Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Alkyl coupling in tertiary amines as analog of Guerbet condensation reaction

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METHODS

Metal supported catalysts Pd/Al_2O_3, Pd/C, Pt/C, Ru/C, Pt/Al_2O_3, Rh/Al_2O_3 containing 5 wt. % of the metal have been purchased from Johnson Matthey. Ni/Al_2O_3 containing 5 wt.% of Ni has been prepared by impregnation of corresponding amount of $Ni(NO_3)\cdot 6H_2O$ with subsequent calcination at 450 ºC and reduction at 550 ºC with subsequent transfer of the catalyst into reactor in inert atmosphere.

The catalytic tests have been conducted in 50 ml batch reactors. The catalysts have been loaded in the reactor (0.1 g) and reduced in the reactor before catalytic tests at 200 ºC during 1 h. Afterwards, the reactor has been charged with 2 g of tertiary amine, pressurized by 5 bar of N_2 or H_2 with subsequent heating to the target temperature for 5-17 h. In some experiment 5 g of cyclohexane has been added as a solvent. The reaction products have been analyzed by GC, GC-MS and ^1H and ^{13}C NMR.

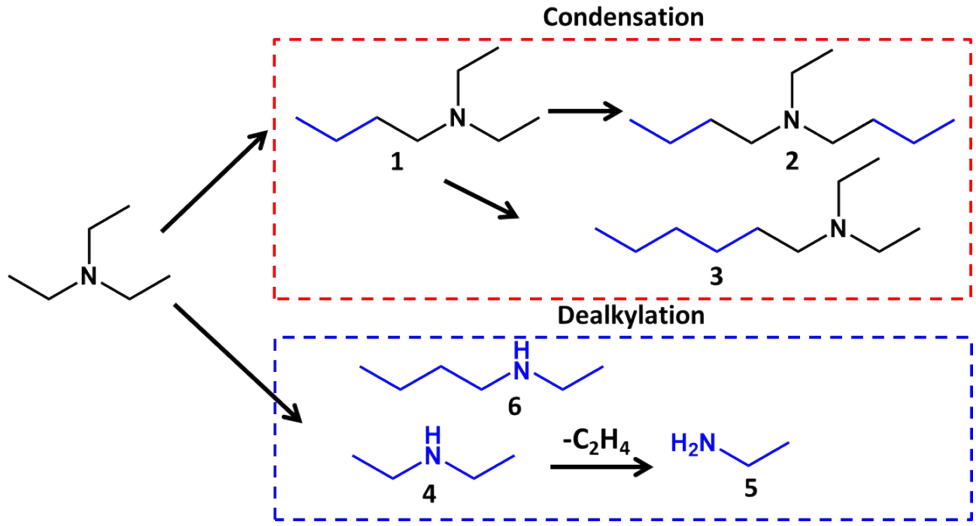
The TEM observations of the samples were performed on a FEI Tecnai F30 electron microscope, operating at 300 kV. CO or O_2 chemisorption measurements were carried out with a Micromeritics ASAP 2020 instrument to evaluate the metal dispersion. Before each measurement, the sample was reduced at 200 ºC. After the reduction, the sample was cool down to 45 ºC with subsequent pulse adsorption of the gas. FTIR measurements were carried out on a Nicolet Protege 380 spectrometer. About 20 mg of the sample was pressed in self-supported wafer. The sample has been activated at 200 ºC under hydrogen atmosphere with subsequent vacuuming and cooled down to r.t. 10 torr of TEA has been adsorbed over the catalyst with subsequent gradually heating till 200 ºC. CO adsorption has been performed by addition of 10 torr of CO at room temperature with subsequent deep vacuuming.

Table S1. *Metal dispersion of the catalysts*

Catalysts	Metal content, wt. %	Adsorption properties				Particle size, nm*
		Gas adsorption	Metal surface area, m^2/g	Dispersion, %	Particle size, nm	
Pd/Al_2O_3	4.5	CO	109	24	5	3
Pt/C	4.9	O_2	120	24	4.6	-
Ru/Al_2O_3	4.7	CO	72	16	6.7	-
Ru/C	5.0	CO	199	42	2.4	2.5
Pd/C	5.3	CO	54	12	8.1	-
Rh/Al_2O_3	4.9	-	-	-	-	-
Pd black	100	CO	26	6	20	-
Ni/Al_2O_3	5.1	CO	83	12	8.1	-

*- analysis by TEM

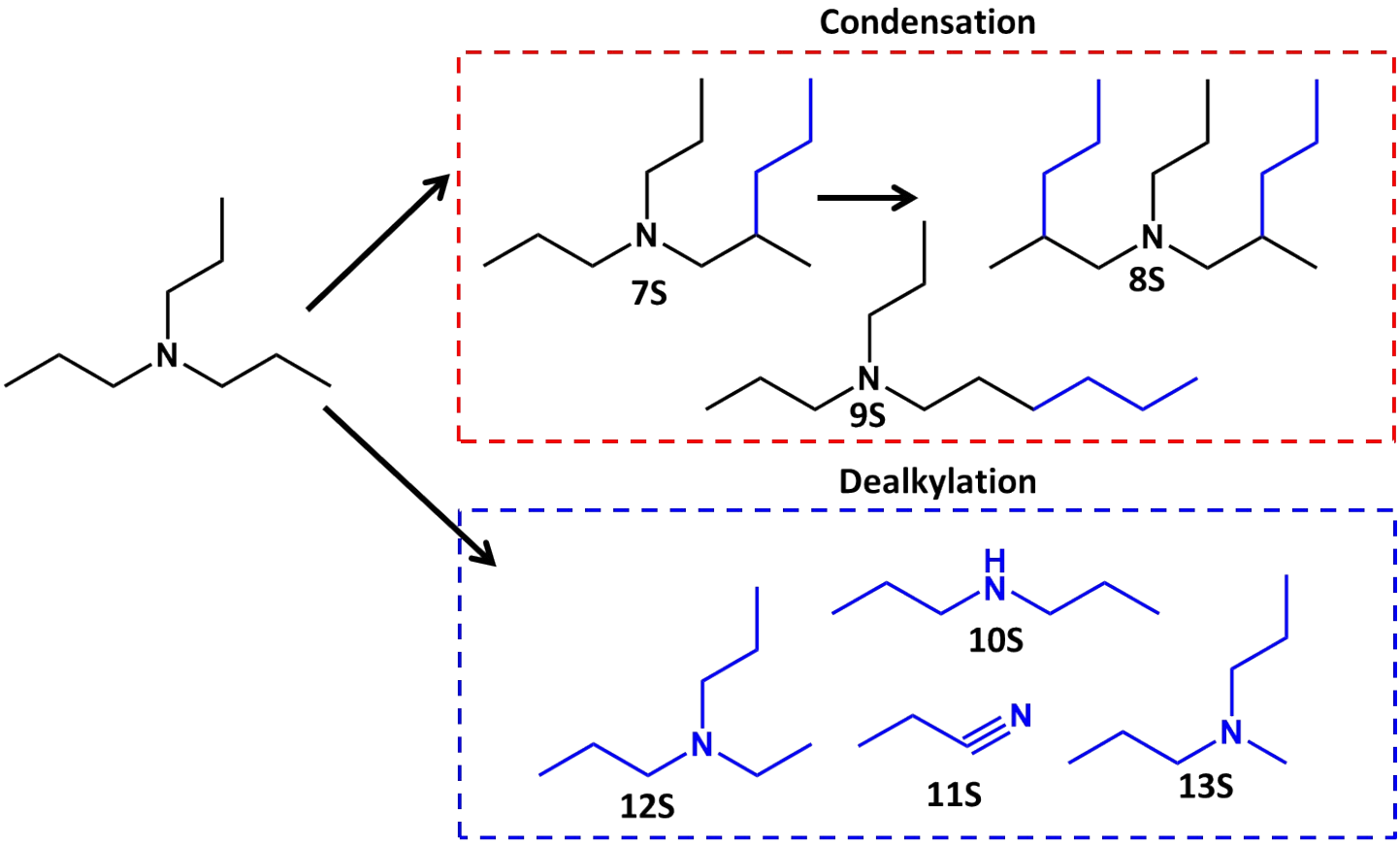
Table S2. *TEA transformation (2 g TEA, p(N_2)=5 bar, 0.1 g catalyst, 5h, 200 °C)*



Catalysts	Conversion, %	Selectivity to amines, mol. %							
		Coupling				Dealkylation			
		1S	**2S**	**3S**	Ethyl group accepted	**4S**	**5S**	**6S**	Ethyl group lost
-	1	-	-	-		-	-	-	
Pd/C	89	20	13	3	**52**	26	11	17	**48**
Pt/C	62	27	5	3	**43**	44	12	8	**68**
Pd/Al_2O_3	47	41	5	1	**53**	42	9	2	**60**
Pd/Al_2O_3[a]	27	39	2	-	**43**	42	11	-	**64**
Ru/Al_2O_3	3	48	-	-	**48**	49	-	-	**49**
Ru/C	13	38	1	4	**48**	55	2	2	**59**
Rh/Al_2O_3	2	-	-	-	**0**	-	-	-	**0**
Pd/Al_2O_3[b]	4	43	-	-	**43**	53	-	2	**53**
Pd/Al_2O_3[c]	88	14	7	4	**36**	30	26	11	**82**

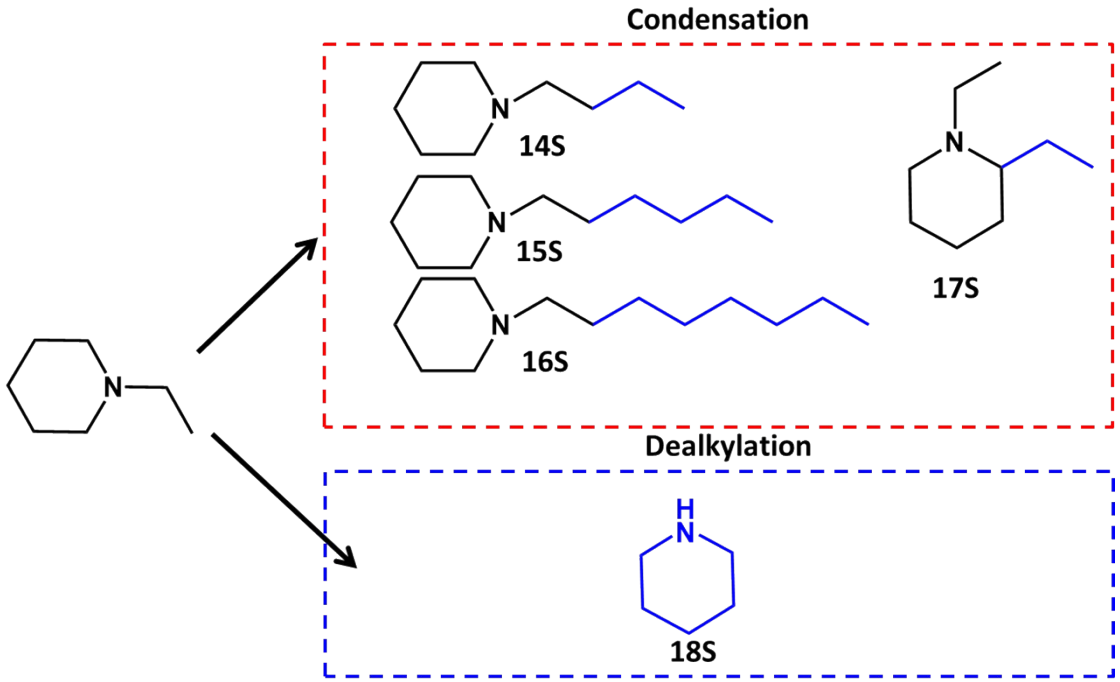
[a] H_2 gas phase, [b] 150 ºC, [c] 250 ºC

Table S3. *TPA transformation (2 g TPA, p(N_2)=5 bar, 0.1 g catalyst, 5h)*



Catalysts	Temperature, °C	Conversion, %	Selectivity to amines, mol. %								
			Coupling				Dealkylation				
			7S	**8S**	**9S**	Propyl group accepted	**10S**	**11S**	**12S**	**13S**	Propyl group lost
Pd/Al_2O_3	200	9	44	-	-	**44**	54	-	-	-	**54**
Pd/Al_2O_3	250	69	29	1	1	**32**	63	5	1	1	**78**

Table S4. *N-ethylpiperidine transformation (2 g N-ethylpiperidine, p(N_2)=5 bar, 0.1 g catalyst, 5h)*



Catalysts	Temperature, °C	Conversion, %	Selectivity to amines, mol. %						
			Coupling					Dealkylation	
			14S	**15S**	**16S**	**17S**	Ethyl group accepted	**18S**	Ethyl group lost
Pd/Al_2O_3	200	36	21	6	4	2	**45**	58	**58**

Figure S1. *GC-MS analysis after 5h during TEA transformation (2 g TEA, p(N_2)=5 bar, 0.1 g Pd/Al_2O_3, 200 °C) with assignment of the products a,b,c,d,e,f in the Figure S2*

