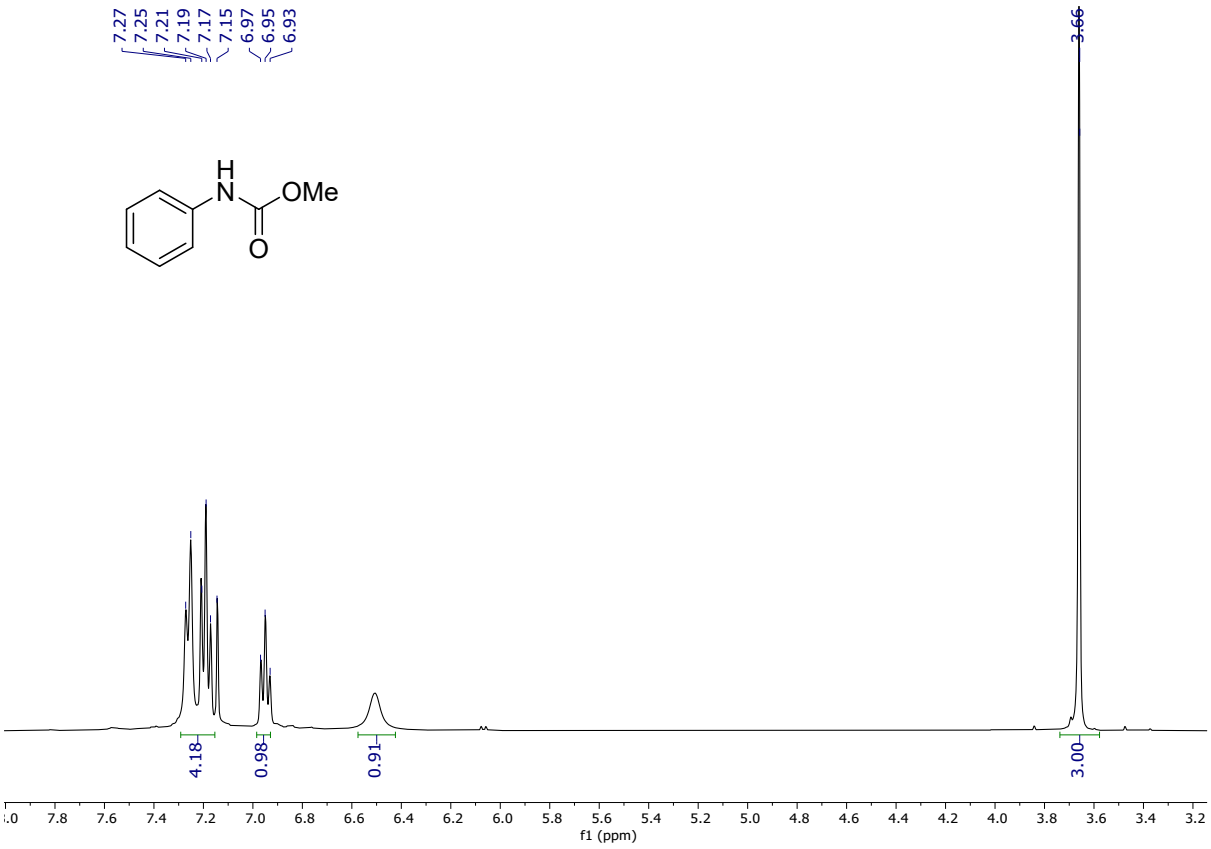


Fig. S1 ^{1}H NMR of methyl *N*-phenyl carbamate in $CDCl_3$

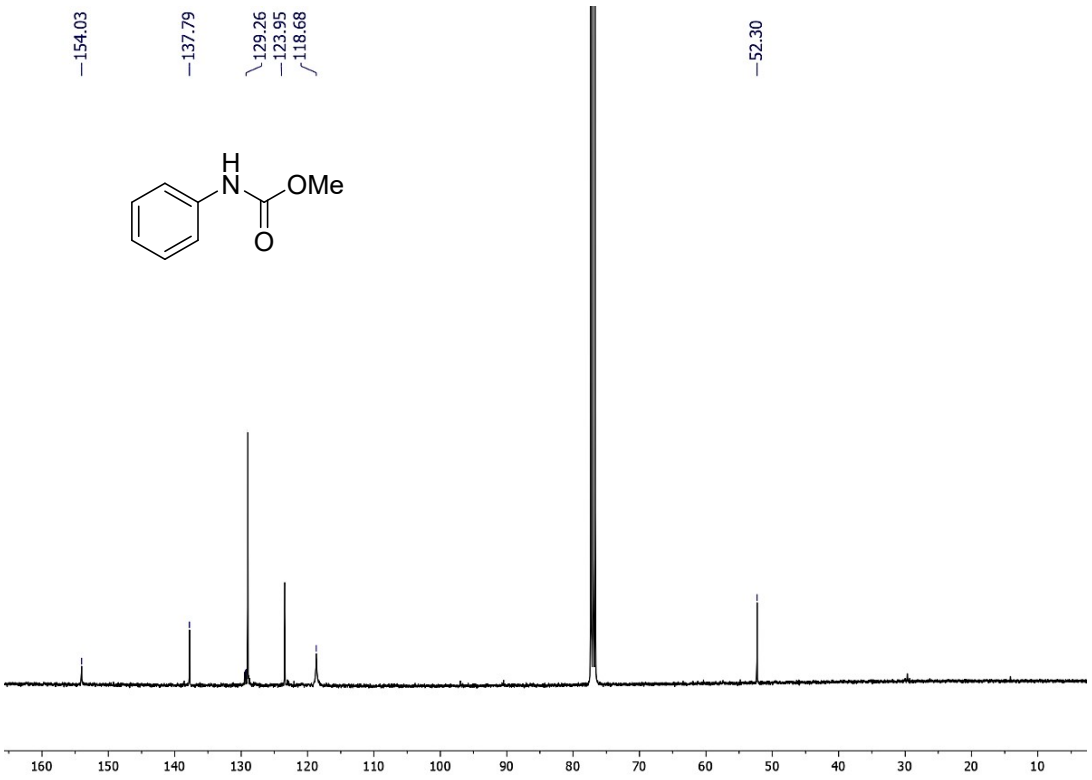


Fig. S2 ^{13}C NMR of methyl *N*-phenyl carbamate in $CDCl_3$

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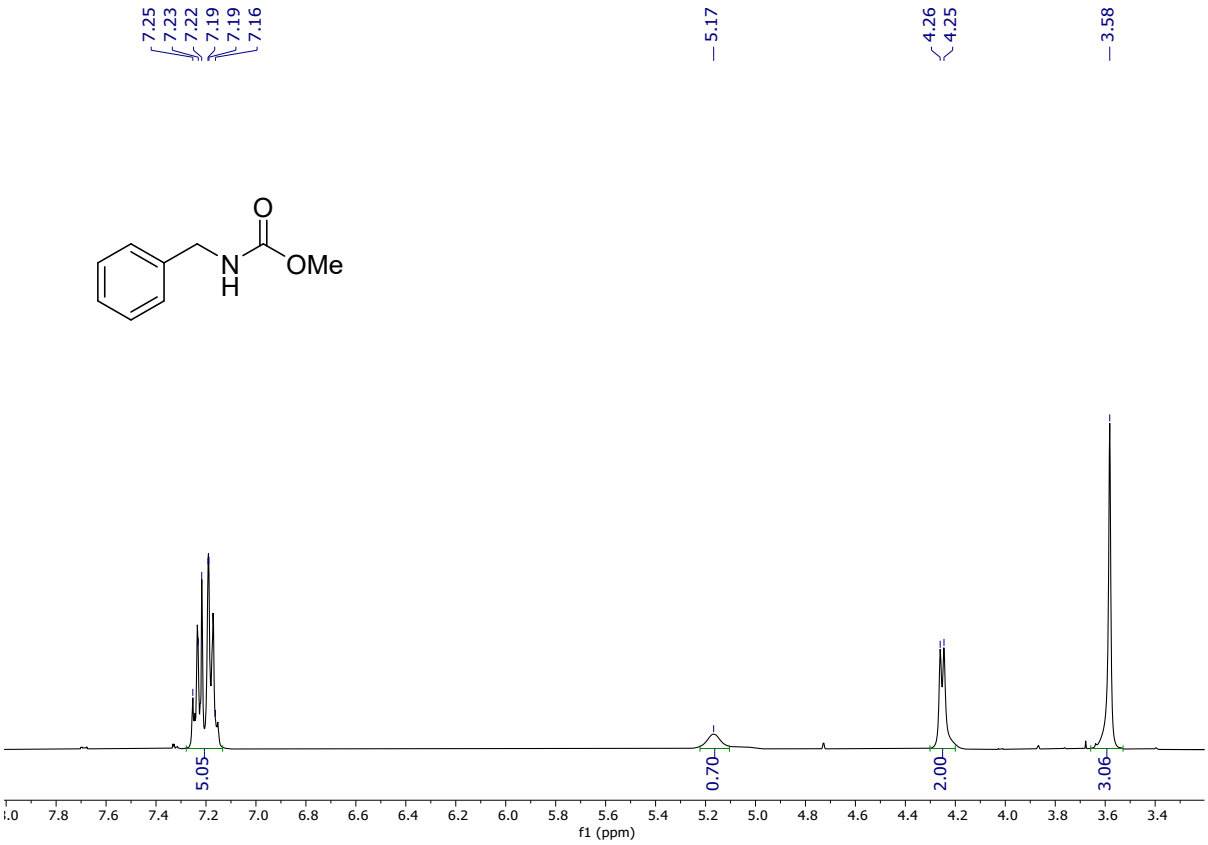