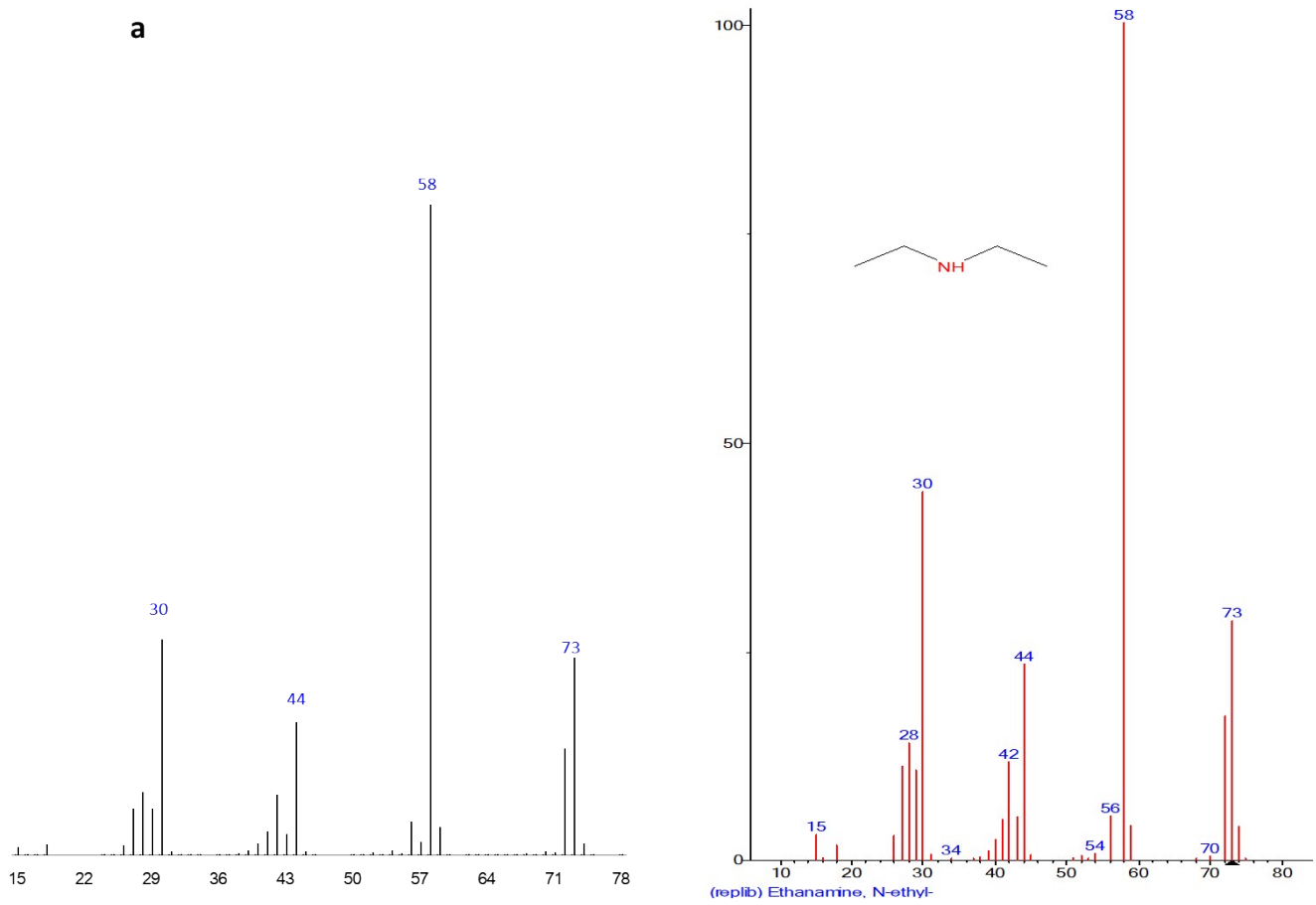


Figure S2-a. *MS spectrum of the product a from Figure S1 in comparison with assignment in NIST library to diethylamine*

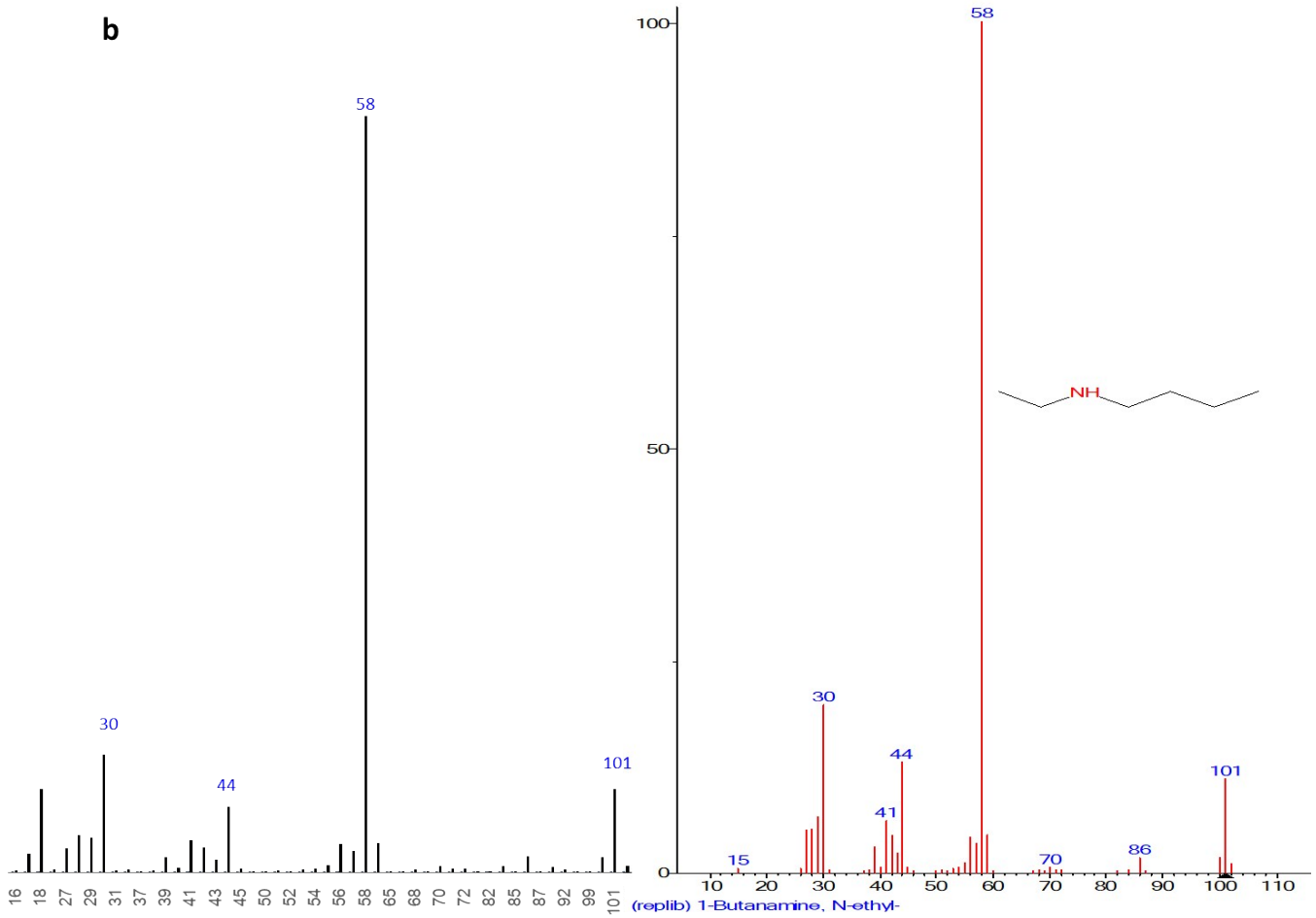


Figure S2-b. *MS spectrum of the product b from Figure S1 in comparison with assignment in NIST library to butylethylamine*

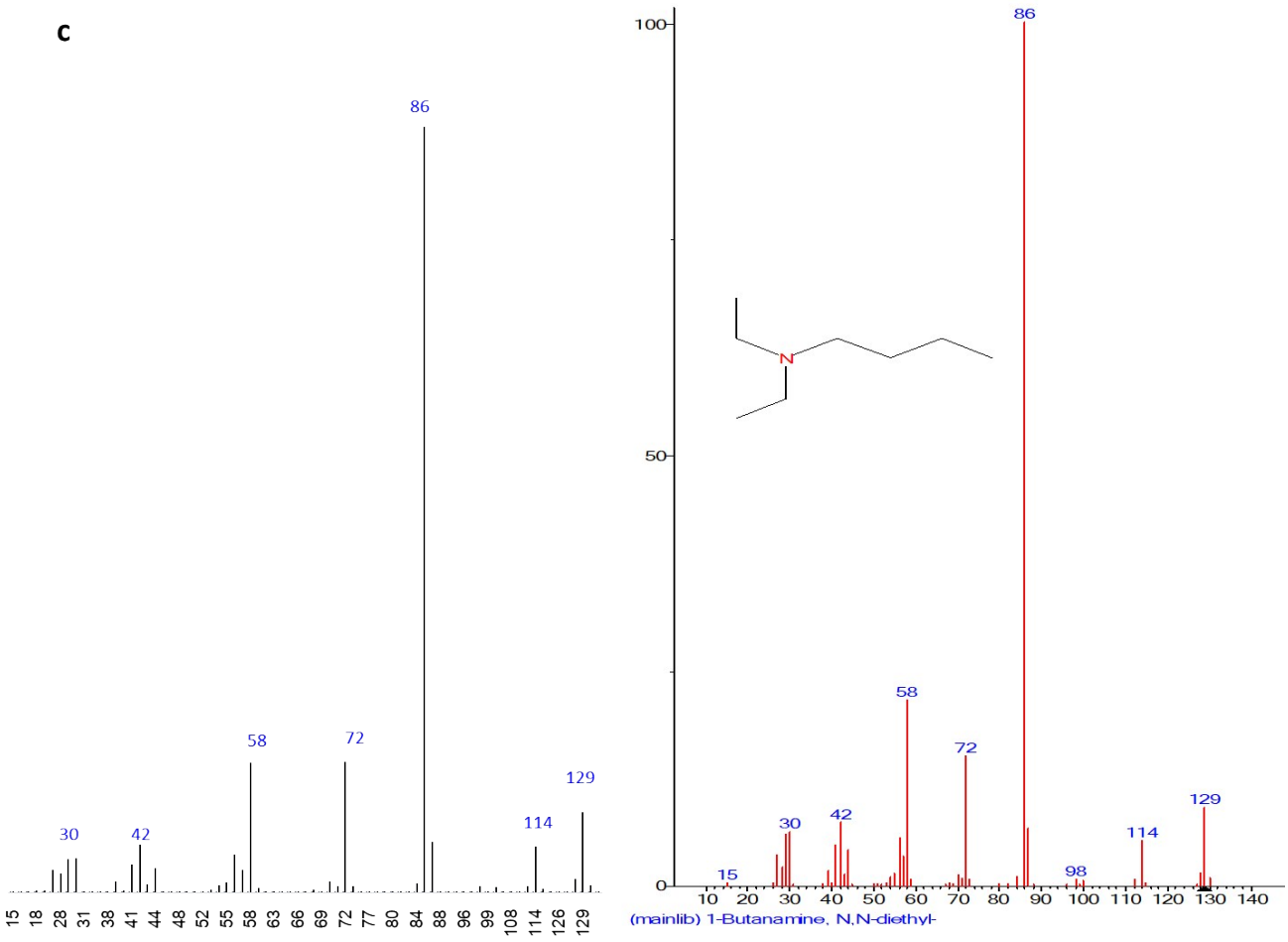


Figure S2-c. *MS spectrum of the product c from Figure S1 in comparison with assignment in NIST library to butyldiethylamine*

d

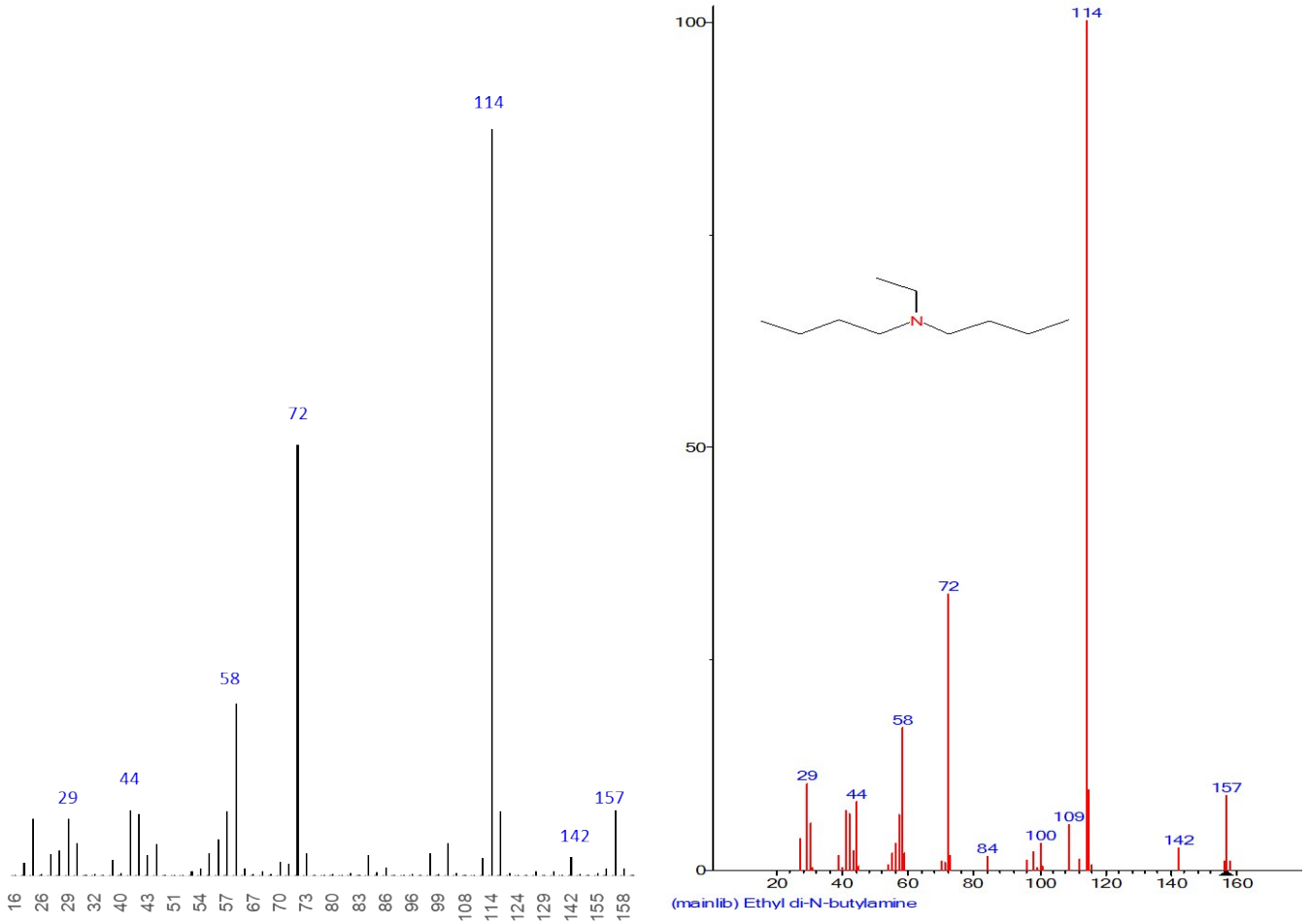


Figure S2-d. *MS spectrum of the product d from Figure S1 in comparison with assignment in NIST library to dibutylethylamine*