Fig. S3 ^{1}H NMR of methyl *N*-benzyl carbamate in $CDCl_3$

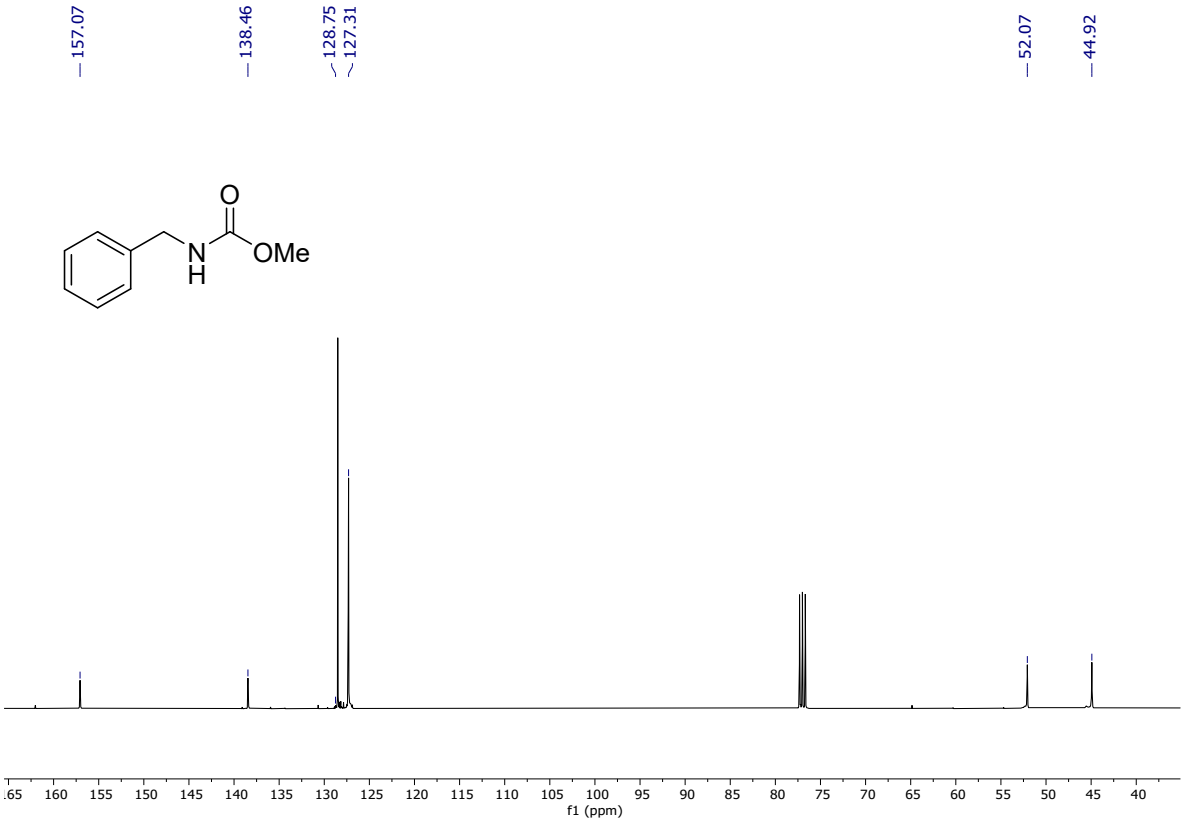

Fig. S4 ^{13}C NMR of methyl *N*-benzyl carbamate in $CDCl_3$

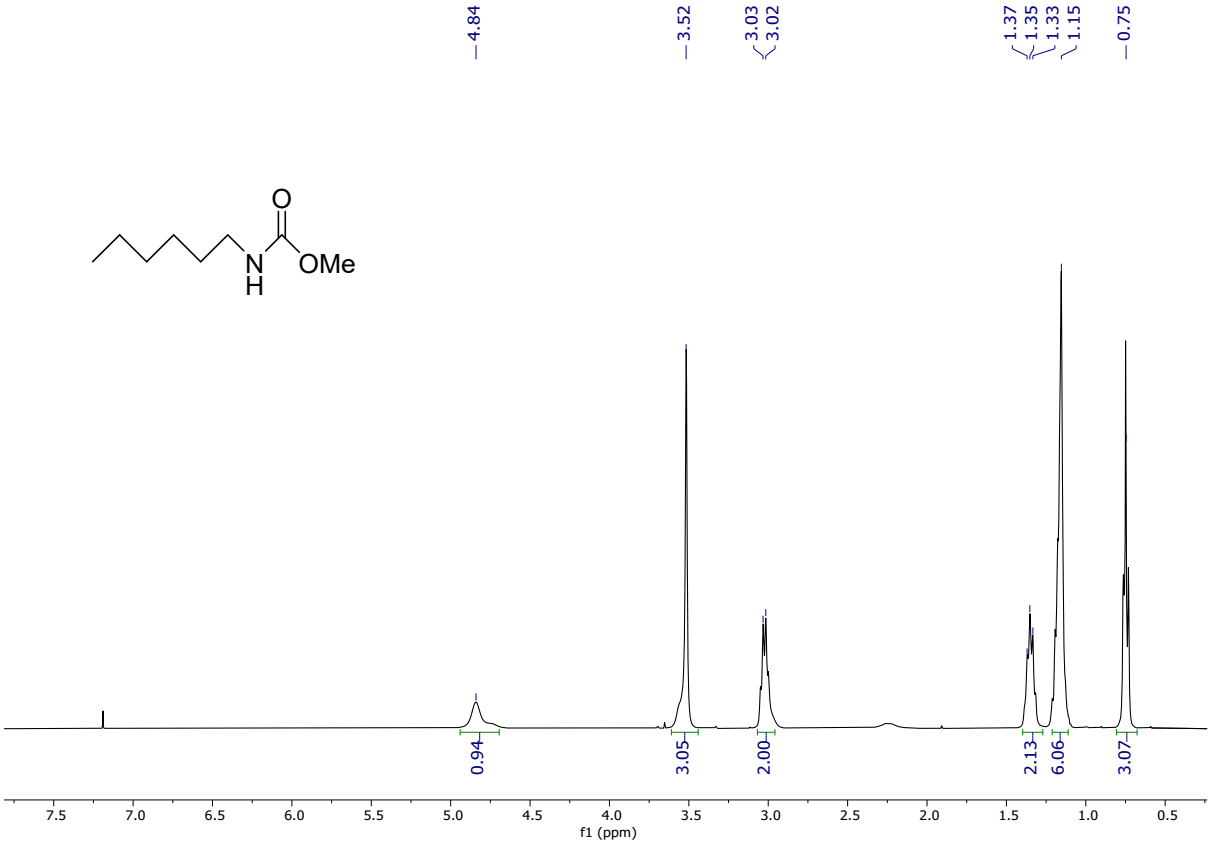

Fig. S5 ^{1}H NMR of methyl *N*-hexyl carbamate in $CDCl_3$

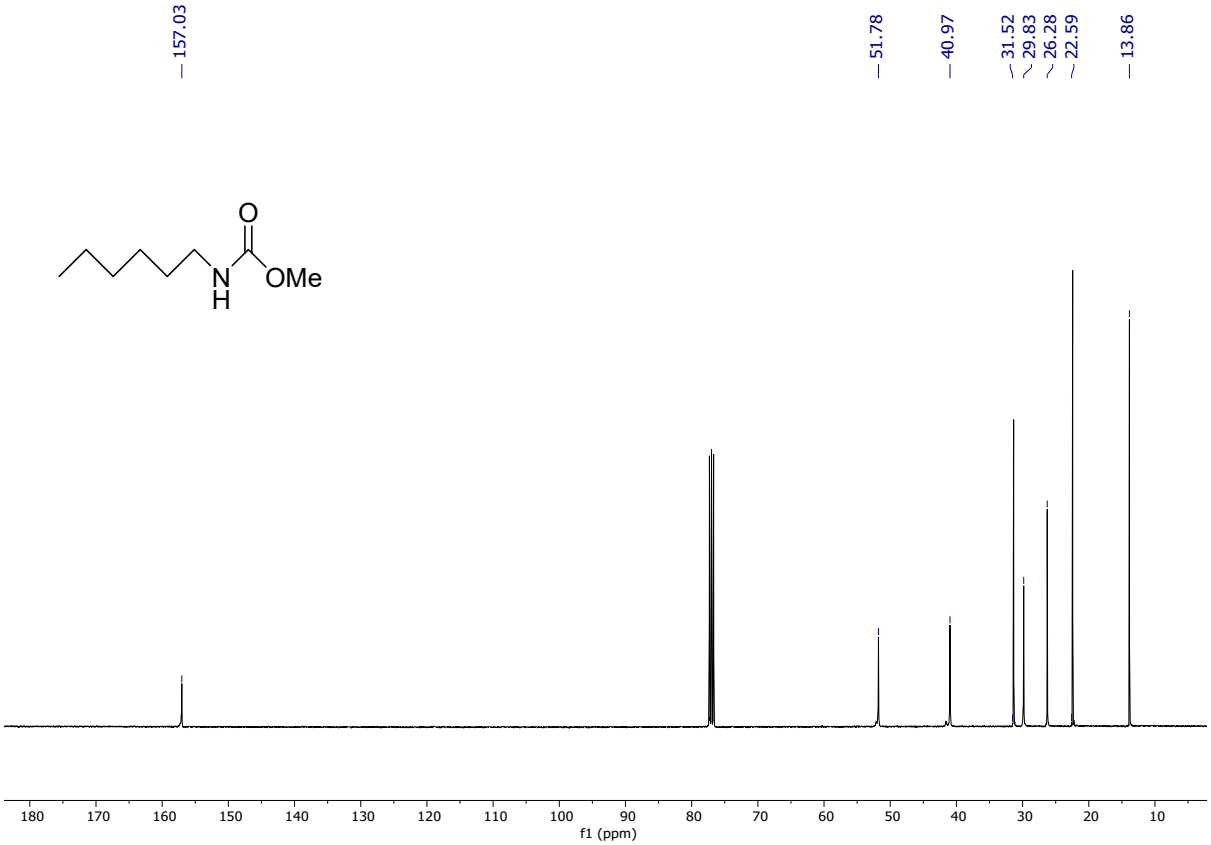

Fig. S6 ^{13}C NMR of methyl *N*-hexyl carbamate in $CDCl_3$

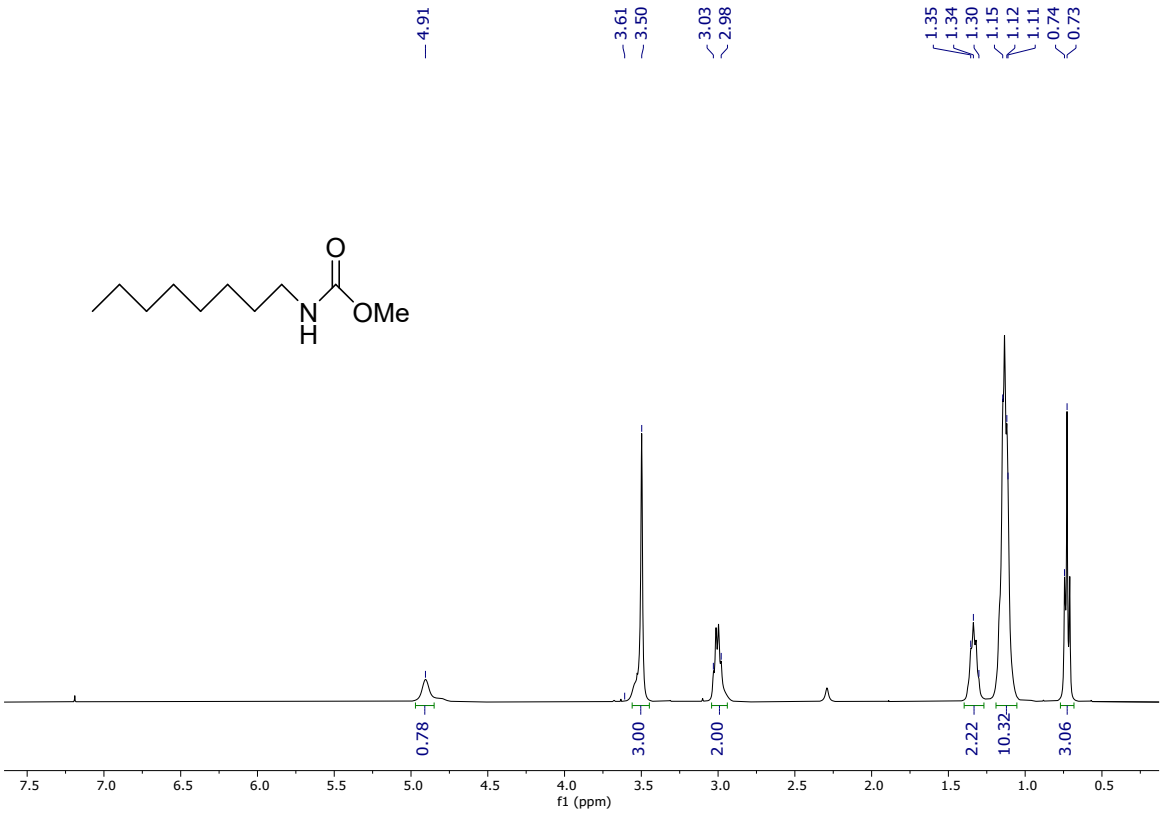

Fig. S7 ^{1}H NMR of methyl *N*-octyl carbamate in $CDCl_3$

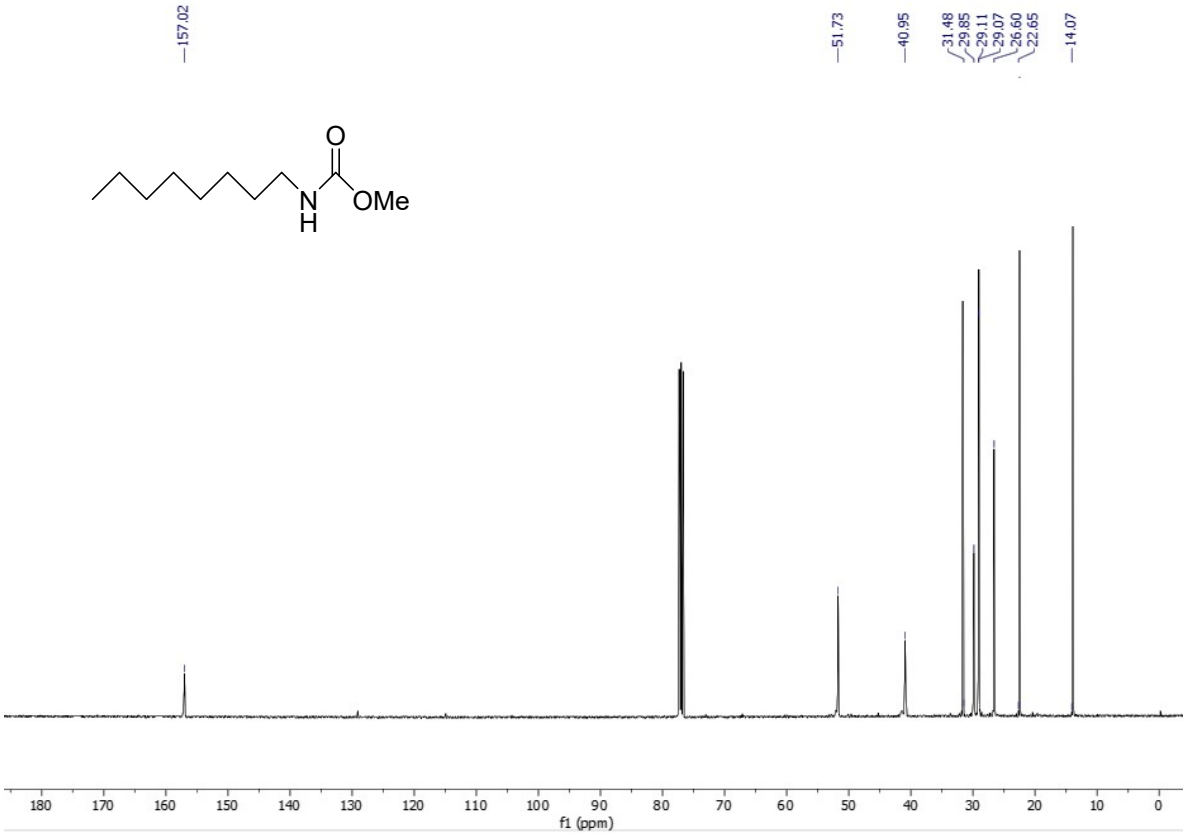

Fig. S8 ^{13}C NMR of methyl *N*-octyl carbamate in $CDCl_3$

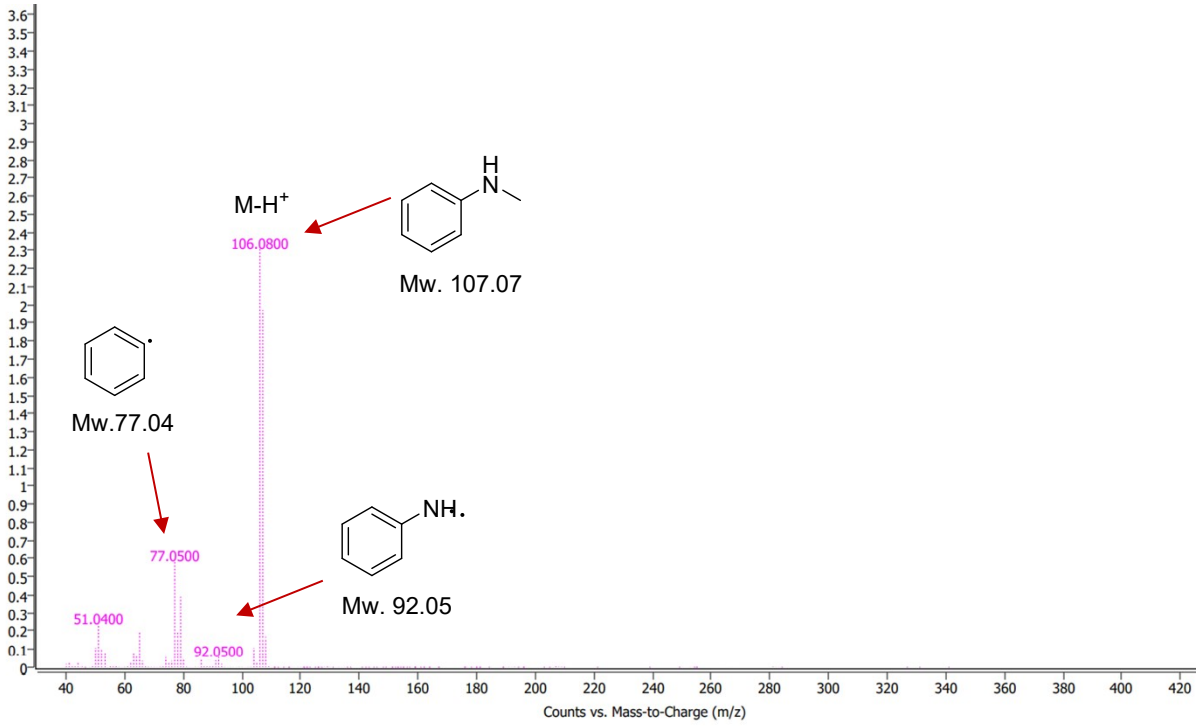

Fig. S9 Mass spectrum (EI) of monomethylation of aniline

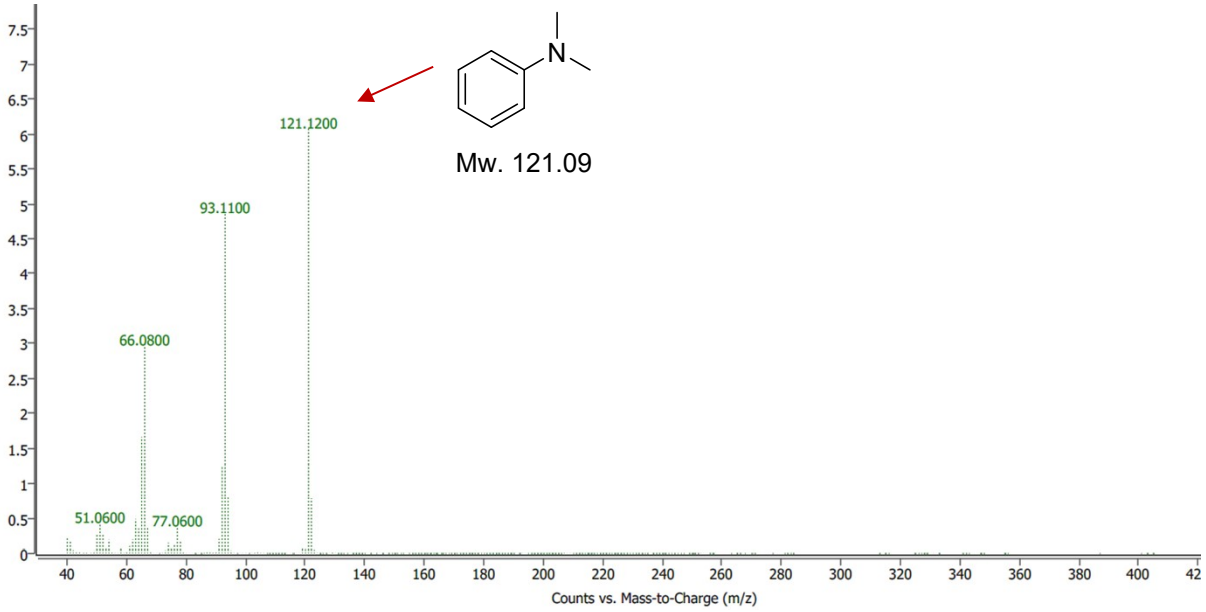

Fig. S10 Mass spectrum (EI) of dimethylation of aniline

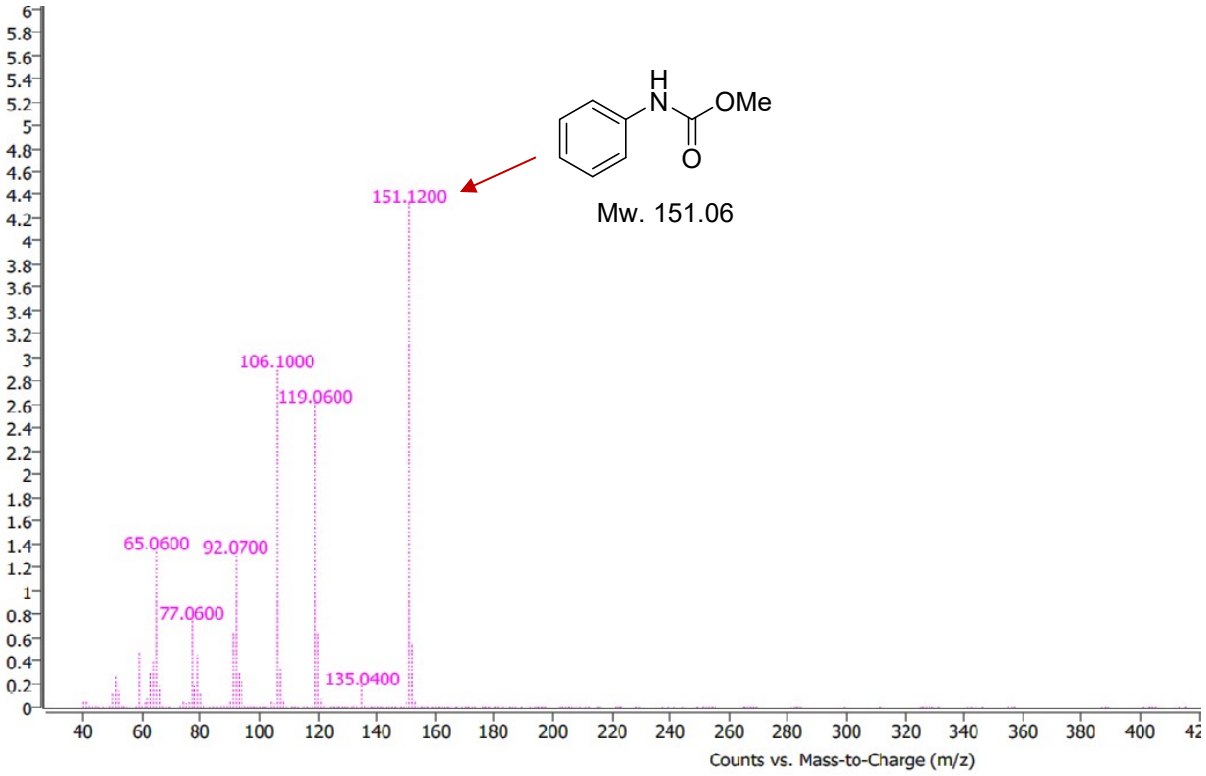

Fig. S11 Mass spectrum (EI) of carboxymethylation of aniline