e

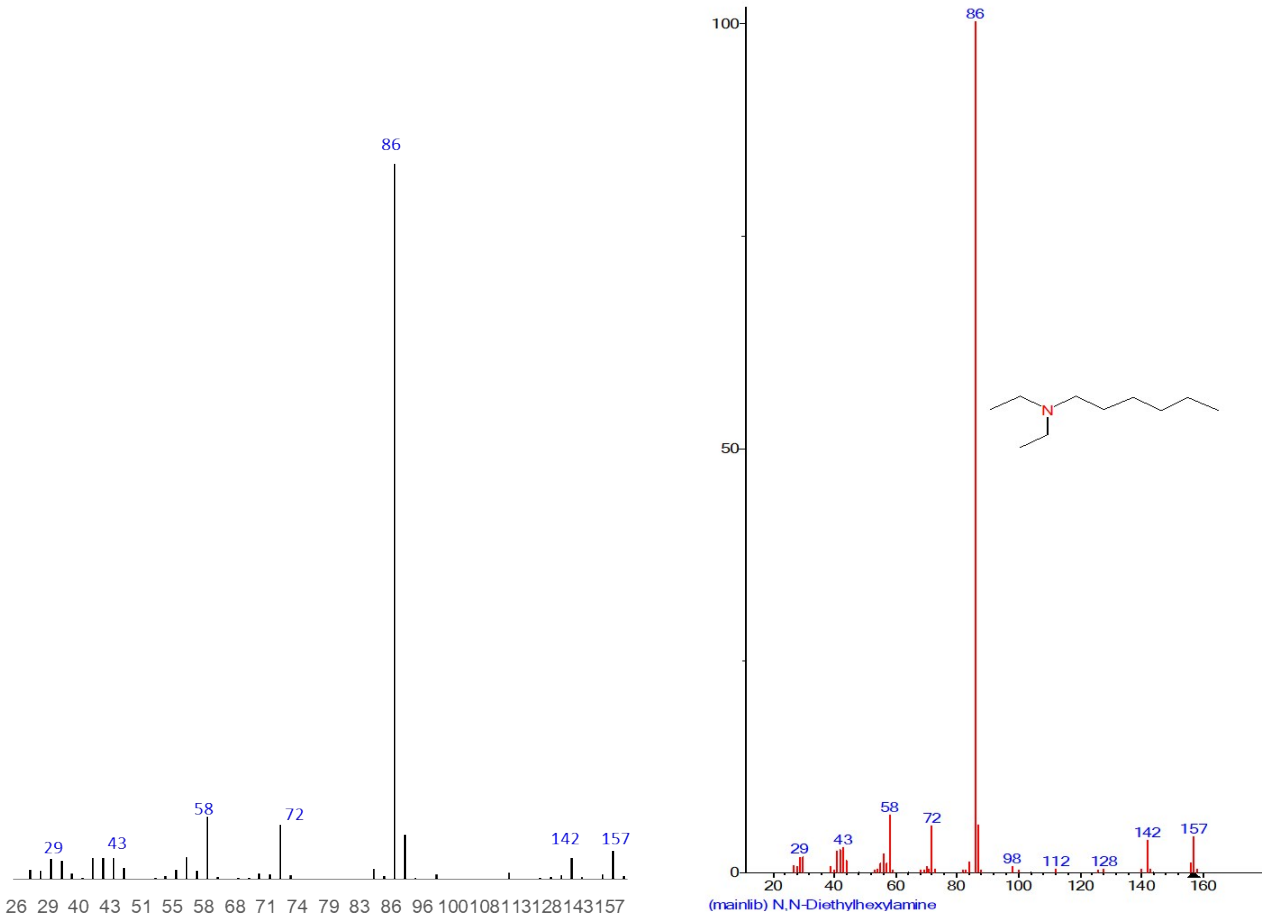


Figure S2-e. *MS spectrum of the product e from Figure S1 in comparison with assignment in NIST library to hexyldiethylamine*

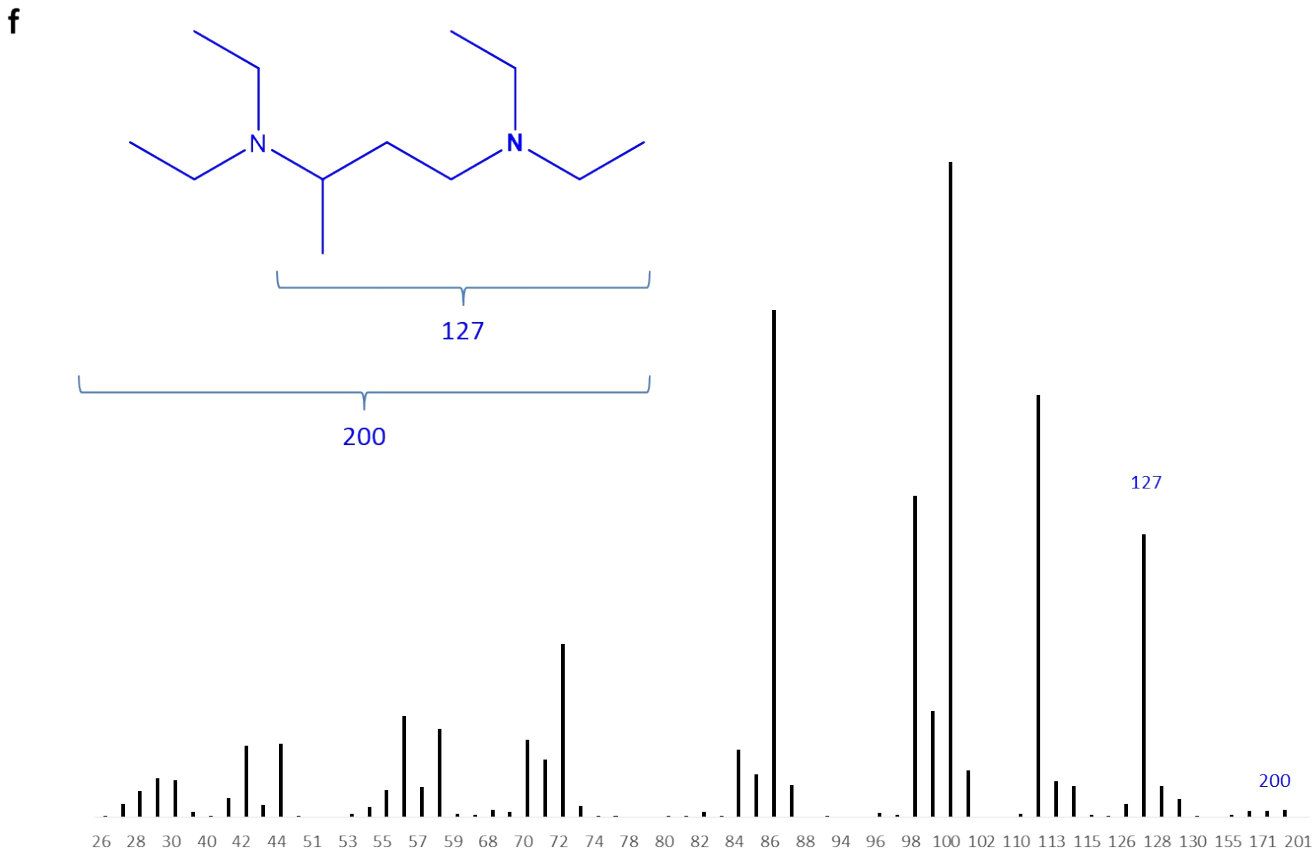


Figure S2-f. *MS spectrum of the product f from Figure S1 indicating on formation of intermediate diamine product*

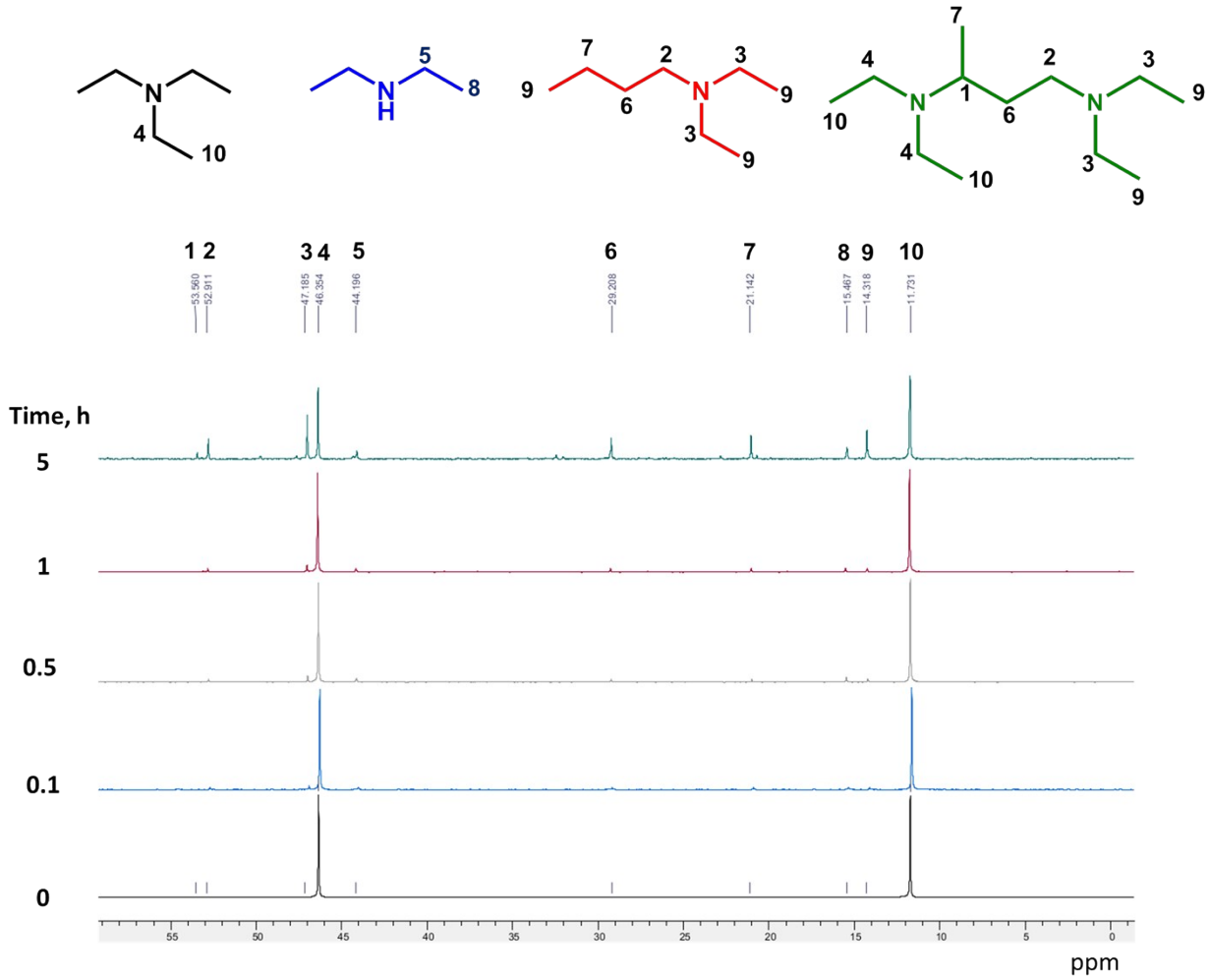


Figure S3. *^{13}C NMR analysis after different reaction time during TEA transformation (2 g TEA, $p(N_2)$=5 bar, 0.1 g Pd/Al_2O_3, 200 °C)*

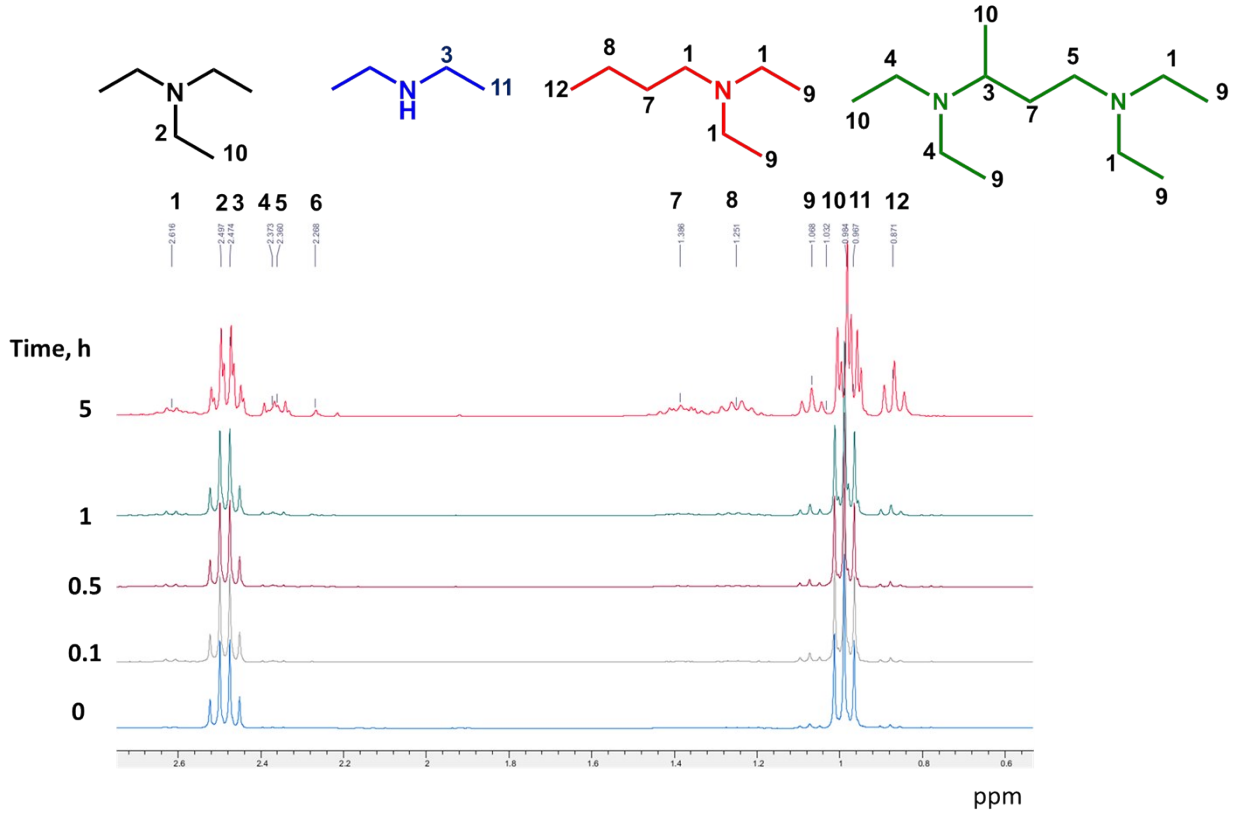


Figure S4. *^{1}H NMR analysis after different reaction time during TEA transformation (2 g TEA, $p(N_2)$=5 bar, 0.1 g Pd/Al_2O_3, 200 °C)*