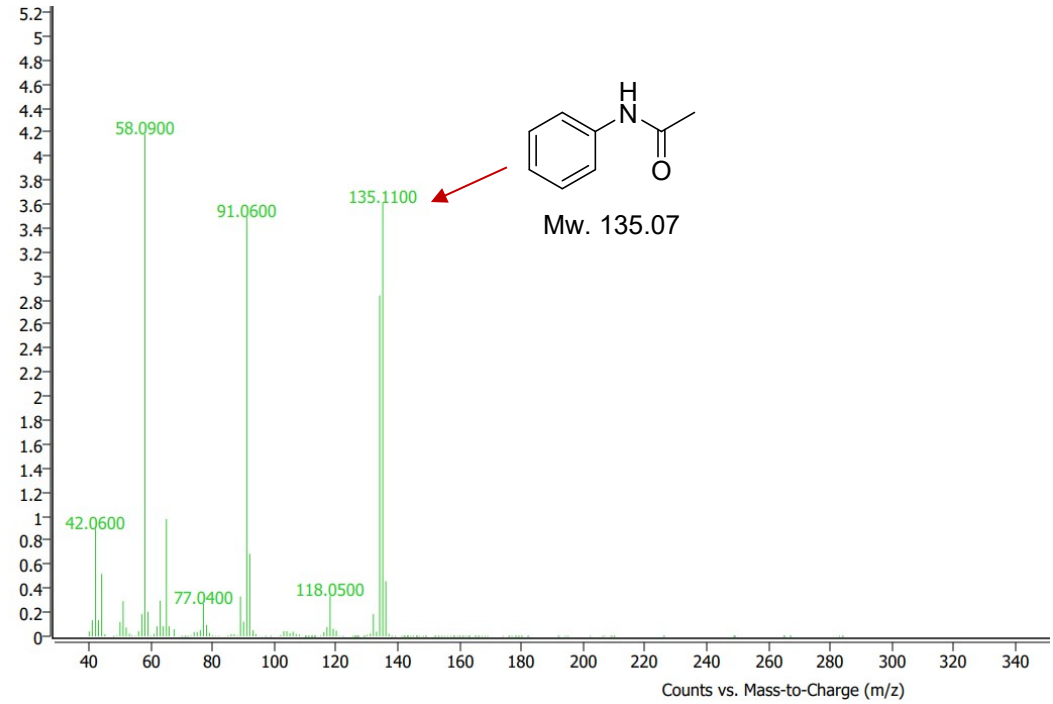

Fig. S12 Mass spectrum (EI) of acetylation of aniline

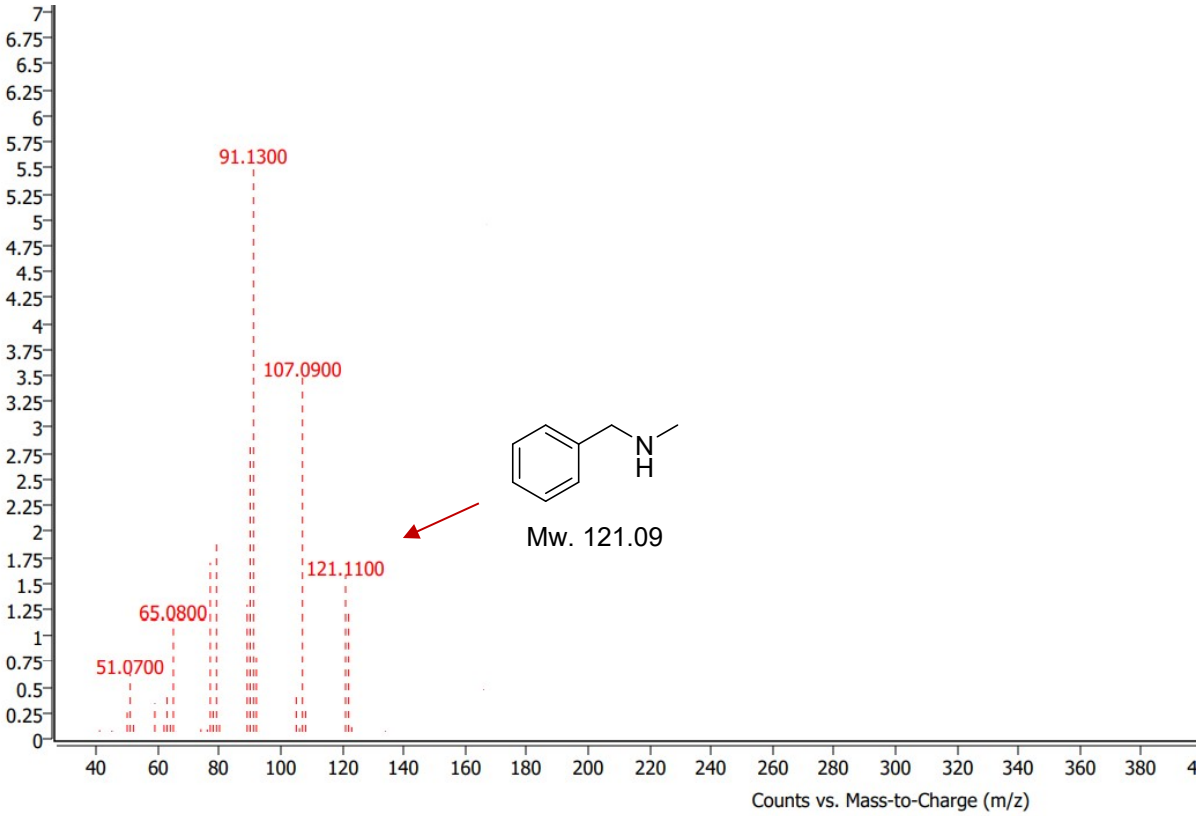

Fig. S13 Mass spectrum (EI) of monomethylation of benzylamine

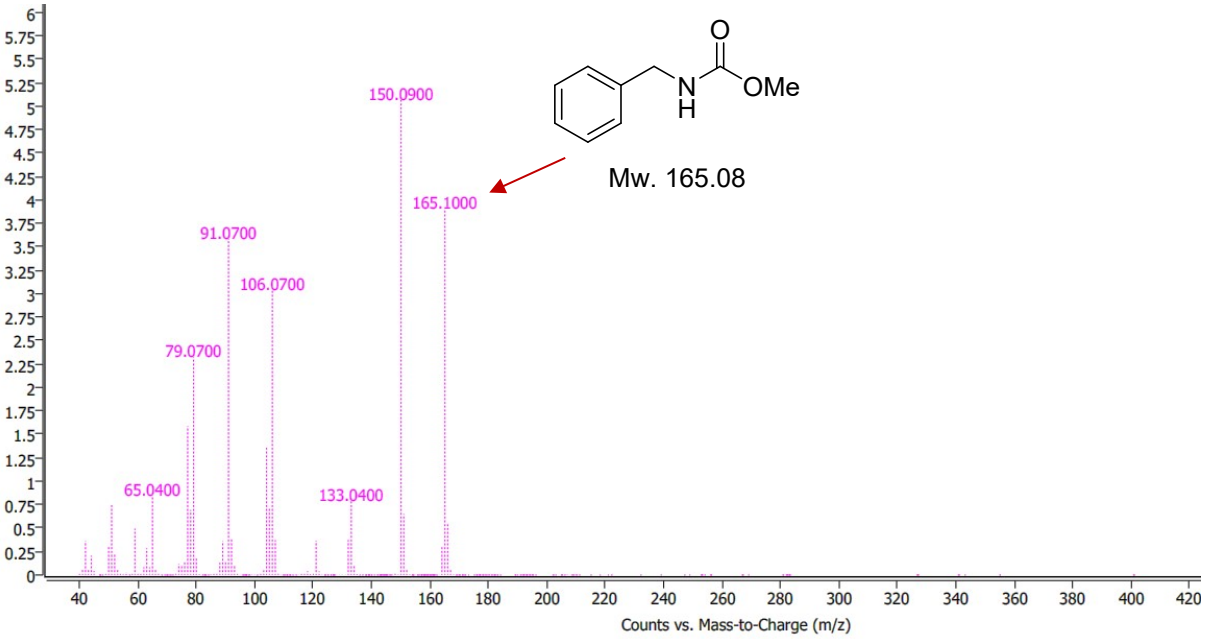

Fig. S14 Mass spectrum (EI) of carboxymethylation of benzylamine.

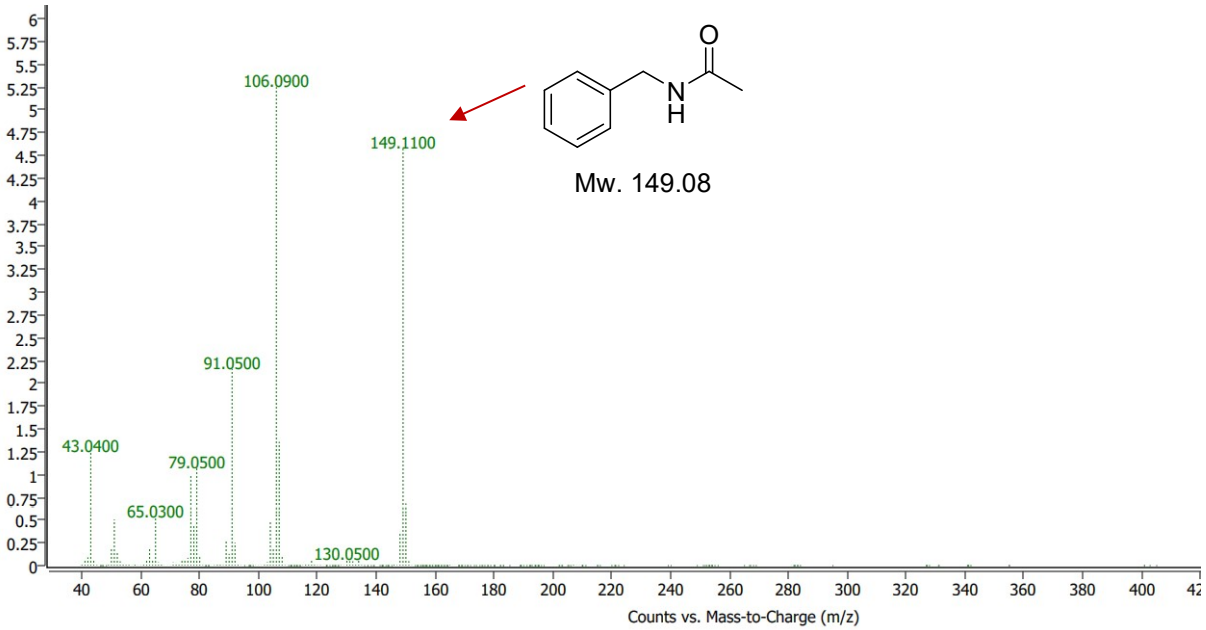

Fig. S15 Mass spectrum (EI) of acetylation of benzylamine.

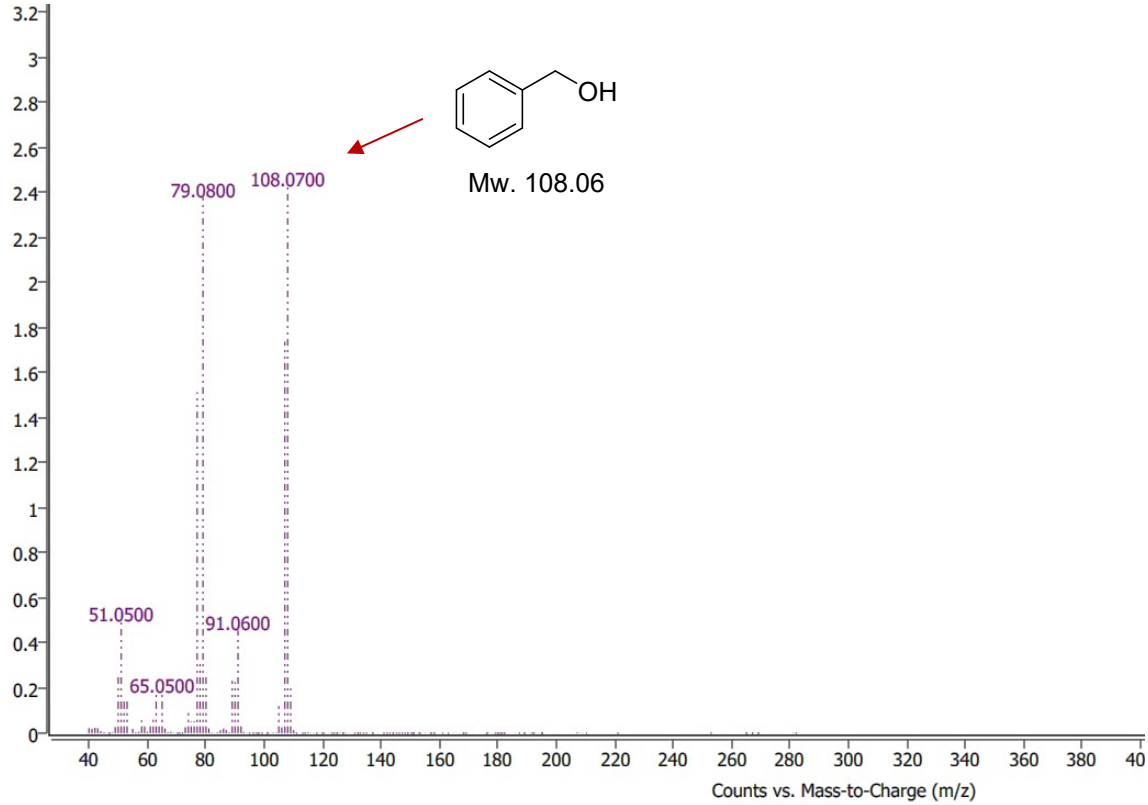

Fig. S16 Mass spectrum (EI) of benzylalcohol

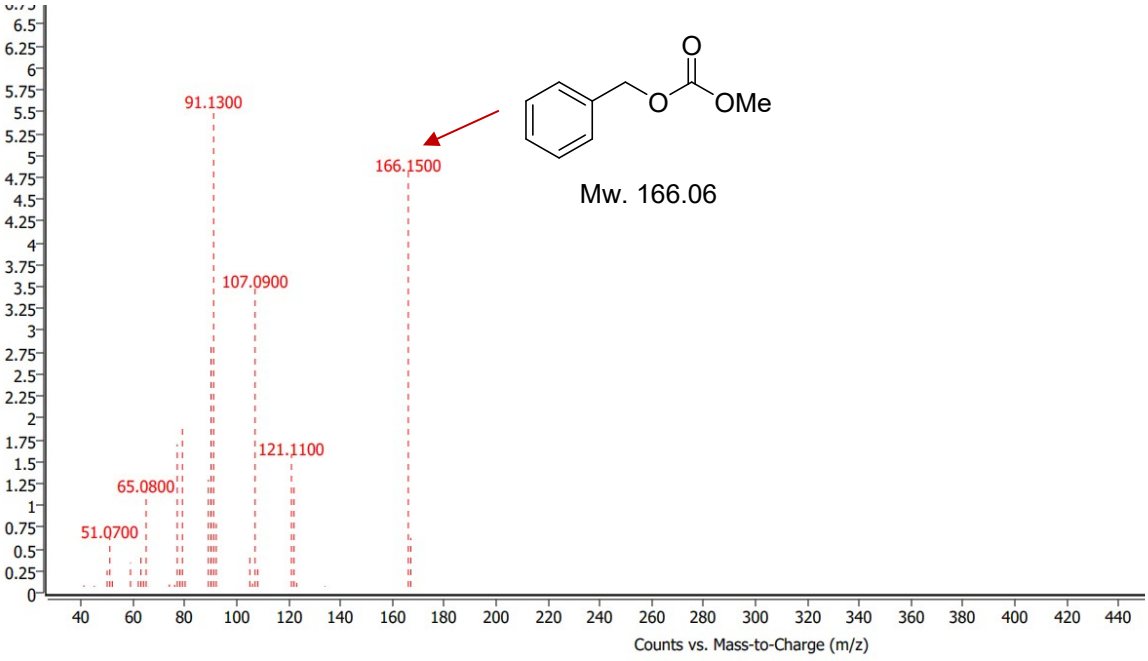

Fig. S17 Mass spectrum (EI) of benzyl methyl carbonate

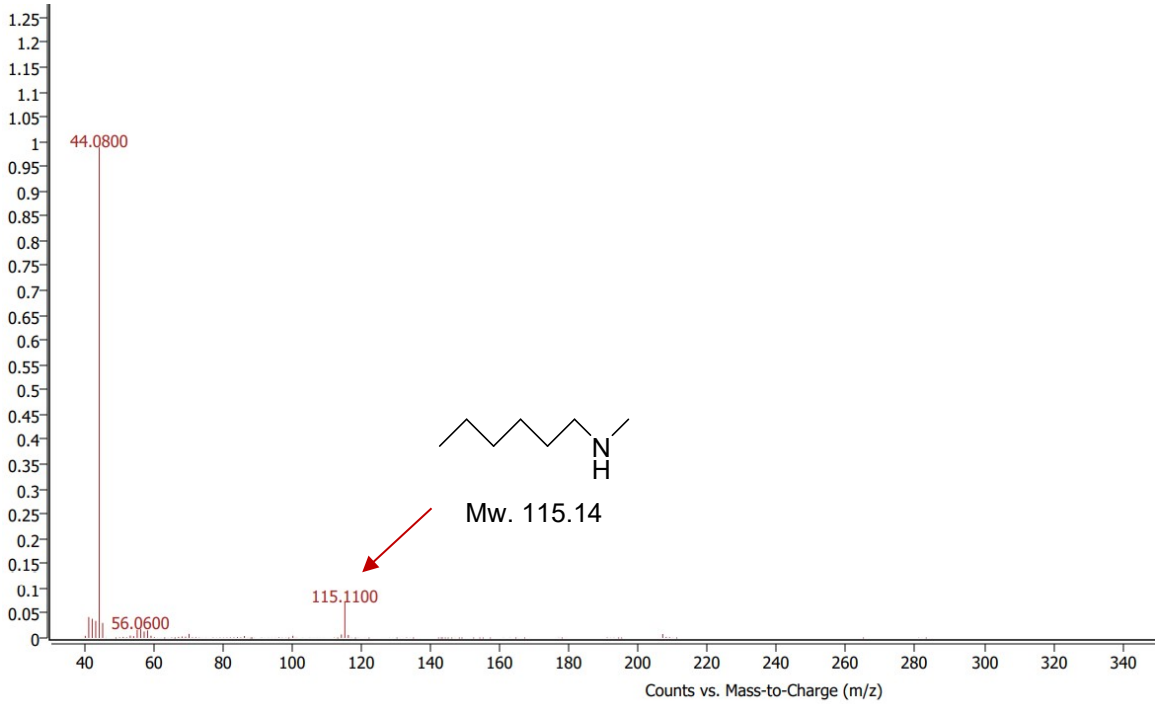

Fig. S18 Mass spectrum (EI) of monomethylation of hexylamine

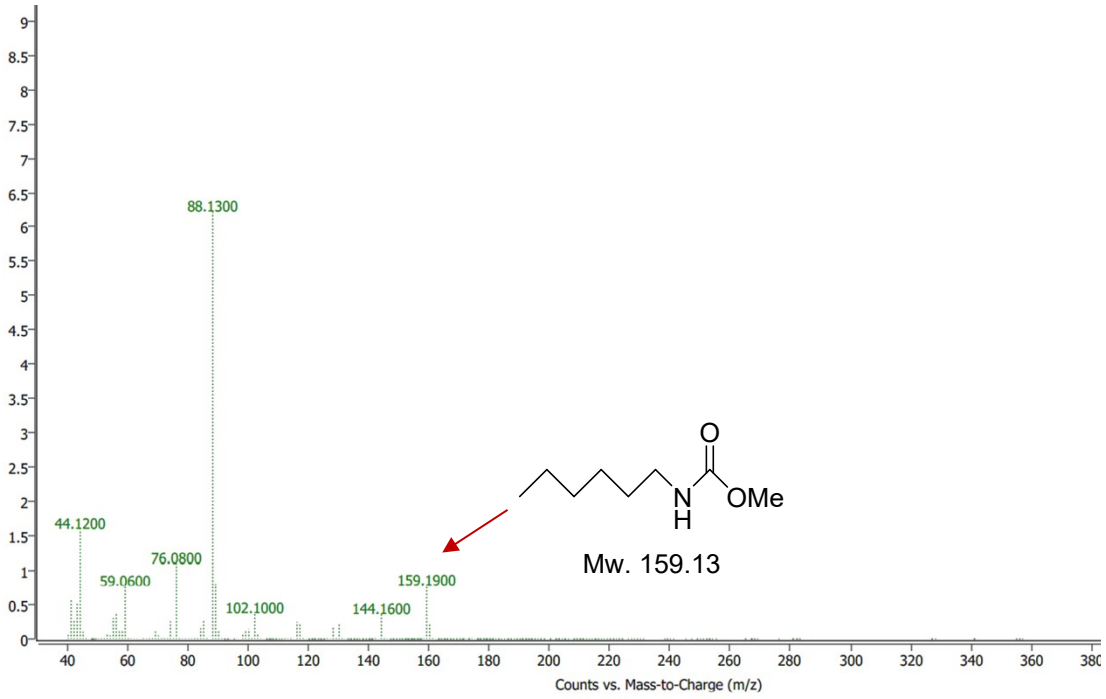

Fig. S19 Mass spectrum (EI) of carboxymethylaion of hexylamine

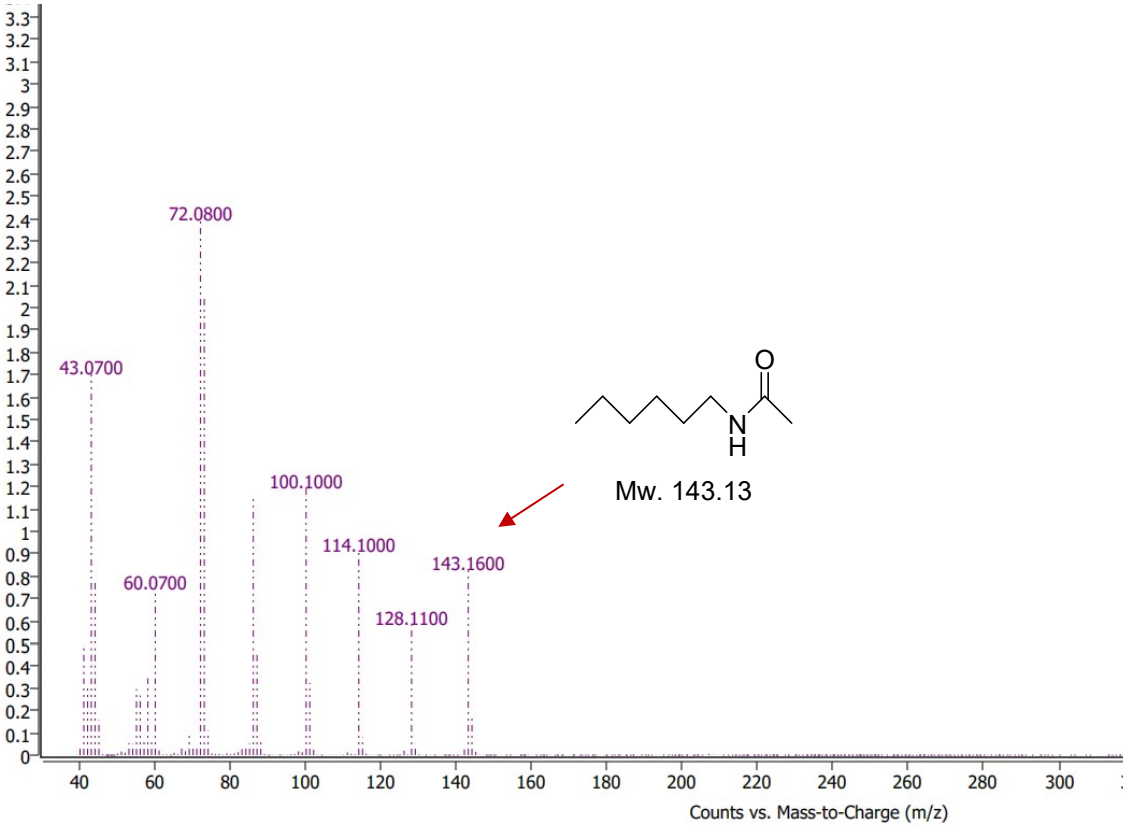

Fig. S20 Mass spectrum (EI) of acetylation of hexylamine

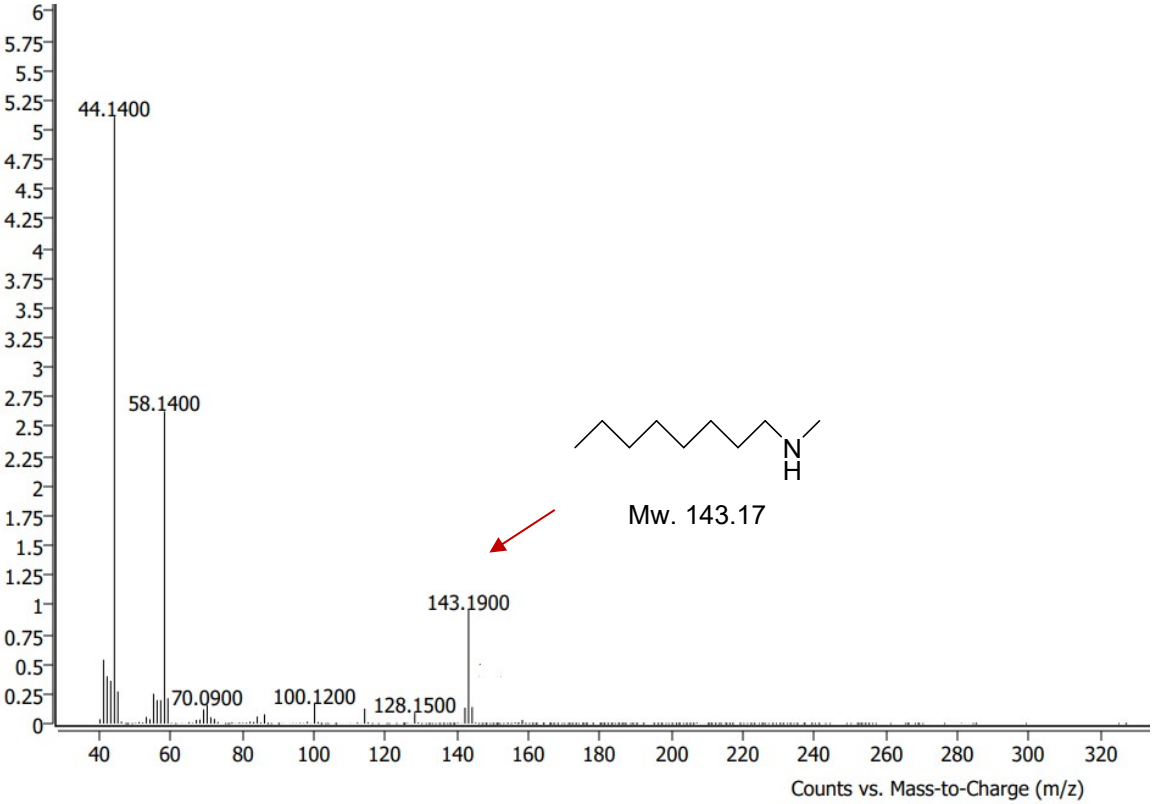

Fig. S21 Mass spectrum (EI) of carboxymethylation of octylamine