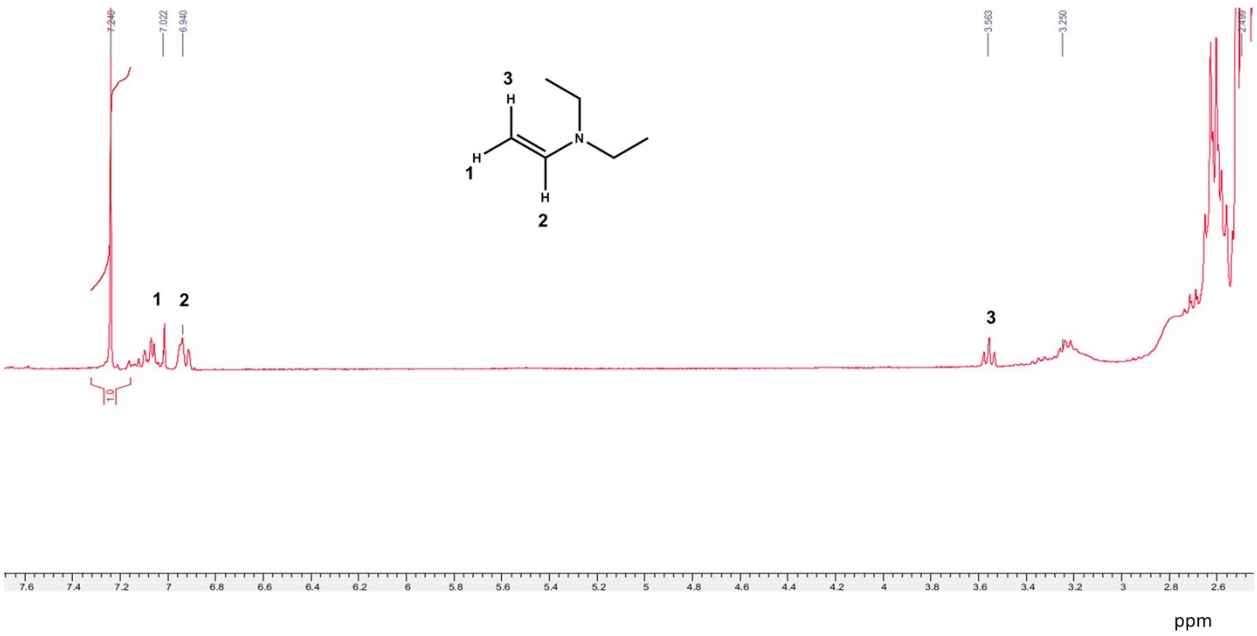


Figure S5. *^{1}H NMR analysis after 5h during TEA transformation (2 g TEA, $p(N_2)$=5 bar, 0.1 g Pd/Al_2O_3, 200 °C)*

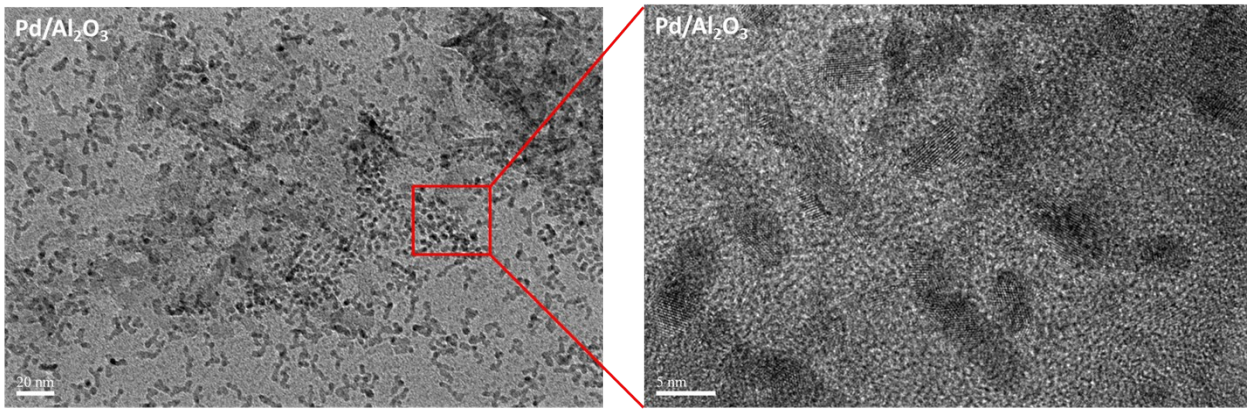


Figure S6. *TEM images of Pd/Al_2O_3*

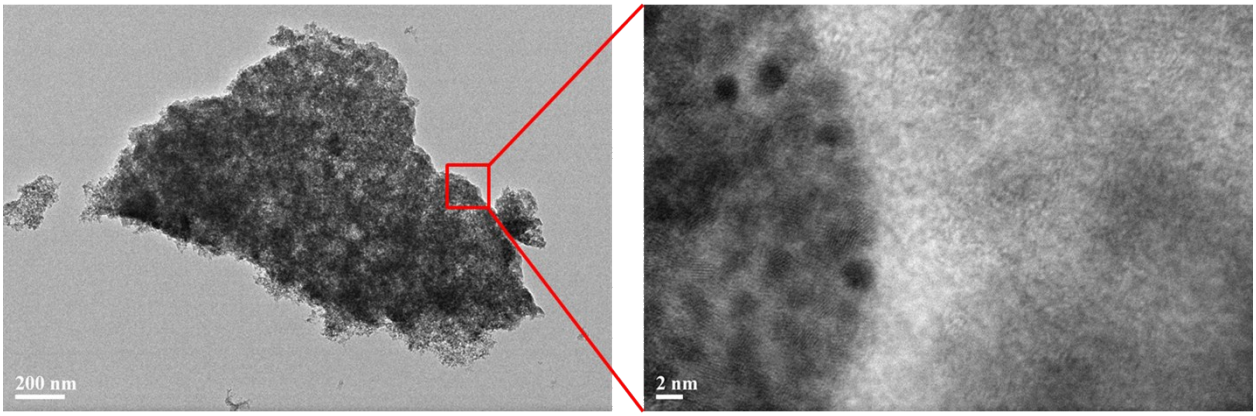


Figure S7. *TEM images of Ru/C*

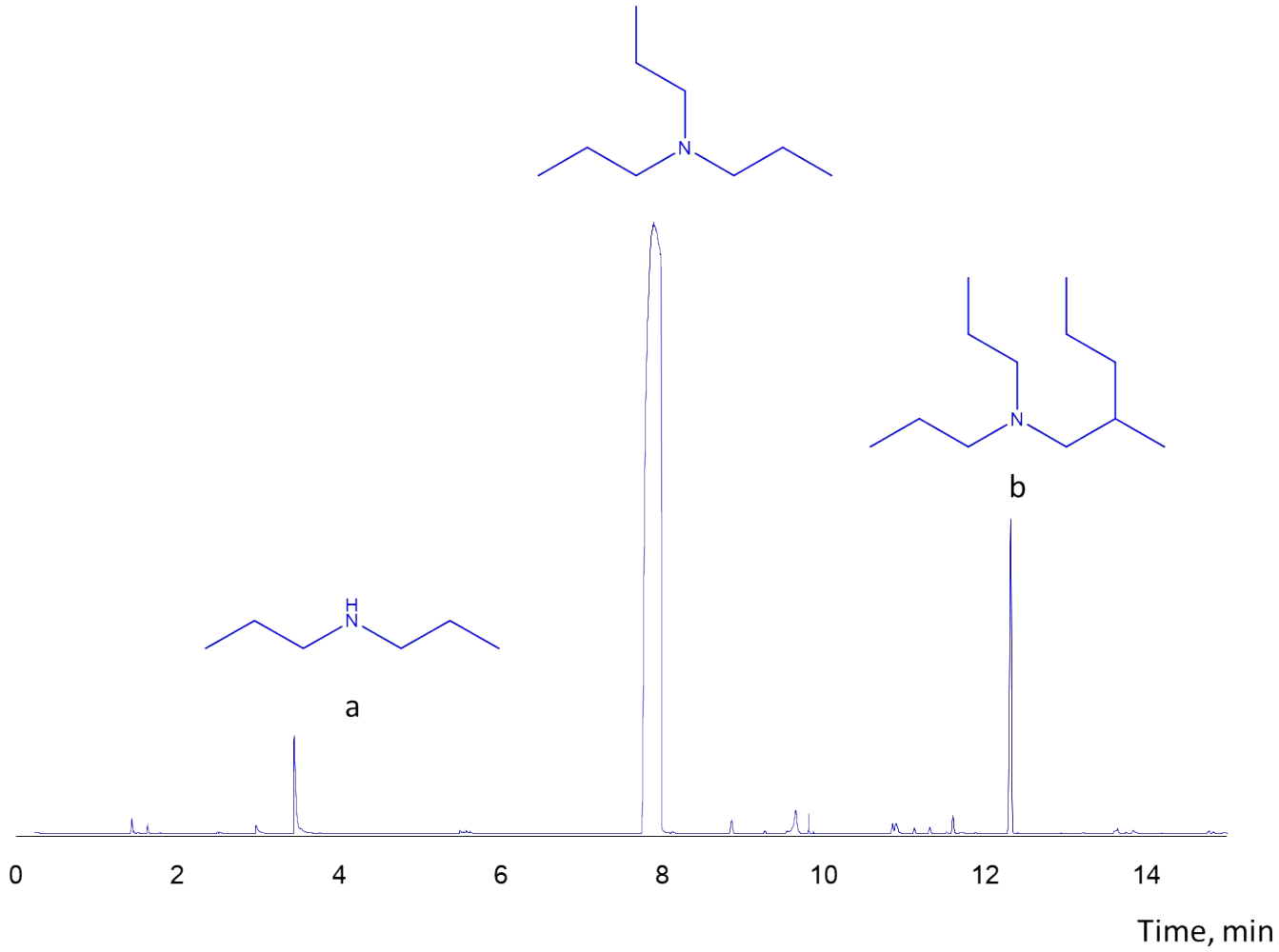


Figure S8. *GC-MS analysis after 5h during TPA transformation (2 g TPA, p(N_2)=5 bar, 0.1 g Pd/Al_2O_3, 200 °C) with assignment of the products a,b in the Figure S9*

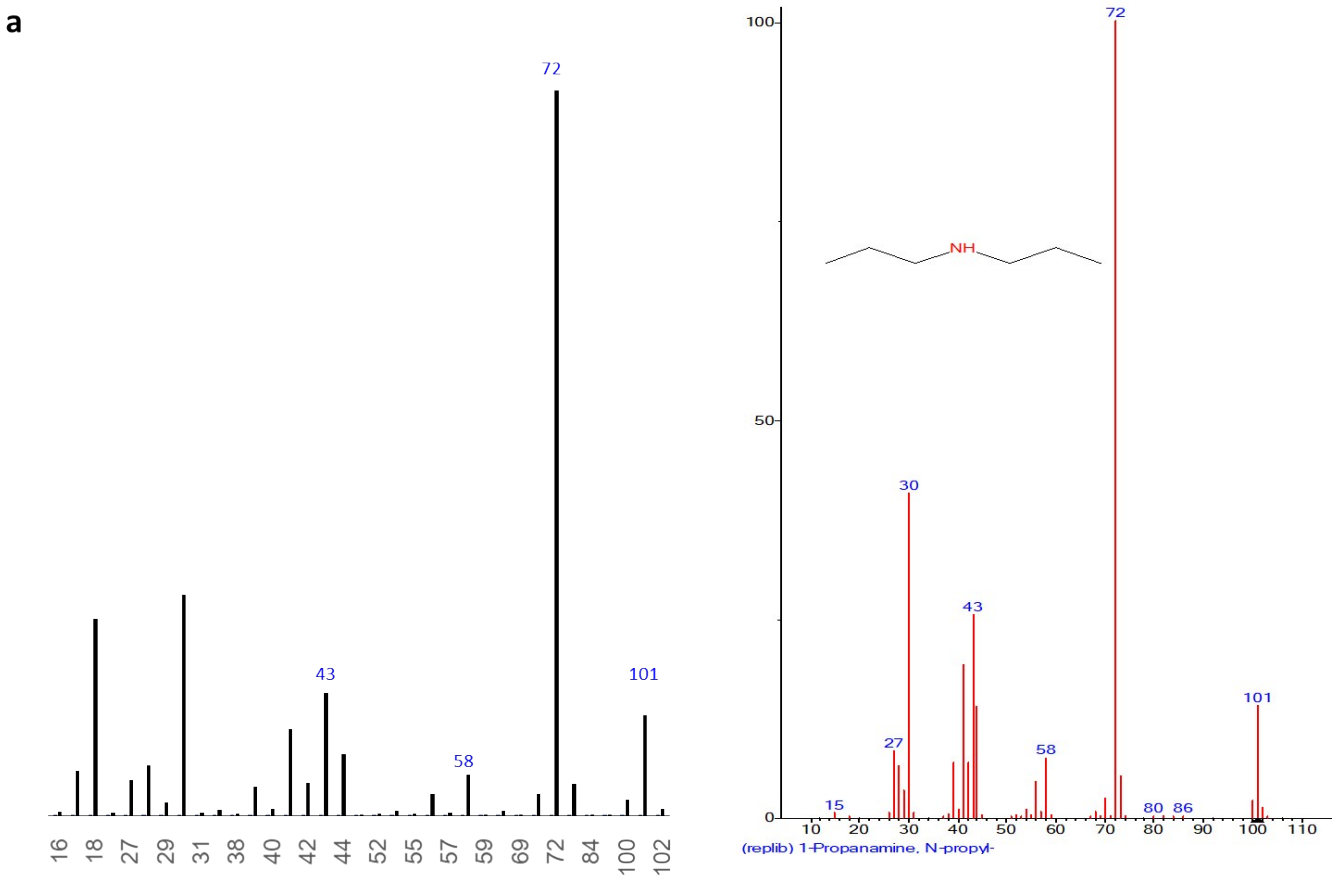


Figure S9-a. *MS spectrum of the product a from Figure S8 in comparison with assignment in NIST library to dipropylamine*

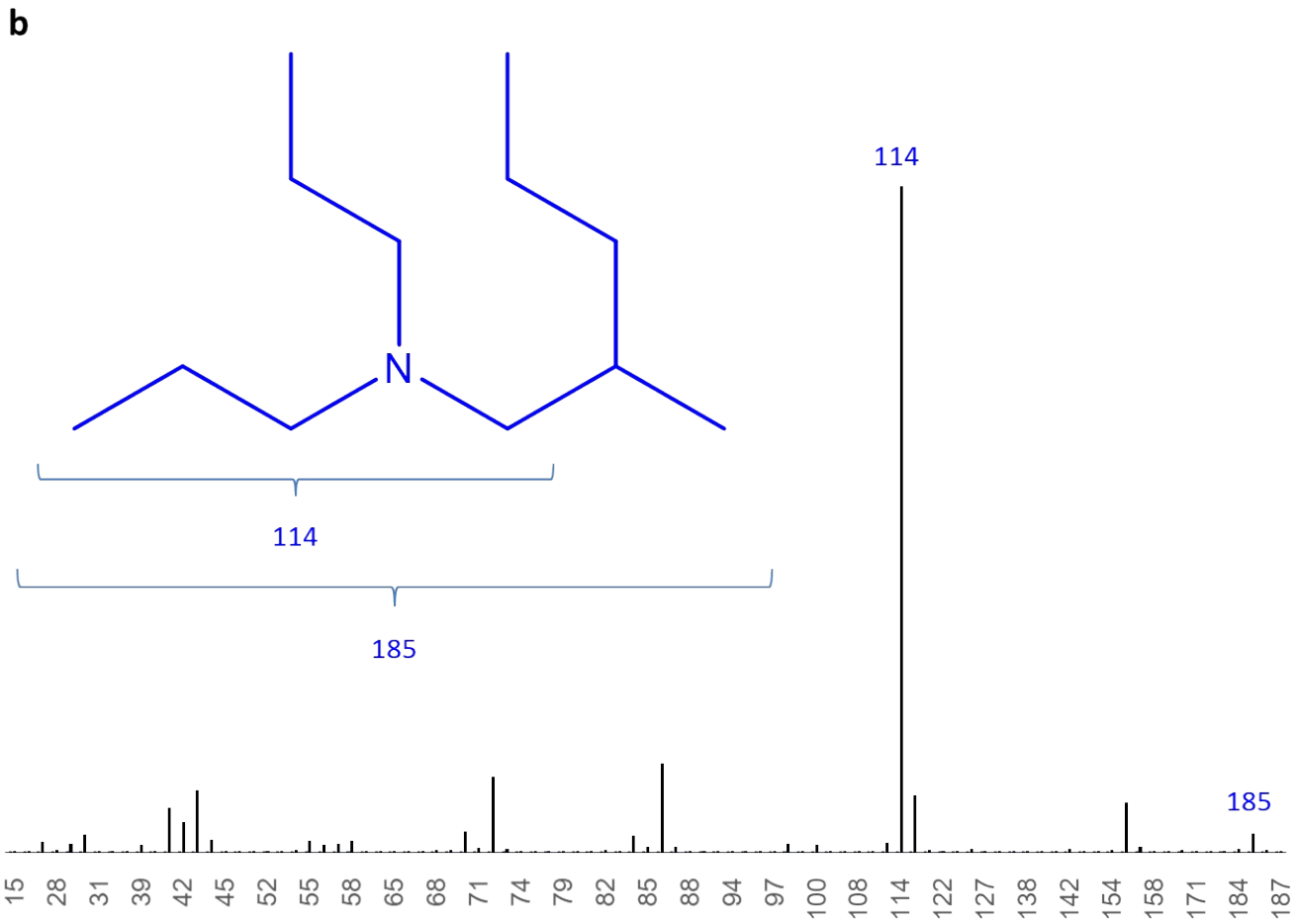


Figure S9-b. *MS spectrum of the product b from Figure S8 indicating on formation of 2-methy-N,N-dipropylpentane-1-amine*

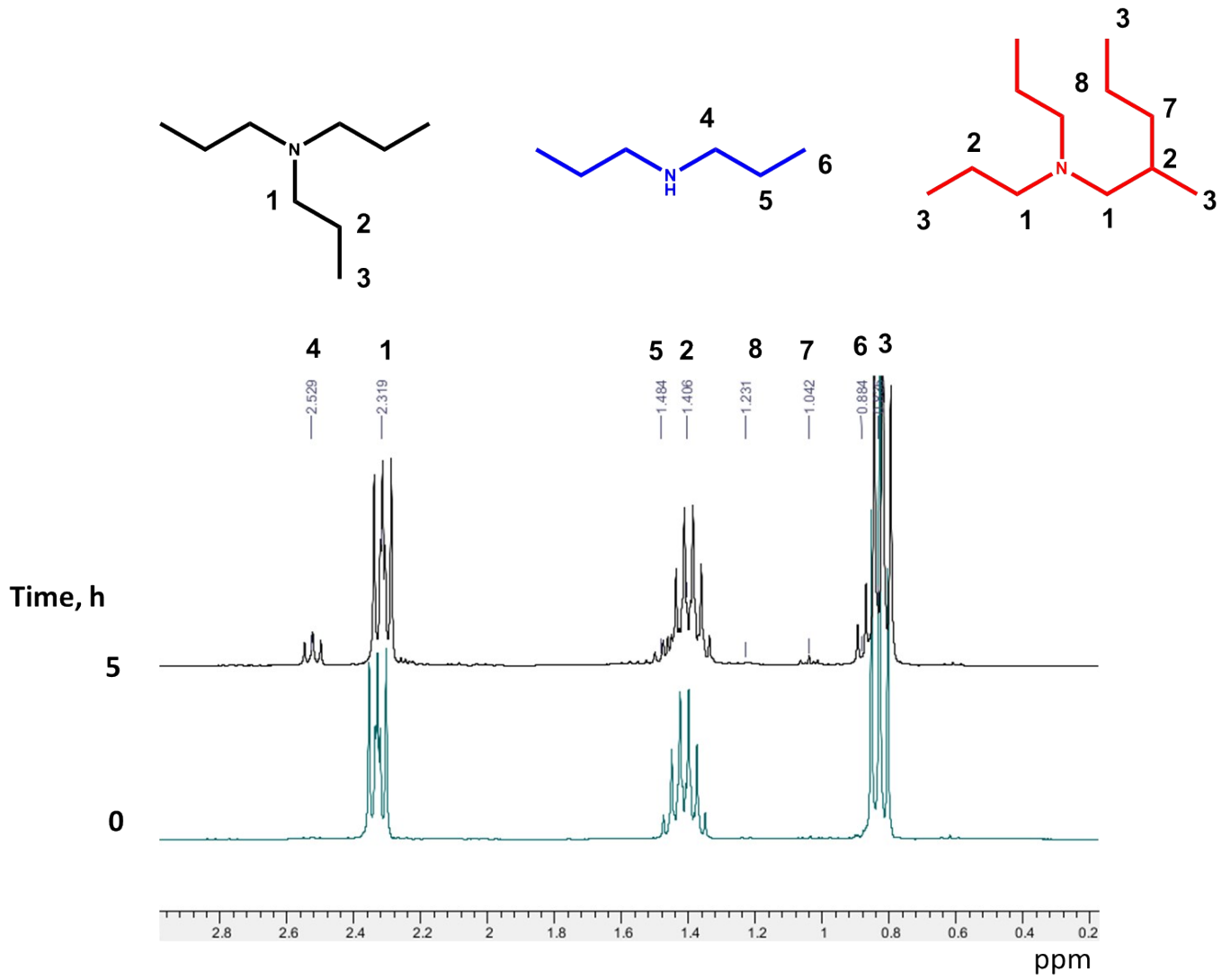


Figure S10. *^{1}H NMR analysis after5 h during TPA transformation (2 g TPA, p(N_2)=5 bar, 0.1 g Pd/Al_2O_3, 200 °C)*

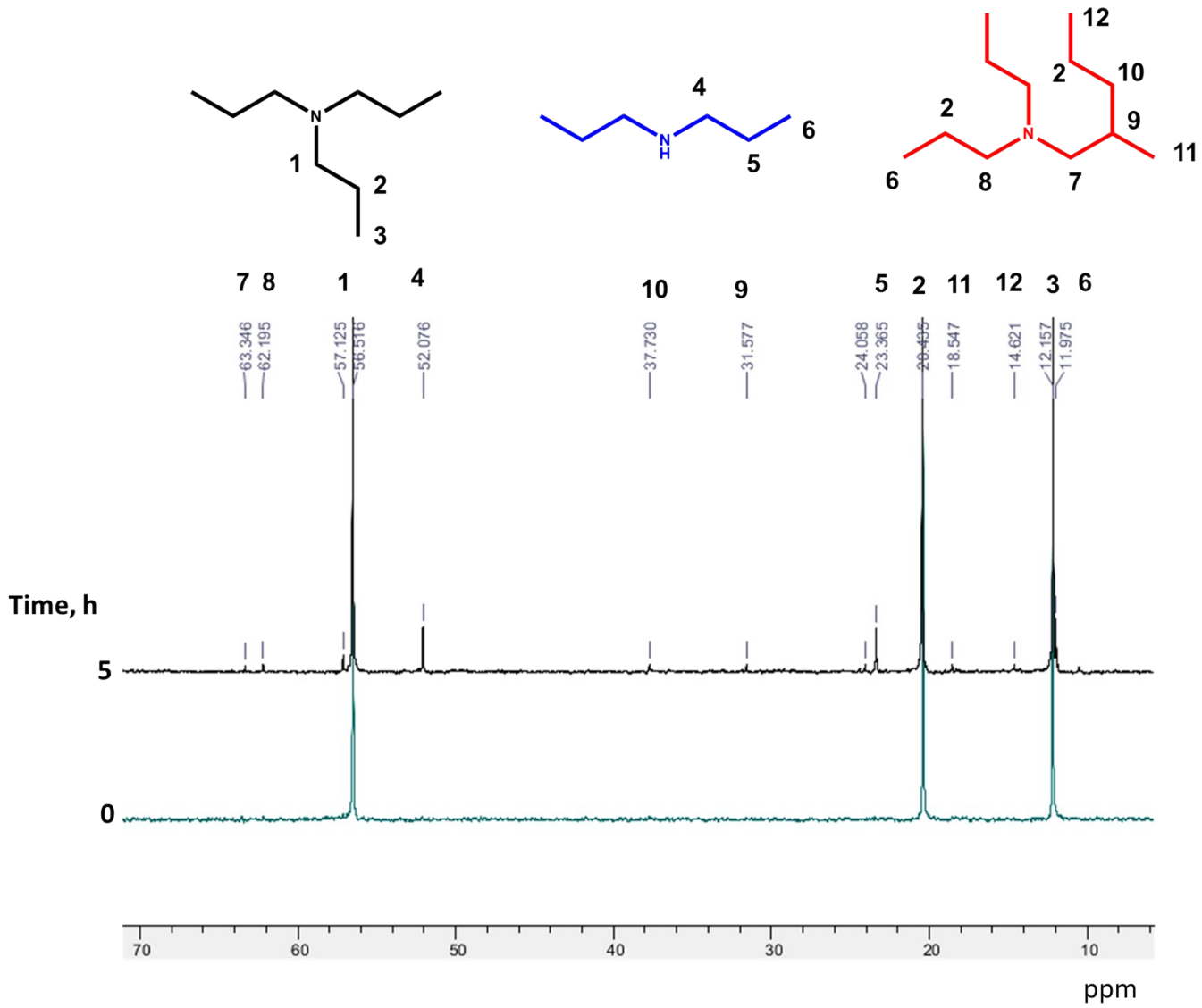


Figure S11. *^{13}C NMR analysis after 5 h during TPA transformation (2 g TPA, $p(N_2)$=5 bar, 0.1 g Pd/Al_2O_3, 200 °C)*

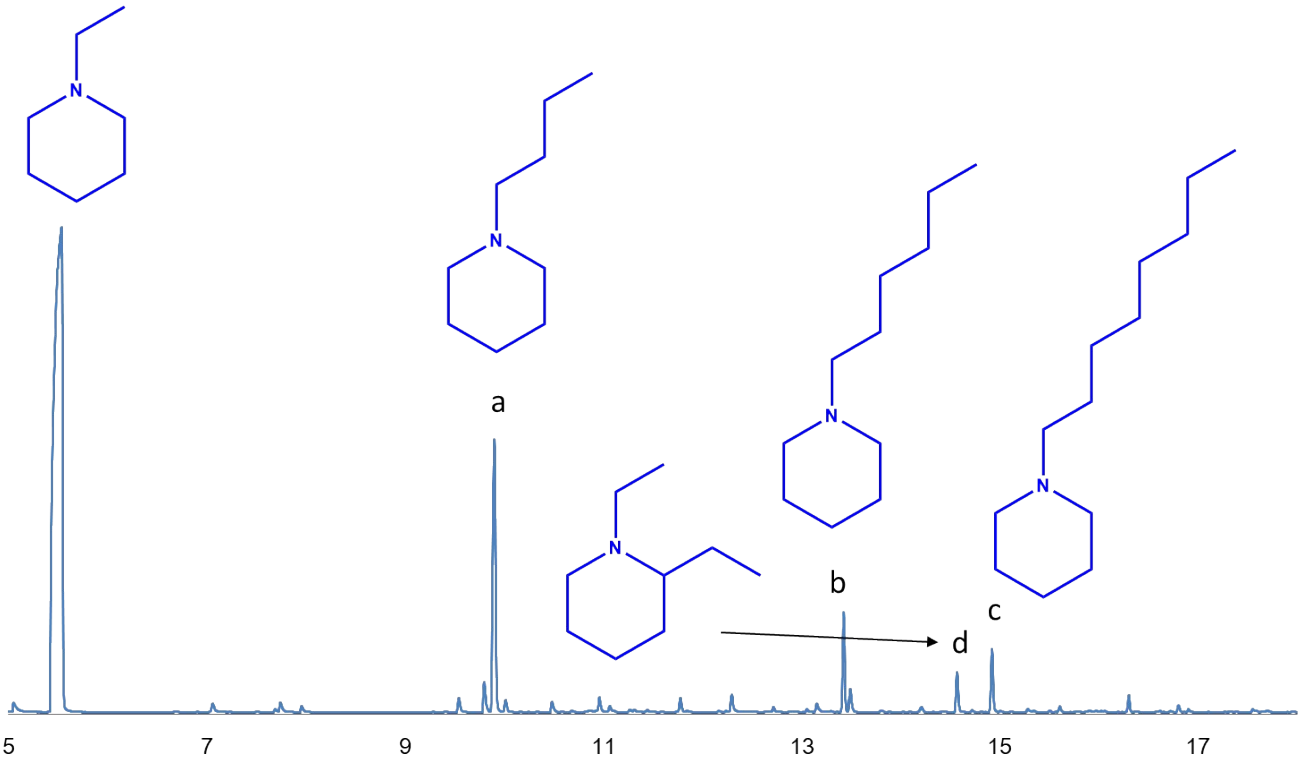


Figure S12. *GC-MS analysis after 5h during N-ethylpiperidine transformation (2 g N-ethylpiperidine, p(N_2)=5 bar, 0.1 g Pd/Al_2O_3, 200 °C) with assignment of the products a,b,c in the Figure S13*