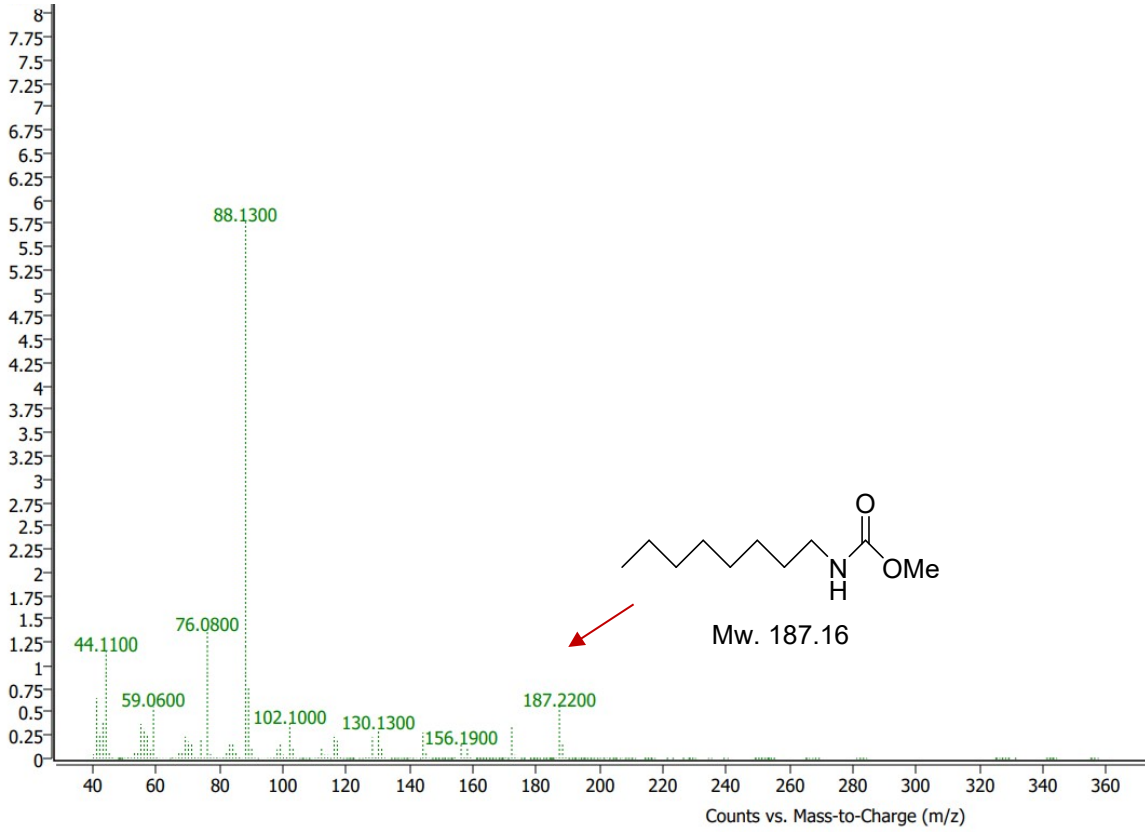

Fig. S22 Mass spectrum (EI) of carboxymethylation of octylamine

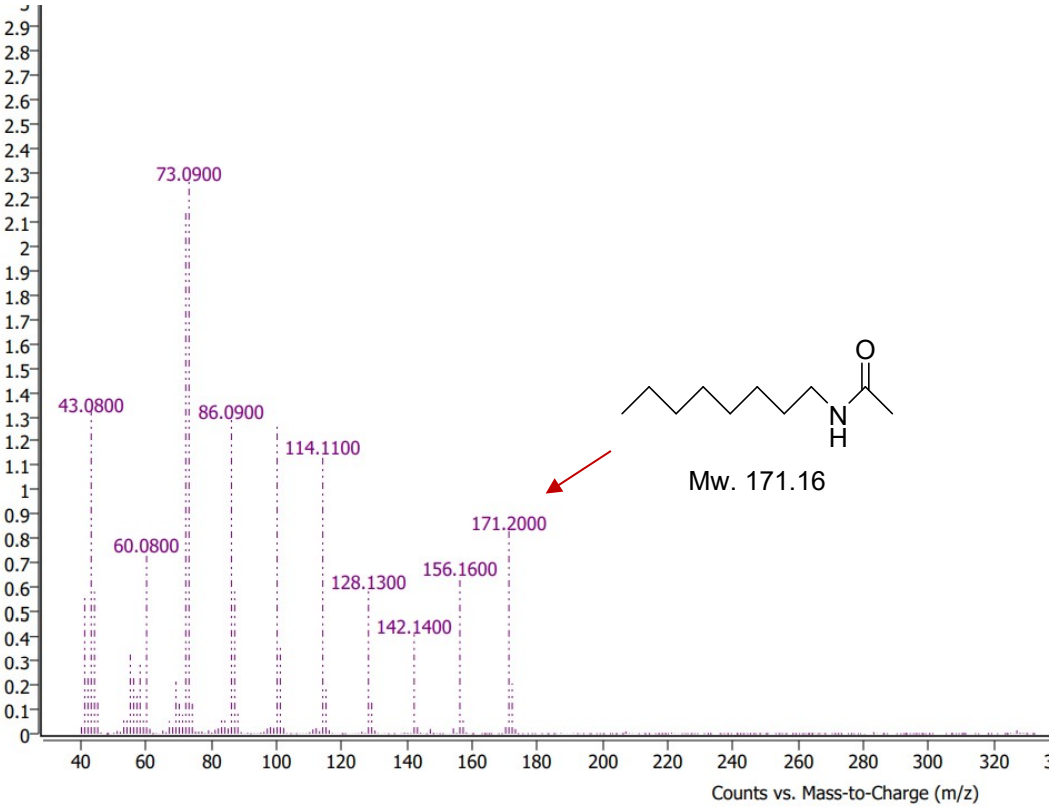

Fig. S23 Mass spectrum (EI) of carboxymethylation of octylamine

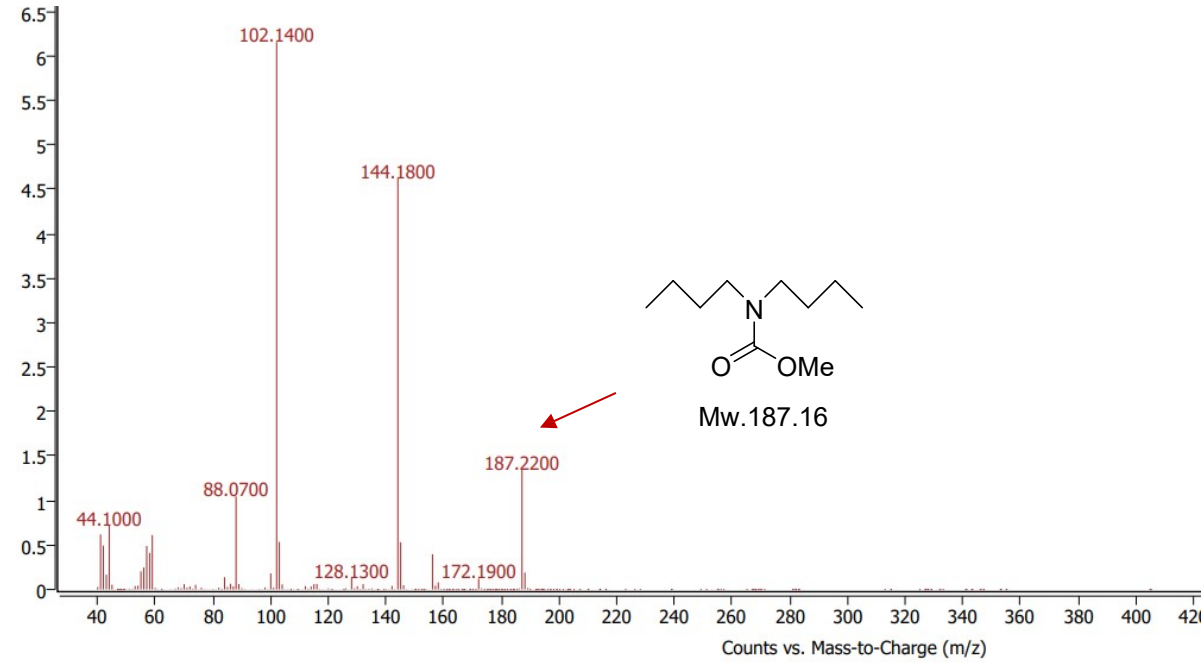

Fig. S24 Mass spectrum (EI) of carboxymethylaion of dibenzylamine

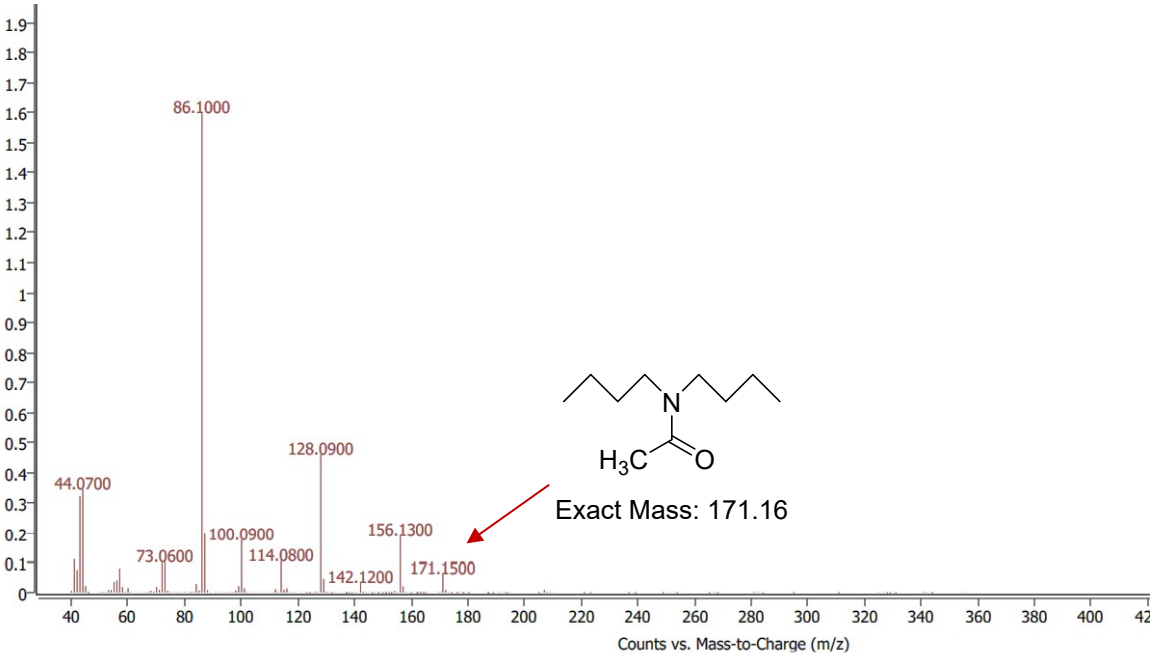

Fig. S25 Mass spectrum (EI) of aceylation of dibenzylamine

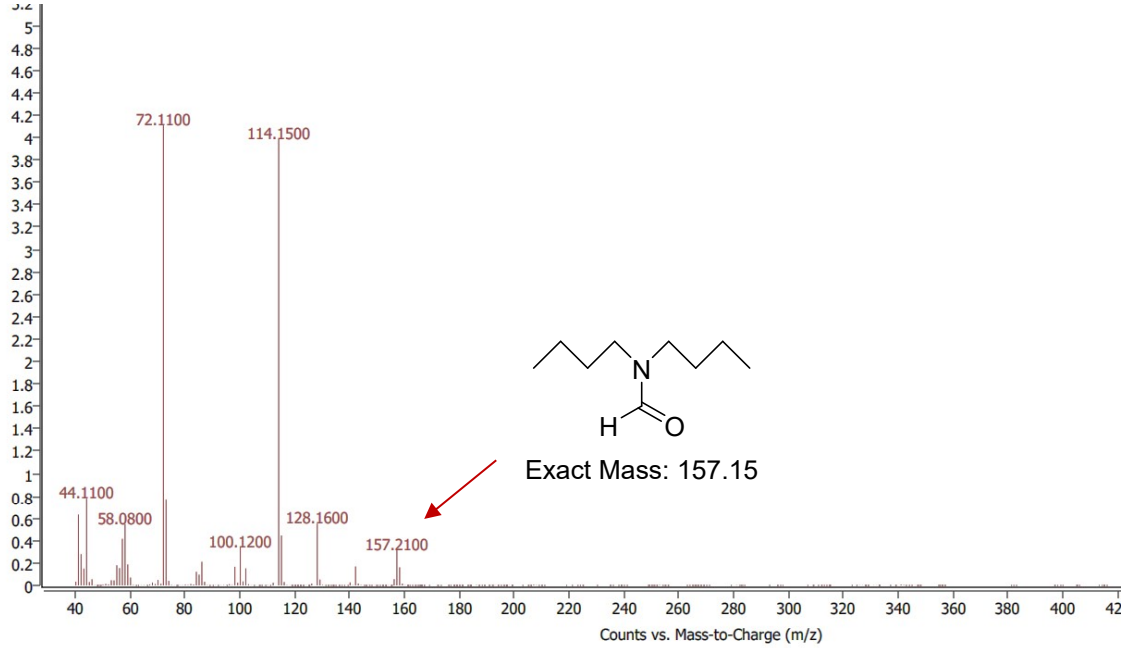

Fig. S26 Mass spectrum (EI) of formylation of dibenzylamine

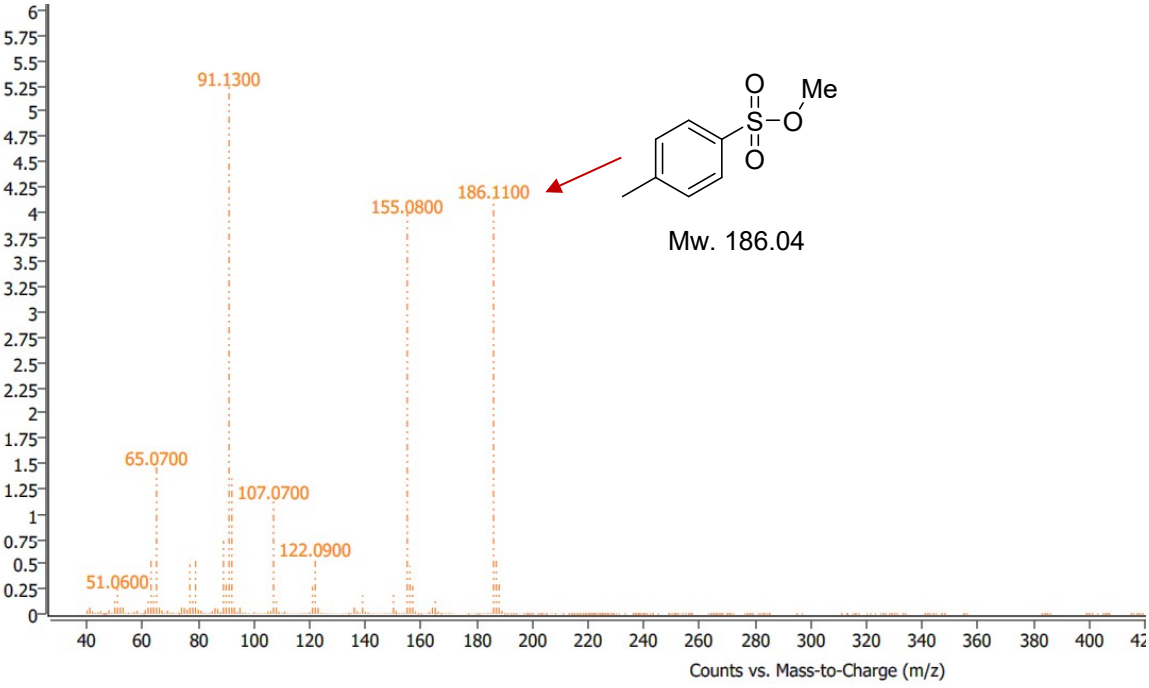

Fig. S27 Mass spectrum (EI) of methyl benzyl sulfonation