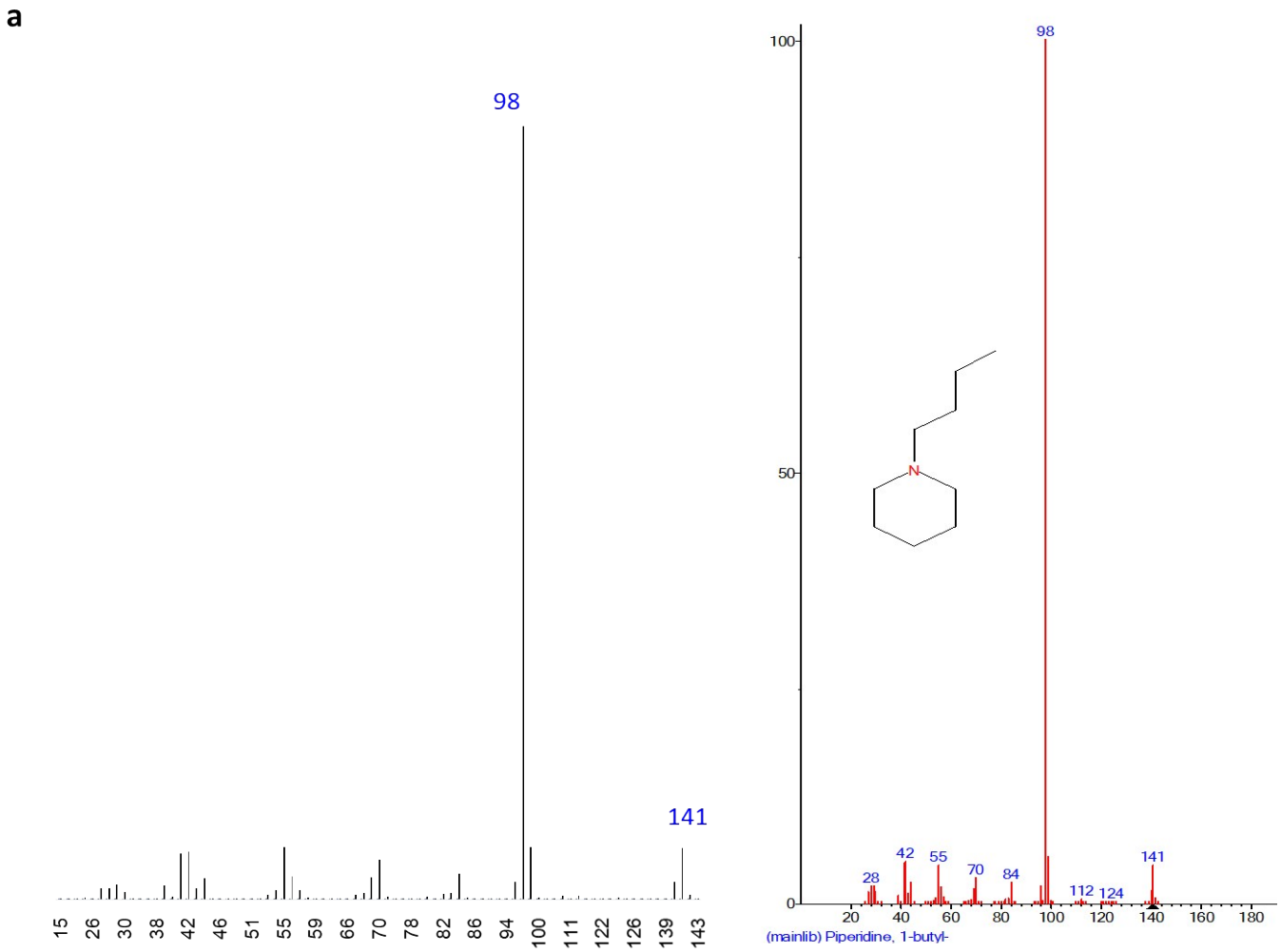


Figure S13-a. *MS spectrum of the product a from Figure S12 in comparison with assignment in NIST library to N-butylpiperidine*

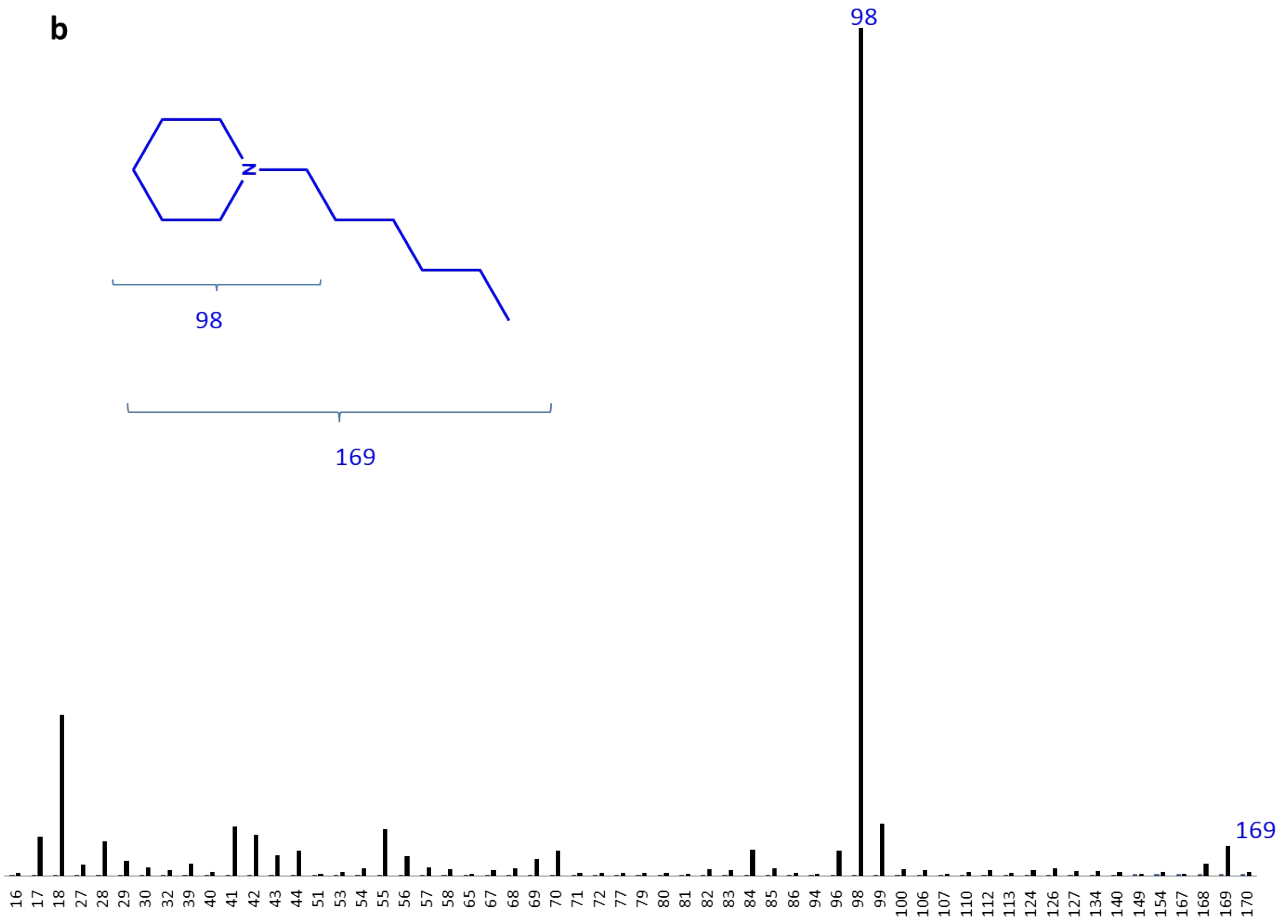


Figure S13-b. *MS spectrum of the product b from Figure S12 indicating on formation of N-hexylpiperidine*

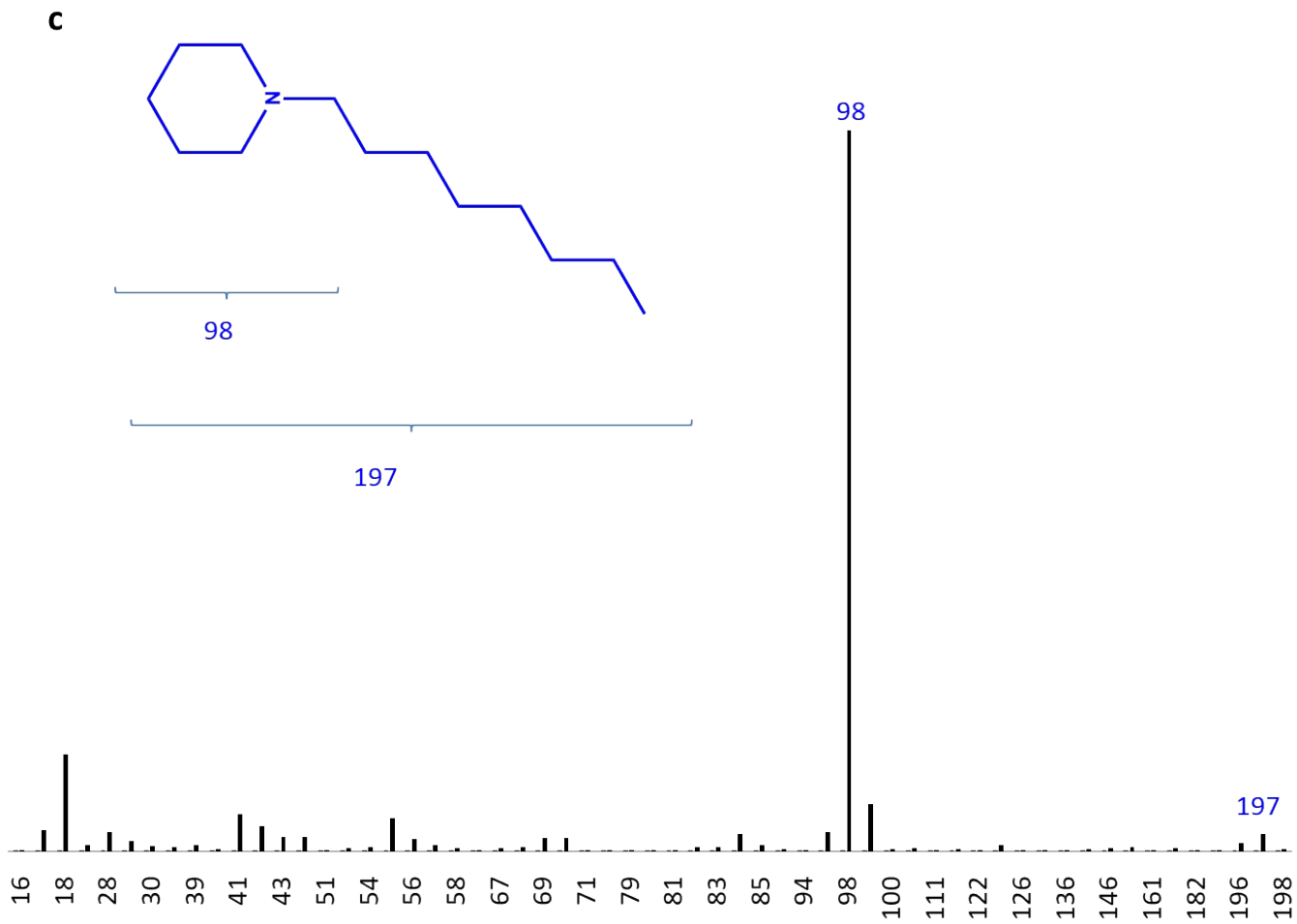


Figure S13-c. *MS spectrum of the product b from Figure S12 indicating on formation of N-octylpiperidine*

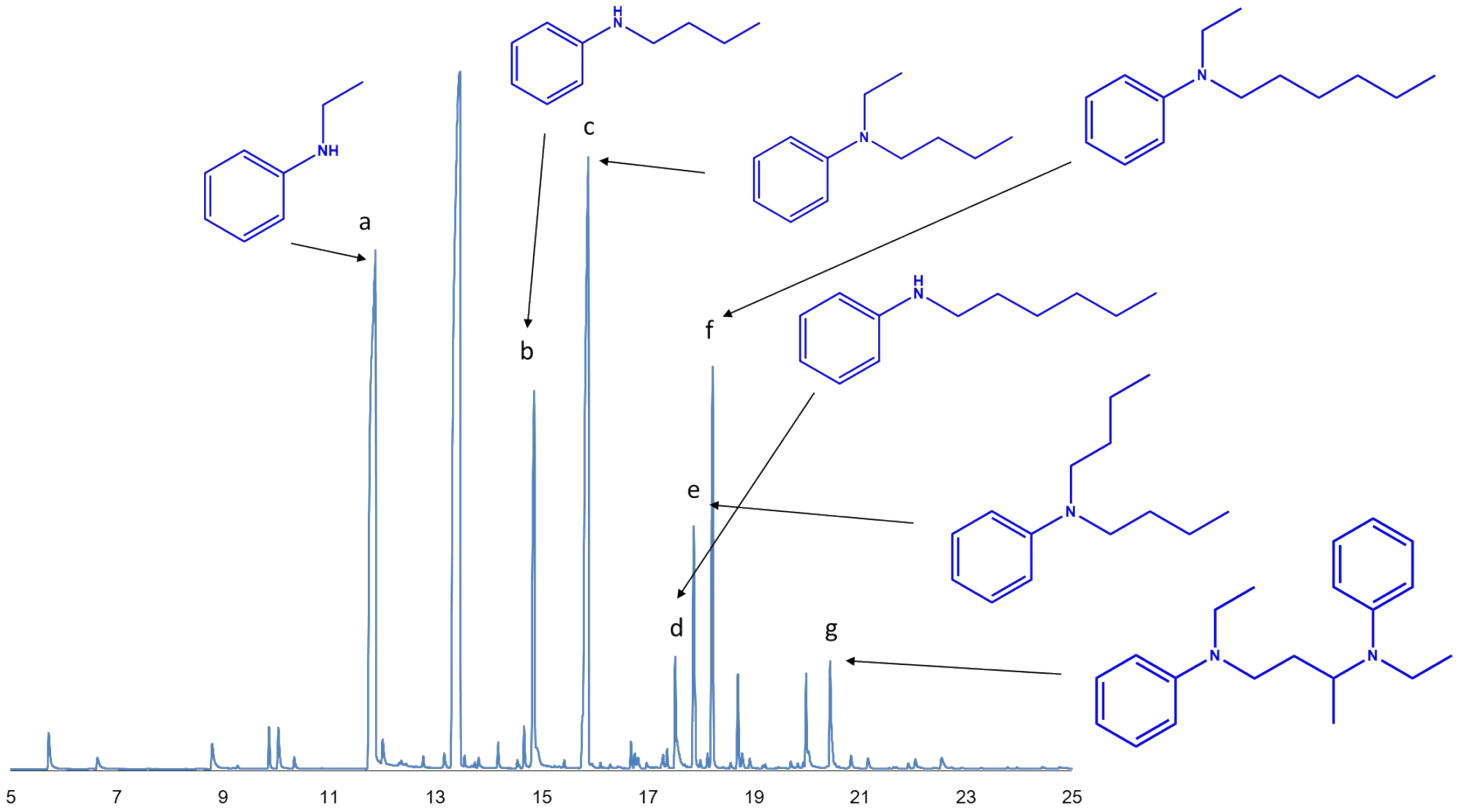


Figure S14. *GC-MS analysis after 5h during N,N-diethylaniline transformation (2 g N,N-diethylaniline, p(N_2)=5 bar, 0.1 g Pd/Al_2O_3, 200 °C) with assignment of the products a,b,c,d,e,f,g in the Figure S15*