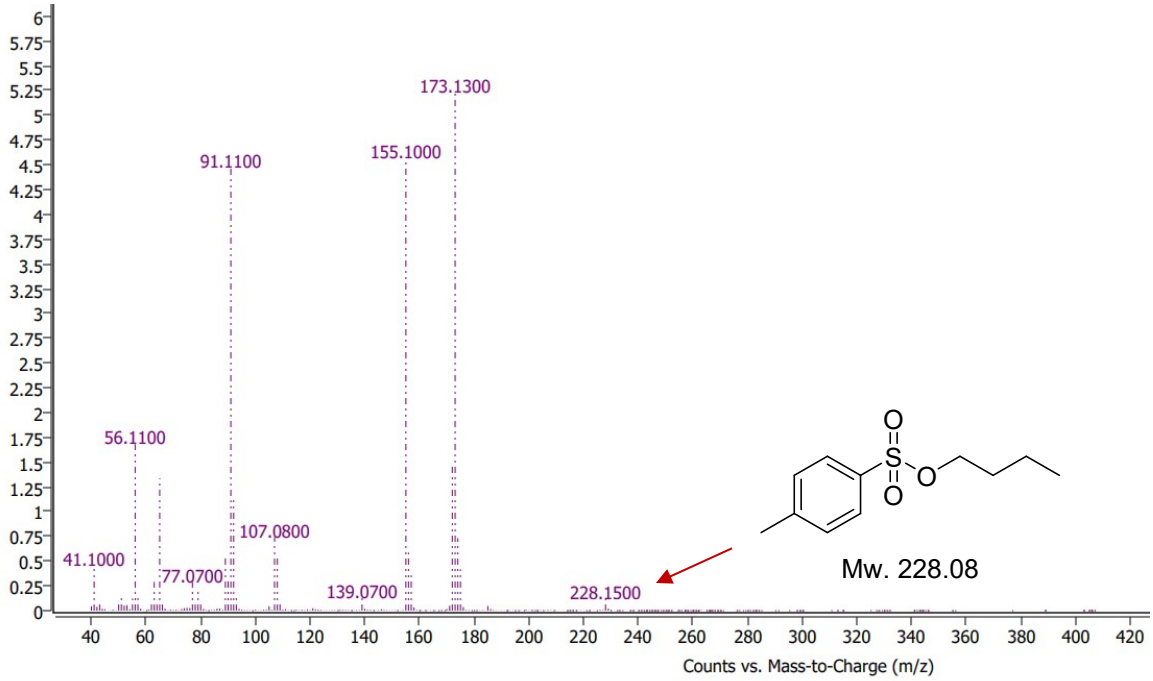

Fig. S28 Mass spectrum (EI) of butyl benzyl sulfonation

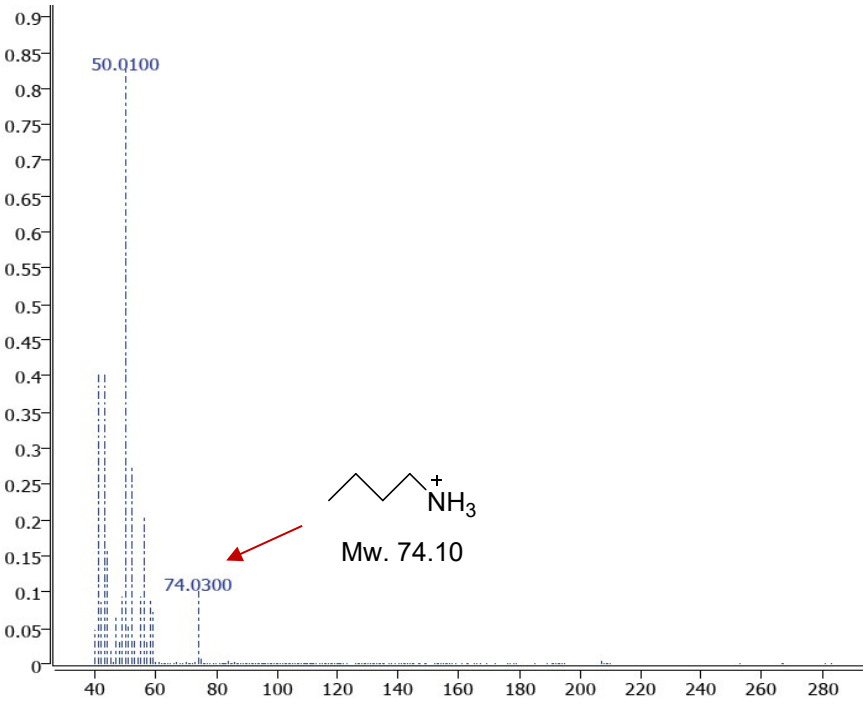

Fig. S29 Mass spectrum (EI) of fragment butylamonium in reaction of dibutylamine by using PTSA catalyst at 150 °C

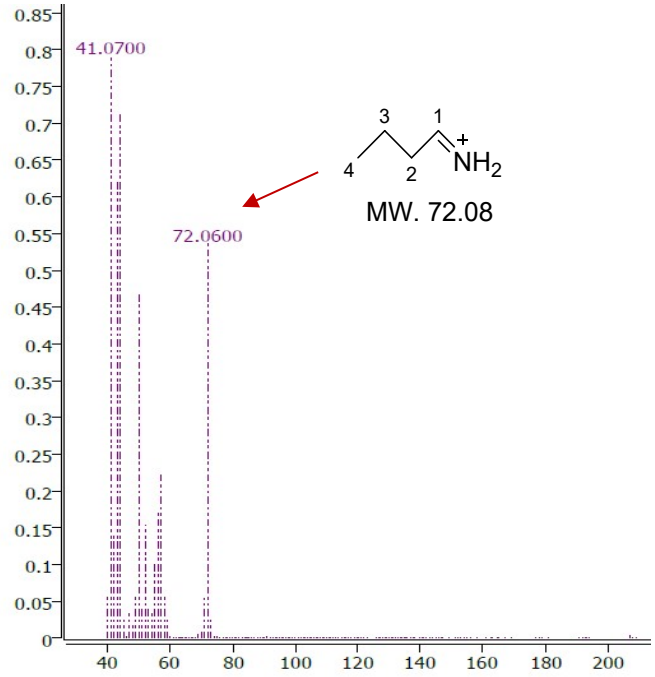

Fig. S30 Mass spectrum (EI) of fragment butan-1-iminium in reaction of dibutylamine by using PTSA catalyst at 150 °C

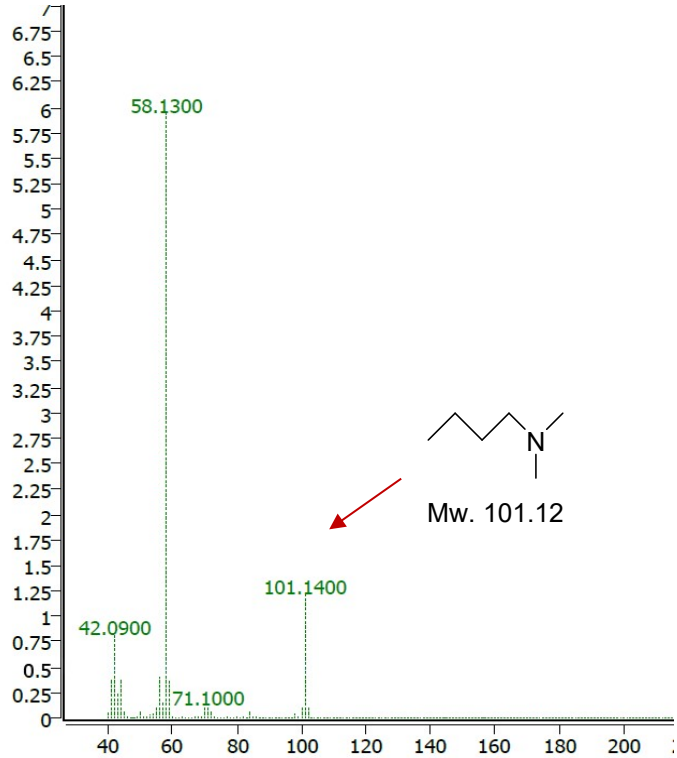

Fig. S31 Mass spectrum (EI) of fragment *N*,*N* dimethyl-butanamine in reaction of dibutylamine by using PTSA catalyst at 150 °C