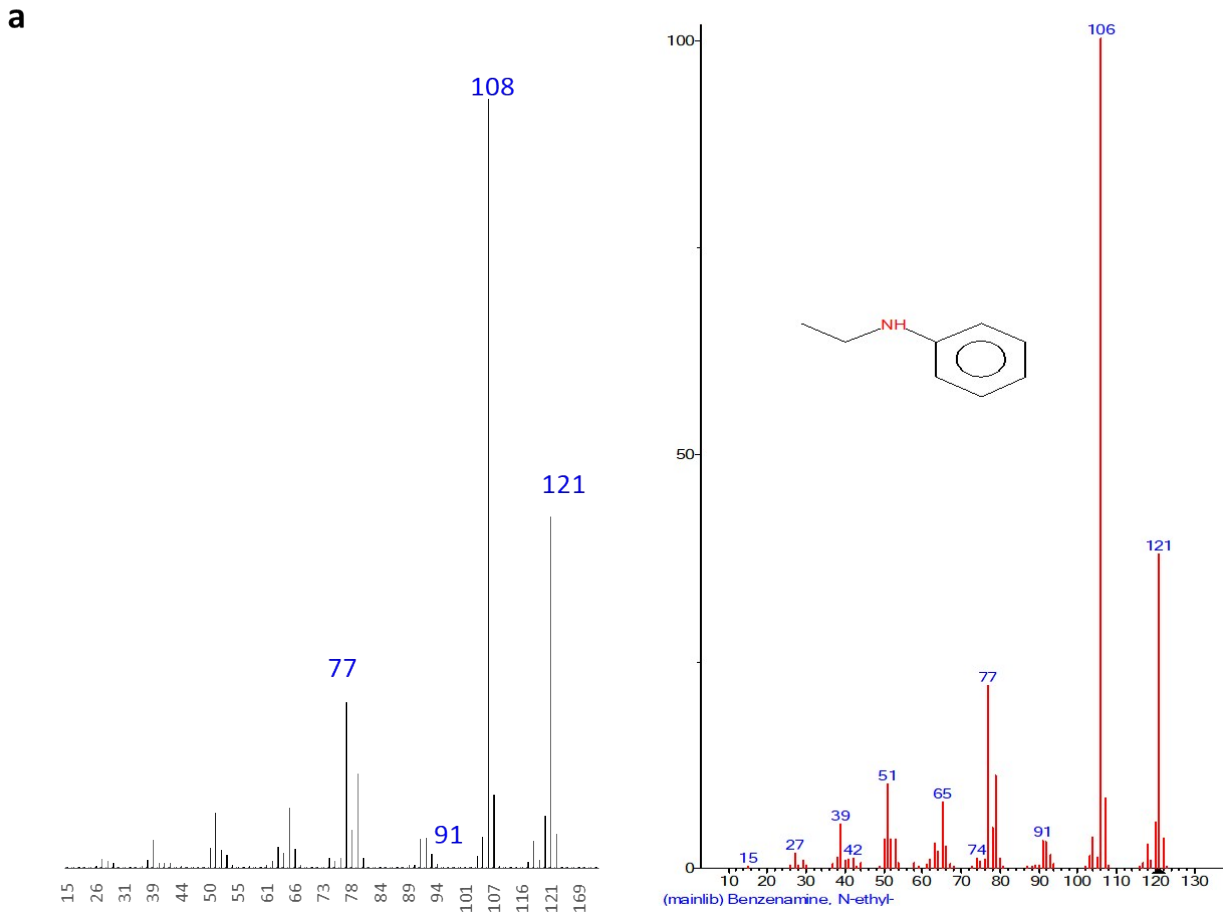


Figure S15-a. *MS spectrum of the product a from Figure S14 in comparison with assignment in NIST library to N-ethylaniline*

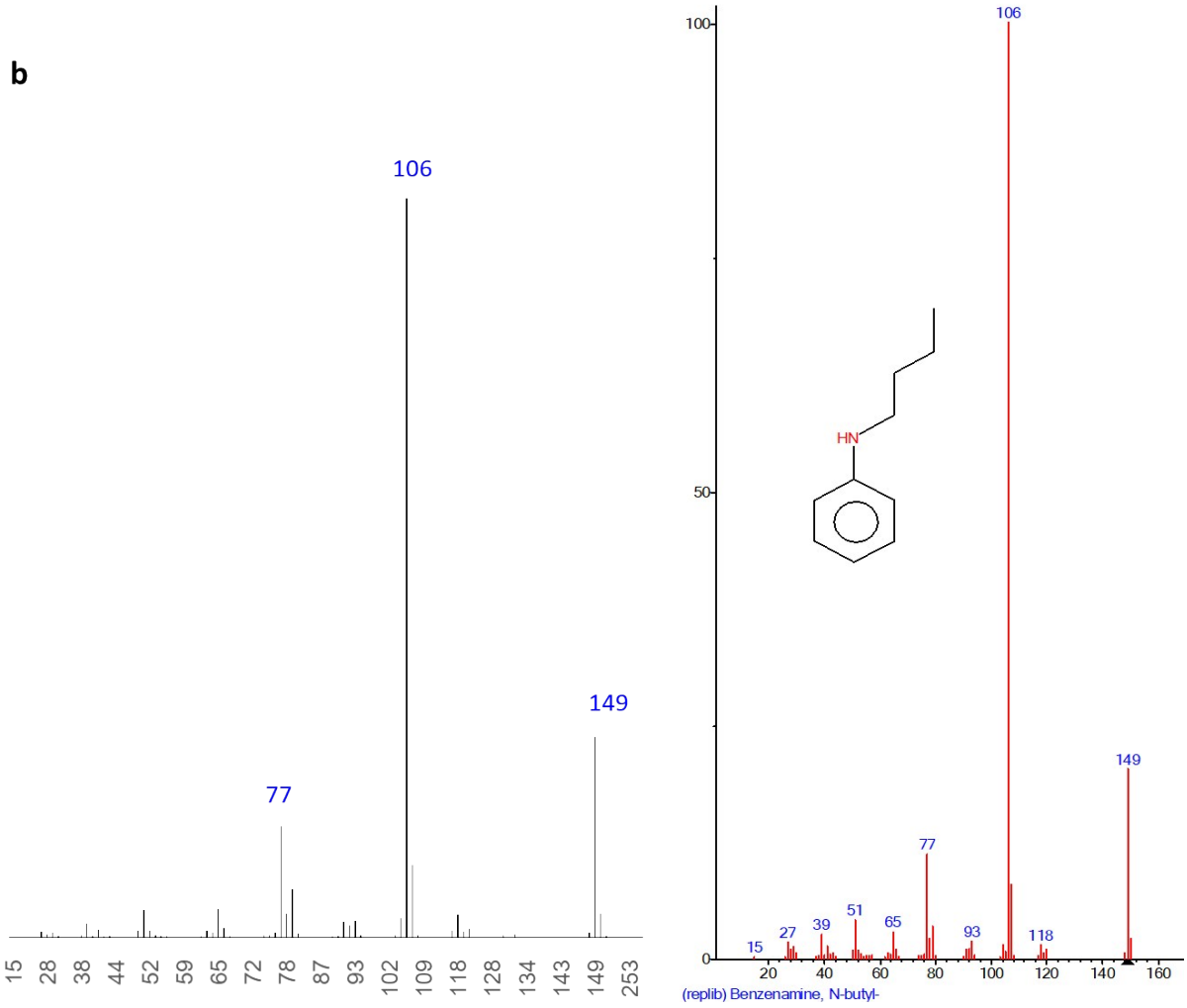


Figure S15-b. *MS spectrum of the product b from Figure S14 in comparison with assignment in NIST library to N-butylaniline*

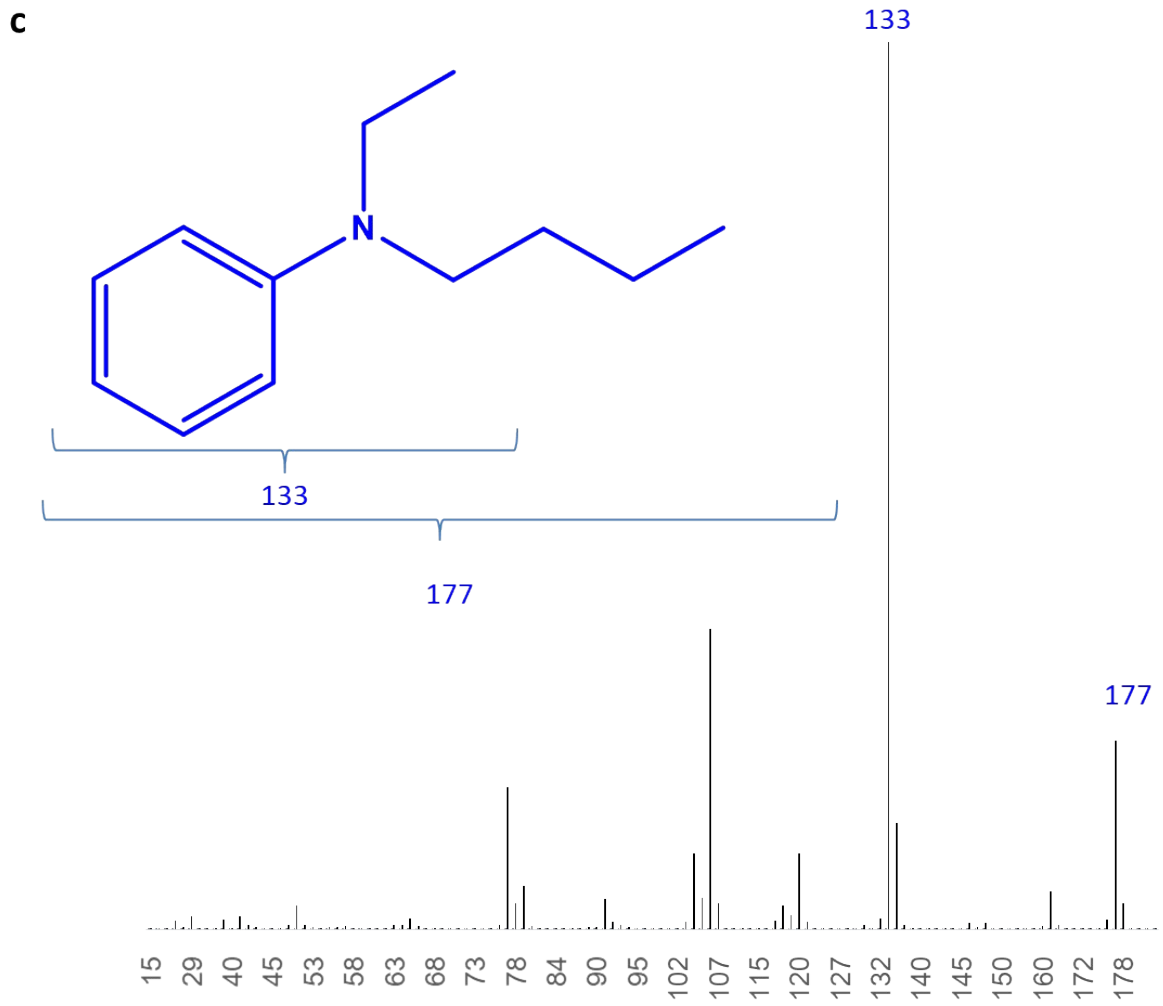


Figure S15-c. *MS spectrum of the product c from Figure S14 in comparison with assignment in NIST library to N-ethylbutylaniline*