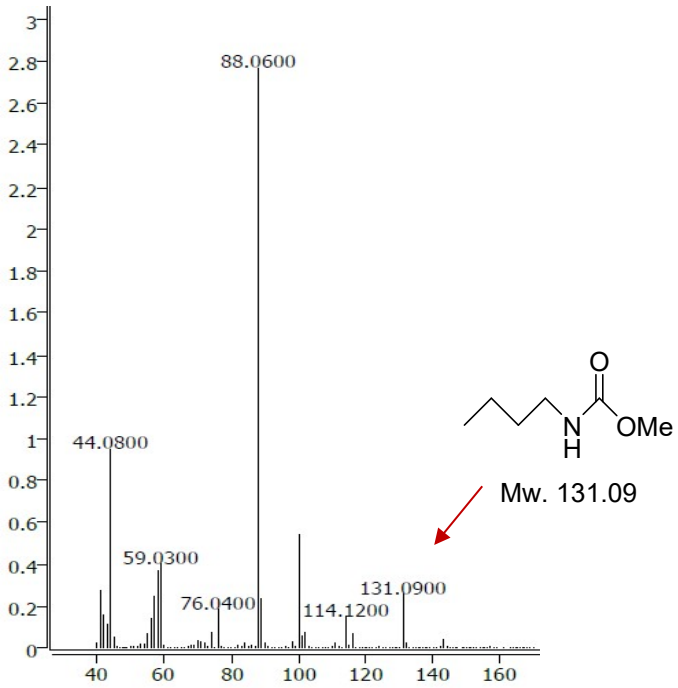

Fig. S32 Mass spectrum (EI) of fragment carboxymethylation of butylamine in reaction of dibutylamine by using PTSA catalyst at 150 °C

4. Green chemistry metrics analysis

The following formulae were used for calculating Process Mass Intensity (PMI), E-factor, Atom Economy (AE) and Water Intensity (WI).[1-12]

$$\text{PMI} = \frac{\text{Total mass of input material in the whole process}}{\text{Mass of product}}$$

$$\text{E-factor} = \frac{\text{Total mass of waste}}{\text{Mass of product}}$$

$$\text{AE} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100$$

$$WI = \frac{\text{Total mass of water used in the whole process}}{\text{Mass of product}}$$

Quantitative evaluation of Green Chemistry Metrics for the reactions between amine and DMC catalysed by acid silica supported catalysts at 90 °C

Experimental procedures: To a 50 mL round bottom flask was added 20 mmol of dimethyl carbonate (DMC) and stoichiometric catalyst (1.00 mmol of H_2SO_4-SiO_2, or $HClO_4$-SiO_2) followed by molecular sieves to eliminate water. Then, the limiting reagent (benzylamine, hexylamine, or octylamine) of 1 mmol was added to the solution mixture. The solution was stirred and refluxed at 90 °C for 24 h. After the reaction was completed, the reaction was allowed to cool to room temperature and filtered by a nylon syringe filter (0.22 μm x 13 mm) to prepare the GC and GC-MS samples. After the GC test, the product from employing H_2SO_4-SiO_2 and $HClO_4$-SiO_2 was obtained by removing the solvent under reduced pressure.

Materials used for metrics calculations: benzylamine (0.1072 g, 1.00 mmol), hexylamine (0.1012 g, 1.00 mmol), octylamine (0.1292 g, 1.00 mmol), dimethyl carbonate (1.8016 g, 20.00 mmol, unrecovered DMC), dimethyl carbonate (0.0901 g, 1.00 mmol, recovered DMC), methyl benzyl carbamate (0.1520 g, 0.92 mmol, H_2SO_4-SiO_2), methyl hexyl carbamate (0.1456 g, 0.91 mmol, H_2SO_4-SiO_2), methyl octyl carbamate (0.1662 g, 0.89 mmol, H_2SO_4-SiO_2), methyl benzyl carbamate (0.1558 g, 0.94 mmol, $HClO_4$-SiO_2), methyl hexyl carbamate (0.1504 g, 0.95 mmol, $HClO_4$-SiO_2), methyl octyl carbamate (0.1682 g, 0.90 mmol, $HClO_4$-SiO_2). Catalysts H_2SO_4-SiO_2 and $HClO_4$-SiO_2 were not included in the calculations because they can be recycled.[1,5]

1. Benzylamine to methyl benzyl carbamate

$$\text{PMI } (H_2SO_4\text{-}SiO_2) = \frac{0.1072 + 1.8016}{0.1520} = 12.6$$

$$\text{PMI } (HClO_4\text{-}SiO_2) = \frac{0.1072 + 1.8016}{0.1558} = 12.3$$

E-Factor (H_2SO_4-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1072 + 1.8016 - 0.1520}{0.1520} = 11.6$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1072 + 0.0901 - 0.1520}{0.1520} = 0.3$$

E-Factor ($HClO_4$-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1072 + 1.8016 - 0.1558}{0.1558} = 11.3$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1072 + 0.0901 - 0.1558}{0.1558} = 0.3$$

$$\text{AE} = \frac{107.156 + 90.078}{165.192} = 0.90$$

$$\text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1520} = 0 \qquad \text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1558} = 0$$

2. Hexylamine to methyl hexyl carbamate

$$\text{PMI } (H_2SO_4\text{-}SiO_2) = \frac{0.1012 + 1.8016}{0.1456} = 13.1 \qquad \text{PMI } (HClO_4\text{-}SiO_2) = \frac{0.1012 + 1.8016}{0.1504} = 12.7$$

E-Factor (H_2SO_4-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1012 + 1.8016 - 0.1456}{0.1456} = 12.1$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1012 + 0.0901 - 0.1456}{0.1456} = 0.3$$

E-Factor ($HClO_4$-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1012 + 1.8016 - 0.1504}{0.1504} = 11.7$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1072 + 0.0901 - 0.1504}{0.1504} = 0.3$$

$$\text{AE} = \frac{101.193 + 90.078}{159.229} = 0.89$$

$$\text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1456} = 0 \qquad \text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1504} = 0$$

3. Octylamine to methyl octyl carbamate

$$\text{PMI } (H_2SO_4\text{-}SiO_2) = \frac{0.1292 + 1.8016}{0.1662} = 11.6 \qquad \text{PMI } (HClO_4\text{-}SiO_2) = \frac{0.1292 + 1.8016}{0.1682} = 11.5$$

E-Factor (H_2SO_4-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1292 + 1.8016 - 0.1662}{0.1662} = 10.6$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1292 + 0.0901 - 0.1662}{0.1662} = 0.3$$

E-Factor ($HClO_4$-SiO_2)

$$\text{E-Factor (Catalyst not included)} = \frac{0.1292 + 1.8016 - 0.1682}{0.1682} = 10.5$$

$$\text{E-Factor (DMC recovery)} = \frac{0.1292 + 0.0901 - 0.1682}{0.1682} = 0.3$$

$$\text{AE} = \frac{129.247 + 90.078}{187.283} = 0.91$$

$$\text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1662} = 0 \qquad \text{WI } (H_2SO_4\text{-}SiO_2) = \frac{0}{0.1682} = 0$$

5. Green Motion™ Analysis[11,13]

Questions

1. Raw materials origin:

a) Natural raw materials

b) Raw material obtained by semisynthesis

c) Raw material obtained by chemical synthesis

2. Renewable carbon percentage:

3. GHS pictograms of the final product:

a) Explosive

b) Toxic

c) Corrosive

d) Dangerous for environment

e) Flammable

f) Nocive (Exclamation point)

g) Dangerous for health (CMR) Cat. 1

h) Dangerous for health (CMR) Cat. 2

i) Combustive

j) Compressed gas

4. Is this process step natural?

5. Tick the solvents used during this step:

a) No solvent

b) Water

Supercritical fluid

c) CO2

d) Tetrafluoroethane

e) Water

Renewable solvent

f) Ethanol

g) Vegetable oil

h) Another renewable solvent

Petrochemical solvent

i) Hexane

j) Cyclohexane, Methylcyclohexane

k) Toluene

l) MTBE

m) THF

n) Acetone

o) Isopropyl acetate

p) Ethyl acetate

q) Another petrochemical solvent

CMR solvent

r) Methanol

s) Methyl chloride

6. Tick GHS pictograms visible on the reagents and solvents lable:

a) Explosive

b) Dangerous for health (CMR) Cat. 1

c) Dangerous for health (CMR) Cat. 2

d) Toxic

e) Combustive

f) Corrosive

g) Dangerous for environmental

h) Flammable

i) Nocive (Exclamation point)

j) Compressed gas

7. Step yield (%):

8. Number of solvents used:

9. Atom economy:

This calculation only applied to synthesis.

The atom economy calculation was simplified by the calculation of the carbon economy. A chain reduction leading to the loss of carbon atoms will be penalized. On the contrary, a rearrangement or addition step in which the total carbon atoms of reactants engaged will be kept is valorised.

Carbon economy definition: Number of carbons of the product at the end of the step / Total number of carbons in the main reagents involved

10. Is it protection or deprotection step?

11. Is it a:

a) Microbiological transformation step?

b) Steam distillation step?

c) None

12. Step duration (in hours):

13. Reaction step under pressure?

a) No

b) Yes

14. Ways of heating:

a) No heating

b) Steam 1 bar

c) Steam up to 3 bars

d) Steam up to 6 bars

e) Steam up to 15 bars

f) Oil

g) Electrical resistance

h) Gas

15. Ways of cooling:

a) No cooling

b) Water

c) Glycol water

d) Brine

e) Dry ice

16. Distillation conditions:

a) No distillation

b) Distillation at atmospheric pressure

c) Distillation under vacuum

17. Does the step belong to the following list? If yes, tick its name:

Hazardous processes

a) Sulfonation

b) Nitrification

c) Chlorination

d) Silylation

e) Polyoxyethylenation with ethylene oxide

f) Process using isocyanate, short alkyl halide or alkyl sulfate

g) Process using phosphorous oxychloride

Energy-intensive processes

h) Crystallization

i) Ozonolysis

j) Liquid-liquid extraction

Other energy-intensive process

18. E-factor:

Table S4. Green Motion results for the reactions between amine and DMC catalysed by acid silica supported catalysts at 90 °C

Question	H_2SO_4-SiO_2			$HClO_4$-SiO_2		
	Benzylamine	Hexylamine	Octylamine	Benzylamine	Hexylamine	Octylamine
1	c	c	c	c	c	c
2	0%	0%	0%	0%	0%	0%
3	f	-	-	f	-	-
4	No	No	No	No	No	No
5	h	h	h	h	h	h
6	h	h	h	h	h	h
7	92.0%	91.4%	88.7%	94.3%	94.5%	89.8%
8	1	1	1	1	1	1
9	0.90	0.89	0.91	0.90	0.89	0.91
10	No	No	No	No	No	No
11	c	c	c	c	c	c
12	24 hours	24 hours	24 hours	24 hours	24 hours	24 hours
13	a	a	a	a	a	a
14	b	b	b	b	b	b
15	a	a	a	a	a	a
16	a	a	a	a	a	a
17	-	-	-	-	-	-
18.1	11.6	12.1	10.6	11.3	11.7	10.5
18.2	0.3	0.3	0.3	0.3	0.3	0.3
Result (18.1)	75	76	76	75	76	76
Result (18.2)	79	80	80	79	80	80

18.1: catalyst recovery, 18.2: DMC recovery

6. Substrate scope and scalable investigations

Table S5 Experimental results for the scalable reactions between ethylamine and butylamine and DMC catalysed by acid silica supported catalysts at 90 °C

Amine	Lewis acid	Equivalent	Conversion (%)	Selectivity (%)		
				Product 1	Product 2	Product 3
Ethylamine	H_2SO_4-SiO_2	1.0	>99.00±0.00	-	-	>99.00±0.00
	$HClO_4$-SiO_2	1.0	>99.00±0.00	-	-	>99.00±0.00
Butylamine	H_2SO_4-SiO_2	1.0	>99.00±0.00	-	-	>99.00±0.00
	$HClO_4$-SiO_2	1.0	>99.00±0.00	-	-	>99.00±0.00

Reaction conditions: Amine/DMC/catalyst = 20.00 mmol : 0.4 mol : 20.00 mmol; T = 90 °C; Reaction time 24 h. Conversion and selectivity were calculated by GC ,^{1}H-NMR and GC-MS.

Table S6 Recycle studies of acid-silica supported catalysts for the reaction of hexylamine with dmc at a gram scale.

Catalyst	Run	Conversion (%)	Selectivity (%)	
			Product 2	Product 3
H_2SO_4-SiO_2	1	>99.00	3.21	96.79
	2	>99.00	0.89	99.11
	3	>99.00	0.53	99.47
	4	>99.00	0.81	99.19
	5	>99.00	0.51	99.49
$HClO_4$-SiO_2	1	>99.00	-	>99.00
	2	>99.00	-	>99.00
	3	>99.00	-	>99.00
	4	>99.00	-	>99.00
	5	>99.00	-	>99.00

Reaction conditions: Amine/DMC/catalyst = 40.00 mmol : 0.8 mol : 40.00 mmol; T = 90 °C; Reaction time 24 h. Conversion and selectivity were calculated by GC ,^{1}H-NMR and GC-MS.

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