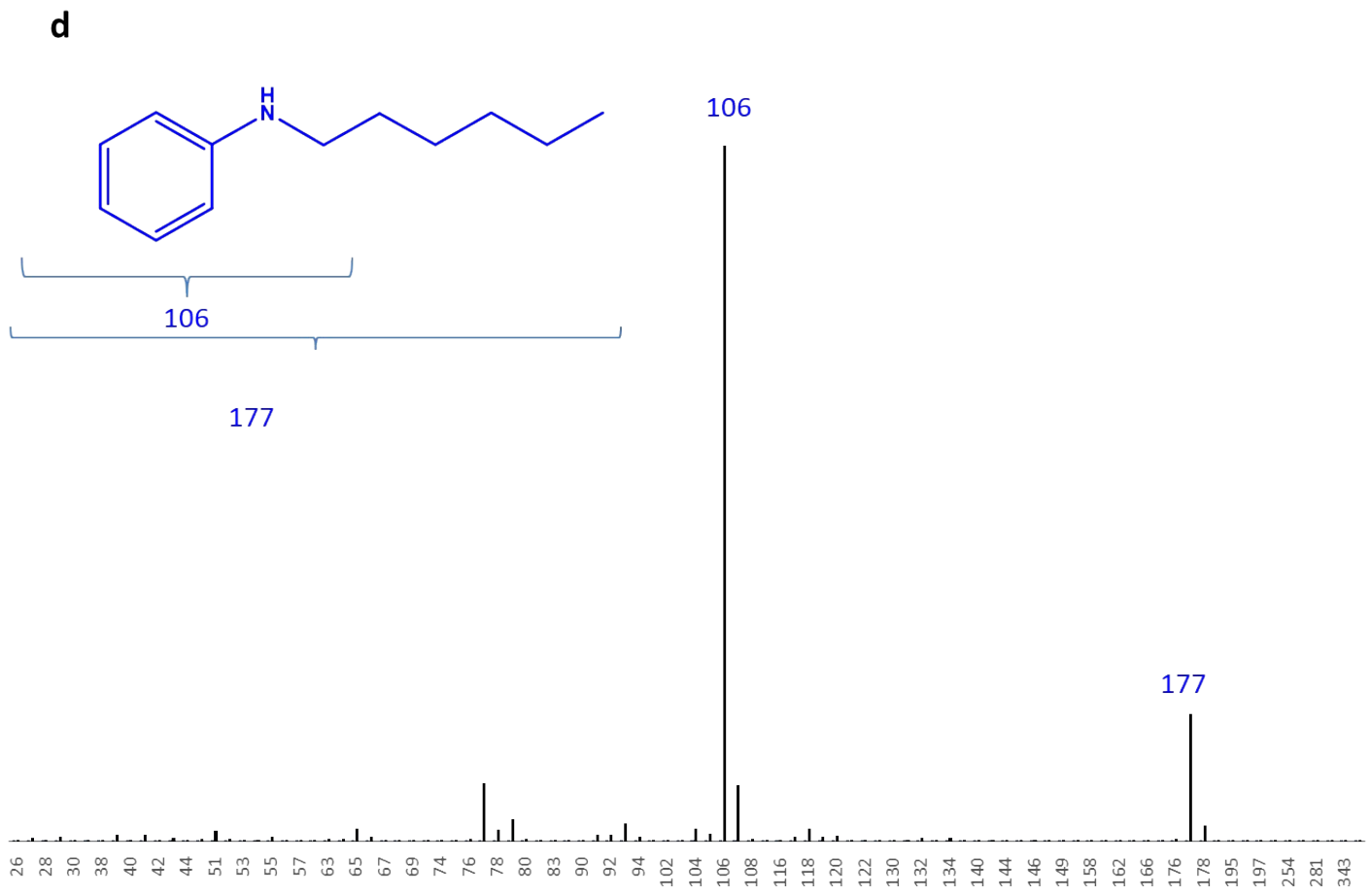


Figure S15-d. *MS spectrum of the product c from Figure S14 in comparison with assignment in NIST library to N-hexylaniline*

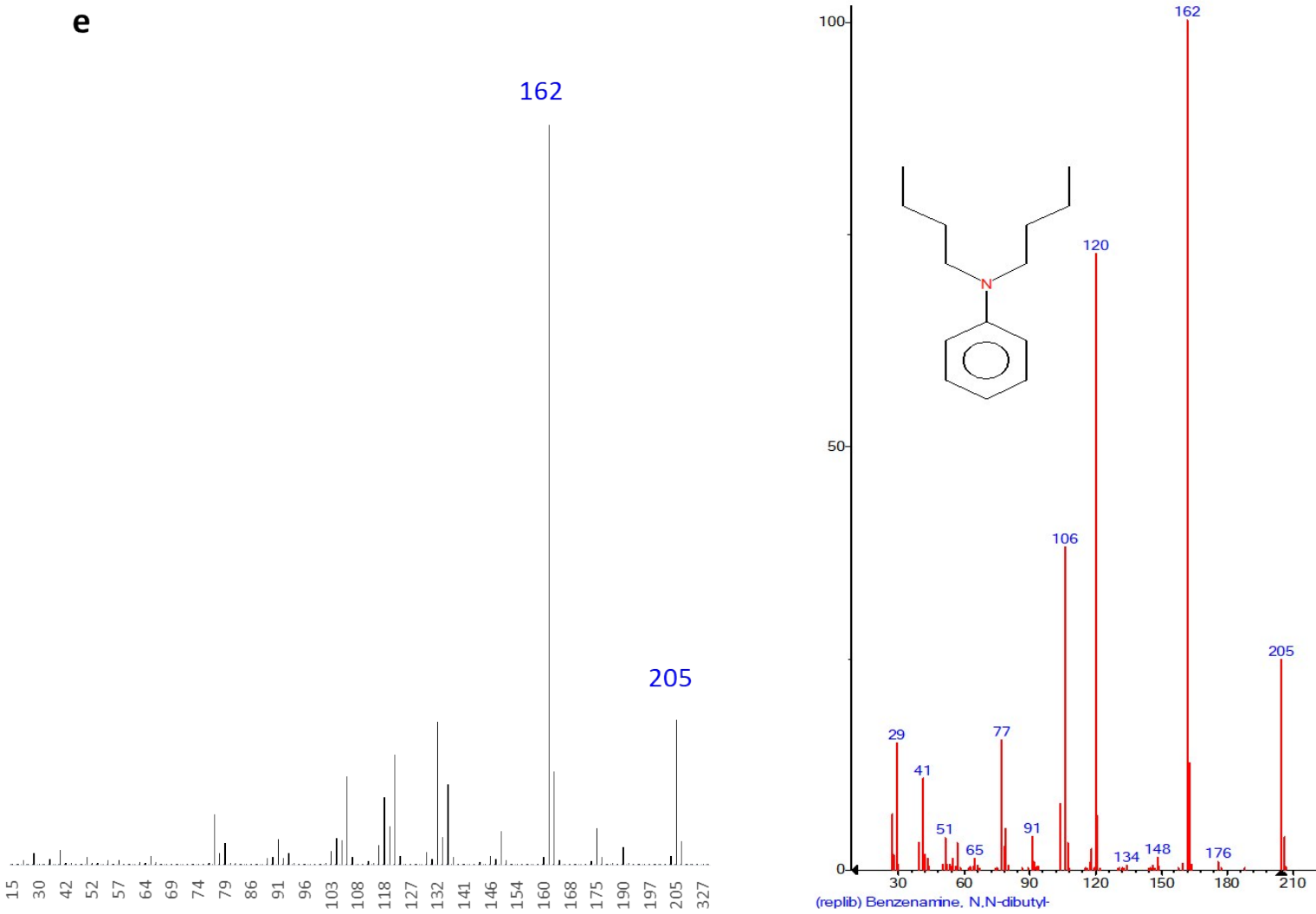


Figure S15-e. *MS spectrum of the product c from Figure S14 in comparison with assignment in NIST library to N,N-dibutylaniline*

f

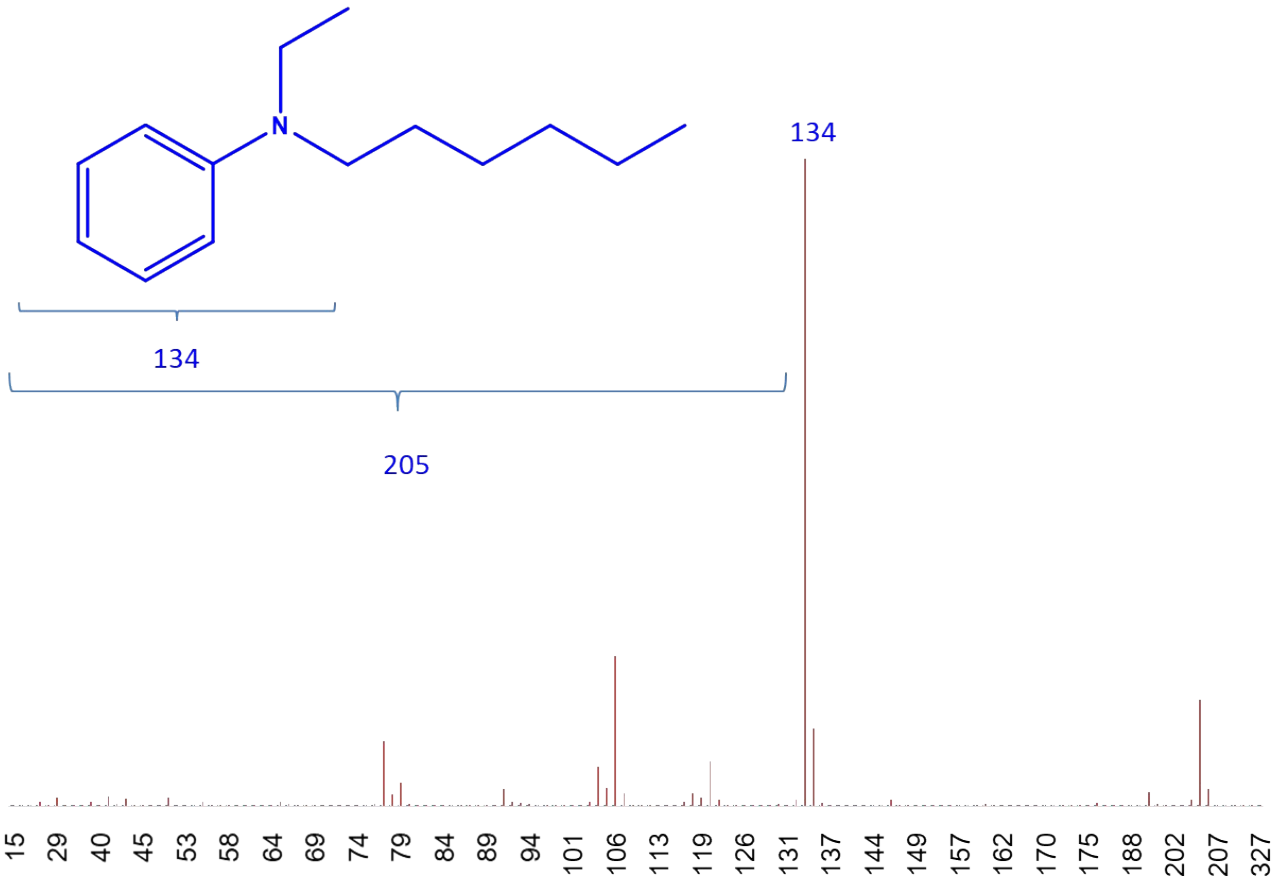


Figure S15-f. *MS spectrum of the product f from Figure S14 indicating on formation of N,N-ethylhexylaniline*

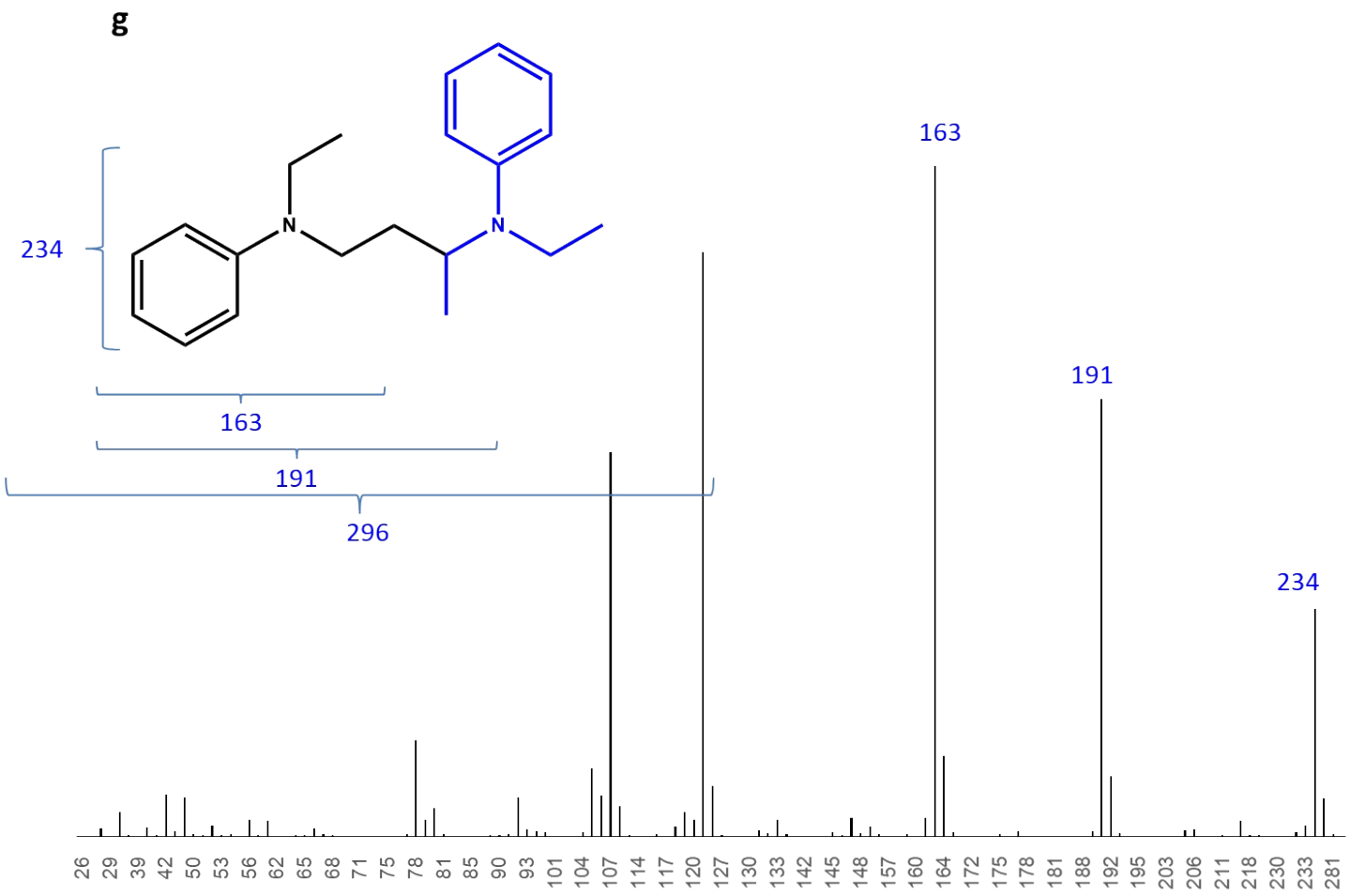


Figure S15-g. *MS spectrum of the product g from Figure S14 indicating on formation of N,N-diethyl-N,N-diphenylbutane-1,3-diamine*